Electronic Supplementary Information

Nickel-Catalyzed Amination of Aryl Fluorides with Primary Amines

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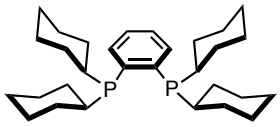
1. Instrumentation and Chemicals

^{1}H (400 MHz), ^{13}C (100.5 MHz) and ^{31}P (161.8 MHz) NMR spectra were recorded on a JEOL JNM-ECXII spectrometer. Chemical shift values for ^{1}H, ^{13}C and ^{31}P NMR spectra are referenced to Me_4Si (0 ppm), the residual solvent resonances (77.0 ppm for $CHCl_3$) and H_3PO_4 (0 ppm), respectively. High-resolution mass spectra were recorded at the Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University (JEOL JMS-T100GCv mass spectrometer for EI-MS) and the GC–MS & NMR Laboratory, Research Faculty of Agriculture, Hokkaido University (JEOL JMS-T100GCv mass spectrometer for FD-MS). IR spectra were measured with a PerkinElmer Frontier instrument. Optical rotations were measured on a JASCO P-2200. Melting points were measured with a Yanaco MP-500D instrument on a micro melting point apparatus using micro cover glass. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$.

All reactions were carried out under argon or nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. [Ni(cod)$_2$] was purchased from Kanto Chemical (if needed, recrystallization from toluene/1,5-cyclooctadiene was carried out before use). DCYPBz,[1] DIPPBz,[2] DETPBz[3] and were known compounds. PS-DPPBz was prepared according to the literature.[4] IPr·HCl, PCy_3, DPPBz, DCYPT, DCYPM, DCYPE, DCYPP·2HBF$_4$, DCYPB and **L1** were commercially available and used as received. NaO*t*Bu was purchased from TCI. Toluene (anhydrous grade) was purchased from Kanto Chemical, and dried and deoxidized by passage through packed columns of neutral alumina and copper(II) oxide under positive argon pressure.

2. Synthesis of DCYPBz

Although DCYPBz was a known compound,[1] its spectroscopic data have not been described: Mg turnings (519 mg, 21.4 mmol, 14.5 equiv) and Et_2O (18 mL) were placed in a 50-mL Schlenk flask equipped with a magnetic stirring bar. Bromocyclohexane (2.2 mL, 18.0 mmol, 12.0 equiv) was added dropwise to the flask at rt, and then the mixture was stirred for further 0.5 h. Next, *o*-bis(dichlorophosphino)benzene (270 μL, 1.47 mmol) was added to the flask at 0 °C. After stirring at rt for 3 h, the reaction was quenched with degassed H_2O (~5 mL) and 1N HCl aq (~5 mL). The organic layer was extracted with hexane under Ar atmosphere, dried over Na_2SO_4, filtered through a cannula equipped with a small filter paper, and evaporated under reduced pressure. The crude product was purified by reprecipitation with Et_2O (~4 mL) and MeOH (~40 mL) to give 1,2-bis(dicyclohexylphosphino)benzene (DCYPBz) as white solids (373.8 mg, 54% yield). The analytically pure compound was obtained by recrystallization from hot degassed *i*PrOH.



White solids. **M.p.** 142.7–145.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.00–1.35 (m, 20H), 1.46–1.82 (m, 16H), 1.82–2.00 (m, 8H), 7.29–7.32 (m, 2H), 7.48–7.52 (m, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$): δ 26.47 (4C), 27.20–27.32 (m, 8C), 29.11 (t, J_{C-P} = 4.7 Hz, 4C), 30.39 (t, J_{C-P} = 8.6 Hz, 4C), 34.89 (t, J_{C-P} = 5.7 Hz, 4C), 127.44 (2C), 132.64 (2C), 144.37 (t, J_{C-P} = 6.6 Hz, 2C). **^{31}P NMR** (161.8 MHz, $CDCl_3$): δ –13.96. **IR** (ATR): 2921, 2847, 1444, 1262, 1177, 1095, 1000, 850, 742 cm^{-1}. **HRMS–FD** (*m/z*): $[M]^+$ Calcd for $C_{30}H_{46}P_2$, 470.32312; found, 470.32227.

3. Preparation of Substrates

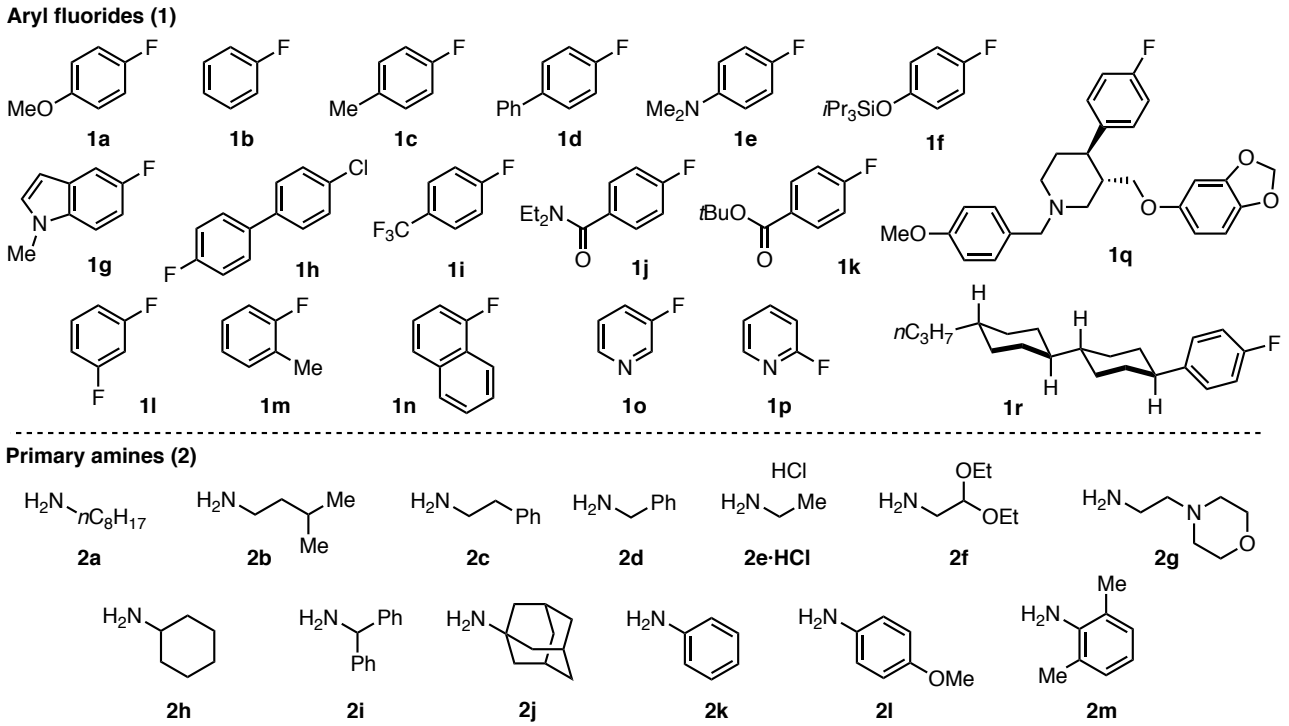
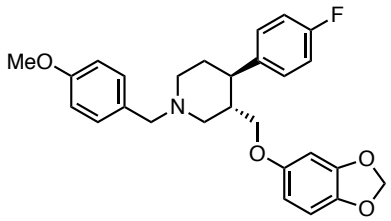


Figure S1. List of Substrates for Catalytic Reactions.

Aryl fluorides **1a–1e**, **1i**, **1l–1p** and **1r** were commercially available. **1f**,[5] **1g**,[6] **1h**,[7] **1j**[6] and **1k**[8] were known compounds. Primary amines **2a–2m** are commercially available.

_N_-PMB-protected Paroxetine (1q)

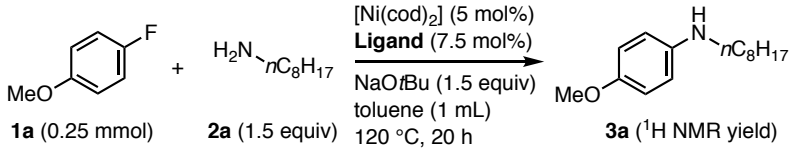
The title compound was synthesized from Paroxetine hydrochloride hemihydrate and *p*-methoxybenzyl chloride (1.2 equiv) with *i*Pr$_2$EtN (3.0 equiv) in CH_2Cl_2 [>99% yield, isolated by silica gel column chromatography with hexane/EtOAc 60:40]



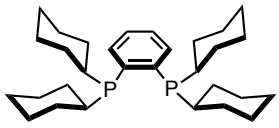
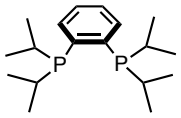
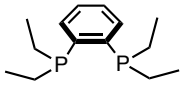
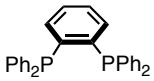
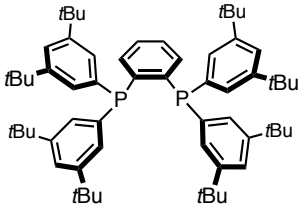
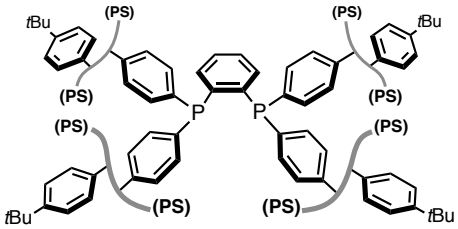
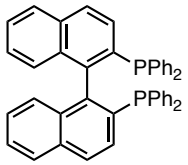
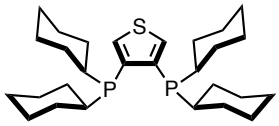
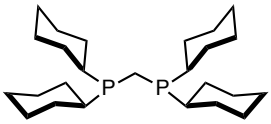
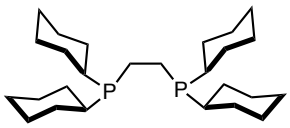
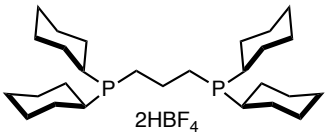
White solids. **M.p.** 94.6–95.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.78–1.86 (m, 2H), 2.00–2.09 (m, 2H), 2.18–2.22 (m, 1H), 2.46 (td, J = 11.2, 4.8 Hz, 1H), 2.97 (br d, J = 10.8 Hz, 1H), 3.23 (br d, J = 10.4 Hz, 1H), 3.40–3.60 (m, 4H), 3.81 (s, 3H), 5.88 (s, 2H), 6.11 (dd, J = 8.0, 2.4 Hz, 1H), 6.32 (d, J = 2.8 Hz, 1H), 6.62 (d, J = 8.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.96 (t, J = 8.4 Hz, 2H), 7.14–7.17 (m, 2H), 7.25–7.27 (m, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$): δ 34.31, 42.12, 44.07, 53.64, 55.23, 57.43, 62.74, 69.55, 97.93, 101.03, 105.47, 107.78, 113.53 (2C), 115.31 ($J_{C–F}$ = 21.1 Hz, 2C), 128.80 ($J_{C–F}$ = 7.7 Hz, 2C), 130.09, 130.42 (2C), 139.80, 141.44, 148.06, 154.36, 158.65, 161.42 ($J_{C–F}$ = 244.4 Hz). **IR** (ATR): 2931, 2762, 1610, 1511, 1488, 1463, 1251, 1220, 1184, 1097, 1030, 934, 850, 812, 784 cm^{-1}. **HRMS–FD** (*m/z*): $[M]^+$ Calcd for $C_{27}H_{28}FNO_4$, 449.20024; found, 449.20030. **$[\alpha]_D^{26}$** –39.74 (c = 1.03, $CHCl_3$).

4. Parameters in Ni-catalyzed Amination of 1a with 2a

Table S1. Effects of Ligands



1a (0.25 mmol) **2a** (1.5 equiv) **3a** (^{1}H NMR yield)

Entry	Ligand		**3a** [%, ^{1}H NMR]
1		**DCYPBz**	**95**
2		DIPPBz	79
3		DETPBz	3
4		DPPBz	0
5		SciOPP	0
6		PS-DPPBz	0
7		BINAP	0
8		DCYPT	68
9		DCYPM	0
10		DCYPE	48
11		DCYPP·2HBF$_4$	6

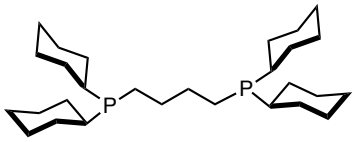
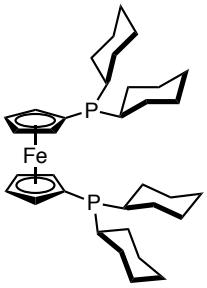
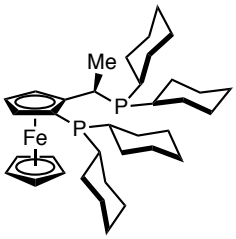
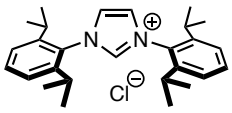
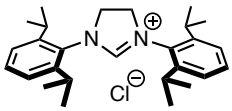
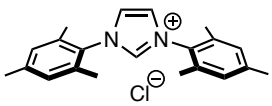
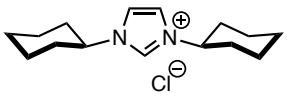
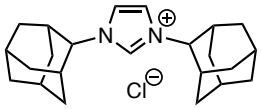
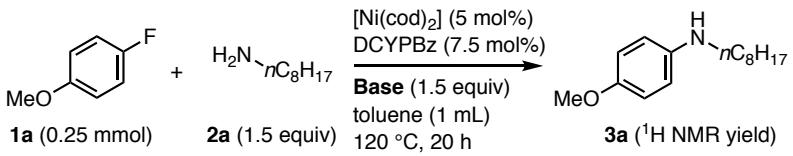
12		DCYPB	0
13		DCYPPF	0
14		**L1**	73
15		IPr·HCl	0
16		IPr·HCl (15 mol%)	0
17		SIPr·HCl	0
18		IMes·HCl	0
19		ICy·HCl	0
20		I(2-Ad)·HCl	0
21		PCy_3 (15 mol%)	0

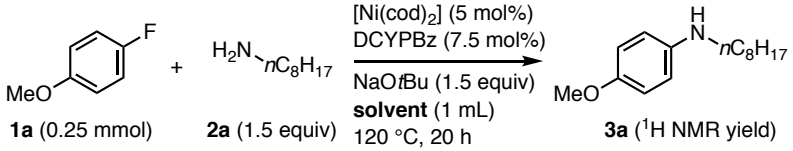
Table S2. Effects of Bases



1a (0.25 mmol) **2a** (1.5 equiv) **3a** (^{1}H NMR yield)

Entry	Base	**3a** [%, ^{1}H NMR]
1	**NaO*t*Bu**	**95**
2	LiO*t*Bu	20
3	KO*t*Bu	17
4	K_2CO_3	0
5	NaHMDS	22

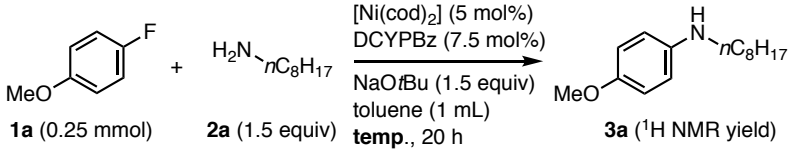
Table S3. Effects of Solvents



1a (0.25 mmol) **2a** (1.5 equiv) **3a** (^{1}H NMR yield)

Entry	Solvent	**3a** [%, ^{1}H NMR]
1	**toluene**	**95**
2	CPME	82
3	octane	75
4	1,4-dioxane	16
5	*t*AmOH	5
6	DMA	0

Table S4. Effects of Reaction Temperature



1a (0.25 mmol) **2a** (1.5 equiv) **3a** (^{1}H NMR yield)

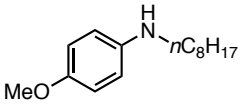
Entry	Temp (°C)	**3a** [%, ^{1}H NMR]
1	**120**	**95**
2	110	62
3	100	15
4	90	4
5	80	1

5. Experimental Procedures

A Typical Procedure for Ni-Catalyzed Amination of Aryl Fluorides with Primary Amines: In a nitrogen-filled glove box, [Ni(cod)$_2$] (3.4 mg, 0.0124 mmol, 5 mol%), DCYPBz (8.8 mg, 0.0187 mmol, 7.5 mol%) and toluene (0.5 mL) were placed in a 10-mL glass tube containing a magnetic stirring bar. After stirring at rt for ca. 5 min, 4-fluoroanisole (**1a**, 31.5 mg, 0.25 mmol), octylamine (**2a**, 48.4 mg, 0.374 mmol), NaO*t*Bu (36.0 mg, 0.375 mmol) and toluene (0.5 mL) were added successively. The tube was sealed with a screw cap and was removed from the glove box. The mixture was stirred at 120 °C for 20 h. After being cooled to rt, the mixture was diluted with Et_2O and filtered through a silica gel pad (eluting with Et_2O). The volatiles were removed under reduced pressure, and then an internal standard (1,2-diphenylethane) was added to determine the yield of 4-methoxy-*N*-octylaniline (**3a**, 95% yield). The crude product was purified by silica gel column chromatography (hexane/EtOAc 100:0 to 95:5) to give **3a** as pale yellow oil (55.3 mg, 0.235 mmol, 94% yield).

6. Characterization of Products

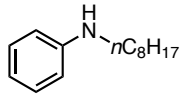
4-Methoxy-*N*-octylaniline (3a)[4]



[Scheme 2: **1a** (0.25 mmol), **2a** (0.374 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3a** (55.3 mg, 0.235 mmol, 94% yield) was isolated by silica gel column chromatography with hexane/EtOAc 100:0 to 95:5.

Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.24–1.44 (m, 10H), 1.57 (quint, J = 6.8 Hz, 2H), 3.05 (t, J = 6.8 Hz, 2H), 3.32 (br s, 1H), 3.74 (s, 3H), 6.56–6.63 (m, 2H), 6.75–6.80 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.10, 22.65, 27.19, 29.25, 29.42, 29.65, 31.81, 44.99, 55.79, 113.96 (2C), 114.82 (2C), 142.84, 151.87.

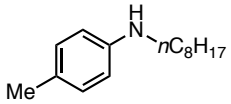
N-Octylaniline (3b)[9]



[Scheme 4: **1b** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3b** (42.4 mg, 0.206 mmol, 83% yield) was isolated by silica gel column chromatography with hexane/EtOAc 100:0 to 95:5.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, J = 7.6 Hz, 3H), 1.22–1.44 (m, 10H), 1.61 (quint, J = 6.8 Hz, 2H), 3.10 (t, J = 7.2 Hz, 2H), 3.59 (br s, 1H), 6.60 (dd, J = 8.0, 0.8 Hz, 2H), 6.68 (td, J = 7.2, 0.8 Hz, 1H), 7.15–7.20 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.09, 22.64, 27.16, 29.25, 29.40, 29.54, 31.81, 43.94, 112.62 (2C), 117.00, 129.17 (2C), 148.50.

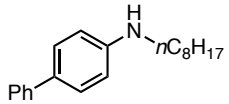
4-Methyl-*N*-octylaniline (3c)[4]



[Scheme 4: **1c** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3c** (49.7 mg, 0.227 mmol, 91% yield) was isolated by silica gel column chromatography with hexane/EtOAc 100:0 to 95:5.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.20–1.42 (m, 10H), 1.60 (quint, J = 7.2 Hz, 2H), 2.23 (s, 3H), 3.07 (t, J = 7.2 Hz, 2H), 3.45 (br s, 1H), 6.53 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.09, 20.34, 22.64, 27.17, 29.25, 29.41, 29.59, 31.81, 44.34, 112.83 (2C), 126.20, 129.65 (2C), 146.27.

N-Octyl-[1,1'-biphenyl]-4-amine (3d)[10]

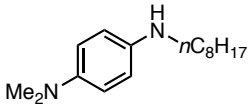


[Scheme 4: **1d** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%),

NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3d** (60.6 mg, 0.215 mmol, 86% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99:1 to 90:10.

Yellow solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.22–1.46 (m, 10H), 1.62 (quint, J = 8.0 Hz, 2H), 3.14 (t, J = 7.2 Hz, 2H), 3.70 (br s, 1H), 6.67 (d, J = 8.8 Hz, 2H), 7.22–7.26 (m, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.54 (dd, J = 8.0, 0.8 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.10, 22.65, 27.15, 29.26, 29.39, 29.52, 31.81, 43.93, 112.82 (2C), 125.90, 126.18 (2C), 127.85 (2C), 128.58 (2C), 129.81, 141.26, 147.90.

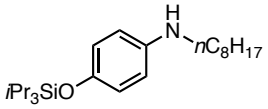
N^1,*N*^{1}-Dimethyl-*N*^{4}-octylbenzene-1,4-diamine (3e)[4]



[Scheme 4: **1e** (0.252 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), *m*-xylene (1 mL), 140 °C, 20 h] **3e** (57.9 mg, 0.233 mmol, 92% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 80:20.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.4 Hz, 3H), 1.20–1.45 (m, 10H), 1.57 (quint, J = 8.0 Hz, 2H), 2.81 (s, 6H), 3.05 (br, 2H+1H), 6.59 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.07, 22.62, 27.18, 29.23, 29.40, 29.72, 31.79, 42.31 (2C), 45.08, 114.19 (2C), 115.96 (2C), 141.19, 143.90.

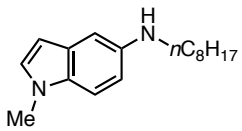
N-Octyl-4-((triisopropylsilyl)oxy)aniline (3f)



[Scheme 4: **1f** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), *m*-xylene (1 mL), 140 °C, 20 h] **3f** (76.7 mg, 0.203 mmol, 81% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99:1 to 95:5.

Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.08 (d, J = 7.2 Hz, 18H), 1.15–1.45 (m, 13H), 1.59 (quint, J = 6.8 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 3.29 (br s, 1H), 6.48–6.52 (m, 2H), 6.69–6.75 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 12.57 (3C), 14.09, 17.91 (6C), 22.65, 27.21, 29.25, 29.44, 29.72, 31.82, 44.96, 113.78 (2C), 120.35 (2C), 142.85, 147.69. **IR** (ATR): 2926, 2866, 1509, 1464, 1234, 919, 907, 883, 820, 758, 734, 679 cm^{-1}. **EI-HRMS** (*m/z*): $[M]^+$ calcd for $C_{23}H_{43}NOSi$ 377.31139; found, 377.31043.

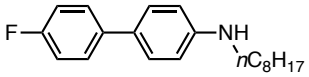
1-Methyl-*N*-octyl-1*H*-indol-5-amine (3g)



[Scheme 4: **1g** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3g** (60.3 mg, 0.233 mmol, 93% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99:1 to 90:10.

Yellow solids. **M.p.** 40.4–41.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.26–1.46 (m, 10H), 1.65 (quint, J = 6.8 Hz, 2H), 3.14 (t, J = 7.6 Hz, 2H), 3.38 (br s, 1H), 3.73 (s, 3H), 6.31 (dd, J = 2.8, 1.2 Hz, 1H), 6.65 (dd, J = 8.8, 2.4 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 3.2 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.09, 22.63, 27.27, 29.26, 29.45, 29.71, 31.81, 32.77, 45.51, 99.59, 102.41, 109.69, 111.79, 128.70, 129.27, 131.18, 142.37. **IR** (ATR): 2953, 2921, 2849, 1625, 1508, 1475, 1422, 1247, 1169, 868, 788, 727, 709 cm^{-1}. **EI-HRMS** (*m/z*): $[M]^+$ calcd for $C_{17}H_{26}N_2$ 258.20960; found, 258.20959.

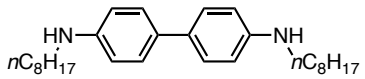
4-Fluoro-*N*-octyl-[1,1'-biphenyl]-4-amine (3h)



[Scheme 4: **1h** (0.25 mmol, contaminated with ~4% of 4,4'-dichlorobiphenyl), **2a** (0.25 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3h** (61.9 mg, 0.206 mmol, 83% yield), contaminated with *N*-octyl-[1,1'-biphenyl]-4-amine (2.9 mg, 4%), was isolated by silica gel column chromatography with hexane/EtOAc 100:0 to 99:1.

Pale yellow solids (viscous). **M.p.** 78.3–82.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.4 Hz, 3H), 1.20–1.50 (m. 10H), 1.62 (quint, J = 7.2 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H), 3.68 (br s, 1H), 6.64 (d, J = 8.4 Hz, 2H), 7.06 (t, J = 8.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.42–7.48 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.10, 22.65, 27.15, 29.26, 29.40, 29.51, 31.82, 43.94, 112.86 (2C), 115.35 (d, J_{C-F} = 21.1 Hz, 2C), 127.60 (d, J_{C-F} = 7.6 Hz, 2C), 127.73 (2C), 128.91, 137.43 (d, J_{C-F} = 2.9 Hz), 147.87, 161.65 (d, J_{C-F} = 245.2 Hz). **IR** (ATR): 2925, 2855, 1611, 1499, 1478, 1328, 1299, 1223, 1158, 813 cm^{-1}. **FD-HRMS** (*m/z*): $[M]^+$ calcd for $C_{20}H_{26}FN$ 299.20493; found, 299.20487.

N^4,$N^{4'}$-Dioctyl-[1,1'-biphenyl]-4,4'-diamine (3h')

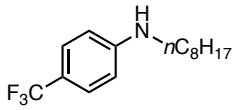


[Scheme 4: **1h** (0.25 mmol, contaminated with ~4% of 4,4'-dichlorobiphenyl), **2a** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3h** (46.5 mg, 0.155 mmol, 62%) and **3h'** (31.3 mg, 0.077 mmol, 31% yield) was isolated by silica gel column chromatography with hexane/EtOAc 100:0 to 95:5.

Yellow solids. **M.p.** 89.5–91.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.4 Hz, 6H), 1.20–1.40 (m. 20H), 1.63 (quint, J = 7.2 Hz, 4H), 3.12 (t, J = 7.2 Hz, 4H), 3.60 (br s, 2H), 6.64 (d, J = 8.8 Hz, 4H), 7.36 (d, J = 8.4 Hz, 4H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.11 (2C), 22.65 (2C), 27.18 (2C), 29.27 (2C), 29.41 (2C), 29.59 (2C), 31.82 (2C), 44.14 (2C), 112.96 (4C), 127.09 (4C),

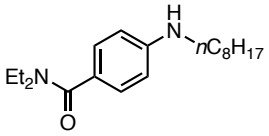
130.47 (2C), 147.00 (2C). **IR** (ATR): 3390, 2954, 2919, 2852, 1614, 1505, 1470, 1328, 1287, 1182, 812, 797 cm^{-1}. **FD-HRMS** (*m/z*): $[M]^+$ calcd for $C_{28}H_{44}N_2$ 408.35045; found, 408.35226.

_N_-Octyl-4-(trifluoromethyl)aniline (3i)[4]



[Scheme 4: **1i** (0.25 mmol), **2a** (0.375 mmol), $[Ni(cod)_2]$ (5 mol%), DCYPBz or DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] Only trace amounts of **3i** was observed in the crude mixture (based on ^1H NMR analysis).

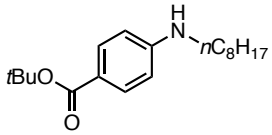
_N,N_-Diethyl-4-(octylamino)benzamide (3j)



[Scheme 4: **1j** (0.25 mmol), **2a** (0.375 mmol), $[Ni(cod)_2]$ (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3j** (50.6 mg, 0.166 mmol, 66% yield) was isolated by silica gel column chromatography with hexane/EtOAc 90:10 to 60:40.

Pale pink solids. **M.p.** 42.5–44.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.4 Hz, 3H), 1.18 (t, J = 6.8 Hz, 6H), 1.26–1.46 (m, 10H), 1.61 (quint, J = 7.6 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H), 3.43 (br m, 4H), 3.86 (br, 1H), 6.55 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 13.53 (br, 2C), 14.05, 22.60, 27.06, 29.18, 29.33, 29.35, 31.75, 40.99 (br m, 2C), 43.62, 111.60 (2C), 125.05, 128.32, 128.41, 149.36, 171.80. **IR** (ATR): 3337, 2927, 2854, 1598, 1425, 1285, 1172, 1096, 833, 762, 730 cm^{-1}. **EI-HRMS** (*m/z*): $[M]^+$ calcd for $C_{19}H_{32}N_2O$ 304.25146; found, 304.25046.

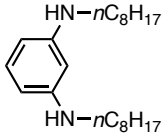
***tert*-Butyl 4-(octylamino)benzoate (3k)**[9]



[Scheme 4: **1k** (0.25 mmol), **2a** (0.375 mmol), $[Ni(cod)_2]$ (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3k** (52.3 mg, 0.171 mmol, 68% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99:1 to 98:2.

White solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3H), 1.22–1.42 (m, 10H), 1.56 (s, 9H), 1.61 (quint, J = 6.8 Hz, 2H), 3.14 (t, J = 7.2 Hz, 2H), 4.06 (br s, 1H), 6.52 (d, J = 6.8 Hz, 2H), 7.80 (d, J = 6.8 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.06, 22.62, 27.04, 28.29 (3C), 29.19, 29.27, 29.32, 31.76, 43.37, 79.70, 111.14 (2C), 119.87, 131.27 (2C), 151.75, 166.19.

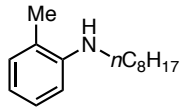
N^1,N^3-Dioctylbenzene-1,3-diamine (3l)[11]



[Scheme 4: **1l** (0.25 mmol), **2a** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3l** (65.8 mg, 0.198 mmol, 79% yield) was isolated by silica gel column chromatography with hexane/CH_2Cl_2 80:20 followed by GPC.

White solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 6H), 1.20–1.50 (m, 20H), 1.59 (quint, J = 7.6 Hz, 4H), 3.07 (t, J = 7.2 Hz, 4H), 3.50 (br s, 2H), 5.86 (t, J = 2.0 Hz, 1H), 5.99 (dd, J = 8.0, 2.0 Hz, 2H), 6.96 (t, J = 8.0 Hz, 1H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.11 (2C), 22.65 (2C), 27.20 (2C), 29.27 (2C), 29.42 (2C), 29.64 (2C), 31.83 (2C), 44.00 (2C), 96.83, 102.54 (2C), 129.87, 149.70 (2C).

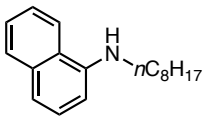
2-Methyl-*N*-octylaniline (3m)[4]



[Scheme 4: **1m** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), *m*-xylene (1 mL), 140 °C, 20 h] **3m** (28.6 mg, 0.130 mmol, 52% yield) was isolated by silica gel column chromatography with hexane/EtOAc 100:0 to 95:5.

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.21–1.43 (m, 10H), 1.66 (quint, J = 7.6 Hz, 2H), 2.13 (s, 3H), 3.14 (t, J = 7.2 Hz, 2H), 3.44 (br s, 1H), 6.60–6.66 (m, 2H), 7.05 (d, J = 6.8 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.10, 17.44, 22.66, 27.24, 29.27, 29.42, 29.58, 31.83, 43.93, 109.55, 116.56, 121.62, 127.10, 129.96, 146.35.

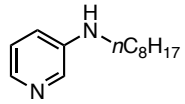
***N*-Octylnaphthalen-1-amine (3n)**[12]



[Scheme 4: **1n** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3n** (58.4 mg, 0.229 mmol, 92% yield) was isolated by silica gel column chromatography with hexane/CH_2Cl_2 90:10 to 80:20.

Brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.21–1.40 (8H), 1.41–1.51 (m, 2H), 1.74 (quint, J = 7.2 Hz, 2H), 3.23 (t, J = 7.2 Hz, 2H), 4.27 (br s, 1H), 6.58 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.37–7.44 (m, 2H), 7.77 (d, J = 8.8 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.11, 22.66, 27.34, 29.27, 29.40, 29.45, 31.83, 44.18, 104.10, 116.96, 119.73, 123.24, 124.51, 125.59, 126.64, 128.61, 134.25, 143.59.

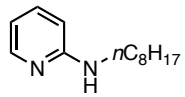
***N*-Octylpyridin-3-amine (3o)**[4]



[Scheme 4: **1o** (0.263 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3o** (45.6 mg, 0.221 mmol, 84% yield) was isolated by silica gel column chromatography with hexane/EtOAc 90:10 to 50:50.

White solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.4 Hz, 3H), 1.20–1.49 (m, 10H), 1.60 (quint, J = 7.2 Hz, 2H), 3.10 (q, J = 6.8 Hz, 2H), 3.71 (br s, 1H), 6.83–6.86 (m, 1H), 7.07 (dd, J = 8.0, 4.4 Hz, 1H), 7.94 (d, J = 4.8 Hz, 1H), 8.02 (d, J = 2.8 Hz, 1H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.05, 22.60, 27.03, 29.18, 29.33 (1C+1C), 31.74, 43.53, 118.19, 123.62, 135.97, 138.43, 144.35.

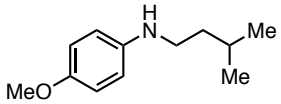
***N*-Octylpyridin-2-amine (3p)**[9]



[Scheme 4: **1p** (0.25 mmol), **2a** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPE (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3p** (37.2 mg, 0.180 mmol, 72% yield) was isolated by silica gel column chromatography with hexane/EtOAc 90:10 followed by PTLC with hexane/EtOAc 90:10.

White solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.20–1.44 (m, 10H), 1.60 (quint, J = 7.6 Hz, 2H), 3.23 (q, J = 6.4 Hz, 2H), 4.50 (br s, 1H), 6.36 (d, J = 8.4 Hz, 1H), 6.54 (dd, J = 6.4, 5.2 Hz, 1H), 7.38–7.43 (m, 1H), 8.07 (dd, J = 5.0, 1.0 Hz, 1H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.09, 22.62, 27.05, 29.23, 29.34, 29.52, 31.79, 42.27, 106.23, 112.55, 137.34, 148.21, 158.91.

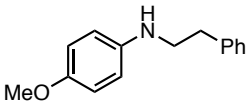
***N*-Isopentyl-4-methoxyaniline (3q)**[4]



[Scheme 5: **1a** (0.25 mmol), **2b** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3q** (43.4 mg, 0.225 mmol, 90% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 85:15.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.94 (d, J = 6.4 Hz, 6H), 1.50 (q, J = 7.2 Hz, 2H), 1.71 (septet, J = 7.2 Hz, 1H), 3.07 (t, J = 7.6 Hz, 2H), 3.37 (br, 1H), 3.75 (s, 3H), 6.56–6.61 (m, 2H), 6.76–6.80 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 22.60 (2C), 25.96, 38.63, 43.11, 55.75, 113.95 (2C), 114.81 (2C), 142.81, 151.88.

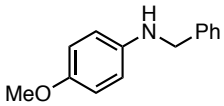
4-Methoxy-*N*-phenethylaniline (3r)[4]



[Scheme 5: **1a** (0.25 mmol), **2c** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3r** (45.2 mg, 0.199 mmol, 80% yield) was isolated by silica gel column chromatography with hexane/EtOAc 90:10.

Brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.92 (t, J = 7.2 Hz, 2H), 3.36 (t, J = 7.2 Hz, 2H), 3.75 (s + br, 3H+1H), 6.60–6.64 (m, 2H), 6.77–6.81 (m, 2H), 7.21–7.26 (m, 3H), 7.30–7.34 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 35.39, 46.18, 55.70, 114.58 (2C), 114.83 (2C), 126.33, 128.53 (2C), 128.74 (2C), 139.25, 141.76, 152.30.

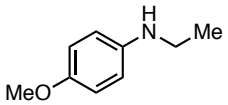
***N*-Benzyl-4-methoxyaniline (3s)**[13]



[Scheme 5: **1a** (0.25 mmol), **2d** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3s** (48.3 mg, 0.226 mmol, 91% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 85:15.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.74 (s, 3H), 3.78 (br s, 1H), 4.28 (s, 2H), 6.59–6.63 (m, 2H), 6.76–6.80 (m, 2H), 7.26–7.29 (m, 1H), 7.32–7.39 (m, 4H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 49.14, 55.72, 114.01 (2C), 114.81 (2C), 127.10, 127.49 (2C), 128.53 (2C), 139.61, 142.38, 152.08.

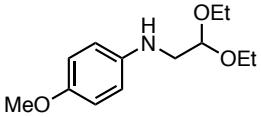
***N*-Ethyl-4-methoxyaniline (3t)**[14]



[Scheme 5: **1a** (0.25 mmol), **2e·HCl** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (1.5 mmol), CPME (1 mL), 120 °C, 20 h] **3t** (29.2 mg, 0.193 mmol, 77% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 85:15.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.24 (t, J = 6.8 Hz, 3H), 3.11 (q, J = 7.6 Hz, 2H), 3.31 (br, 1H), 3.75 (s, 3H), 6.57–6.61 (m, 2H), 6.77–6.81 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.95, 39.43, 55.77, 114.09 (2C), 114.81 (2C), 142.65, 152.00.

***N*-(2,2-Diethoxyethyl)-4-methoxyaniline (3u)**[15]

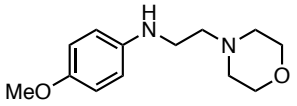


[Scheme 5: **1a** (0.25 mmol), **2f** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3u** (45.3 mg, 0.189 mmol, 76% yield) was

isolated by silica gel column chromatography with hexane/EtOAc 70:30.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.24 (t, J = 6.8 Hz, 6H), 3.21 (d, J = 5.6 Hz, 2H), 3.53–3.61 (m, 2H), 3.64 (br s, 1H), 3.69–3.77 (m, 5H), 4.68 (t, J = 5.6 Hz, 1H), 6.60–6.64 (m, 2H), 6.76–6.80 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 15.34 (2C), 47.30, 55.68, 62.31 (2C), 100.95, 114.43 (2C), 114.77 (2C), 142.05, 152.23.

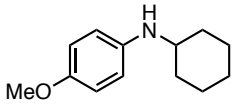
4-Methoxy-*N*-(2-morpholinoethyl)aniline (3v)[16]



[Scheme 5: **1a** (0.25 mmol), **2g** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3v** (27.0 mg, 0.114 mmol, 46% yield) was isolated by silica gel column chromatography with hexane/EtOAc 50:50 to 0:100

Pale yellow solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.47 (br m, 4H), 2.63 (t, J = 6.0 Hz, 2H), 3.13 (t, J = 6.0 Hz, 2H), 3.72 (t, J = 4.4 Hz, 4H), 3.75 (s, 3H), 6.61–6.63 (m, 2H), 6.78–6.80 (m, 2H) (NH proton is missing). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 40.87, 53.33 (2C), 55.77, 57.22, 66.92 (2C), 114.17 (2C), 114.81 (2C), 142.68, 152.08.

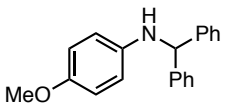
***N*-Cyclohexyl-4-methoxyaniline (3w)**[4]



[Scheme 5: **1a** (0.25 mmol), **2h** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3w** (40.8 mg, 0.199 mmol, 80% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 85:15.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.09–1.14 (m, 2H), 1.15–1.28 (m, 1H), 1.29–1.41 (m, 2H), 1.61–1.67 (m, 1H), 1.72–1.77 (m, 2H), 2.02–2.06 (m, 2H), 3.13–3.24 (m, 2H), 3.74 (s, 3H), 6.55–6.59 (m, 2H), 6.75–6.79 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 25.04 (2C), 25.93, 33.57 (2C), 52.71, 55.75, 114.74 (2C), 114.82 (2C), 141.55, 151.75.

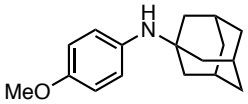
***N*-Benzhydryl-4-methoxyaniline (3x)**[4]



[Scheme 5: **1a** (0.25 mmol), **2i** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3x** (56.5 mg, 0.195 mmol, 78% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99:1 to 90:10.

Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 4.00 (br s, 1H), 5.42 (s, 1H), 6.49–6.52 (m, 2H), 6.69–6.72 (m, 2H), 7.23–7.27 (m, 2H), 7.29–7.40 (m, 8H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 55.63, 63.75, 114.54 (2C), 114.64 (2C), 127.23 (2C), 127.35 (4C), 128.66 (4C), 141.61, 143.14 (2C), 152.04.

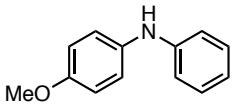
***N*-(4-Methoxyphenyl)adamantan-1-amine (3y)**[4]



[Scheme 5: **1a** (0.25 mmol), **2j** (0.375 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), *o*-xylene (1 mL), 140 °C, 20 h] **3y** (11.3 mg, 0.044 mmol, 18% yield) was isolated by silica gel column chromatography with hexane/EtOAc 70:30.

White solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.63 (q, J = 12.4 Hz, 6H), 1.74 (d, J = 2.4 Hz, 6H), 2.08 (br s, 3H), 3.77 (s, 3H), 6.74−6.78 (m, 2H), 6.81−6.84 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 29.67 (3C), 36.42 (3C), 43.68 (3C), 52.60, 55.43, 113.78 (2C), 124.35 (2C), 138.20, 154.79.

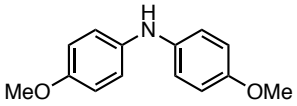
4-Methoxy-*N*-phenylaniline (3z)[17]



[Scheme 5: **1a** (0.25 mmol), **2k** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3z** (44.6 mg, 0.224 mmol, 90% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 85:15.

White solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 5.49 (br s, 1H), 6.81–6.92 (m, 5H), 7.06–7.10 (m, 2H), 7.18–7.24 (m, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 55.51, 114.59 (2C), 115.55 (2C), 119.49, 122.14 (2C), 129.26 (2C), 135.63, 145.09, 155.18.

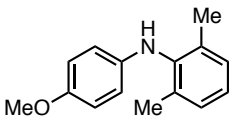
Bis(4-methoxyphenyl)amine (3aa)[18]



[Scheme 5: **1a** (0.25 mmol), **2l** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3aa** (48.5 mg, 0.212 mmol, 85% yield) was isolated by silica gel column chromatography with hexane/EtOAc 90:10 to 80:20.

Yellow solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.78 (s, 6H), 5.28 (br s, 1H), 6.80–6.84 (m, 4H), 6.92–6.96 (m, 4H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 55.58 (2C), 114.63 (4C), 119.45 (4C), 137.86 (2C), 154.14 (2C).

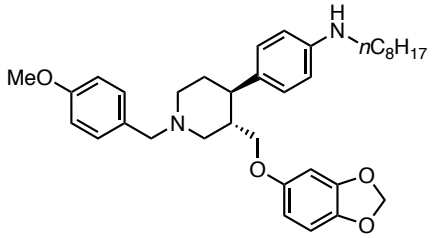
***N*-(4-Methoxyphenyl)-2,6-dimethylaniline (3ab)**[19]



[Scheme 5: **1a** (0.25 mmol), **2m** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3ab** (32.4 mg, 0.143 mmol, 57% yield) was isolated by silica gel column chromatography with hexane/EtOAc 95:5 to 85:15.

Brown solids. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.19 (s, 6H), 3.74 (s, 3H), 5.02 (br s, 1H), 6.42–6.54 (m, 2H), 6.73–6.77 (m, 2H), 7.02–7.05 (m, 1H), 7.10 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): 18.35 (2C), 55.64, 114.63 (2C), 115.22 (2C), 124.97 (2C), 128.54 (2C), 134.83, 139.19, 140.03, 152.66.

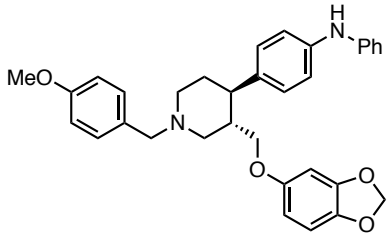
4-((3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-1-(4-methoxybenzyl)piperidin-4-yl)-*N*-octylaniline (3ac)



[Scheme 6: **1q** (0.25 mmol), **2a** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), *m*-xylene (1 mL), 140 °C, 20 h] **3ac** (131.2 mg, 0.234 mmol, 94% yield) was isolated by silica gel column chromatography with hexane/EtOAc 80:20 to 60:40.

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.4 Hz, 3H), 1.22–1.42 (m, 10H), 1.58 (quint, J = 6.8 Hz, 2H), 1.72–1.88 (m, 2H), 2.00 (t, J = 11.2 Hz, 2H), 2.15–2.24 (m, 1H), 2.30 (td, J = 11.6, 4.4 Hz, 1H), 2.94 (br d, J = 11.2 Hz, 1H), 3.04 (t, J = 7.2 Hz, 2H), 3.25 (br d, J = 10.2 Hz, 1H), 3.43–3.47 (br m, 2H+1H), 3.56–3.61 (m, 2H), 3.79 (s, 3H), 5.84 (s, 2H), 6.11 (dd, J = 8.4, 2.4 Hz, 1H), 6.34 (d, J = 2.4 Hz, 1H), 6.52 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): 14.05, 22.59, 27.12, 29.18, 29.34, 29.56, 31.75, 34.34, 41.99, 43.87, 44.08, 53.76, 55.13, 57.69, 62.77, 69.88, 97.96, 100.88, 105.56, 107.68, 112.76 (2C), 113.43 (2C), 128.09 (2C), 130.17, 130.38 (2C), 132.50, 141.23 147.00, 147.94, 154.48, 158.55. **IR** (ATR): 2925, 2855, 1614, 1512, 1502, 1487, 1466, 1243, 1180, 1037, 816, 753, 733 cm^{-1}. **FD-HRMS** (*m/z*): $[M]^+$ calcd for $C_{35}H_{46}N_2O_4$, 558.34576; found, 558.34764. **$[\alpha]_D^{24}$** –47.55 (c = 1.08, $CHCl_3$).

4-((3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-1-(4-methoxybenzyl)piperidin-4-yl)-*N*-phenylaniline (3ad)

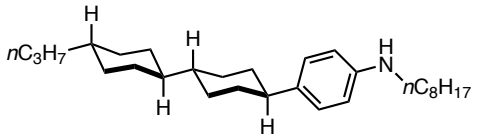


[Scheme 6: **1q** (0.25 mmol), **2k** (0.75 mmol), [Ni(cod)$_2$] (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), *m*-xylene (1 mL), 140 °C, 20 h] **3ad** (121.4 mg, 0.232 mmol, 93% yield) was isolated by silica gel column chromatography with hexane/EtOAc 80:20 to 50:50.

Pale yellow solids. **M.p.** 42.4–44.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.74–1.91 (m, 2H),

1.95–2.09 (m, 2H), 2.14–2.26 (m, 1H), 2.37 (td, J = 11.2, 4.4 Hz, 1H), 2.96 (br d, J = 10.8 Hz, 1H), 3.25 (br d, J = 9.2 Hz, 1H), 3.42–3.50 (m, 2H), 3.52–3.63 (m, 2H), 3.77 (s, 3H), 5.67 (s, 1H), 5.82 (s, 2H), 6.11 (dd, J = 8.8, 2.4 Hz, 1H), 6.34 (d, J = 2.4 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.85–6.90 (m, 3H), 6.94–7.04 (m, 4H), 7.06 (d, J = 8.4 Hz, 2H), 7.18–7.28 (m, 4H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): 34.22, 41.91, 44.03, 53.66, 55.11, 57.54, 62.71, 69.74, 97.90, 100.89, 105.51, 107.70, 113.45 (2C), 117.29 (2C), 118.08 (2C), 120.51, 128.17 (2C), 129.18 (2C), 130.10, 130.37 (2C), 136.70, 141.27 (1C + 1C), 143.24, 147.96, 154.40, 158.55. **IR** (ATR): 3397, 2915, 1597, 1512, 1499, 1487, 1466, 1313, 1242, 1178, 1036, 908, 815, 747, 729 cm^{-1}. **FD-HRMS** (*m/z*): $[M+H]^+$ calcd for $C_{33}H_{34}N_2O_4$ 522.25186; found, 522.25338. **$[\alpha]_D^{26}$** –67.42 (c = 1.00, $CHCl_3$).

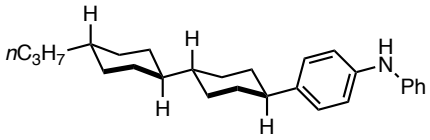
***Trans*,*trans*-4-(4-*N*-octylaminophenyl)-4'-propylbicyclohexyl (3ae)**



[Scheme 6: **1r** (0.25 mmol), **2a** (0.375 mmol), $[Ni(cod)_2]$ (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.375 mmol), toluene (1 mL), 120 °C, 20 h] **3ae** (94.0 mg, 0.228 mmol, 91% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99.5:0.5 to 99:1.

White solids. **M.p.** 146.7–149.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.79–0.90 (m, 8H), 0.91–1.20 (m, 9H), 1.21–1.50 (m, 14H), 1.59 (t, J = 6.8 Hz, 2H), 1.69–1.94 (m, 8H), 2.33 (br t, J = 11.6 Hz, 1H), 3.06 (t, J = 7.6 Hz, 2H), 3.33 (br, 1H), 6.53 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 14.09, 14.43, 20.04, 22.65, 27.20, 29.28, 29.43, 29.66, 30.10 (2C), 30.45 (2C), 31.83, 33.62 (2C), 34.88 (2C), 37.63, 39.84, 42.94, 43.45, 43.67, 44.25, 112.64 (2C), 127.38 (2C), 136.65, 146.57. **IR** (ATR): 2914, 2846, 1615, 1519, 1313, 1186, 815, 721 cm^{-1}. **EI-HRMS** (*m/z*): $[M]^+$ calcd for $C_{29}H_{49}N$, 411.38650; found, 411.38639.

***Trans*,*trans*-4-(4-*N*-phenylaminophenyl)-4'-propylbicyclohexyl (3af)**



[Scheme 6: **1r** (0.25 mmol), **2k** (0.75 mmol), $[Ni(cod)_2]$ (5 mol%), DCYPBz (7.5 mol%), NaO*t*Bu (0.75 mmol), toluene (1 mL), 120 °C, 20 h] **3af** (80.2 mg, 0.213 mmol, 85% yield) was isolated by silica gel column chromatography with hexane/EtOAc 99.5:0.5 to 99:1.

White solids. **M.p.** 130.9–133.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.82–0.91 (m, 5H), 0.95–1.08 (m, 3H), 1.09–1.21 (m, 6H), 1.26–1.44 (m, 4H), 1.72–1.78 (m, 4H), 1.80–1.87 (m, 2H), 1.91 (br d, J = 12.4 Hz, 2H), 2.40 (tt, J = 11.6, 3.2 Hz, 1H), 5.62 (s, 1H), 6.88 (t, J = 7.2 Hz, 1H), 7.01–7.03 (m, 4H), 7.11 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (100.5 MHz, $CDCl_3$): 14.43, 20.04, 30.08 (2C), 30.38 (2C), 33.60 (2C), 34.73 (2C), 37.61, 39.82, 42.90, 43.41, 43.91, 116.96 (2C), 118.49 (2C), 120.28, 127.53 (2C), 129.25 (2C), 140.56, 141.07, 143.74. **IR** (ATR):

2913, 2847, 1597, 1513, 1177, 1029, 934, 746 cm^{-1}. **EI-HRMS** (*m/z*): $[M]^+$ calcd for $C_{27}H_{37}N$ 375.29260; found, 375.29226.

7. References

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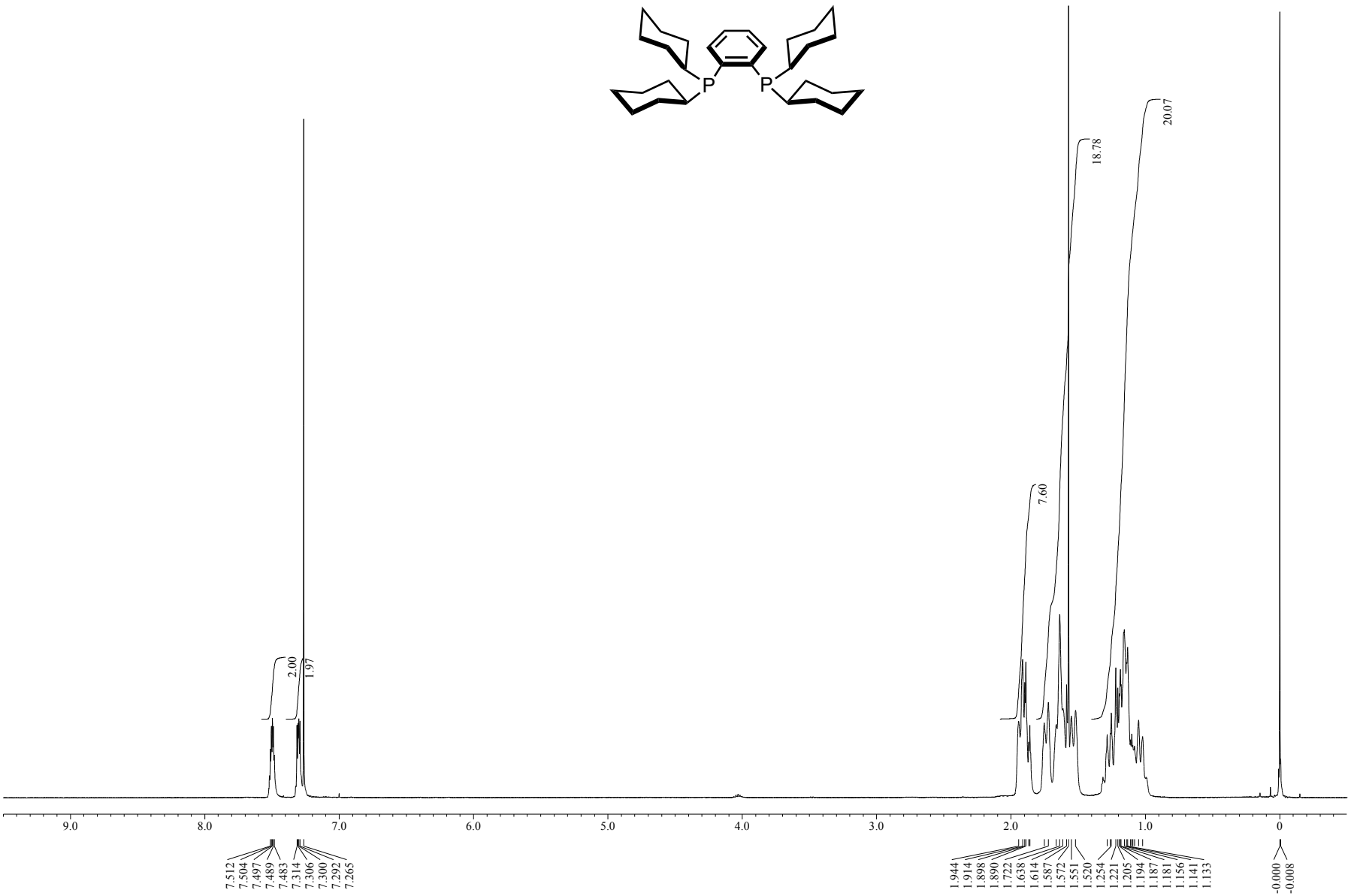
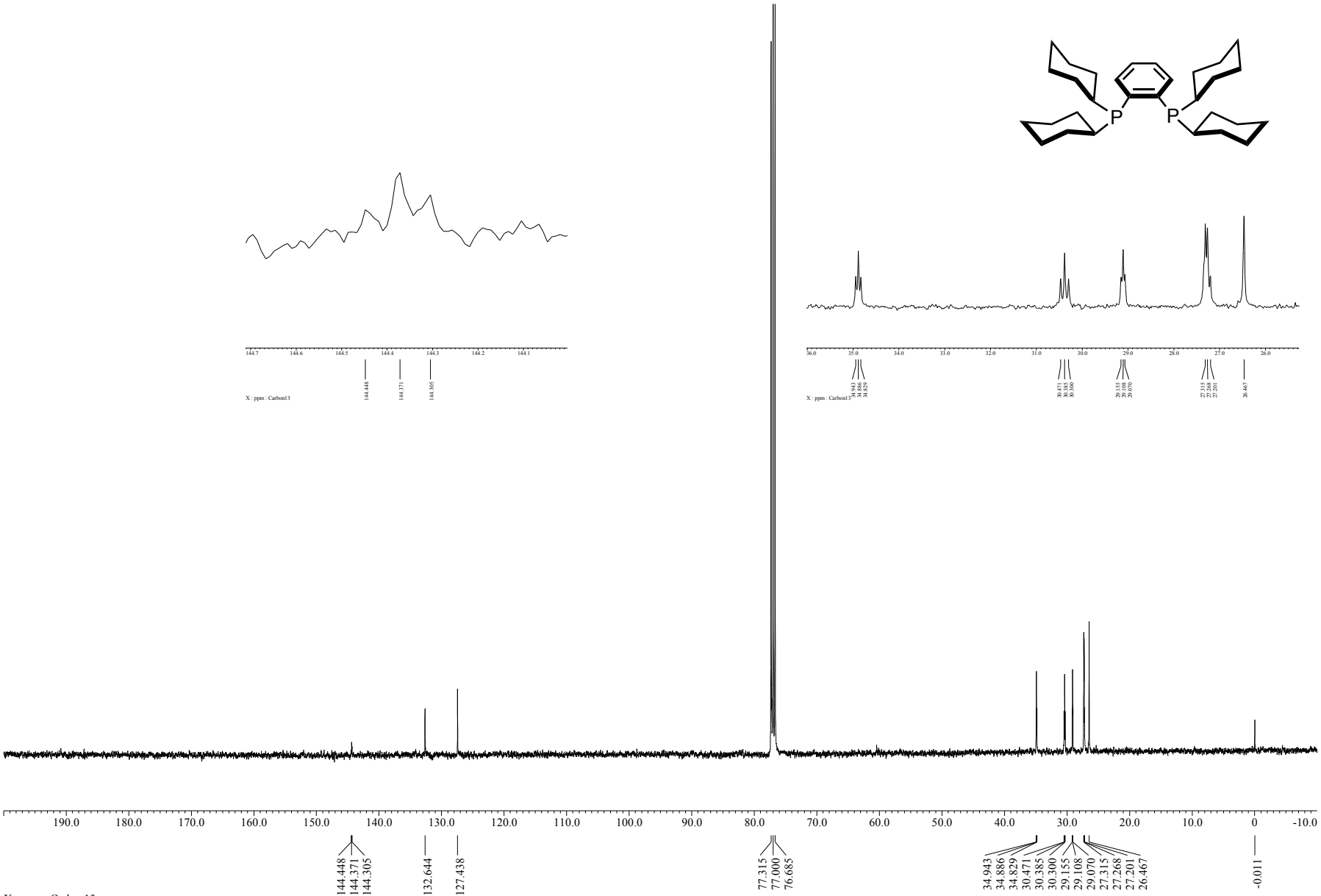


^{1}H NMR spectrum of DCYPBz in $CDCl_3$



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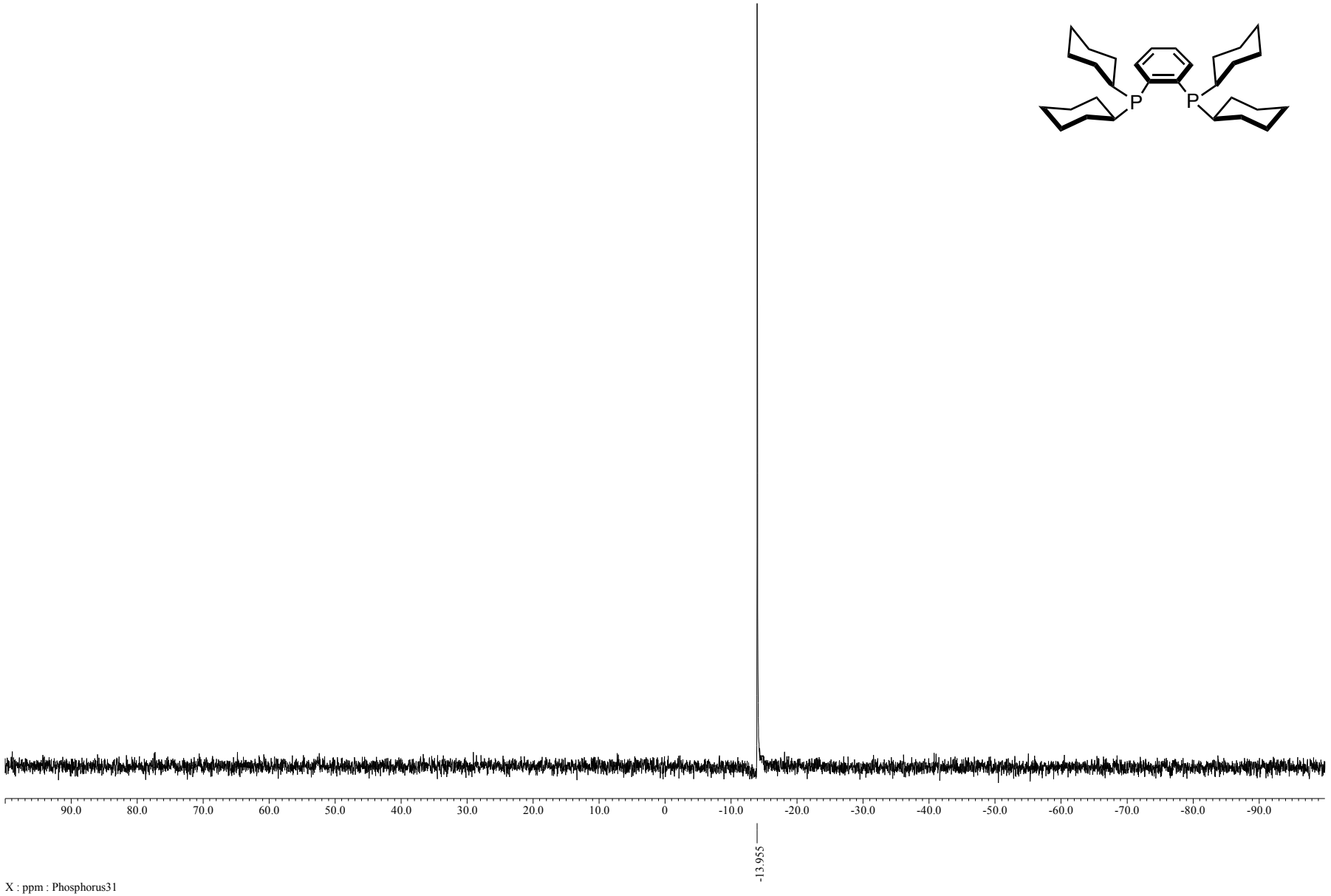

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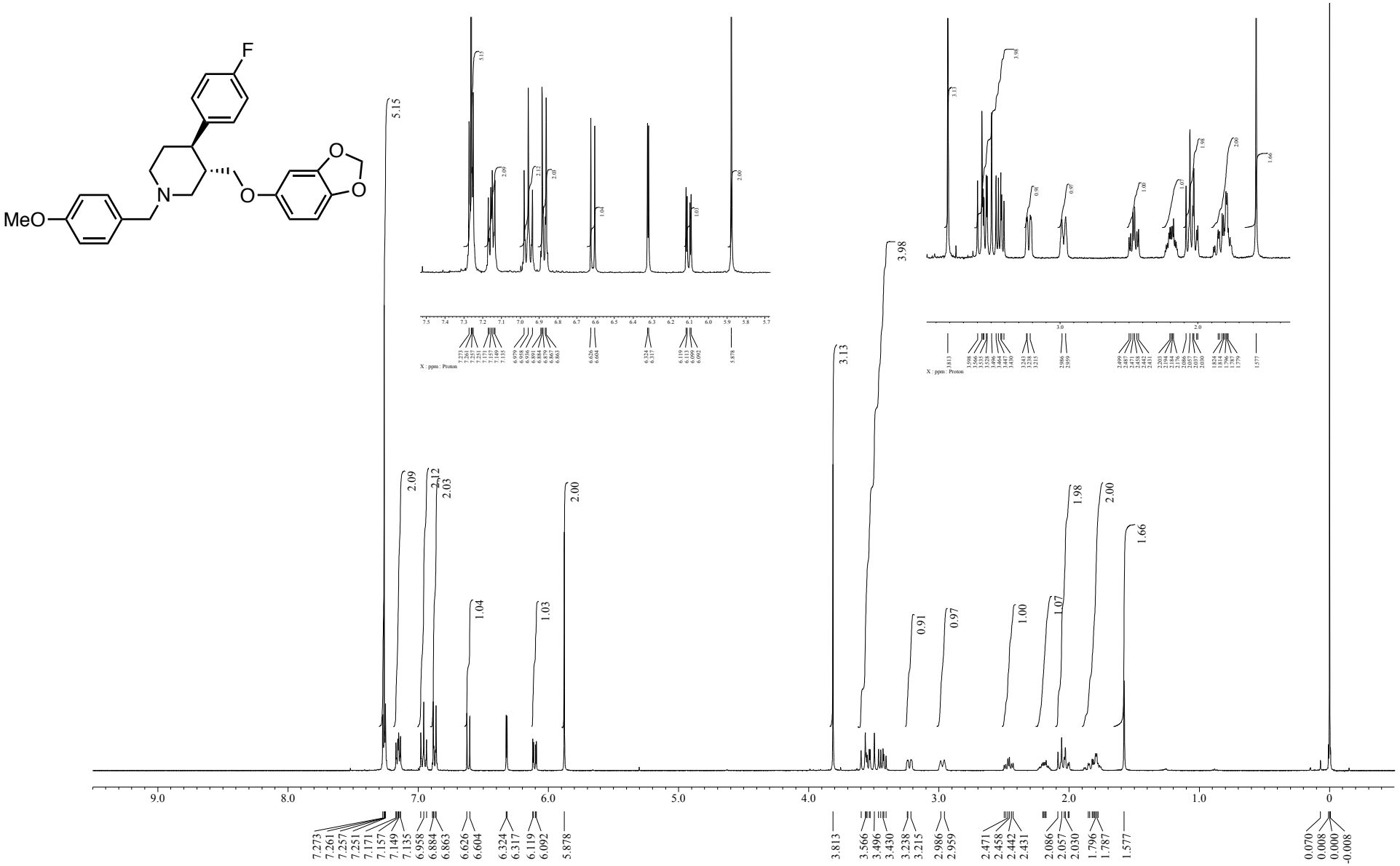

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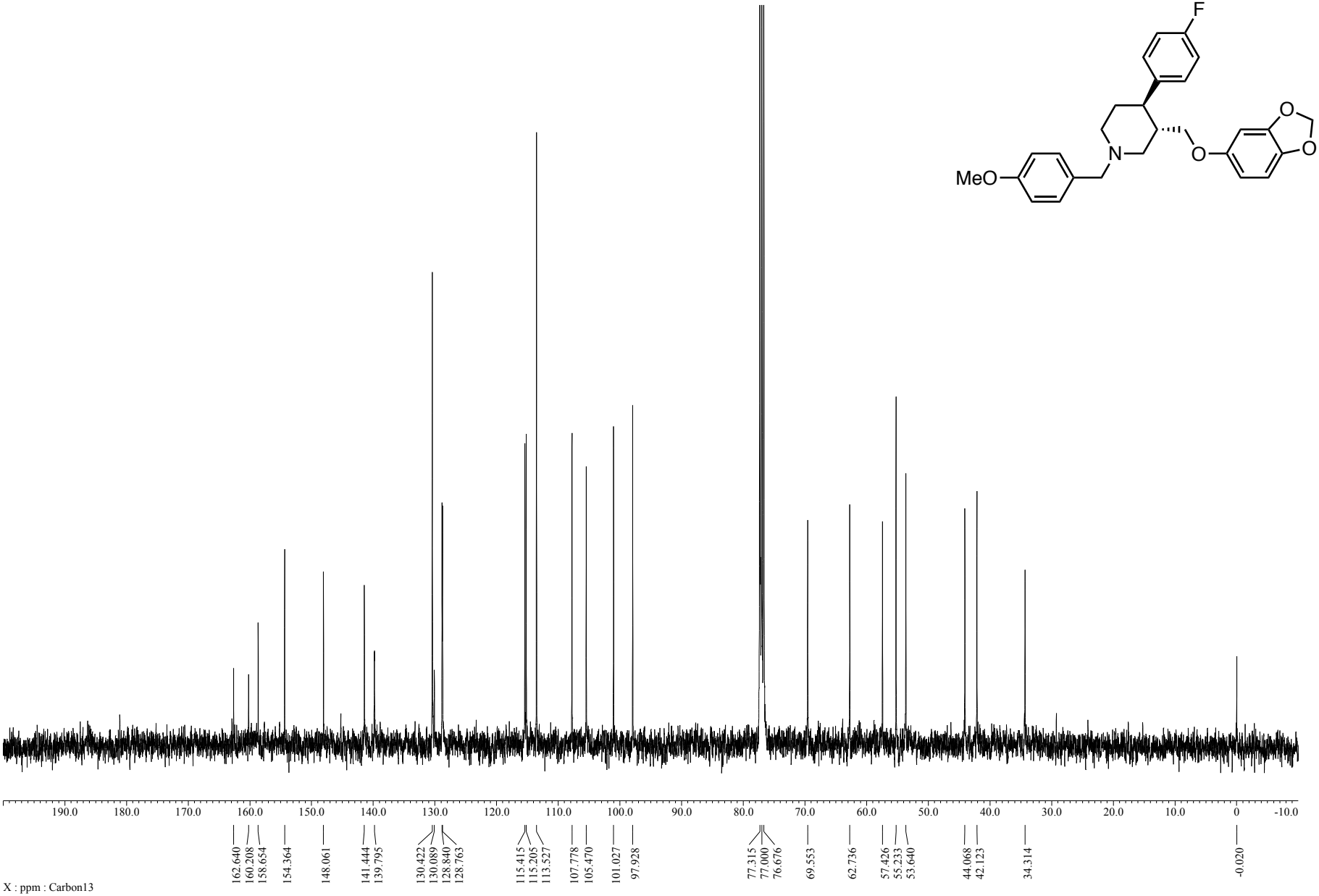

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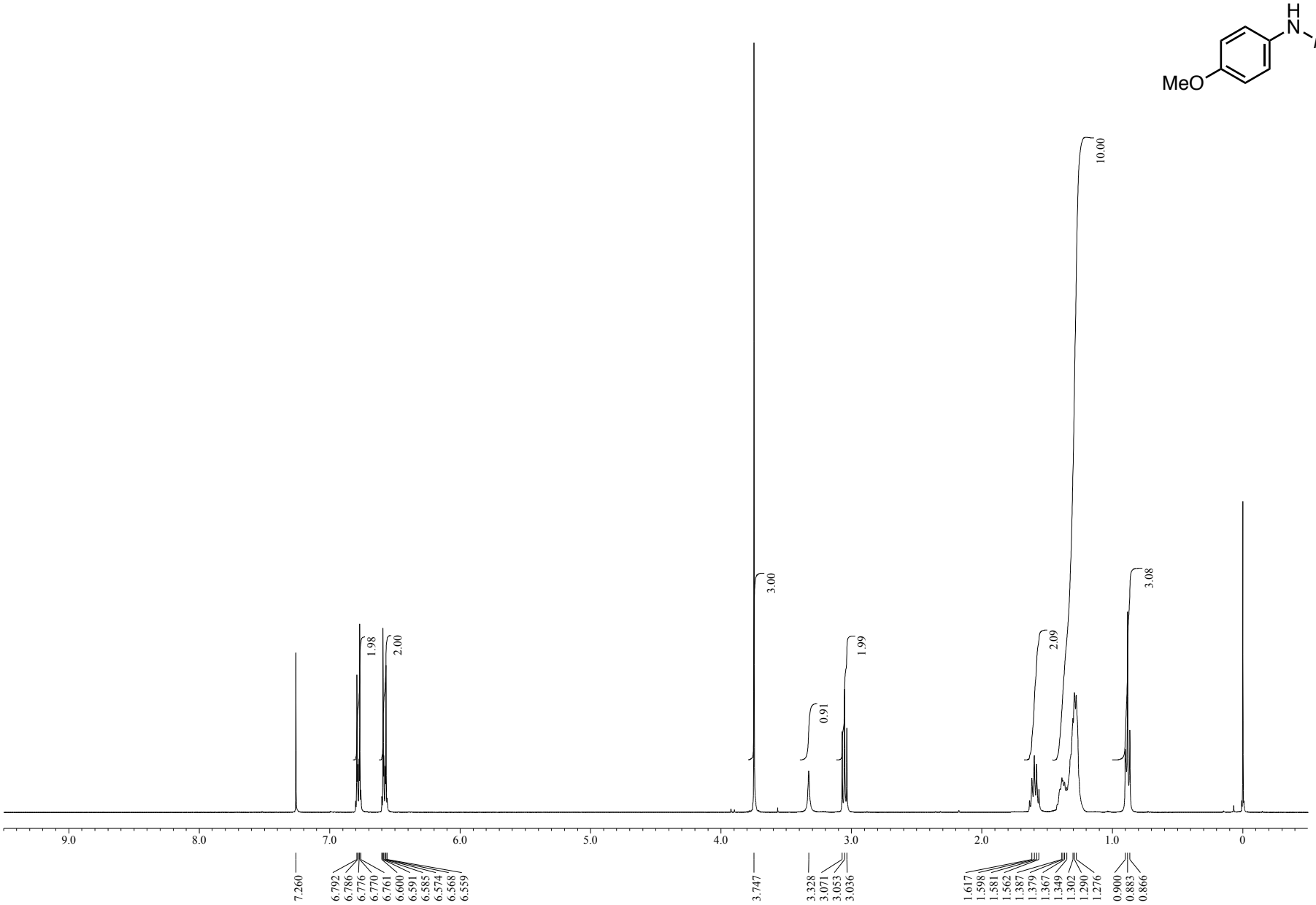

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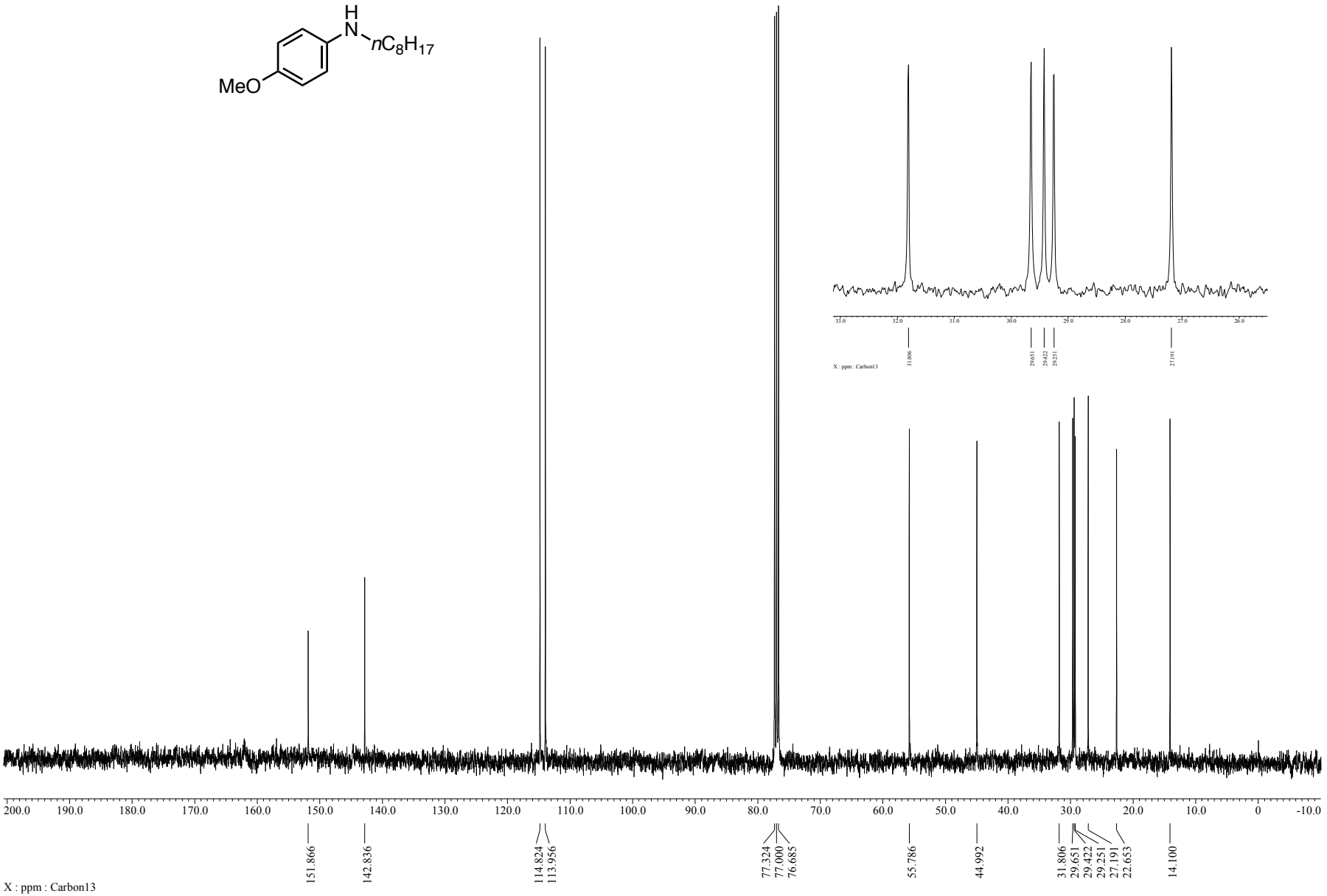

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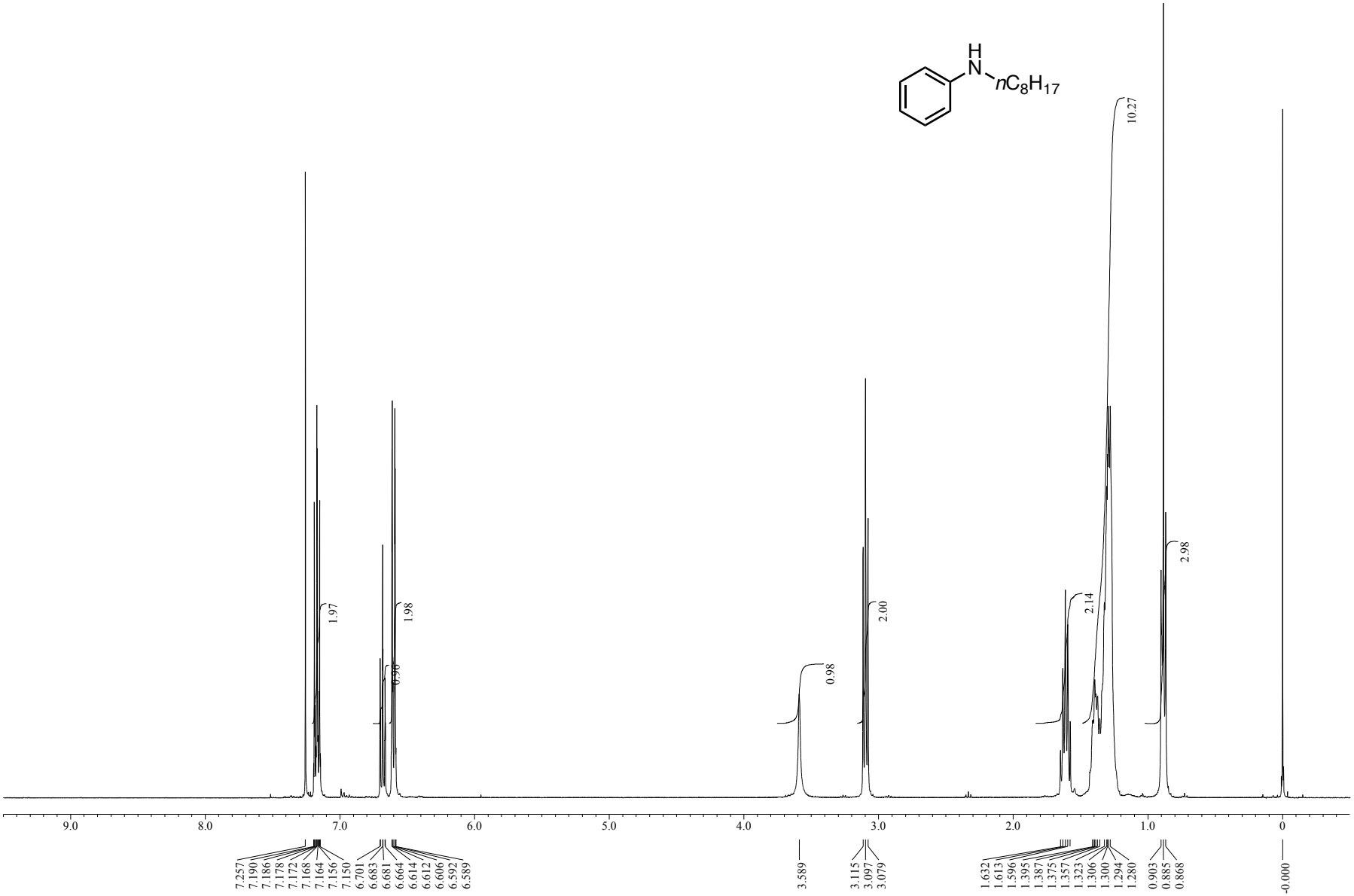

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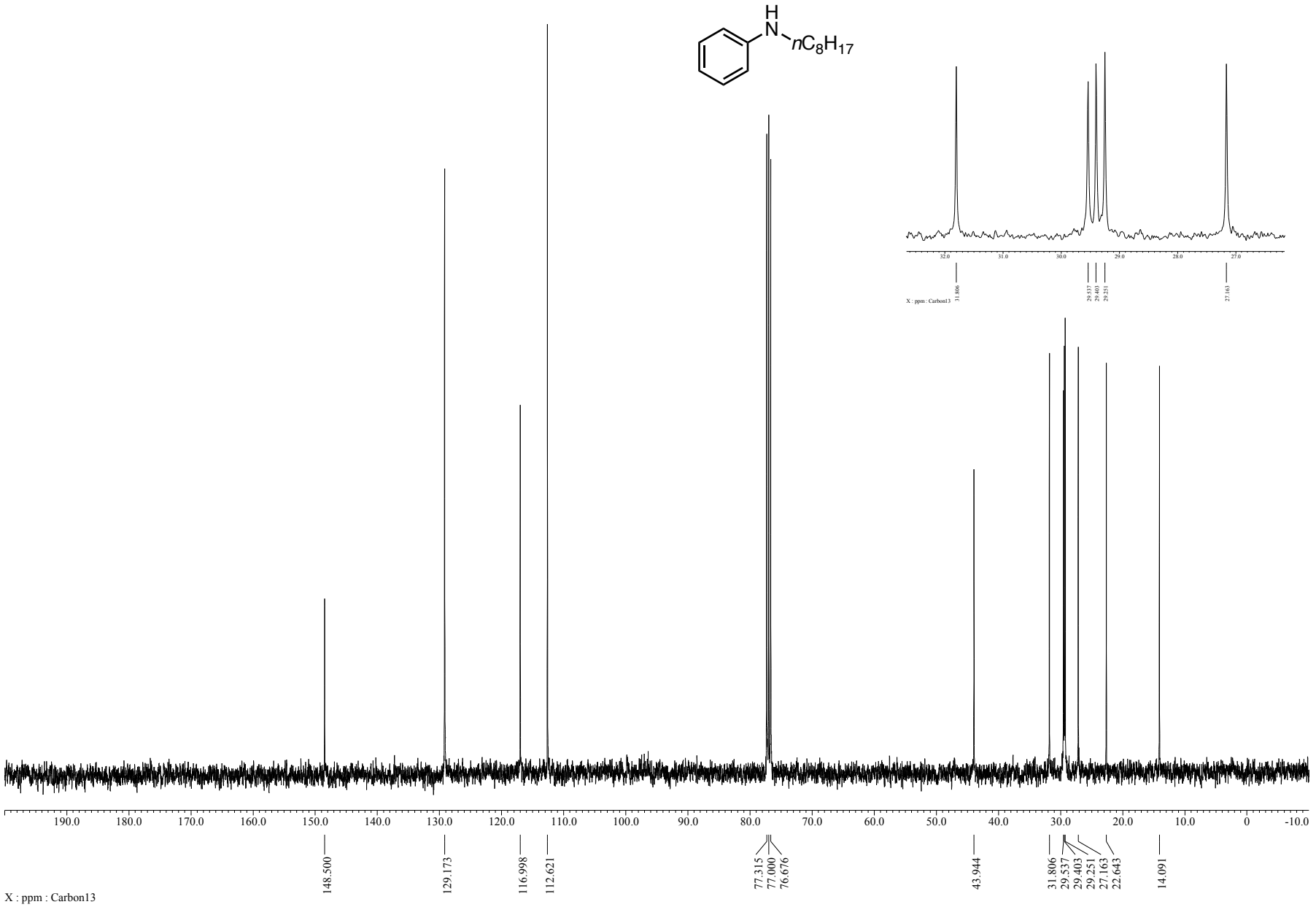

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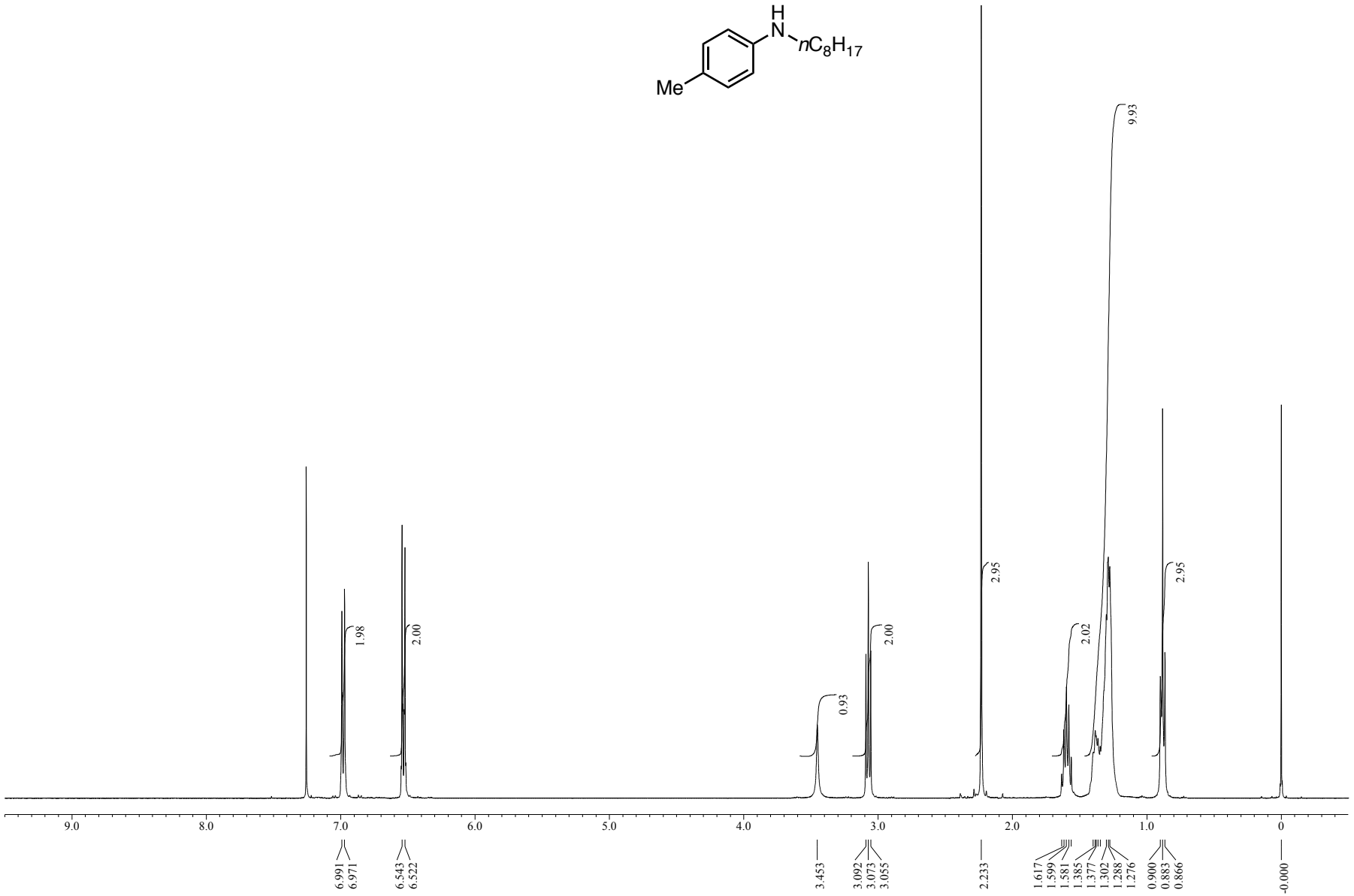
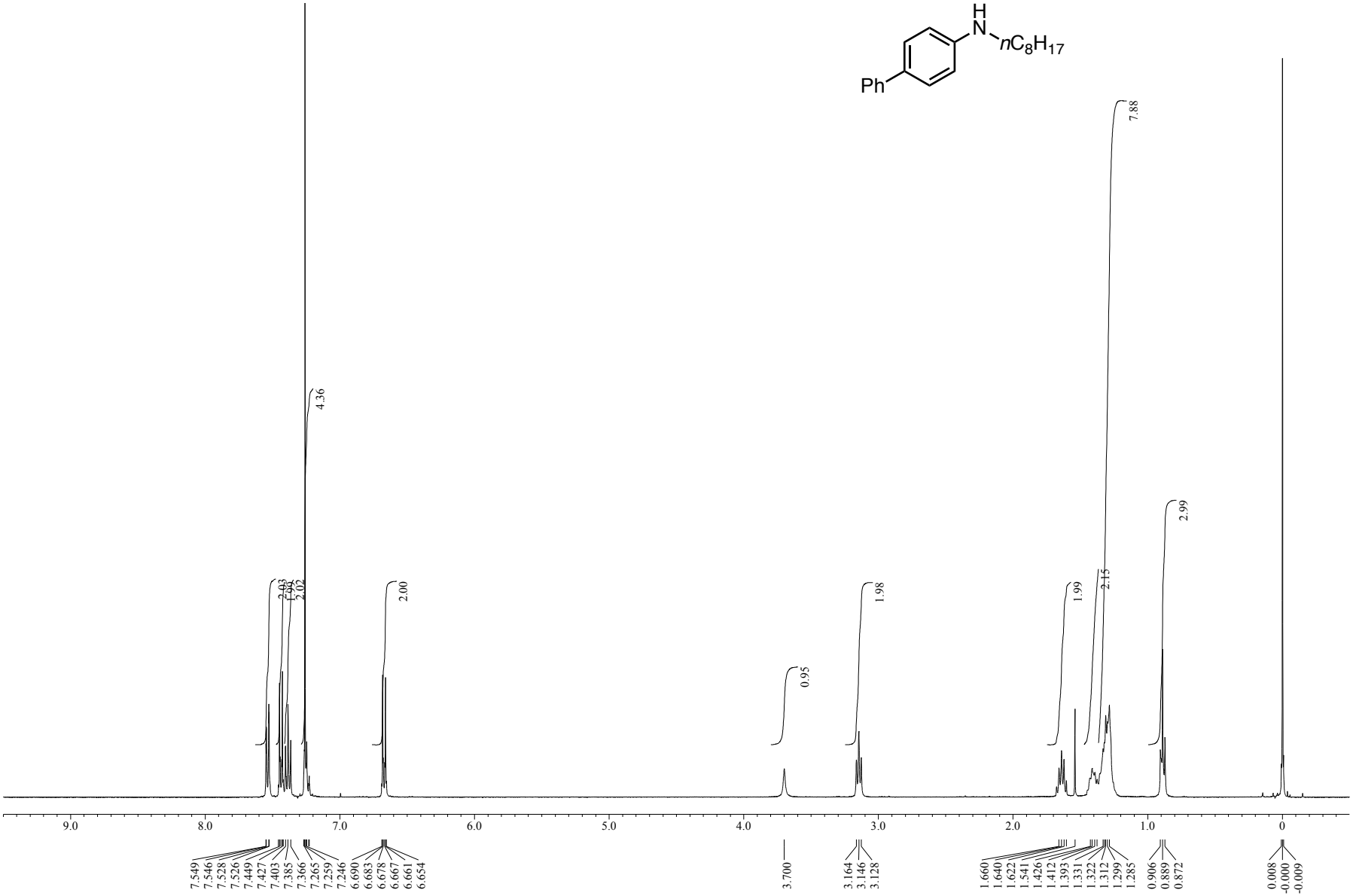


^{1}H NMR spectrum of **3c** in $CDCl_3$

^{13}C NMR spectrum of **3c** in $CDCl_3$



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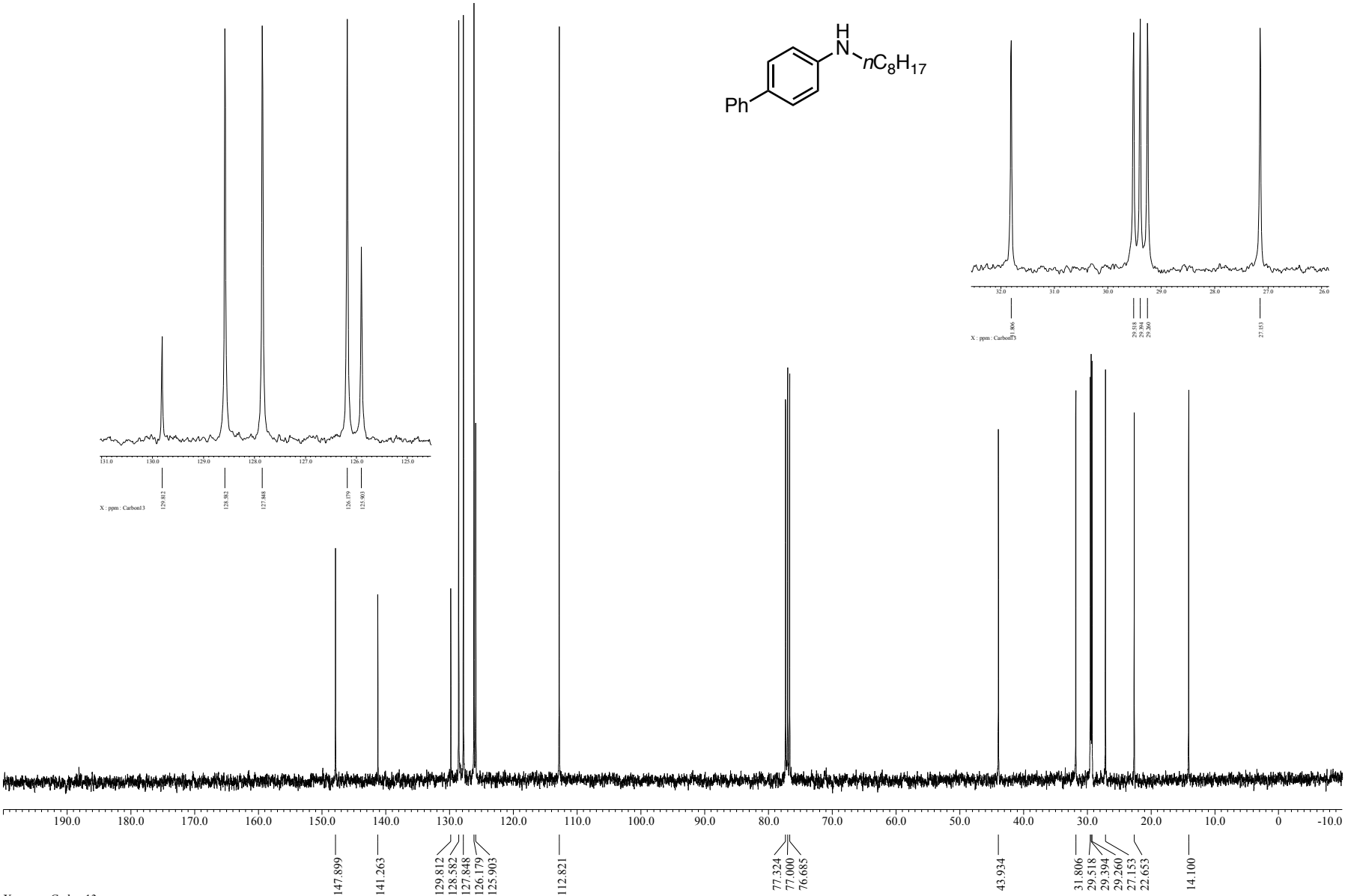

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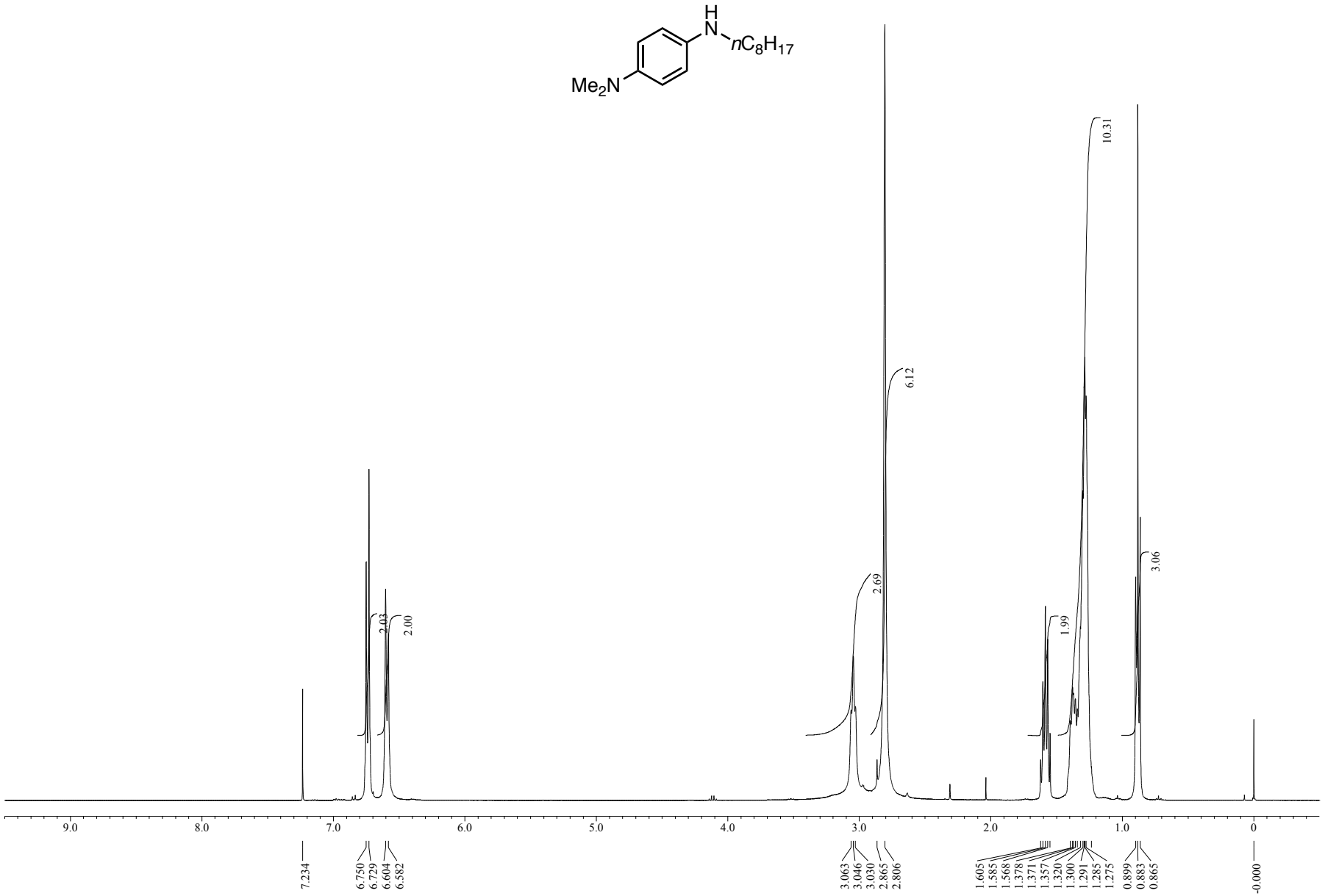

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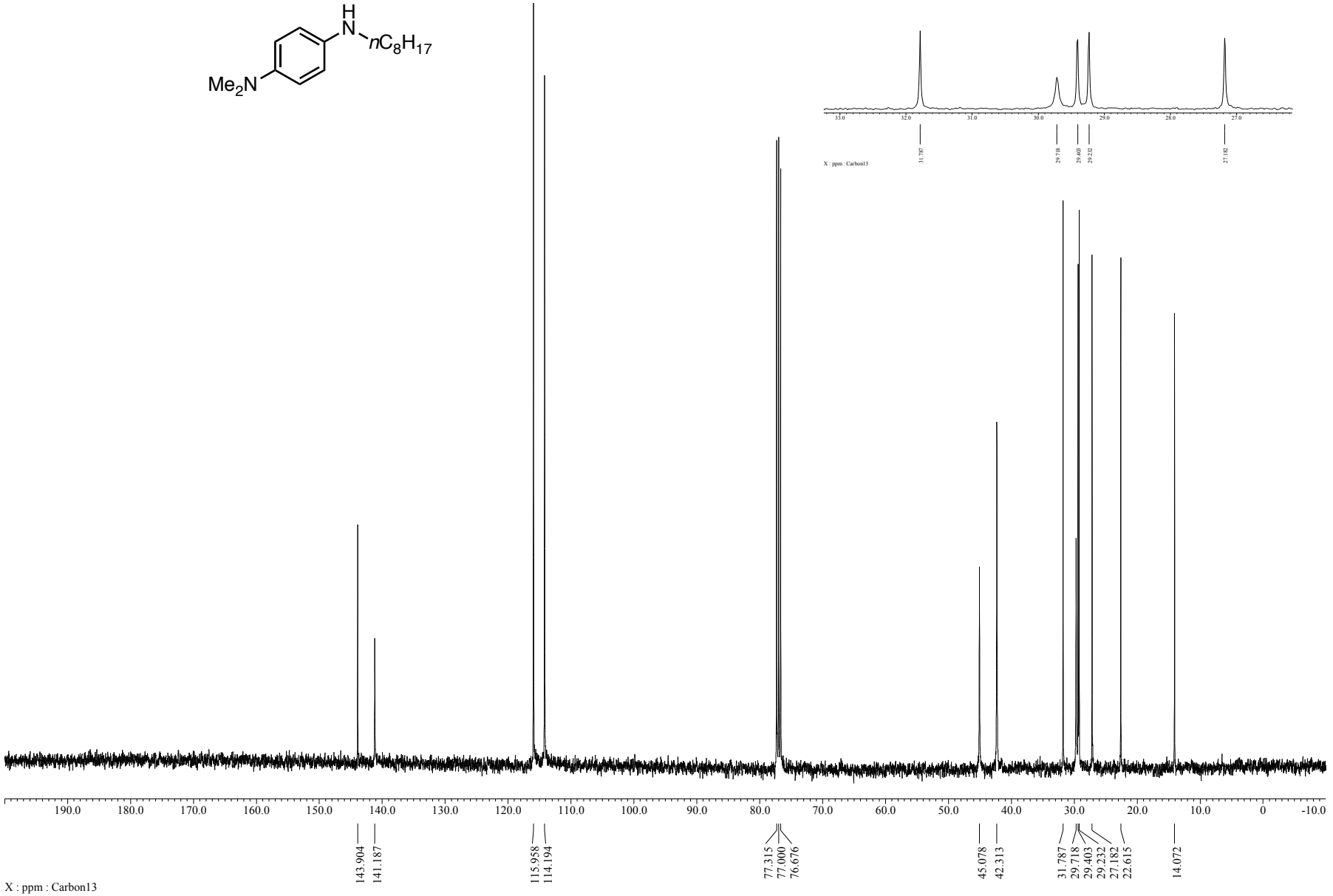

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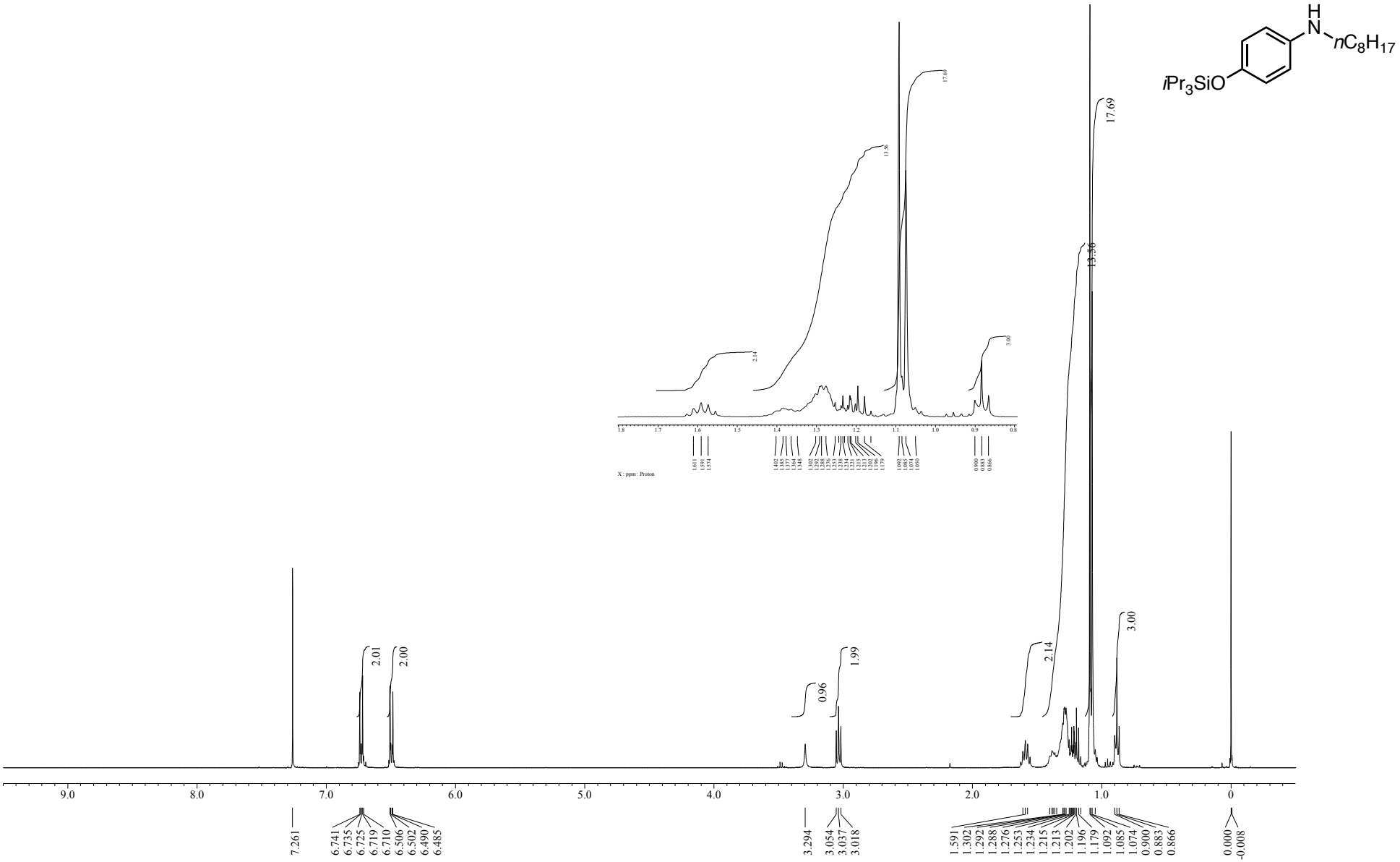

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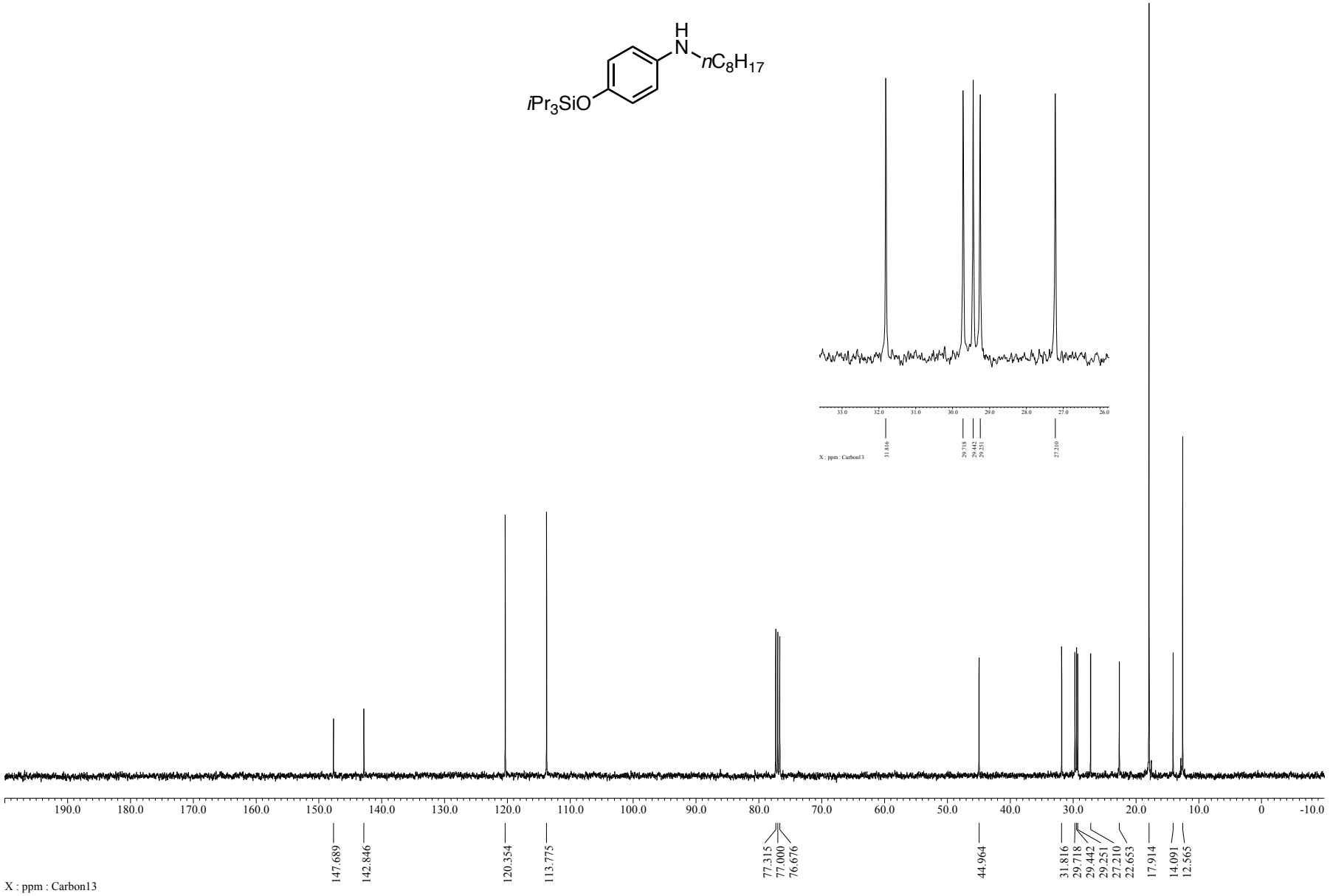

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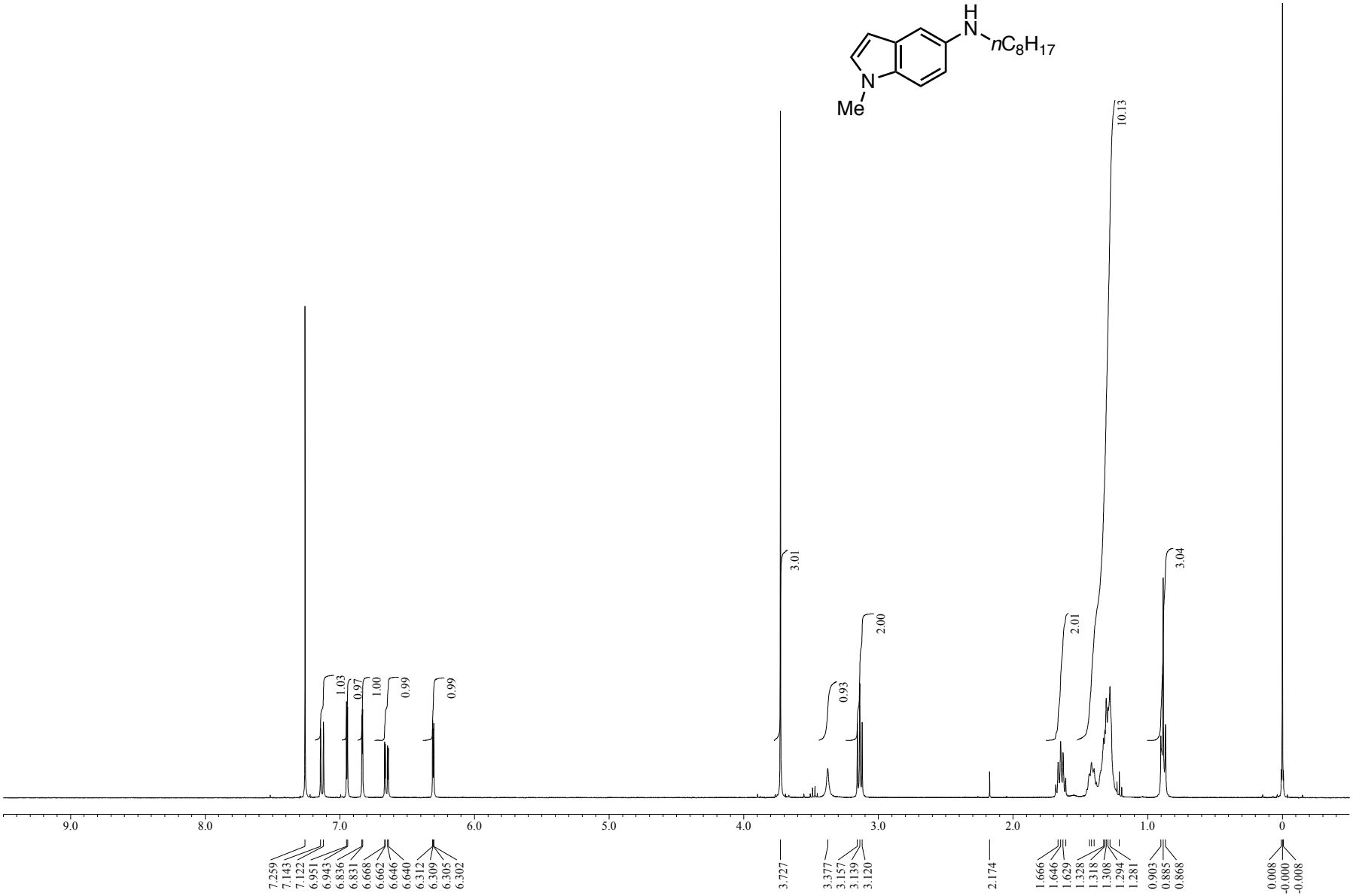

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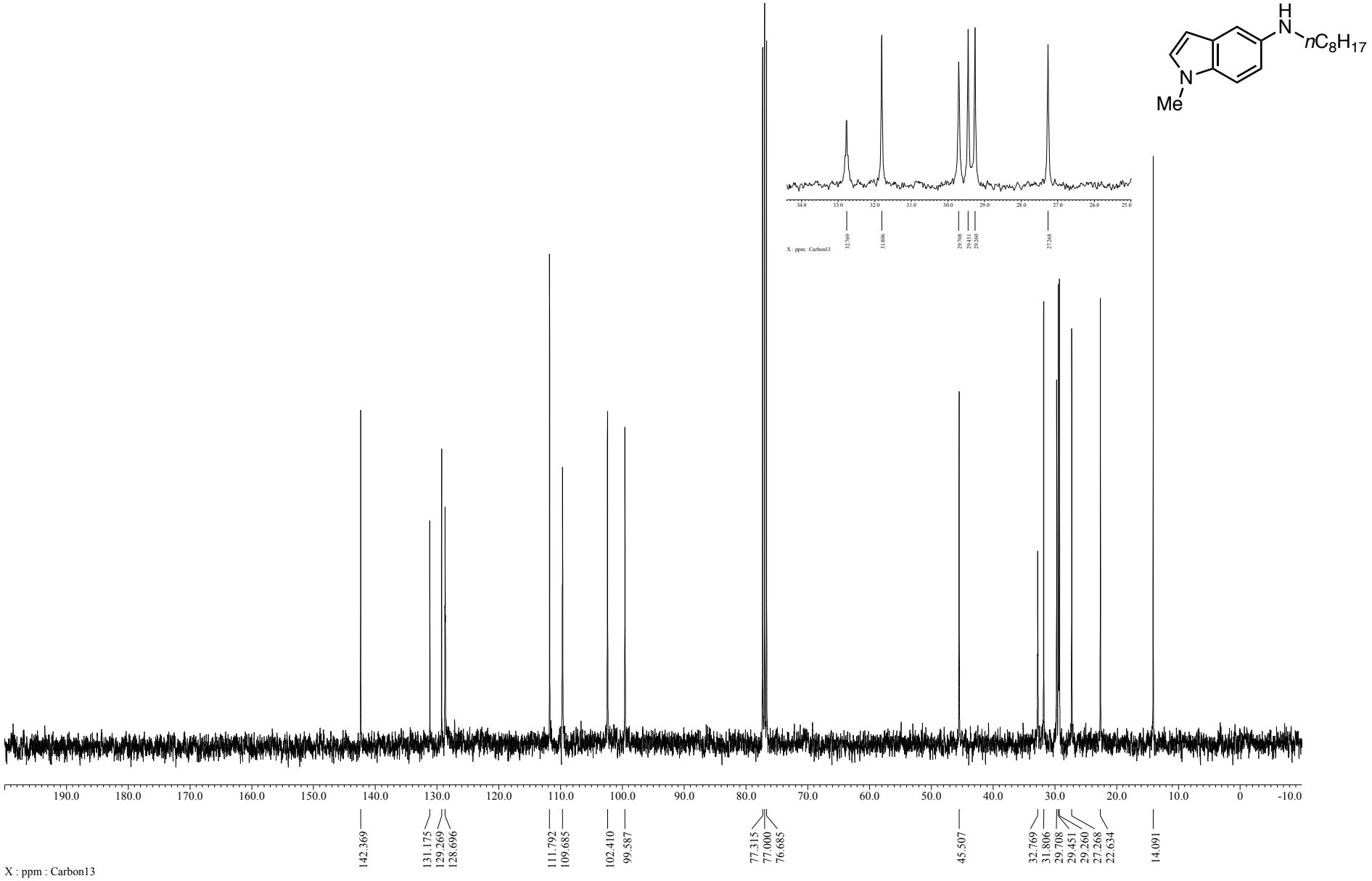

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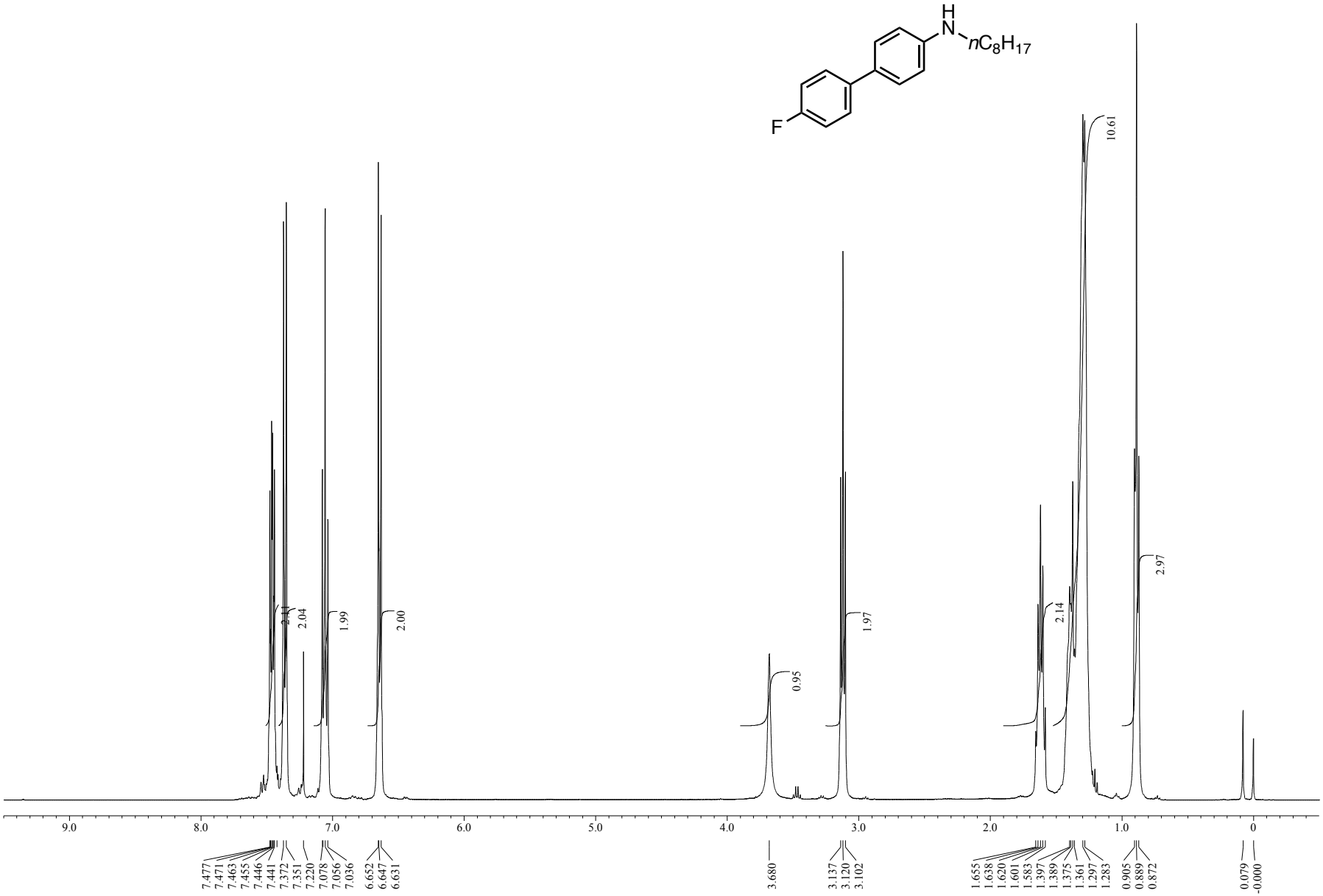

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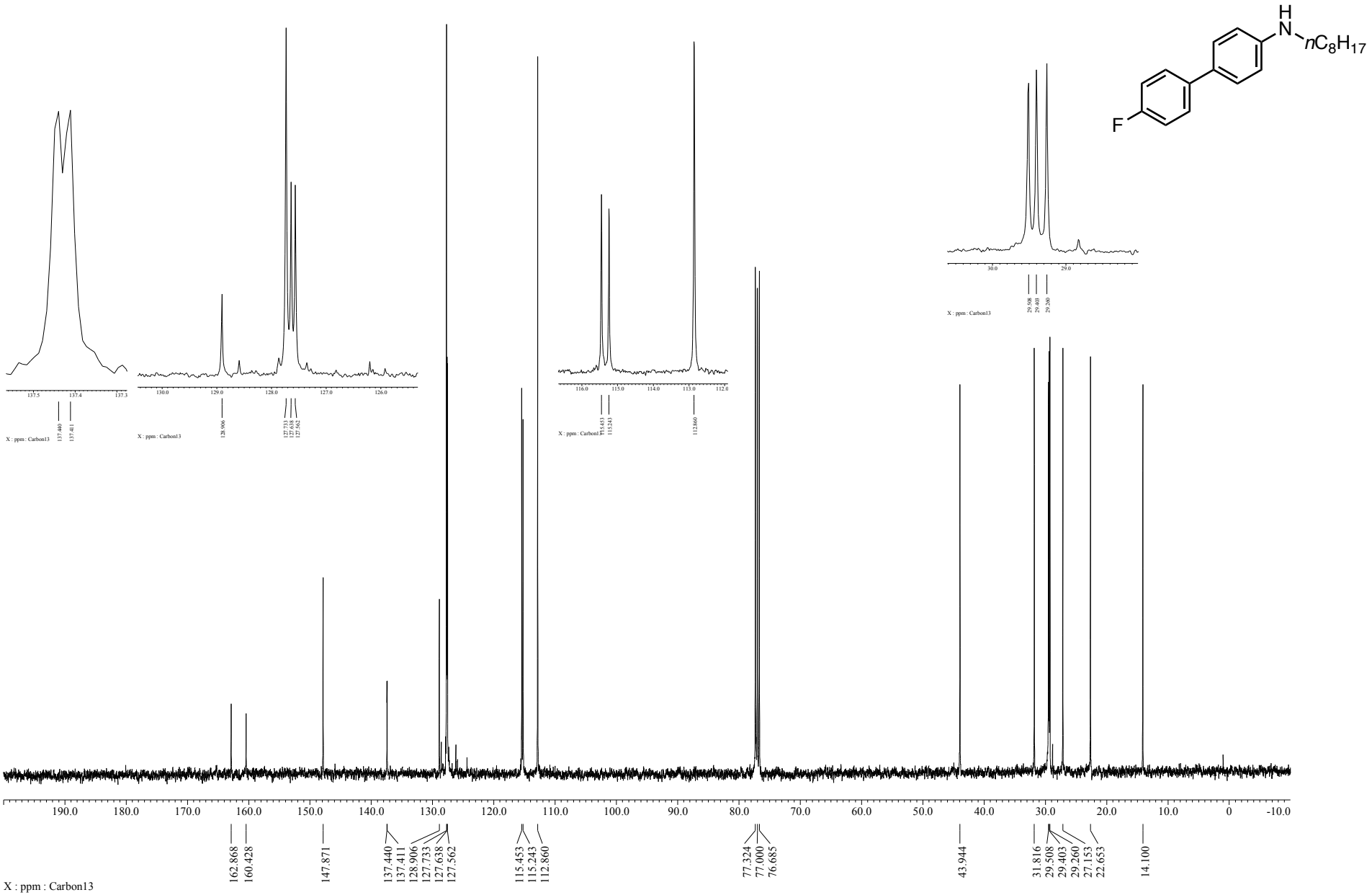

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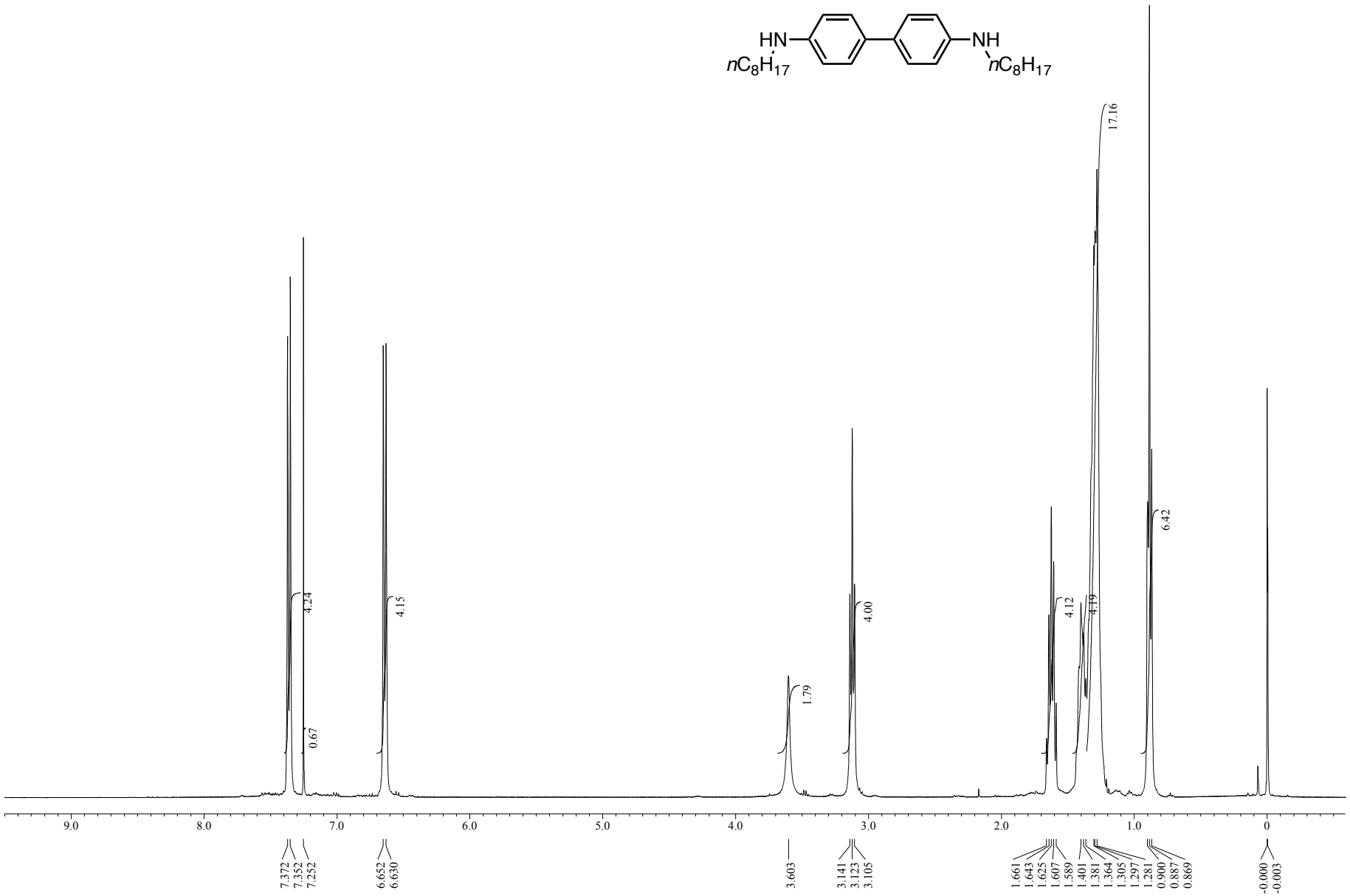

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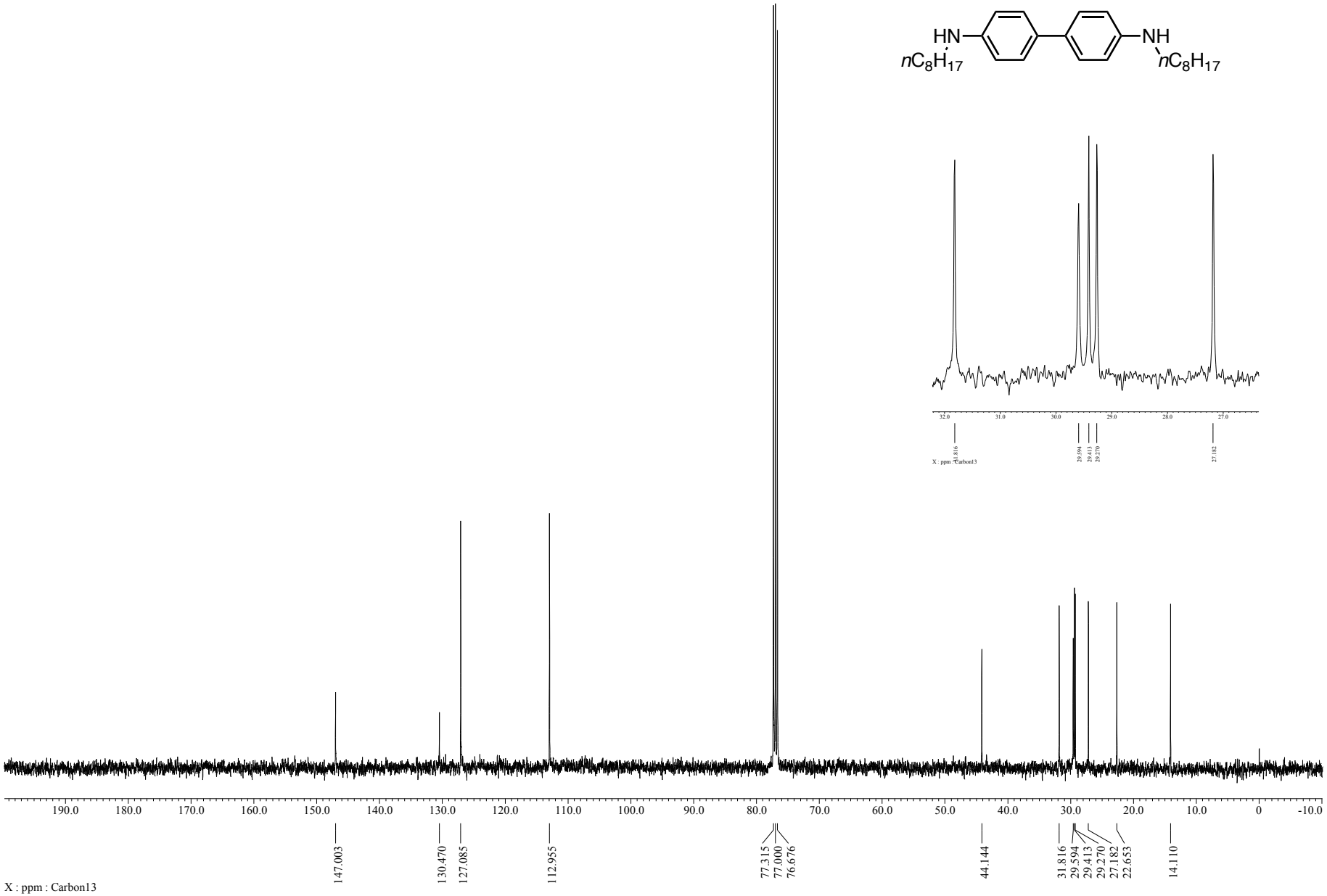

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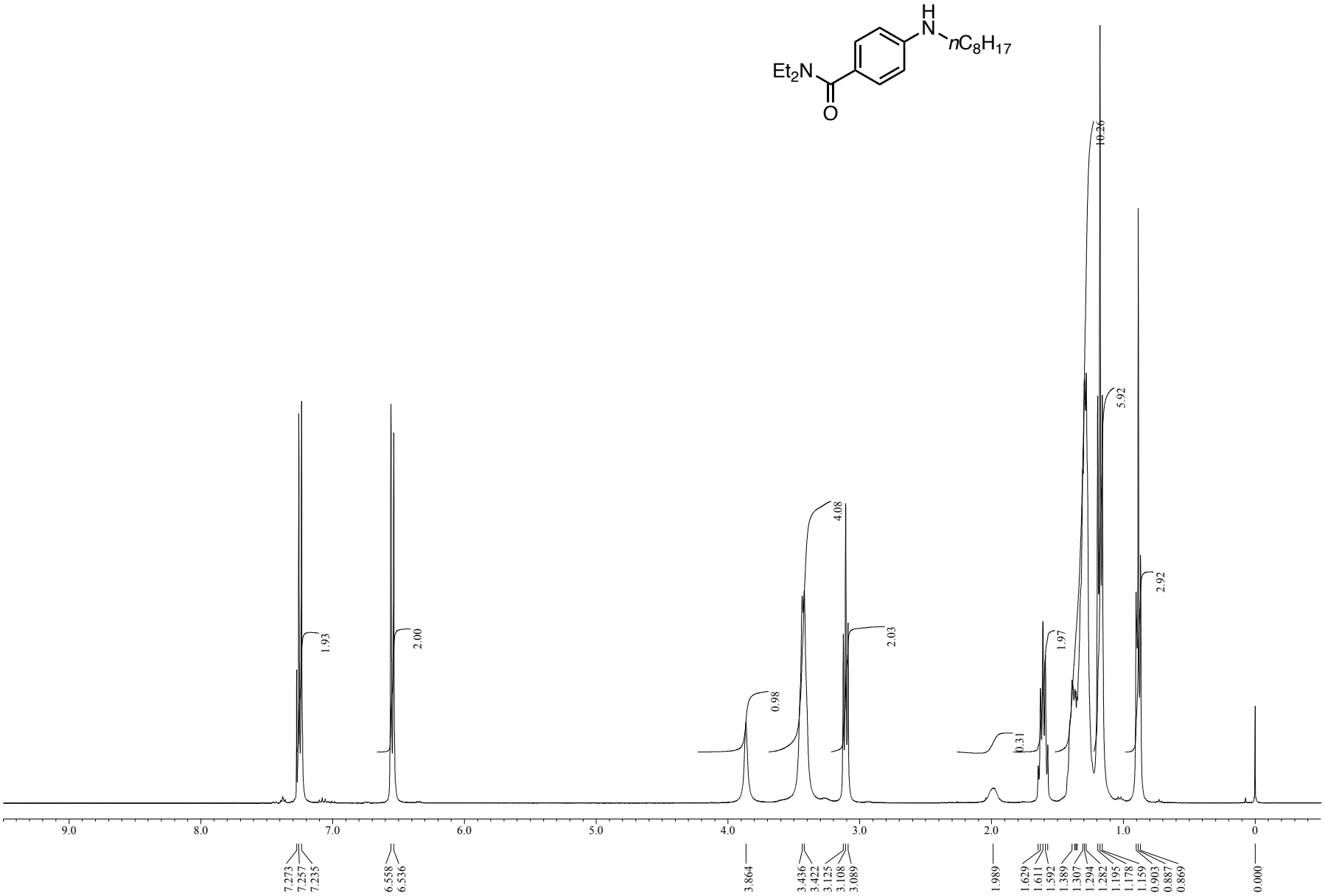

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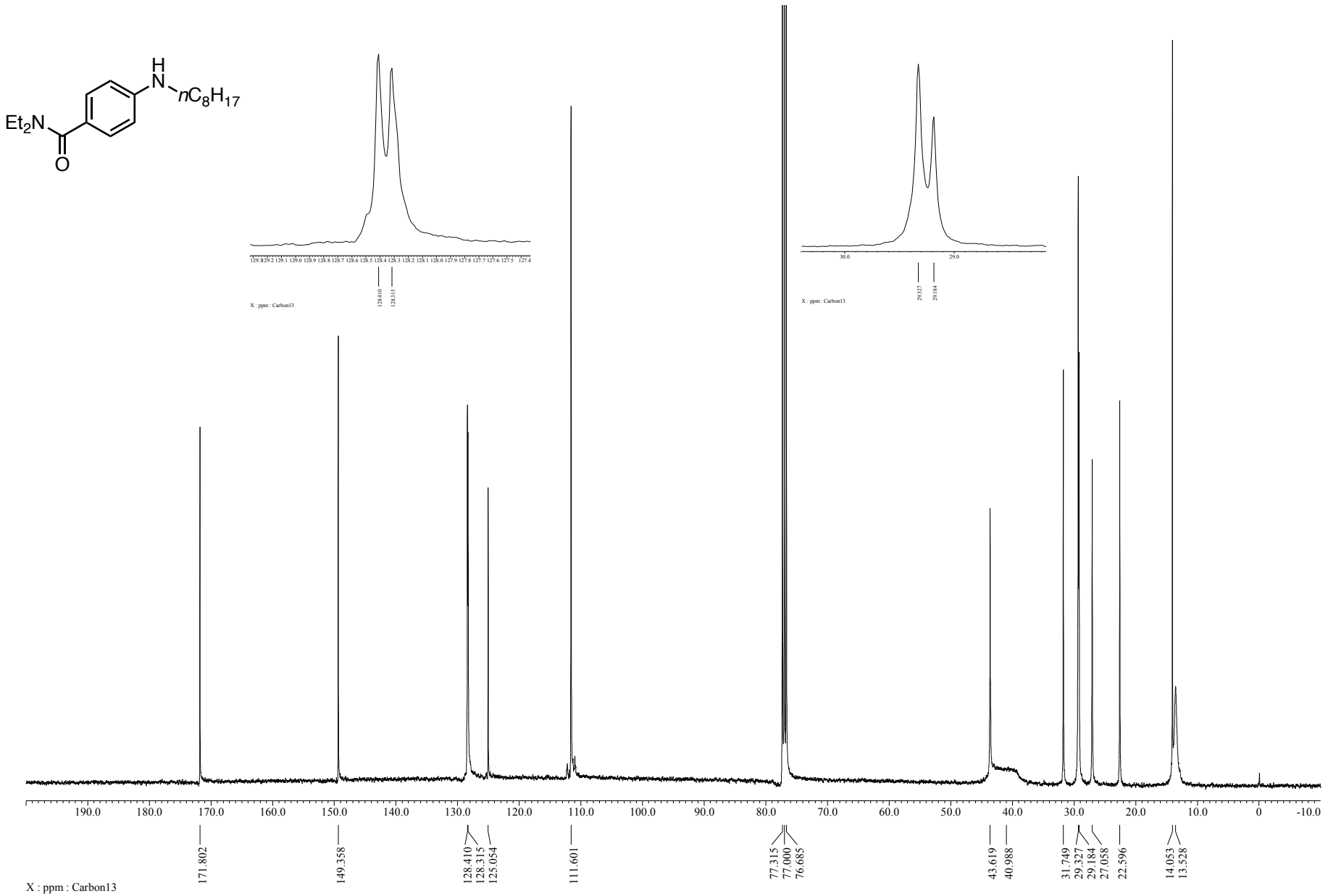

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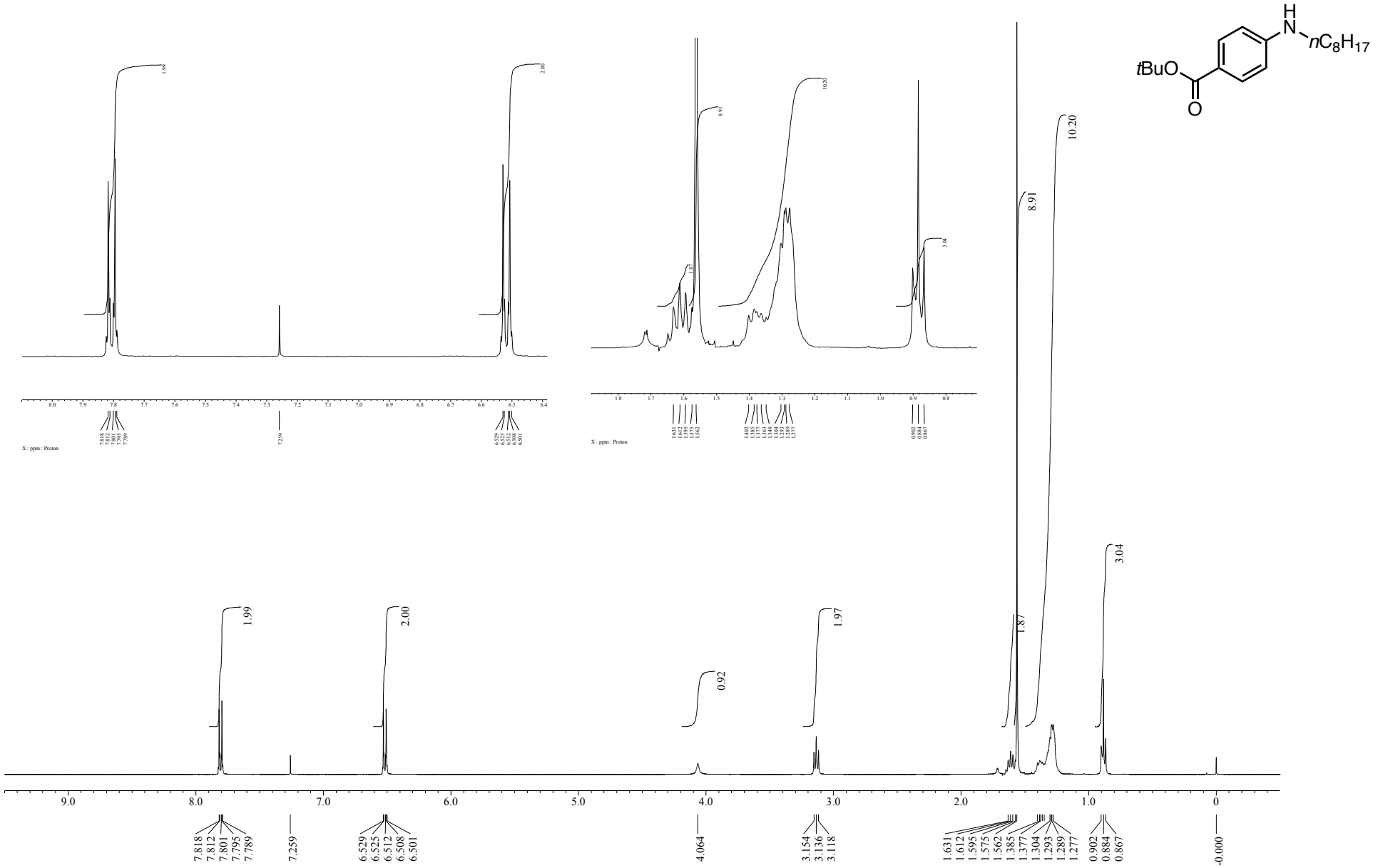

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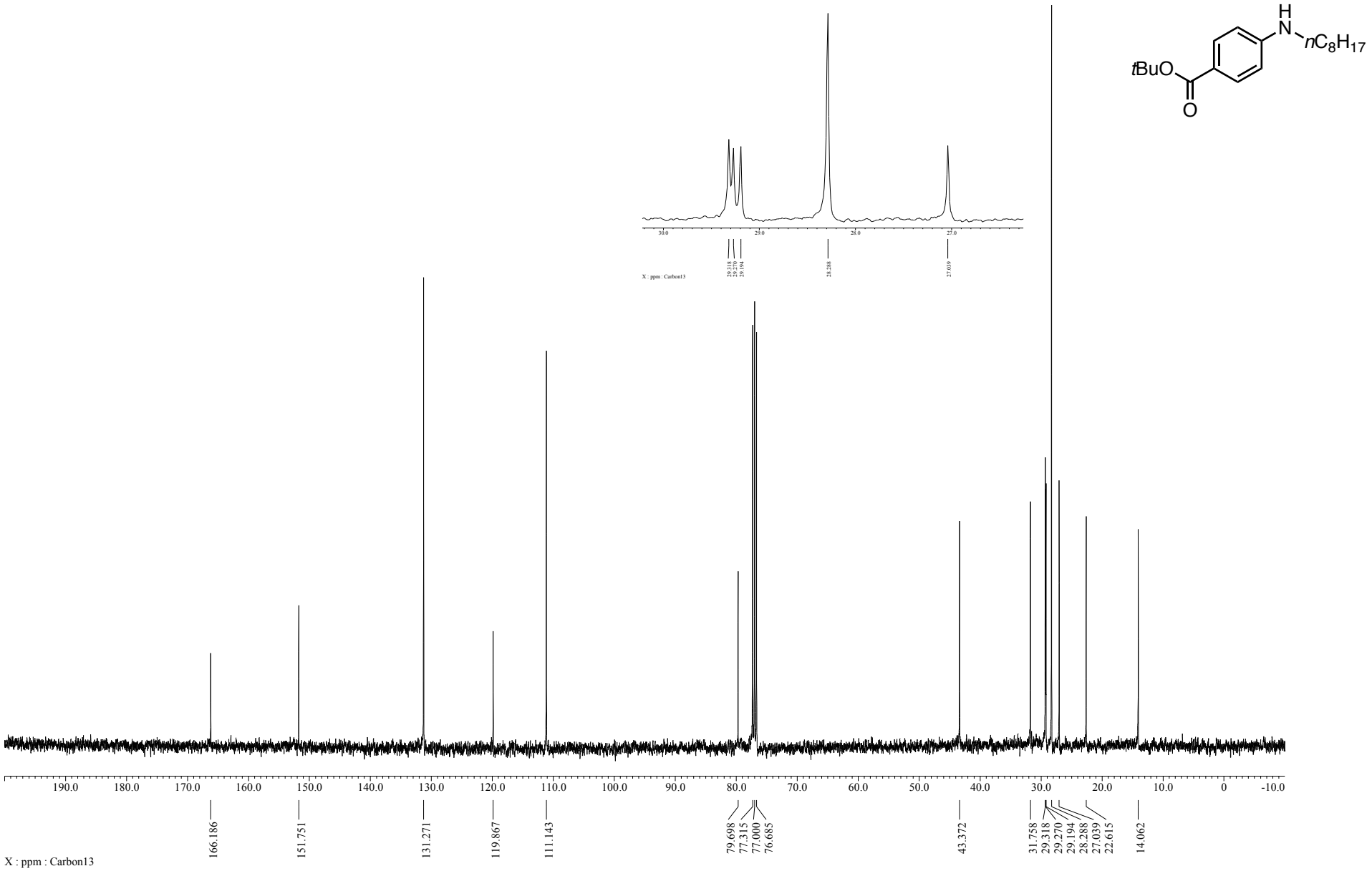

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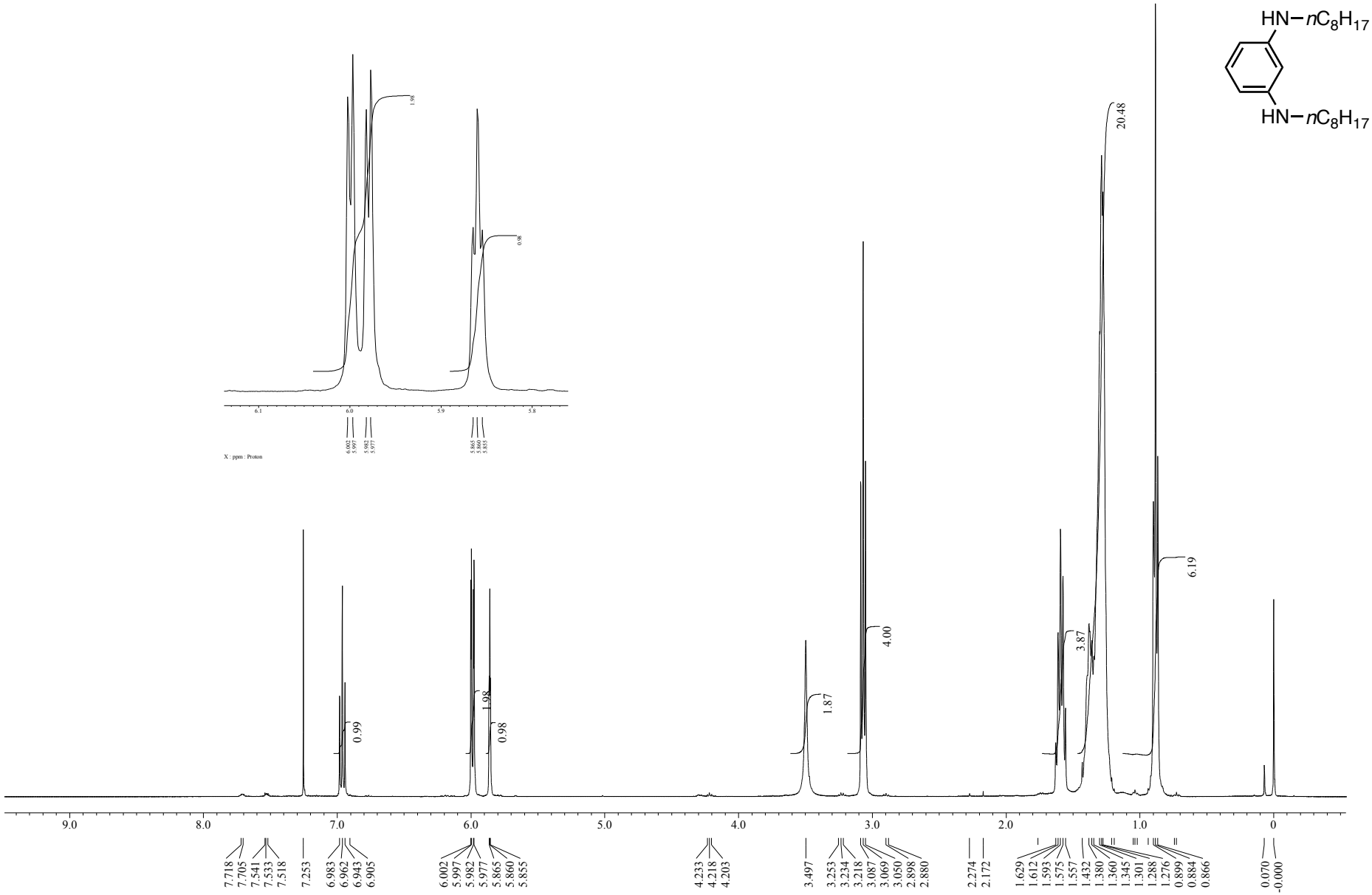

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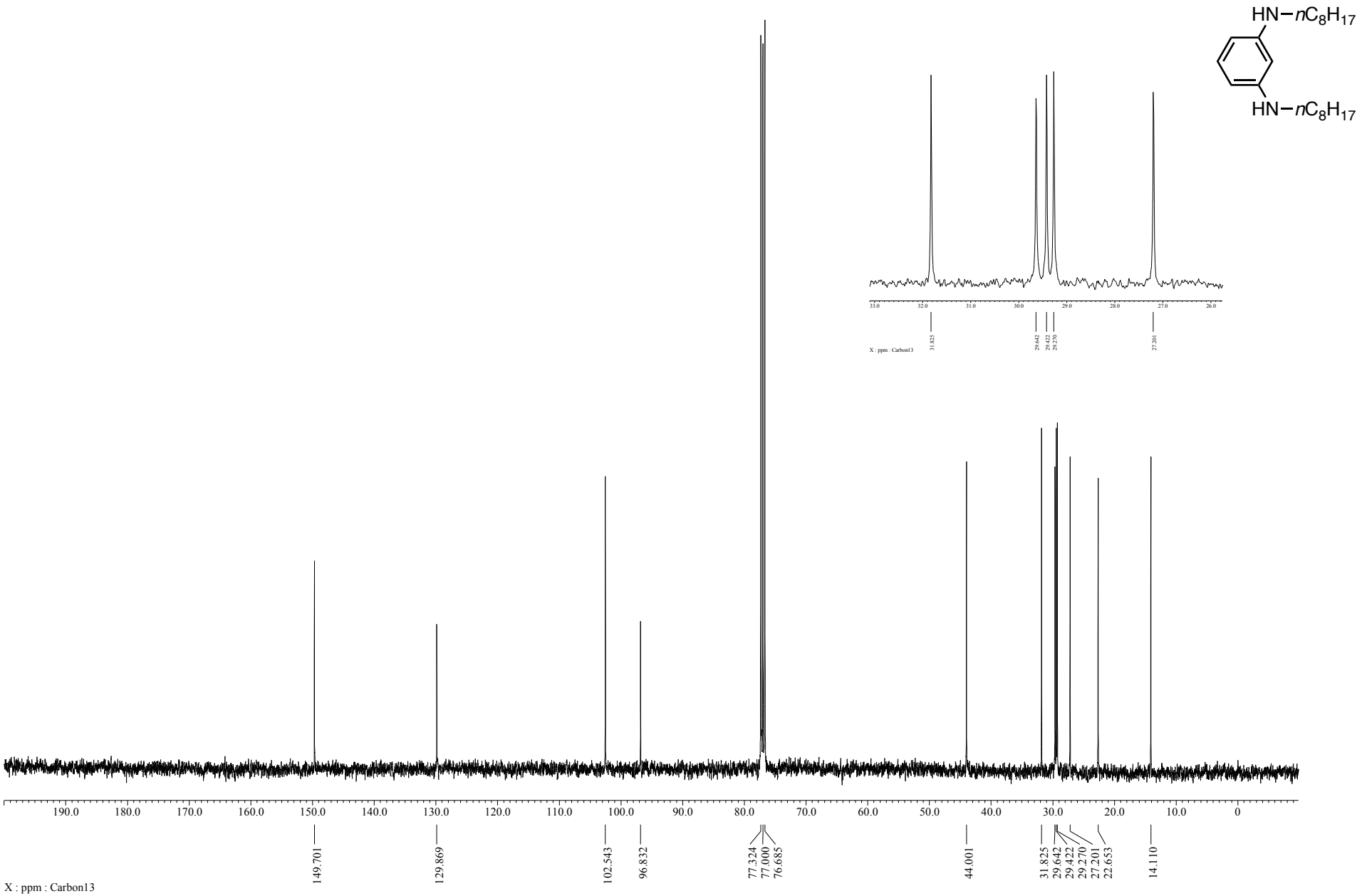

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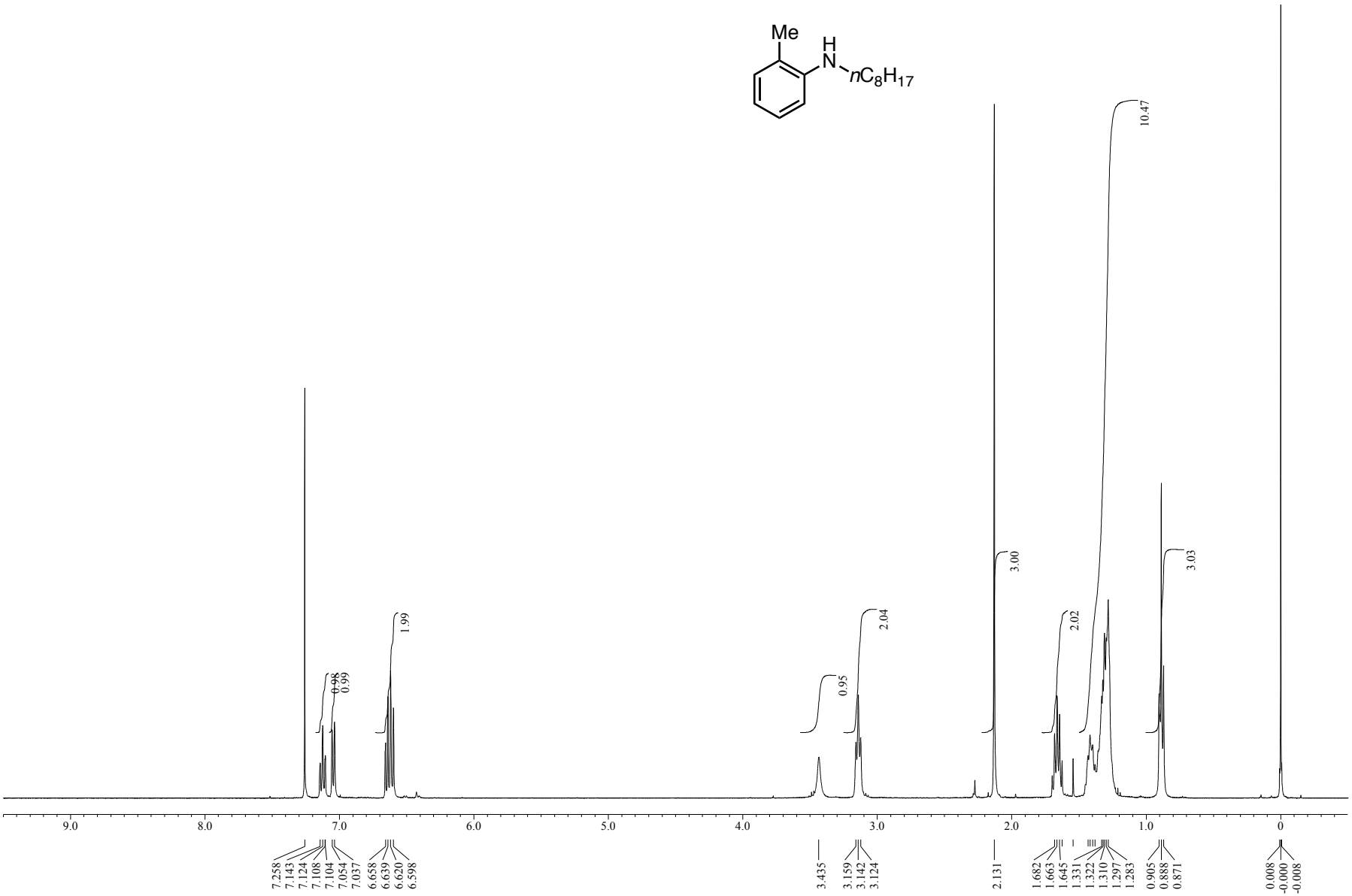

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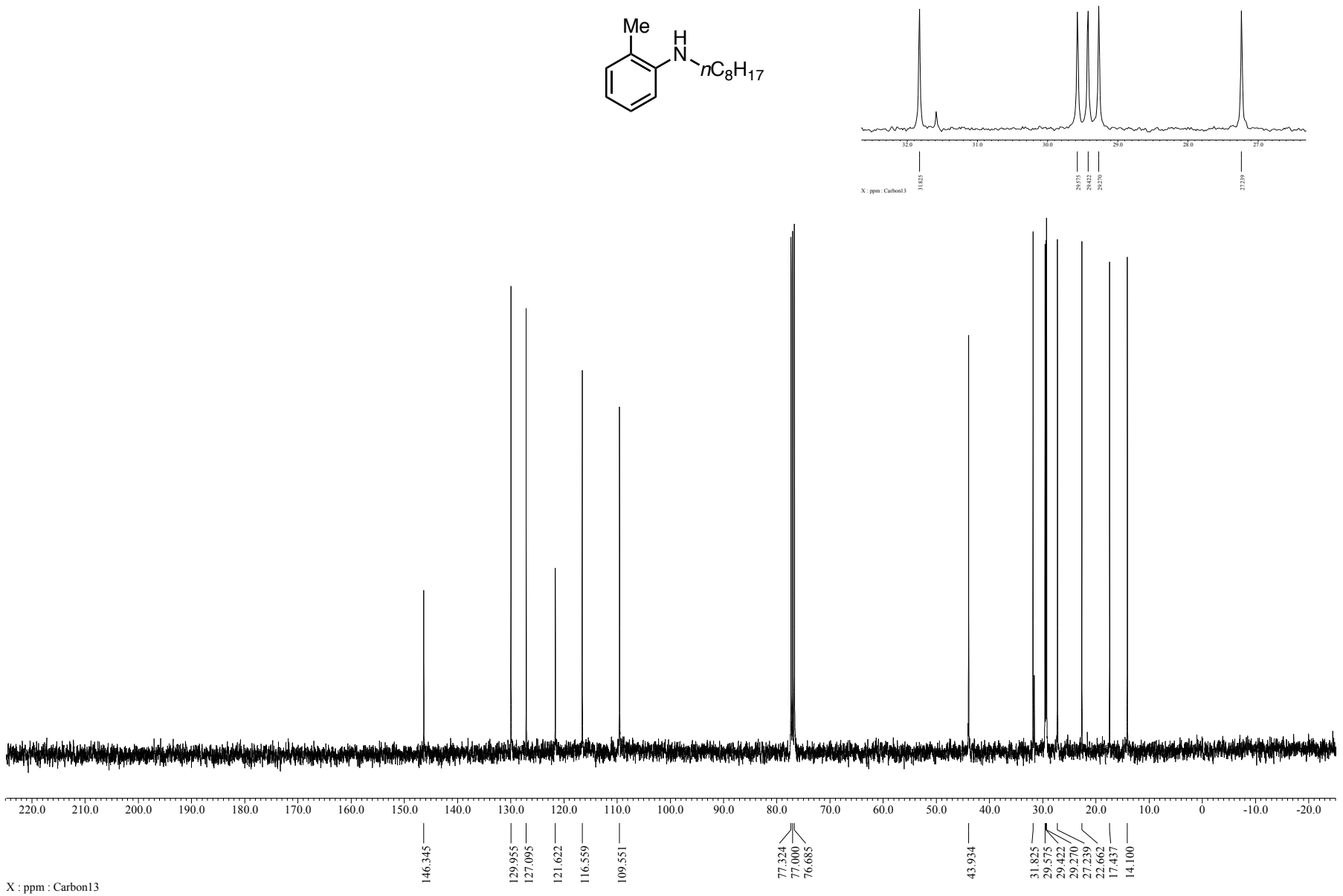

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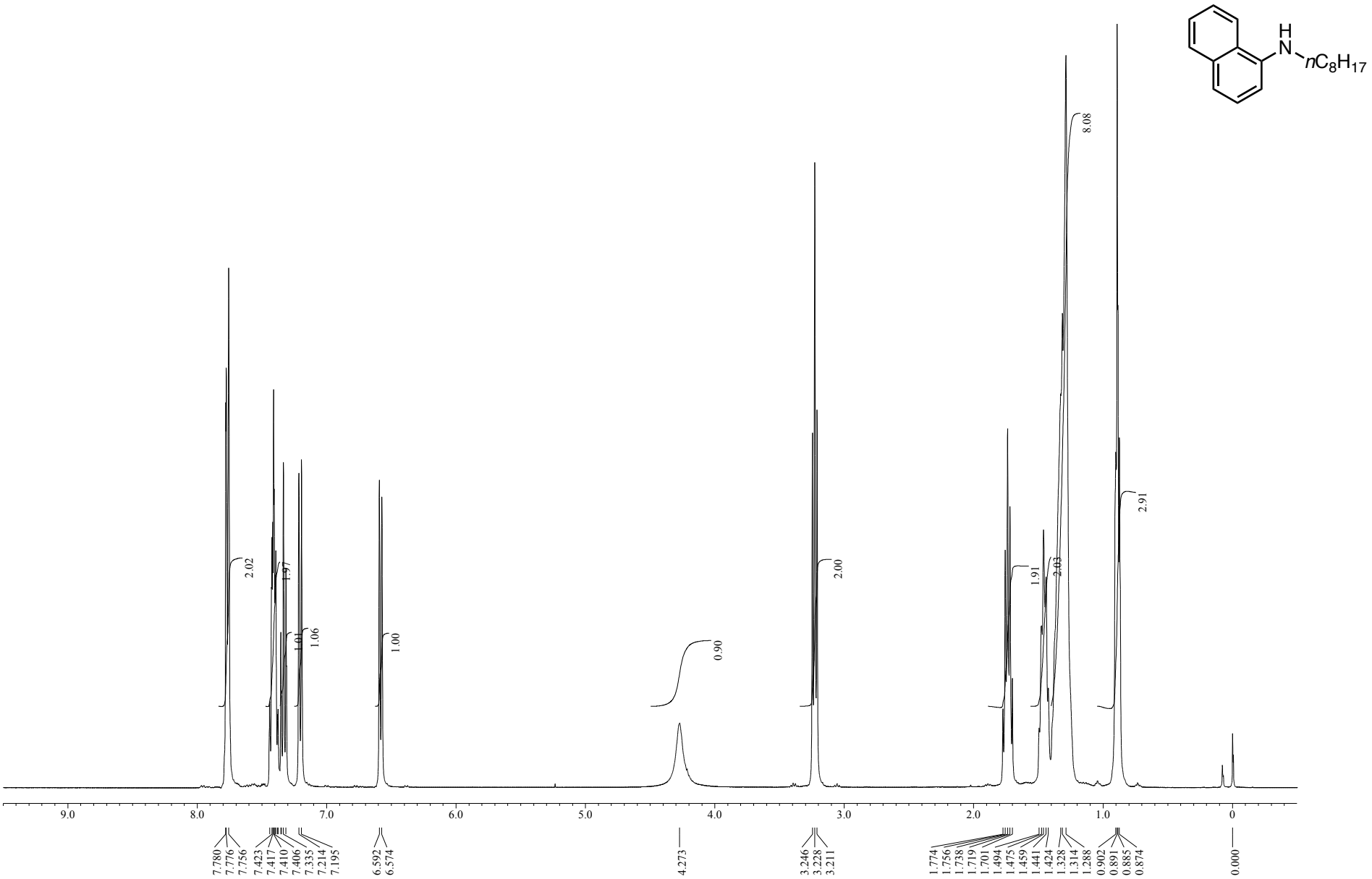

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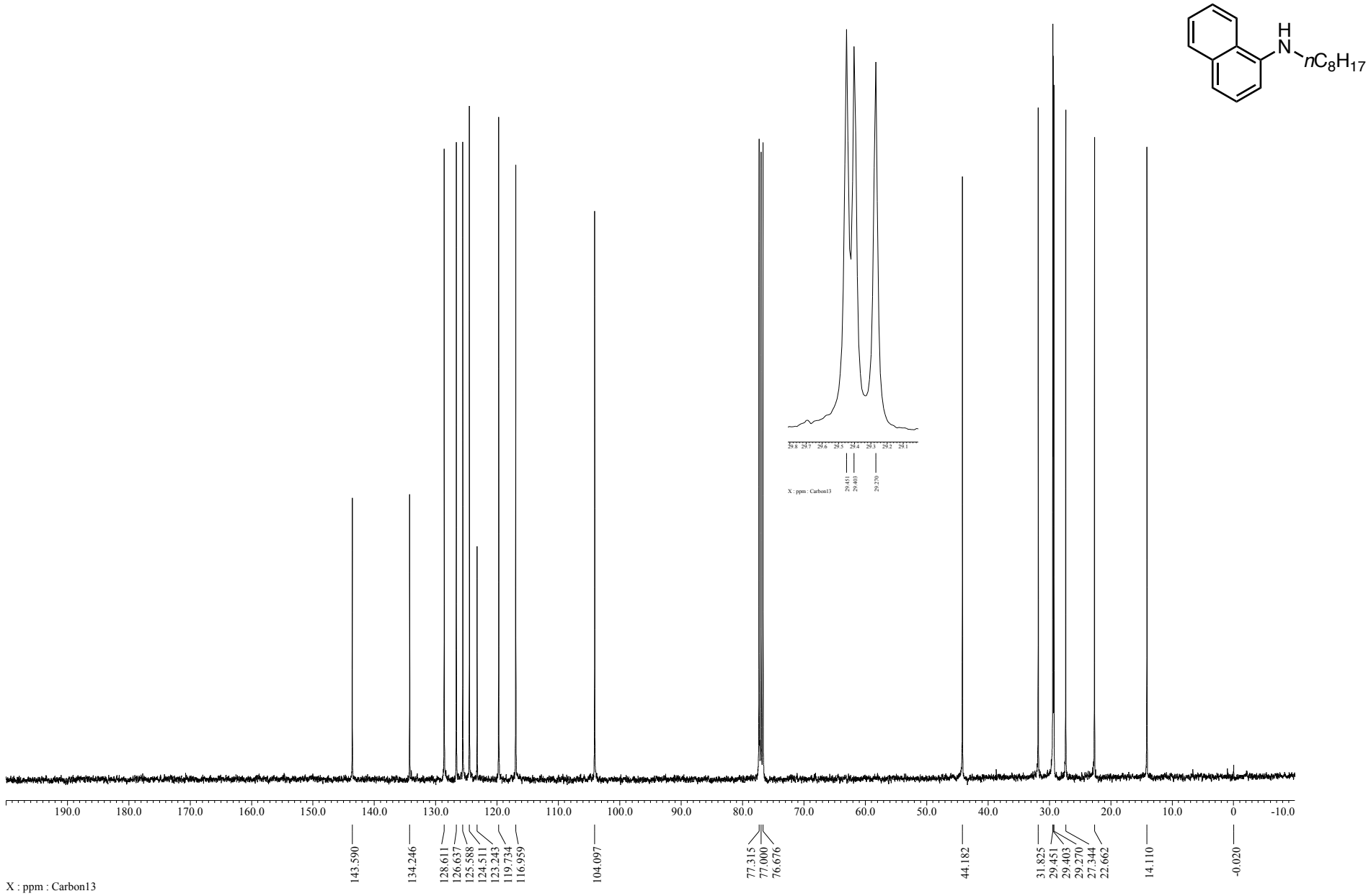

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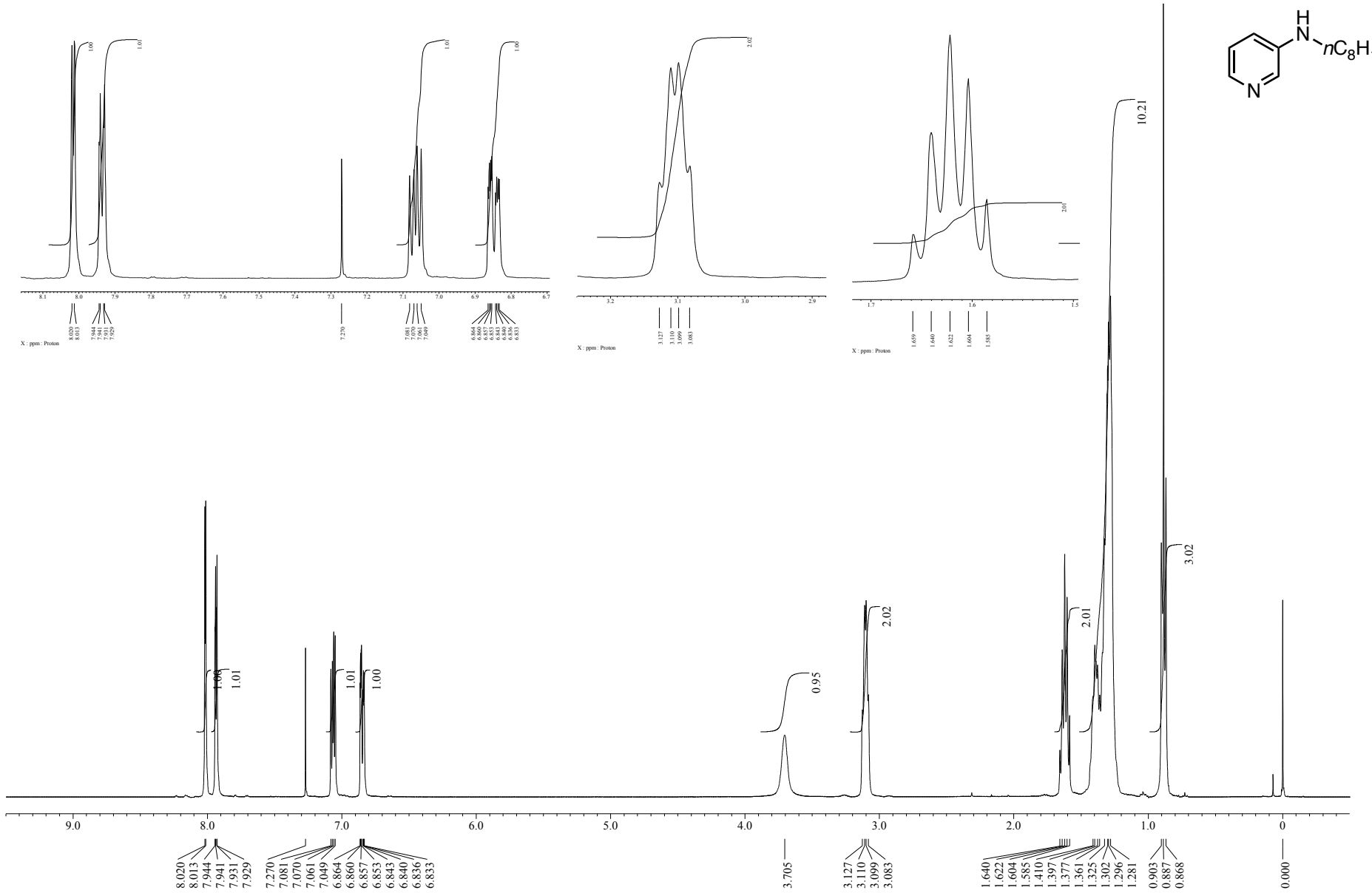

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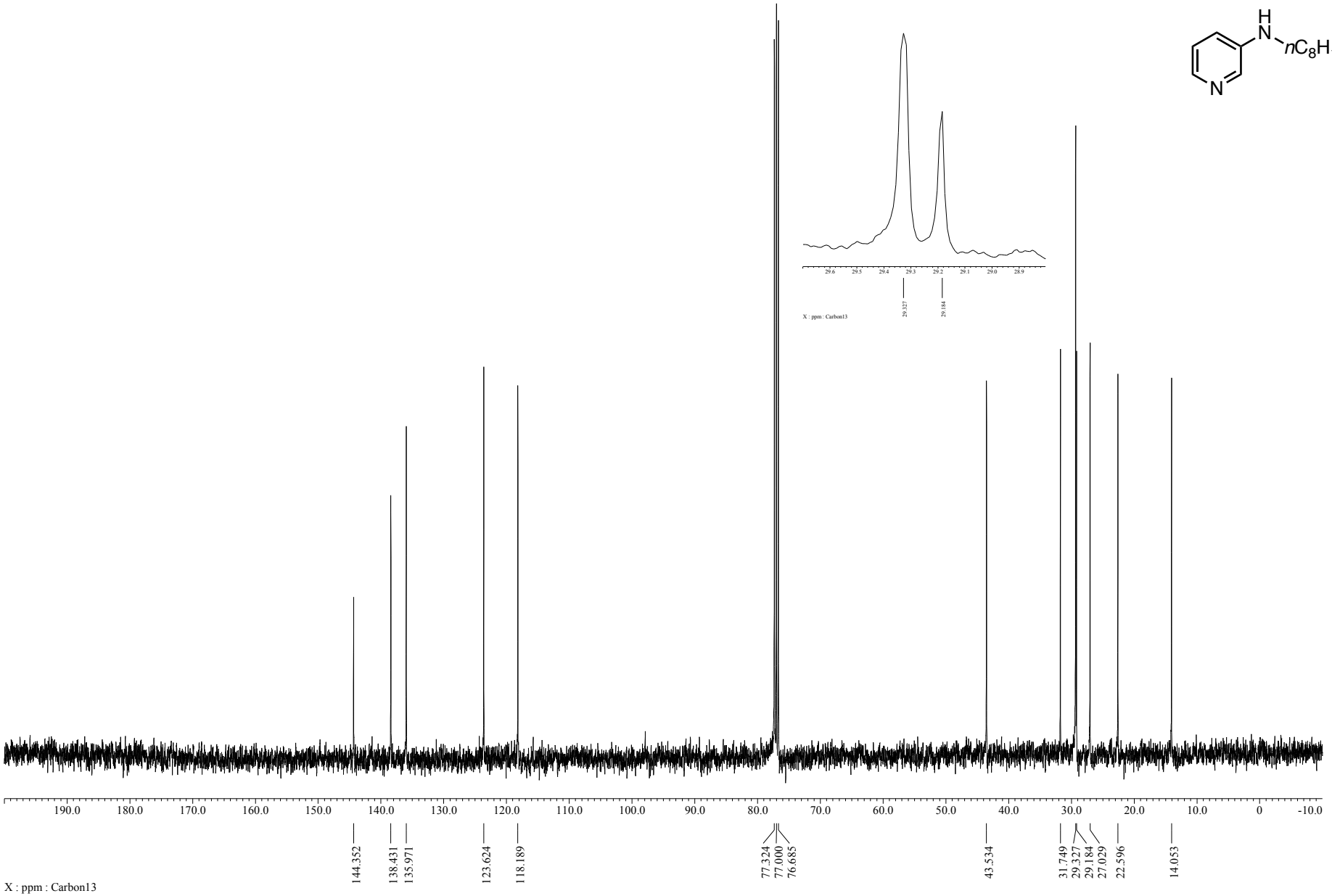

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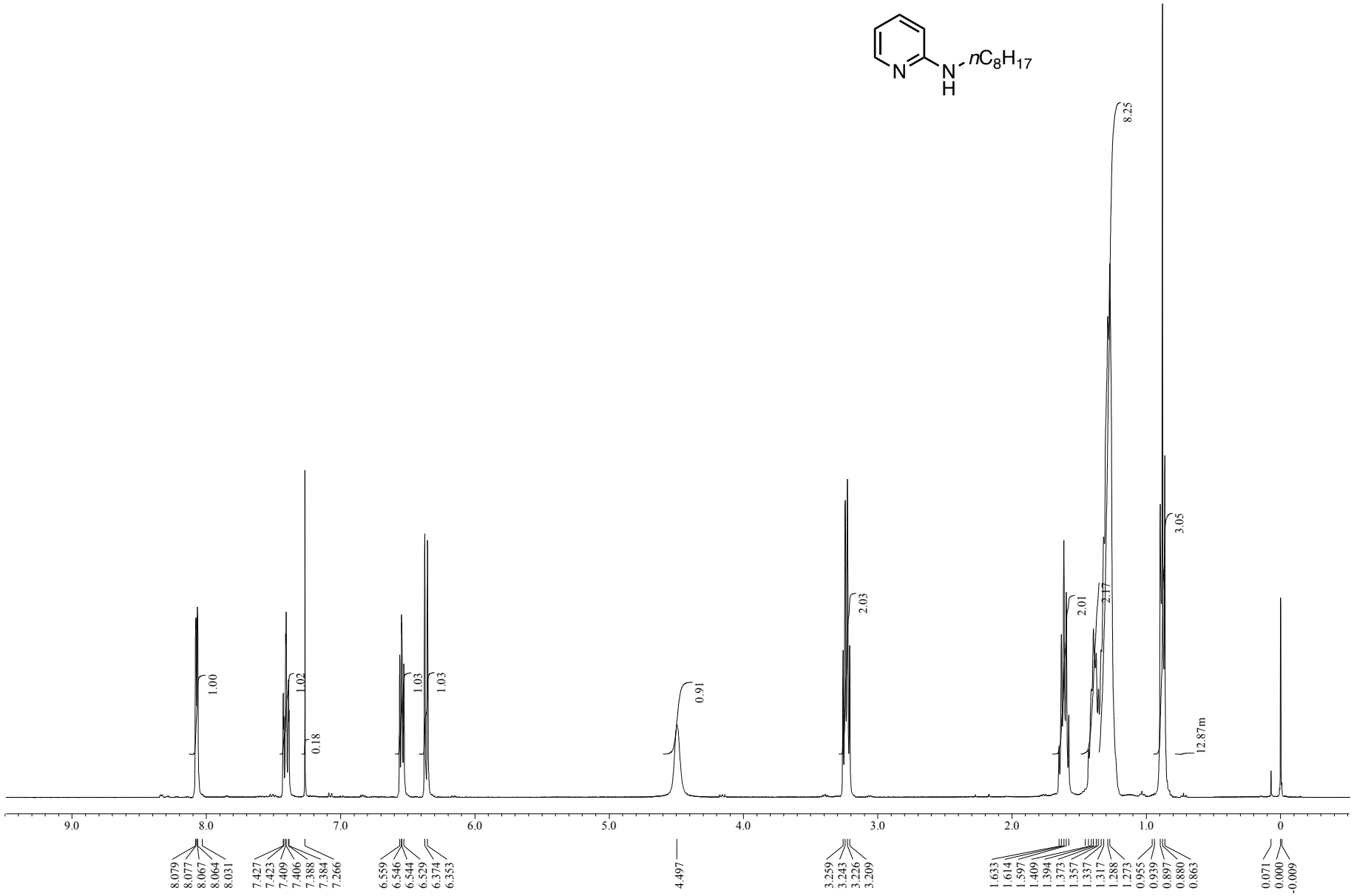

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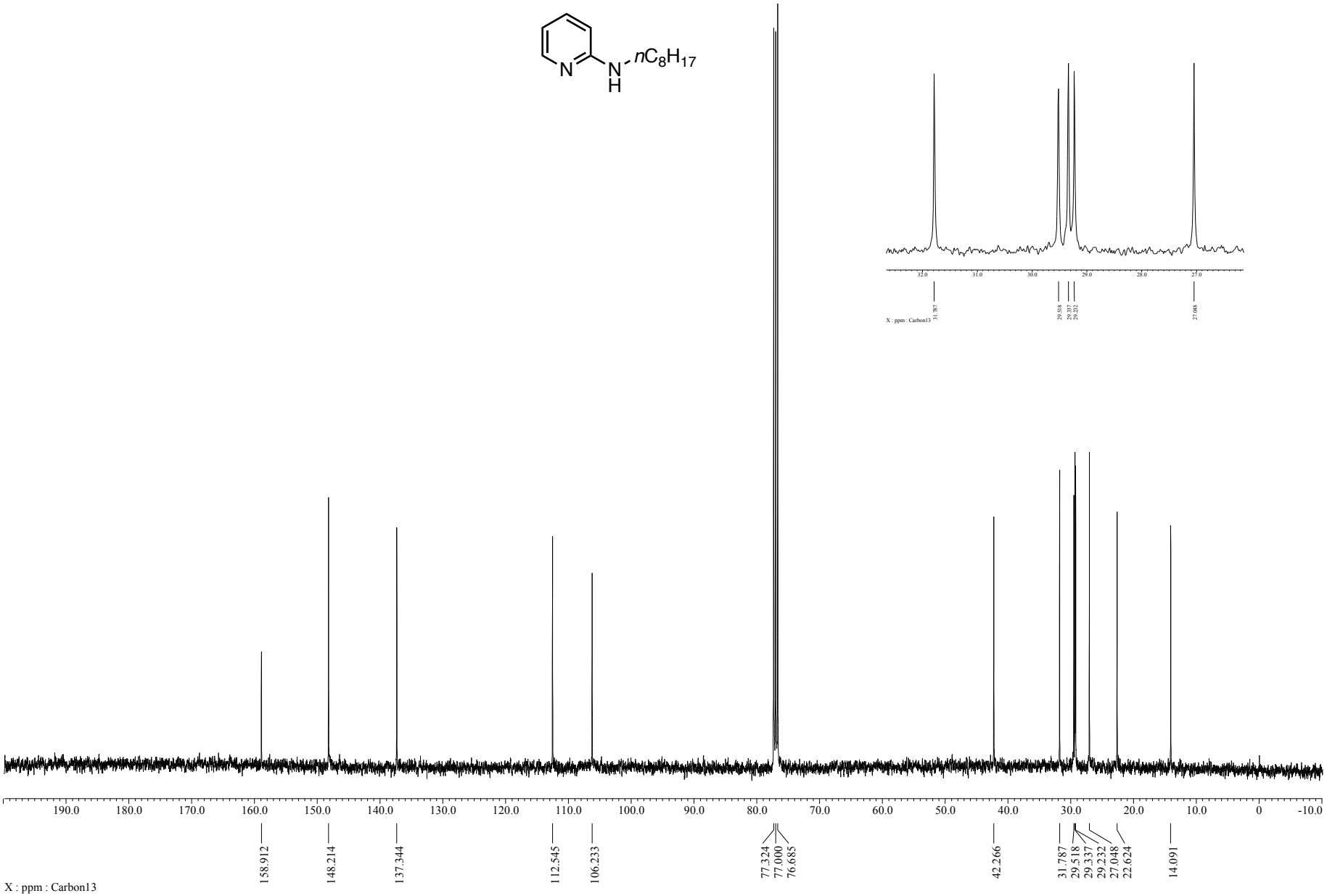

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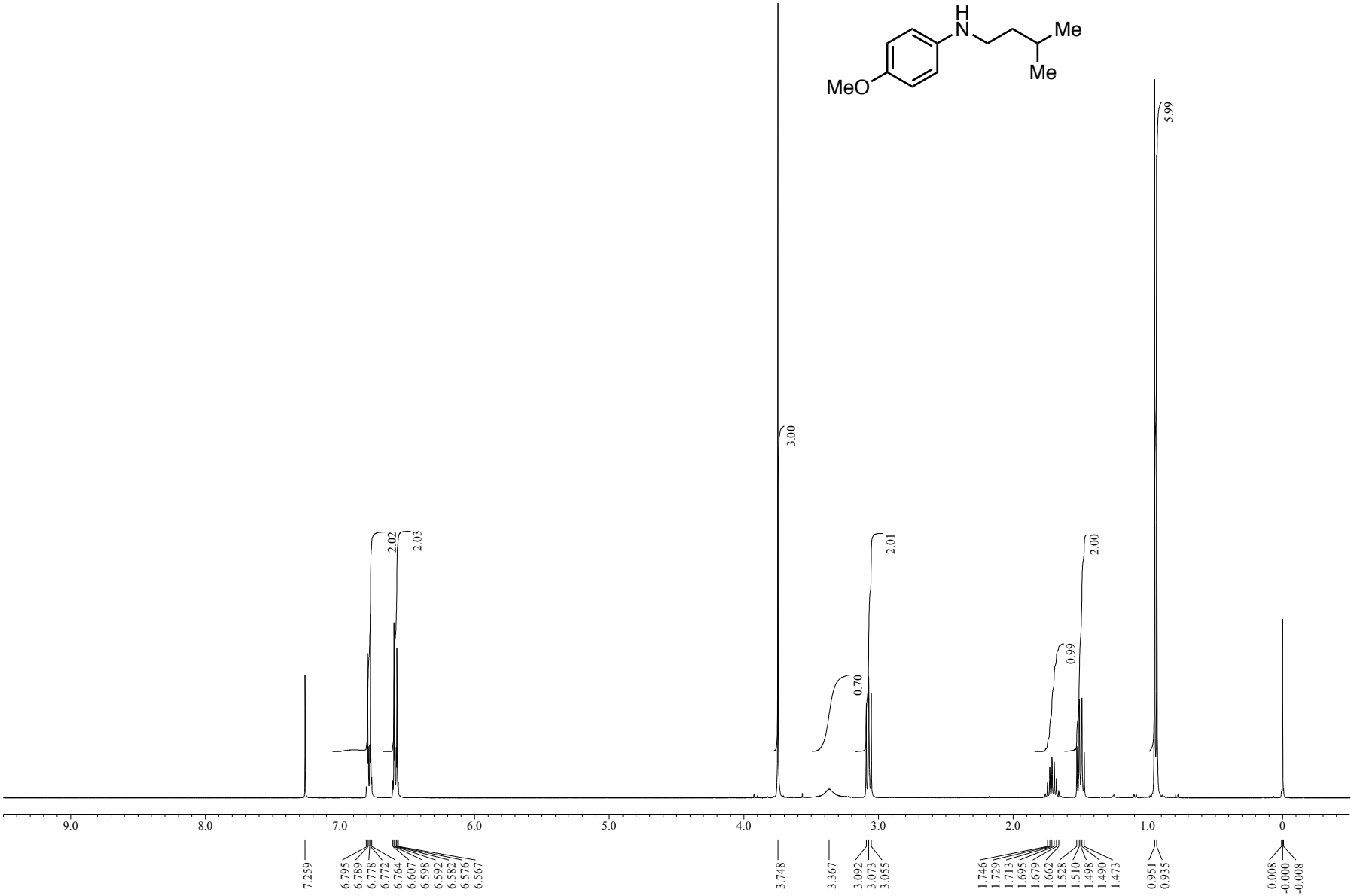

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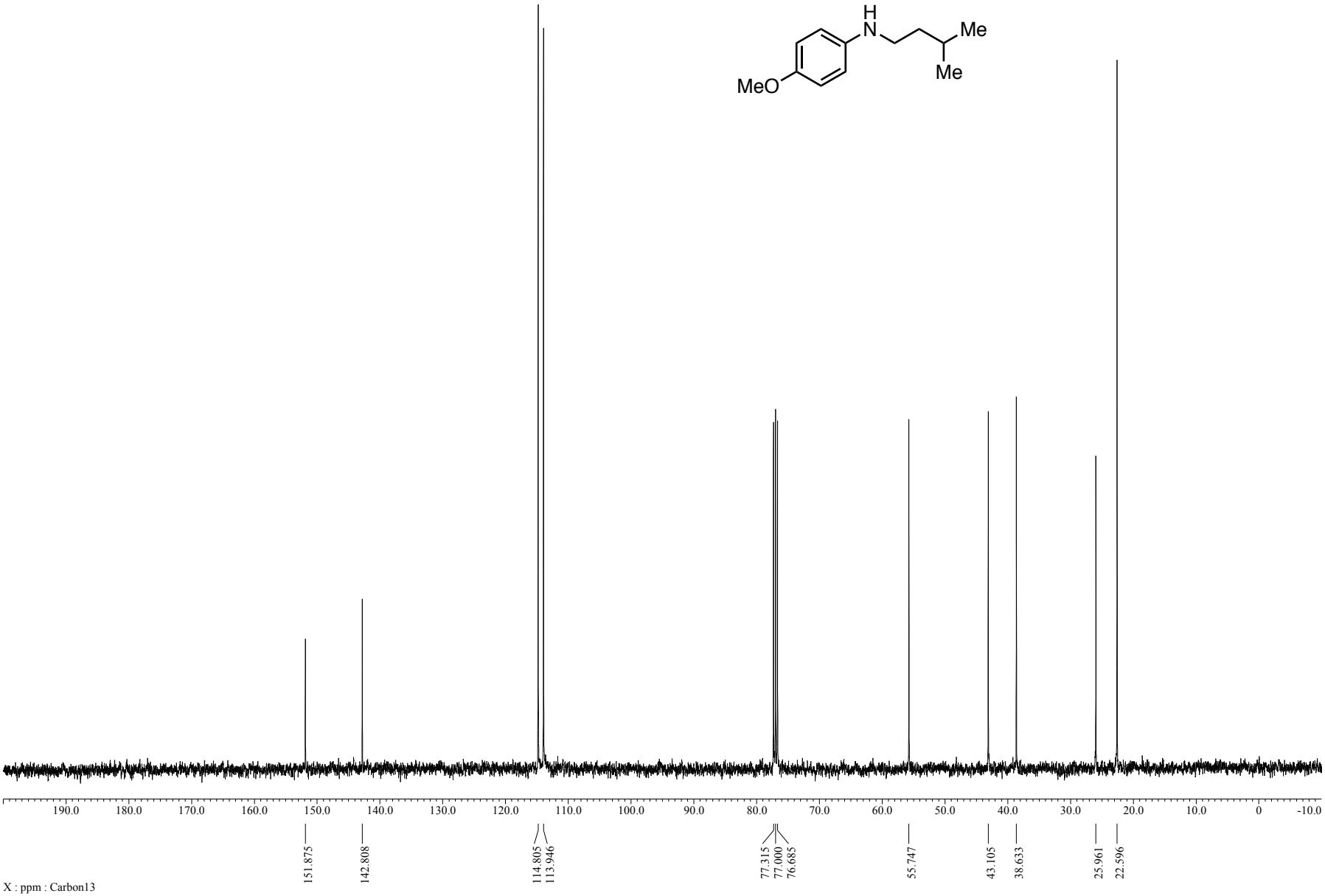

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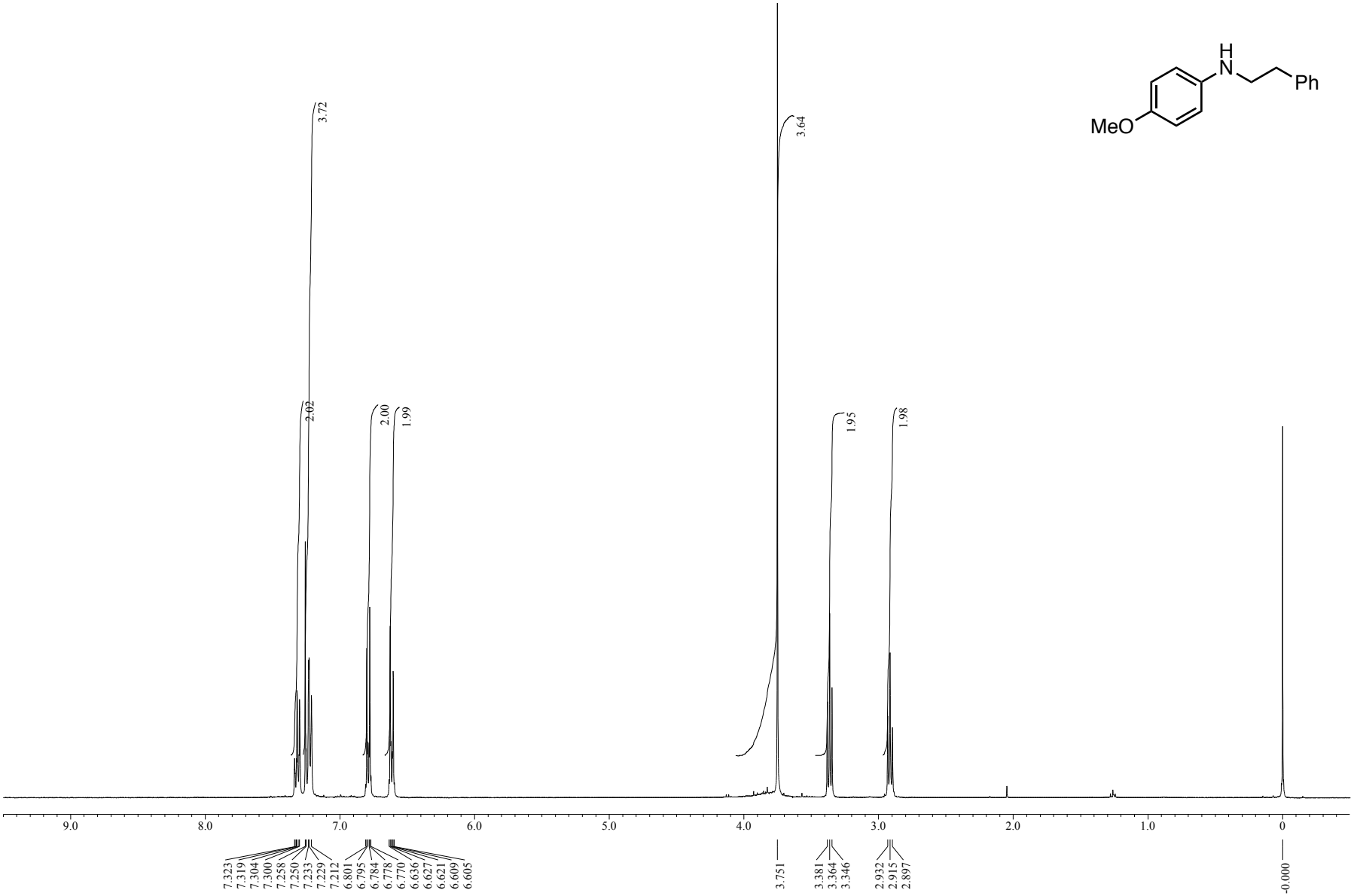

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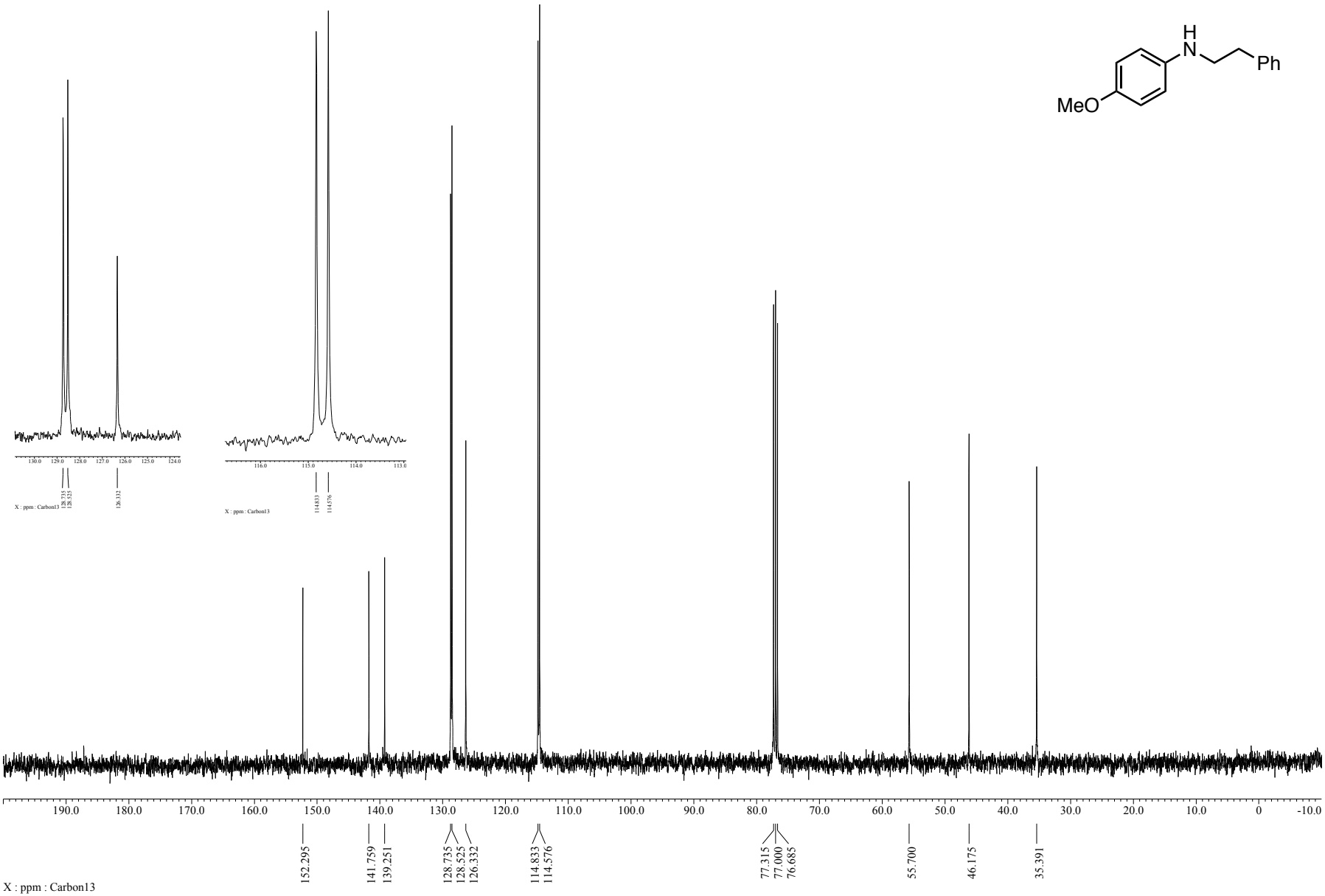

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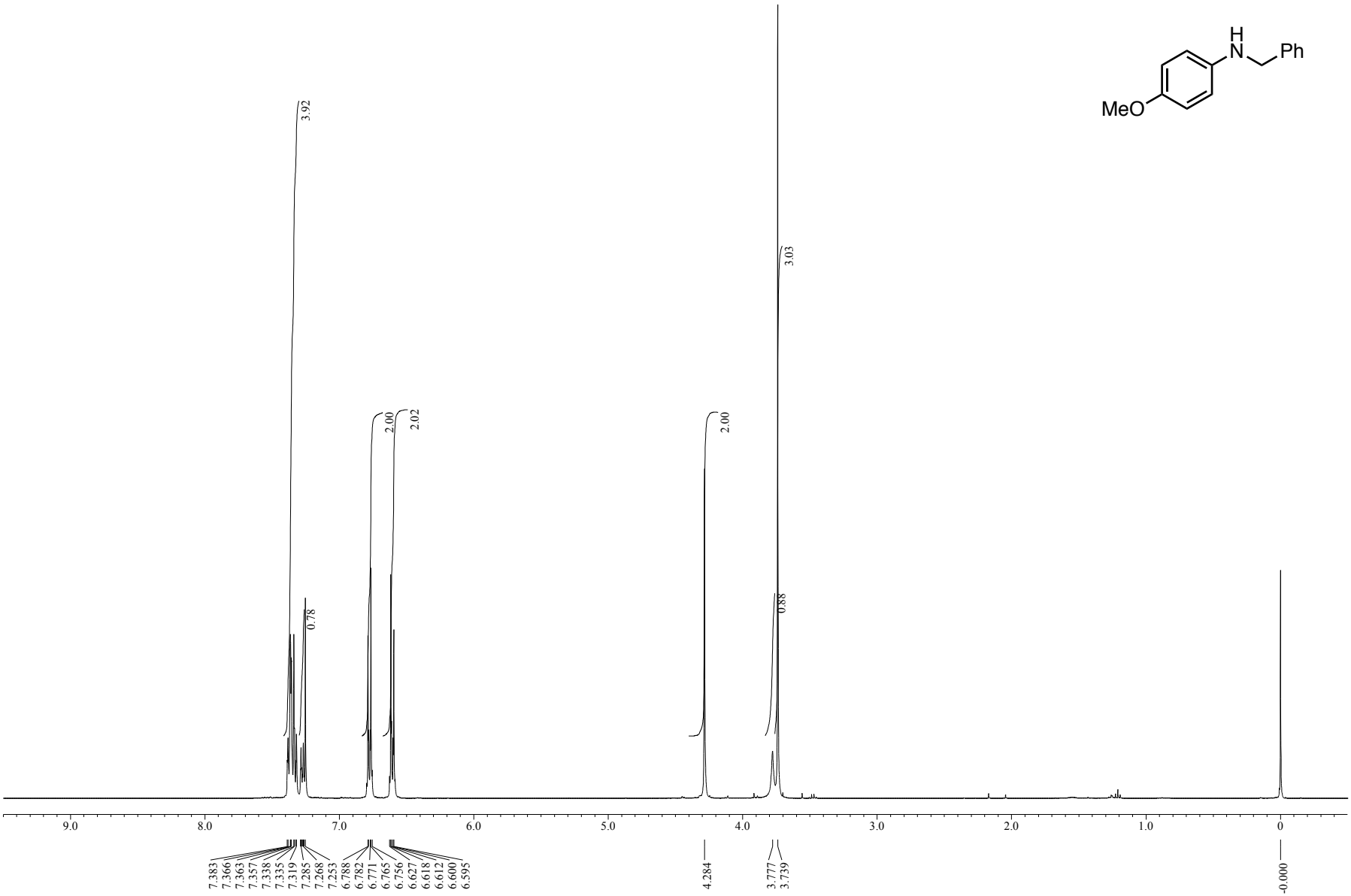

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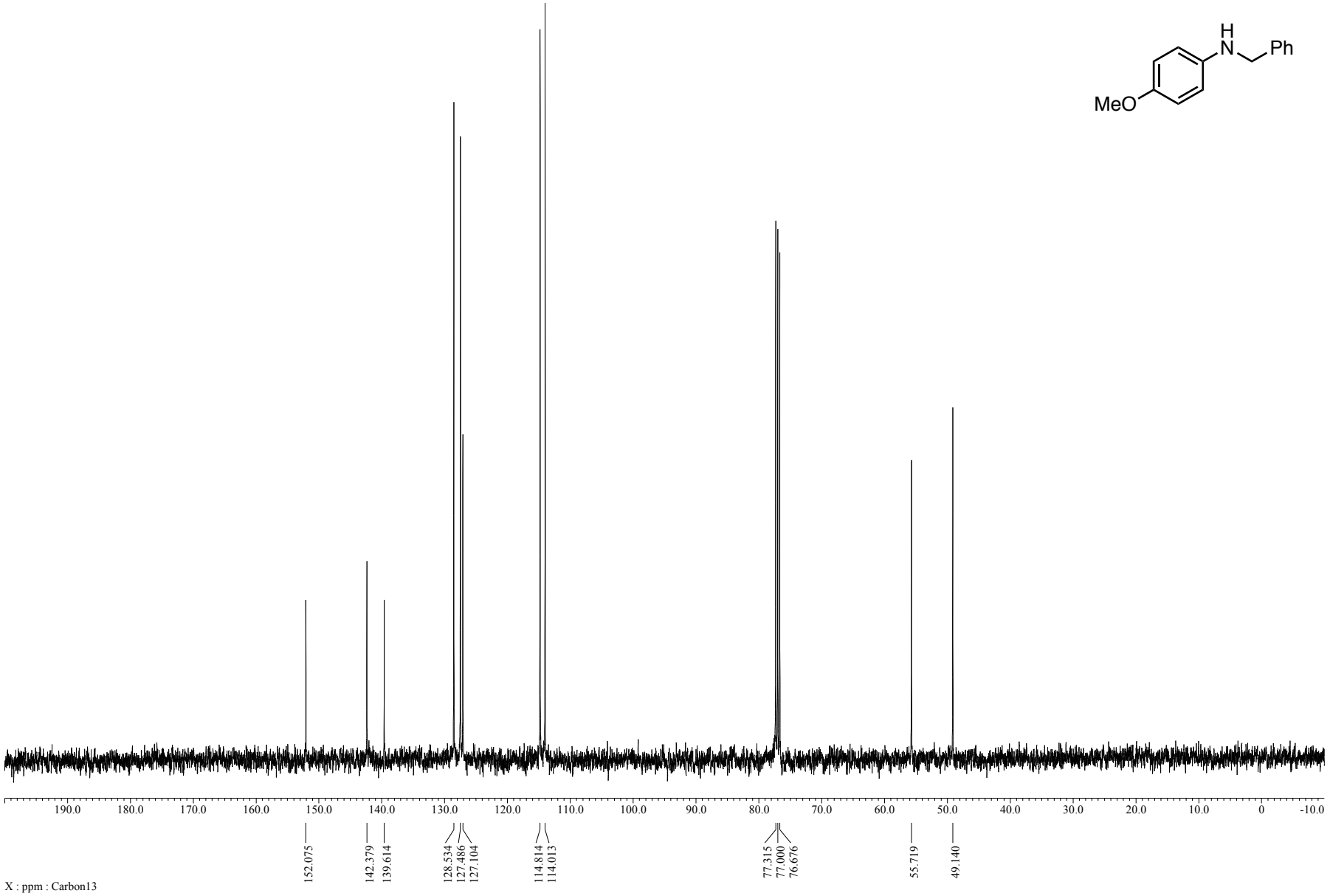

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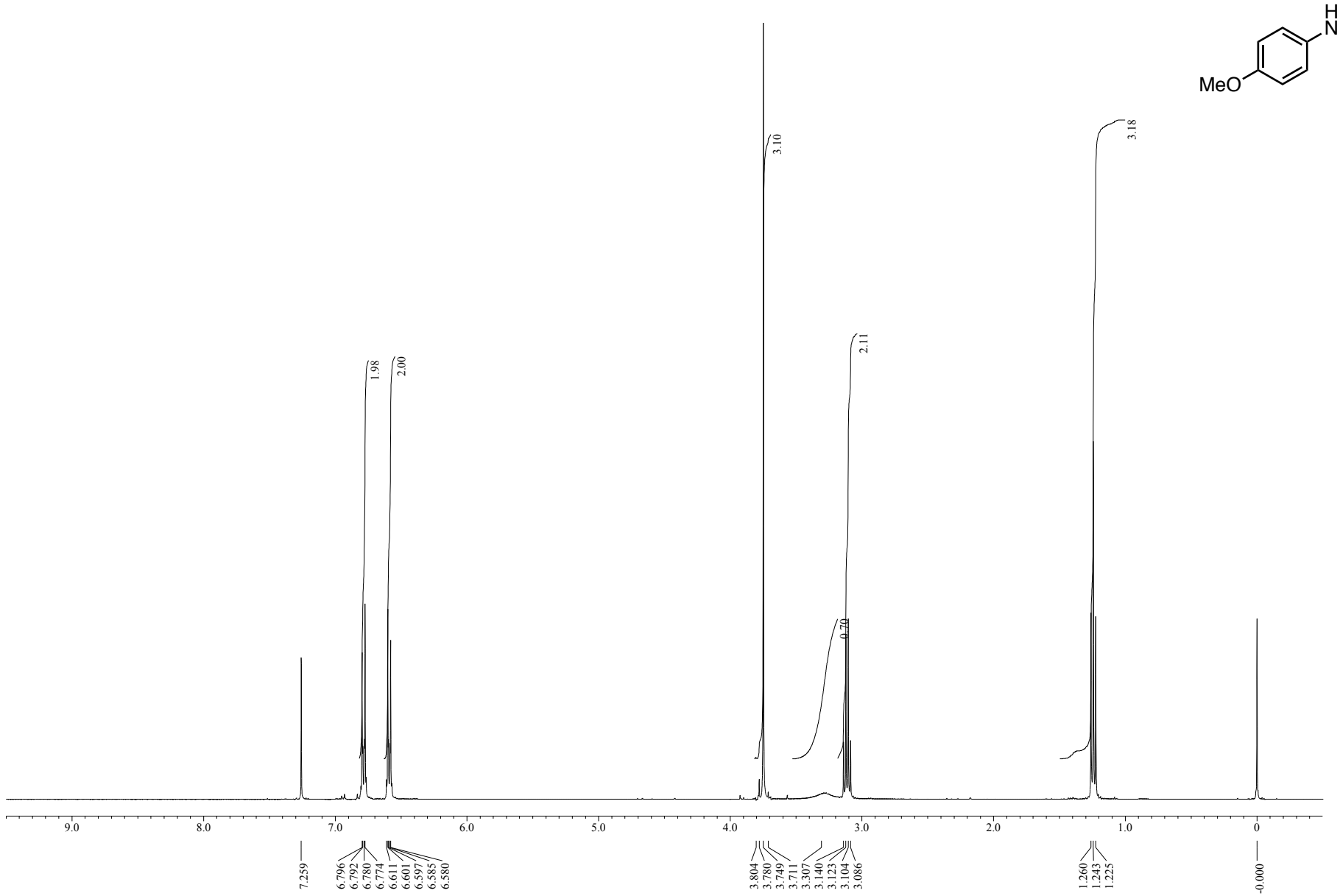

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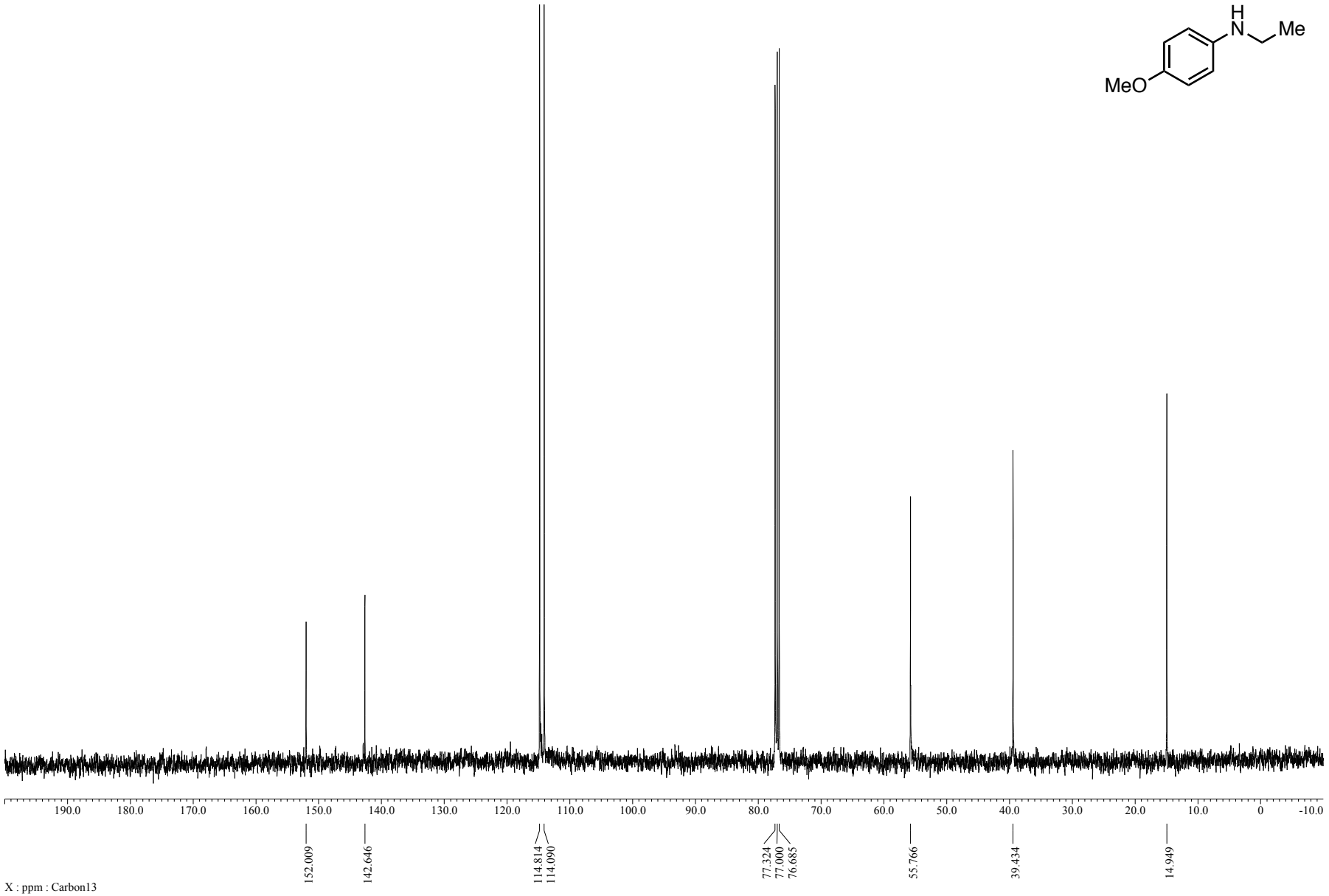

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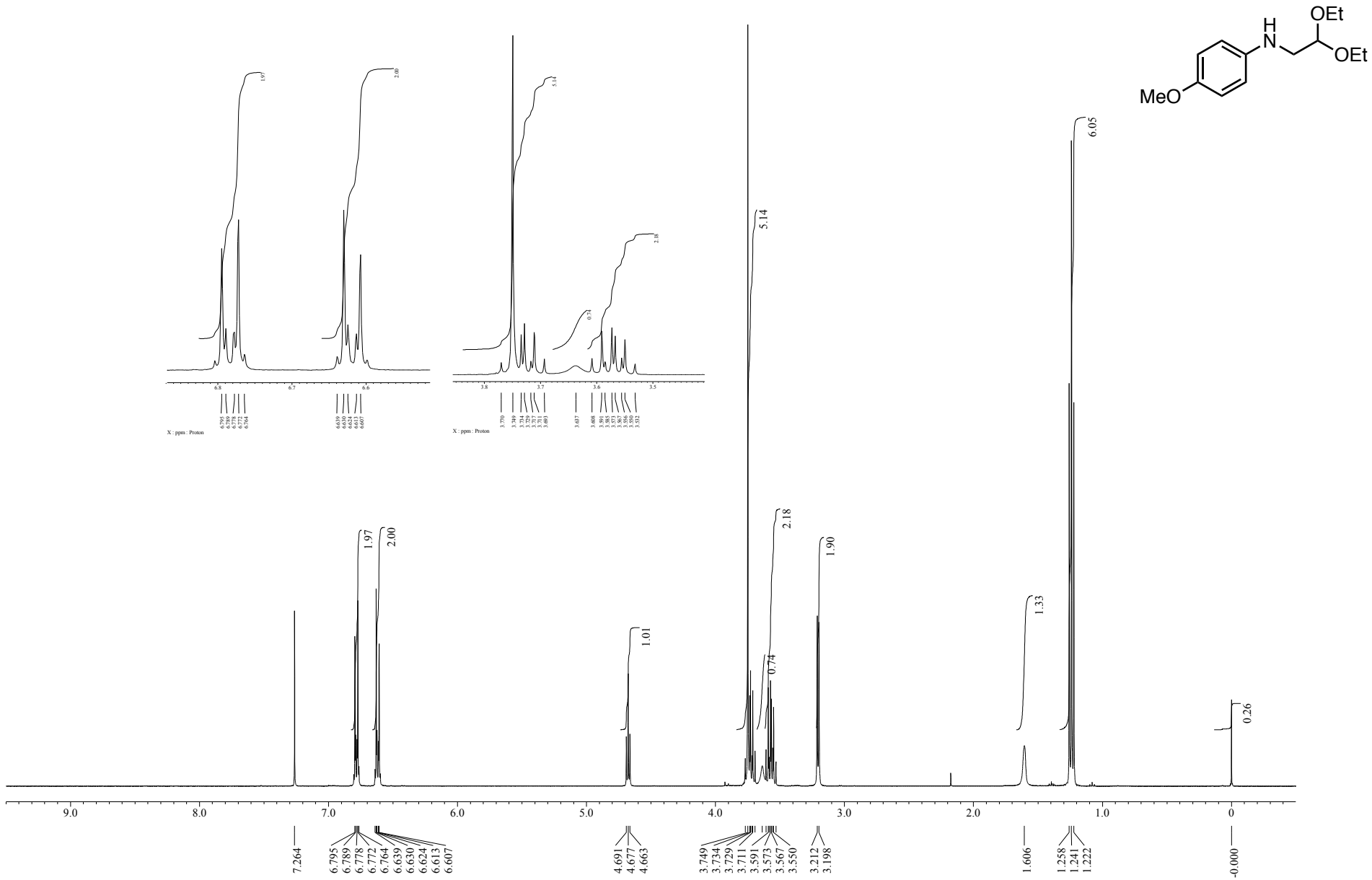

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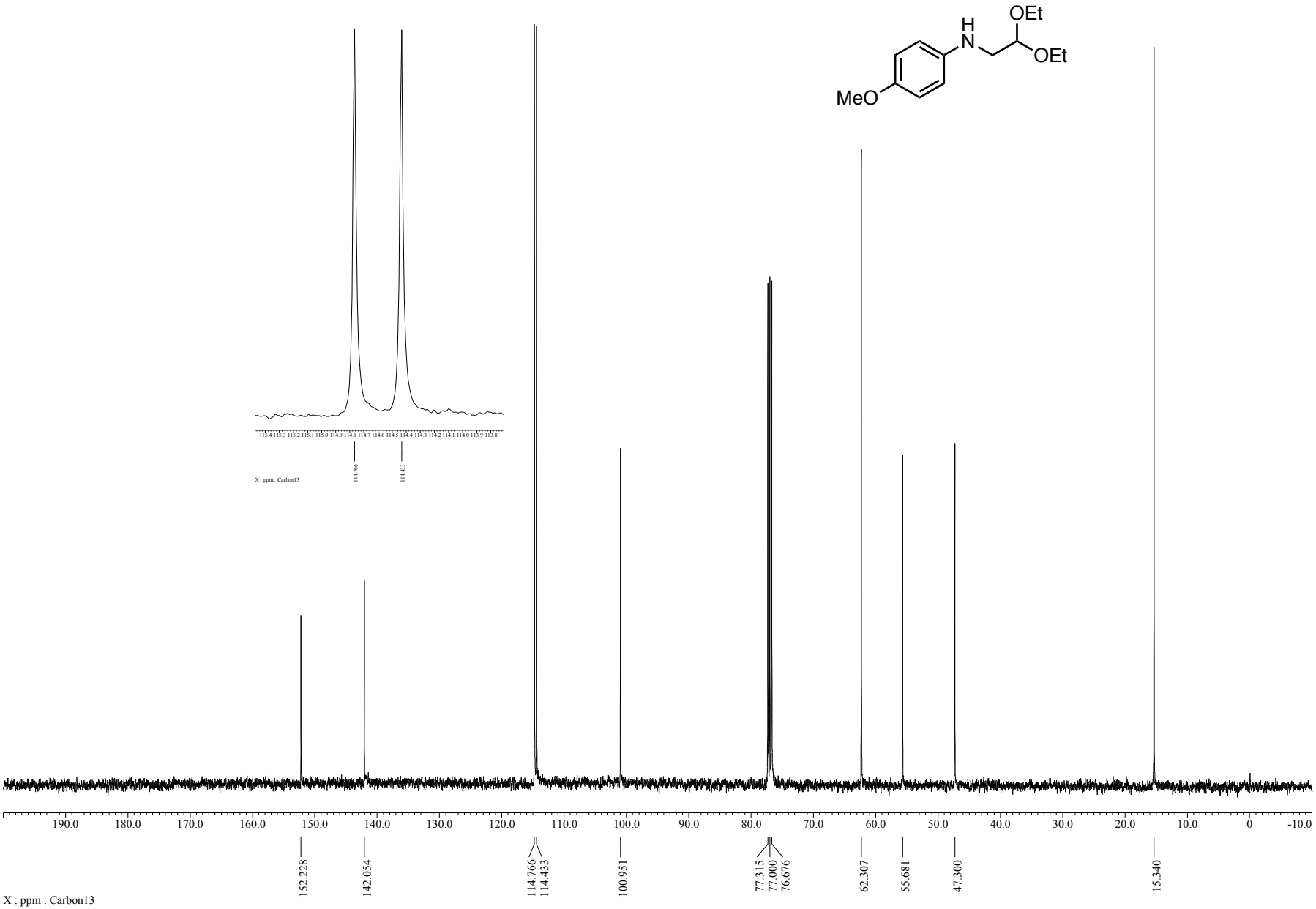
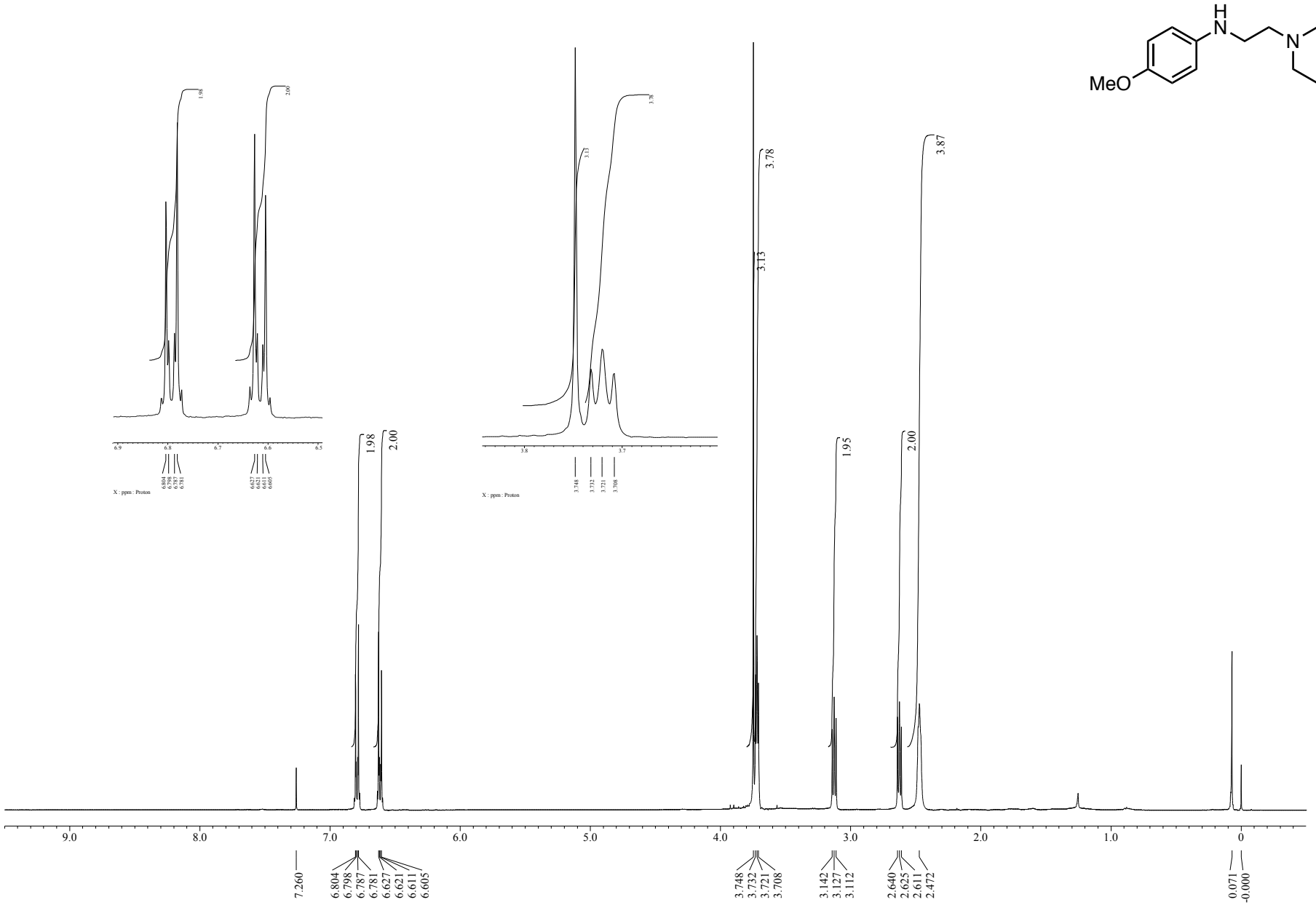
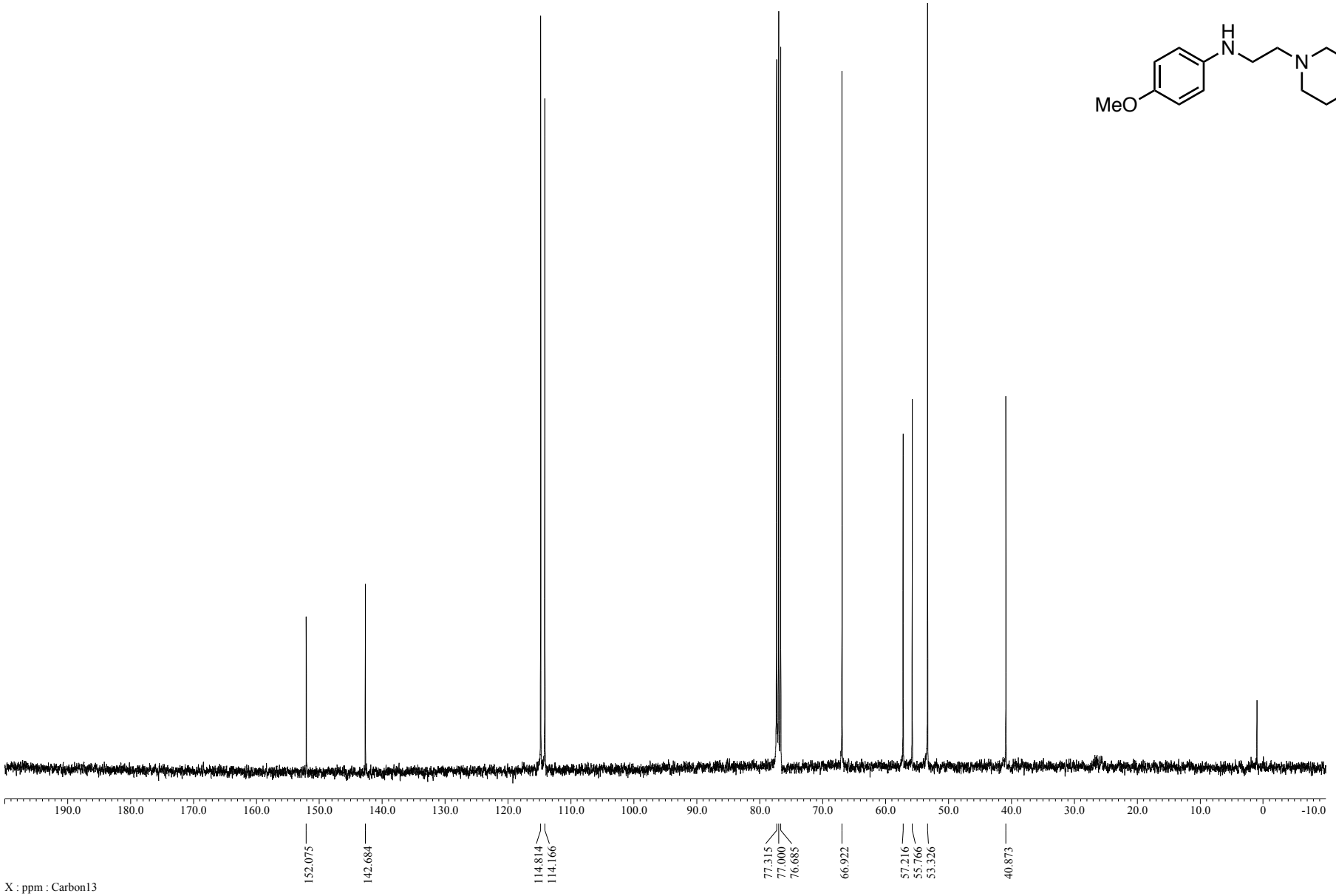


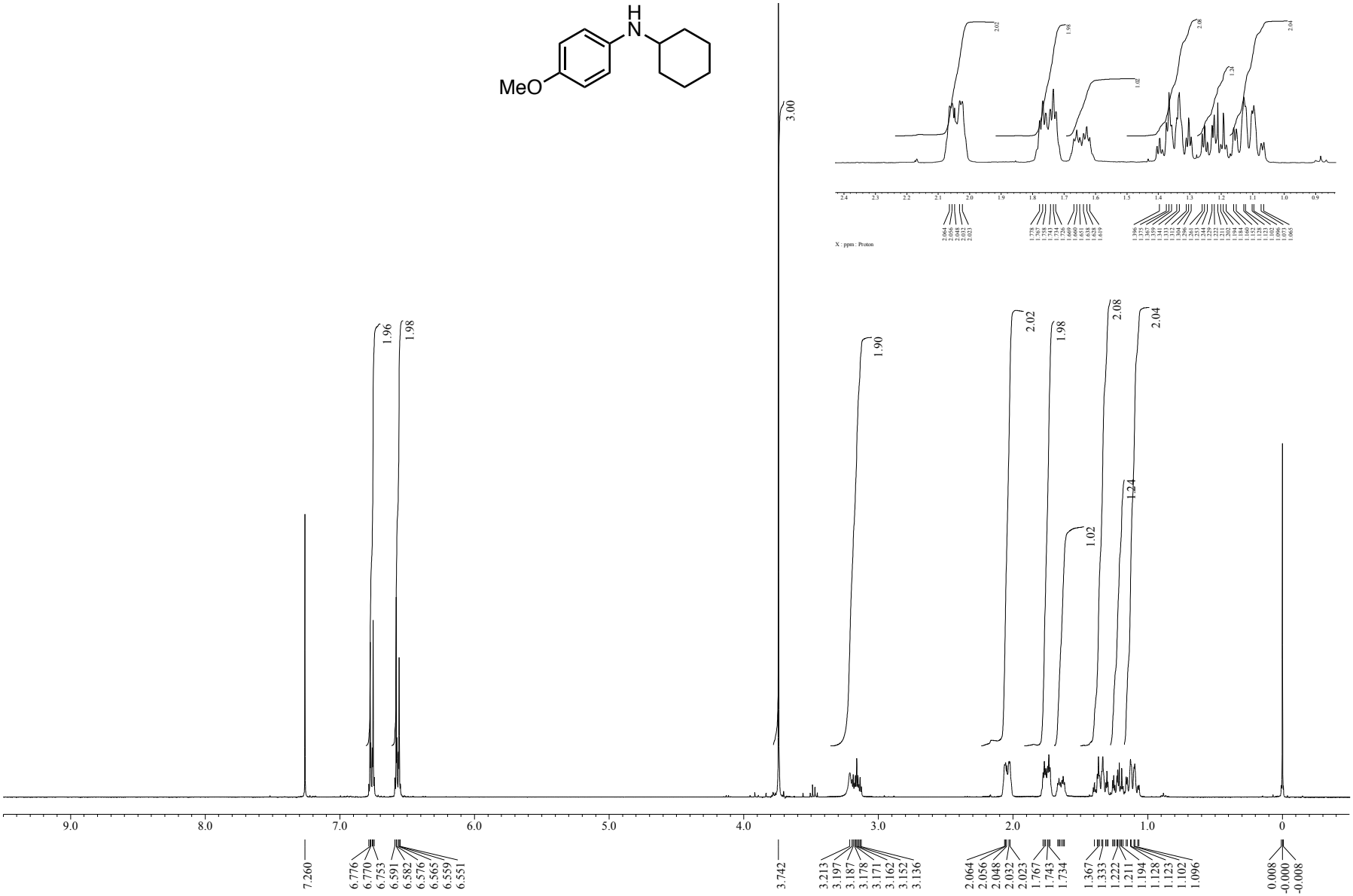
^{13}C NMR spectrum of **3u** in $CDCl_3$



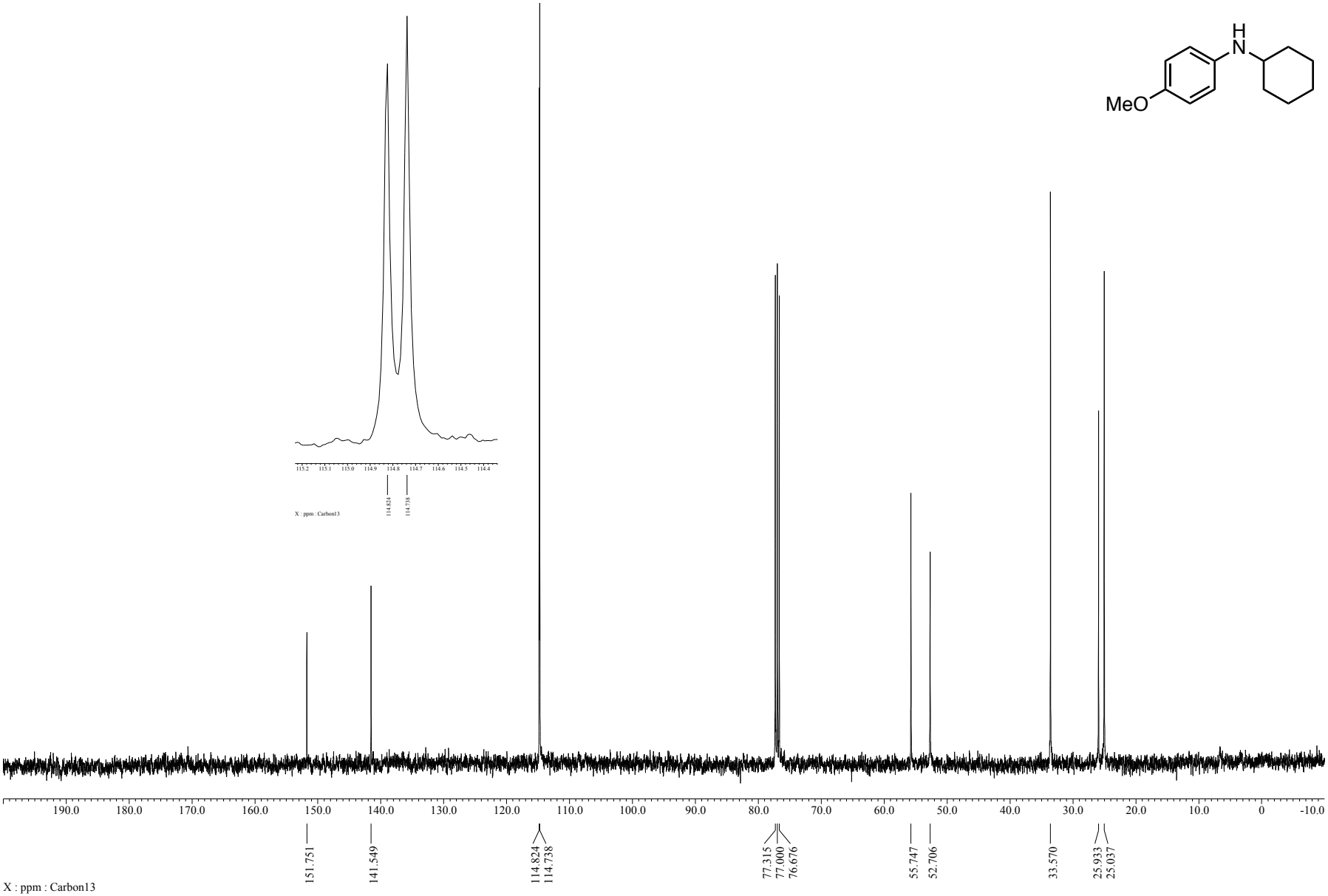
^{1}H NMR spectrum of **3v** in $CDCl_3$



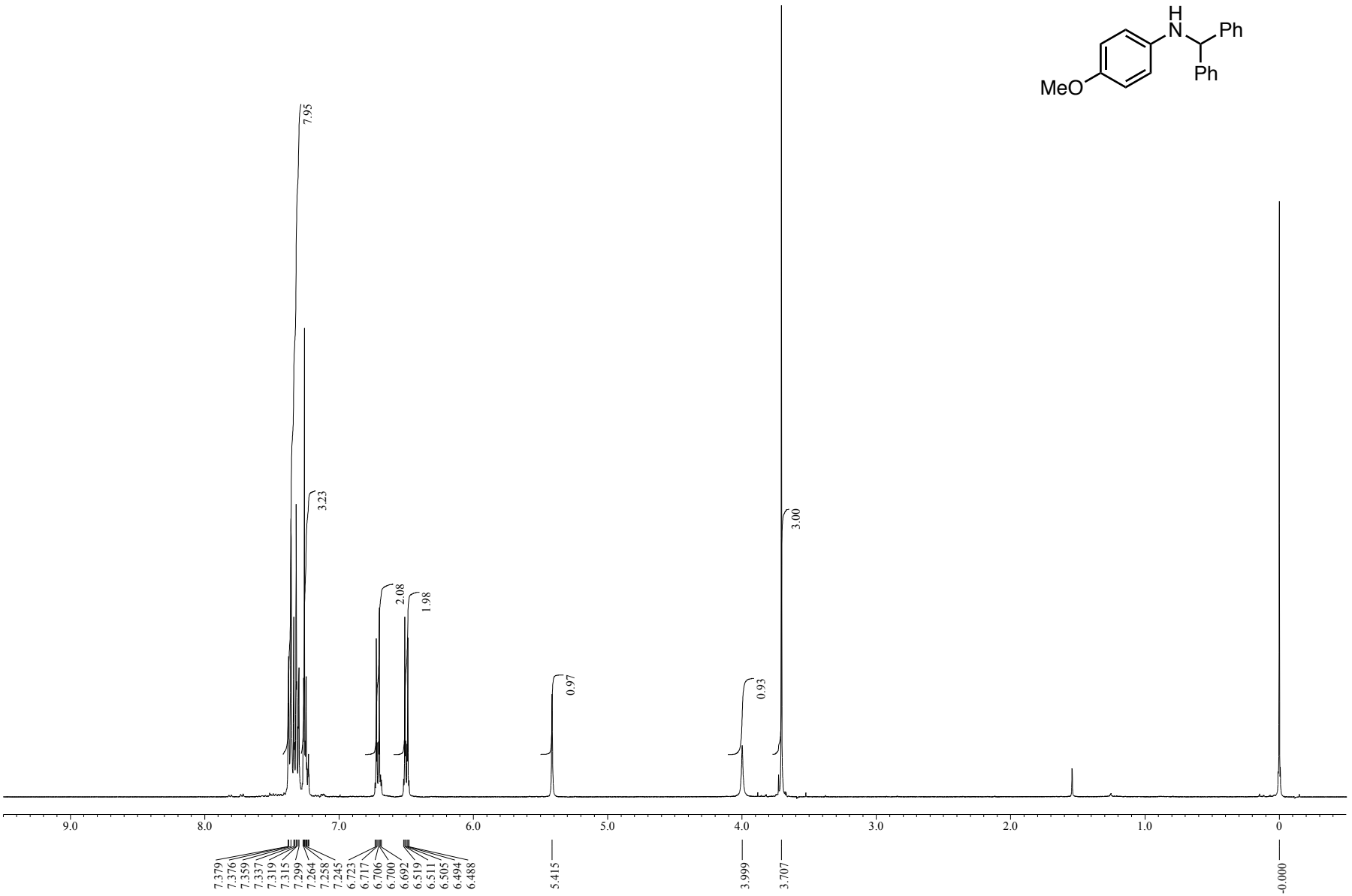
^{13}C NMR spectrum of **3v** in $CDCl_3$



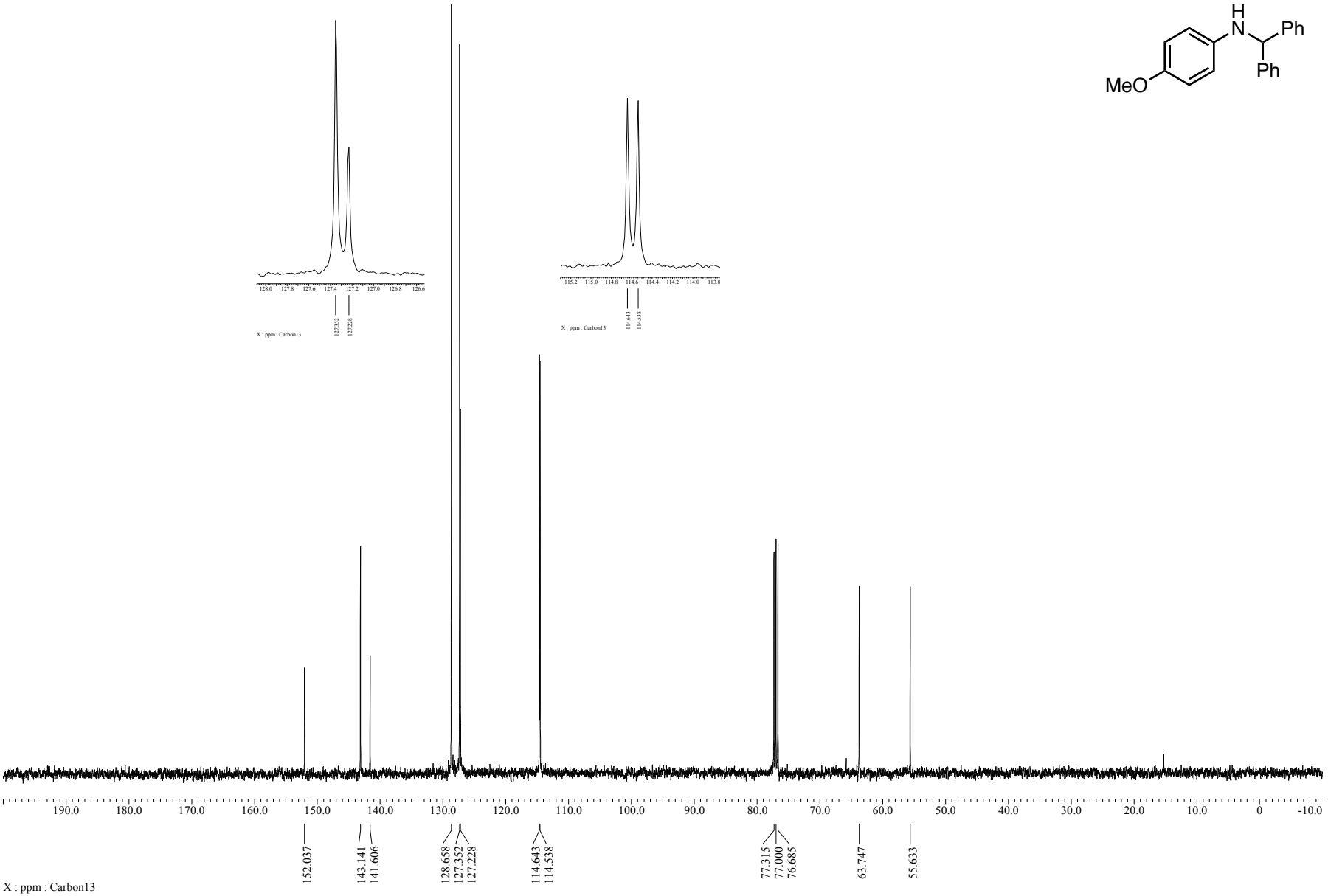
^{1}H NMR spectrum of **3w** in $CDCl_3$



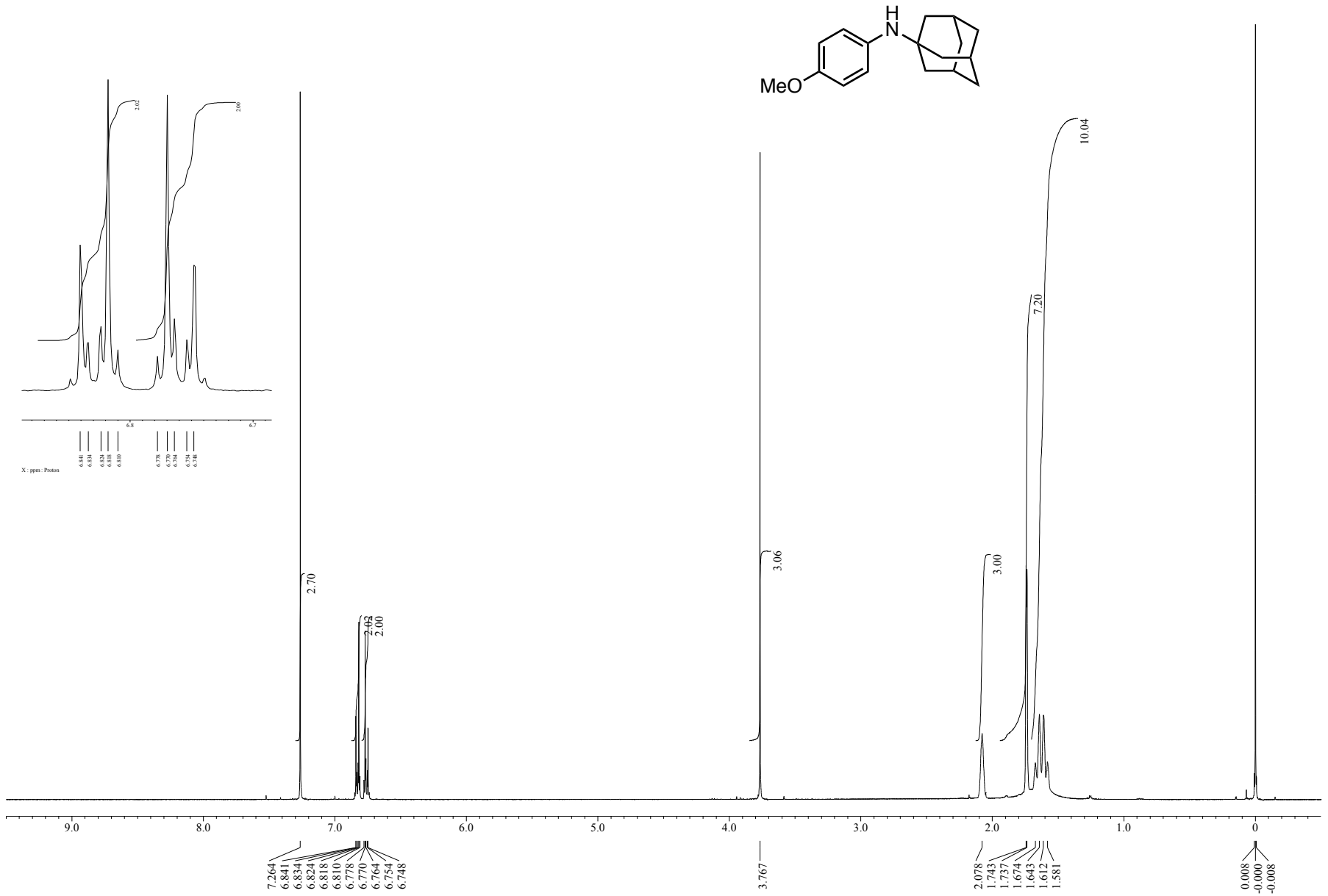
^{13}C NMR spectrum of **3w** in $CDCl_3$



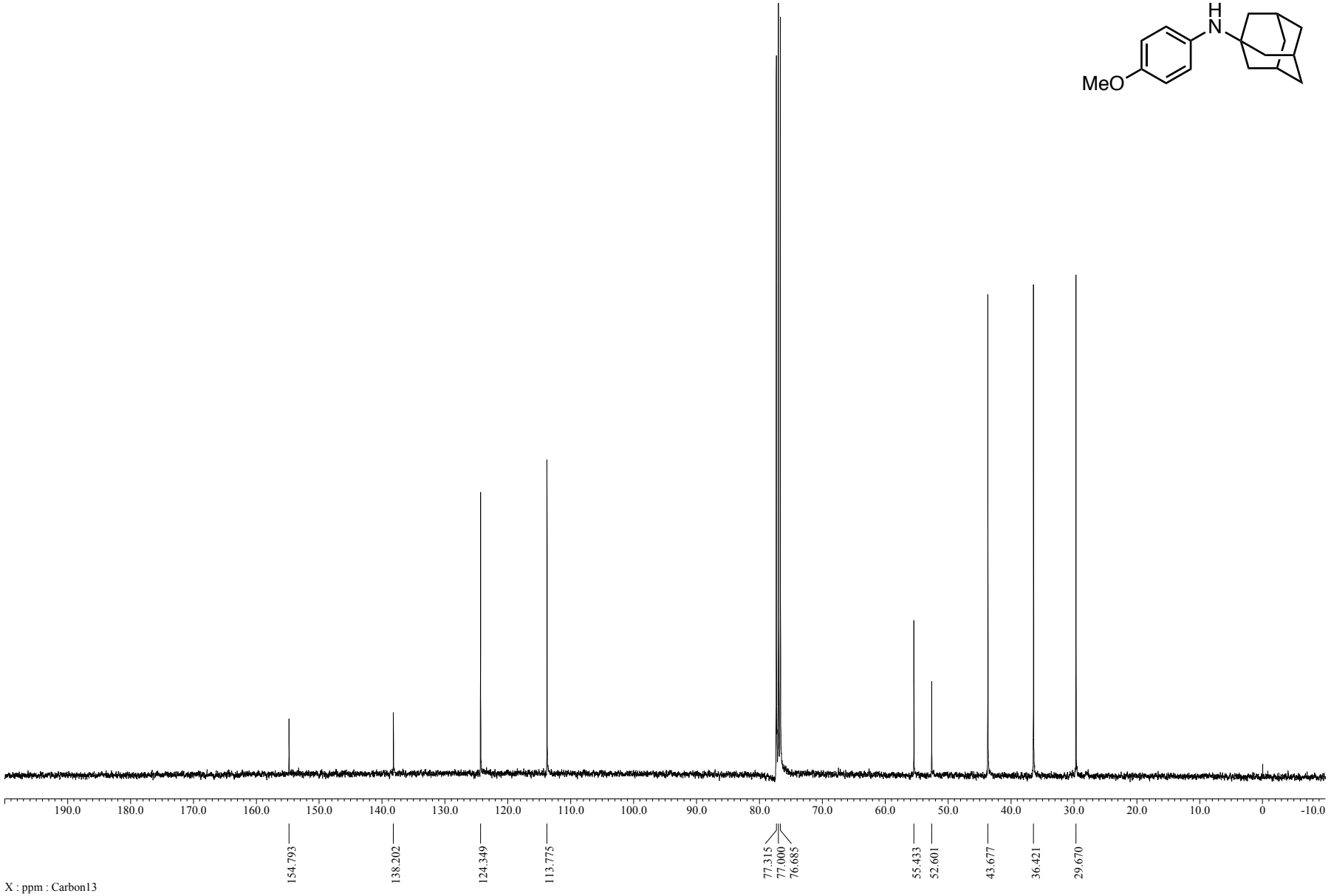
^{1}H NMR spectrum of **3x** in $CDCl_3$



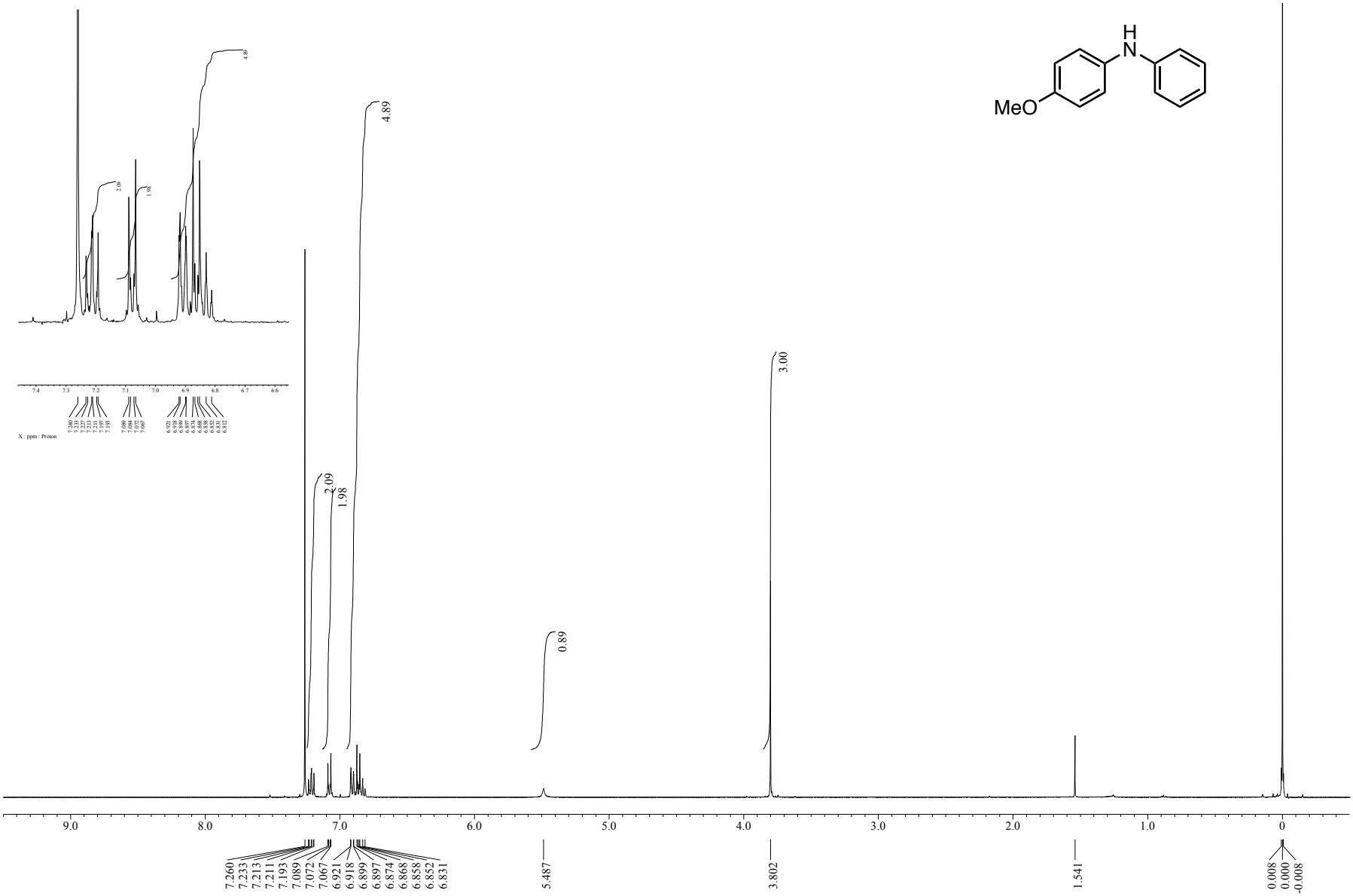
^{13}C NMR spectrum of **3x** in $CDCl_3$



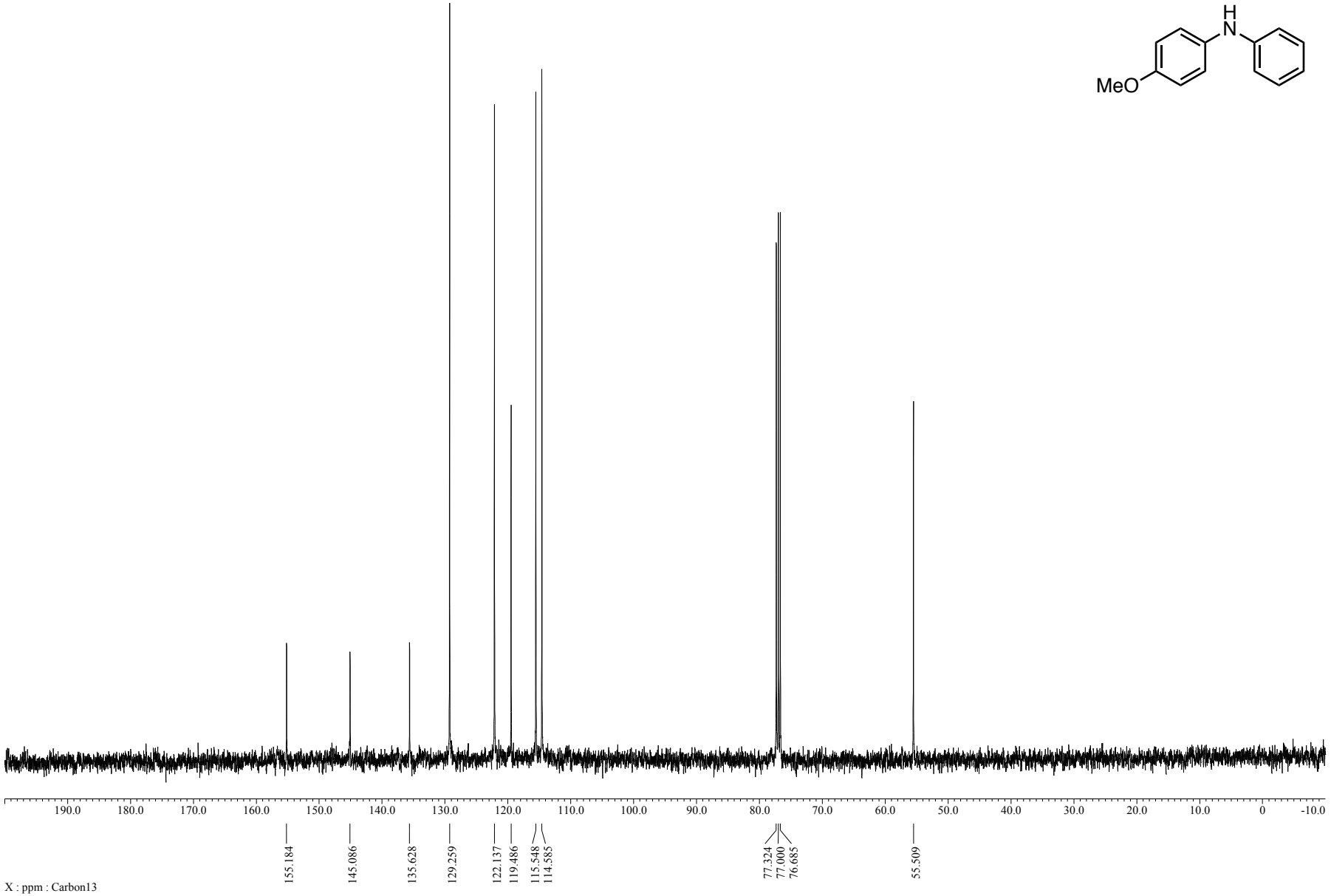
^{1}H NMR spectrum of **3y** in $CDCl_3$



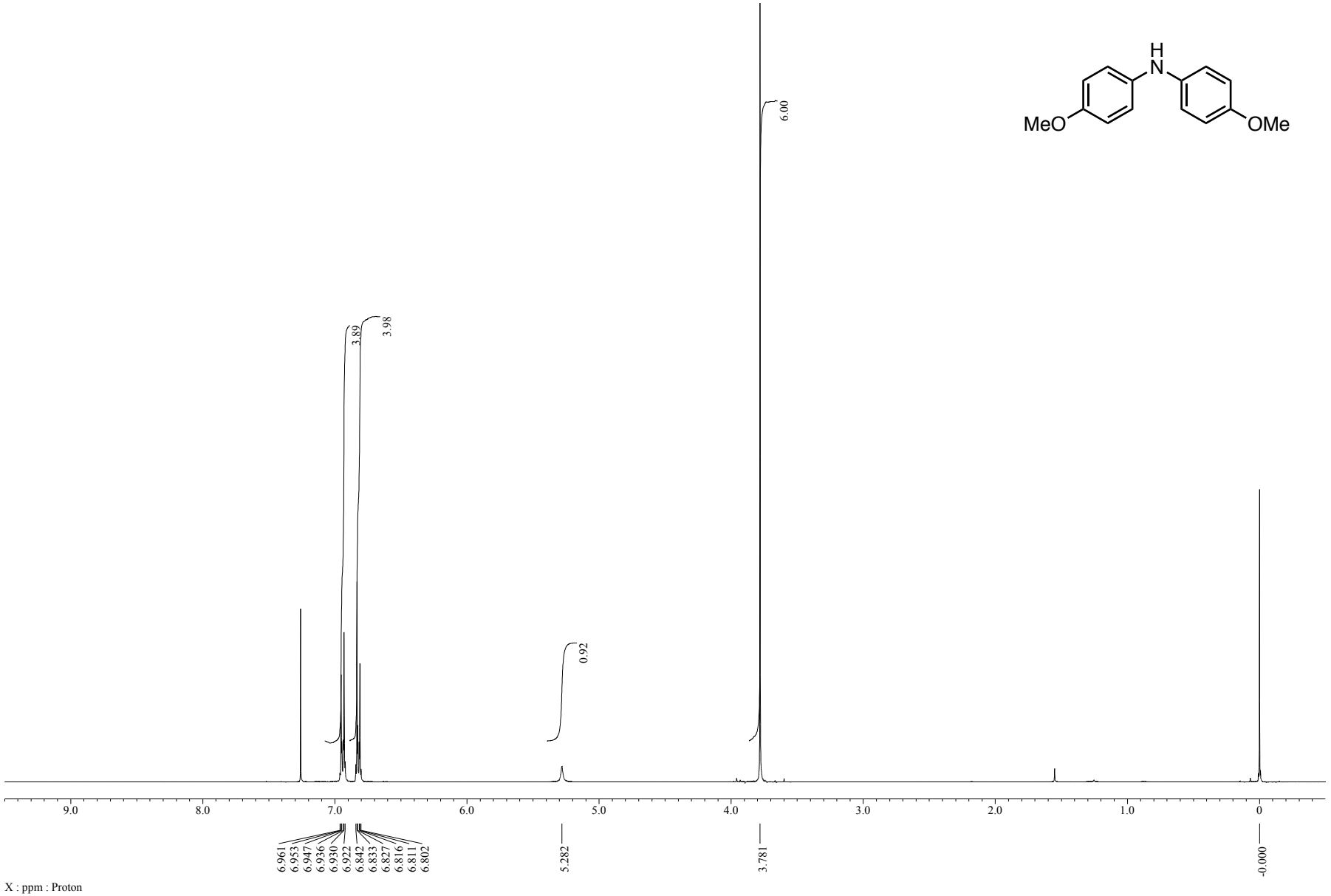
^{13}C NMR spectrum of **3y** in $CDCl_3$



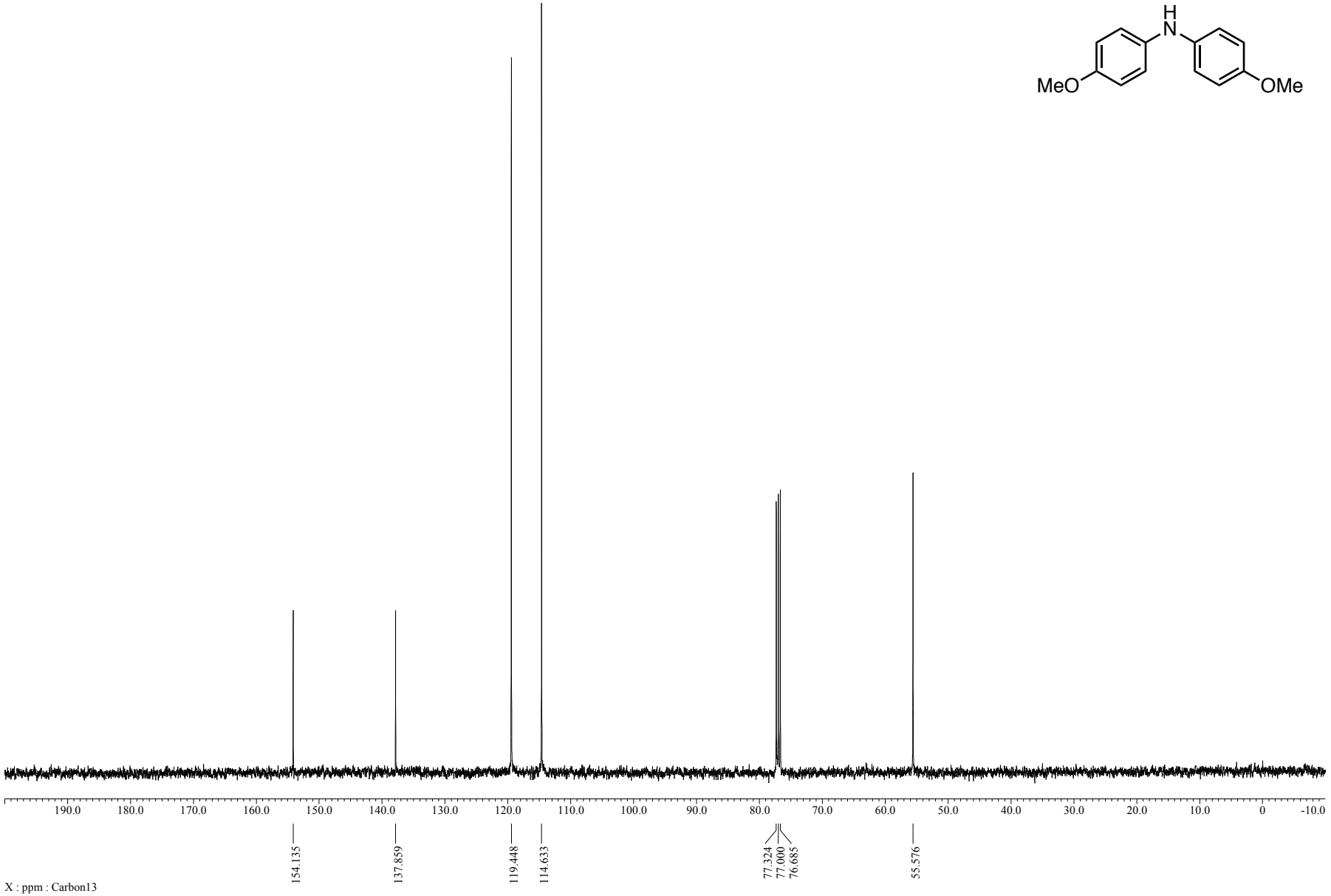
^{1}H NMR spectrum of **3z** in $CDCl_3$



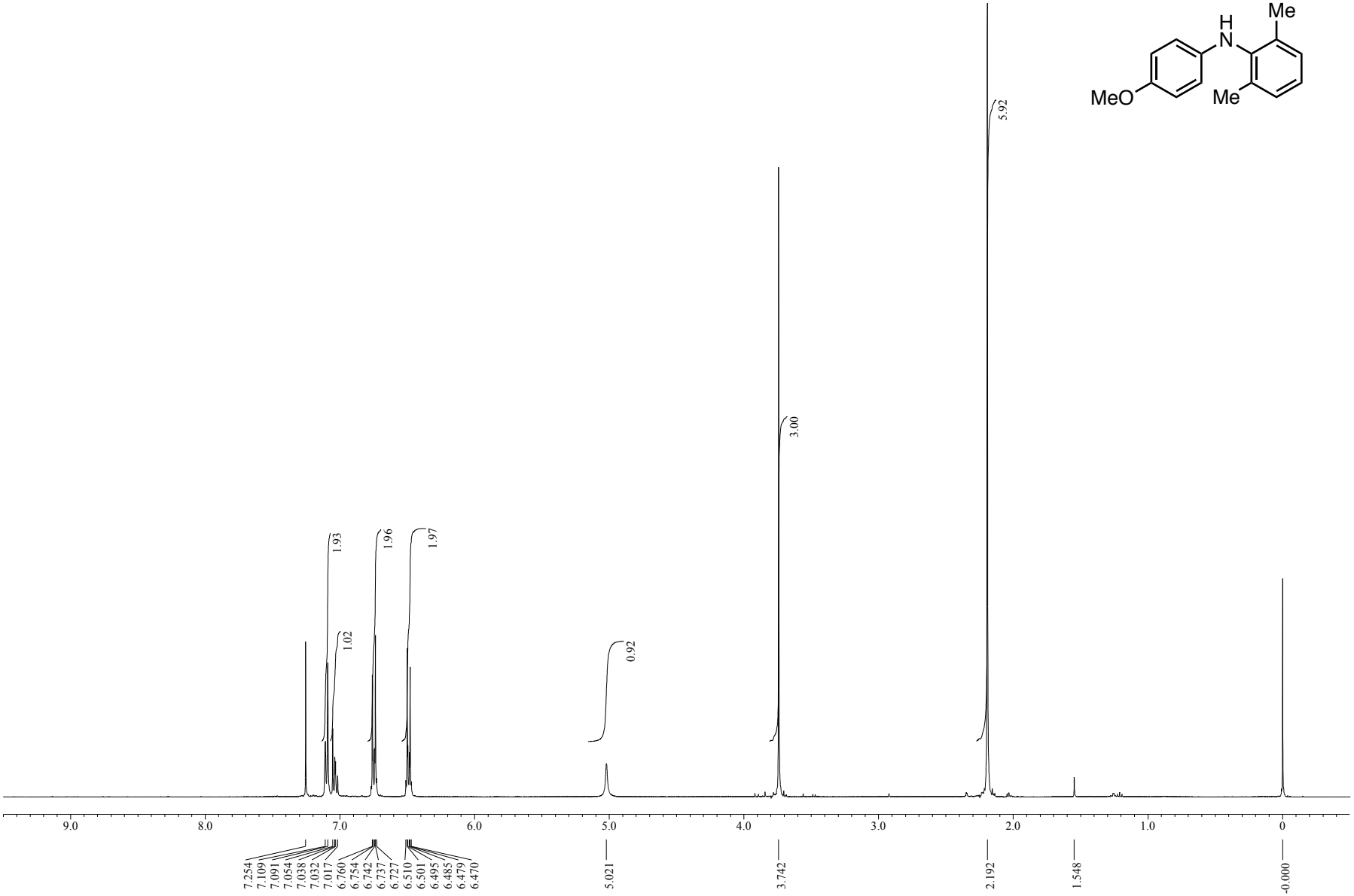
^{13}C NMR spectrum of **3z** in $CDCl_3$



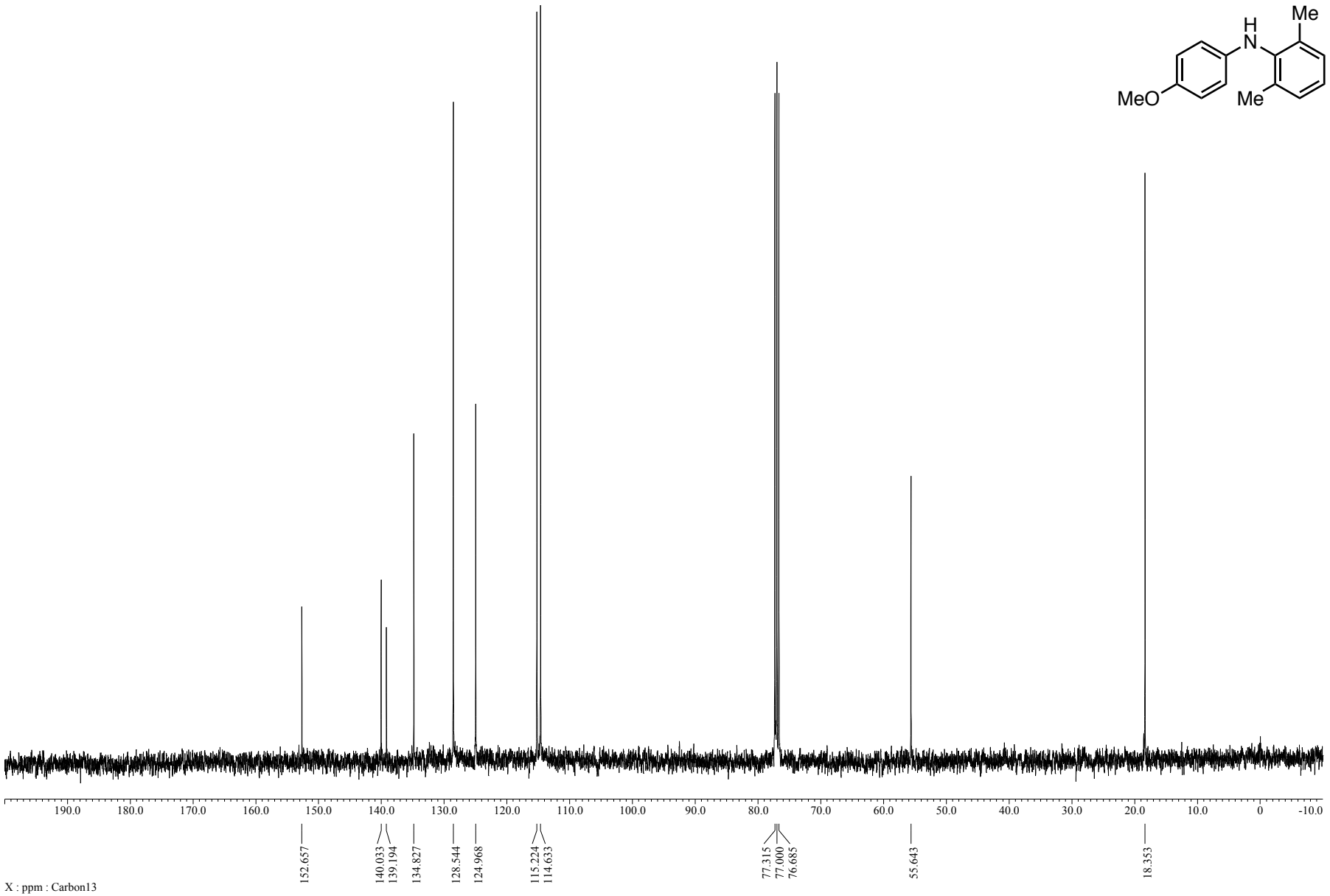
^{1}H NMR spectrum of **3aa** in $CDCl_3$



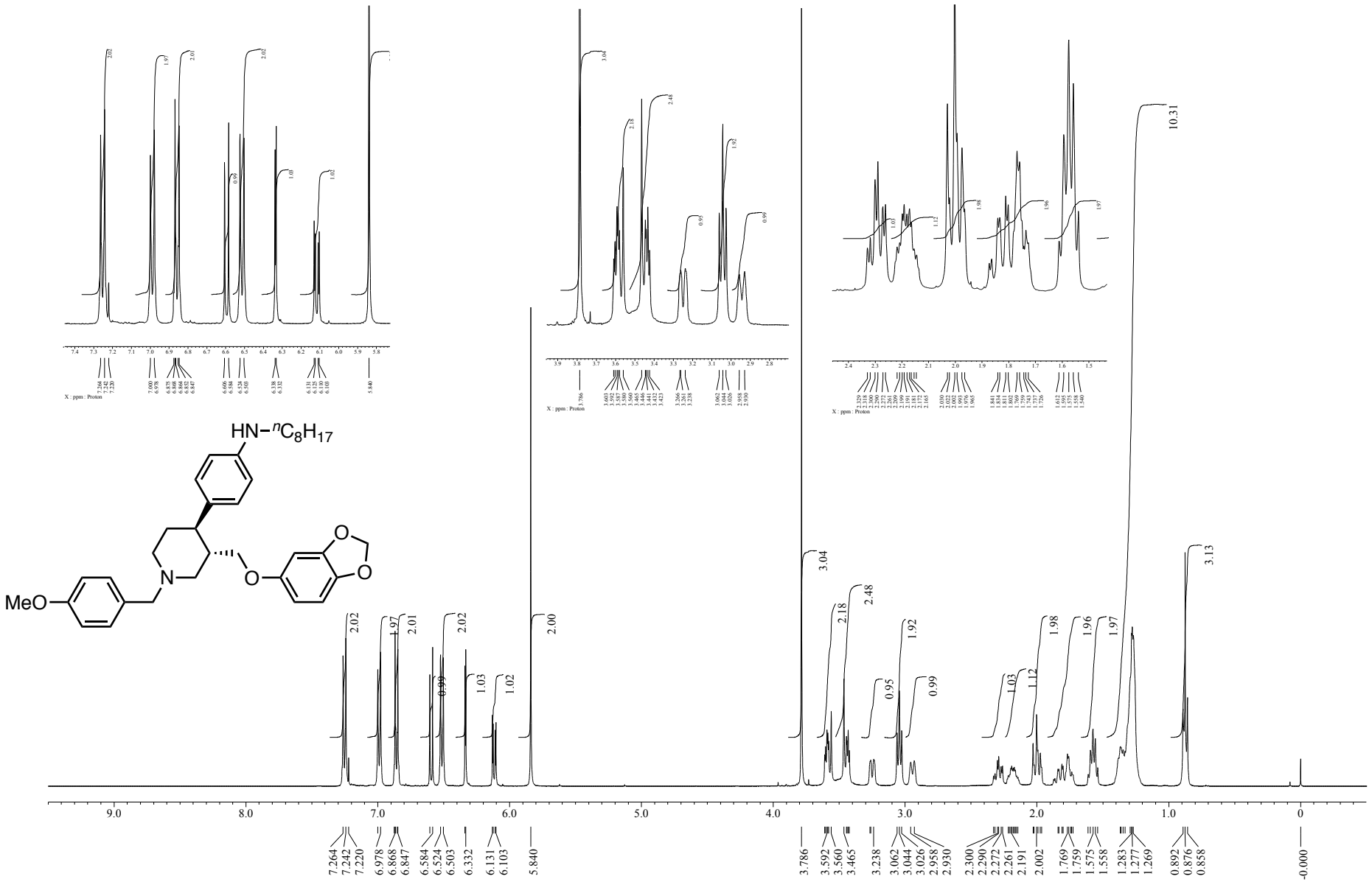
^{13}C NMR spectrum of **3aa** in $CDCl_3$



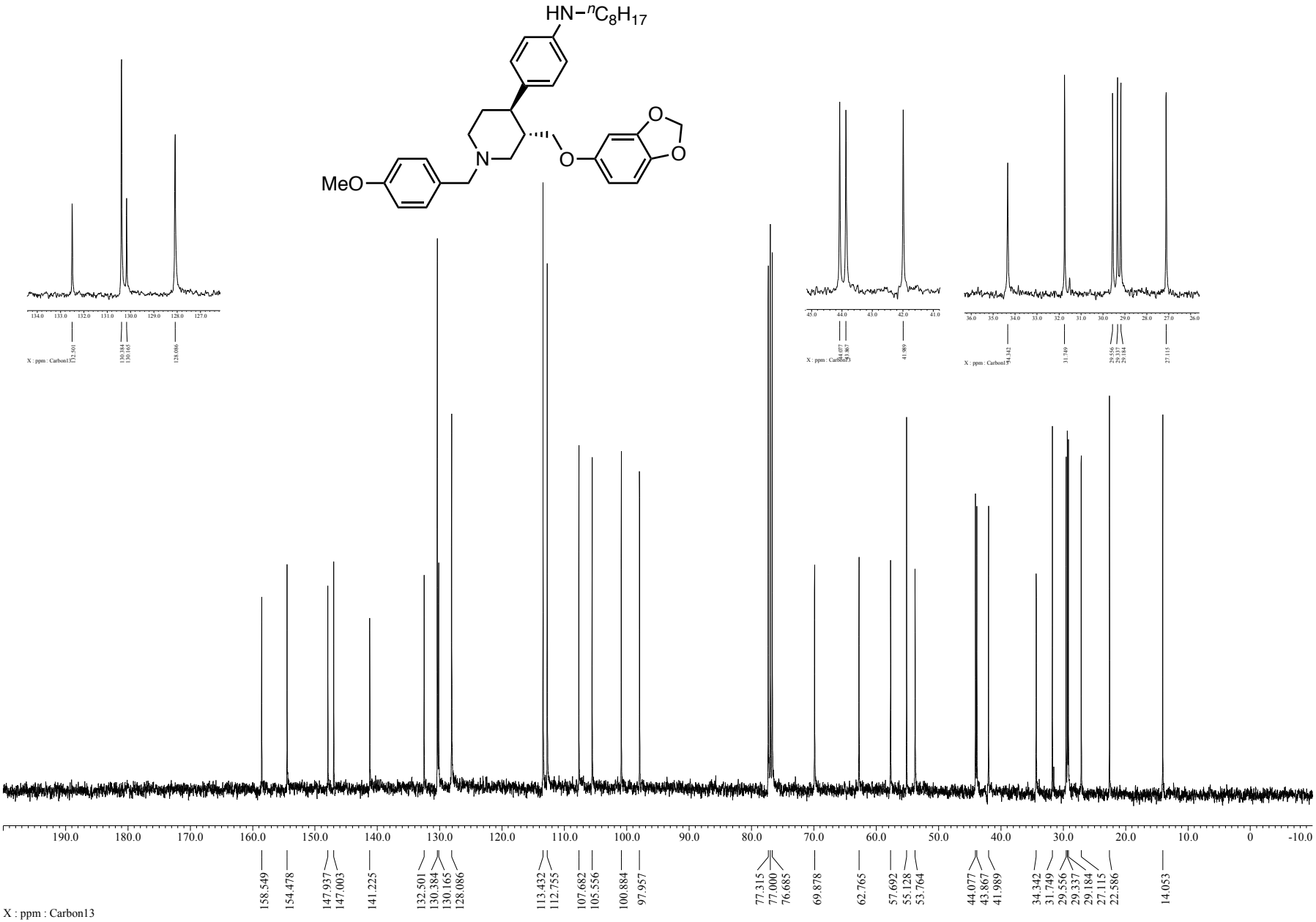
^{1}H NMR spectrum of **3ab** in $CDCl_3$



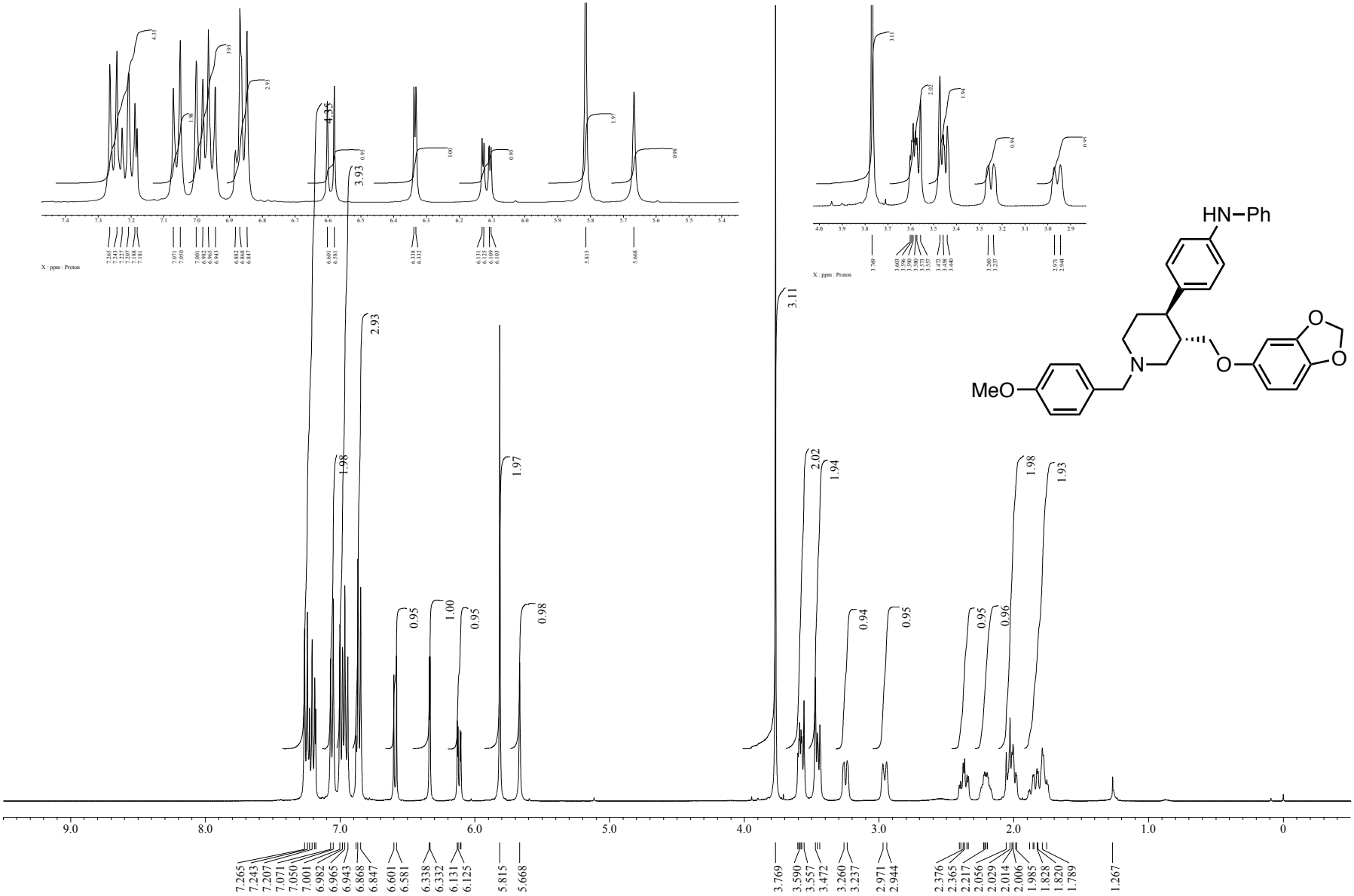
^{13}C NMR spectrum of **3ab** in $CDCl_3$



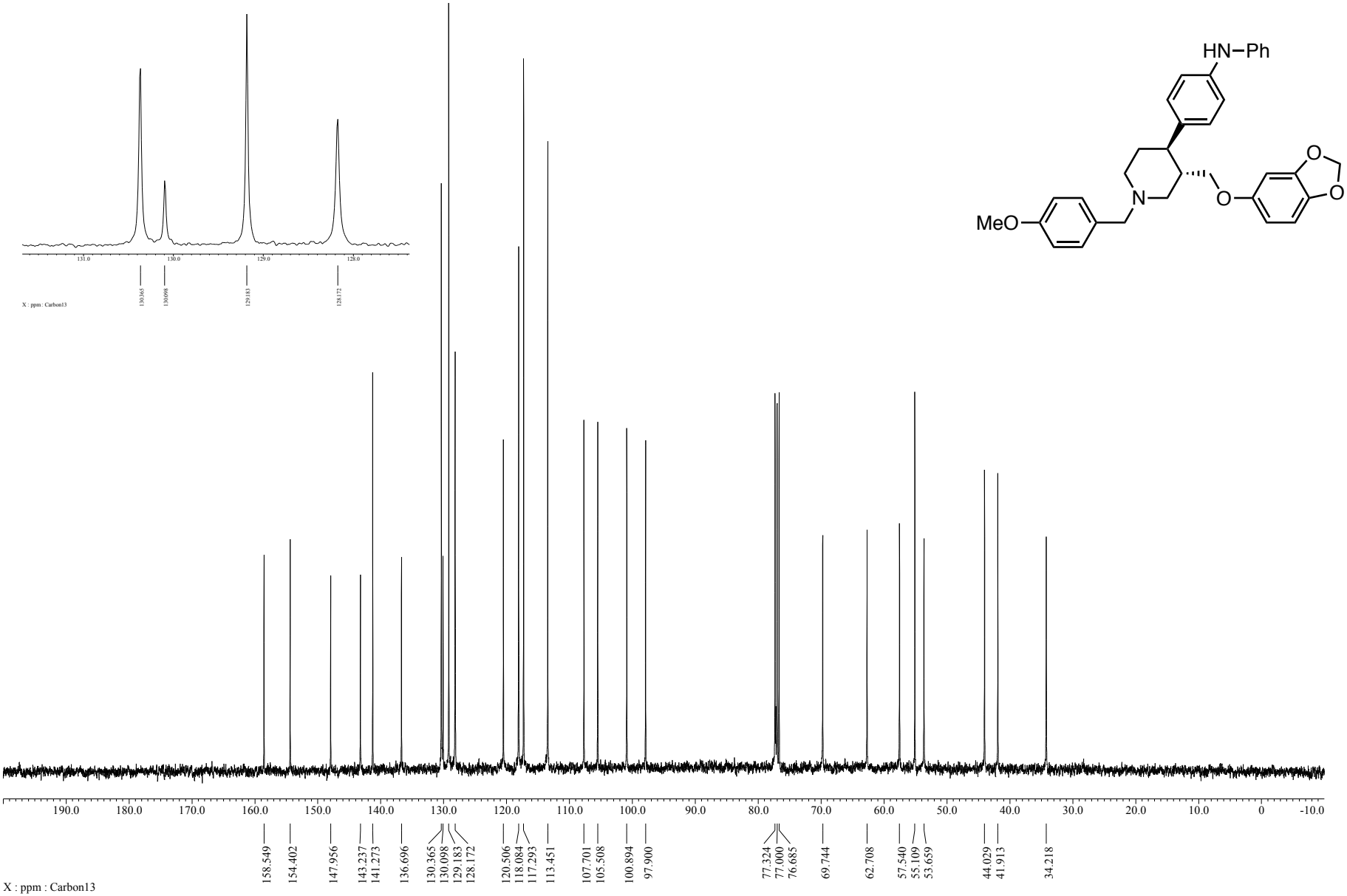
^{1}H NMR spectrum of **3ac** in $CDCl_3$



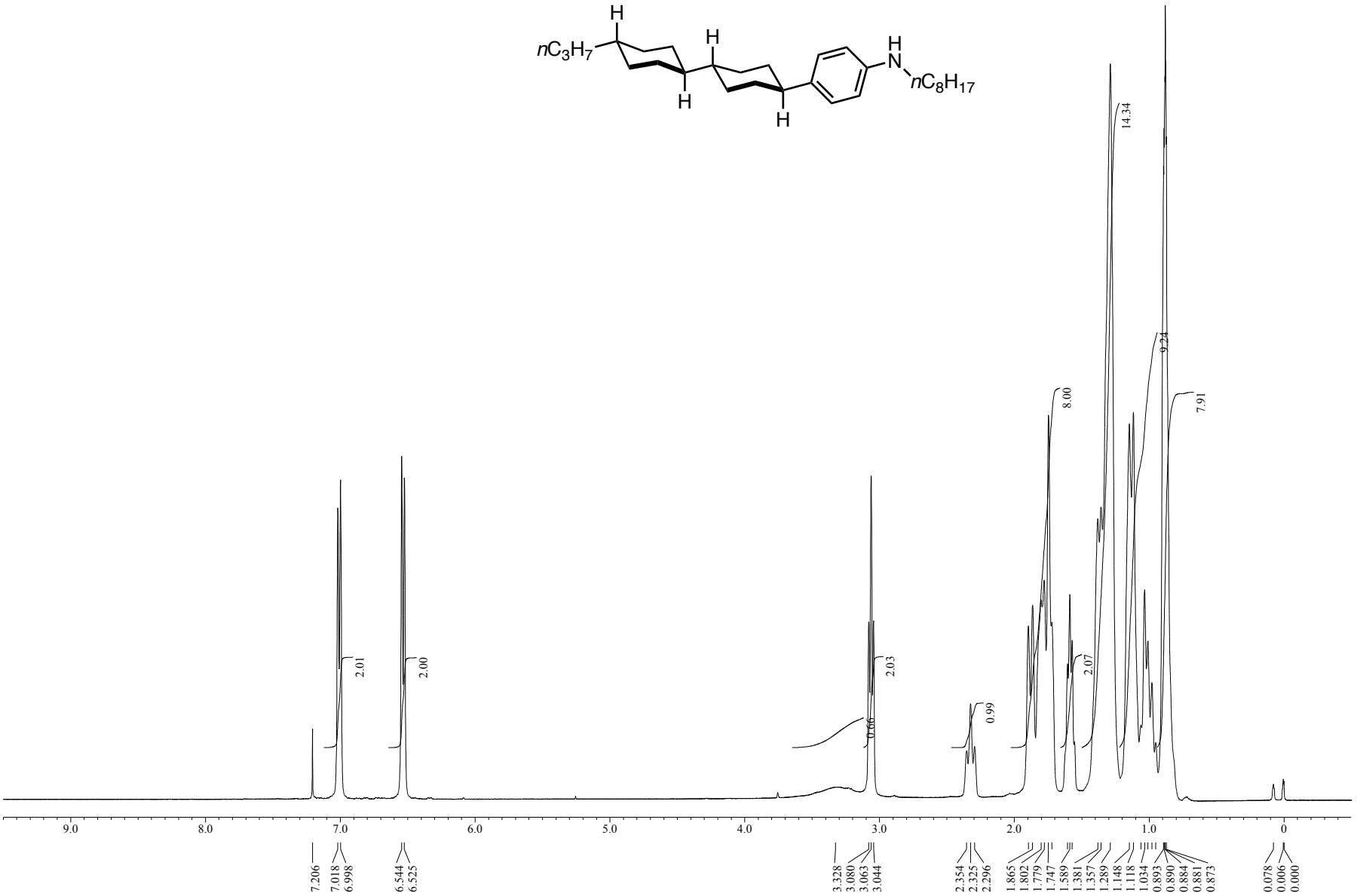
^{13}C NMR spectrum of **3ac** in $CDCl_3$



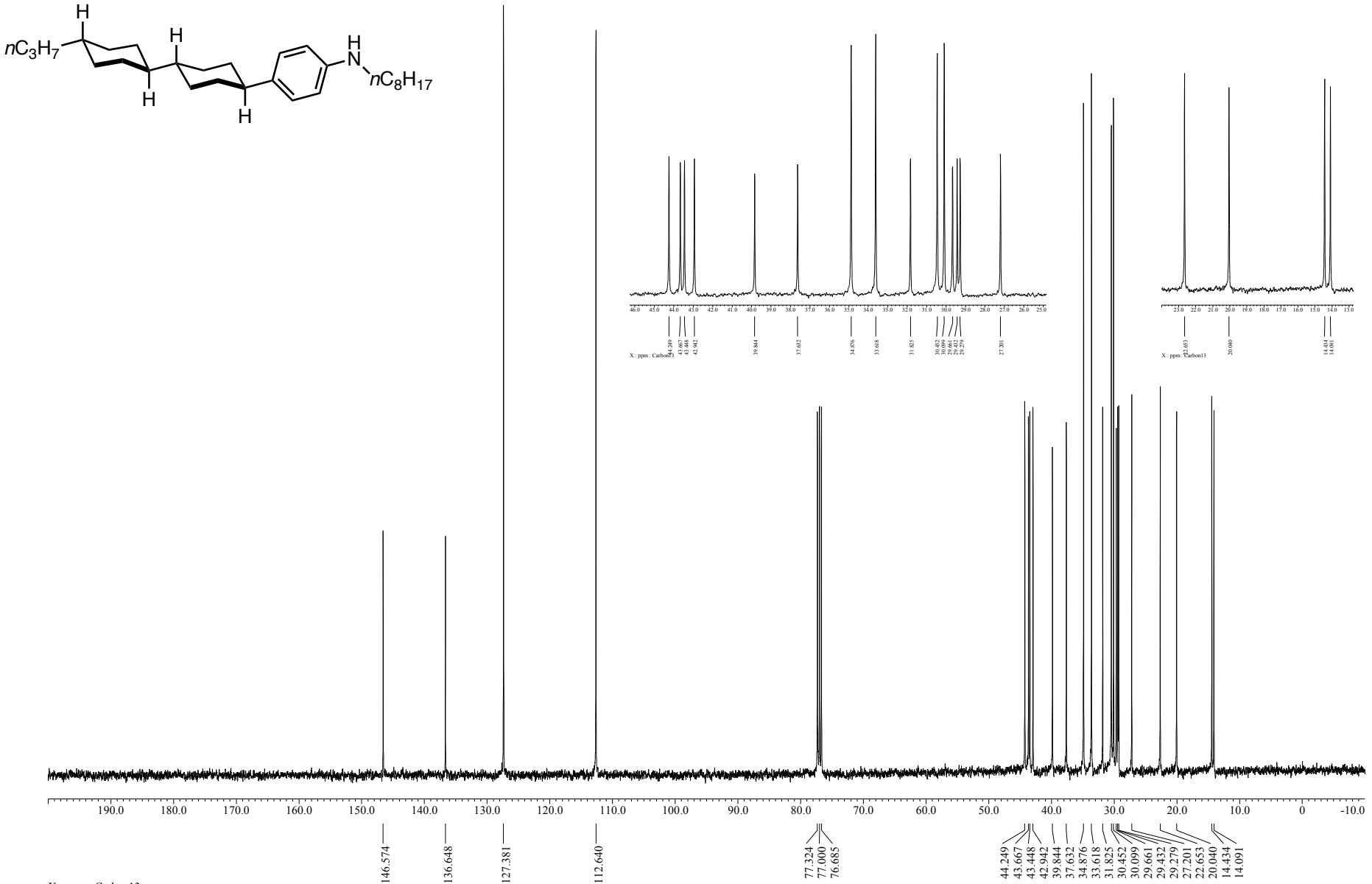
^{1}H NMR spectrum of **3ad** in $CDCl_3$



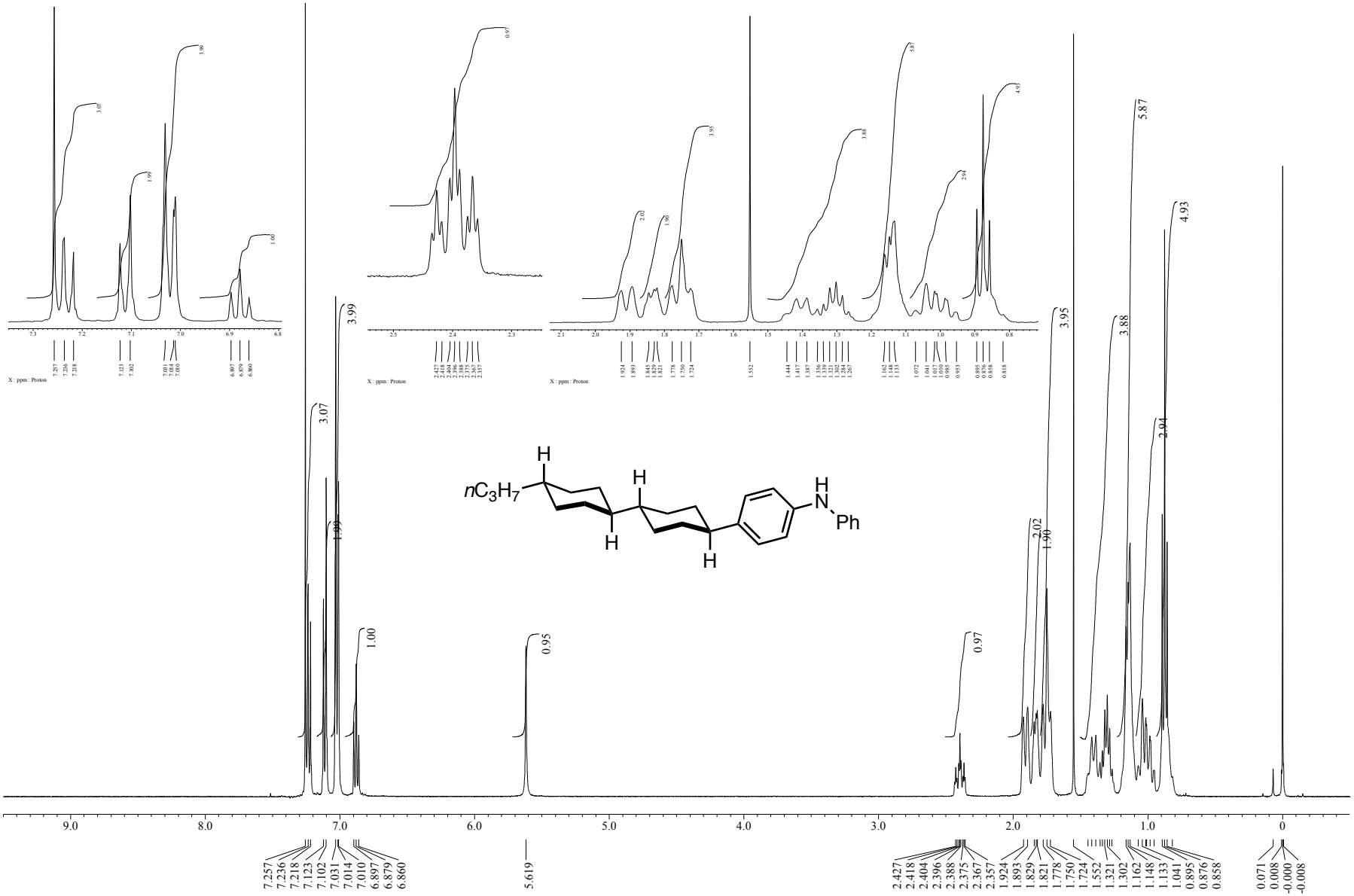
^{13}C NMR spectrum of **3ad** in $CDCl_3$



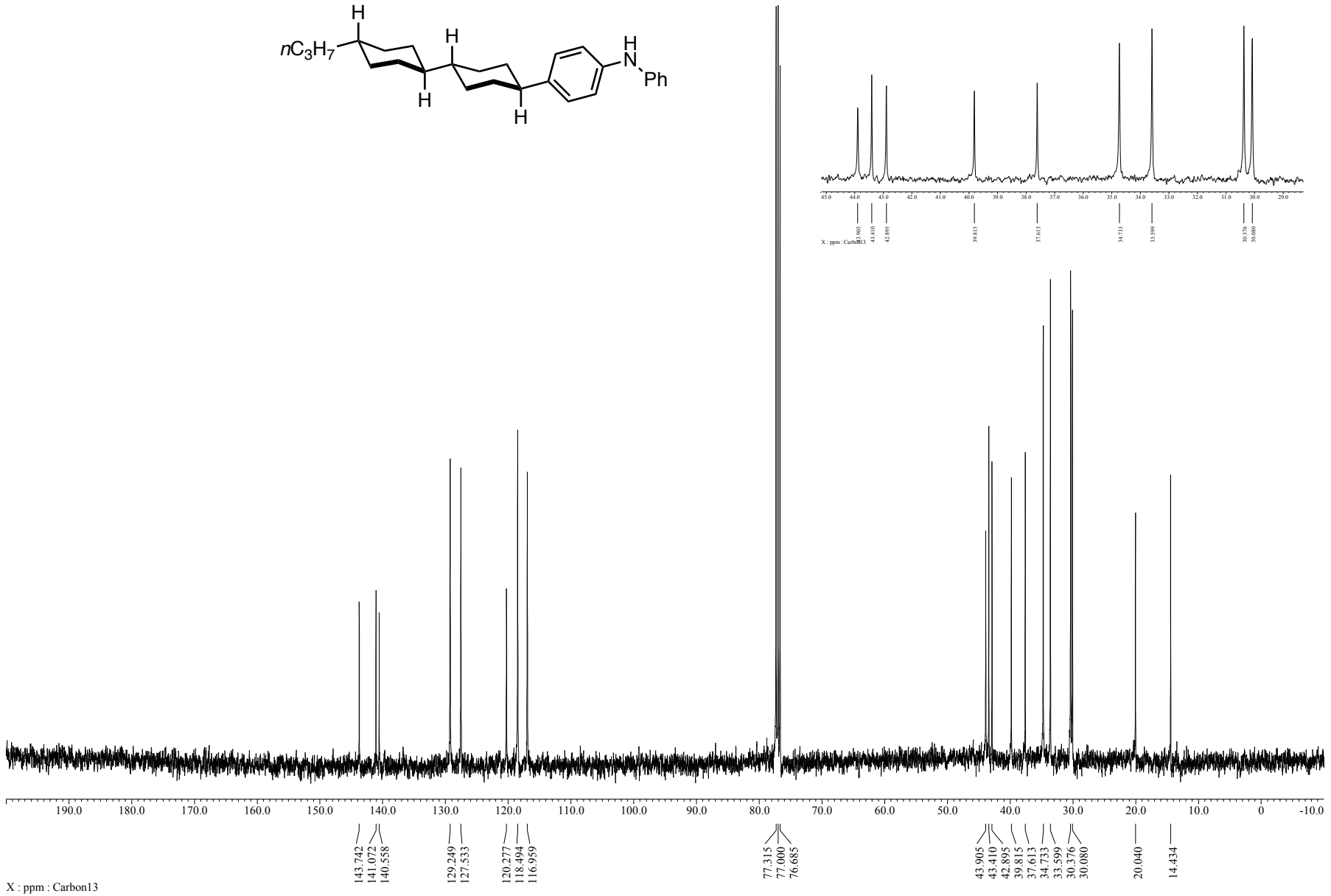
^{1}H NMR spectrum of **3ae** in $CDCl_3$



^{13}C NMR spectrum of **3ae** in $CDCl_3$



^{1}H NMR spectrum of **3af** in $CDCl_3$



^{13}C NMR spectrum of **3af** in $CDCl_3$