SUPPORTING INFORMATION

Thermal and Lewis Acid Catalyzed Diastereoselective Intramolecular Diels-Alder Reaction on α,β-Unsaturated Amides Derived from (-)-8-Amino Menthol

(3R,4aS,6aS,9R,10aR,11aS,11bR)-5-Oxo-3,11b-epoxy-4a,6,6,9-tetramethyl-3,4,4a,11b-tetrahydroisoindolyl-[2,3-a]-perhydro-11,5a-benzoxazine (10). Colorless solid, m.p. 114-116°C (from hexane). $[\alpha]^{25}_D$ = -22.25 (c = 1.0, CH_2Cl_2). ^{1}H NMR (δ): 0.91-1.01 (m, 2H); 0.96 (d, 3H, J = 6.5 Hz); 1.03 (d, 1H, J = 11.7 Hz); 1.08-1.12 (m, 1H); 1.14 (s, 3H); 1.26 (s, 3H); 1.41 (m, 1H); 1.50-1.62 (m, 1H); 1.70-1.76 (m, 2H); 1.72 (s, 3H); 2.04 (m, 1H); 2.38 (dd, 1H, J_1 = 4.7 Hz, J_2 = 11.7 Hz); 3.60 (dt, 1H, J_1 = 4.1 Hz, J_2 = 10.6 Hz); 4.96 (dd, 1H, J_1 =1.5 Hz, J_2 = 4.7 Hz); 5.16 (s, 1H); 6.41 (dd, 1H, J_1 = 1.5 Hz, J_2 = 5.8 Hz); 6.55 (d, 1H, J = 5.8 Hz). ^{13}C NMR (δ): 20.4; 22.0; 22.7; 24.4; 25.3; 31.2; 34.5; 36.0; 41.3; 51.7; 52.5; 57.4; 77.1; 79.7; 84.1; 90.3; 130.8; 136.1; 177.2. IR (nujol): 1680, 1040 cm^{-1}. MS (m/z, %): 317 (M^+, 25); 305 (37); 136 (71); 126 (74); 81 (33); 69 (100); 41 (52). Anal. Calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57; N, 4.41. Found: C, 71.76; H, 8.74; N, 4.52.

(3S,4S,4aS,6aS,9R,10aR,11aS,11bR)-5-Oxo-3,11b-epoxy-4a,6,6,9-tetramethyl-3,4,4a,11b-tetrahydroisoindolyl-[2,3-a]-perhydro-11,5a-benzoxazine (11). Colorless solid, m.p. 98-99°C (from hexane). $[\alpha]^{25}_D$ = -80.06 (c = 1.0, CH_2Cl_2). ^{1}H NMR (δ): 0.83-0.96 (m, 2H); 0.94 (d, 3H, J = 7.1 Hz); 0.95 (d, 3H, J = 6.5 Hz); 1.03-1.19 (m, 1H); 1.25 (s, 3H); 1.35-1.68 (m, 2H); 1.70-1.81 (m, 2H); 1.72 (s, 3H); 2.02 (m, 1H); 2.08 (d, 1H, J = 3.9 Hz); 2.52 (m, 1H); 3.61 (dt, 1H, J_1 = 4.1 Hz, J_2 = 10.6 Hz); 4.86 (dd, 1H, J_1 = 1.5 Hz, J_2 = 4.4 Hz); 5.10 (s, 1H); 6.33 (dd, 1H, J_1 = 1.5 Hz, J_2 =5.9 Hz); 6.66 (d, 1H, J = 5.9 Hz). ^{13}C NMR (δ): 17.1; 20.6; 22.0; 24.4; 25.2; 31.2; 34.5; 36.3; 41.1; 51.5; 55.0; 57.7; 77.2; 83.2; 84.5; 89.7; 133.7; 134.0; 173.5. IR (nujol): 1670, 1050 cm^{-1}. MS (m/z, %): 317 (M^+, 31); 136 (42); 126 (57); 81 (34); 69 (100). Anal. Calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57; N, 4.41. Found: C, 71.76; H, 8.69; N, 4.51.

(3R,4aS,6aS,9R,10aR,11aS,11bR)-3-Ethyl-6,6,9-trimethyl-5-oxo-3,4,4a,11b-tetrahydroisoindolyl-[2,3-a]-perhydro-11,5a-benzoxazine (16). Colorless solid, m.p. 82-84°C (from hexane). $[\alpha]^{25}_D$ = -72.77 (c = 1.0, CH_2Cl_2). ^{1}H NMR (δ): 0.77-0.99 (m, 3H); 0.94 (t, 3H, J = 7.6 Hz); 0.95 (d, 3H, J = 6.8 Hz); 1.01-1.13 (m, 1H); 1.16 (s, 3H); 1.23-1.52 (m, 4H); 1.68-1.78 (m, 2H); 1.74 (s, 3H); 1.93-2.09 (m, 3H); 2.50-2.57 (m, 2H); 3.36 (dt, 1H, J_1 = 4.2 Hz, J_2 = 10.6 Hz); 4.60 (dd, 1H, J_1 = 1.3 Hz, J_2 = 6.3 Hz); 5.74-5.83 (m, 2H). ^{13}C NMR (δ): 11.1; 18.1; 22.0; 23.9; 25.5; 28.6; 29.3; 31.2; 34.5; 36.2; 38.8; 40.5; 41.1; 49.7; 56.7; 76.3; 89.5; 123.8;

135.2; 174.9. IR (nujol): 1680, 1230, 1100 cm^{-1}. MS (m/z, %): 317 (M^+, 11), 182 (100), 137 (19). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.55; H, 9.92; N, 4.31.

(3S,4aR,6aS,9R,10aR,11aS,11bS)-3-Ethyl-6,6,9-trimethyl-5-oxo-3,4,4a,11b-tetrahydroisoindolyl-[2,3-a]-perhydro-11,5a-benzoxazine (17). Colorless solid, m.p. 65-66°C (from pentane). $[\alpha]^{25}_D$ = -32.02 (c = 1.2, CH_2Cl_2). ^1H NMR (δ): 0.87-1.18 (m, 4H); 0.92 (d, 3H, J = 6.6 Hz); 0.94 (t, 3H, J = 7.3 Hz); 1.22 (s, 3H); 1.24-1.65 (m, 4H); 1.65-1.73 (m, 2H); 1.70 (s, 3H); 1.92-2.01 (m, 3H); 2.44 (m, 1H); 2.80 (m, 1H); 3.43 (dt, 1H, J_1 = 4.2 Hz, J_2 = 10.6 Hz); 5.05 (d, 1H, J = 6.5 Hz); 5.63 (ddd, 1H, J_1 = 2.2 Hz, J_2 = 3.5 Hz, J_3 = 10.2 Hz); 5.86 (dt, 1H, J_1 = 2.5 Hz, J_2 = 10.2 Hz). ^{13}C NMR (δ): 11.7; 19.8; 22.0; 24.2; 25.5; 27.9; 28.8; 31.2; 34.5; 35.1; 35.5; 40.8; 41.0; 50.3; 57.3; 76.2; 85.5; 121.5; 134.7; 176.6. IR (nujol): 1680, 1140, 1010 cm^{-1}. MS (m/z, %): 317 (M^+, 13), 182 (100), 137 (16). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.77; H, 10.02; N, 4.59.

N-(8-Mentholyl)-(3aR,6R,7aR)-3a,6-epoxy-7a-methyl-3a,6,7,7a-tetrahydroisoindoline (22). Yield 85%. Colorless solid, m. p. 154-155°C (from hexane). $[\alpha]^{25}_D$ = +15,65 (c = 1.0, CH_2Cl_2). ^1H NMR (δ): 0.85-1.02 (m, 4H); 0.91 (d, 3H, J = 6.5 Hz); 0.96 (s, 6H); 1.20 (s, 3H); 1.35-1.67 (m, 4H); 1.94 (m, 1H); 2.04 (dd, 1H, J_1 = 4.7 Hz, J_2 = 11.4 Hz); 2.62 (d, 1H, J = 8.1 Hz); 3.14 (d, 1H, J = 12.3 Hz); 3.15 (d, 1H, J = 8.1 Hz); 3.40 (d, 1H, J = 12.3 Hz); 3.66 (dt, 1H, J_1 = 3.9 Hz, J_2 = 10.2 Hz); 4.92 (d, 1H, J = 4.6 Hz); 6.35 (s, 2H); 8.42 (s, 1H). ^{13}C NMR (δ): 17.9; 21.6; 22.1; 22.6; 25.8; 31.0; 35.1; 38.7; 44.3; 46.6; 47.6; 48.4; 57.1; 59.4; 72.9; 78.9; 96.4; 134.0; 136.1. IR (nujol) : 3100, 1220, 1180 cm^{-1}. CIMS (m/z, %): 306 (M^++1, 100); 192 (41); 152 (45). Anal. Calcd for $C_{19}H_{31}NO_2$: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.89; H, 10.42; N, 4.46.

N-(8-Mentholyl)-(3aR,6S,7S,7aR)-3a,6-epoxy-7-methyl-3a,6,7,7a-tetrahydroisoindoline (23). Yield 94%. Colorless solid, m. p. 106-107°C (from hexane). $[\alpha]^{25}_D$ = -46.29 (c = 1.0, CH_2Cl_2). ^1H NMR (δ): 0.81 (d, 3H, J = 7.1 Hz); 0.86-1.07 (m, 3H); 0.91 (d, 3H, J = 6.5 Hz); 0.96 (s, 3H); 1.18 (s, 3H); 1.40-1.51 (m, 2H); 1.52-1.62 (m, 2H); 1.68 (m, 1H); 1.93 (m, 1H); 2.10 (m, 1H); 2.25 (m, 1H); 2.88 (d, 1H, J = 11.5 Hz); 3.40-3.47 (m, 2H); 3.65 (dt, 1H, J_1 = 4.0 Hz, J_2 = 10.2 Hz); 4.79 (dd, 1H, J_1 = 1.7 Hz, J_2 = 4.2 Hz); 6.27 (dd, 1H, J_1 = 1.7 Hz, J_2 = 5.8 Hz); 6.45 (d, 1H, J = 5.8 Hz); 8.52 (s, 1H). ^{13}C NMR (δ): 16.6; 17.9; 21.3; 22.1; 25.7; 31.0; 35.1; 37.5; 44.3; 47.9; 48.4; 49.9; 51.0; 59.2; 72.8; 83.6; 95.6; 134.0; 137.0. IR (nujol): 3085, 1180 cm^{-1}. CIMS (m/z, %): 306 (M^++1, 100); 192 (33); 152 (24). Anal. Calcd for $C_{19}H_{31}NO_2$: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.84; H, 10.12; N, 4.76.

N-(8-Mentholyl)-(3aR,6R,7aS)-6-ethyl-3a,6,7,7a-tetrahydroisoindoline (26). Colorless solid, m.p. 67-68°C (from hexane). $[\alpha]^{25}_D$ = -34.26 (c = 1.0, CH_2Cl_2). ^1H NMR (δ): 0.85-1.05 (m, 3H); 0.90 (d, 3H, J = 6.5 Hz); 0.91 (t, 3H, J = 6.7 Hz);

0.93 (s, 3H); 1.16 (s, 3H); 1.22-1.54 (m, 5H); 1.55-1.60 (m, 1H); 1.63-1.68 (m, 2H); 1.89-1.93 (m, 2H); 2.18-2.47 (m, 2H); 2.52 (m,1H); 2.73-3.04 (broad, 2H); 3.44 (m, 1H); 3.61 (dt, 1H, J_1 = 4.0 Hz, J_2 = 10.3 Hz); 5.64 (s, 3H0; 8.62 (broad s, 1H). ^{13}C NMR (δ): 11.5; 16.9; 21.9; 22.1; 25.6; 28.7; 31.0; 34.2; 35.0; 35.1; 36.8; 38.5; 44.3; 48.3; 50.4; 52.1; 59.3; 72.9; 126.2; 133.5. IR (nujol): 3120, 1185, 1165, 1020 cm^{-1}. MS (m/z, %): 305 (M^+, 1); 193 (13); 192 (100). Anal. Calcd for $C_{20}H_{35}NO$: C, 78.63; H, 11.55; N, 4.58. Found: C, 78.79; H, 11.41; N, 4.43.

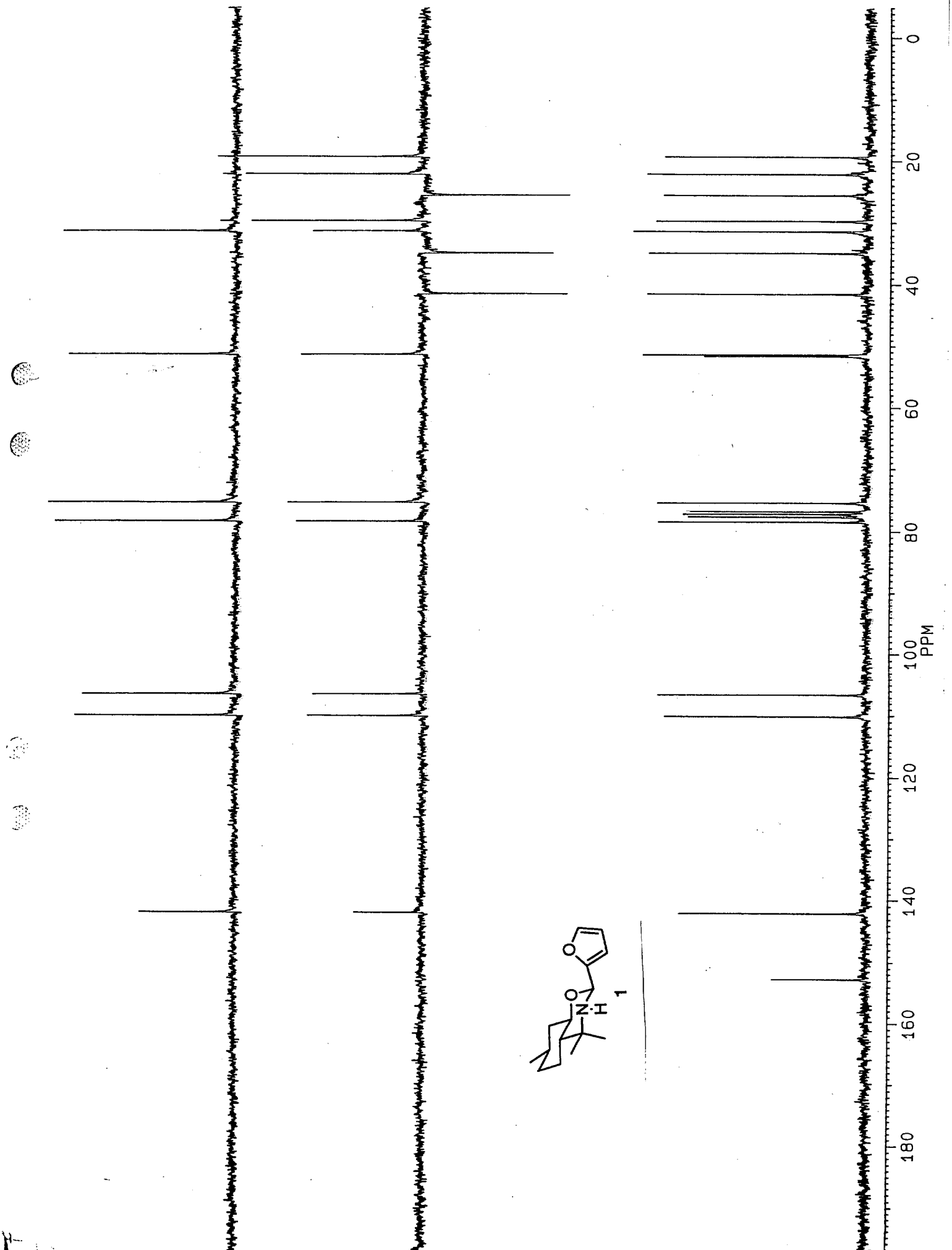
N-(8-Mentholyl)-(3aS,6S,7aR)-6-ethyl-3a,6,7,7a-tetrahydroisoindoline (27). Pale yellow oil. $[\alpha]^{25}_D$ = +54.83 (c = 1.1, CH_2Cl_2). ^{1}H NMR (δ): 0.83-1.07 (m,3H); 0.91 (d, 3H, J = 6.4 Hz); 0.92 (t, 3H, J = 7.0 Hz); 0.92 (s, 3H); 1.14 (s, 3H); 1.23-1.51 (m, 4H); 1.51-1.68 (m, 2H); 1.74 (m, 2H); 1.90 (m, 2H); 2.00-2.29 (m, 3H); 2.52 (m, 1H); 3.18-3.27 (m, 2H); 3.62 (dt, 1H, J_1 = 4.0 Hz, J_2 = 10.2 Hz); 5.63 (m, 2H); 7.90-9.20 (broad s, 1H). ^{13}C NMR (δ): 11.2; 17.2; 21.1; 22.2; 25.7; 28.7; 31.0; 33.9; 35.1; 36.7; 38.1; 44.4; 48.5; 49.6; 52.1; 58.7; 72.6; 72.8; 126.0; 133.2. IR (film): 3140, 1190, 1170, 1030 cm^{-1}. MS (m/z, %): 305 (M^+, 1); 193 (14) 192 (100). Anal. Calcd for $C_{20}H_{35}NO$: C, 78.63; H, 11.55; N, 4.58. Found: C, 78.52; H, 11.46; N, 4.76.

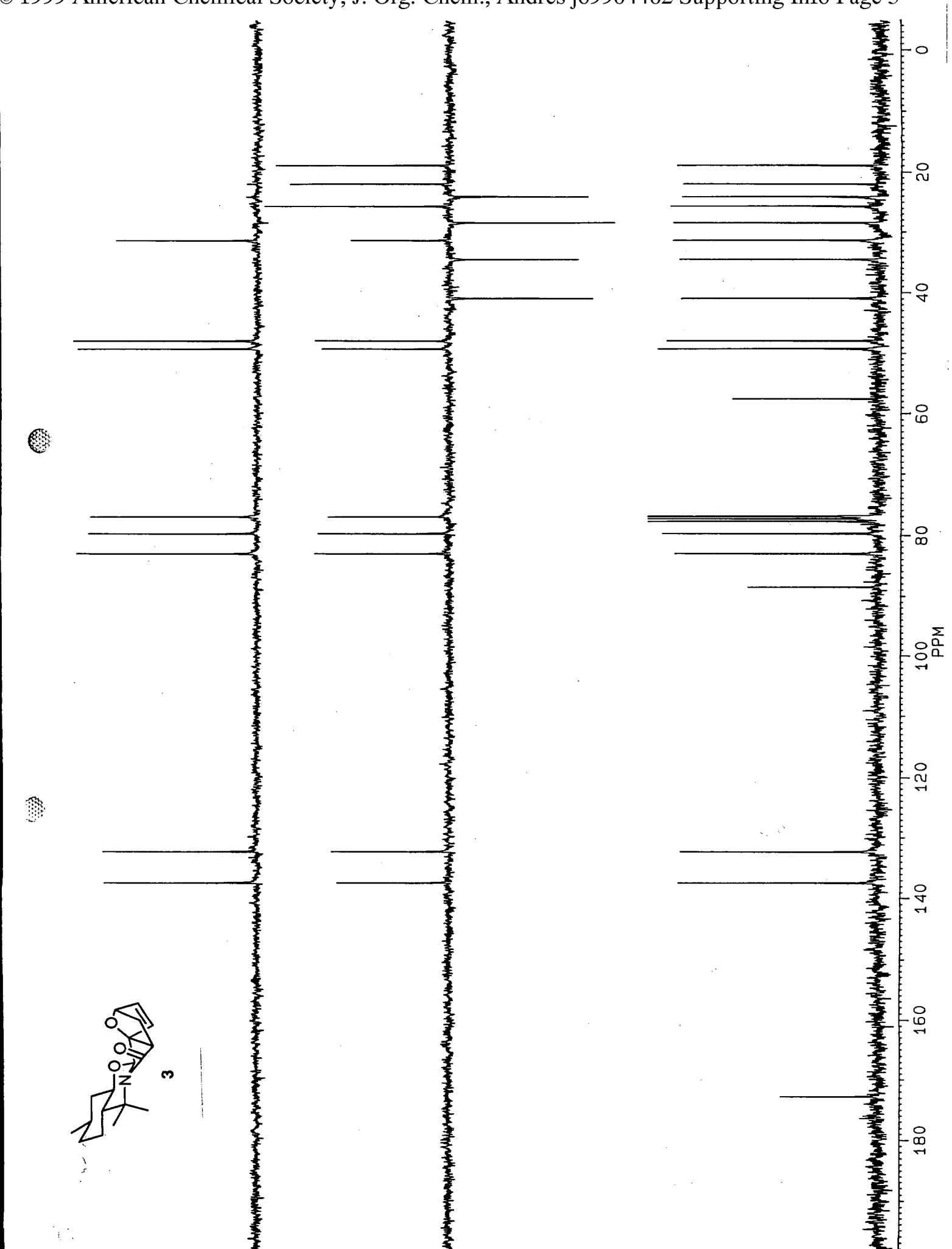
(3aR,6R,7aR)-3a,6-Epoxy-7a-methyl-3a,6,7,7a-tetrahydroisoindoline (ent-28). Yield 66%. Colorless oil. $[\alpha]^{25}_D$ = +23.16 (c = 1.0, CH_2Cl_2). ^{1}H NMR, ^{13}C NMR and IR data are coincident with those reported for **28**. Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.36; H, 8.82; N, 9.39.

(3aR,6S,7S,7aR)-3a,6-Epoxy-7-methyl-3a,6,7,7a-tetrahydroisoindoline. (ent-29). Yield 73%. Colorless oil. $[\alpha]^{25}_D$ = -77.82 (c =1.3, CH_2Cl_2). ^{1}H NMR, ^{13}C NMR and IR data are coincident with those reported for **29**. Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.36; H, 8.52; N, 9.39.

(3aR,6R,7aS)-6-Ethyl-3a,6,7,7a-tetrahydroisoindoline (31). Yield 60%. Pale yellow oil. $[\alpha]^{25}_D$ = -35.13 (c = 0.6, CH_2Cl_2). ^{1}H NMR (δ): 0.93 (t, 3H, J = 7.4 Hz); 1.15 (q, 1H, J = 1.9 Hz); 1.25-1.45 (m, 2H); 1.74 (dt, 1H, J_1 = 4.5 Hz, J_2 = 12.8 Hz); 2.02 (m, 1H); 2.41 (m, 1H); 2.74-2.84 (m, 2H); 3.04 (d, 1H, J = 10.4 Hz); 3.43-3.50 (m, 2H); 5.26 (broad s, 1H) 5.65 (ddd, 1H, J_1 = 2.8 Hz, J_2 = 3.1 Hz, J_3 = 10.0 Hz); 5.73 (d, 1H, J = 10.0 Hz). ^{13}C NMR (δ): 11.1; 28.3; 30.9; 35.9; 36.9; 37.9; 49.1; 50.8; 122.9; 134.1. IR (film) 3420, 1270,1120 cm^{-1}. Anal. Calcd for $C_{10}H_{17}$ N: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.30; H, 11.21; N, 9.32.

(3aS,6S,7aR)-6-Ethyl-3a,6,7,7a-tetrahydroisoindoline (*ent*-31). Yield 58%. Pale yellow oil. $[\alpha]^{25}_D$ = + 36.83 (c = 0.6, CH_2Cl_2). ^{1}H NMR, ^{13}C NMR and IR data are coincident with those reported for **31**. Anal. Calcd for $C_{10}H_{17}$ N: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.48; H, 11.46; N, 9.14.

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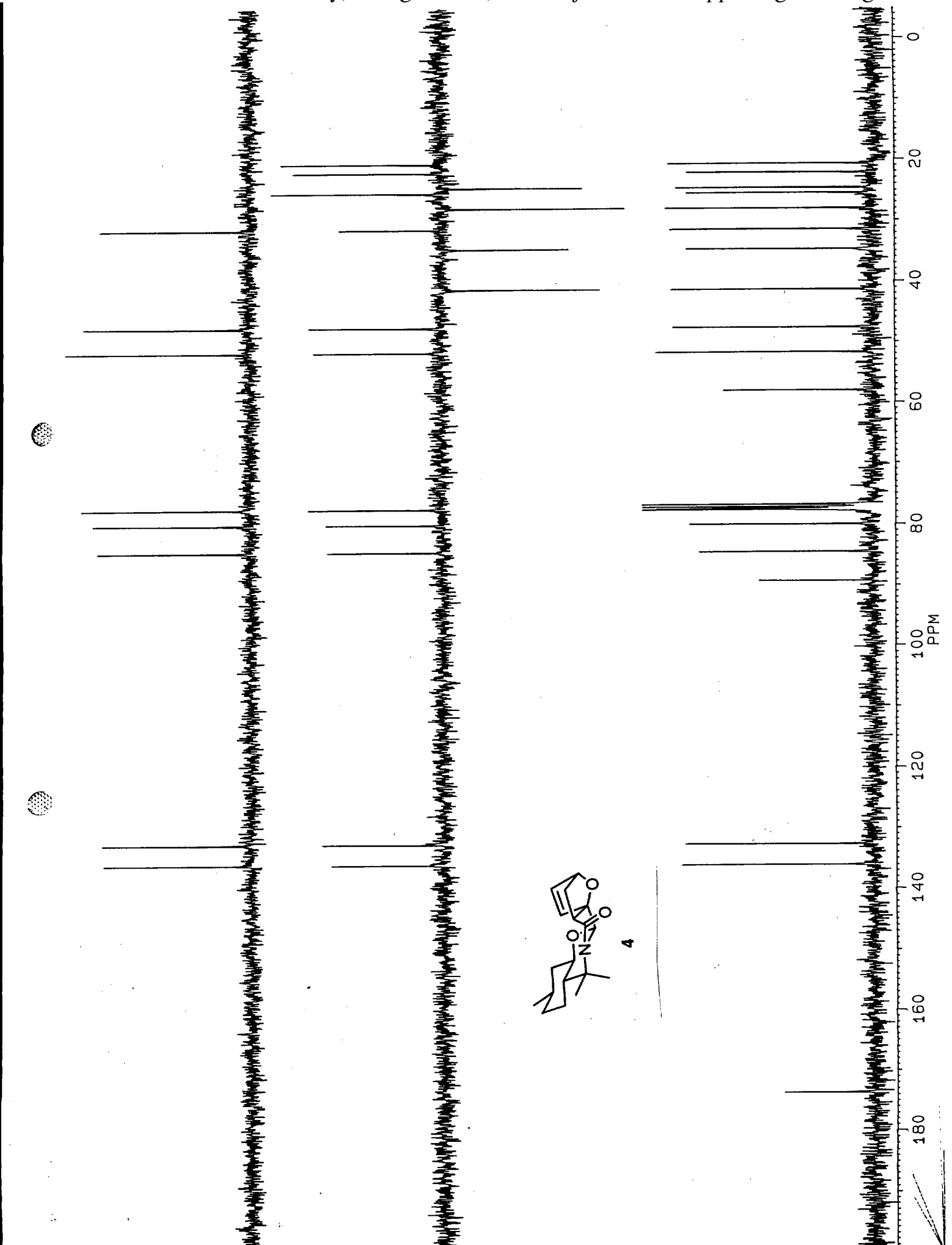

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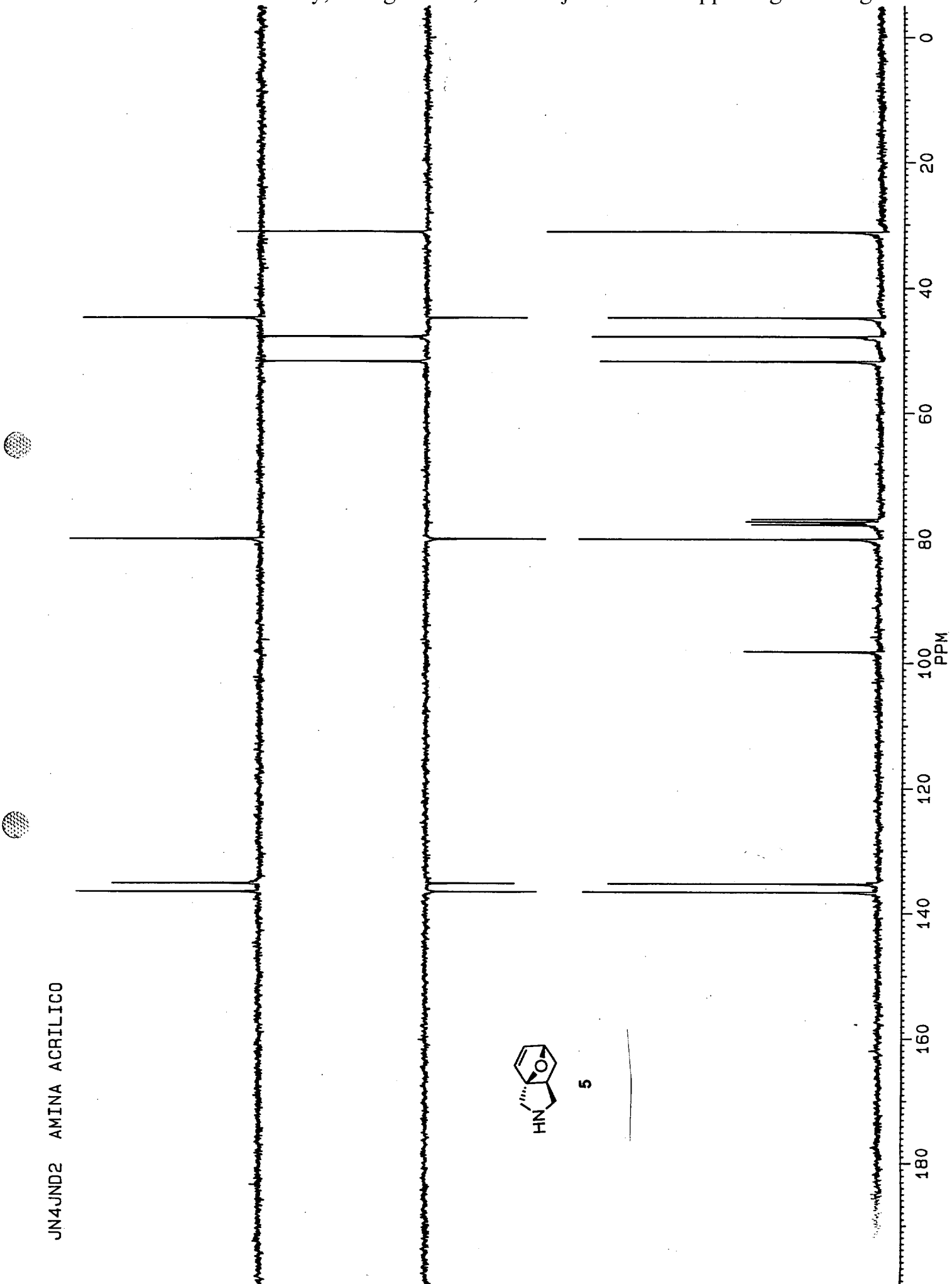

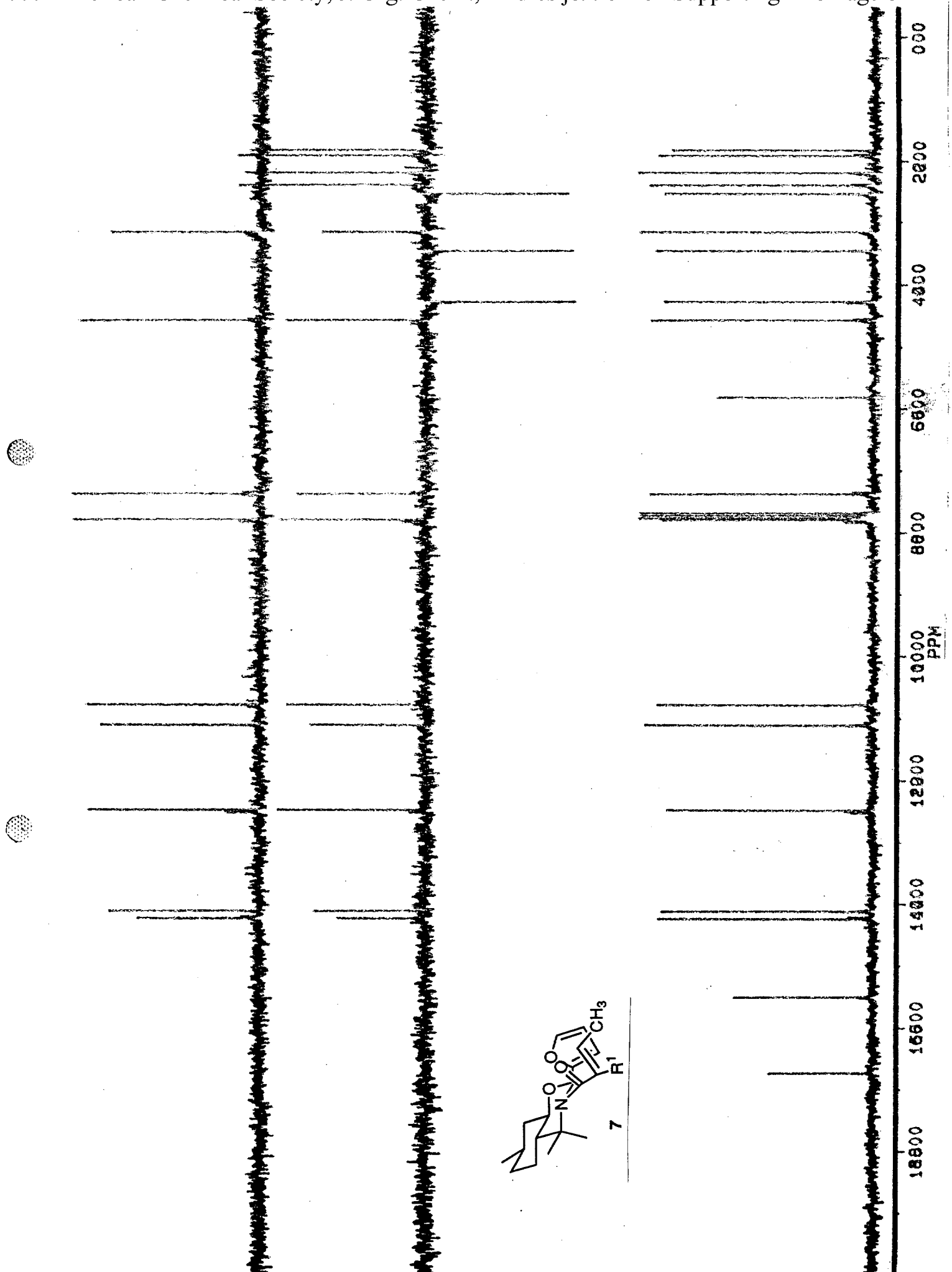

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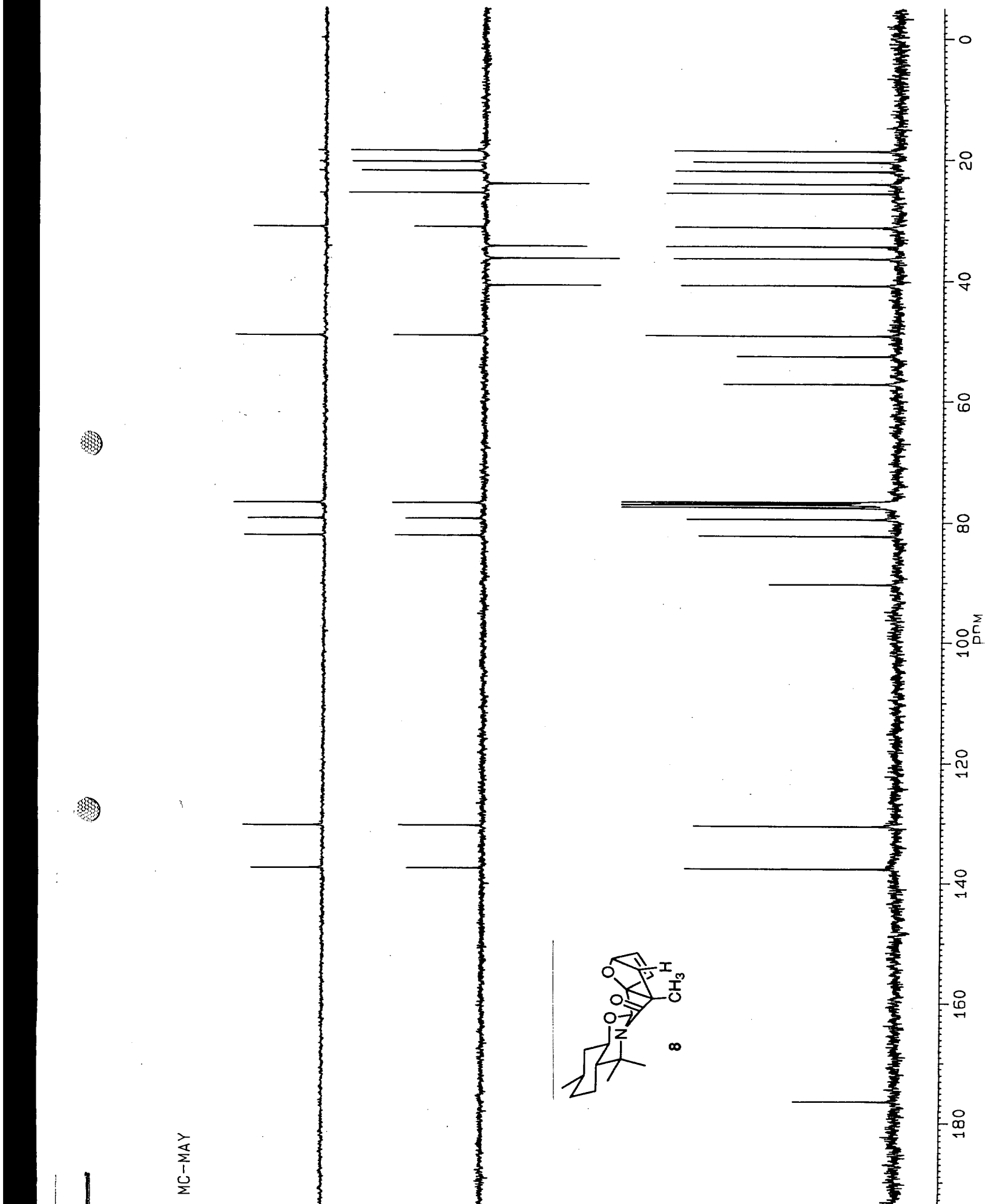

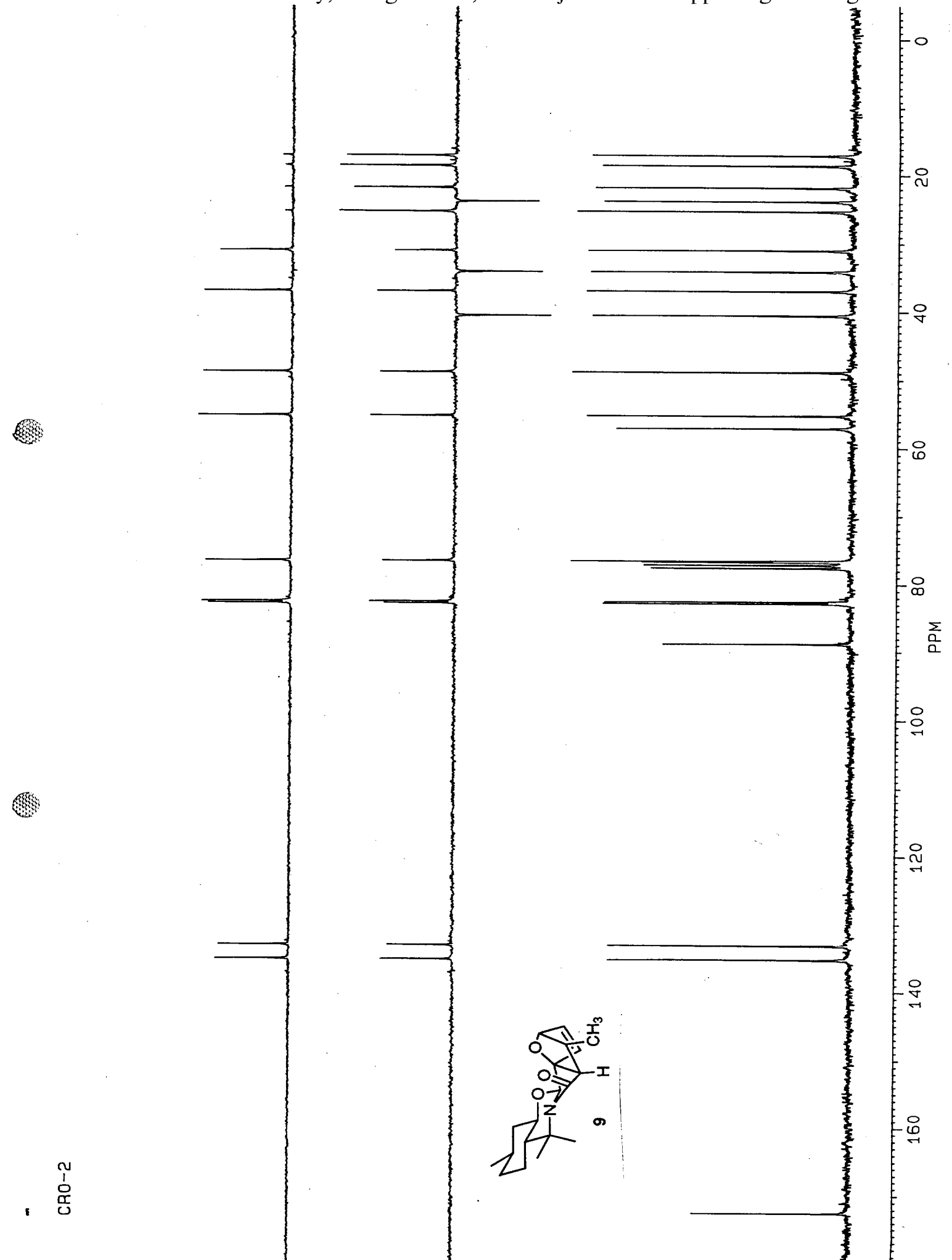

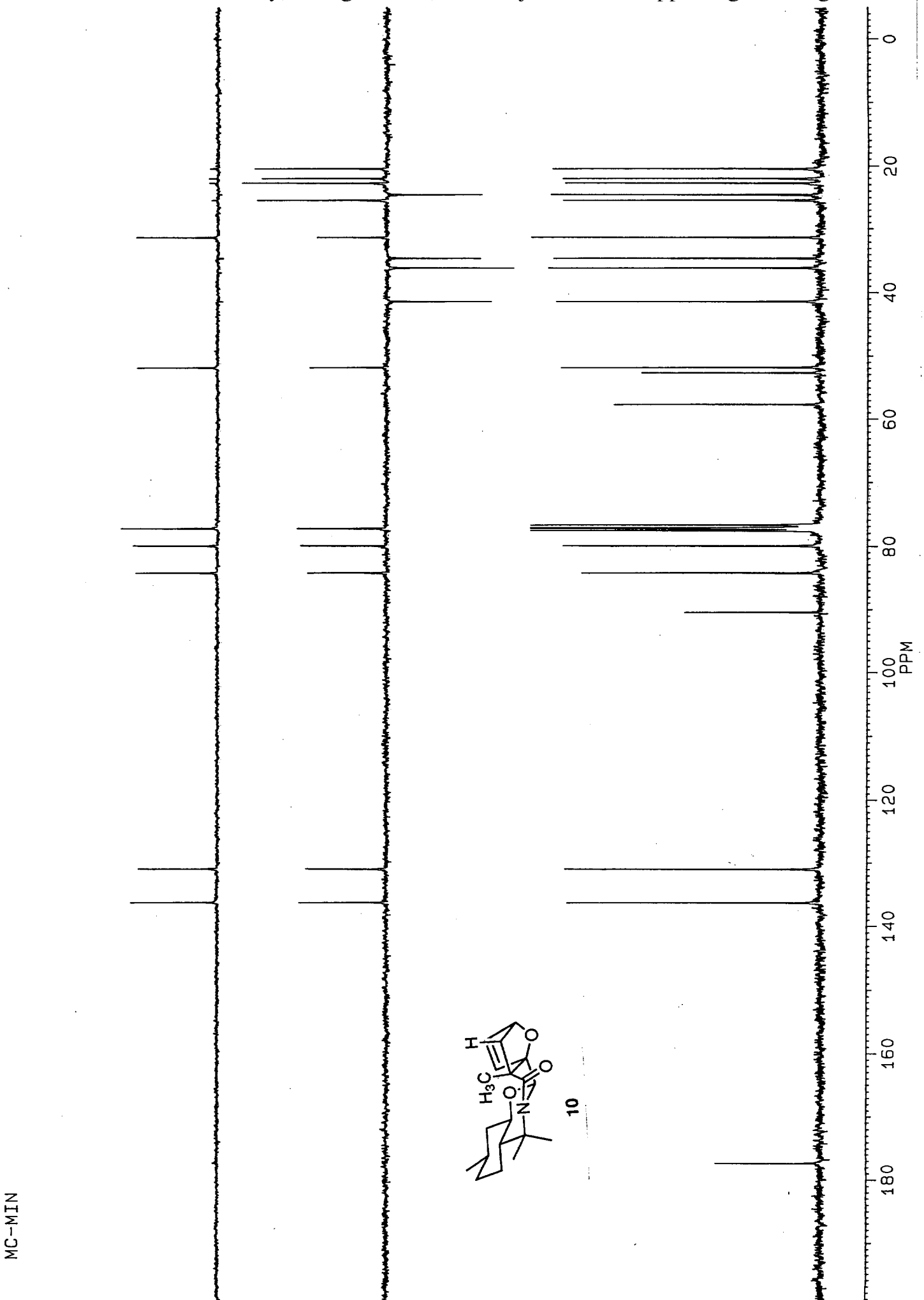

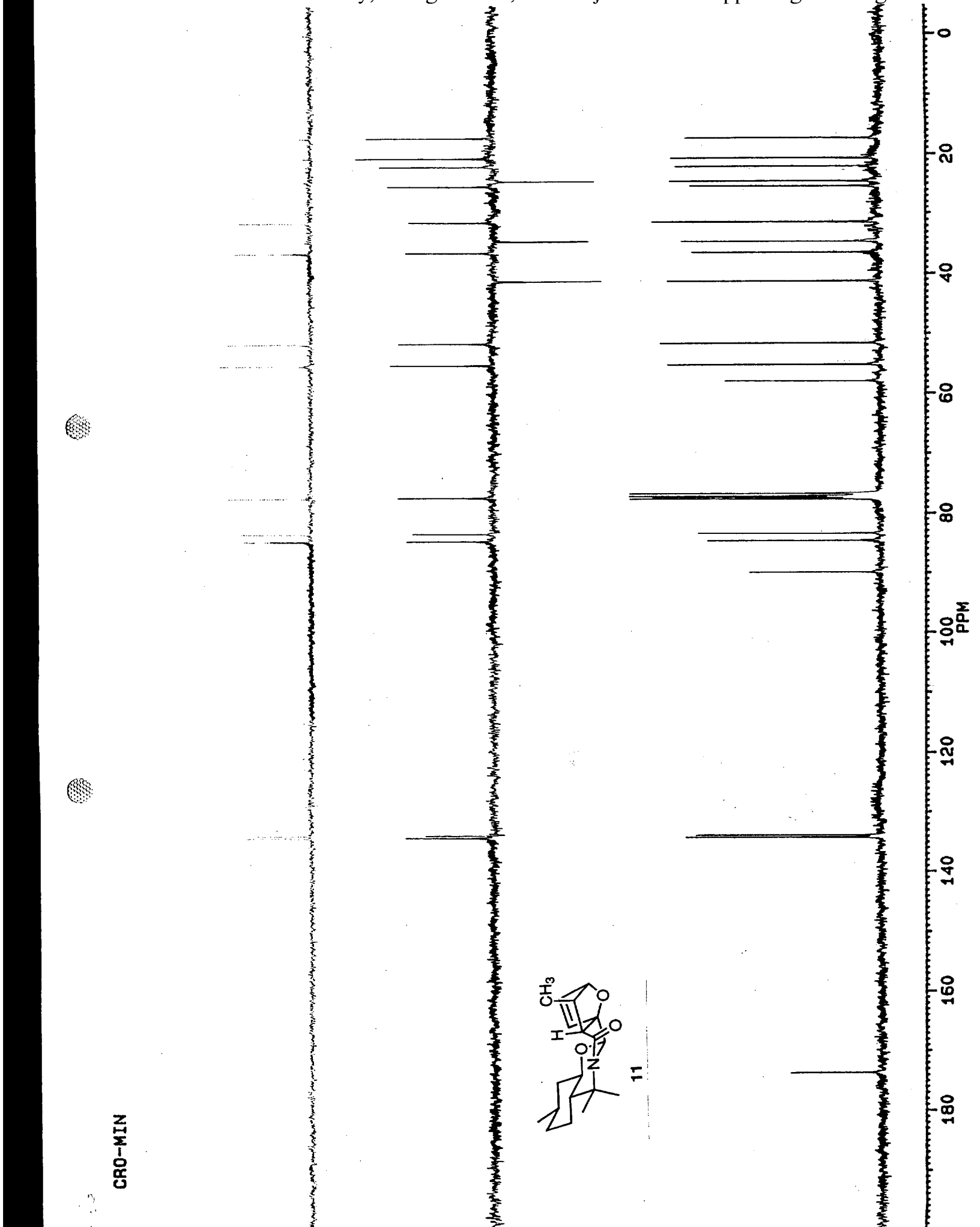

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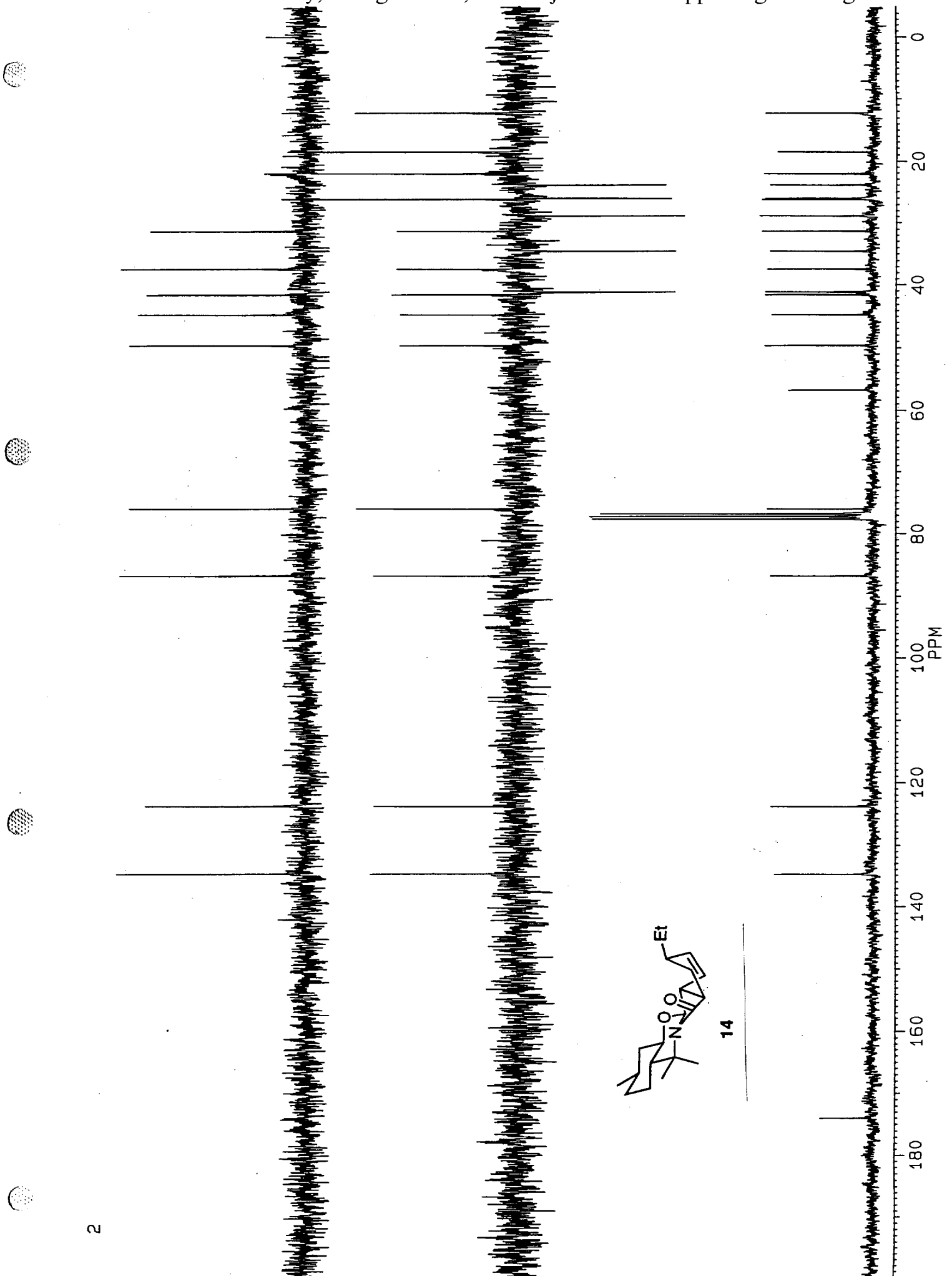

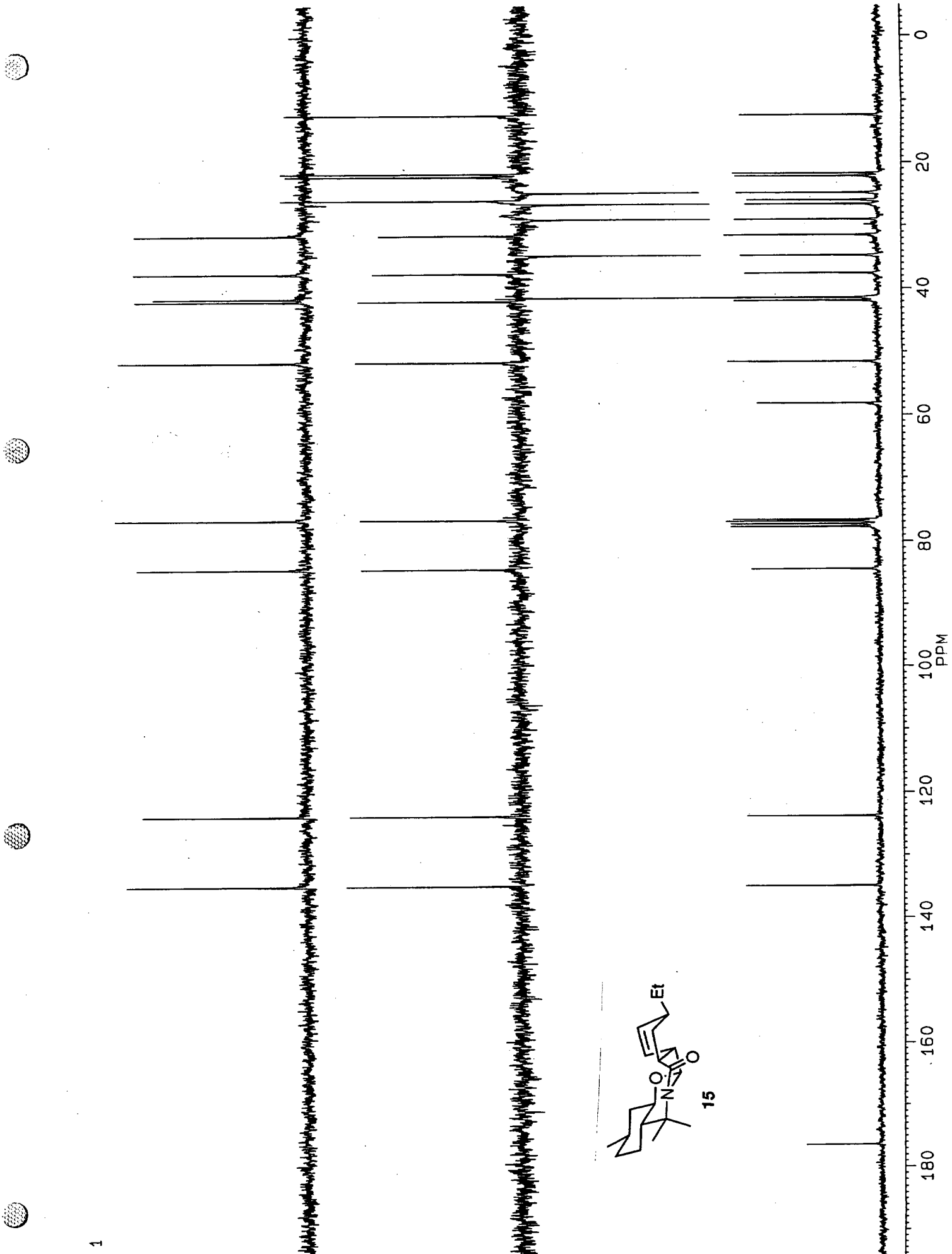

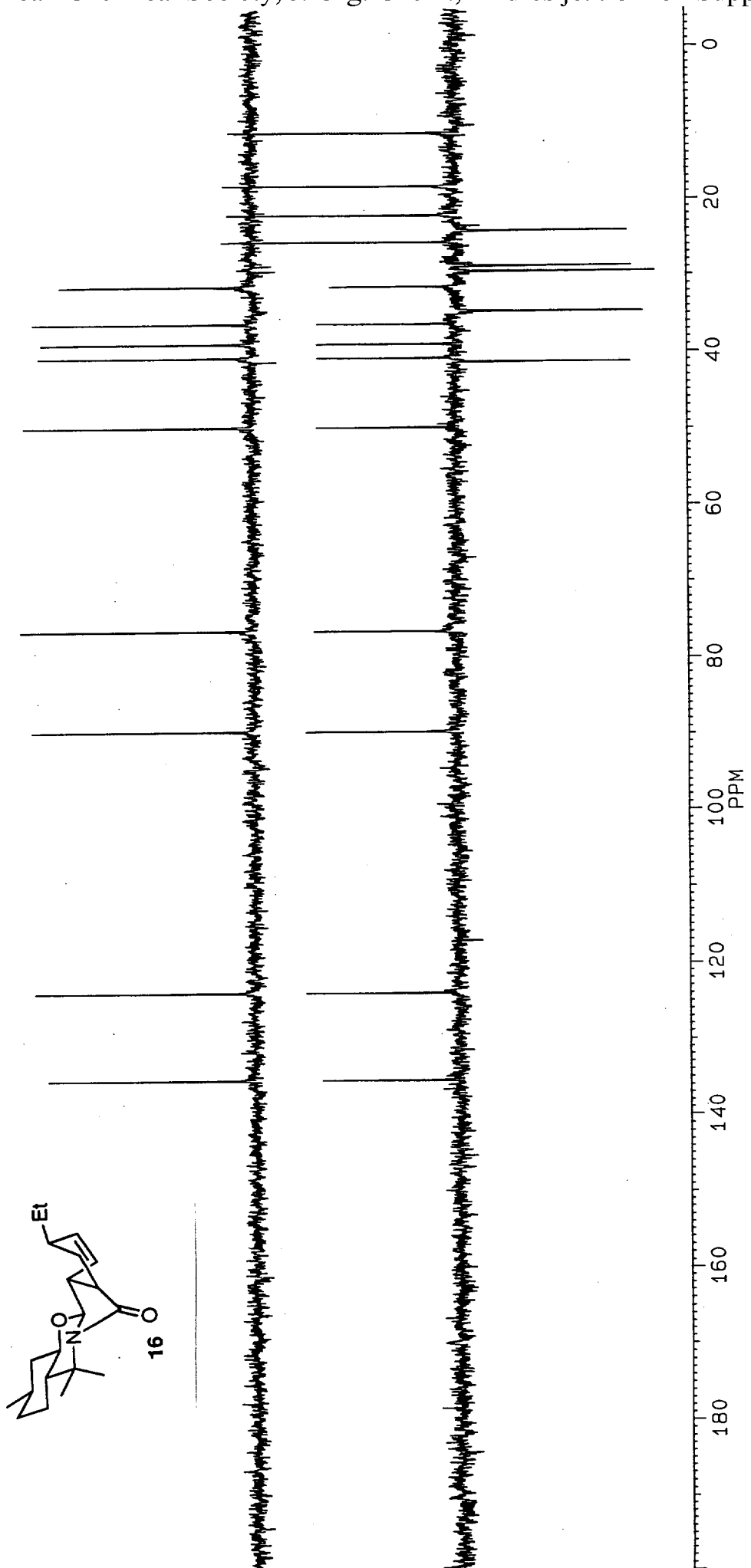

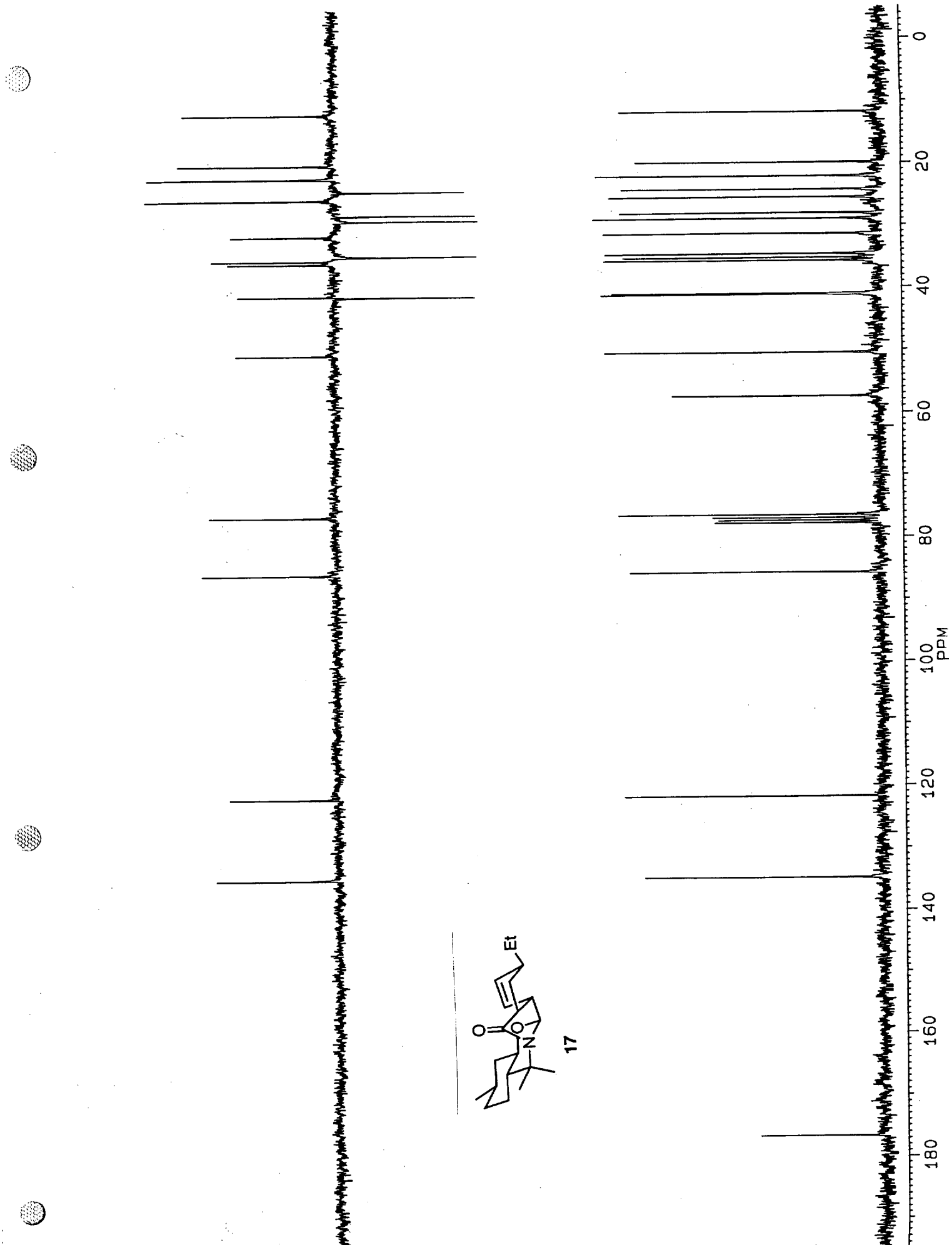
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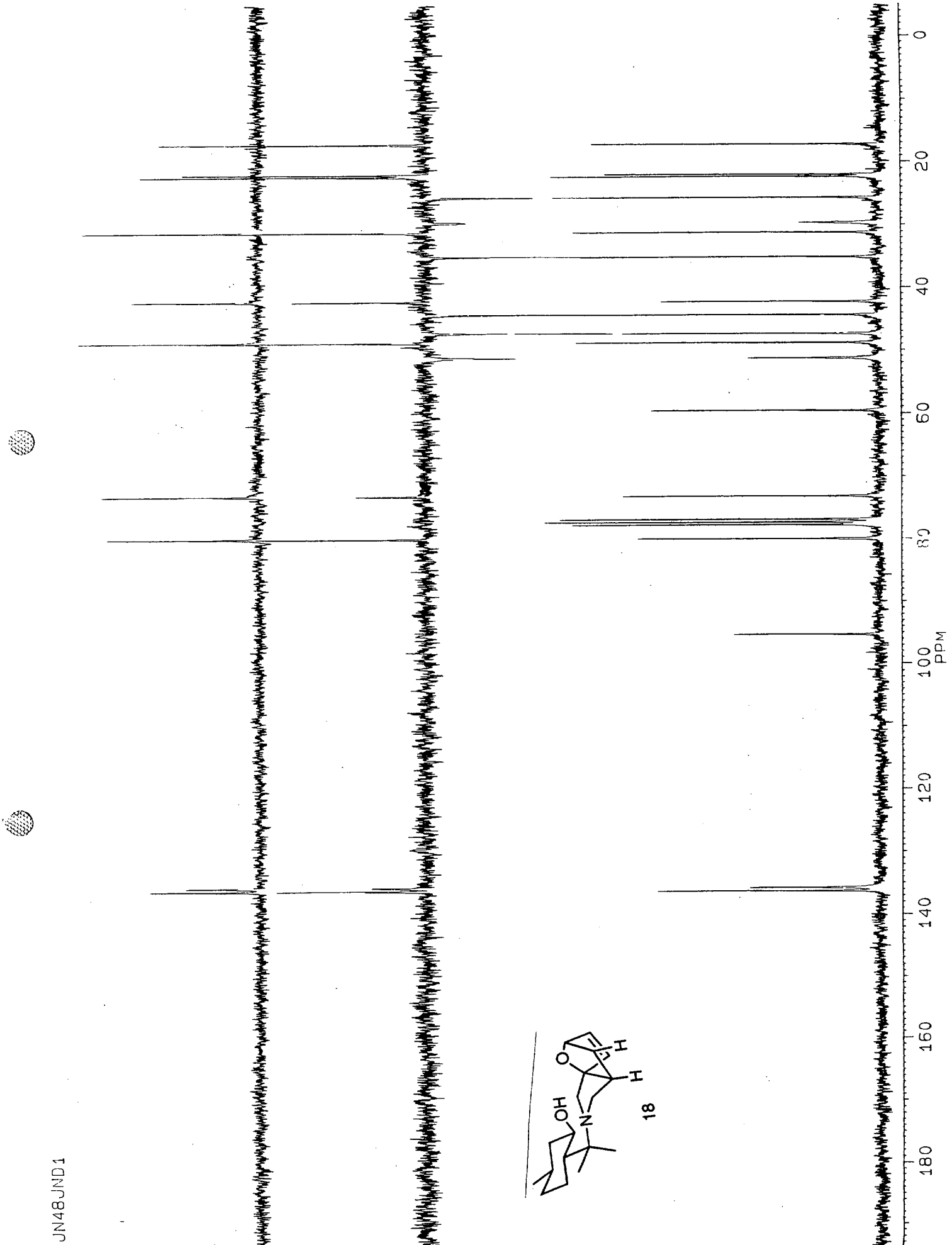

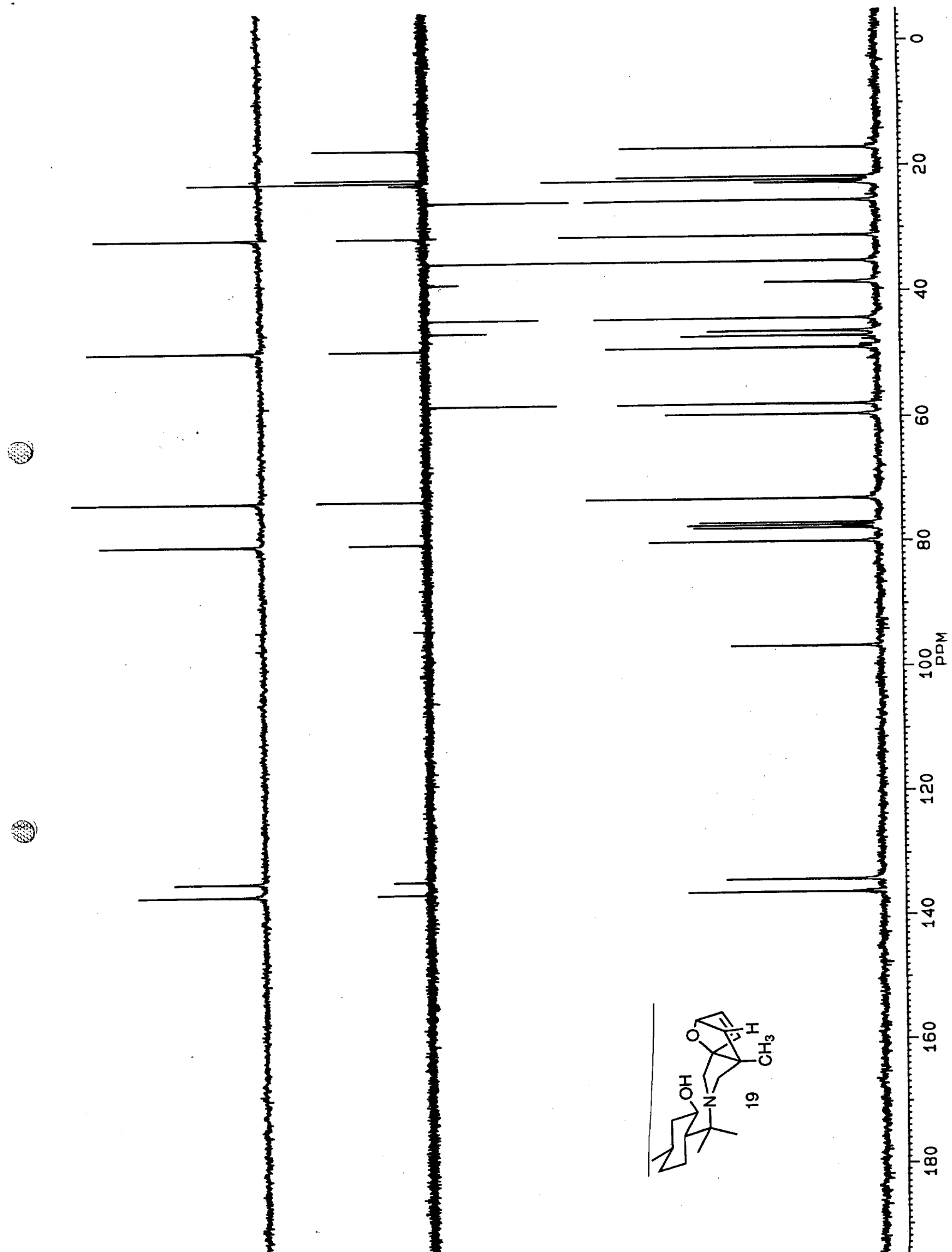

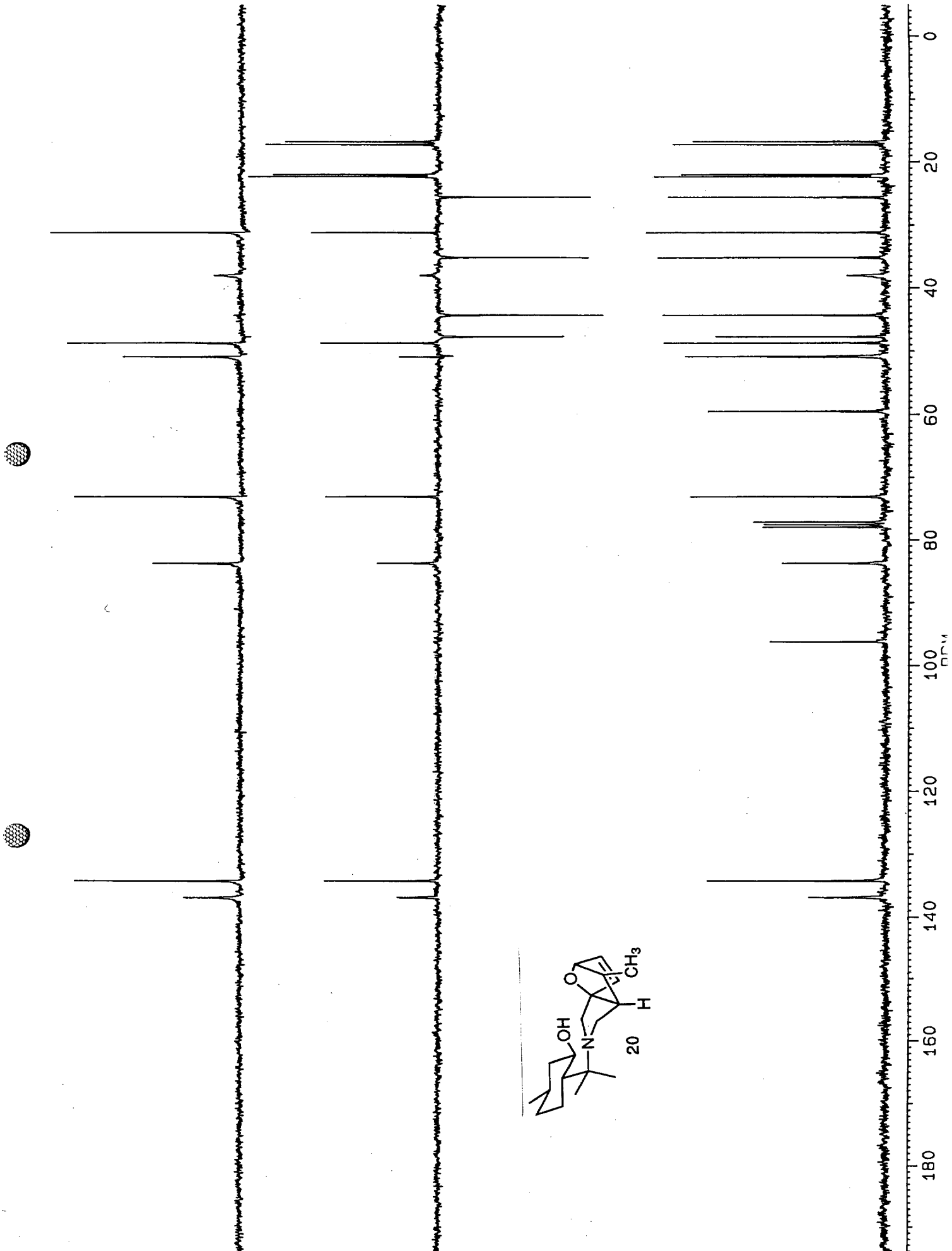

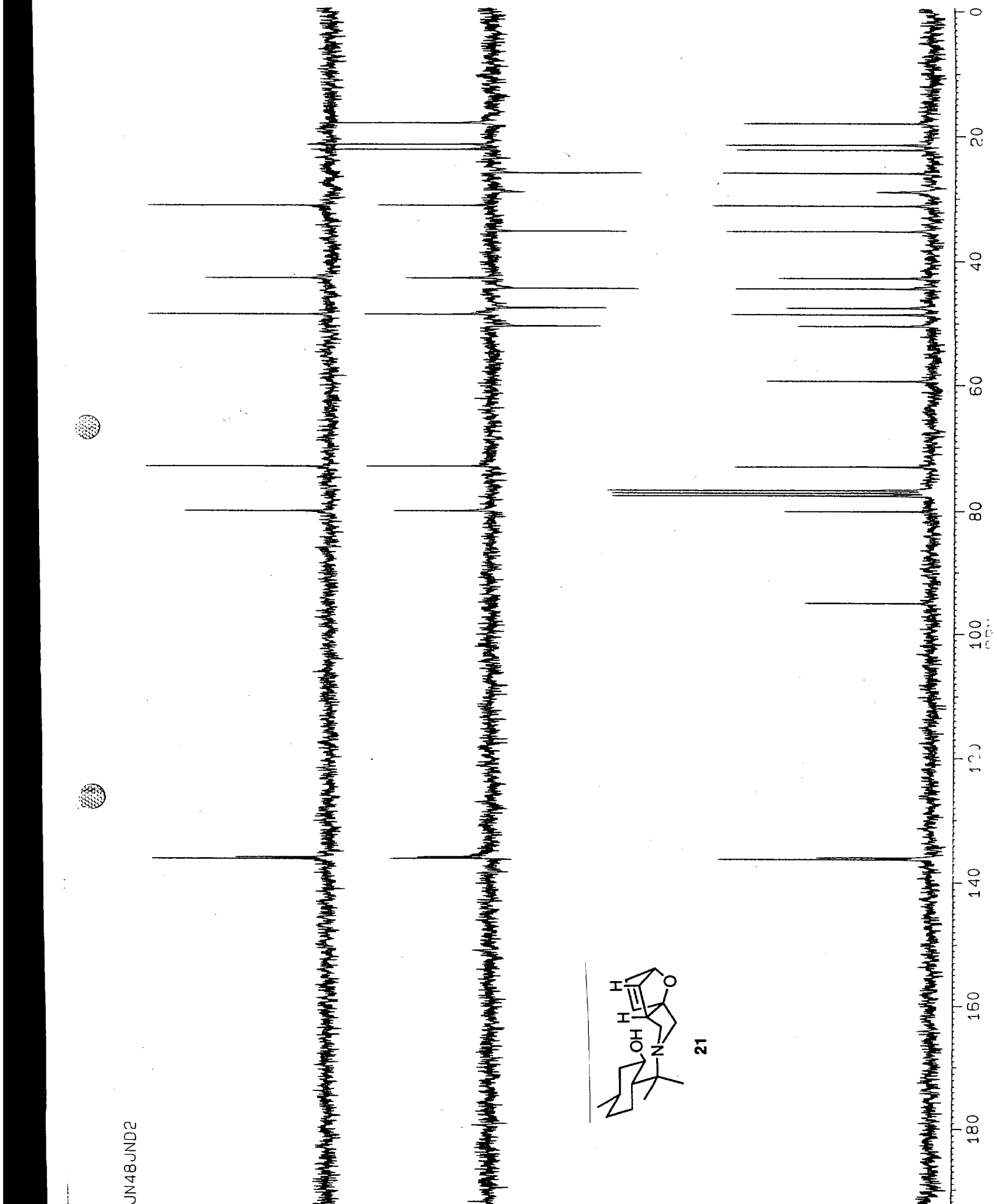

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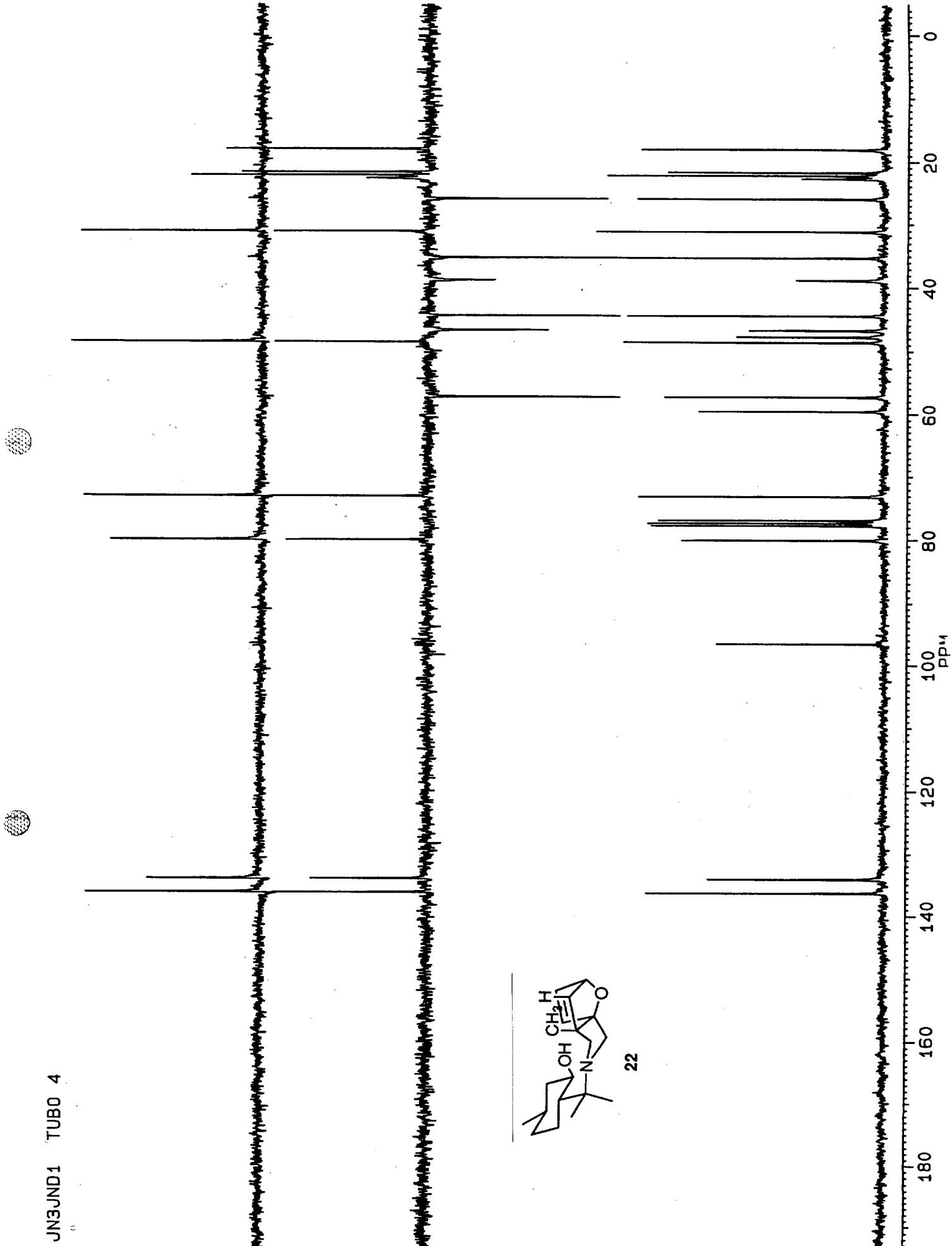

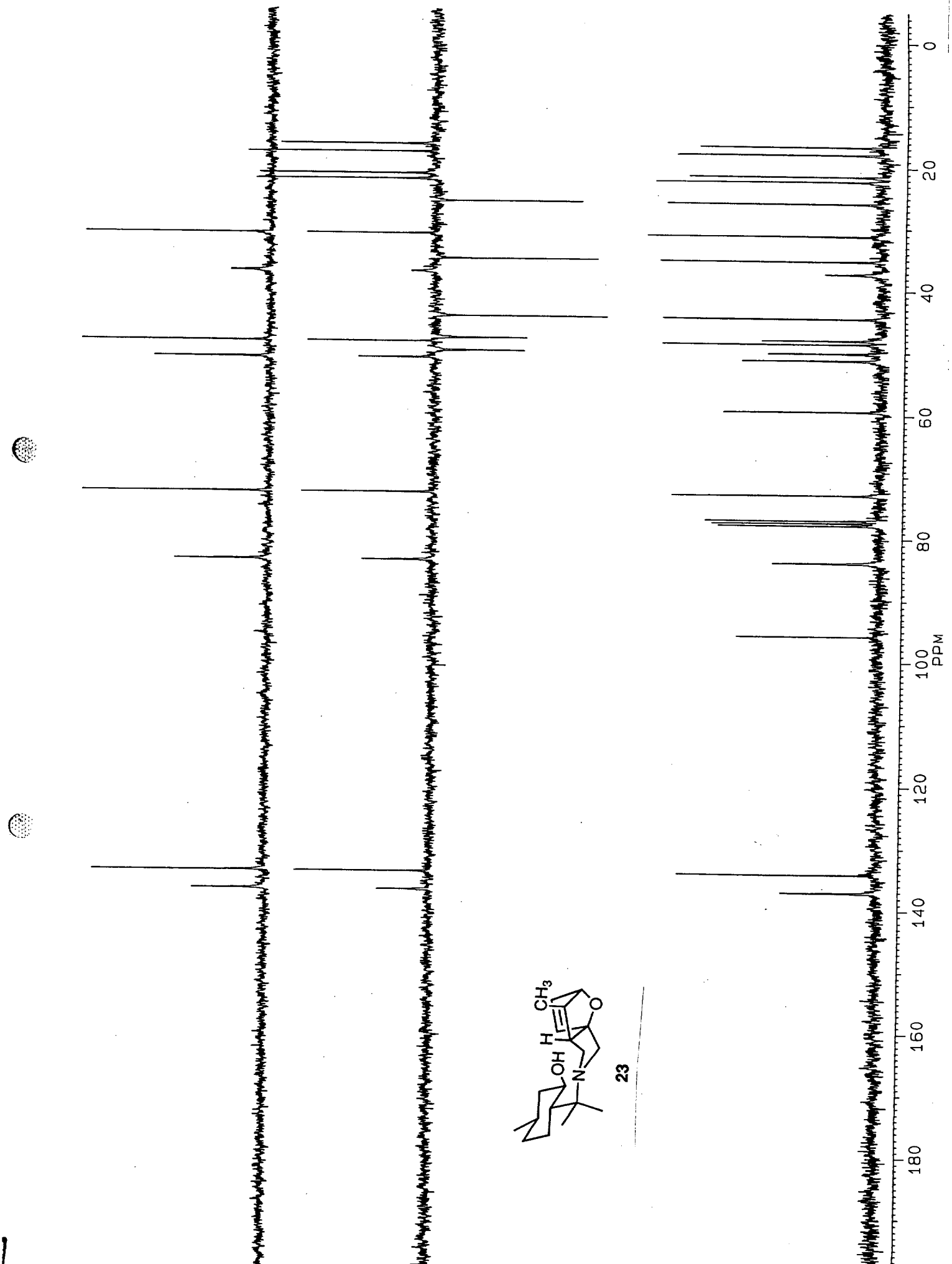

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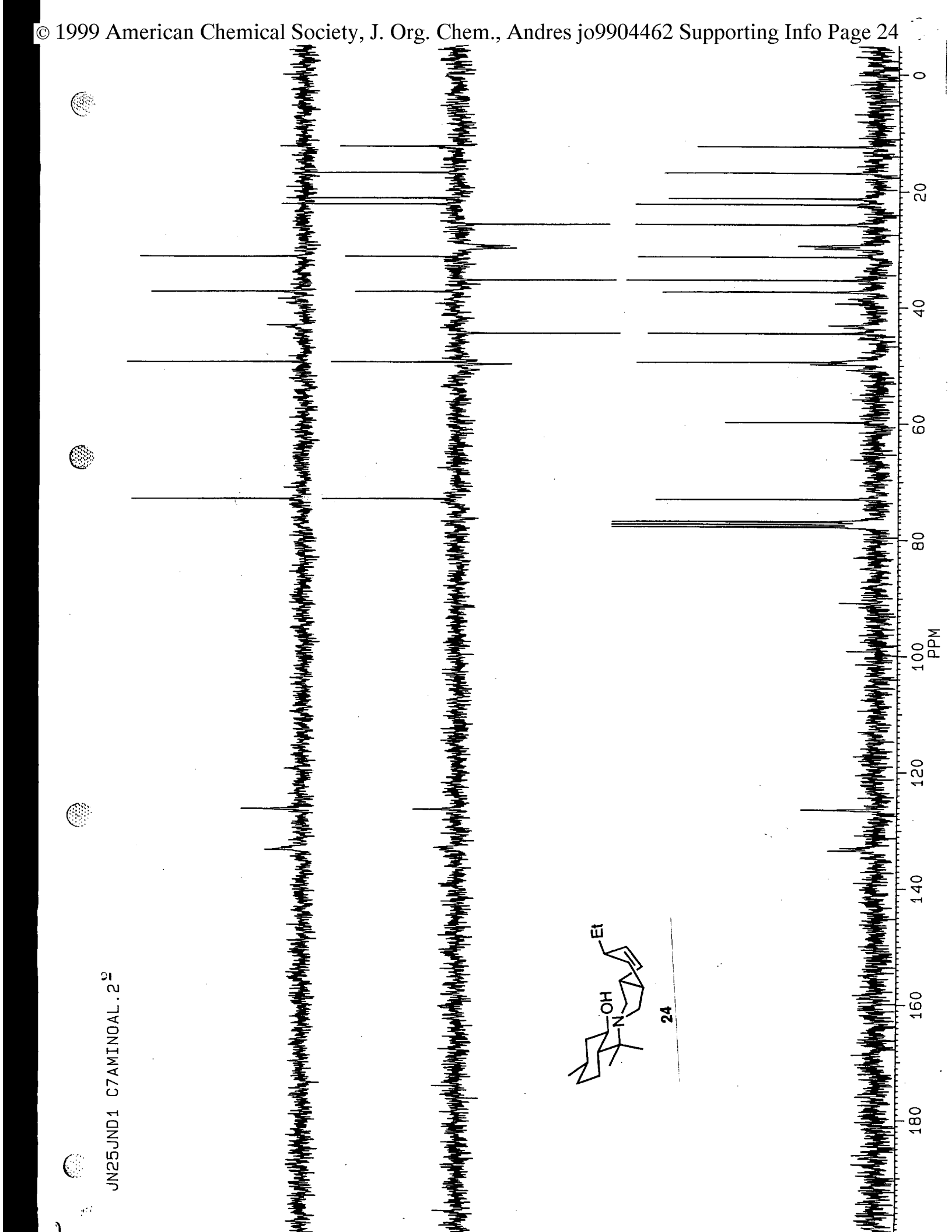

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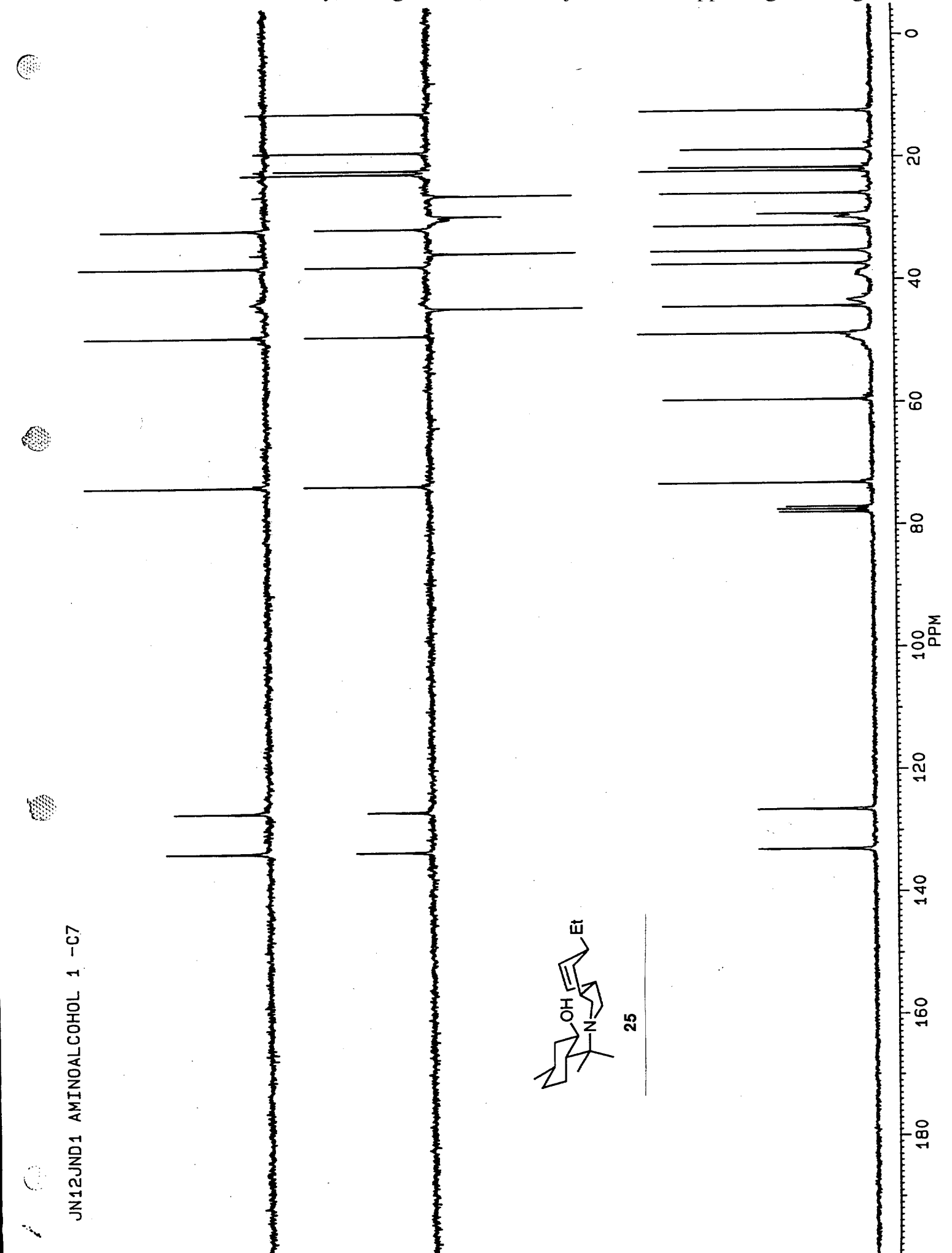

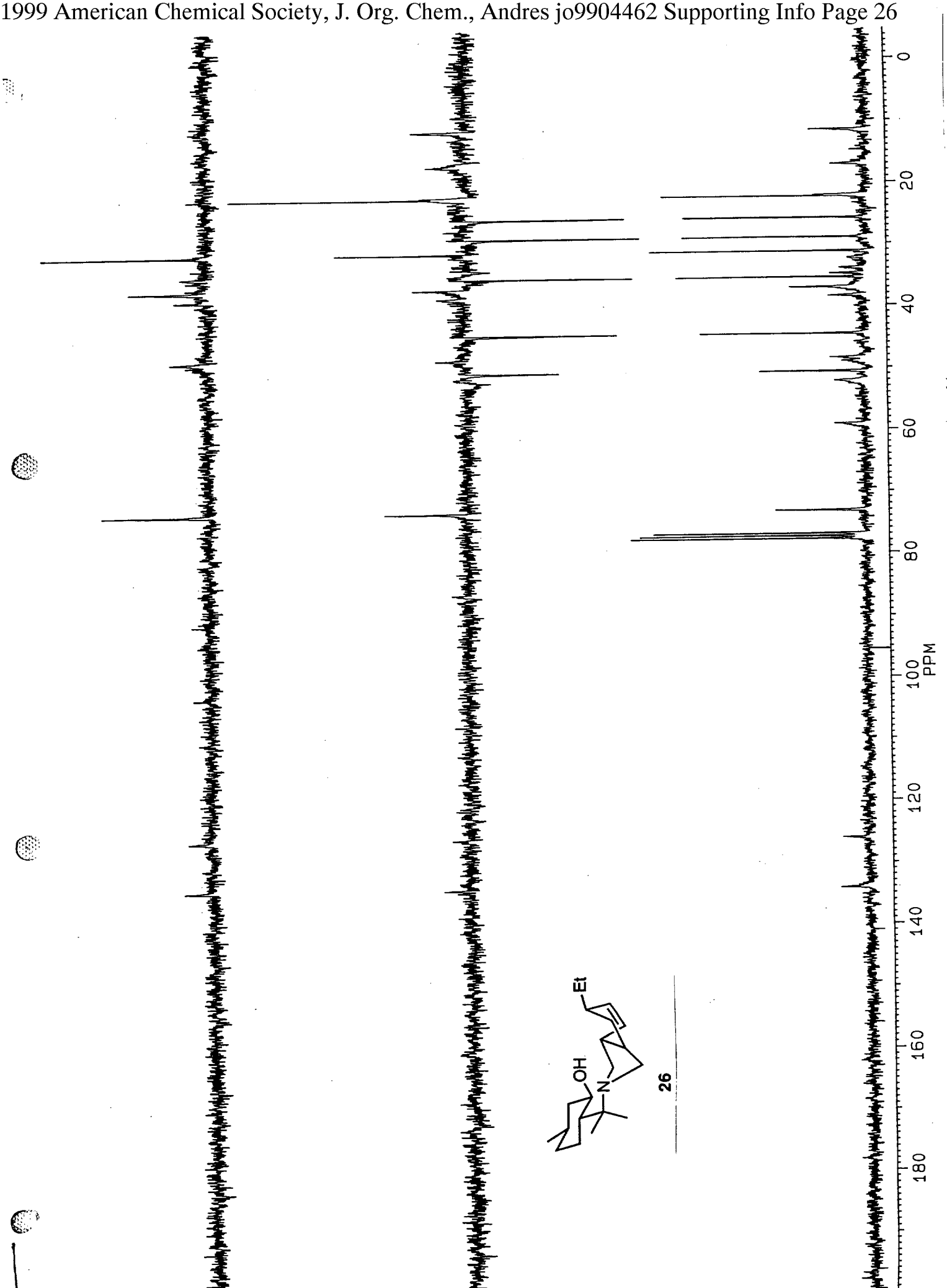

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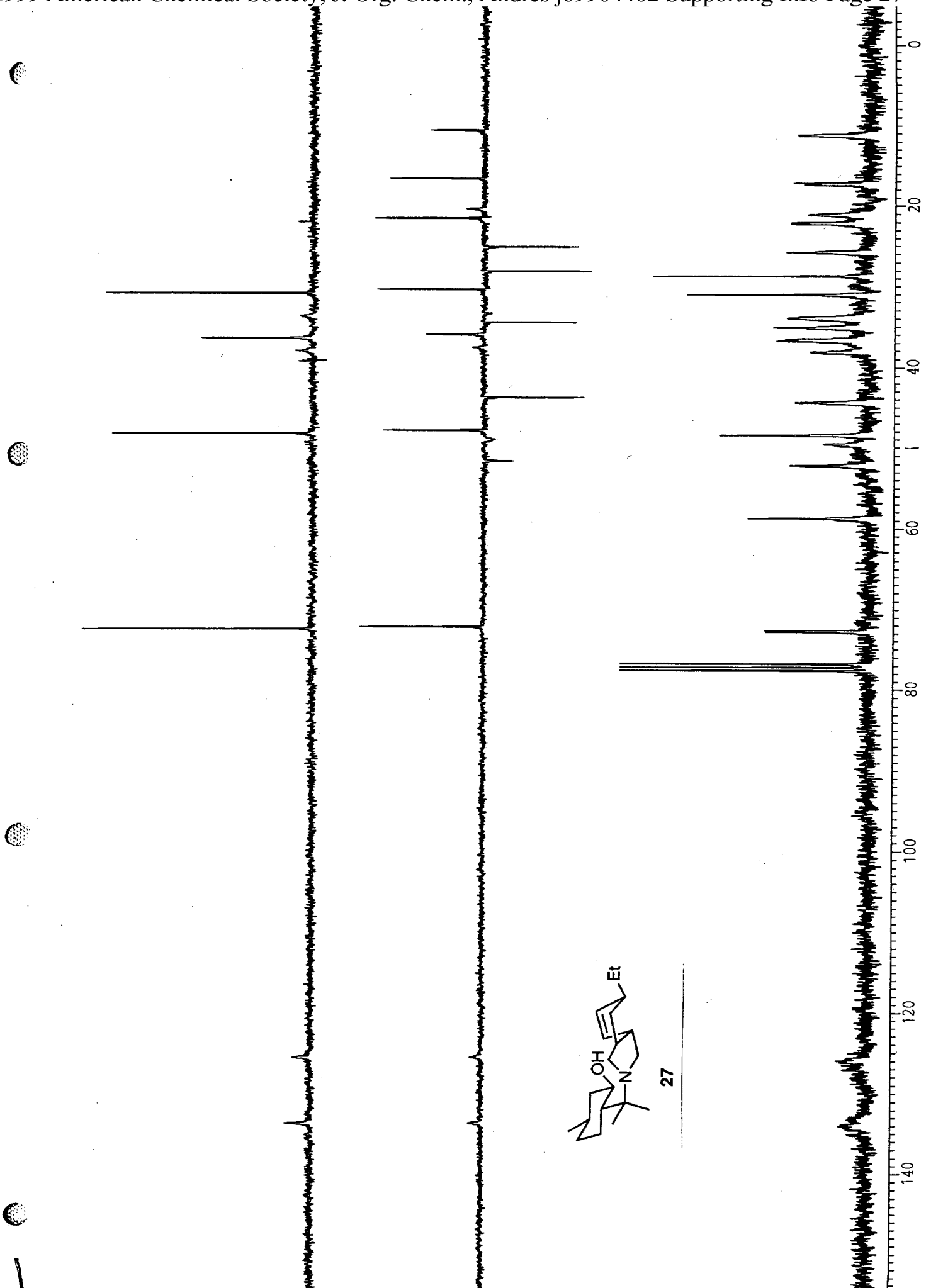

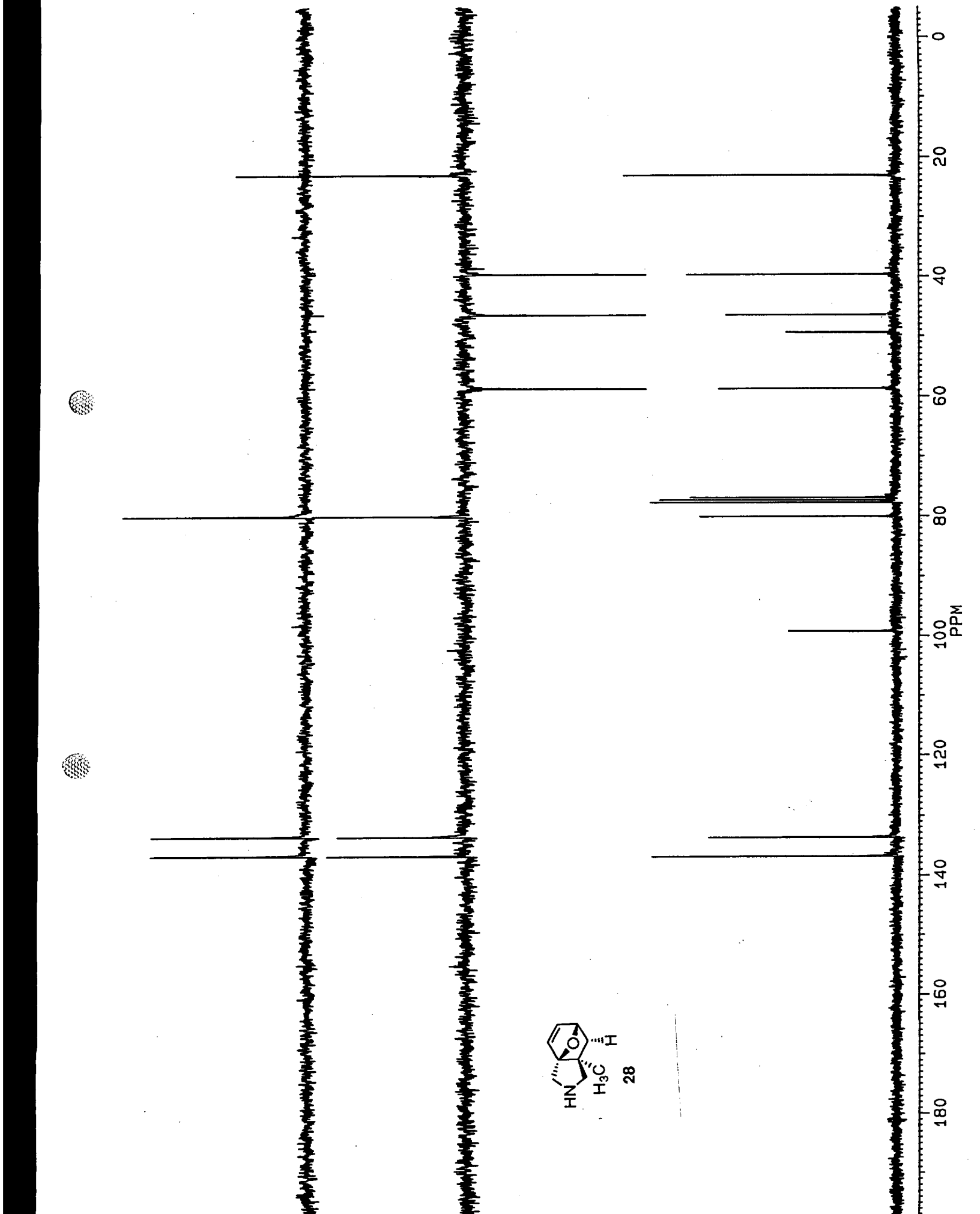

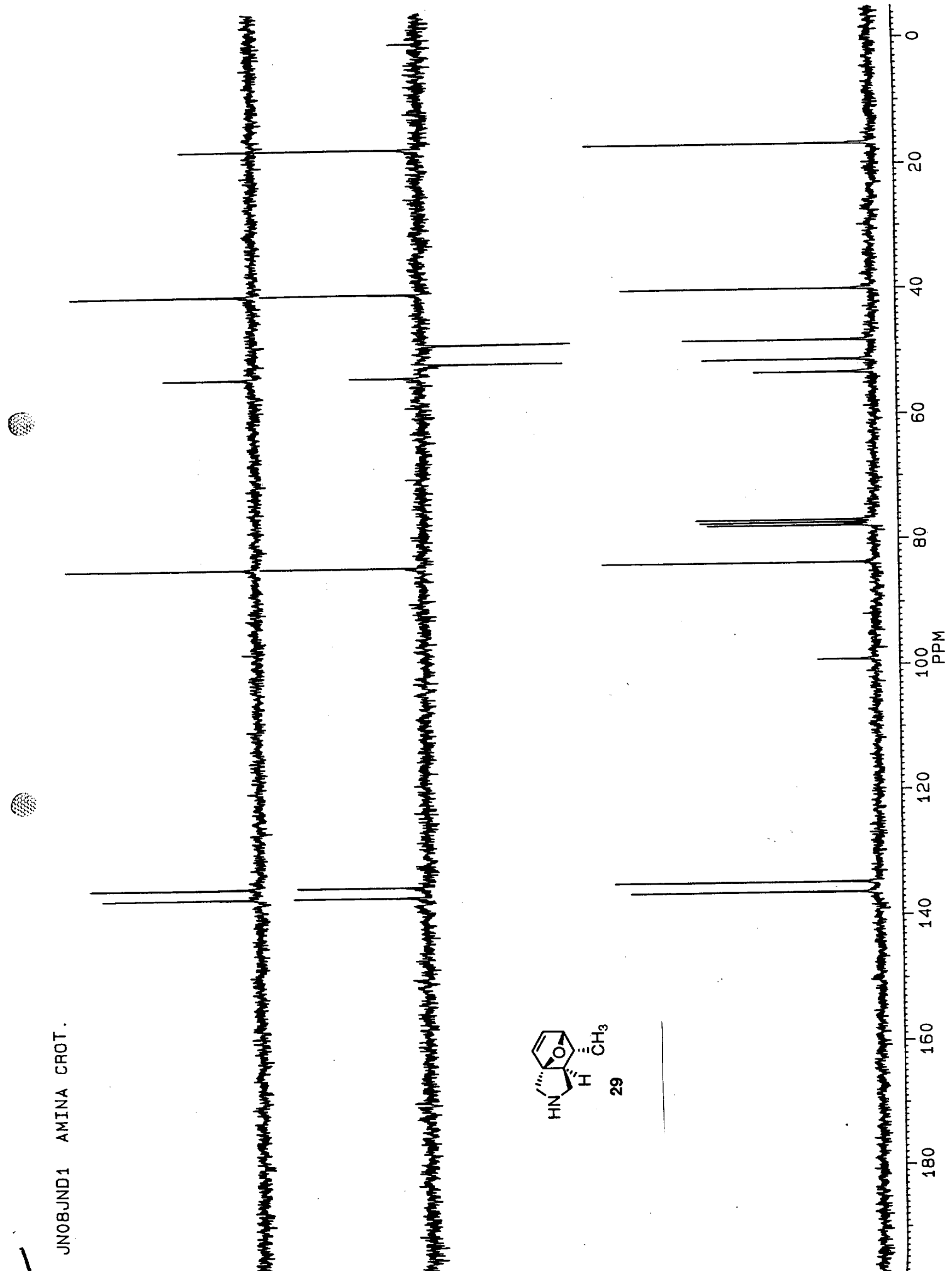
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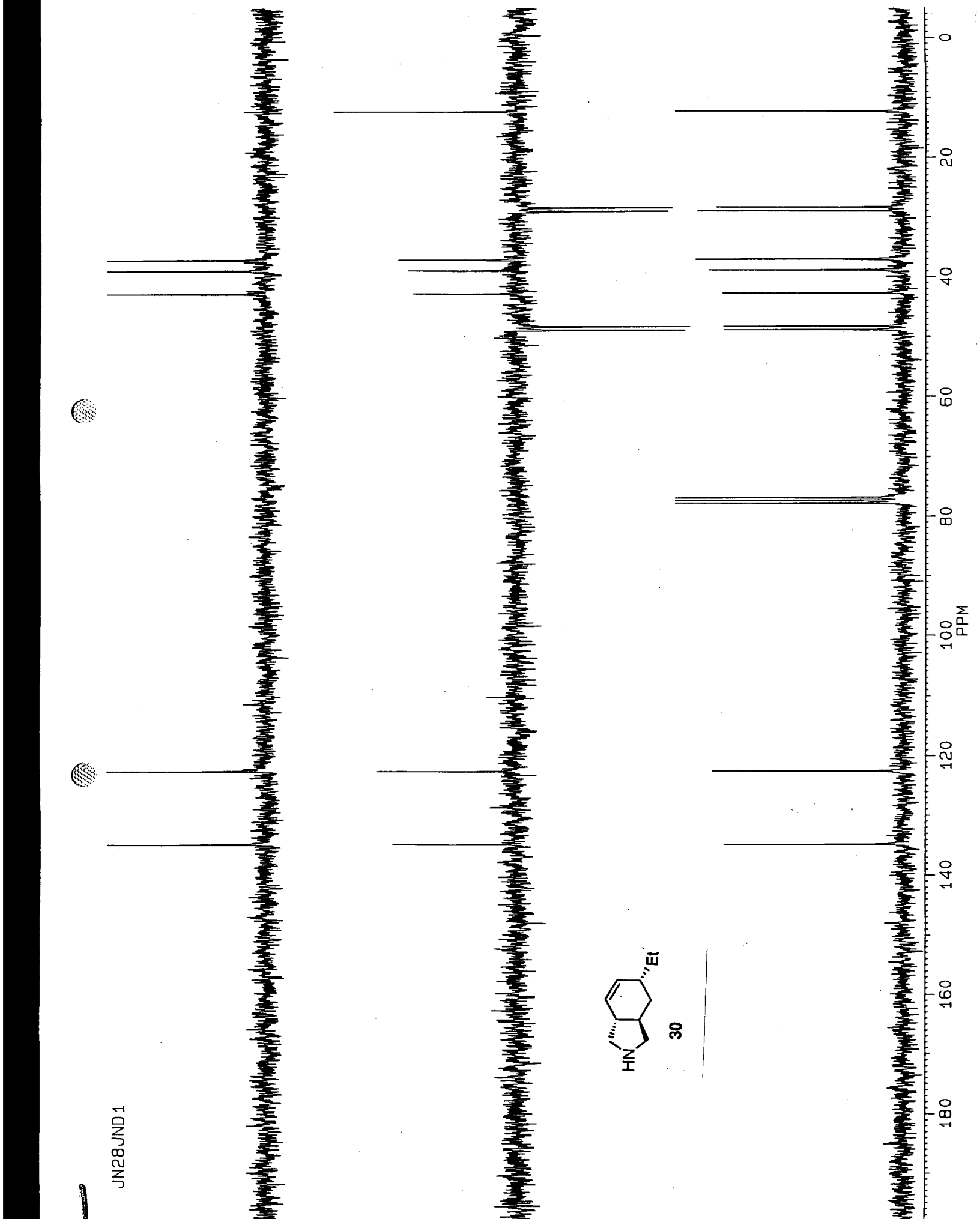

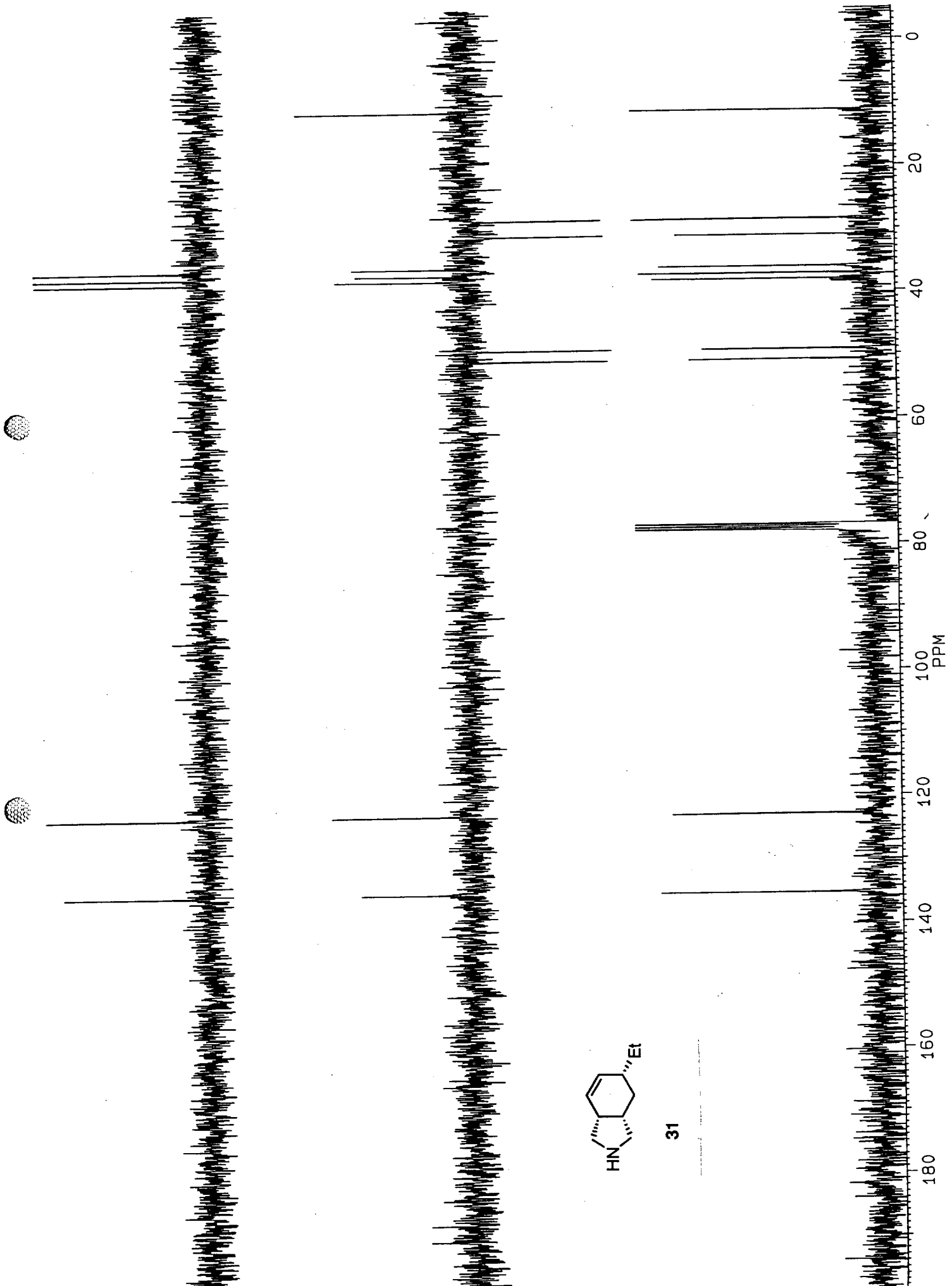

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