Multicomponent Reactions of 1,3-Disubstituted 5-Pyrazolones and Formaldehyde in Environmentally Benign Solvent Systems and Their Variations with More Fundamental Substrates

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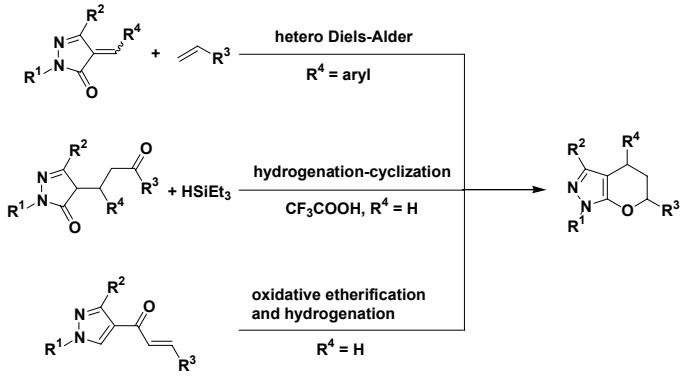
Electronic Supporting Information

General remarks:

Ethyl 4,4-dimethyl-3-oxovalerate, methyl isobutyrylacetate, ethyl butyrylacetate, vinylferrocene, ethyl benzoylacetate, ethyl 4-methoxybenzoylacetate, 2,4,6-trichlorophenylhydrazine, 4-methylstyrene, 4-methoxystyrene, 4-chlorostyrene, 4-fluoro-*a*-methylstyrene, 4-*tert*-butylstyrene, 4-chloro-α-methylstyrene, *tert*-butylhydrazine hydrochloride, 4-chlorophenylhydrazine hydrochloride, 4-fluorophenylhydrazine hydrochloride, 4-methylphenylhydrazine hydrochloride and chloroform-*d* were purchased from Alfa Aesar Chemical Company. 1-Methyl-2-phenylindole and 1-ethyl-2-phenylindole were purchased from TCI Chemical Company. Styrene, *a*-methylstyrene, paraformaldehyde, glycerol, 1-methylimidazole, chloroacetic acid, $NaBF_4$, ethanol, ethyl acetate, *n*-heptane and petroether were purchased from Shanghai Chemical Company. Synthesis of 1,3-disubstituted 5-pyrazolones were performed according to literature methods.[1,2] Ionic liquid, $[MIm\text{-}CO_2H]BF_4$, was prepared according to a reported method.[3] ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me_4Si in $CDCl_3$. IR spectra were recorded on a FT-IR Bruker (VERTEX 70) using KBr technology. HRMS analysis was measured on a VG ZAB HS Instrument.



Scheme S1. Previous methods to access the skeleton of product ***3a***.

Typical procedure of two-step sequential reaction of phenylhydrazine (4a), ethyl

acetoacetate (5b), α-methylstyrene (2a) and paraformaldehyde: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, glycerol (2.5g) was mixed with phenylhydrazine (***4a***, 54.0 mg, 0.50 mmol) and ethyl acetoacetate (***5b***, 75mg, 0.55 mmol) under air. The mixture was then heated at 110 ^{o}C for 4 hours. Then, α-methylstyrene (***2a***, 118.0 mg, 1.00 mmol) and paraformaldehyde (45.0 mg, 0.75 mmol) were added. After 10 hours of stirring at 110 ^{o}C, the mixture was cooled to 75 ^{o}C, and then extracted with ethyl acetate (3 mL × 3). The obtained organic solutions were concentrated and then subjected to isolation with preparative TLC using a mixed solution of ethyl acetate and petro ether as eluting solvent (normally, the ratio of ethyl acetate/petroether is 1/10).

Typical procedure of three-component reaction of 1-ethyl-2-phenylindole (6b), 3-phenyl-1-(4-fluorophenyl)-5-pyrazolone (7a) and paraformaldehyde: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, glycerol (2.0 g) was mixed with 1-ethyl-2-phenylindole (110.5 mg, 0.50 mmol) and 3-phenyl-1-(4-fluorophenyl)-5-pyrazolone (127.0 mg, 0.50 mmol) under air. The mixture was then heated at 110 ^{o}C for 6 hours. Then the mixture was extracted with ethyl acetate (3 mL × 3). The obtained organic solutions were concentrated and then subjected to isolation with preparative TLC using a mixed solution of ethyl acetate and petro ether as eluting solvent (normally, the ratio of ethyl acetate/petroether is 1/10).

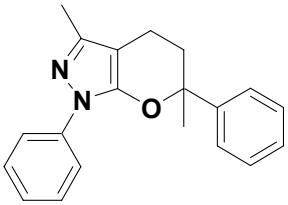
Typical procedure of two-step sequential reaction of phenylhydrazine (4a), ethyl 4-methoxybenzoylacetate (5f), 1-ethyl-2-phenylindole (6b) and paraformaldehyde: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, glycerol (2.5g) was mixed with phenylhydrazine (54.0 mg, 0.50 mmol) and ethyl 4-methoxybenzoylacetate (122.0 mg, 0.55 mmol) under air. The mixture was then heated at 110 ^{o}C for 6 hours. Then, 1-ethyl-2-phenylindole (***6a***, 110.5 mg, 0.50 mmol) and paraformaldehyde (45.0 mg, 0.75 mmol) were added. After 6 hours of stirring at 110 ^{o}C, the mixture was cooled to 75 ^{o}C, and then extracted with ethyl acetate (3 mL × 3). The obtained organic solutions were concentrated and then subjected to isolation with preparative TLC using a mixed solution of ethyl acetate and petro ether as eluting solvent (normally, the ratio of ethyl acetate/petroether is 1/10).

References

1. D. E. Butler, H. A. DeWald, *J. Org. Chem.* **1971**, *36*, 2542–2547.
2. D. Castagnolo, A. De Logu, M. Radi, B. Bechi, F. Manetti, M. Magnani, S. Supino, R. Meleddu, L. Chisu, M. Botta, *Bioorg. Med. Chem*. **2008**, *16*, 8587-8591.
3. J. Li, Y. Peng, G. Song, *Catal. Lett*. **2005**, *102*, 159-162.

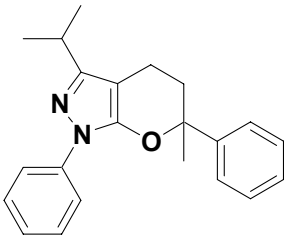
Spectroscopic data of the products

1,4,5,6-Tetrahydro-3,6-dimethyl-1,6-diphenyl-pyrano[2,3-c]pyrazole (3a)



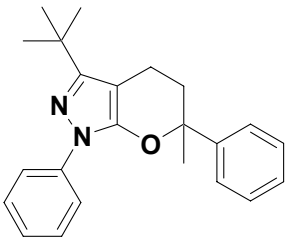
Yellow-pale liquid, ^{1}H NMR ($CDCl_3$): 1.56 (s, 3H), 1.86-1.95 (m, 1H), 2.02 (s, 3H), 2.03-2.11 (s, 1H), 2.17 (dt, J_a = 5.2 Hz, J_b = 13.6 Hz, 1H), 2.30 (dt, J_a = 4.8 Hz, J_b = 14.4 Hz, 1H), 7.03-7.12 (m, 1H), 7.15 (t, J = 7.2 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H); ^{13}C NMR: 12.8, 15.7, 28.8, 33.5, 83.8, 95.8, 119.8, 124.6, 125.0, 127.3, 128.6, 129.1, 139.3, 144.2, 146.5, 150.1; IR (cm^{-1}): 3061, 2978, 2925, 2855, 1605, 1507, 1445, 1393, 1375, 1328, 1266, 1158, 1120, 1102, 1070, 1029, 1004, 900, 866, 758, 697, 658; HRMS (ESI): calcd for $C_{20}H_{20}N_2O$, [M + H^+] = 305.3936; found: 305.3968.

1,4,5,6-Tetrahydro-6-methyl-1,6-diphenyl-3-*iso*-propyl-pyrano[2,3-c]pyrazole (3b)



Yellow liquid; ^{1}H NMR ($CDCl_3$): 1.24 (d, J = 2.4 Hz, 3H), 1.26 (d, J = 2.4 Hz, 3H), 1.68 (s, 3H), 2.01-2.09 (m, 1H), 2.20-2.35 (m, 2H), 2.91 (sept, J = 6.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.18-7.24 (m, 1H), 7.29 (t, J = 8.0 Hz, 2H), 7.31-7.36 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), ^{13}C NMR: 16.5, 21.5, 21.6, 28.3, 28.5, 33.8, 83.5, 94.0, 120.0, 124.6, 124.9, 127.2, 128.6, 129.0, 139.4, 144.4, 150.0, 155.3; IR (cm^{-1}): 3062, 2964, 2929, 2867, 1603, 1511, 1494, 1451, 1399, 1302, 1265, 1151, 1092, 1065, 1029, 904, 866, 759, 696; HRMS Calculated for $C_{22}H_{25}N_2O$ [M + H^+]: 333.1967, Detected: 333.1991.

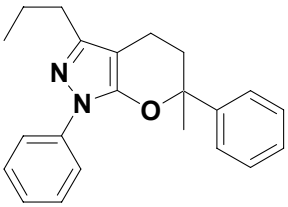
1,4,5,6-Tetrahydro-3-*tert*-butyl-6-methyl-1,6-diphenyl-pyrano[2,3-c]pyrazole (3c)



Yellow-pale solid, mp = 112-113 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.30 (s, 9H), 1.69 (s, 3H), 2.07 (ddd, J_a = 5.6 Hz, J_b = 8.0 Hz, J_c = 14.0 Hz, 1H), 2.28 (dt, J_a = 6.0 Hz, J_b = 14.0 Hz, 1H), 2.41 (ddd, J_a = 5.6 Hz, J_b = 8.0 Hz, J_c = 15.2 Hz, 1H), 2.67 (dt, J_a = 6.0 Hz, J_b = 15.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.23 (tt, J_a = 2,0 Hz, J_b = 7.2 Hz, 1H), 7.27-7.33 (m, 2H), 7.33-7.44 (m, 4H), 7.93 (dd, J_a = 0.8 Hz,

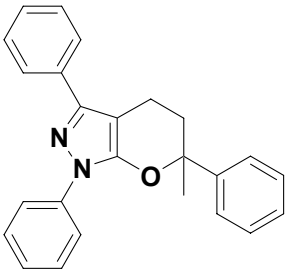
J_b = 8.8 Hz, 2H); ^{13}C NMR: 18.1, 28.2, 29.2, 33.5, 33.9, 83.0, 93.7, 120.0, 124.6, 124,8, 127.2, 128.5, 128.9, 139.5, 144.5, 150.1, 157.3; IR (cm^{-1}): 2977, 2932, 2860, 1600, 1509, 1444, 1385, 1361, 1329, 1269, 1247, 1096, 1065, 1024, 903, 868, 755, 703, 690, 591; anal. calcd for $C_{23}H_{26}N_2O$: C: 79.73, H: 7.56, N: 8.09%; found: C: 80.02, H: 7.67, N: 7.83%.

1,4,5,6-Tetrahydro-6-methyl-1,6-diphenyl-3-*n*-propyl-pyrano[2,3-c]pyrazole (3d)



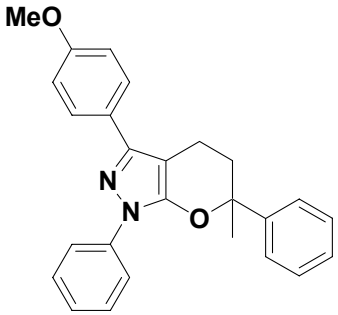
Yellow liquid; ^{1}H NMR ($CDCl_3$): 0.93 (t, J = 7.6 Hz, 3H), 1.60-1.67 (m, 2H), 1.68 (s, 3H), 1.98-2.08 (m, 1H), 2.12-2.31 (m, 2H), 2,41-2,52 (m, 3H), 7.13-7.24 (m, 2H), 7.28 (t, J = 6.8 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 14.1, 16.0, 22.1, 28.4, 30.0, 33.7, 83.6, 95.2, 120.0, 124.6, 125.0, 127.3, 128.6, 129.0, 139.3, 144.3, 149.9, 150.5; IR (cm^{-1}): 3061, 2958, 2930, 2870, 1604, 1512, 1495, 1452, 1398, 1266, 1068, 903, 758, 686; HRMS Calculated for $C_{22}H_{25}N_2O$ [M + H^+]: 333.1967, Detected: 333.1998.

1,4,5,6-Tetrahydro-6-methyl-1,3,6-triphenyl-pyrano[2,3-c]pyrazole (3e)



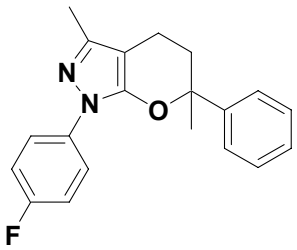
Yellow solid, mp = 124-126 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.72 (s, 3H), 2.08 (ddd, J_a = 5.6 Hz, J_b = 8.8 Hz, J_c = 14.0 Hz, 1H), 2.35 (dt, J_a = 5.2 Hz, J_b = 14.0 Hz, 1H), 2.53 (ddd, J_a = 6.0 Hz, J_b = 8.4 Hz, J_c = 15.2 Hz, 1H), 2.76 (dt, J_a = 5.2 Hz, J_b = 15.2 Hz, 1H), 7.19-7.32 (m, 5H), 7.32-7.39 (m, 4H), 7.45 (t, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H); ^{13}C NMR: 18.0, 28.8, 33.8, 83.7, 95.0, 120.4, 124.6, 125.6, 126.5, 127.4, 127.7, 128.5, 128.7, 129.1, 134.1, 139.3, 144.1, 147.7, 150.6; IR (cm^{-1}): 3057, 2865, 2928, 1600, 1573, 1509, 1448, 1381, 1272, 1139, 1066, 913, 971, 758, 696; anal. calcd for $C_{25}H_{22}N_2O$: C: 81.94, H: 6.05, N: 7.64%; found: C: 81.67, H: 5.84, N: 7.51%.

1,4,5,6-Tetrahydro-6-methyl-3-(4-methoxyphenyl)-1,6-diphenyl-pyrano[2,3-c]pyrazole (3f)



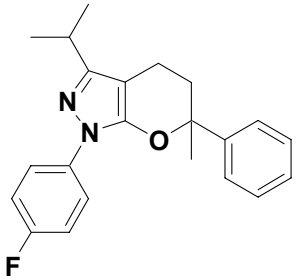
Yellow solid, mp = 154 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.70 (s, 3H), 2.03-2.11 (m, 1H), 2.27-2.37 (m, 1H), 2.44-2.56 (m, 1H), 2.68-2.78 (m, 1H), 3.75 (d, J = 1.2 Hz, 3H), 6.89 (dd, J_a = 1.2 Hz, J_b = 8.4 Hz, 2H), 7.17-7.25 (m, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.32-7.38 (m, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.71 (dd, J_a = 0.8 Hz, J_b = 8.0 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H); ^{13}C NMR: 18.0, 28.7, 33.7, 55.3, 83.7, 94.6, 114.0, 120.3, 124.6, 125.4, 126.8, 127.4, 127.7, 128.7, 129.1, 139.3, 144.1, 147.6, 150.6, 159.4; IR (cm^{-1}): 2929, 1601, 1572, 1509, 1485, 1455, 1379, 1296, 1245, 1178, 1132, 1063, 1052, 838, 763, 695, 587; HRMS Calculated for $C_{26}H_{25}N_2O_2$ [M + H$^+$]: 397.1916, Detected: 397.1951.

1,4,5,6-Tetrahydro-1-(4-fluorophenyl)-3,6-dimethyl-6-phenyl-pyrano[2,3-c]pyrazole (3g)



Yellow-pale solid, mp = 110-111 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.70 (s, 3H), 2.02-2.10 (m, 1H), 2.14 (s, 3H), 2.16-2.26 (m, 1H), 2.32 (dt, J_a = 5.2 Hz, J_b = 14.0 Hz, 1H), 2.45 (dd, J_a = 5.2 Hz, J_b = 14.8 Hz, 1H), 7.11 (t, = 8.4 Hz, 2H), 7.21-7.27 (m, 1H), 7.27-7.37 (m, 4H), 7.84 (q, J = 4.8 Hz, 2H); ^{13}C NMR: 12.6, 15.7, 28.6, 33.5, 83.8, 95.6, 115.6, 115.8, 121.4, 121.5, 124.5, 127.3, 128.6, 135.4, 135.4, 144.1, 146.5, 149.8, 158.9, 161.4; IR (cm^{-1}): 2973, 2922, 1615, 1514, 1445, 1391, 1270, 1220, 1155, 1105, 1071, 900, 835, 762, 700, 594; HRMS Calculated for $C_{20}H_{20}FN_2O$ [M + H$^+$]: 323.1560, Detected: 323.1589.

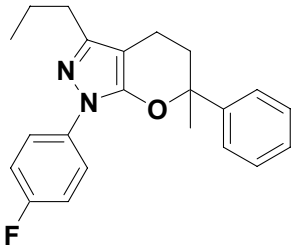
1,4,5,6-Tetrahydro-6-methyl-1-(4-fluorophenyl)-6-phenyl-3-*iso*-propyl-pyrano[2,3-c]pyrazole (3h)



Yellow-pale liquid; ^{1}H NMR ($CDCl_3$): 1.24 (d, J = 1.2 Hz, 3H), 1.25 (d, J = 1.6 Hz, 3H), 1.68 (s, 3H), 2.01-2.10 (m, 1H), 2.23-2.36 (m, 2H), 2.51-2.61 (m, 1H), 2.90 (sept, J = 7.2 Hz, 1H), 7.05-7.13 (m, 2H), 7.19-7.26 (m, 1H), 7.27-7.36 (m, 4H), 7.85 (d, J = 4.8 Hz, 2H), 7.87 (d, J = 4.8

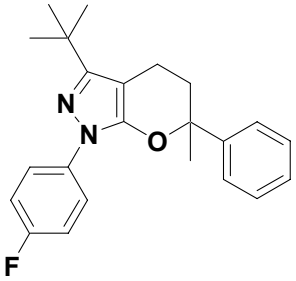
Hz, 2H); ^{13}C NMR: 16.5, 21.5, 21.5, 28.2, 28.5, 33.8, 83.6, 94.0, 115.6, 115.8, 121.6, 121.7, 124.5, 127.3, 128.6, 135.6, 144.3, 149.8, 155.3, 158.9, 161.3; IR (cm^{-1}): 2965, 2930, 1610, 1597, 1516, 1497, 1447, 1423, 1397, 1299, 1265, 1227, 1156, 1084, 1064, 1032, 903, 836, 763, 699, 515; HRMS Calculated for $C_{22}H_{24}FN_2O$ [M + H$^+$]: 351.1873, Detected: 351.1907.

1,4,5,6-Tetrahydro-1-(4-fluorophenyl)-6-methyl-6-phenyl-3-*iso*-propyl-pyrano[2,3-c]pyrazol e (3i)



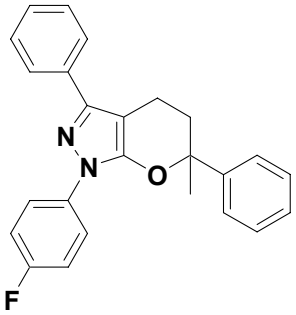
Yellow liquid; ^{1}H NMR ($CDCl_3$): 0.93 (t, J = 7.6 Hz, 3H), 1.64 (sext, J = 8.0 Hz, 2H), 1.69 (s, 3H), 2.00-2.10 (m, 1H), 2.20-2.34 (m, 2H), 2.44-2.53 (m, 3H), 7.10 (t, J = 8.4 Hz, 2H), 7.21-7.27 (m, 1H), 7.27-7.36 (m, 4H), 7.85 (q, J = 4.4 Hz, 2H); ^{13}C NMR: 14.1, 16.0, 22.0, 28.4, 30.0, 33.7, 83.7, 95.1, 115.6, 115.8, 121.6, 121.7, 124.5, 127.3, 128.3, 128.6, 128.6, 135.4, 135.5, 144.2, 149.7, 150.6, 158.9, 161.4; IR (cm^{-1}): 2960, 2931, 2869, 1601, 1447, 1423, 1397, 1266, 1226, 1156, 1104, 1072, 1030, 903, 836, 762, 699, 600; HRMS Calculated for $C_{22}H_{24}FN_2O$ [M + H$^+$]: 351.1873, Detected: 351.1902.

1,4,5,6-Tetrahydro-3-*tert*-butyl-1-(4-fluorophenyl)-6-methyl-6-phenyl-pyrano[2,3-c]pyrazole (3j)



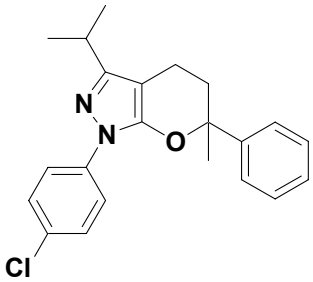
Yellow-pale solid, mp = 106-107 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.29 (s, 9H), 1.69 (s, 3H), 2.07 (ddd, J_a = 5.6 Hz, J_b = 8.0 Hz, J_c = 14.0 Hz, 1H), 2.28 (dt, J_a = 5.6 Hz, J_b = 14.0 Hz, 1H), 2.41 (ddd, J_a = 5.2 Hz, J_b = 8.0 Hz, J_c = 14.8 Hz, 1H), 2.67 (dt, J_a = 5.6 Hz, J_b = 15.2 Hz, 1H), 7.09 (tt, J_a = 2.4 Hz, J_b = 6.8 Hz, 2H), 7.21-7.27 (m, 1H), 7.28-7.37 (m, 4H), 7.86-7.91 (m, 2H); ^{13}C NMR: 18.1, 28.1, 29.2, 33.5, 33.9, 83.1, 93.6, 115.5, 115.7, 121.6, 121.7, 124.5, 127.3, 128.6, 135.6, 135.7, 144.4, 149.9, 157.4; IR (cm^{-1}): 2966, 2935, 2862, 1609, 1590, 1516, 1446, 1419, 1390, 1272, 1226, 1155, 1091, 1067, 1028, 903, 833, 765, 702; HRMS Calculated for $C_{23}H_{26}FN_2O$ [M + H$^+$]: 365.2029, Detected: 365.2068.

1,4,5,6-Tetrahydro-1-(4-fluorophenyl)-6-methyl-3,6-diphenyl-pyrano[2,3-c]pyrazole (3k)



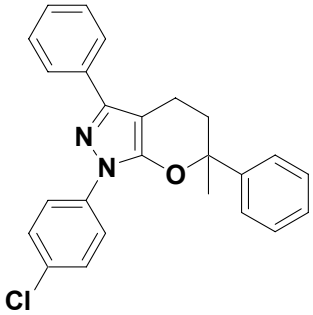
Yellow solid, mp = 133-134 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.73 (s, 3H), 2.10 (ddd, J_a = 5.2 Hz, J_b = 8.4 Hz, 14.0 Hz, 1H), 2.37 (dt, J_a = 5.6 Hz, J_b = 14.0 Hz, 1H), 2.50-2.60 (m, 1H), 2.78 (dt, J_a = 5.6 Hz, J_b = 15.2 Hz, 1H), 7.15 (t, J = 8.8 Hz, 2H), 7.21-7.40 (m, 8H), 7.77 (dd, J_a = 1.6 Hz, J_b = 8.8 Hz, 2H), 7.94-8.01 (m, 2H); ^{13}C NMR: 17.9, 28.7, 33.7, 83.8, 94.9, 115.7, 115.9, 122.1, 122.1, 124.6, 126.4, 127.4, 127.8, 128.5, 128.7, 133.9, 144.0, 147.7, 150.4; IR (cm^{-1}): 3059, 2930, 1595, 1573, 1515, 1446, 1384, 1272, 1225, 1140, 1125, 1063, 988, 915, 835, 773, 760, 735, 697, 601; HRMS Calculated for $C_{25}H_{22}FN_2O$ [M + H$^+$]: 385.1716, Detected: 385.1741.

1,4,5,6-Tetrahydro-1-(4-chlorophenyl)-6-methyl-6-phenyl-3-*iso*-propyl-pyrano[2,3-c]pyrazole (3l)



Yellow-pale solid, mp = 93-94 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.24 (dd, J_a = 2.0 Hz, J_b = 7.2 Hz, 6H), 1.71 (s, 3H), 2.03-2.12 (m, 1H), 2.25-2.36 (m, 2H), 2.51-2.61 (m, 1H), 2.89 (quint, J = 6.8 Hz, 1H), 7.22-7.28 (m, 1H), 7.29-7.39 (m, 6H), 7.86 (dd, J_a = 2.0 Hz, J_b = 6.8 Hz, 2H); ^{13}C NMR: 16.5, 21.4, 21.4, 28.3, 28.5, 33.7, 83.7, 94.3, 121.0, 124.5, 127.3, 128.6, 129.0, 130.0, 137.9, 144.2, 150.0, 155.7; IR (cm^{-1}): 2967, 2928, 1604, 1508, 1447, 1415, 1393, 1268, 1084, 1063, 1034, 896, 866, 828, 762, 699, 514; HRMS Calculated for $C_{22}H_{24}ClN_2O$ [M + H$^+$]: 367.1577, Detected: 367.1611.

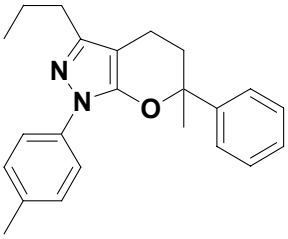
1,4,5,6-Tetrahydro-1-(4-chlorophenyl)-6-methyl-3,6-diphenyl-pyrano[2,3-c]pyrazole (3m)



Yellow-pale solid, mp = 154 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.75 (s, 3H), 2.12 (ddd, J_a = 5.6 Hz, J_b = 8.8 Hz, J_c = 14.4 Hz, 1H), 2.39 (dt, J_a = 5.6 Hz, J_b = 14.0 Hz, 1H), 2.50-2.60 (m, 1H), 2.79 (dt, J_a =

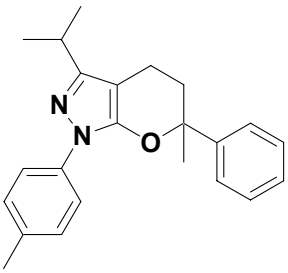
5.6 Hz, J_b = 15.2 Hz, 1H), 7.22-7.45 (m, 10H), 7.74-7.79 (m, 2H), 7.95-8.10 (m, 2H); ^{13}C NMR: 17.9, 28.7, 33.7, 84.0, 95.2, 121.3, 124.5, 126.4, 127.4, 127.9, 128.5, 128.7, 129.1, 130.8, 133.8, 137.8, 143.9, 148.0; IR (cm^{-1}): 3060, 2962, 2933, 1601, 1573, 1505, 1446, 1409, 1383, 1271, 1142, 1126, 1093, 1063, 987, 834, 773, 760, 696, 674; anal. calcd for $C_{25}H_{21}ClN_2O$: C: 74.90, H: 5.28, N: 6.99%; found: C: 74.81, H: 5.01, N: 7.27%.

1,4,5,6-Tetrahydro-6-methyl-1-(4-methylphenyl)-3-*n*-propyl-pyrano[2,3-c]pyrazole (3n)



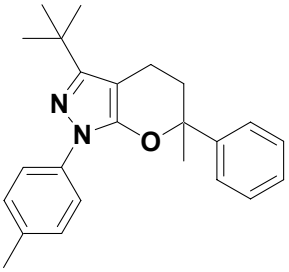
Yellow solid, mp = 93-94 ^{o}C; ^{1}H NMR ($CDCl_3$): 0.93 (t, J = 7.2 Hz, 3H), 1.64 (quint, J = 8.0 Hz, 2H), 1.68 (s, 3H), 2.00-2.09 (m, 1H), 2.18-2.31 (m, 2H), 2.35 (s, 3H), 2.44-2.53 (m, 3H), 7.19-7.25 (m, 3H), 7.26-7.32 (m, 2H), 7.32-7.36 (m, 2H), 7.77 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 14.1, 16.0, 21.0, 22.1, 28.4, 30.0, 33.8, 83.5, 94.9, 120.1, 124.6, 127.2, 128.5, 129.5, 134.6, 136.9, 144.4, 149.7, 150.2; IR (cm^{-1}): 2959; 2928; 2868; 1707, 1520; 1448, 1396, 1316, 1266, 1108, 1072, 1029, 905, 819, 762, 734, 699, 510; HRMS Calculated for $C_{23}H_{27}N_2O$ [M + H^+]: 347.2123, Detected: 347.2157.

1,4,5,6-Tetrahydro-6-methyl-1-(4-methylphenyl)-6-phenyl-3-*iso*-propyl-pyrano[2,3-c]pyrazole (3o)



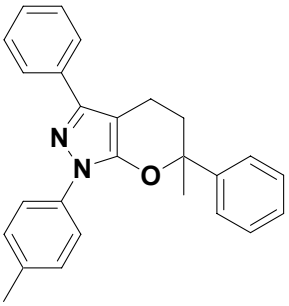
Yellow liquid; ^{1}H NMR ($CDCl_3$): 1.23 (d, J = 3.6 Hz, 3H), 1.26 (d, J = 3.6 Hz, 3H), 1.67 (s, 3H), 2.00-2.09 (m, 1H), 2.22-2.31 (m, 2H), 2.34 (s, 3H), 2.51-2.59 (m, 1H), 2.91 (sept, J = 6.8 Hz, 1H), 7.15-7.25 (m, 3H), 7.26-7.32 (m, 2H), 7.32-7.36 (m, 2H), 7.77 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 16.6, 21.0, 21.5, 21.6, 28.3, 28.6, 33.8, 83.4, 93.8, 120.1, 124.6, 127.2, 128.5, 129.5, 134.5, 137.0, 144.5, 149.8, 155.0; IR (cm^{-1}): 2964, 2927, 1605, 1520, 1496, 1447, 1397, 1302, 1264, 1087, 1065, 1033, 903, 818, 763, 699, 510; HRMS Calculated for $C_{23}H_{27}N_2O$ [M + H^+]: 347.2123, Detected: 347.2155.

1,4,5,6-Tetrahydro-3-*tert*-butyl-6-methyl-1-(4-methylphenyl)-6-phenyl-pyrano[2,3-c]pyrazole (3p)



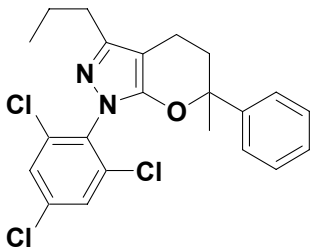
Yellow solid, mp = 83-84 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.30 (s, 9H), 1.66 (s, 3H), 2.00-2.09, 2.25 (dt, J_a = 5.6 Hz, J_b = 13.6 Hz, 1H), 2.33 (s, 3H), 2.40 (ddd, J_a = 5.6 Hz, J_b = 8.0 Hz, J_c = 15.2 Hz, 1H), 2.65 (dt, J_a = 6.0 Hz, J_b = 15.2 Hz, 1H), 7.17-7.25 (m, 3H), 7.28 (t, 7.2 Hz, 2H), 7.31-7.37 (m, 2H), 7.79 (d, J = 8.8 Hz, 2H); ^{13}C NMR: 18.2, 21.1, 28.2, 29.3, 33.5, 34.0, 82.9, 93.4, 120.1, 124.6, 127.2, 128.5, 129.5, 134.4, 137.1, 144.6, 149.9, 156.9; IR (cm^{-1}): 2960, 2928, 2860, 1600, 1521, 1390, 1268, 1091, 1067, 1037, 905, 818, 763, 699; HRMS Calculated for $C_{24}H_{29}N_2O$ [M + H^+]: 361.2280, Detected: 361.2309.

1,4,5,6-Tetrahydro-6-methyl-1-(4-methylphenyl)-3,6-diphenyl-pyrano[2,3-c]pyrazole (3q)



Yellow solid, mp = 126-127 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.79 (s, 3H), 2.17 (ddd, J_a = 5.6 Hz, J_b = 8.4 Hz, J_c = 14.0 Hz, 1H), 2.39-2.48 (m, 4H), 2.56-2.67 (m, 1H), 2.86 (dt, J_a = 5.6 Hz, J_b = 15.2 Hz, 1H), 7.27-7.40 (m, 6H), 7.40-7.46 (m, 2H), 7.83 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 17.9, 21.1, 28.7, 33.8, 83.5, 94.8, 120.5, 124.6, 126.4, 127.3, 127.6, 128.5, 128.6, 129.6, 134.1, 135.3, 136.8, 144.1, 147.4, 150.4; IR (cm^{-1}): 2962, 2927, 1601, 1520, 1447, 1384, 1270, 1142, 1126, 1063, 988, 915, 824, 774, 759, 698; anal. calcd for $C_{26}H_{24}N_2O$: C: 82.07, H: 6.36, N: 7.36%; found: C: 82.33, H: 6.10, N: 7.09%.

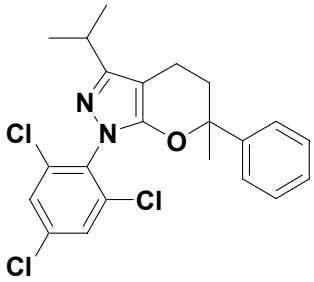
1,4,5,6-Tetrahydro-1-(2,4,6-trichlorophenyl)-6-methyl-6-phenyl-1-*n*-propyl-pyrano[2,3-c]pyrazole (3r)



Yellow liquid; ^{1}H NMR ($CDCl_3$): 0.88-1.04 (m, 3H), 1.20-1.33 (m, 1H), 1.58-1.75 (m, 4H), 1.97-2.07 (m, 1H), 2.20-2.40 (m, 2H), 2.45-2.62 (m, 2H), 7.18-7.38 (m, 4H), 7.39-7.55 (m, 3H); ^{13}C NMR: 13.8, 16.0, 21.7, 27.3, 29.9, 34.3, 83.5, 93.3, 124.6, 127.3, 128.4, 128.5, 128.6, 135.6,

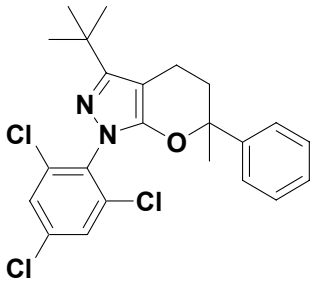
136.4, 136.6, 144.3, 151.1, 151.8; IR (cm^{-1}): 3081, 2960, 2931, 2870, 1725, 1607, 1553, 1518, 1450, 1379, 1266, 1190, 1106, 1085, 1070, 1029, 904, 858, 815, 762, 732, 698; HRMS Calculated for $C_{22}H_{22}Cl_3N_2O$ [M + H^+]: 435.0798, Detected: 435.0829.

1,4,5,6-Tetrahydro-1-(2,4,6-trichlorophenyl)-6-methyl-6-phenyl-3-iso-propyl-pyrano[2,3-c]pyrazole (3s)



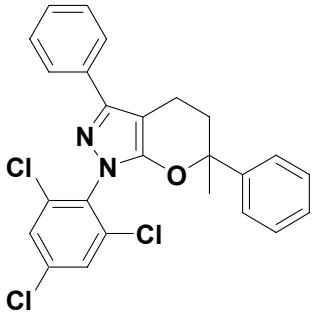
Yellow liquid; ^{1}H NMR ($CDCl_3$): 1.26 (d, J = 7.2 Hz, 6H), 1.61 (s, 3H), 1.96-2.08 (m, 1H), 2.17-2.27 (m, 1H), 2.32-2.43 (m, 1H), 2.51-2.62 (m, 1H), 2.86-2.97 (quint, J = 7.2 Hz, 1H), 7.17-7.26 (m, 1H), 7.26-7.36 (m, 4H), 7.38-7.42 (m, 1H), 7.43-7.48 (m, 1H); ^{13}C NMR: 16.5, 21.5, 27.1, 28.4, 34.4, 83.3, 92.1, 124.6, 127.2, 128.4, 128.5, 128.6, 133.0, 135.5, 136.5, 136.7, 144.4, 151.1, 156.9; IR (cm^{-1}): 2964, 2928, 2863, 1720, 1606, 1517, 1379, 1265, 1089, 1064, 1028, 904, 859, 838, 817, 805, 763, 732, 699, 544; HRMS Calculated for $C_{22}H_{22}Cl_3N_2O$ [M + H^+]: 435.0798, Detected: 435.0835.

1,4,5,6-Tetrahydro-3-*tert*-butyl-1-(2,4,6-trichlorophenyl)-6-methyl-6-phenyl-pyrano[2,3-c]pyrazole (3t)



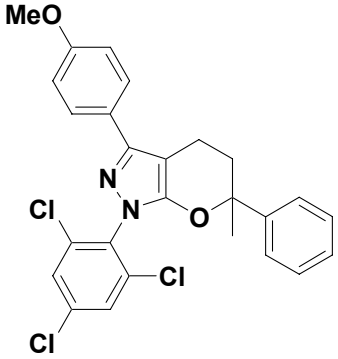
Yellow liquid; ^{1}H NMR ($CDCl_3$): 1.30 (s, 9H), 1.59 (s, 3H), 1.99-2.07 (m, 1H), 2.22 (dt, J_a = 6.0 Hz, J_b = 14.0 Hz, 1H), 2.48 (dt, J_a = 6.4 Hz, J_b = 14.8 Hz, 1H), 2.68 (dt, J_a = 6.4 Hz, J_b = 15.2 Hz, 1H), 7.19-7.25 (m, 1H), 7.26-7.35 (m, 4H), 7.39 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H); ^{13}C NMR: 18.2, 26.9, 29.4, 33.7, 34.6, 82.8, 91.7, 124.6, 127.2, 128.3, 128.5, 128.6, 135.4, 136.5, 136.7, 144.5, 151.1, 158.9; IR (cm^{-1}): 2962, 2929, 1601, 1552, 1518, 1461, 1377, 1267, 1088, 1066, 1026, 855, 819, 804, 762, 698; HRMS Calculated for $C_{23}H_{24}Cl_3N_2O$ [M + H^+]: 449.0954, Detected: 449.0989.

1,4,5,6-Tetrahydro-1-(2,4,6-trichlorophenyl)-6-methyl-3,6-diphenyl-pyrano[2,3-c]pyrazole (3u)



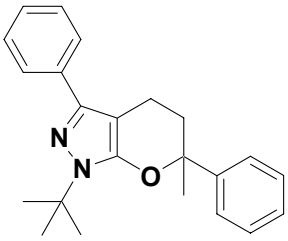
Yellow solid, mp = 98-99 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.71 (s, 3H), 2.09-2.19 (m, 1H), 2.34-2.44 (m, 1H), 2.63-2.73 (m, 1H), 2.87 (dt, J_a = 4.8 Hz, J_b = 14.8 Hz, 1H), 7.26-7.32 (m, 1H), 7.33-7.39 (m, 3H), 7.39-7.46 (m, 4H), 7.49-7.53 (m, 1H), 7.54-7.58 (m, 1H), 7.83 (d, J = 8.0 Hz, 2H); ^{13}C NMR: 18.0, 27.7, 34.3, 83.6, 93.2, 124.7, 126.6, 127.4, 127.9, 128.5, 128.5, 128.6, 128.8, 132.8, 133.9, 136.0, 136.3, 136.6, 144.1, 149.4, 151.7; IR (cm^{-1}):3062, 2929, 1602, 1574, 1552, 1514, 1469, 1376, 1267, 1129, 1061, 859, 766, 697; HRMS Calculated for $C_{25}H_{20}Cl_3N_2O$ [M + H^+]: 469.0641, Detected: 469.0677.

1,4,5,6-Tetrahydro-1-(2,4,6-trichlorophenyl)-6-methyl-3-(4-methoxyphenyl)-6-phenyl-pyrano[2,3-c]pyrazole (**3v**)



Yellow solid, mp = 91-92 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.66 (s, 3H), 2.05-2.14 (m, 1H), 2.27-2.38 (m, 1H), 2.55-2.65 (m, 1H), 2.76-2.85 (m, 1H), 3.81 (s, 3H), 6.90 (d, J = 8.8 Hz, 2H), 7.24-7.28 (m, 1H), 7.29-7.37 (m, 4H), 7.45-7.47 (m, 1H), 7.51 (d, J = 2,4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 17.6, 27.3, 34.0, 55.0, 83.1, 92.4, 113.6, 124.3, 127.0, 127.5, 128.1, 128.3, 128.4, 135.5, 136.0, 136.3, 143.8, 148.9, 151.3, 159.1; IR (cm^{-1}): 3077, 2930, 1726, 1604, 1574, 1553, 1515, 1470, 1379, 1302, 1250, 1175, 1128, 1061, 1031, 837, 699; HRMS Calculated for $C_{26}H_{22}Cl_3N_2O_2$ [M + H^+]: 499.0747, Detected: 499.0733.

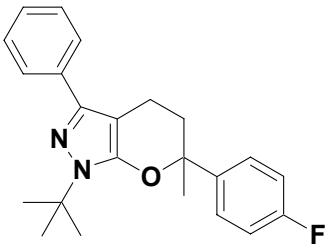
1,4,5,6-Tetrahydro-1-*tert*-butyl-6-methyl-3,6-diphenyl-pyrano[2,3-c]pyrazole (**3w**)



Yellow liquid; ^{1}H NMR ($CDCl_3$): 1.69 (s, 3H), 1.71 (s, 9H), 2.03 (dq, J_a = 5.6 Hz, J_b = 7.2 Hz, 1H), 2.22 (quint, J = 8.0 Hz, 1H), 2.51-2.61 (m, 1H), 2.75 (ddd, J_a = 5.6 Hz, J_b = 6.8 Hz, J_c = 15.2 Hz,

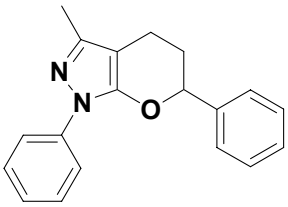
1H), 7.19-7.30 (m, 2H), 7.30-7.38 (m, 4H), 7.41-7.45 (m, 2H), 7.69-7.73 (m, 2H). ^{13}C NMR: 17.9, 27.4, 29.1, 34.3, 58.6, 82.3, 93.9, 124.7, 126.1, 126.8, 127.2, 128.3, 128.5, 128.6, 135.0, 144.0, 145.0, 150.4; IR (cm^{-1}): 2976, 2930, 1594, 1570, 1492, 1448, 1367, 1268, 1214, 1134, 1069, 1025, 766, 697; HRMS Calculated for $C_{23}H_{27}N_2O$ [M + H$^+$]: 347.2123, Detected: 347.2155.

1,4,5,6-Tetrahydro-1-*tert*-butyl-6-methyl-6-(4-fluorophenyl)-3-phenyl-pyrano[2,3-c]pyrazole (3x)



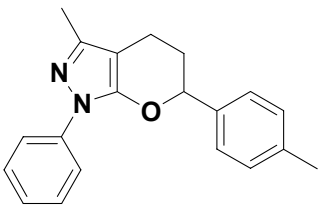
Yellow solid, mp = 83-84 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.68 (s, 3H), 1.71 (s, 9H), 1.98-2.06 (m, 1H), 2.14-2.24 (m, 1H), 2.55 (dt, J_a = 6.8 Hz, J_b = 14.8 Hz, 1H), 2.76 (dt, J_a = 6.4 Hz, J_b = 14.8 Hz, 1H), 7.04 (t, J = 6.0 Hz, 2H), 7.20-7.26 (m, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.40 (dd, J_a = 5.6 Hz, J_b = 8.8 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H); ^{13}C NMR: 17.9, 27.4, 29.1, 34.3, 58.6, 82.2, 93.7, 115.2, 115.4, 126.1, 126.4, 126.5, 126.9, 128.4, 134.9, 140.8, 140.8, 144.1, 150.2, 160.7, 163.1; IR (cm^{-1}): 2980, 2933, 1701, 1602, 1569, 1509, 1489, 1458, 1364, 1268, 1224, 1161, 1135, 1074, 1039, 1022, 922, 908, 836, 774, 698; HRMS Calculated for $C_{23}H_{26}FN_2O$ [M + H$^+$]: 365.2029, Detected: 365.2066.

1,4,5,6-Tetrahydro-3-methyl-1,6-diphenyl-pyrano[2,3-c]pyrazole (3y)



Yellow solid, mp = 134-135 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.01-2.13 (m, 1H), 2.16-2.23 (m, 1H), 2.45 (s, 3H), 2.50-2.58 (m, 1H), 2.59-2.69 (m, 1H), 5.21 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.31-7.38 (m, 3H), 7.38-7.42 (m, 4H), 7.78 (dd, J_a = 0.8 Hz, J_b = 8.4 Hz, 2H); ^{13}C NMR: 12.8, 17.8, 30.4, 81.4, 120.0, 125.1, 126.0, 128.2, 128.6, 129.0, 138.9, 140.2, 146.5, 150.8; IR (cm^{-1}): 3038, 2959, 2920, 2856, 1602, 1513, 1452, 1392, 1321, 1277, 1124, 1068, 966, 882, 761, 723, 695, 656; HRMS Calculated for $C_{19}H_{19}N_2O$ [M + H$^+$]: 291.1497, Detected: 291.1521.

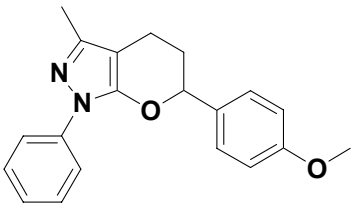
1,4,5,6-Tetrahydro-3-methyl-6-(4-methylphenyl)-1-phenyl-pyrano[2,3-c]pyrazole (3z)



Yellow solid, mp = 100-101 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.00-2.13 (m, 1H), 2.13-2.21 (m, 1H), 2.24 (s,

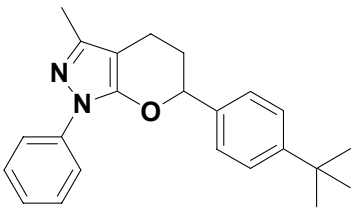
3H), 2.37 (s, 3H), 2.49-2.58 (m, 1H), 2.58-2.68 (m, 1H), 5.17 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H), 7.11-7.16 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.25-7.38 (m, 4H), 7.78 (dd, J_a = 0.8 Hz, J_b = 8.4 Hz, 2H); ^{13}C NMR: 12.8, 17.8, 21.2, 30.3, 81.3, 96.2, 119.9, 125.0, 126.0, 128.9, 129.3, 137.3, 138.0, 129.0, 146.5, 150.9; IR (cm^{-1}): 3035, 2944, 2916, 2854, 1608, 1501, 1450, 1388, 1277, 1118, 1071, 1024, 971, 887, 819, 757, 691; HRMS Calculated for $C_{20}H_{21}N_2O$ [M + H^+]: 305.1654, Detected: 305.1683.

1,4,5,6-Tetrahydro-3-methyl-6-(4-methoxyphenyl)-1-phenyl-pyrano[2,3-c]pyrazole (3aa)



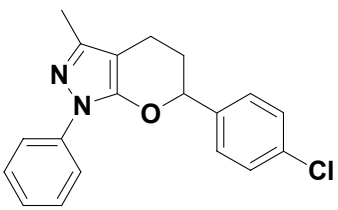
Yellow solid, mp = 120-122 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.03-2.13 (m, 1H), 2.13-2.22 (m, 1H), 2.24 (s, 3H), 2.51-2.60 (m, 1H), 2.60-2.70 (m, 1H), 3.82 (s, 3H), 5.08 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H), 6.85 (dd, J_a = 1.6 Hz, J_b = 6.8 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 8.0 Hz, 4H), 7.69 (dd, J_a = 1.2 Hz, J_b = 8.8 Hz, 2H); ^{13}C NMR: 12.7, 17.8, 30.2, 55.3, 81.2, 96.1, 114.0, 120.0, 125.0, 127.4, 128.9, 132.3, 139.0, 146.5, 150.9, 159.5; IR (cm^{-1}): 2956, 2920, 2852, 1608, 1516, 1451, 1392, 1283, 1245, 1178, 1120, 1070, 1029, 965, 882, 832, 760, 690; HRMS Calculated for $C_{20}H_{21}N_2O$ [M + H^+]: 321.1603, Detected: 321.1637.

1,4,5,6-Tetrahydro-3-methyl-6-(4-*tert*-butylphenyl)-1-phenyl-pyrano[2,3-c]pyrazole (3ab)



Yellow solid, mp = 162 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.33 (s, 9H), 2.00-2.13 (m, 1H), 2.13-2.22 (m, 1H), 2.24 (s, 3H), 2.49-2.58 (m, 1H), 2.58-2.68 (m, 1H), 5.19 (dd, J_a = 1.6 Hz, J_b = 10.0 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 8.0 Hz, 4H), 7.42 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H); ^{13}C NMR: 12.7, 17.8, 30.3, 31.4, 34.6, 81.3, 96.2, 120.0, 125.0, 125.5, 125.7, 128.9, 137.3, 139.0, 146.5, 150.9, 151.2; IR (cm^{-1}): 2959, 2861, 1605, 1514, 1393, 1276, 1119, 1067, 1012, 966, 884, 829, 756, 689; HRMS Calculated for $C_{23}H_{27}N_2O$ [M + H^+]: 347.2123, Detected: 347.2102.

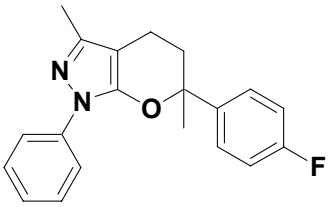
1,4,5,6-Tetrahydro-6-(4-chlorophenyl)-3-methyl-1-phenyl-pyrano[2,3-c]pyrazole (3ac)



Yellow-pale solid, mp = 134 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.95-2.08 (m, 1H), 2.10-2.22 (m, 1H), 2.23 (s,

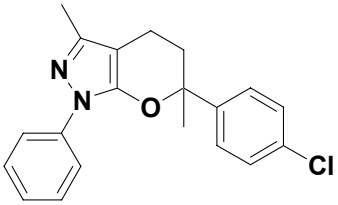
3H), 2.47-2.56 (m, 1H), 2.57-2.67 (m, 1H), 5.16 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.25-7.40 (m, 6H), 7.75 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 12.7, 17.7, 30.2, 80.6, 96.2, 120.0, 125.2, 127.4, 128.8, 129.0, 134.0, 138.7, 138.9, 146.5, 150.4; IR (cm^{-1}): 2948, 2916, 1610, 1515, 1498, 1452, 1389, 1336, 1277, 1119, 1072, 1010, 971, 885, 834, 755, 691, 530; HRMS Calculated for $C_{19}H_{18}ClN_2O$ [M + H$^+$]: 325.1108, Detected: 325.1074.

1,4,5,6-Tetrahydro-6-(4-fluorophenyl)-3,6-dimethyl-1-phenyl-pyrano[2,3-c]pyrazole (3ad)



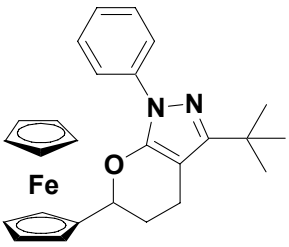
Yellow-pale solid, mp = 106-107 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.72 (s, 3H), 2.04-2.14 (m, 1H), 2.19 (s, 3H), 2.20-2.29 (m, 1H), 2.33 (dt, J_a = 5.2 Hz, J_b = 13.6 Hz, 1H), 2.49 (dt, J_a = 4.8 Hz, J_b = 14.4 Hz, 1H), 7.02 (tt, J_a = 2.0 Hz, J_b = 8.8 Hz, 2H), 7.24 (tt, J_a = 1.2 Hz, J_b = 7.2 Hz, 1H), 7.30-7.37 (m, 2H), 7.45 (tt, J_a = 0.8 Hz, J_b = 7.2 Hz, 2H), 7.91 (dd, J_a = 3.2 Hz, J_b = 8.4 Hz, 2H); ^{13}C NMR: 12.7, 15.7, 28.7, 33.5, 83.3, 95.6, 115.3, 115.5, 119.8, 125.1, 126.3, 126.4, 129.0, 139.1, 140.0, 140.0, 146.4, 149.8, 160.7, 163.1; IR (cm^{-1}): 3044, 2981, 2932, 2902, 2854, 1609, 1514, 1449, 1396, 1267, 1225, 1160, 1125, 1100, 1076, 1018, 904, 834, 753, 689; HRMS Calculated for $C_{20}H_{20}FN_2O$ [M + H$^+$]: 323.1560, Detected: 323.1588.

1,4,5,6-Tetrahydro-6-(4-chlorophenyl)-3,6-dimethyl-1-phenyl-pyrano[2,3-c]pyrazole (3ae)



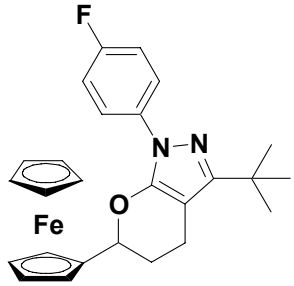
Yellow solid, mp = 142-143 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.69 (s, 3H), 2.02-2.10 (m, 1H), 2.15 (s, 3H), 2.16-2.25 (m, 1H), 2.30 (dt, J_a = 5.2 Hz, J_b = 14.0 Hz, 1H), 2.47 (dt, J_a = 5.2 Hz, J_b = 14.8 Hz, 1H), 7.23 (t, J = 10.0 Hz, 1H), 7.25-7.29 (m, 4H), 7.43 (dt, J_a = 1.6 Hz, J_b = 7.6 Hz, 2H), 7.86 (dd, J_a = 0.8 Hz, J_b = 8.4 Hz, 2H); ^{13}C NMR: 12.7, 15.6, 28.7, 33.4, 83.3, 95.6, 119.8, 125.1, 126.1, 128.7, 129.0, 133.1, 139.1, 142.7, 146.4, 149.7; IR (cm^{-1}): 2975, 2937, 2853, 1611, 1515, 1447, 1395, 1268, 1120, 1094, 1075, 1012, 904, 752, 688; HRMS Calculated for $C_{20}H_{20}ClN_2O$ [M + H$^+$]: 339.1264, Detected: 339.1292.

1,4,5,6-Tetrahydro-3-*tert*-butyl-6-ferrocenyl-1-phenyl-pyrano[2,3-c]pyrazole (3af)



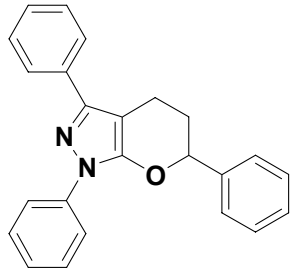
Yellow solid, mp = 133-134 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.37 (s, 9H), 1.91-2.01 (m, 1H), 2.14-2.24 (m, 1H), 2.72-2.79 (m, 2H), 4.14-4.17 (m, 5H), 4.18 (s, 2H), 4.26 (d, J = 13.2 Hz, 2H), 4.96 (dd, J_a = 1.6 Hz, J_b = 10.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.4 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H); ^{13}C NMR: 20.3, 29.3, 30.3, 33.7, 66.4, 66.4, 67.9, 68.0, 68.9, 77.9, 87.9, 94.3, 120.2, 124.9, 128.8, 139.3, 151.0, 157.4; IR (cm^{-1}): 2973, 2851, 1599, 1508, 1452, 1385, 1362, 1320, 1294, 1273, 1247, 1158, 1122, 1103, 1049, 1023, 998, 966, 926, 834, 756, 693, 492; HRMS Calculated for $C_{26}H_{29}FeN_2O$ [M + H^+]: 441.1629, Detected: 441.1666.

1,4,5,6-Tetrahydro-3-*tert*-butyl-6-ferrocenyl-1-(4-fluorophenyl)-pyrano[2,3-c]pyrazole (3ag)



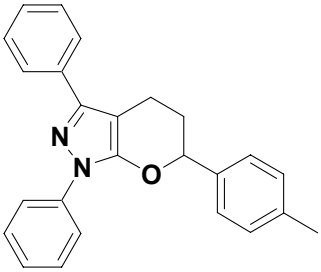
Yellow solid, mp = 103-104 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.36 (s, 9H), 1.91-2.01 (m, 1H), 2.18-2.27 (m, 1H), 2.71-2.79 (m, 2H), 4.09-4.17 (m, 5H), 4.19 (s, 2H), 4.24-4.29 (m, 2H), 4.96 (dd, J_a = 1.2 Hz, J_b = 10.0 Hz, 1H), 7.09 (t, J = 8.8 Hz, 2H), 7.82 (dd, J_a = 4.8 Hz, J_b = 8.8 Hz, 2H); ^{13}C NMR: 20.2, 29.3, 30.1, 33.6, 66.4, 66.5, 68.0, 68.1, 68.8, 78.0, 87.7, 94.2, 115.4, 115.6, 121.8, 121.8, 135.4, 135.5, 150.8, 157.5, 158.9, 161.3; IR (cm^{-1}): 2965, 2926, 2903, 2855, 1590, 1518, 1494, 1387, 1320, 1274, 1245, 1219, 1160, 1125, 1094, 1044, 965, 867, 833, 818, 714, 493; HRMS Calculated for $C_{26}H_{28}FFeN_2O$ [M + H^+]: 459.1535, Detected: 459.1569.

1,4,5,6-Tetrahydro-1,3,6-triphenyl-pyrano[2,3-c]pyrazole (3ah)



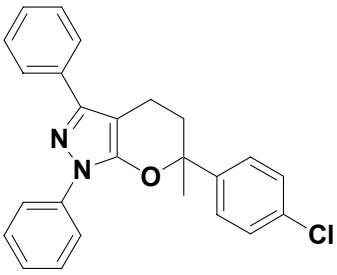
Yellow solid, mp = 161-162 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.03-2.14 (m, 1H), 2.16-2.26 (m, 1H), 2.79-2.87 (m, 1H), 2.89-2.99 (m, 1H), 5.24 (dd, J_a = 2.0 Hz, J_b = 10.4 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.29-7.44 (m, 10H), 7.84 (dd, J_a = 1.2 Hz, J_b = 8.4 Hz, 2H), 7.91 (dd, J_a = 1.2 Hz, J_b = 8.4 Hz, 2H); ^{13}C NMR: 20.0, 30.6, 81.3, 95.5, 120.5, 125.6, 126.0, 126.5, 127.8, 128.3, 128.6, 128.7, 129.0, 134.0, 139.0, 140.1, 147.9, 151.4; IR (cm^{-1}): 3058, 2930, 1602, 1511, 1487, 1453, 1383, 1140, 1070, 1028, 977, 753, 695; HRMS Calculated for $C_{24}H_{21}N_2O$ [M + H^+]: 353.1654, Detected: 353.1682.

1,4,5,6-Tetrahydro-6-(4-methylphenyl)-1,3-diphenyl-pyrano[2,3-c]pyrazole (3ai)



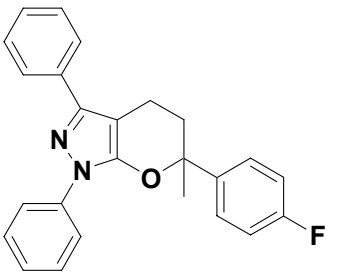
Yellow solid, mp = 204-205 ^{o}C; ^{1}H NMR ($CDCl_3$): 2.08-2.20 (m, 1H), 2.22-2.30 (m, 1H), 2.39 (s, 3H), 2.84-2.94 (m, 1H), 2.94-3.05 (m, 1H), 5.28 (dd, J_a = 2.0 Hz, J_b = 10.4 Hz, 1H), 7.15-7.26 (m, 3H), 7.31-7.46 (m, 7H), 7.85 (dd, J_a = 1.2 Hz, J_b = 8.4 Hz, 2H), 7.91 (dd, J_a = 1.2 Hz, J_b = 8.8 Hz, 2H); ^{13}C NMR: 20.0, 21.2, 30.5, 81.2, 95.3, 120.5, 125.5, 126.0, 126.5, 127.7, 128.5, 129.0, 129.3, 134.1, 137.2, 138.1, 139.0, 147.9, 151.4; IR (cm^{-1}): 3051, 2929, 1601, 1511, 1486, 1456, 1383, 1141, 1070, 1031, 976, 808, 756, 694; HRMS Calculated for $C_{25}H_{23}N_2O$ [M + H^+]: 367.1810, Detected: 367.1839.

1,4,5,6-Tetrahydro-6-(4-chlorophenyl)-6-methyl-3,6-phenyl-pyrano[2,3-c]pyrazole (3aj)



Yellow solid, mp = 111-112 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.71 (s, 3H), 2.09 (ddd, J_a = 5.6 Hz, J_b = 8.2 Hz, J_c = 14.0 Hz, 1H), 2.32 (dt, J_a = 5.6 Hz, J_b = 14.4 Hz, 1H), 2.54 (ddd, J_a = 5.6 Hz, J_b = 8.4 Hz, J_c = 13.2 Hz, 1H), 2.79 (dt, J_a = 5.2 Hz, J_b = 15.2 Hz, 1H), 7.24-7.33 (m, 6H), 7.34-7.40 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.77 (dd, J_a = 1.2 Hz, J_b = 7.2 Hz, 2H), 7.80 (dd, J_a = 1.2 Hz, J_b = 7.6 Hz, 2H); ^{13}C NMR: 17.9, 28.6, 33.6, 83.3, 94.9, 120.4, 125.7, 126.2, 126.4, 127.8, 128.5, 128.8, 128.9, 129.1, 129.8, 133.2, 133.9, 139.1, 142.6, 147.7, 150.3; IR (cm^{-1}): 2931, 1600, 1572, 1508, 1452, 1379, 1272, 1139, 1069, 1008, 985, 913, 872, 823, 756, 696; HRMS Calculated for $C_{25}H_{22}ClN_2O$ [M + H^+]: 401.1421, Detected: 401.1455.

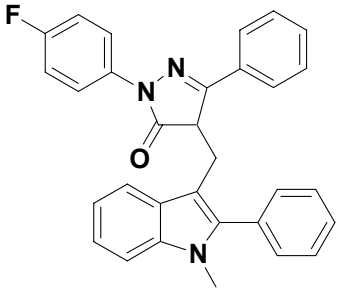
1,4,5,6-Tetrahydro-6-(4-fluorophenyl)-6-methyl-1,3-diphenyl-pyrano[2,3-c]pyrazole (3ak)



Yellow solid, mp = 165-166 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.73 (s, 3H), 2.11 (ddd, J_a = 5.6 Hz, J_b = 8.8 Hz, J_c = 14.4 Hz, 1H), 2.36 (dt, J_a = 5.6 Hz, J_b = 14.0 Hz, 1H), 2.56 (ddd, J_a = 5.6 Hz, J_b = 8.2 Hz, J_c = 14.4 Hz, 1H), 2.81 (dt, J_a = 5.6 Hz, J_b = 15.2 Hz, 1H), 6.70 (t, J = 8.8 Hz, 2H), 7.22-7.42 (m, 6H), 7.47 (t, J = 7.6 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.8 Hz, 2H); ^{13}C NMR: 17.9,

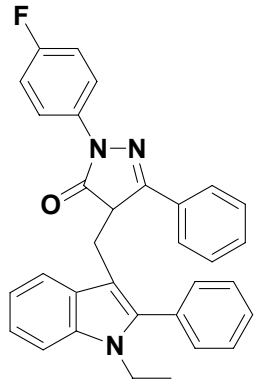
28.8, 33.8, 83.3, 94.9, 115.4, 115.6, 120.4, 125.6, 126.4, 126.4, 127.8, 128.5, 129.1, 133.9, 139.1, 139.8, 139.8, 147.7, 150.4; IR (cm^{-1}): 3061, 2936, 1601, 1574, 1509, 1484, 1454, 1380, 1231, 1140, 1126, 1070, 986, 915, 875, 831, 696; HRMS Calculated for $C_{25}H_{22}FN_2O$ [M + H^+]: 385.1716, Detected: 385.1737.

2,4-Dihydro-4-(1-methyl-2-phenylindol-3-ylmethyl)-2-(4-fluorophenyl)-5-phenyl-3H-pyrazol-3-one (7a)



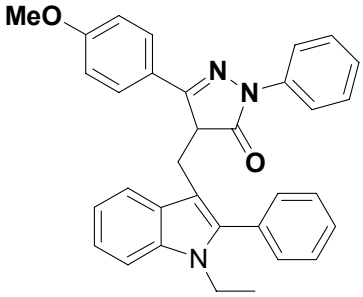
Yellow solid, mp = 159-160 ^oC; ^1H NMR ($CDCl_3$): 2.80 (s, 3H), 2.98 (d, J = 14.4 Hz, 1H), 2.89 (d, J = 14.4 Hz, 1H), 4.96 (s, 1H), 6.59 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.2 Hz, 2H), 7.16 (t, J = 9.2 Hz, 2H), 7.27-7.34 (m, 5H), 7.34-7.46 (m, 5H), 7.98-8.04 (m, 2H), 8.16 (dd, J_a = 1.6 Hz, J_b = 6.8 Hz, 2H); ^{13}C NMR: 29.7, 49.4, 87.0, 91.6, 105.2, 115.7, 116.0, 117.6, 118.1, 120.9, 121.0, 122.9, 127.0, 128.3, 128.7, 128.8, 130.1, 130.5, 131.1, 135.4, 147.7, 156.9, 174.4; IR (cm^{-1}): 3382, 2942, 1688, 1618, 1508, 1471, 1448, 1366, 1339, 1230, 1154, 1077, 1035, 1019, 986, 935, 837, 745, 698, 572; HRMS Calculated for $C_{31}H_{25}FN_3O$ [M + H^+]: 474.1982, Detected: 474.2018.

2,4-Dihydro-4-(1-ethyl-2-phenylindol-3-ylmethyl)-2-(4-fluorophenyl)-5-phenyl-3H-pyrazol-3-one (7b)

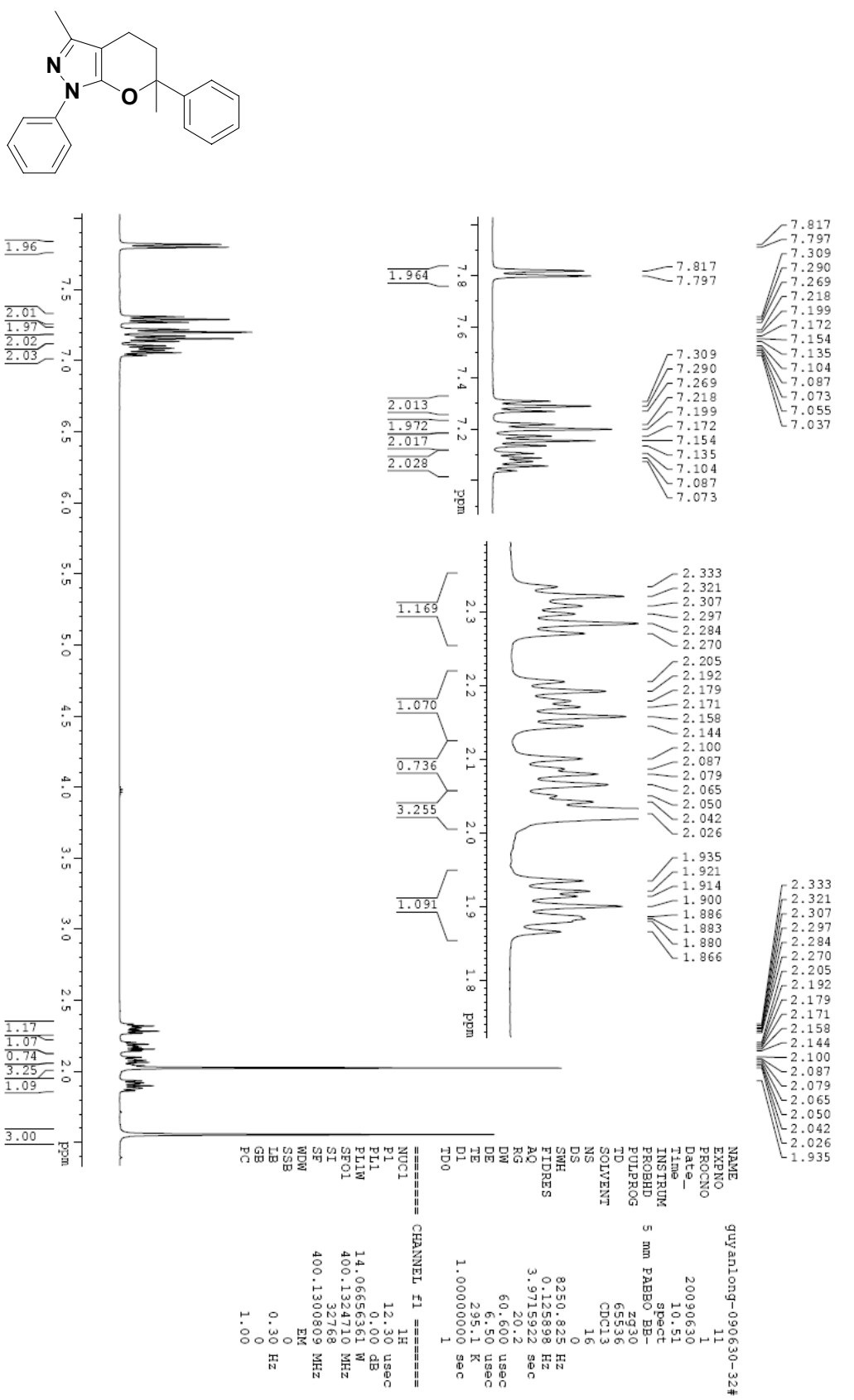


Yellow solid, mp = 105-106 ^oC; ^1H NMR ($CDCl_3$): 1.09 (t, J = 7.2 Hz, 3H), 3.15 (dd, J_a = 8.8 Hz, J_b = 14.4 Hz, 1H), 3.59 (dd, J_a = 5.6 Hz, J_b = 14.4 Hz, 1H), 3.77-3.94 (m, 2H), 4.07-4.13 (m, 1H), 6.77 (bs, 2H), 7.05 (t, J = 8.8 Hz, 2H), 7.09-7.19 (m, 5H), 7.22-7.33 (m, 5H), 7.36 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.84 (dd, J_a = 4.8 Hz, J_b = 9.2 Hz, 2H); ^{13}C NMR: 15.4, 26.8, 38.5, 49.8, 100.0, 107.7, 109.8, 115.3, 115.5, 119.1, 119.7, 120.7, 120.8, 122.0, 126.9, 127.4, 128.2, 128.2, 128.3, 129.9, 130.4, 131.0, 131.2, 134.4, 134.4, 135.9, 139.2, 158.7, 159.7, 161.1, 173.1; IR (cm^{-1}): 3057, 2956, 2931, 1715, 1508, 1464, 1344, 1219, 1155, 835, 743, 699; HRMS Calculated for $C_{32}H_{27}FN_2O$ [M + H^+]: 488.2138, Detected: 488.2177.

2,4-Dihydro-4-(1-ethyl-2-phenylindol-3-ylmethyl)-5-(4-methoxyphenyl)-2-phenyl-3H-pyrazol -3-one (7c)



Yellow solid, mp = 113-114 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.10 (t, J = 7.2 Hz, 3H), 3.13 (dd, J_a = 8.8 Hz, J_b = 14.4 Hz, 1H), 3.58 (dd, J_a = 5.6 Hz, J_b = 14.8 Hz, 1H), 3.77 (s, 3H), 3.80-3.95 (m, 2H), 4.07 (dd, J_a = 5.6 Hz, J_b = 8.4 Hz, 1H), 6.62 (d, J = 8.8 Hz, 2H), 6.78-6.87 (m, 2H), 7.09 (d, J = 7.2 Hz, 2H), 7.15 (q, J = 7.6 Hz, 2H), 7.21-7.32 (m, 4H), 7.36 (t, J = 7.2 Hz, 3H), 7.76 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 15.5, 27.0, 38.5, 50.0, 55.4, 107.9, 109.8, 113.6, 119.0, 119.2, 119.7, 121.9, 124.0, 124.9, 127.5, 128.2, 128.3, 128.4, 128.7, 130.5, 131.3, 135.9, 138.3, 139.1, 159.3, 139.1, 159.3, 161.0, 173.2; IR (cm^{-1}): 3058, 2973, 2933, 1713, 1607, 1516, 1498, 1463, 1344, 1315, 1255, 1176, 1029, 835, 746, 702; HRMS Calculated for $C_{33}H_{30}N_3O_2$ [M + H^+]: 500.2338, Detected: 500.2366.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7.104
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7.055
7.037
2.333
2.321
2.307
2.297
2.284
2.270
2.205
2.192
2.179
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2.158
2.144
2.100
2.087
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1.900
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1.07
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ppm
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EXPNO 11
PROCNO 1
Date_ 20090630
Time 10.51
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PULPROG zg30
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SOLVENT CDCl3
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FIDRES 0.125898 Hz
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DW 60.600 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
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P1 12.30 usec
PL1 0.00 dB
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SF 400.1300809 MHz
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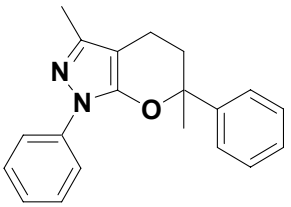

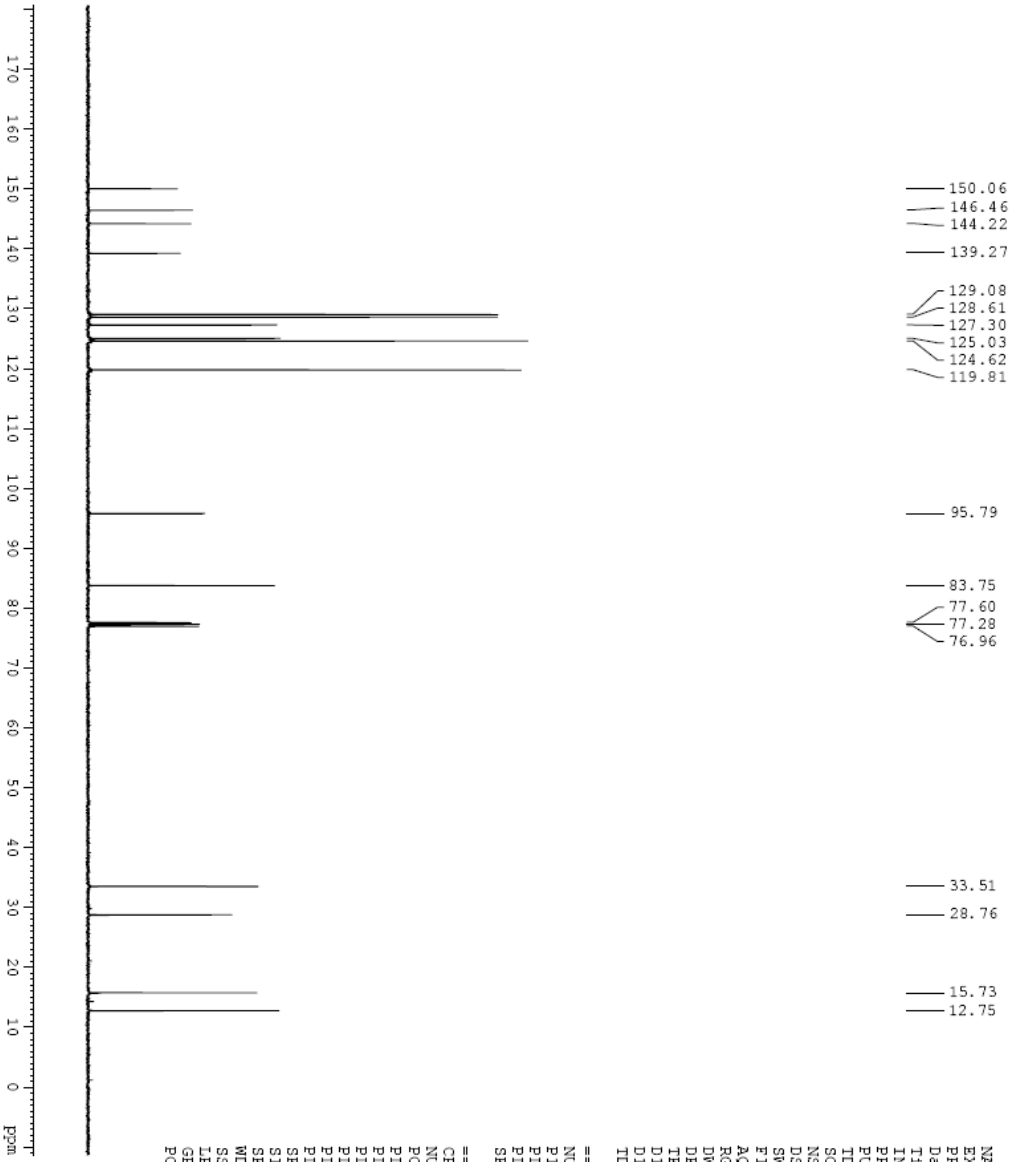


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PROCNO                                  1
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D11                        0.03000000 sec
TD0                                 1

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P1                              12.50 usec
PL1                              6.00 dB
PL1W                    30.15976143 W
SFO1                   100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                       waltz16
NUC2                              1H
PCPD2                       80.00 usec
PL2                           0.00 dB
PL12                         16.85 dB
PL13                         16.50 dB
PL2W                    14.06656361 W
PL12W                    0.29052800 W
PL13W                    0.31491116 W
SFO2                   400.1316005 MHz
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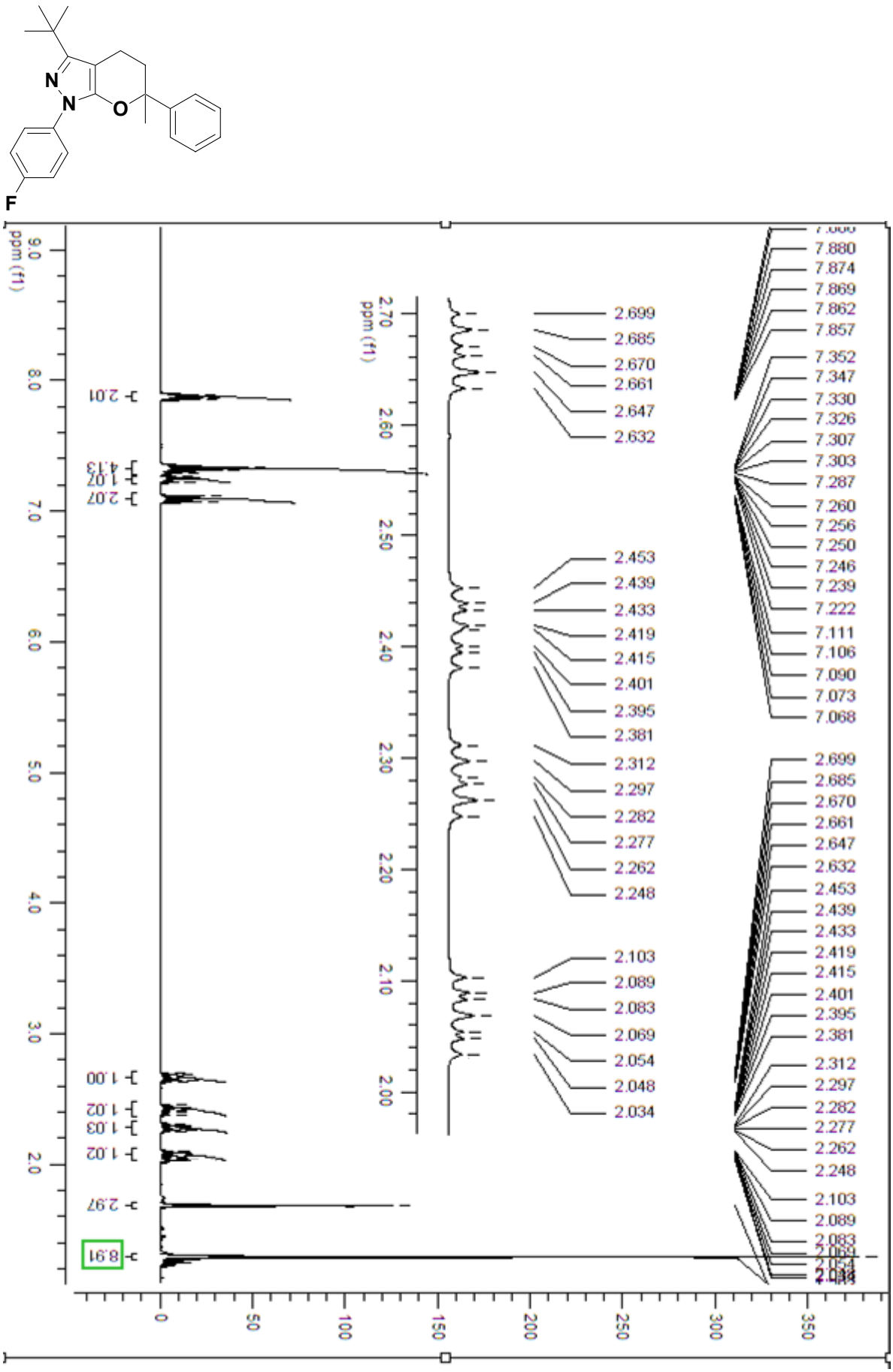
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2.670
2.661
2.647
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2.453
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2.419
2.415
2.401
2.395
2.381
2.312
2.297
2.282
2.277
2.262
2.248
2.103
2.089
2.083
2.069
2.054
2.048
2.034
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7.347
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7.303
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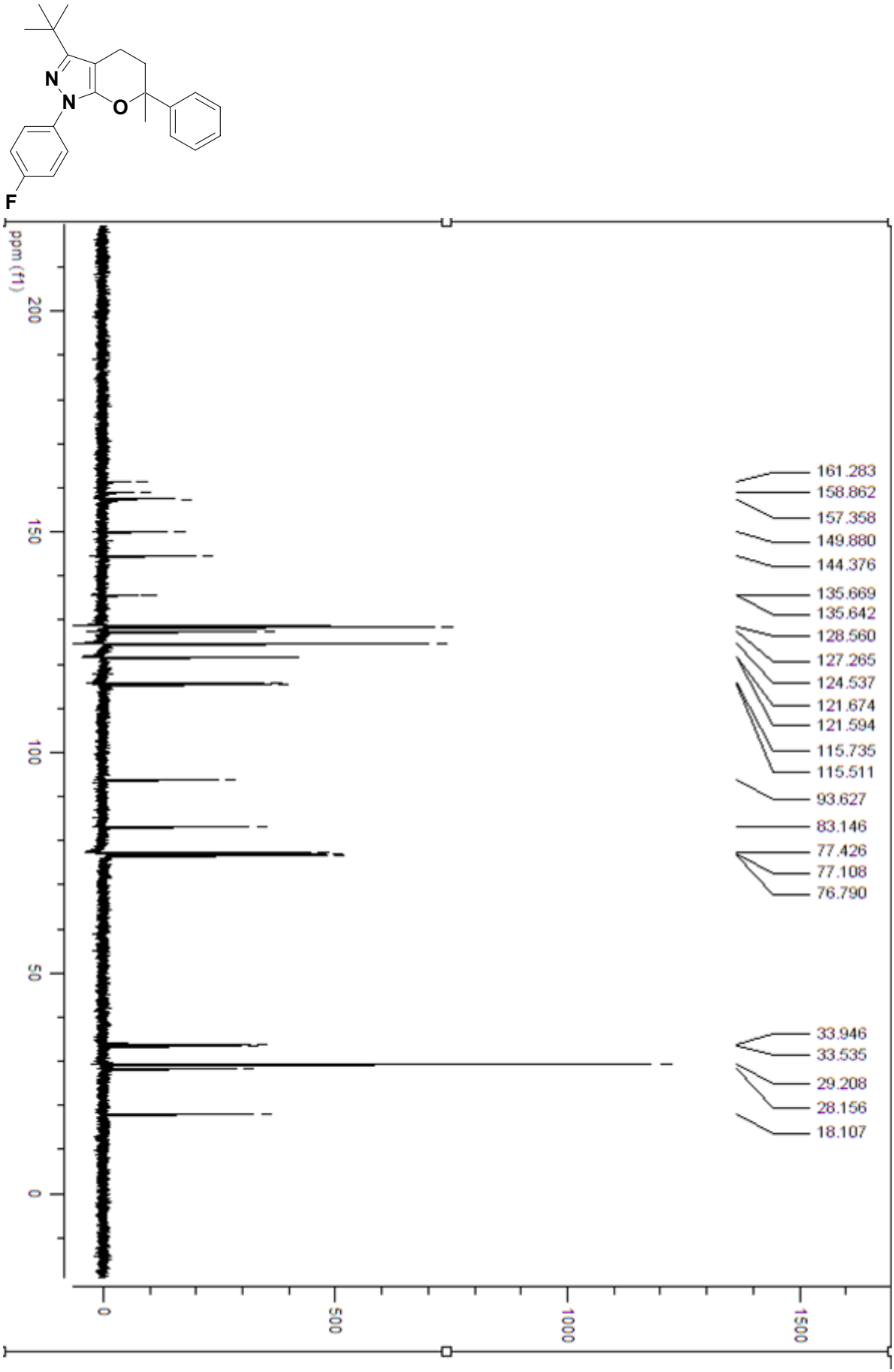
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135.669
135.642
128.560
127.265
124.537
121.674
121.594
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83.146
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77.108
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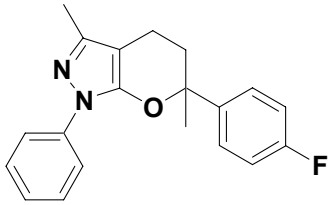
28.156
18.107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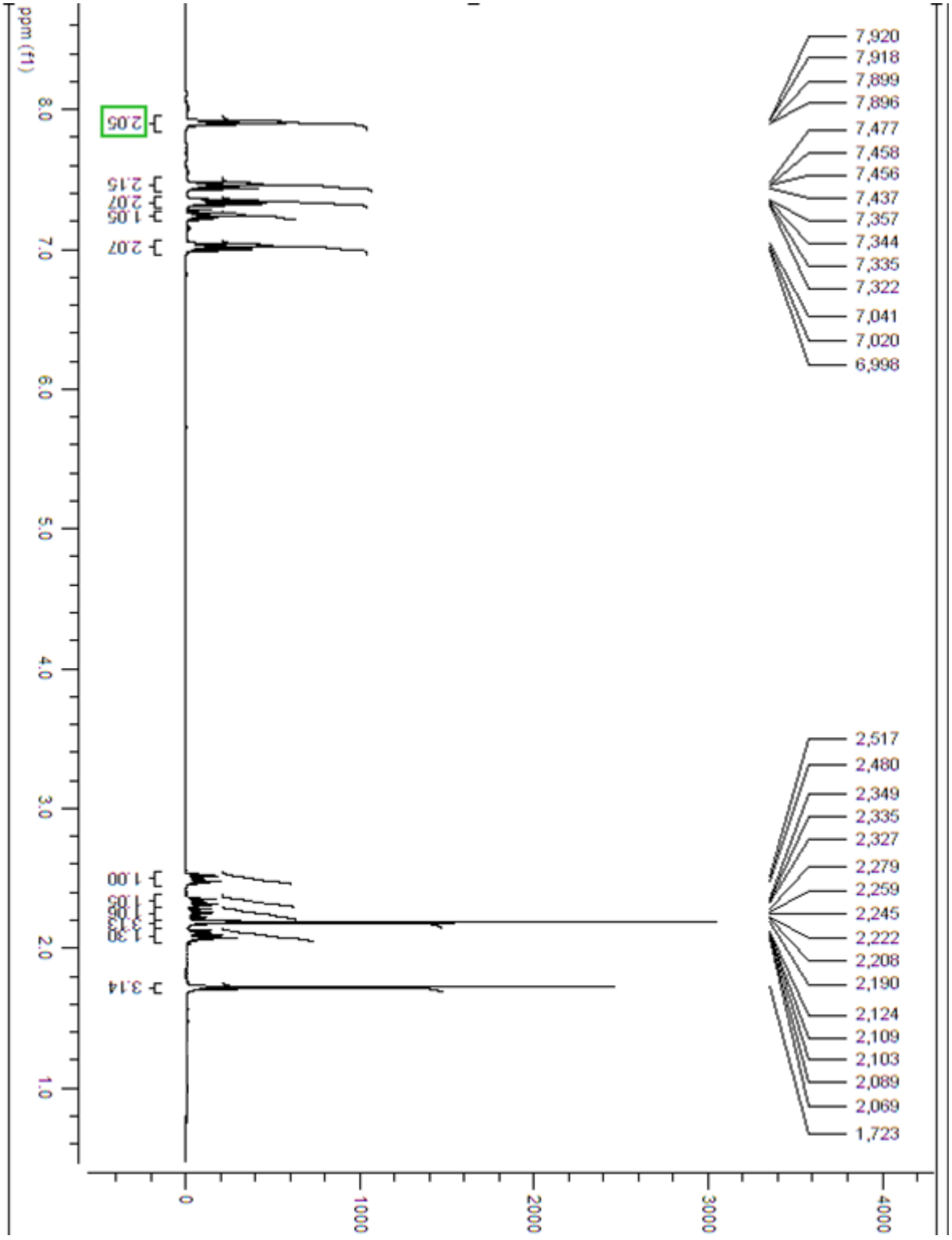
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1.05
2.07
1.00
3.14
0
1000
2000
3000
4000
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7,899
7,896
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7,458
7,456
7,437
7,357
7,344
7,335
7,322
7,041
7,020
6,998
2,517
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2,335
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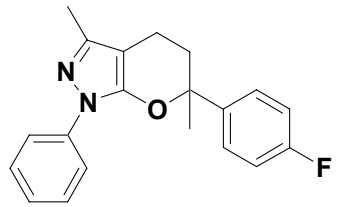
2,069
1,723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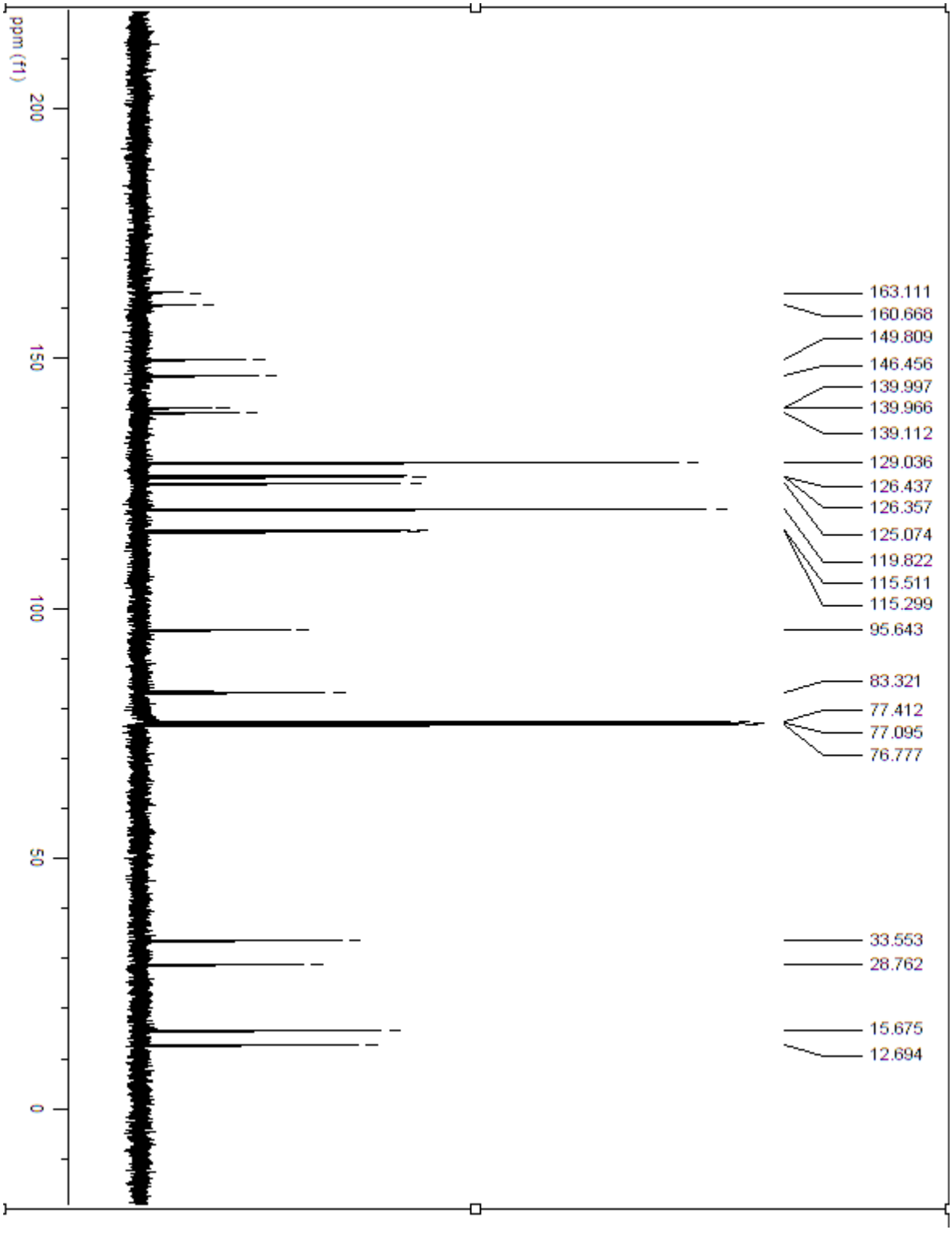
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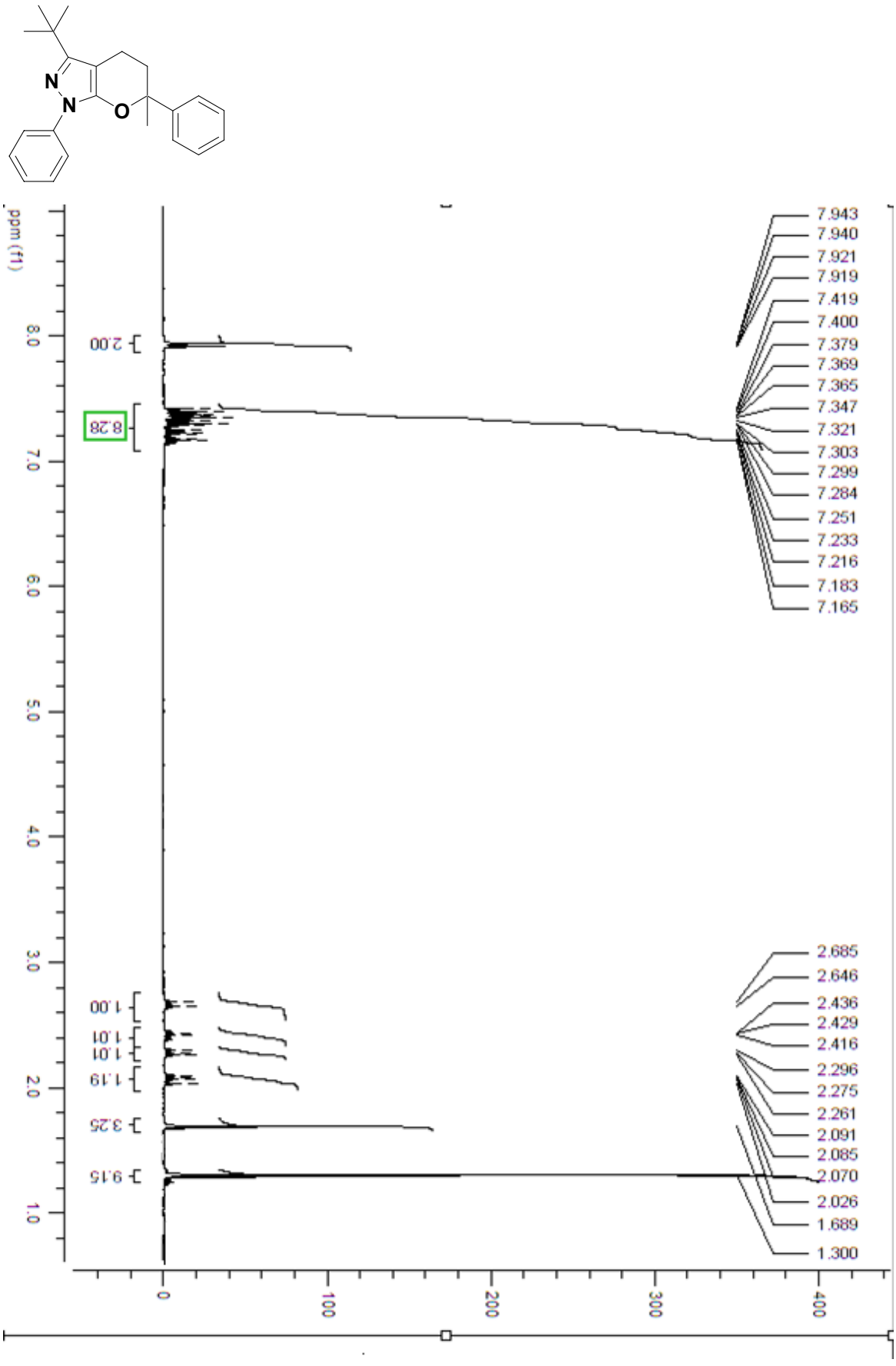
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7.919
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7.369
7.365
7.347
7.321
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7.299
7.284
7.251
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7.216
7.183
7.165
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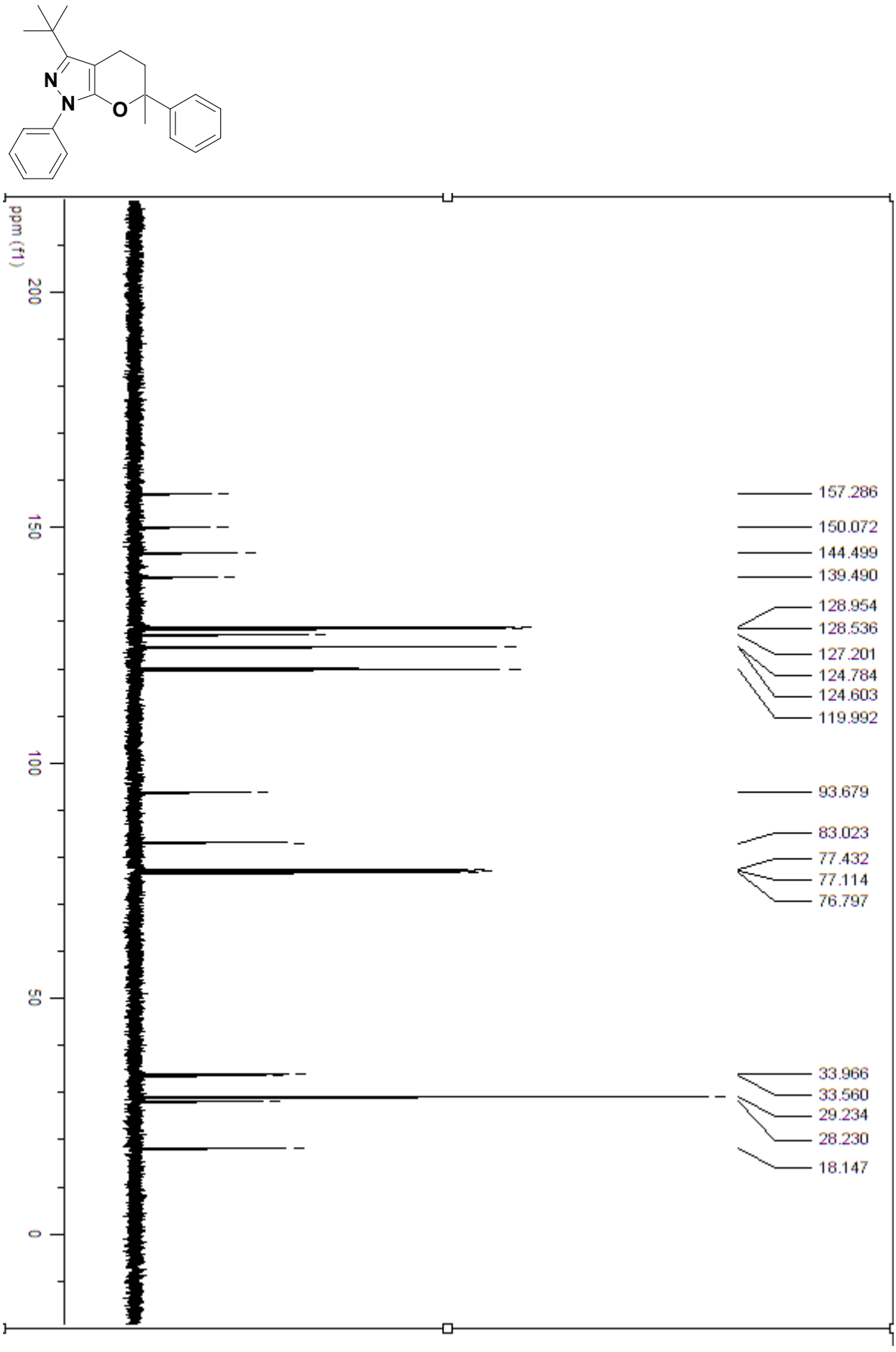
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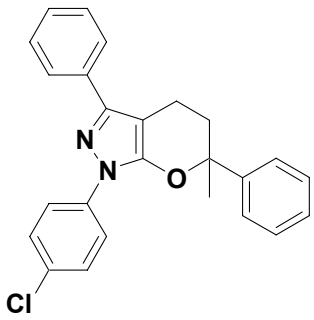
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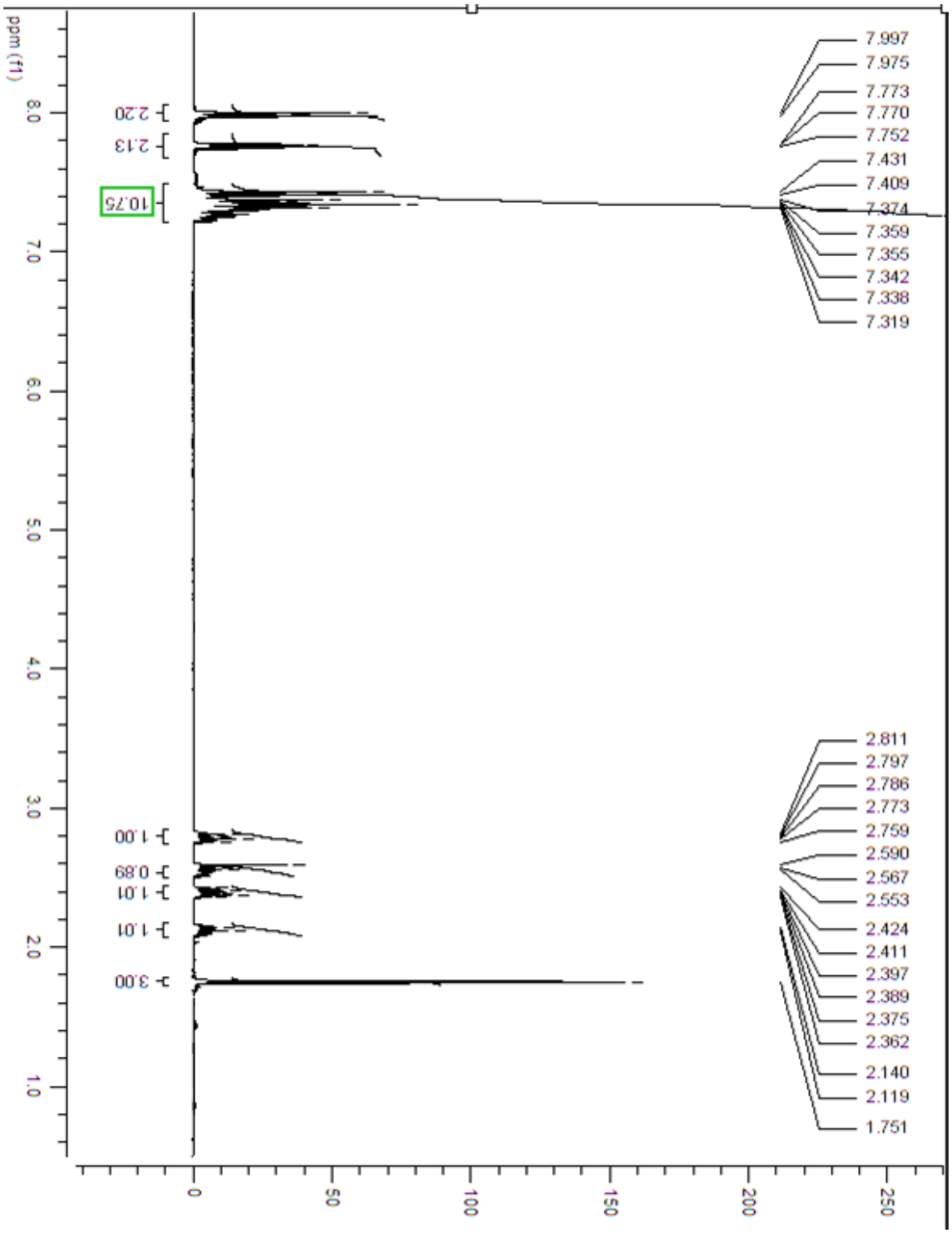
Cl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1.01
1.01
3.00
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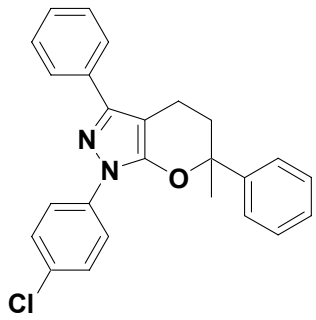
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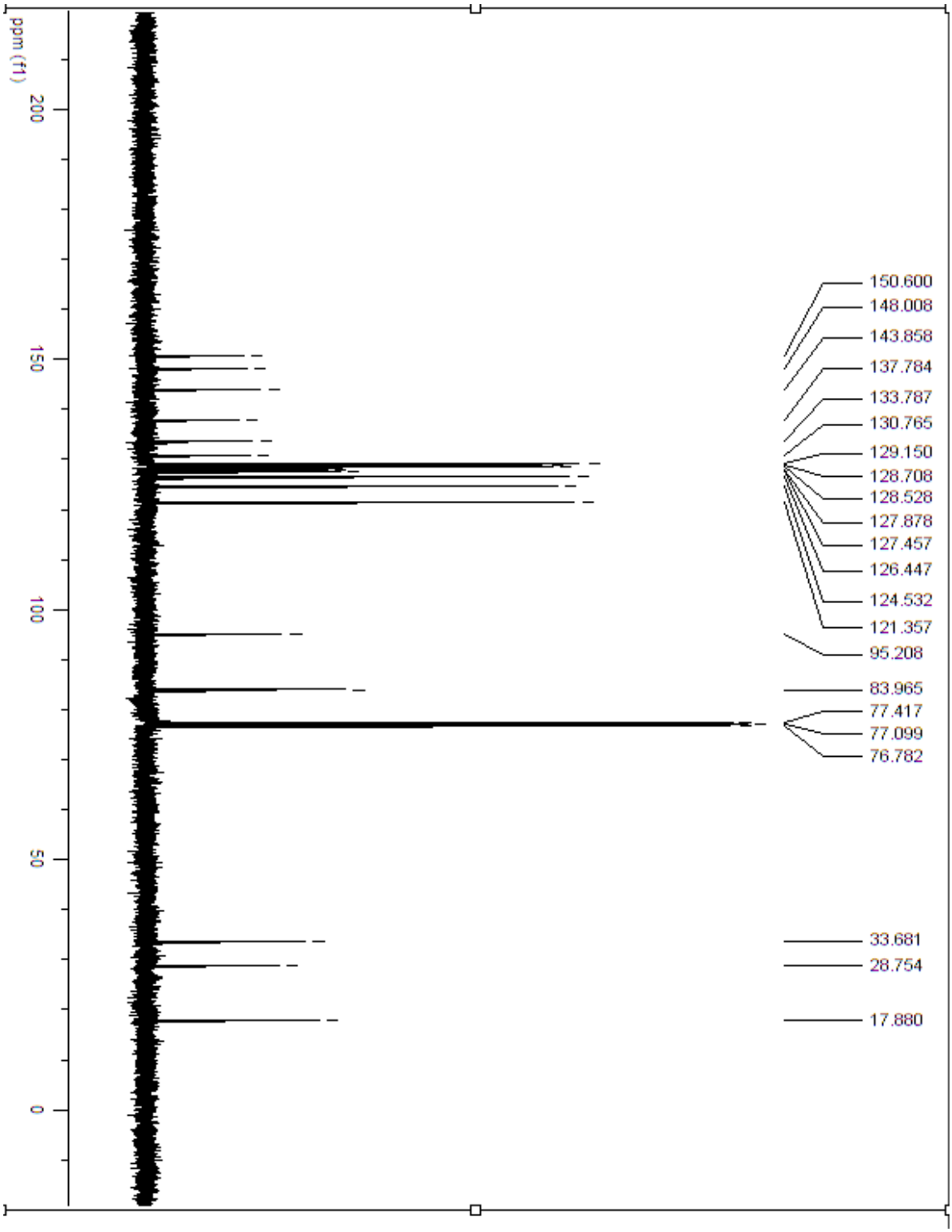
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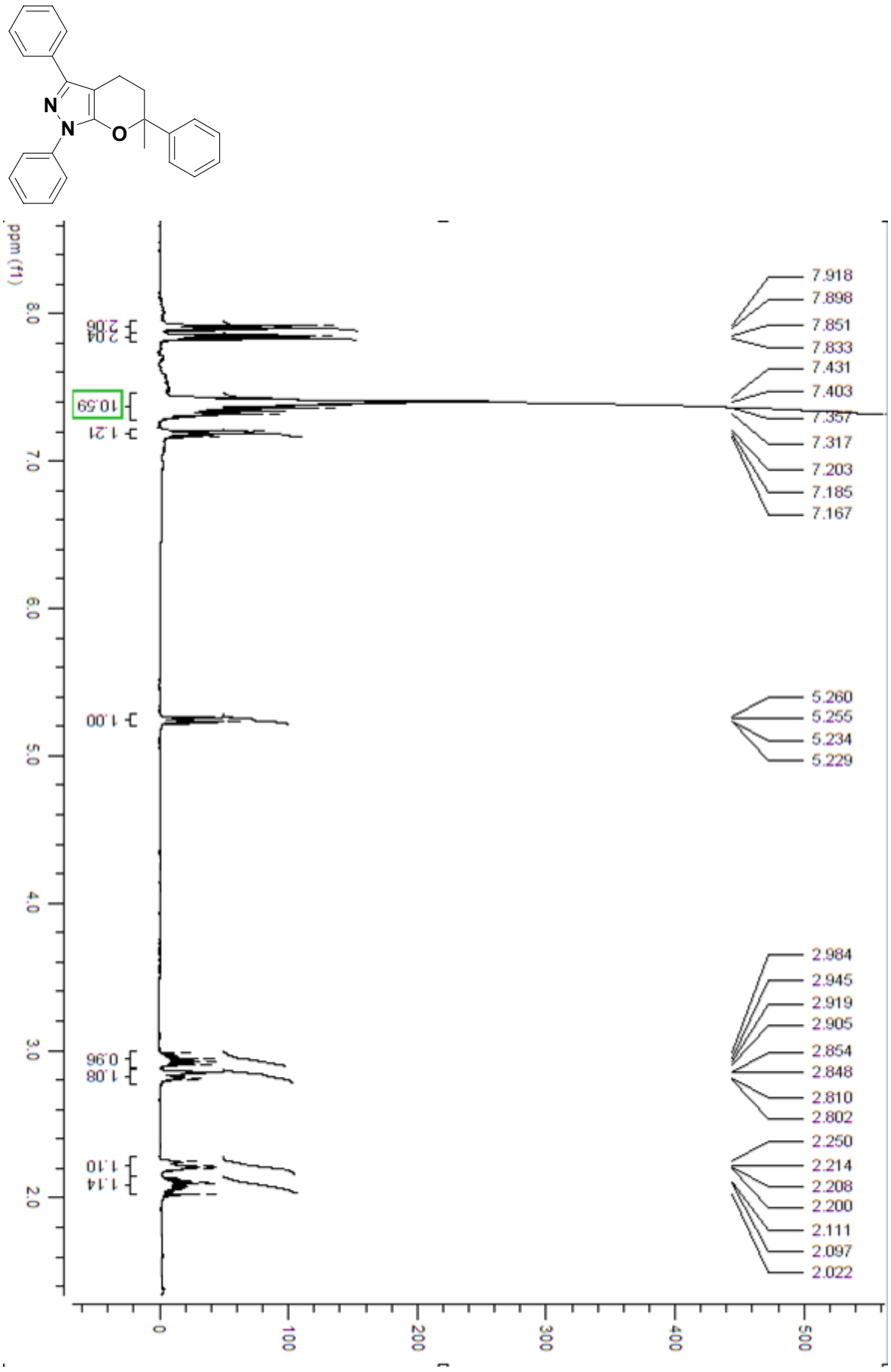
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1.10
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5.234
5.229
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2.905
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2.848
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400
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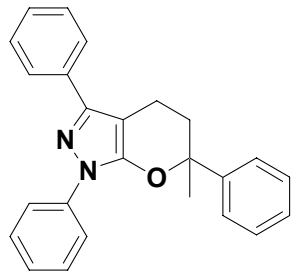
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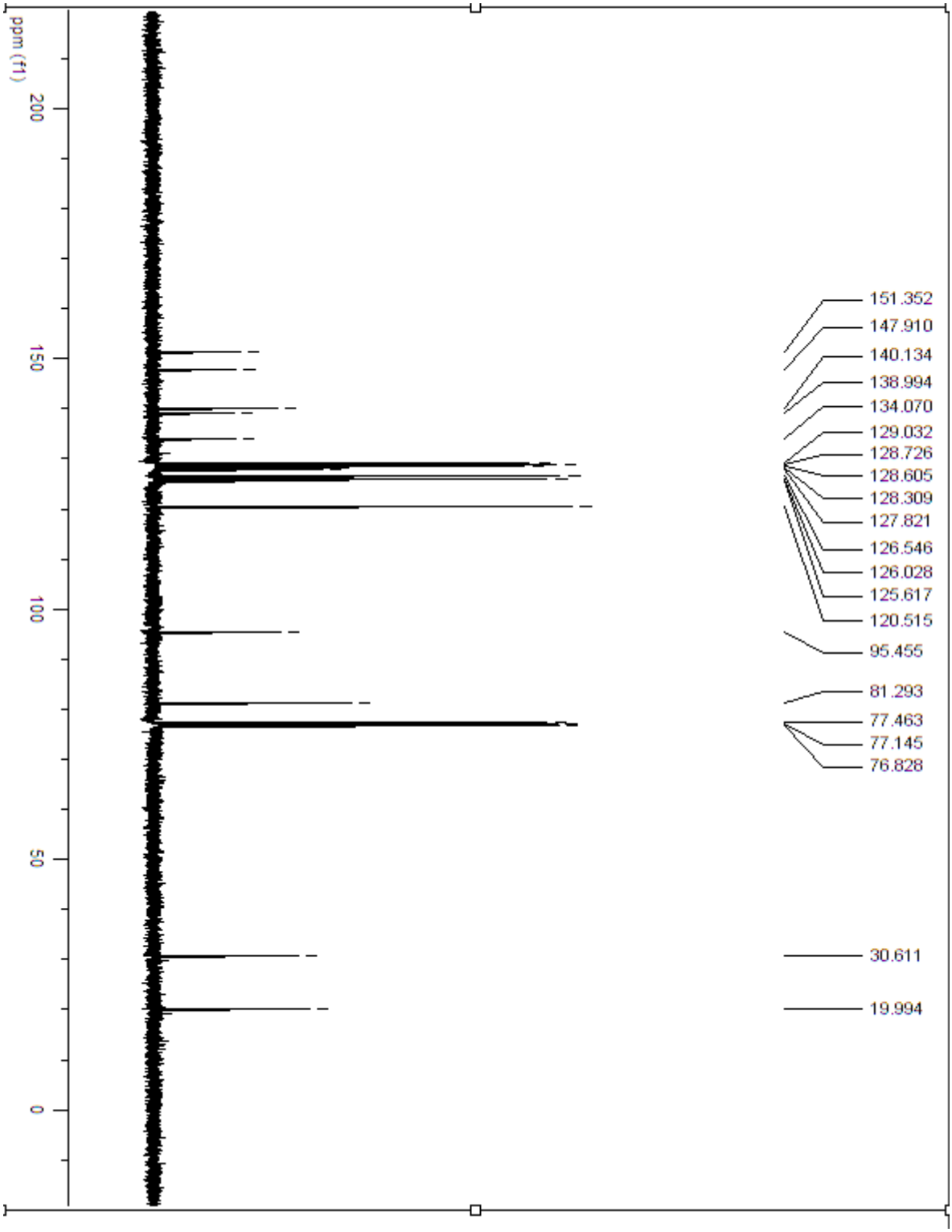
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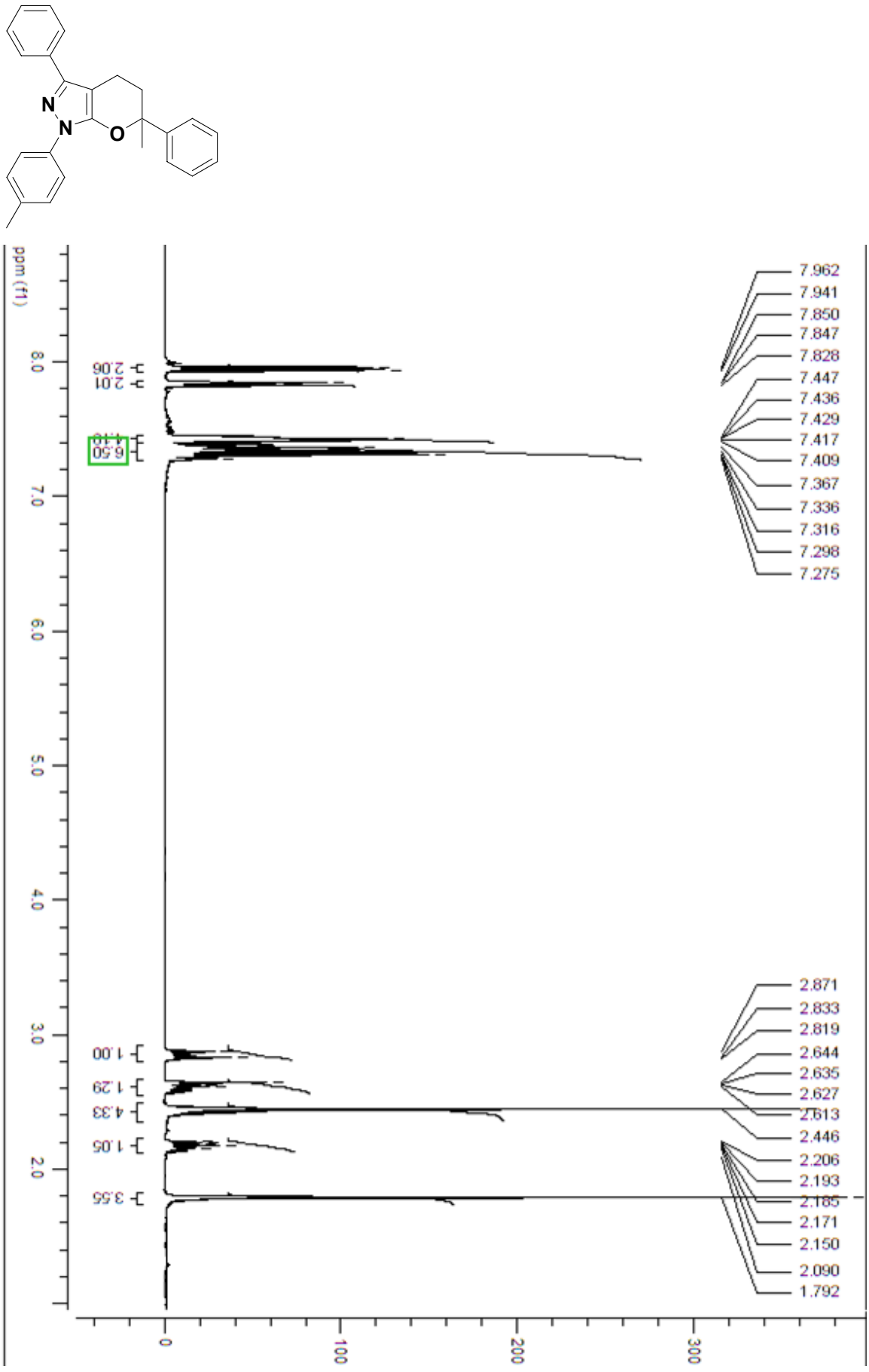
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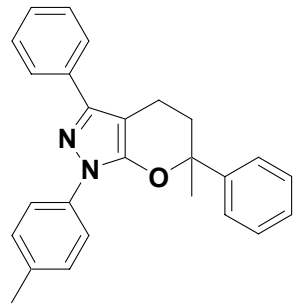
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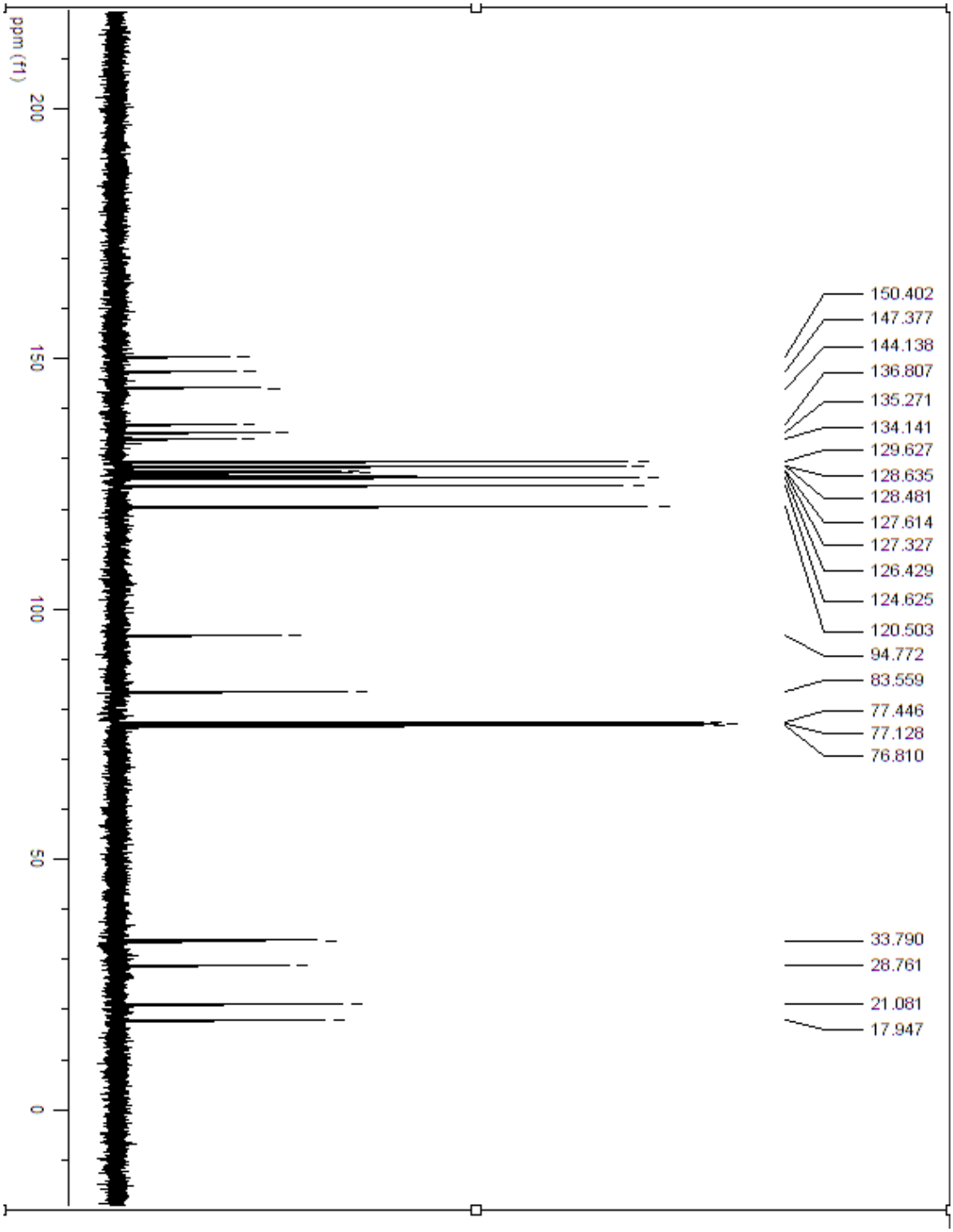
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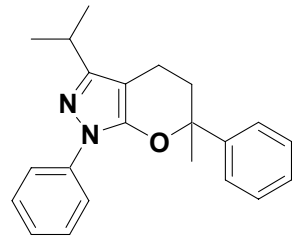
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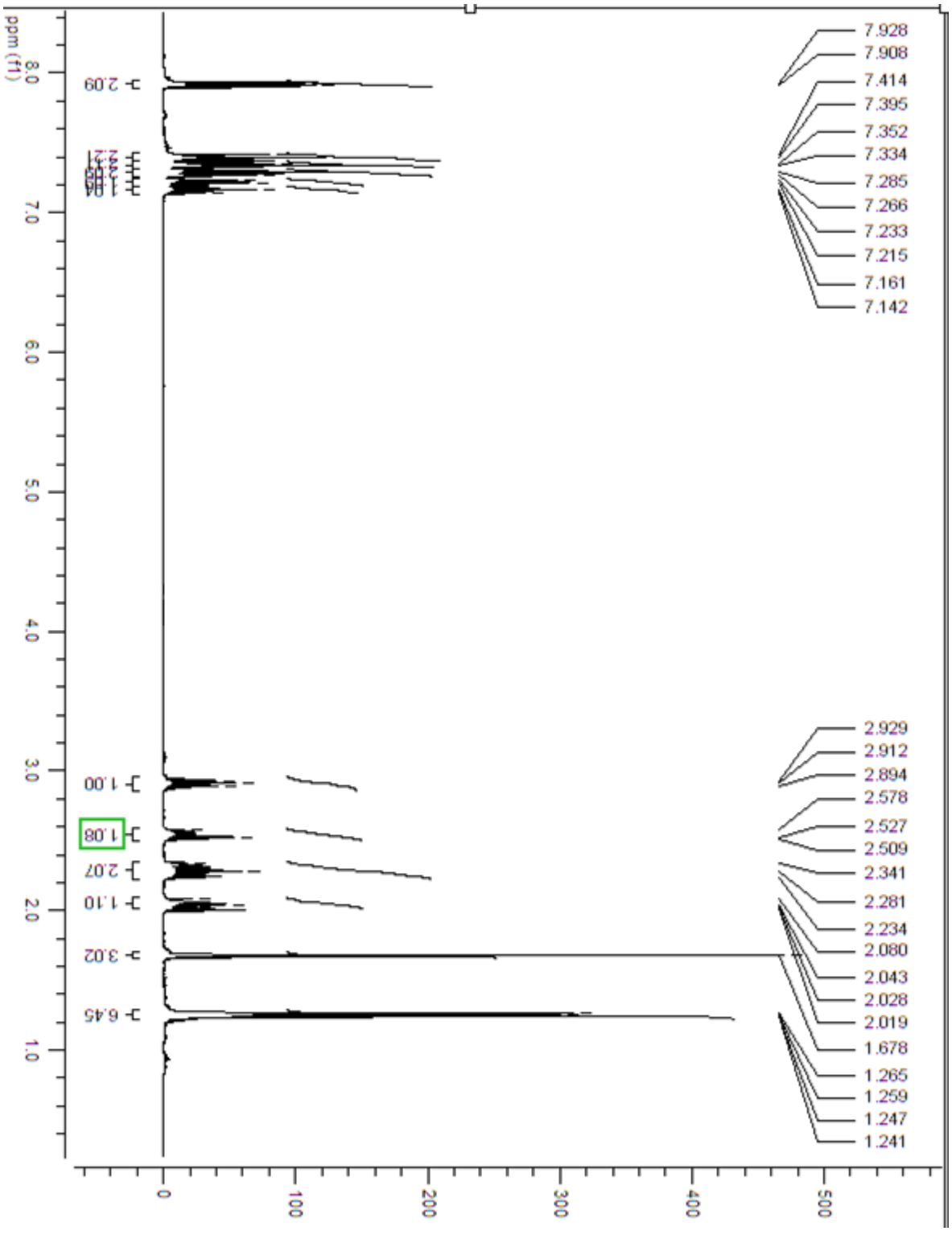
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3.02
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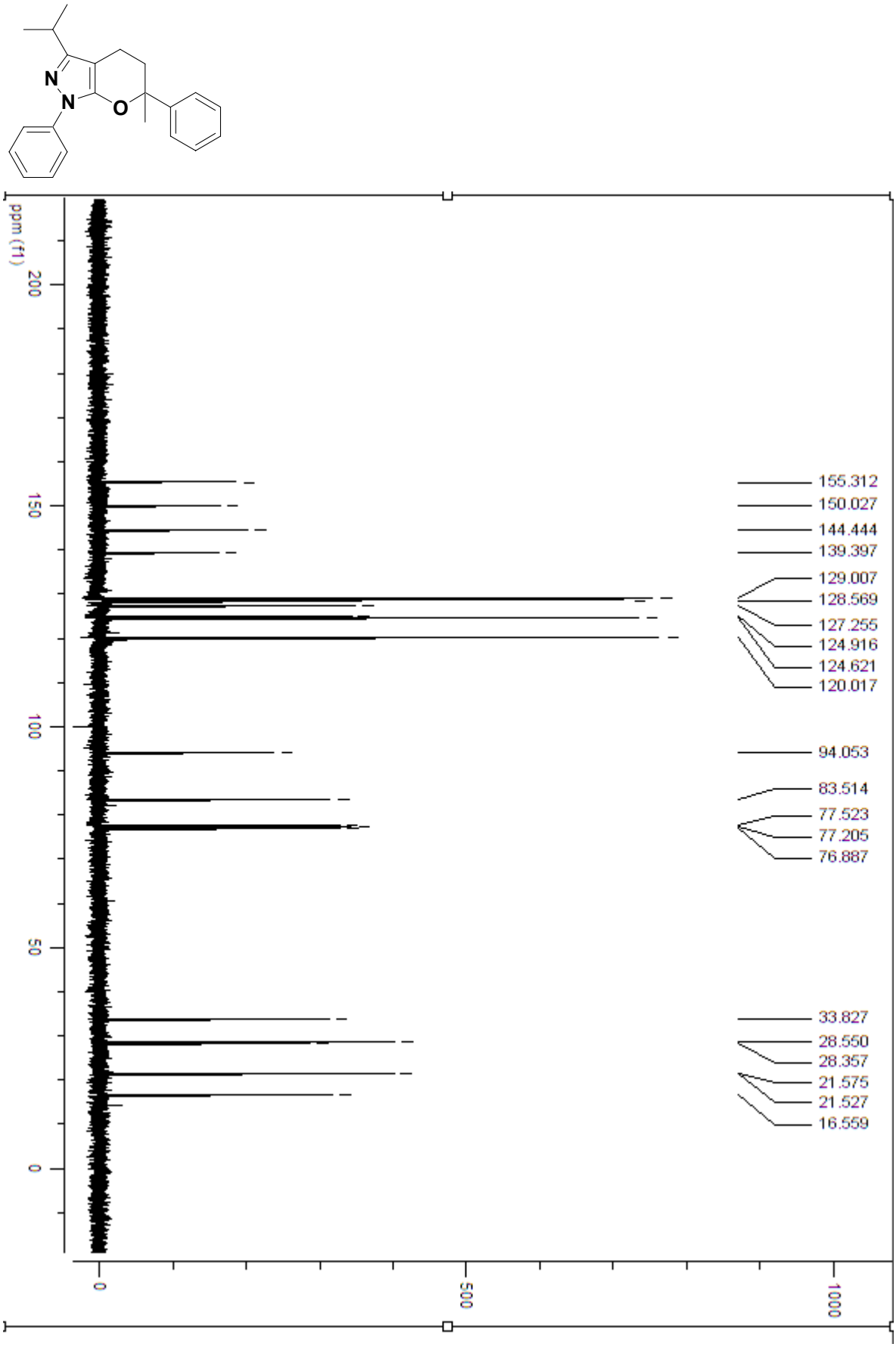
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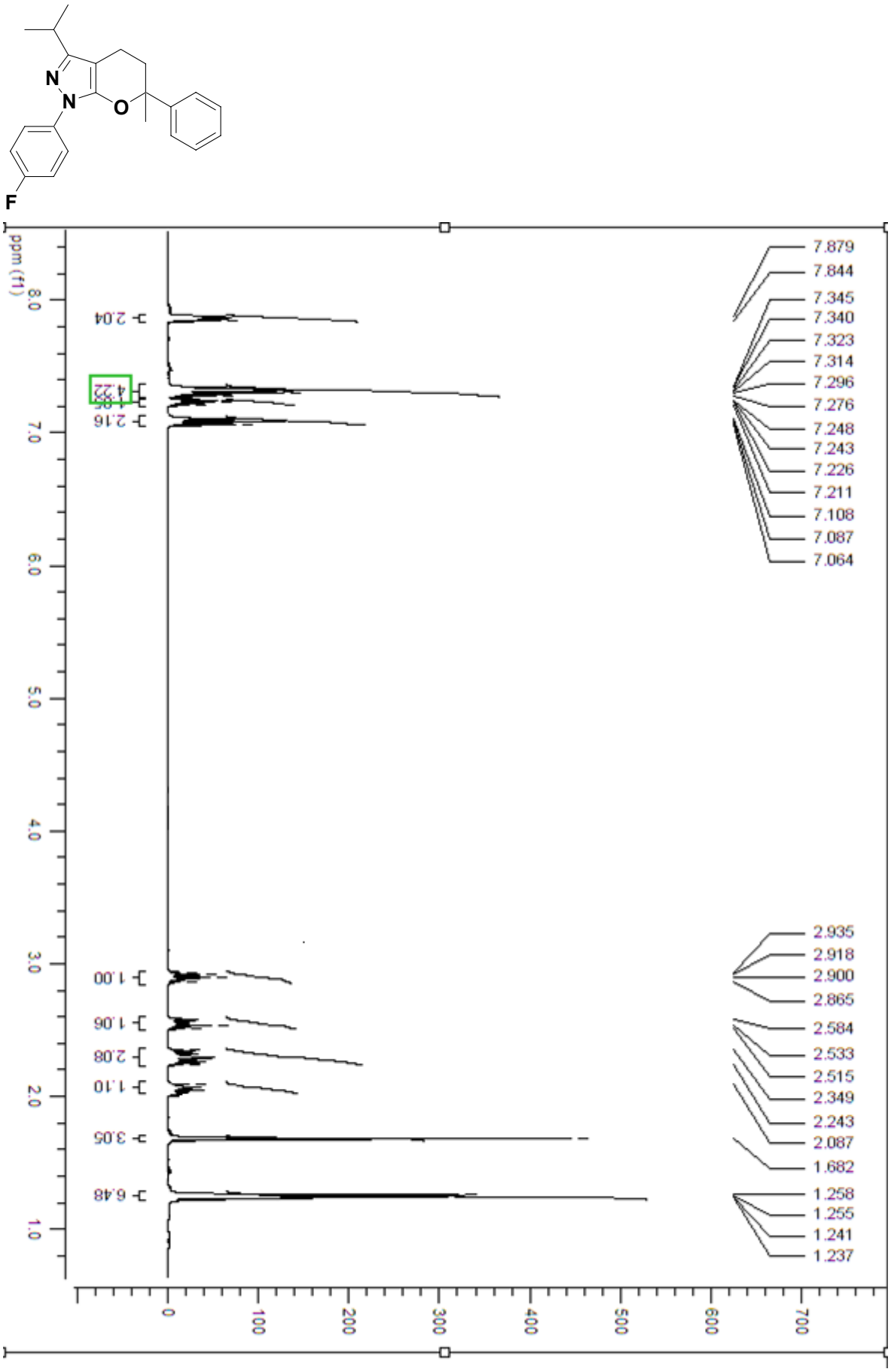
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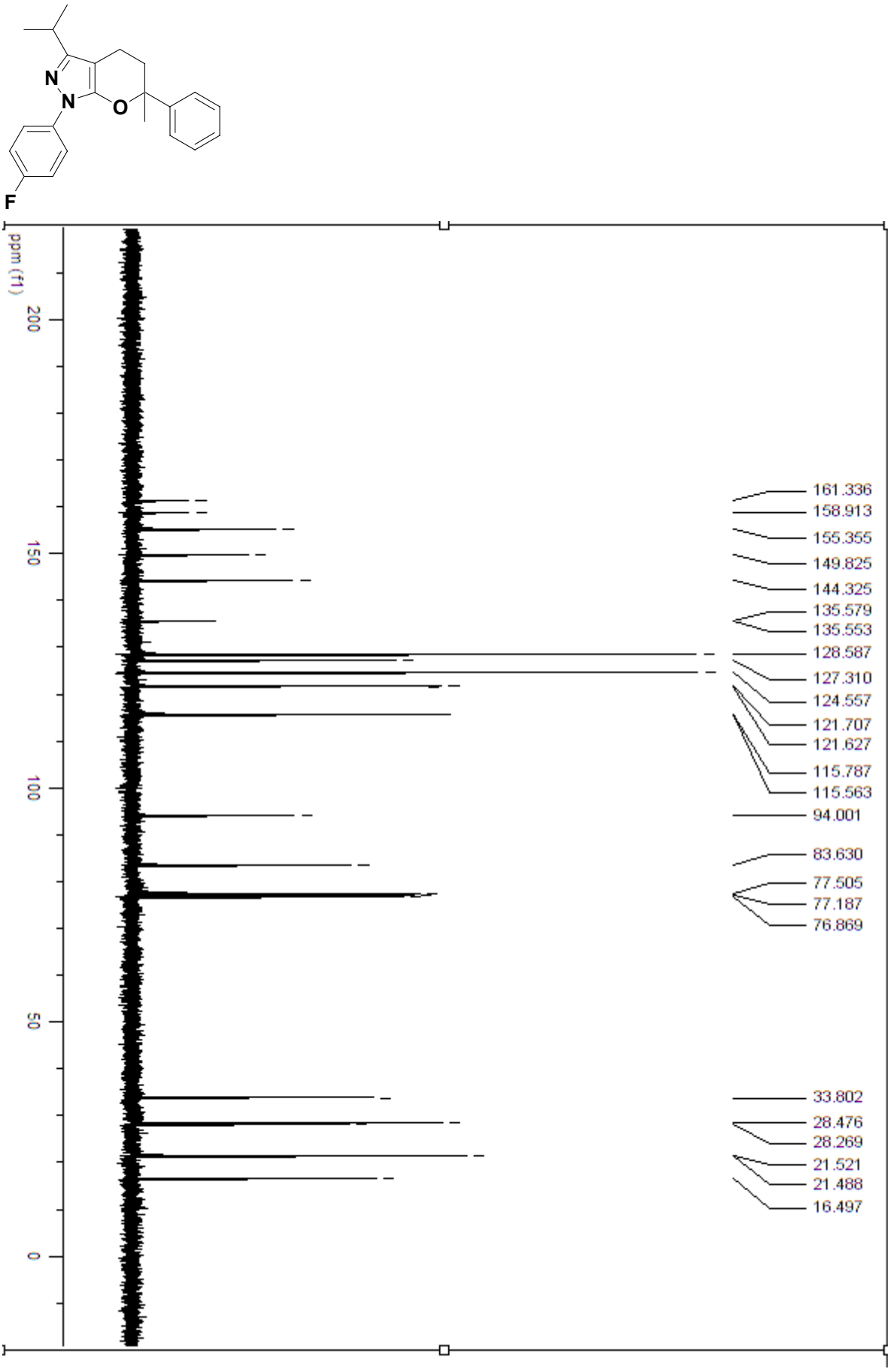
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O
F
ppm (f1)
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150
100
50
0
161.336
158.913
155.355
149.825
144.325
135.579
135.553
128.587
127.310
124.557
121.707
121.627
115.787
115.563
94.001
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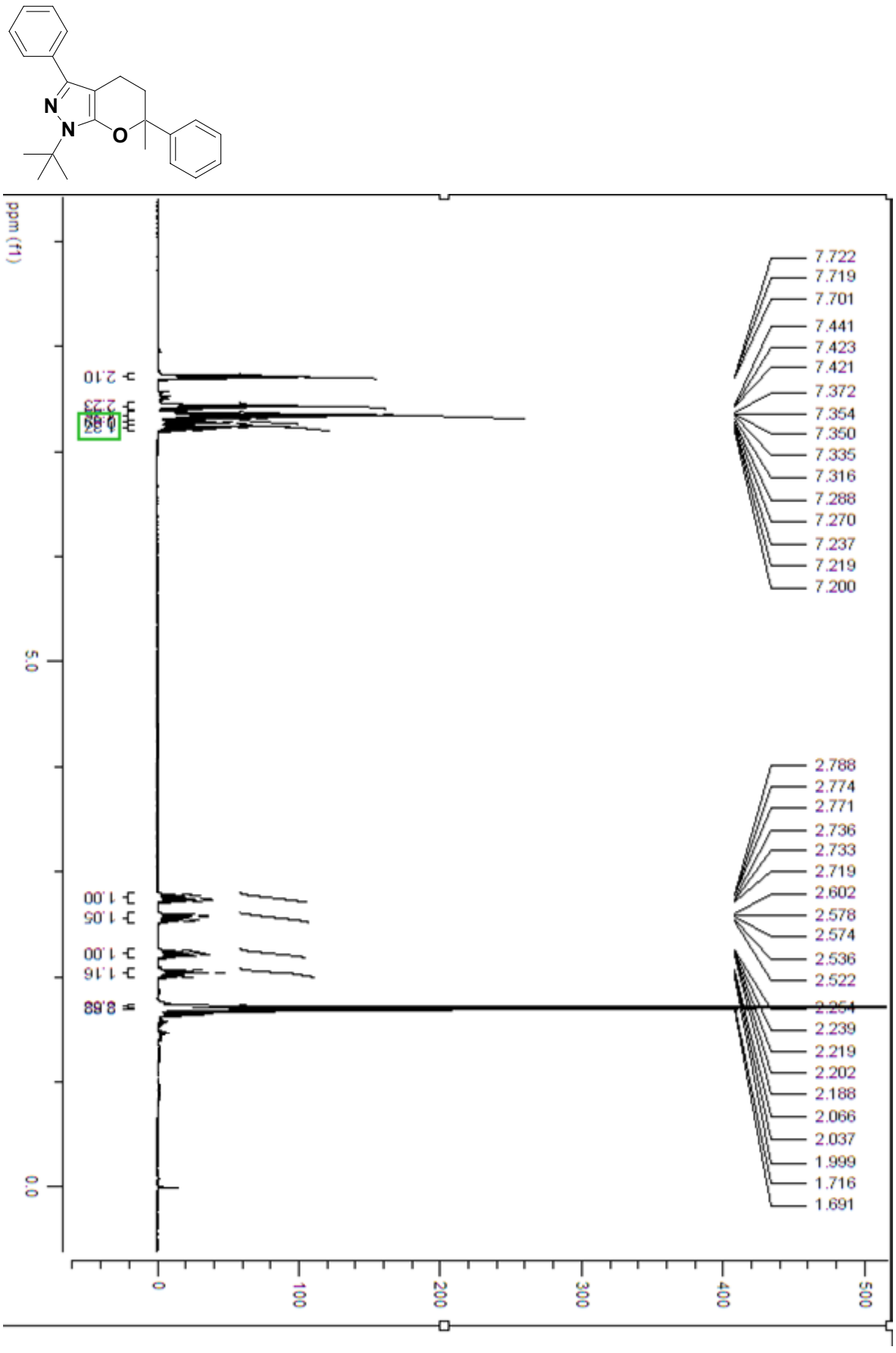
77.505
77.187
76.869
33.802
28.476
28.269
21.521
21.488
16.497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N
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7.423
7.421
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7.354
7.350
7.335
7.316
7.288
7.270
7.237
7.219
7.200
2.788
2.774
2.771
2.736
2.733
2.719
2.602
2.578
2.574
2.536
2.522
2.254
2.239
2.219
2.202
2.188
2.066
2.037
1.999
1.716
1.691
0
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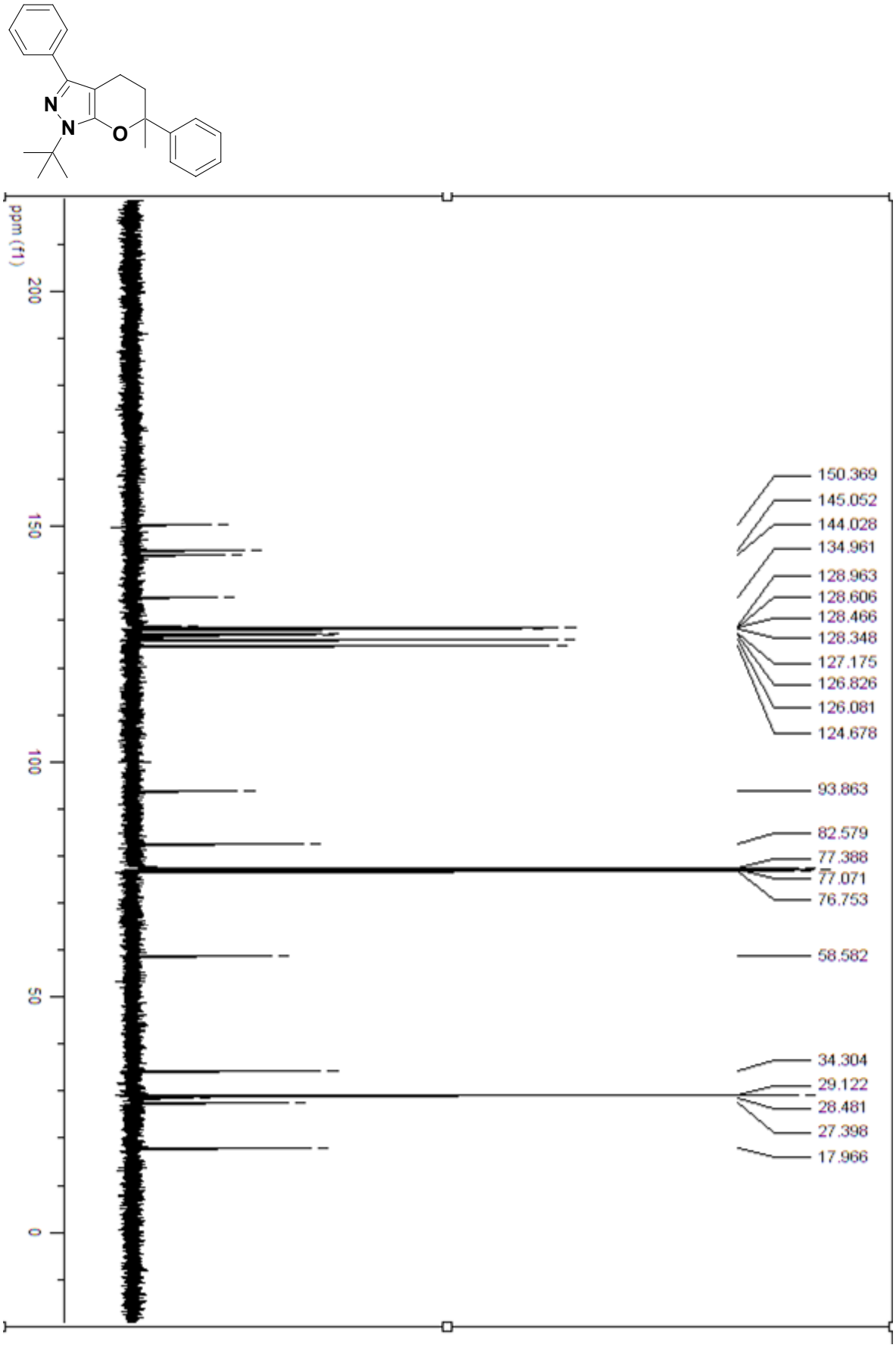
200
300
400
500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50
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128.466
128.348
127.175
126.826
126.081
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77.071
76.753
58.582
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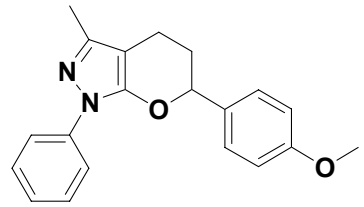
29.122
28.481
27.398
17.966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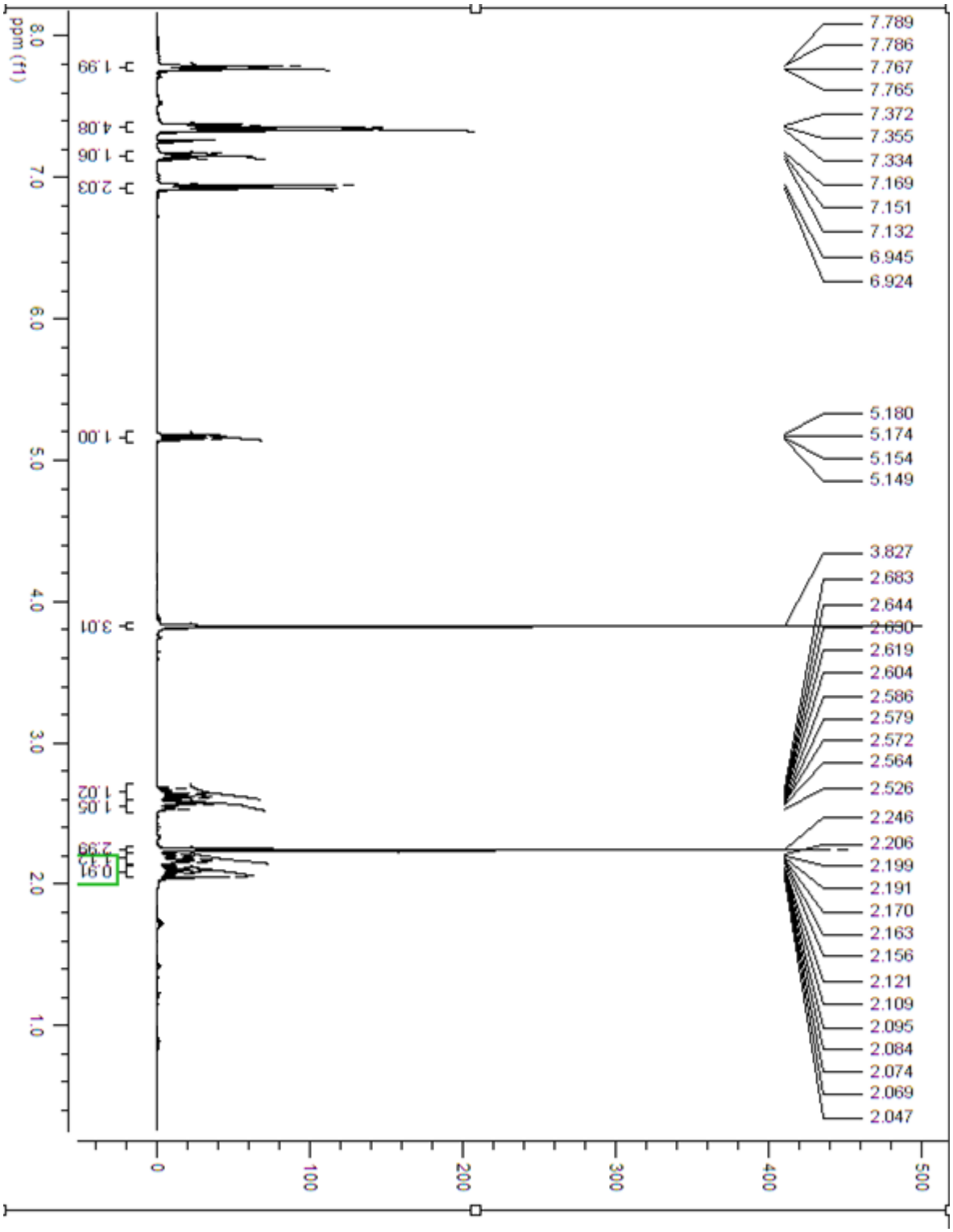
O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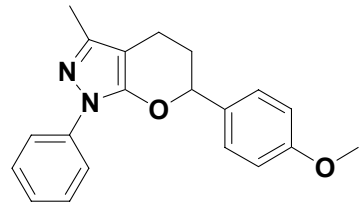
4.0
3.0
2.0
1.0
0
100
200
300
400
500
1.99
4.08
1.06
2.03
1.00
3.01
1.02
1.05
2.99
0.91
7.789
7.786
7.767
7.765
7.372
7.355
7.334
7.169
7.151
7.132
6.945
6.924
5.180
5.174
5.154
5.149
3.827
2.683
2.644
2.619
2.604
2.586
2.579
2.572
2.564
2.526
2.246
2.206
2.199
2.191
2.170
2.163
2.156
2.121
2.109
2.095
2.084
2.074
2.069
2.047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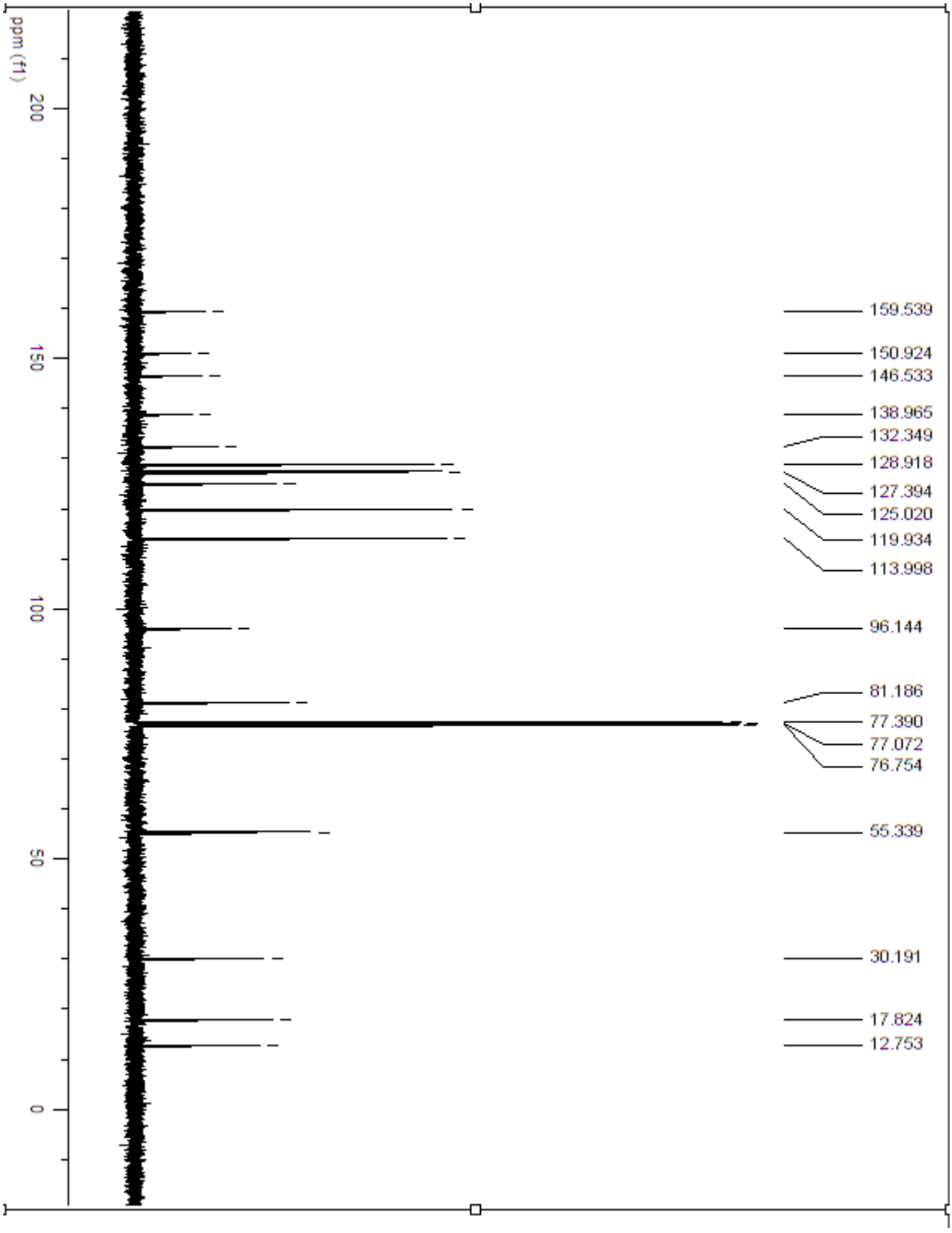
O
O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100
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146.533
138.965
132.349
128.918
127.394
125.020
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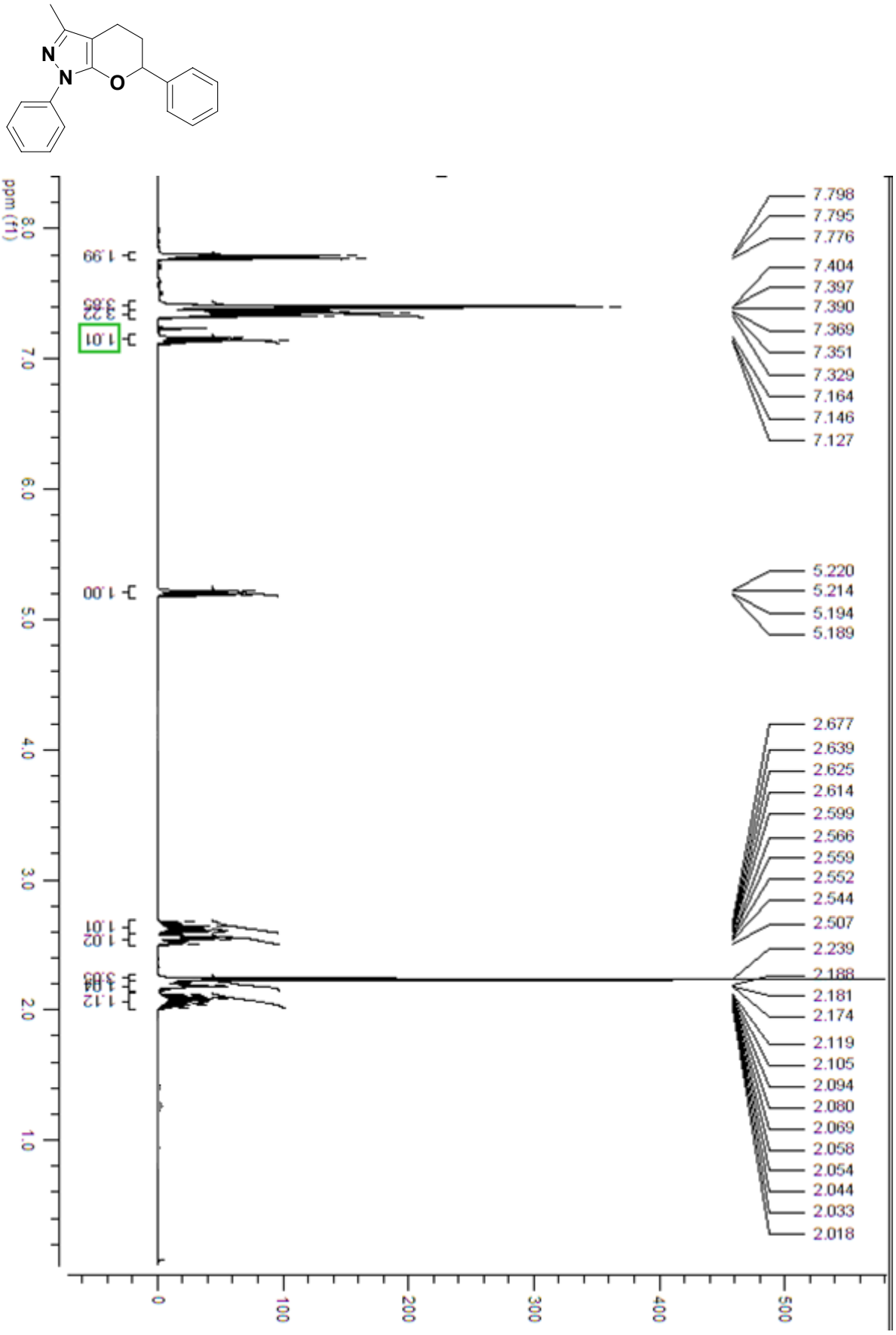
113.998
96.144
81.186
77.390
77.072
76.754
55.339
30.191
17.824
12.753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4.0
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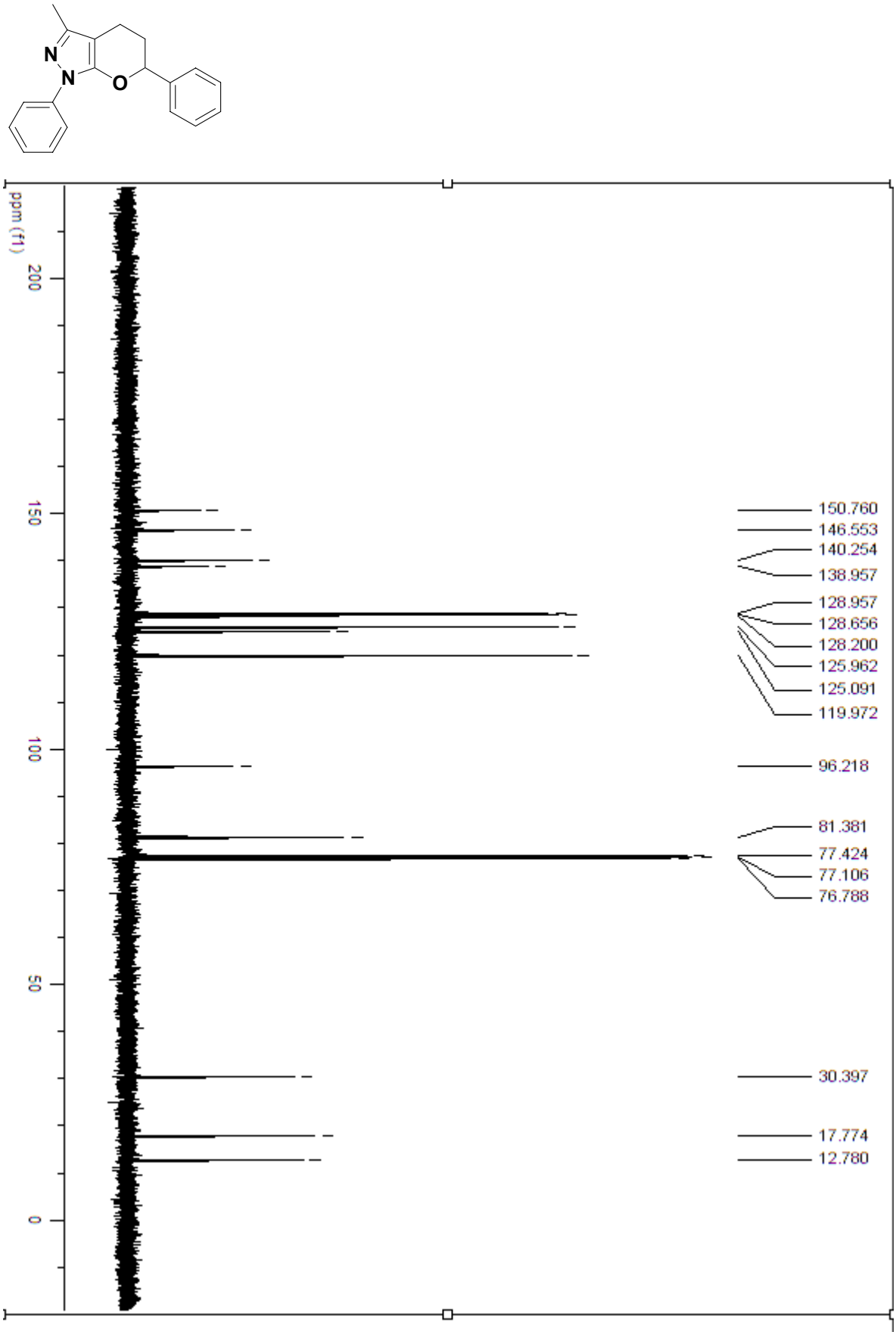
2.0
1.0
1.99
1.01
1.00
0
100
200
300
400
500
7.798
7.795
7.776
7.404
7.397
7.390
7.369
7.351
7.329
7.164
7.146
7.127
5.220
5.214
5.194
5.189
2.677
2.639
2.625
2.614
2.599
2.566
2.559
2.552
2.544
2.507
2.239
2.188
2.181
2.174
2.119
2.105
2.094
2.080
2.069
2.058
2.054
2.044
2.033
2.018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N
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ppm (f1)
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150
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50
0
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146.553
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138.957
128.957
128.656
128.200
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119.972
96.218
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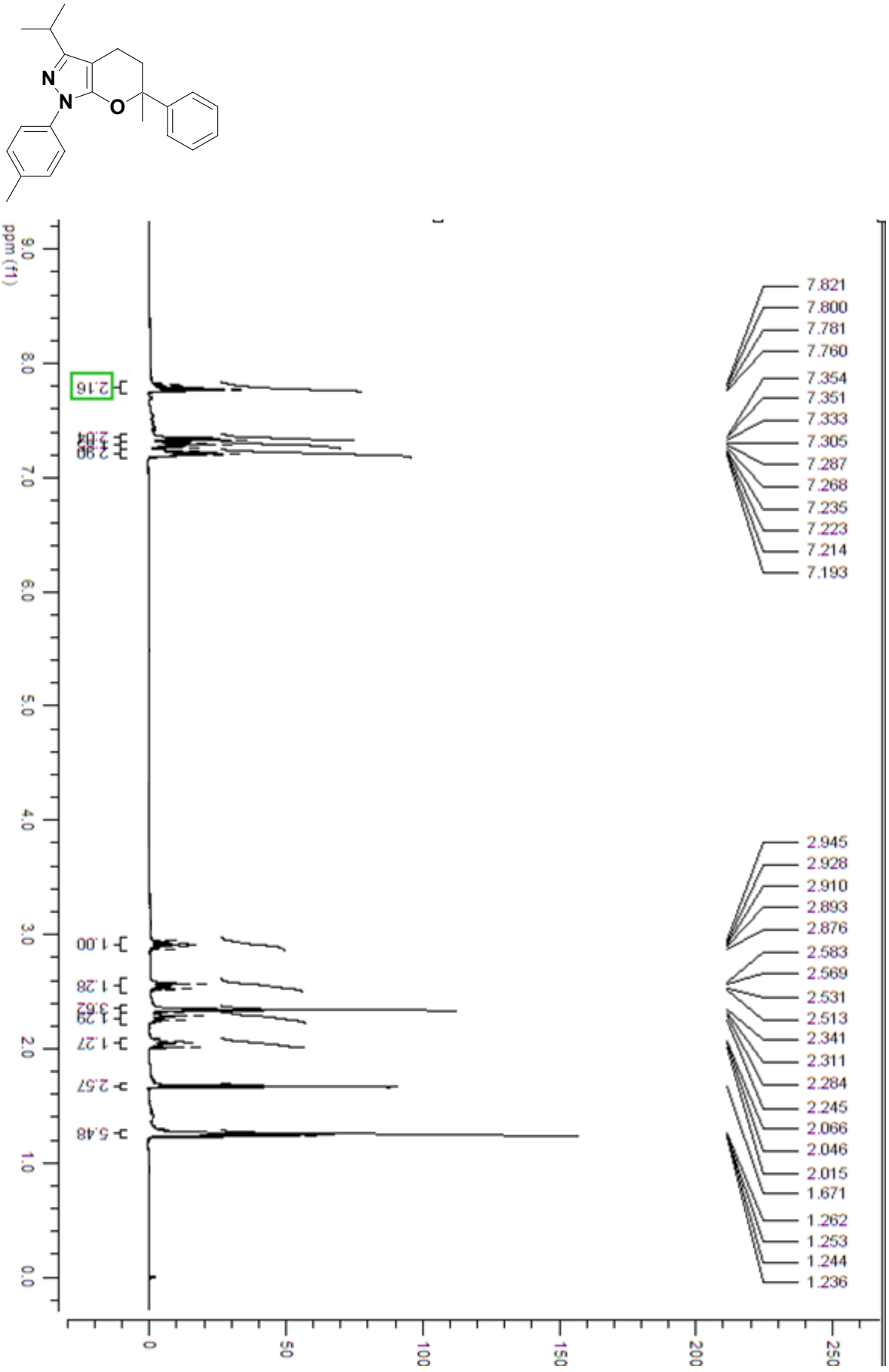
77.424
77.106
76.788
30.397
17.774
12.780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N
O
ppm (f1)
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.16
2.90
2.04
1.00
1.28
3.62
1.29
1.27
2.57
5.48
7.821
7.800
7.781
7.760
7.354
7.351
7.333
7.305
7.287
7.268
7.235
7.223
7.214
7.193
2.945
2.928
2.910
2.893
2.876
2.583
2.569
2.531
2.513
2.341
2.311
2.284
2.245
2.066
2.046
2.015
1.671
1.262
1.253
1.244
1.236
0
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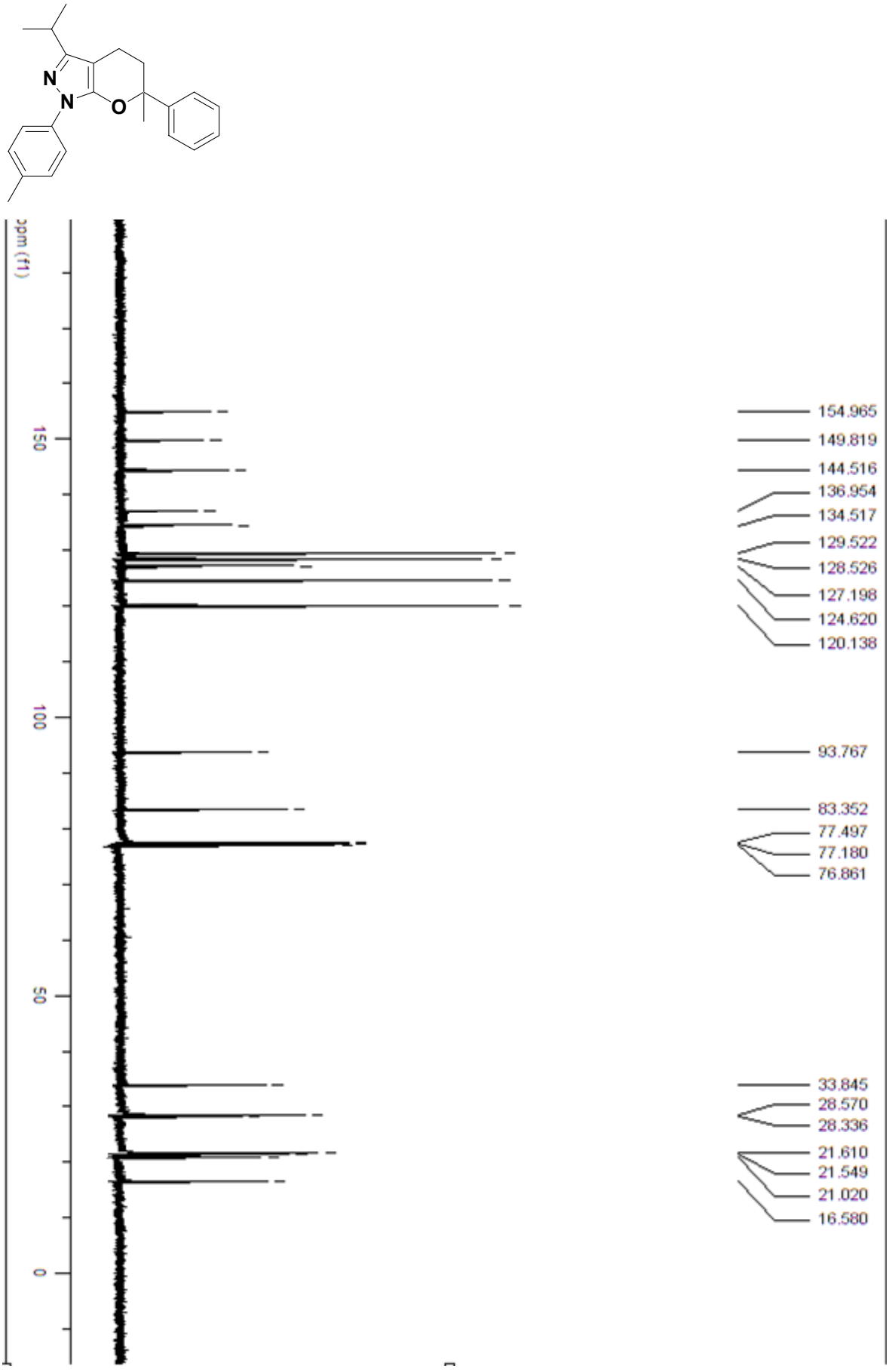
100
150
200
250


ppm (f1)
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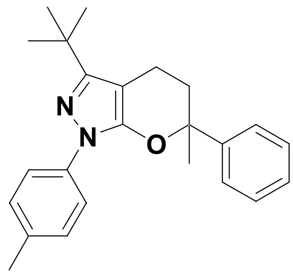
100
50
0
154.965
149.819
144.516
136.954
134.517
129.522
128.526
127.198
124.620
120.138
93.767
83.352
77.497
77.180
76.861
33.845
28.570
28.336
21.610
21.549
21.020
16.580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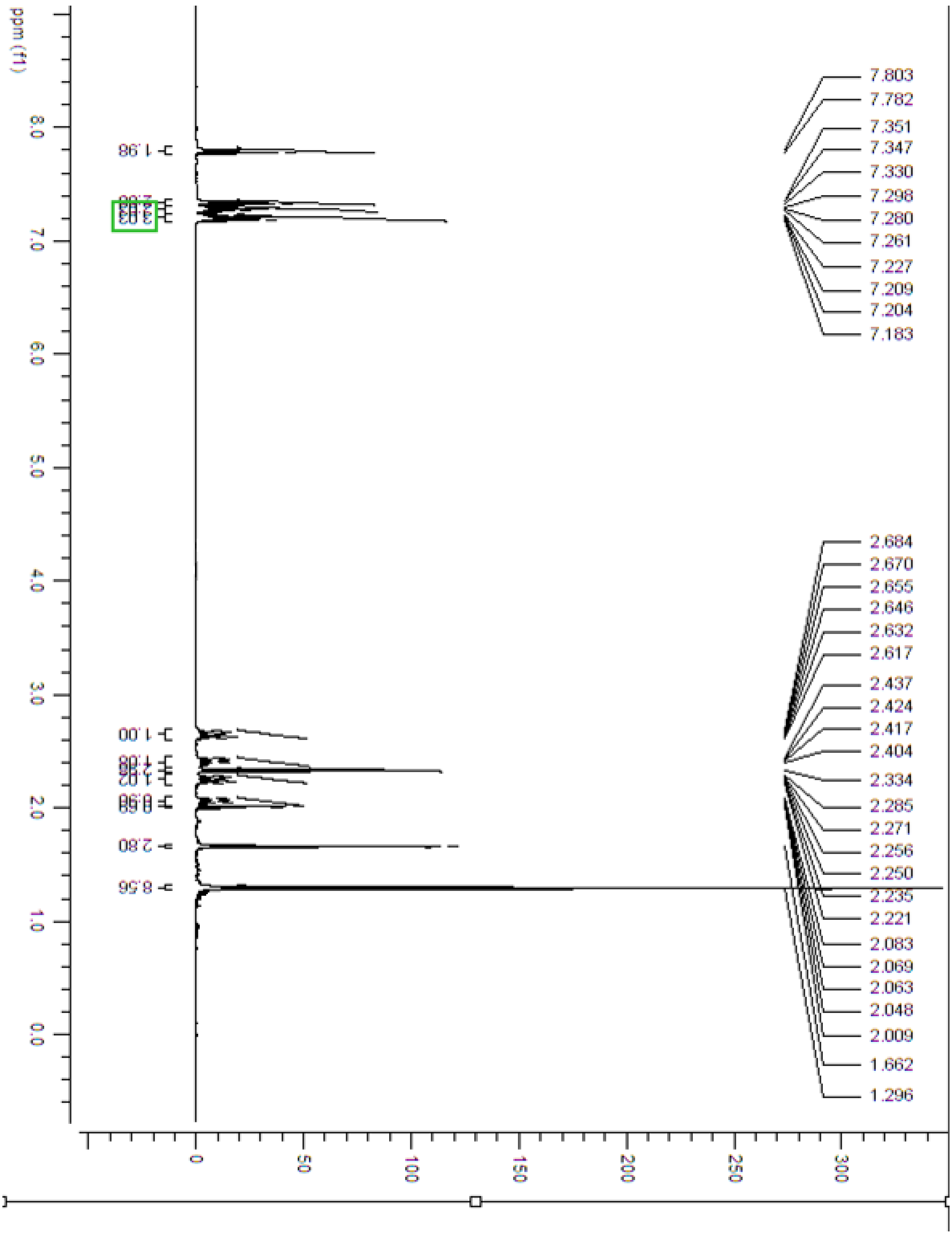
N
O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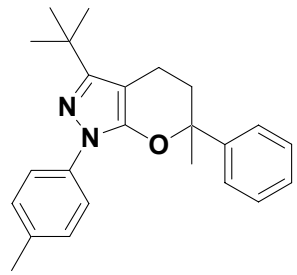
7.351
7.347
7.330
7.298
7.280
7.261
7.227
7.209
7.204
7.183
2.684
2.670
2.655
2.646
2.632
2.617
2.437
2.424
2.417
2.404
2.334
2.285
2.271
2.256
2.250
2.235
2.221
2.083
2.069
2.063
2.048
2.009
1.662
1.296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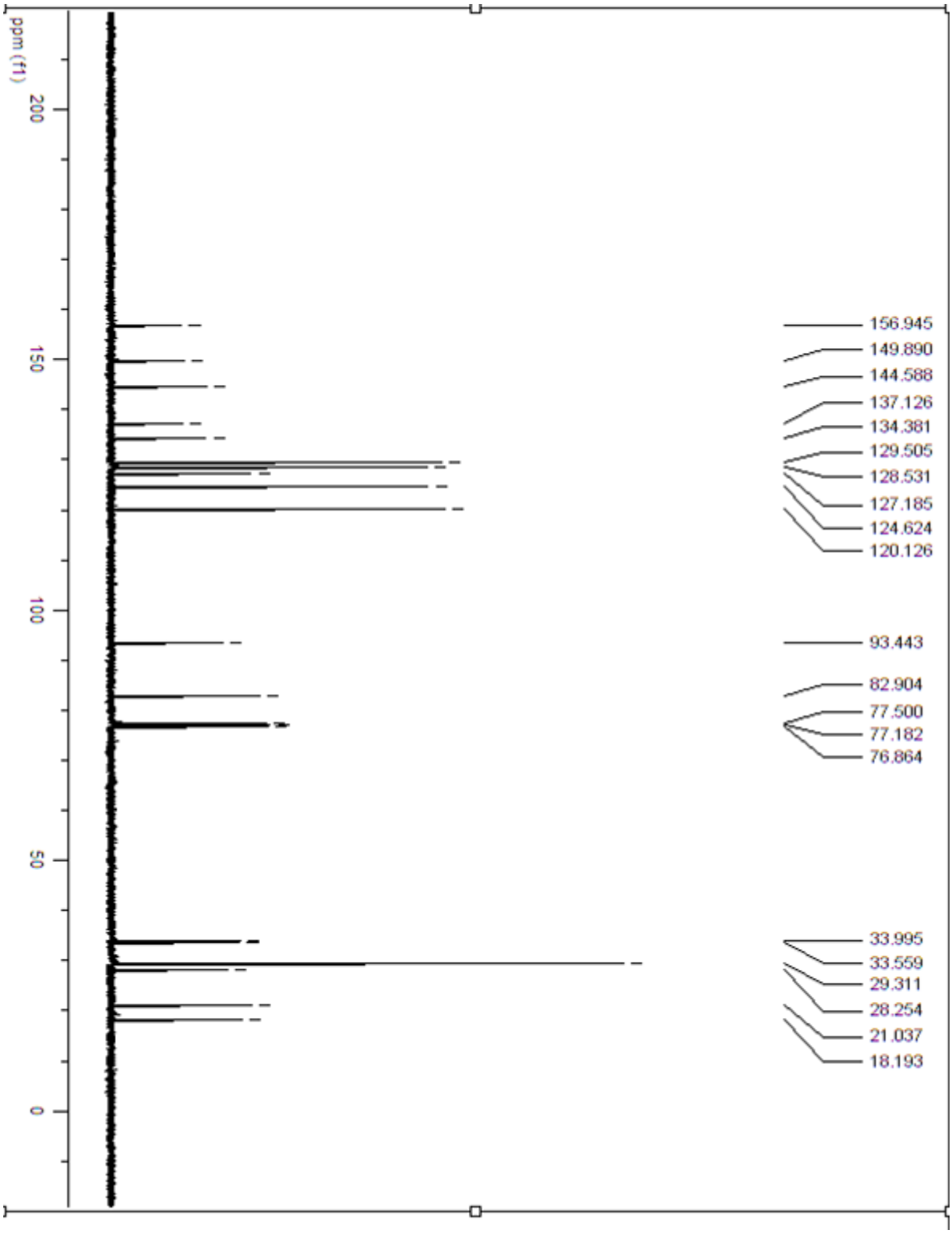
N
O


ppm (f1)
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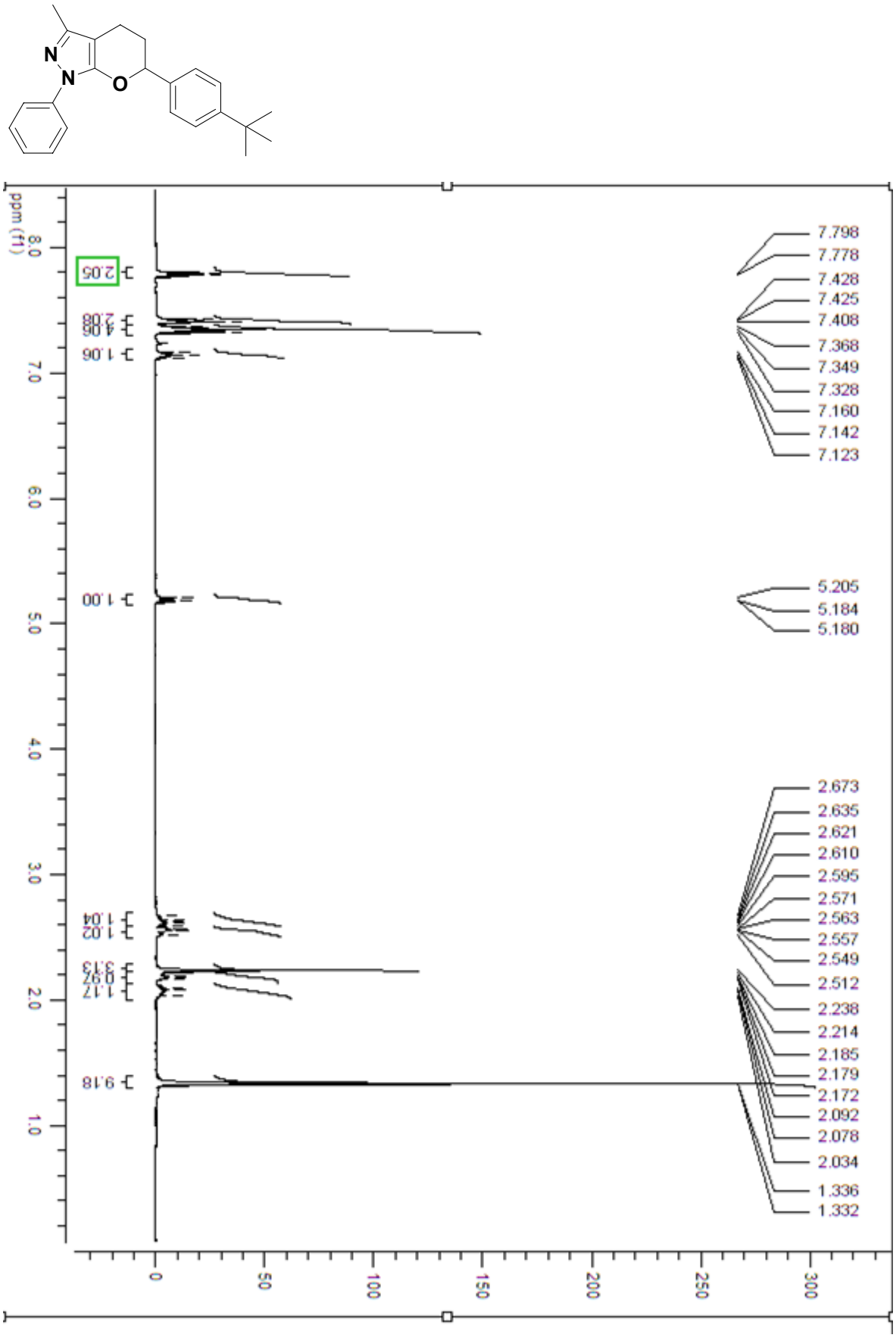
150
100
50
0
156.945
149.890
144.588
137.126
134.381
129.505
128.531
127.185
124.624
120.126
93.443
82.904
77.500
77.182
76.864
33.995
33.559
29.311
28.254
21.037
18.193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N
O
ppm (f1)
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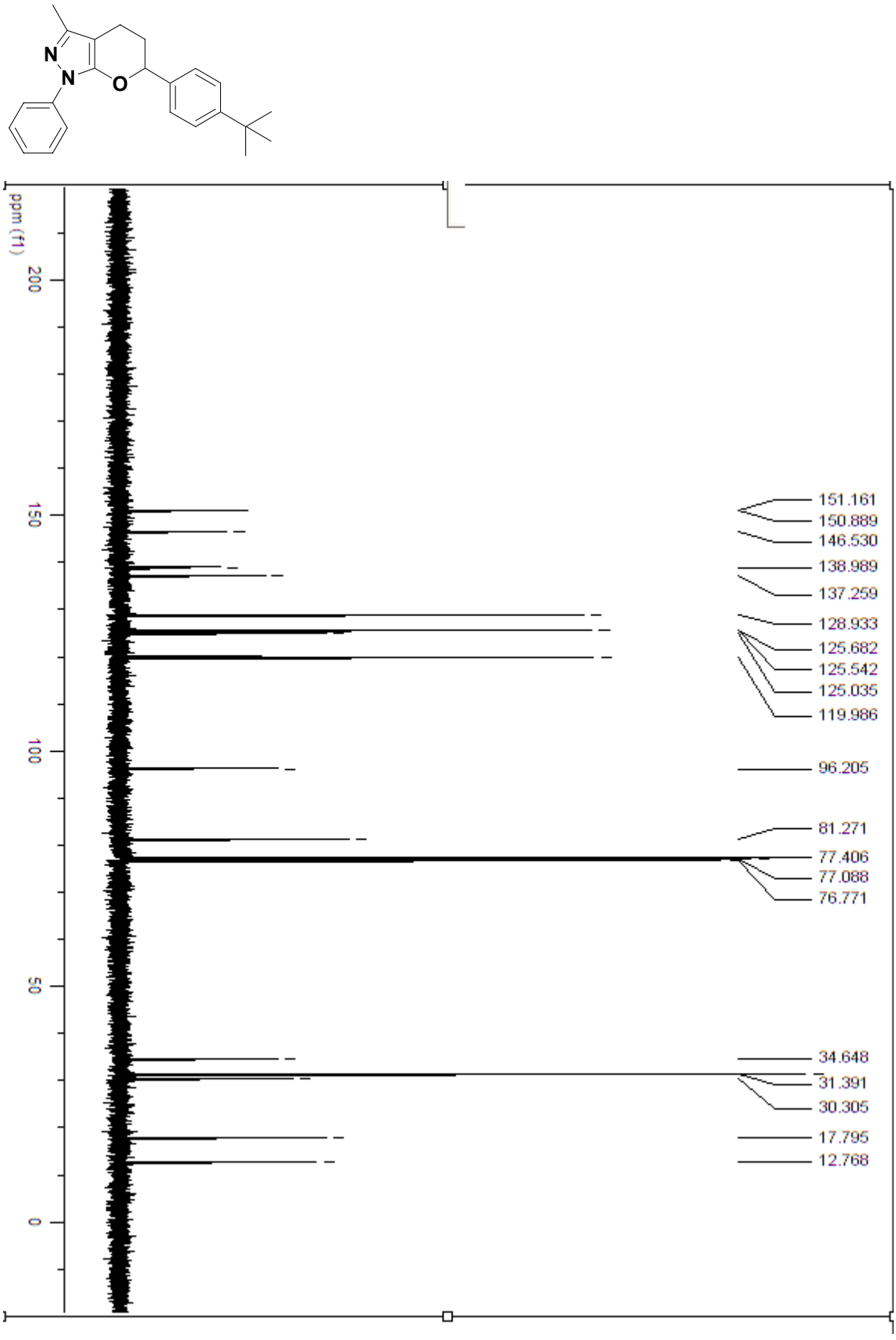
6.0
5.0
4.0
3.0
2.0
1.0
2.05
4.05
2.08
1.06
1.00
1.04
1.02
3.13
0.97
1.17
9.18
7.798
7.778
7.428
7.425
7.408
7.368
7.349
7.328
7.160
7.142
7.123
5.205
5.184
5.180
2.673
2.635
2.621
2.610
2.595
2.571
2.563
2.557
2.549
2.512
2.238
2.214
2.185
2.179
2.172
2.092
2.078
2.034
1.336
1.332
0
50
100
150
200
250
300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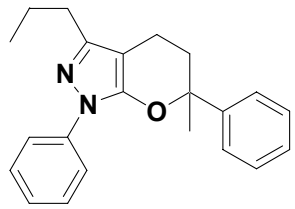
N
O
ppm (f1)
200
150
100
50
0
151.161
150.889
146.530
138.989
137.259
128.933
125.682
125.542
125.035
119.986
96.205
81.271
77.406
77.088
76.771
34.648
31.391
30.305
17.795
12.768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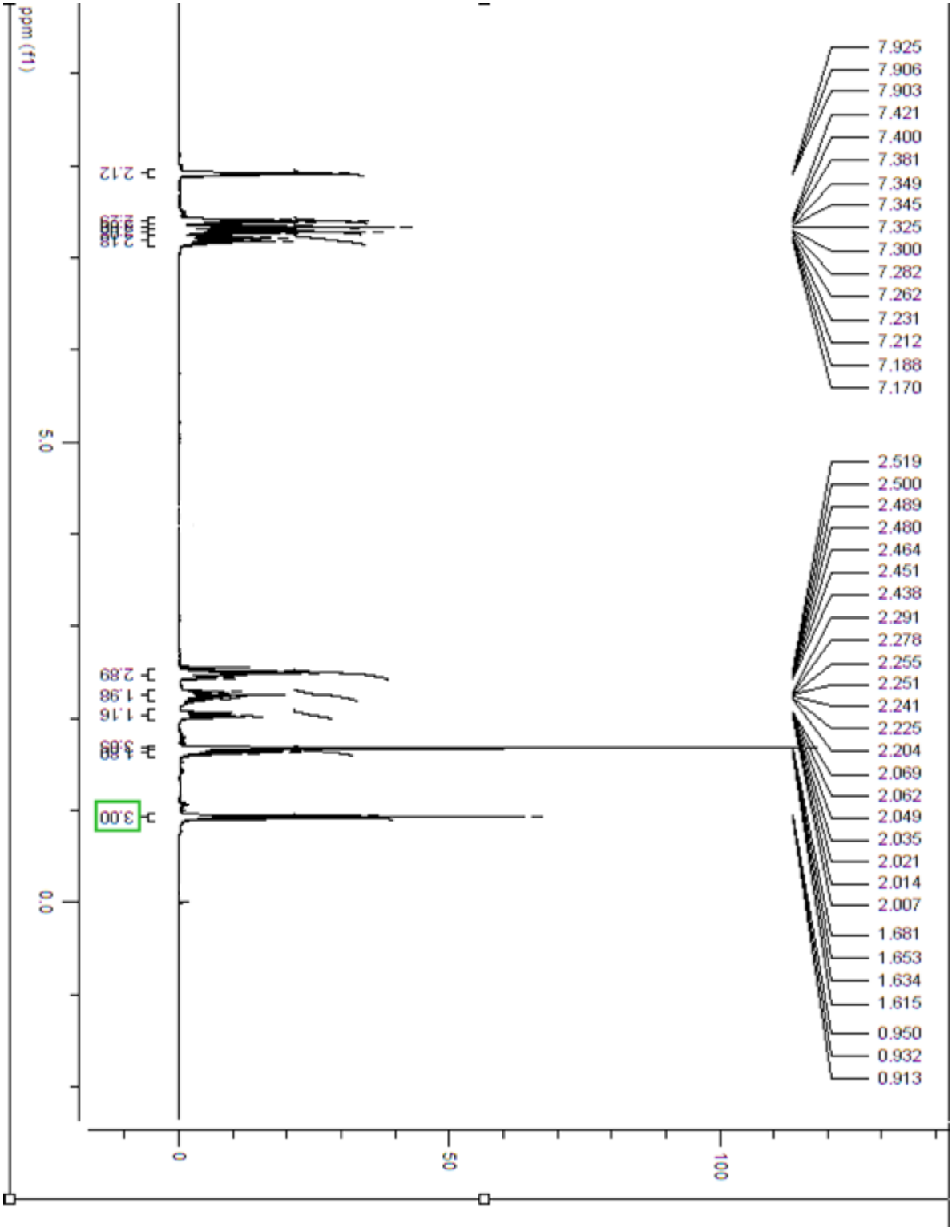
N
O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7.349
7.345
7.325
7.300
7.282
7.262
7.231
7.212
7.188
7.170
2.519
2.500
2.489
2.480
2.464
2.451
2.438
2.291
2.278
2.255
2.251
2.241
2.225
2.204
2.069
2.062
2.049
2.035
2.021
2.014
2.007
1.681
1.653
1.634
1.615
0.950
0.932
0.913
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50
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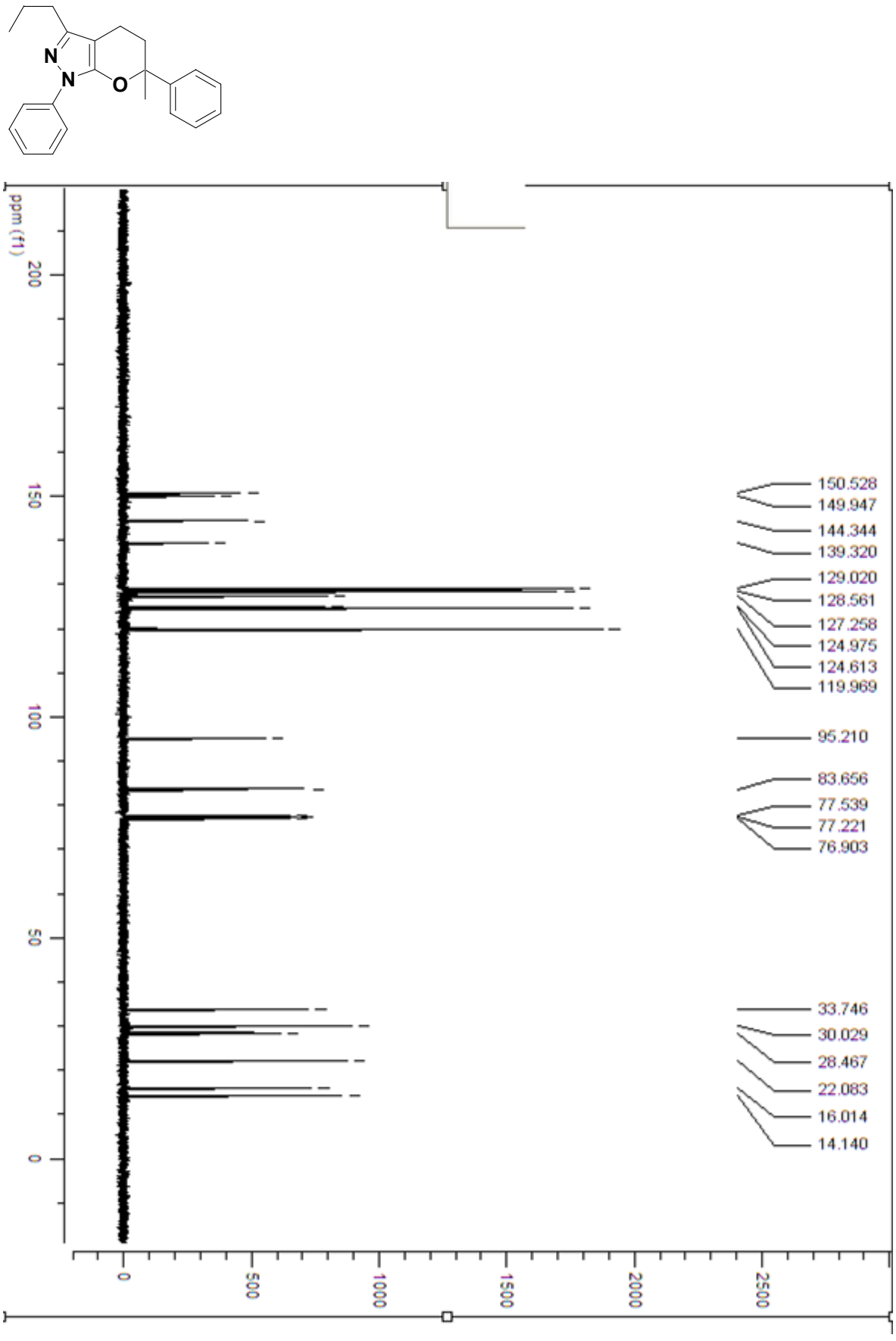
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N
O
ppm (f1)
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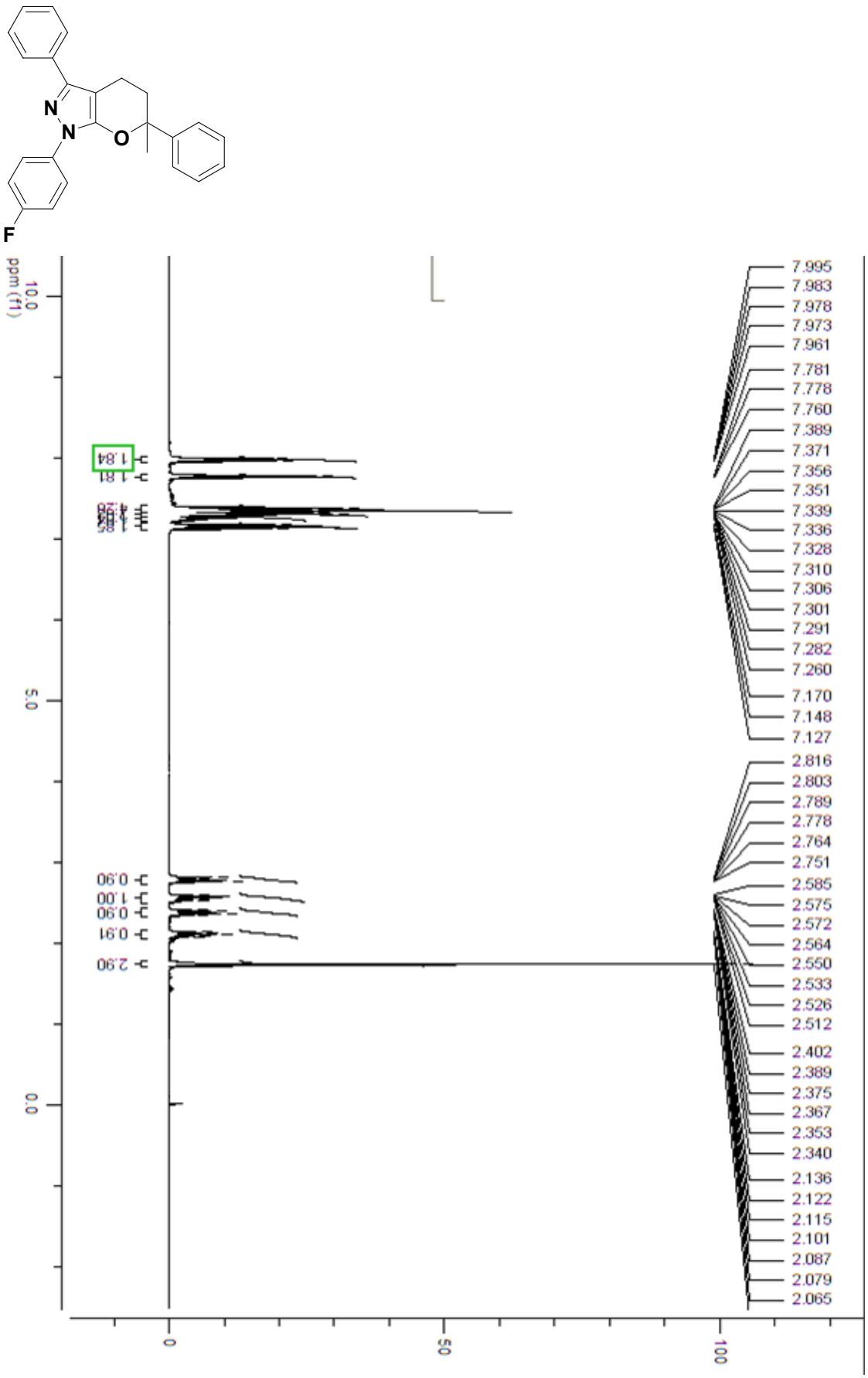
150
100
50
0
0
500
1000
1500
2000
2500
150.528
149.947
144.344
139.320
129.020
128.561
127.258
124.975
124.613
119.969
95.210
83.656
77.539
77.221
76.903
33.746
30.029
28.467
22.083
16.014
14.140


F
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N
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2.90
0.90
1.00
0.90
0.91
7.995
7.983
7.978
7.973
7.961
7.781
7.778
7.760
7.389
7.371
7.356
7.351
7.339
7.336
7.328
7.310
7.306
7.301
7.291
7.282
7.260
7.170
7.148
7.127
2.816
2.803
2.789
2.778
2.764
2.751
2.585
2.575
2.572
2.564
2.550
2.533
2.526
2.512
2.402
2.389
2.375
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2.087
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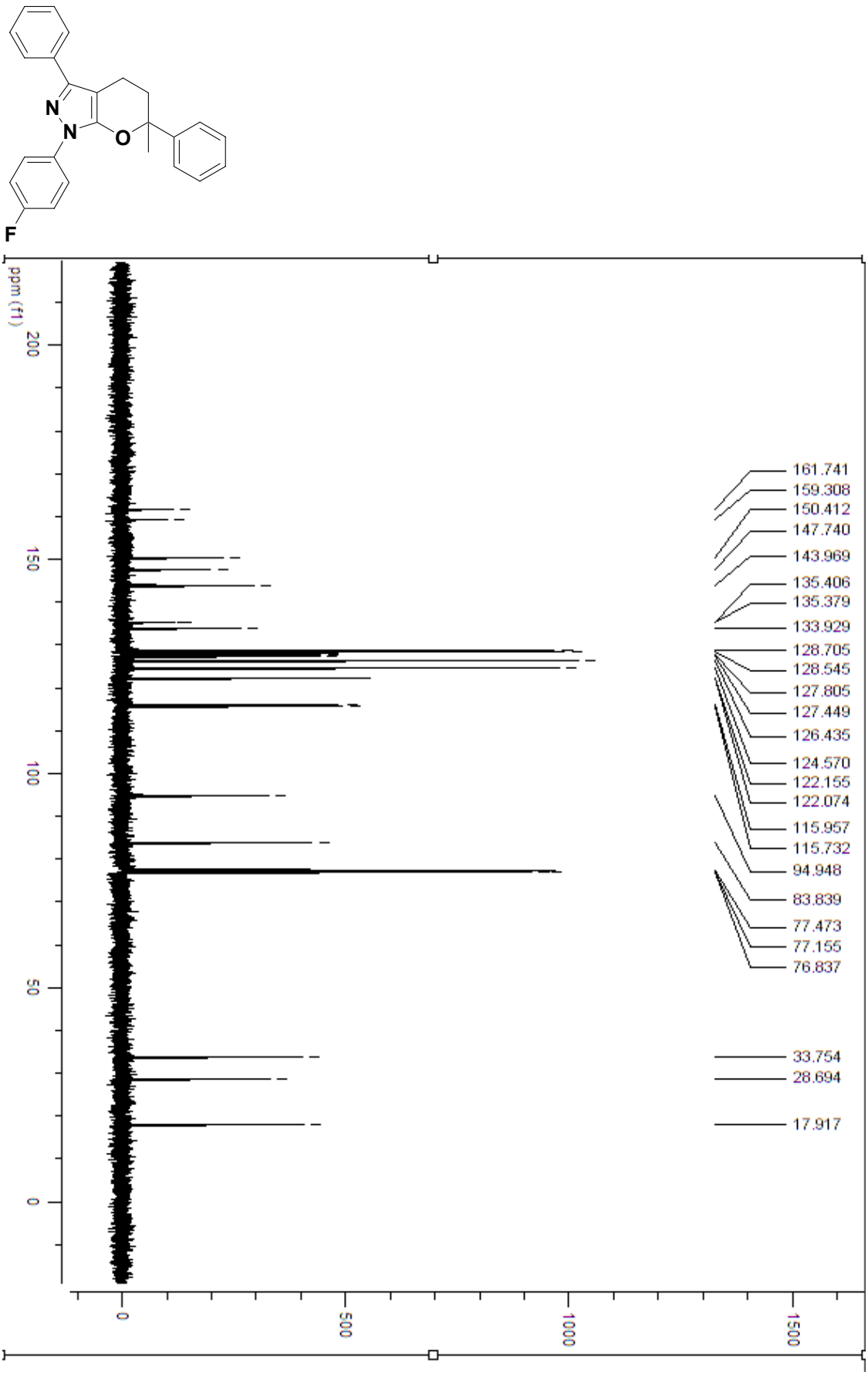
100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N
O
F
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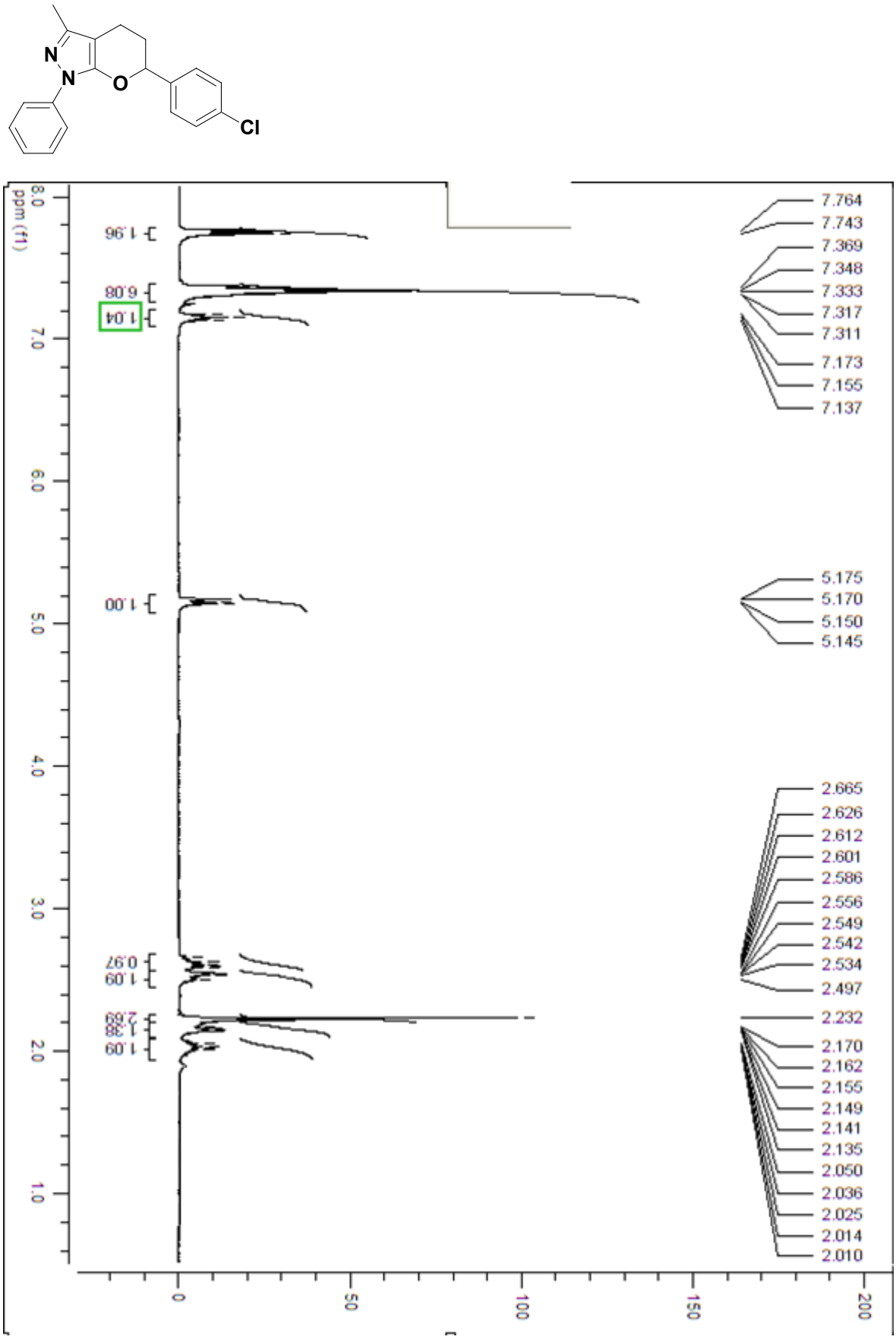
150
100
50
0
0
500
1000
1500
161.741
159.308
150.412
147.740
143.969
135.406
135.379
133.929
128.705
128.545
127.805
127.449
126.435
124.570
122.155
122.074
115.957
115.732
94.948
83.839
77.473
77.155
76.837
33.754
28.694
17.917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O
Cl
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6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
150
200
1.96
6.08
1.04
1.00
0.97
1.09
2.69
1.38
1.09
7.764
7.743
7.369
7.348
7.333
7.317
7.311
7.173
7.155
7.137
5.175
5.170
5.150
5.145
2.665
2.626
2.612
2.601
2.586
2.556
2.549
2.542
2.534
2.497
2.232
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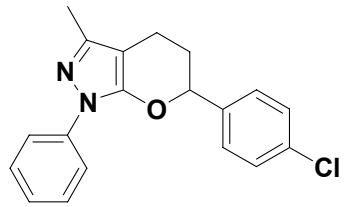
2.155
2.149
2.141
2.135
2.050
2.036
2.025
2.014
2.010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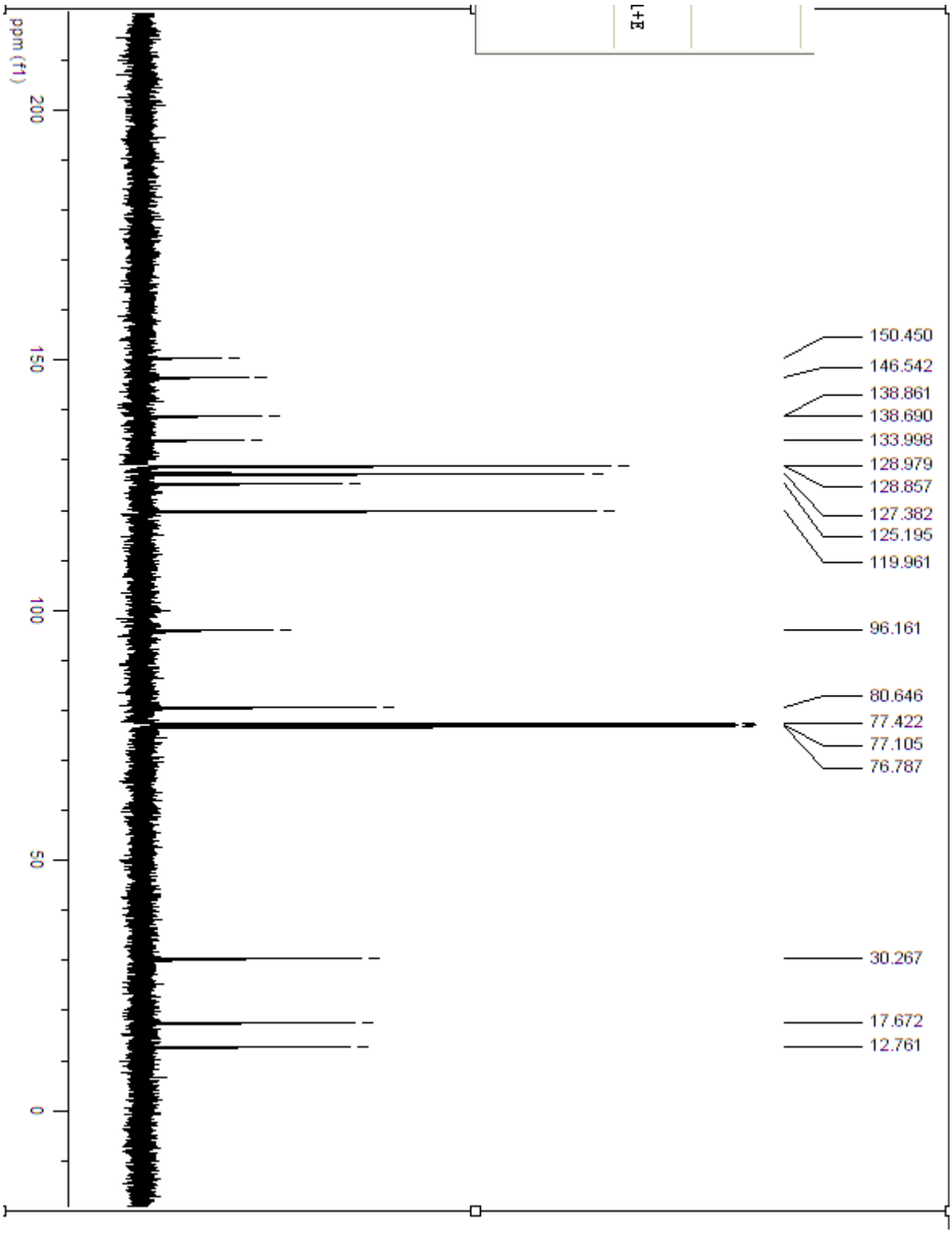
Cl


ppm (f1)
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150
100
50
0
150.450
146.542
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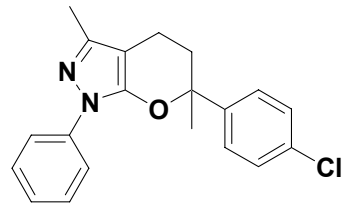
138.690
133.998
128.979
128.857
127.382
125.195
119.961
96.161
80.646
77.422
77.105
76.787
30.267
17.672
12.761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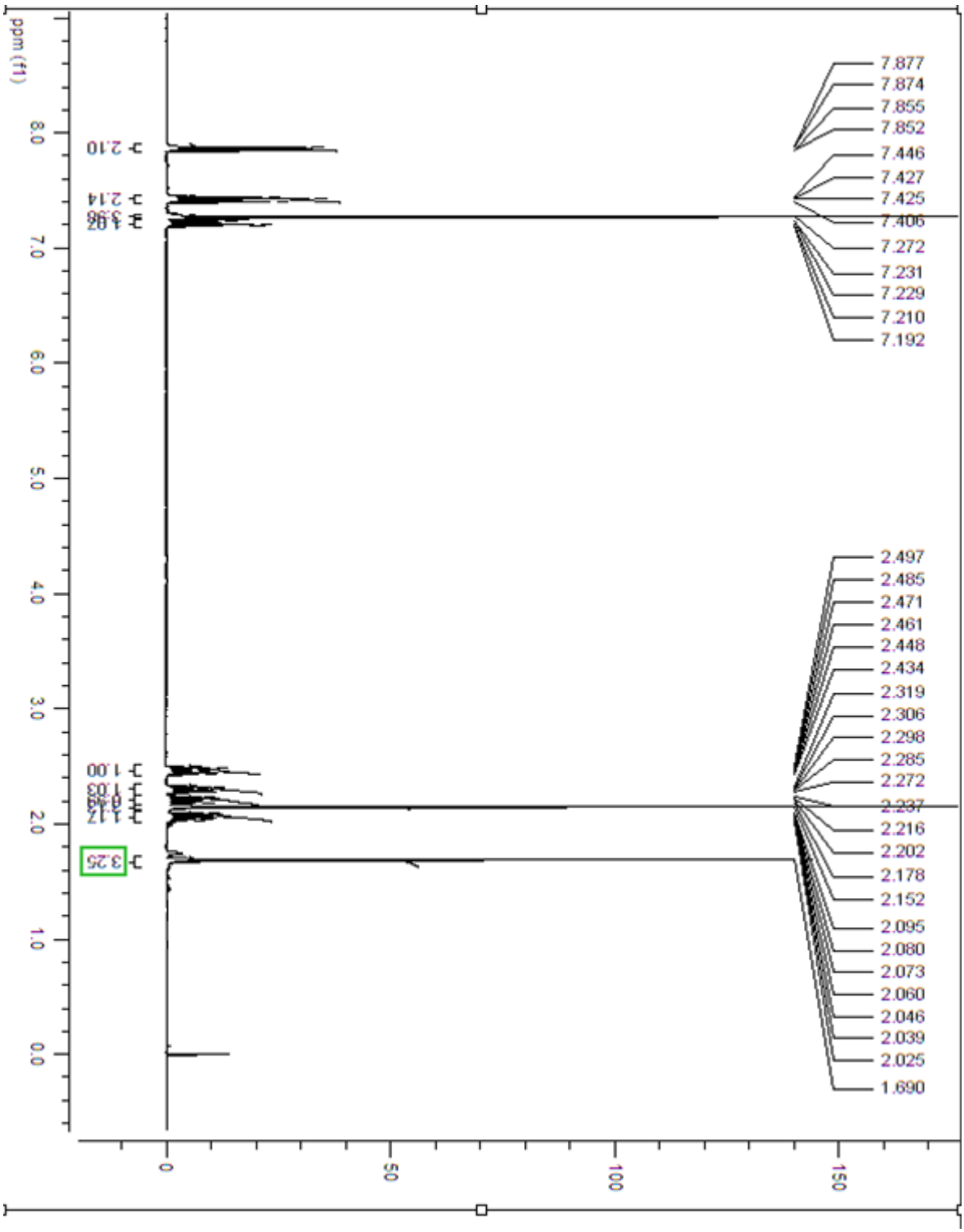
O
Cl


ppm (f1)
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6.0
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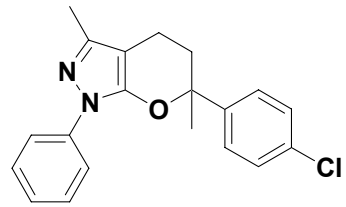
4.0
3.0
2.0
1.0
0.0
0
50
100
150
2.10
2.14
3.25
1.00
7.877
7.874
7.855
7.852
7.446
7.427
7.425
7.406
7.272
7.231
7.229
7.210
7.192
2.497
2.485
2.471
2.461
2.448
2.434
2.319
2.306
2.298
2.285
2.272
2.237
2.216
2.202
2.178
2.152
2.095
2.080
2.073
2.060
2.046
2.039
2.025
1.690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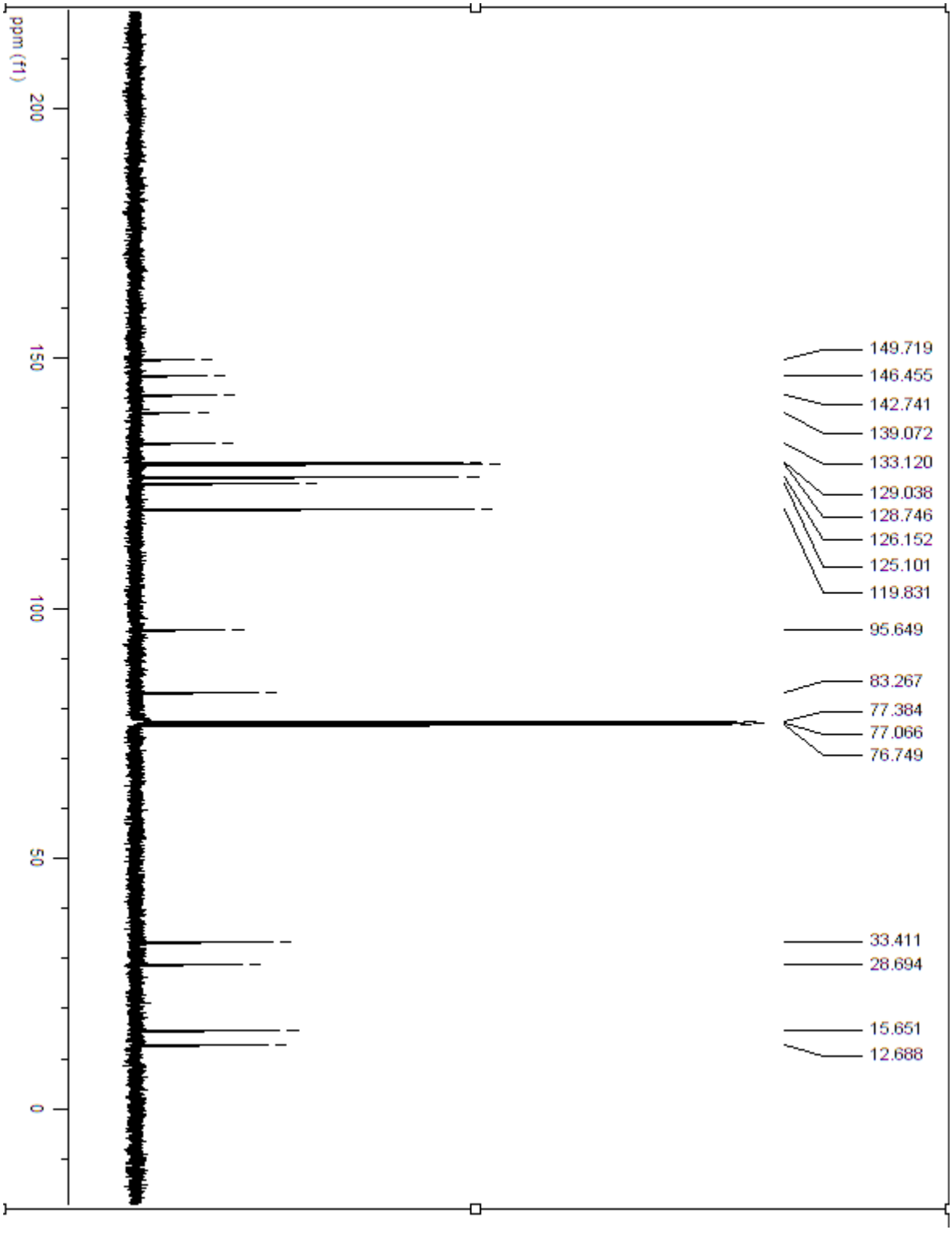
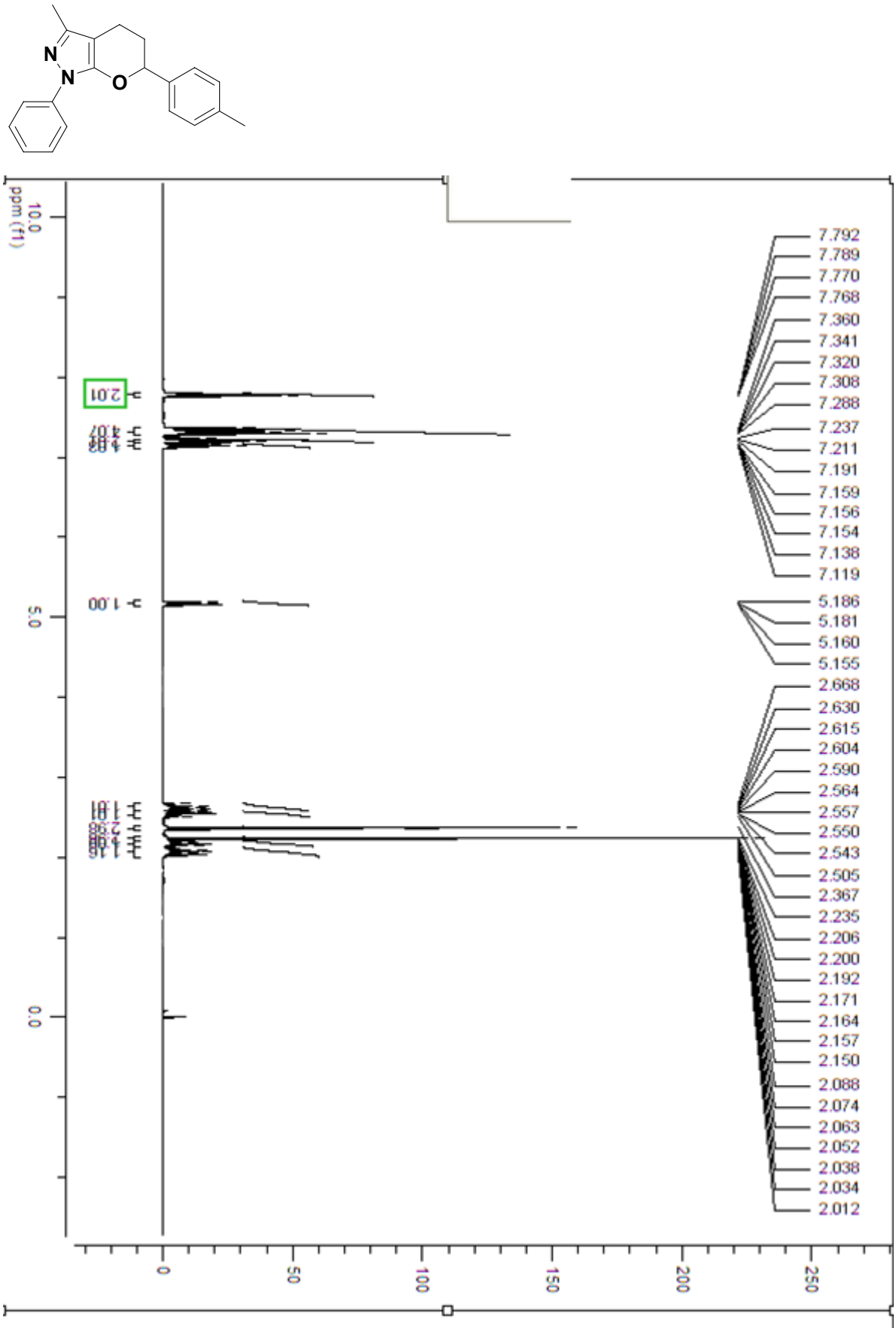
N
O
Cl


ppm (f1)
200
150
100
50
0
149.719
146.455
142.741
139.072
133.120
129.038
128.746
126.152
125.101
119.831
95.649
83.267
77.384
77.066
76.749
33.411
28.694
15.651
12.688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N
O
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ppm (f1)
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0.0
2.01
4.07
1.00
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7.789
7.770
7.768
7.360
7.341
7.320
7.308
7.288
7.237
7.211
7.191
7.159
7.156
7.154
7.138
7.119
5.186
5.181
5.160
5.155
2.668
2.630
2.615
2.604
2.590
2.564
2.557
2.550
2.543
2.505
2.367
2.235
2.206
2.200
2.192
2.171
2.164
2.157
2.150
2.088
2.074
2.063
2.052
2.038
2.034
2.012
0
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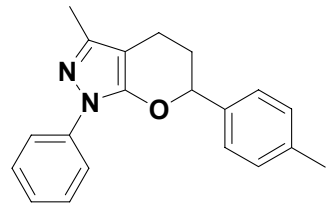
100
150
200
250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N
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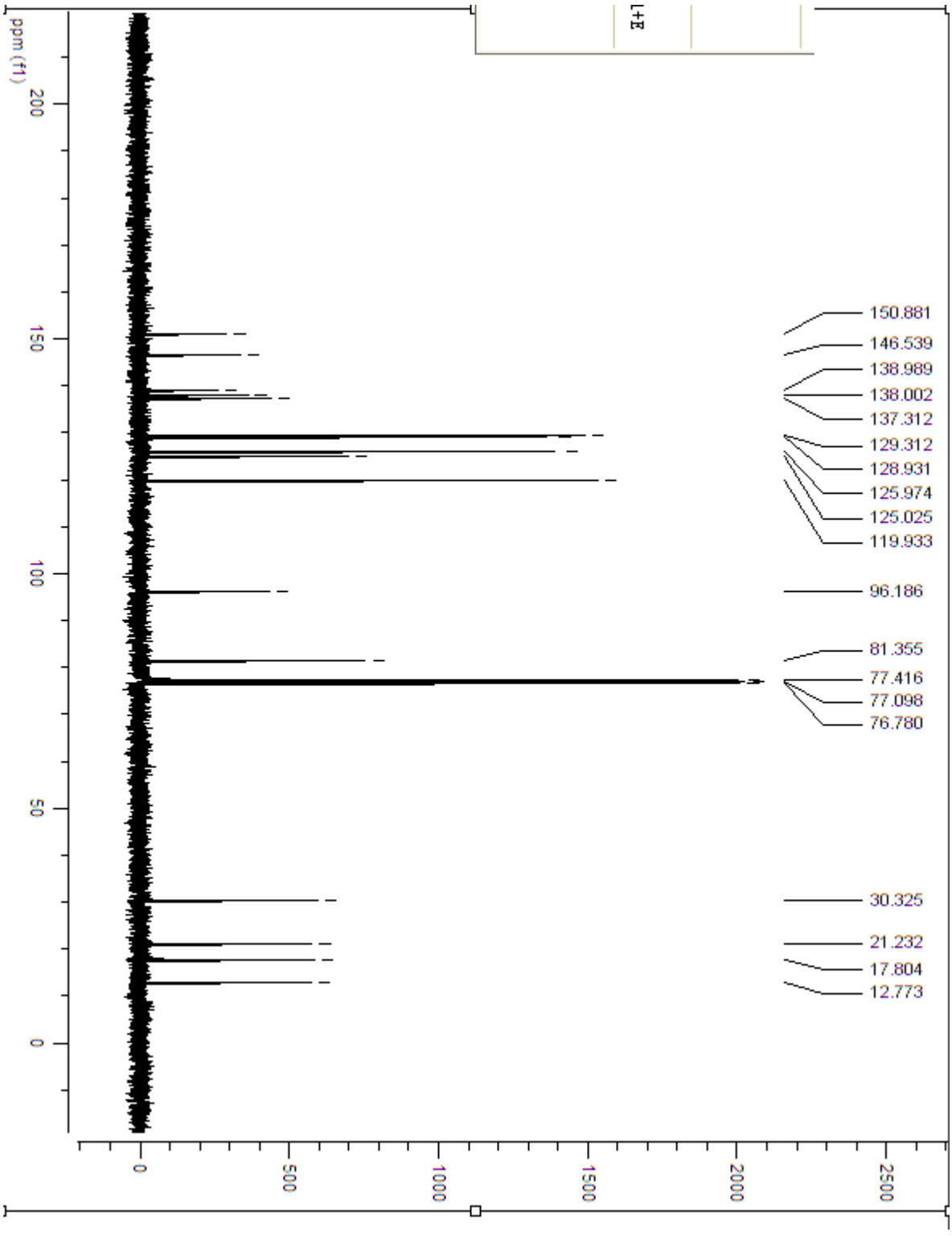
ppm (f1)
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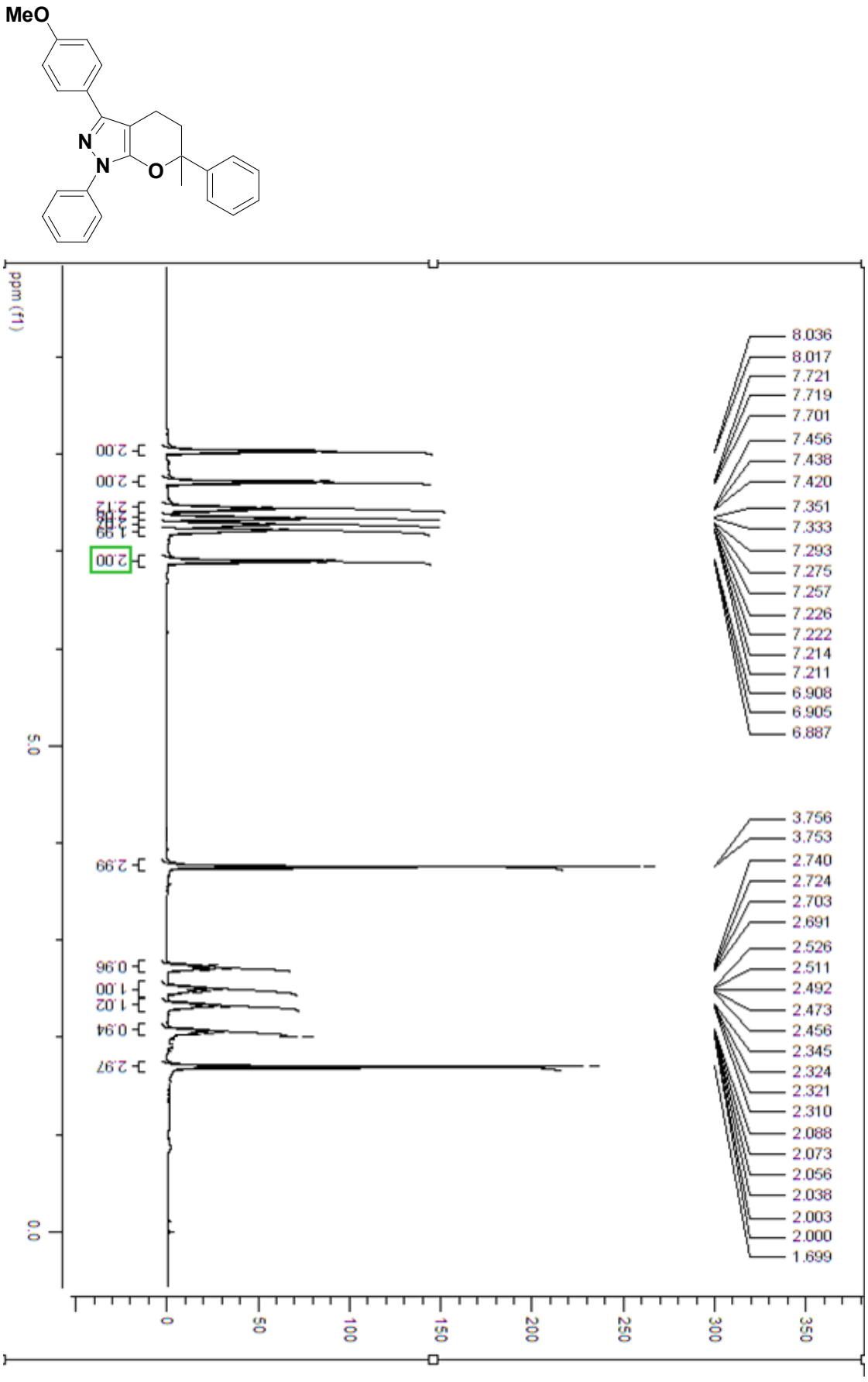
150
100
50
0
0
500
1000
1500
2000
2500
150.881
146.539
138.989
138.002
137.312
129.312
128.931
125.974
125.025
119.933
96.186
81.355
77.416
77.098
76.780
30.325
21.232
17.804
12.773


MeO
N
N
O
ppm (f1)
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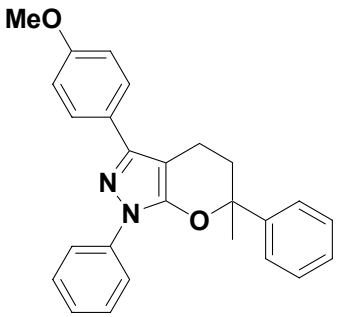
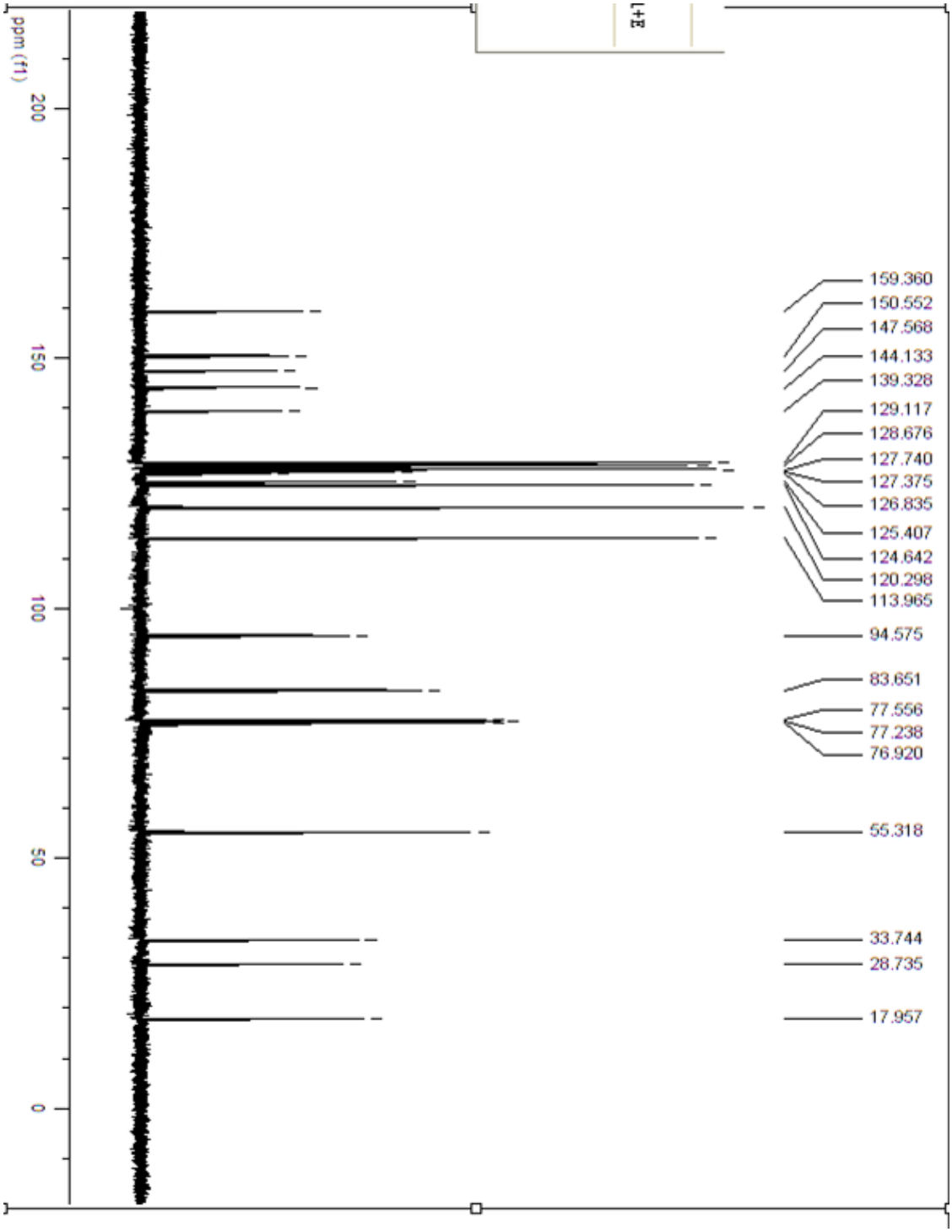
8.017
7.721
7.719
7.701
7.456
7.438
7.420
7.351
7.333
7.293
7.275
7.257
7.226
7.222
7.214
7.211
6.908
6.905
6.887
3.756
3.753
2.740
2.724
2.703
2.691
2.526
2.511
2.492
2.473
2.456
2.345
2.324
2.321
2.310
2.088
2.073
2.056
2.038
2.003
2.000
1.699
2.00
2.00
2.00
2.99
0.96
1.00
1.02
0.94
2.97
5.0
0.0
0
50
100
150
200
250
300
350


MeO
N
N
O


ppm (f1)
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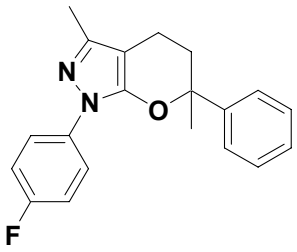
100
50
0
159.360
150.552
147.568
144.133
139.328
129.117
128.676
127.740
127.375
126.835
125.407
124.642
120.298
113.965
94.575
83.651
77.556
77.238
76.920
55.318
33.744
28.735
17.957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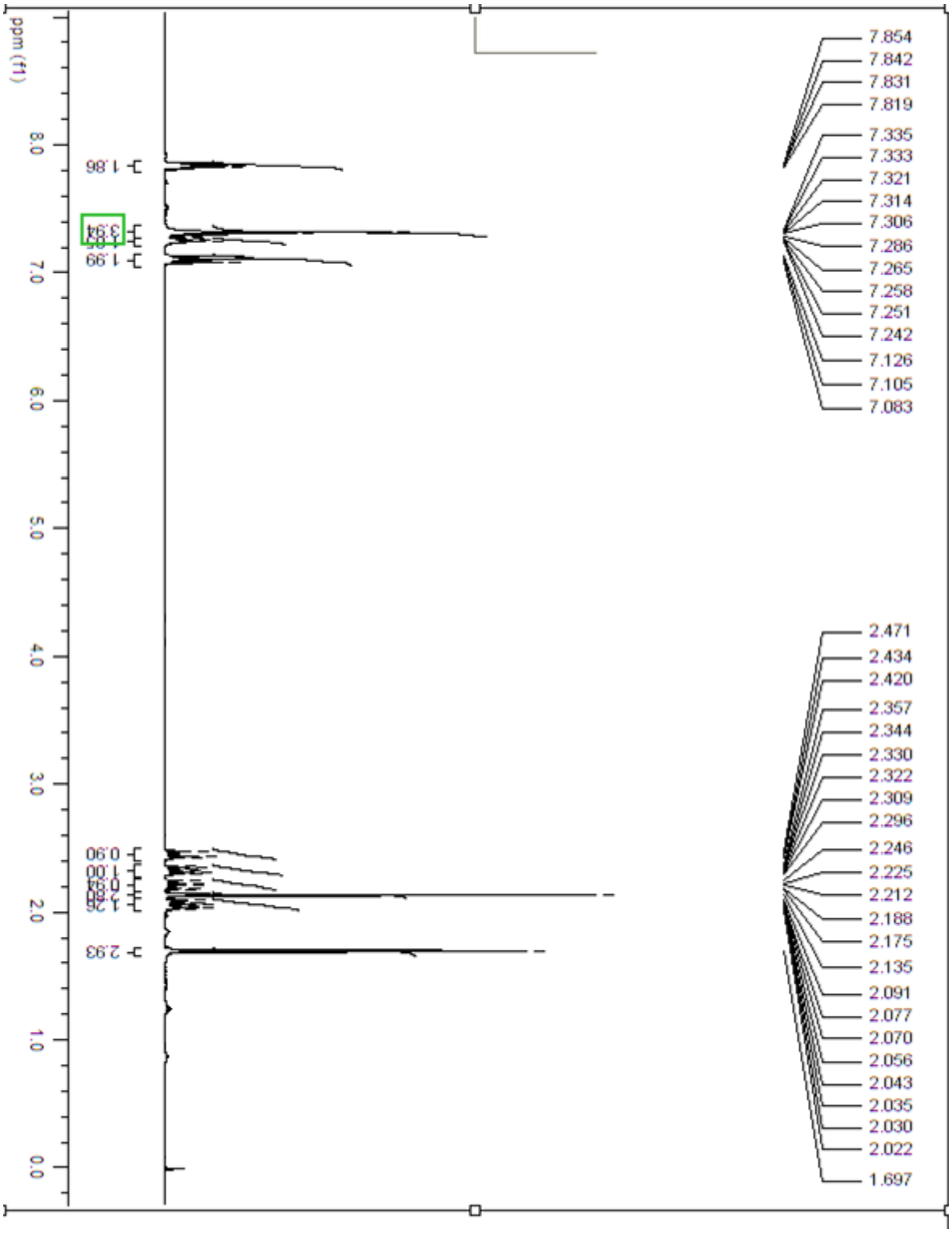
N
O
F


ppm (f1)
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.86
3.92
1.99
0.90
1.00
2.93
7.854
7.842
7.831
7.819
7.335
7.333
7.321
7.314
7.306
7.286
7.265
7.258
7.251
7.242
7.126
7.105
7.083
2.471
2.434
2.420
2.357
2.344
2.330
2.322
2.309
2.296
2.246
2.225
2.212
2.188
2.175
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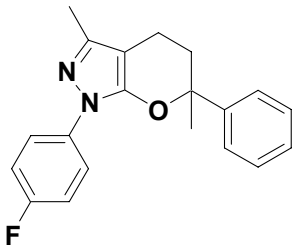
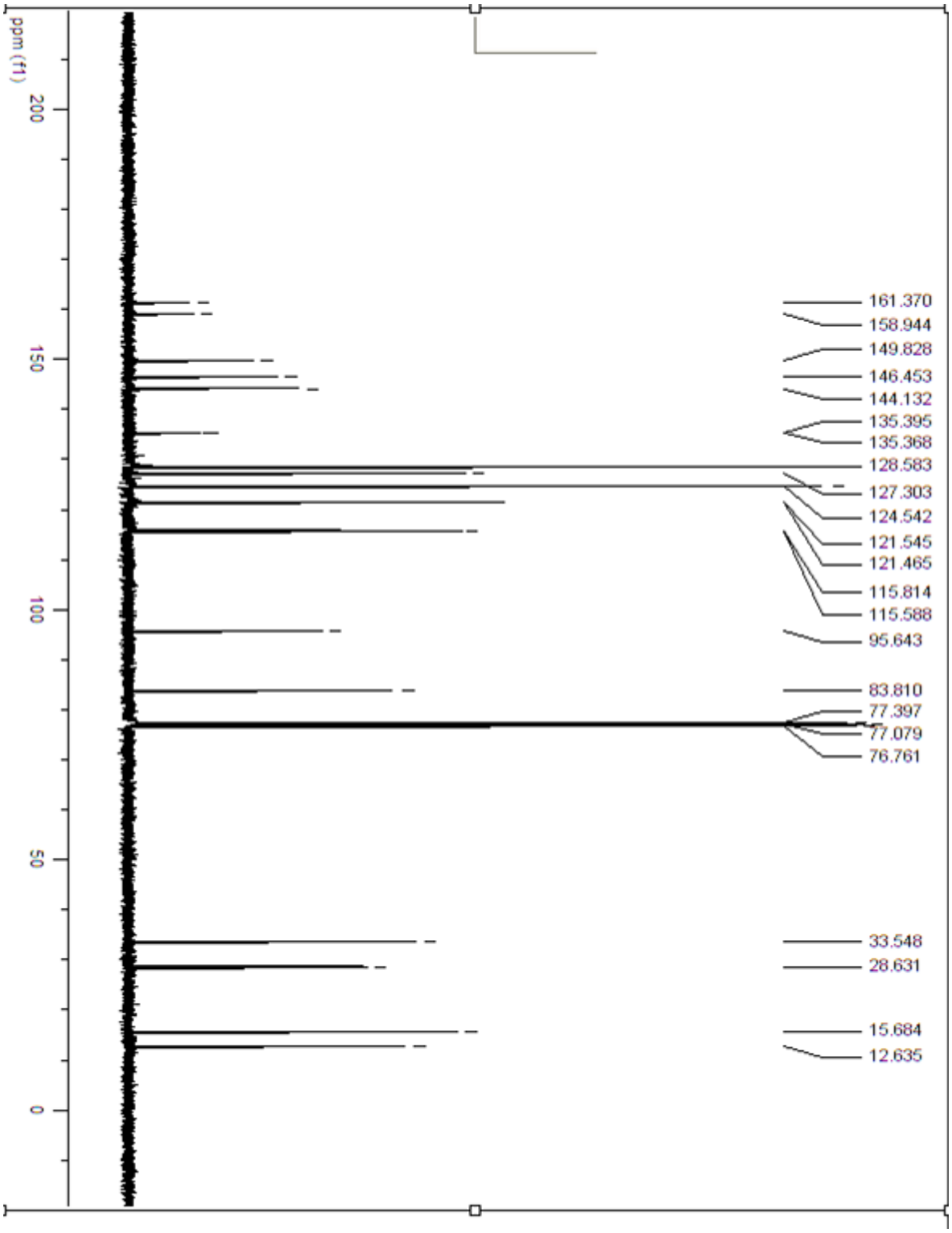
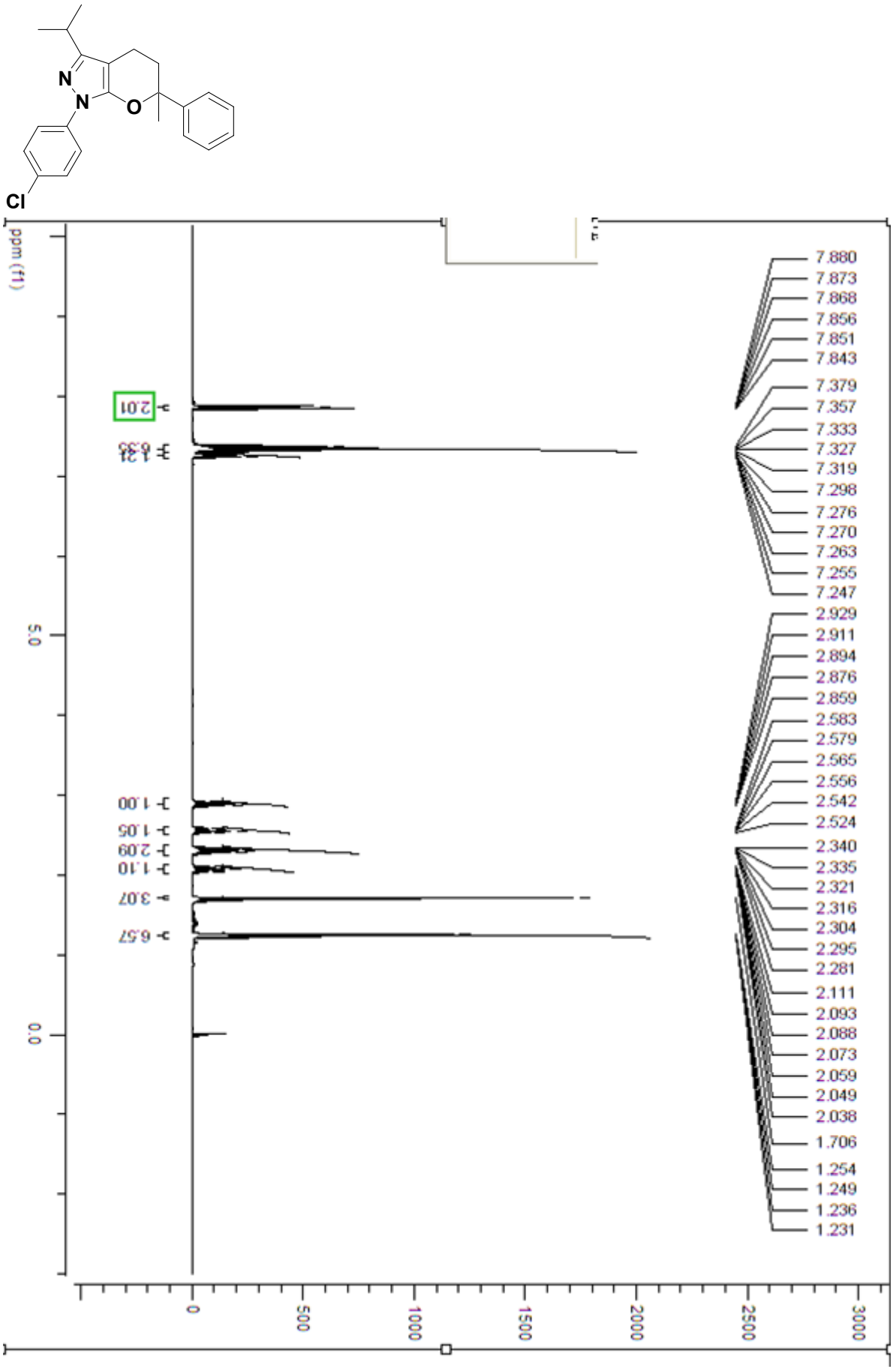
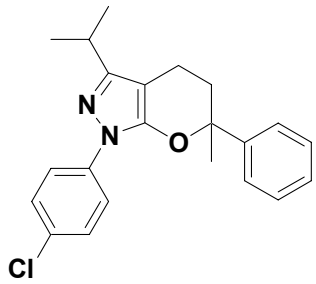
2.056
2.043
2.035
2.030
2.022
1.697


N
N
O
F


ppm (f1)
200
150
100
50
0
161.370
158.944
149.828
146.453
144.132
135.395
135.368
128.583
127.303
124.542
121.545
121.465
115.814
115.588
95.643
83.810
77.397
77.079
76.761
33.548
28.631
15.684
12.635


N
N
O
Cl
ppm (f1)
7.880
7.873
7.868
7.856
7.851
7.843
7.379
7.357
7.333
7.327
7.319
7.298
7.276
7.270
7.263
7.255
7.247
2.929
2.911
2.894
2.876
2.859
2.583
2.579
2.565
2.556
2.542
2.524
2.340
2.335
2.321
2.316
2.304
2.295
2.281
2.111
2.093
2.088
2.073
2.059
2.049
2.038
1.706
1.254
1.249
1.236
1.231
2.01
6.35
1.00
1.05
2.09
1.10
3.07
6.57
5.0
0.0
0
500
1000
1500
2000
2500
3000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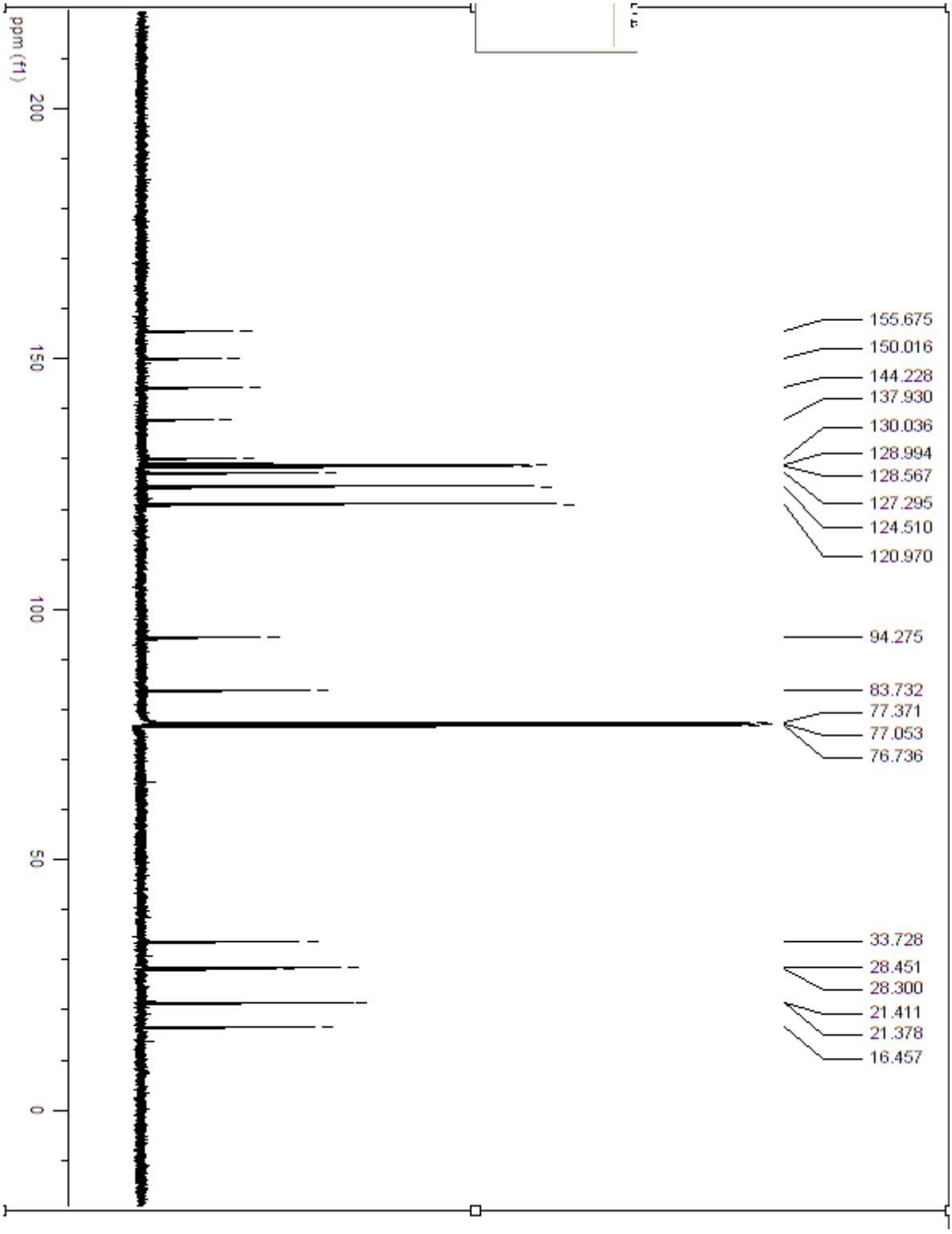
N
O
Cl


ppm (f1)
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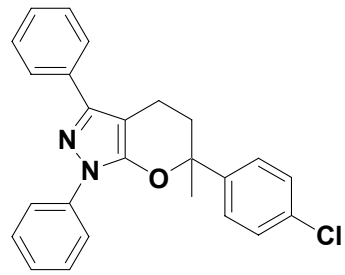
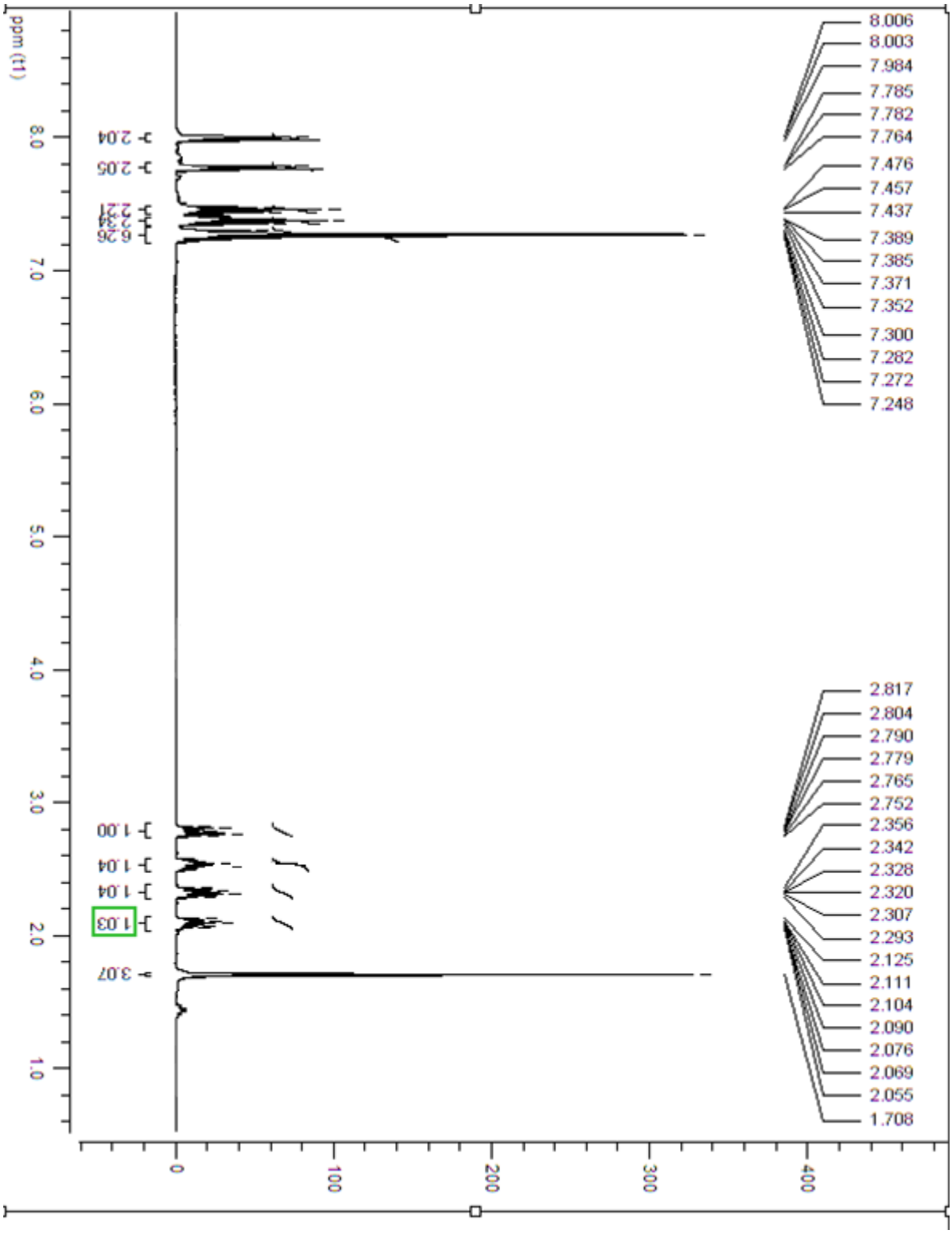
150
100
50
0
155.675
150.016
144.228
137.930
130.036
128.994
128.567
127.295
124.510
120.970
94.275
83.732
77.371
77.053
76.736
33.728
28.451
28.300
21.411
21.378
16.457


N
N
O
Cl


ppm (t1)
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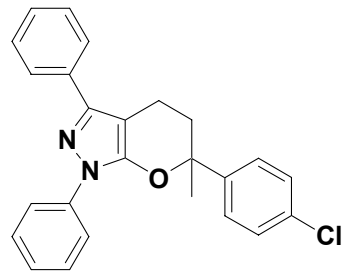
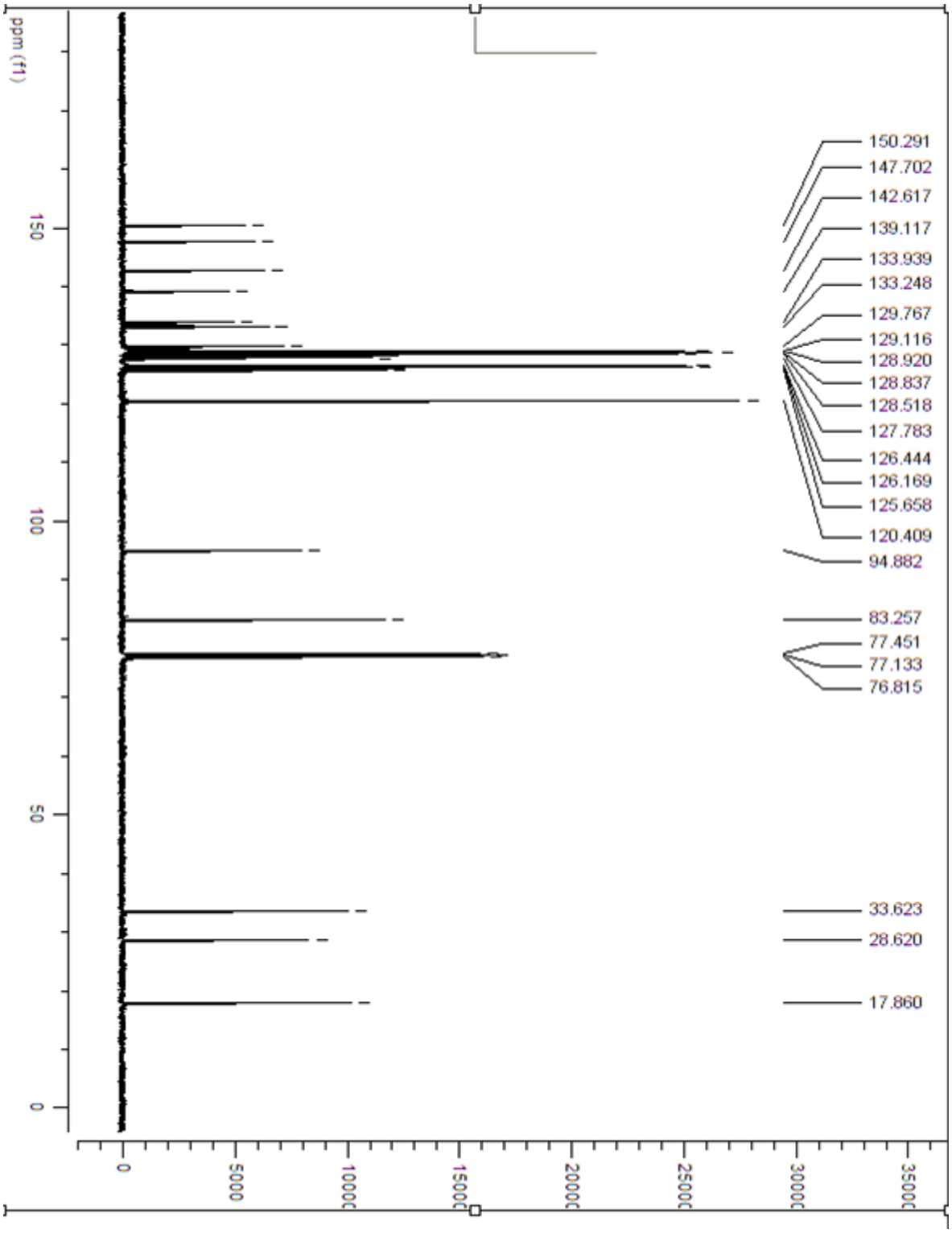
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
100
200
300
400
2.04
2.05
6.26
1.00
1.04
1.04
1.03
3.07
8.006
8.003
7.984
7.785
7.782
7.764
7.476
7.457
7.437
7.389
7.385
7.371
7.352
7.300
7.282
7.272
7.248
2.817
2.804
2.790
2.779
2.765
2.752
2.356
2.342
2.328
2.320
2.307
2.293
2.125
2.111
2.104
2.090
2.076
2.069
2.055
1.708


N
N
O
Cl


ppm (f1)
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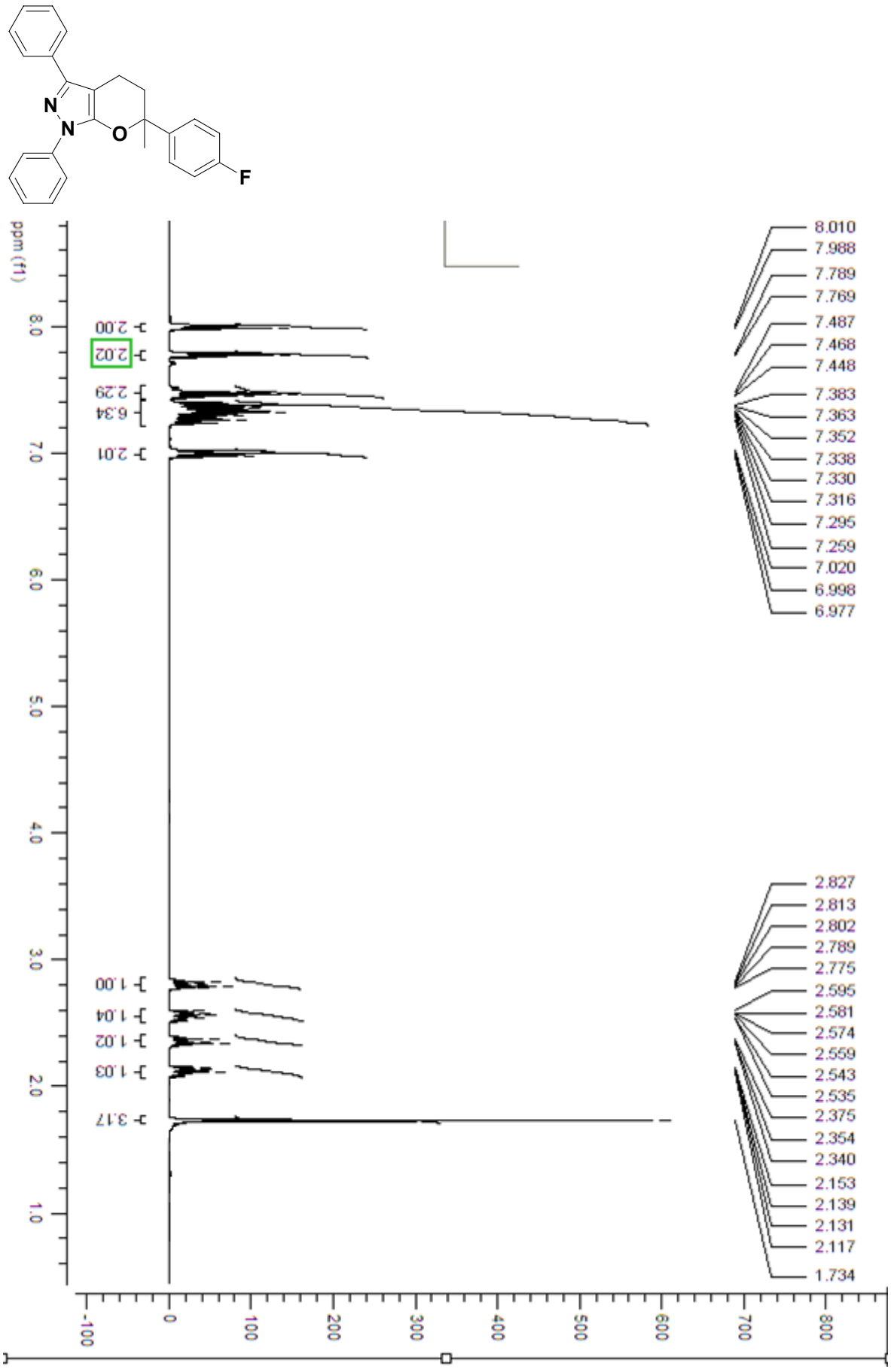
100
50
0
0
5000
10000
15000
20000
25000
30000
35000
150.291
147.702
142.617
139.117
133.939
133.248
129.767
129.116
128.920
128.837
128.518
127.783
126.444
126.169
125.658
120.409
94.882
83.257
77.451
77.133
76.815
33.623
28.620
17.860


N
N
O
F
ppm (f1)
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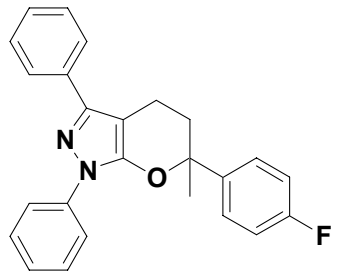
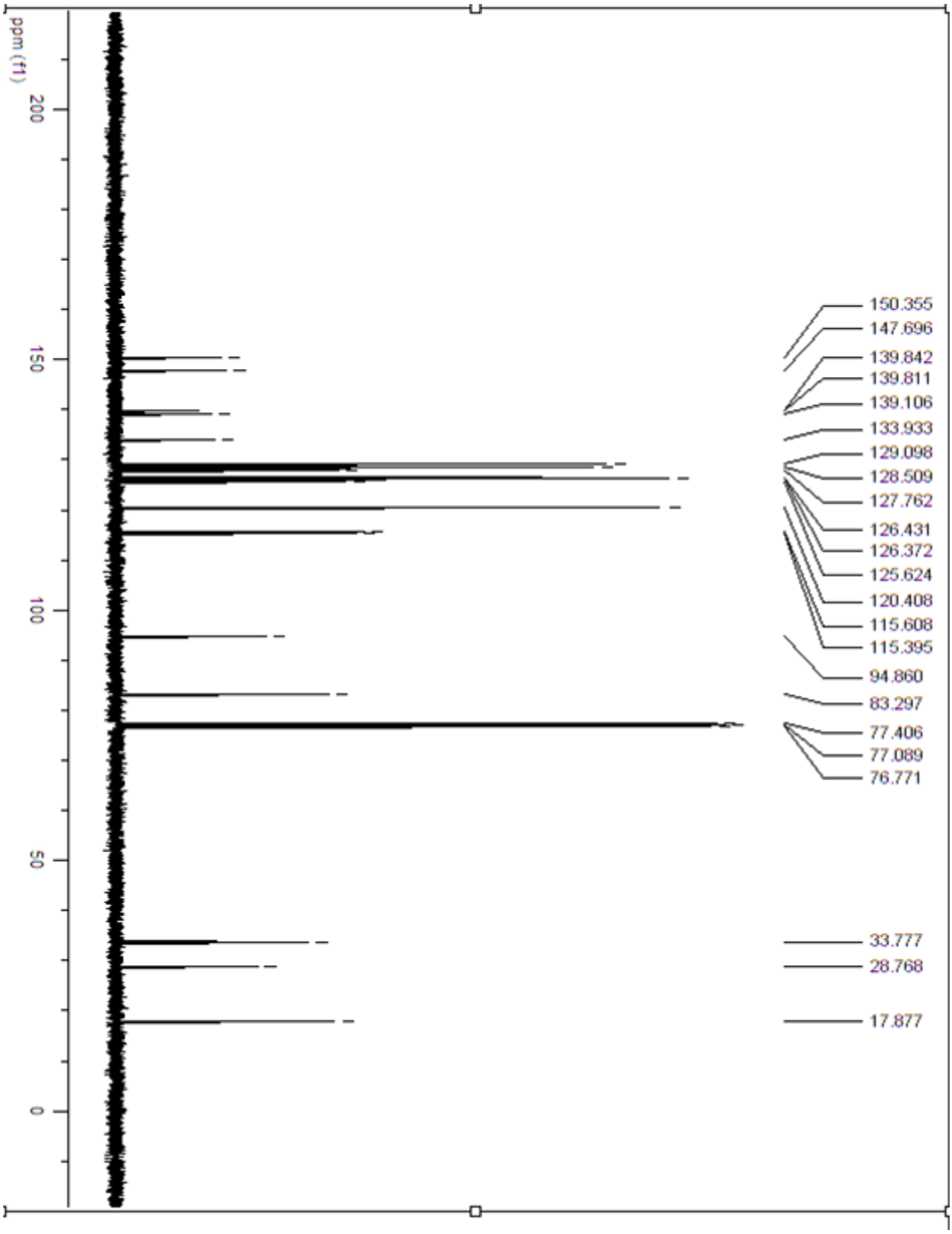
7.0
6.0
5.0
4.0
3.0
2.0
1.0
2.00
2.02
2.29
6.34
2.01
1.00
1.04
1.02
1.03
3.17
8.010
7.988
7.789
7.769
7.487
7.468
7.448
7.383
7.363
7.352
7.338
7.330
7.316
7.295
7.259
7.020
6.998
6.977
2.827
2.813
2.802
2.789
2.775
2.595
2.581
2.574
2.559
2.543
2.535
2.375
2.354
2.340
2.153
2.139
2.131
2.117
1.734
-100
0
100
200
300
400
500
600
700
800


N
N
O
F


ppm (f1)
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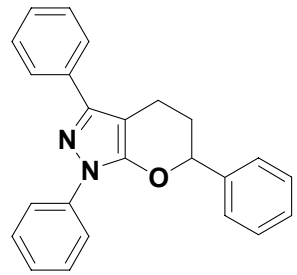
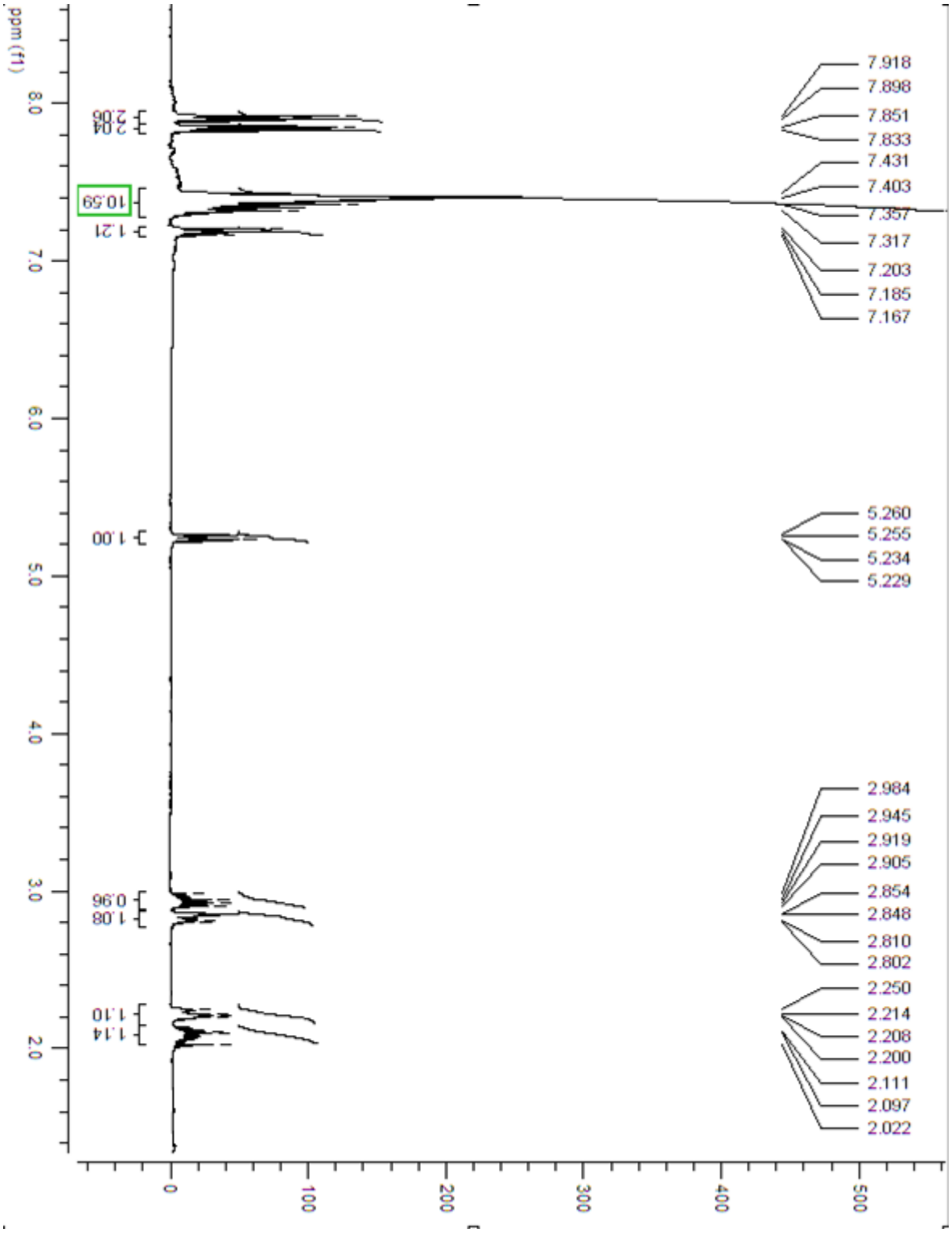
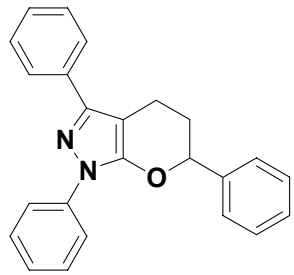
150
100
50
0
150.355
147.696
139.842
139.811
139.106
133.933
129.098
128.509
127.762
126.431
126.372
125.624
120.408
115.608
115.395
94.860
83.297
77.406
77.089
76.771
33.777
28.768
17.877


N
N
O


ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
2.04
2.06
10.59
1.21
1.00
0.96
1.08
1.10
1.14
7.918
7.898
7.851
7.833
7.431
7.403
7.357
7.317
7.203
7.185
7.167
5.260
5.255
5.234
5.229
2.984
2.945
2.919
2.905
2.854
2.848
2.810
2.802
2.250
2.214
2.208
2.200
2.111
2.097
2.022
0
100
200
300
400
500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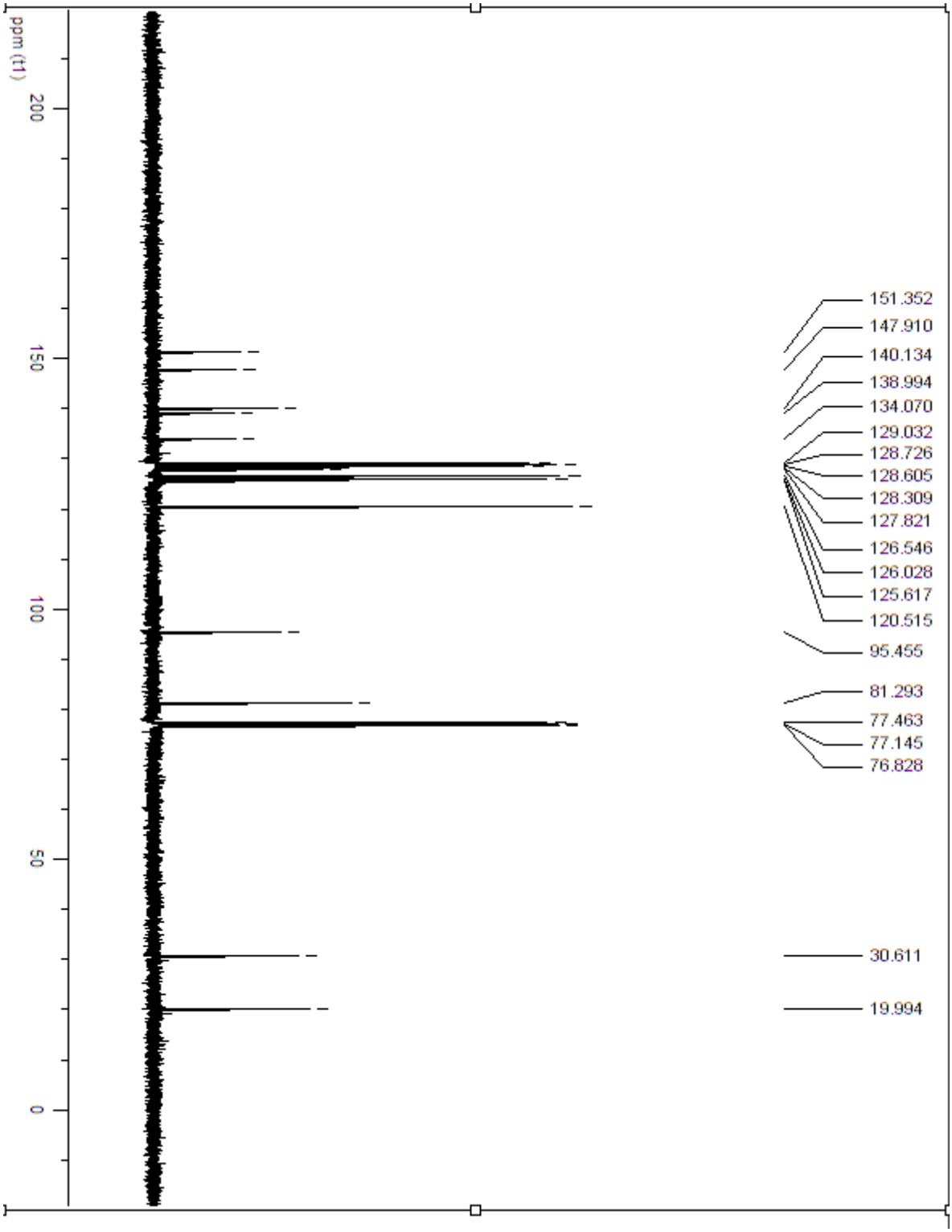
N
O


ppm (t1)
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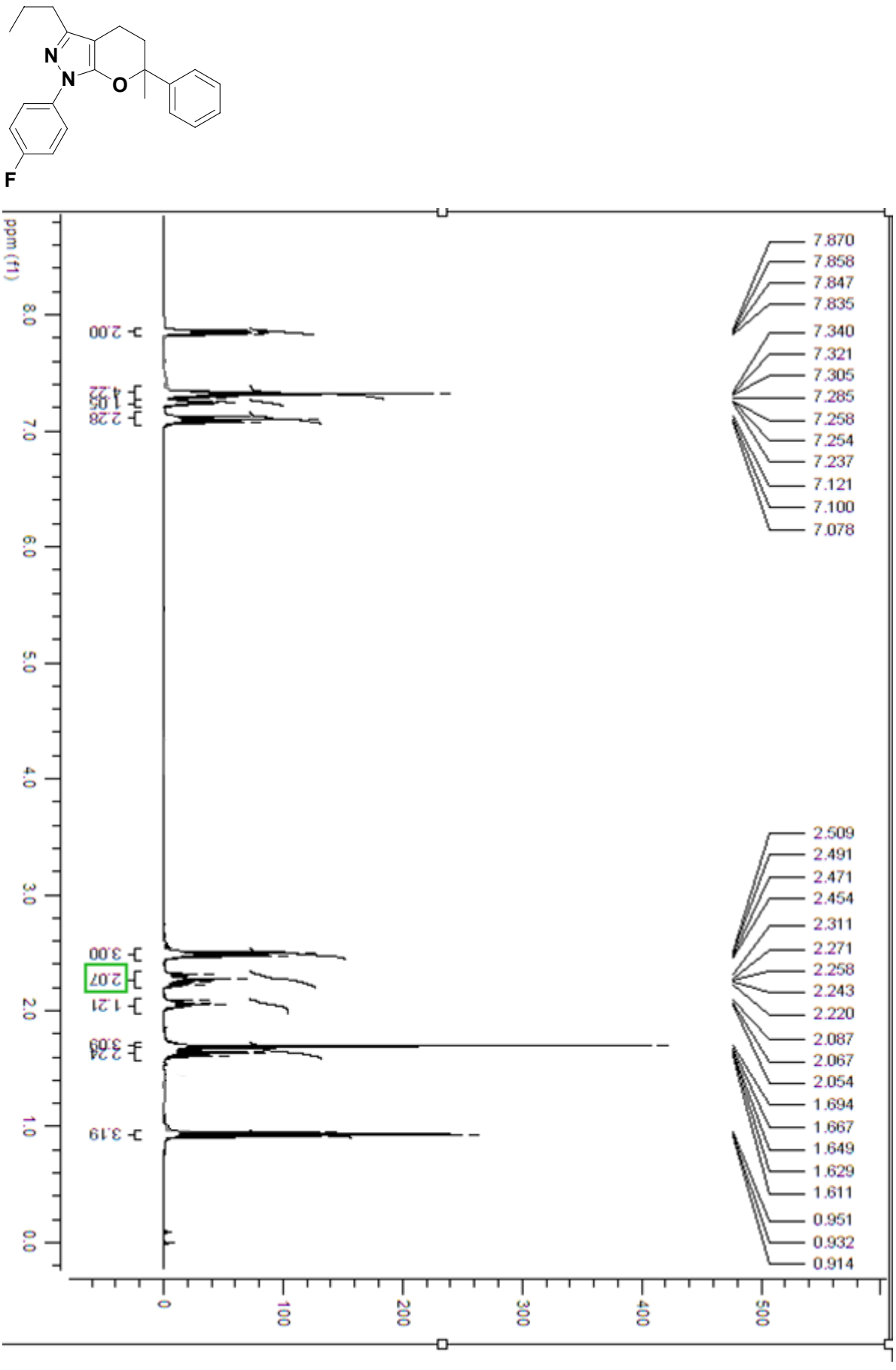
150
100
50
0
151.352
147.910
140.134
138.994
134.070
129.032
128.726
128.605
128.309
127.821
126.546
126.028
125.617
120.515
95.455
81.293
77.463
77.145
76.828
30.611
19.994


N
N
O
F
ppm (f1)
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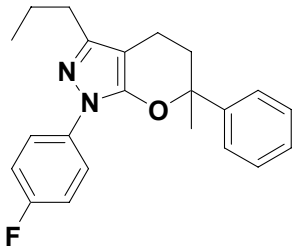
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.00
4.22
1.05
2.28
3.00
2.07
1.21
3.09
2.24
3.19
0
100
200
300
400
500
7.870
7.858
7.847
7.835
7.340
7.321
7.305
7.285
7.258
7.254
7.237
7.121
7.100
7.078
2.509
2.491
2.471
2.454
2.311
2.271
2.258
2.243
2.220
2.087
2.067
2.054
1.694
1.667
1.649
1.629
1.611
0.951
0.932
0.914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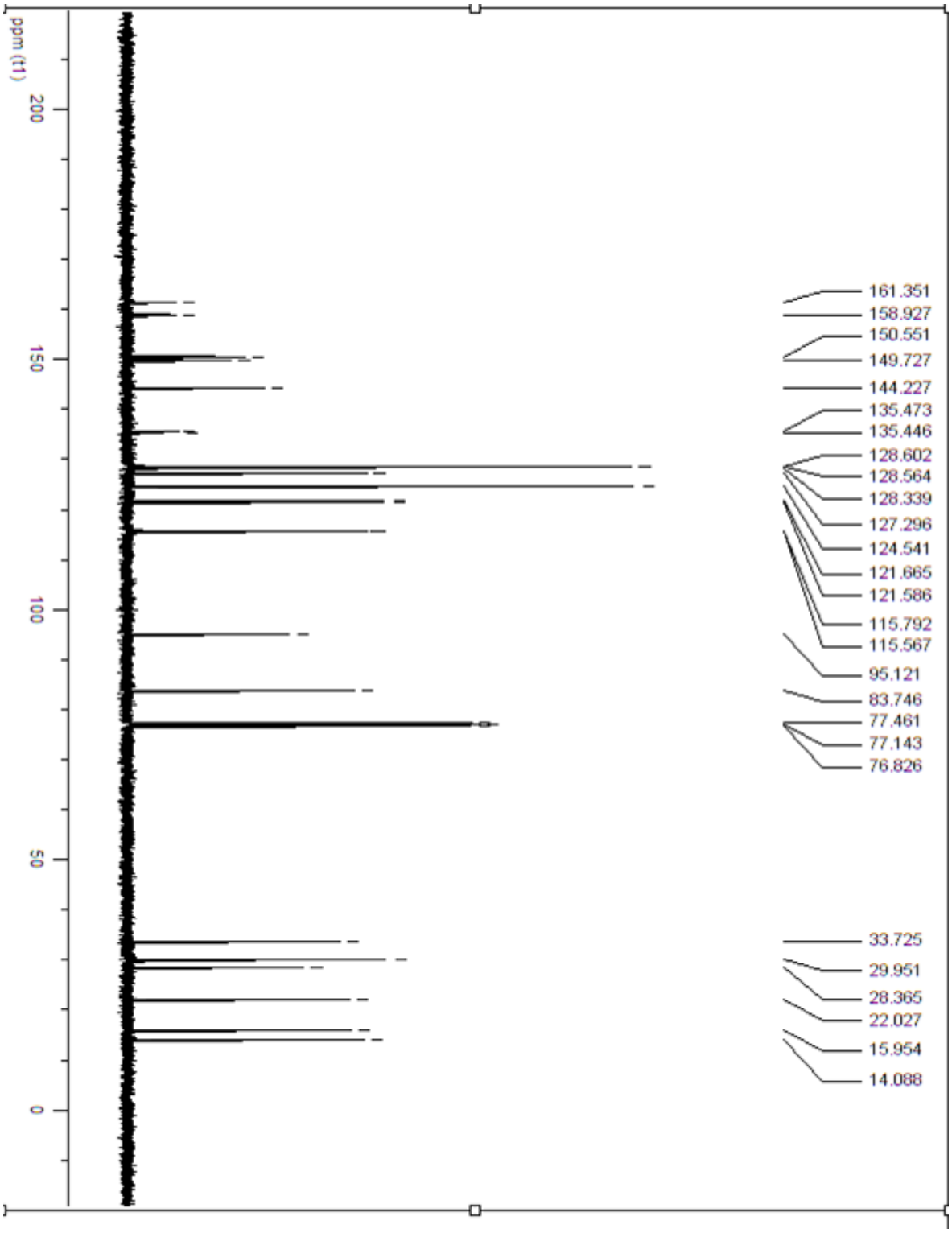
O
F


ppm (t1)
200
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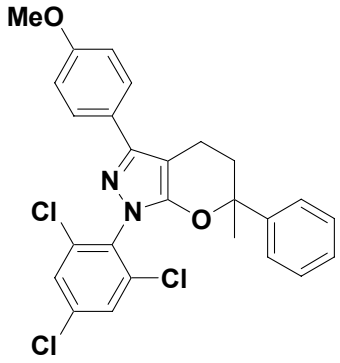
100
50
0
161.351
158.927
150.551
149.727
144.227
135.473
135.446
128.602
128.564
128.339
127.296
124.541
121.665
121.586
115.792
115.567
95.121
83.746
77.461
77.143
76.826
33.725
29.951
28.365
22.027
15.954
14.088


MeO
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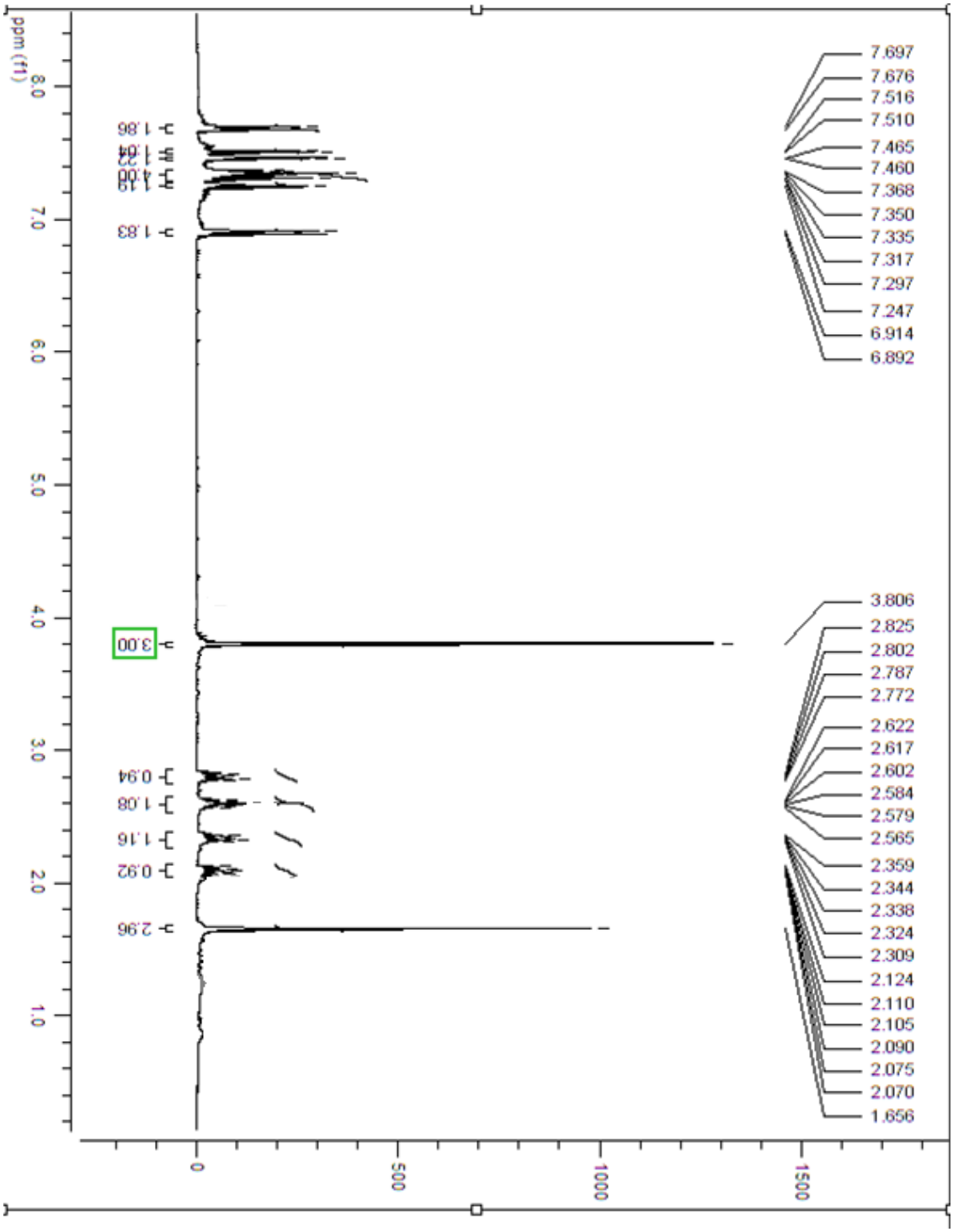
N
O
Cl
Cl
Cl


ppm (f1)
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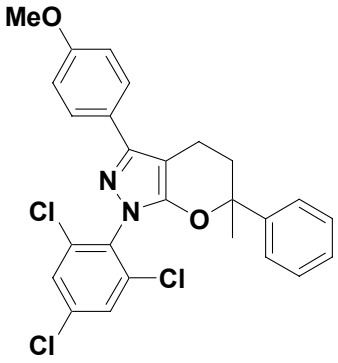
4.0
3.0
2.0
1.0
0
500
1000
1500
1.86
1.83
3.00
0.94
1.08
1.16
0.92
2.96
7.697
7.676
7.516
7.510
7.465
7.460
7.368
7.350
7.335
7.317
7.297
7.247
6.914
6.892
3.806
2.825
2.802
2.787
2.772
2.622
2.617
2.602
2.584
2.579
2.565
2.359
2.344
2.338
2.324
2.309
2.124
2.110
2.105
2.090
2.075
2.070
1.656


MeO
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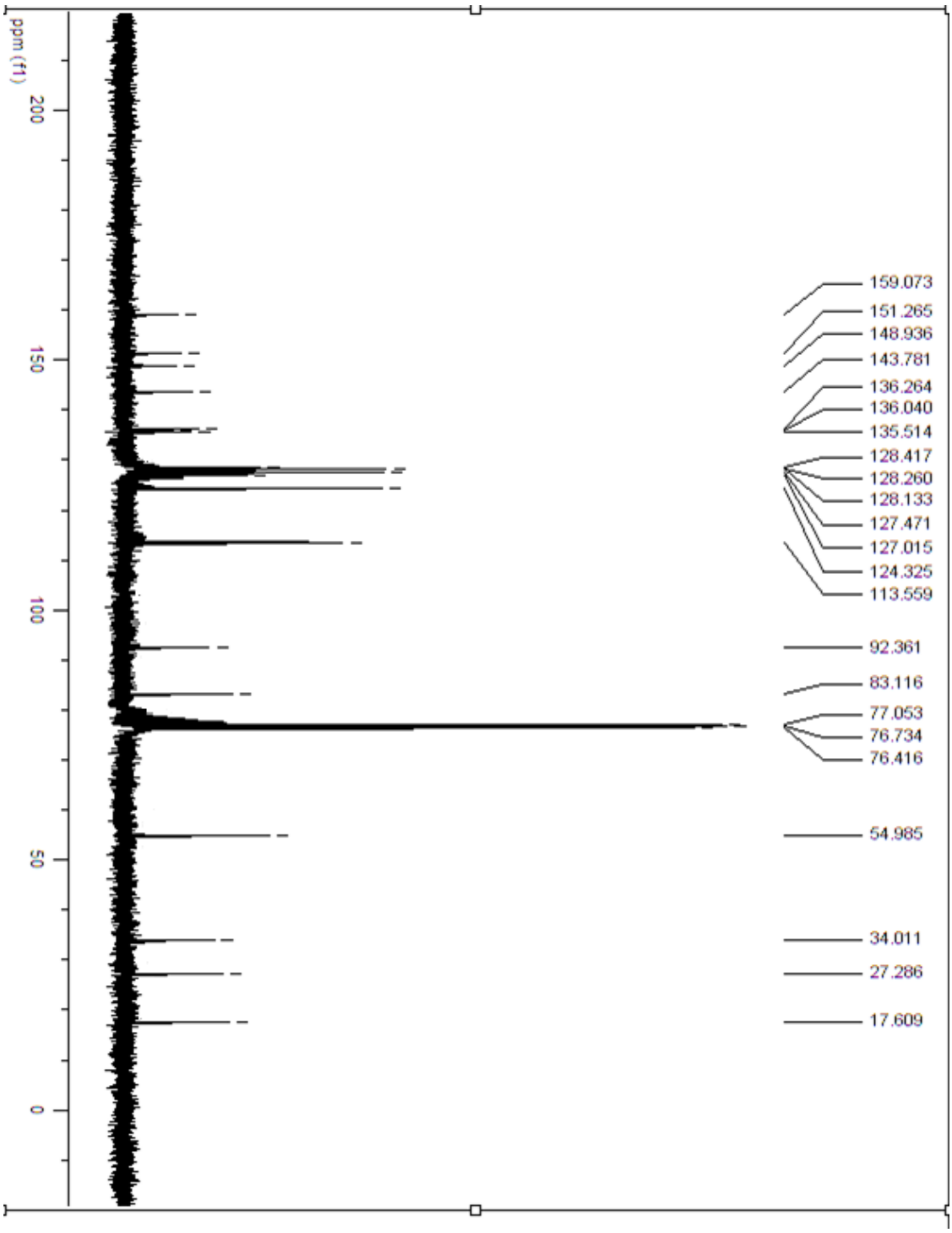
N
O
Cl
Cl
Cl


ppm (f1)
200
150
100
50
0
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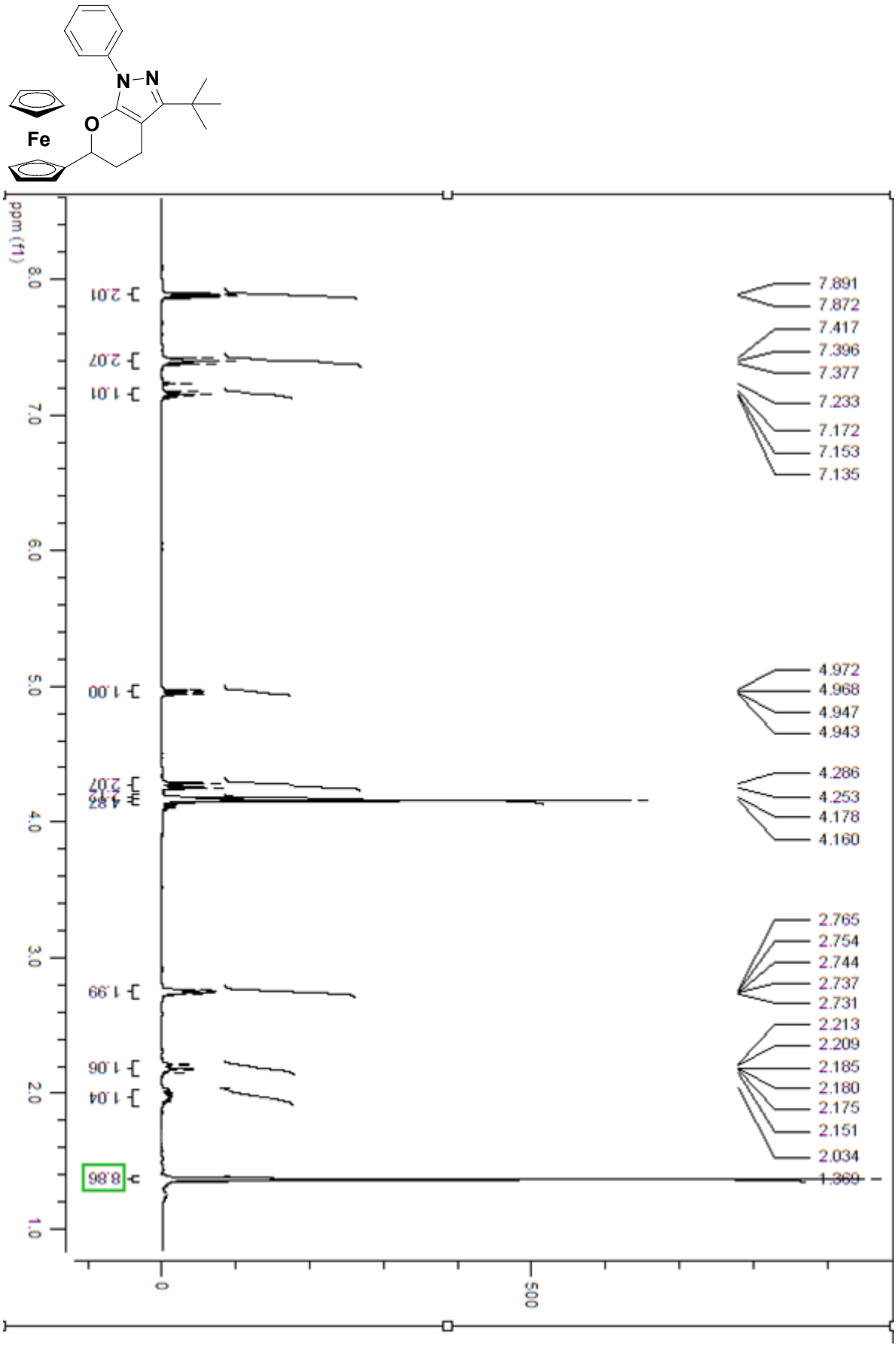
151.265
148.936
143.781
136.264
136.040
135.514
128.417
128.260
128.133
127.471
127.015
124.325
113.559
92.361
83.116
77.053
76.734
76.416
54.985
34.011
27.286
17.609


N–N
O
Fe
ppm (f1)
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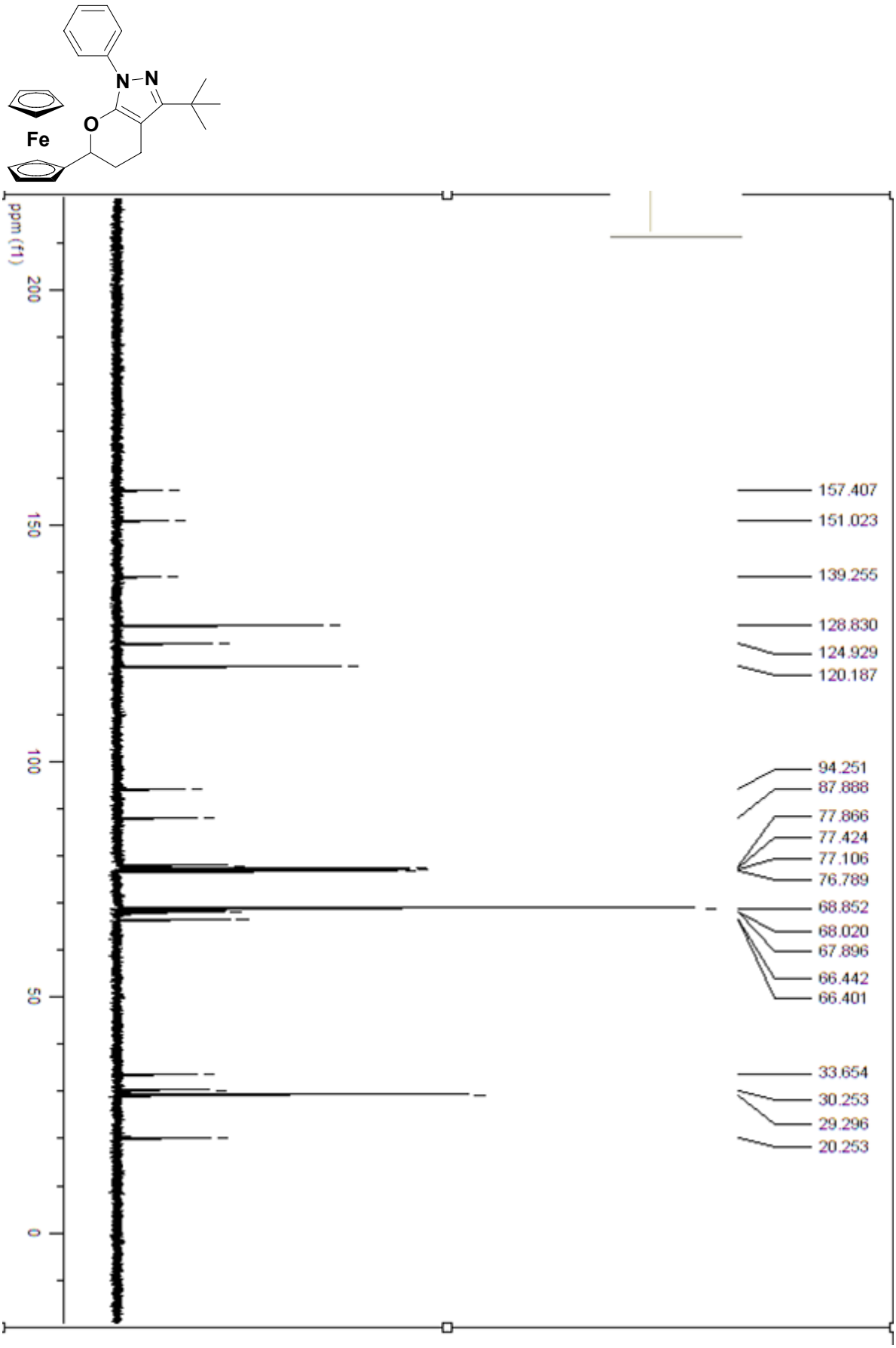
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
500
2.01
2.07
1.01
1.00
4.82
2.07
1.99
1.06
1.04
8.86
7.891
7.872
7.417
7.396
7.377
7.233
7.172
7.153
7.135
4.972
4.968
4.947
4.943
4.286
4.253
4.178
4.160
2.765
2.754
2.744
2.737
2.731
2.213
2.209
2.185
2.180
2.175
2.151
2.034
1.369


N–N
O
Fe
ppm (f1)
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100
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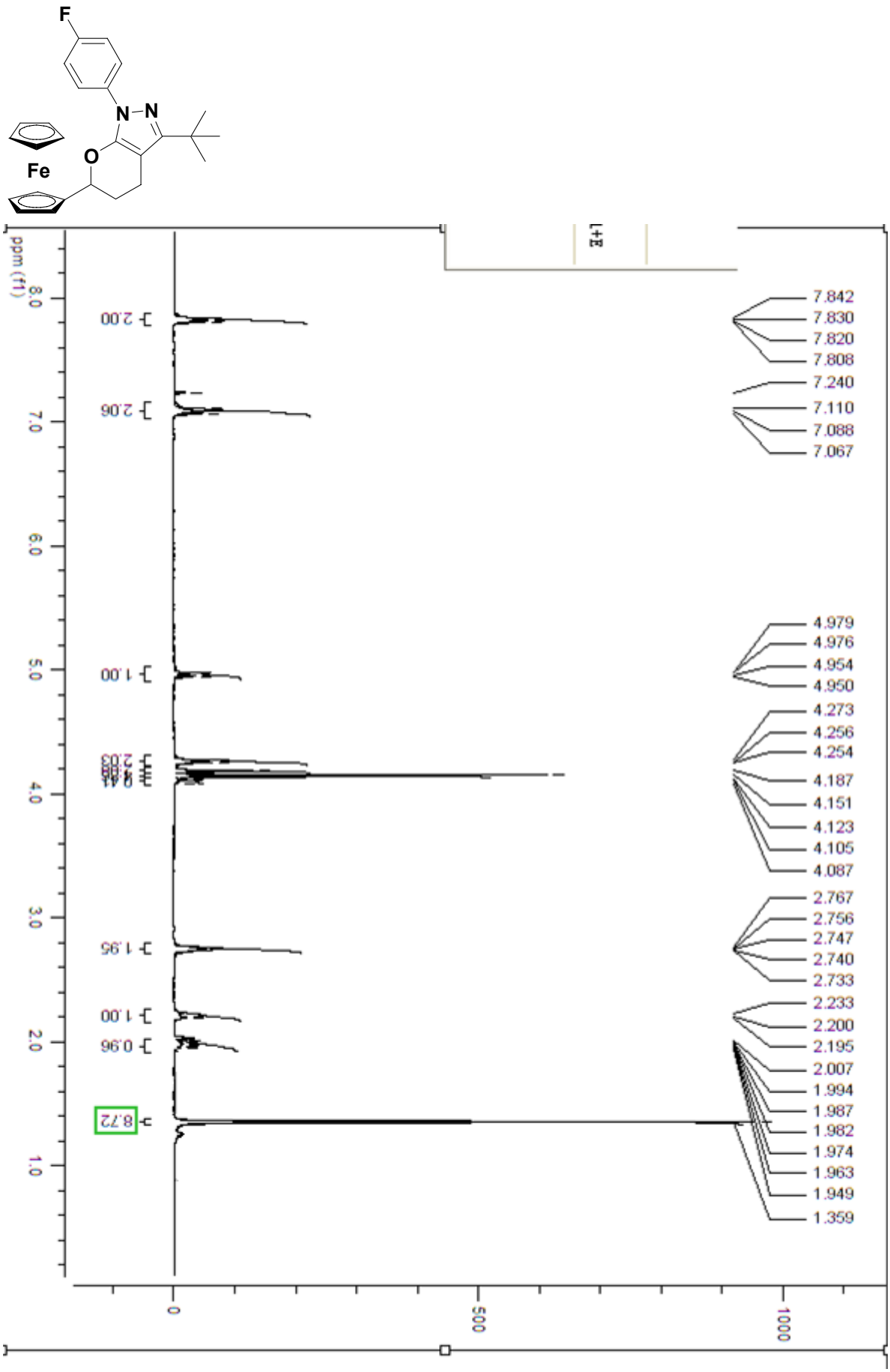
151.023
139.255
128.830
124.929
120.187
94.251
87.888
77.866
77.424
77.106
76.789
68.852
68.020
67.896
66.442
66.401
33.654
30.253
29.296
20.253


F
N–N
O
Fe
ppm (f1)
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
2.00
2.06
1.00
2.03
1.95
1.00
0.96
8.72
0
500
1000
7.842
7.830
7.820
7.808
7.240
7.110
7.088
7.067
4.979
4.976
4.954
4.950
4.273
4.256
4.254
4.187
4.151
4.123
4.105
4.087
2.767
2.756
2.747
2.740
2.733
2.233
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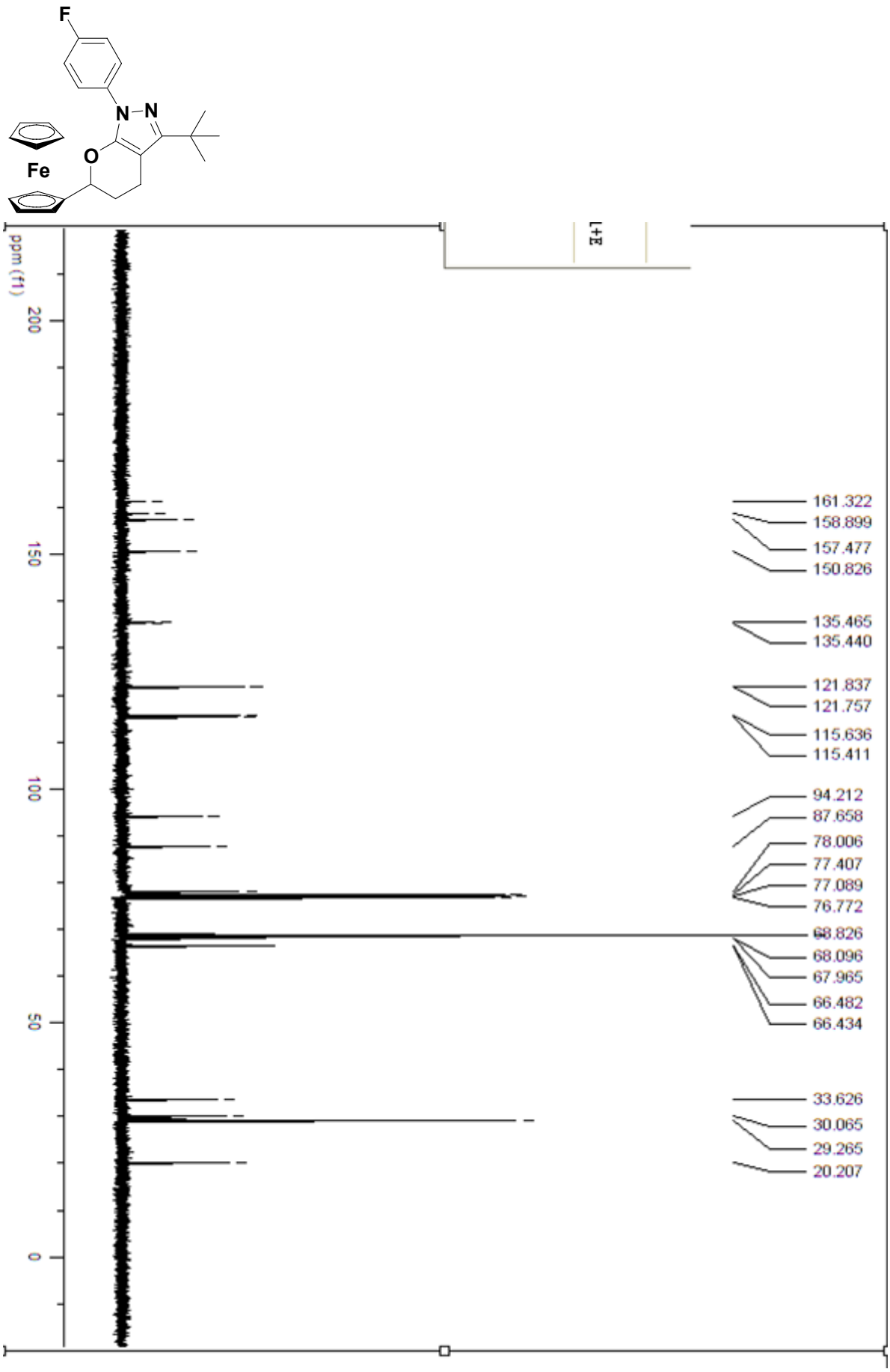
2.195
2.007
1.994
1.987
1.982
1.974
1.963
1.949
1.359


F
N
N
O
Fe
ppm (f1)
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150
100
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150.826
135.465
135.440
121.837
121.757
115.636
115.411
94.212
87.658
78.006
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68.826
68.096
67.965
66.482
66.434
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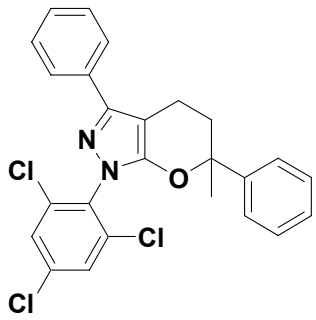
29.265
20.207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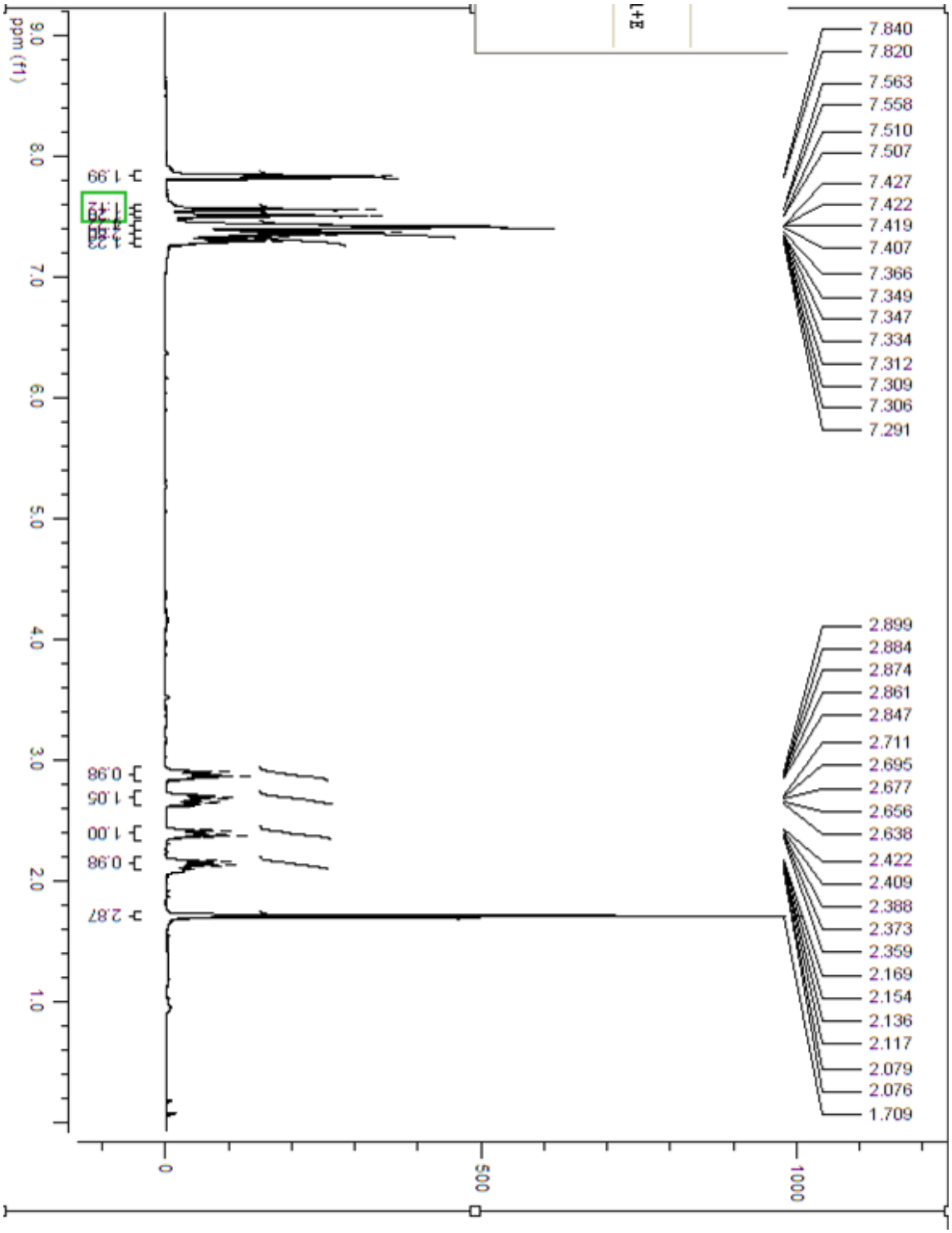
Cl
Cl
Cl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3.0
2.0
1.0
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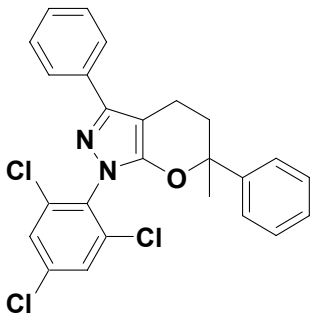
0.98
1.05
1.00
0.98
2.87
7.840
7.820
7.563
7.558
7.510
7.507
7.427
7.422
7.419
7.407
7.366
7.349
7.347
7.334
7.312
7.309
7.306
7.291
2.899
2.884
2.874
2.861
2.847
2.711
2.695
2.677
2.656
2.638
2.422
2.409
2.388
2.373
2.359
2.169
2.154
2.136
2.117
2.079
2.076
1.709
0
500
1000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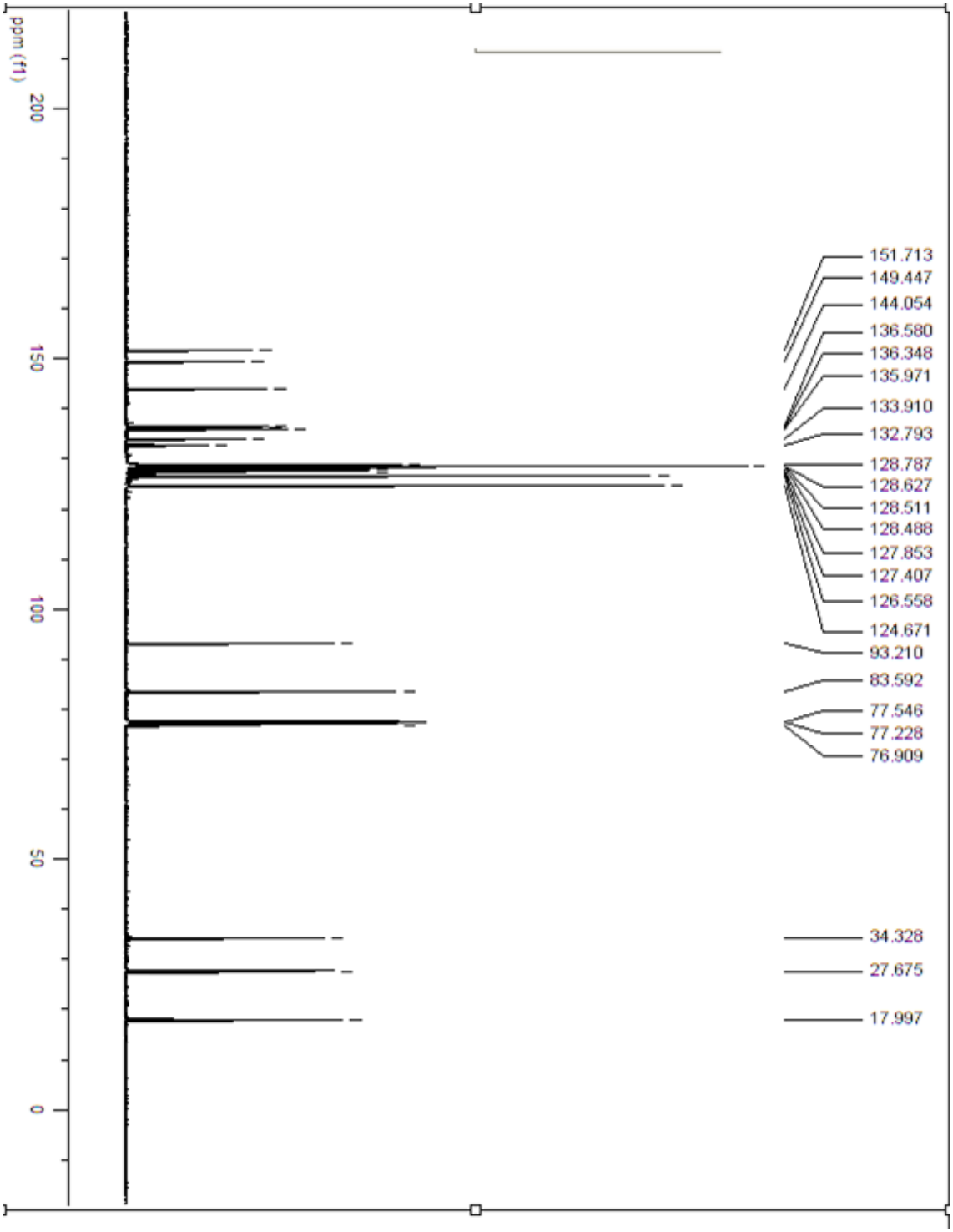
O
Cl
Cl
Cl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100
50
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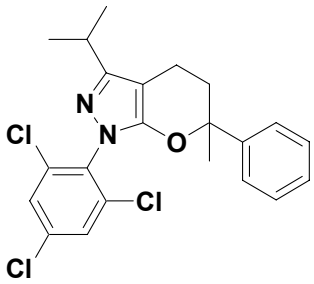
149.447
144.054
136.580
136.348
135.971
133.910
132.793
128.787
128.627
128.511
128.488
127.853
127.407
126.558
124.671
93.210
83.592
77.546
77.228
76.909
34.328
27.675
17.997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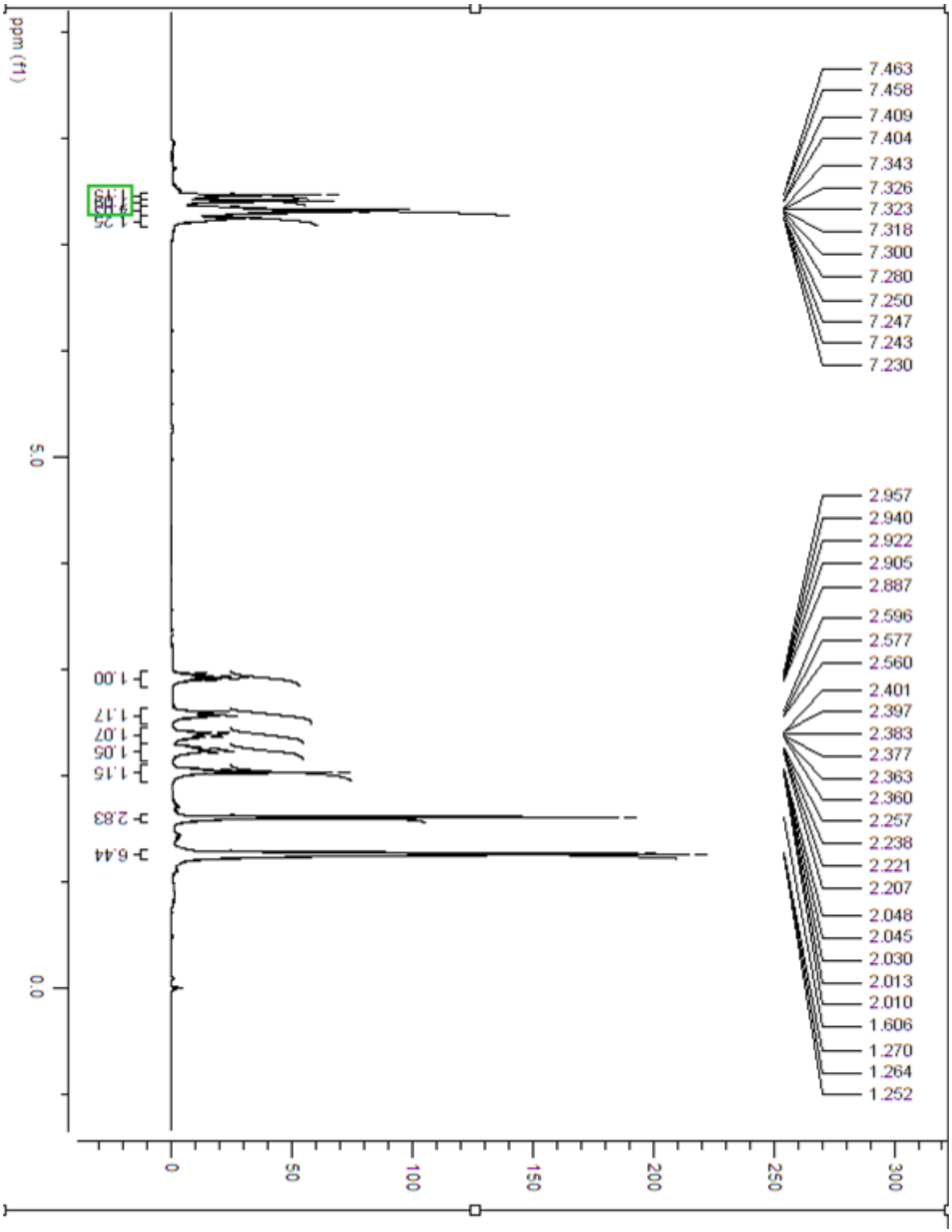
O
Cl
Cl
Cl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0.0
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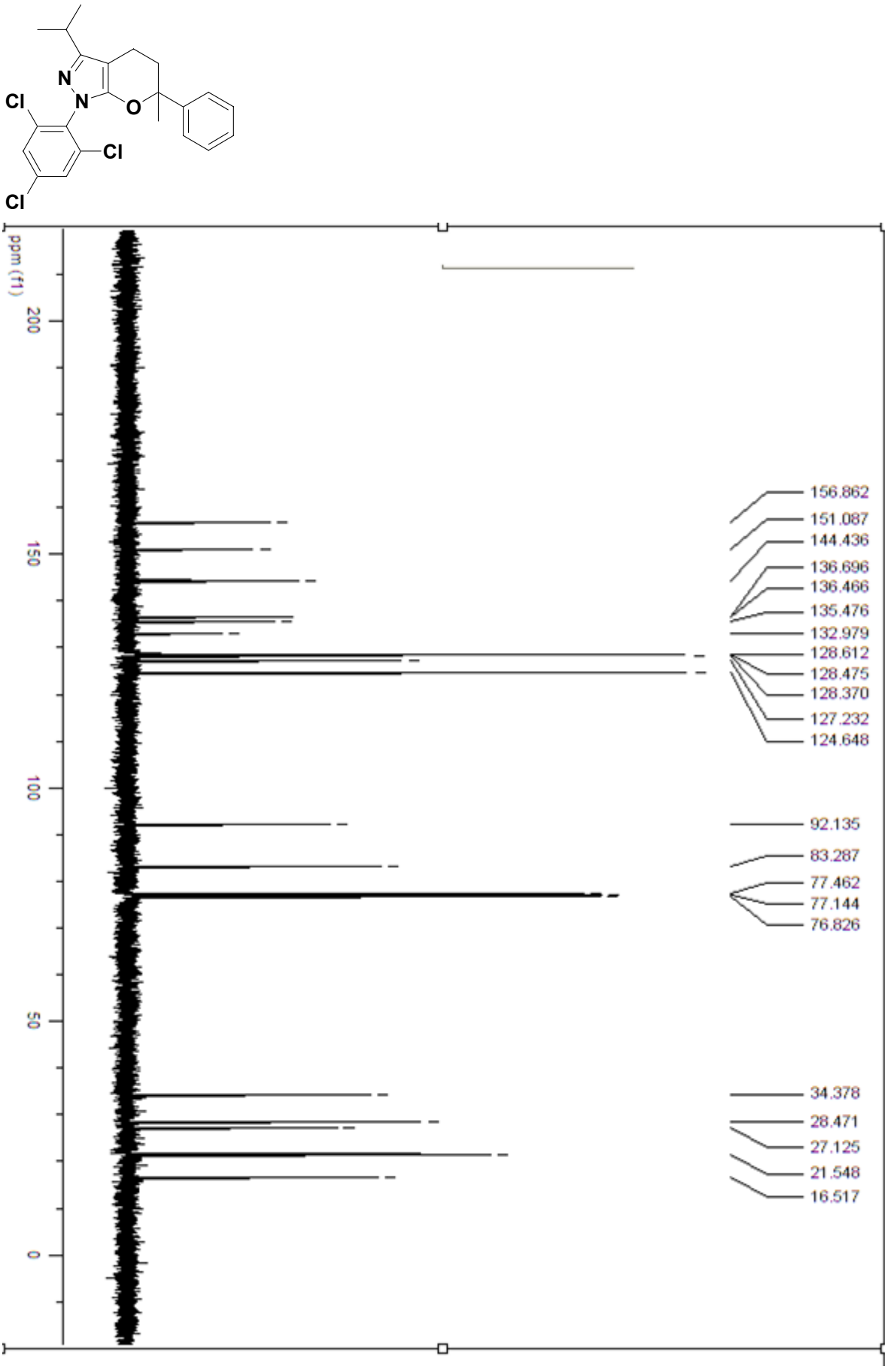
7.458
7.409
7.404
7.343
7.326
7.323
7.318
7.300
7.280
7.250
7.247
7.243
7.230
2.957
2.940
2.922
2.905
2.887
2.596
2.577
2.560
2.401
2.397
2.383
2.377
2.363
2.360
2.257
2.238
2.221
2.207
2.048
2.045
2.030
2.013
2.010
1.606
1.270
1.264
1.252
1.00
1.17
1.07
1.05
1.15
2.83
6.44
0
50
100
150
200
250
300


Cl
N
N
O
Cl
Cl
ppm (f1)
200
150
100
50
0
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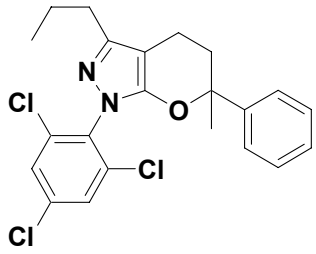
151.087
144.436
136.696
136.466
135.476
132.979
128.612
128.475
128.370
127.232
124.648
92.135
83.287
77.462
77.144
76.826
34.378
28.471
27.125
21.548
16.517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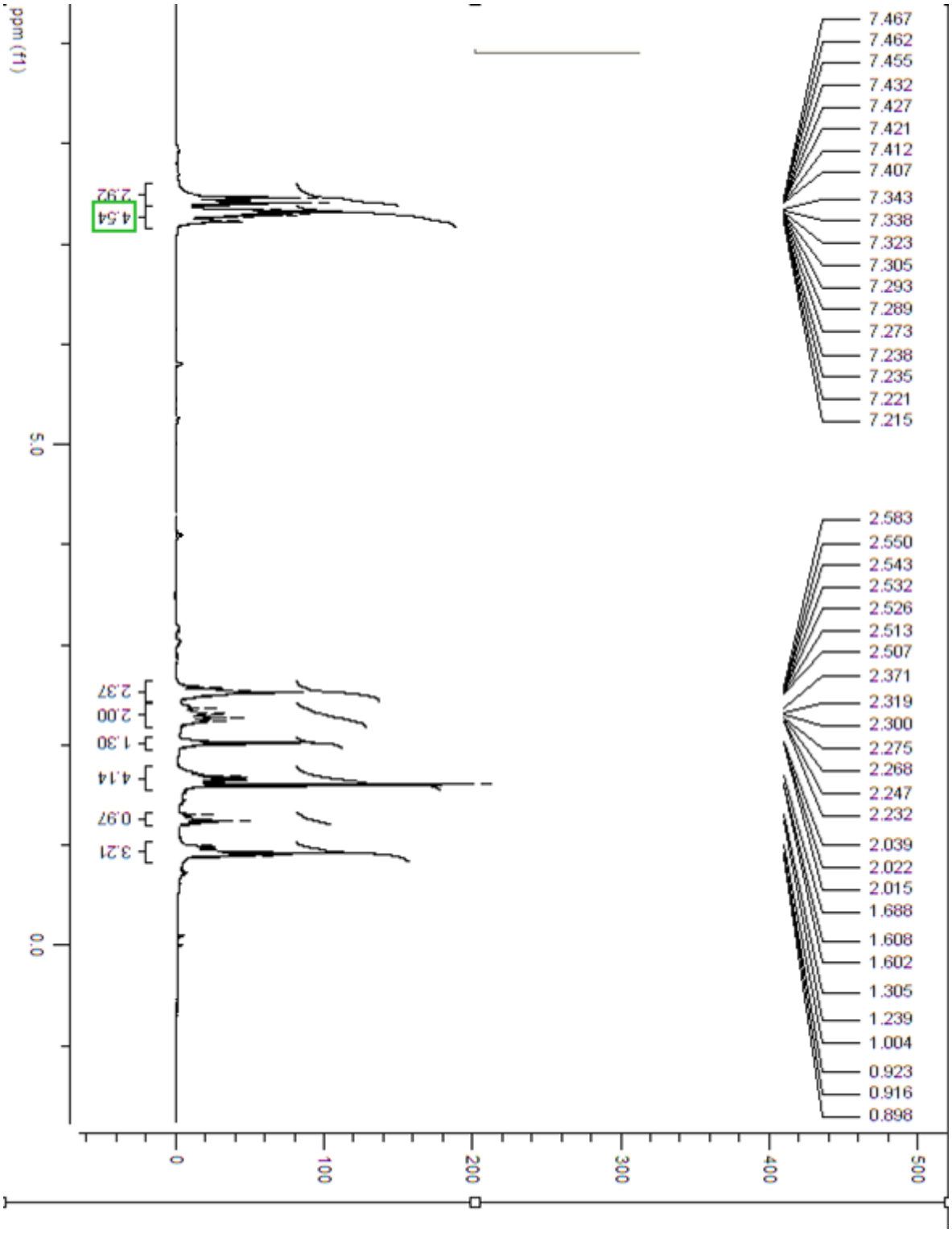
N
O
Cl
Cl
Cl


ppm (f1)
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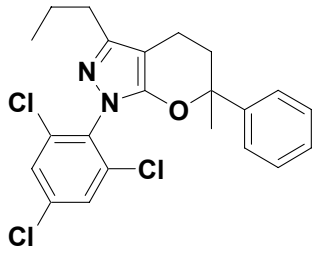
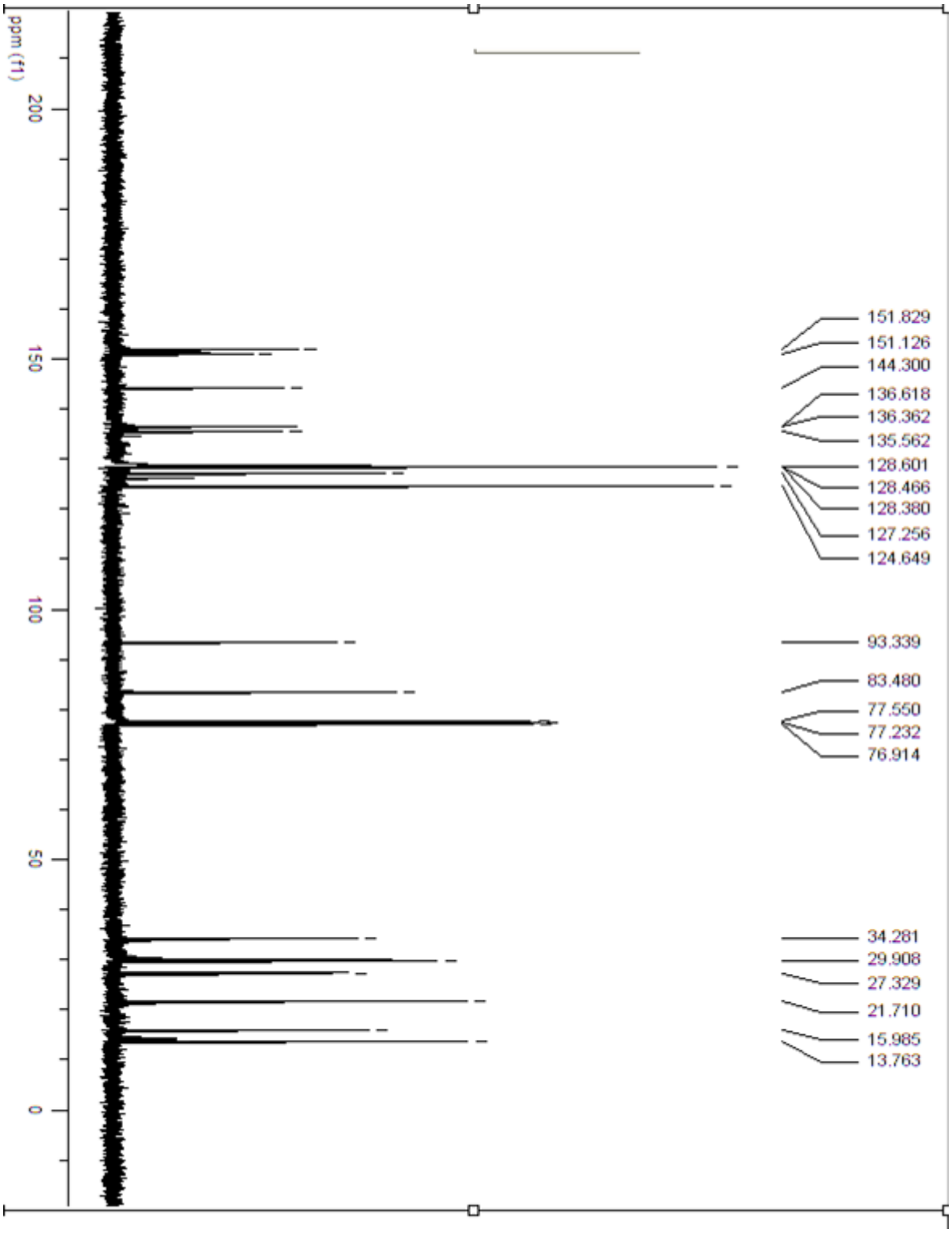
0.0
2.92
4.54
2.37
2.00
1.30
4.14
0.97
3.21
7.467
7.462
7.455
7.432
7.427
7.421
7.412
7.407
7.343
7.338
7.323
7.305
7.293
7.289
7.273
7.238
7.235
7.221
7.215
2.583
2.550
2.543
2.532
2.526
2.513
2.507
2.371
2.319
2.300
2.275
2.268
2.247
2.232
2.039
2.022
2.015
1.688
1.608
1.602
1.305
1.239
1.004
0.923
0.916
0.898
0
100
200
300
400
500


N
N
O
Cl
Cl
Cl


ppm (f1)
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150
100
50
0
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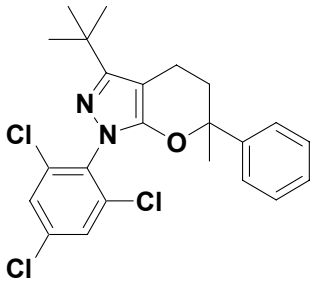
151.126
144.300
136.618
136.362
135.562
128.601
128.466
128.380
127.256
124.649
93.339
83.480
77.550
77.232
76.914
34.281
29.908
27.329
21.710
15.985
13.763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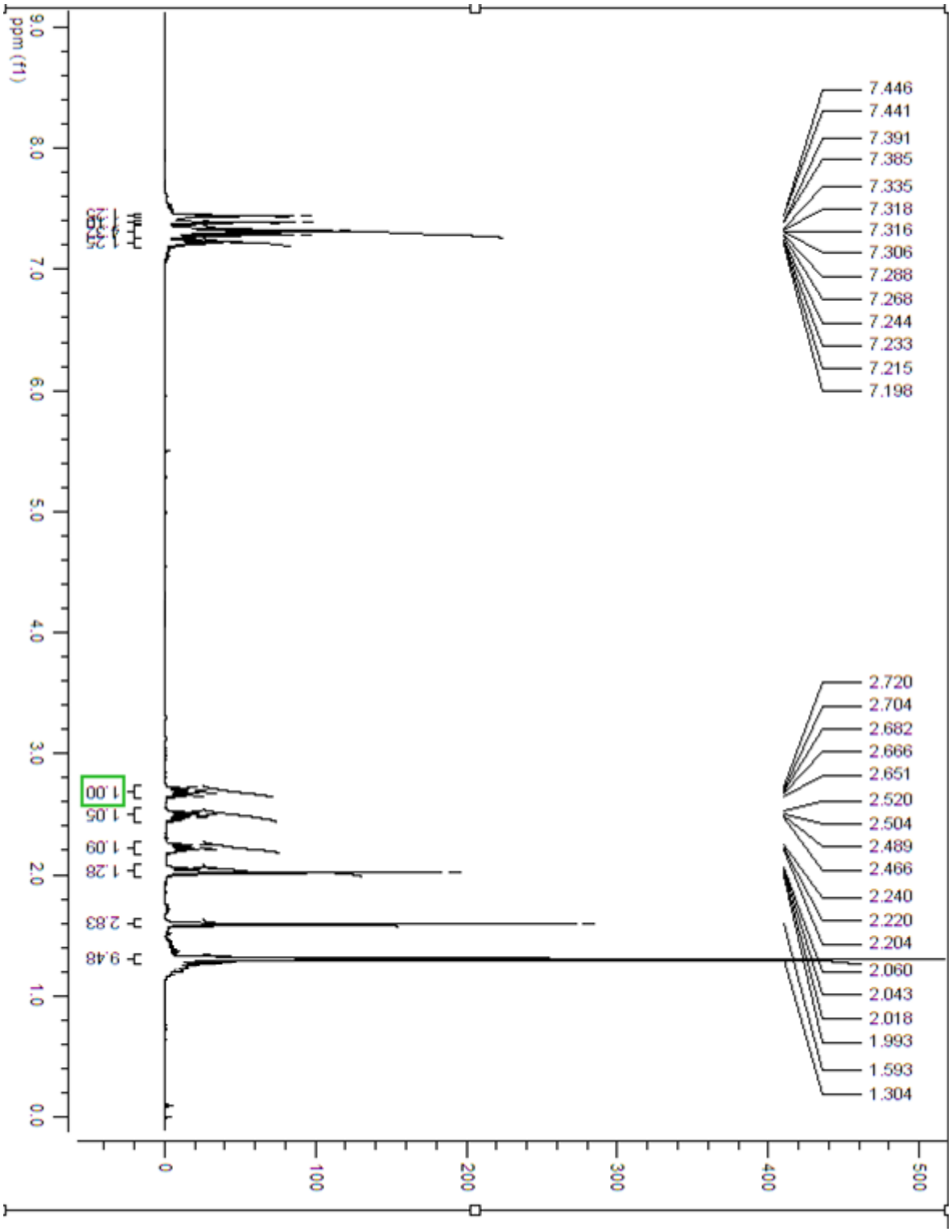
N
O
Cl
Cl
Cl


ppm (f1)
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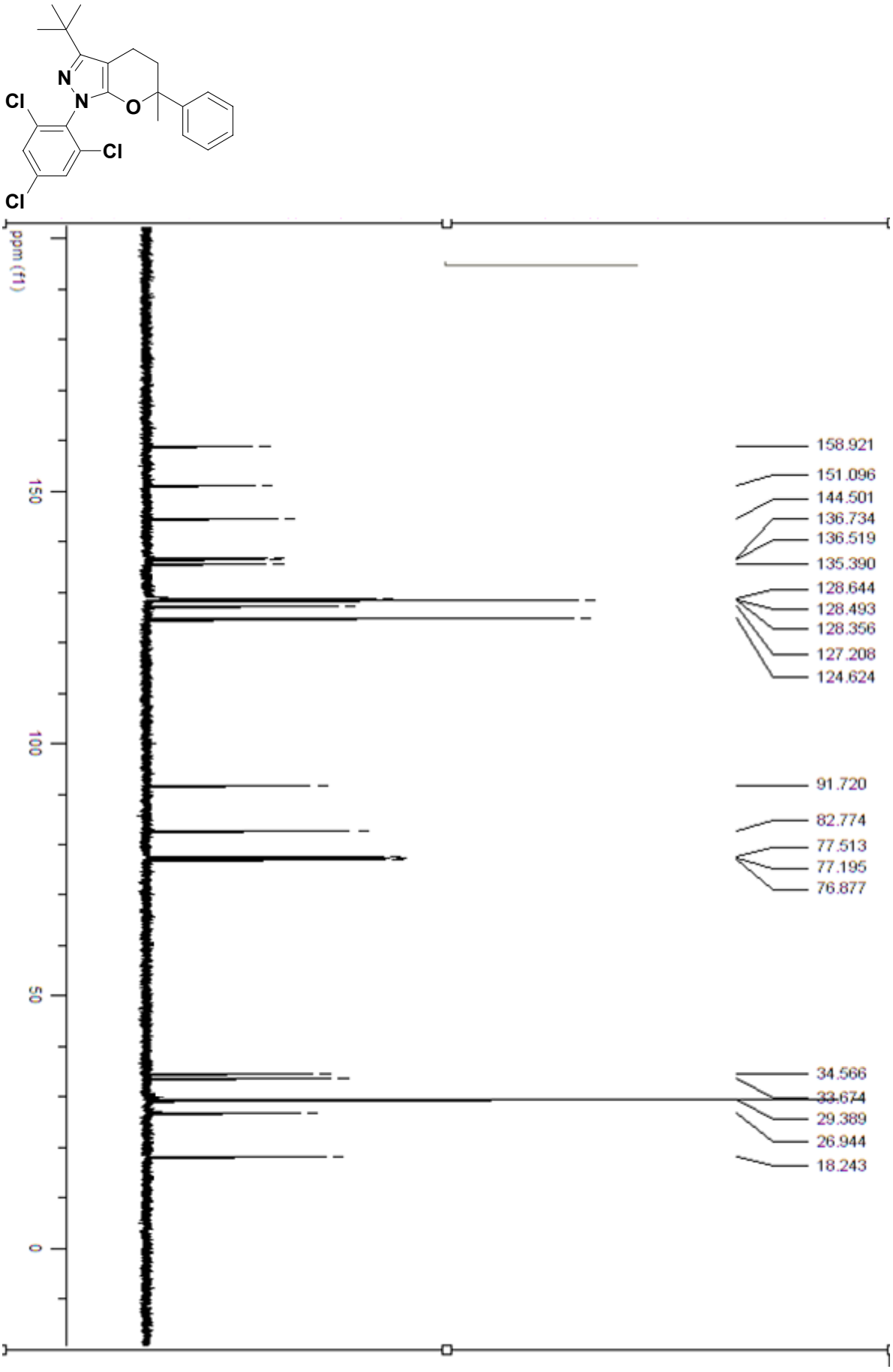
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.446
7.441
7.391
7.385
7.335
7.318
7.316
7.306
7.288
7.268
7.244
7.233
7.215
7.198
2.720
2.704
2.682
2.666
2.651
2.520
2.504
2.489
2.466
2.240
2.220
2.204
2.060
2.043
2.018
1.993
1.593
1.304
1.00
1.05
1.09
1.28
2.83
9.48
0
100
200
300
400
500


Cl
N
N
O
Cl
Cl
ppm (f1)
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100
50
0
158.921
151.096
144.501
136.734
136.519
135.390
128.644
128.493
128.356
127.208
124.624
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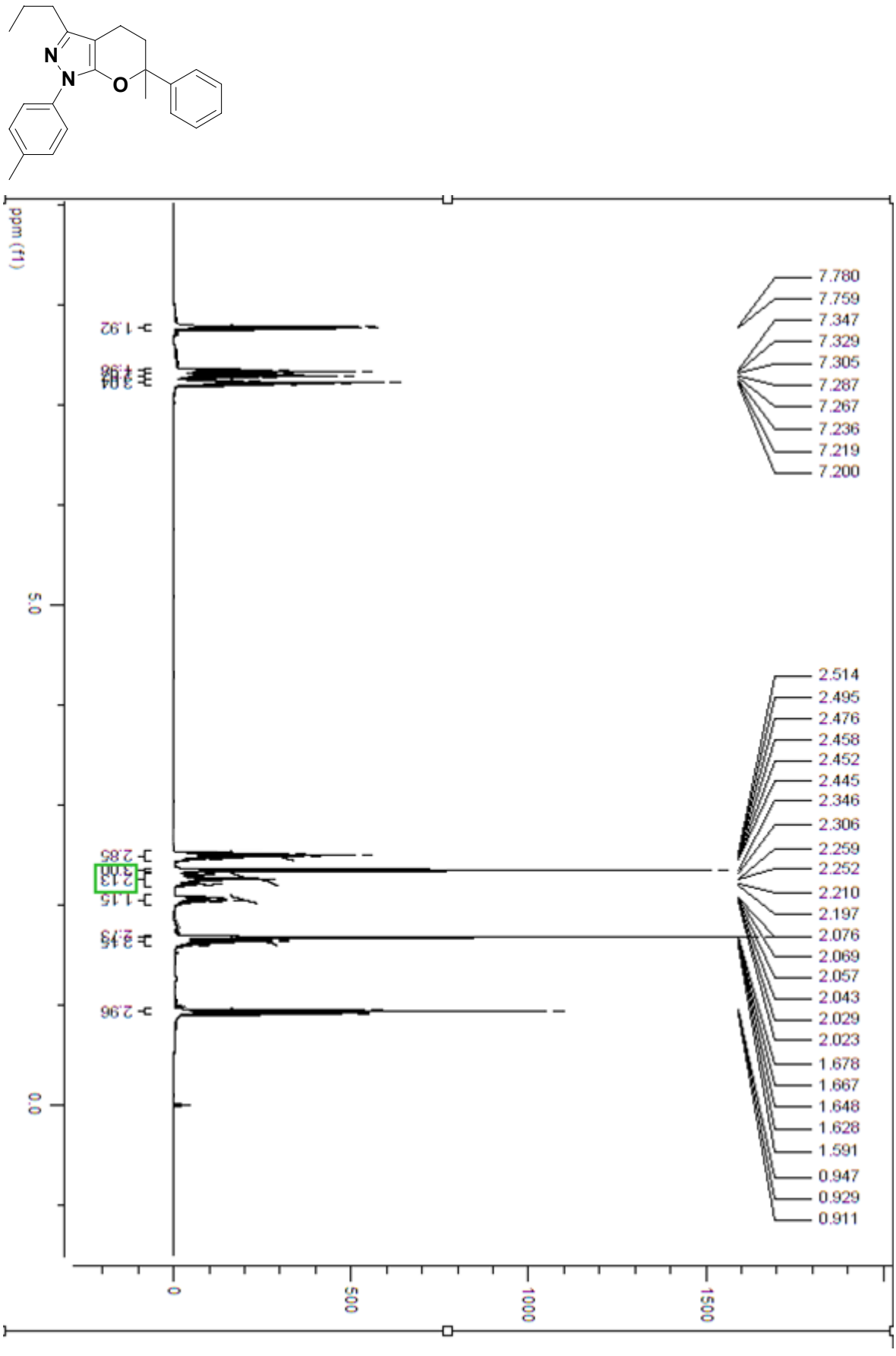
82.774
77.513
77.195
76.877
34.566
33.674
29.389
26.944
18.243


N
N
O
ppm (f1)
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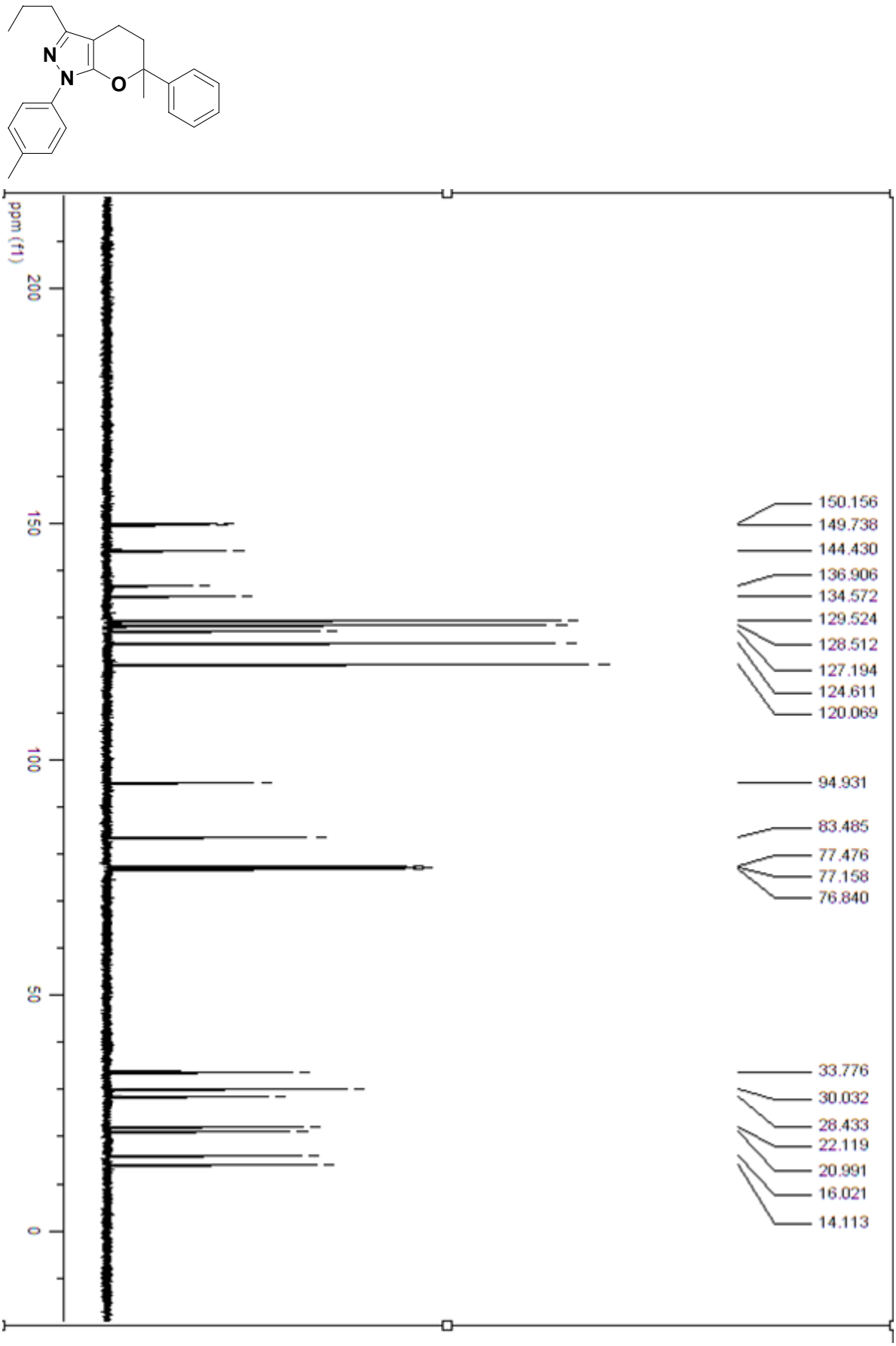
7.347
7.329
7.305
7.287
7.267
7.236
7.219
7.200
2.514
2.495
2.476
2.458
2.452
2.445
2.346
2.306
2.259
2.252
2.210
2.197
2.076
2.069
2.057
2.043
2.029
2.023
1.678
1.667
1.648
1.628
1.591
0.947
0.929
0.911
5.0
0.0
0
500
1000
1500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N
O
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150
100
50
0
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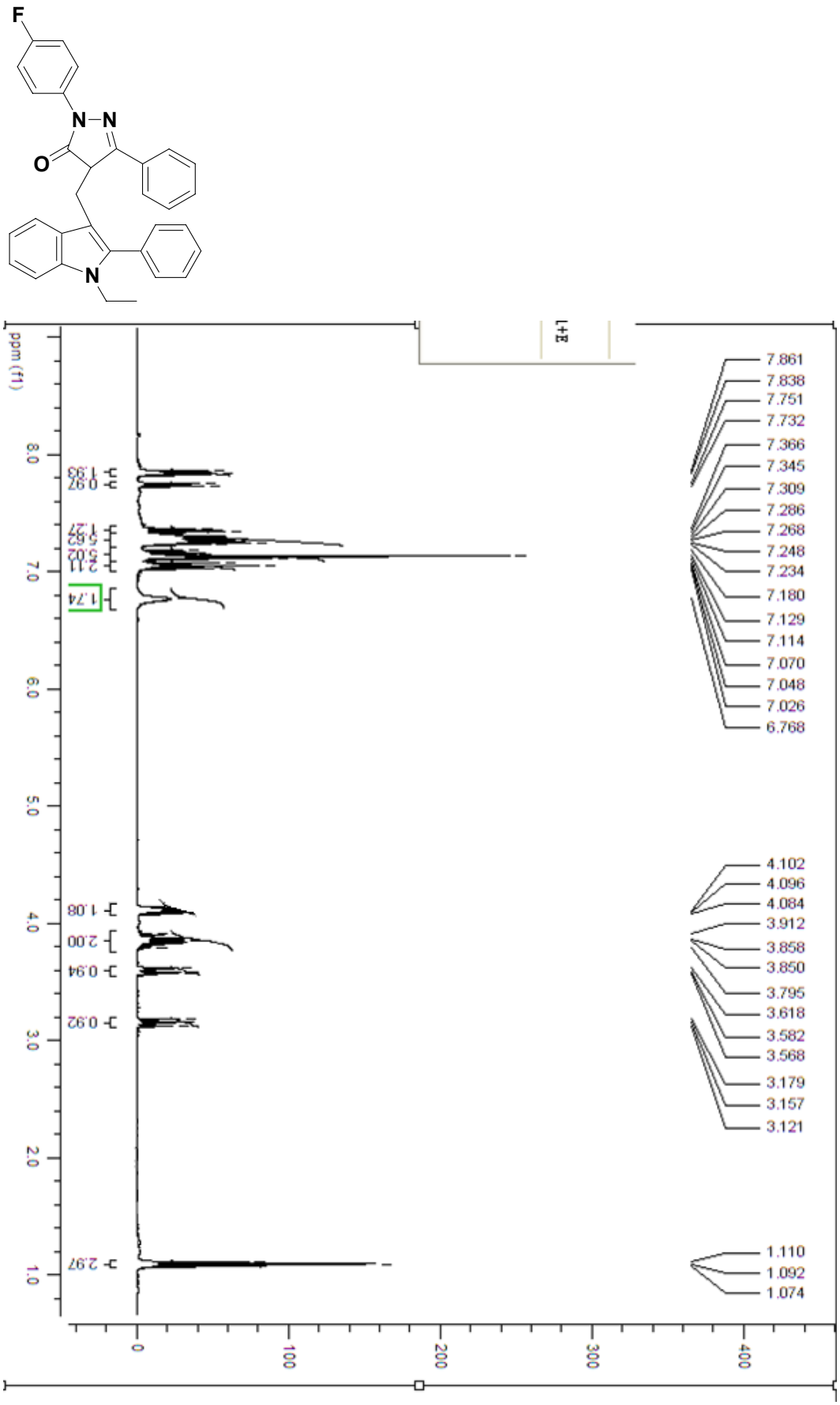
144.430
136.906
134.572
129.524
128.512
127.194
124.611
120.069
94.931
83.485
77.476
77.158
76.840
33.776
30.032
28.433
22.119
20.991
16.021
14.113


F
N
N
O
N
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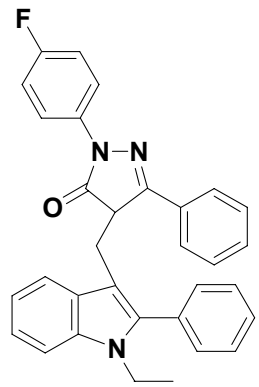
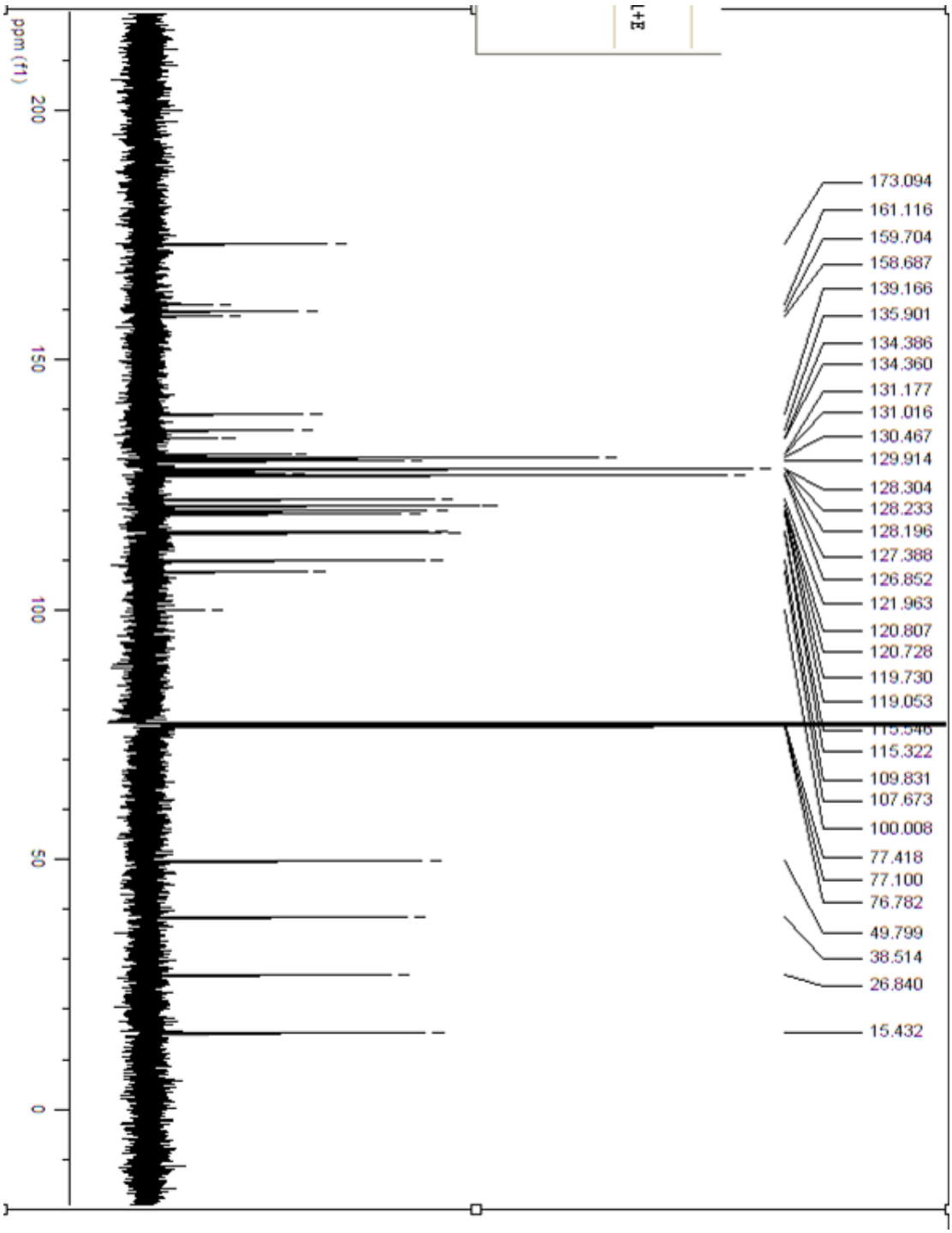
7.732
7.366
7.345
7.309
7.286
7.268
7.248
7.234
7.180
7.129
7.114
7.070
7.048
7.026
6.768
4.102
4.096
4.084
3.912
3.858
3.850
3.795
3.618
3.582
3.568
3.179
3.157
3.121
1.110
1.092
1.074
1.93
0.97
1.27
5.29
5.02
2.11
1.74
1.08
2.00
0.94
0.92
2.97


F
N
N
O
N


ppm (f1)
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150
100
50
0
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161.116
159.704
158.687
139.166
135.901
134.386
134.360
131.177
131.016
130.467
129.914
128.304
128.233
128.196
127.388
126.852
121.963
120.807
120.728
119.730
119.053
115.322
109.831
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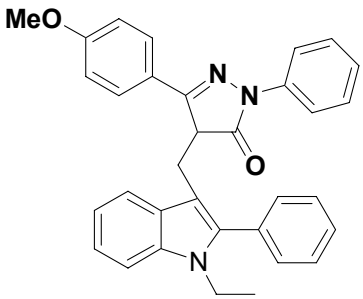
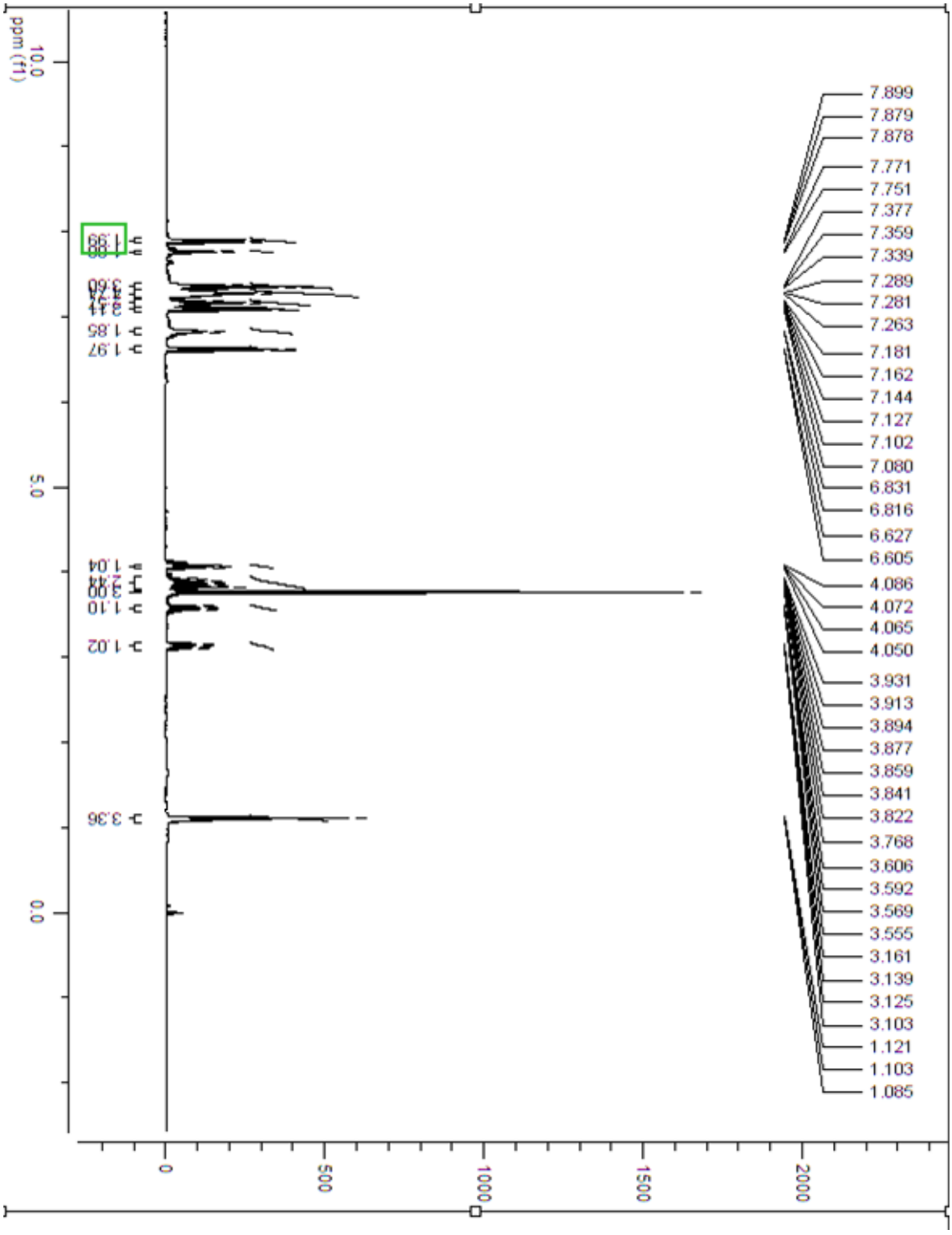
100.008
77.418
77.100
76.782
49.799
38.514
26.840
15.432


MeO
N
N
O
N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7.878
7.771
7.751
7.377
7.359
7.339
7.289
7.281
7.263
7.181
7.162
7.144
7.127
7.102
7.080
6.831
6.816
6.627
6.605
4.086
4.072
4.065
4.050
3.931
3.913
3.894
3.877
3.859
3.841
3.822
3.768
3.606
3.592
3.569
3.555
3.161
3.139
3.125
3.103
1.121
1.103
1.085
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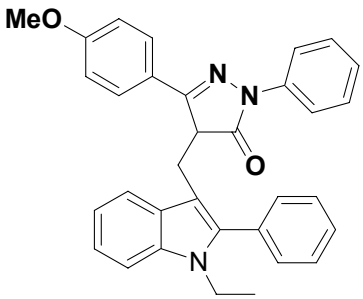
1000
1500
2000


MeO
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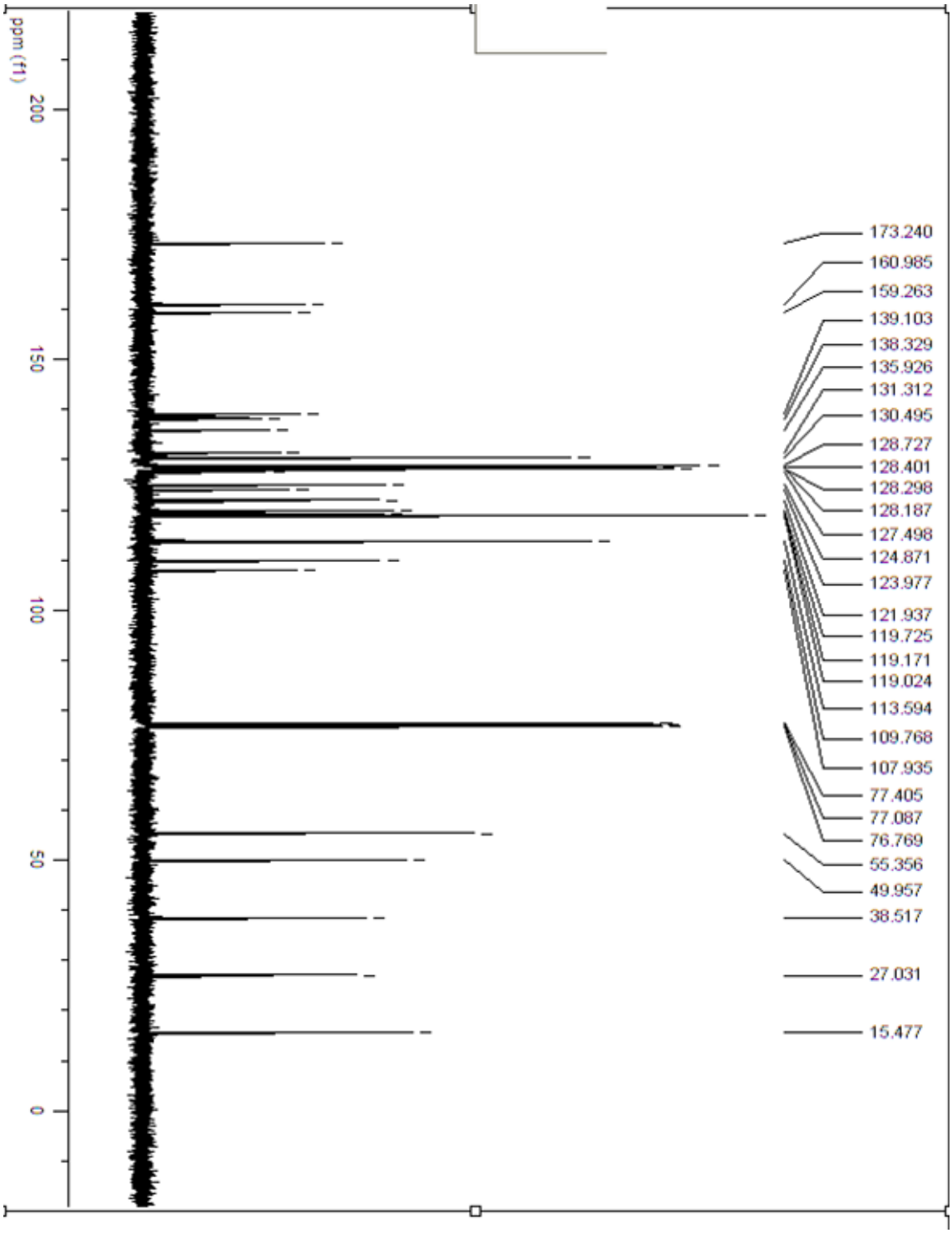
N
O
N


ppm (f1)
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100
50
0
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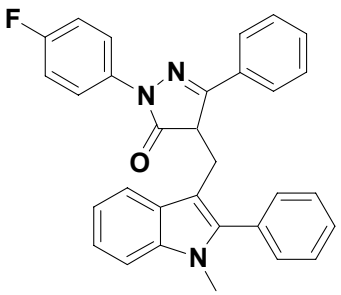
160.985
159.263
139.103
138.329
135.926
131.312
130.495
128.727
128.401
128.298
128.187
127.498
124.871
123.977
121.937
119.725
119.171
119.024
113.594
109.768
107.935
77.405
77.087
76.769
55.356
49.957
38.517
27.031
15.477


F
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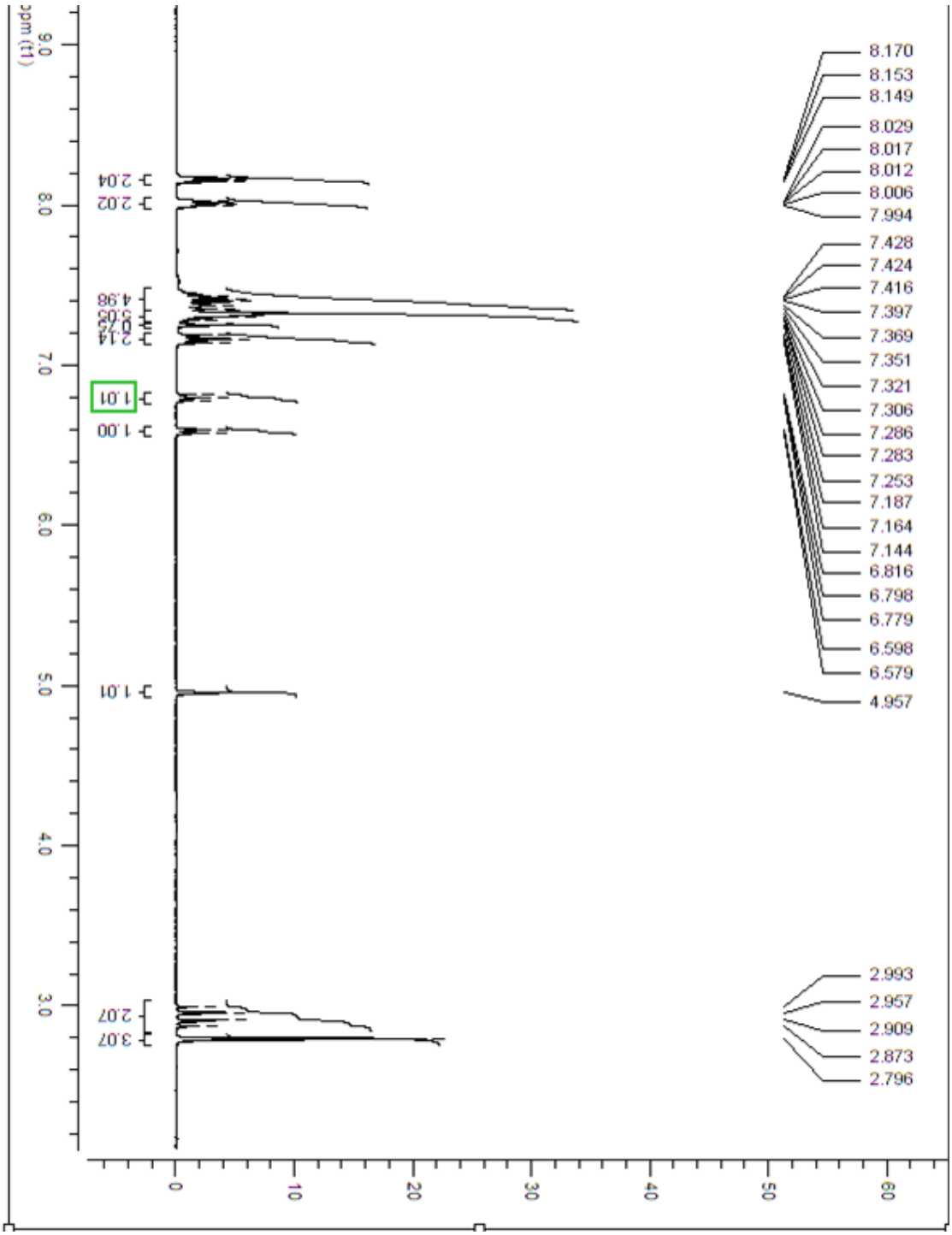
N
O
N


ppm (t1)
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7.0
6.0
5.0
4.0
3.0
2.04
2.02
4.98
2.14
1.01
1.00
1.01
2.07
3.07
8.170
8.153
8.149
8.029
8.017
8.012
8.006
7.994
7.428
7.424
7.416
7.397
7.369
7.351
7.321
7.306
7.286
7.283
7.253
7.187
7.164
7.144
6.816
6.798
6.779
6.598
6.579
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2.993
2.957
2.909
2.873
2.796
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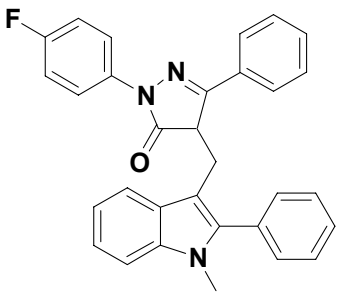
10
20
30
40
50
60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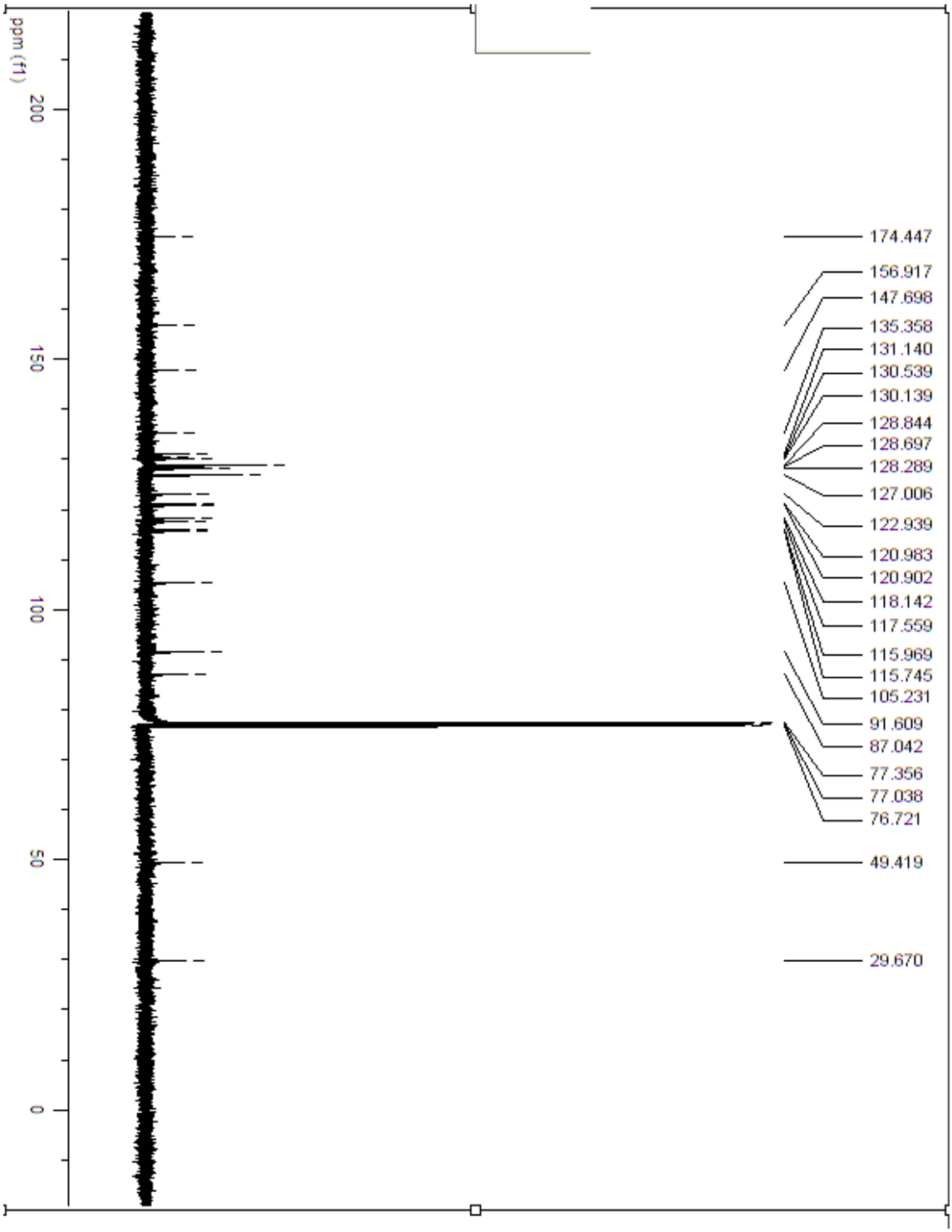
O
N


ppm (f1)
200
150
100
50
0
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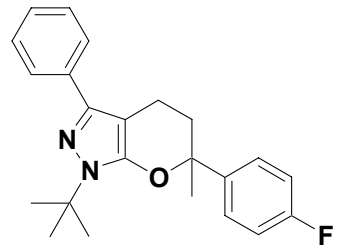
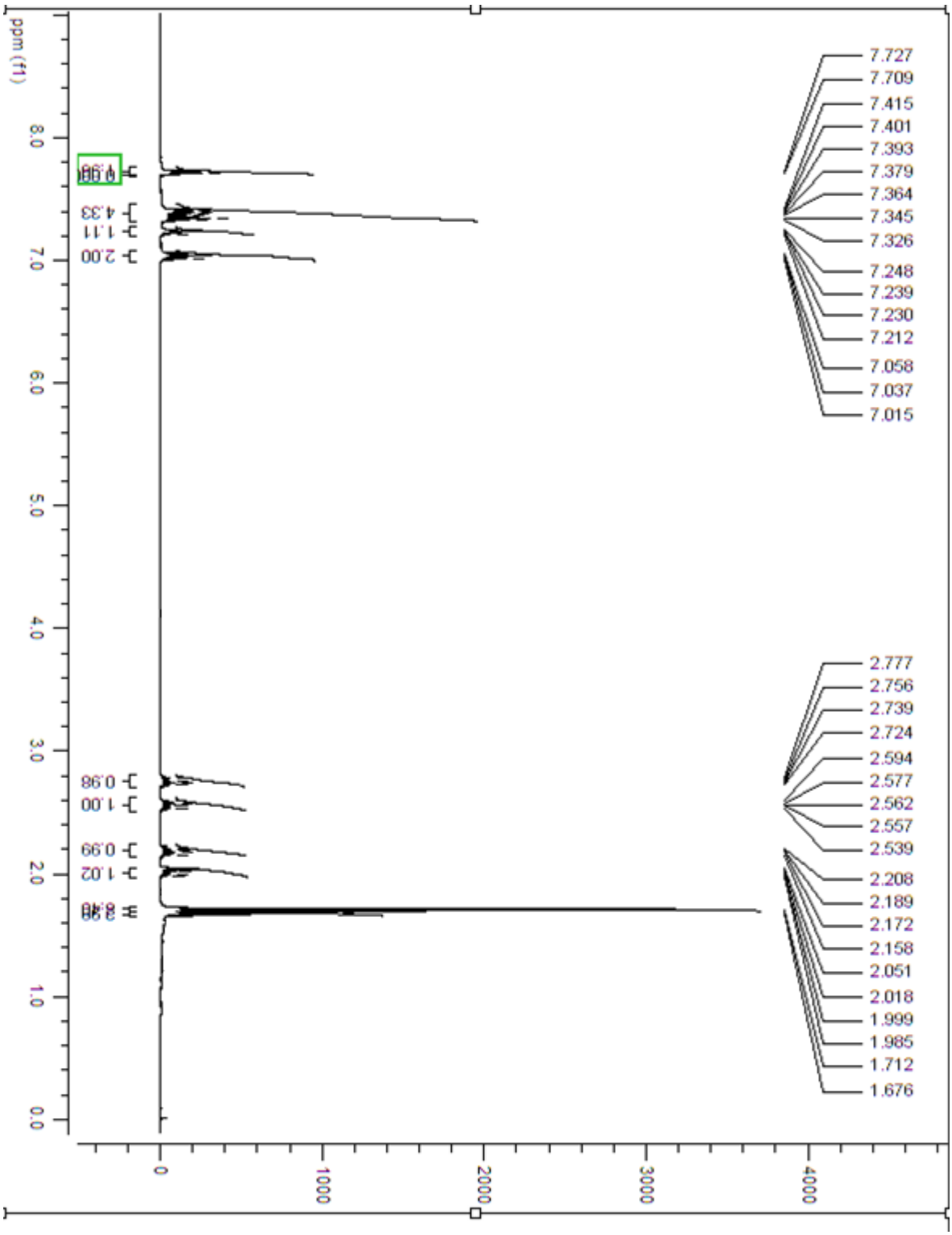
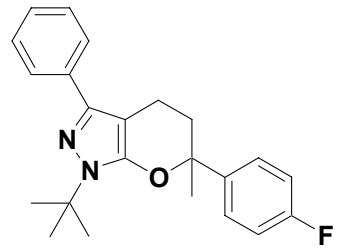
156.917
147.698
135.358
131.140
130.539
130.139
128.844
128.697
128.289
127.006
122.939
120.983
120.902
118.142
117.559
115.969
115.745
105.231
91.609
87.042
77.356
77.038
76.721
49.419
29.670


N
N
O
F


ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
1000
2000
3000
4000
7.727
7.709
7.415
7.401
7.393
7.379
7.364
7.345
7.326
7.248
7.239
7.230
7.212
7.058
7.037
7.015
2.777
2.756
2.739
2.724
2.594
2.577
2.562
2.557
2.539
2.208
2.189
2.172
2.158
2.051
2.018
1.999
1.985
1.712
1.676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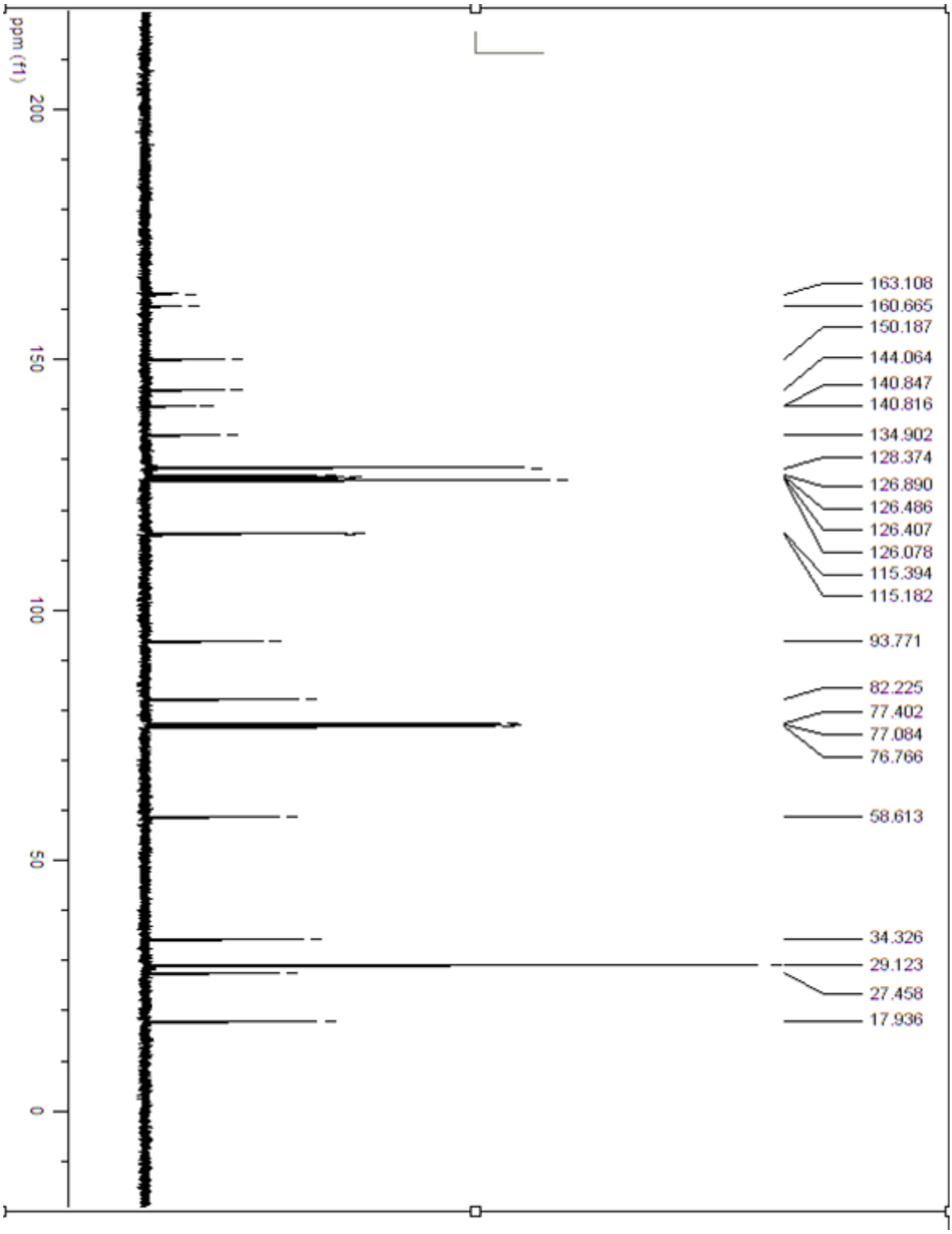
N
O
F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100
50
0
163.108
160.665
150.187
144.064
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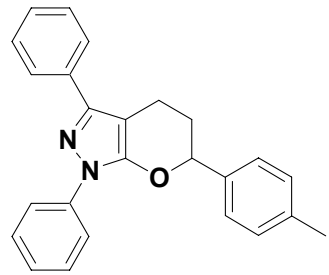
140.816
134.902
128.374
126.890
126.486
126.407
126.078
115.394
115.182
93.771
82.225
77.402
77.084
76.766
58.613
34.326
29.123
27.458
17.936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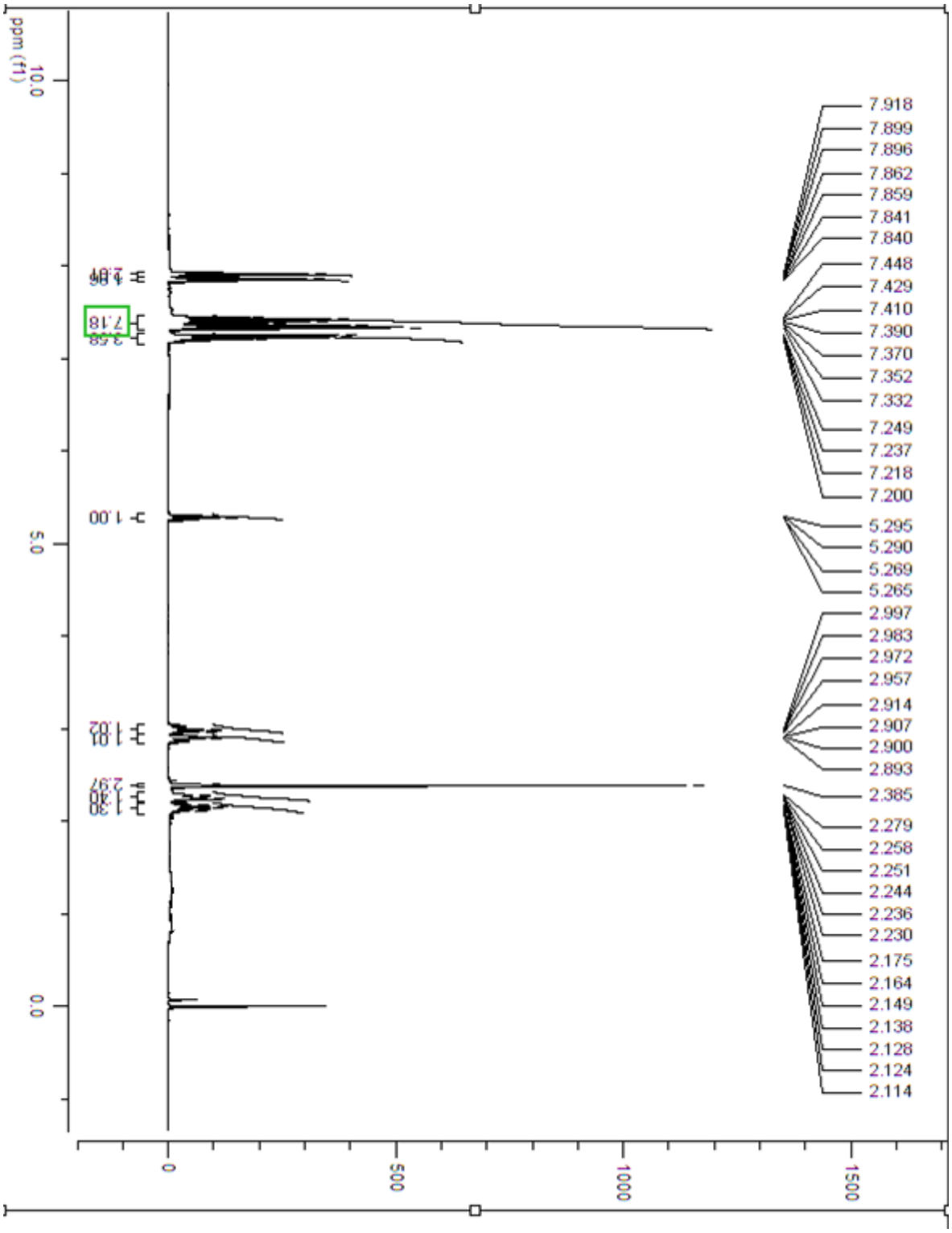
N
O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0
500
1000
1500
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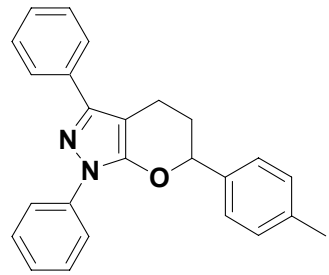
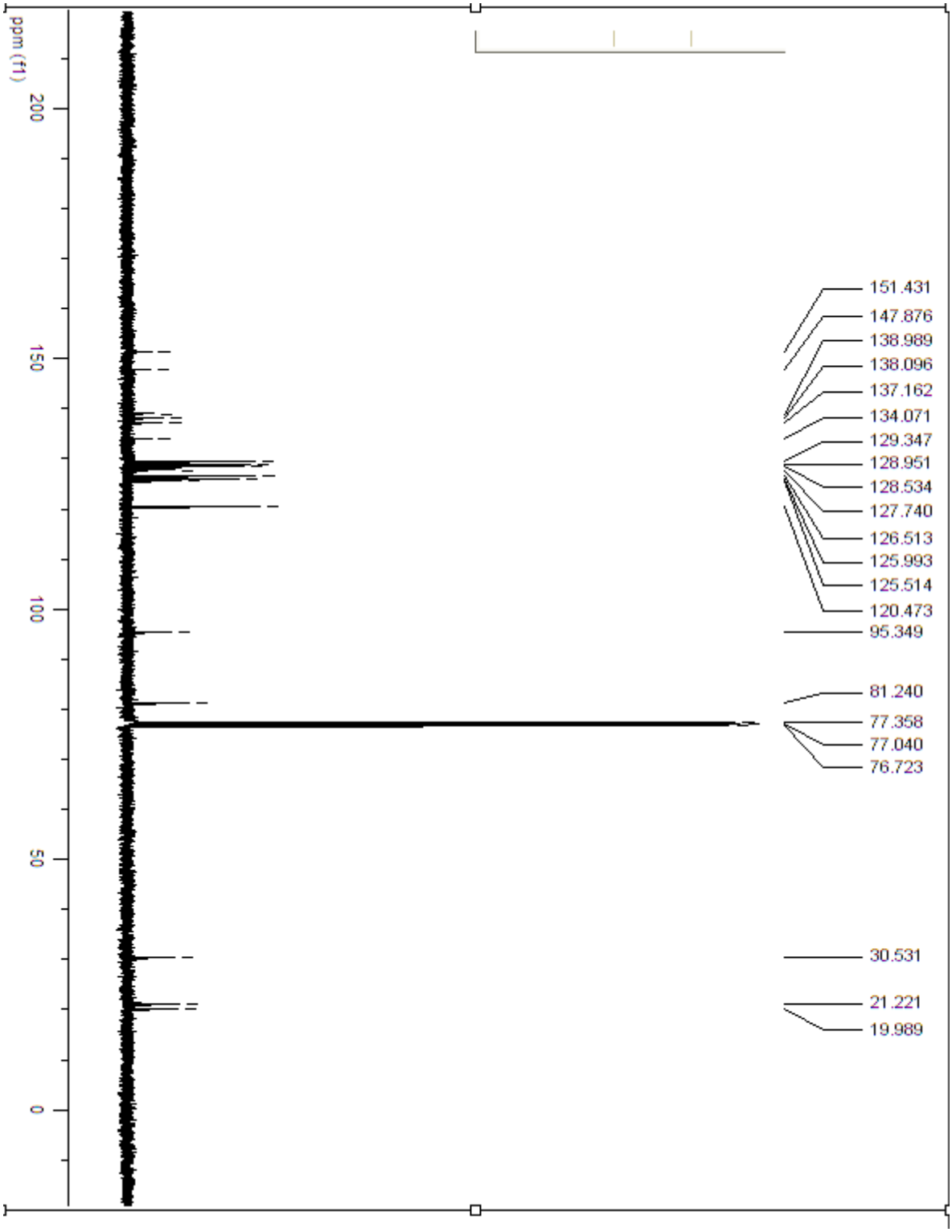
7.862
7.859
7.841
7.840
7.448
7.429
7.410
7.390
7.370
7.352
7.332
7.249
7.237
7.218
7.200
5.295
5.290
5.269
5.265
2.997
2.983
2.972
2.957
2.914
2.907
2.900
2.893
2.385
2.279
2.258
2.251
2.244
2.236
2.230
2.175
2.164
2.149
2.138
2.128
2.124
2.114


N
N
O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100
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127.740
126.513
125.993
125.514
120.473
95.349
81.240
77.358
77.040
76.723
30.531
21.221
19.989