Supporting Information

For

Synthesis and Diversification of 1,2,3-Triazole-Fused 1,4-Benzodiazepine Scaffolds

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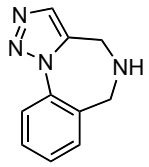
Experimental Section

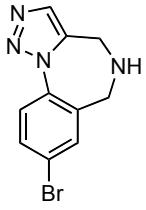
General methods. Unless otherwise noted, solvents and reagents were reagent-grade and used without further purification. Acetonitrile (CH_3CN), dimethylformamide (DMF), tetrahydrofuran (THF) and toluene were dried according to the procedure described by Grubbs.[1] Benzene, dichloromethane (CH_2Cl_2), pyridine and triethylamine were distilled from CaH_2. 1,2-Dichloroethane (DCE) was dried with, and stored over activated ball-type 4 Å molecular sieves. Where required, solvents were degassed by sparging with nitrogen for 20 min prior to use. Molecular sieves were activated by heating (*ca*. 250 ˚C) under high vacuum (*ca*. 0.5 mmHg) for at least 6 h prior to use. Zinc granules were activated by stirring with aqueous HCl (1.0 M) for 10 min, then filtered, rinsed with H_2O, MeOH, then Et_2O, and dried under high vacuum (*ca*. 0.5 mmHg) before use. Zinc chloride was fused under high vacuum (*ca*. 0.5 mmHg) prior to use. Reactions were performed under a nitrogen or argon atmosphere in round-bottom flasks sealed under rubber septa with magnetic stirring, unless otherwise noted. Water sensitive reactions were performed with oven-dried glassware and stir bars. Sensitive reagents and solvents were transferred using plastic syringes and oven-dried steel needles using standard techniques. Reaction temperatures are reported as the temperatures of the bath surrounding the vessel.

Nuclear magnetic resonance spectra were acquired at room temperature in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to either TMS or the residual solvent: $CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C); d_6-DMSO, δ = 2.50 ppm (^{1}H) and 39.5 ppm (^{13}C); CD_3CN, δ = 1.94 ppm (^{1}H) and 1.32 (CD_3CN) ppm (^{13}C).[2] The abbreviations s, d, t, q, m and comp stand for the resonance multiplicities singlet, doublet, triplet, quartet, multiplet, and complex (overlapping multiplets of magnetically nonequivalent protons), respectively. Br = broad; app = apparent. Infrared (IR) spectra were recorded as films on sodium chloride plates and reported as wavenumbers (cm^{-1}). Thin-layer chromatography was performed on Merck Kieselgel 60 F254 silica gel plates eluting with the solvents indicated, visualized by 254 nm UV lamp, and stained with 100 basic $KMnO_4$ solution or *para*-anisaldehyde. Flash chromatography was performed with Silicycle pharmaceutical grade silica gel (Silicycle F60, particle size 43-60 μm).[3]



4

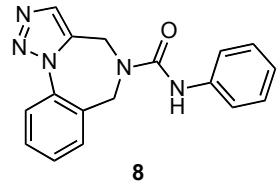
5,6-Dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (4). A mixture of 2-azidobenzaldehyde (**5**) (3.10 g, 21.1 mmol),[4] propargylamine (1.74 g, 2.02 mL, 31.6 mmol), sodium triacetoxyborohydride (8.93 g, 42.1 mmol) and glacial acetic acid (1.27 g, 1.20 mL, 21.1 mmol) in DCE (62 mL) was stirred at room temperature for 3 h. The reaction was diluted with CH_2Cl_2 (150 mL) and saturated aqueous $NaHCO_3$ (150 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 80 mL), and the combined organic layers were concentrated under reduced pressure. The residue was dissolved in Et_2O (80 mL), and the solution was extracted with aqueous HCl (3 × 40 mL, 1.0 M). The combined aqueous extracts were washed with Et_2O (80 mL). The pH of the aqueous layer was then raised to ~ 11-12 by adding aqueous NaOH (1.0 M), and the resulting suspension was extracted with Et_2O (3 × 80 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure and the residue was dissolved in toluene (60 mL), and heated at 100 ˚C for 4.5 h. The cooled reaction was concentrated under reduced pressure, and the residue was purified by recrystallization from hexanes/EtOAc to give 2.57 g (66%) of amine **4** as pale yellow prisms: mp 120-122 ˚C (lit.[5] 124-125 ˚C, Et_2O); ^{1}H NMR (400 MHz) δ 7.97 (d, J = 7.9 Hz, 1 H), 7.72 (s, 1 H), 7.54 (m, 1 H), 7.49-7.40 (comp, 2 H), 4.03 (s, 2 H), 3.82 (s, 2 H), 2.10 (br s, 1 H). All spectroscopic data were consistent with those reported in the literature.[5]



7

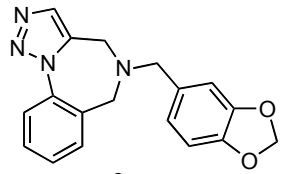
8-Bromo-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (7). A mixture of 2-azido-5-bromobenzaldehyde (**6**) (5.00 g, 22.1 mmol),[6] propargylamine (1.83 g, 2.13 mL, 33.2 mmol), sodium triacetoxyborohydride (9.38 g, 44.2 mmol) and glacial acetic acid (1.33 g, 1.27 mL, 22.1 mmol) in DCE (100 mL) was stirred at room temperature for 2.5 h. The reaction was diluted with CH_2Cl_2 (200 mL) and saturated aqueous $NaHCO_3$ (200 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic layers were concentrated under reduced pressure. The residue was dissolved in Et_2O (300 mL), and the solution was extracted with aqueous HCl (3 × 150 mL, 1.0 M). The pH of the combined aqueous extracts was then raised to ~ 11-12 by adding aqueous NaOH (1.0 M). The resulting suspension was extracted

with Et_2O (4 × 100 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in toluene (120 mL) and the solution heated at 100 ˚C for 4.5 h. The cooled reaction was concentrated under reduced pressure, and the residue was purified by recrystallization from *i*-PrOH to give 4.50 g (77%) of amine **7** as pale brown plates: mp 139-141 ˚C; ^{1}H NMR (300 MHz) δ 7.83 (d, *J* = 8.7 Hz, 1 H), 7.68 (s, 1 H), 7.64 (dd, *J* = 8.7, 2.0 Hz, 1 H), 7.56 (d, *J* = 2.0 Hz, 1 H), 4.06 (s, 2 H), 3.80 (s, 2 H), 2.26 (s, 1 H); ^{13}C NMR (75 MHz) δ 135.7, 135.6, 133.5, 132.9, 132.2, 132.1, 124.4, 122.5, 48.8, 39.4; IR (neat) 3285, 2972, 2919, 2856, 1486, 1466, 1442, 1363, 1227, 1185, 1124, 1094, 1043, 1017 cm^{-1}; mass spectrum (ESI) *m/z* 286.9904 [$C_{10}H_9N_4Na^{79}Br$ (M+Na) requires 286.9903].



8

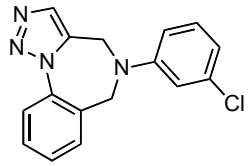
***N*-Phenyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carboxamide (8).** Phenyl isocyanate (45 mg, 41 μL, 0.38 mmol) was added to a solution of amine **4** (35 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 2 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous HCl (10 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc to give 57 mg (99%) of urea **8** as a colorless foam; ^{1}H NMR (600 MHz) δ 7.42 (dd, *J* = 7.5, 1.2 Hz, 1 H), 7.73 (s, 1 H), 7.58 (app td, *J* = 7.5, 1.5 Hz, 1 H), 7.50 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.47 (app td, *J* = 7.5, 1.2 Hz, 1 H), 7.34 (dd, *J* = 8.5, 1.1 Hz, 2 H), 7.26 (dd, *J* = 8.5, 7.4 Hz, 2 H), 7.05 (tt, *J* = 7.4, 1.1 Hz, 1 H), 6.81 (br s, 1 H), 4.71 (s, 2 H), 4.47 (s, 2 H); ^{13}C NMR (150 MHz) δ 154.6, 138.5, 136.2, 133.1, 132.2, 130.7, 130.2, 129.7, 129.0, 128.5, 123.9, 123.1, 120.7, 46.9, 38.8; IR (neat) 3314, 3132, 3060, 2920, 2859, 1643, 1597, 1537, 1499, 1444, 1393, 1367, 1311, 1241 cm^{-1}; mass spectrum (ESI) *m/z* 306.1349 [$C_{17}H_{16}N_5O$ (M+1) requires 306.1349].



9

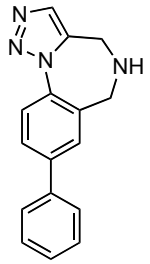
5-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (9). A mixture of sodium triacetoxyborohydride (239 mg, 1.13 mmol), amine **4** (35 mg, 0.19 mmol), piperonal (169 mg, 1.13 mmol) and glacial acetic acid (11 mg, 11 μL, 0.19 mmol) in DCE (3.0 mL) was stirred at room temperature for 18 h. The reaction was diluted with CH_2Cl_2 (20

mL) and saturated aqueous $NaHCO_3$ (20 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic layers were concentrated under reduced pressure. The residue was dissolved in Et_2O (20 mL), and the solution was extracted with aqueous HCl (3 × 10 mL, 1.0 M). The combined aqueous extracts were washed with Et_2O (10 mL). The pH of the aqueous layer was then raised to ~ 11-12 by adding aqueous NaOH (1.0 M), and the resulting solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (1 : 1) to give 58 mg (96%) of amine **9** as a yellow gum: ^{1}H NMR (400 MHz) δ 7.90 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.73 (s, 1 H), 7.55 (app td, *J* = 7.6, 1.6 Hz, 1 H), 7.46 (app td, *J* = 7.6, 1.4 Hz, 1 H), 7.41 (dd, *J* = 7.6, 1.6 Hz, 1 H), 6.92 (s, 1 H), 6.83-6.78 (comp, 2 H), 5.97 (s, 2 H), 3.64 (s, 2 H), 3.61 (s, 2 H), 3.52 (s, 2 H); ^{13}C NMR (75 MHz) δ 148.1, 147.2, 136.8, 133.6, 132.9, 131.8, 131.2, 129.6, 129.1, 129.1, 122.8, 122.3, 109.4, 108.2, 101.2, 60.1, 54.2, 44.5; IR (neat) 2901, 2813, 1491, 1433, 1245, 1098, 1039 cm^{-1}; mass spectrum (ESI) *m/z* 321.1346 [$C_{18}H_{17}N_4O_2$ (M+1) requires 321.1346].



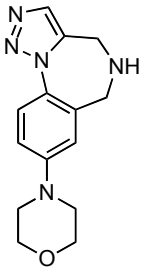
10

5-(3-Chlorophenyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (10). Palladium acetate (2.4 mg, 0.011 mmol) was added to a solution of (±)-BINAP (10 mg, 0.016 mmol) in degassed toluene (1.0 mL) and the mixture was stirred at room temperature for 1 min. Amine **4** (40 mg, 0.21 mmol), 1-bromo-3-chlorobenzene (82 mg, 50 μL, 0.43 mmol) and then sodium *tert*-butoxide (29 mg, 0.30 mmol) were added, and the reaction was heated at 80 ˚C for 2.5 h. The cooled reaction was diluted with Et_2O (5 mL) and filtered through celite, washing with Et_2O (5 mL). The combined filtrate and washings were concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (7 : 3) to give 61 mg (96%) of amine **10** as a yellow glass: ^{1}H NMR (400 MHz) δ 7.99 (d, *J* = 7.5 Hz, 1 H), 7.79 (s, 1 H), 7.55 (app td, *J* = 7.5, 2.1 Hz, 1 H), 7.49-7.40 (comp, 2 H), 7.19 (app t, *J* = 8.2 Hz, 1 H), 6.87 (app t, *J* = 2.2 Hz, 1 H), 6.83-6.76 (comp, 2 H), 4.47 (s, 2 H), 4.33 (s, 2 H); ^{13}C NMR (75 MHz) δ 149.4, 136.3, 135.4, 133.1, 133.1, 130.5, 130.5, 129.9, 129.4, 128.9, 122.9, 118.8, 114.0, 112.1, 50.6, 42.8; IR (neat) 3131, 3062, 2922, 2850, 1594, 1563, 1492, 1385, 1232, 1132, 1102 cm^{-1}; mass spectrum (CI) *m/z* 297.0902 [$C_{16}H_{14}N_4Cl$ (M+1) requires 297.0902].



11

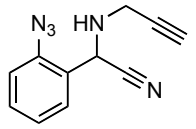
8-Phenyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (11). (All reagents were weighed out in a glove-box). A mixture of amine **7** (500 mg, 1.89 mmol), phenylboronic acid (460 mg, 3.77 mmol), bis(tri-*tert*-butylphosphine)palladium(0) (9.6 mg, 0.019 mmol) and cesium carbonate (1.23 g, 3.77 mmol) in degassed dioxane (12.5 mL) was stirred at 90 ˚C for 5 h. The cooled reaction was diluted with CH_2Cl_2 (20 mL) and filtered through celite, washing with CH_2Cl_2 (80 mL). The combined filtrate and washings were concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with CH_2Cl_2/MeOH (97 : 3 → 19 : 1) to give 414 mg (84%) of biphenyl **11** as a cream colored solid: mp 120-122 ˚C (pale yellow prisms from *i*-PrOH); ^{1}H NMR (300 MHz) δ 7.99 (d, *J* = 8.2 Hz, 1 H), 7.74-7.67 (comp, 2 H), 7.64-7.57 (comp, 3 H), 7.46 (app t, *J* = 7.2 Hz, 2 H), 7.38 (t, *J* = 7.2 Hz, 1 H), 4.05 (s, 2 H), 3.86 (s, 2 H), 2.56 (s, 1 H); ^{13}C NMR (75 MHz) δ 142.1, 139.5, 135.7, 135.6, 132.1, 131.8, 129.0, 128.7, 128.0, 127.8, 127.1, 123.2, 49.1, 39.3; IR (neat) 3302, 3034, 2977, 2681, 1512, 1488, 1453, 1435, 1228, 1142, 1124 cm^{-1}; mass spectrum (ESI) *m/z* 163.1290 [$C_{16}H_{15}N_4$ (M+1) requires 263.1291].



12

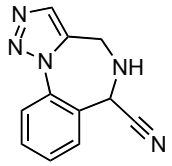
4-(5,6-Dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-8-yl)morpholine (12). Palladium acetate (21 mg, 0.094 mmol) was added to a solution of (±)-BINAP (88 mg, 0.14 mmol) in degassed toluene (12.5 mL) and the mixture was stirred at room temperature for 1 min. Amine **7** (500 mg, 1.89 mmol), morpholine (1.64 g, 1.65 mL, 18.9 mmol) and then sodium *tert*-butoxide (254 mg, 2.64 mmol) were added, and the reaction was heated at 80 ˚C for 1 h. The cooled reaction was filtered through celite, washing with CH_2Cl_2 (50 mL). The combined filtrate and washings were concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with CH_2Cl_2/MeOH (95 : 5 → 93 : 7) to give 354 mg (69%) of amine **12** as a cream colored solid: mp 150-152 ˚C (pale yellow microcrystals from *i*-PrOH); ^{1}H NMR (400 MHz) δ 7.81 (d, *J* = 8.9 Hz,

1 H), 7.67 (s, 1 H), 7.01 (dd, *J* = 8.9, 2.6 Hz, 1 H), 6.89 (d, *J* = 2.6 Hz, 1 H), 4.00 (s, 2 H), 3.88 (t, *J* = 4.8 Hz, 4 H), 3.77 (s, 2 H), 3.25 (t, *J* = 4.8 Hz, 4 H), 2.13 (s, 1 H); ^{13}C NMR (100 MHz) δ 151.7, 135.1, 132.4, 131.9, 128.8, 123.8, 115.9, 115.5, 66.8, 49.4, 48.8, 39.2; IR (neat) 3301, 2979, 2888, 2843, 1610, 1585, 1511, 1451, 1381, 1266, 1246, 1120 cm^{-1}; mass spectrum (ESI) *m/z* 272.15055 [$C_{14}H_{18}N_5O$ (M+1) requires 272.15059].



13

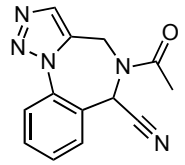
2-(2-(Benzo[*d*][1,3]dioxol-5-ylmethyl)phenyl)-2-(prop-2-ynylamino)-acetonitrile (13). Aqueous HCl (4.28 mL, 1.0 M, 4.28 mmol) was added dropwise to a solution of 2-azido-benzaldehyde (**5**) (600 mg, 4.08 mmol),[4] propargylamine (236 mg, 274 μL, 4.28 mmol) and sodium cyanide (210 mg, 4.28 mmol) in MeOH (8.6 mL) and the reaction stirred at room temperature for 2.5 h. The reaction was diluted with H_2O (50 mL) and the pH raised to 10 with aqueous NaOH (*ca*. 300 μL, 1.0 M). The resulting mixture was extracted with EtOAc (3 × 70 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with hexanes/Et_2O (4 : 1 → 3 : 2) to give 673 mg of amine **13** (78%) as an orange oil: ^{1}H NMR (500 MHz) 7.53 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.45 (ddd, *J* = 8.1, 7.6, 1.5 Hz, 1 H), 7.22 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.20 (app td *J* = 7.6, 1.5 Hz, 1 H), 5.11 (d, *J* = 7.5 Hz, 1 H), 3.62 (m, 2 H), 2.34 (t, *J* = 2.5 Hz, 1 H) 2.00 (m, 1 H); ^{13}C NMR (100 MHz) 138.1, 130.8, 129.4, 125.4, 125.2, 118.7, 117.9, 79.6, 73.2, 48.6, 36.5; IR (neat) 3295, 2132, 1586, 1491, 1452, 1297, 1106 cm^{-1}; mass spectrum (CI) m/z 212.0940 [$C_{11}H_{10}N_5$ (M+1) requires 212.0936], 185, 157.



14

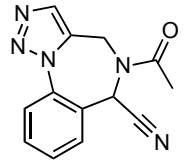
5,6-Dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (14). A solution of amine **13** (667 mg, 3.02 mmol) in toluene (158 mL) was stirred at 60 ˚C for 34 h. The cooled reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with toluene/EtOAc (1 : 1 → 0 : 1) to give 589 mg of amine **14** (88%) as a colorless solid: mp 133 ˚C (dec.) (colorless needles from hexanes/CH_2Cl_2); ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.94 (d, *J* = 7.9 Hz, 1 H), 7.90 (s, 1 H), 7.75-7.66 (comp, 2 H), 7.61 (app t, *J* = 7.2 Hz, 1 H), 5.49 (d, *J* = 5.1 Hz, 1 H), 4.20 (ddd, *J* = 6.3, 5.1, 4.9 Hz, 1 H), 4.10 (dd, *J* = 14.6, 4.9 Hz, 1 H), 3.73 (dd, *J* = 14.6, 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, d_6-DMSO) 135.4, 135.2, 132.2, 131.0, 130.1,

129.7, 127.0, 123.4, 119.2, 48.9, 36.7; IR (neat) 3312, 2920, 2851, 1495, 1469, 1230, 1136, 1095 cm^{-1}; mass spectrum (CI) m/z 212.0940 [$C_{11}H_{10}N_5$ (M+1) requires 212.0936], 185.



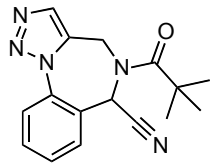
15

5-Acetyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (15). Acetyl chloride (15 mg, 13 μL, 0.19 mmol) was added to a solution of amine **13** (20 mg, 0.095 mmol) and pyridine (22 mg, 23 μL, 0.28 mmol) in anhydrous MeCN (1.0 mL) and the reaction stirred at room temperature for 36 h. The mixture was concentrated under reduced pressure, and the residue purified by flash chromatography eluting with EtOAc to give 23 mg of amide **15** (96 %) as a cream colored solid: mp 196-197 ˚C (colorless needles from toluene); ^{1}H NMR (500 MHz, d_6-DMSO, 120 ˚C) δ 8.00 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.00 (s, 1 H), 7.83 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.79 (app td, *J* = 7.6, 1.4 Hz, 1 H), 7.63 (app td, *J* = 7.6, 1.2 Hz, 1 H), 6.74 (s, 1 H), 5.38 (d, *J* = 15.0 Hz, 1 H), 4.28 (d, *J* = 15.0 Hz, 1 H), 2.28 (s, 3 H); ^{13}C NMR (125 Mz, d_6-DMSO, 120 ˚C) δ 168.6, 134.6, 132.6, 131.4, 131.3, 130.9, 129.3, 123.8, 123.0, 115.6, 47.4, 38.5, 20.7; IR (neat) 2926, 1667, 1661, 1499, 1395, 1233 cm^{-1}; mass spectrum (CI) m/z 254.1044 [$C_{13}H_{12}N_5O$ (M+1) requires 254.1042], 227.



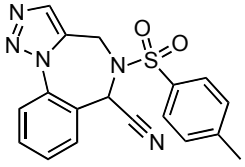
15

5-Acetyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (15). Propargylamine (53 mg, 61 μL, 0.96 mmol) was added to a mixture of 2-azido-benzaldehyde **5** (118 mg, 0.802 mmol),[4] and activated, powdered 4 Å molecular sieves (400 mg, pre-activated weight) in anhydrous MeCN (2.0 mL) and the reaction stirred at room temperature for 18 h. $LiClO_4$ (8.5 mg, 0.080 mmol) and trimethylsilyl cyanide (202 mg, 255 μl, 2.04 mmol) were added, and the mixture was stirred at room temperature for 24 h. Pyridine (381 mg, 389 μL, 4.81 mmol) and then acetyl chloride (252 mg, 228 μL, 3.21 μmol) were added and the reaction was stirred at room temperature for a further 36 h. The mixture was filtered through celite, and washed with MeCN (20 mL). The filtrate was concentrated under reduced pressure, and the residue purified by flash chromatography eluting with EtOAc to give 100 mg of amide **15** (49%) as a cream colored solid. All spectroscopic data were consistent with those previously recorded.



17

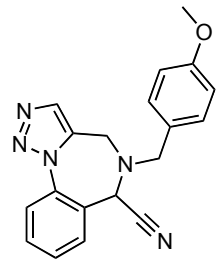
5-Pivaloyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (17). Pivaloyl chloride (69 mg, 70 μL, 0.57 mmol) was added to a solution of amine **14** (60 mg, 0.28 mmol) and pyridine (67 mg, 69 μL, 0.85 mmol) in anhydrous MeCN (1.0 mL) at 0 ˚C, and the reaction was stirred at room temperature for 4 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous HCl (10 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (1 : 1 → 4 : 6) to give 77 mg (92%) of amide **17** as a colorless solid: mp 212-214 ˚C (colorless needles from *i*-PrOH); ^{1}H NMR (400 MHz) δ 8.04 (dd, *J* = 7.8, 0.8 Hz, 1 H), 7.87 (s, 1 H), 7.75 (ddd, *J* = 7.8, 7.0, 2.0 Hz, 1 H), 7.62-7.55 (comp, 2 H), 6.42 (s, 1 H), 5.49 (d, *J* = 15.1 Hz, 1 H), 4.16 (d, *J* = 15.1 Hz, 1 H), 1.42 (s, 9 H); ^{13}C NMR (100 MHz) δ 176.4, 135.5, 132.9, 132.5, 131.6, 131.1, 130.4, 124.2, 123.9, 115.7, 48.8, 39.2, 39.0, 28.2; IR (neat) 2974, 2934, 2235, 1644, 1500, 1475, 1403, 1369, 1318, 1227, 1182, 1134, 1107 cm^{-1}; mass spectrum (ESI) *m/z* 296.1508 [$C_{16}H_{18}N_5O$ (M+1) requires 296.1506].



18

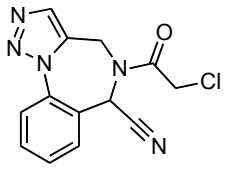
5-Tosyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (18). *p*-Toluenesulfonyl chloride (54 mg, 0.28 mmol) was added to a solution of amine **14** (30 mg, 0.14 mmol) and pyridine (34 mg, 34 μL, 1.4 mmol) in anhydrous MeCN (1.0 mL) and the reaction stirred at room temperature for 2 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous HCl (20 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (20 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (1 : 1 → 4 : 6) to give 45 mg of sulfonamide **18** (87 %) as a colorless glass: mp 127-128.5 ˚C (colorless microcrystals from *i*-PrOH); ^{1}H NMR (400 MHz) δ 7.93 (d, *J* = 7.6 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 2 H), 7.72 (s, 1 H), 7.66 (app t, *J* = 7.6 Hz, 1 H), 7.50 (app t, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 6.13 (s, 1 H), 5.04 (d, *J* = 14.4 Hz, 1 H), 3.99 (d, *J* = 14.4 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz) δ 145.5, 135.0, 134.0, 133.6, 132.6, 130.8, 130.4, 130.3, 129.9, 127.5, 124.4, 123.2, 114.8, 49.6, 38.0, 21.7; IR (neat) 2954, 2925,

2252, 1597 1499, 1361, 1166, 1094, 1010 cm^{-1}; mass spectrum (CI) m/z 366.1028 [$C_{18}H_{16}N_5O_2S$ (M+1) requires 366.1025], 339, 210, 182, 85, 83.



19

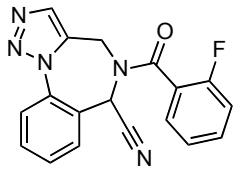
5-(4-Methoxybenzyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (19). Sodium triacetoxyborohydride (2.16 g, 10.2 mmol) was added to a solution of amine **14** (360 mg, 1.70 mmol), *p*-anisaldehyde (1.39 g, 1.24 mL, 10.2 mmol) and glacial acetic acid (102 mg, 97 μL, 1.70 mmol) in DCE (27 mL) and the reaction stirred at room temperature for 18 h. The reaction was diluted with CH_2Cl_2 (30 mL) and saturated aqueous $NaHCO_3$ (30 mL) and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic layers dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with hexanes/EtOAc (9 : 1 → 7 : 3) to give 418 mg of amine **19** (74%) as a colorless solid: mp 155 ˚C (dec.) (colorless microcrystals from *i*-PrOH); ^{1}H NMR (500 MHz) δ 8.00 (dd, *J* = 7.6, 1.1 Hz, 1 H), 7.77 (s, 1 H), 7.68 (app td, *J* = 7.6, 1.6 Hz, 1 H), 7.60 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.56 (app td, *J* = 7.6, 1.1 Hz, 1 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 4.65 (s, 1 H), 3.88 (d, *J* = 12.9 Hz, 1 H), 3.85-3.78 (comp, 5 H), 3.72 (d, *J* = 14.9 Hz, 1 H); ^{13}C NMR (125 MHz) δ 159.6, 135.6, 133.1, 132.3, 131.5, 130.3, 130.3, 129.7, 128.0, 124.5, 123.8, 116.2, 114.3, 58.1, 55.4, 55.3, 42.7; IR (neat) 2933, 2835, 2247, 1611, 1512, 1495, 1468, 1249, 1175, 1032 cm^{-1}; mass spectrum (CI) m/z 332.1510 [$C_{19}H_{18}N_5O$ (M+1) requires 332.1511], 305, 121.



20

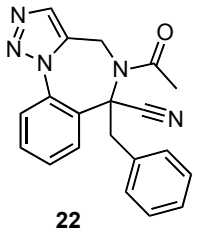
5-(2-Chloroacetyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (20). Chloroacetyl chloride (107 mg, 75 μL, 0.95 mmol) was added to a mixture of amine **14** (100 mg, 0.47 mmol) and pyridine (112 mg, 102 μL, 1.4 mmol) in anhydrous CH_2Cl_2 (3.0 mL), and the reaction was stirred at 0 ˚C for 40 min. The reaction was diluted with CH_2Cl_2 (20 mL) and washed with aqueous HCl (10 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (3 : 7) to give 123 mg (90%) of amide **20** as a

colorless solid: mp 179-181 ˚C (colorless prisms from MeCN); ^{1}H NMR (400 MHz, CD_3CN) (rotamers) δ 7.98, (d, *J* = 7.5 Hz, 1 H), 7.94 (s, 1 H), 7.79 (app t, *J* = 7.5 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.63 (app t, *J* = 7.5 Hz, 1 H), 6.62 (s, 0.9 H), 6.18 (br s, 0.1 H), 5.56 (m, 0.1 H), 5.18 (d, *J* = 14.9 Hz, 0.9 H), 4.48 (d, *J* = 13.8 Hz, 1 H), 4.39 (d, *J* = 13.8 Hz, 1 H), 4.24 (d, *J* = 14.9 Hz, 0.9 H), 3.88 (m, 0.1 H); ^{13}C NMR (75 MHz, CD_3CN) δ 166.8, 136.4, 134.5, 133.4, 132.9, 132.3, 131.3, 125.0, 124.6, 116.9, 47.9, 43.1, 39.0; IR (neat) 2919, 2850, 1672, 1501, 1403, 1327, 1231, 1204, 1134, 1108 cm^{-1}; mass spectrum (ESI) *m/z* 288.0647 [$C_{13}H_{11}N_5OCl$ (M+1) requires 288.0647].



21

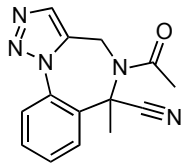
5-(2-Fluorobenzoyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (21). 2-Fluorobenzoyl chloride (90 mg, 68 μL, 0.57 mmol) was added to a solution of amine **14** (60 mg, 0.28 mmol) and pyridine (67 mg, 69 μL, 0.85 mmol) in anhydrous MeCN (1.5 mL) at 0 ˚C, and the reaction was stirred at room temperature for 1 h. The reaction was diluted with CH_2Cl_2 (20 mL) and the mixture was washed with aqueous HCl (10 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (4 : 6) to give 93 mg (98%) of amide **21** as a colorless solid: mp 217-219 ˚C (colorless prisms from hexanes/EtOAc); ^{1}H NMR (500 MHz, d_6-DMSO, 100 ˚C) δ 8.01 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.96 (s, 1 H), 7.93-7.80 (m, 1 H), 7.83 (app td, *J* = 7.8, 1.4 Hz, 1 H), 7.67 (app td, *J* = 7.8, 1.2 Hz, 1 H), 7.66-7.60 (m, 1 H), 7.54 (app, td, *J* = 7.4, 1.8 Hz, 1 H), 7.41-7.32 (comp, 2 H), 6.90-6.52 (m, 1 H), 5.28-4.89 (m, 1 H), 4.33 (d, *J* = 15.3 Hz, 1 H); ^{13}C NMR (125 MHz, d_6-DMSO, 100 ˚C) δ 164.5, 157.6 ($J_{C\text{-}F}$ = 347.6 Hz), 134.7, 132.8, 132.3 ($J_{C\text{-}F}$ = 8.3 Hz), 131.8, 131.3, 131.0, 129.5, 128.6, 124.7 ($J_{C\text{-}F}$ = 3.5 Hz), 123.3, 123.3, 121.5 ($J_{C\text{-}F}$ = 16.7 Hz), 115.8 ($J_{C\text{-}F}$ = 21.0 Hz), 115.3, 47.1, 38.2; IR (neat) 3063, 2923, 1652, 1614, 1450, 1455, 1394, 1325, 1236, 1093 cm^{-1}; mass spectrum (ESI) *m/z* 356.0918 [$C_{18}H_{12}N_5OFNa$ (M+Na) requires 356.0918].



22

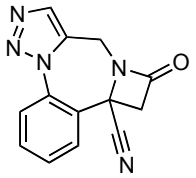
5-Acetyl-6-benzyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (22). A solution of amide **15** (50 mg, 0.20 mmol) in DMF (2.8 mL) was added dropwise

over 2 min to sodium hydride (8.7 mg, 0.22 mmol), and the mixture was stirred at room temperature for 45 min. Benzyl bromide (101 mg, 70 μL, 0.59 mmol) was added, and the reaction was stirred at room temperature for 15 min. The reaction was diluted with toluene (30 mL) and washed with H_2O (3 × 10 mL). The combined aqueous washes were extracted with toluene (3 × 5 mL) and then the combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with EtOAc to give 58 mg (86%) of nitrile **22** as a colorless solid: mp 242-244 ˚C; ^{1}H NMR (400 MHz) δ 8.00 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.86 (s, 1 H), 7.79 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.63 (app td, *J* = 7.8, 1.2 Hz 1 H), 7.34 (app td, *J* = 7.8, 1.2 Hz, 1 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 7.04 (app t, *J* = 7.2, Hz, 2 H), 6.74 (d, *J* = 7.2, 2 H), 5.09 (br d, *J* = 16.4 Hz, 1 H), 4.32 (d, *J* = 16.4 Hz, 1 H), 3.97 (br d, *J* = 13.2 Hz, 1 H), 2.46 (s, 3 H), 2.09 (d, *J* = 13.2 Hz, 1 H); ^{13}C NMR (100 MHz) δ 168.7, 134.0, 132.6, 132.5, 131.7, 131.5, 130.9, 130.1, 129.7, 128.1, 127.7, 125.5, 125.5, 116.3, 66.6, 42.2, 39.8, 24.3; IR (neat) 3031, 2926, 2854, 1666, 1496, 1392, 1353, 1229, 1218, 1133, 1043 cm^{-1}; mass spectrum (ESI) *m/z* 344.1506 [$C_{20}H_{18}N_5O$ (M+1) requires 344.1506].



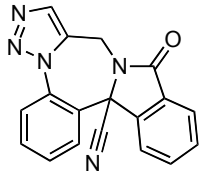
23

5-Acetyl-6-methyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (23). A solution of amide **15** (70 mg, 0.28 mmol) in DMF (3.5 mL) was added dropwise over 3 min to sodium hydride (12 mg, 0.30 mmol), and the mixture was stirred at room temperature for 45 min. Methyl iodide (196 mg, 86 μL, 1.38 mmol) was added and the reaction was stirred at room temperature for 1 h. The reaction was diluted with toluene (30 mL) and washed with H_2O (3 × 10 mL). The combined aqueous washes were extracted with toluene (3 × 5 mL), and then the combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with EtOAc to give 59 mg (80%) of nitrile **23** as a colorless solid: mp 175-177 ˚C; ^{1}H NMR (400 MHz) δ 8.29 (dd, *J* = 7.8, 1.6 Hz, 1 H), 8.03 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.83 (s, 1 H), 7.71 (app td, *J* = 7.8, 1.6 Hz, 1 H), 7.65 (app td, *J* = 7.8, 1.6 Hz, 1 H), 5.05 (d, *J* = 16.6 Hz, 1 H), 4.40 (d, *J* = 16.6 Hz, 1 H), 2.36 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.8, 133.6, 132.7, 131.6, 130.8, 130.3, 129.3, 128.6, 125.7, 117.5, 60.1, 39.7, 26.4, 23.9; IR (neat) 3137, 3003, 2935, 2246, 1668, 1495, 1392, 1353, 1227, 1187, 1127, 1052 cm^{-1}; mass spectrum (ESI) *m/z* 268.1192 [$C_{14}H_{14}N_5O$ (M+1) requires 268.1193].



24

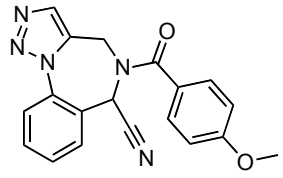
11-Oxo-9,11,12,12a-tetrahydroazeto[1,2-*d*]benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-12*a*-carbonitrile (24). A solution of amide **20** (50 mg, 0.17 mmol) in anhydrous DMF (1.6 mL) was added to a suspension of sodium hydride (7.6 mg, 0.19 mmol, 60% dispersion in mineral oil) in DMF (0.8 mL) and the reaction was stirred at room temperature for 1.5 h. The solution was poured into saturated aqueous NH_4Cl (20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were concentrated under reduced pressure. The residue was partitioned between H_2O (30 mL) and CH_2Cl_2 (10 mL), and the aqueous layer was further extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with CH_2Cl_2/MeOH (99 : 1) to give 34 mg (78%) of β-lactam **24** as a colorless solid: mp 239-240 ˚C; ^{1}H NMR (400 MHz) δ 8.10 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.88 (d, *J* = 1.0 Hz, 1 H), 7.76 (app td, *J* = 7.8, 1.4 Hz, 1 H), 7.64 (app td, *J* = 7.8, 1.2 Hz, 1 H), 7.52 (app d, *J* = 7.8, 1.4 Hz, 1 H), 5.01 (dd, *J* = 14.7, 1.0 Hz, 1 H), 4.48 (app dq, *J* = 14.7, 1.0 Hz, 1 H), 3.93 (dd, *J* = 15.1, 1.0 Hz, 1 H), 3.84 (app dt, *J* = 15.1, 1.0 Hz, 1 H); ^{13}C NMR (100 MHz) δ 162.3, 136.0, 134.0, 132.5, 130.3, 128.6, 127.3, 126.5, 125.5, 116.9, 51.2, 48.4, 35.8; IR (neat) 2923, 2853, 1777, 1493, 1467, 1357, 1263, 1239, 1135, 1106, 1034 cm^{-1}; mass spectrum (ESI) *m/z* 274.0700 [$C_{13}H_9N_5ONa$ (M+Na) requires 274.0699].



25

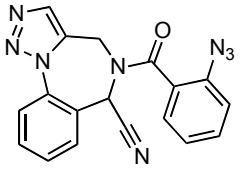
11-Oxo-11,13a-dihydro-9*H*-benzo[*f*]isoindolino[1,2-*d*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-13a-carbonitrile (25). A solution of amide **21** (28 mg, 0.084 mmol) in anhydrous DMF (0.7 mL) was added to a suspension of sodium hydride (3.7 mg, 0.092 mmol, 60% dispersion in mineral oil) in DMF (0.7 mL) and the reaction was stirred at room temperature for 2 h. The solution was diluted with toluene (30 mL) and the mixture was washed with H_2O (3 × 15 mL) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (4 : 6) to give 20 mg (76%) of isoindolinone **25** as a colorless solid: mp 245-247 ˚C; ^{1}H NMR (400 MHz) δ 8.10 (dd, *J* = 8.0, 1.2, Hz, 1 H), 8.02 (d, *J* = 7.6 Hz, 1 H), 7.99 (s, 1 H), 7.87 (app t, *J* = 7.5 Hz, 1 H), 7.82-7.72 (comp, 3 H), 7.50 (app td, *J* = 7.8, 1.2 Hz, 1 H), 7.20 (dd, *J* = 7.8, 1.4 Hz, 1 H),

5.47 (d, J = 15.1 Hz, 1 H), 4.25 (d, J = 15.1 Hz, 1 H); ^{13}C NMR (100 MHz) δ 165.9, 139.2, 135.8, 134.1, 133.7, 132.5, 131.6, 131.3, 130.7, 130.3, 127.0, 126.1, 126.0, 125.4, 125.3, 115.9, 61.0, 35.1; IR (neat) 3084, 2924, 2855, 1714, 1493, 1468, 1358, 1238, 1153, 1104 cm^{-1}; mass spectrum (ESI) m/z 314.1038 [$C_{18}H_{12}N_5O$ (M+1) requires 314.1036].



26

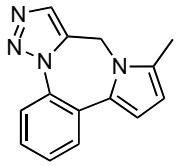
5-(4-Methoxybenzoyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (26). 4-Methoxybenzoyl chloride (48 mg, 38 μL, 0.28 mmol) was added to a solution of amine **14** (30 mg, 0.14 mmol) and pyridine (34 mg, 34 μL, 0.43 mmol) in anhydrous MeCN (1.0 mL) at 0 ˚C, and the reaction was stirred at room temperature for 1 h. The reaction was diluted with CH_2Cl_2 (20 mL) and the mixture was washed with aqueous HCl (20 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (20 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (1 : 1 → 3 : 7) to give 49 mg (quant.) of amide **26** as a colorless foam; ^{1}H NMR (500 MHz, d_6-DMSO, 120 ˚C) δ 8.01 (dd, J = 7.7, 1.2 Hz, 1 H), 7.94 (d, J = 0.9 Hz, 1 H), 7.86 (dd, J = 7.7, 1.2 Hz, 1 H), 7.82 (app td, J = 7.7, 1.2 Hz, 1 H), 7.66 (app td, J = 7.7, 1.2 Hz, 1 H), 7.56 (d, J = 8.9 Hz, 2 H), 7.07 (d, J = 8.9 Hz, 2 H), 6.57 (s, 1 H), 5.18 (d, J = 15.1 Hz, 1 H), 4.44 (dd, J = 15.1, 0.9 Hz, 1 H), 3.86 (s, 3 H); ^{13}C NMR (125 MHz, d_6-DMSO, 120 ˚C) δ 169.0, 161.1, 134.6, 132.6, 131.4, 131.2, 131.2, 129.3, 129.1, 125.1, 123.7, 123.0, 115.6, 113.7, 54.9, 47.6, 39.1; IR (neat) 2939, 1644, 1607, 1512, 1501, 1383, 1252, 1238, 1176 cm^{-1}; mass spectrum (CI) m/z 346.1306 [$C_{19}H_{16}N_5O_2$ (M+1) requires 346.1304].



27

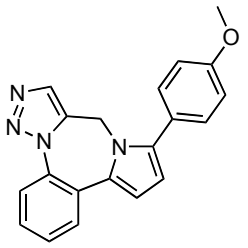
5-(2-Azidobenzoyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (27). A solution of 2-azidobenzoic acid[7] (309 mg, 1.9 mmol) in thionyl chloride (6.52 g, 4.0 mL, 55 mol) was heated under reflux for 3 h. The cooled solution was concentrated under reduced pressure, and the residue was azeotroped with anhydrous benzene (3 × 4.0 mL). The residue was dissolved in anhydrous CH_2Cl_2 (6.0 mL) at 0 ˚C, and amine **14** (200 mg, 0.95 mmol) and pyridine (225 mg, 204 μL, 2.8 mmol) were added and the mixture was stirred at room temperature for 2 h. The reaction was diluted with CH_2Cl_2 (40 mL) and washed with aqueous HCl (20 mL, 1.0

M) and saturated aqueous $NaHCO_3$ (20 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (3 : 7) to give 335 mg (99%) of amide **27** as a pale yellow glass: ^{1}H NMR (400 MHz) (rotamers) δ 8.07 (d, *J* = 8.0 Hz, 1 H), 8.02-7.94 (m, 0.35 H), 7.84-7.14 (comp, 7.49 H), 7.06-6.98 (m, 0.16 H), 6.71 (s, 0.62 H), 5.87-5.44 (comp, 0.72 H), 4.88-4.62 (comp, 0.66 H), 4.44-4.02 (comp, 1 H); ^{13}C NMR (75 MHz) (rotamers) δ 167.0, 136.6, 135.1, 134.7, 133.9, 132.9, 132.3, 131.9, 131.5, 130.5, 130.3, 128.8, 128.3, 127.5, 125.5, 125.0, 124.1, 122.9, 119.0, 118.5, 115.1, 50.7, 46.4, 39.0, 36.7, 35.6; IR (neat) 3143, 3065, 2942, 2132, 1651, 1598, 1500, 1449, 1394, 1323, 1296, 1236, 1153, 1107 cm^{-1}; mass spectrum (ESI) *m/z* 379.1027 [$C_{18}H_{12}N_8ONa$ (M+1) requires 379.1026].



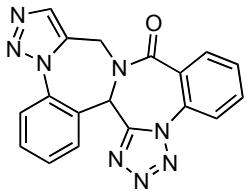
28

11-Methyl-9*H*-benzo[*f*]pyrrolo[1,2-*d*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (28). A solution of amide **15** (55 mg, 0.22 mmol) in degassed DMF (2.5 mL) was added dropwise over 2 min to sodium hydride (9.6 mg, 0.24 mmol), and the mixture was stirred at room temperature for 45 min. A solution of triphenylvinylphosphonium bromide (92 mg, 0.25 mmol) in degassed DMF (1.5 mL) was added, and the reaction was stirred at room temperature for 1.5 h. The reaction was diluted with toluene (30 mL) and washed with H_2O (3 × 15 mL) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (1 : 1) to give 37 mg (72%) of pyrrole **28** as a colorless solid: mp 194-196 ˚C (colorless needles from *i*-PrOH); ^{1}H NMR (500 MHz) δ 8.04 (dd, *J* = 7.4, 1.6 Hz, 1 H), 7.70 (s, 1 H), 7.66 (dd, *J* = 7.4, 1.7 Hz, 1 H), 7.46 (app td, *J* = 7.4, 1.6 Hz, 1 H), 7.43 (app td, *J* = 7.4, 1.7 Hz, 1 H), 6.38 (d, *J* = 3.6 Hz, 1 H), 6.01 (d, *J* = 3.6 Hz, 1 H), 5.03 (s, 2 H), 2.37 (s, 3 H); ^{13}C NMR (125 MHz) δ 134.0, 131.7, 131.0, 129.8, 129.7, 129.4, 129.2, 127.7, 125.1, 123.8, 109.3, 108.6, 36.5, 12.3; IR (neat) 3098, 3002, 2917, 2854, 1607, 1507, 1481, 1444, 1406, 1406, 1345, 1329, 1250, 1228, 1192, 1130, 1043, 1031 cm^{-1}; mass spectrum (ESI) *m/z* 237.1135 [$C_{14}H_{13}N_4$ (M+1) requires 237.1135].



29

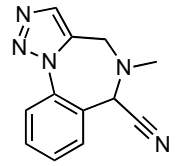
11-(4-Methoxyphenyl)-9*H*-benzo[*f*]pyrrolo[1,2-*d*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (29). A solution of amide **26** (64 mg, 0.19 mmol) in degassed DMF (2.3 mL) was added dropwise over 2 min to sodium hydride (8.2 mg, 0.20 mmol), and the mixture was stirred at room temperature for 45 min. A solution of triphenylvinylphosphonium bromide (79 mg, 0.21 mmol) in degassed DMF (1.4 mL) was added, and the reaction was stirred at room temperature for 1.5 h. The reaction was diluted with toluene (30 mL) and washed with H_2O (3 × 10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (6 : 4) to give 52 mg (85%) of pyrrole **29** as a colorless solid: mp 186-187 ˚C; ^{1}H NMR (400 MHz) δ 8.08 (dd, *J* = 7.5, 1.6 Hz, 1 H), 7.75 (dd, *J* = 7.5, 1.6 Hz, 1 H), 7.70 (s, 1 H), 7.50 (app td, *J* = 7.5, 1.6 Hz, 1 H), 7.46 (app td, *J* = 7.5, 1.6 Hz, 1 H), 7.31 (d, *J* = 6.7 Hz, 2 H), 7.03 (d, *J* = 6.7 Hz, 2 H), 6.54 (d, *J* = 3.7 Hz, 1 H), 6.26 (d, *J* = 3.7 Hz, 1 H), 5.09 (br s, 2 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz) δ 159.5, 135.8, 134.7, 131.9, 131.2, 130.8, 130.6, 129.6, 129.4, 128.1, 124.9, 124.5, 124.0, 114.4, 110.1, 109.9, 55.5, 37.3; IR (neat) 3003, 2932, 2837, 1610, 1550, 1487, 1454, 1395, 1334, 1289, 1250, 1177, 1131, 1032 cm^{-1}; mass spectrum (CI) *m/z* 329.1400 [$C_{20}H_{17}N_4O$ (M+1) requires 329.1402], 330, 328.



30

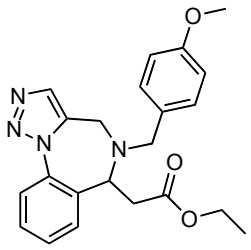
9*H*-Benzo[*f*]tetrazolo[1,5-*a*][1,4]diazepino[1,2-*d*]benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-11(15a*H*)-one (30). A solution of amide **27** (84 mg, 0.24 mmol) in toluene (12 mL) was heated under reflux for 12 h. The reaction was cooled to 0 ˚C, and the precipitate was isolated by vacuum filtration and washed with toluene (20 mL), to give 58 mg (69%) of tetrazole **30** as a cream colored solid: mp 284 ˚C (dec.); ^{1}H NMR (400 MHz, CD_3CN) δ 8.16 (dd, *J* = 7.9, 1.2 Hz, 1 H), 8.10 (d, *J* = 7.9 Hz, 1 H), 7.89 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.86-7.81 (comp, 2 H), 7.73 (app td, *J* = 7.9, 1.2 Hz, 1 H), 7.64-7.56 (comp, 3 H), 6.16 (s, 1 H), 5.93 (d, *J* = 15.2 Hz, 1 H), 3.98 (d, *J* = 15.2 Hz, 1 H); ^{13}C NMR (125 MHz, CD_3CN) δ 165.2, 155.1, 137.9, 134.5, 134.2, 133.7, 133.2, 133.2, 133.2, 131.6, 130.8, 130.6, 127.9, 125.3, 124.0, 123.4, 54.6, 35.8; IR (neat) 3075, 2919, 1639, 1605, 1502,

1470, 1443, 1402, 1355, 1251, 1154, 1132, 1102, 1080 cm^{-1}; mass spectrum (ESI) *m/z* 379.1026 [$C_{18}H_{12}N_8ONa$ (M+Na) requires 379.1026].



31

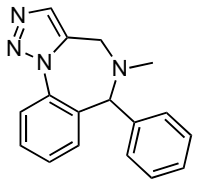
5-Methyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (31). A mixture of sodium triacetoxyborohydride (271 mg, 1.28 mmol), amine **14** (45 mg, 0.21 mmol), paraformaldehyde (64 mg, 2.1 mmol) and glacial acetic acid (13 mg, 12 μL, 0.21 mmol) in DCE (3.4 mL) was stirred at room temperature for 36 h. The reaction was diluted with CH_2Cl_2 (15 mL) and saturated aqueous $NaHCO_3$ (15 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with toluene/EtOAc (7 : 3 → 1 : 1) to give 30 mg (63%) of amine **31** as a colorless solid: mp 161-163 ˚C (colorless needles from *i*-PrOH); ^{1}H NMR (400 MHz) δ 7.97 (d, *J* = 7.9 Hz, 1 H), 7.82 (s, 1 H), 7.78 (d, *J* = 7.5 Hz, 1 H), 7.70 (dd, *J* = 7.9, 7.5 Hz, 1 H), 7.61 (app t, *J* = 7.5, 1 H), 4.42 (s, 1 H), 3.86 (d, *J* = 14.5 Hz, 1 H), 3.68 (d, *J* = 14.5 Hz, 1 H), 3.11 (s, 3 H); ^{13}C NMR (75 MHz) δ 135.5, 133.3, 132.0, 131.5, 130.0, 129.8, 124.4, 123.8, 116.1, 57.1, 45.9, 42.5; IR (neat) 2951, 2856, 2801, 1496, 1469, 1228, 1184, 1135, 1099, 1034 cm^{-1}; mass spectrum (CI) *m/z* 226.1093 [$C_{12}H_{12}N_5$ (M+1) requires 226.1093], 199.



32

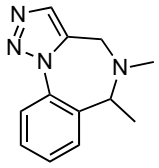
Ethyl 2-(5-(4-methoxybenzyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-6-yl)acetate (32). Glacial acetic acid (0.6 mg, 0.6 μL, 0.1 mmol), was added to a mixture of nitrile **19** (35 mg, 0.11 mmol), ethyl bromoacetate (88 mg, 59 μL, 0.53 mmol) and activated zinc granules (35 mg, 0.53 mmol) in THF (1.0 mL) and the reaction was stirred at 45 ˚C for 2 h. The cooled mixture was diluted with saturated aqueous $NaHCO_3$ (10 mL) and H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (6 : 4) to give 31 mg (75%) of ester **32** as a colorless oil; ^{1}H NMR (400 MHz) δ 7.97 (d, *J* = 7.9 Hz, 1 H), 7.67 (s, 1 H), 7.55 (ddd, *J* = 7.9, 7.5, 1.0 Hz, 1 H), 7.46 (app t, *J* = 7.5 Hz,

1 H), 7.40 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 4.43 (dd, *J* = 8.9, 6.5 Hz, 1 H), 4.08-3.98 (m, 2 H), 3.90 (d, *J* = 13.3 Hz, 1 H), 3.84 (d, *J* = 12.7 Hz, 1 H), 3.81 (s, 3 H), 3.69 (d, *J* = 12.7 Hz, 1 H), 3.21 (d, *J* = 13.3 Hz, 1 H), 2.11 (dd, *J* = 15.4, 8.9 Hz, 1 H), 2.02 (dd, *J* = 15.4, 6.5 Hz, 1 H), 1.14 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz) δ 171.1, 159.2, 135.4, 134.2, 132.9, 131.4, 130.5, 130.2, 130.0, 129.7, 129.2, 123.6, 114.0, 63.5, 61.1, 60.6, 55.4, 43.7, 40.9, 14.2; IR (neat) 2981, 2935, 2836, 1731, 1612, 1512, 1496, 1447, 1371, 1303, 1248, 1178, 1135, 1099, 1034 cm^{-1}; mass spectrum (ESI) *m/z* 393.1920 [$C_{22}H_{25}N_4O_3$ (M+1) requires 393.1921].



33

5-Methyl-6-phenyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (33). Phenylmagnesium bromide solution (164 μL, 0.444 mmol, 2.7 M in Et_2O) was added to a solution of zinc chloride (667 μL, 0.667 mmol, 1.0 M in THF) at 0 ˚C, and the mixture stirred for 10 min. The reaction was diluted with THF (2.0 mL), a solution of nitrile **31** (50 mg, 0.22 mmol) in THF (1.5 mL) was added and the mixture was stirred at 0 ˚C for 5 min, and then room temperature for 1.5 h. The reaction was diluted with saturated aqueous $NaHCO_3$ (10 mL) and H_2O (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (6 : 4) to give 53 mg (86%) of amine **33** as a colorless solid: mp 111-113 ˚C; ^{1}H NMR (400 MHz) δ 7.86 (dd, *J* = 7.8, 1.3 Hz, 1 H), 7.74 (s, 1 H), 7.49 (app td, *J* = 7.8, 1.4 Hz, 1 H), 7.36-7.25 (comp, 6 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 4.16 (s, 1 H), 3.97 (d, *J* = 14.9 Hz, 1 H), 3.76 (d, *J* = 14.9, Hz, 1 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz) δ 139.9, 136.3, 133.5, 132.8, 132.8, 131.3, 129.2, 128.9, 128.6, 128.6, 128.5, 128.5, 127.9, 123.1, 69.3, 46.8, 43.4; IR (neat) 3061, 3029, 2950, 2848, 2785, 1604, 1488, 1468, 1452, 1325, 1226, 1137, 1097, 1076, 1026 cm^{-1}; mass spectrum (ESI) *m/z* 277.1447 [$C_{17}H_{17}N_4$ (M+1) requires 227.1448], 278.



34

5,6-Dimethyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (34). Methylmagnesium bromide solution (298 μL, 0.954 mmol, 3.2 M in Et_2O) was added to a solution of zinc chloride (1.34 mL, 1.34 mmol, 1.0 M in THF) and the mixture was stirred at 0 ˚C for 10 min.

The reaction was diluted with THF (2.0 mL), a solution of nitrile **31** (43 mg, 0.19 mmol) in THF (1.5 mL) was added, and the mixture was stirred at room temperature for 6 h. The reaction was diluted with saturated aqueous $NaHCO_3$ (20 mL) and H_2O (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with EtOAc/MeOH (19 : 1) to give 30 mg (73%) of amine **34** as a colorless oil; ^{1}H NMR (400 MHz) δ 7.90 (d, *J* = 7.2 Hz, 1 H), 7.75 (s, 1 H), 7.58-7.44 (comp, 3 H), 3.77 (d, *J* = 14.0 Hz, 1 H), 3.56 (d, *J* = 14.0 Hz, 1 H), 3.53 (q, *J* = 6.8 Hz, 1 H), 2.41 (s, 3 H), 1.31 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz) δ 136.0, 133.6, 132.6, 132.3, 129.1, 129.0, 128.9, 123.2, 58.5, 47.4, 41.1, 18.3; IR (neat) 2981, 2940, 2850, 2784, 1491, 1468, 1376, 1226, 1139, 1097, 1039 cm^{-1}; mass spectrum (ESI) *m/z* 215.1291 [$C_{12}H_{15}N_4$ (M+1) requires 215.1291].

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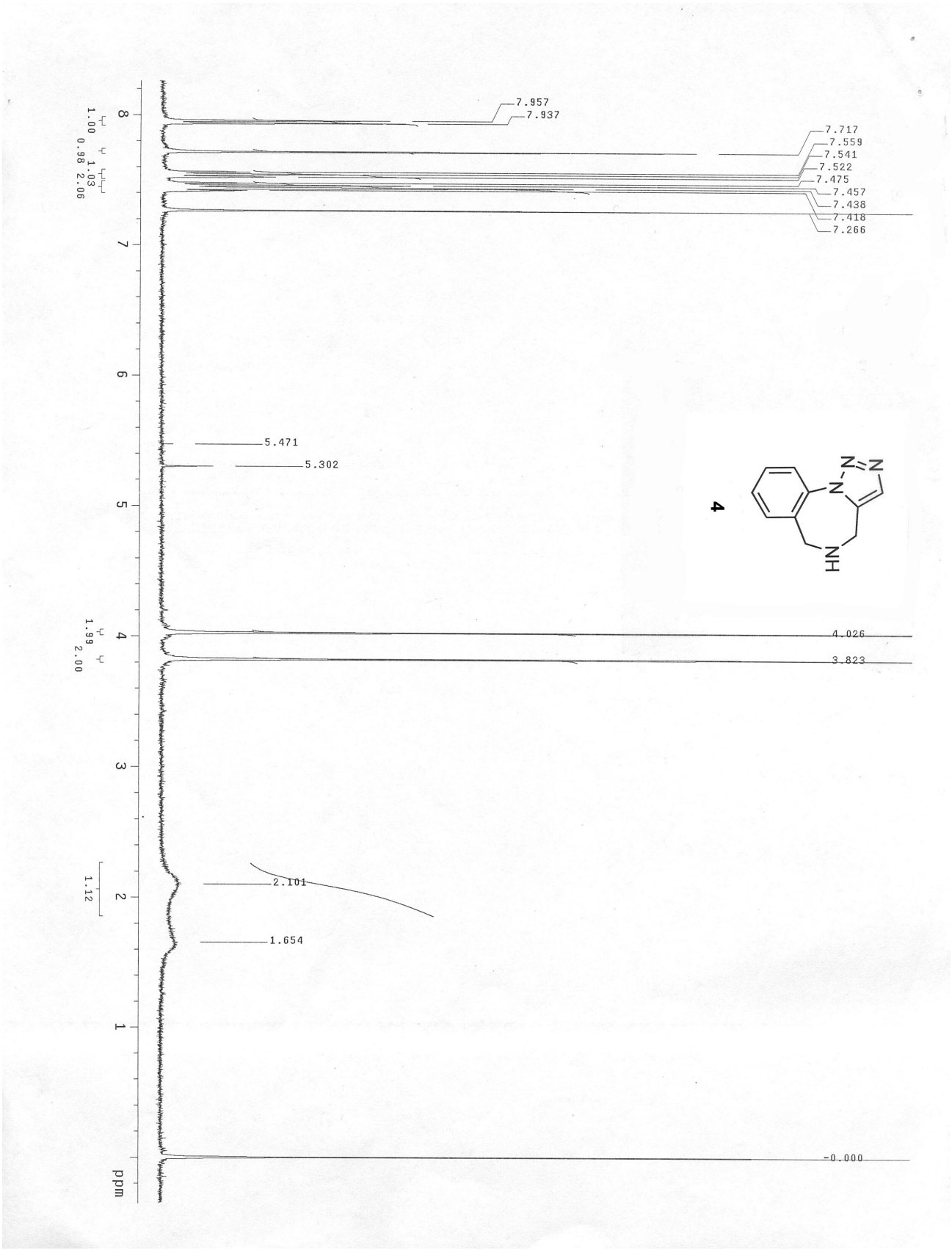
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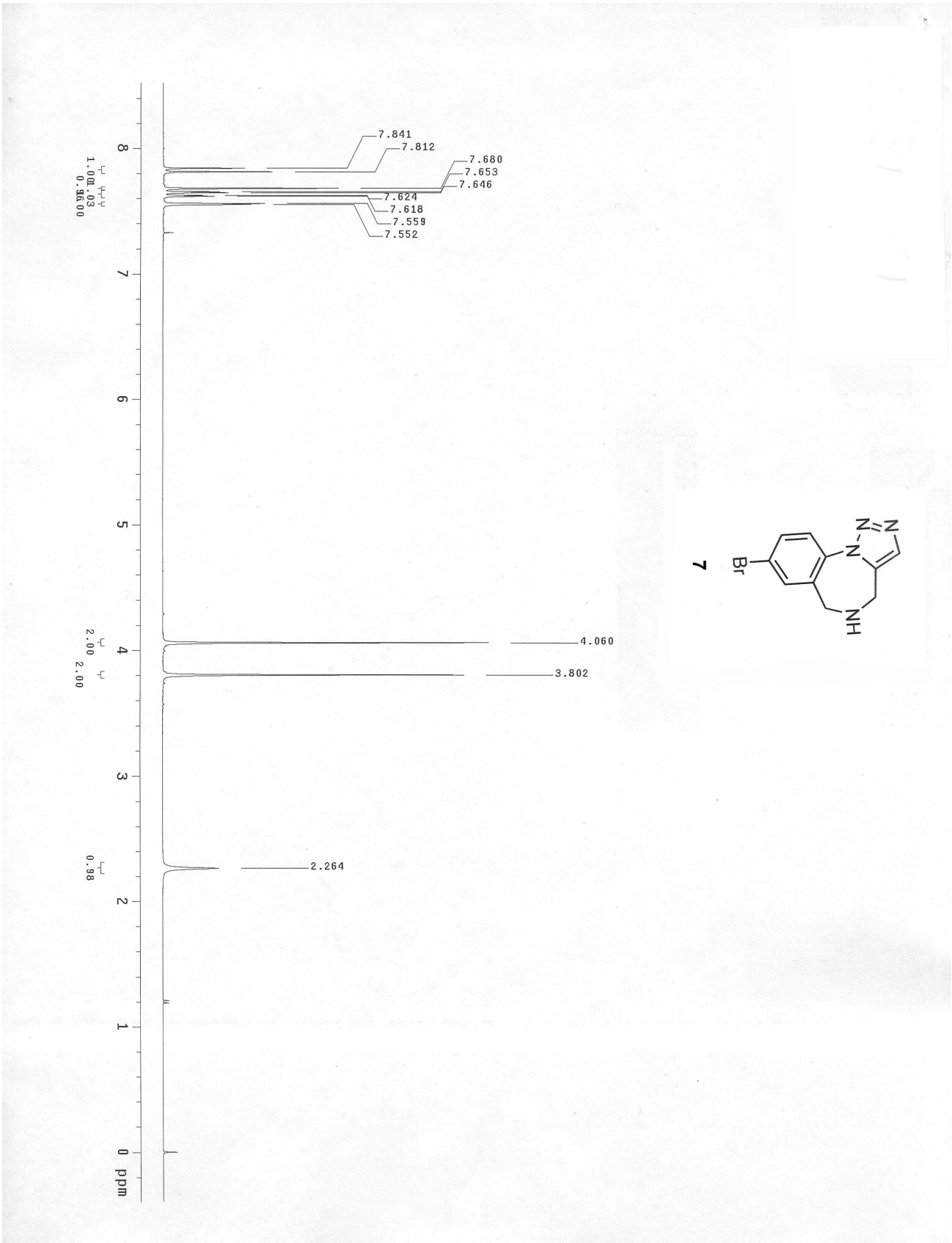
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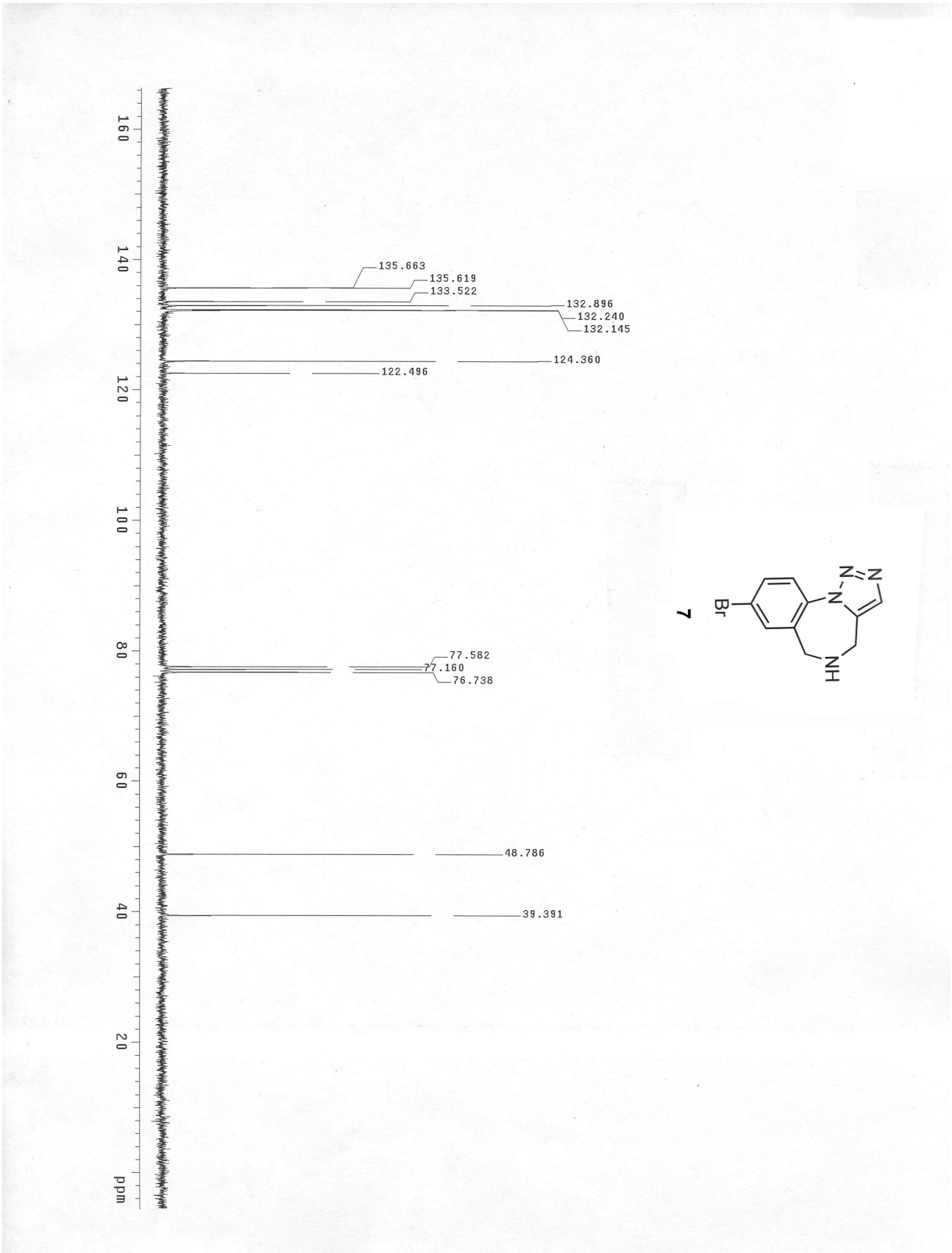
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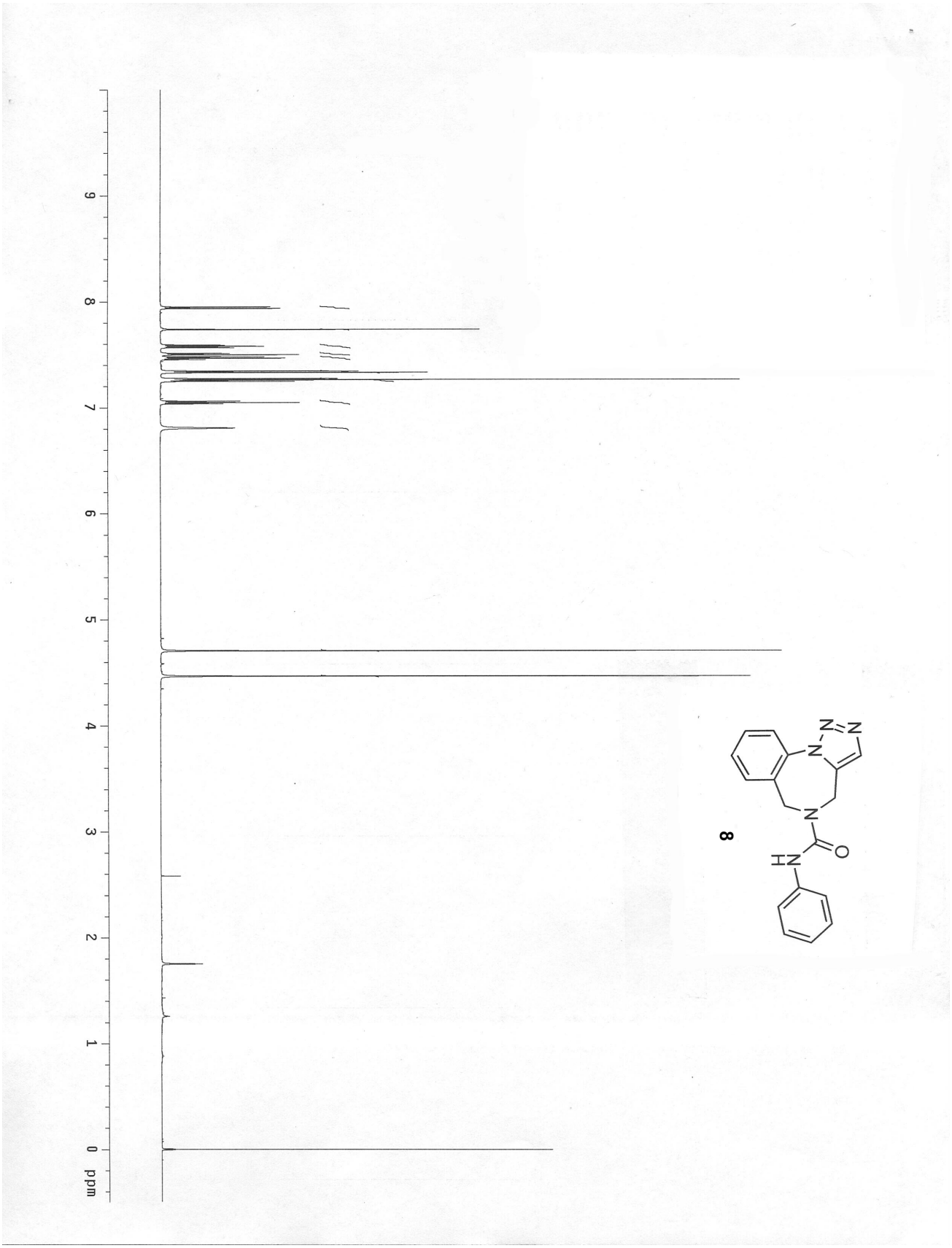

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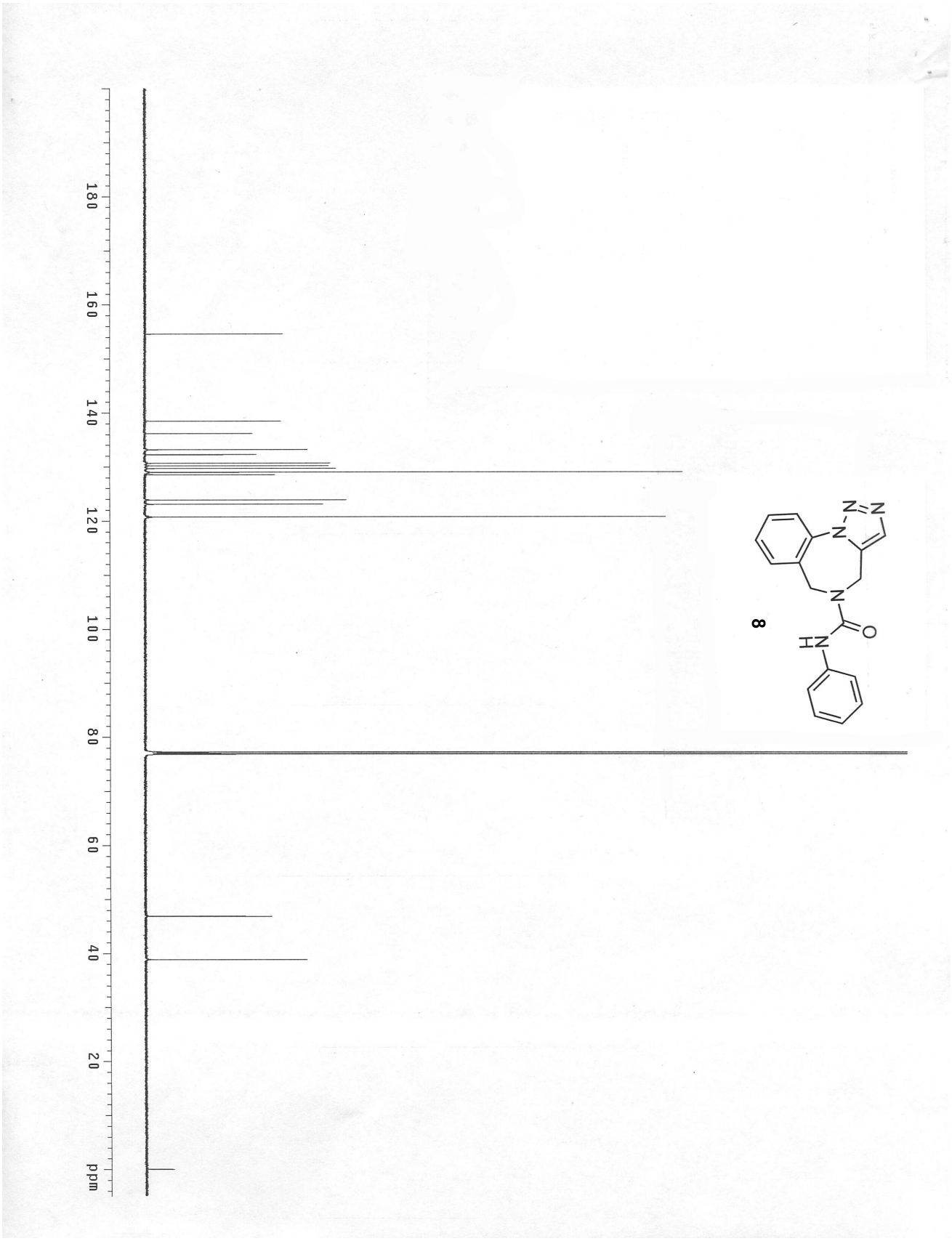
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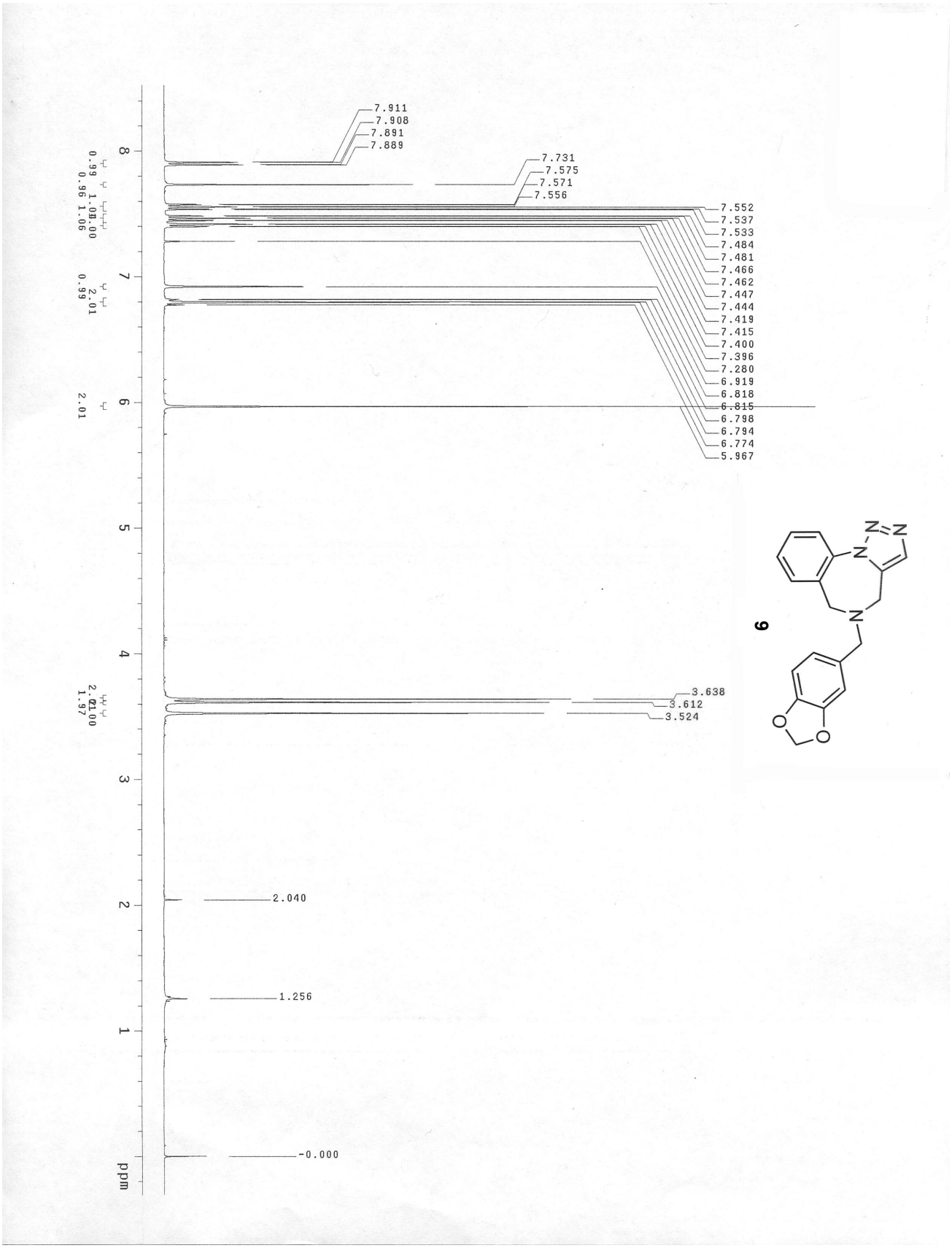
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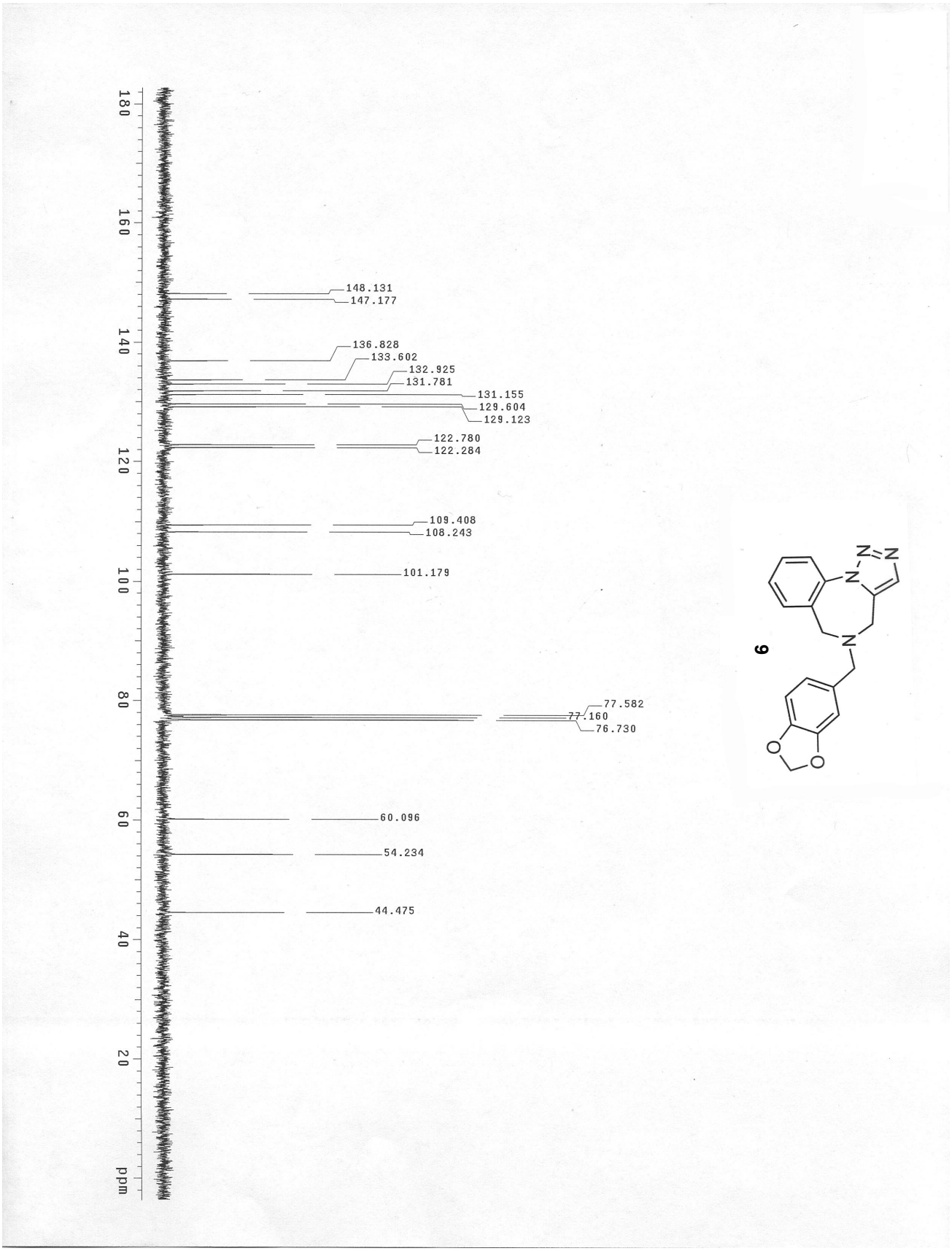
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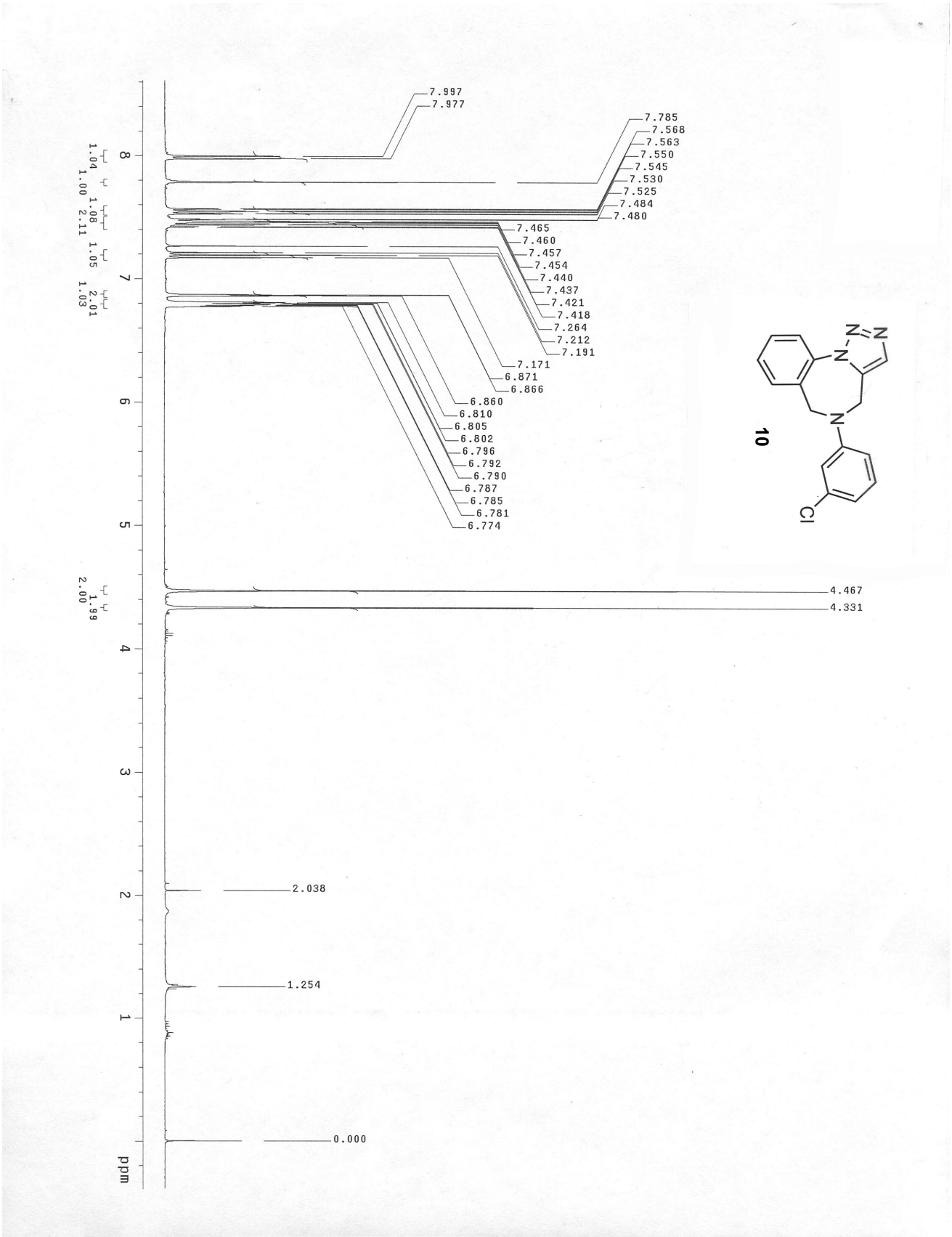
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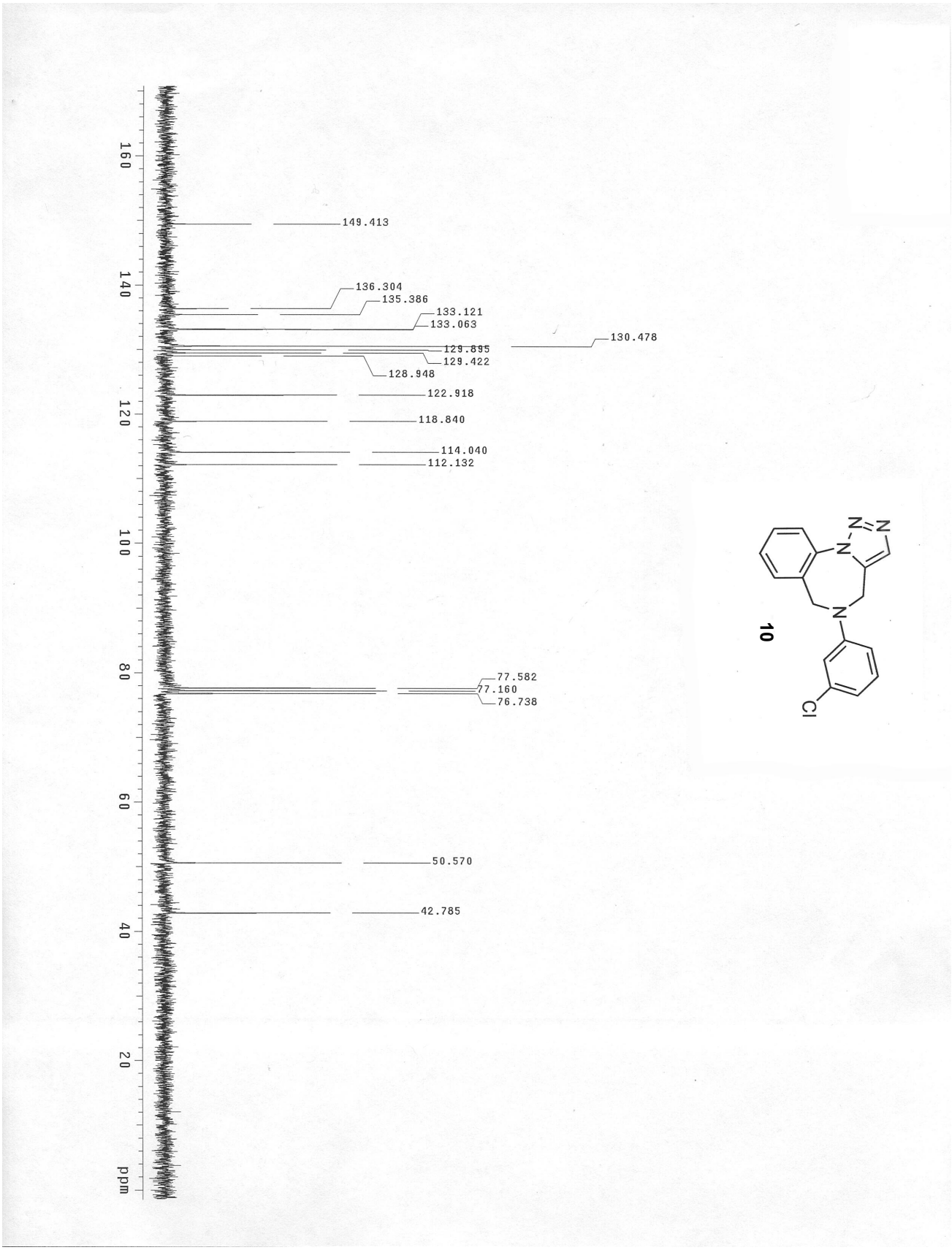
7.460
7.457
7.454
7.440
7.437
7.421
7.418
7.264
7.212
7.191
7.171
6.871
6.866
6.860
6.810
6.805
6.802
6.796
6.792
6.790
6.787
6.785
6.781
6.774
4.467
4.331
2.038
1.254
0.000
ppm
1.04 1.08 1.05 2.01
1.00 2.11 1.03
1.99
2.00
10
Cl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140
120
100
80
60
40
20
ppm
149.413
136.304
135.386
133.121
133.063
130.478
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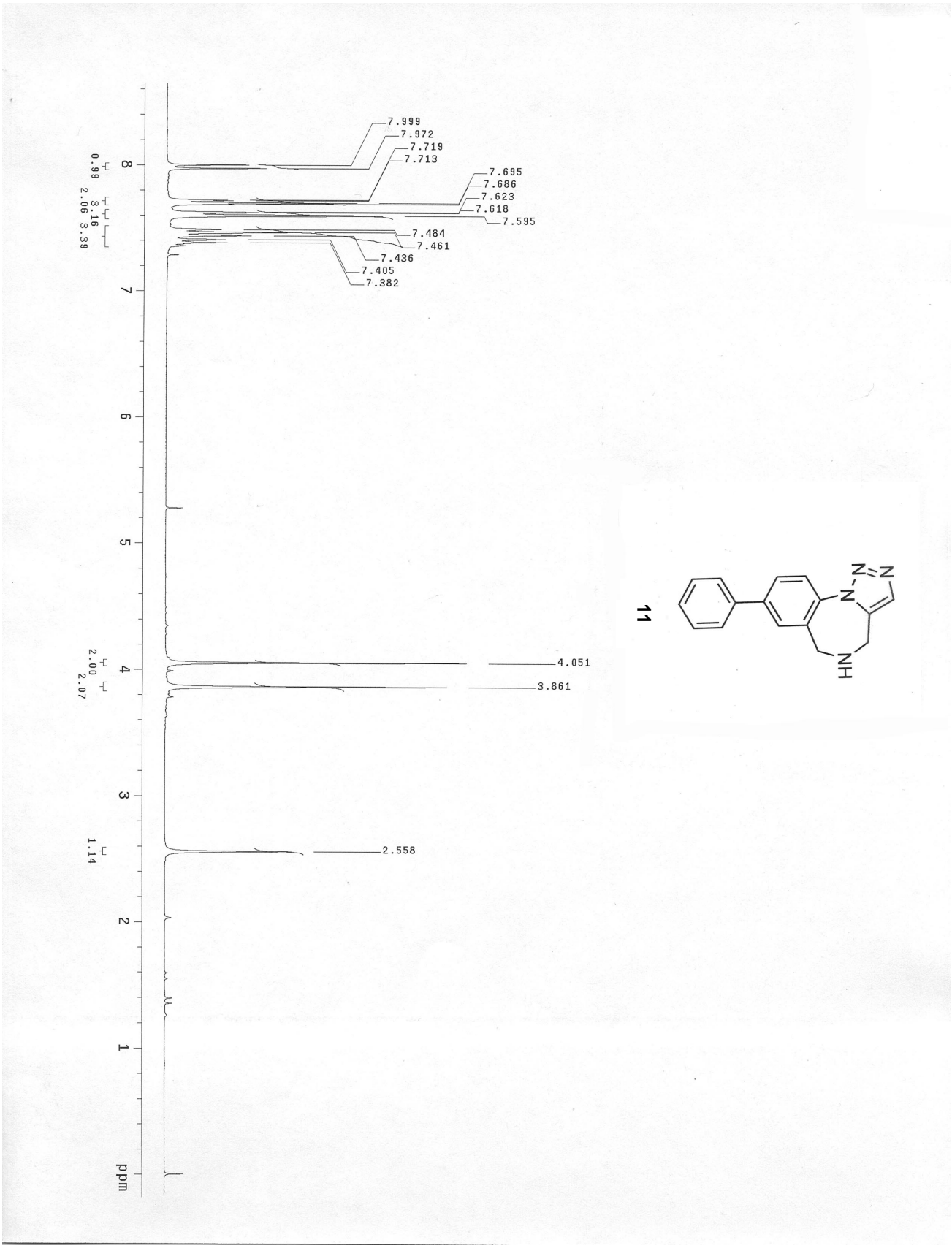
129.422
128.948
122.918
118.840
114.040
112.132
77.582
77.160
76.738
50.570
42.785
10
Cl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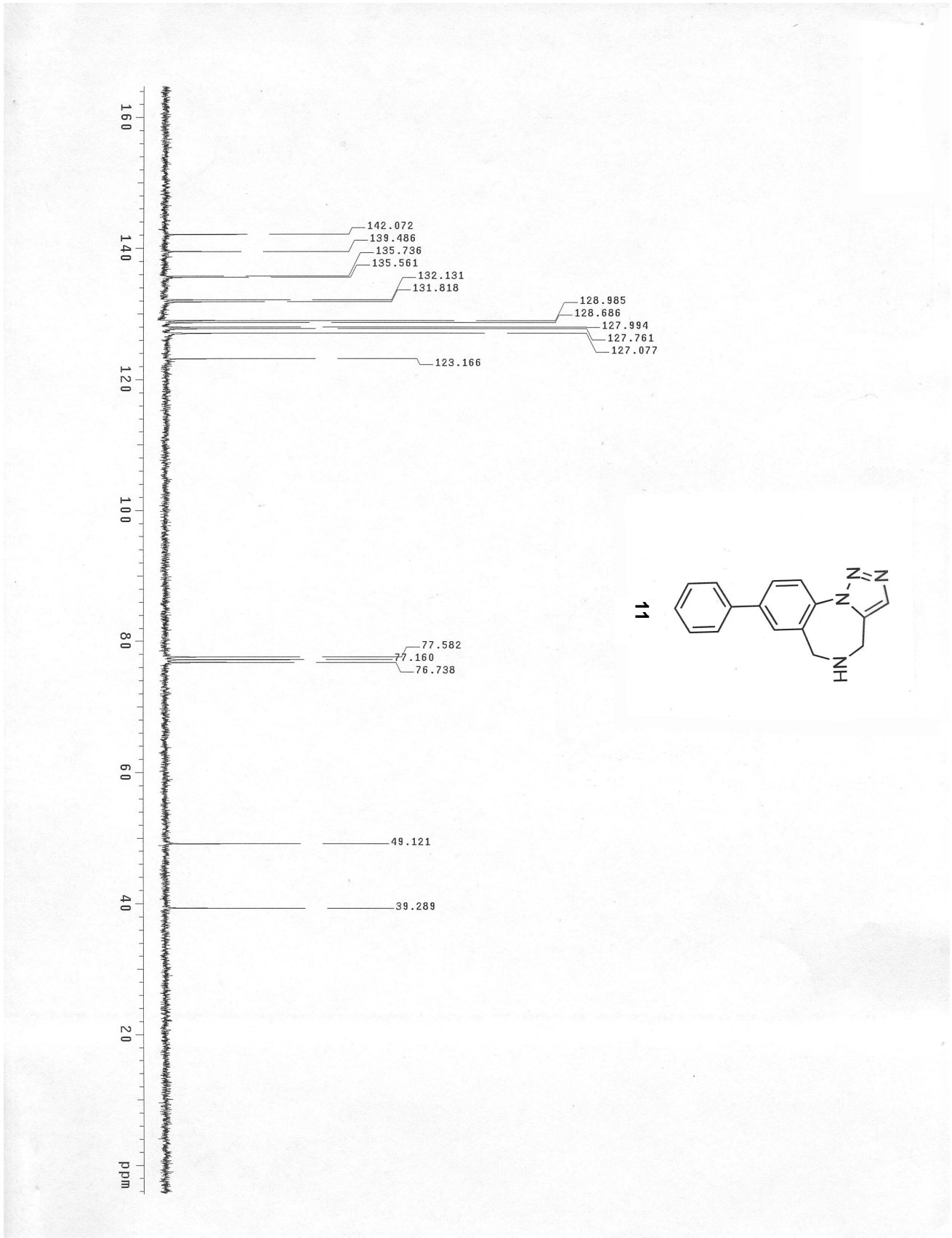
7.972
7.719
7.713
7.695
7.686
7.623
7.618
7.595
7.484
7.461
7.436
7.405
7.382
4.051
3.861
2.558
0.99
3.16
2.06
3.39
2.00
2.07
1.14
ppm
11
NH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140
120
100
80
60
40
20
ppm
142.072
139.486
135.736
135.561
132.131
131.818
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128.686
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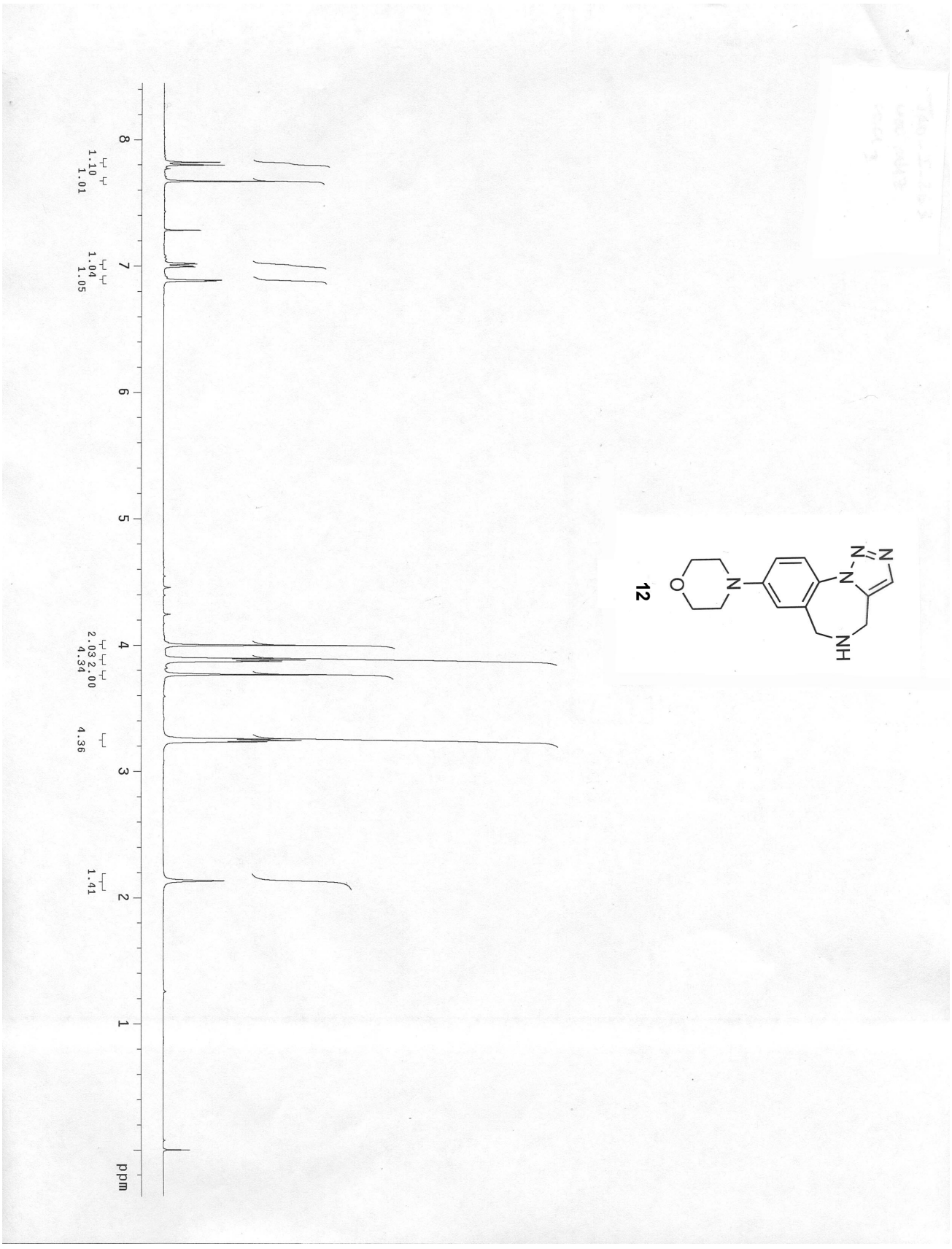
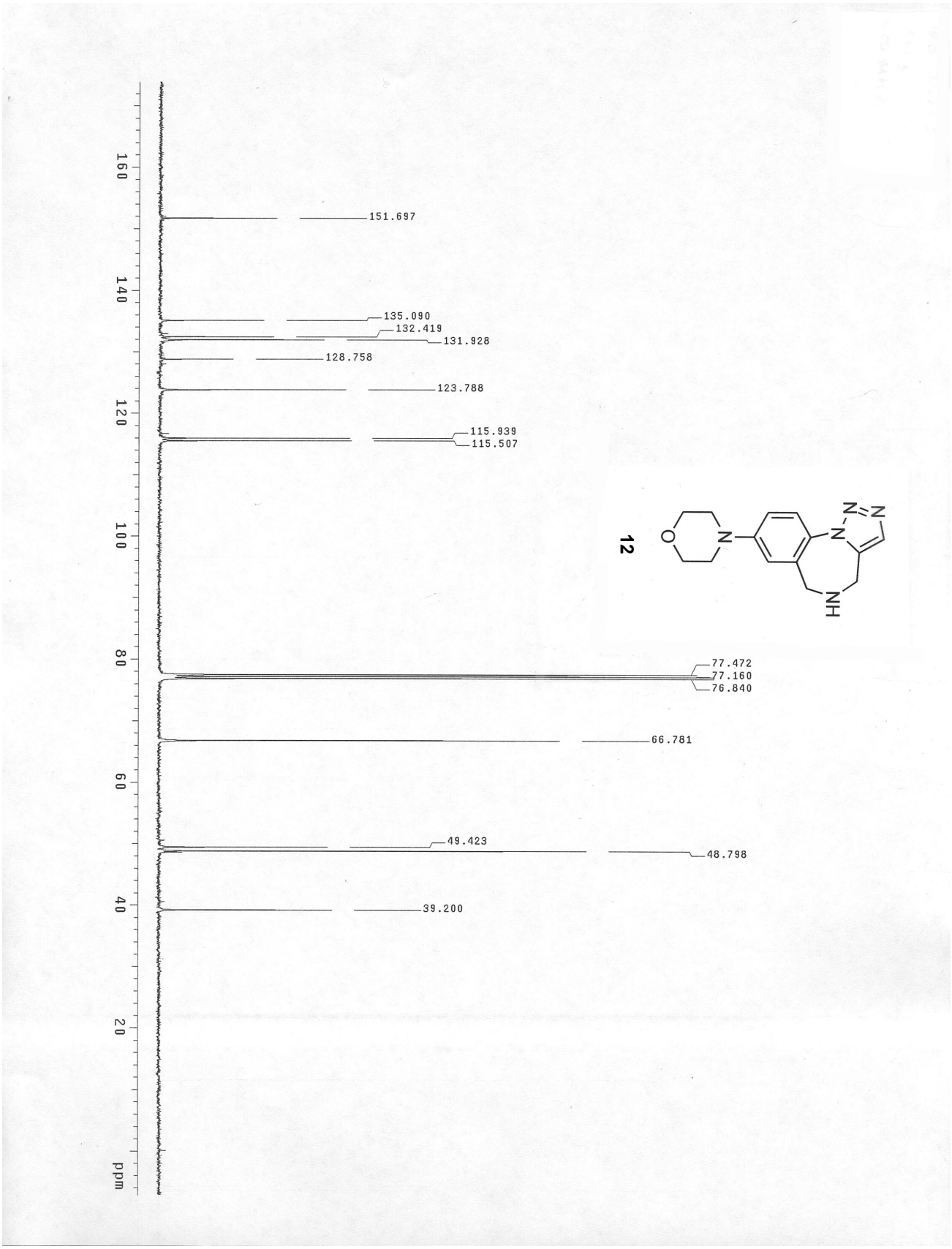
127.761
127.077
123.166
77.582
77.160
76.738
49.121
39.289
11
N
N
N
NH


12
N
O
N
N
N
NH
8
7
6
5
4
3
2
1
ppm
1.10
1.01
1.04
1.05
2.03
2.00
4.34
4.36
1.41


160
140
120
100
80
60
40
20
ppm
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135.090
132.419
131.928
128.758
123.788
115.939
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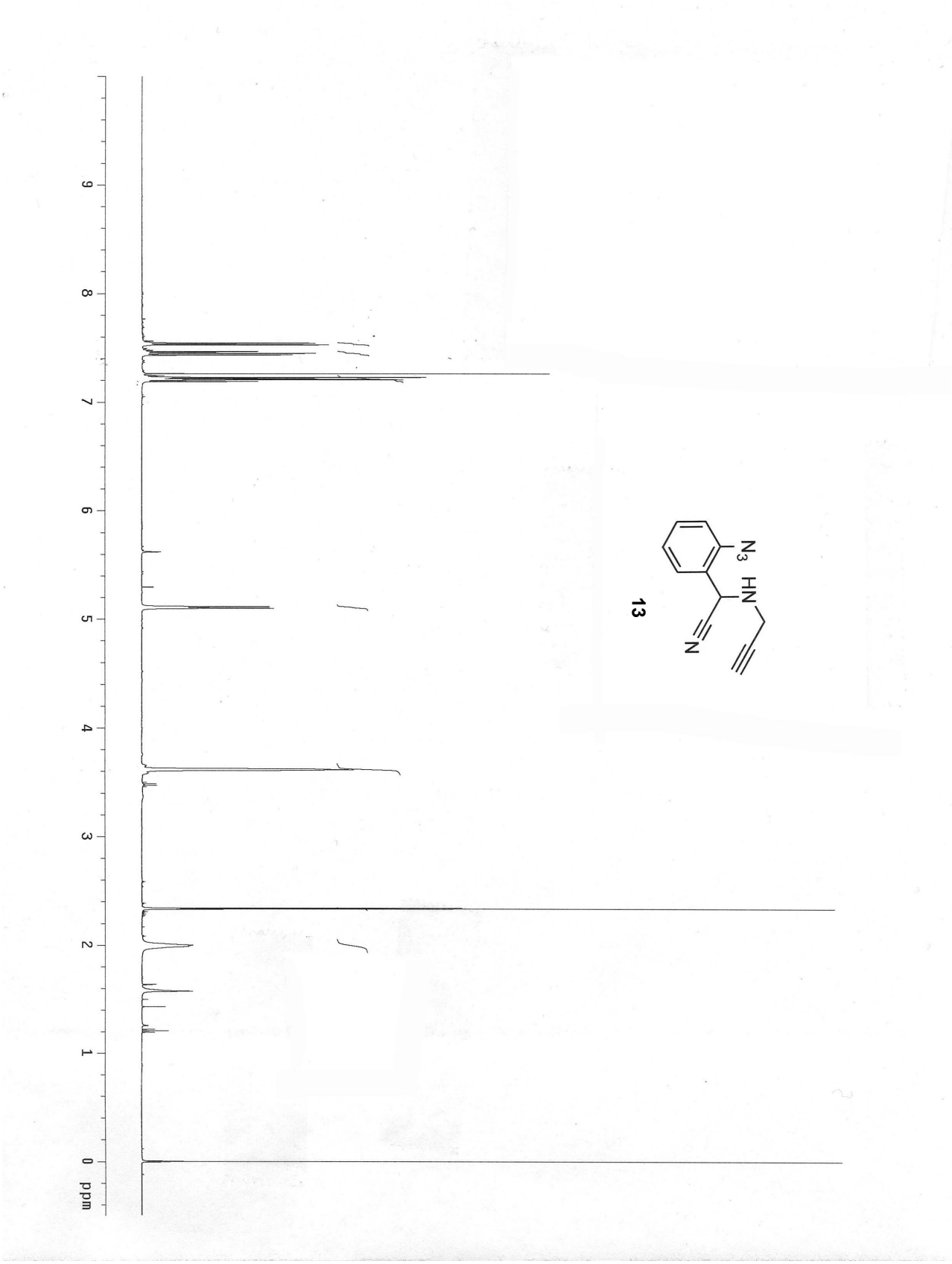
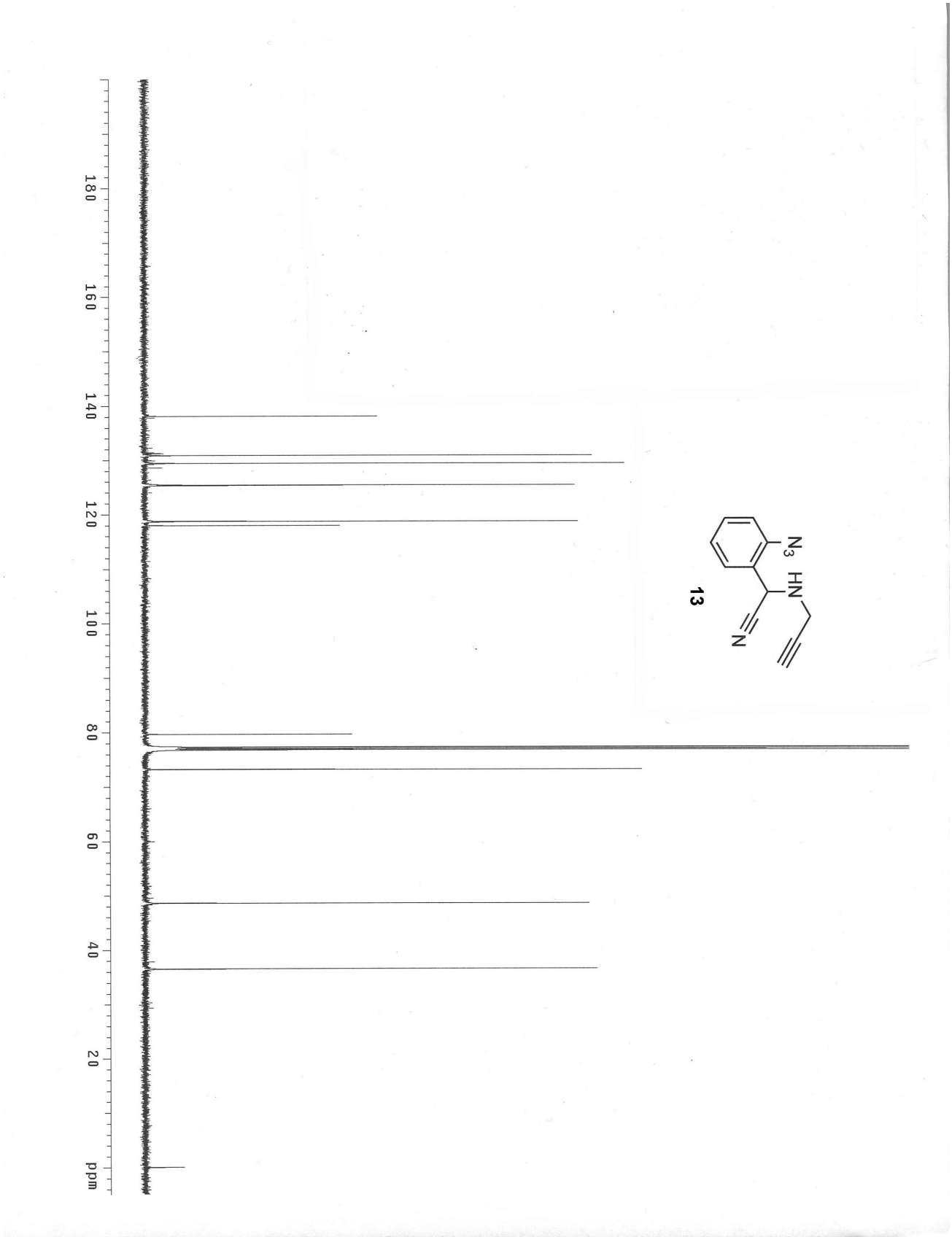
77.472
77.160
76.840
66.781
49.423
48.798
39.200
12
O
N
N
N
NH



13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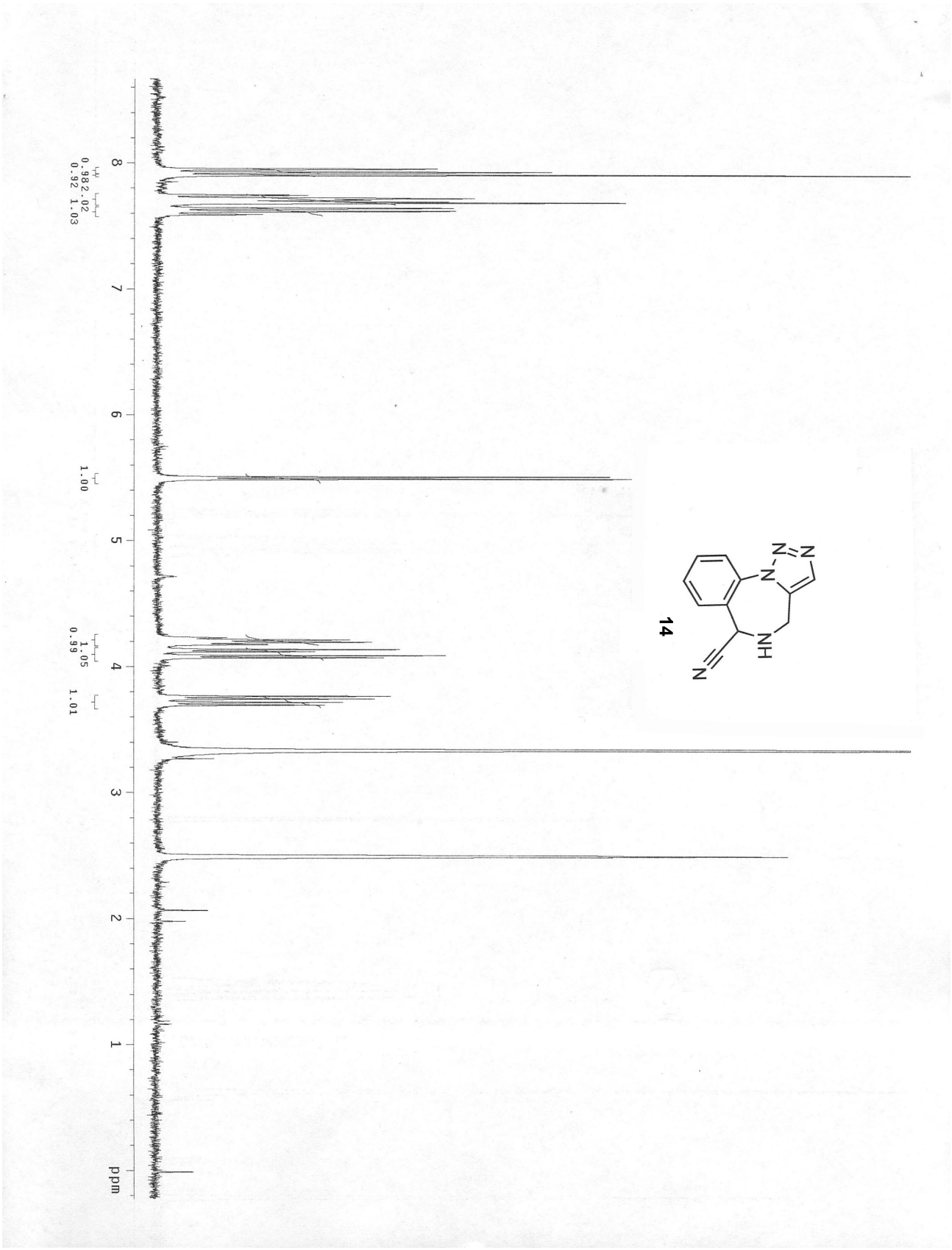
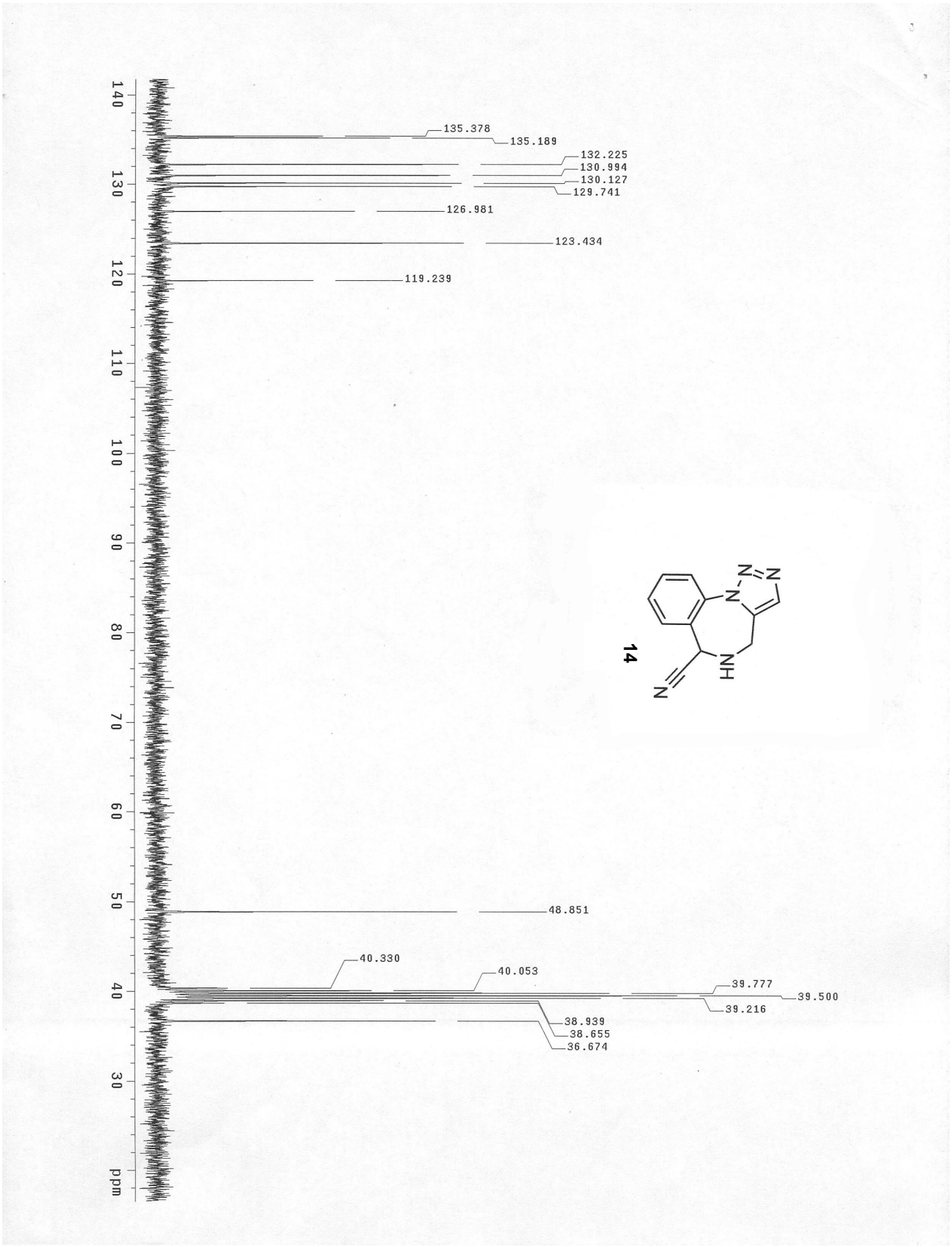
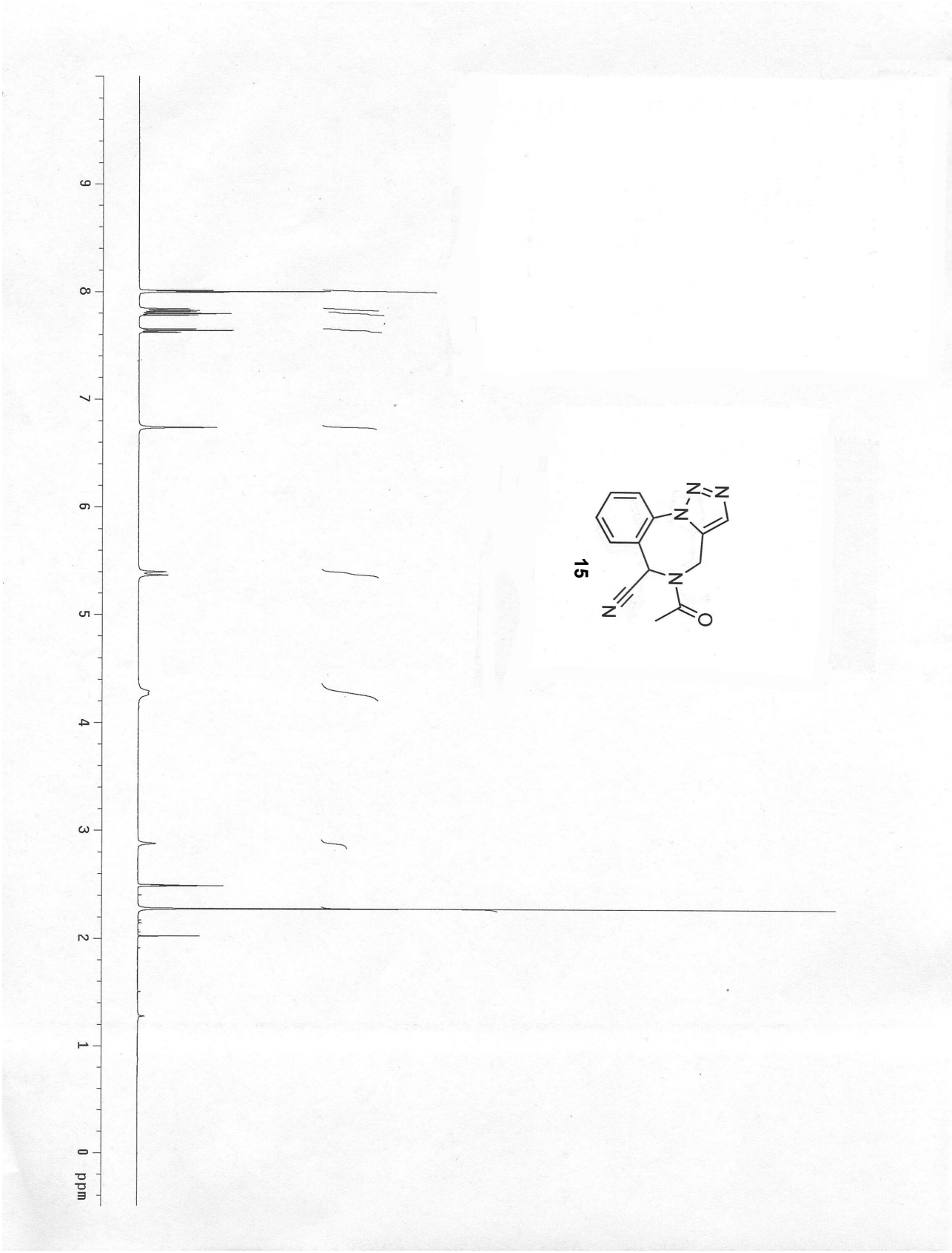
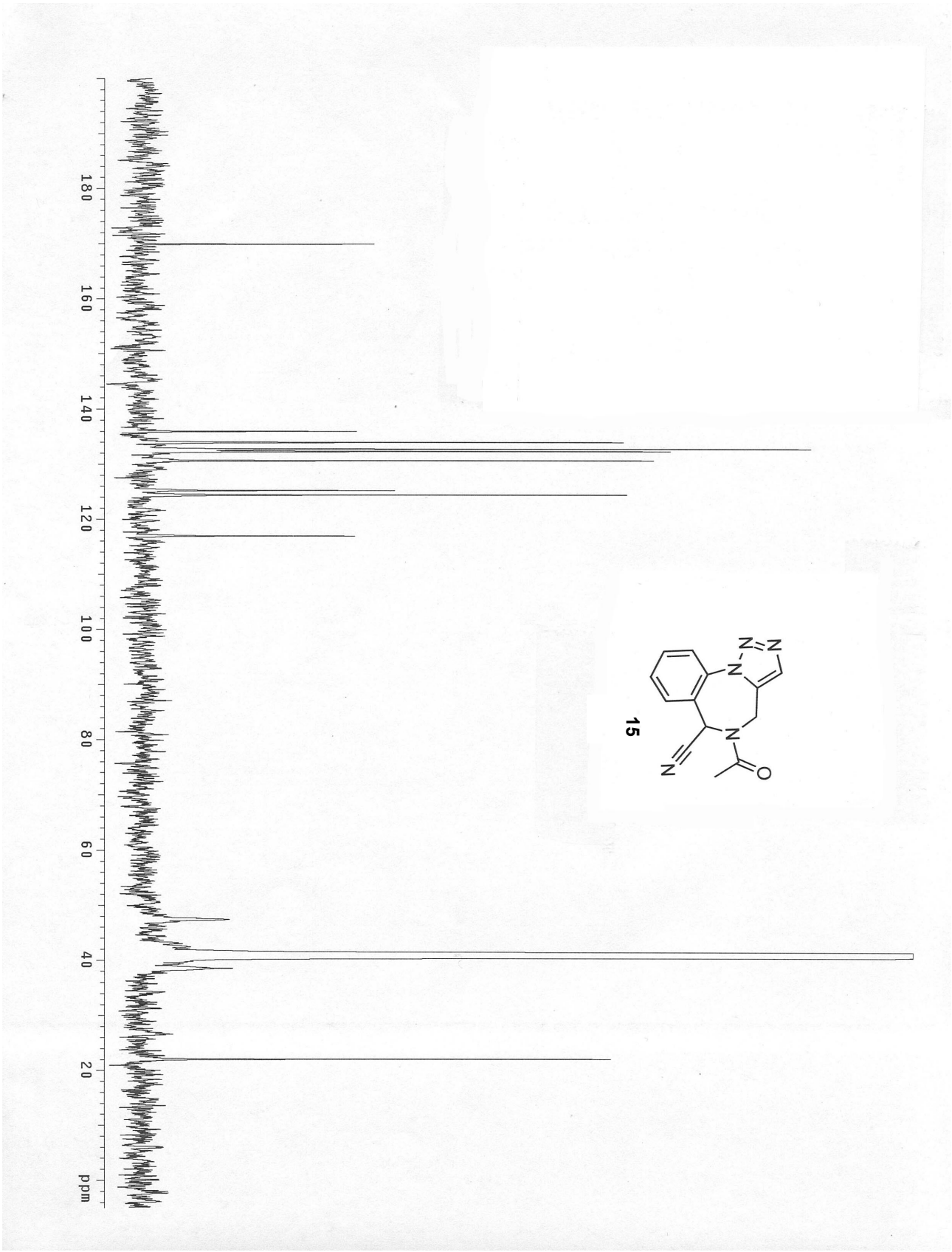
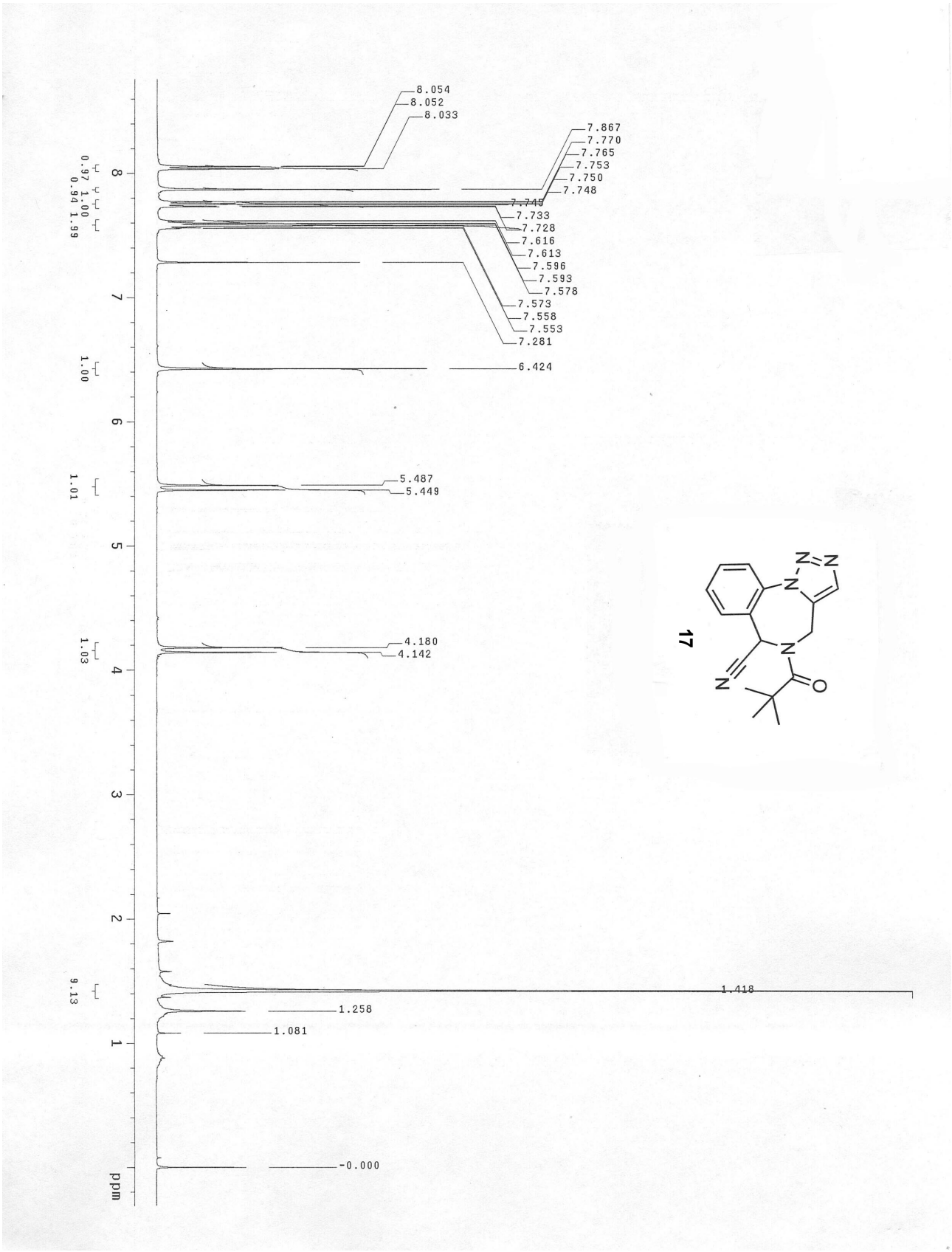
160
140
120
100
80
60
40
20
ppm
N3
HN
N
13

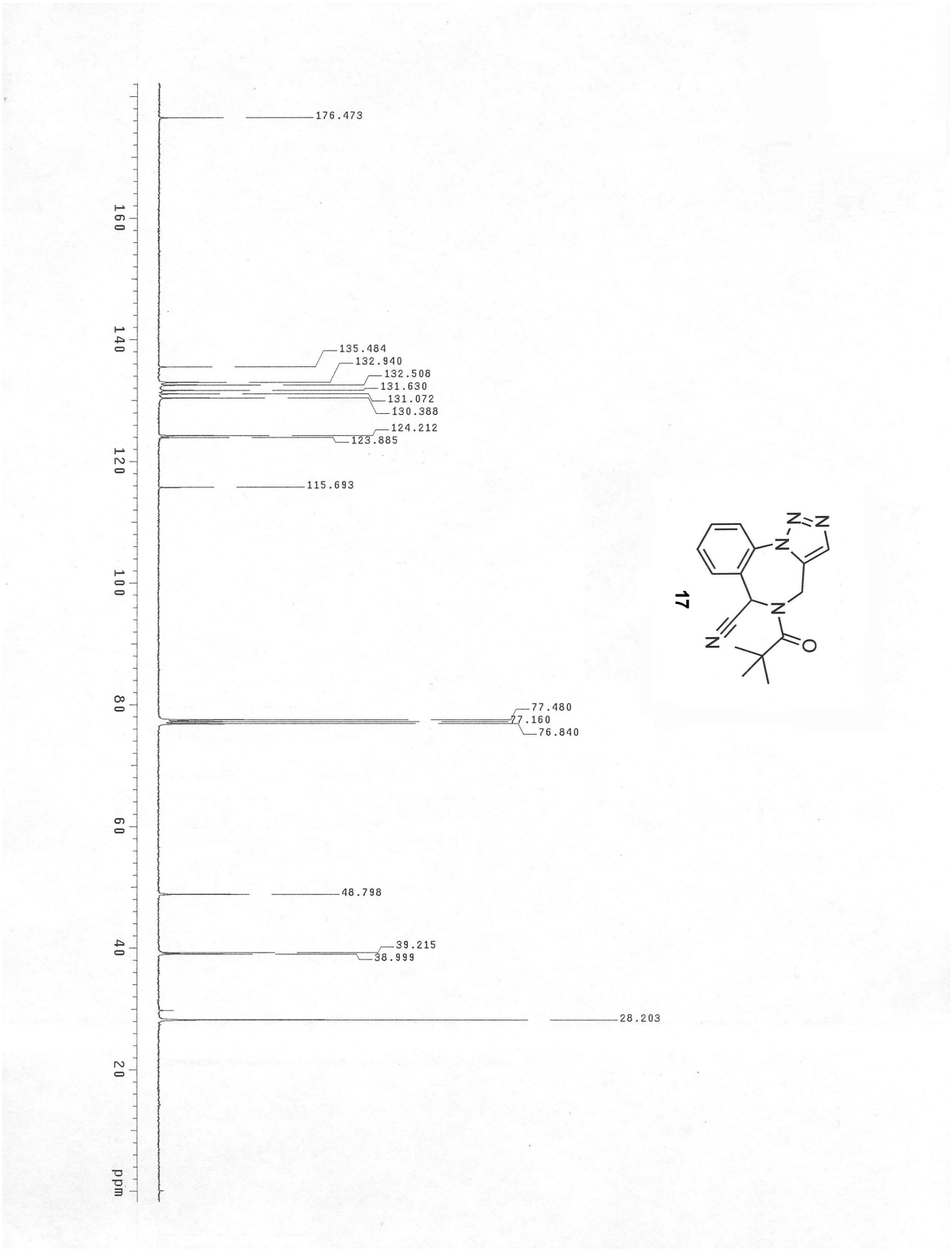

14
N
N
N
NH
N
8
7
6
5
4
3
2
1
ppm
0.98 2.02
0.92 1.03
1.00
1.05
0.99
1.01

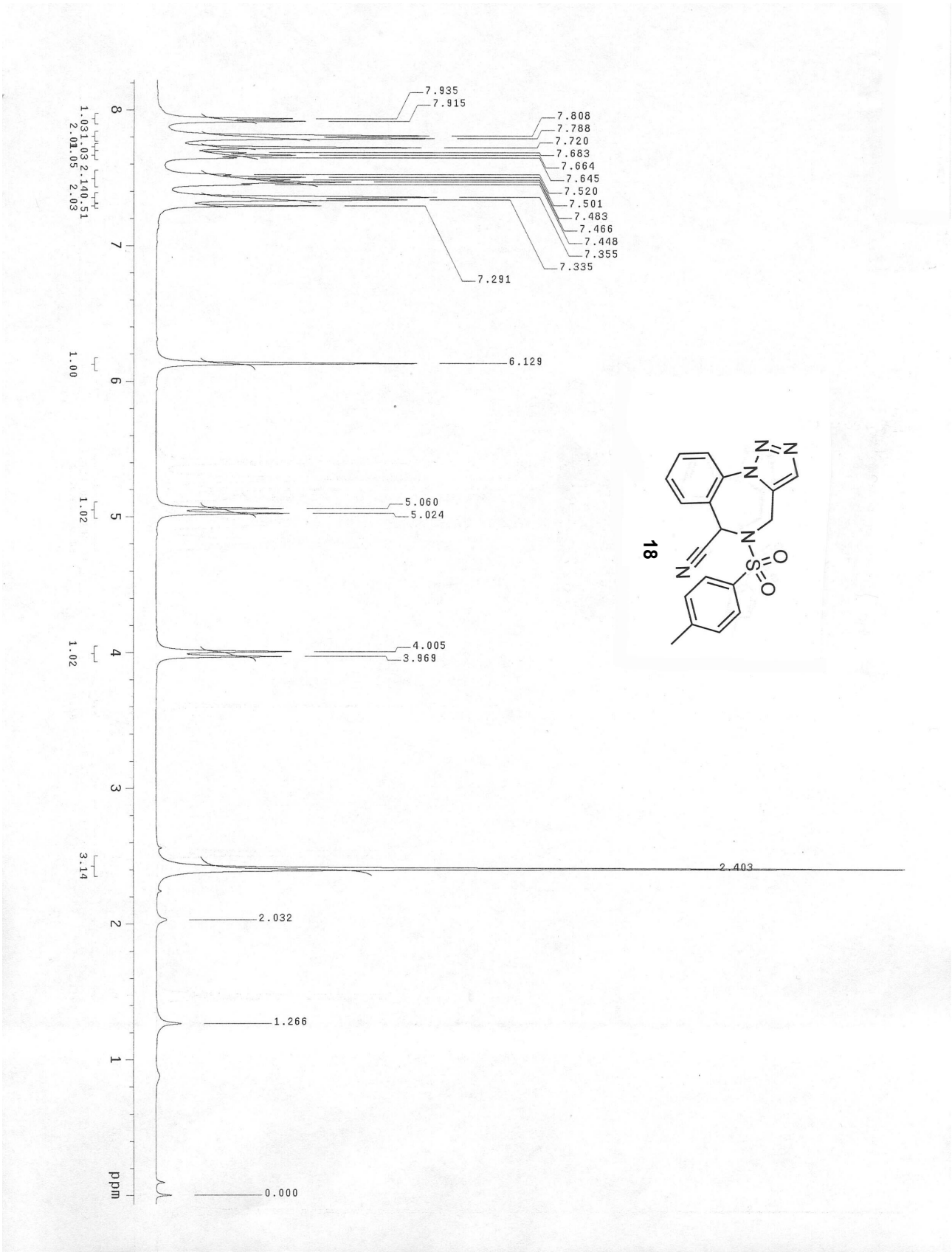

135.378
135.189
132.225
130.994
130.127
129.741
126.981
123.434
119.239
48.851
40.330
40.053
39.777
39.500
39.216
38.939
38.655
36.674
140
130
120
110
100
90
80
70
60
50
40
30
ppm
14
N
N
N
NH
N

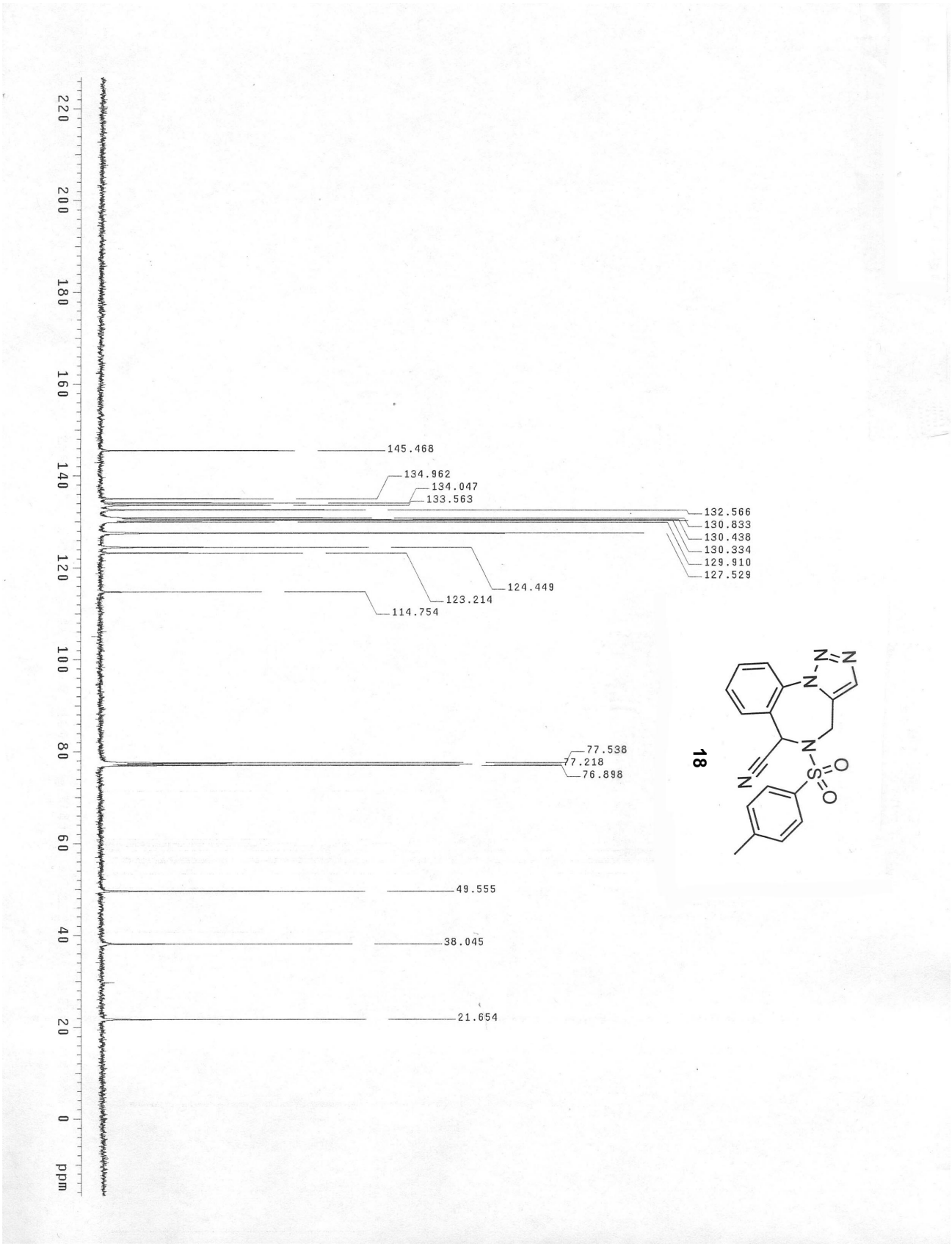

9
8
7
6
5
4
3
2
1
0 ppm
15
N
N
N
N
N
O

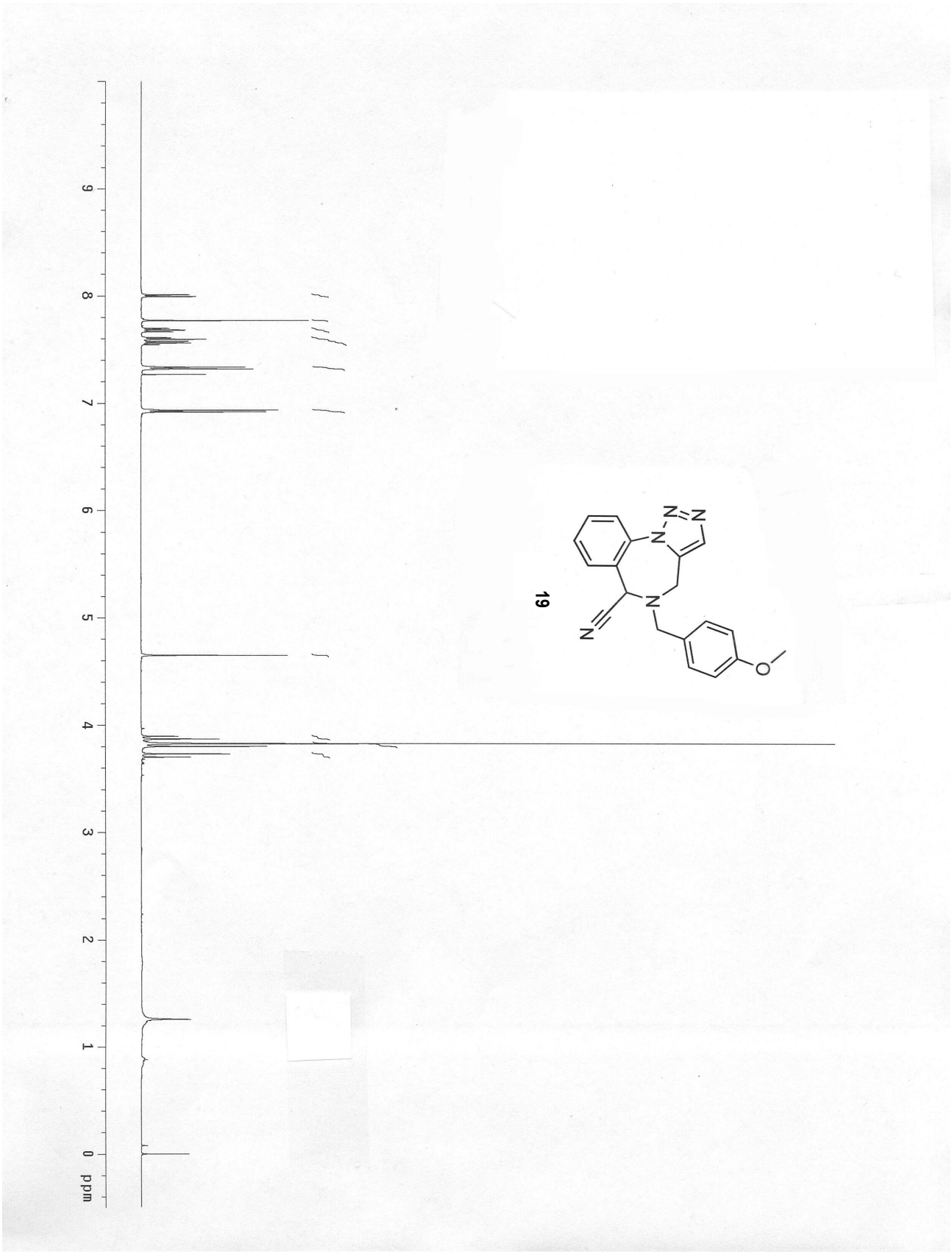

180
160
140
120
100
80
60
40
20
ppm
15
N
N
N
N
N
O


8.054
8.052
8.033
7.867
7.770
7.765
7.753
7.750
7.748
7.745
7.733
7.728
7.616
7.613
7.596
7.593
7.578
7.573
7.558
7.553
7.281
6.424
5.487
5.449
4.180
4.142
1.418
1.258
1.081
-0.000
ppm
0.97 1.00
0.94 1.99
1.00
1.01
1.03
9.13
17
N
N
N
N
N
O

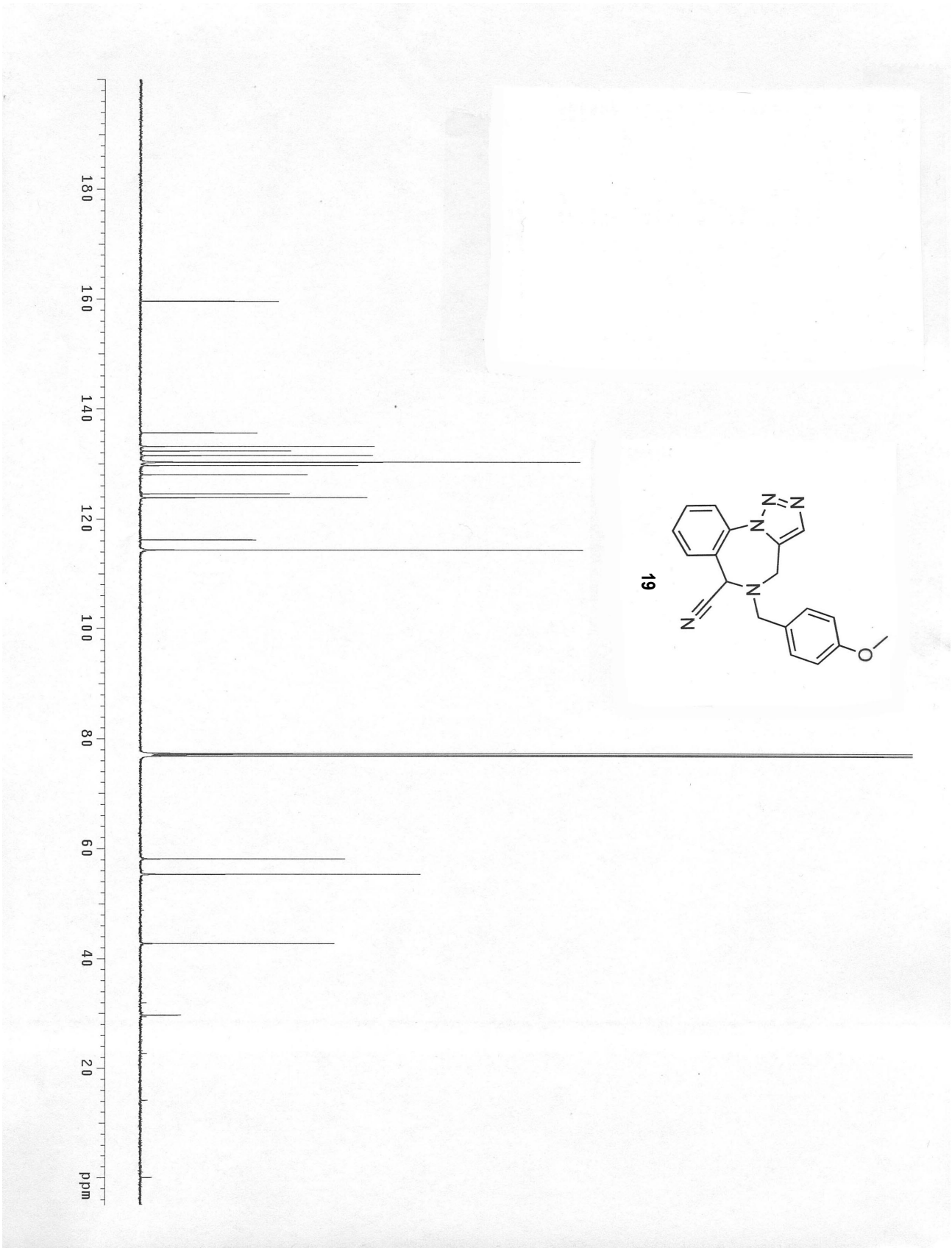

176.473
135.484
132.940
132.508
131.630
131.072
130.388
124.212
123.885
115.693
77.480
77.160
76.840
48.798
39.215
38.999
28.203
160
140
120
100
80
60
40
20
ppm
47

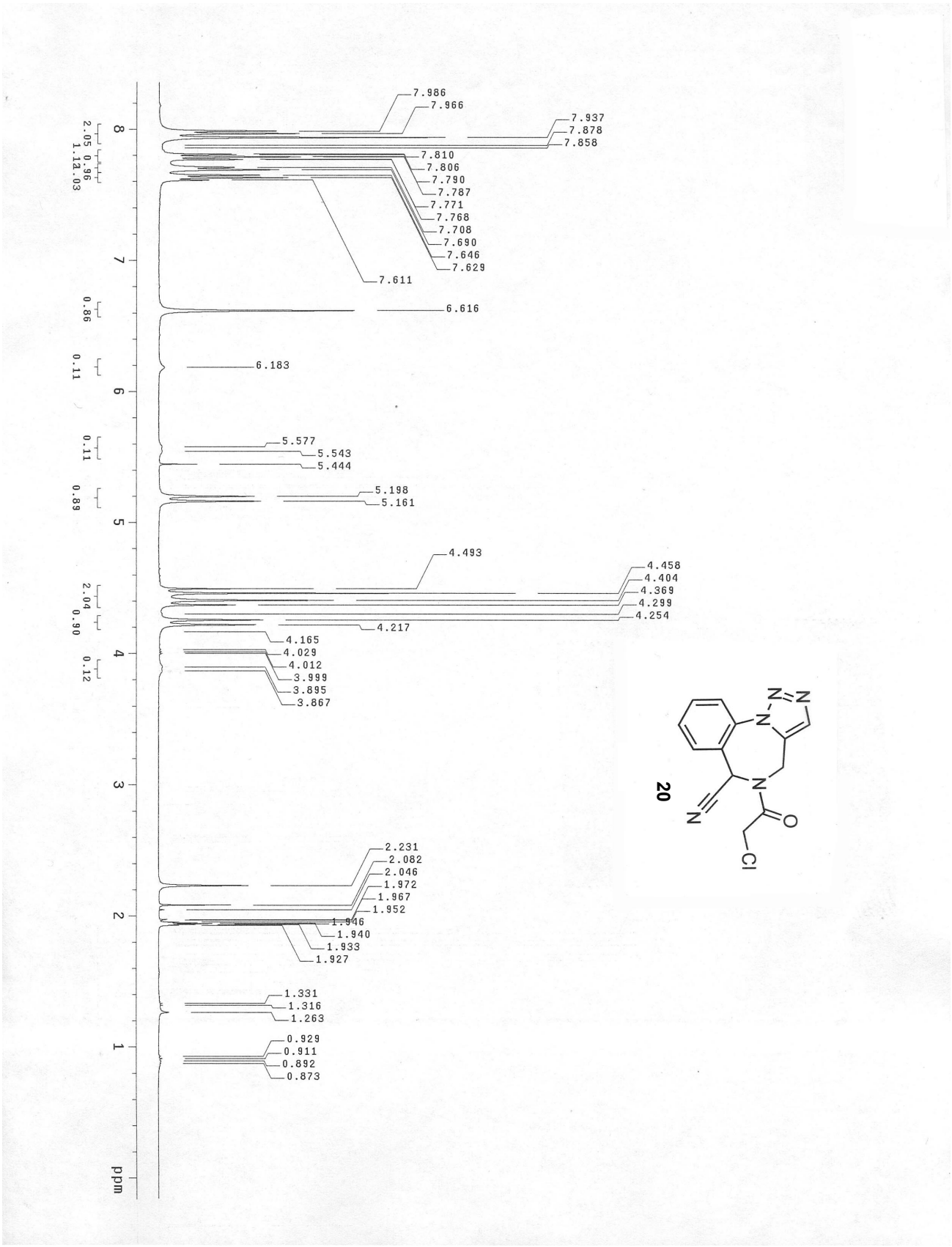

7.935
7.915
7.808
7.788
7.720
7.683
7.664
7.645
7.520
7.501
7.483
7.466
7.448
7.355
7.335
7.291
6.129
5.060
5.024
4.005
3.969
2.403
2.032
1.266
0.000
ppm
1.03 1.03 2.14 0.51
2.01 1.05 2.03
1.00
1.02
1.02
3.14
18


145.468
134.962
134.047
133.563
132.566
130.833
130.438
130.334
129.910
127.529
124.449
123.214
114.754
77.538
77.218
76.898
49.555
38.045
21.654
220
200
180
160
140
120
100
80
60
40
20
0
ppm
18



19


180
160
140
120
100
80
60
40
20
ppm
19
N
N
N
N
N
O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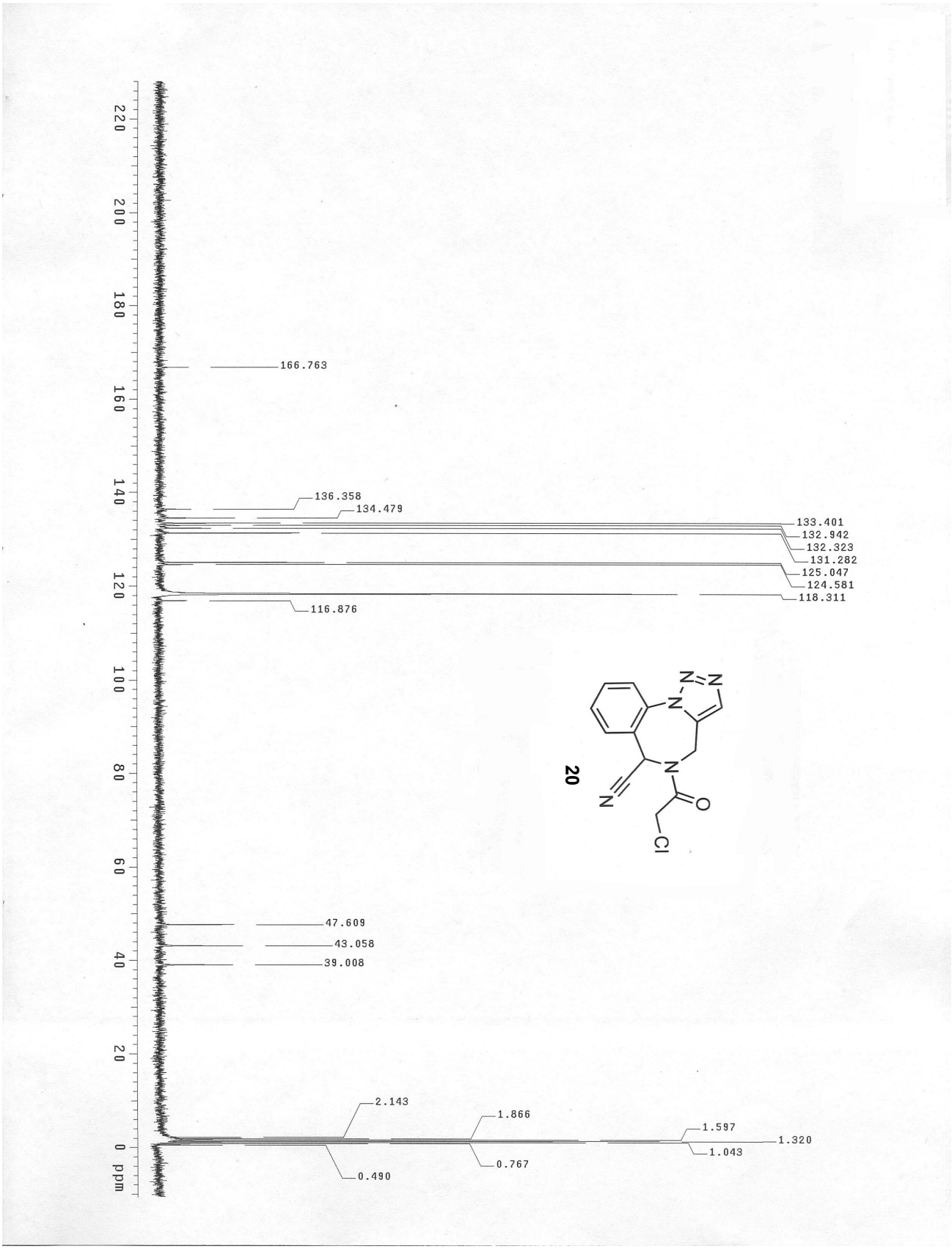
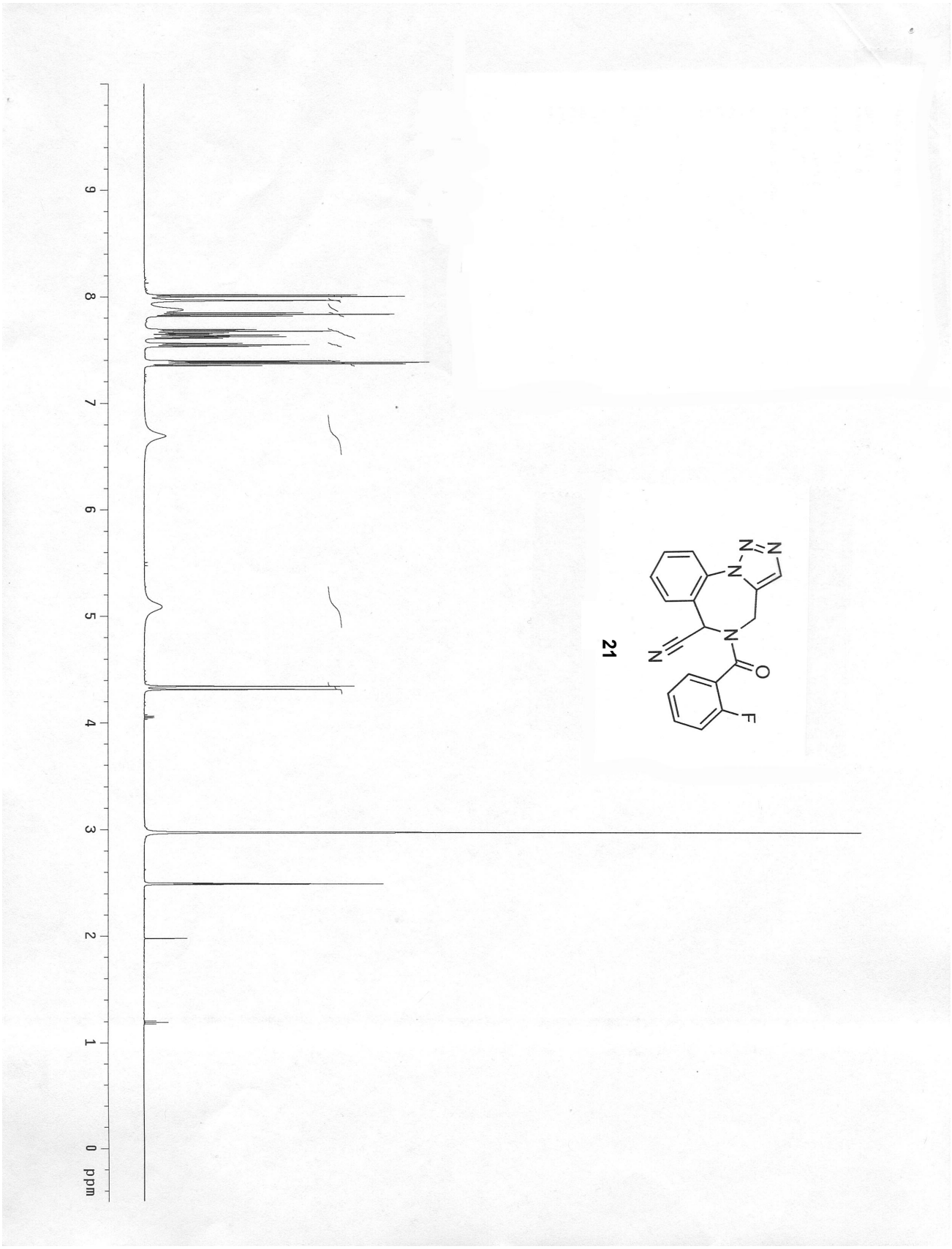
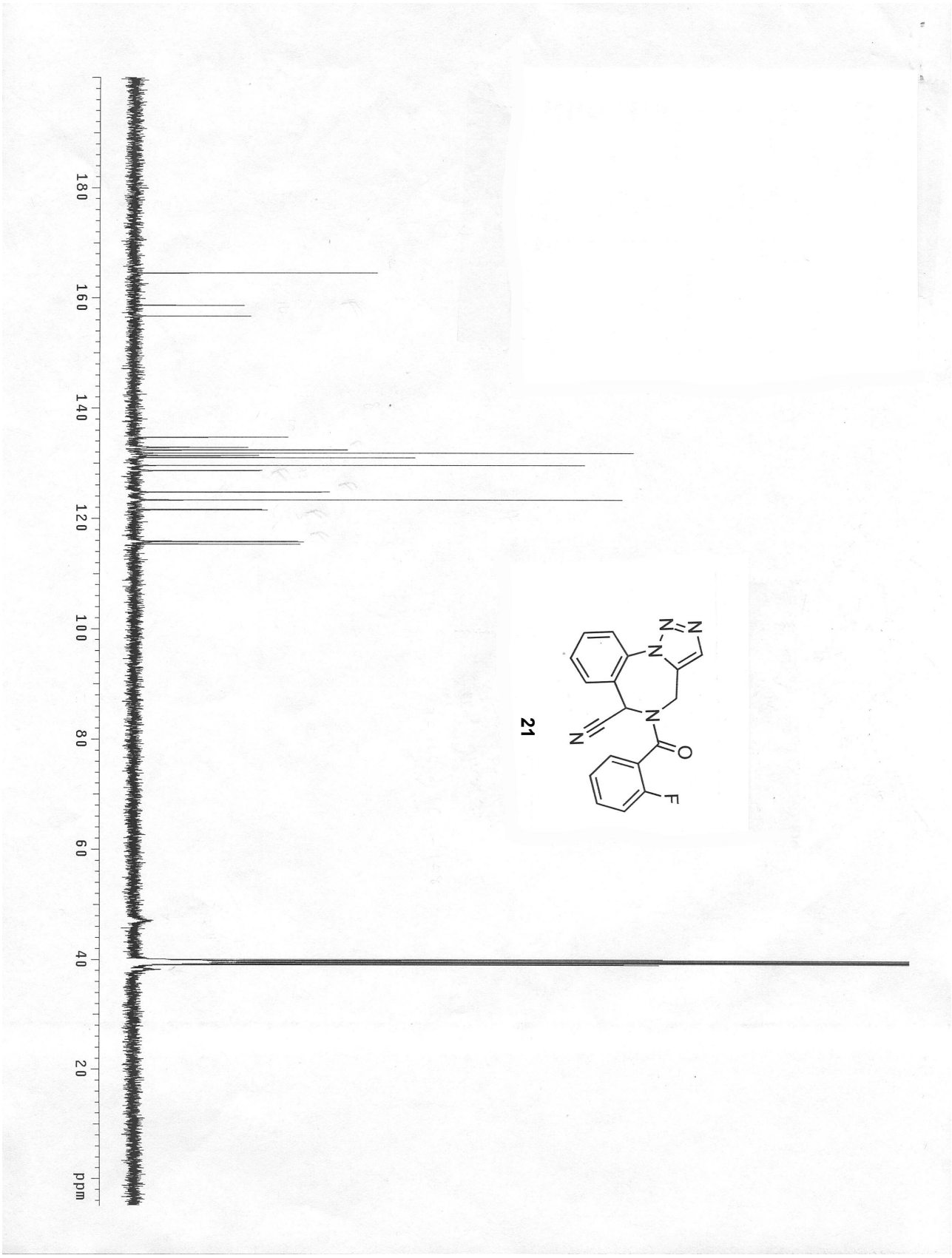
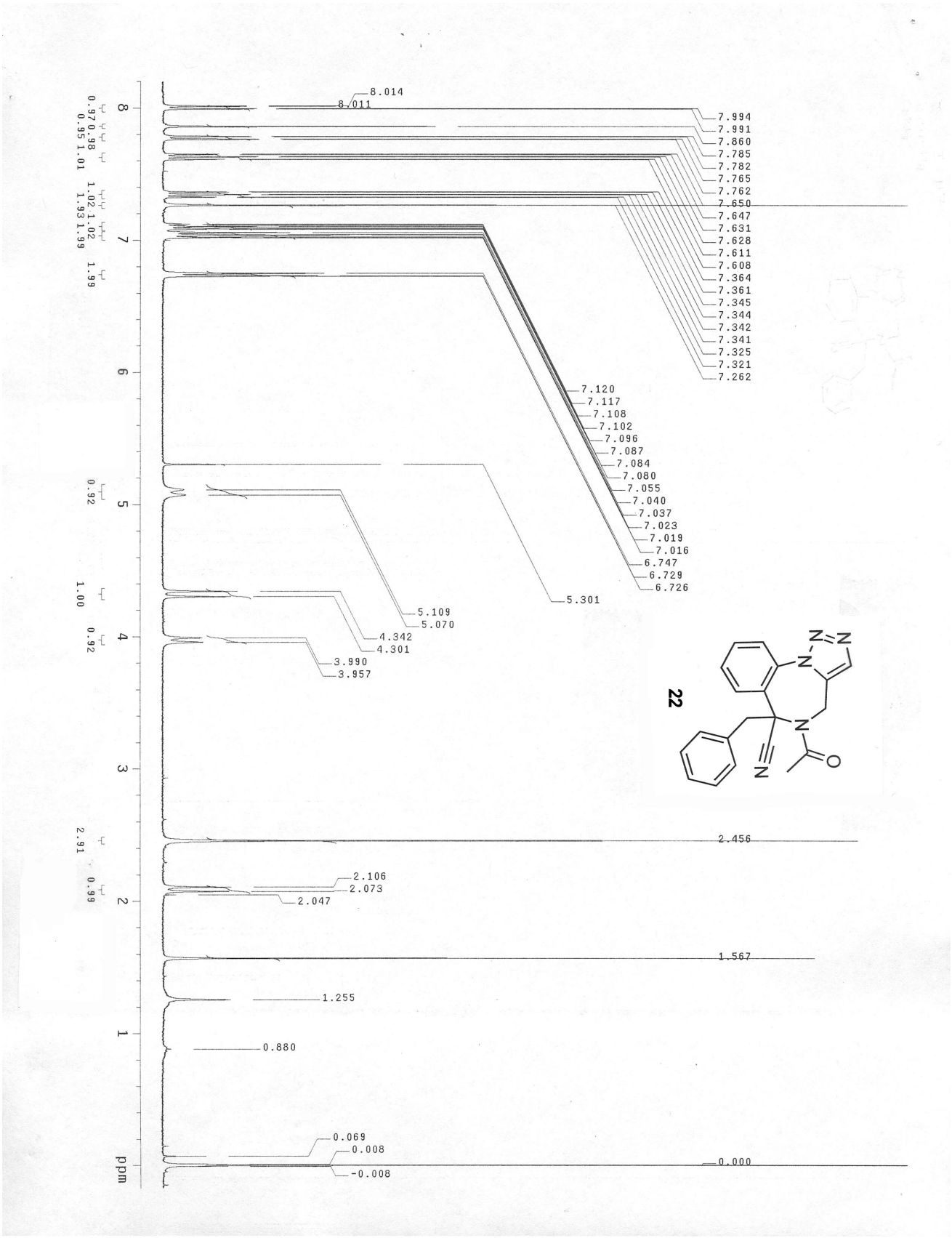
7.966
7.937
7.878
7.858
7.810
7.806
7.790
7.787
7.771
7.768
7.708
7.690
7.646
7.629
7.611
6.616
6.183
5.577
5.543
5.444
5.198
5.161
4.493
4.458
4.404
4.369
4.299
4.254
4.217
4.165
4.029
4.012
3.999
3.895
3.867
2.231
2.082
2.046
1.972
1.967
1.952
1.946
1.940
1.933
1.927
1.331
1.316
1.263
0.929
0.911
0.892
0.873
ppm
20


166.763
136.358
134.479
133.401
132.942
132.323
131.282
125.047
124.581
118.311
116.876
47.609
43.058
39.008
2.143
1.866
1.597
1.320
1.043
0.767
0.490
0 ppm
20
N
N
N
N
O
Cl


9
8
7
6
5
4
3
2
1
0
ppm
21
N
N
N
N
N
O
F


180
160
140
120
100
80
60
40
20
ppm
21
N
N
N
N
N
O
F


8.014
8.011
7.994
7.991
7.860
7.785
7.782
7.765
7.762
7.650
7.647
7.631
7.628
7.611
7.608
7.364
7.361
7.345
7.344
7.342
7.341
7.325
7.321
7.262
7.120
7.117
7.108
7.102
7.096
7.087
7.084
7.080
7.055
7.040
7.037
7.023
7.019
7.016
6.747
6.729
6.726
5.301
5.109
5.070
4.342
4.301
3.990
3.957
2.456
2.106
2.073
2.047
1.567
1.255
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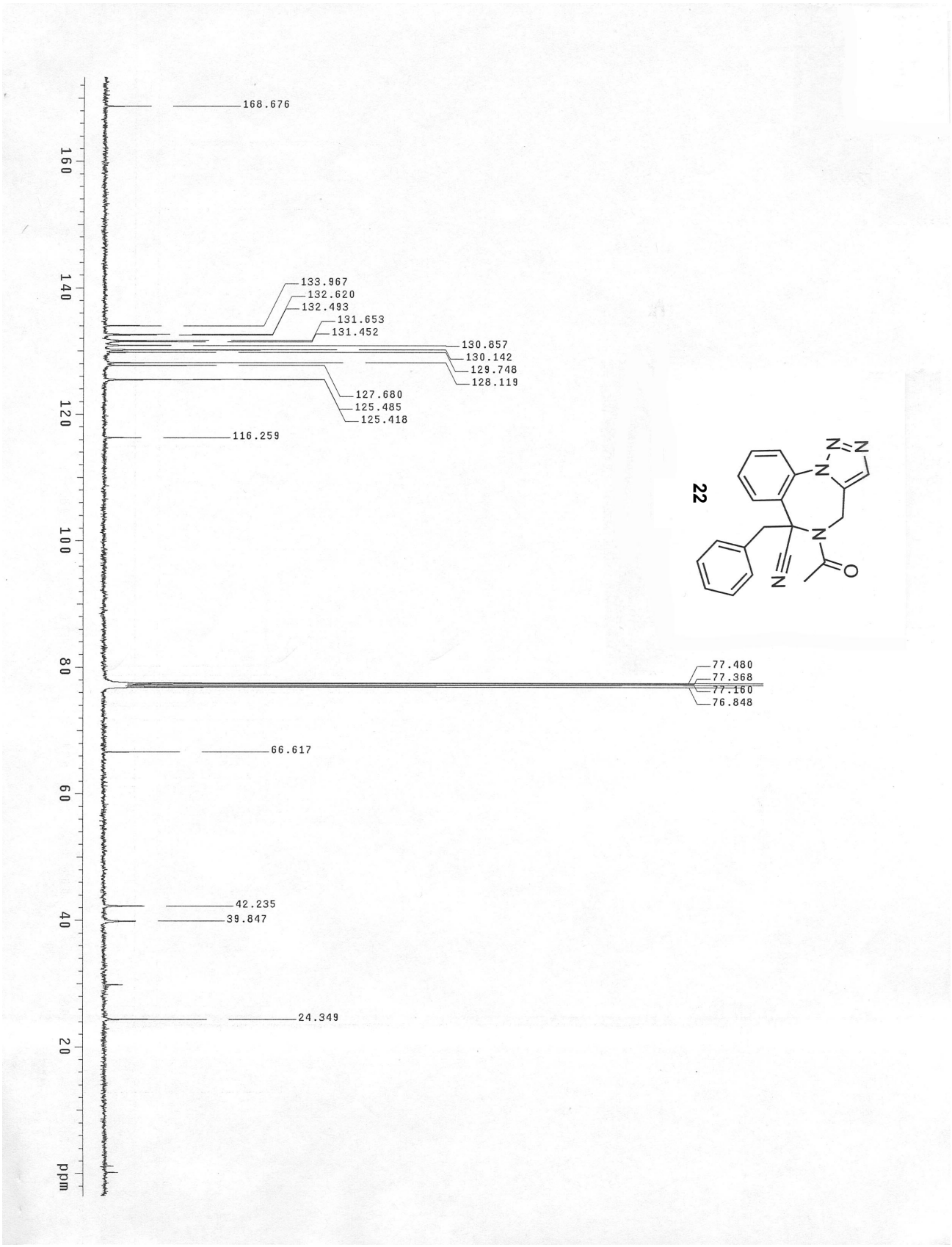
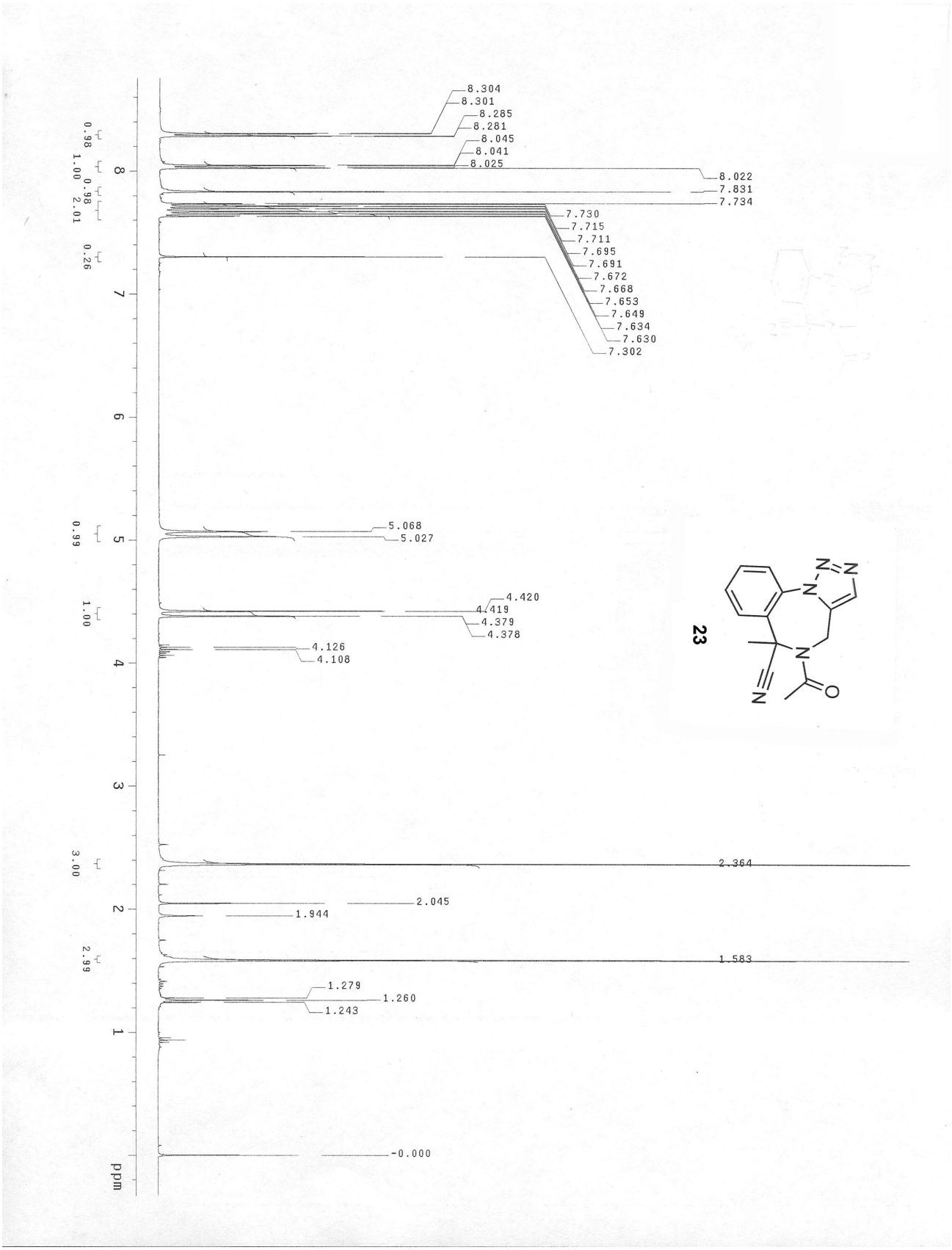
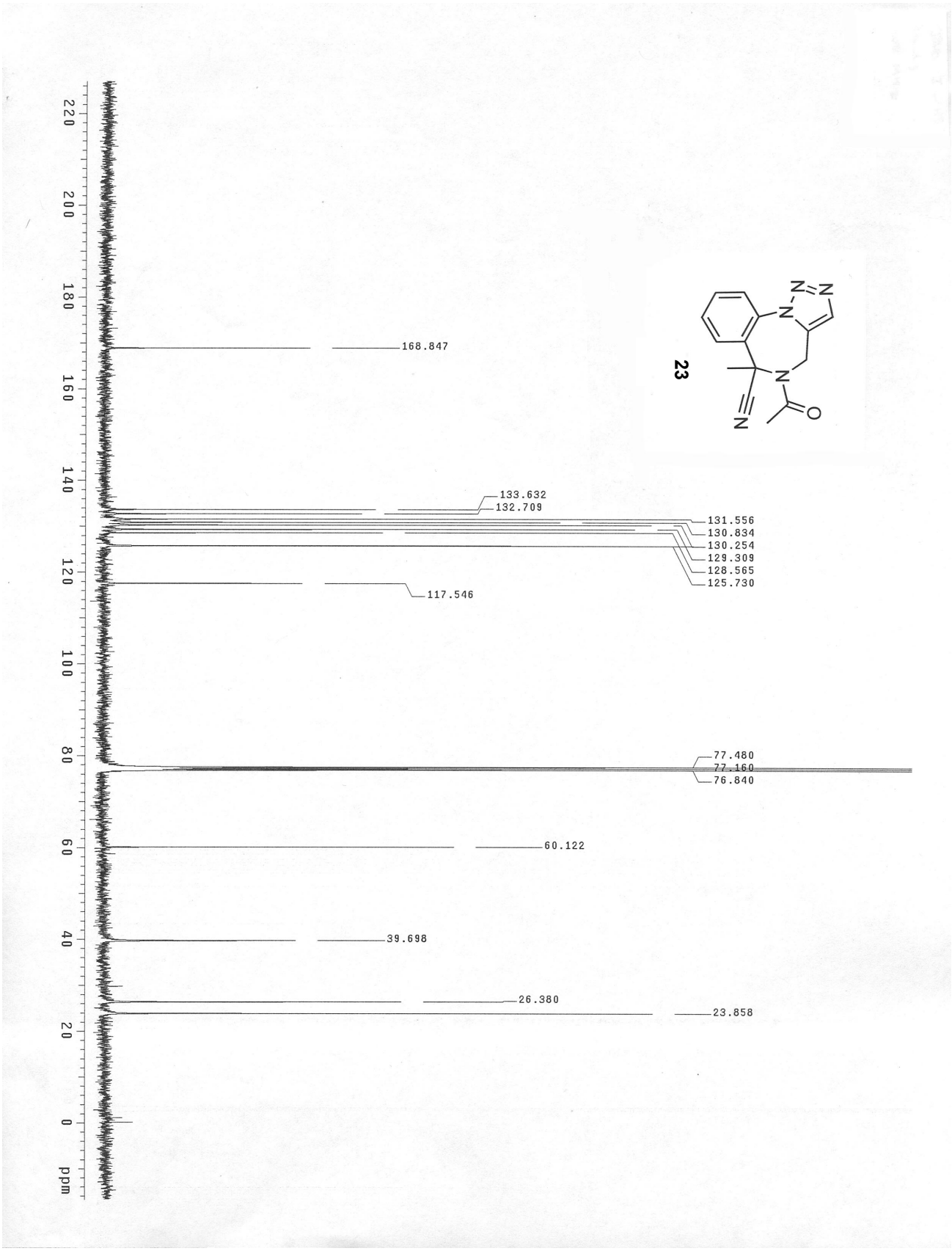
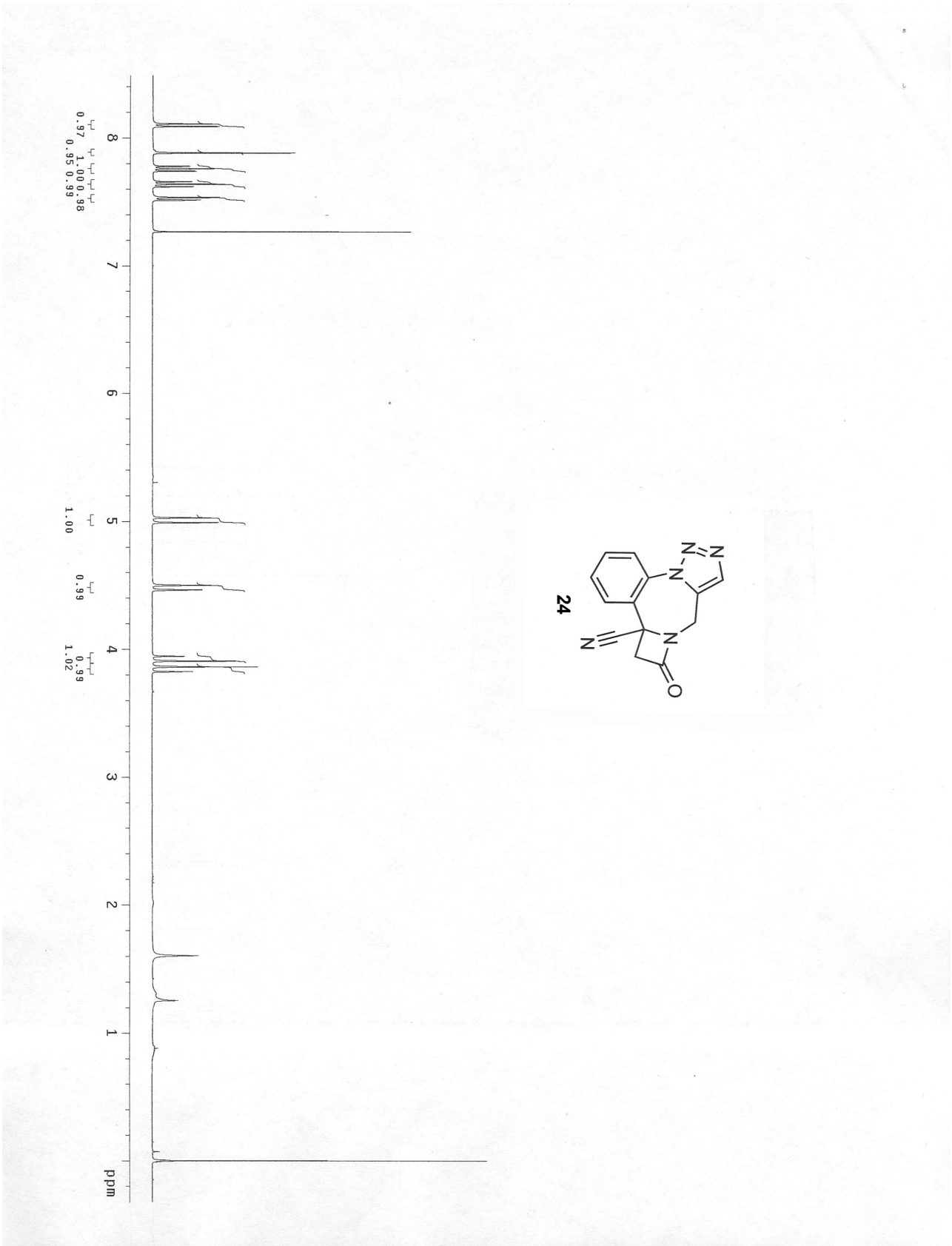
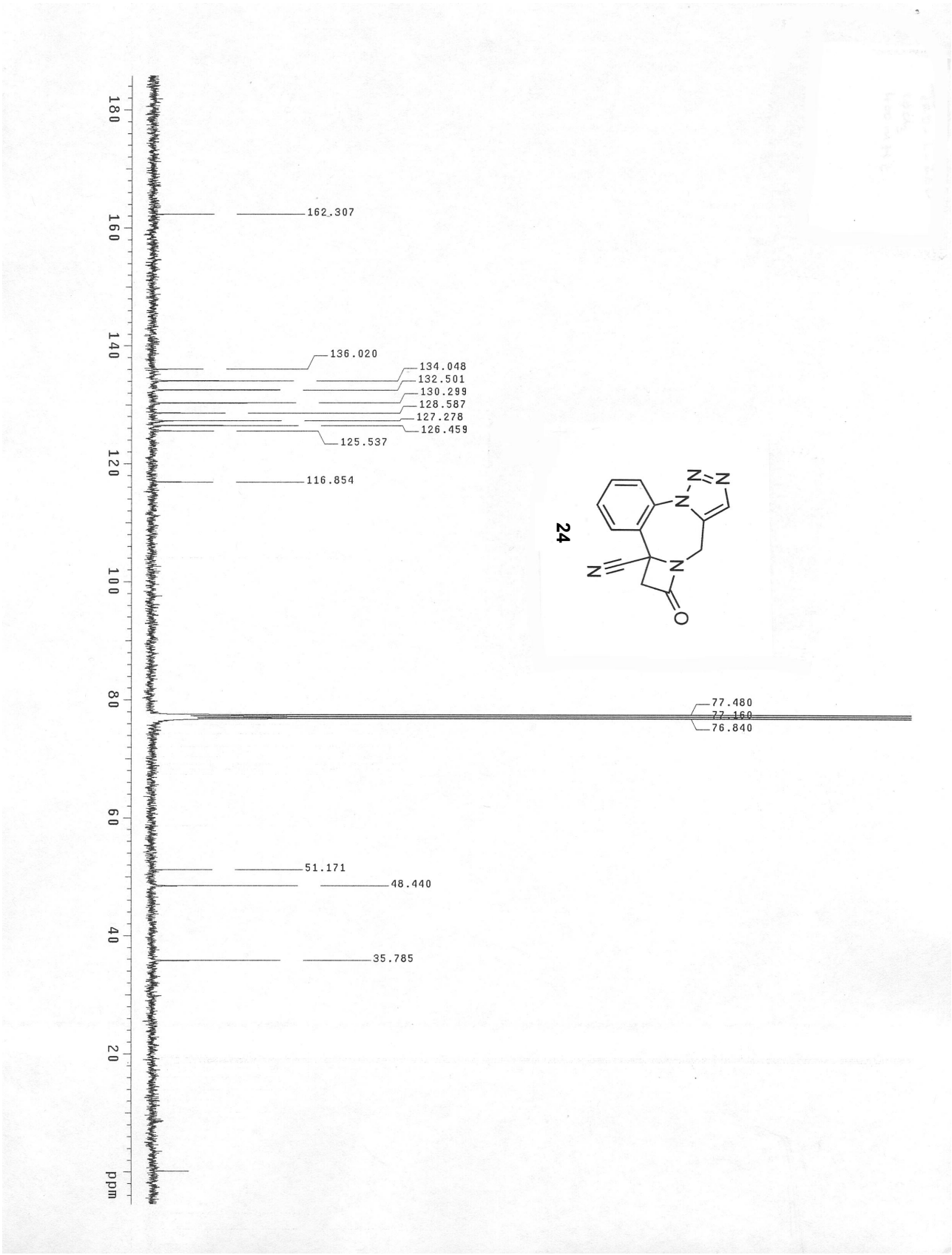
0.069
0.008
-0.008
0.000
ppm
22

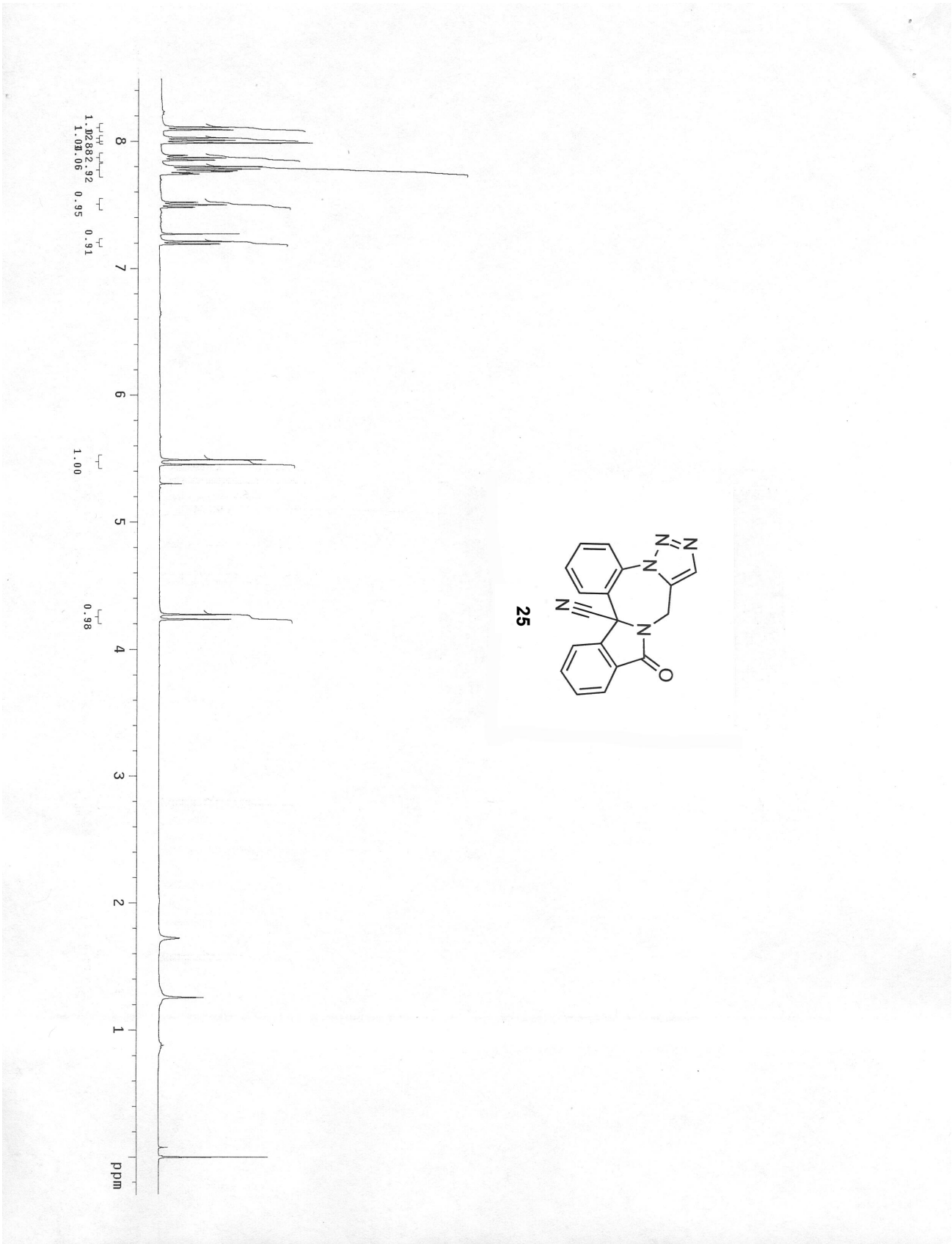

168.676
133.967
132.620
132.493
131.653
131.452
130.857
130.142
129.748
128.119
127.680
125.485
125.418
116.259
77.480
77.368
77.160
76.848
66.617
42.235
39.847
24.349
160
140
120
100
80
60
40
20
ppm
22

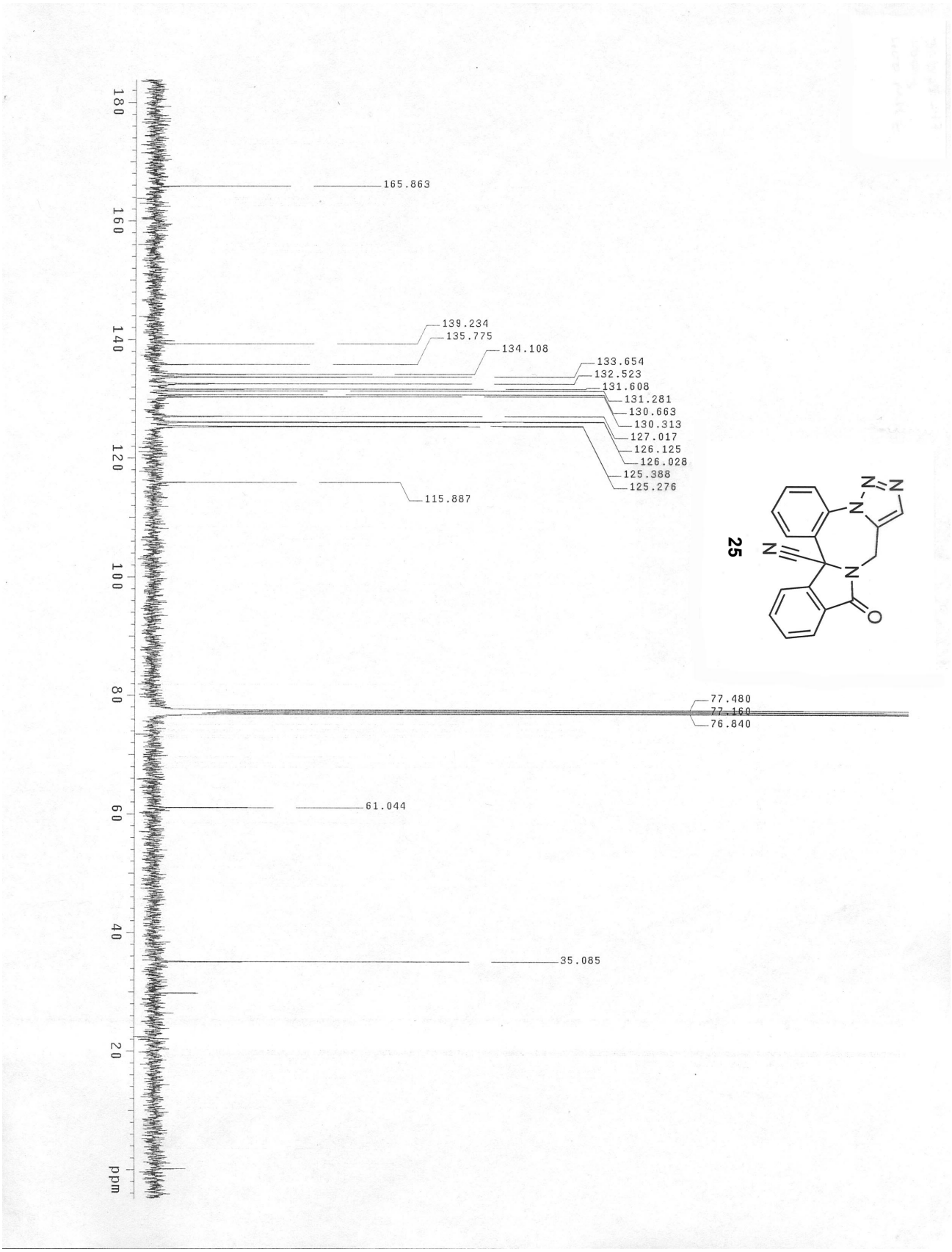

8.304
8.301
8.285
8.281
8.045
8.041
8.025
8.022
7.831
7.734
7.730
7.715
7.711
7.695
7.691
7.672
7.668
7.653
7.649
7.634
7.630
7.302
5.068
5.027
4.420
4.419
4.379
4.378
4.126
4.108
2.364
2.045
1.944
1.583
1.279
1.260
1.243
-0.000
ppm
23


23
168.847
133.632
132.709
131.556
130.834
130.254
129.309
128.565
125.730
117.546
77.480
77.160
76.840
60.122
39.698
26.380
23.858
220
200
180
160
140
120
100
80
60
40
20
0
ppm


24
N
N
N
N
O
8
7
6
5
4
3
2
1
ppm
0.97 1.00 0.98
0.95 0.99
1.00
0.99
0.99
1.02


180
160
140
120
100
80
60
40
20
ppm
162.307
136.020
134.048
132.501
130.299
128.587
127.278
126.459
125.537
116.854
77.480
77.160
76.840
51.171
48.440
35.785
24
N
N
N
N
N
O


25
N
N
N
N
N
O
8
7
6
5
4
3
2
1
ppm
1.00
0.98
0.95
0.91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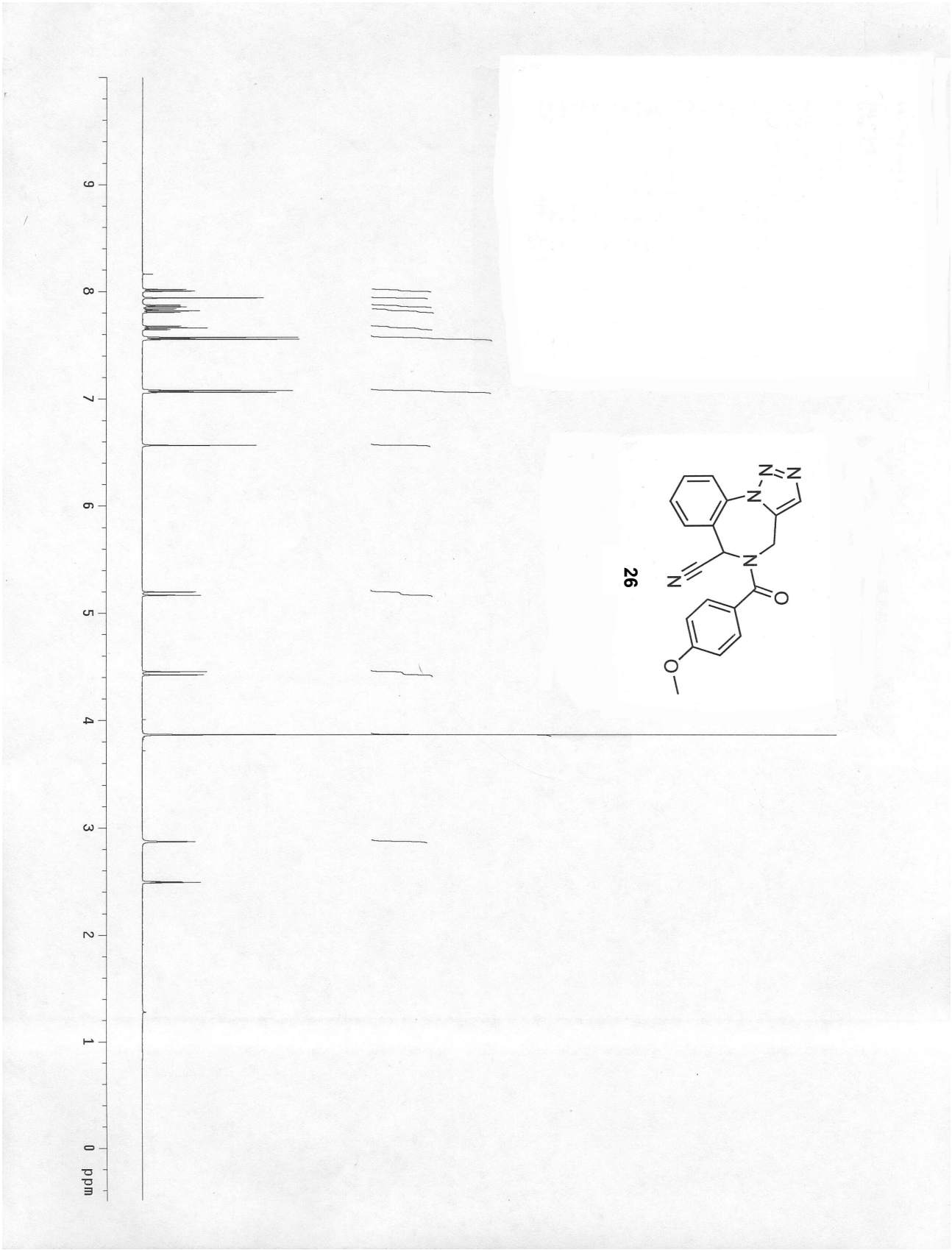
139.234
135.775
134.108
133.654
132.523
131.608
131.281
130.663
130.313
127.017
126.125
126.028
125.388
125.276
115.887
77.480
77.160
76.840
61.044
35.085
180
160
140
120
100
80
60
40
20
ppm
25


26
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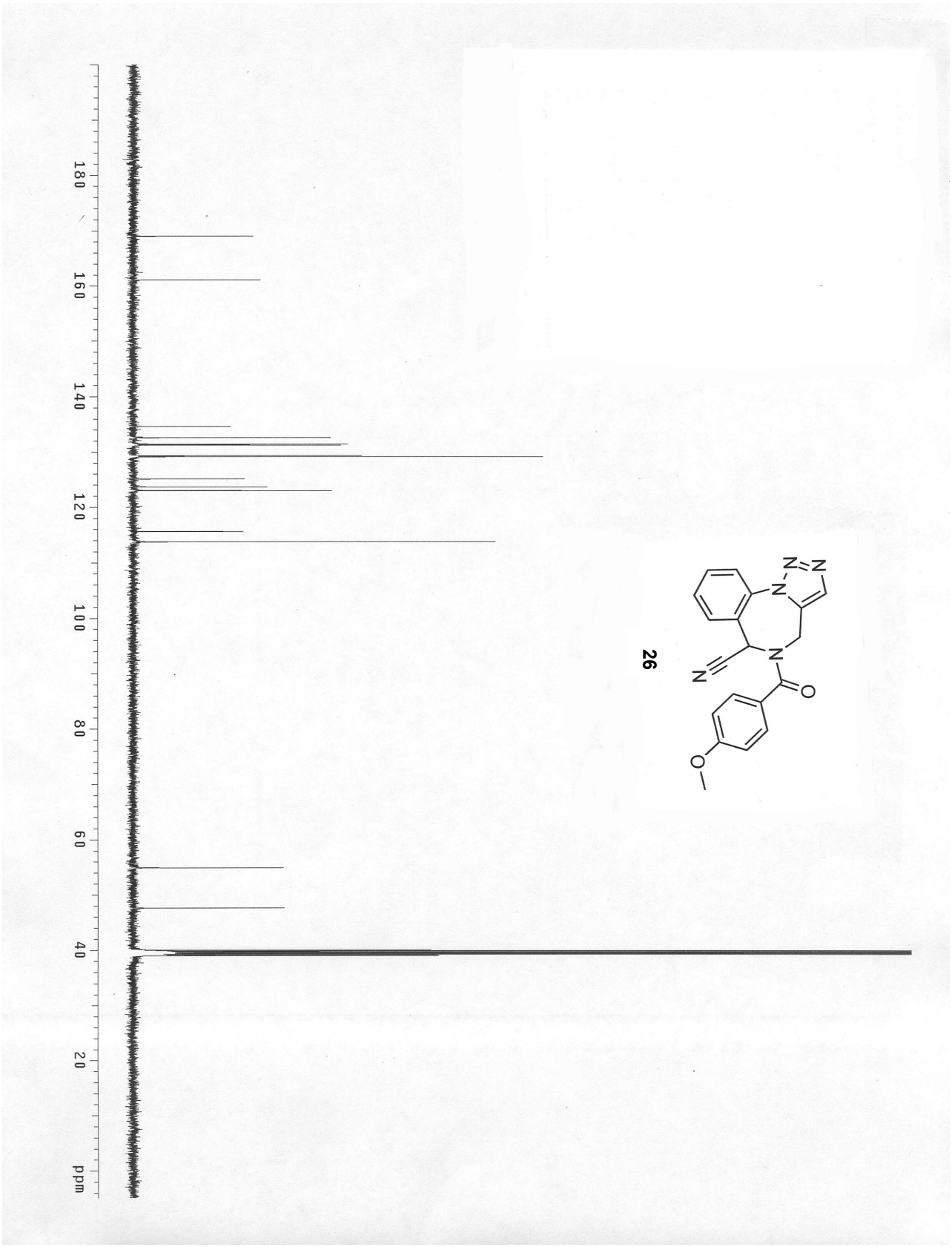
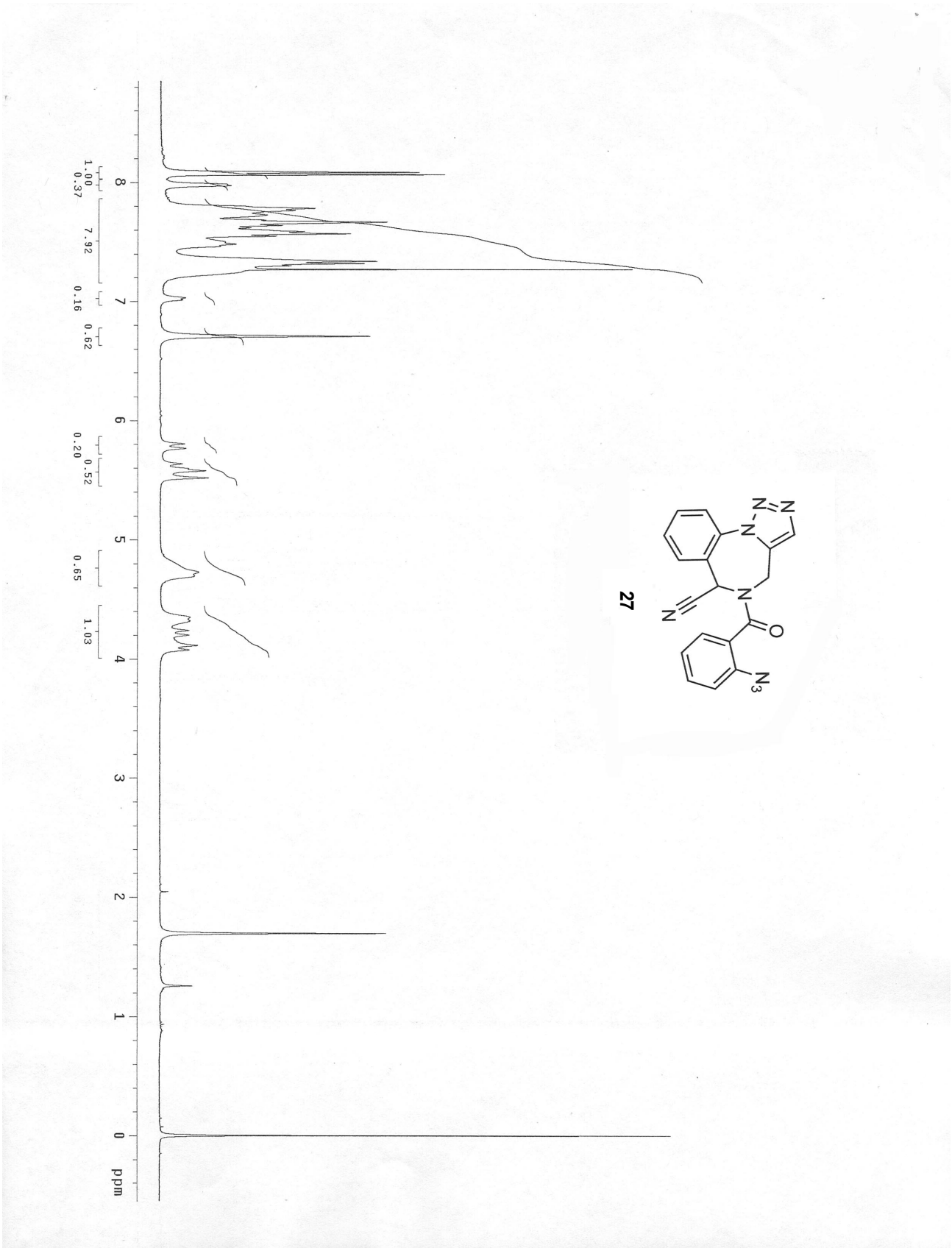
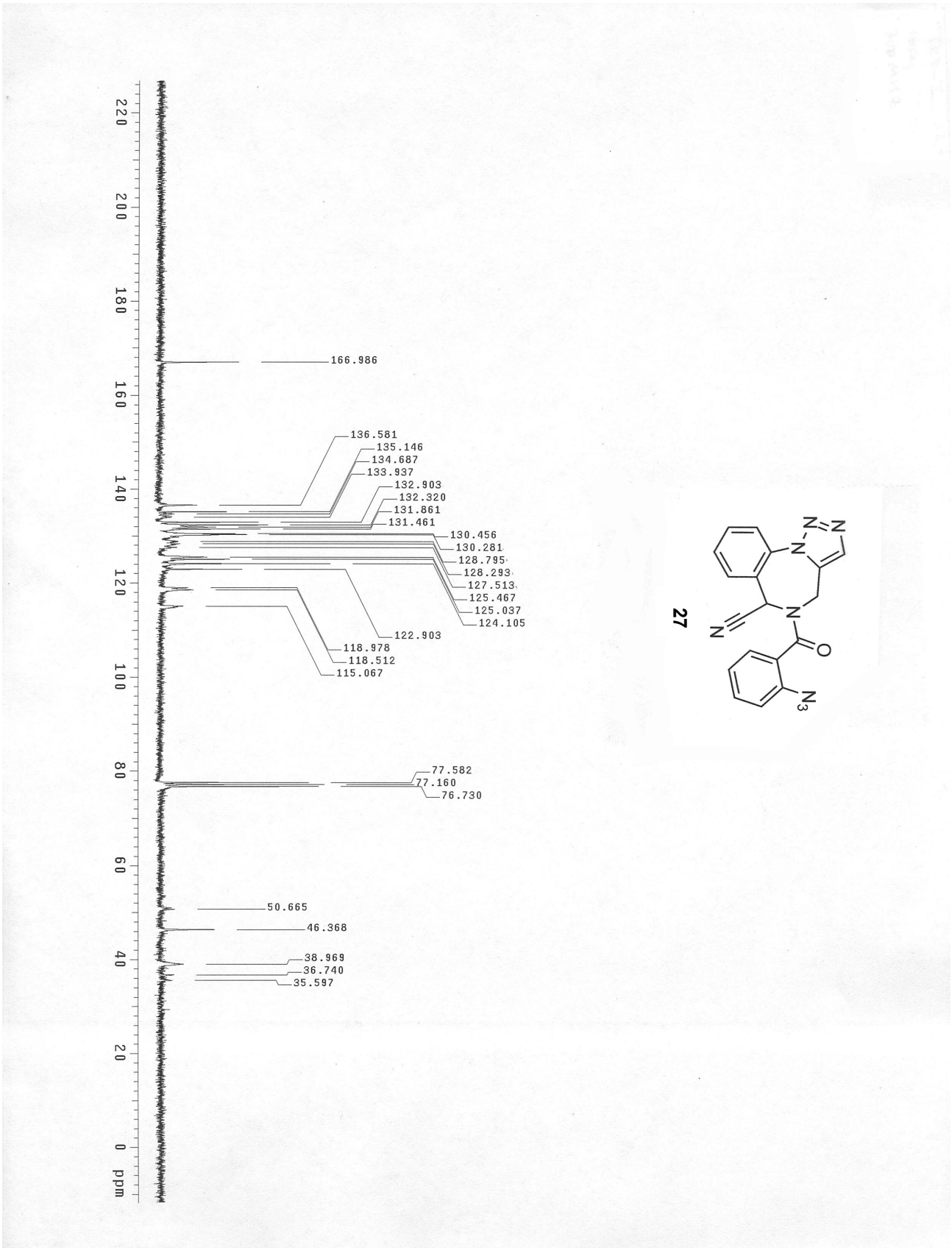
N
N
N
N
O
O
9
8
7
6
5
4
3
2
1
0
ppm


180
160
140
120
100
80
60
40
20
ppm
26


27
ppm
1.00
0.37
7.92
0.16
0.62
0.20
0.52
0.65
1.03


166.986
136.581
135.146
134.687
133.937
132.903
132.320
131.861
131.461
130.456
130.281
128.795
128.293
127.513
125.467
125.037
124.105
122.903
118.978
118.512
115.067
77.582
77.160
76.730
50.665
46.368
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35.597
220
200
180
160
140
120
100
80
60
40
20
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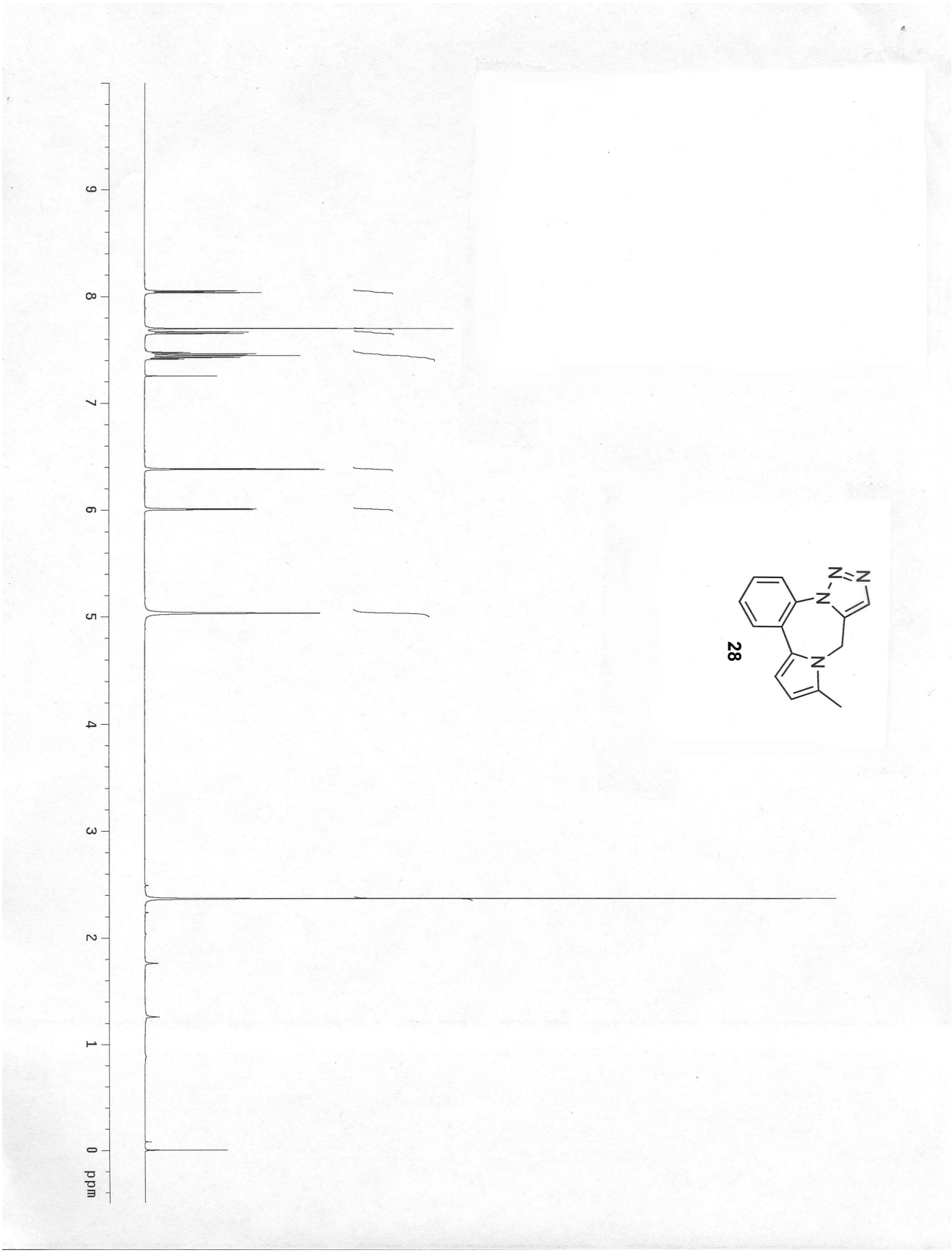
ppm
27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8
7
6
5
4
3
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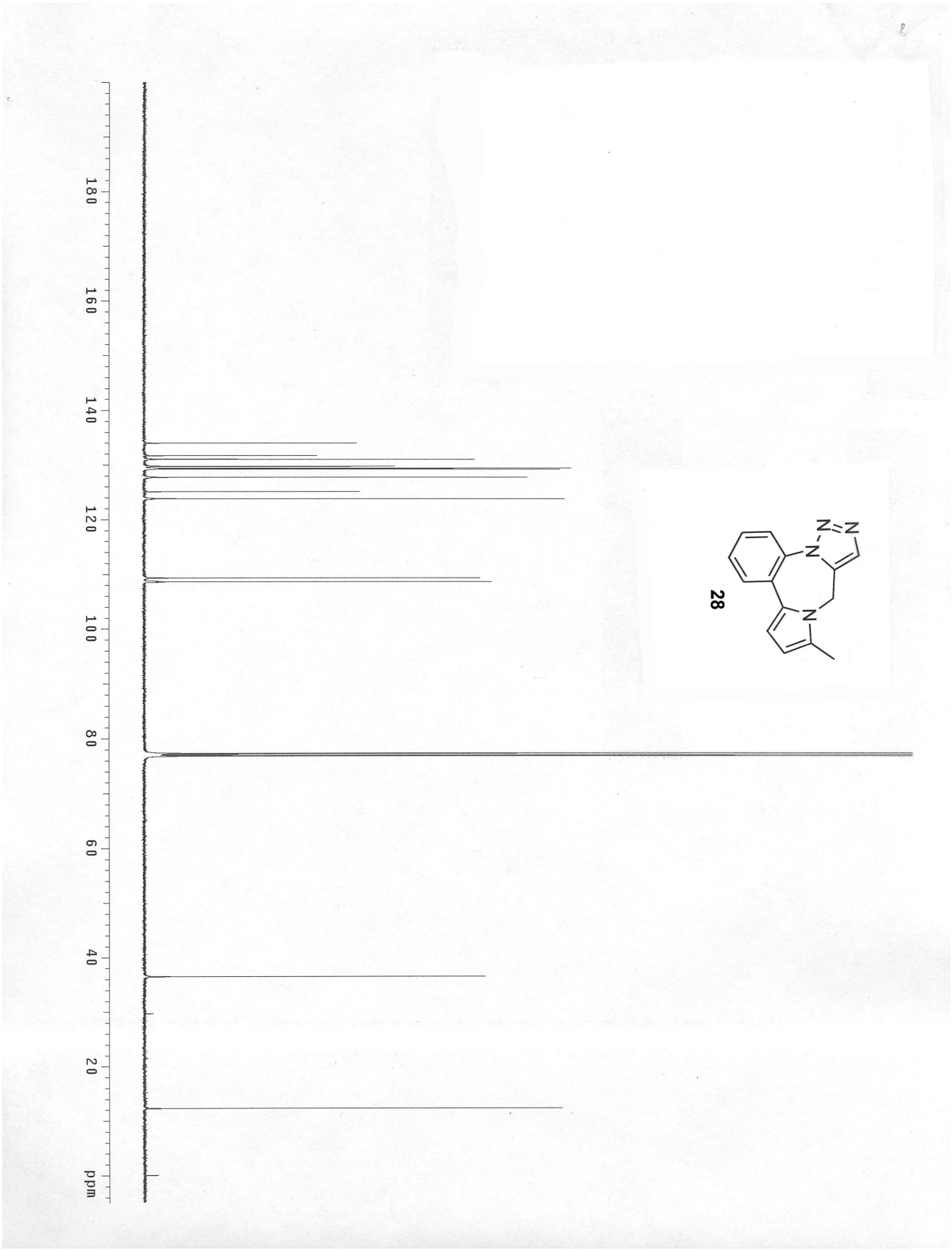
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180
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140
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80
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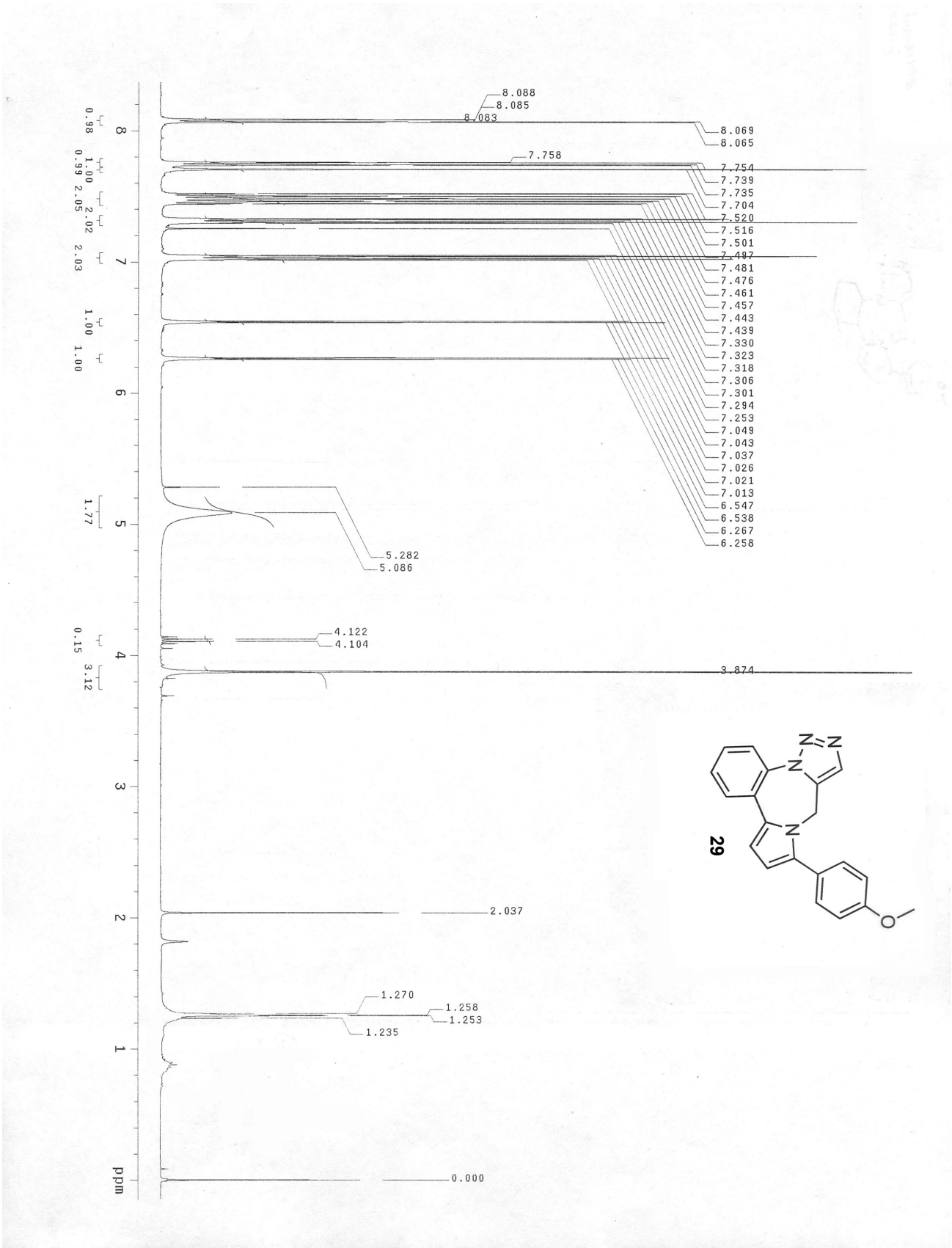
40
20
ppm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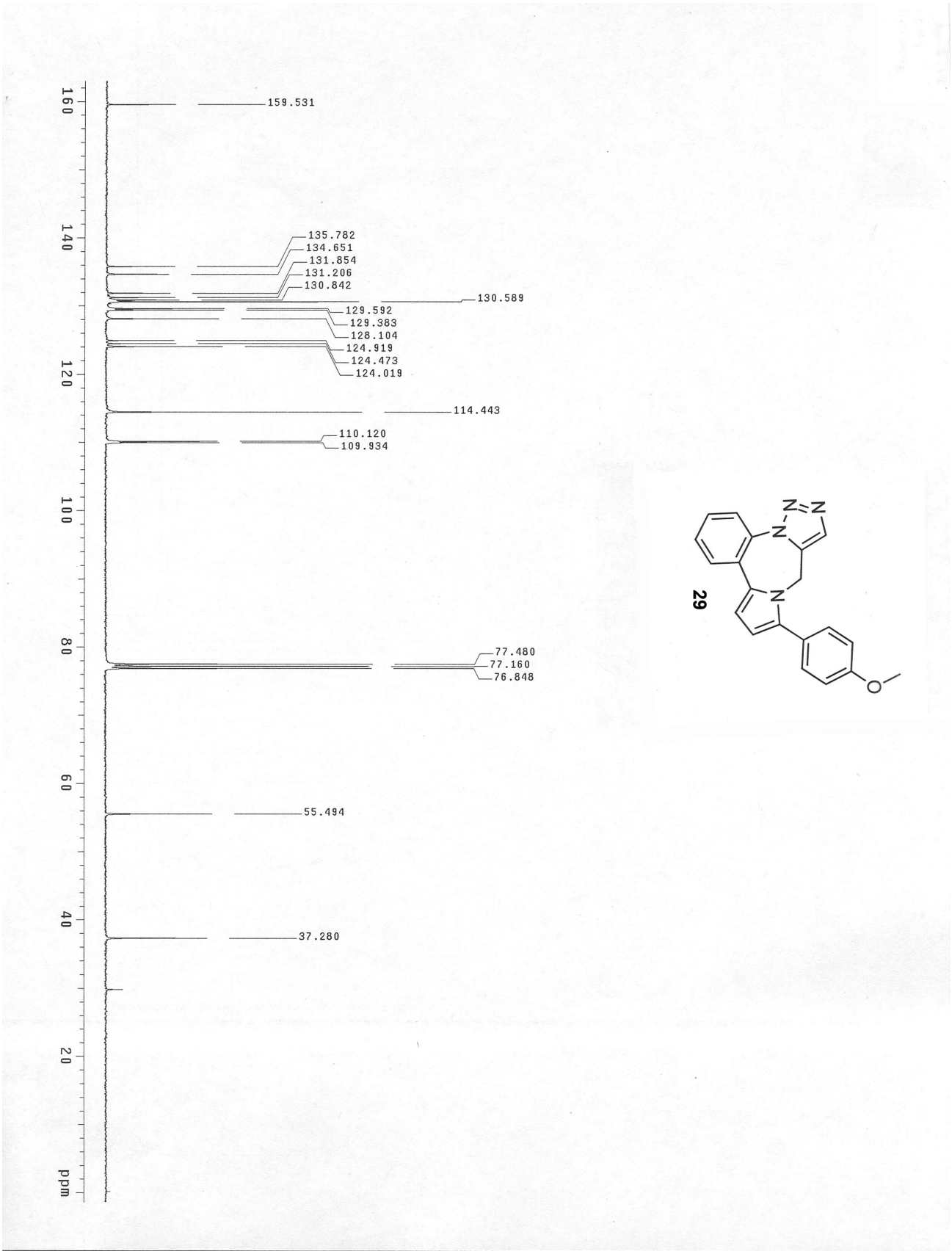
8.085
8.083
8.069
8.065
7.758
7.754
7.739
7.735
7.704
7.520
7.516
7.501
7.497
7.481
7.476
7.461
7.457
7.443
7.439
7.330
7.323
7.318
7.306
7.301
7.294
7.253
7.049
7.043
7.037
7.026
7.021
7.013
6.547
6.538
6.267
6.258
5.282
5.086
4.122
4.104
3.874
2.037
1.270
1.258
1.253
1.235
0.000
ppm
0.98
1.00
0.99
2.05
2.02
2.03
1.00
1.00
1.77
0.15
3.12
29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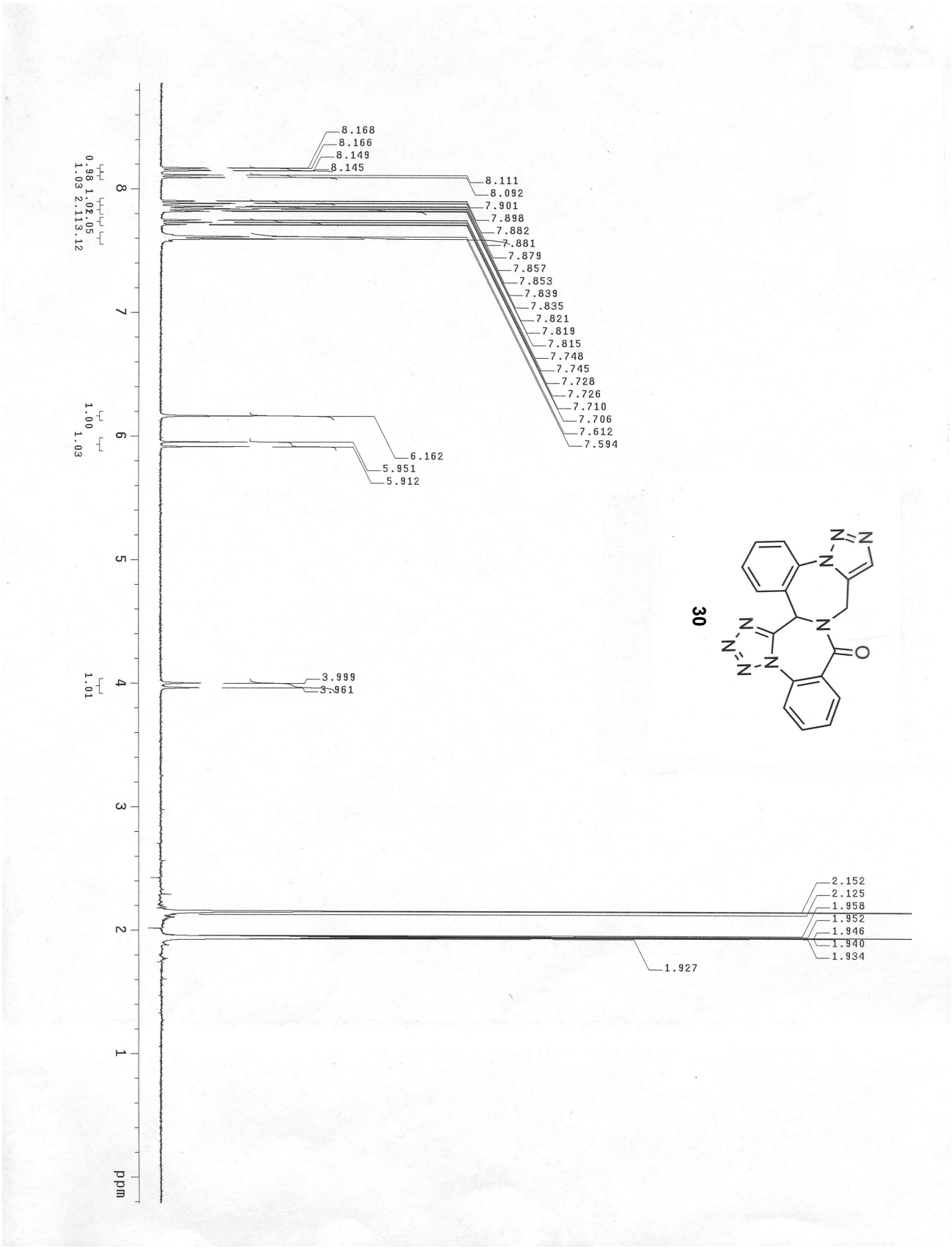
135.782
134.651
131.854
131.206
130.842
130.589
129.592
129.383
128.104
124.919
124.473
124.019
114.443
110.120
109.934
77.480
77.160
76.848
55.494
37.280
160
140
120
100
80
60
40
20
ppm
29


8.168
8.166
8.149
8.145
8.111
8.092
7.901
7.898
7.882
7.881
7.879
7.857
7.853
7.839
7.835
7.821
7.819
7.815
7.748
7.745
7.728
7.726
7.710
7.706
7.612
7.594
6.162
5.951
5.912
3.999
3.961
2.152
2.125
1.958
1.952
1.946
1.940
1.934
1.927
0.98 1.02.05
1.03 2.113.12
1.00
1.03
1.01
ppm
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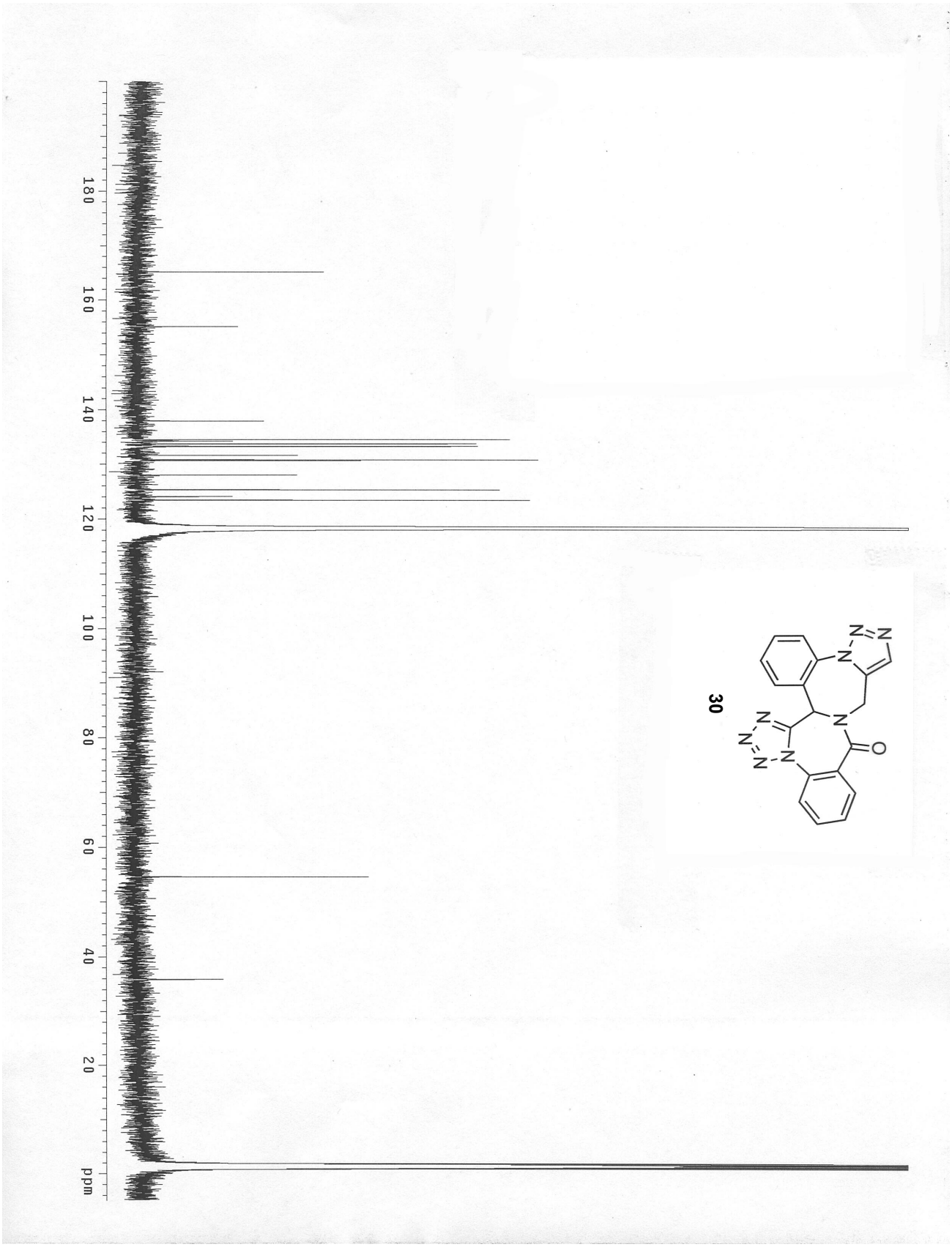

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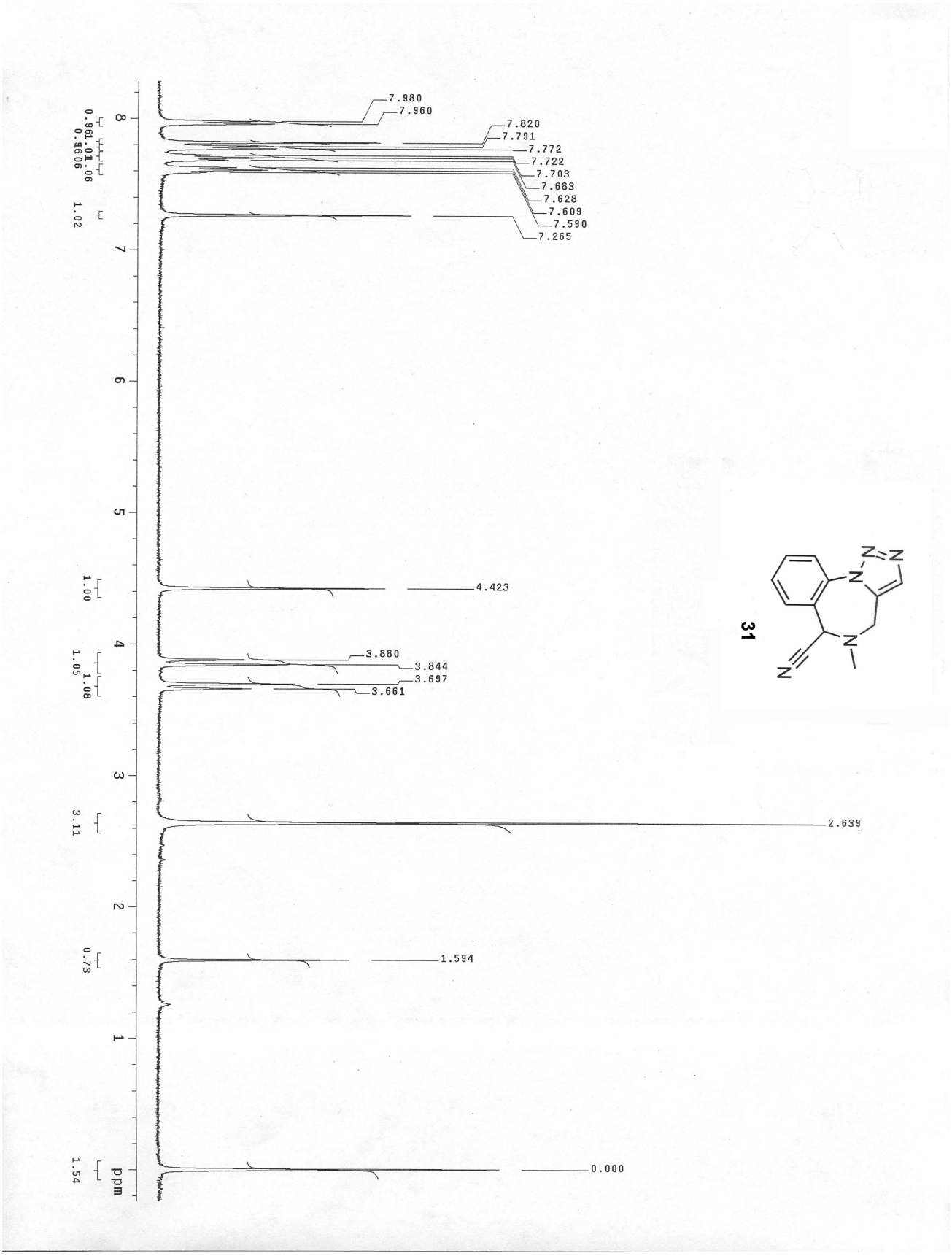
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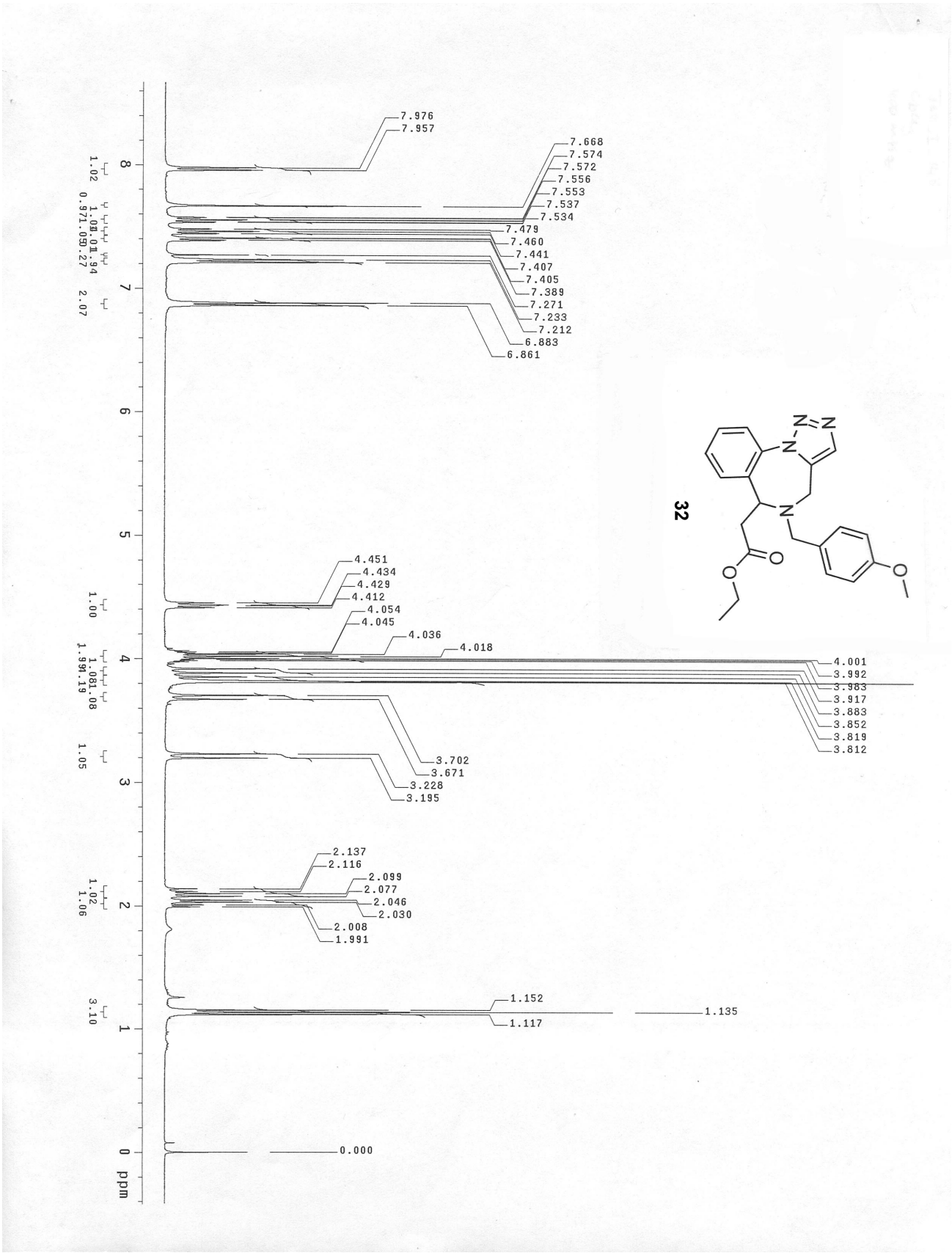
7.960
7.820
7.791
7.772
7.722
7.703
7.683
7.628
7.609
7.590
7.265
4.423
3.880
3.844
3.697
3.661
2.639
1.594
0.000
ppm
31


135.488
133.252
132.043
131.548
129.961
129.837
124.382
123.792
116.058
77.590
77.160
76.738
57.096
45.851
42.472
140
130
120
110
100
90
80
70
60
50
40
ppm
31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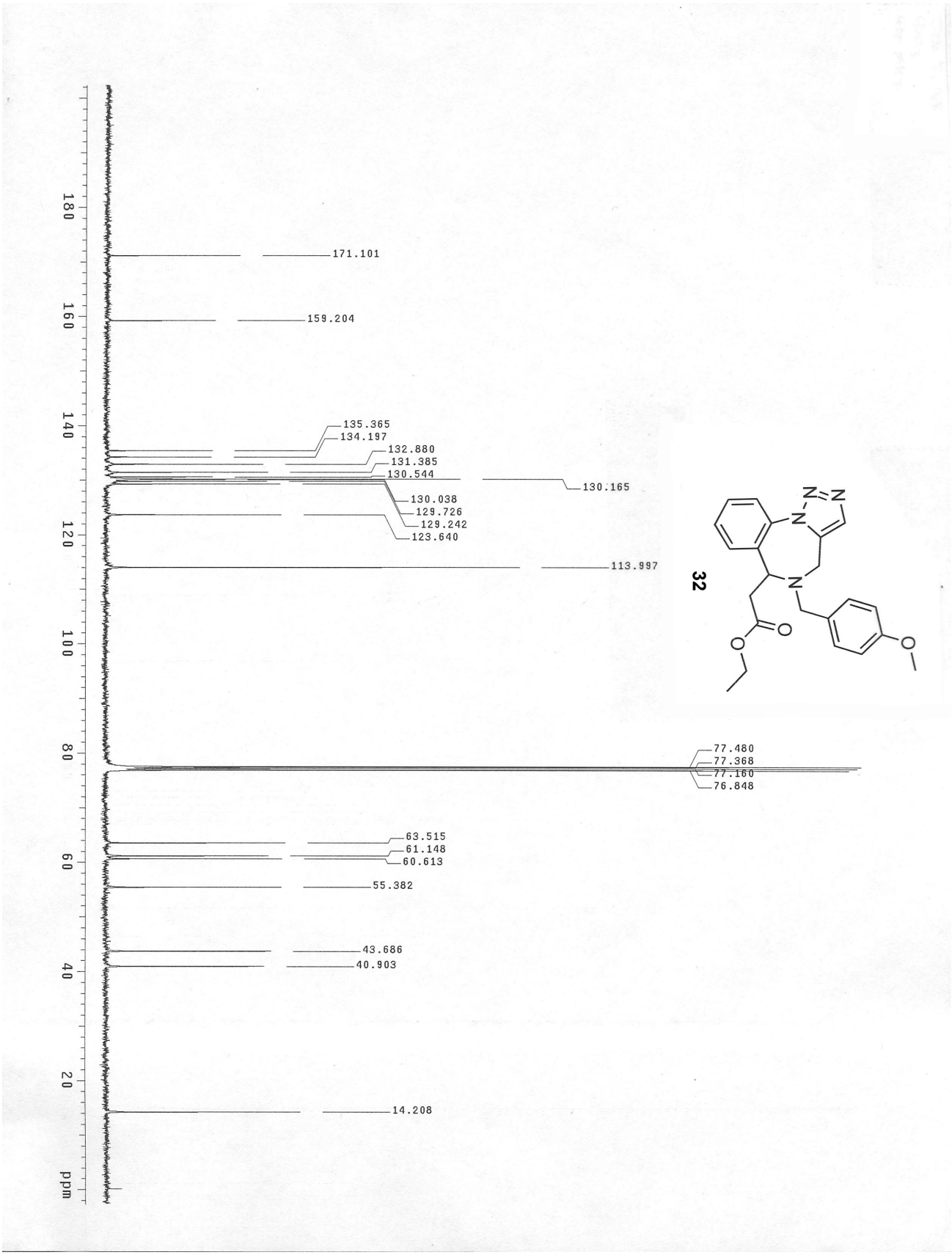
7.668
7.574
7.572
7.556
7.553
7.537
7.534
7.479
7.460
7.441
7.407
7.405
7.389
7.271
7.233
7.212
6.883
6.861
4.451
4.434
4.429
4.412
4.054
4.045
4.036
4.018
4.001
3.992
3.983
3.917
3.883
3.852
3.819
3.812
3.702
3.671
3.228
3.195
2.137
2.116
2.099
2.077
2.046
2.030
2.008
1.991
1.152
1.135
1.117
0.000
ppm
32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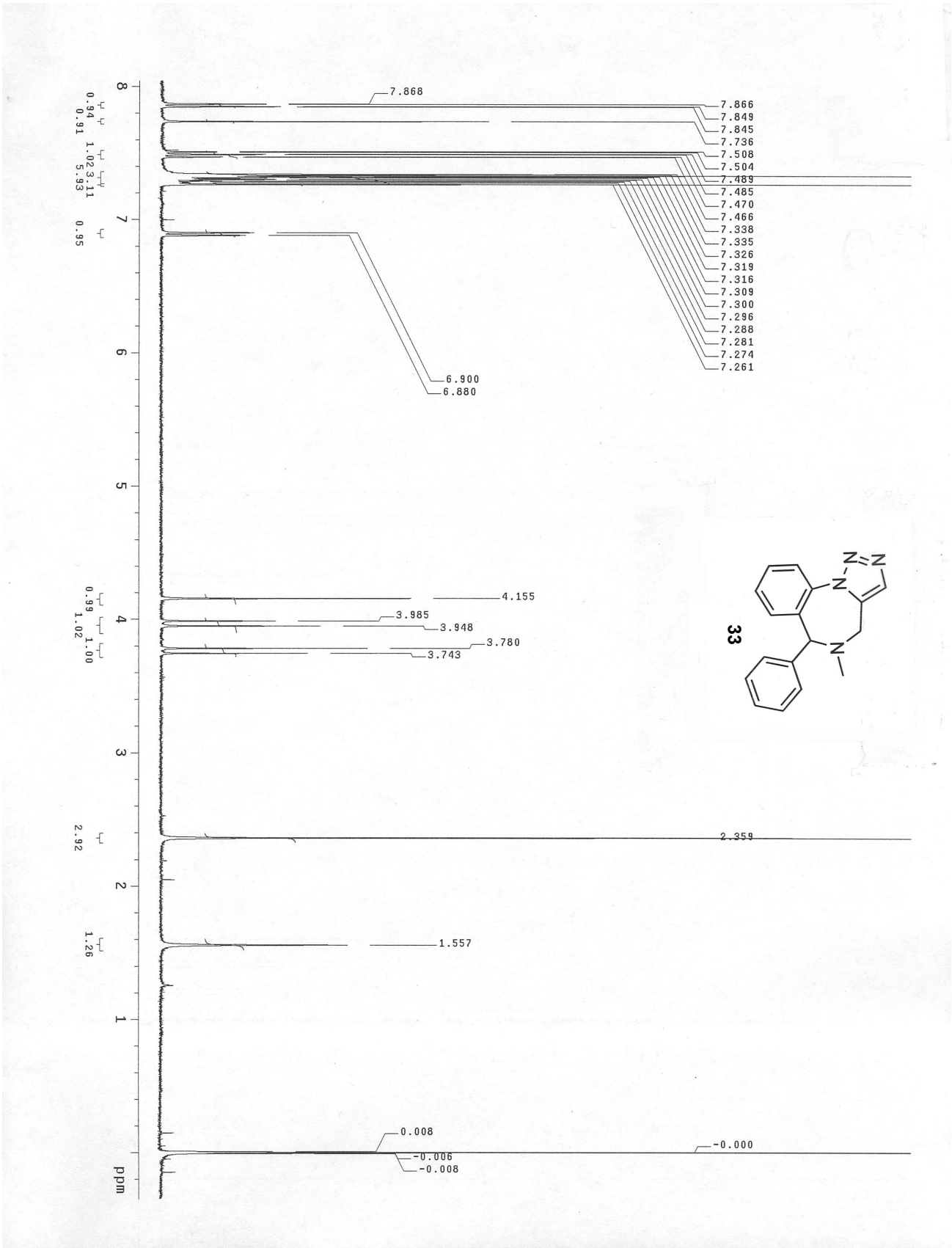
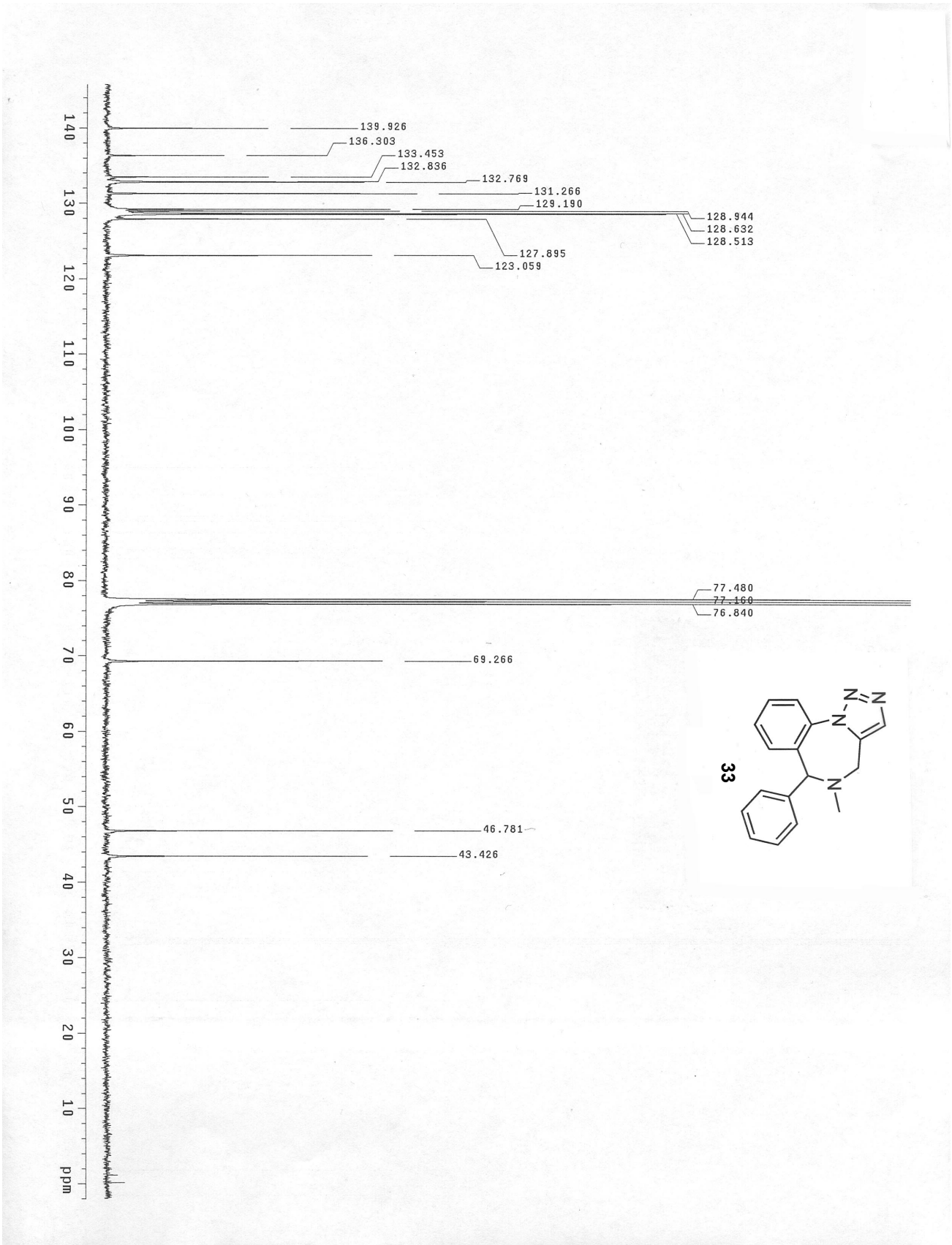
159.204
135.365
134.197
132.880
131.385
130.544
130.165
130.038
129.726
129.242
123.640
113.997
77.480
77.368
77.160
76.848
63.515
61.148
60.613
55.382
43.686
40.903
14.208
ppm
32


7.868
7.866
7.849
7.845
7.736
7.508
7.504
7.489
7.485
7.470
7.466
7.338
7.335
7.326
7.319
7.316
7.309
7.300
7.296
7.288
7.281
7.274
7.261
6.900
6.880
4.155
3.985
3.948
3.780
3.743
2.359
1.557
0.008
-0.006
-0.008
-0.000
ppm
33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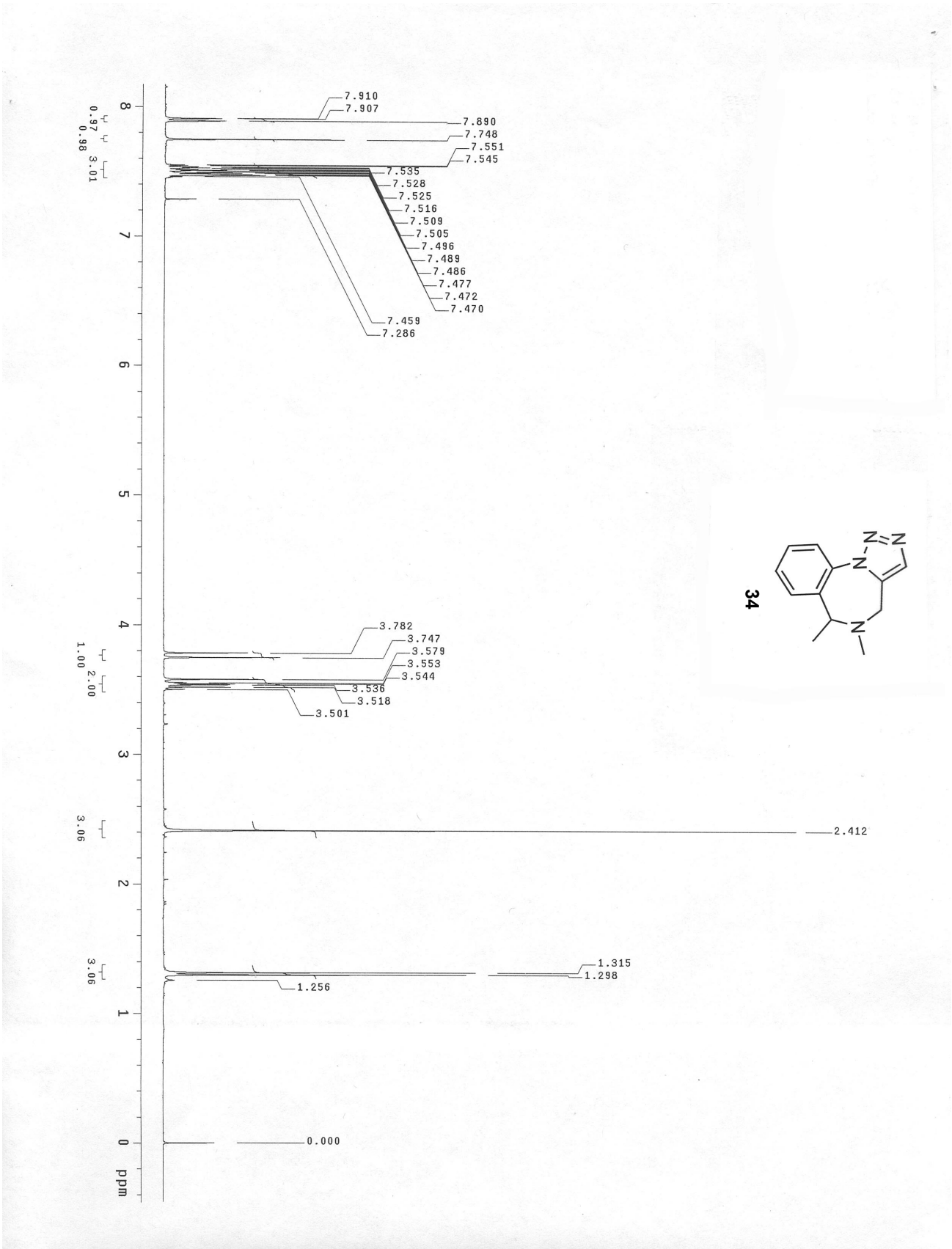
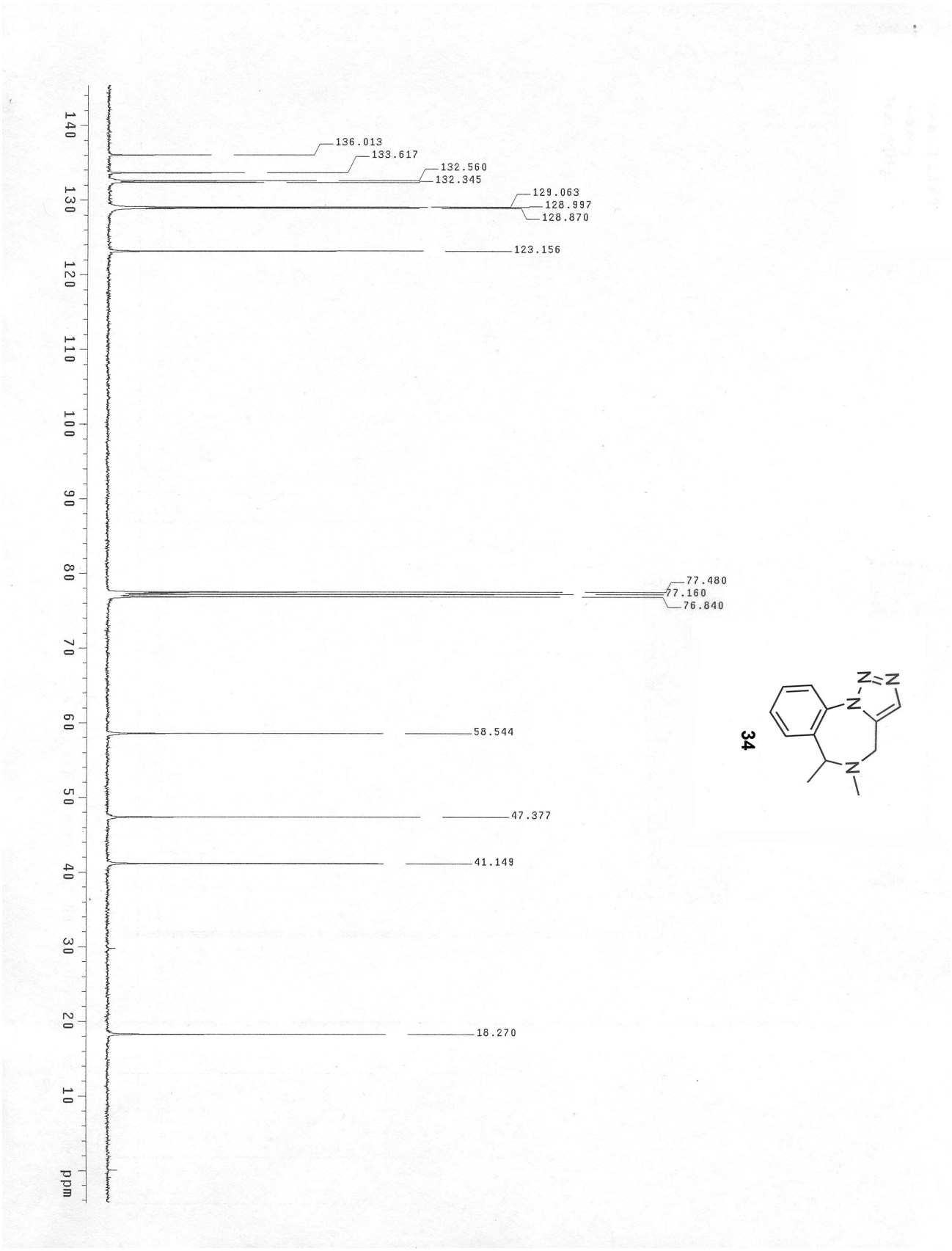
136.303
133.453
132.836
132.769
131.266
129.190
128.944
128.632
128.513
127.895
123.059
77.480
77.160
76.840
69.266
46.781
43.426
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
33


7.910
7.907
7.890
7.748
7.551
7.545
7.535
7.528
7.525
7.516
7.509
7.505
7.496
7.489
7.486
7.477
7.472
7.470
7.459
7.286
3.782
3.747
3.579
3.553
3.544
3.536
3.518
3.501
2.412
1.315
1.298
1.256
0.000
ppm
0.97
0.98
3.01
1.00
2.00
3.06
3.06
34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132.345
129.063
128.997
128.870
123.156
77.480
77.160
76.840
58.544
47.377
41.149
18.270
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
34