Supporting Information for: Rh(I)-Catalyzed Arylation of Heterocycles via C-H Bond Activation: Expanded Scope Through Mechanistic Insight.

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Materials:

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), diethyl ether, methylene chloride (CH_2Cl_2), and toluene were obtained from a Seca Solvent System by GlassContour (solvent dried over alumina under a N_2 atmosphere). Dichlorobenzene (DCB) was stirred over NaH overnight, distilled at 20 mm Hg, and stored over 3 Å molecular sieves in a glove box. THF-d_8 was stirred under N_2 over sodium/benzophenone ketyl, vacuum transferred into a sealable storage vessel, degassed using three consecutive freeze pump thaw cycles, and stored over activated 3 Å molecular sieves. Benzene-d_6 was transferred into a sealable storage vessel, degassed using three consecutive freeze pump thaw cycles, and stored over activated 3 Å molecular sieves. Diisopropylisobutylamine and diisopropylethylamine were stirred over CaH_2 overnight, distilled in vacuo or under N_2, degassed using three consecutive freeze pump thaw cycles, and stored over activated 3 Å molecular sieves. PhBr was stirred over CaH_2 overnight and distilled in vacuo. All liquid aryl bromides and heterocycles were thoroughly degassed using three freeze-pump-thaw cycles prior to introduction to the glove box. Benzoxazole and benzothiazole were distilled under vacuum prior to introduction to the glove box. Complete analytical data and synthesis procedures have been reported in the literature for $[RhCl(coe)_2]_2$ (also available from Strem),[1] 5-(4-fluoro-phenyl)-4-phenyl-1*H*-imidazole, 5-(4-fluoro-phenyl)-4-(4-pyridyl)-1*H*-imidazole,[2] and 5-(4-methoxy-phenyl)-4-phenyl-1*H*-imidazole.[3] 5-(4-Fluoro-phenyl)-4-(4-pyridyl)-1*H*-imidazole was prepared according to the procedure described in reference 2. Phosphines **1a** and **1b** were prepared as previously reported.[4]

For the arylation reactions assembled outside of the glove box, a number of material substitutions were made. THF was purchased from Acros (100 mL bottle, extra dry, <50 ppm water, packaged under N_2) and used as received. Diisopropylisobutylamine (98%) and diisopropylethylamine (99.5%, redistilled) were both purchased from Aldrich and sparged with a N_2 stream for at least 15 min prior to use. $[RhCl(cod)]_2$ was purchased from Strem and used as received. Other than benzoxazole, which was distilled as mentioned above, none of the heterocycles or aryl bromides were distilled or degassed prior to use. All of the chemicals used in these reactions were stored on a bench top with no special handling over the course of the experiments reported (ca. 1 week).

General Procedures:

Unless otherwise specified, all reactions were prepared in flame or oven-dried glassware under an inert N_2 atmosphere using either syringe and cannula techniques or a N_2-filled Vacuum Atmospheres inert atmosphere box. Microwave reactions were conducted in either 5 mL microwave vials (Biotage No. 351521 with No. 355543 stir bars and No. 352298 caps) and heated in a Biotage Initiator Eight Microwave reactor (Biotage No. 355524). Because of the high pressure generated by heating THF to 200 ºC in a sealed tube, a number of precautions were taken when using microwave heating in addition to those recommended by Biotage. First, the "high absorption level" setting was used in order to avoid erratic heating and over pressure errors in the first minutes of the reaction. The "fixed hold time" setting was used in order to ensure heating at the 200 ºC for the specified time. No more than 4 mL THF was used in the 5 mL microwave viles in order to maintain reaction pressures below the instrument maximum setting. Needle punctures in the cap septa led to mechanical failure of the septa and subsequent overpressure errors after about 1.5 h of heating at 200 ºC, so reagents were not injected into the vial through the septum. Overpressure errors were also observed with intact septa after about 12 h of heating. 1,2-Dichlorobenzene/THF mixtures (up to 1:1 v/v) can be used to avoid any problems with high pressures with no decrease in reaction yield or catalyst lifetime.

Flash column chromatography was carried out using a Biotage SP Flash Purification System (Biotage No. SP1-B1A) with Flash+ cartridges (Biotage No. FPK0-1107-16046) using ethyl acetate/hexanes or methanol/CH_2Cl_2 gradients calculated using the TLC data recorded for each compound (vide infra). NMR spectra (^1H, ^{13}C, and ^{31}P) were obtained on a Bruker AMX-400 or AVB-400 spectrometer at

room temperature. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. ^{1}H resonances are referenced to residual protonated solvent ($CHCl_3$, 7.26 ppm; CD_3OD, 3.16; C_6D_6, 7.16 ppm; d_8-THF, 3.58), while ^{31}P resonances are referenced to a trimethylphosphate external standard (3.0 ppm). ^{13}C NMR spectra are included for 2-arylimidazoles not reported in the literature. In some cases rapid tautomerization of the benzimidazole moiety apparently led to broadening and or absence of 1-2 of the expected ^{13}C resonances as has been previously reported.[5] The N-H proton of the arylated benzimidazoles was note observed in many cases due to rapid exchange with solvent or water in the solvent. Mass spectrometry was performed by the University of California, Berkeley mass spectrometry facility.

Experimental Procedures:

Chloro(9-cyclohexyl-9-phosphabicyclo[4.2.1]nonane)((*Z*)-9-cyclohexyl-9-phosphabicyclo[4.2.1] non-3-ene)rhodium (I) (3): In an inert atmosphere box, a glass tube fitted with a Kontes adapter was charged with $[RhCl(coe)_2]_2$ (0.107 g, 0.15 mmol), **1a** (0.135 g, 0.6 mmol), and THF (5 mL). The tube was sealed with a Kontes stopper, removed from the box, heated at 125 °C for 2 h, cooled to room temperature, and returned to the box. The reaction mixture was concentrated to yield a brownish-yellow solid. This solid was washed with pentane to yield 0.147 g of **3** as a bright yellow solid (84%). A sample of this material was placed in a small vial and dissolved in THF. This vial was nested in a larger vial containing pentane. The larger vial was sealed and crystals of **3** suitable for X-ray analysis formed after 1-2 days. ^{1}H NMR (400 MHz, C_6D_6): δ 3.60 (m, 2H), 3.16 (m, 1H), 2.95 (m, 1H), 2.69 (m, 2H), 2.44-1.95 (m, 8H), 1.95-1.76 (m, 4H), 1.76-1.55(m, 10H), 1.55-1.41 (m, 6H), 1.41-1.16 (m, 10H), 1.19-0.99 (4H). ^{31}P NMR (162 MHz, C_6D_6): δ 87.0 (dd, J_1 = 385.2 Hz, J_2 = 133.3 Hz), 48.7 (dd, J_1 = 384.2 Hz, J_2 = 120.5 Hz). HRMS-FAB (m/z): $[M]^+$ calcd for $C_{28}H_{48}P_2ClRh$, 584.197484; found, 584.195910.

(*Z*)-1-Phenyl-2,3,6,7-tetrahydro-1*H*-phosphepine (5a): Prepared using the method described for **5b**. The intermediate **4a** was obtained in 74% yield as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 2H), 7.33 (m, 3H), 5.80 (m, 2H), 2.65 (m, 2H), 2.15 (m, 2H), 1.89 (m, 2H), 1.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.57 (d, J = 95.1 Hz), 132.05, 131.64 (d, J = 2.9 Hz), 129.77 (d, J = 9.5 Hz), 128.57 (d, J = 11.0 Hz), 28.92 (d, J = 65.9 Hz), 19.11 (d, J = 5.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.67. HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{15}PO$, 206.086054; found, 206.085982. Phosphine **5a** (0.36 g, 78%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, d_8-THF): δ 7.43 (t, J = 7.1 Hz, 2H), 7.31 (m, 2H), 7.24 (m, 1H), 5.76 (m, 2H), 2.50 (m, 2H), 2.37 (m, 2H), 1.95 (m, 2H), 1.86 (m, 2H). ^{13}C NMR (125 MHz, d_8-THF): δ 141.6 (d, J = 16.8 Hz), 131.9 (s), 131.1 (d, J = 15.8 Hz), 128.5 (d, J = 5.3 Hz), 127.8 (s), 24.6 (d, J = 14.8 Hz), 24.2 (d, J = 8.6 Hz). ^{31}P NMR (162 MHz, C_6D_6): δ -14.6. HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{15}P$, 190.091139; found, 190.091107.

(*Z*)-1-Cyclohexyl-2,3,6,7-tetrahydro-1*H*-phosphepine (5c): Prepared using the method described for **5b**. The intermediate **4c** was obtained in 79% yield as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (m, 2H), 2.53 (m, 2H), 2.09 (m, 2H), 1.76 (m, 6H), 1.61 (m, 1H), 1.48 (m, 3H), 1.18 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.88, 37.71 (d, J = 67.3 Hz), 26.23 (d, J = 13.2 Hz), 25.78, 24.78 (d, J = 61.5 Hz), 24.83 (d, J = 2.9 Hz), 18.83 (d, J = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 51.84. HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{21}PO$, 212.133004; found, 212.132772. Phosphine **5c** (0.13 g, 62%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 5.70 (m, 2H), 2.29 (m, 4H), 1.64 (m, 8H), 1.34 (m, 3H), 1.17 (m, 4H). ^{13}C NMR (125 MHz, C_6D_6): δ 132.0 (s), 36.9 (d, J = 11.0 Hz), 29.5 (d, J = 13.4 Hz), 27.2 (d, J = 9.6 Hz), 26.9 (s), 24.4 (d, J = 7.7 Hz), 22.1 (d, J = 16.3 Hz). ^{31}P NMR (162 MHz, C_6D_6): δ -11. HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{21}P$, 196.138089; found, 196.138317.

(*Z*)-1-*iso*-Propyl-2,3,6,7-tetrahydro-1*H*-phosphepine (5d): Prepared using the method described for **5b**. The intermediate **4d** was obtained in quantitative yield as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (m, 2H), 2.49 (m, 2H), 2.06 (m, 2H), 1.72 (m, 3H), 1.45 (m, 2H), 1.01 (dd, J_1 = 15.4 Hz,

J_2 = 7.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.83, 27.39 (d, J = 67.3 Hz), 24.51 (d, J = 61.5 Hz), 18.75 (d, J = 5.1 Hz), 15.07 (d, J = 2.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 54.61. HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{17}PO$, 172.101704; found, 172.101401. Phosphine **5d** (0.23 g, 51%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 5.69 (m, 2H), 2.27 (m, 4H), 1.63 (m, 2H), 1.42 (m, 1H), 1.30 (m, 2H), 0.97 (dd, J_1 = 13.1 Hz, J_2 = 6.8 Hz, 6H). ^{31}P NMR (162 MHz, C_6D_6): δ -6.0. ^{13}C NMR (100 MHz, C_6D_6): δ 131.6 (s), 26.0 (d, J = 10.2 Hz), 24.0 (d, J = 7.3 Hz), 22.4 (d, J = 16.8 Hz), 19.2 (d, J = 16.1 Hz). HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{17}P$, 156.106789; found, 156.106420.

(*Z*)-1-Methyl-2,3,6,7-tetrahydro-1*H*-phosphepine (5e): Prepared using the method described for **5b**. The intermediate **4e** was obtained in 78% yield as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (m, 2H), 2.13 (m, 2H), 1.75 (m, 2H), 1.49 (m, 2H), 1.31 (m, 2H), 1.07 (d, J = 12.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.42, 28.67 (d, J = 65.1 Hz), 18.81 (d, J = 4.4 Hz), 14.73 (d, J = 67.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 48.96. HRMS-EI (m/z): $[M]^+$ calcd for $C_7H_{13}PO$, 144.070404; found, 144.070530. Phosphine **5e** (0.16 g, 35%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 5.67 (m, 2H), 2.26 (m, 4H), 1.61 (m, 2H), 1.16 (m, 2H), 0.85 (d, J_1 = 3.2 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 132.0 (s), 26.4 (d, J = 13.4 Hz), 24.0 (d, J = 7.2 Hz), 12.1 (d, J = 15.4 Hz). ^{31}P NMR (162 MHz, C_6D_6): δ -34.4. HRMS-EI (m/z): $[M]^+$ calcd for $C_7H_{13}P$, 128.075489; found, 128.075668.

Chloro[(*Z*)-1-Cyclohexyl-2,3,6,7-tetrahydro-1*H*-phosphepine]rhodium (I) dimer (7): In an inert atmosphere box, a glass tube fitted with a Kontes adapter was charged with $[RhCl(coe)_2]_2$ (0.109 g, 0.15 mmol), **5c** (0.060 g, 0.3 mmol), and THF (12 mL). The tube was sealed with a Kontes stopper, removed from the box, heated at 70 °C for 45 min, cooled to room temperature, and returned to the box. The reaction mixture was concentrated to yield a brownish-yellow solid. This solid was washed with pentane to yield 0.069 g of **7** as a yellow solid (67%). A sample of this material was placed in a small vial and dissolved in THF. This vial was nested in a larger vial containing pentane. The larger vial was sealed and crystals of **7** suitable for X-ray analysis formed after 1-2 days. ^{1}H NMR (400 MHz, C_6D_6): δ 4.38 (br s, 2H), 2.01-1.79 (m, 4H), 1.79-1.00 (m, 11H), 1.00-0.86 (m, 2H), 0.86-0.71 (m, 2H). ^{31}P NMR (162 MHz, C_6D_6): δ 77.1 (dd, J_1 = 170.9 Hz, J_2 = 49.1 Hz).

Typical Procedure for Coupling Benzimidazole and Bromobenzene using Phosphepine Ligands (Conventional Heating Protocol in an NMR Tube): In an inert atmosphere box, $[RhCl(coe)_2]_2$ (0.0029 g, 0.0020 mmol), **5b** (0.0020 g, 0.0060 mmol), and d_8-THF (0.4 mL) were added to a glass vial. The vial was sealed with a septum and the catalyst mixture was agitated until the solids dissolved. Similarly, benzimidazole (0.0473 g, 0.400 mmol), bromobenzene (0.84 mL, 0.80 mmol), diisopropylisobutylamine (0.245 mL, 1.2 mmol), and 2,6-dimethoxytoluene (0.0255 g, 0.168 mmol) were added to a 2 mL volumetric flask. The flask was filled to 2 mL total volume with THF (non-deuterated solvent used), a stir bar was added, the flask was sealed, and the mixture was stirred to give a homogeneous solution. To an NMR tube was added 0.2 mL of the catalyst solution and 0.2 mL of the substrate solution. The tube was fitted with a Cajon adapter, removed from the inert atmosphere box, and flame sealed. The tube was then heated at 150 °C, and the reaction progress was monitored by ^{1}H NMR spectroscopy (see Figure 4.5).

2-phenyl-1*H*-benzo[*d*]imidazole (17): Typical Procedure for Cross-Coupling Azoles and Aryl Bromides (Microwave Protocol). In an inert atmosphere box, a stir bar, the appropriate heterocycle, e.g., benzimidazole (0.0481 g, 0.407 mmol), and 1 mL of THF were added to a 5 mL glass microwave vial. Into a separate vial were weighed **5b** (0.102 g, 0.0599 mmol) and $[RhCl(coe)_2]_2$ (0.0143 g, 0.0200 mmol), and the catalyst was transferred to the microwave vial using 2 mL of THF. The appropriate aryl bromide, e.g., bromobenzene (0.126 g, 0.802 mmol) was transferred to the microwave vial using 1 mL of THF, and *i*-Pr$_2$*i*-BuN (0.245 mL, 1.19 mmol) added directly to the vial via syringe. The vial was sealed, removed from the inert atmosphere box, and heated for 2 h at 200 ºC. The reaction mixture was

then cooled, quenched with excess Et_3N (0.5 mL), and concentrated under reduced pressure. The residue was dissolved in a minimal amount of methanol/methyelene chloride (ca. 1-2 mL), loaded onto a silica gel samplet (Biotage No. SAM-1107-16016), and purified using flash chromatography. A suitable gradient was calculated by the Biotage SP (10-80% ethyl acetate/hexanes) given a product R_f of 0.32 in 40% ethyl acetate/hexanes. The desired product was obtained as 0.0775 g (98% yield, Table 2, entry 7) of a white solid. For other heterocycles, the concentration of the reactants was increased to 0.3 M. The amount of heterocycle (mmol) and the concentration (M) of the reaction is therefore provided for each entry. mp 280-282 °C (lit. 285-286 °C).[6] ^{1}H NMR (400 MHz, CD_3OD): δ 8.10 (m, 2H), 7.61 (br s, 2H), 7.54 (m, 2H), 7.27 (m, 2H).

2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (11): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-80% ethyl acetate/hexanes; R_f = 0.5, 40% ethyl acetate/hexanes) to provide 0.984 g (93%, 0.4 mmol scale) of **11** as an off-white solid. mp 266-267 °C (lit. 264-266 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.50 (br s, 2H), 7.16 (m, 2H).

2-(4-(methylsulfinyl)phenyl)-1*H*-benzo[*d*]imidazole (12): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (0-10% methanol/ethyl acetate; R_f = 0.19, 2% methanol/ethyl acetate) to provide 0.0616 g (60%, 0.4 mmol scale) of **12** as an off-white solid. mp 212-214 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 8.16 (m, 2H), 7.74 (m, 2H), 7.50 (br s, 2H), 7.16 (m, 2H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, CD_3OD): δ 150.33, 146.52, 132.47, 127.28, 124.23, 122.94 (br), 122.33 (br), 42.06. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3177 (br, w), 1420 (s), 1314 (m), 1276 (m), 1082 (m), 1028 (s), 1010 (s). HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{12}N_2OS$, 256.067035; found, 256.067775.

2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (13): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-80% ethyl acetate/hexanes; R_f = 0.42, 40% ethyl acetate/hexanes) to provide 0.0785 g (86%, 0.4 mmol scale) of **13** as an off-white solid. mp 288-290 °C (lit. 288-290 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.46 (br s, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.12 (m, 2H).

1-(4-(1*H*-benzo[*d*]imidazol-2-yl)phenyl)propan-1-one (14): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (R_f = 0.21, 40% ethyl acetate/hexanes) to provide 0.0916 g (91%, 0.4 mmol scale) of **14** as an off-white solid. mp 210-212 °C (lit. 212-213 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 8.06 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.49 (br s, 2H), 7.15 (m, 2H), 2.96 (q, *J* = 7.3 Hz, 2H). 1.06 (t, *J* = 7.1 Hz, 3H).

ethyl 4-(1*H*-benzo[*d*]imidazol-2-yl)benzoate (15): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (R_f = 0.40, 40% ethyl acetate/hexanes) to provide 0.0769 g (96%, 0.3 mmol scale) of **15** as an off-white solid. mp 245-247 °C (lit. 242 °C).[7] ^{1}H NMR (400 MHz, CD_3OD): δ 8.04 (m, 4H), 7.49 (br s, 2H), 7.15 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

4-(1*H*-benzo[*d*]imidazol-2-yl)benzamide (16): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (1-15% methanol/ethyl acetate; R_f = 0.28, 5% methanol/ethyl acetate) to provide 0.0807 g (85%, 0.4 mmol scale) of **16** as an off-white solid. mp 340-341 °C (lit. 336-337 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.49 (br d, 2H), 7.15 (m, 2H).

***N*-(4-(1*H*-benzo[*d*]imidazol-2-yl)phenyl)ethanamide (18)**: The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (1-10% methanol/ethyl acetate; R_f = 0.42, 5% methanol/ethyl acetate) to provide 0.0663 g (88%, 0.3 mmol scale) of **18** as an off-white solid. mp 308-310 °C (lit. 313-314 °C).[8] ^{1}H NMR (400 MHz, CD_3OD): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.44 (br s, 2H), 7.10 (m, 2H), 2.02 (s, 3H).

2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (19): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-80% ethyl acetate/hexanes; R_f = 0.18, 40% ethyl acetate/hexanes) to provide 0.0630 g (69%, 0.4 mmol scale) of **19** as an off-white solid. mp 227-228 °C (lit. 229-230 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 8.05 (m, 2H), 7.59 (br s, 2H), 7.25 (m, 2H), 7.10 (m, 2H), 3.90 (s, 3H).

4-(1*H*-benzo[*d*]imidazol-2-yl)phenol (20): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-100% ethyl acetate/hexanes; R_f = 0.27, 50% ethyl acetate/hexanes) to provide 0.0417 g (66%, 0.3 mmol scale) of **20** as an off-white solid. mp 294-296 °C (lit. 298 °C).[9] ^{1}H NMR (400 MHz, CD_3OD): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.40 (br s, 2H), 7.07 (m, 2H), 6.78 (d, *J* = 8.8 Hz, 2H).

2-(3,5-dimethylphenyl)-1*H*-benzo[*d*]imidazole (21): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-80% ethyl acetate/hexanes; R_f = 0.45, 40% ethyl acetate/hexanes) to provide 0.0604 g (67%, 0.4 mmol scale) of **21** as an off-white solid. mp 260-263 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 7.55 (s, 2H), 7.43 (m, 2H), 7.09 (m, 2H), 6.98 (s, 1H), 2.24 (s, 6H). ^{13}C NMR (100 MHz, CD_3OD): δ 152.3, 138.6, 131.5, 129.4, 128.4, 126.5, 124.2, 122.4, 20.0. HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{14}N_2$, 222.115699; found, 222.115986. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2909 (br, w), 1606 (w), 1537 (w), 1465 (w), 1446 (m), 1405 (m), 1361 (w), 1323 (w), 1273 (m), 1227 (w).

4-(1*H*-benzo[*d*]imidazol-2-yl)-2,6-dimethylaniline (22): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-100% ethyl acetate/hexanes; R_f = 0.55, 2% methanol/ethyl acetate) to provide 0.0402 g (63%, 0.3 mmol scale) of **22** as an off-white solid. mp 260 °C (decomp.). ^{1}H NMR (400 MHz, CD_3OD): δ 7.50 (s, 2H), 7.36 (m, 2H), 7.03 (m, 2H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, CD_3OD): δ 153.4, 146.1, 138.7 (br), 126.4, 121.8, 121.5, 117.7, 113.8, 16.5. HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{15}N_3$, 237.126598; found, 237.126637. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3394 (m), 2916 (br, m), 1622 (s), 1490 (w), 1470 (m), 1450 (m), 1425 (s), 1396 (m), 1361 (m), 1327 (w), 1271 (m), 1230 (w).

2-(1-methyl-1*H*-indol-5-yl)-1*H*-benzo[*d*]imidazole (23): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-100% ethyl acetate/hexanes; R_f = 0.10, 40% ethyl acetate/hexanes) to provide 0.0615 g (63%, 0.4 mmol scale) of **23** as an off-white solid. mp 222-223 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 8.16 (d, *J* = 1.5 Hz, 1H), 7.79 (dd, J_1 = 8.6 Hz, J_2 = 1.7 Hz, 1H), 7.43 (m, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 7.08 (m, 2H), 6.43 (d, *J* = 3.0 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 153.8, 138.7, 137.9, 130.3, 128.8, 122.1, 120.3, 119.9, 119.4, 114.0, 109.5, 101.3, 31.6. HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{13}N_3$, 247.110948; found, 247.111333. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2910 (br, w), 1624 (w), 1550 (m), 1512 (w), 1489 (w), 1457 (s), 1445 (s), 1416 (s), 1402 (s), 1359 (m), 1338 (m), 1318 (m), 1274 (s).

2-(benzofuran-5-yl)-1*H*-benzo[*d*]imidazole (24): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-100% ethyl acetate/hexanes; R_f = 0.32, 40% ethyl acetate/hexanes) to provide 0.0763 g (81%, 0.4 mmol scale) of **24** as an off-white solid. mp 207-209 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 8.21 (d, J = 1.8 Hz, 1H), 7.92 (dd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1H), 7.72 (d, J = 2.3 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.46 (br, s, 2H), 7.11 (m, 2H), 6.84 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD): δ 156.0, 152.5, 146.6, 138.9 (br), 128.2, 124.7, 123.0, 122.4, 119.7, 114.4 (br), 111.5, 106.5. HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{10}N_2O$, 234.079313; found, 234.079549. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3110 (br, w), 2919 (br, w), 2677 (br, w), 1732 (br, w), 1621 (w), 1592 (w), 1554 (w), 1530 (w), 1470 (w), 1442 (s), 1410 (m), 1371 (m).

2-(benzo[*b*]thiophen-5-yl)-1*H*-benzo[*d*]imidazole (25): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-100% ethyl acetate/hexanes; R_f = 0.39, 40% ethyl acetate/hexanes) to provide 0.101 g (100%, 0.4 mmol scale) of **25** as an off-white solid. mp 217-219 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 8.41 (m, 1H), 7.93 (m, 2H), 7.55 (d, J = 5.3 Hz, 1H), 7.47 (br, s, 2H), 7.37 (d, J = 5.6 Hz, 1H), 7.12 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 152.3, 141.5, 140.2, 127.9, 127.6, 127.4, 125.9, 123.8, 122.7, 122.5, 122.2, 121.6. HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{10}N_2S$, 250.056470; found, 250.056226. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2930 (br, w), 1442 (s), 1426 (s), 1412 (m), 1367 (w), 1311 (w), 1281 (m).

2-(thiophen-3-yl)-1*H*-benzo[*d*]imidazole (26): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.1 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-100% ethyl acetate/hexanes; R_f = 0.40, 50% ethyl acetate/hexanes) to provide 0.0385 g (64%, 0.3 mmol scale) of **26** as an off-white solid. mp 320-322 °C (lit. 320 °C).[10] ^{1}H NMR (400 MHz, CD_3OD): δ 7.98 (dd, J_1 = 2.9 Hz, J_2 = 1.1 Hz, 1H), 7.62 (dd, J_1 = 5.1 Hz, J_2 = 1.1 Hz, 1H), 7.46 (dd, J_1 = 5.1 Hz, J_2 = 3.1 Hz, 1H), 7.43 (br s, 2H), 7.10 (m, 2H).

1-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (27): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (5-50% ethyl acetate/hexanes; R_f = 0.20, 20% ethyl acetate/hexanes) to provide 0.159 g (79%, 0.9 mmol scale) of **27** as an off-white solid. mp 93-95 °C (lit. 92-94 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 7.64 (m, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.44 (m, 4H), 7.19 (m, 2H), 3.75 (s, 3H).

2-phenylbenzo[*d*]oxazole (28): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (2-20% ethyl acetate/hexanes; R_f = 0.52, 10% ethyl acetate/hexanes) to provide 0.116 g (66%, 0.9 mmol scale) of **28** as an off-white solid. mp 98-99 °C (lit. 100-102 °C).[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (m, 2H), 7.79 (m, 1H), 7.60 (m, 1H), 7.54 (m, 3H), 7.36 (m, 2H).

2-phenylbenzo[*d*]thiazole (29): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle and heated for 6 h. The crude reaction mixture was purified by flash chromatography (2-20% ethyl acetate/hexanes; R_f = 0.58, 10% ethyl acetate/hexanes) to provide 0.0650 g (38%, 0.9 mmol scale) of **29** as an off-white solid. mp 112-113 °C (lit. 115 °C).[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (m, 3H), 7.92 (d, J = 7.8 Hz, 1H), 7.50 (m, 4H), 7.39 (t, J = 7.6 Hz, 1H).

4-(4-fluorophenyl)-2,5-diphenyl-1*H*-imidazole (30): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (5-50% ethyl acetate/hexanes; R_f = 0.33, 20% ethyl acetate/hexanes) to provide 0.0937 g (91%, 0.9 mmol scale) of **30** as an off-white solid. mp 256-257 °C

(lit. 256-257 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.34 (m, 6H), 7.26 (m, 1H), 7.22 (m, 2H), 7.16 (m, 1H), 6.94 (t, *J* = 8.6 Hz, 2H).

3-(4-(4-fluorophenyl)-2-phenyl-1*H*-imidazol-5-yl)-1*H*-indole (31): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-80% ethyl acetate/hexanes; R_f = 0.33, 40% ethyl acetate/hexanes) to provide 0.257 g (80%, 0.33 mmol scale) of **31** as an off-white solid. mp 249-250 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 7.85 (m, 2H), 7.41 (m, 2H), 7.29 (m, 5H), 6.98 (m, 2H), 6.78 (m, 3H). Analysis of the ^{13}C NMR spectrum was complicated due to poor signal-to-noise ratio resulting from low solubility and ^{19}F coupling. HRMS-EI (m/z): $[M]^+$ calcd for $C_{23}H_{16}N_3F$, 353.132826; found, 353.132764. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3441 (m), 3038 (br, w), 2974 (w), 2917 (w), 2875 (w).

4-(4-(4-fluorophenyl)-2-phenyl-1*H*-imidazol-5-yl)pyridine (32): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (10-80% ethyl acetate/hexanes; R_f = 0.34, 40% ethyl acetate/hexanes) to provide 0.0555 g (28%, 0.9 mmol scale) of **32** as an off-white solid. mp 144-146 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 8.40 (m, 2H), 8.01 (m, 2H), 7.56 (m, 2H), 7.49 (m, 2H), 7.41 (m, 3H), 7.11 (m, 2H). Analysis of the ^{13}C NMR spectrum was complicated due to poor signal-to-noise ratio resulting from low solubility and ^{19}F coupling. GC-MS *m/z* (% relative intensity, ion): 316 (1), 288 (0.10), 185 (0.14), 127 (0.19). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2929 (br, w), 1599 (s), 1543 (m), 1509 (s), 1488 (m), 1450 (m).

4-(4-methoxyphenyl)-2,5-diphenyl-1*H*-imidazole (33): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (5-50% ethyl acetate/hexanes; R_f = 0.25, 20% ethyl acetate/hexanes) to provide 0.0717 g (%, 0.24 mmol scale) of **33** as an off-white solid. mp 225-226 °C (lit. 226-227 °C).[1] ^{1}H NMR (400 MHz, CD_3OD): δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.32 (m, 4H), 7.25 (m, 3H), 7.18 (m, 2H), 7.13 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 3.67 (s, 3H).

4,5-dimethyl-2-phenylthiazole (34): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (2-20% ethyl acetate/hexanes; R_f = 0.5, 10% ethyl acetate/hexanes) to provide 0.0800 g (47%, 0.9 mmol scale) of **34** as a light brown oil. ^{1}H NMR (400 MHz, CD_3OD): δ 7.68 (m, 2H), 7.28 (m, 3H), 2.25 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 164.1, 148.8, 133.3, 129.5, 128.7, 127.0, 125.7, 13.1, 9.9. HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{11}NS$, 189.061221; found, 189.061718. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3061 (m), 3021 (m), 2953 (m), 2920 (s), 2860 (m), 1950 (m), 1710 (w), 1598 (m), 1546 (s), 1499 (s), 1460 (s), 1438 (m).

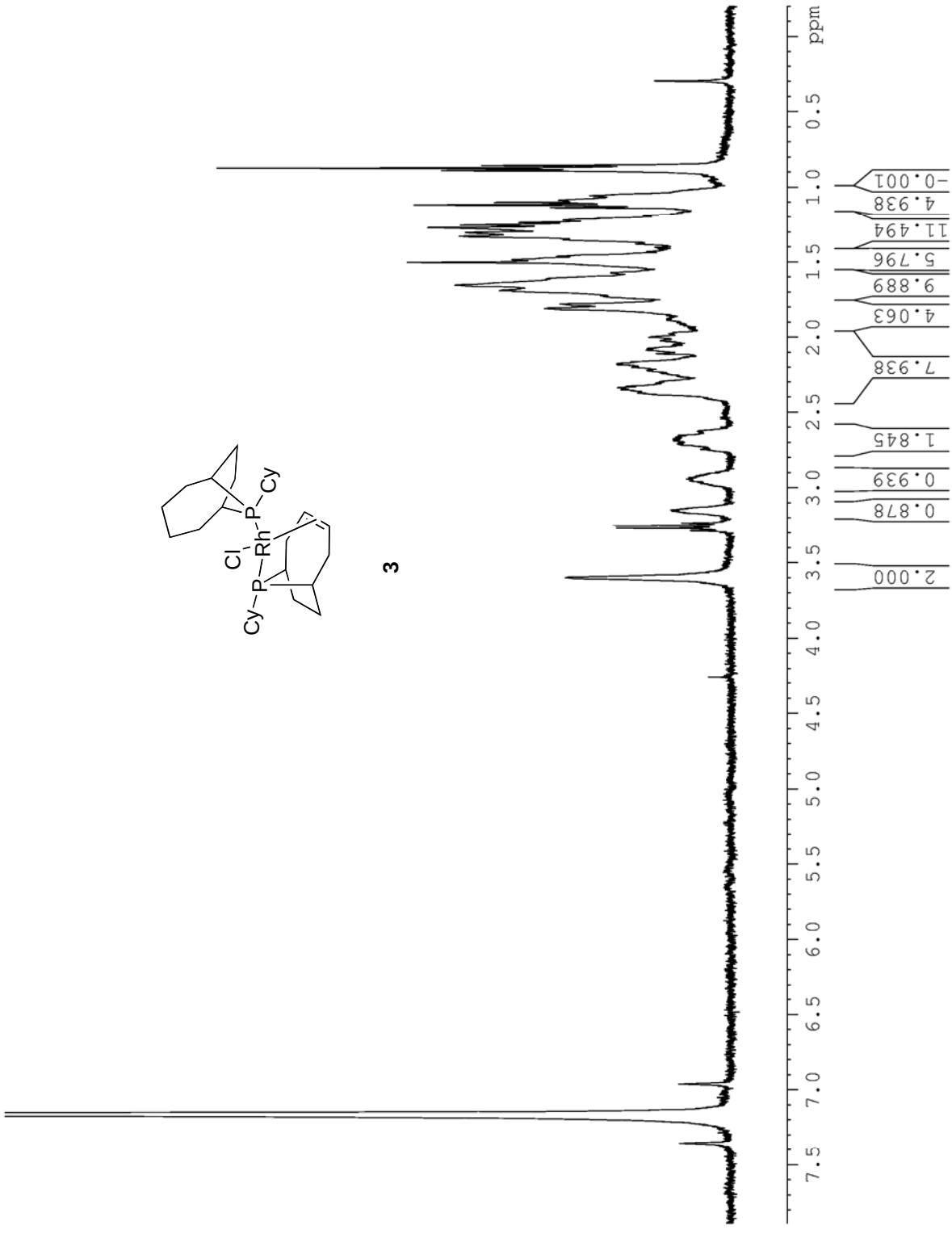
4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (35): The product was synthesized using the typical procedure outlined above. The reaction was conducted at 0.3 M in heterocycle. The crude reaction mixture was purified by flash chromatography (5-50% ethyl acetate/hexanes) to provide 0.0822 g (52%, 0.9 mmol scale) of **35** as a light brown oil. ^{1}H NMR (400 MHz, CD_3OD): δ 7.75 (m, 2H), 7.39 (m, 1H), 7.30 (m, 2H), 4.76 (s, 2H), 1.23 (s, 6H). ^{13}C NMR (100 MHz, CD_3OD): δ 163.3, 131.5, 128.2, 127.8, 127.3, 79.0, 67.0, 27.1. HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{13}NO$, 175.099714; found, 175.100343. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3411 (br, w), 3062 (m), 3032 (m), 2967 (s), 2928 (s), 2892 (s), 2868 (m), 1737 (w), 1650 (s).

Typical Procedure for Cross-Coupling Azoles and Aryl Bromides (Microwave Protocol with $RhCl(cod)]_2$ and 5b•HBF_4). To a dry 2.5 mL glass microwave vial is added a stir bar, the appropriate heterocycle, the appropriate aryl bromide (2.0 equiv) and *i*-Pr_2*i*-BuN (3 equiv). Into a separate vial were weighed **5b•HBF_4** (7.5 mol% for dioxane and 15 mol% for THF, see Table 5) and $[RhCl(cod)]_2$

(2.5 mol% for dioxane and 5 mol% for THF, see Table 5), and the catalyst was transferred to the microwave vial using the appropriate volume of THF or 1,4-dioxane. The microwave vial was placed under a nitrogen atmosphere, sealed and heated for 2 h at 200 ºC. The reaction mixture was then cooled, quenched with excess Et_3N (0.25 mL), and concentrated under reduced pressure. The residue was dissolved in a minimal amount of methanol/methyelene chloride (ca. 1 mL), loaded onto a silica gel samplet (Biotage No. SAM-1107-16016), and purified using flash chromatography as previously described for each product.

Optimized procedure for direct arylation at low catalyst loading (Table 6, entry 5). In an inert atmosphere box, a stir bar, benzimidazole (0.0473 g, 0.4 mmol), bromobenzene (0.1256 g, 0.8 mmol), and *i*-Pr_2*i*-BuN (0.250 mL, 1.2 mmol) were added to a 10 mL glass sealed tube. Into a separate vial were weighed **5b** (0.0020 g, 0.012 mmol) and $[RhCl(coe)_2]_2$ (0.0032 g, 0.004 mmol), and the catalyst was transferred to the sealed tube using 1.4 mL of 1,4-dioxane. The sealed tube was sealed, removed from the inert atmosphere box, and heated for 24 h at 175 ºC in an oil bath. The reaction mixture was then cooled, quenched with excess Et_3N (0.50 mL), and concentrated under reduced pressure. The residue was dissolved in a minimal amount of methanol/methyelene chloride (ca. 1-2 mL), loaded onto a silica gel samplet (Biotage No. SAM-1107-16016), and purified using flash chromatography as previously described. The desired product was obtained as 0.0712 g (92 % yield) of a white solid. A second run according to the same procedure provided a 88% yield. Analytical data for title compound is consistent with that previously reported (vida supra).

Spectra: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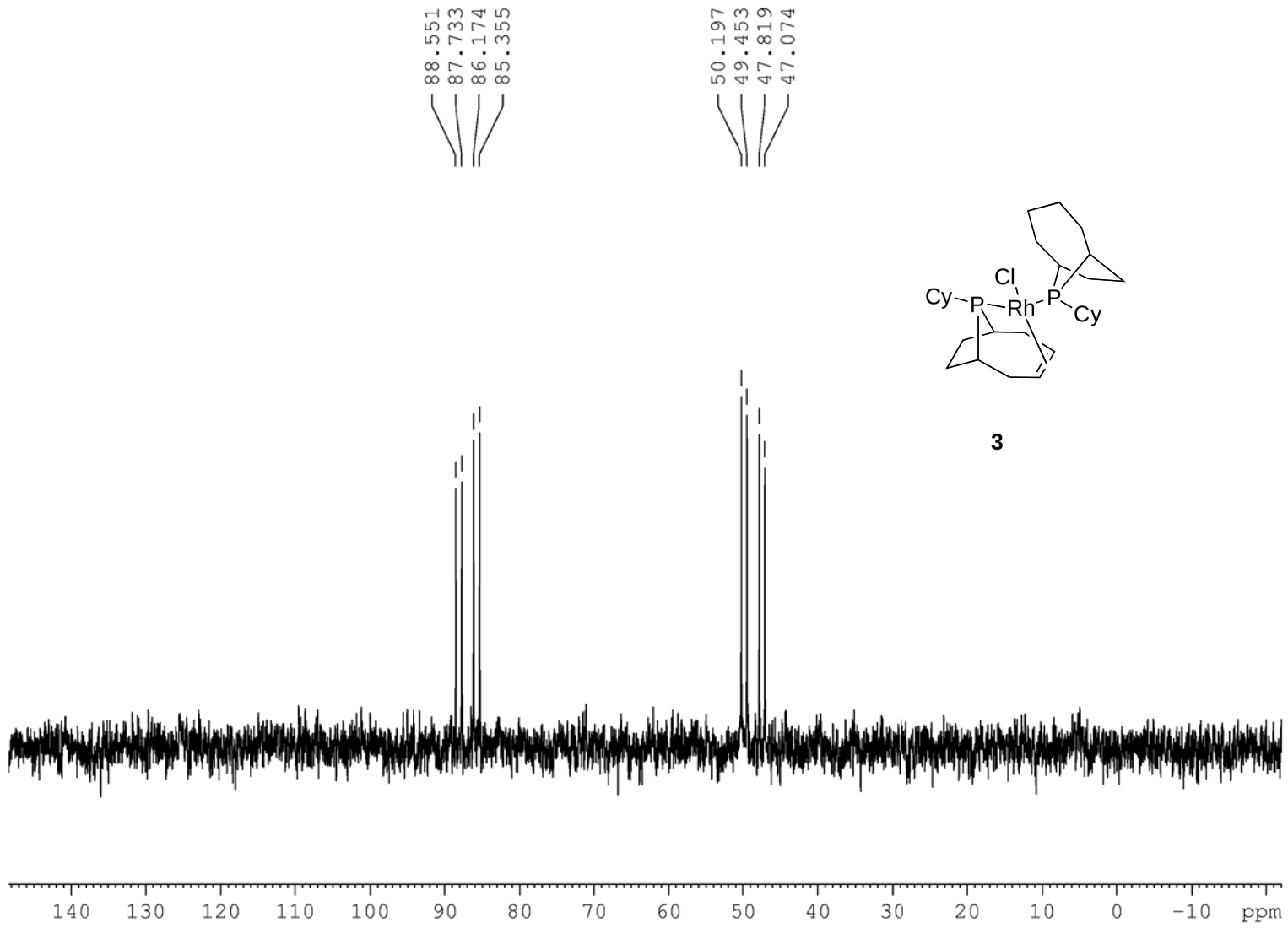
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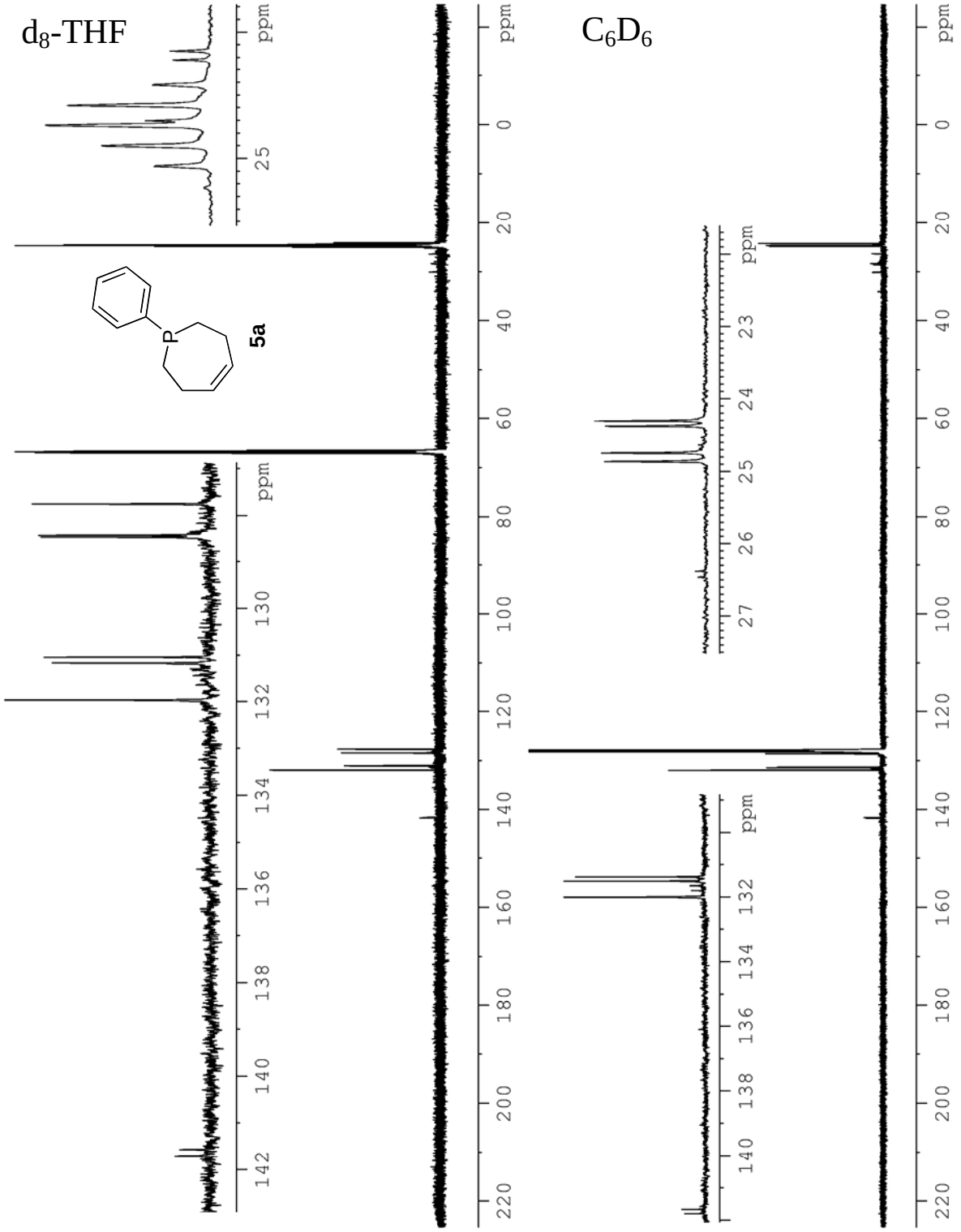
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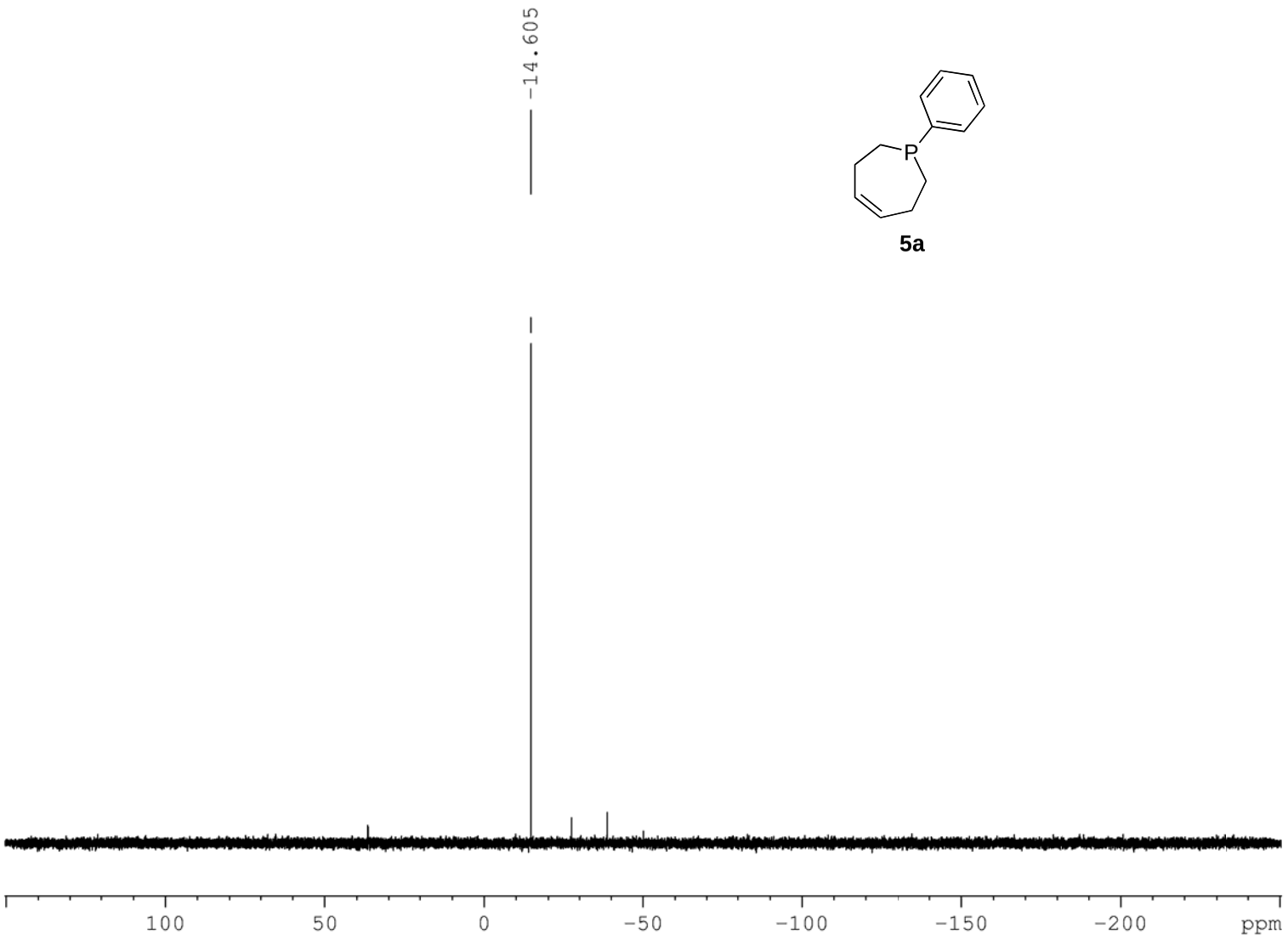

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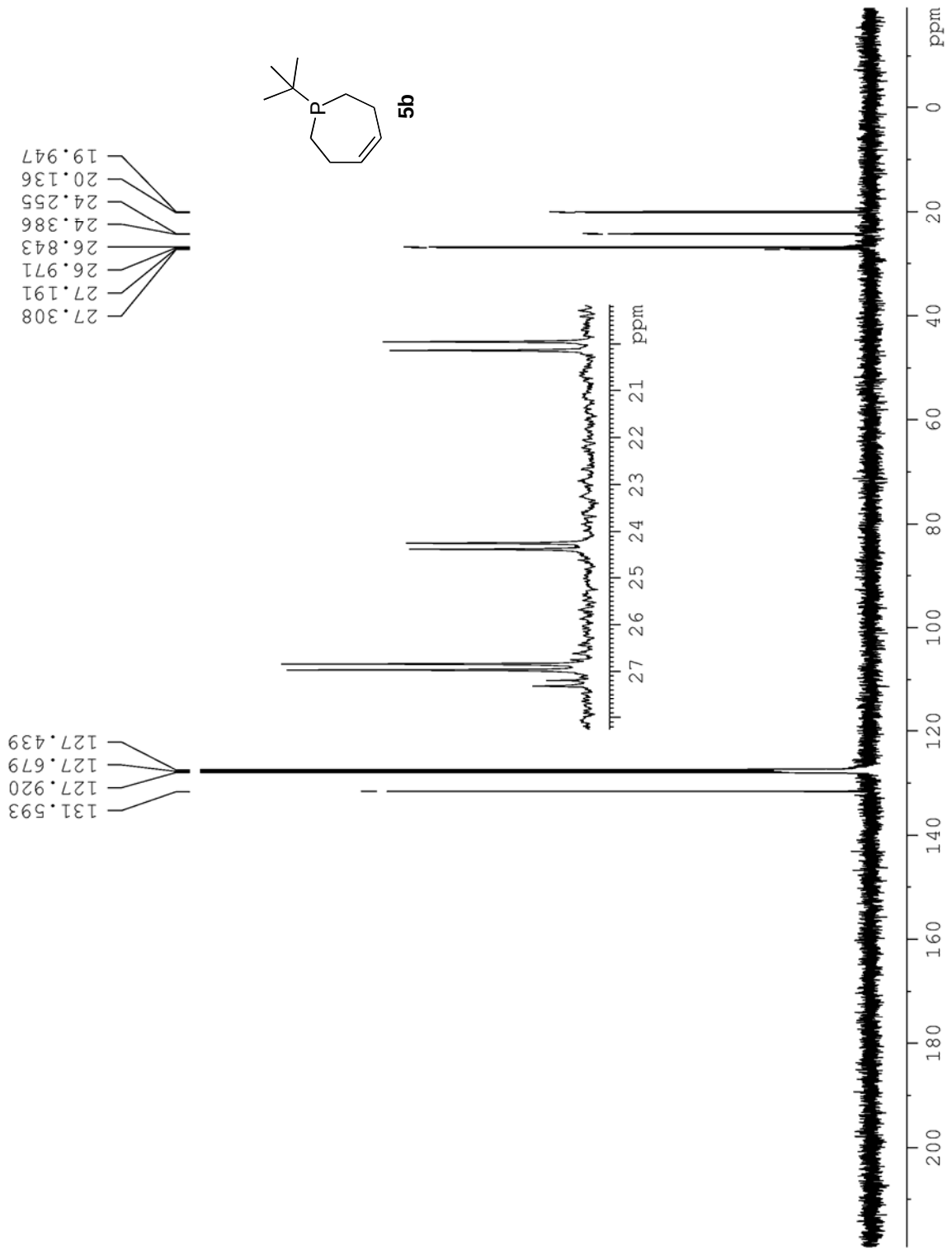
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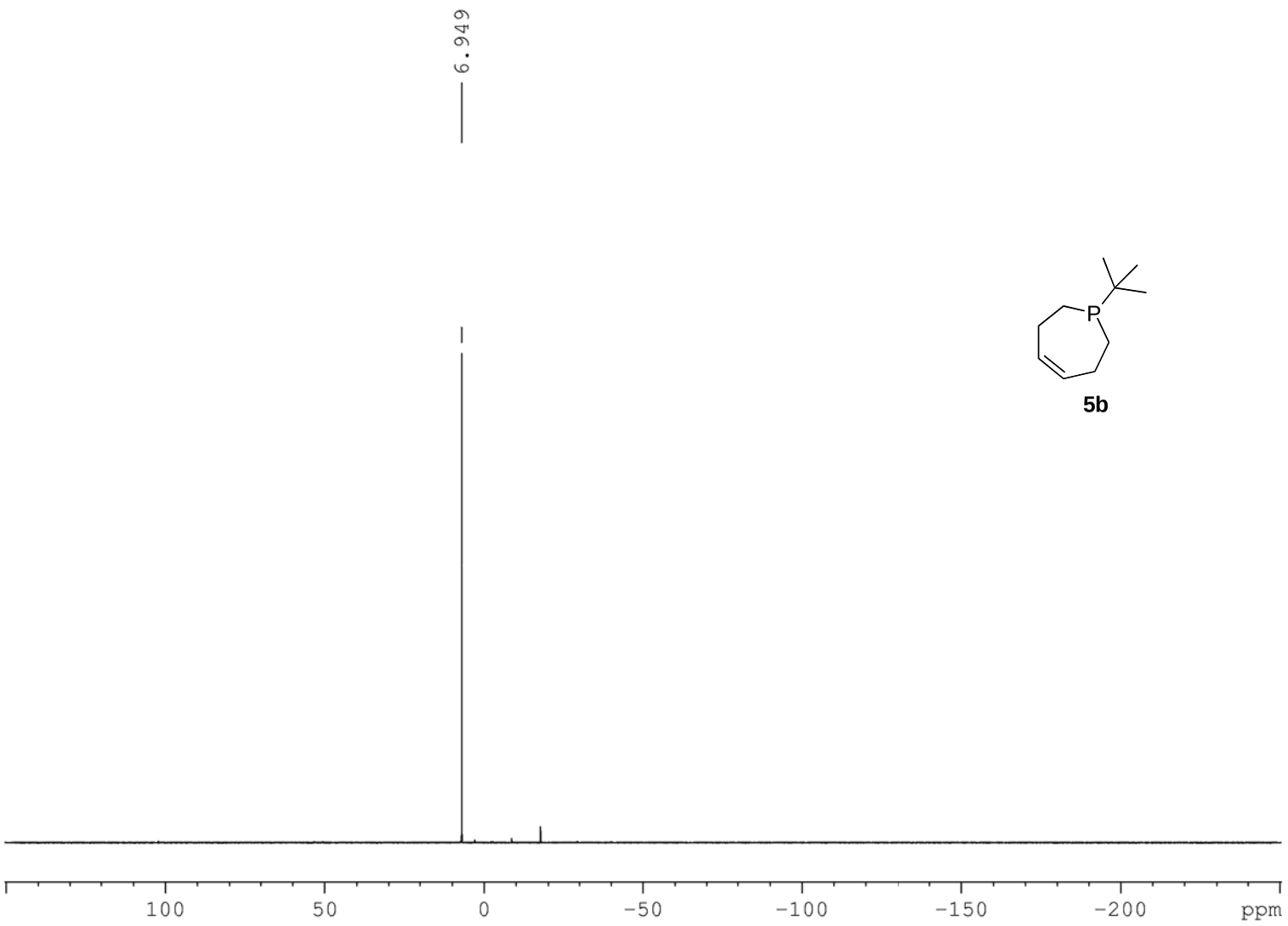

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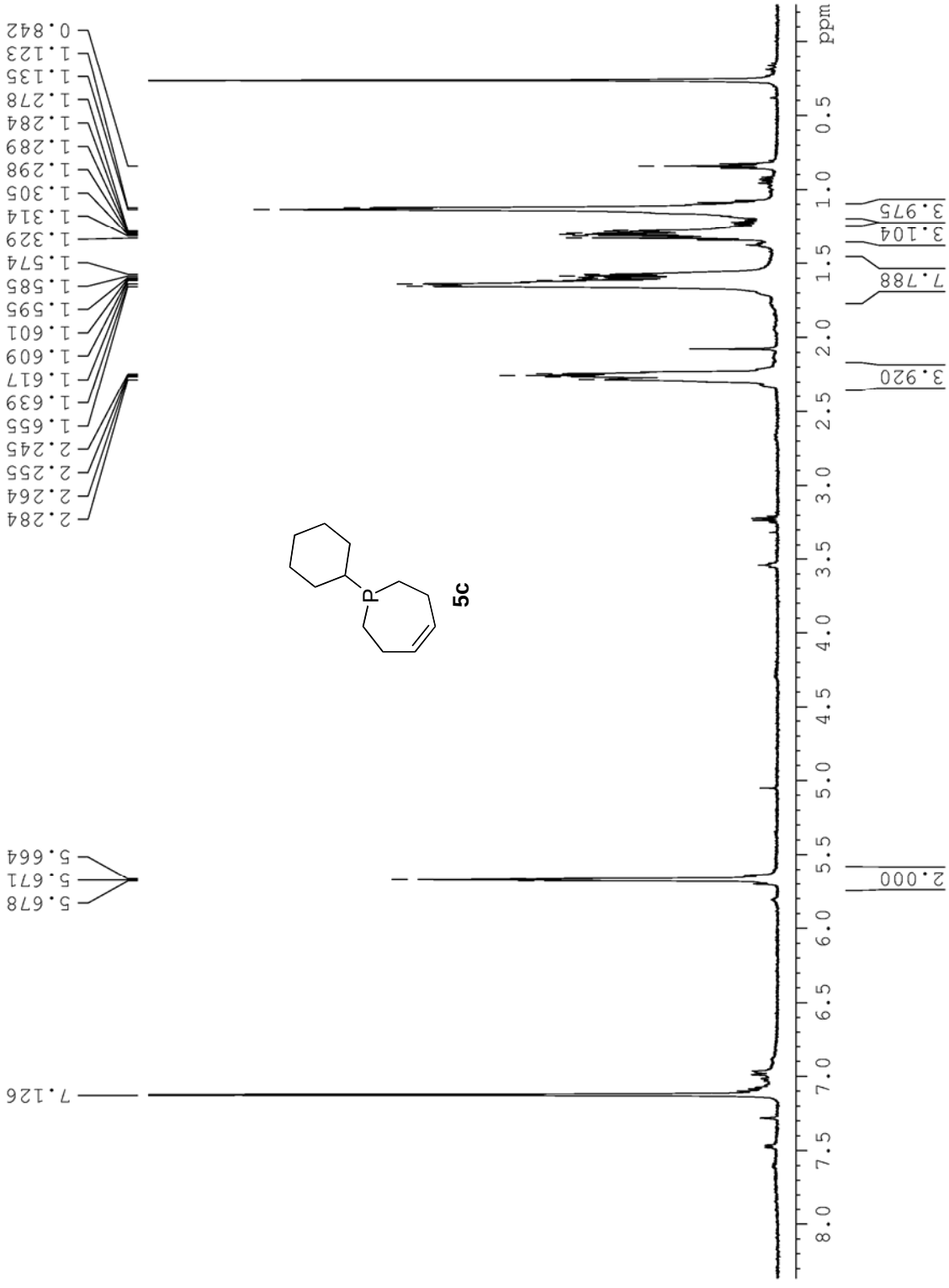
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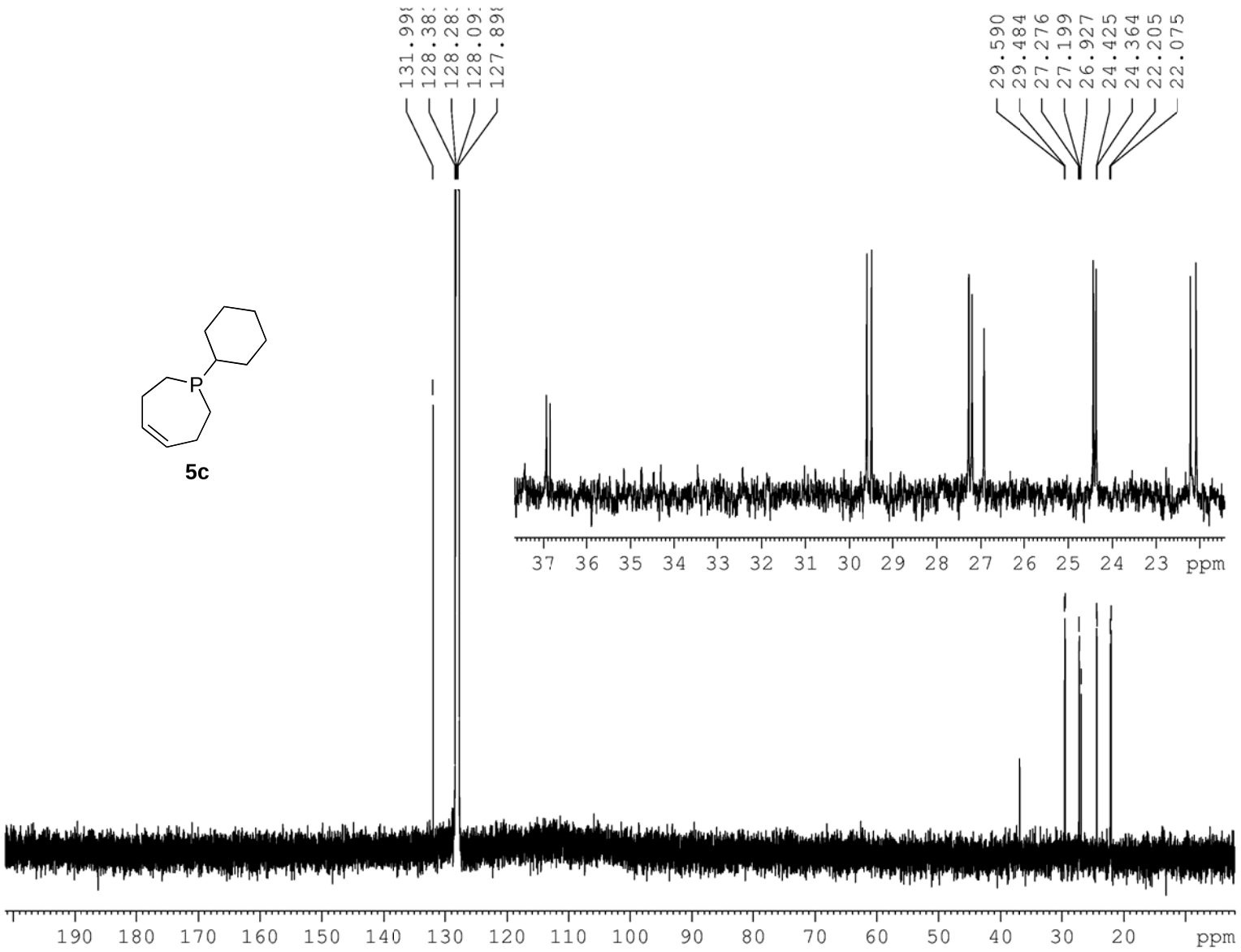
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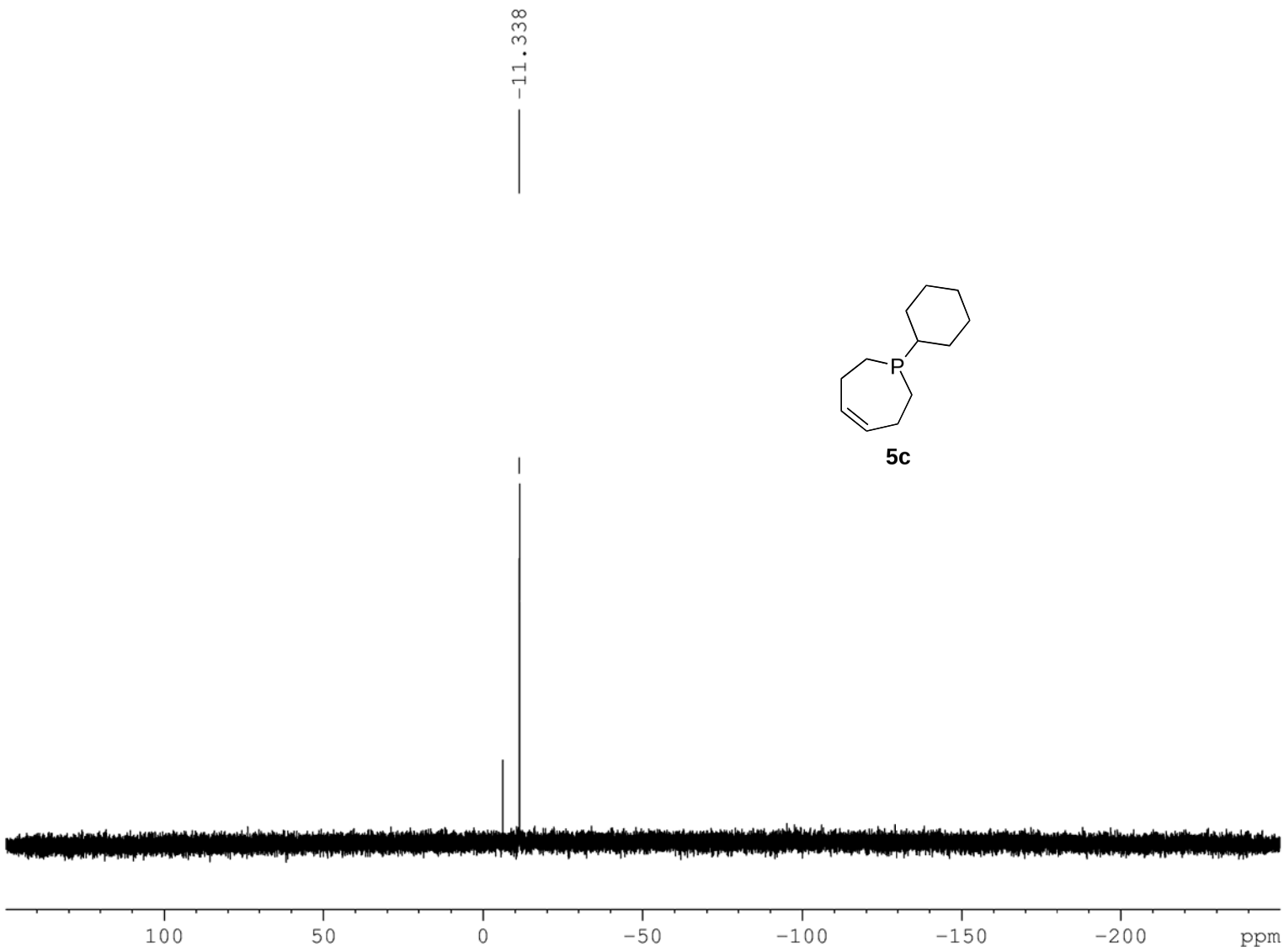

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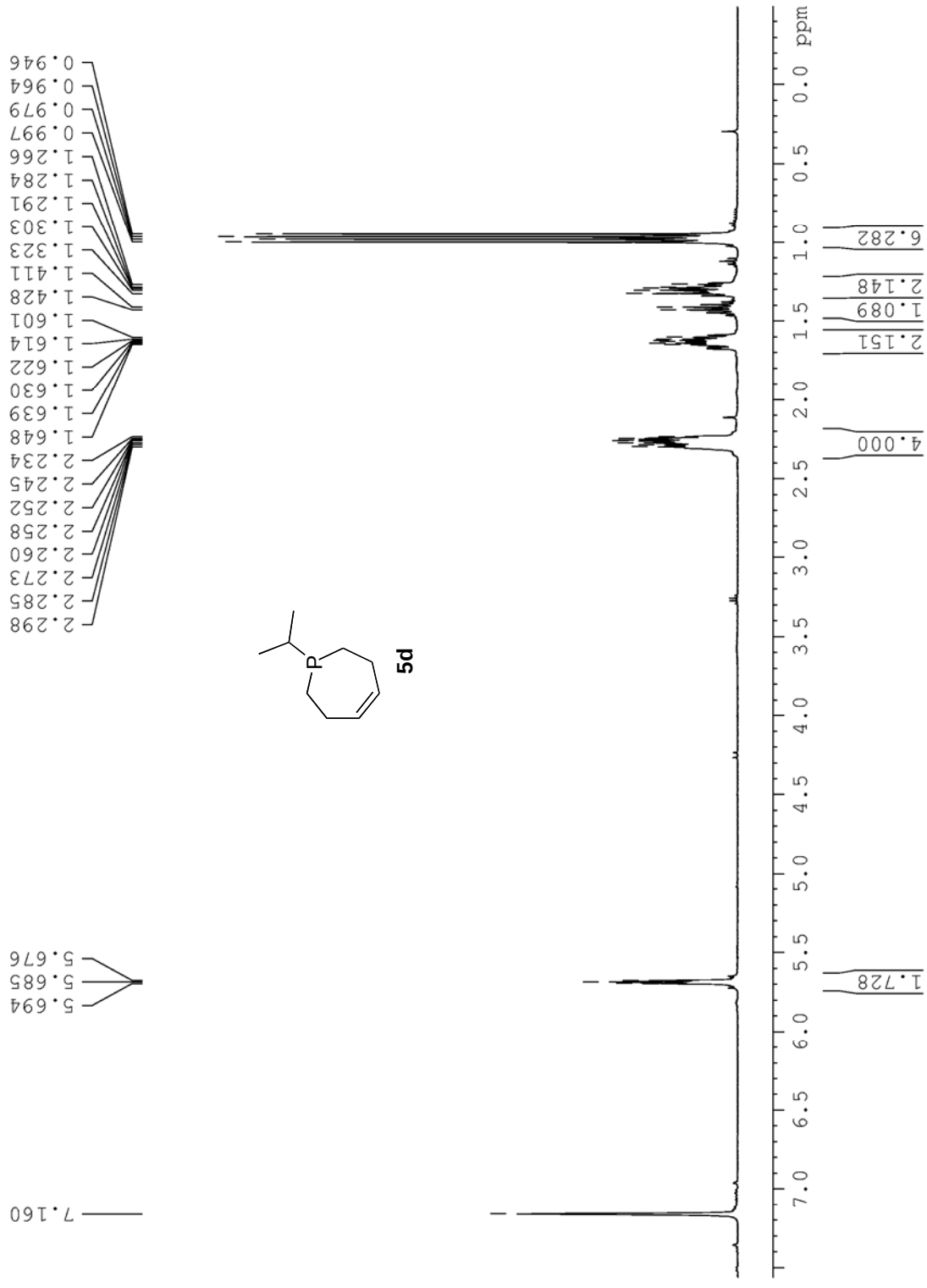
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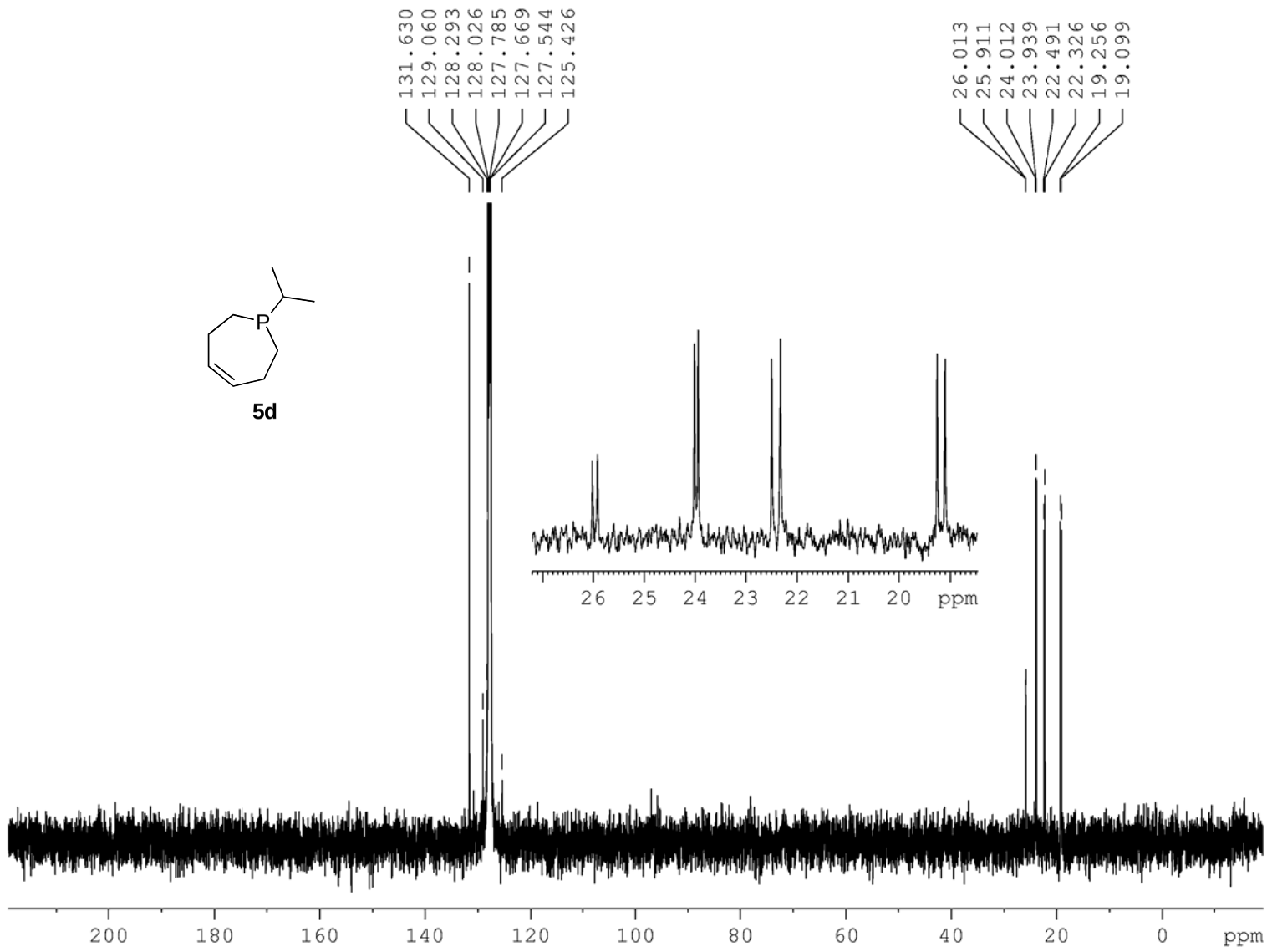
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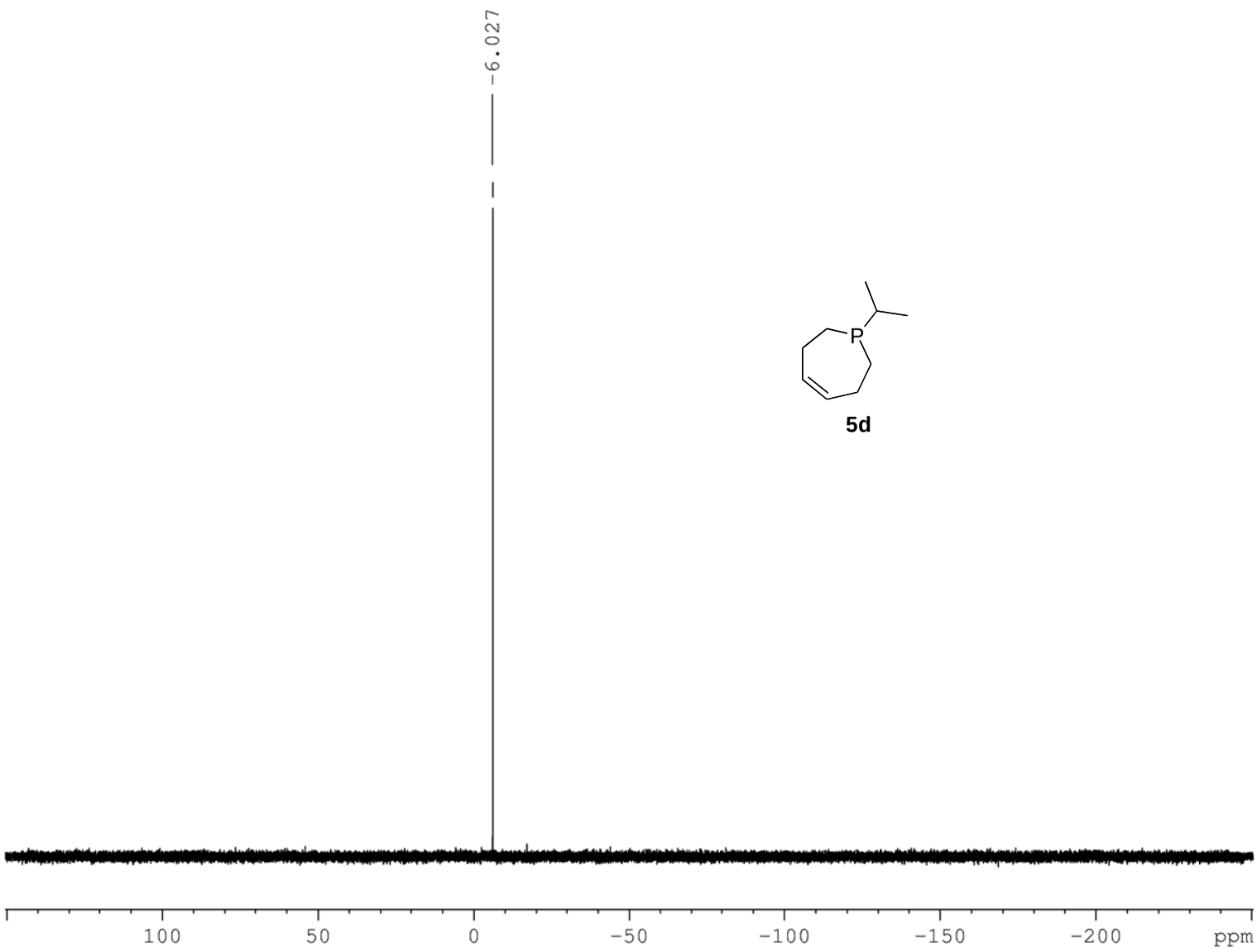
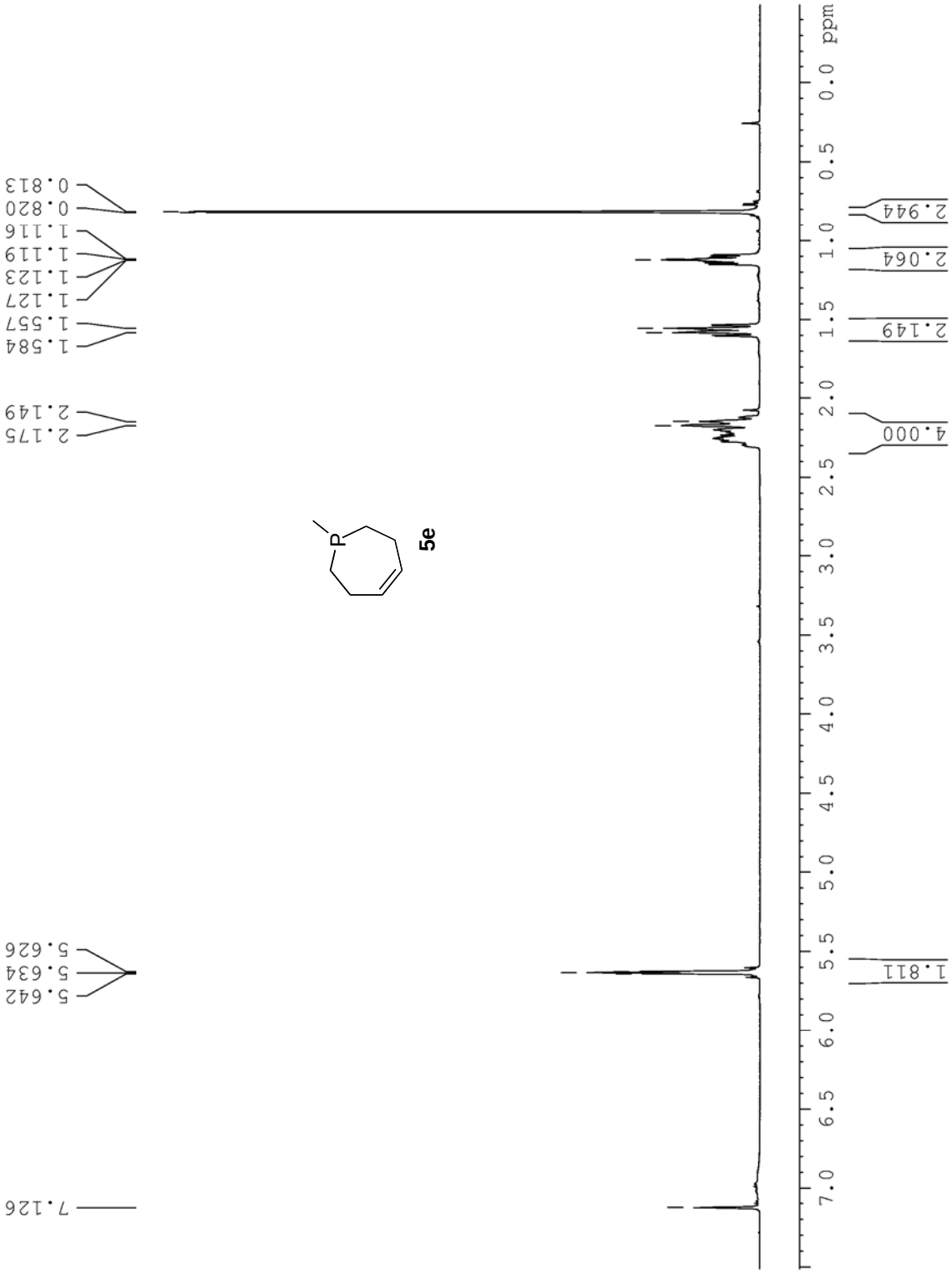
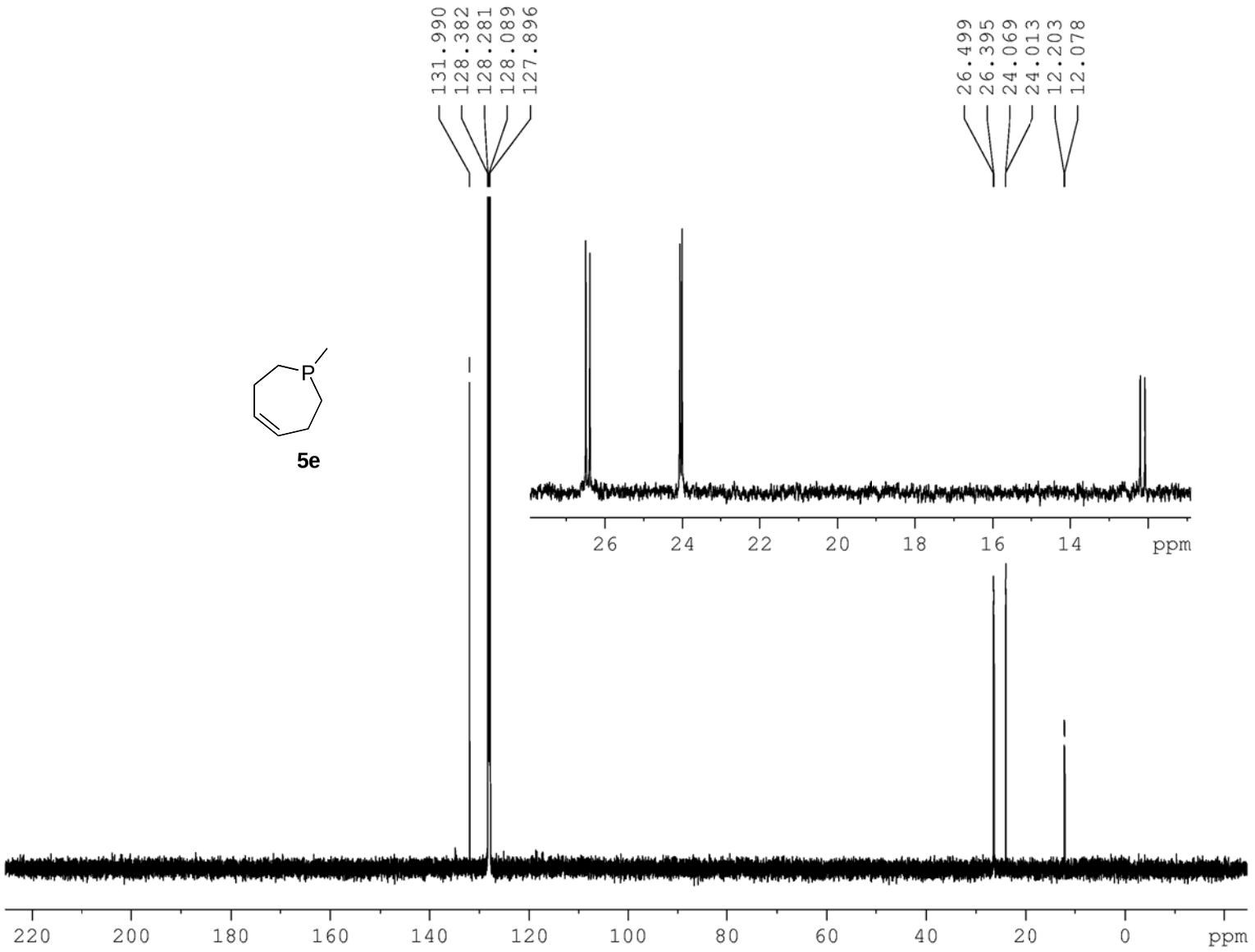
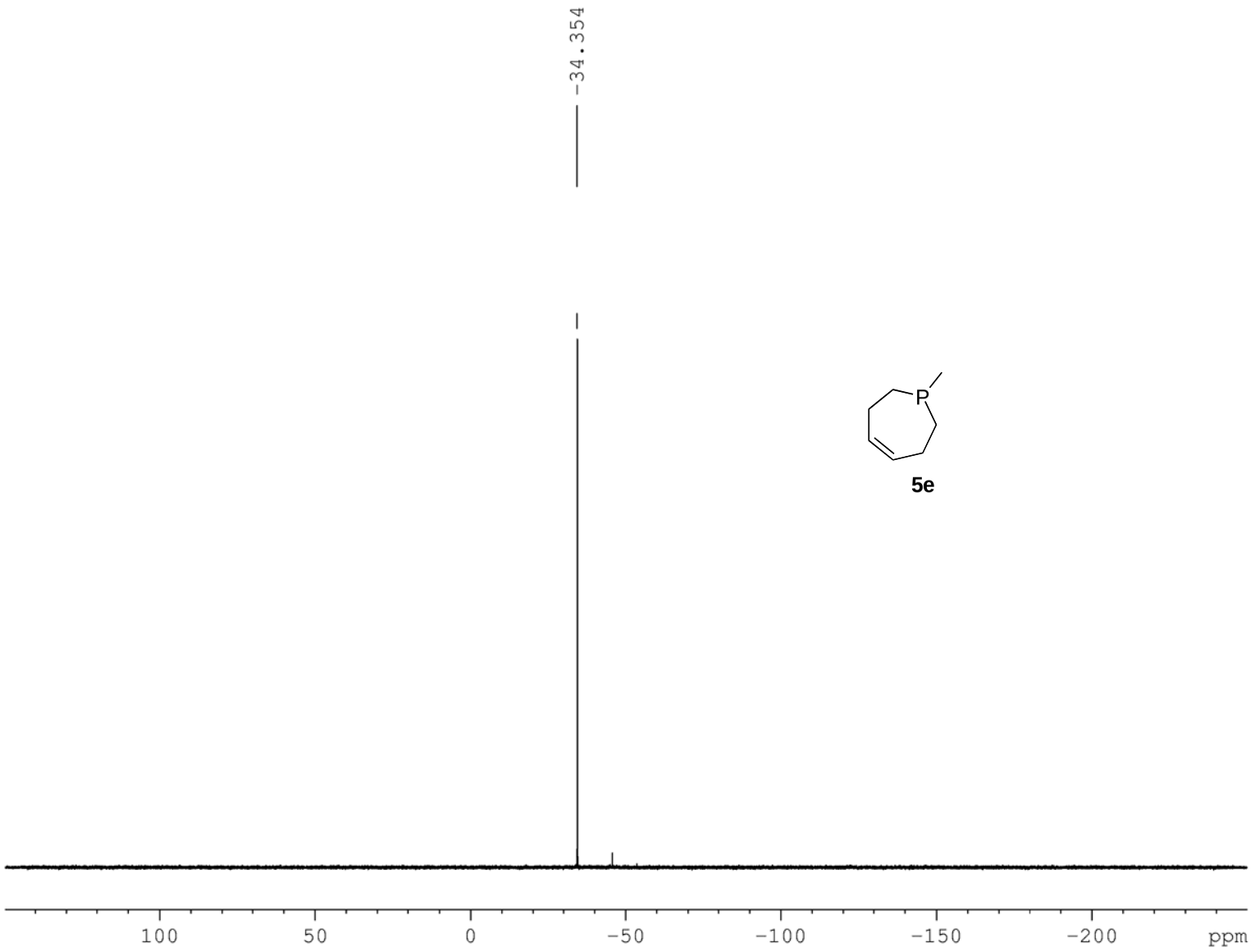
26 25 24 23 22 21 20 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm



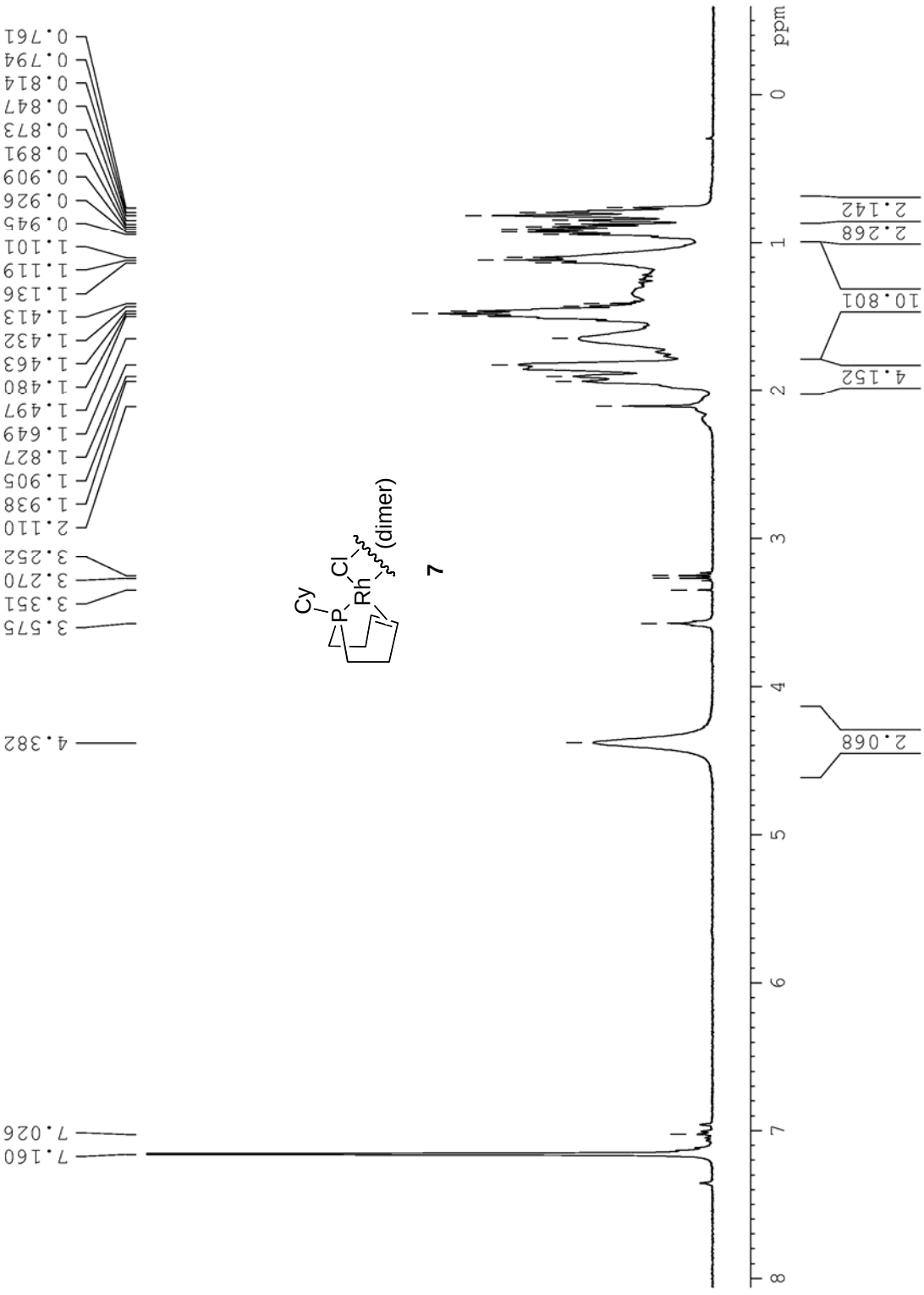
5d

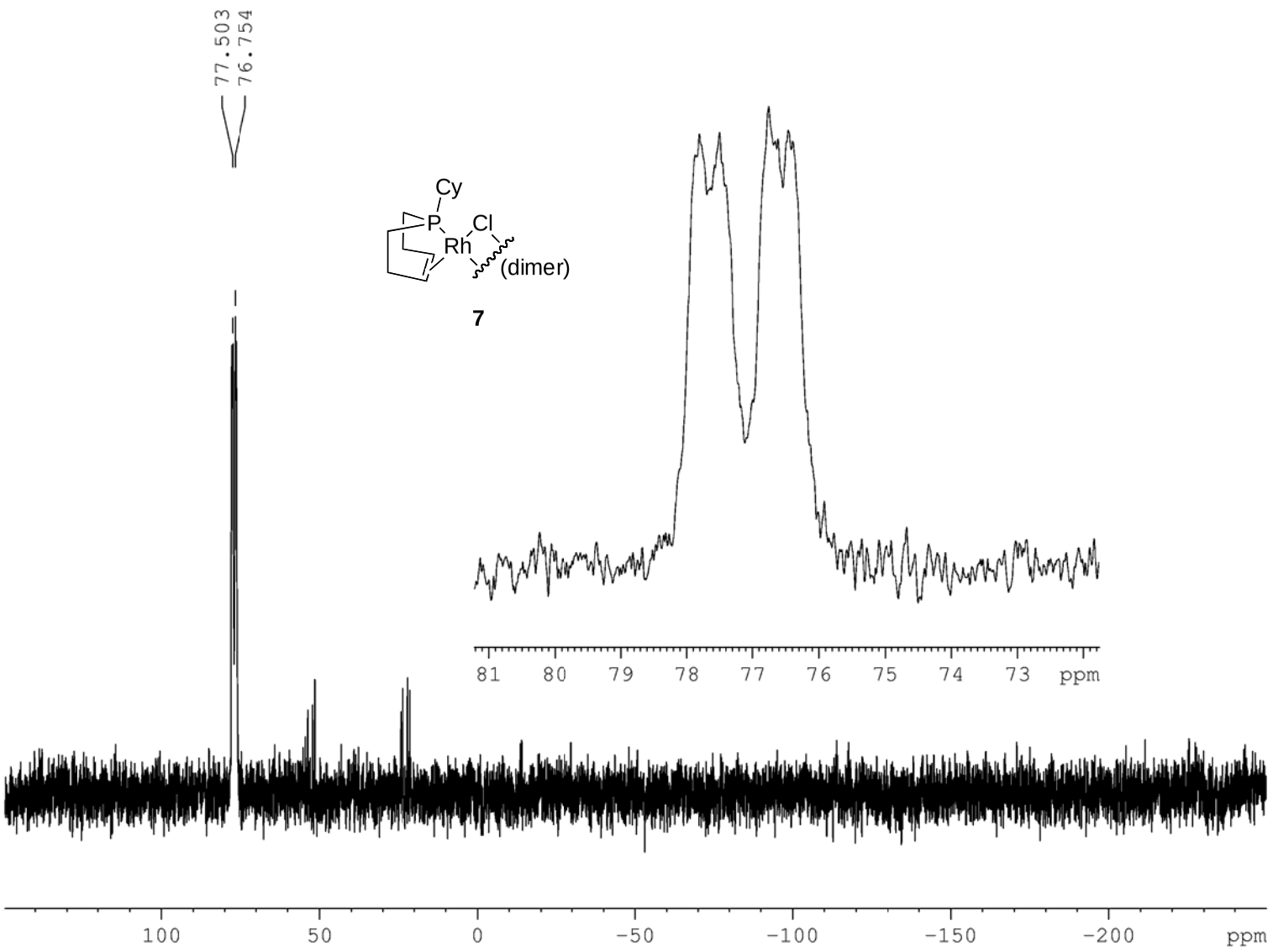

7.126
5.642
5.634
5.626
2.175
2.149
1.584
1.557
1.127
1.123
1.119
1.116
0.820
0.813
P
5e
1.811
4.000
2.149
2.064
2.944
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

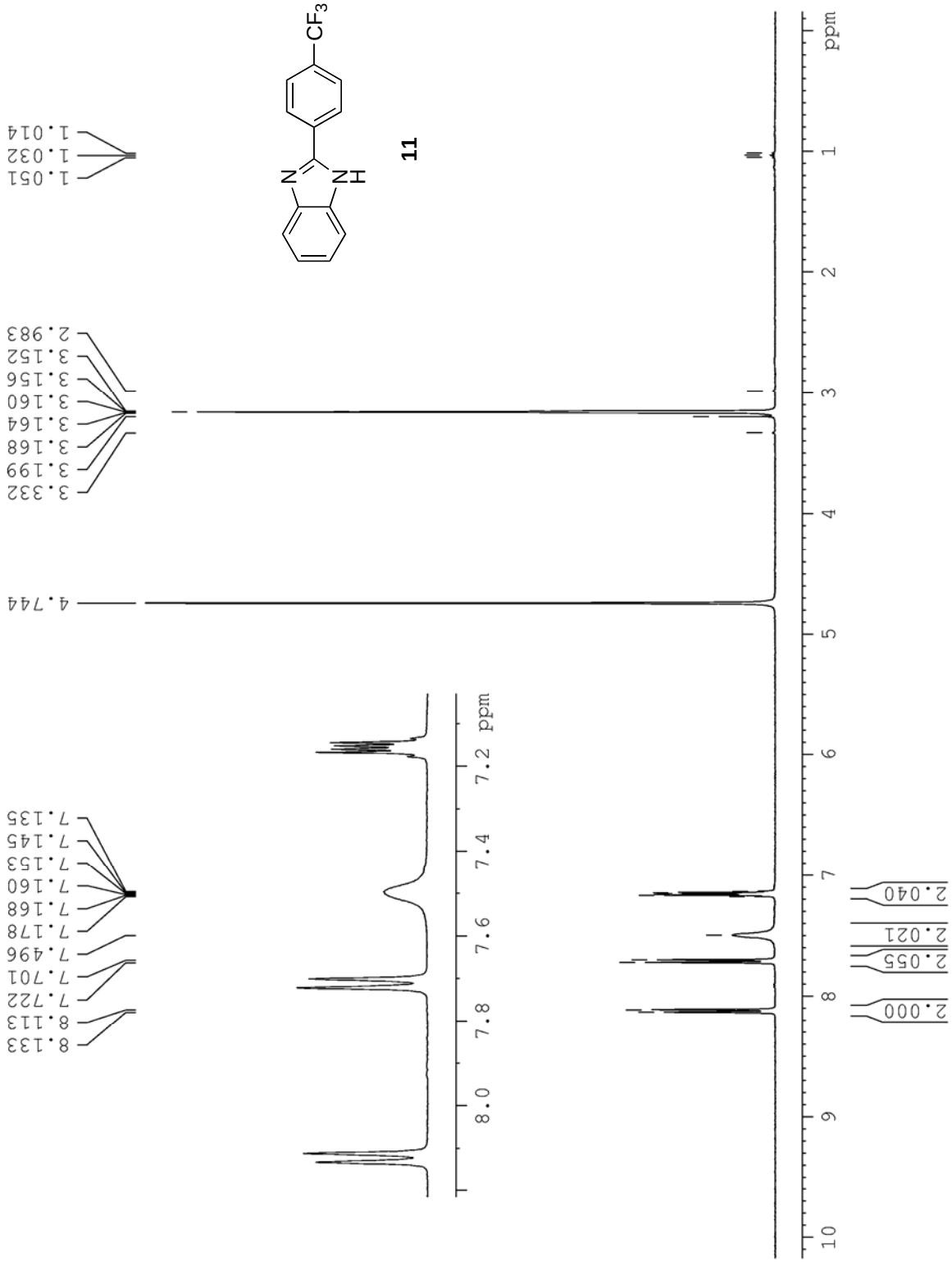

131.990
128.382
128.281
128.089
127.896
26.499
26.395
24.069
24.013
12.203
12.078
P
5e
26
24
22
20
18
16
14
ppm
220
200
180
160
140
120
100
80
60
40
20
0
ppm

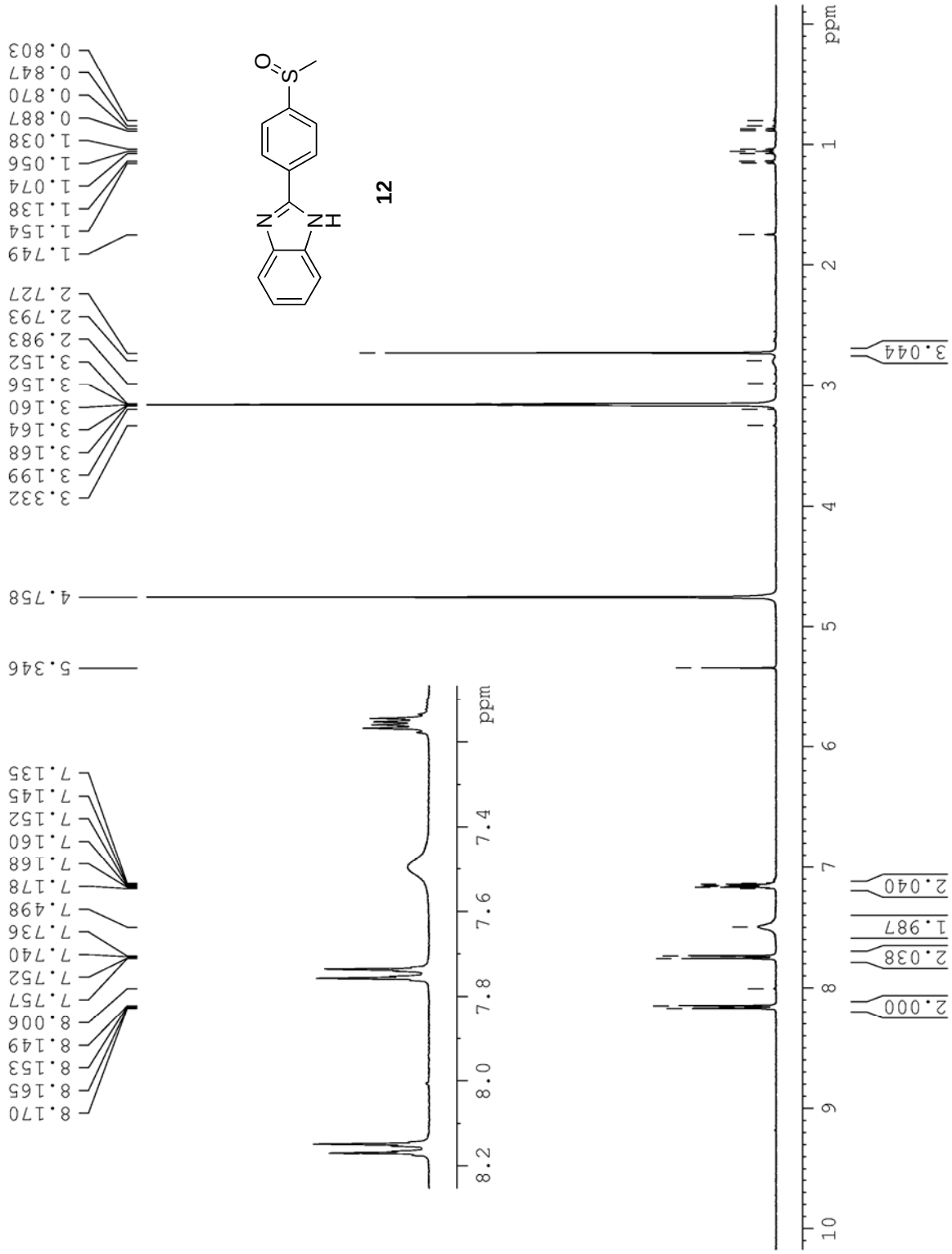


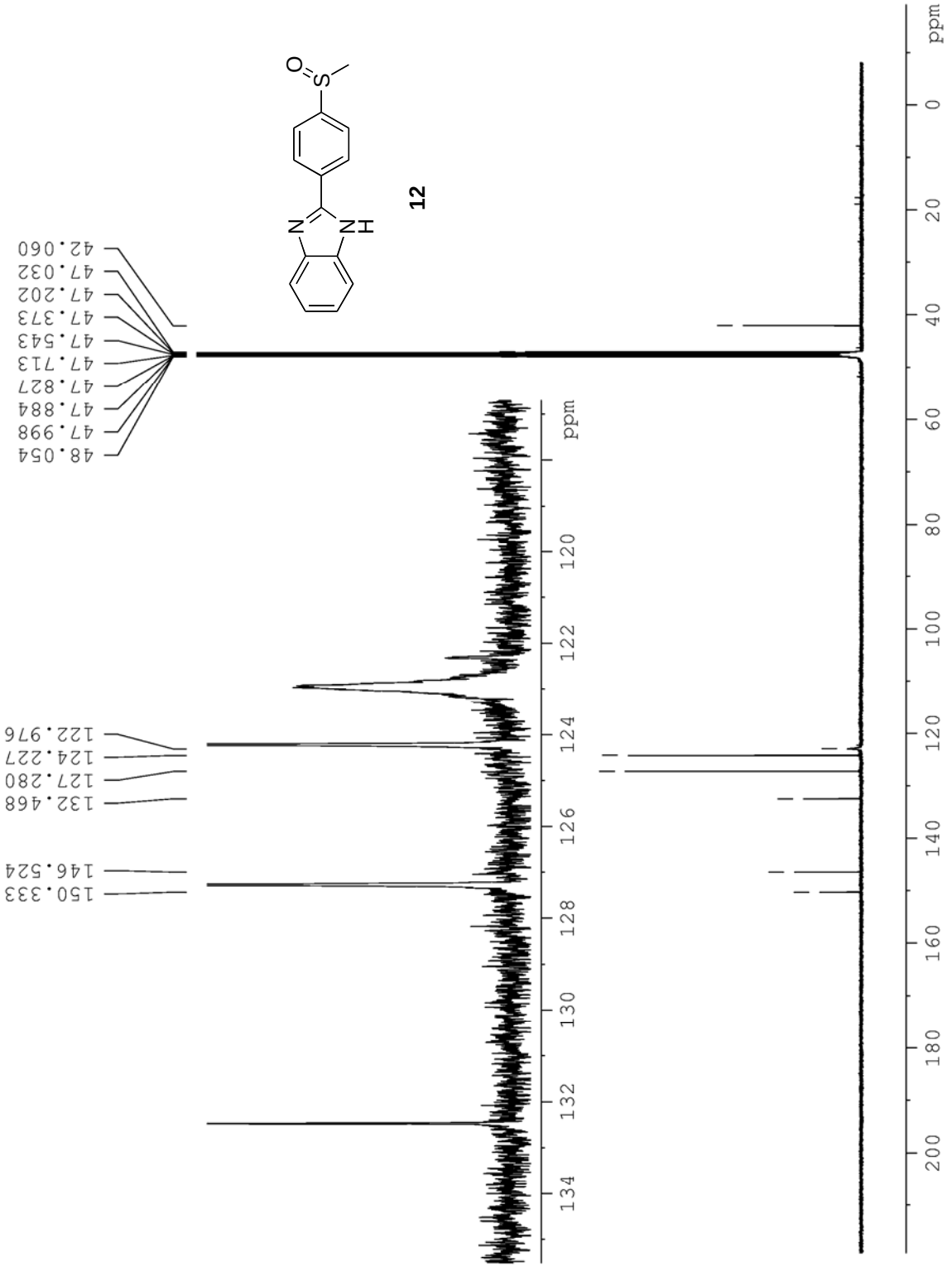
5e

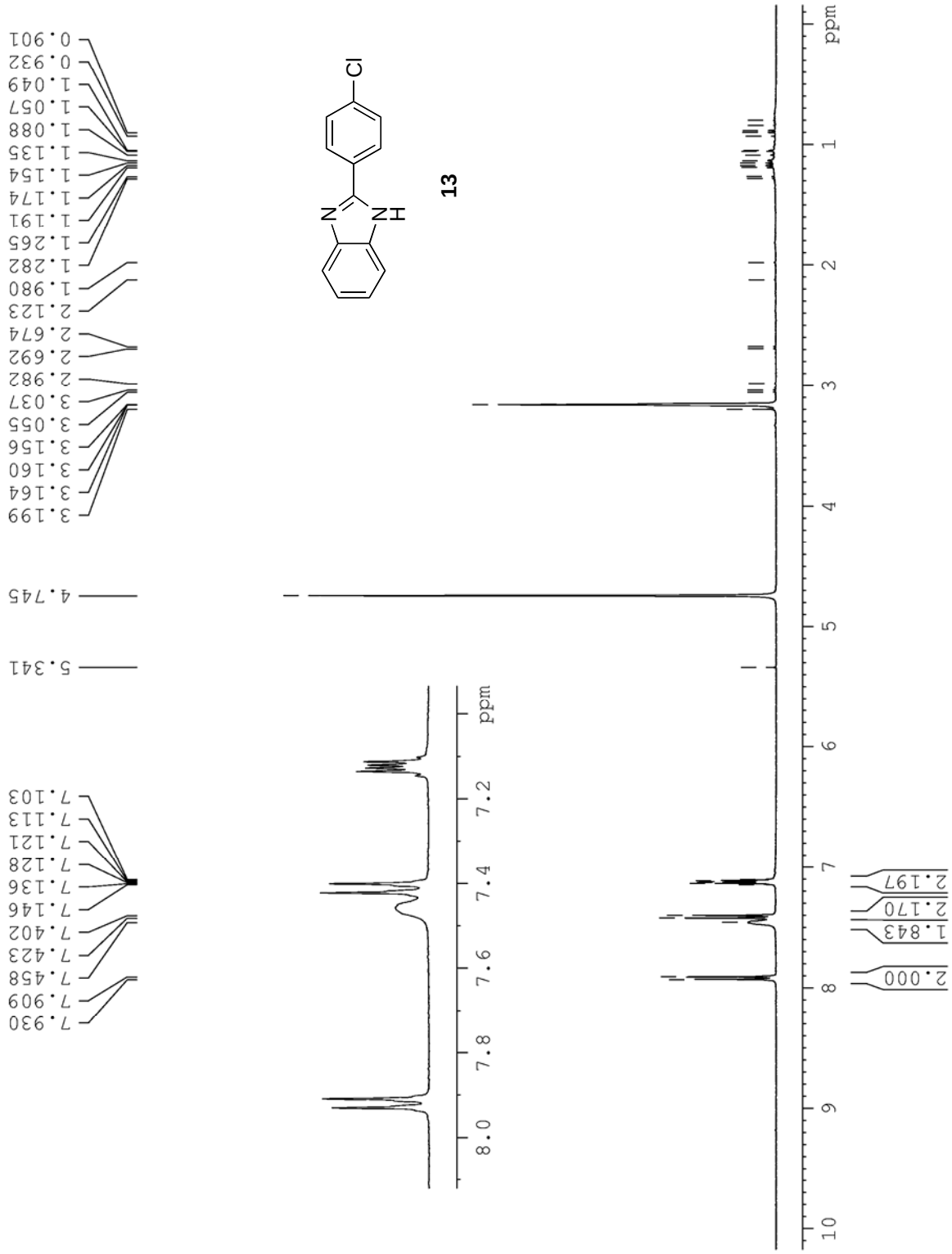

7.160
7.026
4.382
3.575
3.351
3.270
3.252
2.110
1.938
1.905
1.827
1.649
1.497
1.480
1.463
1.432
1.413
1.136
1.119
1.101
0.945
0.926
0.909
0.891
0.873
0.847
0.814
0.794
0.761
Cy
P
Rh
Cl
(dimer)
7
ppm
0
1
2
3
4
5
6
7
8
2.068
4.152
10.801
2.268
2.142

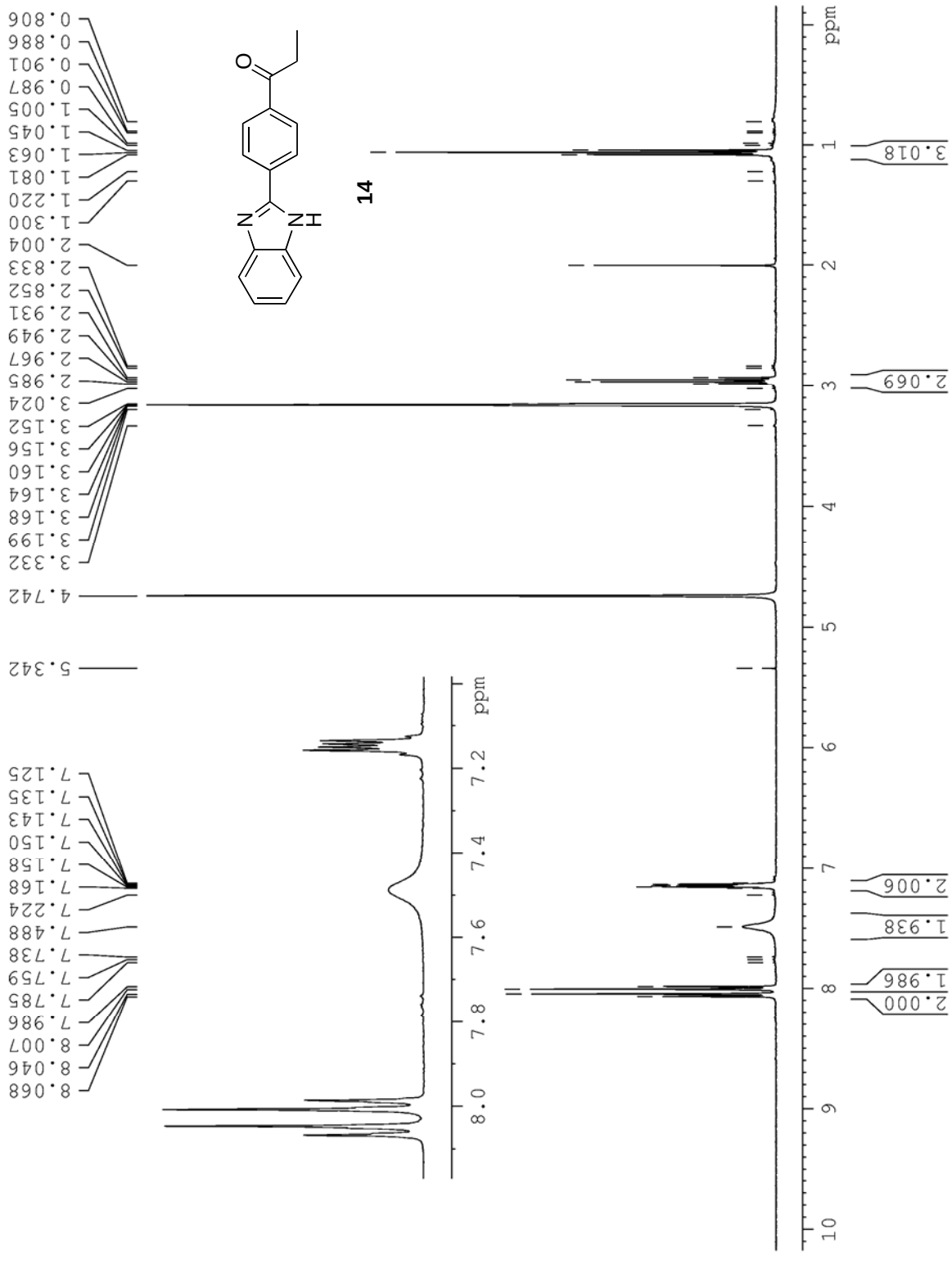

77.503
76.754
Cy
P
Cl
Rh
(dimer)
7
81 80 79 78 77 76 75 74 73 ppm
100 50 0 -50 -100 -150 -200 ppm

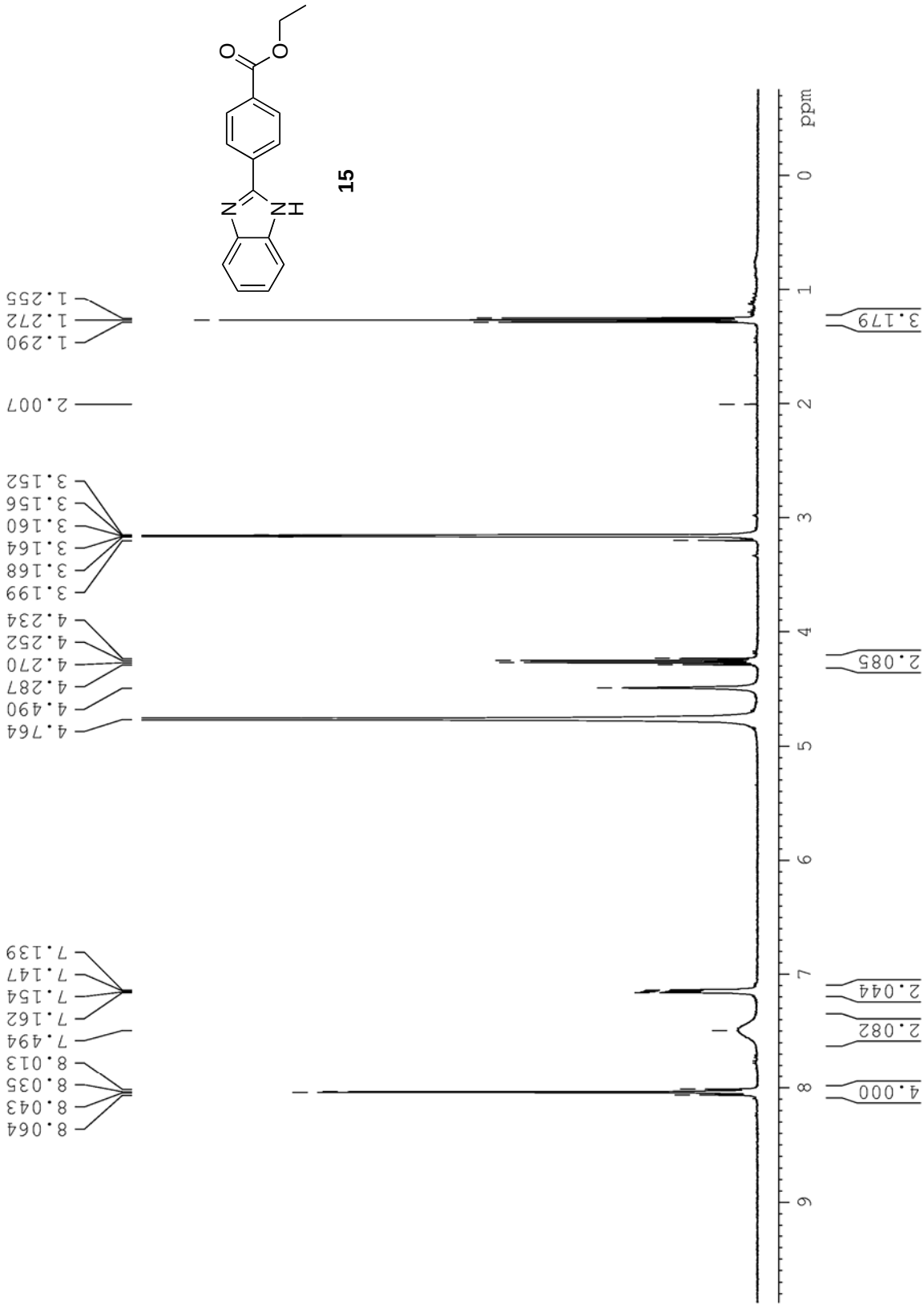

11
CF3
N
H
ppm
8.133
8.113
7.722
7.701
7.496
7.178
7.168
7.160
7.153
7.145
7.135
4.744
3.332
3.199
3.168
3.164
3.160
3.156
3.152
2.983
1.051
1.032
1.014
2.000
2.055
2.021
2.040

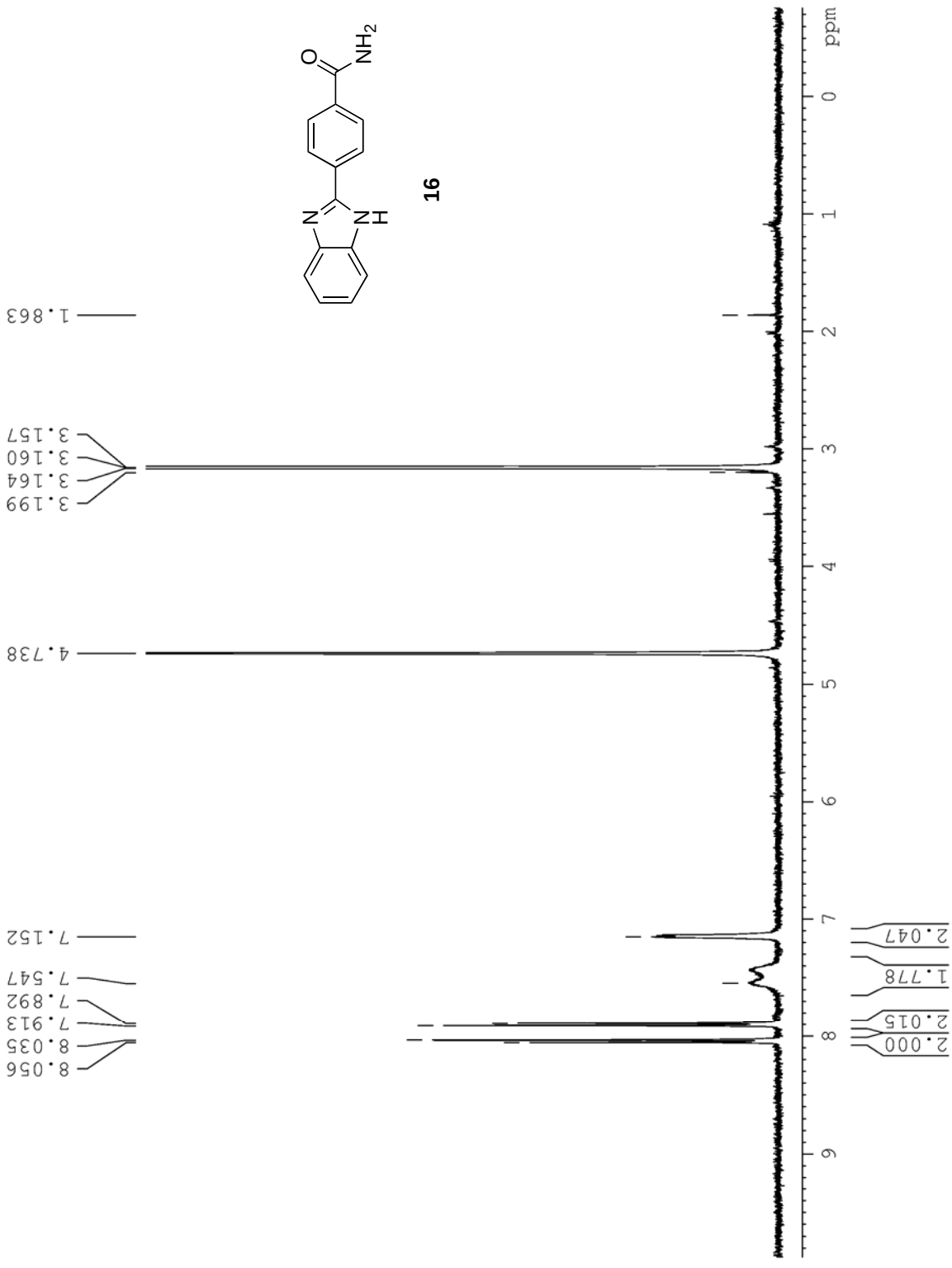

12
ppm
8.2
8.0
7.8
7.6
7.4
2.000
2.038
1.987
2.040
3.044
0.803
0.847
0.870
0.887
1.038
1.056
1.074
1.138
1.154
1.749
2.727
2.793
2.983
3.152
3.156
3.160
3.164
3.168
3.199
3.332
4.758
5.346
7.135
7.145
7.152
7.160
7.168
7.178
7.498
7.736
7.740
7.752
7.757
8.006
8.149
8.153
8.165
8.170

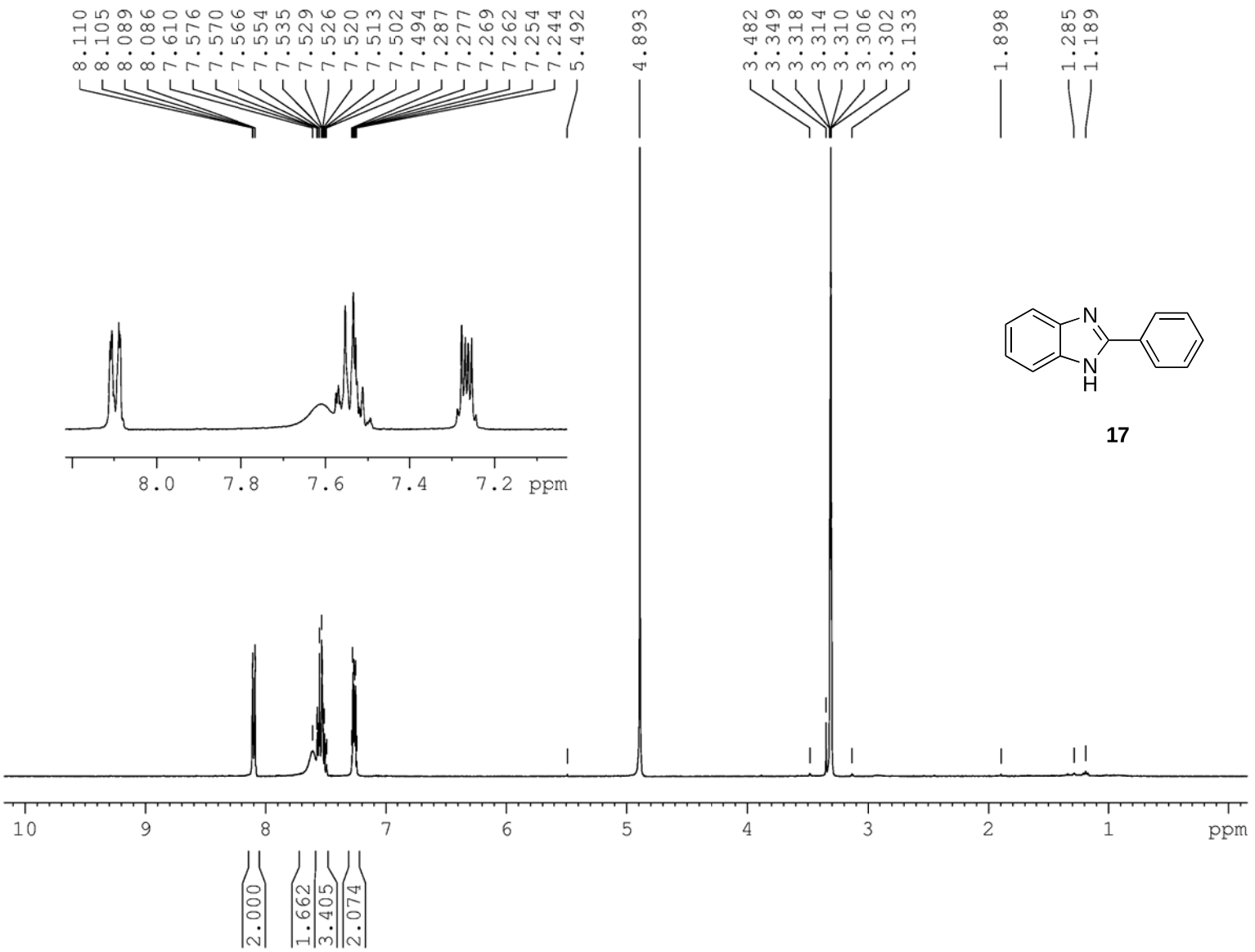

12
42.060
47.032
47.202
47.373
47.543
47.713
47.827
47.884
47.998
48.054
122.976
124.227
127.280
132.468
146.524
150.333
ppm
ppm


13
Cl
N
H
ppm
0.901
0.932
1.049
1.057
1.088
1.135
1.154
1.174
1.191
1.265
1.282
1.980
2.123
2.674
2.692
2.982
3.037
3.055
3.156
3.160
3.164
3.199
4.745
5.341
7.103
7.113
7.121
7.128
7.136
7.146
7.402
7.423
7.458
7.909
7.930
2.000
1.843
2.170
2.197

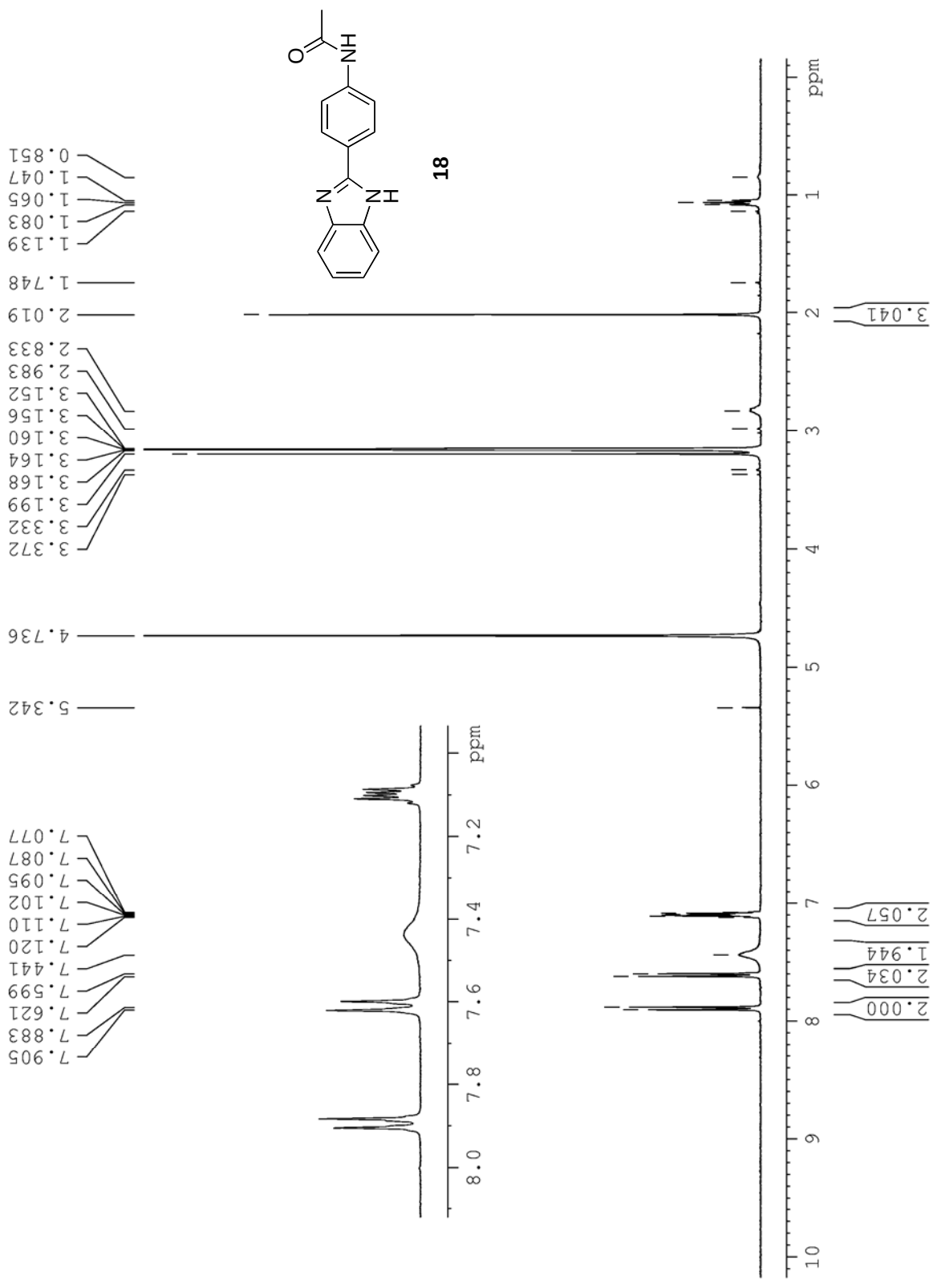

14
O
N
H
N
ppm
0.806
0.886
0.901
0.987
1.005
1.045
1.063
1.081
1.220
1.300
2.004
2.833
2.852
2.931
2.949
2.967
2.985
3.024
3.152
3.156
3.160
3.164
3.168
3.199
3.332
4.742
5.342
7.125
7.135
7.143
7.150
7.158
7.168
7.224
7.488
7.738
7.759
7.785
7.986
8.007
8.046
8.068
2.000
1.986
1.938
2.006
2.069
3.018

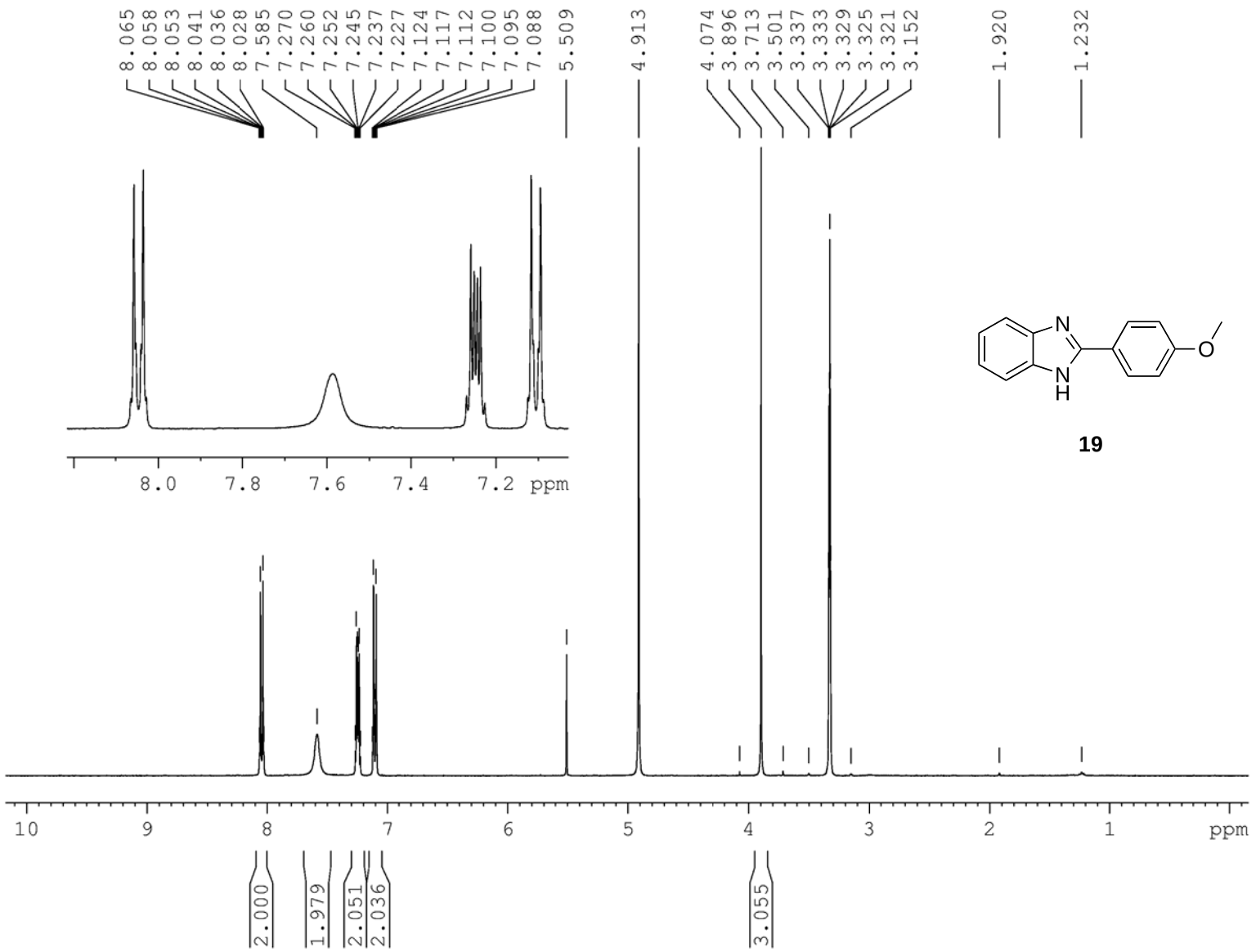

15
ppm
0
1
2
3
4
5
6
7
8
9
1.255
1.272
1.290
2.007
3.152
3.156
3.160
3.164
3.168
3.199
4.234
4.252
4.270
4.287
4.490
4.764
7.139
7.147
7.154
7.162
7.494
8.013
8.035
8.043
8.064
3.179
2.085
2.044
2.082
4.000


16
1.863
3.157
3.160
3.164
3.199
4.738
7.152
7.547
7.892
7.913
8.035
8.056
2.047
1.778
2.015
2.000
ppm

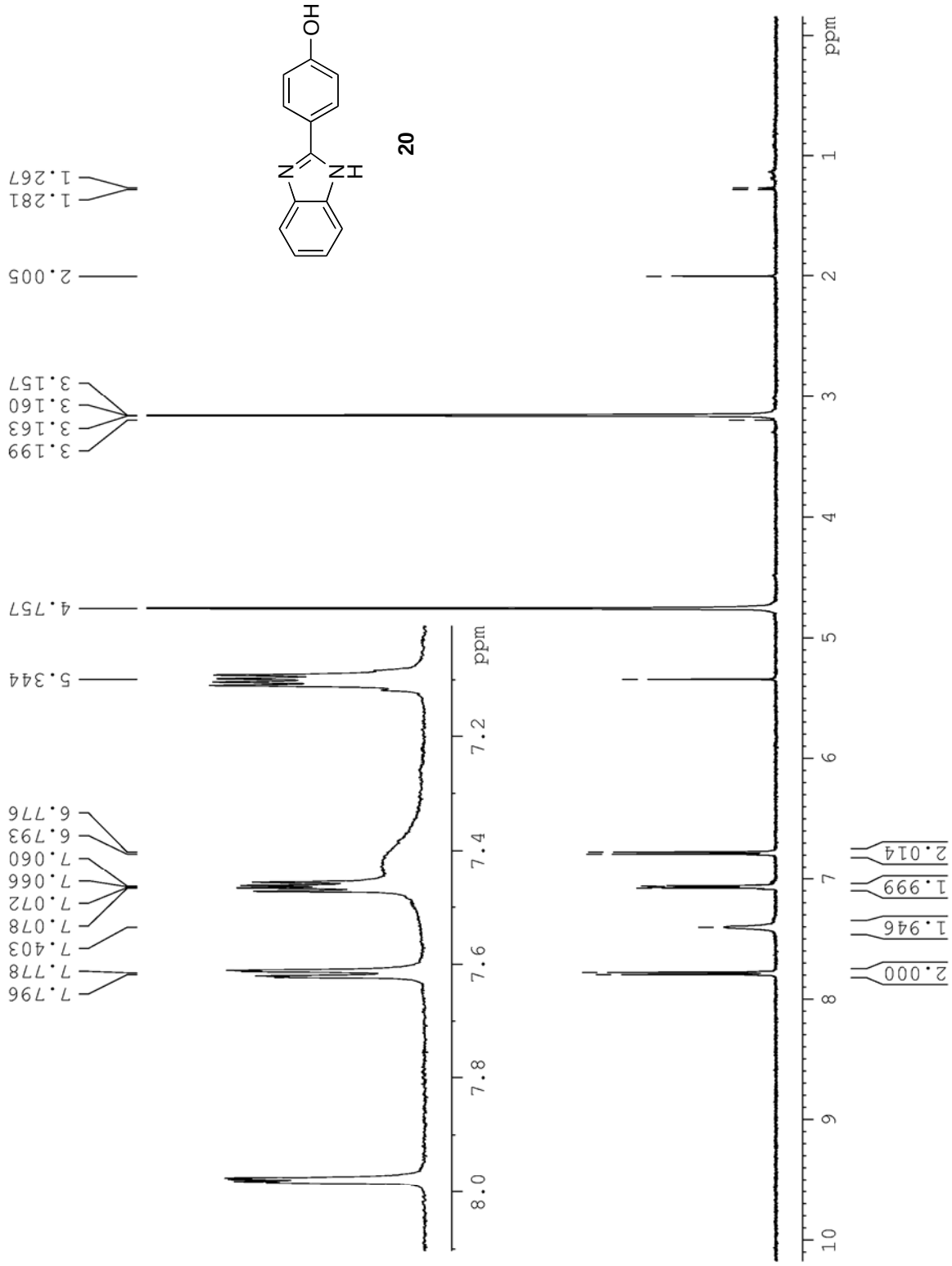

8.110
8.105
8.089
8.086
7.610
7.576
7.570
7.566
7.554
7.535
7.529
7.526
7.520
7.513
7.502
7.494
7.287
7.277
7.269
7.262
7.254
7.244
5.492
4.893
3.482
3.349
3.318
3.314
3.310
3.306
3.302
3.133
1.898
1.285
1.189
8.0
7.8
7.6
7.4
7.2 ppm
10
9
8
7
6
5
4
3
2
1
ppm
2.000
1.662
3.405
2.074
N
N
H

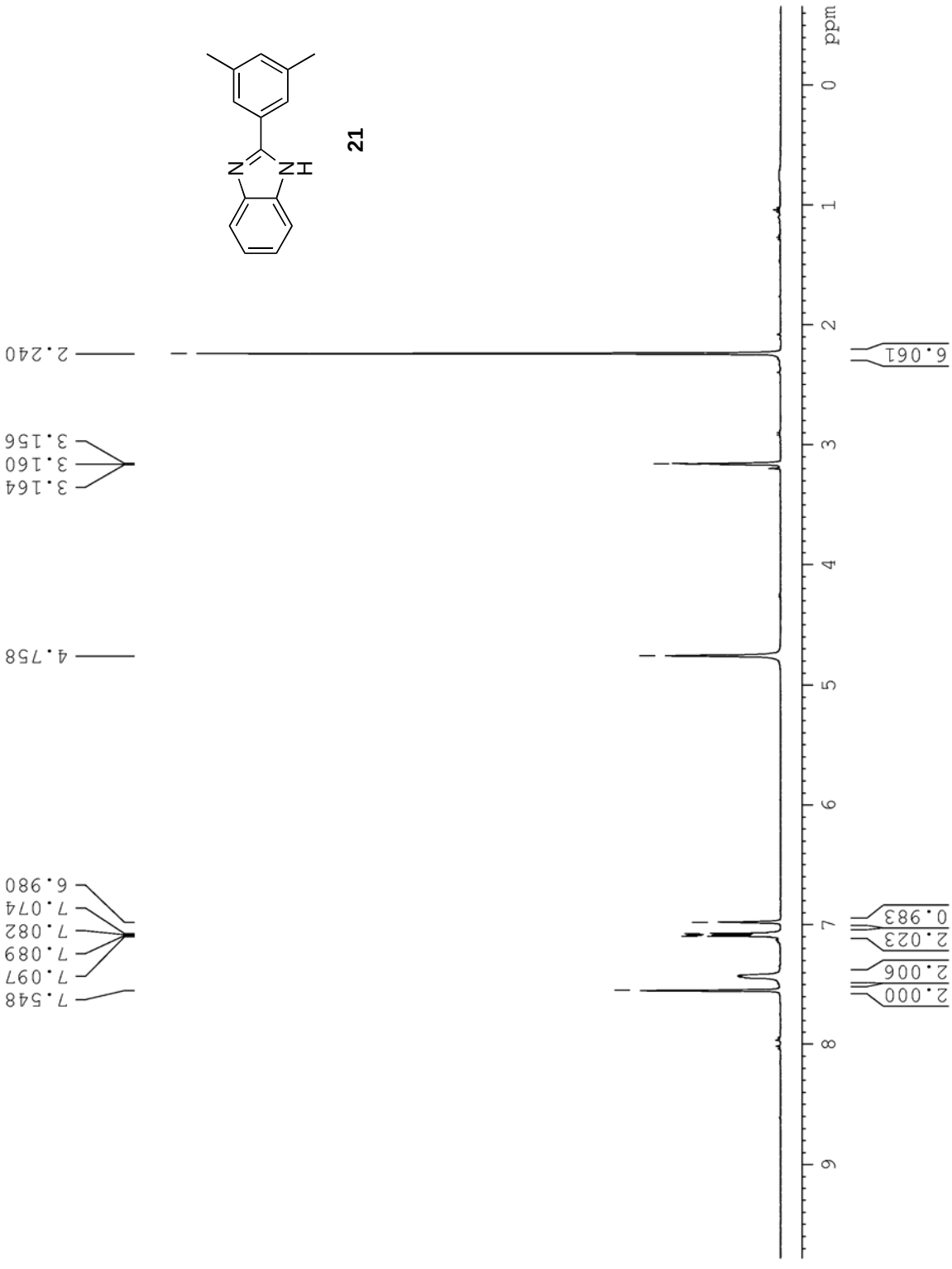
17

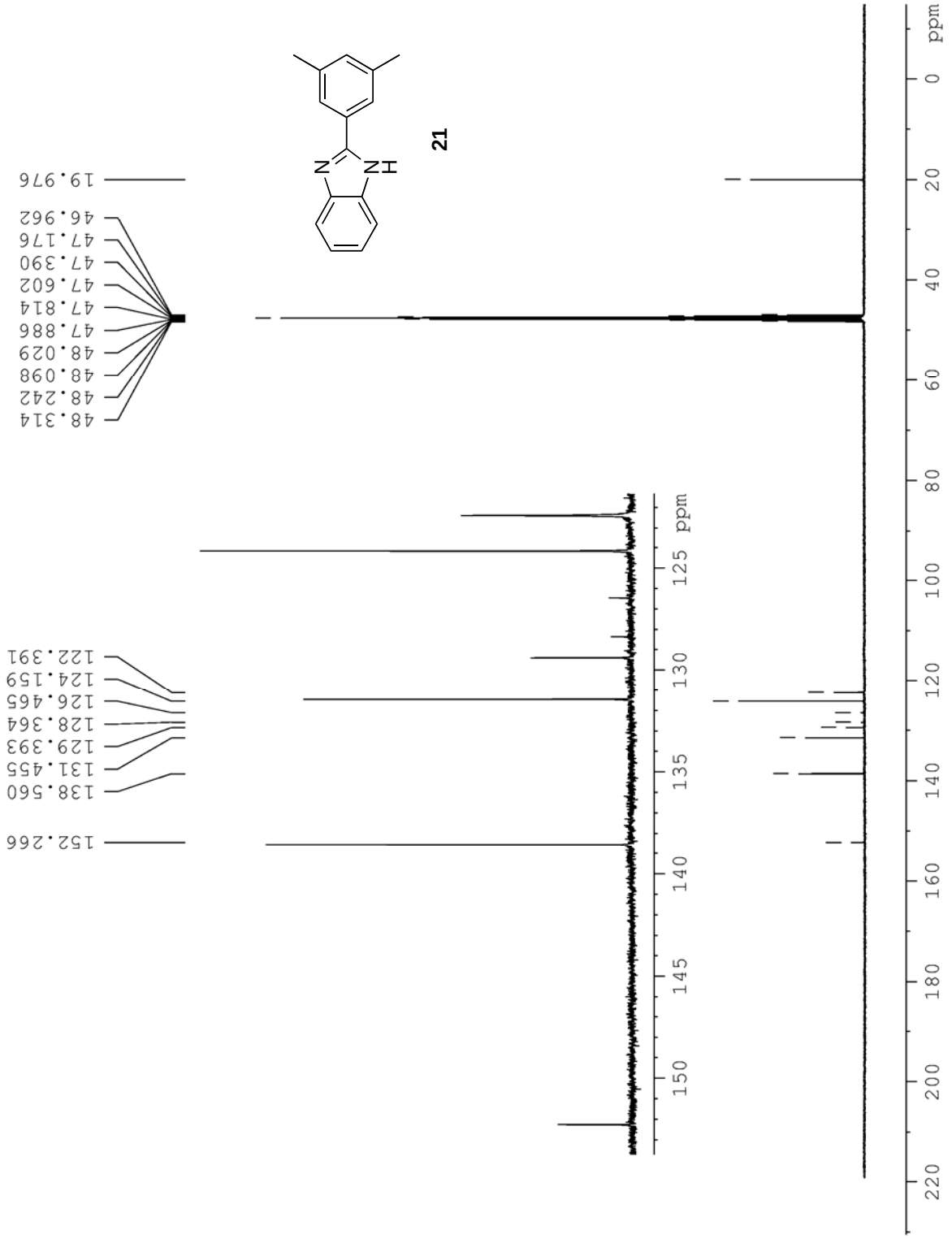

18
O
NH
N
H
N
ppm
1
2
3
4
5
6
7
8
9
10
3.041
2.057
1.944
2.034
2.000
7.905
7.883
7.621
7.599
7.441
7.120
7.110
7.102
7.095
7.087
7.077
5.342
4.736
3.372
3.332
3.199
3.168
3.164
3.160
3.156
3.152
2.983
2.833
2.019
1.748
1.139
1.083
1.065
1.047
0.851
8.0
7.8
7.6
7.4
7.2
ppm

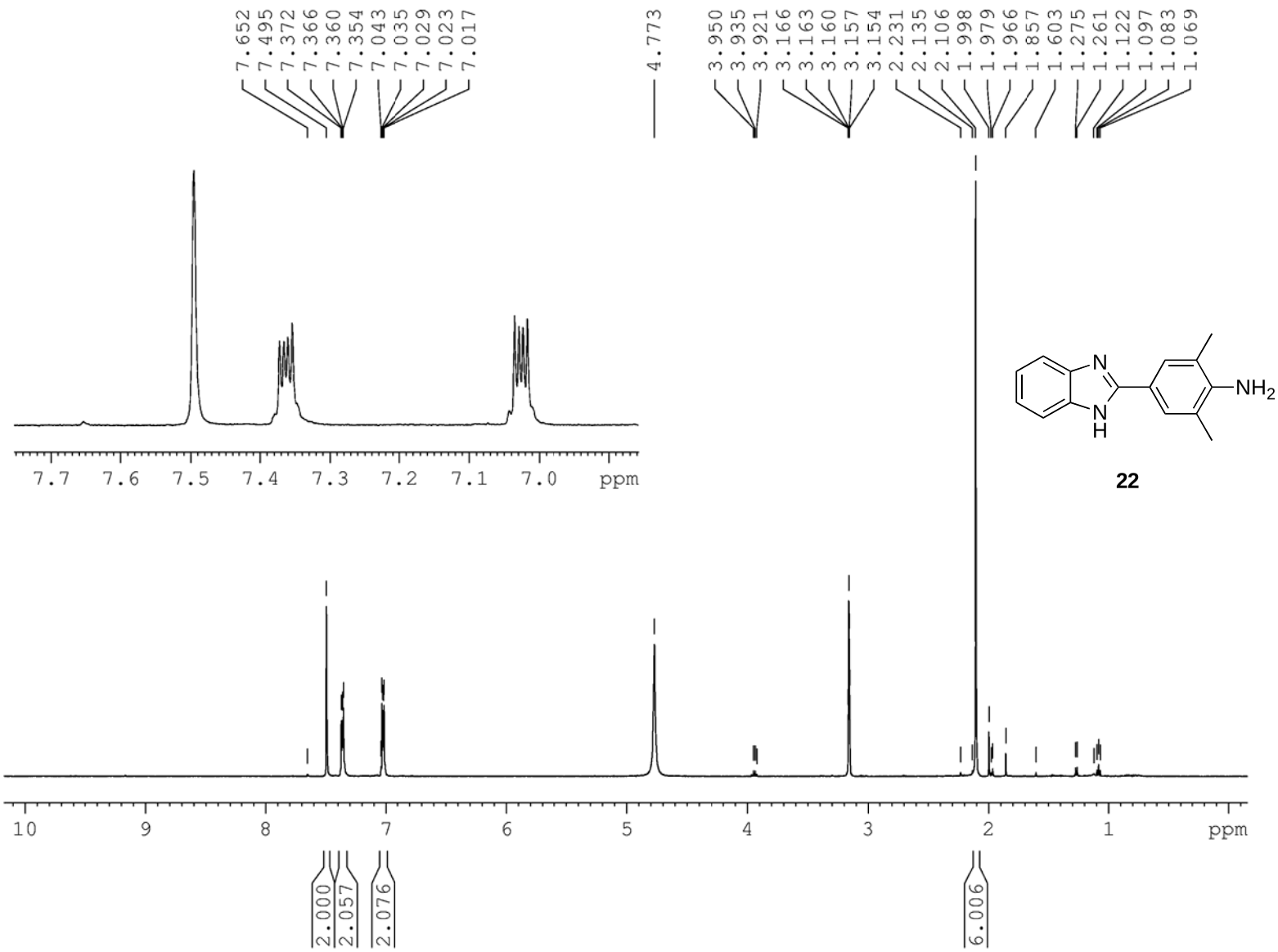

8.065
8.058
8.053
8.041
8.036
8.028
7.585
7.270
7.260
7.252
7.245
7.237
7.227
7.124
7.117
7.112
7.100
7.095
7.088
5.509
4.913
4.074
3.896
3.713
3.501
3.337
3.333
3.329
3.325
3.321
3.152
1.920
1.232
8.0
7.8
7.6
7.4
7.2
ppm
10
9
8
7
6
5
4
3
2
1
ppm
2.000
1.979
2.051
2.036
3.055
N
N
H
O

19

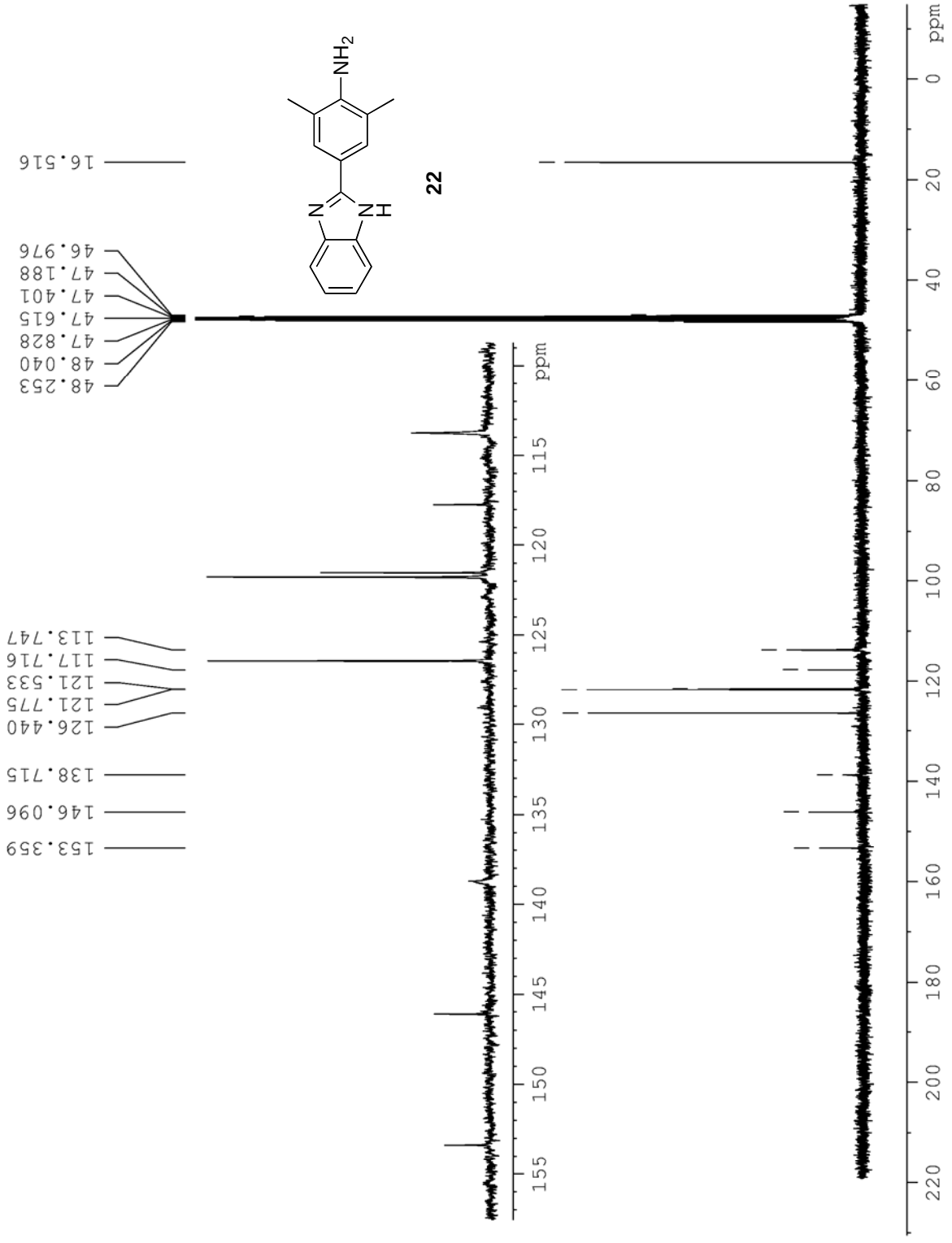

20
OH
N
H
N
ppm
1.267
1.281
2.005
3.157
3.160
3.163
3.199
4.757
5.344
6.776
6.793
7.060
7.066
7.072
7.078
7.403
7.778
7.796
2.000
1.946
1.999
2.014

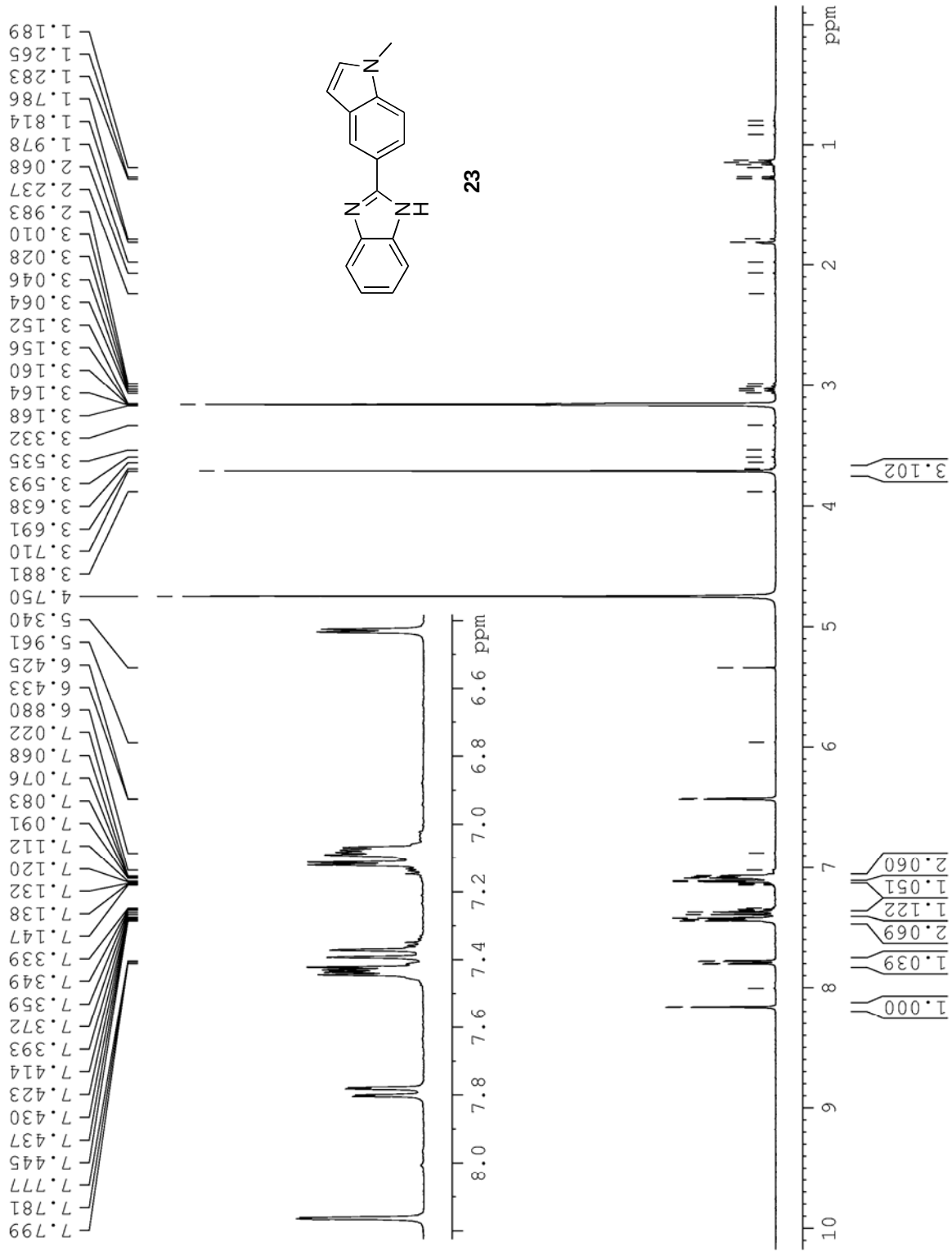

21
ppm
0
1
2
3
4
5
6
7
8
9
2.240
3.156
3.160
3.164
4.758
6.980
7.074
7.082
7.089
7.097
7.548
6.061
0.983
2.023
2.006
2.000

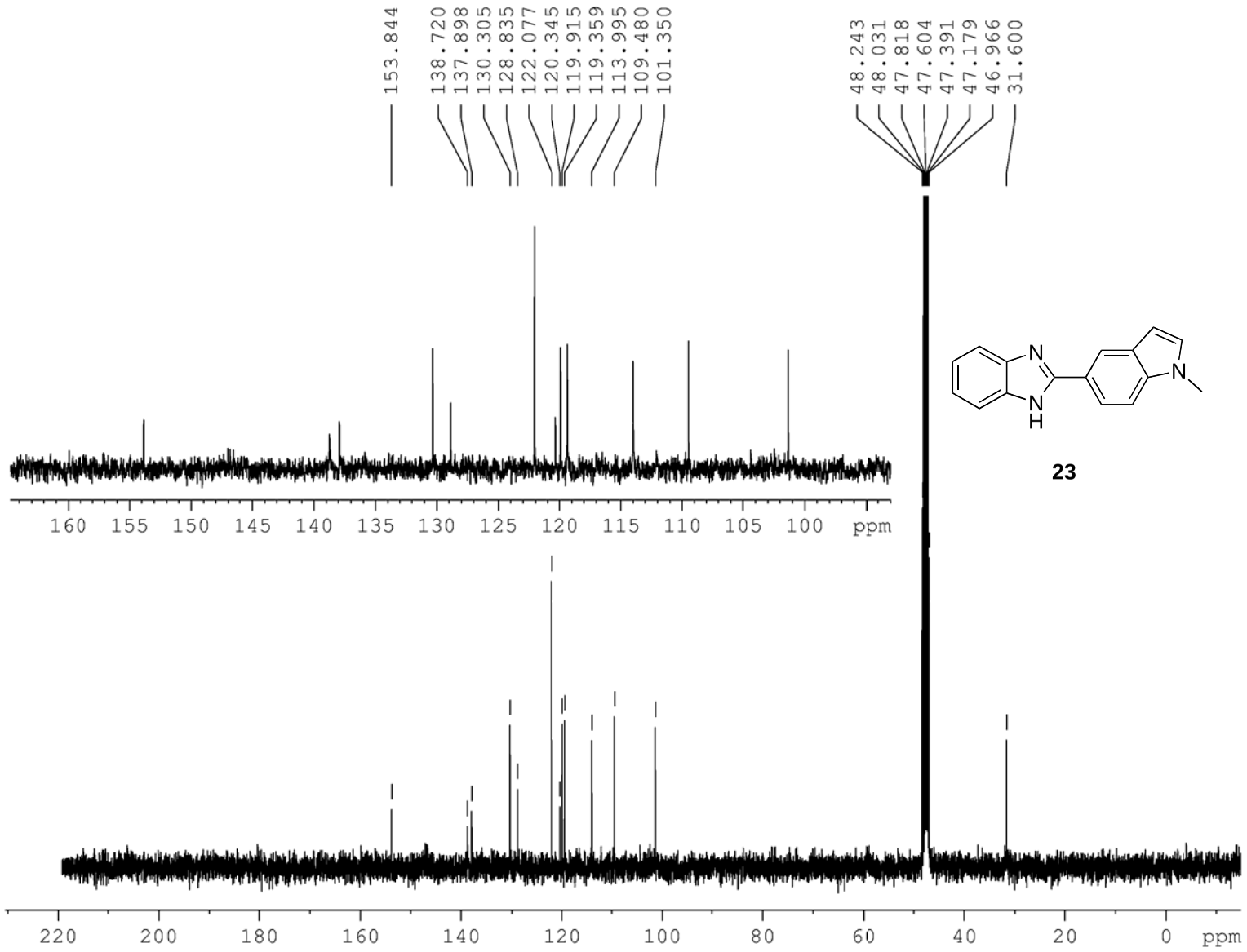

21
19.976
46.962
47.176
47.390
47.602
47.814
47.886
48.029
48.098
48.242
48.314
122.391
124.159
126.465
128.364
129.393
131.455
138.560
152.266
ppm
0
20
40
60
80
100
120
125
130
135
140
145
150
160
180
200
220

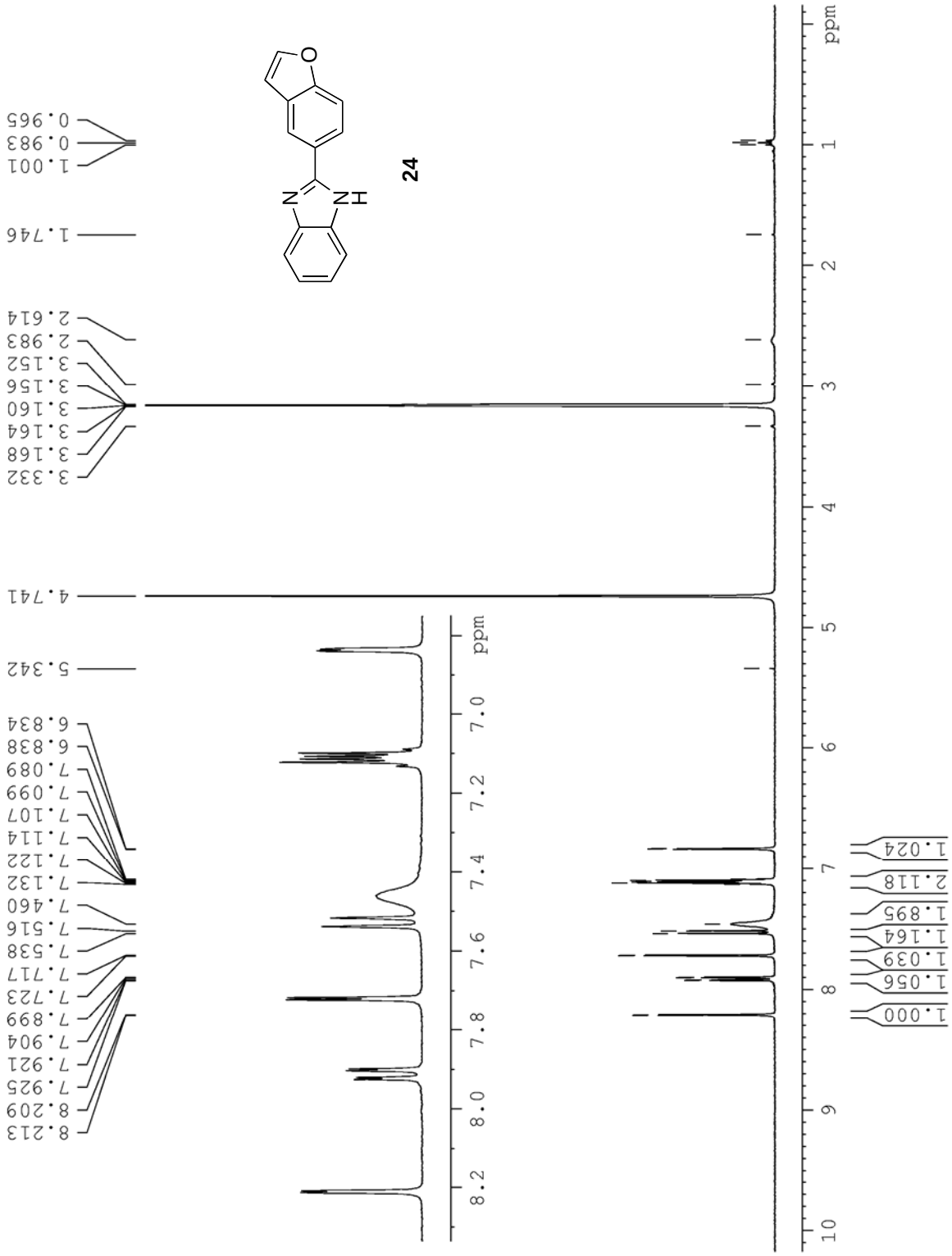

7.652
7.495
7.372
7.366
7.360
7.354
7.043
7.035
7.029
7.023
7.017
4.773
3.950
3.935
3.921
3.166
3.163
3.160
3.157
3.154
2.231
2.135
2.106
1.998
1.979
1.966
1.857
1.603
1.275
1.261
1.122
1.097
1.083
1.069
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
10 9 8 7 6 5 4 3 2 1 ppm
2.000
2.057
2.076
6.006
N
N
H
NH2

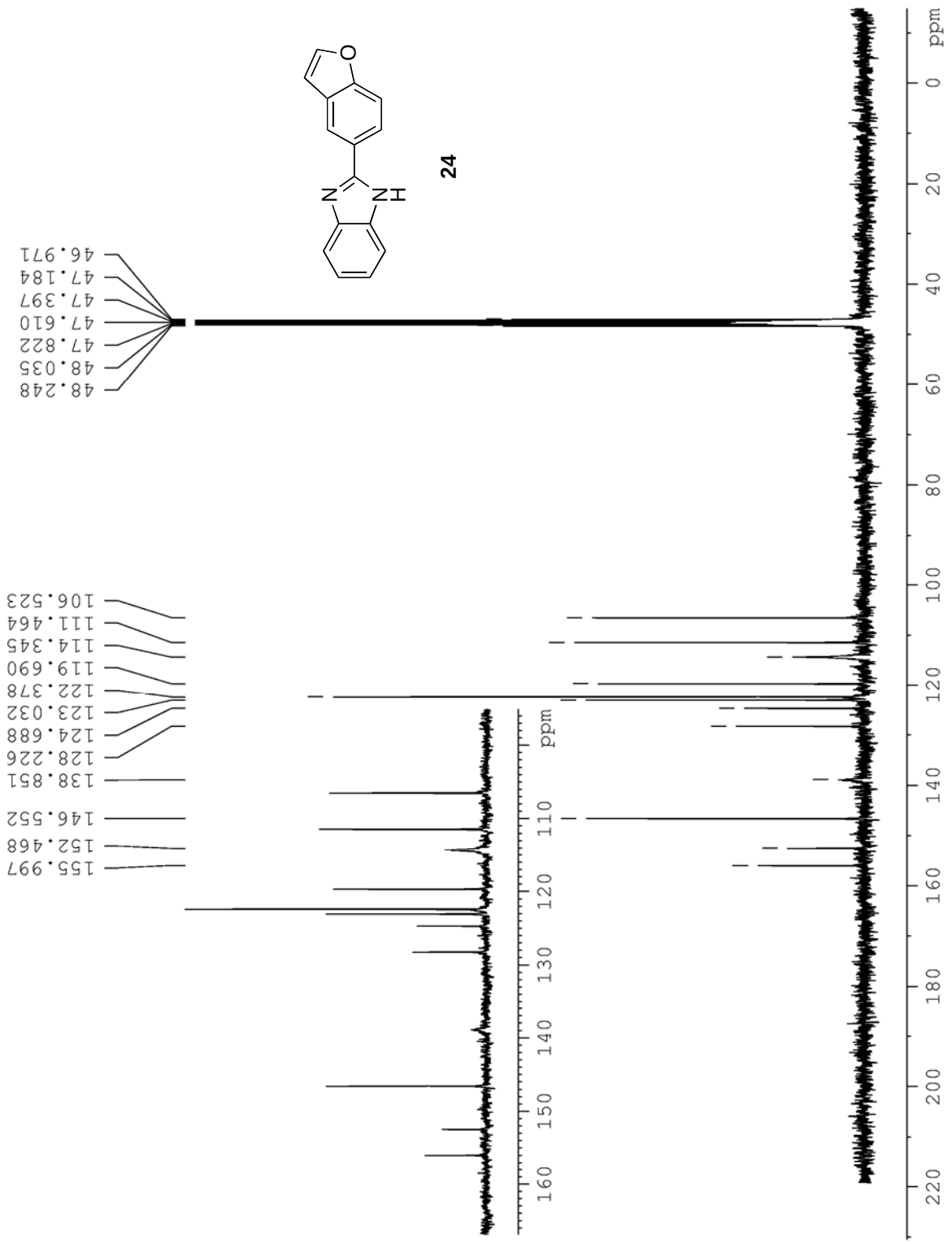
22

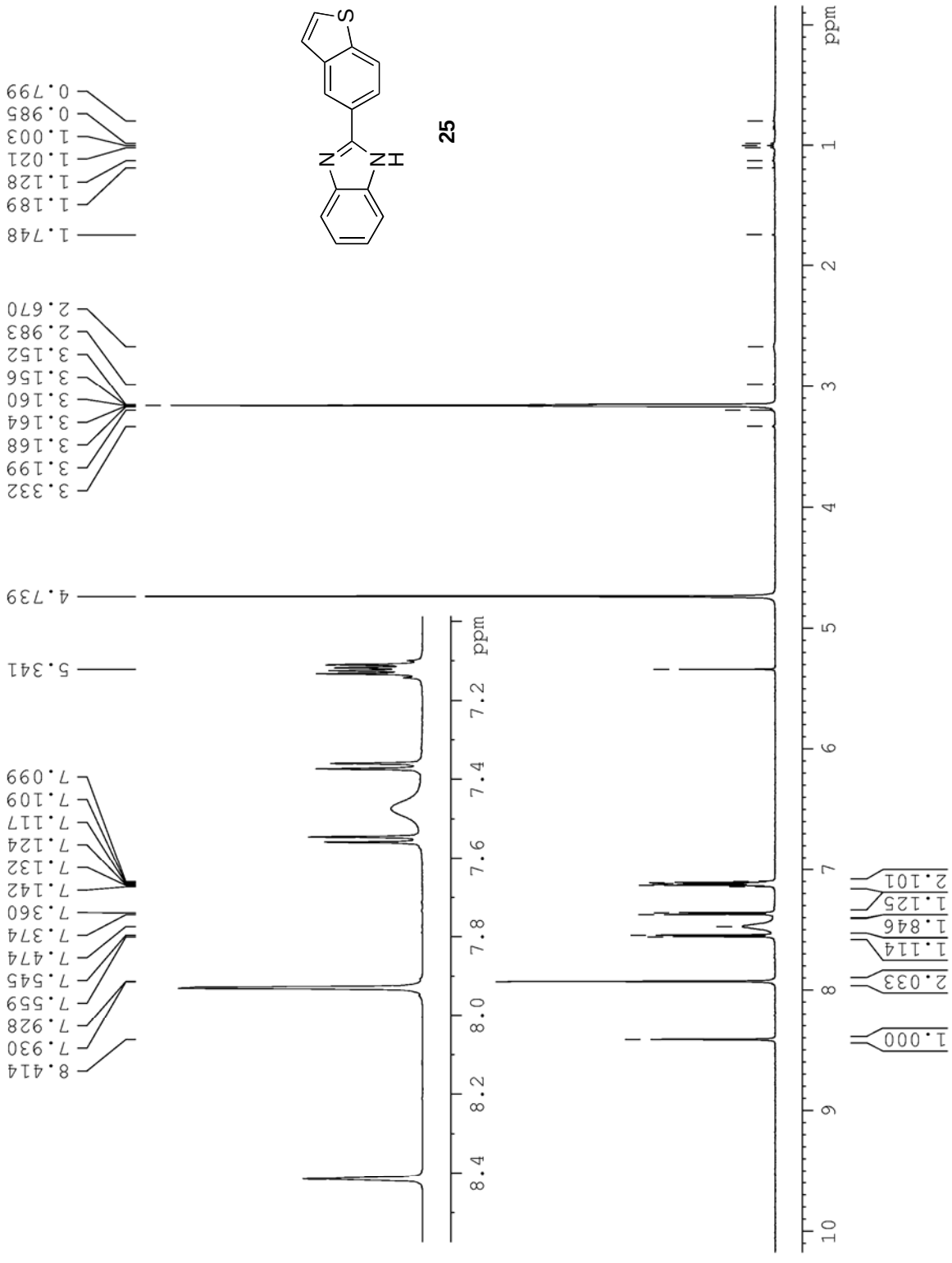

NH2
N
H
N
22
16.516
46.976
47.188
47.401
47.615
47.828
48.040
48.253
113.747
117.716
121.533
121.775
126.440
138.715
146.096
153.359
ppm
ppm

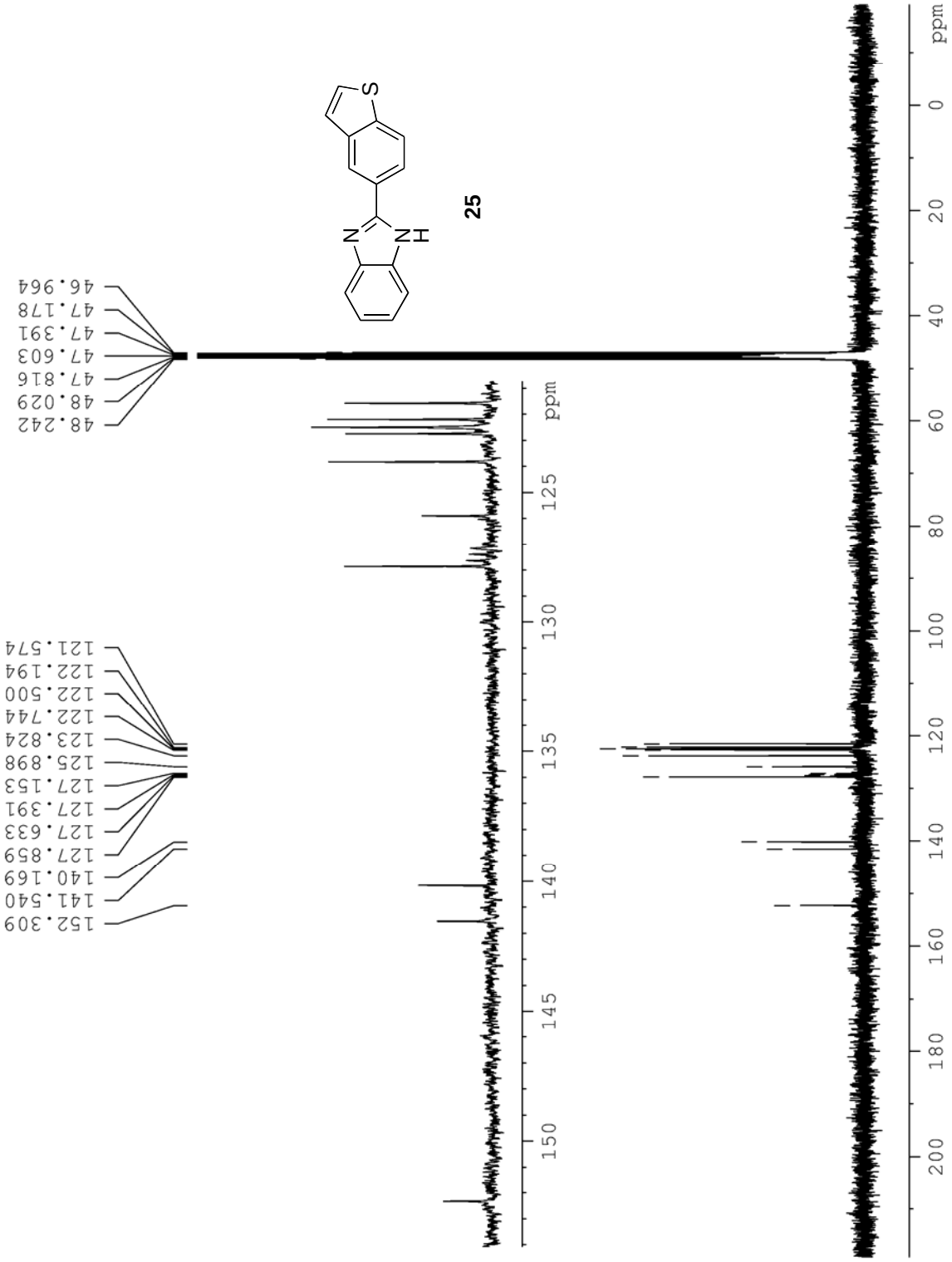

23
ppm
1.000
1.039
2.069
1.122
1.051
2.060
3.102

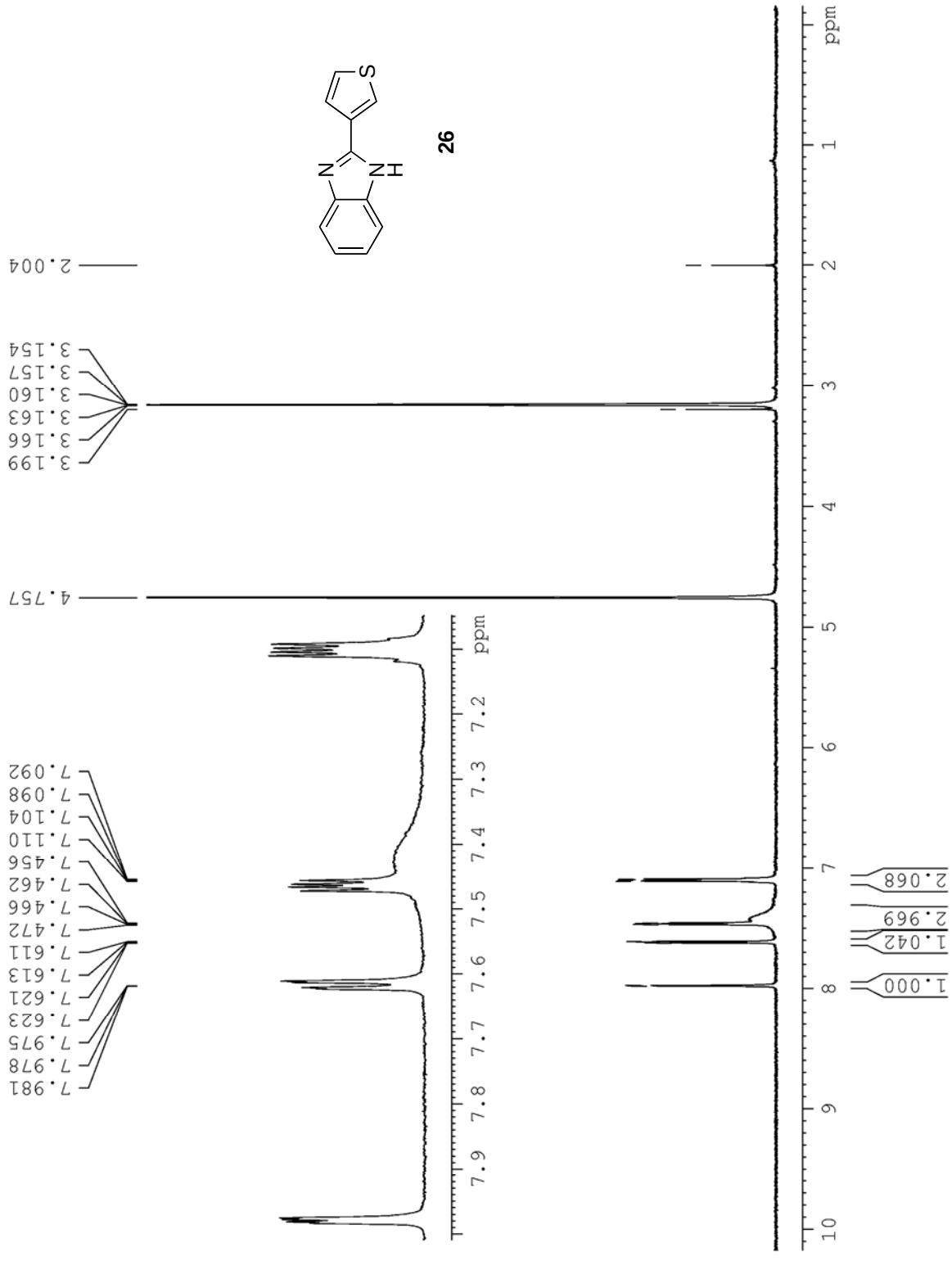

153.844
138.720
137.898
130.305
128.835
122.077
120.345
119.915
119.359
113.995
109.480
101.350
48.243
48.031
47.818
47.604
47.391
47.179
46.966
31.600
N
N
H
N
23
160 155 150 145 140 135 130 125 120 115 110 105 100 ppm
220 200 180 160 140 120 100 80 60 40 20 0 ppm

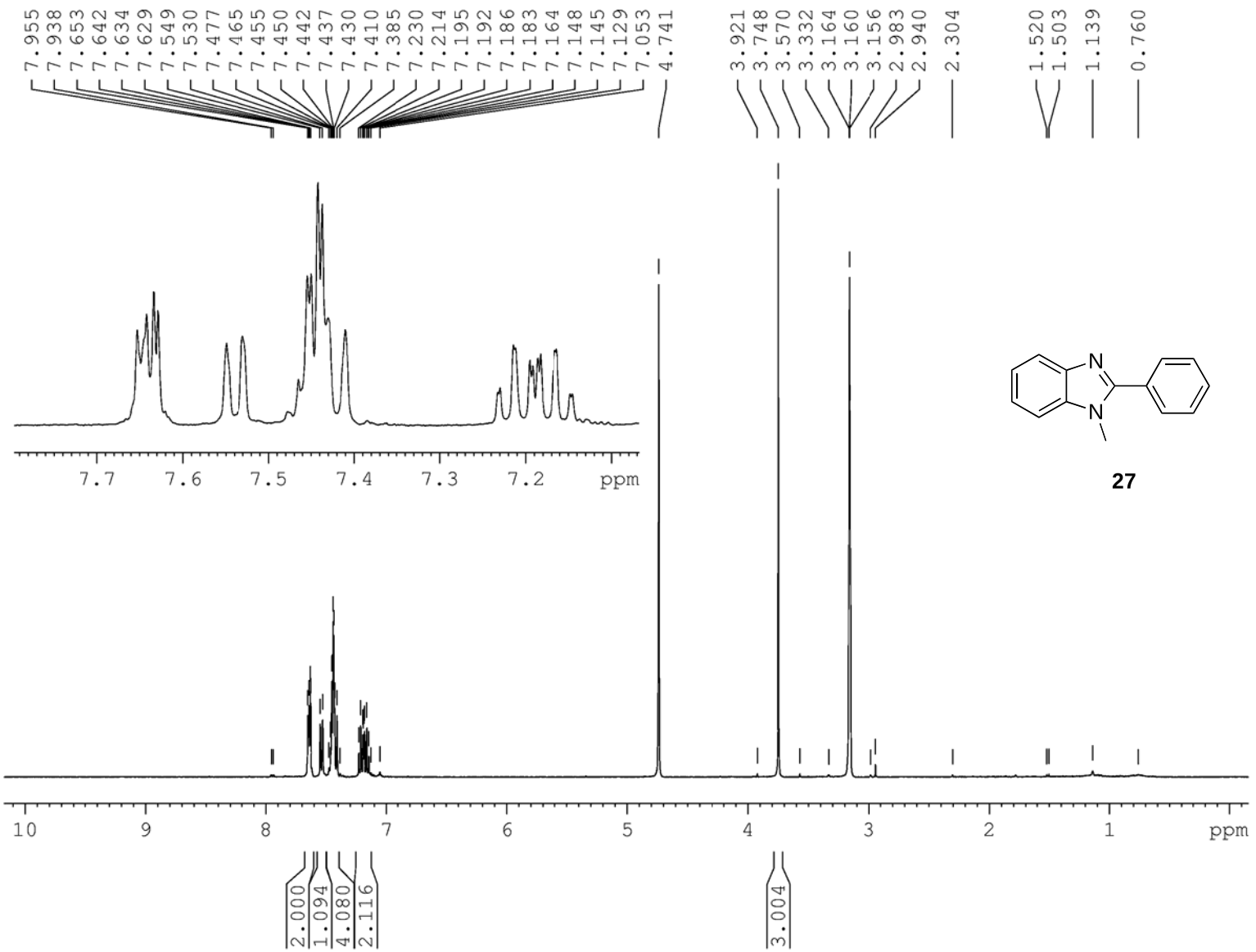

24
8.213
8.209
7.925
7.921
7.904
7.899
7.723
7.717
7.538
7.516
7.460
7.132
7.122
7.114
7.107
7.099
7.089
6.838
6.834
5.342
4.741
3.332
3.168
3.164
3.160
3.156
3.152
2.983
2.614
1.746
1.001
0.983
0.965
1.000
1.056
1.039
1.164
1.895
2.118
1.024
ppm


24
155.997
152.468
146.552
138.851
128.226
124.688
123.032
122.378
119.690
114.345
111.464
106.523
48.248
48.035
47.822
47.610
47.397
47.184
46.971
ppm
ppm

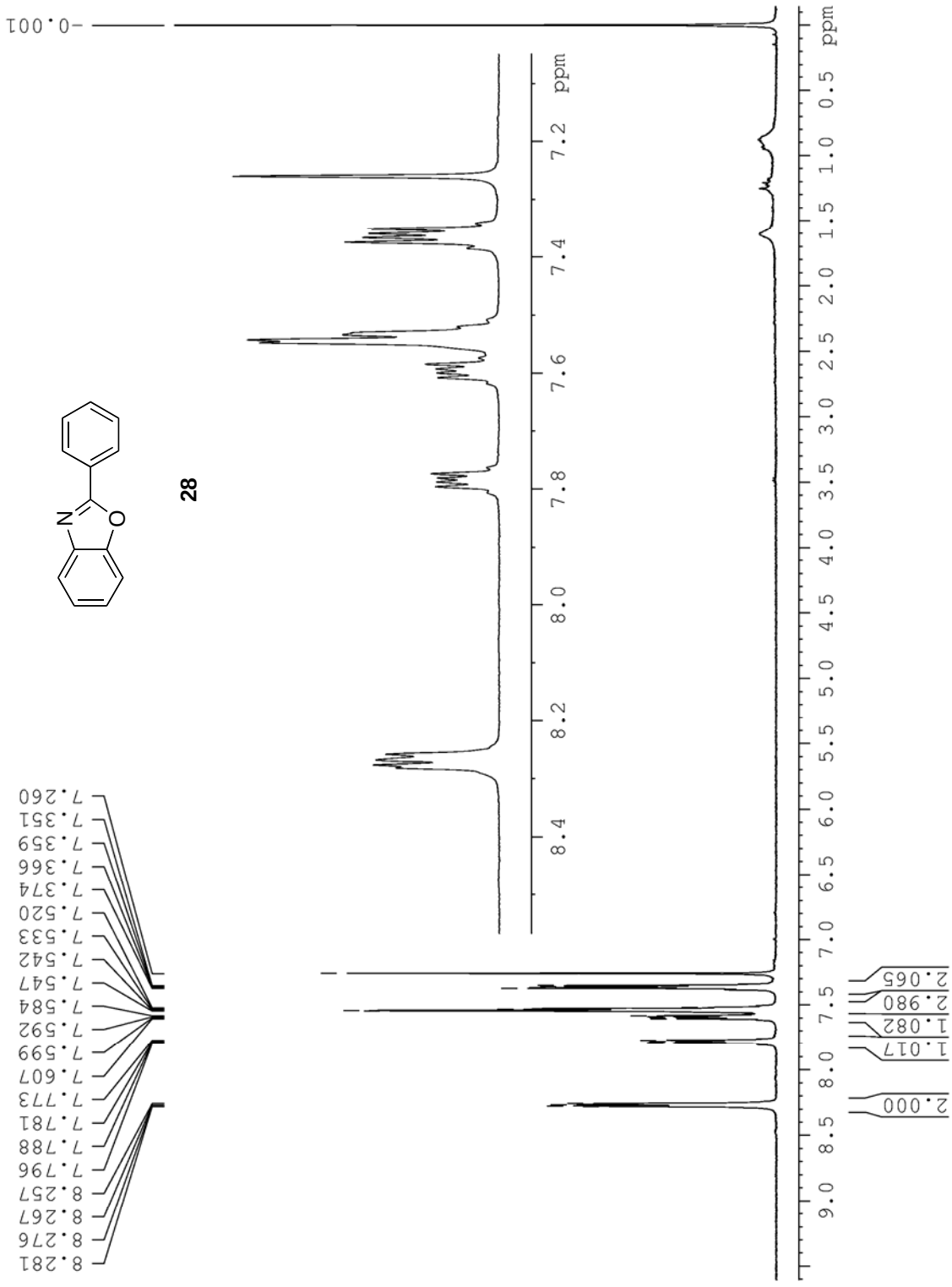

25
8.414
7.930
7.928
7.559
7.545
7.474
7.374
7.360
7.142
7.132
7.124
7.117
7.109
7.099
5.341
4.739
3.332
3.199
3.168
3.164
3.160
3.156
3.152
2.983
2.670
1.748
1.189
1.128
1.021
1.003
0.985
0.799
1.000
2.033
1.114
1.846
1.125
2.101
ppm

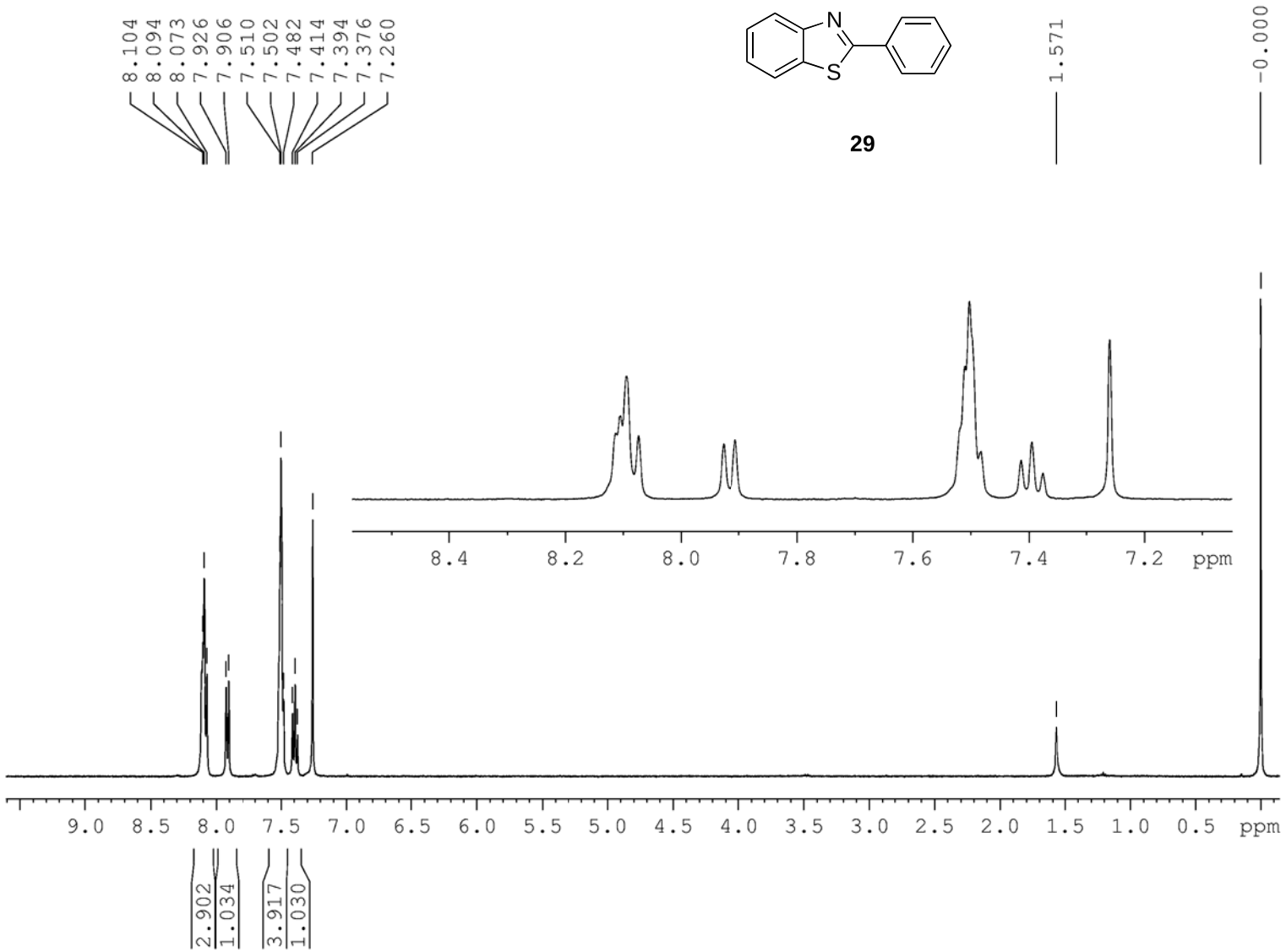

S
N
H
N
25
152.309
141.540
140.169
127.859
127.633
127.391
127.153
125.898
123.824
122.744
122.500
122.194
121.574
48.242
48.029
47.816
47.603
47.391
47.178
46.964
ppm
ppm

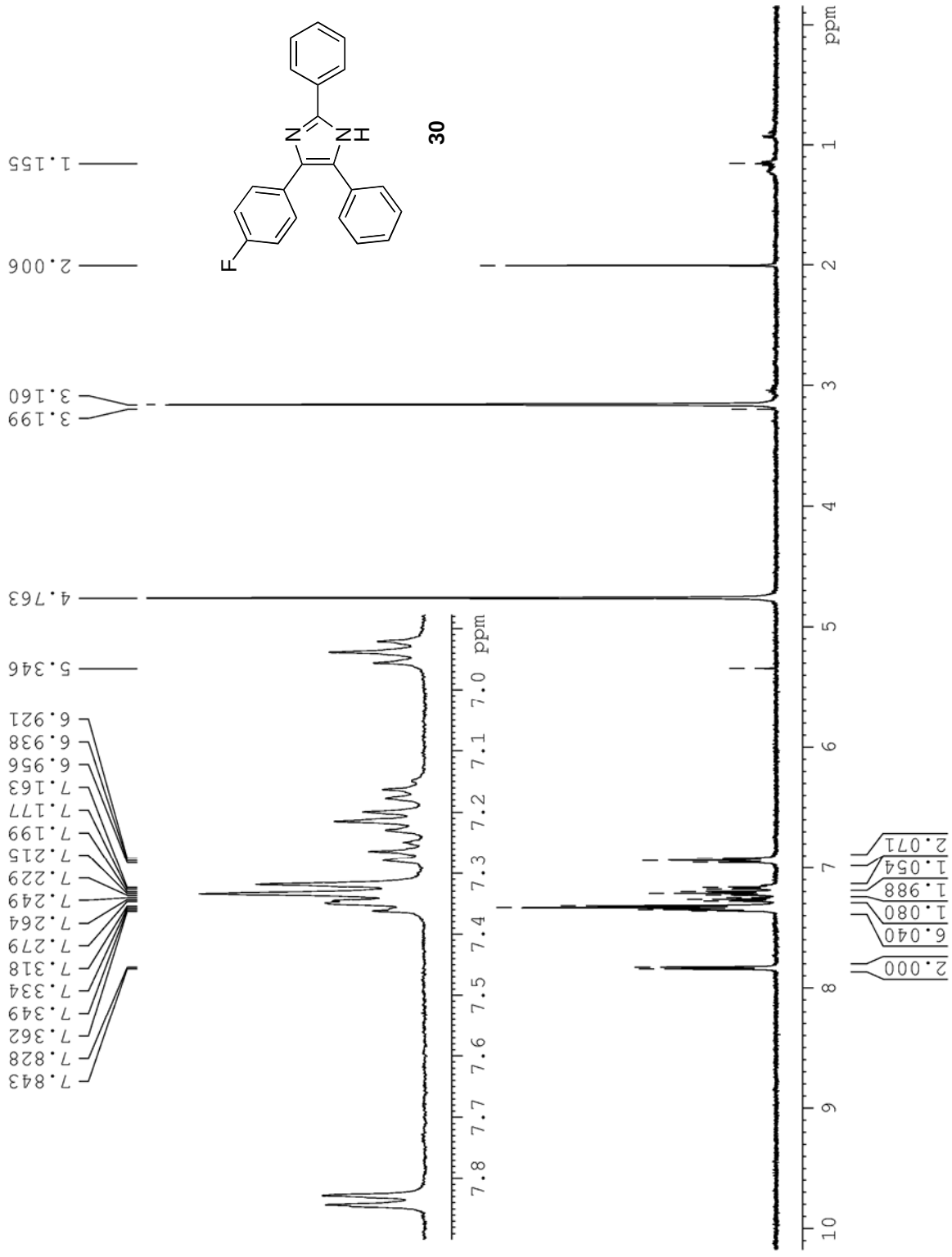

26
7.981
7.978
7.975
7.623
7.621
7.613
7.611
7.472
7.466
7.462
7.456
7.110
7.104
7.098
7.092
4.757
3.199
3.166
3.163
3.160
3.157
3.154
2.004
1.000
1.042
2.969
2.068
ppm

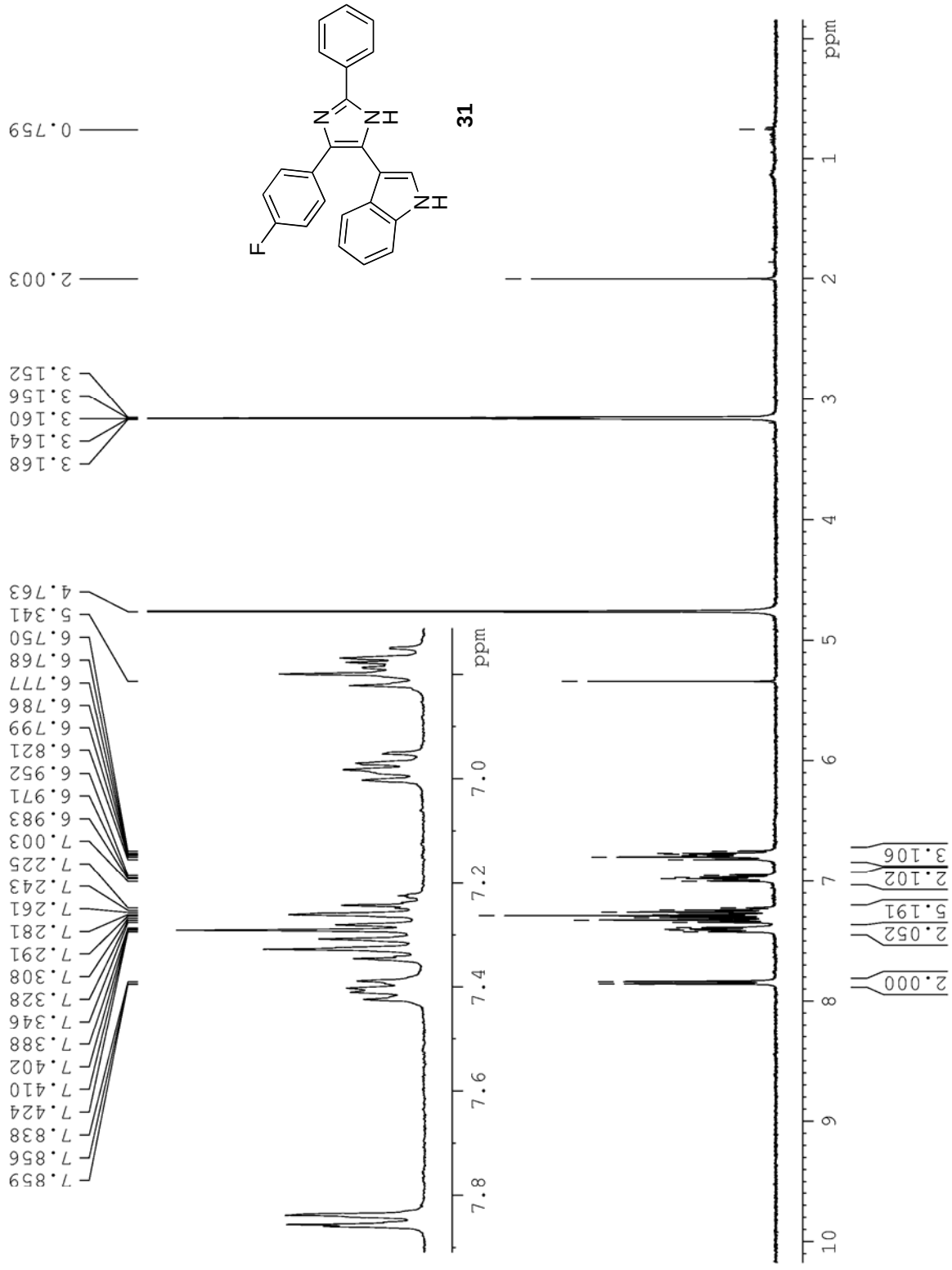

7.955
7.938
7.653
7.642
7.634
7.629
7.549
7.530
7.477
7.465
7.455
7.450
7.442
7.437
7.430
7.410
7.385
7.230
7.214
7.195
7.192
7.186
7.183
7.164
7.148
7.145
7.129
7.053
4.741
3.921
3.748
3.570
3.332
3.164
3.160
3.156
2.983
2.940
2.304
1.520
1.503
1.139
0.760
7.7
7.6
7.5
7.4
7.3
7.2
ppm
10
9
8
7
6
5
4
3
2
1
ppm
2.000
1.094
4.080
2.116
3.004
N
N

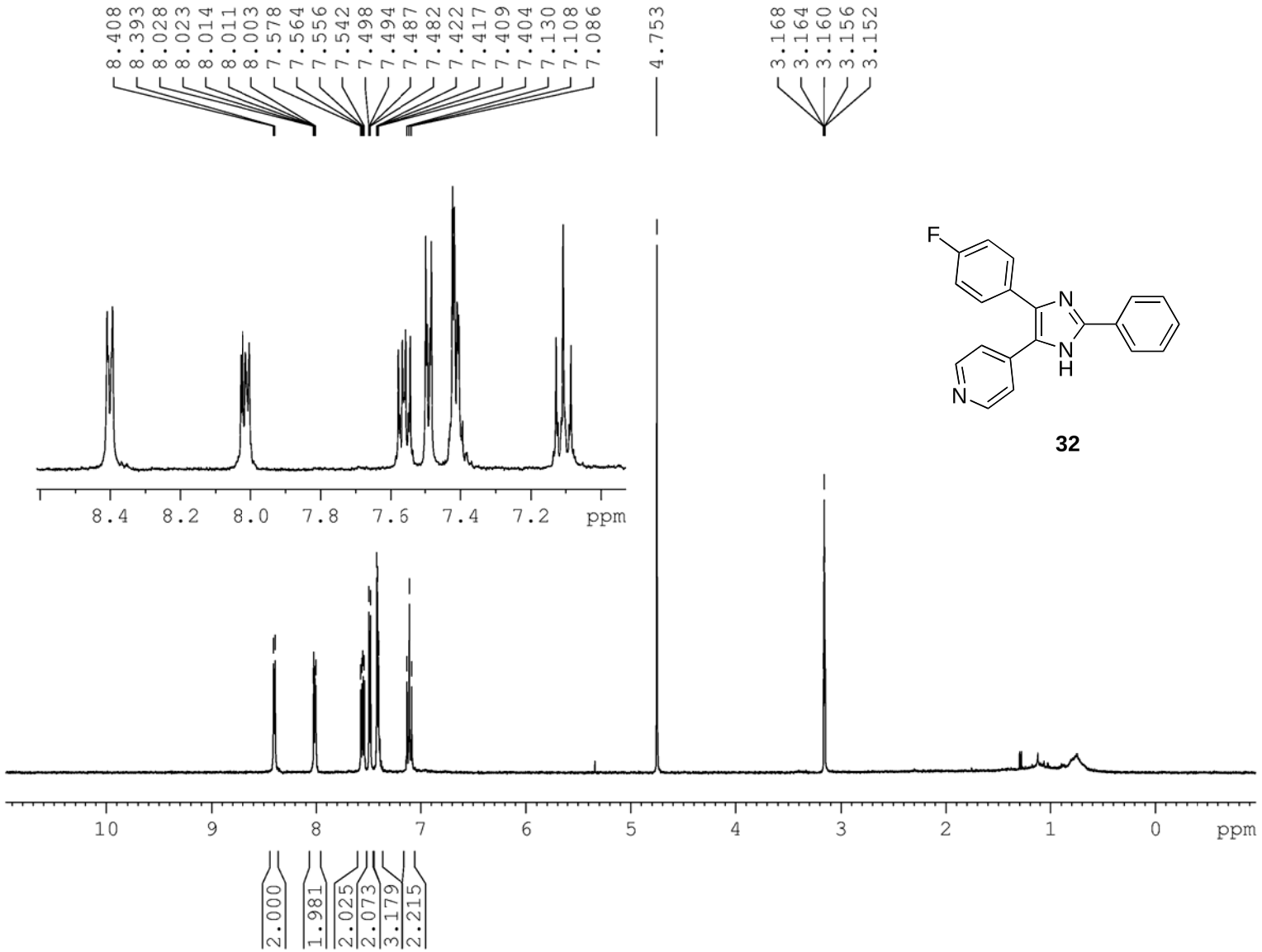
27

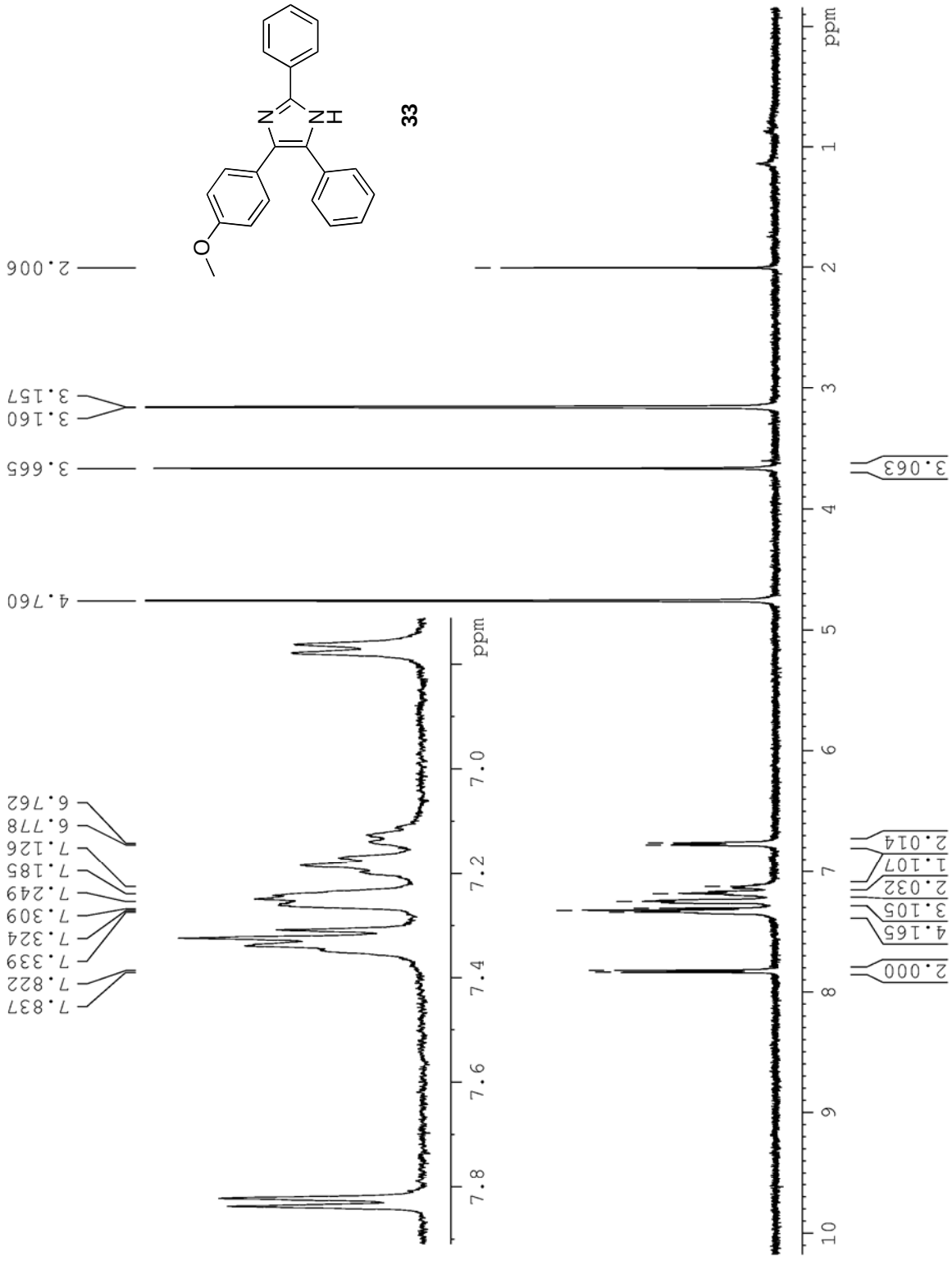

28
N
O
8.281
8.276
8.267
8.257
7.796
7.788
7.781
7.773
7.607
7.599
7.592
7.584
7.547
7.542
7.533
7.520
7.374
7.366
7.359
7.351
7.260
2.000
1.017
1.082
2.980
2.065
ppm

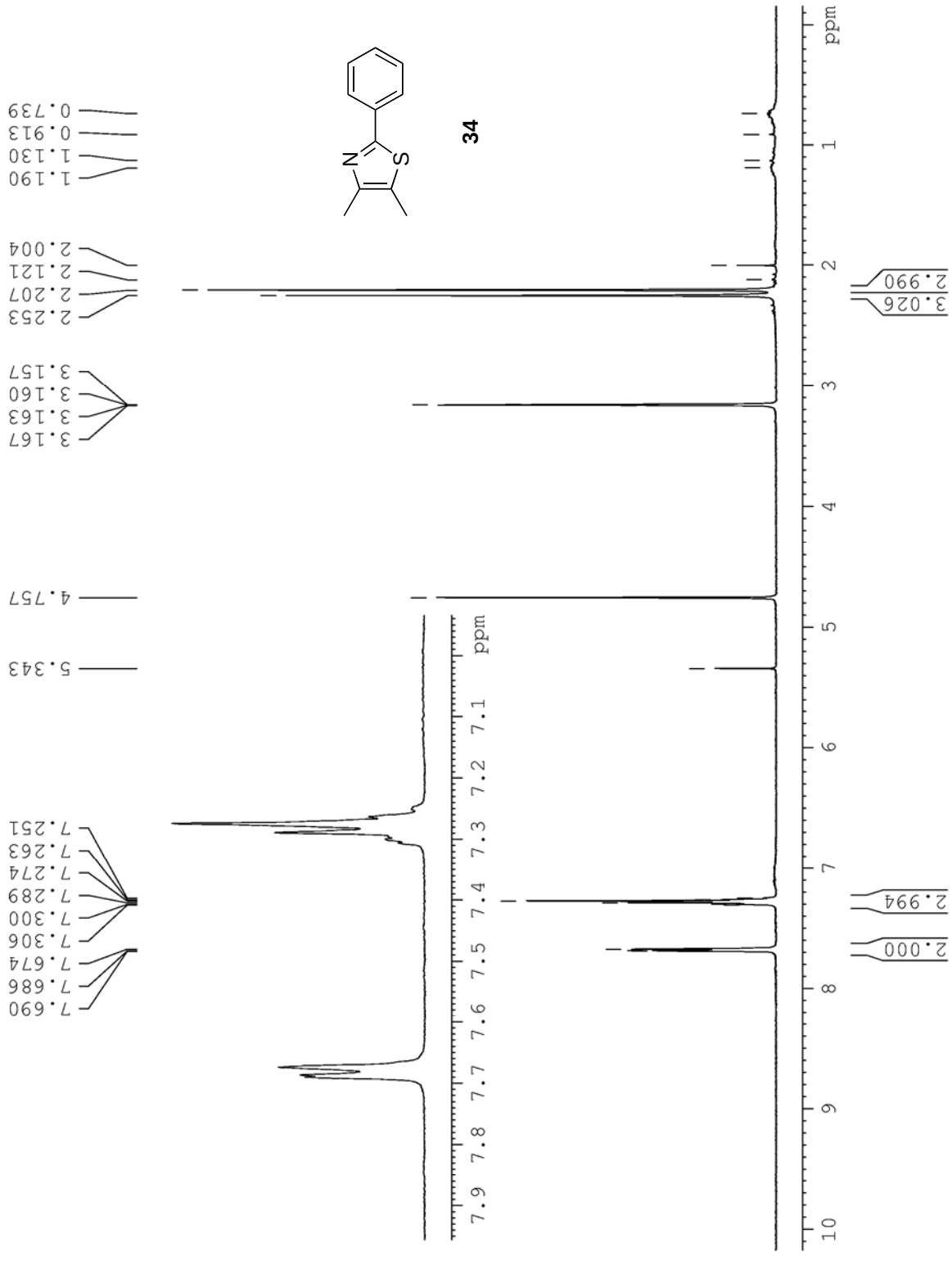

8.104
8.094
8.073
7.926
7.906
7.510
7.502
7.482
7.414
7.394
7.376
7.260
N
S
29
1.571
-0.000
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.902
1.034
3.917
1.030

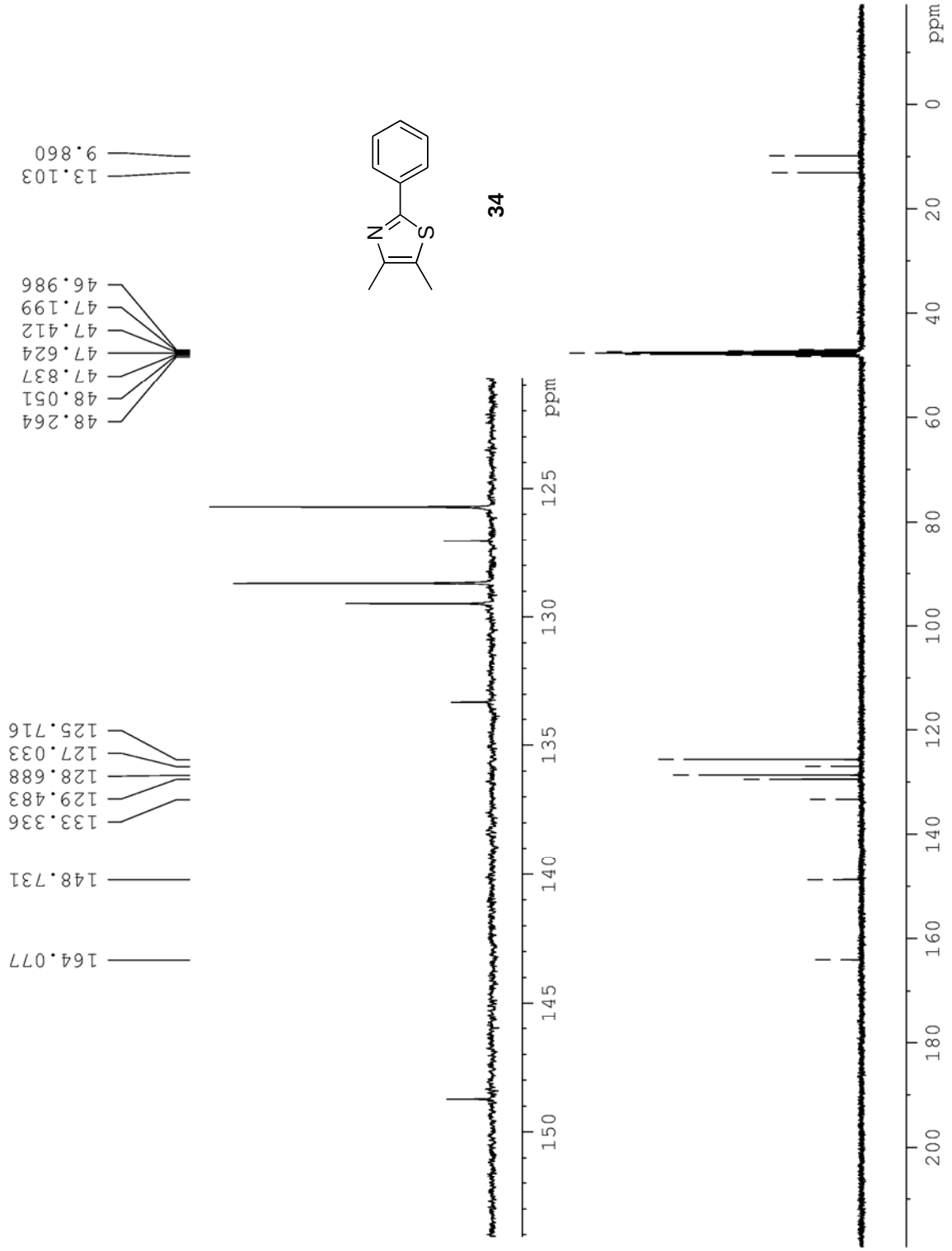

30
F
N
H
1.155
2.006
3.160
3.199
4.763
5.346
6.921
6.938
6.956
7.163
7.177
7.199
7.215
7.229
7.249
7.264
7.279
7.318
7.334
7.349
7.362
7.828
7.843
2.000
6.040
1.080
1.988
1.054
2.071
ppm
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm

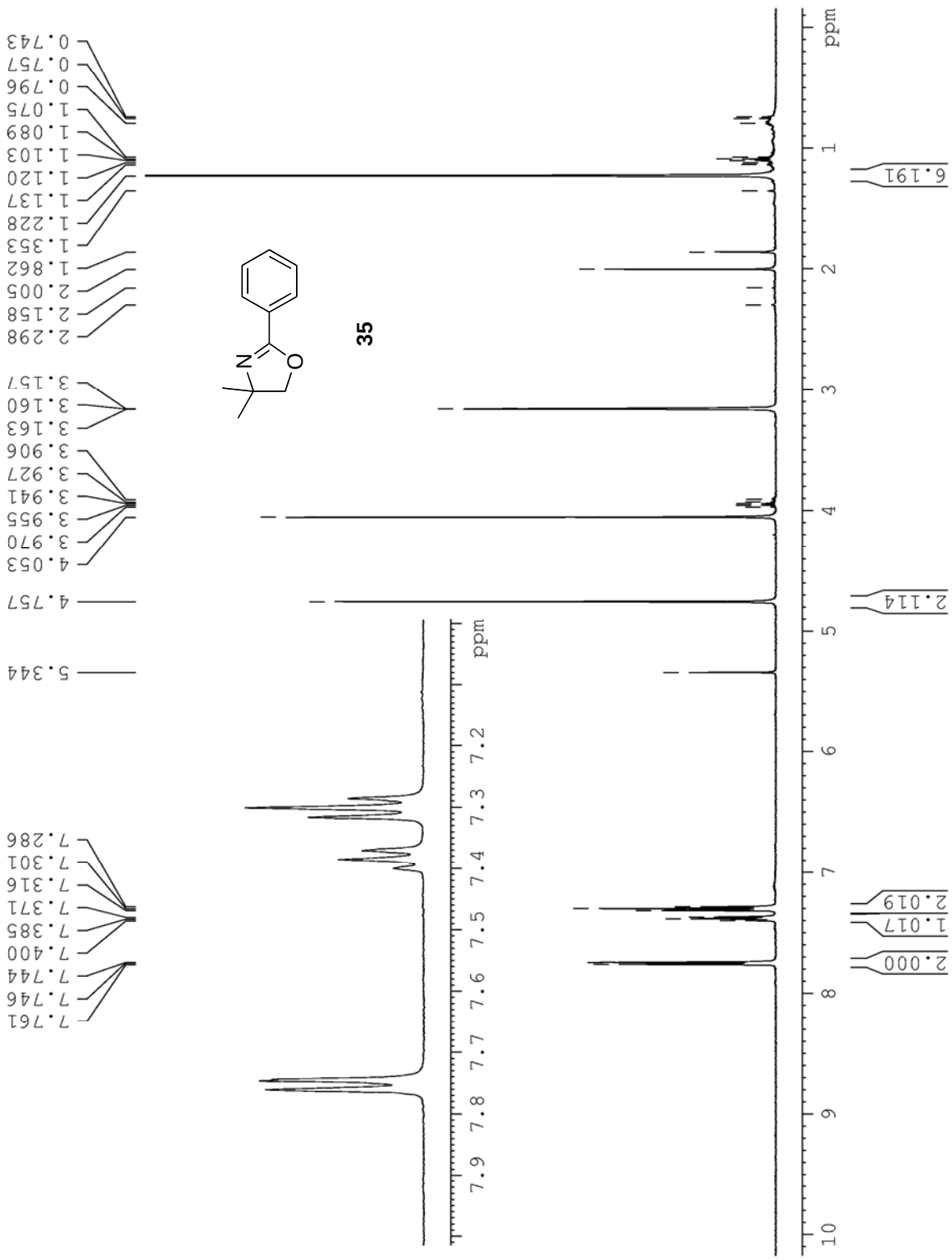

31
0.759
2.003
3.168
3.164
3.160
3.156
3.152
4.763
5.341
6.750
6.768
6.777
6.786
6.799
6.821
6.952
6.971
6.983
7.003
7.225
7.243
7.261
7.281
7.291
7.308
7.328
7.346
7.388
7.402
7.410
7.424
7.838
7.856
7.859
ppm
2.000
2.052
5.191
2.102
3.106

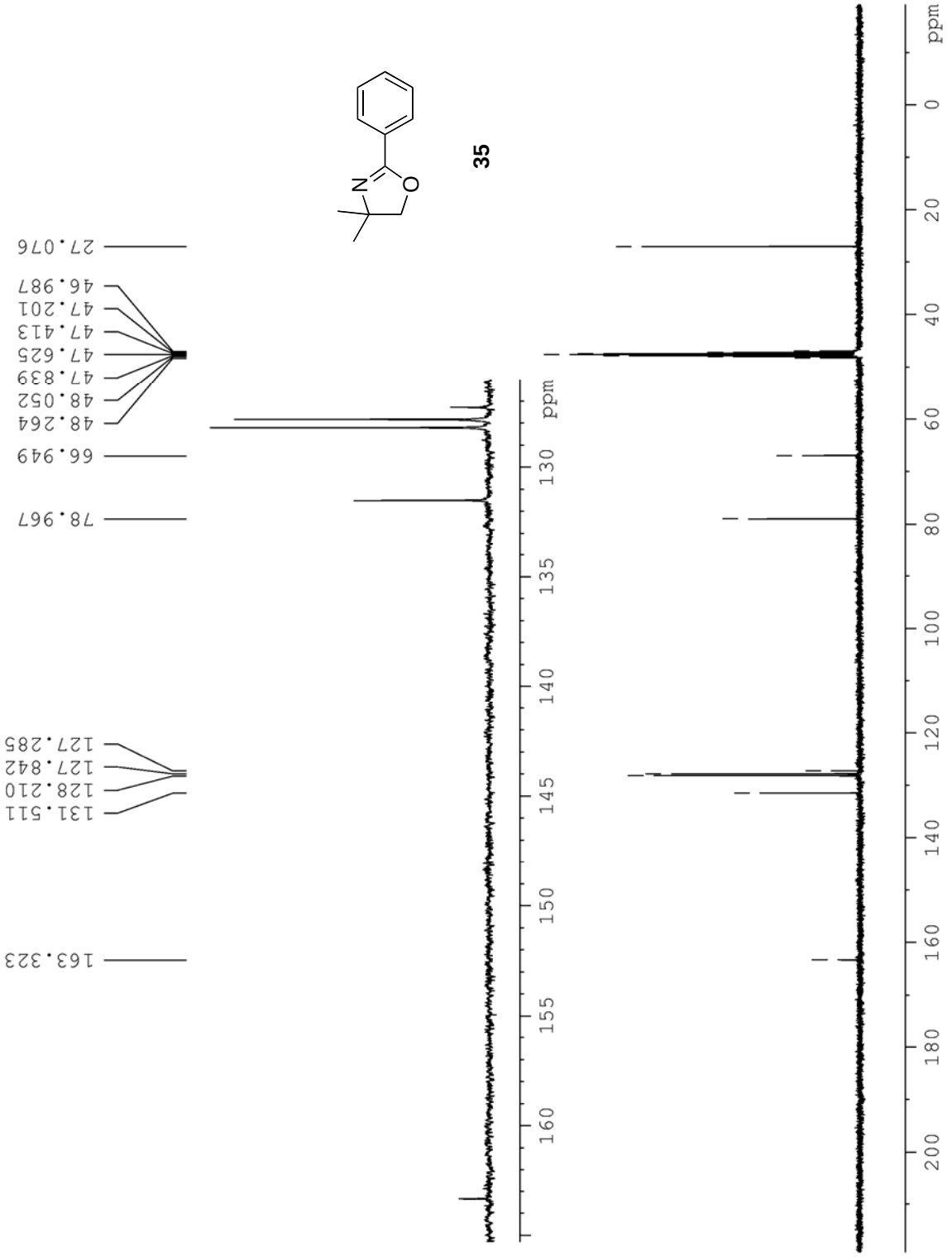

8.408
8.393
8.028
8.023
8.014
8.011
8.003
7.578
7.564
7.556
7.542
7.498
7.494
7.487
7.482
7.422
7.417
7.409
7.404
7.130
7.108
7.086
4.753
3.168
3.164
3.160
3.156
3.152
F
N
N
H
N
32
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
1.981
2.025
2.073
3.179
2.215


33
N
H
O
2.006
3.157
3.160
3.665
4.760
6.762
6.778
7.126
7.185
7.249
7.309
7.324
7.339
7.822
7.837
2.000
4.165
3.105
2.032
1.107
2.014
3.063
ppm
ppm


34
N
S
ppm
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
10 9 8 7 6 5 4 3 2 1 ppm
7.690
7.686
7.674
7.306
7.300
7.289
7.274
7.263
7.251
5.343
4.757
3.167
3.163
3.160
3.157
2.253
2.207
2.121
2.004
1.190
1.130
0.913
0.739
2.000
2.994
2.990
3.026


34
N
S
9.860
13.103
46.986
47.199
47.412
47.624
47.837
48.051
48.264
125.716
127.033
128.688
129.483
133.336
148.731
164.077
ppm
ppm


35
O
N
ppm
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm
10
9
8
7
6
5
4
3
2
1
ppm
6.191
2.114
2.000
1.017
2.019
7.761
7.746
7.744
7.400
7.385
7.371
7.316
7.301
7.286
5.344
4.757
4.053
3.970
3.955
3.941
3.927
3.906
3.163
3.160
3.157
2.298
2.158
2.005
1.862
1.353
1.228
1.137
1.120
1.103
1.089
1.075
0.796
0.757
0.743


35
27.076
46.987
47.201
47.413
47.625
47.839
48.052
48.264
66.949
78.967
127.285
127.842
128.210
131.511
163.323
ppm
ppm

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