Supplementary Information

Copper-Catalyzed Benzylic C(sp^3)-H Alkoxylation of Heterocyclic Compounds

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General. All reactions were carried out in a dry solvent under an argon atmosphere. Chlorobenzene, 4,7-dimethoxy-1,10-phenanthroline, *tert*-butyl peroxide, and (-)-sparteine were purchased from Sigma-Aldlich Co. and were used without further purification. CuBr and $CuBr_2$ were purchased from nacalai tesque and were used without further purification. 5,6-Dimethyl-1,10-phenanthroline was purchased from Tokyo Chemical Industry Co. and were used without further purification. NMR spectra were recorded on JEOL ECX500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR), and JEOL ECS400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer. Proton chemical shifts are reported relative to residual solvent peaks ($CDCl_3$ at δ 7.26 ppm, DMSO-d_6 at δ 2.50 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm or DMSO-d_6 at δ 39.50 ppm. IR spectra were recorded on a JASCO FT/IR-410. ESI-mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). The enantiomeric excesses (*ee*'s) were determined by HPLC analysis conducted by JASCO HPLC systems with Daicel CHIRALPAK column.

Preparation of 1a (1d, 1e, 1f, 1g, and 1k were synthesized by the same method). To a suspension of 2-methyl-1*H*-benzo[*d*]imidazole[1] (430 mg, 3.25 mmol), 2,2-diphenyloxirane[2] (1.30 g, 6.62 mmol) in ethanol (3.0 mL) was added sodium acetate (270 mg, 3.29 mmol). After heating under reflux conditions for 12 h, the solvent was removed in vacuo. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated in vacuo to give a white solid. This residue was washed with ethyl acetate and dried in vacuo to give **1a** (755 mg, 71% yield).

Preparation of 1b (1c, 1l, 1m, and 1n were synthesized by the same method). To a solution of 2-methyl-1*H*-benzo[*d*]imidazole[1] (430 mg, 3.25 mmol) in DMF (5.0 mL) was added sodium hydride (60% in mineral oil, 143 mg, 3.58 mmol) at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. Then, 2-(4-methoxyphenyl)-2-phenyloxirane[2] (810 mg, 3.58 mmol) was added. The reaction mixture was stirred at 60 °C for 12 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated in vacuo to give a white solid. This residue was washed with ethyl acetate/hexane and dried in vacuo to give **1b** (569 mg, 49% yield).

Preparation of 1h (1i and 1j were synthesized by the same method). A mixture of 1-fluoro-2-nitro-4-(trifluoromethyl)benzene (344 mg, 1.65 mmol), 2-amino-1,1-diphenylethanol[3] (351 mg, 1.65 mmol), *N*,*N*-diisopropylethylamine (213 mg, 1.65 mmol), and acetonitrile (2.0 mL) was stirred at 80 °C for 12 h. Then, the solvent was removed in vacuo. After filtering over a short pad of silica gel and concentration, yellow solid was obtained and used without further purification. This intermediate was dissolved in ethanol (5.0 mL), and 10% Pd/C (50% wet type, 100 mg) was added. Then the mixture was stirred under a hydrogen atmosphere for 3 h, and the mixture was filtered through celite. Then, the solvent was removed in vacuo. A mixture of the residue, 1,1,1-trimethoxyethane (207 mg, 1.72 mmol), *p*-toluenesulfonic acid monohydrate (22.0 mg, 0.116 mmol), and toluene (5.0 mL) was stirred under an argon atmosphere at 50 °C for 3 h. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give **1h** (280 mg, 43% yield).

Preparation of 1o. A mixture of 1-fluoro-2-nitrobenzene (474 mg, 3.36 mmol), 4-amino-2-methyl-2-butanol (520 mg, 5.04 mmol), *N*,*N*-diisopropylethylamine (651 mg, 5.04 mmol), and acetonitrile (3.0 mL) was stirred at 80 °C for 12 h. Then, the solvent was removed in vacuo. After filtering over a short pad of silica gel and concentration, yellow solid was obtained and used without further purification. This intermediate was dissolved in ethanol (10 mL), and 10% Pd/C (50% wet type, 100 mg) was added. Then stirred under a hydrogen atmosphere at 50 ^{o}C for 3 h, and the mixture was filtered through celite. Then, the solvent was removed in vacuo. A mixture of the residue,

1,1,1-trimethoxyethane (604 mg, 5.03 mmol), *p*-toluenesulfonic acid monohydrate (64.0 mg, 0.336 mmol), and toluene (10 mL) was stirred under an argon atmosphere at 50 °C for 12 h. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (ethyl acetate/methanol = 10/1) to give **1o** (601 mg, 82% yield).

Preparation of 1p.
Boron tribromide (1.0 M dichloromethane solution, 1.01 mL, 1.01 mmol) was added drop-wise to a solution of 1-(2-methoxyphenyl)-2-methyl-1*H*-benzo[*d*]imidazole[4] (100 mg, 0.420 mmol) in dichloromethane (3.0 mL) at 0 °C. The reaction mixture was stirred for 24 h at 25 °C. Water was added and the crude mixture was extracted with dichloromethane. The combined organic extracts were washed with water, dried over Na_2SO_4. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (ethyl acetate/methanol = 20/1) to give **1p** (77.0 mg, 82% yield).

Preparation of 1q. To a solution of 5-methyl-1*H*-tetrazole (1.00 g, 11.9 mmol), 2-methyl-2-phenyloxirane (1.92 g, 14.3 mmol) in DMF (10 mL) was added cesium carbonate (5.81 g, 17.8 mmol). The reaction mixture was stirred at 100 °C for 12 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give **1q** (1.51 g, 58% yield).

Preparation of 1r (1s was synthesized by the same method). To a solution of 2-methylquinazolin-4(3*H*)-one (1.00 g, 6.24 mmol), 2-methyl-2-phenyloxirane (1.01 g, 7.53 mmol) in DMF (10 mL) was added cesium carbonate (3.05 g, 9.36 mmol). The reaction mixture was stirred at 100 °C for 12 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give **1r** (0.930 g, 51% yield)

Preparation of 1t. To a solution of 2-methyl-1*H*-benzo[*d*]imidazole (1.00 g, 7.57 mmol) in DMF (10 mL) was added sodium hydride (60% in mineral oil, 363 mg, 9.08 mmol) at 0 °C and the reaction mixture was stirred at 0 °C for 0.5 h. Then, 1-bromo-2-propanone (1.14 g, 8.33 mmol) was added. The reaction mixture was stirred at 25 °C 2 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated in vacuo to give a white solid. This residue was washed with ethyl acetate/hexane and dried in vacuo. Pale yellow solid was obtained and used without further purification. This intermediate was dissolved in methanol (10 mL), and sodium borohydride (163 mg, 4.31 mmol) was added at 0 °C and the reaction mixture was stirred at 0 °C for 2 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated in vacuo to give a white solid. This residue was washed with ethyl acetate and dried in vacuo to give **1t** (633 mg, 49% yield).

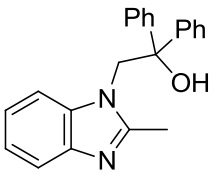
Preparation of 1u. To a solution of 2-methyl-1*H*-benzo[*d*]imidazole (1.00 g, 7.57 mmol) and 2-bromoethanol (1.13 g, 9.04 mmol) in DMF (20 mL) was added potassium carbonate (2.10 g, 15.2 mmol). The reaction mixture was stirred at 60 °C for 8 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (ethyl acetate /methanol = 10/1) to give **1u** (0.643 g, 48% yield) as a white powder. The spectroscopic data were identical to the reported.[5]

Preparation of 3. To a solution of 2-methyl-1*H*-benzo[*d*]imidazole (3.00 g, 22.7 mmol) in DMF (30 mL) was added sodium hydride (60% in mineral oil, 1.09 g, 27.2 mmol) at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. Then, iodomethane (3.55 g, 25.0 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated in vacuo to give a white solid. This residue was washed with ethyl acetate/hexane and dried in vacuo to give **3** (2.16 g, 65% yield) as a pale yellow solid. The spectroscopic data were

identical to the reported.[6]

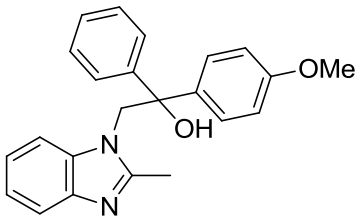
Preparation of 6. To a solution of 2-methylquinazolin-4(3H)-one (1.00 g, 6.24 mmol) in DMF (10 mL) was added sodium hydride (60% in mineral oil, 0.30 g, 7.49 mmol) at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. Then, iodomethane (0.974 g, 6.86 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h. Water was added and the crude mixture was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na_2SO_4. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give **6** (0.919 g, 84% yield) as a white powder. The spectroscopic data were identical to the reported.[7]

2-(2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1a).



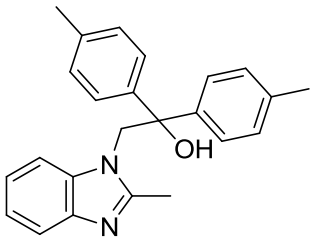
71%, white powder, TLC (ethyl acetate/methanol = 10/1): R_f = 0.39, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.64 (s, 1H), 4.85 (s, 2H), 7.02–7.12 (m, 2H), 7.16 (ddd, *J* = 8.0, 6.9, and 1.4 Hz, 1H), 7.26–7.40 (m, 10H), 7.61 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 54.1, 78.8, 110.7, 118.6, 121.6, 121.7, 126.4 (4C), 128.1 (2C), 128.6 (4C), 136.5, 142.3, 144.2 (2C), 153.2; IR (KBr, ν / cm^{-1}) 3137, 1614, 1494, 1463, 1397, 1237, 1158, 1071, 1003, 953, 743, 700; HRMS (ESI^+) Calcd for $C_{22}H_{20}N_2ONa$ ($M+Na^+$) 351.1473, Found 351.1461.

1-(4-Methoxyphenyl)-2-(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)-1-phenylethanol (1b).



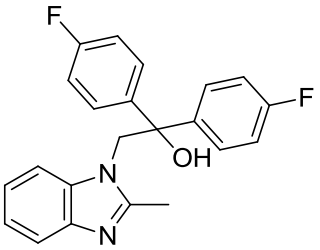
49%, white powder, TLC (ethyl acetate): R_f = 0.38, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (s, 3H), 2.60 (s, 1H), 3.79 (s, 3H), 4.81 (s, 2H), 6.81–6.85 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.12–7.20 (m, 3H), 7.26–7.35 (m, 5H), 7.61 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 54.2, 55.3, 78.5, 110.9, 113.8 (2C), 118.5, 121.6, 121.7, 126.5 (2C), 127.8 (2C), 127.9, 128.4 (2C), 136.4, 136.5, 142.2, 144.4, 153.2, 159.3; IR (KBr, ν / cm^{-1}) 3055, 1607, 1508, 1464, 1399, 1252, 1177, 1033, 835, 744, 703; HRMS (ESI^+) Calcd for $C_{23}H_{22}N_2O_2Na$ ($M+Na^+$) 381.1579, Found 381.1567.

2-(2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-di-*p*-tolylethanol (1c).



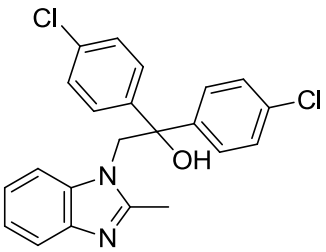
66%, white powder, TLC (ethyl acetate): R_f = 0.47, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.34 (s, 6H), 2.73 (s, 1H), 4.79 (s, 2H), 7.05 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.09–7.18 (m, 10H), 7.59 (dd, *J* = 7.5, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 21.0 (2C), 54.1, 78.7, 111.0, 118.5, 121.6 (3C), 126.3 (4C), 129.1 (4C), 136.6, 137.8, 141.4 (2C), 142.3, 153.2; IR (KBr, ν / cm^{-1}) 3158, 1738, 1614, 1509, 1397, 1288, 1235, 1158, 1085, 1004, 813, 740; HRMS (ESI^+) Calcd for $C_{24}H_{24}N_2ONa$ ($M+Na^+$) 379.1786, Found 379.1774.

1,1-Bis(4-fluorophenyl)-2-(2-methyl-1*H*-benzo[d]imidazol-1-yl)ethanol (1d).



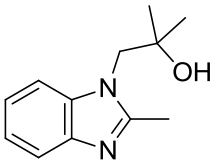
64%, white powder, TLC (ethyl acetate): R_f = 0.54, ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.00 (s, 3H), 4.88 (s, 2H), 6.25 (s, 1H), 6.94 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.07–7.14 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.31–7.36 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 13.6, 53.4, 77.1, 111.5, 114.5 (*J* = 21.5 Hz, 4C), 117.5, 120.6 (2C), 128.9 (*J* = 8.4 Hz, 4C), 136.6, 141.5 (2C), 141.9, 153.0, 161.3 (*J* = 242 Hz, 2C); IR (KBr, ν / cm^{-1}) 3158, 1604, 1508, 1464, 1399, 1231, 1159, 1078, 1013, 839, 745; HRMS (ESI^+) Calcd for $C_{22}H_{18}F_2N_2ONa$ ($M+Na^+$) 387.1285, Found 387.1283.

1,1-Bis(4-chlorophenyl)-2-(2-methyl-1*H*-benzo[d]imidazol-1-yl)ethanol (1e).



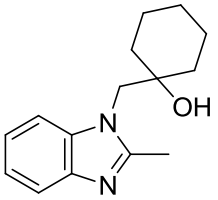
61%, white powder, TLC (ethyl acetate/methanol = 10/1): R_f = 0.47, ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.99 (s, 3H), 4.89 (s, 2H), 6.32 (s, 1H), 6.94 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.02 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.30–7.37 (m, 8H), 7.39 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 13.6, 53.1, 77.1, 111.5, 117.5, 120.6 (2C), 127.8 (4C), 128.7 (4C), 132.1 (2C), 136.5, 141.9, 144.0 (2C), 152.9; IR (KBr, ν / cm^{-1}) 3065, 1736, 1615, 1490, 1464, 1400, 1234, 1159, 1094, 1013, 823, 741; HRMS (ESI^+) Calcd for $C_{22}H_{18}Cl_2N_2ONa$ ($M+Na^+$) 419.0694, Found 419.0681.

2-Methyl-1-(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)-2-propanol (1f).



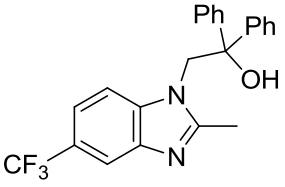
87%, pale yellow powder, TLC (ethyl acetate/methanol = 10/1): R_f = 0.27, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 6H), 2.41 (s, 1H), 2.60 (s, 3H), 4.07 (s, 2H), 7.14–7.22 (m, 2H), 7.35–7.40 (m, 1H), 7.57–7.62 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 28.1 (2C), 54.3, 72.2, 110.5, 118.5, 121.8 (2C), 136.0, 142.1, 153.0; IR (KBr, ν / cm^{-1}) 3174, 2978, 1615, 1403, 1287, 1239, 1186, 1012, 938, 907, 848, 743; HRMS (ESI^+) Calcd for $C_{12}H_{17}N_2O$ ($M+H^+$) 205.1341, Found 205.1333.

1-((2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)methyl)cyclohexanol (1g).



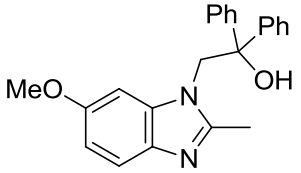
61%, white powder, TLC (hexane/ethyl acetate = 1/1): R_f = 0.10, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15-1.75 (m, 10H), 2.61 (s, 3H), 4.03 (s, 2H), 7.13–7.20 (m, 2H), 7.35–7.40 (m, 1H), 7.55–7.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 21.3 (2C), 25.5, 35.8 (2C), 54.9, 72.9, 110.5, 118.7, 121.7, 121.8, 136.3, 142.4, 153.1; IR (KBr, ν / cm^{-1}) 3280, 2937, 1522, 1400, 1287, 1248, 1175, 997, 744; HRMS (ESI^+) Calcd for $C_{15}H_{21}N_2O$ ($M+H^+$) 245.1654, Found 245.1644.

2-(2-Methyl-5-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1h).



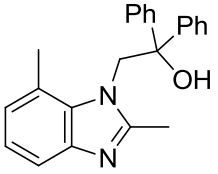
43%, white powder, TLC (ethyl acetate): R_f = 0.50, ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00 (s, 3H), 3.08 (s, 1H), 4.86 (s, 2H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.24–7.40 (m, 11H), 7.75 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 54.2, 78.8, 111.3, 116.1 (d, *J* = 4.8 Hz), 118.6 (d, *J* = 3.6 Hz), 124.0 (q, *J* = 32.4 Hz), 124.9 (q, *J* = 271 Hz), 126.4 (4C), 128.3 (2C), 128.7 (4C), 138.5, 141.6, 144.0 (2C), 155.3; IR (KBr, ν / cm^{-1}) 3136, 1629, 1446, 1327, 1245, 1124, 1068, 890, 811, 755, 698, 622; HRMS (ESI^+) Calcd for $C_{23}H_{19}F_3N_2O$ Na($M+Na^+$) 419.1347, Found 419.1330.

2-(6-Methoxy-2-methyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1i).



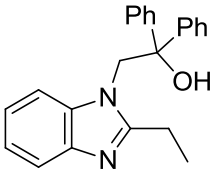
23%, white powder, TLC (hexane/ethyl acetate = 3/1): R_f = 0.09, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 3.00 (s, 1H), 3.67 (s, 3H), 4.80 (s, 2H), 6.44 (d, *J* = 2.3 Hz, 1H), 6.74 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.27–7.39 (m, 10H), 7.41 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 54.2, 55.8, 78.7, 94.5, 110.9, 118.9, 126.5 (4C), 128.1 (2C), 128.5 (4C), 136.6, 136.9, 144.4 (2C), 152.4, 155.9; IR (KBr, ν / cm^{-1}) 3374, 1618, 1485, 1448, 1400, 1216, 1092, 1025, 808, 759, 700, 633; HRMS (ESI^+) Calcd for $C_{23}H_{22}N_2O_2Na$ ($M+Na^+$) 381.1579, Found 381.1578.

2-(2,7-Dimethyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1j).



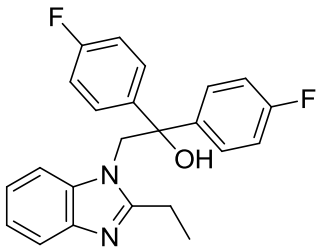
24%, white powder, TLC (hexane/ethyl acetate = 1/1): R_f = 0.09, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 3H), 2.54 (s, 3H), 2.76 (s, 1H), 5.06 (s, 2H), 6.87 (d, *J* = 7.3 Hz, 1H), 7.08 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.20–7.27 (m, 4H), 7.28–7.35 (m, 6H), 7.49 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.5, 54.1, 78.4, 117.0, 121.8 (2C), 125.3, 126.4 (4C), 128.1 (2C), 128.5 (4C), 134.9, 142.8, 144.3 (2C), 153.5; IR (KBr, ν / cm^{-1}) 3062, 1594, 1396, 1294, 1072, 951, 745, 700, 604; HRMS (ESI^+) Calcd for $C_{23}H_{23}N_2O$ ($M+H^+$) 343.1810, Found 343.1795.

2-(2-Ethyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1k).



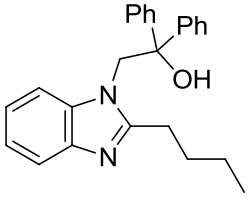
83%, white powder, TLC (hexane/ethyl acetate = 1/1): R_f = 0.20, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.5 Hz, 3H), 2.21 (q, *J* = 7.5 Hz, 2H), 2.61 (s, 1H), 4.86 (s, 2H), 7.03–7.10 (m, 2H), 7.11–7.18 (m, 1H), 7.26–7.40 (m, 10H), 7.67 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.4, 20.3, 53.6, 78.8, 110.7, 118.8, 121.5, 121.7, 126.4 (4C), 128.1 (2C), 128.5 (4C), 136.5, 142.4, 144.2 (2C), 157.6 ; IR (KBr, ν / cm^{-1}) 3060, 1509, 1461, 1412, 1069, 743, 700; HRMS (ESI^+) Calcd for $C_{23}H_{22}N_2ONa$ ($M+Na^+$) 365.1630, Found 365.1644.

2-(2-Ethyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-bis(4-fluorophenyl)ethanol (1l).



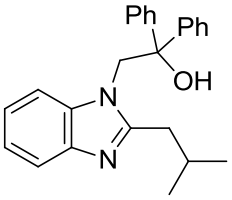
39%, pale yellow solid, TLC (hexane/ethyl acetate = 1/1): R_f = 0.40, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.5 Hz, 3H), 2.33 (q, *J* = 7.5 Hz, 2H), 3.15 (s, 1H), 4.82 (s, 2H), 6.96–7.04 (m, 5H), 7.05 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.15 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.24–7.31 (m, 4H), 7.62 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.5, 20.4, 53.7, 78.1, 110.5, 115.4 (*J* = 21.5 Hz, 4C), 118.8, 121.7, 121.9, 128.3 (*J* = 8.4 Hz, 4C), 136.2, 139.9, 142.2 (2C), 157.4, 162.4 (*J* = 245 Hz, 2C); IR (KBr, ν / cm^{-1}) 3186, 1603, 1506, 1460, 1226, 1159, 1087, 834, 750; HRMS (ESI^+) Calcd for $C_{23}H_{20}F_2N_2ONa$ ($M+Na^+$) 401.1441, Found 401.1429.

2-(2-Butyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1m).



42%, white powder, TLC (hexane/ethyl acetate = 1/1): R_f = 0.33, ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.5 Hz, 3H), 1.21 (qt, *J* = 7.5 Hz, 2H), 1.55–1.64 (m, 2H), 2.07–2.12 (m, 2H), 3.00 (s, 1H), 4.83 (s, 2H), 7.01 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.25–7.31 (m, 10H), 7.60 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.6, 26.6, 29.3, 53.6, 78.7, 110.8, 118.7, 121.5, 121.6, 126.4 (4C), 128.0 (2C), 128.5 (4C), 136.3, 142.3, 144.2 (2C), 156.7; IR (KBr, ν / cm^{-1}) 3091, 2929, 1614, 1507, 1461, 1267, 1101, 1073, 1026, 956, 735, 700; HRMS (ESI^+) Calcd for $C_{25}H_{26}N_2ONa$ ($M+Na^+$) 393.1943, Found 393.1930.

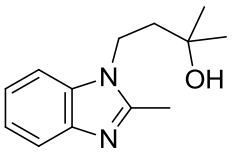
2-(2-Isobutyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (1n).



49%, white powder, TLC (ethyl acetate): R_f = 0.61, ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.9 Hz, 6H), 2.04 (d, *J* = 6.9 Hz, 2H), 2.15–2.24 (m, 1H), 2.76 (s, 1H), 4.88 (s, 2H), 7.03 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0, 8.0 Hz, 1H), 7.26–7.36 (m, 10H), 7.64 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6 (2C), 27.4, 35.7, 78.7, 110.7, 118.8, 121.5, 121.6, 126.4 (4C), 128.0 (2C), 128.5 (4C), 136.3, 142.5 (2C), 144.3, 155.9; IR (KBr, ν / cm^{-1}) 3339, 2956, 1508, 1459, 1406, 1327, 1189, 1069, 742, 704, 647; HRMS (ESI^+) Calcd for $C_{25}H_{26}N_2ONa$

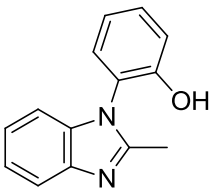
($M+Na^+$) 393.1943, Found 393.1929.

2-Methyl-4-(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)butan-2-ol (1o).



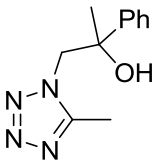
82%, white powder, TLC (ethyl acetate/methanol = 10/1): R_f = 0.21, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 6H), 1.91 (t, *J* = 8.0 Hz, 2H), 2.61 (s, 3H), 4.27 (t, *J* = 8.0 Hz, 2H), 7.20–7.26 (m, 2H), 7.28–7.34 (m, 1H), 7.66–7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 29.7 (2C), 39.5, 42.6, 69.7, 109.0, 119.0, 121.7, 121.9, 134.9, 142.7, 151.3; IR (KBr, ν / cm^{-1}) 3182, 2962, 1513, 1476, 1413, 1365, 1285, 1233, 1163, 918, 732; HRMS (ESI^+) Calcd for $C_{13}H_{17}N_2O$ ($M+H^+$) 219.1497, Found 219.1488.

2-(2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)phenol (1p).



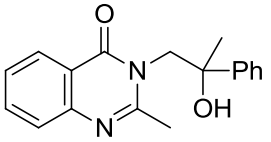
82%, pale yellow solid, TLC (ethyl acetate): R_f = 0.63, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (s, 3H), 7.00 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.03–7.07 (m, 2H), 7.10 (dd, *J* = 6.9, 6.9 Hz, 1H), 7.15 (dd, *J* = 6.9, 6.9 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.45 (ddd, *J* = 8.6, 7.5, and 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.1, 110.7, 118.2, 119.5, 120.4, 122.2, 122.7, 122.9, 128.6, 130.9, 135.3, 141.4, 152.5, 153.6; IR (KBr, ν / cm^{-1}) 3060, 2864, 2696, 2558, 1598, 1517, 1457, 1326, 1295, 1249, 1229, 1021, 752; HRMS (ESI^+) Calcd for $C_{14}H_{13}N_2O$ ($M+H^+$) 225.1028, Found 225.1029.

1-(5-Methyl-1*H*-tetrazol-1-yl)-2-phenyl-2-propanol (1q).



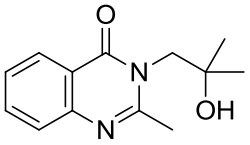
58%, white solid, TLC (hexane/ethyl acetate = 1/1): R_f = 0.14, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 3H), 2.22 (s, 3H), 3.48 (s, 1H), 4.30 (d, *J* = 14.2 Hz, 1H), 4.44 (d, *J* = 14.2 Hz, 1H), 7.20–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.8, 26.8, 57.6, 74.3, 124.8 (2C), 127.9, 128.6 (2C), 143.7, 153.1; IR (KBr, ν / cm^{-1}) 3346, 1527, 1407, 1262, 1221, 1069, 874, 762, 701; HRMS (ESI^+) Calcd for $C_{11}H_{14}N_4ONa$ ($M+Na^+$) 241.1065, Found 241.1062.

3-(2-Hydroxy-2-phenylpropyl)-2-methylquinazolin-4(3*H*)-one (1r).



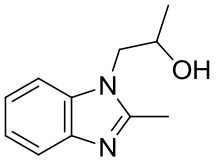
51%, white powder, TLC (hexane/ethyl acetate = 1/1): R_f = 0.21, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69 (s, 3H), 2.29 (s, 3H), 4.15 (d, *J* = 14.4 Hz, 1H), 4.31 (s, 1H), 4.68 (d, *J* = 14.4 Hz, 1H), 7.26–7.30 (m, 1H), 7.31–7.37 (m, 2H), 7.43–7.51 (m, 3H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.74 (ddd, *J* = 8.6, 6.9, and 1.2 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 27.6, 55.8, 75.6, 120.0, 125.1, 126.6, 126.7, 127.0, 127.5, 128.5, 134.7, 145.3, 147.1, 154.8, 164.8; IR (KBr, ν / cm^{-1}) 3441, 1661, 1592, 1473, 1384, 1148, 768, 702; HRMS (ESI^+) Calcd for $C_{18}H_{18}N_2O_2Na$ ($M+Na^+$) 317.1266, Found 317.1257.

3-(2-Hydroxy-2-methylpropyl)-2-methylquinazolin-4(3*H*)-one (1s).



21%, white powder, TLC (hexane/ethyl acetate = 1/2): R_f = 0.19, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 6H), 2.70 (s, 3H), 3.57 (s, 1H), 4.25 (s, 2H), 7.45 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.74 (dd, *J* = 8.0, 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.3, 28.4 (2C), 54.7, 71.9, 120.2, 126.6 (2C), 126.9, 134.6, 147.2, 154.8, 164.2; IR (KBr, ν / cm^{-1}) 3422, 2972, 1649, 1592, 1478, 1386, 1342, 1191, 1138, 979, 780, 694; HRMS (ESI^+) Calcd for $C_{13}H_{17}N_2O_2$ ($M+H^+$) 233.1290, Found 233.1291.

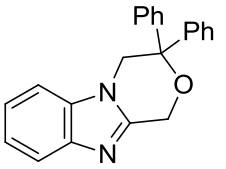
1-(2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)-2-propanol (1t).



49%, white powder, TLC (ethyl acetate): R_f = 0.12, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (d, *J* = 6.3 Hz, 3H), 2.44 (s, 3H), 3.96 (dd, *J* = 14.9, 9.2 Hz, 1H), 4.02 (dd, *J* = 14.9, 3.4 Hz, 1H), 4.28-4.34 (m, 1H), 6.98 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.09 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 20.9, 51.5, 65.7, 109.1, 118.3, 121.9 (2C), 134.7, 141.6, 152.1; IR (KBr, ν / cm^{-1}) 3136, 2974, 1411, 1288, 1135, 1083, 754; HRMS (ESI^+) Calcd for $C_{11}H_{14}N_2ONa$ ($M+Na^+$) 213.1004, Found 213.1011.

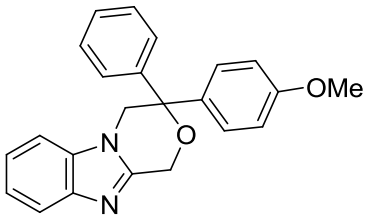
Typical procedure for copper-catalyzed C(sp^3)-H alkoxylation. A mixture of 2-(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (**1a**, 41.1 mg, 0.125 mmol), CuBr (0.9 mg, 6.3 μ mol), 5,6-dimethyl-1,10-phenanthroline (1.6 mg, 7.7 μ mol), (^{t}BuO)$_2$ (23.8 mg, 0.163 mmol), and chlorobenzene (1.25 mL) was stirred at 100 °C for 6 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give 3,3-diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine **2a** (30.8 mg, 75% yield).

3,3-Diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2a).



yellow solid, TLC (hexane/ethyl acetate = 1/1): R_f = 0.32, ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (s, 2H), 4.93 (s, 2H), 7.26–7.32 (m, 12H), 7.35–7.45 (m, 1H), 7.65–7.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.0, 60.8, 78.9, 108.5, 119.5, 122.2, 122.7, 126.6 (4C), 128.1 (2C), 128.7 (4C), 133.6, 141.1 (2C), 143.1, 147.7; IR (neat, ν / cm^{-1}) 3404, 1617, 1524, 1476, 1453, 1338, 1227, 1076, 745, 699; HRMS (ESI$^+$) Calcd for $C_{22}H_{19}N_2O$ (M+H$^+$) 327.1497, Found 327.1499.

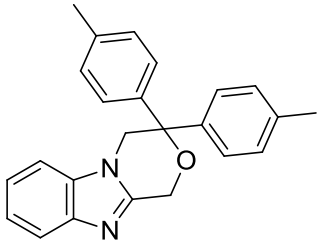
3-(4-Methoxyphenyl)-3-phenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2b).



Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 6 h.

71%, yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.36, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.58 (d, *J* = 12.9 Hz, 1H), 4.68 (d, *J* = 12.9 Hz, 1H), 4.87 (d, *J* = 16.4 Hz, 1H), 4.95 (d, *J* = 16.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.23–7.35 (m, 7H), 7.40–7.46 (m, 1H), 7.67–7.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.2, 55.2, 60.7, 78.7, 108.5, 114.0 (2C), 119.5, 122.2, 122.7, 126.5 (2C), 128.0, 128.1 (2C), 128.6 (2C), 132.7, 133.6, 141.8, 143.1, 147.8, 159.3; IR (neat, ν / cm^{-1}) 2360, 1510, 1454, 1249, 1179, 1076, 747; HRMS (ESI$^+$) Calcd for $C_{23}H_{21}N_2O_2$ (M+H$^+$) 357.1603, Found 357.1594.

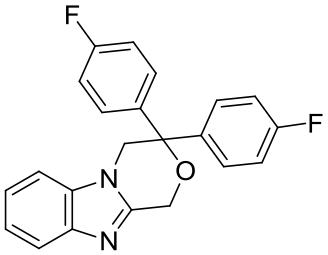
3,3-Di-*p*-tolyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2c).



Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 6 h.

55%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.43, ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 6H), 4.62 (s, 2H), 4.91 (s, 2H), 7.11 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 7.27–7.32 (m, 2H), 7.40–7.47 (m, 1H), 7.69–7.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0 (2C), 49.2, 60.7, 78.7, 108.5, 119.5, 122.1 (2C), 122.6, 126.5 (4C), 129.3 (4C), 133.6, 137.9, 138.3 (2C), 143.1, 147.9; IR (neat, ν / cm^{-1}) 2920, 1617, 1510, 1454, 1227, 1087, 810, 744; HRMS (ESI$^+$) Calcd for $C_{24}H_{23}N_2O$ (M+H$^+$) 355.1810, Found 355.1804.

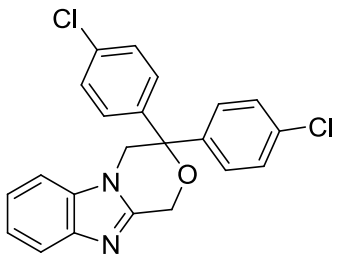
3,3-Bis(4-fluorophenyl)-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2d).



Reaction conditions: CuBr (5.0 mol %), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 6 h.

81%, pale yellow oil, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.49, ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.56 (s, 2H), 4.85 (s, 2H), 6.95 (dd, *J* = 8.6, 8.6 Hz, 4H), 7.15–7.30 (m, 6H), 7.33–7.40 (m, 1H), 7.61–7.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.2, 60.8, 78.2, 108.5, 115.7 (d, *J* = 21.5 Hz, 4C), 119.6, 122.4, 122.9, 128.5 (d, *J* = 8.4 Hz, 4C), 133.4, 136.8 (d, *J* = 3.6 Hz, 2C), 143.1, 147.2, 162.4 (d, *J* = 247 Hz, 2C); IR (neat, ν / cm^{-1}) 1605, 1508, 1454, 1372, 1228, 1160, 1085, 1014, 836, 745; HRMS (ESI$^+$) Calcd for $C_{22}H_{17}F_3N_2O$ (M+H$^+$) 363.1309, Found 363.1297.

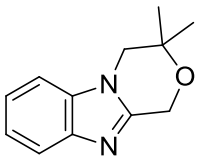
3,3-Bis(4-chlorophenyl)-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2e).



Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 6 h.

81%, pale yellow solid, purification: silica gel column chromatography (hexane/ ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.46, ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.60 (s, 2H), 4.91 (s, 2H), 7.23 (d, *J* = 8.6 Hz, 4H), 7.29 (d, *J* = 8.6 Hz, 4H), 7.30–7.35 (m, 2H), 7.41–7.46 (m, 1H), 7.70–7.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 48.9, 60.9, 78.2, 108.5, 119.7, 122.5 (2C), 123.0, 128.0 (4C), 129.0 (4C), 133.4, 134.4, 139.2 (2C), 143.1, 147.1; IR (neat, ν / cm^{-1}) 1489, 1454, 1401, 1227, 1090, 1012, 831, 746; HRMS (ESI$^+$) Calcd for $C_{22}H_{17}Cl_2N_2O$ (M+H$^+$) 395.0718, Found 395.0700.

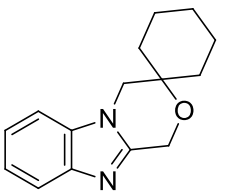
3,3-Dimethyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2f).



Reaction conditions: CuBr (5.0 mol%), 4,7-dimethoxy-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 4 h.

55%, yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/2), TLC (hexane/ethyl acetate = 1/2): R_f = 0.19, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 6H), 3.96 (s, 2H), 5.05 (s, 2H), 7.26–7.35 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.3 (2C), 51.2, 59.9, 70.6, 108.6, 119.3, 122.0, 122.5, 134.1, 143.0, 147.2; IR (neat, ν / cm^{-1}) 3391, 2976, 1740, 1477, 1453, 1386, 1271, 1215, 1157, 1081, 867, 744; HRMS (ESI$^+$) Calcd for $C_{12}H_{15}N_2O$ (M+H$^+$) 203.1184, Found 203.1182.

1,4-Dihydrospiro[benzo[4,5]imidazo[2,1-*c*][1,4]oxazine-3,1'-cyclohexane] (2g).

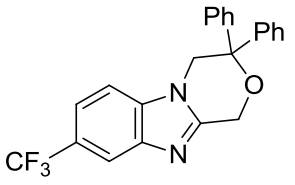


Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (2.0 equiv), 100 °C, 4 h.

52%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f =

0.39, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32–1.44 (m, 1H), 1.47–1.60 (m, 4H), 1.65–1.75 (m, 3H), 1.89–1.95 (m, 2H), 3.92 (s, 2H), 5.02 (s, 2H), 7.23–7.33 (m, 3H), 7.72 (d, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (2C), 25.7, 32.8 (2C), 50.8, 59.1, 71.5, 108.7, 119.3, 122.0, 122.4, 134.2, 143.1, 147.7; IR (neat, ν / cm^{-1}) 2935, 1740, 1477, 1454, 1338, 1228, 1157, 1079, 887, 744; HRMS (ESI^+) Calcd for $C_{15}H_{19}N_2O$ ($M+H^+$) 243.1497, Found 243.1500.

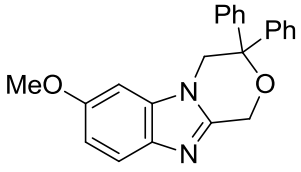
3,3-Diphenyl-8-(trifluoromethyl)-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2h).



Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 6 h.

45%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 2/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.80, ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 2H), 4.96 (s, 2H), 7.27–7.35 (m, 10H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.2, 60.7, 78.9, 108.9, 117.2 (d, *J* = 3.6 Hz), 119.3 (d, *J* = 3.6 Hz), 127.7 (q, *J* = 272 Hz), 125.3 (q, *J* = 32.4 Hz), 126.5 (4C), 128.3 (2C), 128.8 (4C), 135.6, 140.8 (4C), 142.6, 149.8; IR (neat, ν / cm^{-1}) 1628, 1448, 1330, 1161, 1117, 1051, 913, 755, 699, 671; HRMS (ESI^+) Calcd for $C_{23}H_{17}F_3N_2ONa$ ($M+Na^+$) 417.1191, Found 417.1185.

7-Methoxy-3,3-diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2i).



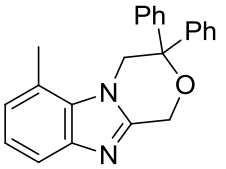
Reaction conditions: CuBr (10 mol%), 5,6-dimethyl-1,10-phenanthroline (12 mol%), (^{t}BuO)$_2$ (2.6 equiv), 100 °C, 6 h.

70%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 3/1): R_f = 0.20, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 3H), 4.61 (s, 2H), 4.89 (s, 2H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.26–7.35 (m, 10H), 7.58 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 49.1, 55.9, 60.8, 78.9, 92.6, 111.5, 119.9, 126.6 (4C), 128.1 (2C), 128.6 (4C), 134.1, 137.5, 141.2 (2C), 146.7, 156.3; IR (neat, ν / cm^{-1})

2955, 1624, 1451, 1355, 1274, 1211, 1147, 1075, 816, 754, 699, 639; HRMS (ESI^+) Calcd for $C_{23}H_{21}N_2O$ ($M+H^+$) 357.1603, Found 357.1591.

6-Methyl-3,3-diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2j).

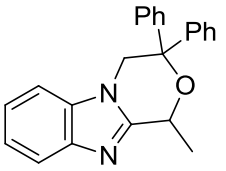
Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 6 h.



80%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.39, ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.80 (s, 3H), 4.92 (s, 2H), 4.99 (s, 2H), 7.01 (d, *J* = 6.9 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.27–7.40 (m, 10H), 7.54 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5, 51.6, 60.9, 78.9, 117.4, 120.9, 122.5, 124.5, 126.8 (4C), 128.1 (2C), 128.7 (4C), 132.5, 141.2 (2C), 143.2, 147.5; IR (neat, ν / cm^{-1}) 1651, 1526, 1474, 1448, 1336, 1272, 1218, 1081, 748, 699, 650, 608; HRMS (ESI^+) Calcd for $C_{23}H_{21}N_2O$ ($M+H^+$) 341.1654, Found 341.1641.

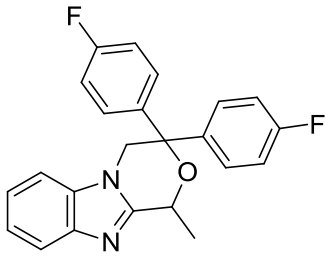
1-Methyl-3,3-diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2k).

Reaction conditions: CuBr (10 mol%), 4,7-dimethoxy-1,10-phenanthroline (12 mol%), (^{t}BuO)$_2$ (2.6 equiv), 100 °C, 4 h.



70%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 2/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.53, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (d, *J* = 6.6 Hz, 3H), 4.28 (d, *J* = 12.6 Hz, 1H), 4.74 (q, *J* = 6.6 Hz, 1H), 5.09 (d, *J* = 12.6 Hz, 1H), 7.20–7.29 (m, 5H), 7.30–7.36 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.44–7.50 (m, 3H), 7.79 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 49.2, 66.7, 78.6, 108.7, 119.6, 122.3, 122.7, 125.5 (2C), 127.6 (2C), 127.7, 128.2, 128.4 (2C), 128.8 (2C), 133.7, 139.1, 143.0, 144.4, 151.8; IR (neat, ν / cm^{-1}) 3420, 1455, 1101, 748, 699; HRMS (ESI^+) Calcd for $C_{23}H_{21}N_2O$ ($M+H^+$) 341.1654, Found 341.1656.

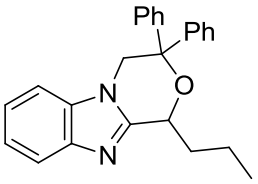
3,3-Bis(4-fluorophenyl)-1-methyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2l).



Reaction conditions: CuBr (10 mol%), 4,7-dimethoxy-1,10-phenanthroline (12 mol%), (^{t}BuO)$_2$ (2.6 equiv), 100 °C, 4 h.

67%, yellow oil, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.55, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (d, *J* = 6.3 Hz, 3H), 4.23 (d, *J* = 12.6 Hz, 1H), 4.66 (q, *J* = 6.3 Hz, 1H), 4.98 (d, *J* = 12.6 Hz, 1H), 6.94 (dd, *J* = 8.6, 8.6 Hz, 2H), 7.06 (dd, *J* = 8.6, 8.6 Hz, 2H), 7.16 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.29–7.36 (m, 2H), 7.37–7.47 (m, 3H), 7.73–7.80 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 49.4, 66.8, 78.0, 108.6, 115.3 (*J* = 21.5 Hz, 2C), 115.9 (*J* = 21.5 Hz, 2C), 119.8, 122.5, 122.9, 127.4 (*J* = 8.4 Hz, 2C), 129.5 (*J* = 8.4 Hz, 2C), 133.6, 134.8 (*J* = 3.6 Hz), 140.0 (*J* = 3.6 Hz), 143.0, 151.4, 162.2 (*J* = 246 Hz), 162.4 (*J* = 248 Hz); IR (neat, ν / cm^{-1}) 1606, 1507, 1455, 1373, 1319, 1230, 1159, 1103, 836, 748; HRMS (ESI$^+$) Calcd for $C_{23}H_{19}F_2N_2O$ (M+H$^+$) 377.1465, Found 377.1451.

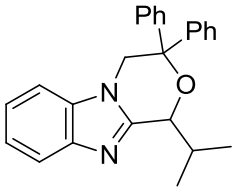
3,3-Diphenyl-1-propyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2m).



Reaction conditions: CuBr (10 mol%), 4,7-dimethoxy-1,10-phenanthroline (12 mol%), (^{t}BuO)$_2$ (2.6 equiv), 100 °C, 4 h.

71%, yellow oil, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.67, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.5 Hz, 3H), 1.73 (q, *J* = 7.5 Hz, 2H), 2.13–2.22 (m, 1H), 2.30–2.40 (m, 1H), 4.28 (d, *J* = 12.6 Hz, 1H), 4.67 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 7.21–7.31 (m, 5H), 7.32–7.44 (m, 5H), 7.45–7.53 (m, 3H), 7.78 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 18.3, 35.8, 49.0, 69.9, 78.4, 108.6, 119.6, 122.2, 122.6, 125.4 (2C), 127.5 (2C), 127.7, 128.2, 128.4 (2C), 128.8, 133.7, 139.1, 143.1, 144.6, 151.2; IR (neat, ν / cm^{-1}) 2959, 1518, 1474, 1455, 1428, 1375, 1327, 1218, 1072, 744, 699; HRMS (ESI$^+$) Calcd for $C_{25}H_{25}N_2O$ (M+H$^+$) 369.1967, Found 369.1956.

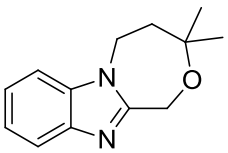
1-Isopropyl-3,3-diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2n).



Reaction conditions: CuBr (10 mol%), 4,7-dimethoxy-1,10-phenanthroline (12 mol%), (^{t}BuO)$_2$ (2.6 equiv), 100 °C, 4 h.

41%, yellow oil, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.66, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (d, *J* = 6.9 Hz, 3H), 1.28 (d, *J* = 6.9 Hz, 3H), 2.70–2.80 (m, 1H), 4.23 (d, *J* = 12.9 Hz, 1H), 4.57 (s, 1H), 5.06 (d, *J* = 12.9 Hz, 1H), 7.15–7.25 (m, 5H), 7.27–7.42 (m, 5H), 7.44–7.50 (m, 3H), 7.75 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.4, 19.0, 32.4, 49.0, 74.5, 78.2, 108.5, 119.6, 122.2, 122.6, 125.4 (2C), 127.4 (2C), 127.7, 128.2, 128.4 (2C), 128.8 (2C), 133.7, 139.0, 143.1, 144.7, 150.7; IR (neat, ν / cm^{-1}) 2964, 1454, 1227, 1064, 1024, 753, 699; HRMS (ESI$^+$) Calcd for $C_{25}H_{25}N_2O$ (M+H$^+$) 369.1967, Found 369.1951.

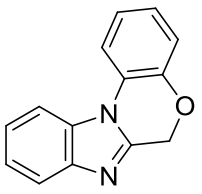
3,3-Dimethyl-1,3,4,5-tetrahydrobenzo[4,5]imidazo[2,1-*c*][1,4]oxazepine (2o).



Reaction conditions: CuBr (5.0 mol%), 5,6-dimethyl-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 12 h.

21%, yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/3), TLC (hexane/ethyl acetate = 1/2): R_f = 0.25, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (s, 6H), 2.21 (t, *J* = 5.2 Hz, 2H), 4.24 (t, *J* = 5.2 Hz, 2H), 4.94 (s, 2H), 7.21–7.34 (m, 3H), 7.70 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.3 (2C), 38.7, 39.8, 59.9, 75.7, 108.9, 119.5, 122.0, 122.3, 135.5, 142.5, 153.9; IR (neat, ν / cm^{-1}) 1455, 1374, 1085, 747; HRMS (ESI$^+$) Calcd for $C_{13}H_{16}N_2O$ (M+H$^+$) 217.1341, Found 217.1350.

6*H*-Benzo[*b*]benzo[4,5]imidazo[1,2-*d*][1,4]oxazine (2p).

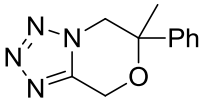


Reaction conditions: CuBr (20 mol%), 5,6-dimethyl-1,10-phenanthroline (24 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 12 h.

59%, yellow solid, purification: silica gel column chromatography

(hexane/ethyl acetate = 1/3), TLC (ethyl acetate): R_f = 0.72, ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (s, 2H), 7.19–7.22 (m, 3H), 7.34–7.42 (m, 2H), 7.80–7.88 (m, 2H), 7.90 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.5, 111.3, 116.2, 118.4, 120.6, 123.2, 123.3, 124.0, 126.0, 126.4, 131.3, 143.7, 146.4, 146.6; IR (neat, ν / cm^{-1}) 1621, 1550, 1504, 1465, 1399, 1343, 1237, 1215, 1031, 738; HRMS (ESI^+) Calcd for $C_{14}H_{11}N_2O$ ($M+H^+$) 223.0871, Found 223.0871.

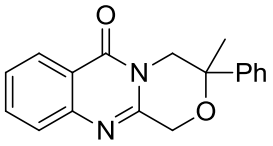
6-Methyl-6-phenyl-6,8-dihydro-5*H*-tetrazolo[5,1-*c*][1,4]oxazine (2q).



Reaction conditions: $CuBr_2$ (10 mol%), 4,7-dimethoxy-1,10-phenanthroline (12 mol%), (^{t}BuO)$_2$ (2.6 equiv), 100 °C, 6 h.

44%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.45, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 3H), 4.47 (d, *J* = 13.4 Hz, 1H), 4.74 (d, *J* = 16.6 Hz, 1H), 5.09 (d, *J* = 13.4 Hz, 1H), 5.11 (d, *J* = 16.6 Hz, 1H), 7.27–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5, 51.8, 57.9, 75.5, 125.3, 128.8, 129.2, 138.5, 149.1; IR (neat, ν / cm^{-1}) 2981, 1448, 1380, 1346, 1295, 1158, 1065, 836, 765, 701; HRMS (ESI^+) Calcd for $C_{11}H_{12}N_4ONa$ ($M+Na^+$) 239.0909, Found 239.0915.

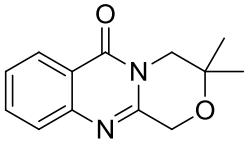
3-Methyl-3-phenyl-3,4-dihydro-[1,4]oxazino[3,4-b]quinazolin-6(1*H*)-one (2r).



Reaction conditions: $CuBr_2$ (5.0 mol%), 4,7-dimethoxy-1,10-phenanthroline (6.0 mol%), (^{t}BuO)$_2$ (1.3 equiv), 100 °C, 12 h.

49%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/2), TLC (hexane/ethyl acetate = 1/1): R_f = 0.39, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66 (s, 3H), 3.96 (d, *J* = 14.4 Hz, 1H), 4.58 (d, *J* = 16.9 Hz, 1H), 4.82 (d, *J* = 16.9 Hz, 1H), 5.01 (d, *J* = 14.4 Hz, 1H), 7.24–7.29 (m, 1H), 7.30–7.38 (m, 4H), 7.45 (td, *J* = 7.4, 1.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.71 (td, *J* = 6.9, 1.1 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 46.8, 63.4, 75.7, 120.3, 125.3 (2C), 126.5, 126.6, 126.8, 128.1, 129.1 (2C), 134.6, 140.3, 147.1, 150.8, 161.2; IR (neat, ν / cm^{-1}) 3442, 1673, 1600, 1469, 1335, 1088, 765, 699; HRMS (ESI^+) Calcd for $C_{18}H_{16}N_2O_2Na$ ($M+Na^+$) 315.1109, Found 315.1099.

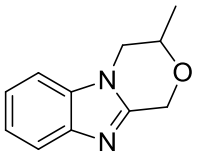
3,3-Dimethyl-3,4-dihydro-[1,4]oxazino[3,4-*b*]quinazolin-6(1*H*)-one (2s).



Reaction conditions: $CuBr_2$ (5.0 mol%), 4,7-dimethoxy-1,10-phenanthroline (6.0 mol%), ($^tBuO)_2$ (1.3 equiv), 100 °C, 12 h.

50%, white solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/2), TLC (hexane/ethyl acetate = 1/2): R_f = 0.53, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 6H), 3.94 (s, 2H), 4.78 (s, 2H), 7.47 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.7 (2C), 49.3, 62.9, 71.3, 120.5, 126.5, 126.7, 126.8, 134.6, 147.2, 151.0, 161.5; IR (neat, ν / cm^{-1}) 3420, 1671, 1596, 1475, 1381, 1323, 1215, 1163, 1102, 770, 697; HRMS (ESI^+) Calcd for $C_{13}H_{14}N_2O_2Na$ ($M+Na^+$) 253.0953, Found 253.0956.

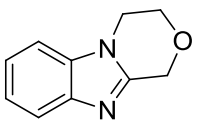
3-Methyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2t).



Reaction conditions: $CuBr_2$ (10 mol%), 4,7-dimethoxy -1,10-phenanthroline (12 mol%), ($^tBuO)_2$ (2.6 equiv), 100 °C, 4 h.

40%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/2), TLC (hexane/ethyl acetate = 1/2): R_f = 0.18, ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (d, *J* = 6.3 Hz, 3H), 3.81 (dd, *J* = 10.4, 10.4 Hz, 1H), 4.05-4.15 (m, 2H), 4.96 (d, *J* = 16.1 Hz, 1H), 5.15 (d, *J* = 16.1 Hz, 1H), 7.23-7.33 (m, 3H), 7.71 (dd, *J* = 6.3, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.7, 47.9, 64.9, 70.1, 108.7, 119.4, 122.3, 122.6, 133.8, 142.7, 147.8; IR (neat, ν / cm^{-1}) 2872, 1480, 1424, 1329, 1280, 1097, 862, 744; HRMS (ESI^+) Calcd for $C_{11}H_{13}N_2O$ ($M+H^+$) 189.1028, Found 189.1021.

3,4-Dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine (2u).



Reaction conditions: CuBr (10 mol%), 5,6-dimethyl-1,10-phenanthroline (12 mol%), ($^tBuO)_2$ (2.6 equiv), 100 °C, 4 h.

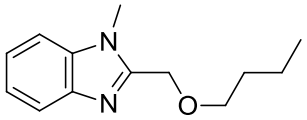
24%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/3), TLC (hexane/ethyl acetate = 1/1): R_f = 0.10, ^{1}H NMR (500 MHz,

$CDCl_3$) δ 4.15-4.23 (m, 4H), 5.04 (s, 2H), 7.27-7.36 (m, 3H), 7.70-7.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.0, 64.0, 65.5, 108.7, 119.5, 122.3, 122.6, 134.0, 142.7, 147.8; IR (neat, ν / cm^{-1}) 2923, 1523, 1451, 1373, 1321, 1096, 984, 920, 878, 745; HRMS (ESI^+) Calcd for $C_{10}H_{11}N_2O$ ($M+H^+$) 175.0871, Found 175.0865.

Gram-scale procedure for copper-catalyzed C(sp^3)-H alkoxylation. A mixture of 2-(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-diphenylethanol (**1a**, 1.64 g, 5.00 mmol), CuBr (35.9 mg, 0.25 mmol), 5,6-dimethyl-1,10-phenanthroline (62.5 mg, 0.300 mmol), (^{t}BuO)$_2$ (0.950 g, 6.50 mmol), and chlorobenzene (50 mL) was stirred at 100 °C for 6 h. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give 3,3-diphenyl-3,4-dihydro-1*H*-benzo[4,5]imidazo[2,1-*c*][1,4]oxazine **2a** (1.37 g, 84% yield).

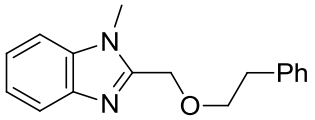
Typical procedure for intermolecular alkoxylation. A mixture of 1,2-dimethyl-1H-benzo[d]imidazole[5] (**3**, 18.3 mg, 0.125 mmol), 2-phenylethyl alcohol (**4b**, 30.5 mg, 0.250 mmol), CuBr (3.6 mg, 25.0 μmol), 5,6-dimethyl-1,10-phenanthroline (6.2 mg, 30.0 μmol), (^{t}BuO)$_2$ (73.3 mg, 0.501 mmol), and chlorobenzene (2.50 mL) was stirred at 100 °C for 3 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/2) to give **5b** (12.2 mg, 37% yield).

2-(Butoxymethyl)-1-methyl-1*H*-benzo[*d*]imidazole (5a).



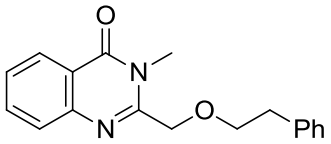
33%, yellow oil, purification: silica gel column chromatography (hexane/ethyl acetate = 1/2), TLC (hexane/ethyl acetate = 1/1): R_f = 0.30, ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.5 Hz, 3H), 1.35 (qt, *J* = 7.5, 7.5 Hz, 2H), 1.54–1.61 (m, 2H), 3.50 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 4.80 (s, 2H), 7.26–7.33 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 19.2, 27.4, 31.6, 65.7, 70.5, 109.2, 119.9, 122.1, 122.9, 136.3, 142.2, 191.0; IR (KBr, ν / cm^{-1}) 2957, 2870, 1617, 1477, 1398, 1333, 1238, 1096, 1005, 741; HRMS (ESI^+) Calcd for $C_{13}H_{19}N_2O$ ($M+H^+$) 219.1497, Found 219.1501.

1-Methyl-2-(phenethoxymethyl)-1*H*-benzo[*d*]imidazole (5b).



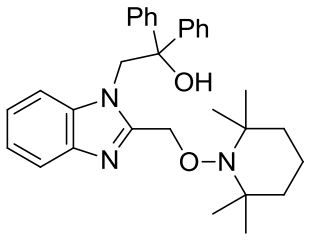
37%, yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.13, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, *J* = 6.7 Hz, 2H), 3.56 (s, 3H), 3.71 (t, *J* = 6.7 Hz, 2H), 4.77 (s, 2H), 7.08–7.31 (m, 8H), 7.71 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.8, 36.1, 65.7, 71.1, 109.3, 119.9, 122.1, 122.9, 126.2, 128.3 (2C), 128.8 (2C), 136.2, 138.8, 142.1, 150.6; IR (neat, ν / cm^{-1}) 2936, 1705, 1477, 1397, 1333, 1097, 743, 700; HRMS (ESI^+) Calcd for $C_{17}H_{19}N_2O$ ($M+H^+$) 267.1497, Found 267.1496.

3-Methyl-2-(phenethoxymethyl)quinazolin-4(3*H*)-one (7).



30%, yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.45, ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92 (t, *J* = 8.6 Hz, 2H), 3.52 (s, 3H), 3.82 (t, *J* = 8.6 Hz, 4.61 (s, 2H), 7.15-7.29 (m, 5H), 7.49 (dt, *J* = 1.8, 8.6 Hz, 1H), 7.67 (d, *J* = 10.9 Hz, 1H), 7.74 (dt, *J* = 1.7, 10.9 Hz, 1H), 8.27 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.4, 36.2, 71.7, 72.7, 120.9, 126.4, 126.7, 127.2, 127.3, 128.4 (2C), 128.8 (2C), 134.1, 138.4, 146.8, 152.7, 162.4; IR (neat, ν / cm^{-1}) 2924, 1679, 1603, 1474, 1367, 1107, 776, 698, 611; HRMS (ESI^+) Calcd for $C_{18}H_{19}N_2O_2$ ($M+H^+$) 295.1447, Found 295.1433.

1,1-Diphenyl-2-(2-(((2,2,6,6-tetramethyl-1-piperidinyl)oxy)methyl)-1*H*-benzo[*d*]imidazol-1-yl)ethanol (8).

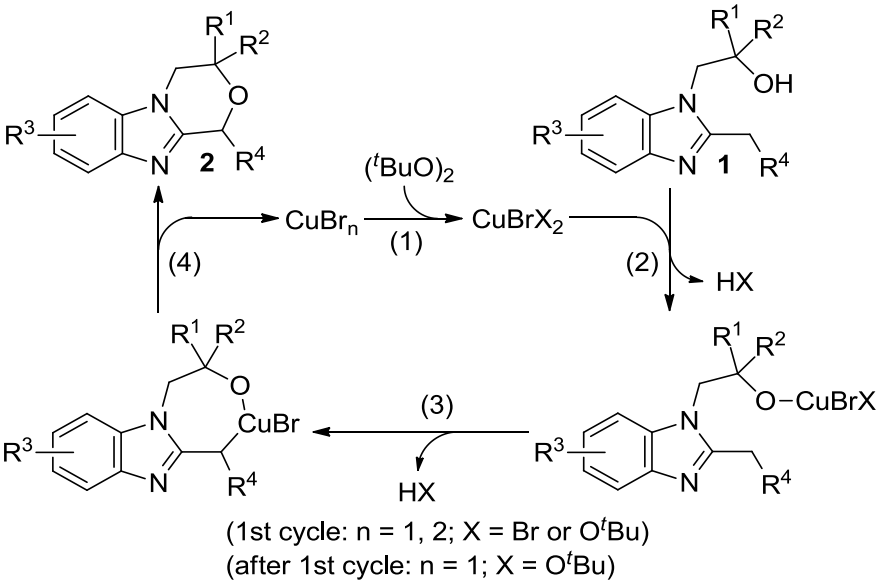


45%, pale yellow solid, purification: silica gel column chromatography (hexane/ethyl acetate = 1/1), TLC (hexane/ethyl acetate = 1/1): R_f = 0.45, ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (s, 6H), 1.14 (s, 6H), 1.20-1.55 (m, 6H), 3.88 (s, 1H), 4.76 (s, 2H), 5.13 (s, 2H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.89 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.20-7.39 (m, 10H), 7.67 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.9, 20.2 (4C), 33.1 (2C), 39.8 (2C), 54.9, 60.1, 72.6, 111.2, 119.6, 121.7, 122.4, 126.4 (4C), 127.6 (2C), 128.4 (4C),

136.1, 142.0, 145.4 (2C), 151.2; IR (neat, ν / cm^{-1}) 3191, 2932, 1463, 1415, 1361, 1242, 1132, 1030, 752, 700; HRMS (ESI^+) Calcd for $C_{31}H_{38}N_3O_2$ ($M+H^+$) 484.2964, Found 484.2986.

Another possible mechanism for the alkoxylation reaction: (1) oxidation of a copper catalyst CuBr (or $CuBr_2$) by (^{t}BuO)$_2$;[8] (2) formation of an alkoxycopper intermediate via the elimination of ^{t}BuOH (in the case of $CuBr_2$: ^{t}BuOH or HBr);[9] (3) formation of a metalacyclic intermediate via the elimination of ^{t}BuOH (in the case of $CuBr_2$: ^{t}BuOH or HBr) (C-H bond activation); and (4) reductive elimination to give the product and regenerate CuBr.

Scheme S1 Proposed mechanism for the catalytic benzylic C(sp^3)-H alkoxylation.



Asymmetric alkoxylation reaction. A mixture of 2-(2-ethyl-1*H*-benzo[*d*]imidazol-1-yl)-1,1-bis(4-fluorophenyl)ethanol (**1l**, 23.7 mg, 62.6 μmol), $CuBr_2$ (1.4 mg, 6.3 μmol), (-)-spartaine (1.8 mg, 7.7 μmol), (^{t}BuO)$_2$ (23.8 mg, 0.163 mmol), and chlorobenzene (1.25 mL) was stirred at 100 °C for 12 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 1/1) to give **2l*** (3.4 mg, 14% yield). The enantiomeric excesses (11% *ee*) were determined by HPLC analysis on a CHIRAPAK AD-H column (hexane/ethanol = 12/1) with retention time; 6.92 min (minor), 34.4 min (major).

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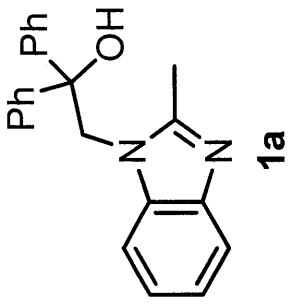
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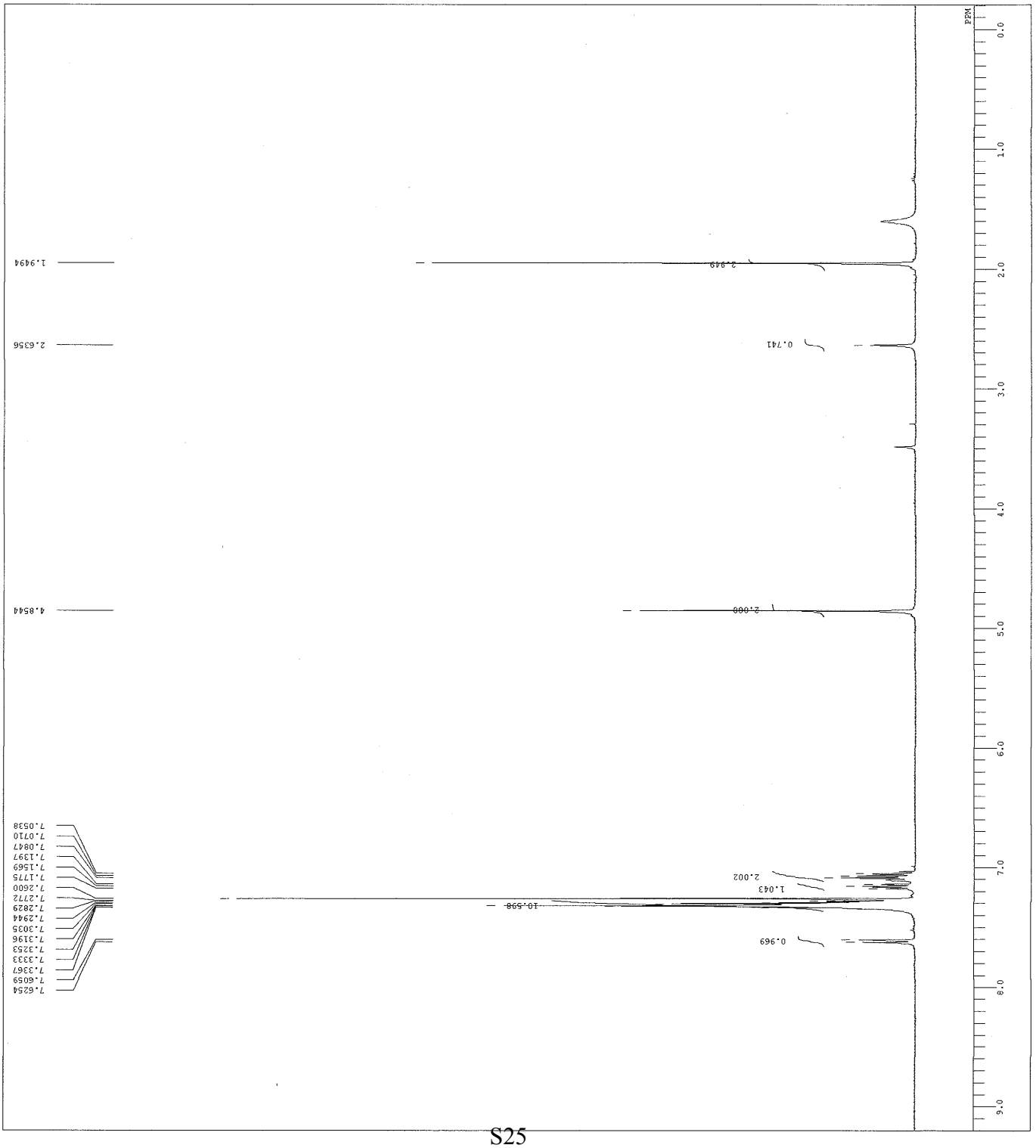
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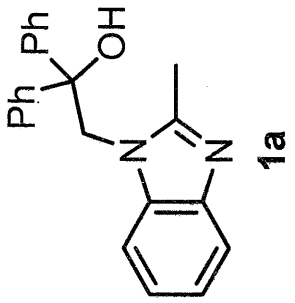
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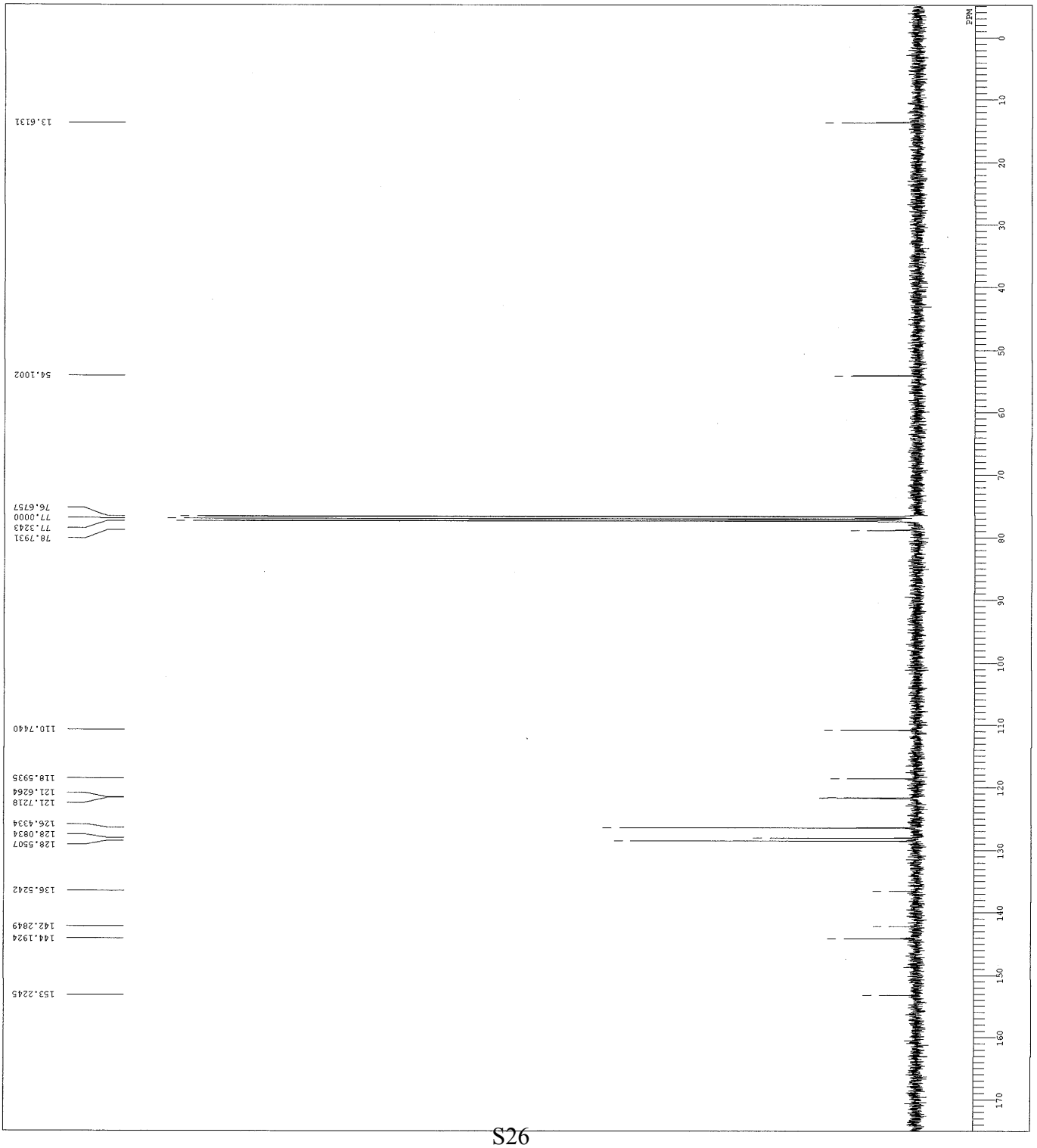
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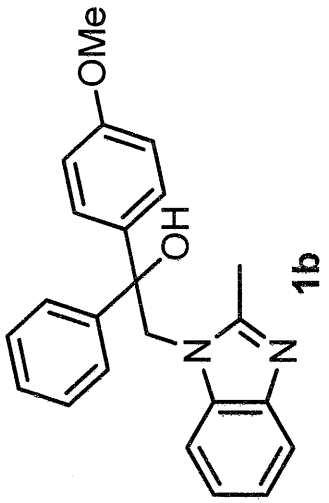
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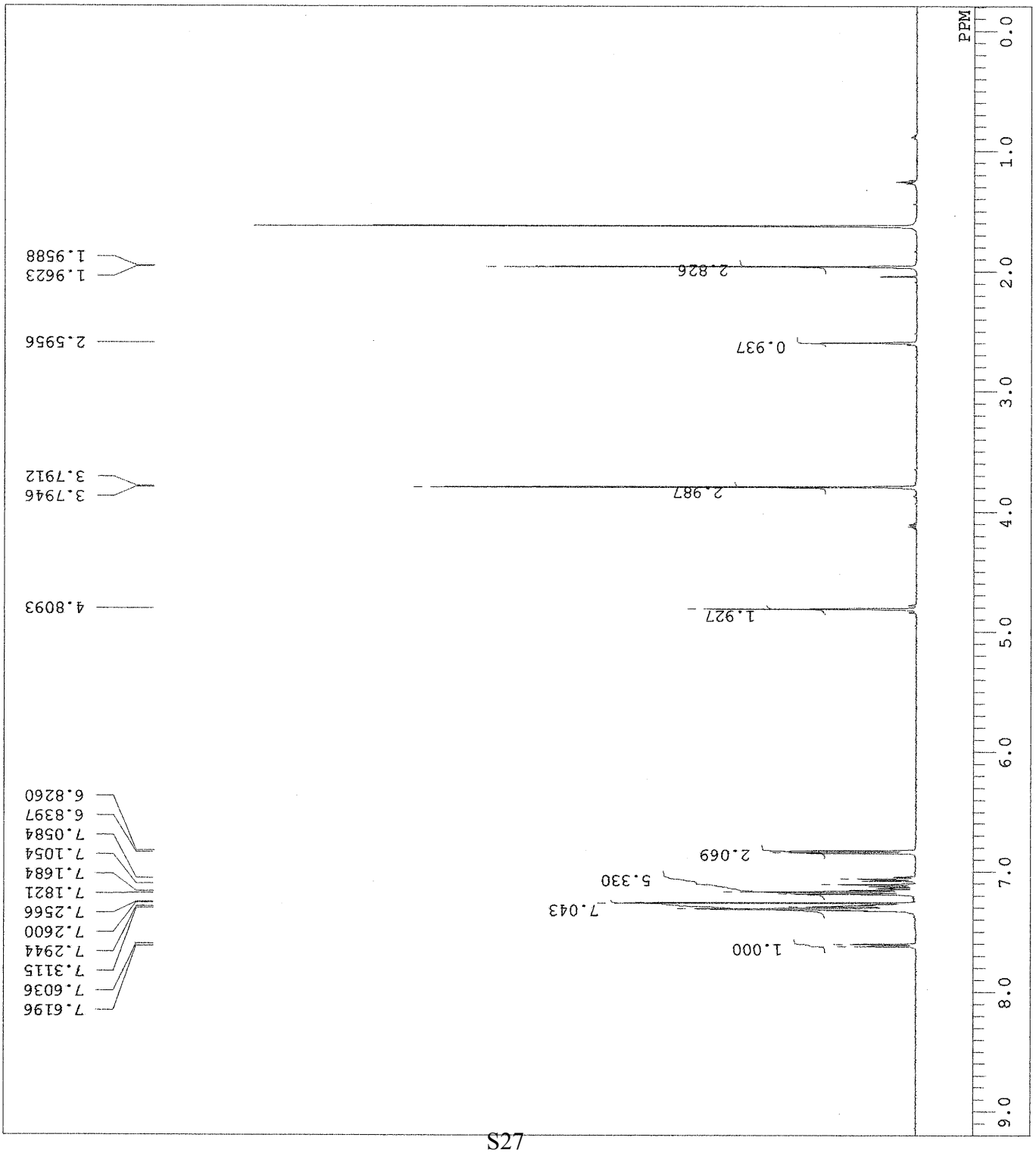
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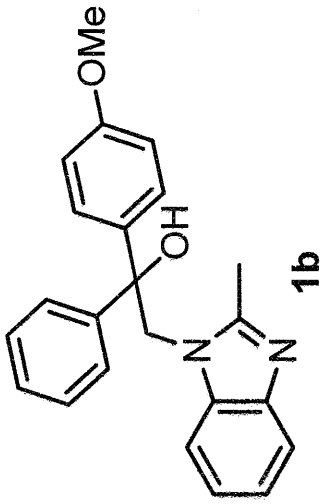
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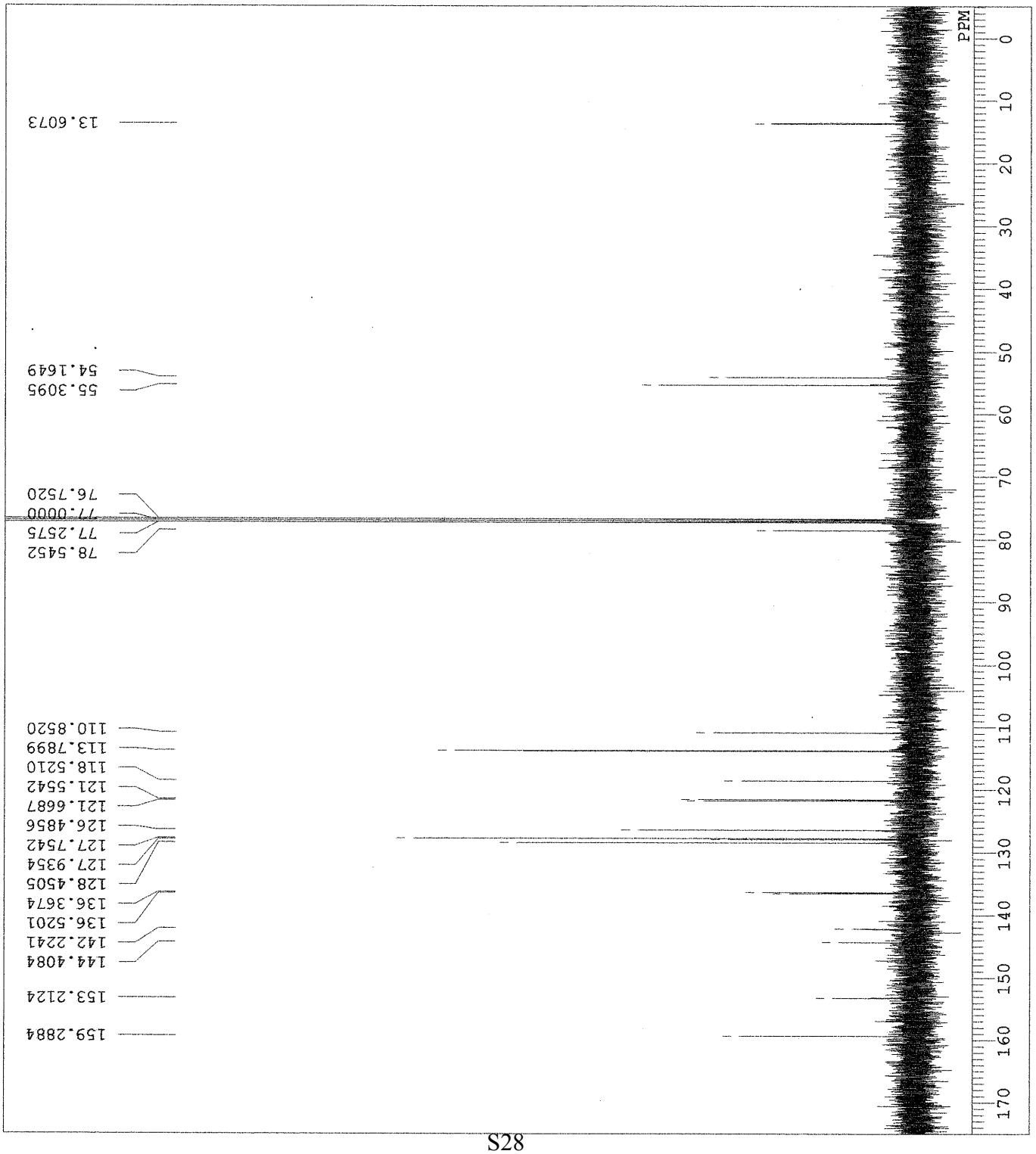
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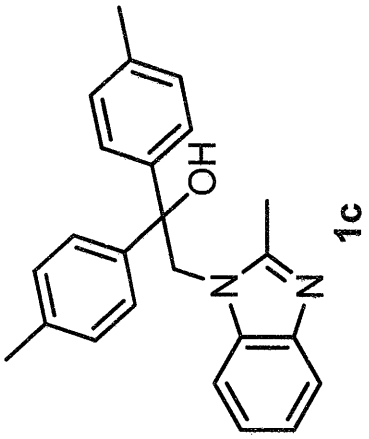
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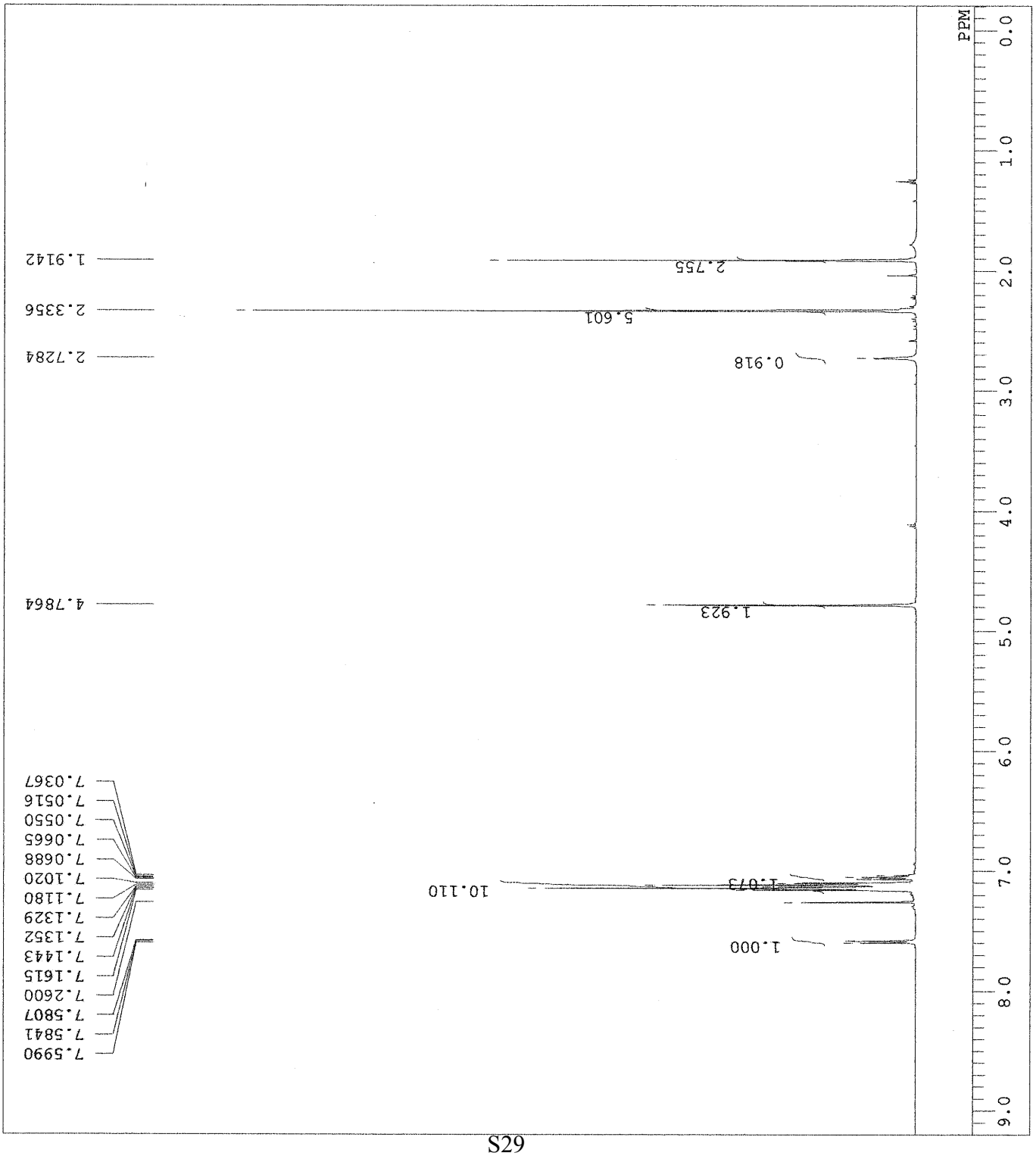
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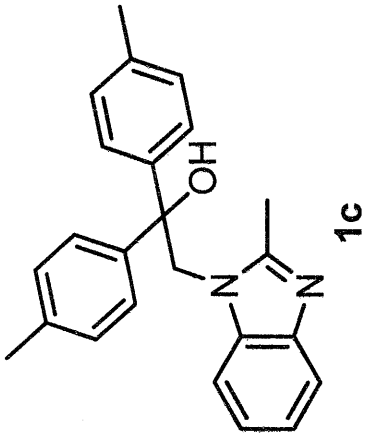
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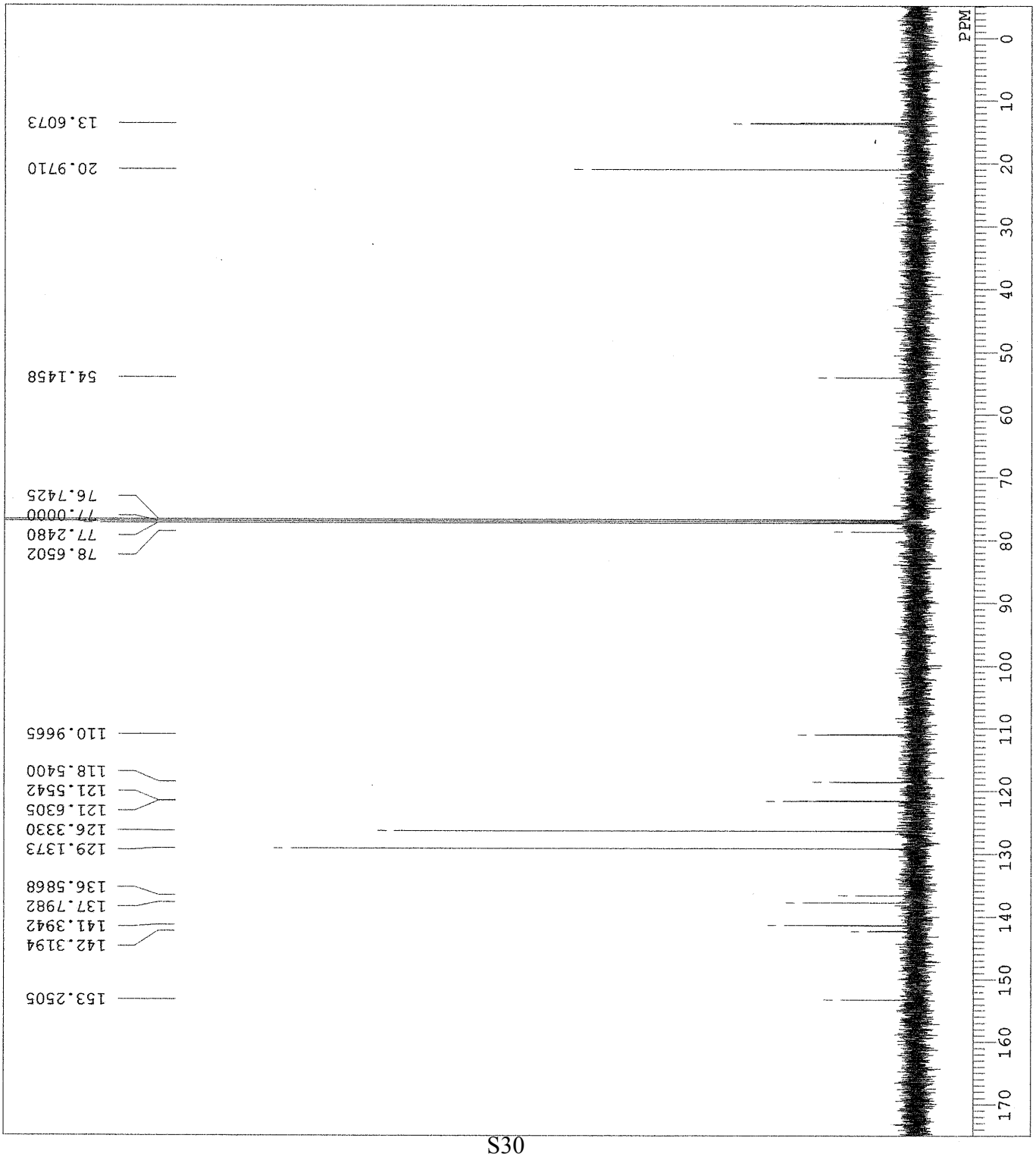
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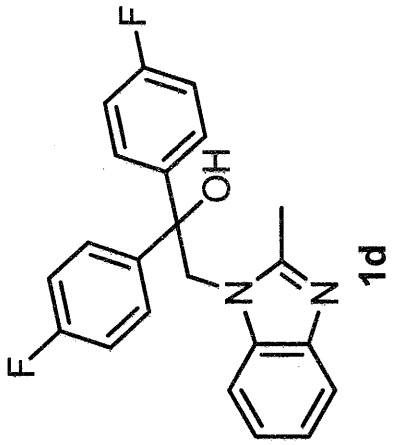
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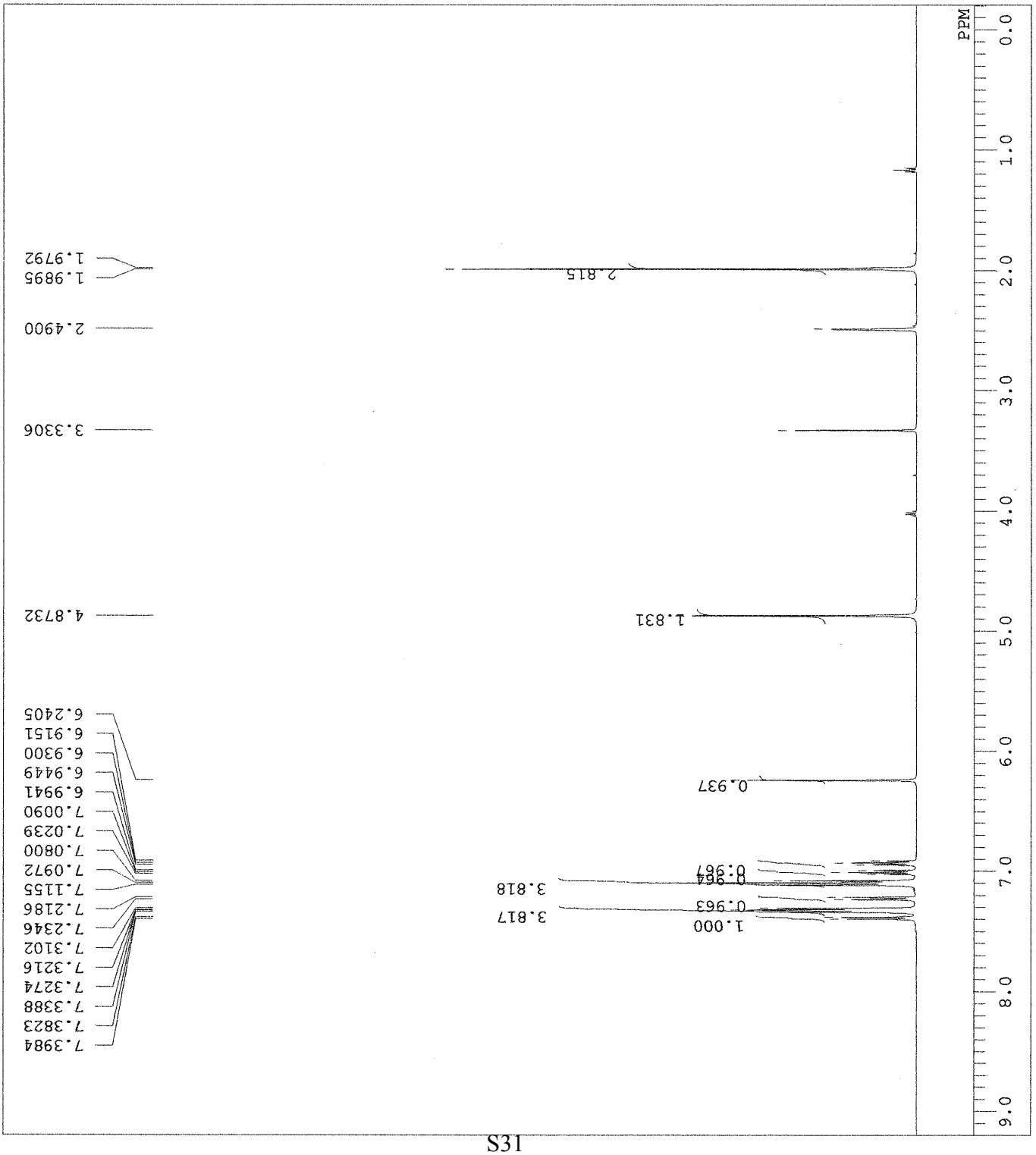
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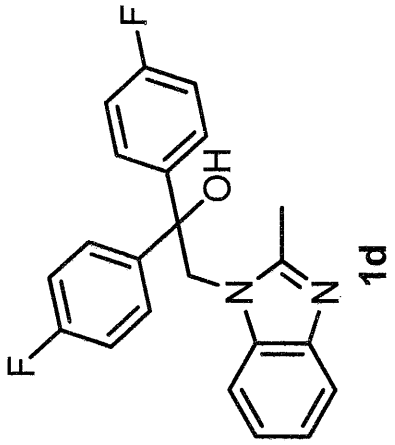
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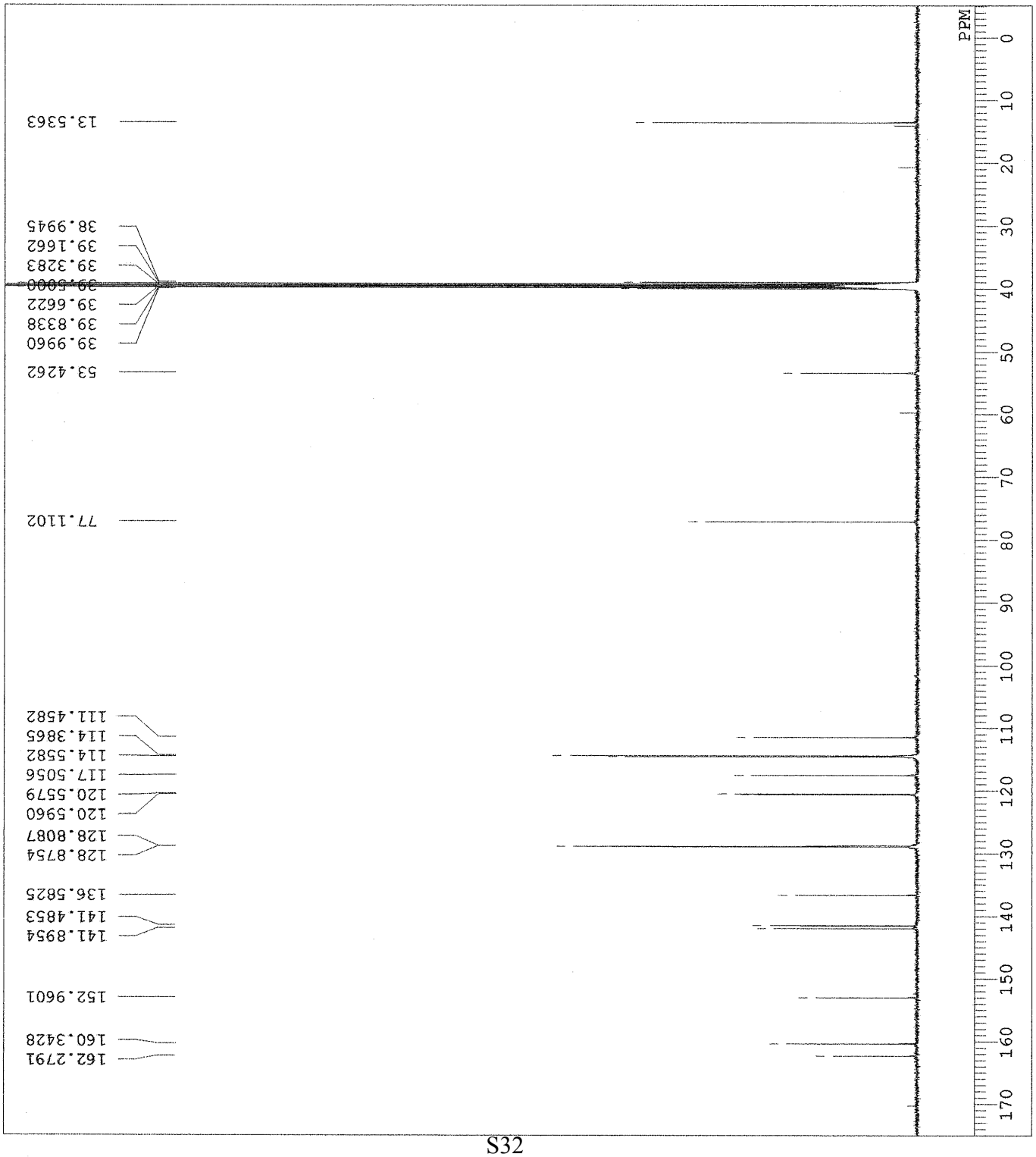
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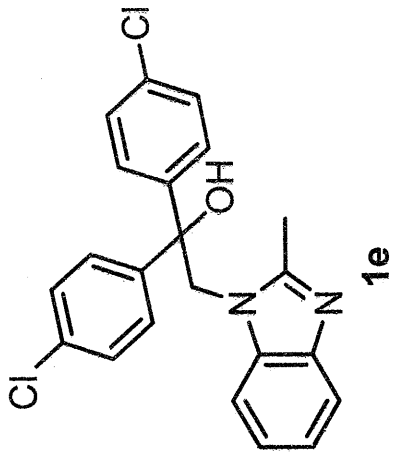
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Cl

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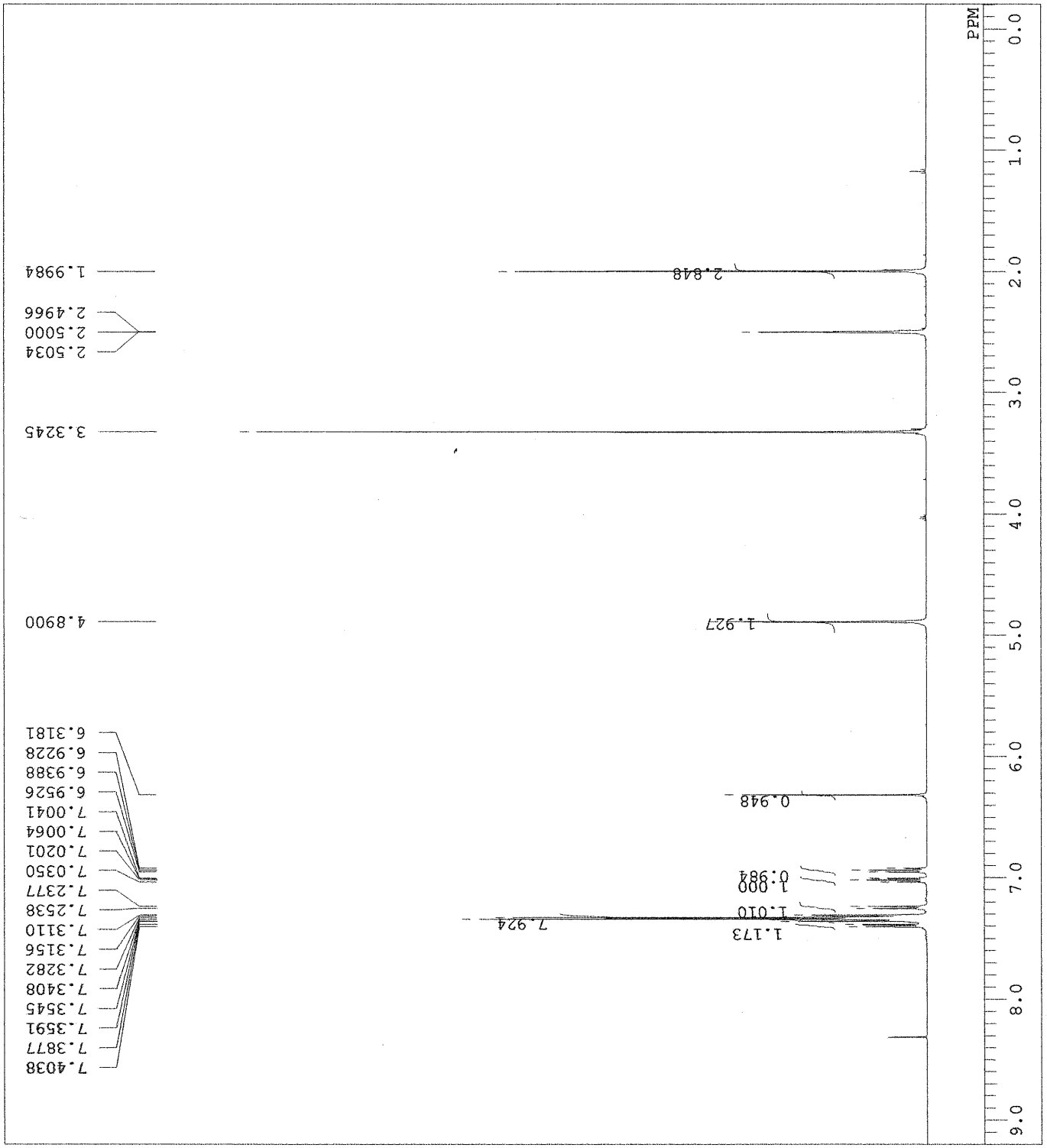
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7.0064
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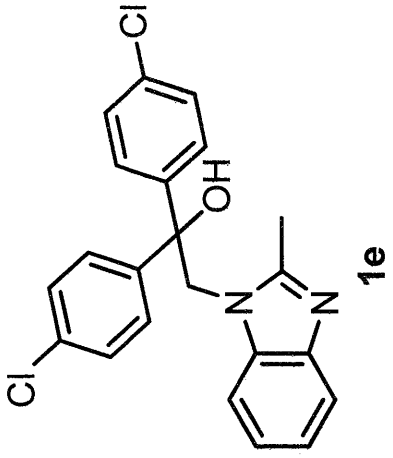
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Cl

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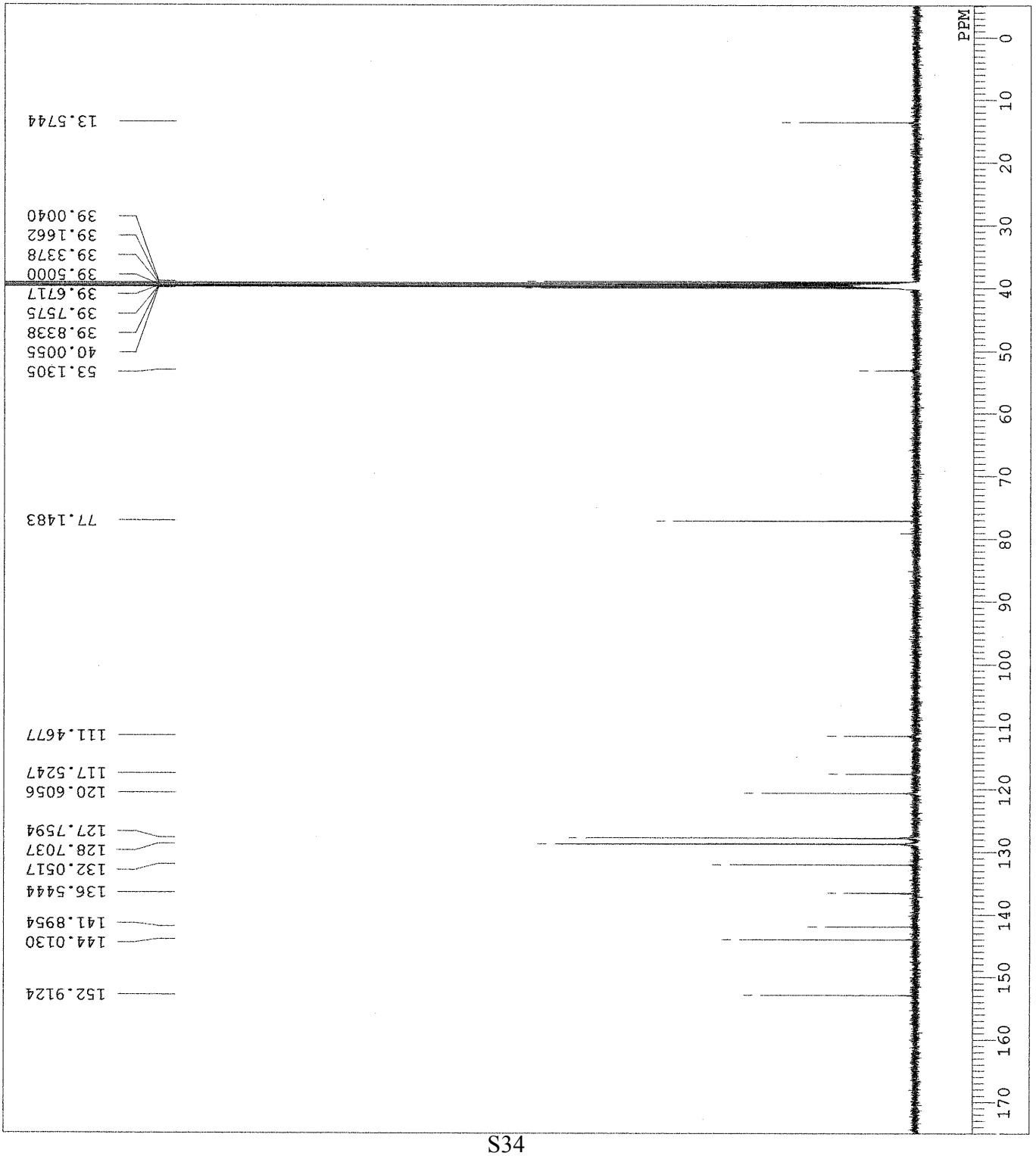
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132.0517
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144.0130
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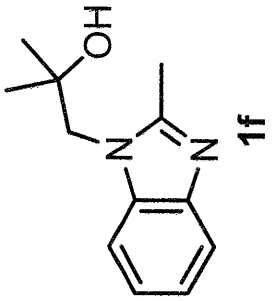
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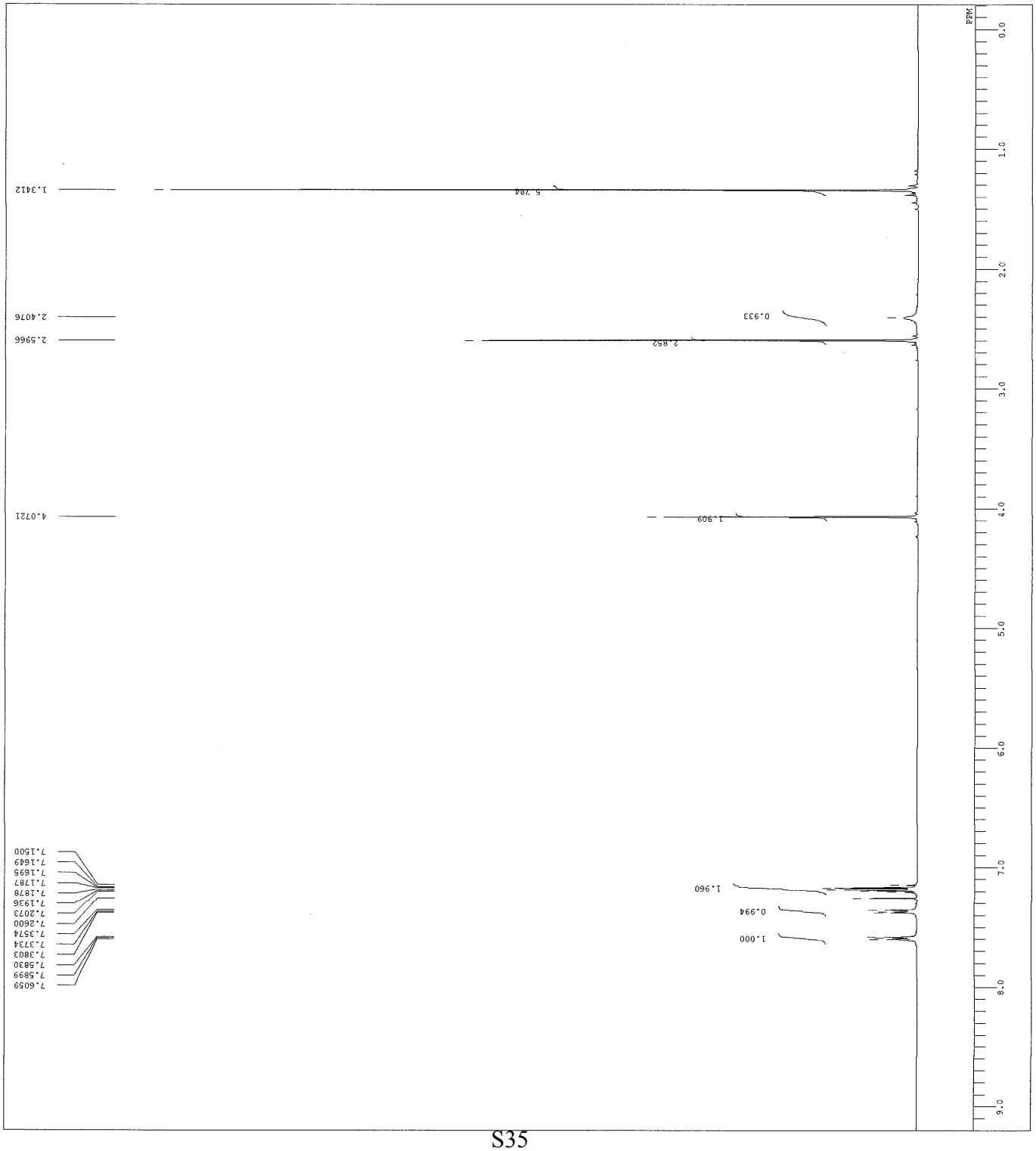
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1.909
1.960
0.994
1.000
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7.5899
7.5830
7.3803
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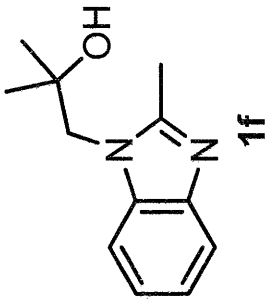
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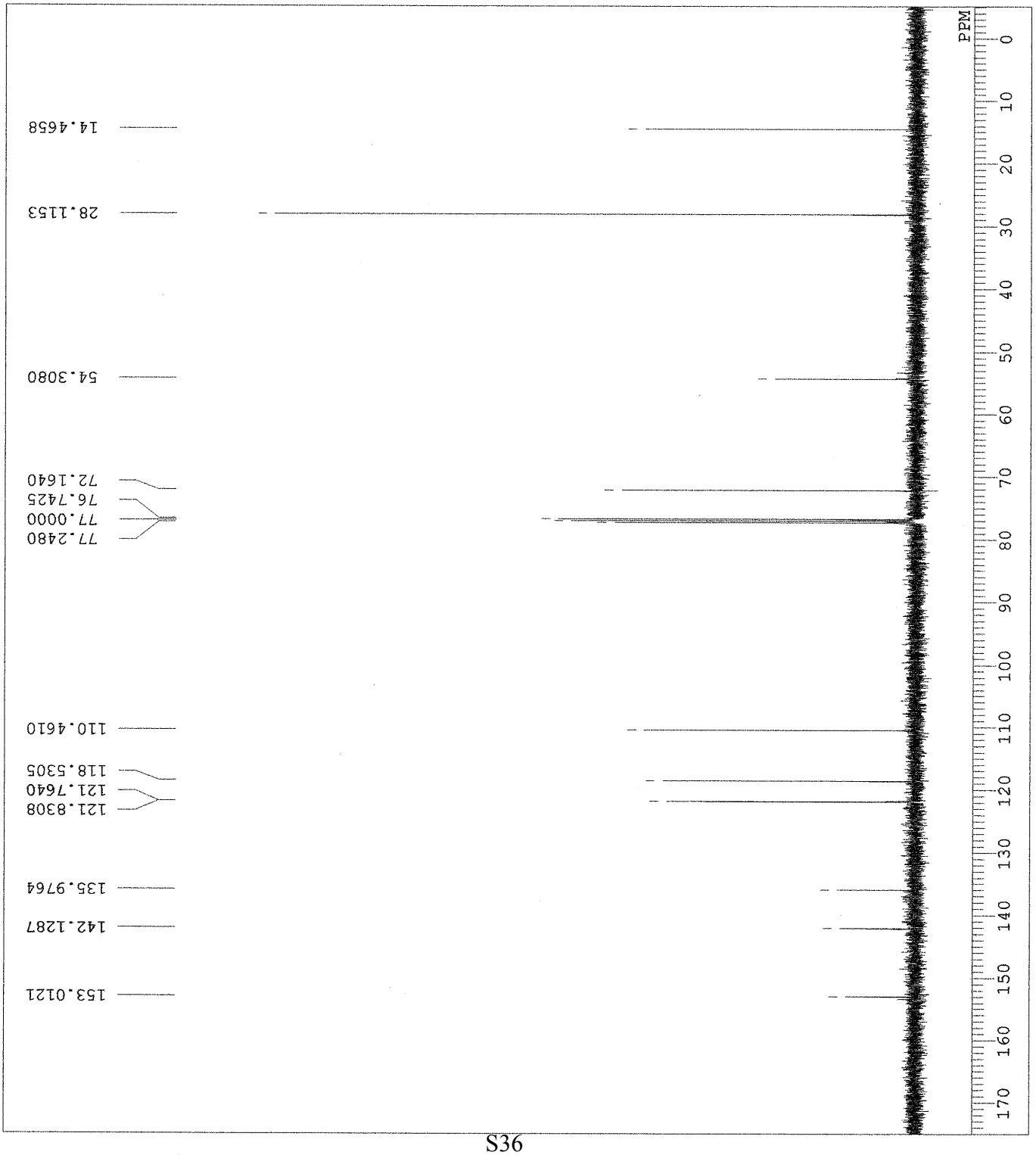
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121.8308
135.9764
142.1287
153.0121
PPM
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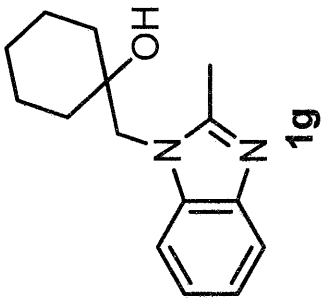
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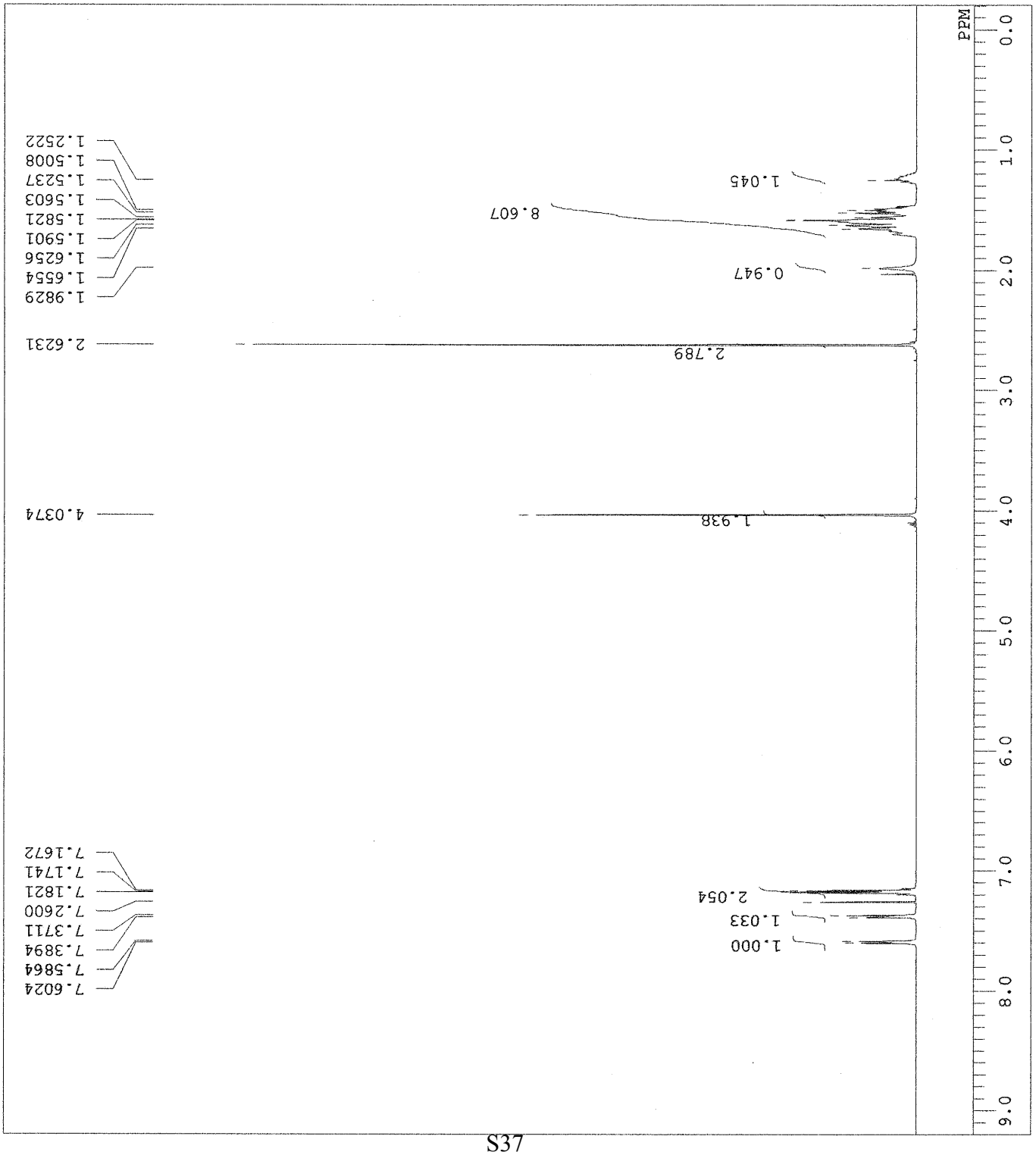
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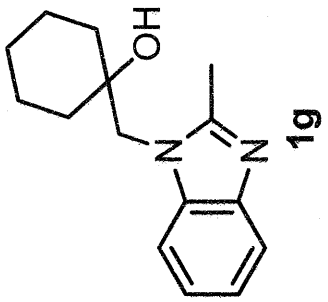
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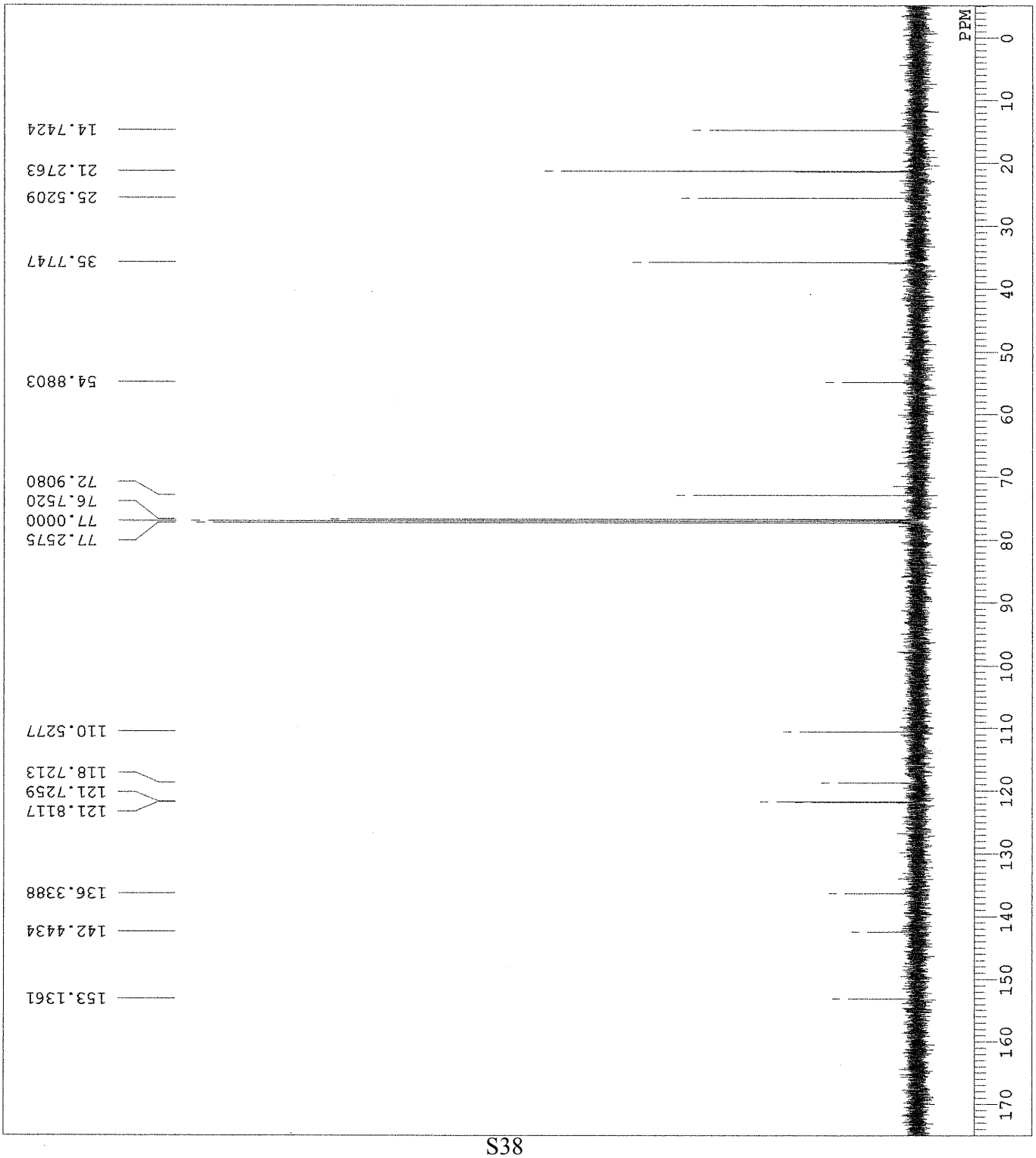
N
1g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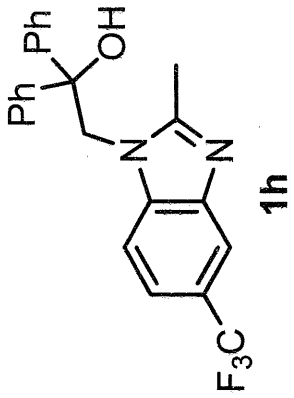
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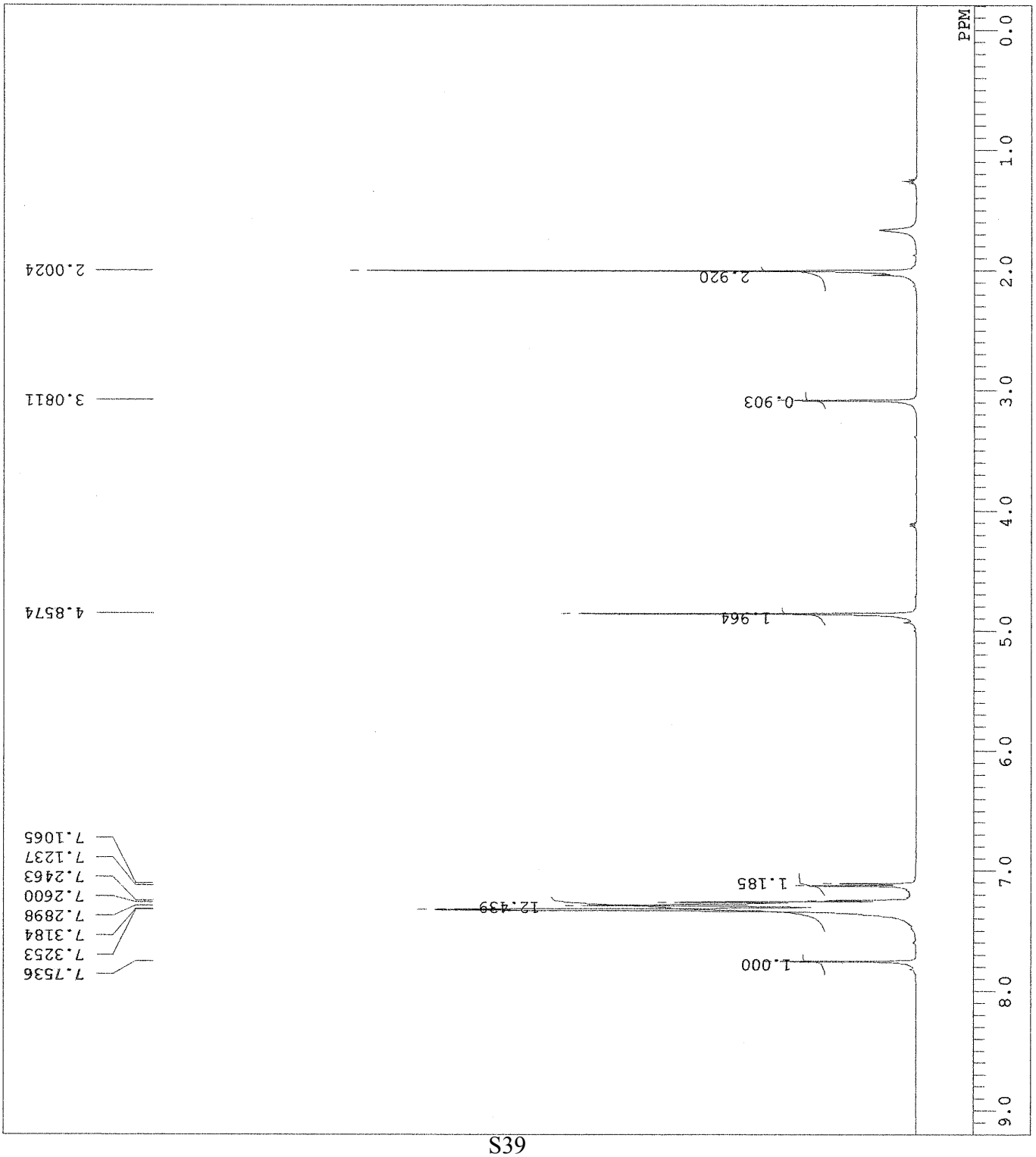
N
F3C

1h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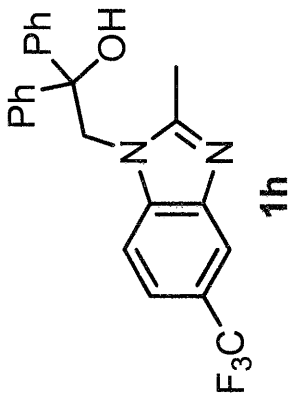
2.920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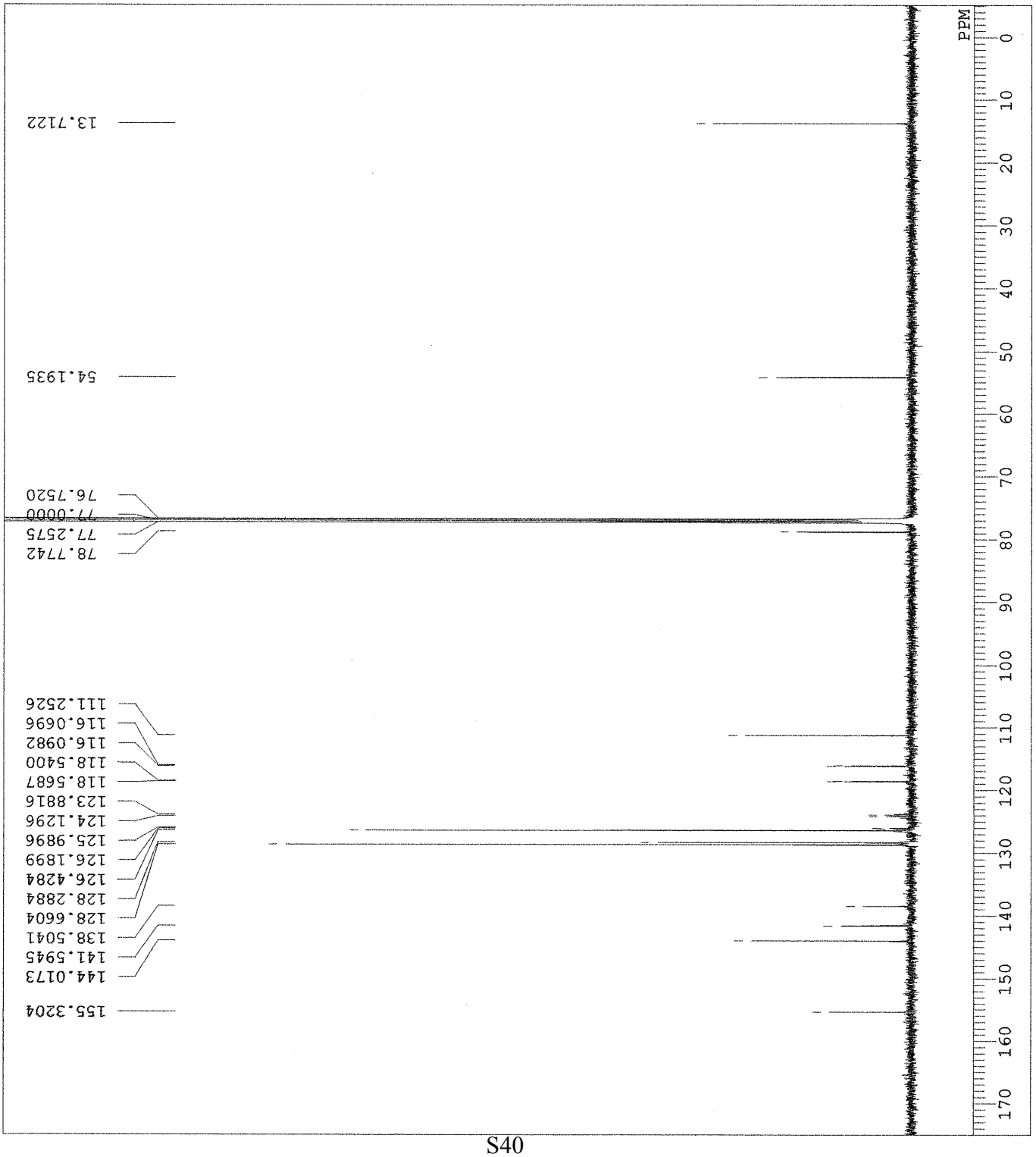
N
F3C

1h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125.9896
126.1899
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128.6604
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141.5945
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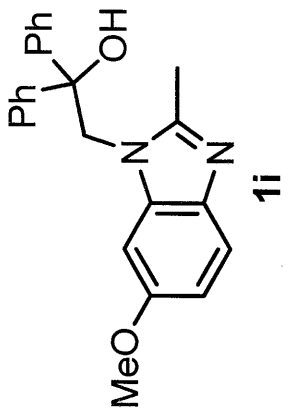
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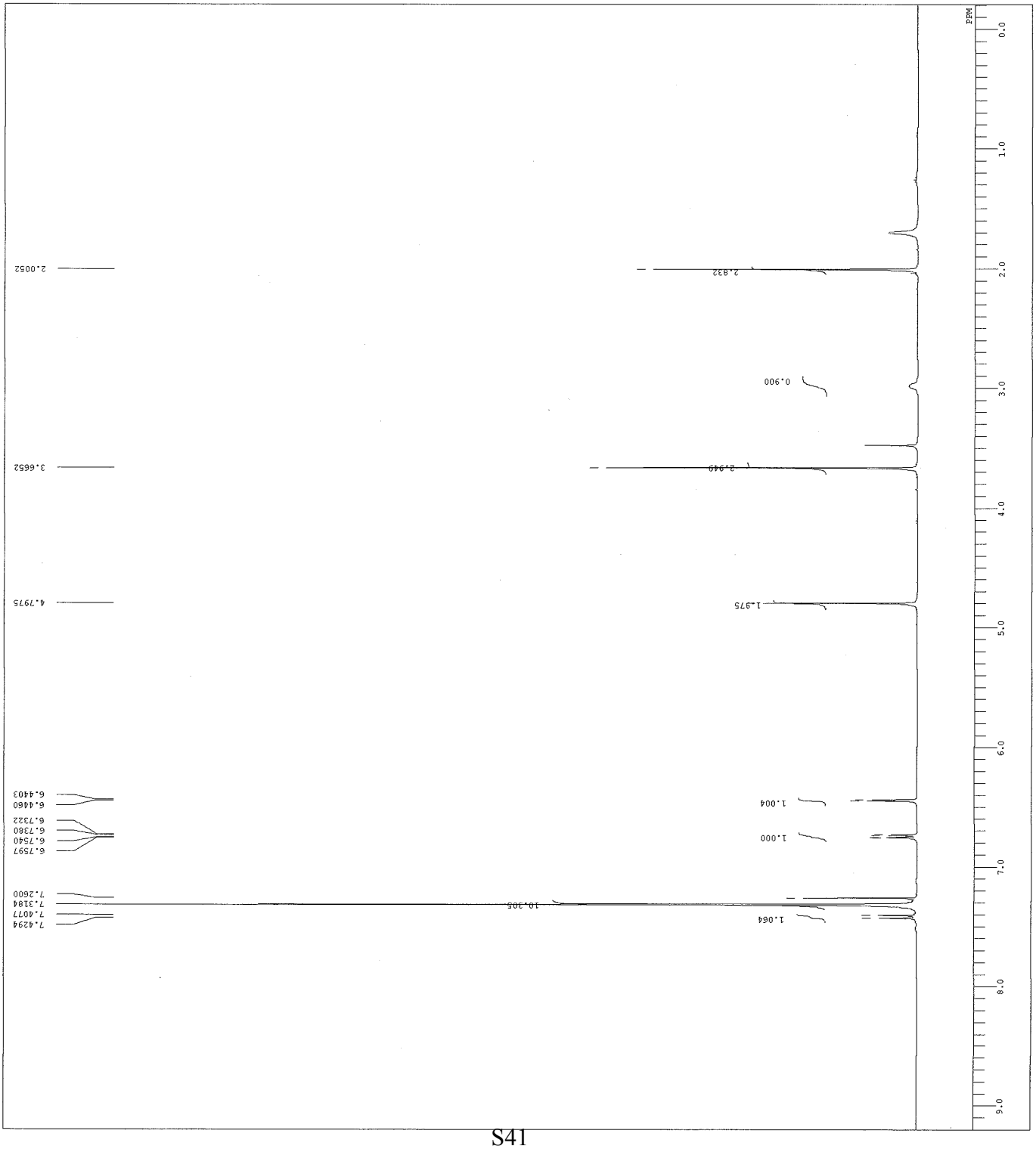
N
MeO

1i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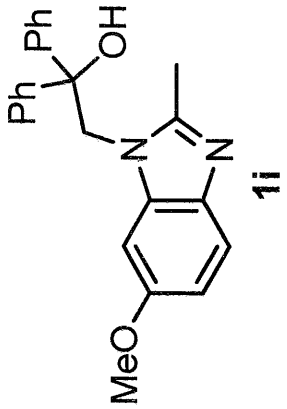
PPM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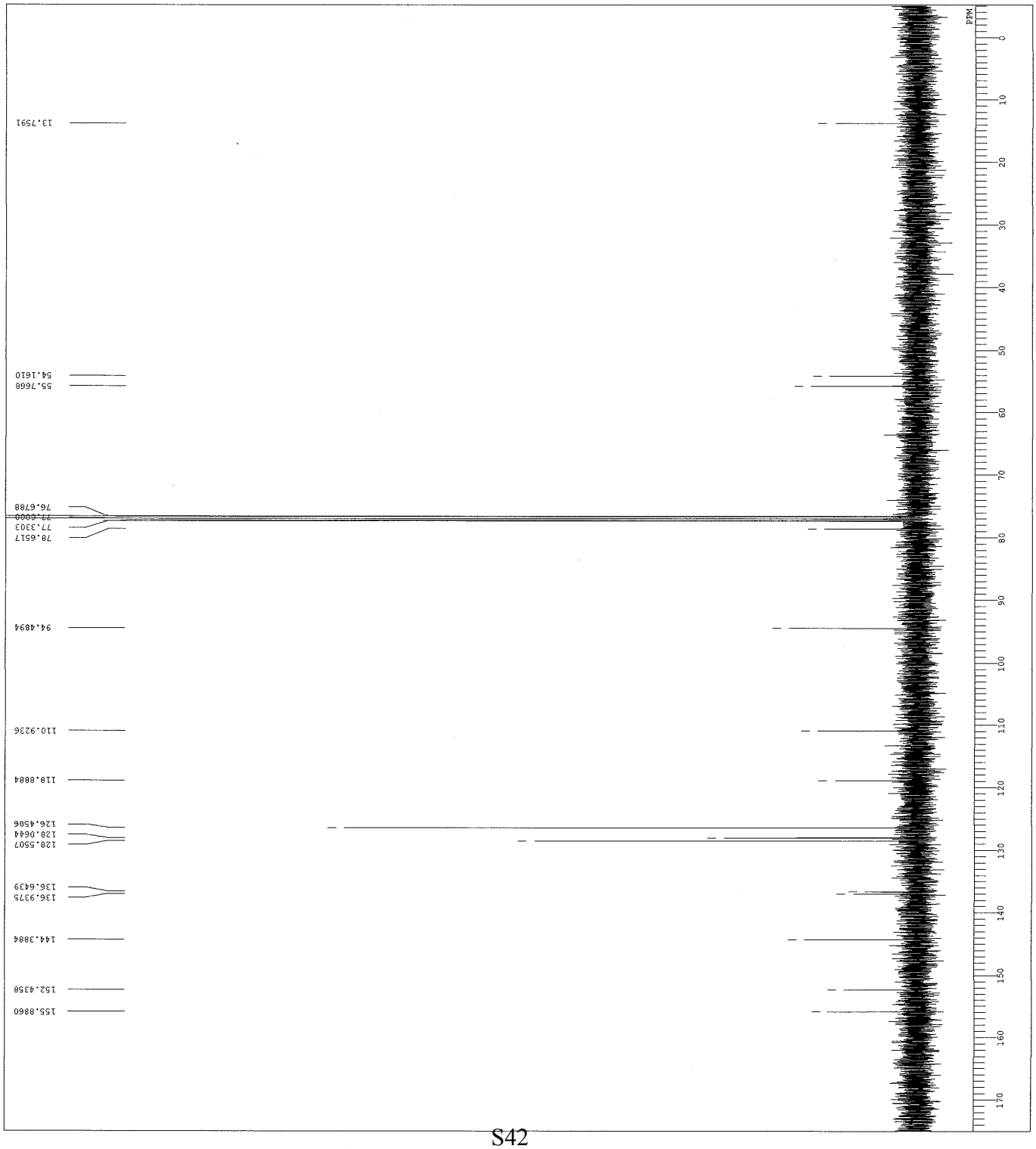
MeO

1i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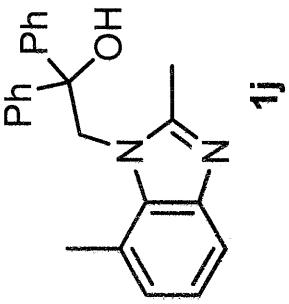
PPM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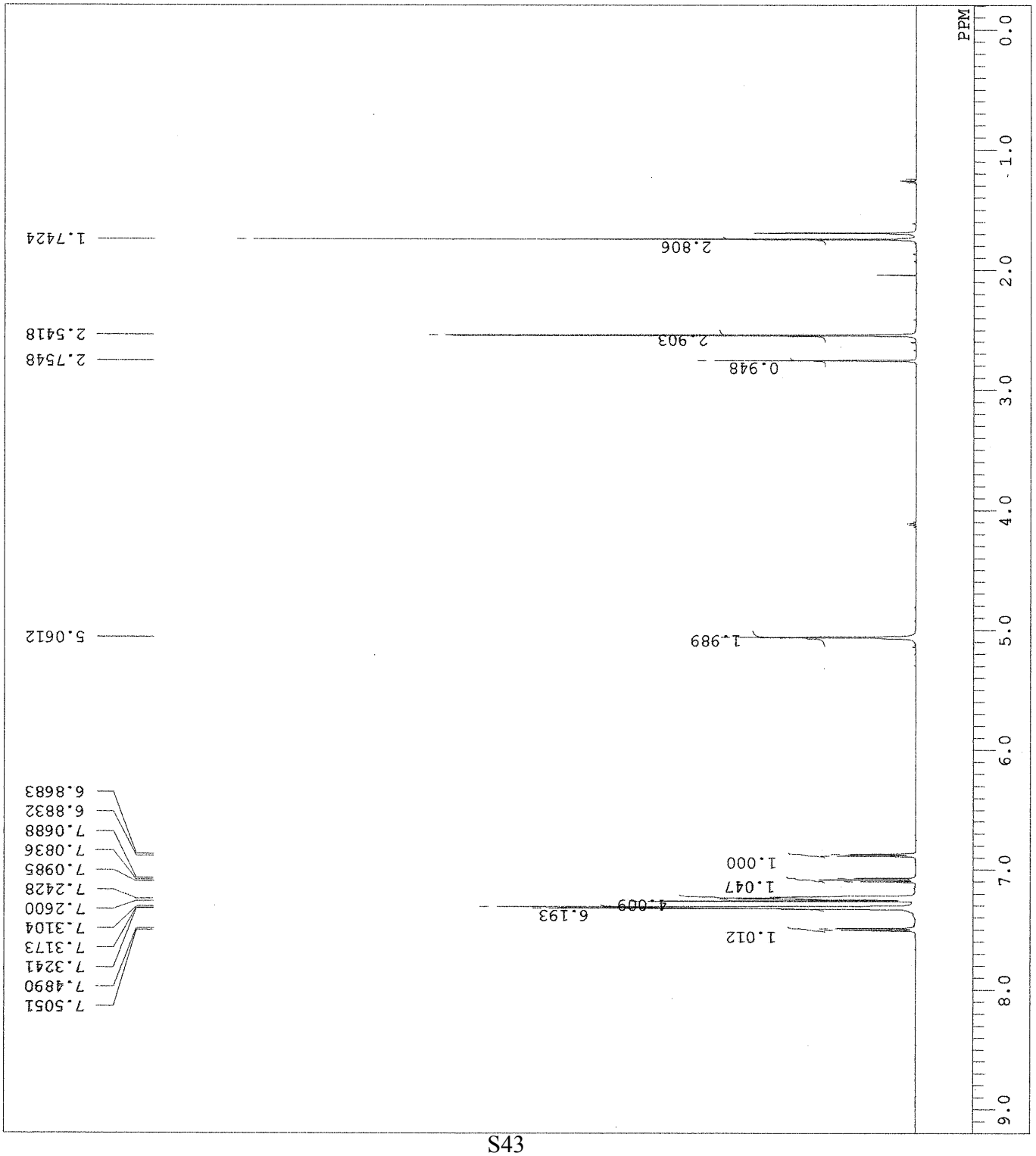
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7.0688
7.0836
7.0985
7.2428
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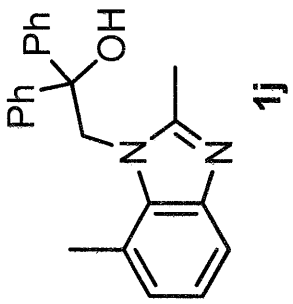
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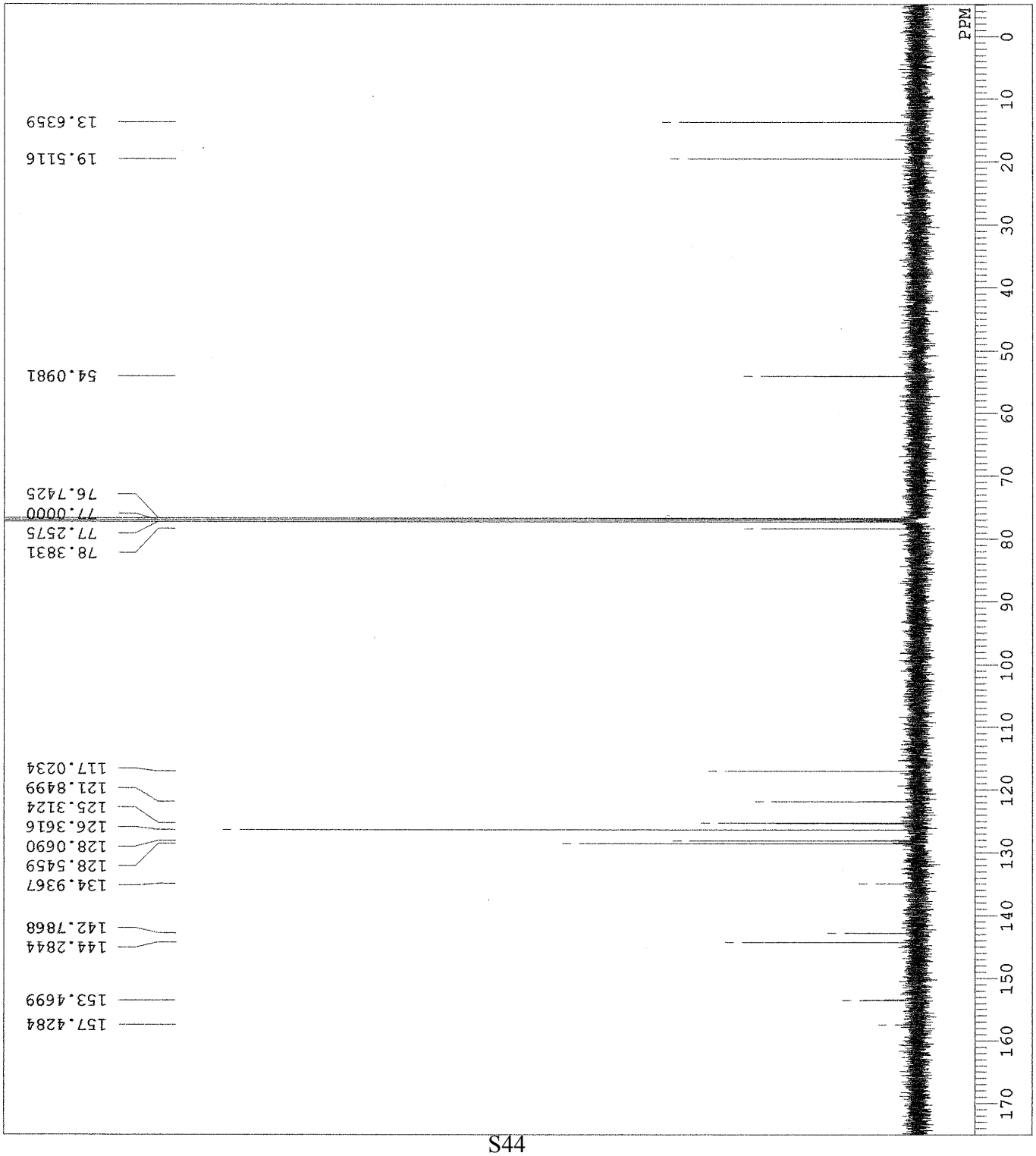
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144.2844
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157.4284
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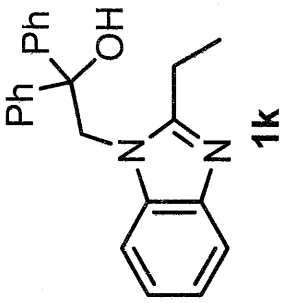
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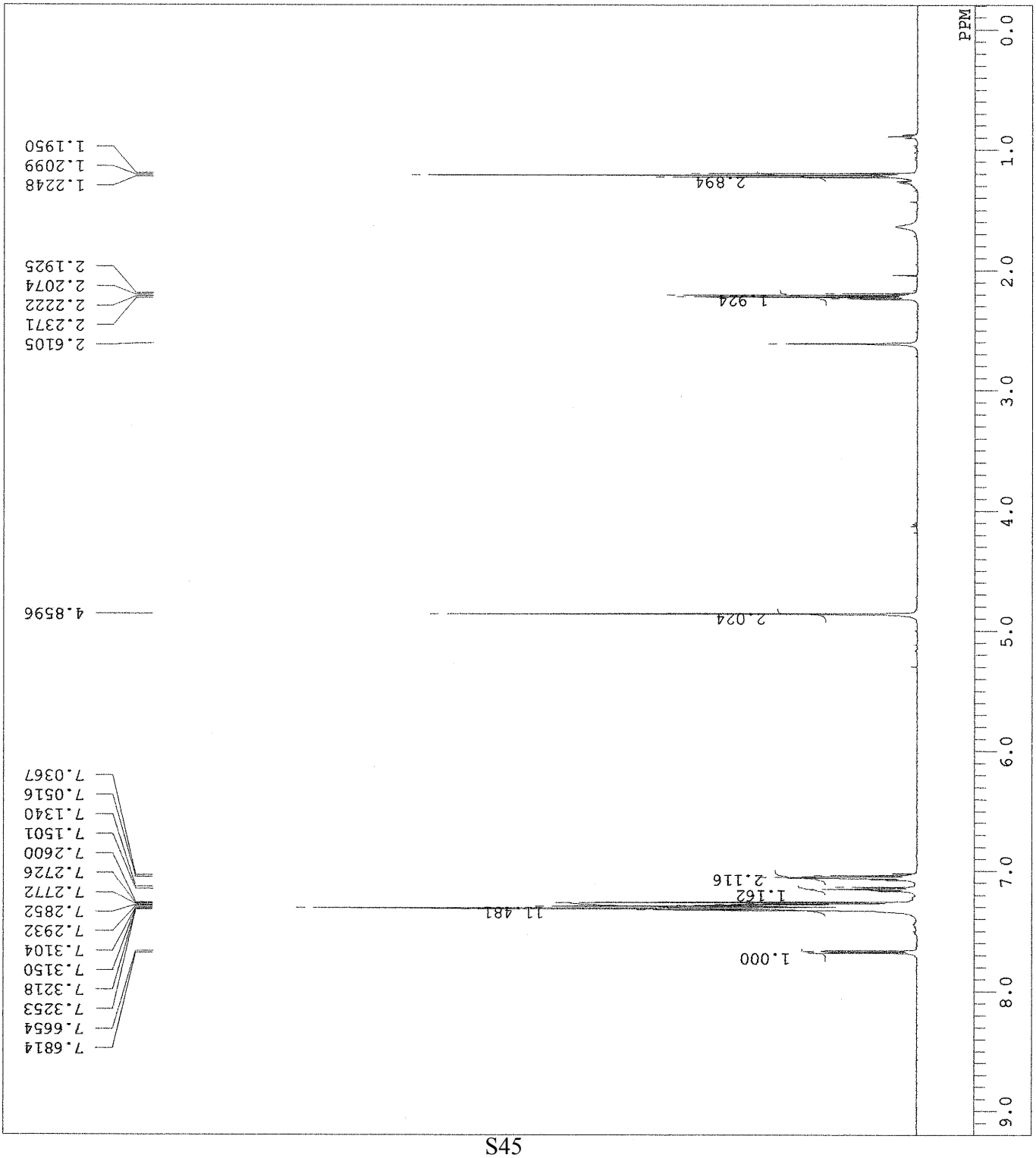
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7.3253
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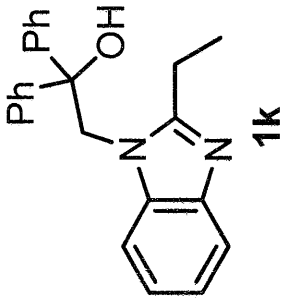
2.6105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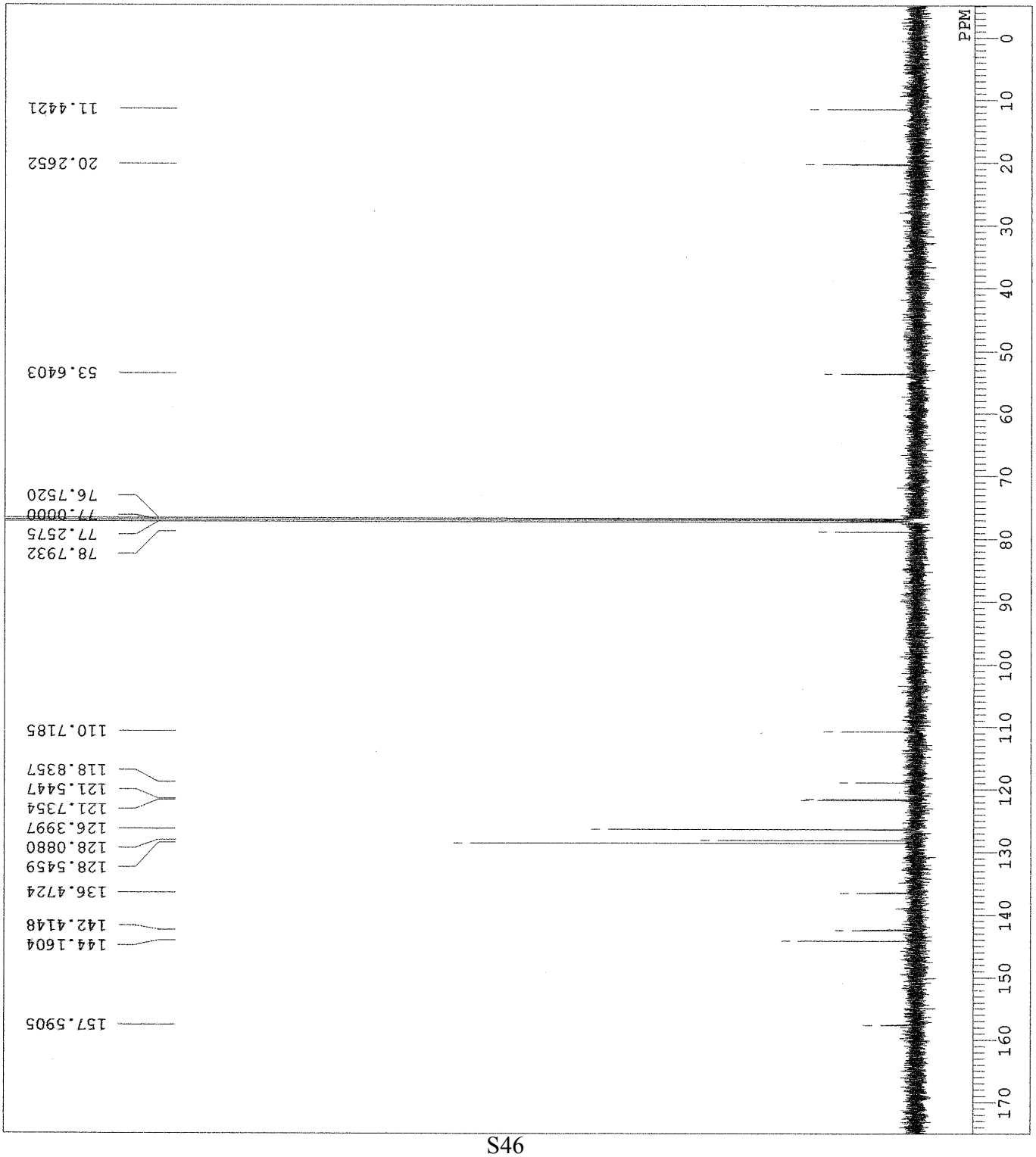
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121.7354
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128.5459
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142.4148
144.1604
157.5905
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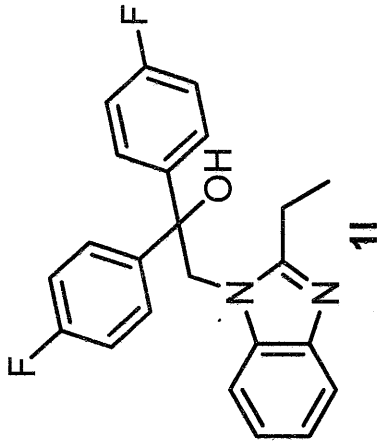
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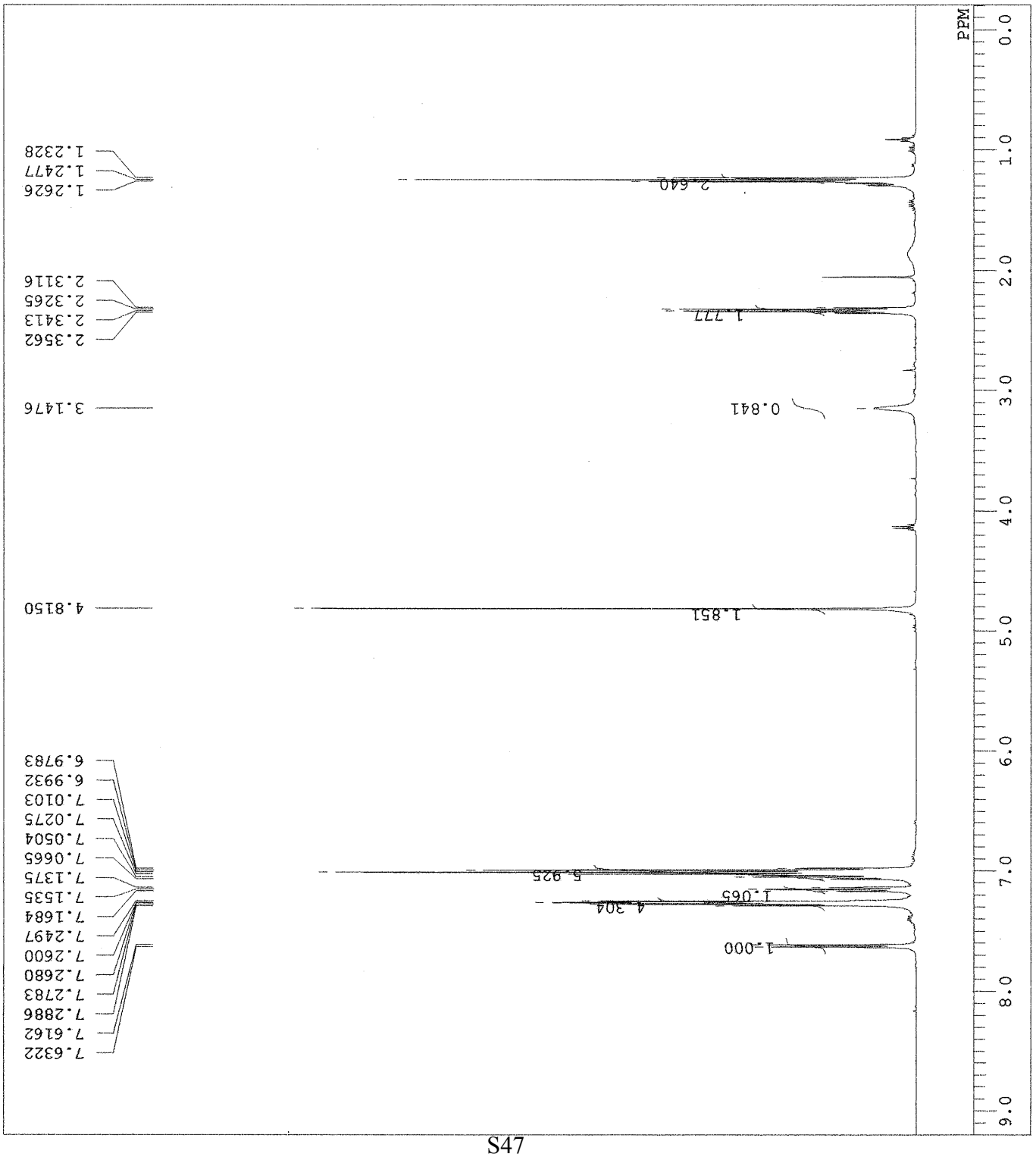
N
F

11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3.1476
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4.8150
1.851
6.9783
6.9932
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7.0504
7.0665
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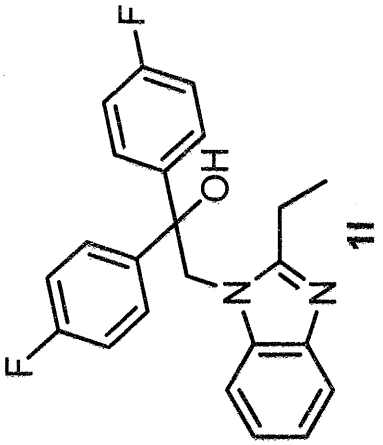
1.000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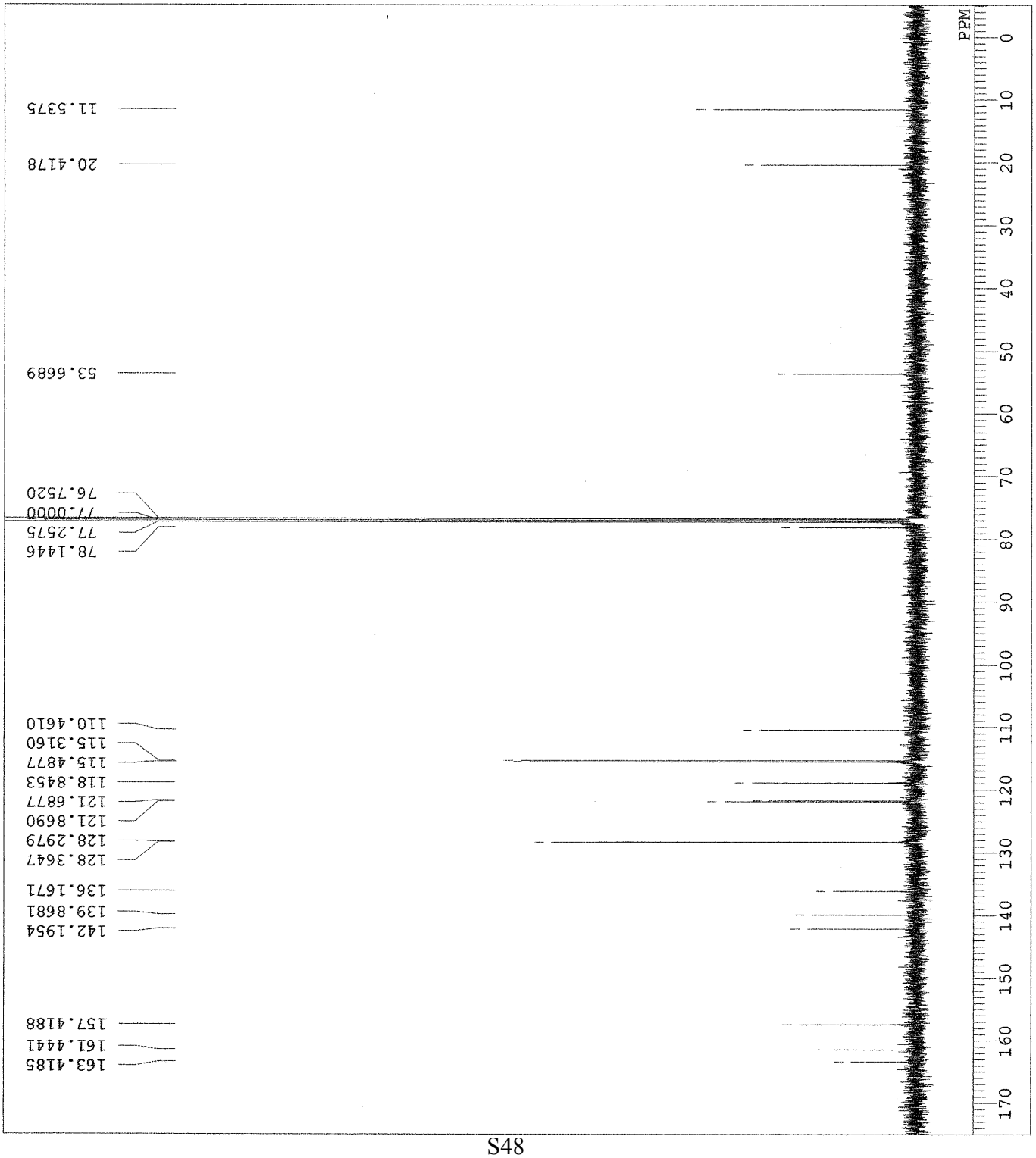
11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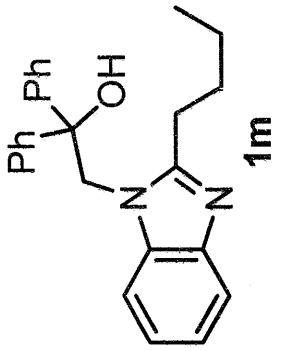
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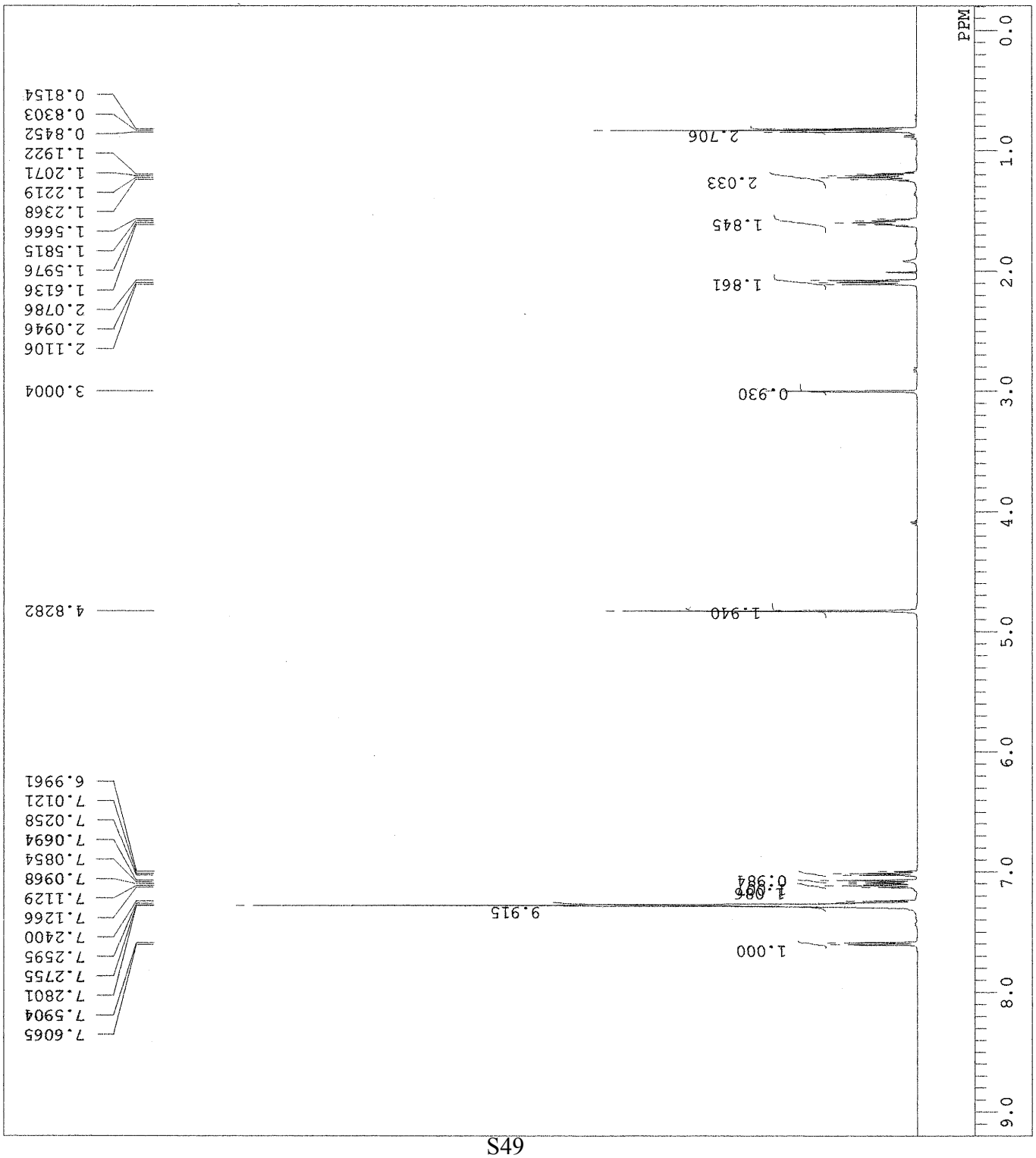
1m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1.1922
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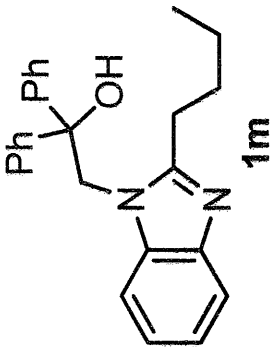
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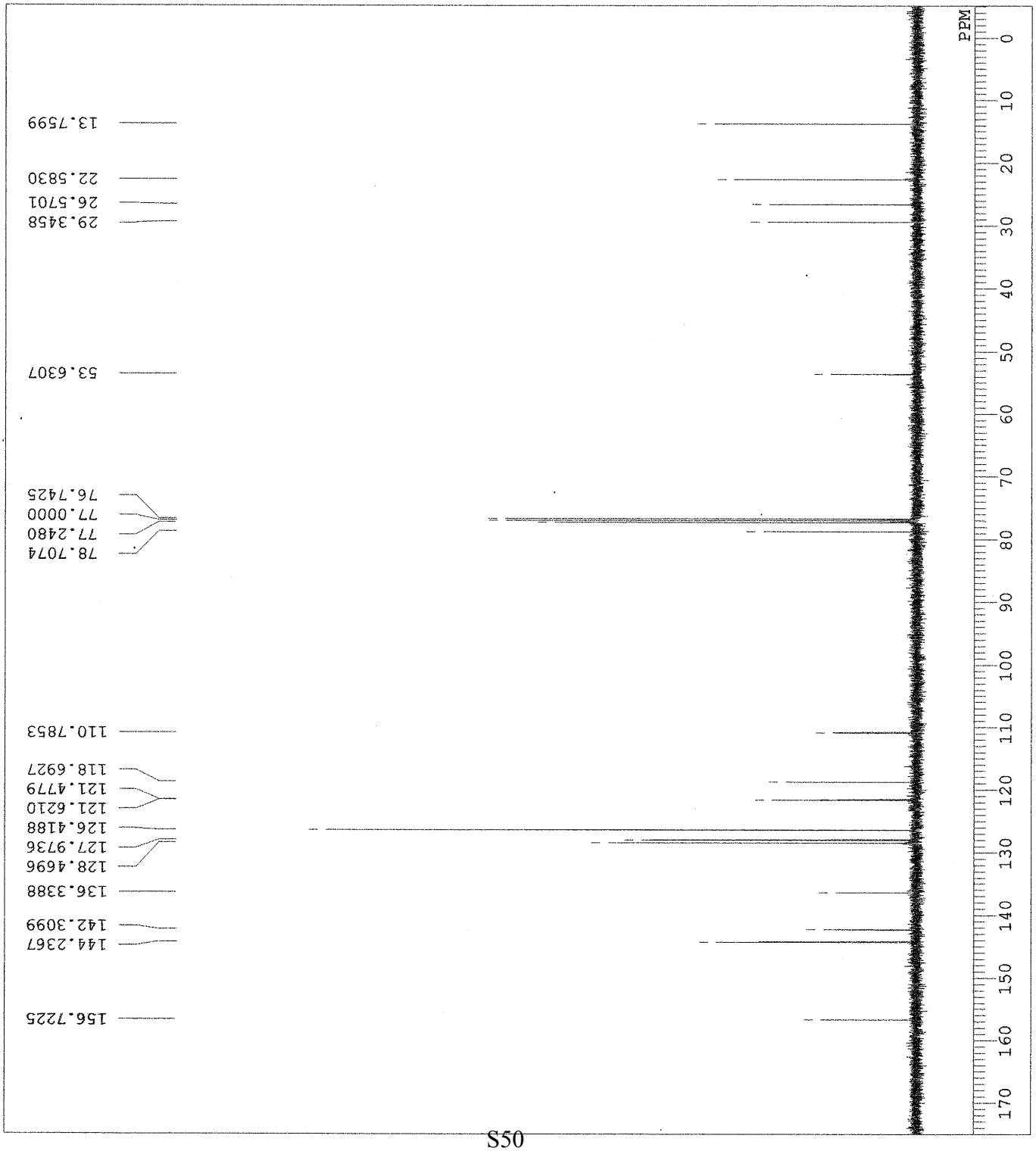
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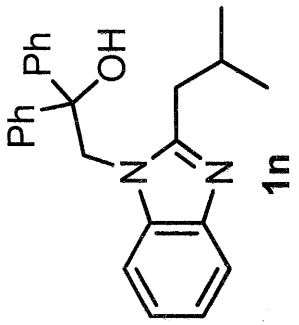
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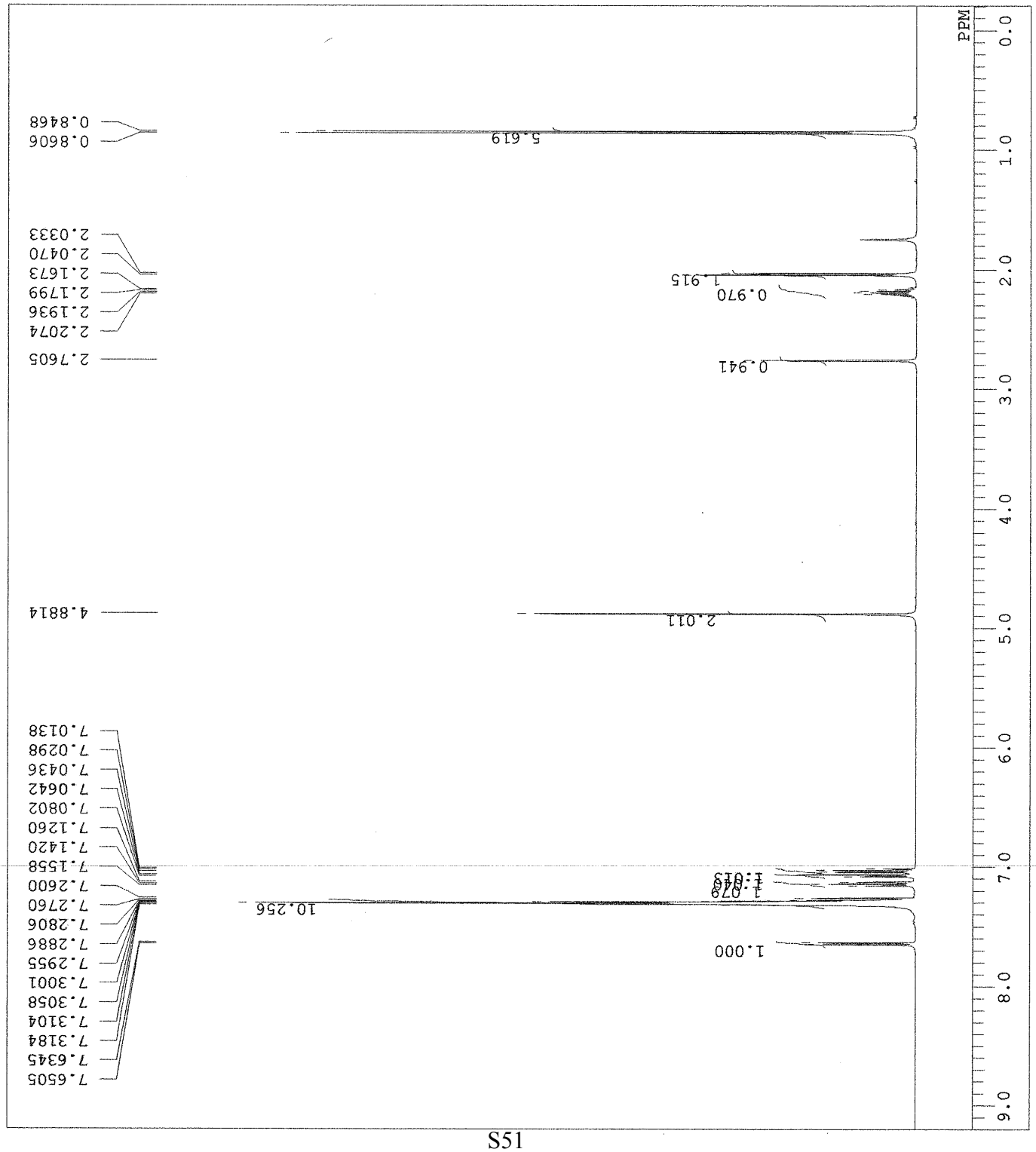
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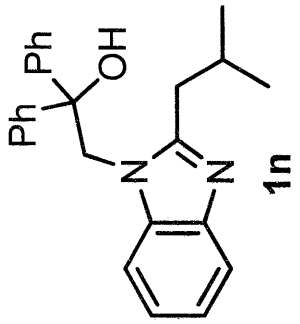
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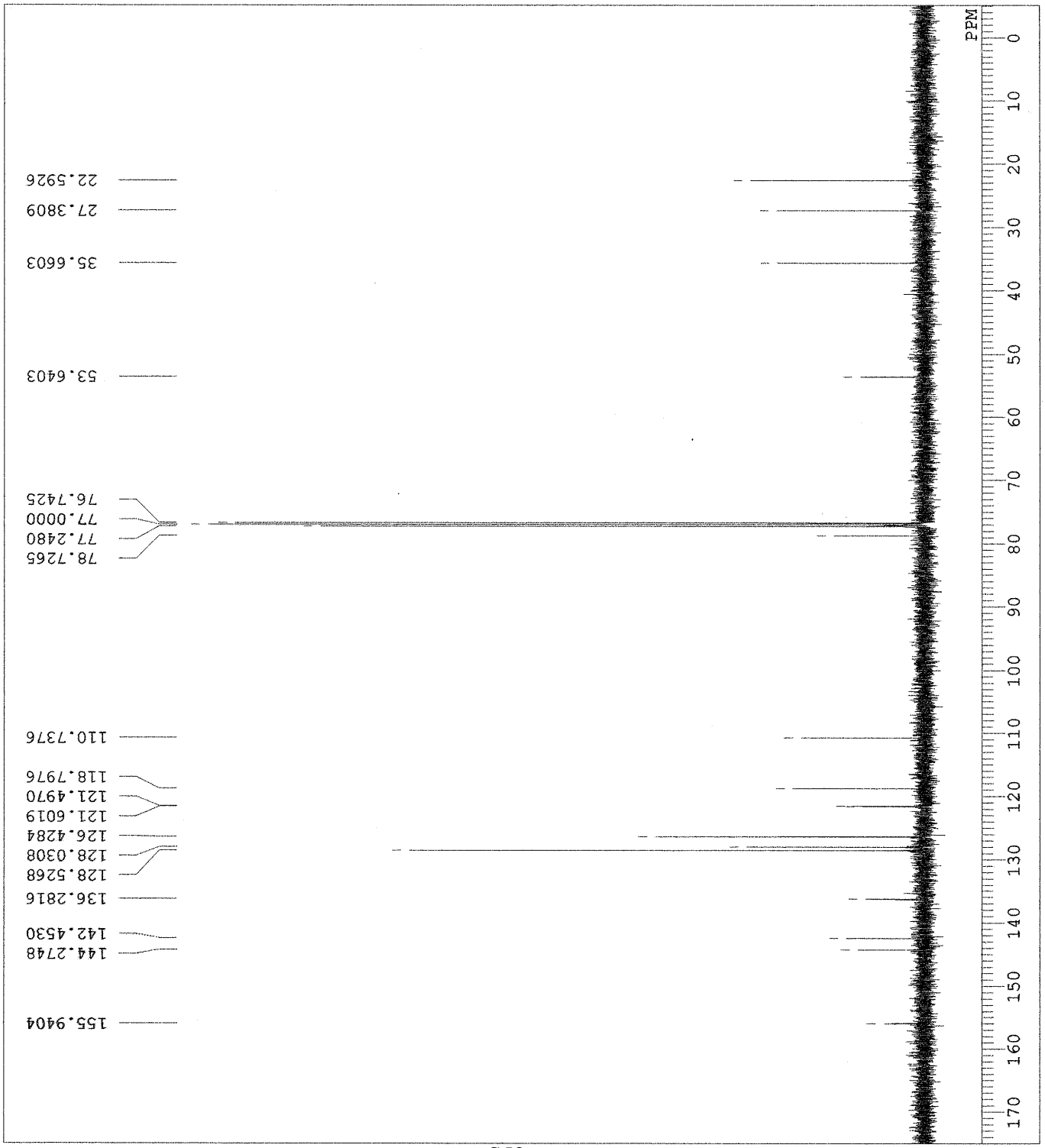
N

1n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144.2748
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PPM
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70
80
90
100
110
120
130
140
150
160
170

OH
N
N
1o

PPM
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4.0
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6.0
7.0
8.0
9.0
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1.964
2.945
5.862
1.3576
1.8913
1.9073
1.9245
2.6116
4.2550
4.2710
4.2882
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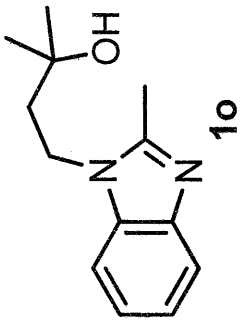
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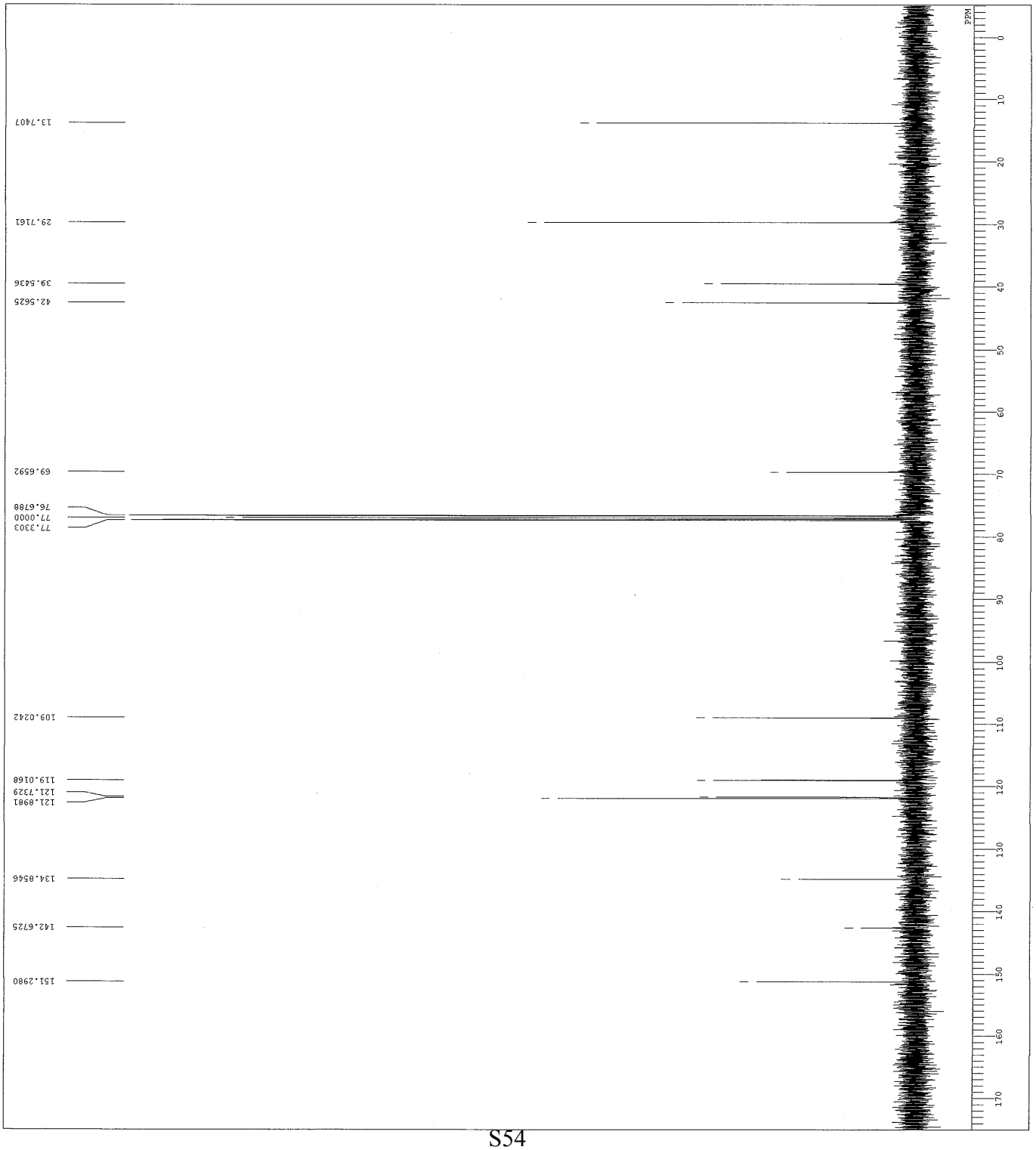
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PPM
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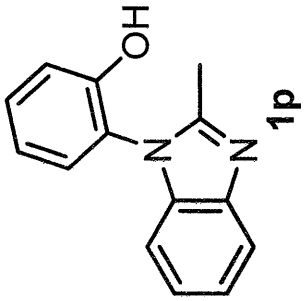
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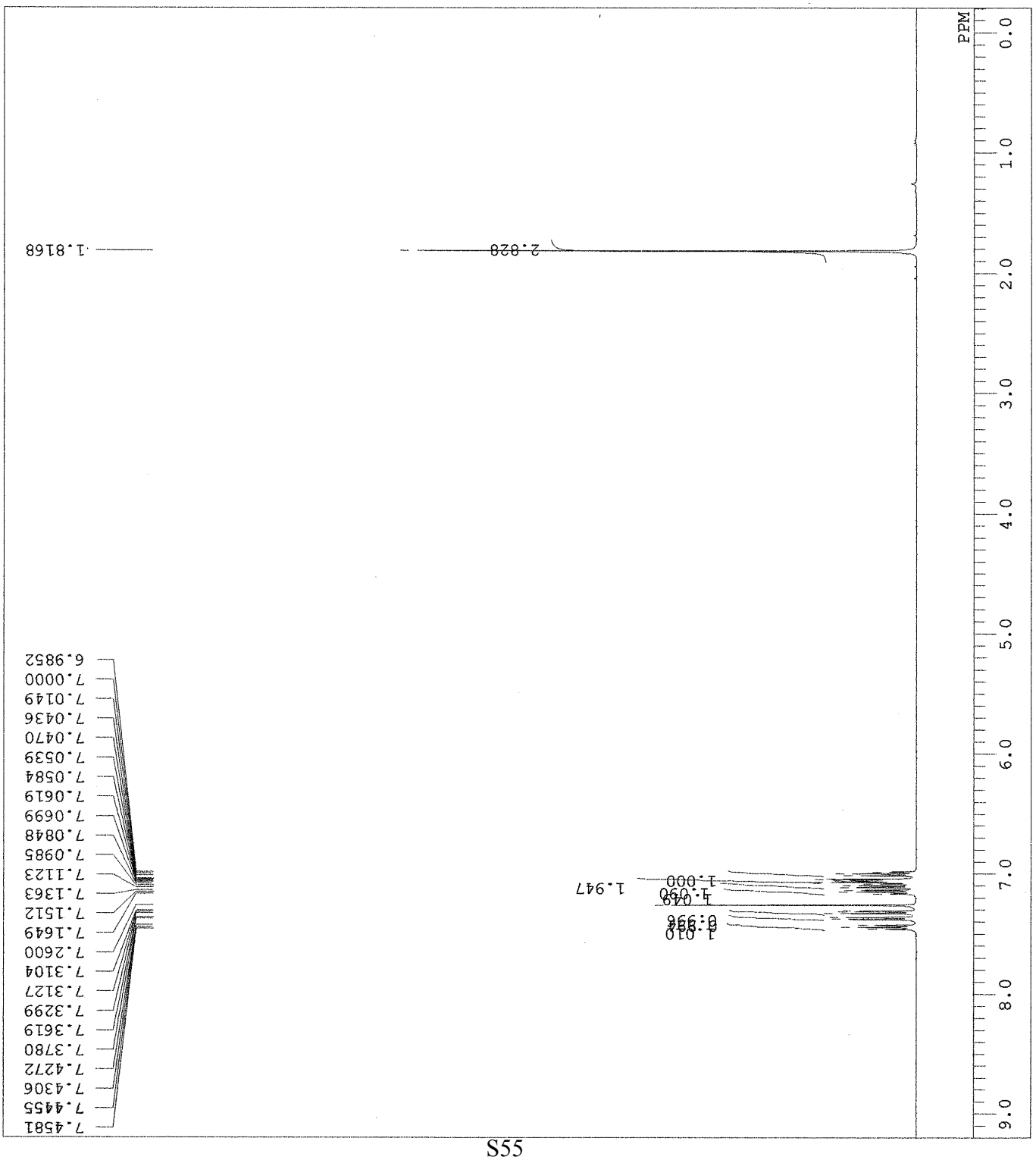
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7.0619
7.0699
7.0848
7.0985
7.1123
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7.1512
7.1649
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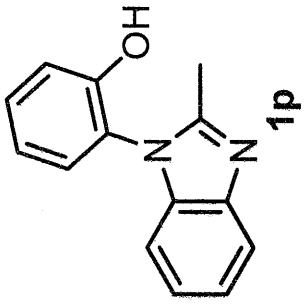
7.4581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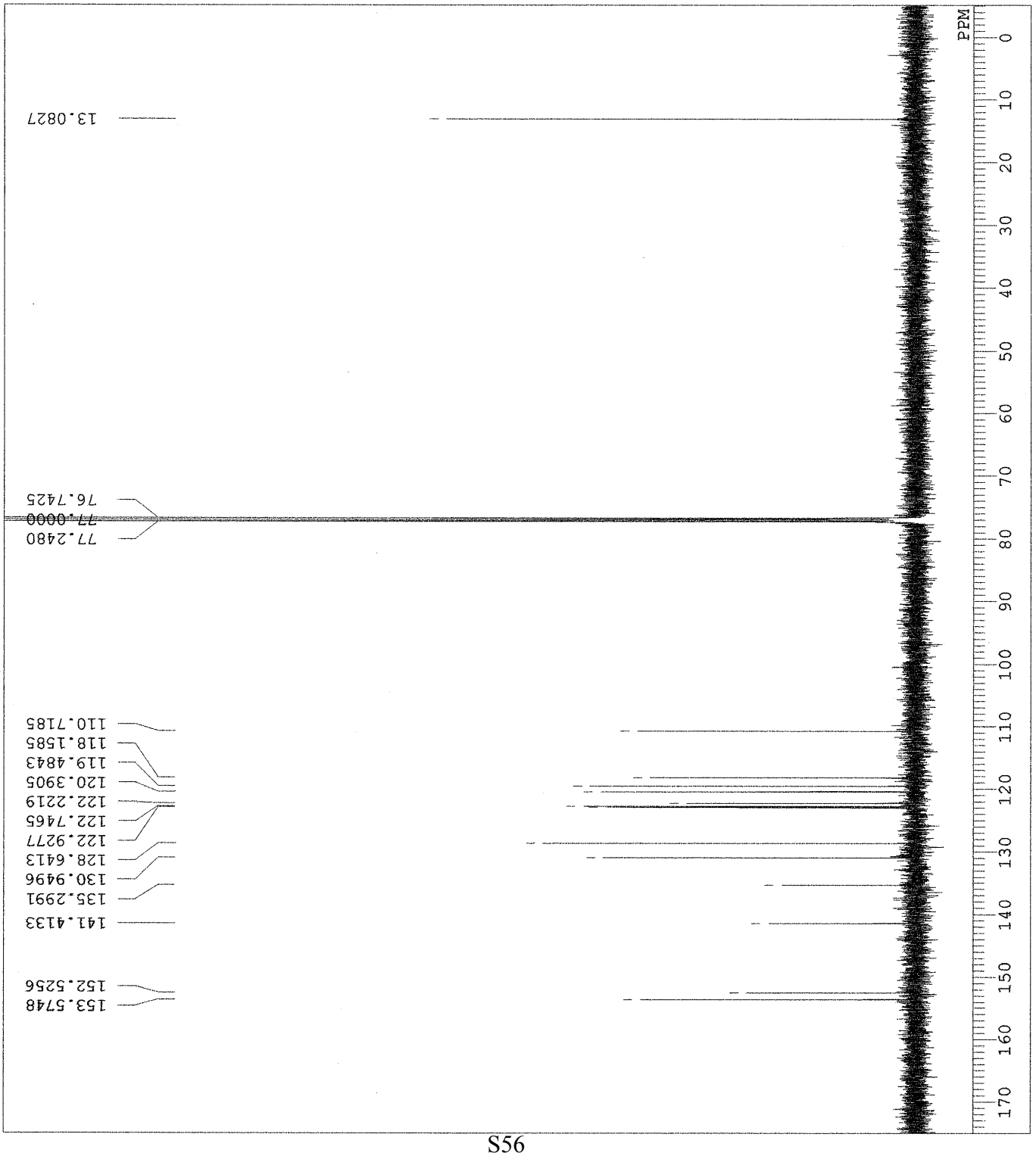
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150
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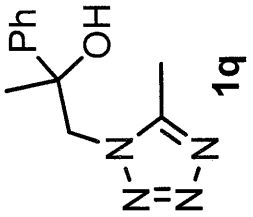
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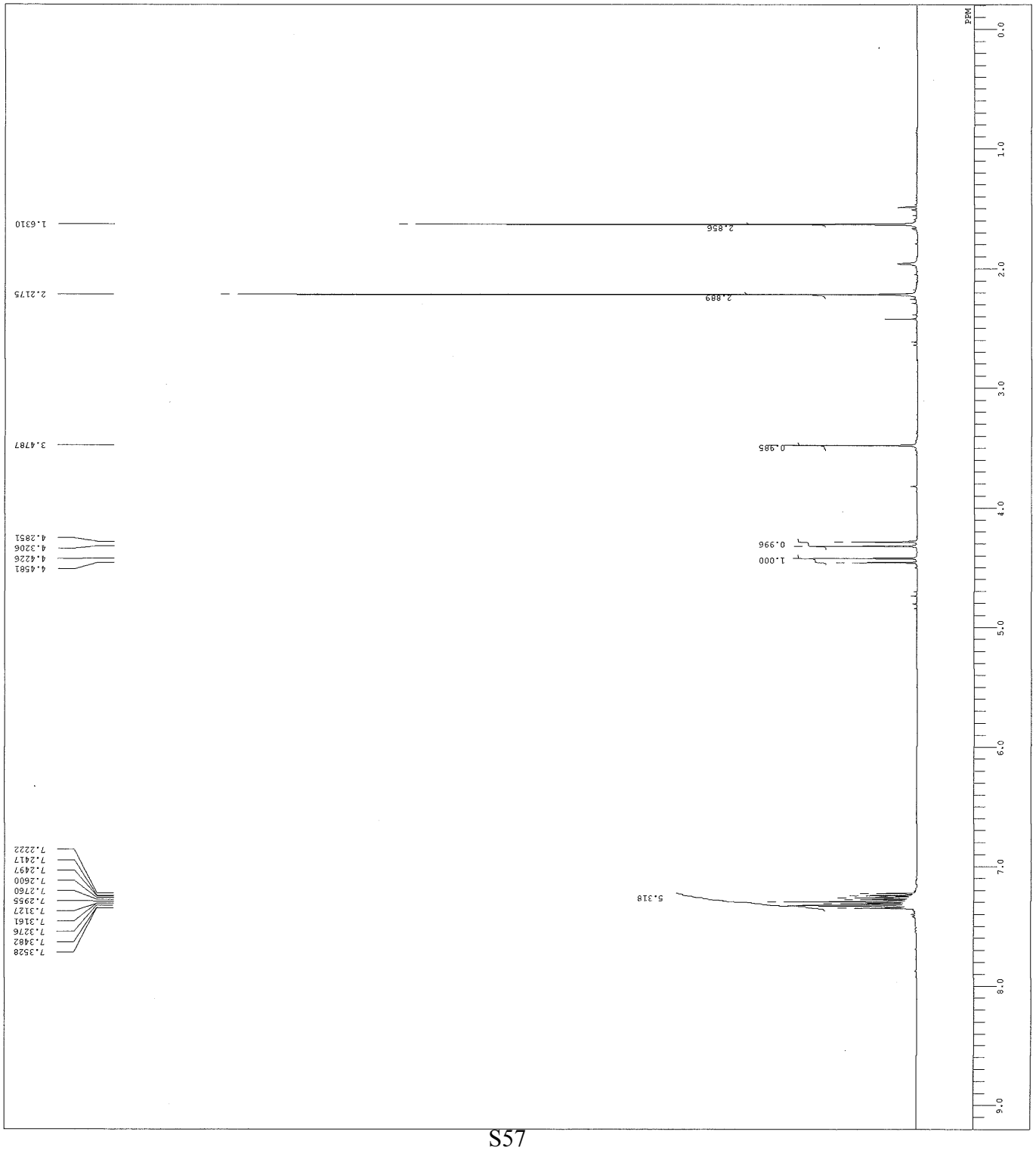
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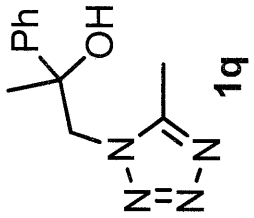
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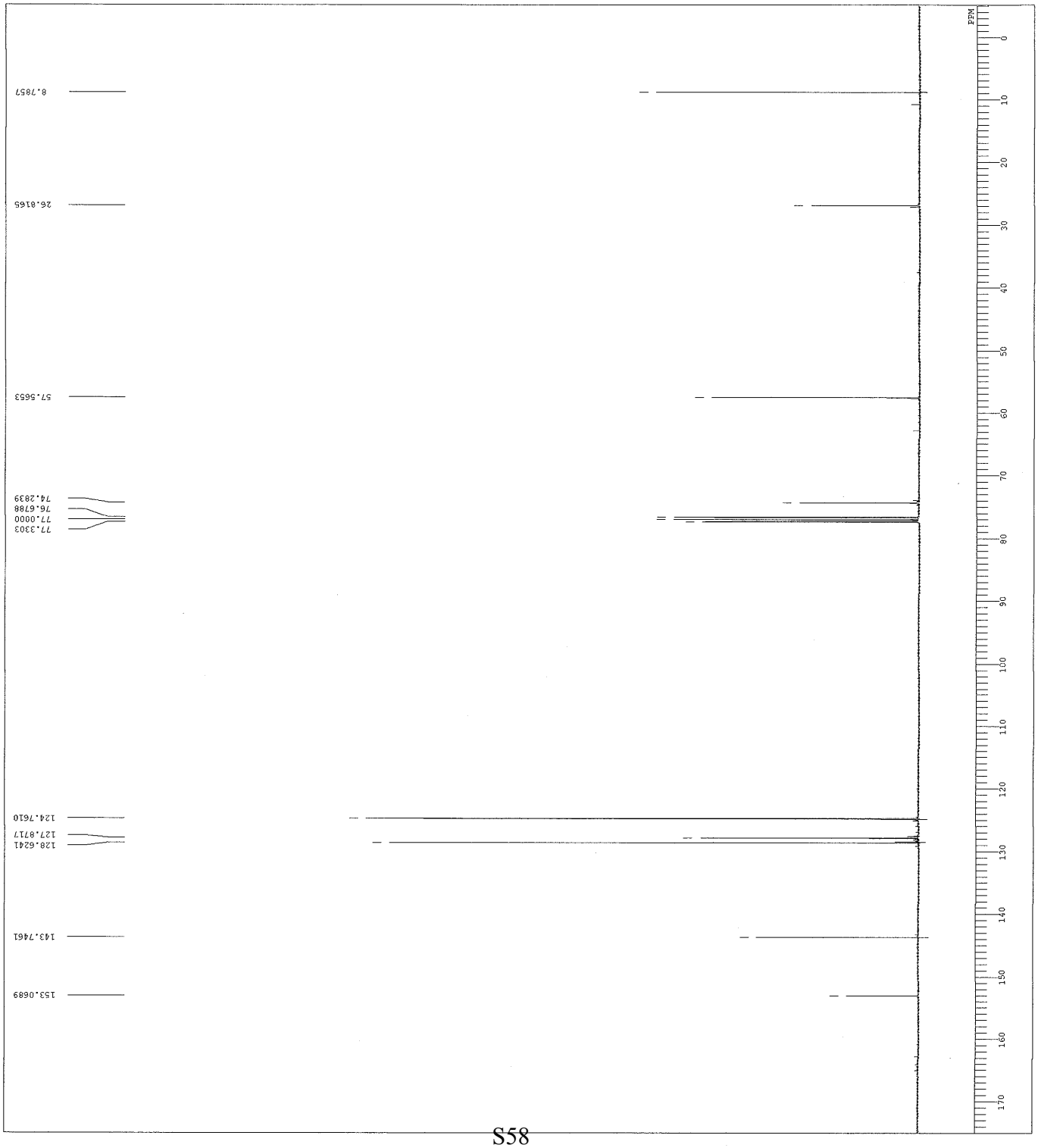
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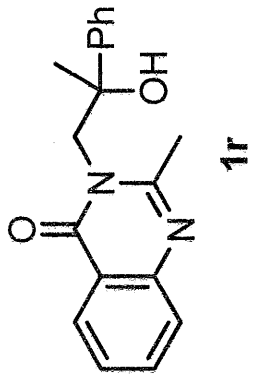
143.7461
153.0689
PPM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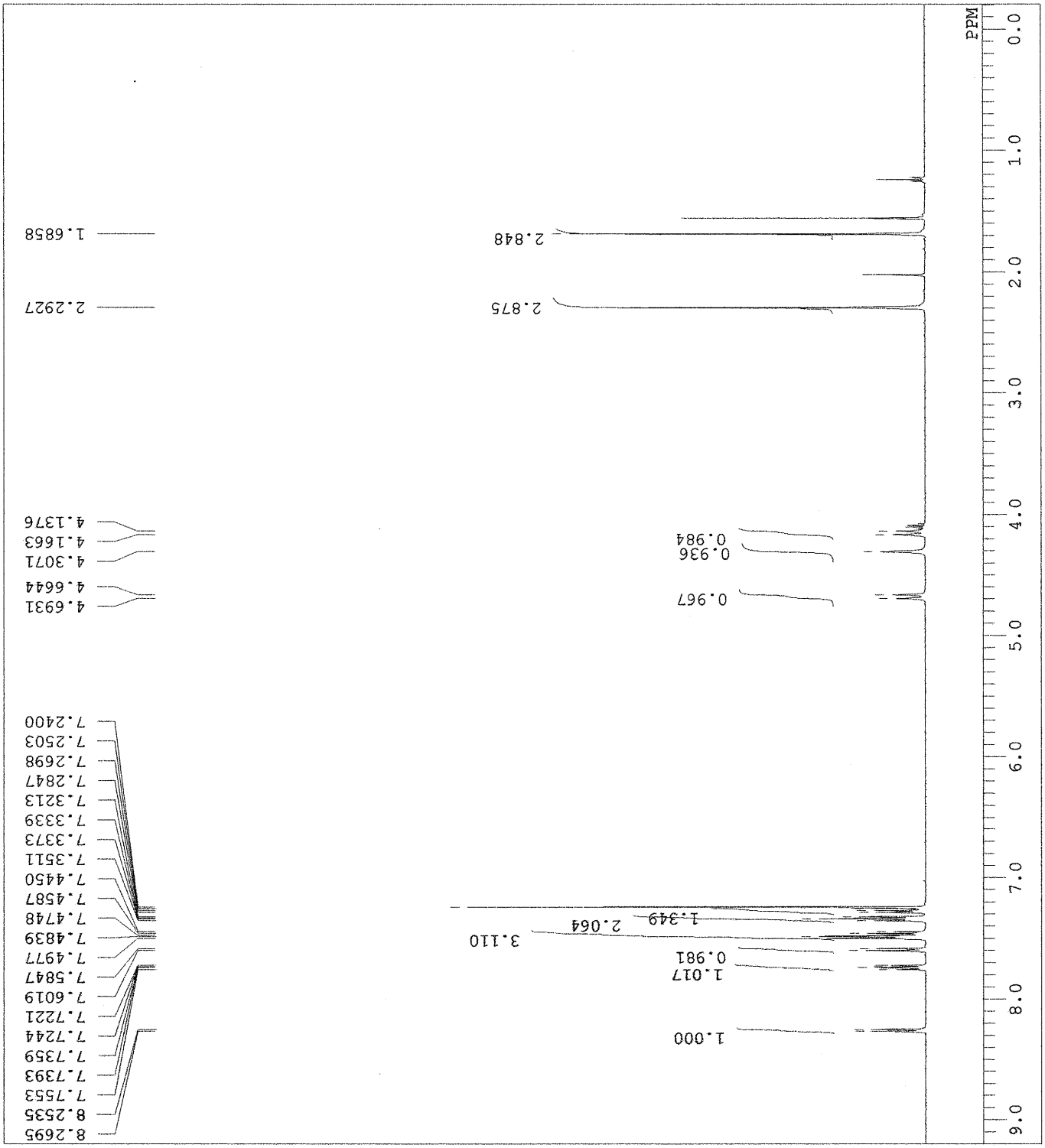
N
O

1r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7.7359
7.7244
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7.3339
7.3213
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7.2503
7.2400
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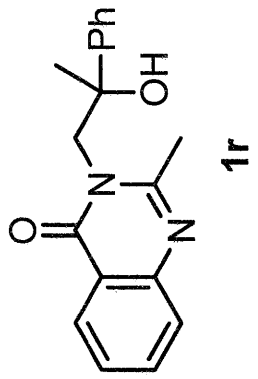
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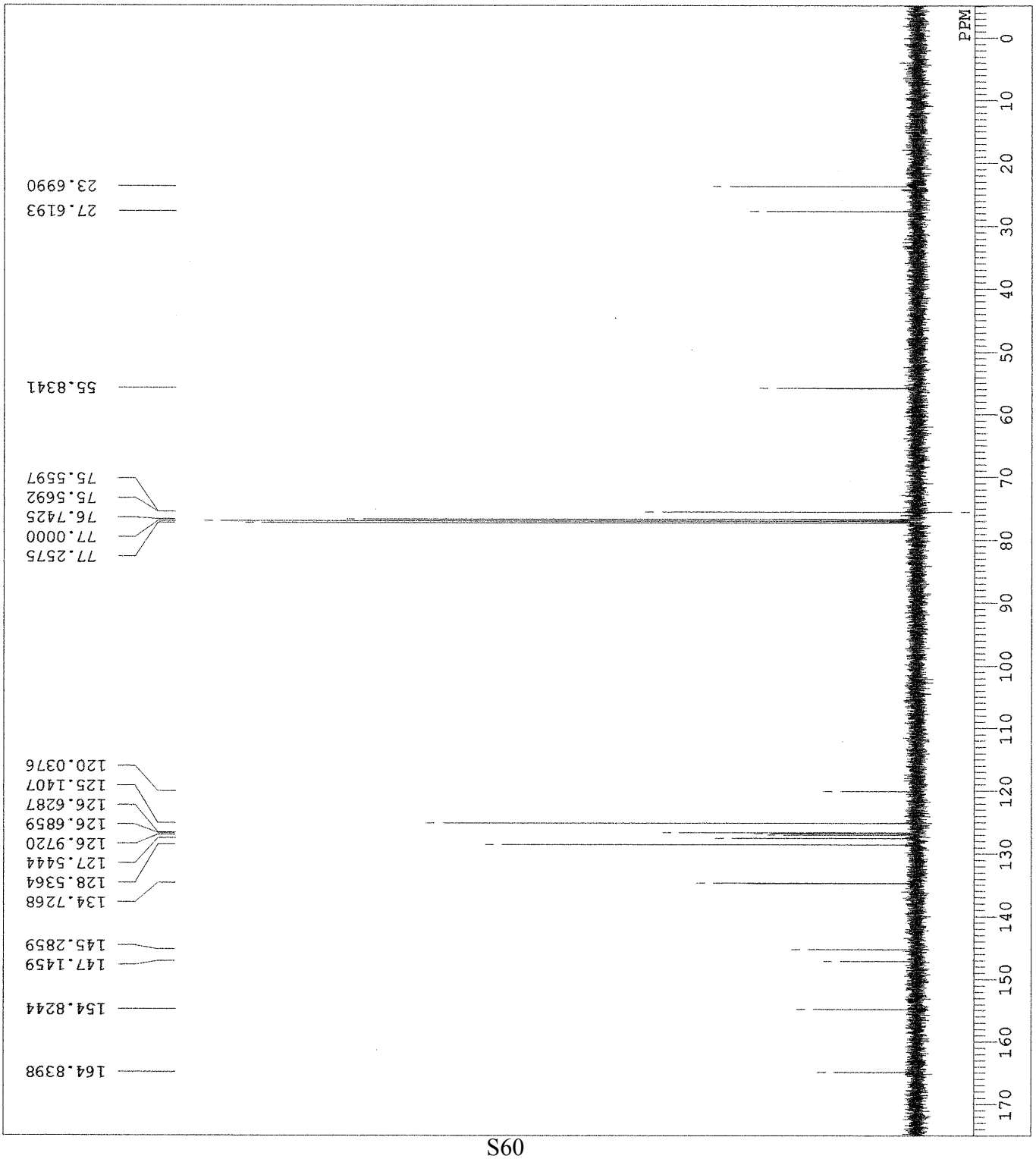
O

1r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126.6859
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147.1459
154.8244
164.8398
PPM
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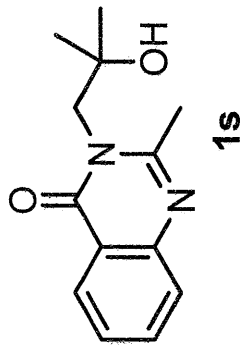
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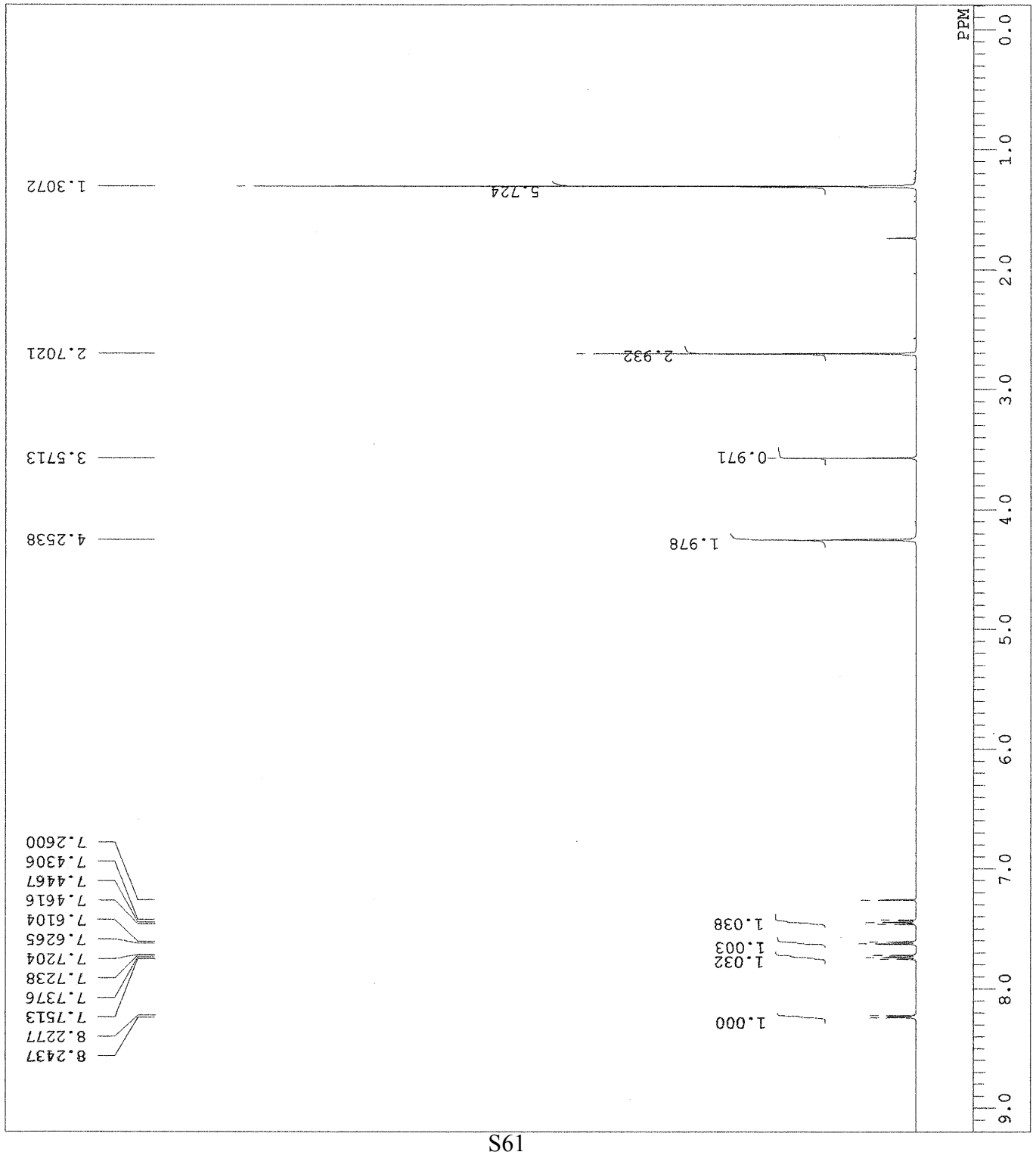
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1.978
1.038
1.032
1.003
1.000
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8.2277
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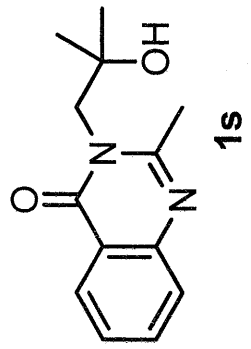
7.4306
7.2600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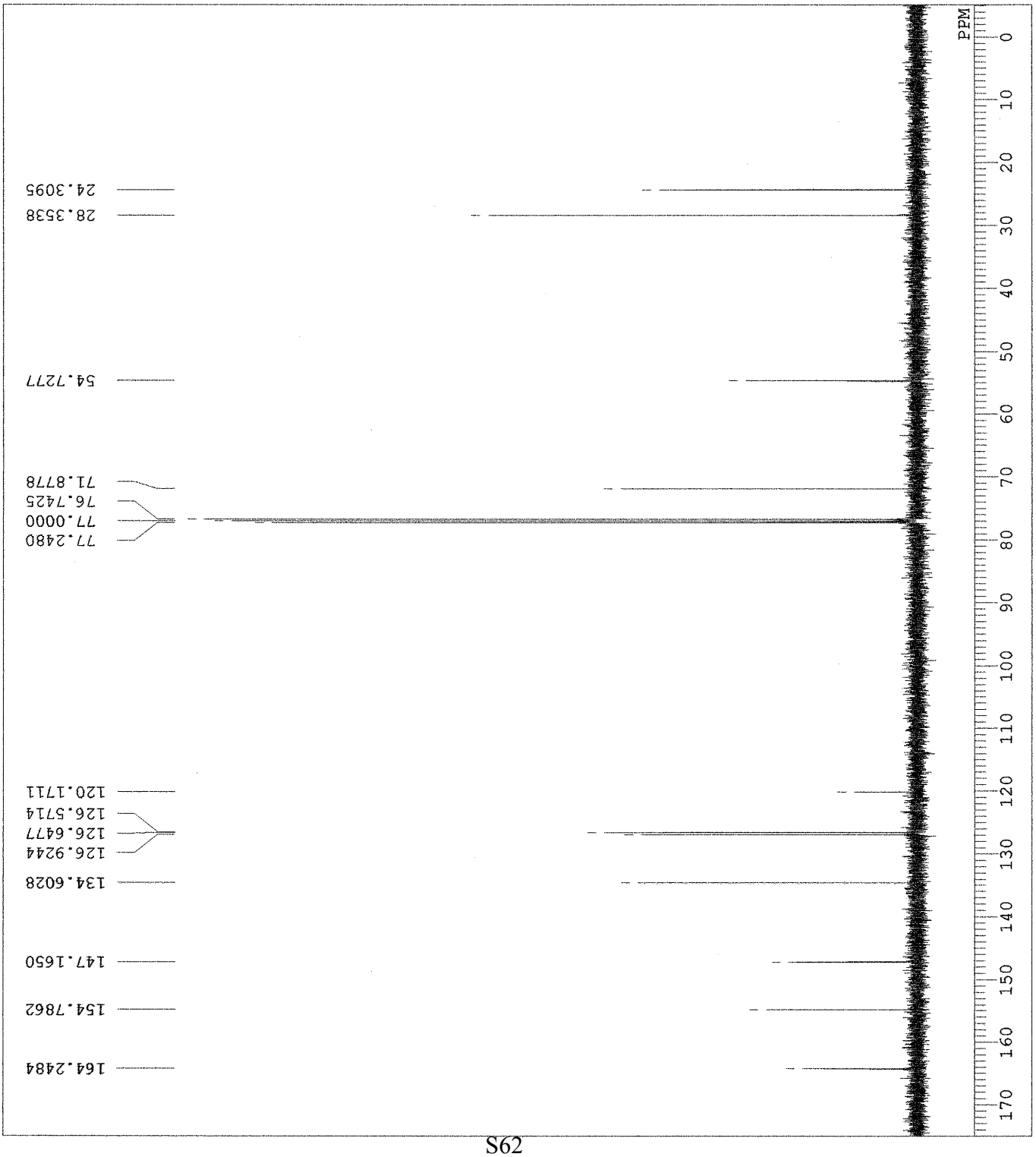
N
O

1s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147.1650
154.7862
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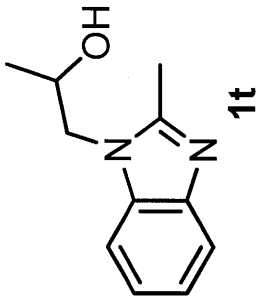
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N
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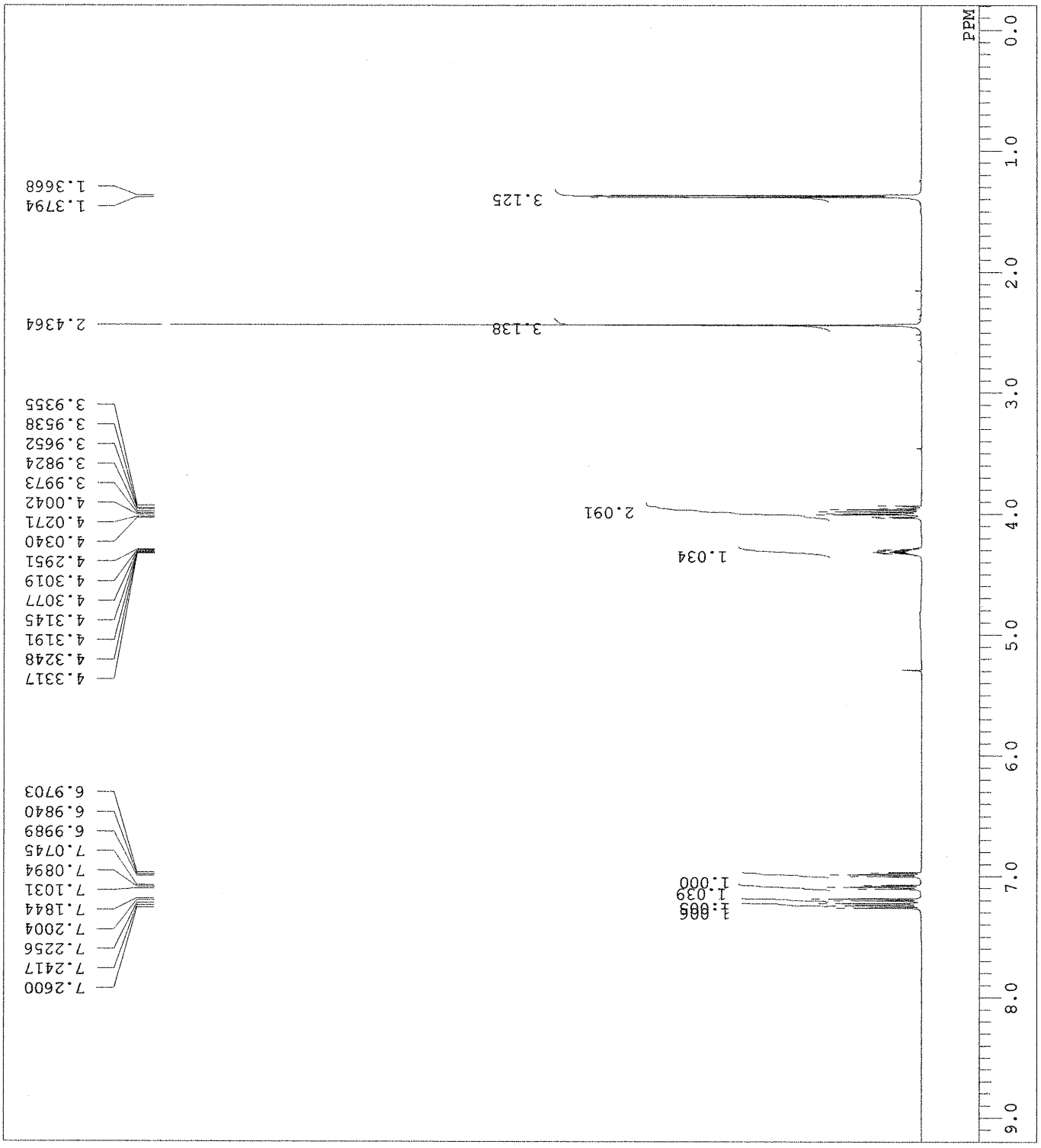
PPM
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8.0
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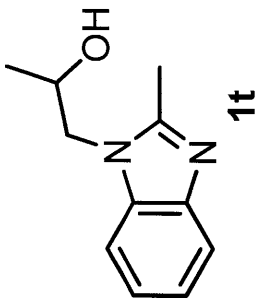
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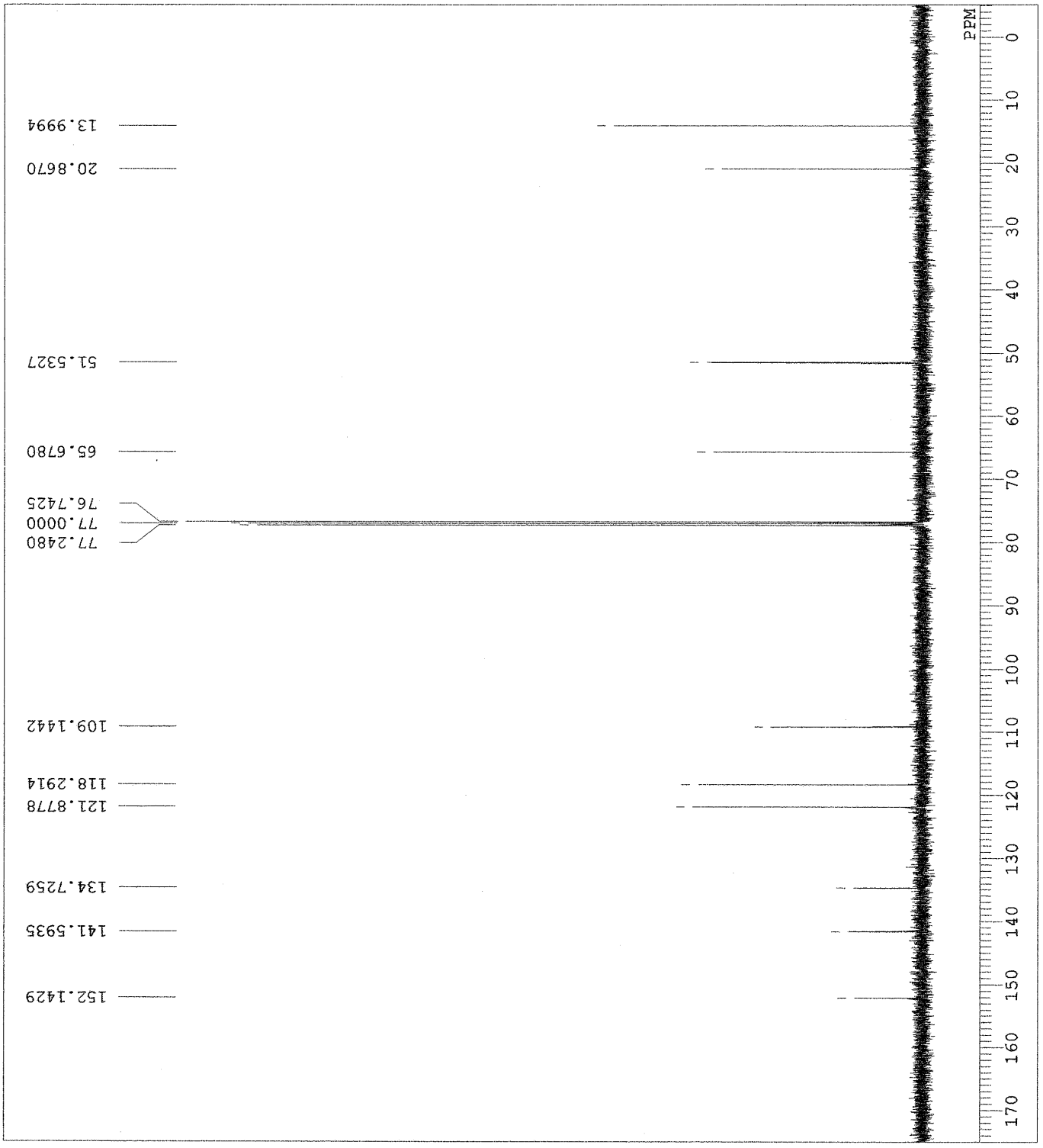
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118.2914
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141.5935
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PPM
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100
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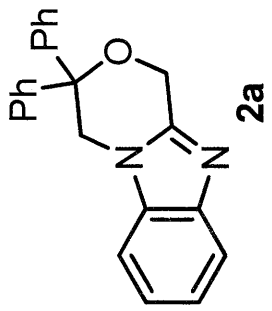
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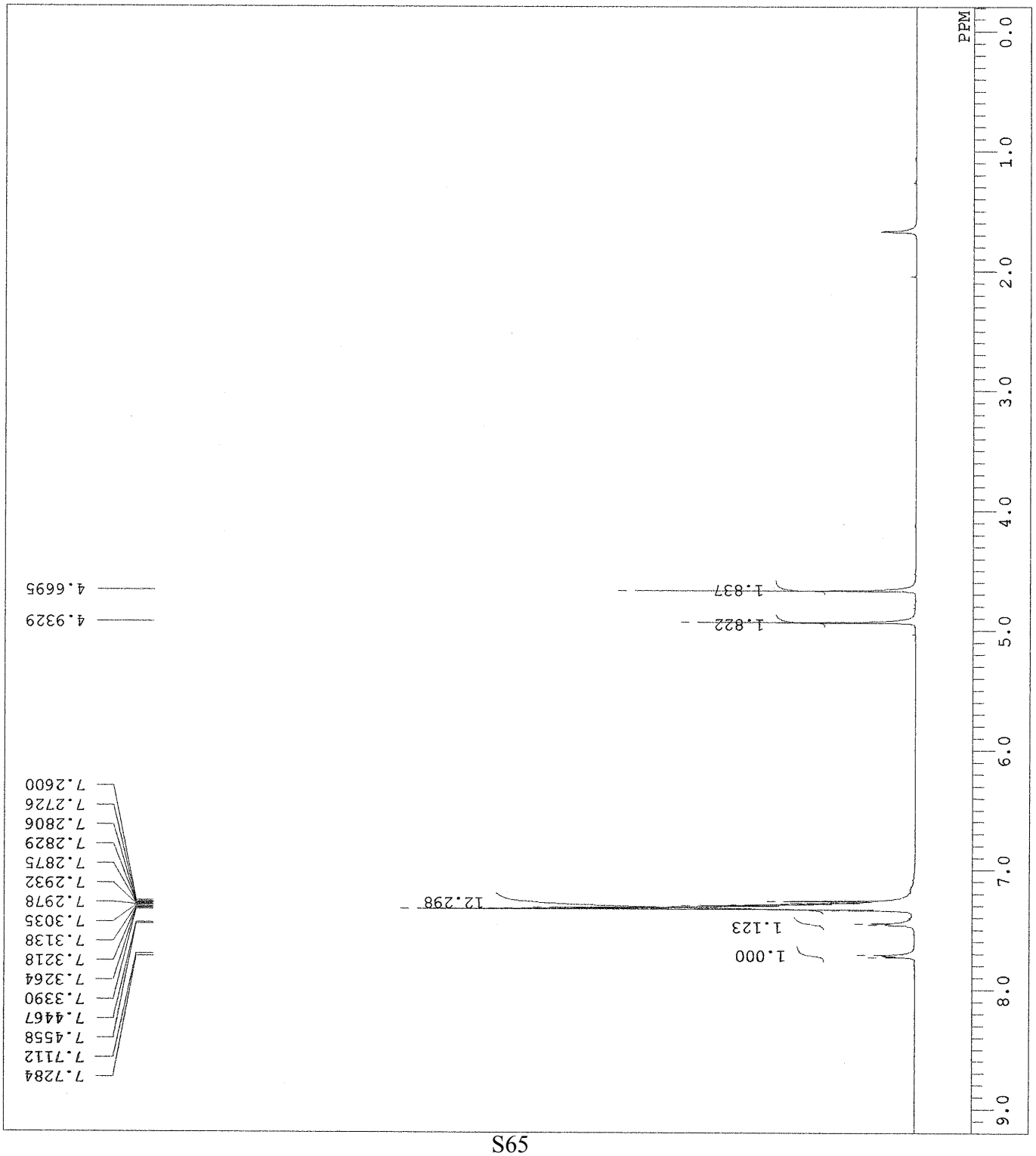
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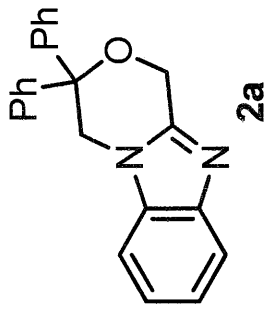
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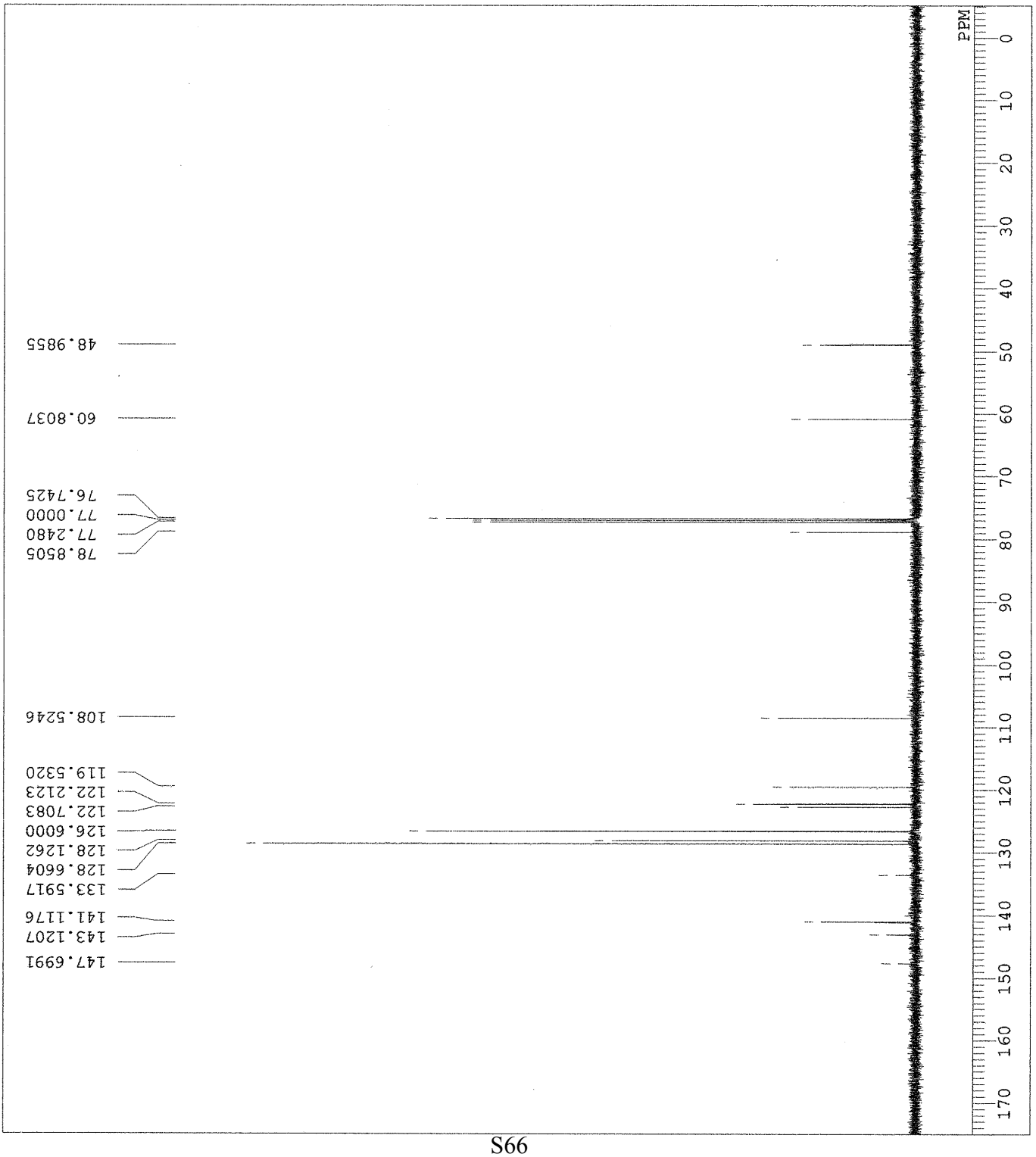
N
2a


PPM
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150
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170
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76.7425
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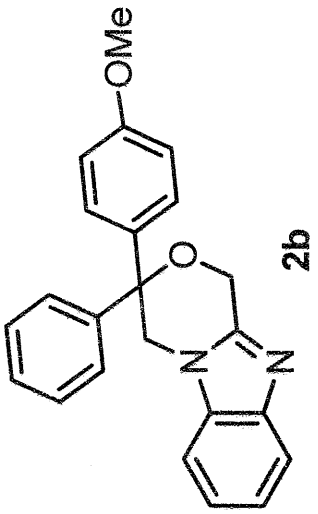
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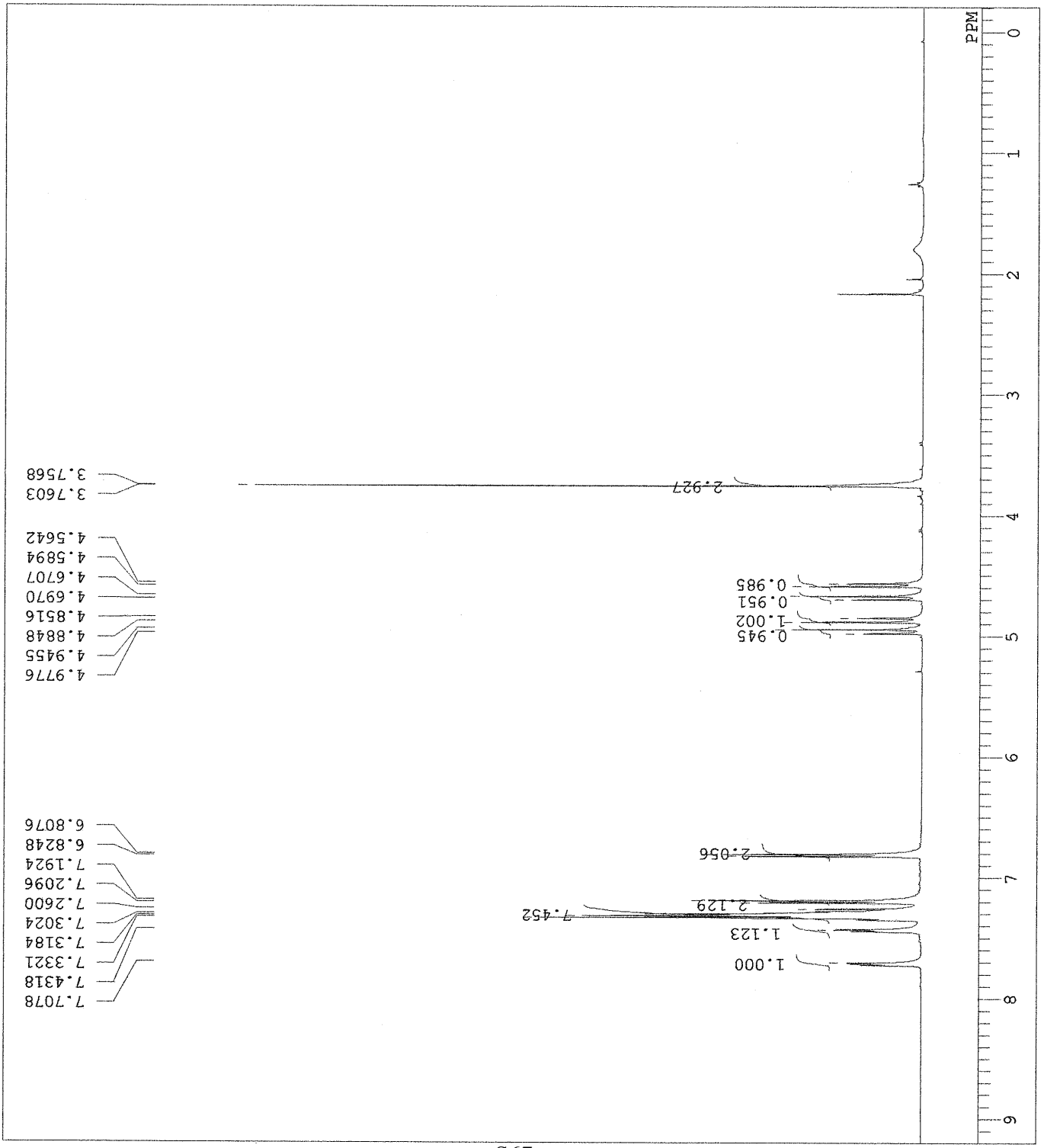
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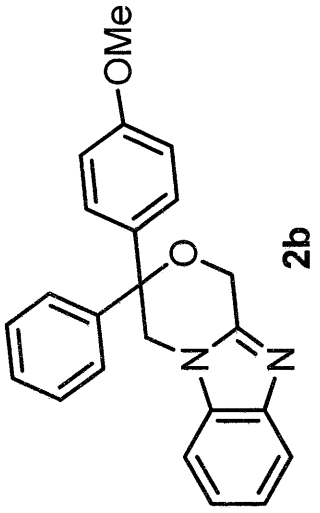
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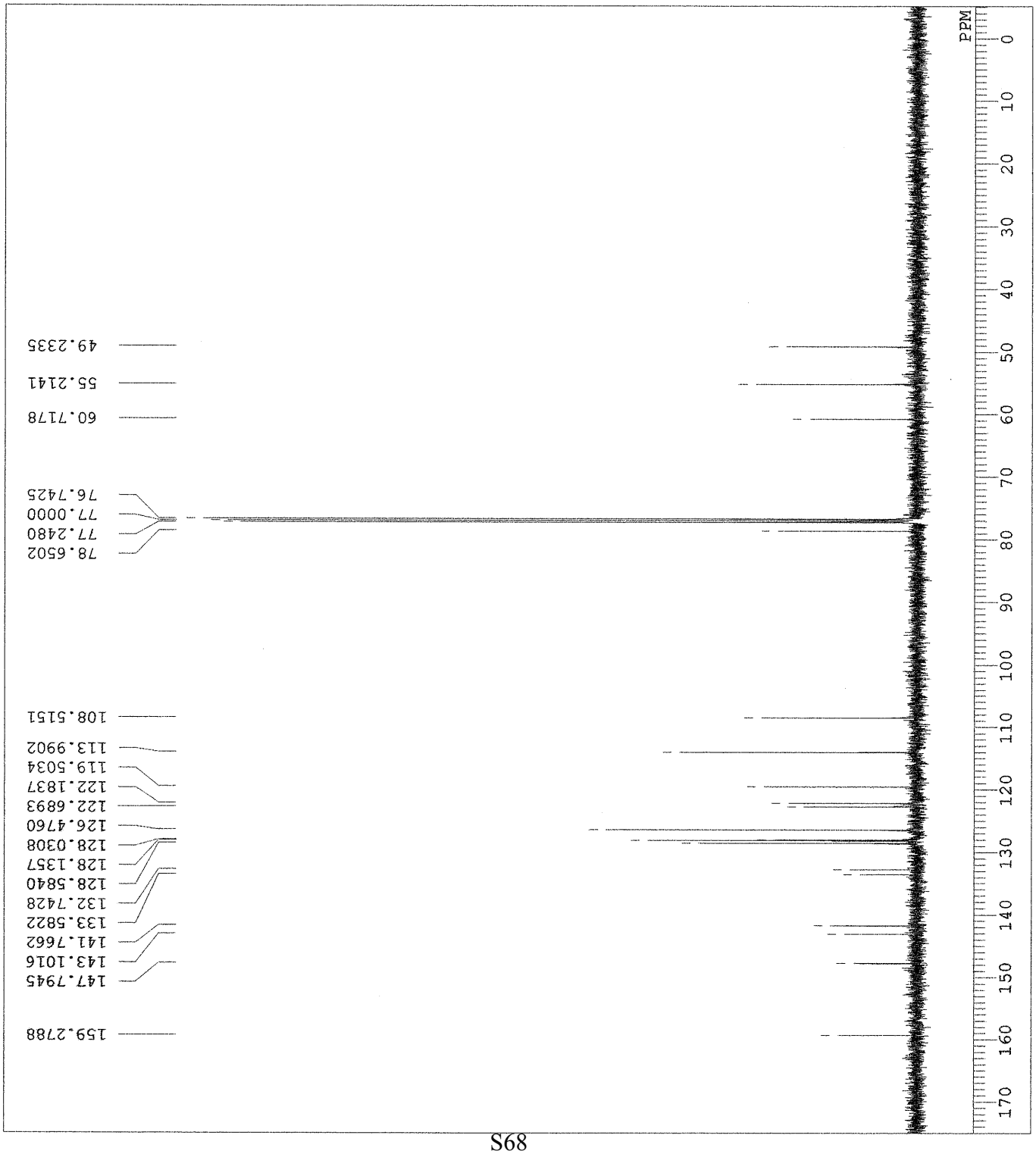
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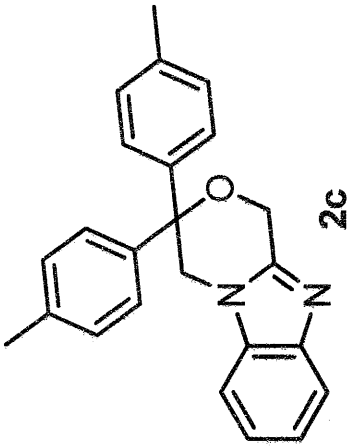
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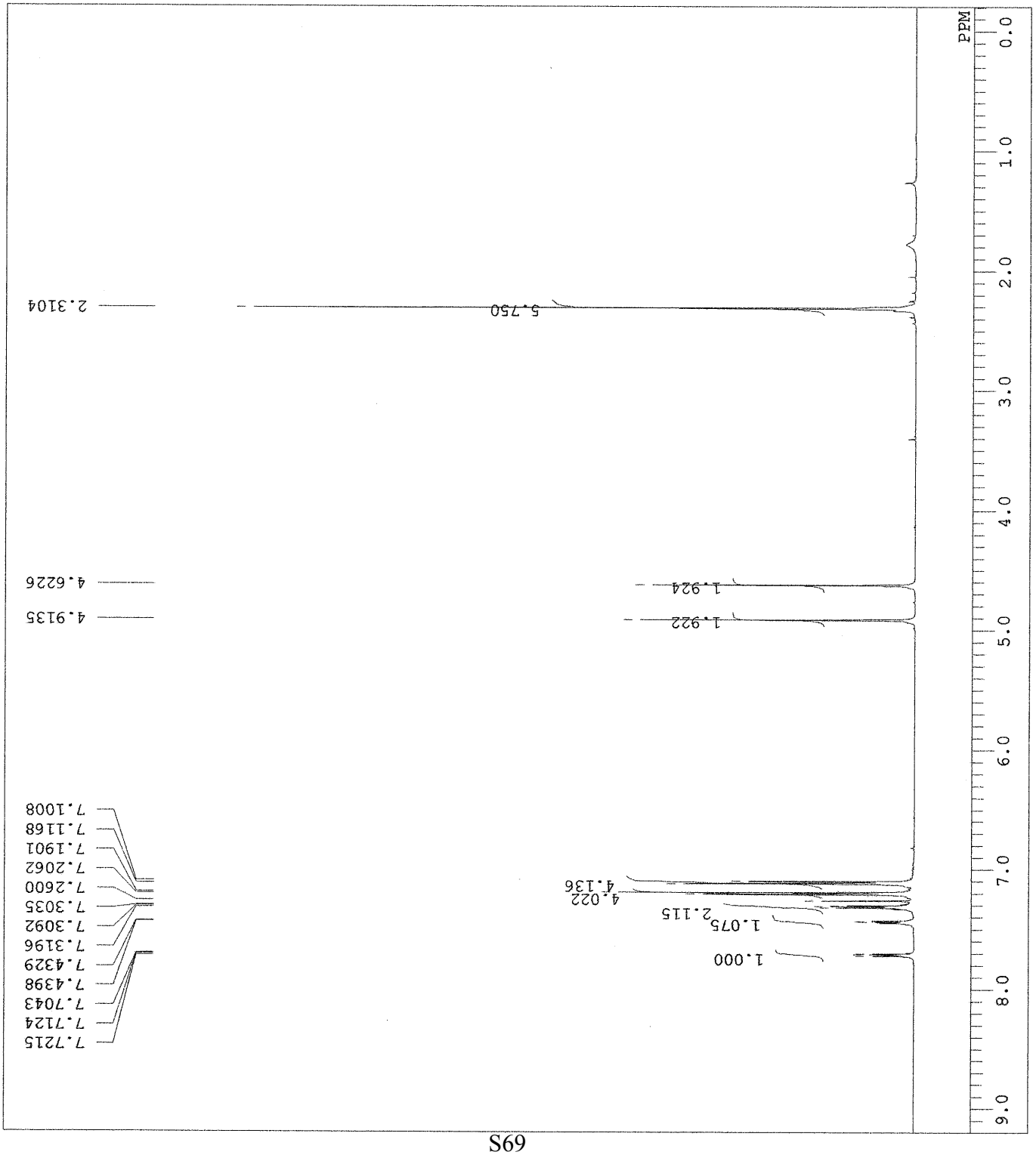
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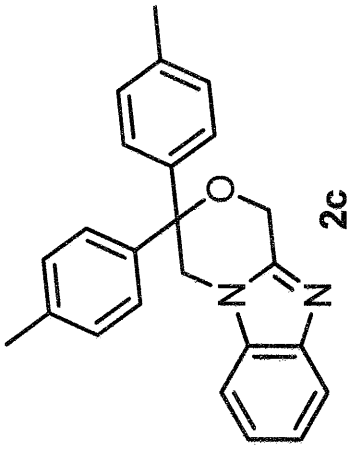
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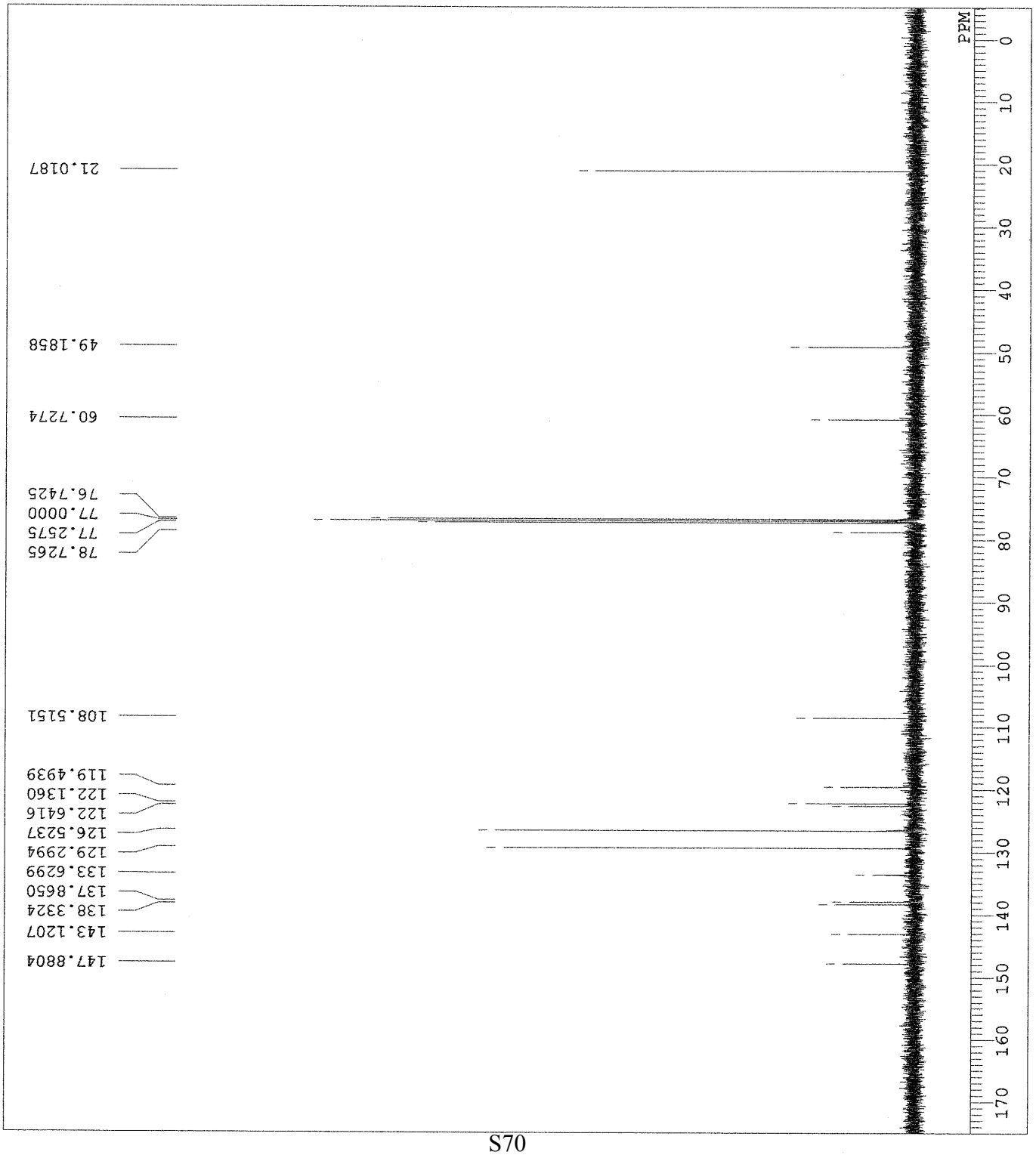
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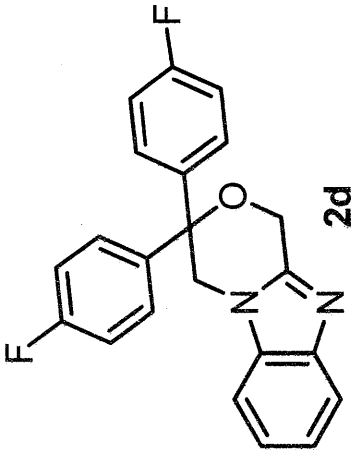
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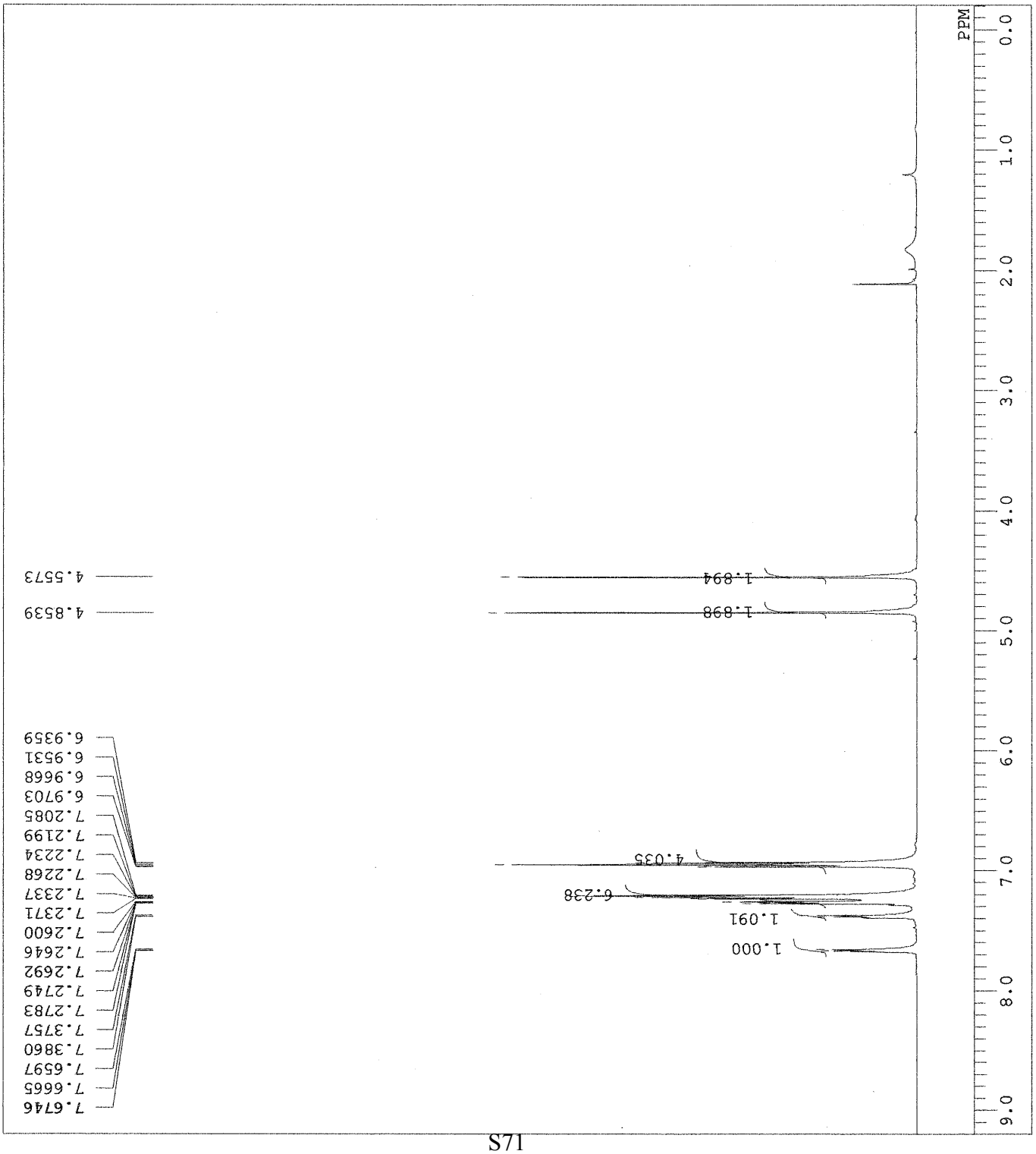
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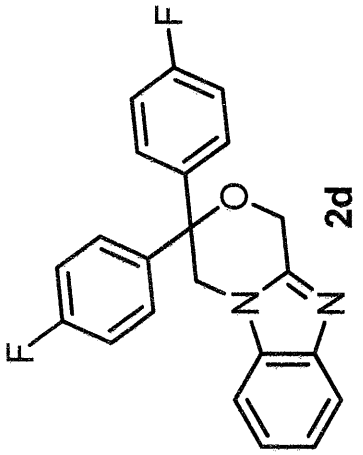
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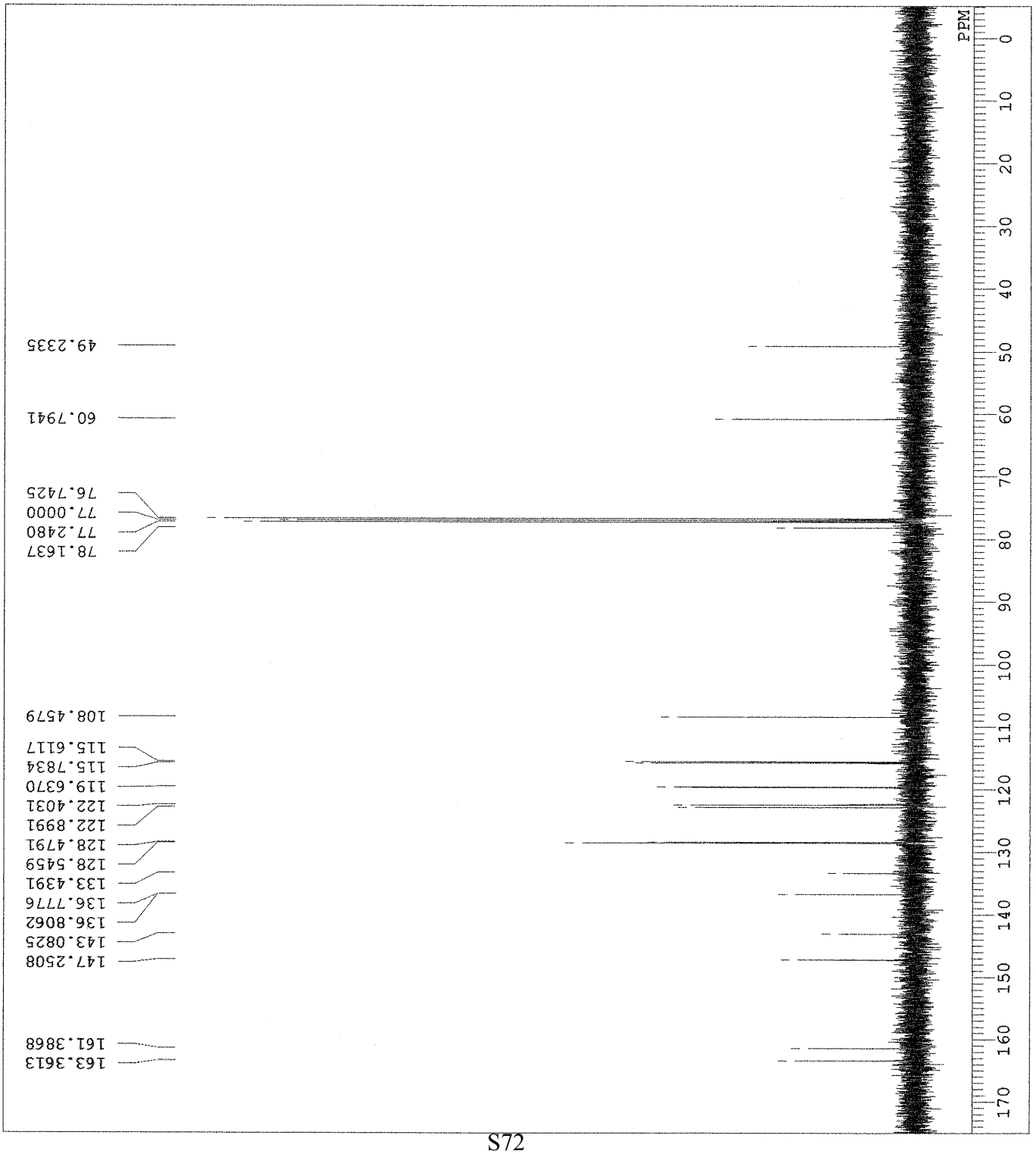
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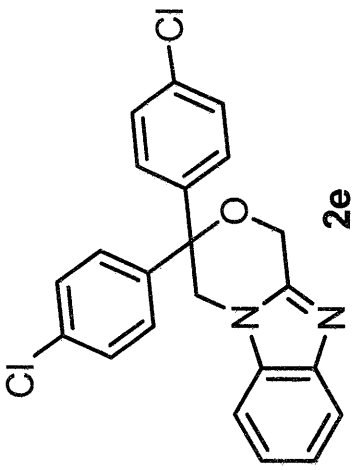
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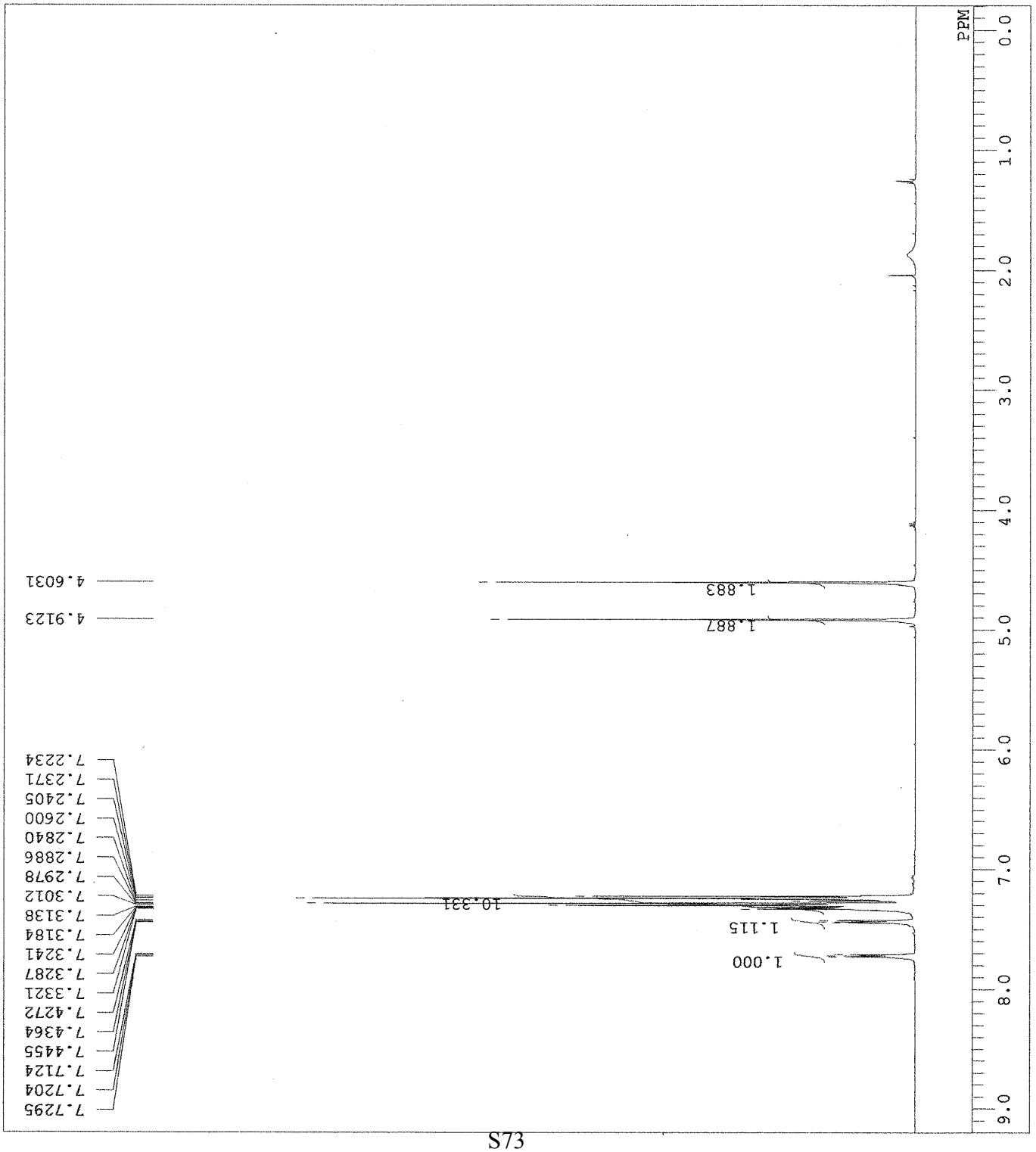
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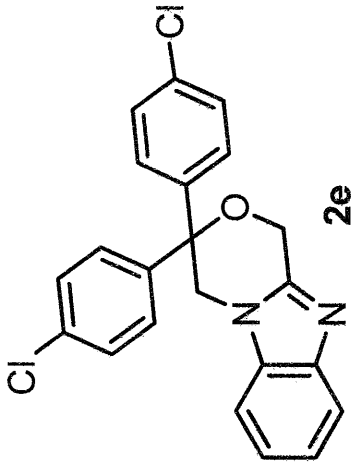
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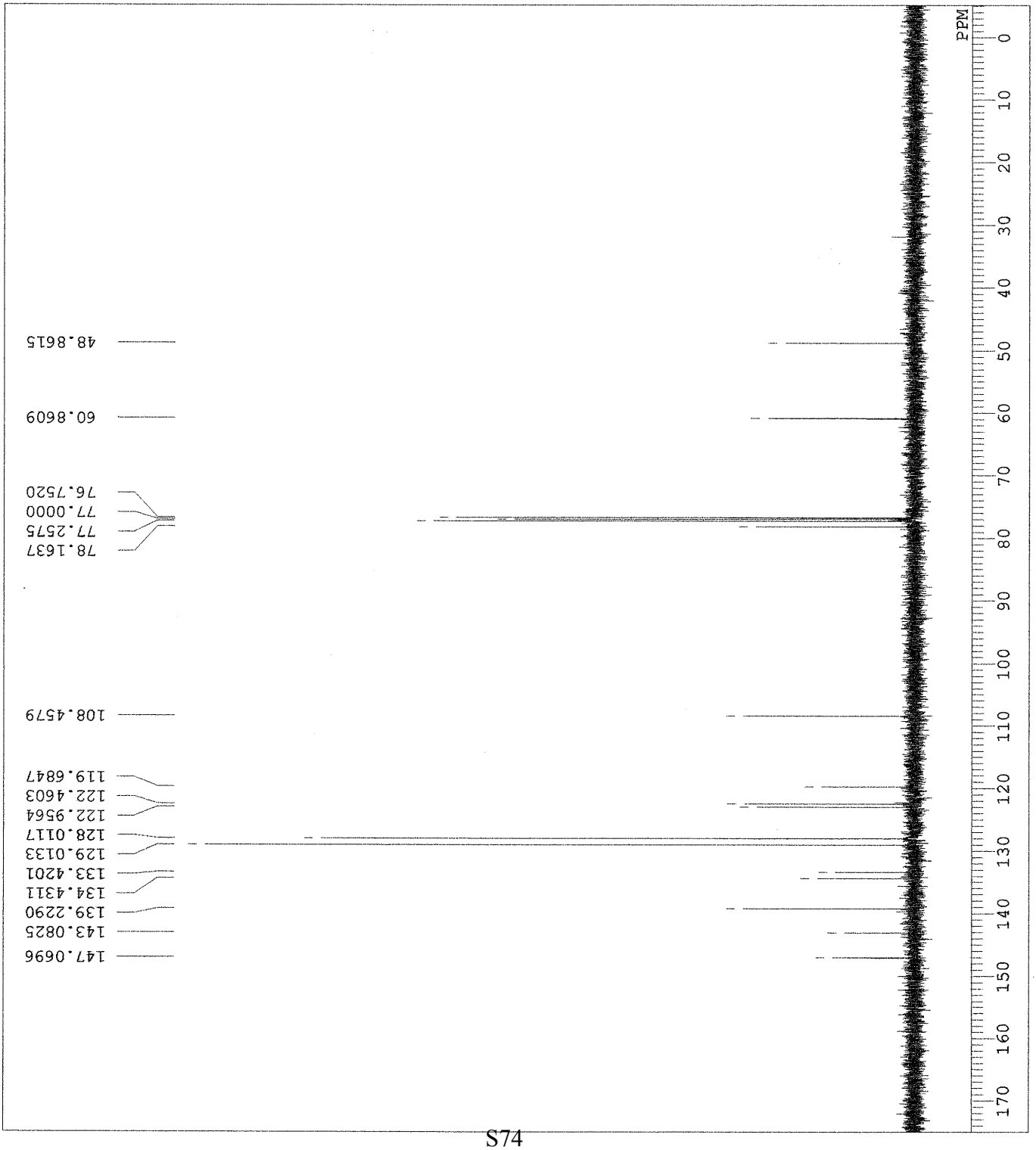
2e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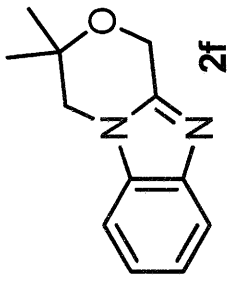
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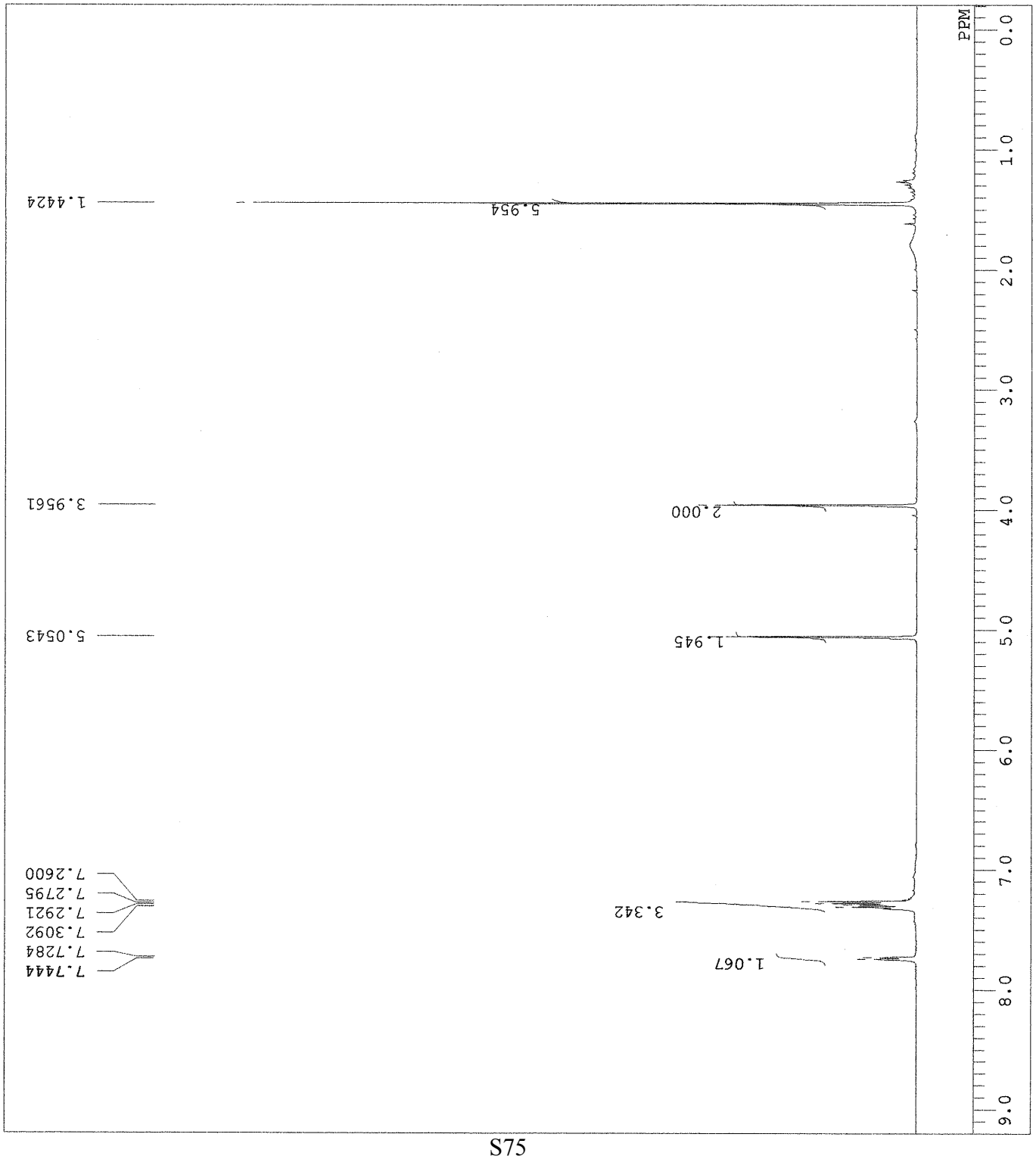
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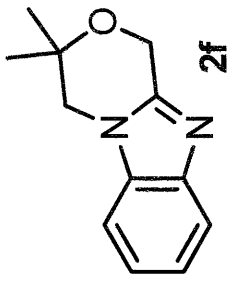
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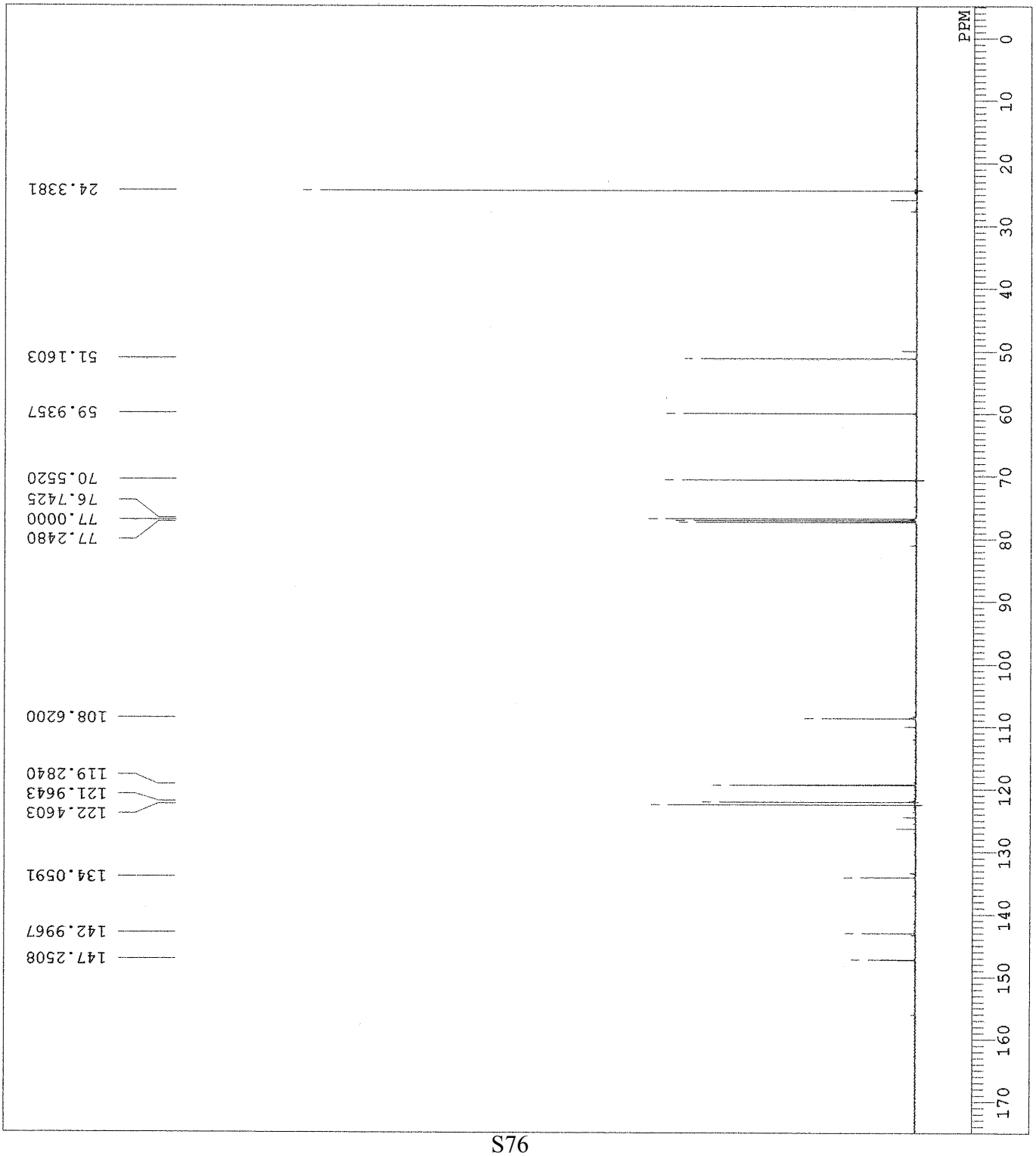
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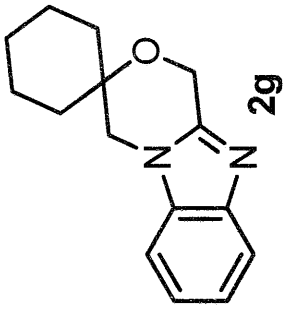
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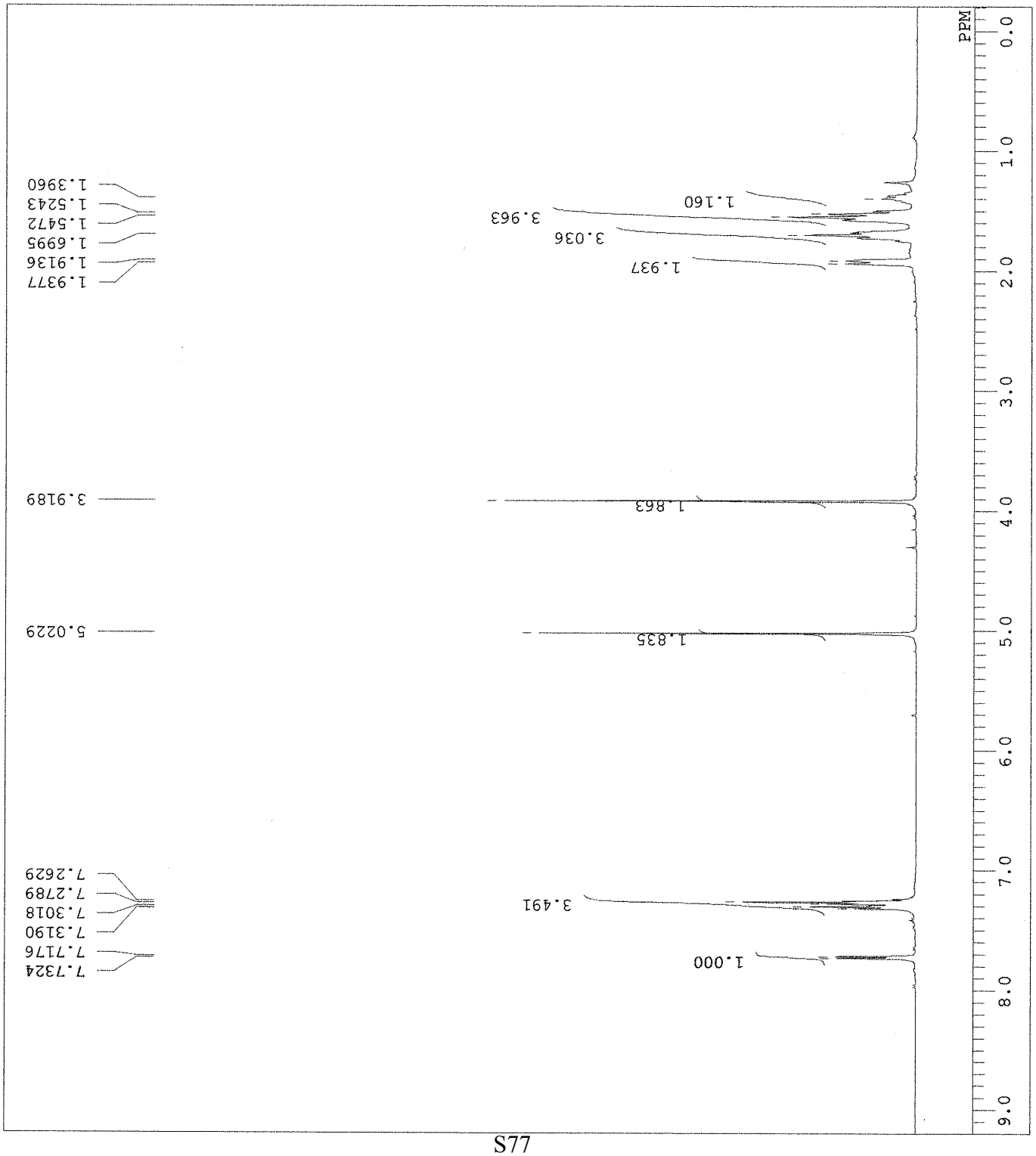
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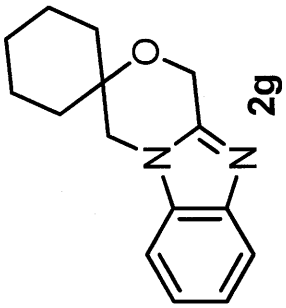
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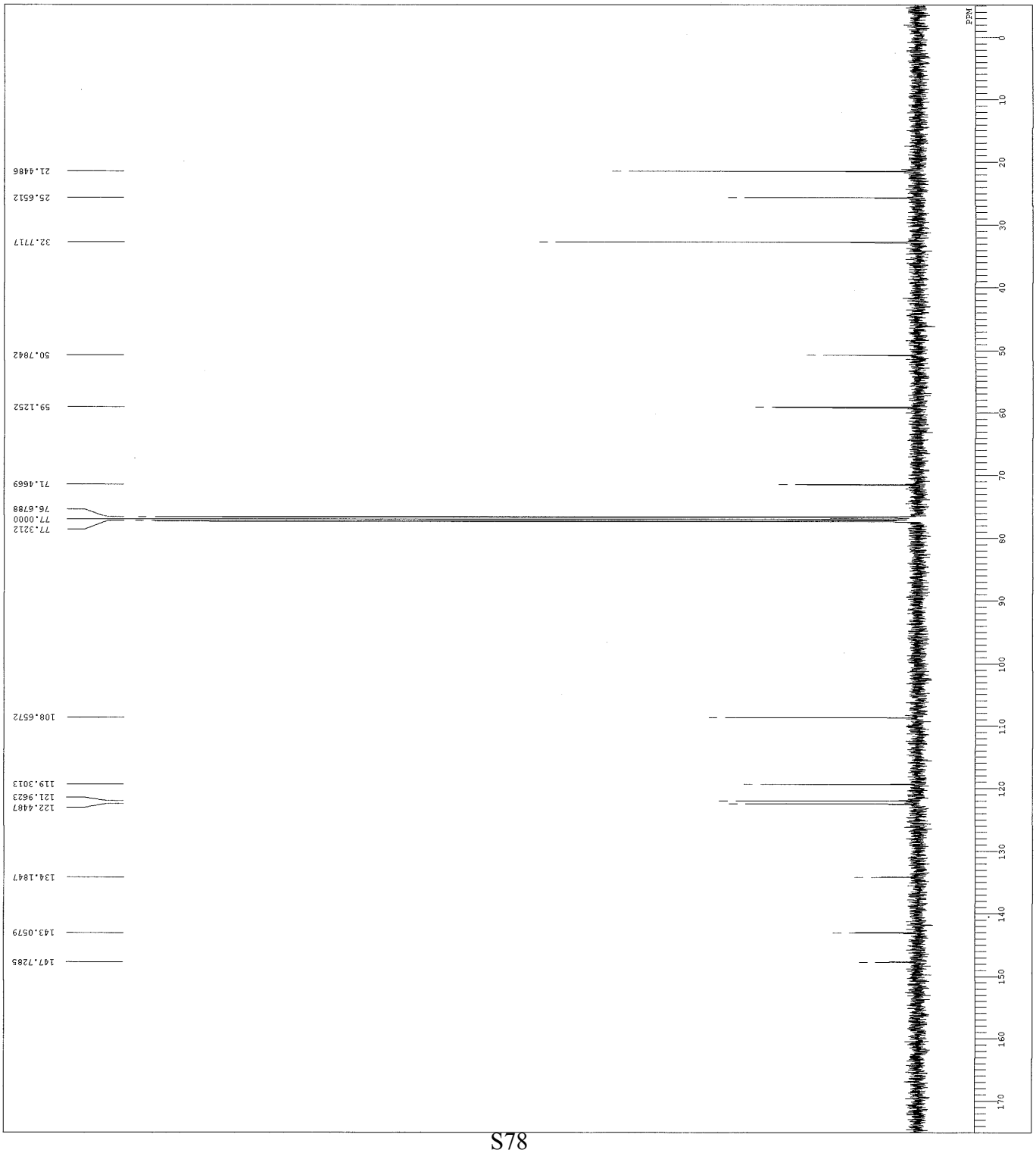
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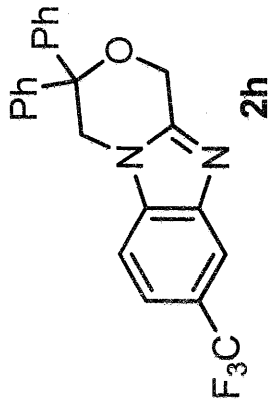
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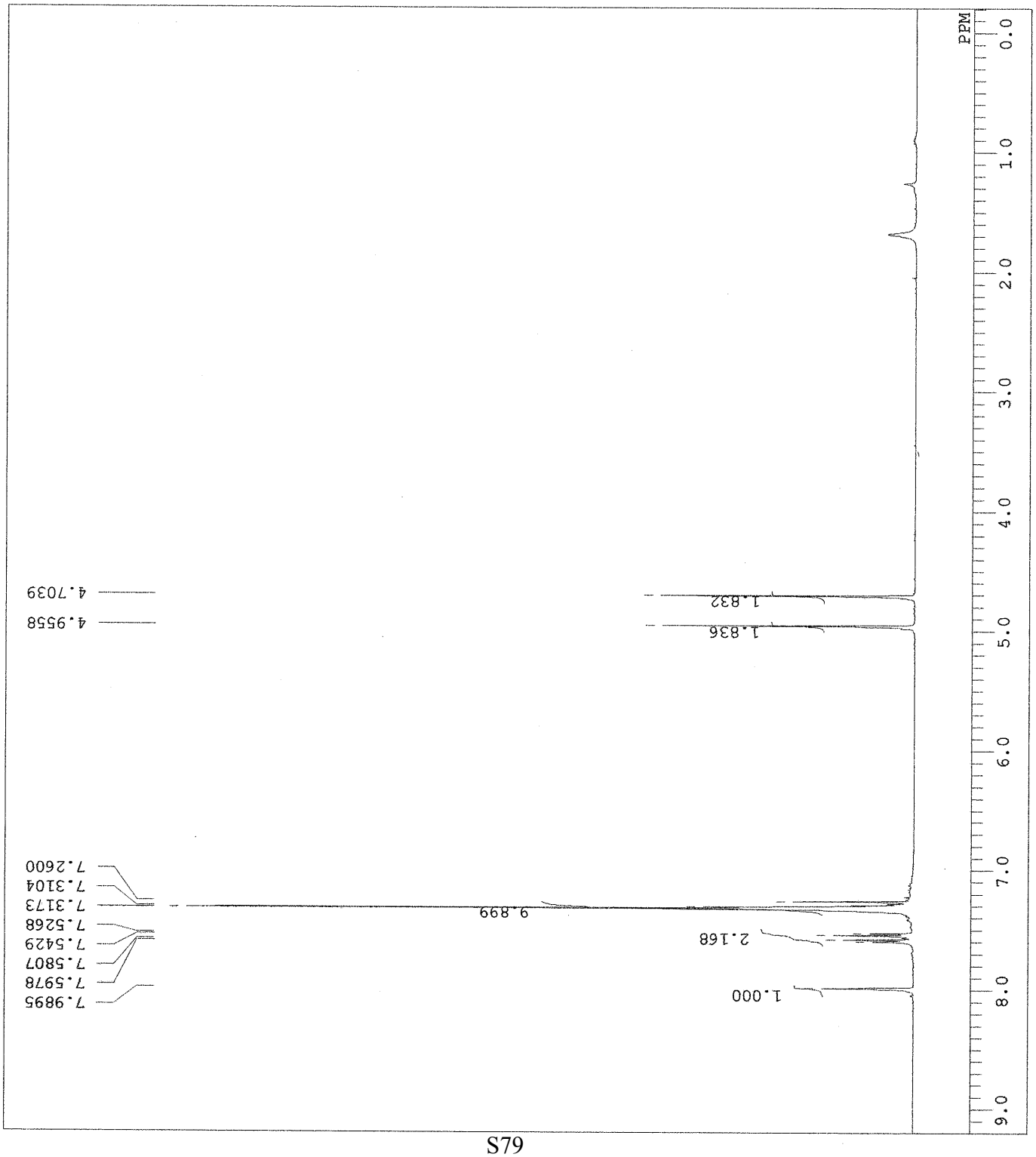
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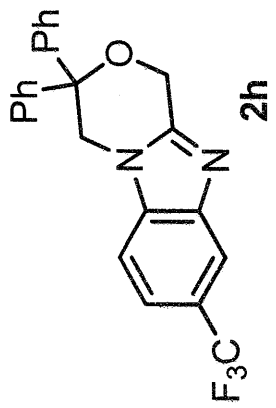
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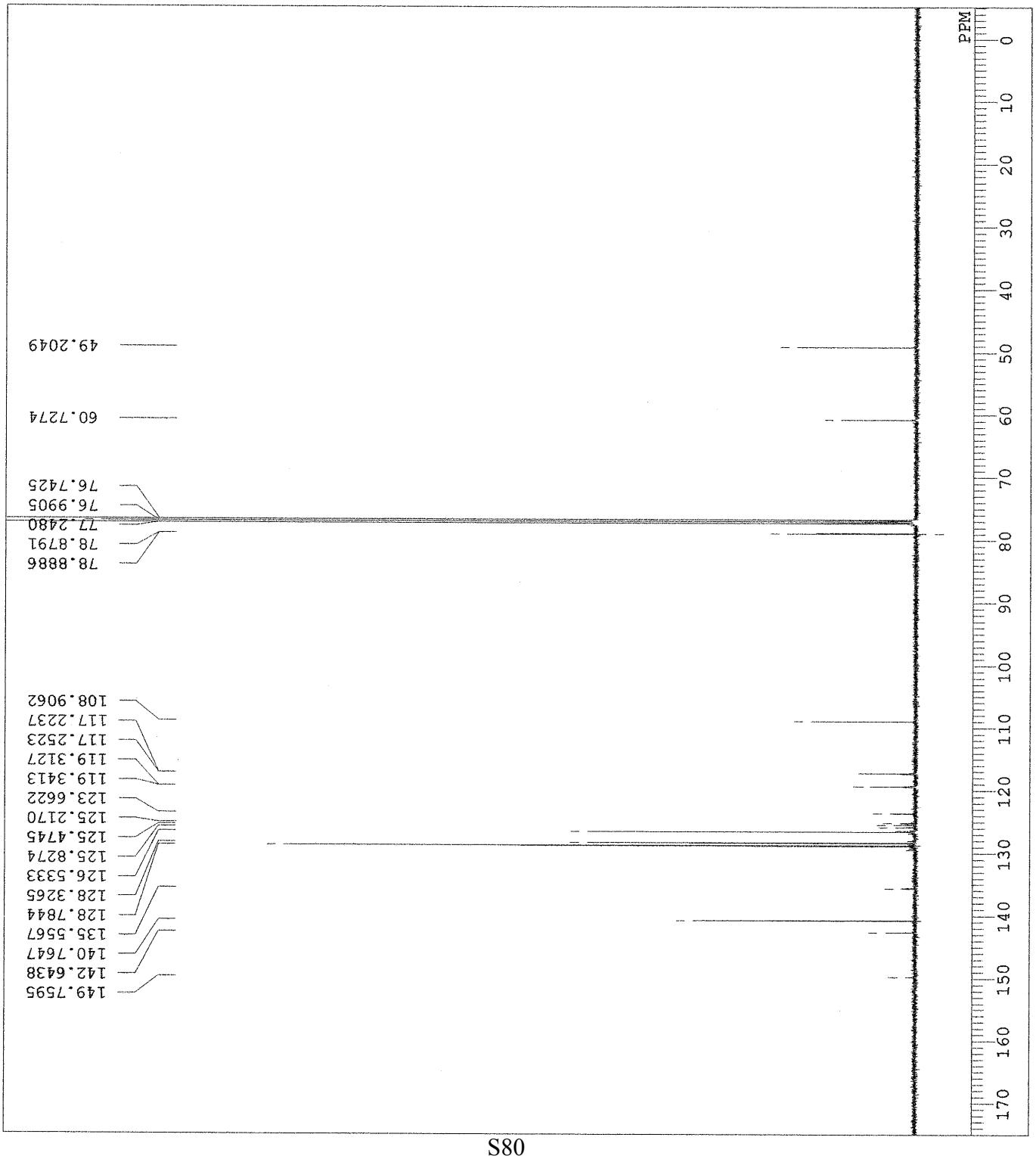
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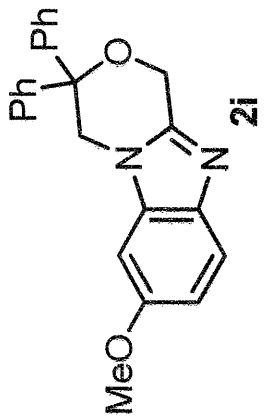
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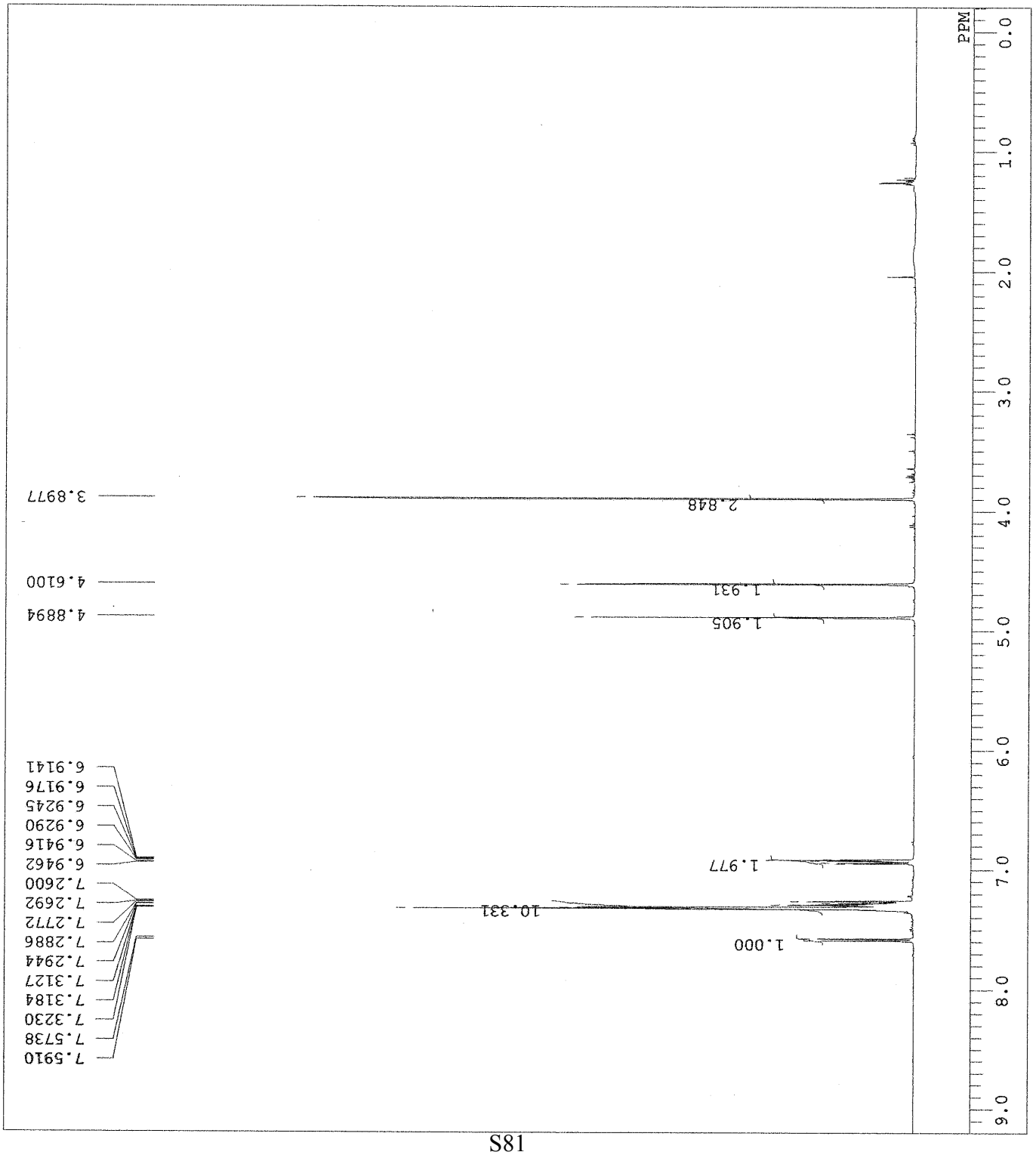
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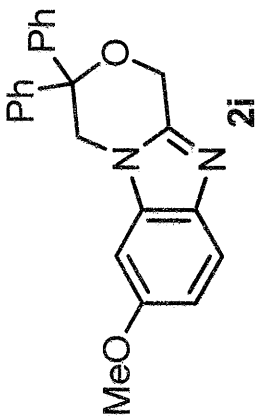
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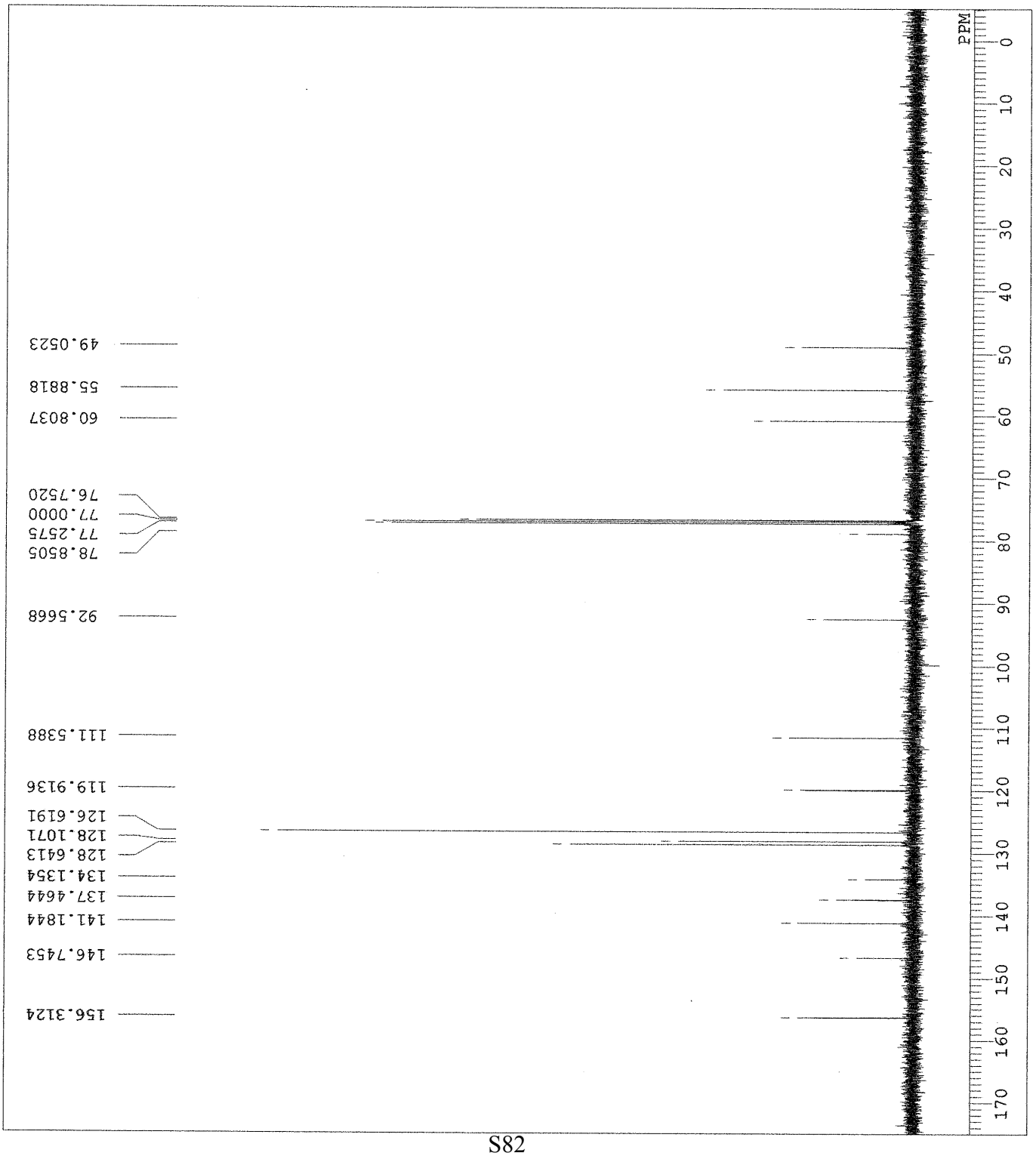
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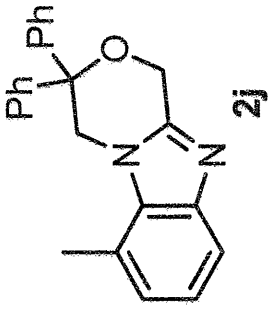
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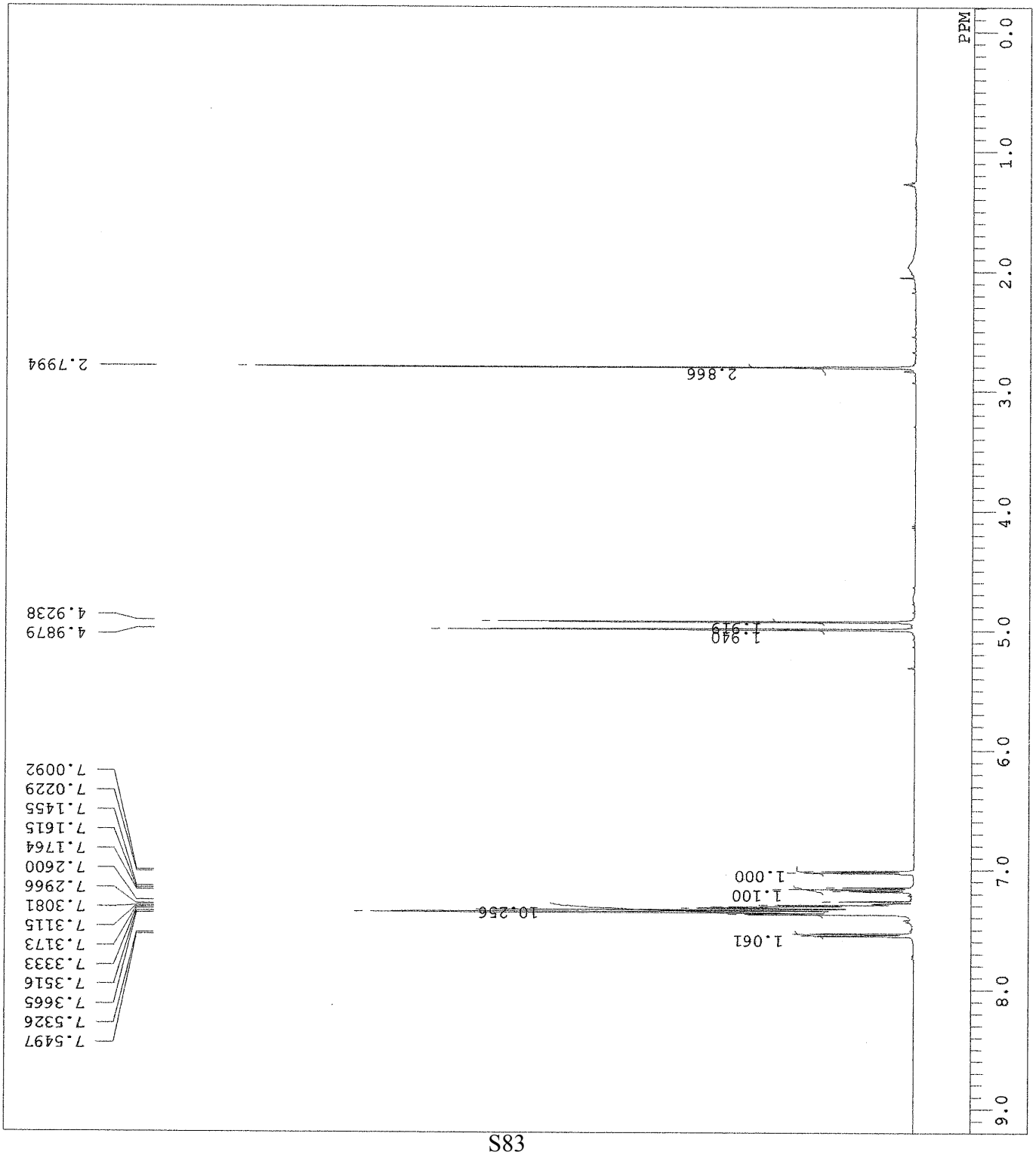
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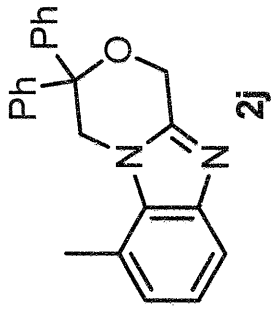
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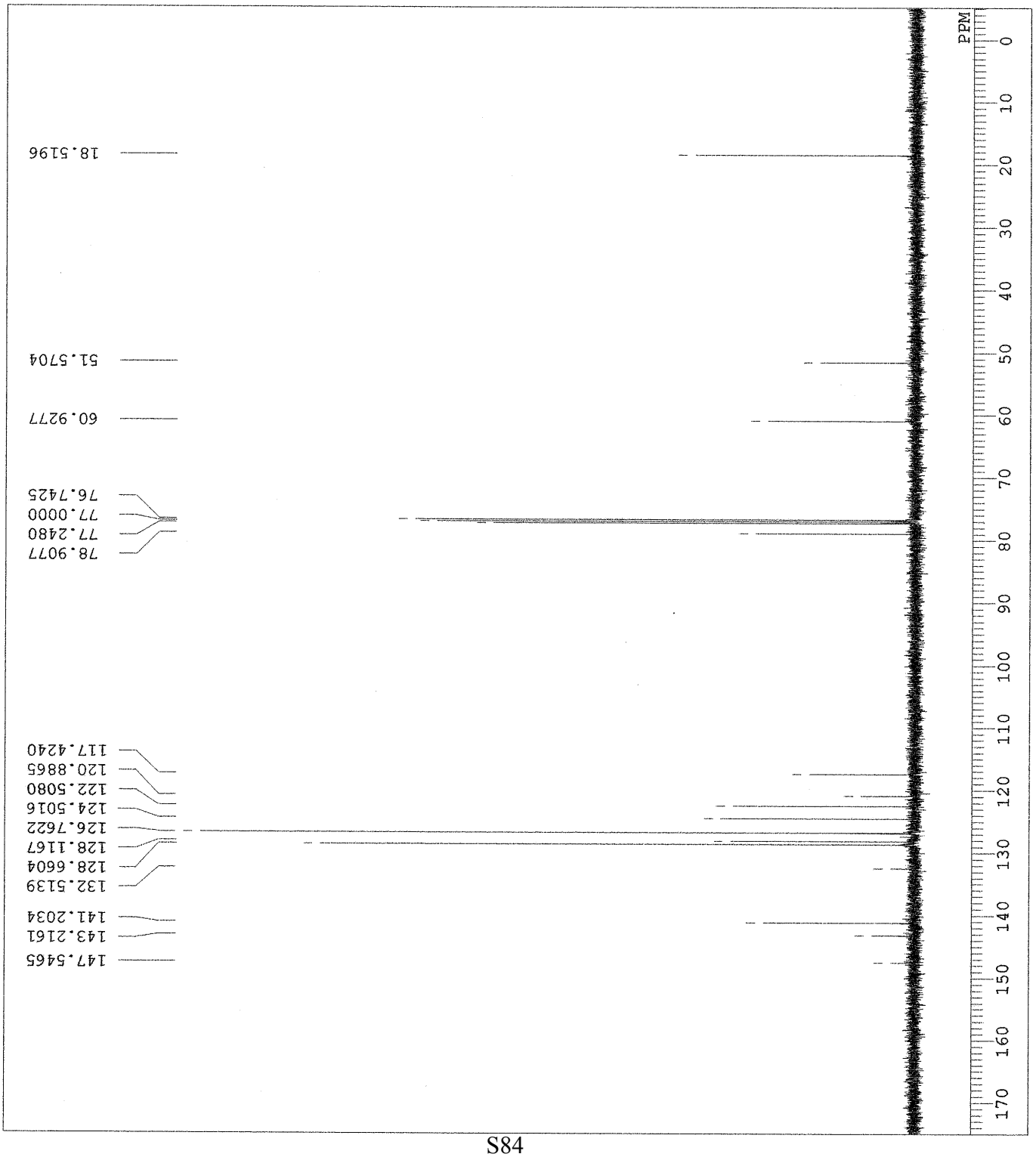
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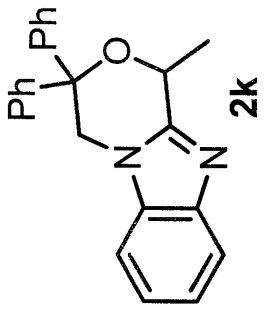
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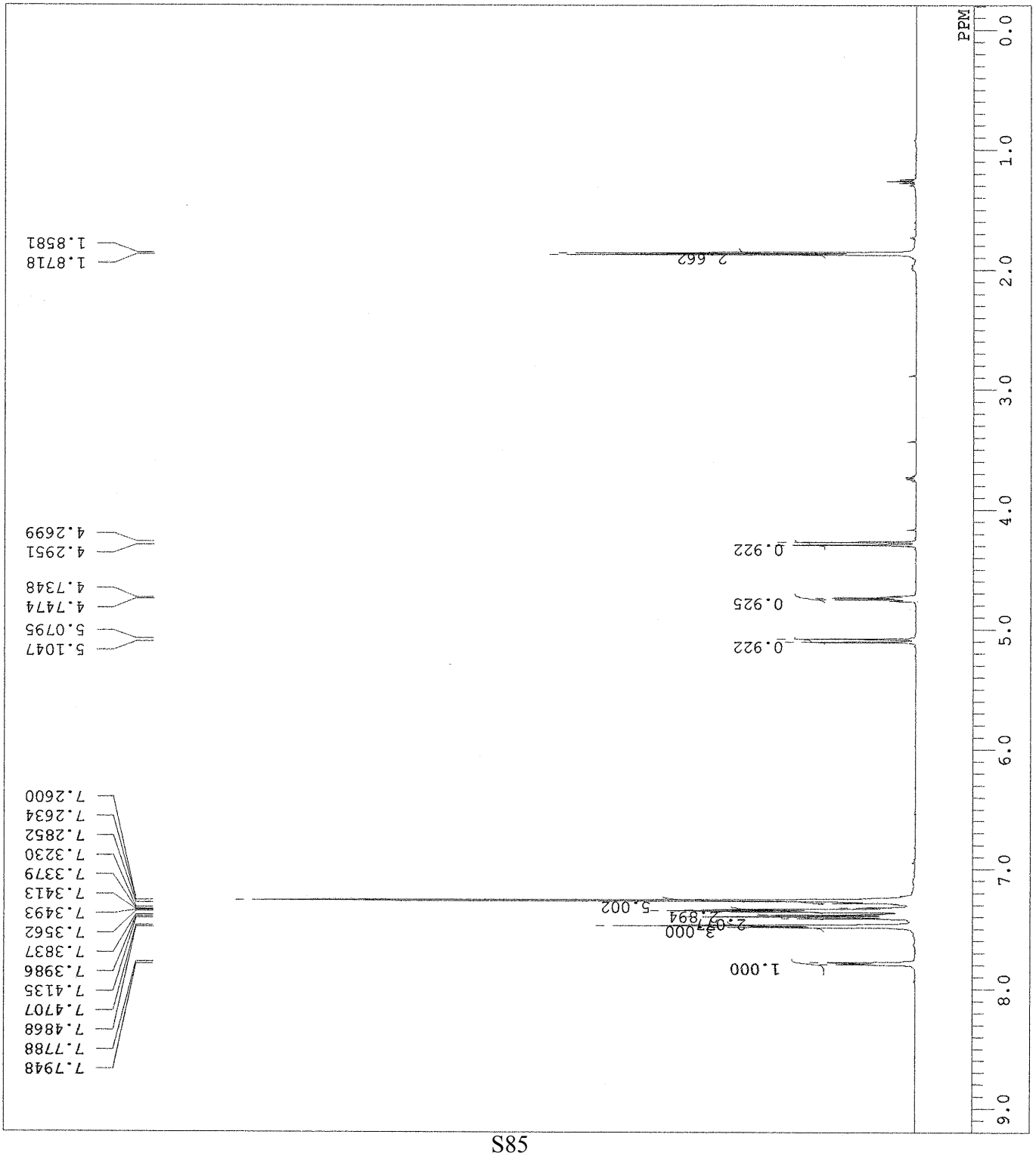
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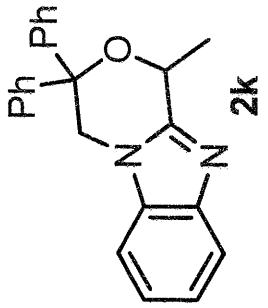
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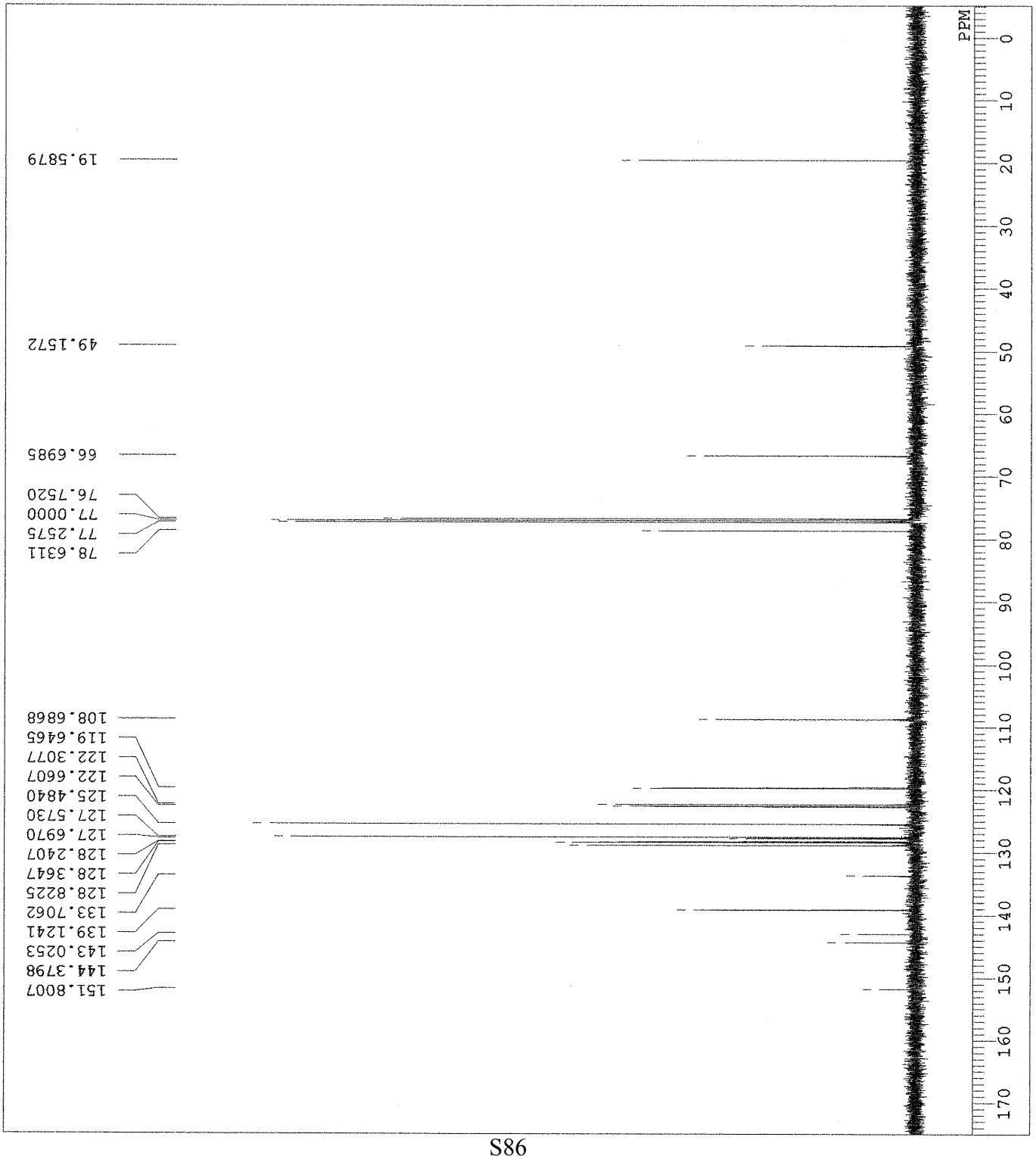
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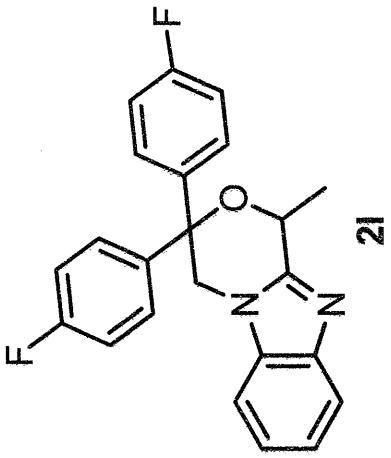
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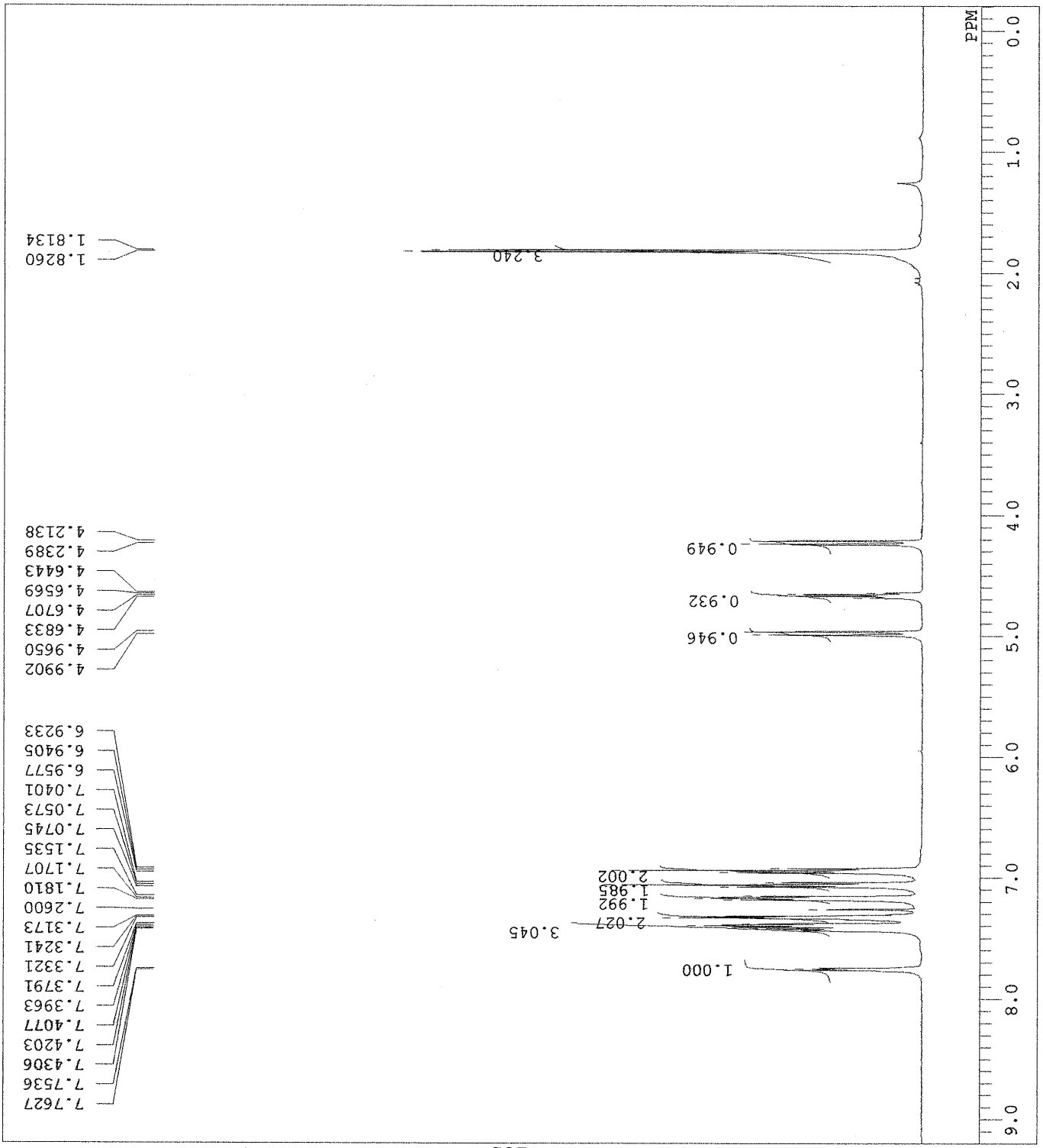
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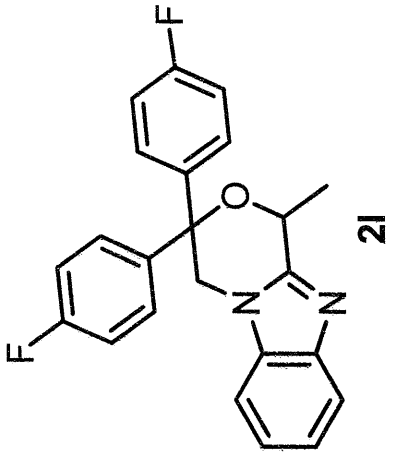
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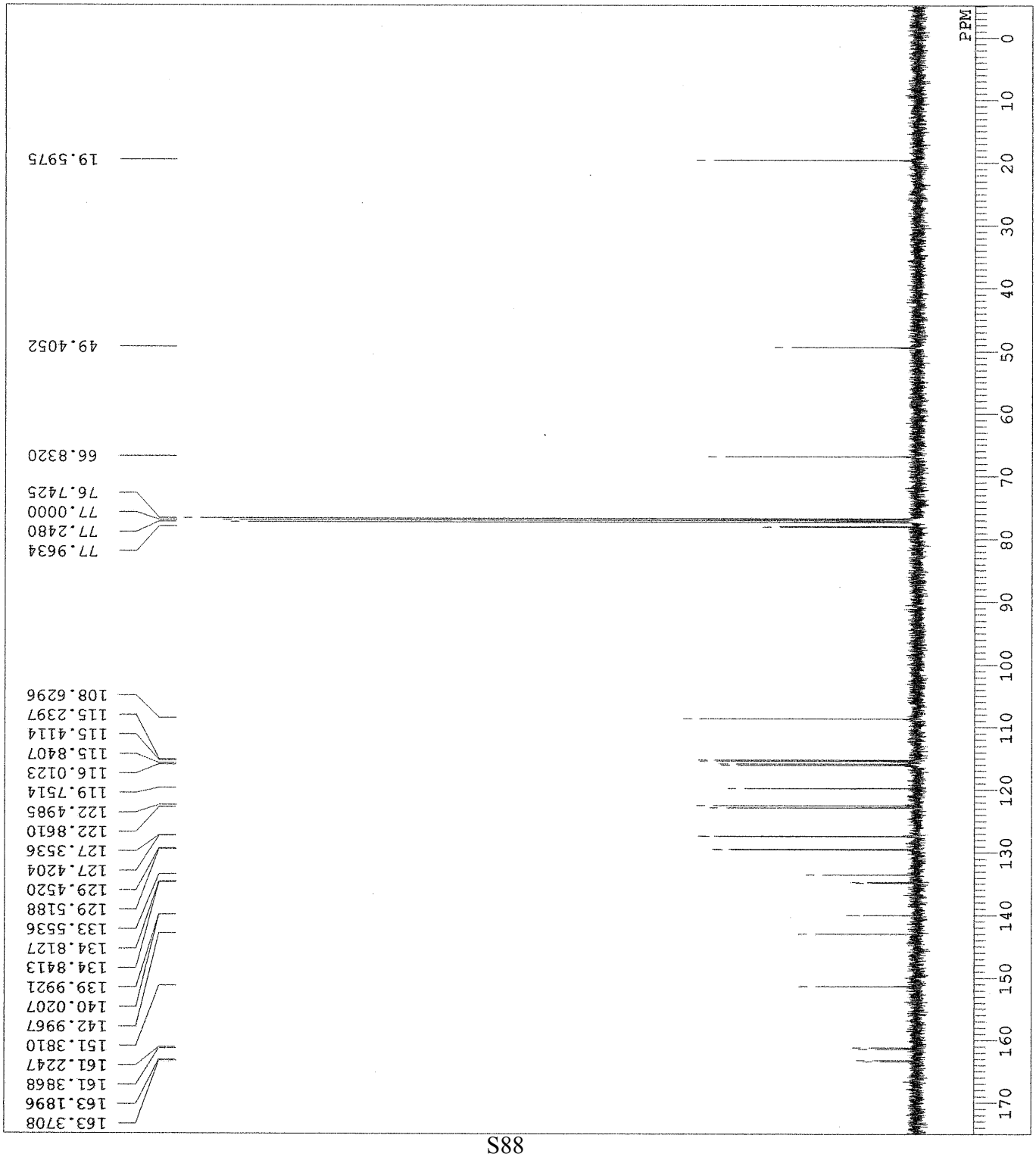
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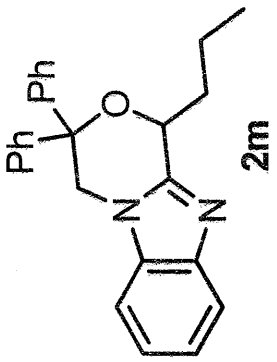
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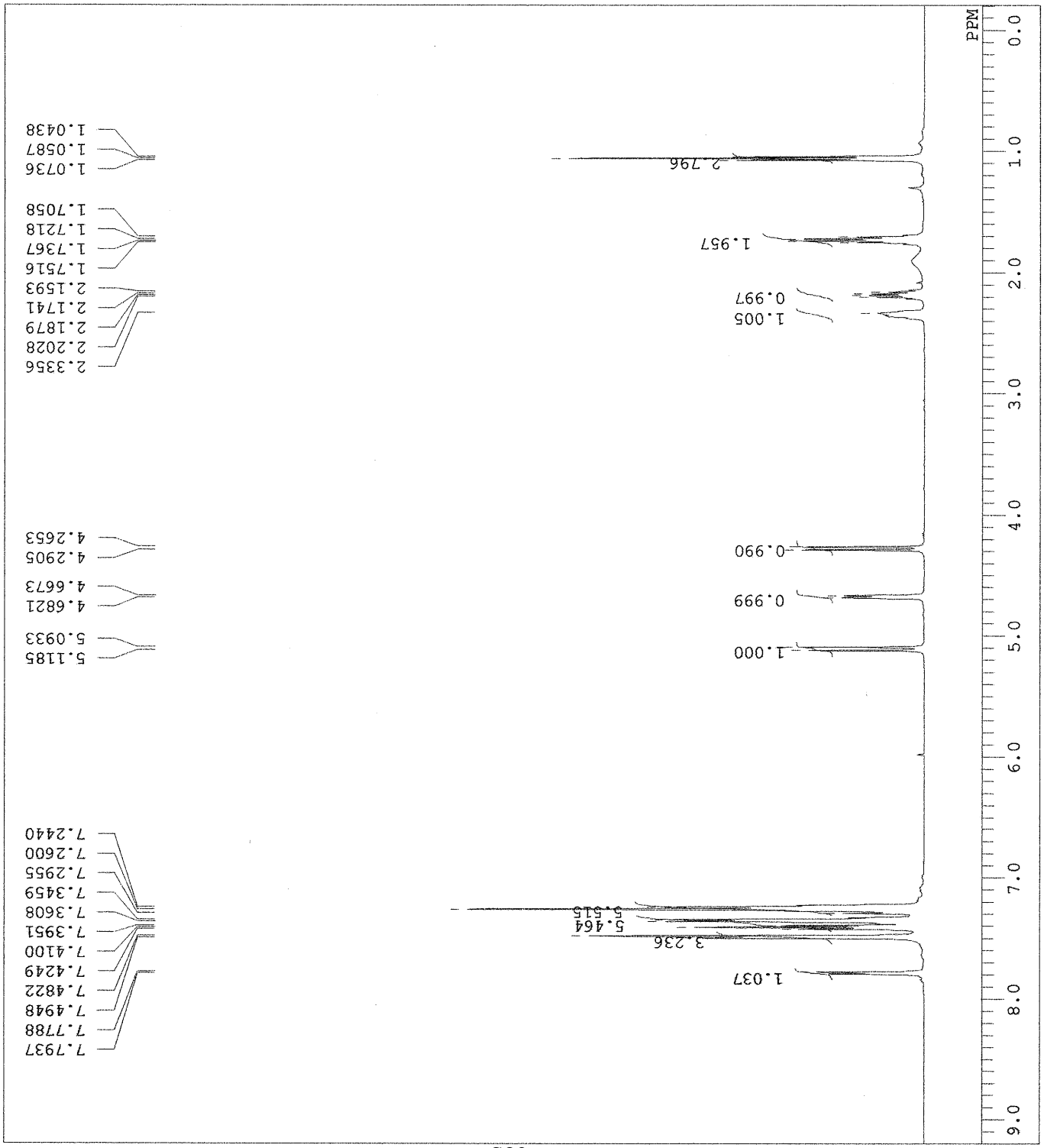
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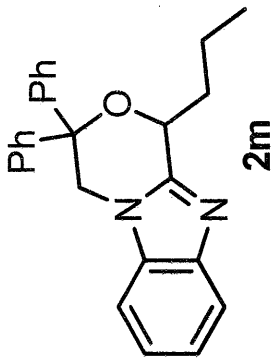
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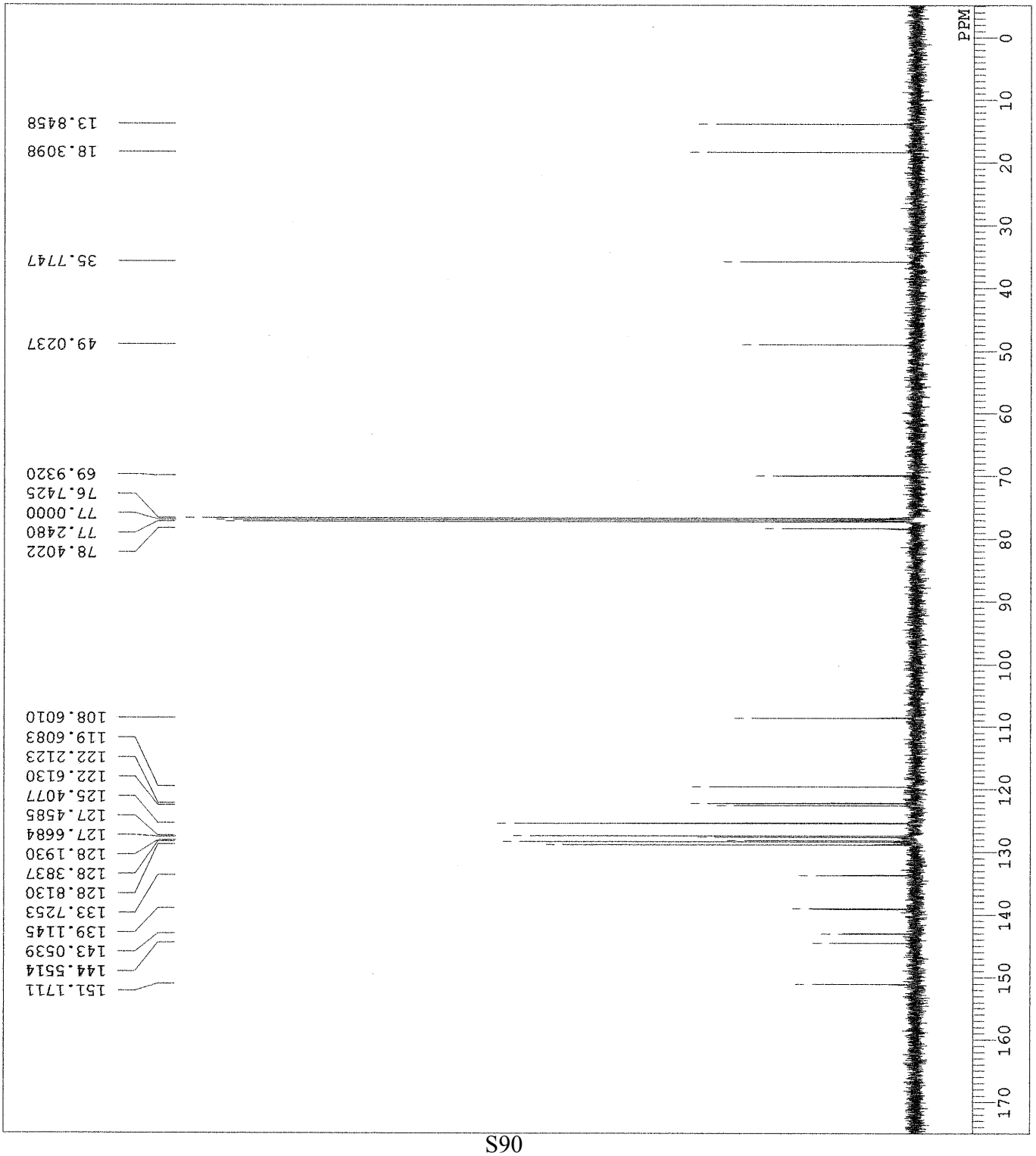
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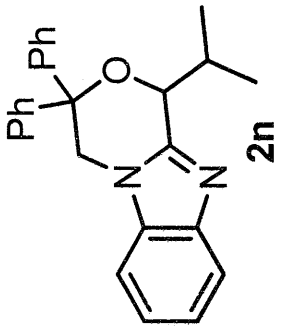
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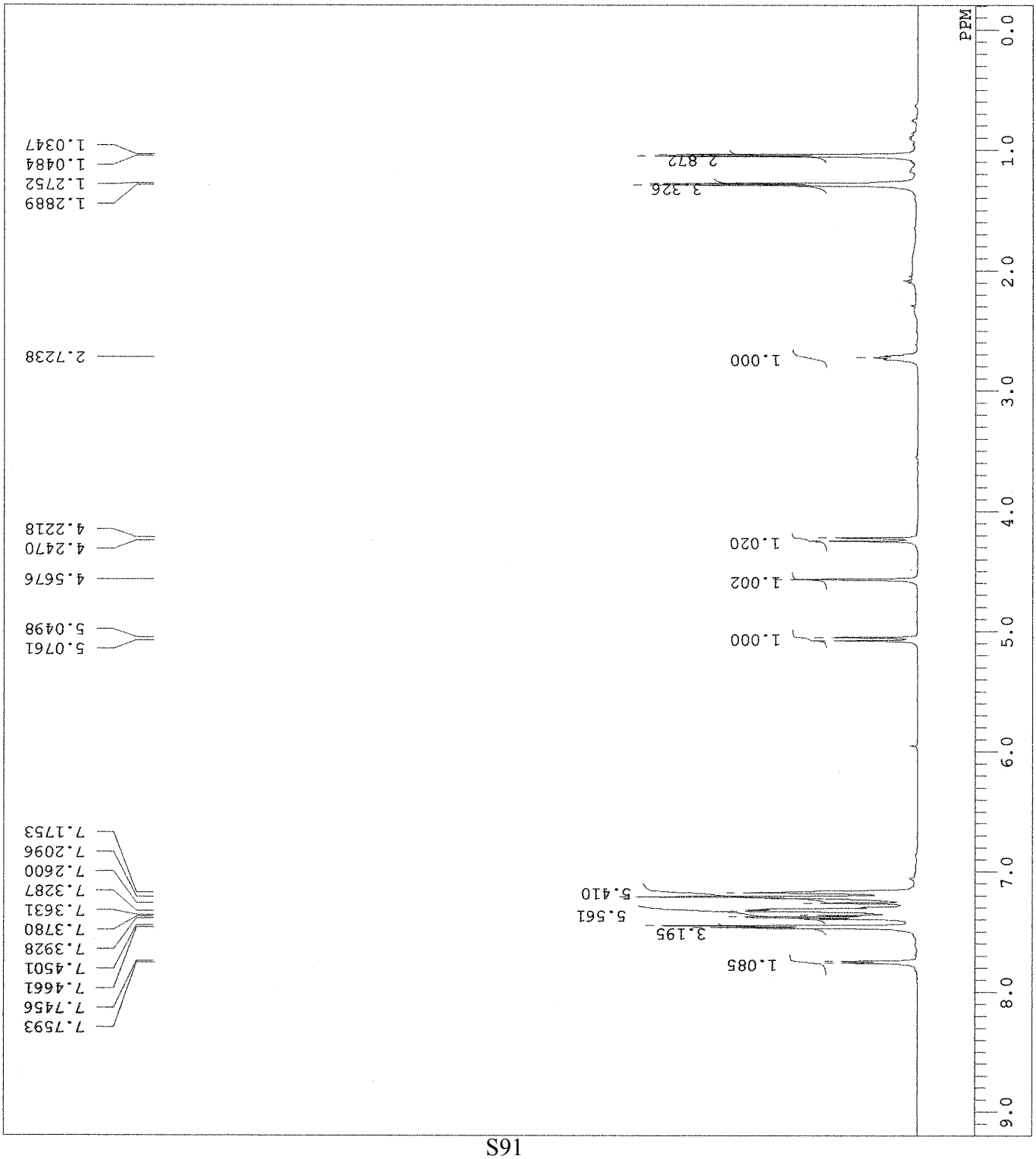
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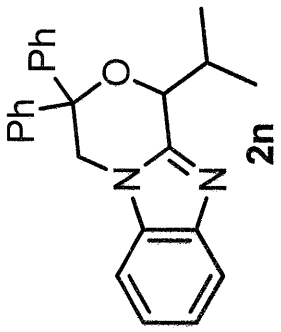
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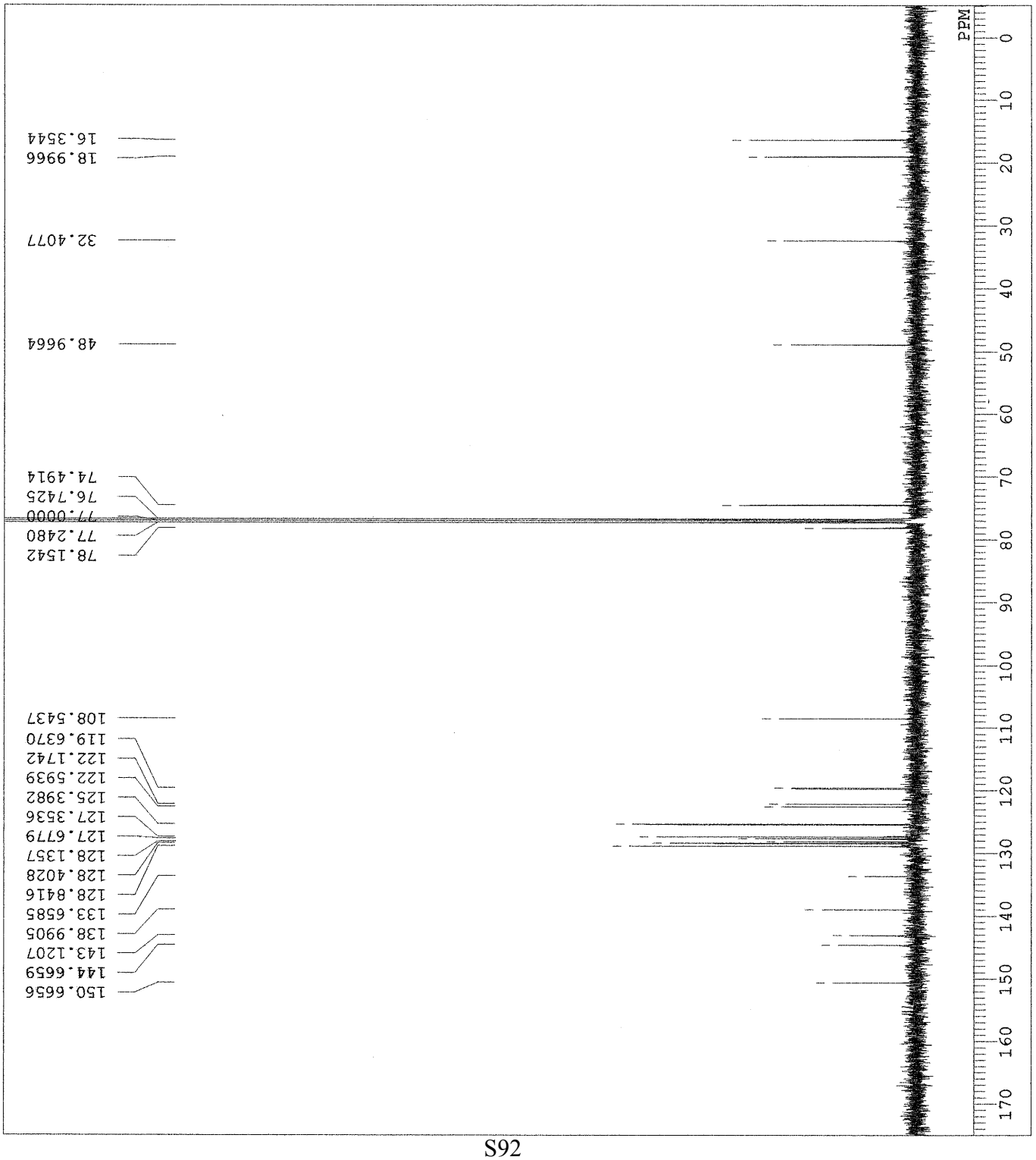
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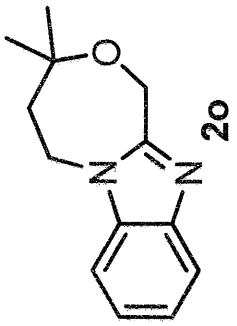
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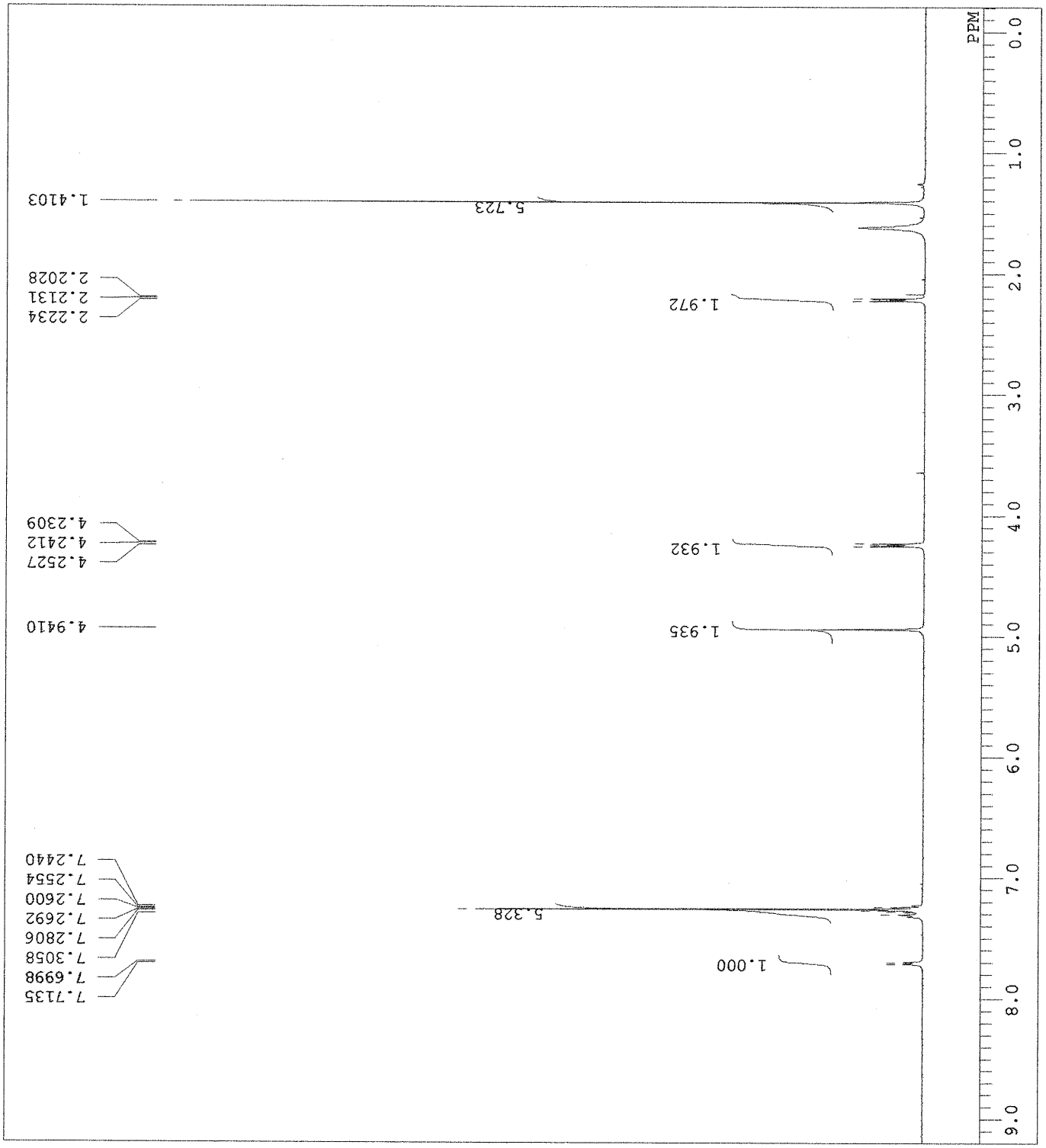
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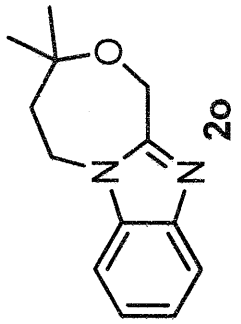
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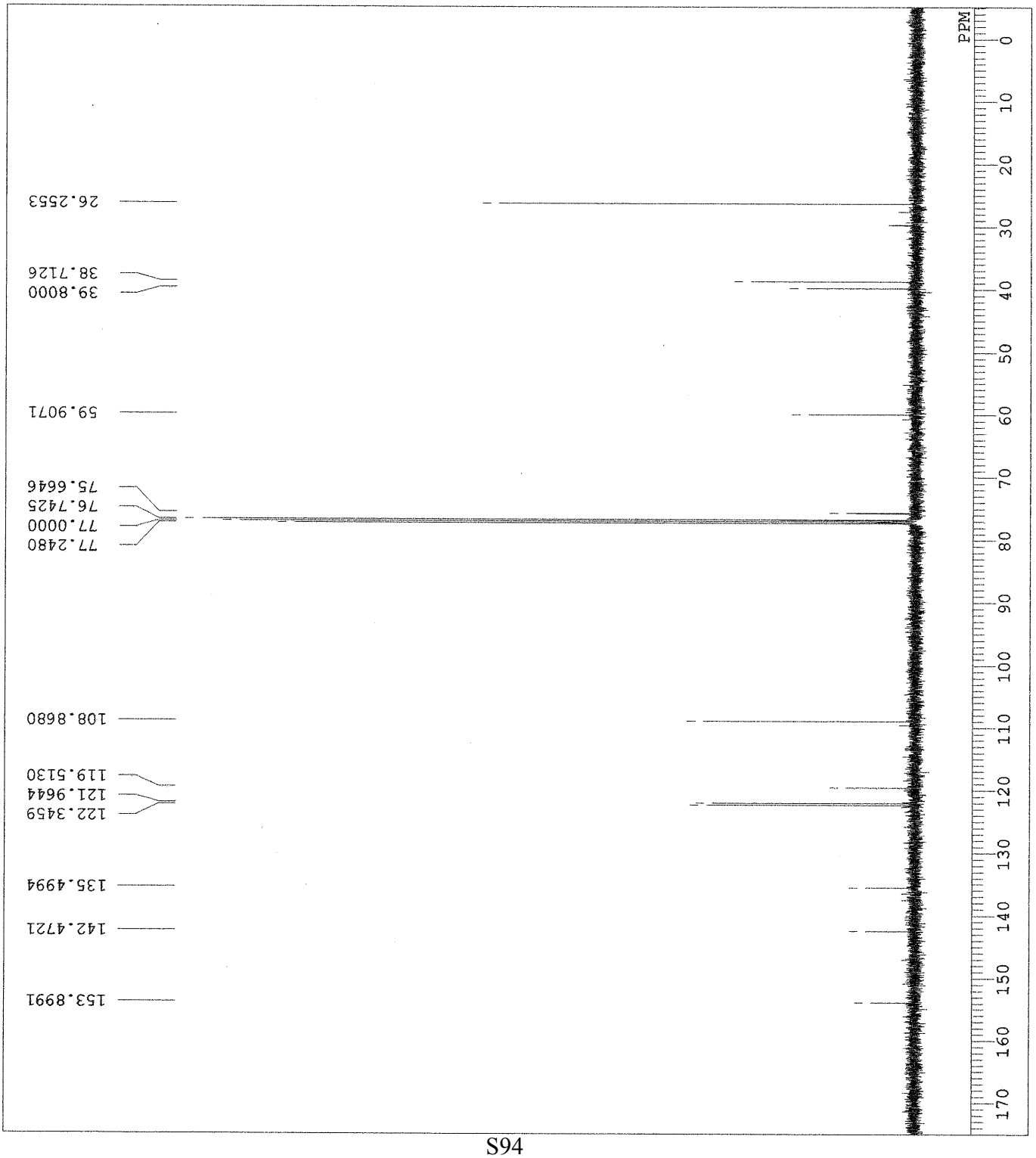
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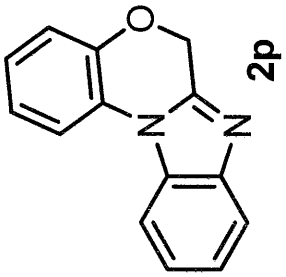
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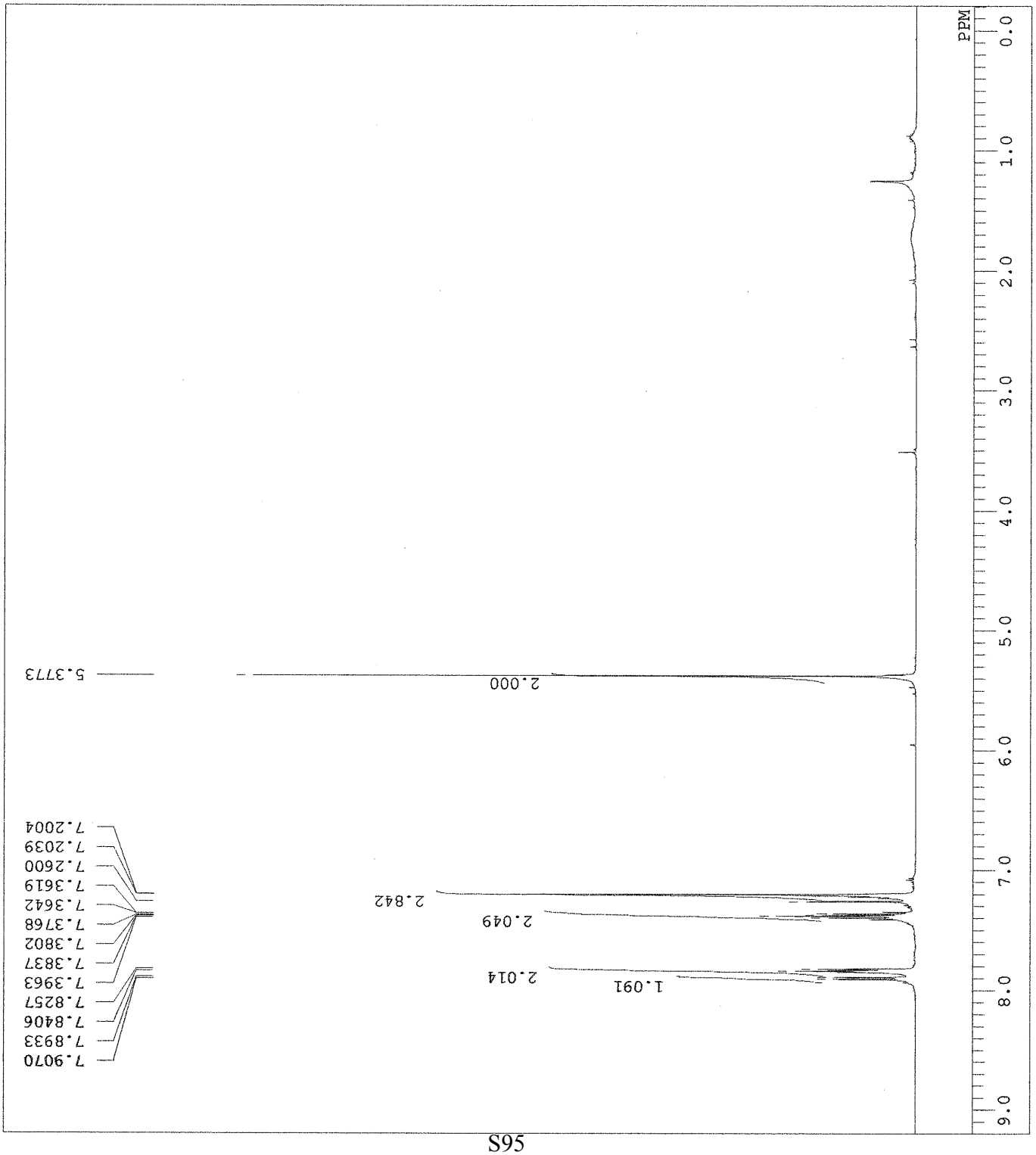
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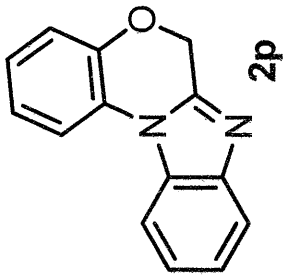
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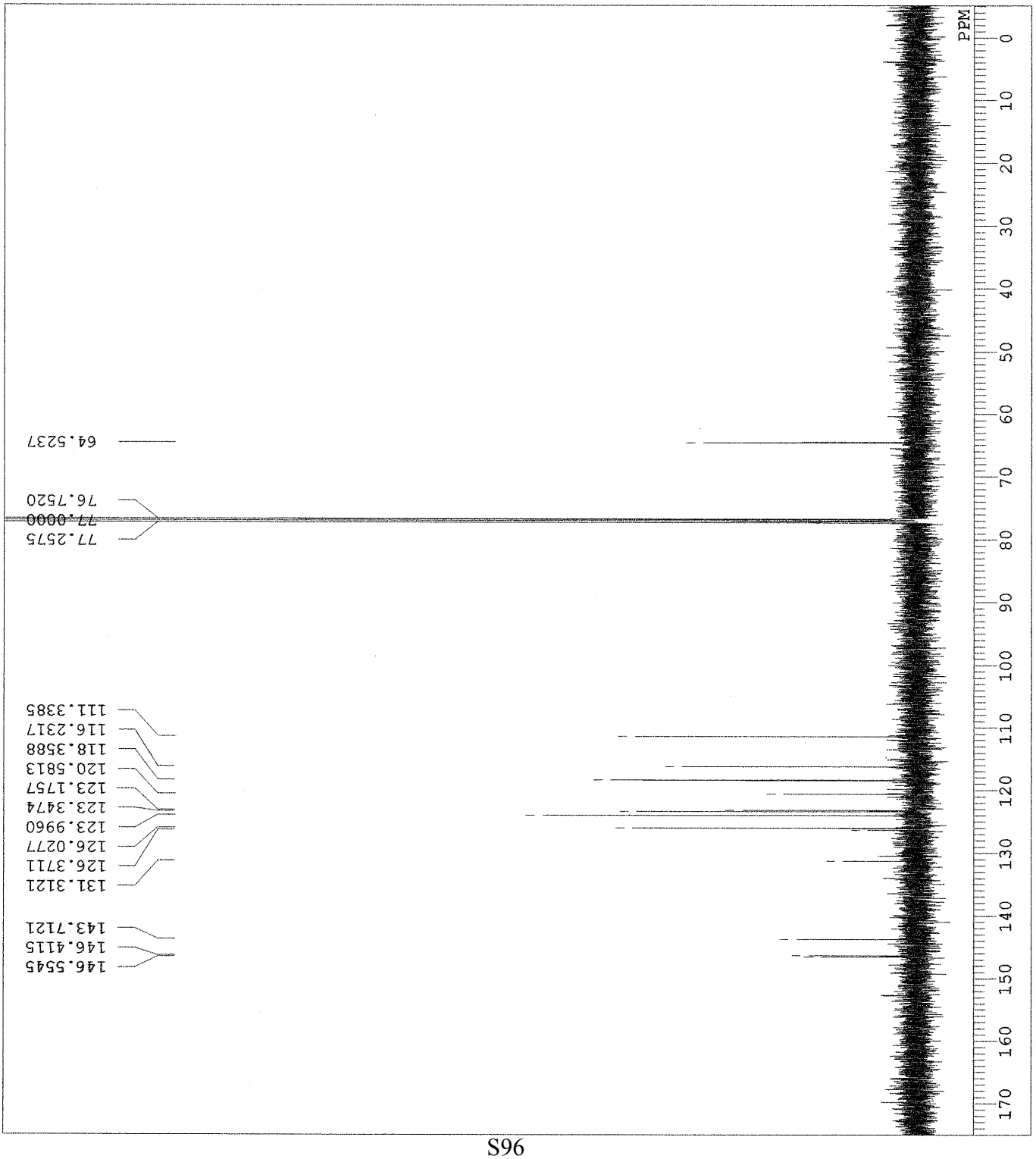
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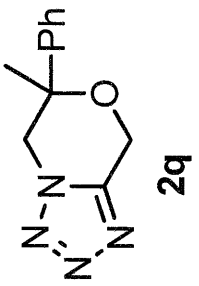
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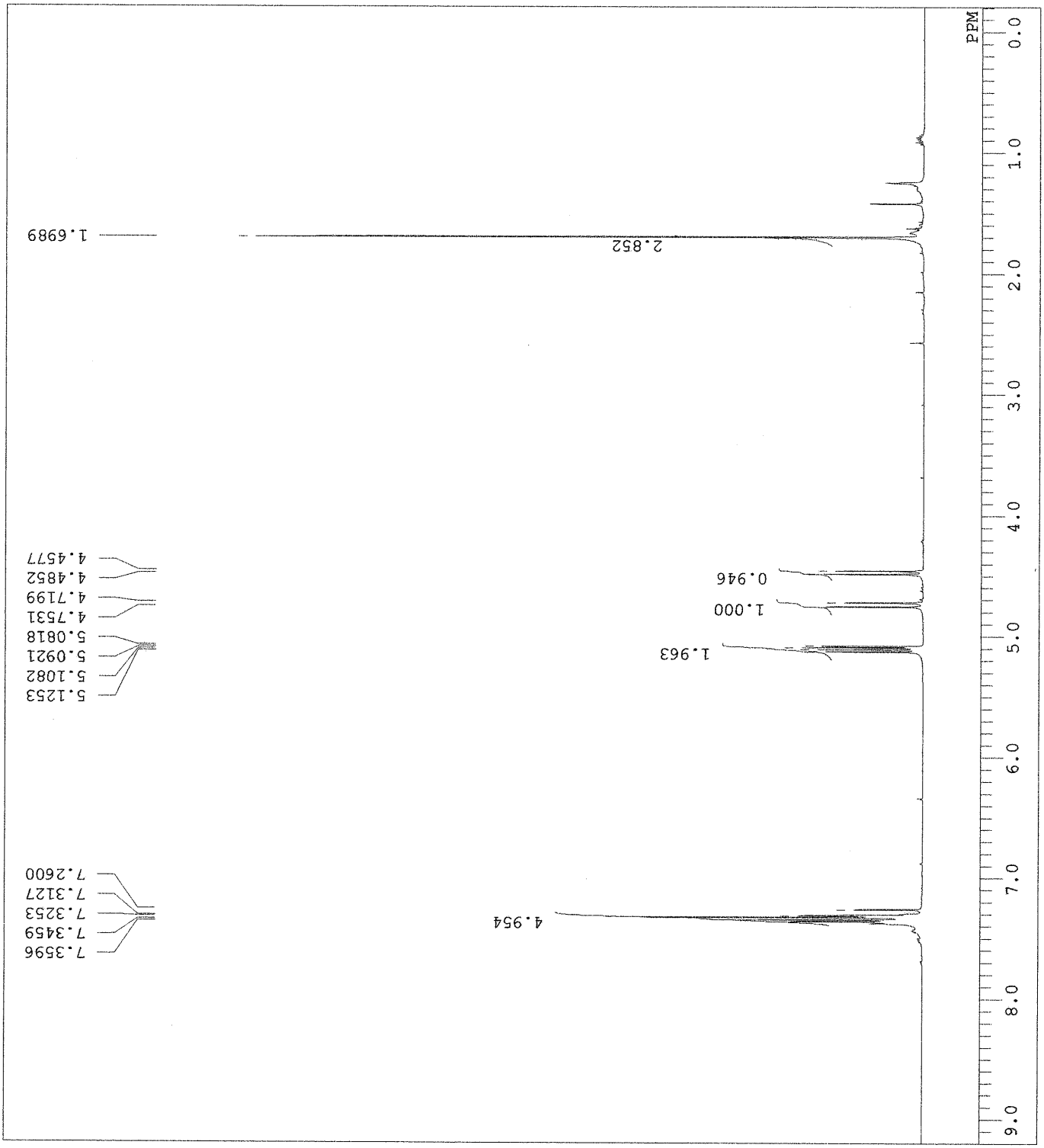
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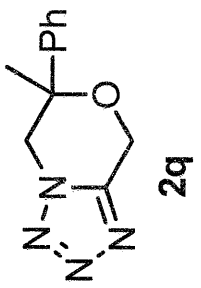
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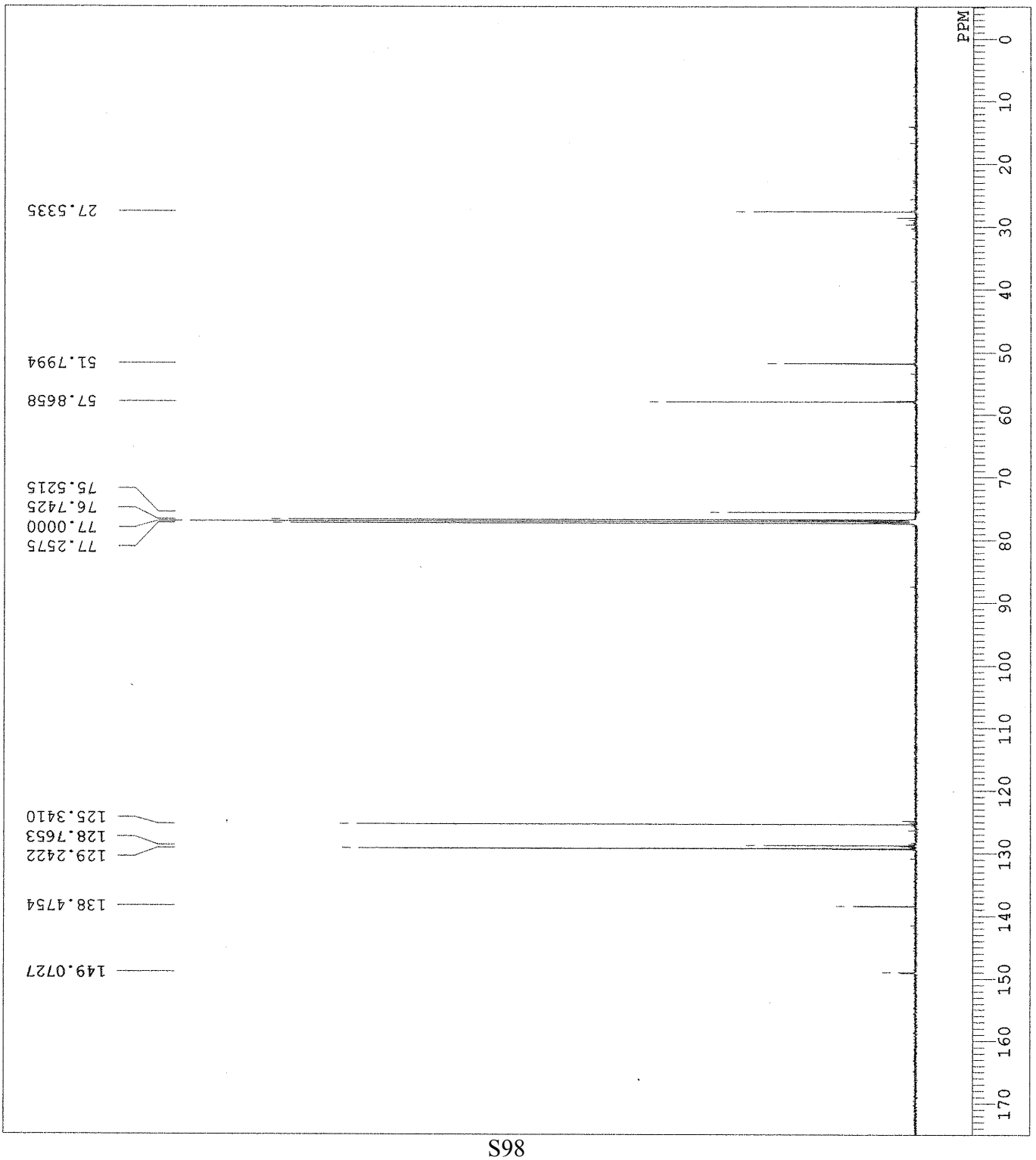
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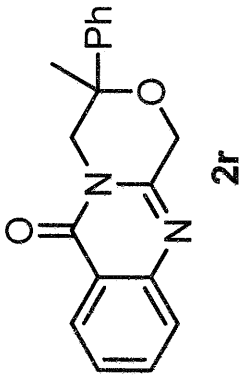
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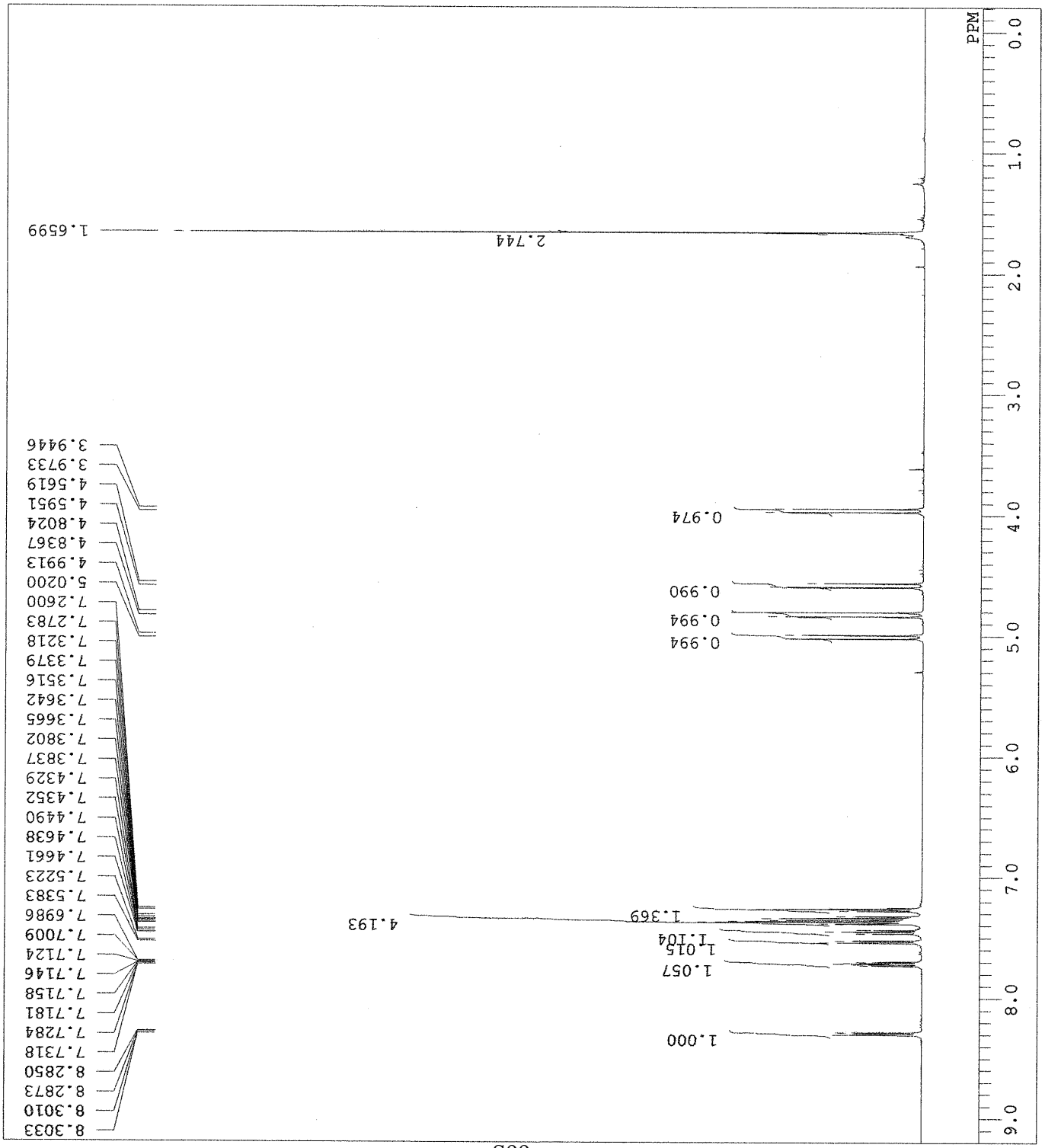
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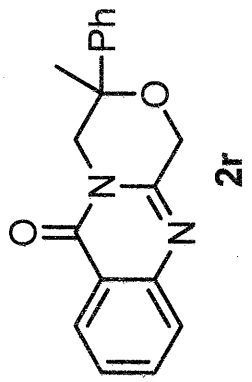
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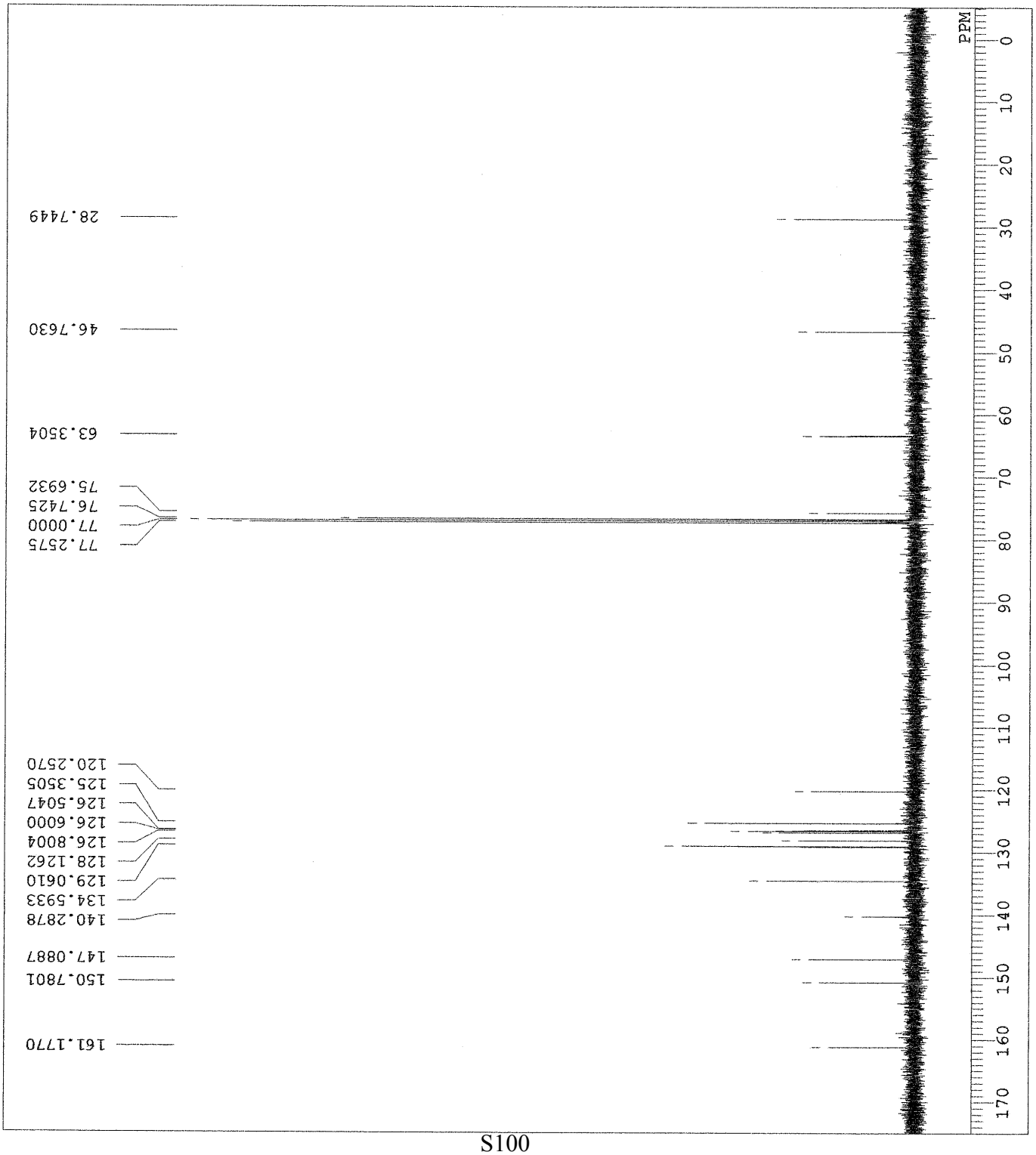
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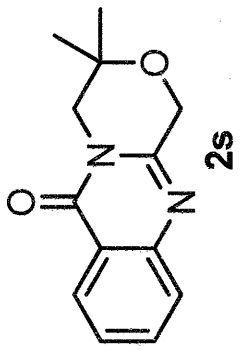
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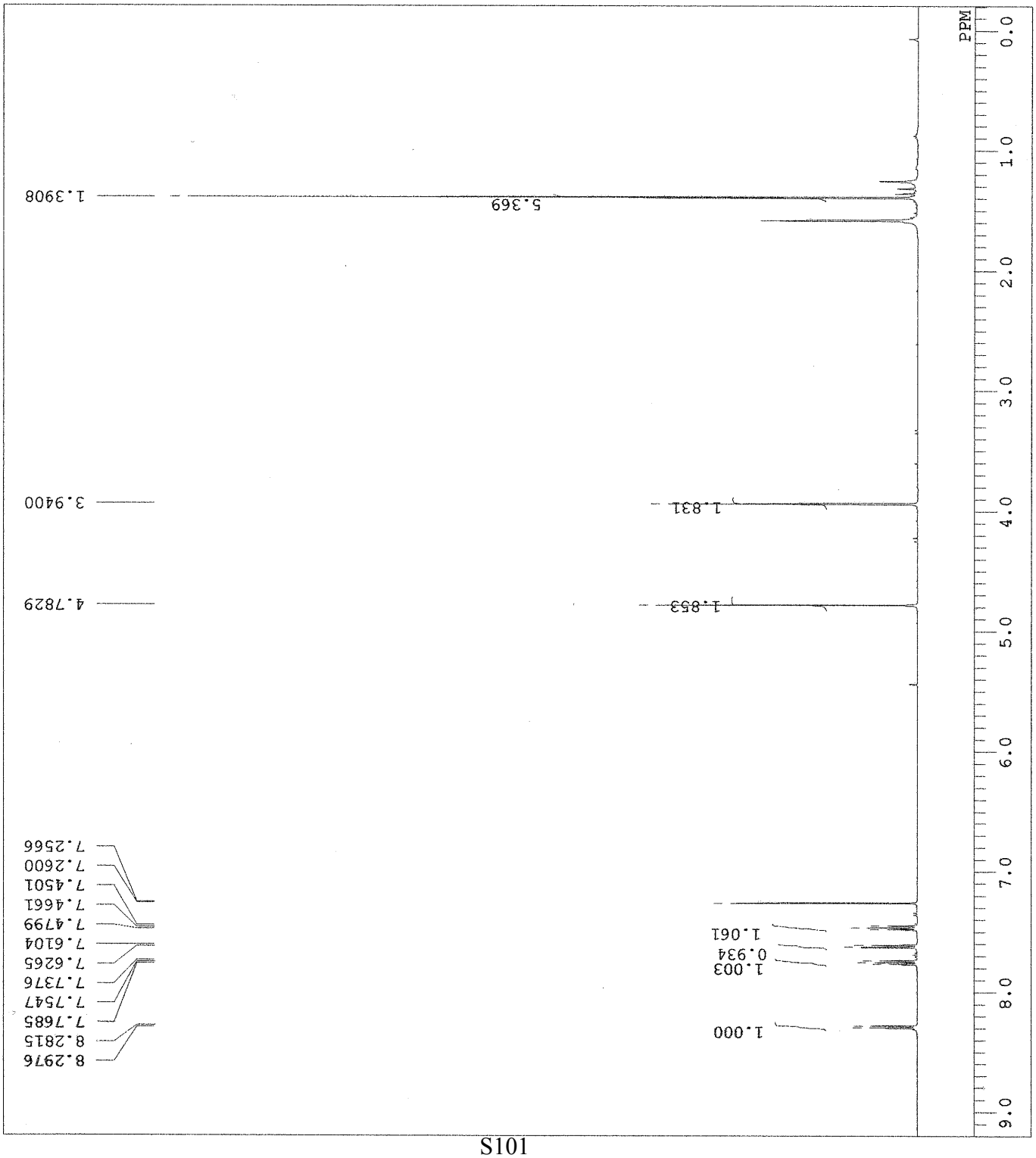
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3.0
4.0
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7.0
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1.831
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7.2600
7.4501
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7.4799
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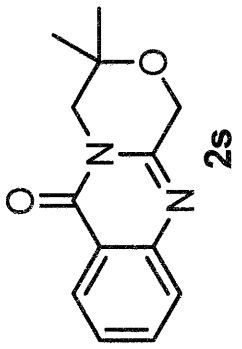
1.000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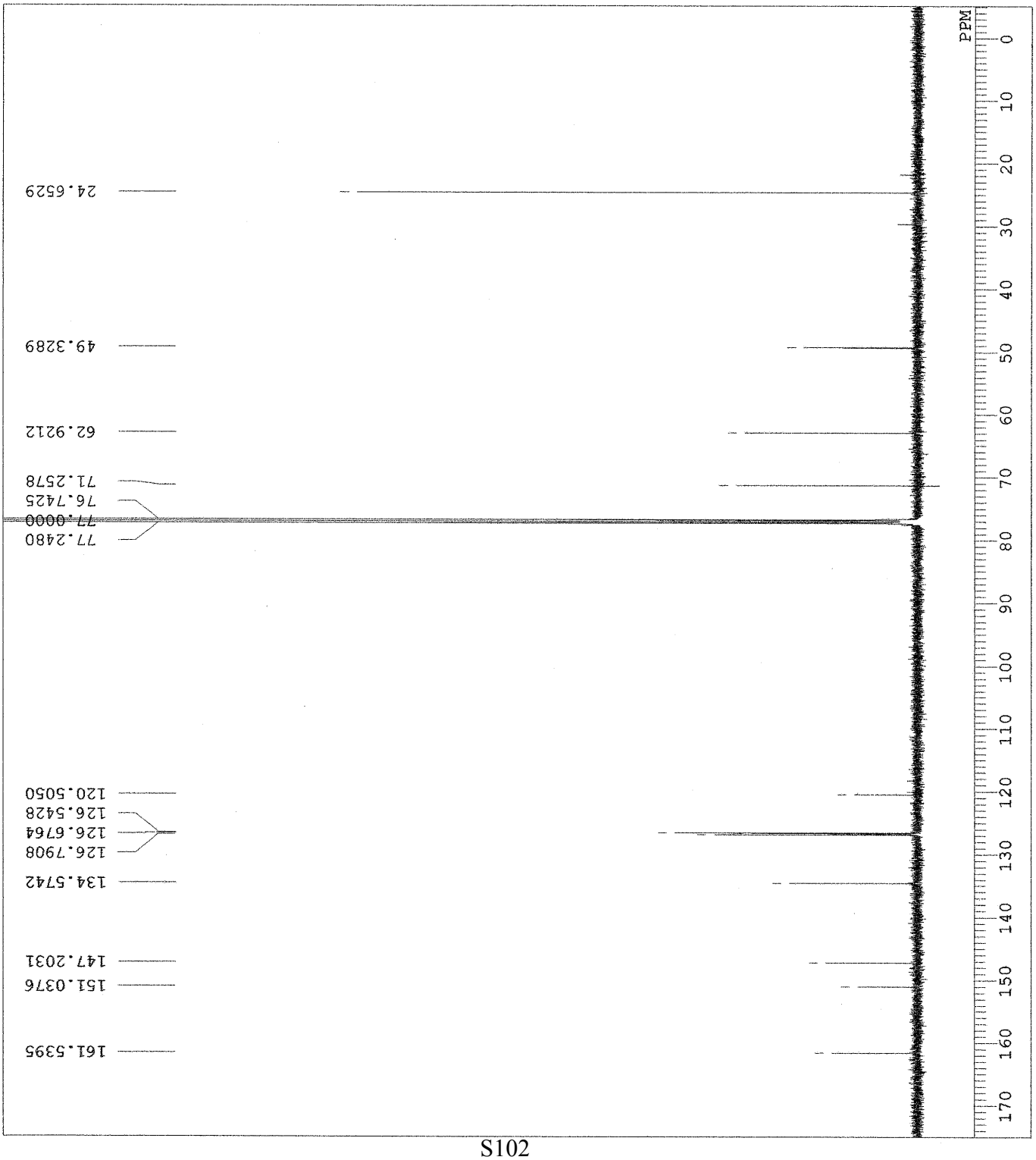
2s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100
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150
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49.3289
62.9212
71.2578
76.7425
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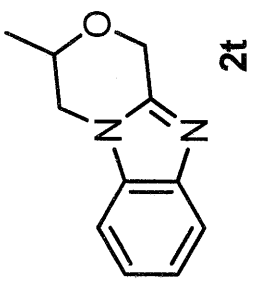

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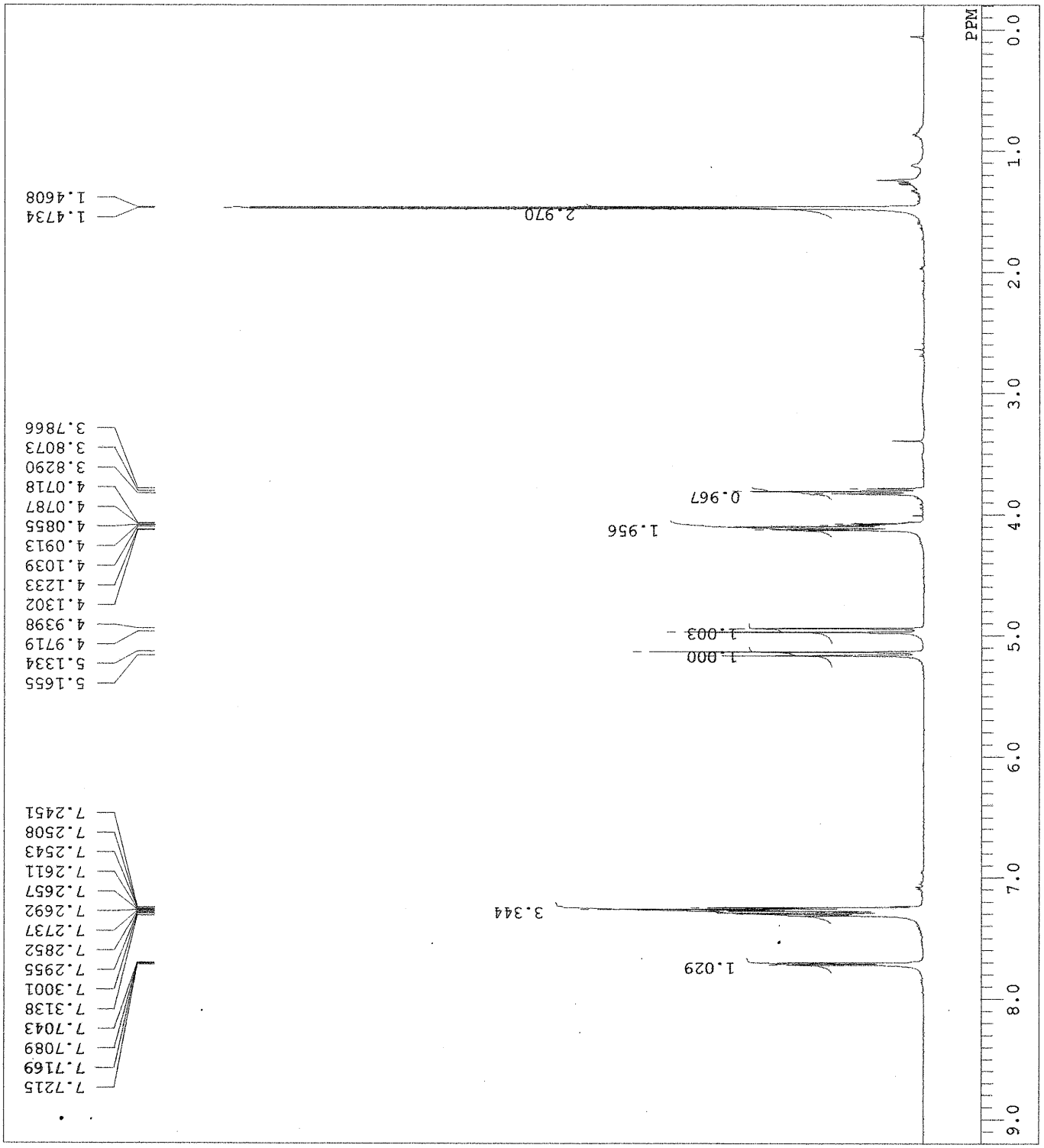
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7.2451
7.2508
7.2543
7.2611
7.2657
7.2692
7.2737
7.2852
7.2955
7.3001
7.3138
7.7043
7.7089
7.7169
7.7215
1.000
1.003
1.956
0.967
2.970
1.4734
1.4608
5.1655
5.1334
4.9719
4.9398
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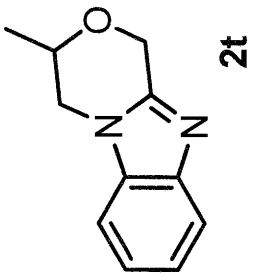

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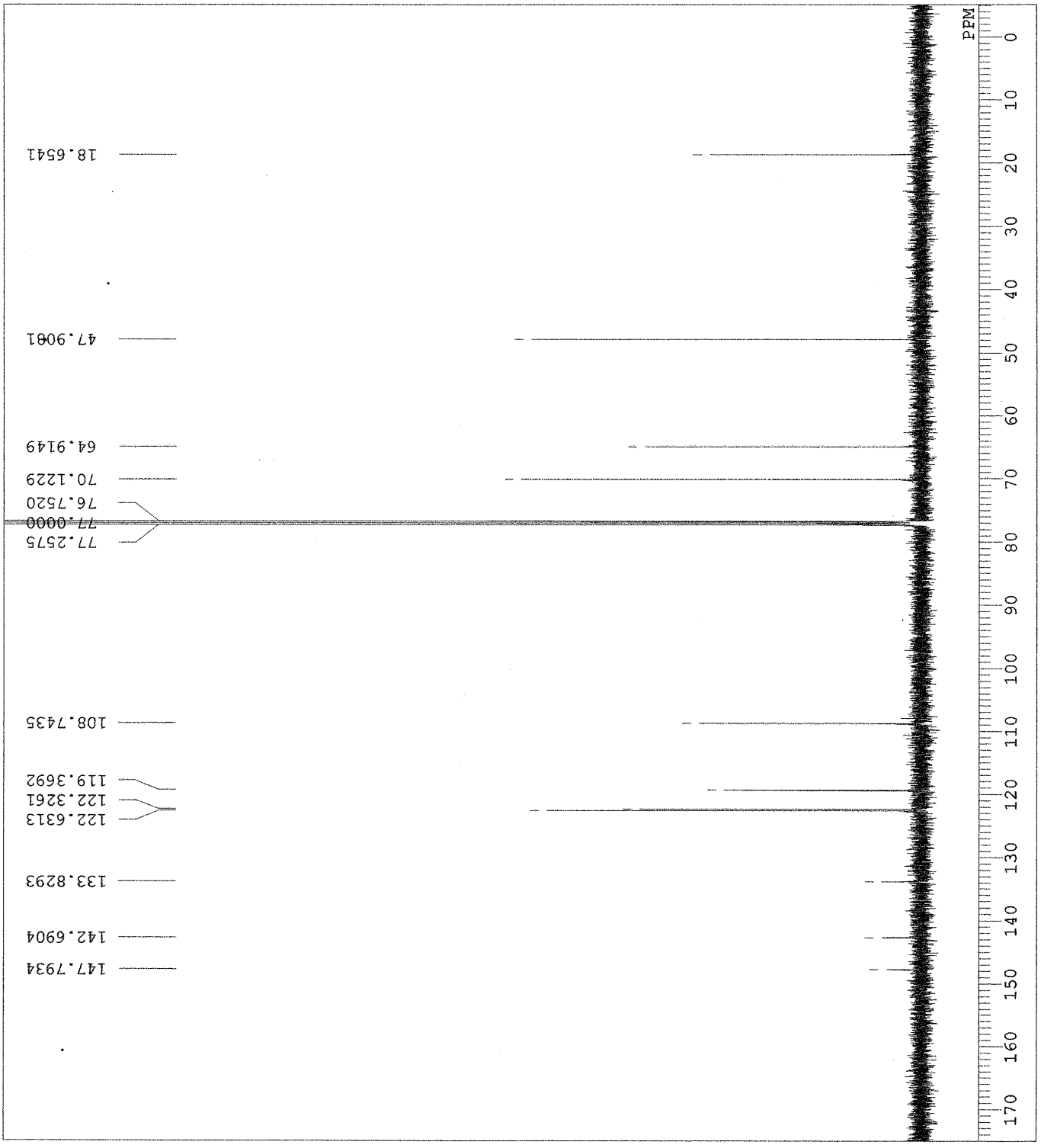
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122.6313
133.8293
142.6904
147.7934
PPM
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20
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100
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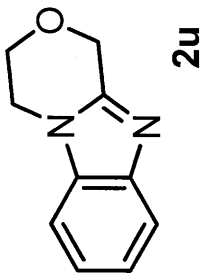
170



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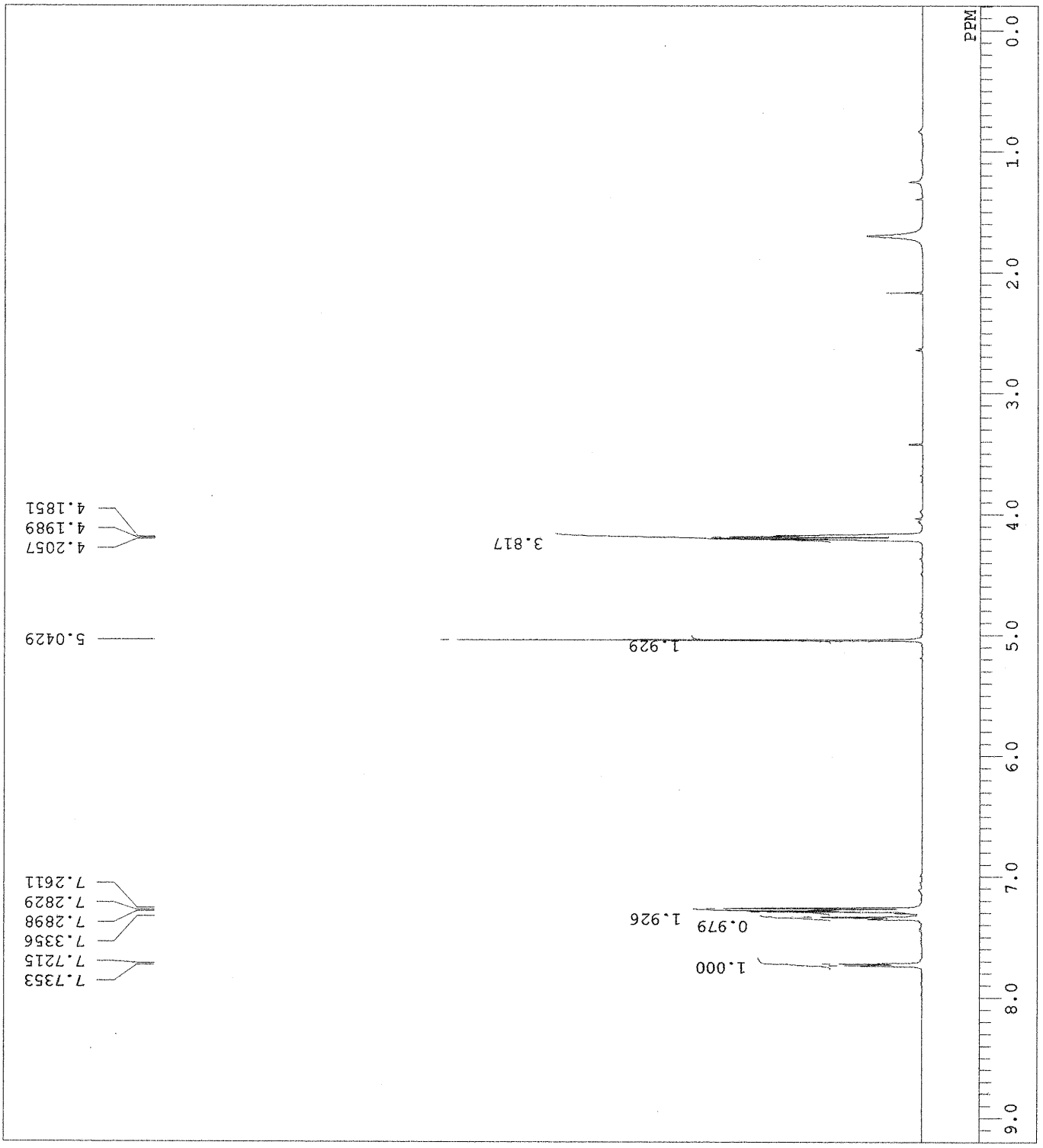
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1.926
1.929
3.817
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7.2898
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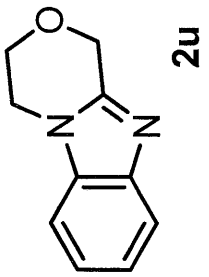
7.7215
7.7353



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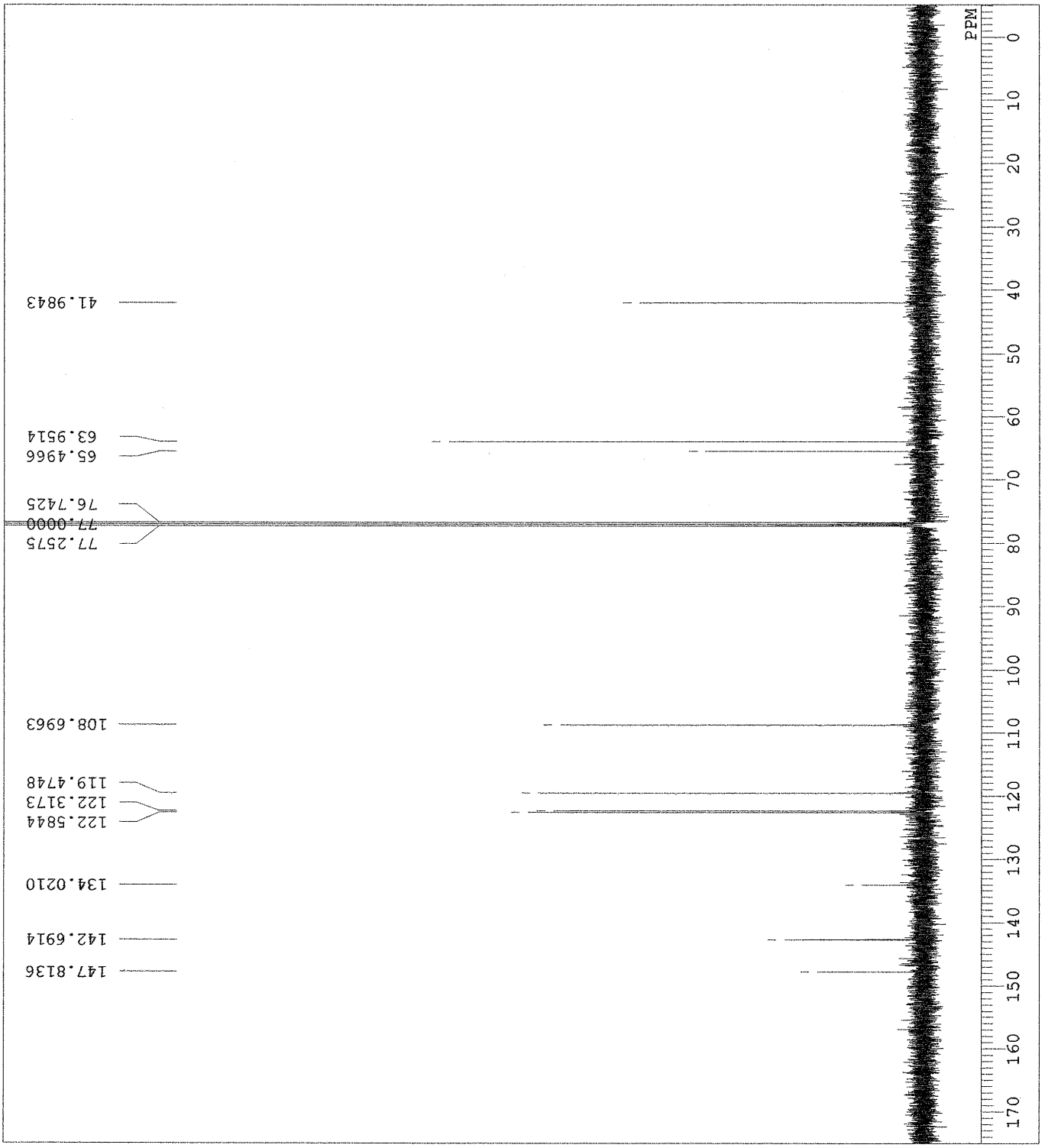
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122.5844
134.0210
142.6914
147.8136
PPM
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20
30
40
50
60
70
80
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100
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140
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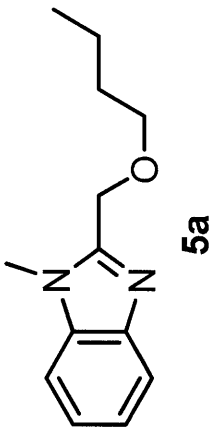
160
170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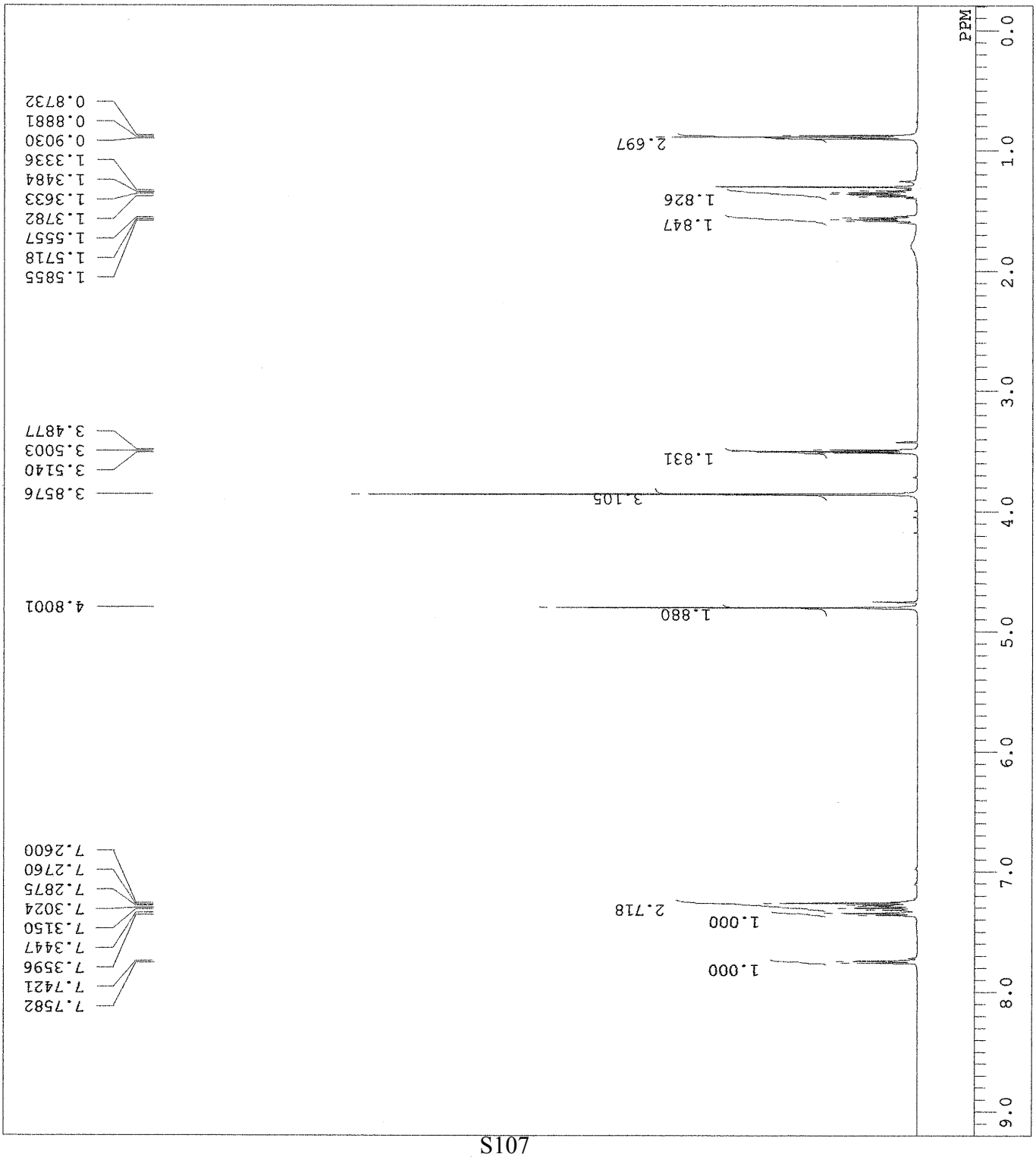
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6.0
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0.9030
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1.3484
1.3633
1.3782
1.5557
1.5718
1.5855
3.4877
3.5003
3.5140
3.8576
4.8001
7.2600
7.2760
7.2875
7.3024
7.3150
7.3447
7.3596
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1.831
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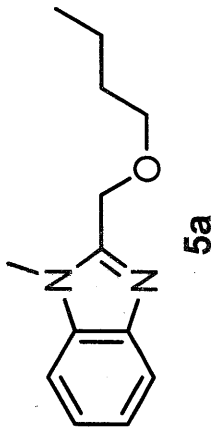
1.880
2.718
1.000
1.000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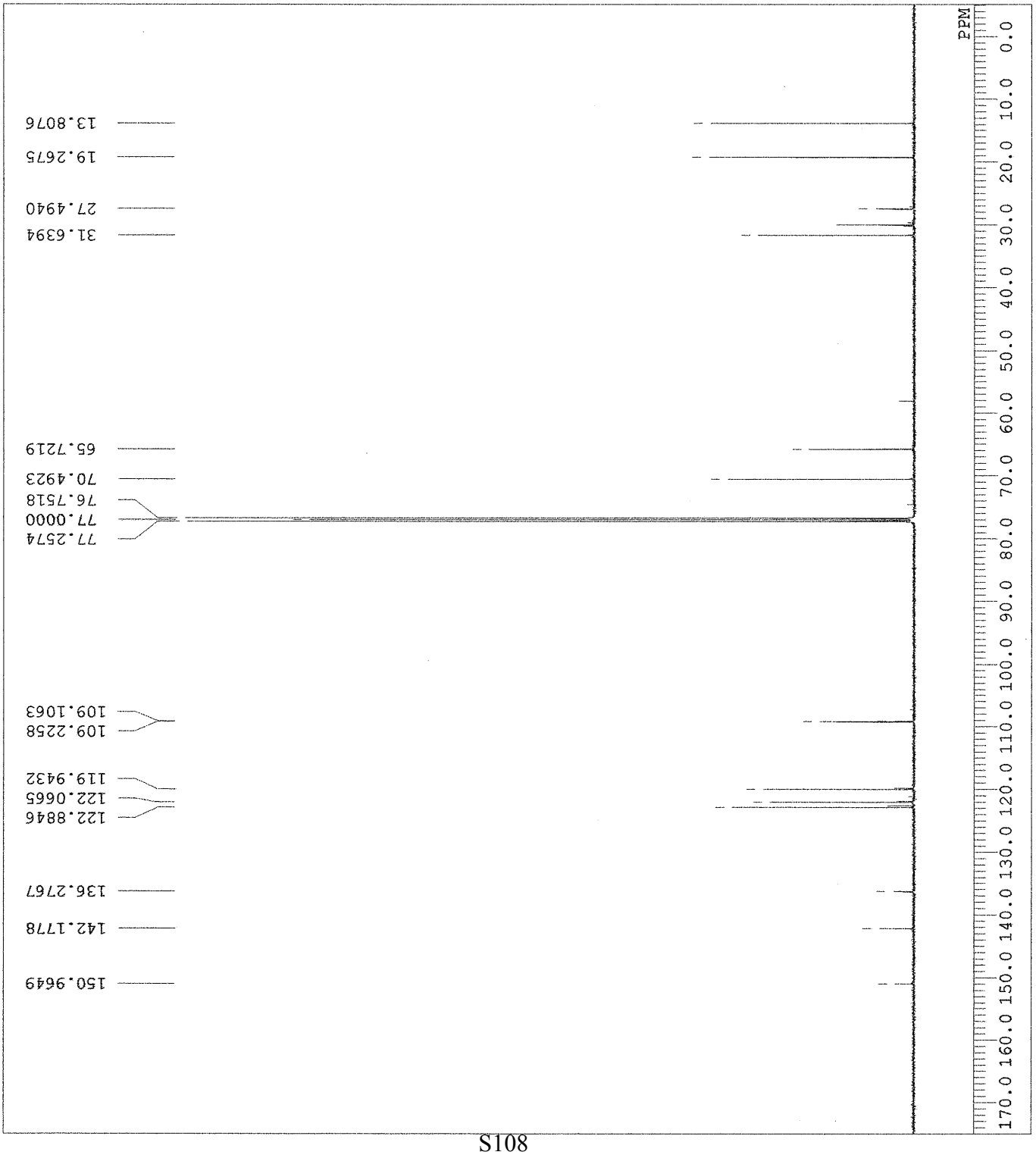
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31.6394
65.7219
70.4923
76.7518
77.0000
77.2574
109.1063
109.2258
119.9432
122.0665
122.8846
136.2767
142.1778
150.9649
PPM
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10.0
20.0
30.0
40.0
50.0
60.0
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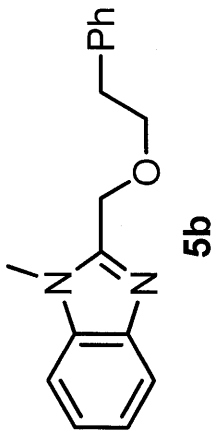
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0


Ph
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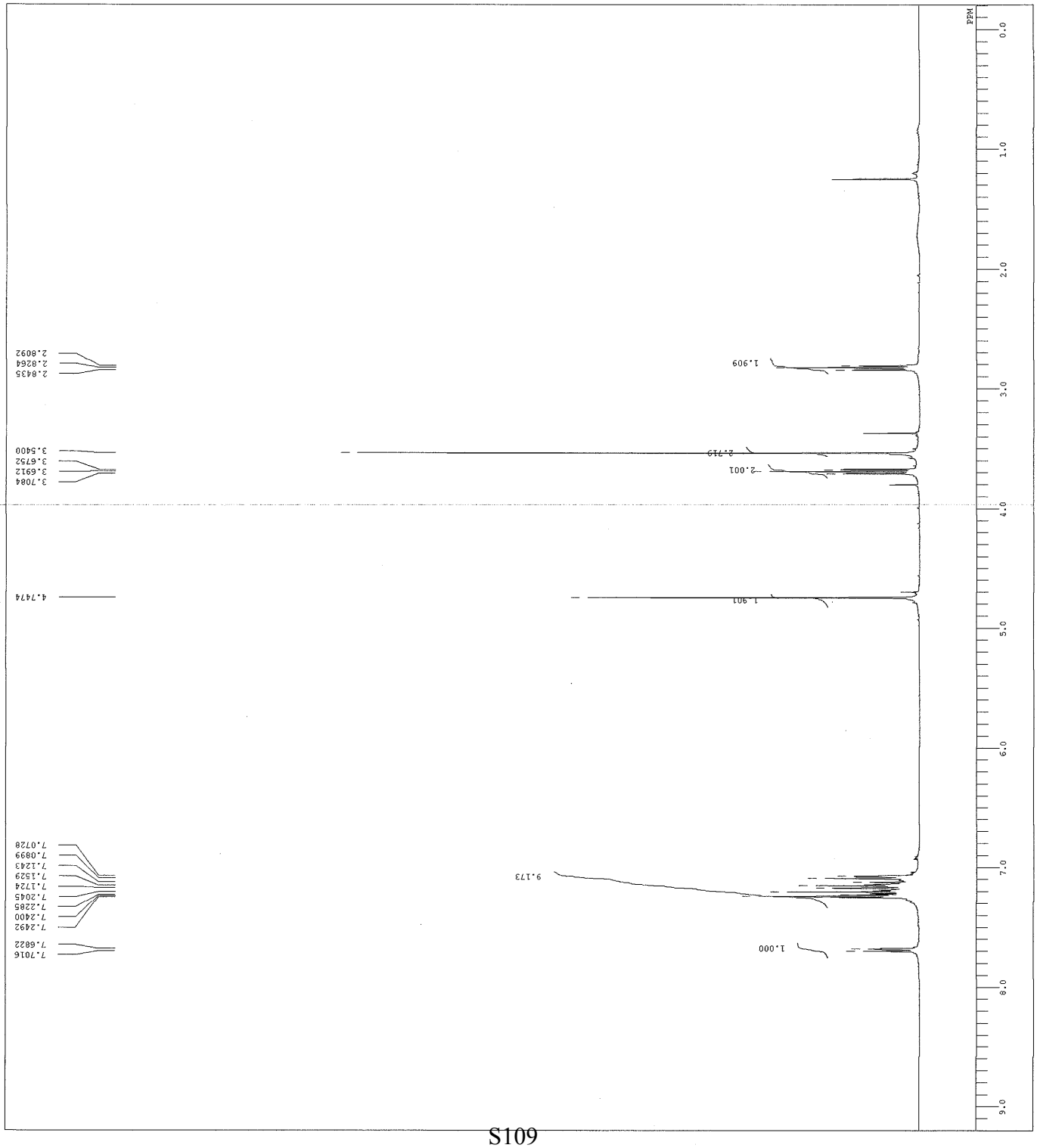
N
N

5b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2.001
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1.909
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7.0899
7.1243
7.1529
7.1724
7.2045
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7.2400
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3.6912
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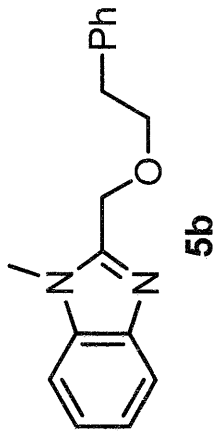
2.8092
2.8264
2.8435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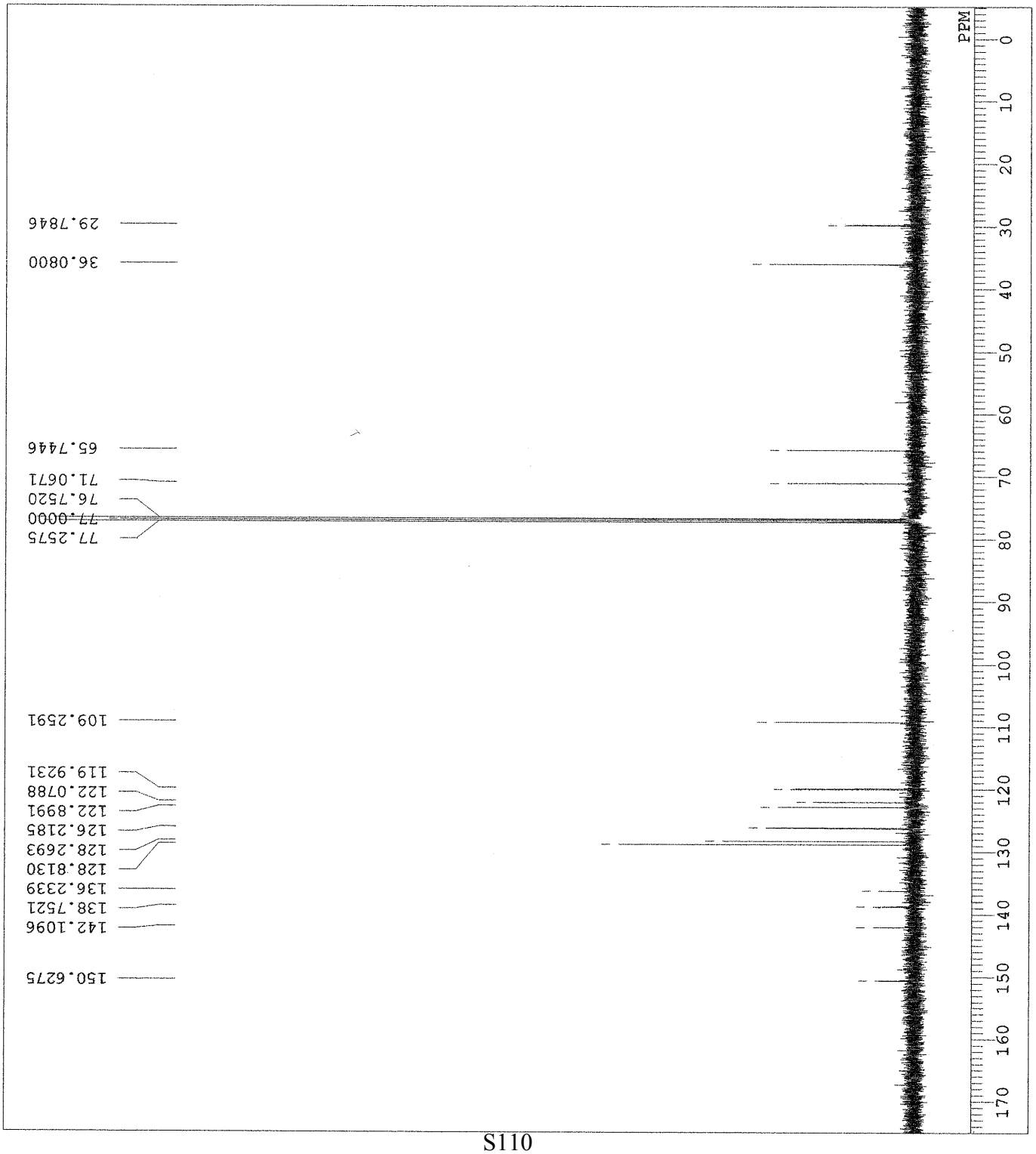
N
5b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122.8991
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128.2693
128.8130
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138.7521
142.1096
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PPM
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100
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160
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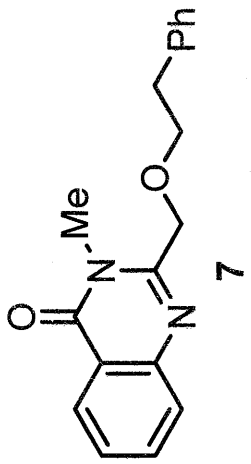
Ph
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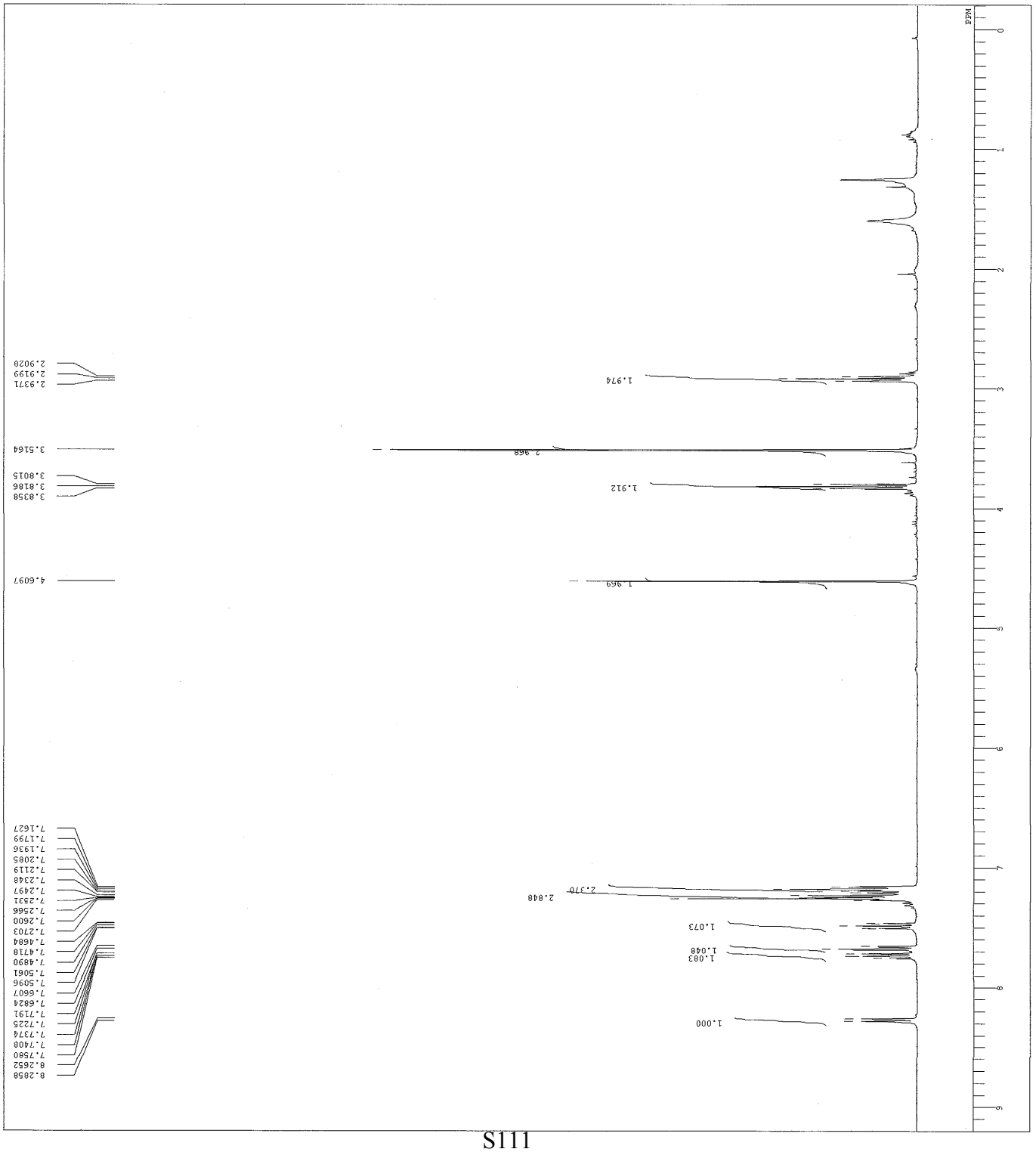
Me
N
N
O

7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4.609
1.912
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3.835
3.818
3.801
2.937
2.919
2.902
8.285
8.265
7.758
7.740
7.737
7.722
7.713
7.682
7.660
7.509
7.506
7.489
7.506
7.471
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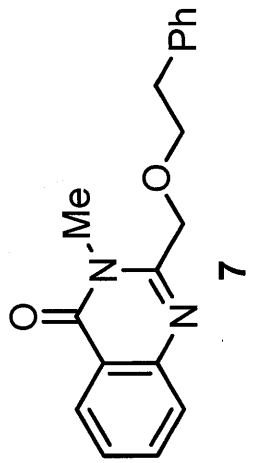
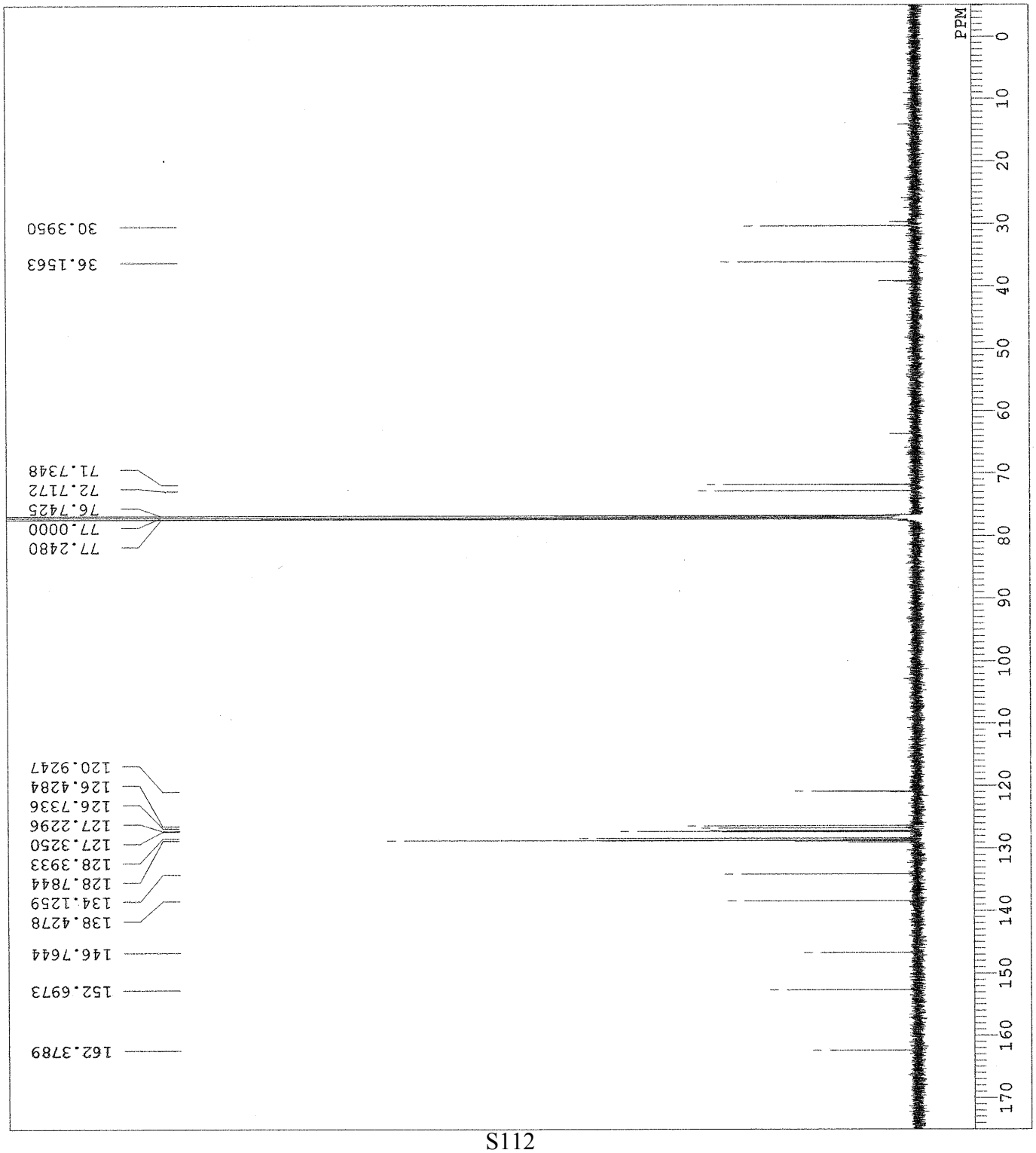

Ph
O
Me
N
N
O

7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150
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72.7172
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77.2480
120.9247
126.4284
126.7336
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128.7844
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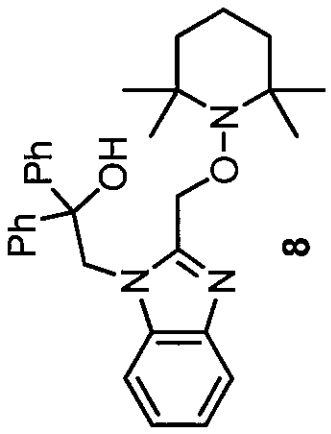
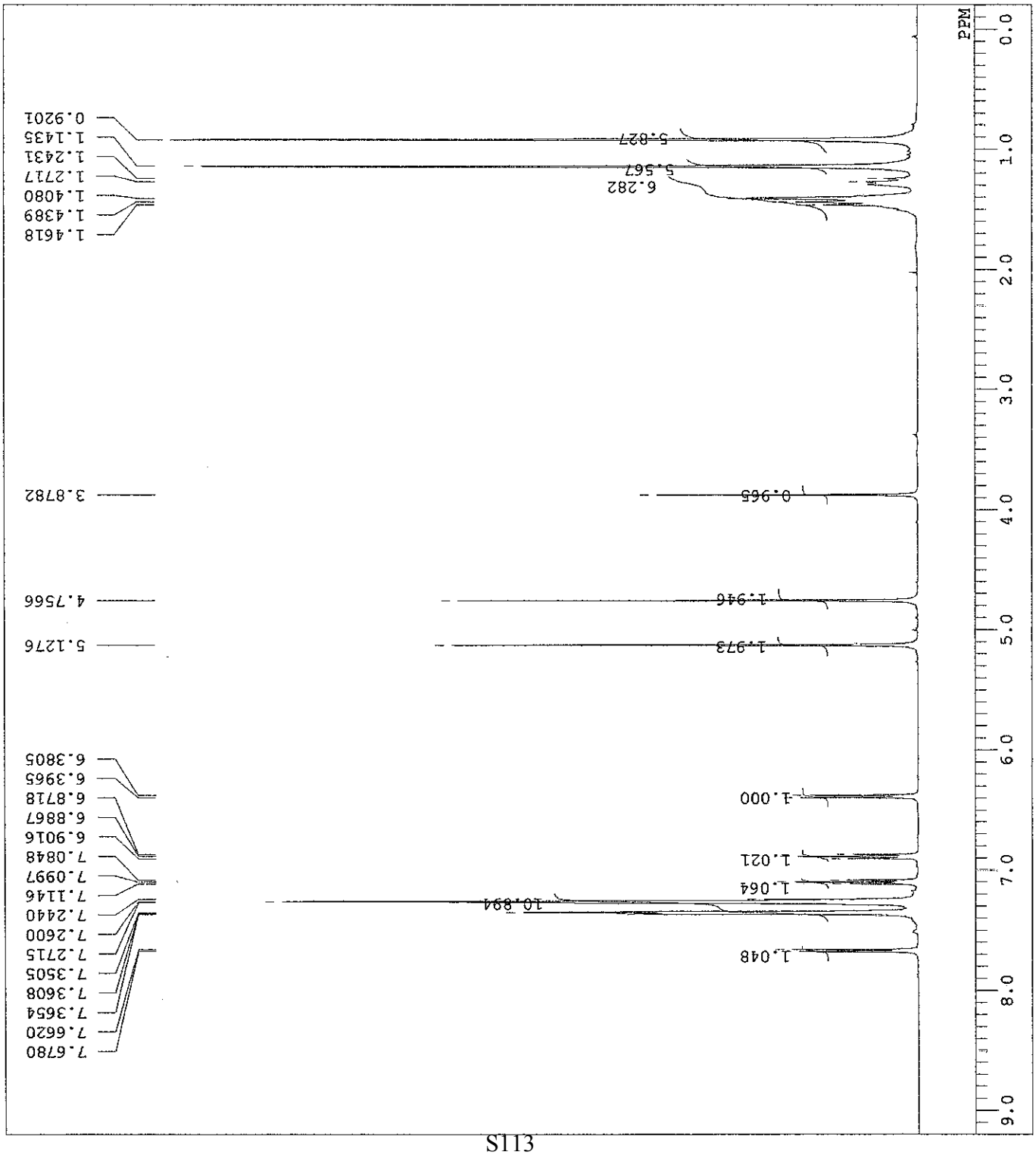
162.3789


Ph
Ph
OH
N
O
N
N

8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1.2431
1.2717
1.4080
1.4389
1.4618
5.827
5.567
6.282
3.8782
0.965
4.7566
1.946
5.1276
1.973
6.3805
6.3965
6.8718
6.8867
6.9016
7.0848
7.0997
7.1146
7.2440
7.2600
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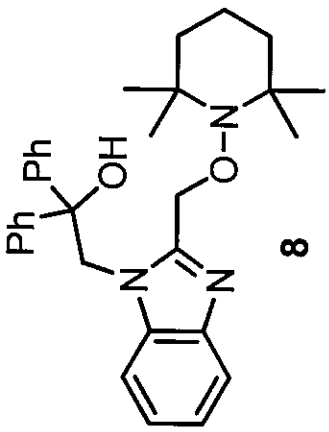
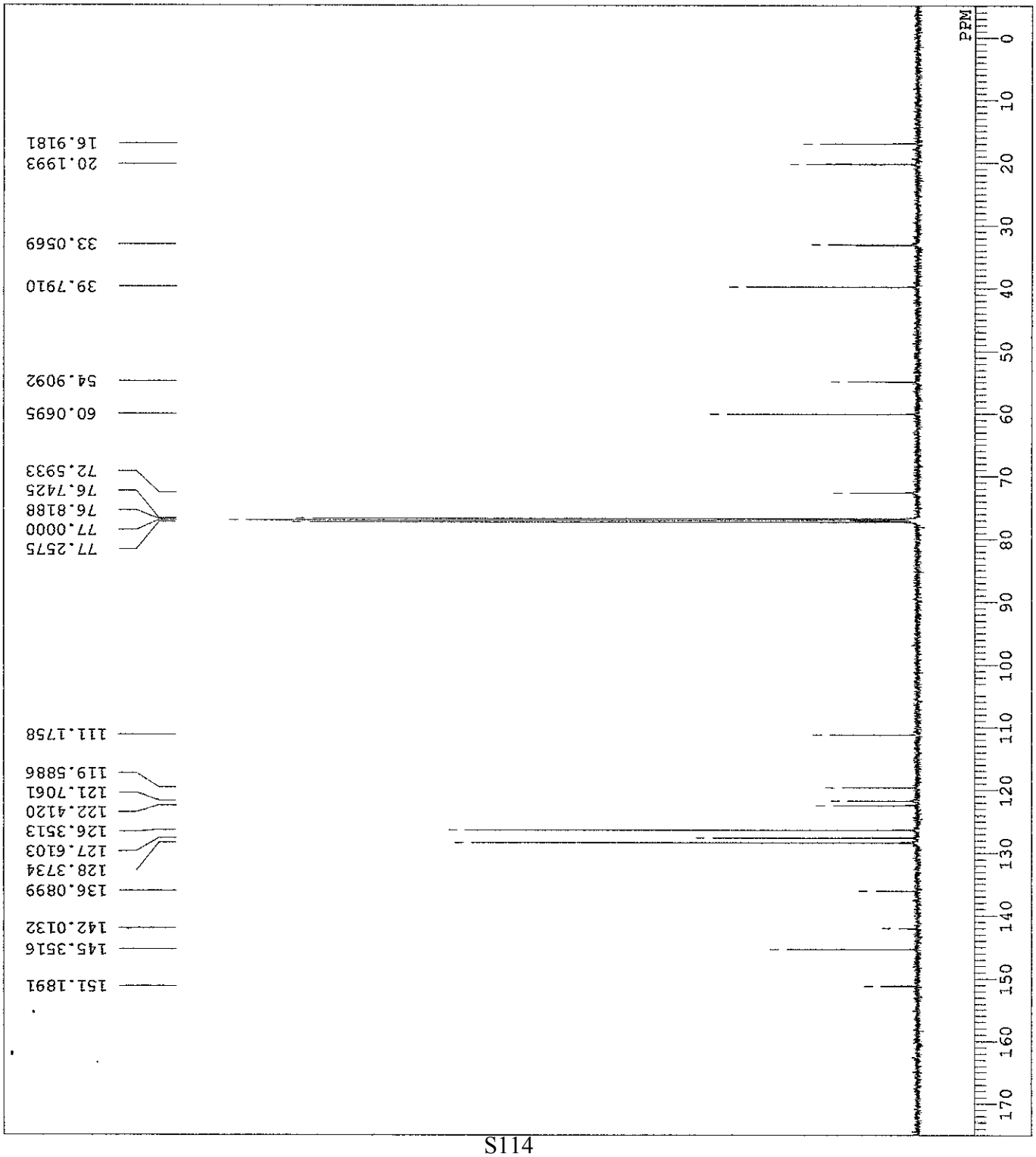
1.021
1.064
10.894
1.048


Ph
Ph
OH
O
N
N
N

8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121.7061
122.4120
126.3513
127.6103
128.3734
136.0899
142.0132
145.3516
151.1891
PPM
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90
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150
160
170