Supplementary Information

Double Carbonylation of Aryl Iodides with Amines under an Atmospheric Pressure of Carbon Monoxide Using Sulfur-Modified Au-Supported Palladium

Nozomi Saito,[a,c]* Takahisa Taniguchi,[a] Naoyuki Hoshiya,[b,d] Satoshi Shuto,[b] Mitsuhiro Arisawa,[b,c,e]* Yoshihiro Sato[a,c]*

[a] Laboratory of Fine Synthetic Chemistry, Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan

[b] Laboratory of Organic Chemistry for Drug Development, Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan

[c] ACT-C, Japan Science and Technology Agency (JST), Sapporo 060-0812, Japan

[d] Present address: Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607-8412, Japan

[e] Present address: Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-oka, Suita, Osaka 565-0862, Japan

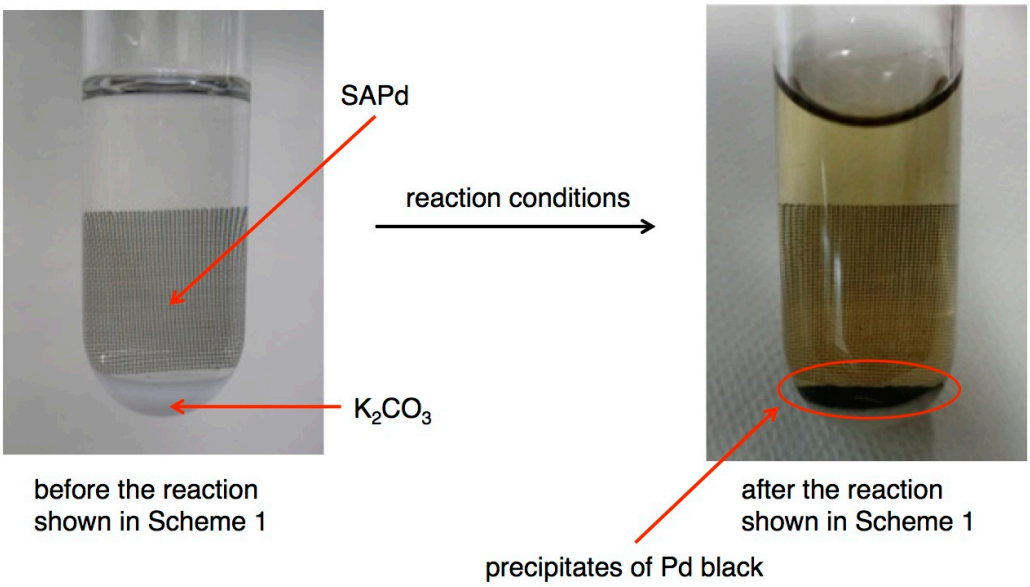
General Information

All manipulations were performed under an argon atmosphere unless stated otherwise. Solvents were purified under argon using The Ultimate Solvent System (Glass Counter Inc.) (CH_3CN, DMF, THF, Toluene). All other solvents and reagents were purified when necessary by standard procedures. Column chromatography was performed on silica gel 60 N (spherical, neutral; Kanto Kagaku, 45-50 μm) with the indicated solvent as eluent. TLC and PTLC were performed on Silica gel 60 PF_{254} (Merck). IR spectra were obtained on a JASCO FT/IR 460Plus spectrometer. ^1H NMR spectroscopy was recorded on JEOL ECA500 (500 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent as the internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectroscopy was recorded on JEOL ECA500 (125 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent as the internal standard ($CDCl_3$: δ = 77.00 ppm). Mass spectra were obtained on JEOL JMS-T100LP and JMS-T100GCV and JEOL JMS-FAB mate mass spectrometer, and Thermo Scientific Exactive mass spectrometer. GC was performed using a gas chromatograph Shimadzu GC-17A equipped with an Agilent J&W DB-5MS column and a FID detector. Sulfur-Modified Au-Supported Pd (SAPd) Material was prepared according to the literature.[1]

[1] M. Al-Amin, S. Arai, N. Hoshiya, T. Honma, Y. Tamenori, T. Sato, M. Yokoyama, A. Ishii, M. Takeuchi, T.Maruko, S. Shuto, M. Arisawa, *J. Org. Chem.* **2013**, *78*, 7575-7581.

Experimental Procedure for Double Carbonylation Using SAPd Shown in Scheme 1

A flame-dried test tube was charged with **1a** (117.8 mg, 0.503 mmol), K_2CO_3 (138.7 mg, 1.00 mmol), bibenzyl (48.9 mg, 0.268 mmol, as an internal standard) and degassed DMF (3 mL). To this were added a sheet of SAPd and **2a** (130.0 μL, 1.49 mmol), and the test tube was immersed in a liquid nitrogen bath. After the mixture had been frozen, the flask was evacuated to 0.05 mmHg. The flask was backfilled with CO in a plastic balloon and the frozen mixture was thawed at room temperature. Then, the resulting reaction mixture was heated at 80 °C for 24 hours and analyzed by GC with an internal standard (bibenzyl). GC Yield (**3aa**: 40%, **4aa**: 9%, **1a**: 47%). After the reaction, the immobilized Pd NPs seemed to come off the Au-mesh, and the precipitation of Pd-black was observed in the reaction mixture as following pictures.



Typical Procedure for Double Carbonylation Using SAPd (Scheme 2). A mixture of **1a** (117.0 mg, 0.500 mmol), K_2CO_3 (137.6 mg, 1.00 mmol), bibenzyl (43.5 mg, 0.239 mmol, internal standard for GC analysis) and a sheet of SAPd in DMF (3 mL) was heated at 80 °C for 2 hours under an argon atmosphere without stirring (1 atm). After removal of SAPd from the reaction vessel, **2a** (130.0 μL, 1.49 mmol) and a stirring bar were added to the vessel. The vessel was immersed in a liquid nitrogen bath. After the mixture had been frozen, the flask was evacuated to 0.05 mmHg. The flask was backfilled with CO in a plastic balloon and the frozen mixture was thawed at room temperature. Then, the resulting reaction mixture was stirred at 80 °C for 24 hours. To the mixture was added 10% HCl at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 1/1~1/2) to give **3aa** (106.0 mg, 85%) as a colorless solid and **4aa** (11.7 mg, 11%) as a yellow oil, respectively. ^{1}H and ^{13}C NMR data of 1-(4-Methoxyphenyl)-2-morpholinoethane-1,2-dione (**3aa**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 6.99-6.97 (m, 2H), 3.89 (s, 3H), 3.78 (m, 4H), 3.65 (t, J = 4.9 Hz, 2H), 3.38 (t, J = 4.9 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 189.8, 165.8, 165.0, 132.1, 126.1, 114.4, 66.8, 66.7, 55.7, 46.3, 41.5. These data were identical to those reported previously.[2] ^{1}H and ^{13}C NMR data of *N*-(4-Methoxybenzoyl)morpholine (**4aa**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H),

[2] J. Liu, R. Zhang, S. Wang, W. Sun, C. Xia, *Org. Lett.* **2009**, *11*. 1321-1324.

6.91-6.89 (m, 2H), 3.81 (s, 3H), 3.85-3.33 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 160.8, 129.2, 127.3, 113.7, 66.9, 55.3, 48.2 (br), 43.0 (br). These data were identical to those reported previously.[3]

1-(4-Methoxyphenyl)-2-pyrrolidin-1-ylethane-1,2-dione (3ab) and *N*-(4-Methoxybenzoyl)-pyrrolidine (4ab) (Table 1, run 1). A crude product, which was obtained from **1a** (117.4 mg, 0.502 mmol), K_2CO_3 (139.1 mg, 1.01 mmol), **2b** (123.0 μL, 1.50 mmol), and bibenzyl (47.3 mg, 0.260 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3ab** (95.7 mg, 82%) as a colorless solid and **4ab** (10.4 mg, 10%) as a colorless solid, respectively. ^{1}H and ^{13}C NMR data of **3ab**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 6.93-6.91 (m, 2H), 3.83 (s, 3H), 3.59 (t, *J* = 6.7 Hz, 2H), 3.36 (t, *J* = 6.7 Hz, 2H), 1.93-1.85 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 165.2, 164.6, 132.2, 125.8, 114.1, 55.5, 46.5, 45.0, 25.8, 23.9. These data were identical to those reported previously.[4] ^{1}H and ^{13}C-NMR data of **4ab**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 6.90-6.88 (m, 2H), 3.83 (s, 3H), 3.64-3.62 (m, 2H), 3.49-3.46 (m, 2H), 1.90-1.85 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 160.7, 129.4, 129.1, 113.4, 55.3, 49.8, 46.3, 26.5, 24.4. These data were identical to those reported previously.[5]

1-(4-Methoxyphenyl)-2-piperidin-1-ylethane-1,2-dione (3ac) and *N*-(4-Methoxybenzoyl)-piperidine (4ac) (Table 1, run 2). A crude product, which was obtained from **1a** (117.8 mg, 0.503 mmol), K_2CO_3 (137.6 mg, 0.996 mmol), bibenzyl (50.8 mg, 0.279 mmol, internal standard for GC analysis), and **2c** (150.0 μL, 1.52 mmol) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3ac** (117.3 mg, 94%) as a yellow oil and **4ac** (7.0 mg, 6%) as a yellow oil, respectively. ^{1}H and ^{13}C NMR data of **3ac**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.86 (m 2H), 7.00-6.93 (m, 2H), 3.85 (s, 3H), 3.67-3.64 (m, 2H), 3.26-3.24 (m, 2H), 1.66-1.64 (m, 4H), 1.51-1.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 165.7, 164.7, 131.9, 126.2, 114.2, 55.5, 46.9, 41.9, 26.1, 25.3, 24.3. These data were identical to those reported previously.[6] ^{1}H and ^{13}C NMR data of **4ac**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.85-3.3.21 (br, 4H), 1.85-1.40 (br, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 160.5, 128.8, 128.6, 113.6, 55.3, 49.0 (br), 43.4 (br), 26.4 (br), 25.7 (br), 24.6. These data were identical to those reported previously.[7]

1-(4-Methoxyphenyl)-2-(4-methylpiperazin-1-yl)ethane-1,2-dione (3ad) and 1-(4-Methoxybenzoyl)-4-methylpiperazine (4ad) (Table 1, run 3). A crude product, which was obtained from **1a** (119.9 mg, 0.512 mmol), K_2CO_3 (138.4 mg, 1.00 mmol)、**2d** (166.0 μL, 1.50 mmol), and bibenzyl (46.8 mg, 0.257 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (AcOEt/MeOH = 100/1~1/1) to give **3ad** (115.4 mg, 86%) as a yellow oil and **4ad** (13.8 mg, 11%) as a yellow oil, respectively. Spectral data of **3ad**: IR (neat) 1637, 1599 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 6.95-6.93 (m, 2H), 3.85 (s, 3H), 3.85-3.82 (m, 2H), 3.44-3.42 (m, 2H), 2.64 (t, *J* = 5.2 Hz, 2H), 2.52 (t, *J* = 5.2 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 165.6, 164.9, 132.0, 125.8, 114.3, 55.6, 54.4, 54.0, 45.4, 45.0, 40.3; EI-LRMS *m/z* 262 (M^+), 135; EI-HRMS calcd for

---

[3] J. R. Martinelli, D. A. Watson, D. M. M. Freckmann, T. E. Barder, S. L. Buchwald, *J. Org. Chem.* **2008**, *73*, 7102-7107.

[4] M. Iizuka, Y. Kondo, *Chem. Commun.* **2006**, 1739-1741.

[5] K. Ekoue-Kovi, C. Wolf, *Org. Lett.* **2007**, *9*, 3429-3432.

[6] J. Zhang, Y. Wei, S. Lin, F. Liang, P. Liu, *Org. Biomol. Chem.* **2012**, *10*, 9237-9242.

[7] J. Li, F. Xu, Y. Zhang, Q. Shen, *J. Org. Chem.* **2009**, *74*, 2575-2577.

$C_{14}H_{18}O_3N_2$ 262.1317, found 262.1326. Spectral data of **4ad**: IR (neat): 1626, 1610; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.63-3.47 (br, 4H), 2.48-2.35 (br, 4H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 160.9, 129.1, 128.2, 113.8, 55.4, 55.3, 55.1, 46.0; EI-LRMS *m/z* 234 (M^+), 135; EI-HRMS calcd for $C_{13}H_{18}N_2O_2$ 234.13683, found 234.13675.

1-(4-Methoxyphenyl)-2-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)ethane-1,2-dione (3ae) and 1-(4-Methoxybenzoyl)-4-piperidone ethylene ketal (4ae) (Table 1, run 4). A crude product, which was obtained from **1a** (118.5 mg, 0.506 mmol), K_2CO_3 (139.7 mg, 1.01 mmol), **2e** (166.0 μL, 1.50 mmol), and bibenzyl (49.6 mg, 0.272 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3ae** (134.9 mg, 87%) as a colorless solid and **4ae** (12.6 mg, 9%) as a colorless oil, respectively. Spectral data of **3ae**: mp 127 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1671, 1639, 1600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.99-3.92 (m, 4H), 3.86 (s, 3H), 3.82 (t, *J* = 5.7 Hz, 2H), 3.40 (t, *J* = 5.7 Hz, 2H), 1.79 (t, *J* = 5.7 Hz, 2H), 1.66 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 165.7, 164.8, 132.0, 126.1, 114.3, 106.6, 64.5, 55.6, 44.0, 39.2, 35.3, 34.6; EI-LRMS *m/z* 305 (M^+), 135; EI-HRMS calcd for $C_{16}H_{19}NO_5$ 305.1263, found 305.1249. ^{1}H and ^{13}C NMR data of **4ae**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.32 (m, 2H), 6.86-6.84 (m, 2H), 3.92 (s, 4H), 3.76 (s, 3H), 3.80-3.40 (br, 4H), 1.83-1.42 (br, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 160.5, 128.7, 127.9, 113.5, 106.8, 64.3, 55.1, 45.7 (br), 40.3 (br), 35.3 (br), 34.9 (br) These data were identical to those reported previously.[8]

1-[3,4-Dihydroisoquinolin-2(1*H*)-yl]-2-(4-methoxyphenyl)ethane-1,2-dione (3af) (Table 1, run 5). A crude product, which was **1a** (117.4 mg, 0.502 mmol), K_2CO_3 (138.5 mg, 1.00 mmol), **2f** (190.0 μL, 1.49 mmol), and bibenzyl (47.6 mg, 0.261 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 3/2~0/1) to give **3af** (150.9 mg, quant) as a colorless solid. ^{1}H and ^{13}C NMR data of **3af**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2H), 7.25-6.93 (m, 6H), 4.89 (s, 1.3H), 4.53 (s, 0.7H), 3.97 (t, *J* = 6.0 Hz, 0.7H), 3.88 (s, 1.9H), 3.86 (s, 1.1H), 3.61 (t, *J* = 6.0 Hz, 1.3H), 2.99 (t, *J* = 6.0 Hz, 0.7H), 2.85 (t, *J* = 6.0 Hz, 1.3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 190.0, 166.4, 166.0, 164.9, 164.8, 133.4, 132.1, 131.8, 128.9, 128.7, 127.1, 126.7, 126.6, 126.5, 126.1, 126.0, 114.3, 55.6, 47.3, 43.4, 43.3, 39.2, 29.2, 28.2. These data were identical to those reported previously.[9]

***N*-Butyl-4-methoxyphenylglyoxamide (3ag) and *N*-Butyl-4-methoxyphenylbenzamide (4ag) (Table 1, run 6).** A crude product, which was obtained from **1a** (117.5 mg, 0.502 mmol), K_2CO_3 (139.3 mg, 1.01 mmol), **2g** (148.0 μL, 1.50 mmol), and bibenyl (47.1 mg, 0.258 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 6/1) to give **3ag** (87.8 mg, 74%) as a colorless solid and **4ag** (23.4 mg, 22%) as a yellow oil, respectively. ^{1}H and ^{13}C NMR data of **3ag**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.8 Hz, 2H), 7.12 (brs, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.40-3.36 (m, 2H), 1.62-1.56 (m, 2H), 1.44-1.37 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.8, 164.6, 162.3, 133.8, 126.3, 113.7, 55.5, 39.0, 31.3, 20.0, 13.6. These data were identical to those reported previously[4] ^{1}H and ^{13}C NMR data of **4ag**: ^{1}H NMR (500 MHz,

[8] D. L. Boger, M. D. Mullican, *J. Org. Chem.* **1984**, *49*, 4033-4044.

[9] M. Genelot, N. Villandier, A. Bendjeriou, P. Jaithong, L. Djakovitch, V. Dufaud, *Catal. Sci. Technol.* **2012**, *2*, 1886-1893.

$CDCl_3$) δ 7.73-7.71 (m, 2H), 6.92-6.91 (m, 2H), 6.02 (brs, 1H), 3.85 (s, 3H), 3.46-3.42 (m, 2H), 1.62-1.56 (m, 2H), 1.45-1.37 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 162.0, 128.6, 127.1, 113.7, 55.4, 39.7, 31.8, 20.2, 13.8. These data were identical to those reported previously.[10]

2-(4-Methoxyphenyl)-2-oxo-*N*,*N*-dipropylacetamide (3ah) and 4-Methoxy-*N*,*N*-dipropylbenzamide (4ah) (Table 1, run 7). A crude product, which was obtained from **1a** (118.9 mg, 0.508 mmol), K_2CO_3 (139.7 mg, 1.01 mmol), **2h** (205.0 μL, 1.50 mmol), and bibenzyl (48.0 mg, 0.263 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 6/1) to give **3ah** (99.8 mg, 75%) as a yellow oil and **4ah** (12.6 mg, 20%) as a yellow oil, respectively. Spectral data of **3ah**: IR (neat) 1671, 1637, 1599 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.44 (t, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.7 Hz, 2H), 1.74-1.67 (m, 2H), 1.61-1.53 (m, 2H) 0.99 (t, *J* = 7.5 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 167.5, 164.6, 132.0, 126.4, 114.2, 55.6, 49.3, 45.7, 21.8, 20.6, 11.4, 11.0; EI-LRMS m/z 263 (M^+), 135; EI-HRMS calcd. for $C_{15}H_{21}NO_3$ 263.15214, found 263.15184. Spectral data of **4ah**: IR data; 1630 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 6.90-6.87 (m, 2H), 3.82 (s, 3H), 3.59-3.30 (br, 4H), 1.74-1.43 (br, 4H), 1.07-0.59 (br, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 160.1, 129.6, 128.3, 113.6, 55.3, 50.9 (br), 46.5 (br), 21.9 (br), 20.6 (br), 11.2 (br); EI-LRMS *m/z* 235 (M^+), 135; EI-HRMS calcd. for $C_{14}H_{20}NO_2$ 234.14940, found 234.14945

***N*-Benzyl-2-(4-methoxyphenyl)-*N*-methyl-2-oxoacetamide (3ai) (Table 1, run 8).** A crude product, which was obtained from **1a** (116.3 mg, 0.497 mmol), K_2CO_3 (139.2 mg, 1.01 mmol), **2i** (195.0 μL, 1.51 mmol), and bibenzyl (45.6 mg, 0.250 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1~1/2) followed by preparative thin-layer chromatography on silica gel (hexane/AcOEt = 3/1) to give **3ai** (134.9 mg, 87%) as an colorless oil. Spectral data of **3ai**: IR (neat) 1668, 1643, 1599 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.40-7.25 (m, 5H) 6.99-6.97 (m, 2H), 4.72 (s, 1.1H), 4.39 (s, 0.9H), 3.88 (m, 3H), 2.97 (s, 1.4H), 2.84 (s, 1.6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 167.6, 167.4, 164.8, 135.9, 135.0, 132.2, 132.1, 128.8, 128.3, 128.1, 127.8, 126.8, 126.3, 126.1, 114.3, 55.6, 53.5, 49.7, 34.5, 31.3; EI-LRMS *m/z* 283 (M^+), 135; EI-HRMS calcd. for $C_{17}H_{17}NO_3$ 283.12084, found 283.12021.

***N*-(2-*tert*-Butyldimethylsiloxyethyl)-2-(4-methoxyphenyl)-*N*-methyl-2-oxoacetamide (3aj) (Table 1, run 9).** A crude product, which was obtained from **1a** (118.7 mg, 0.507 mmol), K_2CO_3 (141.4 mg, 1.02 mmol), **2j** (342 μL, 1.50 mmol), and bibenzyl (45.8 mg, 0.251mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1~1/1) to give **3aj** (124.3 mg, 70%) as a colorless oil. Spectral data of **3aj**: IR (neat) 1672, 1646, 1600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.89 (m, 2H), 6.96-6.93 (m, 2H), 3.90 (t, *J* = 5.3 Hz, 1H), 3.87 (s, 3H), 3.70 (t, *J* = 5.7 Hz, 1H), 3.63 (t, *J* = 5.3 Hz, 1H), 3.34 (t, *J* = 5.7 Hz, 1H), 3.15-3.02 (m, 3H), 0.90-0.83 (m, 9H), 0.09--0.03 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 167.7, 167.5, 164.7, 132.2, 132.1, 126.3, 126.1, 114.2, 61.6, 61.1, 55.6, 51.8, 49.3, 37.0, 33.4, 25.8, 25.8, 18.1; EI-LRMS: *m/z* 351 (M^+), 336, 294, 216, 135; EI-HRMS calcd. for $C_{18}H_{29}NO_4Si$ 354.18658, found 351.18670.

4-Methoxy-*N*-phenylbenzamide (4ak) (Table 1, run 10). A crude product was obtained from **1a**

[10] P. Nordeman, L. R. Odell, M. Larhed, *J. Org. Chem.* **2012**, *77*, 11393-11398.

(117.0 mg, 0.500 mmol), K_2CO_3 (138.9 mg, 1.00 mmol), **2k** (140 μL, 1.54 mmol), and bibenzyl (48.8 mg, 0.268 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours. The yield of **4ak** was determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene (δ = 6.1 ppm in $CDCl_3$, 3H) as an internal standard (55%). Analytically pure samples were obtained by recycle preparative thin-layer chromatography on silica gel (hexane/AcOEt = 5/1).^{1}H and ^{13}C NMR data of **4ak**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.9 Hz, 2H), 7.70 (brs, 1H), 7.63 (d, *J* = 7.4 Hz), 7.39-7.36 (m, 2H), 7.16-7.13 (m, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 152.4, 138.1, 129.0, 128.9, 127.1, 124.3, 120.1, 113.9, 55.5. These data were identical to those reported previously.[11]

1-(3-Methoxyphenyl)-2-morpholinoethane-1,2-dione (3ba) and *N*-(3-Methoxybenzoyl)-morpholine (4ba) (Table 2, run 1). A crude product, which was obtained from **1b** (117.2 mg, 0.502 mmol), K_2CO_3 (138.9 mg, 1.01 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (48.8 mg, 0.268 mmol) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/1) to give **3ba** (104.6 mg, 84%) as a colorless solid and**4ba** (15.6 mg, 14%) as a colorless oil, respectively. ^{1}H and ^{13}C NMR data of **3ba**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.40 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.17 (m, 1H), 3.83 (s, 3 H), 3.78-3.74 (br, 4H), 3.62 (t, *J* = 4.9 Hz, 2H), 3.34 (t, *J* = 4.87, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 165.3, 160.0, 134.2, 130.1, 122.7, 121.7, 112.6, 66.6, 66.5, 55.4, 46.1, 41.5. These data were identical to those reported previously.[12] ^{1}H and ^{13}C NMR data of **4ba**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 1H), 6.96-6.94 (m, 3H). 3.81 (s, 3H), 3.87-3.26 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 159.7, 136.6, 129.7, 119.1, 115.6, 112.5, 66.9, 55.4, 48.2 (br), 42.5 (br). These data were identical to those reported previously.[5]

1-(2-Methoxyphenyl)-2-morpholinoethane-1,2-dione (3ca) and *N*-(2-Methoxybenzoyl)-morpholine (4ca) (Table 2, run 2). A crude product, which was obtained from **1c** (118.1 mg, 0.502 mmol), K_2CO_3 (137.7 mg, 1.01 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (48.1 mg, 0.268 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1~1/2) to give an inseparable mixture of **3ca** and **4ca** (97.4 mg, **3ca**: 29%, **4ca**: 55%) as a yellow oil. Analytically pure samples were obtained by recycle preparative thin-layer chromatography on silica gel (hexane/AcOEt = 1/1). ^{1}H and ^{13}C NMR data of **3ca**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (ddd, *J* = 8.7, 8.2, 1.7 Hz, 1H), 7.09 (dd, *J* = 8.2, 7.9 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 3.79 (t, *J* = 4.6 Hz, 2H), 3.72-3.69 (m, 4H), 3.40 (t, *J* = 4.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 167.4, 160.1, 136.2, 131.1, 123.5, 121.5, 112.2, 66.5, 66.3, 56.2, 45.9, 41.4. These data were identical to those reported previously.[2] ^{1}H and ^{13}C NMR data of **4ca**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 1H), 7.24 (m, 1H), 7.00 (m, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 3.83 (s, 3H), 3.90-3.72 (m, 4H), 3.63-3.56 (m, 2H), 3.29-3.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.8, 155.2, 130.6, 128.0, 125.2, 121.0, 110.8, 66.9, 66.8, 55.5, 47.2, 42.1. These data were identical to those reported previously.[7]

1-(3,5-Dimethylphenyl)-2-morpholinoethane-1,2-dione (3da) and *N*-(3,5-Dimethylbenzoyl)-morpholine (4da) (Table 2, run 3). A crude product, which was obtained from **1d** (120.0 mg, 0.517 mmol), K_2CO_3 (140.9 mg, 1.02 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (51.8 mg,

[11] E. Racine, F. Monnier, J. P. Vors, M. Taillefer, *Org. Lett.* **2011**, *13*, 2818-2821.

[12] W. Wei, Y. Shao, H. Hu, F. Zhang, C. Zhang, Y. Xu, X. Wan, *J. Org. Chem.* **2012**, *77*, 7157-7165.

0.284 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3da** (97.2 mg, 76%) as a white solid and **4da** (7.9 mg, 7%) as a yellow amorphous solid, respectively. Spectral data of **3da**: mp 101 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1677, 1643 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.28 (s, 1H), 3.80-3.76 (m, 4H), 3.64 (t, *J* = 4.9 Hz, 2H), 3.35 (t, *J* = 4.9 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 165.7, 138.9, 136.7, 133.0, 127.3, 66.7, 66.6, 46.2, 41.5, 21.1; EI-LRMS *m/z* 247 (M^+), 133; EI-HRMS calcd. for $C_{14}H_{17}NO_3$ 247.12084, found 247.12042. ^1H and ^{13}C NMR data of **4da**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.99 (s, 2H), 4.01-3.24 (br, 8H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 138.3, 135.3, 131.3, 124.6, 66.9, 48.2, 42.5, 21.2. These data were identical to those reported previously.[3]

1-Morpholino-2-(3,4,5-trimethoxyphenyl)ethane-1,2-dione (3ea) and *N*-(3,4,5-Trimethoxybenzoyl)morpholine (4ea) (Table 2, run 4). A crude product, which was obtained from **1e** (146.9 mg, 0.496 mmol), K_2CO_3 (140.4 mg, 1.02 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (48.0 mg, 0.263 mmol) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/5) to give **3ea** (132.6 mg, 86%) as a colorless solid and **4ea** (4.8 mg, 4%) as a yellow oil, respectively. Spectral data of **3ea**: mp 133 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1673, 1644 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 3.75 (s, 4H), 3.63 (t, *J* = 4.9 Hz, 2H), 3.35 (t, *J* = 4.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 165.2, 153.3, 144.1, 127.9, 106.8, 66.7, 66.6, 60.9, 56.3, 46.2, 41.6; EI-LRMS *m/z* 309 (M^+), 195; EI-HRMS calcd. for $C_{15}H_{19}NO_6$ 309.12124, found 309.12109. ^1H NMR data of **4ea**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.61 (s, 2H), 3.86 (s, 6H), 3.84 (s, 3H), 3.85-3.47 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 153.3, 139.2, 130.6, 104.3, 66.9, 60.9, 56.2, 48.3 (br), 42.7 (br). These data were identical to those reported previously.[13]

1-Morpholino-2-phenylethane-1,2-dione (3fa) and *N*-Benzoylmorpholine (4fa) (Tbale 2, run 5). A crude product, which was obtained from **1f** (104.2 mg, 0.511 mmol), K_2CO_3 (141.3 mg, 1.02 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (46.6 mg, 0.256 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3fa** (77.7 mg, 69%) as a colorless solid and **4fa** (21.1 mg, 22%) as a yellow oil, respectively. ^1H and ^{13}C NMR data of **3fa**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.66 (m, 1H), 7.54-7.51 (m, 2H), 3.82-3.78 (m, 4H), 3.65 (t, *J* = 4.7 Hz, 2H), 3.38 (t, *J* = 4.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 165.2, 134.7, 132.7, 129.4, 128.9, 66.4, 46.0, 41.3. These data were identical to those reported previously.[2] ^1H and ^{13}C NMR data of **4fa**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.41 (m, 5H), 4.05-3.20 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 135.3, 129.9, 128.6, 127.1, 66.9, 48.2 (br), 42.5 (br). These data were identical to those reported previously.[7]

1-(4-Chlorophenyl)-2-morpholinoethane-1,2-dione (3ga) and *N*-(4-Chlorobenzoyl)morpholine (4ga) (Table 2, run 6). A crude product, which was obtained from **1g** (120.2 mg, 0.504 mmol), K_2CO_3 (138.8 mg, 1.00 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (48.0 mg, 0.263 mmol, internal standard for GC analysis), DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3ga** (82.7 mg, 0.326 mmol, 65%) as a colorless solid and **4ga** (30.6 mg, 0.136 mmol, 27%) as a colorless solid, respectively. ^1H and

[13] G. R. Pettit, M. P. Grealish, D. L. Herald, M. R. Boyd, E. Hamel, R. K. Pettit, *J. Med. Chem.* **2000**, *43*, 2731-2737.

^{13}C NMR data of **3ga**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.50-7.47 (m, 2H), 3.79-3.75 (m, 4H), 3.65-3.63 (m, 2H), 3.38-3.36 (m, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 189.6, 164.8, 141.5, 131.4, 131.0, 129.4, 66.7, 66.6, 46.2, 41.6. These data were identical to those reported previously.[2] ^{1}H and ^{13}C NMR data of **4ga**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 4.04-3.15 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 136.0, 133.6, 128.8, 128.6, 66.8, 48.2 (br), 42.6 (br). These data were identical to those reported previously.[14]

1-(4-Methoxycarbonylphenyl)-2-morpholinoethane-1,2-dione (3ha) and *N*-(4-Methoxycarbonylbenzoyl)morpholine (4ha) (Table 2, run 7). A crude product, which was obtained from **1h** (132.5 mg, 0.506 mmol), K_2CO_3 (140.8 mg, 1.02 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (47.2 mg, 0.259 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 1/1~1/2) to give **3ha** (63.9 mg, 46%) as a yellowish solid and **4ha** (53.5 mg, 42%) as a yellow solid, respectively. Spectral data of **3ha**: mp 139 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1724, 1685, 1646 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 2H), 3.95 (s, 3H), 3.79 (brs, 4H), 3.66 (t, *J* = 4.9 Hz, 2H), 3.38 (t, *J* = 4.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 165.8, 164.8, 136.1, 135.3, 130.1, 129.5, 66.7, 66.6, 52.6, 46.2, 41.7; EI-LRMS *m/z* 277 (M^+), 246, 163, 135; EI-HRMS calcd. for $C_{14}H_{15}NO_5$ 277.09502, found 277.09458. ^{1}H and ^{13}C NMR data of **4ha**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 3.88-3.21 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 166.2, 139.5, 131.3, 129.9, 127.0, 66.8, 52.3, 48.0, 42.5. These data were identical to those reported previously.[15]

1-(2,2-Dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-6-yl)-2-morpholinoethane-1,2-dione (3ia) and 2,2-Dimethyl-6-(morpholine-4-carbonyl)-4*H*-benzo[*d*][1,3]dioxin-4-one (4ia) (Table 2, run 8). A crude product, which was obtained from **1i** (154.4 mg, 0.507 mmol), K_2CO_3 (142.0 mg, 1.03 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (51.5 mg, 0.283 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/5) to give **3ia** (70.6 mg, 44%) as a colorless solid and **4ia** (76.8 mg, 52%) as a colorless solid, respectively. Spectral data of **3ia**: mp 127 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1747, 1682, 1644, 1612; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.3 Hz, 1H), 8.21 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 3.82-3.77 (m, 4H), 3.68 (t, *J* = 4.9 Hz, 2H), 3.41 (t, *J* = 4.9 Hz, 2H), 1.76 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.6, 160.6, 159.6, 136.9, 132.8, 128.0, 118.4, 113.4, 107.4, 66.7, 66.6, 46.3, 41.8, 25.9; EI-LRMS *m/z* 319 (M^+), 205; EI-HRMS calcd. for $C_{16}H_{17}NO_6$ 319.10559, found 319.10511. Spectral data of **4ia**: mp 124 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1743, 1632; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1 H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 3.99-3.22 (br, 8H), 1.72 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 160.2, 157.0, 135.7, 129.6, 128.5, 117.8, 113.0, 106.8, 66.7, 48.3 (br), 42.8 (br), 25.7; EI-LRMS *m/z* 291 (M^+), 205; EI-HRMS calcd. for $C_{15}H_{17}NO_5$ 291.11067, found 291.11070

1-Morpholino-2-(thiophen-3-yl)ethane-1,2-dione (3ja) and Morpholino(thiophen-3-yl)-methanone (4ja) (Table 2, run 9). A crude product, which was obtained from **1j** (104.7 mg, 0.498 mmol), K_2CO_3 (138.3 mg, 1.00 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (48.6 mg,

[14] J. Zhu, Y. Zhang, F. Shi, Y. Deng, *Tetrahedron Lett*. **2012**, *53*, 3178-3180.

[15] R. Cadoni, A. Porcheddu, G. Giacomelli, L. D. Luca, *Org. Lett*. **2012**, *14*, 5014-5017.

0.267 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/2) to give **3ja** (94.1 mg, 84%) as a colorless oil and **4ja** (16.0 mg, 16%) as a colorless oil, respectively. Spectral data of **3ja**: IR (film, $CHCl_3$) 1672, 1642 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.57 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.37 (dd, *J* = 5.2, 2.9 Hz, 1H), 3.77-3.72 (m, 4H), 3.65 (t, *J* = 4.9 Hz, 2H), 3.42 (t, *J* = 4.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.3, 165.1, 138.4, 136.7, 127.3, 126.8, 66.7, 66.6, 46.3, 41.7; EI-LRMS *m/z* 225 (M^+), 111; EI-HRMS calcd. for $C_{10}H_{11}NO_3S$ 225.04596, found 225.04567. ^1H and ^{13}C NMR data of **4ja**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.17 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.00-3.30 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 135.9, 126.9, 126.6, 126.1, 66.8, 47.9 (br), 42.6 (br). These data were identical to those reported previously.[13]

1-(1-Methyl-1*H*-indol-3-yl)-2-morpholinoethane-1,2-dione (3ka) and (1-Methyl-1*H*-indol-3-yl)(morpholino)methanone (4ka) (Table 2, run 10). A crude product, which was obtained from **1k** (129.9 mg, 0.505 mmol), K_2CO_3 (141.8 mg, 1.03 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (50.4 mg, 0.277 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1~1/2) to give **3ka** (129.7 mg, 94%) and colorless solid **4ka** (6.8 mg, 6%) as a yellowish solid. Spectral data of **3ka**: mp 157 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1662, 1642, 1607 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.2 Hz, 1H), 7.82 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 2.9 Hz, 1H), 6.58 (d, *J* = 2.9 Hz, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 3.60 (t, *J* = 4.9 Hz, 2H), 3.36 (t, *J* = 4.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 166.4, 139.9, 131.0, 128.0, 125.3, 124.8, 122.1, 109.8, 103.3, 66.6, 66.5, 46.2, 41.3, 32.9; EI-LRMS *m/z* 272 (M^+), 158; EI-HRMS calcd. for $C_{15}H_{16}N_2O_3$ 272.11609, found 272.11587. Spectral data of **4ka**: mp 132 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1621 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.32-7.27 (m, 2H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 3.76 (s, 3H), 3.79-3.55 (br, 8H); ^{13}C NMR δ 171.7, 137.1, 129.9, 127.7, 126.0, 120.9, 120.4, 109.0, 101.5, 66.8, 48.2, 43.0 (br), 32.8 (br); EI-LRMS m/z 244 (M^+), 158; EI-HRMS calcd. for $C_{14}H_{16}N_2O_2$ 244.12118, found 244.12010.

1-Morpholino-2-(quinolin-6-yl)ethane-1,2-dione (3la) and Morpholino(quinolin-6-yl)methanone (4la) (Table 2, run 11). A crude product, which was obtained from **1l** (128.4 mg, 0.503 mmol), K_2CO_3 (138.9 mg, 1.01 mmol), **2a** (130.0 μL, 1.49 mmol), and bibenzyl (48.8 mg, 0.268 mmol, internal standard for GC analysis) in DMF at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1~1/2) to give **3la** (108.9 mg, 0.403 mmol, 80%) as a colorless solid and **4la** (20.3 mg, 0.167 mmol, 17%) as a colorless solid, respectively. Spectral data of **3la**: mp 127 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1680, 1645 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.45 (d, *J* = 1.7 Hz, 1H), 8.27 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.23 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.81 (s, 4H), 3.65 (t, *J* = 4.9 Hz, 2H), 3.41 (t, *J* = 4.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 165.0, 153.4, 150.7, 137.7, 132.6, 130.7 (2C), 127.4 (2C), 122.3, 66.7, 66.6, 46.3, 41.7; EI-LRMS *m/z* 270 (M^+), 156; EI-HRMS calcd. for $C_{15}H_{14}N_2O_3$ 270.10044, found 270.10024. Spectral data of **4la**: mp 121 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1633 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.99 (brs, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.93 (s, 1H), 7.73 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.48 (m, 1H), 4.00-3.34 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 151.6, 148.4, 136.5, 133.4, 130.1 (2C), 127.8, 127.1, 122.0, 66.9, 48.3 (br), 42.7 (br); ESI-LRMS m/z 265.09 ($[M+Na]^+$); ESI-HRMS calcd. for $C_{14}H_{14}O_2N_2Na$ 265.09475, found 265.09476.

1-(4-Benzoylpiperazin-1-yl)-2-(naphthalen-2-yl)ethane-1,2-dione (3ml) and [4-(2-Naphthoyl) piperazin-1-yl](phenyl)methanone (4ml) (Scheme 3). A crude product, which was obtained from **1m** (131.7 mg, 0.518 mmol), K_2CO_3 (138.2 mg, 1.00 mmol), **2l** (285.6 mg, 1.50 mmol), and bibenzyl (48.7 mg, 0.267 mmol, internal standard for GC analysis) in DMF (3 mL) at 80 °C for 24 hours, was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1~2/1) to give **3ml** (159.7 mg, 83%) as a colorless solid and **4ml** (27.3 mg, 15%) as a colorless slid, respectively. Spectral data of **3ml**: mp 144 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1673, 1638 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.99-7.87 (m, 4H), 7.64 (m, 1H) 7.57 (m, 1H), 7.40 (s, 5H), 4.20-3.03 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 170.6, 165.6, 136.4, 134.8, 133.1, 132.3, 130.2, 129.8, 129.6, 129.2, 128.6, 127.9, 127.2, 126.9, 123.4, 47.2 (br), 45.9 (br), 42.0 (br), 41.4 (br); EI-LRMS *m/z* 372 (M^+), 189, 155; EI-HRMS calcd. for $C_{23}H_{20}N_2O_3$ 372.14739, found 372.14628. Spectral data of **4mk**: mp 184 °C (recrystallized from $CHCl_3$/hexane); IR (film, $CHCl_3$) 1629 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92-7.87 (m, 4H), 7.55-7.42 (m, 8H), 4.20-3.14 (br, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 135.1, 133.7, 132.6, 132.3, 130.1, 128.6, 128.5, 128.4, 127.8, 127.3, 127.2, 127.1, 127.0, 126.8, 124.0, 47.7 (br), 42.5 (br); EI-LRMS *m/z* 344 (M^+), 189, 155; EI-HRMS calcd. for $C_{22}H_{20}N_2O_2$ 344.15248, found 344.15248.

Large-scale reactions.

For the reaction of 1a and 2a (Scheme 4, Eq 1). A mixture of **1a** (2.34 g, 10.0 mmol), K_2CO_3 (2.78 g, 20.1 mmol), **2a** (2.6 mL, 30.1 mmol) and 2 sheets of SAPd in DMF (10 mL) was stirred at 80 °C for 24 hours. After the usual work-up, the crude product was purified by flash column chromatography on silica gel (hexane/AcOEt = 2/1~1/1) to give **3aa** (2.13 g, 85%) and **4aa** (105.2 mg, 5%), respectively

For the reaction of 1m and 2l (Scheme 4, Eq 2). A mixture of **1m** (2.54 g, 10.0 mmol), K_2CO_3 (2.77 g, 20.0 mmol), **2l** (5.71 g, 30.0 mmol) and 2 sheets of SAPd in DMF (10 mL) was stirred at 80 °C for 24 hours. After the usual work-up, the crude product was purified by flash column chromatography on silica gel (hexane/AcOEt = 1/1~1/2) to give **3ml** (3.06 g, 82%) and **4mk** (569.4 mg, 17%), respectively

Examination of reusability of SAPd (Table 3)

After the solution of **1a** in DMF in the presence of K_2CO_3 and SAPd was heated at 80 °C for 2 hours, SAPd was removed and reused to the next reaction without purification. The yields shown in Table 3 were calculated by GC analysis using bibenzyl as an internal standard.

Run 1		cycle 1	cycle 2	cycle 3	cycle 4	cycle 5
1a (mg)		117.3	117.0	118.3	117.5	117.3
2a (μL)		130.0	130.0	130.0	130.0	130.0
bibenzyl (mg)		47.8	47.8	47.9	49.5	48.8
K_2CO_3 (mg)		139.0	138.0	139.5	138.3	138.2
yields (%)	**3aa**	88	90	90	90	89
	4aa	7	7	8	8	6

Run 2		cycle 1	cycle 2	cycle 3	cycle 4	cycle 5
1a (mg)		117.8	117.5	116.7	117.2	117.1
2a (μL)		130.0	130.0	130.0	130.0	130.0
bibenzyl (mg)		47.0	46.7	50.6	47.9	48.7
K_2CO_3 (mg)		138.4	138.3	139.1	138.3	138.2
yields (%)	**3aa**	89	90	91	93	91
	4aa	7	8	7	7	7

Run 3		cycle 1	cycle 2	cycle 3	cycle 4	cycle 5
1a (mg)		117.5	117.8	117.5	117.5	117.7
2a (μL)		130.0	130.0	130.0	130.0	130.0
bibenzyl (mg)		45.7	51.2	48.3	49.1	50.3
K_2CO_3 (mg)		139.1	138.7	138.5	138.4	138.7
yields (%)	**3aa**	84	84	92	90	89
	4aa	6	8	6	8	7

Data of ICP-MS analysis

Amount of palladium in the reaction mixture of **1a** and **2a**[a], and in SAPd

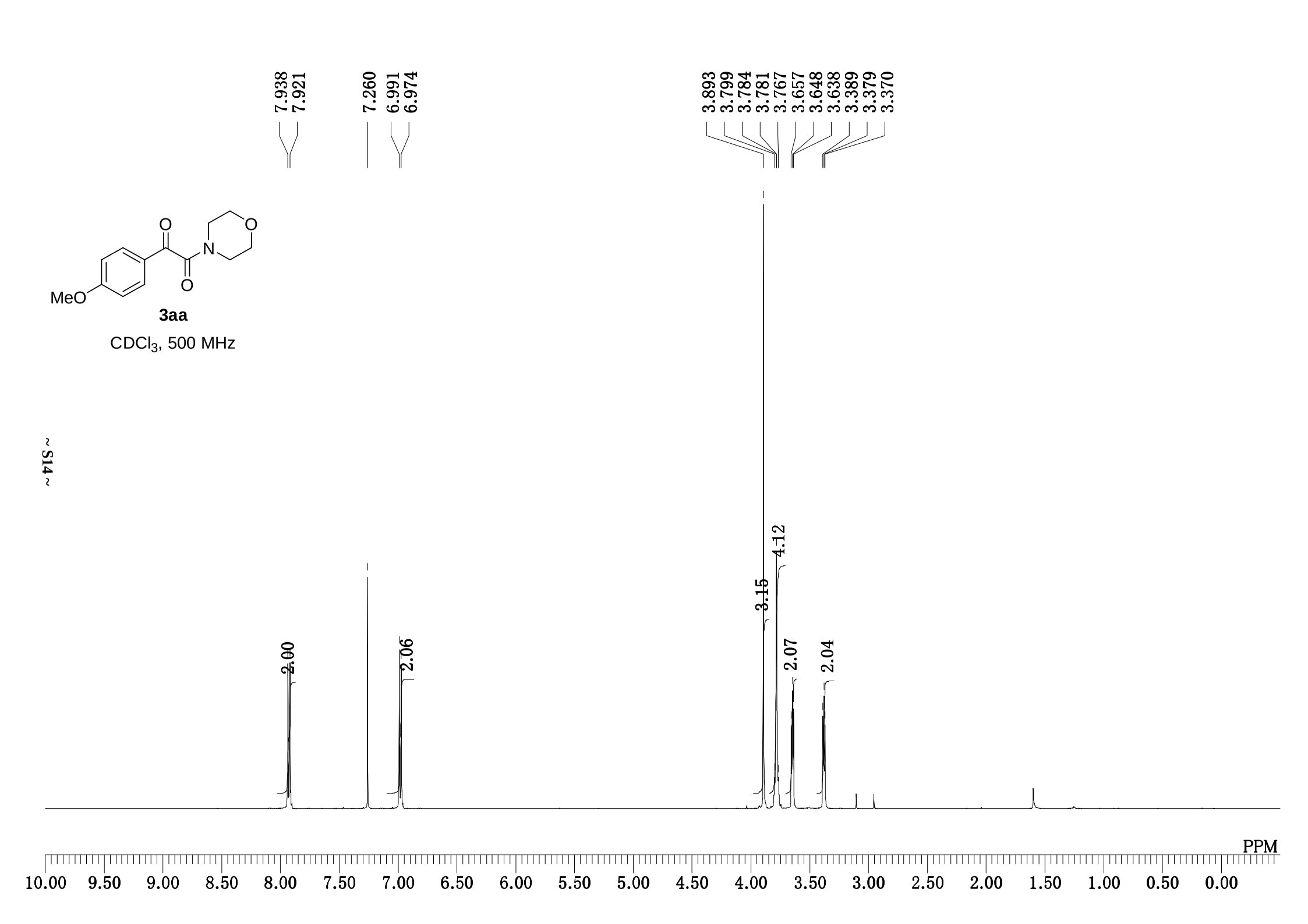
Amount of leached Pd (μg) in the reaction mixture[b]							Immobilized Pd on SAPd (μg)	
		cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	after use	before use
leached Pd (μg) (mol%)[c]	run 1	10 (0.019)	11 (0.021)	22 (0.041)	15 (0.028)	5 (0.009)	87	408
	run 2	62 (0.116)	63 (0.118)	35 (0.066)	46 (0.086)	28 (0.053)	40	338
	run 3	96 (0.180)	78 (0.146)	29 (0.054)	28 (0.052)	36 (0.067)	136	329
average (μg)		56	50	28	30	23	88	358
standard deviation[c]		43	35	7	16	16	48	43

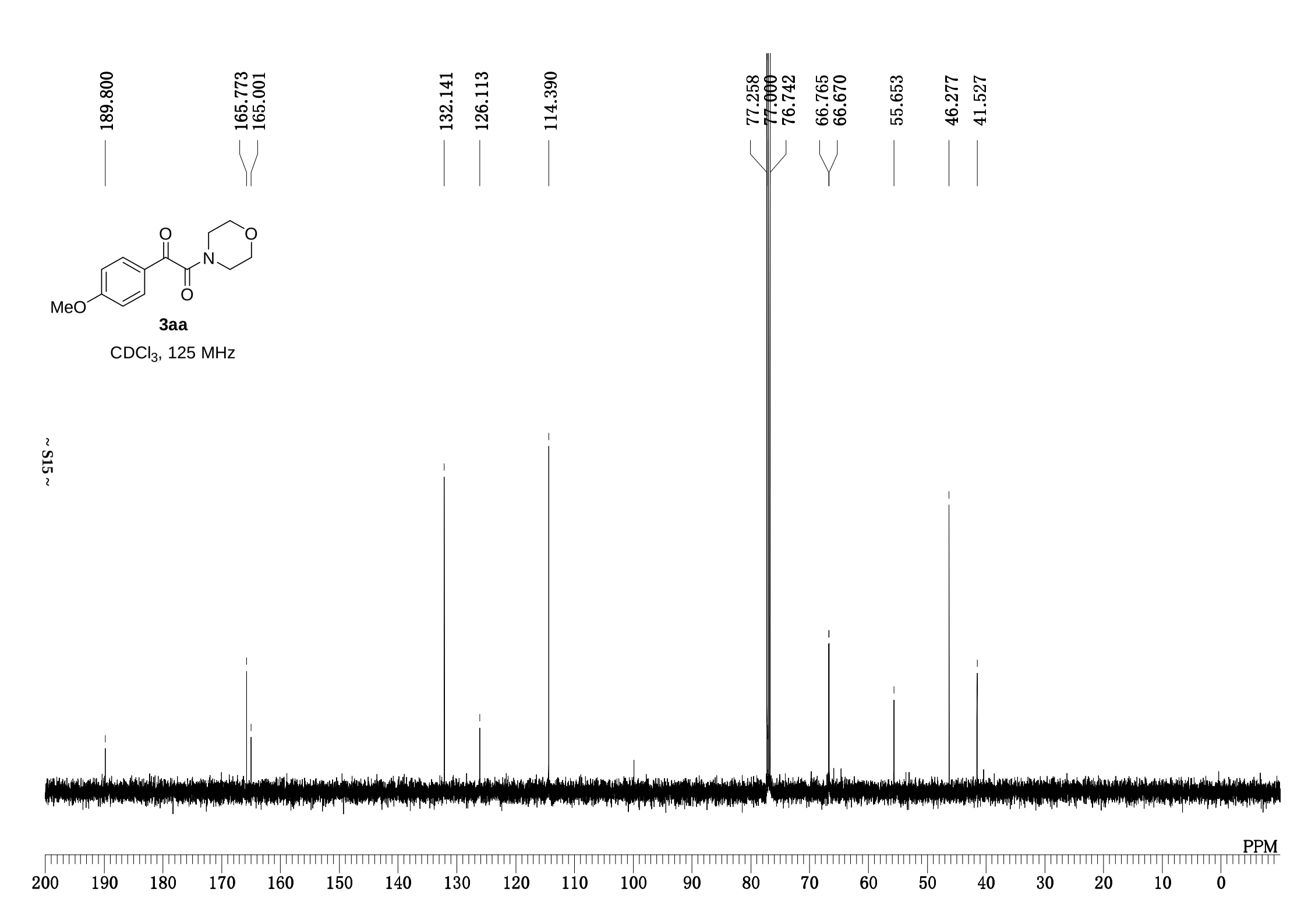
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3 equiv), K_2CO_3 (2 equive), bibenzyl (0.5 equiv, internal standard) DMF (3 mL), 80 °C, 24 hours

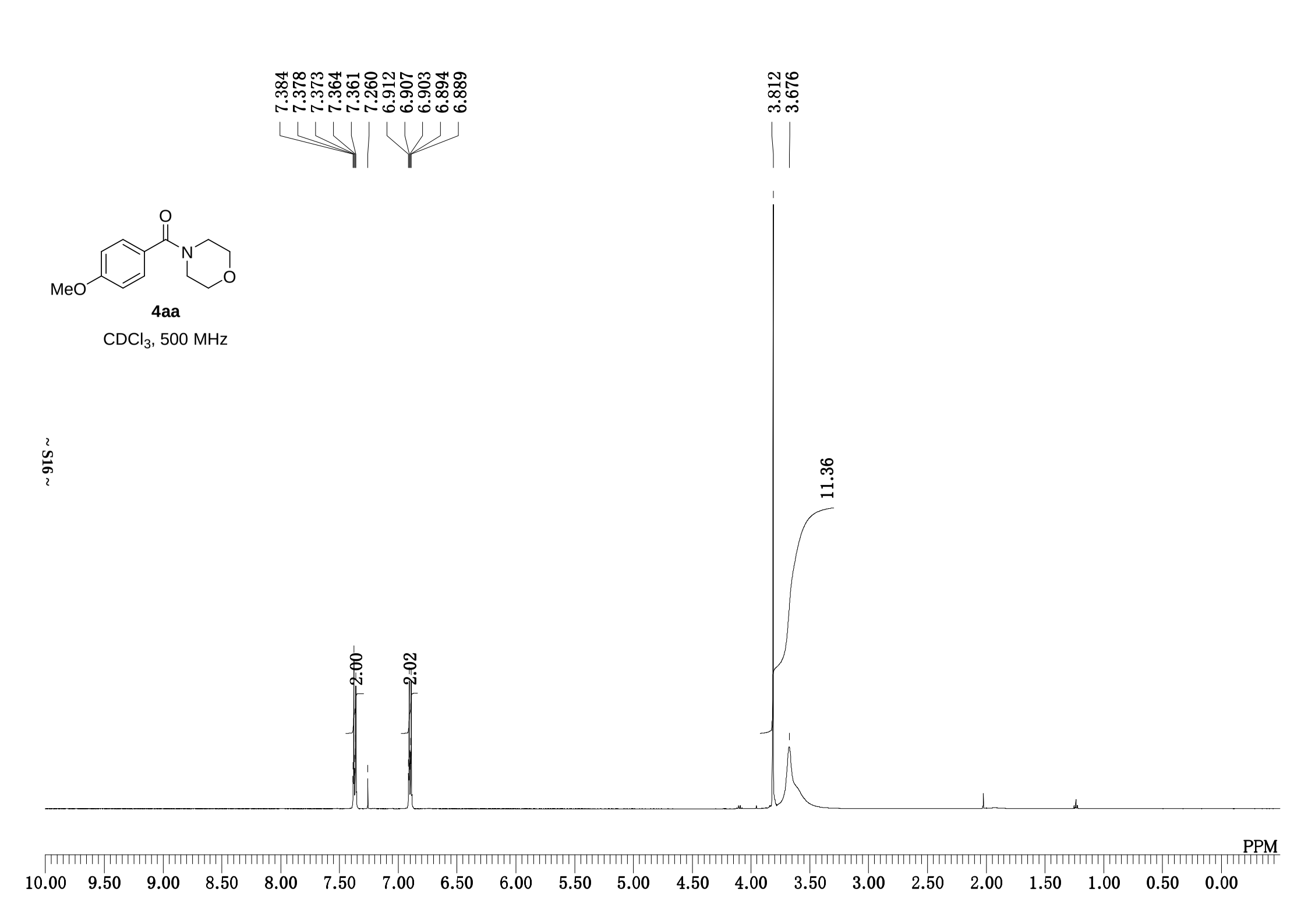
[b] The reaction mixture was acidified and subjected directly to ICP-MS.

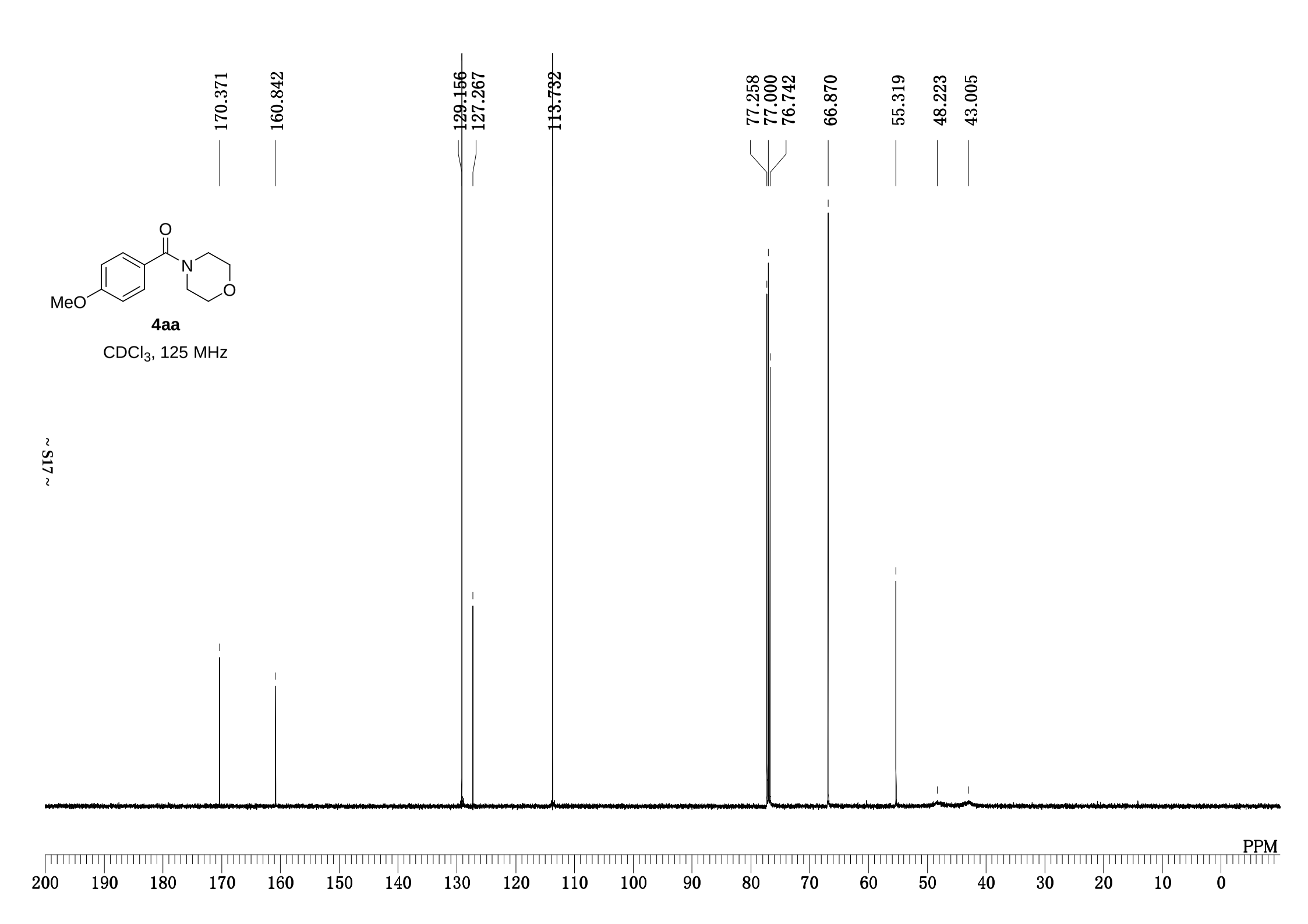
[c] Value in parentheses indicats the loading of Pd catalyst (mol%).

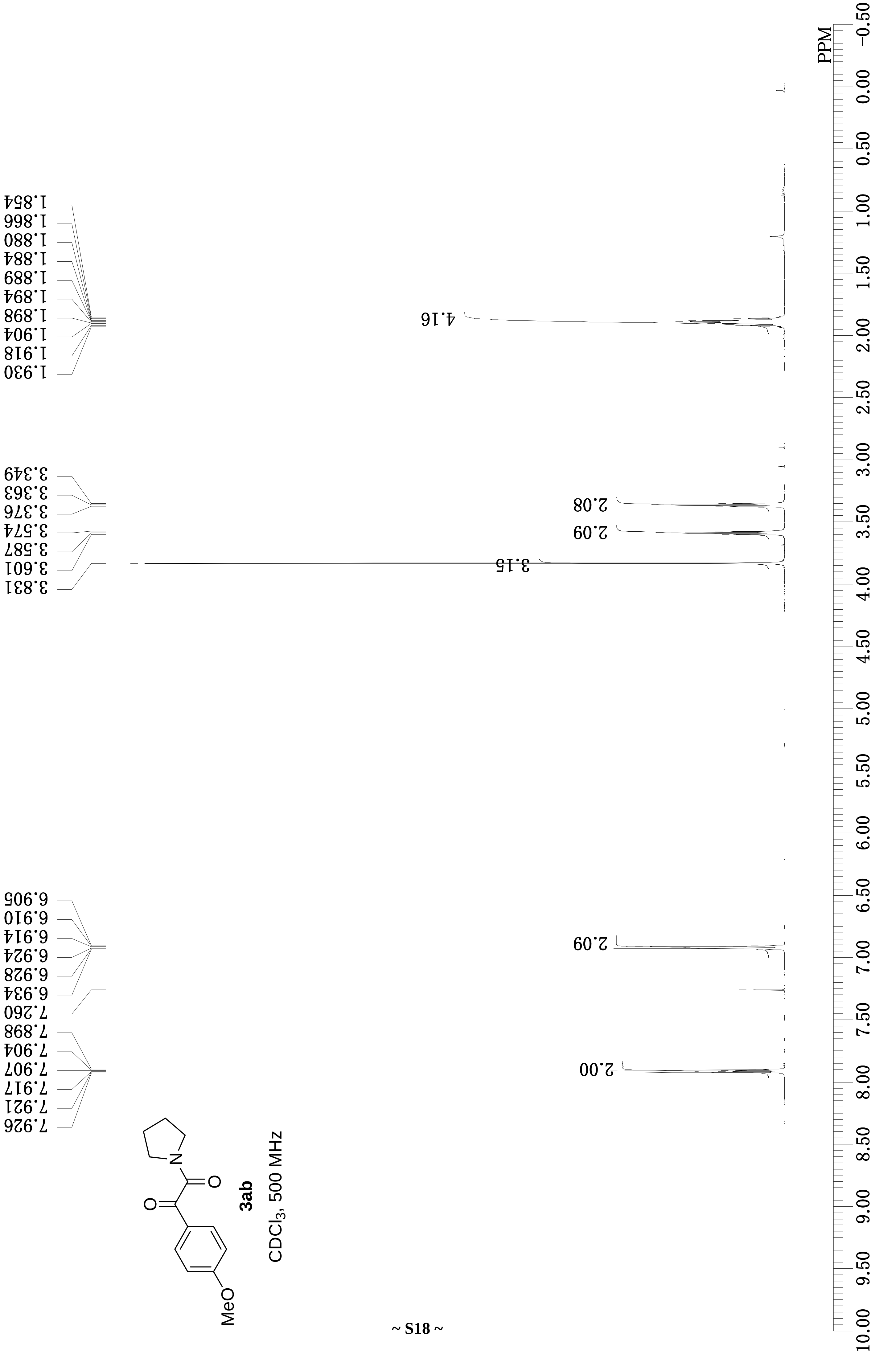
[d] The standard deviation was calculated from three sets of samples.

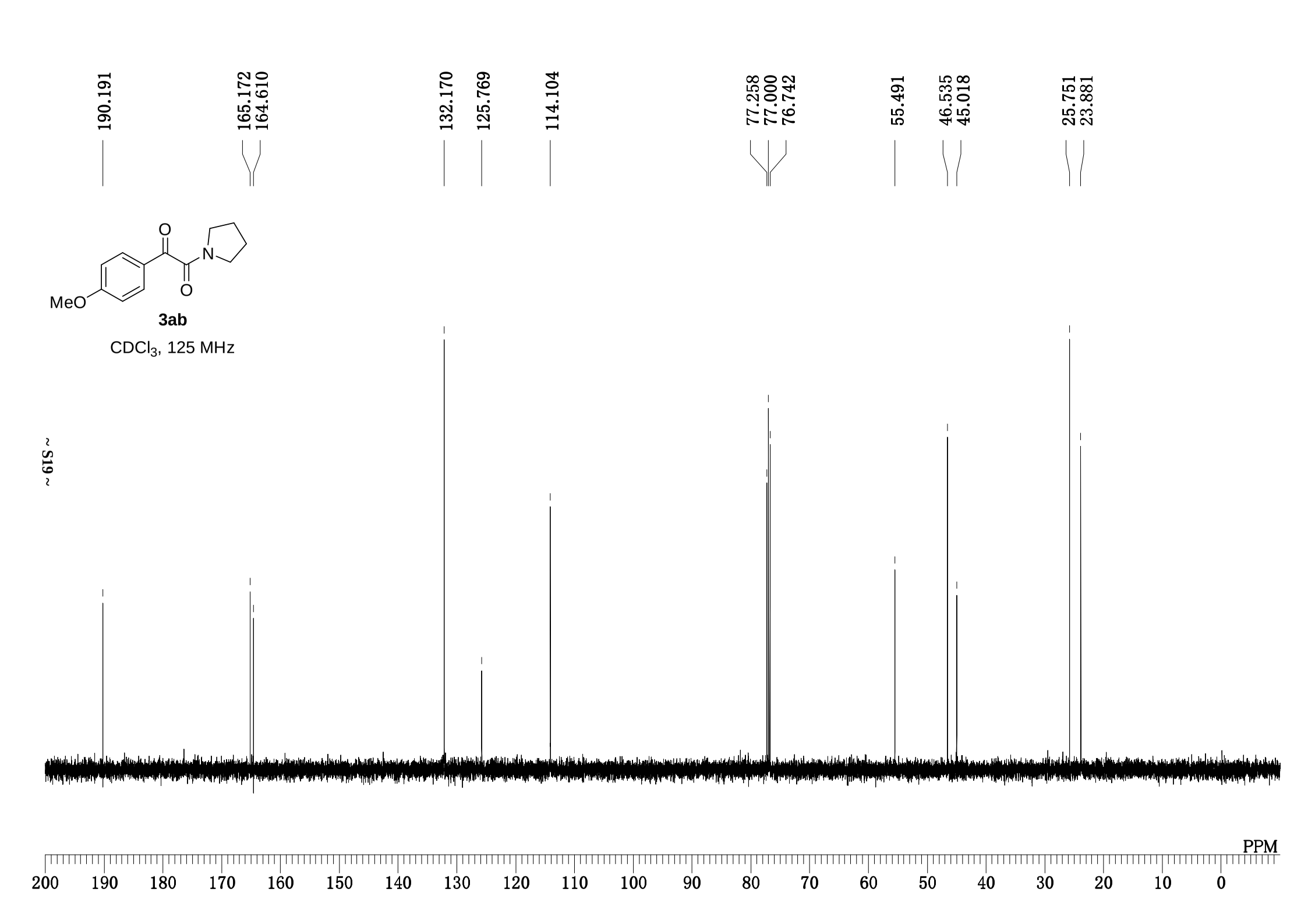

7.938
7.921
7.260
6.991
6.974
3.893
3.799
3.784
3.781
3.767
3.657
3.648
3.638
3.389
3.379
3.370
O
O
N
O
MeO
3aa
CDCl3, 500 MHz
2.00
2.06
3.15
4.12
2.07
2.04
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00

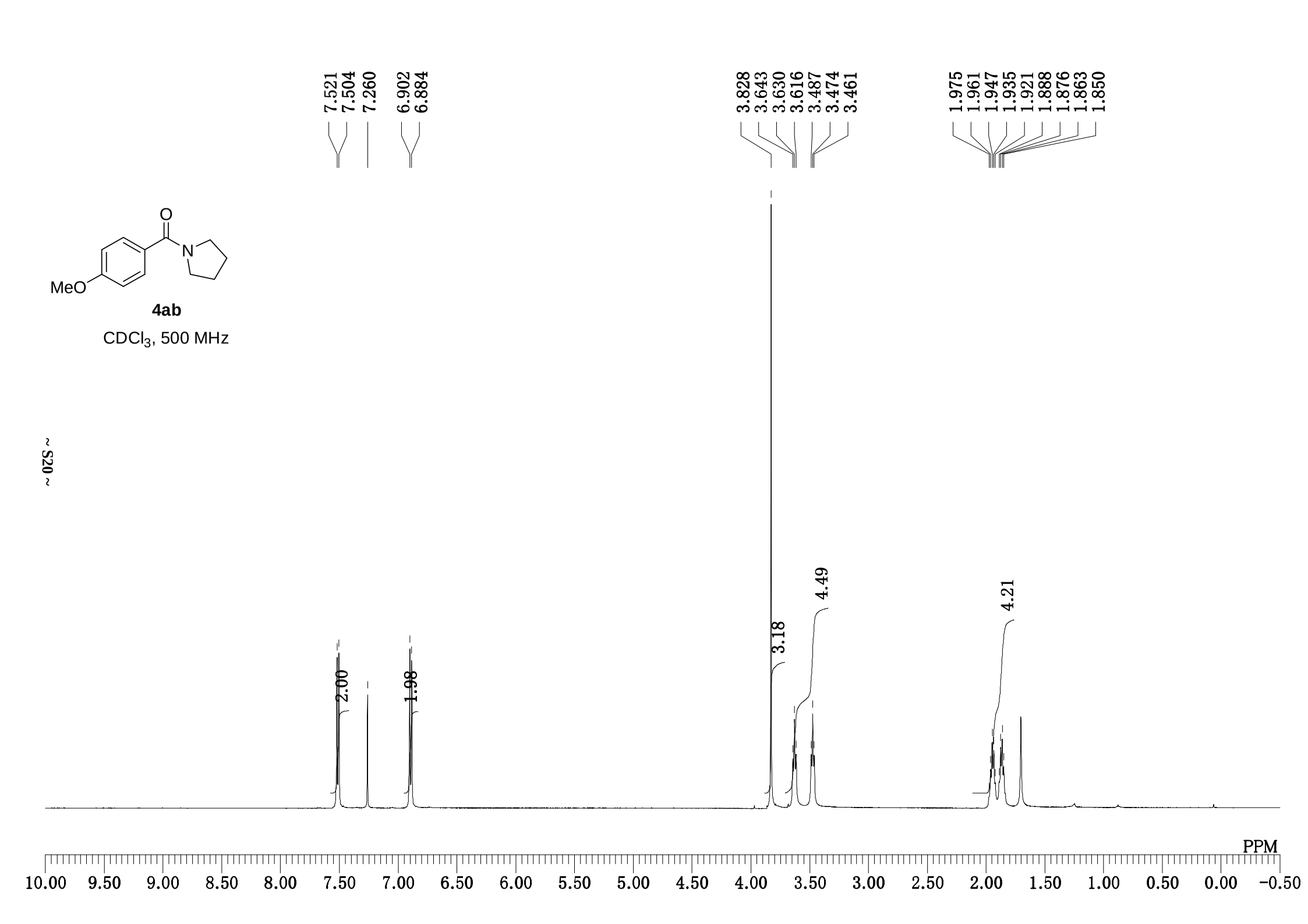

189.800
165.773
165.001
132.141
126.113
114.390
77.258
77.000
76.742
66.765
66.670
55.653
46.277
41.527
O
O
N
O
MeO
3aa
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

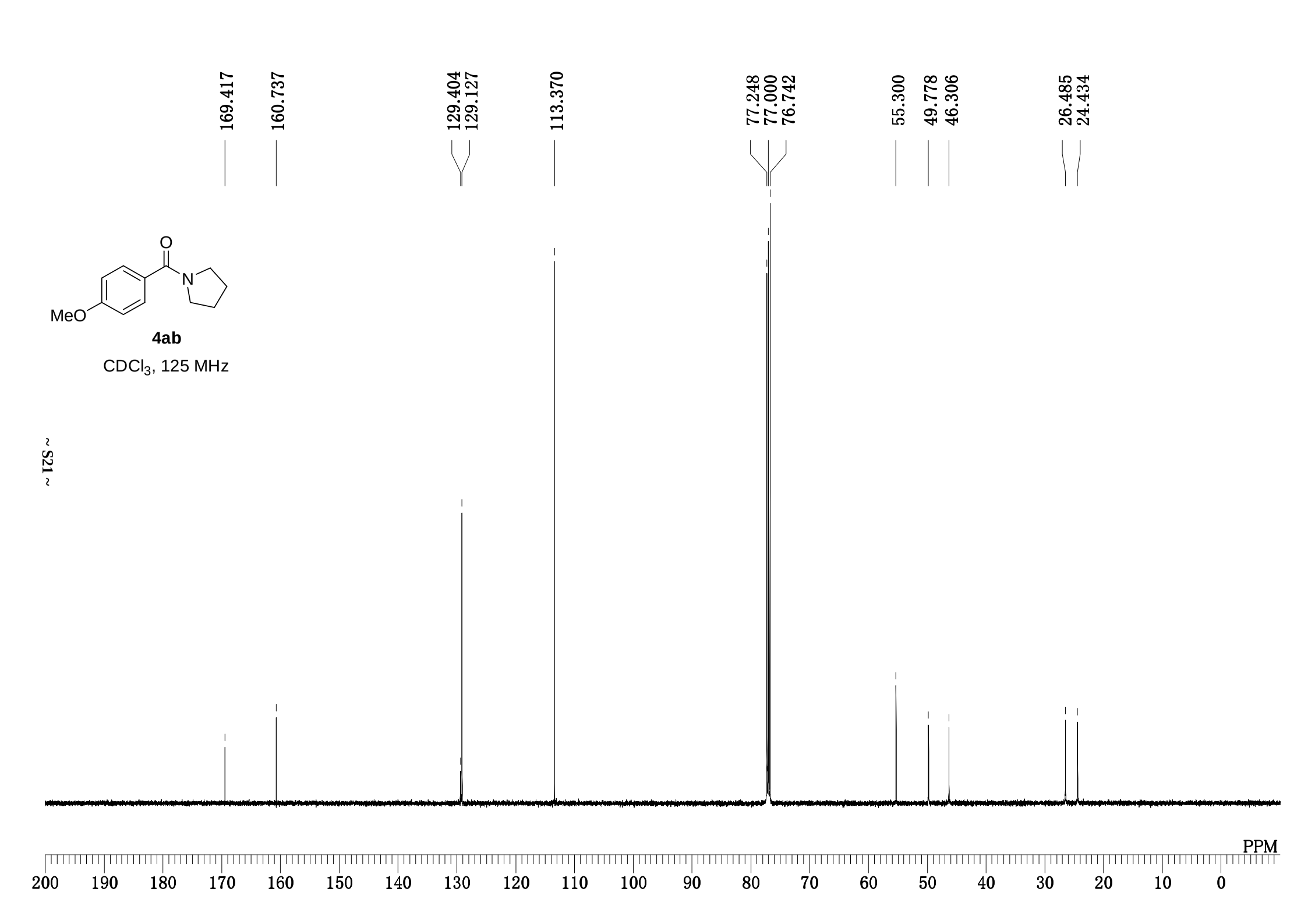

7.384
7.378
7.373
7.364
7.361
7.260
6.912
6.907
6.903
6.894
6.889
3.812
3.676
O
N
O
MeO
4aa
CDCl3, 500 MHz
11.36
2.00
2.02
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00

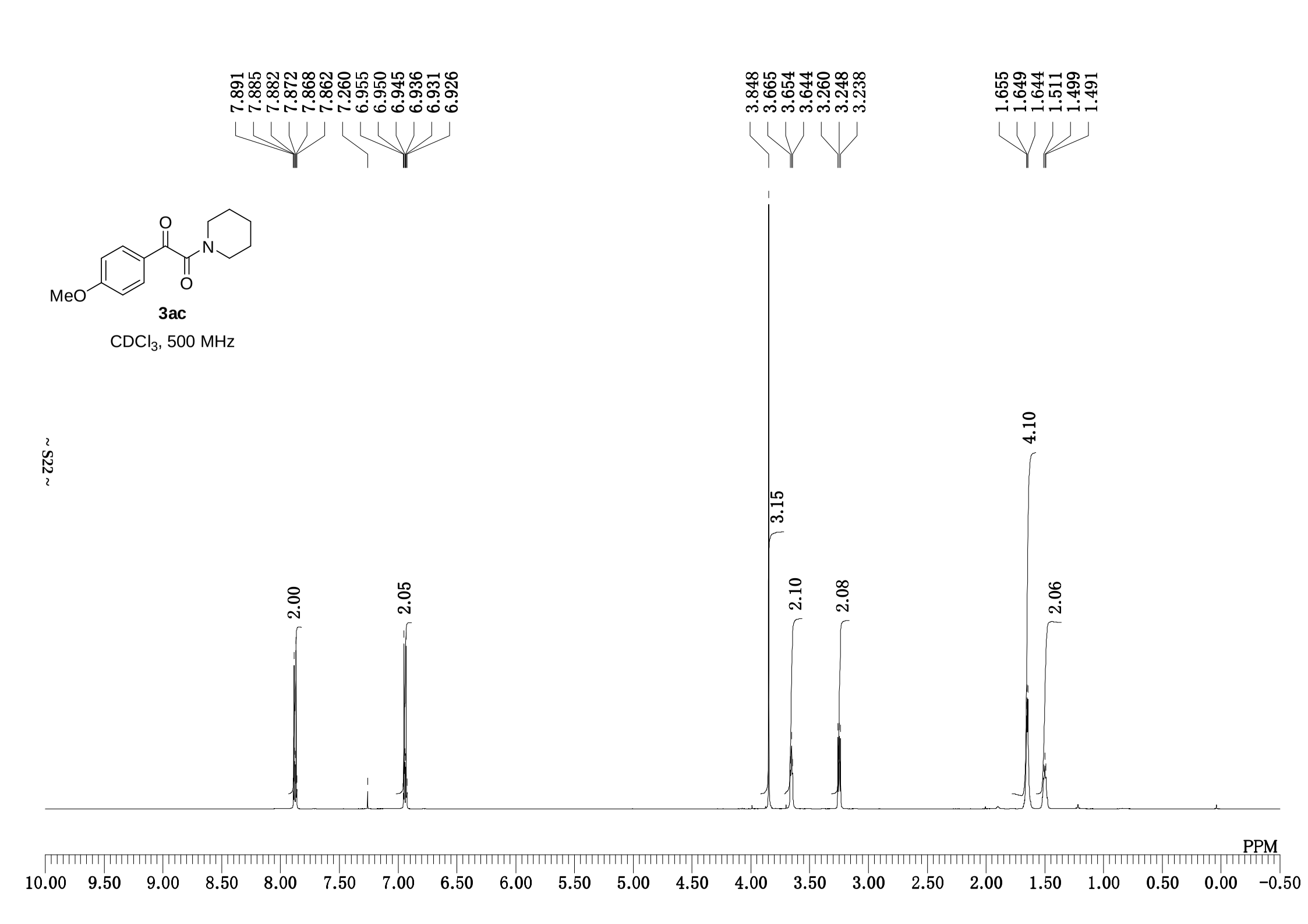

170.371
160.842
129.156
127.267
113.732
77.258
77.000
76.742
66.870
55.319
48.223
43.005
O
N
O
MeO
4aa
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

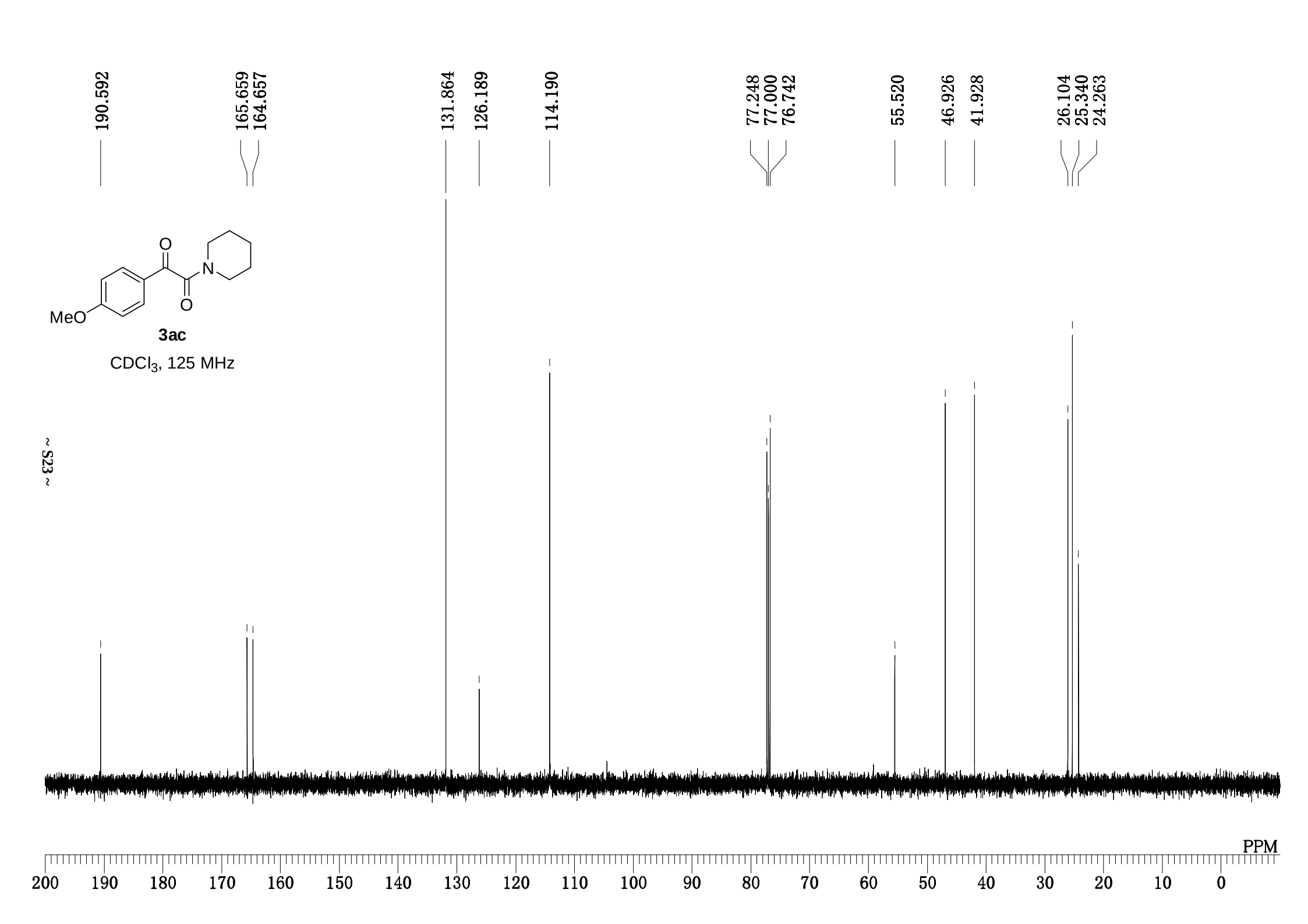

1.854
1.866
1.880
1.884
1.889
1.894
1.898
1.904
1.918
1.930
3.349
3.363
3.376
3.574
3.587
3.601
3.831
6.905
6.910
6.914
6.924
6.928
6.934
7.260
7.898
7.904
7.907
7.917
7.921
7.926
4.16
2.08
2.09
3.15
2.09
2.00
PPM
MeO
N
O
3ab
CDCl3, 500 MHz

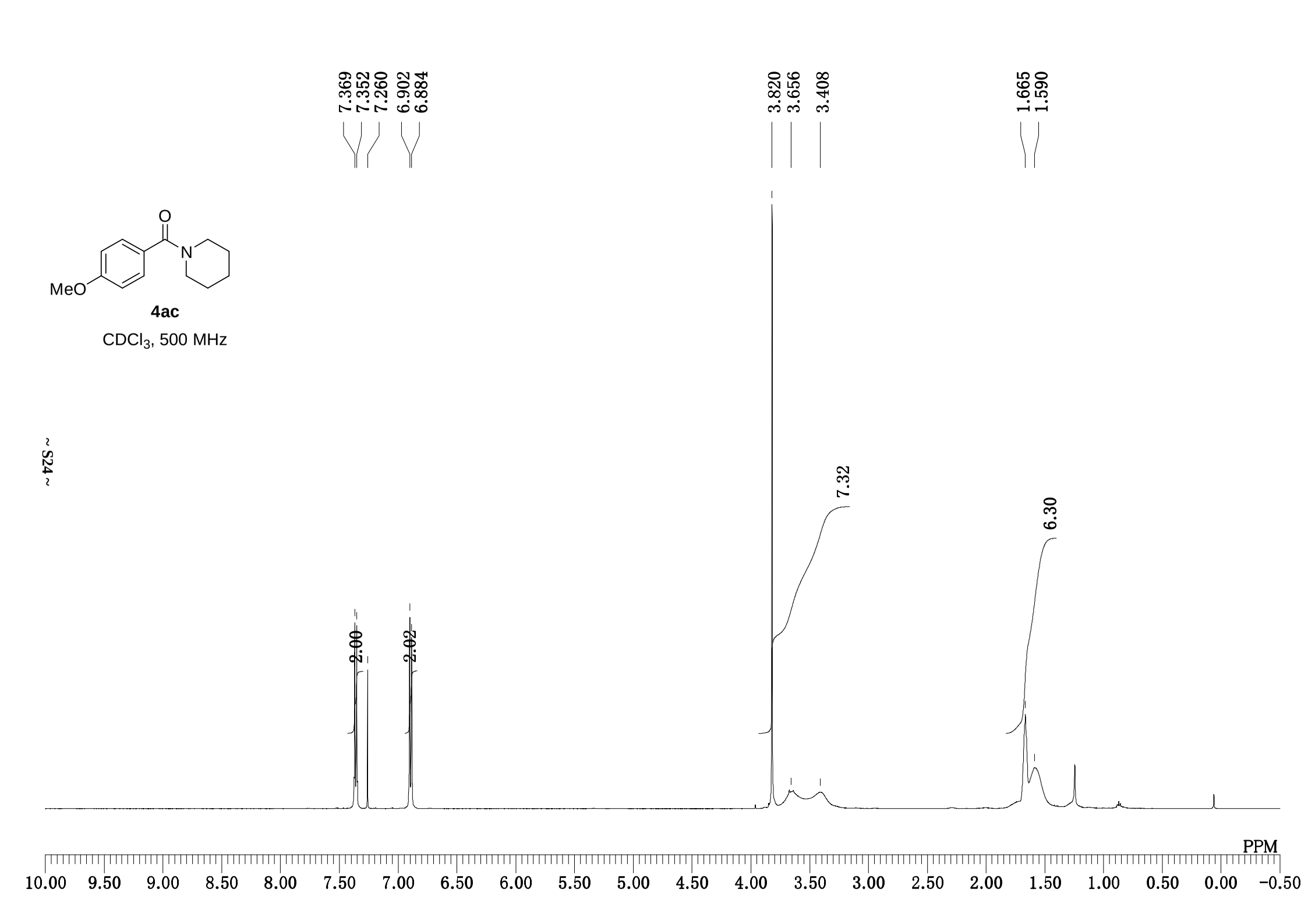

190.191
165.172
164.610
132.170
125.769
114.104
77.258
77.000
76.742
55.491
46.535
45.018
25.751
23.881
O
N
O
MeO
3ab
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

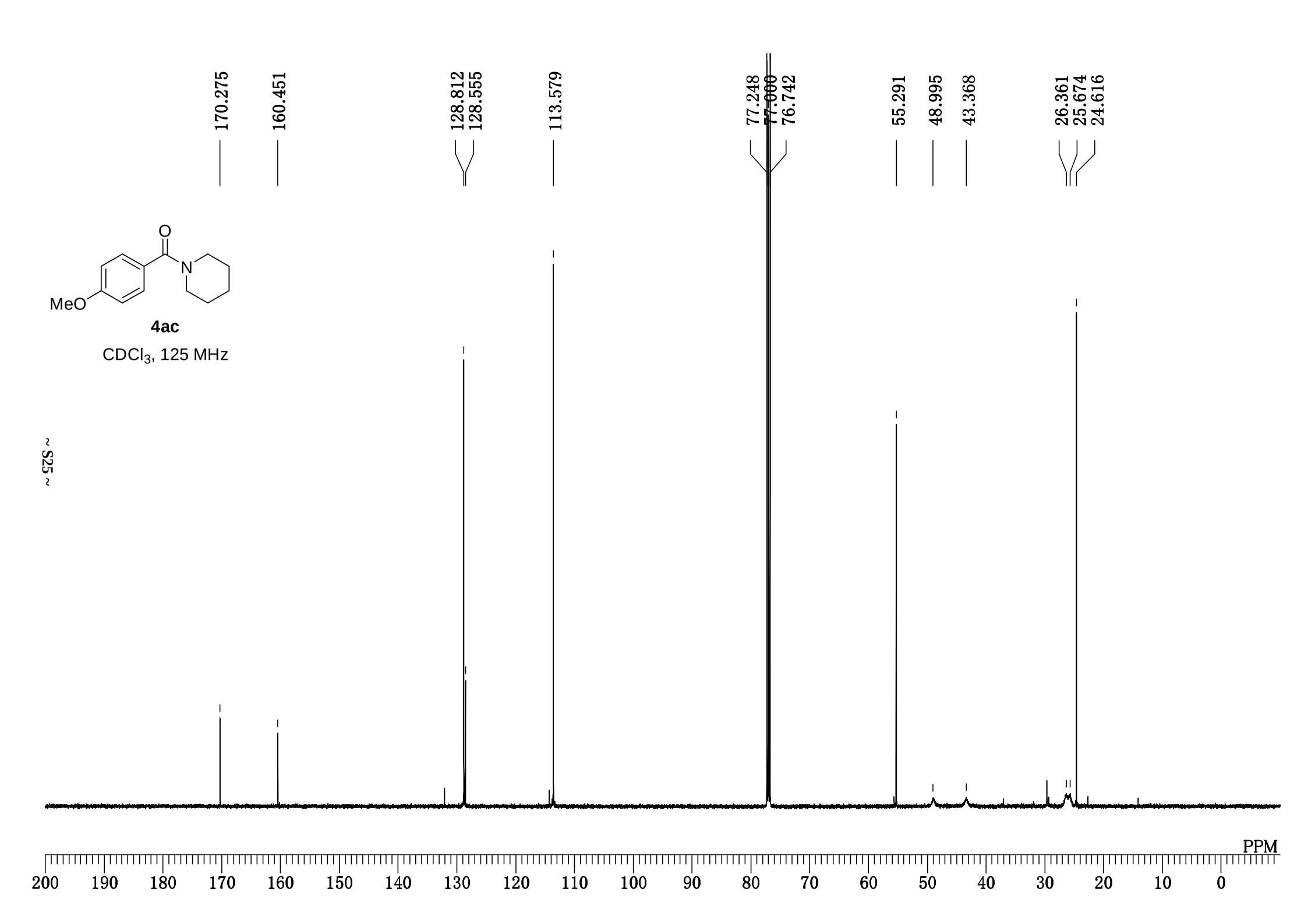

7.521
7.504
7.260
6.902
6.884
3.828
3.643
3.630
3.616
3.487
3.474
3.461
1.975
1.961
1.947
1.935
1.921
1.888
1.876
1.863
1.850
O
N
MeO
4ab
CDCl3, 500 MHz
2.00
1.98
3.18
4.49
4.21
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

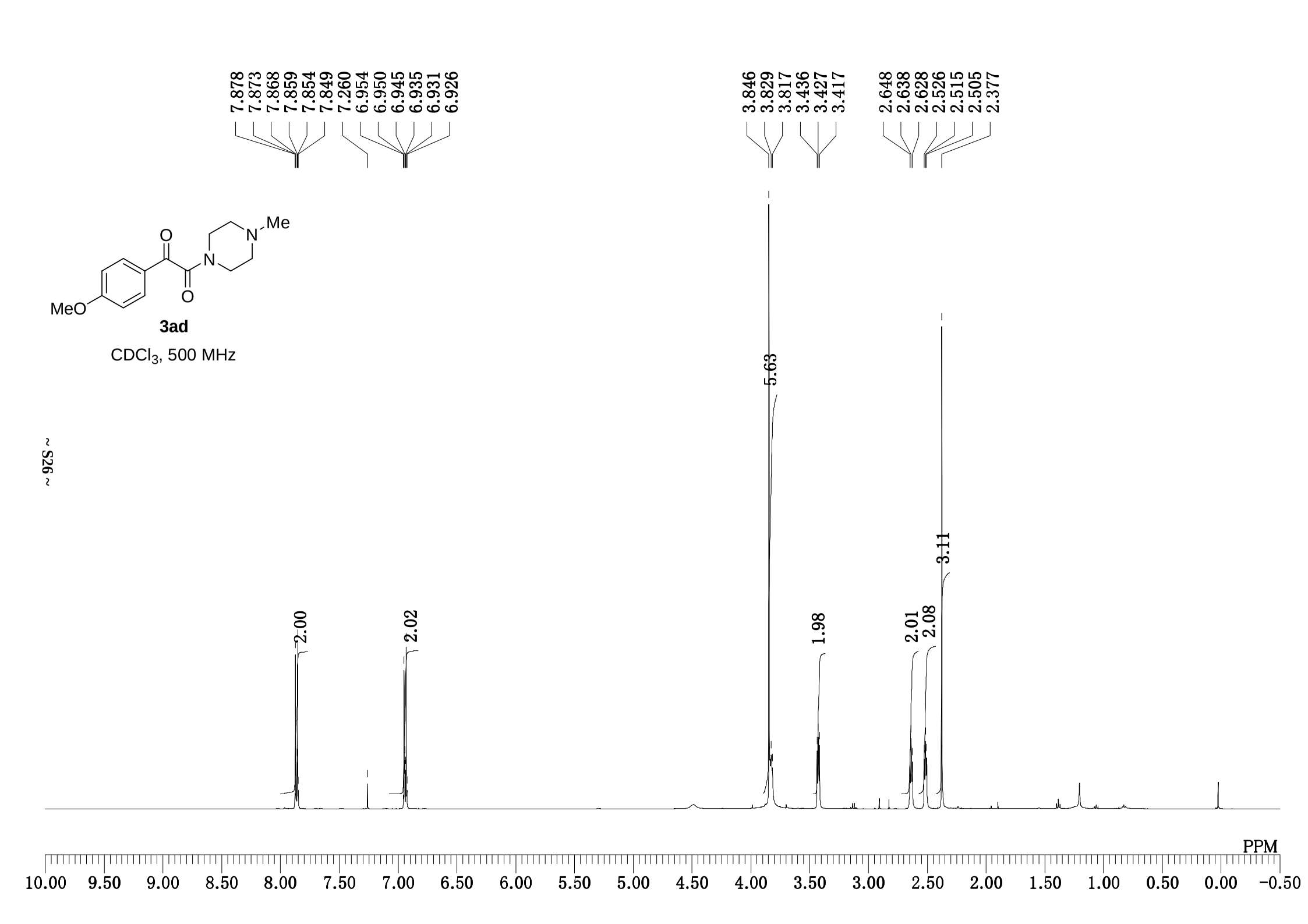

169.417
160.737
129.404
129.127
113.370
77.248
77.000
76.742
55.300
49.778
46.306
26.485
24.434
O
N
MeO
4ab
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

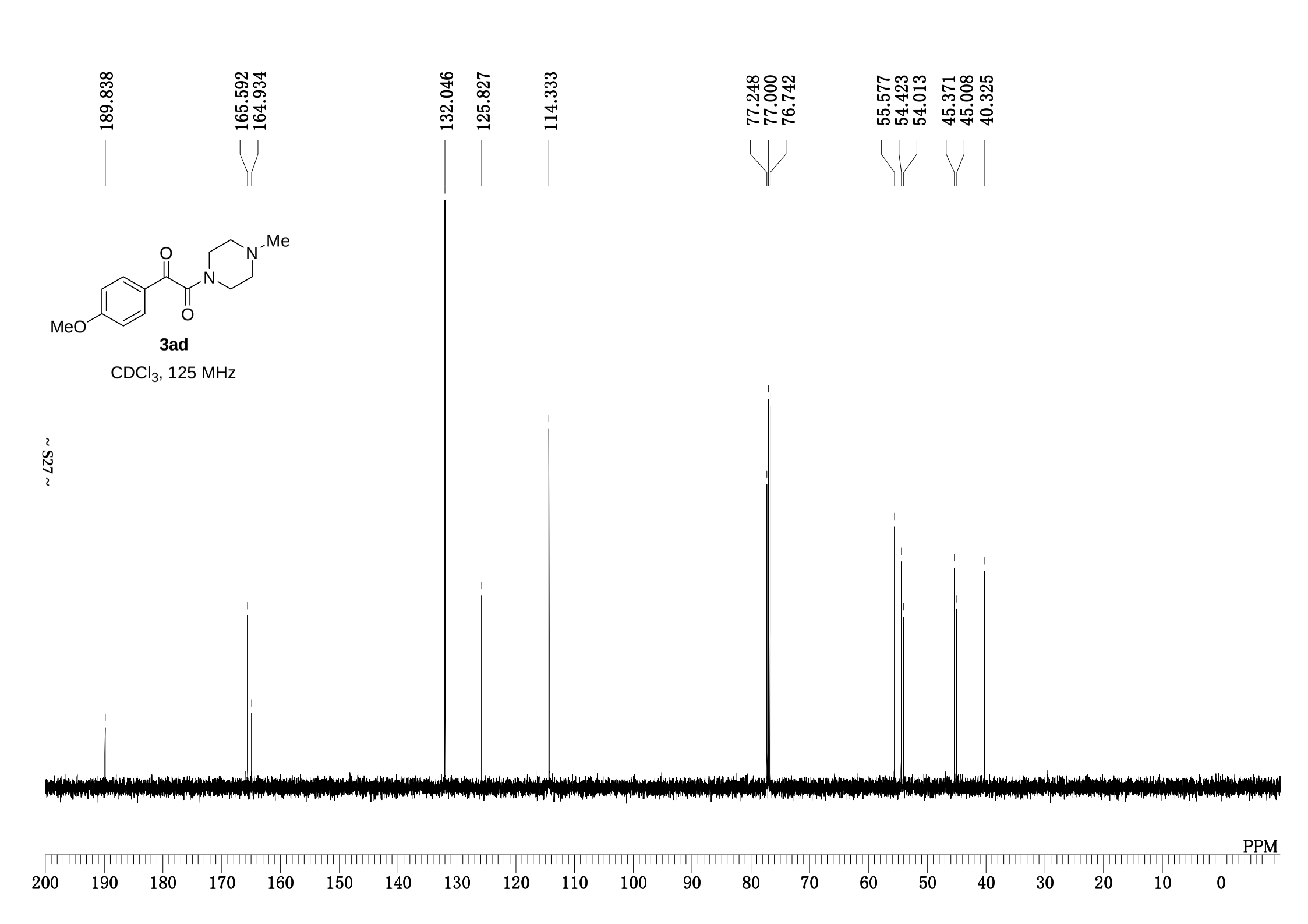

7.891
7.885
7.882
7.872
7.868
7.862
7.260
6.955
6.950
6.945
6.936
6.931
6.926
3.848
3.665
3.654
3.644
3.260
3.248
3.238
1.655
1.649
1.644
1.511
1.499
1.491
O
N
O
MeO
3ac
CDCl3, 500 MHz
~ S22 ~
2.00
2.05
3.15
2.10
2.08
4.10
2.06
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

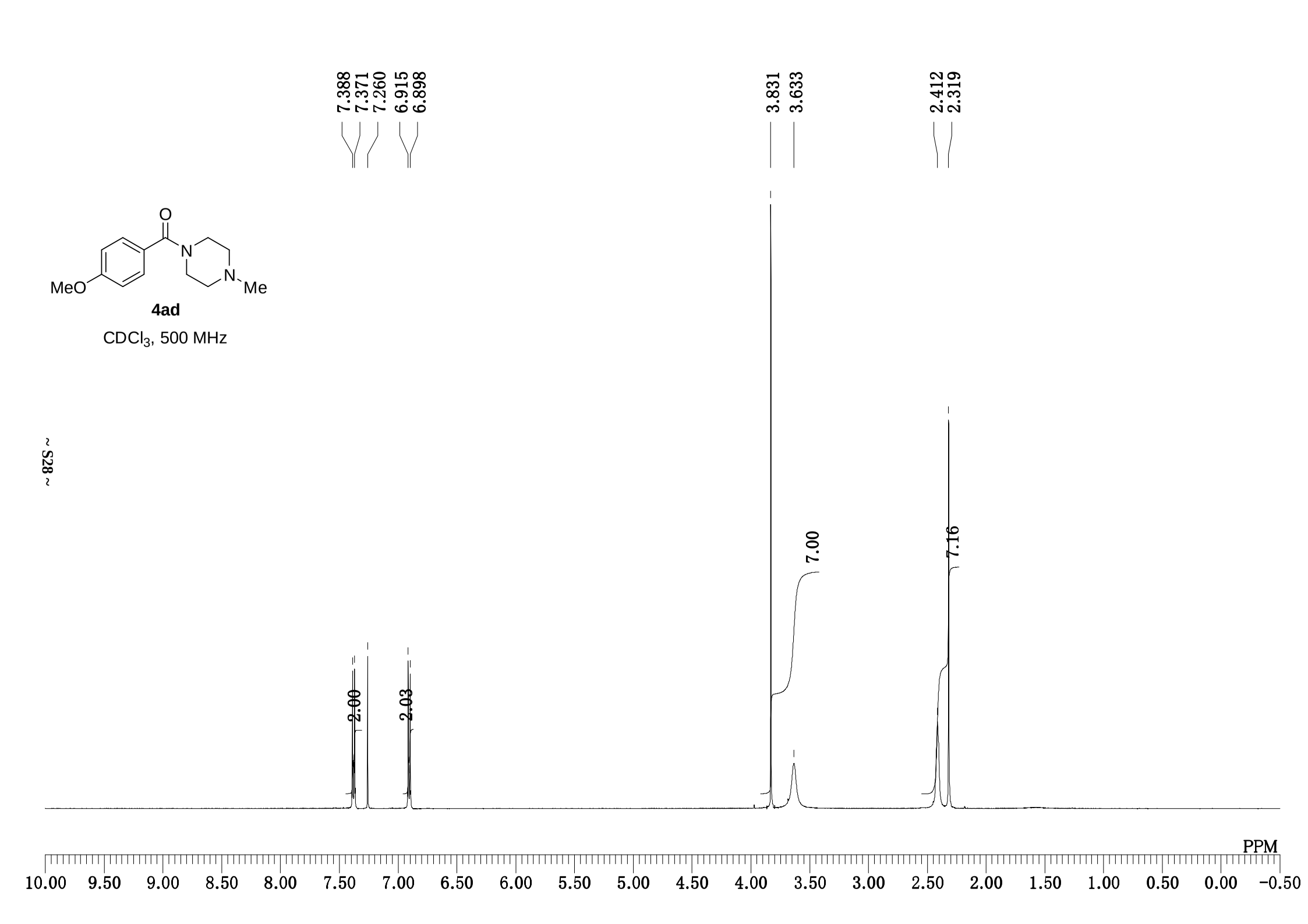

190.592
165.659
164.657
131.864
126.189
114.190
77.248
77.000
76.742
55.520
46.926
41.928
26.104
25.340
24.263
O
N
O
MeO
3ac
CDCl3, 125 MHz
~ S23 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

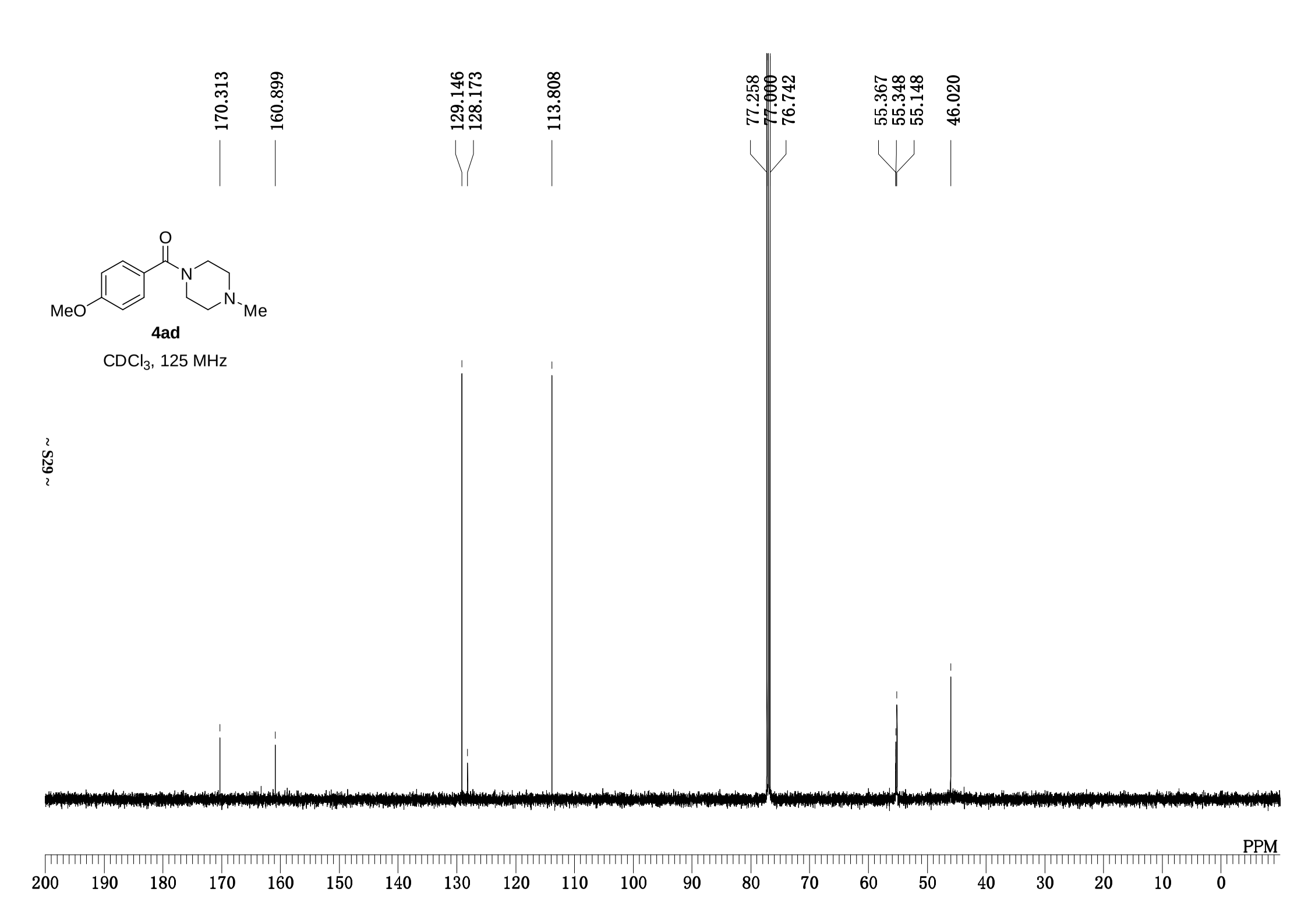

7.369
7.352
7.260
6.902
6.884
3.820
3.656
3.408
1.665
1.590
O
N
MeO
4ac
CDCl3, 500 MHz
~ S24 ~
2.00
2.02
7.32
6.30
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

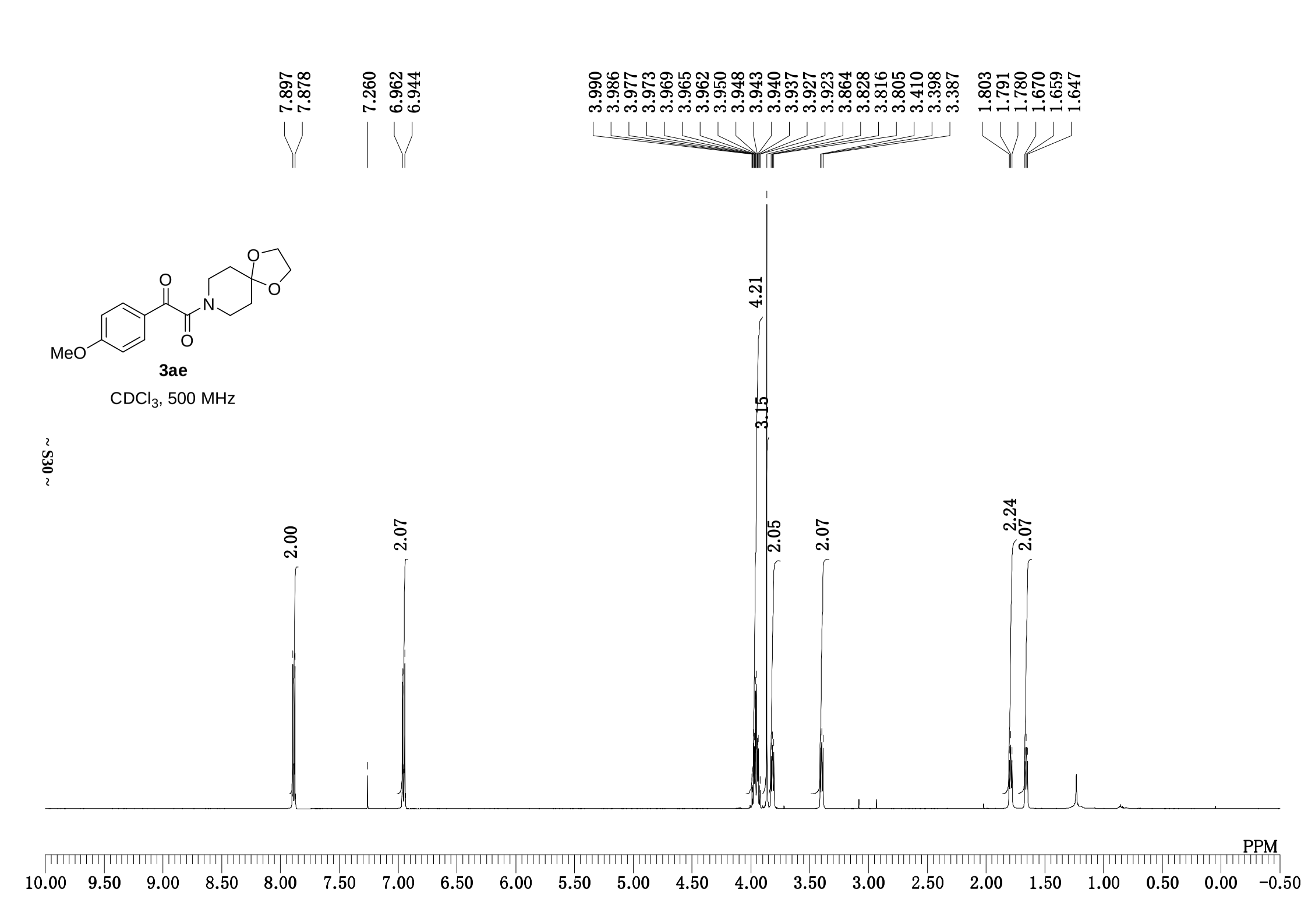

170.275
160.451
128.812
128.555
113.579
77.248
77.000
76.742
55.291
48.995
43.368
26.361
25.674
24.616
O
N
MeO
4ac
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

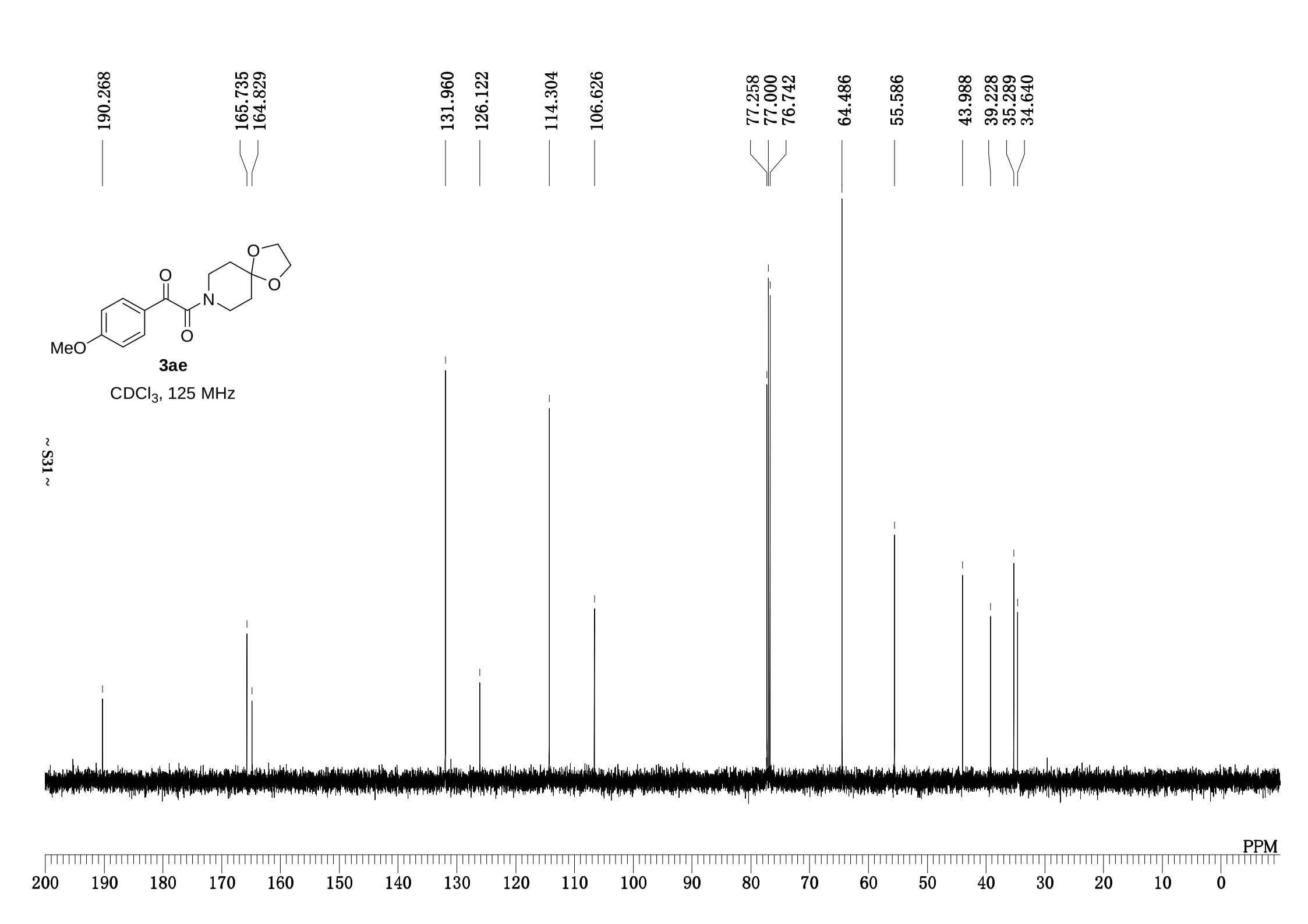

7.878
7.873
7.868
7.859
7.854
7.849
7.260
6.954
6.950
6.945
6.935
6.931
6.926
3.846
3.829
3.817
3.436
3.427
3.417
2.648
2.638
2.628
2.526
2.515
2.505
2.377
O
N
Me
O
N
MeO
3ad
CDCl3, 500 MHz
5.63
2.00
2.02
1.98
2.01
2.08
3.11
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

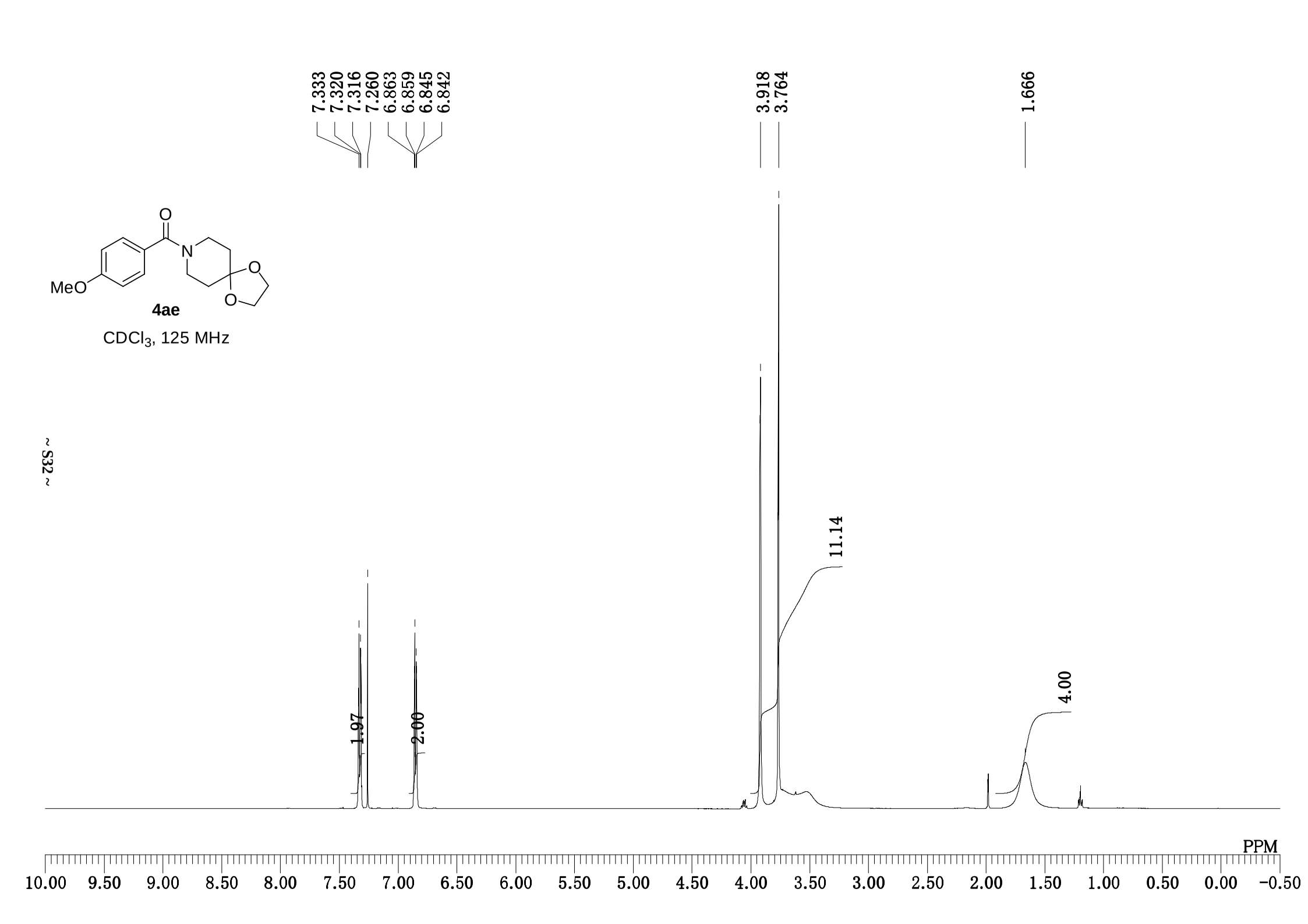

189.838
165.592
164.934
132.046
125.827
114.333
77.248
77.000
76.742
55.577
54.423
54.013
45.371
45.008
40.325
O
N
Me
N
O
MeO
3ad
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

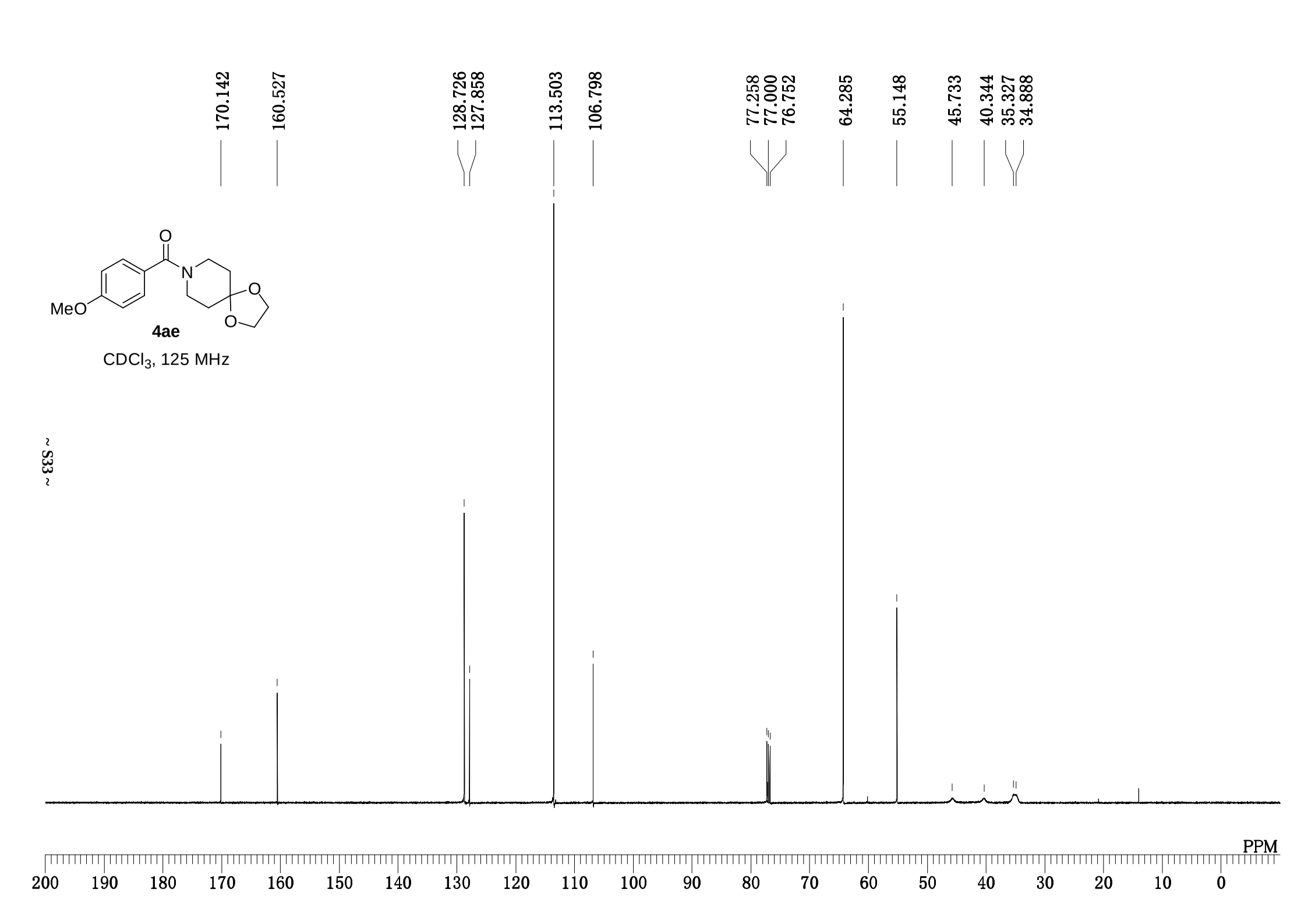

7.388
7.371
7.260
6.915
6.898
3.831
3.633
2.412
2.319
MeO
N
N
Me
O
4ad
CDCl3, 500 MHz
2.00
2.03
7.00
7.16
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

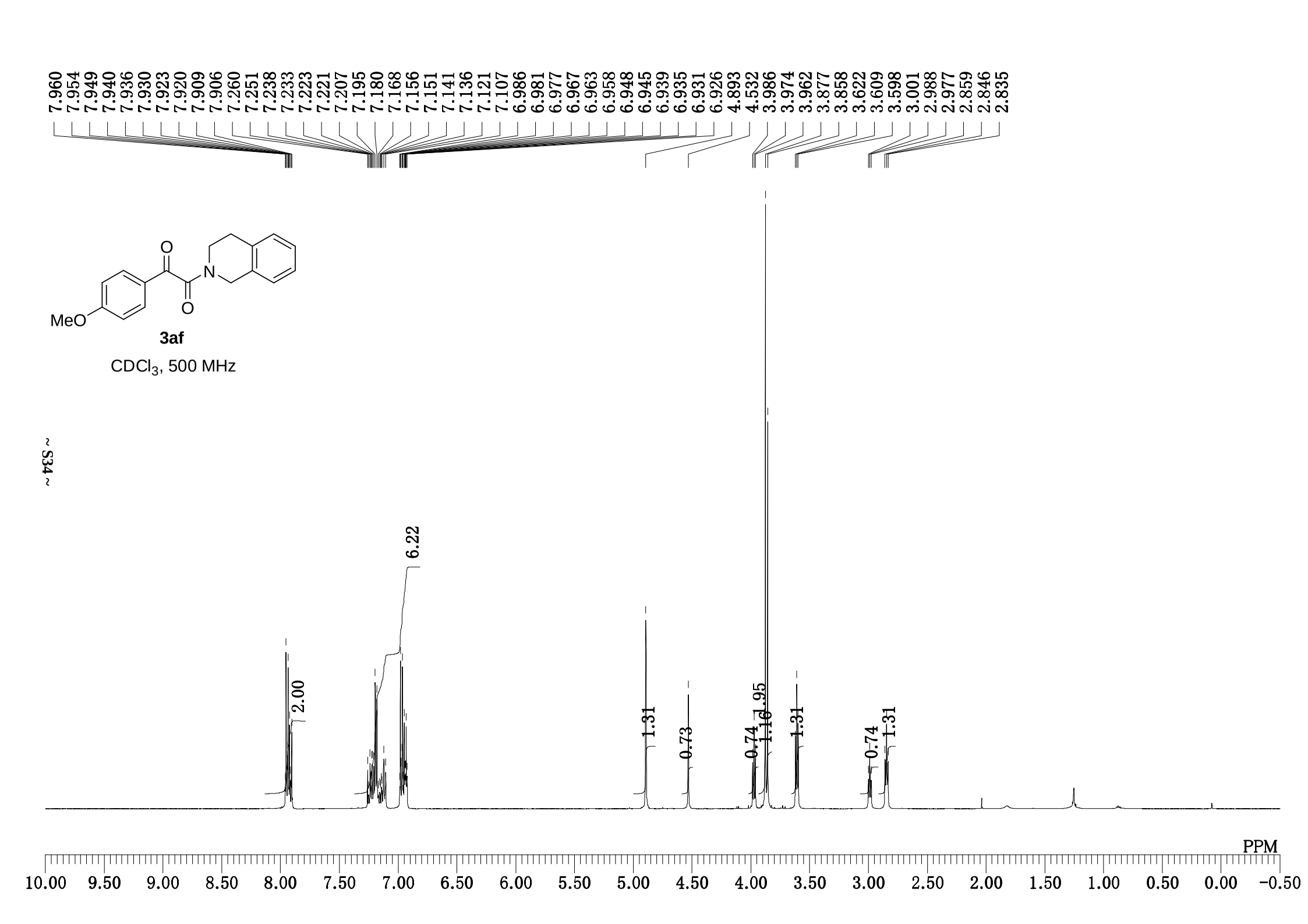

170.313
160.899
129.146
128.173
113.808
77.258
77.000
76.742
55.367
55.348
55.148
46.020
O
N
N
MeO
Me
4ad
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

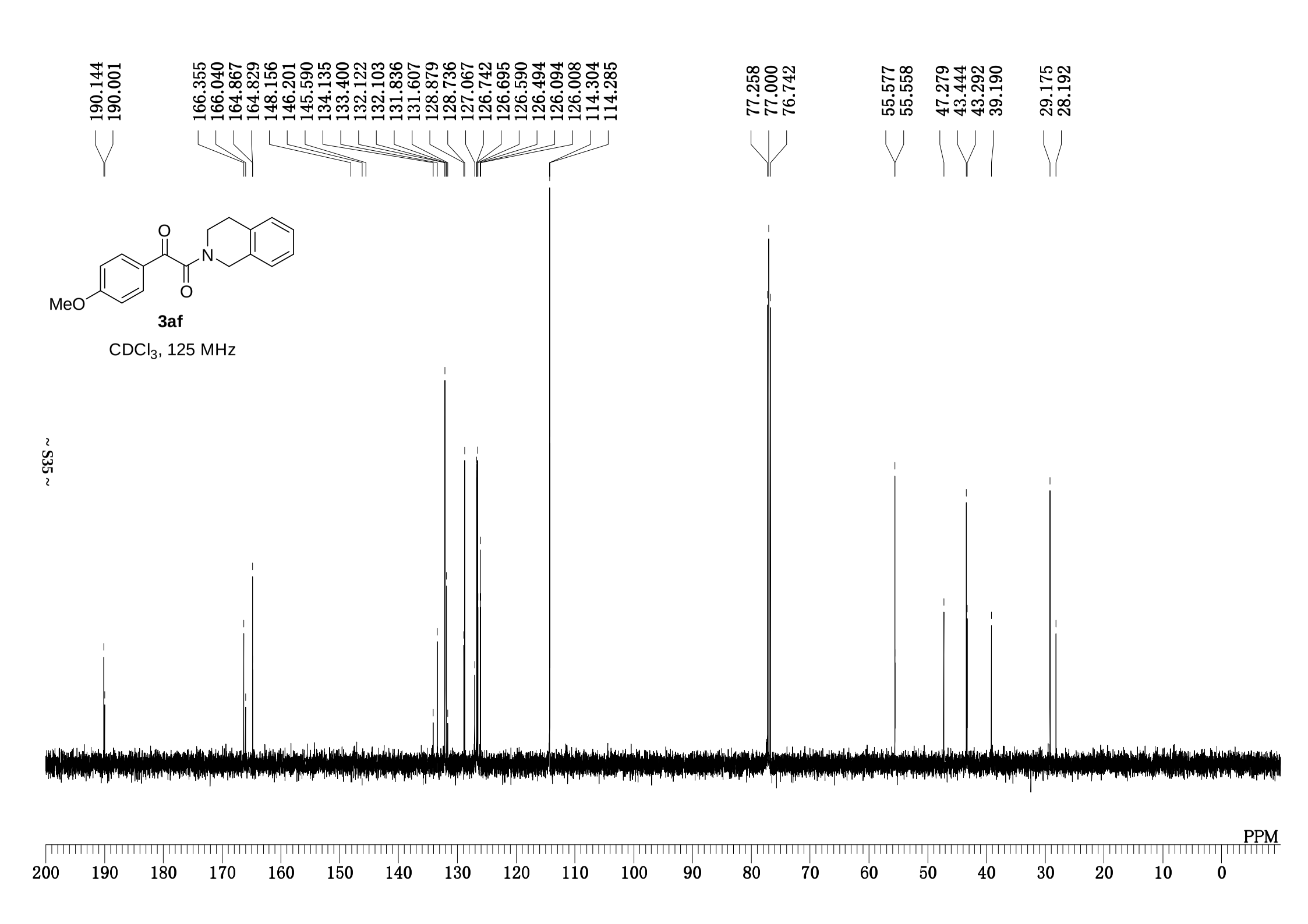

7.897
7.878
7.260
6.962
6.944
3.990
3.986
3.977
3.973
3.969
3.965
3.962
3.950
3.948
3.943
3.940
3.937
3.927
3.923
3.864
3.828
3.816
3.805
3.410
3.398
3.387
1.803
1.791
1.780
1.670
1.659
1.647
4.21
3.15
2.00
2.07
2.05
2.07
2.24
2.07
O
O
N
O
O
MeO
3ae
CDCl3, 500 MHz
~ S30 ~
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

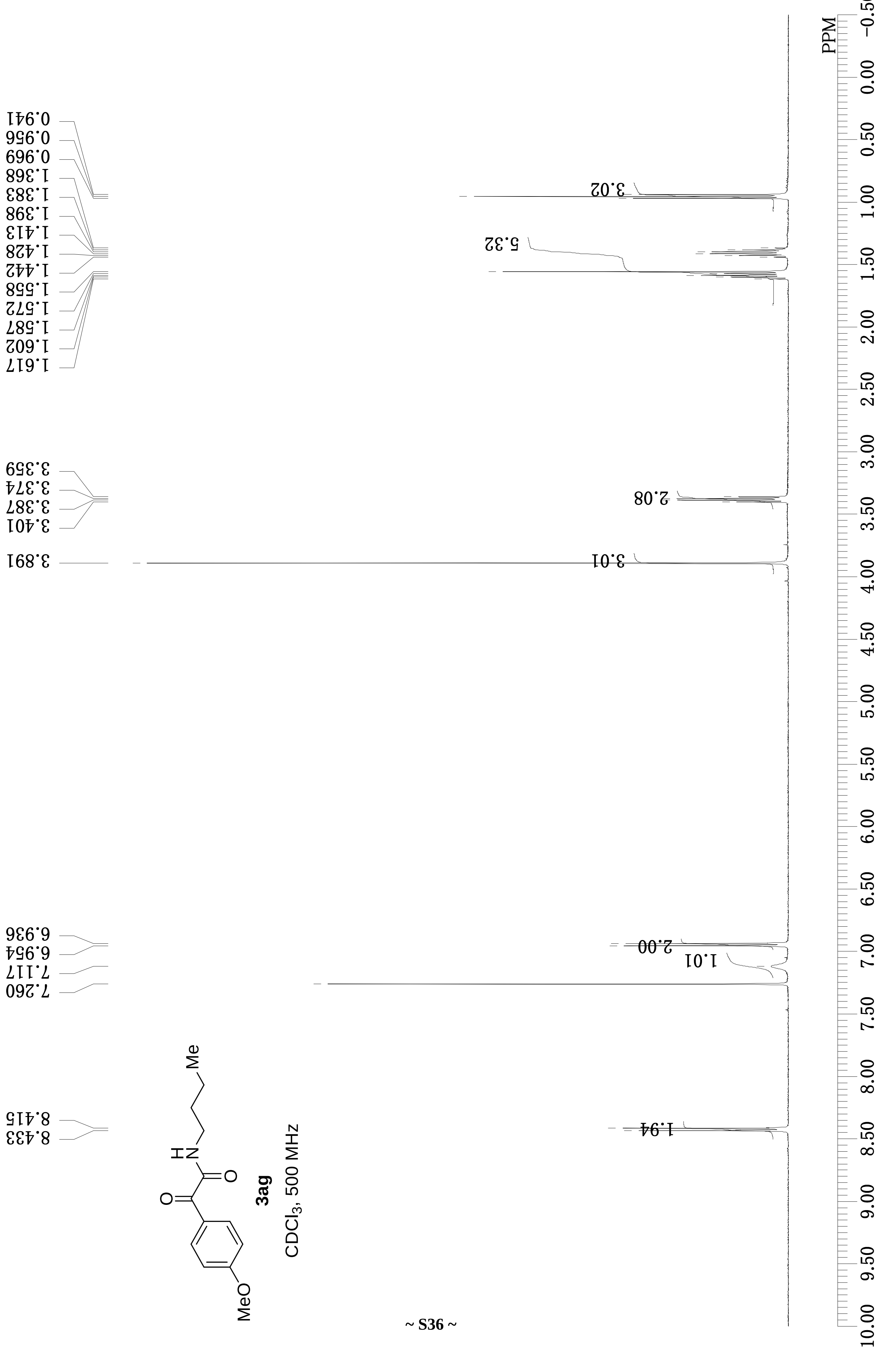

190.268
165.735
164.829
131.960
126.122
114.304
106.626
77.258
77.000
76.742
64.486
55.586
43.988
39.228
35.289
34.640
MeO
3ae
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

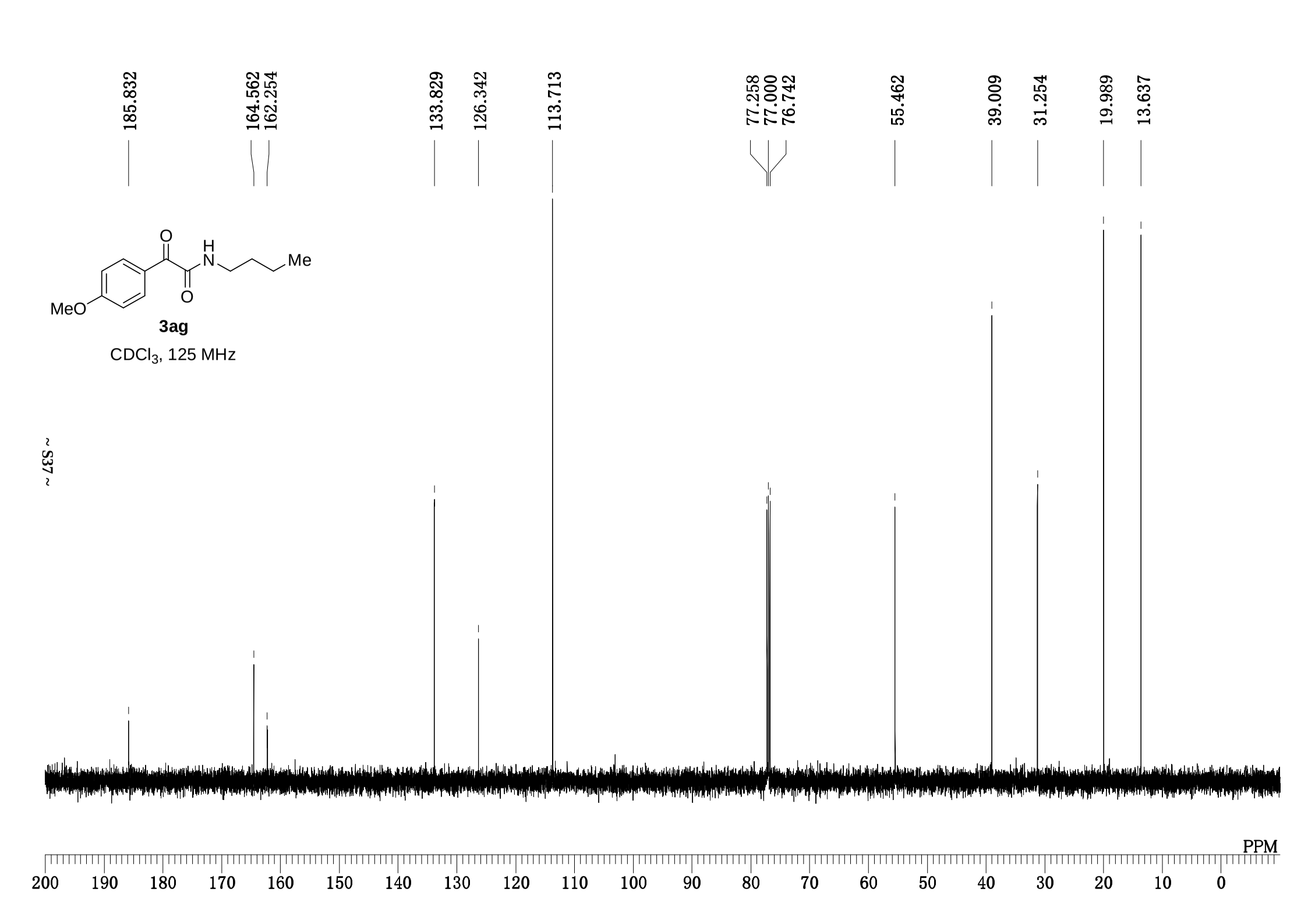

7.333
7.320
7.316
7.260
6.863
6.859
6.845
6.842
3.918
3.764
1.666
O
N
O
O
MeO
4ae
CDCl3, 125 MHz
11.14
4.00
1.97
2.00
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

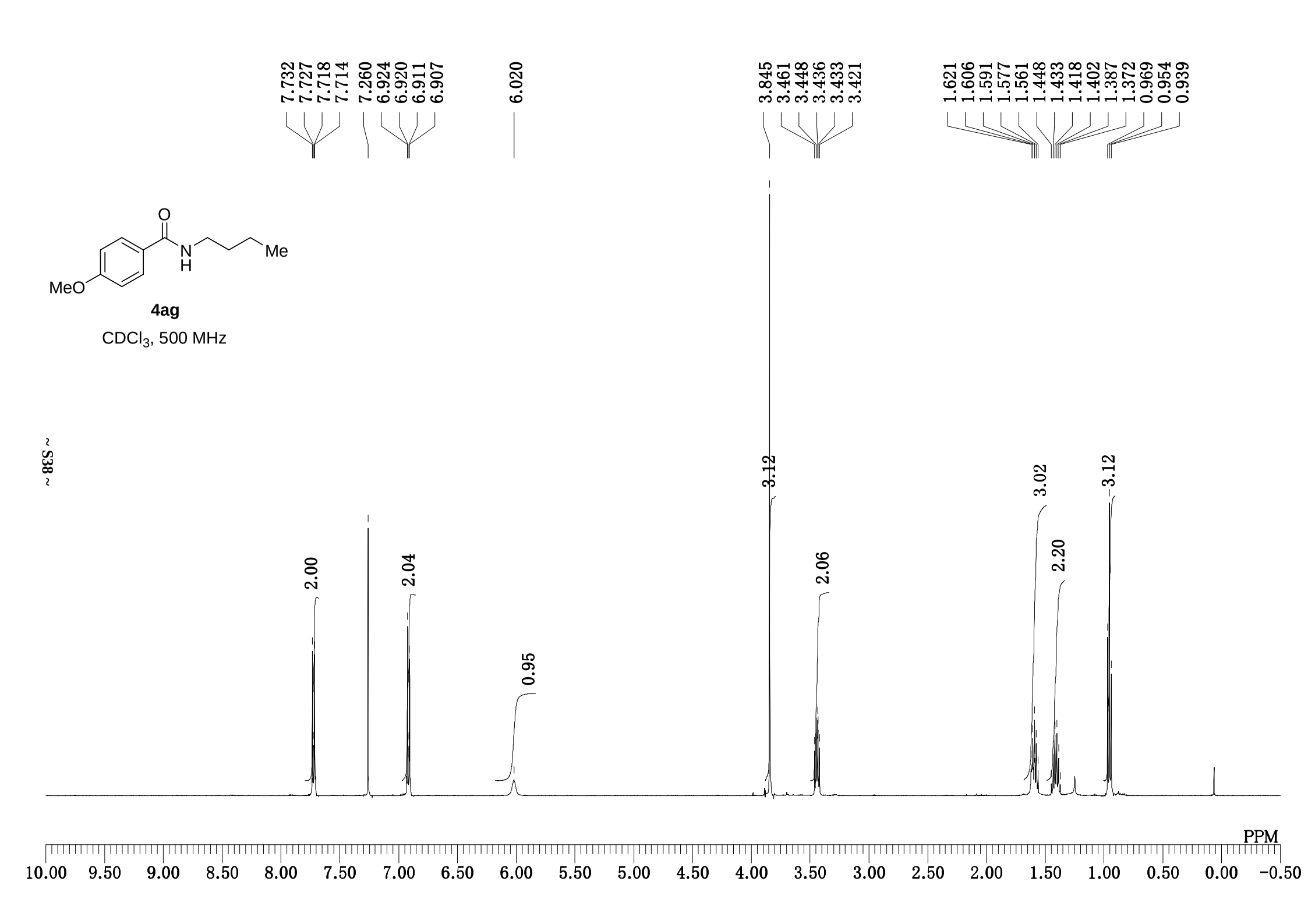

170.142
160.527
128.726
127.858
113.503
106.798
77.258
77.000
76.752
64.285
55.148
45.733
40.344
35.327
34.888
MeO
4ae
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

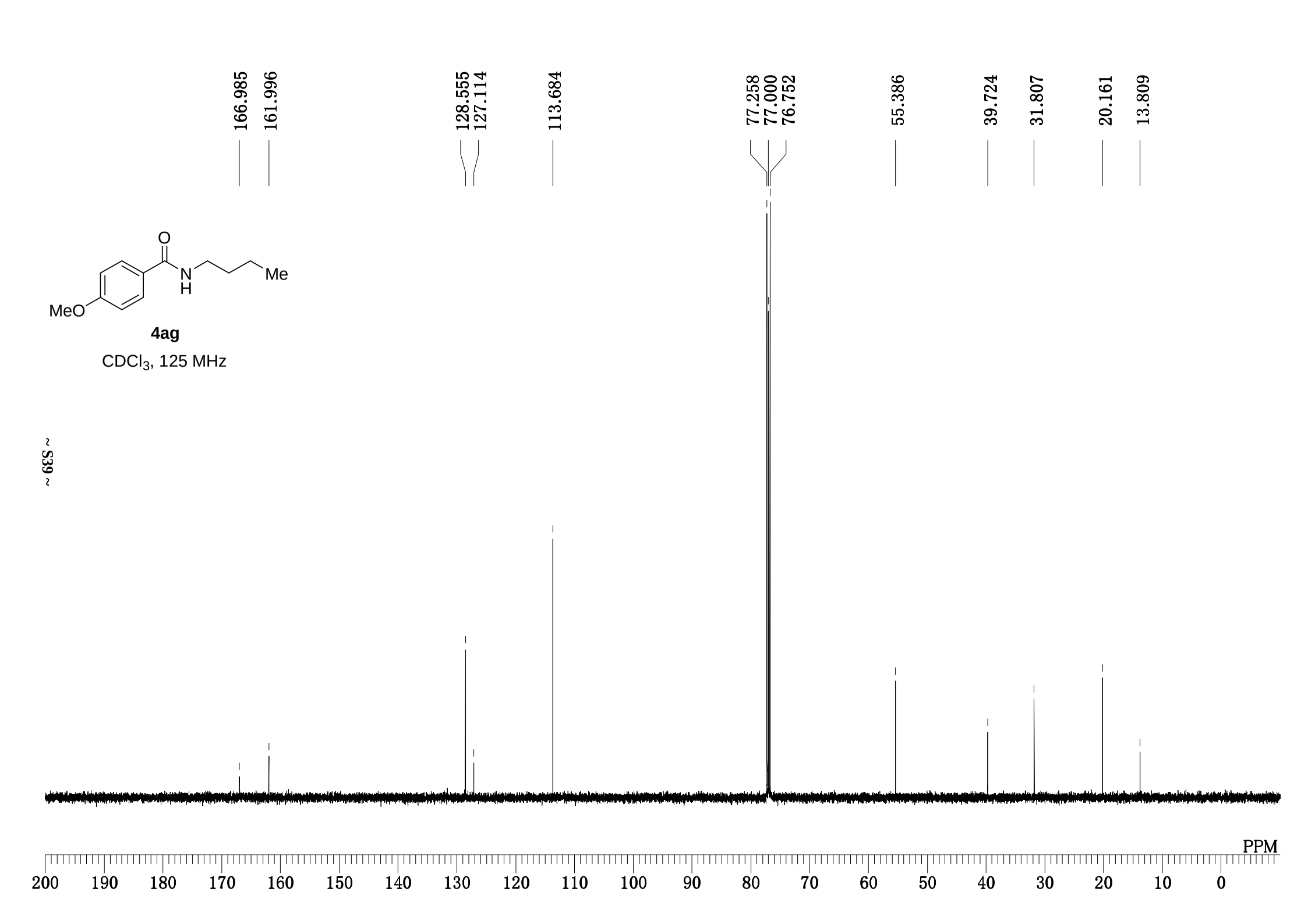

7.960
7.954
7.949
7.940
7.936
7.930
7.923
7.920
7.909
7.906
7.260
7.251
7.238
7.233
7.223
7.221
7.207
7.195
7.180
7.168
7.156
7.151
7.141
7.136
7.121
7.107
6.986
6.981
6.977
6.967
6.963
6.958
6.948
6.945
6.939
6.935
6.931
6.926
4.893
4.532
3.986
3.974
3.962
3.877
3.858
3.622
3.609
3.598
3.001
2.988
2.977
2.859
2.846
2.835
O
N
O
MeO
3af
CDCl3, 500 MHz
~ S34 ~
6.22
2.00
1.31
0.73
0.74
1.16
1.95
1.31
0.74
1.31
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

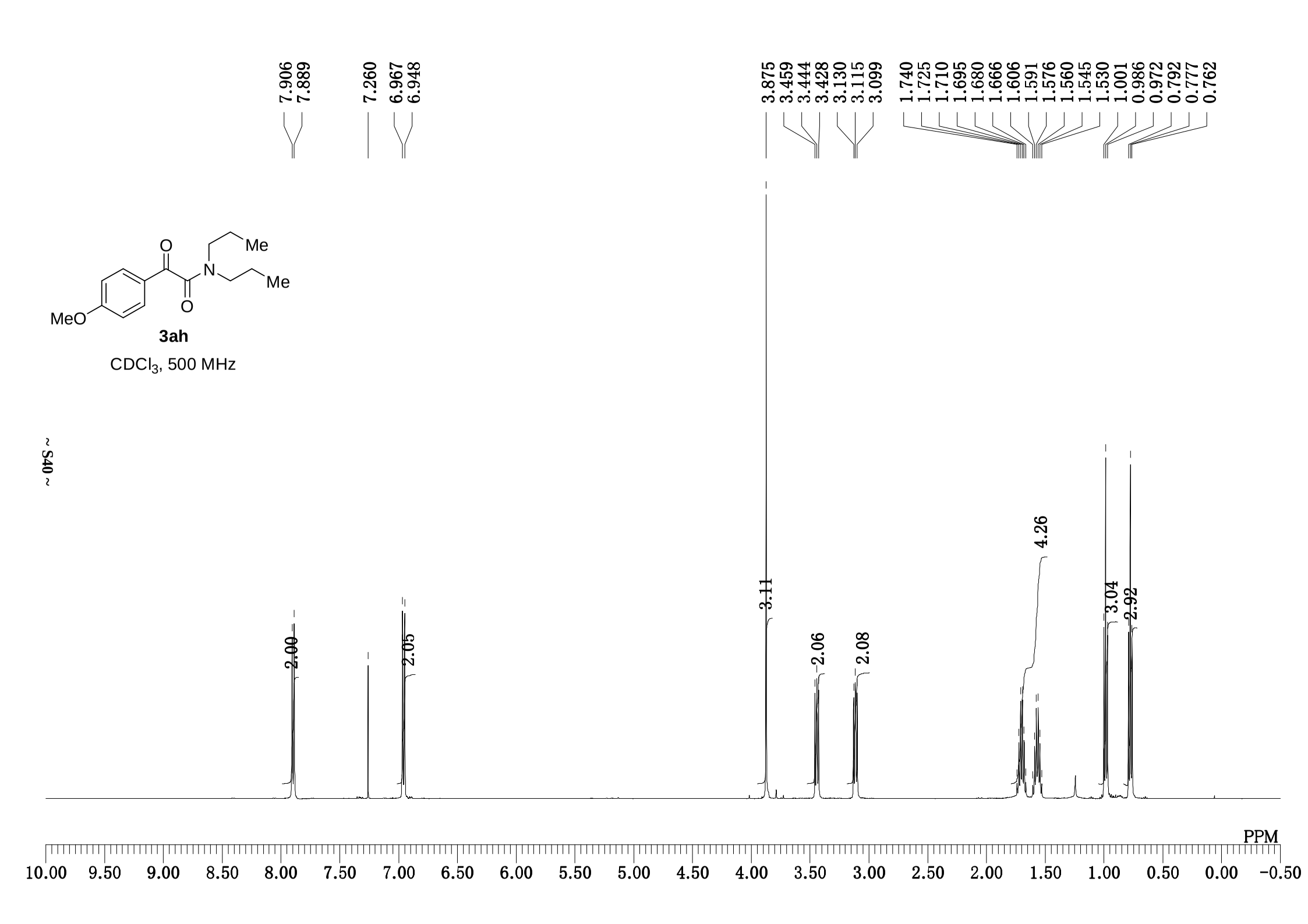

190.144
190.001
166.355
166.040
164.867
164.829
148.156
146.201
145.590
134.135
133.400
132.122
132.103
131.836
131.607
128.879
128.736
127.067
126.742
126.695
126.590
126.494
126.094
126.008
114.304
114.285
77.258
77.000
76.742
55.577
55.558
47.279
43.444
43.292
39.190
29.175
28.192
O
N
O
MeO
3af
CDCl3, 125 MHz
~ S35 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


0.941
0.956
0.969
1.368
1.383
1.398
1.413
1.428
1.442
1.558
1.572
1.587
1.602
1.617
3.359
3.374
3.387
3.401
3.891
6.936
6.954
7.117
7.260
8.415
8.433
3.02
5.32
2.08
3.01
2.00
1.01
1.94
PPM
MeO
O
O
H
N
Me
3ag
CDCl3, 500 MHz

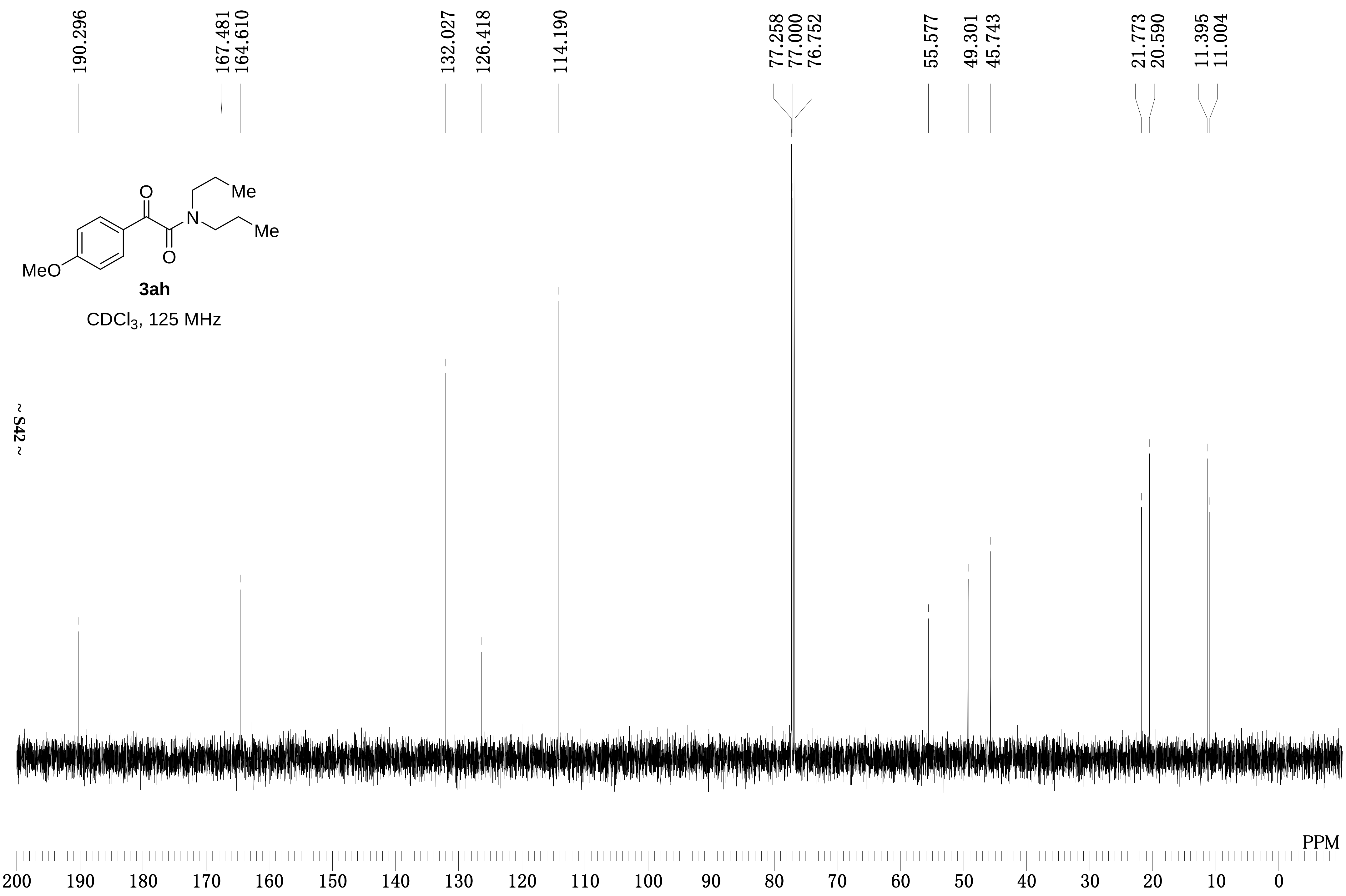

185.832
164.562
162.254
133.829
126.342
113.713
77.258
77.000
76.742
55.462
39.009
31.254
19.989
13.637
O
H
N
Me
O
MeO
3ag
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

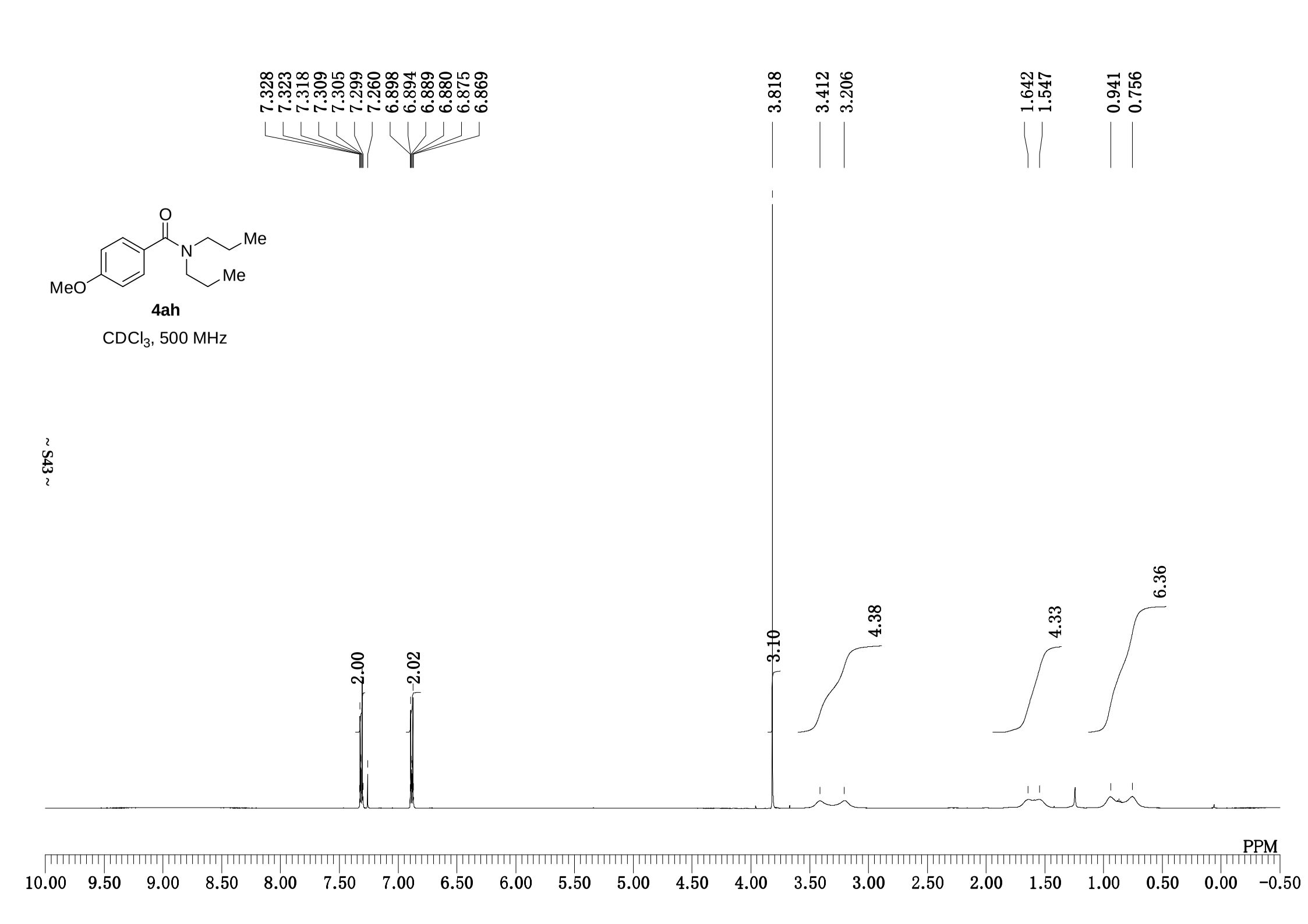

7.732
7.727
7.718
7.714
7.260
6.924
6.920
6.911
6.907
6.020
3.845
3.461
3.448
3.436
3.433
3.421
1.621
1.606
1.591
1.577
1.561
1.448
1.433
1.418
1.402
1.387
1.372
0.969
0.954
0.939
O
N
H
Me
MeO
4ag
CDCl3, 500 MHz
~ S38 ~
2.00
2.04
0.95
3.12
2.06
3.02
2.20
3.12
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

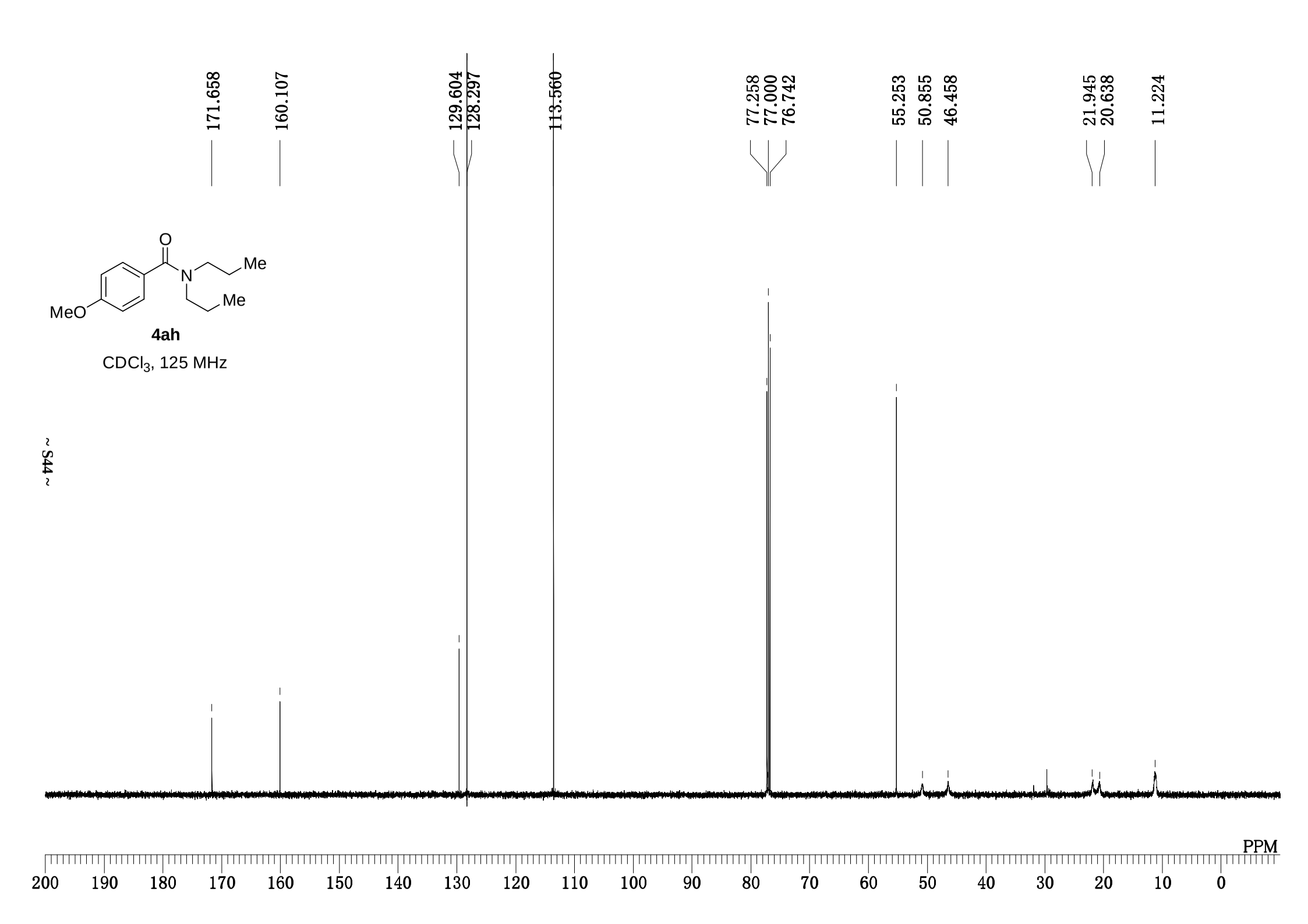

166.985
161.996
128.555
127.114
113.684
77.258
77.000
76.752
55.386
39.724
31.807
20.161
13.809
O
N
H
Me
MeO
4ag
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

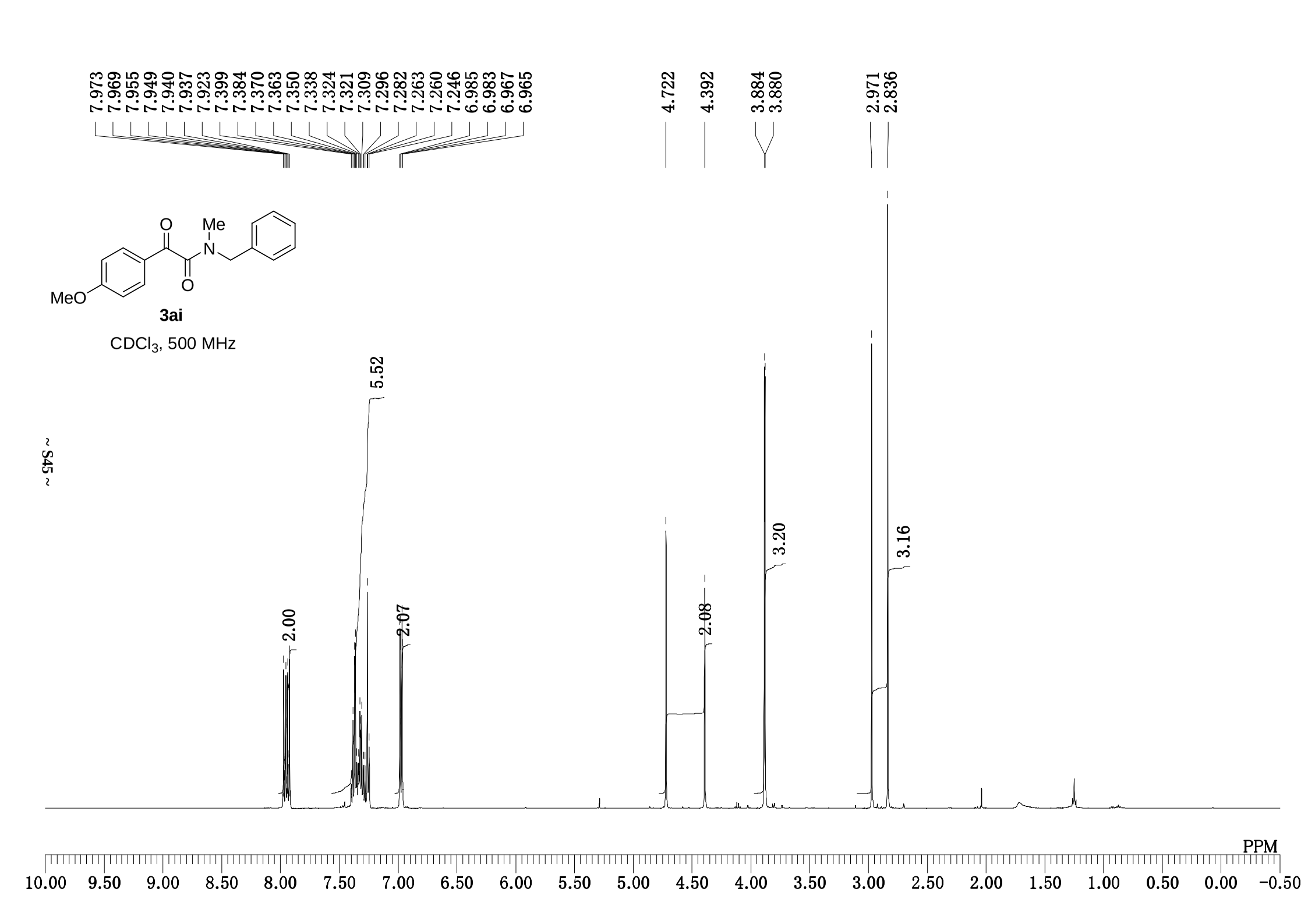

7.906
7.889
7.260
6.967
6.948
3.875
3.459
3.444
3.428
3.130
3.115
3.099
1.740
1.725
1.710
1.695
1.680
1.666
1.606
1.591
1.576
1.560
1.545
1.530
1.001
0.986
0.972
0.792
0.777
0.762
O
Me
N
Me
O
MeO
3ah
CDCl3, 500 MHz
~ S40 ~
2.00
2.05
3.11
2.06
2.08
4.26
3.04
2.92
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

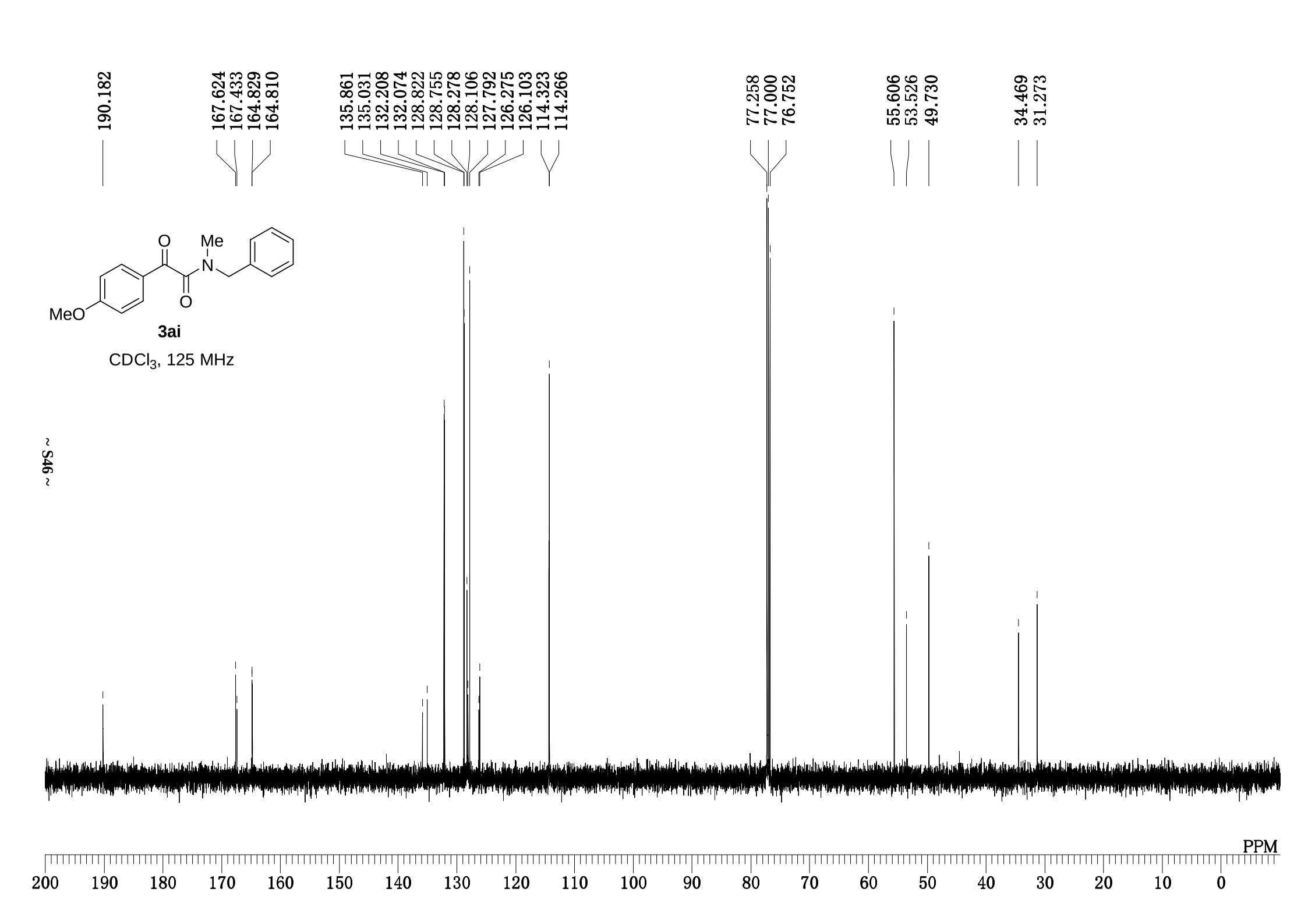
0.762
0.777
0.792
0.972
0.986
1.001
1.244
1.530
1.545
1.560
1.576
1.591
1.606
1.666
1.680
1.695
1.710
1.725
1.740
3.099
3.115
3.130
3.428
3.444
3.459
3.875
7.906
7.889
7.260
6.967
6.948
2.92
3.04
2.20
2.06
2.09
2.07
3.11
2.05
2.00
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50
Me
Me
N
O
O
MeO
3ah
CDCl3, 500 MHz


190.296
167.481
164.610
132.027
126.418
114.190
77.258
77.000
76.752
55.577
49.301
45.743
21.773
20.590
11.395
11.004
O
Me
N
Me
O
MeO
3ah
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

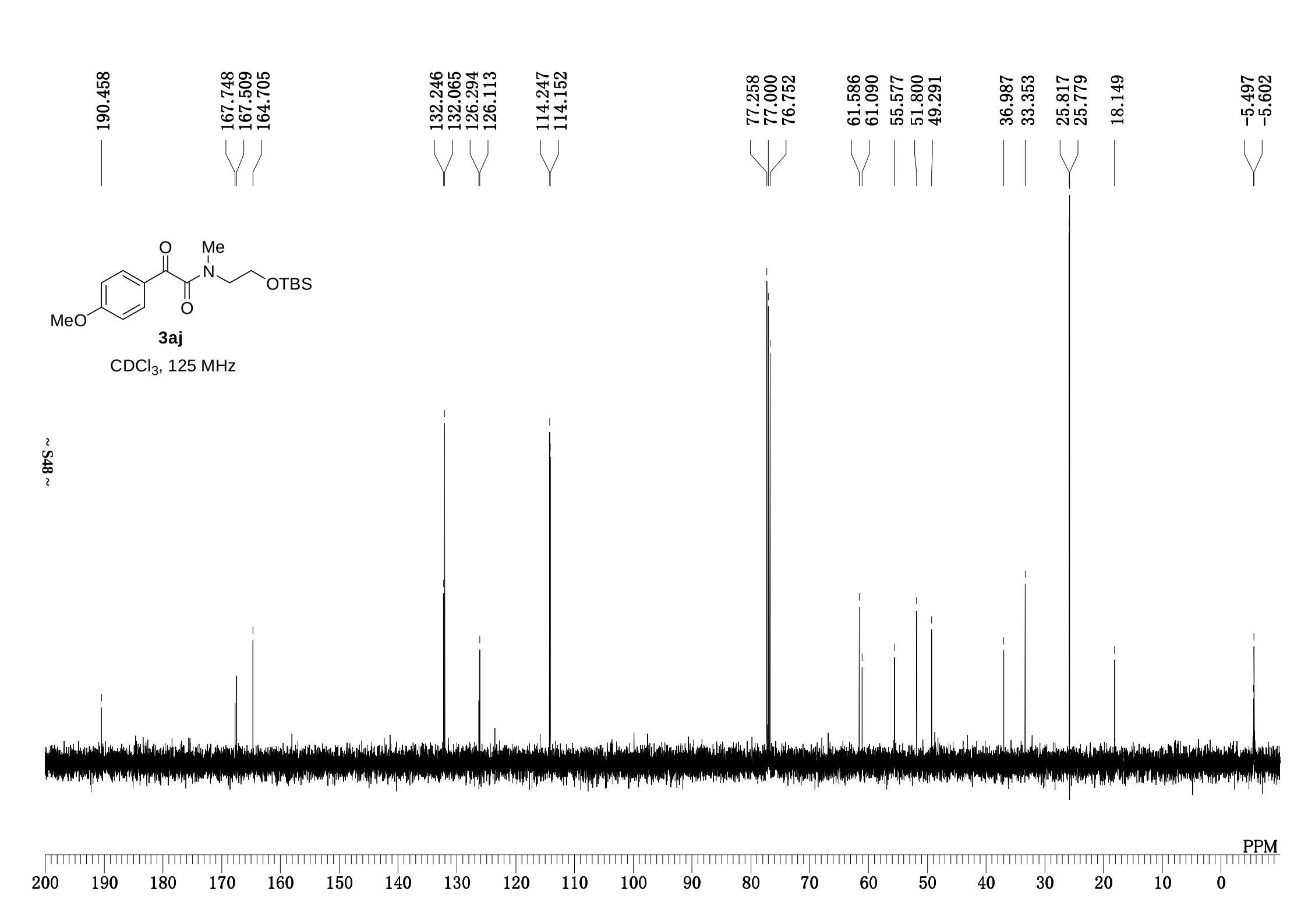

7.328
7.323
7.318
7.309
7.305
7.299
7.260
6.898
6.894
6.889
6.880
6.875
6.869
3.818
3.412
3.206
1.642
1.547
0.941
0.756
O
N
Me
Me
MeO
4ah
CDCl3, 500 MHz
2.00
2.02
3.10
4.38
4.33
6.36
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

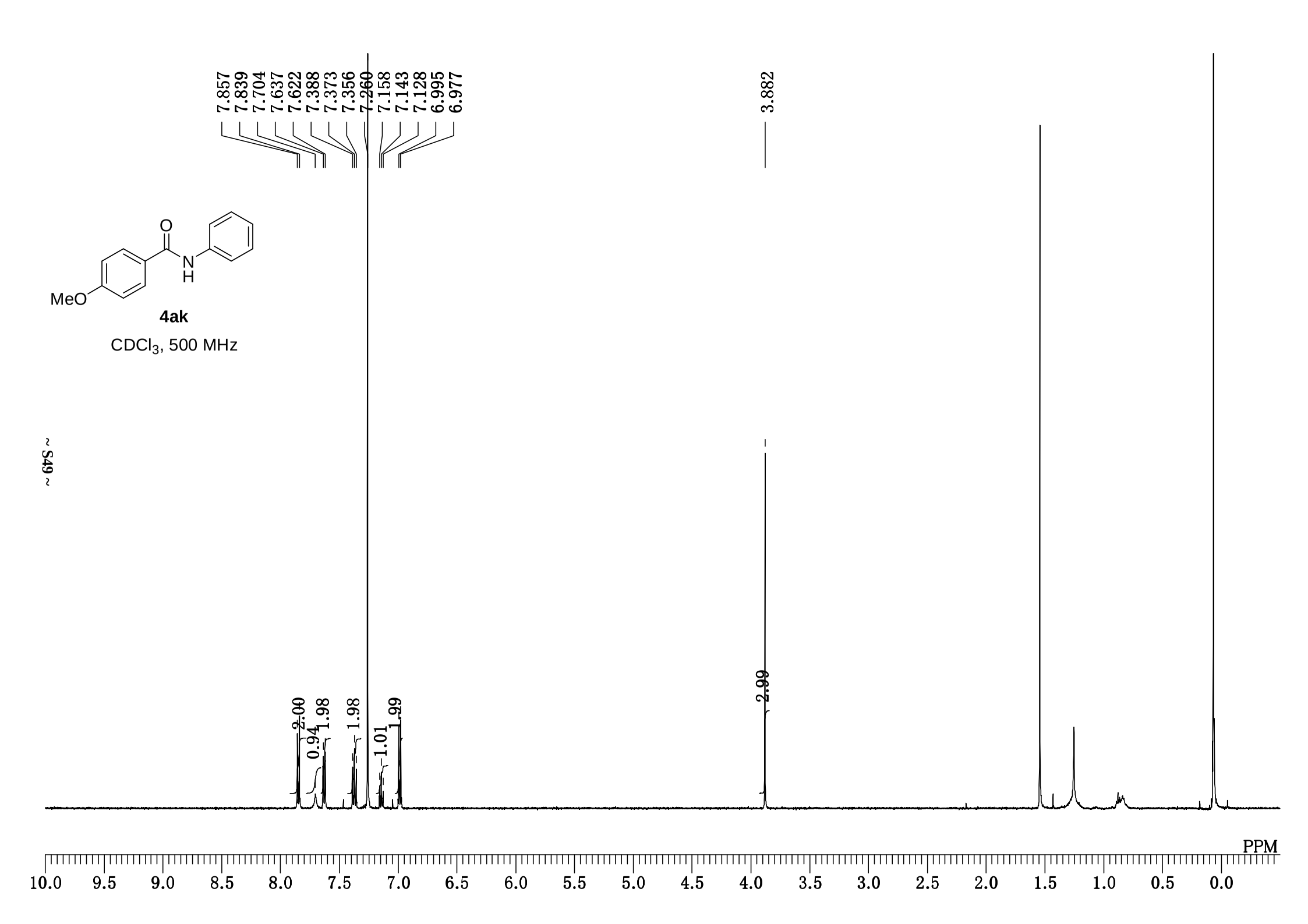

171.658
160.107
129.604
128.297
113.560
77.258
77.000
76.742
55.253
50.855
46.458
21.945
20.638
11.224
O
N
Me
Me
MeO
4ah
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

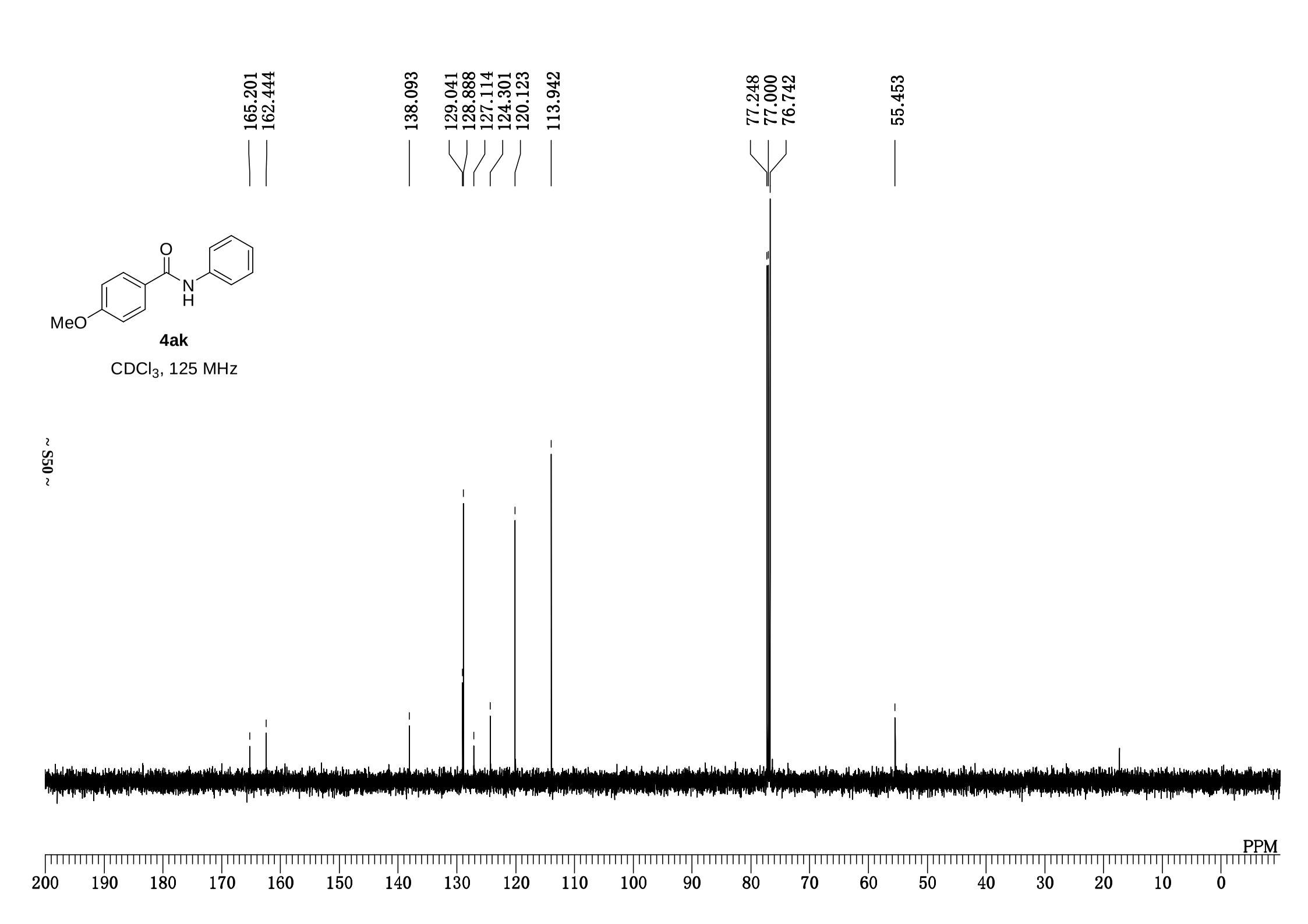

7.973
7.969
7.955
7.949
7.940
7.937
7.923
7.399
7.384
7.370
7.363
7.350
7.338
7.324
7.321
7.309
7.296
7.282
7.263
7.260
7.246
6.985
6.983
6.967
6.965
4.722
4.392
3.884
3.880
2.971
2.836
O
Me
N
O
MeO
3ai
CDCl3, 500 MHz
5.52
2.00
2.07
2.08
3.20
3.16
~ S45 ~
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

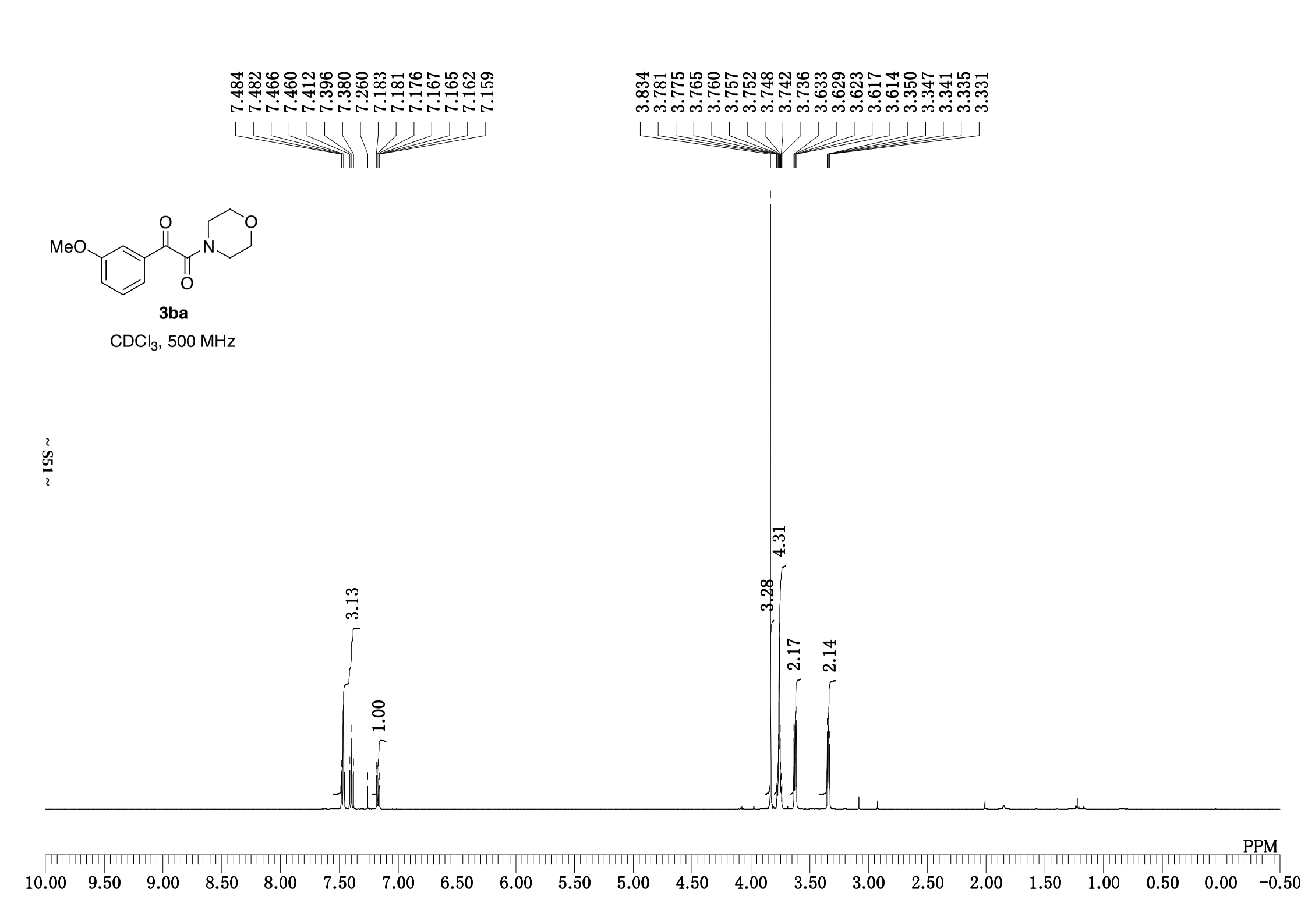

190.182
167.624
167.433
164.829
164.810
135.861
135.031
132.208
132.074
128.822
128.755
128.278
128.106
127.792
126.275
126.103
114.323
114.266
77.258
77.000
76.752
55.606
53.526
49.730
34.469
31.273
O
Me
N
O
MeO
3ai
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

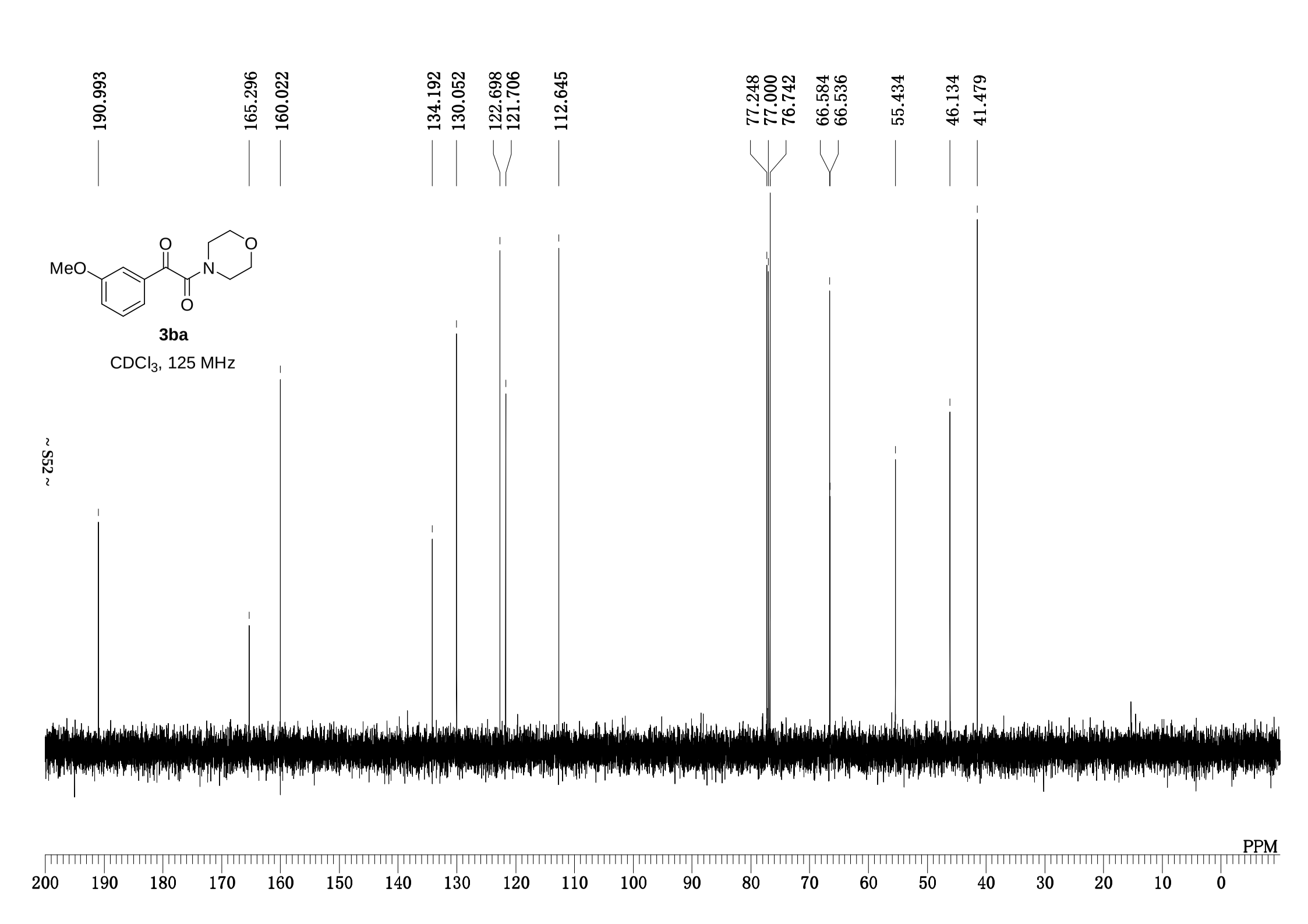
7.927
7.921
7.915
7.910
7.907
7.904
7.897
7.891
7.260
6.961
6.957
6.951
6.947
6.943
6.937
6.934
3.910
3.900
3.888
3.872
3.867
3.713
3.702
3.690
3.643
3.633
3.623
3.351
3.340
3.328
3.147
3.018
0.896
0.831
9.50
0.091
−0.025
6.18
2.00
2.07
1.11
3.02
0.96
1.02
0.97
1.47
1.59
Me
N
OTBS
O
O
MeO
3aj
CDCl3, 500 MHz
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

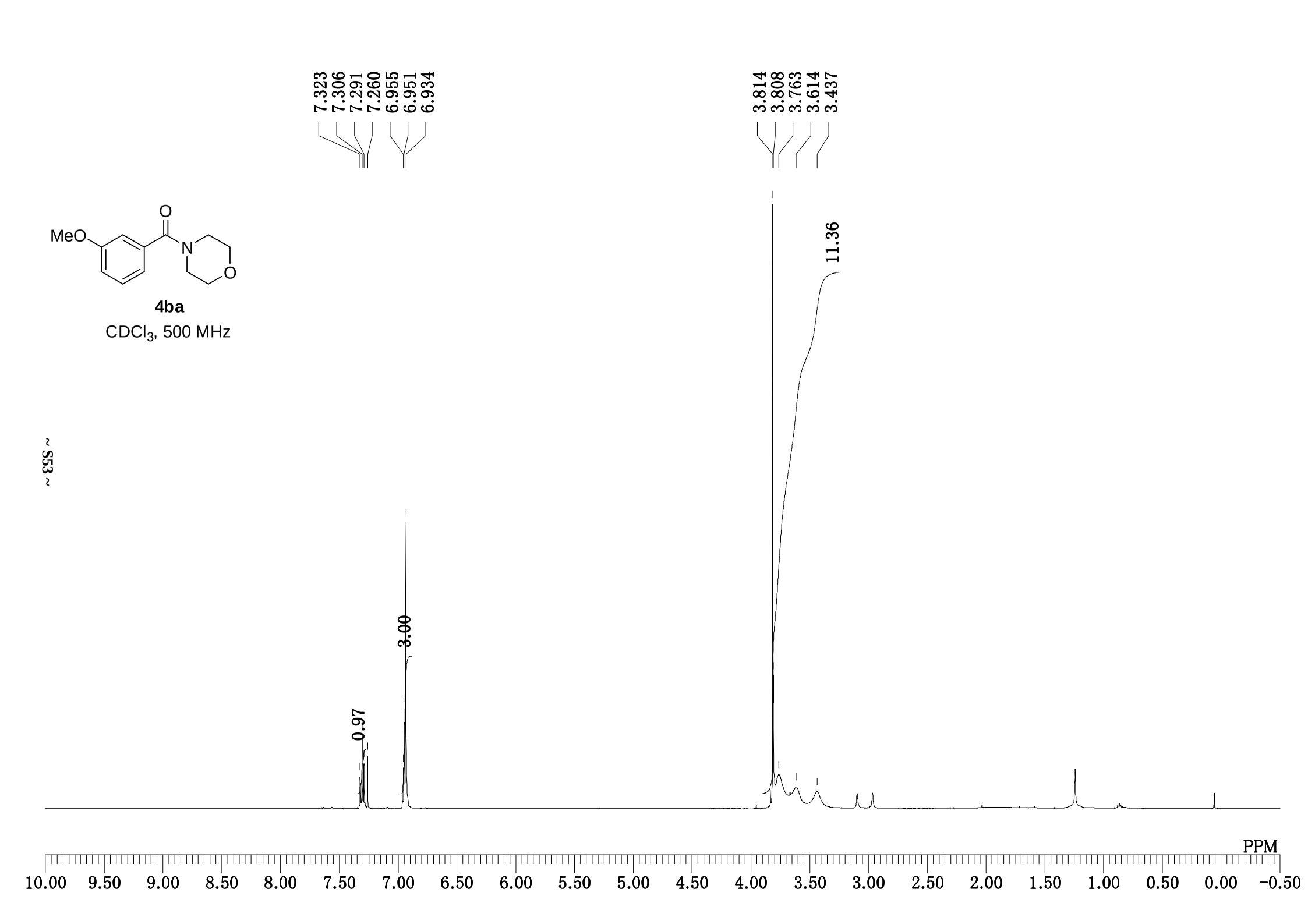

190.458
167.748
167.509
164.705
132.246
132.065
126.294
126.113
114.247
114.152
77.258
77.000
76.752
61.586
61.090
55.577
51.800
49.291
36.987
33.353
25.817
25.779
18.149
−5.497
−5.602
O
Me
N
OTBS
O
MeO
3aj
CDCl3, 125 MHz
~ S48 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

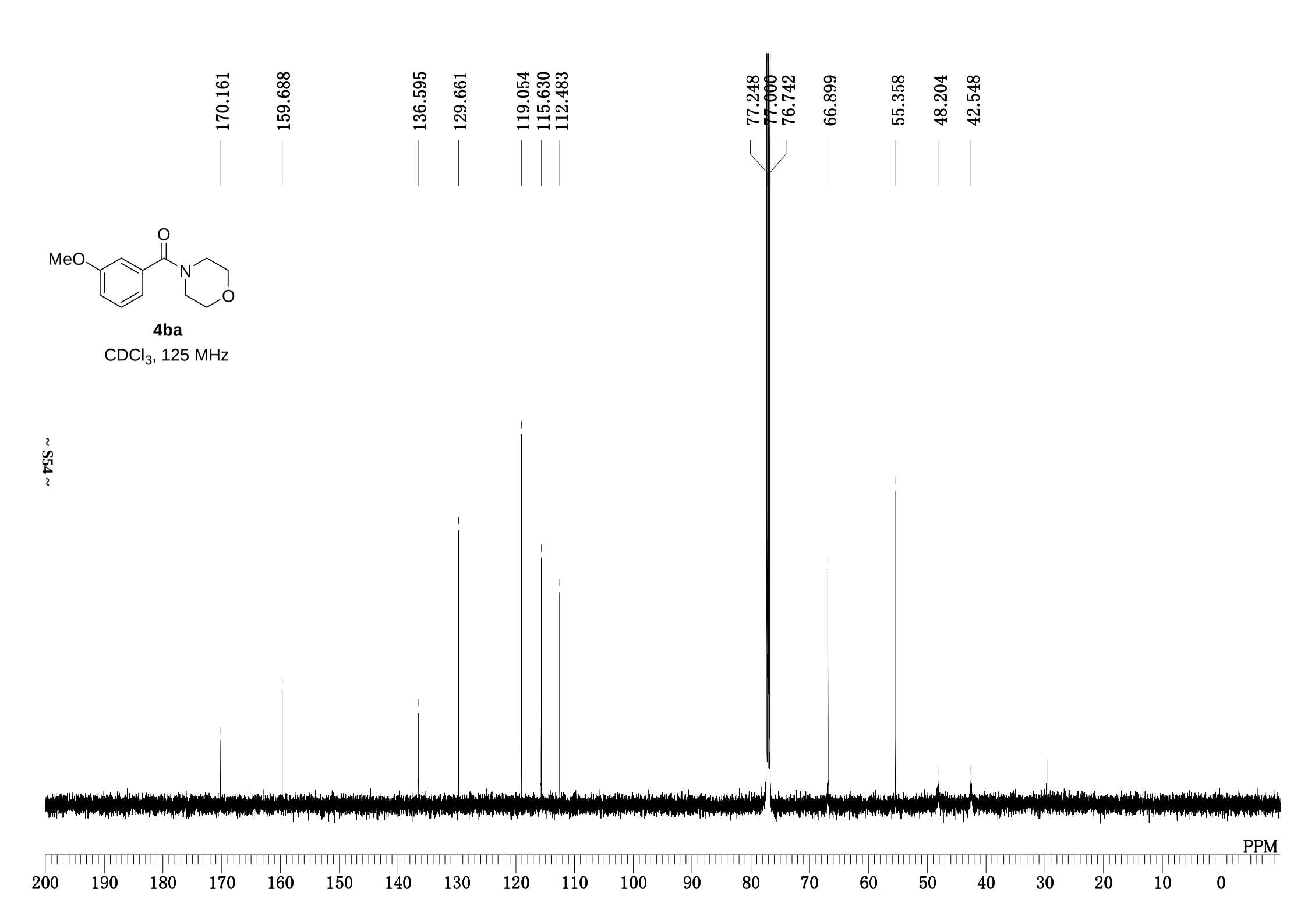

7.857
7.839
7.704
7.637
7.622
7.388
7.373
7.356
7.260
7.158
7.143
7.128
6.995
6.977
3.882
2.00
0.94
1.98
1.98
1.01
1.99
2.99
MeO
O
N
H
4ak
CDCl3, 500 MHz
PPM
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

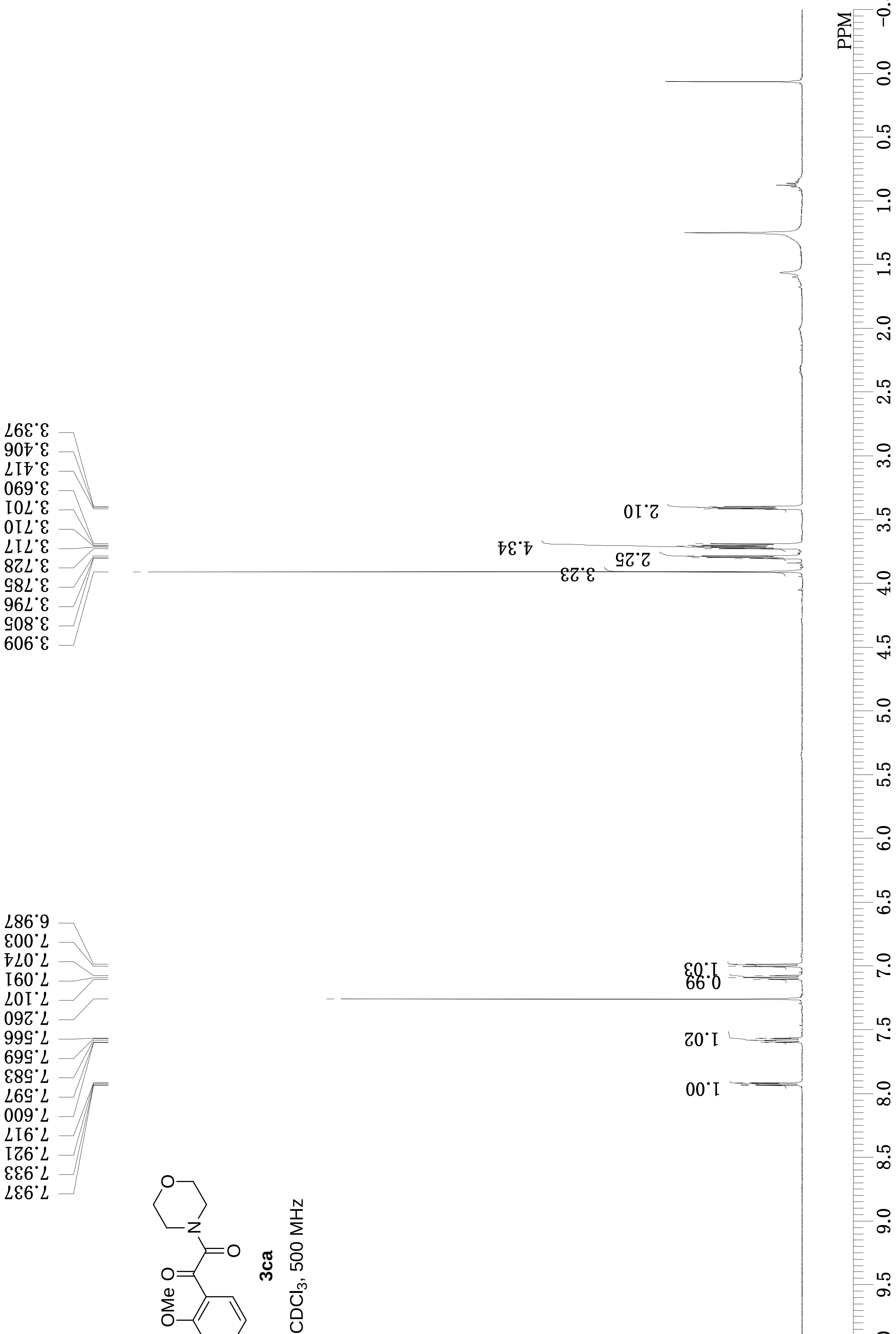

165.201
162.444
138.093
129.041
128.888
127.114
124.301
120.123
113.942
77.248
77.000
76.742
55.453
O
N
H
MeO
4ak
CDCl3, 125 MHz
~ S50 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

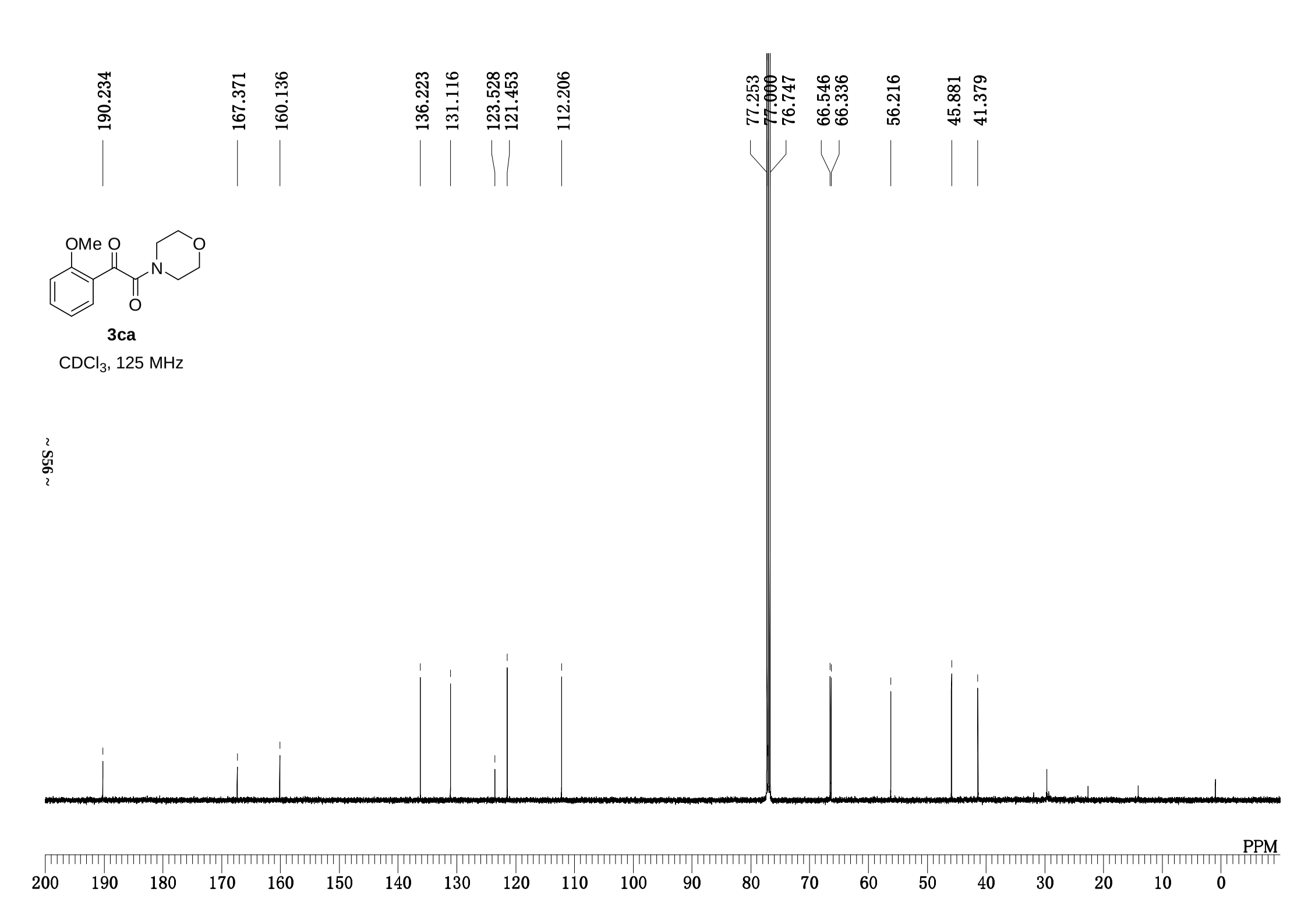

7.484
7.482
7.466
7.460
7.412
7.396
7.380
7.260
7.183
7.181
7.176
7.167
7.165
7.162
7.159
3.834
3.781
3.775
3.765
3.760
3.757
3.752
3.748
3.742
3.736
3.633
3.629
3.623
3.617
3.614
3.350
3.347
3.341
3.335
3.331
MeO
O
O
N
O
3ba
CDCl3, 500 MHz
3.13
1.00
3.28
4.31
2.17
2.14
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

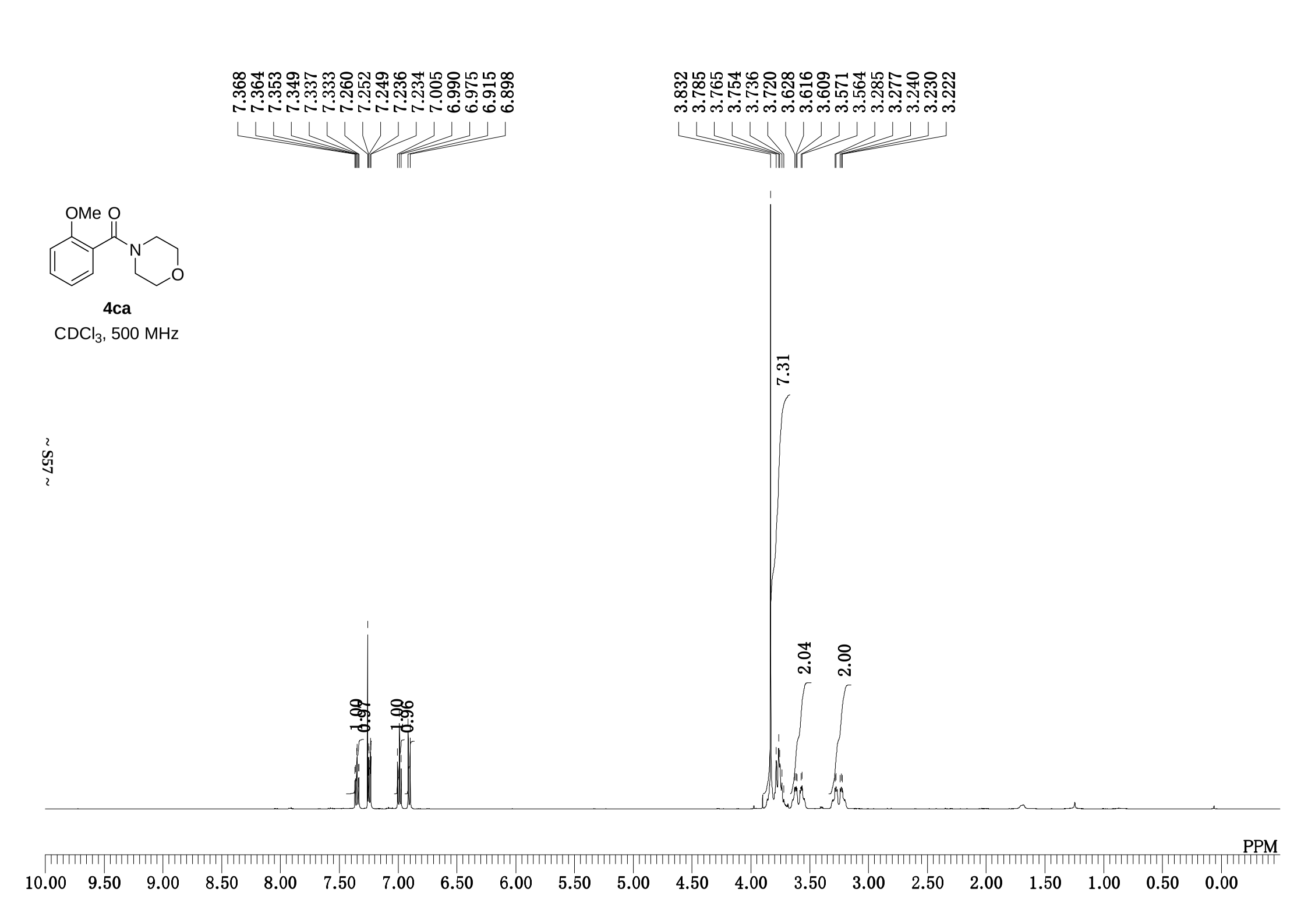

190.993
165.296
160.022
134.192
130.052
122.698
121.706
112.645
77.248
77.000
76.742
66.584
66.536
55.434
46.134
41.479
MeO
O
N
O
O
3ba
CDCl3, 125 MHz
~ S52 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

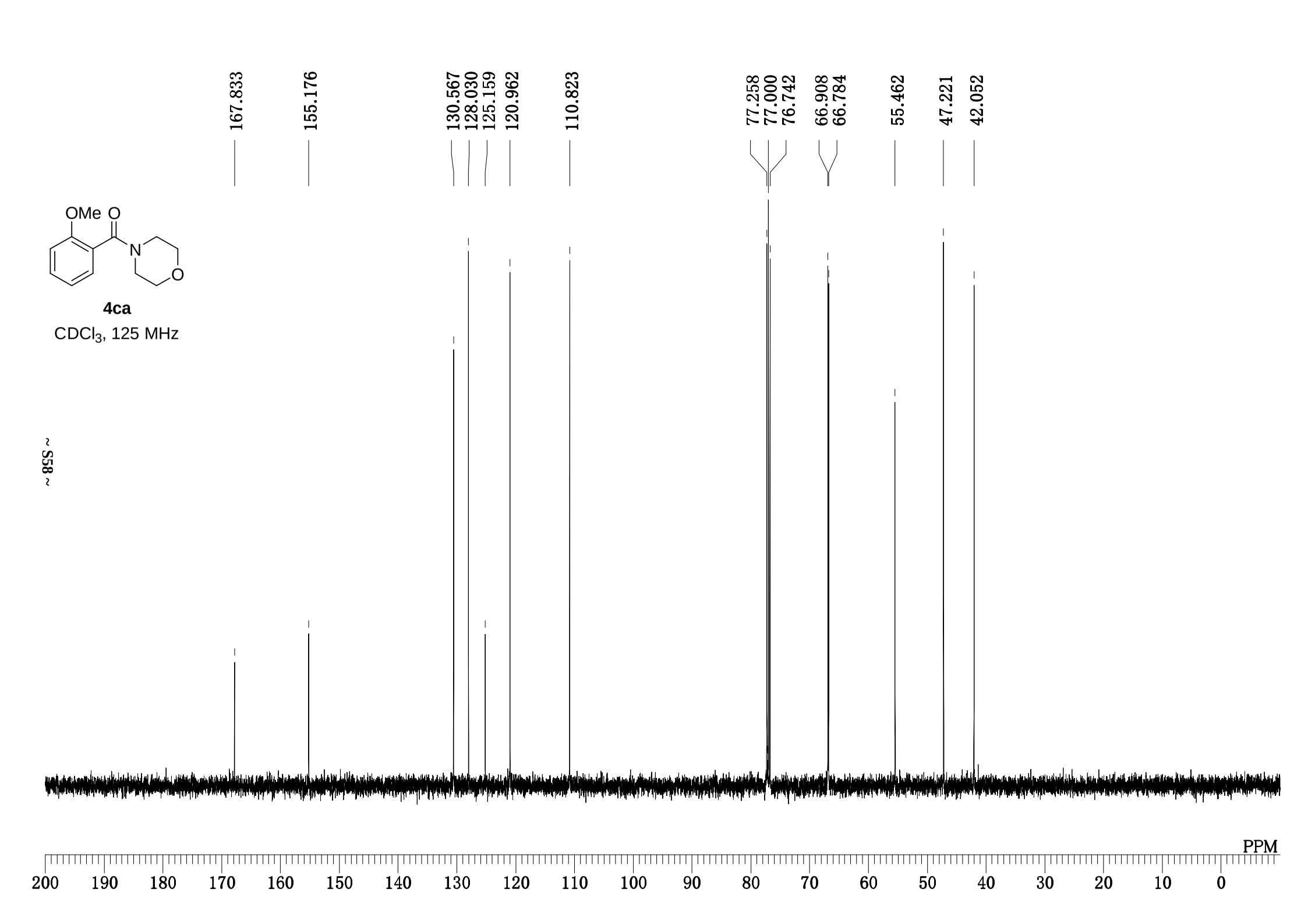

7.323
7.306
7.291
7.260
6.955
6.951
6.934
3.814
3.808
3.763
3.614
3.437
11.36
3.00
0.97
MeO
O
N
O
4ba
CDCl3, 500 MHz
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

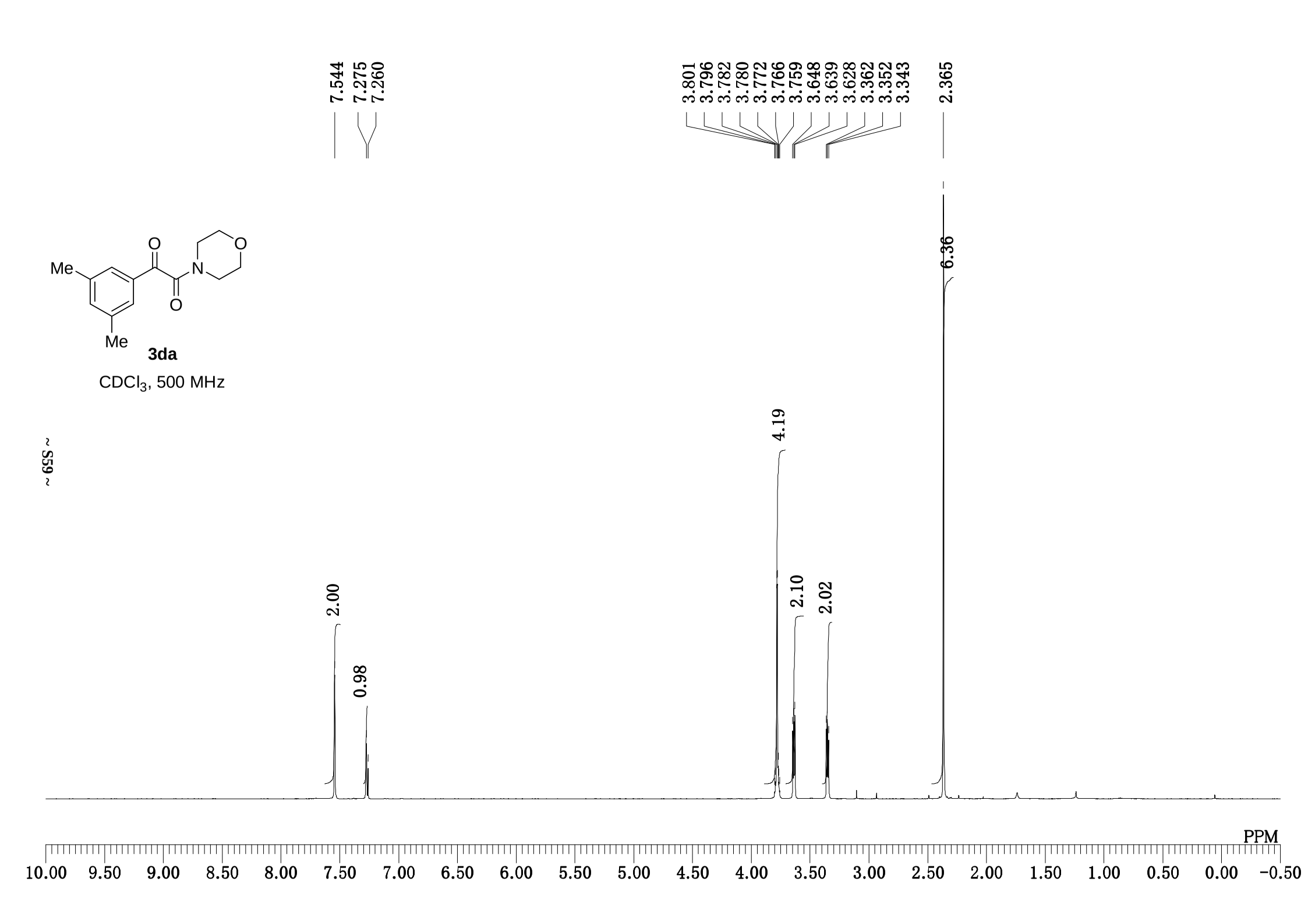

170.161
159.688
136.595
129.661
119.054
115.630
112.483
77.248
77.000
76.742
66.899
55.358
48.204
42.548
MeO
O
N
O
4ba
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

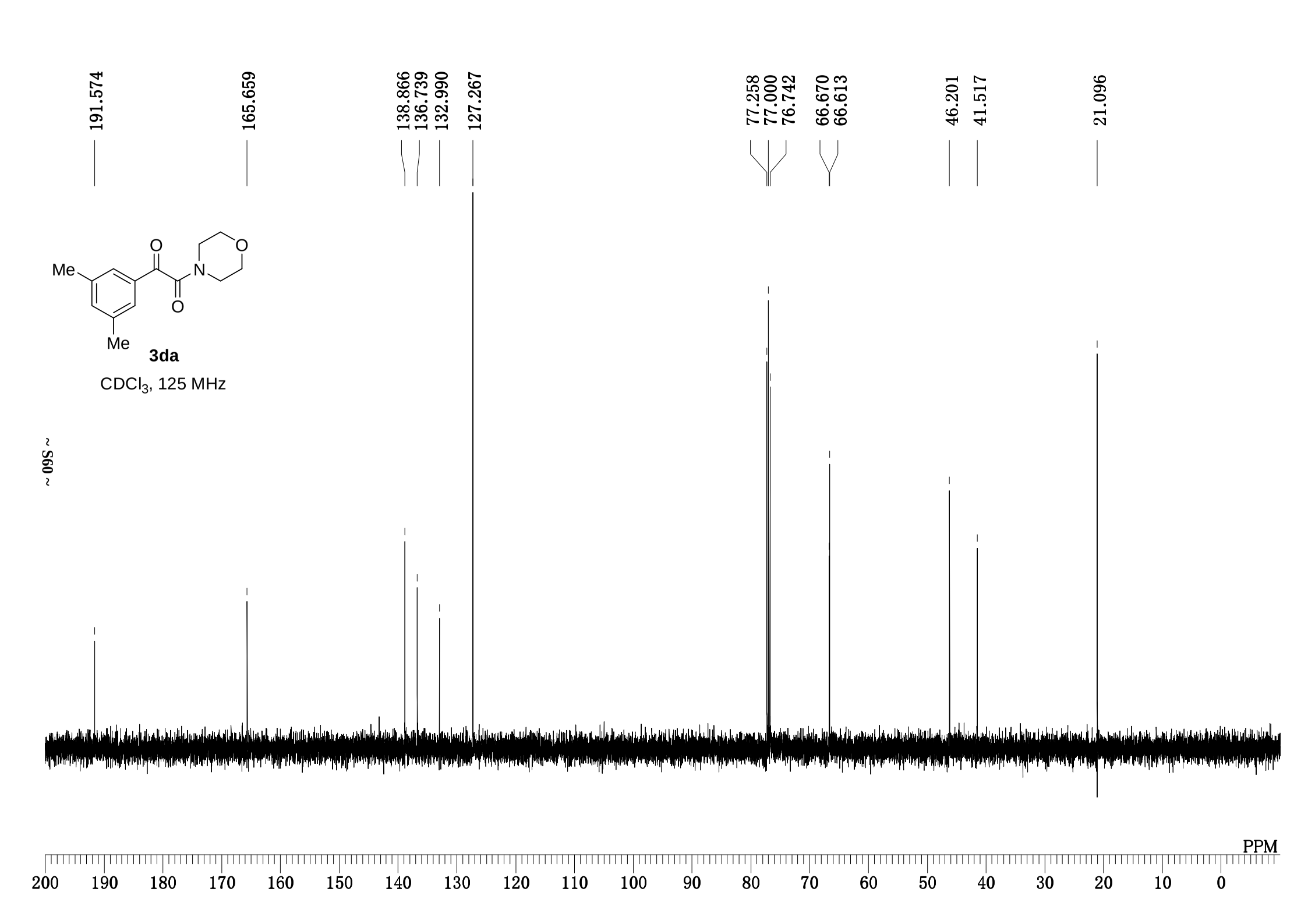

3ca
CDCl3, 500 MHz
OMe
O
N
PPM
7.937
7.933
7.921
7.917
7.600
7.597
7.583
7.569
7.566
7.260
7.107
7.091
7.074
7.003
6.987
3.909
3.805
3.796
3.785
3.728
3.717
3.710
3.701
3.690
3.417
3.406
3.397
1.00
1.02
0.99
1.03
3.23
2.25
4.34
2.10

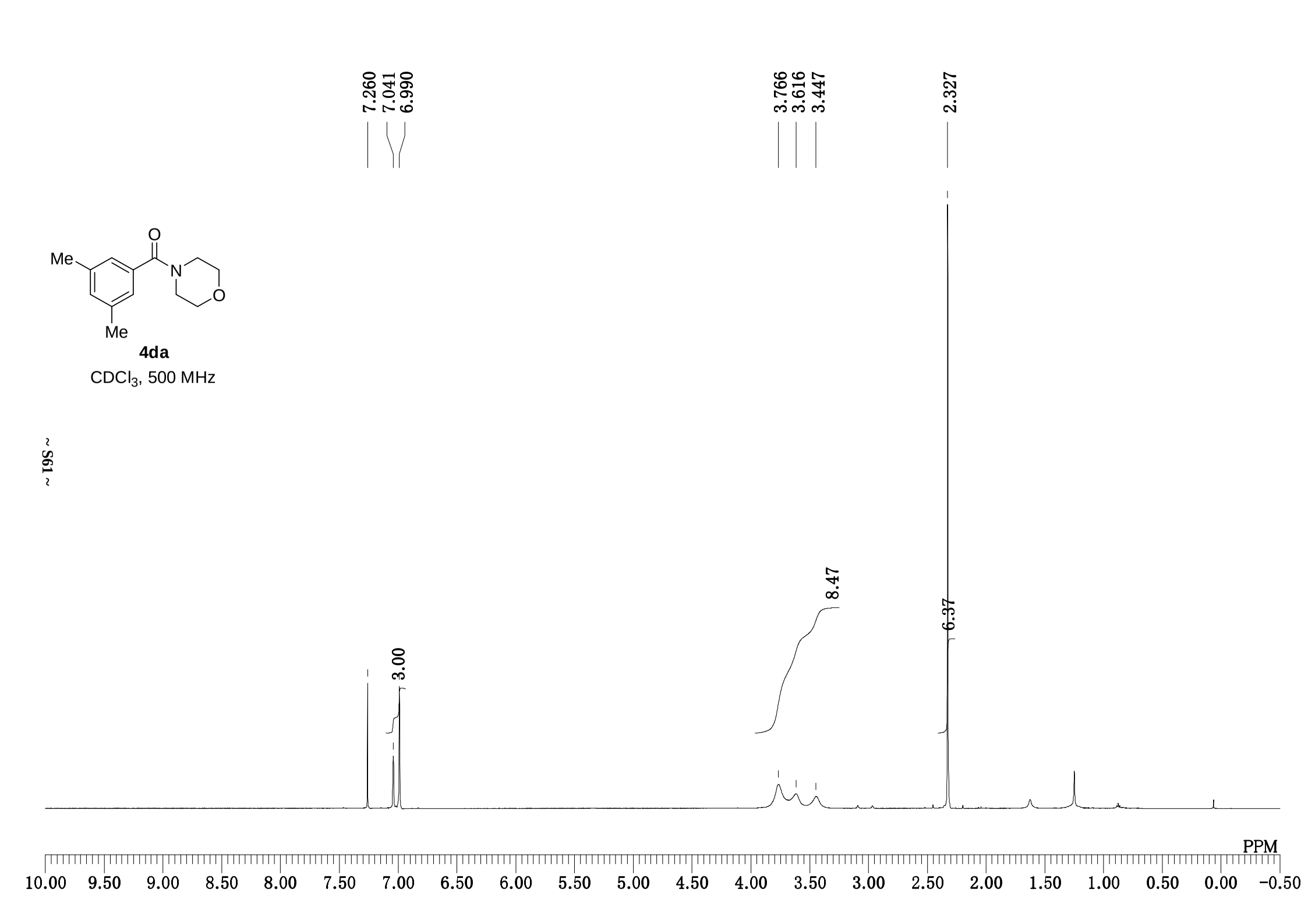

190.234
167.371
160.136
136.223
131.116
123.528
121.453
112.206
77.253
77.000
76.747
66.546
66.336
56.216
45.881
41.379
OMe
O
O
N
O
3ca
CDCl3, 125 MHz
~ S56 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

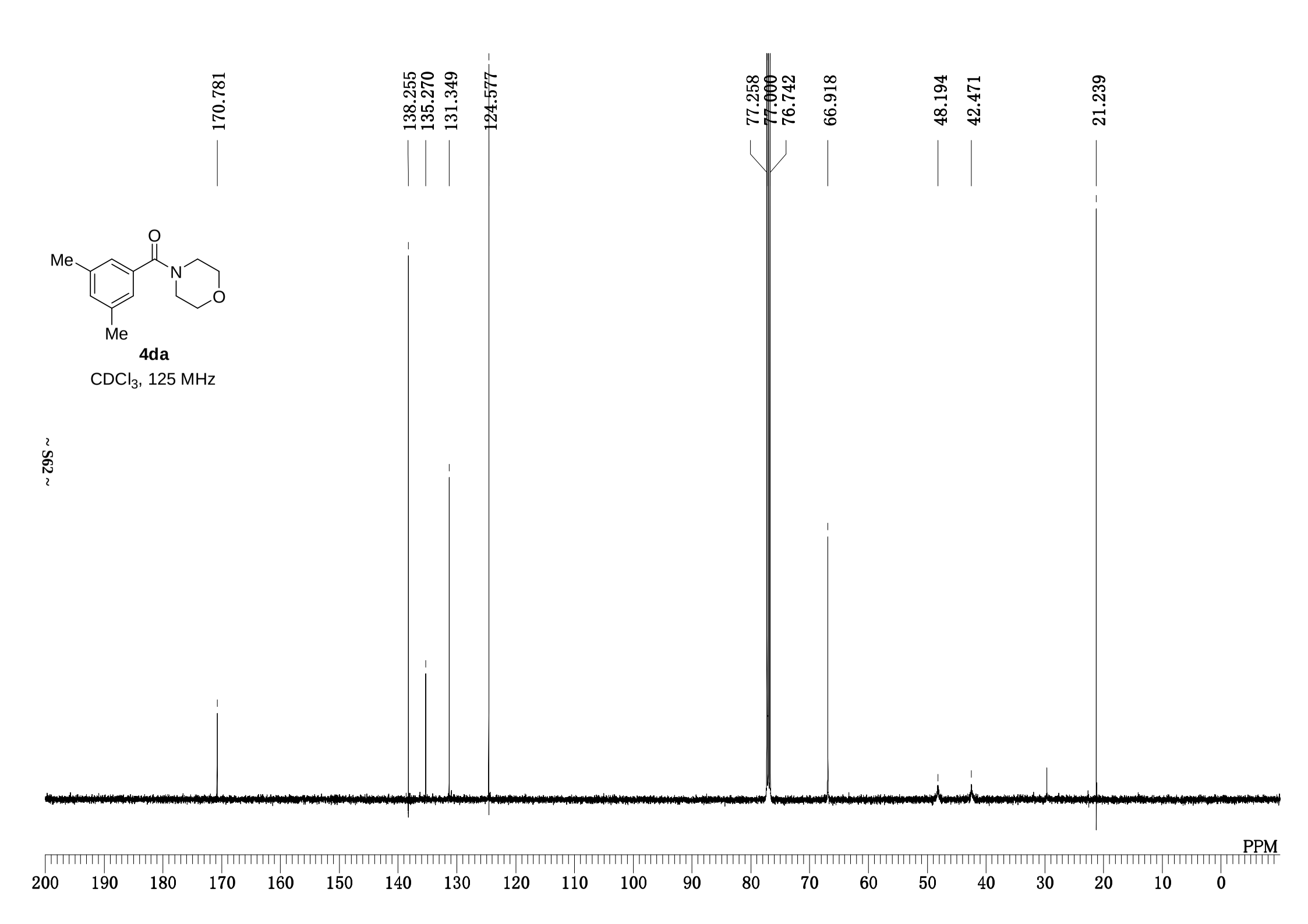

7.368
7.364
7.353
7.349
7.337
7.333
7.260
7.252
7.249
7.236
7.234
7.005
6.990
6.975
6.915
6.898
3.832
3.785
3.765
3.754
3.736
3.720
3.628
3.616
3.609
3.571
3.564
3.285
3.277
3.240
3.230
3.222
OMe O
N
O
4ca
CDCl3, 500 MHz
7.31
2.04
2.00
1.00
0.97
1.00
0.96
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00

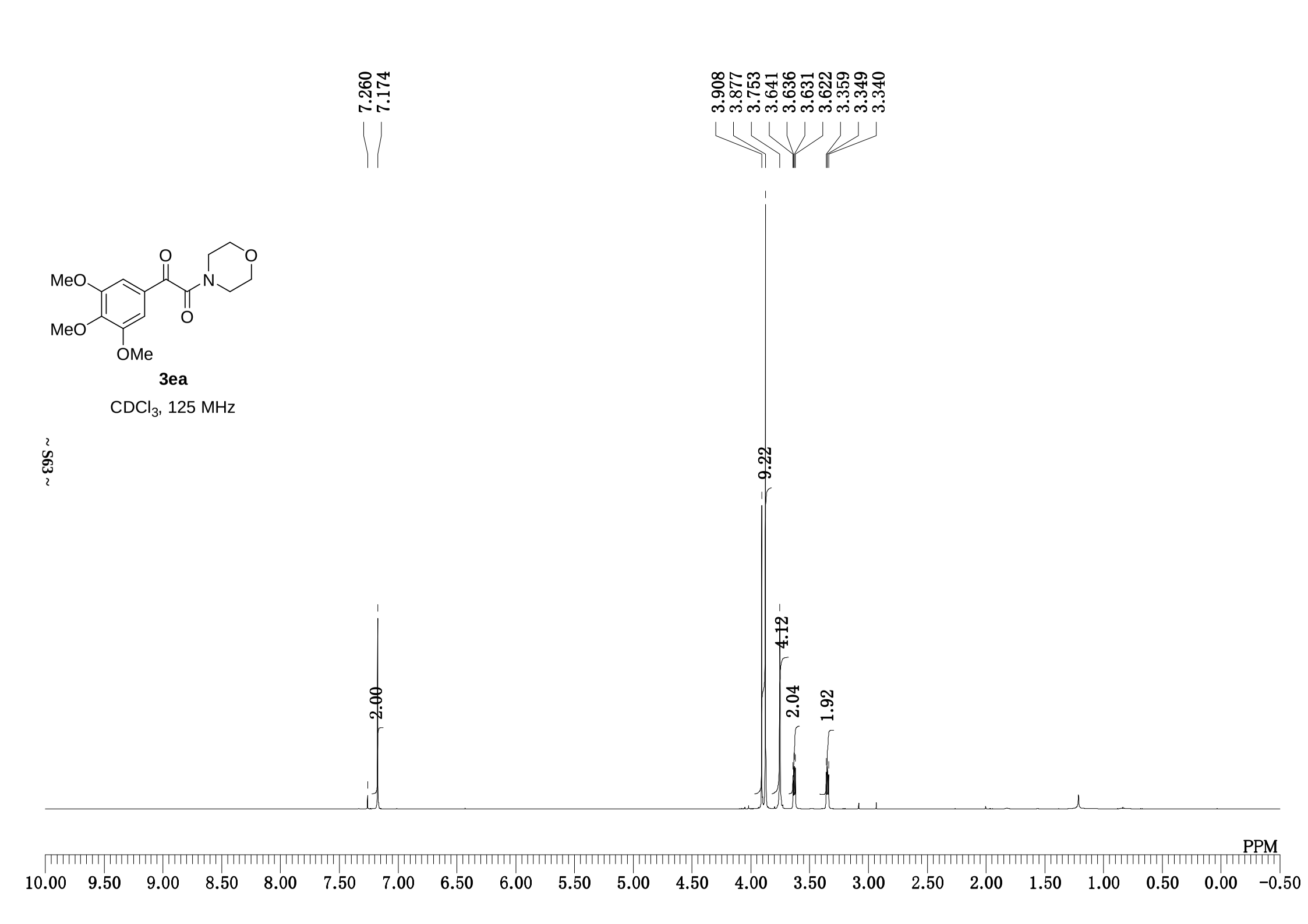

167.833
155.176
130.567
128.030
125.159
120.962
110.823
77.258
77.000
76.742
66.908
66.784
55.462
47.221
42.052
OMe O
N
O
4ca
CDCl3, 125 MHz
PPM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

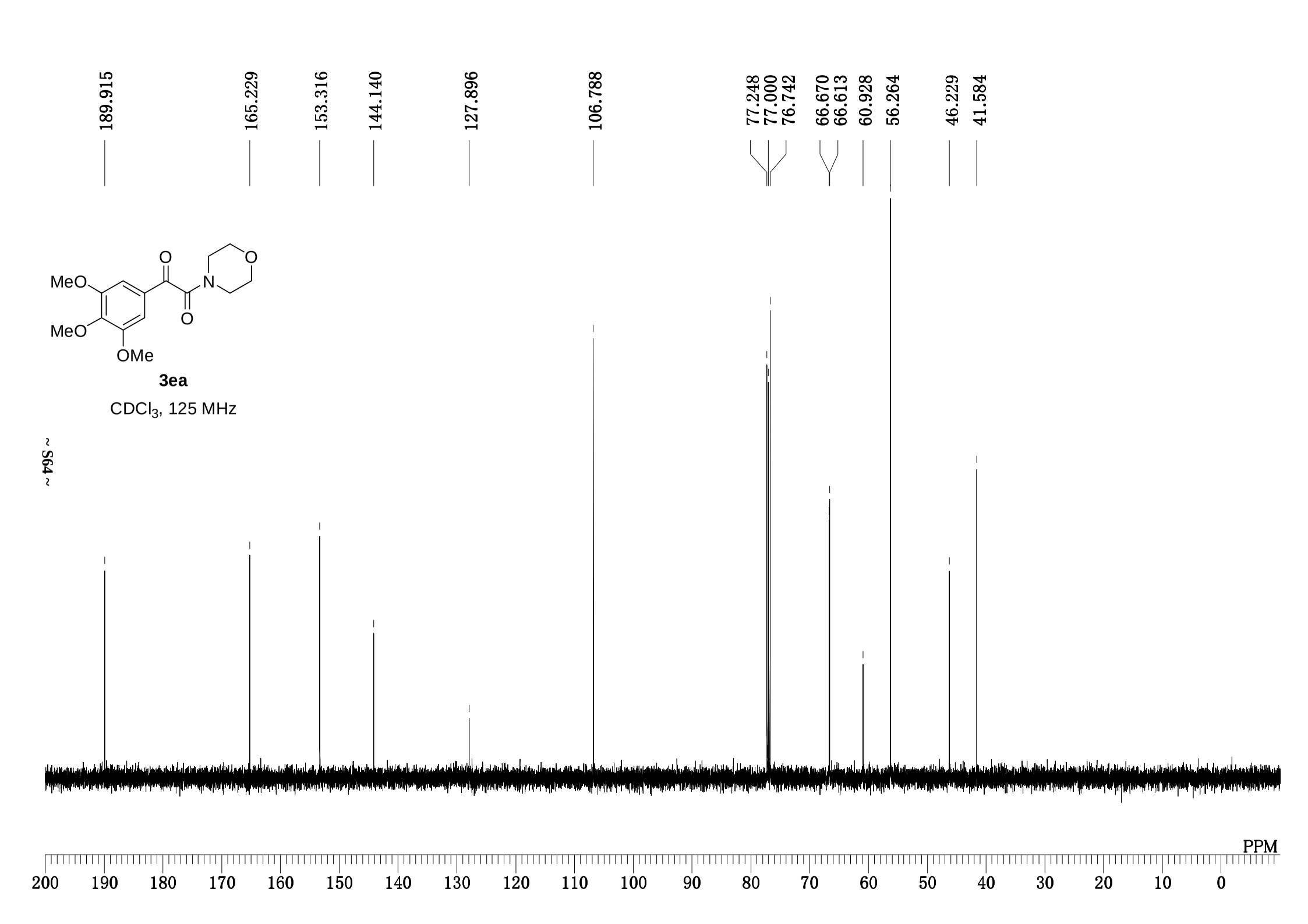

7.544
7.275
7.260
3.801
3.796
3.782
3.780
3.772
3.766
3.759
3.648
3.639
3.628
3.362
3.352
3.343
2.365
6.36
4.19
2.10
2.02
2.00
0.98
Me
Me
O
O
N
O
3da
CDCl3, 500 MHz
~ S59 ~
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

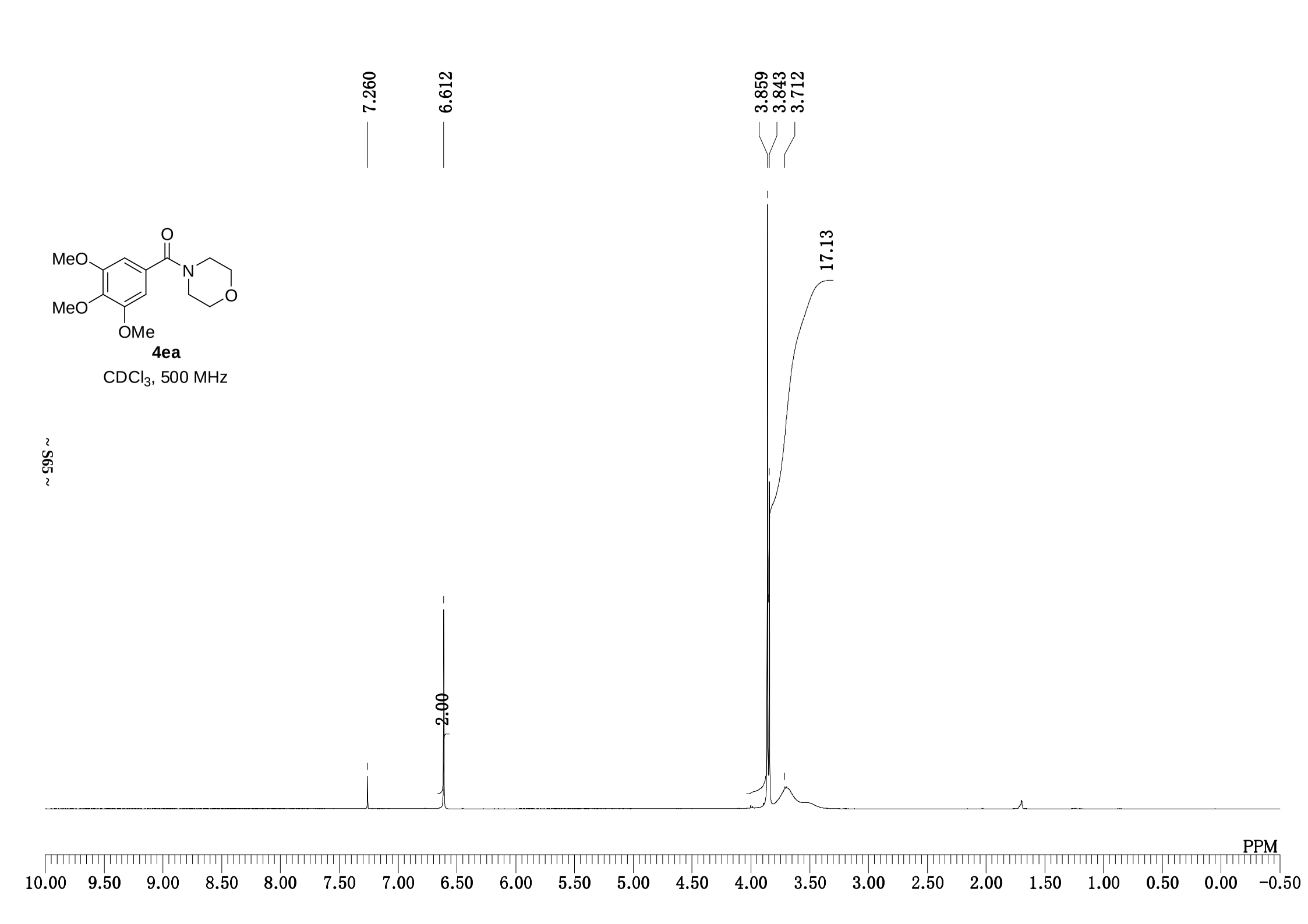

191.574
165.659
138.866
136.739
132.990
127.267
77.258
77.000
76.742
66.670
66.613
46.201
41.517
21.096
Me
Me
O
O
N
O
3da
CDCl3, 125 MHz
~ S60 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

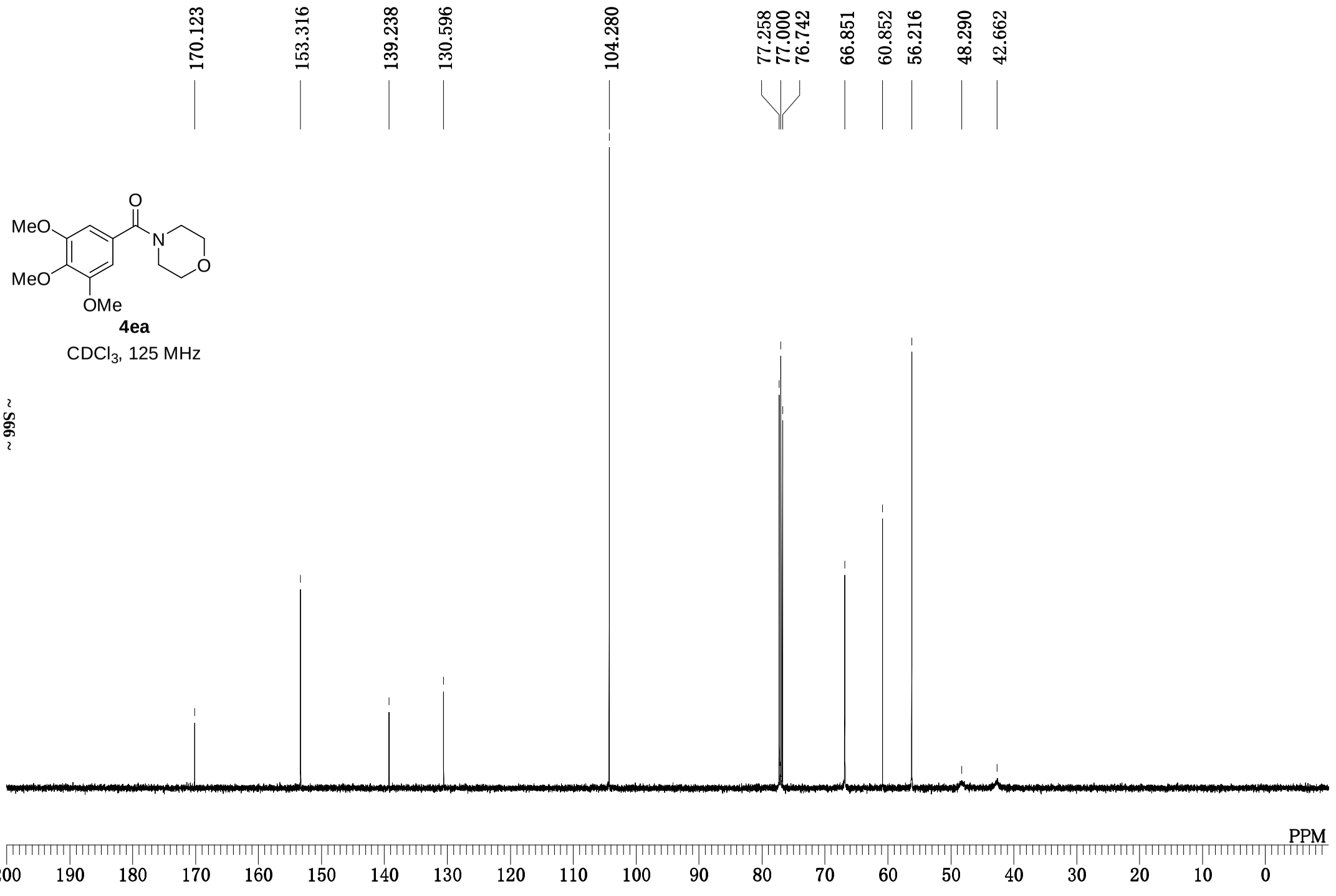

7.260
7.041
6.990
3.766
3.616
3.447
2.327
Me
O
N
O
Me
4da
CDCl3, 500 MHz
8.47
6.37
3.00
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00 −0.50

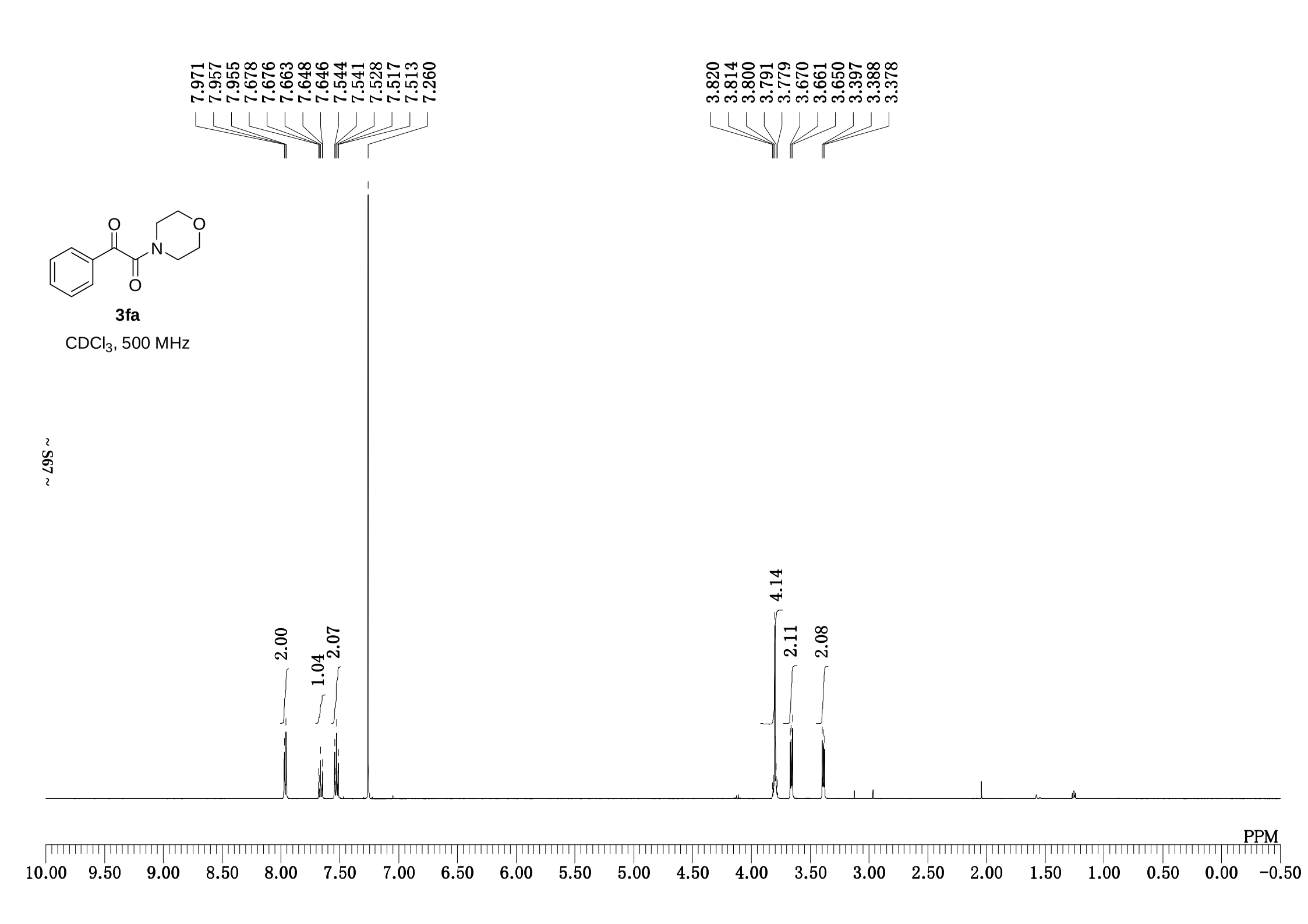

170.781
138.255
135.270
131.349
124.577
77.258
77.000
76.742
66.918
48.194
42.471
21.239
Me
Me
O
N
O
4da
CDCl3, 125 MHz
~S62~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

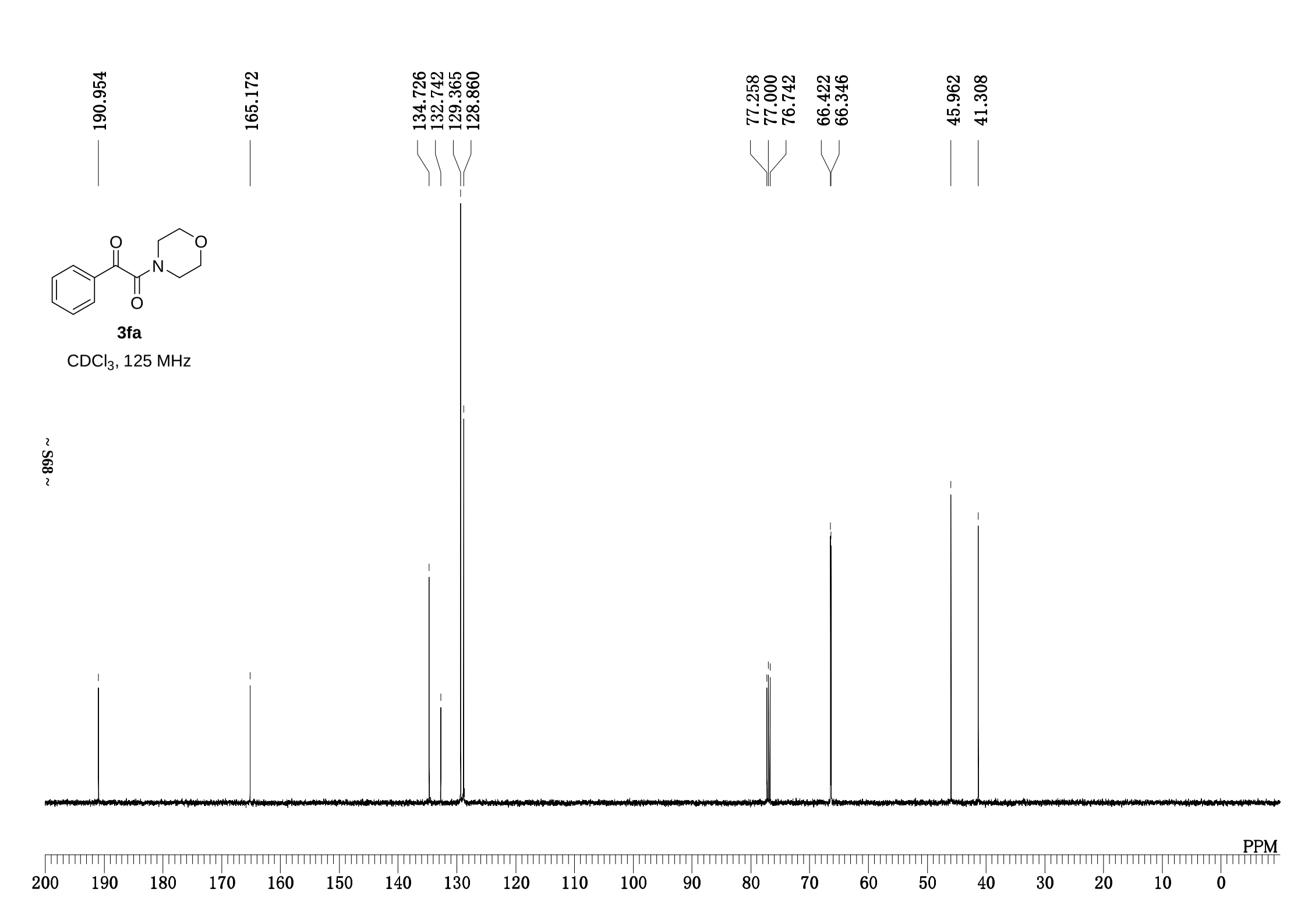

7.260
7.174
3.908
3.877
3.753
3.641
3.636
3.631
3.622
3.359
3.349
3.340
MeO
MeO
OMe
O
O
N
O
3ea
CDCl3, 125 MHz
S63
9.22
4.12
2.04
1.92
2.00
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

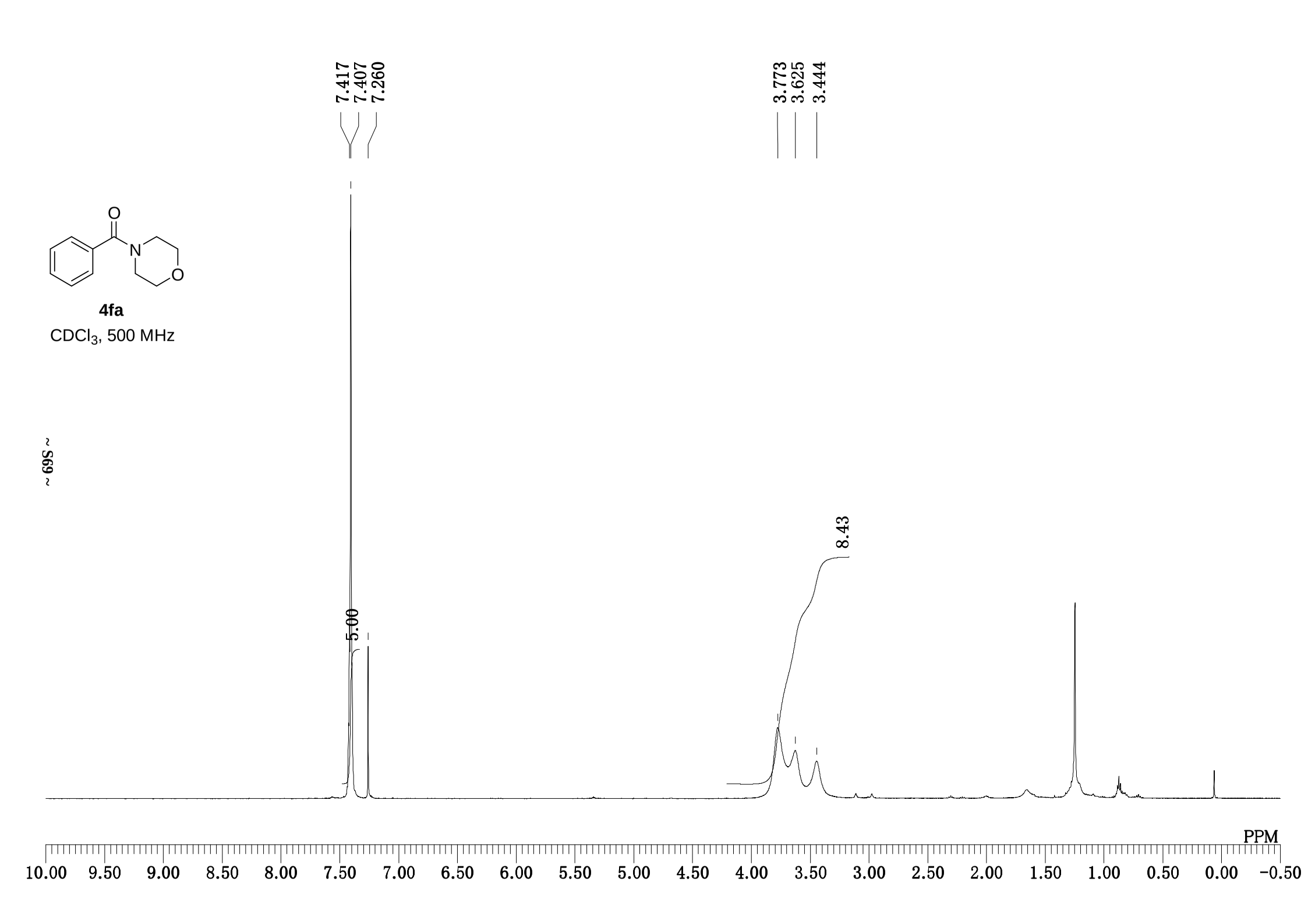

189.915
165.229
153.316
144.140
127.896
106.788
77.248
77.000
76.742
66.670
66.613
60.928
56.264
46.229
41.584
MeO
MeO
OMe
O
O
N
O
3ea
CDCl3, 125 MHz
~ S94 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

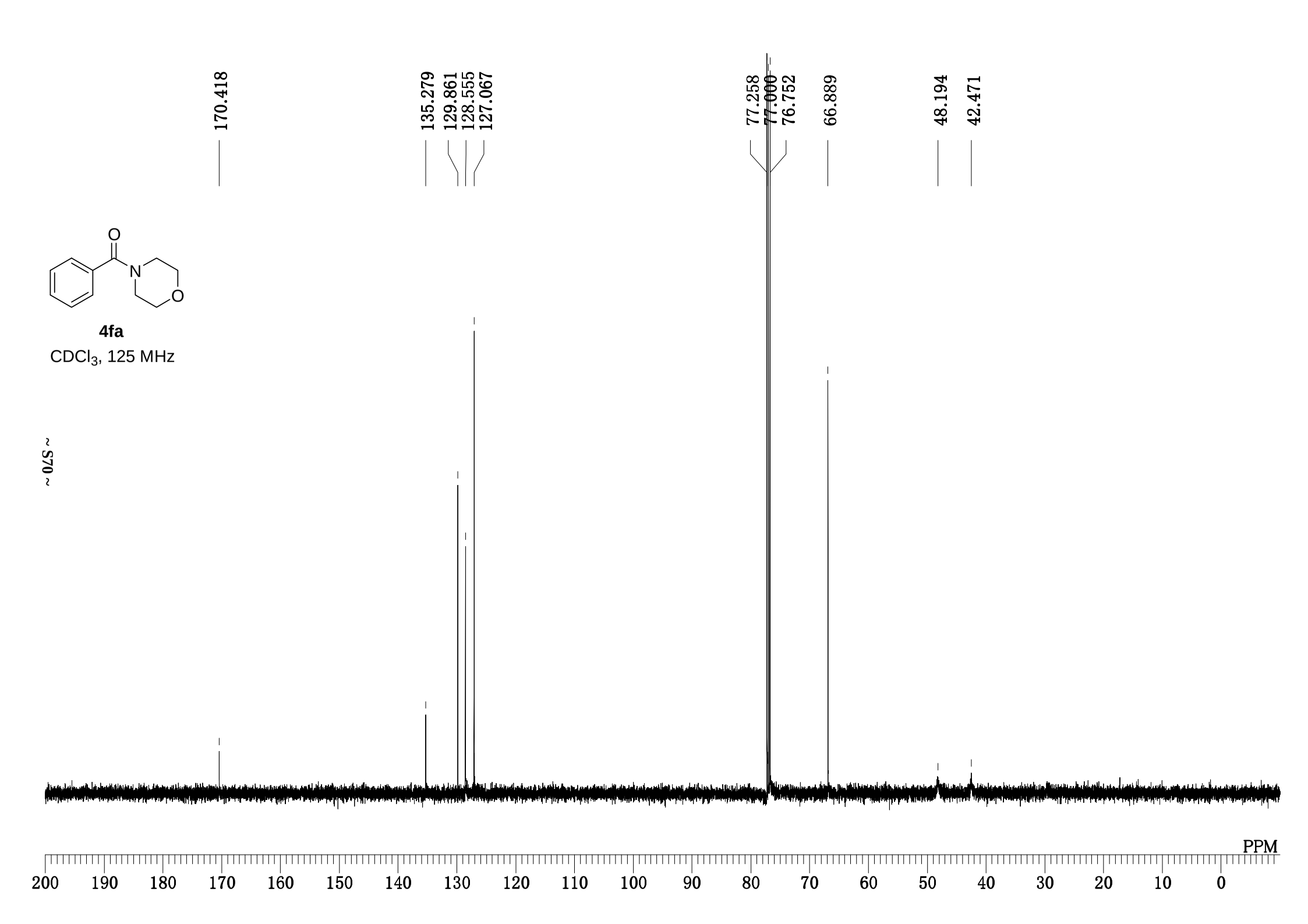

7.260
6.612
3.859
3.843
3.712
17.13
2.00
MeO
MeO
OMe
O
N
O
4ea
CDCl3, 500 MHz
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

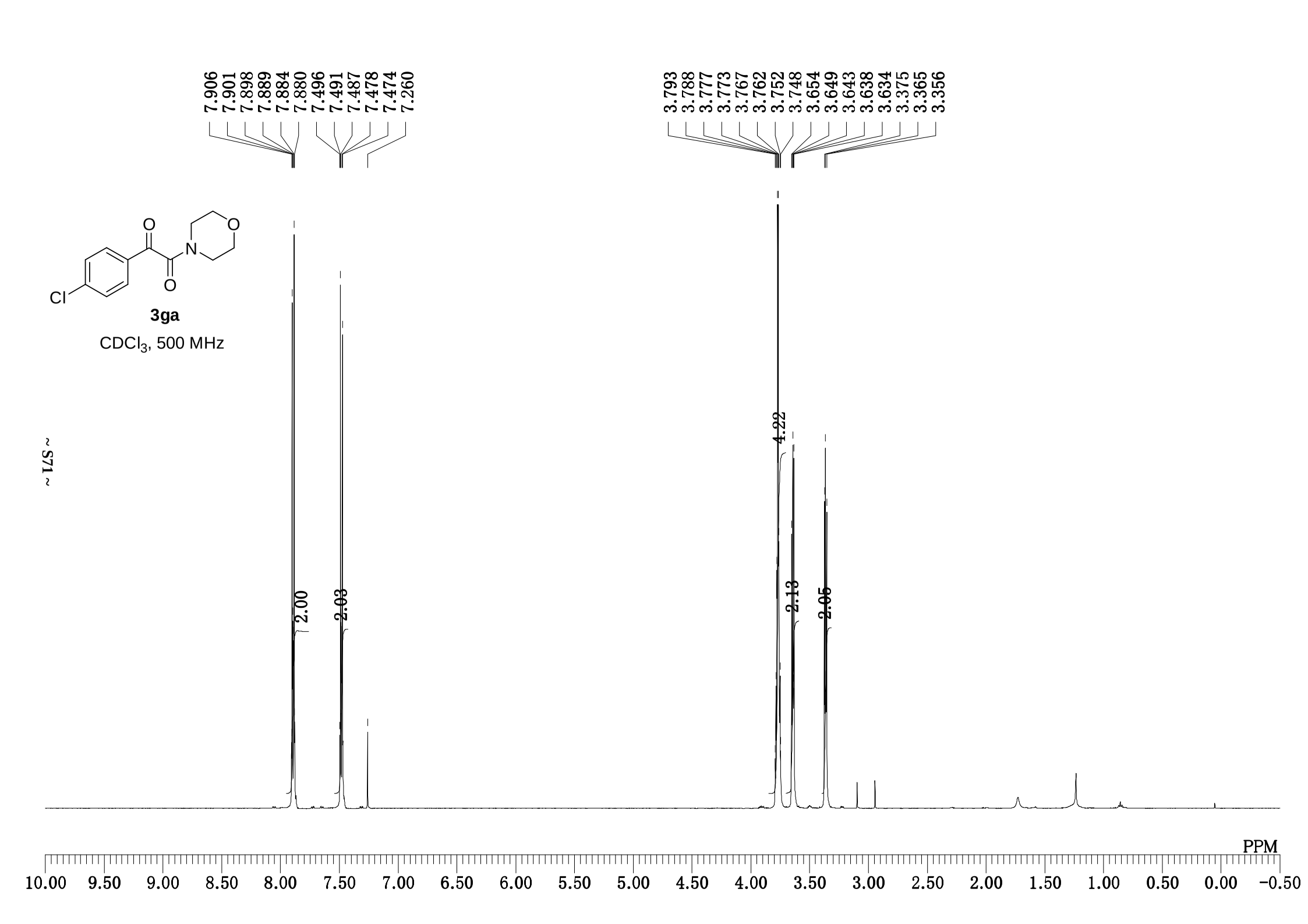

170.123
153.316
139.238
130.596
104.280
77.258
77.000
76.742
66.851
60.852
56.216
48.290
42.662
MeO
MeO
OMe
O
N
O
4ea
CDCl3, 125 MHz
~ S66 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

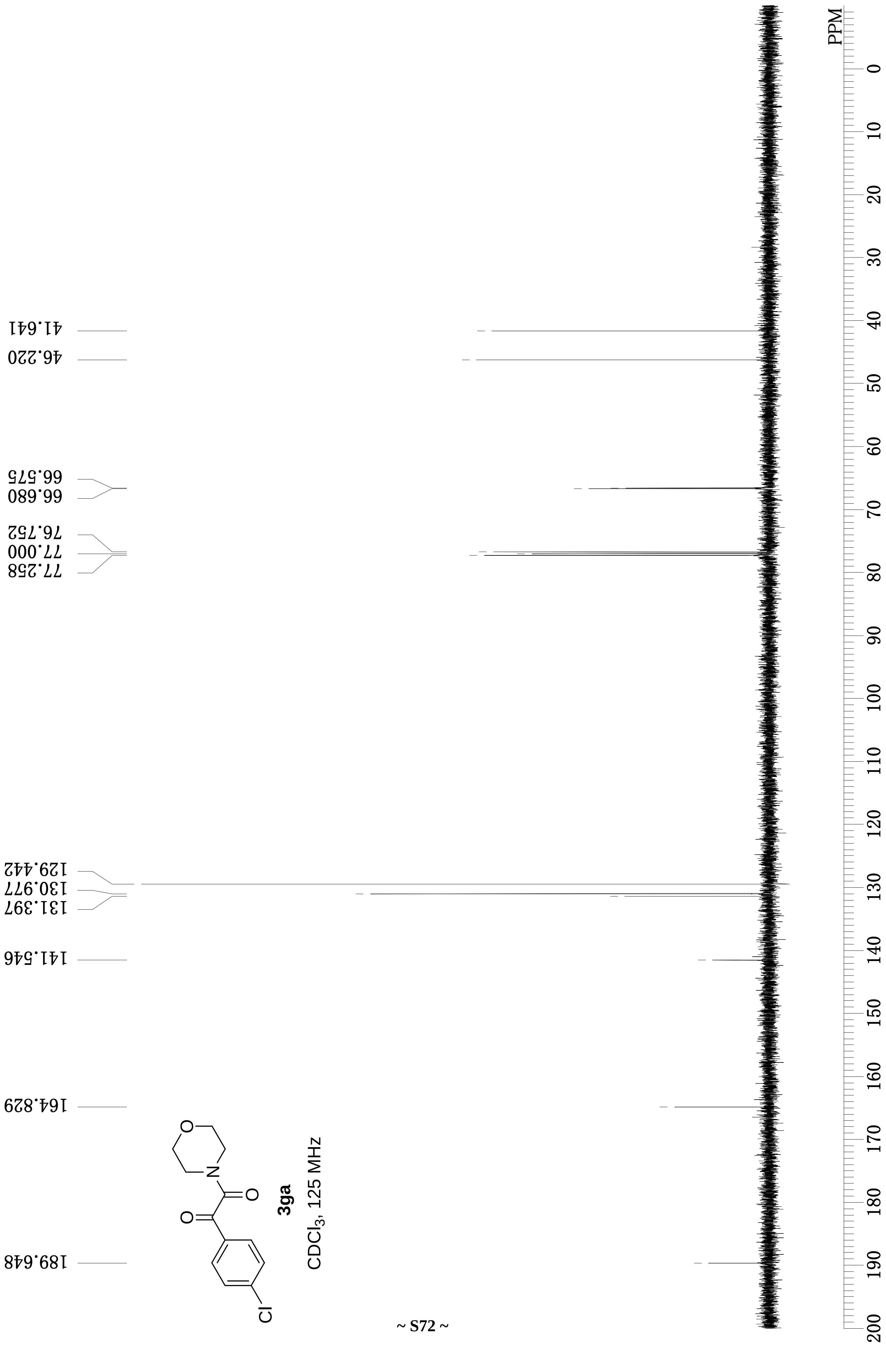

7.971
7.957
7.955
7.678
7.676
7.663
7.648
7.646
7.544
7.541
7.528
7.517
7.513
7.260
3.820
3.814
3.800
3.791
3.779
3.670
3.661
3.650
3.397
3.388
3.378
O
O
N
O
3fa
CDCl3, 500 MHz
~ S67 ~
2.00
1.04
2.07
4.14
2.11
2.08
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

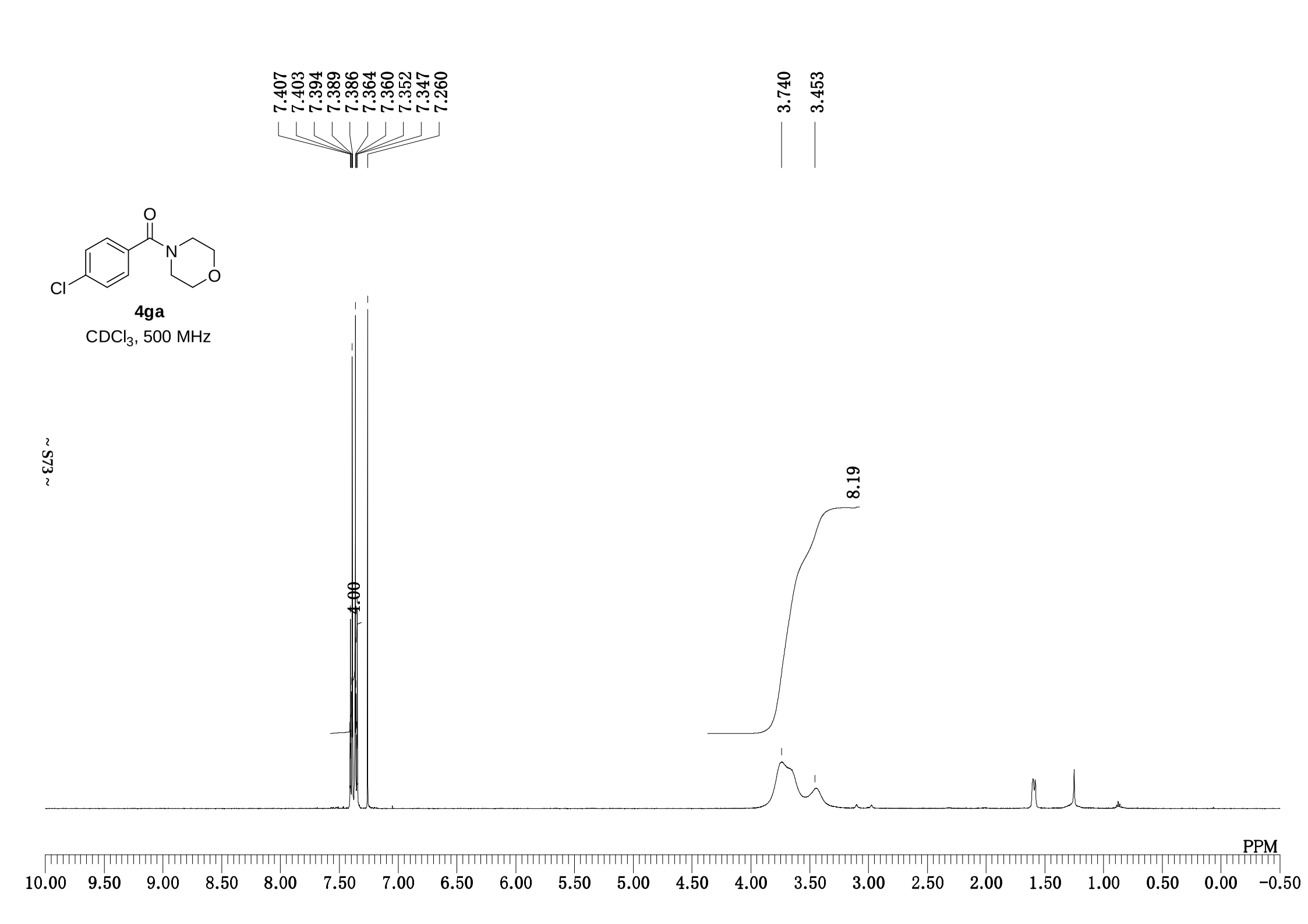

190.954
165.172
134.726
132.742
129.365
128.860
77.258
77.000
76.742
66.422
66.346
45.962
41.308
O
O
N
O
3fa
CDCl3, 125 MHz
~ S68 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

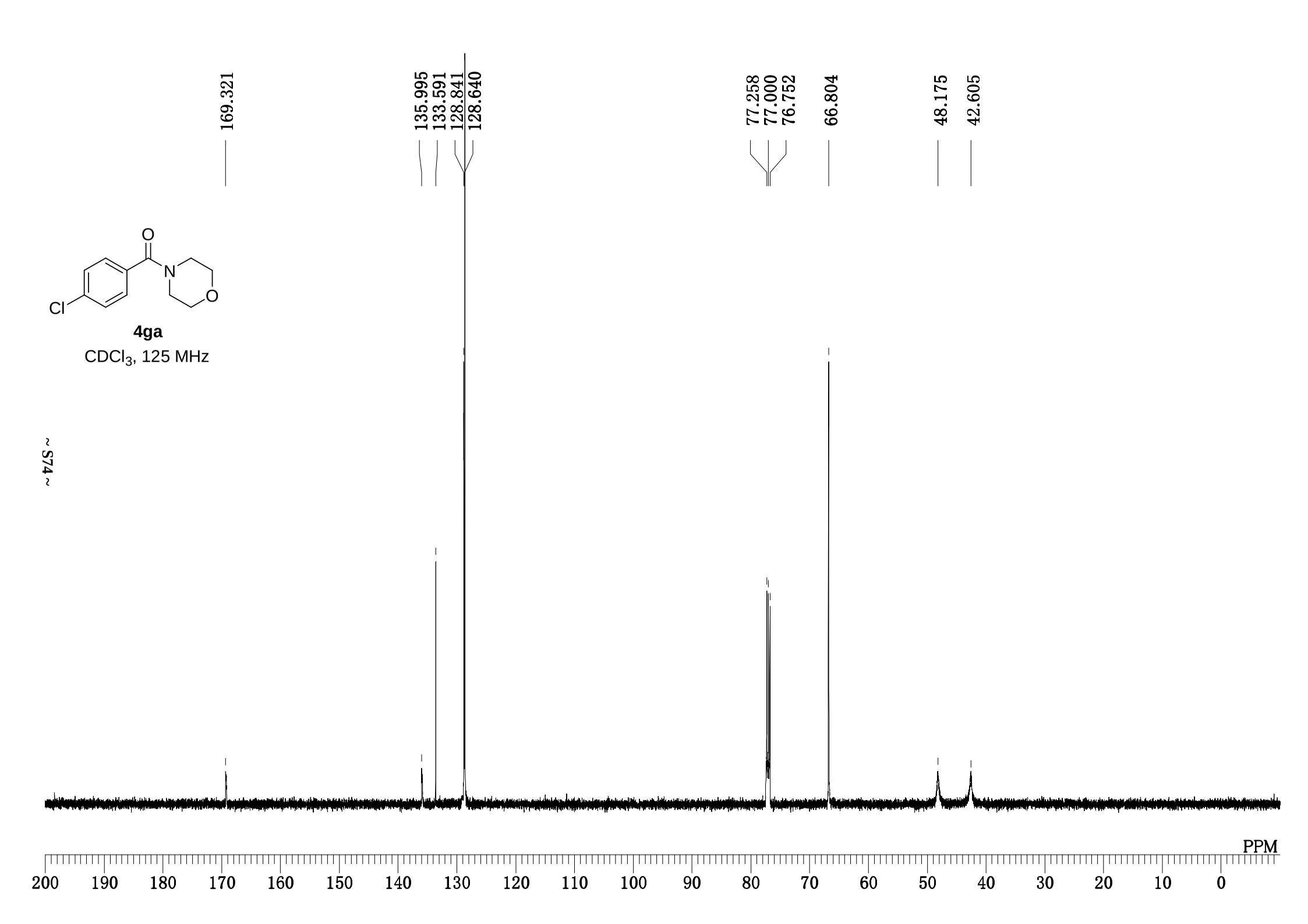

7.417
7.407
7.260
3.773
3.625
3.444
O
N
O
4fa
CDCl3, 500 MHz
~ S69 ~
8.43
5.00
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

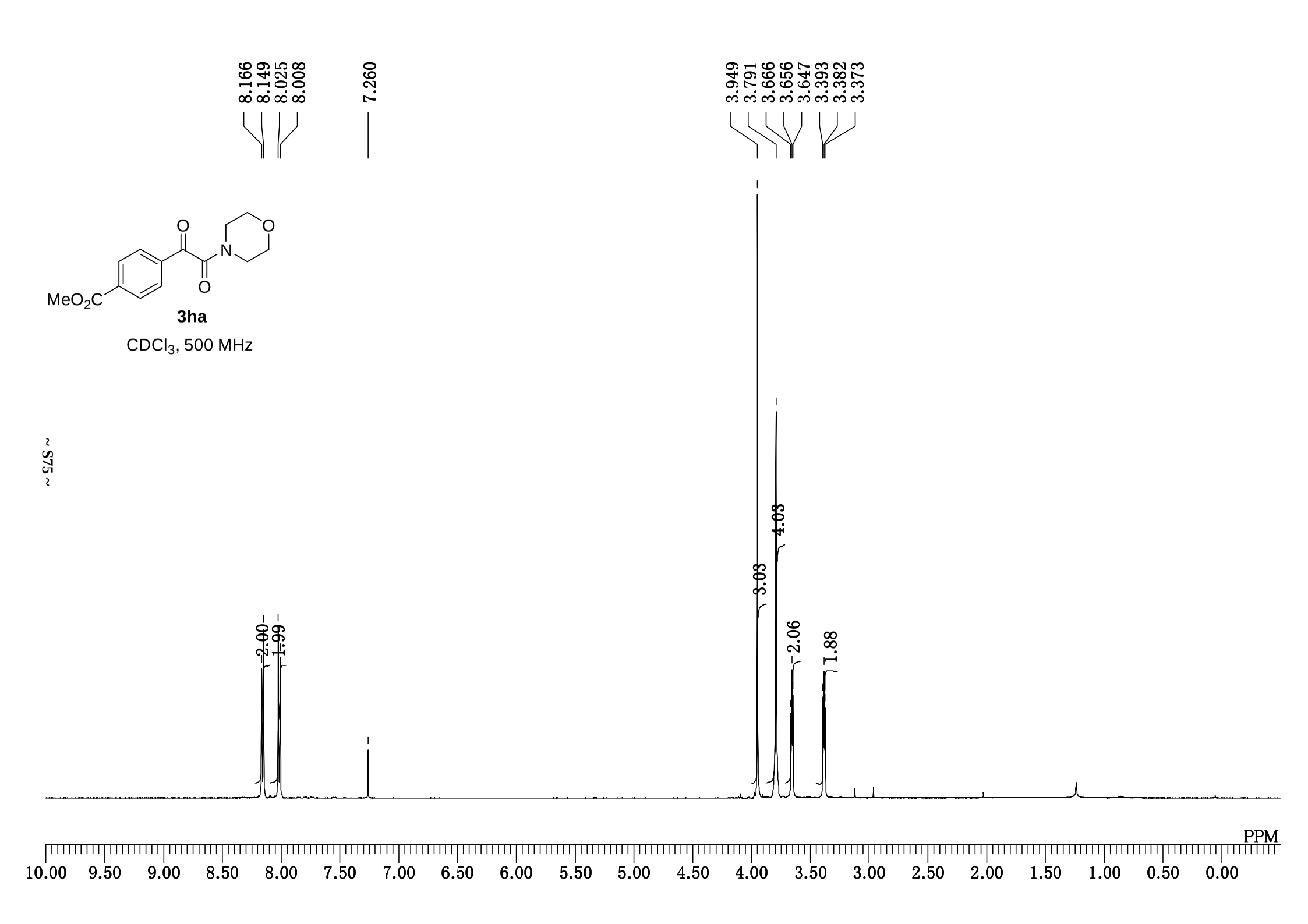

170.418
135.279
129.861
128.555
127.067
77.258
77.000
76.752
66.889
48.194
42.471
O
N
O
4fa
CDCl3, 125 MHz
~570~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

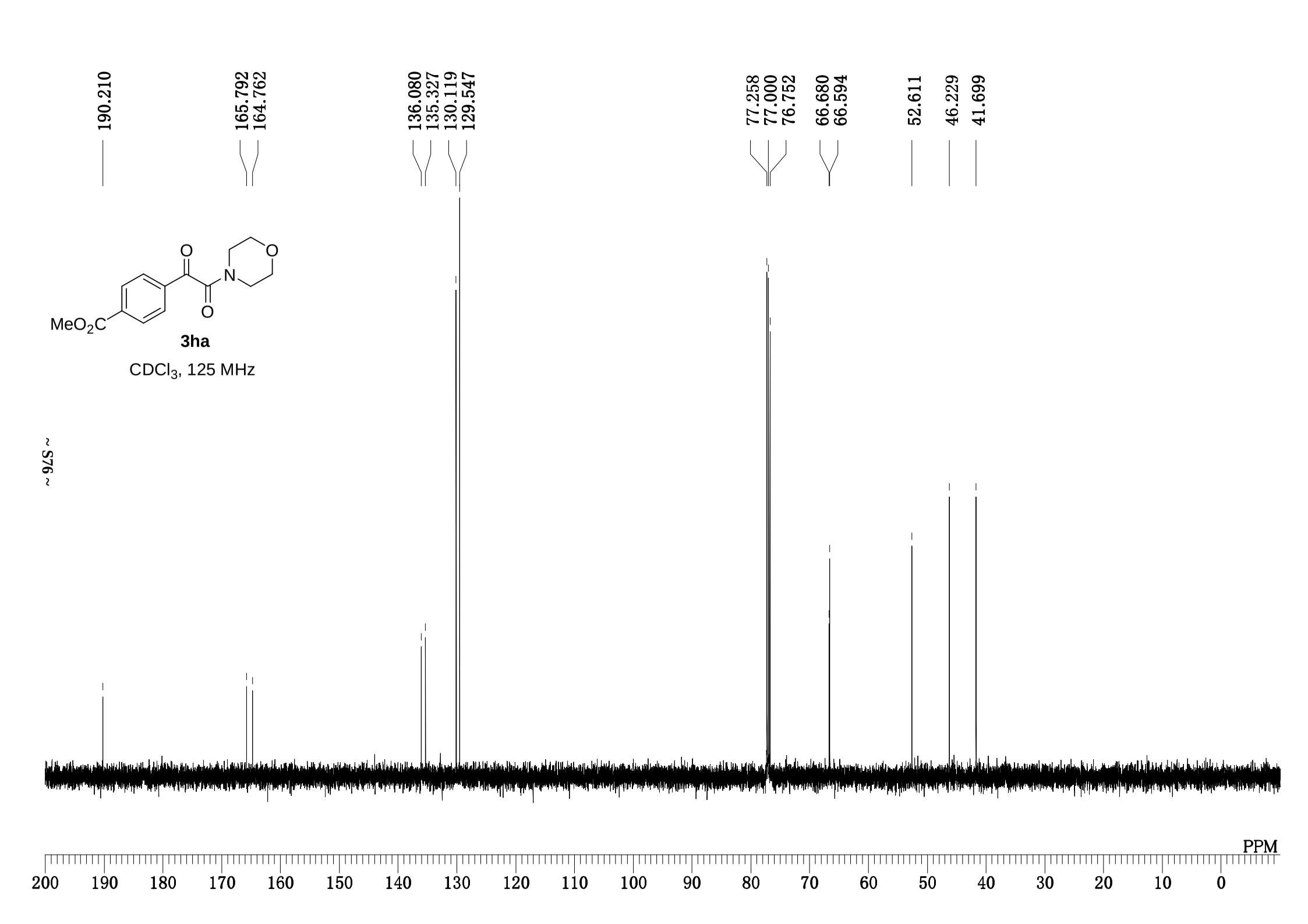

7.906
7.901
7.898
7.889
7.884
7.880
7.496
7.491
7.487
7.478
7.474
7.260
3.793
3.788
3.777
3.773
3.767
3.762
3.752
3.748
3.654
3.649
3.643
3.638
3.634
3.375
3.365
3.356
O
O
N
O
Cl
3ga
CDCl3, 500 MHz
2.00
2.03
4.22
2.13
2.05
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

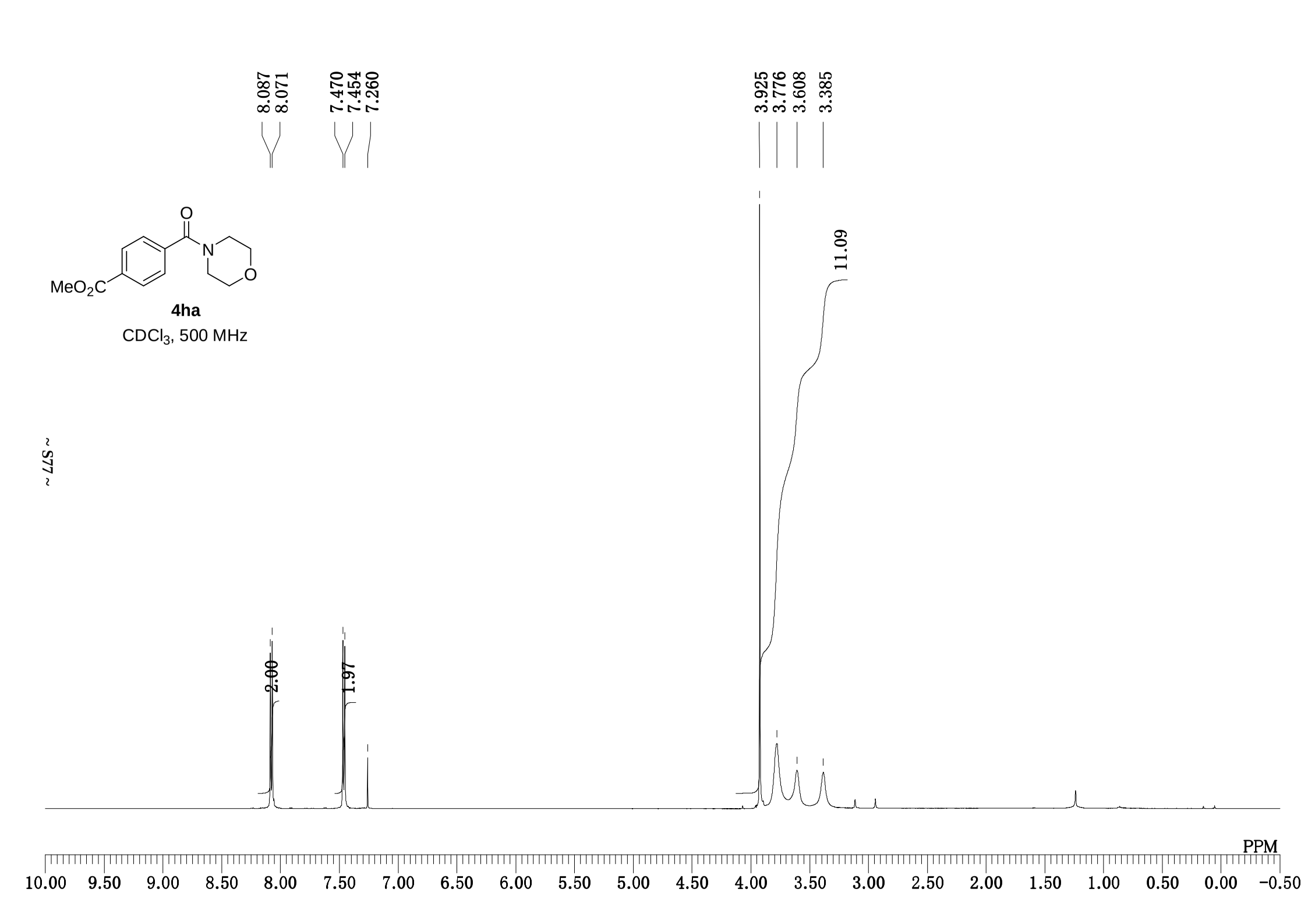

3ga
CDCl$_3$, 125 MHz
189.648
164.829
141.546
131.397
130.977
129.442
77.258
77.000
76.752
66.680
66.575
46.220
41.641
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

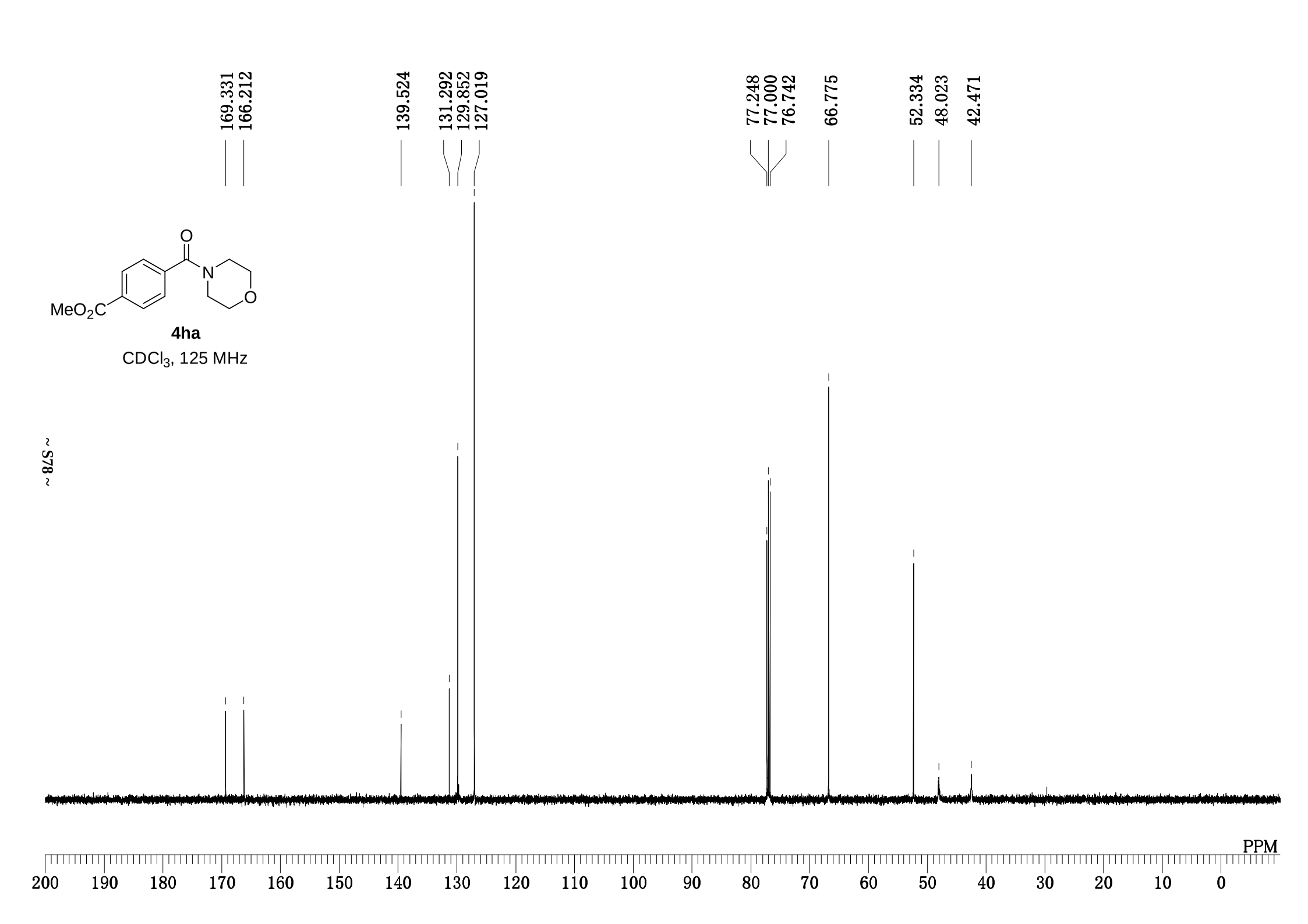

7.407
7.403
7.394
7.389
7.386
7.364
7.360
7.352
7.347
7.260
3.740
3.453
O
N
O
Cl
4ga
CDCl3, 500 MHz
~ S73 ~
4.00
8.19
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50


169.321
135.995
133.591
128.841
128.640
77.258
77.000
76.752
66.804
48.175
42.605
O
N
O
Cl
4ga
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

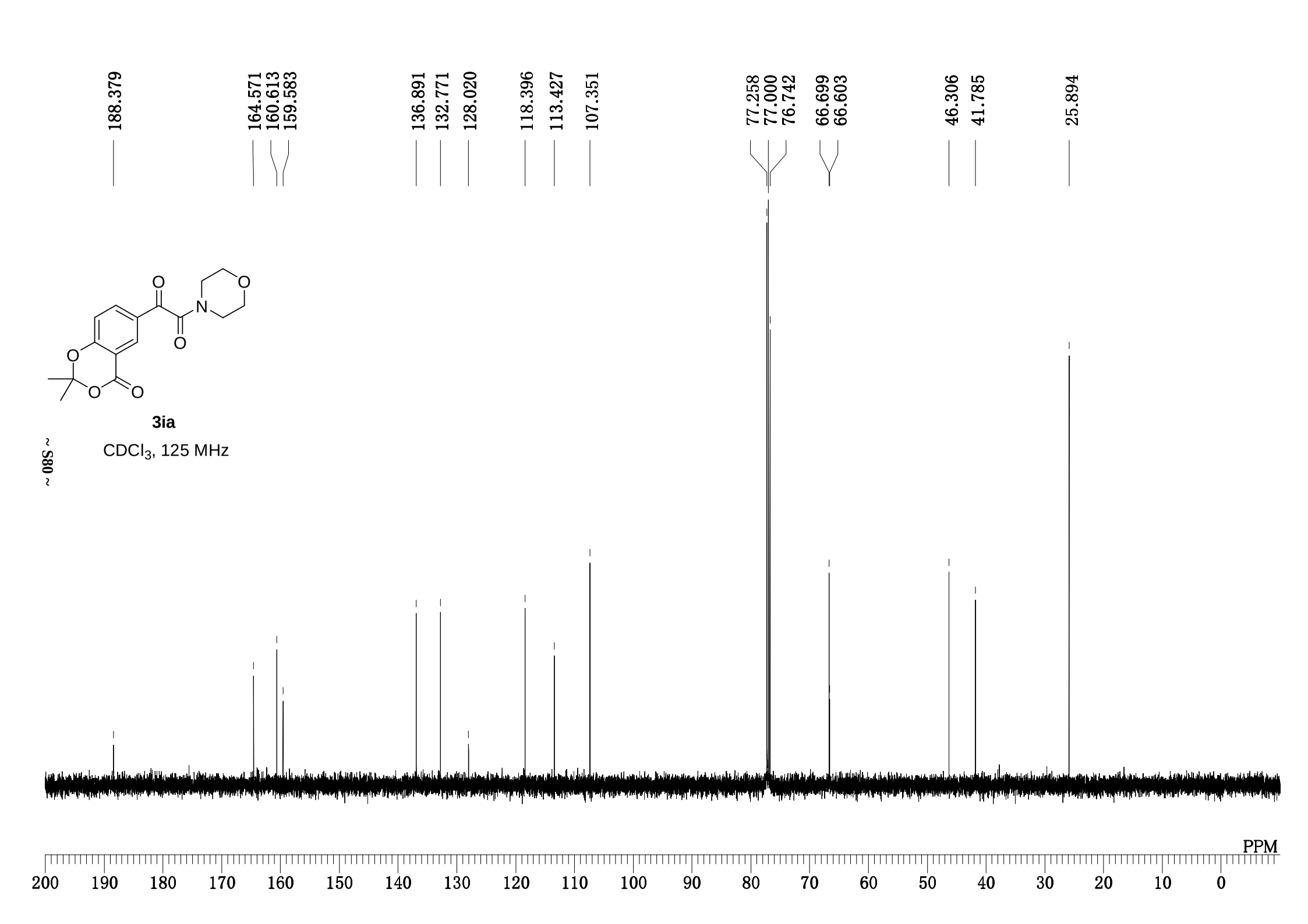

8.166
8.149
8.025
8.008
7.260
3.949
3.791
3.666
3.656
3.647
3.393
3.382
3.373
O
O
N
O
MeO2C
3ha
CDCl3, 500 MHz
2.00
1.99
3.03
4.03
2.06
1.88
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00

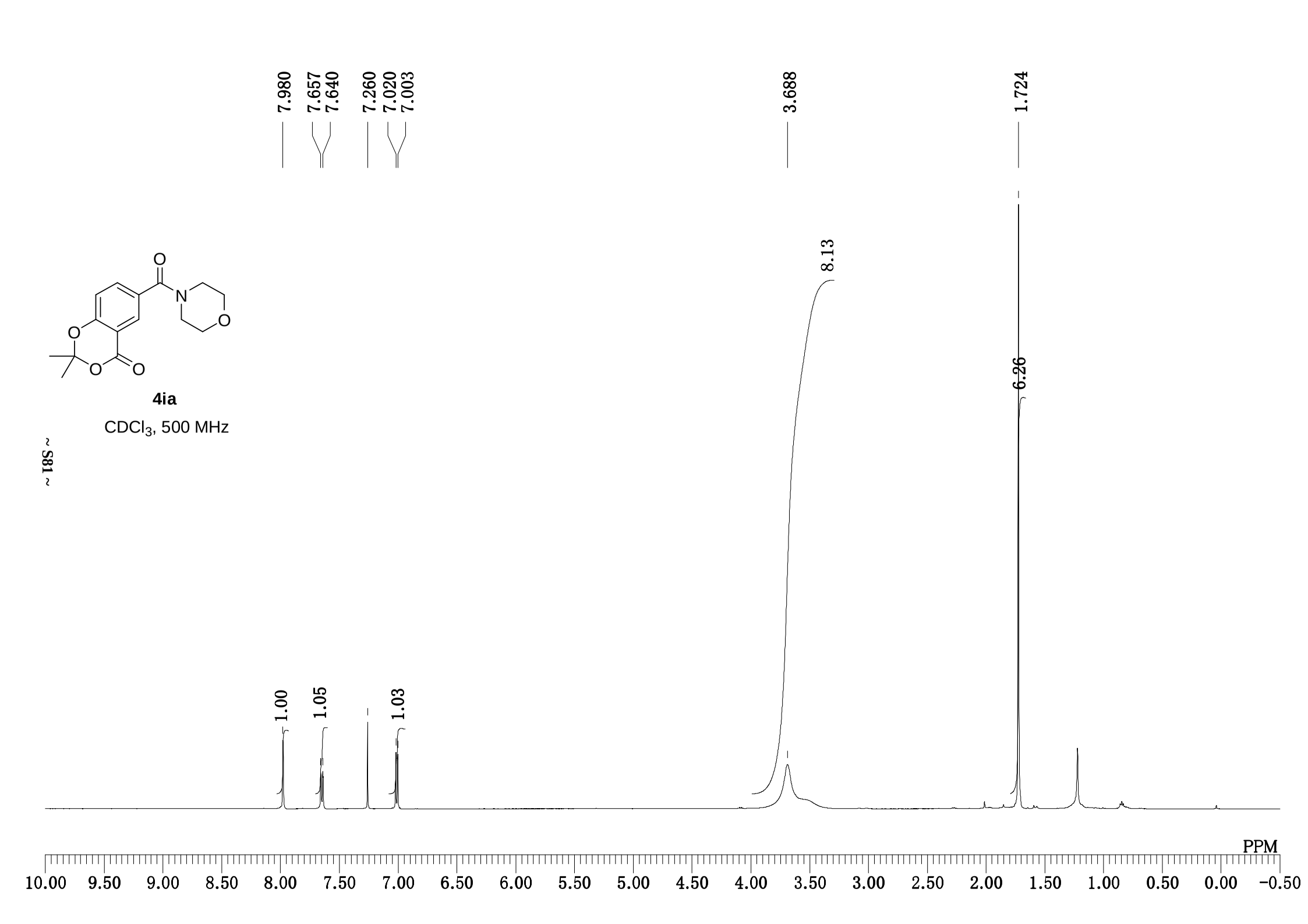

190.210
165.792
164.762
136.080
135.327
130.119
129.547
77.258
77.000
76.752
66.680
66.594
52.611
46.229
41.699
O
O
N
O
O
MeO2C
3ha
CDCl3, 125 MHz
~S76~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

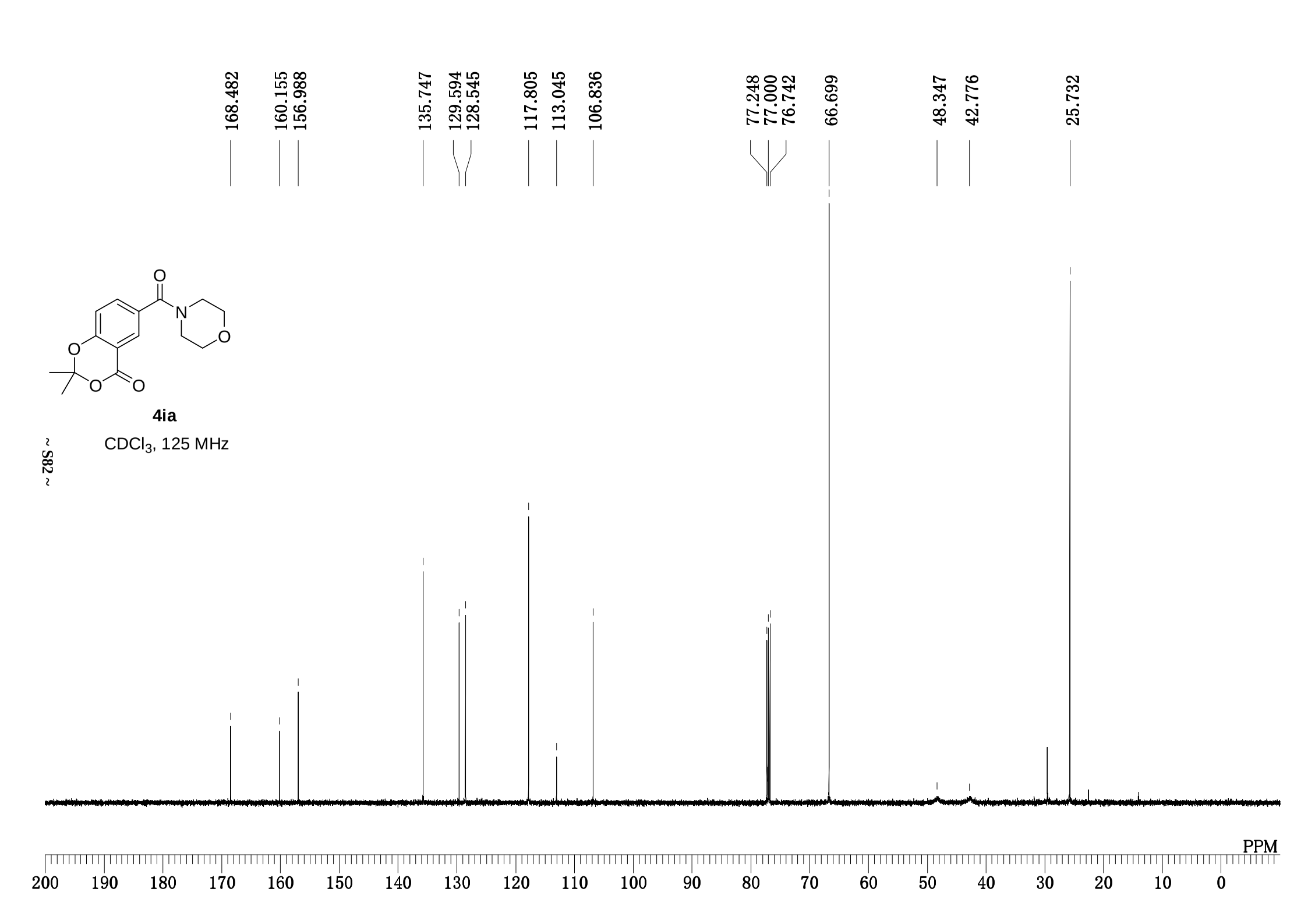

8.087
8.071
7.470
7.454
7.260
3.925
3.776
3.608
3.385
11.09
2.00
1.97
O
N
O
MeO2C
4ha
CDCl3, 500 MHz
~ S77 ~
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

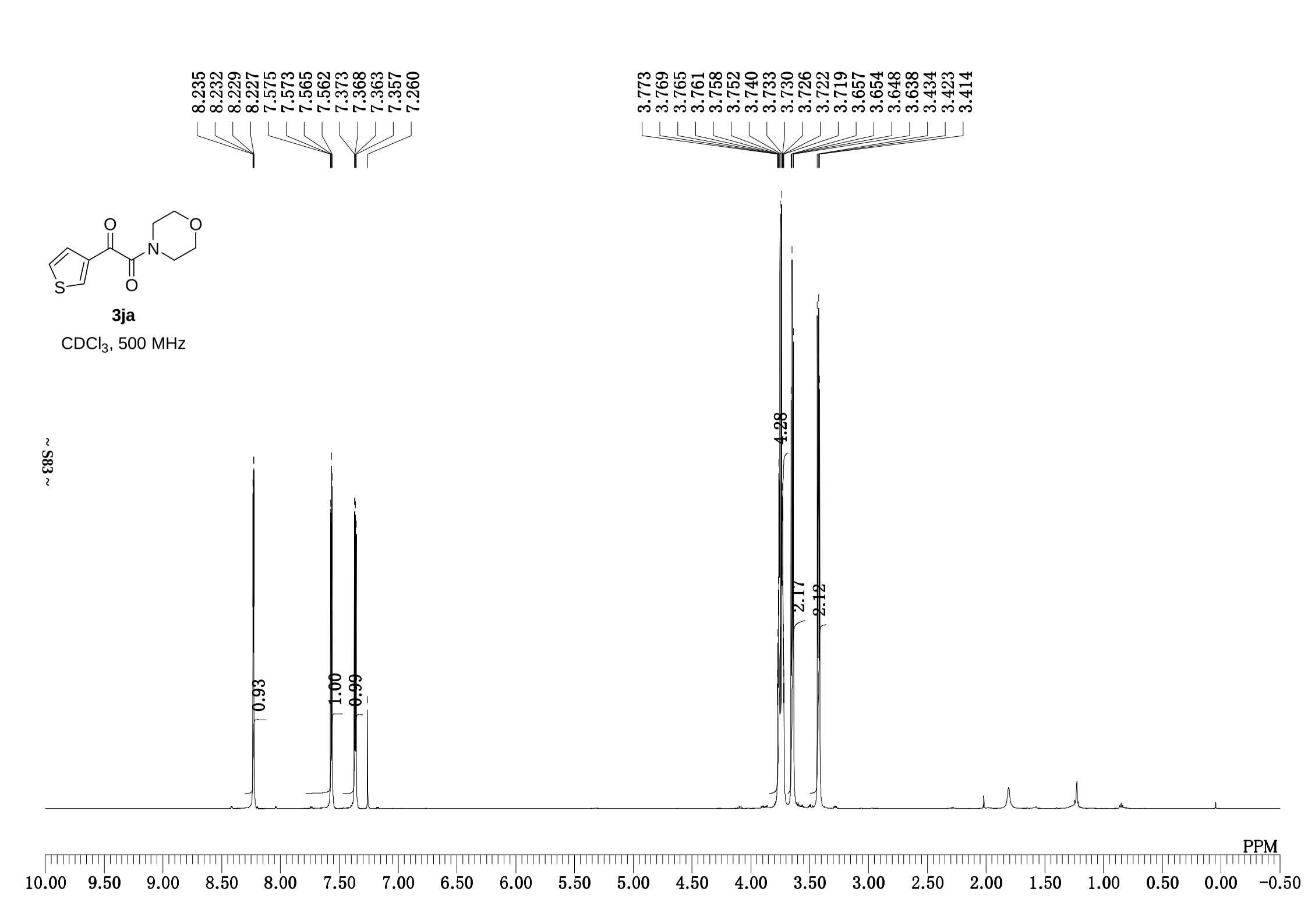

169.331
166.212
139.524
131.292
129.852
127.019
77.248
77.000
76.742
66.775
52.334
48.023
42.471
O
N
O
MeO2C
4ha
CDCl3, 125 MHz
~ S78 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

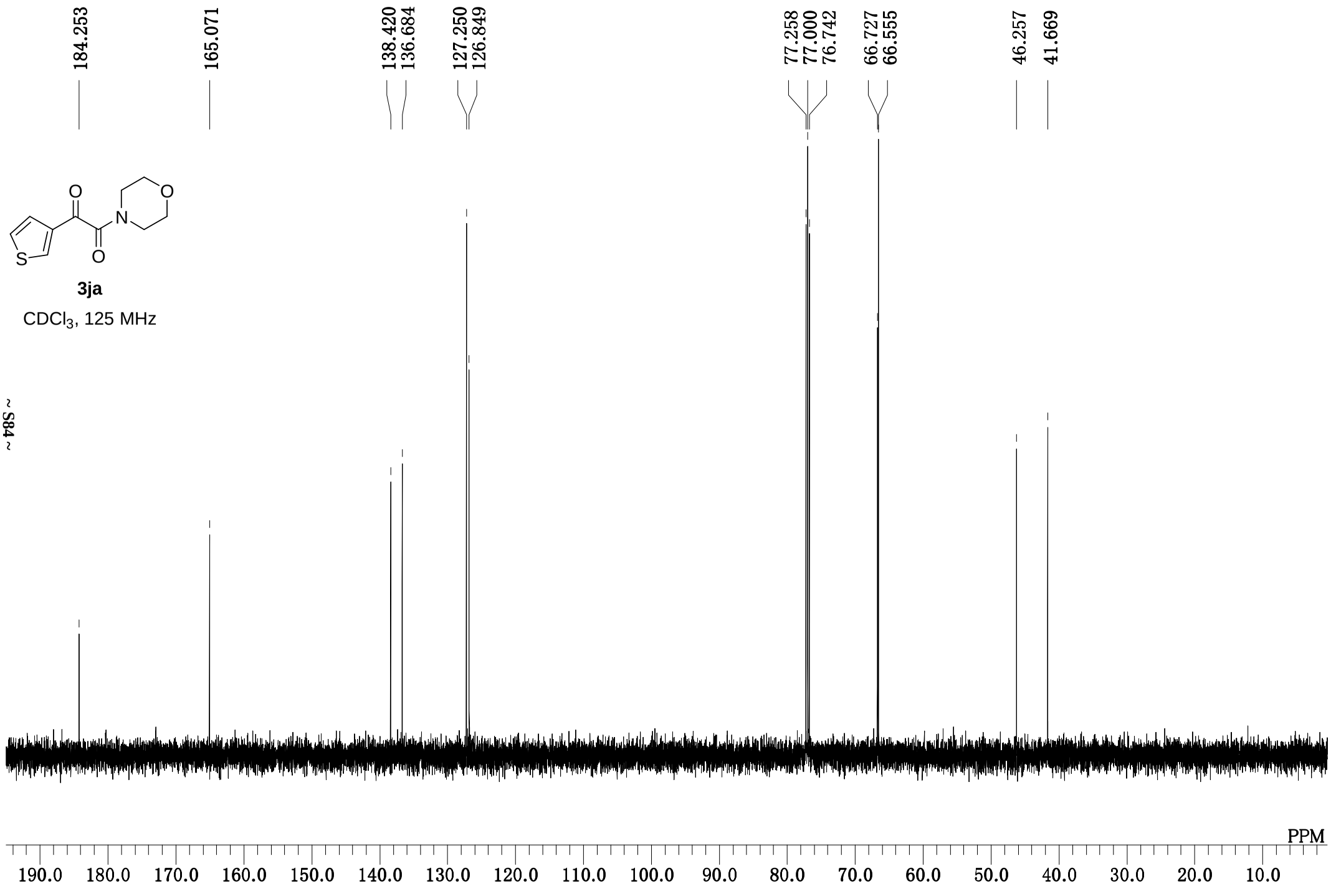
8.525
8.521
8.216
8.212
8.199
8.195
7.260
7.109
7.092
3.817
3.814
3.811
3.806
3.803
3.797
3.788
3.782
3.774
3.767
3.686
3.675
3.666
3.415
3.405
3.396
2.945
1.763
6.43
4.16
2.09
2.03
1.02
1.00
0.92
3ia
CDCl3, 500 MHz
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

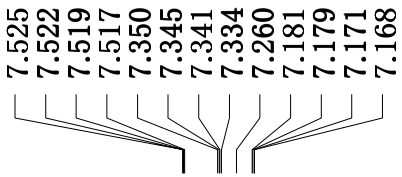

188.379
164.571
160.613
159.583
136.891
132.771
128.020
118.396
113.427
107.351
77.258
77.000
76.742
66.699
66.603
46.306
41.785
25.894
O
O
N
O
O
O
O
3ia
CDCl3, 125 MHz
~S80~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

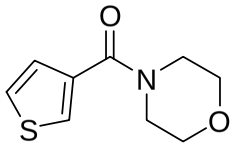

7.980
7.657
7.640
7.260
7.020
7.003
3.688
1.724
8.13
6.26
1.00
1.05
1.03
O
N
O
O
O
O
4ia
CDCl3, 500 MHz
~ S81 ~
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50


168.482
160.155
156.988
135.747
129.594
128.545
117.805
113.045
106.836
77.248
77.000
76.742
66.699
48.347
42.776
25.732
O
N
O
O
O
O
4ia
CDCl3, 125 MHz
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.235
8.232
8.229
8.227
7.575
7.573
7.565
7.562
7.373
7.368
7.363
7.357
7.260
3.773
3.769
3.765
3.761
3.758
3.752
3.740
3.733
3.730
3.726
3.722
3.719
3.657
3.654
3.648
3.638
3.434
3.423
3.414
O
O
N
S
O
3ja
CDCl3, 500 MHz
~ S83 ~
0.93
1.00
0.99
4.28
2.17
2.12
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

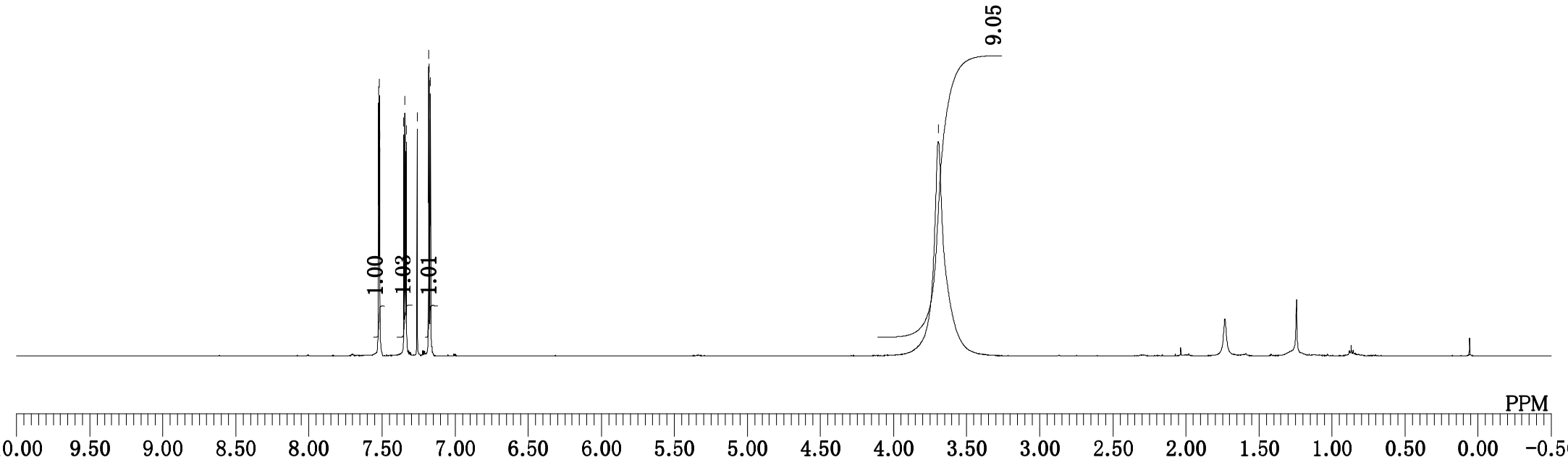

184.253
165.071
138.420
136.684
127.250
126.849
77.258
77.000
76.742
66.727
66.555
46.257
41.669
O
O
N
O
S
3ja
CDCl3, 125 MHz
PPM
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0

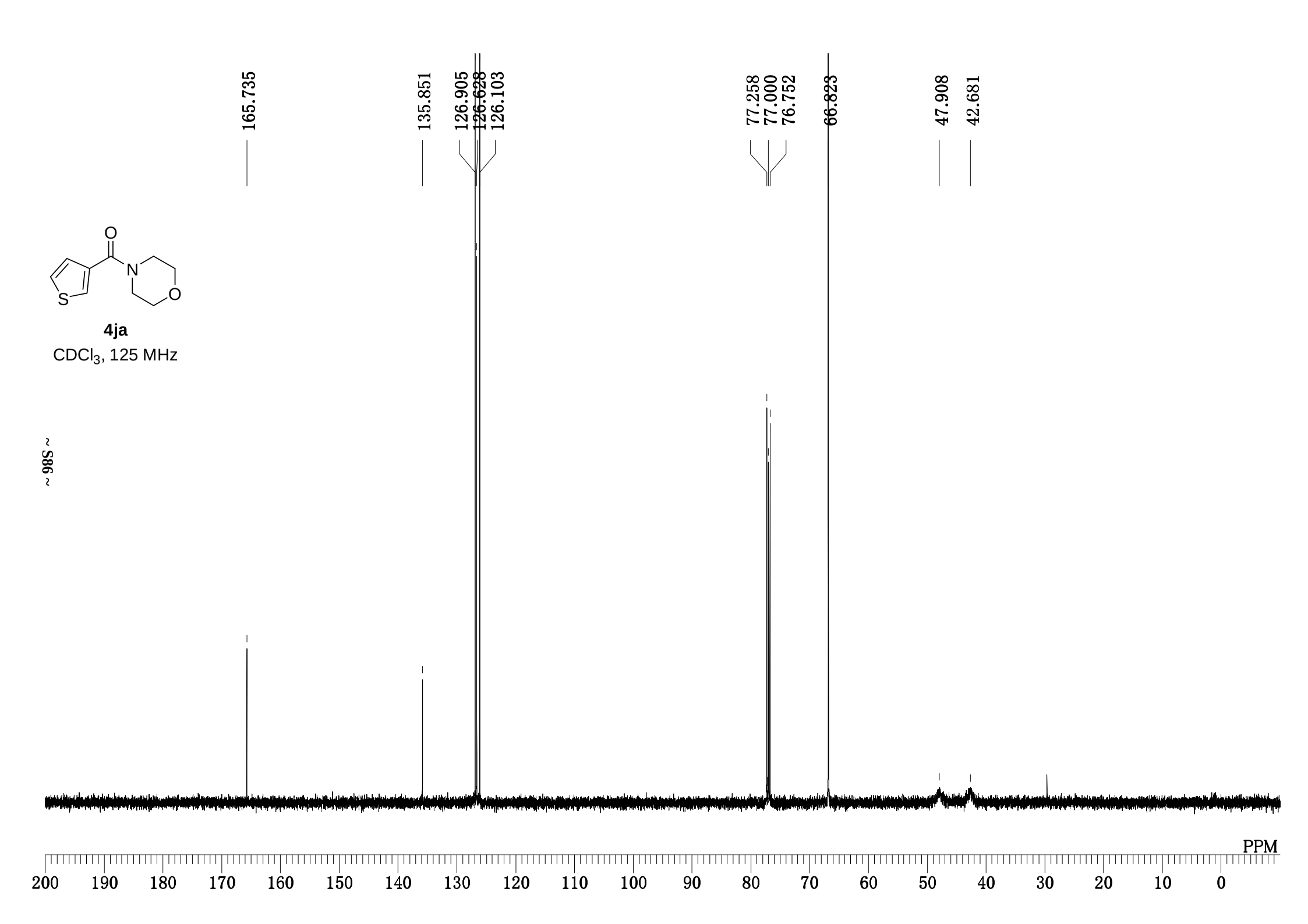


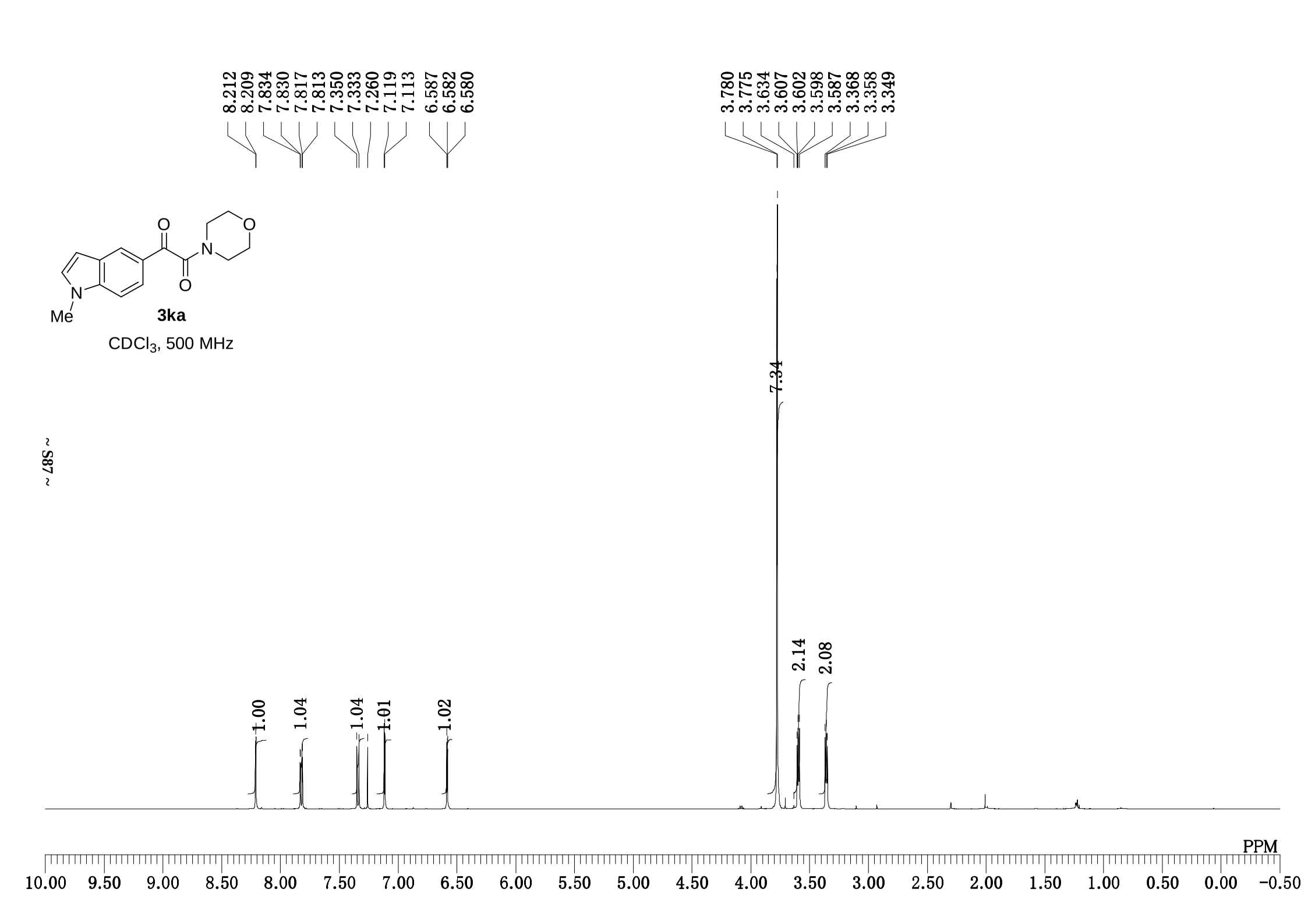


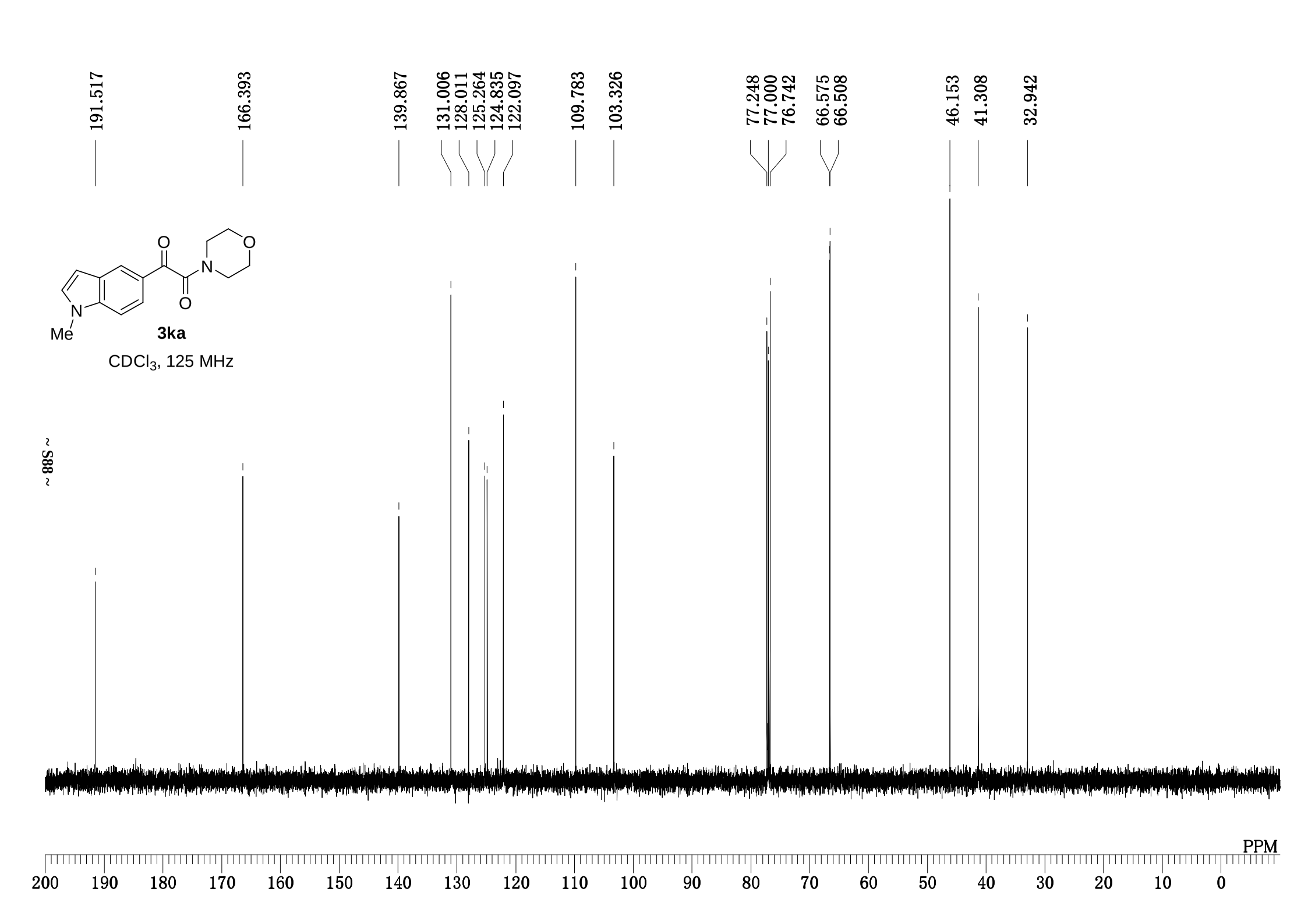
4ja

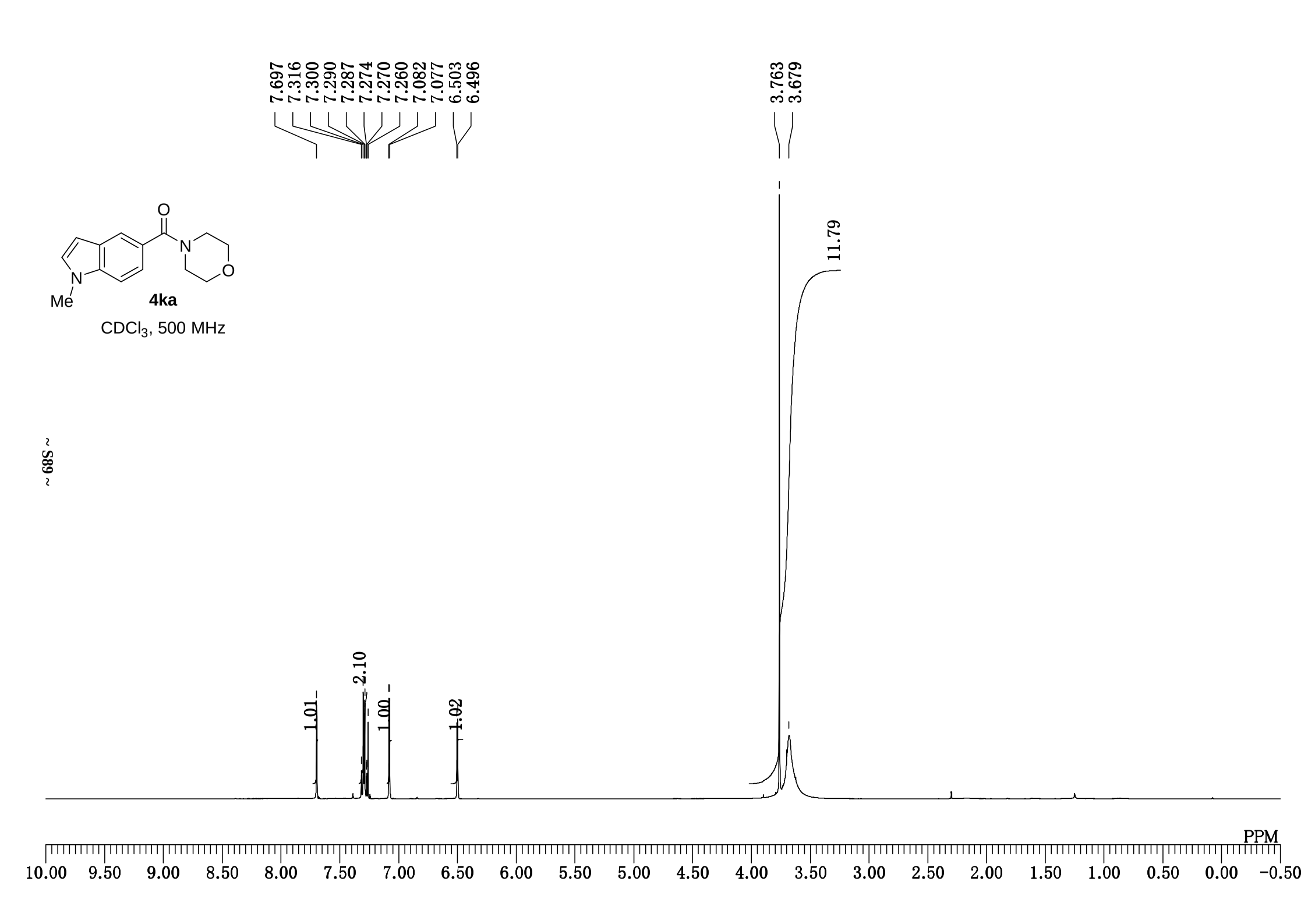
$CDCl_3$, 500 MHz

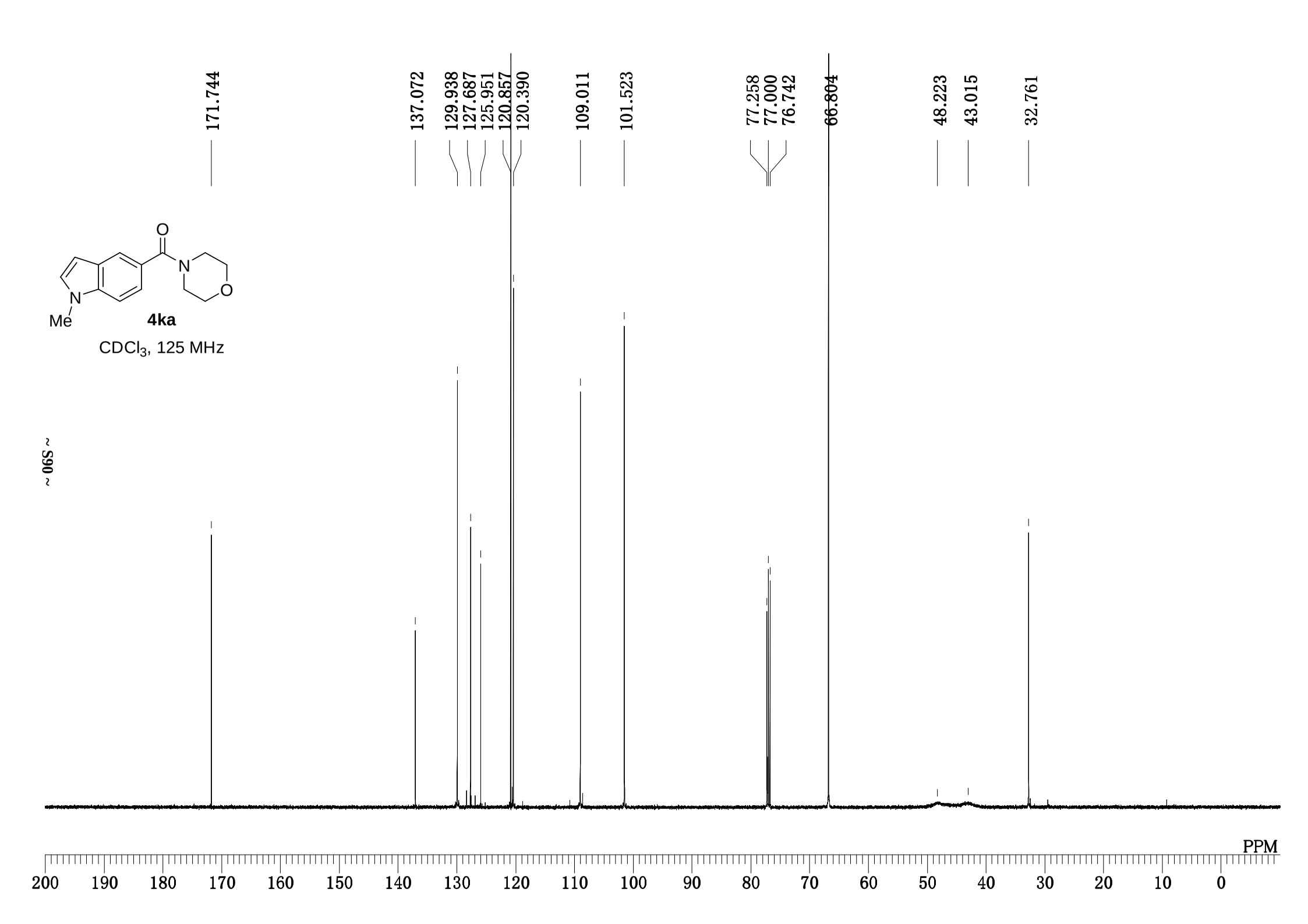


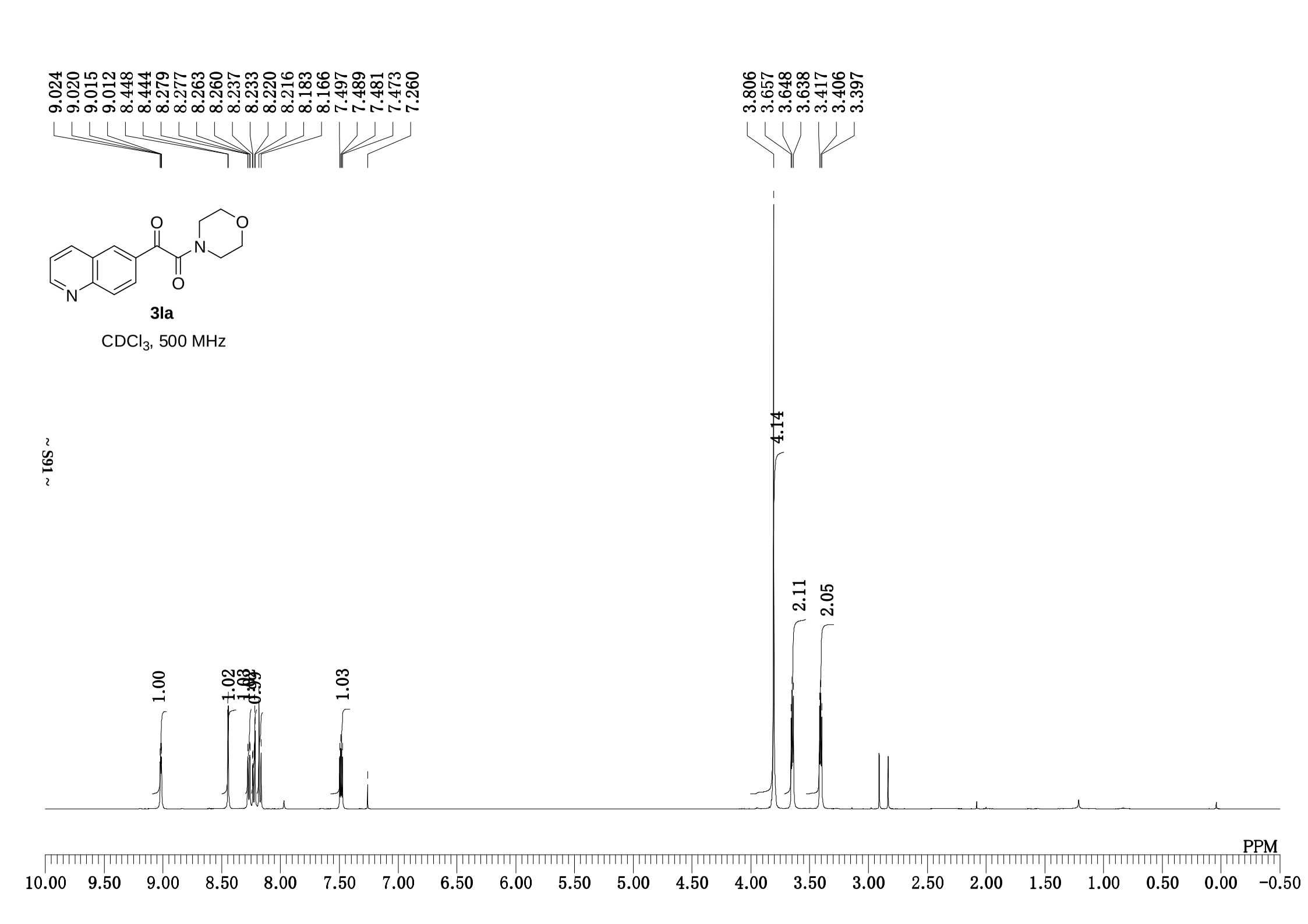

165.735
135.851
126.905
126.628
126.103
77.258
77.000
76.752
66.823
47.908
42.681
O
N
S
O
4ja
CDCl3, 125 MHz
~S86~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

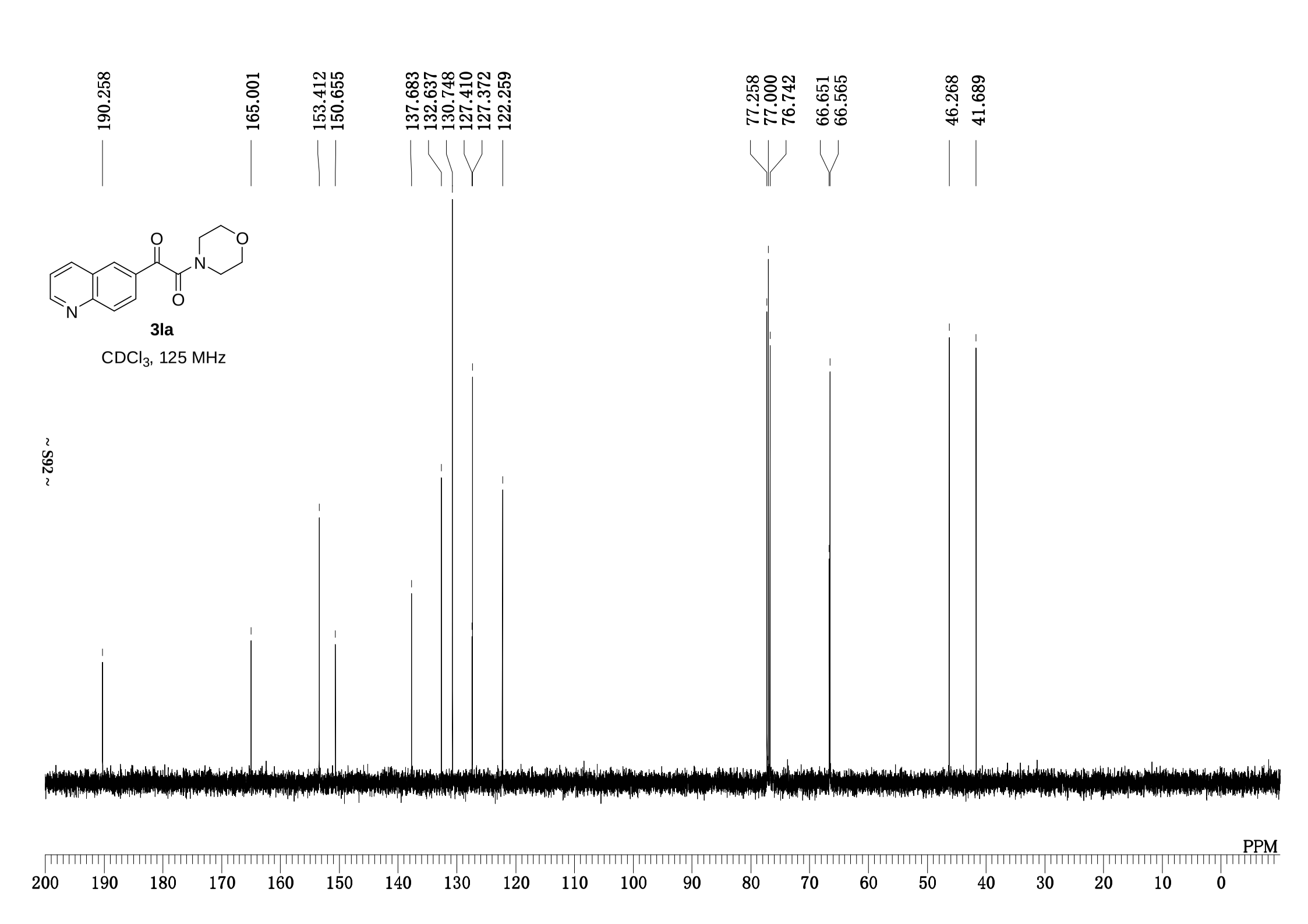

8.212
8.209
7.834
7.830
7.817
7.813
7.350
7.333
7.260
7.119
7.113
6.587
6.582
6.580
3.780
3.775
3.634
3.607
3.602
3.598
3.587
3.368
3.358
3.349
O
O
N
O
N
Me
3ka
CDCl3, 500 MHz
7.34
2.14
2.08
1.00
1.04
1.04
1.01
1.02
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

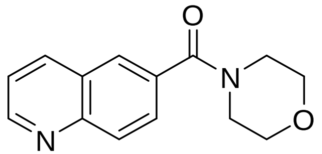

191.517
166.393
139.867
131.006
128.011
125.264
124.835
122.097
109.783
103.326
77.248
77.000
76.742
66.575
66.508
46.153
41.308
32.942
O
O
N
O
N
Me
3ka
CDCl3, 125 MHz
~ S88 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.697
7.316
7.300
7.290
7.287
7.274
7.270
7.260
7.082
7.077
6.503
6.496
3.763
3.679
11.79
2.10
1.01
1.00
1.02
O
N
N
O
Me
4ka
CDCl3, 500 MHz
~ S89 ~
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


171.744
137.072
129.938
127.687
125.951
120.857
120.390
109.011
101.523
77.258
77.000
76.742
66.804
48.223
43.015
32.761
O
N
N
O
Me
4ka
CDCl3, 125 MHz
~ S90 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

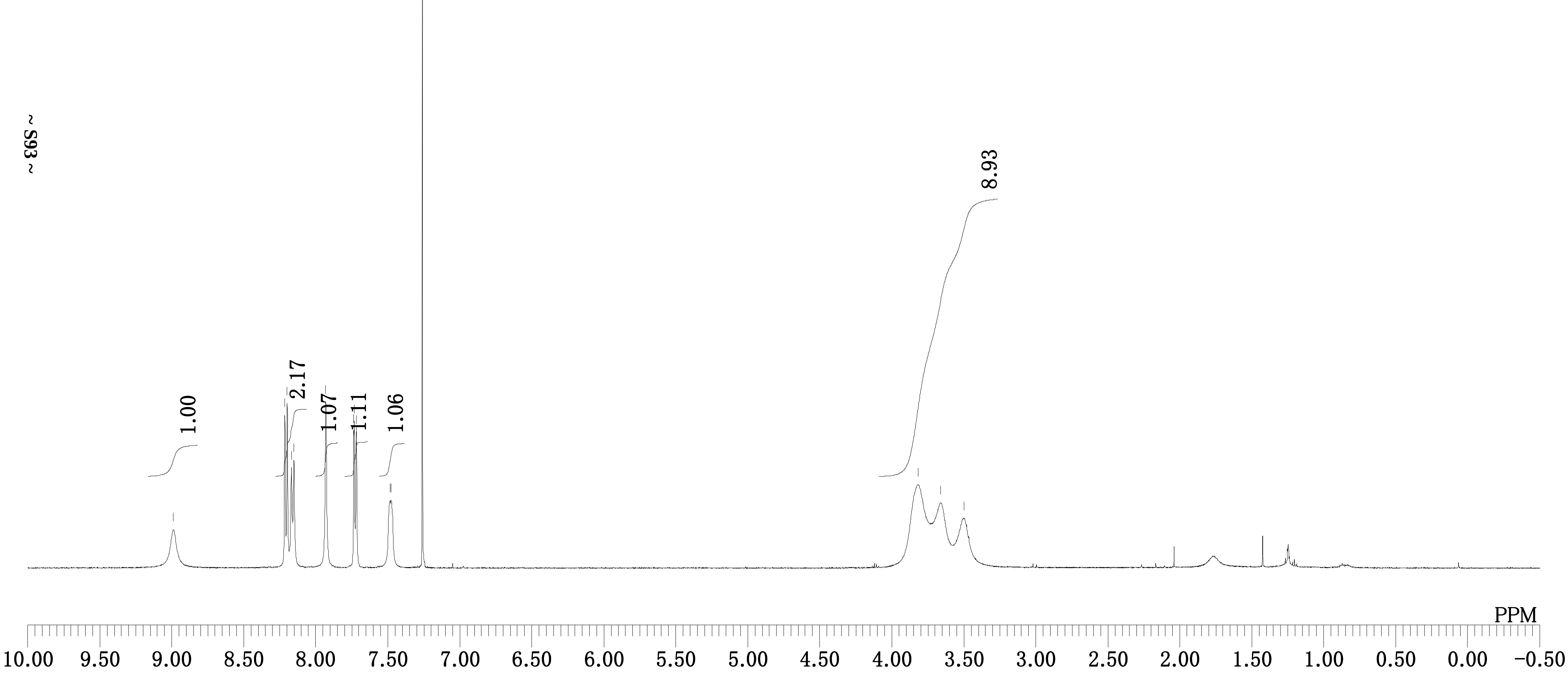

9.024
9.020
9.015
9.012
8.448
8.444
8.279
8.277
8.263
8.260
8.237
8.233
8.220
8.216
8.183
8.166
7.497
7.489
7.481
7.473
7.260
3.806
3.657
3.648
3.638
3.417
3.406
3.397
O
O
N
O
N
3la
CDCl3, 500 MHz
~ S91 ~
4.14
2.11
2.05
1.00
1.02
1.03
1.03
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
−0.50

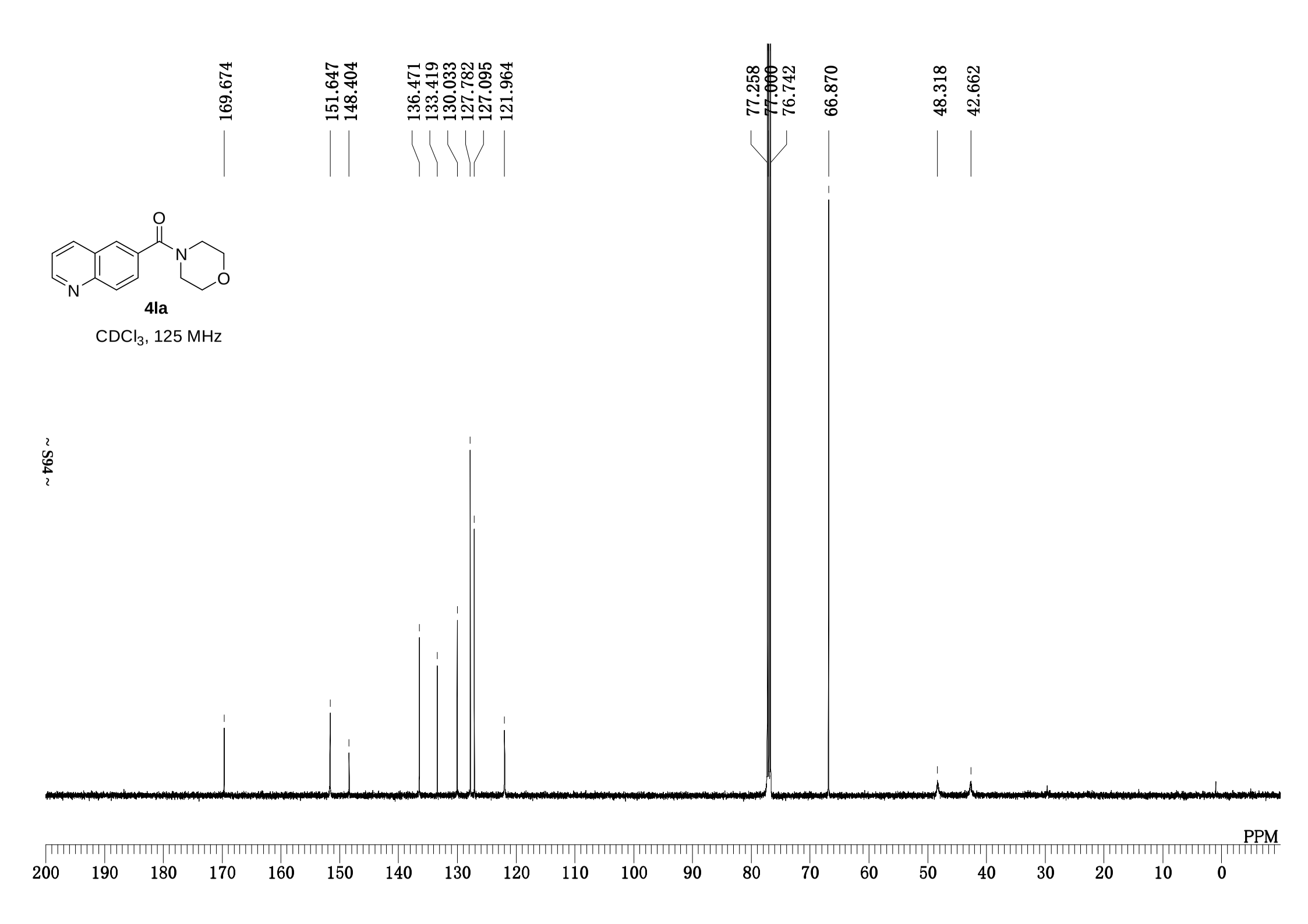

190.258
165.001
153.412
150.655
137.683
132.637
130.748
127.410
127.372
122.259
77.258
77.000
76.742
66.651
66.565
46.268
41.689
O
O
N
O
N
3la
CDCl3, 125 MHz
~ S92 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

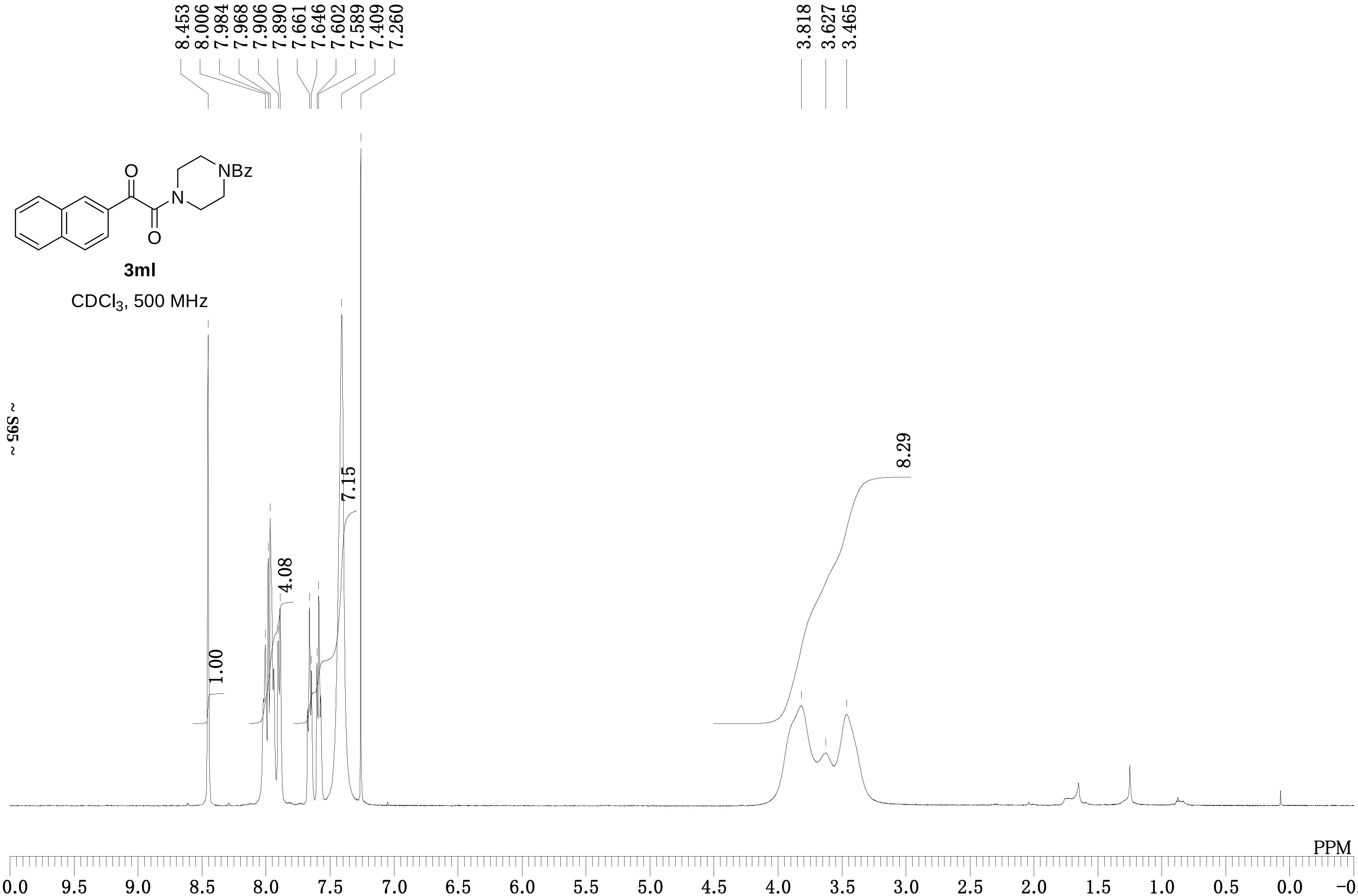


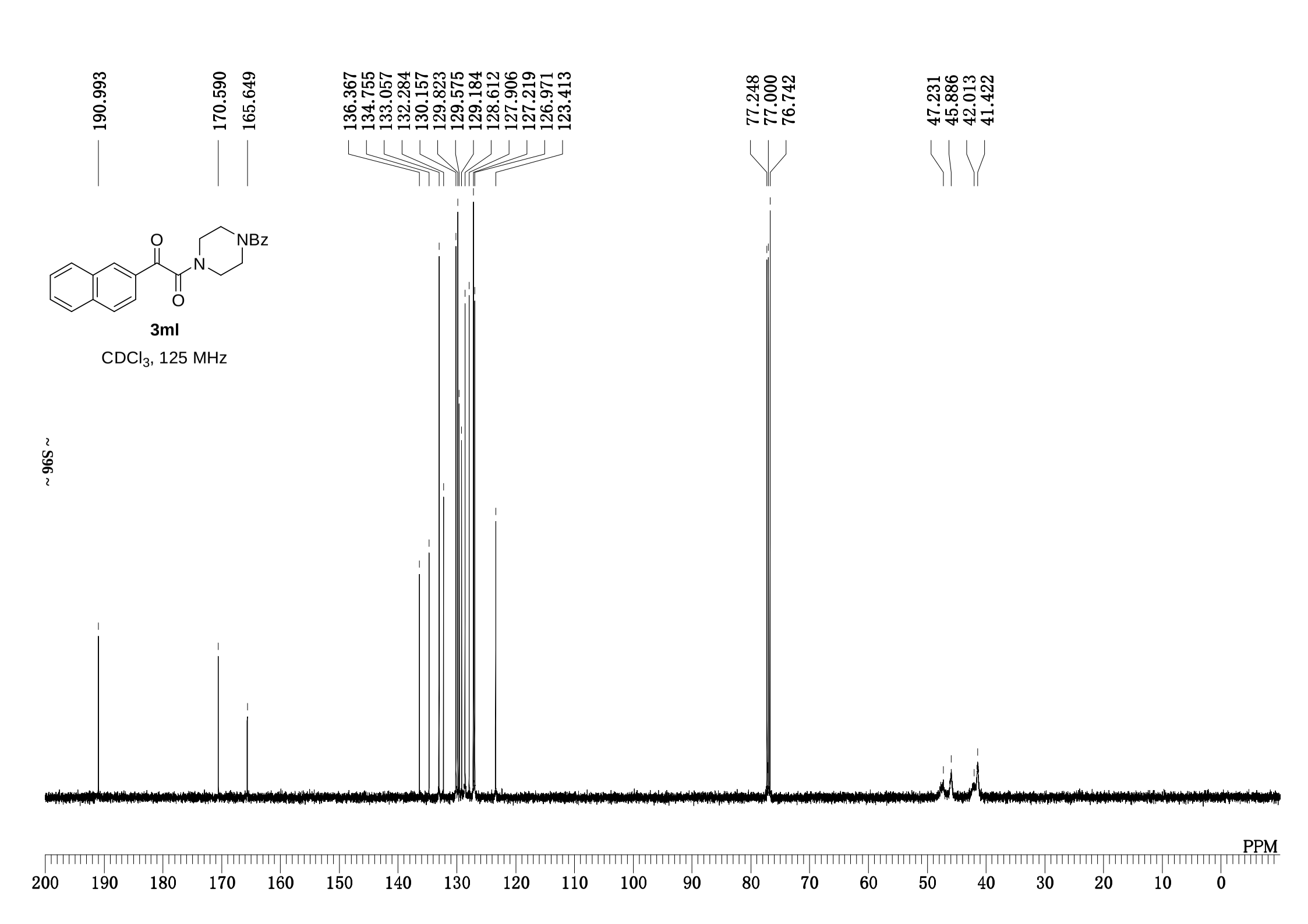
4la

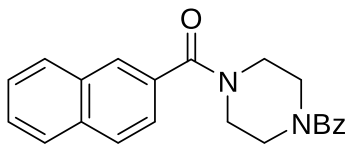
CDCl$_3$, 500 MHz




169.674
151.647
148.404
136.471
133.419
130.033
127.782
127.095
121.964
77.258
77.000
76.742
66.870
48.318
42.662
O
N
N
O
4la
CDCl3, 125 MHz
~ S94 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

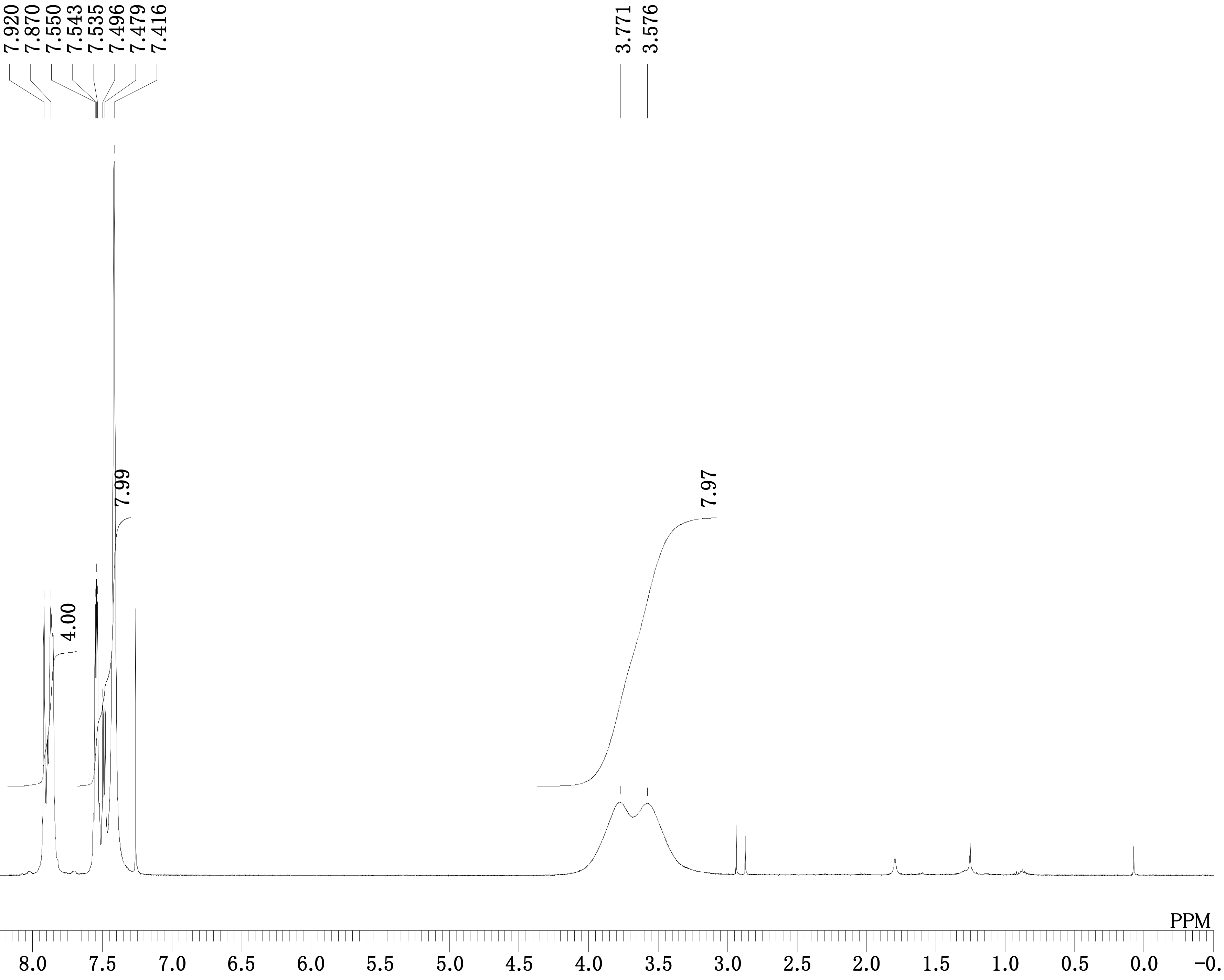

8.453
8.006
7.984
7.968
7.906
7.890
7.661
7.646
7.602
7.589
7.409
7.260
3.818
3.627
3.465
NBz
3ml
CDCl3, 500 MHz
1.00
4.08
7.15
8.29
PPM
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5

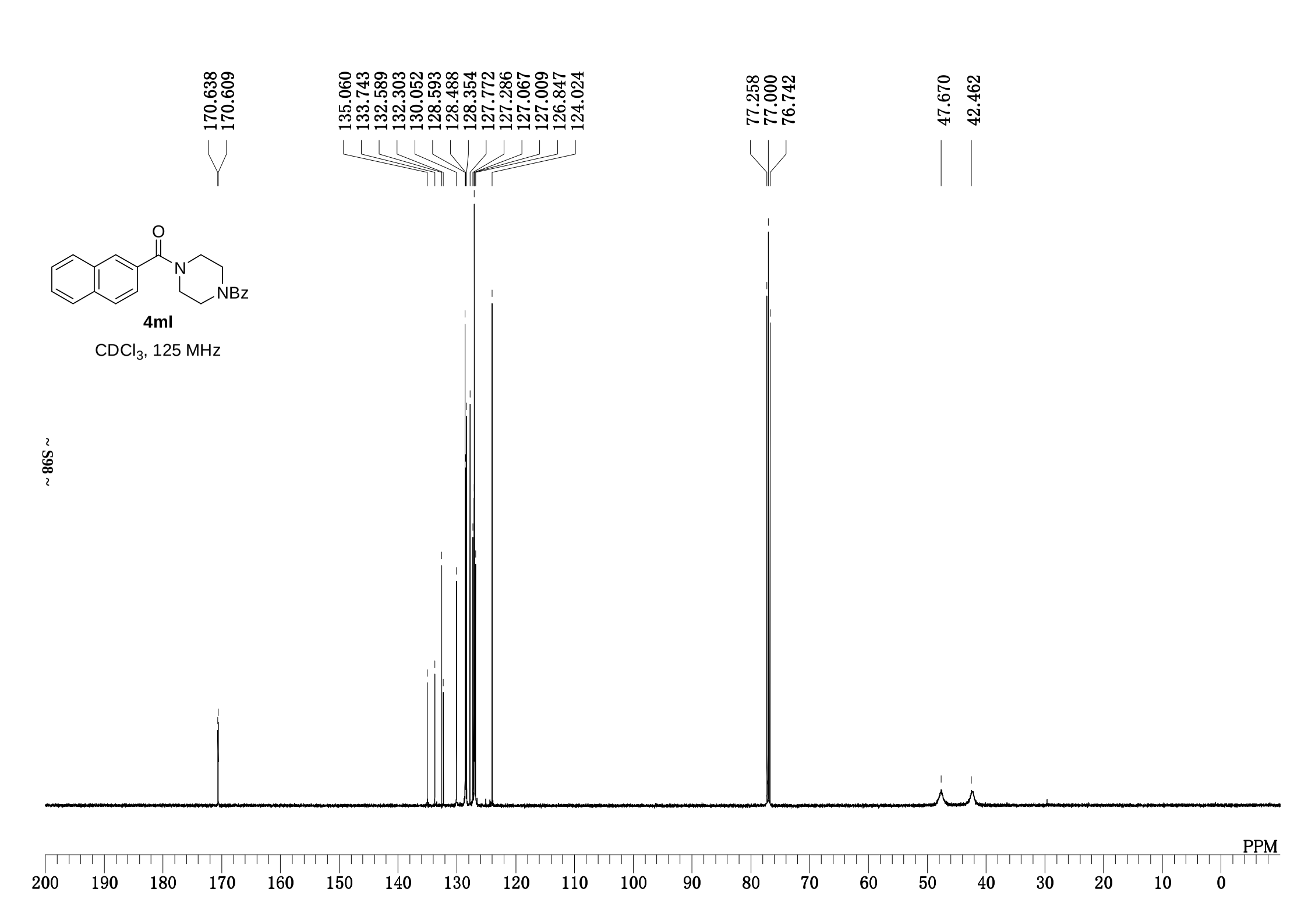

190.993
170.590
165.649
136.367
134.755
133.057
132.284
130.157
129.823
129.575
129.184
128.612
127.906
127.219
126.971
123.413
77.248
77.000
76.742
47.231
45.886
42.013
41.422
O
N
NBz
O
3ml
CDCl3, 125 MHz
~ S96 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



4ml

CDCl$_3$, 500 MHz




170.638
170.609
135.060
133.743
132.589
132.303
130.052
128.593
128.488
128.354
127.772
127.286
127.067
127.009
126.847
124.024
77.258
77.000
76.742
47.670
42.462
O
N
NBz
4ml
CDCl3, 125 MHz
~ S98 ~
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0