Supporting Information For

Application of a Sequential Multicomponent Assembly Process/Huisgen Cycloaddition Strategy to the Preparation of Libraries of 1,2,3-Triazole-Fused 1,4-Benzodiazepines

James R. Donald, Rebekah R. Wood and Stephen F. Martin*

Department of Chemistry and Biochemistry and
The Texas Institute for Drug and Diagnostic Development
The University of Texas, Austin, Texas 78712

sfmartin@mail.utexas.edu

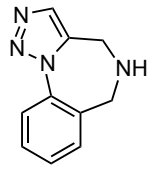
Table of Contents:

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] 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.

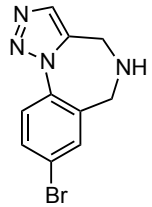
Nuclear magnetic resonance spectra were acquired at room temperature in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to either TMS or the residual solvent: $CDCl_3$, δ = 7.26 ppm (^{1}H) 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] Purity was determined using an LCMS system comprised of an Agilent 1200 Series HPLC and an Agilent 6130 single quadrupole mass spectrometer. Samples were injected onto a Phenomenex Gemini C18 column (5 micron, 2.1 x 50 mm) and eluted at 0.7 ml/min using a gradient of 10-90% acetonitrile, 0.1% formic acid (11 minute linear ramp). Positive mode

electrospray ionization was used to verify the identity of the major component, and a UV chromatogram recorded at 214 nm was integrated to determine compound purity.



6

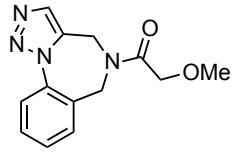
5,6-Dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (6). A mixture of 2-azidobenzaldehyde (**4**) (3.10 g, 21.1 mmol),[4] propargylamine (1.74 g, 2.02 mL, 31.6 mmol), sodium triacetoxyborohydride (8.93 g, 42.1 mmol) and glacial acetic acid (1.27 g, 1.20 mL, 21.1 mmol) in DCE (62 mL) was 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 **6** 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] LCMS purity 97%



7

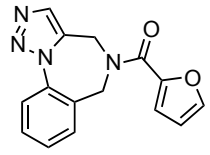
8-Bromo-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (7). A mixture of 2-azido-5-bromobenzaldehyde (**5**) (5.00 g, 22.1 mmol),[6] propargylamine (1.83 g, 2.13 mL, 33.2 mmol), sodium triacetoxyborohydride (9.38 g, 44.2 mmol) and glacial acetic acid (1.33 g, 1.27 mL, 22.1 mmol) in 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]; LCMS purity 100%.



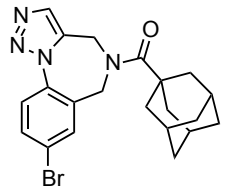
8{*2*}

1-(4H-Benzo[f][1,2,3]triazolo[1,5-a][1,4]diazepin-5(6H)-yl)-2-methoxyethanone (8{*2*}). Methoxyacetyl chloride (**20**{*2*}) (39 μL, 0.43 mmol) was added to a solution of amine **6** (40 mg, 0.21 mmol) and triethylamine (90 μL, 0.64 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 3 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 EtOAc to give 53 mg (96%) of amide **8**{*2*} as a colorless solid: mp 110-112 ˚C; ^{1}H NMR (400 MHz) (rotamers) δ 8.01-7.93 (comp, 1 H), 7.81 (s, 1 H), 7.66-7.46 (comp, 3 H), 4.75 (s, 0.7 H), 4.72 (s, 1.3 H), 4.58 (s, 0.7 H), 4.49 (s, 1.3 H), 4.29 (s, 1.3 H), 4.21 (s, 0.7 H), 3.47 (s, 2 H), 3.44 (s, 1 H); ^{13}C NMR (400 MHz) (rotamers) δ 168.1, 168.0, 136.3, 133.8, 133.0, 131.1, 131.8, 131.3, 130.5, 130.3, 129.8, 129.7, 128.2, 123.3, 123.0, 72.5, 59.3, 47.3, 45.4, 39.0, 38.0; IR (neat) 2926, 2824, 1660, 1497, 1454, 1431, 1235, 1198, 1130, 1109; mass spectrum (ESI) *m/z* 259.1187 [$C_{13}H_{15}N_4O_2$ (M+1) requires 259.1190]; LCMS purity 100%.



8{*11*}

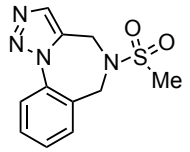
(4*H*-Benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-5(6*H*)-yl)(furan-2-yl)methanone (8{*11*}**).** 2-Furoyl chloride (**20**{*11*}) (49 mg, 40 μL, 0.38 mmol) was added to a solution of amine **6** (35 mg, 0.19 mmol) and triethylamine (57 mg, 79 μL, 0.56 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 2.5 h. The mixture was diluted with CH_2Cl_2 (20 mL), and the mixture was 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 hexanes/EtOAc (4 : 6) to give 50 mg (95%) of amide **8**{*11*} as a colorless solid: mp 107-109 °C; ^{1}H NMR (400 MHz) (rotamers) δ 7.98 (d, *J* = 7.9 Hz, 1 H), 7.83 (s, 1 H), 7.65-7.42 (comp, 4 H), 7.18 (d, *J* = 3.4 Hz, 1 H), 6.57 (m, 1 H), 5.24-4.50 (comp, 4 H); ^{13}C NMR (500 MHz) (rotamers) δ 158.9, 147.4, 144.5, 136.2, 133.6, 131.9, 131.2, 130.3, 129.7, 128.2, 123.0, 118.1, 111.8, 48.4, 46.3, 40.8, 38.5; IR (neat) 3133, 2923, 2857, 1624, 1574, 1496, 1481, 1416, 1247, 1175, 1107, 1014 cm^{-1}; mass spectrum (CI) *m/z* 281.1040 [$C_{15}H_{13}N_4O_2$ (M+1) requires 281.1039]; LCMS purity 99%.



9{*12*}

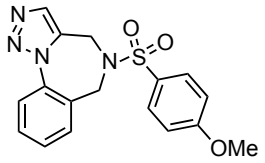
Adamantan-1-yl(8-bromo-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-5(6*H*)-yl)methanone (9{*12*}**).** 1-Adamantanecarbonyl chloride (60 mg, 0.30 mmol) was added to a solution amine **7** (40 mg, 0.15 mmol) and triethylamine (46 mg, 63 μL, 0.45 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 2.5 h. The mixture 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 recrystallization from *i*-PrOH to give 43 mg (67%) of amide **9**{*12*} as colorless microcrystals: mp 218-219 °C; ^{1}H NMR (400 MHz) δ 7.88 (d, *J* = 8.5 Hz, 1 H), 7.80 (s, 1 H), 7.72 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.68 (d, *J* = 2.2 Hz, 1 H), 4.79 (s, 2 H), 4.57 (s, 2 H) 2.16-2.09 (m, 3 H), 2.09-2.04 (m, 6 H), 1.84-1.71 (m, 6H); ^{13}C NMR (100 MHz) δ 176.2, 135.4, 133.7, 133.4 (2C), 132.7, 130.4,

124.4, 123.1, 48.2, 42.4, 40.1, 39.3, 36.6, 28.5; IR (neat) 2907, 2852, 1623, 1493, 1452, 1384, 1232, 1205, 1179, 1102, 1077 cm^{-1}; mass spectrum (ESI) *m/z* 427.1134 [$C_{21}H_{24}N_4O_{Br}$ (M+1) requires 427.1128]; LCMS purity 100%.



10{*1*}

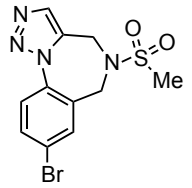
5-(Methylsulfonyl)-5,6-dihydro-4H-benzo[f][1,2,3]triazolo[1,5-a][1,4]diazepine (10{*1*}**).** Methanesulfonyl chloride (**21**{*1*}) (33 μL, 0.43 mmol) was added to a solution of amine **6** (40 mg, 0.21 mmol) and triethylamine (90 μL, 0.64 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 3 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 (6 : 4 → 4 : 6) to give 55 mg (97%) of sulfonamide **10**{*1*} as a colorless solid: mp 170-172 ˚C; ^{1}H NMR (400 MHz) δ 7.95 (d, *J* = 7.8 Hz, 1 H), 7.86 (s, 1 H), 7.69-7.61 (m, 1 H), 7.59-7.52 (comp, 2 H), 4.52 (s, 2 H), 4.32 (s, 2 H), 2.84 (s, 3 H); ^{13}C NMR (400 MHz) δ 136.3, 133.3, 131.0 (2C), 130.9, 130.2, 126.8, 123.6, 48.3, 39.1, 37.4; IR (neat) 3011, 2928, 2854, 1497, 1471, 1334, 1233, 1156, 1022; mass spectrum (ESI) *m/z* 265.0754 [$C_{11}H_{13}N_4O_2S$ (M+1) requires 265.0753]; LCMS purity 100%.



10{*7*}

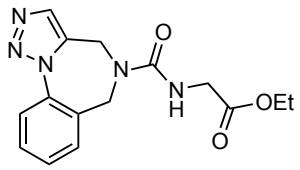
5-(4-Methoxyphenylsulfonyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (10{*7*}**).** 4-Methoxybenzenesulfonyl chloride (**21**{*7*}) (67 mg, 0.32 mmol) was added to a solution of amine **6** (30 mg, 0.16 mmol) and triethylamine (49 mg, 67 μL, 0.48 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 18 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 (6 : 4) to give 54 mg (94%) of sulfonamide **10**{*7*} as a colorless solid: mp 144-146 ˚C; ^{1}H NMR (400 MHz) δ 7.82 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 9.0

Hz, 2 H), 7.60-7.53 (m, 1 H), 7.52 (s, 1 H), 7.50-7.43 (comp, 2 H), 6.96 (d, J = 9.0 Hz, 2 H), 4.48 (s, 2 H), 4.20 (s, 2 H), 3.85 (s, 3 H); ^{13}C NMR (300 MHz) δ 163.6, 136.1, 133.0, 131.4, 130.9, 130.6, 129.9, 129.7, 129.0, 126.6, 123.2, 114.7, 55.8, 48.5, 39.1; IR (neat) 3074, 3006, 2925, 2843, 1596, 1578, 1497, 1462, 1355, 1338, 1309, 1262, 1159, 1093, 1021 cm^{-1}; mass spectrum (ESI) *m/z* 357.1016 [$C_{17}H_{17}N_4O_3S$ (M+1) requires 357.1016]; LCMS purity 99%.



11{*1*}

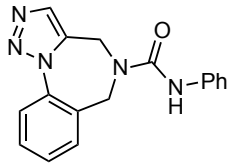
8-Bromo-5-(methylsulfonyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (11{*1*}). Methanesulfonyl chloride (**21**{*1*}) (26 mg, 18 μL, 0.23 mmol) was added to a solution of amine **7** (30 mg, 0.11 mmol) and triethylamine (34 mg, 47 μL, 0.34 mmol) in anhydrous CH_2Cl_2 (1.0 mL), 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 CH_2Cl_2/MeOH (98 : 2) to give 33 mg (85%) of sulfonamide **11**{*1*} as a colorless solid: mp 229-231 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.12 (s, 1 H), 8.10 (d, J = 1.6 Hz, 1 H), 7.89 (dd, 8.5, 1.6 Hz, 1 H), 7.85 (d, 8.5 Hz, 1 H), 4.55 (s, 2 H), 4.29 (s, 2 H), 3.00 (s, 3 H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 135.3, 134.0, 133.6, 133.3, 131.9, 129.5, 124.8, 122.3, 47.0, 38.3, 36.4; IR (neat) 2921, 2851, 1492, 1352, 1336, 1231, 1193, 1162, 1138, 1099, 1023 cm^{-1}; mass spectrum (ESI) *m/z* 364.9679 [$C_{11}H_{11}N_4O_2NaSBr$ (M+Na) requires 364.9678]; LCMS purity 100%.



12{*2*}

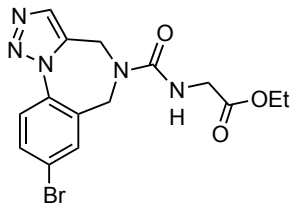
Ethyl 2-(5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5-carboxamido)acetate (12{*2*}). Ethyl isocyanatoacetate (**22**{*2*}) (42 mg, 36 μL, 0.32 mmol) was added to a solution of amine **6** (30 mg, 0.16 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 3 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 EtOAc to give 40 mg (79%) of urea **12**{*2*} as a colorless glass: ^{1}H NMR (400 MHz) δ 7.95 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.79 (s, 1 H), 7.58 (app td, *J* = 7.6, 1.6 Hz, 1 H), 7.53 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.47 (app td, *J* = 7.6, 1.4 Hz, 1 H), 5.35 (t, *J* = 5.2 Hz, 1 H), 4.66 (s, 2 H), 4.43 (s, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 4.03 (d, *J* = 5.1 Hz, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (500 MHz) δ 171.0, 156.4, 136.2, 133.1, 132.2, 130.6, 130.1, 129.6, 128.6, 123.1, 61.6, 46.7, 42.9, 38.7, 14.2; IR (neat) 3346, 3073, 2985, 2937, 1747, 1644, 1538, 1497, 1395, 1201, 1025 cm^{-1}; mass spectrum (CI) *m/z* 316.1412 [$C_{15}H_{18}N_5O_3$ (M+1) requires 316.1410]; LCMS purity 98%.



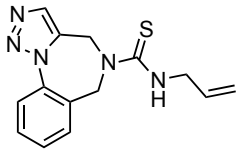
12{*4*}

***N*-Phenyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carboxamide (12{*4*}).** Phenyl isocyanate (**22**{*4*}) (45 mg, 41 μL, 0.38 mmol) was added to a solution of amine **6** (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 **12**{*4*} 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]; LCMS purity 97%.



13{*2*}

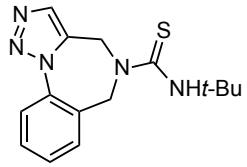
Ethyl 2-(8-bromo-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5-carboxamido)acetate (13{*2*}**).** Ethyl isocyanatoacetate (**22**{*2*}) (39 mg, 34 μL, 0.30 mmol) was added to a solution of amine **7** (40 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 2.5 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 : 2) to give 34 mg (57%) of urea **12**{*2*} as a colorless solid: mp 164-166 ˚C; ^{1}H NMR (400 MHz) δ 7.88-7.84 (m, 1 H), 7.80 (s, 1 H), 7.72-7.65 (comp, 2 H), 5.15-5.08 (m, 1 H), 4.67 (s, 2 H), 4.20 (s, 2 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 4.04 (d, *J* = 5.1 Hz, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 171.0, 156.3, 135.3, 133.6 (2C), 133.3, 132.2, 130.7, 124.7, 123.3, 61.8, 46.2, 43.0, 39.1, 14.3; IR (neat) 3333, 3060, 2925, 2852, 1745, 1642, 1632, 1547, 1535, 1494, 1391, 1197 cm^{-1}; mass spectrum (ESI) *m/z* 394.0509 [$C_{15}H_{17}N_5O_3Br$ (M+1) requires 394.0510]; LCMS purity 100%.



14{*1*}

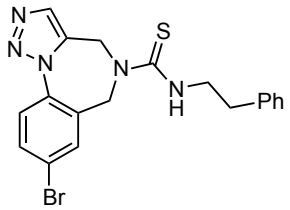
***N*-Allyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carbothioamide (14**{*1*}**).** Allyl isothiocyanate (**23**{*1*}) (24 mg, 24 μL, 0.24 mmol) was added to a solution of amine **6** (35 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 3 h. The mixture was diluted with CH_2Cl_2 (20 mL) and 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 hexanes/EtOAc (4 : 6) to give 53 mg (99%) of thiourea **14**{*1*} as a colorless solid: mp 149-151 ˚C; ^{1}H NMR (400 MHz) δ 7.93 (d, *J* = 7.6 Hz, 1 H), 7.79 (s, 1 H), 7.64 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.59 (app td, *J* = 7.6, 1.2 Hz, 1 H), 7.49 (app, t, *J* = 7.6 Hz, 1 H), 6.18 (br s, 1 H), 5.93 (ddt, *J* = 17.0, 10.5, 5.7 Hz, 1 H), 5.21 (d, *J* = 17.0 Hz, 1 H), 5.16 (d, *J* = 10.5 Hz, 1 H), 5.05 (s, 2 H), 4.92 (s, 2 H), 4.33 (t, *J* = 5.7 Hz, 2 H); ^{13}C NMR (500 MHz) d 181.7, 135.9, 133.6, 133.4, 131.6,

131.0, 130.4, 129.7, 127.9, 122.9, 117.8, 50.1, 49.2, 42.4; IR (neat) 3289, 3063, 2986, 2922, 1531, 1496, 1455, 1370, 1232, 1191, 1111 cm^{-1}; mass spectrum (CI) *m/z* 286.1130 [$C_{14}H_{16}N_5S$ (M+1) requires 286.1126]; LCMS purity 99%.



14{*4*}

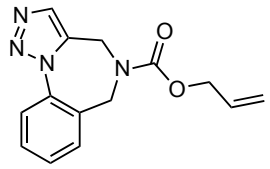
***N*-tert-butyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carbothioamide (14{*4*}).** *tert*-Butyl isothiocyanate (**23**{*4*}) (24 mg, 26 μL, 0.21 mmol) was added to a solution of amine **6** (35 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 18 h. The mixture was diluted with CH_2Cl_2 (20 mL) and 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 hexanes/EtOAc (4 : 6) to give 47 mg (83%) of thiourea **14**{*4*} as a colorless solid: mp 152-154 ˚C; ^{1}H NMR (400 MHz) δ 8.00 (d, *J* = 8.2 Hz, 1 H), 7.79 (s, 1 H), 7.62-7.55, (comp, 2 H), 7.48 (app t, *J* = 7.4 Hz, 1 H), 5.51 (s, 1 H), 5.04 (s, 2 H), 4.80 (s, 2 H), 1.57 (s, 9 H); ^{13}C NMR (500 MHz) δ 180.5, 136.2, 133.4, 132.1, 130.6, 130.3, 129.4, 127.9, 123.0, 55.0, 49.9, 42.6, 29.1 ; IR (neat) 3403, 3060, 2966, 2925, 1532, 1496, 1396, 1354, 1247, 1204, 1176, 1109 cm^{-1}; mass spectrum (CI) *m/z* 302.1439 [$C_{15}H_{20}N_5S$ (M+1) requires 302.1439]; LCMS purity 99%.



15{*3*}

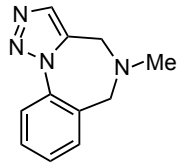
8-bromo-*N*-phenethyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carbothioamide (15{*3*}). Phenethyl isothiocyanate (**23**{*3*}) (49 mg, 45 μL, 0.30 mmol) was added to a solution of amine **7** (40 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (1.0 mL), and the reaction was stirred at room temperature for 2 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with 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 : 1 → 0 : 1) to give 54 mg (83%) of thiourea **15**{*3*} as a colorless solid: mp 133-135 ˚C; ^{1}H NMR (400 MHz) δ

7.86-7.82 (m, 1 H), 7.73 (s, 1 H), 7.72-7.67 (m, 1 H), 7.65 (m, 1 H), 7.34 (app t, *J* = 8.0 Hz, 2 H), 7.27 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.22 (m, 2 H), 5.66 (t, *J* = 6.1 Hz, 1 H), 4.84 (s, 2 H), 4.77 (s, 2 H), 3.95 (app q, *J* = 6.1 Hz, 2 H), 2.99 (t, *J* = 6.1 Hz, 2 H); ^{13}C NMR (100 MHz) δ 181.7, 138.6, 135.0, 133.7 (2C), 133.5, 131.6, 129.8, 129.1, 128.9, 127.1, 124.3, 123.2, 49.5, 47.4, 42.5, 34.9; IR (neat) 3320, 3060, 2930, 1531, 1493, 1451, 1373, 1342, 1233, 1172, cm^{-1}; mass spectrum (ESI) *m/z* 428.0539 [$C_{19}H_{19}N_5SBr$ (M+1) requires 428.0540]; LCMS purity 99%.



16{*2*}

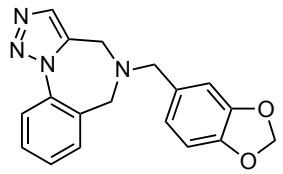
Allyl 4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carboxylate (16{*2*}). Allyl chloroformate (**24**{*2*}) (78 mg, 69 μL, 0.64 mmol) was added to a solution of amine **6** (60 mg, 0.32 mmol) and triethylamine (98 mg, 135 μL, 0.97 mmol) in anhydrous CH_2Cl_2 (2.0 mL) at 0 ºC, and the 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 (1 : 1) to give 83 mg (95%) of carbamate **16**{*2*} as a colorless oil: ^{1}H NMR (300 MHz) (rotamers) δ 7.95 (d, *J* = 7.7 Hz, 1 H), 7.80 (s, 1 H), 7.63-7.43 (comp, 3 H), 6.06-5.88 (m, 1 H), 5.42-5.18 (comp, 2 H), 4.76-4.58 (comp, 4 H), 4.48 (s, 1 H), 4.47 (s, 1 H); ^{13}C NMR (300 MHz) (rotamers) δ 154.6, 136.2, 133.2, 132.4, 132.2, 131.9, 130.7, 130.4, 130.0, 129.6, 129.4, 128.7, 128.5, 123.1, 122.9, 118.1, 118.0, 66.7, 46.8, 46.5, 38.9, 38.6; IR (neat) 3132, 3085, 2989, 2941, 2867, 1696, 1496, 1470, 1413, 1347, 1295, 1235, 1123, 1085 cm^{-1}; mass spectrum (ESI) *m/z* 293.1011 [$C_{14}H_{14}N_4O_2Na$ (M+Na) requires 293.1009]; LCMS purity 99%.



17{*1*}

5-Methyl-5,6-dihydro-4H-benzo[f][1,2,3]triazolo[1,5-a][1,4]diazepine (17{*1*}). A mixture of sodium triacetoxyborohydride (478 mg, 2.26 mmol), amine **6** (70 mg, 0.38 mmol), paraformaldehyde (**25**{*1*}) (113 mg, 3.76 mmol) and glacial acetic acid (22 μL, 0.38 mmol) in DCE (5.5 mL) was stirred at

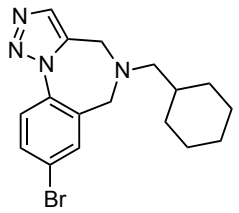
room temperature for 24 h. The reaction was diluted with CH_2Cl_2 (20 mL) and saturated aqueous $NaHCO_3$ (30 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were concentrated under reduced pressure. The residue was dissolved in Et_2O (20 mL), extracted with aqueous HCl (3 × 10 mL, 1.0 M) and the combined aqueous extracts washed with Et_2O (20 mL). The pH of the aqueous layer was then raised to ~ 11-12 through the addition of aqueous NaOH (1.0 M) and the resulting solution 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 CH_2Cl_2/MeOH (98 : 2 → 95 : 5) to give 54 mg (71%) of amine **17**{*1*} as a colorless solid: mp 85-87 ˚C; ^{1}H NMR (400 MHz) δ 7.89 (d, *J* = 8.0 Hz, 1 H), 7.76 (s, 1 H), 7.56 (ddd, *J* = 8.0, 6.5, 2.5 Hz, 1 H), 7.5-7.43 (comp, 2 H), 3.65 (s, 2 H), 3.49 (s, 2 H), 2.48 (s, 3 H); ^{13}C NMR (400 MHz) δ 136.7, 133.4, 132.9, 131.1, 129.7, 129.2, 129.1, 122.8, 56.8, 46.8, 44.1; IR (neat) 3057, 2942, 2848, 2788, 1492, 1468, 1370, 1227, 1138, 1126, 1098, 1079, 1031; mass spectrum (ESI) *m/z* 201.1136 [$C_{11}H_{13}N_4$ (M+1) requires 201.1135]; LCMS purity 100%.



17{*9*}

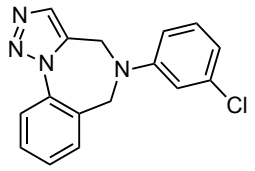
5-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (17{*9*}). A mixture of sodium triacetoxyborohydride (239 mg, 1.13 mmol), amine **6** (35 mg, 0.19 mmol), piperonal (**25**{*9*}) (169 mg, 1.13 mmol) and glacial acetic acid (11 mg, 11 μL, 0.19 mmol) 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 **17**{*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]; LCMS purity 99%.



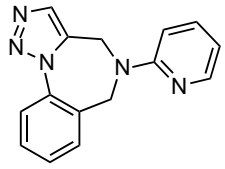
18{*12*}

8-bromo-5-(cyclohexylmethyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (18{*12*}). A mixture of sodium triacetoxyborohydride (192 mg, 0.91 mmol), amine **7** (40 mg, 0.15 mmol), cyclohexanecarboxaldehyde (**25**{*12*}) (102 mg, 110 μL, 0.91 mmol) and glacial acetic acid (9 mg, 9 μL, 0.15 mmol) in DCE (3.0 mL) was stirred at room temperature for 3 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 (2 : 1) to give 30 mg (55%) of amine **18**{*12*} as a colorless glass: ^{1}H NMR (400 MHz) δ 7.80 (d, *J* = 8.5 Hz, 1 H), 7.75 (s, 1 H), 7.67 (dd, *J* = 8.5, 1.8 Hz, 1 H), 7.58 (d, *J* = 1.8 Hz, 1 H), 3.68 (s, 2 H), 3.52 (s, 2 H), 2.39 (d, *J* = 7.0 Hz, 2 H), 1.88-1.65 (comp, 5 H), 1.58-1.44 (m, 1 H), 1.34-1.12 (comp, 3 H), 1.00-0.85 (comp, 2.0 Hz); ^{13}C NMR (100 MHz) δ 135.8, 134.0, 133.2, 132.6, 131.3, 124.2, 122.7, 63.2, 55.2, 45.6, 35.8, 31.7, 26.8, 26.1; IR (neat) 2923, 2849, 1489, 1447, 1358, 1260, 1230, 1182, 1100 cm^{-1}; mass spectrum (ESI) *m/z* 361.1022 [$C_{17}H_{22}N_4Br$ (M+1) requires 361.1023]; LCMS purity 99%.



19{*1*}

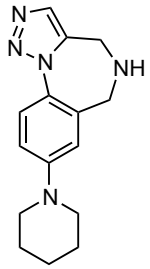
5-(3-Chlorophenyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (19{*1*}). Palladium acetate (2.4 mg, 0.011 mmol) was added to a solution of (±)-BINAP (10 mg, 0.016 mmol) in degassed toluene (1.0 mL) and the mixture was stirred at room temperature for 1 min. Amine **6** (40 mg, 0.21 mmol), 1-bromo-3-chlorobenzene (**26**{*1*}) (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 **19**{*1*} 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]; LCMS purity 95%.



19{*6*}

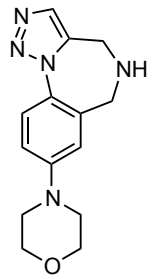
5-(Pyridin-2-yl)-5,6-dihydro-4H-benzo[f][1,2,3]triazolo[1,5-a][1,4]diazepine (19{*6*}). A mixture of amine **6** (40 mg, 0.21 mmol), 2-bromopyridine (**26**{*6*}) (25 μL, 0.26 mmol), tris(dibenzylideneacetone)dipalladium(0) (7.8 mg, 8.6 μmol), 1,3-Bis(diphenylphosphino)propane (6.8 mg, 17 μmol) and sodium *t*-butoxide (29 mg, 0.30 mmol) in degassed toluene was stirred at 70 ˚C for 3 h. The cooled reaction was diluted with Et_2O (20 mL) and washed with saturated aqueous NaCl (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 48 mg (85%) of 2-aminopyridine **19**{*6*} as a cream colored solid: mp 139-141 ˚C (colorless needles from *i*-PrOH); ^{1}H

NMR (400 MHz) δ 8.23 (dd, *J* = 5.1, 1.0 Hz, 1 H), 7.97 (d, *J* = 8.2 Hz, 1 H), 7.80 (s, 1 H), 7.58-7.49 (comp, 3 H), 7.42 (app td, *J* = 7.5, 1.0 Hz, 1 H), 6.70-6.63 (comp, 2 H), 4.74 (s, 2 H), 4.65 (s, 2 H); ^{13}C NMR (400 MHz) δ 157.3, 148.1, 137.9, 136.5, 133.5, 133.2, 130.7, 129.7, 129.6, 129.3, 122.9, 113.7, 106.4, 47.3, 40.2; IR (neat) 3056, 3008, 2924, 2853, 1594, 1564, 1483, 1436, 1388, 1311, 1293, 1232, 1163, 1133; mass spectrum (CI) *m/z* 264.1248 [$C_{15}H_{14}N_5$ (M+1) requires 264.1249]; LCMS purity 96%.



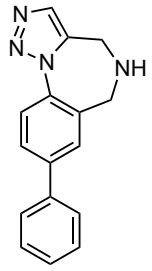
27{*1*}

8-(Piperidin-1-yl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (27{*1*}). Palladium acetate (29 mg, 0.13 mmol) was added to a solution of (±)-BINAP (122 mg, 0.195 mmol) in degassed toluene (17 mL) and the mixture was stirred at room temperature for 1 min. Bromide **7** (690 mg, 2.60 mmol), piperidine (**29**{*1*}) (2.22 g, 2.57 mL, 26.0 mmol) and then sodium *tert*-butoxide (350 mg, 3.64 mmol) were added, and the reaction was heated at 80 ˚C for 1 h. The reaction was cooled and filtered through a Celite® pad 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/Et_3N (98 : 1 : 1 → 94 : 5 : 1) to give 525 mg (75%) of amine **27**{*1*} as a pale brown colored solid: mp 120-122 ˚C (pale yellow needles from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz) δ 7.75 (d, *J* = 8.8 Hz, 1 H), 7.67 (s, 1 H), 7.00 (dd, *J* = 8.8, 2.7 Hz, 1 H), 6.89 (d, *J* = 2.7 Hz, 1 H), 4.00 (s, 2 H), 3.75 (s, 2 H), 3.26 (t, *J* = 5.5 Hz, 4 H), 2.74 (s, 1 H), 1.76-1.67 (m, 4 H), 1.66-1.58 (m, 2 H); ^{13}C NMR (100 MHz) δ 152.4, 134.7, 132.0, 131.9, 127.6, 123.6, 116.3, 115.9, 49.9, 49.3, 39.0, 25.6, 24.2; IR (neat) 3312, 2934, 2852, 2810, 1608, 1583, 1509, 1451, 1384, 1247, 1226, 1124 cm^{-1}; mass spectrum (CI) *m/z* 270.1719 [$C_{15}H_{20}N_5$ (M+1) requires 270.1719]; LCMS purity 96%.



27{*2*}

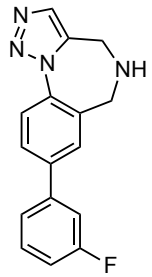
4-(5,6-Dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-8-yl)morpholine (27{*2*}). Palladium acetate (21 mg, 0.094 mmol) was added to a solution of (±)-BINAP (88 mg, 0.14 mmol) in degassed toluene (12.5 mL) and the mixture was stirred at room temperature for 1 min. Amine **7** (500 mg, 1.89 mmol), morpholine (**29**{*2*}) (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 **27**{*2*} 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]; LCMS purity 94%.



28{*1*}

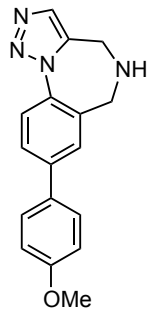
8-Phenyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (28{*1*}). (All reagents were weighed out in a glove-box). A mixture of amine **7** (500 mg, 1.89 mmol), phenylboronic acid (**30**{*1*}) (460 mg, 3.77 mmol), bis(tri-*tert*-butylphosphine)palladium(0) (9.6 mg, 0.019 mmol) and 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 **28**{*1*} 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]; LCMS purity 100%.



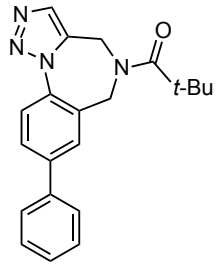
28{*2*}

8-Phenyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (28{*2*}). A mixture of bromide **7** (350 mg, 1.32 mmol), 3-fluorophenylboronic acid (**30**{*2*}) (369 mg, 2.64 mmol), bis(tri-*tert*-butylphosphine)palladium(0) (6.7 mg, 0.013 mmol) and cesium carbonate (860 mg, 2.64 mmol) in degassed dioxane (9.0 mL) was stirred at 90 ˚C for 5 h. The reaction was cooled, and diluted with water (20 mL), and the mixture 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 CH_2Cl_2/MeOH (19 : 1) to give 344 mg (93%) of biphenyl **28**{*2*} as a colorless solid: mp 162-164 ˚C (colorless prisms from *i*-PrOH); ^{1}H NMR (400 MHz) δ 8.02 (d, *J* = 8.2 Hz, 1 H), 7.73-7.68 (comp, 2 H), 7.60 (d, *J* = 2.2 Hz, 1 H), 7.48-7.38 (comp, 2 H), 7.32 (dd, *J* = 9.8, 1.8 Hz, 1 H), 7.12-7.06 (m, 1 H), 4.08 (s, 2 H), 3.90 (s, 2 H), 2.24 (s, 1 H); ^{13}C NMR (100 MHz) δ 161.2 (d, $J_{C\text{-}F}$ = 246.8 Hz), 141.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 140.8 (d, $J_{C\text{-}F}$ = 2.2 Hz), 136.3, 135.7, 132.2, 132.1, 130.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 128.8, 127.8, 123.4, 122.8 (d, $J_{C\text{-}F}$ = 2.2 Hz), 114.9 (d, $J_{C\text{-}F}$ = 20.9 Hz), 114.1 (d, $J_{C\text{-}F}$ = 21.7 Hz), 49.3, 39.5; IR (neat) 3282, 3058, 2921, 1613, 1581, 1512, 1484, 1439, 1402, 1265, 1229, 1200, 1164, 1127 cm^{-1}; mass spectrum (CI) *m/z* 281.1203 [$C_{16}H_{14}N_4F$ (M+1) requires 281.1202]; LCMS purity 99%.



28{*5*}

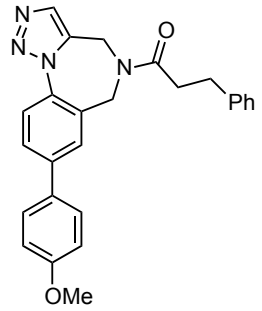
8-(4-Methoxyphenyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (28{*5*}). (All reagents were weighed out in a glove-box). A mixture of amine **7** (500 mg, 1.89 mmol), 4-methoxyphenylboronic acid (**30**{*5*}) (573 mg, 3.77 mmol), bis(tri-*tert*-butylphosphine)palladium(0) (9.6 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 reaction was cooled and diluted with CH_2Cl_2 (20 mL) and the solids were removed by vacuum filtration through Celite®, washing with CH_2Cl_2 (100 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 430 mg (78%) of biphenyl **28**{*5*} as a colorless solid: mp 184-185 ˚C (colorless plates from *i*-PrOH); ^{1}H NMR (400 MHz) δ 7.99 (d, *J* = 8.2 Hz, 1 H), 7.72 (s, 1 H), 7.70 (dd, *J* = 8.2, 2.1 Hz, 1 H), 7.60-7.55 (comp, 3 H), 7.02 (d, *J* = 8.9 Hz, 2 H), 4.07 (s, 2 H), 3.89 (s, 2 H), 3.88 (s, 3 H); ^{13}C NMR (300 MHz) δ 159.8, 141.8, 135.6, 135.3, 132.2, 132.1, 131.8, 128.3 (2C), 127.4, 123.3, 114.5, 55.5, 49.3, 39.4; IR (neat) 3334, 2911, 2838, 1605, 1496, 1433, 1361, 1244, 1226, 1182, 1139, 1188, 1017 cm^{-1}; mass spectrum (ESI) *m/z* 293.1399 [$C_{17}H_{17}N_4O$ (M+1) requires 293.1397]; LCMS purity 100%.



32{*1,4*}

2,2-Dimethyl-1-(8-phenyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-5(6*H*)-yl)propan-1-one (32{*1,4*}). A solution of pivaloyl chloride (**20**{*4*}) (28 mg, 28 μL, 0.23 mmol), amine **28**{*1*} (30 mg, 0.11 mmol) and triethylamine (35 mg, 48 μL, 0.34 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was

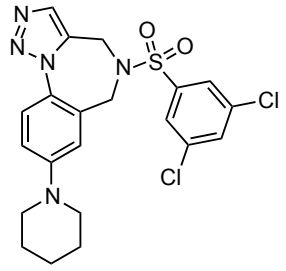
stirred at room temperature for 16 h. The reaction was diluted with CH_2Cl_2 (20 mL), and the mixture washed with aqueous HCl (10 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (1 : 1) to give 40 mg (quant.) of amide **32**{*1*,*4*} as a colorless solid: mp 169-171 ˚C; ^{1}H NMR (400 MHz) δ 8.04 (d, *J* = 8.2 Hz, 1 H), 7.83-7.78 (comp, 2 H), 7.71 (d, *J* = 2.0 Hz, 1 H), 7.61 (d, *J* = 7.4 Hz, 2 H), 7.49 (app t, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 7.4 Hz, 1 H), 4.76 (s, 2 H), 4.62 (s, 2 H), 1.43 (s, 9 H); ^{13}C NMR (75 MHz) 176.7, 142.8, 139.3, 135.4, 133.3, 132.5, 129.3, 129.2, 128.9, 128.7, 128.4, 127.3, 123.3, 48.5, 39.5, 39.2, 28.7; IR (neat) 2973, 1628, 1489, 1407, 1383, 1366, 1174 cm^{-1}; mass spectrum (ESI) *m/z* 347.1867 [$C_{21}H_{23}N_4O$ (M+1) requires 347.1866]; LCMS purity 99%.



32{*5*,*13*}

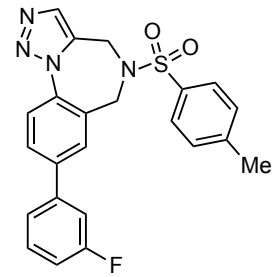
3-Phenyl-1-(8-phenyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-5(6*H*)-yl)propan-1-one (32{*5*,*13*}**).** A solution of hydrocinnamoyl chloride (**20**{*13*}) (29 mg, 25 μL, 0.23 mmol), amine **28**{*5*} (25 mg, 0.086 mmol) and triethylamine (26 mg, 36 μL, 0.26 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was stirred at room temperature for 16 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 31 mg (85%) of amide **32**{*5*,*13*} as a colorless oil: ^{1}H NMR (400 MHz) (rotamers) δ 8.00 (d, *J* = 8.2 Hz, 0.6 H), 7.95 (d, *J* = 8.8 Hz, 0.4 H), 7.79 (s, 1 H), 7.76-7.71 (comp, 1.4 H), 7.68 (s, 1 H), 7.58 (d, *J* = 8.7 Hz, 0.8 H), 7.52 (d, *J* = 8.7 Hz, 1.2 H), 7.45 (d, *J* = 2.0 Hz, 0.6 H), 7.31-7.15 (comp, 5 H), 7.01 (d, *J* = 8.7 Hz, 1 H), 3.08-2.98 (m, 2 H), 2.85 (t, *J* = 7.7 Hz, 1.2 H), 2.70 (t, *J* = 7.5 Hz, 0.8 H); ^{13}C NMR (75 MHz) 171.2, 171.1, 160.0, 142.5, 140.9, 140.8, 134.7, 133.6, 133.2, 132.4, 131.6, 131.4, 129.2, 129.1, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 126.6, 123.7, 123.2, 114.6, 55.5, 48.5, 44.9, 40.0, 37.8, 35.9, 31.4; IR (neat) 2925, 2853,

1649, 1607, 1499, 1454, 1417, 1250 cm^{-1}; mass spectrum (ESI) *m/z* 425.1975 [$C_{26}H_{25}N_4O_2$ (M+1) requires 425.1972]; LCMS purity 98%.



33{*1*,*11*}

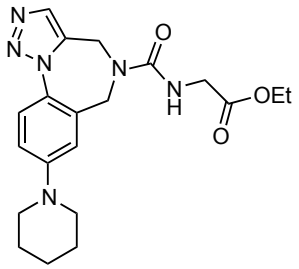
5-(3,5-Dichlorophenylsulfonyl)-8-(piperidin-1-yl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine. (33{*1*,*11*}**).** A solution of 3,5-dichlorobenzenesulfonyl chloride (**21**{*11*}) (37 mg, 0.15 mmol), amine **27**{*1*} (20 mg, 0.074 mmol) and triethylamine (23 mg, 31 μL, 0.22 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was stirred at room temperature for 4 h. The reaction was diluted with CH_2Cl_2 (20 mL), and the mixture was 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 hexanes/EtOAc (7 : 3) to give 31 mg (87%) of sulfonamide **33**{*1*,*11*} as a colorless solid: mp 219-220 ˚C; ^{1}H NMR (400 MHz) δ 7.69 (d, *J* = 1.8 Hz, 2 H), 7.66 (d, *J* = 8.8 Hz, 1 H), 7.61 (s, 1 H), 7.54 (t, *J* = 1.8 Hz, 1 H), 7.01 (dd, *J* = 8.8, 2.7 Hz, 1 H), 6.84 (d, *J* = 2.7 Hz, 1 H), 4.50 (s, 2 H), 4.18 (s, 2 H), 3.27 (t, *J* = 5.4 Hz, 4 H), 1.78-1.60 (comp, 6 H); ^{13}C NMR (100 MHz) 152.7, 140.8, 136.5, 133.3, 132.8, 130.0, 126.7, 126.3, 125.8, 124.1, 116.9, 116.6, 49.6, 49.3, 39.6, 25.6, 24.2; IR (neat) 3076, 2936, 2854, 1609, 1568, 1514, 1361, 1344, 1248, 1171, 1140 cm^{-1}; mass spectrum (ESI) *m/z* 478.0869 [$C_{21}H_{22}N_5O_2SCl_2$ (M+1) requires 478.0866]; LCMS purity 96%.



34{*2*,*5*}

8-(3-Fluorophenyl)-5-tosyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (34{*2*,*5*}**).** A solution of tosyl chloride (**21**{*5*}) (34 mg, 0.18 mmol), amine **28**{*2*} (25 mg, 0.089 mmol)

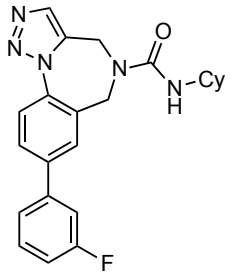
and triethylamine (27 mg, 37 μL, 0.27 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was stirred at room temperature for 4 h. The reaction was diluted with CH_2Cl_2 (20 mL), and the mixture was washed with aqueous HCl (10 mL, 1.0 M) and saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (6 : 4 → 4 : 6) to give 39 mg (quant.) of sulfonamide **34**{*2*,*5*} as a colorless solid: mp 207 ˚C (dec.); ^{1}H NMR (400 MHz) δ 7.90 (d, *J* = 8.2 Hz, 1 H), 7.76-7.70 (comp, 3 H), 7.58 (s, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.47 (app td, *J* = 8.1, 6.0 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.24 (app dt, *J* = 10.0, 2.2 Hz, 1 H), 7.13 (app tdd, *J* = 8.1, 2.2, 0.7 Hz, 1 H), 4.55 (s, 2 H), 4.26 (s, 2 H), 2.37 (s, 3 H); ^{13}C NMR (75 MHz) 163.3 (d, $J_{C\text{-}F}$ = 245.3 Hz), 144.7, 141.5, 141.3, (d, $J_{C\text{-}F}$ = 7.7 Hz), 135.5, 134.7, 133.3, 130.9, 130.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 130.2, 129.9, 129.1, 127.6, 127.0, 123.6, 122.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 115.3 (d, $J_{C\text{-}F}$ = 20.7 Hz), 114.2 (d, $J_{C\text{-}F}$ = 21.9 Hz), 48.6, 39.4, 21.6; IR (neat) 3065, 2923, 2853, 1612.6, 1582, 1485, 1355, 1338, 1164, 1090 cm^{-1}; mass spectrum (ESI) *m/z* 435.1287 [$C_{23}H_{20}N_4O_2FS$ (M+1) requires 435.1286]; LCMS purity 100%.



35{*1*,*2*}

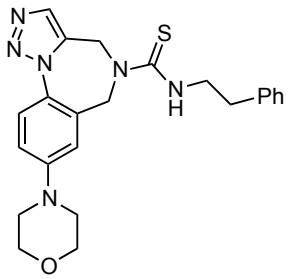
Ethyl 2-(8-(piperidin-1-yl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5-carboxamido)acetate (35{*1*,*2*}). A solution of ethyl isocyanatoacetate (**22**{*2*}) (24 mg, 21 μL, 0.19 mmol) and amine **27**{*1*} (25 mg, 0.093 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was stirred at room temperature for 6 h. The reaction was diluted with CH_2Cl_2 (20 mL) and the mixture was washed with 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 : 9) to give 34 mg (92%) of urea **35**{*1*,*2*} as a colorless foam: ^{1}H NMR (400 MHz) δ 7.75 (d, *J* = 8.8 Hz, 1 H), 7.74 (s, 1 H), 7.01 (dd, *J* = 8.8, 2.6 Hz, 1 H), 6.96 (d, *J* = 2.6 Hz, 1 H), 5.33 (t, *J* = 5.1 Hz, 1 H), 4.61 (s, 2 H), 4.36 (s, 2 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 4.03 (d, *J* = 5.1 Hz, 2 H), 3.27 (t, *J* = 5.4 Hz, 4 H), 1.75-1.66 (comp, 4 H), 1.66-1.58 (comp, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 171.1, 156.5, 152.1, 132.9, 131.8, 129.6, 127.2, 123.9, 116.8, 116.5, 61.6, 50.1, 47.2, 43.0, 38.7, 25.5, 24.2,

14.3; IR (neat) 3332, 2936, 2855, 1747, 1643, 1609, 1538, 1516, 1388, 1248, 1196, 1023 cm^{-1}; mass spectrum (ESI) *m/z* 399.2142 [$C_{20}H_{27}N_6O_3$ (M+1) requires 399.2139]; LCMS purity 95%.



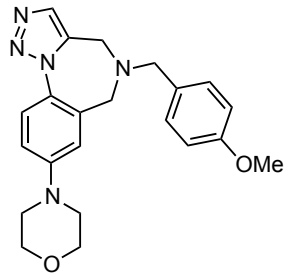
36{*2*,*3*}

***N*-Cyclohexyl-8-(3-fluorophenyl)-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carboxamide (36{*2*,*3*}).** A solution of cyclohexyl isocyanate (**22**{*3*}) (22 mg, 23 μL, 0.18 mmol) and amine **28**{*2*} (25 mg, 0.089 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was stirred at room temperature for 4 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 (3 : 7) to give 36 mg (quant.) of urea **36**{*2*,*3*} as a colorless solid: mp 175 ˚C (dec.); ^{1}H NMR (400 MHz) δ 8.04 (d, *J* = 8.2 Hz, 1 H), 7.80 (s, 1 H), 7.75 (dd, *J* = 8.2, 2.1 Hz, 1 H), 7.71 (d, *J* = 2.1 Hz, 1 H), 7.48-7.38 (comp, 2 H), 7.32 (app dt, *J* = 9.8, 1.9 Hz, 1 H), 7.14-7.07 (m, 1 H), 4.65 (s, 2 H), 4.48 (s, 2 H), 4.40 (d, *J* = 7.4 Hz, 1 H), 3.68 (tdt, *J* = 11.0, 7.4, 3.8 Hz, 1 H), 1.97 (dd, *J* = 8.4, 3.8 Hz, 2 H), 1.78-1.56 (comp, 3 H), 1.45-1.29 (m, 2 H), 1.24-1.05 (comp, 3 H); ^{13}C NMR (100 MHz) δ 163.3 (d, $J_{C\text{-}F}$ = 244.8 Hz), 156.1, 141.5 (d, $J_{C\text{-}F}$ = 8.2 Hz), 141.3, 135.8, 133.3, 132.6, 130.7 (d, $J_{C\text{-}F}$ = 8.9 Hz), 129.7, 129.3, 128.5, 123.6, 123.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 115.2 (d, $J_{C\text{-}F}$ = 20.9 Hz), 114.2 (d, $J_{C\text{-}F}$ = 22.3 Hz), 50.1, 46.7, 39.0, 34.1, 25.7, 25.1; IR (neat) 3240, 2930, 2853, 1624, 1614, 1538, 1485, 1451, 1395, 1249, 1238 cm^{-1}; mass spectrum (ESI) *m/z* 406.2042 [$C_{23}H_{25}N_5OF$ (M+1) requires 406.2038]; LCMS purity 99%.



37{*2,3*}

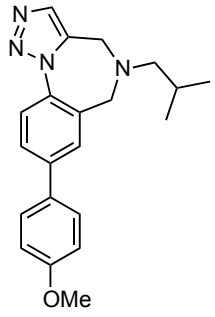
8-Morpholino-*N*-phenethyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-5(6*H*)-carbothioamide (37{*2,3*}). A solution of phenethyl isothiocyanate (**23**{*3*}) (26 mg, 24 μL, 0.16 mmol) and amine **27**{2} (22 mg, 0.081 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was stirred at room temperature for 3.5 h. The reaction was diluted with CH_2Cl_2 (20 mL) and the mixture was washed with 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 33 mg (92%) of thiourea **37**{*2,3*} as a colorless glass: ^{1}H NMR (400 MHz) δ 7.82 (d, *J* = 8.8 Hz, 1 H), 7.71 (s, 1 H), 7.31 (app t, *J* = 7.1 Hz, 2 H), 7.27-7.19 (comp, 3 H), 7.09 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.05 (d, *J* = 2.4 Hz, 1 H), 5.77-5.70 (m, 1 H), 4.80 (s, 2 H), 4.78 (s, 2 H), 3.98-3.87 (comp, 6 H), 3.25 (t, *J* = 4.8 Hz, 4 H), 2.98 (t, *J* = 6.9 Hz, 2 H); ^{13}C NMR (100 MHz) δ 181.6, 151.2, 138.8, 133.3, 131.1, 129.2, 128.9 (2C), 128.2, 126.9, 123.7, 117.0, 116.5, 66.5, 50.5, 49.0, 47.4, 42.2, 35.0; IR (neat) 3286, 2963, 2924, 2857, 1609, 1588, 1516, 1451, 1379, 1342, 1248, 1225, 1121 cm^{-1}; mass spectrum (ESI) *m/z* 435.1963 [$C_{23}H_{27}N_6OS$ (M+1) requires 435.1962]; LCMS purity 94%.



39{*2,14*}

4-(5-(4-Methoxybenzyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepin-8-yl)morpholine (39{*2,14*}). A mixture of sodium triacetoxyborohydride (141 mg, 0.663 mmol), amine **27**{*2*} (30 mg, 0.11 mmol), *p*-anisaldehyde (**25**{*14*}) (90 mg, 81 μL, 0.66 mmol) and glacial acetic acid (7 mg, 6 μL, 0.1 mmol) in DCE (3.0 mL) was stirred at room temperature for 14 h. The reaction was diluted with CH_2Cl_2 (30 mL) and saturated aqueous $NaHCO_3$ (20 mL), and the layers were separated.

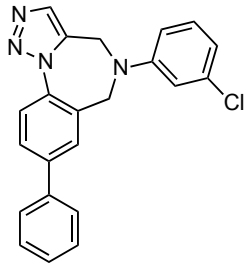
The aqueous layer was extracted with CH_2Cl_2 (10 mL), and the combined organic layers were concentrated under reduced pressure. The residue was dissolved in Et_2O (20 mL), and the solution was extracted with aqueous HCl (3 × 20 mL, 1.0 M). The combined aqueous extracts were washed with Et_2O (20 mL). 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 (3 : 7 → 1 : 9) to give 34 mg (79%) of amine **39**{*2*,*14*} as a pale yellow oil: ^{1}H NMR (400 MHz) δ 7.78 (d, *J* = 8.9 Hz, 1 H), 7.70 (s, 1 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 7.03 (dd, *J* = 8.9, 2.7 Hz, 1 H), 6.91 (d, *J* = 8.89 Hz, 2 H), 6.87 (d, *J* = 2.7 Hz, 1 H), 3.89 (t, *J* = 4.8 Hz, 4 H), 3.83 (s, 3 H), 3.67 (s, 2 H), 3.65 (s, 2 H), 3.49 (s, 2 H), 3.26 (t, *J* = 4.8 Hz, 4 H); ^{13}C NMR (100 MHz) δ 159.2, 151.5, 132.8, 132.7, 130.3, 129.8, 129.6, 128.6, 123.4, 116.9, 115.6, 114.0 66.7, 59.8, 55.3, 54.9, 48.7, 44.3; IR (neat) 2960, 2912, 2835, 1611, 1512, 1452, 1247, 1123 cm^{-1}; mass spectrum (ESI) *m/z* 392.2083 [$C_{22}H_{26}N_5O_2$ (M+1) requires 392.2081]; LCMS purity 97%.



40{*5*,*2*}

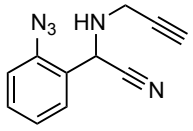
5-Isobutyl-8-(4-methoxyphenyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (40{*5*,*2*}**).** A mixture of sodium triacetoxyborohydride (139 mg, 0.657 mmol), amine **28**{*5*} (32 mg, 0.11 mmol), isobutyraldehyde (**25**{*2*}) (47 mg, 60 μL, 0.66 mmol) and glacial acetic acid (7 mg, 6 μL, 0.1 mmol) in DCE (3.0 mL) was stirred at room temperature for 14 h. The reaction was diluted with CH_2Cl_2 (30 mL) and saturated aqueous $NaHCO_3$ (20 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_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 hexanes/EtOAc (6 : 4) to give 36 mg (94%) of amine **40**{*5*,*2*} as a colorless oil: ^{1}H NMR (400 MHz) δ 7.94 (d, *J* = 8.2 Hz, 1 H), 7.75 (s, 1 H), 7.70 (dd, *J* = 8.2, 2.1 Hz, 1 H), 7.61-7.54 (comp, 3 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.70 (s, 2 H), 3.58 (s, 2 H), 2.31 (d, *J* = 6.8 Hz, 2 H), 1.84 (app nonet, *J* = 6.8 Hz, 1 H), 0.97 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz) δ 159.8, 141.7, 135.3, 133.8, 133.0, 132.2,

129.6, 129.2, 128.4, 127.6, 123.0, 114.6, 64.6, 55.6, 55.5, 45.5, 26.3, 20.9; IR (neat) 2956, 2870, 2836, 1608, 1497, 1463, 1250, 1182 cm^{-1}; mass spectrum (ESI) *m/z* 349.2025 [$C_{21}H_{25}N_4O$ (M+1) requires 349.2023]; LCMS purity 95%.



42{*1*,*1*}

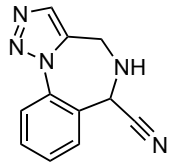
5-(3-Chlorophenyl)-8-phenyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (42{*1*,*1*}**).** Palladium acetate (1.3 mg, 5.7 μmol) was added to a solution of (±)-BINAP (5.3 mg, 8.6 μmol) in degassed toluene (1.0 mL), and the mixture was stirred at room temperature for 1 min. Amine **28**{*1*} (30 mg, 0.11 mmol), 1-bromo-3-chlorobenzene (**26**{*1*}) (44 mg, 27 μL, 0.23 mmol) and then sodium *tert*-butoxide (15 mg, 0.16 mmol) were added, and the reaction was heated at 80 ˚C for 2 h. The reaction was cooled and diluted with CH_2Cl_2 (5 mL), and the mixture was filtered through a Celite® pad washing with CH_2Cl_2 (40 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 40 mg (94%) of amine **42**{*1*,*1*} as a colorless solid: mp 184 ˚C (dec.); ^{1}H NMR (400 MHz) δ 8.07 (d, *J* = 8.4 Hz, 1 H), 7.81 (s, 1 H), 7.75 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.66 (d, *J* = 2.0 Hz, 1 H), 7.60 (d, *J* = 7.2 Hz, 1 H), 7.48 (app t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.2 Hz, 1 H), 7.21 (app t, *J* = 8.1 Hz, 1 H), 6.90 (app t, *J* = 2.2 Hz, 1 H), 6.84-6.79 (comp, 2 H), 4.52 (s, 2 H), 4.42 (s, 2 H); ^{13}C NMR (100 MHz) δ 149.3, 142.4, 139.3, 135.4, 135.2, 133.1, 133.0, 130.4, 129.2, 129.0 (2C), 128.4, 128.2, 127.2, 123.2, 118.9, 114.1, 112.1, 50.9, 42.8; IR (neat) 3060, 2924, 2851, 1594, 1564, 1488, 1383, 1230, 1102 cm^{-1}; mass spectrum (ESI) *m/z* 373.1215 [$C_{22}H_{18}N_4Cl$ (M+1) requires 373.1215]; LCMS purity 95%.



43

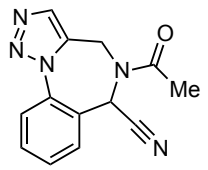
2-(2-(Benzo[*d*][1,3]dioxol-5-ylmethyl)phenyl)-2-(prop-2-ynylamino)-acetonitrile (43). Aqueous HCl (4.28 mL, 1.0 M, 4.28 mmol) was added dropwise to a solution of 2-azido-benzaldehyde (**4**) (600 mg, 4.08 mmol),[4] propargylamine (236 mg, 274 μL, 4.28 mmol) and sodium cyanide (210 mg,

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 **43** (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.



44

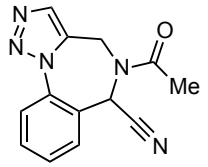
5,6-Dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (44). A solution of amine **43** (667 mg, 3.02 mmol) in toluene (158 mL) was stirred at 60 ˚C for 34 h. The cooled reaction was concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with toluene/EtOAc (1 : 1 → 0 : 1) to give 589 mg of amine **44** (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; LCMS purity 93%.



45{*1*}

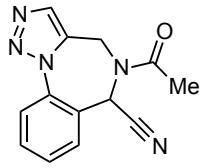
5-Acetyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*1*}). Acetyl chloride (**20**{*1*}) (15 mg, 13 μL, 0.19 mmol) was added to a solution of amine **43** (20 mg, 0.095

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 **45**{*1*} (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.



45{*1*}

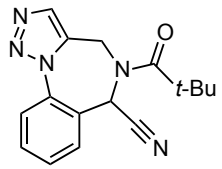
5-Acetyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*1*}). Propargylamine (53 mg, 61 μL, 0.96 mmol) was added to a mixture of 2-azido-benzaldehyde **4** (118 mg, 0.802 mmol),[4] and activated, powdered 4 Å molecular sieves (400 mg, pre-activated weight) in anhydrous 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 (**20**{*1*}) (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 **45**{*1*} (49%) as a cream colored solid. All spectroscopic data were consistent with those previously recorded.



45{*1*}

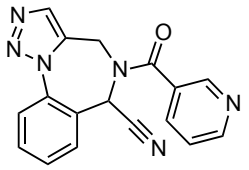
5-Acetyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*1*}). Acetyl chloride (**20**{*1*}) (37 mg, 34 μL, 0.47 mmol) was added to a solution of amine **44** (50 mg, 0.24 mmol)

and pyridine (56 mg, 57 μL, 0.71 mmol) in anhydrous MeCN (1.25 mL) at 0 ˚C, and the reaction was stirred at room temperature for 3 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 EtOAc/toluene (6 : 4 → 7 : 3) to give 55 mg of amide **45**{*1*} (92 %) as a cream colored solid. All spectroscopic data were consistent with those previously recorded; LCMS purity 100%.



45{*4*}

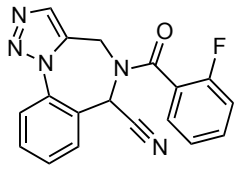
5-Pivaloyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*4*}). Pivaloyl chloride (**20**{*4*}) (69 mg, 70 μL, 0.57 mmol) was added to a solution of amine **44** (60 mg, 0.28 mmol) and pyridine (67 mg, 69 μL, 0.85 mmol) in anhydrous MeCN (1.0 mL) at 0 ˚C, and the 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 **45**{*4*} 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]; LCMS purity 100%.



45{*10*}

5-nicotinoyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*10*}). A mixture of amine **44** (110 mg, 0.52 mmol), nicotinoyl chloride hydrochloride (**20**{*10*}) (185 mg, 1.0

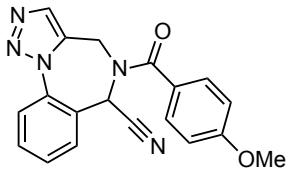
mmol) and pyridine (164 mg, 168 μL, 2.1 mmol) in anhydrous CH_2Cl_2 (3.0 mL) was stirred at room temperature for 2 h. Saturated aqueous $NaHCO_3$ (5 mL) was added and the reaction was stirred at room temperature for 20 min. The reaction was then diluted with CH_2Cl_2 (30 mL) and washed with saturated 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 dichloromethane/MeOH (24 : 1 → 19 : 1) to give 153 mg (92%) of amide **45**{*10*} as a colorless solid: mp 187-189 ˚C (colorless microcrystals from *i*-PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) (rotamers) δ 8.88-8.76, (comp, 2 H), 8.09 (d, *J* = 8.2 Hz, 1 H), 7.95 (app dt, *J* = 7.9, 2.0 Hz, 1 H), 7.90-7.74 (comp, 2 H), 7.70-7.46 (comp, 2 H), 7.51 (dd, *J* = 7.9, 5.0 Hz, 1 H), 6.49 (br s, 1 H), 5.10 (br s, 1 H), 4.34 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 152.7, 148.4, 135.9, 135.5, 133.8, 132.9, 131.5, 130.6, 130.2, 129.2, 124.7, 124.1, 123.3, 115.1, 47.7, 40.9; IR (neat) 2941, 2361, 1651, 1589, 1501, 1391, 1326, 1238, 1102 cm^{-1}; mass spectrum (CI) *m/z* 317.1154 [$C_{17}H_{13}N_6O$ (M+1) requires 317.1151]; LCMS purity 92%.



45{*14*}

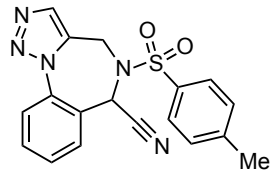
5-(2-Fluorobenzoyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*14*}). 2-Fluorobenzoyl chloride (**20**{*14*}) (90 mg, 68 μL, 0.57 mmol) was added to a solution of amine **44** (60 mg, 0.28 mmol) and pyridine (67 mg, 69 μL, 0.85 mmol) in anhydrous MeCN (1.5 mL) 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 **45**{*14*} 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]; LCMS purity 99%.



45{*16*}

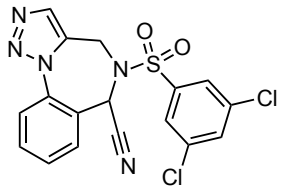
5-(4-Methoxybenzoyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (45{*16*}). 4-Methoxybenzoyl chloride (**20**{*16*}) (48 mg, 38 μL, 0.28 mmol) was added to a solution of amine **44** (30 mg, 0.14 mmol) and pyridine (34 mg, 34 μL, 0.43 mmol) in anhydrous MeCN (1.0 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 **45**{*16*} 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]; LCMS purity 100%.



46{*5*}

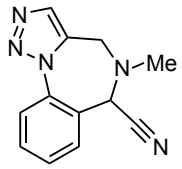
5-Tosyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (46{*5*}). Tosyl chloride (**21**{*5*}) (54 mg, 0.28 mmol) was added to a solution of amine **44** (30 mg, 0.14 mmol) and pyridine (34 mg, 34 μL, 1.4 mmol) in anhydrous MeCN (1.0 mL) and the reaction stirred at room 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 **46**{*5*} (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; LCMS purity 100%.



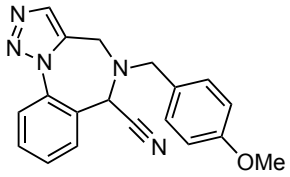
46{*11*}

5-(3,5-Dichlorophenylsulfonyl)-5,6-dihydro-4H-benzo[f][1,2,3]triazolo[1,5-a][1,4]diazepine-6-carbonitrile (46{*11*}). 3,5-Dichlorobenzenesulfonyl chloride (**21**{*11*}) (232 mg, 0.947 mmol) was added to a solution of amine **44** (100 mg, 0.473 mmol) and pyridine (115 μL, 1.42 mmol) in anhydrous MeCN (2.5 mL), and the reaction was stirred at room temperature for 18 h. The mixture was diluted with CH_2Cl_2 (15 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) to give 160 mg (80%) of sulfonamide **46**{*11*} as a colorless solid: mp 175-176 ˚C (colorless microcrystals from *i*-PrOH); ^{1}H NMR (400 MHz) δ 8.01 (d, *J* = 7.8 Hz, 1 H), 7.84-7.70 (comp, 4 H), 7.66-7.56 (comp, 2 H), 7.53 (d, *J* = 7.4 Hz, 1 H), 6.07 (s, 1 H), 5.04 (d, *J* = 14.7 Hz, 1 H), 4.11 (d, *J* = 14.7 Hz, 1 H); ^{13}C NMR (400 MHz) δ 140.1, 136.9, 135.1, 134.3, 133.7, 133.0, 130.8, 130.7, 129.4, 125.8, 124.9, 122.9, 114.0, 49.8, 38.5; IR (neat) 3079, 2955, 1570, 1500, 1422, 1369, 1174, 1143, 1100, 1021; mass spectrum (CI) *m/z* 420.0091 [$C_{17}H_{12}N_5O_2SCl_2$ (M+1) requires 420.0089], 422, 395, 393, 210; LCMS purity 97%.



47{*1*}

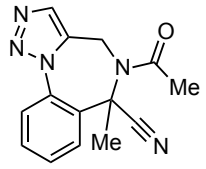
5-Methyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (47{*1*}). A mixture of sodium triacetoxyborohydride (271 mg, 1.28 mmol), amine **44** (45 mg, 0.21 mmol), paraformaldehyde (**25**{*1*}) (64 mg, 2.1 mmol) and glacial acetic acid (13 mg, 12 μL, 0.21 mmol) in DCE (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 **47**{*1*} 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; LCMS purity 98%.



47{*14*}

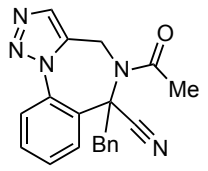
5-(4-Methoxybenzyl)-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (47{*14*}). Sodium triacetoxyborohydride (2.16 g, 10.2 mmol) was added to a solution of amine **44** (360 mg, 1.70 mmol), *p*-anisaldehyde (**25**{*14*}) (1.39 g, 1.24 mL, 10.2 mmol) and glacial acetic 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 **47**{*14*}

(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. LCMS purity 99%.



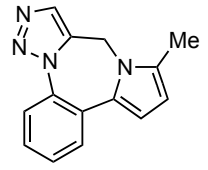
48{*1*,*1*}

5-Acetyl-6-methyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (48{*1*,*1*}). A solution of amide **45**{*1*} (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 (**50**{*1*}) (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 **48**{*1*,*1*} 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]; LCMS purity 100%.



48{*1*,*2*}

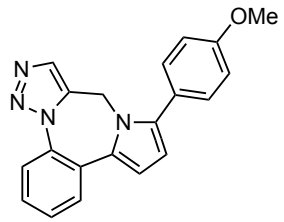
5-Acetyl-6-benzyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine-6-carbonitrile (48{*1*,*2*}). A solution of amide **45**{*1*} (50 mg, 0.20 mmol) in DMF (2.8 mL) was added dropwise over 2 min to sodium hydride (8.7 mg, 0.22 mmol), and the mixture was stirred at room temperature for 45 min. Benzyl bromide (**50**{*2*}) (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 **48**{*1*,*2*} 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]; LCMS purity 100%.



49{*1*}

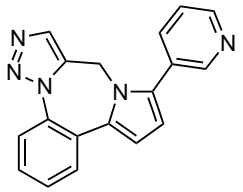
11-Methyl-9*H*-benzo[*f*]pyrrolo[1,2-*d*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (49{*1*}). A solution of amide **45**{*1*} (55 mg, 0.22 mmol) in degassed DMF (2.5 mL) was added dropwise over 2 min to sodium hydride (9.6 mg, 0.24 mmol), and the mixture was stirred at room temperature for 45 min. A solution of triphenylvinylphosphonium bromide (**51**) (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 **49**{*16*} 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]; LCMS purity 100%.



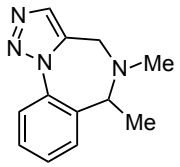
49{*16*}

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 **45**{*16*} (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 (**51**) (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 **45**{*16*} 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; LCMS purity 100%.



49{*10*}

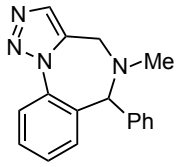
11-(pyridin-3-yl)-9*H*-benzo[*f*]pyrrolo[1,2-*d*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (49{*10*}). A solution of amide **45**{*10*} (78 mg, 0.25 mmol) in DMF (2.8 mL) was added dropwise over 2 min to sodium hydride (10.8 mg, 0.27 mmol), and the mixture was stirred at room temperature for 45 min. A solution of triphenylvinylphosphonium bromide (**51**) (105 mg, 0.28 mmol) in DMF (1.8 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 toluene/EtOAc/MeOH (50 : 50 : 1) to give 67 mg (91%) of pyrrole **49**{*10*} as a pale yellow solid: mp 182-184 ˚C (pale yellow needles from hexanes/EtOAc); ^{1}H NMR (400 MHz) δ 8.72-8.67 (m, 1 H), 8.67-8.62 (m, 1 H), 8.13-8.06 (m, 1 H), 7.79-7.74 (comp, 2 H), 7.72 (app dt, *J* = 7.8, 2.0 Hz, 1 H), 7.56-7.48 (comp, 2 H), 7.45 (dd, *J* = 7.8, 4.9 Hz, 1 H), 6.60 (d, *J* = 3.9 Hz, 1 H), 6.39 (d, *J* = 3.9 Hz, 1 H), 5.12 (br s, 2 H); ^{13}C NMR (100 MHz) δ 149.7, 148.9, 136.2, 134.2, 132.7, 132.0, 131.9, 130.9, 129.7, 129.5, 128.6, 128.1, 124.4, 124.0, 123.8, 111.5, 110.7, 37.5; IR (neat) 3031, 2924, 2854, 1567, 1482, 1454, 1421, 1335, 1253, 1231 cm^{-1}; mass spectrum (ESI) *m/z* 300.1245 [$C_{18}H_{14}N_5$ (M+1) requires 300.1244]; LCMS purity 100%.



52{*1,1*}

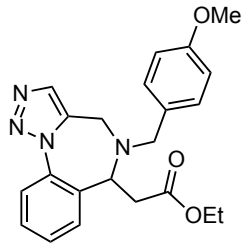
5,6-Dimethyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (52{*1*,*1*}). Methylmagnesium bromide solution (**54**{*1*}) (298 μL, 0.954 mmol, 3.2 M in Et_2O) was added to a solution of zinc chloride (1.34 mL, 1.34 mmol, 1.0 M in THF) and the mixture was stirred at 0 ˚C for 10 min. The reaction was diluted with THF (2.0 mL), a solution of nitrile **47**{*1*} (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 **52**{*1*,*1*} 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]; LCMS purity 92%.



52{*1*,*2*}

5-Methyl-6-phenyl-5,6-dihydro-4*H*-benzo[*f*][1,2,3]triazolo[1,5-*a*][1,4]diazepine (52{*1*,*2*}). Phenylmagnesium bromide solution (**54**{*2*}) (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 **47**{*1*} (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 **52**{*1*,*2*} 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, 128.5, 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; LCMS purity 99%.



53{*14*}

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 (53{*14*}). Glacial acetic acid (0.6 mg, 0.6 μL, 0.1 mmol), was added to a mixture of nitrile **47**{*14*} (35 mg, 0.11 mmol), ethyl bromoacetate (**55**) (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 **53**{*14*} 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]; LCMS purity 97%.

Lipinski Data

Compound #	Molecular Weight	ClogP[a]	H-bond donors	H-bond acceptors	Lipinski Rule of 5
6	186.21	0.91	1	3	Satisfied
7	265.11	1.68	1	3	Satisfied
8{*2*}	258.28	0.34	0	4	Satisfied
8{*8*}	359.21	3.58	0	3	Satisfied
8{*10*}	291.31	1.15	0	4	Satisfied
9{*9*}	427.34	3.89	0	3	Satisfied
9{12}	427.34	3.89	0	3	Satisfied
10{*4*}	376.43	3.12	0	4	Satisfied
10{*9*}	383.42	1.36	1	5	Satisfied
10{*10*}	368.45	3.67	0	4	Satisfied

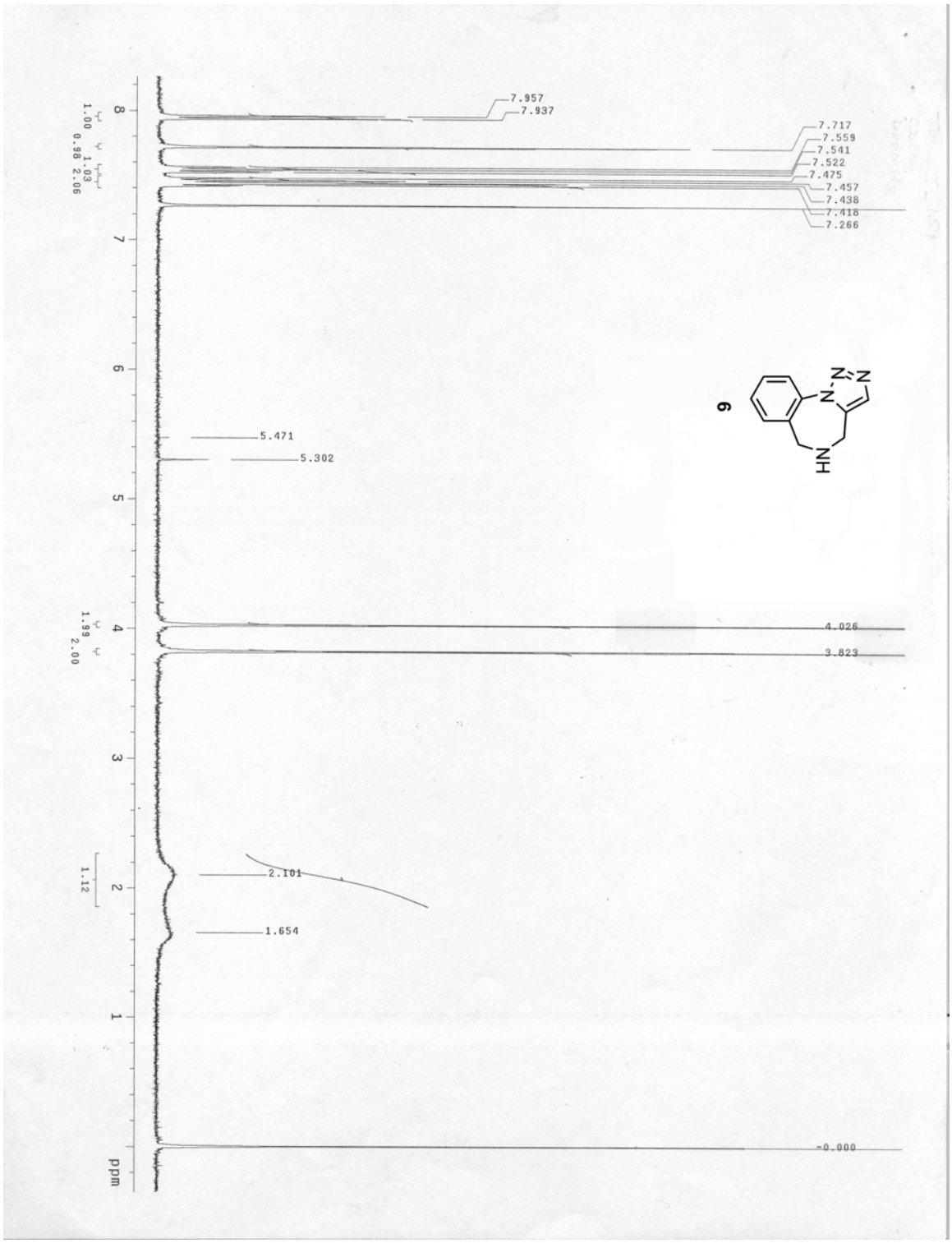
11{*1*}	343.20	0.78	0	4	Satisfied
11{*6*}	439.71	3.50	0	4	Satisfied
12{*2*}	315.33	0.39	1	4	Satisfied
12{*4*}	305.33	2.43	1	3	Satisfied
12{*8*}	323.32	2.57	1	3	Satisfied
13{*3*}	390.28	2.98	1	3	Satisfied
13{*4*}	384.23	3.19	1	3	Satisfied
14{*1*}	285.37	2.03	1	2	Satisfied
14{*4*}	301.41	2.35	1	2	Satisfied
14{*7*}	346.41	3.17	1	3	Satisfied
15{*3*}	428.35	4.08	1	2	Satisfied
15{*7*}	425.31	3.94	1	3	Satisfied
16{*1*}	244.25	1.14	0	3	Satisfied
16{*2*}	270.29	1.87	0	3	Satisfied
16{*3*}	286.33	2.38	0	3	Satisfied
17{*1*}	200.24	1.29	0	3	Satisfied
17{*8*}	352.43	4.66	0	3	Satisfied
17{*10*}	277.32	1.88	0	4	Satisfied
18{*5*}	424.12	4.99	0	3	Satisfied
18{*12*}	361.28	4.17	0	3	Satisfied
19{*1*}	296.75	3.79	0	3	Satisfied
19{*3*}	280.30	3.32	0	3	Satisfied
19{*6*}	263.30	2.56	0	4	Satisfied
27{*1*}	269.35	1.87	1	4	Satisfied
27{*2*}	271.32	0.80	1	5	Satisfied
30{*1*}	262.31	2.55	1	3	Satisfied
30{*2*}	280.30	2.70	1	3	Satisfied
30{*5*}	292.34	2.40	1	4	Satisfied
31{*1,4*}	353.46	3.28	0	4	Satisfied
31{*2,13*}	403.48	2.69	0	5	Satisfied
32{*1,13*}	394.47	4.44	0	3	Satisfied
32{*2,4*}	364.42	4.11	0	3	Satisfied
33{*1,5*}	423.53	3.60	0	5	Satisfied
33{*2,11*}	480.37	3.22	0	6	Satisfied
34{*2,5*}	434.49	4.43	0	4	Satisfied
34{*5,11*}	501.39	4.82	0	5	One violation
35{*1,3*}	394.51	3.17	1	4	Satisfied
35{*2,2*}	400.43	0.28	1	6	Satisfied
36{*1,2*}	391.42	2.04	1	4	Satisfied
36{*5,3*}	417.50	3.70	1	4	Satisfied
37{*1,3*}	432.58	4.27	1	3	Satisfied
37{*2,3*}	434.56	3.20	1	4	Satisfied
38{*1,3*}	425.55	4.96	1	2	Satisfied
38{*2,3*}	443.54	5.10	1	2	Satisfied
39{*1,2*}	325.45	3.49	0	4	Satisfied
39{*2,14*}	391.47	2.75	0	6	Satisfied

40{*2,2*}	336.41	4.33	0	3	Satisfied
40{*5,14*}	412.48	4.35	0	5	Satisfied
41{*1,1*}	379.89	4.74	0	4	Satisfied
41{*2,1*}	381.86	3.68	0	5	Satisfied
42{*2,1*}	390.84	5.58	0	3	One violation
42{*5,1*}	402.88	5.28	0	4	One violation
45{*7*}	329.36	2.63	0	4	Satisfied
45{*15*}	340.34	1.98	0	5	Satisfied
46{*3*}	351.38	1.88	0	5	Satisfied
46{*7*}	381.41	1.72	0	6	Satisfied
47{*1*}	225.25	1.04	0	4	Satisfied
47{*5*}	370.24	3.97	0	4	Satisfied
48{*1,1*}	267.29	0.70	0	4	Satisfied
48{*1,2*}	343.38	2.35	0	4	Satisfied
48{*15,1*}	354.37	2.41	0	5	Satisfied
48{*15,2*}	430.46	4.06	0	5	Satisfied
49{*1*}	236.27	2.42	0	2	Satisfied
49{10}	299.33	2.57	0	3	Satisfied
49{*13*}	326.39	4.52	0	2	Satisfied
49{*15*}	323.35	3.64	0	3	Satisfied
52{*1,1*}	214.27	1.71	0	3	Satisfied
52{*12,2*}	358.48	5.19	0	3	One violation
53{*1*}	286.33	1.57	0	4	Satisfied
53{*14*}	392.45	3.14	0	5	Satisfied

[a] ClogP was calculated using the default weighted method of ChemAxon's logP plugin.

References.

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
2. Gottlieb, H. E.; Kotlyar, V.; Nudelman A. *J. Org. Chem.* **1997**, *62*, 7512-7515.
3. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
4. Pelkey, E. T.; Gribble, G. W. *Tetrahedron Lett.* **1997**, *38,* 5603-5606.
5. Alajarín, M.; Cabrera, J.; Pastor, A.; Villalgordo, J. M. *Tetrahedron Lett.* **2007**, *48*, 3495-3499.
6. Main, C. A.; Petersson, H. M.; Rahman, S. S.; Hartley, R. C. *Tetrahedron* **2008**, *64,* 901-914.
7. Cledera, P.; Avendaño, C.; Menéndez, J. C. *Tetrahedron* **1998**, *54,* 12349-12360.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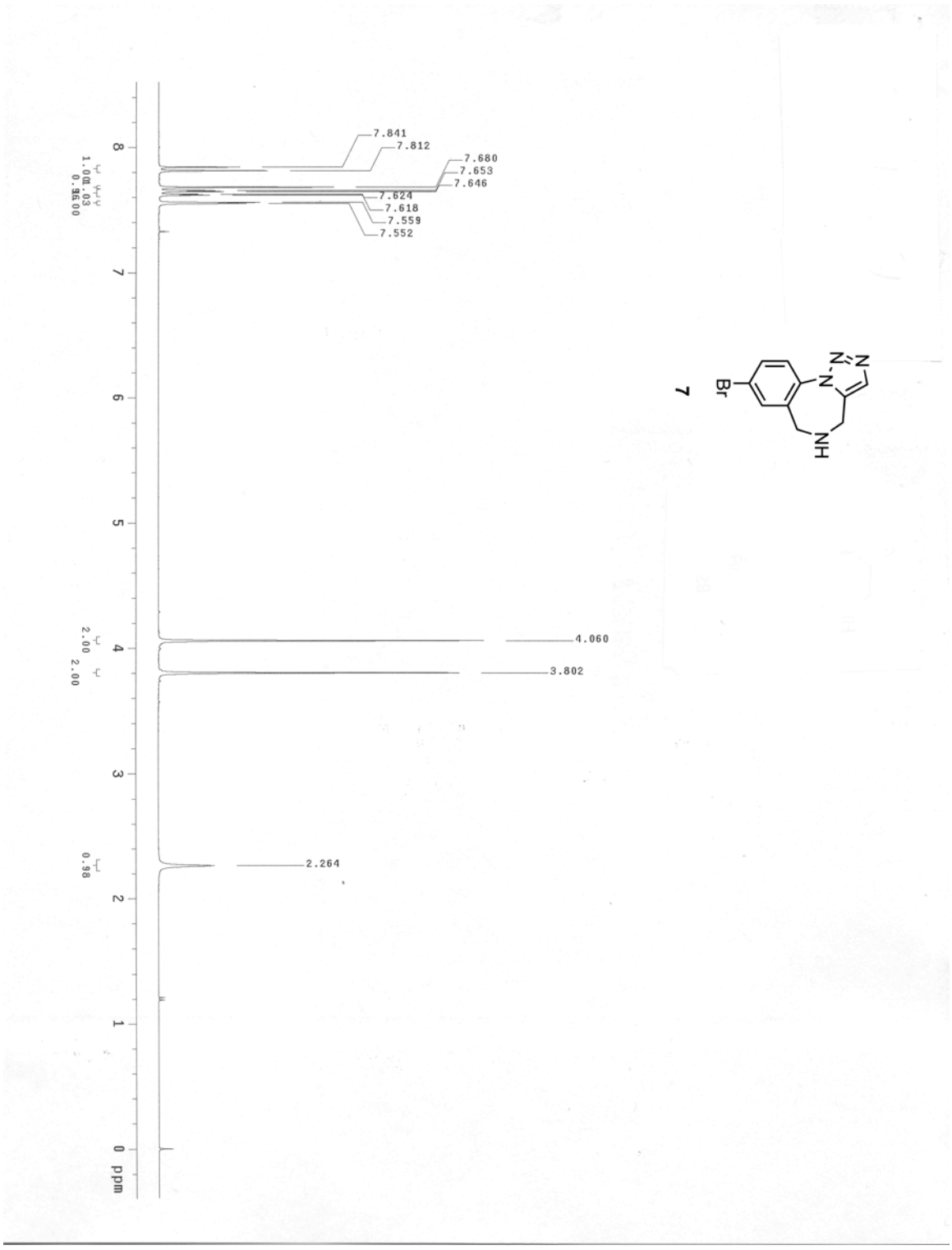
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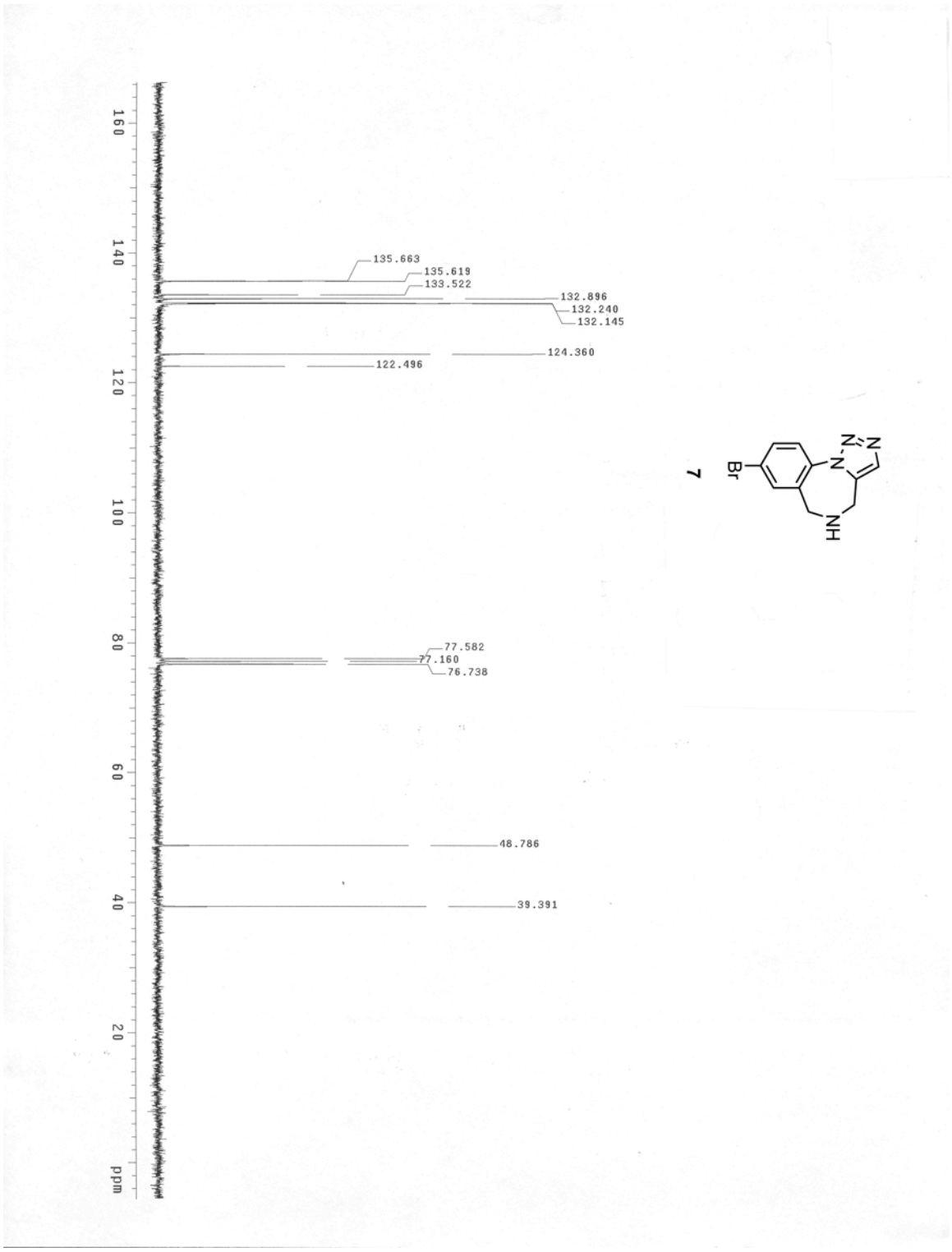
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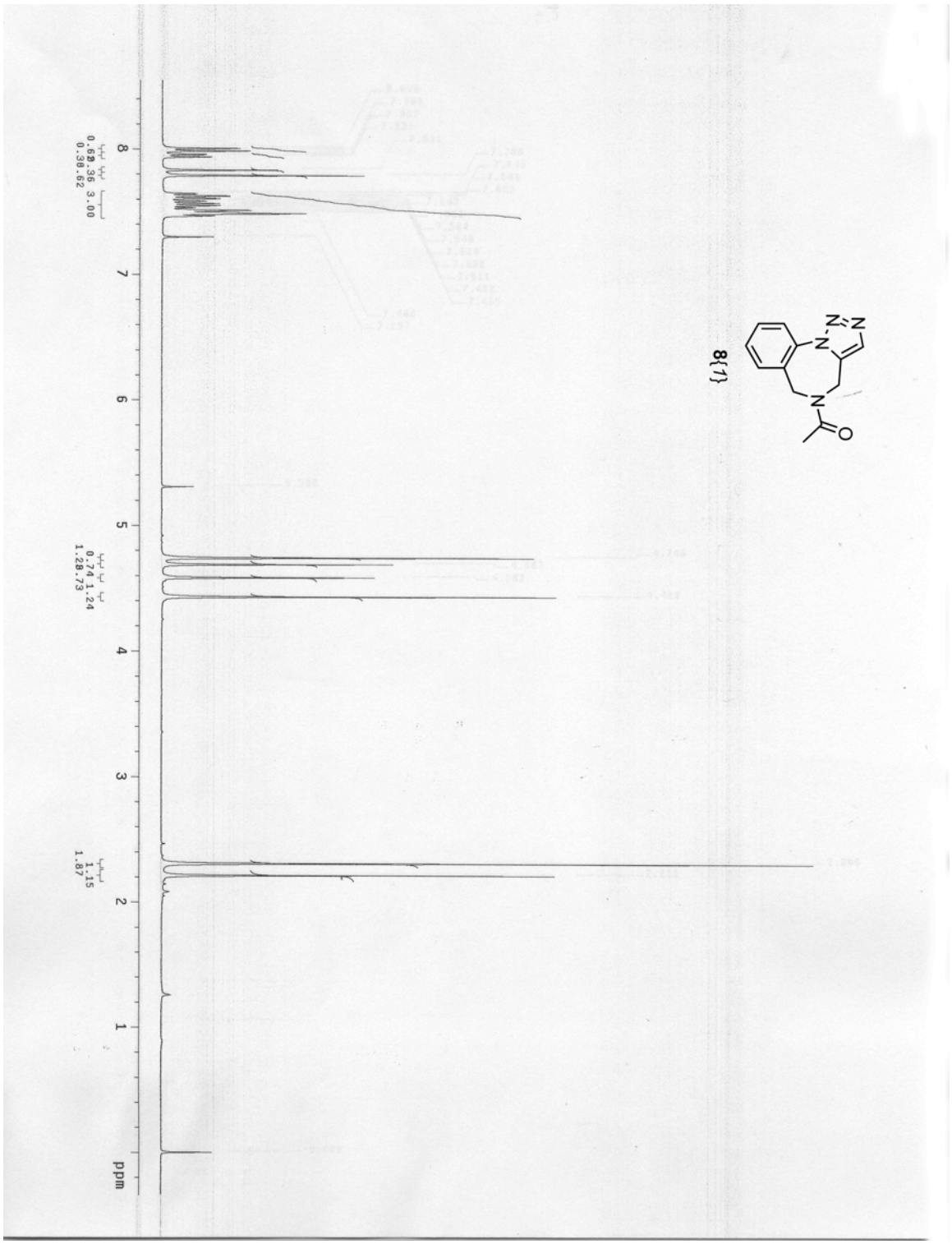
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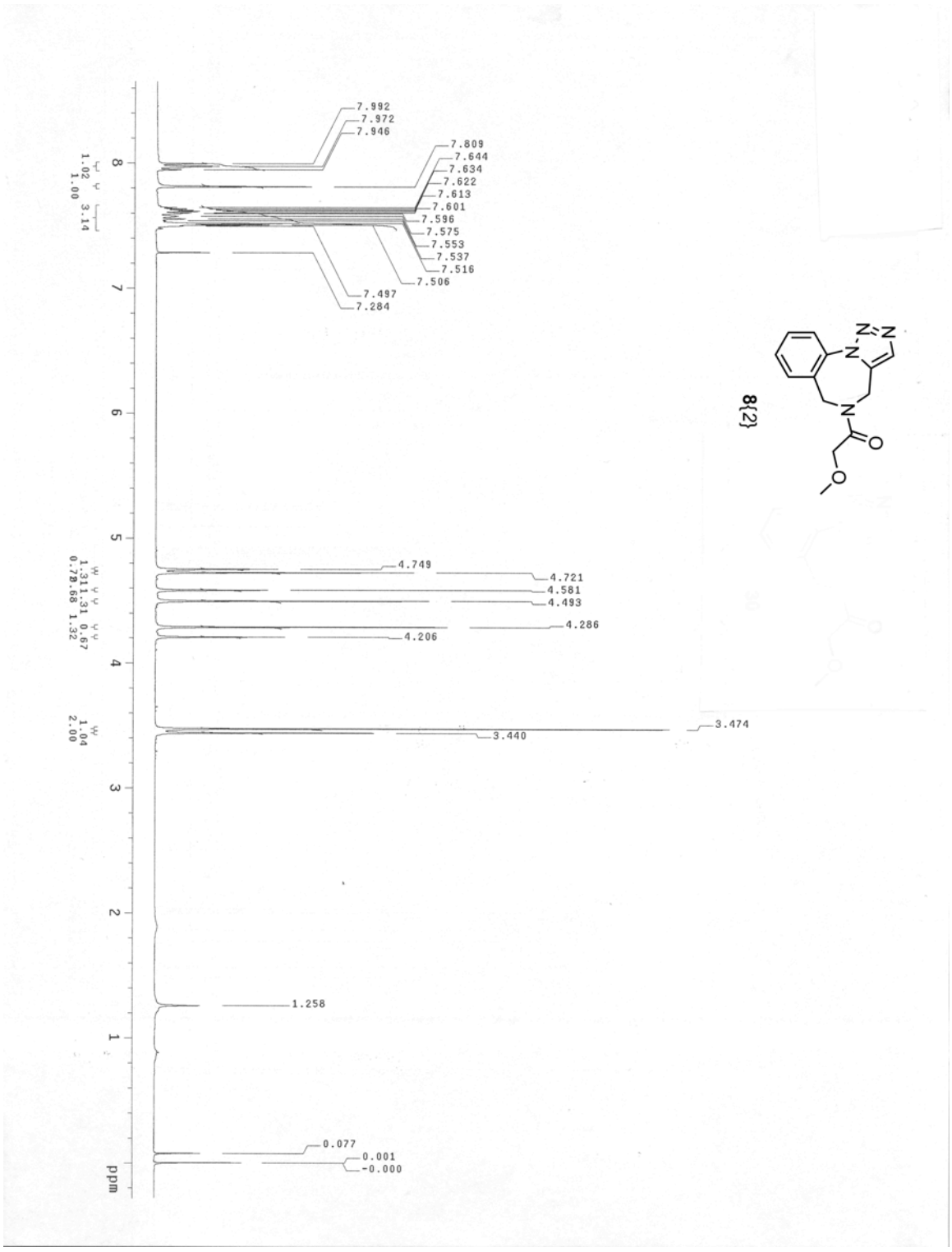
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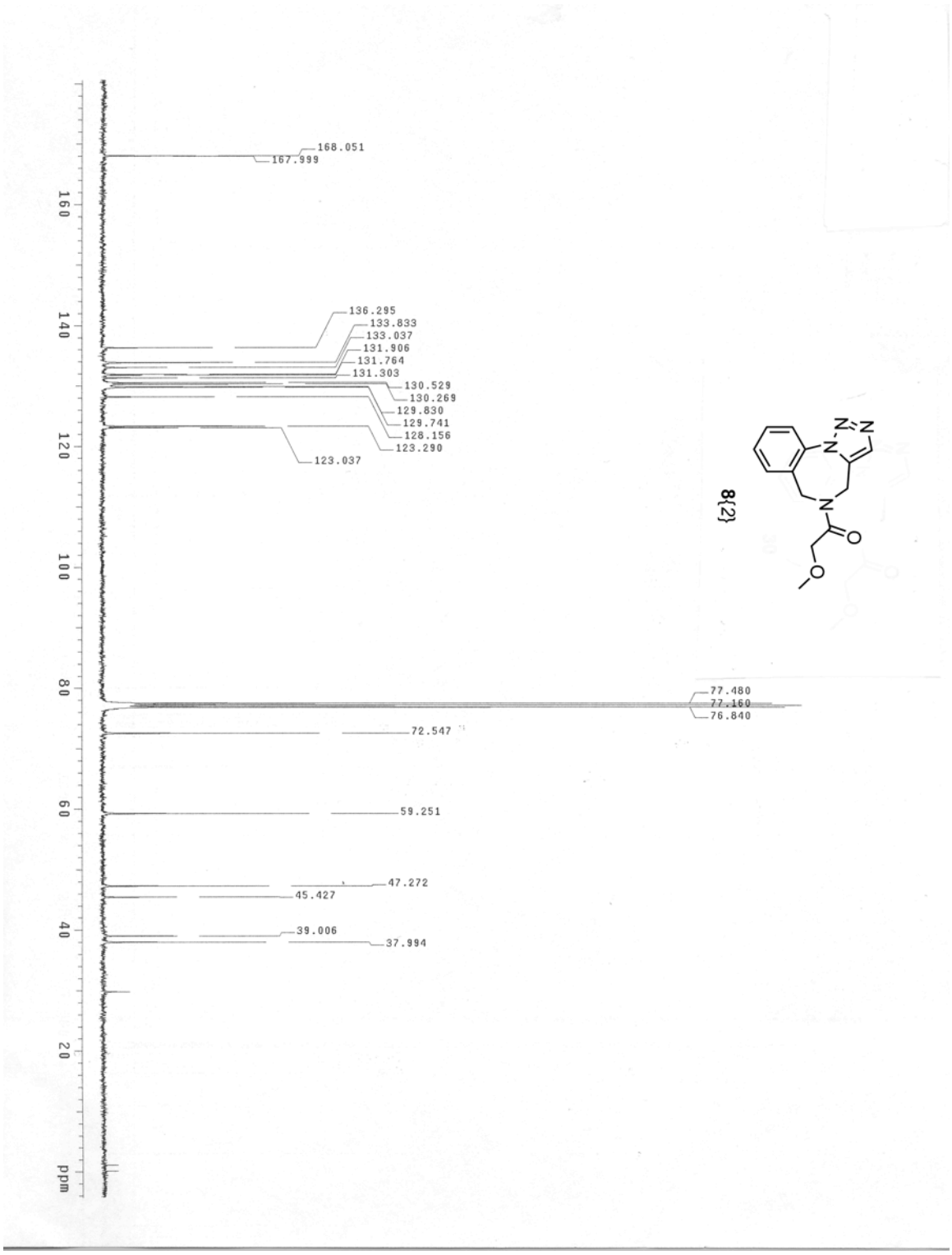
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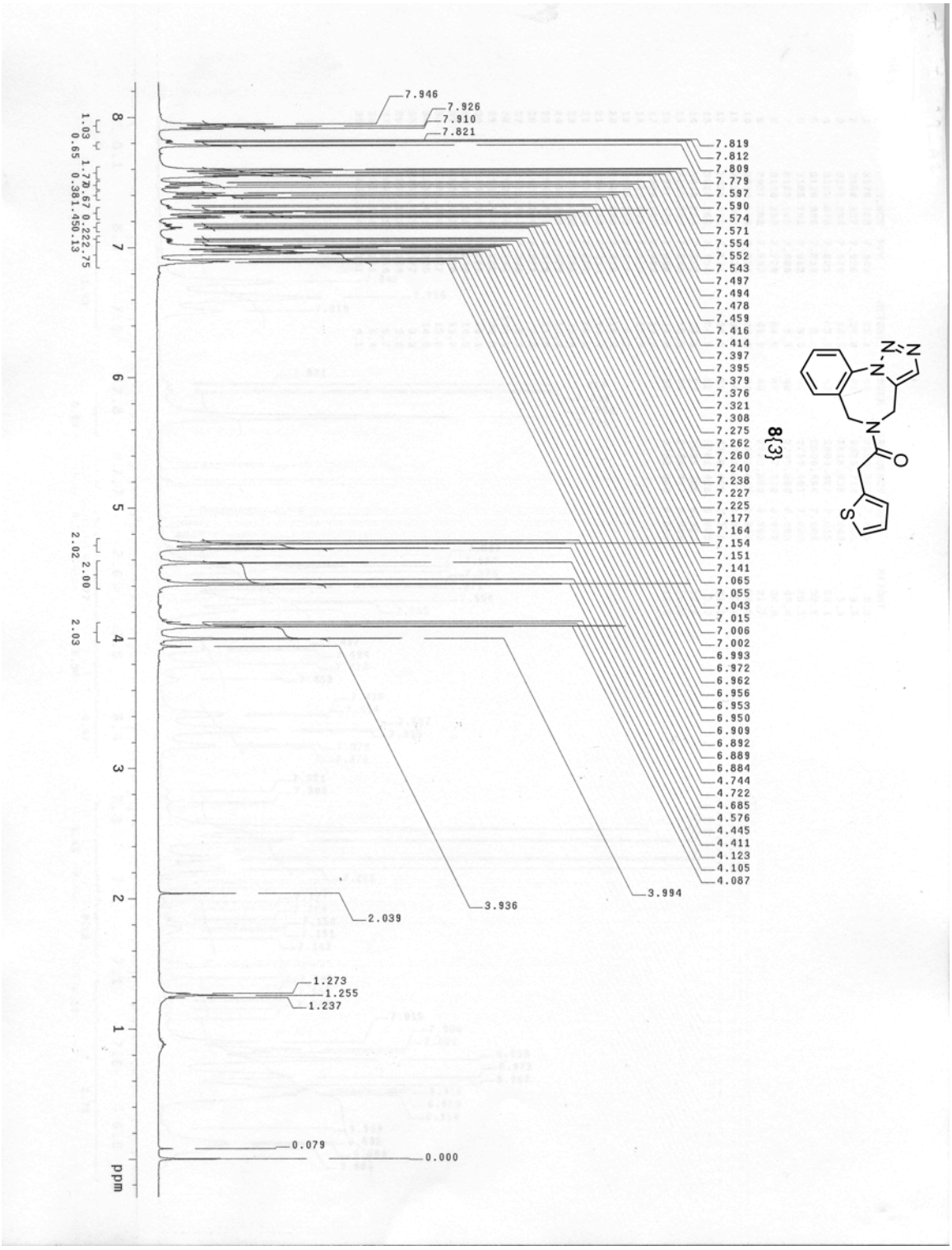
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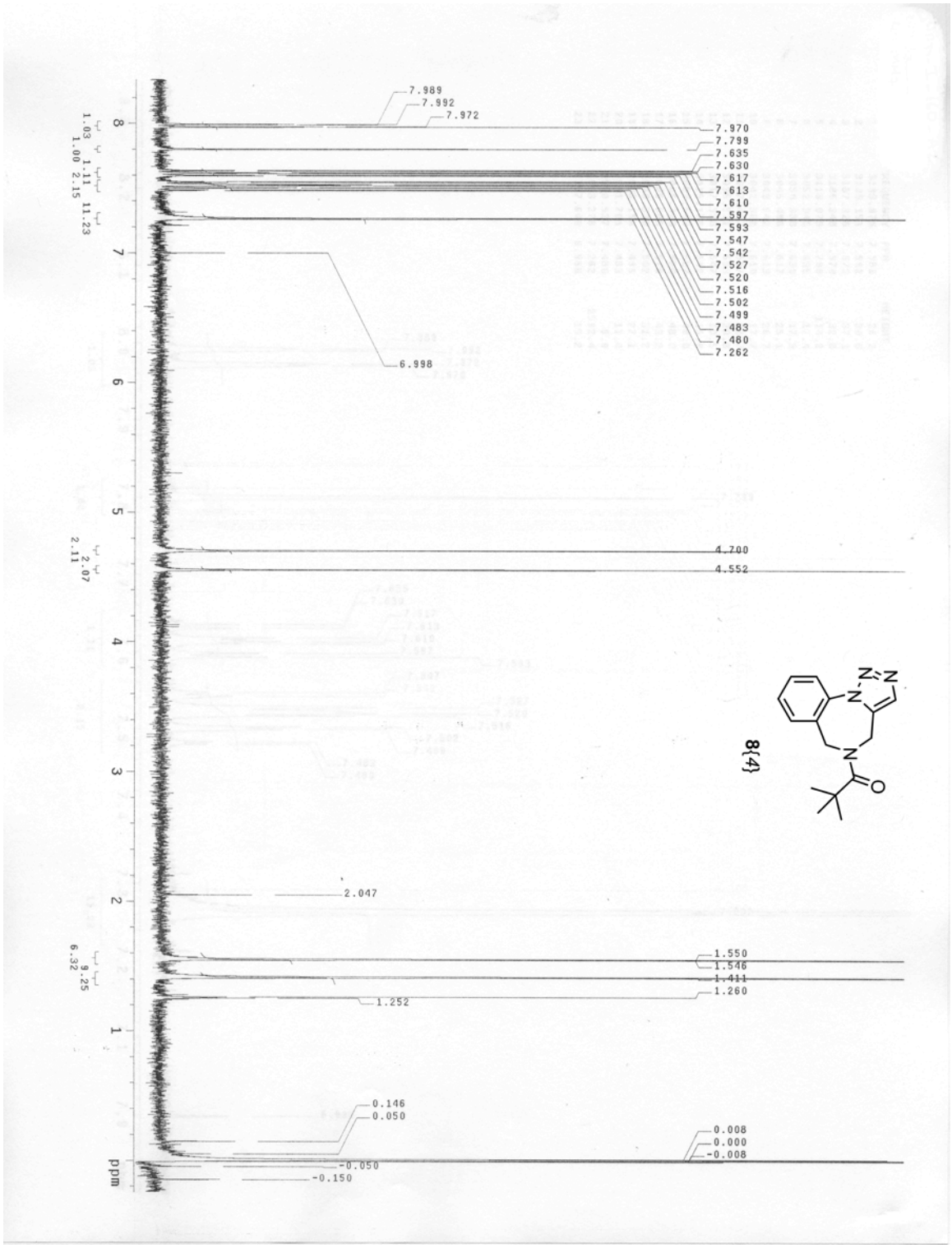
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7.610
7.597
7.593
7.547
7.542
7.527
7.520
7.516
7.502
7.499
7.483
7.480
7.262
6.998
4.700
4.552
2.047
1.550
1.546
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0.000
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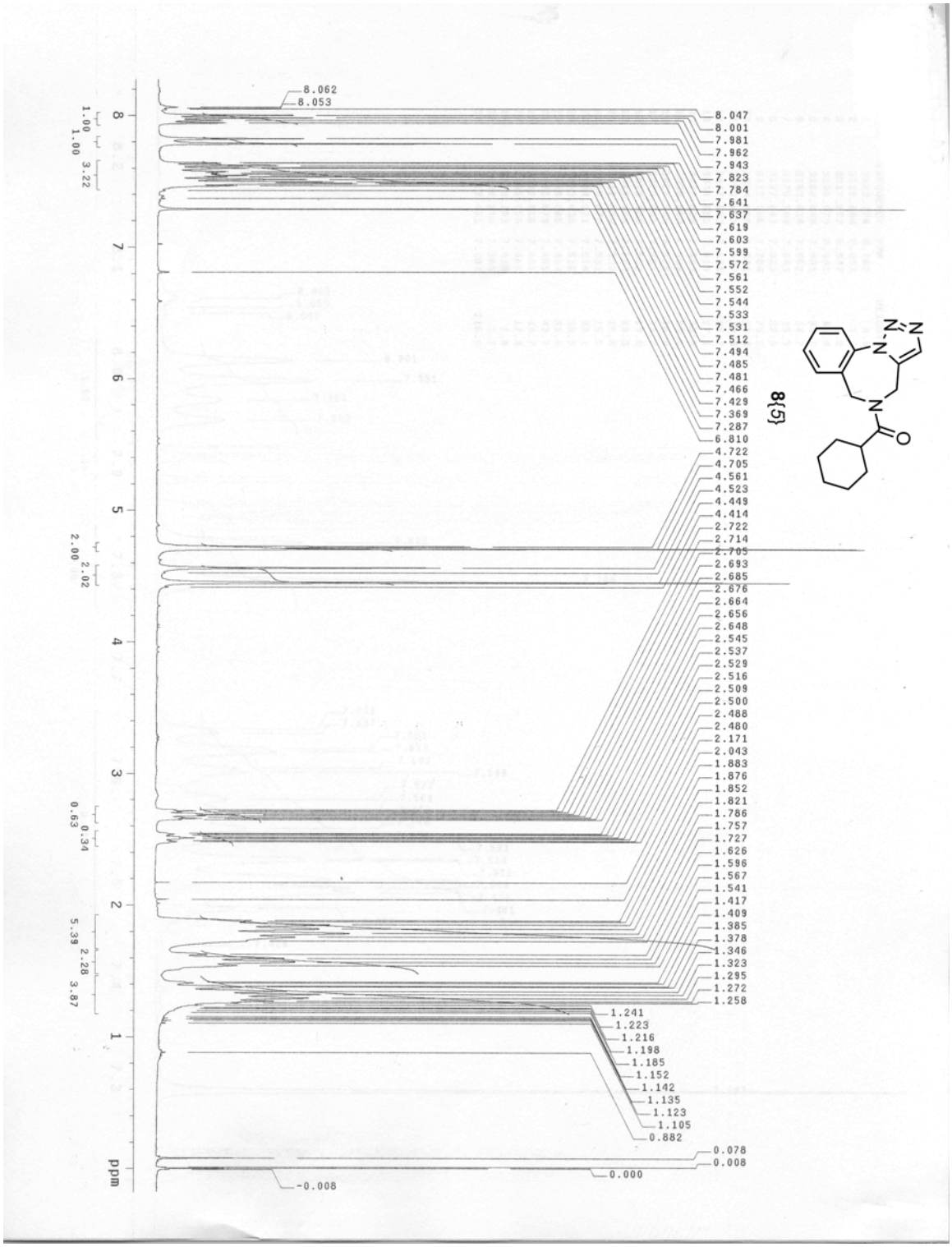
8{4}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7.823
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7.603
7.599
7.572
7.561
7.552
7.544
7.533
7.531
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7.494
7.485
7.481
7.466
7.429
7.369
7.287
6.810
4.722
4.705
4.561
4.523
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4.414
2.722
2.714
2.705
2.693
2.685
2.676
2.664
2.656
2.648
2.545
2.537
2.529
2.516
2.509
2.500
2.488
2.480
2.171
2.043
1.883
1.876
1.852
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1.786
1.757
1.727
1.626
1.596
1.567
1.541
1.417
1.409
1.385
1.378
1.346
1.323
1.295
1.272
1.258
1.241
1.223
1.216
1.198
1.185
1.152
1.142
1.135
1.123
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0.078
0.008
0.000
-0.008
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3.87
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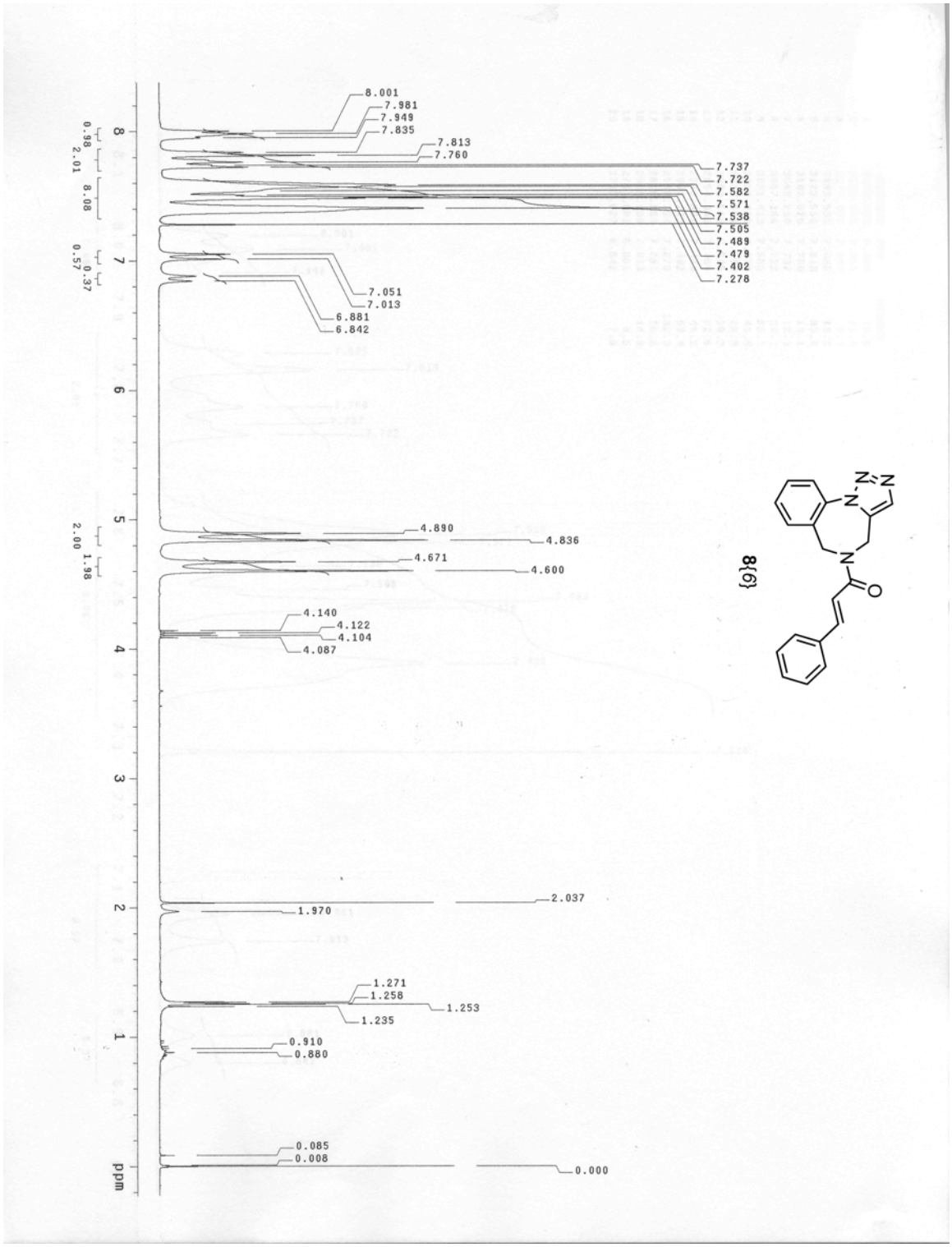
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7.813
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7.737
7.722
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7.571
7.538
7.505
7.489
7.479
7.402
7.278
7.051
7.013
6.881
6.842
4.890
4.836
4.671
4.600
4.140
4.122
4.104
4.087
2.037
1.970
1.271
1.258
1.253
1.235
0.910
0.880
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ppm
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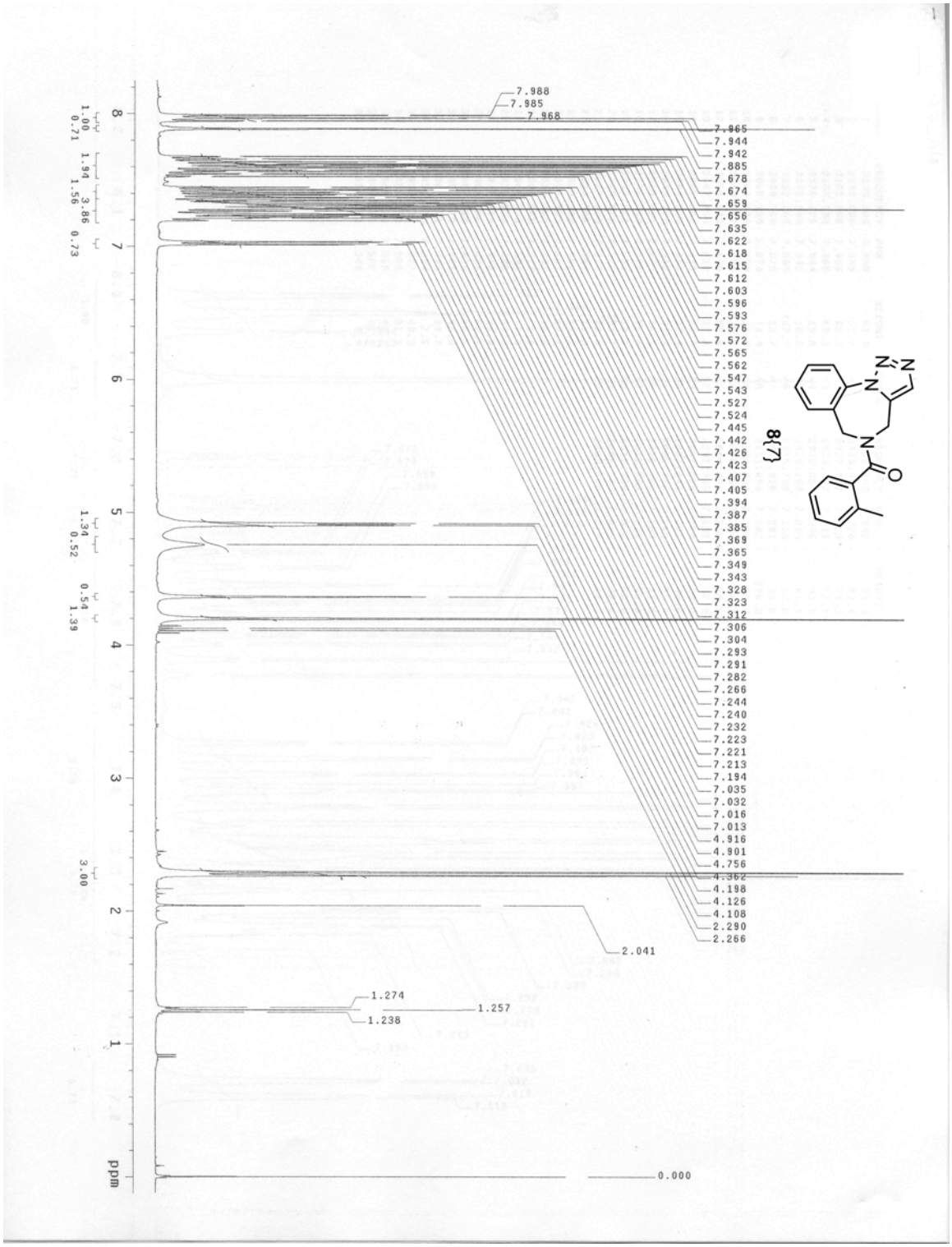
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7.674
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7.656
7.635
7.622
7.618
7.615
7.612
7.603
7.596
7.593
7.576
7.572
7.565
7.562
7.547
7.543
7.527
7.524
7.445
7.442
7.426
7.423
7.407
7.405
7.394
7.387
7.385
7.369
7.365
7.349
7.343
7.328
7.323
7.312
7.306
7.304
7.293
7.291
7.282
7.266
7.244
7.240
7.232
7.223
7.221
7.213
7.194
7.035
7.032
7.016
7.013
4.916
4.901
4.756
4.362
4.198
4.126
4.108
2.290
2.266
2.041
1.274
1.257
1.238
0.000
8{7}
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1.94
1.56
3.86
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0.52
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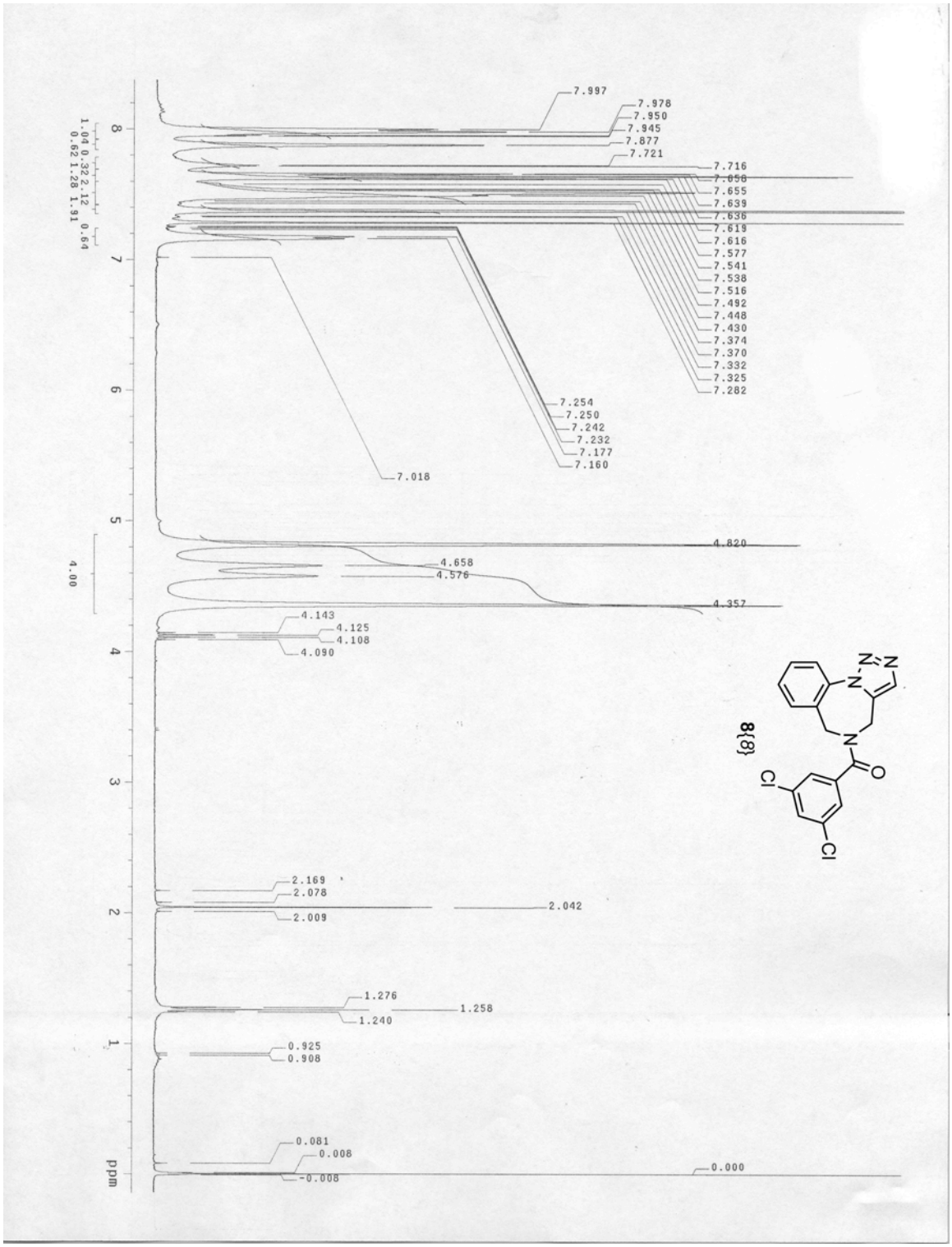
1.39
3.00
ppm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7.636
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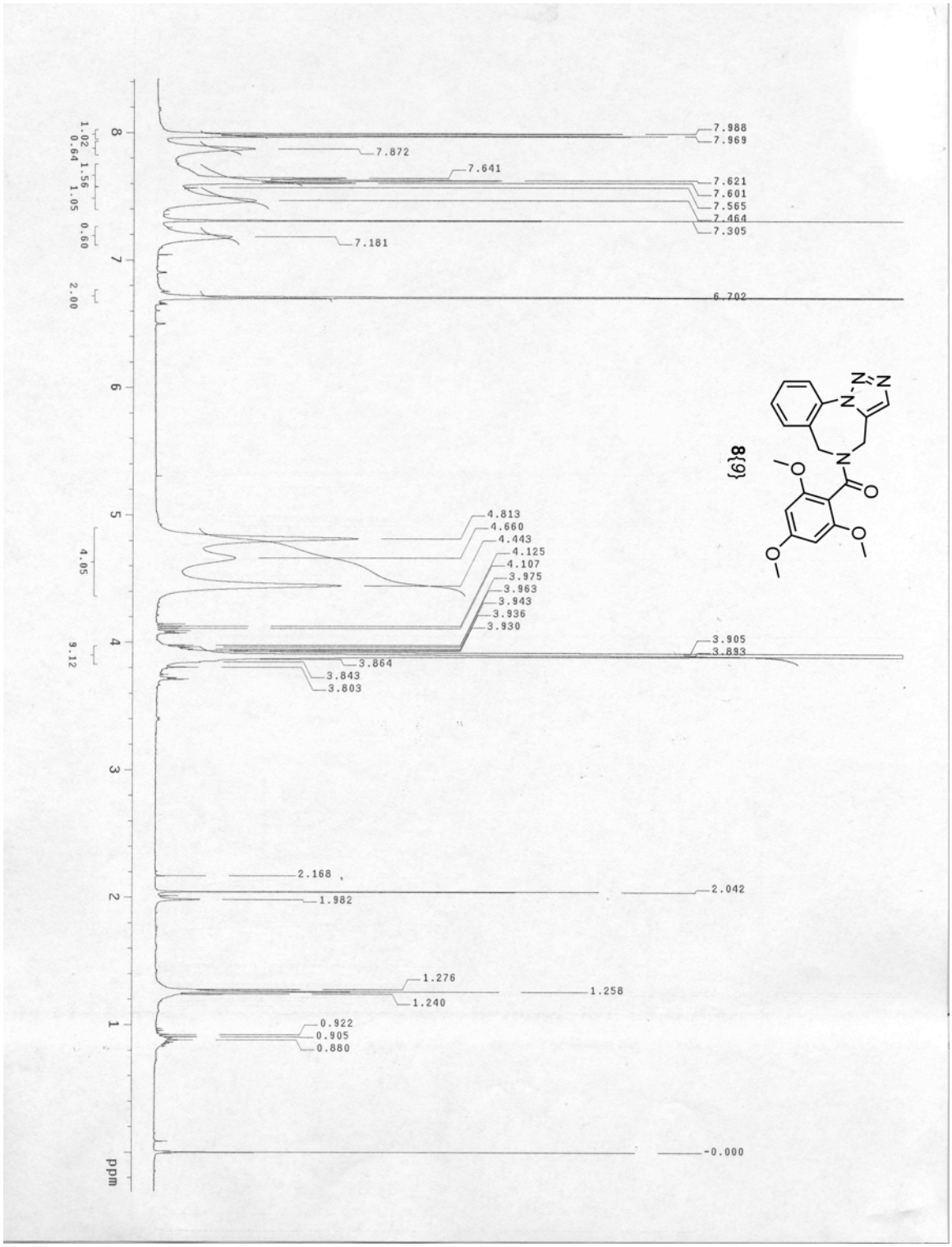
7.616
7.577
7.541
7.538
7.516
7.492
7.448
7.430
7.374
7.370
7.332
7.325
7.282
7.254
7.250
7.242
7.232
7.177
7.160
7.018
4.820
4.658
4.576
4.357
4.143
4.125
4.108
4.090
2.169
2.078
2.042
2.009
1.276
1.258
1.240
0.925
0.908
0.081
0.008
-0.008
0.000
ppm
8{8}
Cl
Cl
O
N
N
N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7.305
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6.702
4.813
4.660
4.443
4.125
4.107
3.975
3.963
3.943
3.936
3.930
3.905
3.893
3.864
3.843
3.803
2.168
2.042
1.982
1.276
1.258
1.240
0.922
0.905
0.880
-0.000
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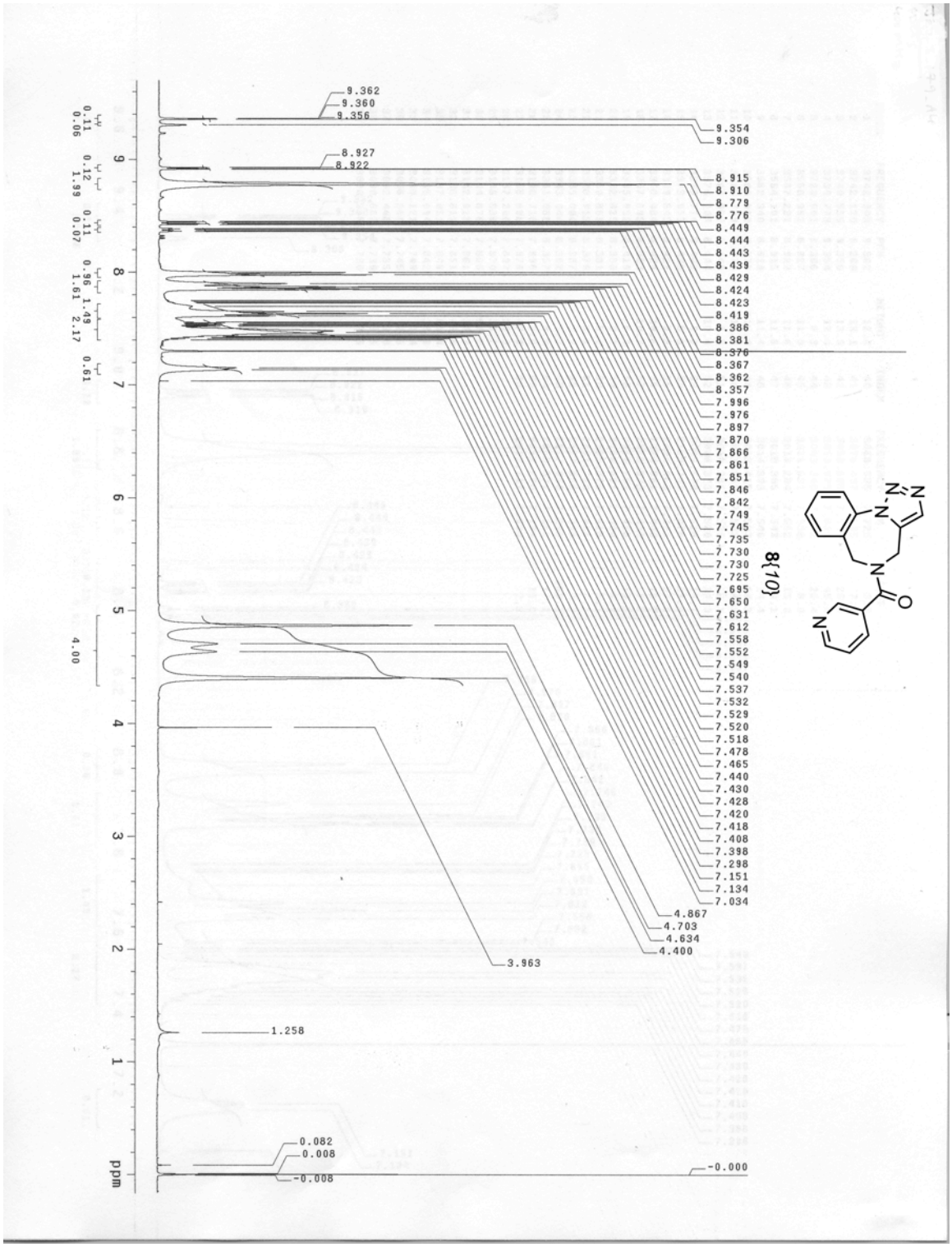
0.64
1.56
1.05
0.60
2.00
4.05
9.12
{6}8
{9}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9.360
9.356
9.354
9.306
8.927
8.922
8.915
8.910
8.779
8.776
8.449
8.444
8.443
8.439
8.429
8.424
8.423
8.419
8.386
8.381
8.370
8.367
8.362
8.357
7.996
7.976
7.897
7.870
7.866
7.861
7.851
7.846
7.842
7.749
7.745
7.735
7.730
7.730
7.725
7.695
7.650
7.631
7.612
7.558
7.552
7.549
7.540
7.537
7.532
7.529
7.520
7.518
7.478
7.465
7.440
7.430
7.428
7.420
7.418
7.408
7.398
7.298
7.151
7.134
7.034
4.867
4.703
4.634
4.400
3.963
1.258
0.082
0.008
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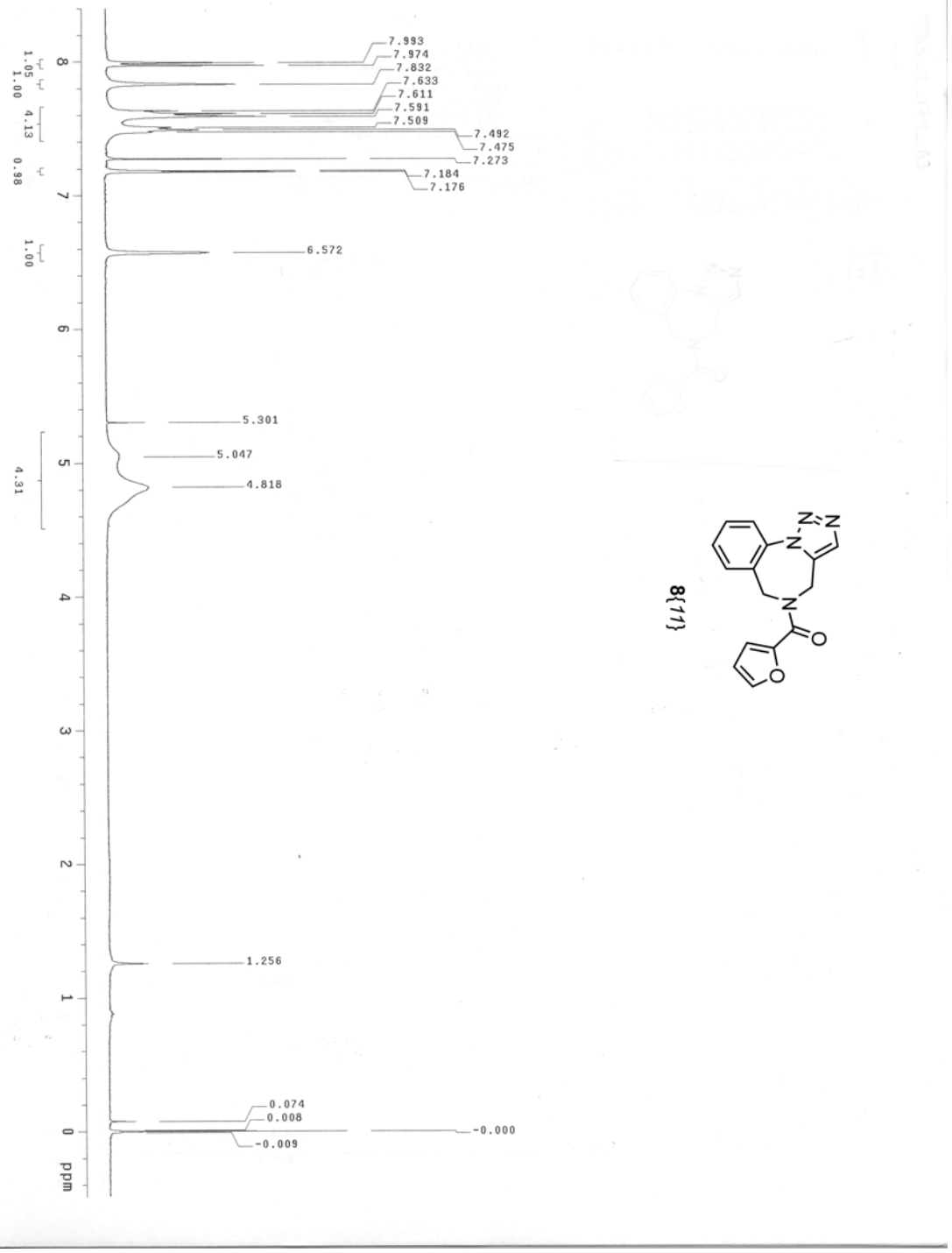
-0.000
ppm
8{10}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7.832
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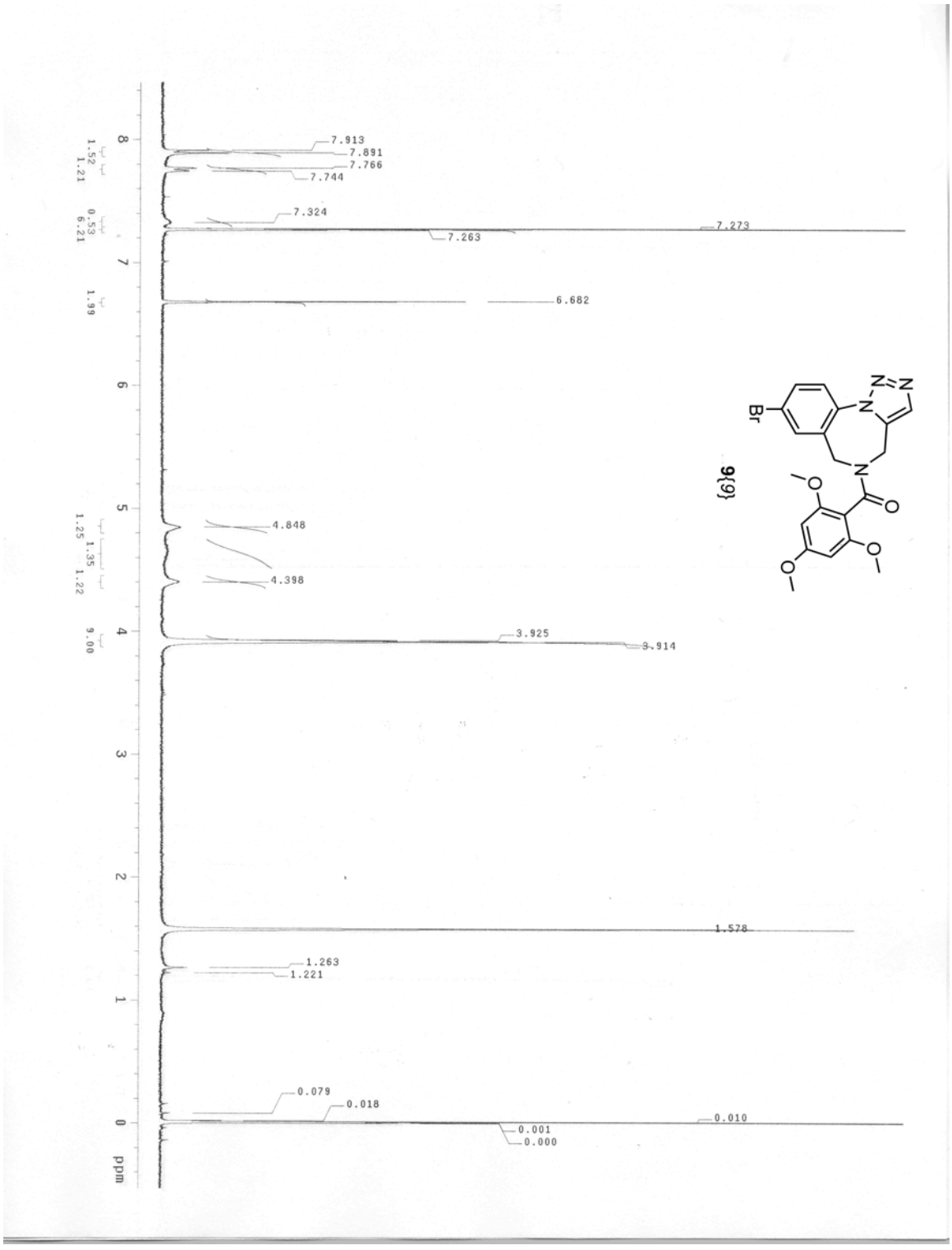
7.611
7.591
7.509
7.492
7.475
7.273
7.184
7.176
6.572
5.301
5.047
4.818
1.256
0.074
0.008
-0.000
-0.009
ppm
1.05
1.00
4.13
0.98
1.00
4.31
8{11}

8(11)
180
160
140
120
100
80
60
40
20
ppm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7.891
7.766
7.744
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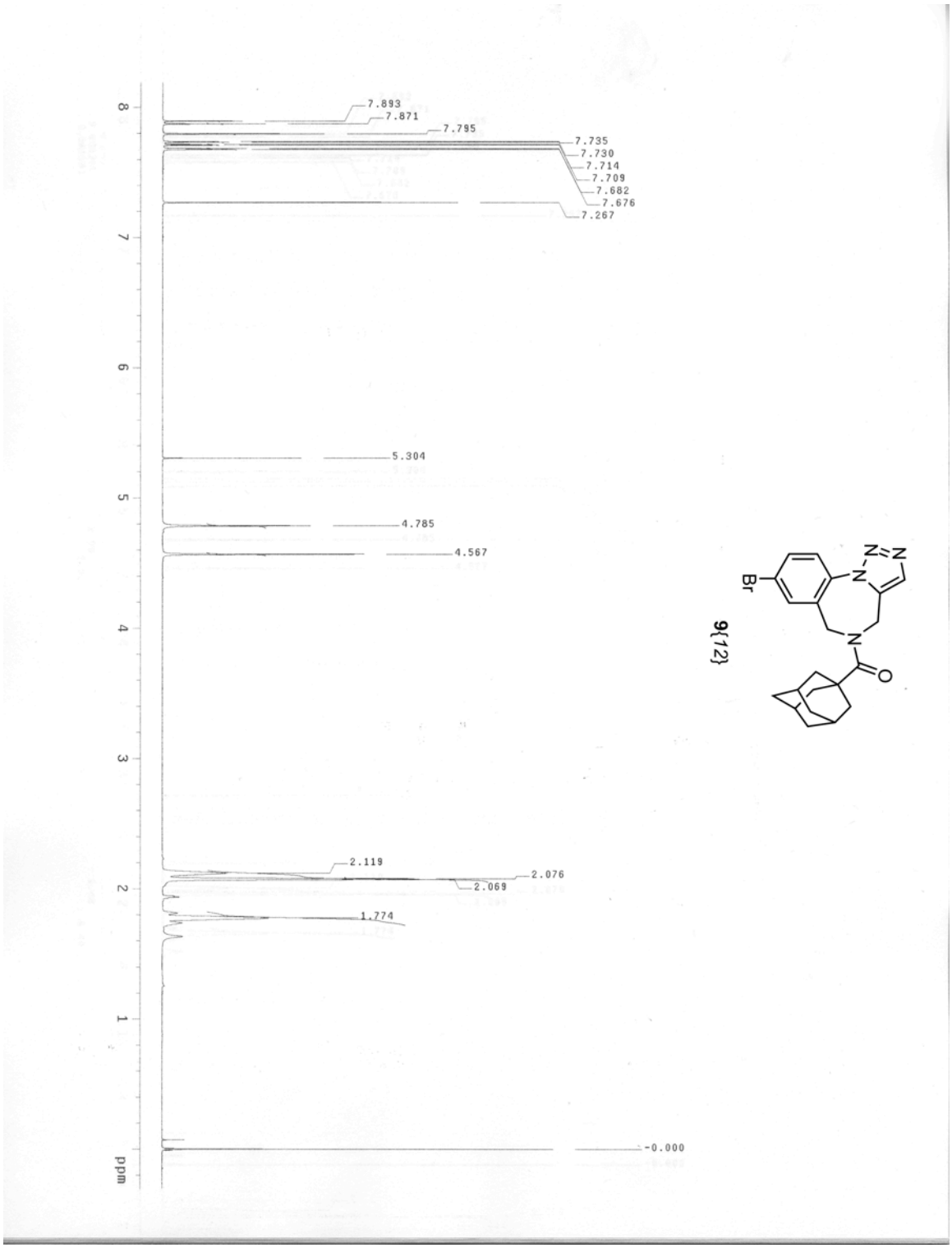
7.273
6.682
4.848
4.398
3.925
3.914
1.578
1.263
1.221
0.079
0.018
0.010
0.001
0.000
ppm
Br
9{9}


7.893
7.871
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7.730
7.714
7.709
7.682
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7.267
5.304
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4.567
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2.076
2.069
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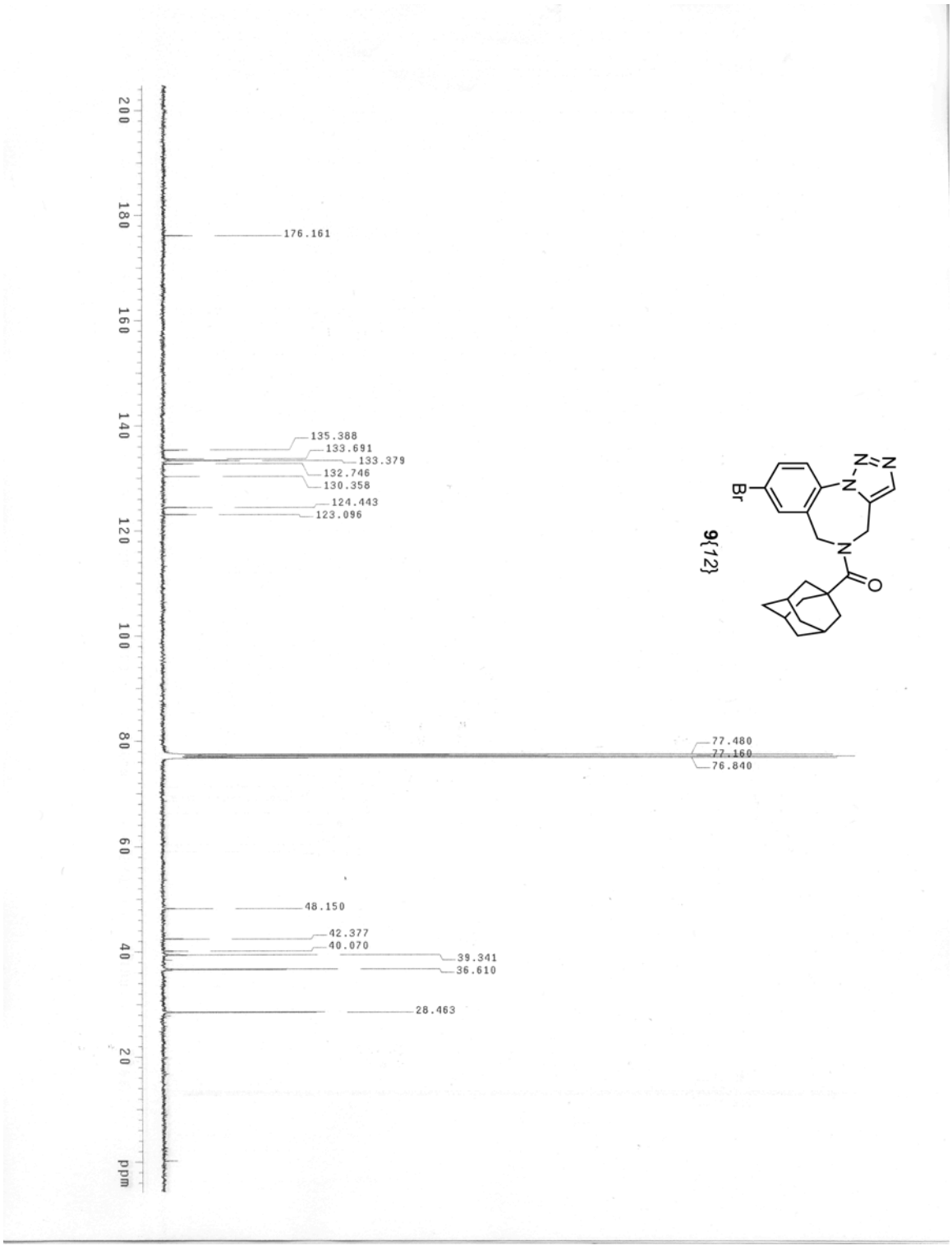
9{12}
Br
N
N
N
O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133.379
132.746
130.358
124.443
123.096
77.480
77.160
76.840
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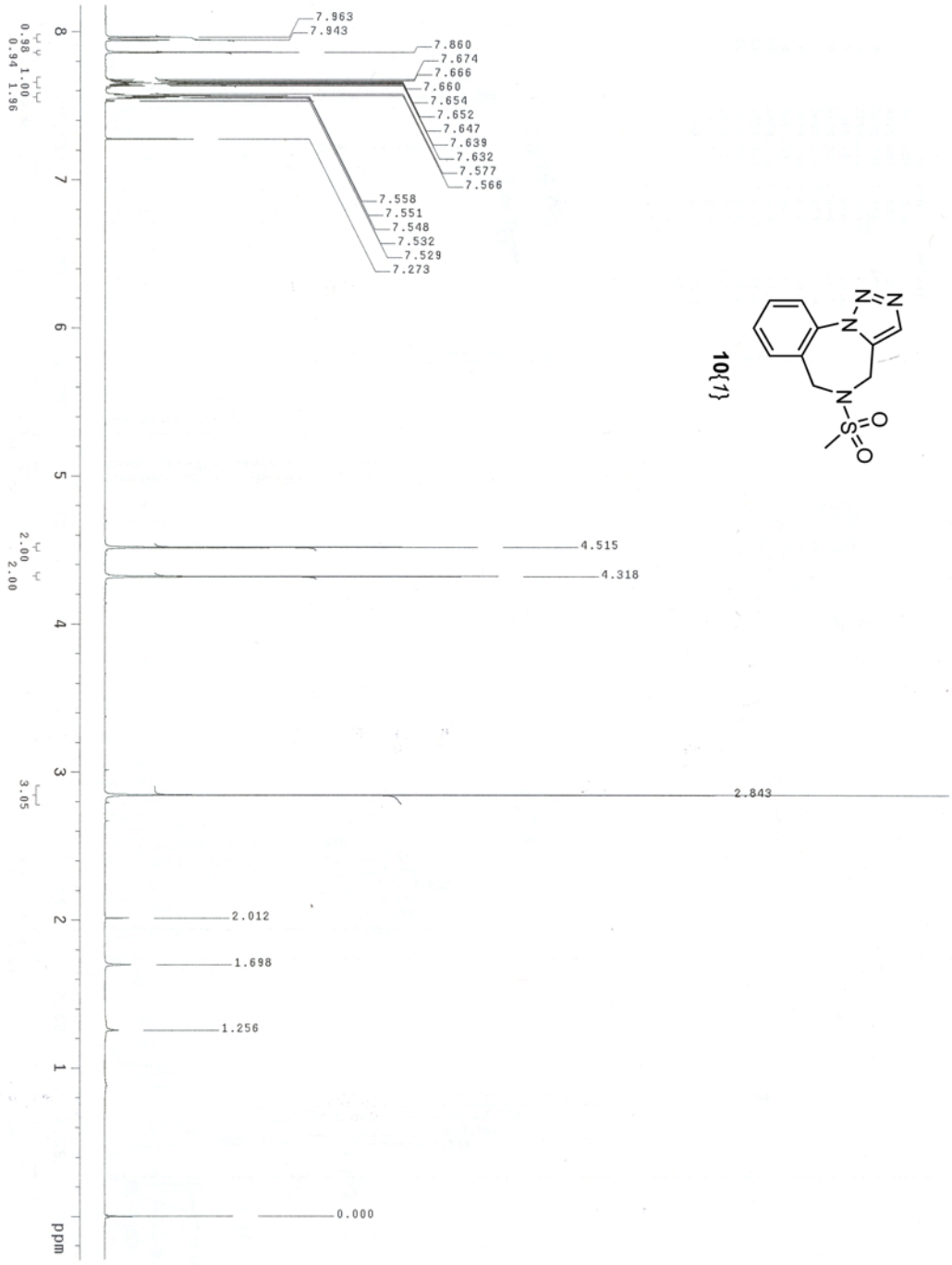
42.377
40.070
39.341
36.610
28.463
ppm
Br
N
N
N
O
9{12}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7.652
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7.639
7.632
7.577
7.566
7.558
7.551
7.548
7.532
7.529
7.273
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1.698
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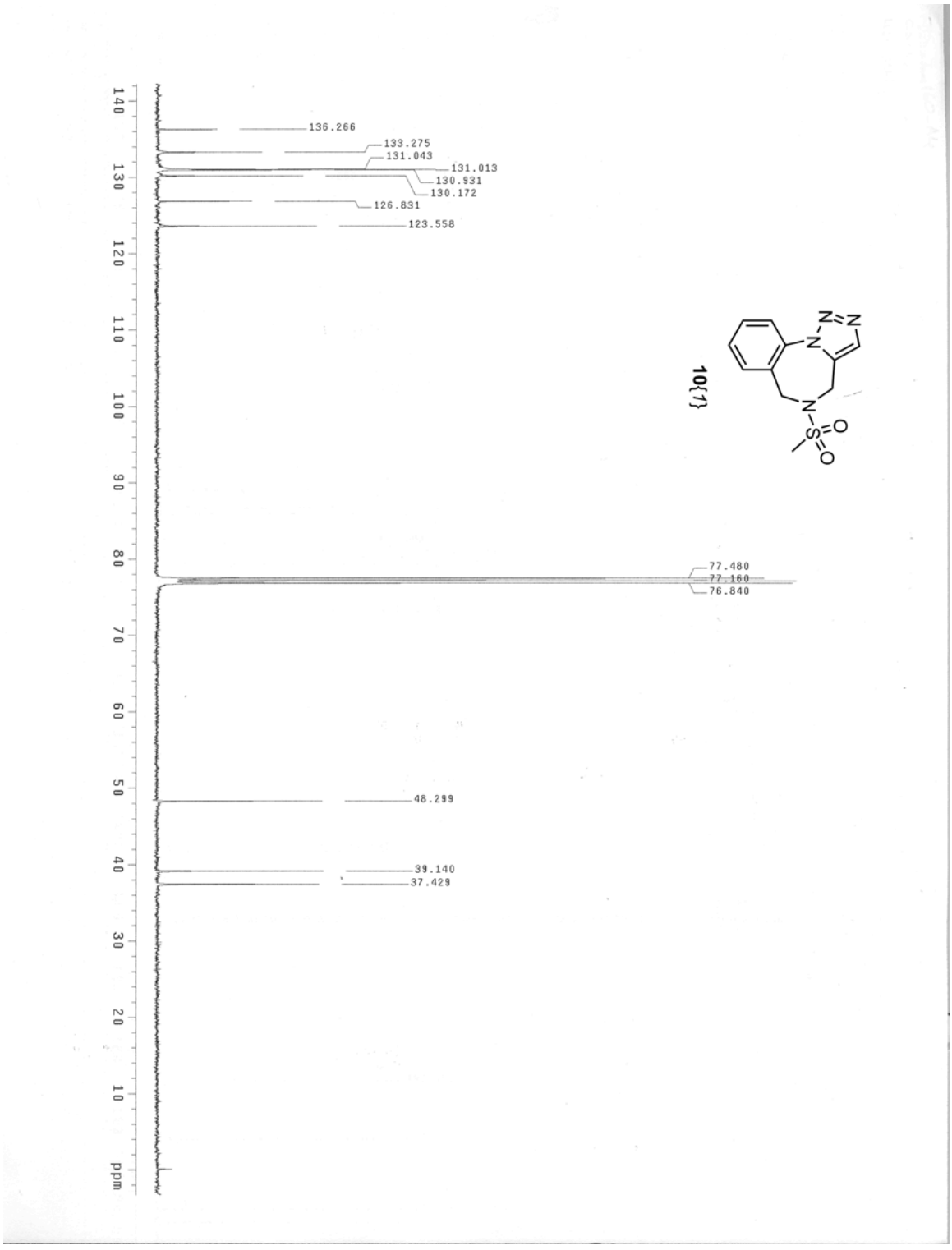
ppm
10{1}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123.558
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77.160
76.840
48.299
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130
120
110
100
90
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70
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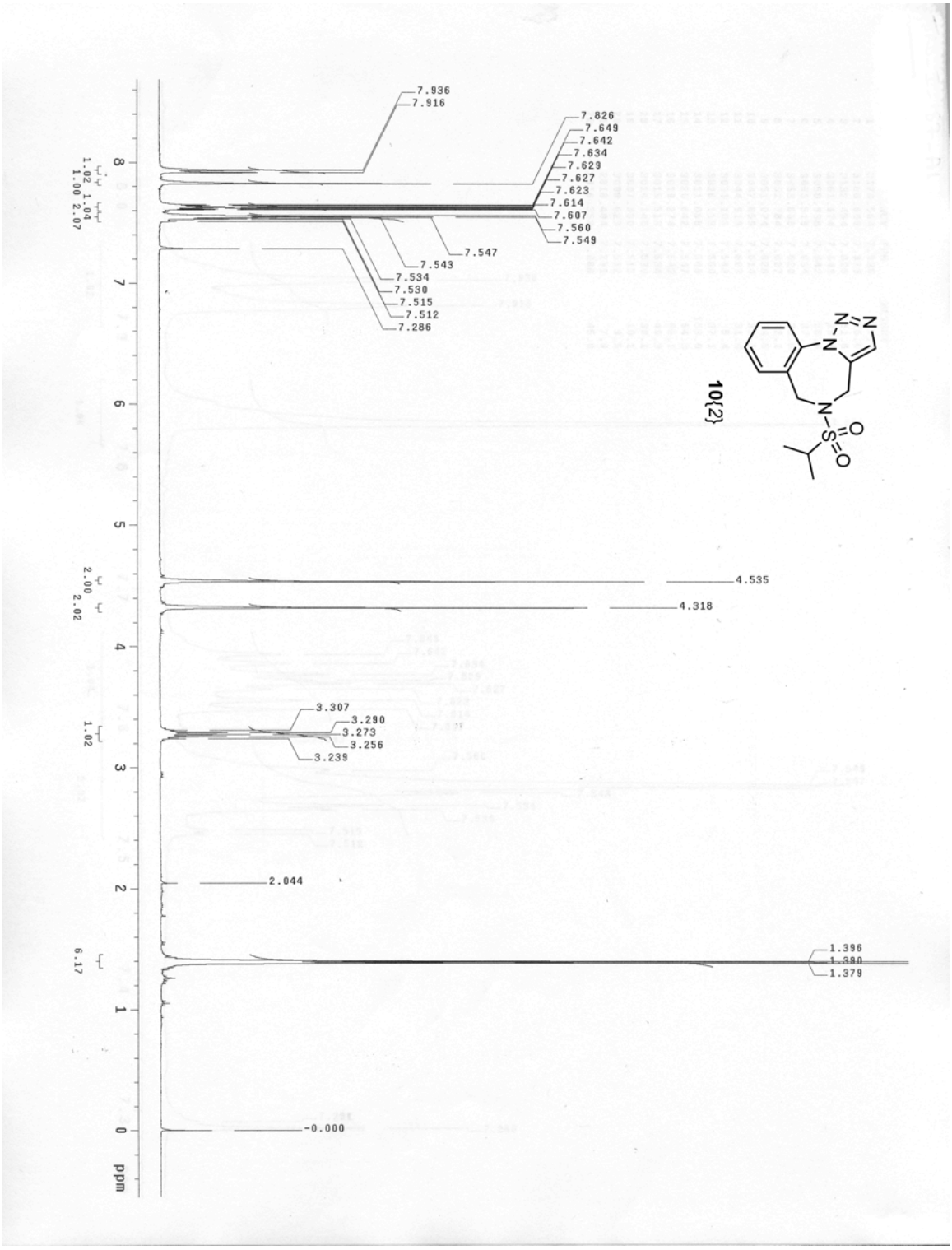
50
40
30
20
10
ppm
10{7}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7.916
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7.642
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7.627
7.623
7.614
7.607
7.560
7.549
7.547
7.543
7.534
7.530
7.515
7.512
7.286
10{2}
4.535
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3.290
3.273
3.256
3.239
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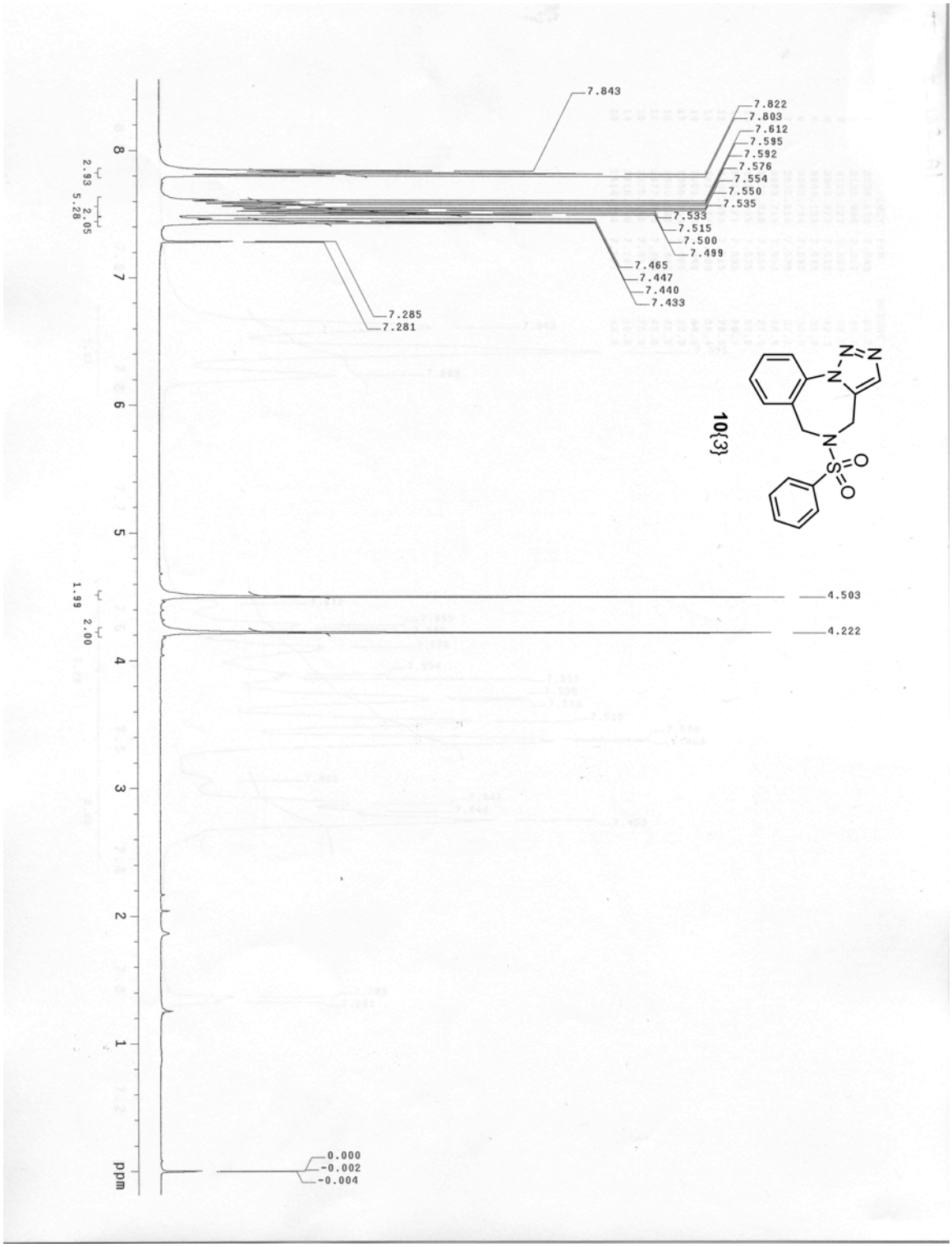
ppm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7.576
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7.533
7.515
7.500
7.499
7.465
7.447
7.440
7.433
7.285
7.281
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-0.004
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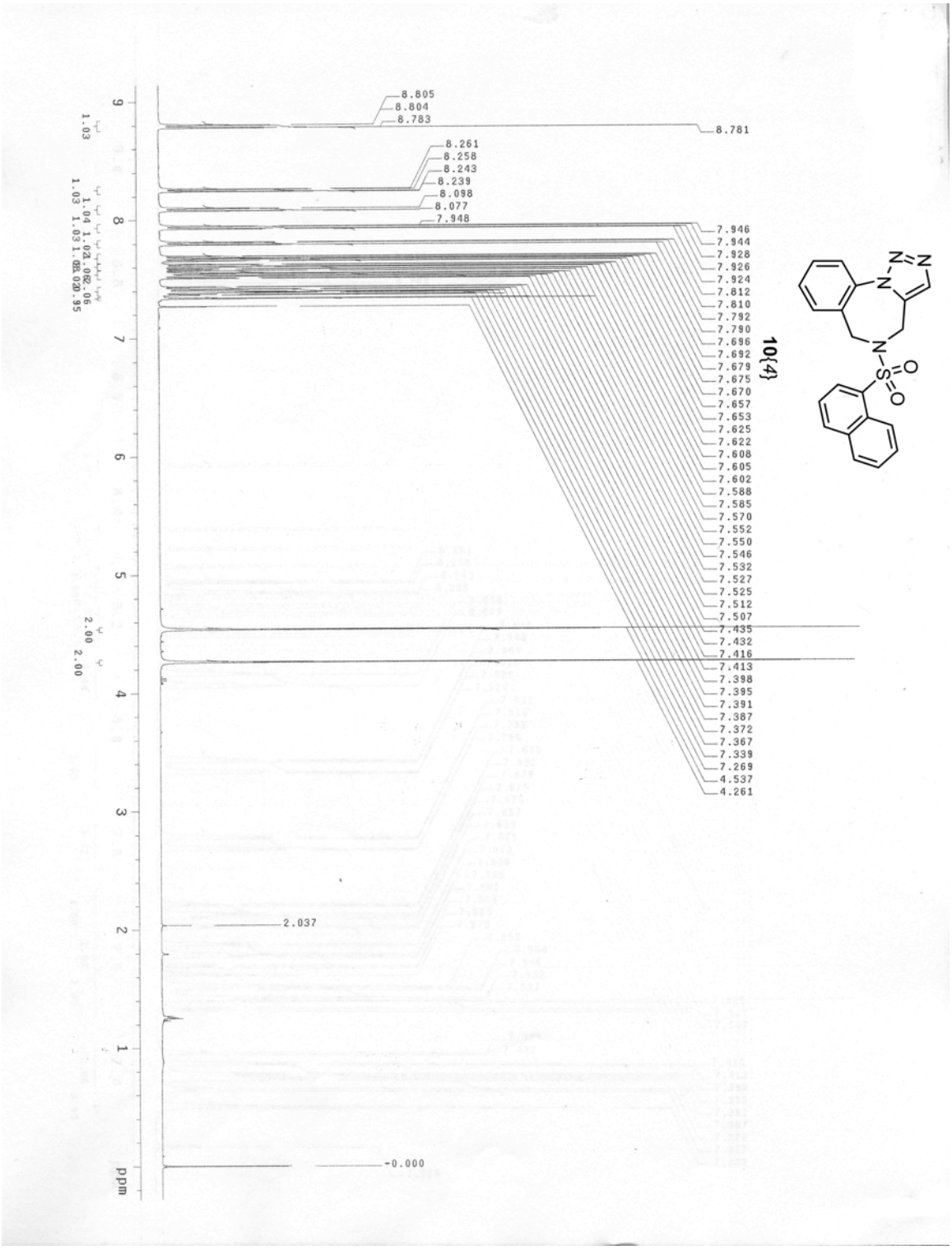
2.00
10{3}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8.077
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7.944
7.928
7.926
7.924
7.812
7.810
7.792
7.790
7.696
7.692
7.679
7.675
7.670
7.657
7.653
7.625
7.622
7.608
7.605
7.602
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7.570
7.552
7.550
7.546
7.532
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7.525
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7.432
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7.413
7.398
7.395
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7.269
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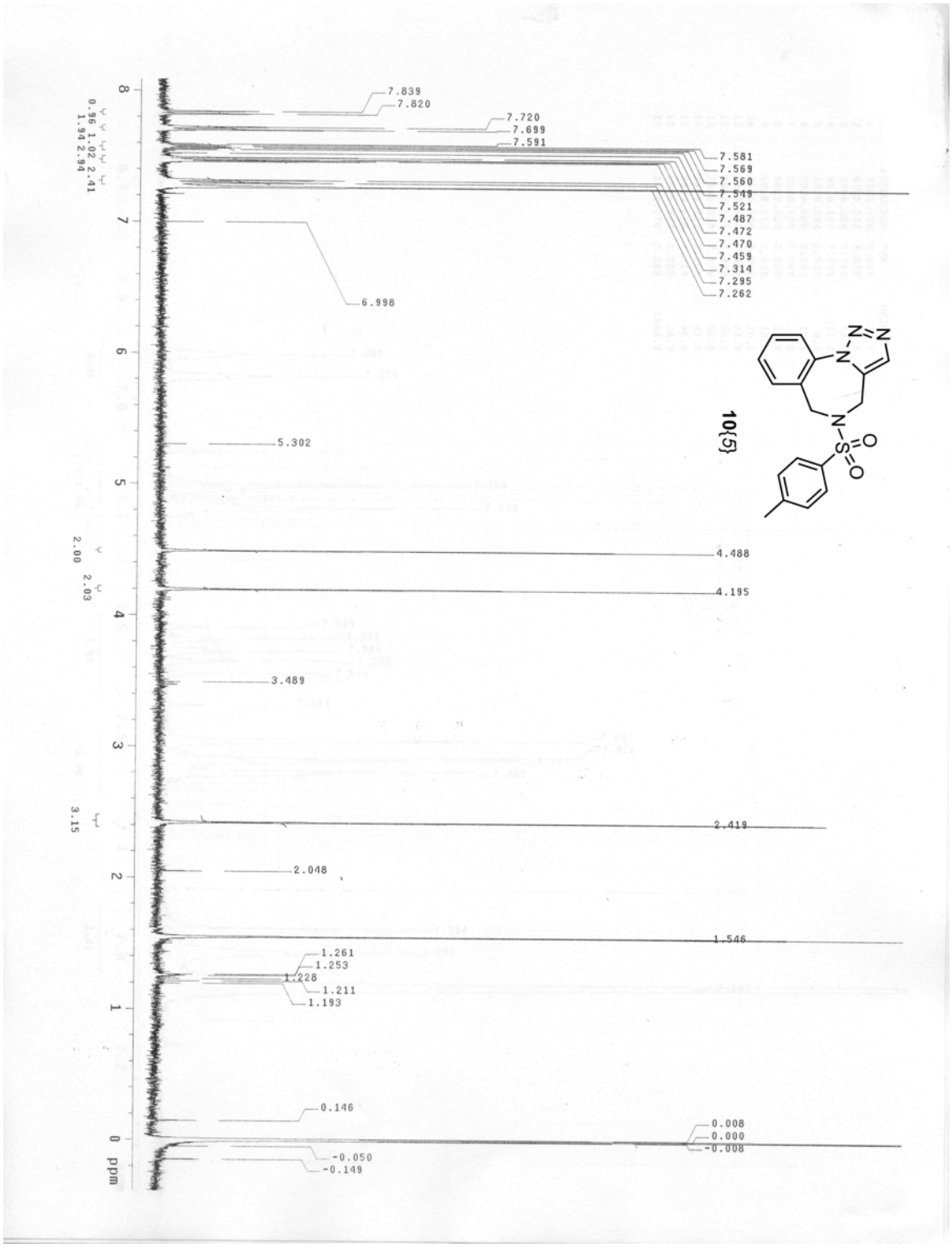
ppm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7.720
7.699
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7.560
7.549
7.521
7.487
7.472
7.470
7.459
7.314
7.295
7.262
6.998
5.302
4.488
4.195
3.489
2.419
2.048
1.546
1.261
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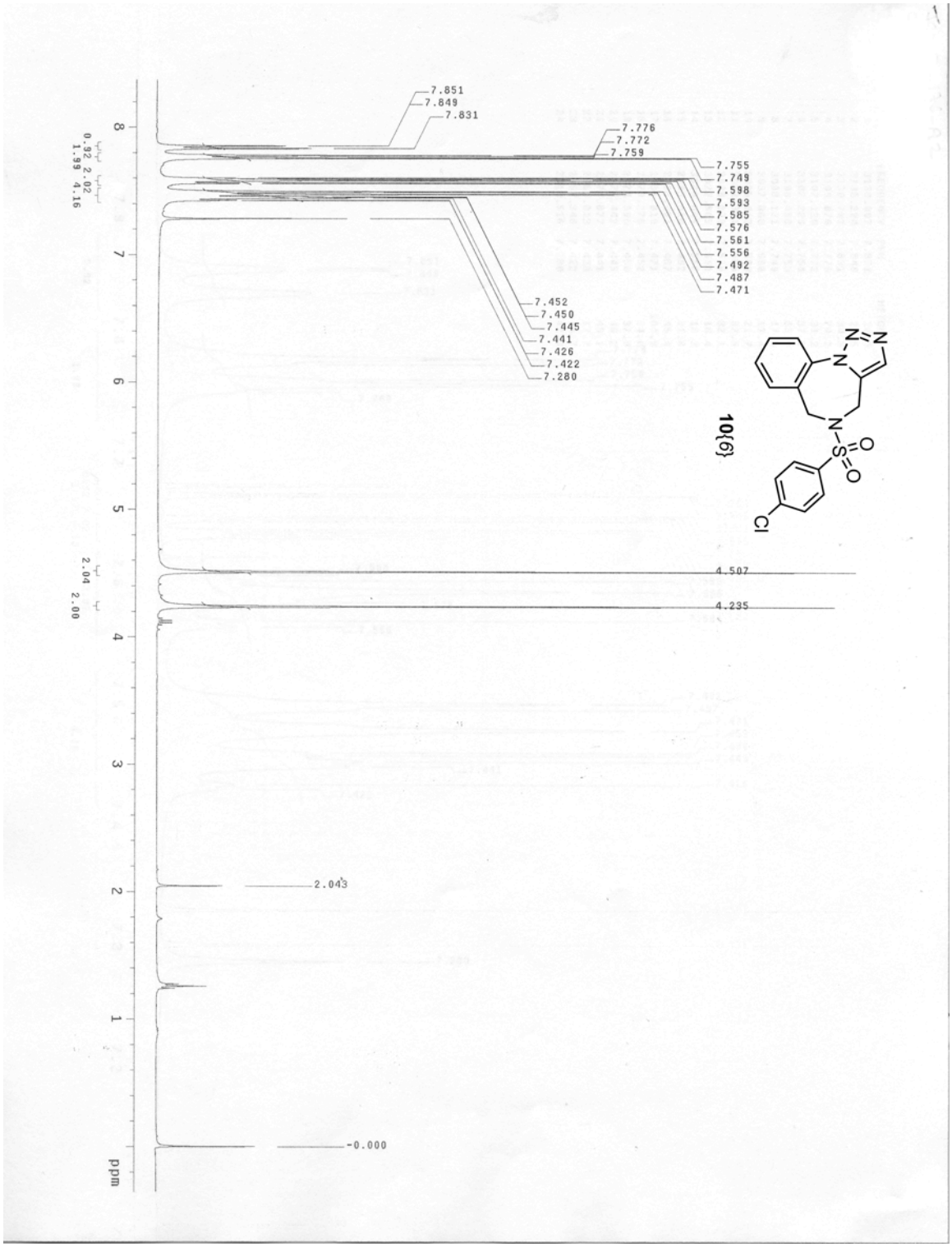
10(5)
ppm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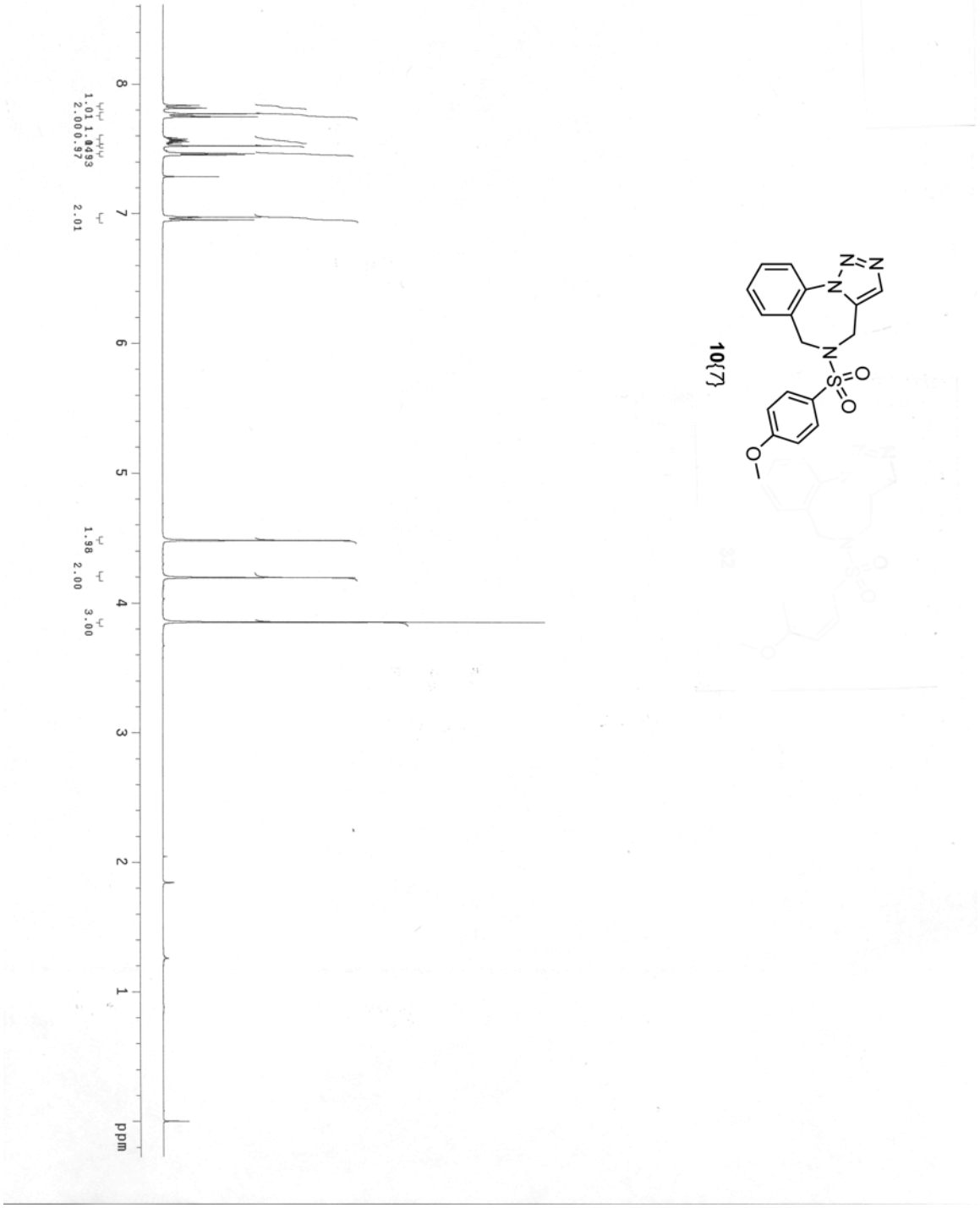
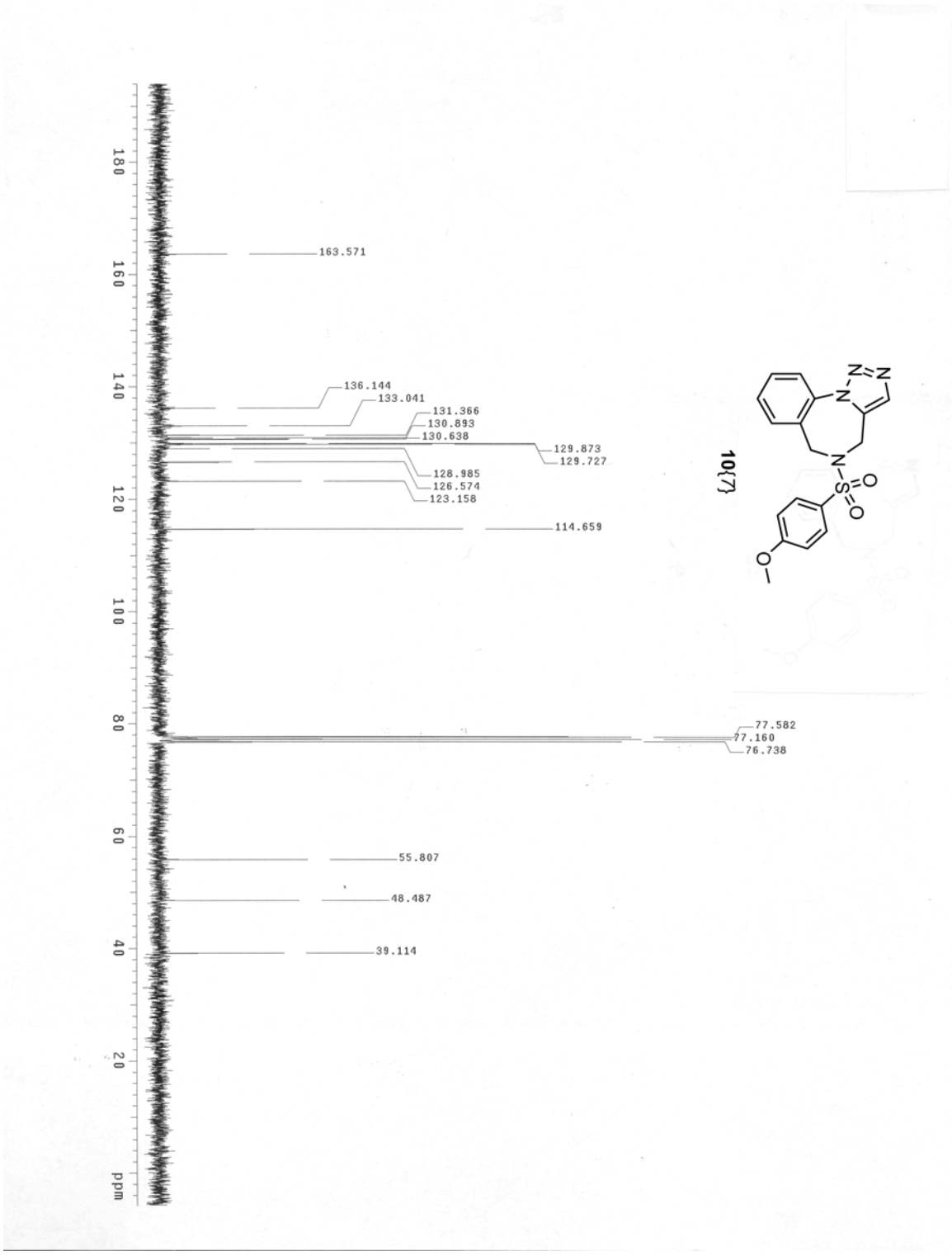
7.598
7.593
7.585
7.576
7.561
7.556
7.492
7.487
7.471
7.452
7.450
7.445
7.441
7.426
7.422
7.280
4.507
4.235
2.043
-0.000
0.92 2.02
1.99 4.16
2.04 2.00
ppm
10{6}
Cl


10(7)
ppm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130.638
129.873
129.727
128.985
126.574
123.158
114.659
77.582
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48.487
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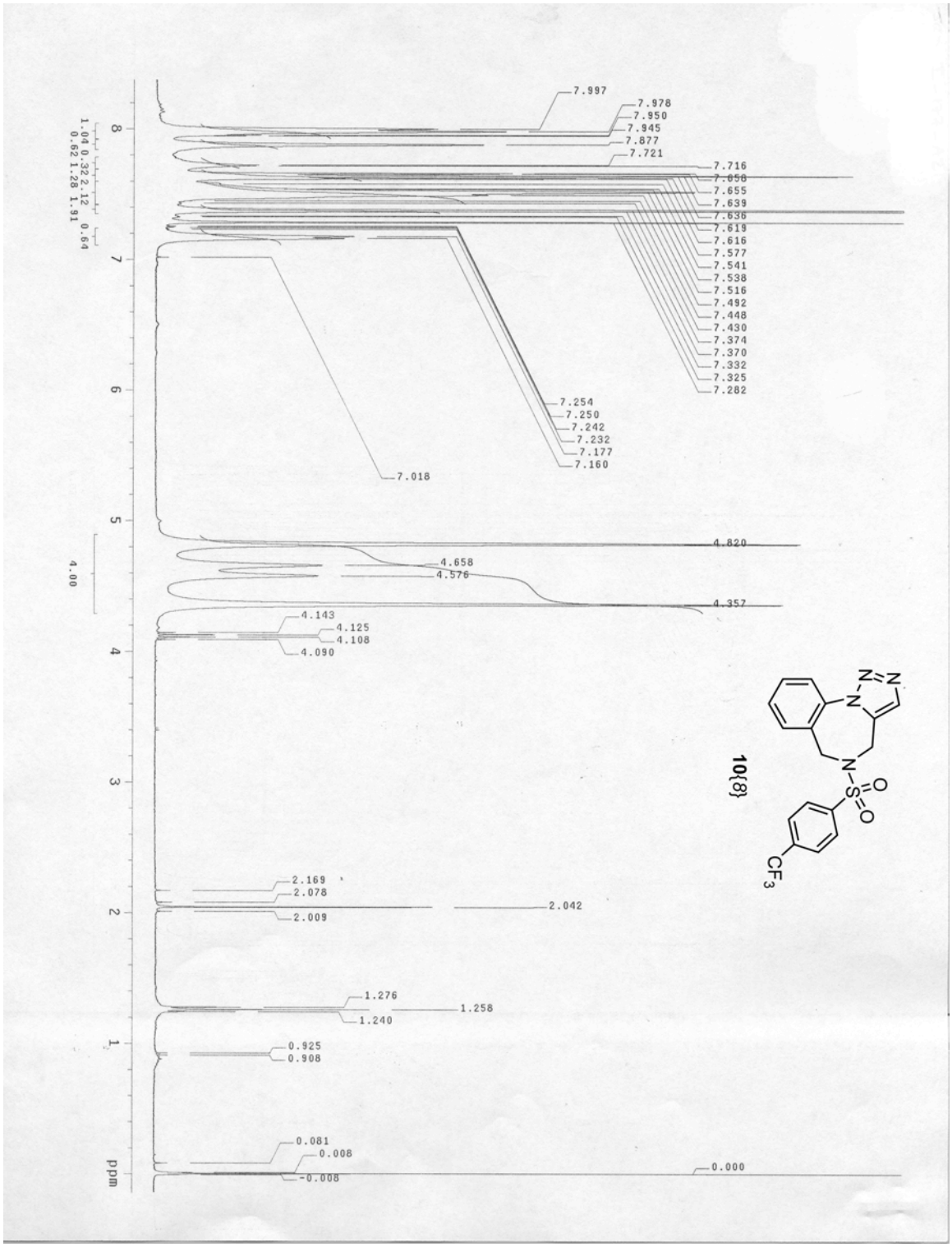
180
160
140
120
100
80
60
40
20
ppm
10{7}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7.978
7.950
7.945
7.877
7.721
7.716
7.658
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7.616
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7.516
7.492
7.448
7.430
7.374
7.370
7.332
7.325
7.282
7.254
7.250
7.242
7.232
7.177
7.160
7.018
4.820
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4.357
4.143
4.125
4.108
4.090
2.169
2.078
2.042
2.009
1.276
1.258
1.240
0.925
0.908
0.081
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0.62 1.28 1.91
4.00
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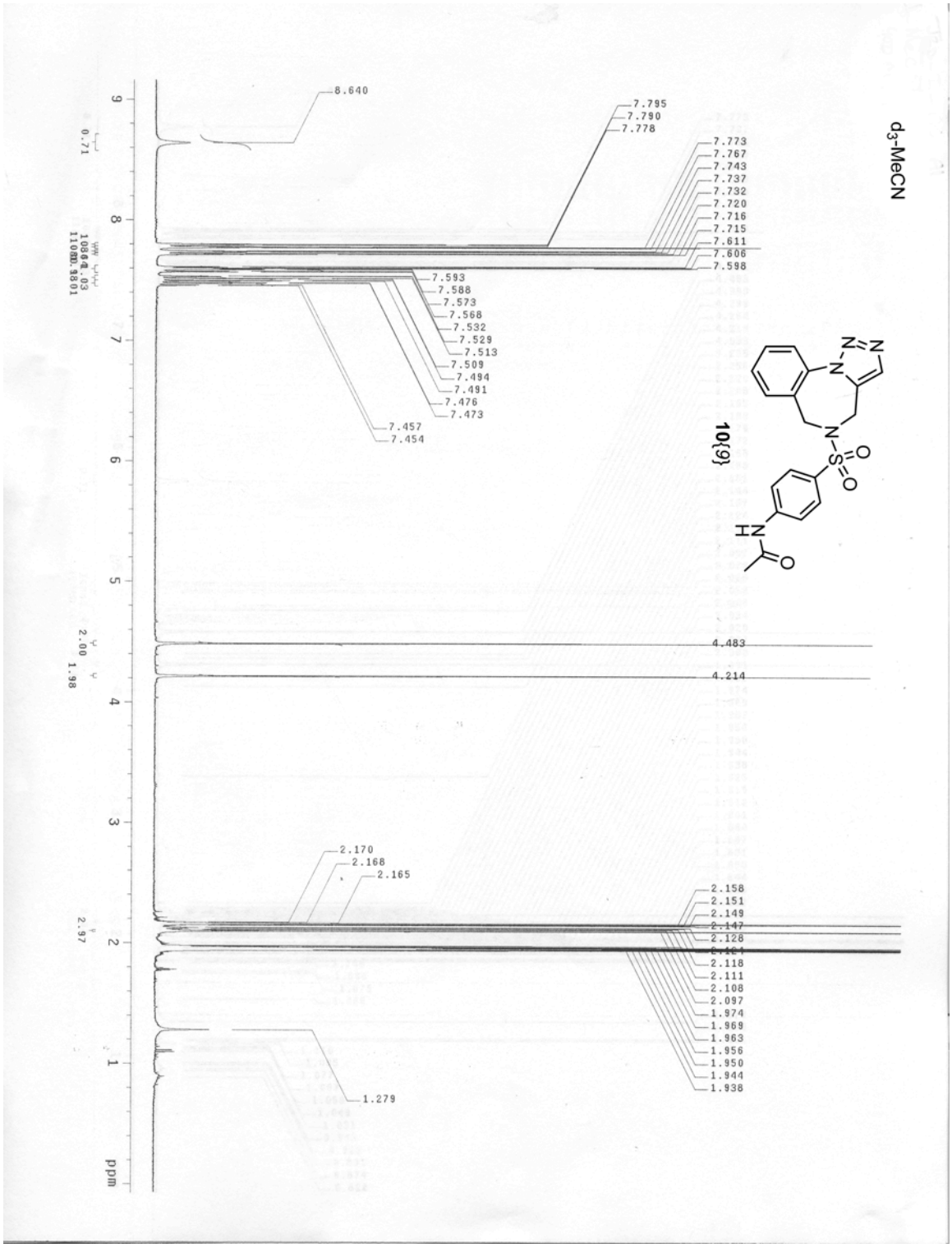
CF3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7.743
7.737
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7.720
7.716
7.715
7.611
7.606
7.598
7.593
7.588
7.573
7.568
7.532
7.529
7.513
7.509
7.494
7.491
7.476
7.473
7.457
7.454
4.483
4.214
2.170
2.168
2.165
2.158
2.151
2.149
2.147
2.128
2.118
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1.963
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1.950
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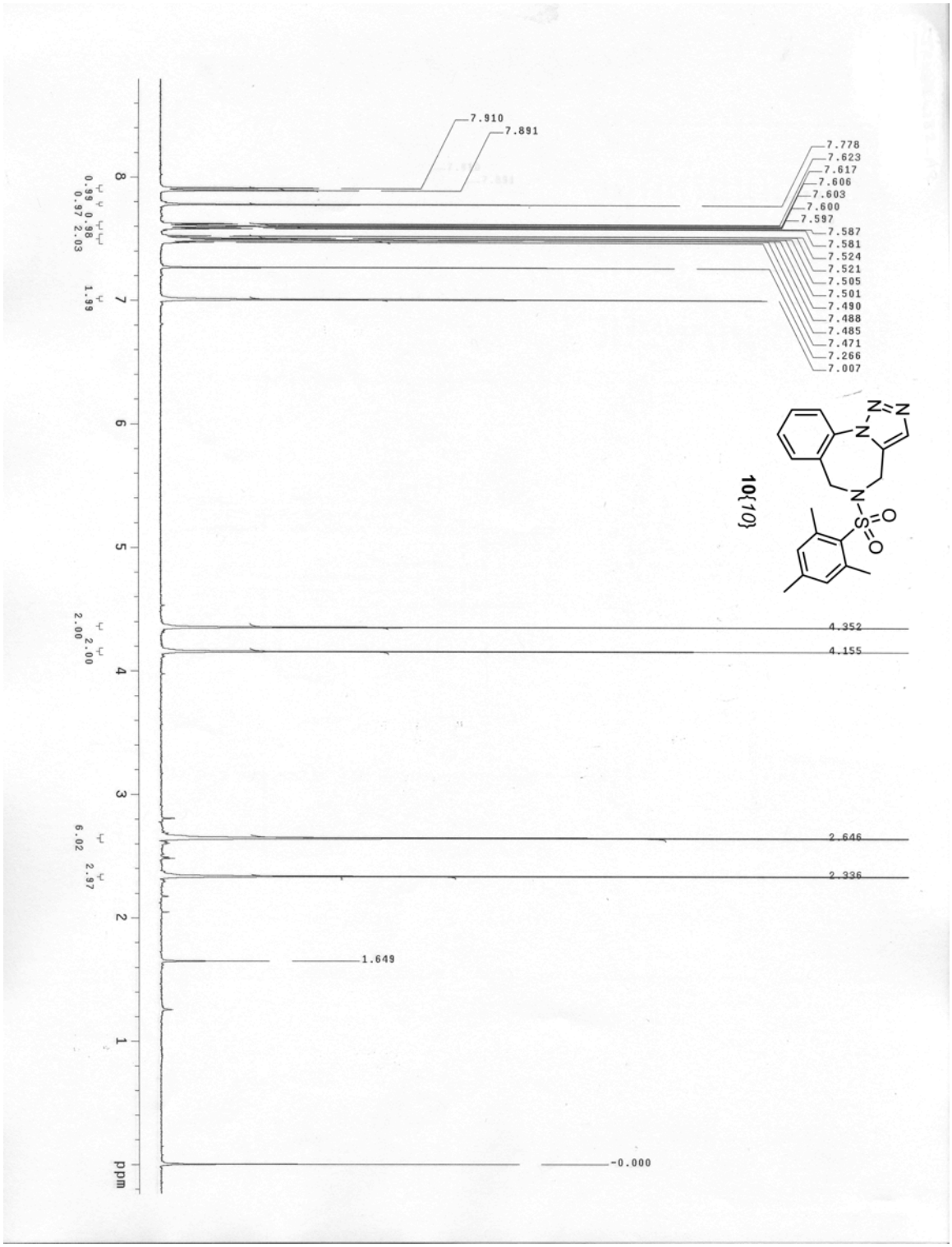
1.279
ppm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7.778
7.623
7.617
7.606
7.603
7.600
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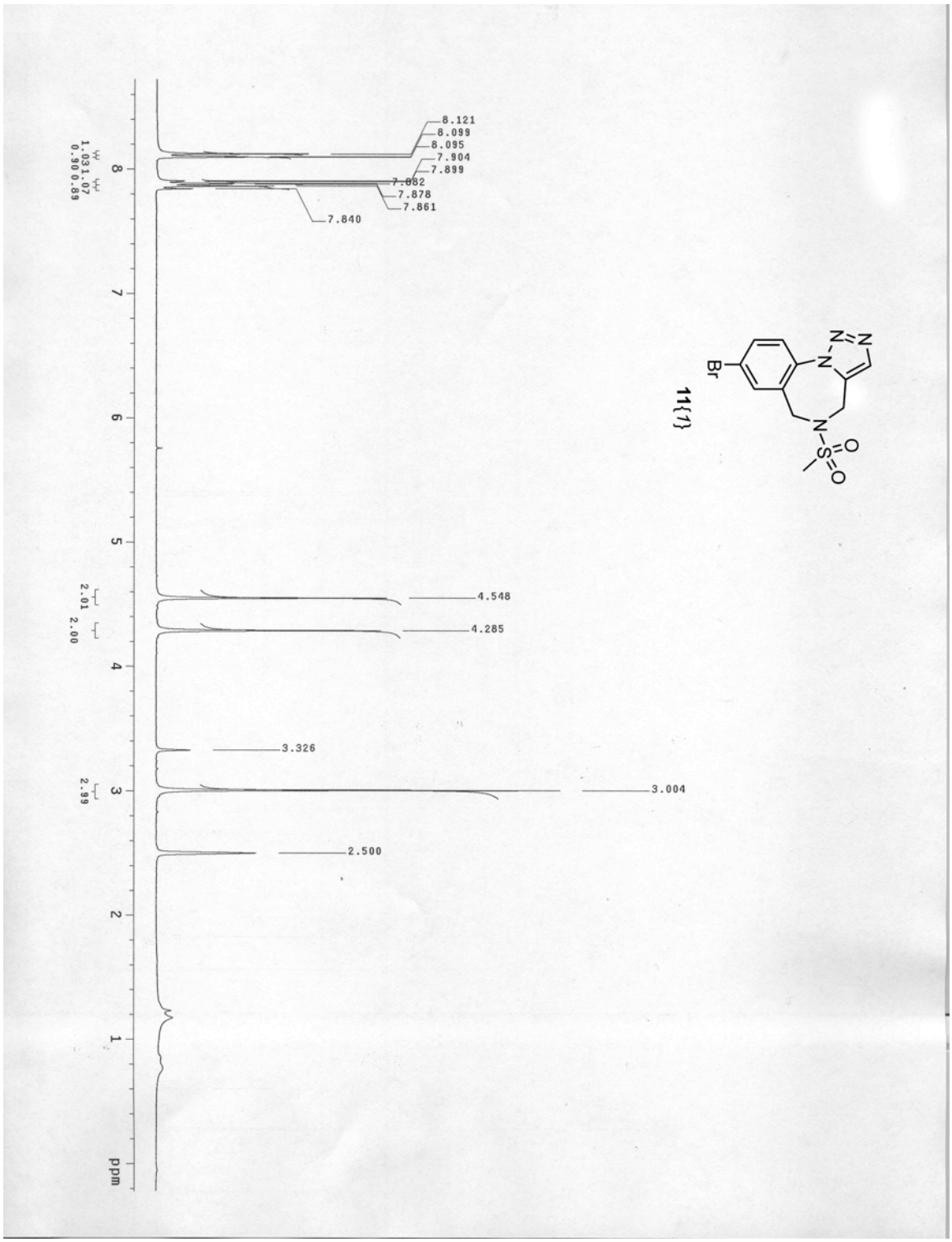
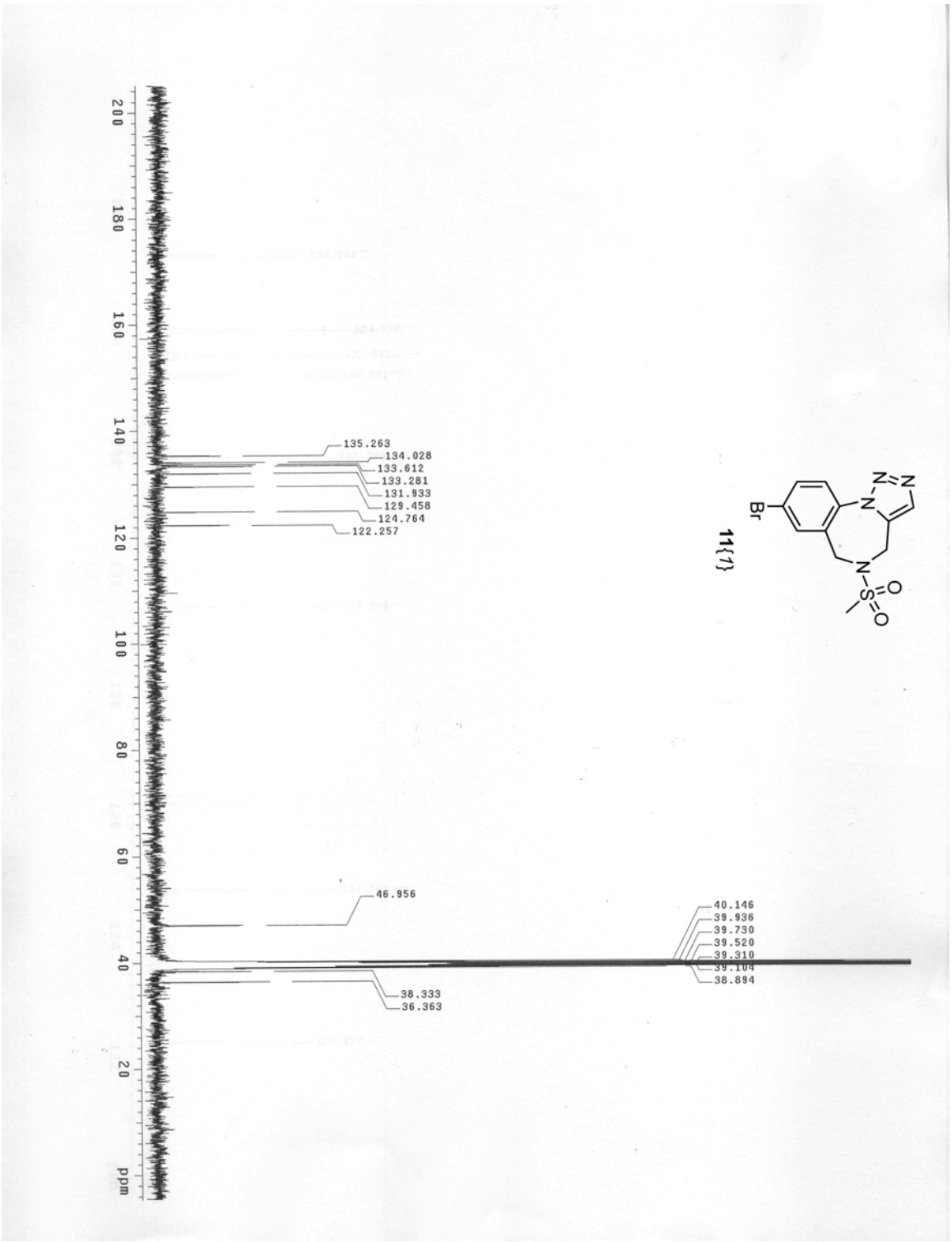
7.587
7.581
7.524
7.521
7.505
7.501
7.490
7.488
7.485
7.471
7.266
7.007
4.352
4.155
2.646
2.336
1.649
-0.000
ppm
10{10}


8.121
8.099
8.095
7.904
7.899
7.882
7.878
7.861
7.840
4.548
4.285
3.326
3.004
2.500
1.03
0.90
1.07
0.89
2.01
2.00
2.99
ppm
Br
N
N
N
S
O
O
11{1}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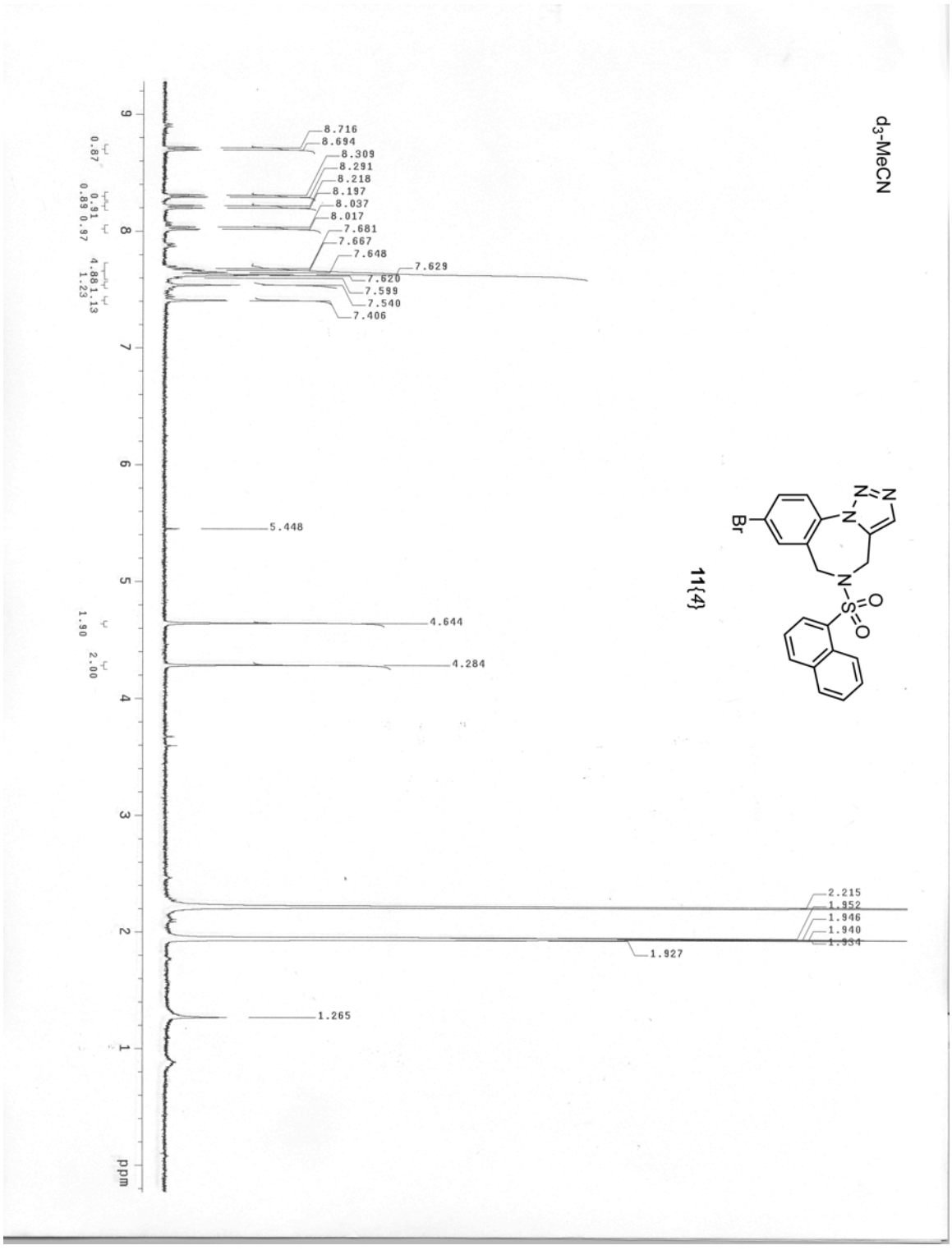
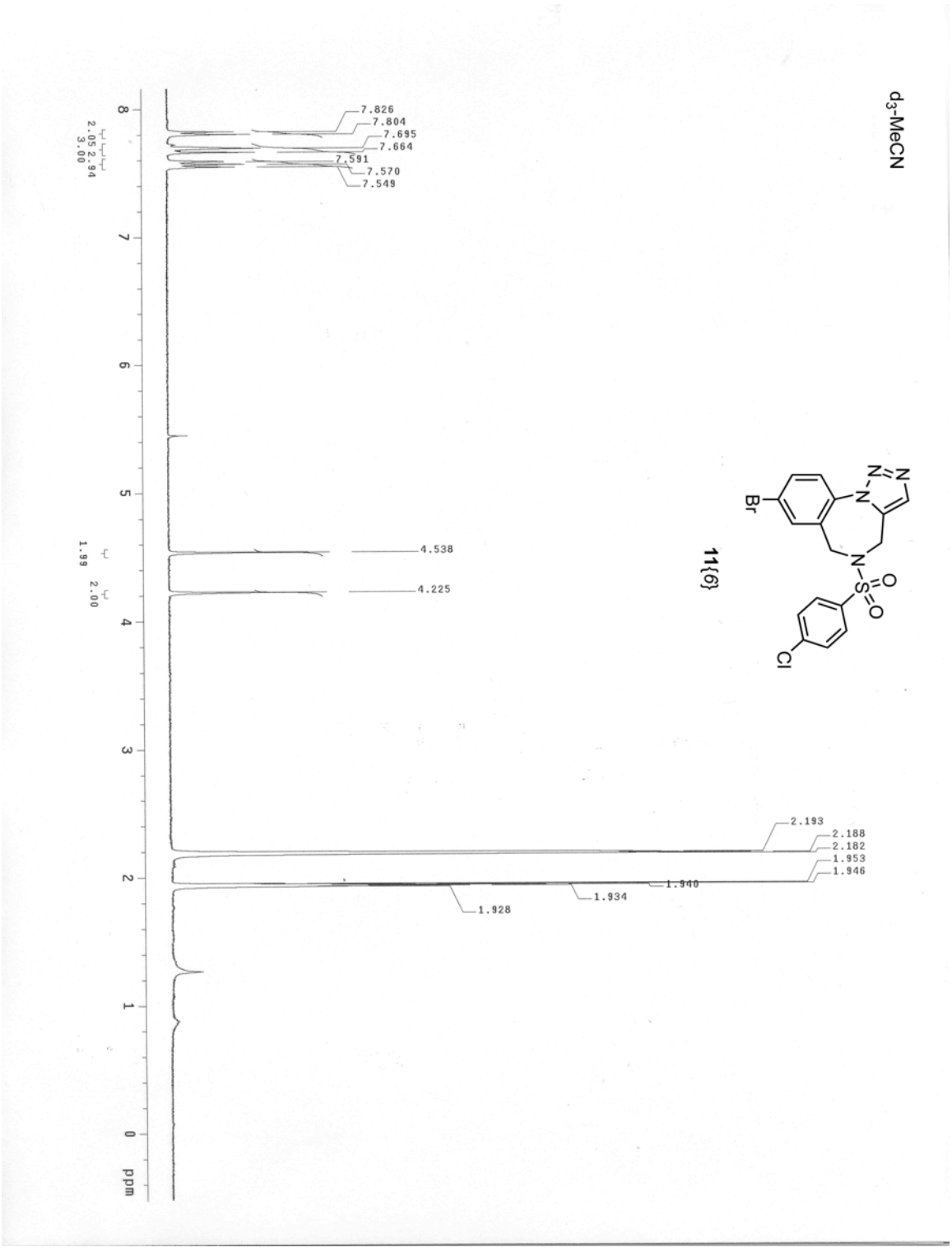
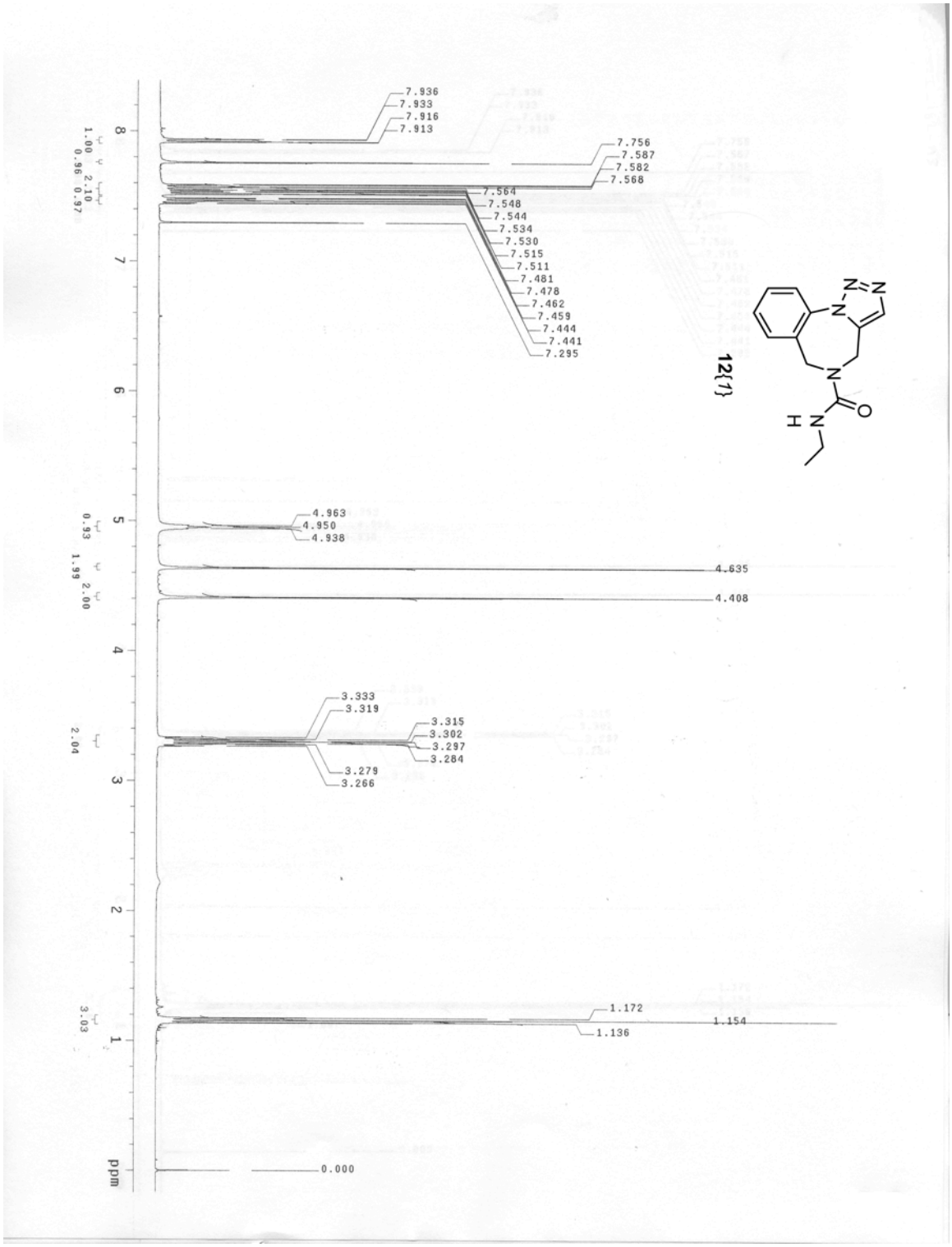
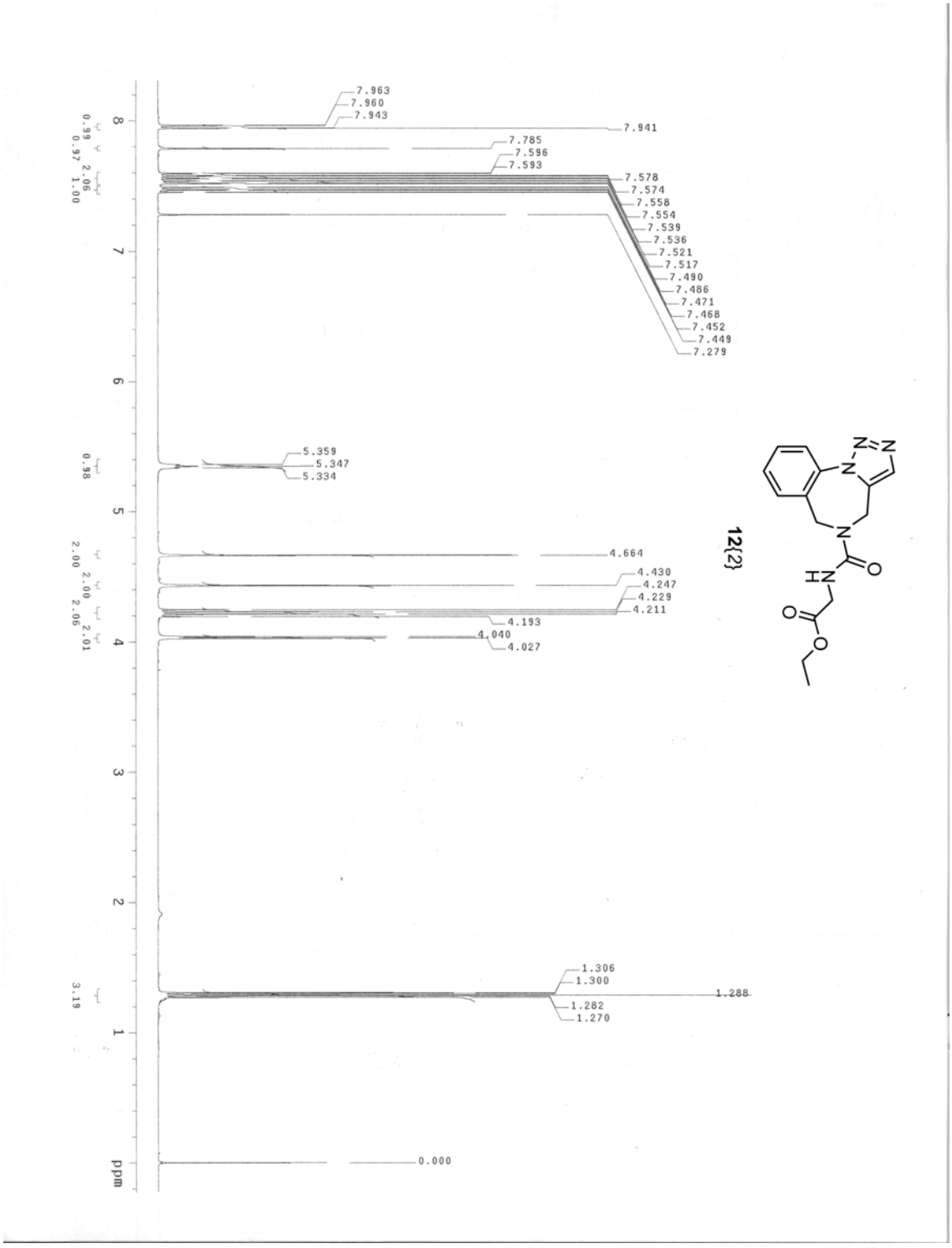
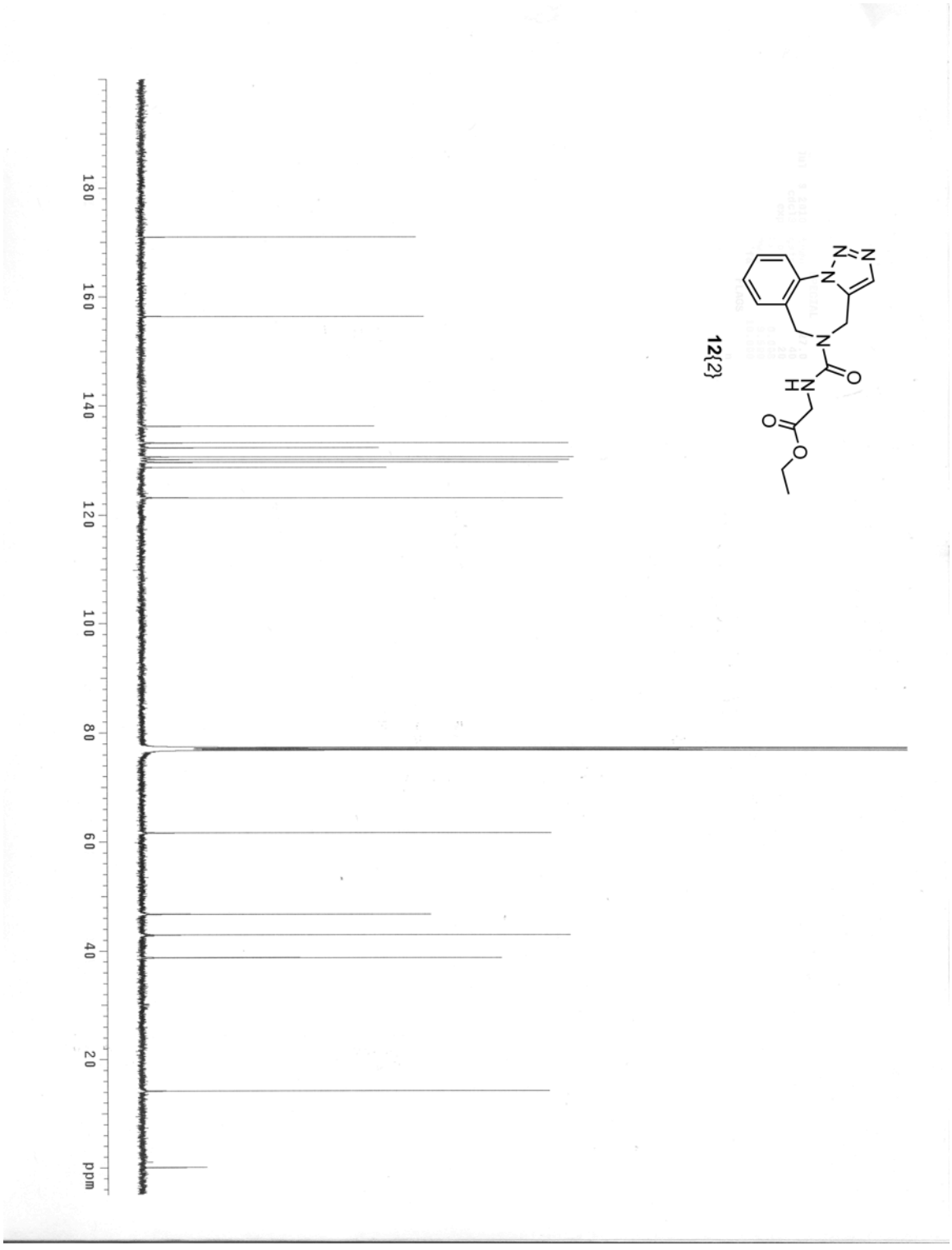
134.028
133.612
133.281
131.933
129.458
124.764
122.257
46.956
40.146
39.936
39.730
39.520
39.310
39.104
38.894
38.333
36.363
200
180
160
140
120
100
80
60
40
20
ppm
Br
N
N
N
N
S
O
O
11{1}

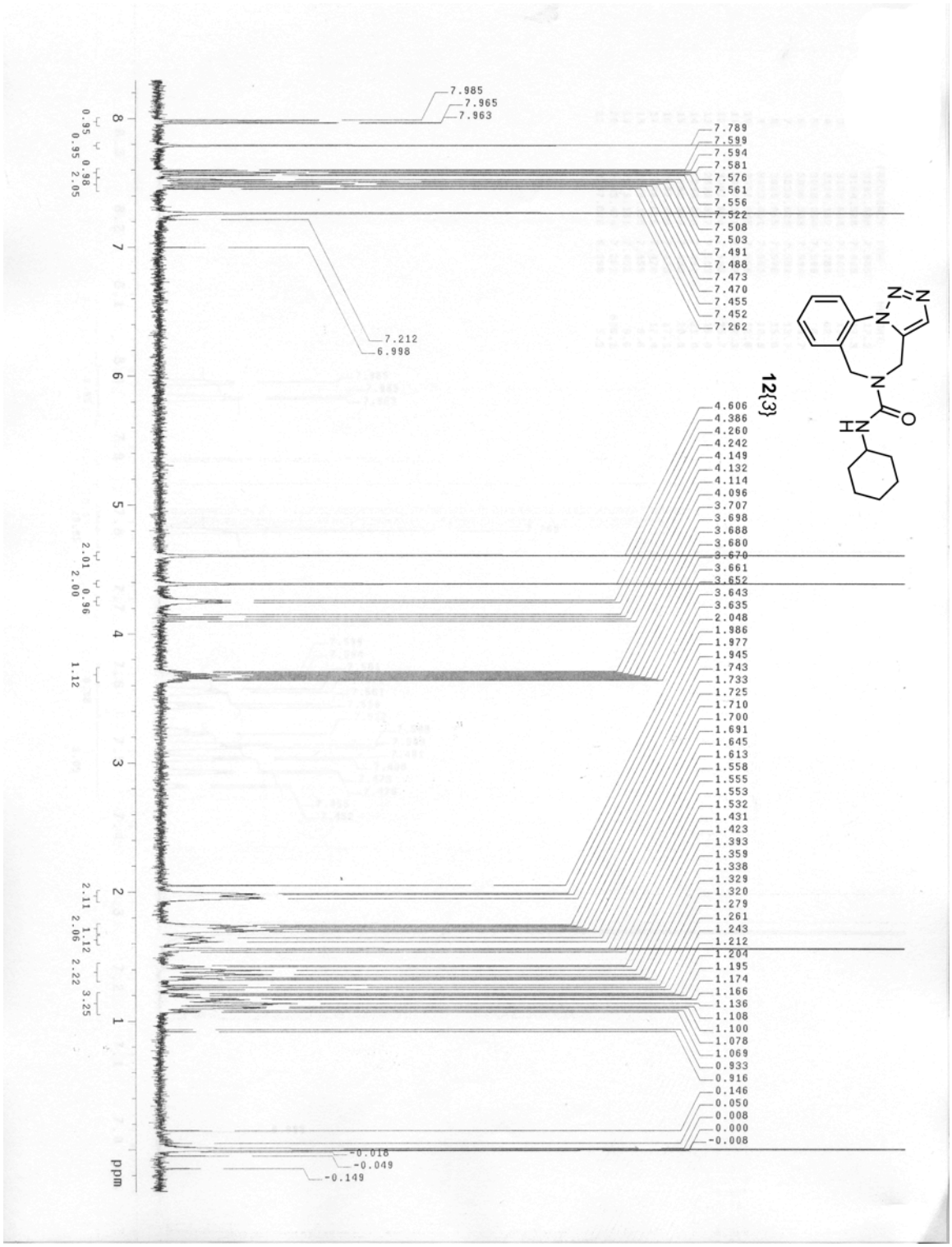

d3-MeCN
11{4}
Br
N
N
N
S
O
O
8.716
8.694
8.309
8.291
8.218
8.197
8.037
8.017
7.681
7.667
7.648
7.629
7.620
7.599
7.540
7.406
5.448
4.644
4.284
2.215
1.952
1.946
1.940
1.934
1.927
1.265
ppm


d3-MeCN
11{6}
Br
Cl
7.826
7.804
7.695
7.664
7.591
7.570
7.549
4.538
4.225
2.193
2.188
2.182
1.953
1.946
1.940
1.934
1.928
ppm


7.936
7.933
7.916
7.913
7.756
7.587
7.582
7.568
7.564
7.548
7.544
7.534
7.530
7.515
7.511
7.481
7.478
7.462
7.459
7.444
7.441
7.295
12{1}
4.963
4.950
4.938
4.635
4.408
3.333
3.319
3.315
3.302
3.297
3.284
3.279
3.266
1.172
1.154
1.136
0.000
ppm


7.963
7.960
7.943
7.941
7.785
7.596
7.593
7.578
7.574
7.558
7.554
7.539
7.536
7.521
7.517
7.490
7.486
7.471
7.468
7.452
7.449
7.279
5.359
5.347
5.334
4.664
4.430
4.247
4.229
4.211
4.193
4.040
4.027
1.306
1.300
1.288
1.282
1.270
0.000
ppm
12(2)


12{2}
180
160
140
120
100
80
60
40
20
ppm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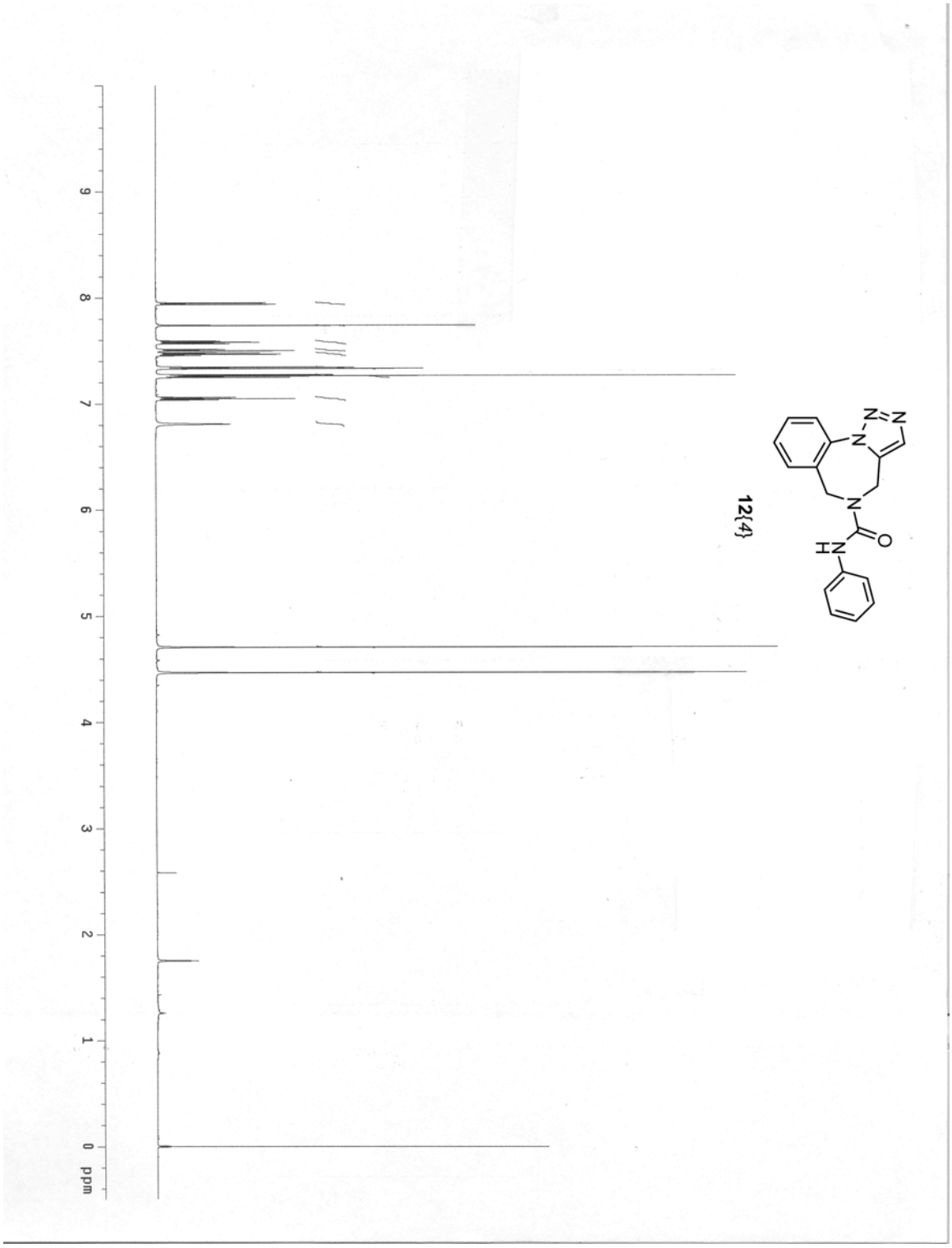
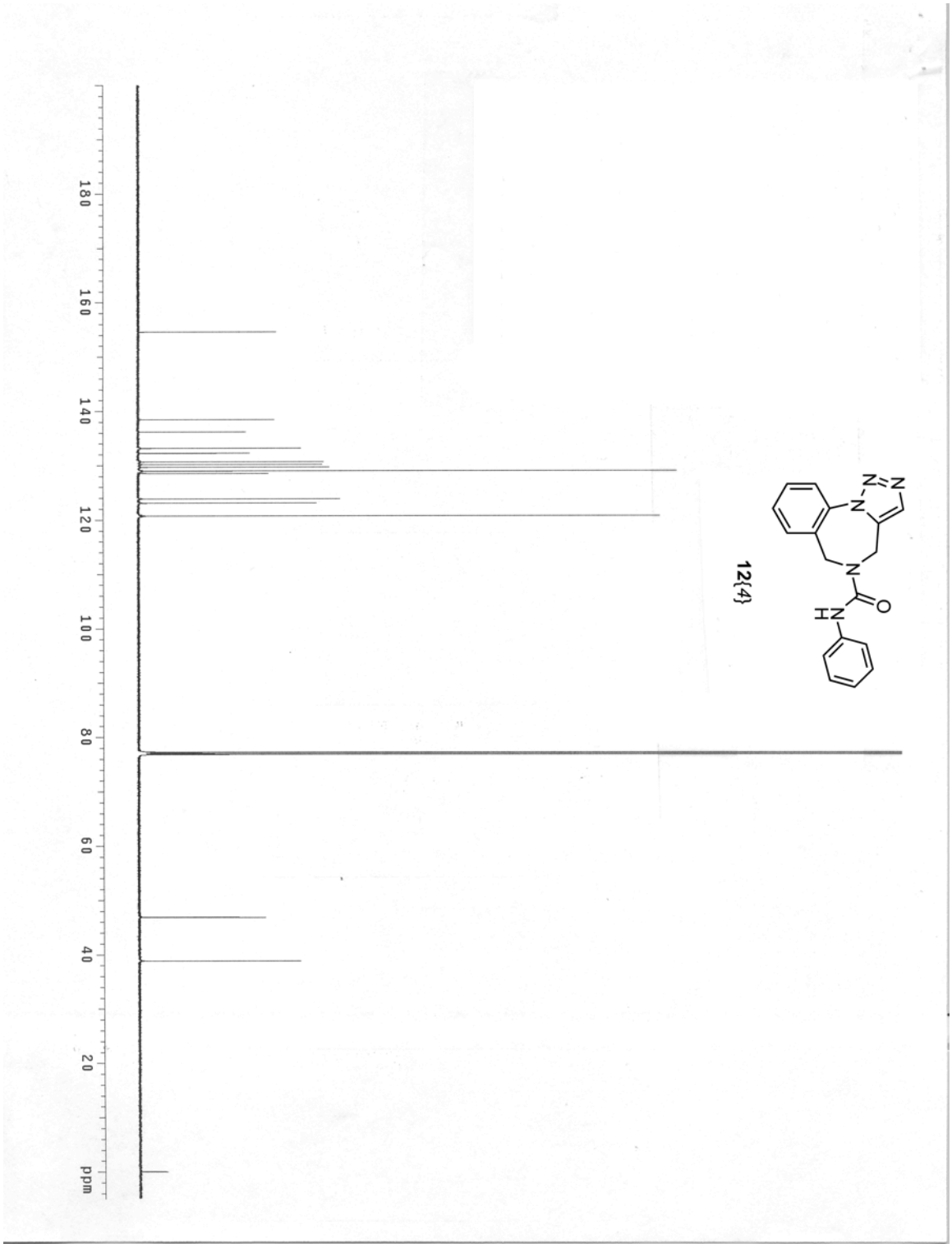
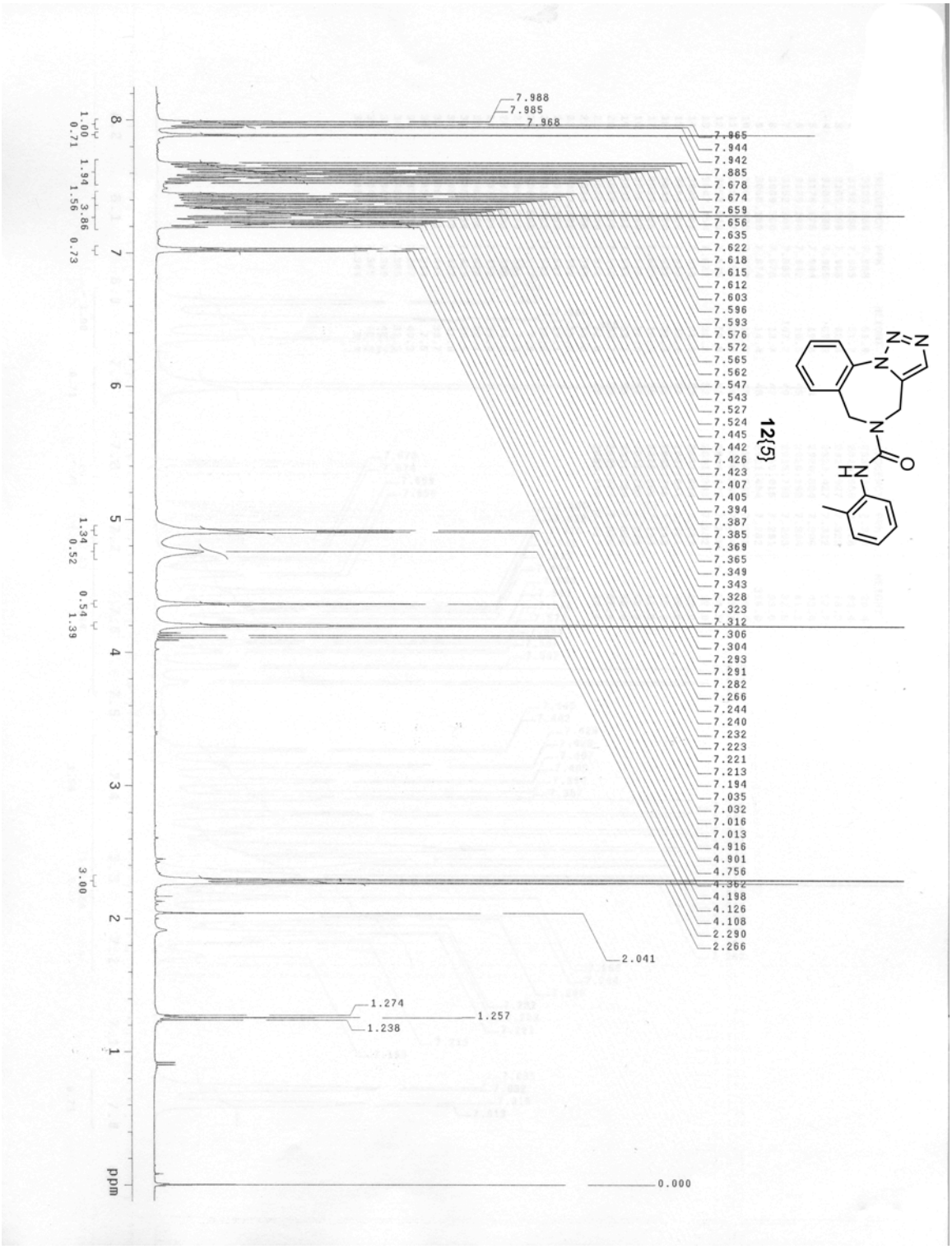
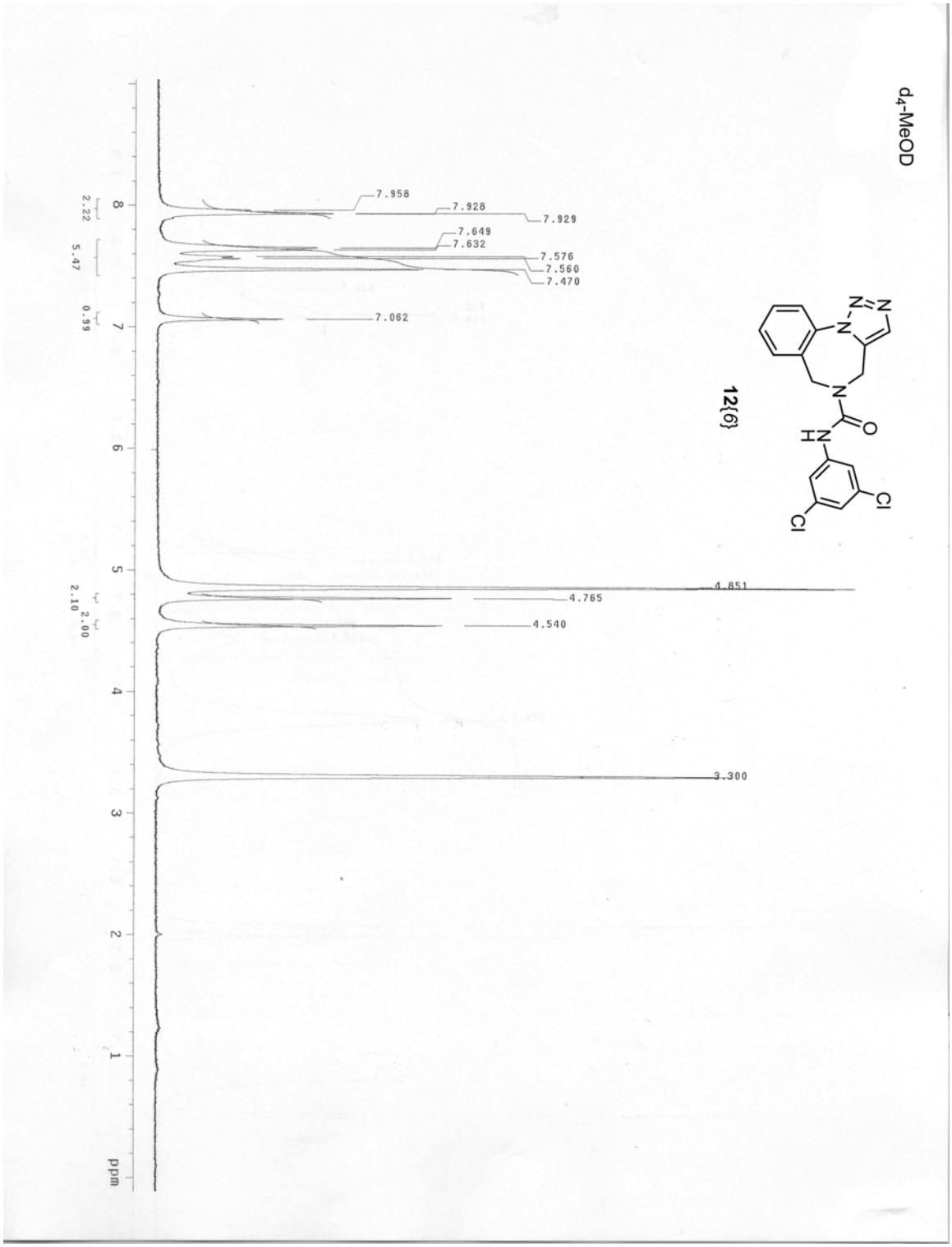
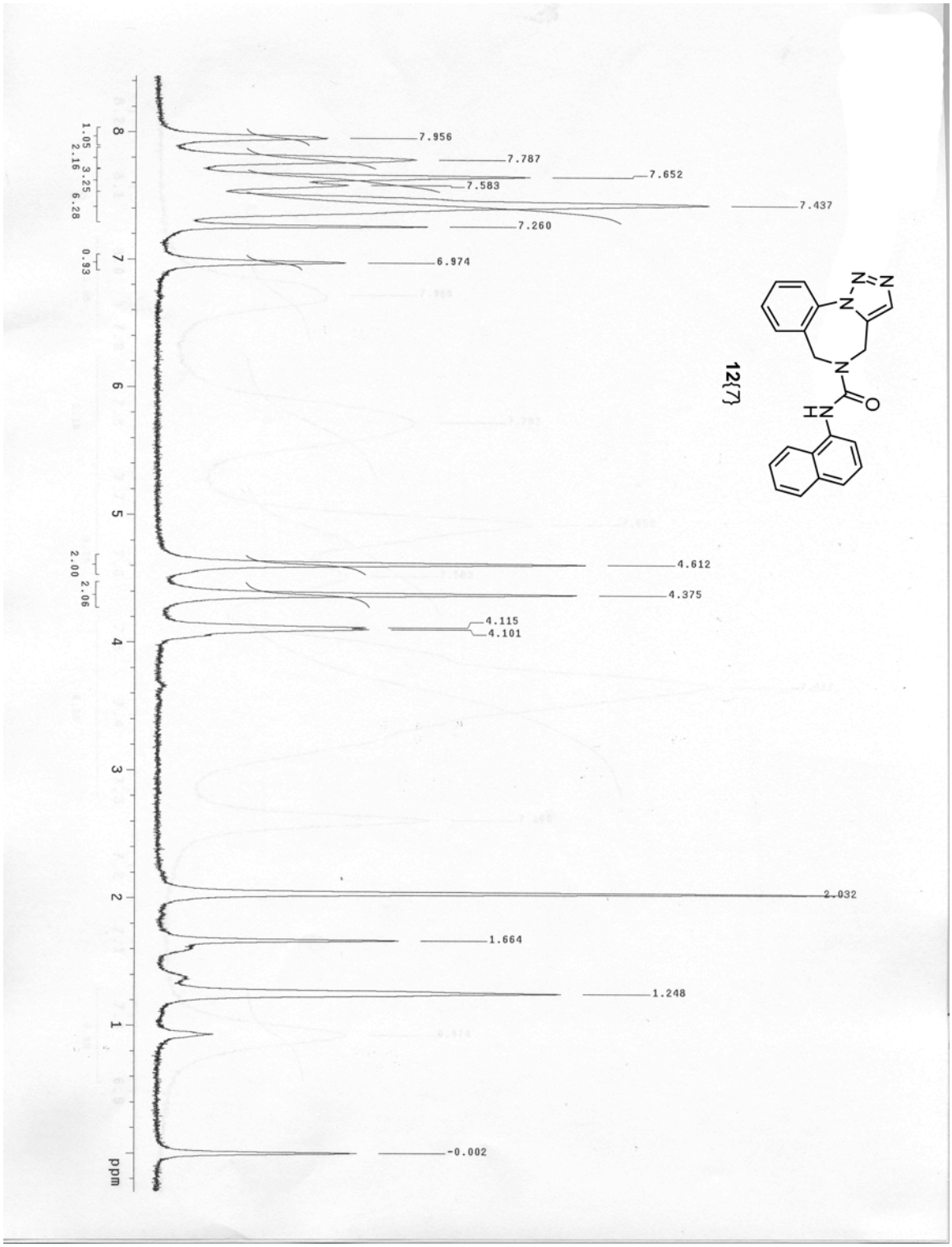
7.965
7.963
7.789
7.599
7.594
7.581
7.576
7.561
7.556
7.522
7.508
7.503
7.491
7.488
7.473
7.470
7.455
7.452
7.262
7.212
6.998
12{3}
4.606
4.386
4.260
4.242
4.149
4.132
4.114
4.096
3.707
3.698
3.688
3.680
3.670
3.661
3.652
3.643
3.635
2.048
1.986
1.977
1.945
1.743
1.733
1.725
1.710
1.700
1.691
1.645
1.613
1.558
1.555
1.553
1.532
1.431
1.423
1.393
1.359
1.338
1.329
1.320
1.279
1.261
1.243
1.212
1.204
1.195
1.174
1.166
1.136
1.108
1.100
1.078
1.069
0.933
0.916
0.146
0.050
0.008
0.000
-0.008
-0.016
-0.049
-0.149
ppm

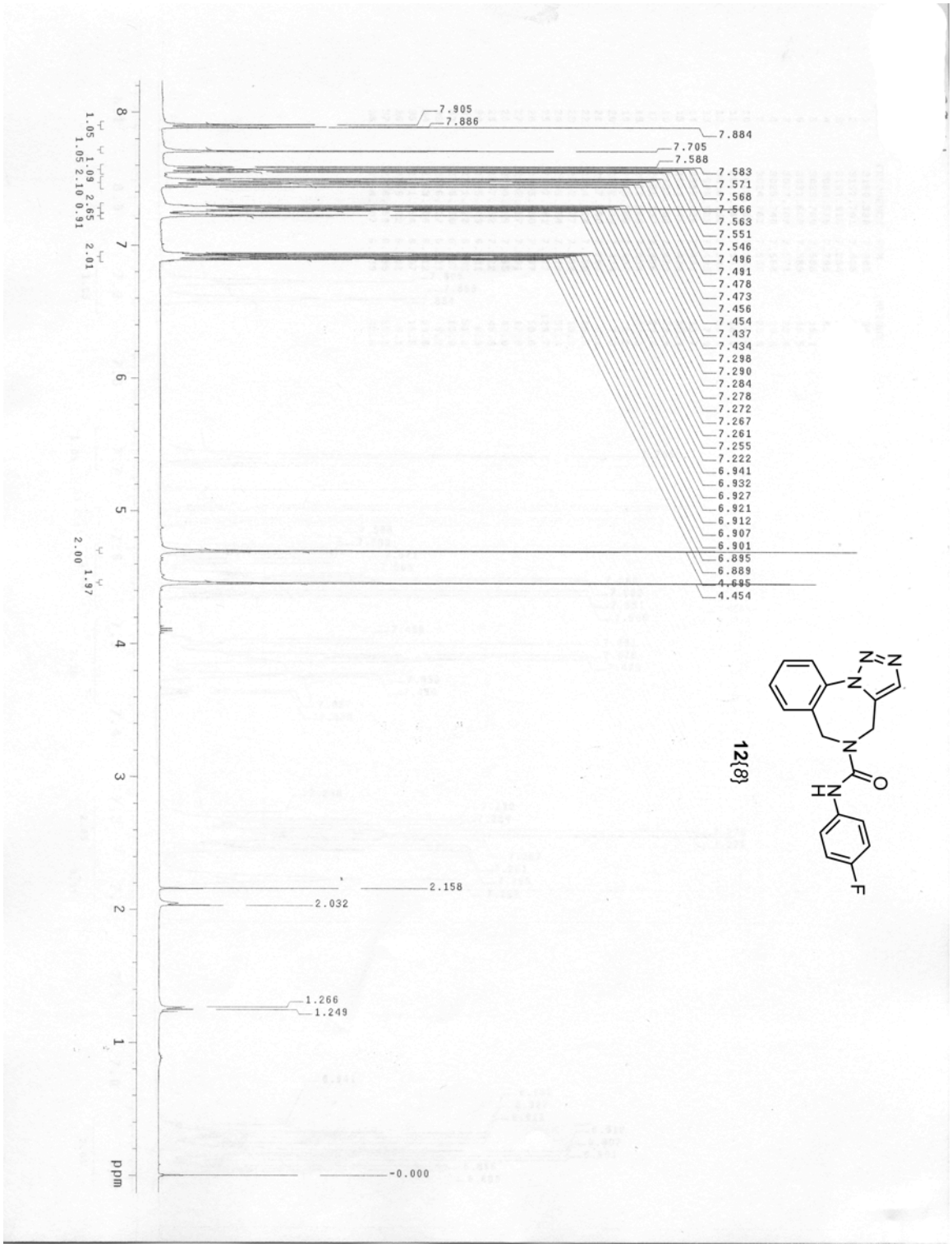

12{4}
9
8
7
6
5
4
3
2
1
0
ppm

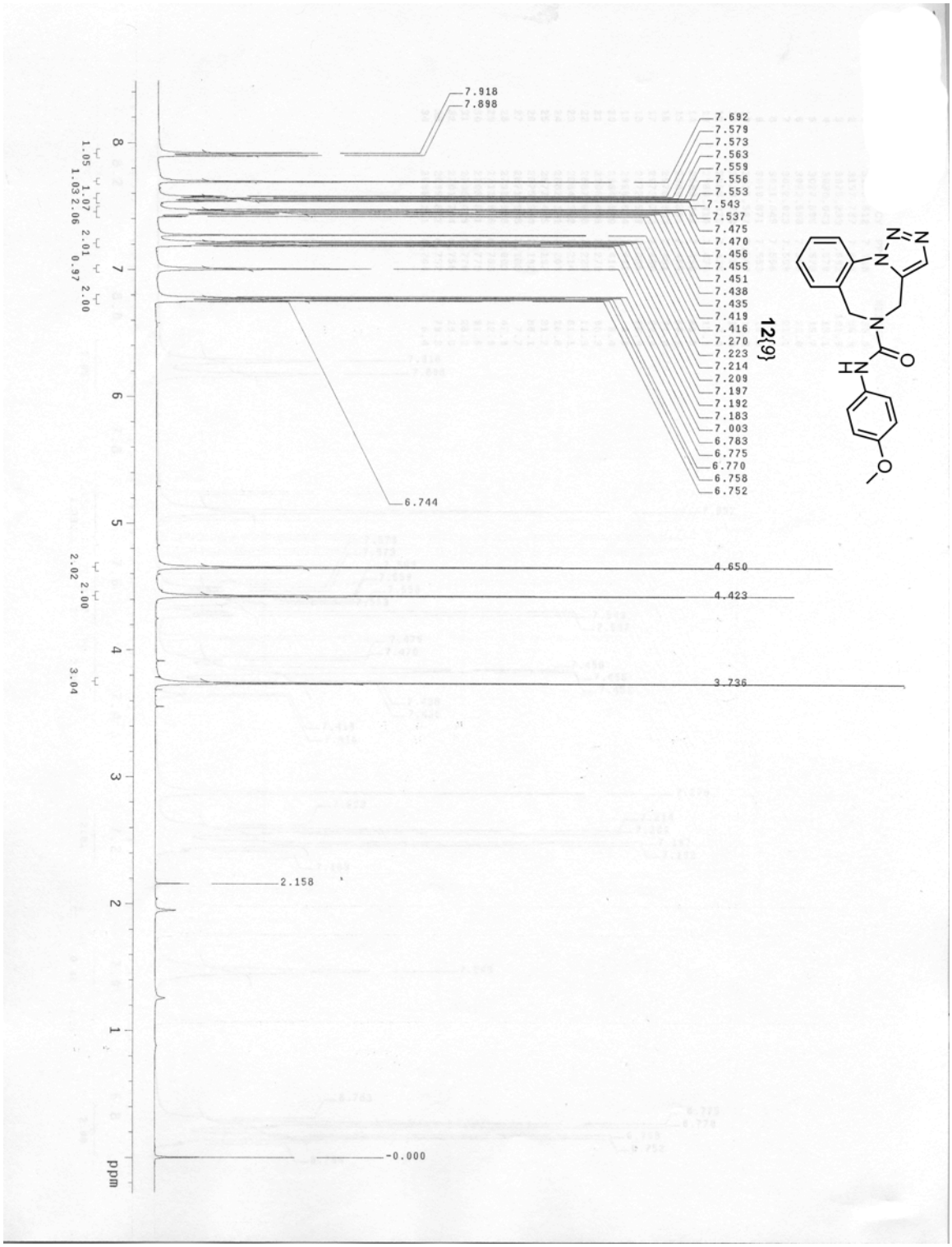

12(4)
180
160
140
120
100
80
60
40
20
ppm

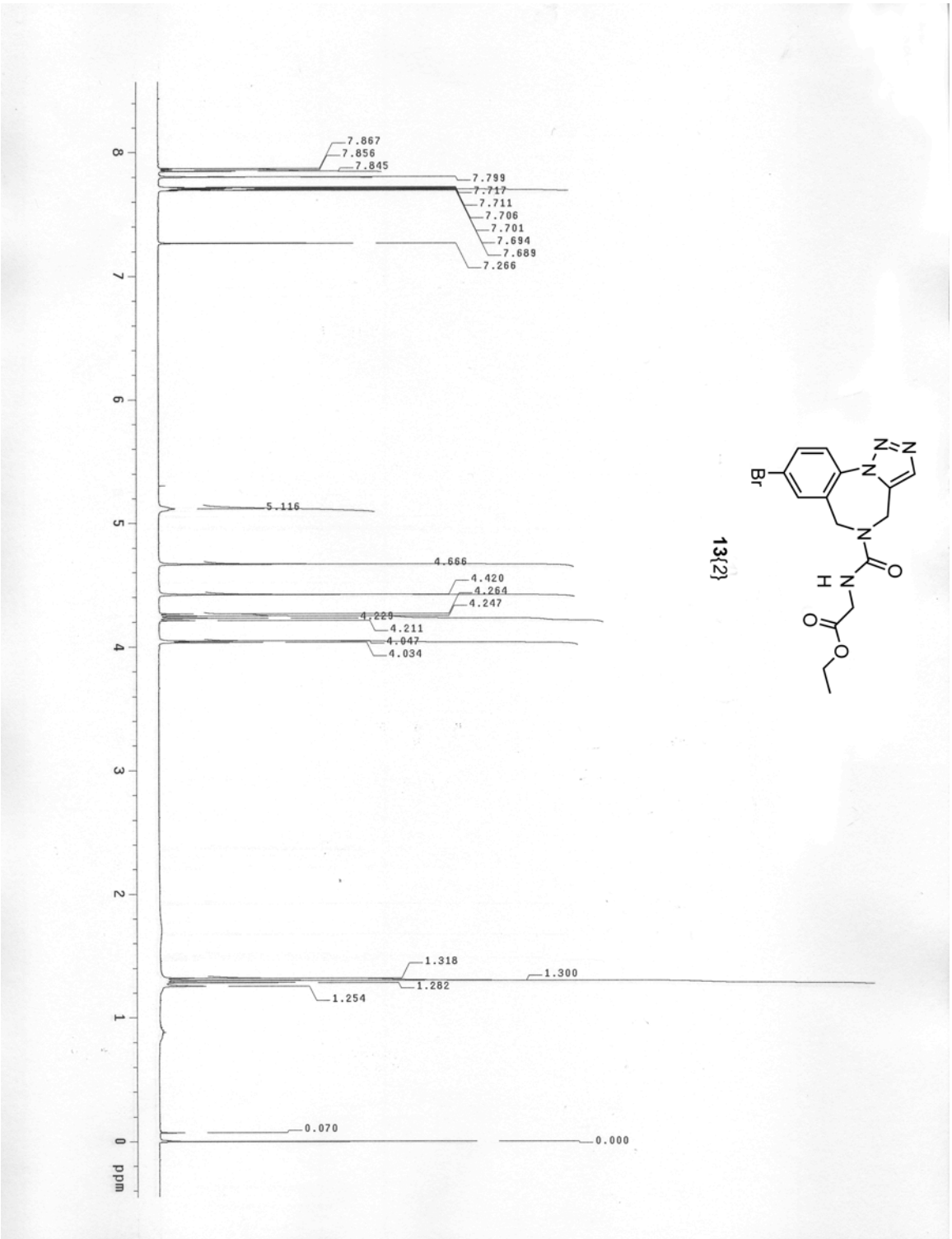

7.988
7.985
7.968
7.965
7.944
7.942
7.885
7.678
7.674
7.659
7.656
7.635
7.622
7.618
7.615
7.612
7.603
7.596
7.593
7.576
7.572
7.565
7.562
7.547
7.543
7.527
7.524
7.445
7.442
7.426
7.423
7.407
7.405
7.394
7.387
7.385
7.369
7.365
7.349
7.343
7.328
7.323
7.312
7.306
7.304
7.293
7.291
7.282
7.266
7.244
7.240
7.232
7.223
7.221
7.213
7.194
7.035
7.032
7.016
7.013
4.916
4.901
4.756
4.362
4.198
4.126
4.108
2.290
2.266
2.041
1.274
1.257
1.238
0.000
12{5}
1.00
0.71
1.94
3.86
1.56
0.73
1.34
0.52
0.54
1.39
3.00
ppm

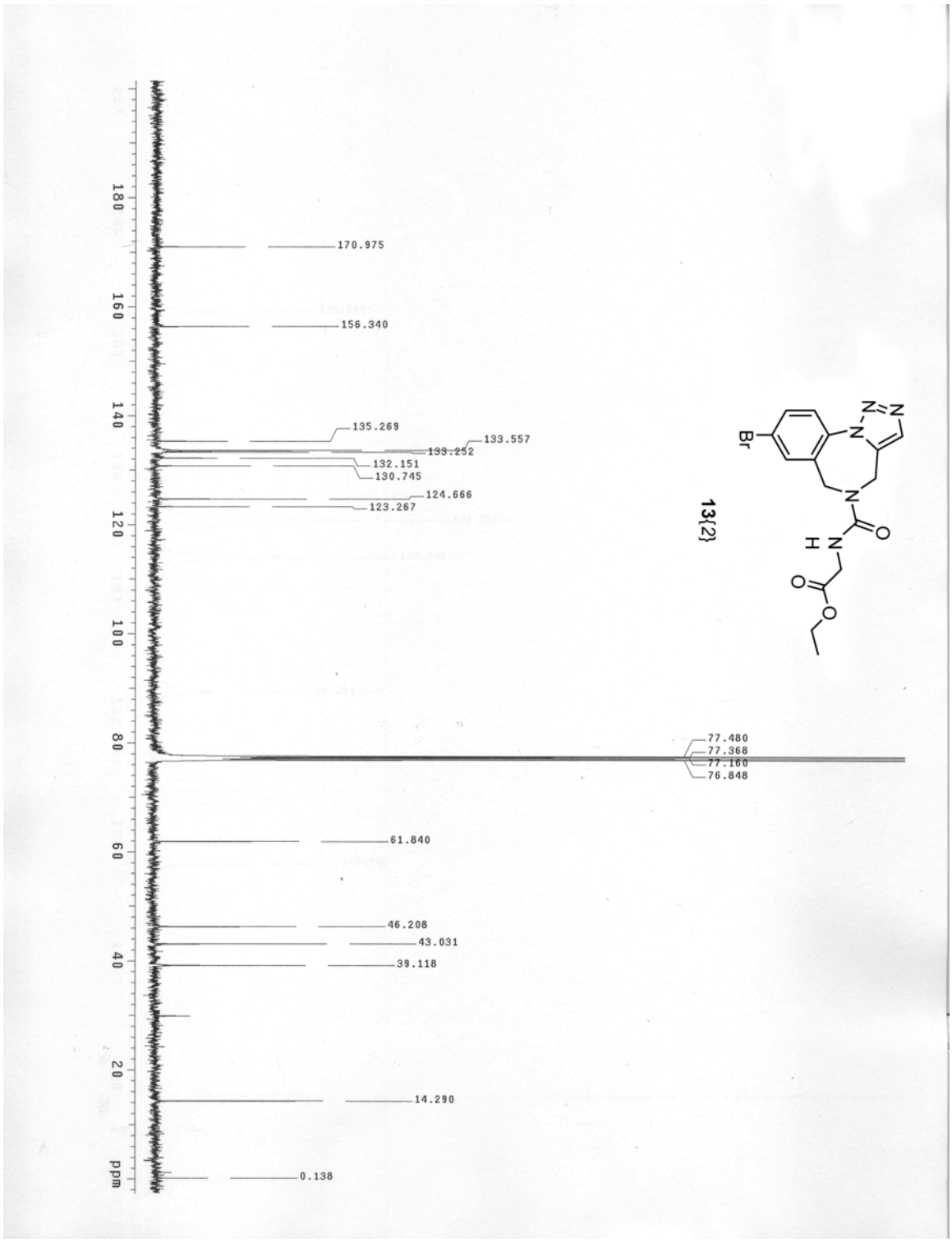

d4-MeOD
12(6)
7.958
7.928
7.929
7.649
7.632
7.576
7.560
7.470
7.062
4.851
4.765
4.540
3.300
2.22
5.47
0.99
2.10
2.00
ppm

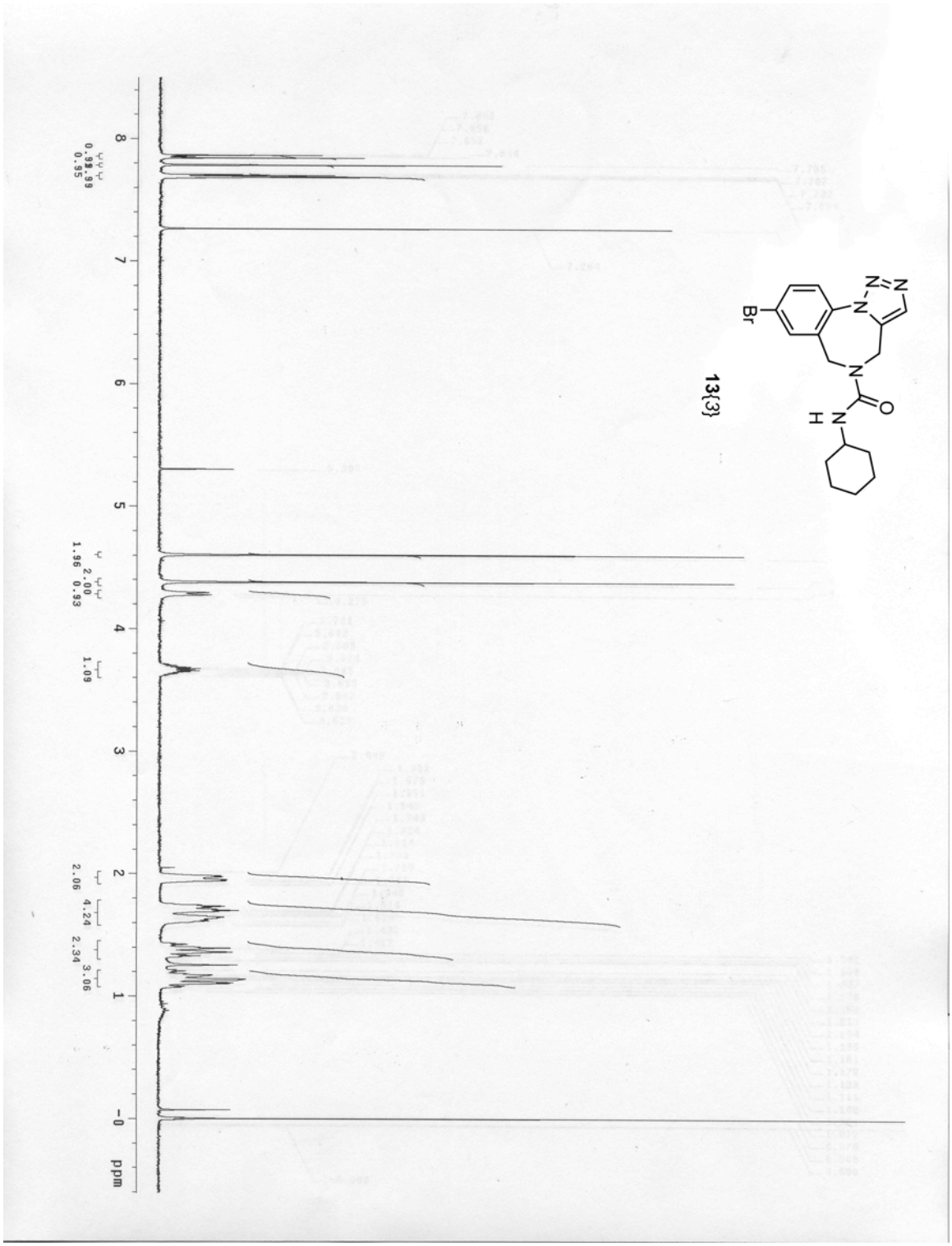

7.956
7.787
7.652
7.583
7.437
7.260
6.974
4.612
4.375
4.115
4.101
2.032
1.664
1.248
-0.002
ppm
1.05
2.16
3.25
6.28
0.93
2.00
2.06
12{7}

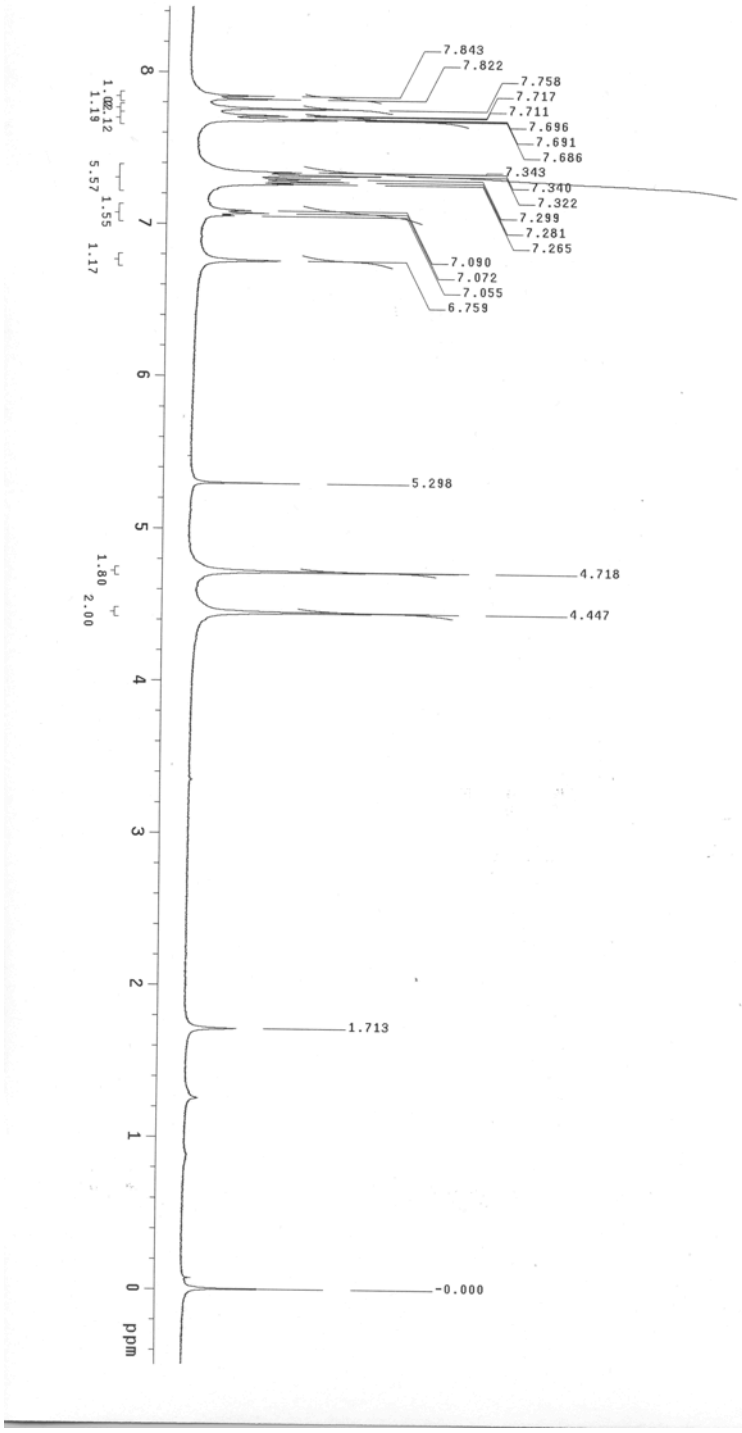

7.905
7.886
7.884
7.705
7.588
7.583
7.571
7.568
7.566
7.563
7.551
7.546
7.496
7.491
7.478
7.473
7.456
7.454
7.437
7.434
7.298
7.290
7.284
7.278
7.272
7.267
7.261
7.255
7.222
6.941
6.932
6.927
6.921
6.912
6.907
6.901
6.895
6.889
4.695
4.454
2.158
2.032
1.266
1.249
-0.000
ppm
12{8}


7.918
7.898
7.692
7.579
7.573
7.563
7.559
7.556
7.553
7.543
7.537
7.475
7.470
7.456
7.455
7.451
7.438
7.435
7.419
7.416
7.270
7.223
7.214
7.209
7.197
7.192
7.183
7.003
6.783
6.775
6.770
6.758
6.752
6.744
4.650
4.423
3.736
2.158
-0.000
12(9)
ppm

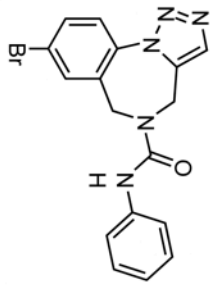

7.867
7.856
7.845
7.799
7.717
7.711
7.706
7.701
7.694
7.689
7.266
5.116
4.666
4.420
4.264
4.247
4.229
4.211
4.047
4.034
1.318
1.300
1.282
1.254
0.070
0.000
ppm
13{2}
Br
N
N
N
O
H
N
O
O

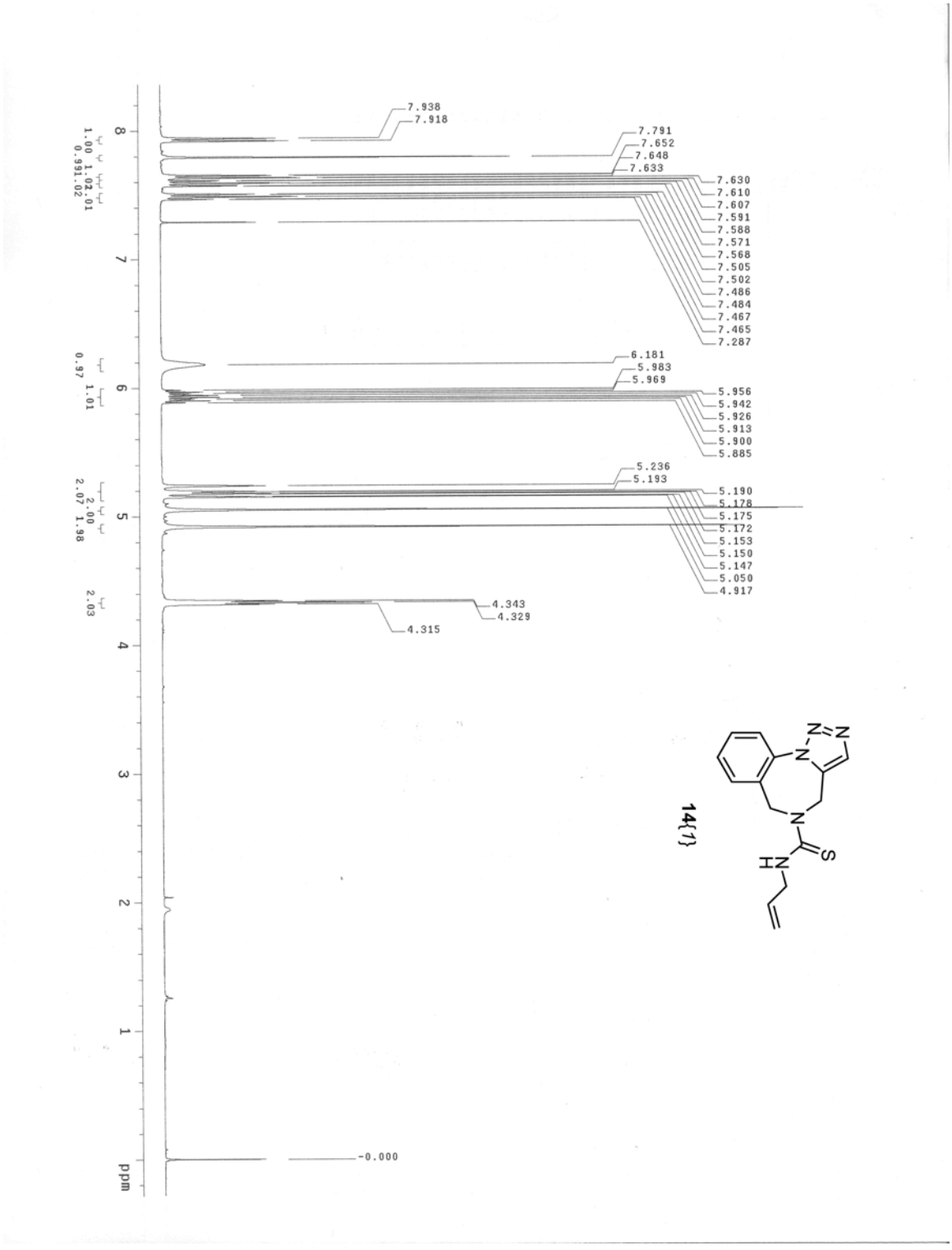

170.975
156.340
135.269
133.557
133.252
132.151
130.745
124.666
123.267
77.480
77.368
77.160
76.848
61.840
46.208
43.031
39.118
14.290
0.138
ppm
13{2}
Br
N
N
N
O
H
O
O

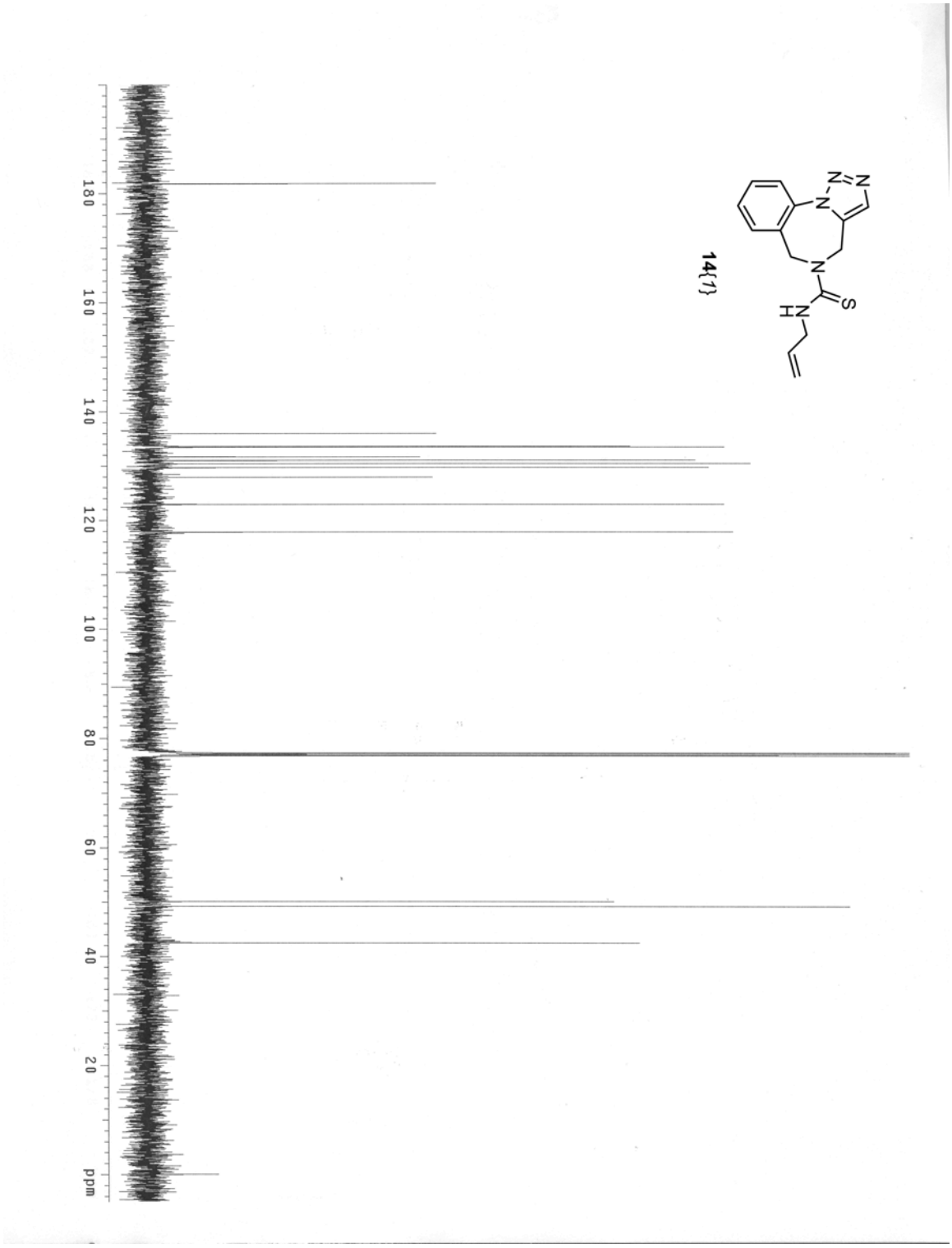

13{3}
Br
N
N
N
N
O
H
8
7
6
5
4
3
2
1
-0
ppm
0.98 0.99
0.95
1.96 0.93
2.00
1.09
2.06
4.24
2.34
3.06

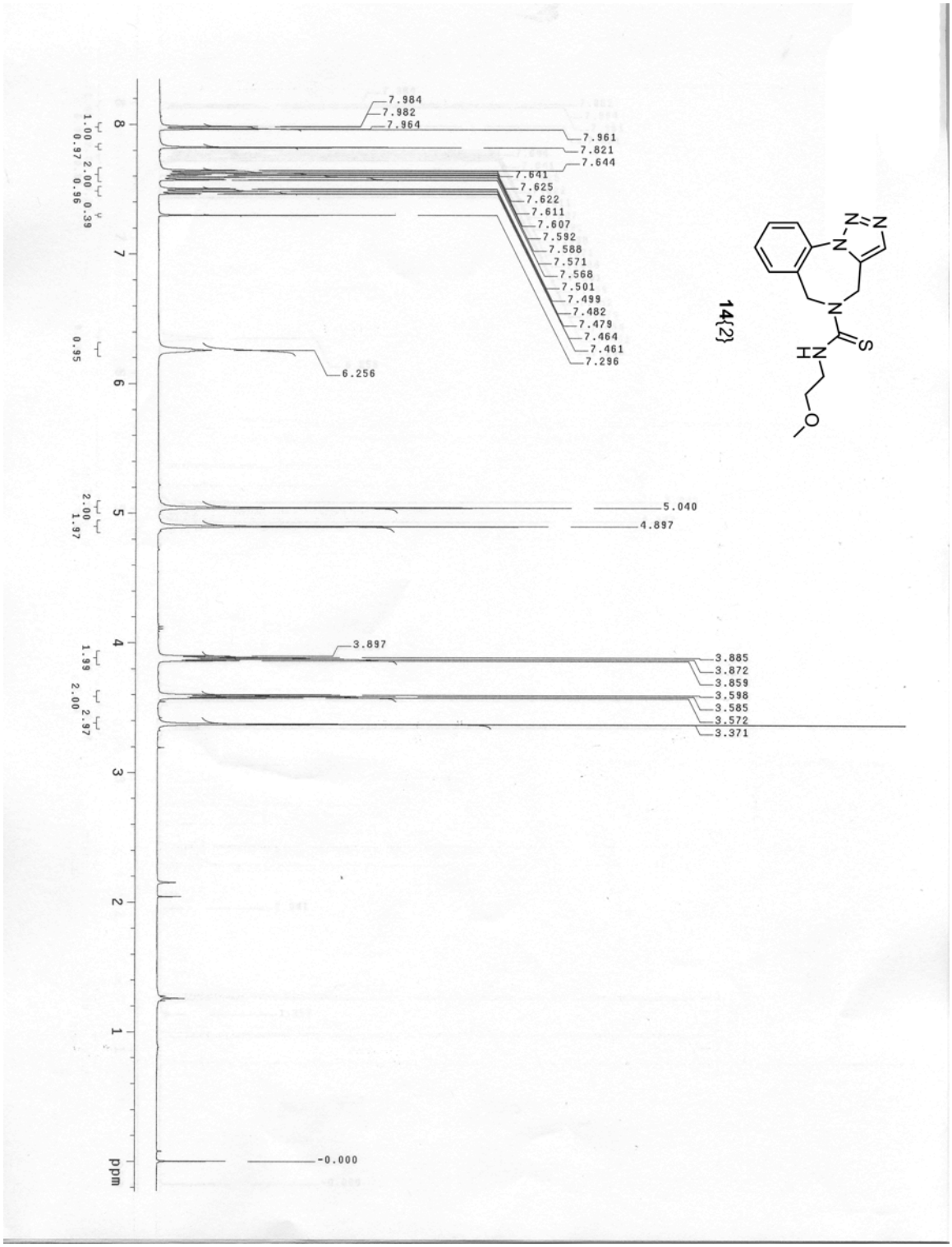

7.843
7.822
7.758
7.717
7.711
7.696
7.691
7.686
7.343
7.340
7.322
7.299
7.281
7.265
7.090
7.072
7.055
6.759
5.298
4.718
4.447
1.713
-0.000
ppm
1.19
2.12
5.57
1.55
1.17
1.80
2.00

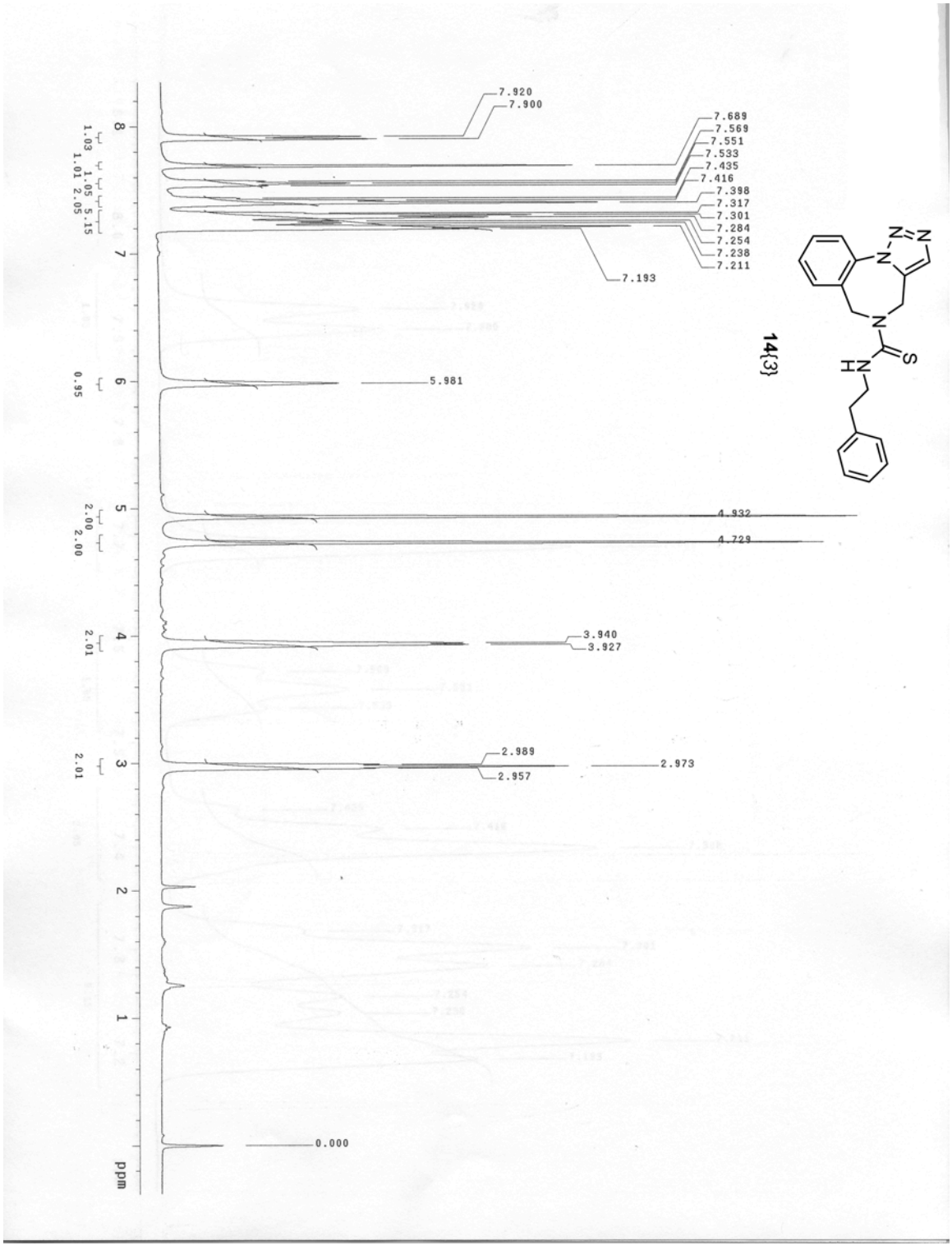
13{4}

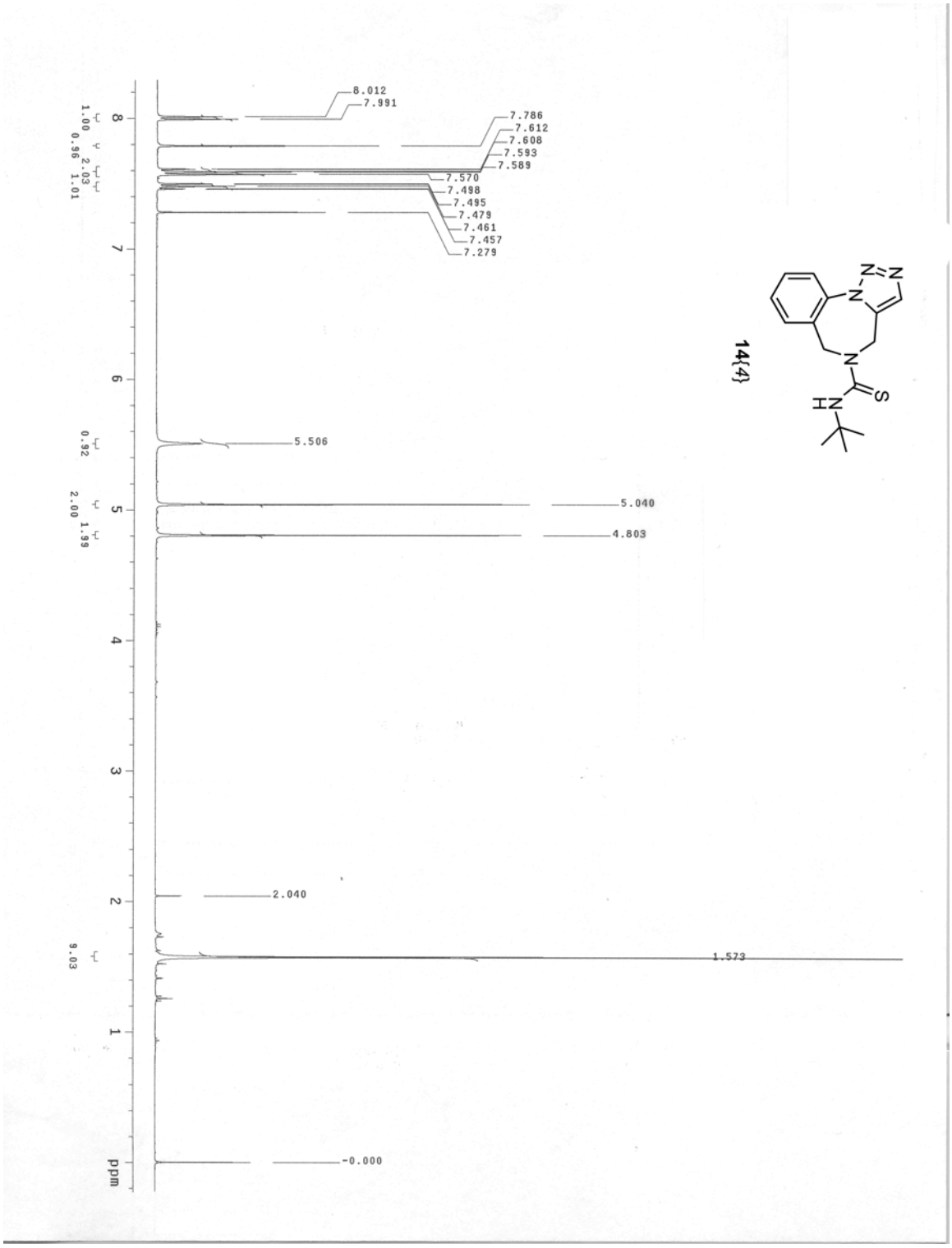

Br
N
N
N
O
H
N

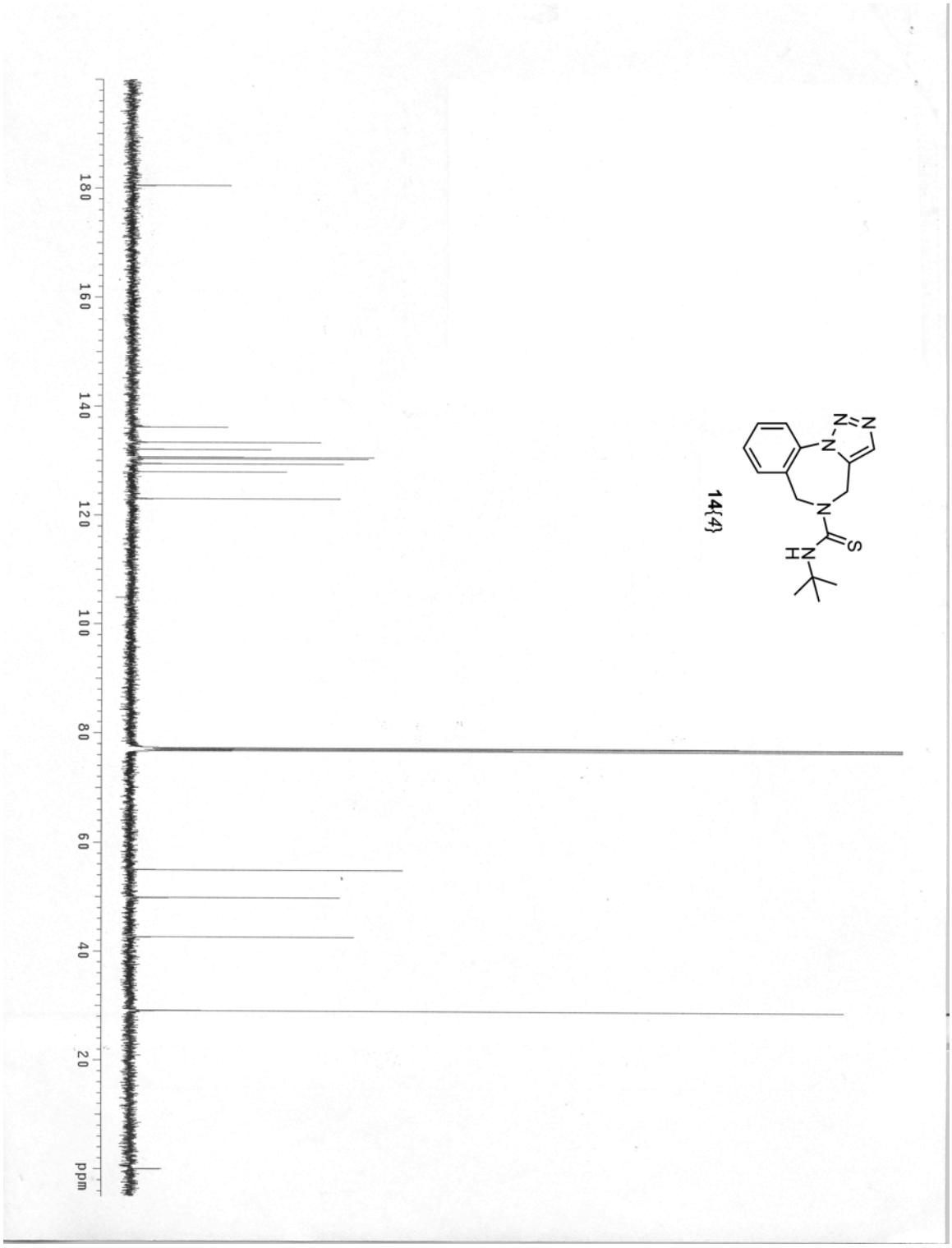

7.938
7.918
7.791
7.652
7.648
7.633
7.630
7.610
7.607
7.591
7.588
7.571
7.568
7.505
7.502
7.486
7.484
7.467
7.465
7.287
6.181
5.983
5.969
5.956
5.942
5.926
5.913
5.900
5.885
5.236
5.193
5.190
5.178
5.175
5.172
5.153
5.150
5.147
5.050
4.917
4.343
4.329
4.315
-0.000
ppm
1.00 1.02 1.01
0.99 1.02
0.97 1.01
2.07 2.00 1.98
2.03
14{7}

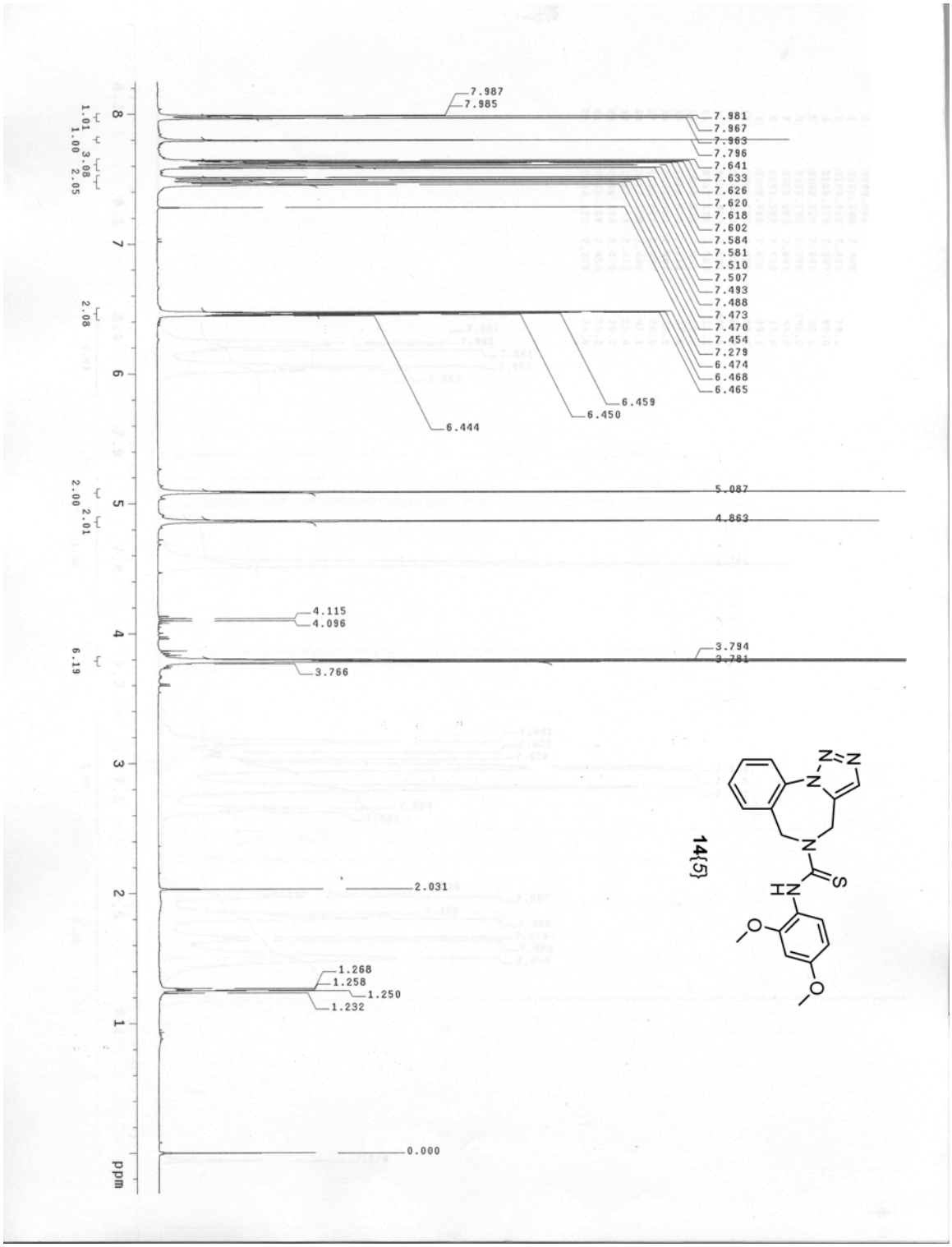

14{1}
180
160
140
120
100
80
60
40
20
ppm

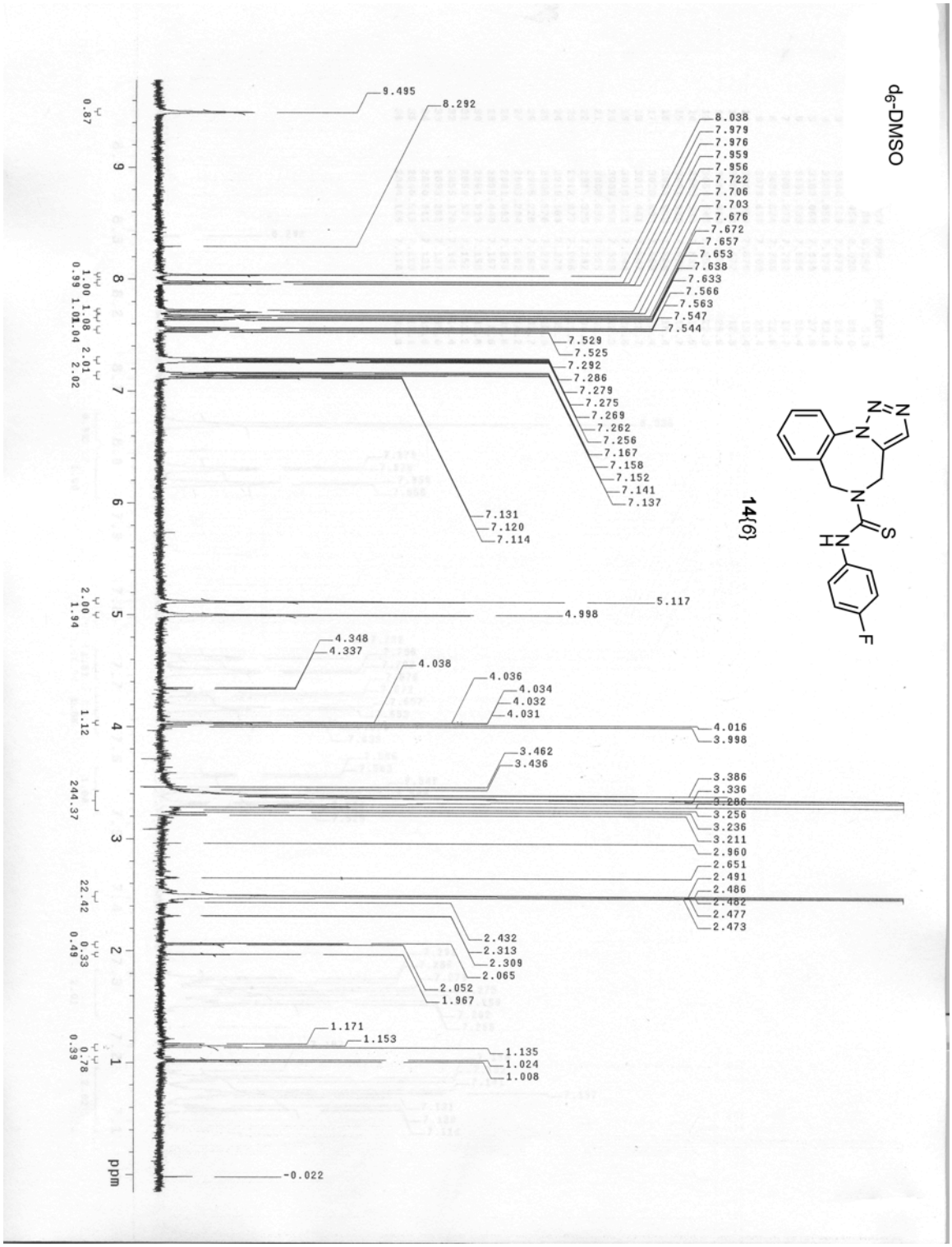

7.984
7.982
7.964
7.961
7.821
7.644
7.641
7.625
7.622
7.611
7.607
7.592
7.588
7.571
7.568
7.501
7.499
7.482
7.479
7.464
7.461
7.296
6.256
5.040
4.897
3.897
3.885
3.872
3.859
3.598
3.585
3.572
3.371
-0.000
ppm
14{2}

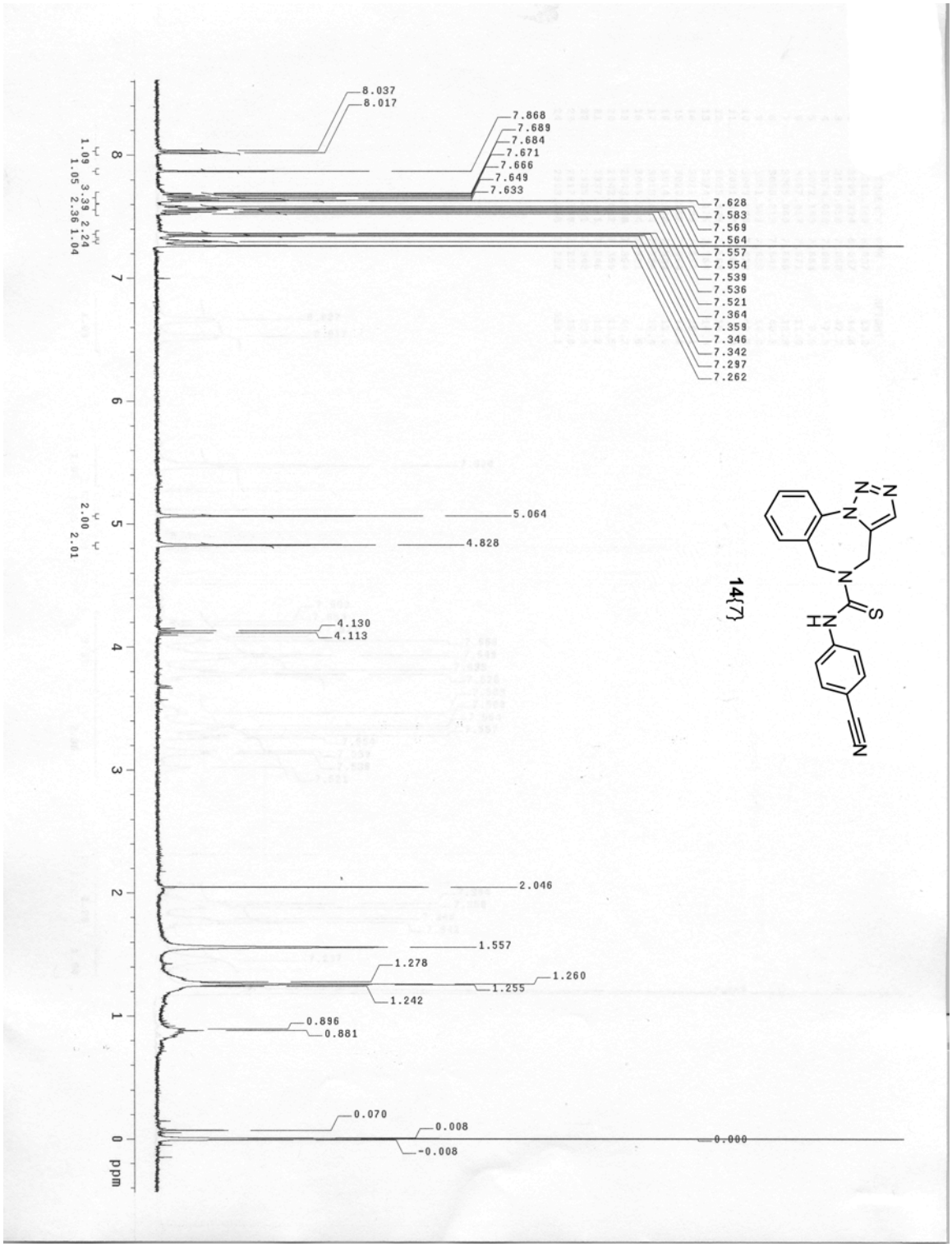

7.920
7.900
7.689
7.569
7.551
7.533
7.435
7.416
7.398
7.317
7.301
7.284
7.254
7.238
7.211
7.193
5.981
4.932
4.729
3.940
3.927
2.989
2.973
2.957
0.000
ppm
14{3}


8.012
7.991
7.786
7.612
7.608
7.593
7.589
7.570
7.498
7.495
7.479
7.461
7.457
7.279
5.506
5.040
4.803
2.040
1.573
-0.000
ppm
1.00
0.96
2.03
1.01
0.92
2.00
1.99
9.03
14{4}


14{4}
180
160
140
120
100
80
60
40
20
ppm


7.987
7.985
7.981
7.967
7.963
7.796
7.641
7.633
7.626
7.620
7.618
7.602
7.584
7.581
7.510
7.507
7.493
7.488
7.473
7.470
7.454
7.279
6.474
6.468
6.465
6.459
6.450
6.444
5.087
4.863
4.115
4.096
3.794
3.781
3.766
2.031
1.268
1.258
1.250
1.232
0.000
ppm
1.01 3.08
1.00 2.05
2.08
2.00 2.01
6.19
14(5)


d6-DMSO
14{6}
9.495
8.292
8.038
7.979
7.976
7.959
7.956
7.722
7.706
7.703
7.676
7.672
7.657
7.653
7.638
7.633
7.566
7.563
7.547
7.544
7.529
7.525
7.292
7.286
7.279
7.275
7.269
7.262
7.256
7.167
7.158
7.152
7.141
7.137
7.131
7.120
7.114
5.117
4.998
4.348
4.337
4.038
4.036
4.034
4.032
4.031
4.016
3.998
3.462
3.436
3.386
3.336
3.286
3.256
3.236
3.211
2.960
2.651
2.491
2.486
2.482
2.477
2.473
2.432
2.313
2.309
2.065
2.052
1.967
1.171
1.153
1.135
1.024
1.008
-0.022
ppm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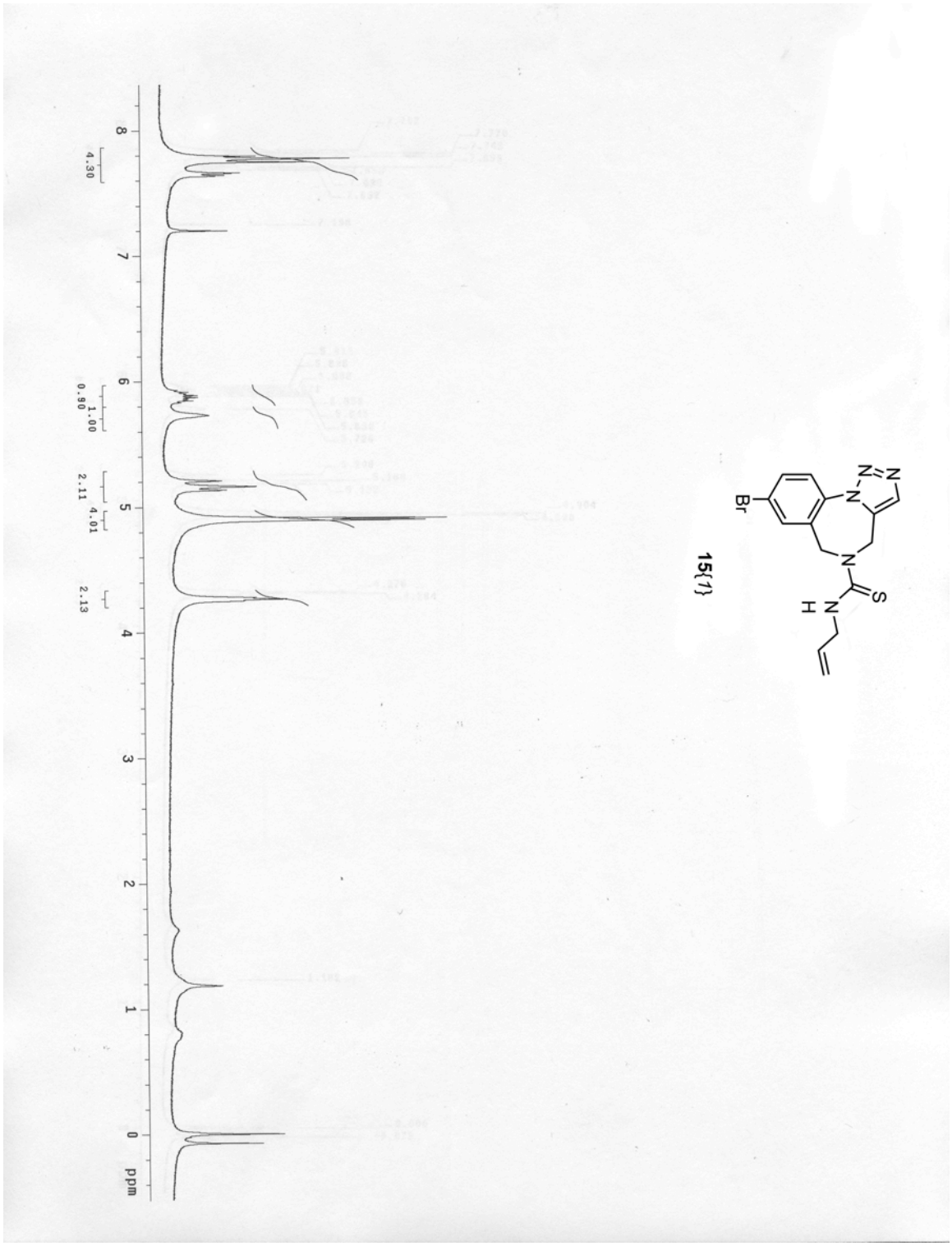
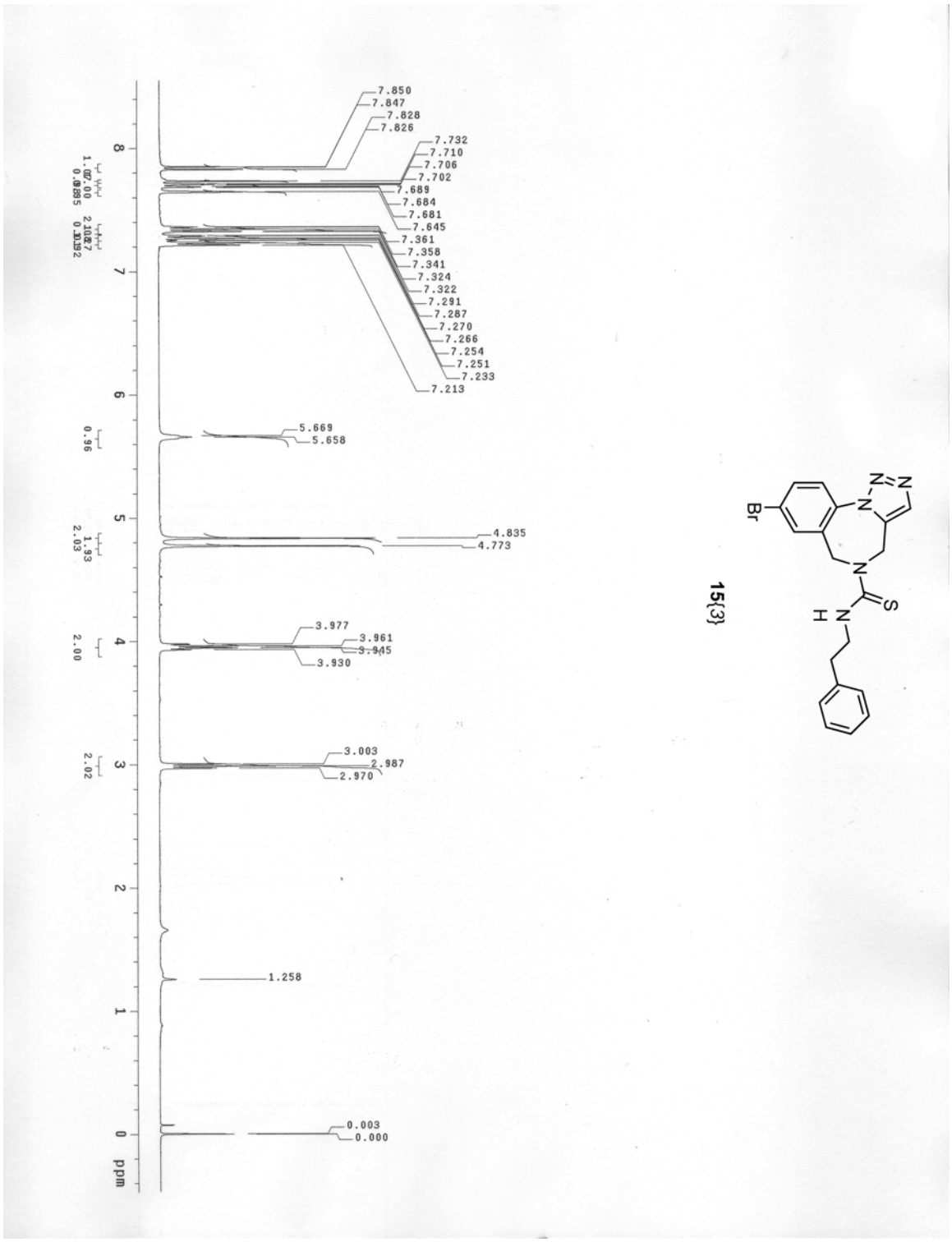
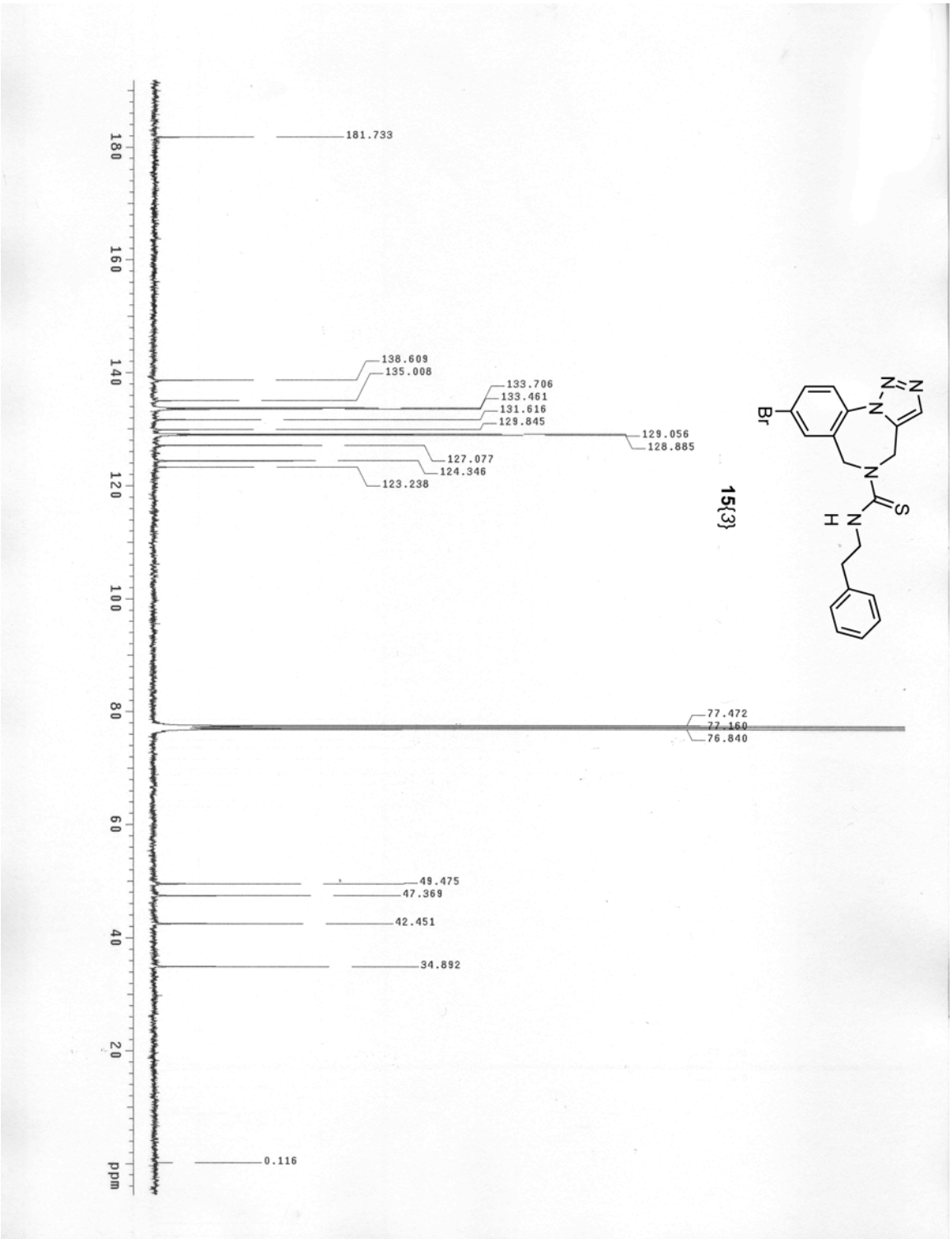
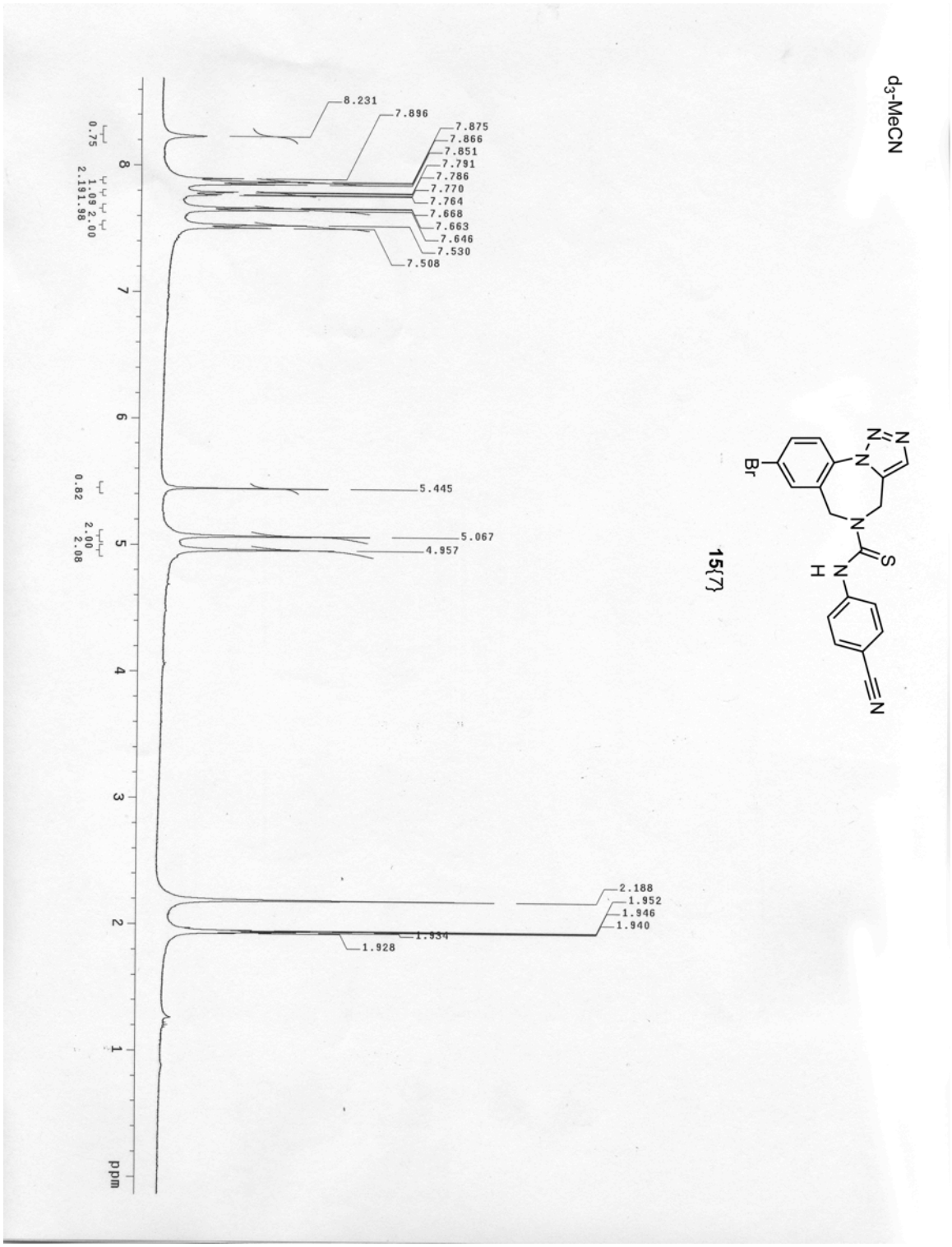
8.017
7.868
7.689
7.684
7.671
7.666
7.649
7.633
7.628
7.583
7.569
7.564
7.557
7.554
7.539
7.536
7.521
7.364
7.359
7.346
7.342
7.297
7.262
5.064
4.828
4.130
4.113
2.046
1.557
1.278
1.260
1.255
1.242
0.896
0.881
0.070
0.008
0.000
-0.008
ppm
14{7}

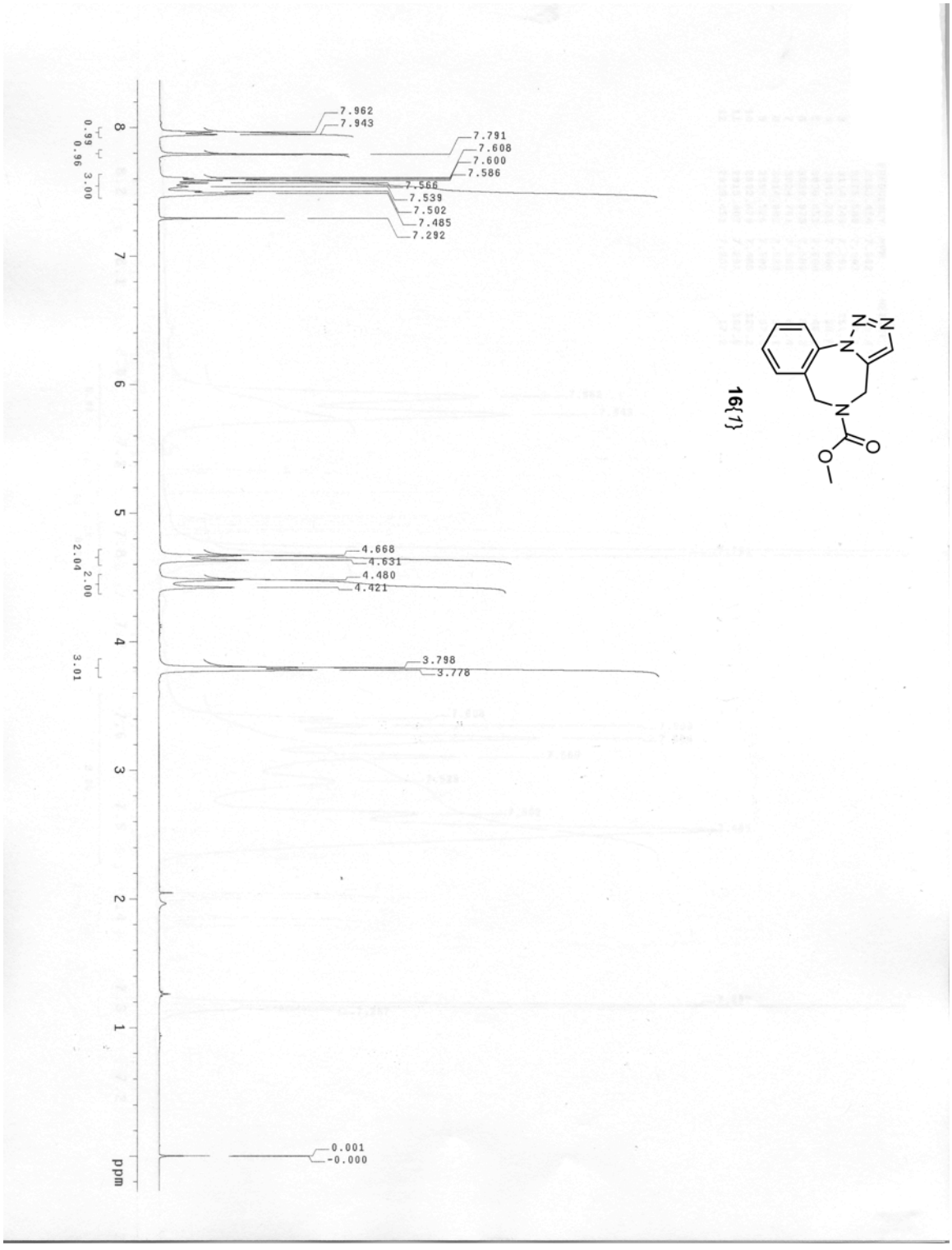

Br
N
N
N
S
N
H
15{1}
8
7
6
5
4
3
2
1
0
ppm
4.30
0.90
1.00
2.11
4.01
2.13

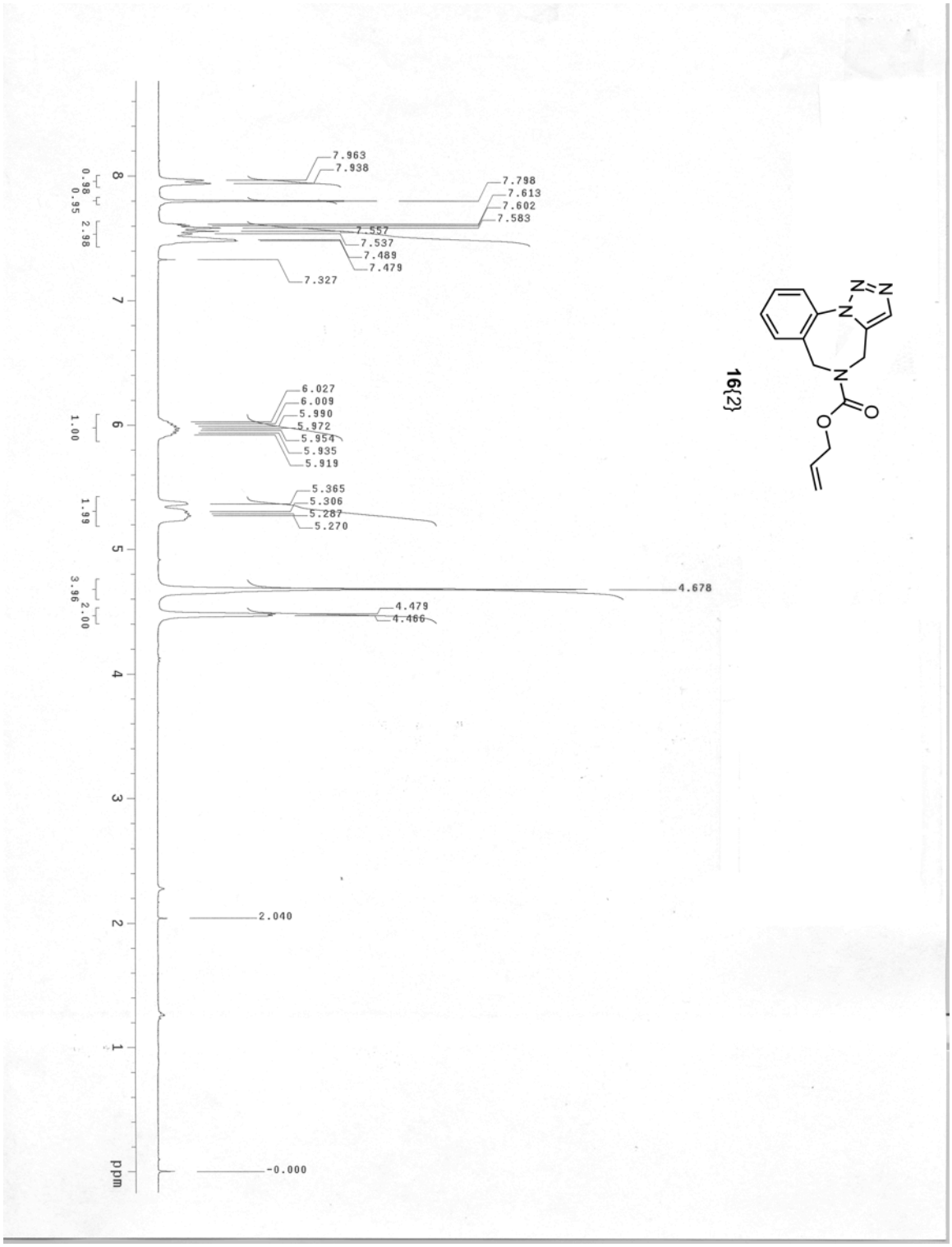

7.850
7.847
7.828
7.826
7.732
7.710
7.706
7.702
7.689
7.684
7.681
7.645
7.361
7.358
7.341
7.324
7.322
7.291
7.287
7.270
7.266
7.254
7.251
7.233
7.213
5.669
5.658
4.835
4.773
3.977
3.961
3.945
3.930
3.003
2.987
2.970
1.258
0.003
0.000
ppm
Br
N
S
H

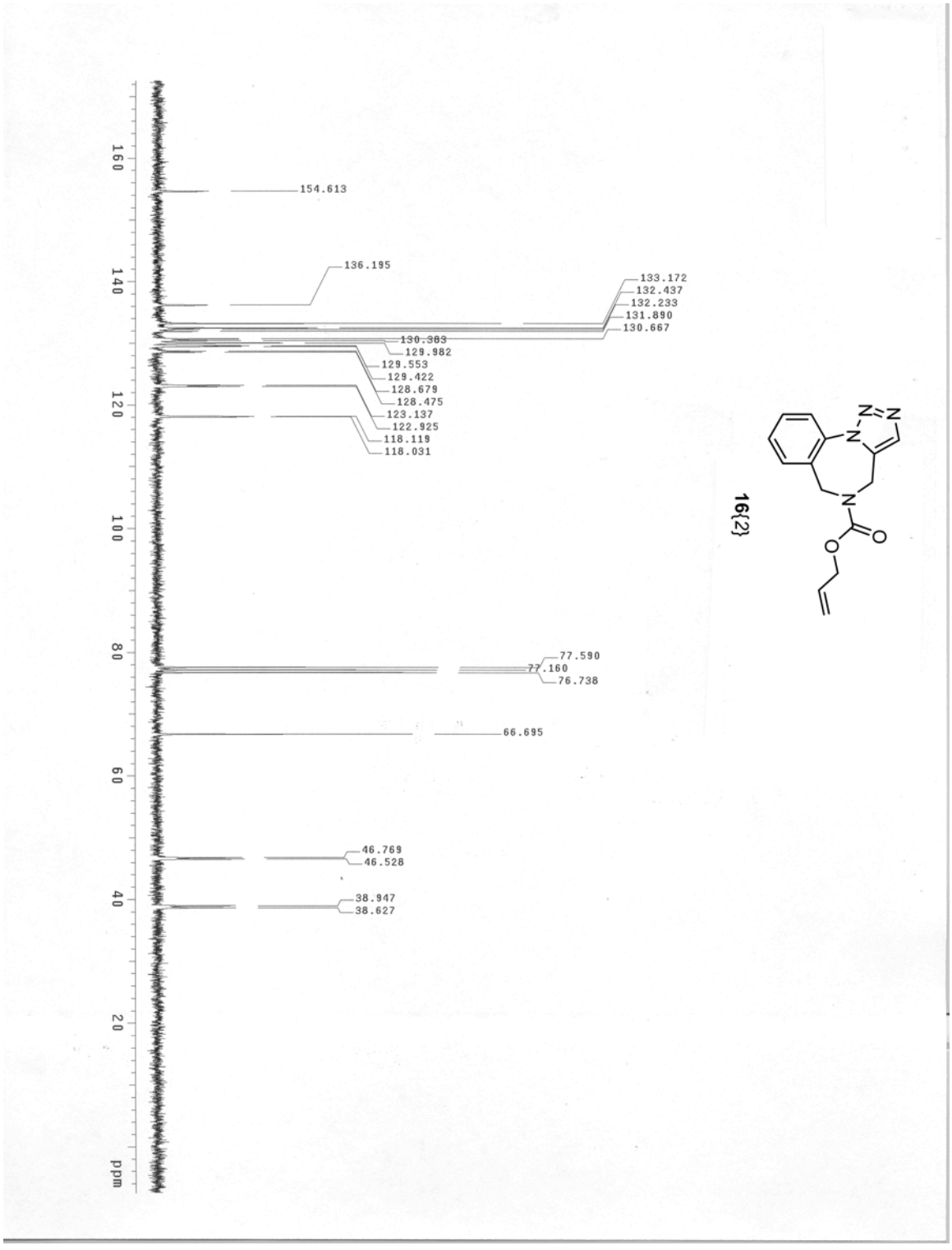
15(3)

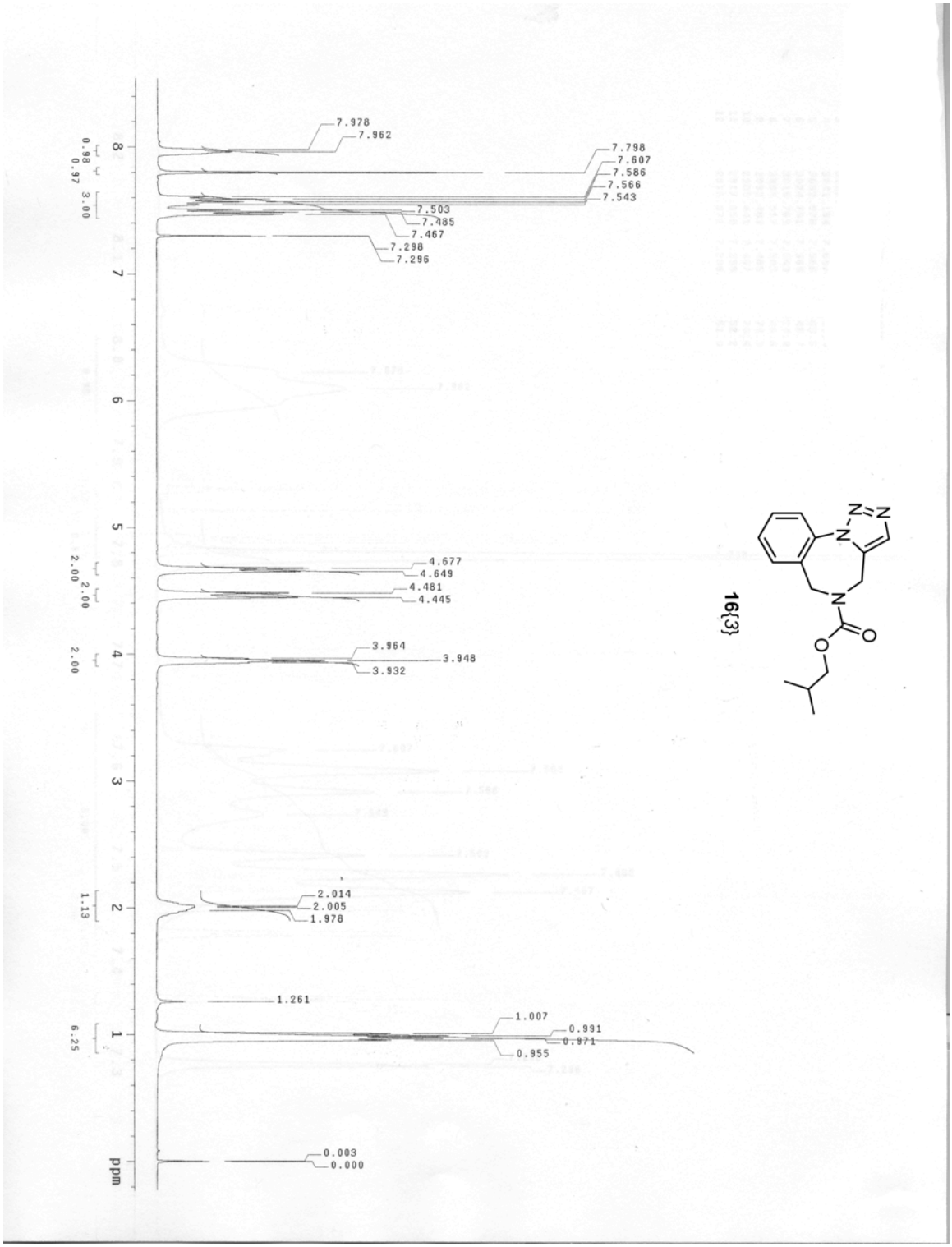

181.733
138.609
135.008
133.706
133.461
131.616
129.845
129.056
128.885
127.077
124.346
123.238
77.472
77.160
76.840
49.475
47.369
42.451
34.892
0.116
ppm
180
160
140
120
100
80
60
40
20
15{3}
Br
N
N
N
S
H
N

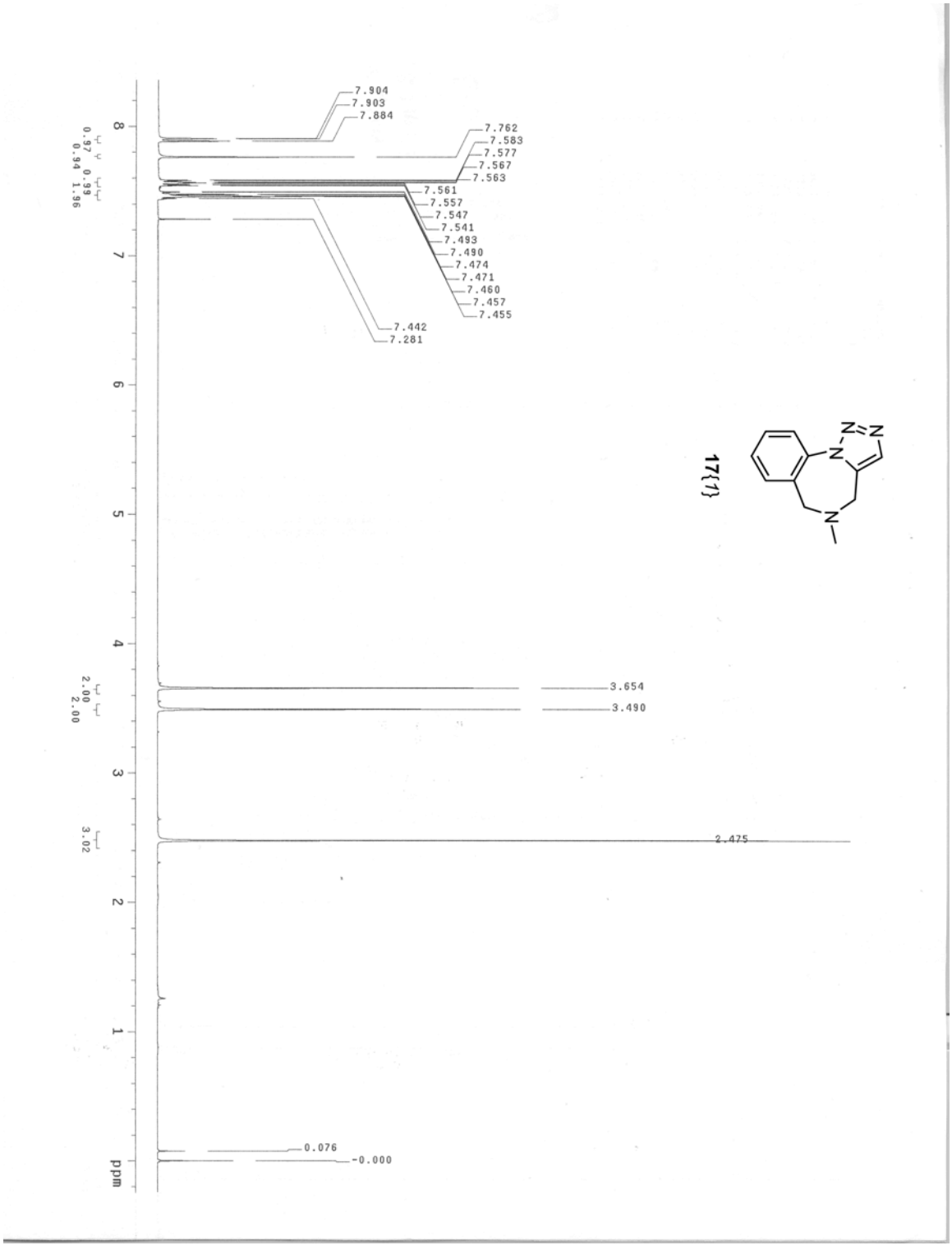

d3-MeCN
8.231
7.896
7.875
7.866
7.851
7.791
7.786
7.770
7.764
7.668
7.663
7.646
7.530
7.508
5.445
5.067
4.957
2.188
1.952
1.946
1.940
1.934
1.928
ppm
Br
N
S
H
15(7)

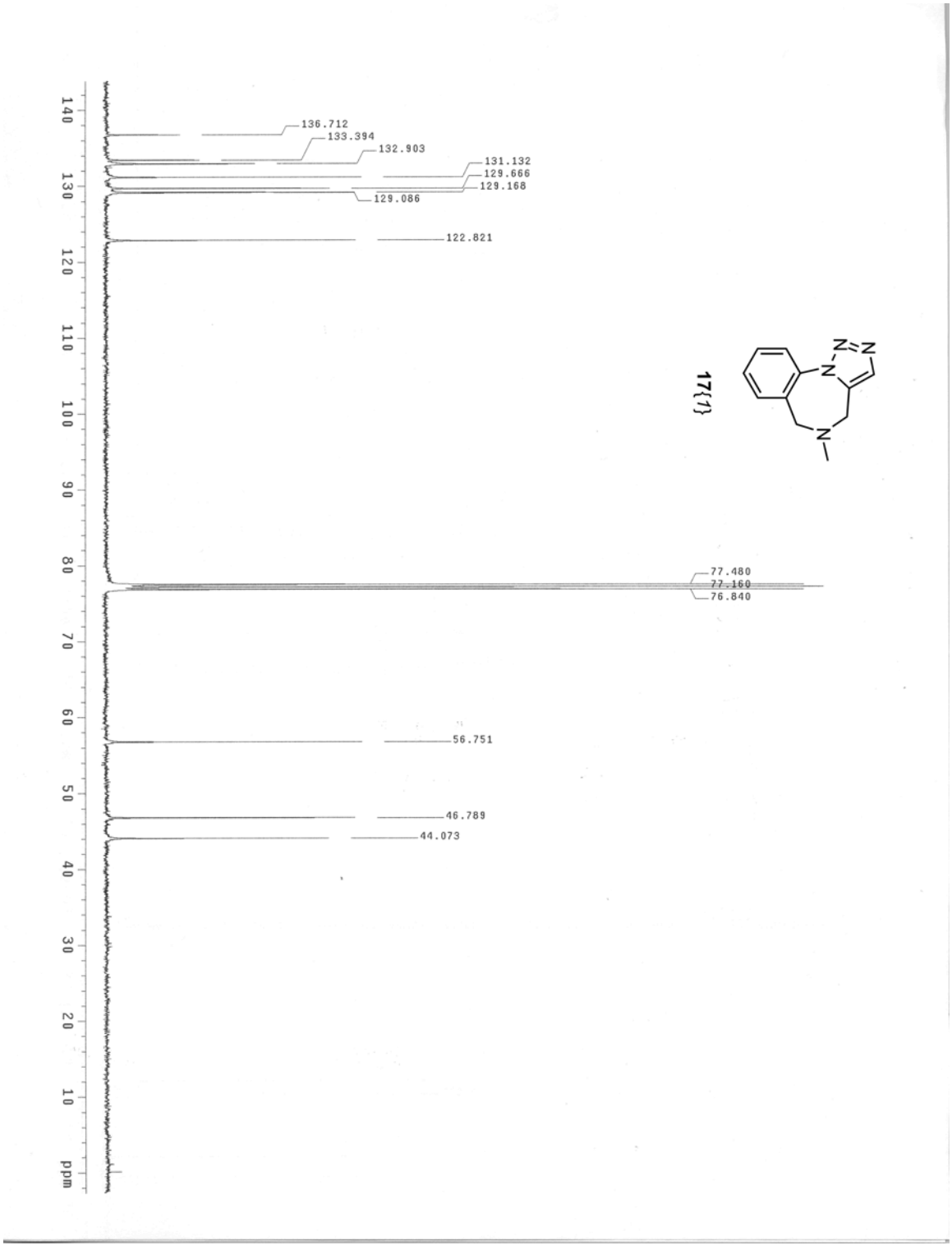

7.962
7.943
7.791
7.608
7.600
7.586
7.566
7.539
7.502
7.485
7.292
4.668
4.631
4.480
4.421
3.798
3.778
0.001
-0.000
ppm
16{1}

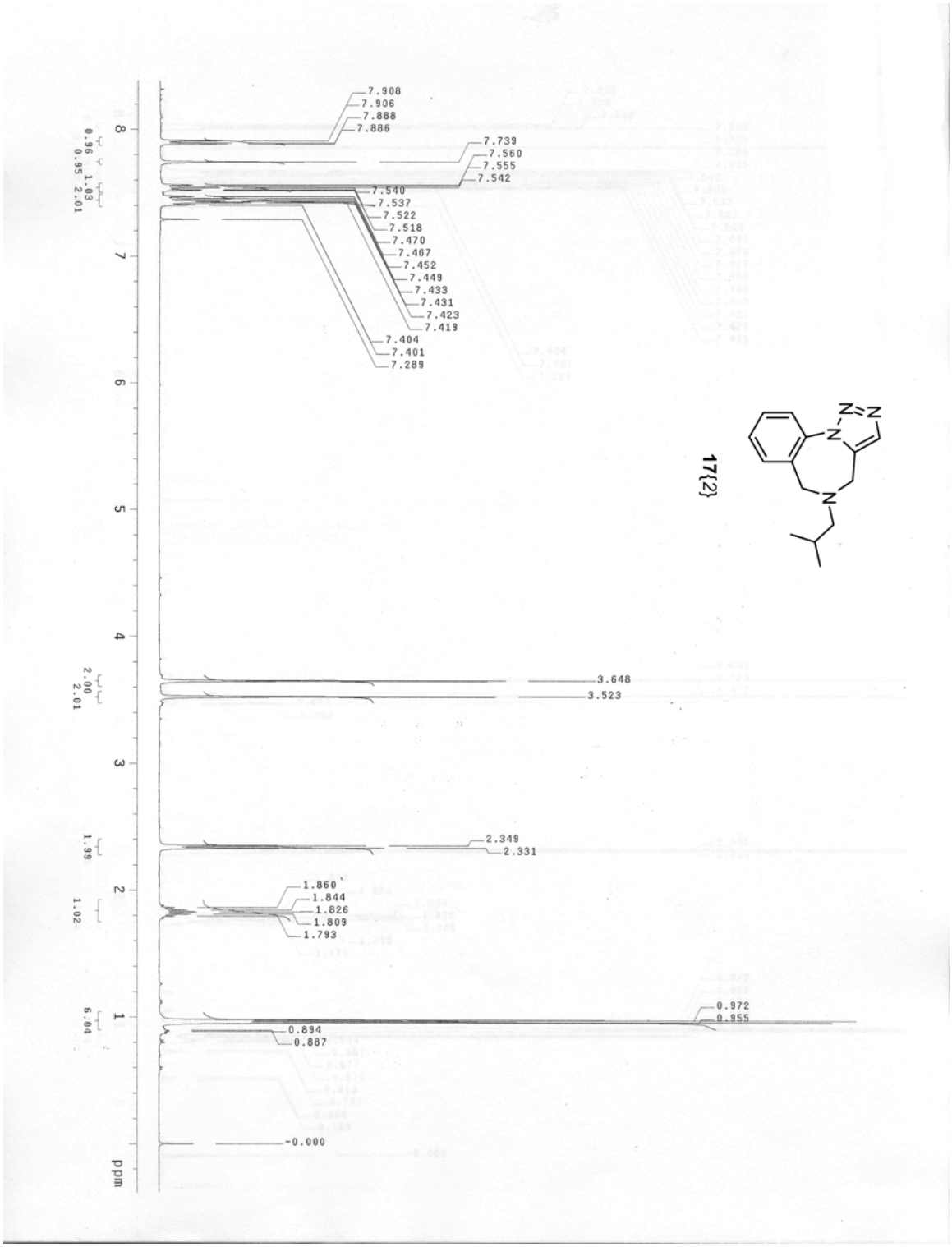

7.963
7.938
7.798
7.613
7.602
7.583
7.557
7.537
7.489
7.479
7.327
6.027
6.009
5.990
5.972
5.954
5.935
5.919
5.365
5.306
5.287
5.270
4.678
4.479
4.466
2.040
-0.000
0.98
0.95
2.98
1.00
1.99
3.96
2.00
ppm
16{2}

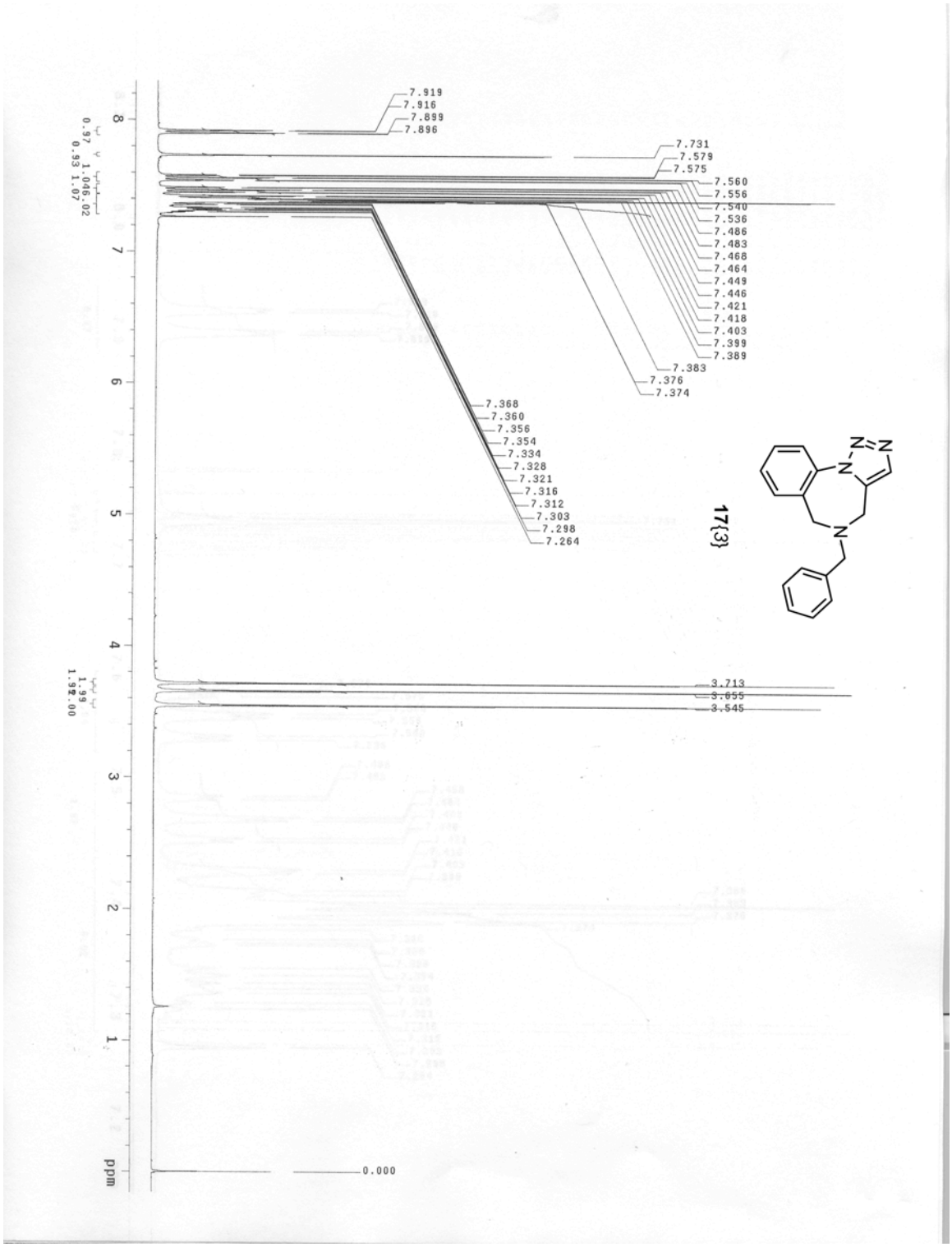

154.613
136.195
133.172
132.437
132.233
131.890
130.667
130.383
129.982
129.553
129.422
128.679
128.475
123.137
122.925
118.119
118.031
77.590
77.160
76.738
66.695
46.769
46.528
38.947
38.627
160
140
120
100
80
60
40
20
ppm
16{2}

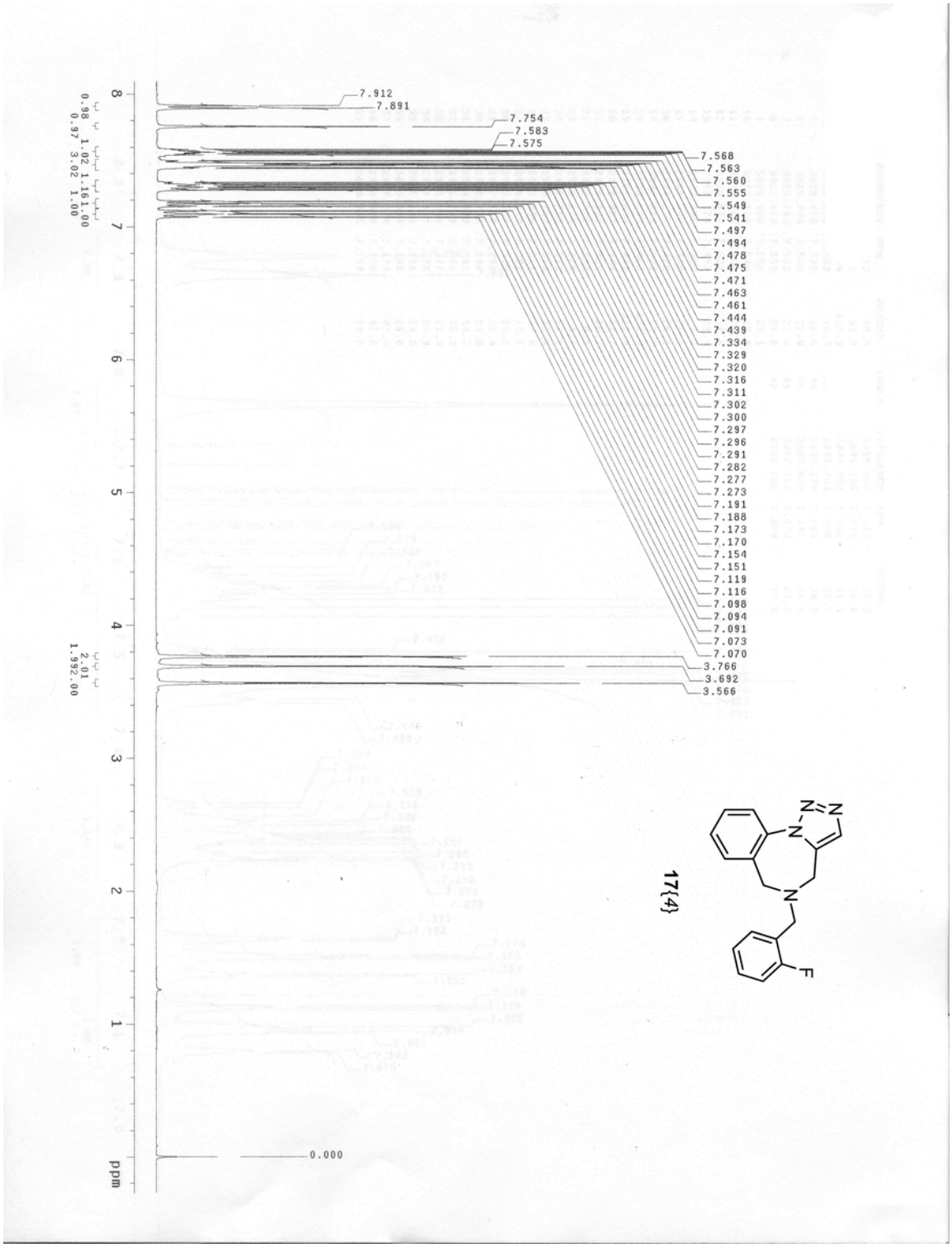

7.978
7.962
7.798
7.607
7.586
7.566
7.543
7.503
7.485
7.467
7.298
7.296
4.677
4.649
4.481
4.445
3.964
3.948
3.932
2.014
2.005
1.978
1.261
1.007
0.991
0.971
0.955
0.003
0.000
ppm
16{3}

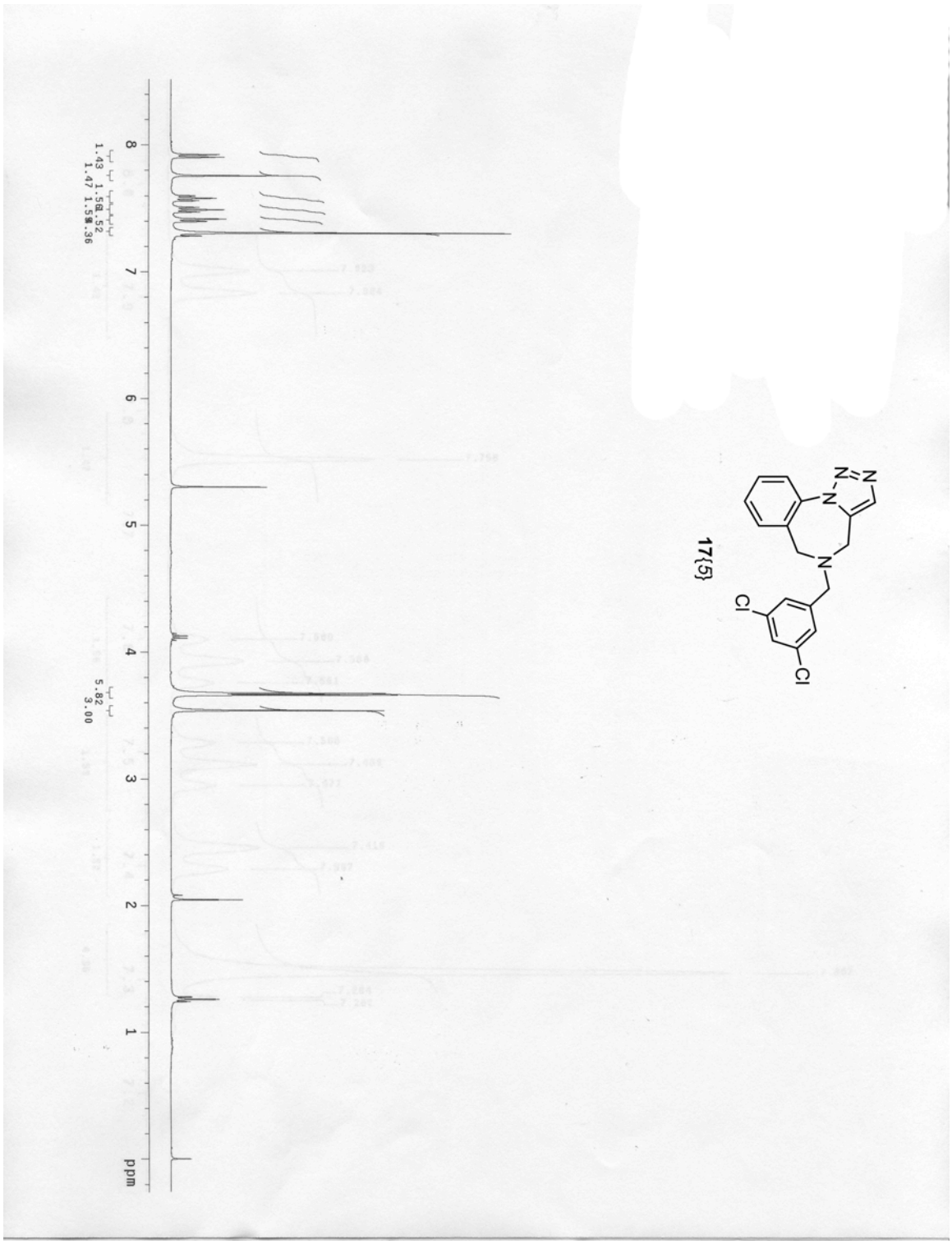

7.904
7.903
7.884
7.762
7.583
7.577
7.567
7.563
7.561
7.557
7.547
7.541
7.493
7.490
7.474
7.471
7.460
7.457
7.455
7.442
7.281
3.654
3.490
2.475
0.076
-0.000
ppm
0.97 0.99
0.94 1.96
2.00
2.00
3.02
17{1}

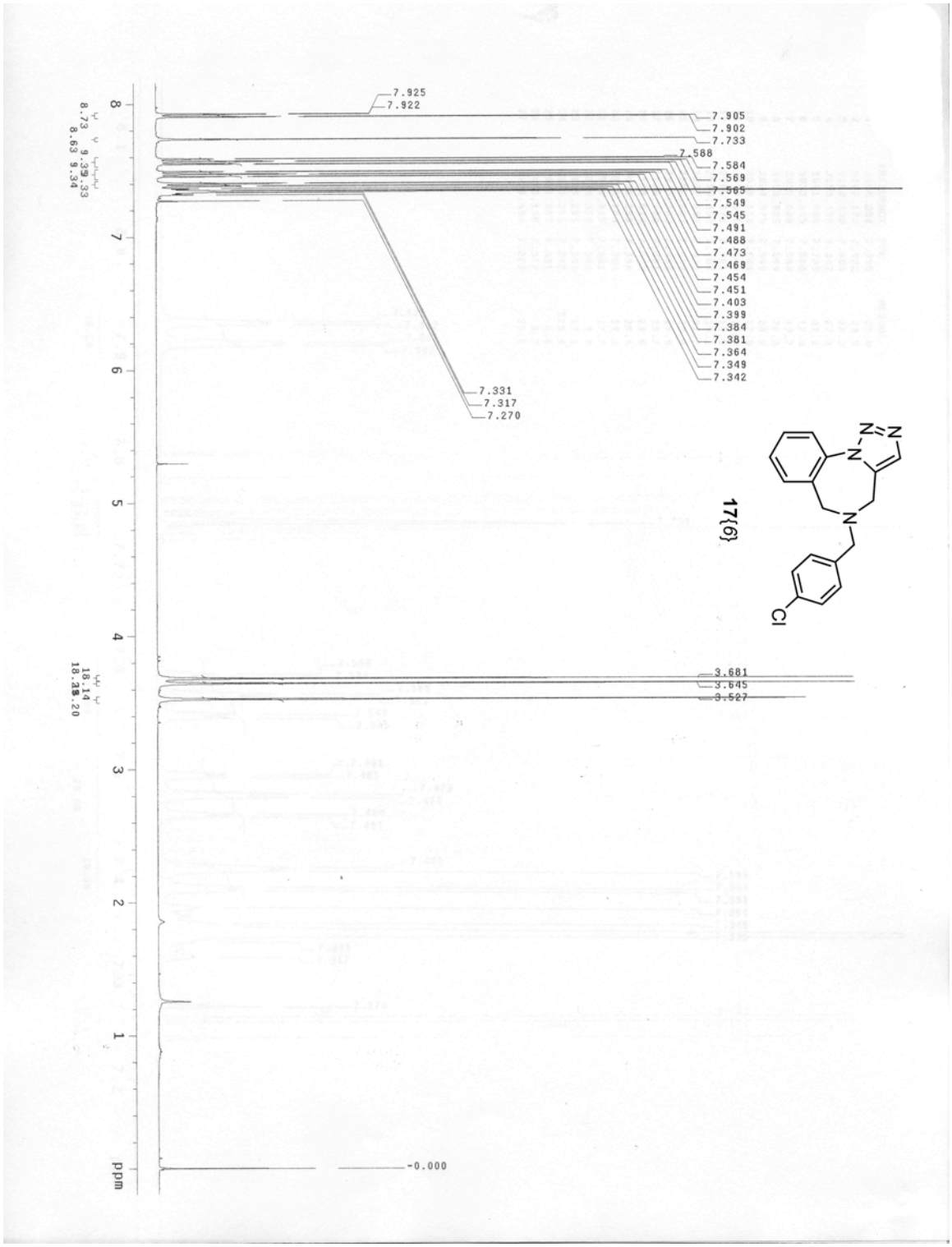

136.712
133.394
132.903
131.132
129.666
129.168
129.086
122.821
77.480
77.160
76.840
56.751
46.789
44.073
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
17{1}

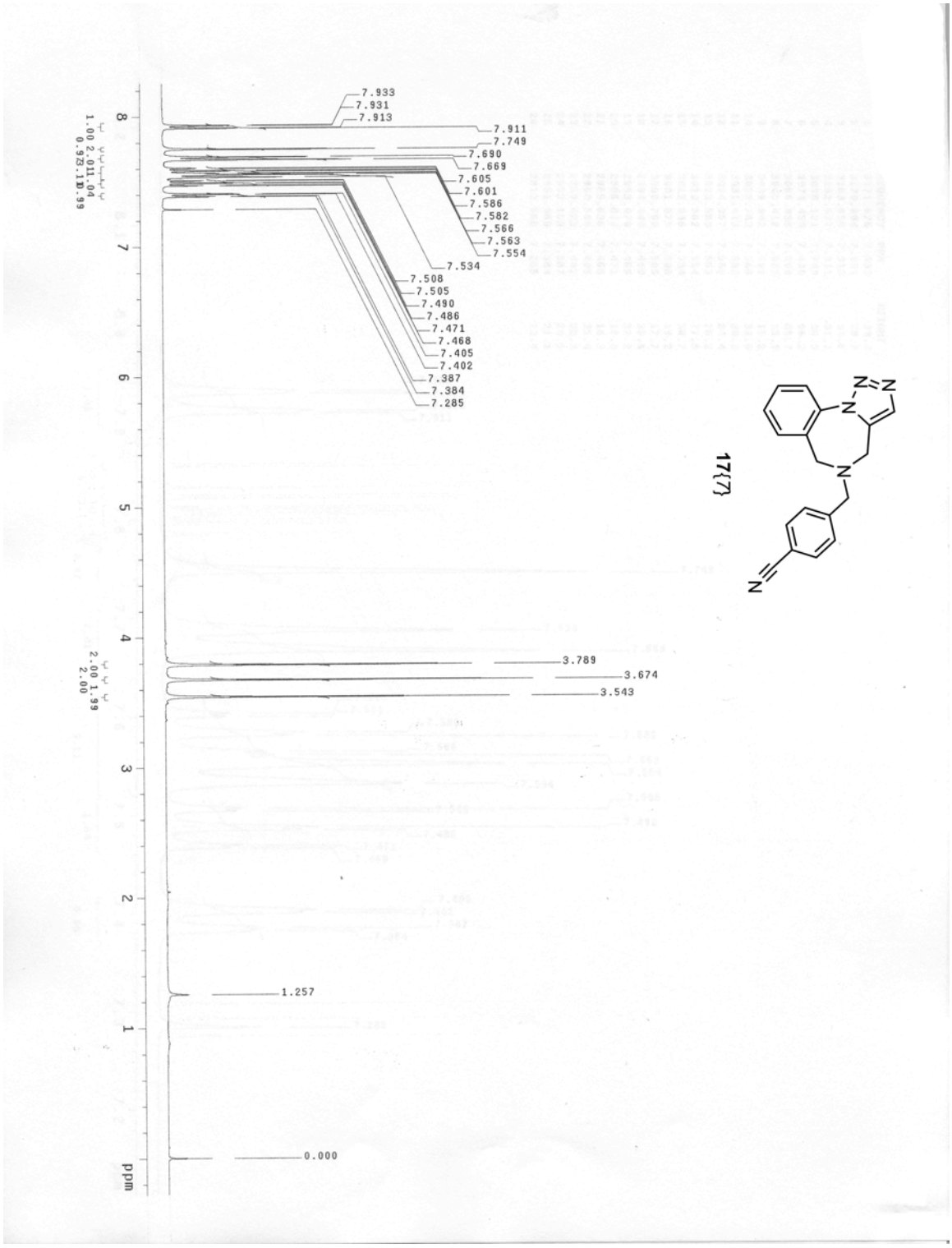

7.908
7.906
7.888
7.886
7.739
7.560
7.555
7.542
7.540
7.537
7.522
7.518
7.470
7.467
7.452
7.449
7.433
7.431
7.423
7.419
7.404
7.401
7.289
3.648
3.523
2.349
2.331
1.860
1.844
1.826
1.809
1.793
0.972
0.955
0.894
0.887
-0.000
ppm
17{2}

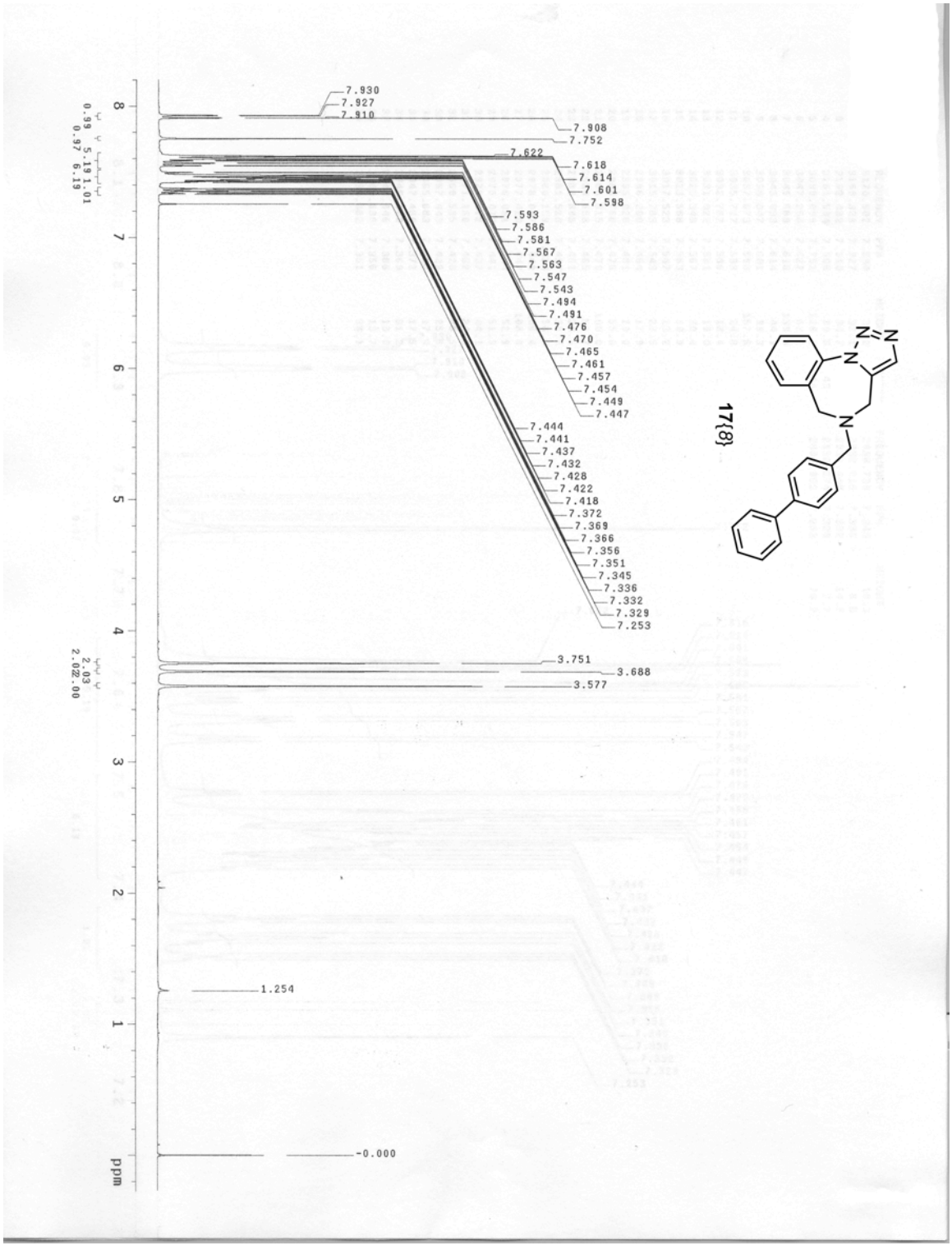

7.919
7.916
7.899
7.896
7.731
7.579
7.575
7.560
7.556
7.540
7.536
7.486
7.483
7.468
7.464
7.449
7.446
7.421
7.418
7.403
7.399
7.389
7.383
7.376
7.374
7.368
7.360
7.356
7.354
7.334
7.328
7.321
7.316
7.312
7.303
7.298
7.264
3.713
3.655
3.545
0.000
ppm
17{3}

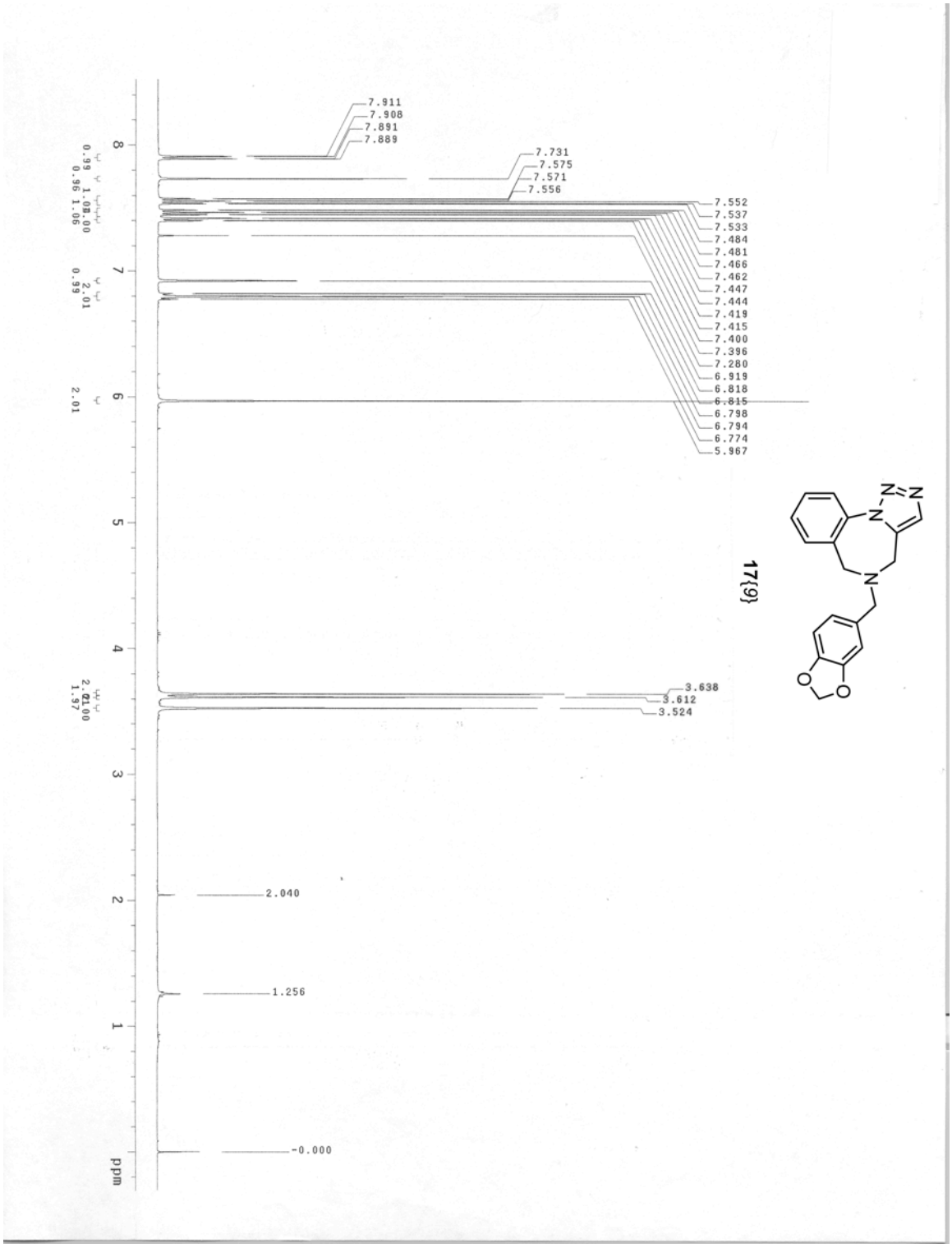

7.912
7.891
7.754
7.583
7.575
7.568
7.563
7.560
7.555
7.549
7.541
7.497
7.494
7.478
7.475
7.471
7.463
7.461
7.444
7.439
7.334
7.329
7.320
7.316
7.311
7.302
7.300
7.297
7.296
7.291
7.282
7.277
7.273
7.191
7.188
7.173
7.170
7.154
7.151
7.119
7.116
7.098
7.094
7.091
7.073
7.070
3.766
3.692
3.566
0.000
ppm
0.98 1.02 1.16 1.00
0.97 3.02 1.00
2.01
1.992.00
17(4)
N
N
N
N
F

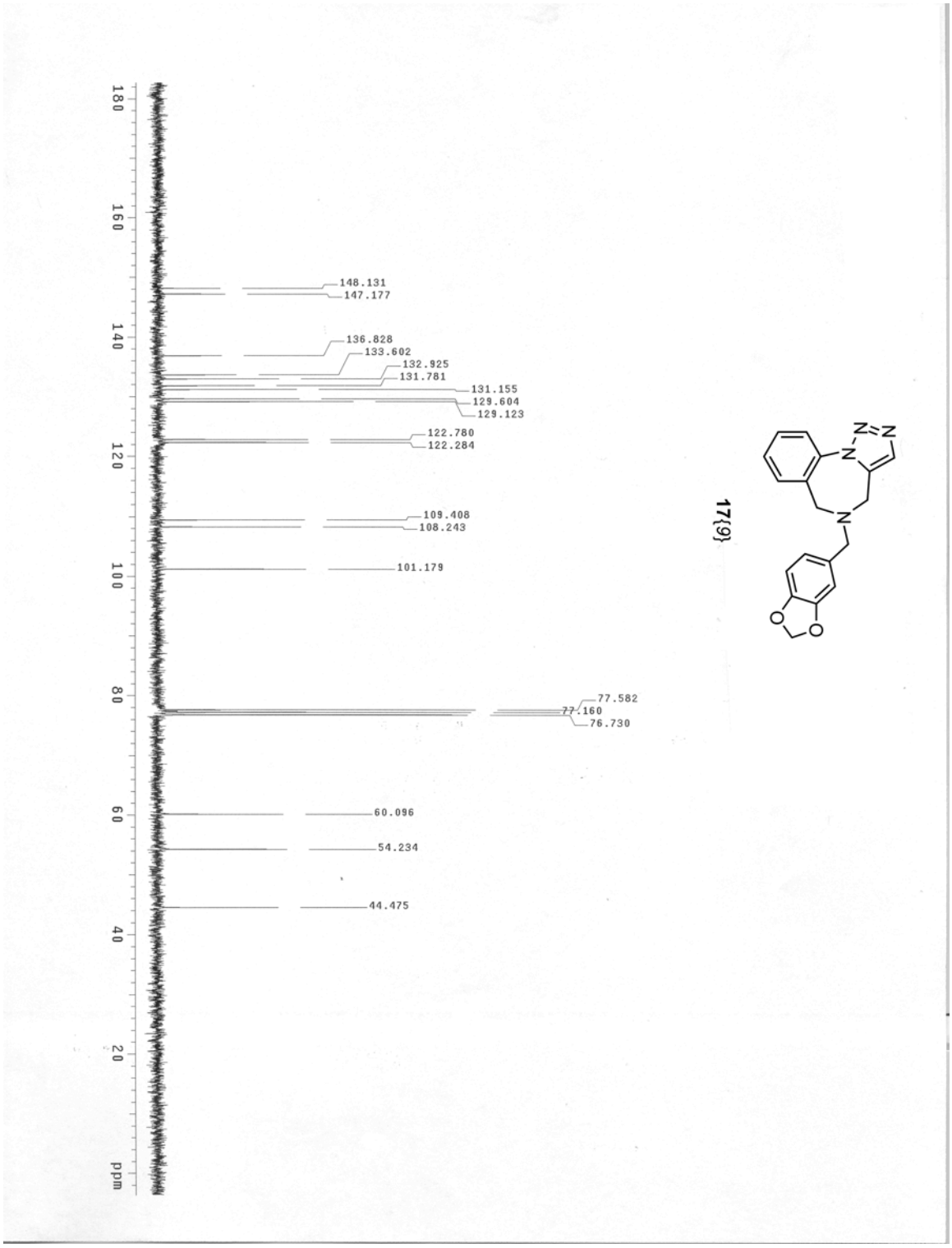

17(5)
Cl
Cl
N
N
N
ppm
1
2
3
4
5
6
7
8
1.43 1.52
1.47 1.52
1.52
1.56
1.96
5.82
3.00


7.925
7.922
7.905
7.902
7.733
7.588
7.584
7.569
7.565
7.549
7.545
7.491
7.488
7.473
7.469
7.454
7.451
7.403
7.399
7.384
7.381
7.364
7.349
7.342
7.331
7.317
7.270
3.681
3.645
3.527
-0.000
ppm
17{6}
Cl

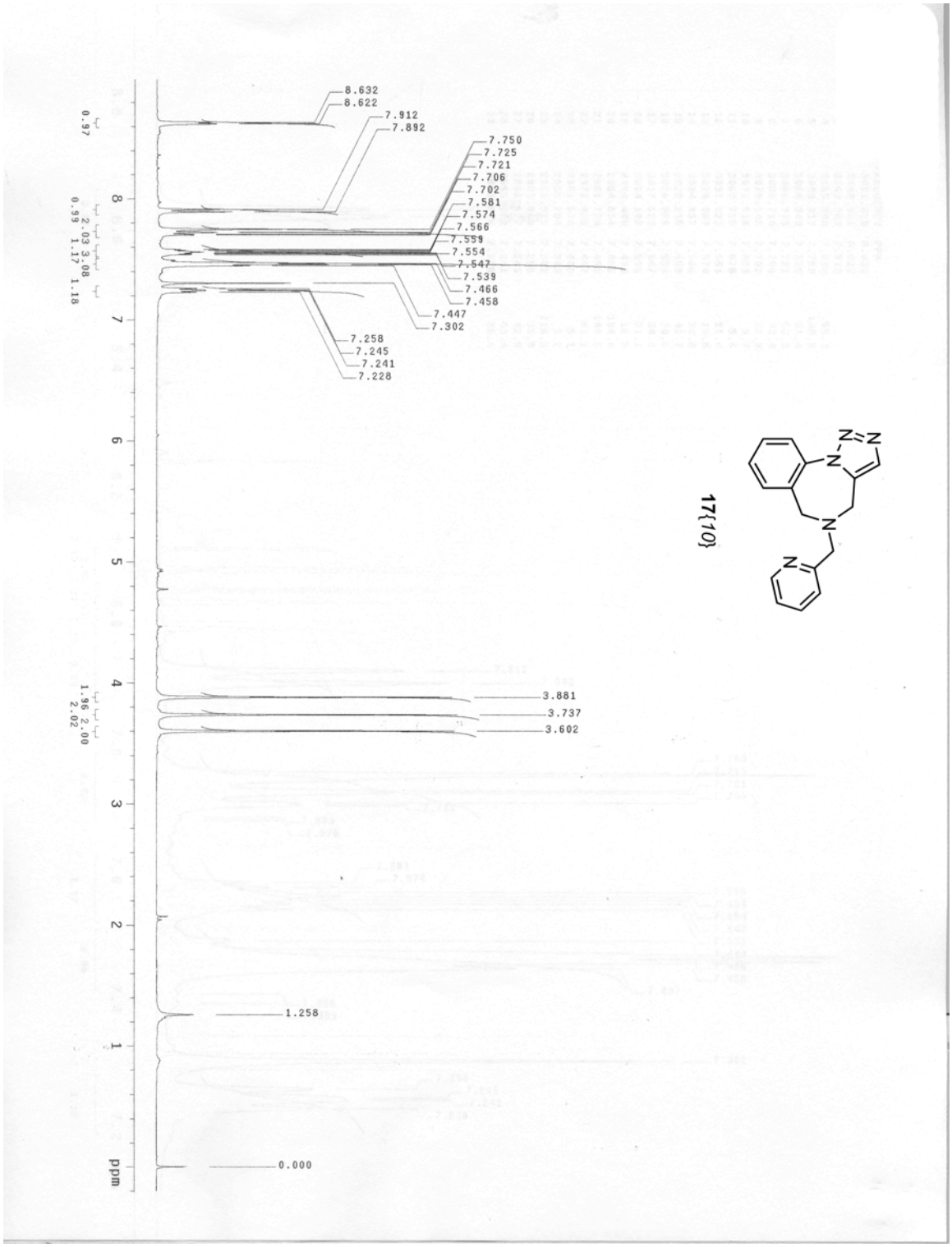

7.933
7.931
7.913
7.911
7.749
7.690
7.669
7.605
7.601
7.586
7.582
7.566
7.563
7.554
7.534
7.508
7.505
7.490
7.486
7.471
7.468
7.405
7.402
7.387
7.384
7.285
3.789
3.674
3.543
1.257
0.000
ppm
1.00 2.01 1.04
0.97 1.00 0.99
2.00 1.99
2.00
17{7}

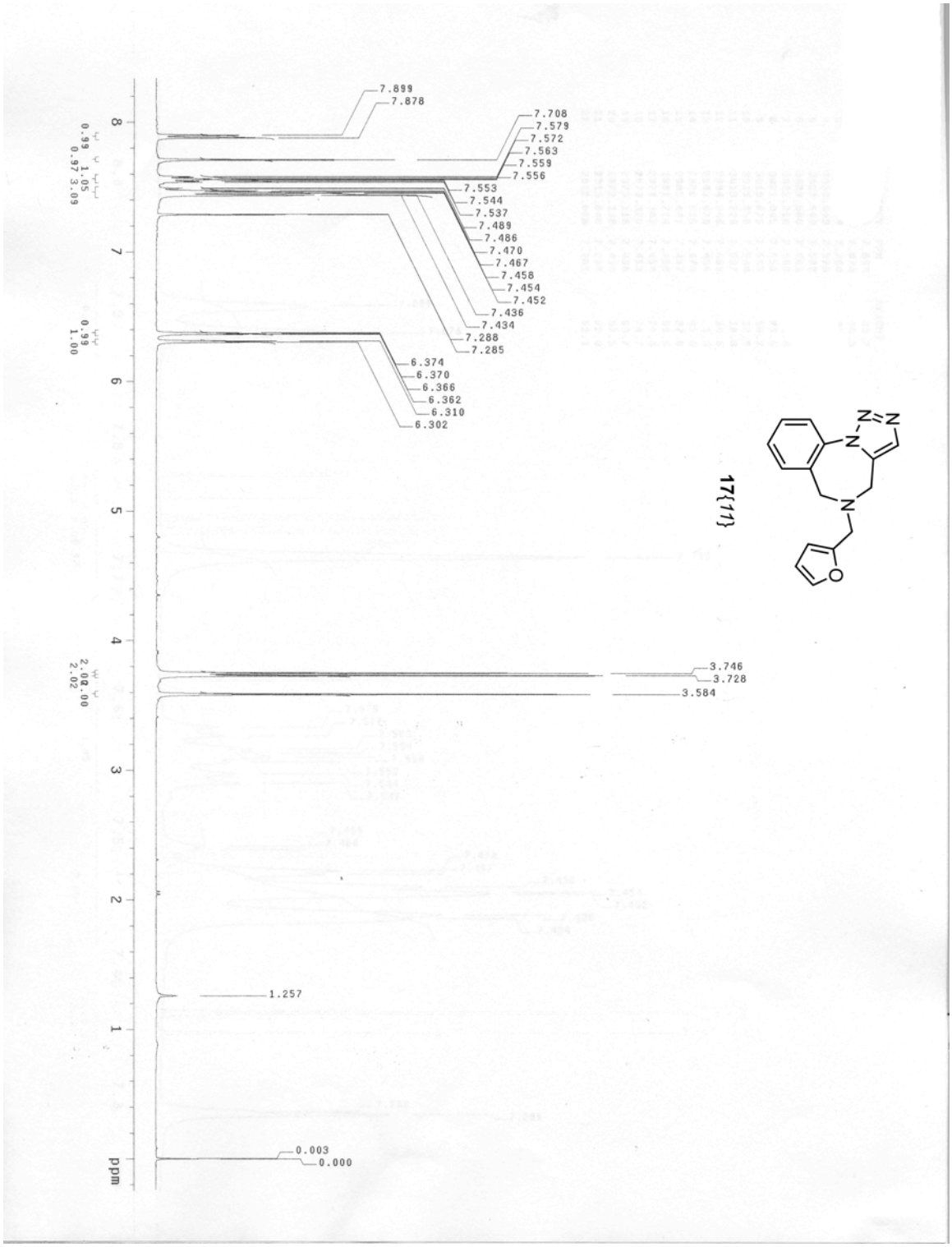

7.930
7.927
7.910
7.908
7.752
7.622
7.618
7.614
7.601
7.598
7.593
7.586
7.581
7.567
7.563
7.547
7.543
7.494
7.491
7.476
7.470
7.465
7.461
7.457
7.454
7.449
7.447
7.444
7.441
7.437
7.432
7.428
7.422
7.418
7.372
7.369
7.366
7.356
7.351
7.345
7.336
7.332
7.329
7.253
3.751
3.688
3.577
1.254
-0.000
ppm
0.99 5.19 1.01
0.97 6.19
2.03
2.02.00
17{8}

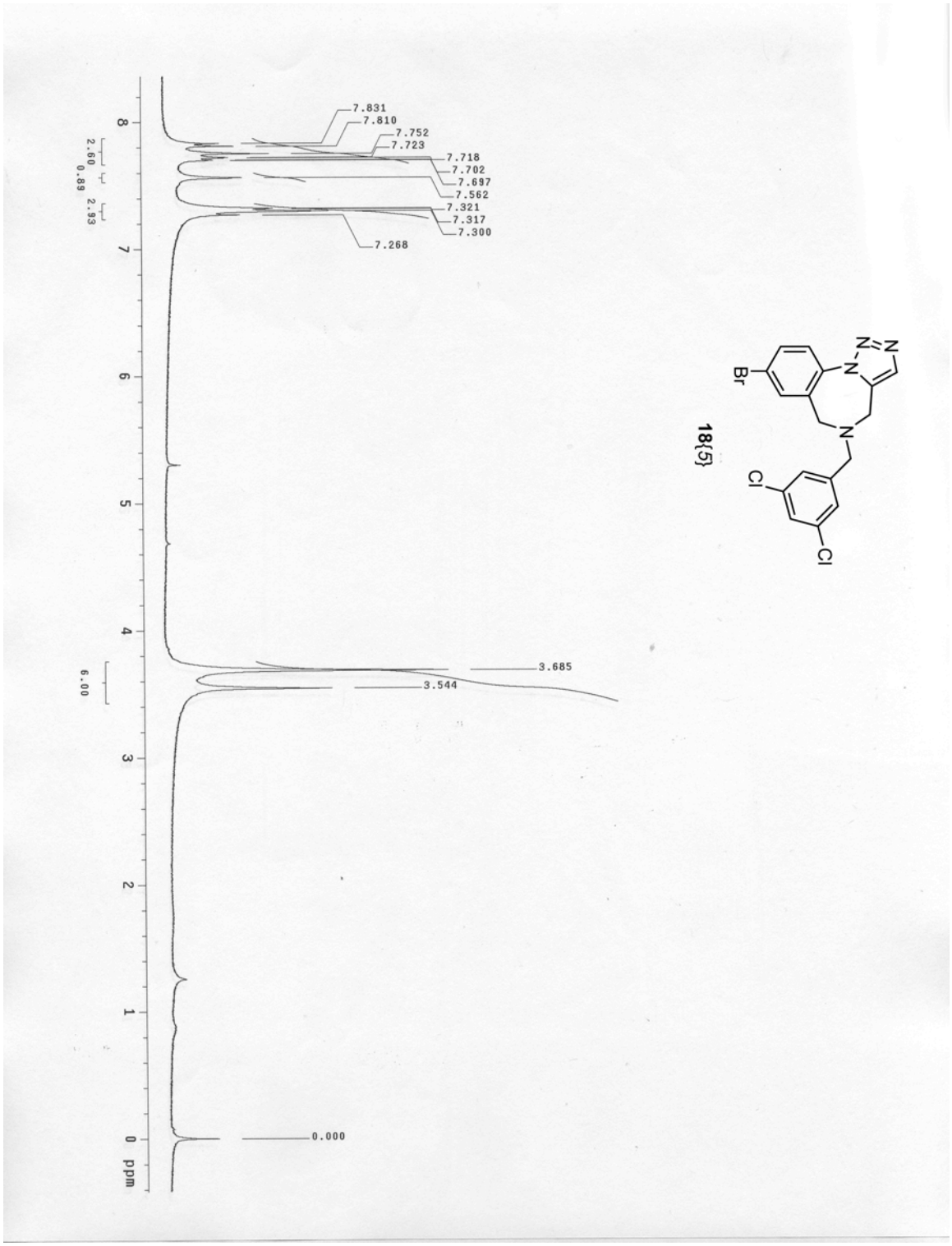

7.911
7.908
7.891
7.889
7.731
7.575
7.571
7.556
7.552
7.537
7.533
7.484
7.481
7.466
7.462
7.447
7.444
7.419
7.415
7.400
7.396
7.280
6.919
6.818
6.815
6.798
6.794
6.774
5.967
3.638
3.612
3.524
2.040
1.256
-0.000
ppm
1719

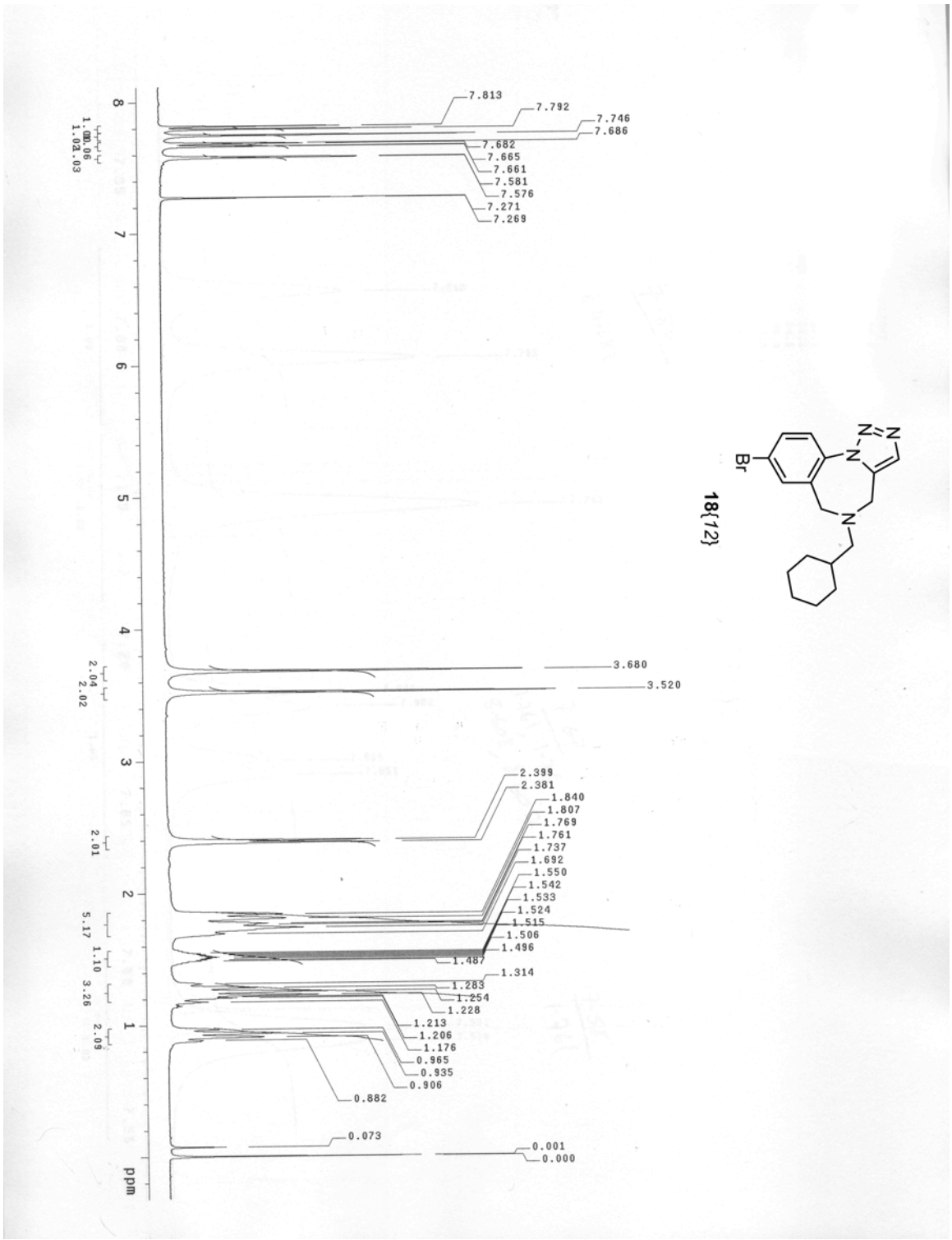

180
160
140
120
100
80
60
40
20
ppm
148.131
147.177
136.828
133.602
132.925
131.781
131.155
129.604
129.123
122.780
122.284
109.408
108.243
101.179
77.582
77.160
76.730
60.096
54.234
44.475

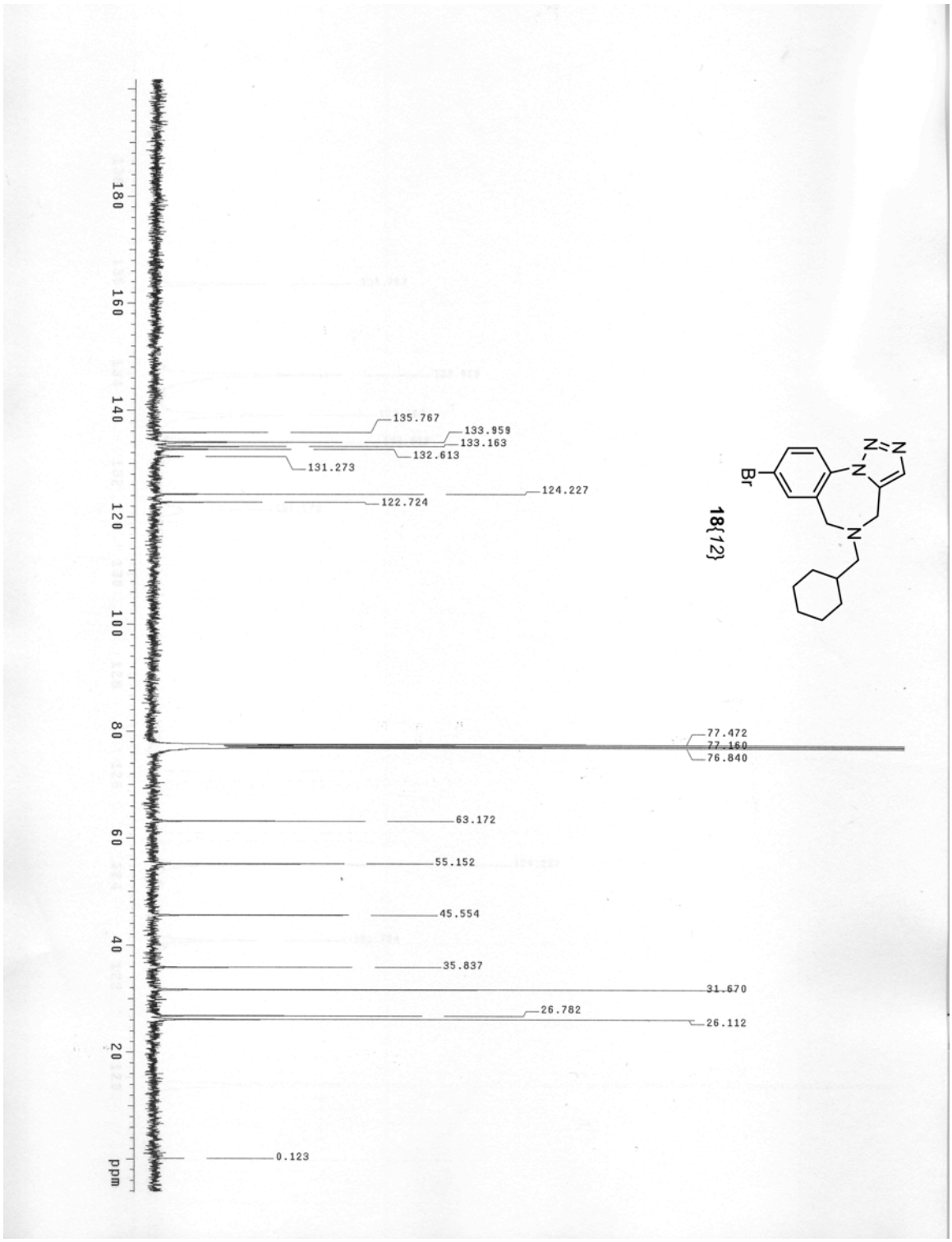
17{9}

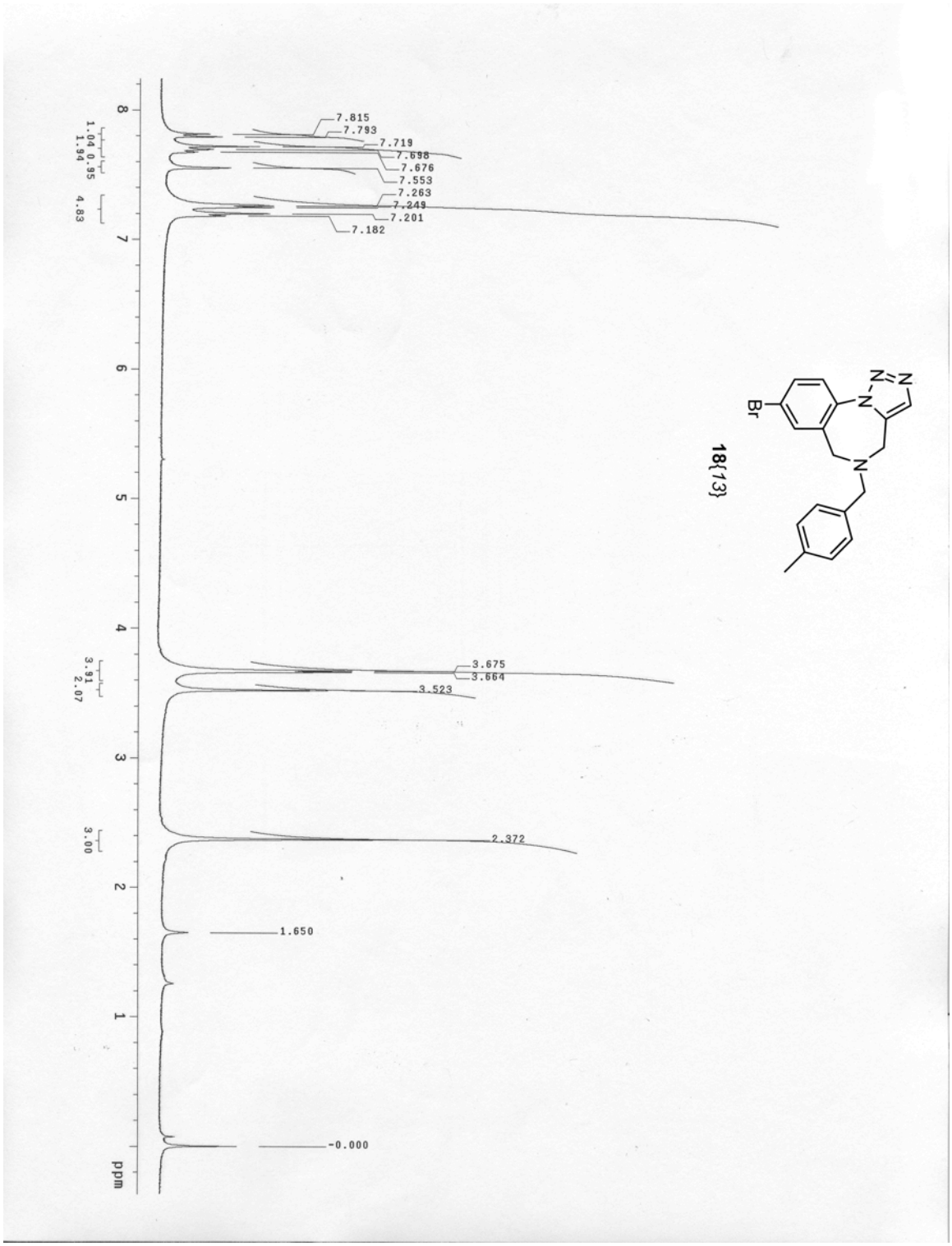

8.632
8.622
7.912
7.892
7.750
7.725
7.721
7.706
7.702
7.581
7.574
7.566
7.559
7.554
7.547
7.539
7.466
7.458
7.447
7.302
7.258
7.245
7.241
7.228
3.881
3.737
3.602
1.258
0.000
ppm
0.97
2.03
3.08
0.99
1.17
1.18
1.96
2.00
2.02
17{10}


7.899
7.878
7.708
7.579
7.572
7.563
7.559
7.556
7.553
7.544
7.537
7.489
7.486
7.470
7.467
7.458
7.454
7.452
7.436
7.434
7.288
7.285
6.374
6.370
6.366
6.362
6.310
6.302
3.746
3.728
3.584
1.257
0.003
0.000
ppm
17{11}

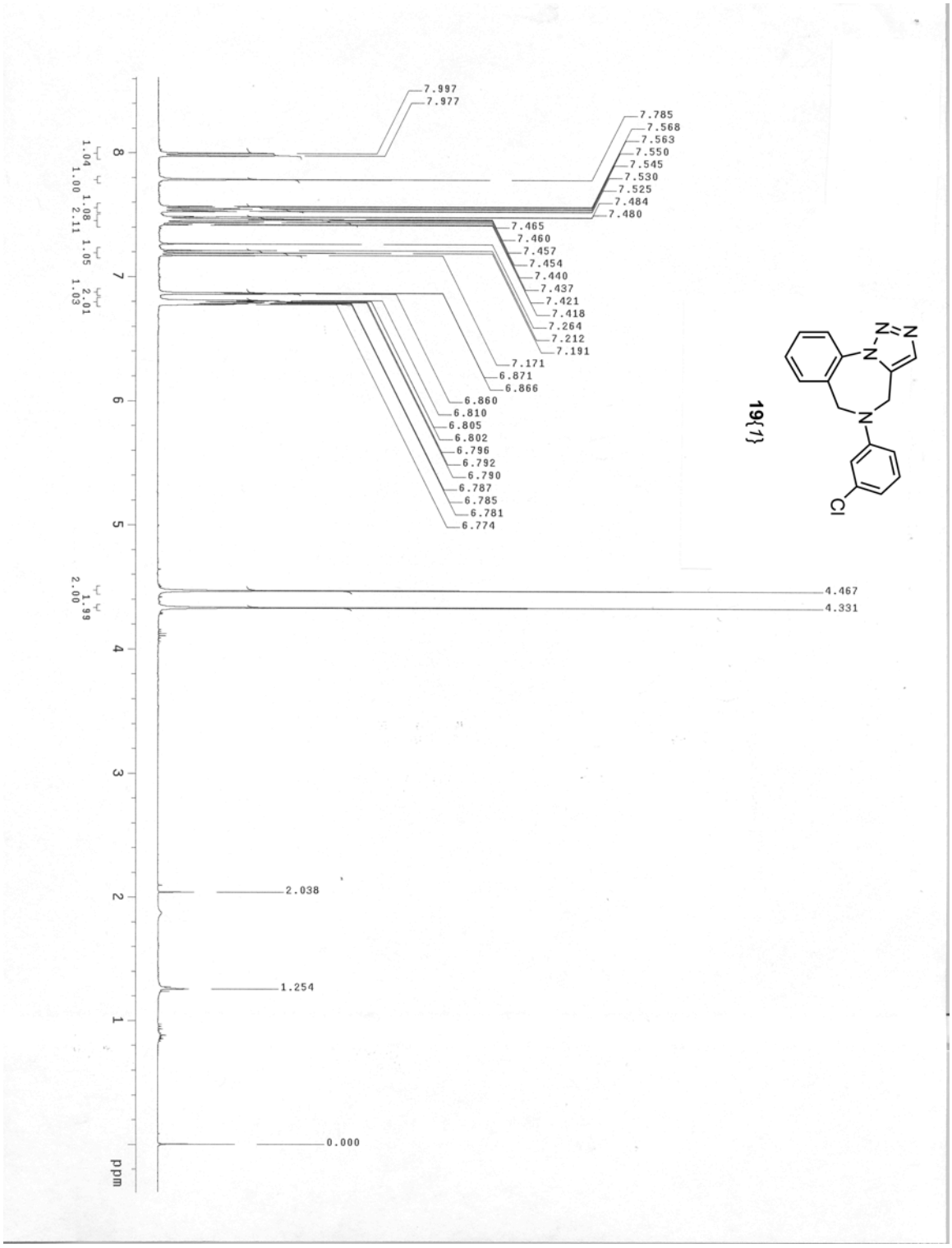

7.831
7.810
7.752
7.723
7.718
7.702
7.697
7.562
7.321
7.317
7.300
7.268
3.685
3.544
0.000
2.60
0.89
2.93
6.00
ppm
Br
N
N
N
N
Cl
Cl
18{5}

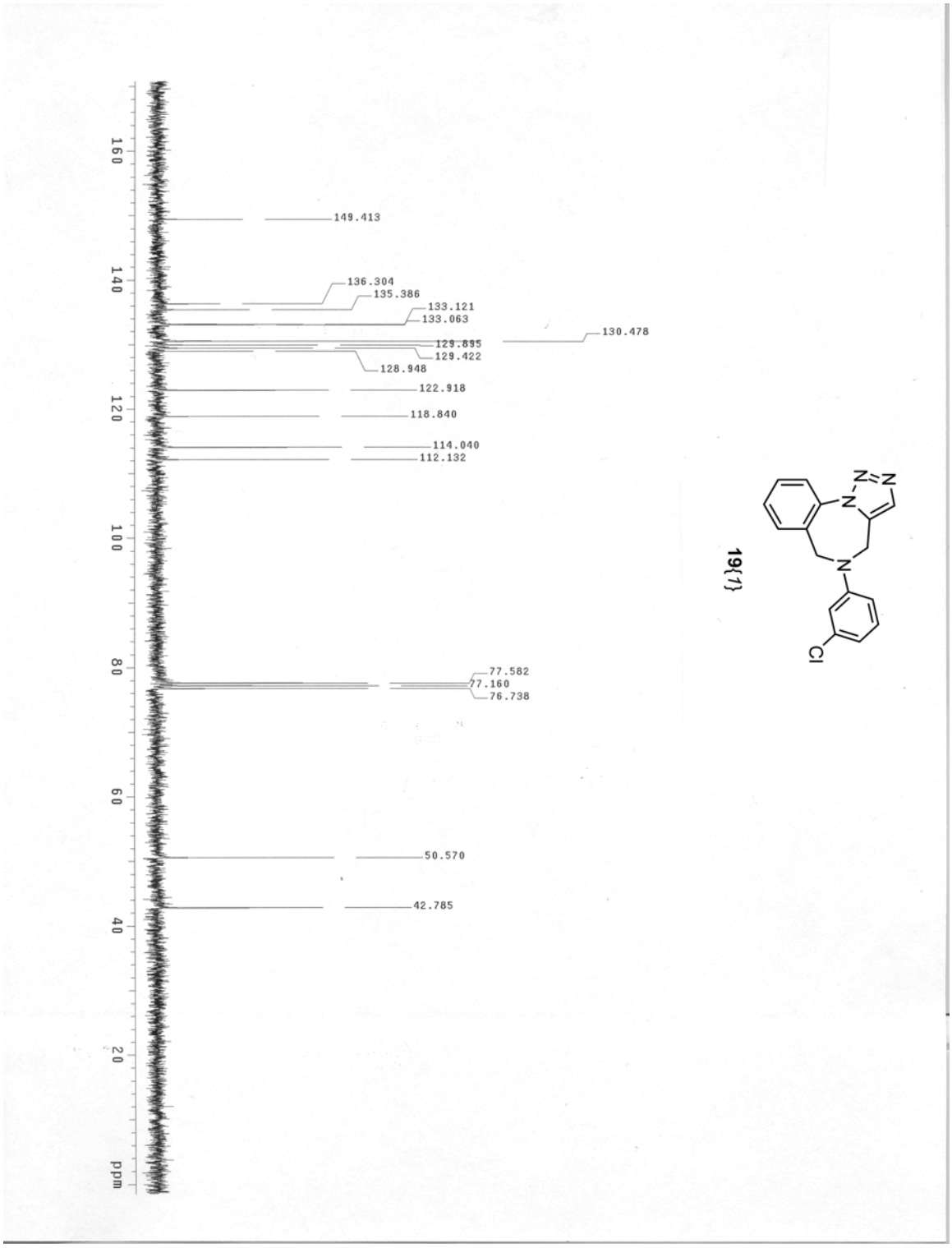

7.813
7.792
7.746
7.686
7.682
7.665
7.661
7.581
7.576
7.271
7.269
3.680
3.520
2.399
2.381
1.840
1.807
1.769
1.761
1.737
1.692
1.550
1.542
1.533
1.524
1.515
1.506
1.496
1.487
1.314
1.283
1.254
1.228
1.213
1.206
1.176
0.965
0.935
0.906
0.882
0.073
0.001
0.000
ppm
18{12}
Br

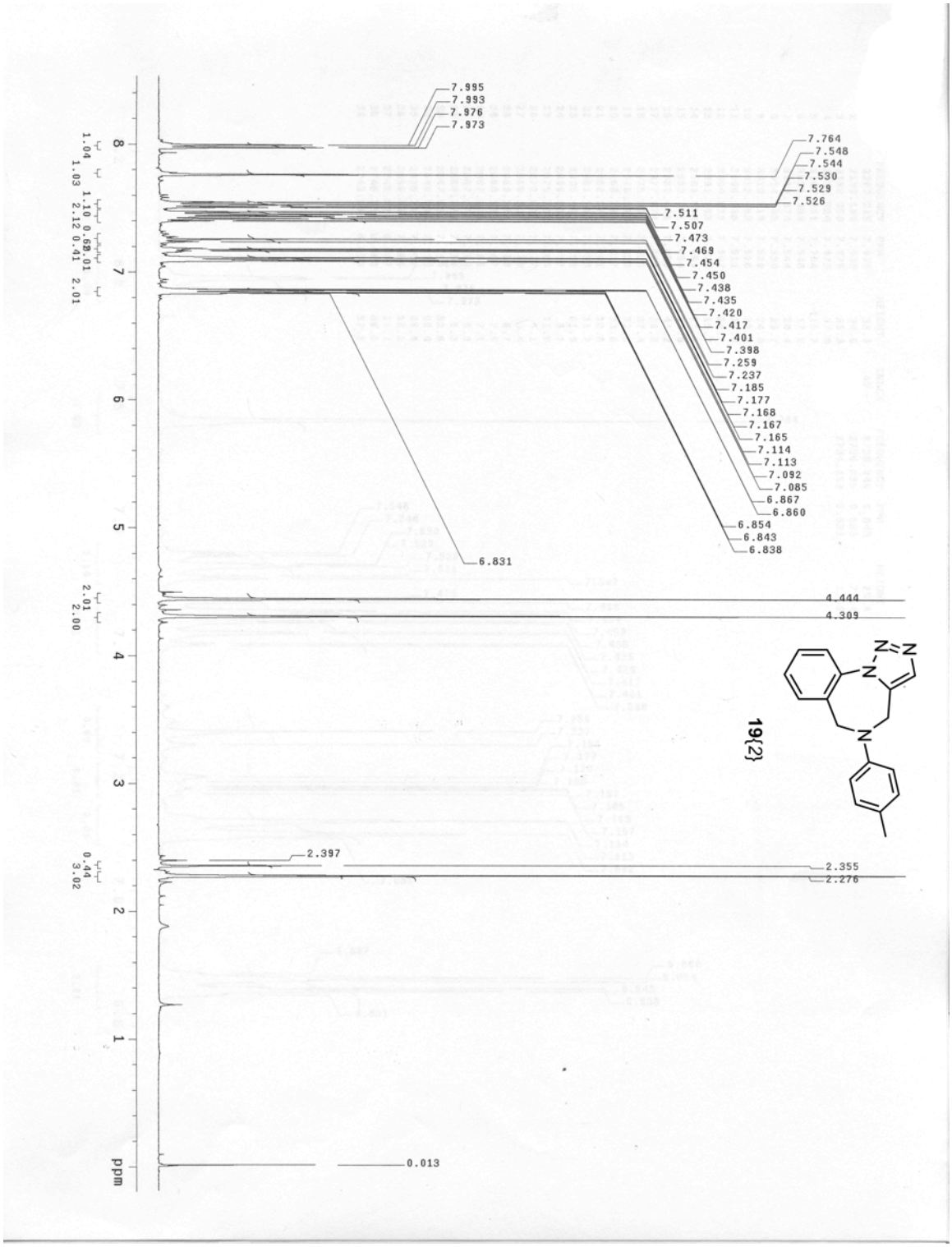

135.767
133.959
133.163
132.613
131.273
124.227
122.724
77.472
77.160
76.840
63.172
55.152
45.554
35.837
31.670
26.782
26.112
0.123
ppm
Br
18{12}

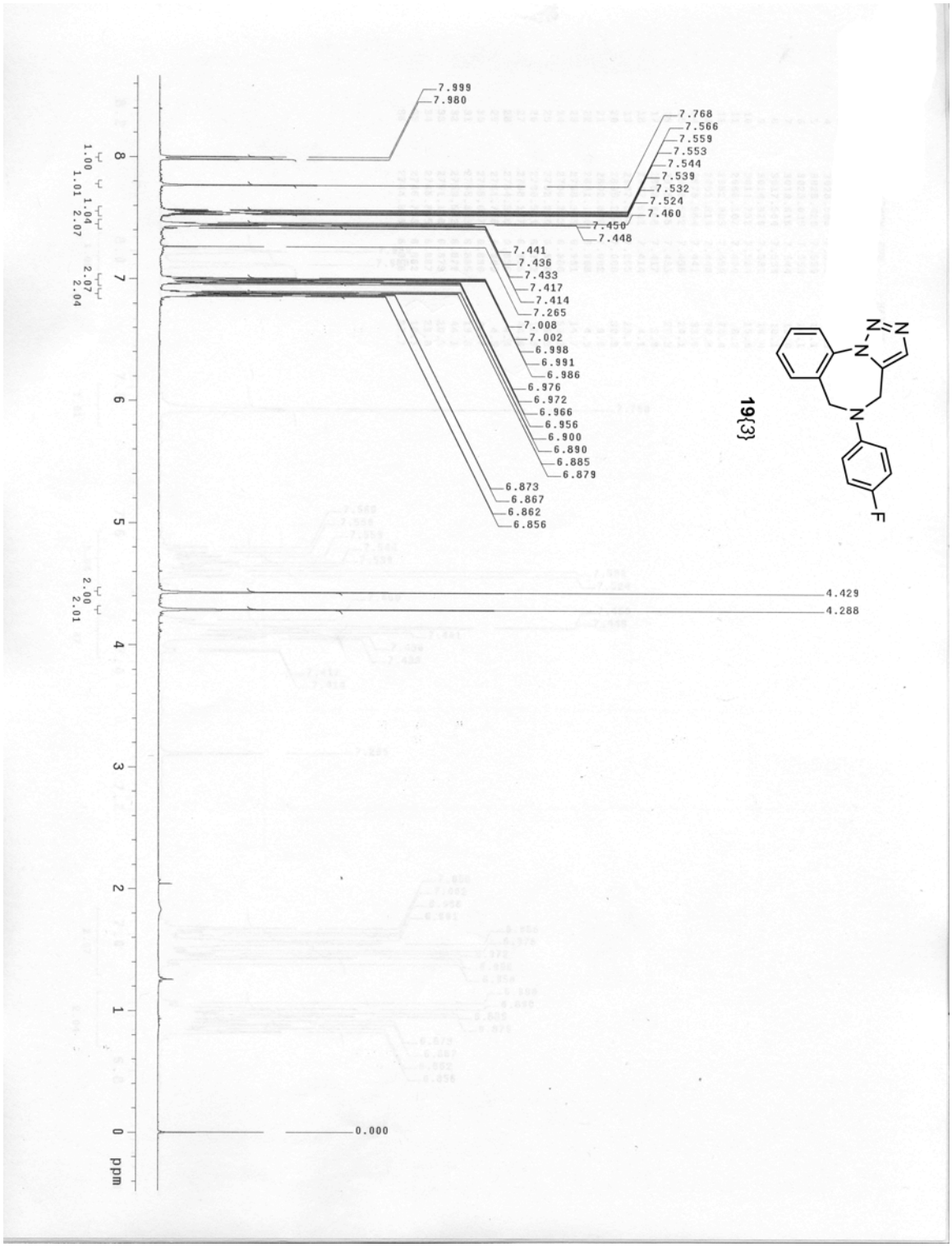

7.815
7.793
7.719
7.698
7.676
7.553
7.263
7.249
7.201
7.182
3.675
3.664
3.523
2.372
1.650
-0.000
ppm
1.04 0.95
1.94
4.83
3.91
2.07
3.00
Br
N
N
N
N

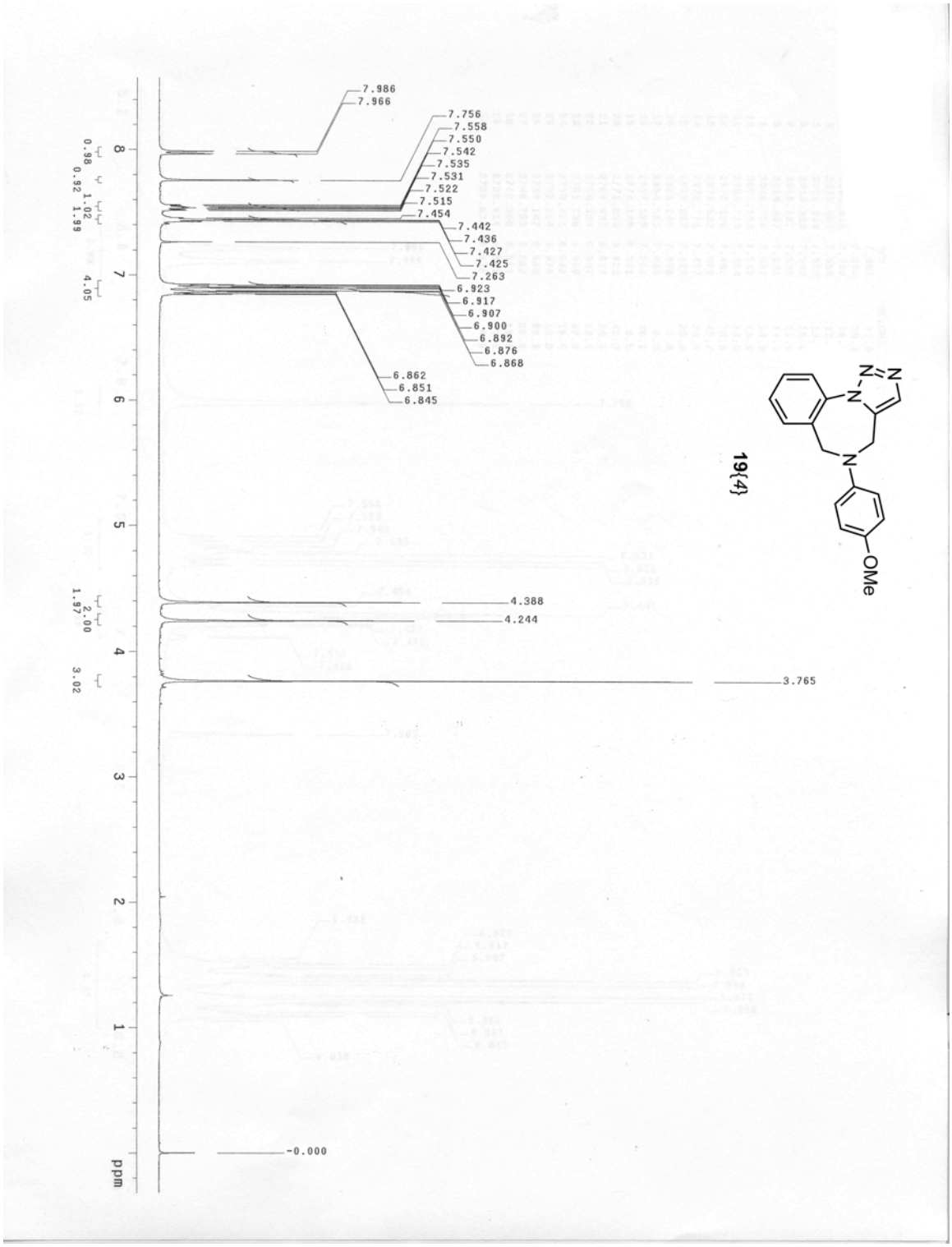
18{13}

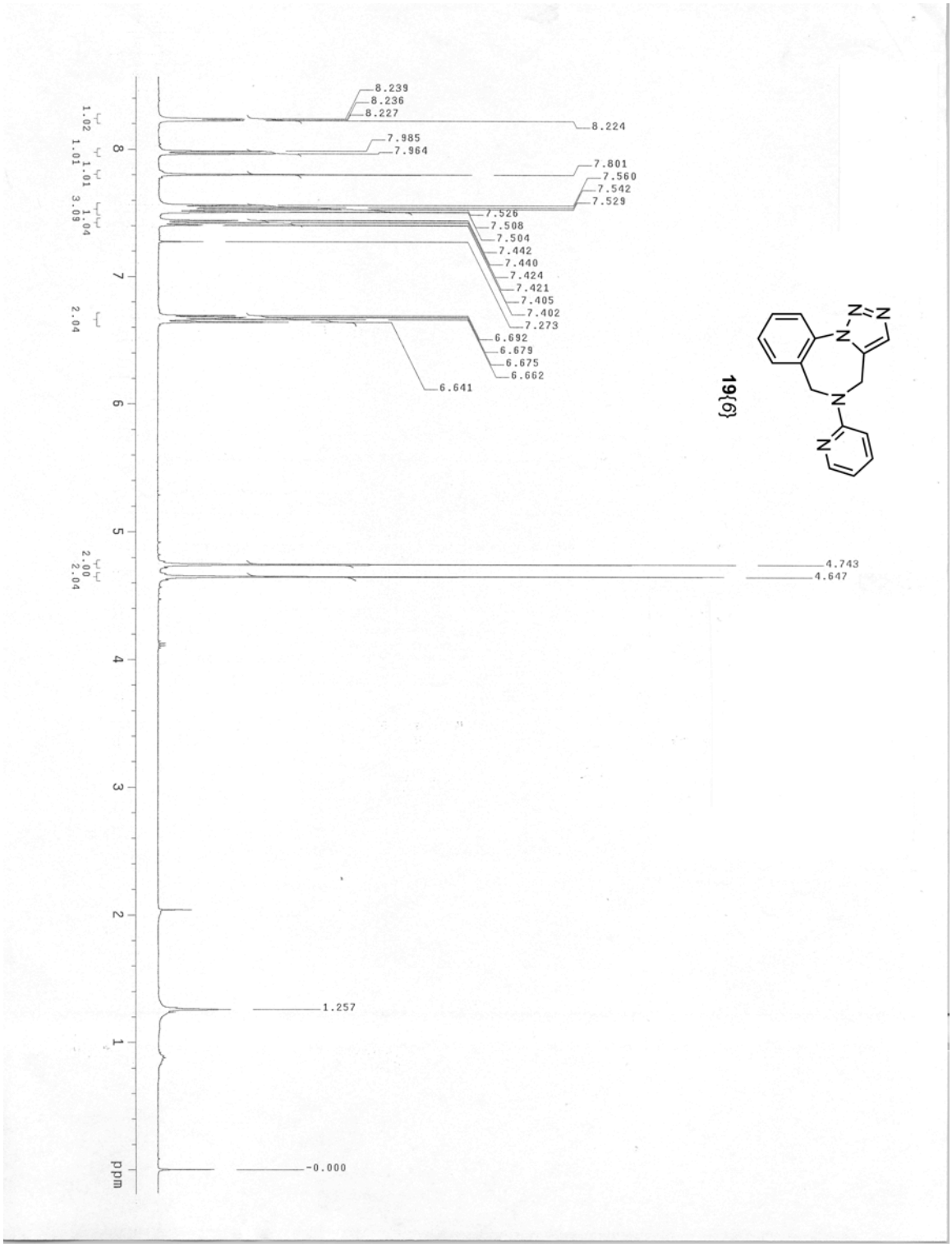

7.997
7.977
7.785
7.568
7.563
7.550
7.545
7.530
7.525
7.484
7.480
7.465
7.460
7.457
7.454
7.440
7.437
7.421
7.418
7.264
7.212
7.191
7.171
6.871
6.866
6.860
6.810
6.805
6.802
6.796
6.792
6.790
6.787
6.785
6.781
6.774
4.467
4.331
2.038
1.254
0.000
ppm
19{1}
Cl

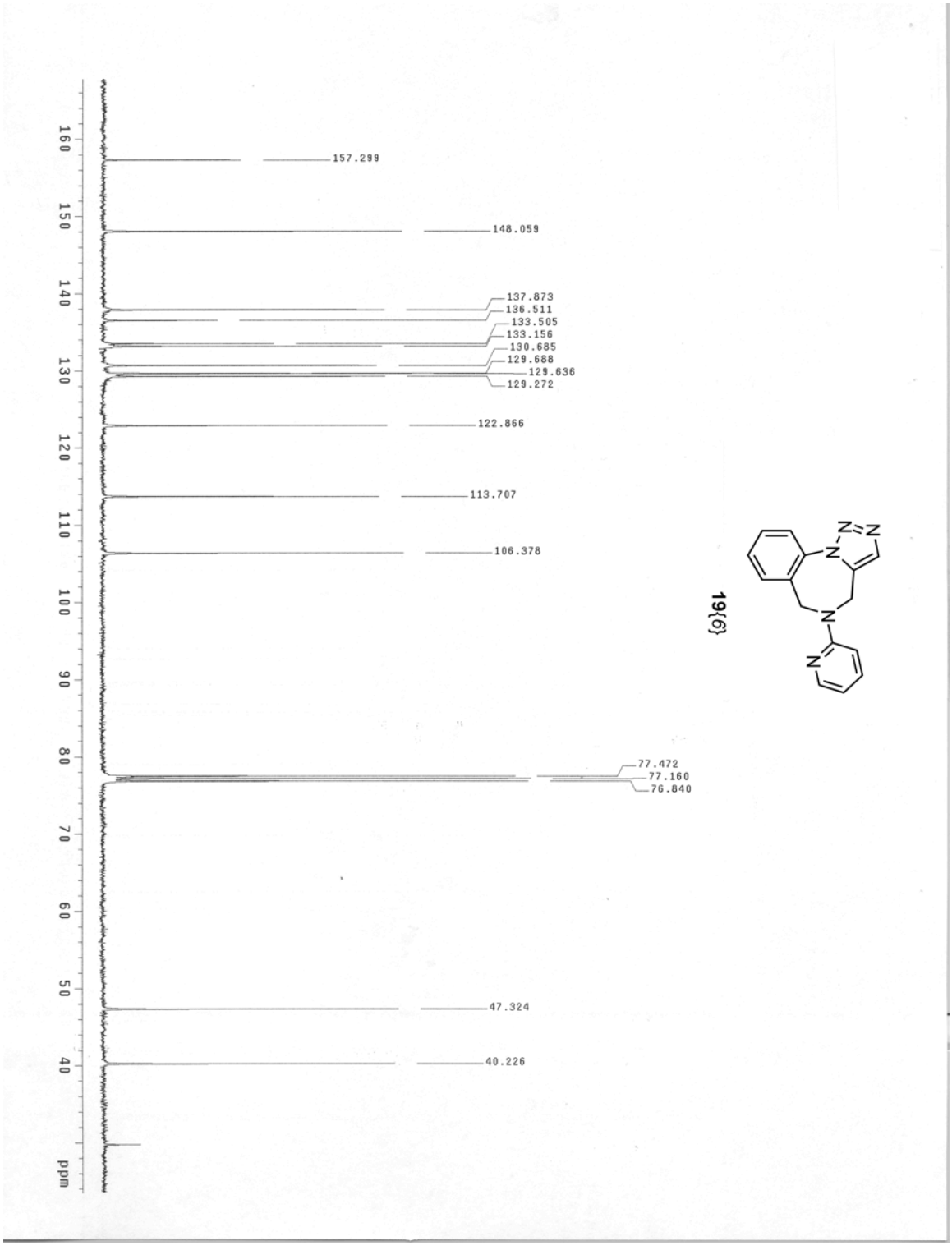

160
140
120
100
80
60
40
20
ppm
149.413
136.304
135.386
133.121
133.063
130.478
129.895
129.422
128.948
122.918
118.840
114.040
112.132
77.582
77.160
76.738
50.570
42.785
19{1}
N
N
N
N
Cl


7.995
7.993
7.976
7.973
7.764
7.548
7.544
7.530
7.529
7.526
7.511
7.507
7.473
7.469
7.454
7.450
7.438
7.435
7.420
7.417
7.401
7.398
7.259
7.237
7.185
7.177
7.168
7.167
7.165
7.114
7.113
7.092
7.085
6.867
6.860
6.854
6.843
6.838
6.831
4.444
4.309
2.397
2.355
2.276
0.013
ppm
19{2}


7.999
7.980
7.768
7.566
7.559
7.553
7.544
7.539
7.532
7.524
7.460
7.450
7.448
7.441
7.436
7.433
7.417
7.414
7.265
7.008
7.002
6.998
6.991
6.986
6.976
6.972
6.966
6.956
6.900
6.890
6.885
6.879
6.873
6.867
6.862
6.856
4.429
4.288
0.000
ppm
19{3}
F

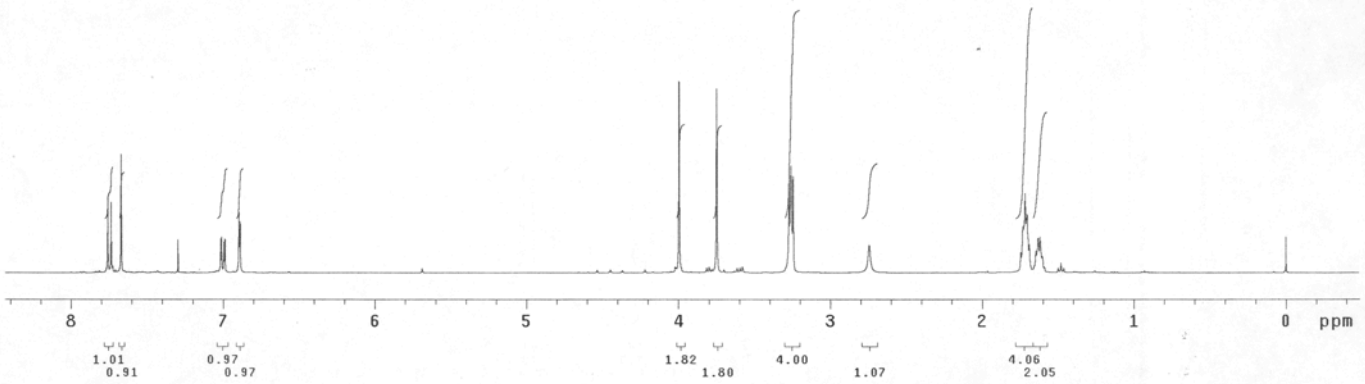

7.986
7.966
7.756
7.558
7.550
7.542
7.535
7.531
7.522
7.515
7.454
7.442
7.436
7.427
7.425
7.263
6.923
6.917
6.907
6.900
6.892
6.876
6.868
6.862
6.851
6.845
4.388
4.244
3.765
-0.000
ppm
19{4}
OMe

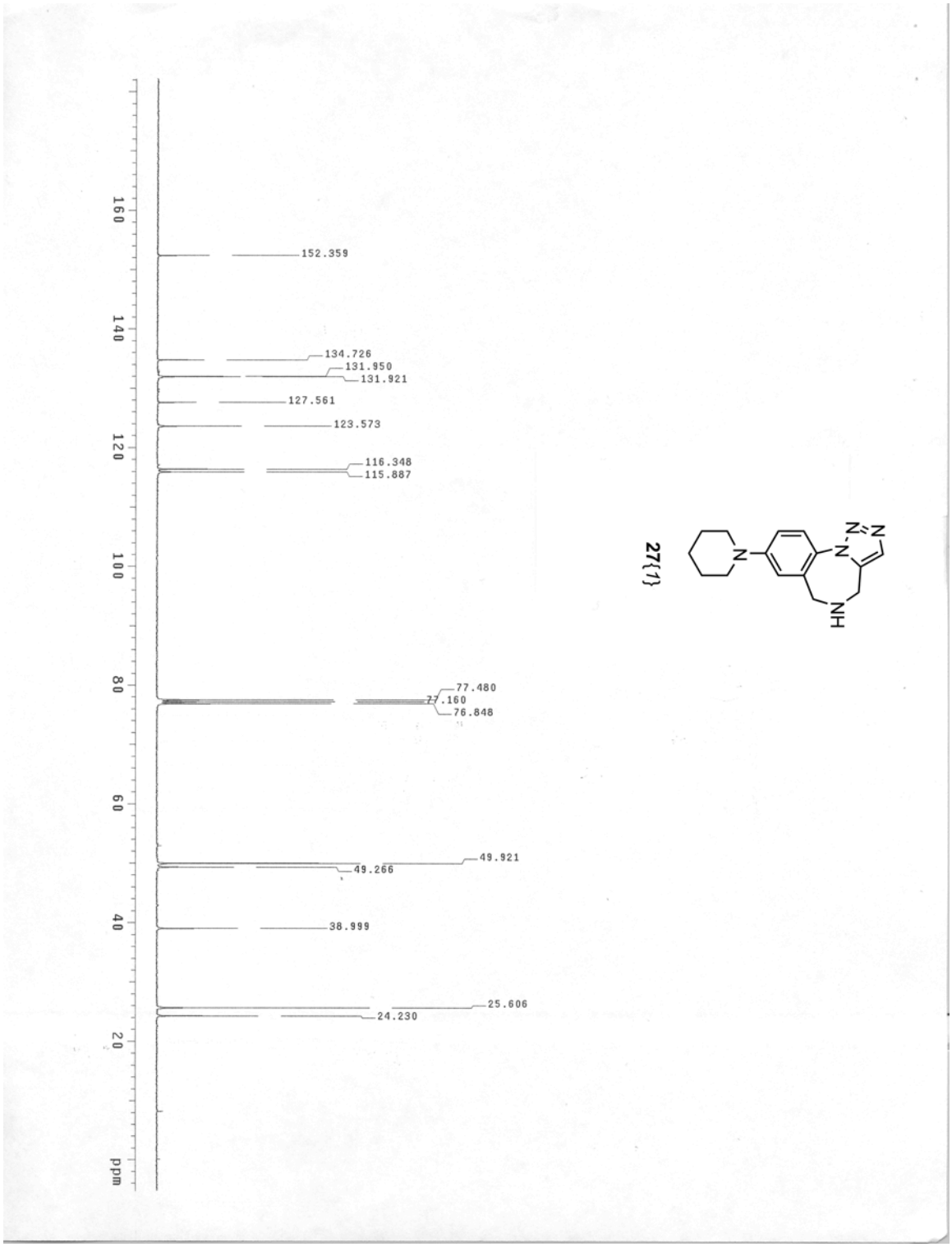

8.239
8.236
8.227
8.224
7.985
7.964
7.801
7.560
7.542
7.529
7.526
7.508
7.504
7.442
7.440
7.424
7.421
7.405
7.402
7.273
6.692
6.679
6.675
6.662
6.641
4.743
4.647
1.257
-0.000
ppm
1.02
1.01
1.01
3.09
1.04
2.04
2.00
2.04
19{9}

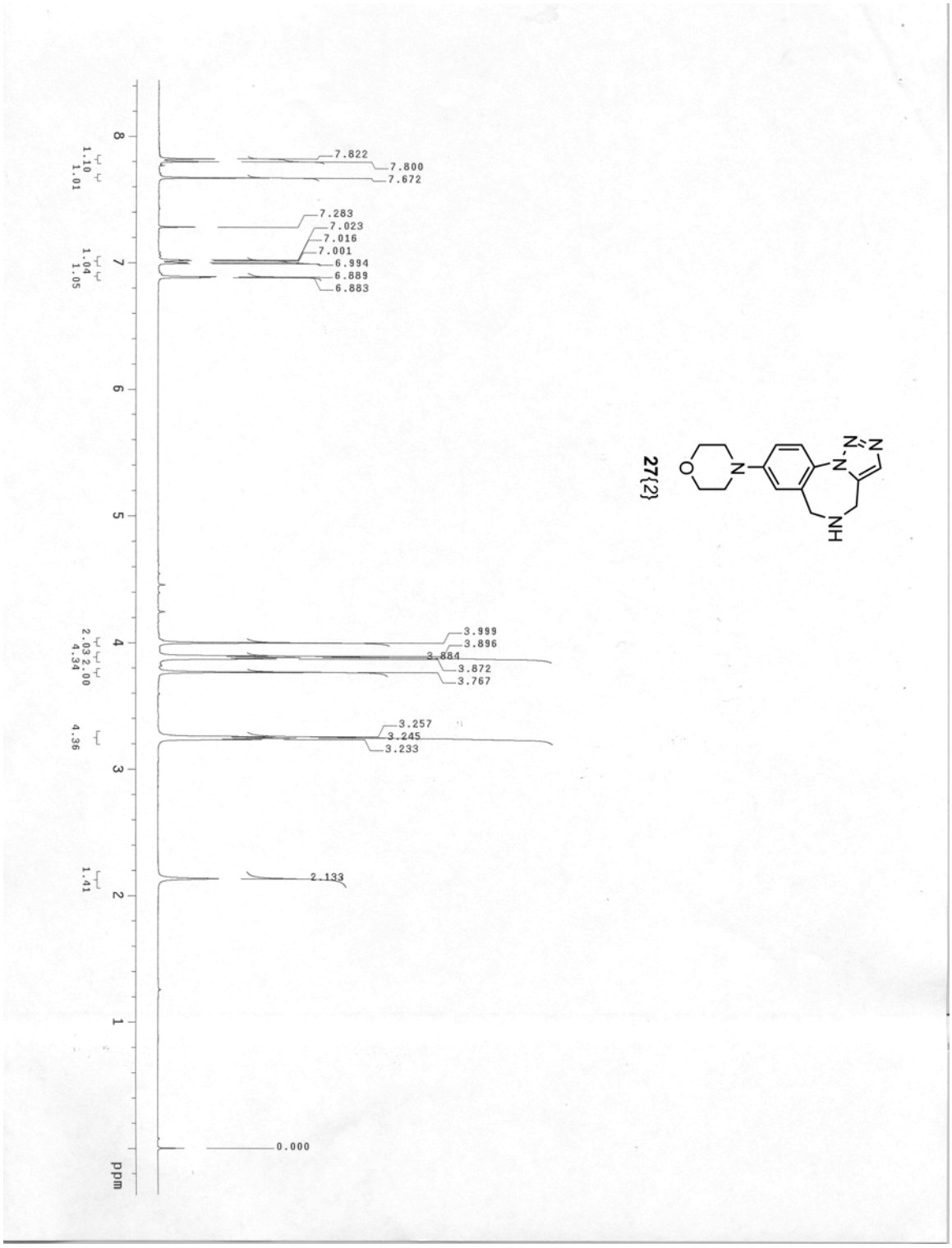

157.299
148.059
137.873
136.511
133.505
133.156
130.685
129.688
129.636
129.272
122.866
113.707
106.378
77.472
77.160
76.840
47.324
40.226
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

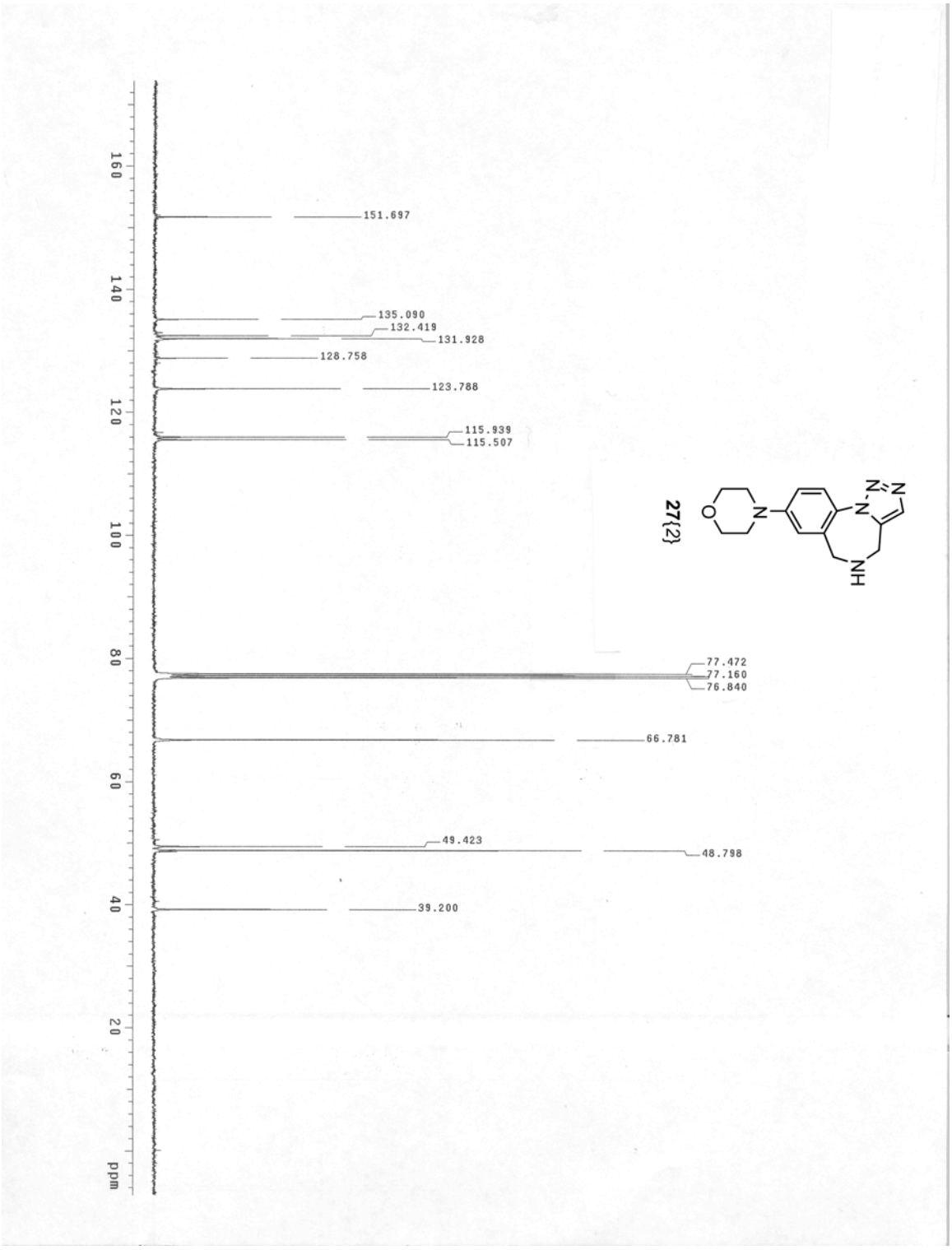
19{9}

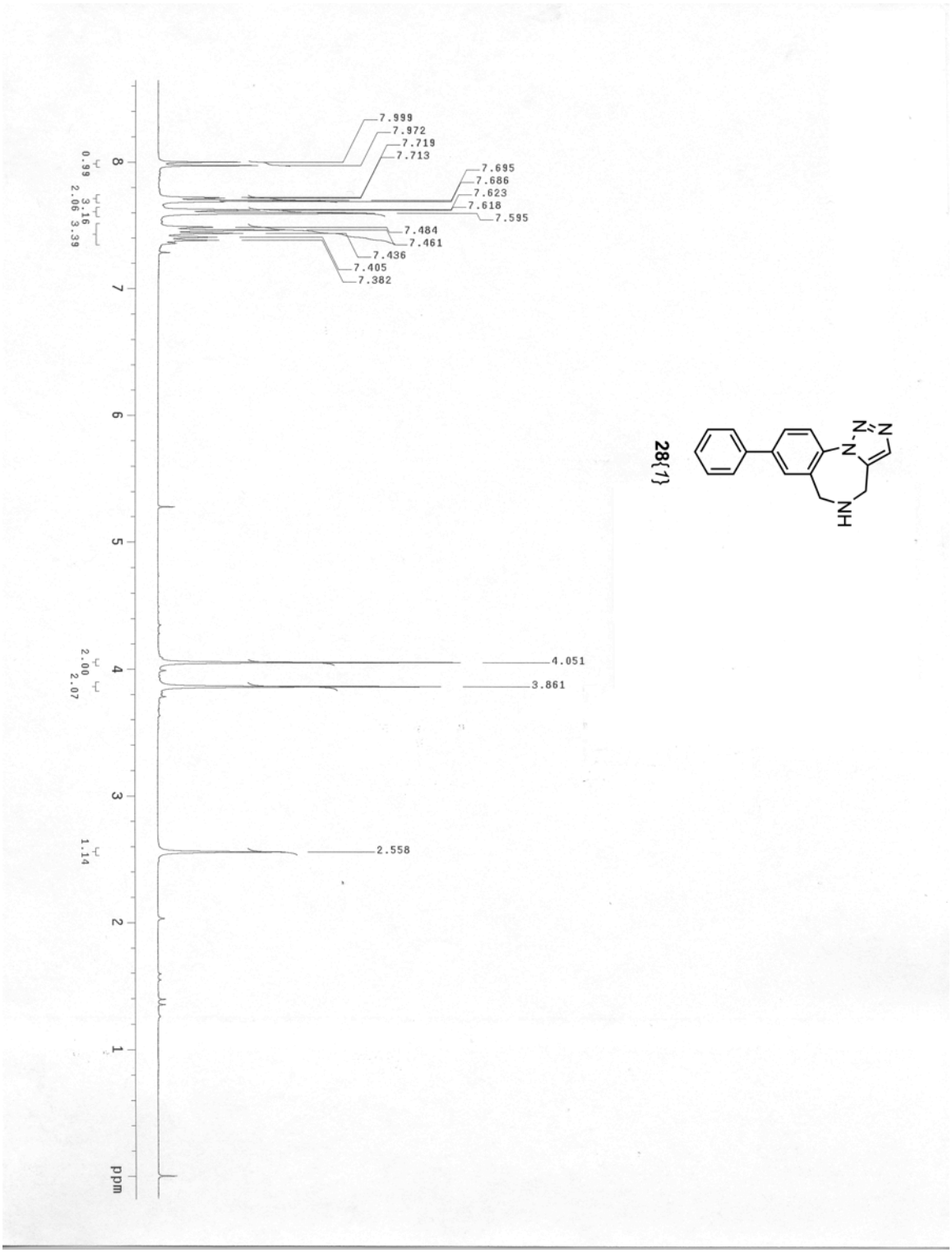
27{*1*}

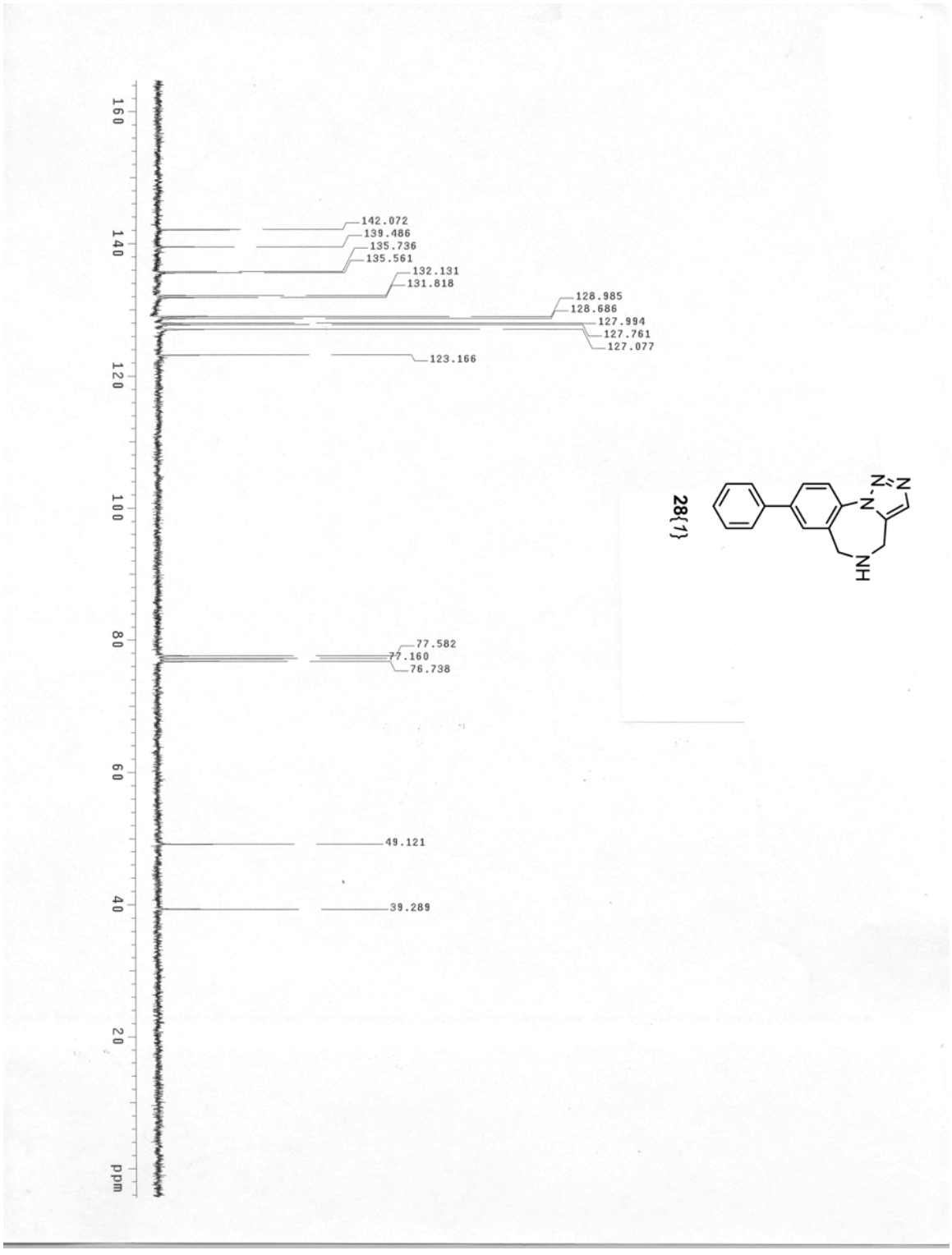


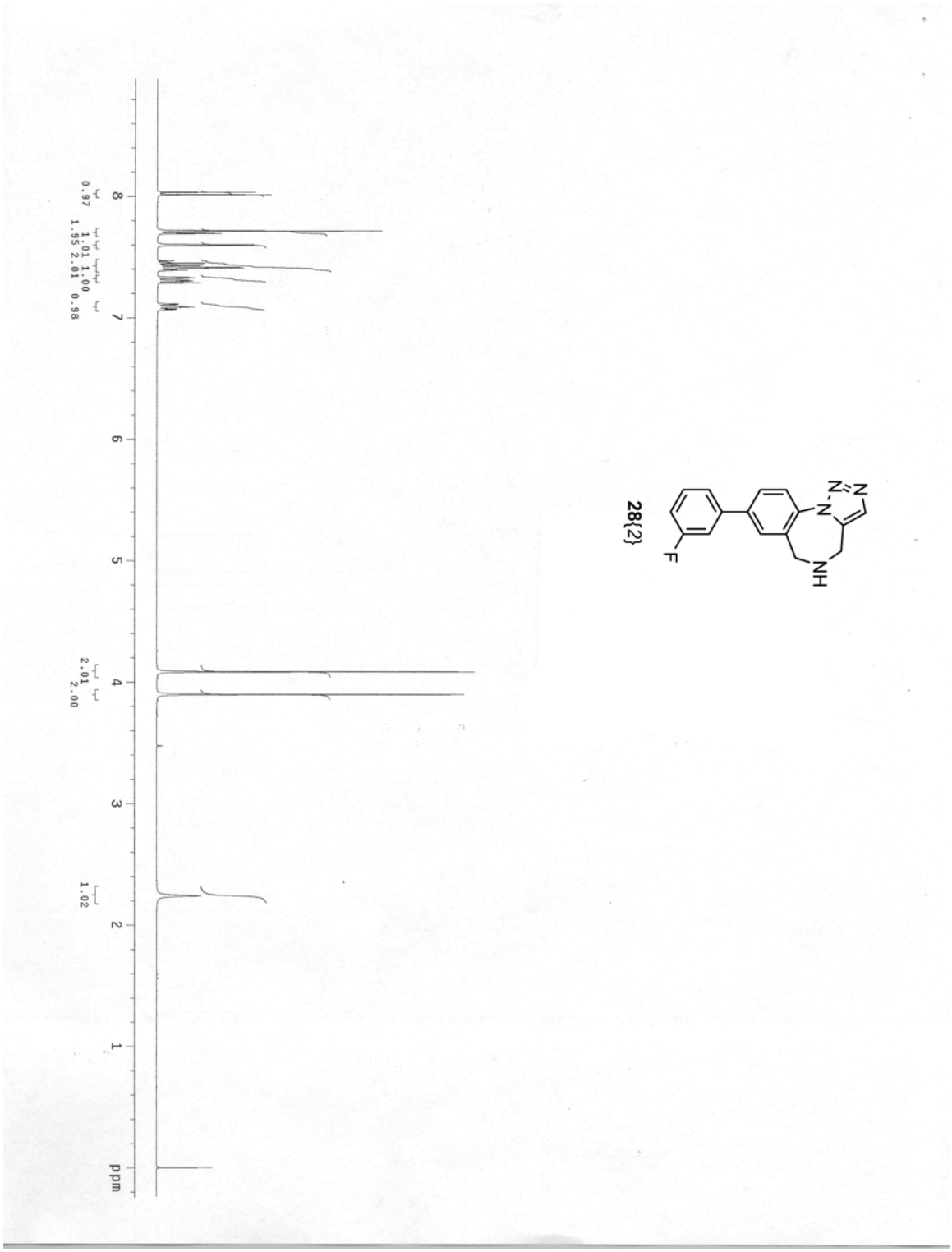

152.359
134.726
131.950
131.921
127.561
123.573
116.348
115.887
77.480
77.160
76.848
49.921
49.266
38.999
25.606
24.230
160
140
120
100
80
60
40
20
ppm
27{1}
N
N
N
NH

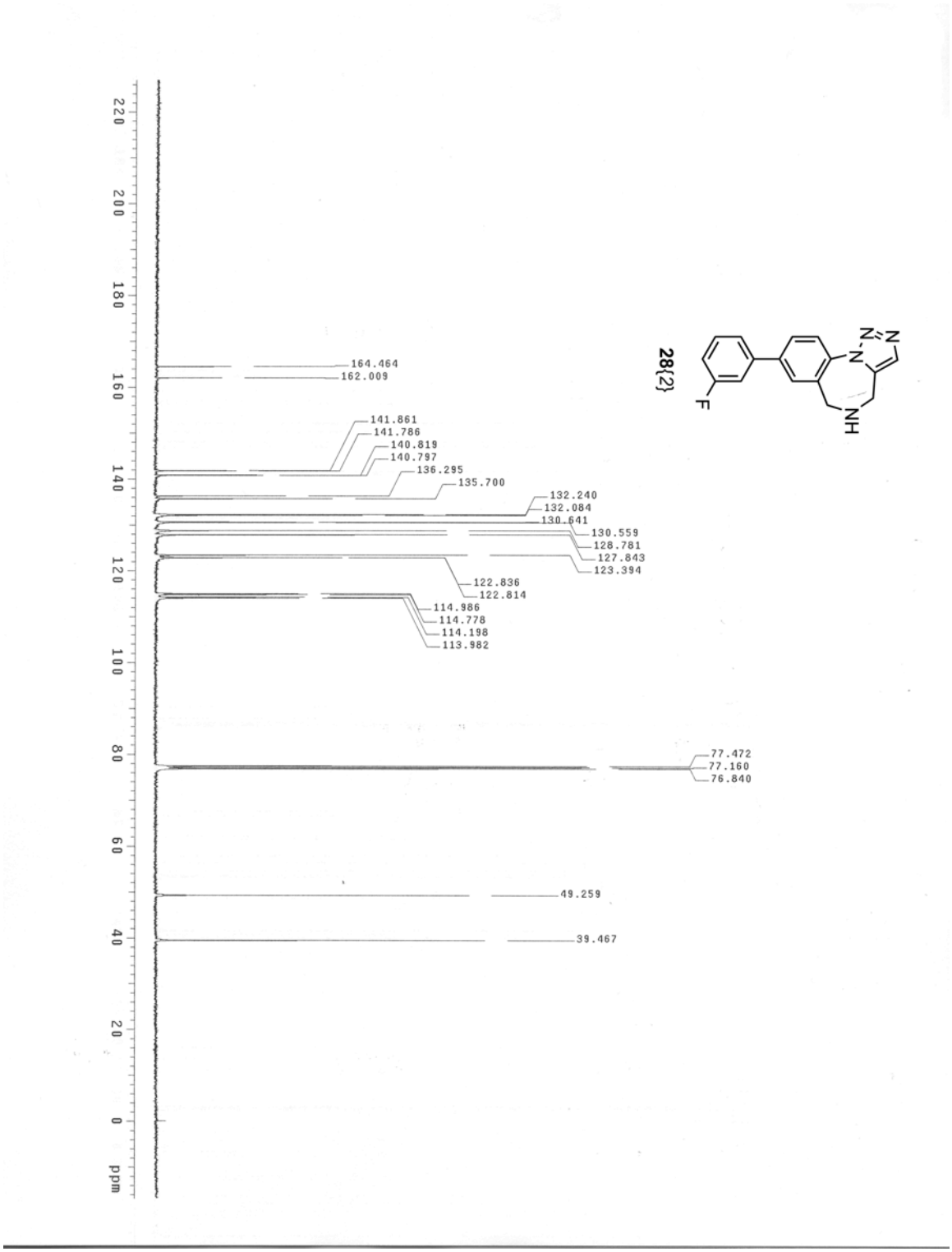

7.822
7.800
7.672
7.283
7.023
7.016
7.001
6.994
6.889
6.883
3.999
3.896
3.884
3.872
3.767
3.257
3.245
3.233
2.133
0.000
ppm
27(2)

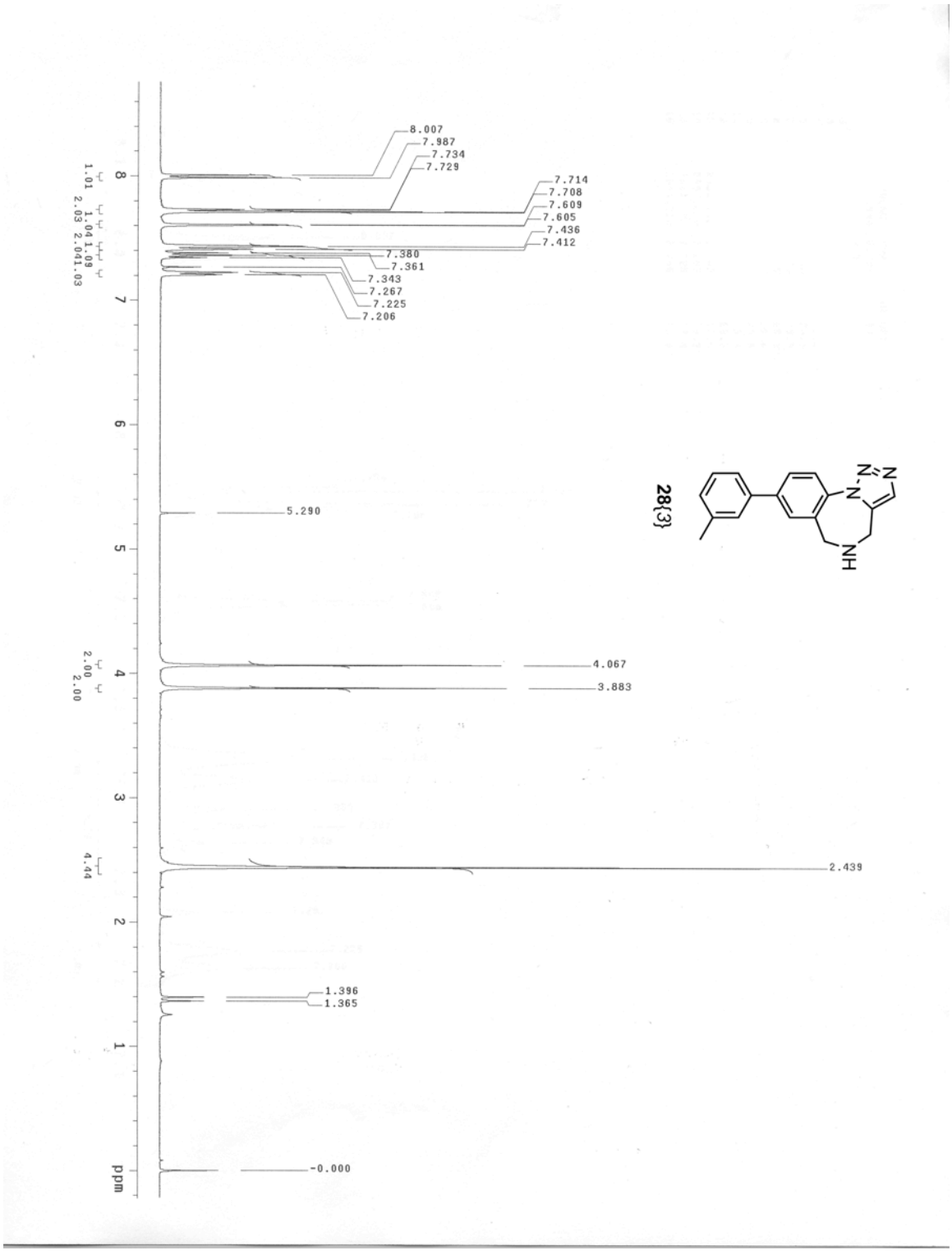

151.697
135.090
132.419
131.928
128.758
123.788
115.939
115.507
77.472
77.160
76.840
66.781
49.423
48.798
39.200
160
140
120
100
80
60
40
20
ppm
27{2}

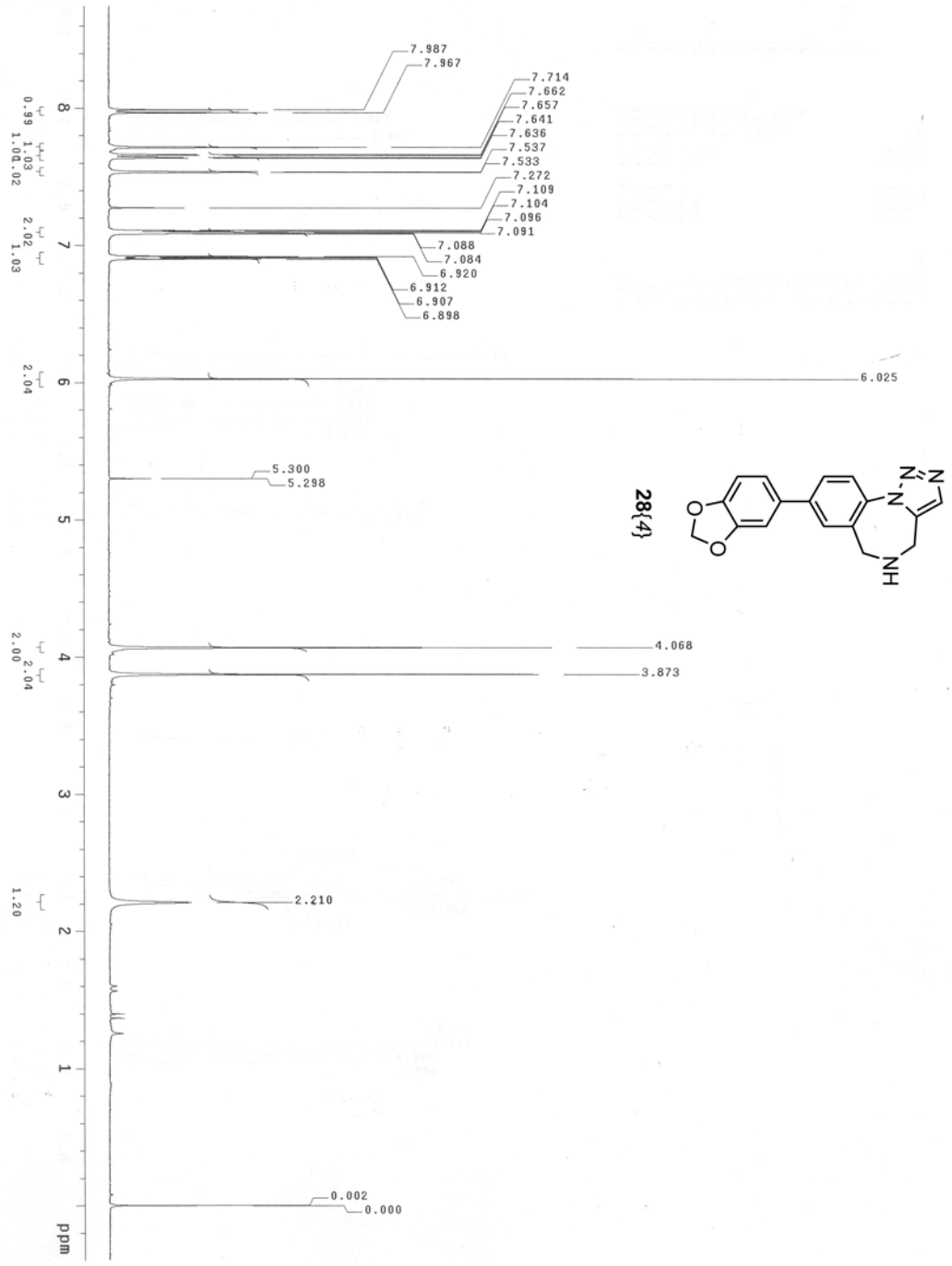

7.999
7.972
7.719
7.713
7.695
7.686
7.623
7.618
7.595
7.484
7.461
7.436
7.405
7.382
4.051
3.861
2.558
ppm
28{1}

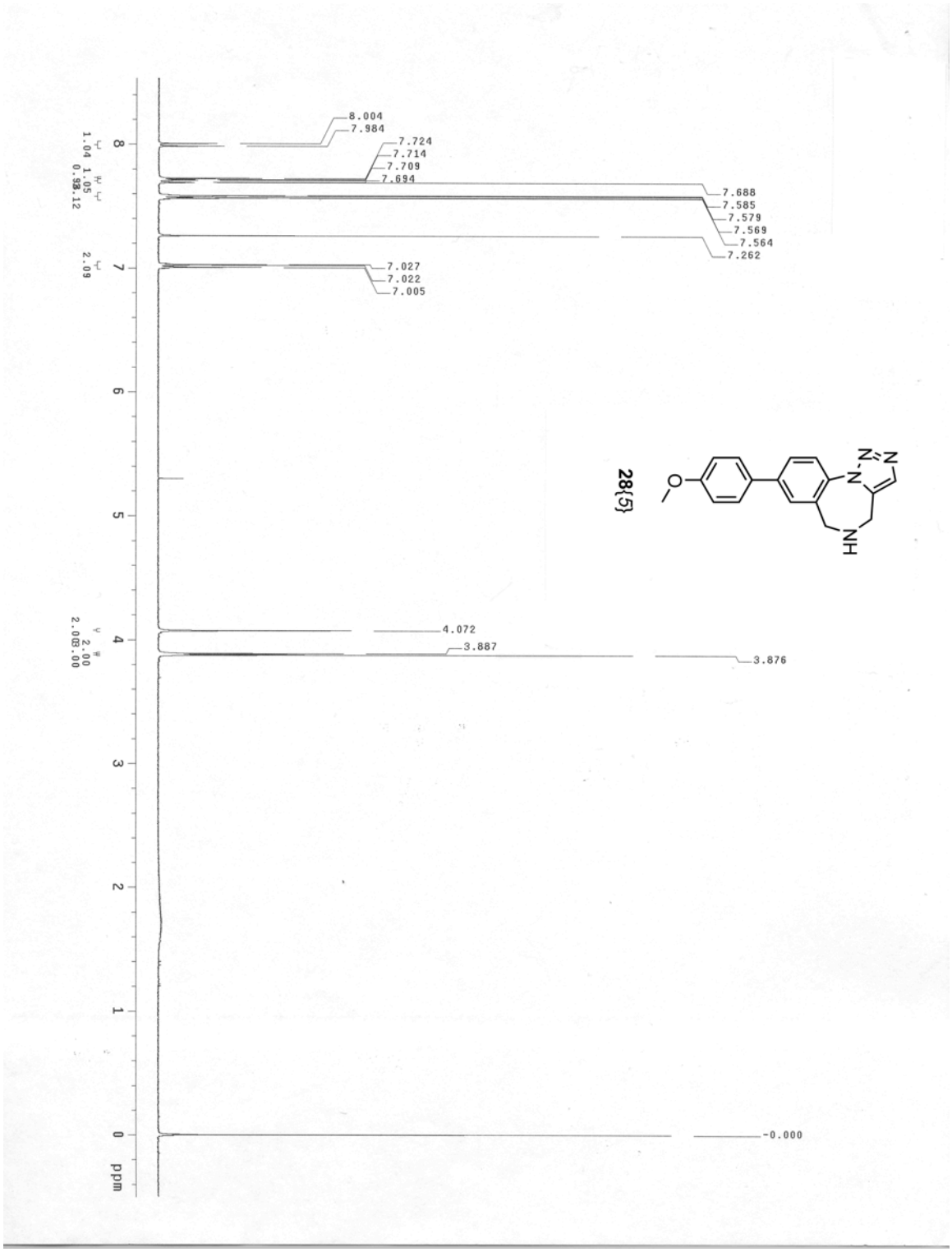

160
140
120
100
80
60
40
20
ppm
142.072
139.486
135.736
135.561
132.131
131.818
128.985
128.686
127.994
127.761
127.077
123.166
77.582
77.160
76.738
49.121
39.289
28{1}
N
N
N
NH

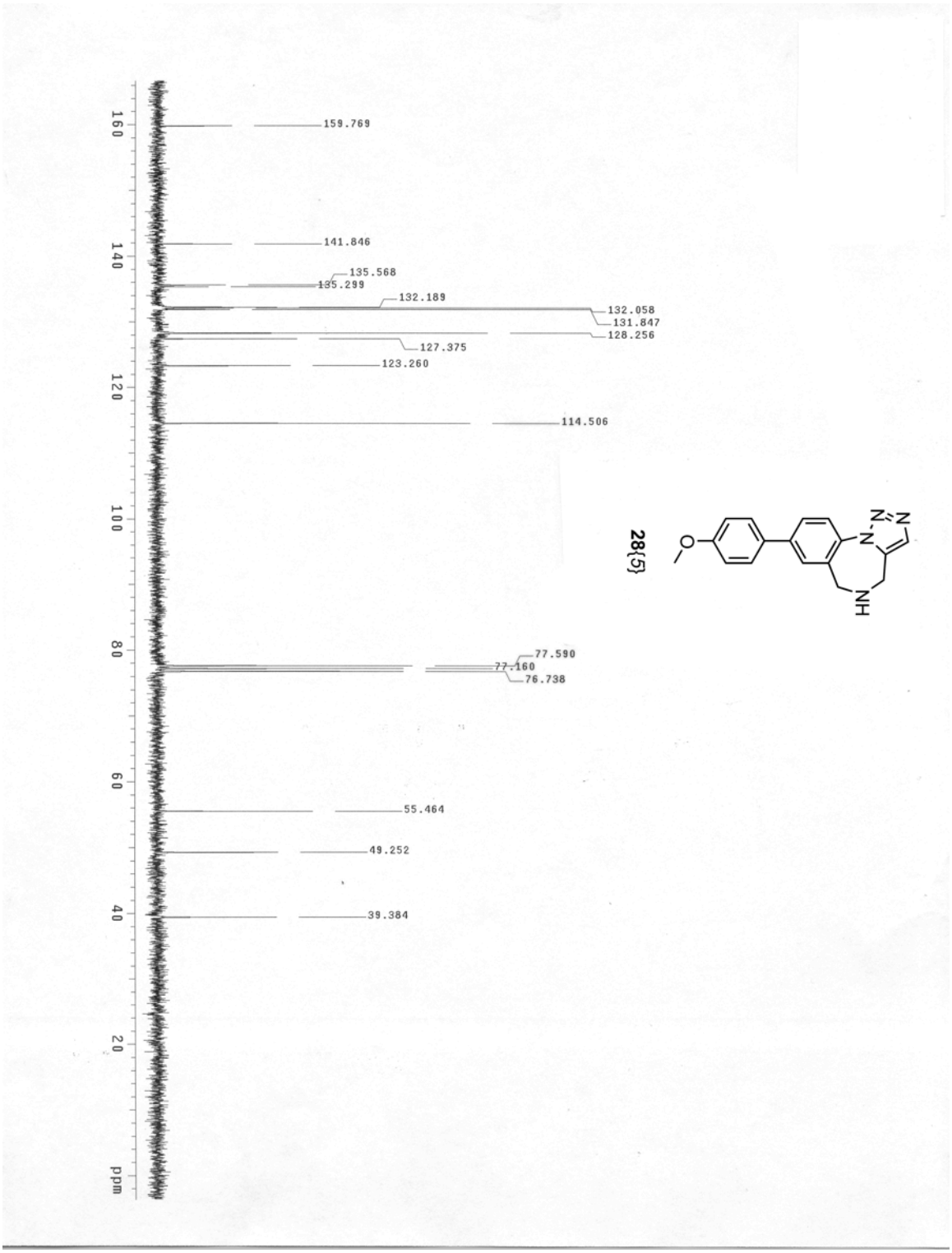

28{2}
F
NH
N
N
N
ppm
8
7
6
5
4
3
2
1
0.97
1.01
1.00
1.95
2.01
0.98
2.01
2.00
1.02

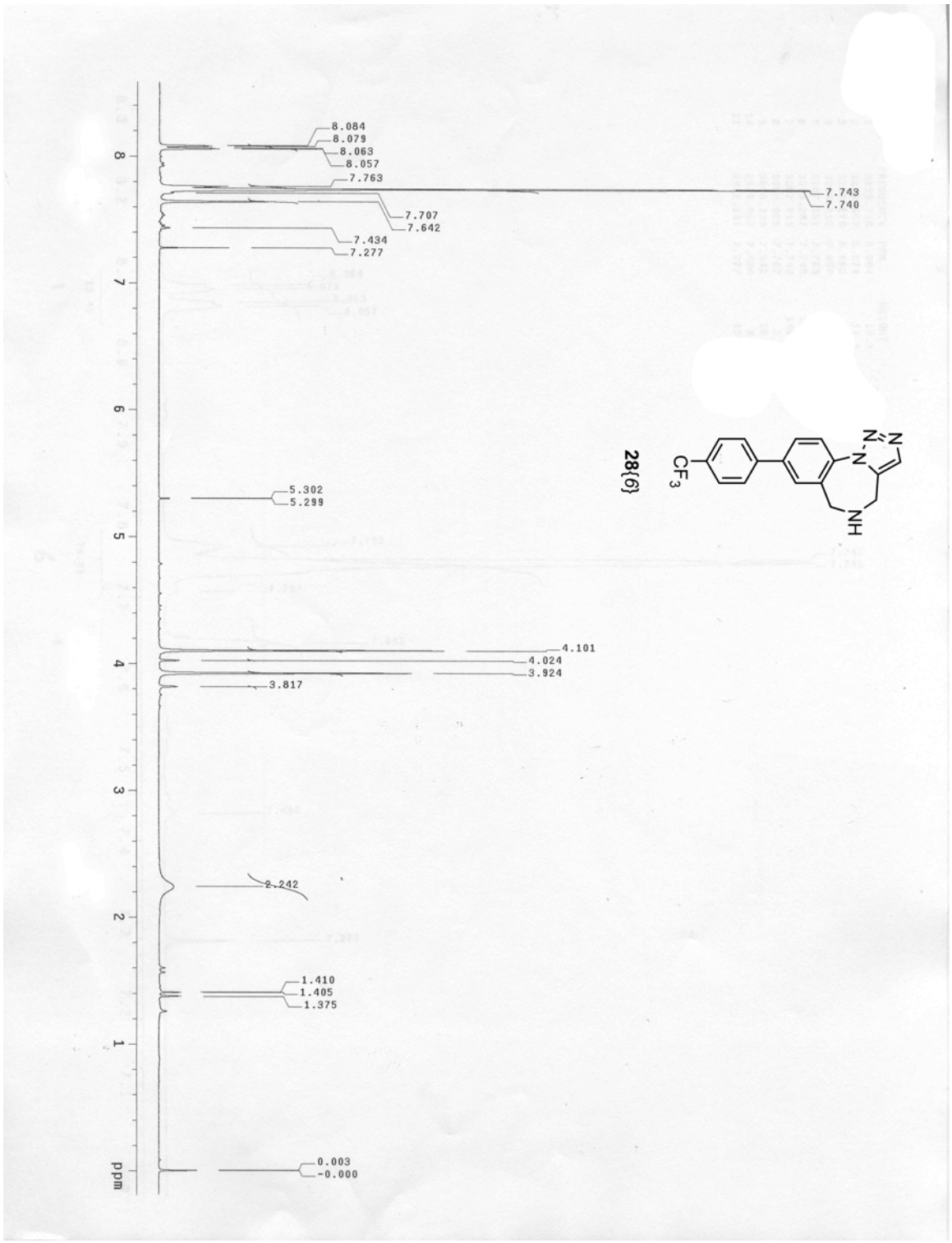

28{2}
164.464
162.009
141.861
141.786
140.819
140.797
136.295
135.700
132.240
132.084
130.641
130.559
128.781
127.843
123.394
122.836
122.814
114.986
114.778
114.198
113.982
77.472
77.160
76.840
49.259
39.467
ppm

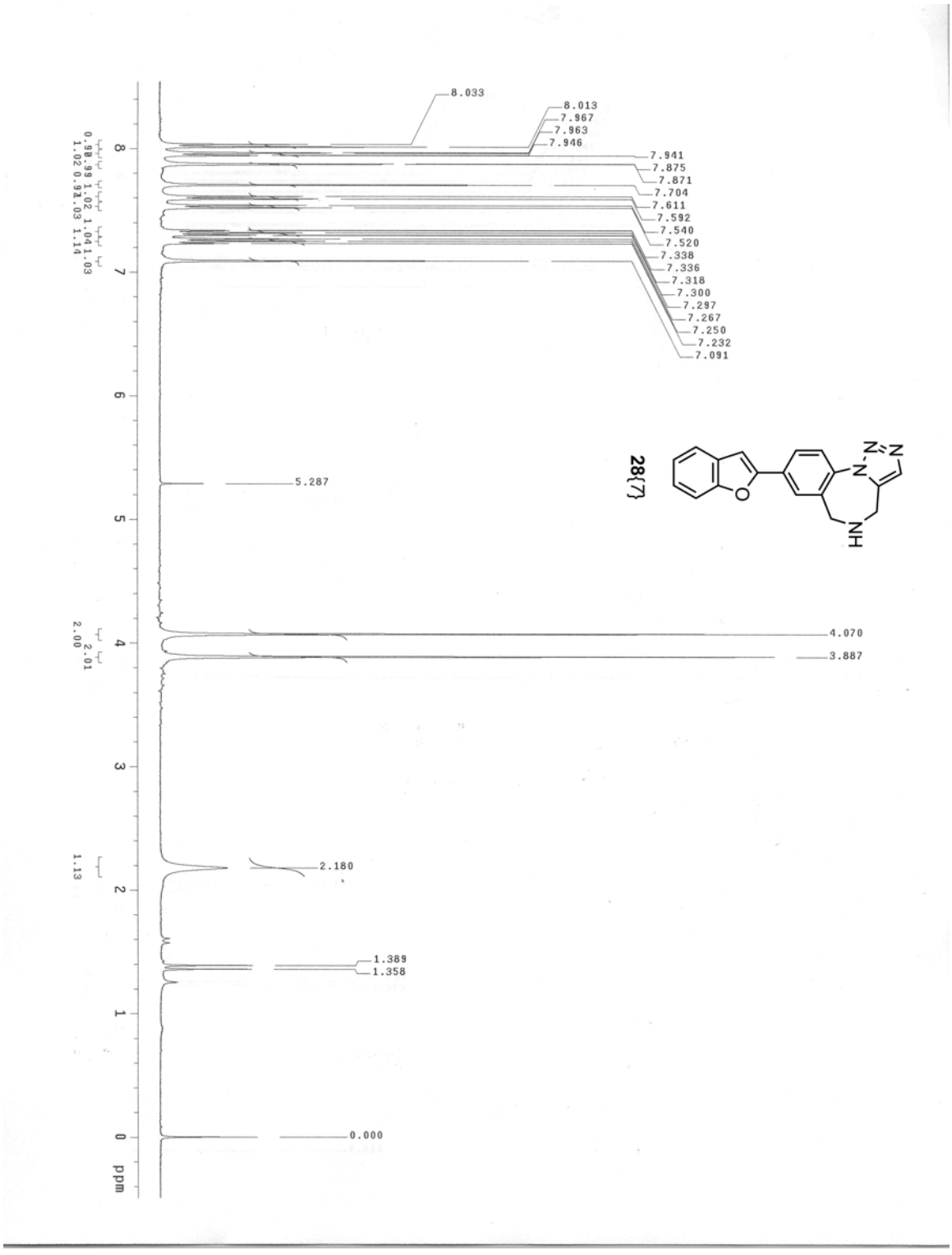

8.007
7.987
7.734
7.729
7.714
7.708
7.609
7.605
7.436
7.412
7.380
7.361
7.343
7.267
7.225
7.206
5.290
4.067
3.883
2.439
1.396
1.365
-0.000
ppm
28{3}
N
N
N
HN

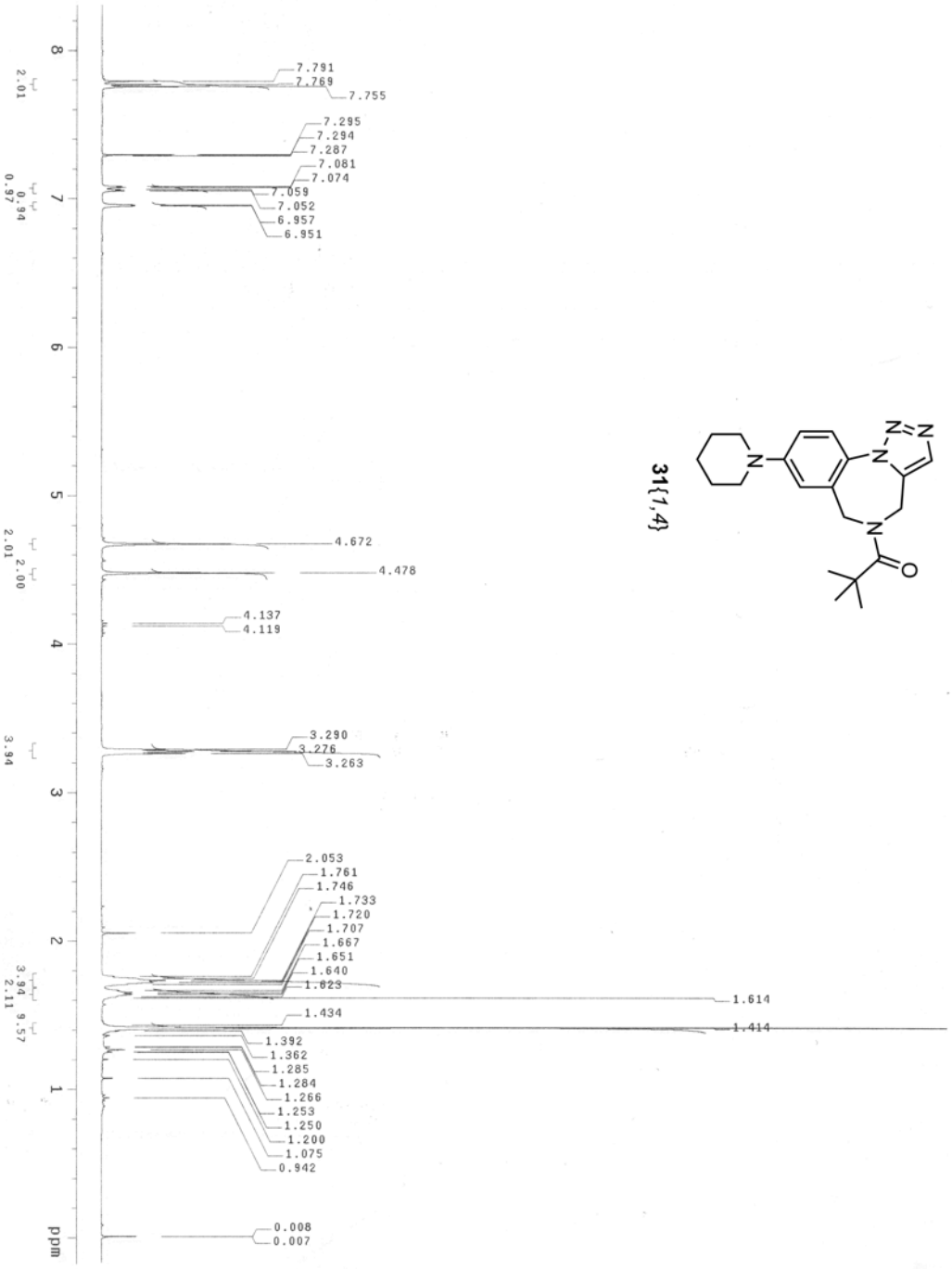

7.987
7.967
7.714
7.662
7.657
7.641
7.636
7.537
7.533
7.272
7.109
7.104
7.096
7.091
7.088
7.084
6.920
6.912
6.907
6.898
6.025
5.300
5.298
4.068
3.873
2.210
0.002
0.000
ppm
28{4}


8.004
7.984
7.724
7.714
7.709
7.694
7.688
7.585
7.579
7.569
7.564
7.262
7.027
7.022
7.005
4.072
3.887
3.876
-0.000
ppm
28{5}
O
N
N
N
NH

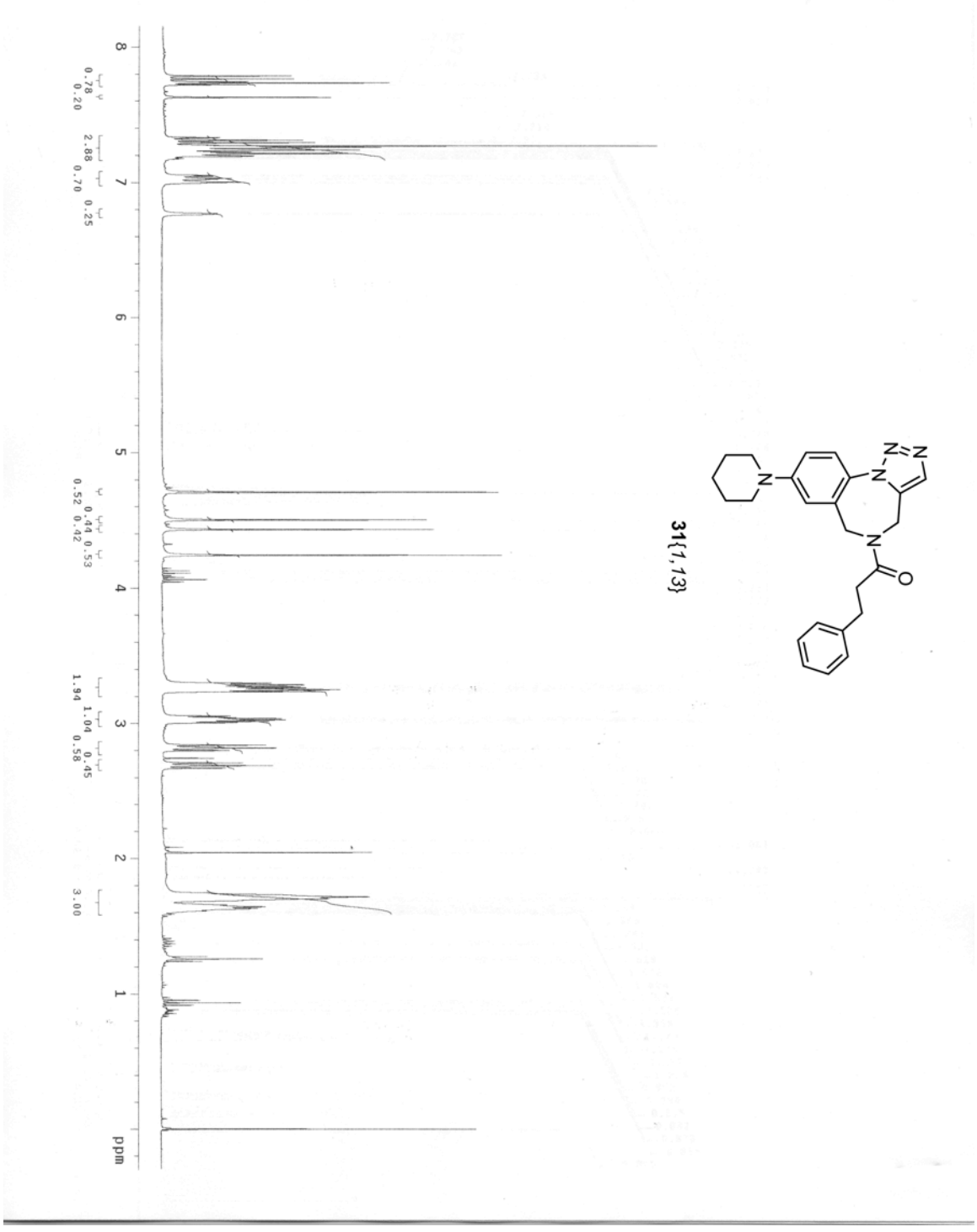

159.769
141.846
135.568
135.299
132.189
132.058
131.847
128.256
127.375
123.260
114.506
77.590
77.160
76.738
55.464
49.252
39.384
160
140
120
100
80
60
40
20
ppm
28{5}
O
N
N
NH


8.084
8.079
8.063
8.057
7.763
7.743
7.740
7.707
7.642
7.434
7.277
5.302
5.299
4.101
4.024
3.924
3.817
2.242
1.410
1.405
1.375
0.003
-0.000
ppm
28{6}
CF3
N
N
NH

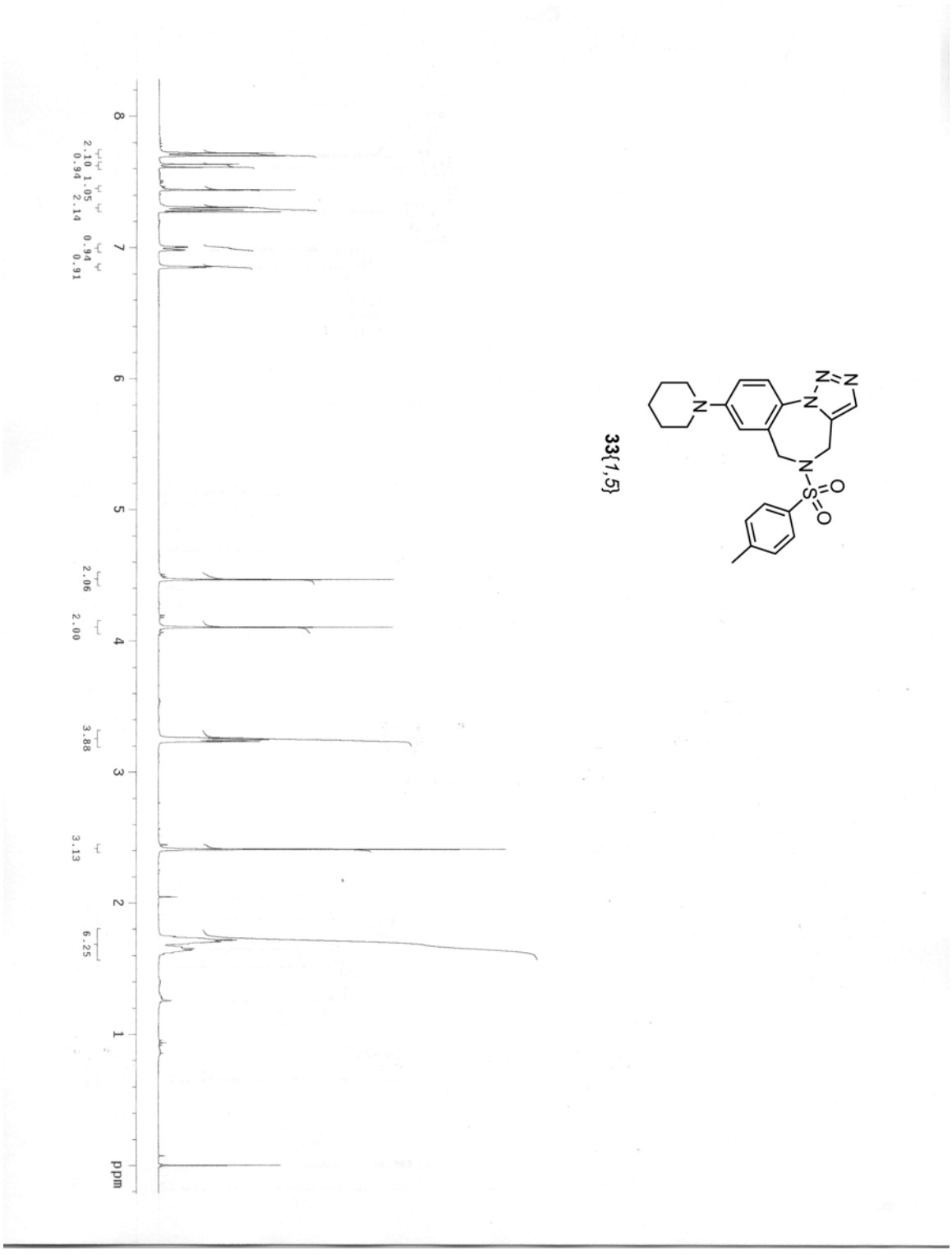

8.033
8.013
7.967
7.963
7.946
7.941
7.875
7.871
7.704
7.611
7.592
7.540
7.520
7.338
7.336
7.318
7.300
7.297
7.267
7.250
7.232
7.091
5.287
4.070
3.887
2.180
1.389
1.358
0.000
ppm
28(7)

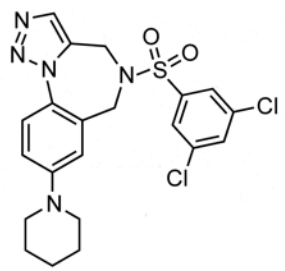

7.791
7.769
7.755
7.295
7.294
7.287
7.081
7.074
7.059
7.052
6.957
6.951
4.672
4.478
4.137
4.119
3.290
3.276
3.263
2.053
1.761
1.746
1.733
1.720
1.707
1.667
1.651
1.640
1.623
1.614
1.434
1.414
1.392
1.362
1.285
1.284
1.266
1.253
1.250
1.200
1.075
0.942
0.008
0.007
ppm
2.01
0.97
0.94
2.01
2.00
3.94
3.94
2.11
9.57

31{1,4}

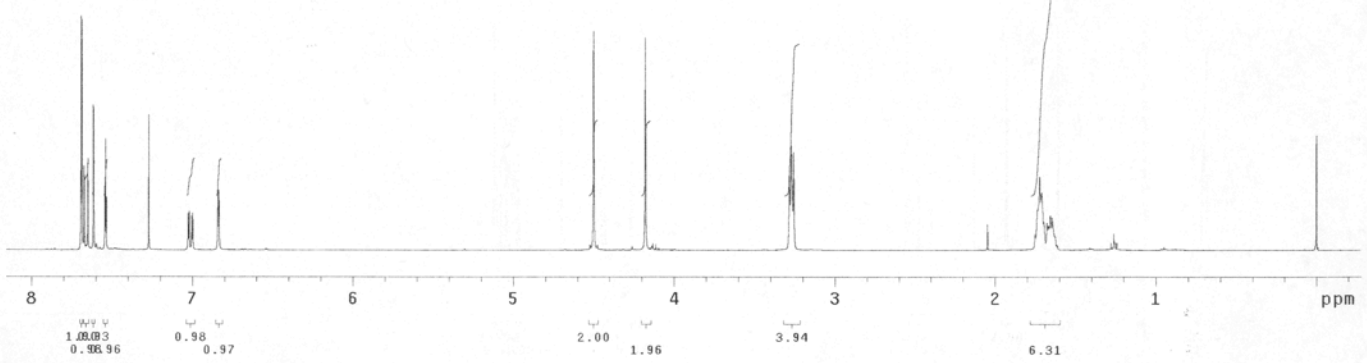

8
7
6
5
4
3
2
1
ppm
0.78
0.20
2.88
0.70
0.25
0.44
0.53
0.52
0.42
1.04
0.45
1.94
0.58
3.00

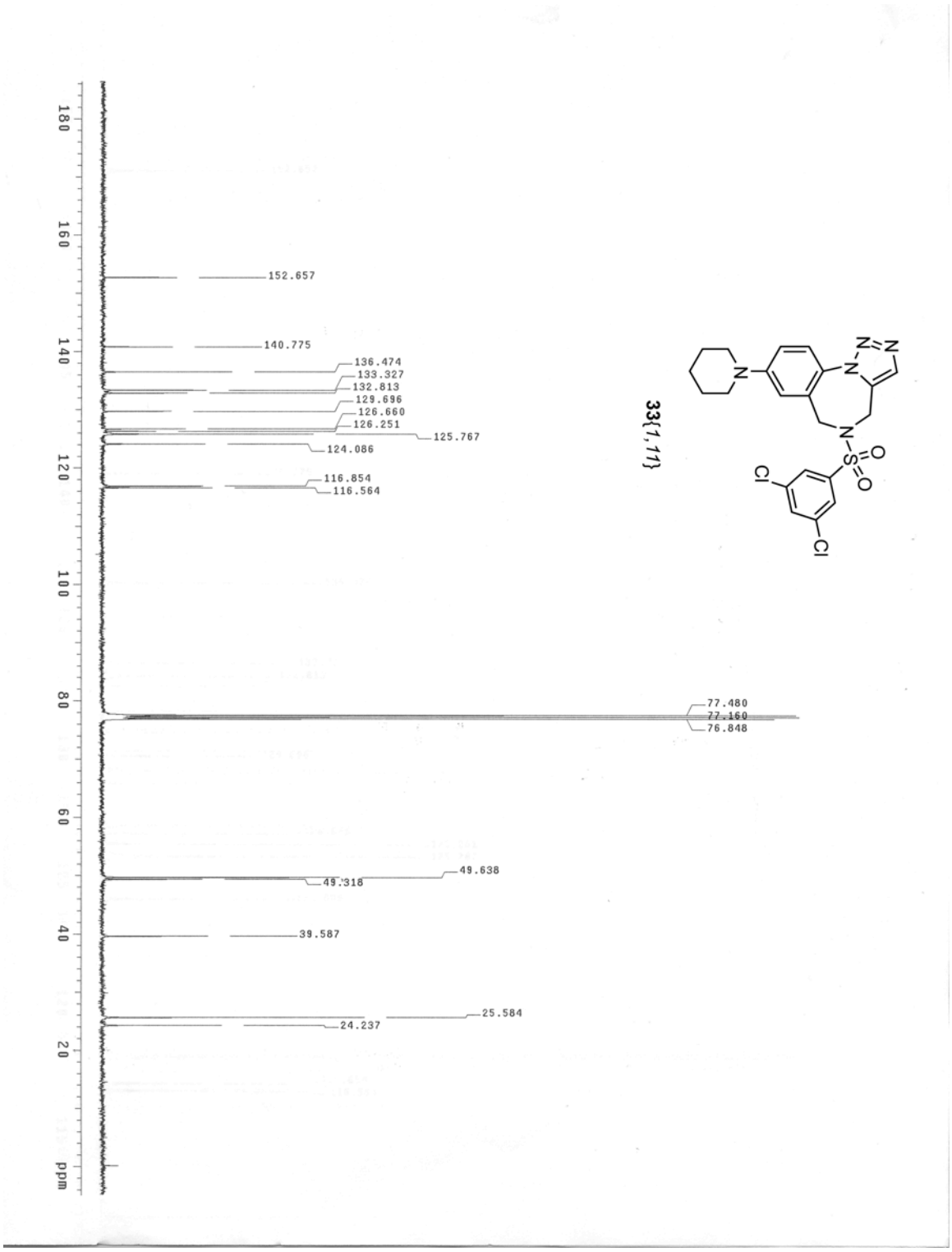
31{*1,13*}

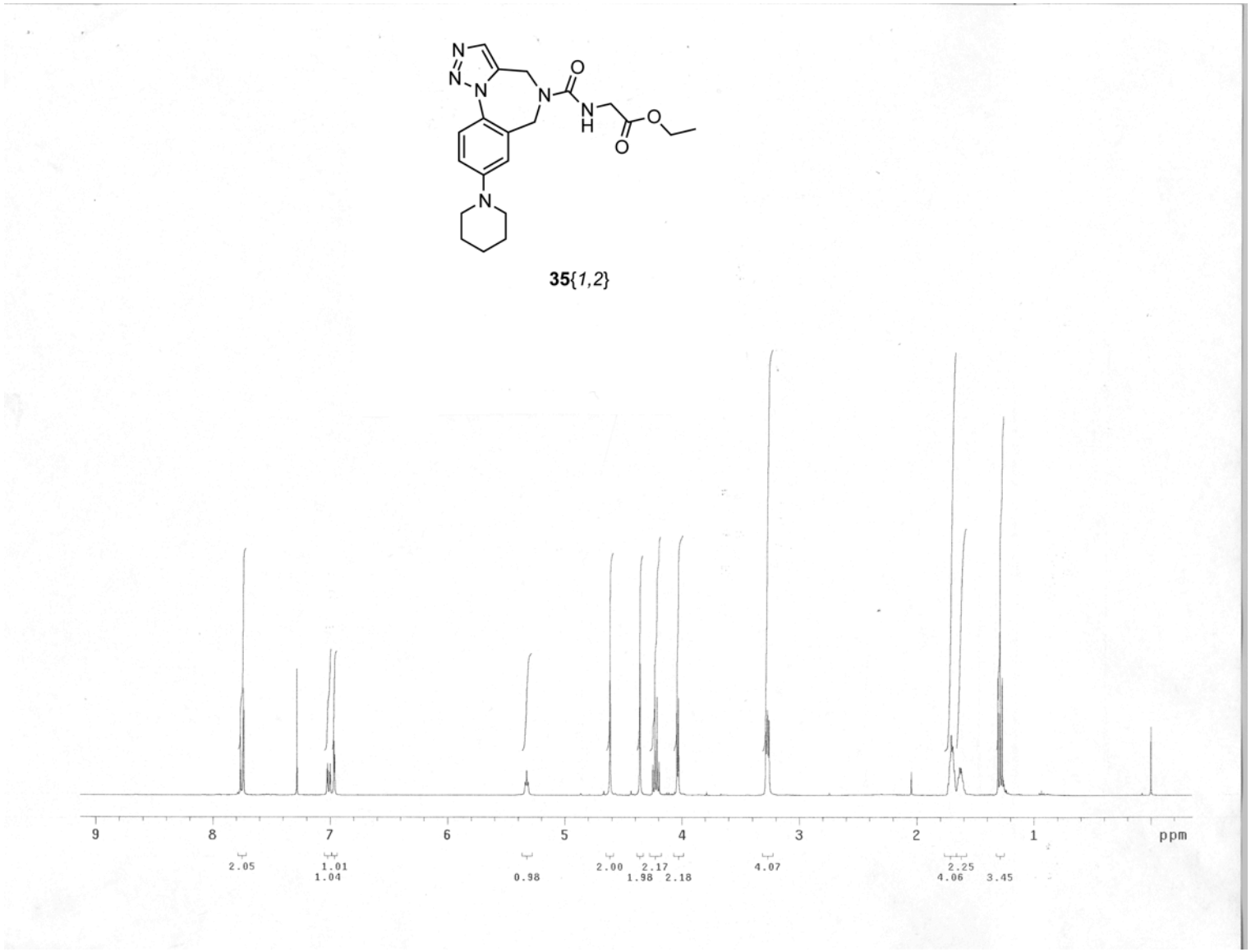

33{1,5}
ppm



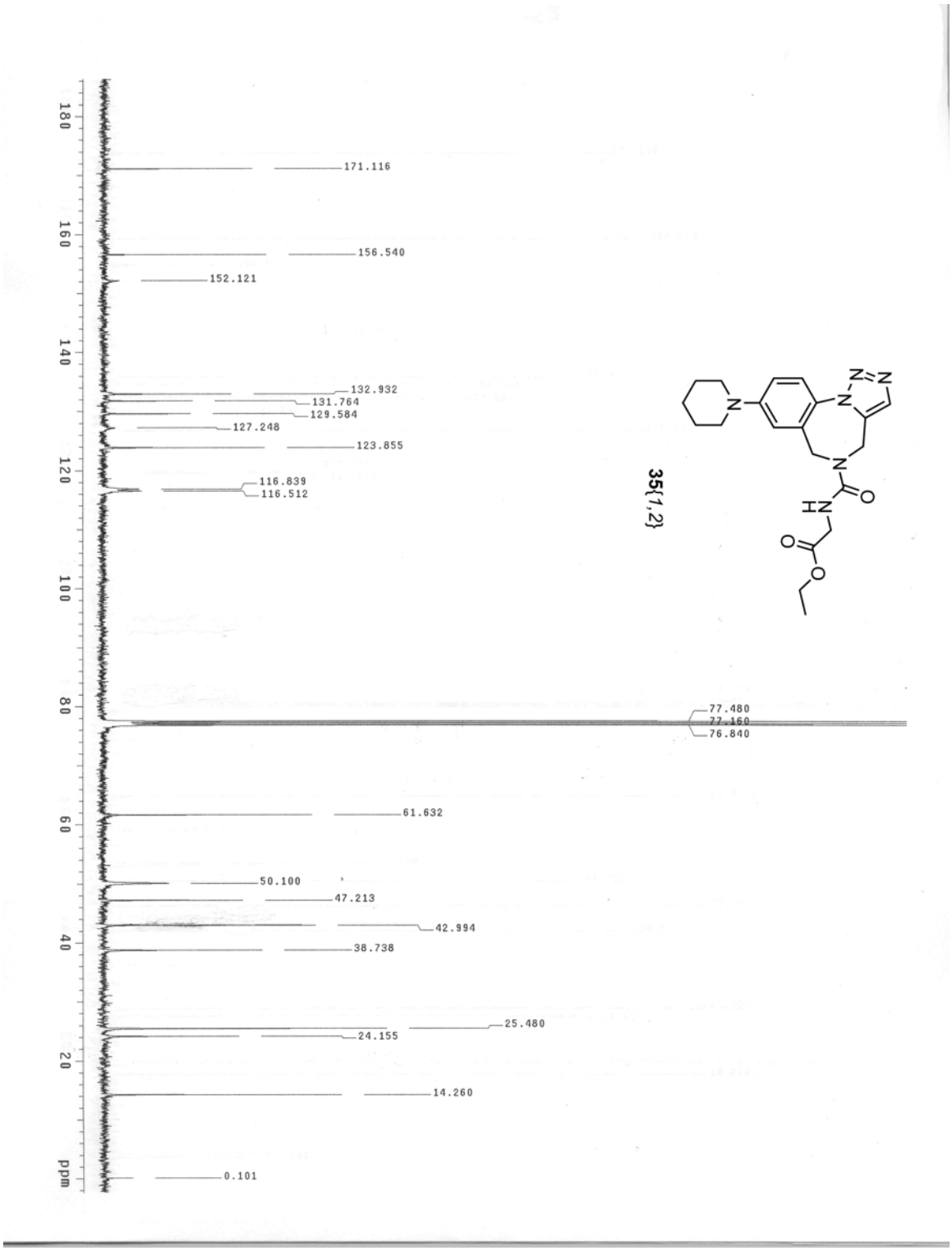
33{*1,11*}

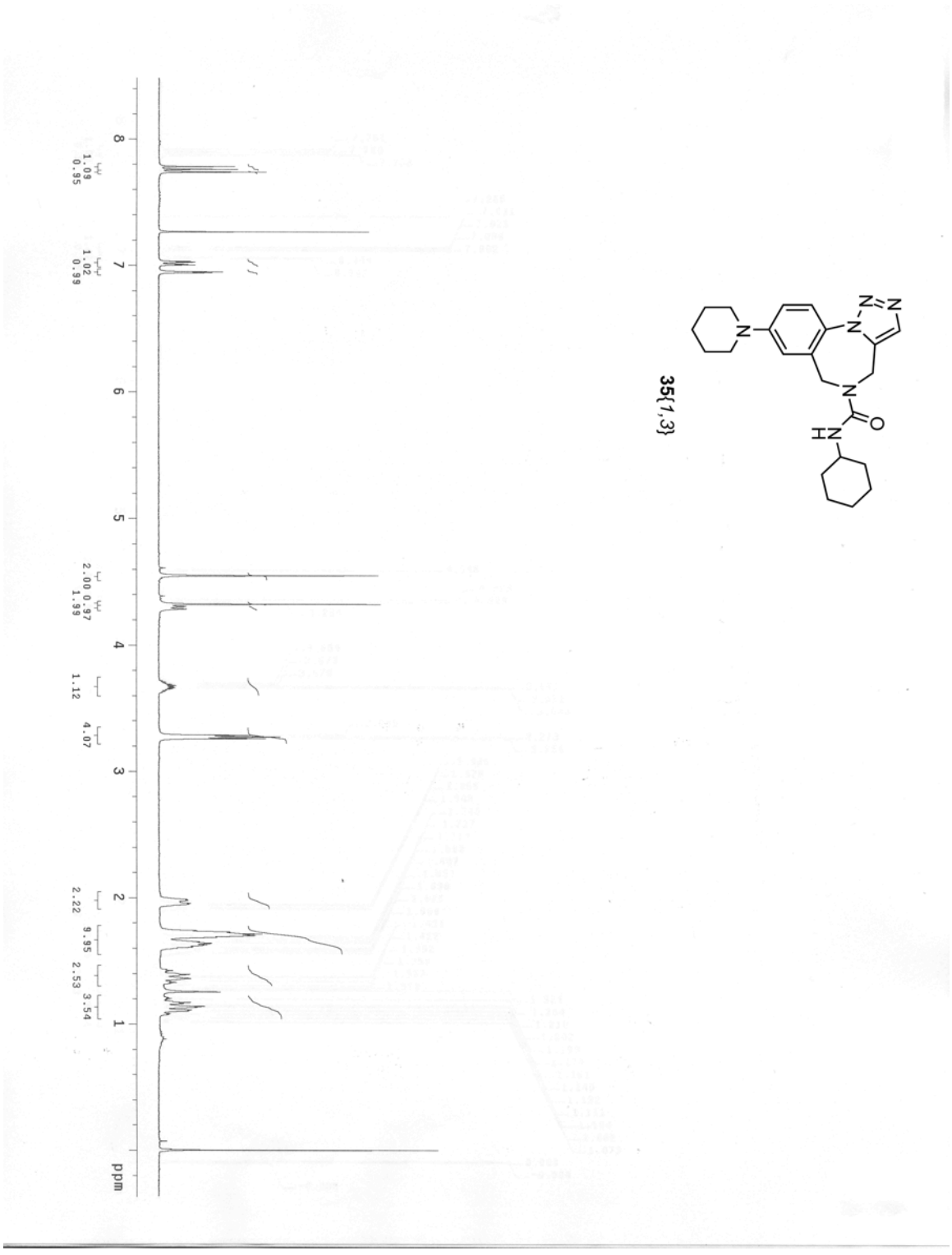


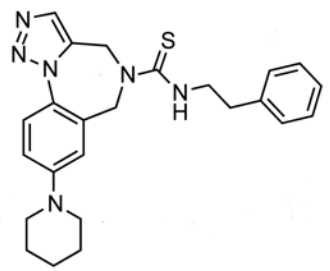

152.657
140.775
136.474
133.327
132.813
129.696
126.660
126.251
125.767
124.086
116.854
116.564
77.480
77.160
76.848
49.638
49.318
39.587
25.584
24.237
180
160
140
120
100
80
60
40
20
ppm
33{1,11}
N
N
N
N
S
O
O
Cl
Cl


N
N
N
O
N
H
O
O
N
9
8
7
6
5
4
3
2
1
ppm
2.05
1.01
1.04
0.98
2.00
2.17
1.98
2.18
4.07
2.25
4.06
3.45

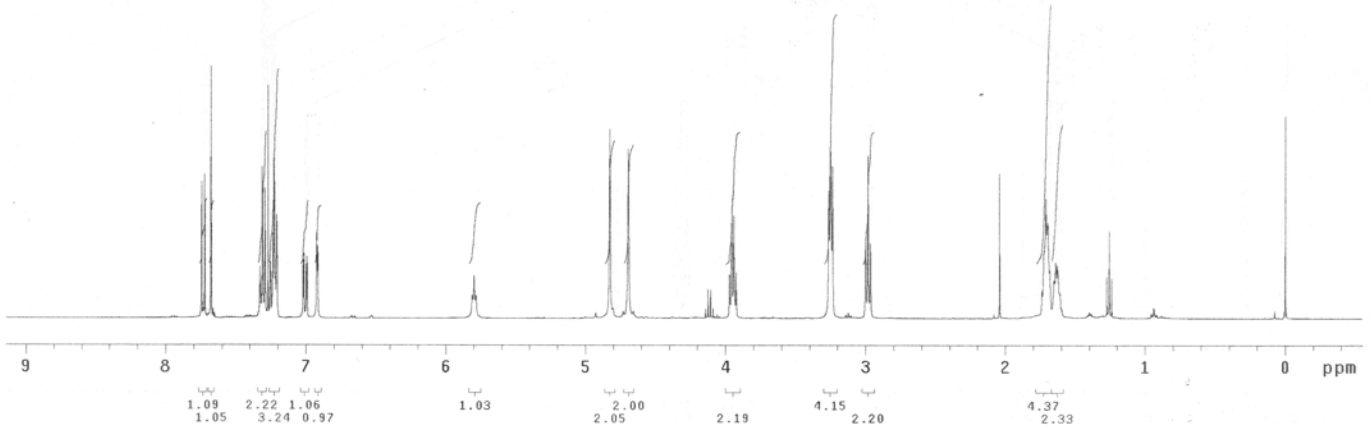
35{*1,2*}

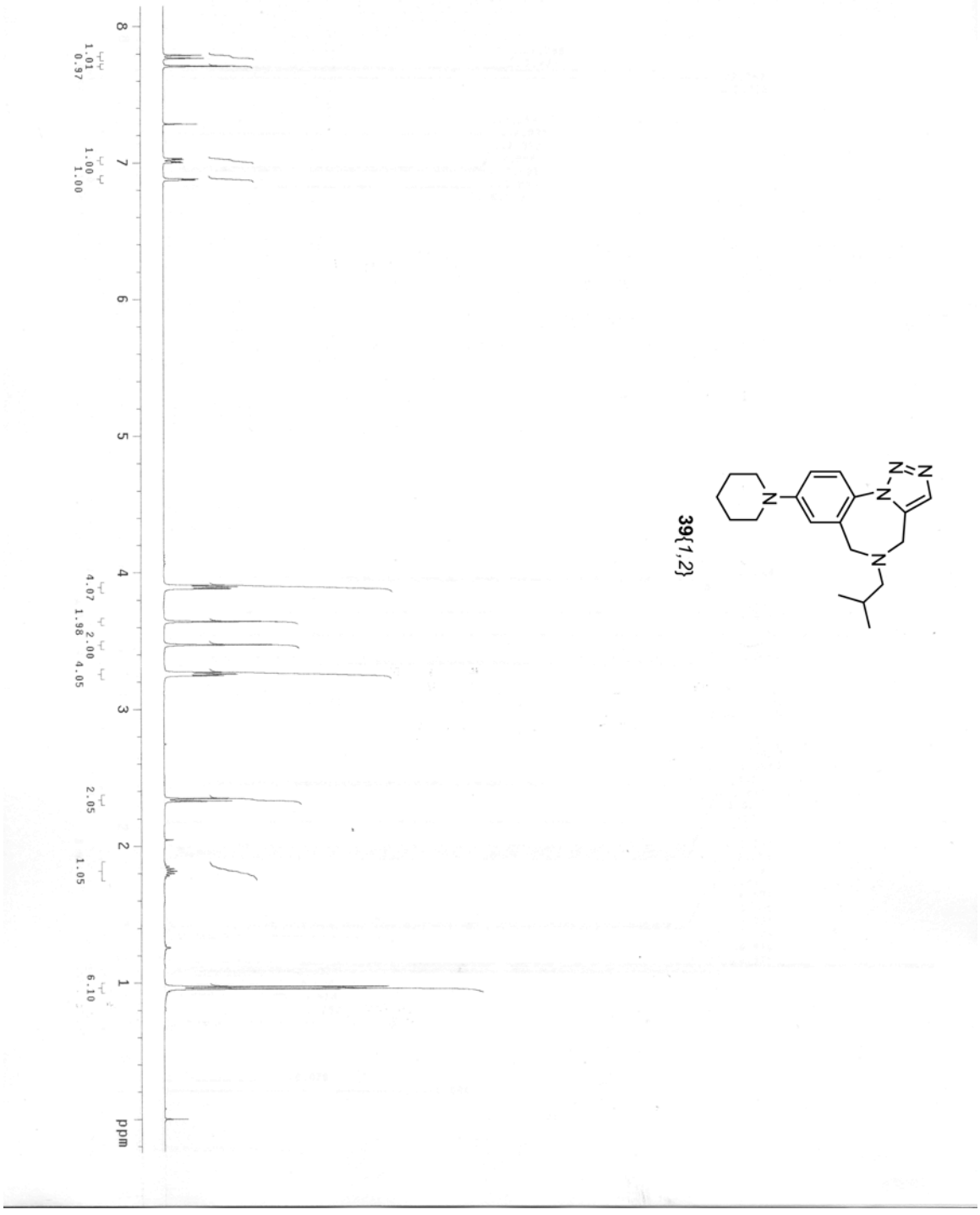

171.116
156.540
152.121
132.932
131.764
129.584
127.248
123.855
116.839
116.512
77.480
77.160
76.840
61.632
50.100
47.213
42.994
38.738
25.480
24.155
14.260
0.101
ppm
35{1,2}


35{1,3}
8
7
6
5
4
3
2
1
ppm
1.09
0.95
1.02
0.99
2.00
0.97
1.99
1.12
4.07
2.22
9.95
2.53
3.54

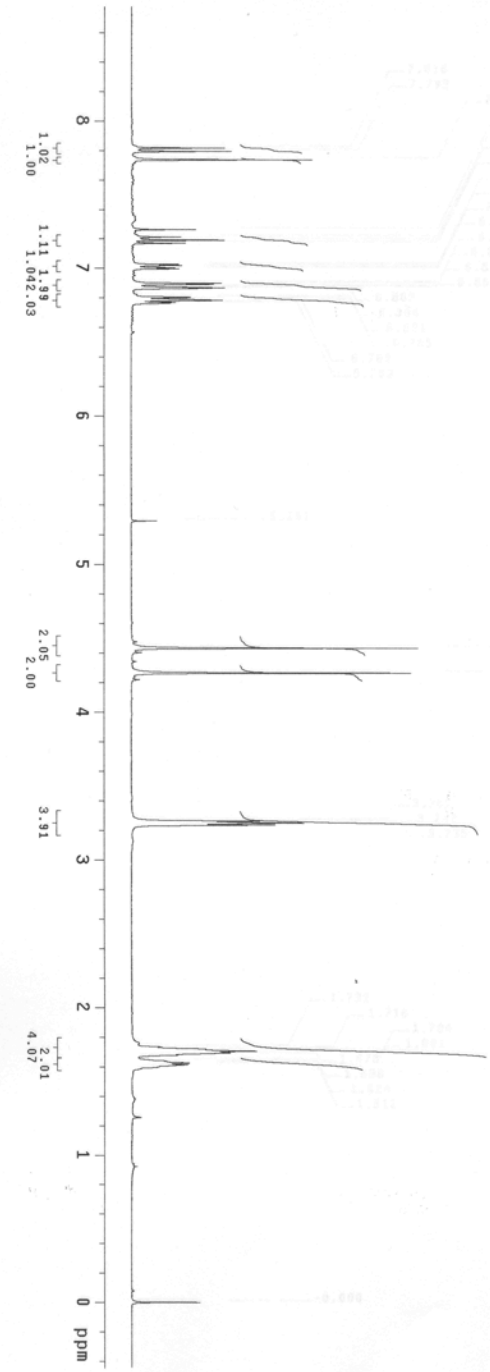


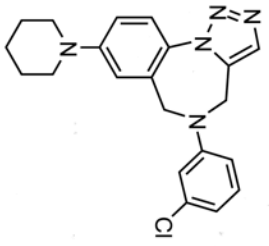
37{*1,3*}


9
8
7
6
5
4
3
2
1
0
ppm
1.09
1.05
2.22
3.24
1.06
0.97
1.03
2.00
2.05
2.19
4.15
2.20
4.37
2.33

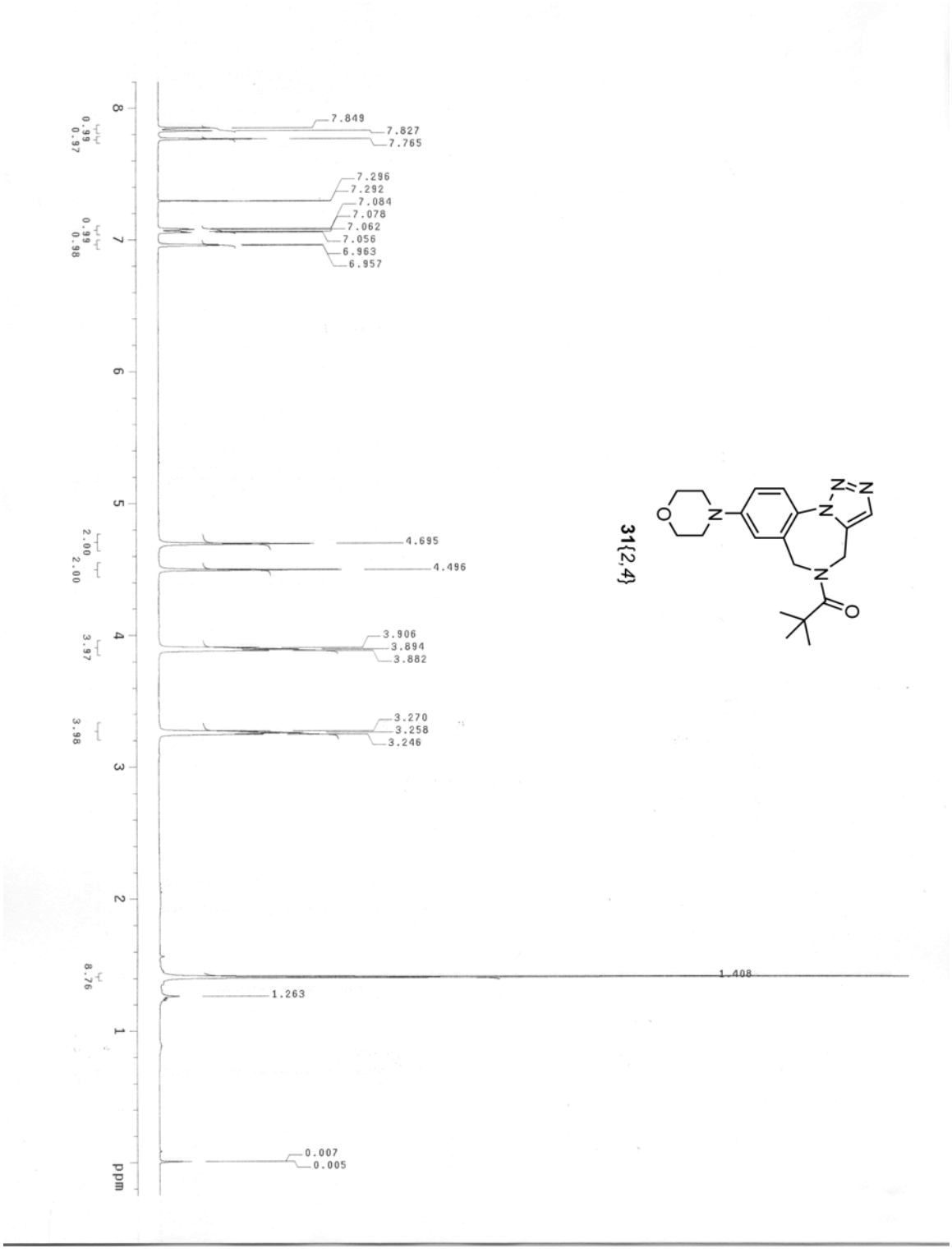

39{1,2}
8
7
6
5
4
3
2
1
ppm
1.01
0.97
1.00
1.00
4.07
1.98
2.00
4.05
2.05
1.05
6.10

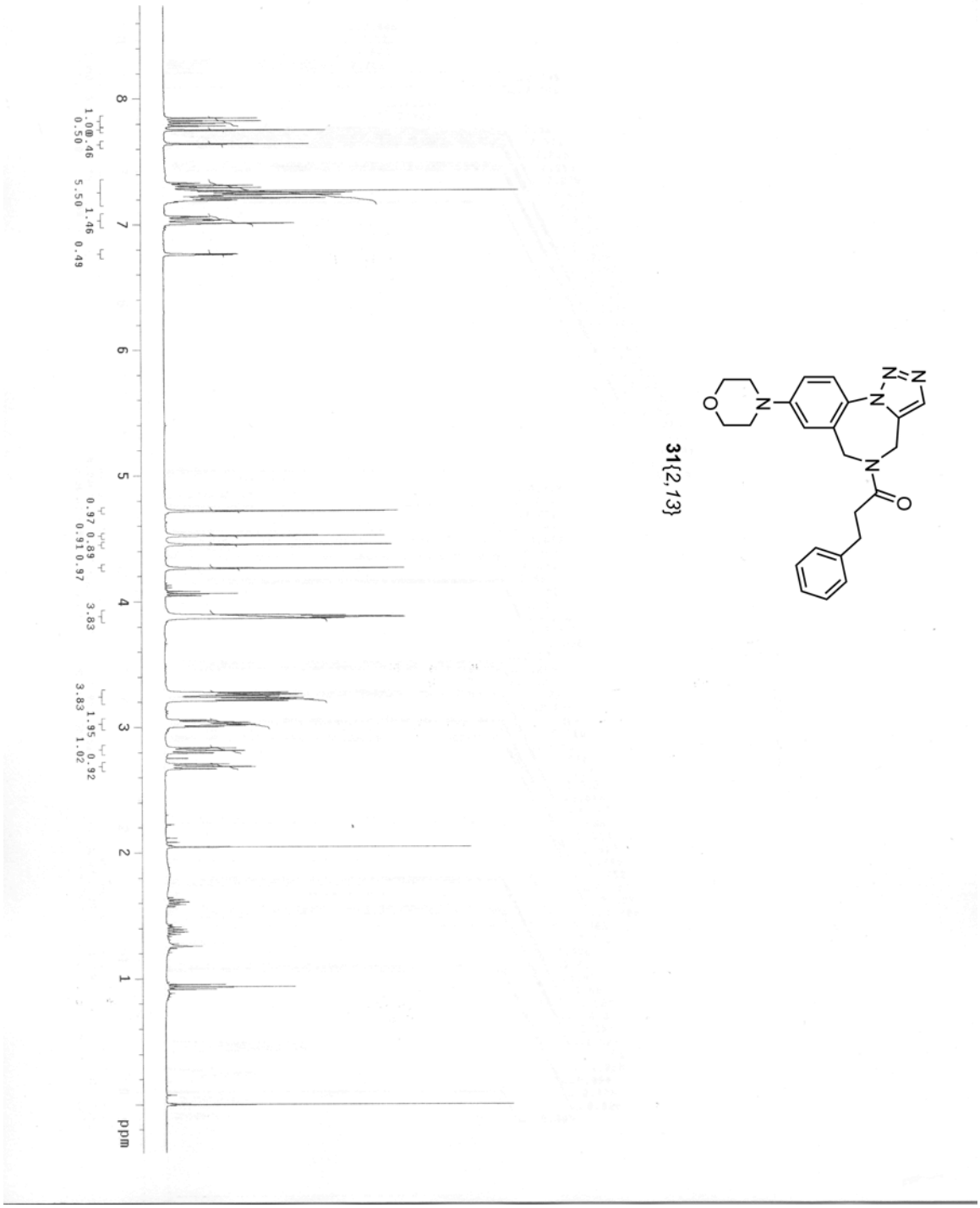

39(1,14)
8
7
6
5
4
3
2
1
ppm
1.03
1.04
2.13
2.15
1.04
1.10
3.25
2.06
4.13
2.18
2.00
2.41
4.30

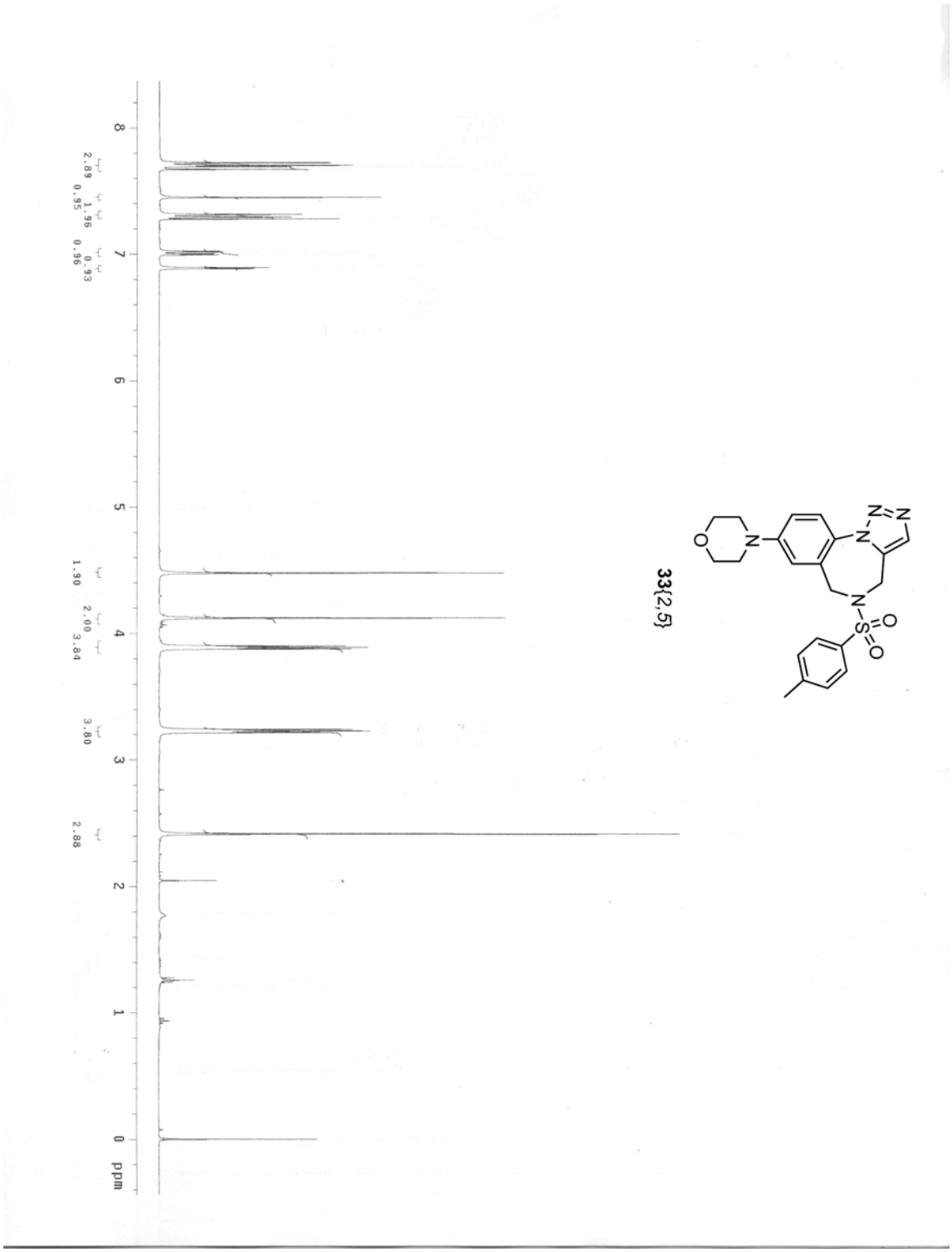

8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
1.11
1.99
1.04
2.03
2.05
2.00
3.91
2.01
4.07

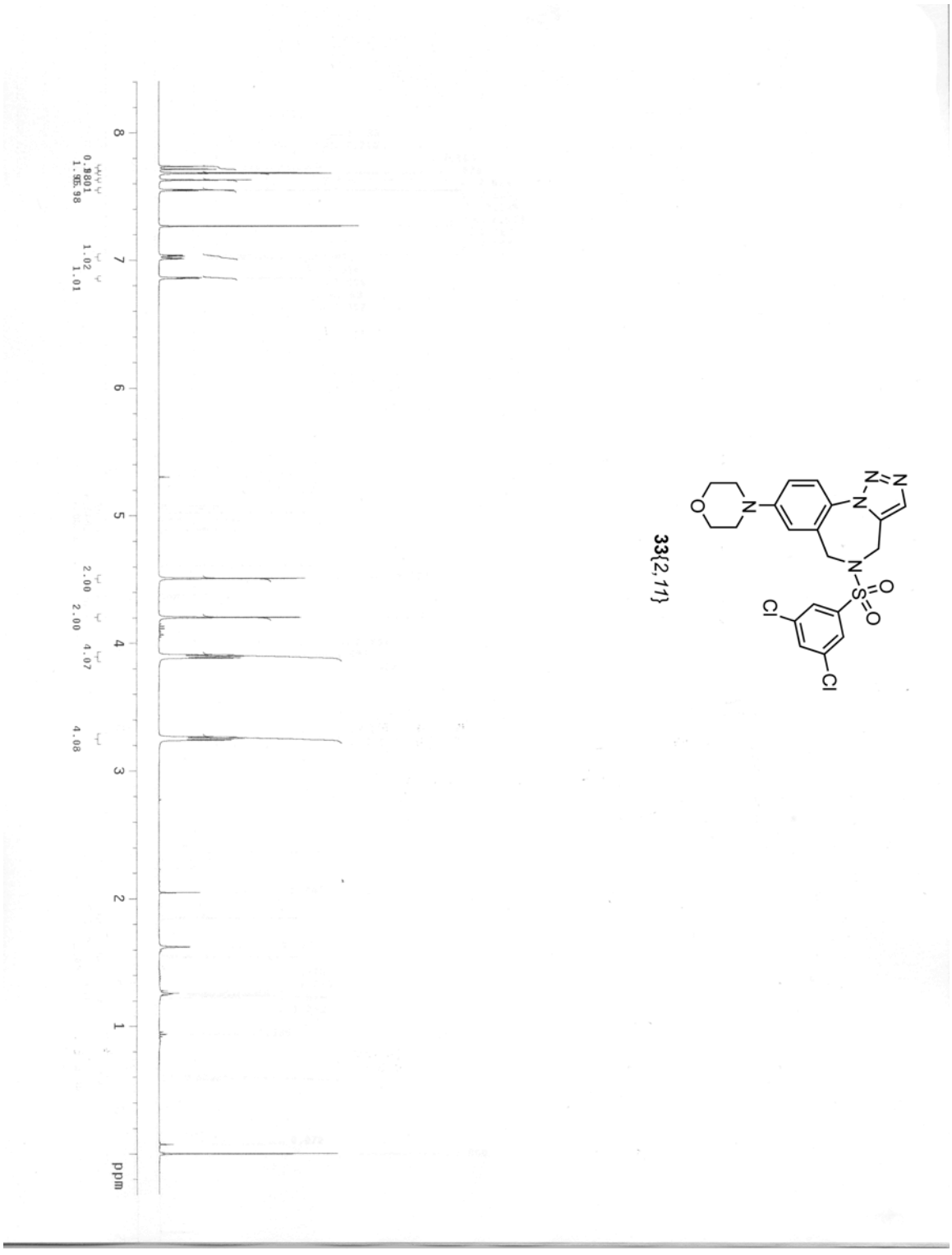

N
N
N
N
Cl

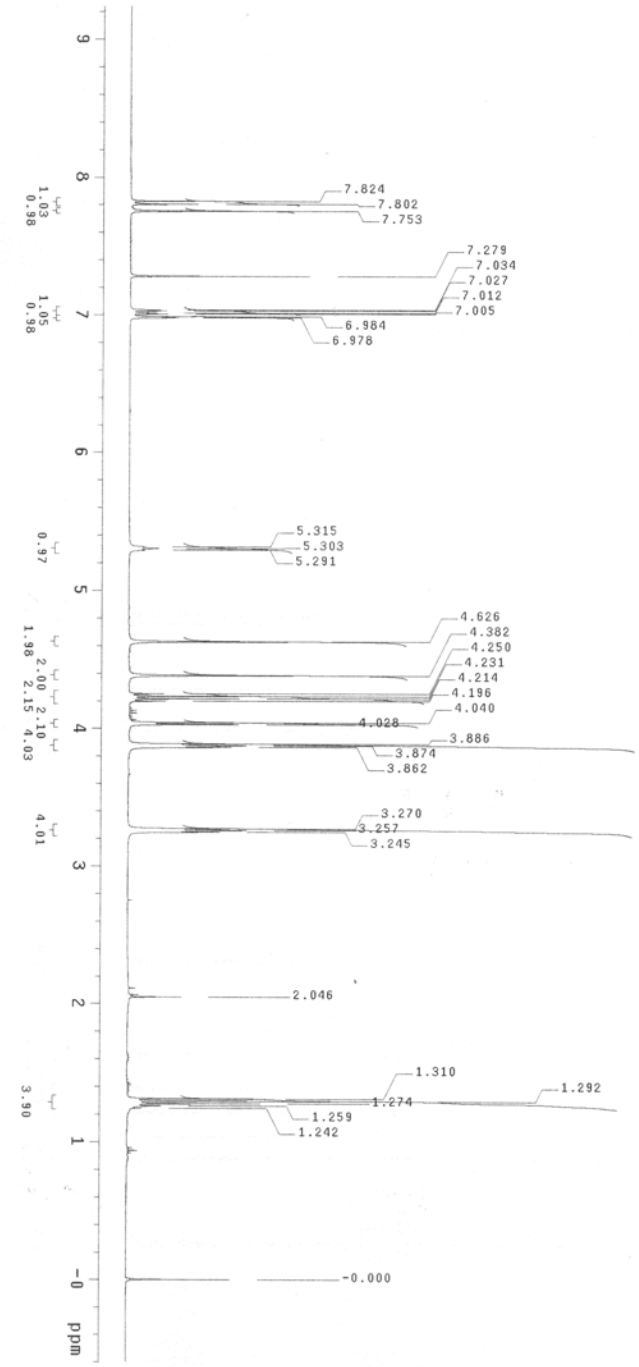
41{*1,1*}


7.849
7.827
7.765
7.296
7.292
7.084
7.078
7.062
7.056
6.963
6.957
4.695
4.496
3.906
3.894
3.882
3.270
3.258
3.246
1.408
1.263
0.007
0.005
ppm
31{2,4}

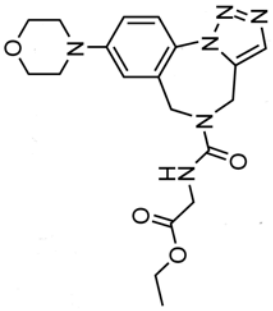

31{2,13}
ppm

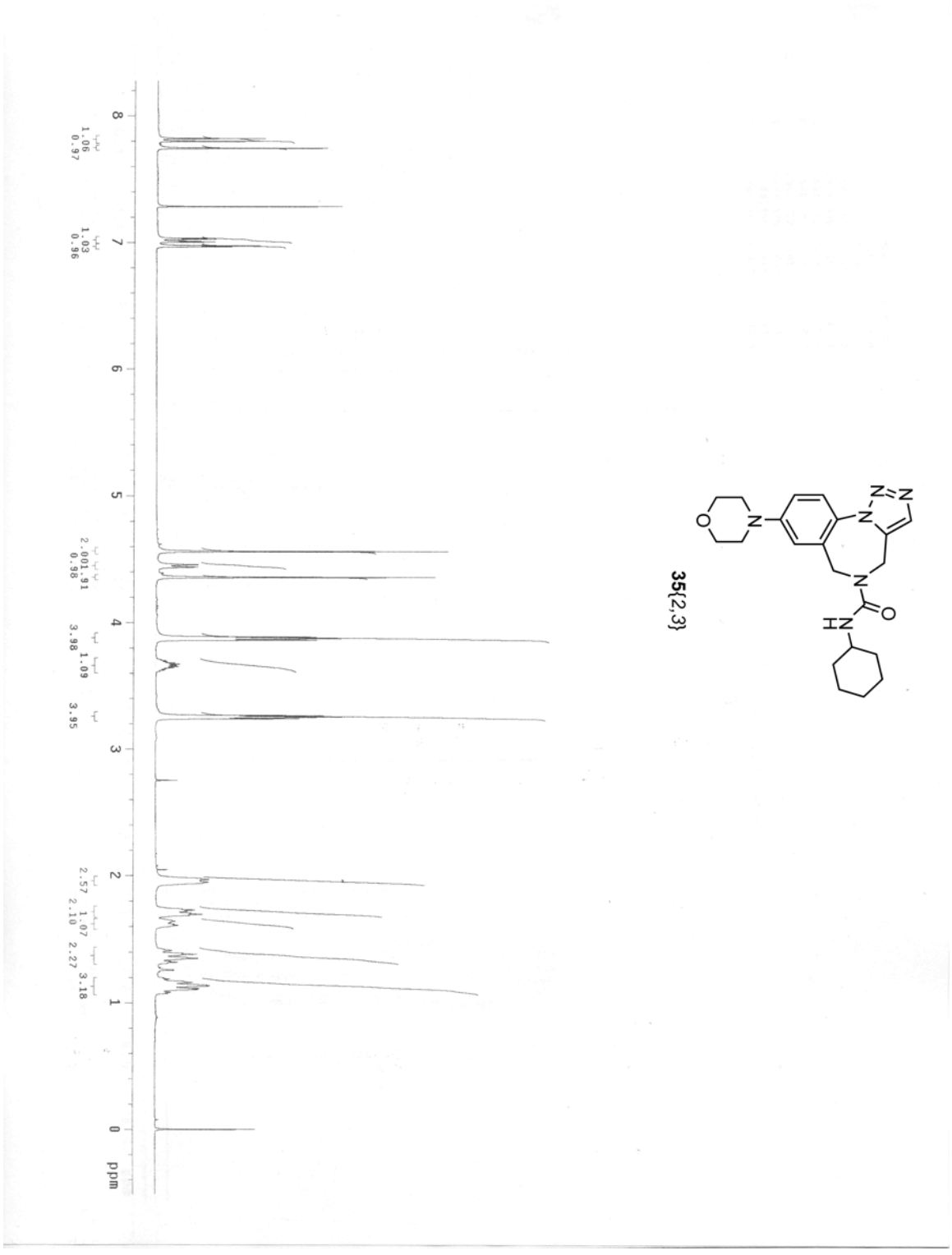

33(2,5)
8
7
6
5
4
3
2
1
0
ppm
2.89
1.96
0.93
0.95
0.96
1.90
2.00
3.84
3.80
2.88

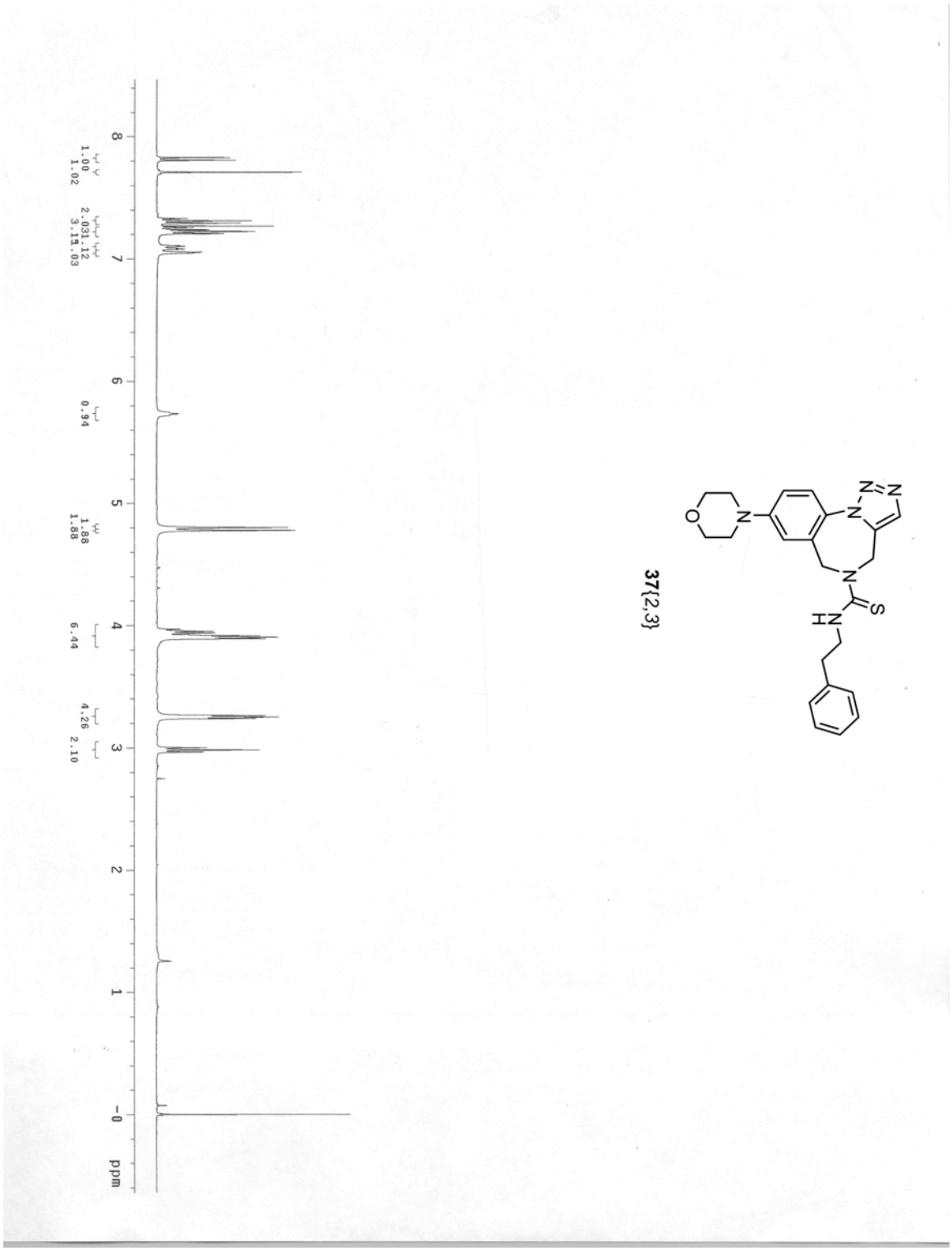

33(2,11)
8
7
6
5
4
3
2
1
ppm
1.98
1.02
1.01
2.00
2.00
4.07
4.08

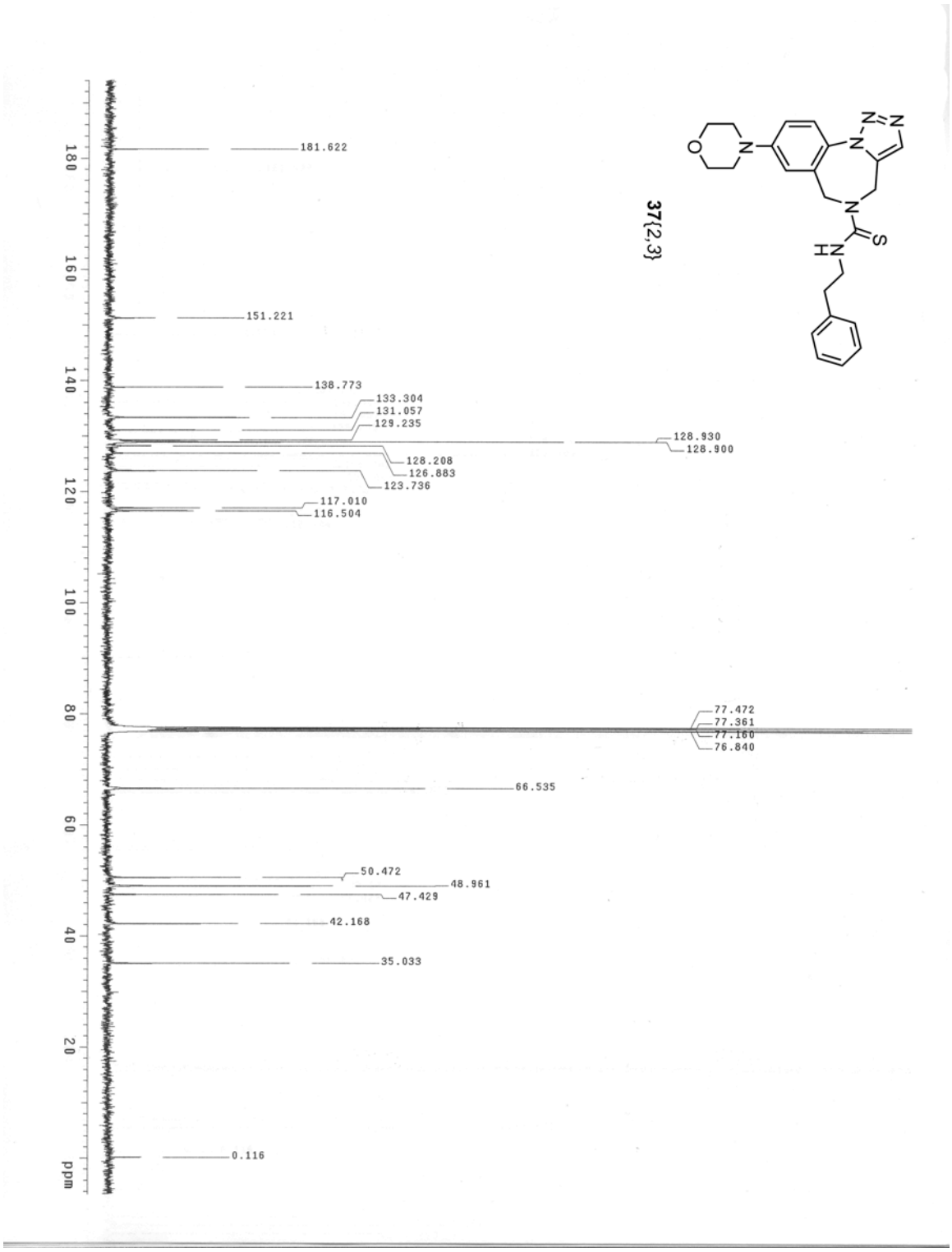

7.824
7.802
7.753
7.279
7.034
7.027
7.012
7.005
6.984
6.978
5.315
5.303
5.291
4.626
4.382
4.250
4.231
4.214
4.196
4.040
4.028
3.886
3.874
3.862
3.270
3.257
3.245
2.046
1.310
1.292
1.274
1.259
1.242
-0.000
ppm

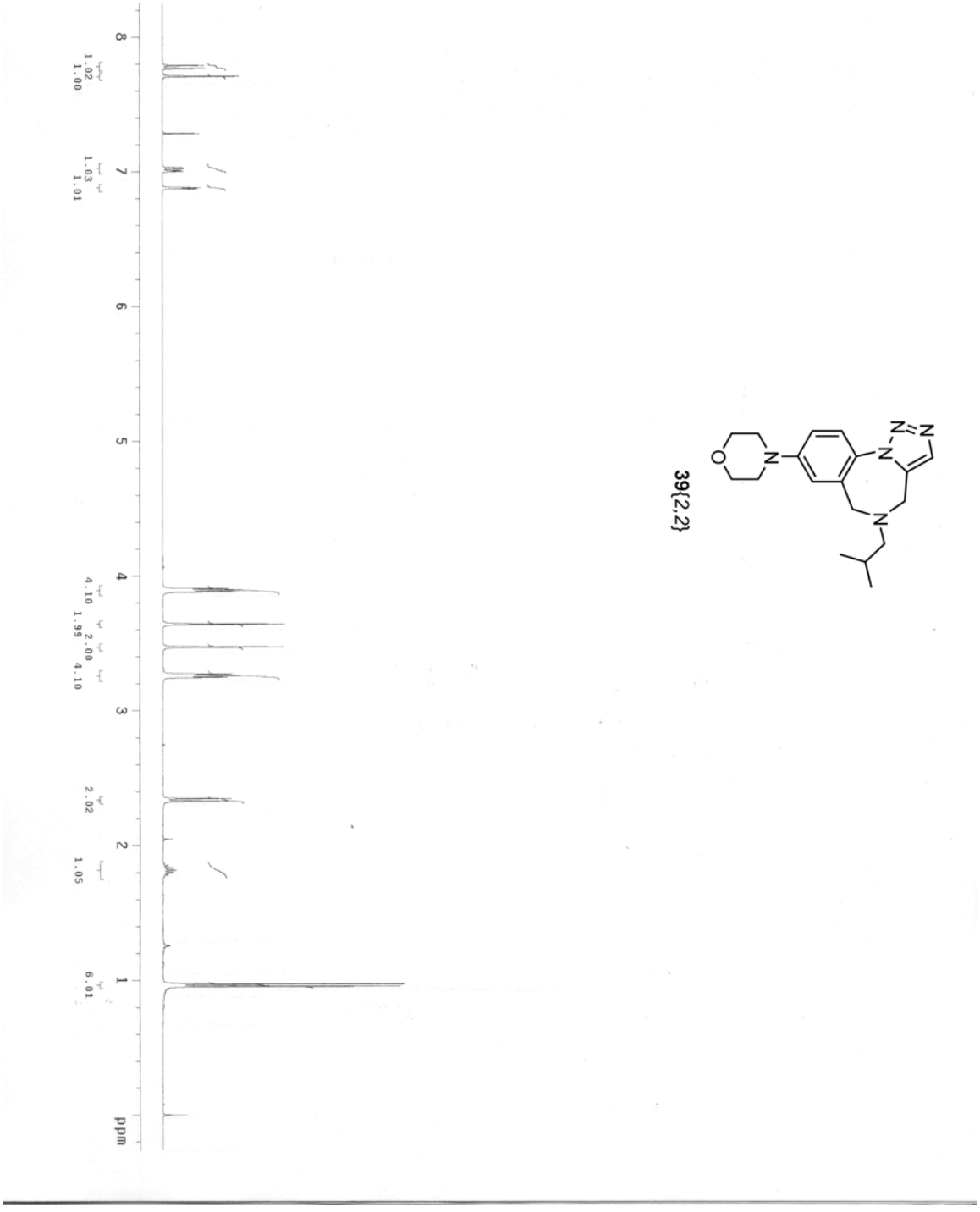
35(2,2)

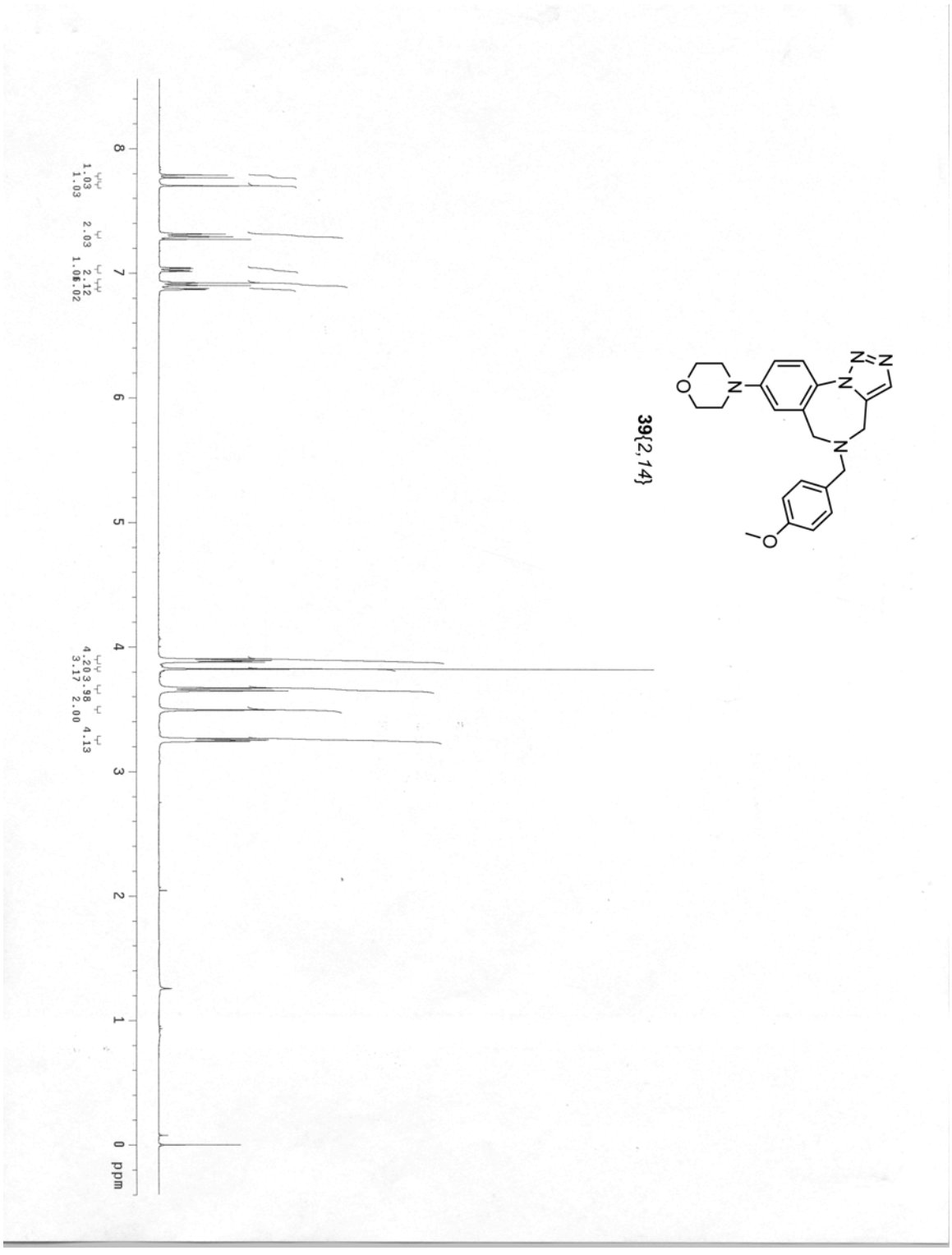


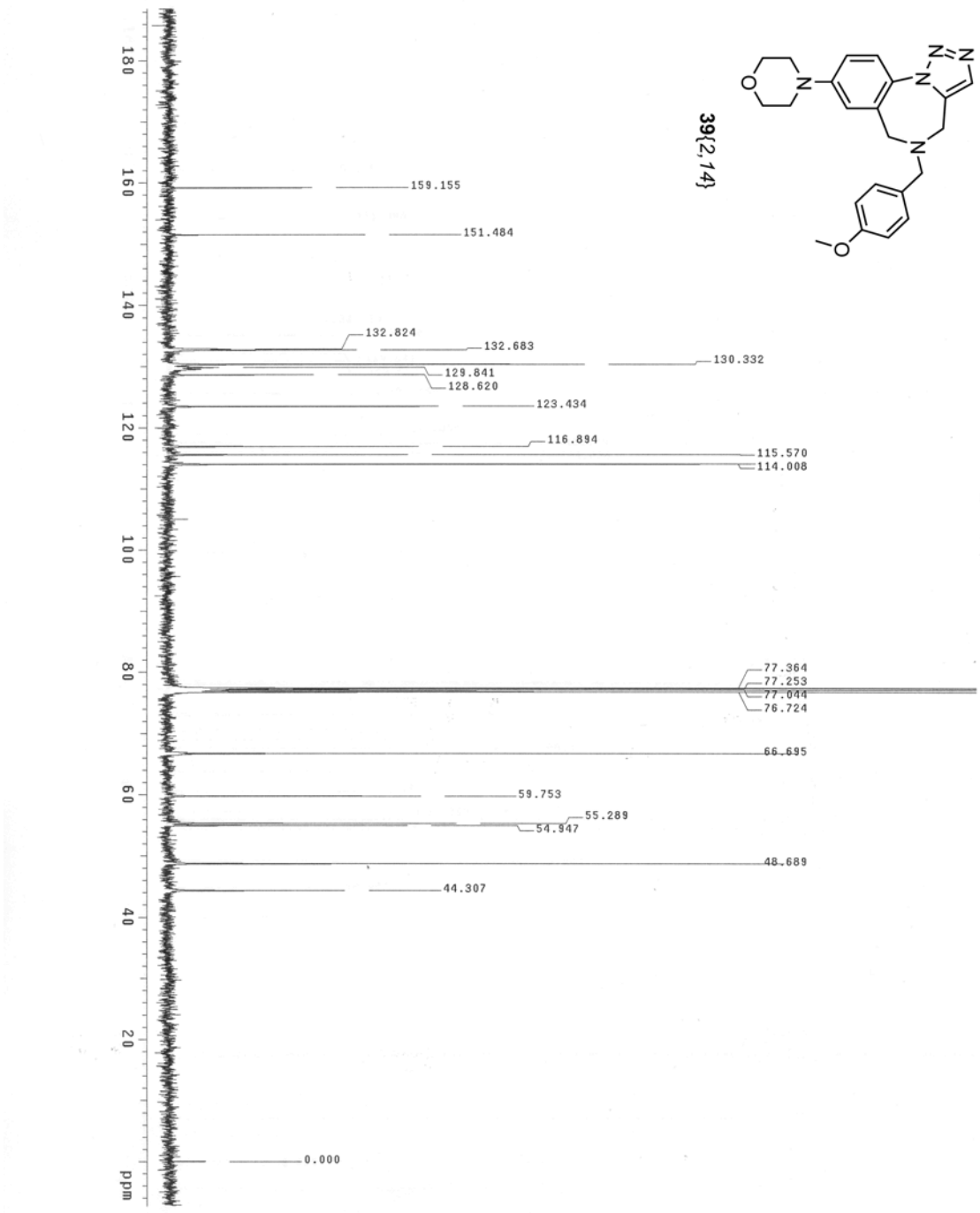

35{2,3}
8
7
6
5
4
3
2
1
0
ppm
1.06
0.97
1.03
0.96
2.00
1.91
0.98
3.98
1.09
3.95
2.57
1.07
2.10
2.27
3.18

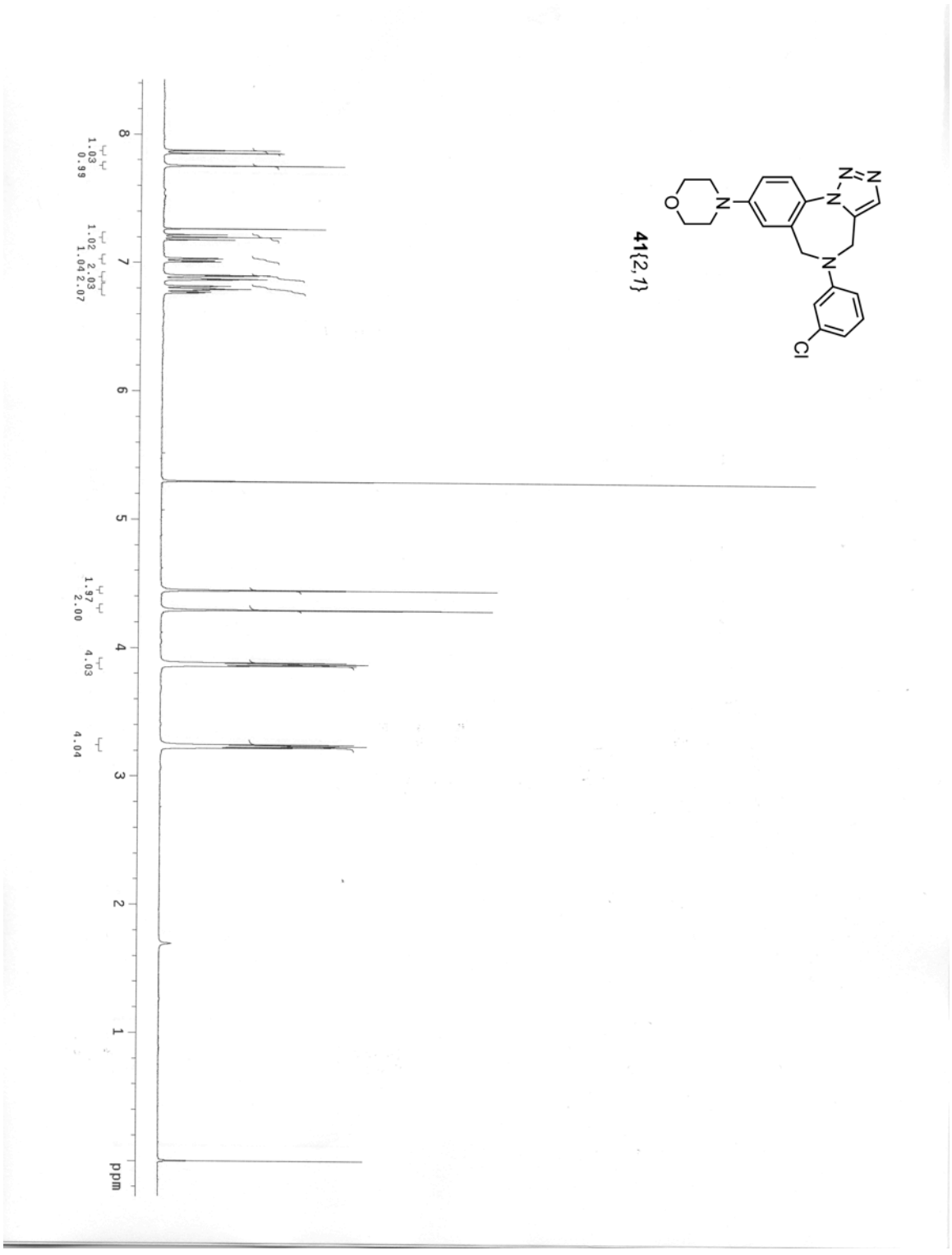

37{2,3}
8
7
6
5
4
3
2
1
-0
ppm
1.00
1.02
2.03
1.12
3.19
3.03
0.94
1.88
1.88
6.44
4.26
2.10

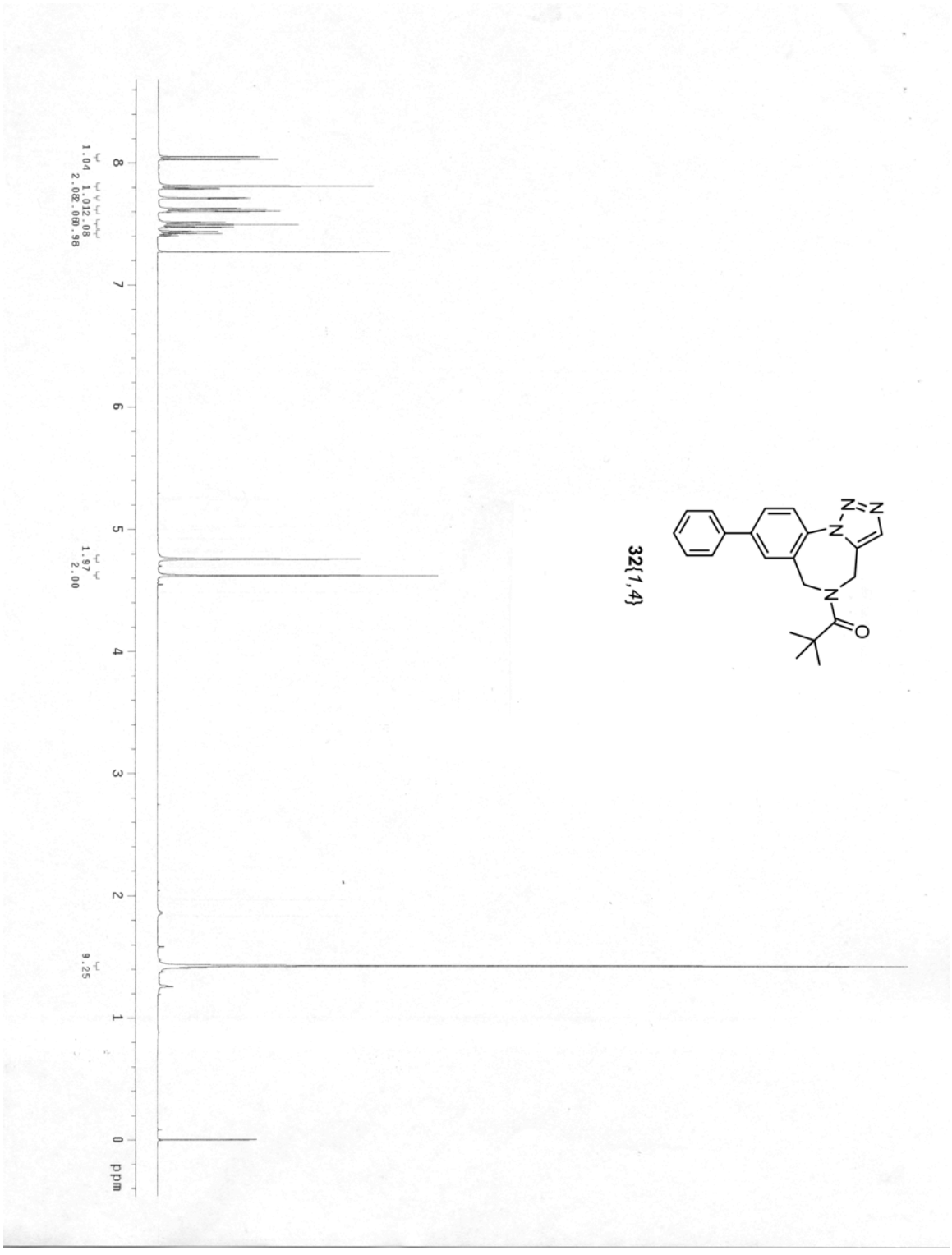

37{2,3}
181.622
151.221
138.773
133.304
131.057
129.235
128.930
128.900
128.208
126.883
123.736
117.010
116.504
77.472
77.361
77.160
76.840
66.535
50.472
48.961
47.429
42.168
35.033
0.116
ppm

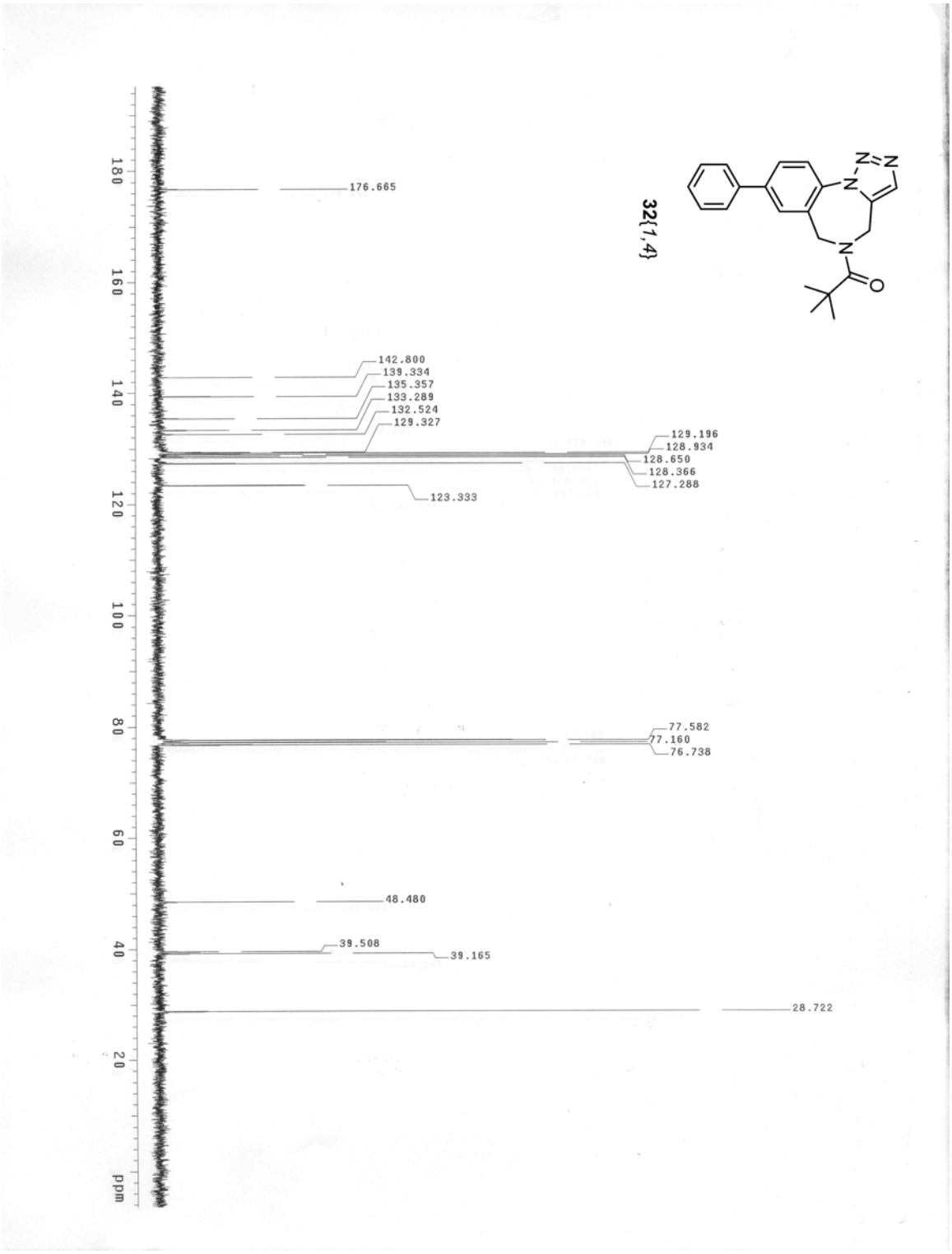

39{2,2}
8
7
6
5
4
3
2
1
ppm
1.02
1.00
1.03
1.01
4.10
1.99
2.00
4.10
2.02
1.05
6.01

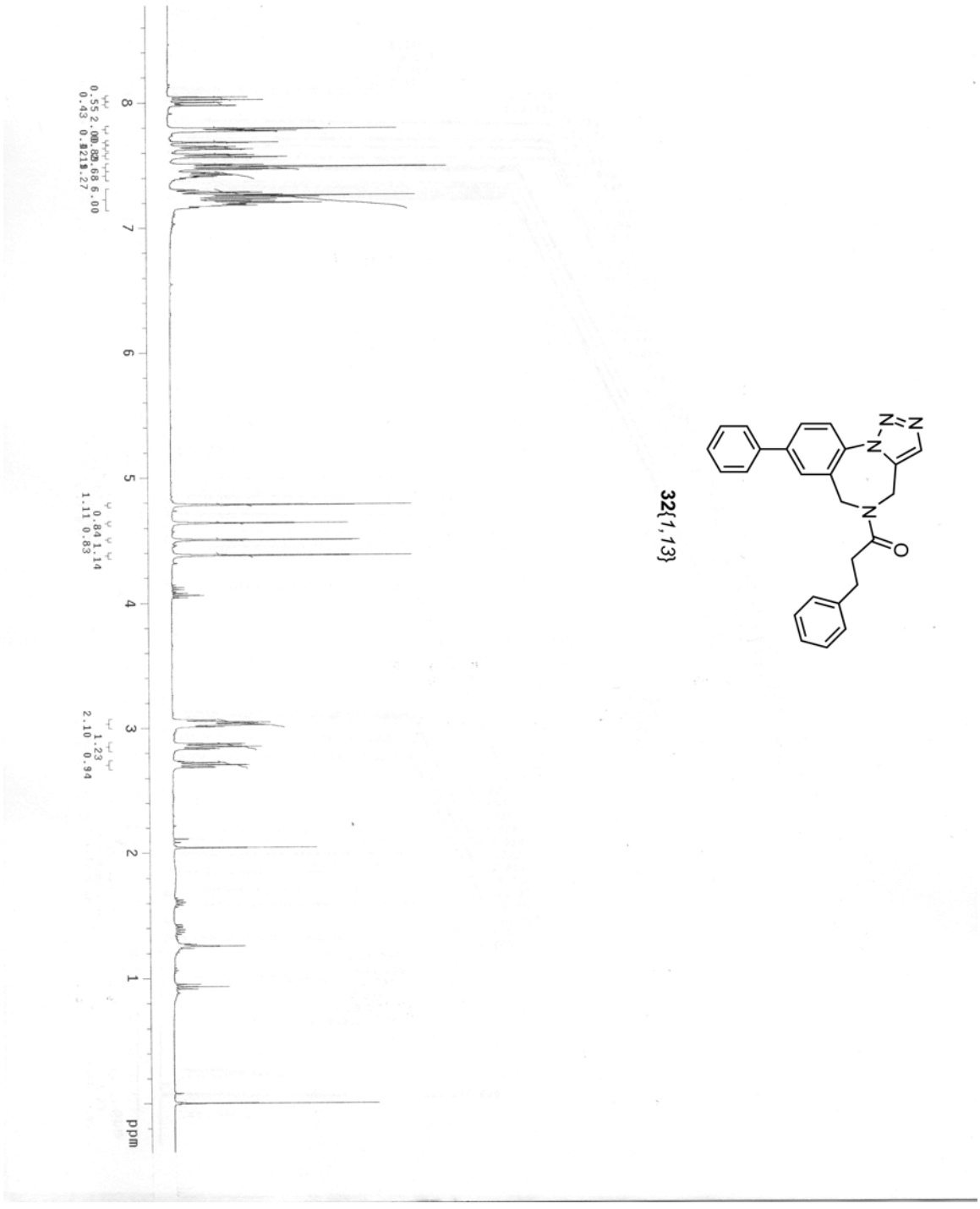

39{2,14}
8
7
6
5
4
3
2
1
0 ppm
1.03
1.03
2.03
2.12
1.06
1.02
4.20
3.98
4.13
3.17
2.00

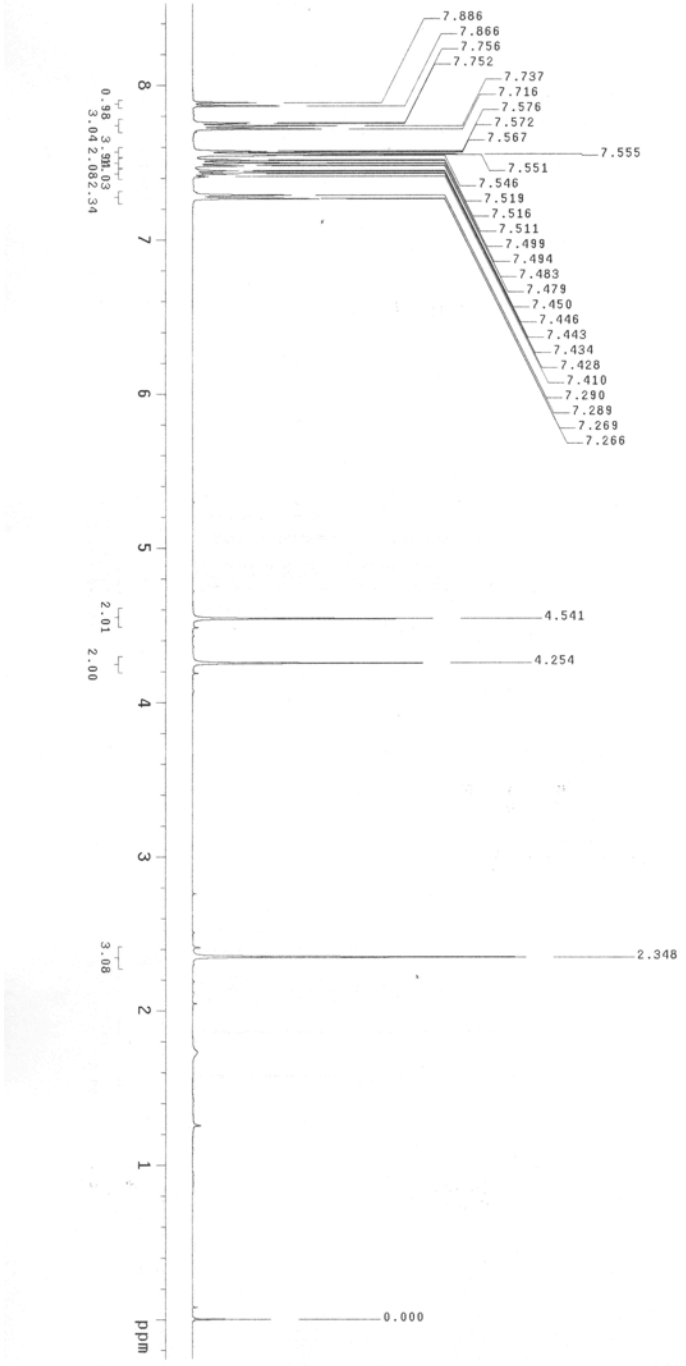

39(2,14)
159.155
151.484
132.824
132.683
130.332
129.841
128.620
123.434
116.894
115.570
114.008
77.364
77.253
77.044
76.724
66.695
59.753
55.289
54.947
48.689
44.307
0.000
ppm


41{2,1}
Cl
ppm
1.03
0.99
1.02
2.03
1.04
2.07
1.97
2.00
4.03
4.04

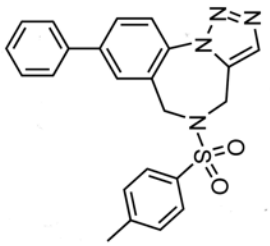

32{1,4}
8
7
6
5
4
3
2
1
0
ppm
1.04 1.012.08
2.08.00.98
1.97
2.00
9.25

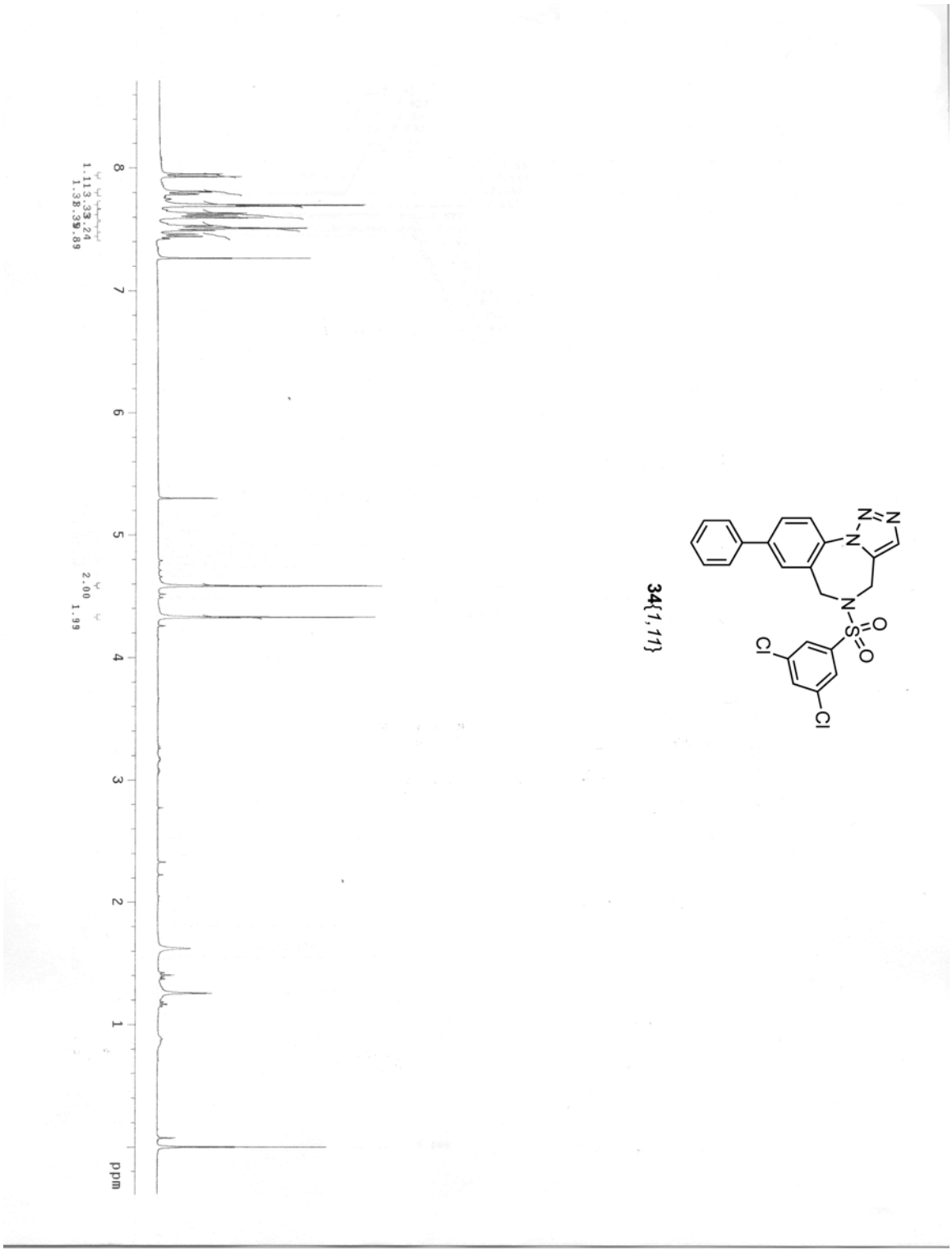

32{1,4}
176.665
142.800
139.334
135.357
133.289
132.524
129.327
129.196
128.934
128.650
128.366
127.288
123.333
77.582
77.160
76.738
48.480
39.508
39.165
28.722
180
160
140
120
100
80
60
40
20
ppm

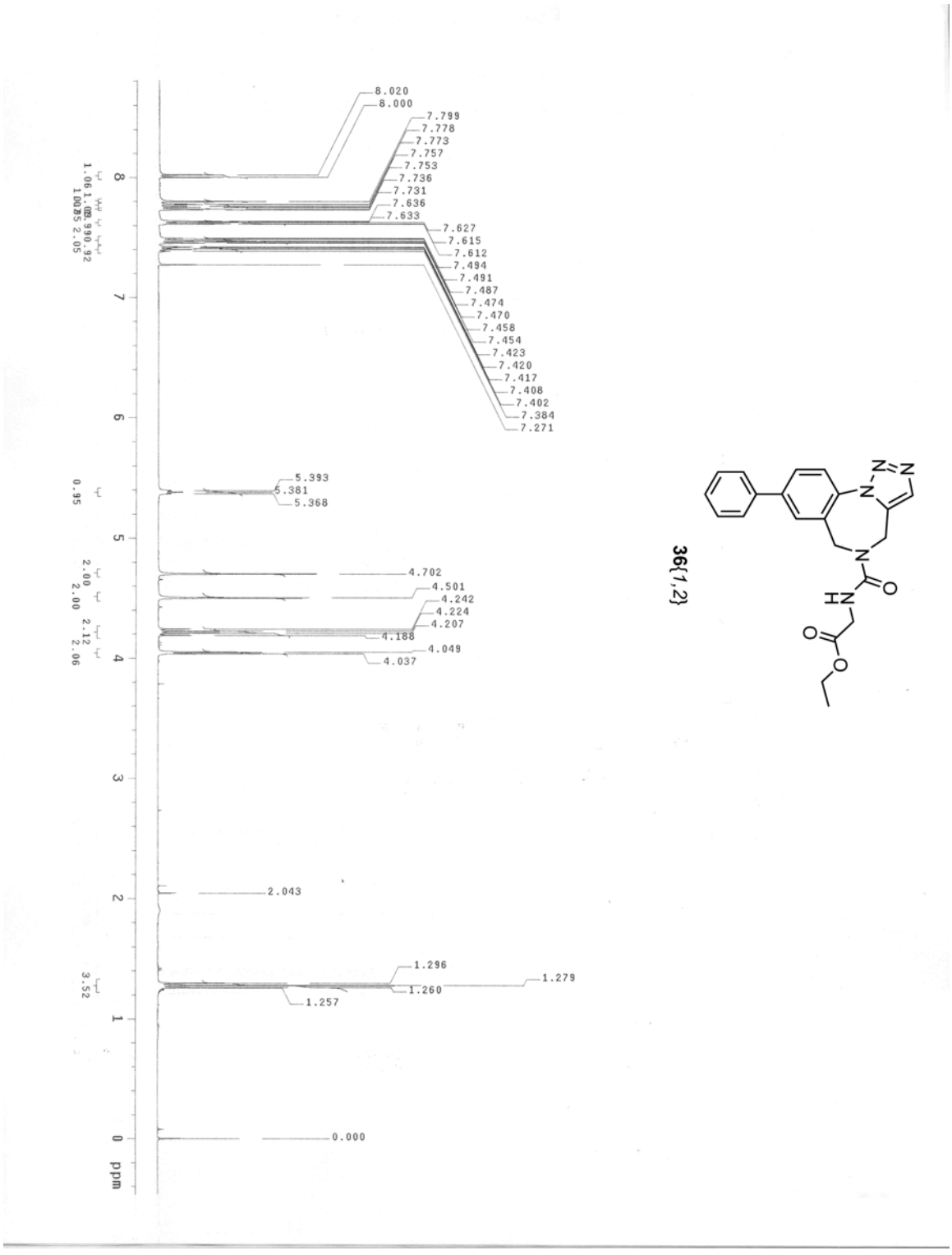

32(1,13)
ppm

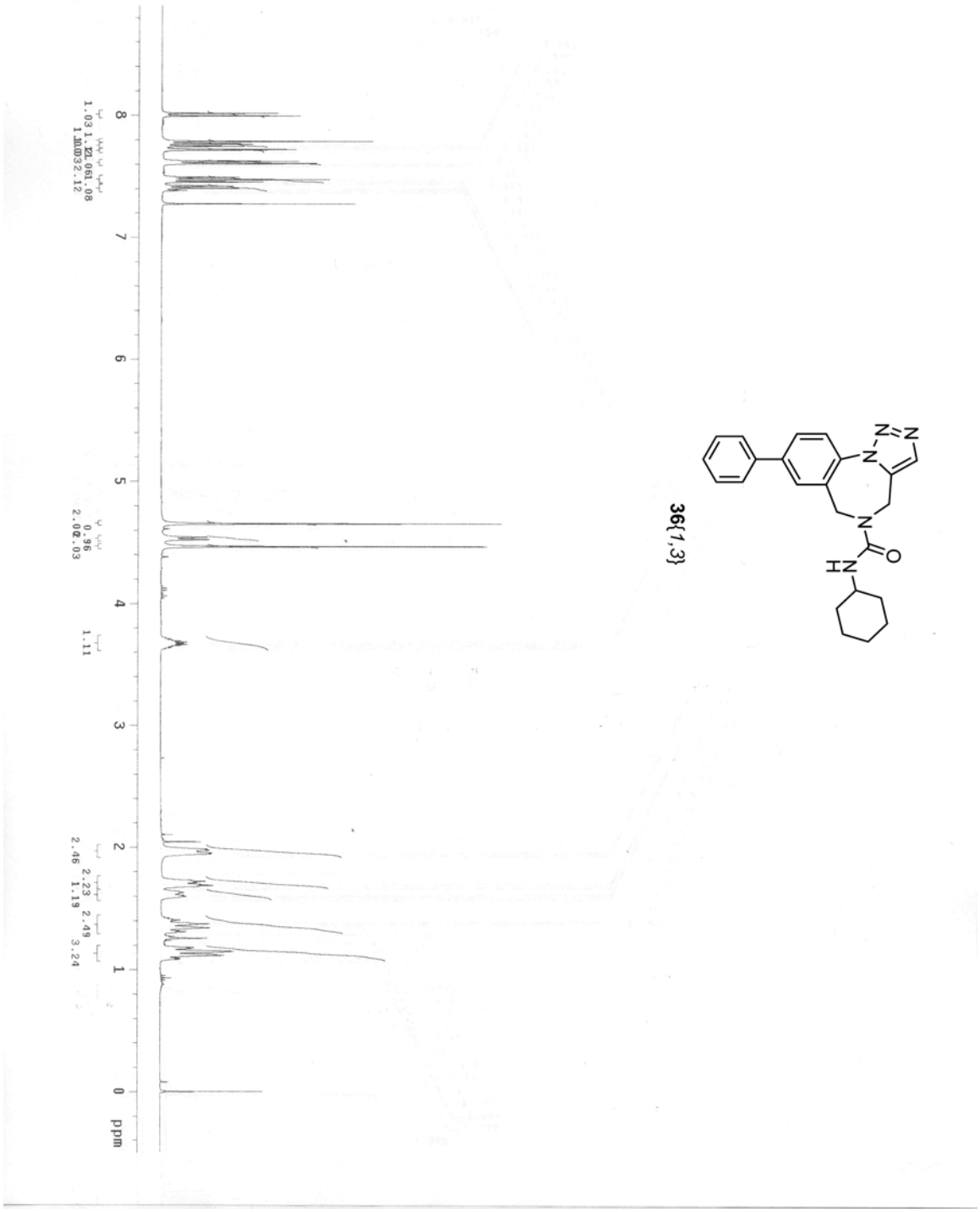

7.886
7.866
7.756
7.752
7.737
7.716
7.576
7.572
7.567
7.555
7.551
7.546
7.519
7.516
7.511
7.499
7.494
7.483
7.479
7.450
7.446
7.443
7.434
7.428
7.410
7.290
7.289
7.269
7.266
4.541
4.254
2.348
0.000
ppm

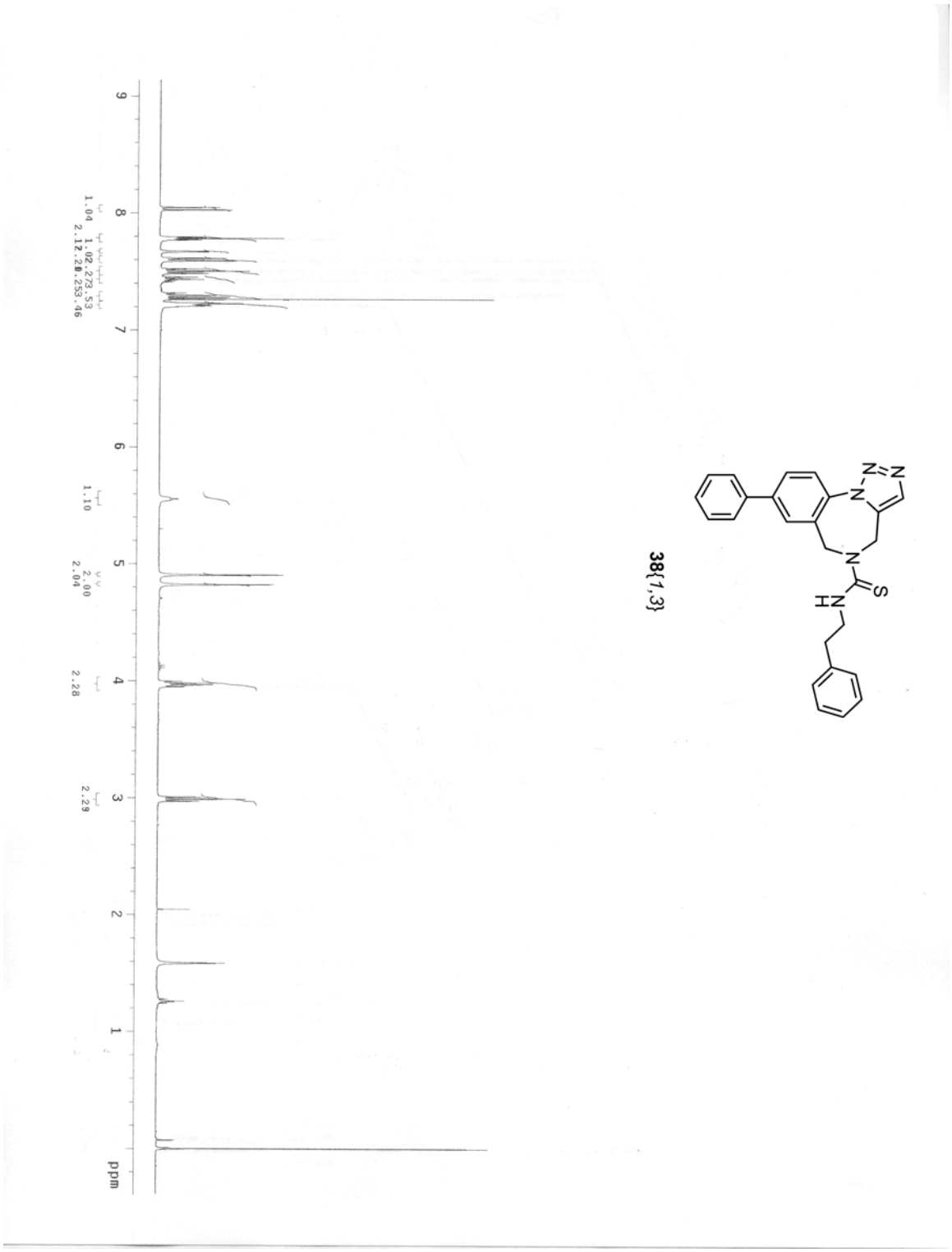
34{*1,5*}

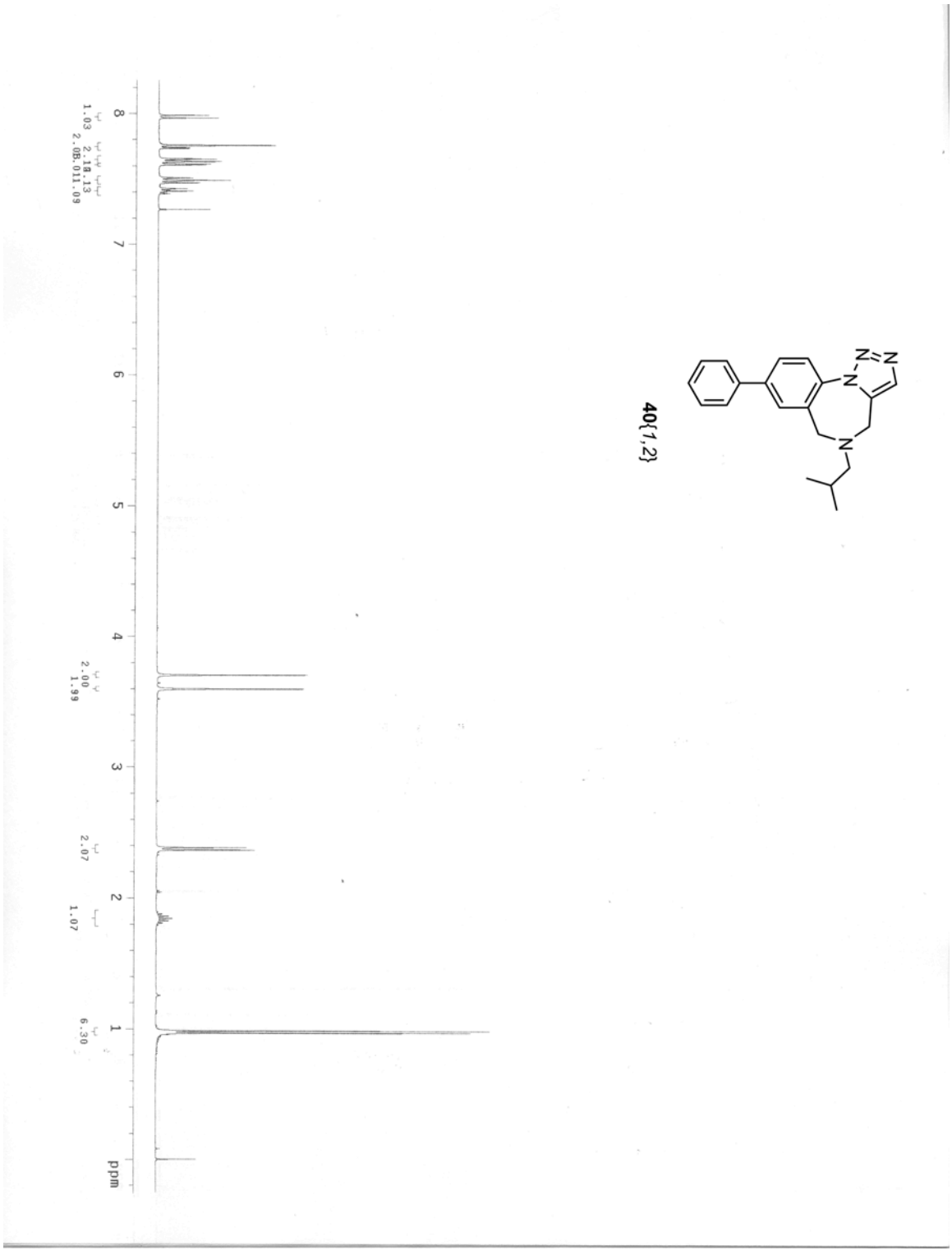


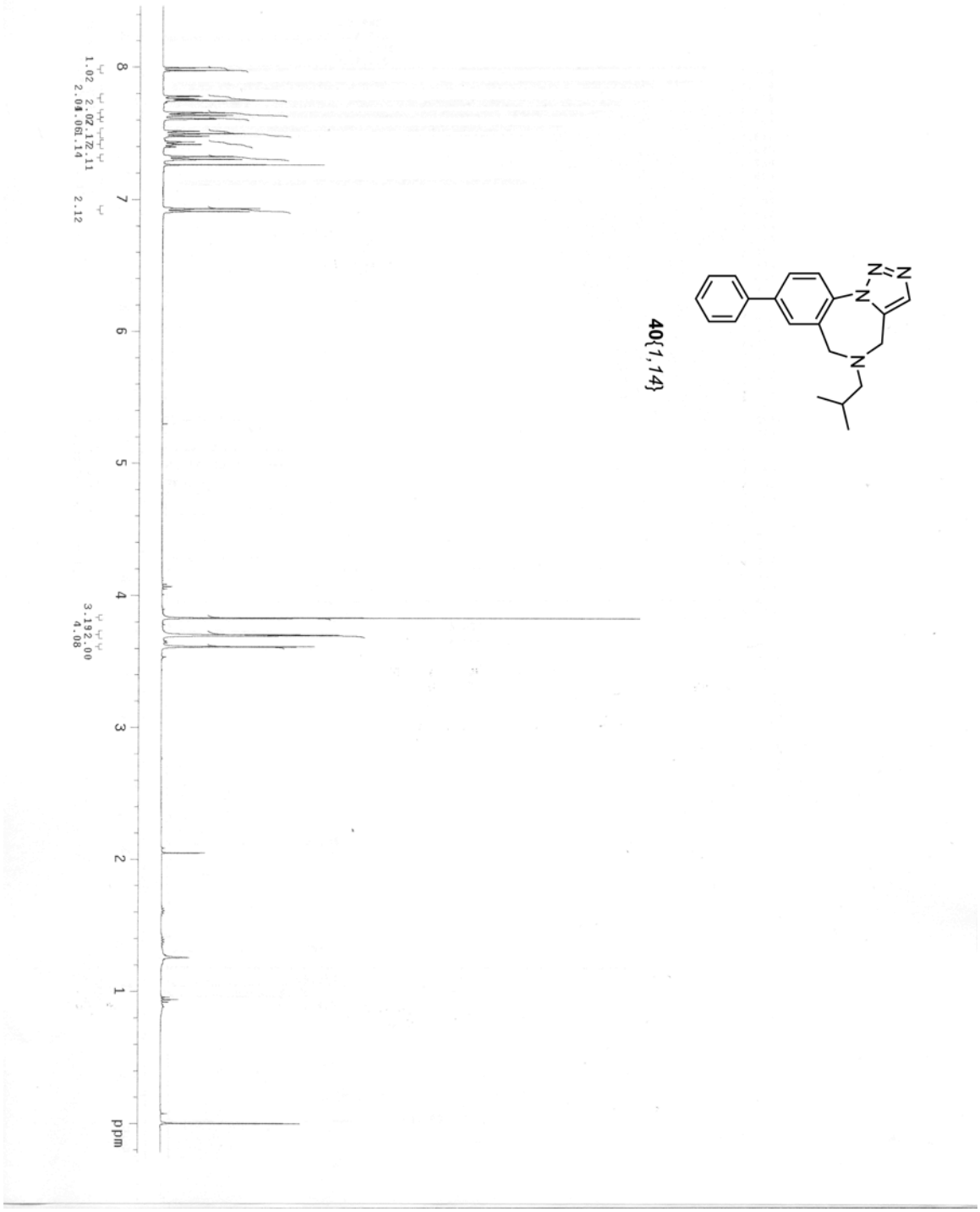

34{1,11}
Cl
Cl
O
O
S
N
N
N
8
7
6
5
4
3
2
1
ppm
2.00
1.99
1.13.33.24
1.38.39.89


8.020
8.000
7.799
7.778
7.773
7.757
7.753
7.736
7.731
7.636
7.633
7.627
7.615
7.612
7.494
7.491
7.487
7.474
7.470
7.458
7.454
7.423
7.420
7.417
7.408
7.402
7.384
7.271
5.393
5.381
5.368
4.702
4.501
4.242
4.224
4.207
4.188
4.049
4.037
2.043
1.296
1.279
1.260
1.257
0.000
ppm
36{1,2}

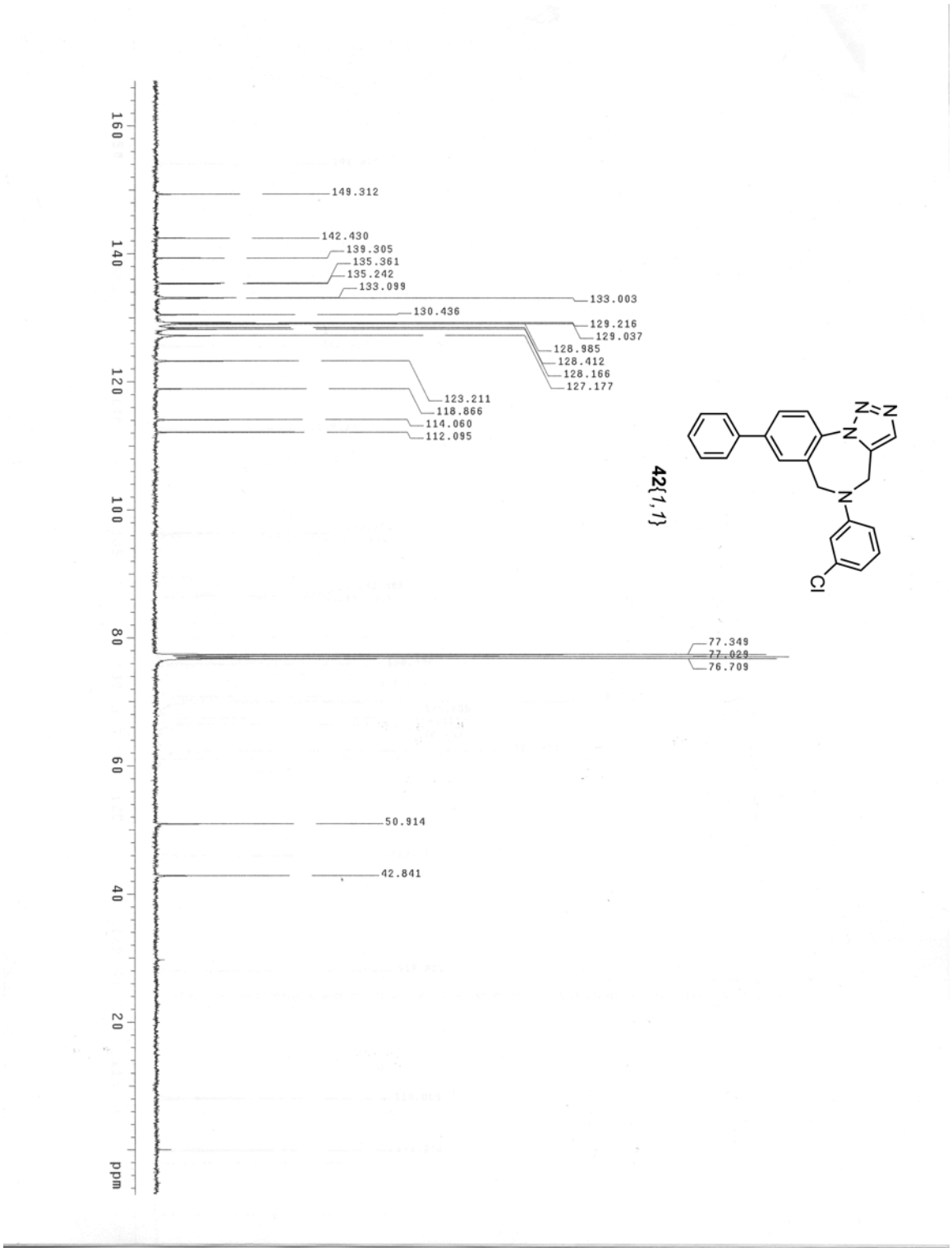

36{1,3}
8
7
6
5
4
3
2
1
0
ppm

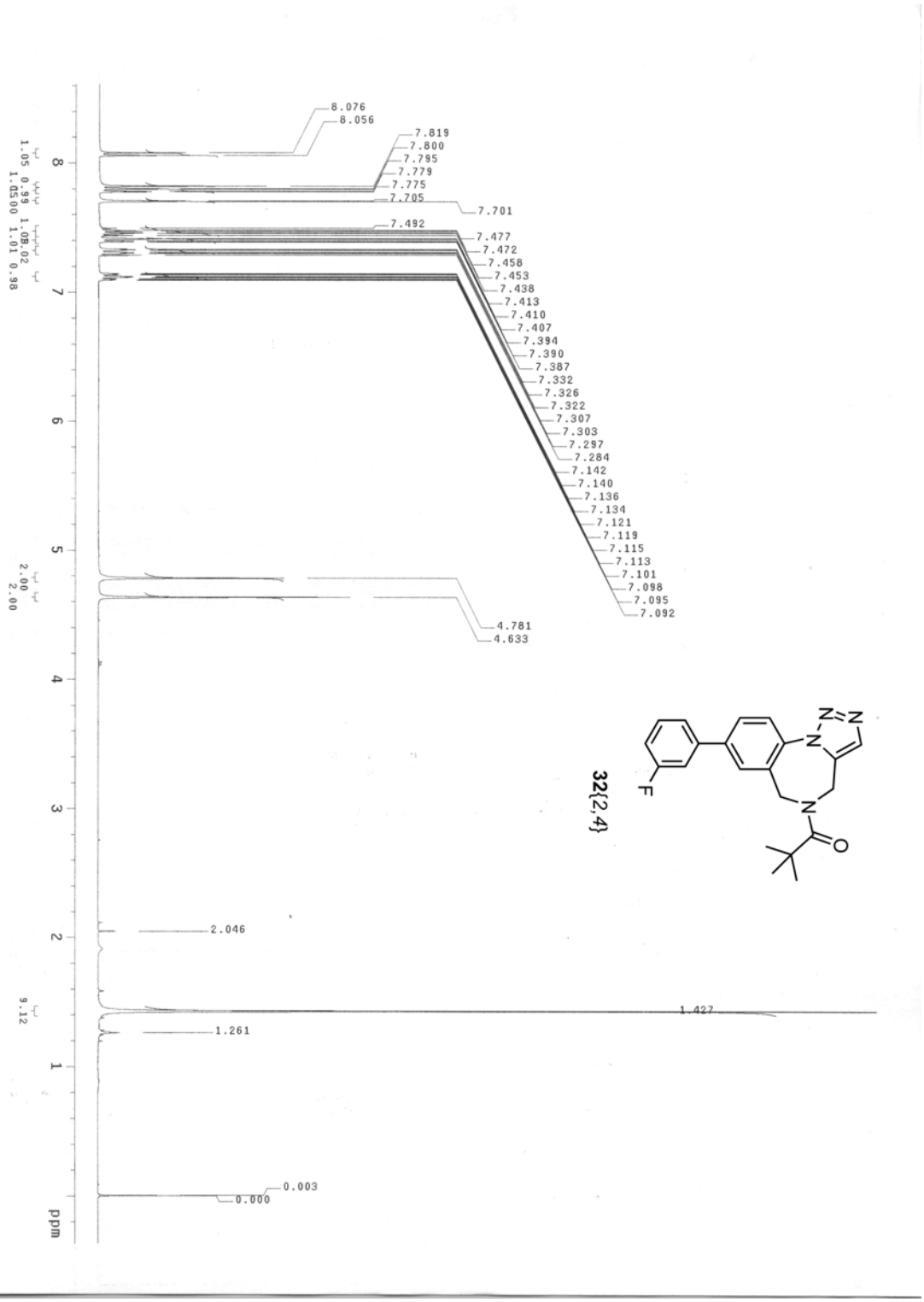

38{1,3}
N
N
N
S
H
N
9
8
7
6
5
4
3
2
1
ppm
1.04
1.02
2.73
3.53
2.12
2.28
1.25
3.46
1.10
2.00
2.04
2.28
2.29

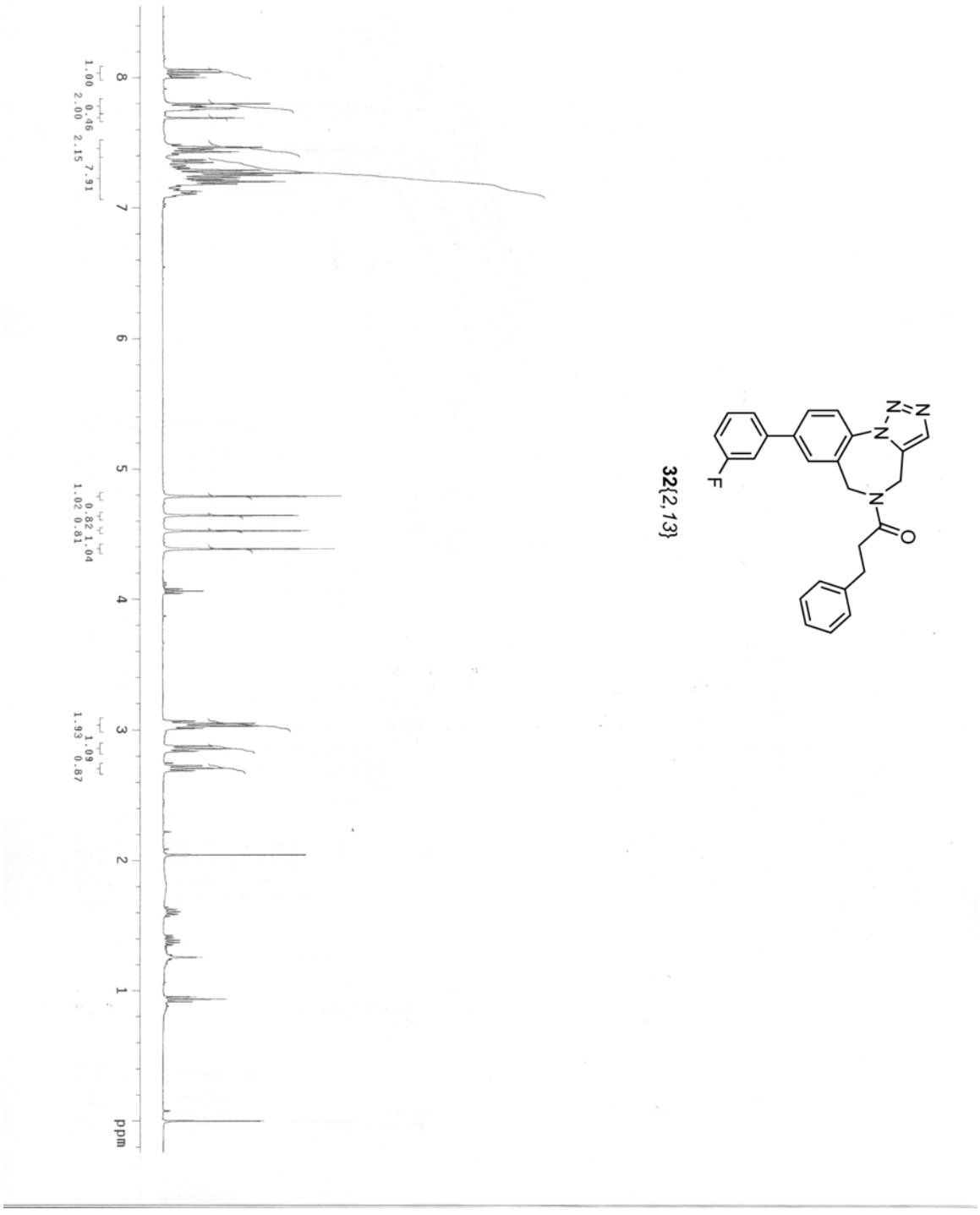

40{1,2}
8
7
6
5
4
3
2
1
ppm
1.03
2.18
2.08
2.11
2.09
2.00
1.99
2.07
1.07
6.30

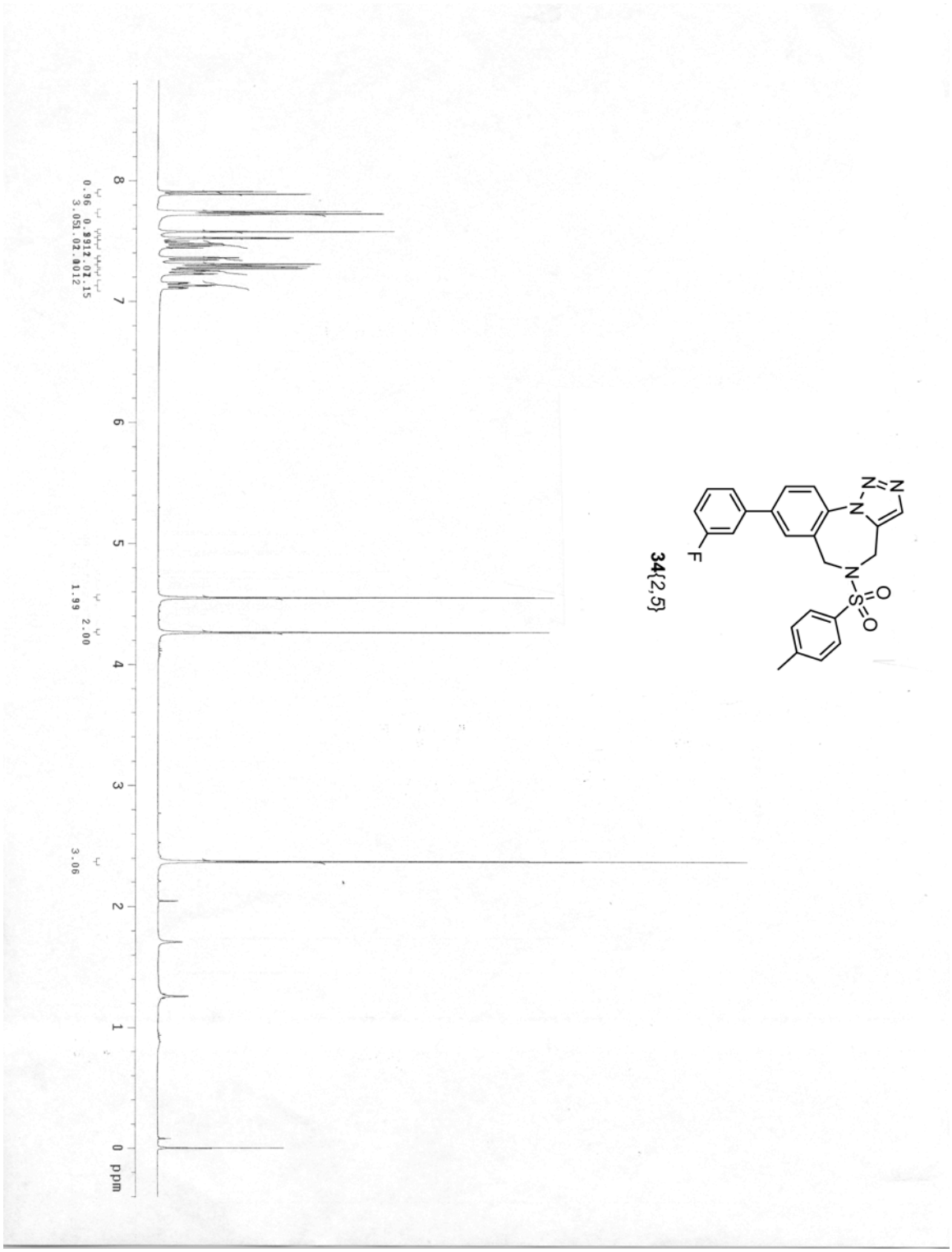

40(1,14)
8
7
6
5
4
3
2
1
ppm
1.02
2.02
2.12
2.11
2.04
2.08
2.14
2.12
3.19
2.00
4.08

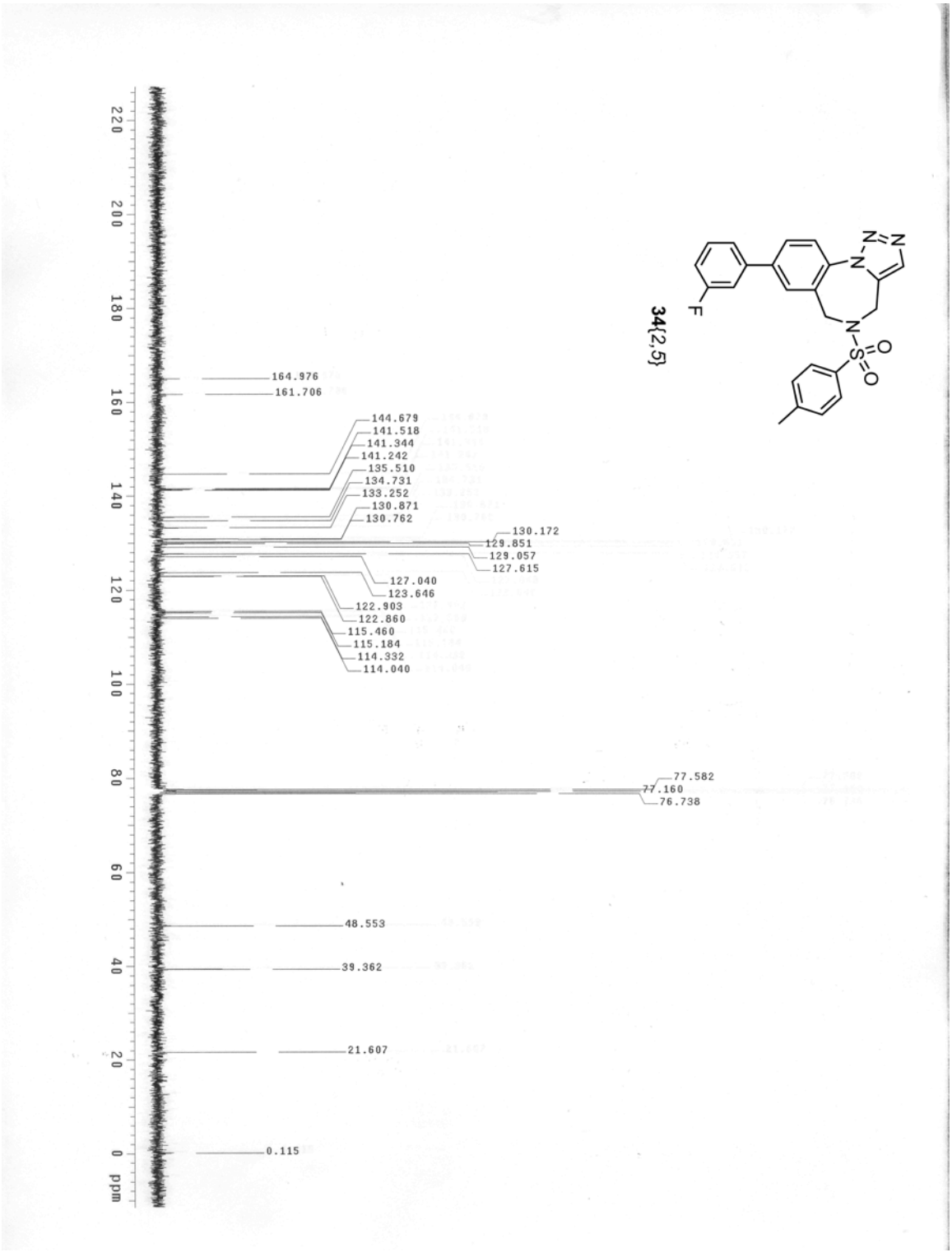
42{1,1}
Cl
N
N
N
8
7
6
5
4
3
2
1
ppm
1.04 1.05 1.91 2.23 1.05 2.20
1.09 1.02 2.35 1.15
2.00
2.04

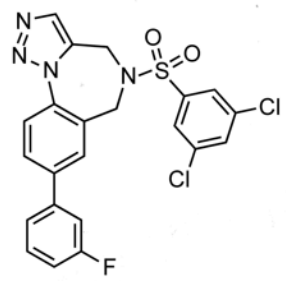

149.312
142.430
139.305
135.361
135.242
133.099
133.003
130.436
129.216
129.037
128.985
128.412
128.166
127.177
123.211
118.866
114.060
112.095
77.349
77.029
76.709
50.914
42.841
160
140
120
100
80
60
40
20
ppm
42{1,1}
Cl


8.076
8.056
7.819
7.800
7.795
7.779
7.775
7.705
7.701
7.492
7.477
7.472
7.458
7.453
7.438
7.413
7.410
7.407
7.394
7.390
7.387
7.332
7.326
7.322
7.307
7.303
7.297
7.284
7.142
7.140
7.136
7.134
7.121
7.119
7.115
7.113
7.101
7.098
7.095
7.092
4.781
4.633
2.046
1.427
1.261
0.003
0.000
ppm
32{2,4}
F
O

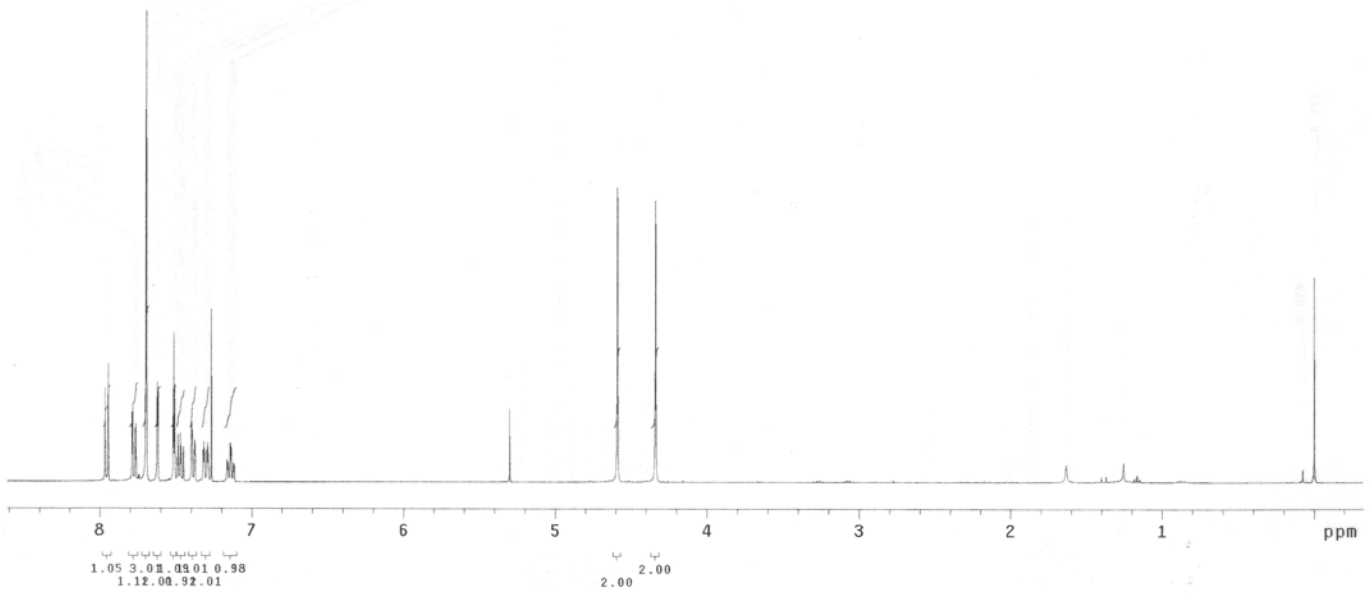

F
N
N
N
O
32{2,13}
8
7
6
5
4
3
2
1
ppm
1.00 0.46 7.91
2.00 2.15
0.82 1.04
1.02 0.81
1.09
1.93 0.87

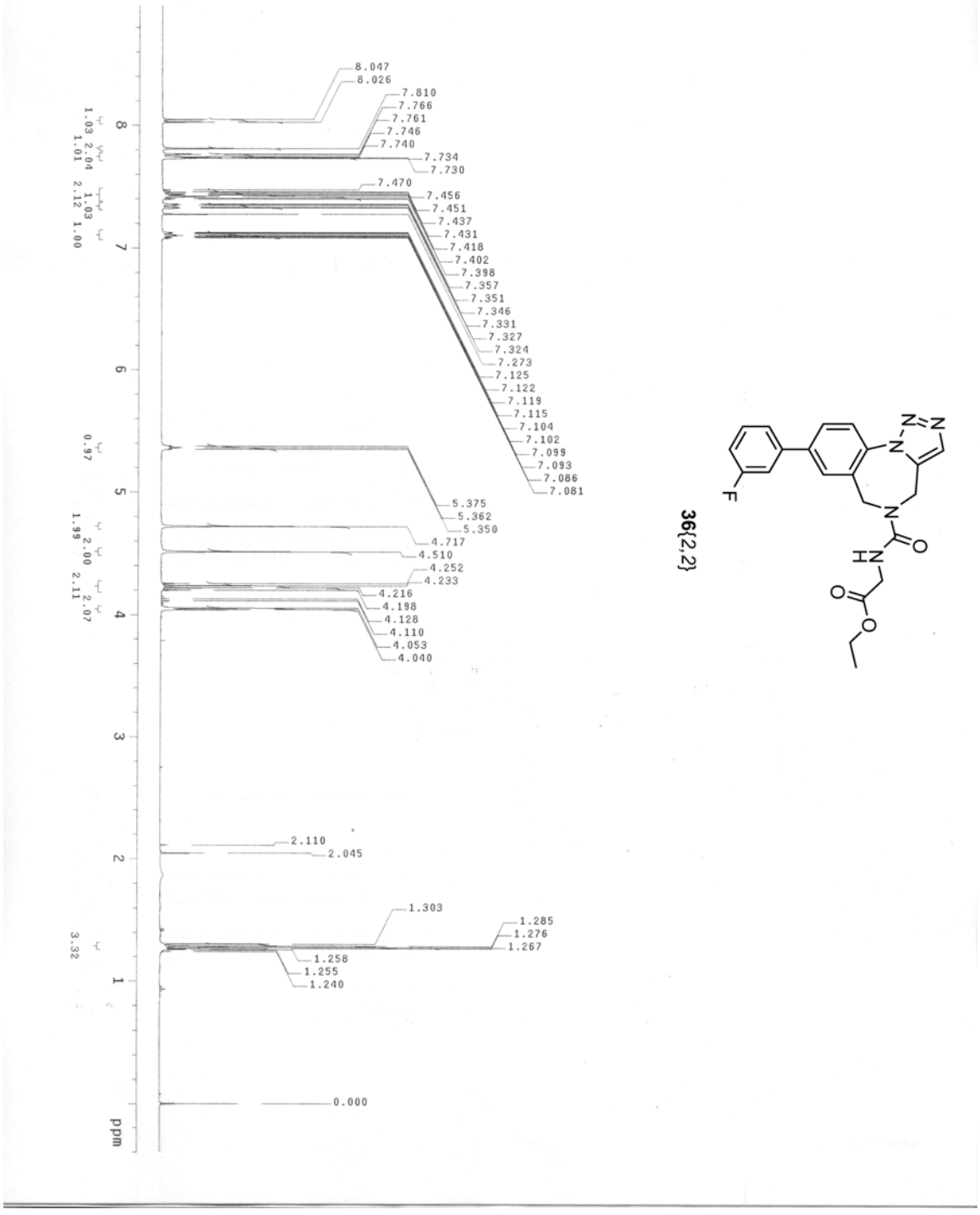

34{2,5}
F
N
N
N
O
S
O
8
7
6
5
4
3
2
1
0
ppm
0.96
0.9912.07.15
3.051.02.8012
2.00
1.99
3.06

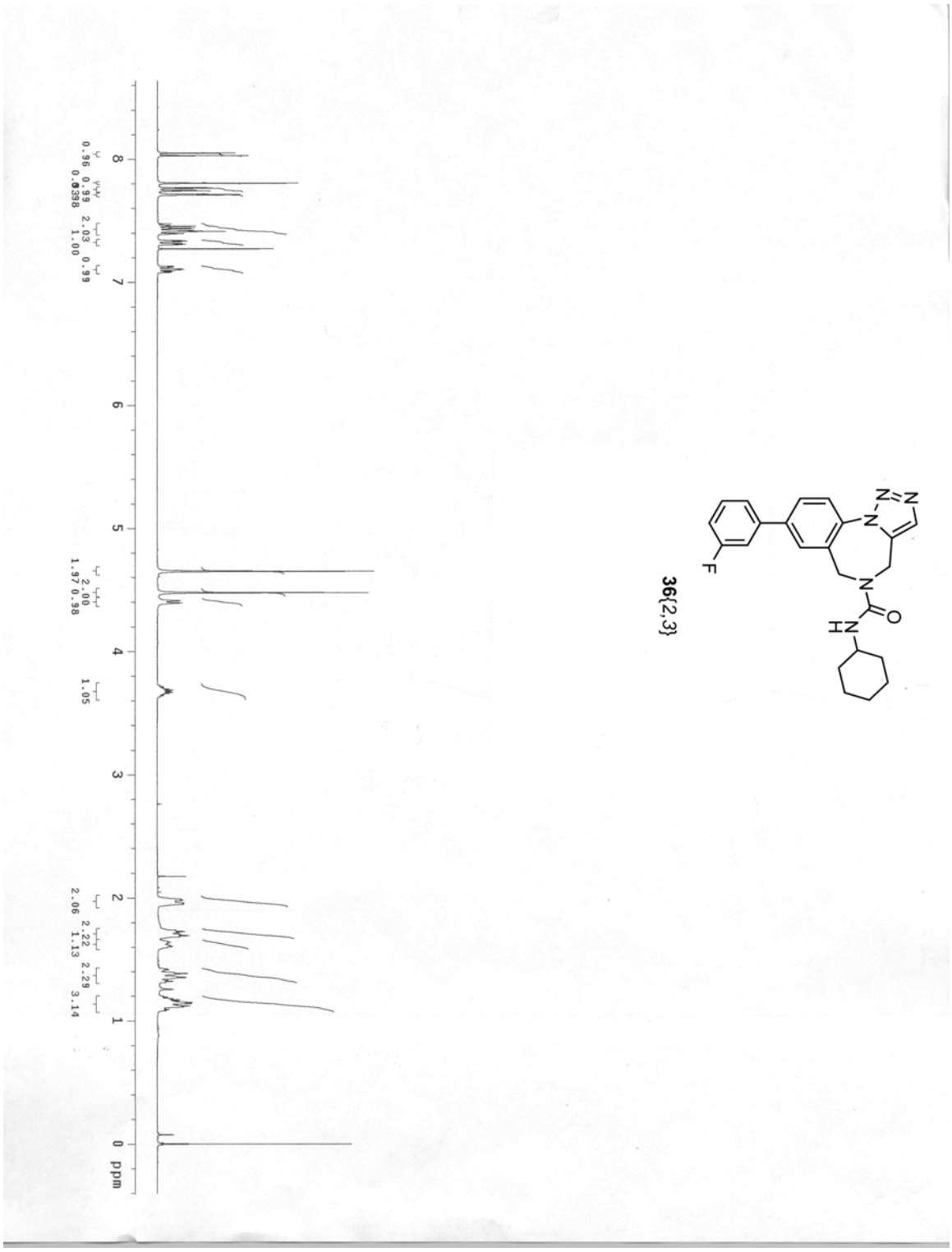

34(2,5)
F
N
N
N
S
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm
164.976
161.706
144.679
141.518
141.344
141.242
135.510
134.731
133.252
130.871
130.762
130.172
129.851
129.057
127.615
127.040
123.646
122.903
122.860
115.460
115.184
114.332
114.040
77.582
77.160
76.738
48.553
39.362
21.607
0.115

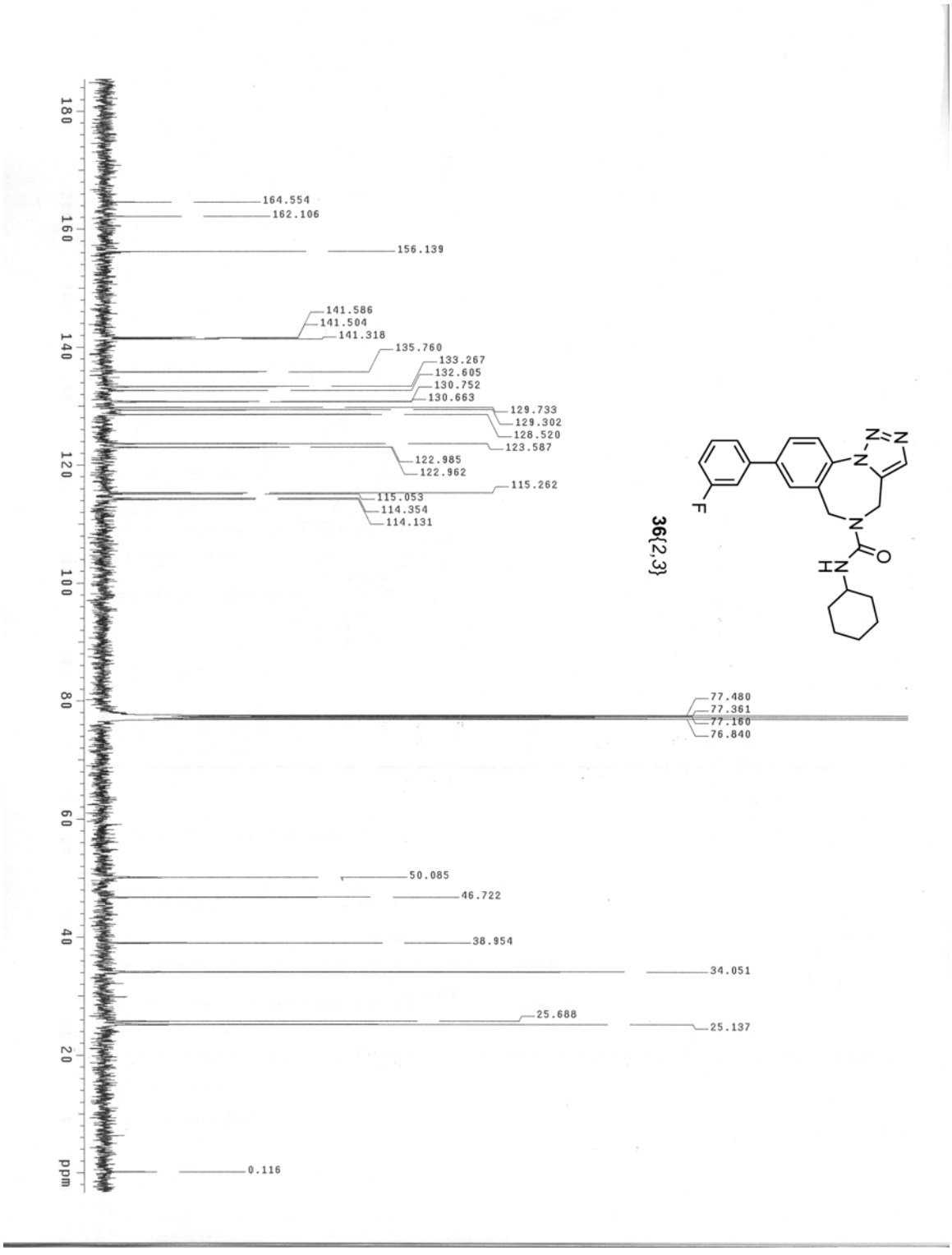

N
N
N
O
O
S
N
Cl
Cl
F

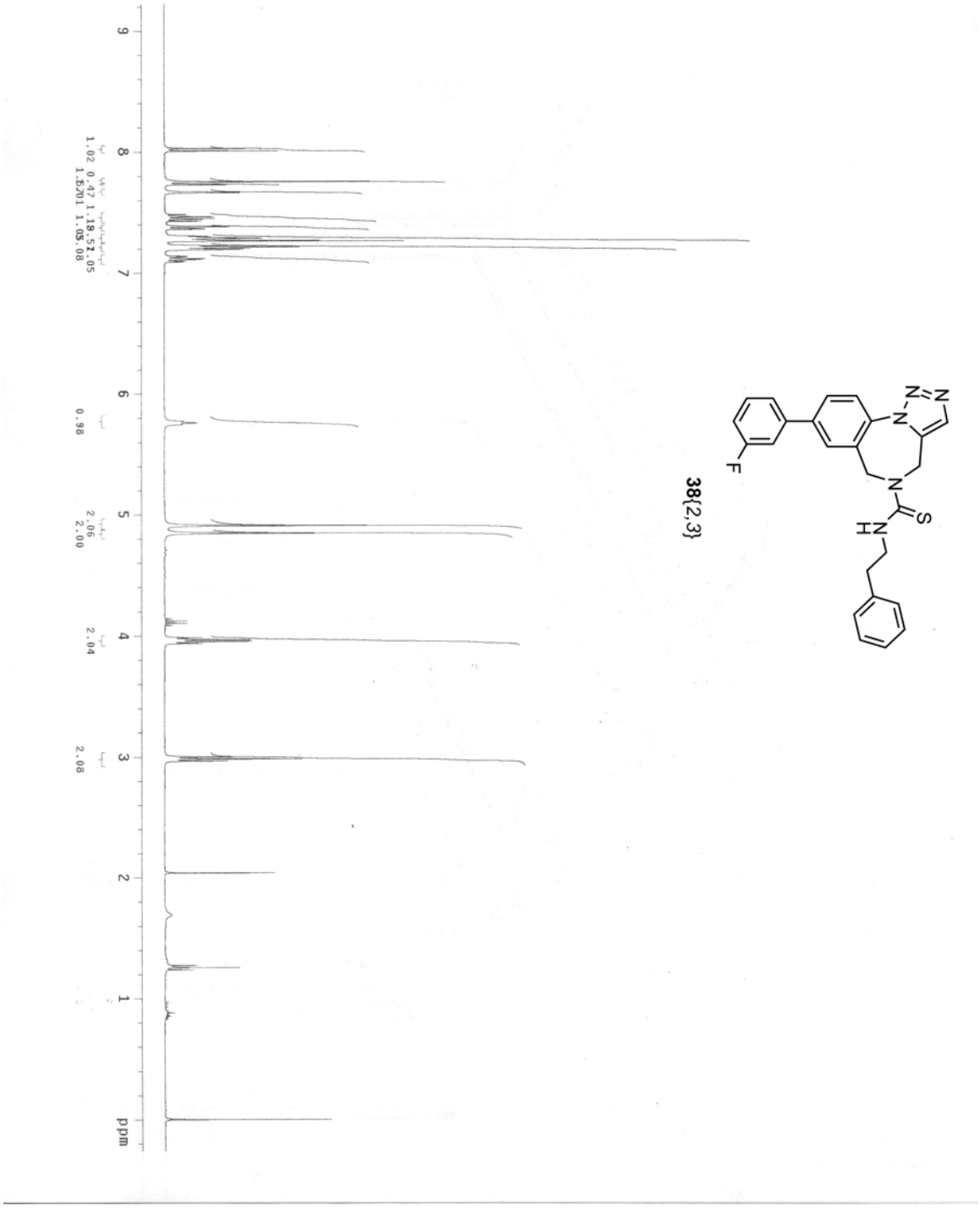
34{*2,11*}

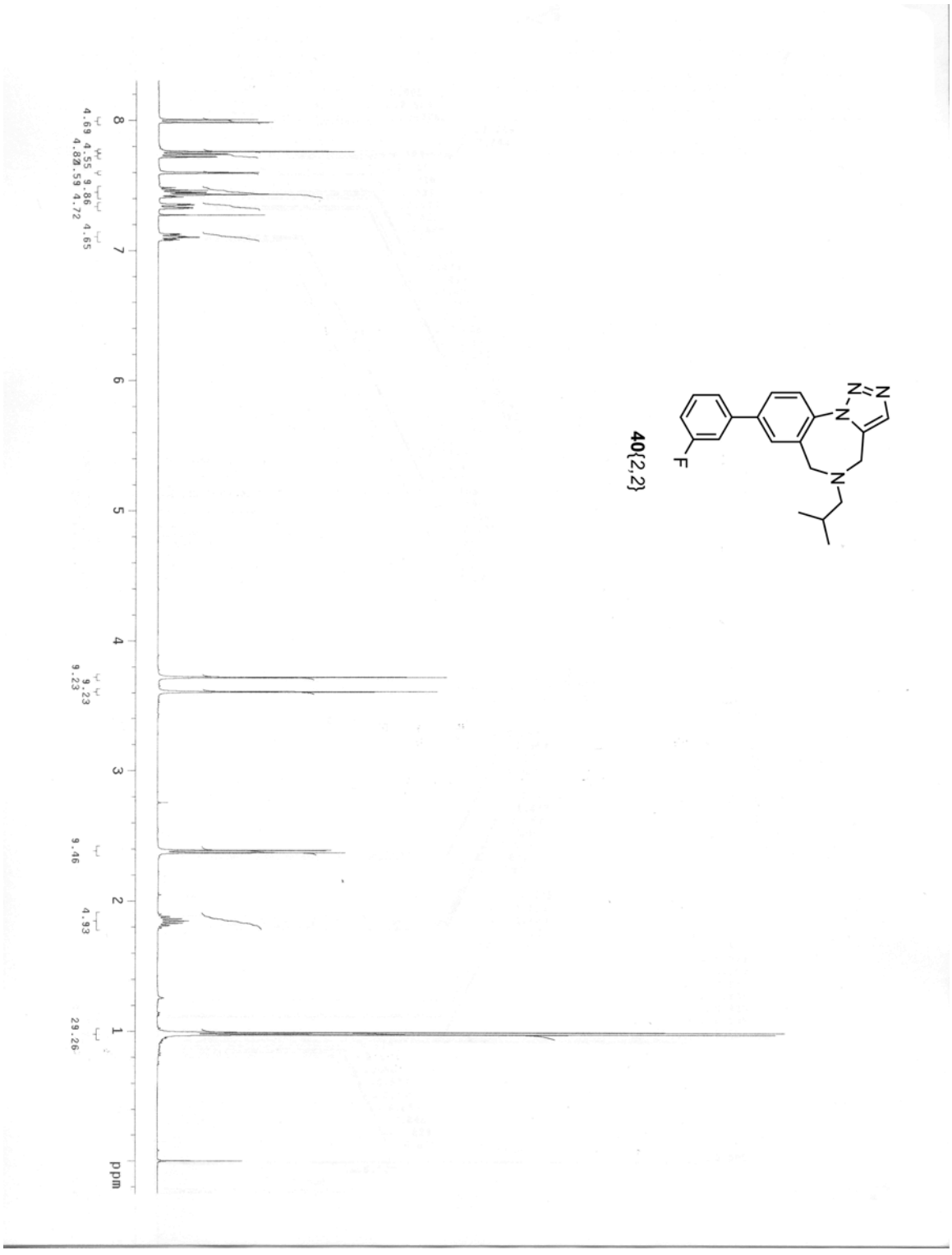

8
7
6
5
4
3
2
1
ppm
1.05 3.01 1.03 1.01 0.98
1.12 1.00 0.92 2.01
2.00
2.00

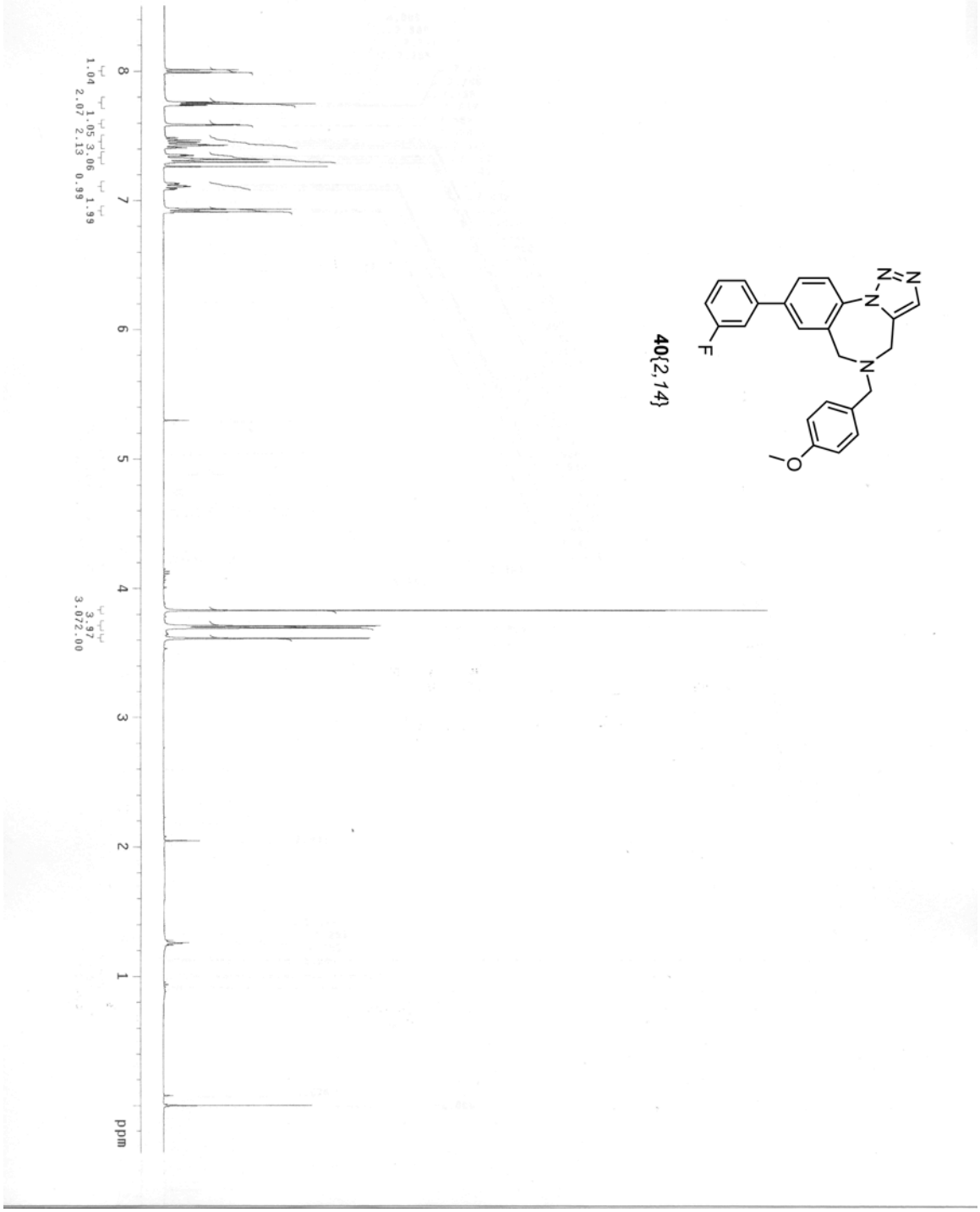

8.047
8.026
7.810
7.766
7.761
7.746
7.740
7.734
7.730
7.470
7.456
7.451
7.437
7.431
7.418
7.402
7.398
7.357
7.351
7.346
7.331
7.327
7.324
7.273
7.125
7.122
7.119
7.115
7.104
7.102
7.099
7.093
7.086
7.081
5.375
5.362
5.350
4.717
4.510
4.252
4.233
4.216
4.198
4.128
4.110
4.053
4.040
2.110
2.045
1.303
1.285
1.276
1.267
1.258
1.255
1.240
0.000
ppm
1.03 2.04 1.03
1.01 2.12 1.00
0.97
1.99 2.00 2.07
2.11
3.32
36{2,2}
F
N
N
N
O
H
N
O
O

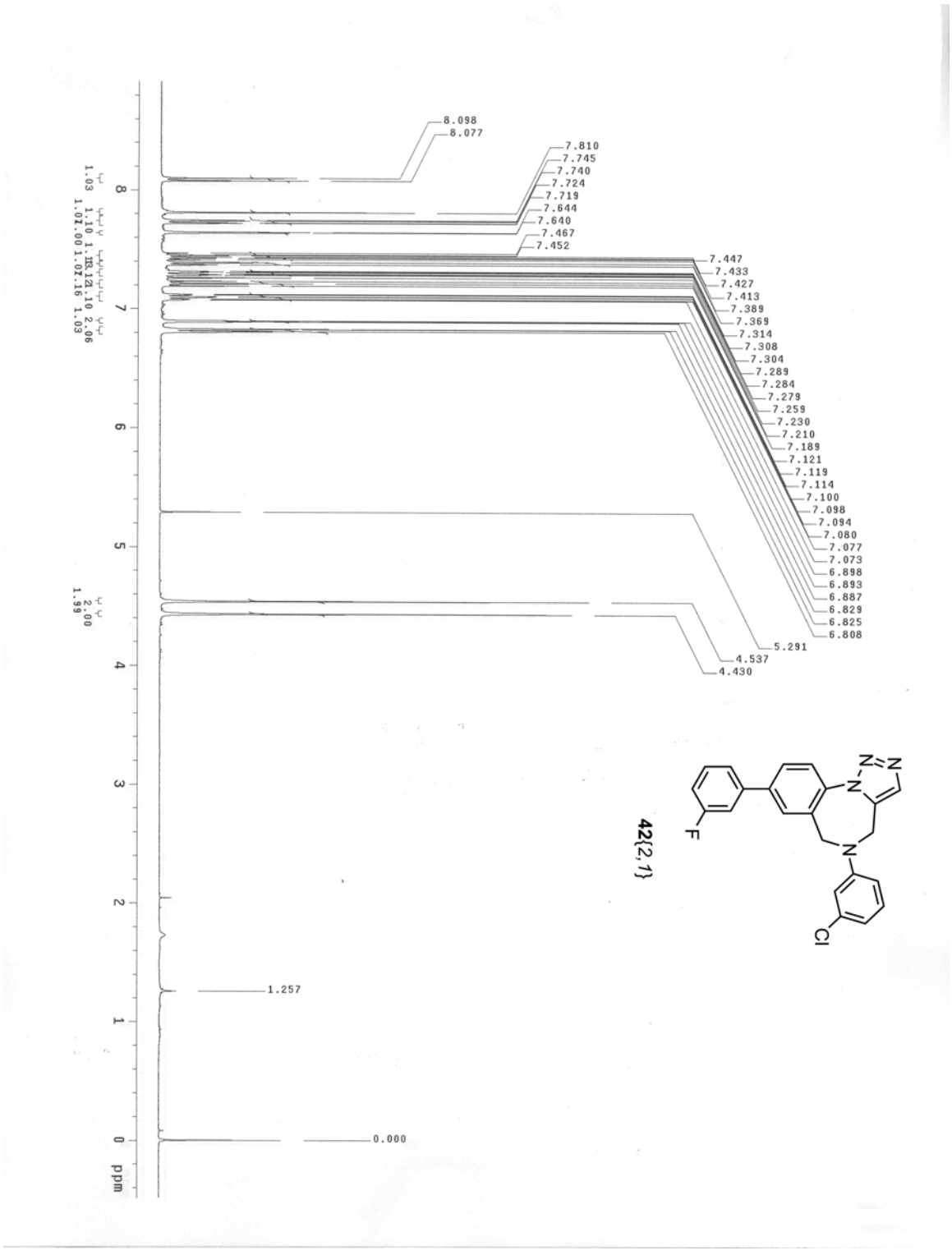

F
N
N
N
N
O
H
36{2,3}
8
7
6
5
4
3
2
1
0 ppm
0.96 0.99 2.03 0.99
0.98 1.00
1.97 0.98
1.05
2.06 1.13 2.29 3.14

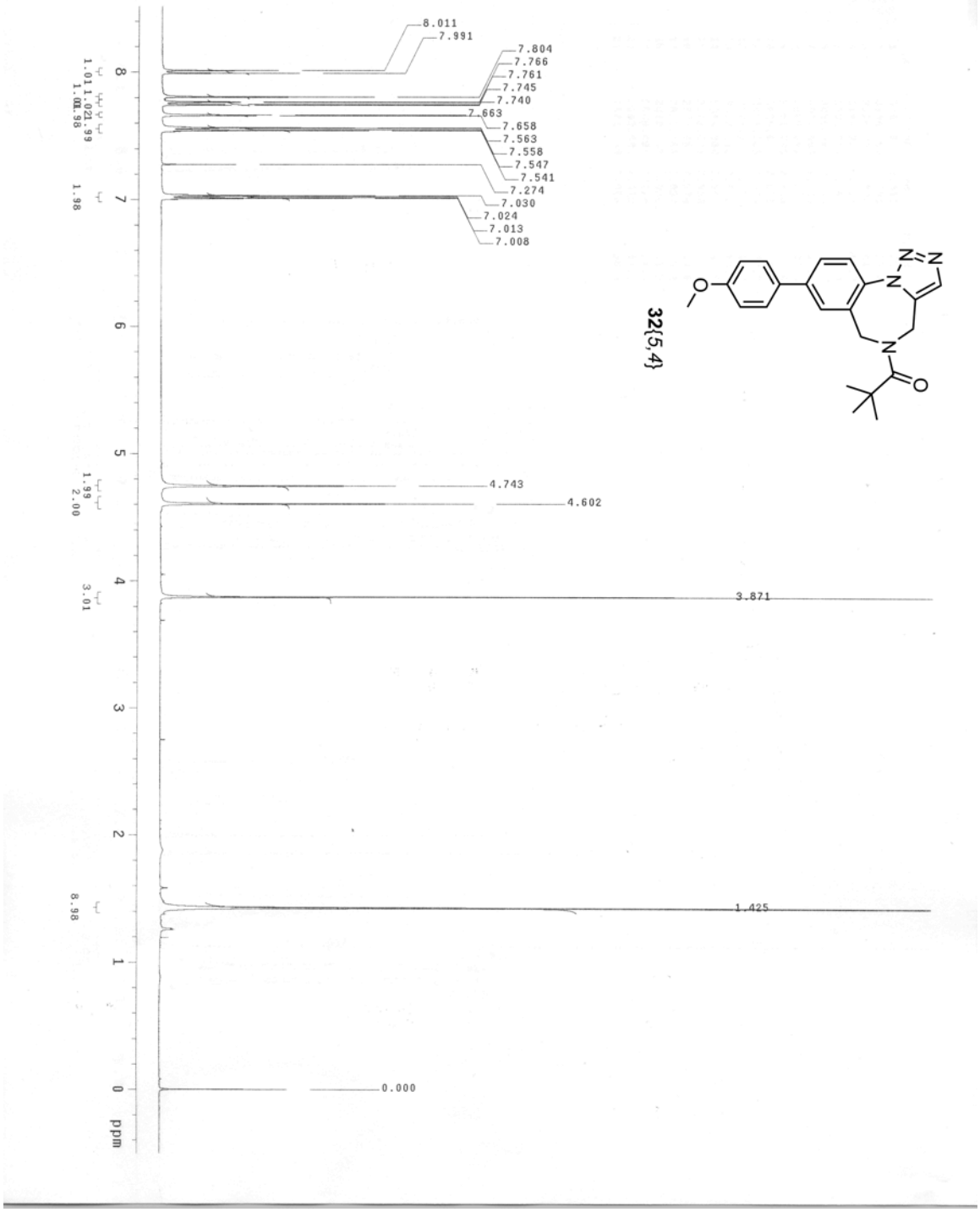

164.554
162.106
156.139
141.586
141.504
141.318
135.760
133.267
132.605
130.752
130.663
129.733
129.302
128.520
123.587
122.985
122.962
115.262
115.053
114.354
114.131
77.480
77.361
77.160
76.840
50.085
46.722
38.954
34.051
25.688
25.137
0.116
ppm
36{2,3}

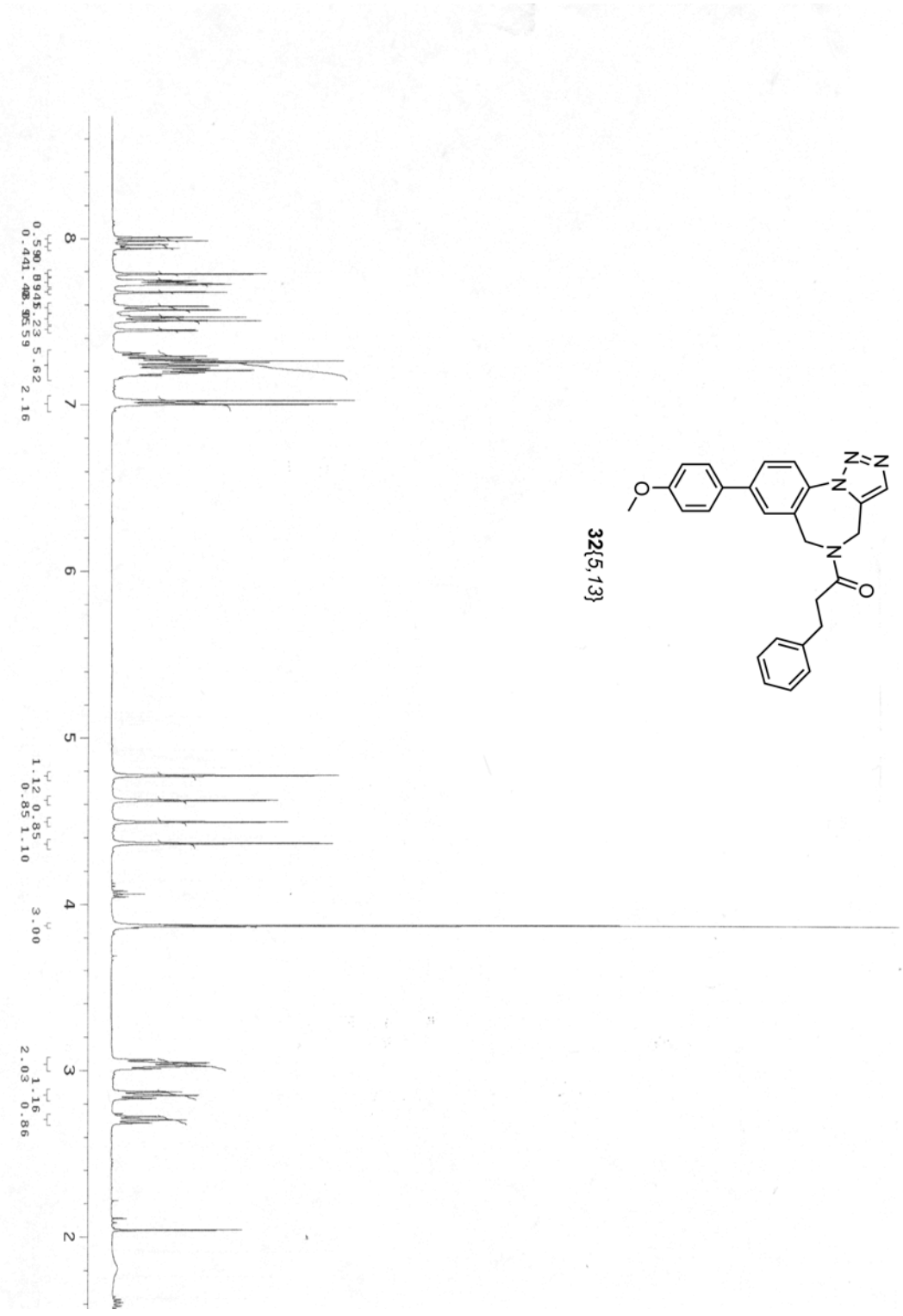

38(2,3)
F
N
N
N
S
H
N
9
8
7
6
5
4
3
2
1
ppm
1.02 0.47 1.18 7.05
1.52 1.01 1.03 3.08
0.98
2.06
2.00
2.04
2.08


40(2,2)
F
N
N
N
8
7
6
5
4
3
2
1
ppm
4.69
4.55
9.86
4.65
4.82
4.59
4.72
9.23
9.23
9.46
4.93
29.26

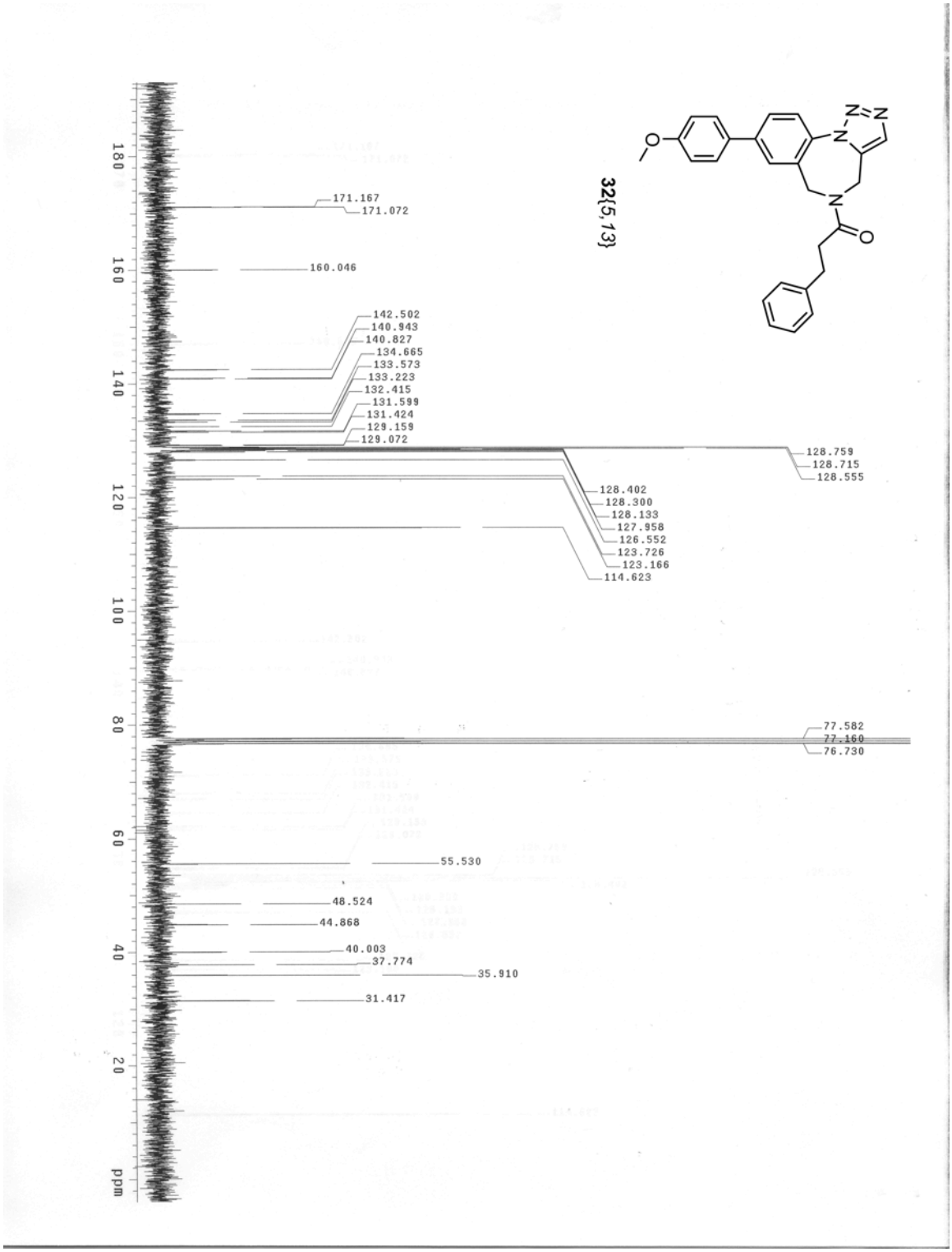

40{2,14}
F
O
N
N
N
8
7
6
5
4
3
2
1
ppm
1.04 1.05 3.06 1.99
2.07 2.13 0.99
3.97
3.072.00

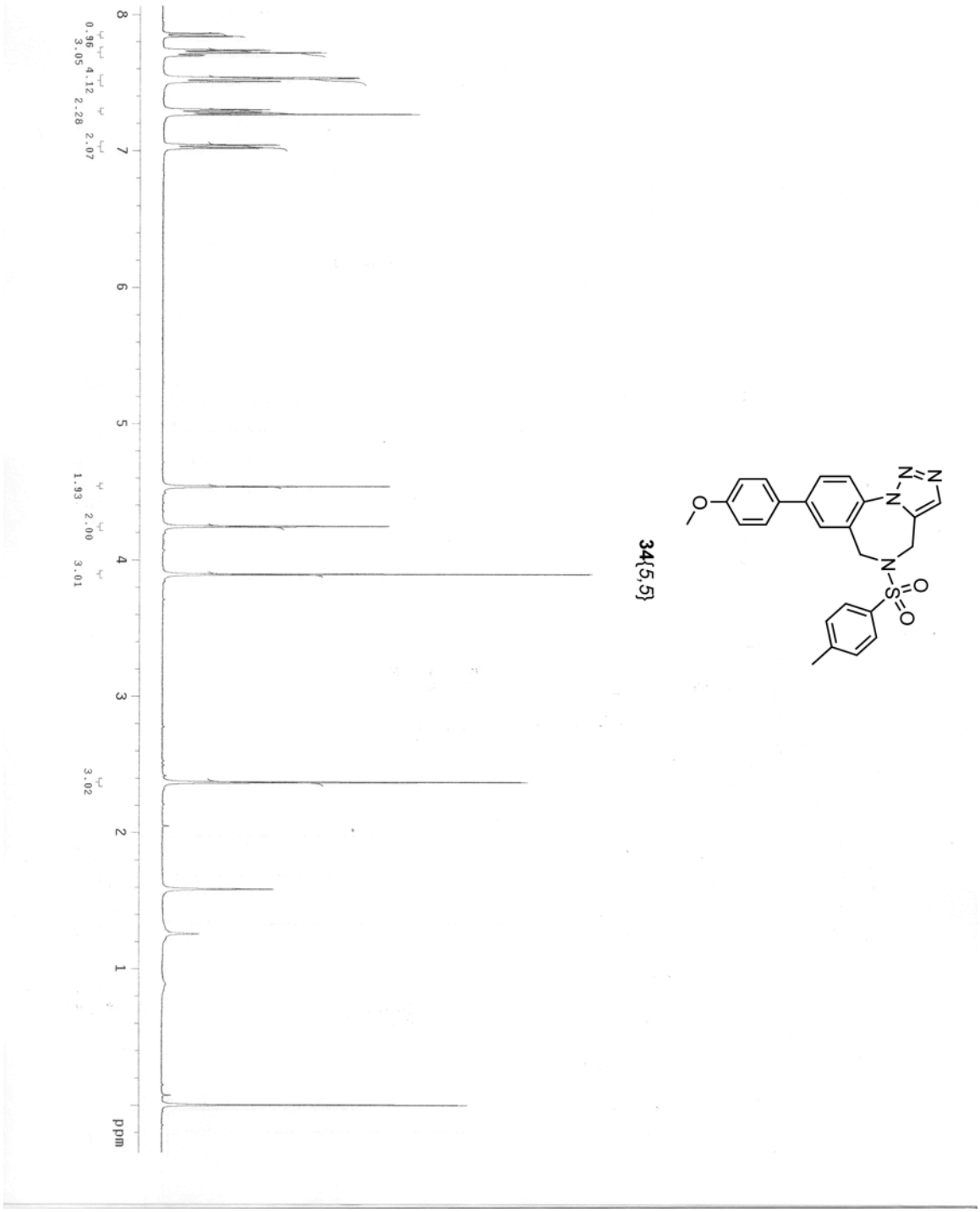

8.098
8.077
7.810
7.745
7.740
7.724
7.719
7.644
7.640
7.467
7.452
7.447
7.433
7.427
7.413
7.389
7.369
7.314
7.308
7.304
7.289
7.284
7.279
7.259
7.230
7.210
7.189
7.121
7.119
7.114
7.100
7.098
7.094
7.080
7.077
7.073
6.898
6.893
6.887
6.829
6.825
6.808
5.291
4.537
4.430
1.257
0.000
ppm
42{2,1}
F
Cl

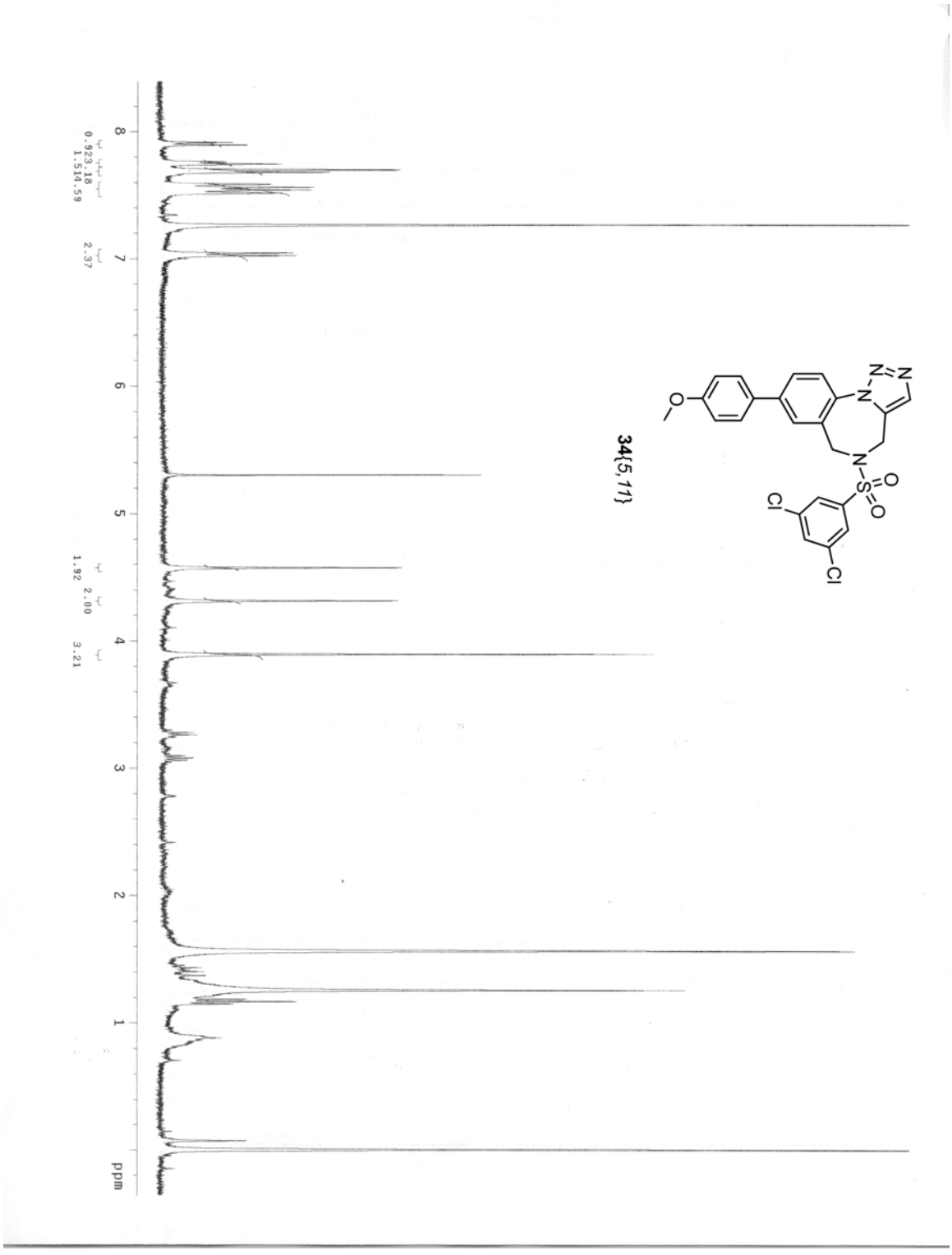

8.011
7.991
7.804
7.766
7.761
7.745
7.740
7.663
7.658
7.563
7.558
7.547
7.541
7.274
7.030
7.024
7.013
7.008
4.743
4.602
3.871
1.425
0.000
ppm
32(5,4)

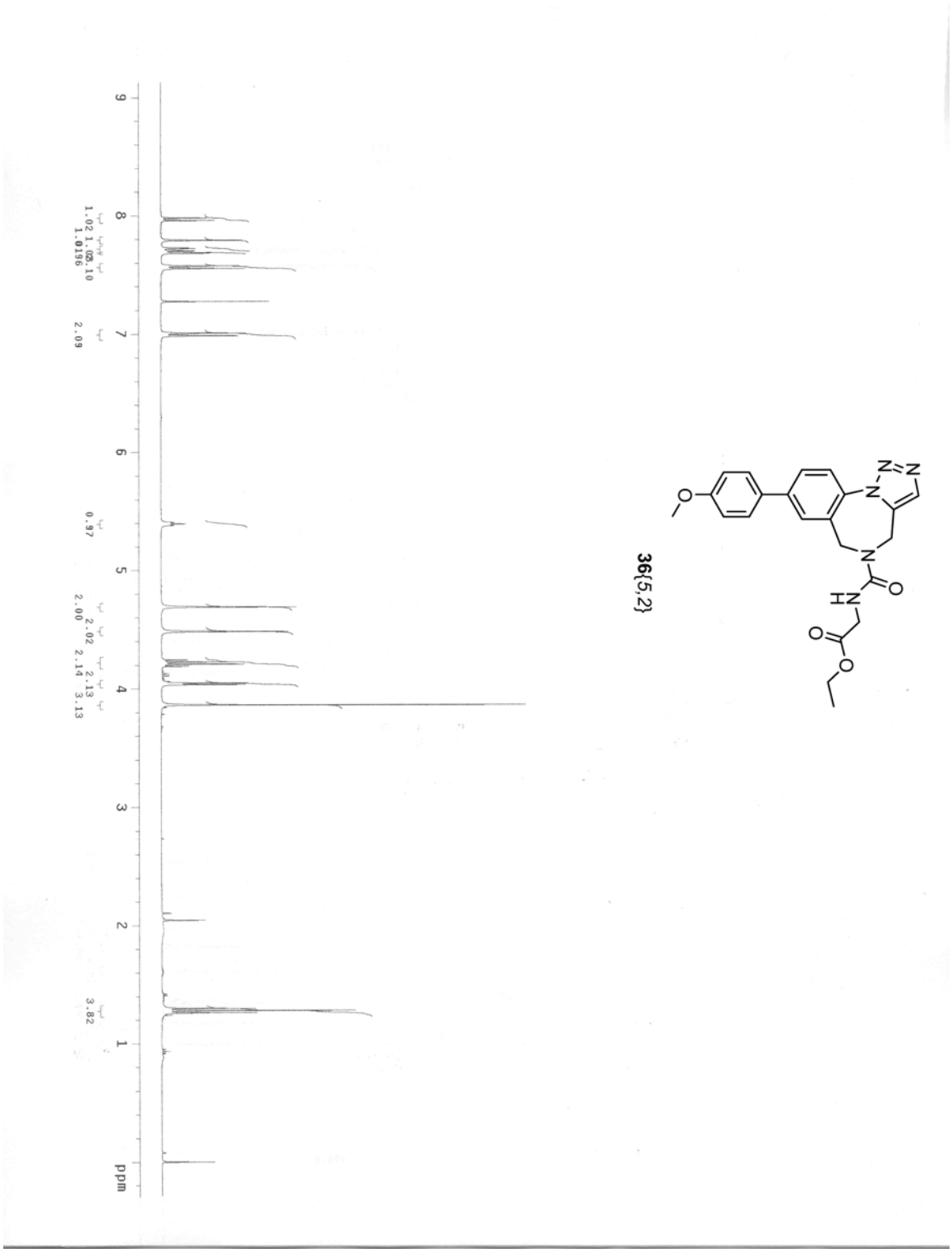

8
7
6
5
4
3
2
0.59 0.89 45.23 5.62 2.16
0.44 1.48 48.95 5.59
1.12 0.85
0.85 1.10
3.00
1.16
2.03 0.86

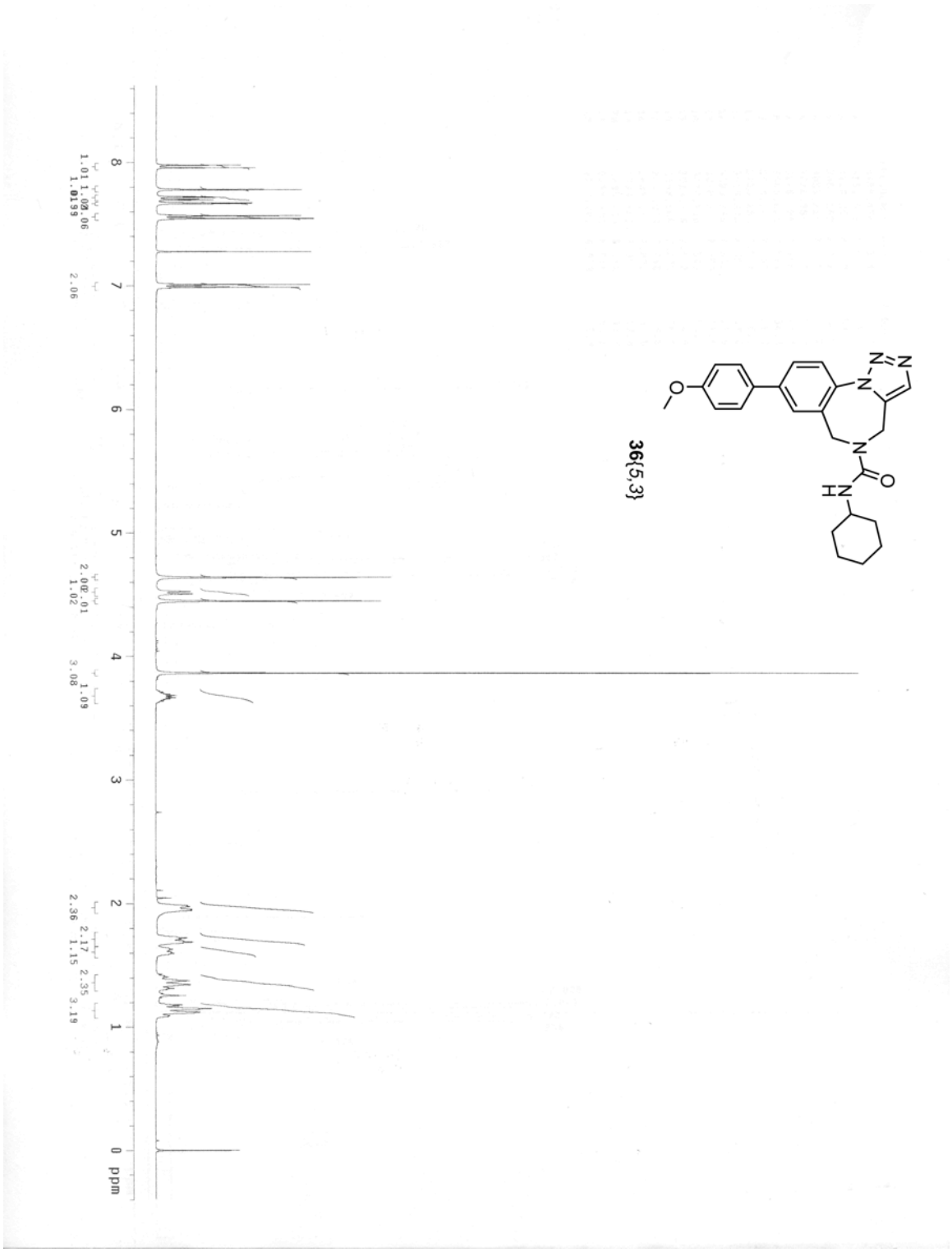
32{*5,13*}

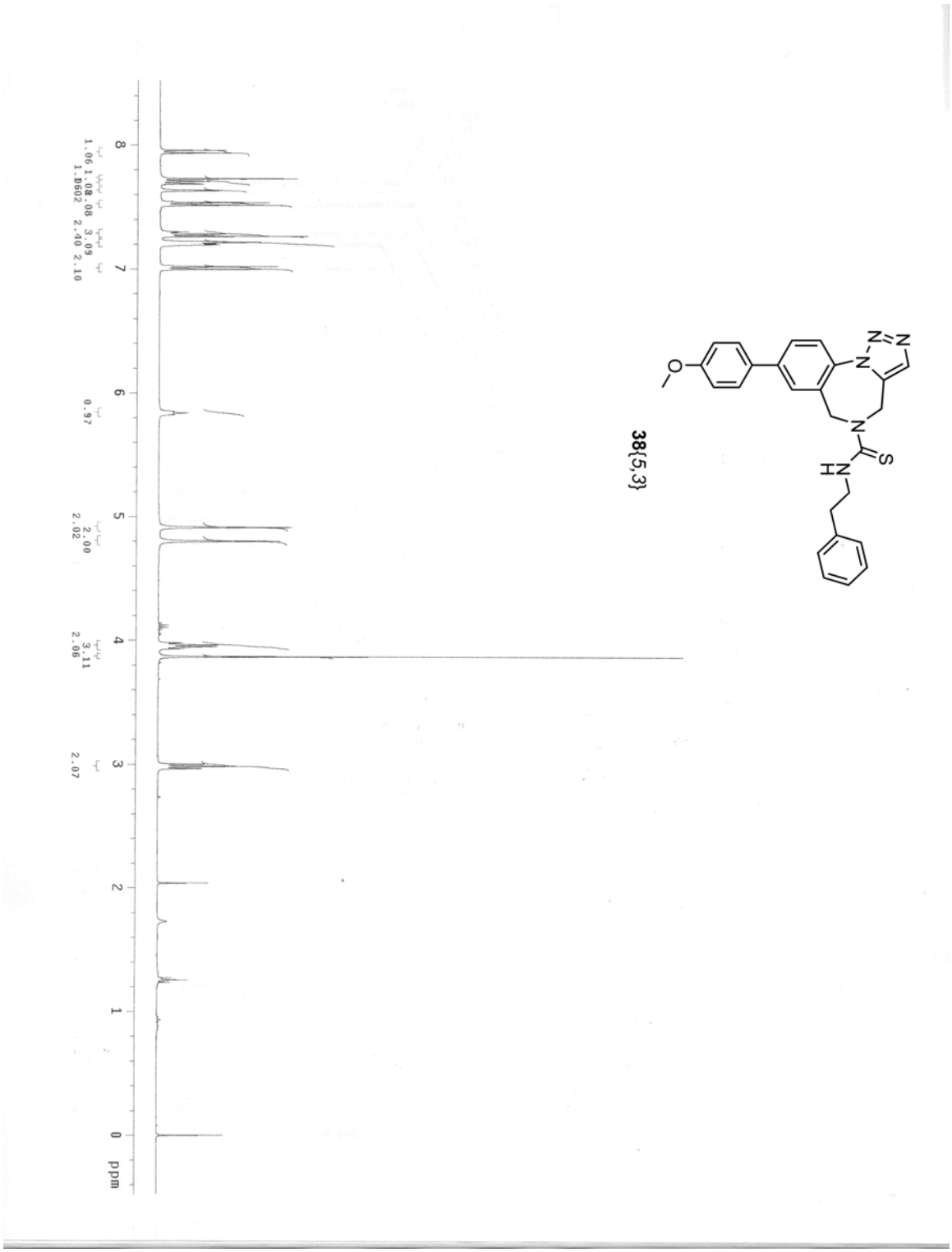

32{5,13}
171.167
171.072
160.046
142.502
140.943
140.827
134.665
133.573
133.223
132.415
131.599
131.424
129.159
129.072
128.759
128.715
128.555
128.402
128.300
128.133
127.958
126.552
123.726
123.166
114.623
77.582
77.160
76.730
55.530
48.524
44.868
40.003
37.774
35.910
31.417
180
160
140
120
100
80
60
40
20
ppm

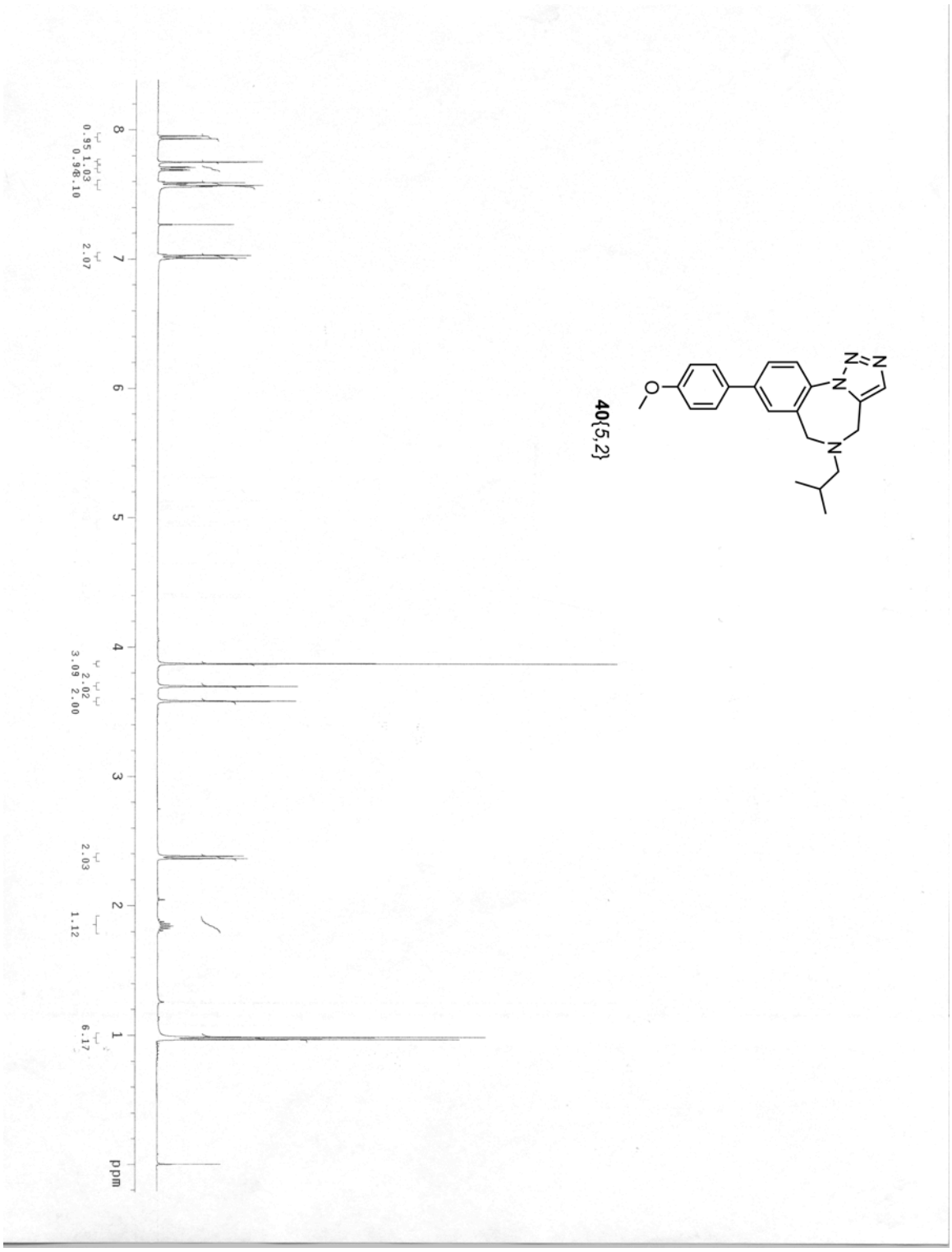

34{5,5}
ppm

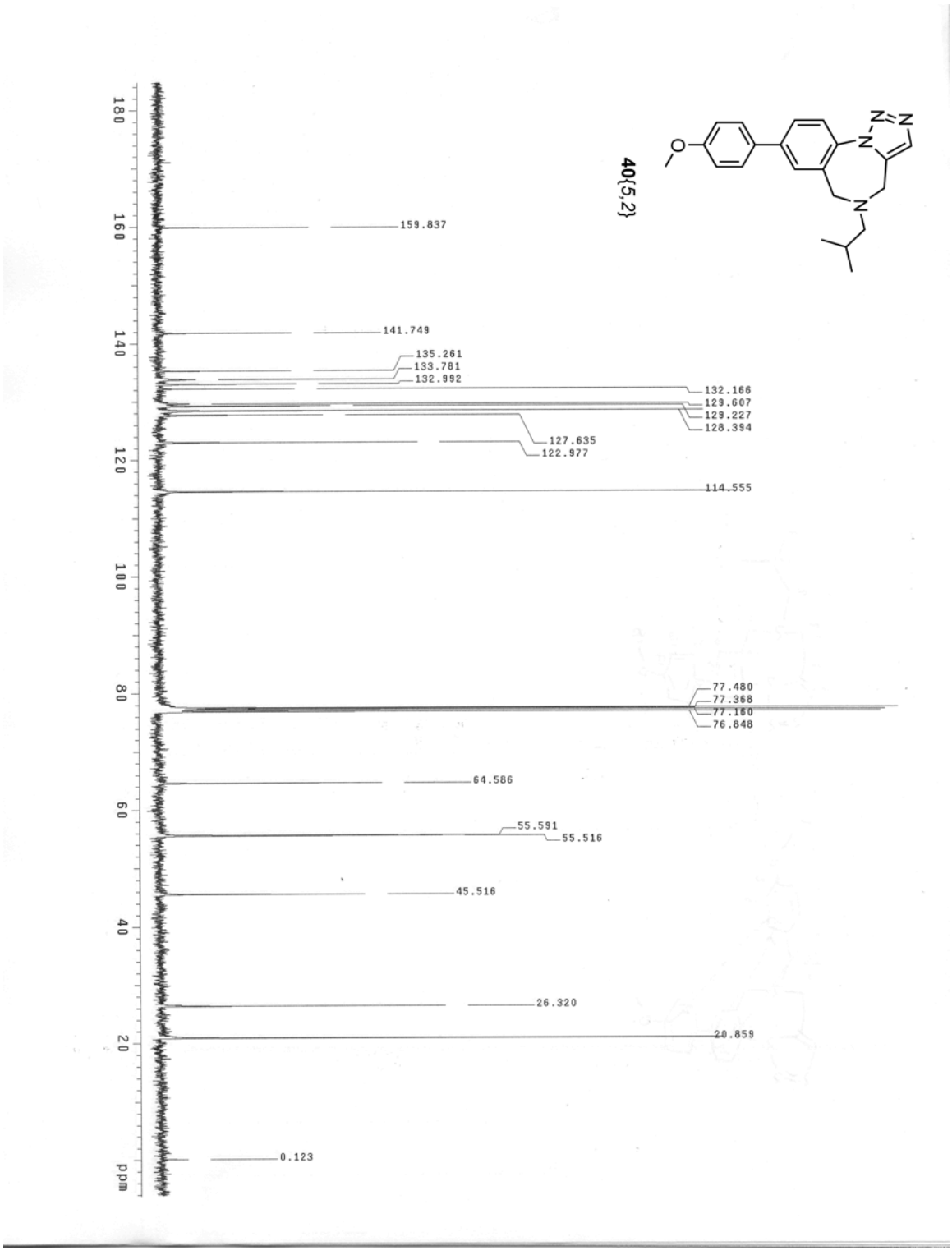

34{5,11}
ppm

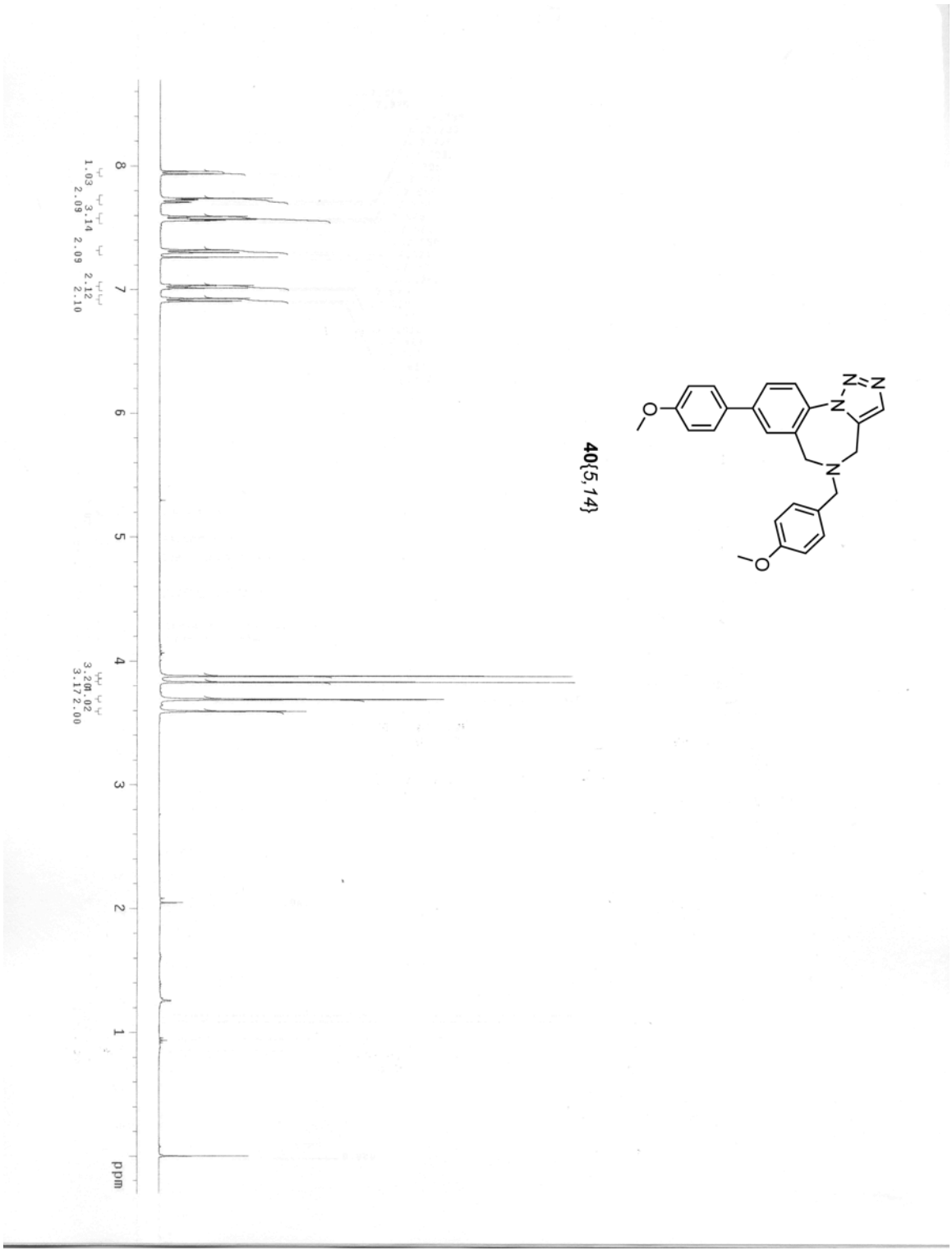

36{5,2}
ppm
9
8
7
6
5
4
3
2
1
1.02
1.02
2.10
1.01
96
2.09
0.97
2.00
2.02
2.14
2.13
3.13
3.82

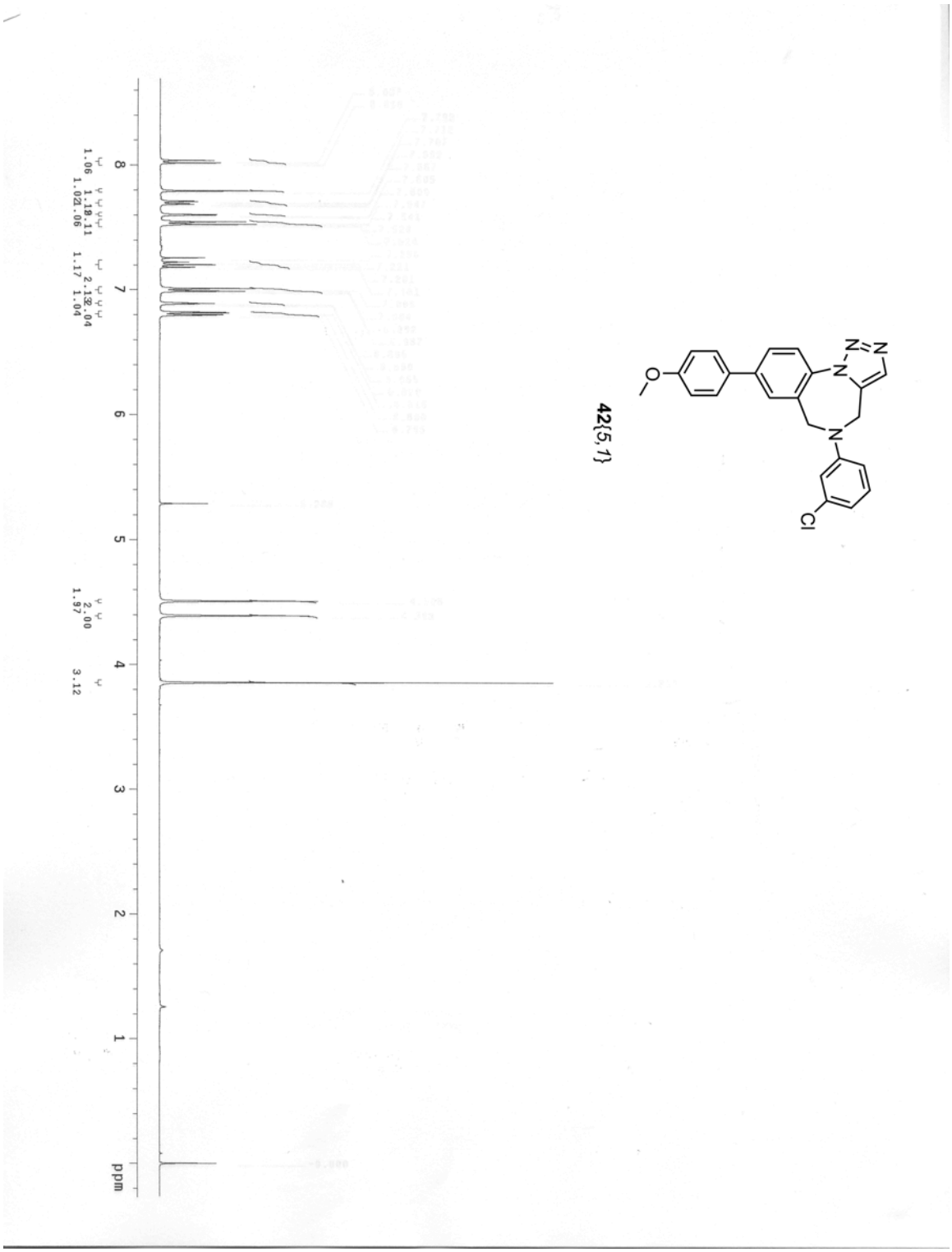

36{5,3}
8
7
6
5
4
3
2
1
0
ppm

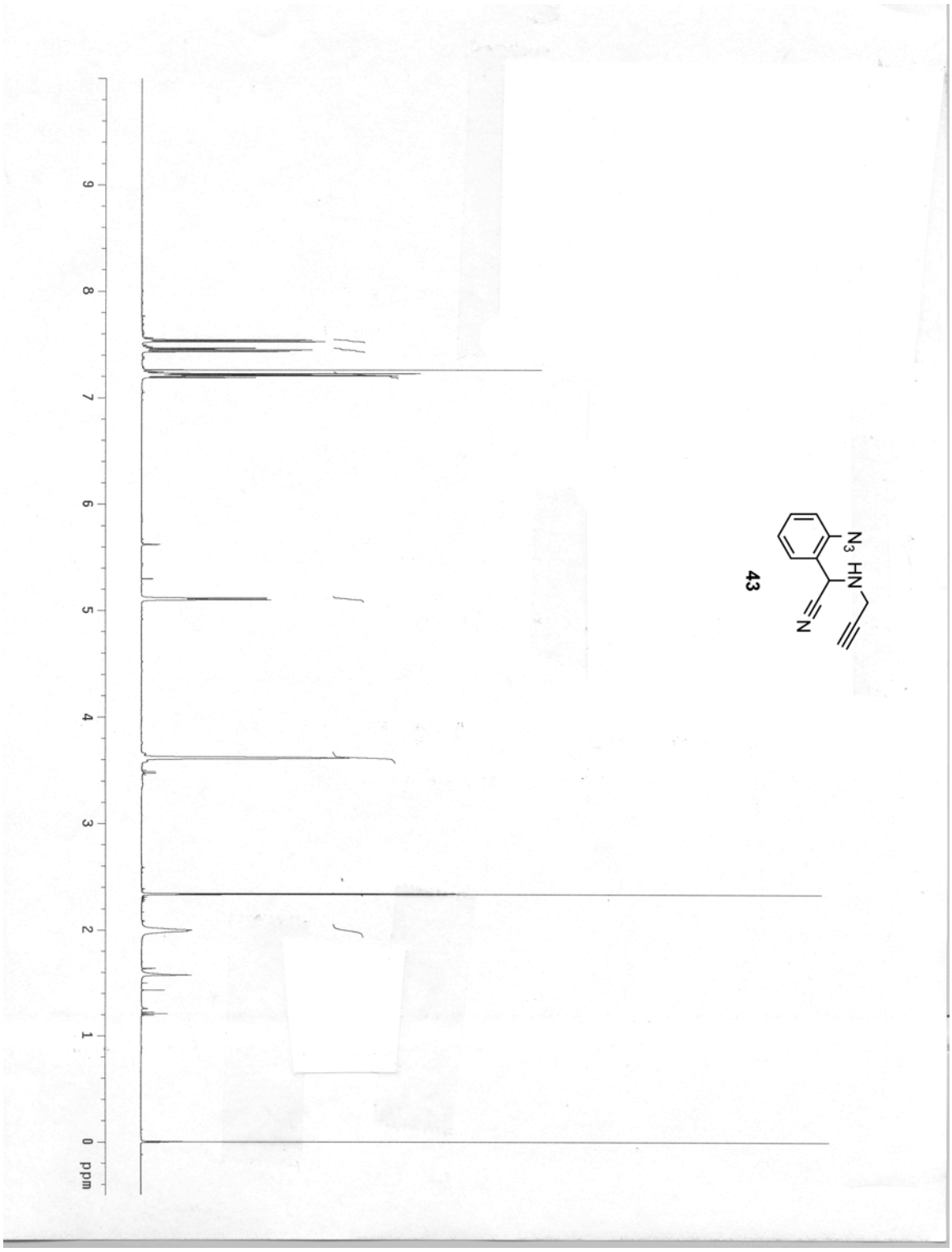

38(5,3)
8
7
6
5
4
3
2
1
0
ppm
1.06 1.08 3.09
1.8602 2.40 2.10
0.97
2.00
2.02
3.11
2.06
2.07

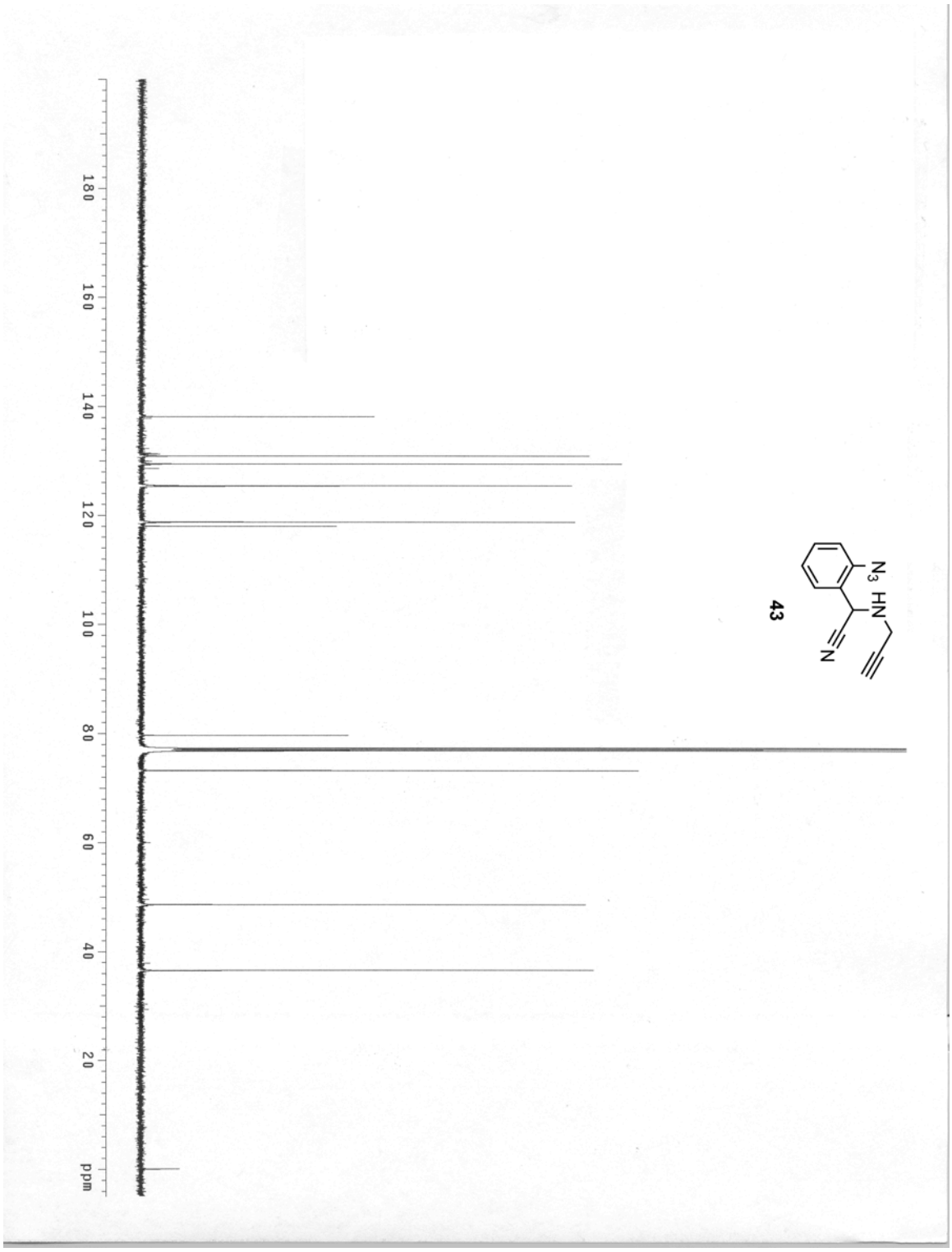

40{5,2}
8
7
6
5
4
3
2
1
ppm
0.95 1.03
0.98 1.10
2.07
2.02
3.09 2.00
2.03
1.12
6.17

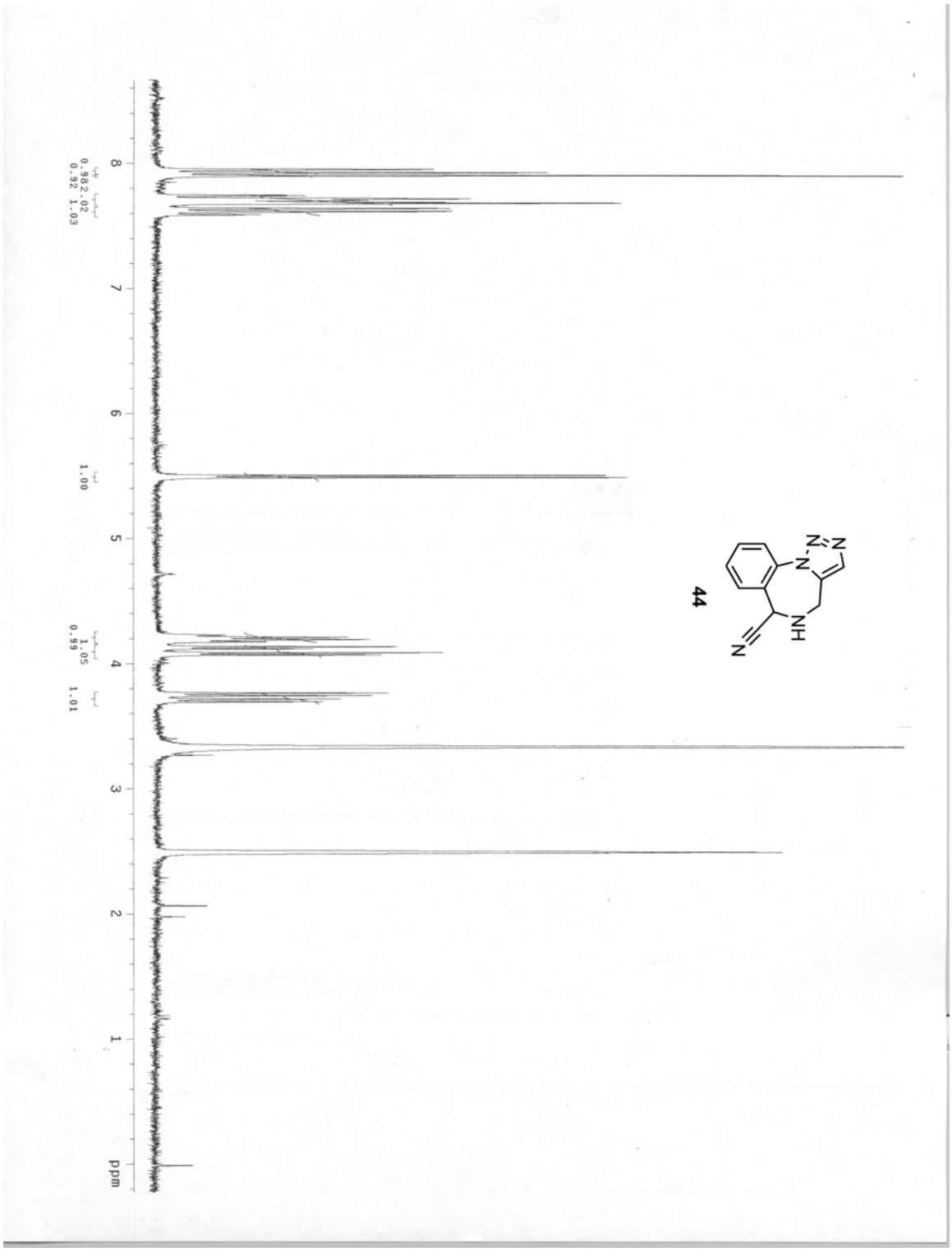

40{5,2}
159.837
141.749
135.261
133.781
132.992
132.166
129.607
129.227
128.394
127.635
122.977
114.555
77.480
77.368
77.160
76.848
64.586
55.591
55.516
45.516
26.320
20.859
0.123
ppm

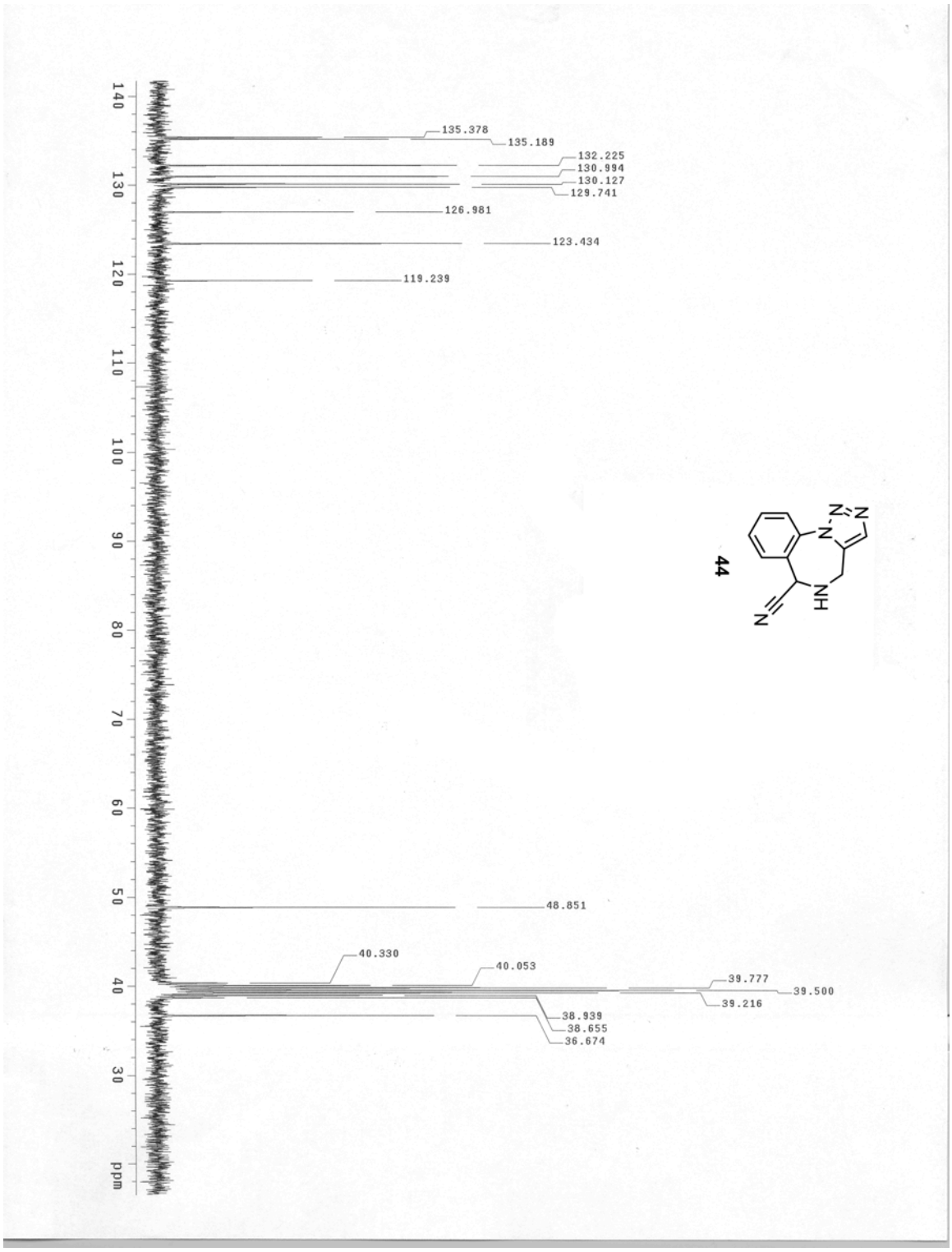

40(5,14)
8
7
6
5
4
3
2
1
ppm
1.03
3.14
2.09
2.09
2.12
2.10
3.20
3.17
1.02
2.00

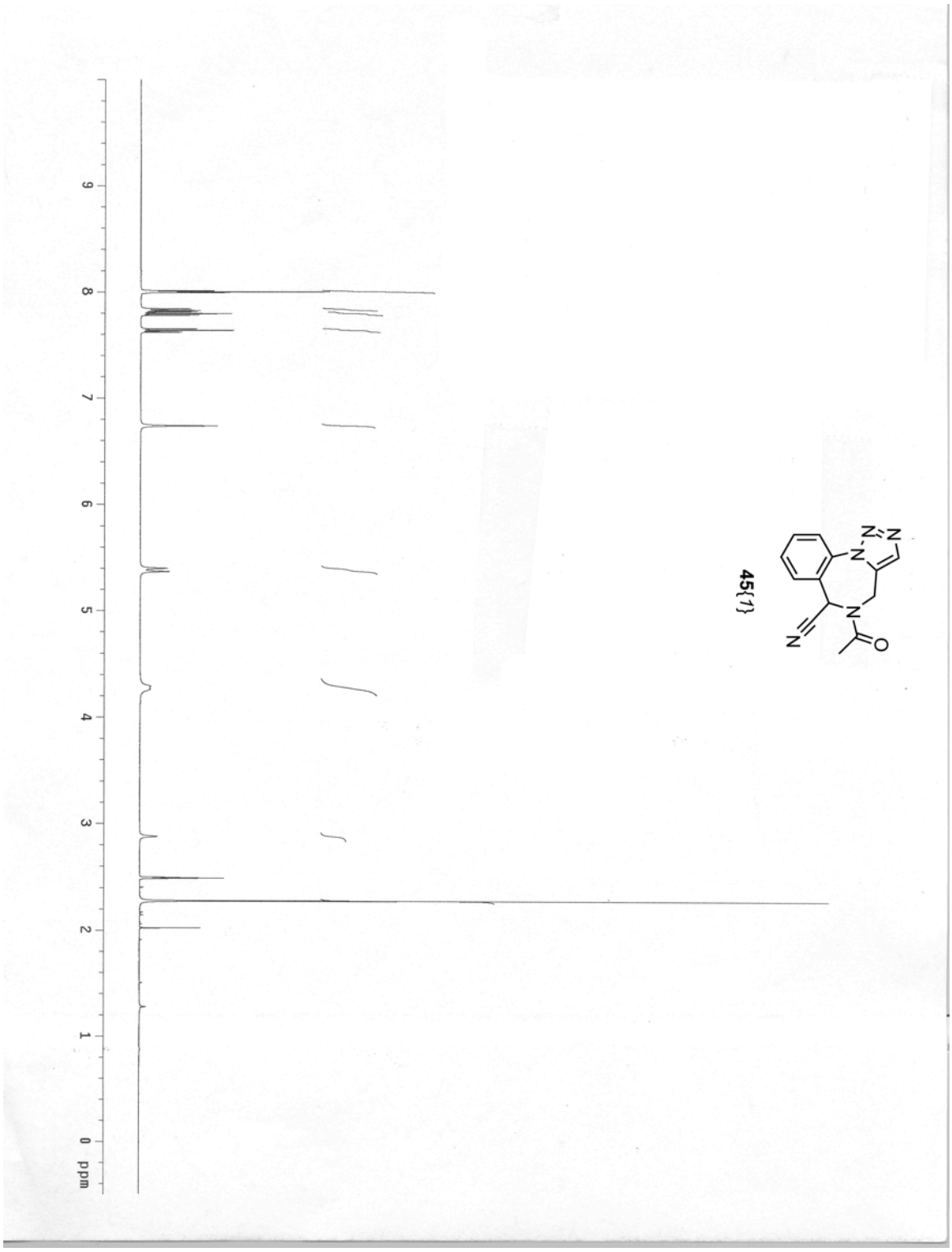

42{5,1}
O
N
N
N
N
Cl
ppm

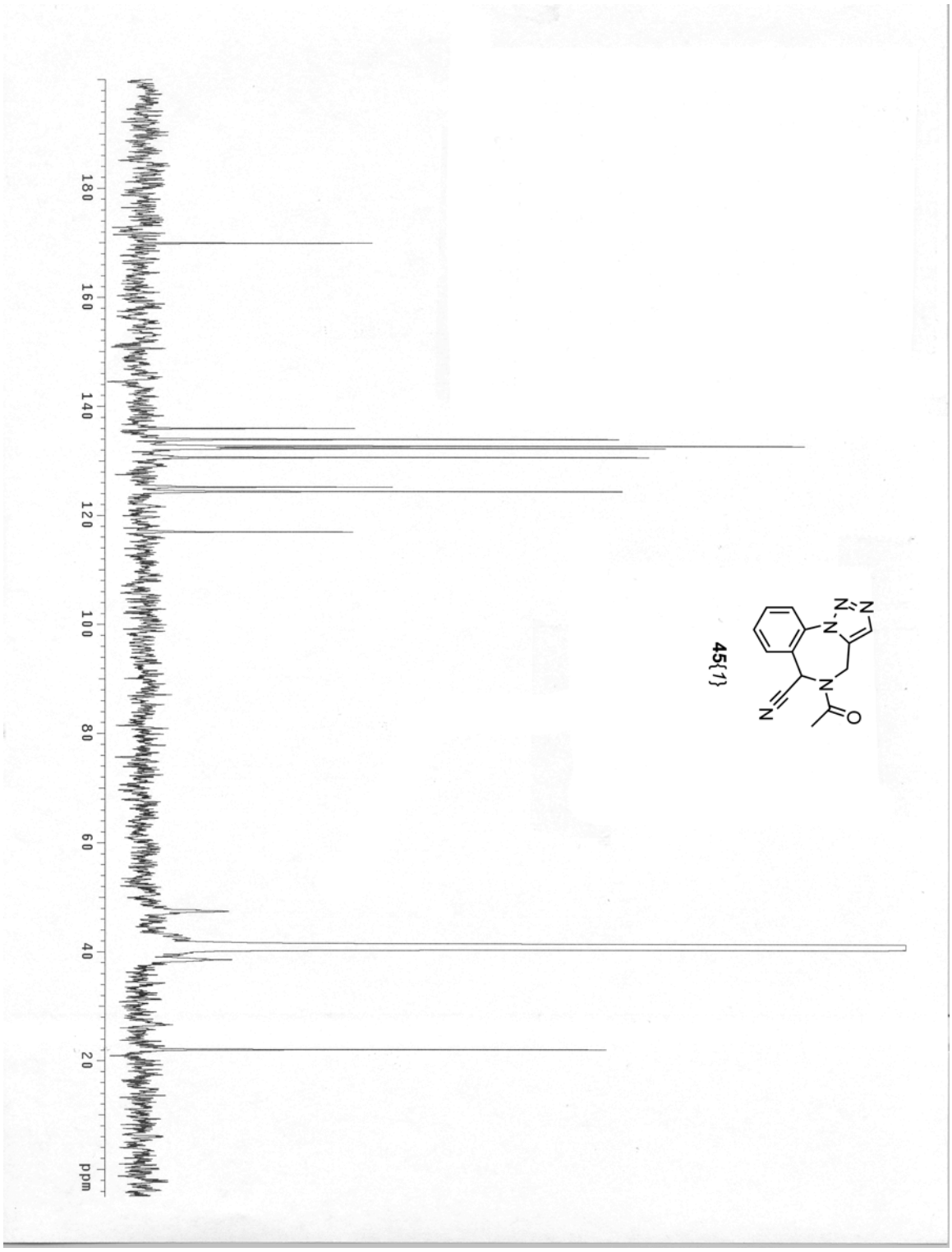

N3
HN
N
43
9
8
7
6
5
4
3
2
1
0
ppm

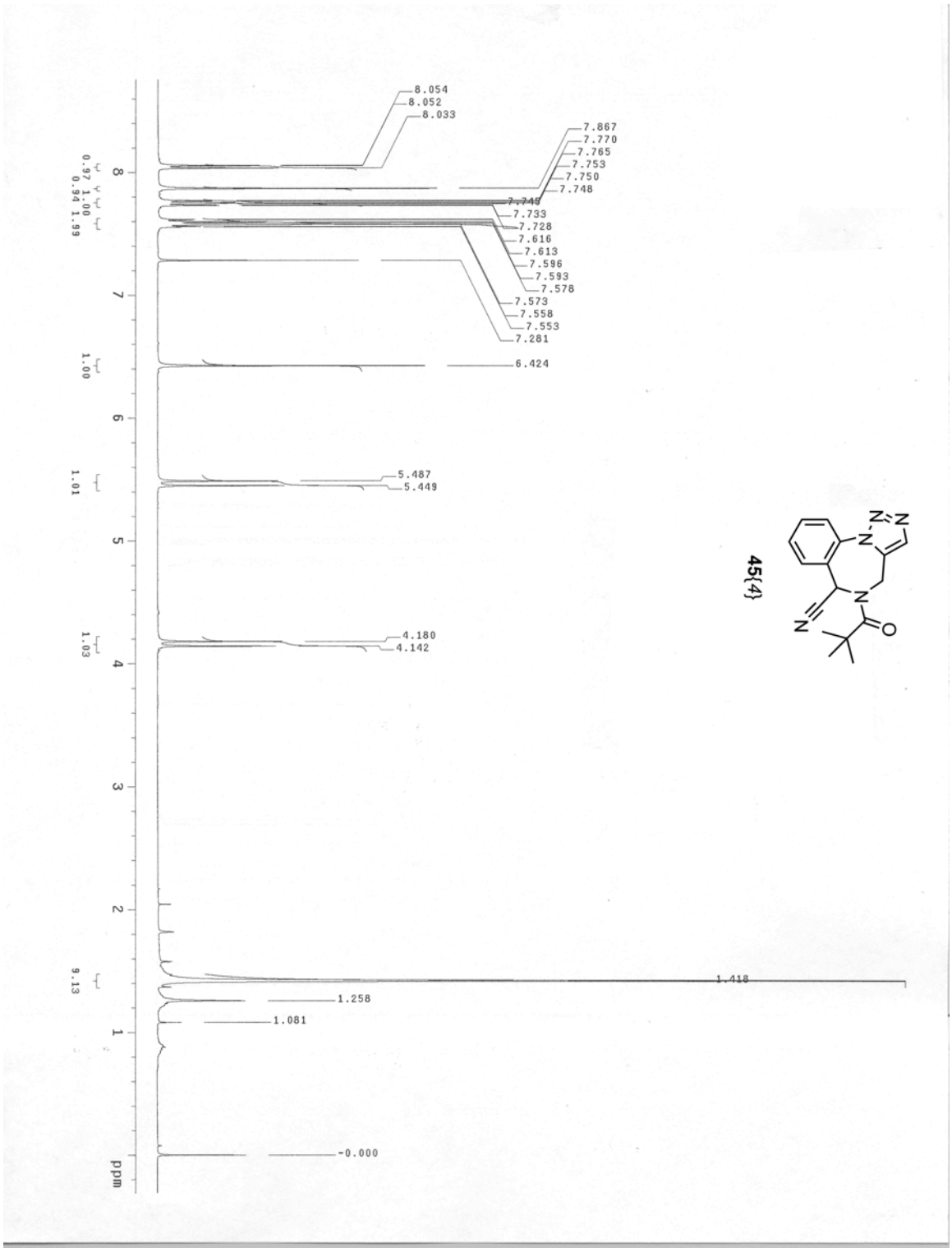

N3
HN
N
43
180
160
140
120
100
80
60
40
20
ppm

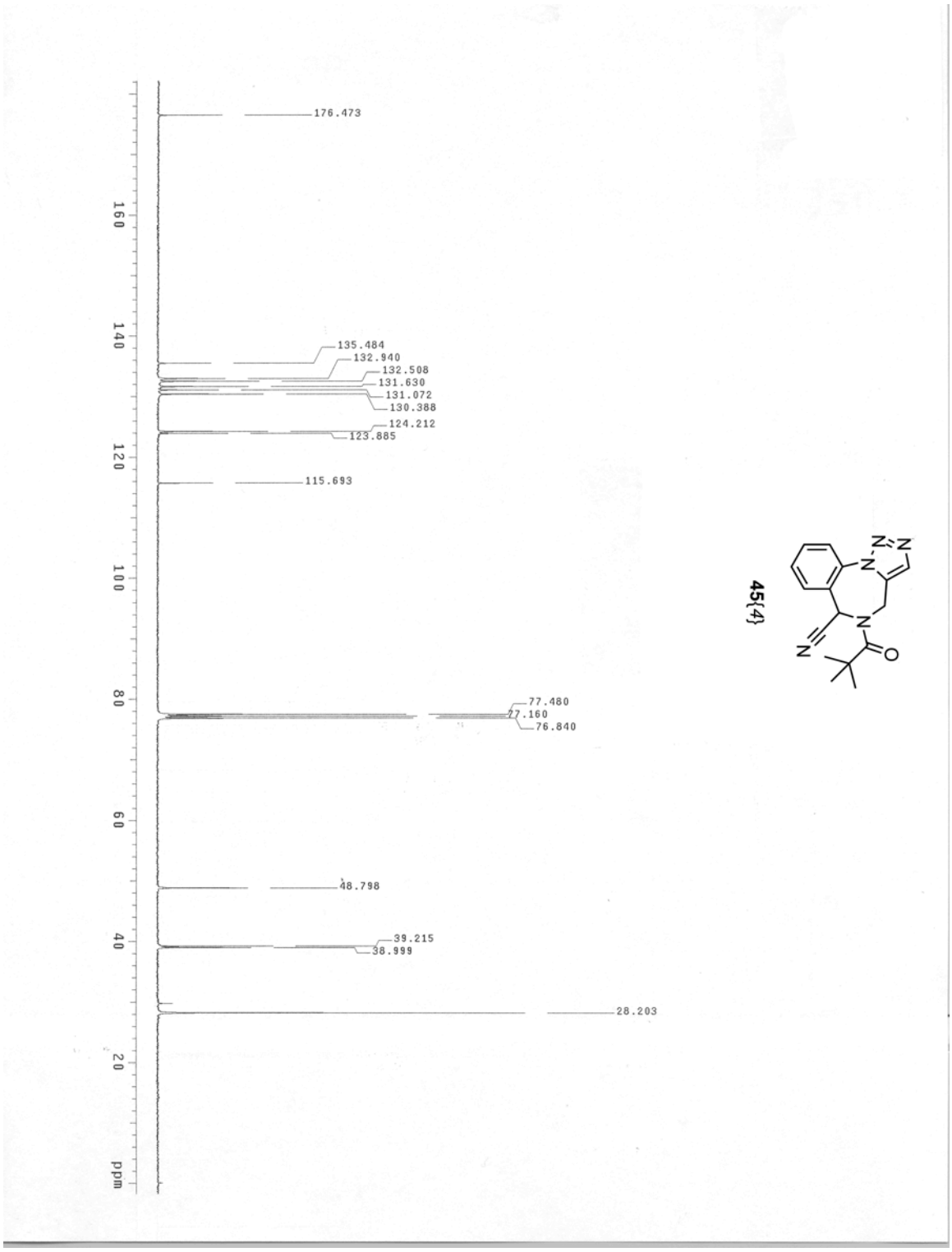

44
NH
N
N
N
ppm
1
2
3
4
5
6
7
8
1.00
1.05
0.99
1.01
0.98
2.02
0.92
1.03

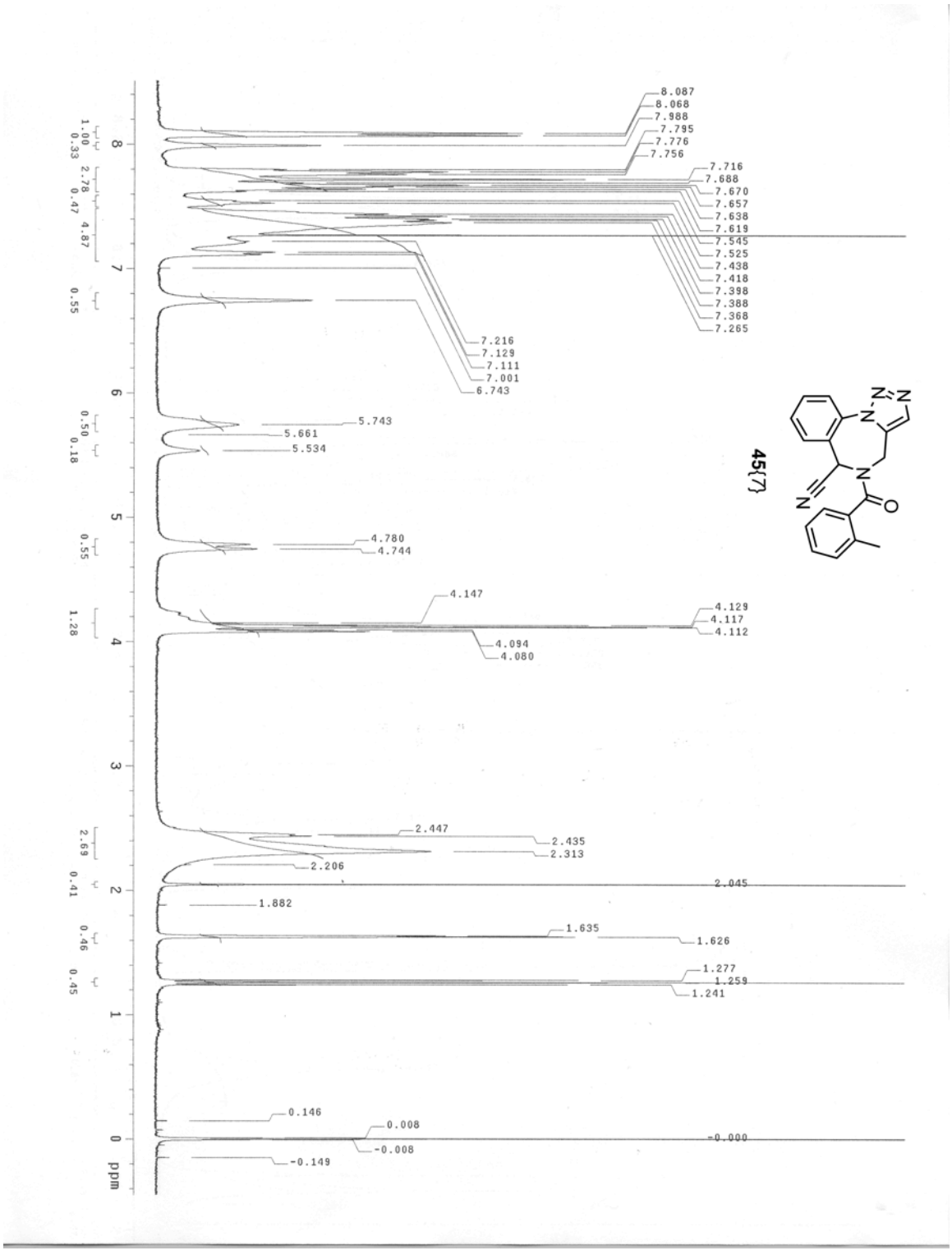

140
130
120
110
100
90
80
70
60
50
40
30
ppm
135.378
135.189
132.225
130.994
130.127
129.741
126.981
123.434
119.239
48.851
40.330
40.053
39.777
39.500
39.216
38.939
38.655
36.674
44
N
N
N
NH
N

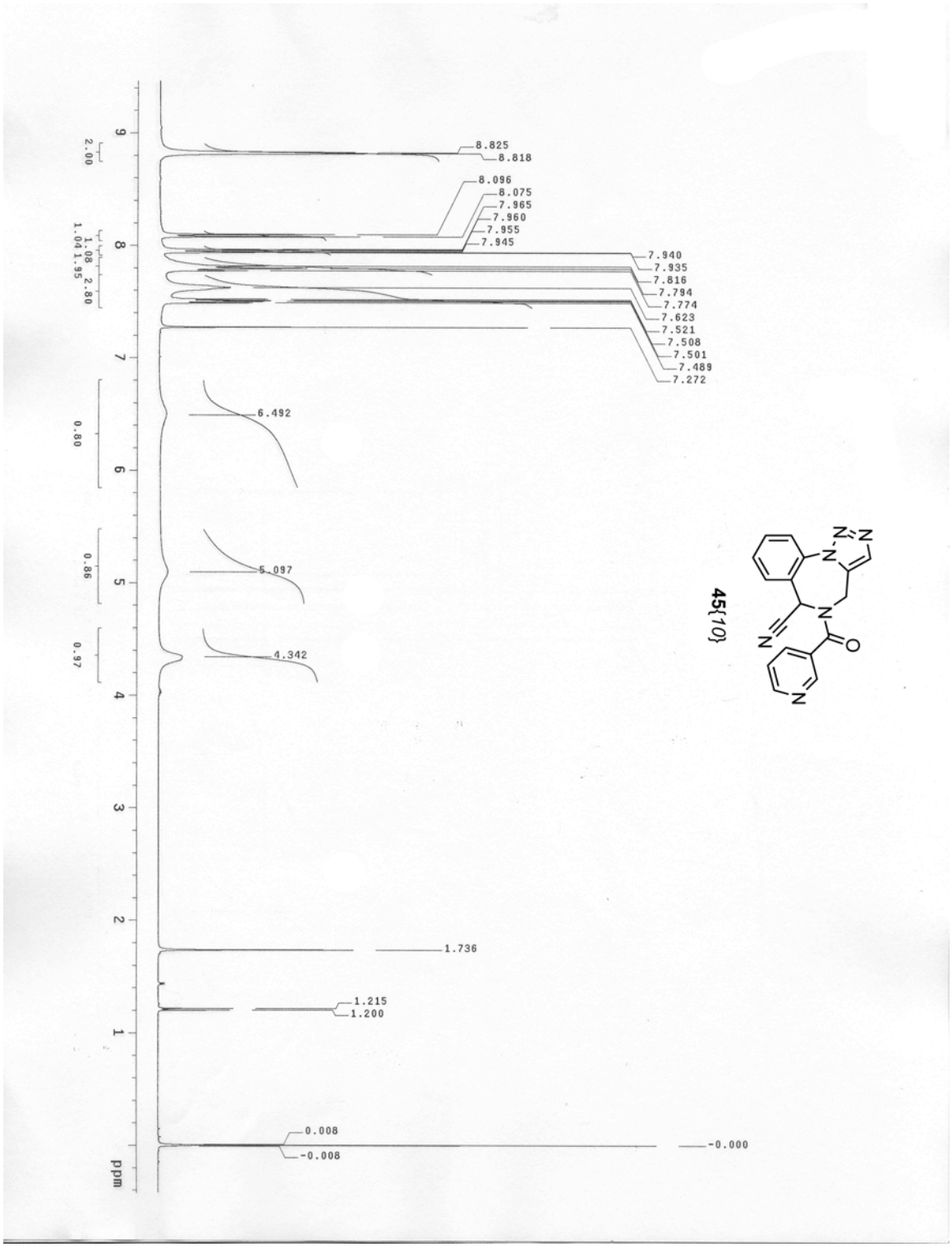

45{1}
9
8
7
6
5
4
3
2
1
0 ppm

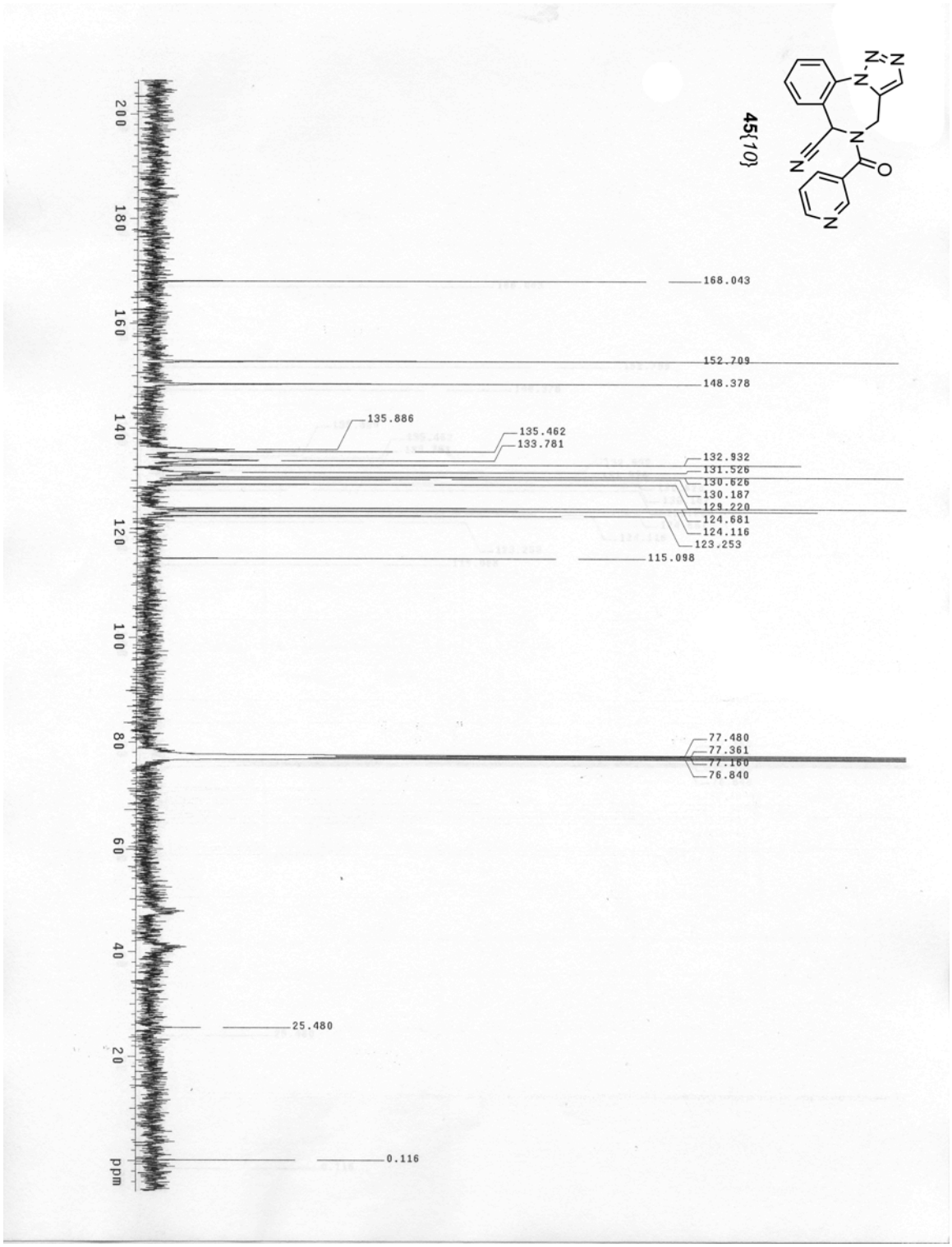

45{1}
180
160
140
120
100
80
60
40
20
ppm

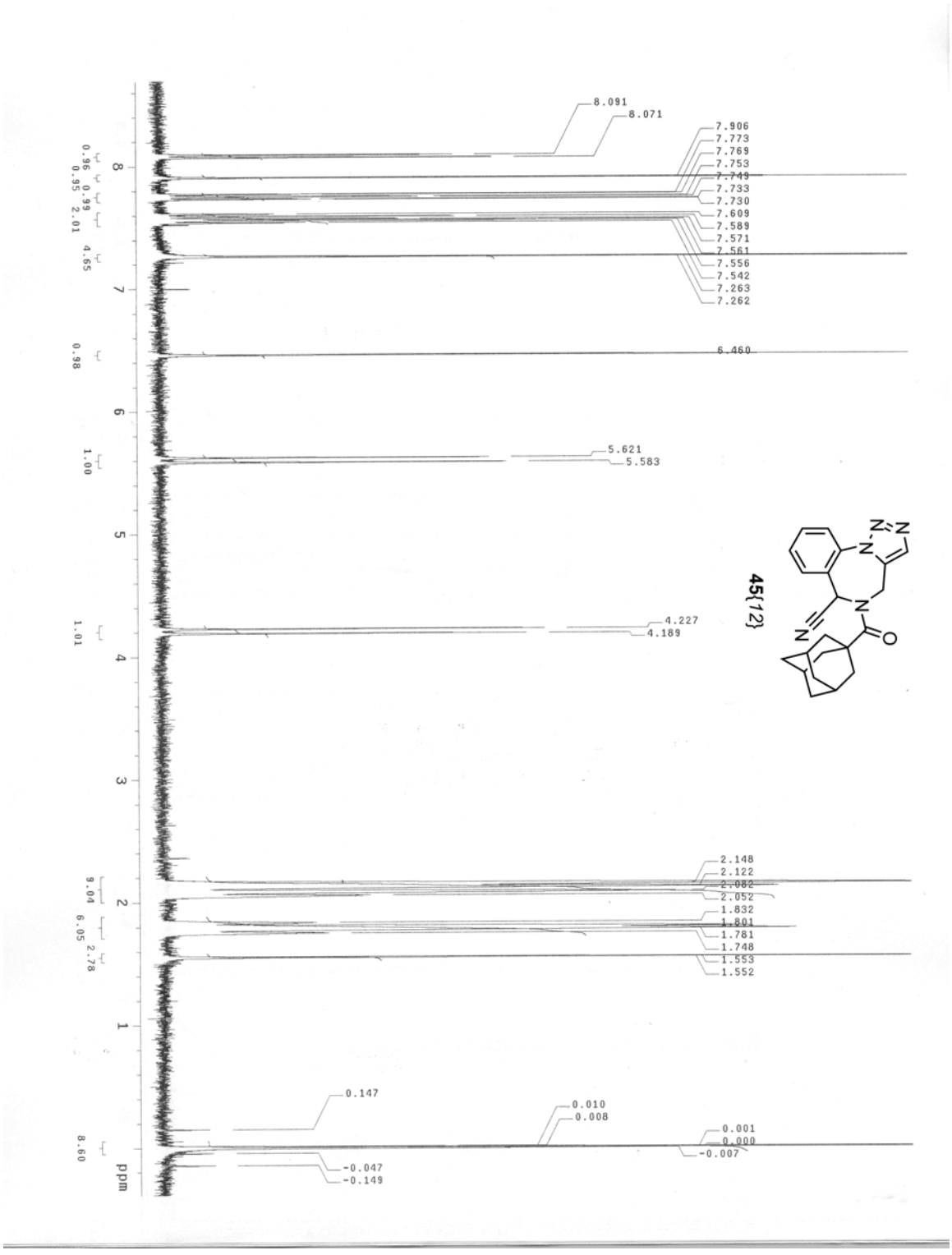

8.054
8.052
8.033
7.867
7.770
7.765
7.753
7.750
7.748
7.748
7.733
7.728
7.616
7.613
7.596
7.593
7.578
7.573
7.558
7.553
7.281
6.424
5.487
5.449
4.180
4.142
1.418
1.258
1.081
-0.000
ppm
45{4}

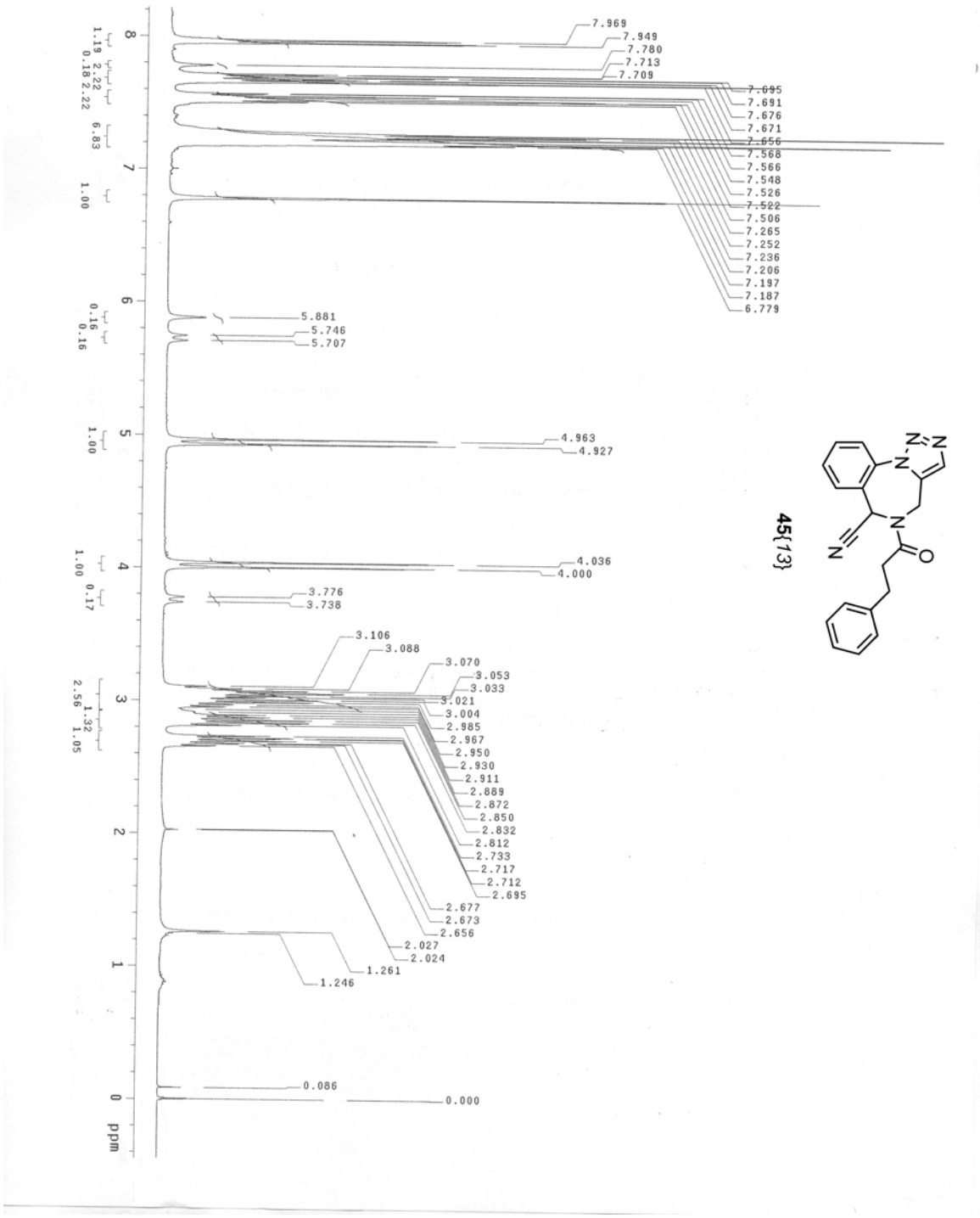

176.473
135.484
132.940
132.508
131.630
131.072
130.388
124.212
123.885
115.693
77.480
77.160
76.840
48.798
39.215
38.999
28.203
160
140
120
100
80
60
40
20
ppm
45{4}

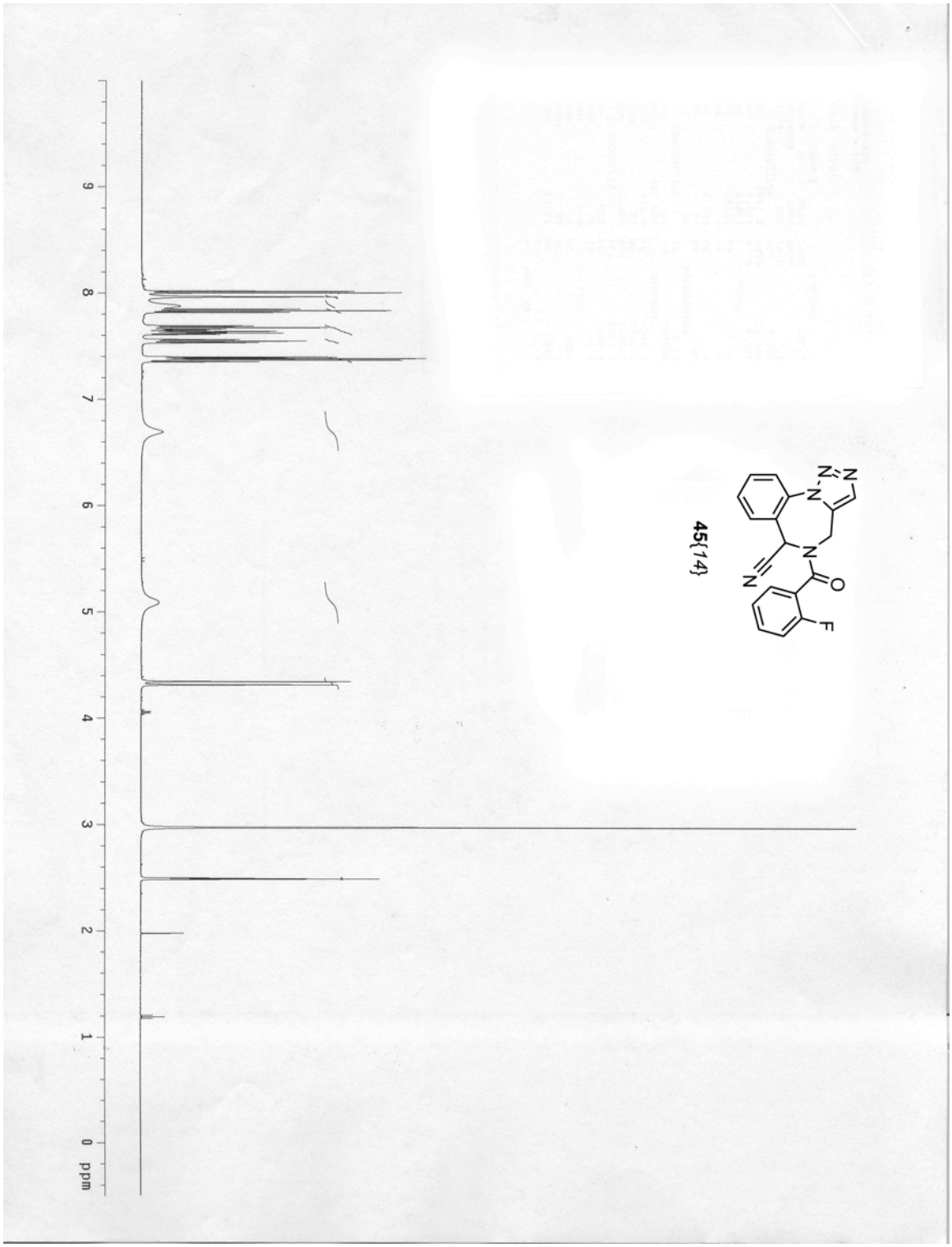

8.087
8.068
7.988
7.795
7.776
7.756
7.716
7.688
7.670
7.657
7.638
7.619
7.545
7.525
7.438
7.418
7.398
7.388
7.368
7.265
7.216
7.129
7.111
7.001
6.743
5.743
5.661
5.534
4.780
4.744
4.147
4.129
4.117
4.112
4.094
4.080
2.447
2.435
2.313
2.206
2.045
1.882
1.635
1.626
1.277
1.259
1.241
0.146
0.008
-0.000
-0.008
-0.149
ppm
45{7}

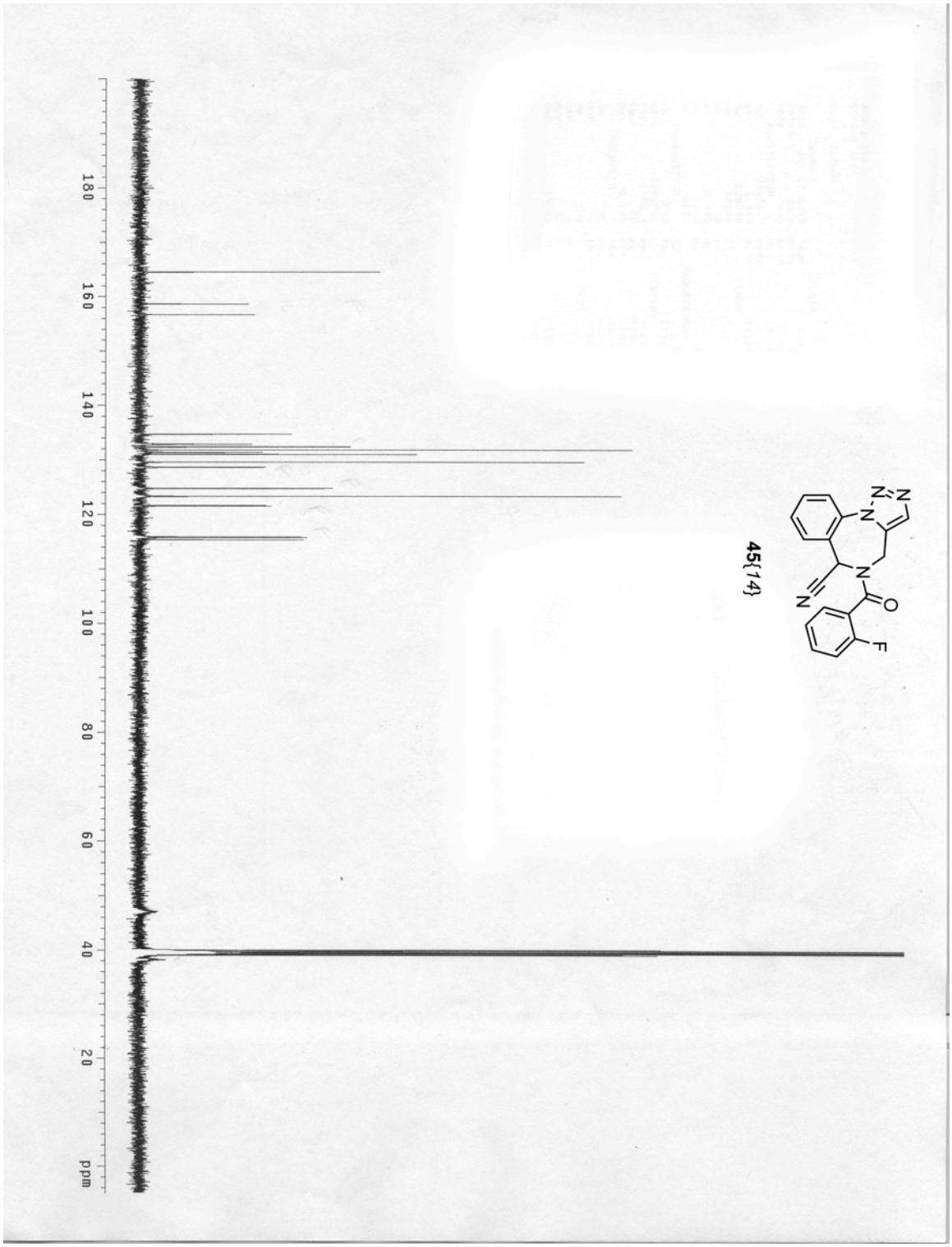

8.825
8.818
8.096
8.075
7.965
7.960
7.955
7.945
7.940
7.935
7.816
7.794
7.774
7.623
7.521
7.508
7.501
7.489
7.272
6.492
5.097
4.342
1.736
1.215
1.200
0.008
-0.008
-0.000
ppm
2.00
1.04
1.95
1.08
2.80
0.80
0.86
0.97
45{10}

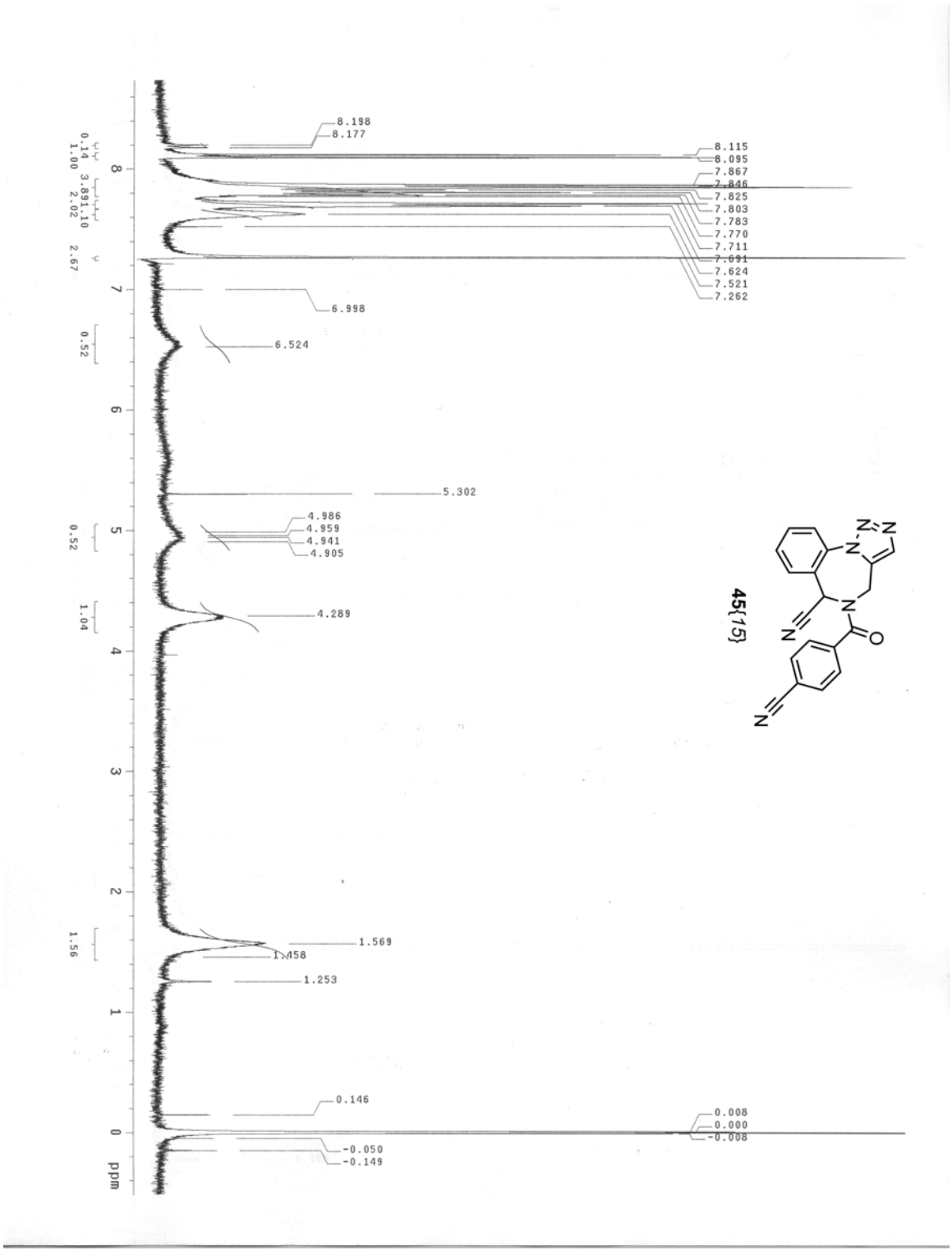

45{10}
168.043
152.709
148.378
135.886
135.462
133.781
132.932
131.526
130.626
130.187
129.220
124.681
124.116
123.253
115.098
77.480
77.361
77.160
76.840
25.480
0.116
ppm

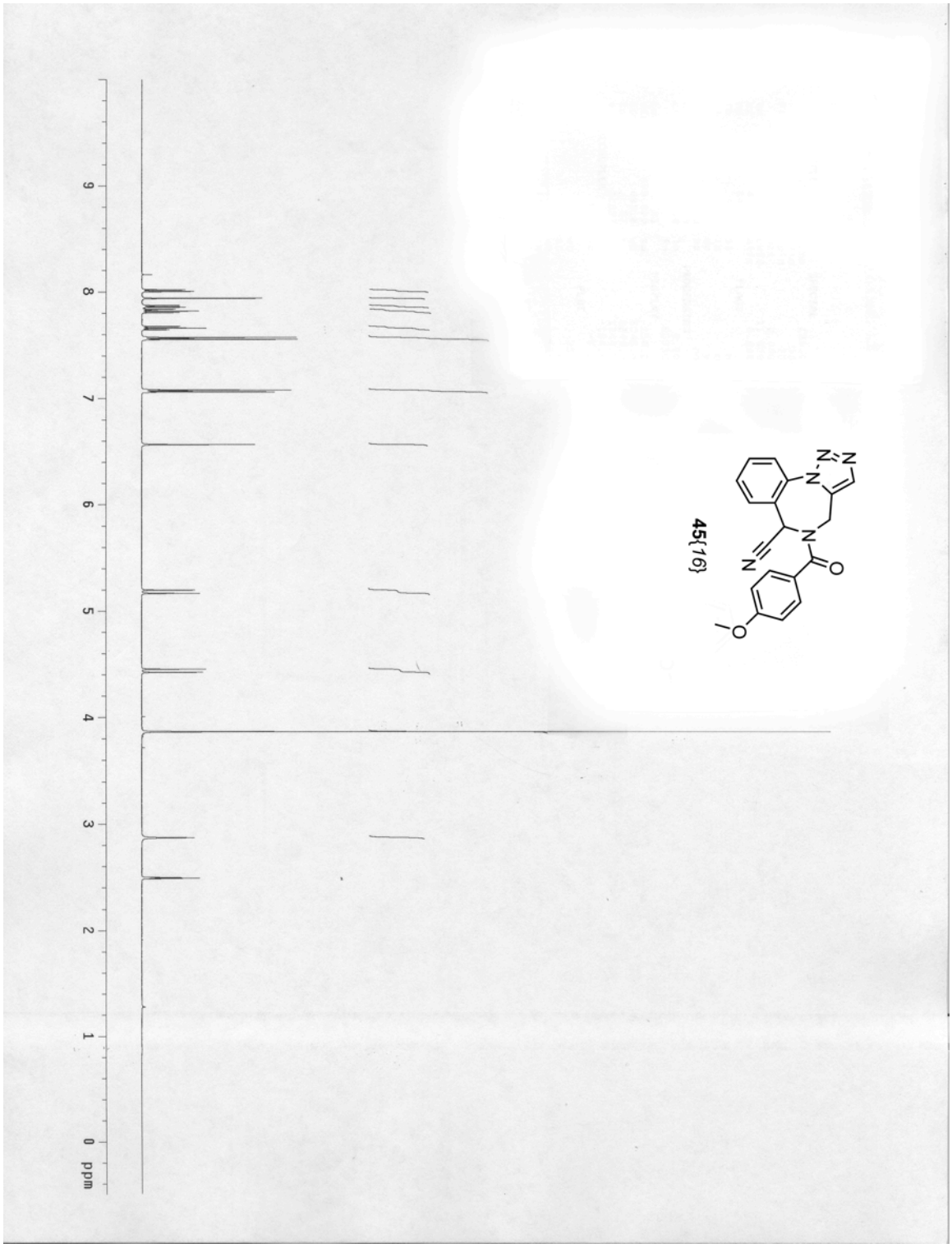

8.091
8.071
7.906
7.773
7.769
7.753
7.749
7.733
7.730
7.609
7.589
7.571
7.561
7.556
7.542
7.263
7.262
6.460
5.621
5.583
4.227
4.189
2.148
2.122
2.082
2.052
1.832
1.801
1.781
1.748
1.553
1.552
0.147
0.010
0.008
0.001
0.000
-0.007
-0.047
-0.149
ppm
45{12}

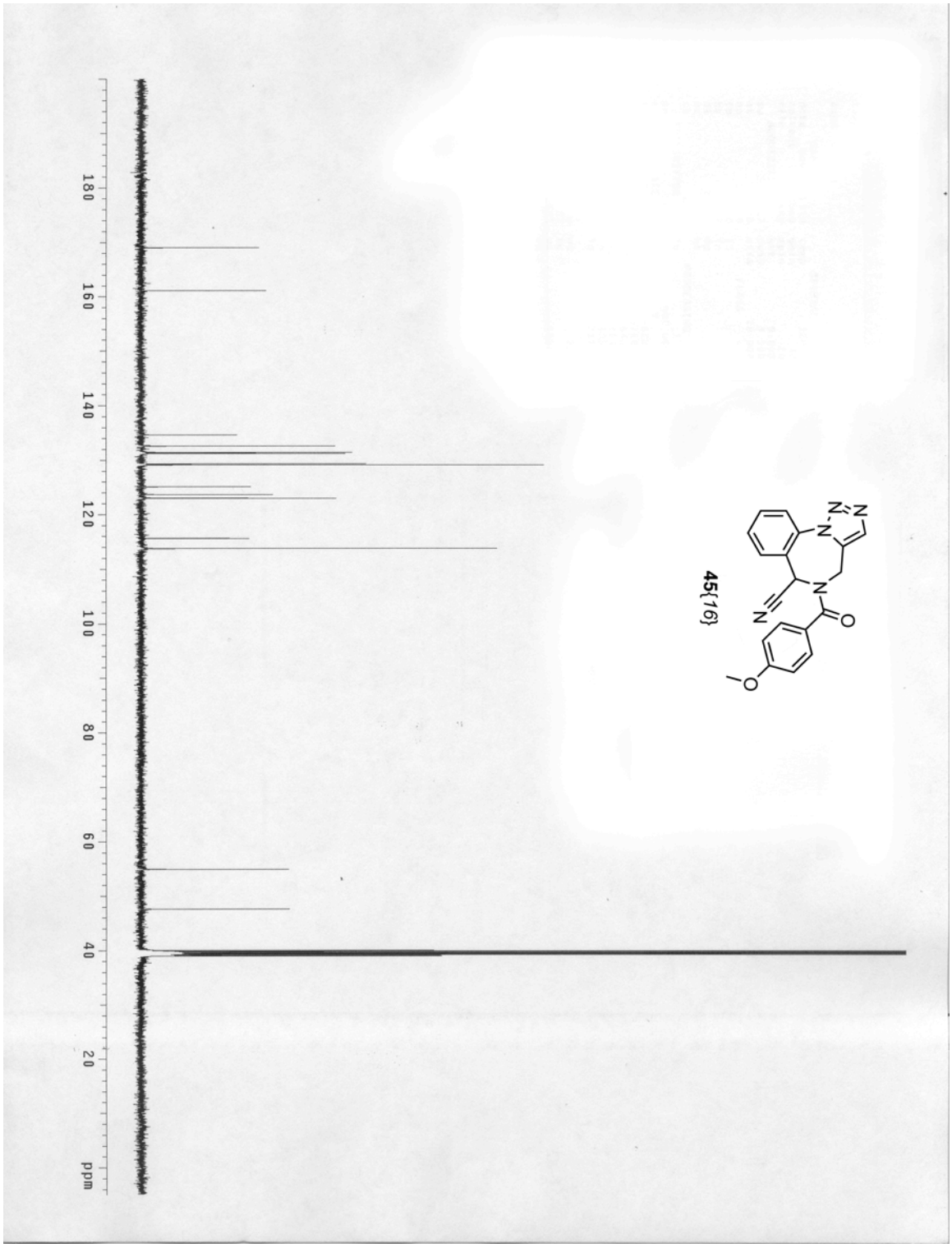

7.969
7.949
7.780
7.713
7.709
7.695
7.691
7.676
7.671
7.656
7.568
7.566
7.548
7.526
7.522
7.506
7.265
7.252
7.236
7.206
7.197
7.187
6.779
5.881
5.746
5.707
4.963
4.927
4.036
4.000
3.776
3.738
3.106
3.088
3.070
3.053
3.033
3.021
3.004
2.985
2.967
2.950
2.930
2.911
2.889
2.872
2.850
2.832
2.812
2.733
2.717
2.712
2.695
2.677
2.673
2.656
2.027
2.024
1.261
1.246
0.086
0.000
ppm
45{13}

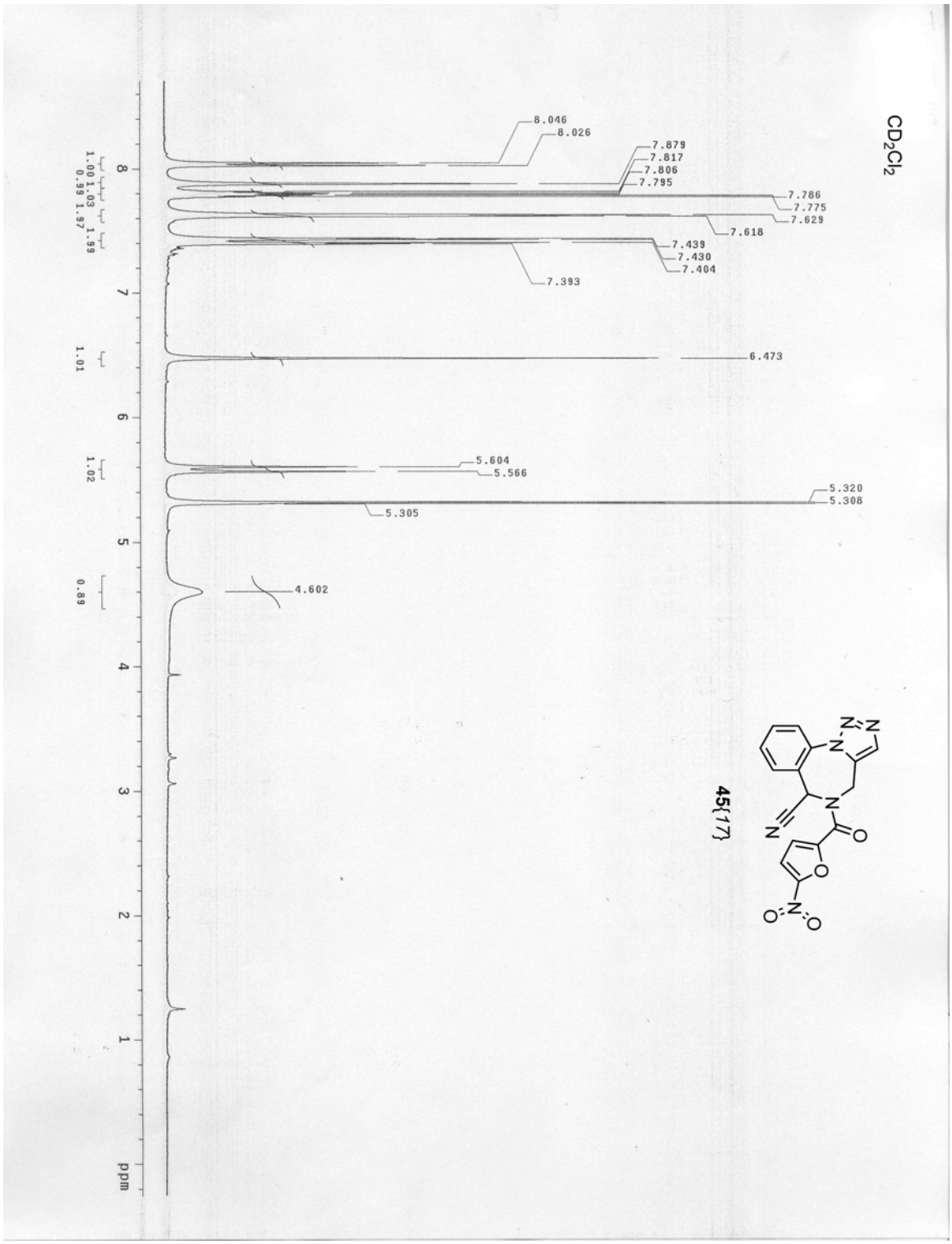

45{14}
N
N
N
N
O
F
9
8
7
6
5
4
3
2
1
0 ppm

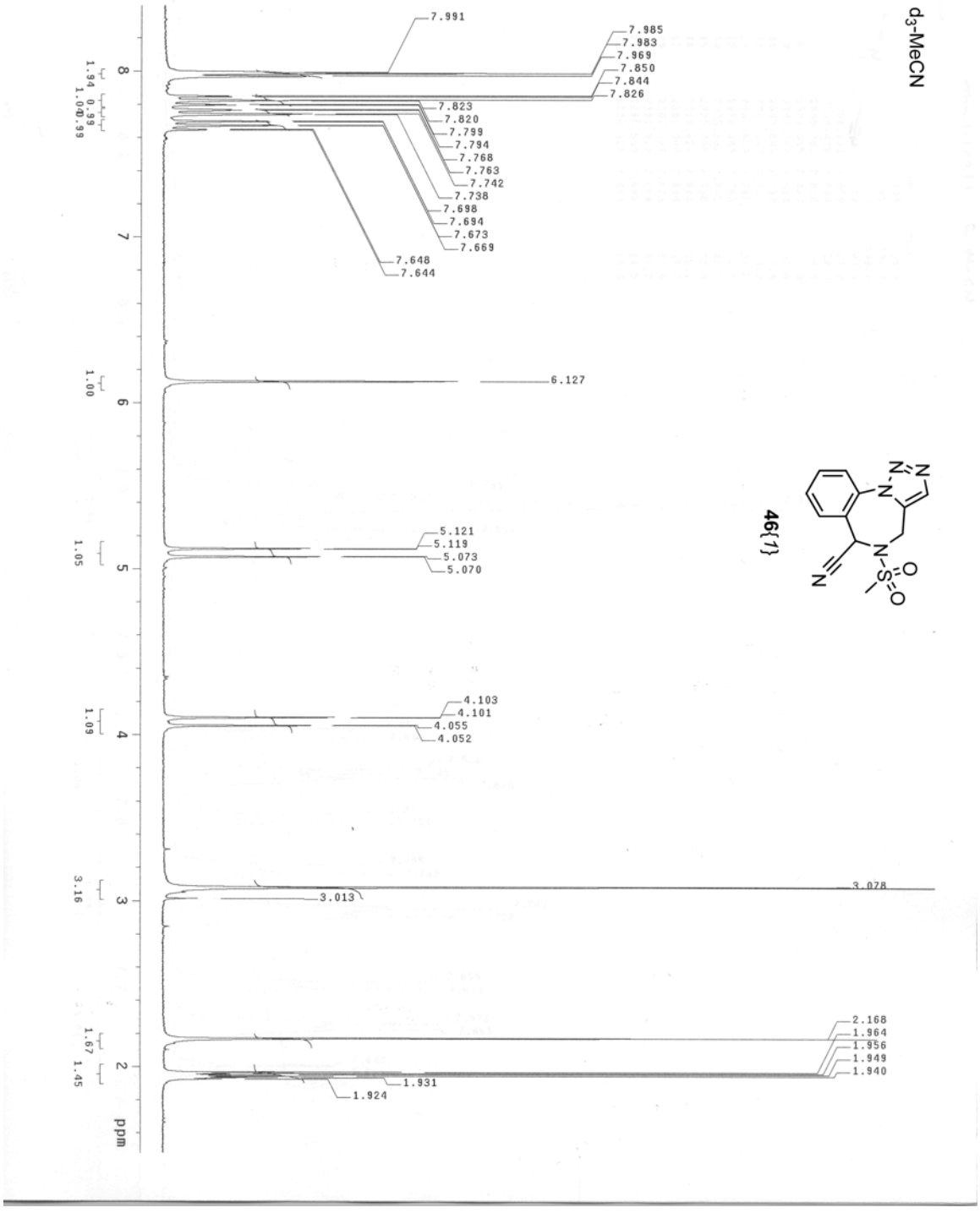

45(14)
180
160
140
120
100
80
60
40
20
ppm

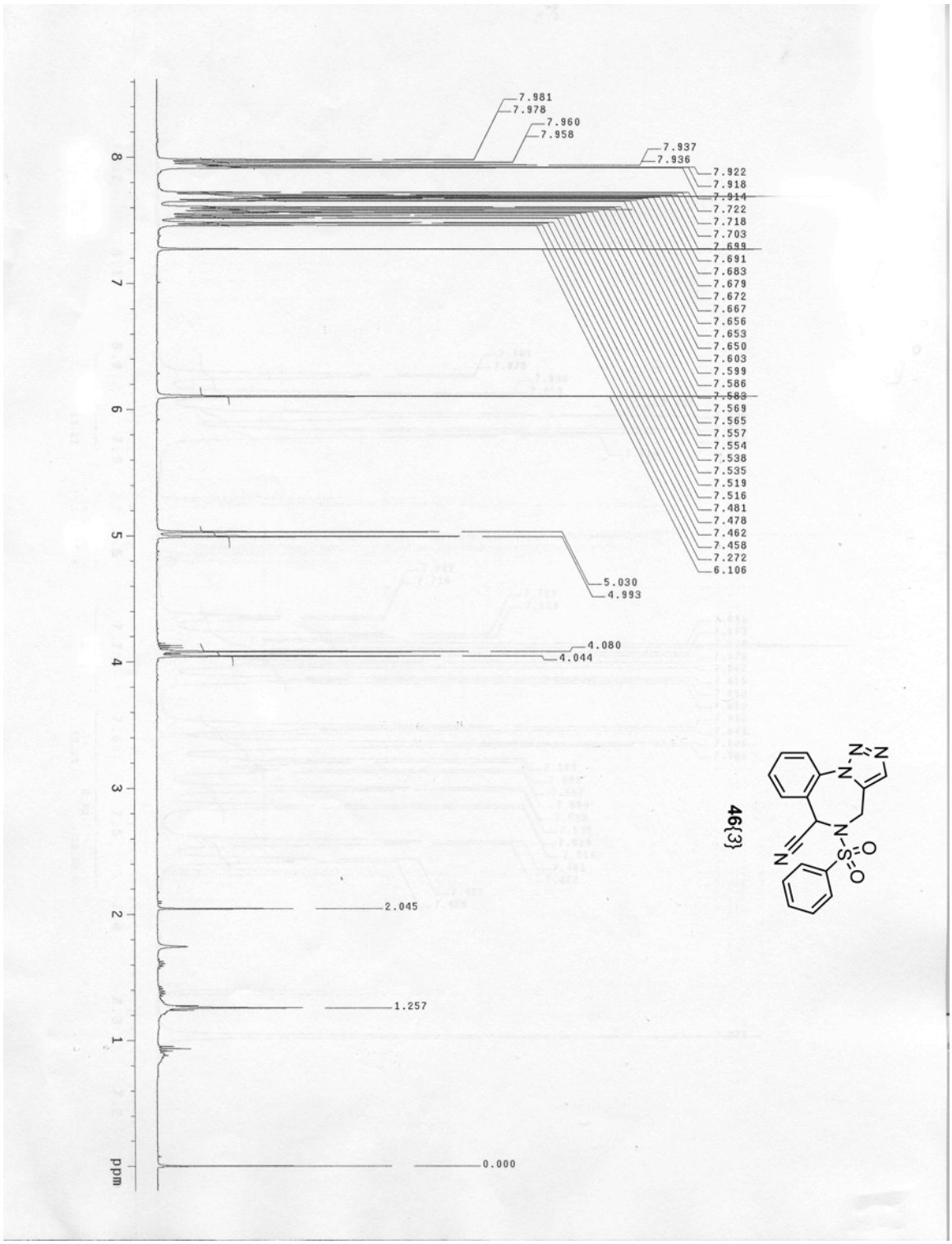

8.198
8.177
8.115
8.095
7.867
7.846
7.825
7.803
7.783
7.770
7.711
7.691
7.624
7.521
7.262
6.998
6.524
5.302
4.986
4.959
4.941
4.905
4.289
1.569
1.458
1.253
0.146
0.008
0.000
-0.008
-0.050
-0.149
ppm
45(15)

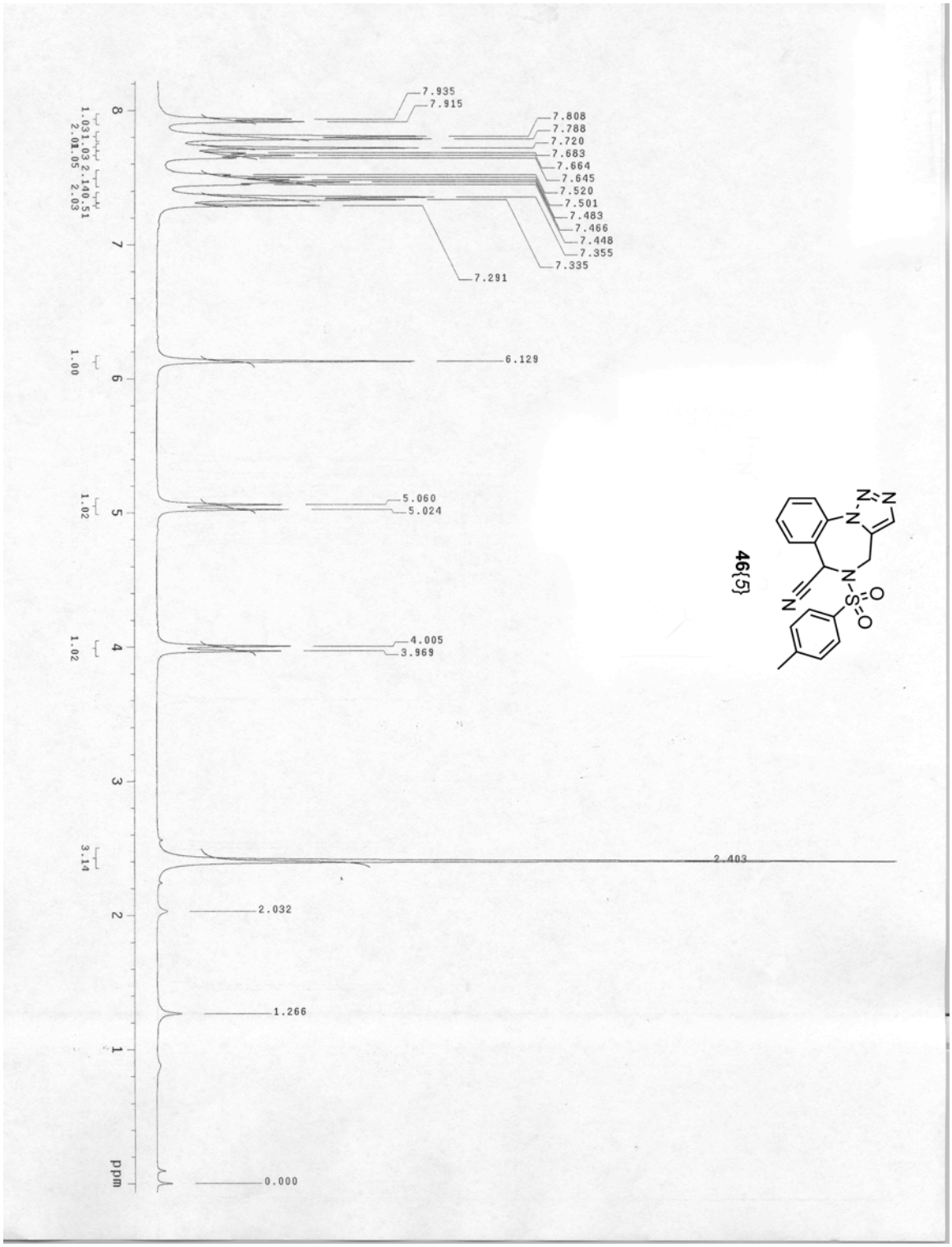

45{16}
9
8
7
6
5
4
3
2
1
0 ppm

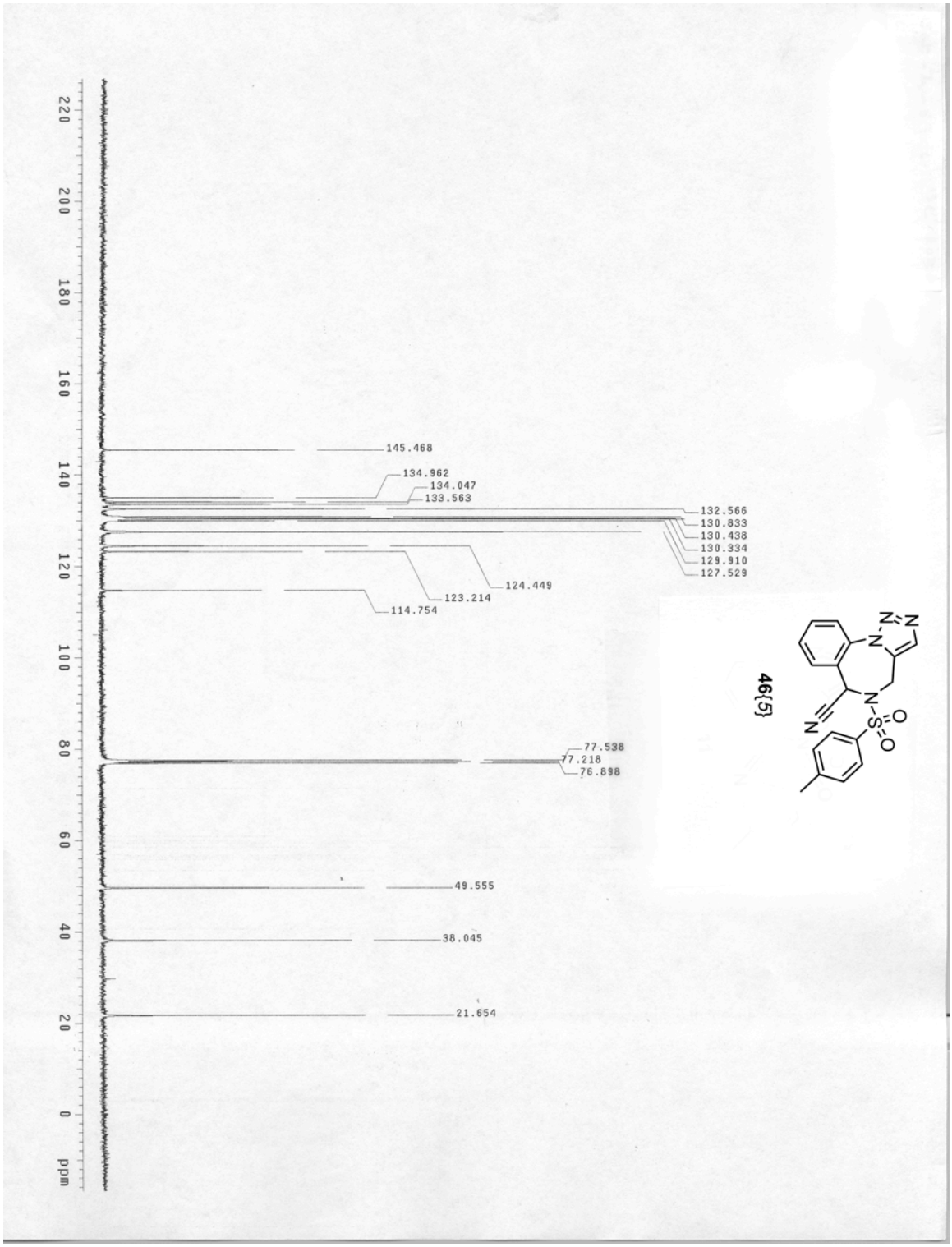

45{16}
180
160
140
120
100
80
60
40
20
ppm

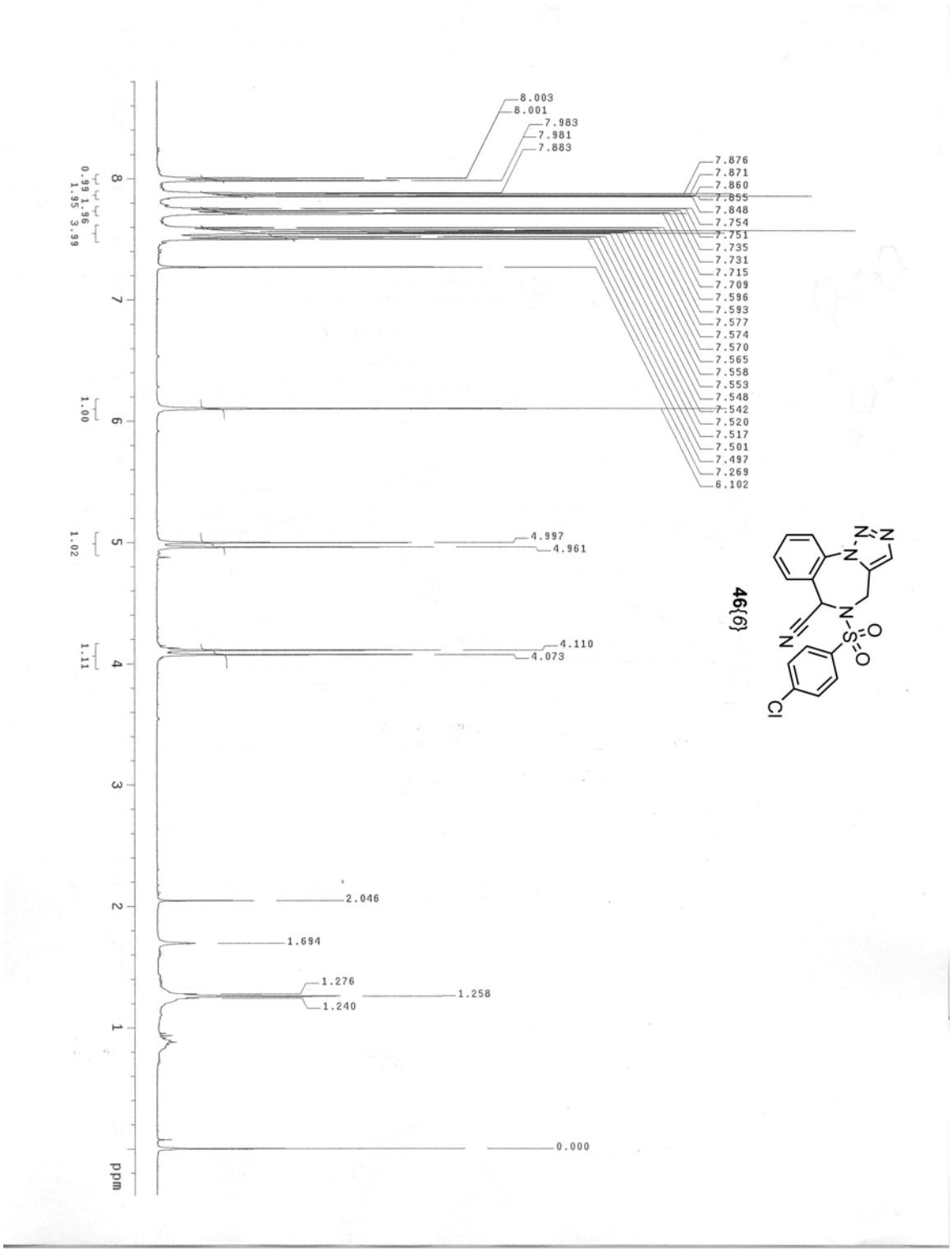

CD2Cl2
8.046
8.026
7.879
7.817
7.806
7.795
7.786
7.775
7.629
7.618
7.439
7.430
7.404
7.393
6.473
5.604
5.566
5.320
5.308
5.305
4.602
1.00 1.03 1.99
0.99 1.97
1.01
1.02
0.89
ppm
45{17}

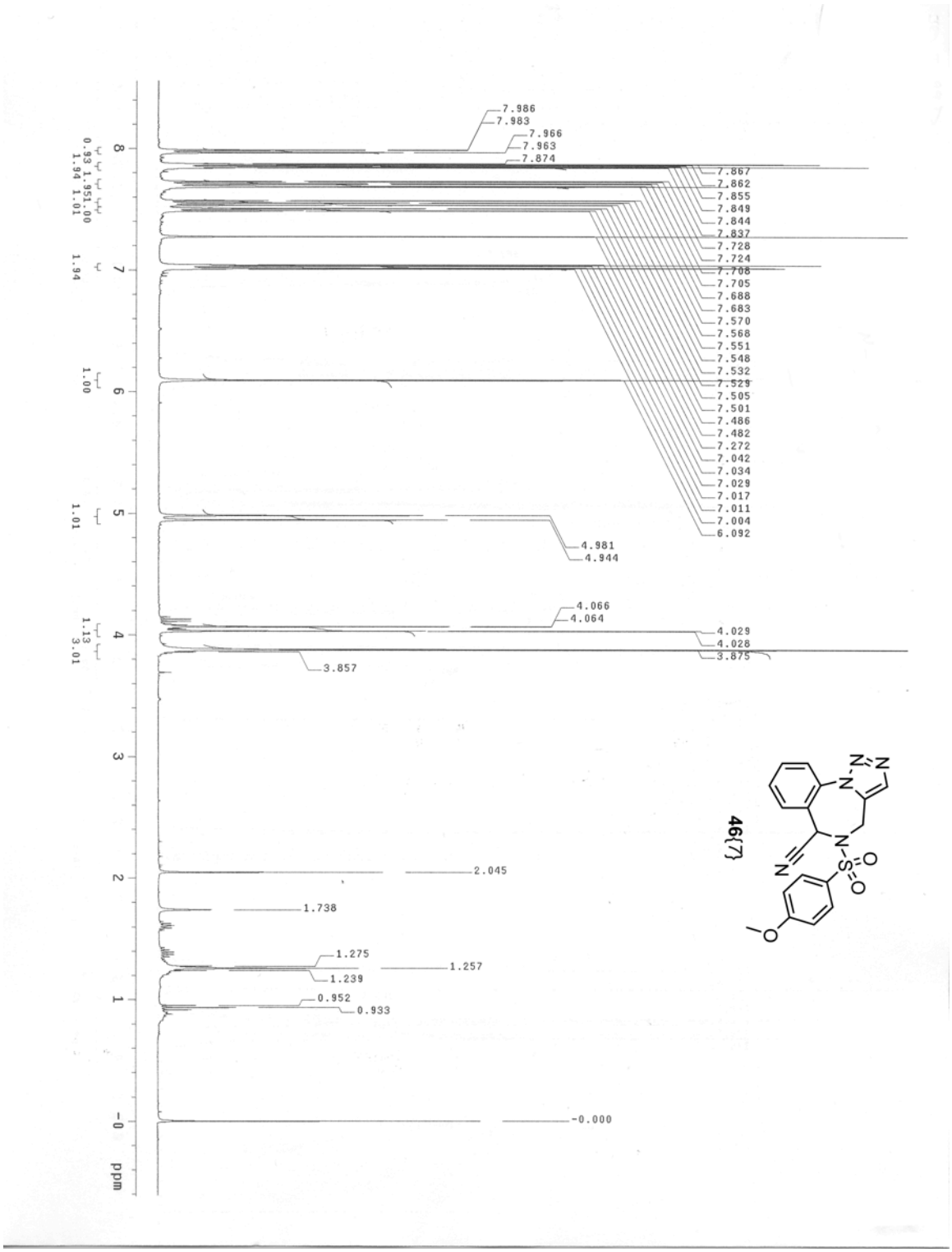

d3-MeCN
46{1}
7.991
7.985
7.983
7.969
7.850
7.844
7.826
7.823
7.820
7.799
7.794
7.768
7.763
7.742
7.738
7.698
7.694
7.673
7.669
7.648
7.644
6.127
5.121
5.119
5.073
5.070
4.103
4.101
4.055
4.052
3.078
3.013
2.168
1.964
1.956
1.949
1.940
1.931
1.924
1.94
0.99
1.04
0.99
1.00
1.05
1.09
3.16
1.67
1.45
ppm

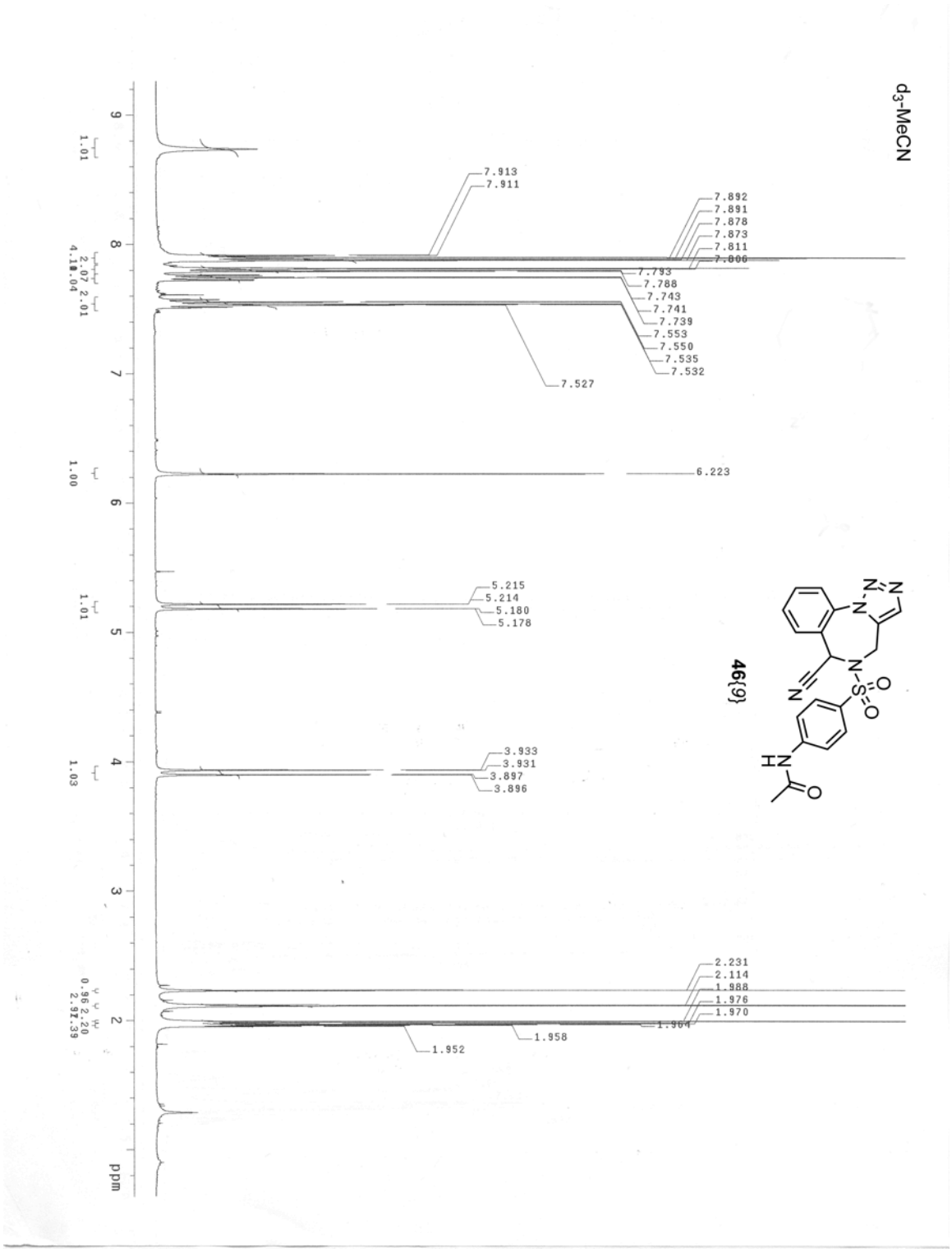

7.981
7.978
7.960
7.958
7.937
7.936
7.922
7.918
7.914
7.722
7.718
7.703
7.699
7.691
7.683
7.679
7.672
7.667
7.656
7.653
7.650
7.603
7.599
7.586
7.583
7.569
7.565
7.557
7.554
7.538
7.535
7.519
7.516
7.481
7.478
7.462
7.458
7.272
6.106
5.030
4.993
4.080
4.044
2.045
1.257
0.000
ppm
46{3}

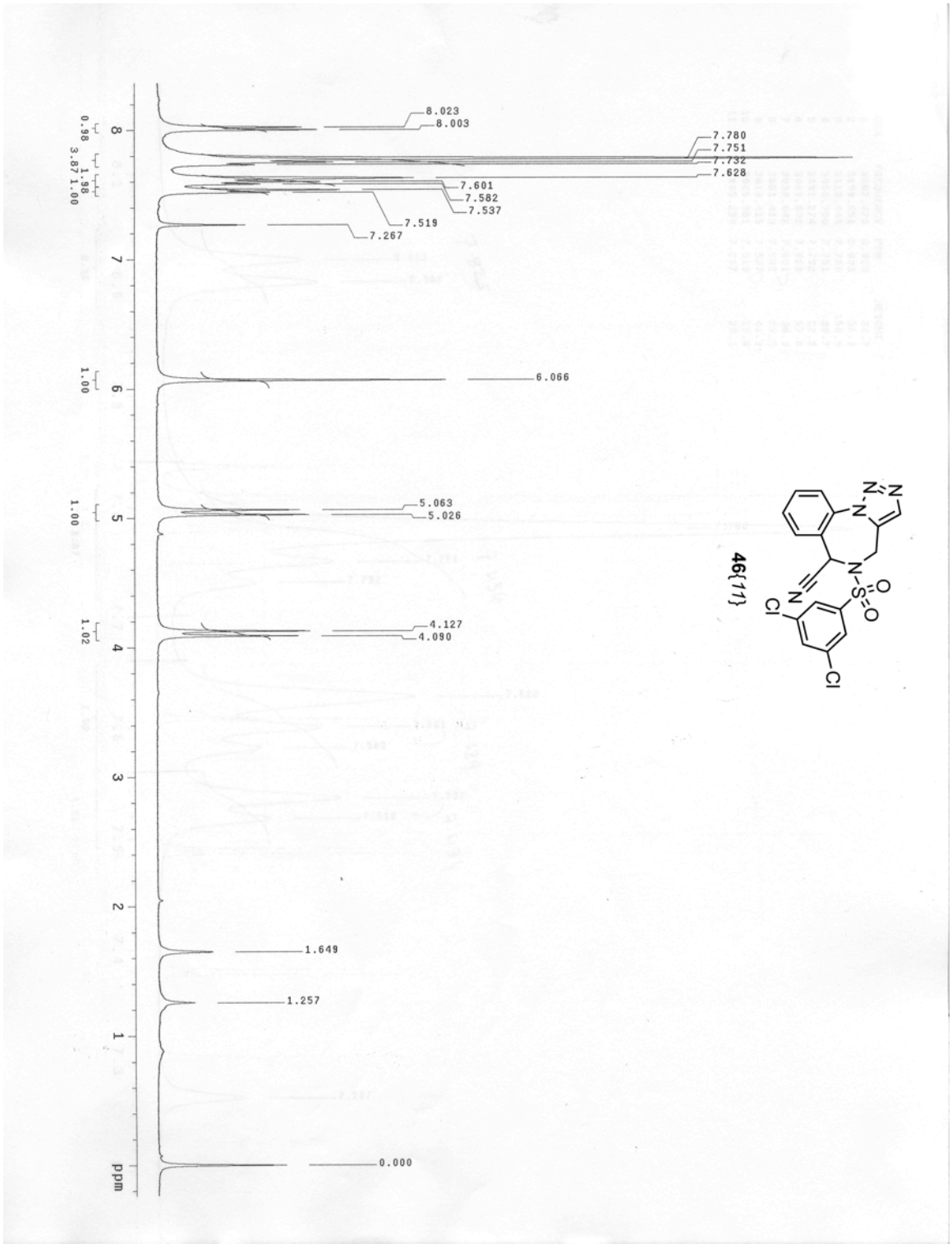

7.935
7.915
7.808
7.788
7.720
7.683
7.664
7.645
7.520
7.501
7.483
7.466
7.448
7.355
7.335
7.291
6.129
5.060
5.024
4.005
3.969
2.403
2.032
1.266
0.000
ppm
1.00
1.02
1.02
3.14
1.03
2.14
0.51
2.01
2.05
2.03
46{5}

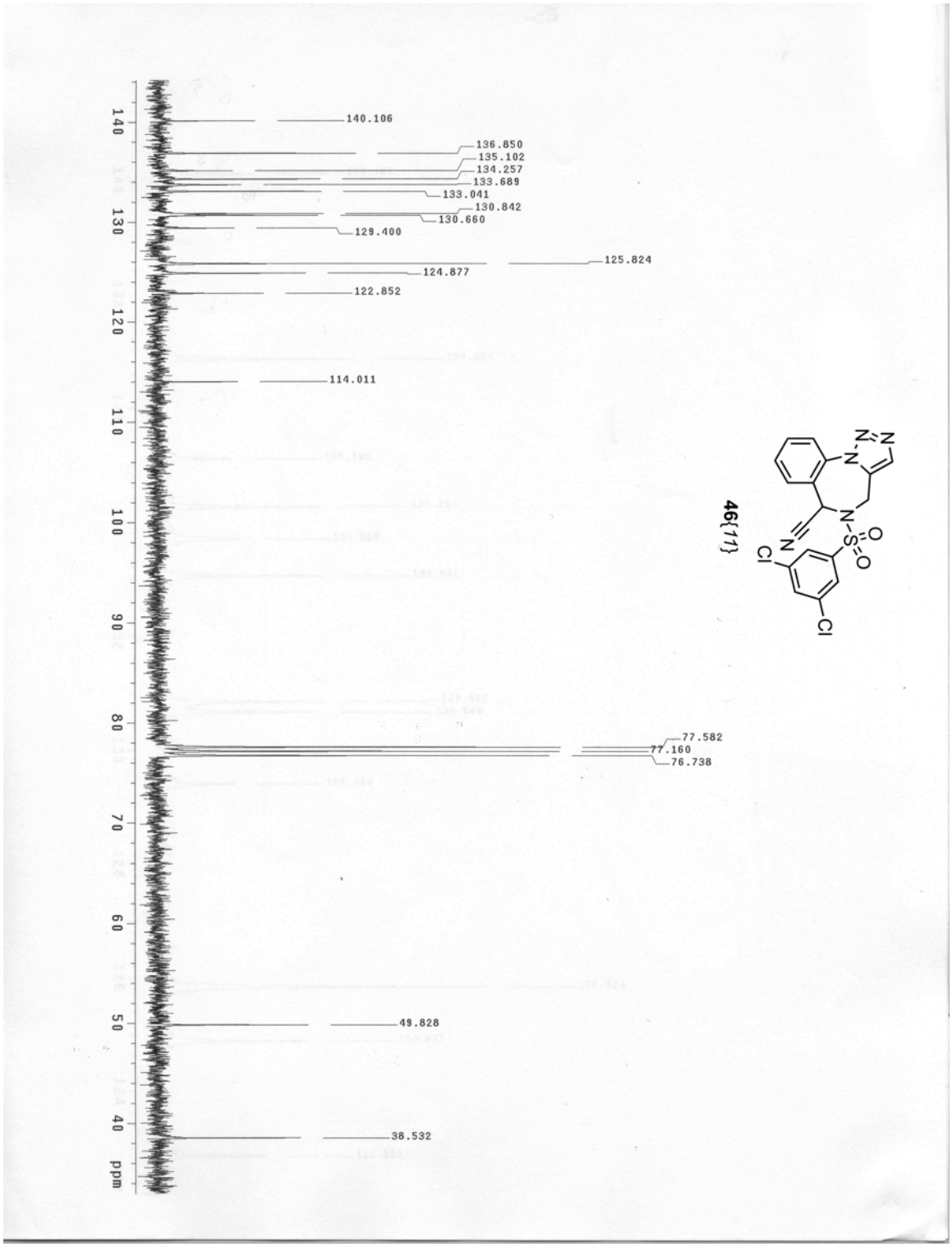

145.468
134.962
134.047
133.563
132.566
130.833
130.438
130.334
129.910
127.529
124.449
123.214
114.754
77.538
77.218
76.898
49.555
38.045
21.654
220
200
180
160
140
120
100
80
60
40
20
0
ppm
46{5}

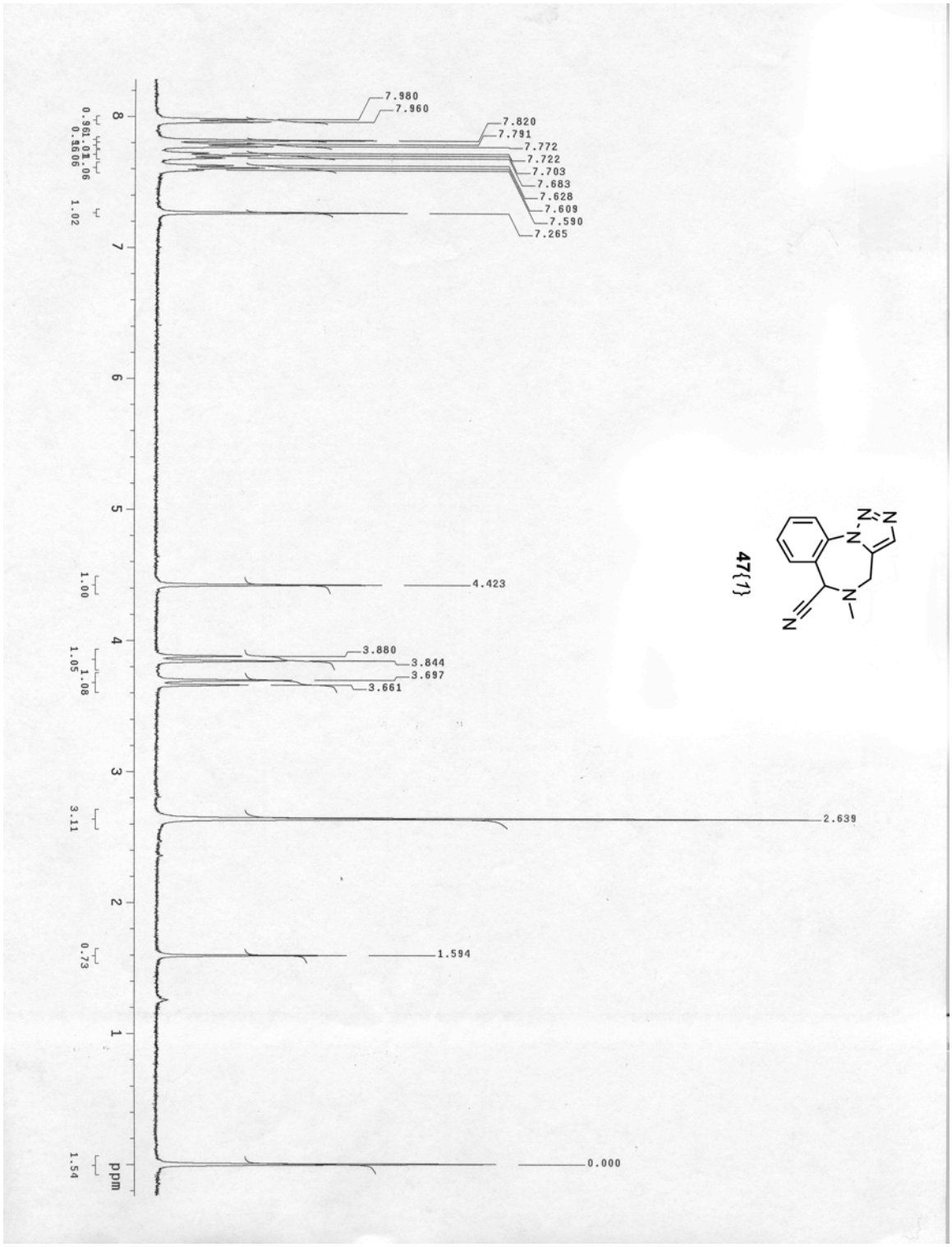

8.003
8.001
7.983
7.981
7.883
7.876
7.871
7.860
7.855
7.848
7.754
7.751
7.735
7.731
7.715
7.709
7.596
7.593
7.577
7.574
7.570
7.565
7.558
7.553
7.548
7.542
7.520
7.517
7.501
7.497
7.269
6.102
4.997
4.961
4.110
4.073
2.046
1.694
1.276
1.258
1.240
0.000
0.99 1.96
1.95 3.99
1.00
1.02
1.11
ppm
46{6}
N
N
N
O
S
O
N
Cl

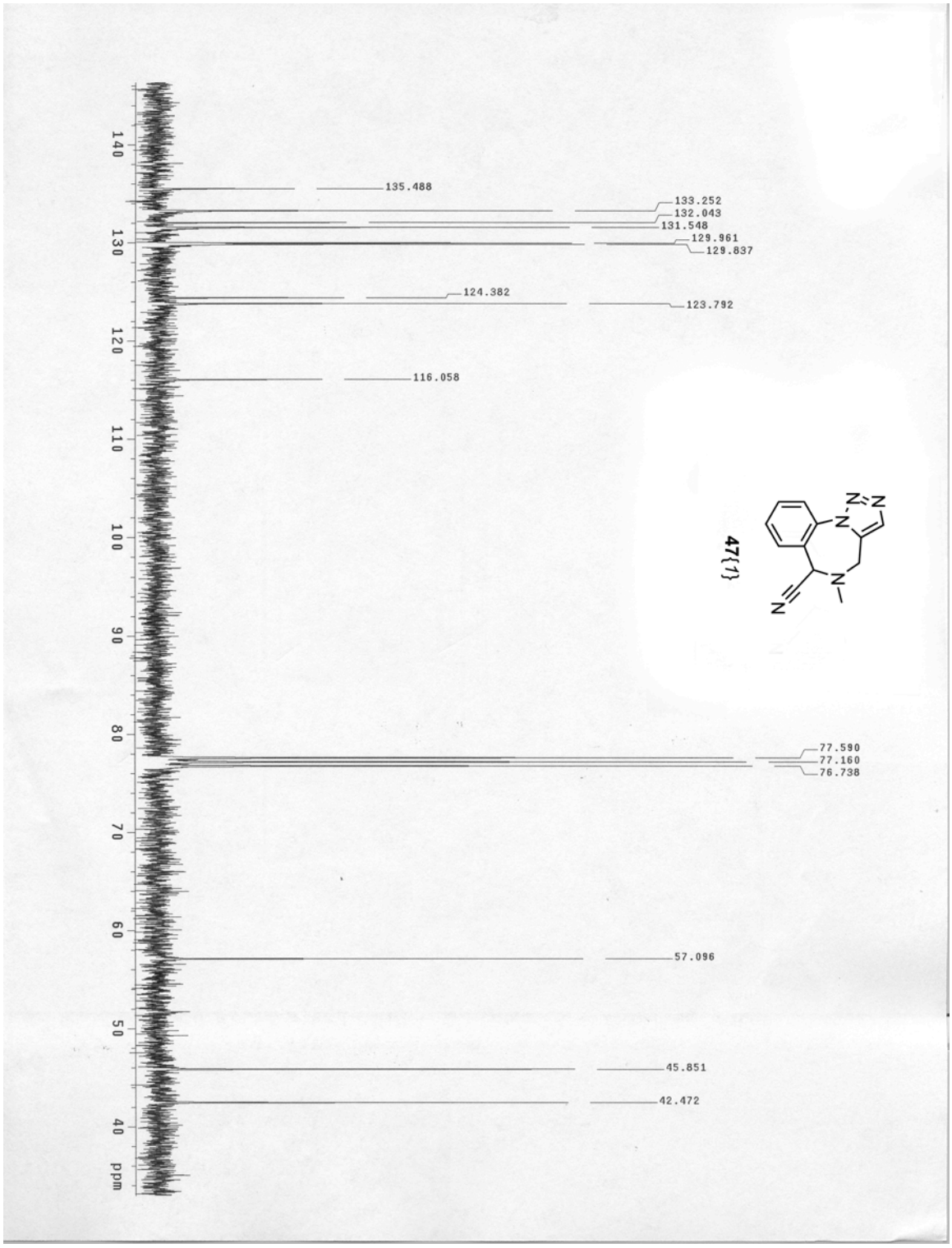

7.986
7.983
7.966
7.963
7.874
7.867
7.862
7.855
7.849
7.844
7.837
7.728
7.724
7.708
7.705
7.688
7.683
7.570
7.568
7.551
7.548
7.532
7.529
7.505
7.501
7.486
7.482
7.272
7.042
7.034
7.029
7.017
7.011
7.004
6.092
4.981
4.944
4.066
4.064
4.029
4.028
3.875
3.857
2.045
1.738
1.275
1.257
1.239
0.952
0.933
-0.000
ppm
46{7}

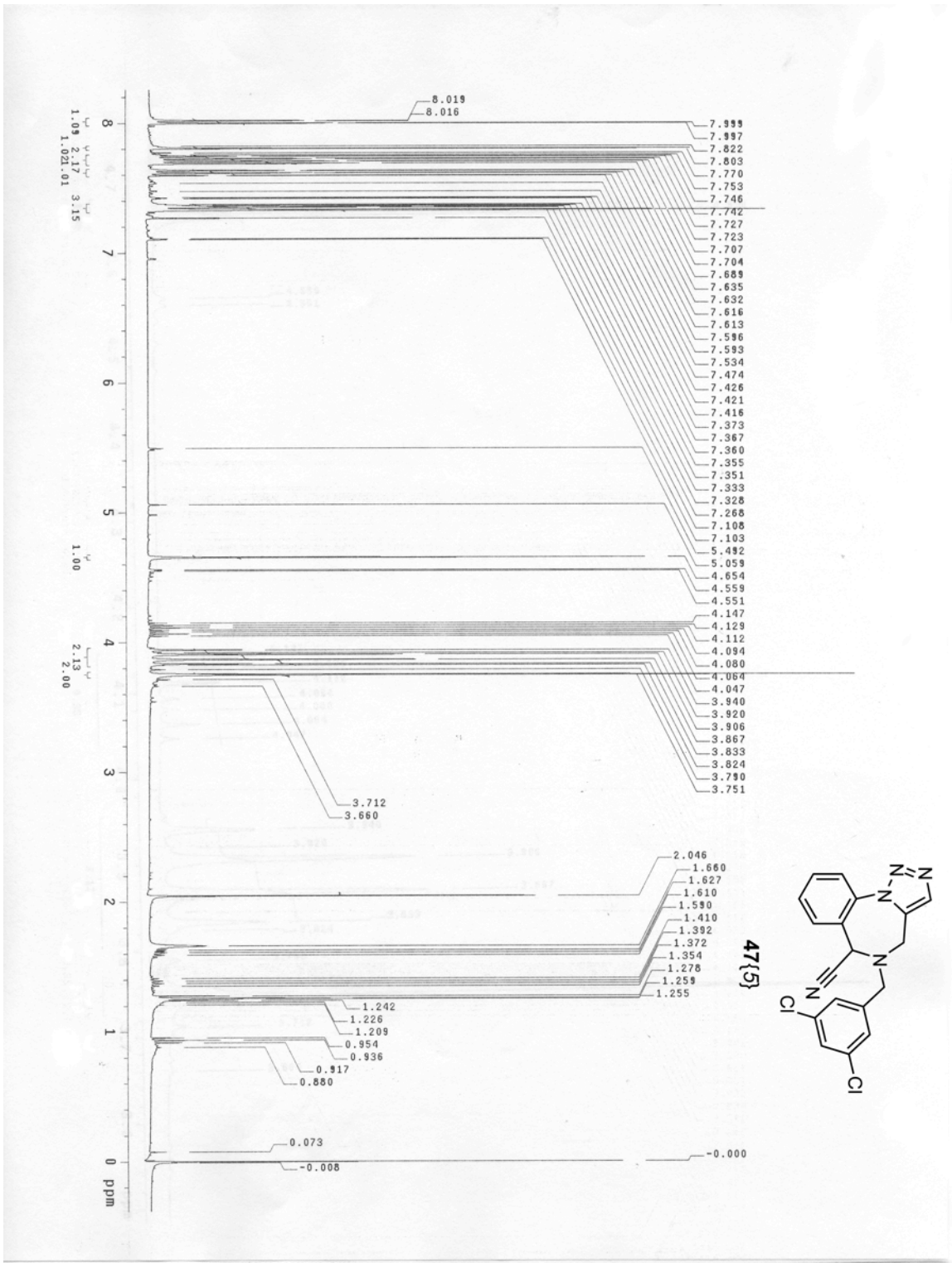

d3-MeCN
7.913
7.911
7.892
7.891
7.878
7.873
7.811
7.806
7.793
7.788
7.743
7.741
7.739
7.553
7.550
7.535
7.532
7.527
6.223
5.215
5.214
5.180
5.178
3.933
3.931
3.897
3.896
2.231
2.114
1.988
1.976
1.970
1.964
1.958
1.952
ppm
46{9}

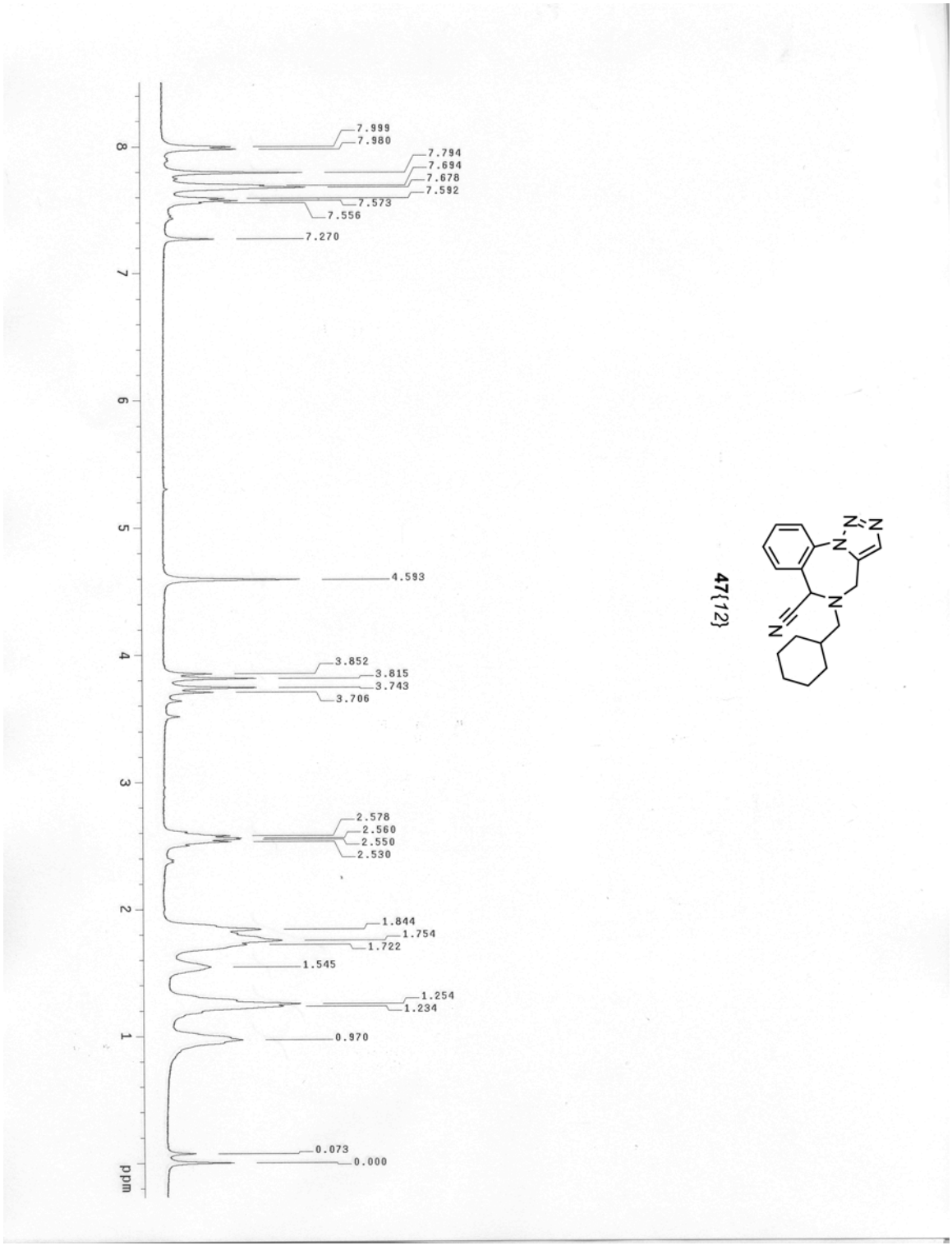

8.023
8.003
7.780
7.751
7.732
7.628
7.601
7.582
7.537
7.519
7.267
6.066
5.063
5.026
4.127
4.090
1.649
1.257
0.000
ppm
0.98 3.87 1.98 1.00
1.00
1.00
1.02
46{11}


140.106
136.850
135.102
134.257
133.689
133.041
130.842
130.660
129.400
125.824
124.877
122.852
114.011
77.582
77.160
76.738
49.828
38.532
ppm
46{11}

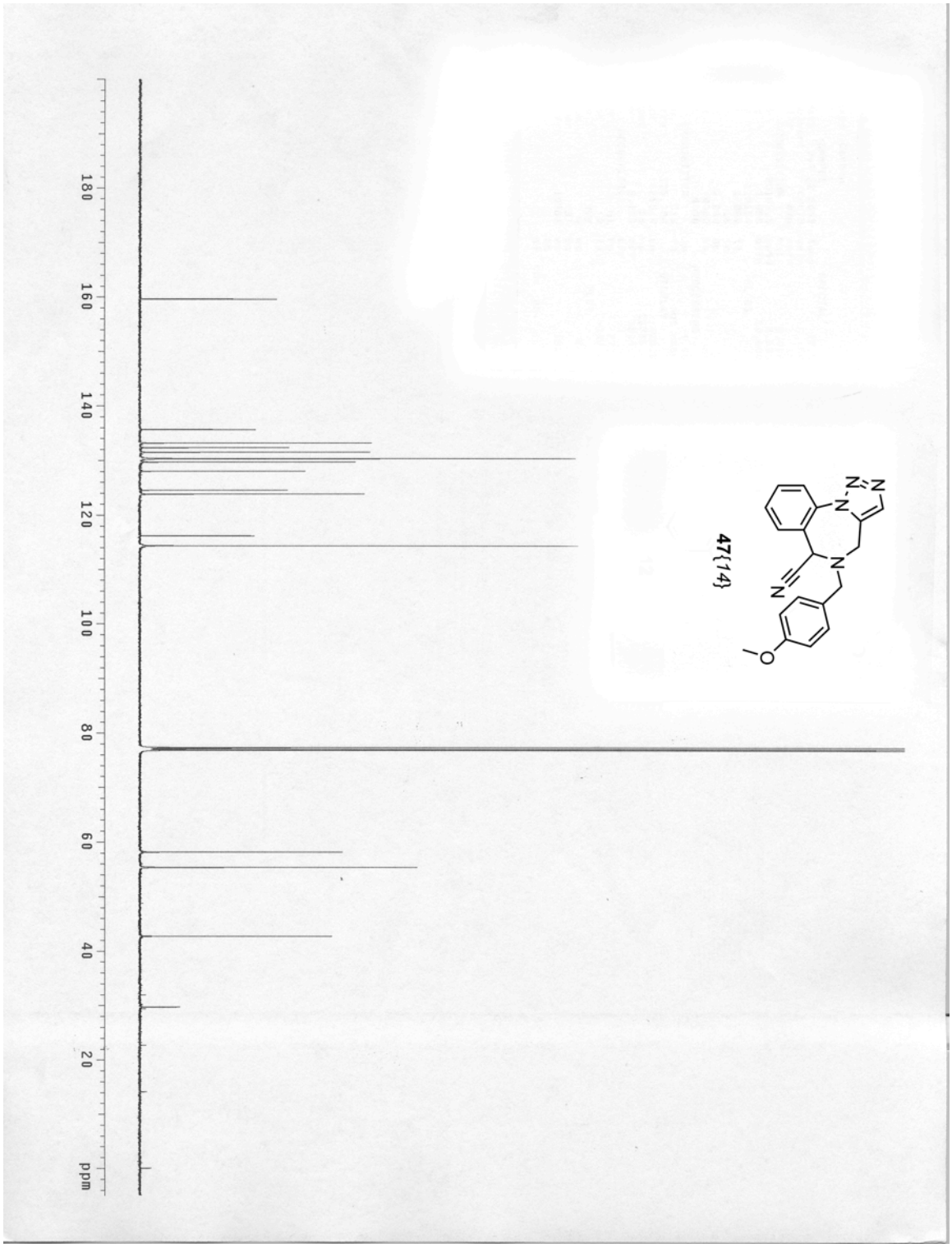

7.980
7.960
7.820
7.791
7.772
7.722
7.703
7.683
7.628
7.609
7.590
7.265
4.423
3.880
3.844
3.697
3.661
2.639
1.594
0.000
ppm
47{1}

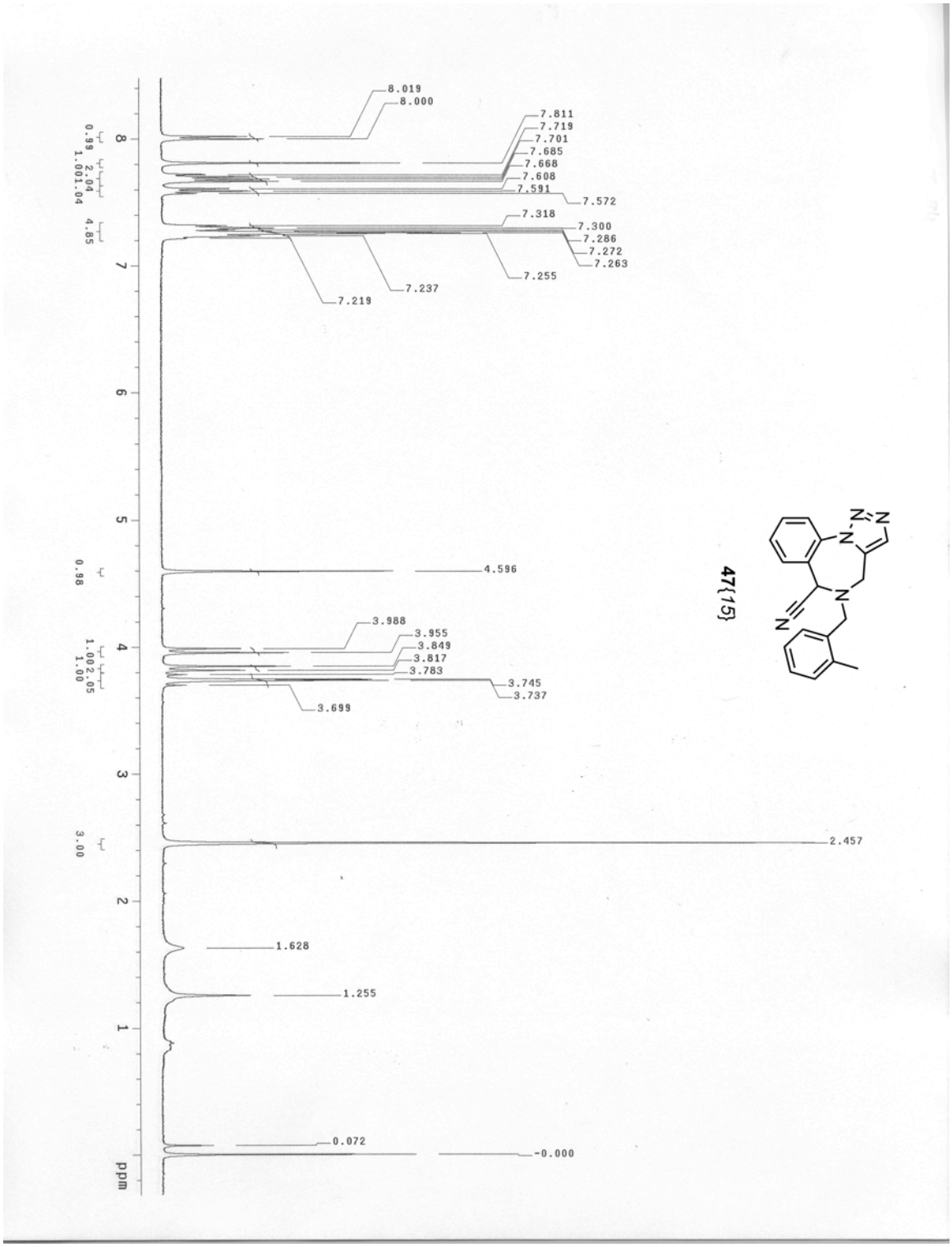

135.488
133.252
132.043
131.548
129.961
129.837
124.382
123.792
116.058
77.590
77.160
76.738
57.096
45.851
42.472
140
130
120
110
100
90
80
70
60
50
40
ppm
47{1}

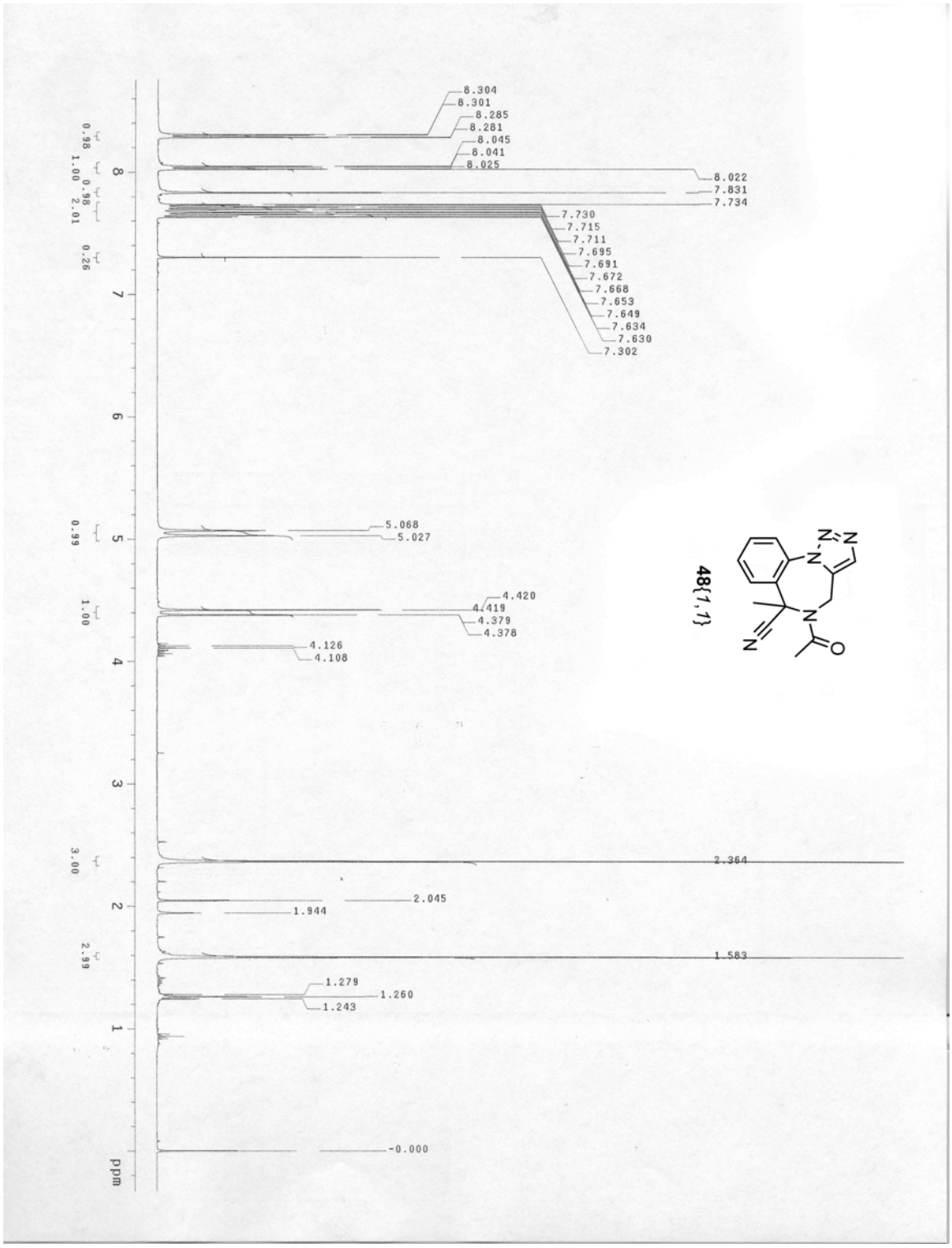

8.019
8.016
7.999
7.997
7.822
7.803
7.770
7.753
7.746
7.742
7.727
7.723
7.707
7.704
7.689
7.635
7.632
7.616
7.613
7.596
7.593
7.534
7.474
7.426
7.421
7.416
7.373
7.367
7.360
7.355
7.351
7.333
7.328
7.268
7.108
7.103
5.492
5.059
4.654
4.559
4.551
4.147
4.129
4.112
4.094
4.080
4.064
4.047
3.940
3.920
3.906
3.867
3.833
3.824
3.790
3.751
3.712
3.660
2.046
1.660
1.627
1.610
1.590
1.410
1.392
1.372
1.354
1.278
1.259
1.255
1.242
1.226
1.209
0.954
0.936
0.917
0.880
0.073
-0.008
-0.000
47{5}
Cl
Cl
N
N
N
N
ppm

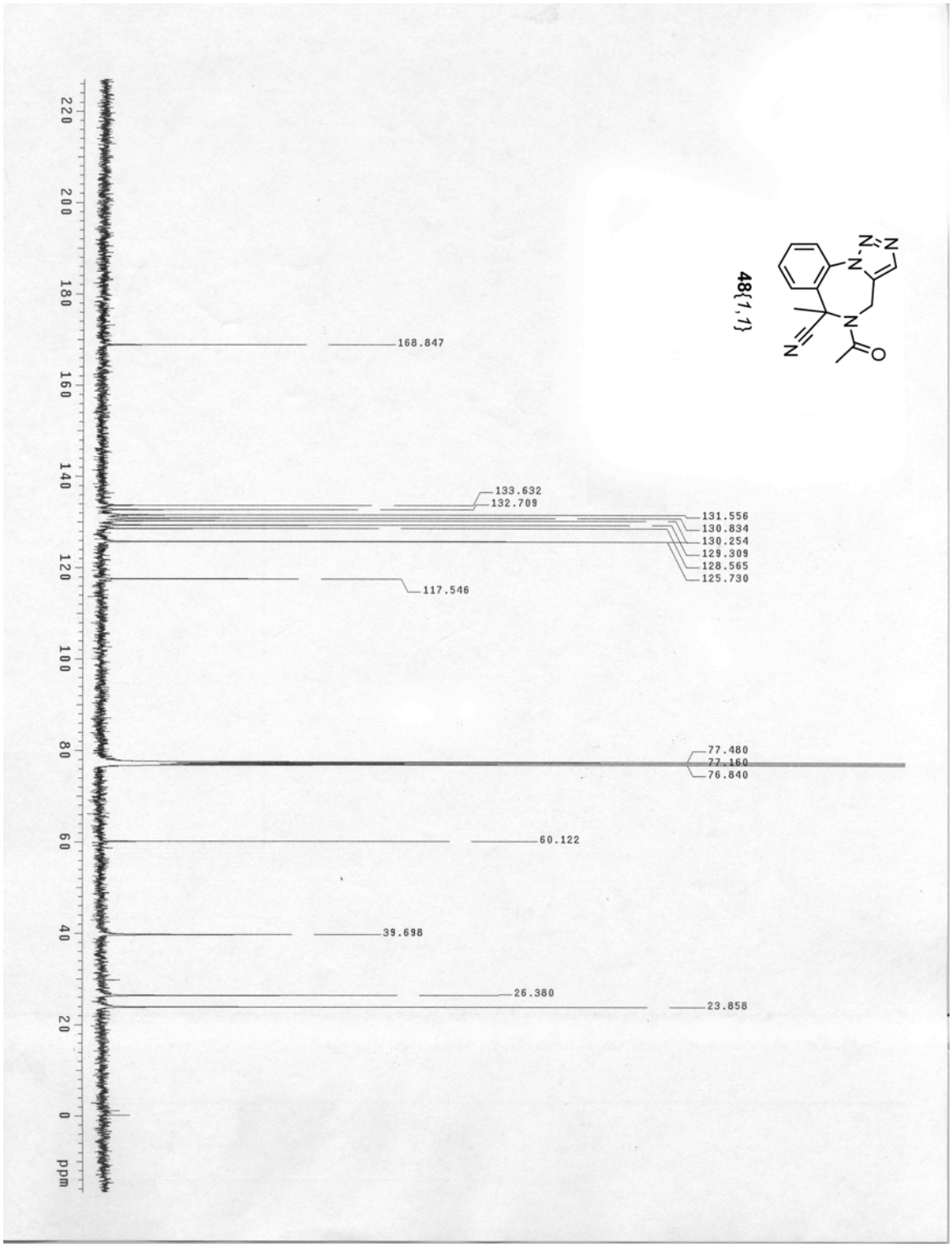

7.999
7.980
7.794
7.694
7.678
7.592
7.573
7.556
7.270
4.593
3.852
3.815
3.743
3.706
2.578
2.560
2.550
2.530
1.844
1.754
1.722
1.545
1.254
1.234
0.970
0.073
0.000
ppm
47{12}

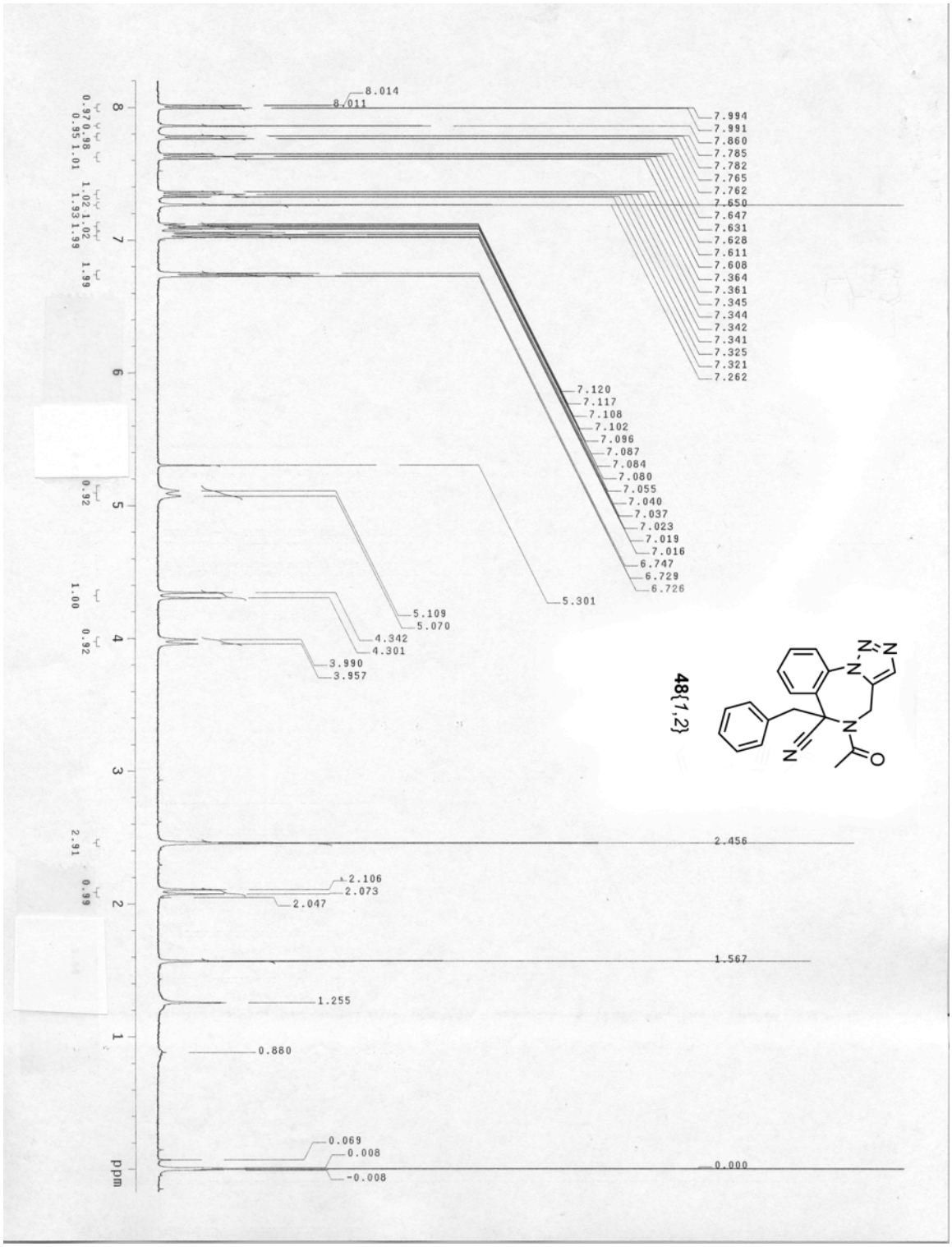

47{14}
9
8
7
6
5
4
3
2
1
0 ppm

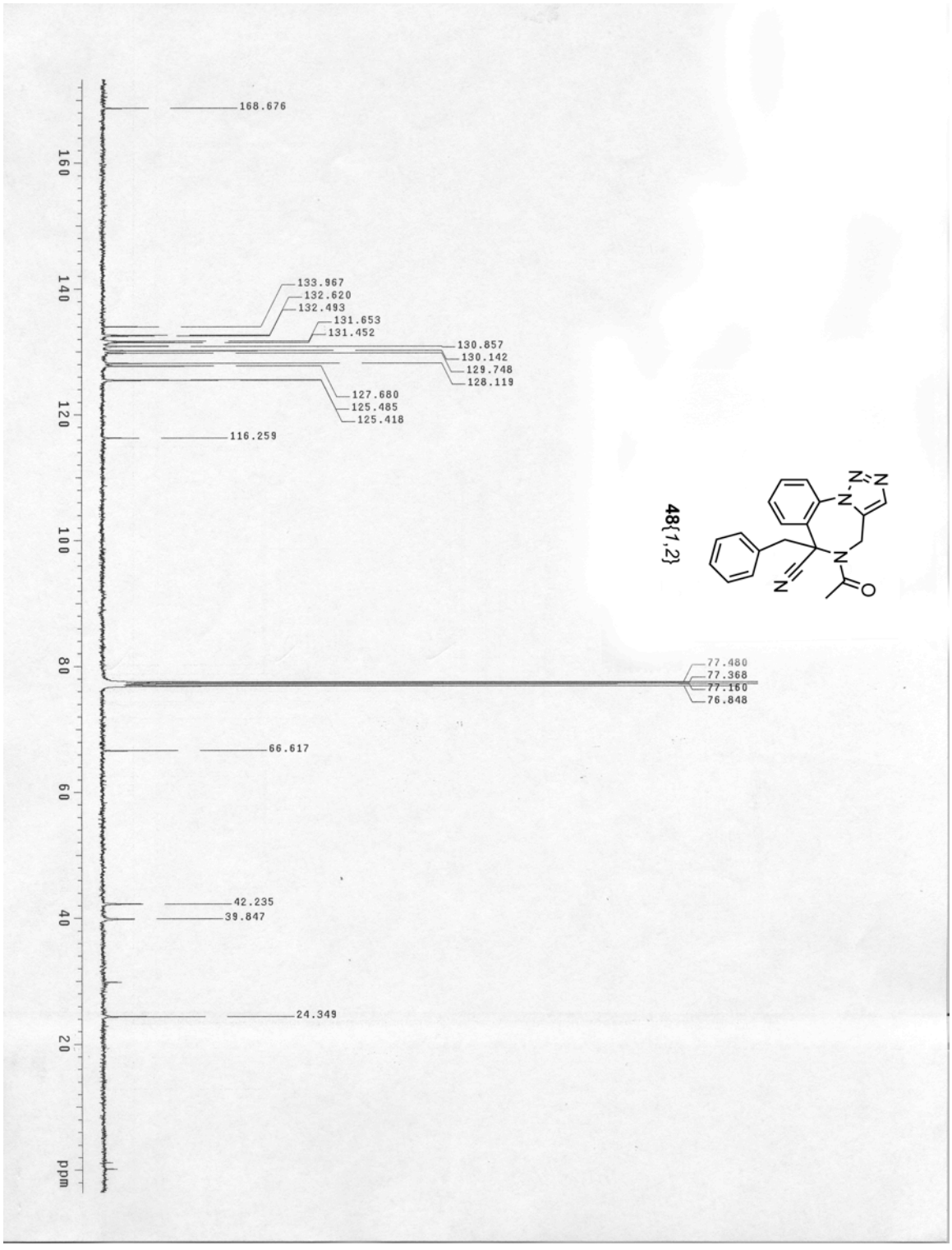

47{14}
180
160
140
120
100
80
60
40
20
ppm

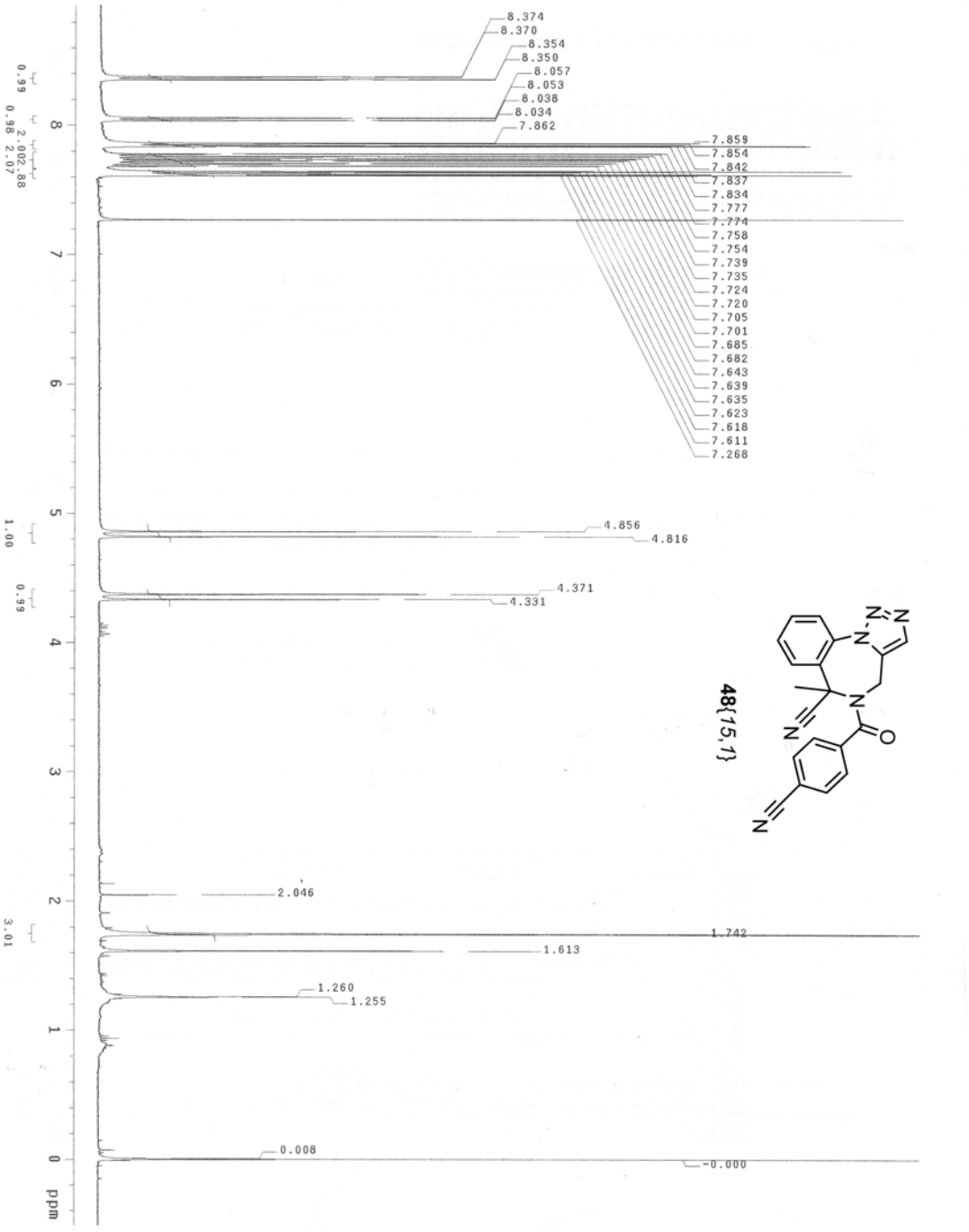

8.019
8.000
7.811
7.719
7.701
7.685
7.668
7.608
7.591
7.572
7.318
7.300
7.286
7.272
7.263
7.255
7.237
7.219
4.596
3.988
3.955
3.849
3.817
3.783
3.745
3.737
3.699
2.457
1.628
1.255
0.072
-0.000
ppm
47{15}

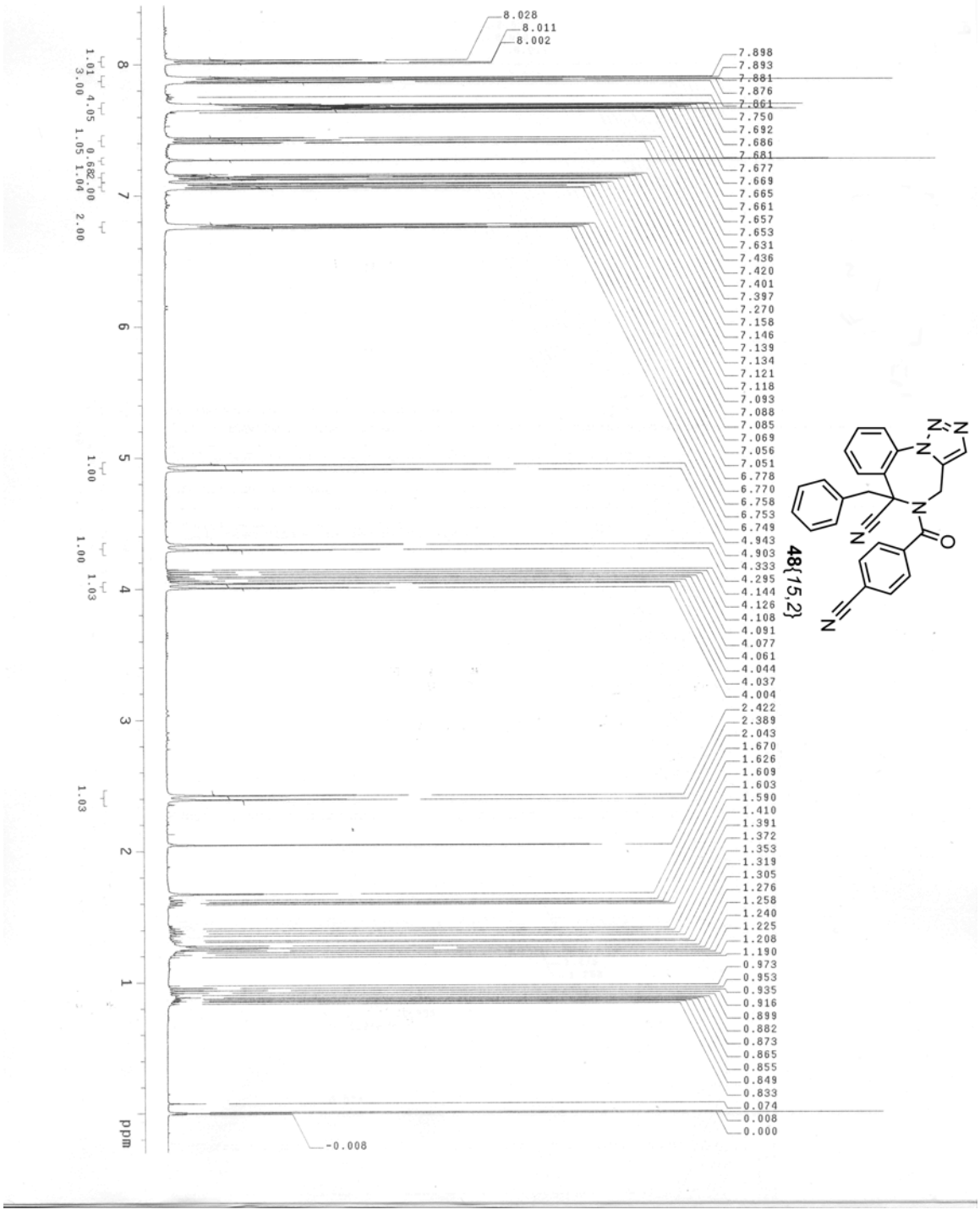

8.304
8.301
8.285
8.281
8.045
8.041
8.025
8.022
7.831
7.734
7.730
7.715
7.711
7.695
7.691
7.672
7.668
7.653
7.649
7.634
7.630
7.302
5.068
5.027
4.420
4.419
4.379
4.378
4.126
4.108
2.364
2.045
1.944
1.583
1.279
1.260
1.243
-0.000
ppm
48{1,1}


48{1,1}
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
ppm


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
0.880
0.069
0.008
-0.008
0.000
ppm
48{1,2}


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
48{1,2}


8.374
8.370
8.354
8.350
8.057
8.053
8.038
8.034
7.862
7.859
7.854
7.842
7.837
7.834
7.777
7.774
7.758
7.754
7.739
7.735
7.724
7.720
7.705
7.701
7.685
7.682
7.643
7.639
7.635
7.623
7.618
7.611
7.268
4.856
4.816
4.371
4.331
2.046
1.742
1.613
1.260
1.255
0.008
-0.000
0.99
0.98
2.00
2.88
2.07
1.00
0.99
3.01
ppm
48{15,1}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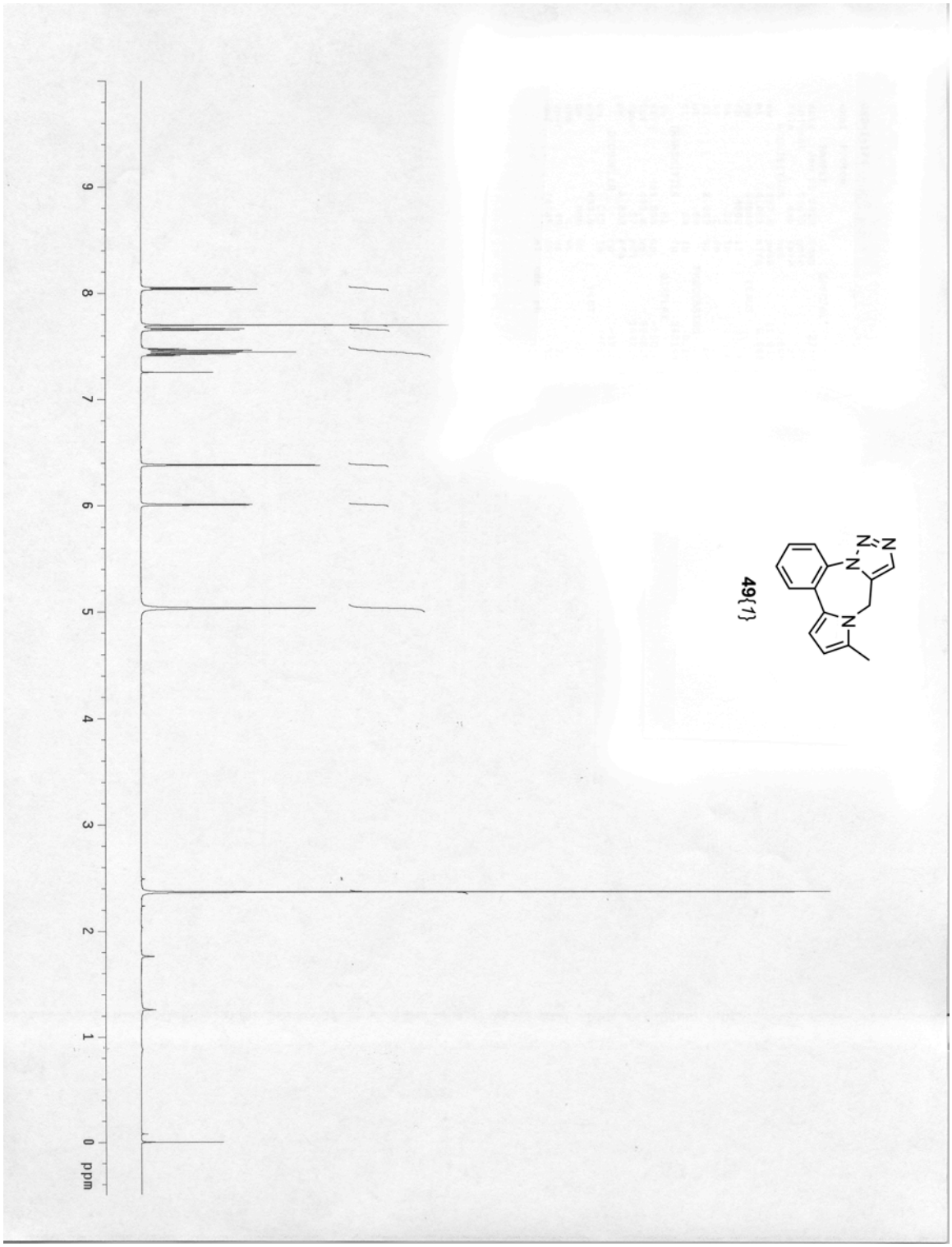
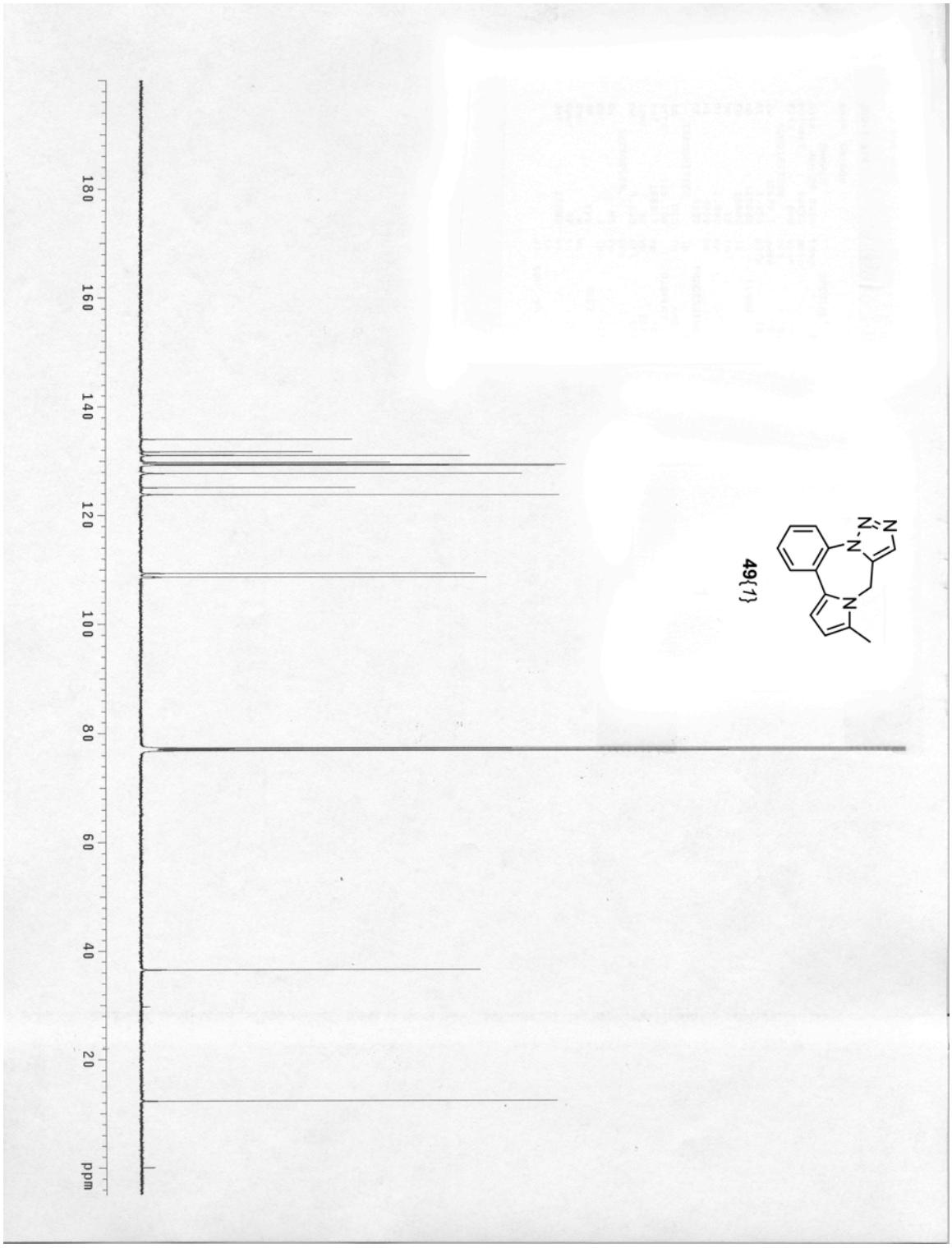
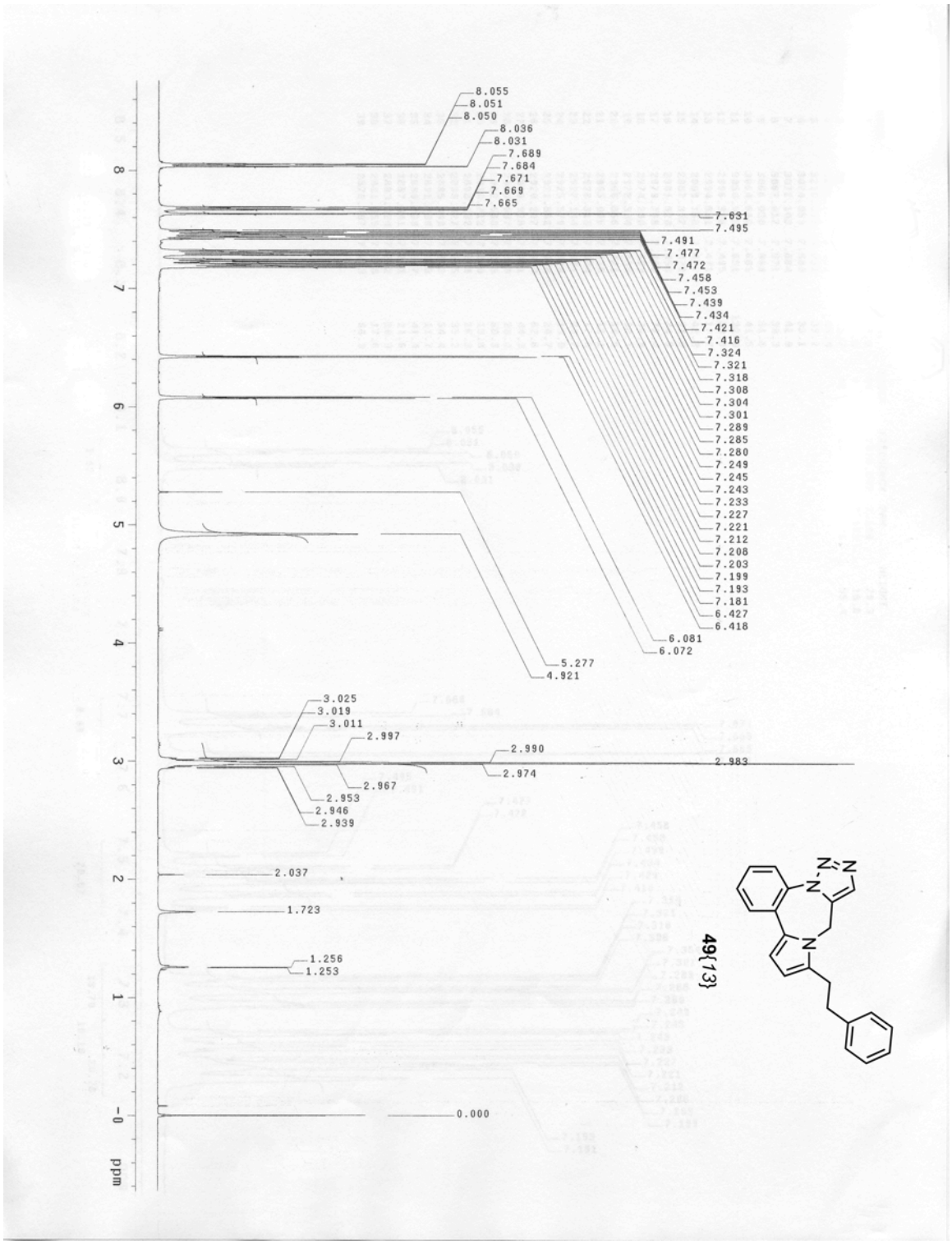
8.011
8.002
7.898
7.893
7.881
7.876
7.861
7.750
7.692
7.686
7.681
7.677
7.669
7.665
7.661
7.657
7.653
7.631
7.436
7.420
7.401
7.397
7.270
7.158
7.146
7.139
7.134
7.121
7.118
7.093
7.088
7.085
7.069
7.056
7.051
6.778
6.770
6.758
6.753
6.749
4.943
4.903
4.333
4.295
4.144
4.126
4.108
4.091
4.077
4.061
4.044
4.037
4.004
2.422
2.389
2.043
1.670
1.626
1.609
1.603
1.590
1.410
1.391
1.372
1.353
1.319
1.305
1.276
1.258
1.240
1.225
1.208
1.190
0.973
0.953
0.935
0.916
0.899
0.882
0.873
0.865
0.855
0.849
0.833
0.074
0.008
0.000
-0.008
ppm
48{15,2}


49{1}
9
8
7
6
5
4
3
2
1
0 ppm


49{1}
180
160
140
120
100
80
60
40
20
ppm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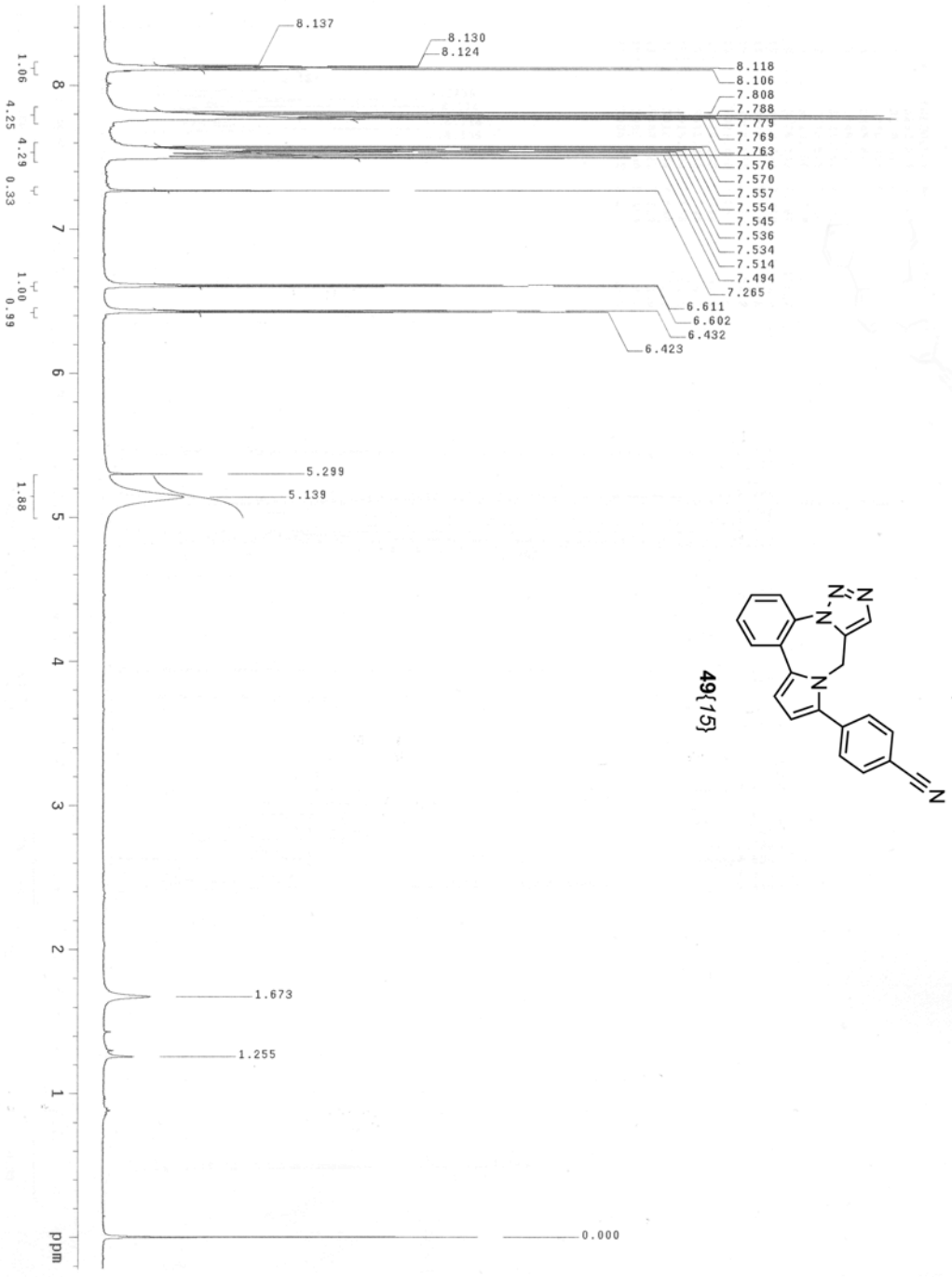
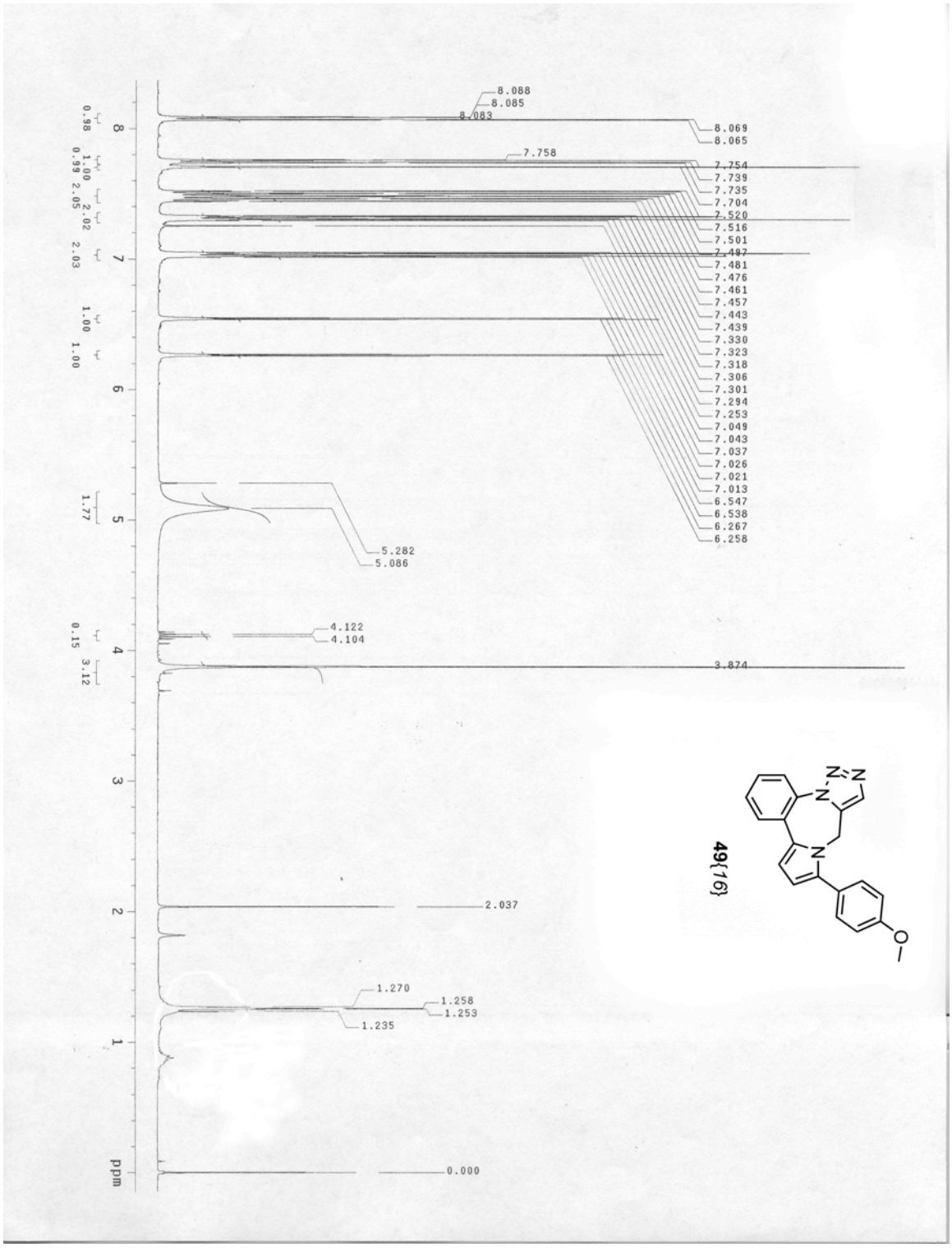
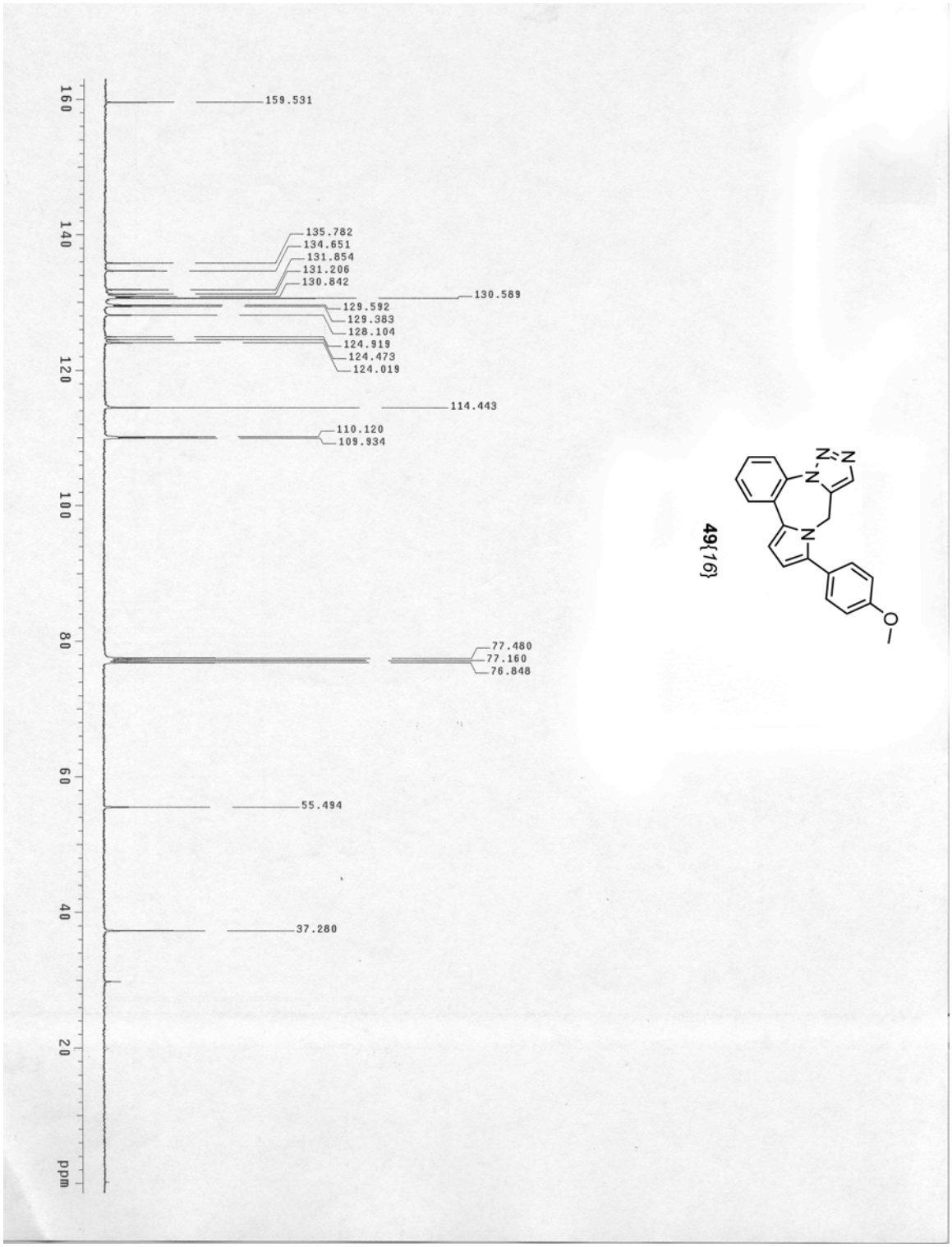
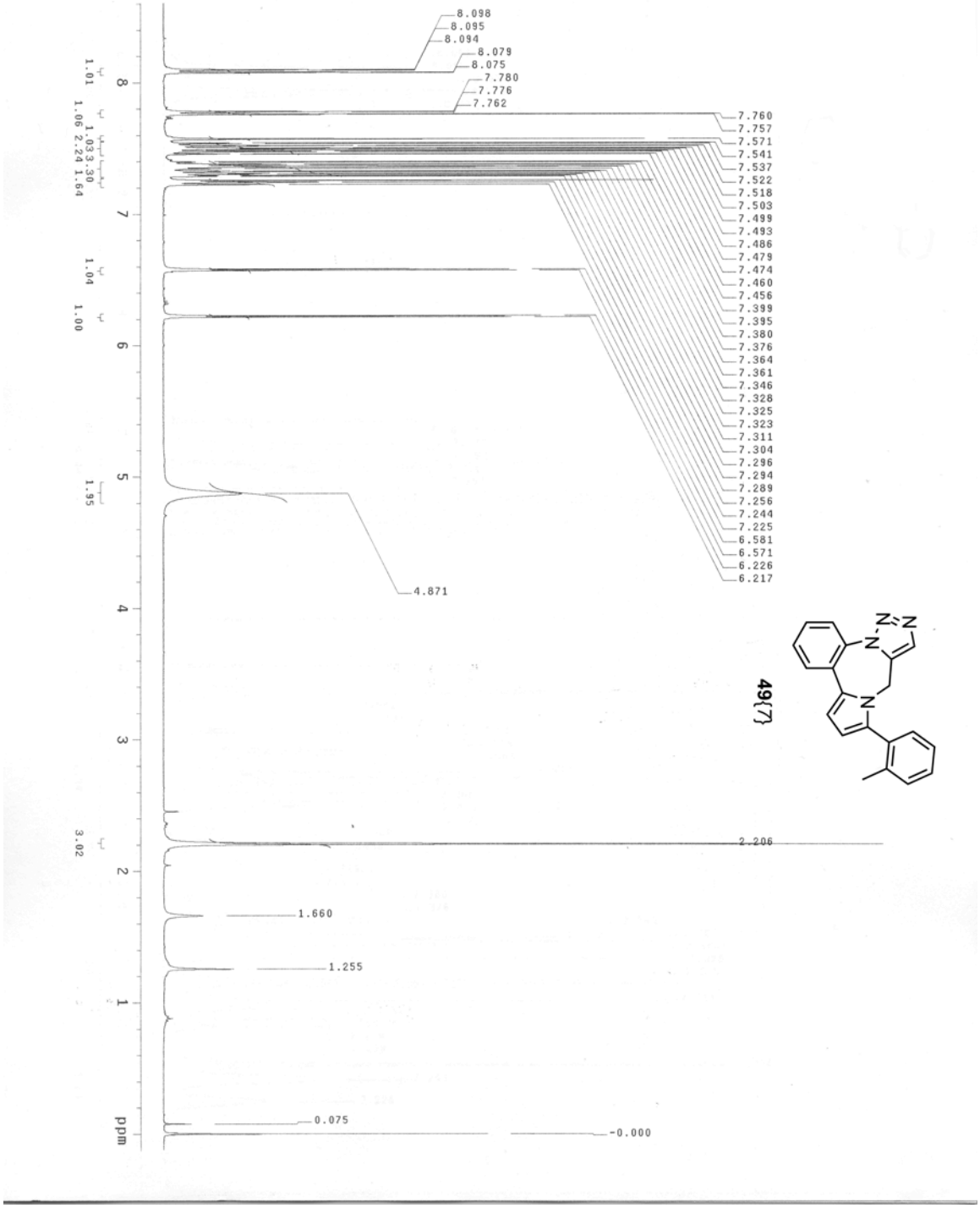
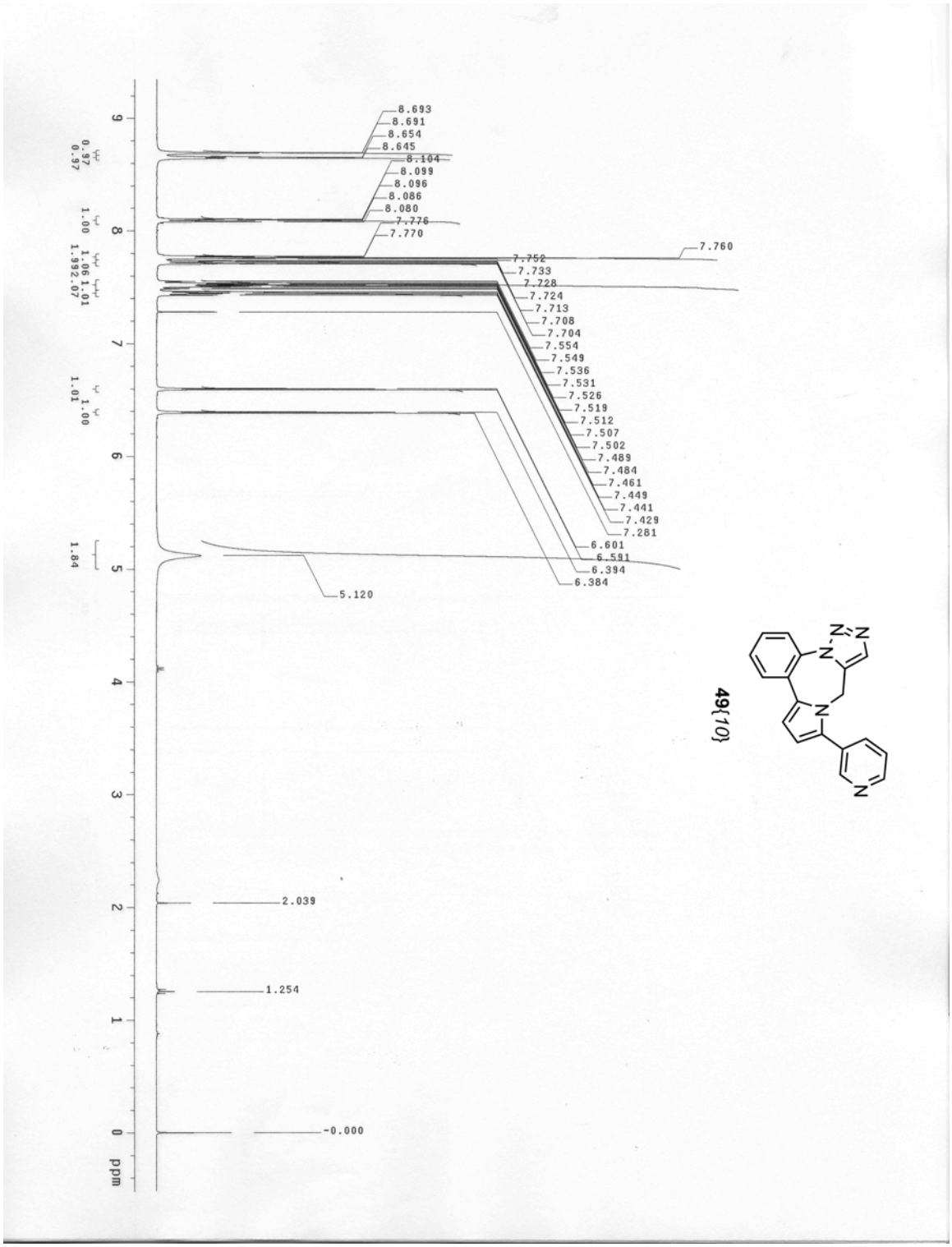
8.051
8.050
8.036
8.031
7.689
7.684
7.671
7.669
7.665
7.631
7.495
7.491
7.477
7.472
7.458
7.453
7.439
7.434
7.421
7.416
7.324
7.321
7.318
7.308
7.304
7.301
7.289
7.285
7.280
7.249
7.245
7.243
7.233
7.227
7.221
7.212
7.208
7.203
7.199
7.193
7.181
6.427
6.418
6.081
6.072
5.277
4.921
3.025
3.019
3.011
2.997
2.990
2.983
2.974
2.967
2.953
2.946
2.939
2.037
1.723
1.256
1.253
0.000
ppm
49{13}


8.137
8.130
8.124
8.118
8.106
7.808
7.788
7.779
7.769
7.763
7.576
7.570
7.557
7.554
7.545
7.536
7.534
7.514
7.494
7.265
6.611
6.602
6.432
6.423
5.299
5.139
1.673
1.255
0.000
ppm
1.06
4.25
4.29
0.33
1.00
0.99
1.88
49{15}


8.088
8.085
8.083
8.069
8.065
7.758
7.754
7.739
7.735
7.704
7.520
7.516
7.501
7.487
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
49{16}


159.531
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
49{19}


8.098
8.095
8.094
8.079
8.075
7.780
7.776
7.762
7.760
7.757
7.571
7.541
7.537
7.522
7.518
7.503
7.499
7.493
7.486
7.479
7.474
7.460
7.456
7.399
7.395
7.380
7.376
7.364
7.361
7.346
7.328
7.325
7.323
7.311
7.304
7.296
7.294
7.289
7.256
7.244
7.225
6.581
6.571
6.226
6.217
4.871
2.206
1.660
1.255
0.075
-0.000
ppm
1.01
1.06
1.03
2.24
3.30
1.64
1.04
1.00
1.95
3.02
49{7}


8.693
8.691
8.654
8.645
8.104
8.099
8.096
8.086
8.080
7.776
7.770
7.760
7.752
7.733
7.728
7.724
7.713
7.708
7.704
7.554
7.549
7.536
7.531
7.526
7.519
7.512
7.507
7.502
7.489
7.484
7.461
7.449
7.441
7.429
7.281
6.601
6.591
6.394
6.384
5.120
2.039
1.254
-0.000
ppm
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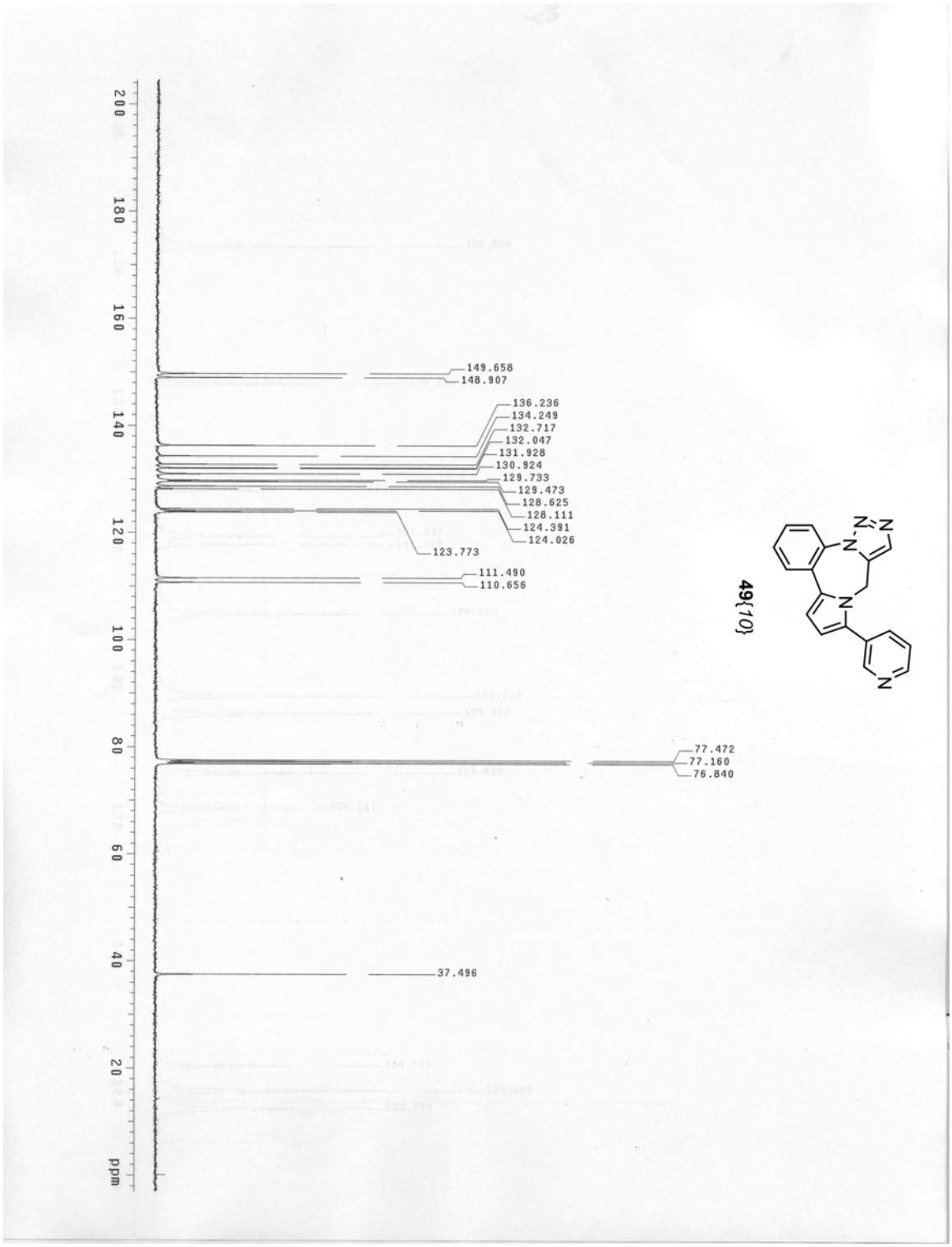
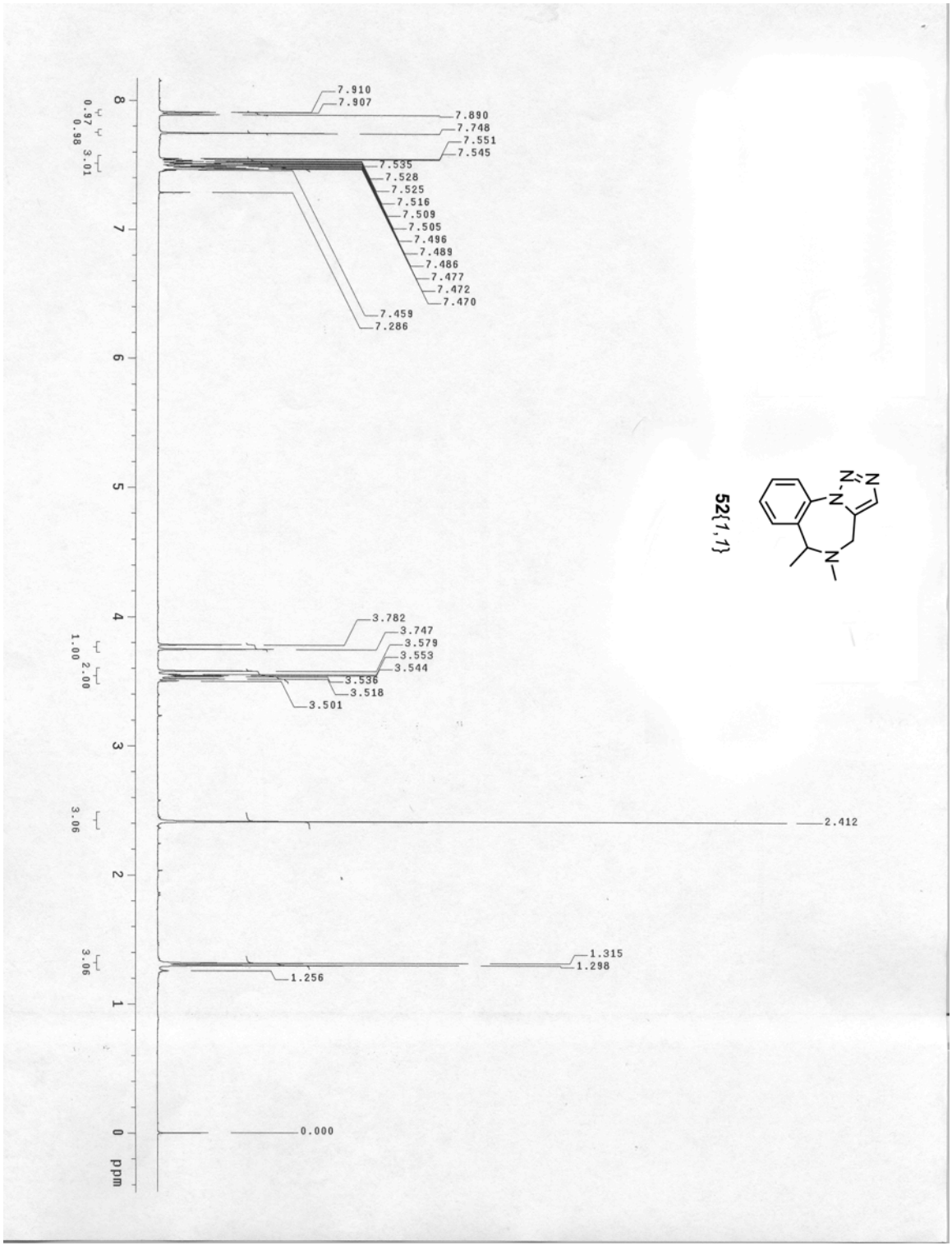
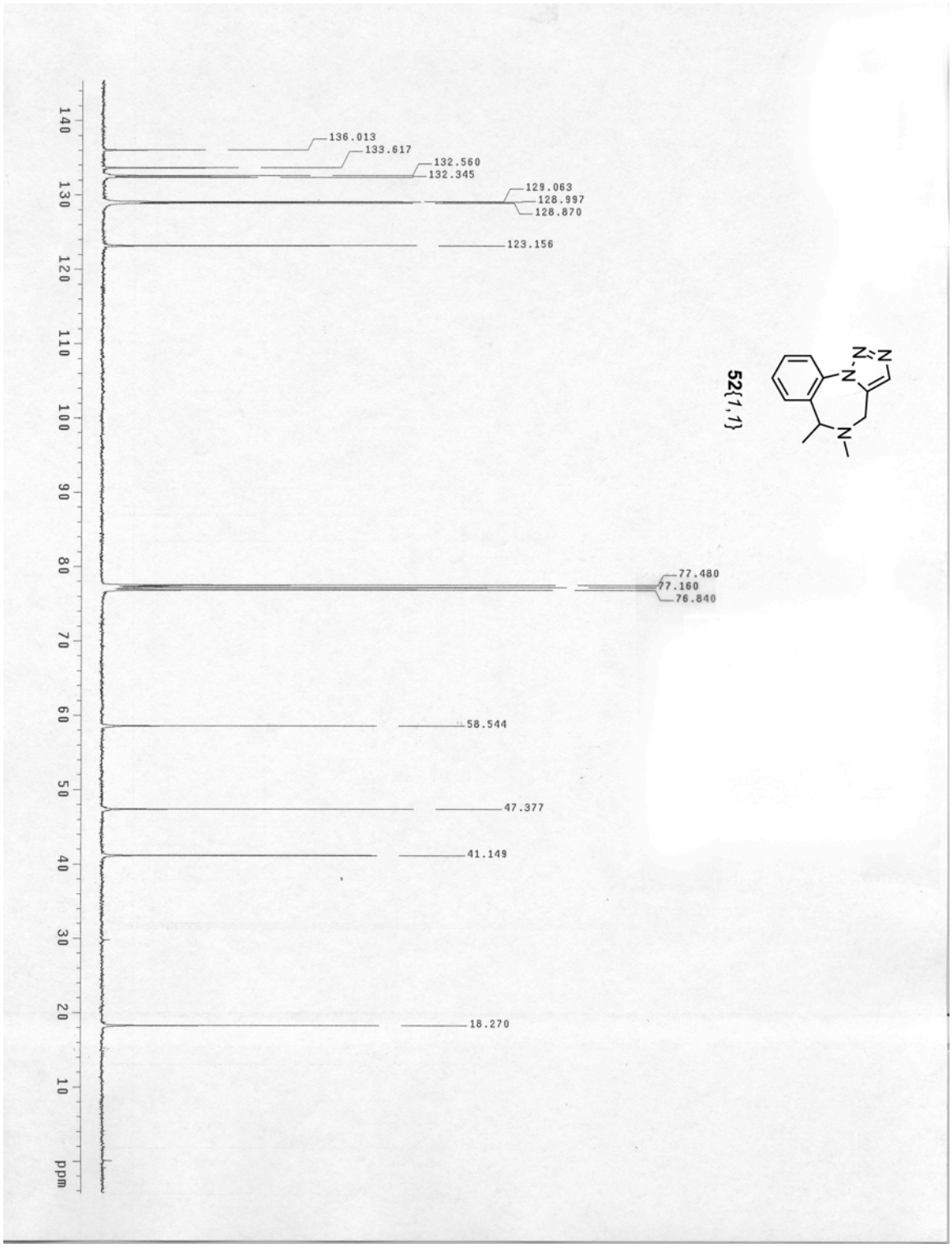
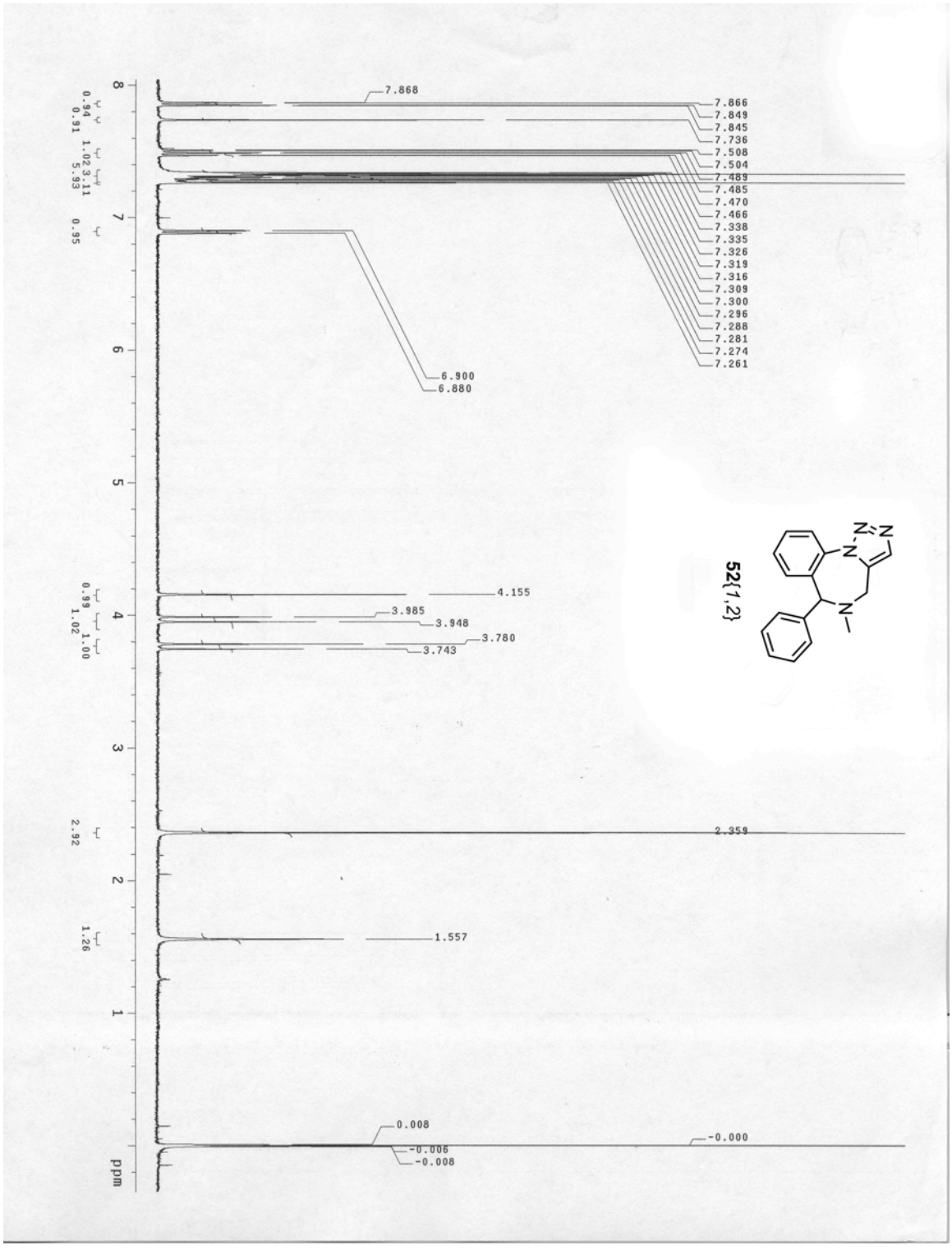
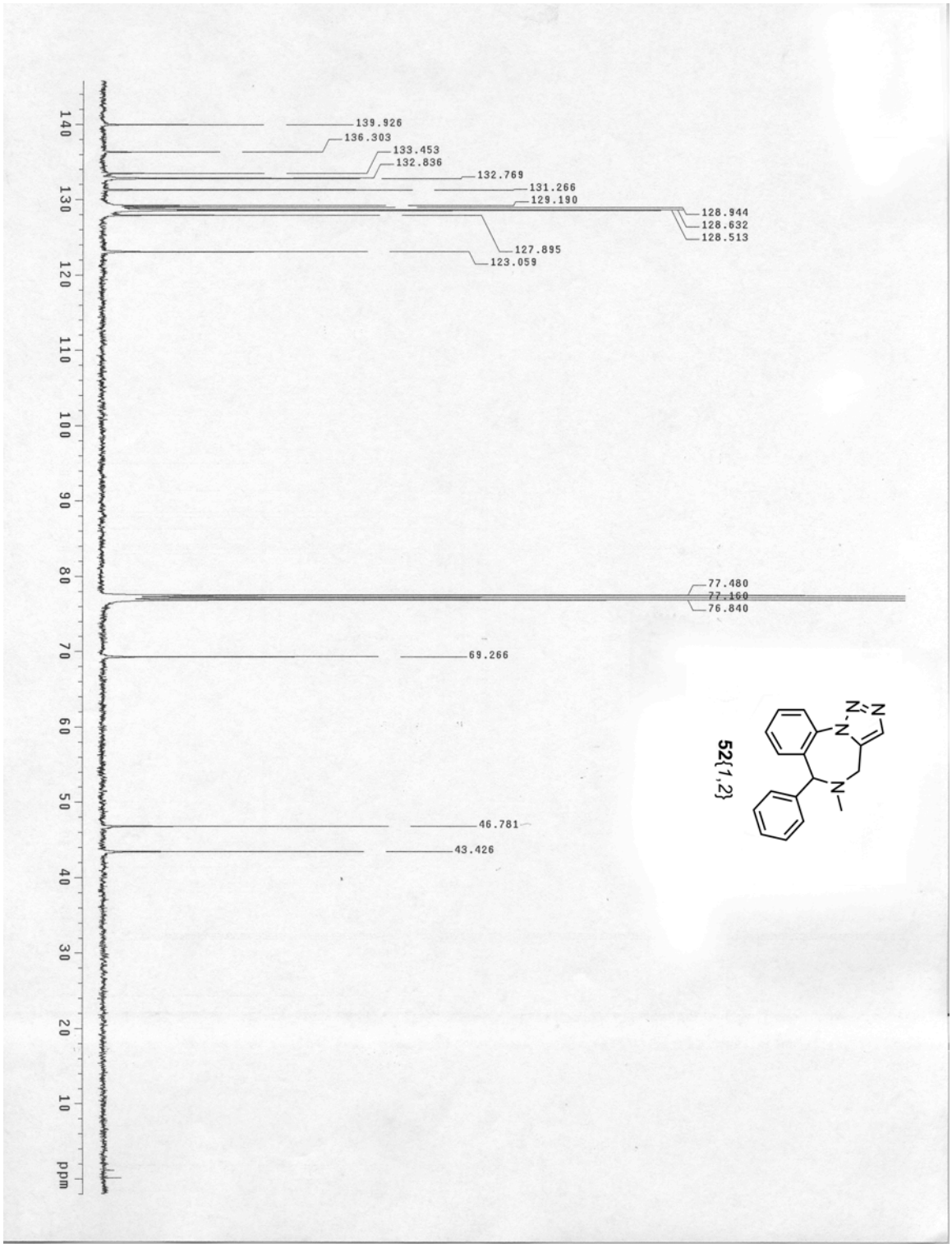
0.97
1.00
1.06
1.01
1.992.07
1.01
1.00
1.84
49{10}

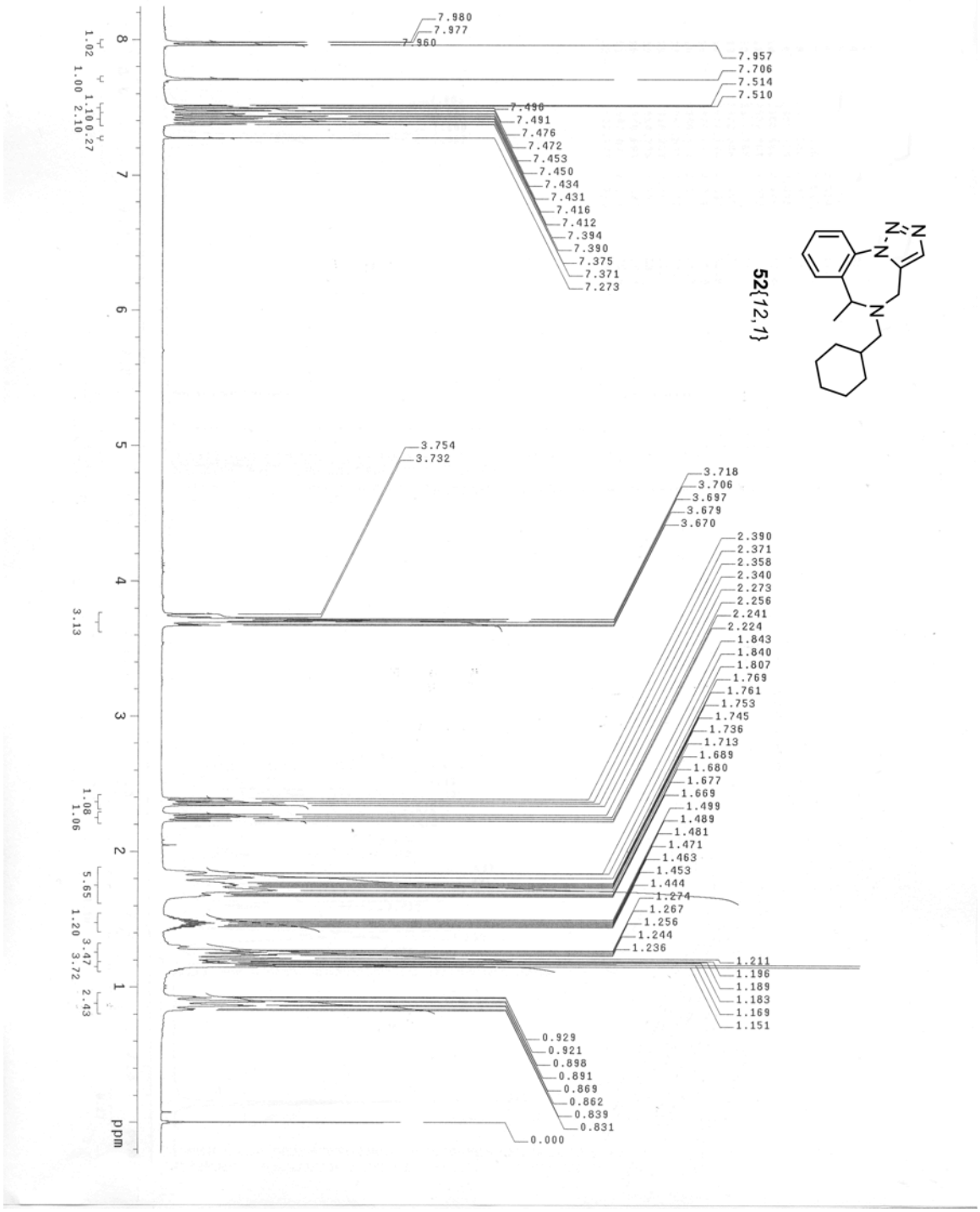

149.658
148.907
136.236
134.249
132.717
132.047
131.928
130.924
129.733
129.473
128.625
128.111
124.391
124.026
123.773
111.490
110.656
77.472
77.160
76.840
37.496
200
180
160
140
120
100
80
60
40
20
ppm
49{10}


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
52{1,1}


136.013
133.617
132.560
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
52{1,1}


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
-0.000
-0.006
-0.008
ppm
52{1,2}


139.926
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
52{1,2}


7.980
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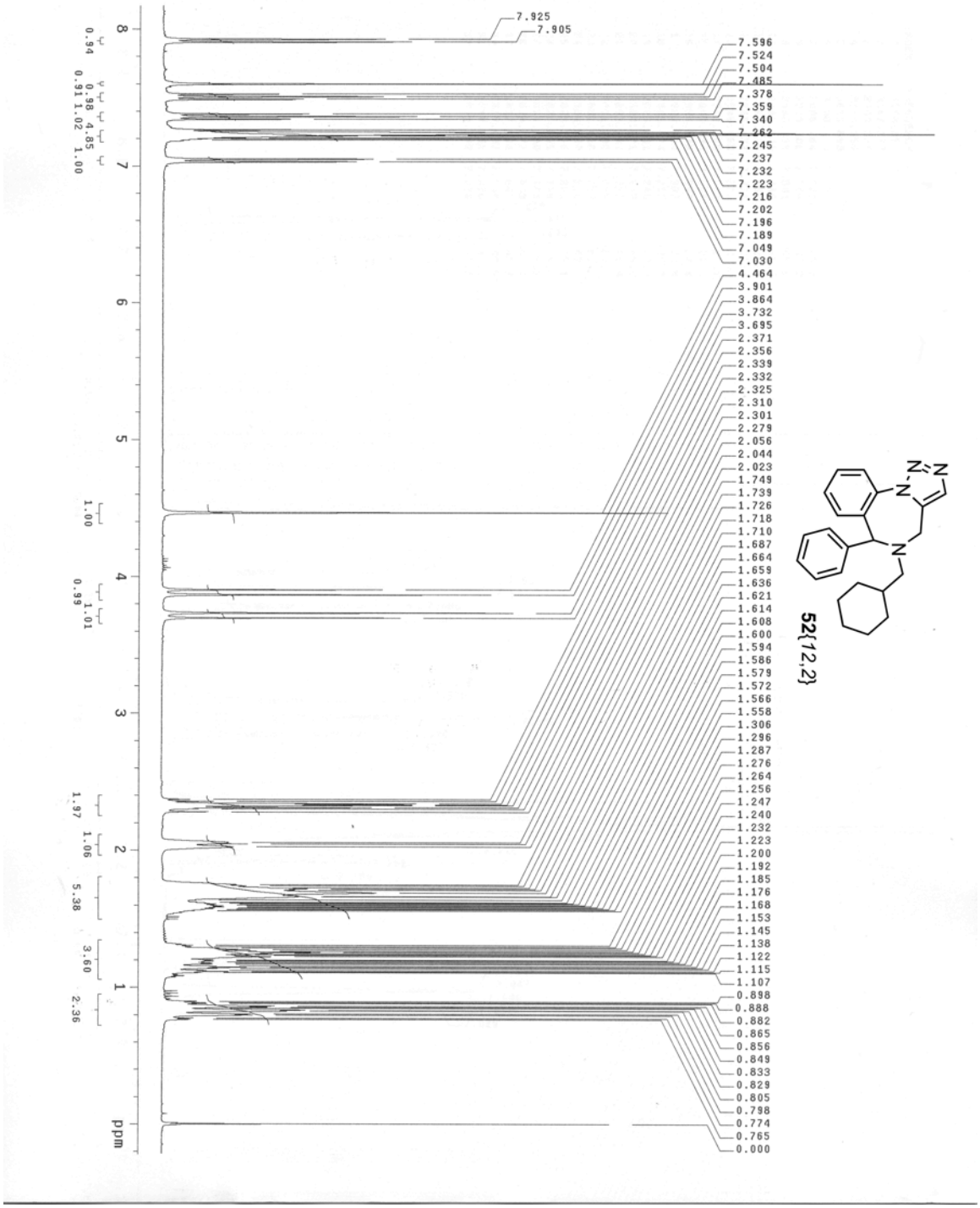
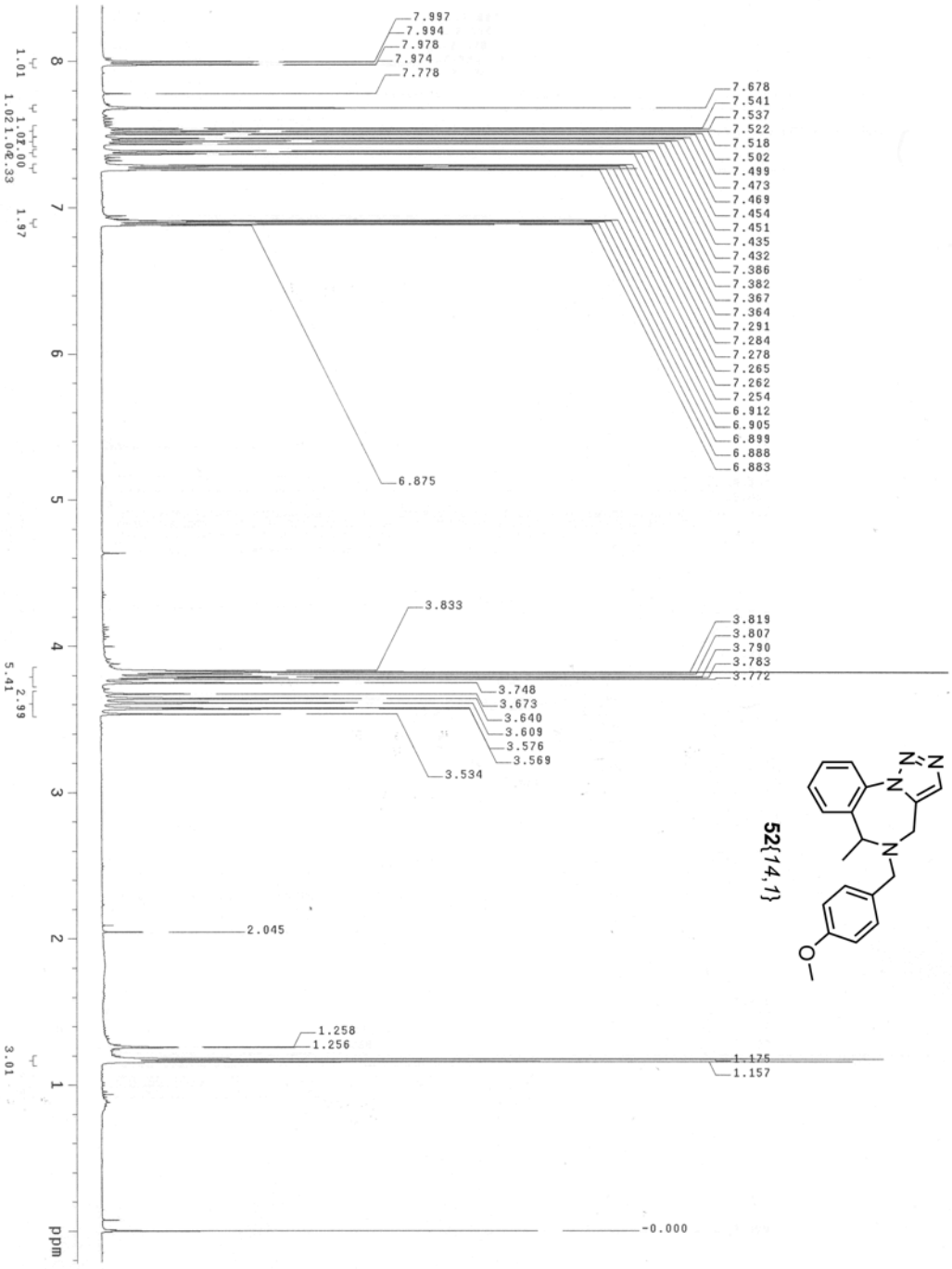
7.960
7.957
7.706
7.514
7.510
7.490
7.491
7.476
7.472
7.453
7.450
7.434
7.431
7.416
7.412
7.394
7.390
7.375
7.371
7.273
52{12,1}
3.754
3.732
3.718
3.706
3.697
3.679
3.670
2.390
2.371
2.358
2.340
2.273
2.256
2.241
2.224
1.843
1.840
1.807
1.769
1.761
1.753
1.745
1.736
1.713
1.689
1.680
1.677
1.669
1.499
1.489
1.481
1.471
1.463
1.453
1.444
1.274
1.267
1.256
1.244
1.236
1.211
1.196
1.189
1.183
1.169
1.151
0.929
0.921
0.898
0.891
0.869
0.862
0.839
0.831
0.000
ppm


7.925
7.905
7.596
7.524
7.504
7.485
7.378
7.359
7.340
7.262
7.245
7.237
7.232
7.223
7.216
7.202
7.196
7.189
7.049
7.030
4.464
3.901
3.864
3.732
3.695
2.371
2.356
2.339
2.332
2.325
2.310
2.301
2.279
2.056
2.044
2.023
1.749
1.739
1.726
1.718
1.710
1.687
1.664
1.659
1.636
1.621
1.614
1.608
1.600
1.594
1.586
1.579
1.572
1.566
1.558
1.306
1.296
1.287
1.276
1.264
1.256
1.247
1.240
1.232
1.223
1.200
1.192
1.185
1.176
1.168
1.153
1.145
1.138
1.122
1.115
1.107
0.898
0.888
0.882
0.865
0.856
0.849
0.833
0.829
0.805
0.798
0.774
0.765
0.000
0.94
0.98
4.85
0.91
1.02
1.00
1.00
0.99
1.01
1.97
1.06
5.38
3.60
2.36
ppm
52{12,2}


7.997
7.994
7.978
7.974
7.778
7.678
7.541
7.537
7.522
7.518
7.502
7.499
7.473
7.469
7.454
7.451
7.435
7.432
7.386
7.382
7.367
7.364
7.291
7.284
7.278
7.265
7.262
7.254
6.912
6.905
6.899
6.888
6.883
6.875
3.833
3.819
3.807
3.790
3.783
3.772
3.748
3.673
3.640
3.609
3.576
3.569
3.534
2.045
1.258
1.256
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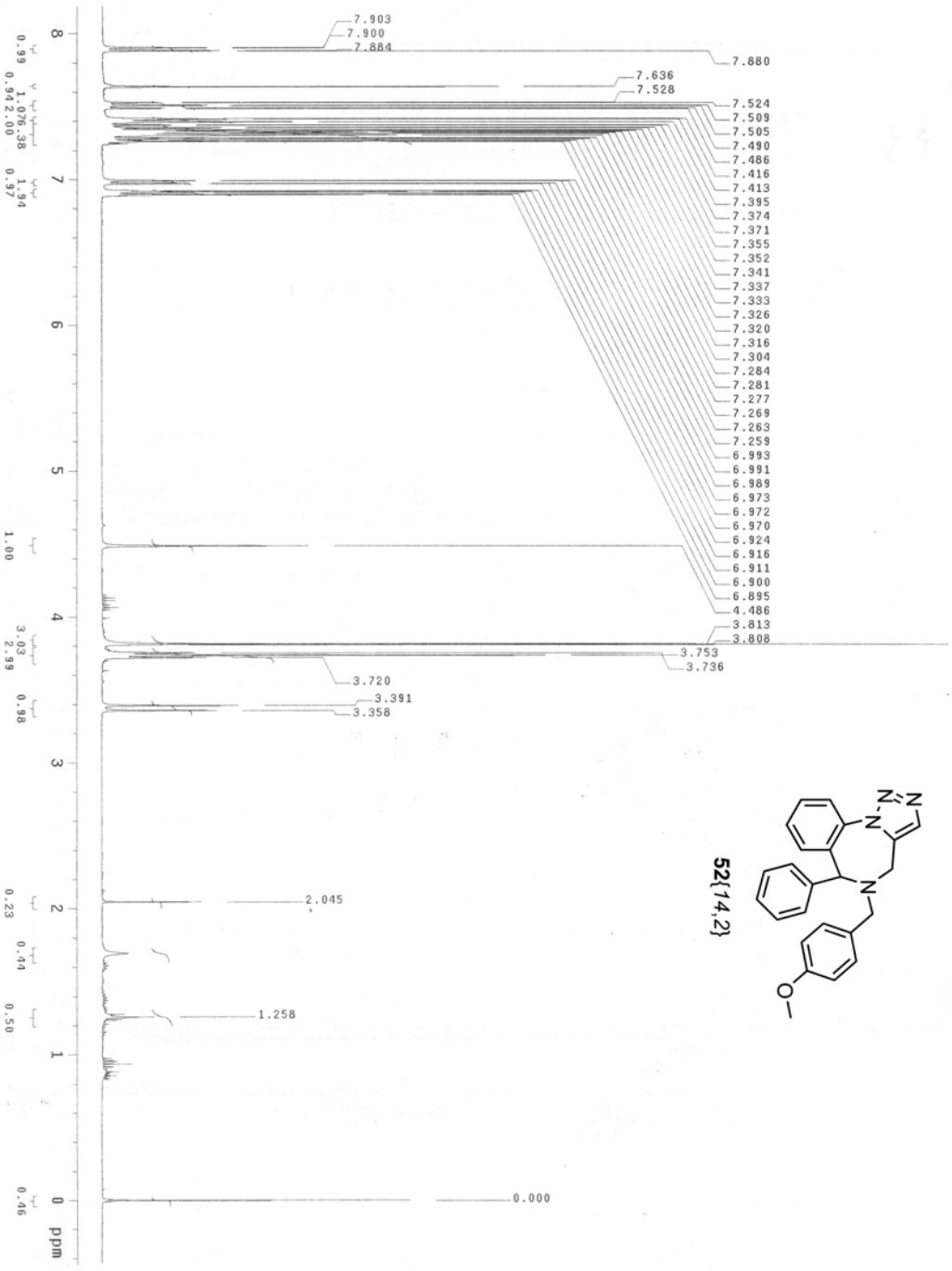
1.157
-0.000
ppm
52{14,1}


7.903
7.900
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7.880
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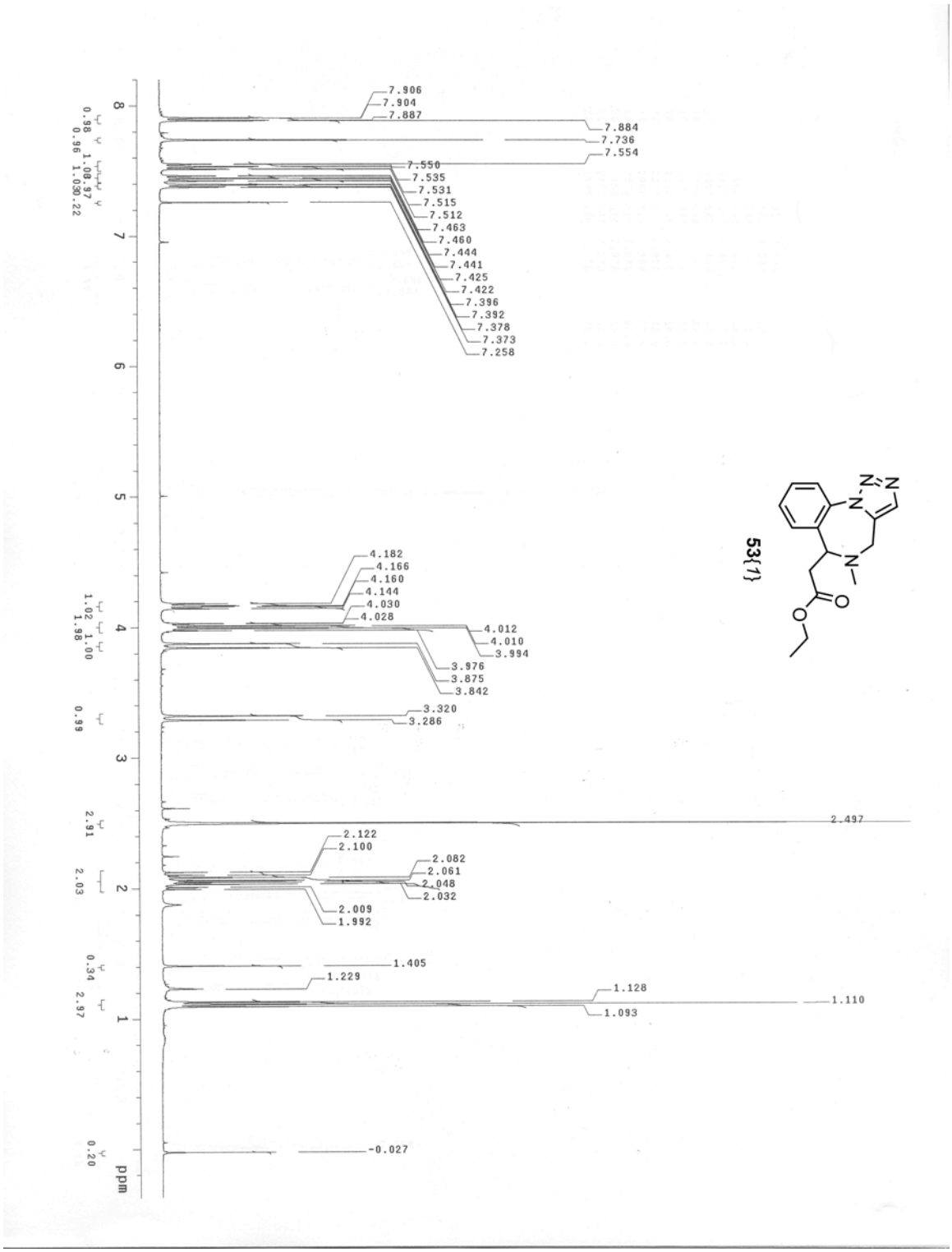
7.528
7.524
7.509
7.505
7.490
7.486
7.416
7.413
7.395
7.374
7.371
7.355
7.352
7.341
7.337
7.333
7.326
7.320
7.316
7.304
7.284
7.281
7.277
7.269
7.263
7.259
6.993
6.991
6.989
6.973
6.972
6.970
6.924
6.916
6.911
6.900
6.895
4.486
3.813
3.808
3.753
3.736
3.720
3.391
3.358
2.045
1.258
0.000
ppm
52(14,2)


7.906
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7.887
7.884
7.736
7.554
7.550
7.535
7.531
7.515
7.512
7.463
7.460
7.444
7.441
7.425
7.422
7.396
7.392
7.378
7.373
7.258
4.182
4.166
4.160
4.144
4.030
4.028
4.012
4.010
3.994
3.976
3.875
3.842
3.320
3.286
2.497
2.122
2.100
2.082
2.061
2.048
2.032
2.009
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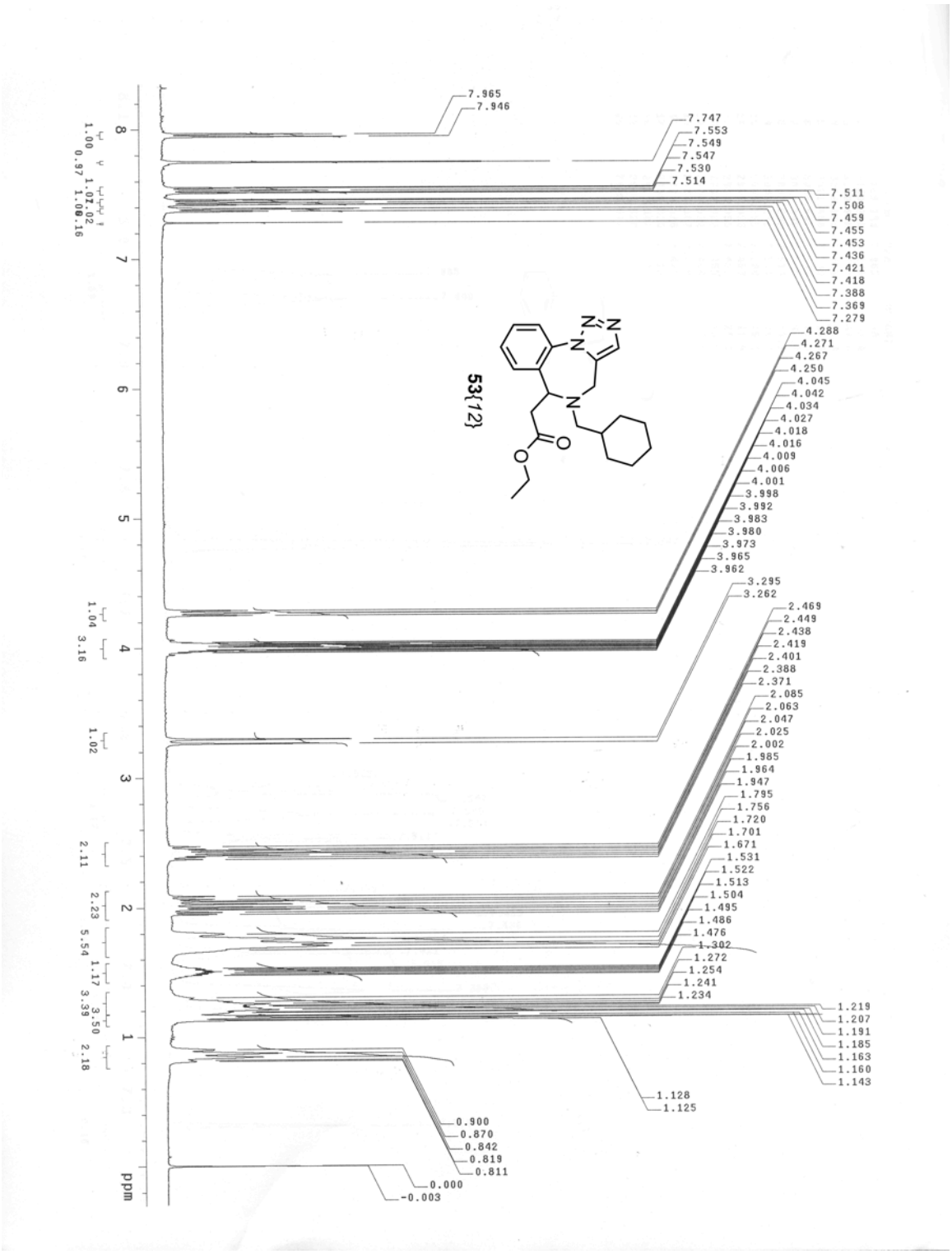
1.405
1.229
1.128
1.110
1.093
-0.027
ppm
53{1}


7.965
7.946
7.747
7.553
7.549
7.547
7.530
7.514
7.511
7.508
7.459
7.455
7.453
7.436
7.421
7.418
7.388
7.369
7.279
53{12}
4.288
4.271
4.267
4.250
4.045
4.042
4.034
4.027
4.018
4.016
4.009
4.006
4.001
3.998
3.992
3.983
3.980
3.973
3.965
3.962
3.295
3.262
2.469
2.449
2.438
2.419
2.401
2.388
2.371
2.085
2.063
2.047
2.025
2.002
1.985
1.964
1.947
1.795
1.756
1.720
1.701
1.671
1.531
1.522
1.513
1.504
1.495
1.486
1.476
1.302
1.272
1.254
1.241
1.234
1.219
1.207
1.191
1.185
1.163
1.160
1.143
1.128
1.125
0.900
0.870
0.842
0.819
0.811
0.000
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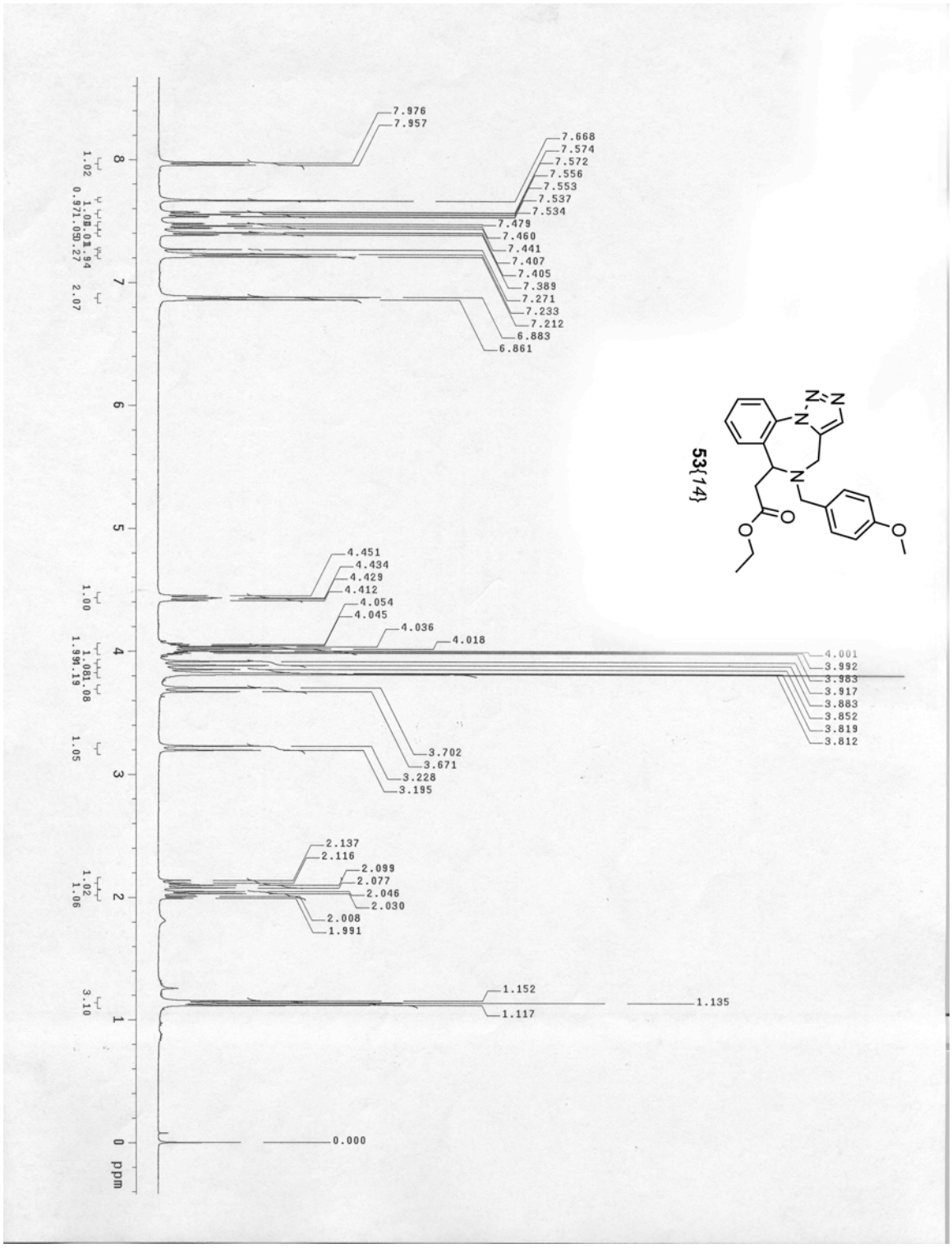
ppm


7.976
7.957
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
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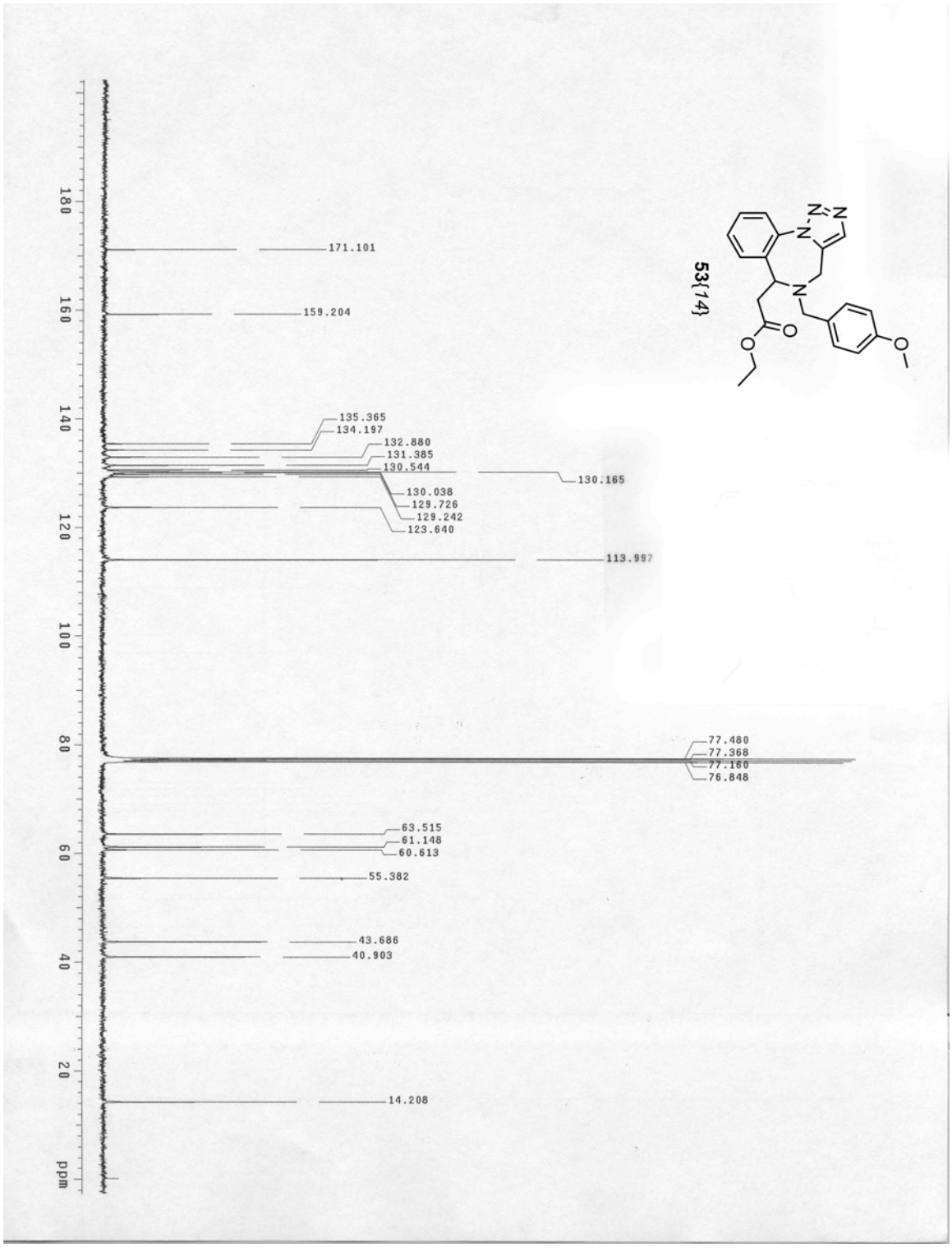
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61.148
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ppm