SUPPORTING INFORMATION

Direct C–H photoarylation of diazines using aryldiazonium salts and visible-light

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1. GENERAL INFORMATION

All reactions were carried out under an oxygen atmosphere, unless specified. Dimethylsulfoxide (DMSO) was purified by distillation before use. Aryldiazonium salts were prepared according to the literature.[1] Reagents and starting materials were purchased from Sigma-Aldrich and used without further purification. Thin-layer chromatography (TLC) in silica gel 60 with F_{254} (0.25 mm) was used to identify product formation using UV light in 254 and 365 nm as the visualizing agent. The purification of the products was carried out by column chromatography (silica gel, pore size 60 Å, 230–400 mesh). ^{1}H NMR and ^{13}C{1H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, operating at 400.15 and 100.62 MHz, respectively, using $CDCl_3$ as solvent. Chemical shifts are reported in δ(ppm) relative to tetramethylsilane (TMS) and the coupling constants (*J*) in Hertz (Hz). The following abbreviations are used to define multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s. = broad singlet. High-resolution mass spectra (HRMS) were recorded on an Agilent LC-6545, Q-TOF MS with Jet Stream ESI ionization. UV-Vis spectra were recorded on a PerkinElmer Lambda 25 UV-visible absorption spectrometer. Melting points were recorded on a Microquímica MQAPF-301 apparatus.

2. GENERAL PROCEDURES

Aryldiazonium salts: To a solution of the aniline (10 mmol) in distilled H_2O (4 mL), aq. HBF_4 50 wt% was added (3.4 mL) and the mixture was stirred while cooled to 0 °C. Subsequently, a solution of $NaNO_2$ (10 mmol, 690 mg) in H_2O (2 mL) was added dropwise. After addition, the reaction mixture was stirred for 45 min, and then the solid filtered off under vacuum. The precipitate was re-dissolved in

a minimal amount of acetone, and diethyl ether was added until precipitation of the aryldiazonium salt. The solid was filtered off, washed with diethyl ether, and dried under vacuum. The NMR data were consistent with those previously reported in the literature.[1]

Photoarylation general procedure: To a test tube (borosilicate, 10 mm internal diameter, and 1mm thick walls) diazine hydrochloride (**1b**–**1d**, 7.5 mmol, 15 equiv) was added to 3 mL of freshly distilled DMSO. The test tube was then sonicated to remove the solubilized air and then saturated with pure oxygen by bubbling this gas for 10 min. The aryldiazonium salt (**2a**–**2u**, 0.5 mmol, 1 equiv) was quickly added. The tube was closed and sealed with a rubber septum and polytetrafluoroethylene (PTFE) tape. The reaction mixture was stirred and irradiated using a homemade temperature controlled photoreactor (blue LED, 4 x 30 W chip LED) at 33 °C for 14h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine (1 x 10 mL), dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude reaction product was purified by chromatography over silica gel (70–230 mesh) and an appropriated mixture of hexane and ethyl acetate to afford the aryl-diazine in 5–84% yields.

3. EXPERIMENTAL DATA

*2-(4-methoxyphenyl)pyrazine (**3a**)*. The compound **3a** (known compound)[2] was obtained following the general procedure. It was obtained in 78% yield (0.391 mmol, 72.8 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = 9/1 (v/v)). mp 85–86 °C (lit. mp 86–87 °C).[2] ^{1}H

NMR (400 MHz, $CDCl_3$): δ 8.97 (d, *J* = 1.5 Hz, 1H), 8.58 (dd, *J* = 2.5, 1.5, 1H), 8.44 (d, *J* = 2,5 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 152.6, 144.0, 142.1, 141.6, 128.9, 128.3, 114.5, 55.4.

*2-(3-methoxyphenyl)pyrazine (**3b**)*. The compound **3b** (known compound)[2] was obtained following the general procedure. It was obtained in 41% yield (0.103 mmol, 19.2 mg) as an orange oil after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). ^1H NMR (400 MHz, $CDCl_3$): δ 8.95 (br.s., 1H), 8.56 (br.s., 1H), 8.43 (br.s., 1H), 7.53–7.48 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 6.97–6.93 (m, 1H), 3.82 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 152.7, 144.1, 142.9, 142.2, 137.7, 130.1, 119.2, 116.1, 112.1, 55.4.

*2-(2-methoxyphenyl)pyrazine (**3c**)*. The compound **3c** (known compound)[2] was obtained following the general procedure. It was obtained in 38% yield (0.192 mmol, 35.8 mg) as a yellow oil after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 7/3 (v/v)). ^1H NMR (400 MHz, $CDCl_3$): δ 9.14 (br.s., 1H), 8.63 (br.s., 1H), 8.44 (br.s., 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.1, 152.0, 146.5, 144.1, 142.1, 131.2, 131.0, 125.8, 121.3, 111.4, 55.6.

*2-(4-fluorophenyl)pyrazine (**3d**)*. The compound **3d** (known compound)[2,3] was obtained following the general procedure. It was obtained in 72% yield (0.362 mmol, 63.0 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 93–95 °C (lit. mp 97–98 °C).[31] ^1H NMR (400 MHz, $CDCl_3$): δ 9.00 (br.s., 1H), 8.64 (br.s., 1H),

8.52 (br.s., 1H), 8.07–7.98 (dd, *J* = 7.7, 5.5 Hz, 2H), 7.25–7.16 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 164.2 (d, $J_{C\text{-}F}$ = 250.8 Hz), 152.0, 144.2, 142.5, 141.6, 132.4, 128.9 (d, $J_{C\text{-}F}$ = 8.5 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.0 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -110.9.

*2-(3-fluorophenyl)pyrazine (**3e**)*. The compound **3e** (known compound)[2] was obtained following the general procedure. It was obtained in 66% yield (0.328 mmol, 57.2 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = 9/1 (v/v)). mp 55–57 °C (lit. mp 56–57 °C)[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (br.s., 1H), 8.64 (br.s., 1H), 8.56–8.51 (m, 1H), 8.82–7.74 (m, 2H), 7.52–7.44 (m, 1H), 7.21–7.13 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 163.4 (d, $J_{C\text{-}F}$ = 247.6 Hz), 151.5, 144.3, 143.4, 142.1, 138.5 (d, $J_{C\text{-}F}$ = 7.7 Hz), 130.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 122.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 116.8 (d, $J_{C\text{-}F}$ = 21.1 Hz), 113.9 (d, $J_{C\text{-}F}$ = 22.8 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -111.9.

*2-(2-fluorophenyl)pyrazine (**3f**)*. The compound **3f** (known compound)[2] was obtained following the general procedure. It was obtained in 45% yield (0.226 mmol, 39.3 mg) as yellow oil after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (br.s., 1H), 8.70 (br.s., 1H), 8.54 (br.s., 1H), 8.04–7.97 (m, 1H), 7.49–7.42 (m, 1H), 7.35–7.28 (m, 1H), 7.25–7.18 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5 (d, $J_{C\text{-}F}$ = 251.2 Hz), 149.5, 145.5 (d, $J_{C\text{-}F}$ = 12.2 Hz), 144.5, 143.0, 131.6 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.0 (d, $J_{C\text{-}F}$ = 2.6 Hz), 124.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 124.3 (d, $J_{C\text{-}F}$ = 11.9 Hz), 116.4 (d, $J_{C\text{-}F}$ = 22.6 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -115.8.

*2-(4-ethylphenyl)pyrazine (**3g**)*. The compound **3g** (new compound) was obtained following the general procedure. It was obtained in 71% yield (0.360 mmol, 66.4

mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = 9/1 (v/v)). mp 43–44 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (br.s., 1H), 8.55 (br.s., 1H), 8.40 (br.s., 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.0, 146.5, 144.1, 142.4, 141.9, 133.7, 128.6, 126.9, 28.7, 15.4. HRMS-ESI-TOF: *m/z* calcd for $C_{12}H_{12}N_2$ $[M+H]^+$ 185.1079, found 185.1073.

*2-(3-ethylphenyl)pyrazine (**3h**)*. The compound **3h** (new compound) was obtained following the general procedure. It was obtained in 40% yield (0.205 mmol, 37.7 mg) as a yellow oil after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (br.s., 1H), 8.63 (br.s., 1H), 8.51 (br.s., 1H), 7.87 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 145.2, 144.1, 142.8, 142.4, 136.4, 129.6, 129.1, 126.6, 124.3, 28.9, 15.6. HRMS-ESI-TOF: *m/z* calcd for $C_{12}H_{12}N_2$ $[M+H]^+$ 185.1079, found 185.1076.

*2-(2-ethylphenyl)pyrazine (**3i**)*. The compound **3i** (known compound)[4] was obtained following the general procedure. It was obtained in 16% yield (0.080 mmol, 14.7 mg) as an orange oil after purification over silica gel column chromatography (hexane/EtOAc = 9/1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (br.s., 1H), 8.60 (br.s., 1H), 8.48 (br.s., 1H), 7.37–7.21 (m, 4H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 144.9, 143.9, 142.6, 142.3, 136.3, 130.0, 129.5, 129.4, 126.1, 26.0, 15.7.

*2-(4-nitrophenyl)pyrazine (**3j**)*. The compound **3j** (known compound)[2] was obtained following the general procedure. It was obtained in 60% yield (0.300 mmol, 60.4 mg) as a yellow solid after purification over silica gel column

chromatography (hexane/EtOAc = from 9/1 (v/v) to 7/3 (v/v)). mp 181–182 °C (lit. mp 178-179 °C).[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (dd, *J* = 1.6, 0.2 Hz, 1H), 8.72 (dd, *J* = 2.4, 1.6 Hz, 1H), 8.63 (*dd*, *J* = 2.4, 0.2 Hz, 1H), 8.38 (d, *J* = 9.0 Hz, 2H), 8.23 (d, *J* = 9.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.3, 148.7, 144.5, 144.4, 142.5, 142.2, 127.8, 124.2.

*2-(3-nitrophenyl)pyrazine (**3k**)*. The compound **3k** (known compound)[5] was obtained following the general procedure. It was obtained in 54% yield (0.269 mmol, 54.2 mg) as an orange solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 133–135 °C (lit. mp 133–134 °C).[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (br.s., 1H), 8.95–8.92 (m, 1H), 8.71 (br.s., 1H), 8.63 (br.s., 1H), 8.41–8.32 (m, 2H), 7.72 (t, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.3, 149.0, 144.5, 144.2, 142.1, 138.1, 132.5, 130.1, 124.5, 121.9.

*2-phenylpyrazine (**3l**)*. The compound **3l** (known compound)[2] was obtained following the general procedure. It was obtained in 72% yield (0.358 mmol, 55.9 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 66–67 °C (lit. mp 73–74 °C)[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (br.s., 1H), 8.63 (br.s., 1H), 8.50 (br.s., 1H), 8.04–7.99 (m, 2H), 7.54–7.44 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.8, 144.2, 142.9, 142.2, 136.3, 129.9, 129.1, 126.9.

*2-(3-(trifluoromethyl)phenyl)pyrazine (**3m**)*. The compound **3m** (new compound) was obtained following the general procedure. It was obtained in 74% yield (0.368 mmol, 82.5 mg) as a red solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 47–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (br.s., 1H), 8.69 (br.s., 1H), 8.59 (br.s., 1H), 8.33

(s, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 151.3, 144.4, 143.6, 142.0, 137.1, 131.7 (q, $J_{C\text{-}F}$ = 32 Hz), 130.0, 129.6, 126.5 (q, $J_{C\text{-}F}$ = 3 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272 Hz), 123.9 (q, $J_{C\text{-}F}$ = 4 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ-62.7. HRMS-ESI-TOF: *m/z* calcd for $C_{11}H_7F_3N_2$ $[M+H]^+$ 225.0640, found 225.0628.

*2-(2-(trifluoromethyl)phenyl)pyrazine (**3n**)*. The compound **3n** (known compound)[6] was obtained following the general procedure. It was obtained in 15% yield (0.074 mmol, 16.6 mg) as a red oil after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (br.s., 1H), 8.68 (br.s., 1H), 8.62 (br.s., 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 153.7, 144.7, 143.8, 143.6, 136.4, 131.8, 131.7, 129.3, 128.8 (q, $J_{C\text{-}F}$ = 32 Hz), 126.6 (q, $J_{C\text{-}F}$ = 5 Hz), 123.9 (q, $J_{C\text{-}F}$ = 273 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ-56.7.

*2-(p-tolyl)pyrazine (**3o**)*. The compound **3o** (known compound)[2] was obtained following the general procedure. It was obtained in 75% yield (0.376 mmol, 64 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 9.5/0.5 (v/v) to 9/1 (v/v)). mp 52–53 °C (lit. mp 56–57 °C).[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (br.s., 1H), 8.63 (br.s., 1H), 8.48 (br.s., 1H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 153.0, 144.2, 142.2, 141.8, 140.3, 133.4, 129.8, 126.8, 21.4.

*2-(4-chlorophenyl)pyrazine (**3p**)*. The compound **3p** (known compound)[4,6] was obtained following the general procedure. It was obtained in 75% yield (0.375 mmol, 71.5 mg) as an orange solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 73–74 °C (lit.

72–73 °C).[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (br.s., 1H), 8.64 (br.s., 1H), 8.53 (br.s., 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.7, 144.3, 143.1, 141.8, 136.3, 134.7, 129.3, 128.2.

*2-(benzo[d][1,3]dioxol-5-yl)pyrazine (**3q**)*. The compound **3q** (known compound)[7] was obtained following the general procedure. It was obtained in 45% yield (0.227 mmol, 45.4 mg) as a red solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 122–123 °C (lit. 115–116 °C).[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (br.s., 1H), 8.59 (br.s., 1H), 8.46 (br.s., 1H), 7.55–7.52 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.05 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.5, 149.4, 148.6, 144.0, 142.0, 141.4, 130.5, 121.3, 108.8, 107.2, 101.6.

*2-(2-(methylthio)phenyl)pyrazine (**3r**)*. The compound **3r** (new compound) was obtained following the general procedure. It was obtained in 7% yield (0.035 mmol, 7.1 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 8/2 (v/v)). mp 48–49 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (br.s., 1H), 8.72 (br.s., 1H), 8.56 (br.s., 1H), 7.50–7.39 (m, 3H), 7.33–7.28 (m, 1H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 144.8, 143.8, 142.1, 138.0, 136.0, 130.2, 130.0, 126.9, 125.4, 16.7. HRMS-ESI-TOF: *m/z* calcd for $C_{11}H_{10}N_2S$ $[M+H]^+$ 203.0643, found 203.0636.

*2-(2,6-dichlorophenyl)pyrazine (**3s**)*. The compound **3s** (new compound) was obtained following the general procedure. It was obtained in 5% yield (0.023 mmol, 5.2 mg) as an orange oil after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 7/3 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (br.s., 1H), 8.68–8.62 (m, 2H), 7.47–7.43 (m, 2H), 7.37–7.32 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.6, 145.9, 144.4, 143.7, 135.1, 135.0,

130.8, 128.4. HRMS-ESI-TOF: *m/z* calcd for $C_{10}H_6Cl_2N_2$ $[M+H]^+$ 224.9986, found 224.9979.

methyl 3-(4-methoxyphenyl)pyrazine-2-carboxylate and *methyl 5-(4-methoxyphenyl)pyrazine-2-carboxylate* (*regioisomeric mixture* ***3v***).[8] These compounds were obtained following the general procedure. The 3-aryl substituted product (known compound) was obtained in 24%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (d, *J* = 1.2 Hz, 1H), 9.05 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 4.03 (s, 3H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.8, 162.3, 155.0, 145.8, 140.8, 140.2, 129.4, 127.9, 114.9, 55.6, 53.1. The compound 5-aryl substituted (known compound) was obtained in 17% ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 2.4 Hz, 1H), 8.51 (d, *J* = 2.3 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.2, 161.2, 153.2, 145.3, 144.1, 141.2, 130.2, 129.2, 114.3, 55.5, 53.1.

2-(4-methoxyphenyl)pyrimidine and 4-(4-methoxyphenyl)pyrimidine (regioisomeric mixture ***3w****)*. The 2-aryl substituted product (known compound)[9,10] was obtained following the general procedure and in 16% yield (0.079 mmol, 14.7 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1 (v/v) to 7/3 (v/v)). mp 58–59 °C (lit. mp 65–66 °C)[10]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.39 (d, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 4.8 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.5, 161.9, 157.2, 130.2, 129.8, 118.3, 114.0, 55.4. The 4-aryl substituted product (known compound)[11,12] was obtained following the general procedure. It was obtained in 53% (0.267 mmol, 49.8 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 9/1

(v/v) to 7/3 (v/v)). mp 80–81 °C (lit. mp 79.7–80.3 °C).[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.63 (d, *J* = 5.3 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 5.3 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.6, 162.3, 158.7, 156.8, 128.8, 116.1, 114.5, 55.5.

*3-(4-methoxyphenyl)pyridazine and 4-(4-methoxyphenyl)pyridazine (regioisomeric mixture **3x**).* The 3-aryl substituted product (known compound)[13] was obtained following the general procedure and in 30% yield (0.150 mmol, 27.9 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 2/8 (v/v) to 1/9 (v/v)). mp 104–106 °C (lit. mp 111–112 °C)[13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, *J* = 4.6 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.48 (dd, *J* = 8.6, 4.6 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4, 159.0, 149.5, 128.8, 128.5, 126.7, 123.2, 114.4, 55.4. The 4-aryl substituted product (known compound)[11] was obtained following the general procedure. It was obtained in 54% yield (0.272 mmol, 50.7 mg) as a yellow solid after purification over silica gel column chromatography (hexane/EtOAc = from 2/8 (v/v) to 1/9 (v/v)). mp 79–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45–9.42 (m, 1H), 9.16 (d, *J* = 5.4 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.63–7.59 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4, 151.3, 149.6, 138.1, 128.3, 126.4, 122.4, 115.0, 55.5.

4. PHOTOCHEMICAL REACTOR

These studies were performed in a home-made blue-LED photoreactor emitting between 400 and 500 nm with 120 W of power (Figure S1), and built from commercial materials.

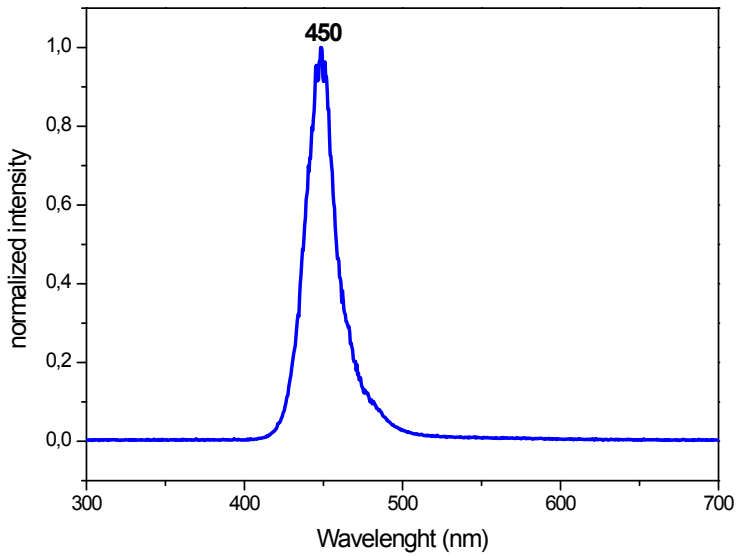

Figure S1: Emission spectra of the blue-LED chip photoreactor.

The reactor structure was assembled with four aluminum heatsink plates (12 x 12 cm each), which were coated with aluminum foil to reflect the internal light of the reactor (Figure S2-A, upper). A blue-LED chip was attached with adhesive thermal paste at center of the bottom of each plate (Figure S2-A, bottom). Subsequently, small holes were made above each blue-LED chip to allow the installation of the electrical wirings, which were soldered on each terminal of the blue-LED chip (Figure S2-B, left) and isolated with liquid insulating paste (Figure S2-B, right). Then, at each corner of the aluminum plates a hole was made (Figure S2-C, upper), and a steel angle was attached in each hole with nuts and bolts (Figure S2-C, bottom). Subsequently, the 4 plates were bolted together by the steel angles to form a square of 12x12 cm (Figure S2-D). Next, two steel angles were attached at the top to support a fan (12 x 12 cm), and 4 rubber feet were screwed in the base of the structure to raise by 6 cm from the bench (Figure S2-E). This structure was assembled to allow air re-circulation inside the photoreactor (Figure S2-F).

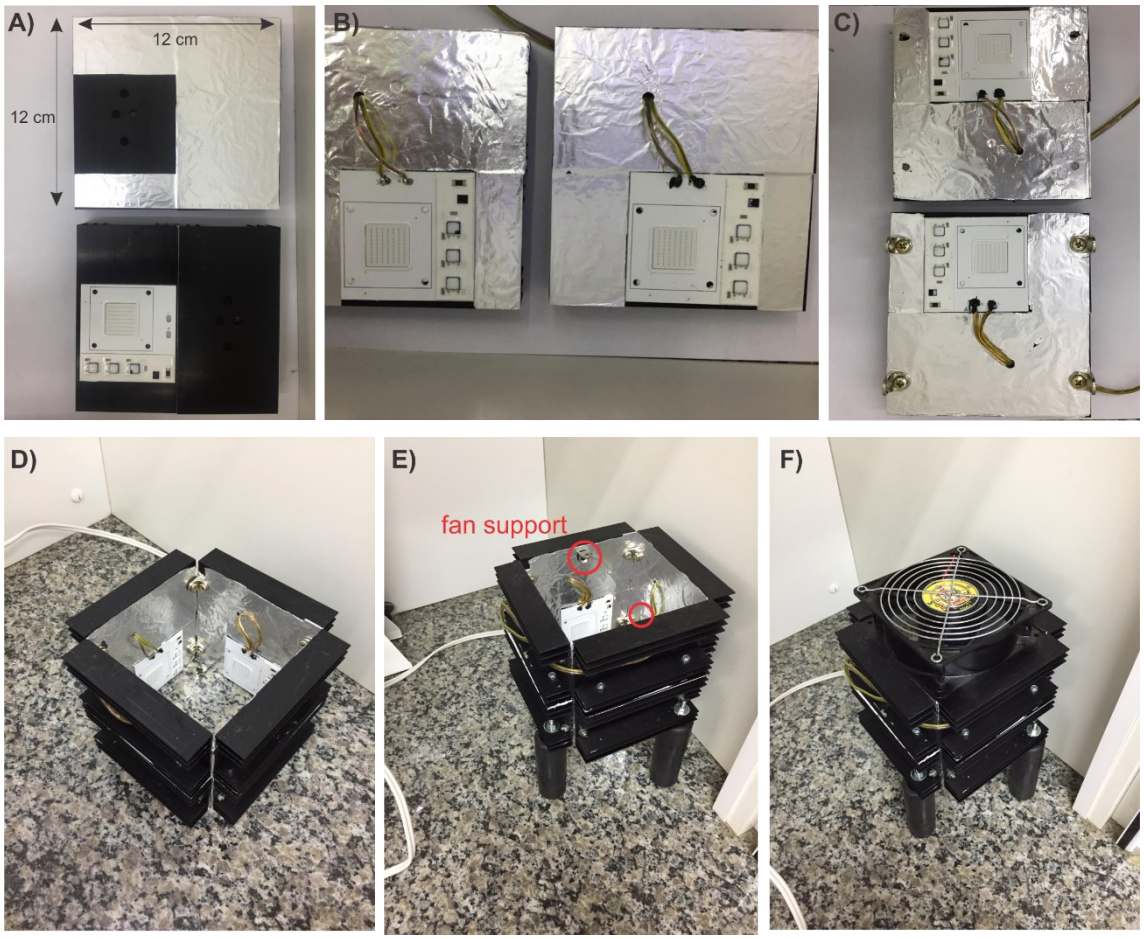

Figure S2: Step-by-step photoreactor assembly: **A)** aluminum heatsink plates with the aluminum foil attached; **B)** Connection of the electrical wires; **C)** Installation of the steels angles in the aluminum plates; **D)** Assembly of the structure of the photoreactor; **E)** Installation of the fan support and rubber feet; **F)** Structure assembled. Assembly of the stirring system; **G)** Display of the automatic system showing the irradiation time and temperature of the photoreactor; and **H)** Internal image of the photoreactor assembled.

Commercial stirrers were not able to promote the stirring of the magnetic bar inside the test tubes due to the distance of 7 cm between the stirrers and the test tubes. Because of this, a stirring system was assembled with one DC motor, one magnet, and one voltage controller (Figure S3-A). The magnet was attached to the DC motor axis by a hex screw. Subsequently, the electrical poles of the DC motor were connected to the voltage controller, already connected to the electrical power (Figure S3-B and C). This system was installed close to the test

tube. The test tube was supported at the center of the photoreactor by a metal clamp (Figure S3-D).

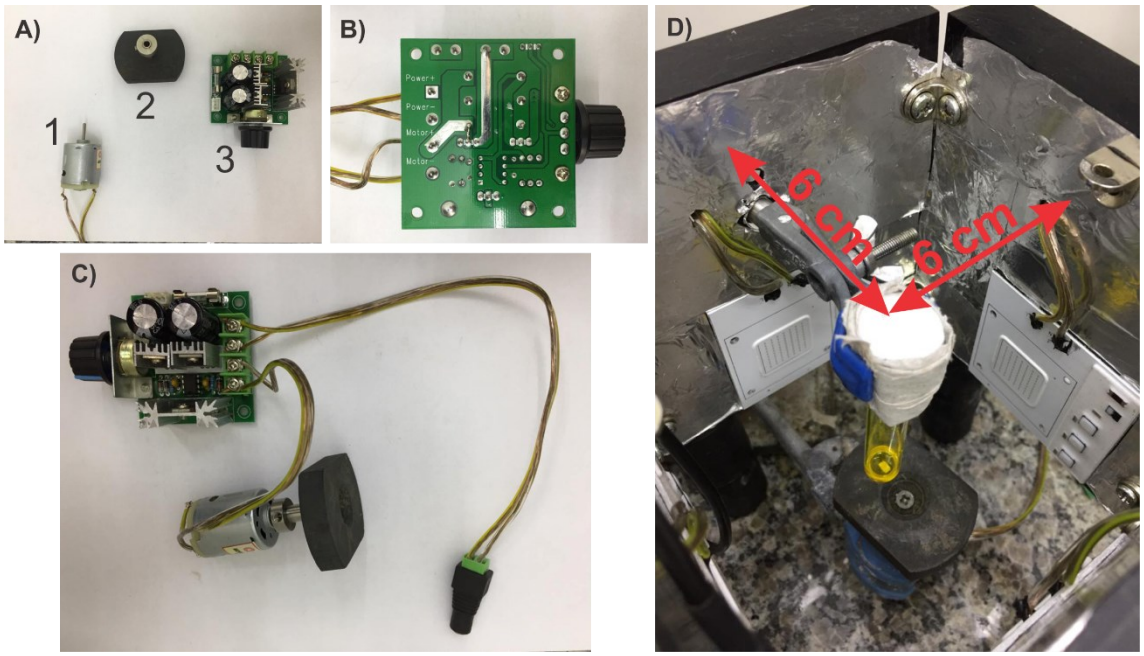

Figure S3: Step-by-step stirring system assembly: **A)** components of the stirring system: 1) DC motor, 2) magnet and 3) voltage controller; **B)** Connection of voltage controller with both DC motor and electrical power; **C)** Stirring system assembled; **D)** Installation of the stirring system in the photoreactor.

After the assembly of the photoreactor, an automated system (Arduino platform) was coupled to the photoreactor to monitor the temperature, reaction time, and luminosity of the photoreactor. This system was assembled using jumper wires, relay, 16x2 LCD module, waterproof temperature sensor (DS18B20), mini photocell (LDR 5 mm), push-button, 220 ohms resistor, and Arduino pro mini 328 (Figure S4-A). These components were connected in a standard protoboard following its corresponding datasheets (Figure S4-B). Subsequently, this system was programmed to turn off the irradiation after the desired reaction time, or if the internal temperature of the photoreactor reaches 40 °C (Figure S4-C).

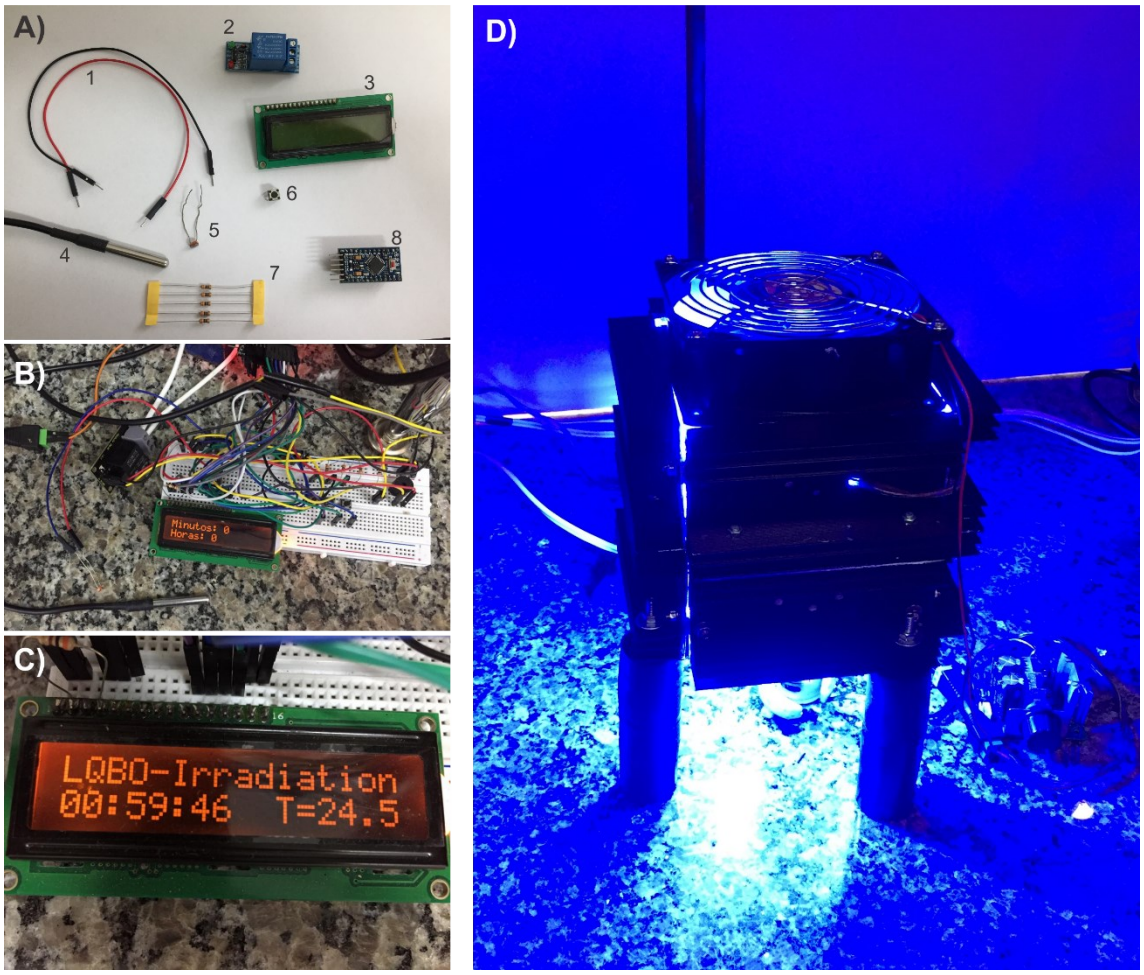

Figure S4: Step-by-step automated system assembly: **A)** components used to assembly: 1) jumper wires, 2) relay 110-220V, 3) 16x2 LCD module, 4) waterproof temperature sensor (DS18B20), 5) mini photocell (LDR 5 mm), 6) push-button, 7) 220 ohms resistor, and 8) Arduino pro mini 328; **B)** Automated system assembled; **C)** LCD module showing reaction time and temperature inside photoreactor; **D)** Photoreactor assembled.

In this setup, we are able to stabilize the temperature of the reaction mixture (inside the test tube), at 33 °C after 10 min of irradiation (Figure S5), as long as the external temperature (laboratory) is maintained below 24 °C.

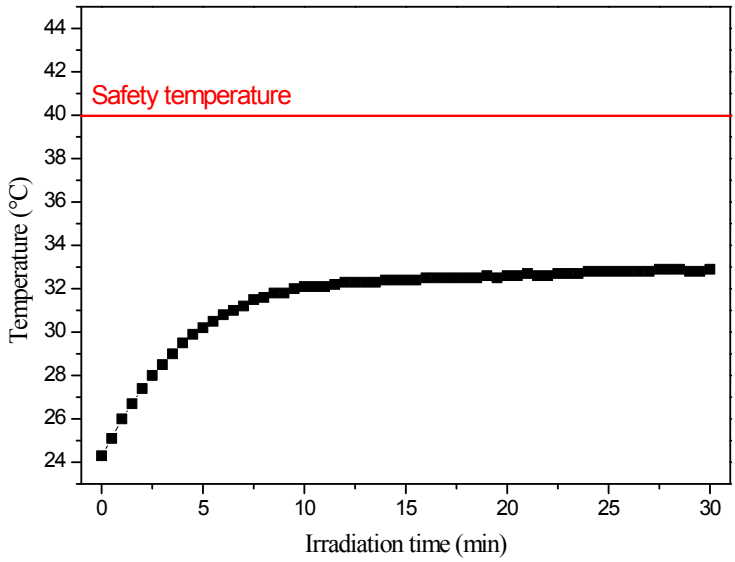

Figure S5: Evolution of the reaction mixture temperature with the irradiation time. External temperature: 24 °C.

5. GC MS and CHROMATOGRAPHIC DATA

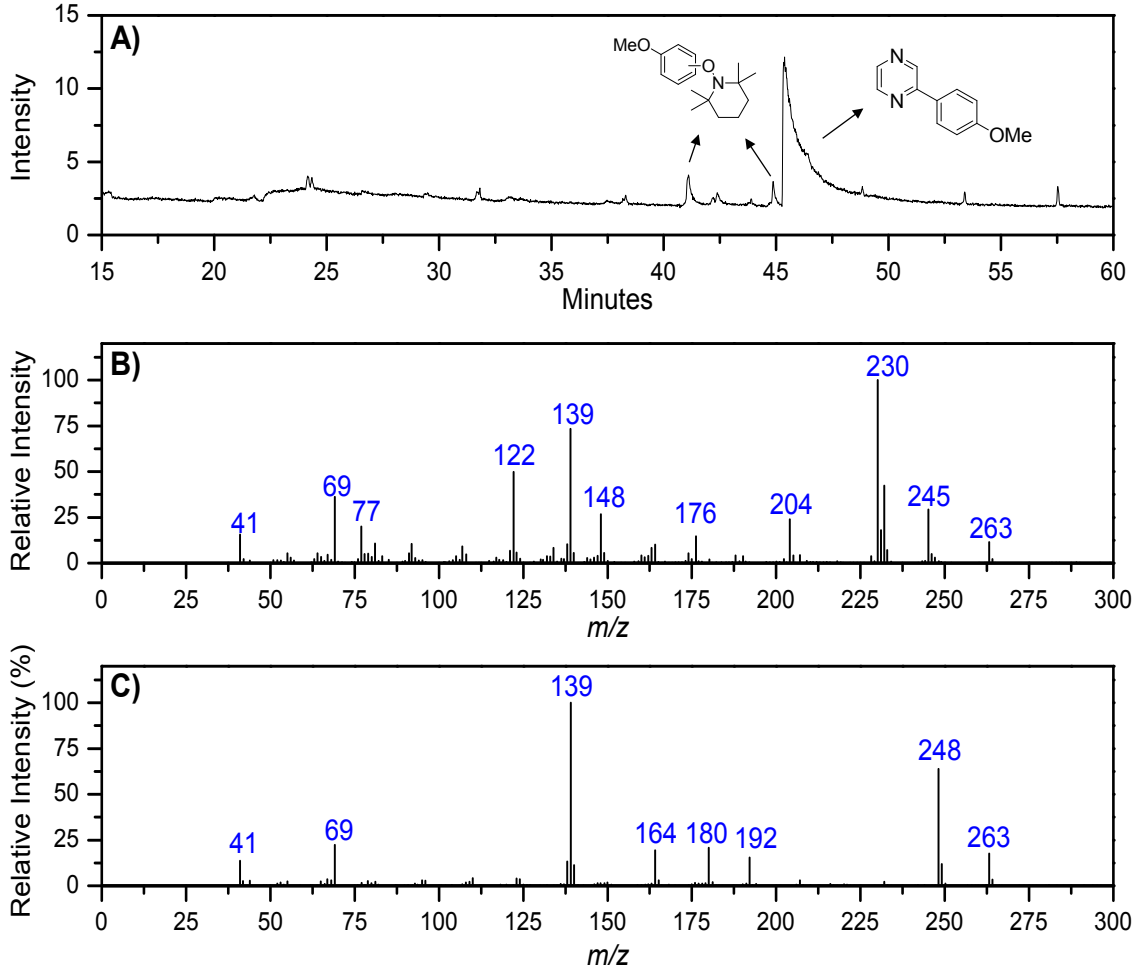

Figure S6: A) Chromatogram of the crude reaction mixture. **B)** and **C)** GC-MS spectrum of the isomers of *O*-arylated-TEMPO product.

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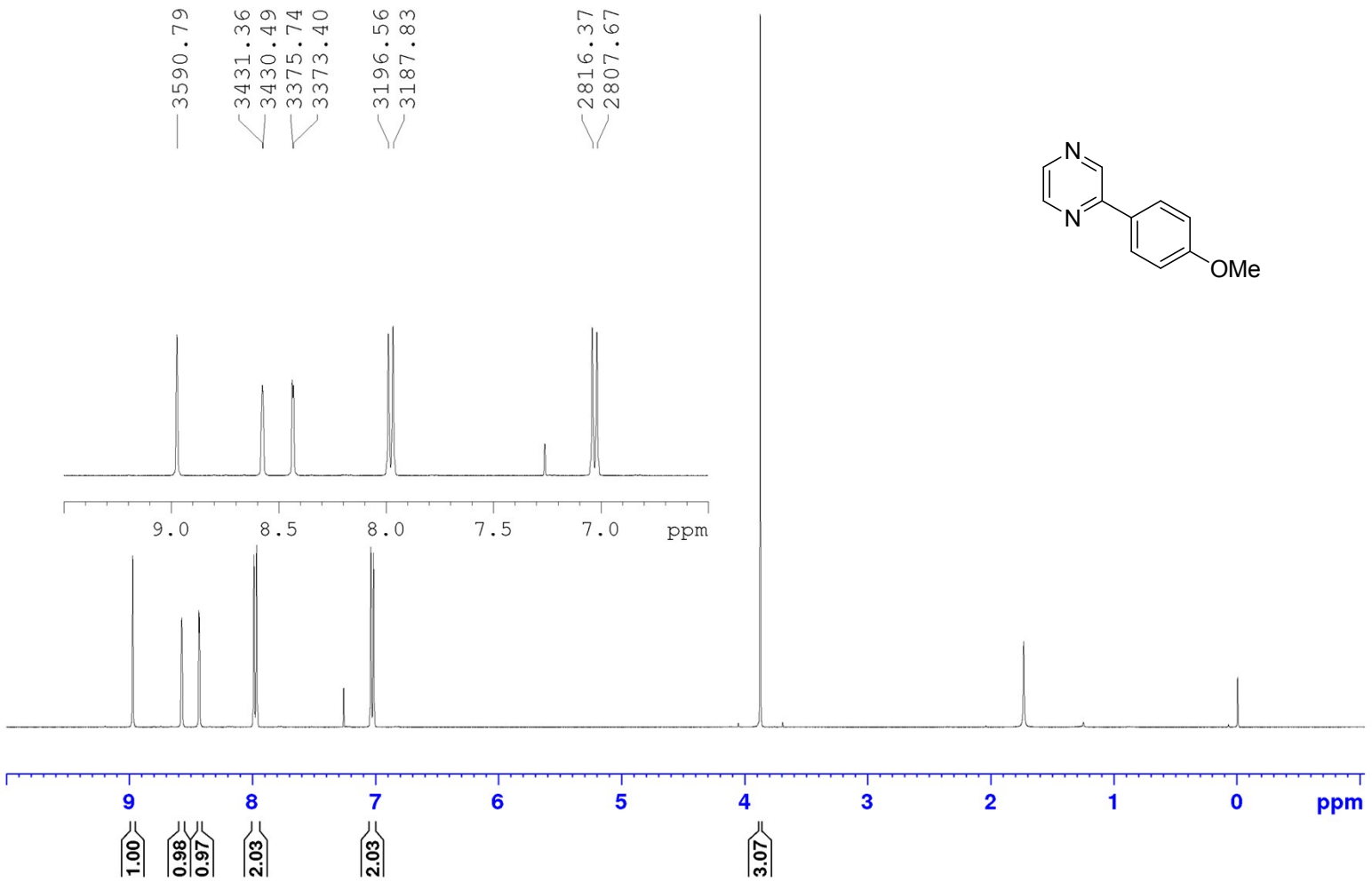
6. NMR DATA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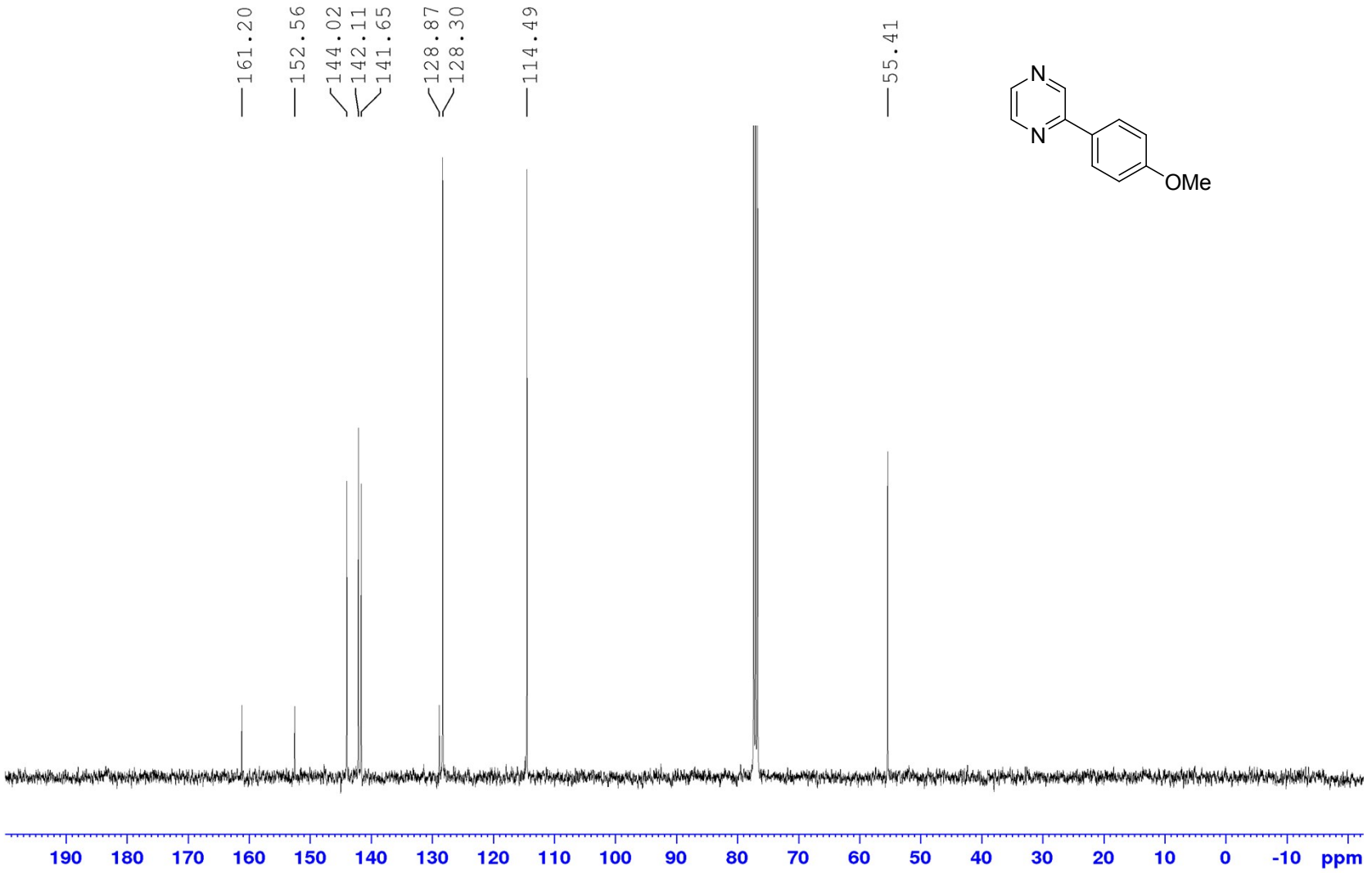
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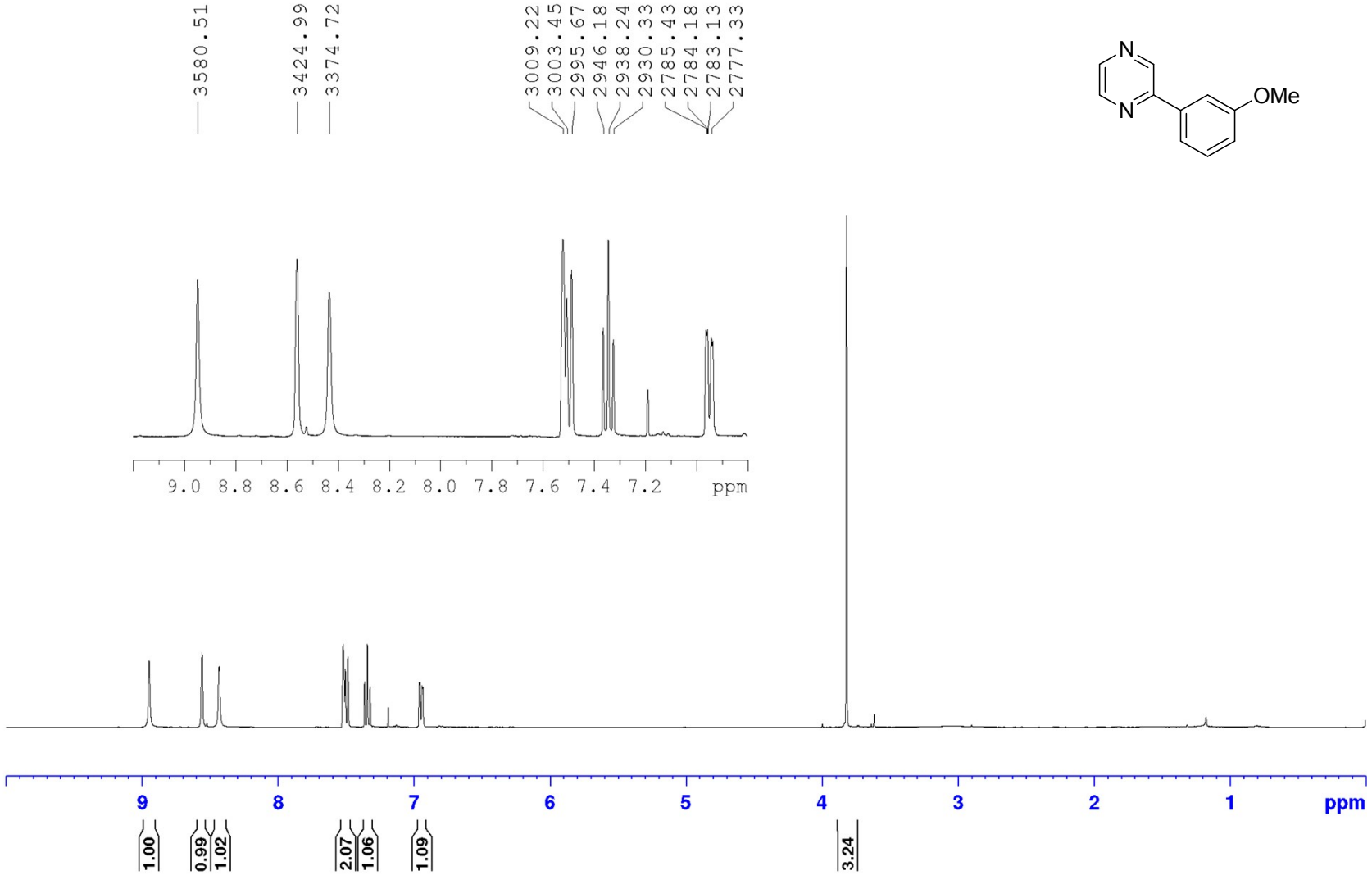
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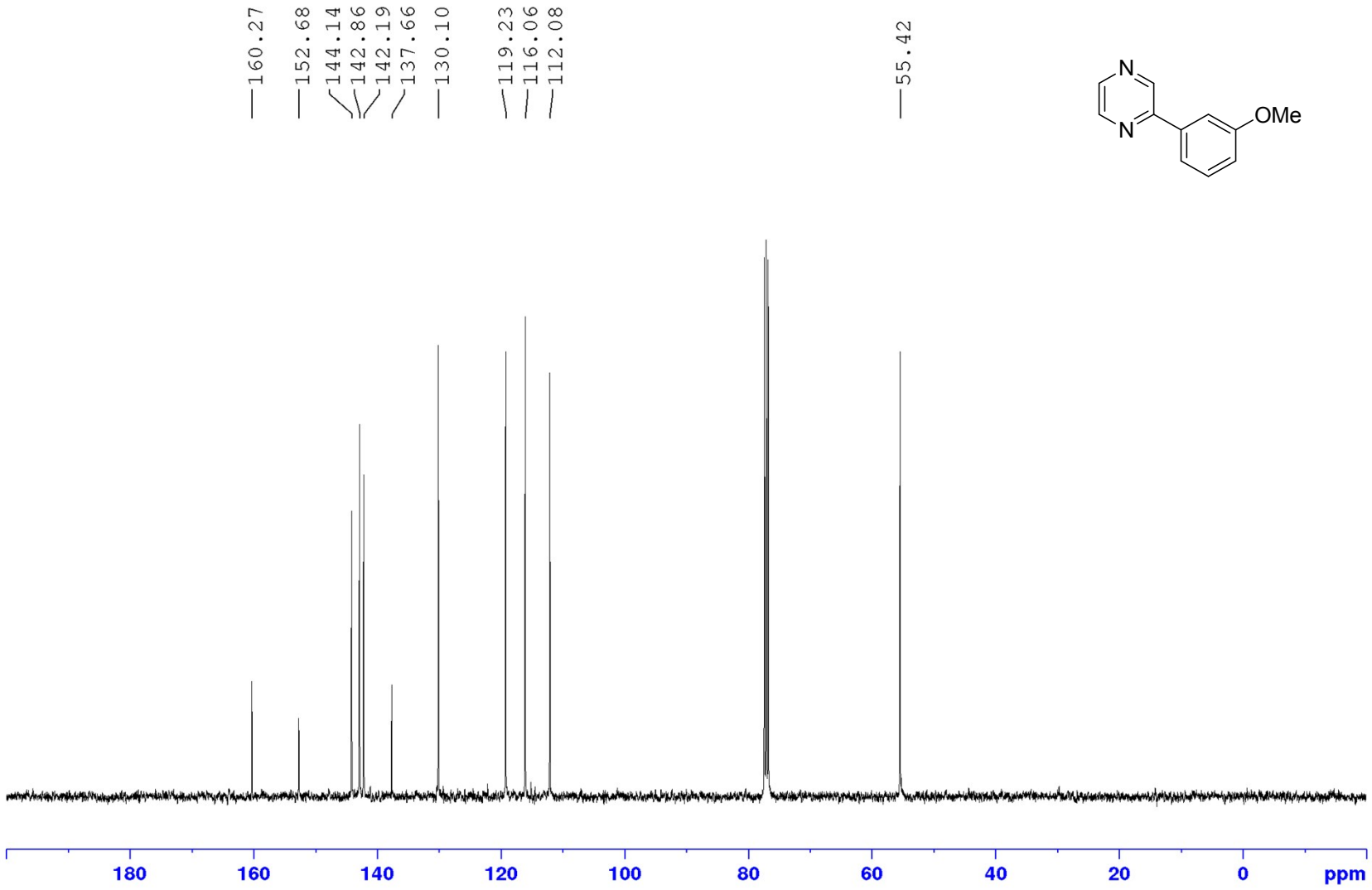
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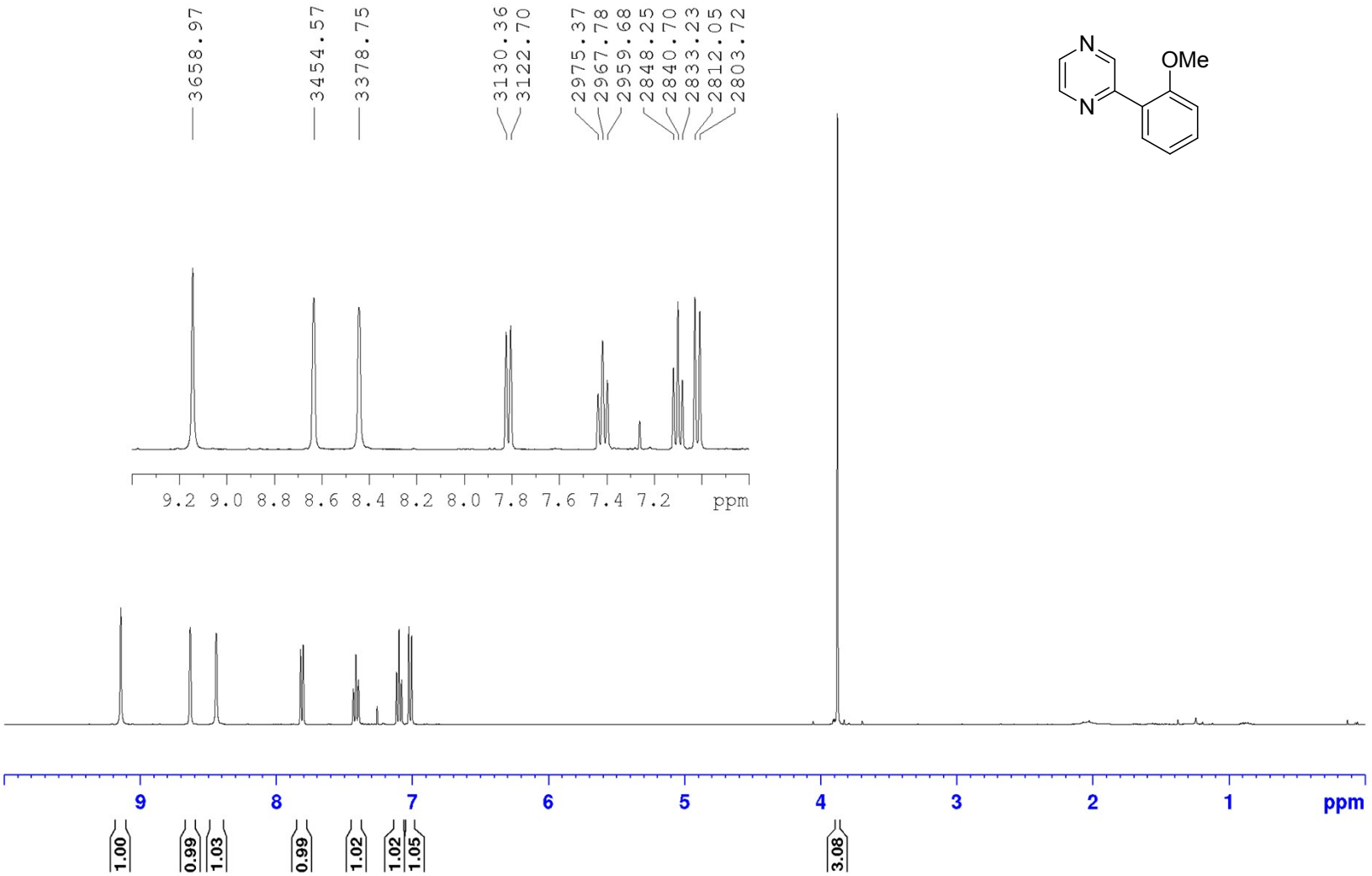
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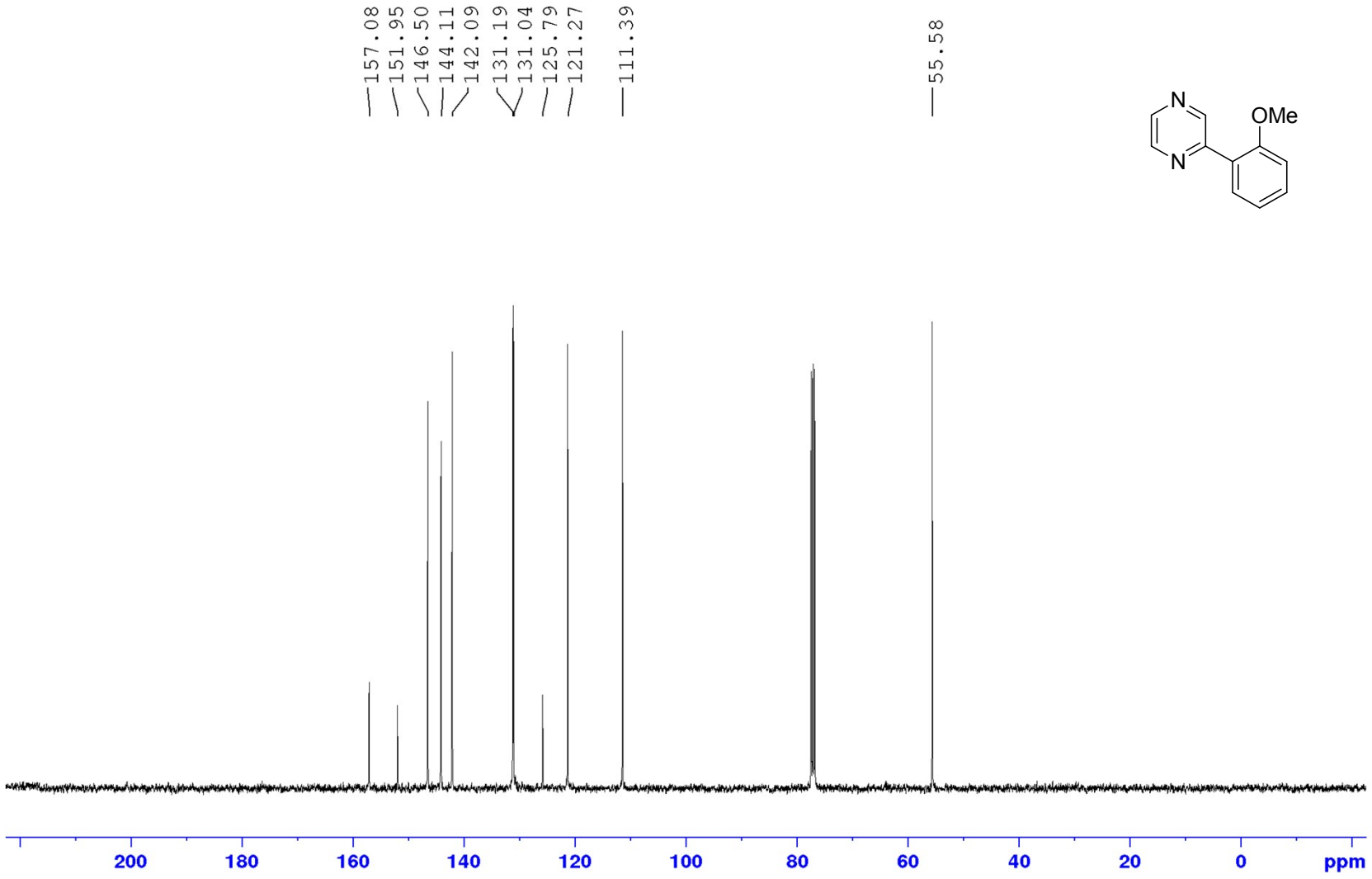
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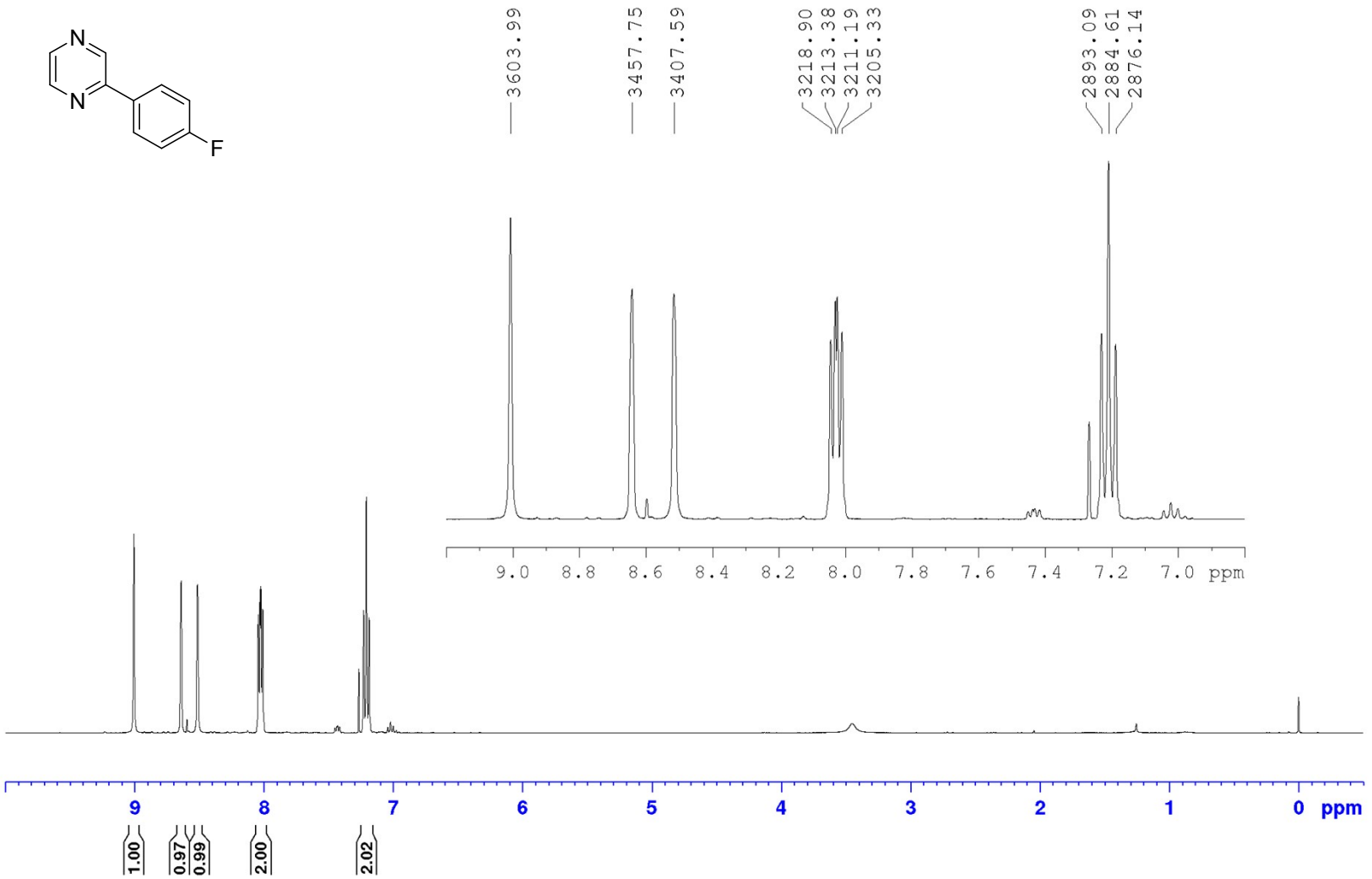
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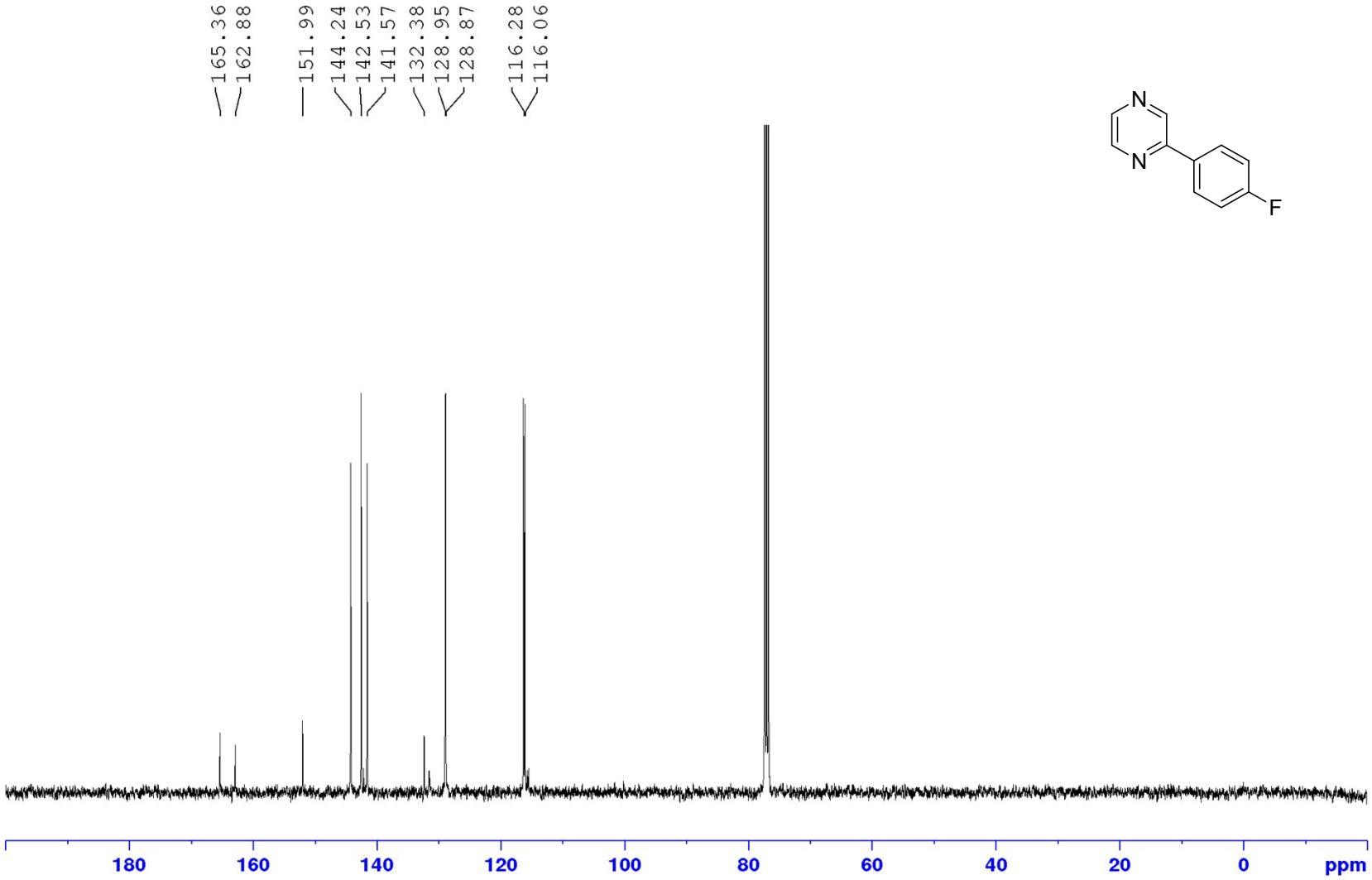
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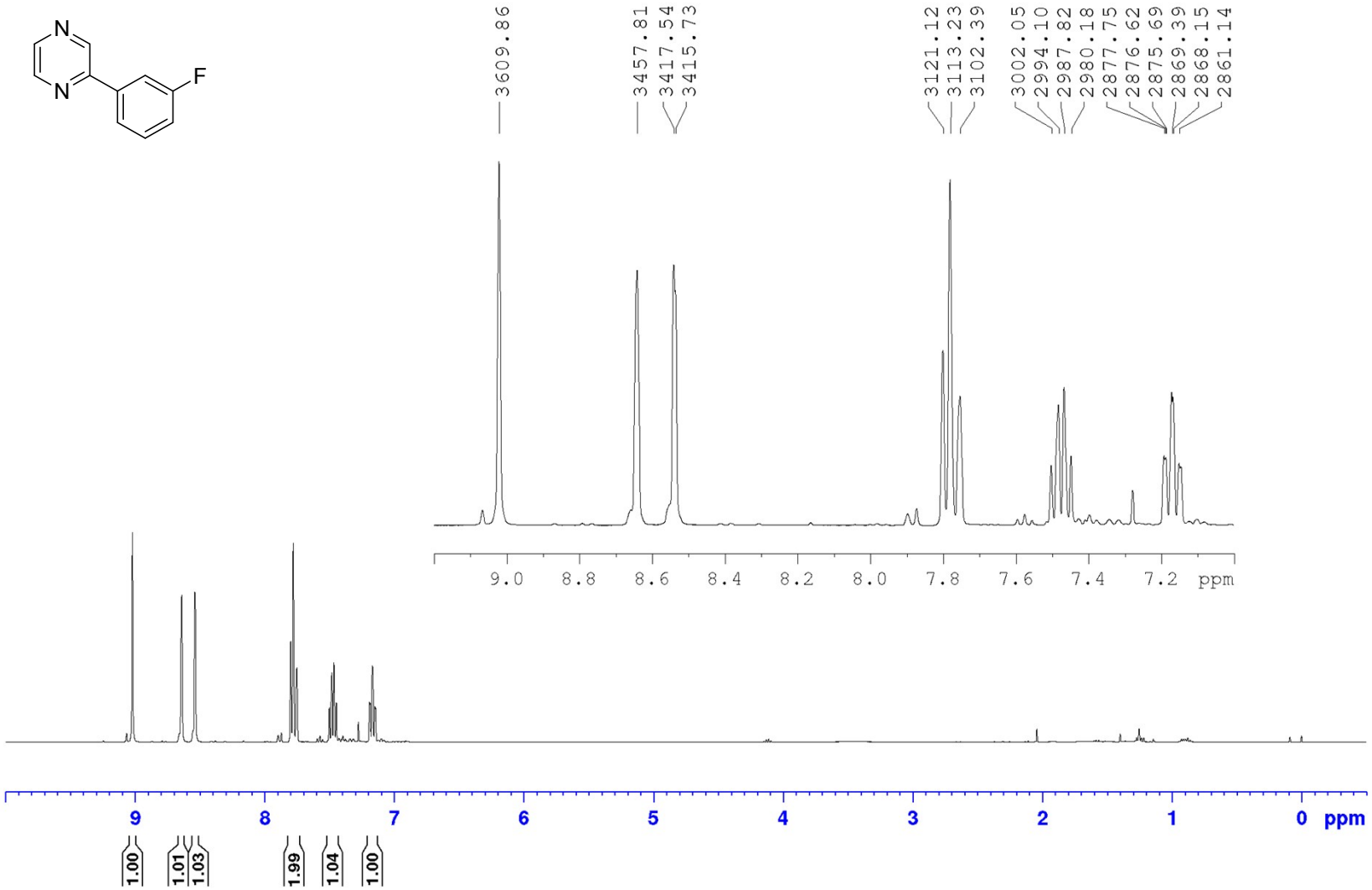
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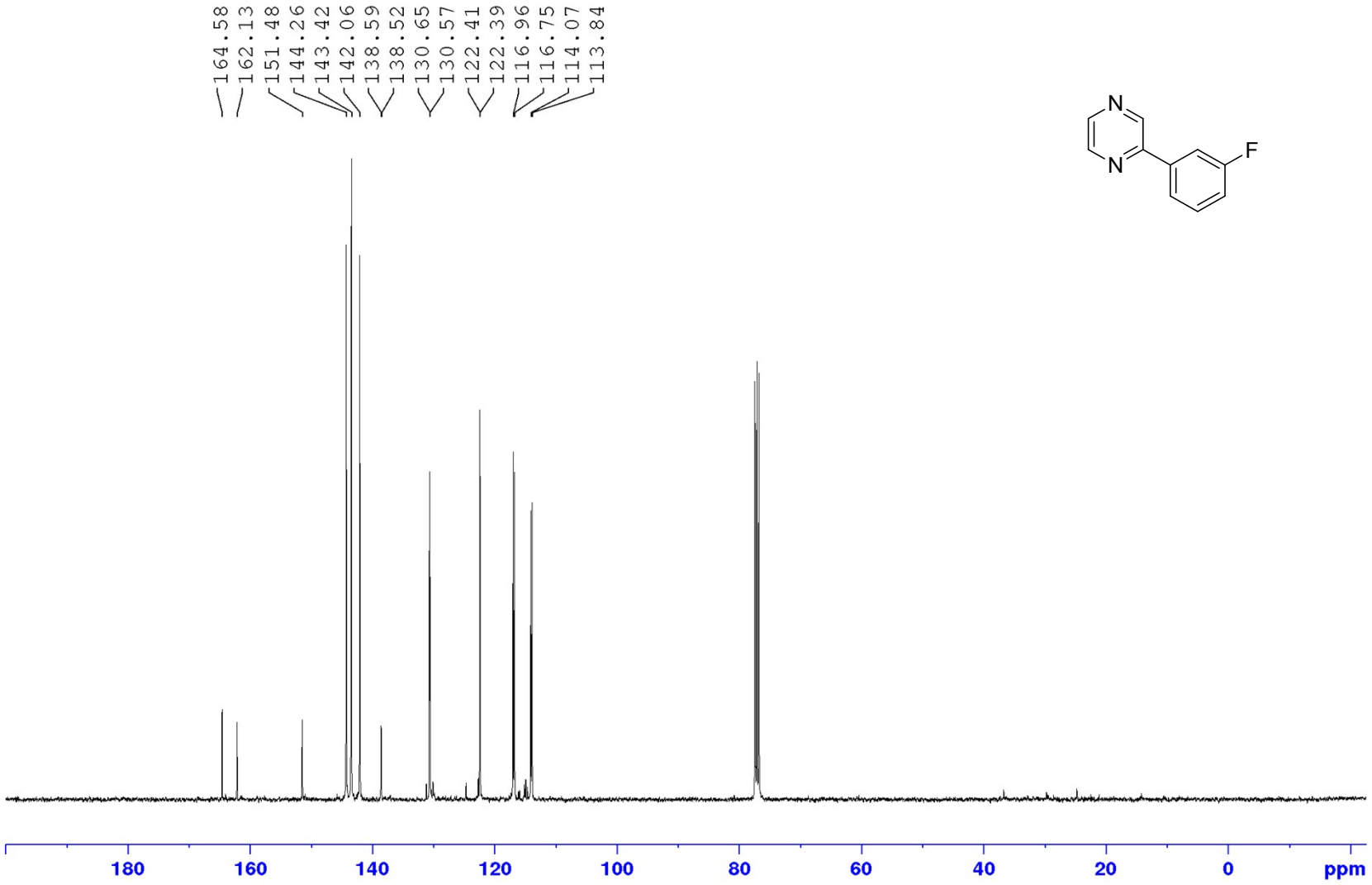
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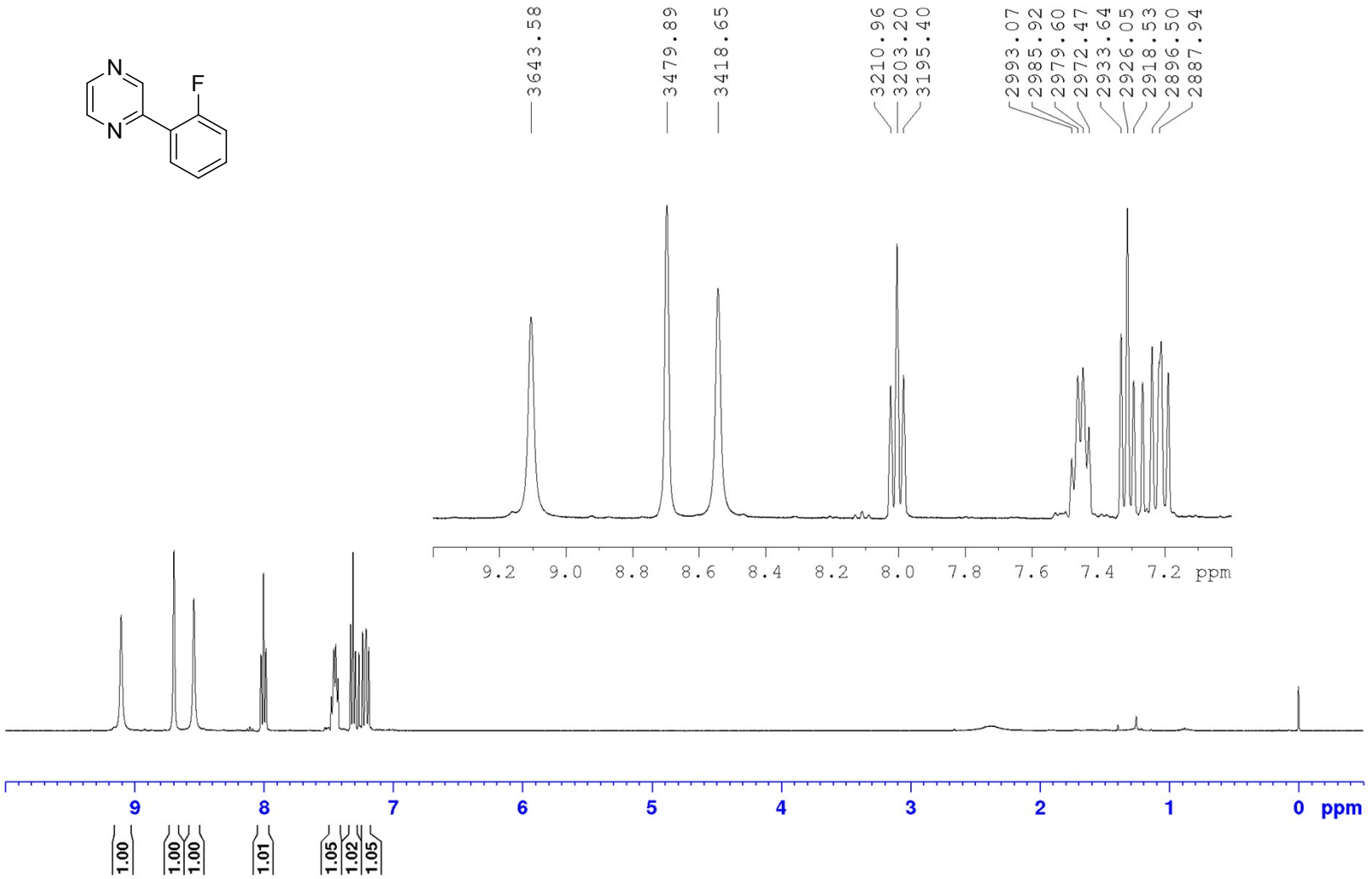
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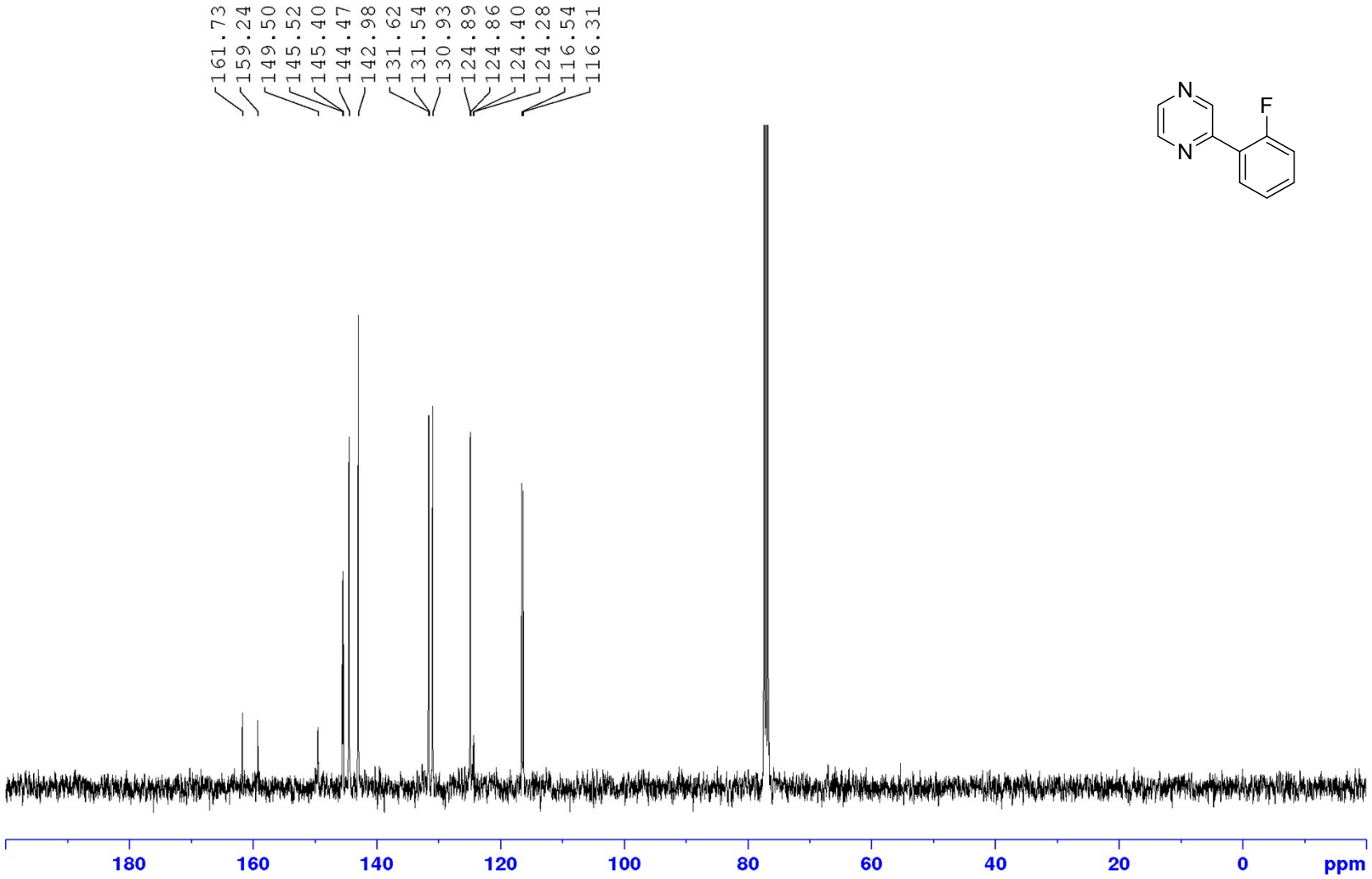
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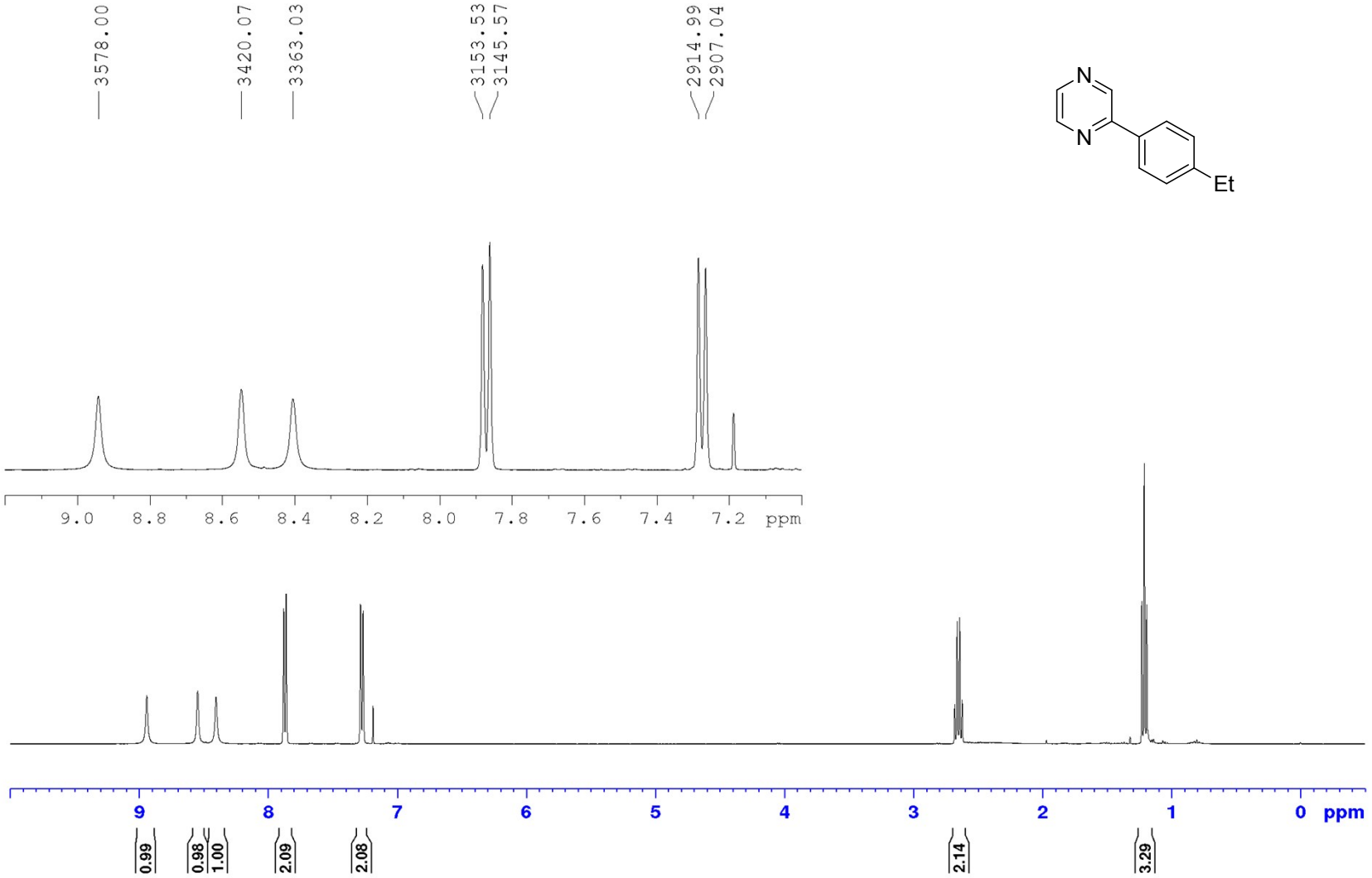
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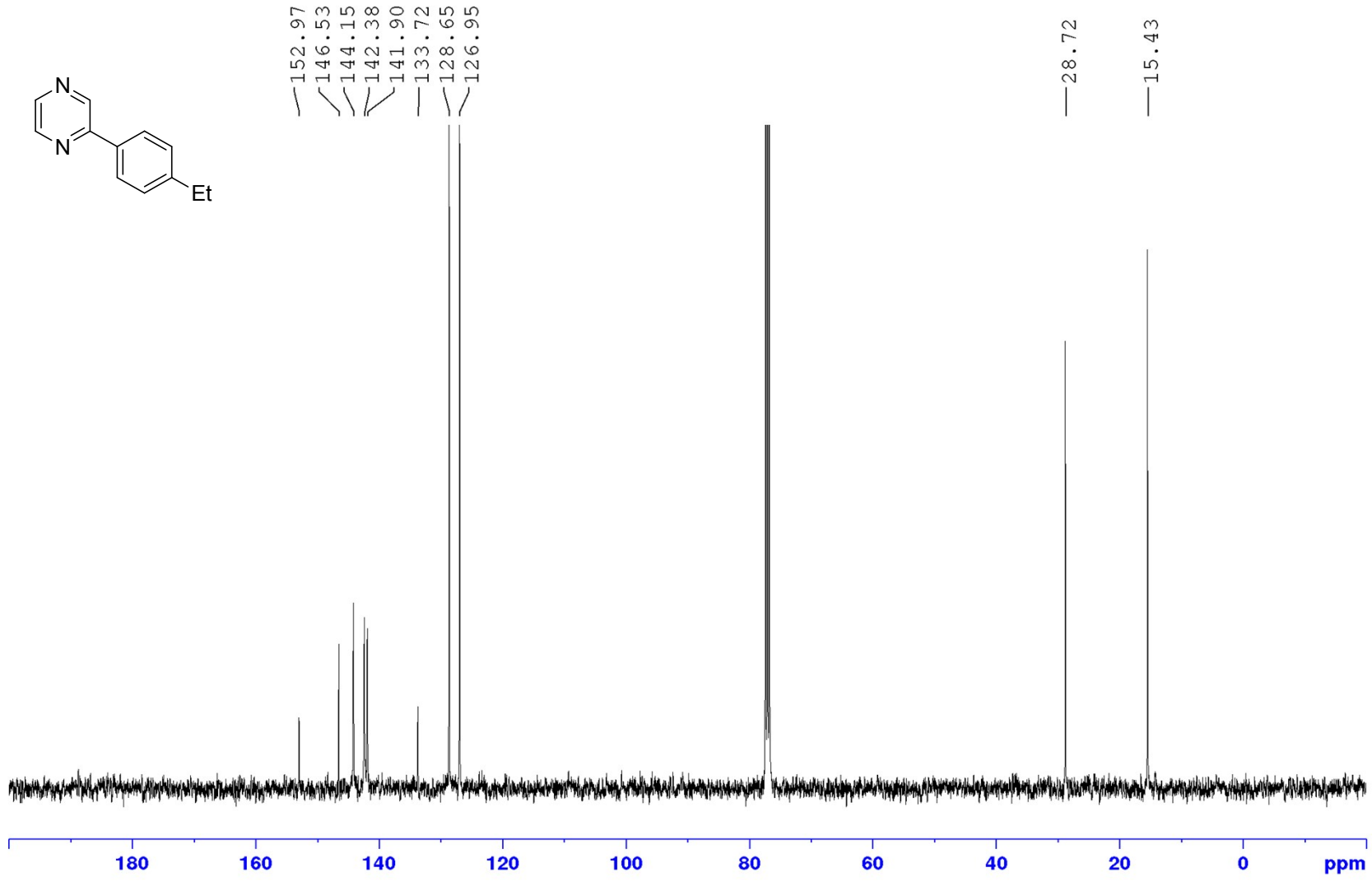
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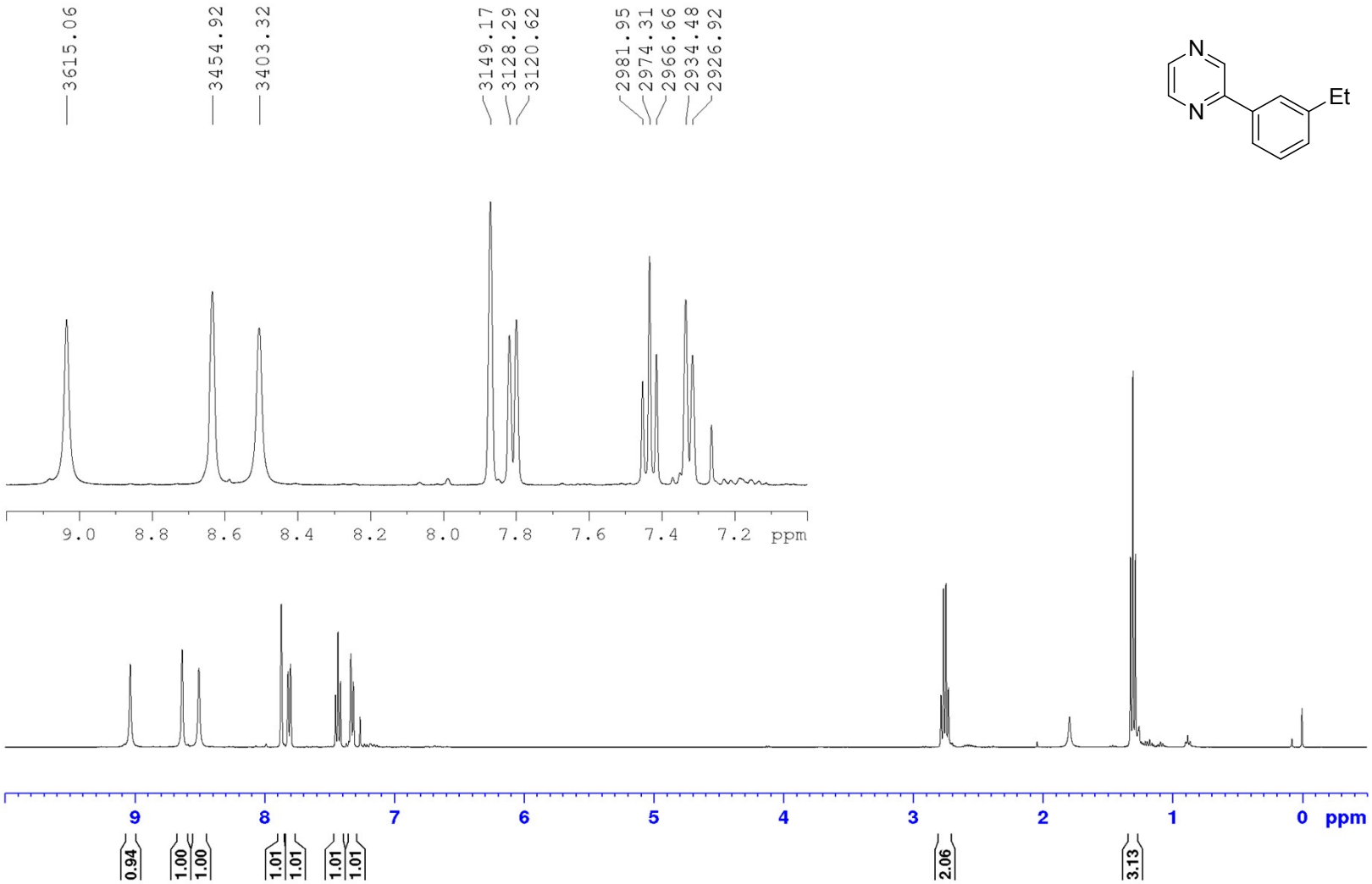
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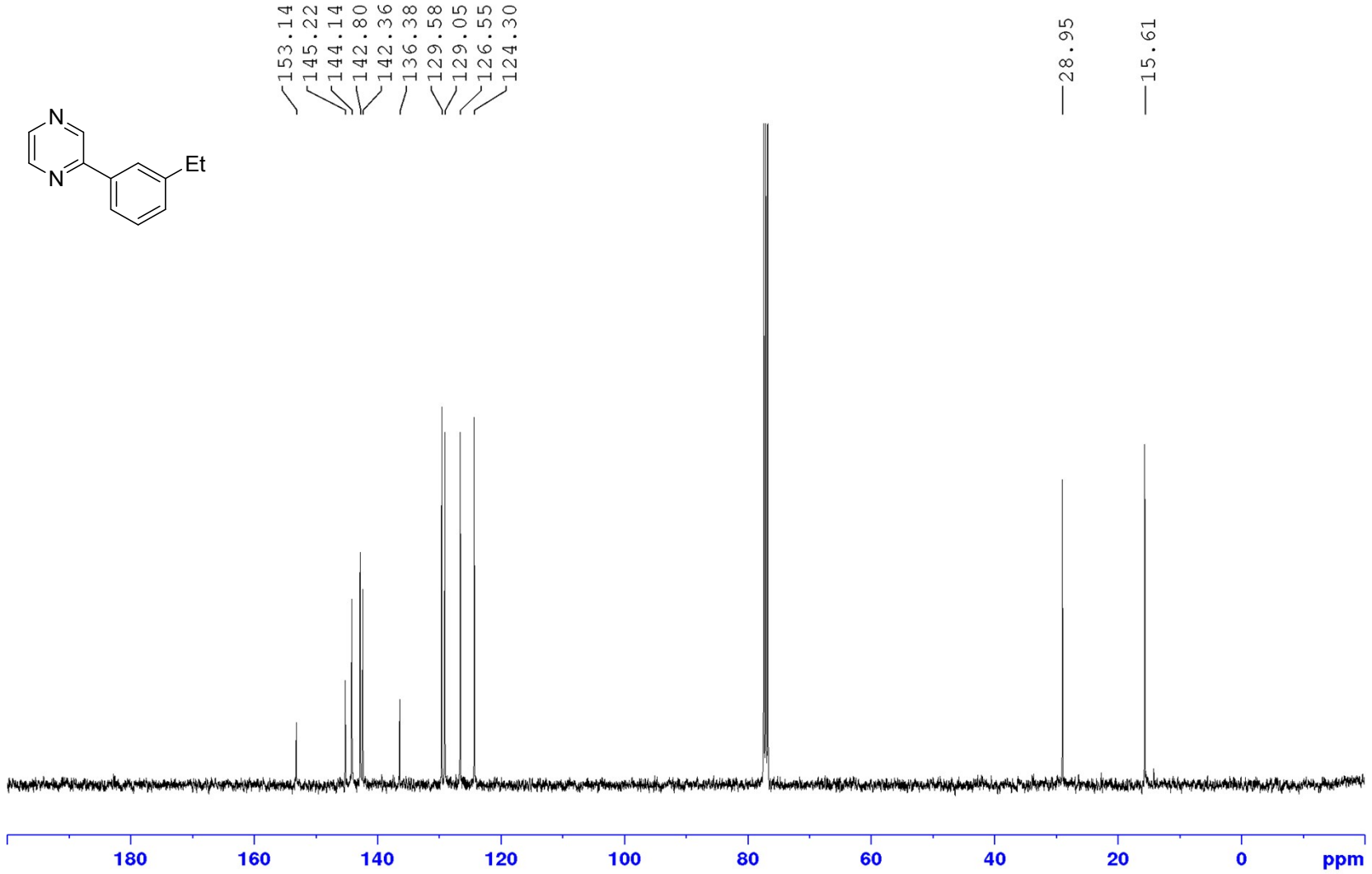
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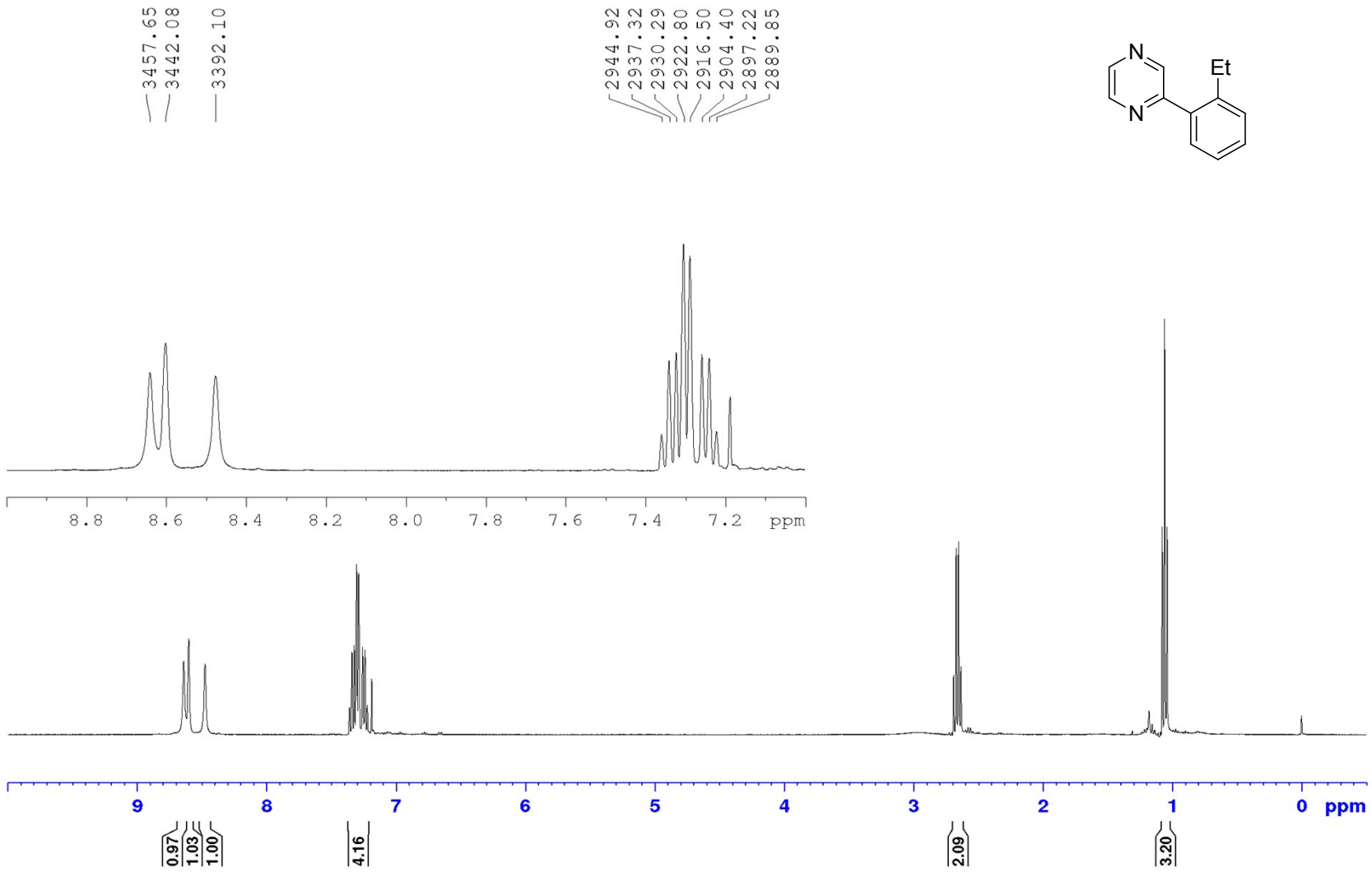
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2944.92
2937.32
2930.29
2922.80
2916.50
2904.40
2897.22
2889.85
N
N
Et
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
9
8
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5
4
3
2
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ppm
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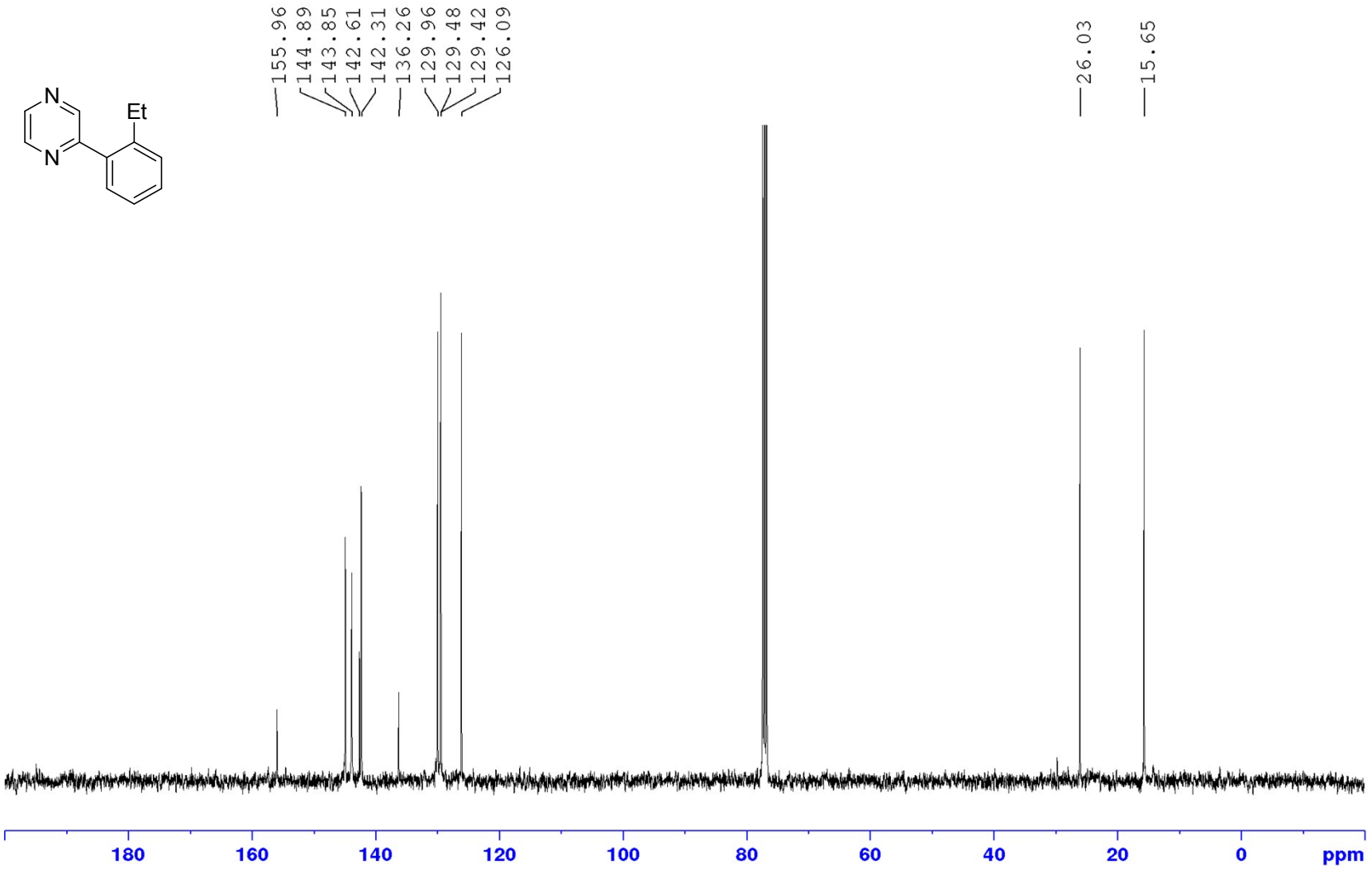
1.03
1.00
4.16
2.09
3.20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144.89
143.85
142.61
142.31
136.26
129.96
129.48
129.42
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N
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Et
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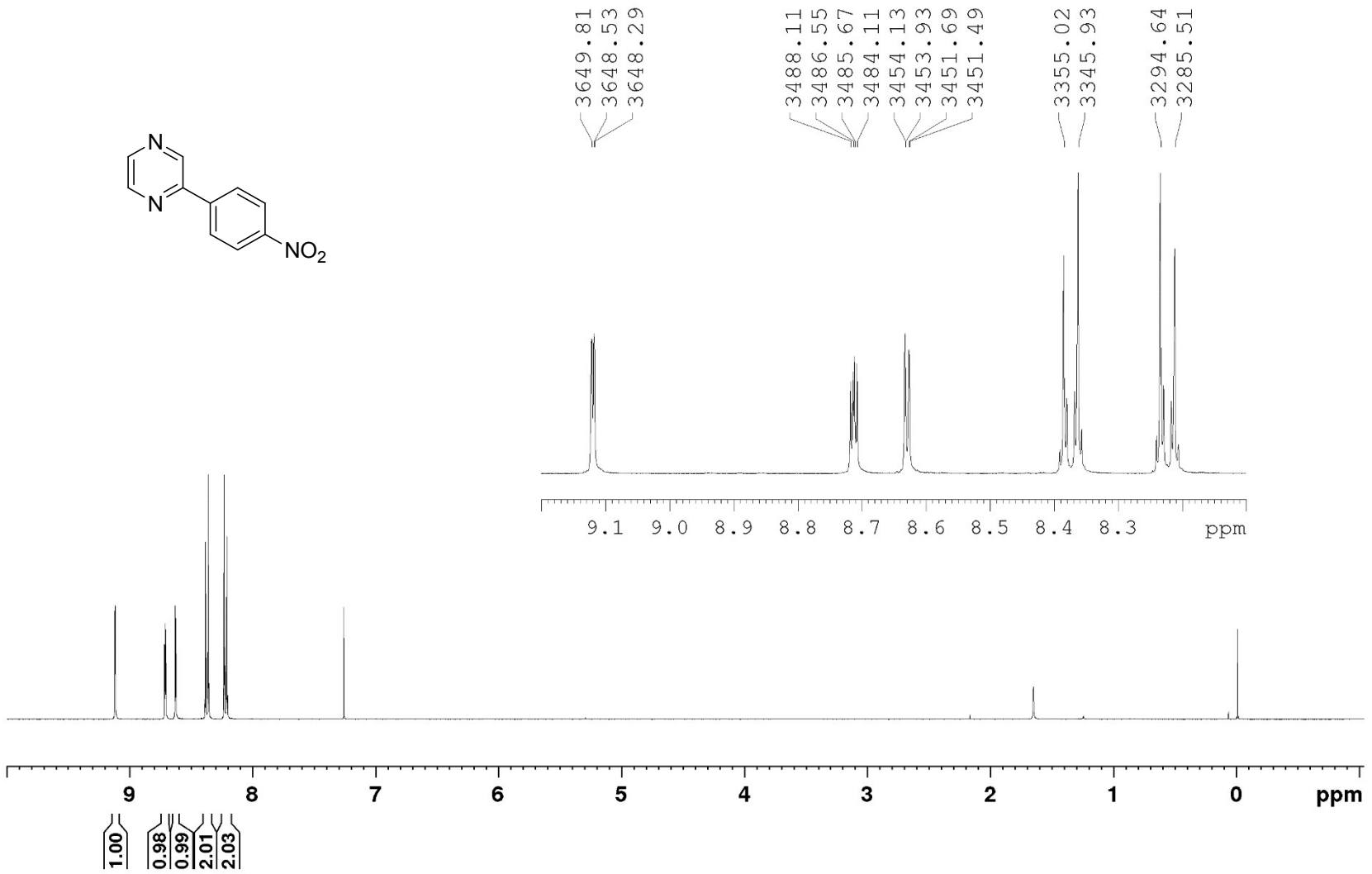
140
120
100
80
60
40
20
0
ppm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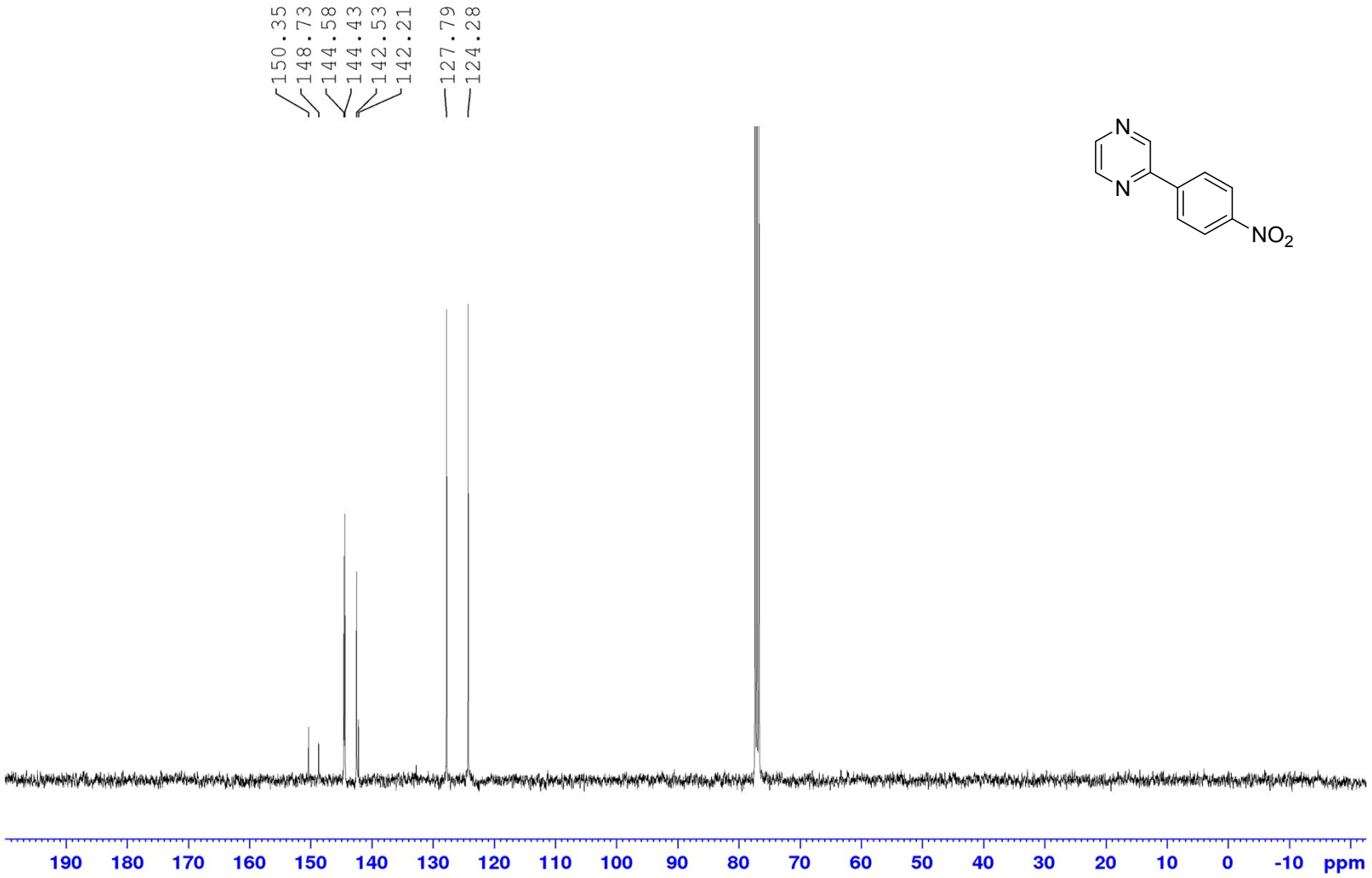
3486.55
3485.67
3484.11
3454.13
3453.93
3451.69
3451.49
3355.02
3345.93
3294.64
3285.51
N
N
NO2
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.98
0.99
2.01
2.03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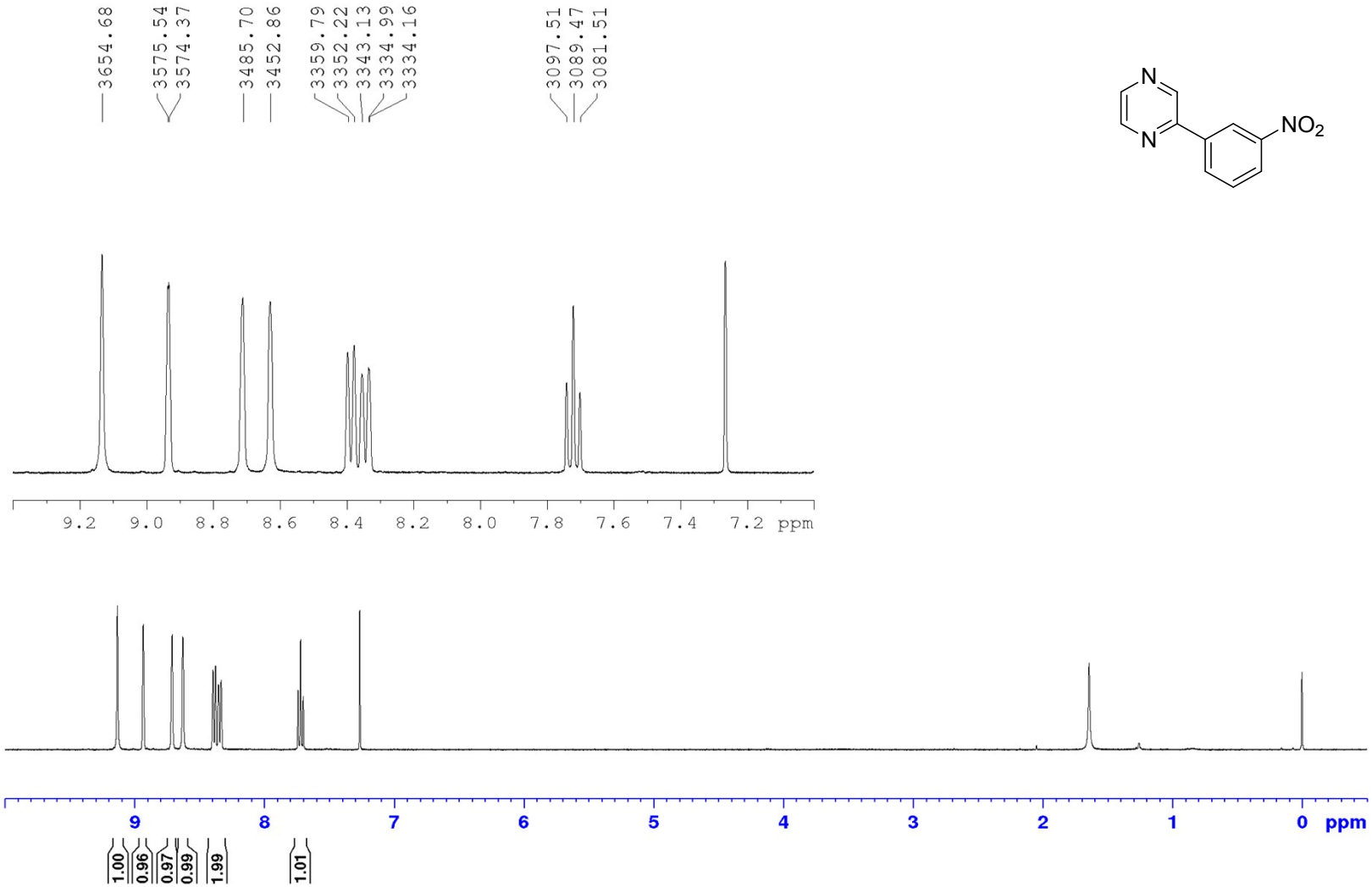
148.73
144.58
144.43
142.53
142.21
127.79
124.28
N
N
NO2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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3574.37
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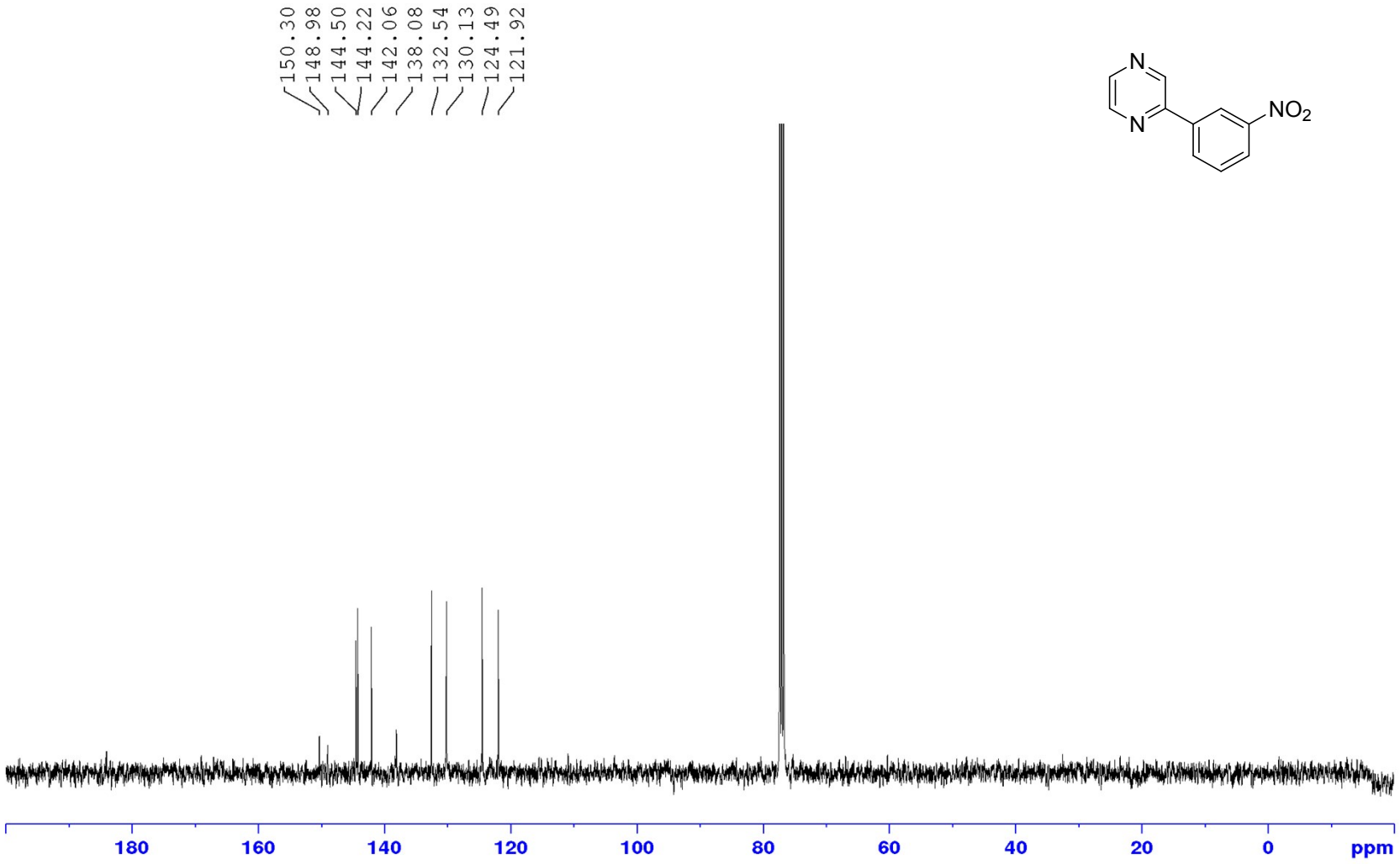
3452.86
3359.79
3352.22
3343.13
3334.99
3334.16
3097.51
3089.47
3081.51
N
N
NO2
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.96
0.97
0.99
1.99
1.01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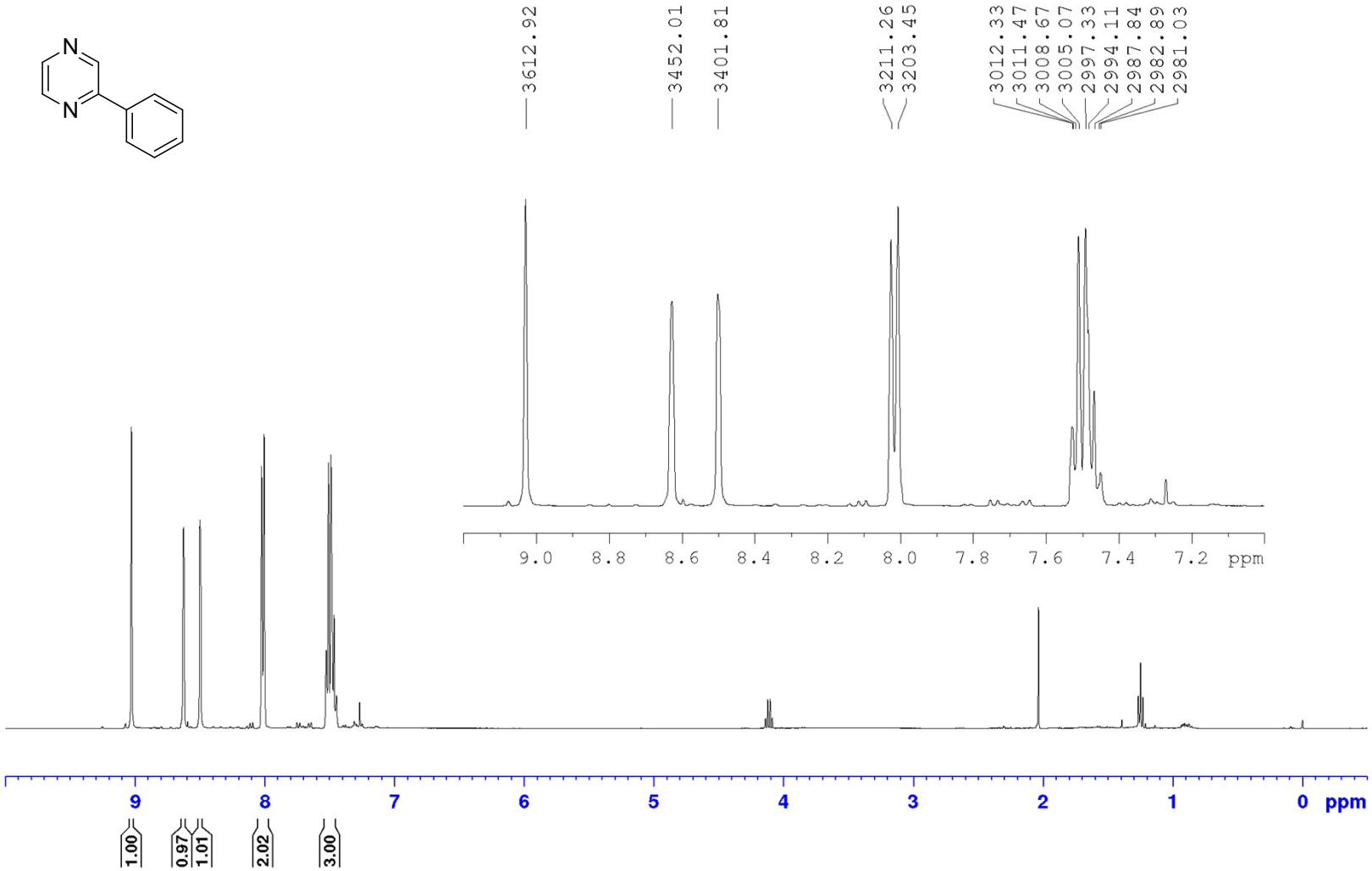
148.98
144.50
144.22
142.06
138.08
132.54
130.13
124.49
121.92
N
N
NO2
180
160
140
120
100
80
60
40
20
0
ppm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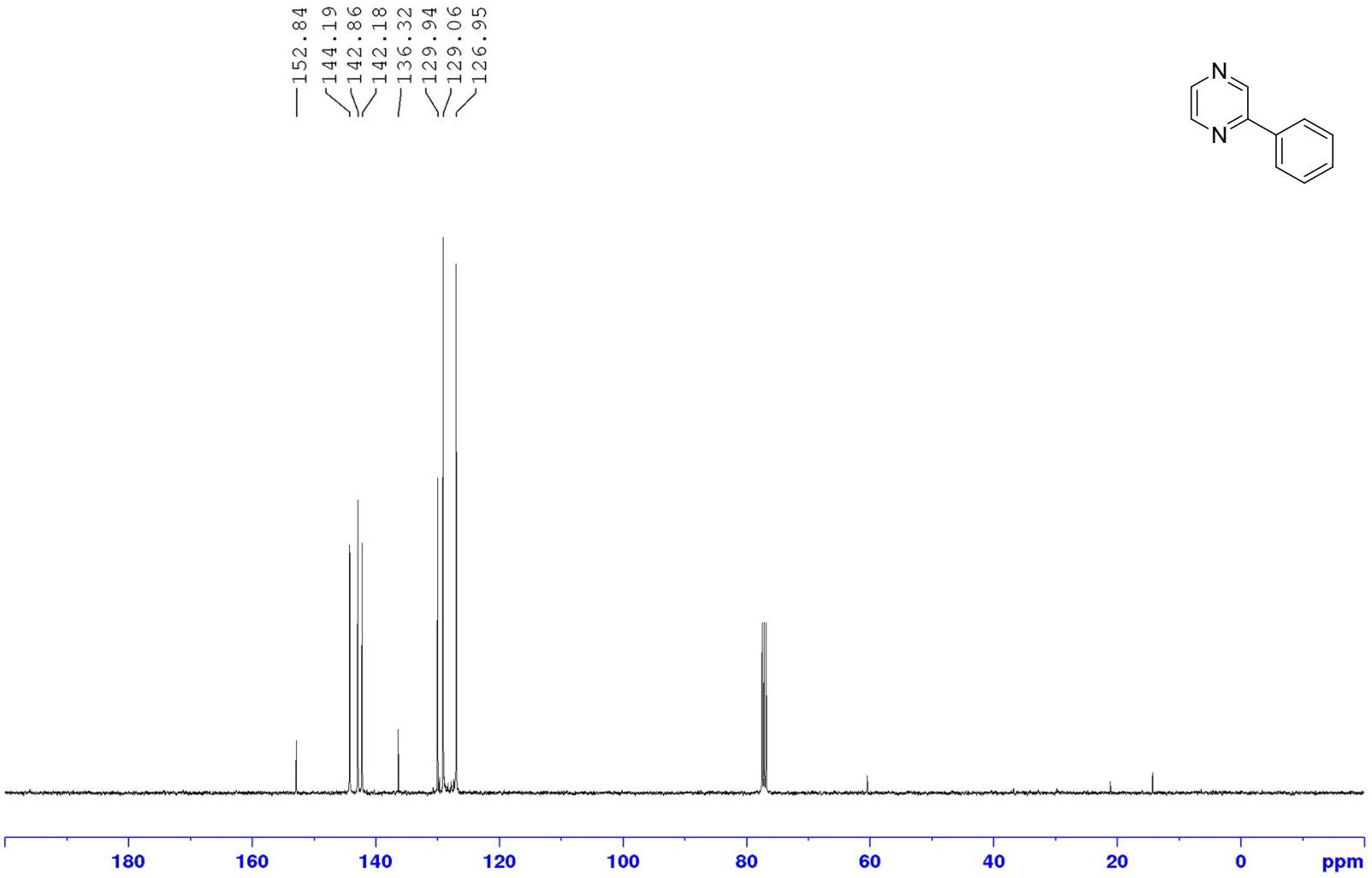
3203.45
3012.33
3011.47
3008.67
3005.07
2997.33
2994.11
2987.84
2982.89
2981.03
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.97
1.01
2.02
3.00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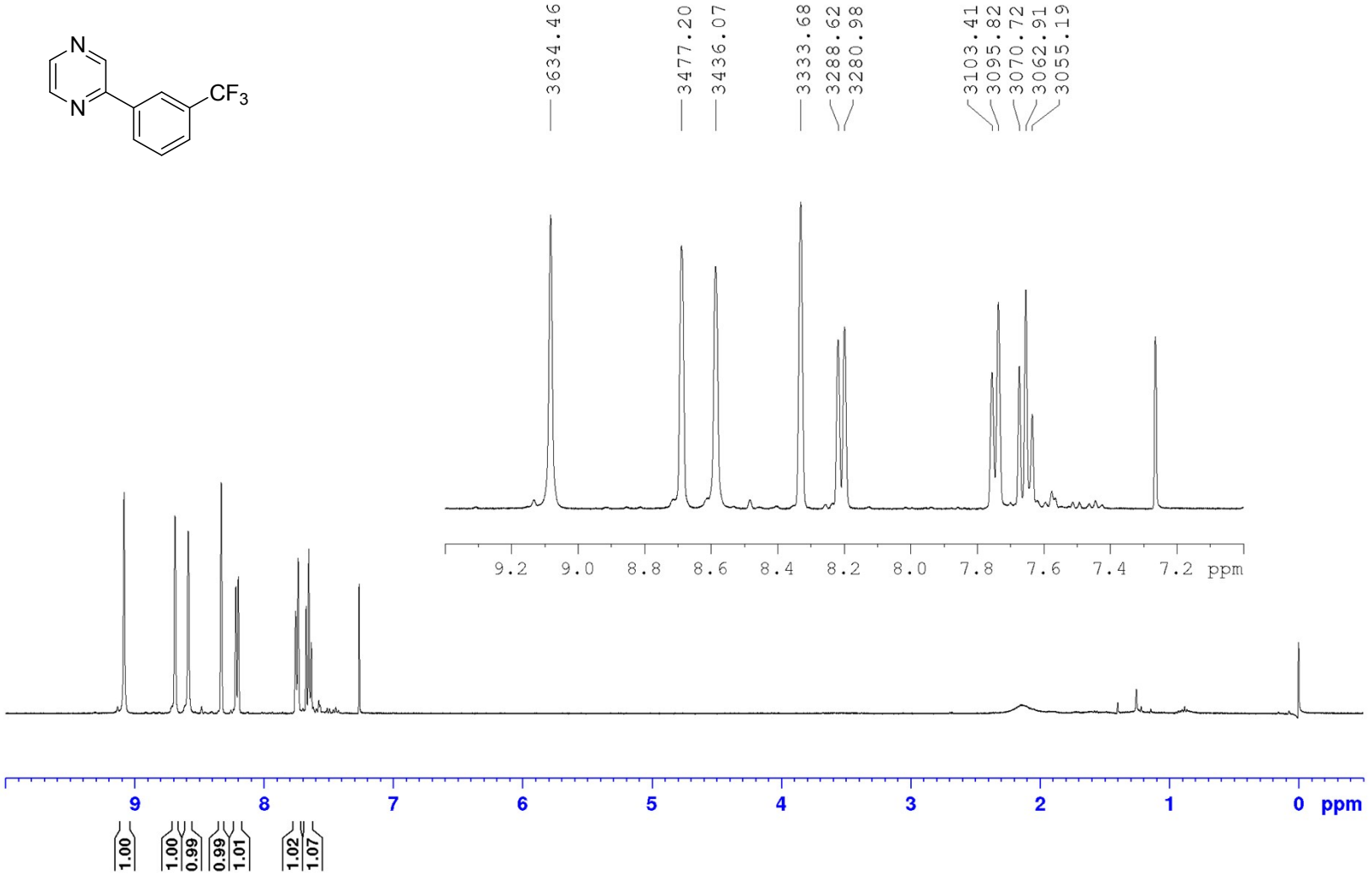
144.19
142.86
142.18
136.32
129.94
129.06
126.95
N
N
180
160
140
120
100
80
60
40
20
0
ppm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N
CF3
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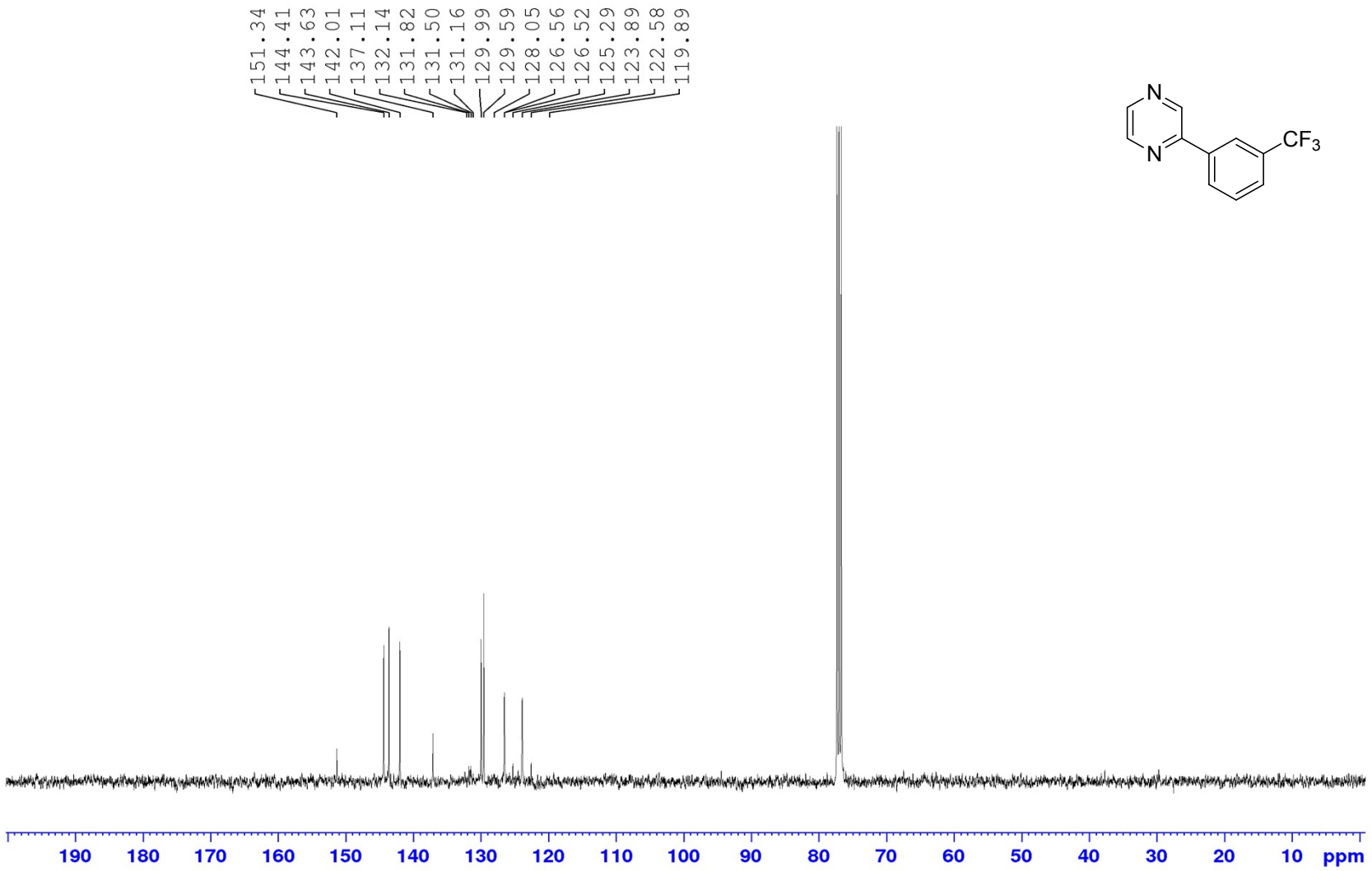
3436.07
3333.68
3288.62
3280.98
3103.41
3095.82
3070.72
3062.91
3055.19
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.00
0.99
0.99
1.01
1.02
1.07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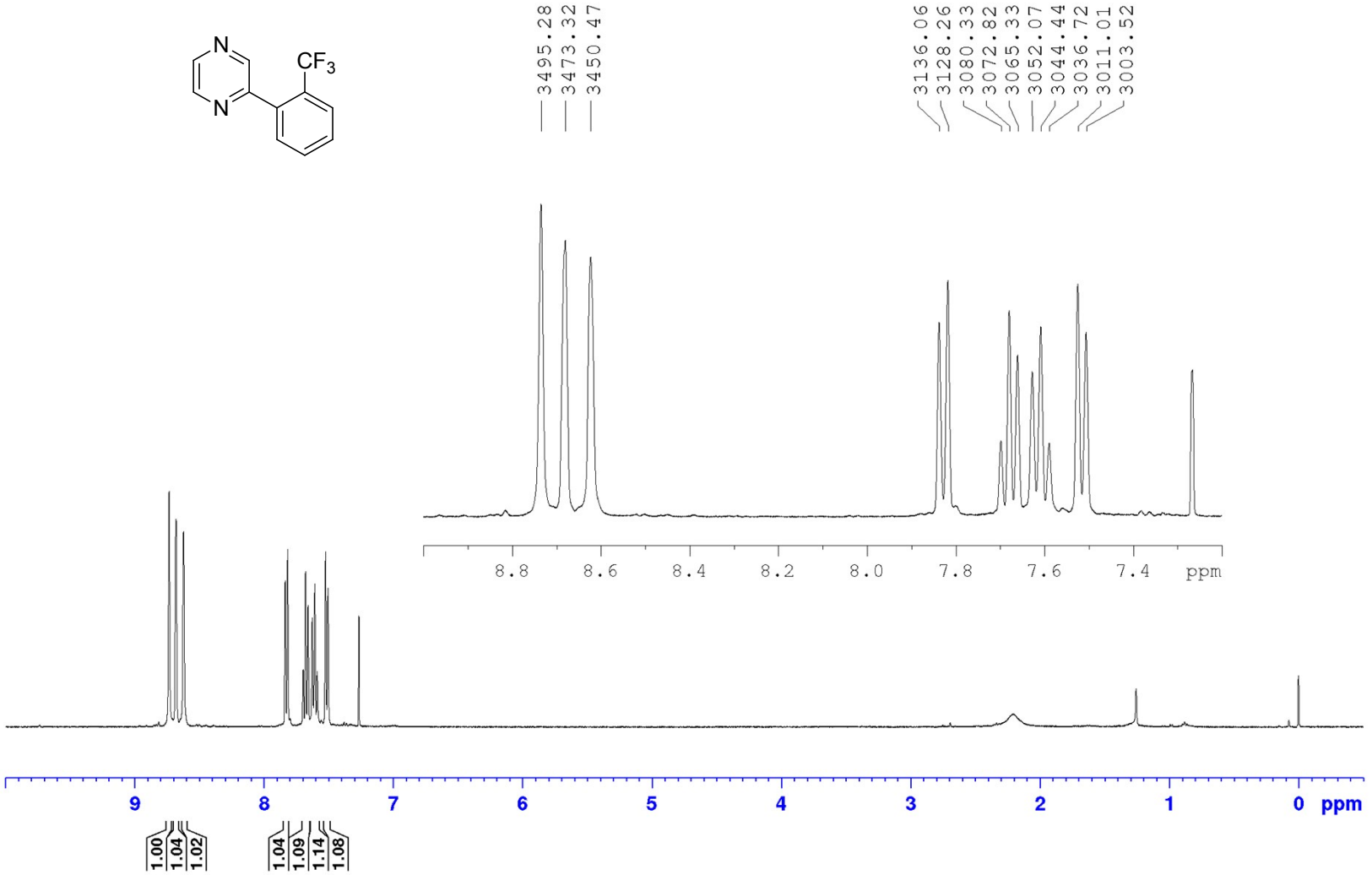
144.41
143.63
142.01
137.11
132.14
131.82
131.50
131.16
129.99
129.59
128.05
126.56
126.52
125.29
123.89
122.58
119.89
N
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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N
CF3
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3128.26
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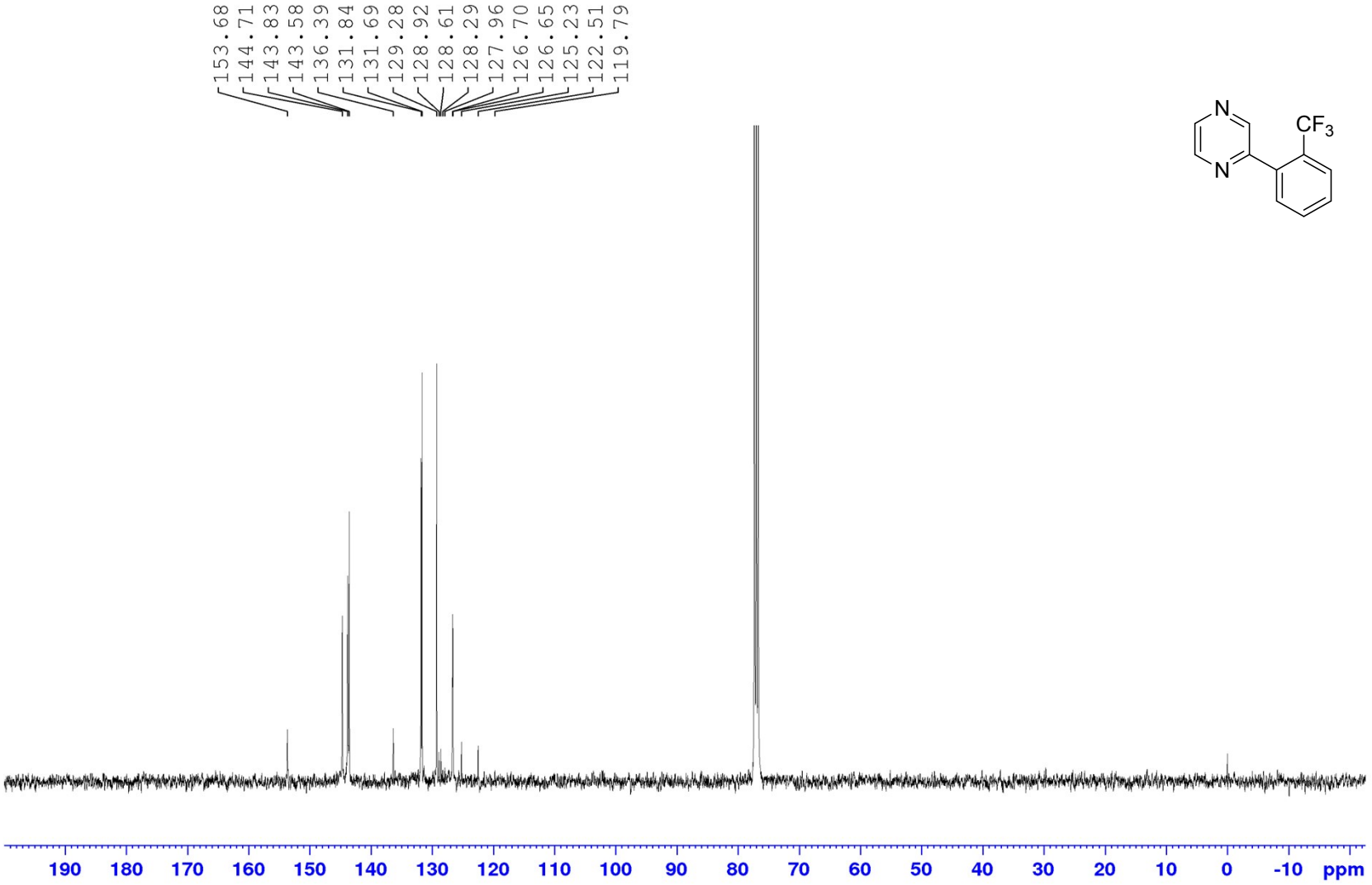
3072.82
3065.33
3052.07
3044.44
3036.72
3011.01
3003.52
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.02
1.04
1.09
1.14
1.08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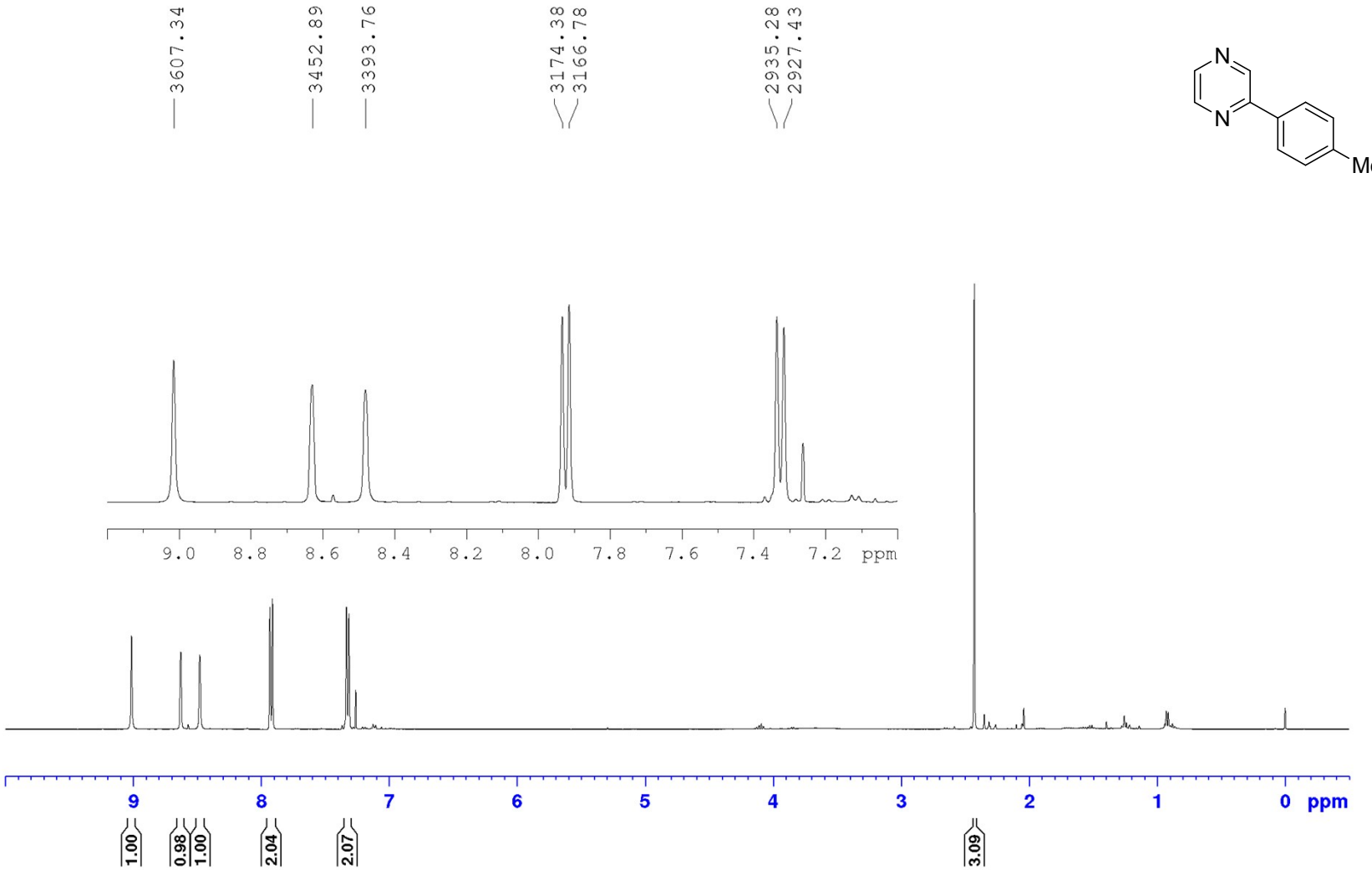
143.58
136.39
131.84
131.69
129.28
128.92
128.61
128.29
127.96
126.70
126.65
125.23
122.51
119.79
N
N
CF3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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3393.76
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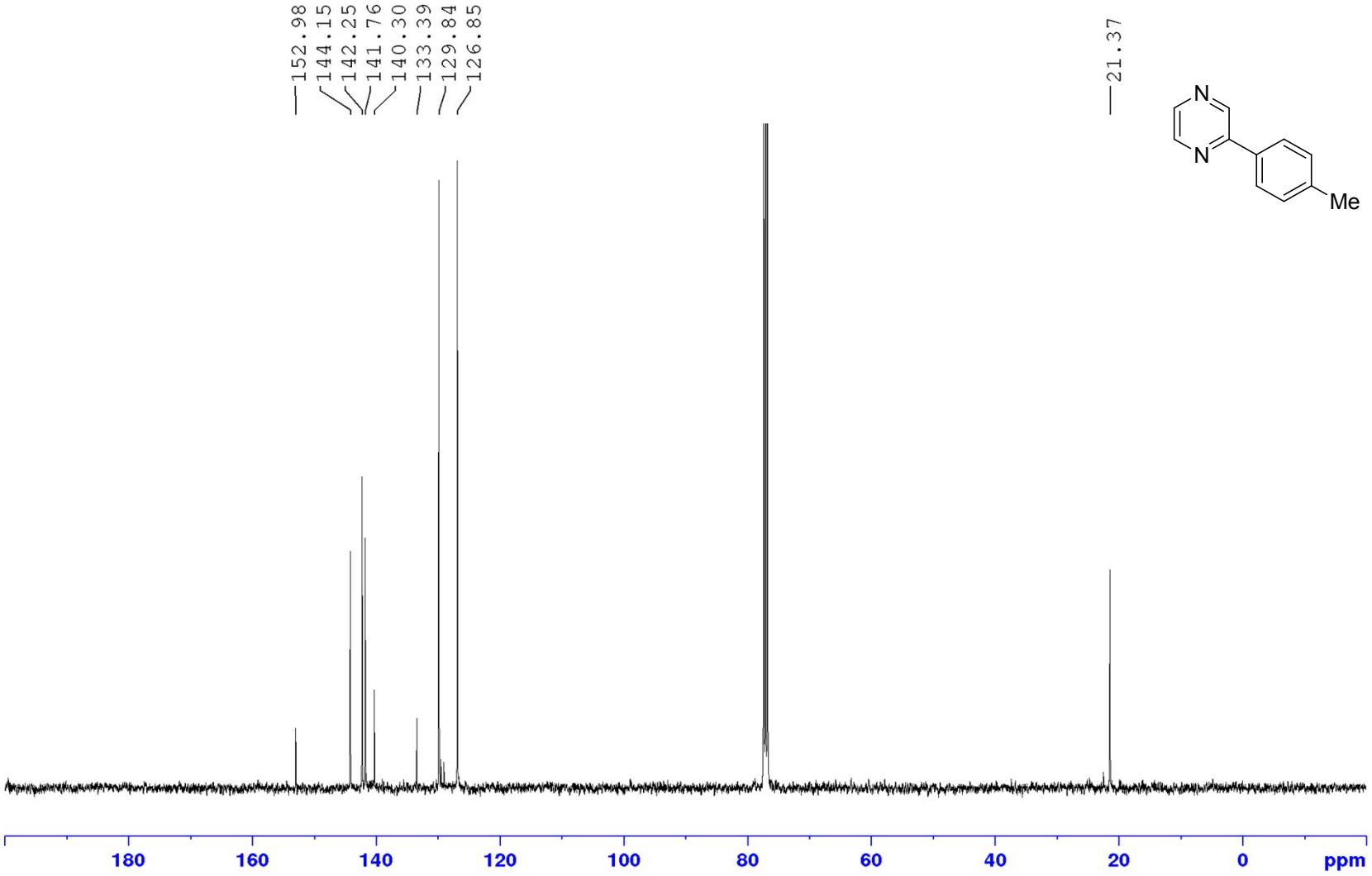
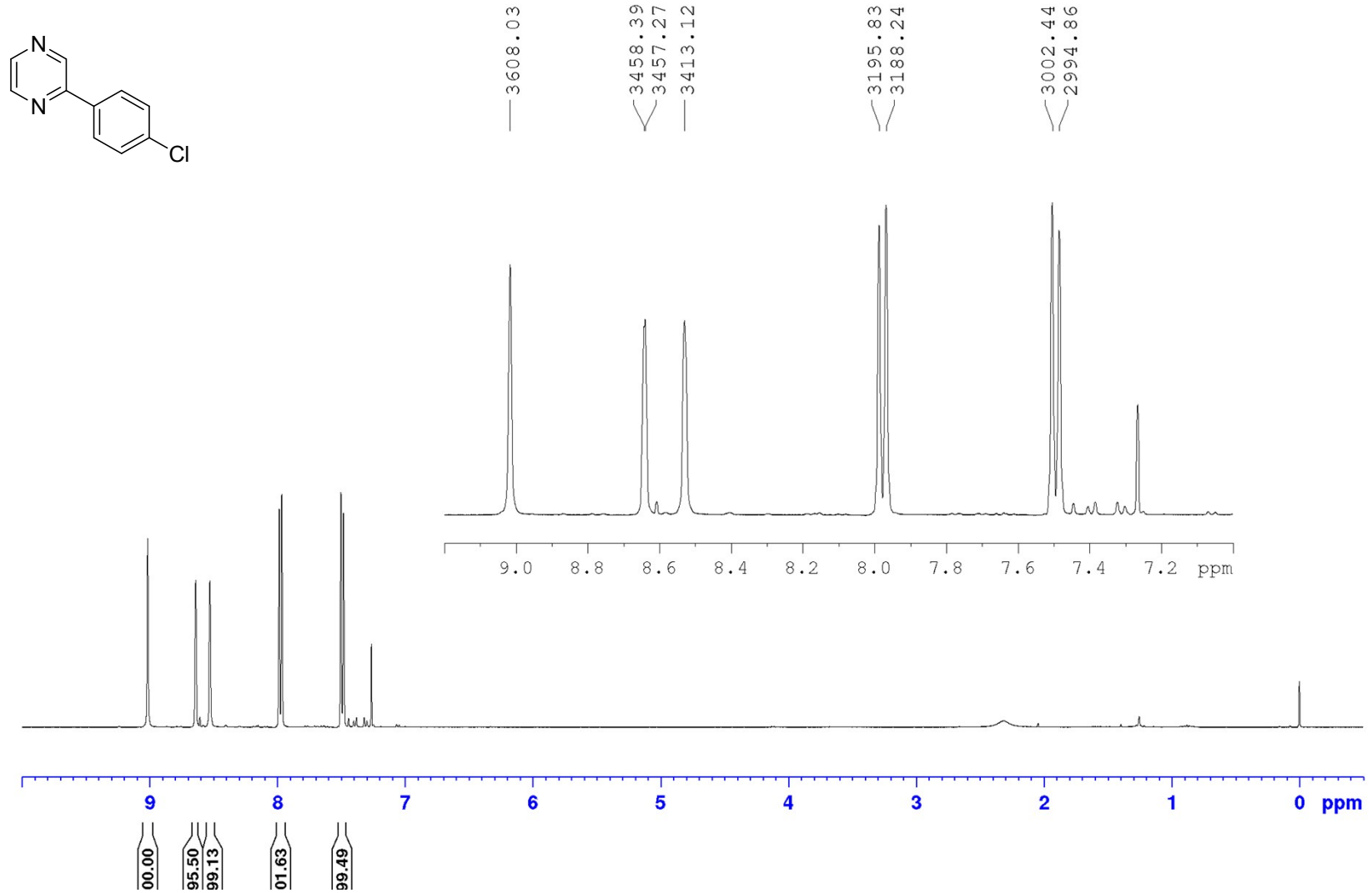
3166.78
2935.28
2927.43
N
N
Me
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
1.00
2.04
2.07
3.09


152.98
144.15
142.25
141.76
140.30
133.39
129.84
126.85
21.37
N
N
Me
180
160
140
120
100
80
60
40
20
0
ppm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N
Cl
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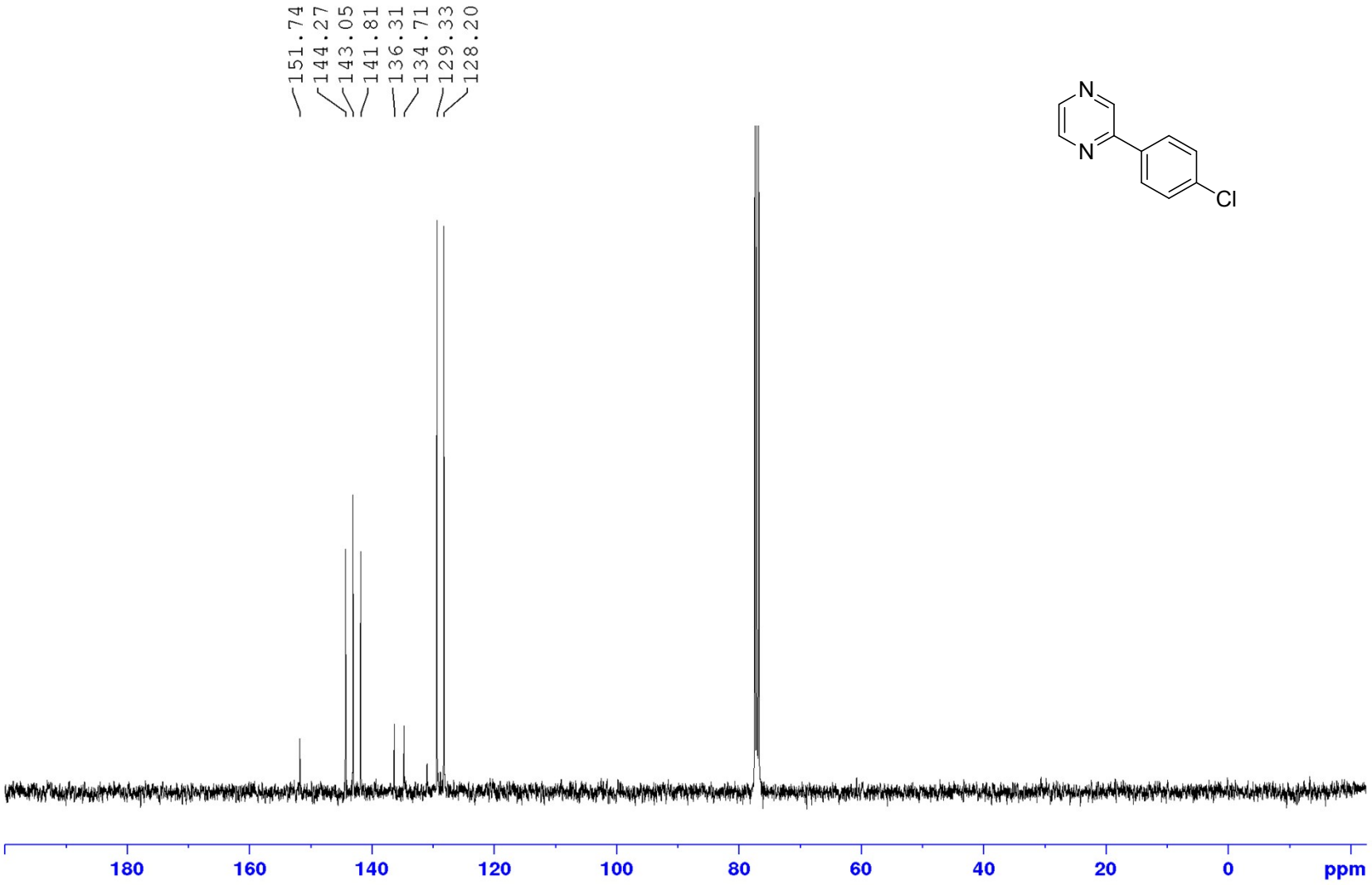
3457.27
3413.12
3195.83
3188.24
3002.44
2994.86
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm
00.00
95.50
99.13
01.63
99.49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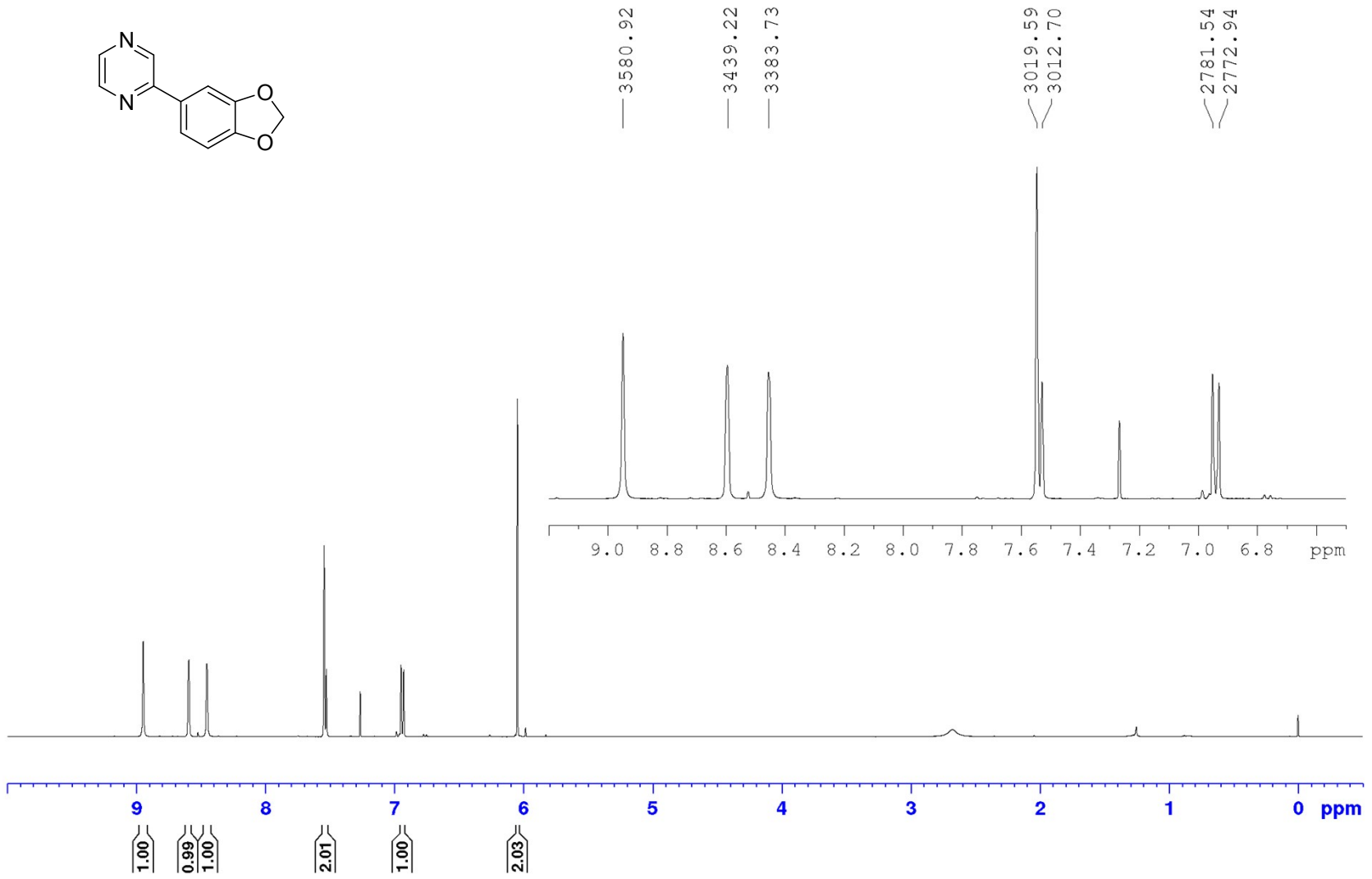
144.27
143.05
141.81
136.31
134.71
129.33
128.20
N
N
Cl
180
160
140
120
100
80
60
40
20
0
ppm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3383.73
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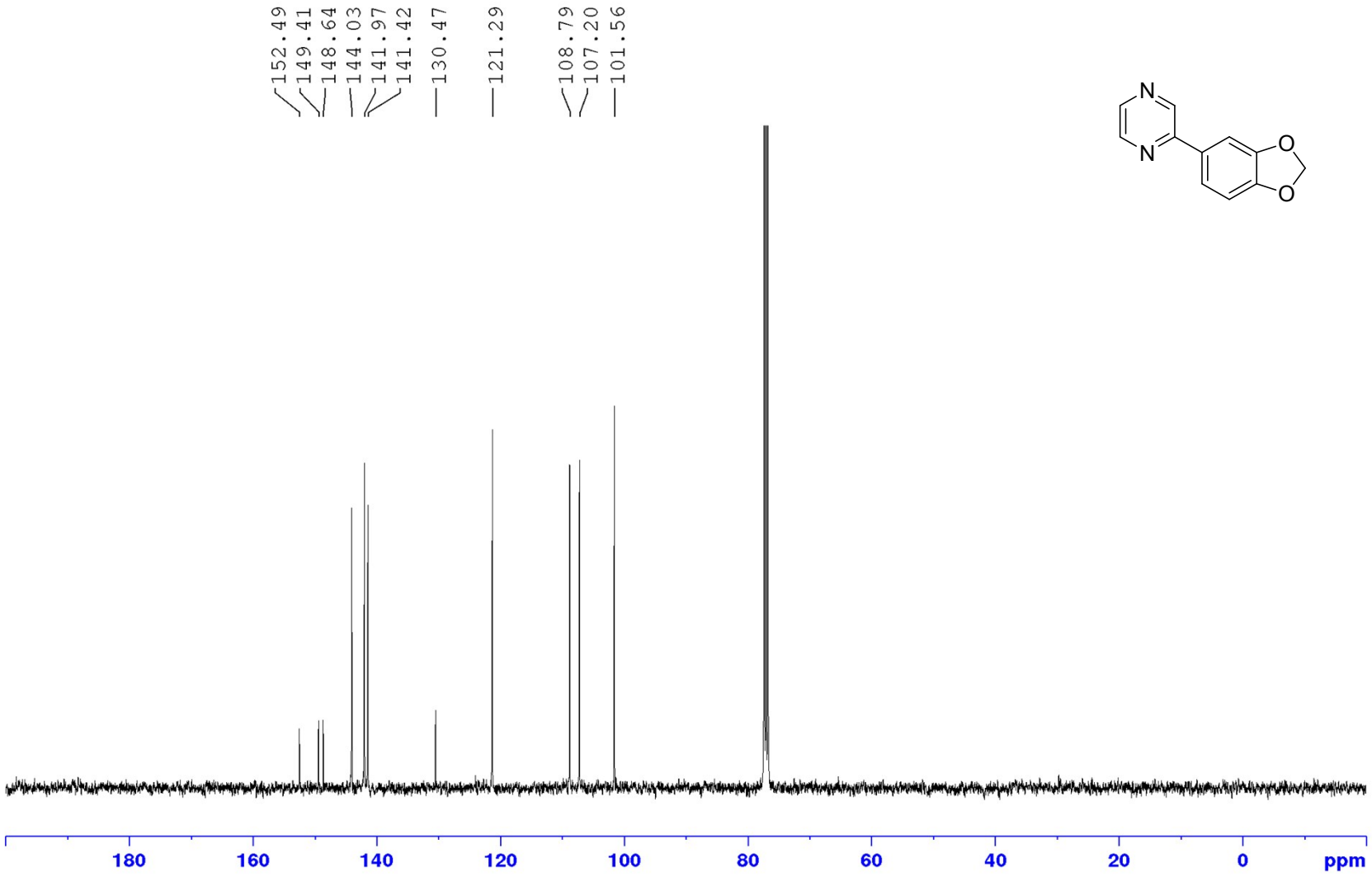
3012.70
2781.54
2772.94
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.99
1.00
2.01
1.00
2.03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149.41
148.64
144.03
141.97
141.42
130.47
121.29
108.79
107.20
101.56
N
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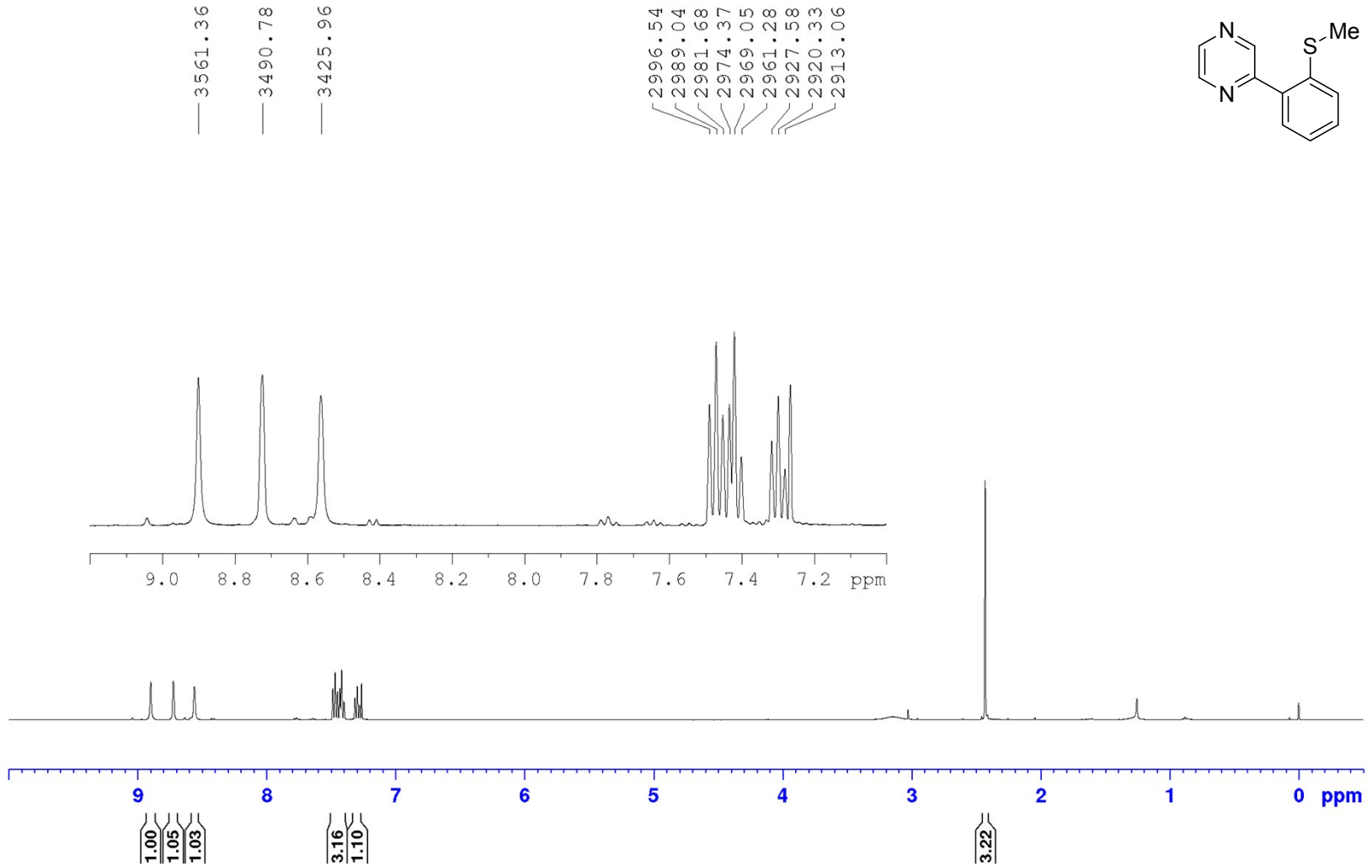
O
O
180
160
140
120
100
80
60
40
20
0
ppm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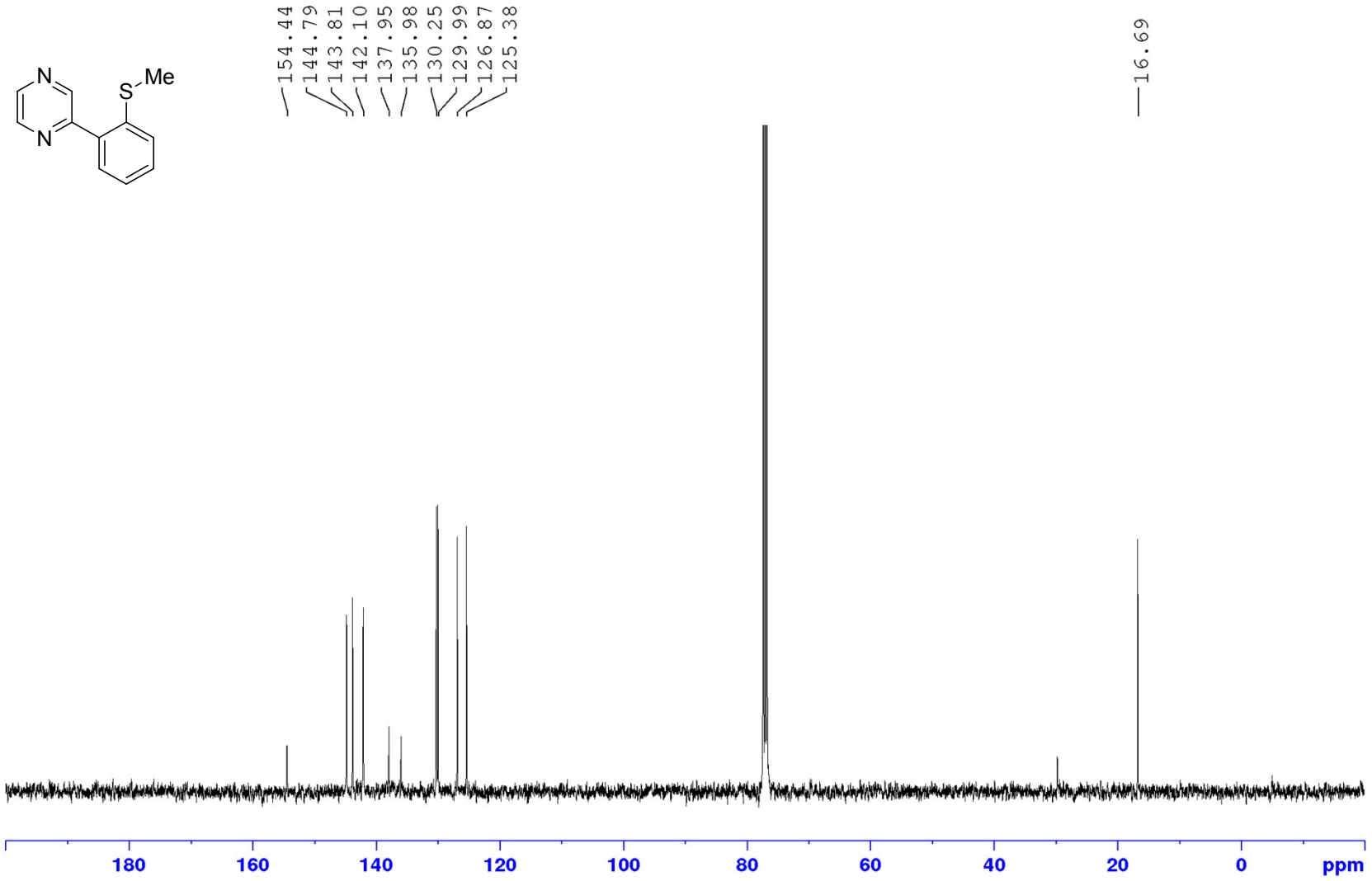
3425.96
2996.54
2989.04
2981.68
2974.37
2969.05
2961.28
2927.58
2920.33
2913.06
N
N
S
Me
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
1.03
3.16
1.10
3.22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142.10
137.95
135.98
130.25
129.99
126.87
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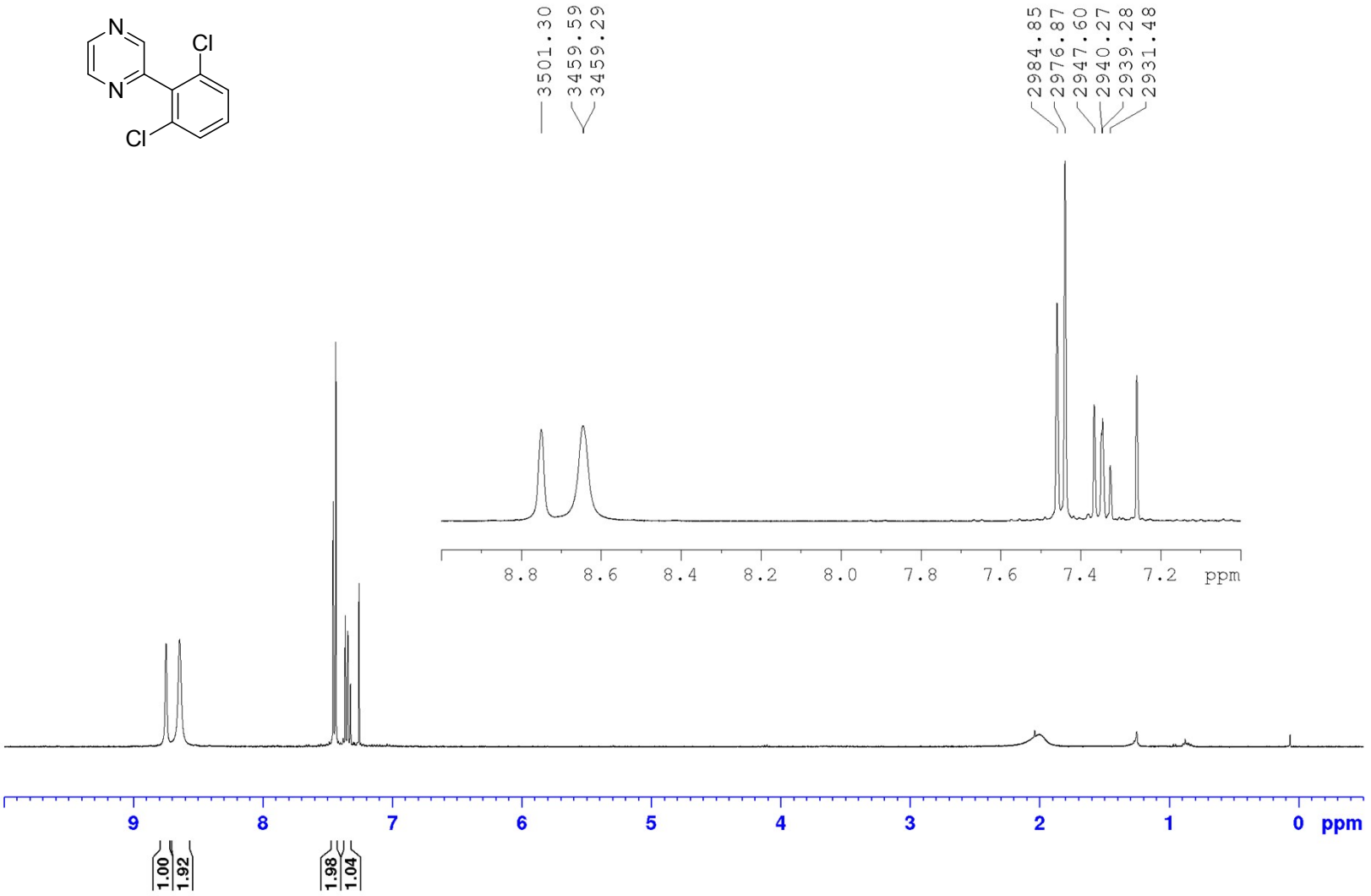
16.69
N
N
S
Me
180
160
140
120
100
80
60
40
20
0
ppm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N
Cl
Cl
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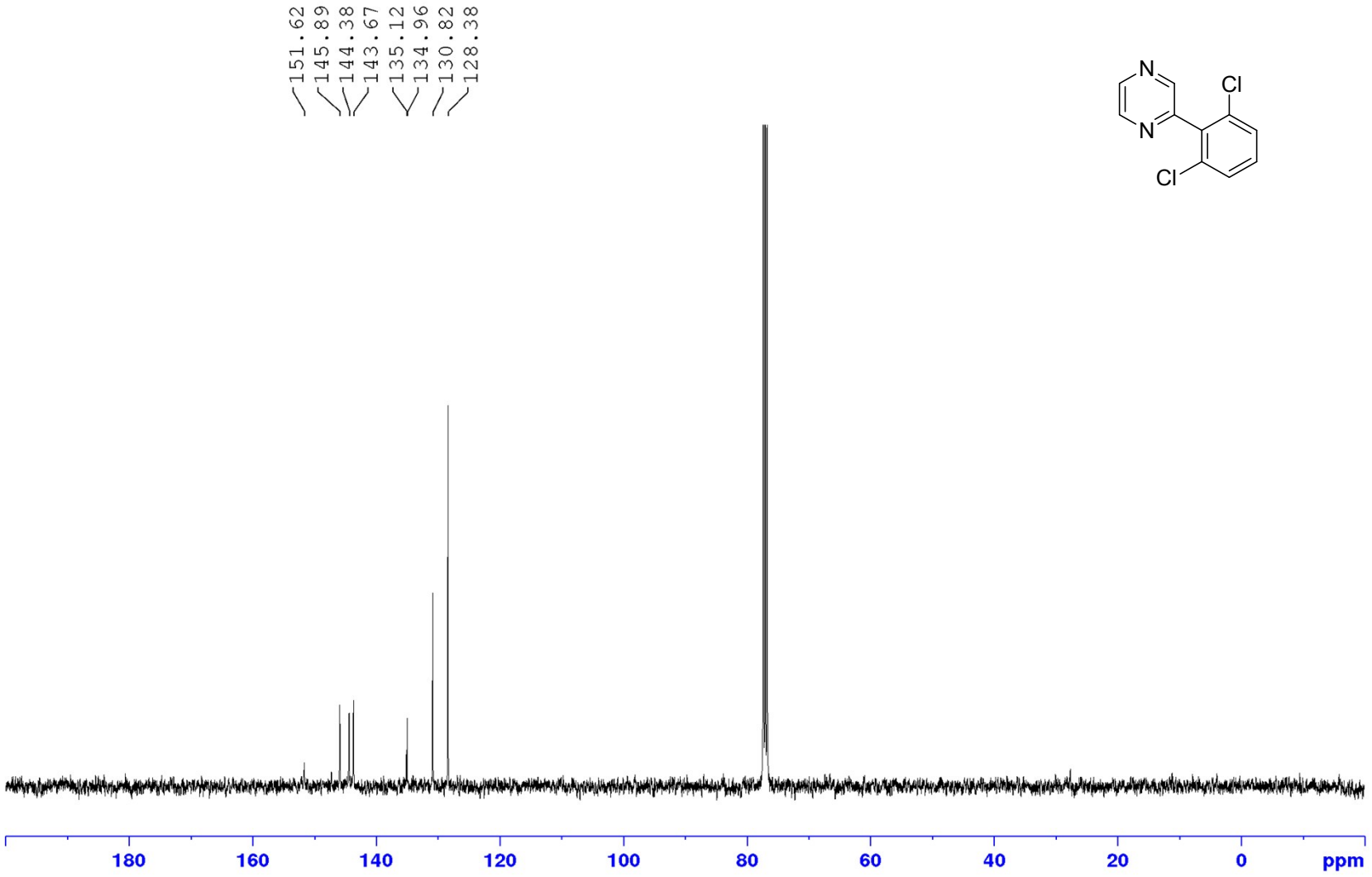
3459.59
3459.29
2984.85
2976.87
2947.60
2940.27
2939.28
2931.48
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.92
1.98
1.04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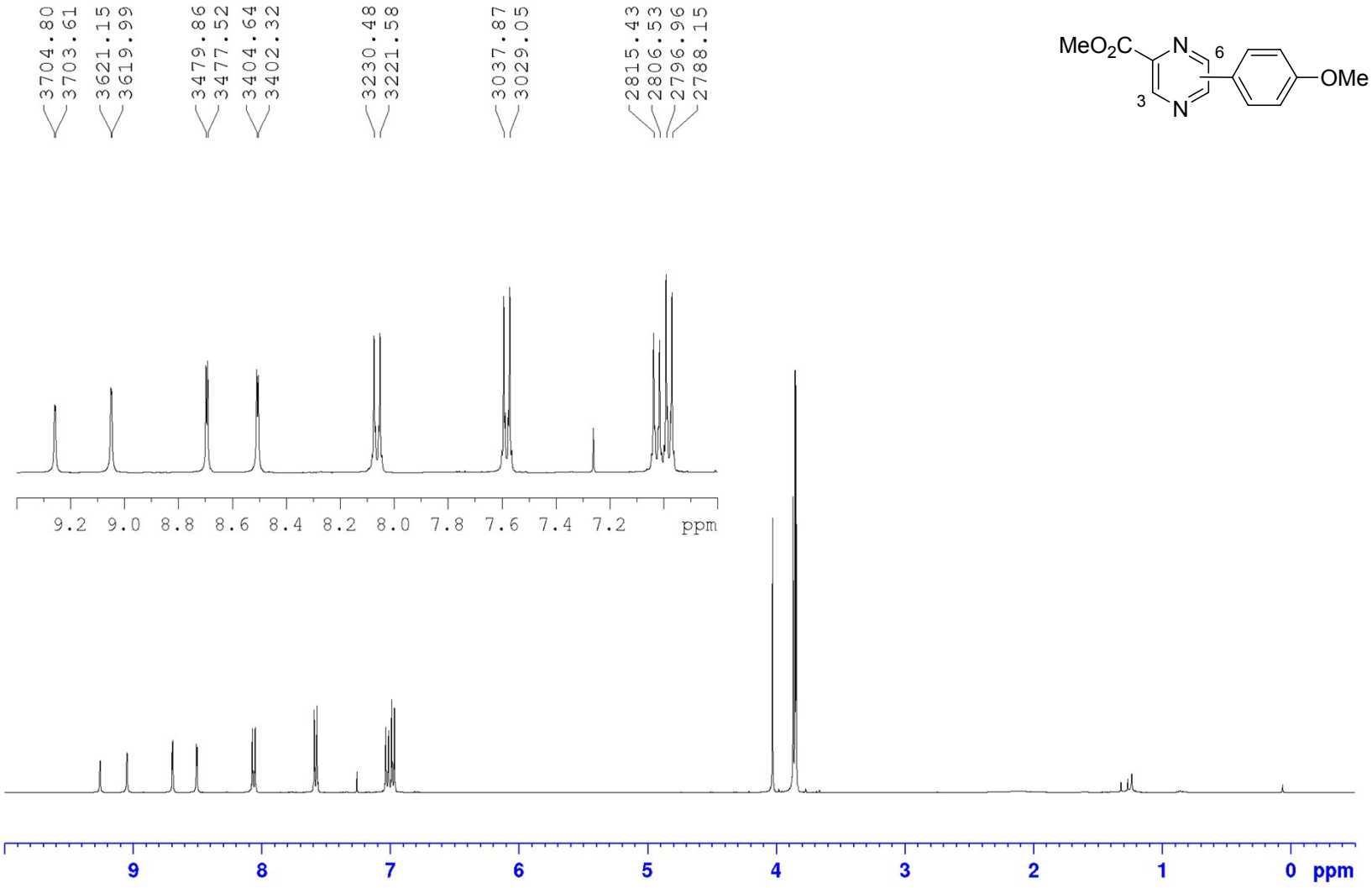
145.89
144.38
143.67
135.12
134.96
130.82
128.38
N
N
Cl
Cl
180
160
140
120
100
80
60
40
20
0
ppm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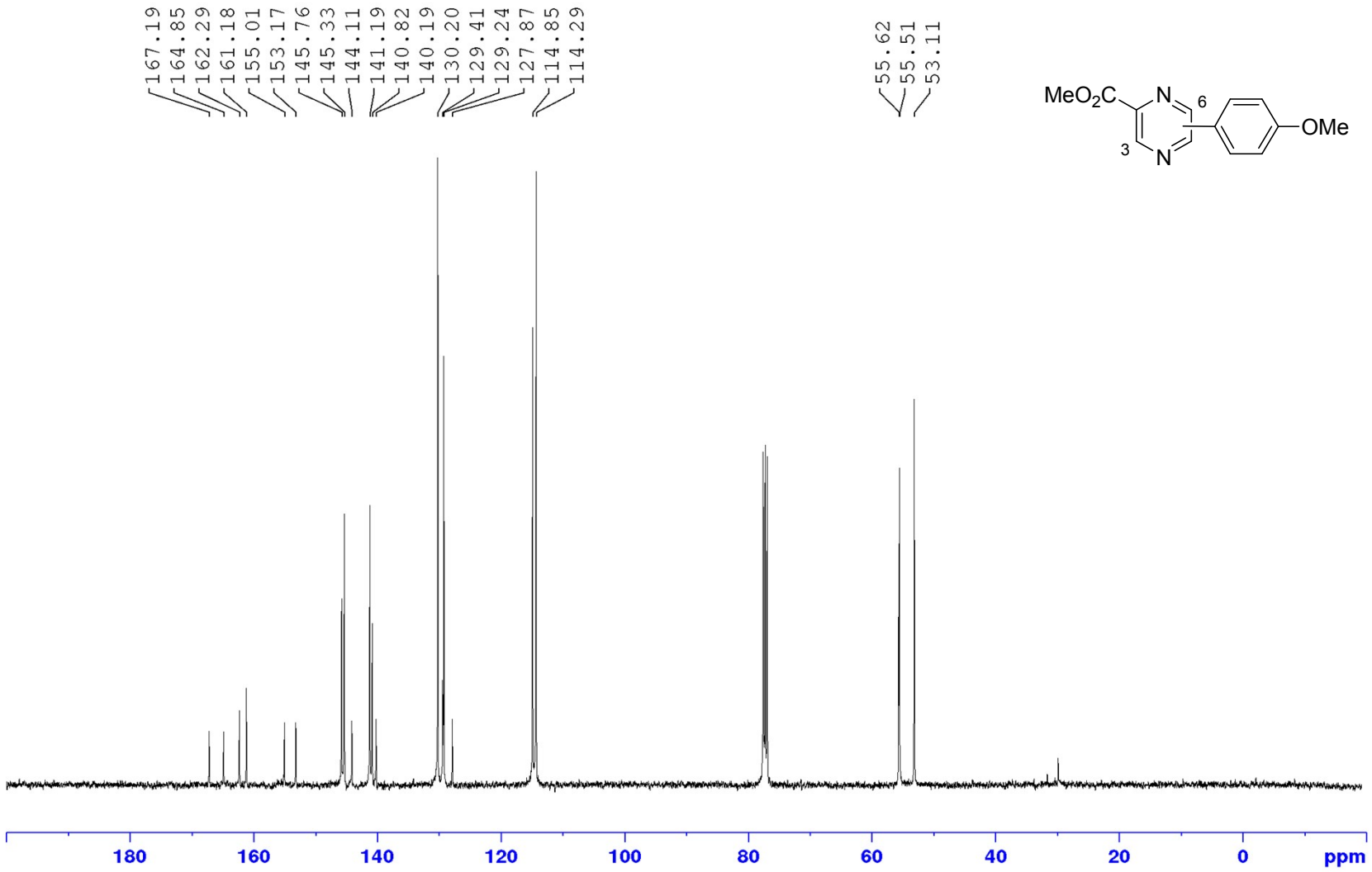
3619.99
3479.86
3477.52
3404.64
3402.32
3230.48
3221.58
3037.87
3029.05
2815.43
2806.53
2796.96
2788.15
MeO2C
N
6
3
N
OMe
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm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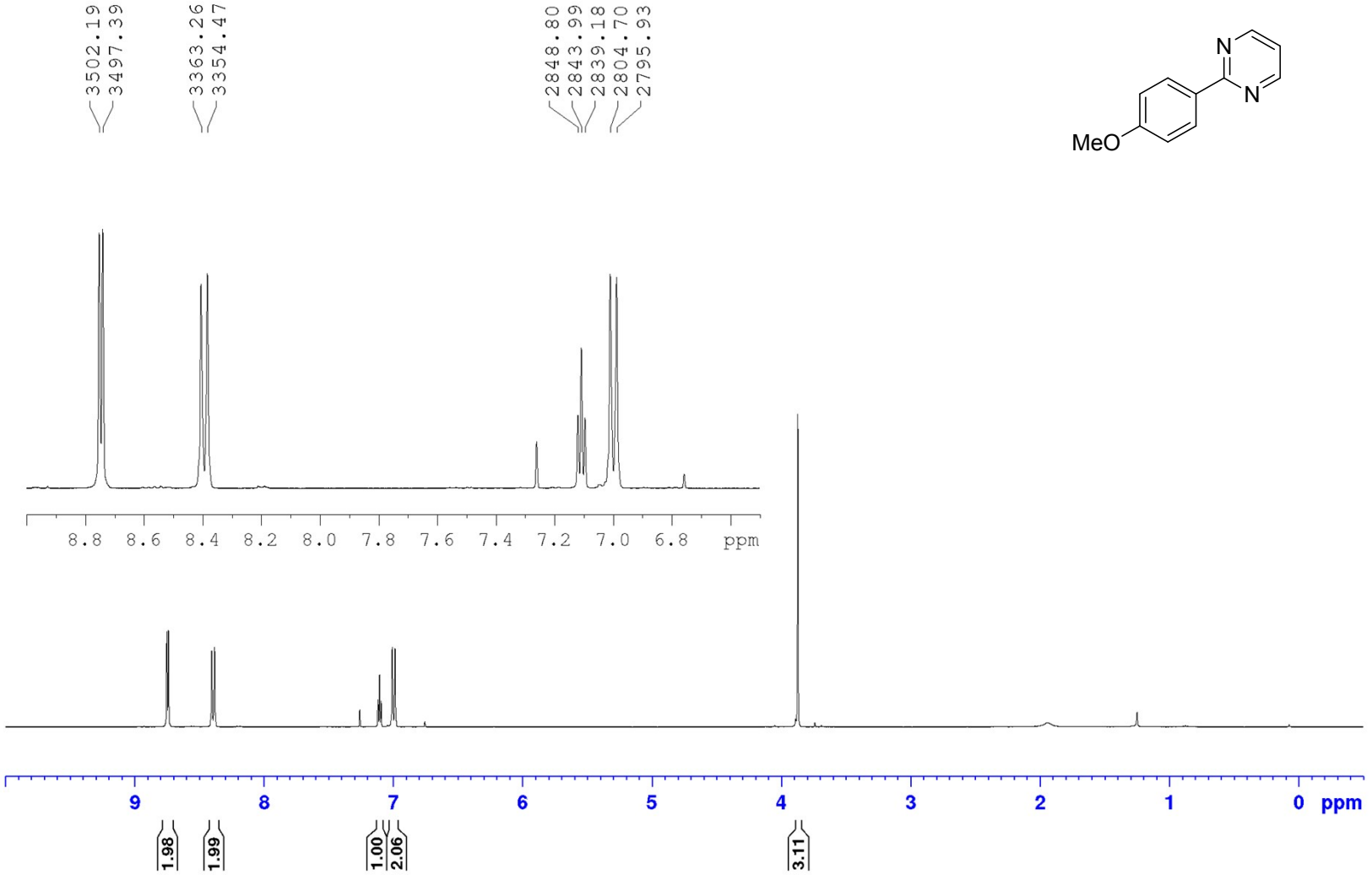
164.85
162.29
161.18
155.01
153.17
145.76
145.33
144.11
141.19
140.82
140.19
130.20
129.41
129.24
127.87
114.85
114.29
55.62
55.51
53.11
MeO2C
N
6
3
N
OMe
180
160
140
120
100
80
60
40
20
0
ppm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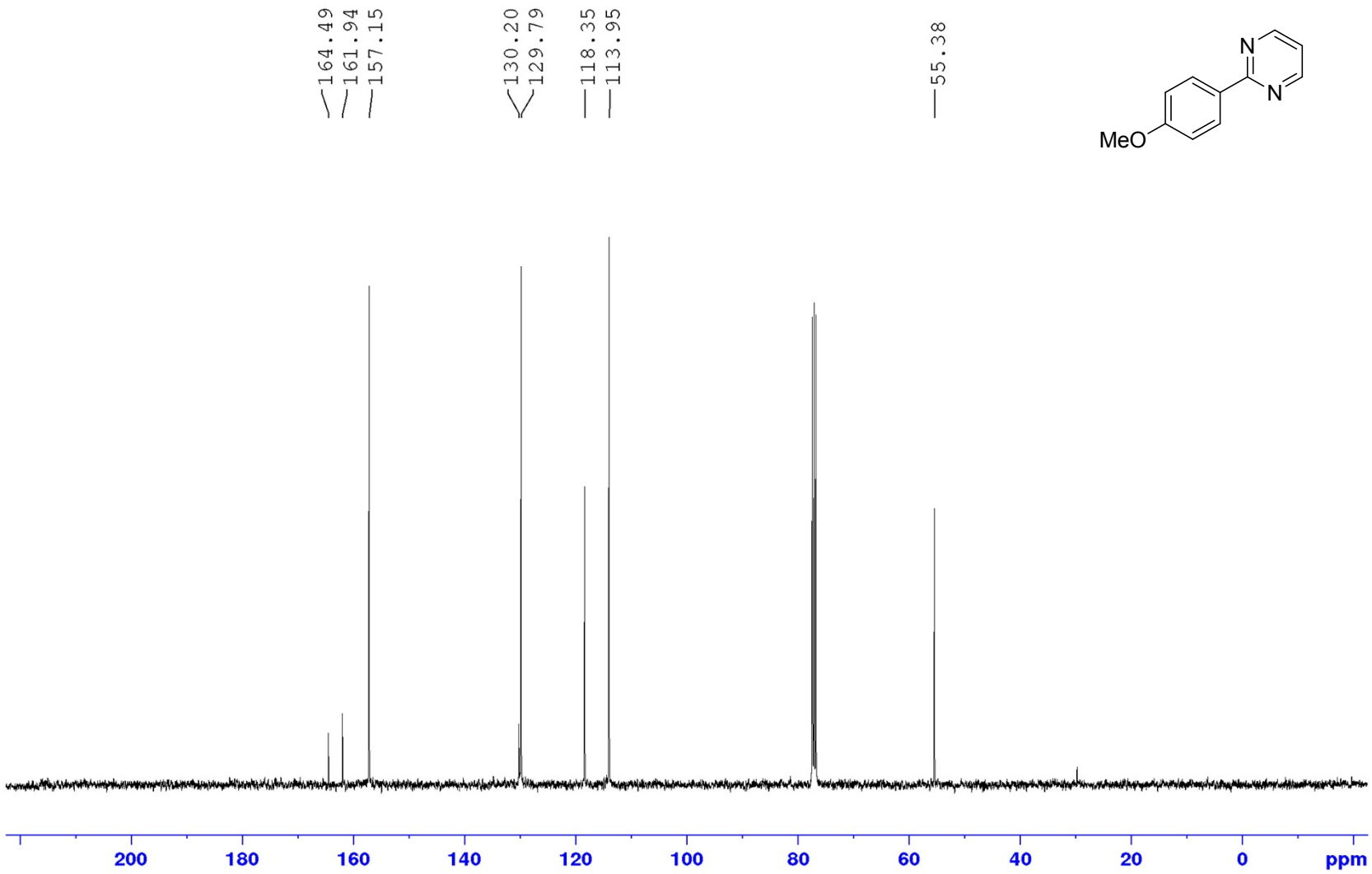
3363.26
3354.47
2848.80
2843.99
2839.18
2804.70
2795.93
N
N
MeO
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.98
1.99
1.00
2.06
3.11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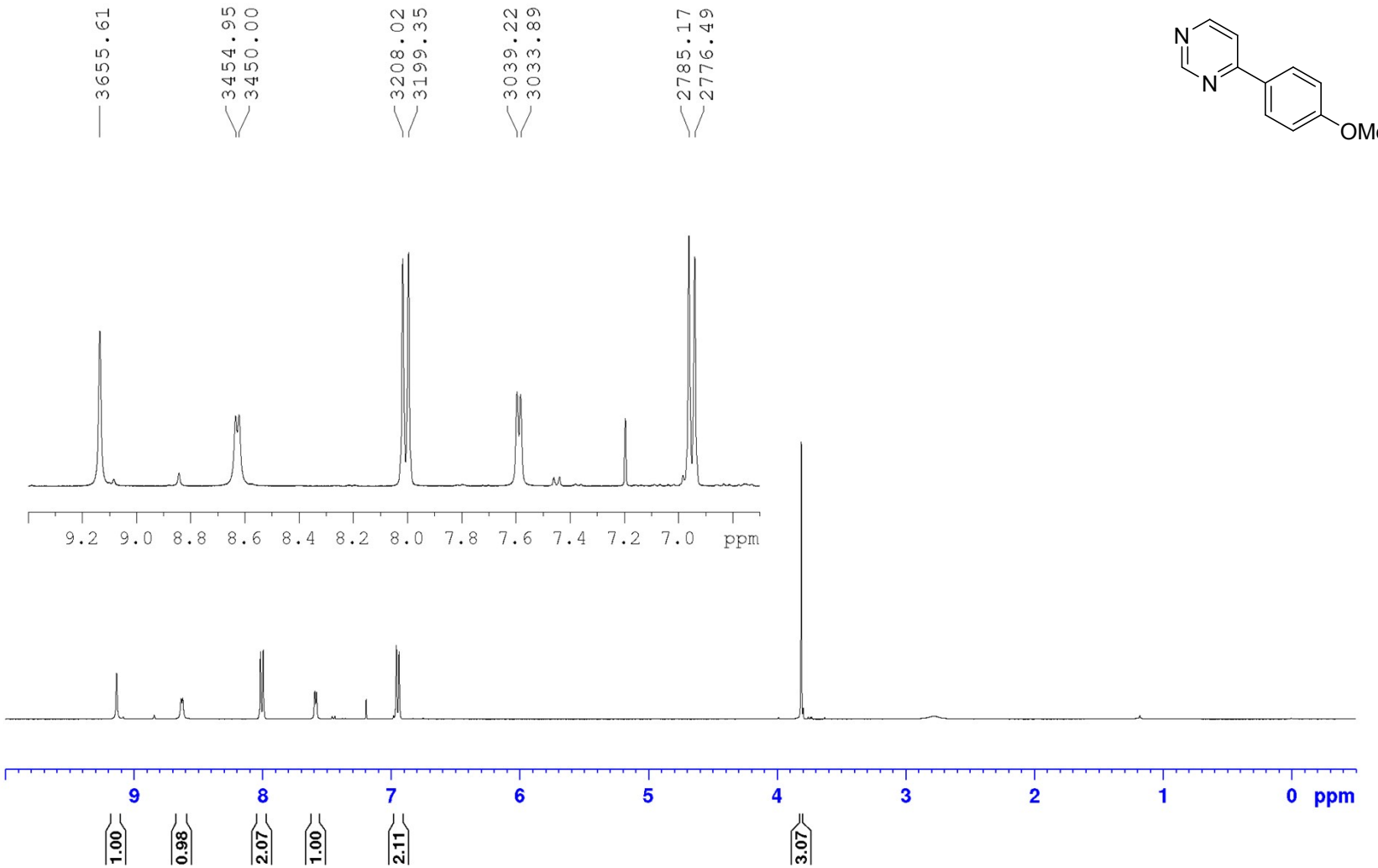
161.94
157.15
130.20
129.79
118.35
113.95
55.38
N
N
MeO
200
180
160
140
120
100
80
60
40
20
0
ppm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3450.00
3208.02
3199.35
3039.22
3033.89
2785.17
2776.49
N
N
OMe
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 ppm
9 8 7 6 5 4 3 2 1 0 ppm
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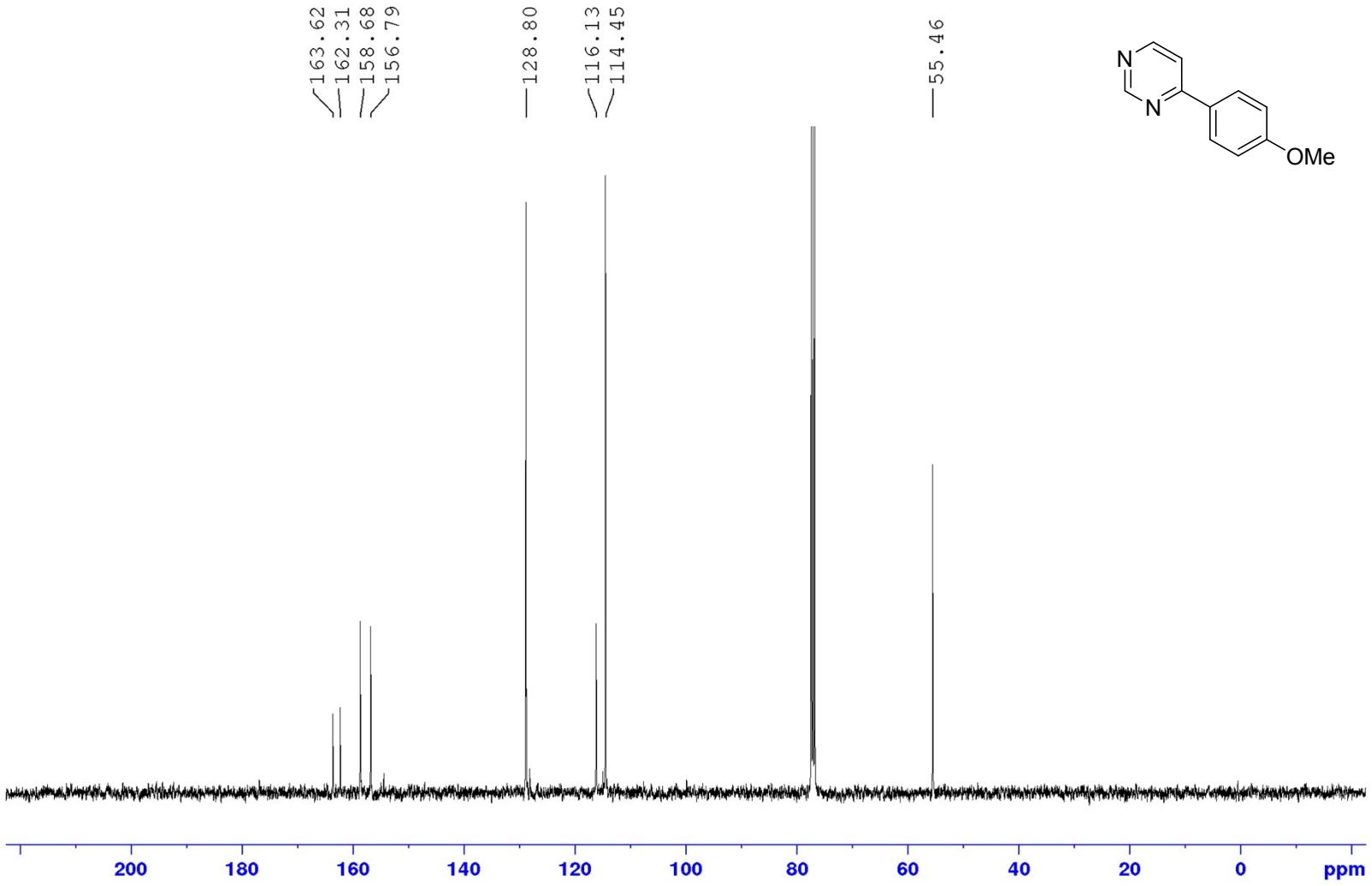
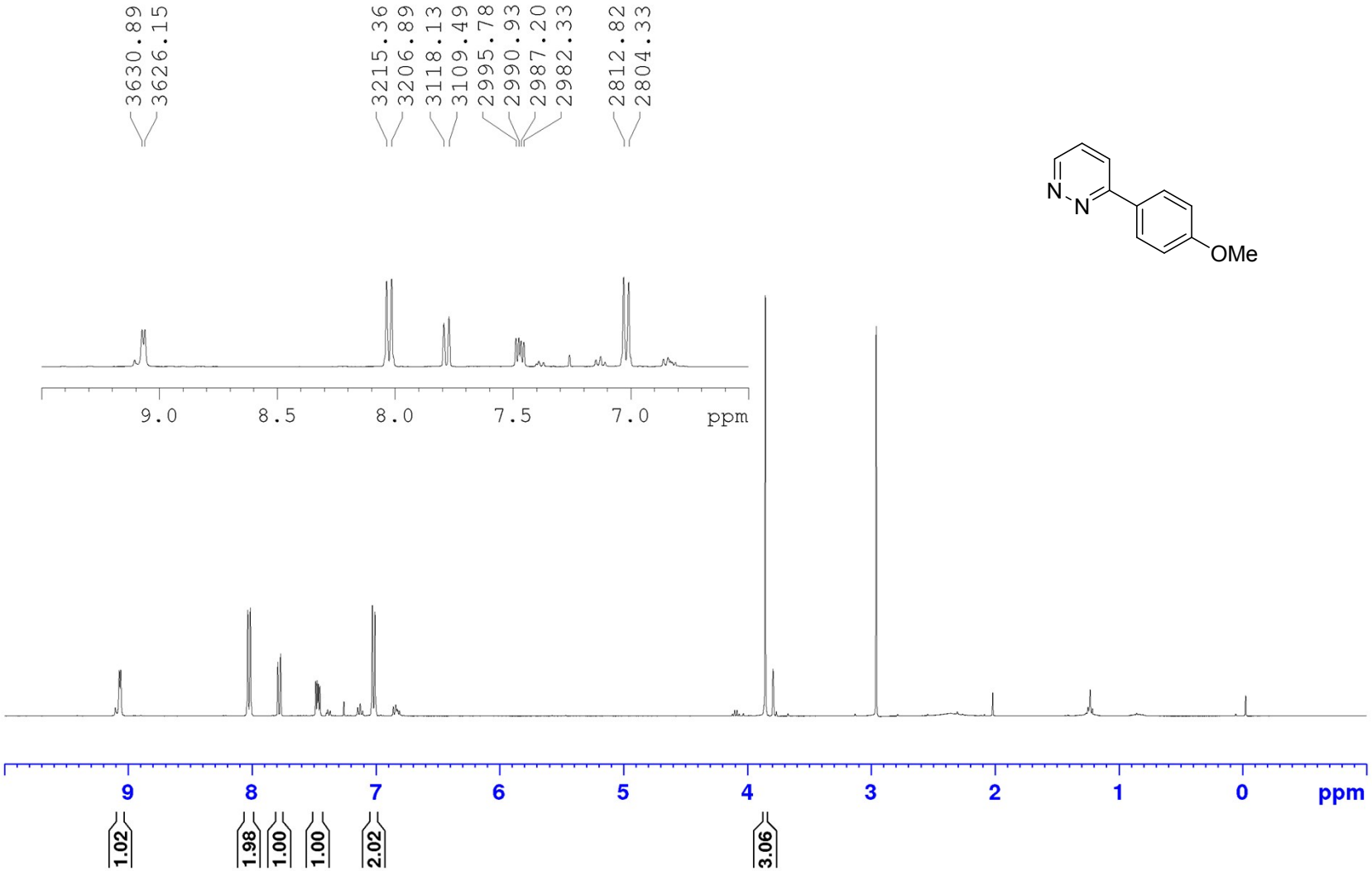
0.98
2.07
1.00
2.11
3.07


163.62
162.31
158.68
156.79
128.80
116.13
114.45
55.46
N
N
OMe
200
180
160
140
120
100
80
60
40
20
0
ppm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3626.15
3215.36
3206.89
3118.13
3109.49
2995.78
2990.93
2987.20
2982.33
2812.82
2804.33
N
N
OMe
9.0
8.5
8.0
7.5
7.0
ppm
9
8
7
6
5
4
3
2
1
0
ppm
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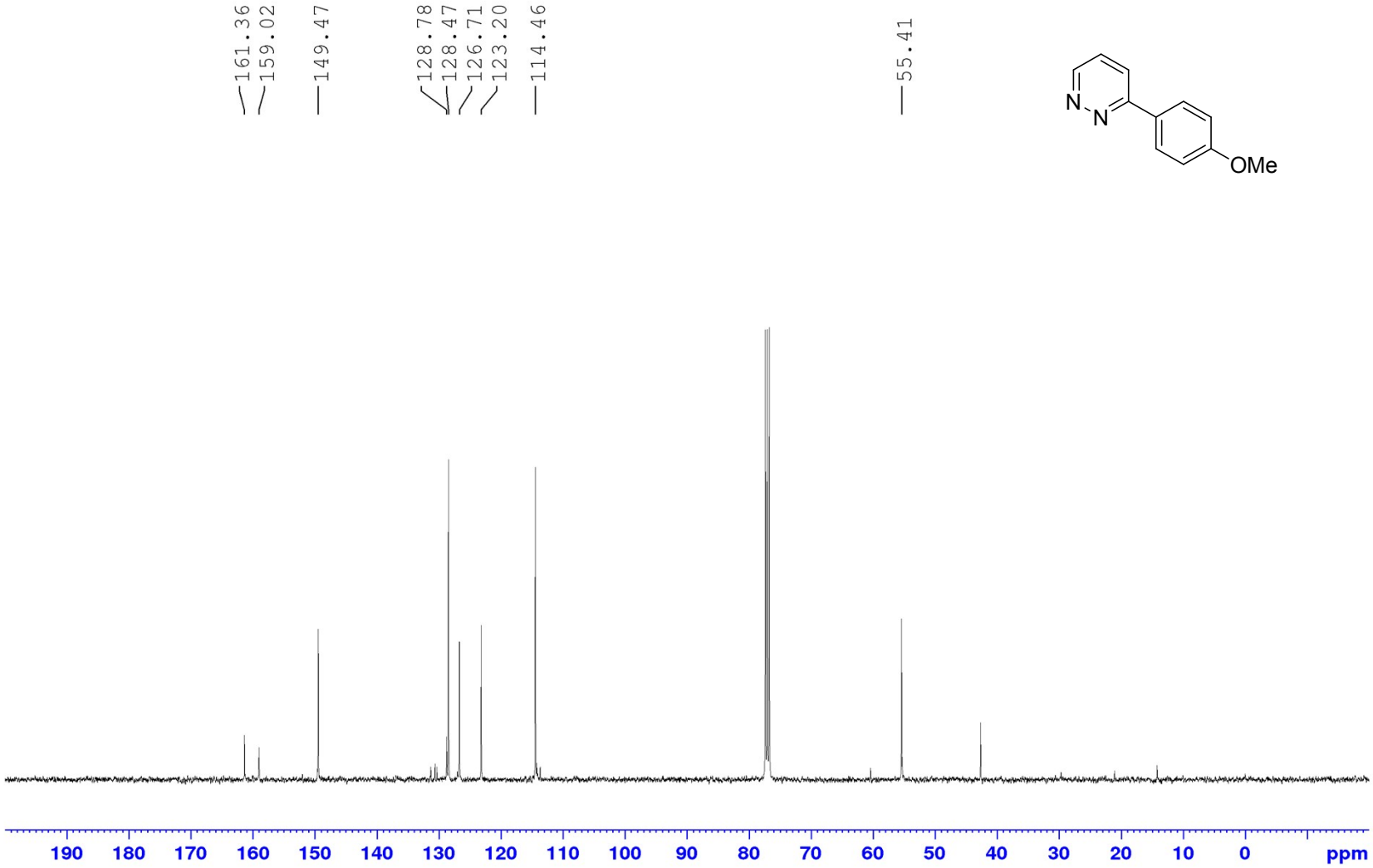
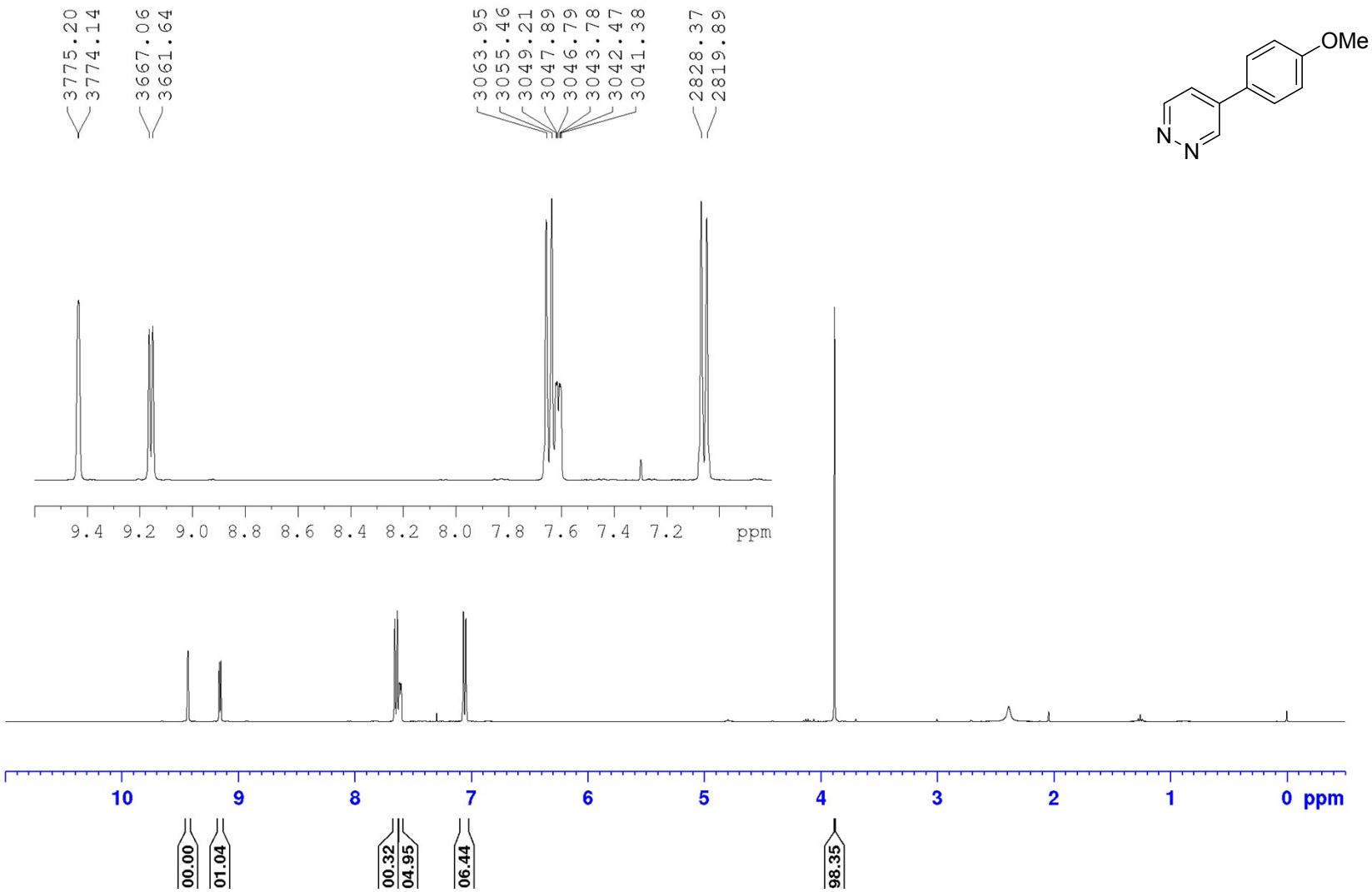
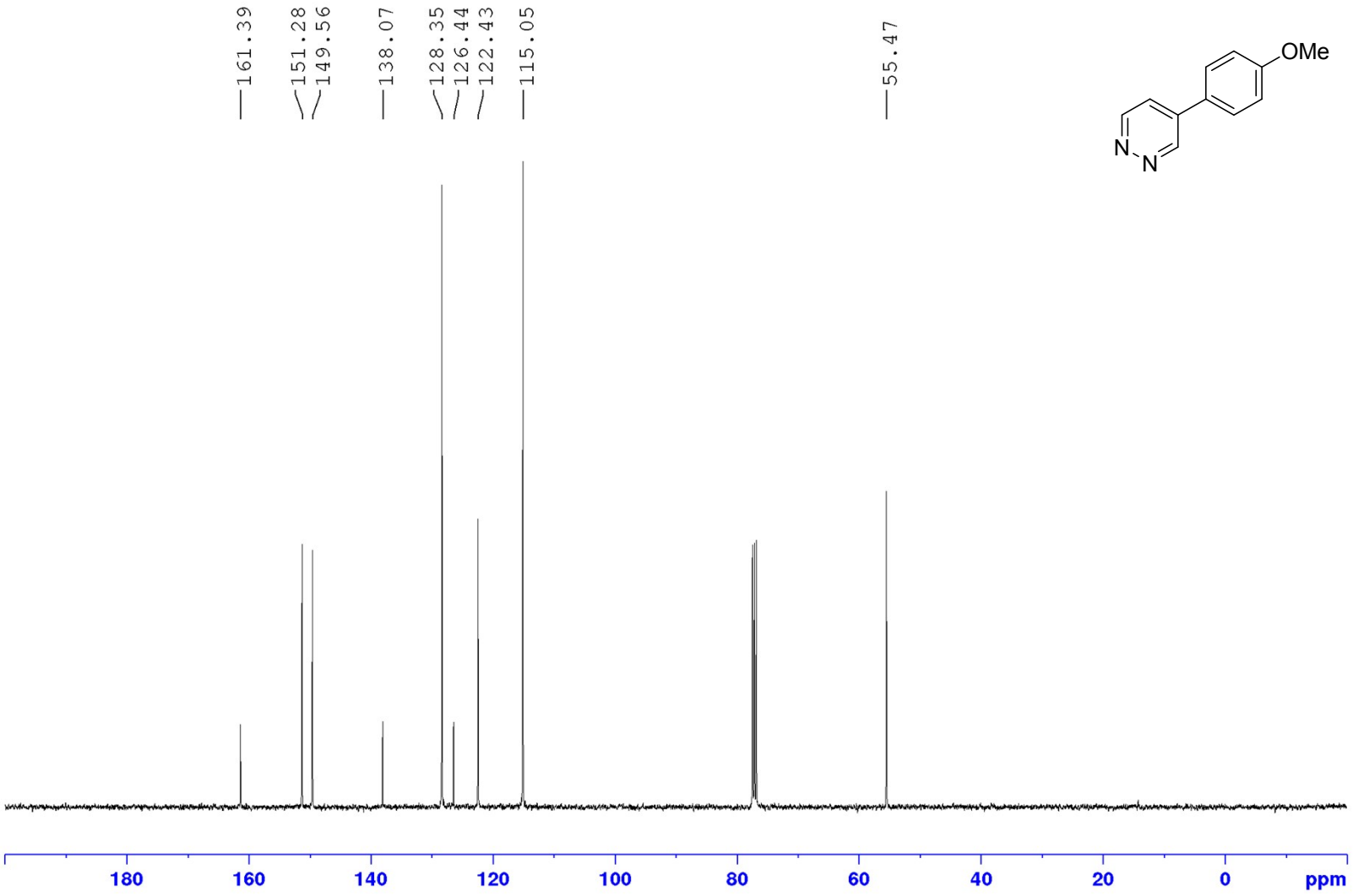
1.98
1.00
1.00
2.02
3.06


161.36
159.02
149.47
128.78
128.47
126.71
123.20
114.46
55.41
N
N
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3775.20
3774.14
3667.06
3661.64
3063.95
3055.46
3049.21
3047.89
3046.79
3043.78
3042.47
3041.38
2828.37
2819.89
OMe
N
N
9.4 9.2 9.0 8.8 8.6 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
00.00
01.04
00.32
04.95
06.44
98.35


161.39
151.28
149.56
138.07
128.35
126.44
122.43
115.05
55.47
OMe
N
N
180
160
140
120
100
80
60
40
20
0
ppm