Supporting information

Cp*Co(III)-Catalyzed Direct Amination of Secondary Alcohols

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1. General: Unless otherwise mentioned, all reactions were carried out using Schlenk techniques. Toluene and THF were dried and deoxygenated by distillation over the drying agents (Na) under nitrogen. ^{1}H and ^{13}C NMR were recorded on JEOL spectrometers (400 and 500 MHz) using $CDCl_3$ as a solvent. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_C = 77 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminium sheets pre-coated with silica gel. Chromatography was conducted on silica gel (Merck, 100-200 mesh). The ESI-MS spectra were recorded on a Waters- Micromass Quattro Micro triplequadrupole mass spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories. The $Cp^*Co(CO)I_2$ catalyst[1] and the aminoalcohol[2] for the intramolecular cyclization were prepared according to the literature procedures. All other chemicals were used as received from the commercial sources.

2. General procedure A: Cobalt-catalyzed alkylation of amines

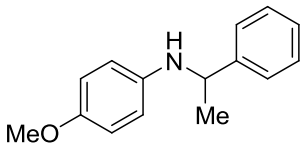
An oven-dried Schlenk tube was charged with $Cp^*Co(CO)I_2$ (14.3 mg, 0.03 mmol), PCy_3 (8.4 mg, 0.03 mmol), alcohol (0.6 mmol), amine (0.3 mmol) and 2 mL of toluene. The closed Schlenk tube containing the reaction mixture was stirred at 150 ^{o}C for 24 h, after which the mixture was cooled to room temperature. All the volatiles were removed under vacuum and purified by flash column chromatography to obtain pure compound.

3. General procedure B: Cobalt-catalyzed Intramolecular alkylation of amines

An oven-dried Schlenk tube was charged with $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol), PCy_3 (5.6 mg, 0.02 mmol), amino alcohol (0.2 mmol) and 2 mL of toluene. The closed Schlenk tube containing the reaction mixture was stirred at 150 ^{o}C for 24 h, after which the mixture was cooled to room temperature. All the volatiles were removed under vacuum and purified by flash column chromatography to obtain pure compound.

4. Analytical data of compounds

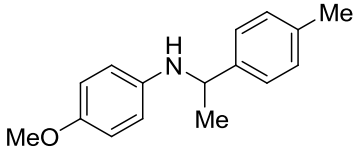
4-methoxy-*N*-(1-phenylethyl)aniline (3aa): Compound **3aa** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 81% (55.2 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[3]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.40 (m, 2H), 7.37-7.34 (m, 2H), 7.28-7.25 (m, 1H), 6.75-6.73 (m, 2H), 6.52-6.51 (m, 2H), 4.46 (q, J = 6.5 Hz, 1H), 3.73 (s, 3H), 1.54 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.8, 145.4, 141.5, 128.5, 126.7, 125.8, 114.7, 114.4, 55.6, 54.1, 25.0.

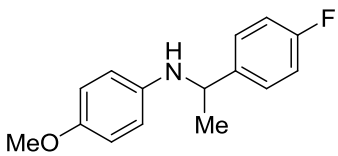
4-methoxy-*N*-(1-*p*-tolylethyl)aniline (3ba): Compound **3ba** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 92% (66.7 mg) yield as a colourless oil. The NMR data are in accordance with the literature.[3]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.26 (m, 2H), 7.15-7.13 (m, 2H), 6.72-6.70 (m, 2H), 6.51-6.49 (m, 2H), 4.41 (q, J = 6.6 Hz, 1H), 3.71 (s, 3H), 2.34 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.1, 142.3, 141.5, 136.3, 129.2, 125.7, 114.6, 114.5, 55.6, 53.9, 25.0, 21.0.

***N*-(1-(4-fluorophenyl)ethyl)-4-methoxyaniline (3ca):** Compound **3ca** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 53% (39.2 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[3]



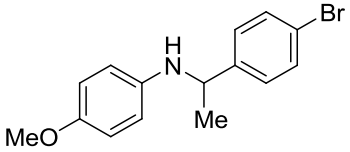
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.32 (m, 2H), 7.03-6.99 (m, 2H), 6.73-6.70 (m, 2H), 6.48-6.46 (m, 2H), 4.41 (q, J = 6.7 Hz, 1H), 3.71 (s, 3H), 1.49 (d, J = 6.7

Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8, 160.4, 151.9, 141.2, 141.0 (d, ^4J = 3 Hz), 127.3 (d, ^3J = 8 Hz), 115.3 (d, ^1J = 22 Hz), 114.6 (d, ^2J = 16 Hz), 55.6, 53.6, 25.1.

^{19}F NMR ($CDCl_3$, 373 MHz): δ (-116.2).

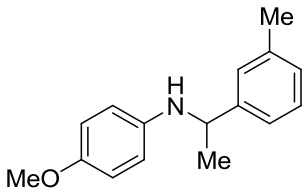
***N*-(1-(4-bromophenyl)ethyl)-4-methoxyaniline (3da):** Compound **3da** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 3:97) and the product was recovered in 61% (56.1 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[3]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 2H), 7.27-7.25 (m, 2H), 6.73-6.70 (m, 2H), 6.47-6.44 (m, 2H), 4.38 (q, J = 6.7 Hz, 1H), 3.71 (s, 3H), 1.48 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.0, 144.5, 141.1, 131.6, 127.6, 120.3, 114.7, 114.5, 55.6, 53.7, 25.0.

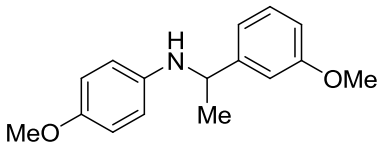
4-methoxy-*N*-(1-*m*-tolylethyl)aniline (3ea): Compound **3ea** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 70% (50.6 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[4]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.18 (m, 3H), 7.08-7.06 (m, 1H), 6.74-6.72 (m, 2H), 6.53-6.50 (m, 2H), 4.43 (q, J = 6.5 Hz, 1H), 3.72 (s, 3H), 2.37 (s, 3H), 1.52 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 145.4, 141.5, 138.1, 128.4, 127.5, 126.5, 122.8, 114.6, 114.4, 55.6, 54.2, 25.0, 21.4.

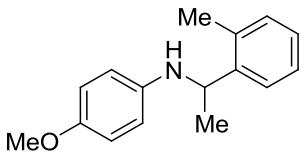
4-methoxy-*N*-(1-(3-methoxyphenyl)ethyl)aniline (3fa): Compound **3fa** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 79% (60.9 mg) yield as a colourless oil. The NMR data are in accordance with the literature.[5]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.22 (m, 1H), 6.97-6.93 (m, 2H), 6.78-6.75 (m, 1H), 6.71-6.69 (m, 2H), 6.49-6.47 (m, 2H), 4.41 (q, J = 6.7 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.8, 151.8, 147.3, 141.4, 129.5, 118.2, 114.6, 114.4, 111.8, 111.6, 55.6, 55.1, 54.2, 25.0.

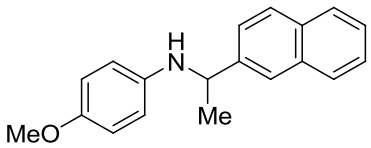
4-methoxy-*N*-(1-*o*-tolylethyl)aniline (3ga): Compound **3ga** was prepared according to the general procedure **A**. The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 1:99) and the product was recovered in 44% (31.8 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[4]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.43 (m, 1H), 7.18-7.13 (m, 3H), 6.71-6.69 (m, 2H), 6.44-6.41 (m, 2H), 4.62 (q, J = 6.6 Hz, 1H), 3.70 (s, 3H), 2.43 (s, 3H), 1.47 (d, J = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 142.9, 141.5, 134.5, 130.5, 126.55, 126.53, 124.6, 114.7, 114.1, 55.7, 50.4, 23.0, 18.9.

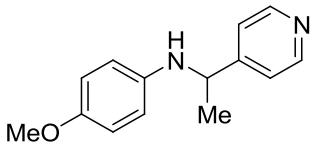
4-methoxy-*N*-(1-(naphthalene-2-yl)ethyl)aniline (3ha): Compound **3ha** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 20:80) and the product was recovered in 40% (33.4 mg) yield as a yellow solid. The NMR data are in accordance with the literature.[3]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.81 (m, 4H), 7.53-7.45 (m, 3H), 6.71-6.69 (m, 2H), 6.55-6.53 (m, 2H), 4.59 (q, J = 6.6 Hz, 1H), 3.69 (s, 3H), 1.59 (d, J = 7.0 Hz, 3H),

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.9, 142.9, 141.5, 133.5, 132.6, 128.3, 127.7, 127.6, 125.9, 125.4, 124.4, 124.2, 114.7, 114.6, 55.6, 54.4, 25.0.

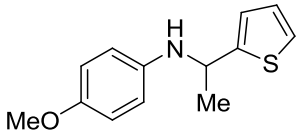
4-methoxy-*N*-(1-(pyridyin-4-yl)ethyl)aniline (3ia): Compound **3ia** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 5:95) and the product was recovered in 74% (50.6 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[6]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (brs, 2H), 7.30-7.29 (m, 2H), 6.69-6.67 (m, 2H), 6.41-6.39 (m, 2H), 4.36 (q, J = 6.7 Hz, 1H), 3.68 (s, 3H), 1.47 (d, J = 6.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.8, 152.0, 149.8, 140.7, 121.2, 114.6, 114.3, 55.5, 53.3, 24.4.

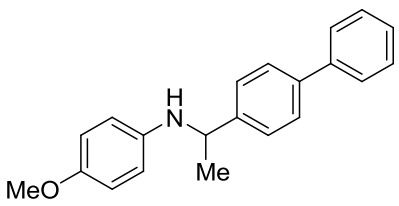
4-methoxy-*N*-(1-(thiophen-2-yl)ethyl)aniline (3ja): Compound **3ja** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 4:96) and the product was recovered in 50% (35.1 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[3]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17-7.16 (m, 1H), 6.97-6.93 (m, 2H), 6.76-6.74 (m, 2H), 6.61-6.59 (m, 2H), 4.75 (q, J = 6.5 Hz, 1H), 3.73 (s, 3H), 1.61 (d, J = 6.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.3, 150.4, 140.9, 126.6, 123.5, 122.9, 115.1, 114.7, 55.6, 50.5, 24.6.

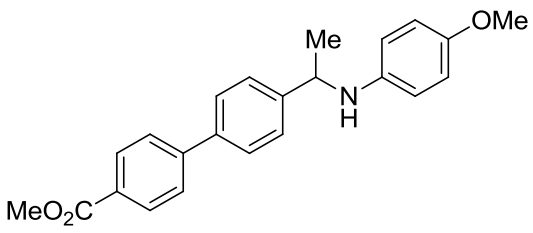
***N*-(1-biphenyl-4-yl)ethyl-4-methoxyaniline (3ka):** Compound **3ka** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 28% (25.4 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[7]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.53 (m, 4H), 7.44-7.40 (m, 4H), 7.34-7.30 (m, 1H), 6.72-6.70 (m, 2H), 6.52-6.49 (m, 2H), 4.46 (q, J = 6.6 Hz, 1H), 3.70 (s, 3H), 1.54 (d, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.9, 144.5, 141.5, 140.9, 139.7, 128.6, 127.3, 127.0, 127.0, 126.3, 114.7, 114.5, 55.7, 53.9, 25.0.

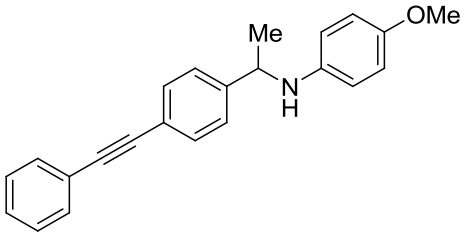
Methyl-4'-(1-(4-methoxyphenylamino)ethyl)biphenyl-4-carboxylate (3la): Compound **3la** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 40 % (43.3 mg) yield as yellow oil. HRMS (ESI) calculated for $C_{23}H_{24}NO_3$ is 362.1756; found 362.1755.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07-8.10 (m, 2H), 7.63-7.65 (m, 2H), 7.48-7.51 (m, 2H), 7.45-7.49 (m, 2H), 6.69-6.72 (m, 2H), 6.48-6.51 (m, 2H), 4.47 (q, J = 6.5 Hz, 1H), 3.93 (s, 3H), 3.69 (S, 3H), 1.54 (d, J = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 151.9, 145.6, 145.3, 141.3, 138.4, 130.0, 128.6, 127.4, 126.8, 126.4, 114.7, 114.5, 55.6, 53.9, 52.0, 25.1.

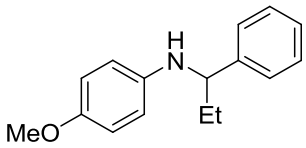
4-methoxy-*N*-(1-(4-(phenylethynyl)phenyl)ethyl)aniline (3ma): Compound **3ma** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 50% (49.1 mg) yield as a brown oil. HRMS (ESI) calculated for $C_{23}H_{22}NO$ is 328.1701; found 328.1704.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.53 (m, 4H), 7.32-7.36 (m, 5H), 6.68-6.70 (m, 2H), 6.44-6.46 (m, 2H), 4.42 (q, J = 6.9 Hz, 1H), 3.70 (s, 3H), 1.50 (d, J = 6.6 Hz, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.2, 146.2, 141.5, 132.2, 131.8, 128.6, 128.4, 126.2, 123.6, 121.9, 115.0, 114.8, 89.6, 89.3, 56.0, 54.4, 25.3.

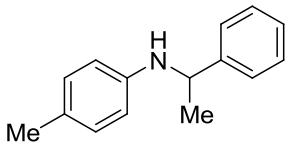
4-methoxy-*N*-(1-phenylpropyl)aniline (3na): Compound **3na** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 1:99) and the product was recovered in 53% (38.4 mg) yield as a colourless oil. The NMR data are in accordance with the literature.[7]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.30 (m, 4H), 7.25-7.21 (m, 2H), 6.71-6.69 (m, 2H), 6.50-6.48 (m, 2H), 4.17 (t, J = 6.4 Hz, 1H), 3.70 (s, 3H), 1.89-1.78 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 144.0, 141.7, 128.4, 126.7, 126.5, 114.7, 114.4, 60.5, 55.6, 31.6, 10.7.

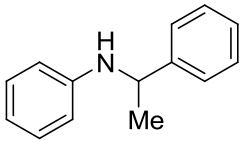
4-methyl-*N*-(1-phenylethyl)aniline (3ab): Compound **3ab** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 3:97) and the product was recovered in 87% (55.1 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[10]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.38 (m, 2H), 7.35-7.31 (m, 2H), 7.25-7.22 (m, 1H), 6.93-6.91 (m, 2H), 6.47-6.45 (m, 2H), 4.49 (q, J = 6.5 Hz, 1H), 2.21 (s, 3H), 1.52 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.3, 144.9, 129.5, 128.5, 126.7, 126.4, 125.8, 113.4, 53.7, 24.9, 20.3.

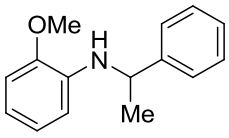
***N*-(1-phenylethyl)aniline (3ac):** Compound **3ac** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 3:97) and the product was recovered in 697% (40.7 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[10]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-73 (m, 2H), 7.41-7.37 (m, 2H), 7.31-7.28 (m, 1H), 7.19-7.15 (m, 2H), 6.74-6.71 (m, 1H), 6.60-6.58 (m, 2H), 4.56 (q, J = 7.1 Hz, 1H), 4.04 (s, 1H), 1.59 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.1, 145.1, 129.0, 128.5, 126.7, 125.7, 117.1, 113.2, 53.3, 24.9.

2-methoxy-*N*-(1-phenylethyl)aniline (3ad): Compound **3ad** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 3:97) and the product was recovered in 53% (36.1 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[3]

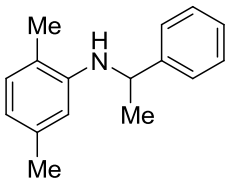


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.40 (m, 2H), 7.37-7.33 (m, 2H), 7.27-7.23 (m, 1H),

6.81-6.79 (m, 1H), 6.76-6.72 (m, 1H), 6.62-6.67 (m, 1H), 6.39-6.38 (m, 1H), 4.67 (brs, 1H), 4.51 (q, *J* = 7.0 Hz, 1H), 3.92 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.0, 145.0, 136.8, 128.2, 126.4, 125.4, 120.7, 115.9, 110.6, 108.8, 55.0, 52.9, 24.8.

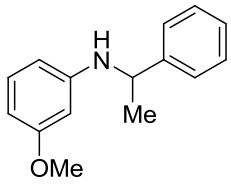
2,5-dimethyl-*N*-(1-phenylethyl)aniline (3ae): Compound **3ae** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 3:97) and the product was recovered in 63% (42.6 mg) yield as a yellow oil. HRMS (ESI) calculated for $C_{16}H_{20}NO$ is 226.1596; found 226.1594.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.19 (m, 6H), 7.01 (brs, 1H), 6.85 (brs, 1H), 4.09 (q, *J* = 7.05 Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.8, 139.7, 129.2, 129.2, 128.6, 127.4, 127.0, 126.2, 125.6, 122.6, 40.3, 22.1, 20.7, 17.6.

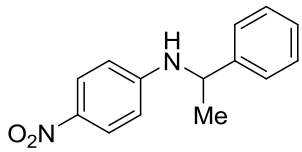
3-methoxy-*N*-(1-phenylethyl)aniline (3af): Compound **3af** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 2:98) and the product was recovered in 70% (47.7 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[10]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.39 (m, 2H), 7.36-7.31 (m, 2H), 7.27-7.23 (m, 2H), 7.03-6.99 (m, 1H), 6.52-6.50 (m, 1H), 6.40 (brs, 1H), 6.35-6.33 (m, 1H), 4.50 (q, *J* = 6.6 Hz, 1H), 2.24 (s, 3H), 1.53 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.3, 145.3, 138.9, 129.1, 128.7, 126.9, 125.9, 118.3, 114.3, 110.4, 53.5, 25.0, 21.7.

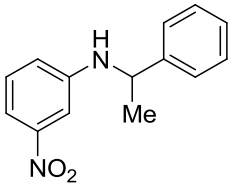
4-nitro-*N*-(1-phenylethyl)aniline (3ag): Compound **3ag** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 6:94) and the product was recovered in 83% (60.3 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[11]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 9.17 Hz, 2H), 7.36-7.28 (m, 5H), 6.46 (d, *J* = 9.1 Hz, 2H), 4.93 (brs, 1H), 4.60-4.57 (m, 1H), 1.58 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.2, 143.2, 137.9, 128.9, 127.4, 126.1, 125.5, 111.7, 53.2, 24.5.

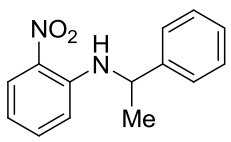
3-nitro-*N*-(1-phenylethyl)aniline (3ah): Compound **3ah** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 4:96) and the product was recovered in 78% (56.6 mg) yield as a yellow oil. The NMR data is in accordance with the literature.[12]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.45 (m, 1H), 7.38-7.33 (m, 5H), 7.28-7.25 (m, 1H), 7.20-7.17 (m, 1H), 6.78-6.76 (m, 1H), 4.57-4.53 (m, 1H), 4.46 (brs, 1H), 1.58 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 147.8, 143.7, 129.5, 128.8, 127.3, 125.7, 118.8, 111.8, 107.2, 53.4, 24.6.

2-nitro-*N*-(1-phenylethyl)aniline (3ai): Compound **3ai** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 5:95) and the product was recovered in 75% (54.6 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[13]

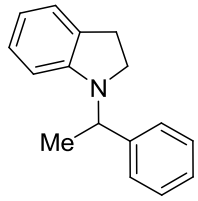


^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (brs, 1H), 8.18-8.15 (m, 1H), 7.34-7.33 (m, 3H), 7.28-

7.23 (m, 2H), 6.64-6.58 (m, 2H), 4.69 (p, J = 6.7 Hz, 1H), 1.65 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 143.5, 135.9, 132.1, 128.9, 127.3, 126.7, 125.5, 115.5, 115.1, 53.1, 25.0.

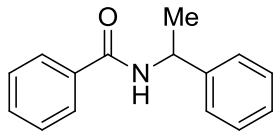
1-(1-phenylethyl)indoline (3aj): Compound **3aj** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 1:99) and the product was recovered in 49% (32.8 mg) yield as a yellow oil. The NMR data are in accordance with the literature.[14]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.11-7.01 (m, 2H), 6.67-6.63 (m, 1H), 6.41-6.39 (m, 1H), 4.76 (q, *J* = 6.8 Hz, 1H), 3.47-3.33 (m, 2H), 3.01-2.96 (m, 2H), 1.58 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.3, 142.8, 130.0, 128.3, 127.1, 127.0, 126.8, 124.3, 116.9, 107.1, 54.4, 47.8, 28.1, 16.4.

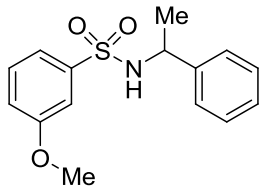
N-(1-phenylethyl)benzamide (3ak): Compound **3ak** was prepared according to the general procedure **A** and the reaction mixture was purified by flash column chromatography (EtOAc : hexane = 15:85) and the product was recovered in 45% (30.4 mg) yield as a yellow solid. The NMR data are in accordance with the literature.[15]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.76 (m, 2H), 7.50-7.46 (m, 1H), 7.43-7.33 (m, 6H), 7.29-7.27 (m, 1H), 6.40 (brs, 1H), 5.35 (p, *J* = 7.1 Hz, 1H), 1.61-1.59 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 143.0, 134.5, 131.4, 128.7, 128.5, 127.4, 126.8, 126.2, 49.1, 21.6.

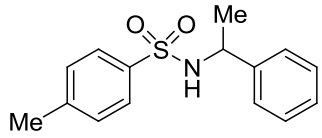
3-methoxy-*N*-(1-phenylehtyl)benzenesulfonamide (3al): Compound **3al** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 15:85) and the product was recovered in 62% (54.2 mg) yield as a pale yellow solid. HRMS (ESI) calculated for $C_{15}H_{18}NO_3S$ is 292.1007 and found 292.1005.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.33 (m, 1H), 7.29-7.27 (m, 1H), 7.20-7.16 (m, 4H), 7.10-7.07 (m, 2H), 7.00-6.98 (m, 1H), 5.25 (brs, 1H), 4.52-4.45 (m, 1H), 3.73 (s, 3H), 1.43 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 141.8, 141.6, 129.8, 128.4, 127.4, 126.0, 119.1, 119.0, 111.4, 55.4, 53.7, 23.6.

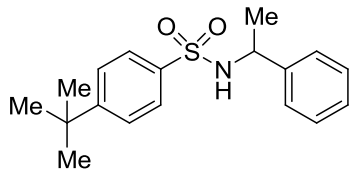
4-methyl-*N*-(1-phenylehtyl)benzenesulfonamide (3am): Compound **3am** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 10:90) and the product was recovered in 60% (49.6 mg) yield as a brown solid. The NMR data are in accordance with the literature.[16]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.61 (m, 2H), 7.18-7.15 (m, 5H), 7.11-7.09 (m, 2H), 5.24 (d, *J* = 6.5 Hz, 1H), 4.45 (p, *J* = 6.5 Hz, 1H), 2.37 (s, 3H), 1.41 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.0, 142.0, 137.5, 129.3, 128.4, 127.3, 127.0, 126.0, 53.5, 23.5, 21.4.

4-tertbutyl-*N*-(1-phenylehtyl)benzenesulfonamide (3an): Compound **3an** was prepared according to the general procedure **A.** The reaction mixture was purified by flash column chromatography (EtOAc : hexane = 12:88) and the product was recovered in 65% (61.8 mg) yield as a yellow solid. HRMS (ESI) calculated for $C_{18}H_{24}NO_2S$ is 318.1528, found 318.1527.

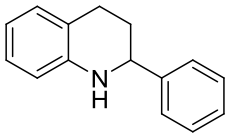


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.60 (m, 2H), 7.34-7.32 (m, 2H), 7.13-7.11

(m, 3H), 7.06-7.04 (m, 2H), 5.42 (brs, 1H), 4.51-4.44 (m, 1H), 1.42 (d, J = 6.7 Hz, 3H), 1.30 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.8, 141.9, 137.3, 128.3, 127.2, 126.8, 126.0, 125.6, 53.6, 34.9, 31.0, 23.6.

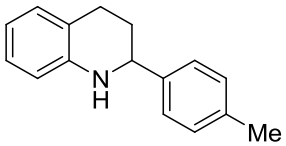
2-phenyl-1,2,3,4-tetrahydroquinoline (5a): Compound **5a** was prepared according to the general procedure **B.** The reaction mixture was purified by flash column chromatography (Et_2O : hexane = 1:99) and the product was recovered in 94% (39.2 mg) yield as a colourless oil. The NMR data are in accordance with the literature.[8]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.40 (m, 4H), 7.36-7.28 (m, 1H), 7.05-7.01 (m, 2H), 6.69-6.65 (m, 1H), 6.56-6.54 (m, 1H), 4.46 (dd, J = 5.9, 3.3 Hz, 1H), 4.04 (brs, 1H), 2.98-2.90 (m, 1H), 2.78-2.72 (m, 1H), 2.17-2.11 (m, 1H), 2.06-1.96 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 137.6, 129.2, 128.5, 127.3, 126.8, 126.4, 120.8, 117.1, 113.9, 56.2, 30.9, 26.3.

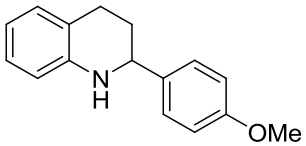
2-p-tolyl-1,2,3,4,-tetrahydroquinoline (5b): Compound **5b** was prepared according to the general procedure **B.** The reaction mixture was purified by flash column chromatography (Et_2O : hexane = 2:98) and the product was recovered in 93% (41.5 mg) yield as colourless oil. The NMR data are in accordance with the literature.[8]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.31 (m, 2H), 7.21-7.19 (m, 2H), 7.06-7.02 (m, 2H), 6.70-6.66 (m, 1H), 6.57-6.55 (m, 1H), 4.44 (dd, J = 6.1, 3.2 Hz, 1H), 4.02 (s, 1H), 3.00-2.92 (m, 1H), 2.81-2.74 (m, 1H), 2.39 (s, 3H), 2.17-2.10 (m, 1H), 2.06-1.97 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 141.7, 137.0, 129.1, 126.8, 126.8, 126.4, 120.8, 117.0, 113.8, 55.9, 30.9, 26.4, 21.0.

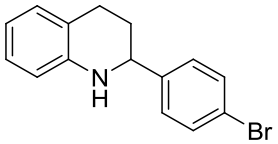
2-(4-methoxyphenyl)-1,2,3,4,-tetrahydroquinoline (5c): Compound **5c** was prepared according to the general procedure **B.** The reaction mixture was purified by flash column chromatography (Et_2O : hexane = 2:98) and the product was recovered in 96% (45.9 mg) yield as colourless oil. The NMR data are in accordance with the literature.[8]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.32 (m, 2H), 7.05-7.01 (m, 2H), 6.93-6.90 (m, 2H), 6.69-6.66 (m, 1H), 6.55-6.53 (m, 1H), 4.41 (dd, J = 6.5, 3.1 Hz, 1H), 4.01 (brs, 1H), 3.84 (s, 3H), 2.99-2.91 (m, 1H), 2.80-2.73 (m, 1H), 2.14-2.08 (m, 1H), 2.04-1.96 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 144.7, 136.8, 129.2, 127.5, 126.8, 120.8, 117.0, 113.9, 113.8, 55.6, 55.2, 31.0, 26.4.

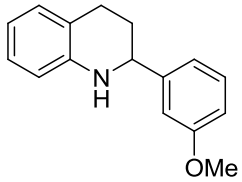
2-(4-bromophenyl)-1,2,3,4-tetrahydroquinoline (5d): Compound **5d** was prepared according to the general procedure **B.** The reaction mixture was purified by flash column chromatography (Et_2O : hexane = 2:98) and the product was recovered in 74% (42.6 mg) yield as yellow oil. The NMR data are in accordance with the literature.[9]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.35 (m, 3H), 7.31-7.27 (m, 1H), 7.03-7.00 (m, 2H), 6.68-6.64 (m, 1H), 6.56-6.53 (m, 1H), 4.45 (dd, J = 5.8, 3.3 Hz, 1 H), 4.04 (s, 1H), 2.97-2.89 (m, 1H), 2.78-2.71 (m, 1H), 2.16-2.10 (m, 1H), 2.05-1.95 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 144.6, 129.2, 128.5, 127.4, 126.8, 126.5, 120.8, 117.1, 113.9, 56.2, 30.9, 26.3.

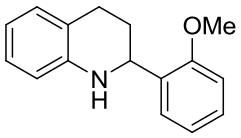
2-(3-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (5e): Compound **5e** was prepared according to the general procedure **B.** The reaction mixture was purified by flash column chromatography (Et_2O : hexane = 2:98) and the product was recovered in 95% (45.4 mg) yield as colourless oil. The NMR data are in accordance with the literature.[9]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.27 (m, 1H), 7.05-7.03 (m, 4H), 6.87-6.84 (m, 1H), 6.69-6.65 (m, 1H), 6.67-6.65 (m, 1H), 4.44 (dd, J = 6.2, 3.1 Hz, 1H), 3.83 (s, 3H), 2.99-2.91 (m, 1H), 2.79-2.73 (m, 1H), 2.18-2.11 (m, 1H), 2.07-1.96 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.8, 146.5, 144.6, 129.5, 129.2, 126.8, 120.8, 118.8, 117.1, 113.9, 112.7, 112.0, 56.2, 55.1, 30.9, 26.3.

2-(2-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (5f): Compound **5f** was prepared according to the general procedure **B.** The reaction mixture was purified by flash column chromatography (Et_2O : hexane = 2:98) and the product was recovered in 80% (38.3 mg) yield as a pale yellow oil. The NMR data are in accordance with the literature.[9]



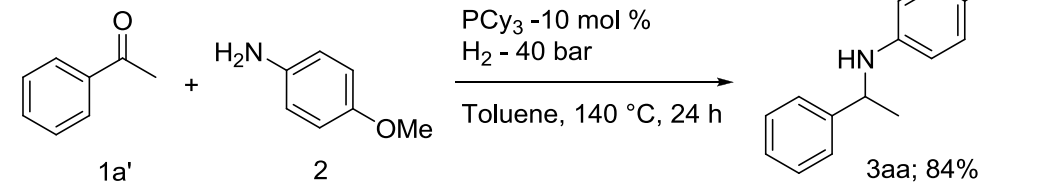
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.45 (m, 1H), 7.30-7.28 (m, 1H), 7.05-6.96 (m, 3H). 6.93-6.91 (m, 1H), 6.68-6.65 (m, 1H), 6.59-6.57 (m, 1H), 4.91-4.89 (m, 1H), 3.88 (s, 3H), 2.94-2.87 (m, 1H), 2.75-2.69 (m, 1H), 2.21-2.14 (m, 1H), 2.08-1.96 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.3, 145.0, 132.6, 129.1, 127.9, 126.7, 126.7, 121.0, 120.6, 116.8, 113.9, 110.2, 55.2, 48.9, 27.9, 25.9.

5. Control experiments

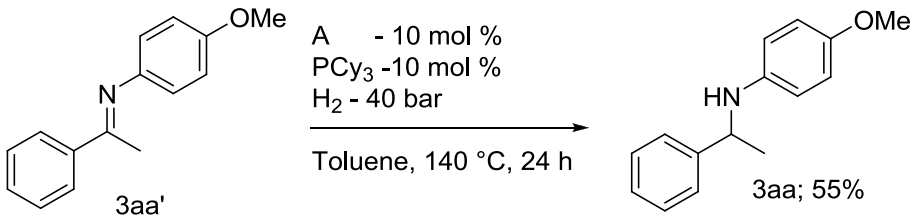
(a) Reductive amination using molecular hydrogen:

(i)



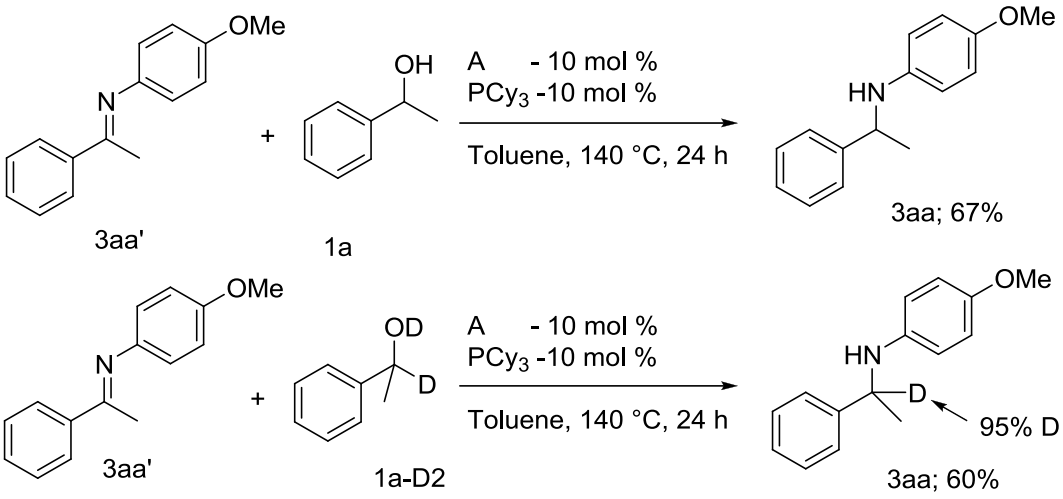
1a' 2 3aa; 84%

(ii)

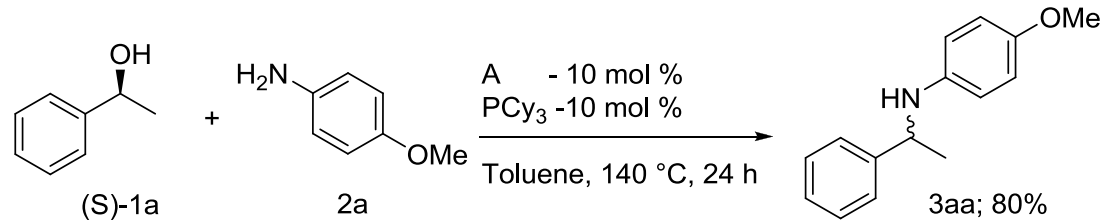


3aa' 3aa; 55%

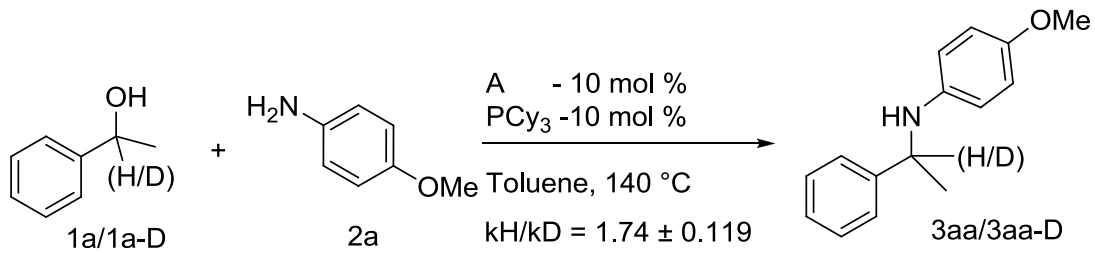
(b) Transfer hydrogenation using 1a:



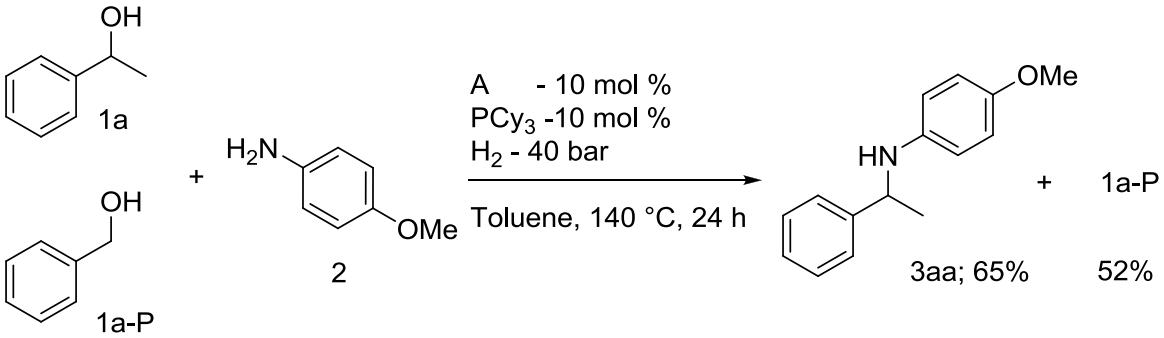
(c) Racemization of (S)-1a through borrowing hydrogen



(d) KIE experiment (parallel):

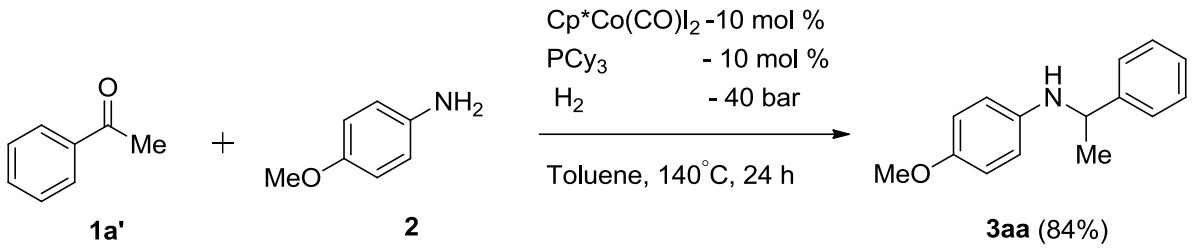


(e) Intermolecular Competitive Experiment:



a) Reductive amination using molecular hydrogen

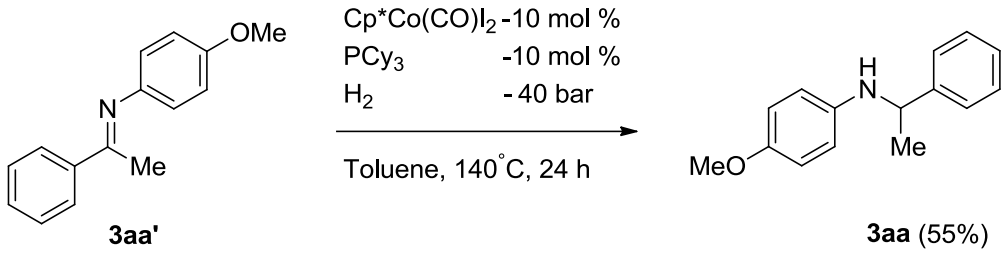
i)



1a' **2** **3aa** (84%)

A 4 mL glass vial containing a stirring bar was sequentially charged with Cp*Co(CO)I_2 (14.3 mg, 0.03 mmol), tricyclohexylphosphine (8.4 mg, 0.03 mmol), acetophenone **1a'** (36 mg, 0.3 mmol), *p*-anisidine **2** (36.9 mg, 0.3 mmol) and toluene (1.5 mL). Afterwards, the reaction vial was capped with a septum equipped with a syringe and the setup was placed into an autoclave and sealed. Then the autoclave was purged 3 times with hydrogen, then pressurized to 40 bar and placed on the stirring plate, which was preheated at 140 °C. After 24 h, the autoclave was cooled in an ice bath and the residual gas was released. All the volatiles were removed under vacuum and the residue was purified by flash column chromatography to yield the pure compound.

ii)

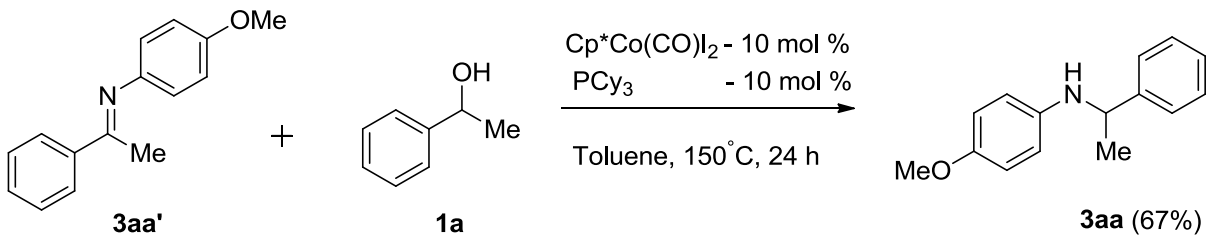


3aa' **3aa** (55%)

A 4 mL glass vial containing a stirring bar was sequentially charged with Cp*Co(CO)I_2 (14.3 mg, 0.03 mmol), tricyclohexylphosphine (8.4 mg, 0.03 mmol), imine **3aa'** (67.5 mg, 0.3 mmol) and toluene (1.5 mL). Afterwards, the reaction vial was capped with a septum equipped with a syringe and kept in the alloy plate, and the setup is placed into an autoclave and sealed. Then the autoclave was purged 3 times with hydrogen, then pressurized to 40 bar and placed into stirring plate, which was preheated at 140 °C. After 24 h, the autoclave was cooled in an ice bath, and the remaining gas was released. All the volatiles were removed under vacuum and purified by flash column chromatography to get pure compound.

b) Transfer hydrogenation

(i)

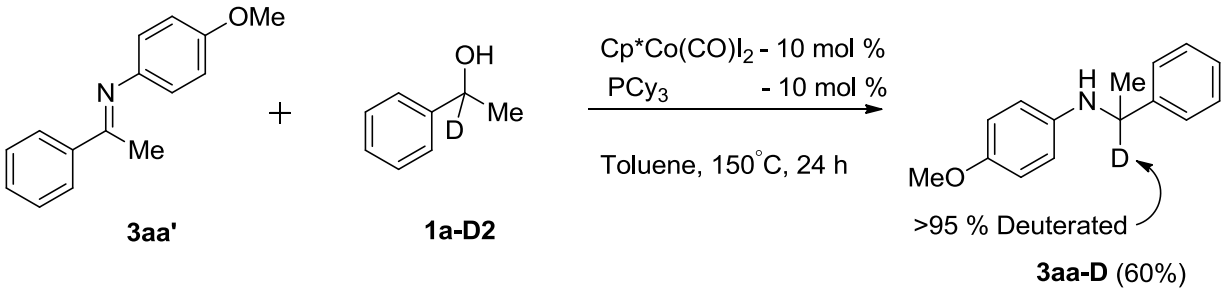


3aa' **1a** **3aa** (67%)

An oven dried Schlenk tube was charged with Cp*Co(CO)I_2 (14.3 mg, 0.03 mmol), tricyclohexylphosphine (8.4 mg, 0.03 mmol), alcohol **1a** (73.2 mg, 0.6 mmol), imine **3aa'** (67.5 mg, 0.3 mmol) and 2 mL of toluene. The closed

Schlenk tube containing the reaction mixture was stirred at 150 °C for 24 h, after which the mixture was cooled to room temperature. All the volatiles were removed under vacuum and the residue was purified by flash column chromatography to yield the pure compound.

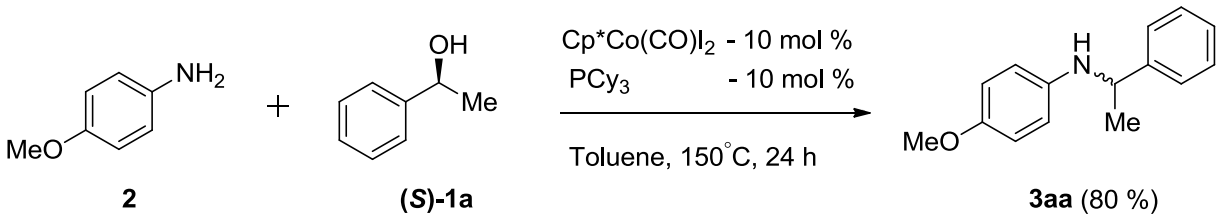
ii)



3aa' **1a-D2** **3aa-D** (60%)

An oven dried Schlenk tube was charged with $Cp^*Co(CO)I_2$ (14.3 mg, 0.03 mmol), tricyclohexylphosphine (8.4 mg, 0.03 mmol), alcohol **1a-D2** (73.8 mg, 0.6 mmol), imine **3aa'** (67.5 mg, 0.3 mmol) and 2 mL of toluene. The closed Schlenk tube containing the reaction mixture was stirred at 150 °C for 24 h, after which the mixture was cooled to room temperature. All the volatiles were removed under vacuum and the residue was purified by flash column chromatography to yield the pure compound.

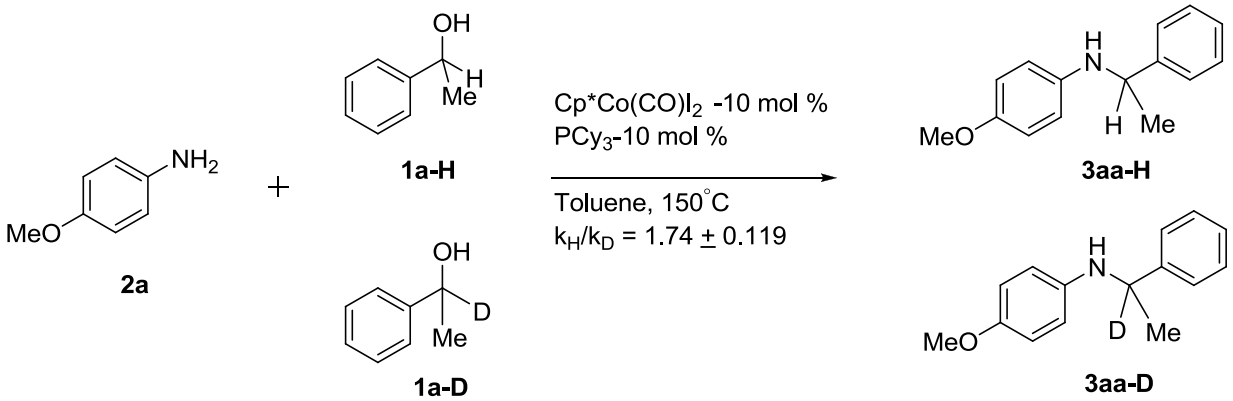
c) Racemization of (*S*)-1a through borrowing hydrogen



2 **(*S*)-1a** **3aa** (80 %)

An oven dried Schlenk tube was charged with $Cp^*Co(CO)I_2$ (14.3 mg, 0.03 mmol), tricyclohexylphosphine (8.4 mg, 0.03 mmol), alcohol **(*S*)-1a** (73.2 mg, 0.6 mmol), amine **2** (36.9 mg, 0.3 mmol) and 2 mL of toluene. The closed Schlenk tube containing the reaction mixture was stirred at 150 °C for 24 h, after which the mixture was cooled to room temperature. All the volatiles were removed under vacuum and the residue was purified by flash column chromatography to yield the pure compound.

d) KIE Experiment (Parallel):



2a **1a-H** **1a-D** **3aa-H** **3aa-D**

An oven-dried Schlenk tube equipped with a teflon coated magnetic stirring bar was evacuated and filled with argon, then charged with Cp*Co(CO)I_2 (2.3 mg, 0.005mmol, 10 mol%), tricyclohexylphosphine (1.4 mg, 0.005 mmol, 10 mol%), 1-phenyl ethanol (12.2 mg, 0.1 mmol, 2 eq), and *p*-anisidine (6.1 mg, 0.05 mmol, 1 eq) in 0.3 mL of toluene. In parallel, a second Schlenk tube was charged with Cp*Co(CO)I_2 (2.3 mg, 0.005mmol, 10 mol%), tricyclohexylphosphine (1.4 mg, 0.005 mmol, 10 mol%), 1- deuterated phenyl ethanol (12.3 mg, 0.1 mmol, 2 eq), and *p*-anisidine (6.1 mg, 0.05 mmol, 1 eq) in 0.3 mL of toluene. Both Schlenks were closed and placed in a preheated oil bath for 1h. The same protocol was repeated for different reaction times (2h, 3h and 4h). At regular intervals (see Table below), the reaction mixture was diluted with 5 mL of EtOAc and filtered using a silica pad. The solvent was then removed under reduced pressure and a ^{1}H NMR spectrum was recorded using mesitylene (7 mg) as the internal standard. The k_H/k_D value was determined from the slope ratio of the kinetics plots (^{1}H NMR yield vs time) as 1.74 ± 0.119.

Time (h)	1	2	3	4
Yield of H (%)	2	2.7	5	7.8
Yield of D (%)	0.38	1.29	2.9	3.6

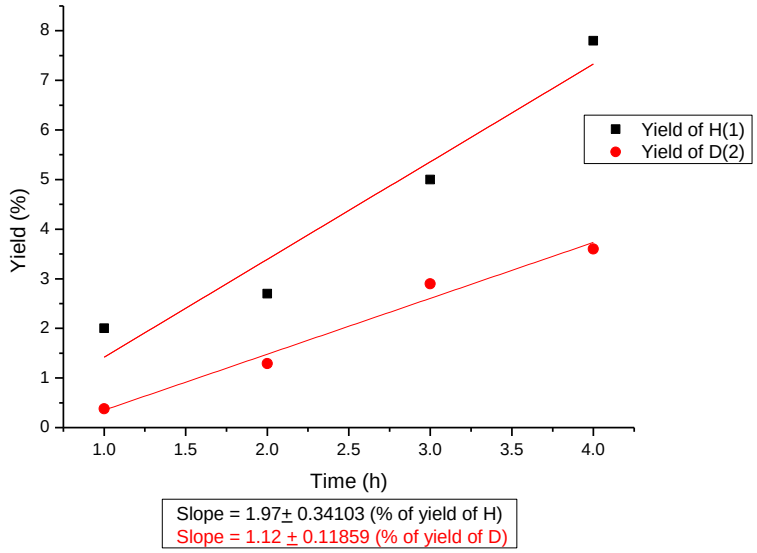
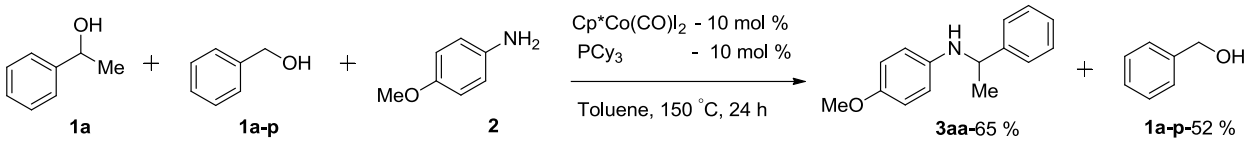


Figure S1. Determination of k_H/K_D value from parallel experiments

e) Intermolecular competition experiment:



An oven-dried Schlenk tube was charged with Cp*Co(CO)I_2 (14.3 mg, 0.03 mmol), tricyclohexylphosphine (8.4 mg, 0.03 mmol), 1-phenyl ethanol **1a** (36.6 mg, 0.3 mmol), benzylalcohol **1a-p** (32.4 mg, 0.3 mmol), amine **2** (36.9 mg, 0.3 mmol) and 2 mL of toluene. The closed Schlenk tube containing the reaction mixture was stirred at 150 °C for 24 h, after which the mixture was cooled to room temperature. All volatiles were removed under vacuum and the residue was purified by flash column chromatography to yield the pure compound.

6. Computational Details

The computational work was carried out using the Gaussian09 suite of programs.[17] Gas-phase geometry optimizations were performed without any symmetry constraint using the B3LYP functional[18] and the 6-31G(d,p) basis functions for all light atoms (H, C, N, O), whereas the Co and I atoms were treated with the SDD basis set augmented by an f polarization function (α = 2.780 for Co)[19] or a d polarization function (α = 0.289 for I).[20] Corrections for dispersion were carried out at the fixed B3LYP optimized geometries using Grimme's GD3 empirical method (B3LYP-D3), using standard SR6 and S8 parameters.[21] All final geometries were characterized as local minima by verifying that all second derivatives of the energy were positive. Thermochemical corrections were obtained at 298.15 K and at 423.15 K on the basis of frequency calculations, using the standard approximations (ideal gas, rigid rotor and harmonic oscillator). Solvation corrections in toluene (ε = 2.3741), acetonitrile (ε = 35.688) and water (ε = 78.3553) were carried out using the SMD polarizable continuum model.[22] An additional correction of 1.95 kcal/mol was applied to all G values to change the standard state from the gas phase (1 atm) to solution (1 M).[23] For the QM/MM calculations, the UFF approach[24] was used for the molecular mechanics part, with the P and P-bonded C atoms of the cyclohexyl groups treated quanto-mechanically. The rest of the cyclohexyl rings and the Cp* methyl groups were handled at the molecular mechanics level.

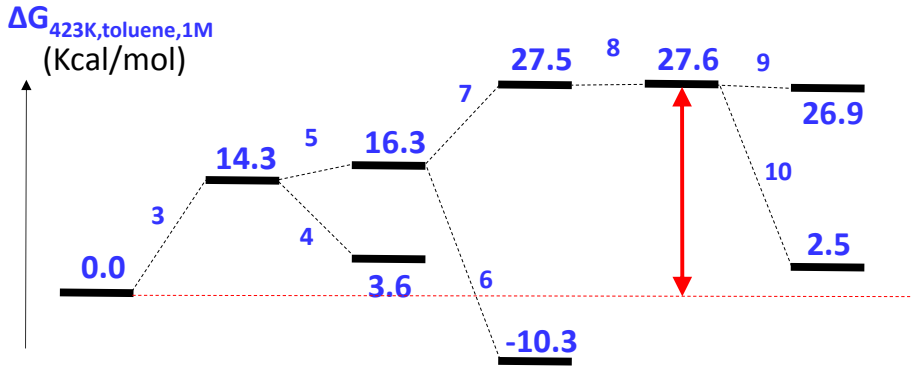
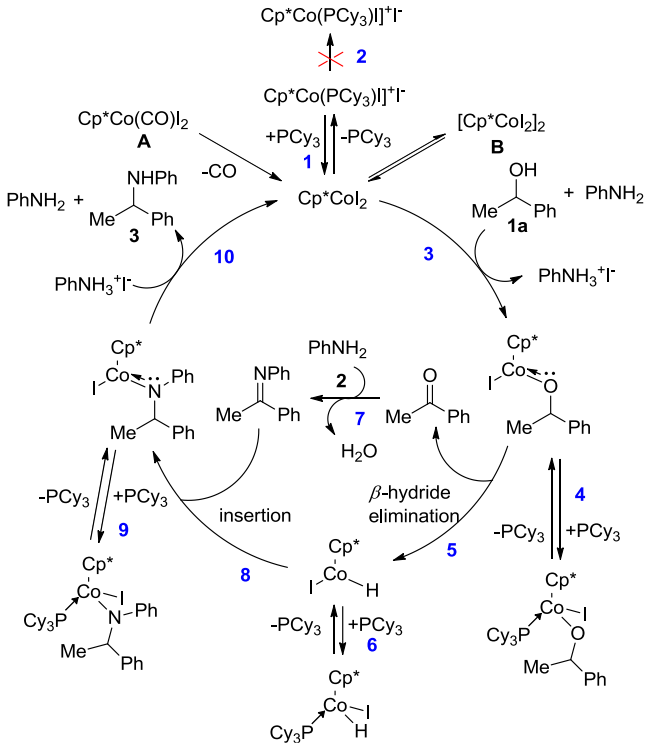


Figure S2. Calculated $\Delta G_{toluene,1M}$ changes at 150°C for the reactions illustrated in Scheme 5 using the computational model (PMe_3 and Cp used in place of PCy_3 and Cp*).

All previous computational work on the analogous Cp*Ir(III) system,[25-28] as well as the above-described experimental work on the Cp*Co(III) system, is suggestive of alcohol dehydrogenation with proton delivery to a spectator ligand (*e.g.* carbonato,[25] alkoxo or aryloxo[26-27]) or to an external base[28] to produce a key hydride intermediate followed by the mirror processes for the imine substrate, which is produced in the meantime by the non-catalyzed condensation of the ketone intermediate with the amine. A vacant coordination site is needed on the metal center to host the hydride ligand. In the present case, the similar activities of the pre-catalysts **A** and **B** (Table S2) suggests the formation of a common active species, which may be either $[Cp^*CoI_2]$ of $[Cp^*CoI(PCy_3)]^+I^-$. The presence of the 18-electron $[Cp^*CoI_2(PCy_3)]$ may also be questioned because numerous examples of $Cp^*CoI_2(PR_3)$ adducts are known in the literature.[29-31] However, the PCy_3 adduct is not among them. The DFT calculations indicate favorable association of the small PMe_3 to $[CpCoI_2]$ (-27.7 kcal/mol at 25°C, -22.9 kcal/mol at 150°C), but an unfavorable one for the bulkier PCy_3 with the bulkier $[Cp^*CoI_2]$ (+4.0 and +10.4 kcal/mol at 25 and 150°C, respectively).

Figure S3: Possible mechanism for the [Cp*CoI$_2$]-catalyzed acetophenone amination by PhNH$_2$.



The role of PCy$_3$ is presumably the stabilization of the hydride intermediate (*vide infra*). The possible iodide dissociation to generate [CpCoI(PMe$_3$)]$^+$I$^-$ is quite costly in toluene (+52.6 and +48.5 kcal/mol at 25 and 150°C and the same process on the real Cp*/PCy$_3$ would undoubtedly also be unfavorable (this process is very solvent-dependent, with the cost dropping to +13.2 and +12.3 kcal/mol in MeCN and H$_2$O, respectively, at 25°C). Hence, the rest of the cycle was explored on the assumption that the alcohol activating species is the unsaturated [Cp*CoI$_2$] monomer.

The alcohol activation (reaction 3), presumably taking place *via* alcohol coordination followed by deprotonation by the external base, yields the 16-electron alkoxide [CpCoI(OCHMePh)] with a cost of 14.3 kcal/mol at 150°C. The anilinium iodide product is ion-paired in toluene (dissociation to the free ions requires 35.5 kcal/mol). The alternative elimination of HI without aniline intervention would require 17.3 kcal/mol. The alkoxide complex is slightly stabilized by PMe$_3$ coordination (reaction 4, -10.7 kcal/mol), lower than the stabilization of [CpCoI$_2$] (-22.9 kcal/mol) because the additional π donation of the alkoxide ligand is greater than that of iodide. Therefore, the real Cp*Co/PCy$_3$ system would undoubtedly not enjoy any stabilization by phosphine association at this stage. The next step (*β*-H elimination, reaction 5) is thermodynamically quite facile. The 16-electron [CpCoHI] intermediate is now greatly stabilized by PMe$_3$ coordination (reaction 6, -26.6 kcal/mol), because the vacant metal orbital can only interact with a lone pair of the residual iodide, a weak π-donor. This stabilization is greater than for [CpCoI$_2$], presumably for both steric and electronic reasons. Therefore, it appears possible that the real Cp*Co/PCy$_3$ system could benefit from a slight stabilization of this intermediate by phosphine coordination. The imine formation (reaction 7) is endoergic by +11.2 kcal/mol, but the subsequent coordination and insertion into the Co-H bond is essentially neutral. The 16-electron [CpCoI(NPhCMePh)] is the highest-energy intermediate of the catalytic cycle, at 27.6 kcal/mol from the starting point. This intermediate is essentially not stabilized at all by PMe$_3$ coordination (reaction 9, -0.7 kcal/mol), because of the strong π-donor power of the amido ligand and of steric impediments. Final protonation and product release (reaction 10) stabilize the system to yield an overall thermodynamic cost of 2.5 kcal/mol. The unsuitability of this number (the process is thermodynamically favorable) may be associated to the

neglect of H-bonding (stronger homo- and hetero-interactions in the PhNHCHMePh + H_2O products than in the PhCH(OH)Me + $PhNH_2$ reactants, a neglect that may also affect the calculated energies of the other intermediates of the cycle. Taking the energy difference between highest and lowest points in the cycle (27.6 kcal/mol at 150°C) as a low limit of the energy span, a TOF of ≤ 180 h^{-1} can be calculated from the Eyring equation, which does not appear unreasonable considering the observed catalytic activities (table 1 and schemes 1-3) and the Cp* ligand simplification.

Table S2. Energies (in hartrees), views and Cartesian coordinates for all geometry optimized systems.

A. Small organic and inorganic molecules/ions

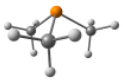
I^-
$E\text{-}D_3$ = -11.5700566182
$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -11.583895
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -11.591948
$G\text{-}D_{3,MeCN,1M,\ 298.15K}$ = -11.621170
$G\text{-}D_{3,water,1M,\ 298.15K}$ = -11.624298

53	0.000000000	0.000000000	0.000000000

HI
$E\text{-}D_3$ = -12.0211720813
$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -12.034087
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -12.043916

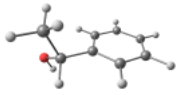
53	0.000000000	0.000000000	0.029998000
1	0.000000000	0.000000000	-1.589912000

PMe_3
$E\text{-}D_3$ = -461.169244883
$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -461.085767
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -461.101263



15	0.000614000	0.001092000	-0.610448000
6	-0.273853000	-1.610503000	0.281780000
1	-0.255165000	-1.486964000	1.369552000
1	-1.239611000	-2.030953000	-0.008593000
1	0.501165000	-2.325157000	-0.005310000
6	-1.259508000	1.041203000	0.282661000
1	-2.264761000	0.727619000	-0.008829000
1	-1.165469000	0.959237000	1.370454000
1	-1.140513000	2.088702000	-0.004274000
6	1.532508000	0.567921000	0.283193000
1	1.416737000	0.523523000	1.371080000
1	2.378198000	-0.059784000	-0.007640000
1	1.765331000	1.595673000	-0.005515000

PhCH(Me)OH
$E\text{-}D_3$ = -386.211528991
$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -386.091225
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -386.108965



8	2.299410000	0.881942000	0.745878000
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1	1.856705000	-1.135623000	0.979874000
6	2.297859000	-0.636768000	-1.063186000
1	3.378022000	-0.744695000	-0.942597000
1	1.887693000	-1.563031000	-1.471286000
1	2.103258000	0.172941000	-1.770376000
6	0.149923000	-0.138410000	0.163586000
6	-0.395912000	1.100362000	-0.184344000
6	-0.707303000	-1.223250000	0.363045000
6	-1.772860000	1.249518000	-0.332341000
6	-2.084478000	-1.077498000	0.211719000
6	-2.621143000	0.160817000	-0.136755000
1	0.270242000	1.942714000	-0.329750000
1	-0.293978000	-2.187726000	0.642799000
1	-2.184232000	2.216414000	-0.600832000
1	-2.738679000	-1.927321000	0.372462000
1	-3.693080000	0.277204000	-0.250367000
1	1.885714000	1.135070000	1.577858000

$PhNH_2$
$E\text{-}D_3$ = -287.688728745
$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -287.607653
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -287.622724

6	1.170264000	1.200299000	0.003362000
6	-0.220246000	1.206026000	-0.004495000
6	1.879178000	0.000013000	0.007372000
1	-0.759621000	2.148218000	-0.013044000
1	2.962497000	-0.000087000	0.014051000
6	-0.938418000	0.000050000	-0.007588000
6	1.170184000	-1.200351000	0.003328000
1	1.703393000	-2.144941000	0.007221000
6	-0.220226000	-1.206032000	-0.004431000
1	-0.759744000	-2.148155000	-0.012654000
1	1.703366000	2.144951000	0.007295000
7	-2.333501000	0.000065000	-0.076032000
1	-2.779956000	0.835578000	0.272669000
1	-2.779841000	-0.836045000	0.271396000

$PhNH_3^+$
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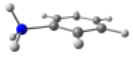
$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -288.006570
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -288.022718



6	-1.227348000	1.209707000	0.001538000
6	0.166439000	1.221327000	-0.005605000
6	-1.916854000	-0.001203000	0.005699000
1	0.707915000	2.161484000	-0.008465000
1	-2.999746000	-0.002677000	0.009253000
6	0.825180000	0.001534000	-0.010625000
6	-1.223893000	-1.211502000	0.001505000
1	-1.763032000	-2.150297000	0.001192000
6	0.168883000	-1.220730000	-0.005591000

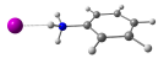
1	0.713710000	-2.158795000	-0.008378000
1	-1.767862000	2.147687000	0.001400000
7	2.323118000	0.000298000	0.007951000
1	2.696856000	0.895755000	-0.321757000
1	2.703475000	-0.730330000	-0.602607000
1	2.692419000	-0.159715000	0.952179000

$PhNH_3^+I^-$

$E\text{-}D_3$ = -299.724827075

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -299.652458

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -299.671265



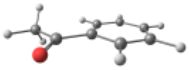
6	-3.940121000	0.406854000	-0.493801000
6	-2.831748000	1.212933000	-0.244492000
6	-3.881425000	-0.960168000	-0.230396000
1	-2.870760000	2.278225000	-0.446791000
1	-4.744501000	-1.585198000	-0.426468000
6	-1.677418000	0.631042000	0.265872000
6	-2.712265000	-1.526303000	0.274969000
1	-2.659984000	-2.591369000	0.465226000
6	-1.595413000	-0.733082000	0.524409000
1	-0.666260000	-1.162087000	0.880155000
1	-4.844853000	0.848527000	-0.893642000
7	-0.491177000	1.450159000	0.524128000
1	-0.504514000	2.326562000	0.003716000
1	0.482991000	0.897589000	0.232834000
1	-0.377081000	1.668393000	1.514719000
53	2.253840000	-0.132442000	-0.105245000

PhCOMe

$E\text{-}D_3$ = -385.007012018

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -384.910801

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -384.928169



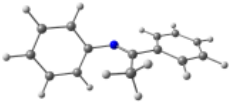
8	2.212008000	-1.306764000	-0.000267000
6	1.698799000	-0.205542000	0.000007000
6	2.556364000	1.047479000	0.000221000
1	3.603765000	0.751348000	0.000176000
1	2.348703000	1.660458000	-0.881572000
1	2.349307000	1.660024000	0.882576000
6	0.204474000	-0.054870000	-0.000082000
6	-0.577121000	-1.217998000	0.000046000
6	-0.431865000	1.192874000	-0.000117000
6	-1.963304000	-1.136262000	0.000190000
6	-1.822005000	1.274710000	-0.000150000
6	-2.588995000	0.111552000	0.000087000
1	-0.069640000	-2.174760000	-0.000071000
1	0.150119000	2.106325000	-0.000219000
1	-2.559030000	-2.042017000	0.000385000
1	-2.306004000	2.244706000	-0.000436000
1	-3.671369000	0.176369000	0.000093000

PhN=CMePh

$E\text{-}D_3$ = -596.23288975

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -596.056579

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -596.079195



7	-0.425117000	-0.477289000	0.086434000
6	0.412117000	0.449742000	-0.187746000
6	0.035185000	1.841354000	-0.653503000
1	-1.036781000	1.926031000	-0.818470000
1	0.331510000	2.591879000	0.085268000
1	0.554959000	2.079611000	-1.585123000
6	1.864563000	0.124166000	-0.064279000
6	2.261255000	-1.180129000	0.272380000
6	2.858072000	1.092109000	-0.264621000
6	3.604823000	-1.503115000	0.399908000
6	4.207036000	0.767738000	-0.132799000
6	4.585338000	-0.529644000	0.198139000
1	1.491470000	-1.924587000	0.429270000
1	2.591163000	2.109592000	-0.520120000
1	3.891968000	-2.516474000	0.657555000
1	4.960553000	1.531385000	-0.289466000
1	5.634822000	-0.782804000	0.298687000
6	-1.815756000	-0.298119000	0.073150000
6	-2.461235000	0.528035000	1.005165000
6	-2.591441000	-1.037188000	-0.831303000
6	-3.850084000	0.623133000	1.016906000
6	-3.977117000	-0.921022000	-0.825039000
6	-4.615349000	-0.092974000	0.098698000
1	-1.864038000	1.075888000	1.725205000
1	-2.090288000	-1.693385000	-1.533195000
1	-4.334697000	1.262284000	1.746953000
1	-4.563038000	-1.487949000	-1.540234000
1	-5.696233000	-0.014961000	0.108298000

H_2O

$E\text{-}D_3$ = -76.4474559123

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -76.444876

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -76.453860

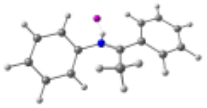
8	0.000000000	0.000000000	0.118702000
1	0.000000000	0.757090000	-0.474807000
1	0.000000000	-0.757090000	-0.474807000

$[PhNHCMePh]^+I^-$

$E\text{-}D_3$ = -608.280209711

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -608.107992

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -608.133685



7	0.310675000	0.843750000	0.078396000
6	-0.673179000	1.693213000	0.167848000
6	-0.404918000	3.163611000	0.334717000
1	0.587153000	3.340084000	0.746447000
1	-0.460629000	3.676966000	-0.629915000
1	-1.156418000	3.603643000	0.989354000
6	-2.063813000	1.226293000	0.135800000
6	-2.416701000	-0.075708000	0.533280000
6	-3.075092000	2.103781000	-0.302999000
6	-3.743250000	-0.485256000	0.480617000
6	-4.394822000	1.681245000	-0.364441000
6	-4.732394000	0.385605000	0.030493000
1	-1.666591000	-0.773574000	0.882994000
1	-2.830491000	3.108454000	-0.624222000
1	-3.995688000	-1.492336000	0.788963000
1	-5.160741000	2.359486000	-0.721256000
1	-5.765061000	0.058876000	-0.012821000
6	1.712737000	1.128965000	0.076188000
6	2.267105000	2.046335000	-0.817829000

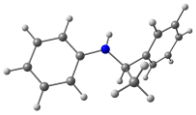
6	2.523787000	0.376116000	0.927122000
6	3.643642000	2.245779000	-0.824361000
6	3.898703000	0.588112000	0.913581000
6	4.458959000	1.523371000	0.045890000
1	1.632908000	2.570867000	-1.521139000
1	2.076714000	-0.373531000	1.565996000
1	4.079068000	2.952581000	-1.520573000
1	4.532254000	0.007081000	1.572585000
1	5.531636000	1.677034000	0.034008000
1	0.129553000	-0.211974000	-0.029696000
53	0.345038000	-2.490919000	-0.190282000

PhNHCHMePh

$E\text{-}D_3$ = -597.450861502

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -597.251024

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -597.273851



7	-0.474383000	0.331071000	0.366616000
6	0.443453000	-0.799512000	0.191439000
6	1.851230000	-0.272347000	-0.024005000
6	2.433298000	0.600987000	0.903674000
6	2.597014000	-0.659151000	-1.139043000
6	3.727371000	1.077879000	0.715202000
6	3.896240000	-0.189598000	-1.325992000
6	4.464425000	0.681602000	-0.400066000
1	1.866692000	0.908420000	1.776074000
1	2.157054000	-1.331759000	-1.868048000
1	4.163001000	1.754991000	1.441568000
1	4.461206000	-0.500991000	-2.197524000
1	5.473641000	1.049861000	-0.545460000
6	-1.835455000	0.255884000	0.083102000
6	-2.590615000	1.445610000	0.069902000
6	-2.505284000	-0.953016000	-0.171312000
6	-3.953291000	1.423697000	-0.185410000
6	-3.876800000	-0.960898000	-0.421405000
6	-4.614147000	0.218204000	-0.431438000
1	-2.091486000	2.389012000	0.269806000
1	-1.965366000	-1.890179000	-0.180046000
1	-4.506134000	2.356980000	-0.190820000
1	-4.368466000	-1.908513000	-0.614178000
1	-5.679637000	0.202685000	-0.626537000
1	-0.062352000	1.223258000	0.138770000
1	0.161139000	-1.367025000	-0.706457000
6	0.390734000	-1.747052000	1.404015000
1	1.035106000	-2.613999000	1.236498000
1	0.733784000	-1.227356000	2.300928000
1	-0.626540000	-2.096626000	1.587144000

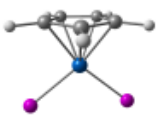
B. Cobalt complexes (models)

$CpCoI_2$

$E\text{-}D_3$ = -362.345241009

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -362.306455

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -362.325763



27	-0.000419000	0.670727000	-0.000994000
6	-0.662298000	2.343757000	-1.009055000
6	-1.170939000	2.363192000	0.314545000
6	-0.058009000	2.332488000	1.204225000
6	1.140281000	2.354806000	0.429966000
6	0.768210000	2.342116000	-0.937430000
1	-0.111925000	2.247257000	2.278852000
1	2.144371000	2.285120000	0.814653000
1	1.443477000	2.264141000	-1.774884000
1	-1.250860000	2.268377000	-1.910009000
1	-2.209318000	2.301879000	0.595414000
53	1.913108000	-0.943712000	0.000062000
53	-1.915144000	-0.941091000	0.000113000

$CpCoI_2(PMe_3)$

$E\text{-}D_3$ = -823.58027914

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -823.436383

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -823.463555

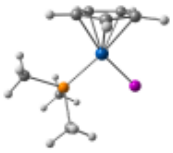
27	-0.000119000	0.073724000	0.705157000
6	-1.151125000	0.440052000	2.433813000
6	-0.004057000	1.274197000	2.463198000
6	1.147440000	0.445814000	2.434591000
6	0.703021000	-0.918418000	2.481212000
6	-0.699897000	-0.922046000	2.480368000
1	1.341154000	-1.784942000	2.436038000
1	-1.333621000	-1.791769000	2.434597000
1	2.173741000	0.771854000	2.391019000
1	-2.178982000	0.760926000	2.388958000
1	-0.006813000	2.352881000	2.450979000
53	2.008009000	-0.956766000	-0.636031000
53	-2.008690000	-0.955123000	-0.636906000
6	-1.451660000	2.957076000	-0.323814000
1	-1.410132000	3.834819000	-0.972849000
1	-2.352829000	2.381450000	-0.538079000
1	-1.481624000	3.280502000	0.717300000
6	1.452977000	2.957579000	-0.319225000
1	1.478498000	3.282639000	0.721518000
1	2.355034000	2.381626000	-0.528848000
1	1.414296000	3.834297000	-0.969813000
15	0.001304000	1.869614000	-0.608870000
6	0.004313000	1.637674000	-2.423349000
1	-0.876651000	1.066364000	-2.711134000
1	-0.001409000	2.615498000	-2.911582000
1	0.893006000	1.077608000	-2.709418000

$CpCoI(PMe_3)^+$

$E\text{-}D_3$ = -811.872092623

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -811.768743

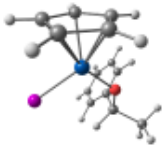
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -811.794265



27	-0.149378000	-0.676882000	-0.000007000
6	-0.744064000	-2.284670000	1.146463000
6	-1.578423000	-2.199107000	-0.000056000
6	-0.743942000	-2.284727000	-1.146480000
6	0.602657000	-2.517020000	-0.702456000
6	0.602576000	-2.517004000	0.702585000
1	-1.062050000	-2.192777000	-2.174204000
1	1.472225000	-2.583665000	-1.337732000

1	1.472085000	-2.583485000	1.337961000
1	-1.062284000	-2.192732000	2.174153000
1	-2.645016000	-2.046864000	-0.000124000
53	1.845262000	0.742267000	-0.000001000
15	-1.604022000	1.066007000	0.000008000
6	-1.411661000	2.151472000	1.460163000
1	-2.140988000	2.963513000	1.414513000
1	-1.570512000	1.575393000	2.373155000
1	-0.402549000	2.561687000	1.474435000
6	-3.383549000	0.621289000	0.000003000
1	-3.629165000	0.040468000	0.890311000
1	-3.985377000	1.532899000	0.000178000
1	-3.629221000	0.040795000	-0.890502000
6	-1.411667000	2.151422000	-1.460186000
1	-2.141047000	2.963420000	-1.414610000
1	-0.402581000	2.561702000	-1.474427000
1	-1.570436000	1.575290000	-2.373159000

CpCoI(OCHMePh)



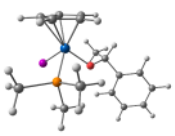
E-D_3 = -736.507921041

G-$D_{3,toluene,1M,\ 298.15K}$ = -736.335874

G-$D_{3,toluene,1M,\ 423.15K}$ = -736.363184

27	-1.228575000	0.597843000	0.115310000
6	-2.660624000	2.128070000	0.266482000
6	-1.702145000	2.458543000	-0.711291000
6	-1.704704000	1.417494000	-1.697184000
6	-2.723622000	0.484247000	-1.349556000
6	-3.284961000	0.892828000	-0.118691000
1	-1.036218000	1.339973000	-2.540527000
1	-2.938110000	-0.435176000	-1.867769000
1	-4.017833000	0.346836000	0.453986000
1	-2.830975000	2.660038000	1.189778000
1	-1.001255000	3.276537000	-0.659955000
53	-0.820315000	-1.903545000	0.034109000
8	0.113838000	1.115877000	1.133021000
6	1.282148000	0.446748000	1.576886000
1	1.031358000	-0.566844000	1.907514000
6	1.834867000	1.241178000	2.764188000
1	1.084463000	1.293595000	3.556544000
1	2.735737000	0.763195000	3.158065000
1	2.086967000	2.257526000	2.451940000
6	2.292692000	0.342564000	0.445812000
6	2.537821000	1.441507000	-0.382627000
6	2.998772000	-0.839950000	0.225700000
6	3.474694000	1.360268000	-1.408828000
6	3.941174000	-0.923626000	-0.798074000
6	4.181138000	0.175727000	-1.618975000
1	1.980215000	2.356631000	-0.219007000
1	2.795758000	-1.705017000	0.847347000
1	3.656721000	2.220117000	-2.044854000
1	4.477877000	-1.851641000	-0.961659000
1	4.909282000	0.109766000	-2.419778000

CpCoI(OCHMePh)(PMe_3)



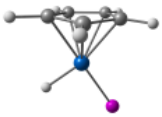
E-D_3 = -1197.72828648

G-$D_{3,toluene,1M,\ 298.15K}$ = -1197.448176

G-$D_{3,toluene,1M,\ 423.15K}$ = -1197.481716

27	1.003093000	0.465222000	0.528742000
6	1.061036000	2.106834000	1.858014000
6	2.313344000	2.043252000	1.175327000
6	2.911341000	0.799102000	1.462711000
6	2.057989000	0.107001000	2.386798000
6	0.938928000	0.918701000	2.639747000
1	2.223476000	-0.889161000	2.762484000
1	0.092177000	0.653285000	3.250675000
1	3.827546000	0.414926000	1.046135000
1	0.346124000	2.912467000	1.811794000
1	2.706337000	2.793392000	0.506550000
53	1.709961000	-1.875363000	-0.421887000
6	0.024201000	2.966702000	-1.432572000
1	-0.157201000	3.366164000	-2.433116000
1	-0.923699000	2.831958000	-0.910128000
1	0.647753000	3.664531000	-0.872243000
6	2.388190000	1.566609000	-2.431204000
1	3.044176000	2.243488000	-1.881838000
1	2.882043000	0.597899000	-2.521169000
1	2.198712000	1.977411000	-3.425748000
15	0.820824000	1.316562000	-1.511218000
6	-0.250652000	0.391369000	-2.661040000
1	-1.221035000	0.283234000	-2.180910000
1	-0.340524000	0.939948000	-3.602157000
1	0.173051000	-0.596171000	-2.835407000
8	-0.850669000	0.287382000	0.242448000
6	-1.757813000	-0.161971000	1.214541000
1	-1.800096000	0.539438000	2.068001000
6	-1.423998000	-1.556962000	1.763244000
1	-0.433417000	-1.560210000	2.222359000
1	-2.163945000	-1.868233000	2.506719000
1	-1.405468000	-2.286326000	0.951968000
6	-3.134625000	-0.153081000	0.563561000
6	-3.342925000	-0.857372000	-0.628096000
6	-4.201977000	0.550506000	1.120867000
6	-4.590380000	-0.859360000	-1.243170000
6	-5.456767000	0.548662000	0.509263000
6	-5.653995000	-0.155086000	-0.675415000
1	-2.513442000	-1.400843000	-1.065111000
1	-4.051816000	1.106643000	2.041331000
1	-4.737070000	-1.411906000	-2.165191000
1	-6.276566000	1.100692000	0.956500000
1	-6.626966000	-0.156321000	-1.154286000

CpCoHI



E-D_3 = -351.465767818

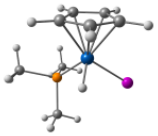
G-$D_{3,toluene,1M,\ 298.15K}$ = -351.415013

G-$D_{3,toluene,1M,\ 423.15K}$ = -351.432106

27	0.633562000	-0.421904000	0.007150000
6	2.311744000	-0.054194000	1.133564000
6	2.651617000	-0.814349000	-0.018238000
6	2.282012000	-0.040114000	-1.152244000
6	1.832202000	1.250235000	-0.692764000
6	1.849876000	1.241500000	0.701788000
1	2.341714000	-0.357119000	-2.182186000

1	1.444670000	2.036941000	-1.320811000
1	1.478848000	2.020464000	1.349212000
1	2.397689000	-0.383812000	2.157712000
1	3.035474000	-1.821381000	-0.029349000
53	-1.768934000	0.042482000	0.000119000
1	0.384209000	-1.853683000	-0.006576000

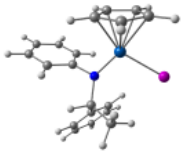
CpCoHI(PMe$_3$)



E-D$_3$ = -812.706400845
G-D$_{3,\text{toluene,1M, 298.15K}}$ = -812.550718
G-D$_{3,\text{toluene,1M, 423.15K}}$ = -812.575653

27	0.369324000	0.620108000	-0.303030000
6	1.945104000	1.982722000	-0.249302000
6	1.502109000	1.797606000	1.105609000
6	0.154777000	2.183941000	1.177945000
6	-0.247035000	2.643170000	-0.123302000
6	0.867758000	2.558764000	-0.985382000
1	-1.239730000	2.962786000	-0.395136000
1	0.881660000	2.811812000	-2.033103000
1	-0.491987000	2.093053000	2.035422000
1	2.934140000	1.780528000	-0.628940000
1	2.090234000	1.386561000	1.911856000
53	-2.012282000	-0.389264000	0.013074000
1	0.355128000	0.200563000	-1.691437000
6	3.166117000	-1.274674000	-0.235909000
1	3.595840000	-2.268457000	-0.088233000
1	3.394148000	-0.930149000	-1.245857000
1	3.614135000	-0.581276000	0.477414000
6	1.139896000	-2.032108000	1.667913000
1	1.565396000	-1.352814000	2.408745000
1	0.072678000	-2.136003000	1.866088000
1	1.631965000	-3.005364000	1.739914000
15	1.339140000	-1.305282000	-0.008128000
6	0.816525000	-2.652965000	-1.133570000
1	1.031562000	-2.357694000	-2.161312000
1	1.344344000	-3.579577000	-0.895409000
1	-0.258931000	-2.795392000	-1.033191000

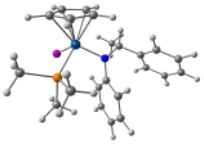
CpCoI(NPhCHMePh)



E-D$_3$ = -947.739193958
G-D$_{3,\text{toluene,1M, 298.15K}}$ = -947.480999
G-D$_{3,\text{toluene,1M, 423.15K}}$ = -947.511127

27	-1.328619000	-0.626376000	0.142815000
6	-1.707210000	-2.475669000	-0.892010000
6	-1.616190000	-2.670743000	0.506053000
6	-2.639698000	-1.885828000	1.131686000
6	-3.357445000	-1.221975000	0.106127000
6	-2.763506000	-1.556284000	-1.141440000
1	-2.817797000	-1.797980000	2.191883000
1	-4.149715000	-0.507606000	0.252896000
1	-3.039587000	-1.143910000	-2.098165000
1	-1.026933000	-2.878964000	-1.624768000
1	-0.869732000	-3.261533000	1.011967000
53	-2.097697000	1.814320000	-0.286587000
7	0.411653000	-0.429163000	0.570082000
6	1.184696000	0.520305000	1.411368000
1	1.756631000	-0.113076000	2.101494000
6	0.342898000	1.447680000	2.286277000
1	-0.454972000	0.885019000	2.777518000
1	0.991699000	1.886250000	3.049091000
1	-0.109219000	2.253849000	1.715861000
6	2.214804000	1.275634000	0.578568000
6	1.840232000	1.951096000	-0.586657000
6	3.552103000	1.305183000	0.977318000
6	2.787125000	2.650670000	-1.328994000
6	4.501190000	2.008268000	0.236857000
6	4.120202000	2.683688000	-0.919683000
1	0.805976000	1.925887000	-0.905404000
1	3.856069000	0.768783000	1.870911000
1	2.482646000	3.172273000	-2.229828000
1	5.536427000	2.021239000	0.559814000
1	4.856246000	3.228600000	-1.500316000
6	1.242867000	-1.507152000	0.137998000
6	1.496852000	-1.665570000	-1.229758000
6	1.819778000	-2.411797000	1.041792000
6	2.295739000	-2.710882000	-1.685453000
6	2.610108000	-3.460253000	0.582180000
6	2.852751000	-3.614514000	-0.782959000
1	1.069795000	-0.943765000	-1.914833000
1	1.619952000	-2.304725000	2.102076000
1	2.489553000	-2.812972000	-2.747381000
1	3.034599000	-4.162150000	1.291506000
1	3.473656000	-4.429011000	-1.137415000

CpCoI(NPhCHMePh)(PMe$_3$)



E-D$_3$ = -1408.94234711
G-D$_{3,\text{toluene,1M, 298.15K}}$ = -1408.576315
G-D$_{3,\text{toluene,1M, 423.15K}}$ = -1408.613483

27	1.148763000	-0.770058000	0.370475000
6	0.633077000	-2.612037000	1.379585000
6	1.693489000	-2.004991000	2.082805000
6	2.826813000	-1.942995000	1.210392000
6	2.457214000	-2.538858000	-0.012493000
6	1.095827000	-2.923399000	0.067201000
1	3.077632000	-2.606015000	-0.889917000
1	0.529333000	-3.385197000	-0.723191000
1	3.792389000	-1.523491000	1.434717000
1	-0.370543000	-2.740169000	1.749011000
1	1.650809000	-1.652449000	3.100523000
53	2.254962000	0.268742000	-1.770243000
6	0.758095000	1.205123000	3.205220000
1	0.973944000	2.161083000	3.688190000
1	-0.316265000	1.106223000	3.064456000
1	1.108910000	0.395091000	3.844637000
6	3.371016000	1.221281000	2.013512000
1	3.641657000	0.392716000	2.667809000
1	3.964443000	1.166119000	1.100061000
1	3.579063000	2.161844000	2.528643000
15	1.587652000	1.122113000	1.564426000
6	1.288829000	2.797177000	0.879217000
1	0.224570000	3.014716000	0.852984000
1	1.792694000	3.523895000	1.521724000

1	1.690428000	2.854099000	-0.130660000
7	-0.769076000	-0.412534000	0.122816000
6	-1.556624000	-1.380136000	-0.689871000
1	-1.304881000	-2.366493000	-0.299310000
6	-1.260189000	-1.432127000	-2.197702000
1	-0.198269000	-1.618840000	-2.359907000
1	-1.840167000	-2.232986000	-2.667835000
1	-1.505143000	-0.499410000	-2.705922000
6	-3.042263000	-1.204502000	-0.373856000
6	-3.907734000	-0.448333000	-1.167066000
6	-3.549287000	-1.771217000	0.800042000
6	-5.239096000	-0.263184000	-0.797910000
6	-4.878217000	-1.595007000	1.173153000
6	-5.730384000	-0.834859000	0.372652000
1	-3.540494000	0.020715000	-2.070808000
1	-2.885881000	-2.352073000	1.433380000
1	-5.891173000	0.334676000	-1.425364000
1	-5.249958000	-2.049408000	2.085440000
1	-6.766320000	-0.691066000	0.659184000
6	-1.246392000	0.919169000	-0.023595000
6	-1.069597000	1.712386000	-1.170604000
6	-2.005510000	1.463924000	1.027017000
6	-1.606938000	2.995048000	-1.249195000
6	-2.542204000	2.746048000	0.952497000
6	-2.339767000	3.523285000	-0.187626000
1	-0.483100000	1.326387000	-1.990489000
1	-2.201709000	0.832101000	1.884818000
1	-1.445683000	3.587039000	-2.144055000
1	-3.132046000	3.131941000	1.777166000
1	-2.756023000	4.522469000	-0.251589000
6	-0.444904000	3.947946000	0.693317000
6	0.192283000	2.731559000	0.008990000
1	-0.736684000	1.223948000	1.213219000
1	-2.741021000	0.892776000	-0.200686000
1	-2.042850000	1.933109000	-1.484134000
1	-3.718519000	3.163640000	-0.152144000
1	-2.874899000	2.749698000	1.381173000
1	-2.306680000	5.058942000	0.702822000
1	-1.785512000	4.498973000	-0.926657000
1	0.191137000	4.842477000	0.519044000
1	-0.497798000	3.774424000	1.790948000
1	1.176261000	2.571937000	0.492126000
1	0.362964000	2.960925000	-1.066265000
6	-0.854370000	-1.533064000	-0.338399000
6	-1.977744000	-1.811569000	-1.333761000
6	-2.676191000	-3.142322000	-1.016888000
6	-3.186203000	-3.170508000	0.429829000
6	-2.049197000	-2.886901000	1.420031000
6	-1.371183000	-1.548983000	1.100916000
1	-0.140832000	-2.352321000	-0.464148000
1	-1.557271000	-1.866660000	-2.361558000
1	-2.730299000	-0.999524000	-1.325200000
1	-3.532923000	-3.281933000	-1.710738000
1	-1.966836000	-3.983969000	-1.177468000
1	-3.621351000	-4.169709000	0.646542000
1	-3.989503000	-2.411563000	0.556505000
1	-2.460897000	-2.853572000	2.451686000
1	-1.299567000	-3.707573000	1.376523000
1	-0.532969000	-1.386144000	1.809733000
1	-2.108124000	-0.736765000	1.261571000

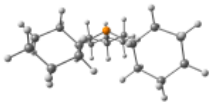
C. Cobalt complexes (full molecules, QM/MM)

PCy_3

$E\text{-}D_3$ = -461.157393622

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -460.660579

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -460.683928



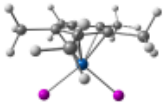
15	0.110132000	0.034111000	-0.841853000
6	1.817098000	-0.108890000	0.034774000
6	2.853229000	0.572832000	-0.861590000
6	4.250756000	0.541572000	-0.231786000
6	4.685175000	-0.899021000	0.051268000
6	3.653470000	-1.612393000	0.929375000
6	2.253079000	-1.552662000	0.302130000
1	1.774553000	0.405003000	1.001543000
1	2.576608000	1.629644000	-1.049851000
1	2.887143000	0.063648000	-1.850622000
1	4.978220000	1.013607000	-0.926757000
1	4.249170000	1.127317000	0.713902000
1	5.668526000	-0.892734000	0.568772000
1	4.804316000	-1.449709000	-0.907821000
1	3.953626000	-2.674747000	1.057153000
1	3.631721000	-1.140353000	1.936488000
1	1.556490000	-2.035111000	1.016225000
1	2.249059000	-2.134589000	-0.645986000
6	-0.672797000	1.473811000	0.146818000
6	-2.080022000	1.758248000	-0.385934000
6	-2.722636000	2.969392000	0.301247000
6	-1.847718000	4.213493000	0.146639000

Cp^*CoI_2

$E\text{-}D_3$ = -362.343533548

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -362.153225

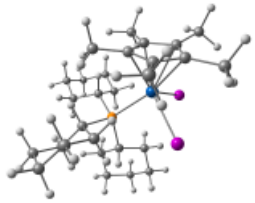
$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -362.171742



27	0.002827000	0.647062000	0.019505000
6	-0.644893000	2.319142000	-1.012614000
6	-1.179083000	2.377585000	0.308439000
6	-0.079606000	2.354806000	1.217609000
6	1.138689000	2.369455000	0.459914000
6	0.791197000	2.335319000	-0.918067000
53	1.842544000	-1.038053000	-0.247334000
53	-1.864275000	-1.030017000	0.106144000
6	2.526514000	2.352177000	1.023904000
1	2.512270000	2.212456000	2.123779000
1	3.123480000	1.534409000	0.575756000
1	3.022241000	3.318579000	0.796994000
6	-0.168170000	2.250500000	2.708314000
1	-1.221845000	2.206847000	3.049993000
1	0.351273000	1.330409000	3.048082000
1	0.314727000	3.136733000	3.169766000
6	-2.628908000	2.368311000	0.683247000
1	-3.273698000	2.222728000	-0.207205000
1	-2.836980000	1.555038000	1.407360000
1	-2.889022000	3.339110000	1.153421000
6	-1.445312000	2.196007000	-2.271166000
1	-0.787318000	2.099289000	-3.158412000
1	-2.095947000	1.299117000	-2.216795000
1	-2.077370000	3.099519000	-2.396051000

6	1.738420000	2.228573000	-2.071513000
1	2.791694000	2.191882000	-1.727180000
1	1.522470000	1.306125000	-2.649385000
1	1.614098000	3.111196000	-2.732495000

$Cp^*CoI_2(PCy_3)$



$E\text{-}D_3$ = -823.53562656

$G\text{-}D_{3,toluene,1M,\ 298.15K}$ = -822.807379

$G\text{-}D_{3,toluene,1M,\ 423.15K}$ = -822.839182

27	-1.520389000	-0.494180000	-1.511120000
6	-2.458658000	1.129857000	-2.779046000
6	-2.710083000	1.426680000	-1.410739000
6	-3.500130000	0.362365000	-0.865936000
6	-3.777095000	-0.557394000	-1.920346000
6	-3.094434000	-0.119834000	-3.076425000
53	-1.933832000	-3.025738000	-0.819343000
53	0.280216000	-1.107612000	-3.345839000
15	0.255118000	-0.061739000	0.211252000
6	1.000023000	1.661834000	-0.154690000
6	1.162502000	1.833205000	-1.655401000
6	1.581838000	3.263420000	-2.020133000
6	2.884942000	3.646072000	-1.312101000
6	2.761207000	3.441292000	0.201454000
6	2.328979000	2.004584000	0.527835000
1	0.247656000	2.368238000	0.199361000
1	1.924541000	1.120778000	-2.039459000
1	0.203922000	1.612885000	-2.144627000
1	1.725724000	3.334531000	-3.119665000
1	0.778888000	3.977145000	-1.733825000
1	3.120530000	4.711412000	-1.522569000
1	3.719550000	3.024815000	-1.705558000
1	3.742989000	3.647719000	0.679742000
1	2.020339000	4.159421000	0.617433000
1	2.246914000	1.928123000	1.626232000
1	3.128265000	1.315164000	0.181709000
6	-0.656238000	0.117647000	1.872296000
6	0.053333000	0.958967000	2.933764000
6	-0.793301000	1.101437000	4.205271000
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6	-1.945272000	-1.072468000	3.701127000
6	-1.101386000	-1.231855000	2.430760000
1	-1.551720000	0.655580000	1.571094000
1	0.219692000	1.983262000	2.545337000
1	1.029427000	0.510034000	3.202006000
1	-0.210933000	1.653712000	4.974030000
1	-1.708756000	1.692547000	3.980240000
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1	-0.280854000	-0.823267000	5.078852000
1	-2.189460000	-2.077086000	4.108693000
1	-2.902326000	-0.561678000	3.455338000
1	-1.720572000	-1.755915000	1.686102000
1	-0.232823000	-1.876572000	2.659084000
6	1.759609000	-1.230872000	0.289380000
6	1.391850000	-2.669662000	-0.046370000
6	2.633170000	-3.570023000	-0.121955000
6	3.435502000	-3.517531000	1.180472000
6	3.798747000	-2.072560000	1.531237000
6	2.539900000	-1.200604000	1.611635000
1	2.394006000	-0.854200000	-0.517418000
1	0.905229000	-2.709817000	-1.034155000
1	0.694276000	-3.072126000	0.718693000
1	2.315483000	-4.617502000	-0.314259000
1	3.277358000	-3.247573000	-0.969724000
1	4.365670000	-4.114432000	1.065264000
1	2.838636000	-3.964943000	2.005718000
1	4.322650000	-2.054987000	2.511307000
1	4.491973000	-1.661538000	0.764325000
1	2.862745000	-0.183483000	1.877133000
1	1.915836000	-1.572970000	2.445493000
6	-2.356162000	2.693328000	-0.692003000
1	-3.239553000	3.364371000	-0.690661000
1	-2.073258000	2.491197000	0.356767000
1	-1.516278000	3.221609000	-1.178042000
6	-4.078272000	0.270120000	0.511644000
1	-5.185901000	0.283060000	0.445006000
1	-3.760494000	-0.677971000	0.988813000
1	-3.770297000	1.123424000	1.146403000
6	-4.808841000	-1.644157000	-1.897615000
1	-4.433328000	-2.549060000	-2.417294000
1	-5.082041000	-1.915808000	-0.857404000
1	-5.718946000	-1.291736000	-2.425693000
6	-3.097616000	-0.832709000	-4.392223000
1	-2.422828000	-0.339419000	-5.120707000
1	-2.762266000	-1.881147000	-4.251035000
1	-4.126782000	-0.835170000	-4.807245000
6	-1.785781000	1.997328000	-3.802888000
1	-1.390926000	2.933728000	-3.365580000
1	-0.952238000	1.455507000	-4.290103000
1	-2.525651000	2.275302000	-4.581860000

7. References

1. B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Adv. Synth. Catal*., 2014, **356**, 1491-1495.
2. W.-C. Gao, S. Jiang, R. L. Wang, C. Zhang, *Chem. Commun*., 2013, **49**, 4890-4892.
3. M. H. Juarez, J.–L. Serraho, P. Lara, J. P. Morales-Cerón, M. Vaquero, E. Álvarez, V. Salazar, A. Suárez, *Chem. Eur. J*., 2015, **21**, 7540-7555.
4. W. Tang, S. Johnston, S. Li, S. Iggo, J. Bacsa, J. Xiao, *Chem. Eur. J*., **2013**, *19*, 14187-14193.
5. E. D. Julian, E. –M. Pedregal, M. Claros, M. Vaquero, J. Diez, E. Lastra, P. Gamasa, A. Pizzano. *Org. Chem. Front*, **2018**, *5*, 841-849.
6. A. V. Malkov, K. Vranková, S. Stončius, P. Kočovský, *J. Org. Chem*., **2009**, *74*, 5839-5849.
7. X. Zhu, H. Du, *Org. Biomol. Chem*., **2015**, *13*, 1013-1016.
8. D. Pi, H. Zhou, P. Cui, R. He, Y. Sui, *ChemistrySelect*, **2017**, *2*, 3967-3979.
9. T. Wang, L.-G. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, A. S. C. Chan, *J. Am. Chem. Soc*., **2011**, *133*, 9878-9891.
10. X- Y. Zhou, M. Bao, Y.-G. Zhou, *Adv. Synth. Catal*., **2011**, *353*, 84-88.
11. G. Tseberlidis, P. Zardi, A. Caselli, D. Cancogni, M. Fusari, L. Lay, E. Gallo, *Organometallics*, **2015**, *34*, 3774-3781.
12. T. Vaijayanthi, A. Chadha, *Tetrahedron: Asymmetry*., **2008**, *19*, 93-96.
13. D. R. Wallach, P. C. Stege, J. P. Shah, J. D. Chisholm, *J. Org. Chem*., **2015**, *80*, 1993-2000.
14. X- Y. Liu, Z. Guo, S. S. Dong, X- H. Li, C.-M. Che, *Chem. Eur. J*., **2011**, *17*, 12932-12945.
15. X. Xu, H. Feng, L. Huang, X. Liu, *J.Org. Chem*., **2018**, *83*, 7962-7969.
16. T. Verdelet, R. M. Ward, D. G. Hall, *Eur. J. Org. Chem*, **2017**, *38*, 5729-5738.
17. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01*. Gaussian, Inc.: Wallingford CT, 2009.
18. M. Reiher, *Inorg. Chem.* **2002,** *41*, 6928-6935.
19. A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Hoellwarth, V. Jonas, K. F. Koehler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111-114.
20. A. Höllwarth, M. Böhme, S. Dapprich, A. Ehlers, A. Gobbi, V. Jonas, K. Kohler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 237-240.
21. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*.
22. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
23. V. S. Bryantsev, M. S. Diallo, W. A. Goddard III, *J. Phys. Chem. B* **2008**, *112*, 9709-9719.
24. A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skiff, Uff, *J. Am. Chem. Soc.* **1992**, *114*, 10024-10035.
25. D. Balcells, A. Nova, E. Clot, D. Gnanamgari, R. H. Crabtree, O. *Organometallics* **2008**, *27*, 2529-2535.
26. H. Li, G. Lu, J. Jiang, F. Huang, Z.-X. Wang, *Organometallics* **2011**, *30*, 2349-2363.
27. A. Bartoszewicz, G. G. Miera, R. Marcos, P. –O. Norrby, B. Martin-Matute, *ACS Catal.* **2015**, *5*, 3704-3716.
28. D.-D. Zhang, X.-K. Chen, H.-L. Liu, H.-L. Huang, *RSC Adv*., **2016**, *6*, 87362-67372.
29. M. L. H. Green, R. B. A. Pardy, *J. Chem. Soc., Dalton Trans*. **1979**, (1972-1979), 355-360.
30. J.O kuda, K. H. Zimmermann, *Chem. Ber*. **1990**, *123*, 1641-1648.
31. H. Werner, L. Scheller, *Polyhedron*, **2012**, *34*, 13-23.

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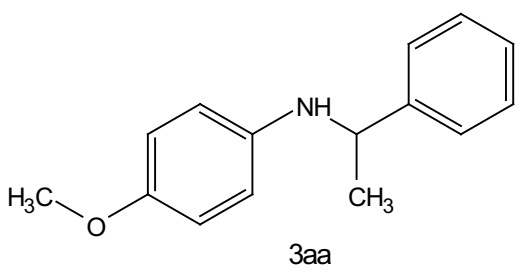
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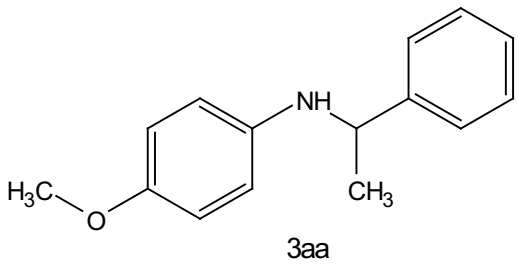
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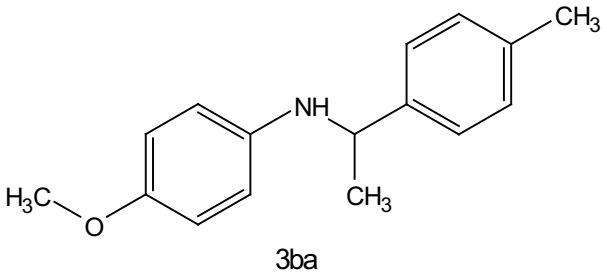
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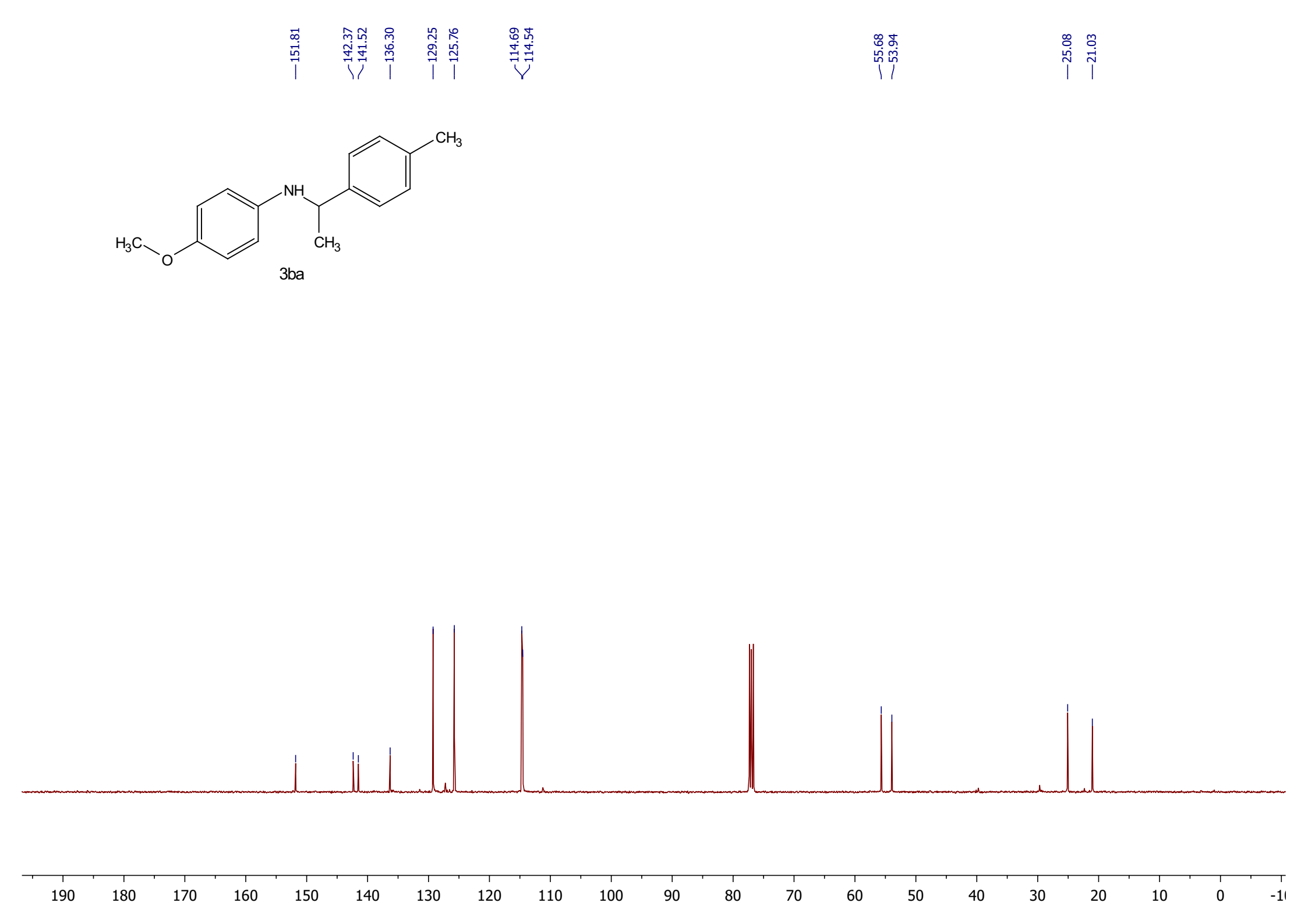
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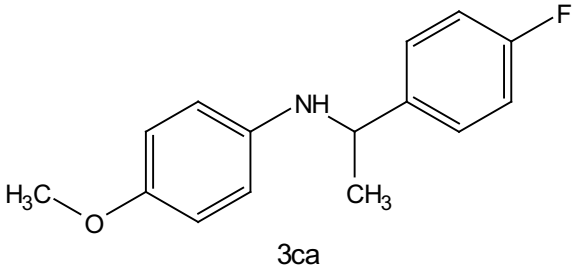
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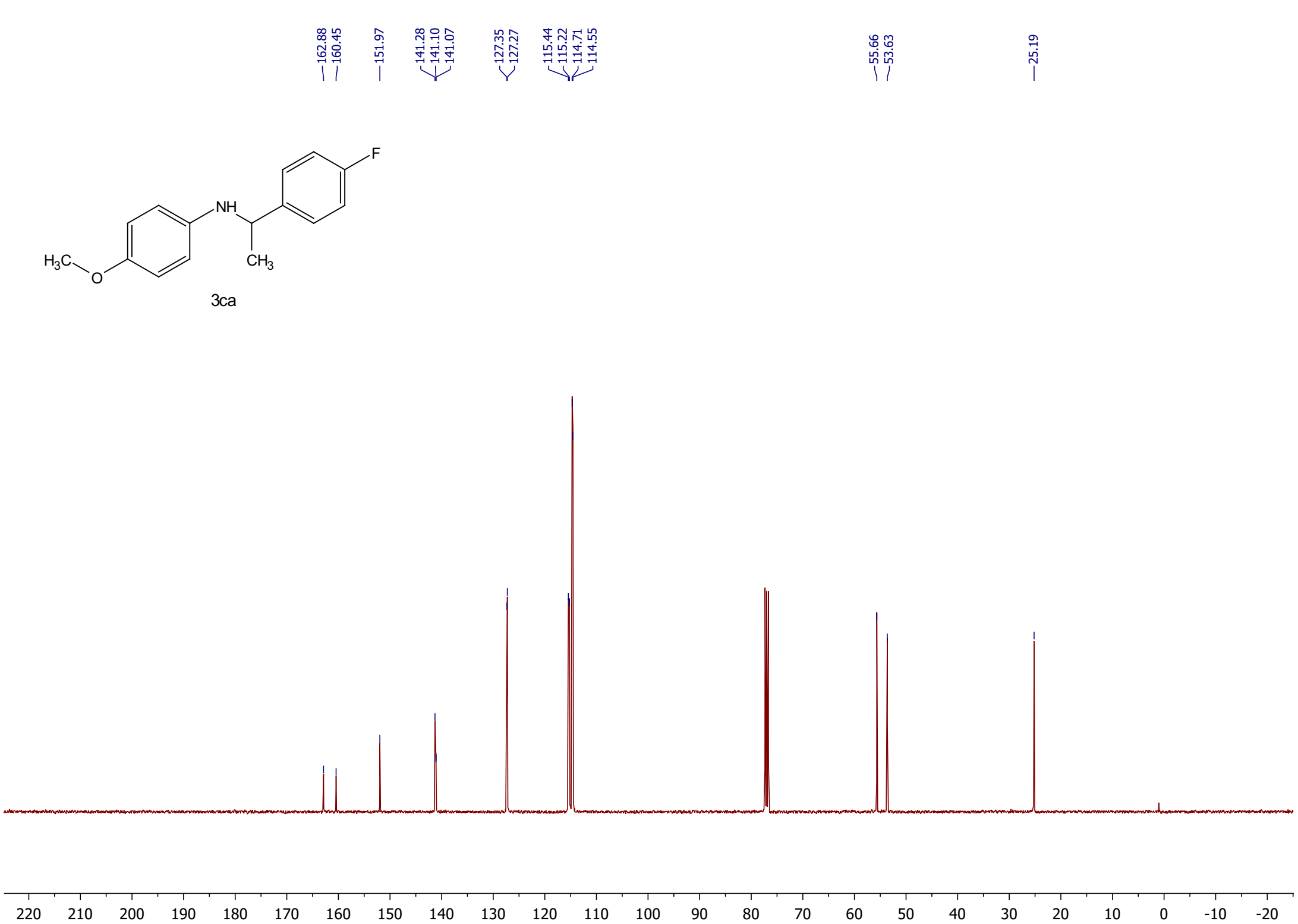
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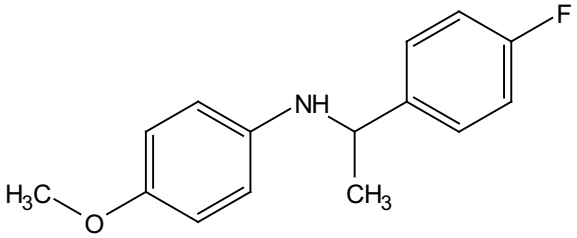

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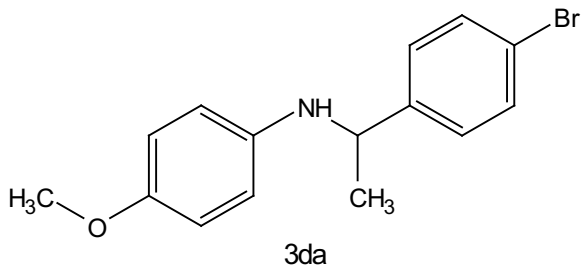
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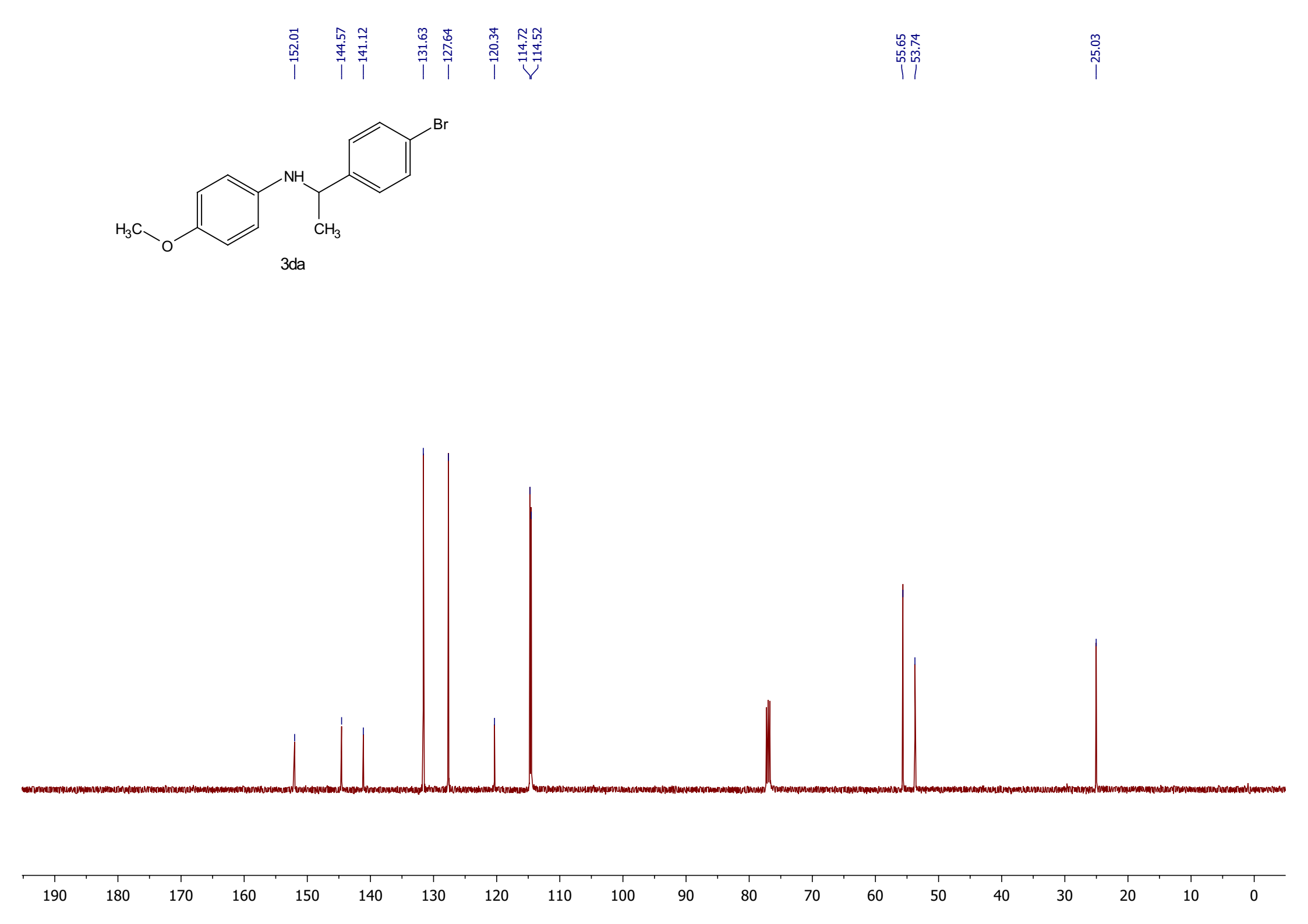
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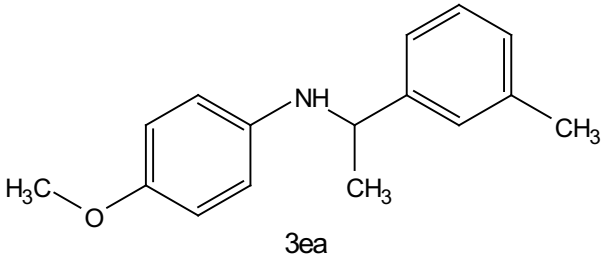
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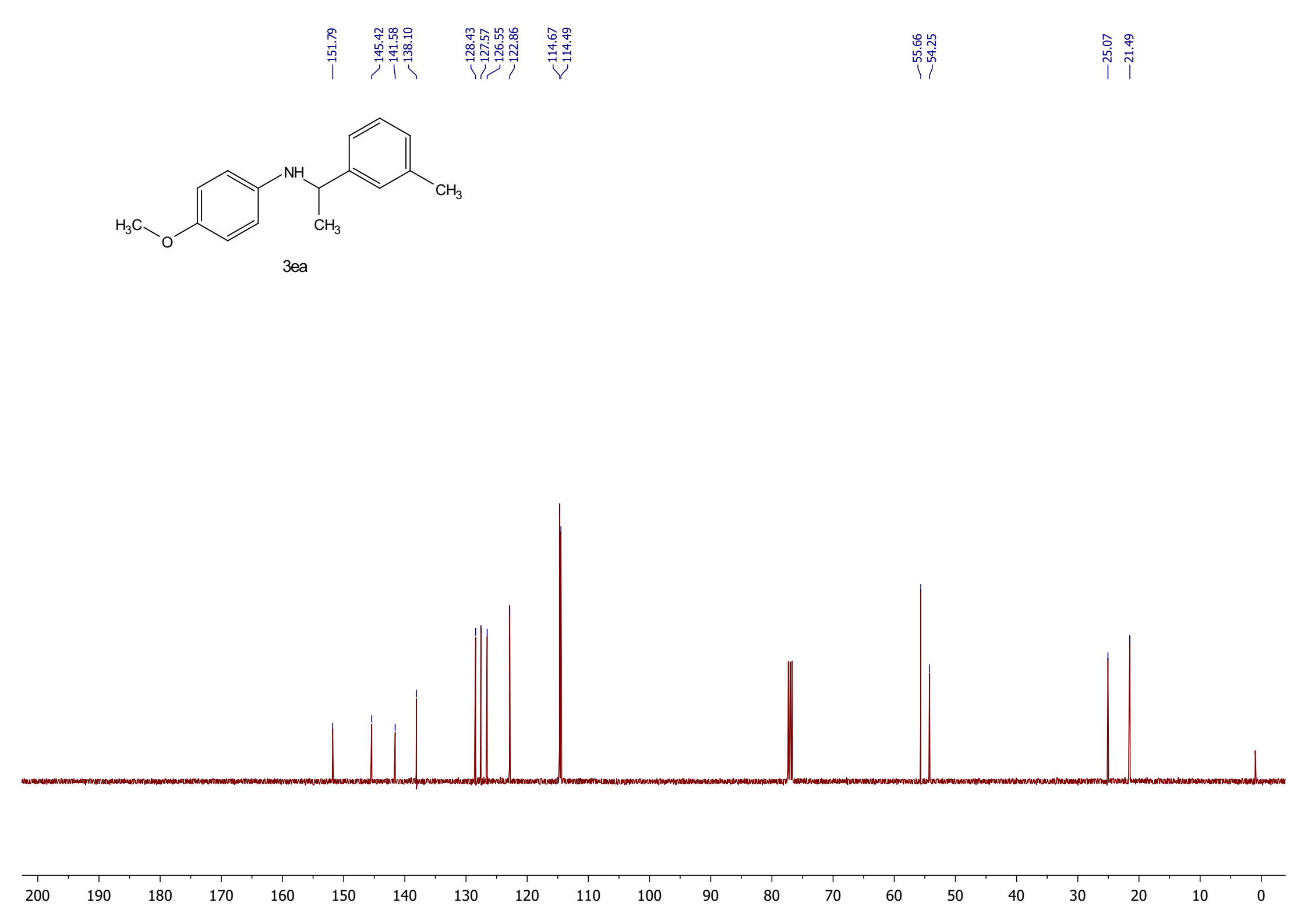
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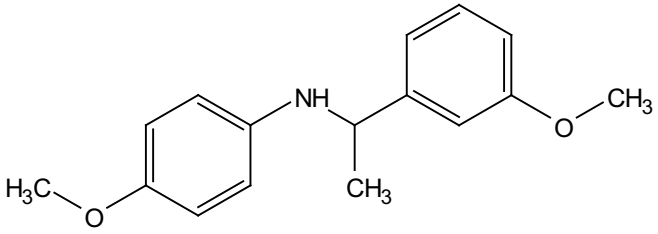
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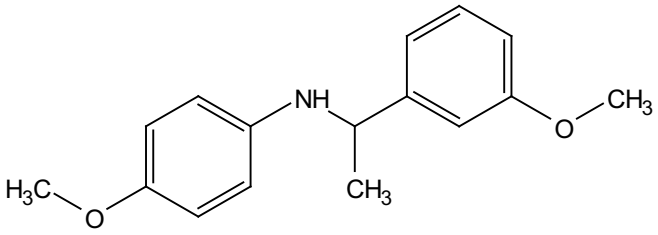
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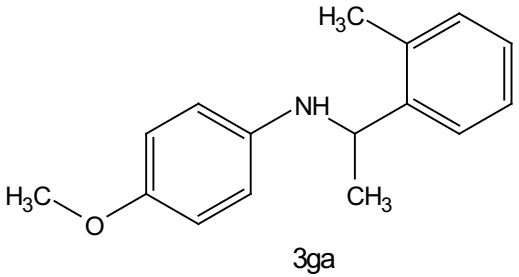
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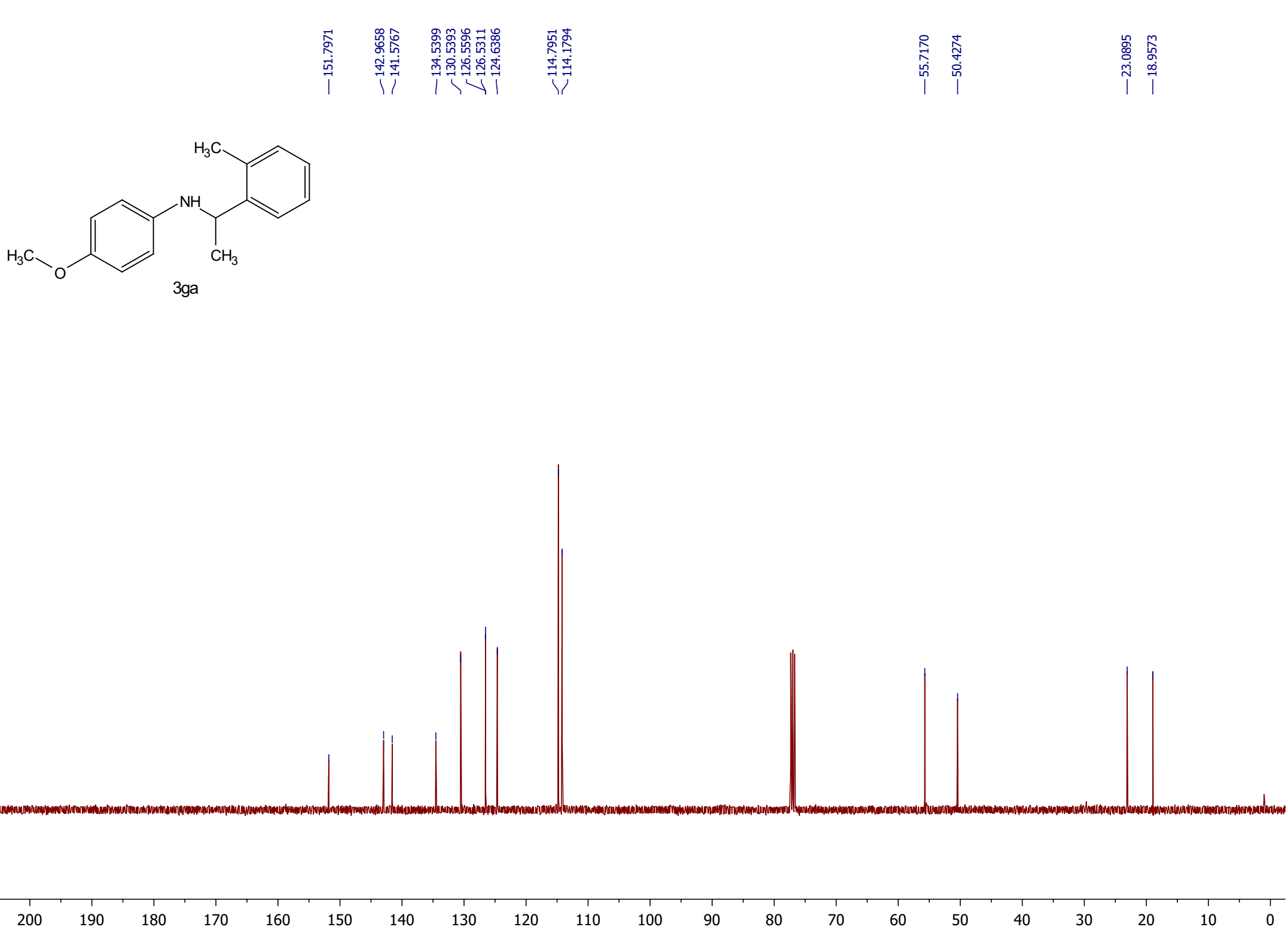
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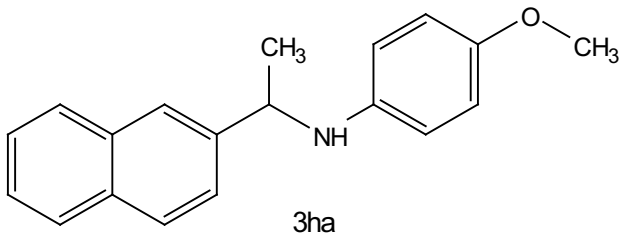
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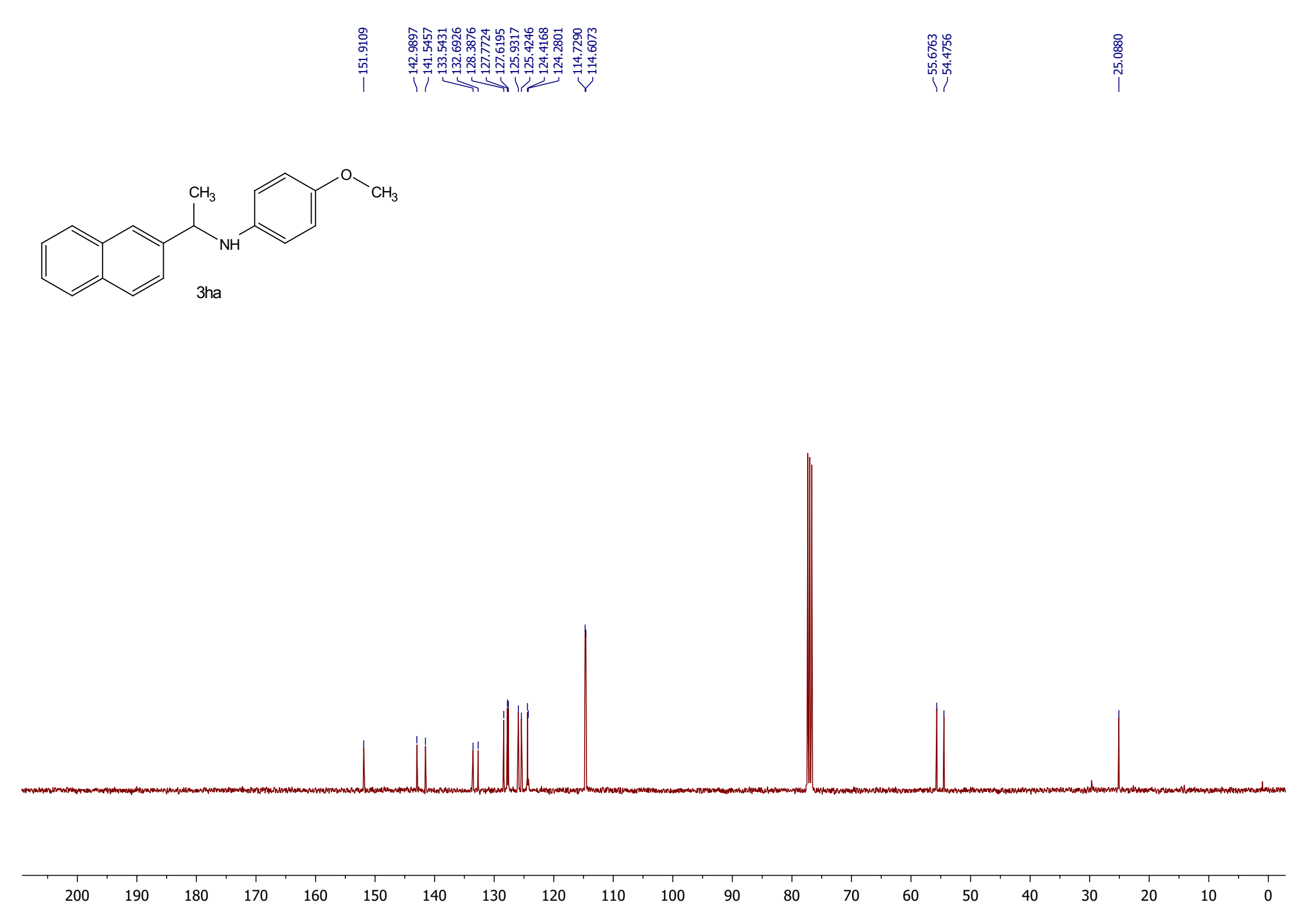
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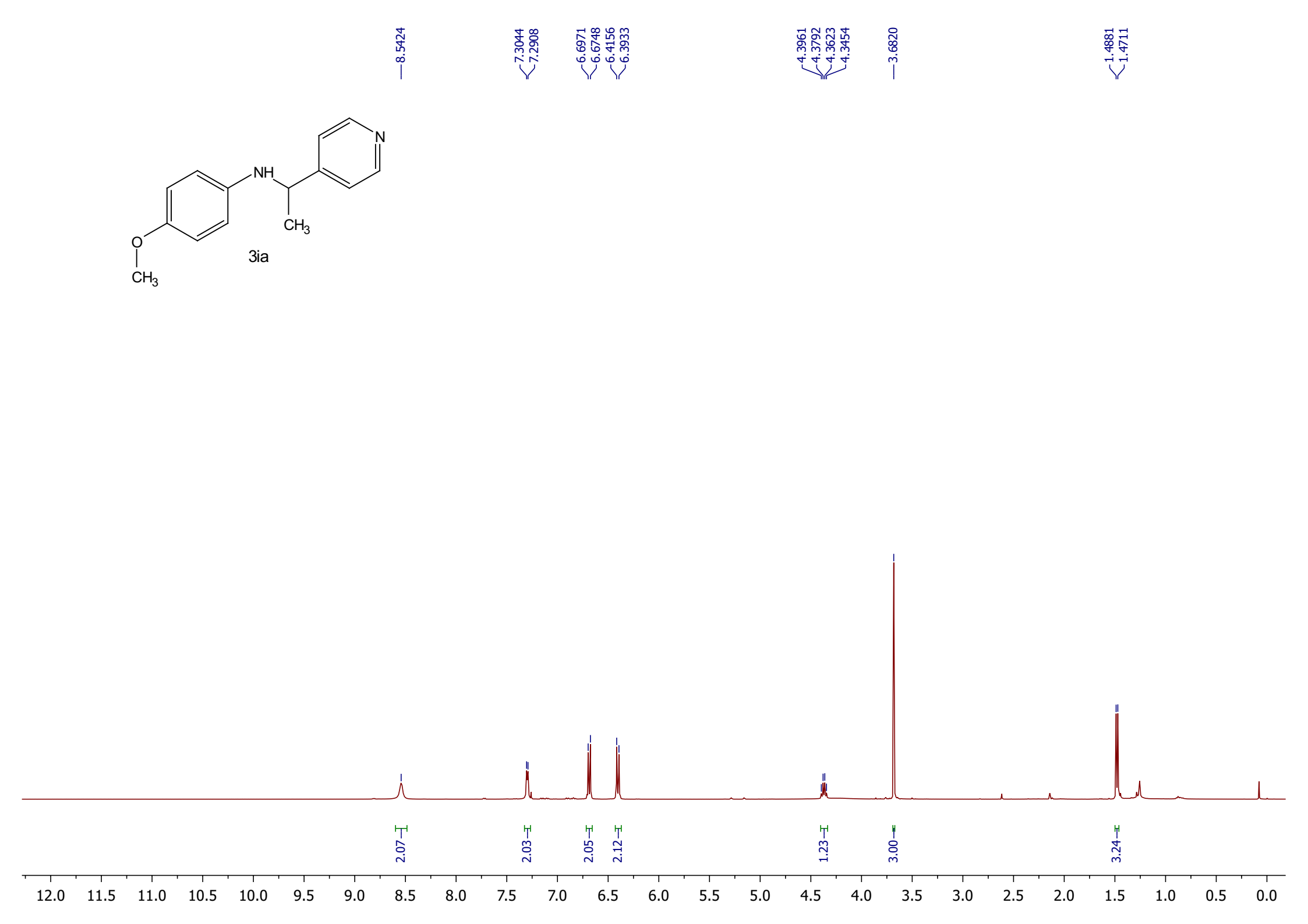
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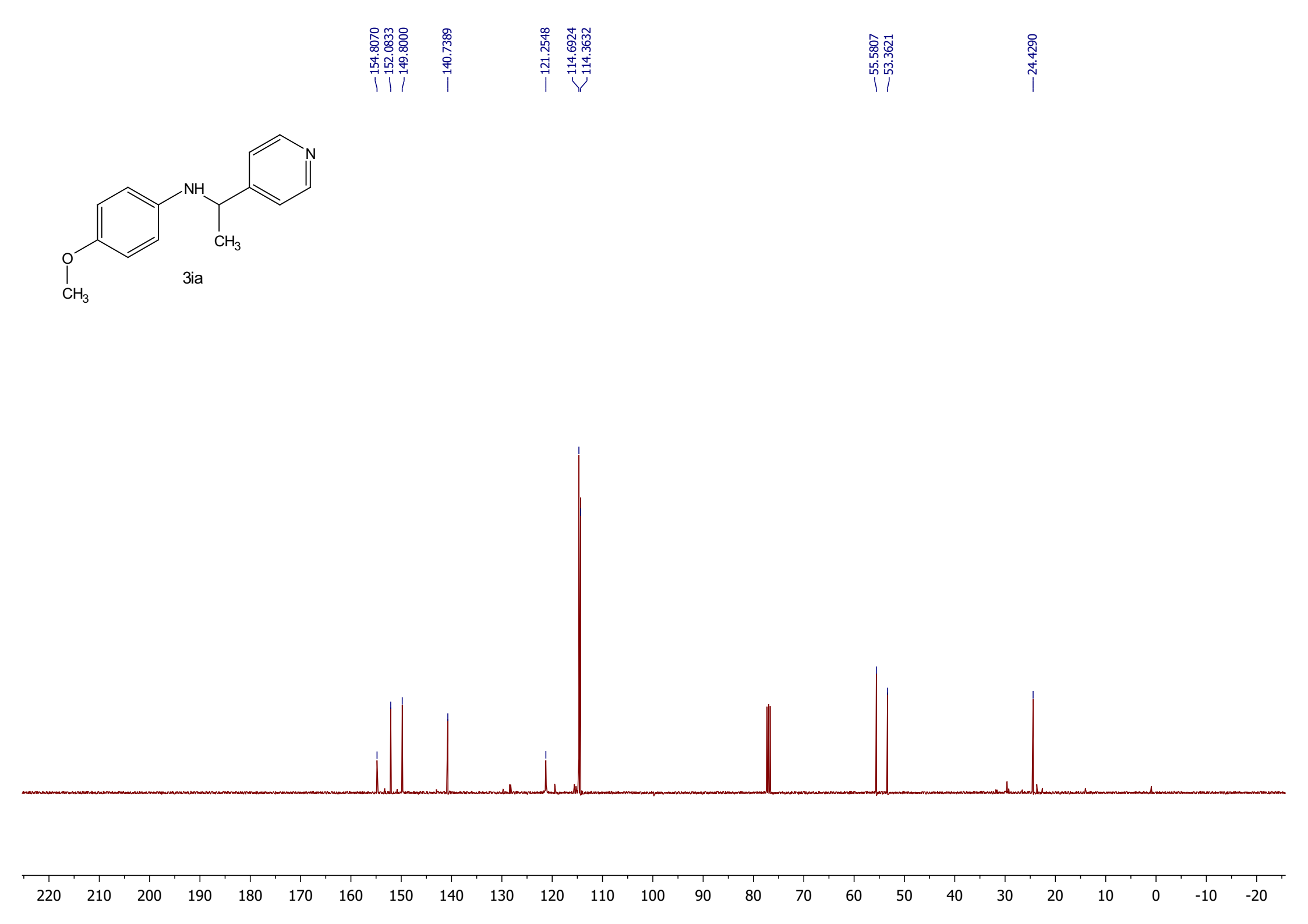
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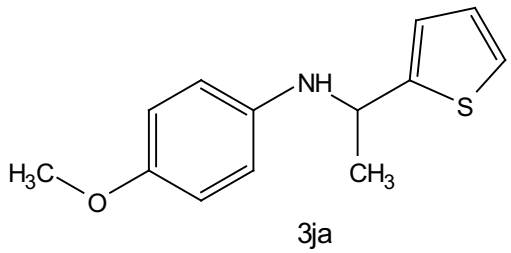
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6.74
6.61
6.59
4.77
4.75
4.72
3.73
1.62
1.60
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1.83
1.97
1.93
0.98
2.93
3.04
10.5
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8.0
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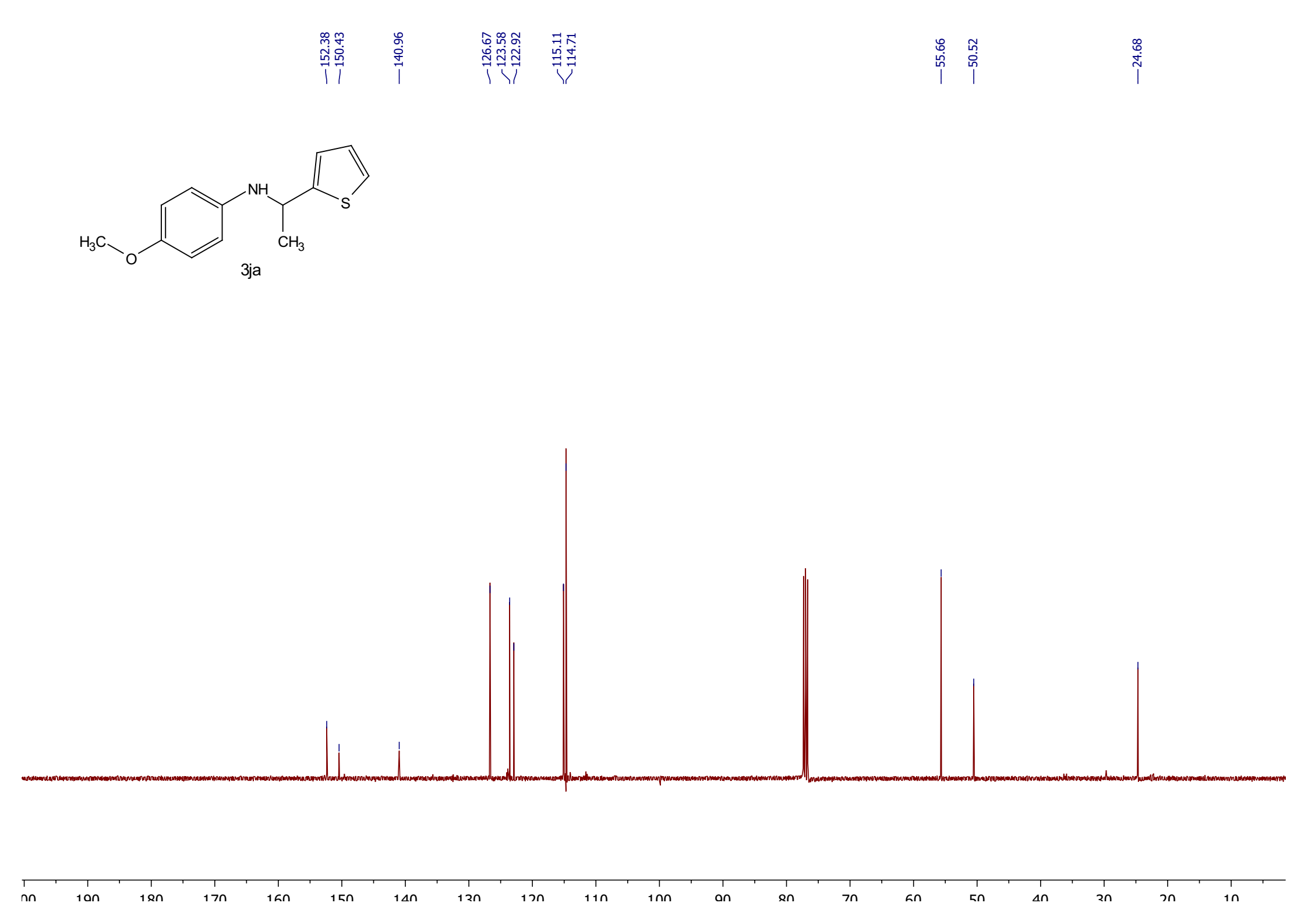
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NH
S
H_3C
O
CH_3
3ja
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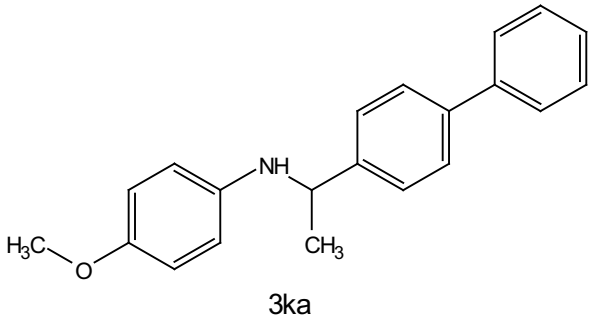
NH
H3C
O
CH3

3ka

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4.4892
4.4726
4.4558
4.4391
3.7018
1.5477
1.5309
3.93
3.90
1.10
1.70
1.78
1.00
2.72
3.05
12.0
11.5
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9.5
9.0
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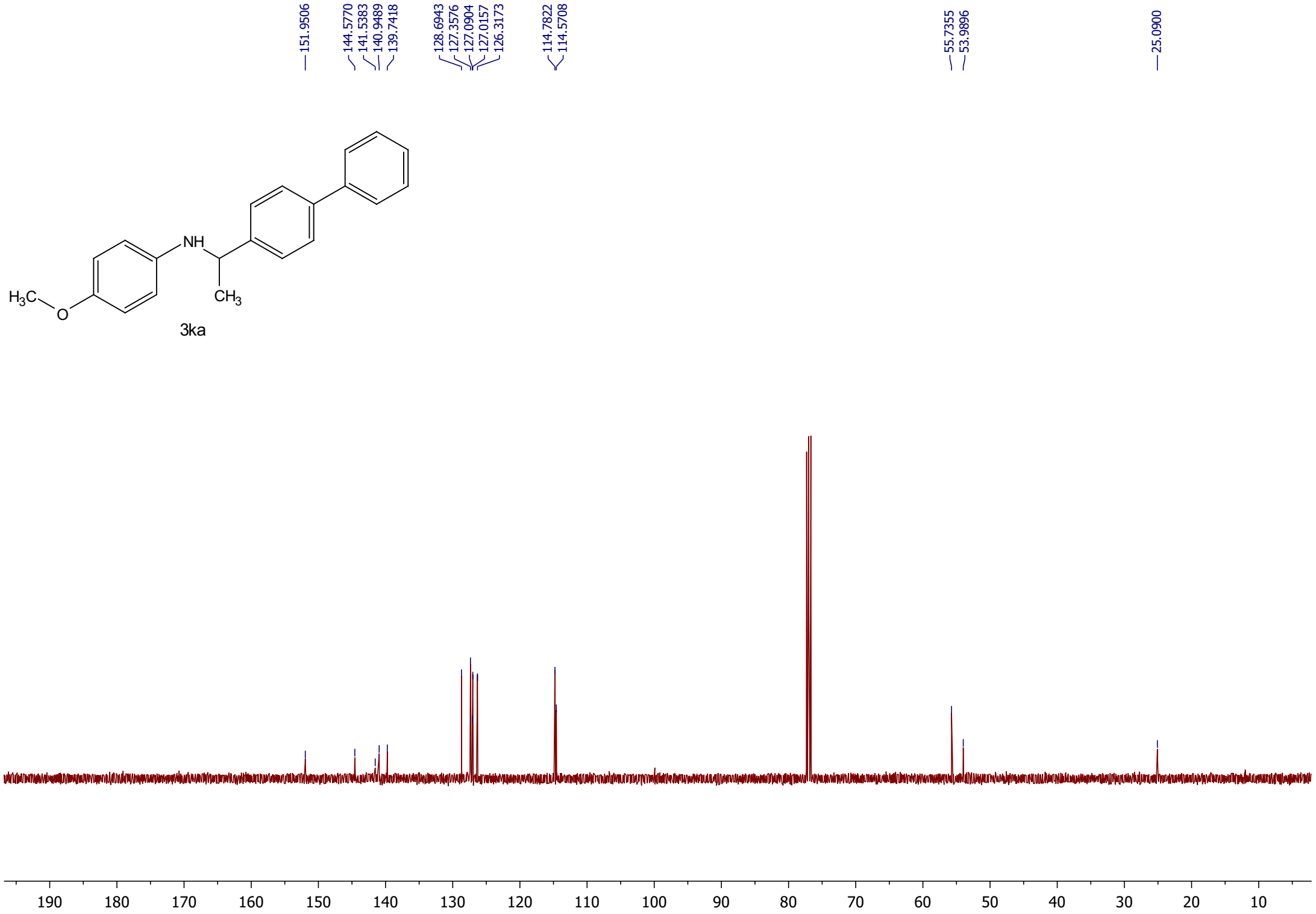
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53.9896
25.0900
NH
H3C
O
CH3
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120
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20
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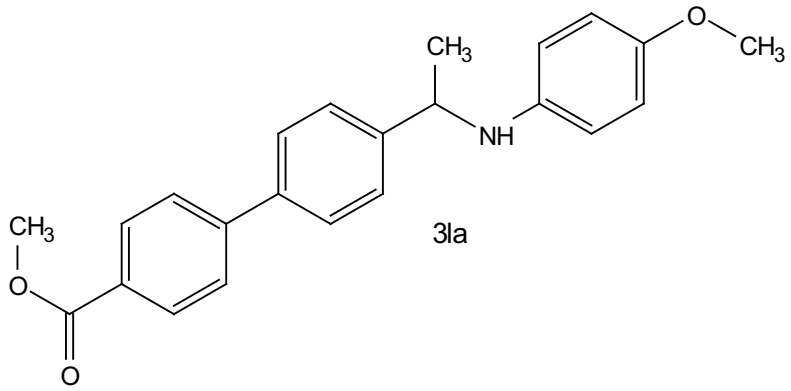
CH3
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CH3
NH
CH3
O
O

3la

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6.7203
6.7146
6.6979
6.5198
6.5108
6.4884
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4.4625
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3.6977
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2.19
1.94
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1.84
1.00
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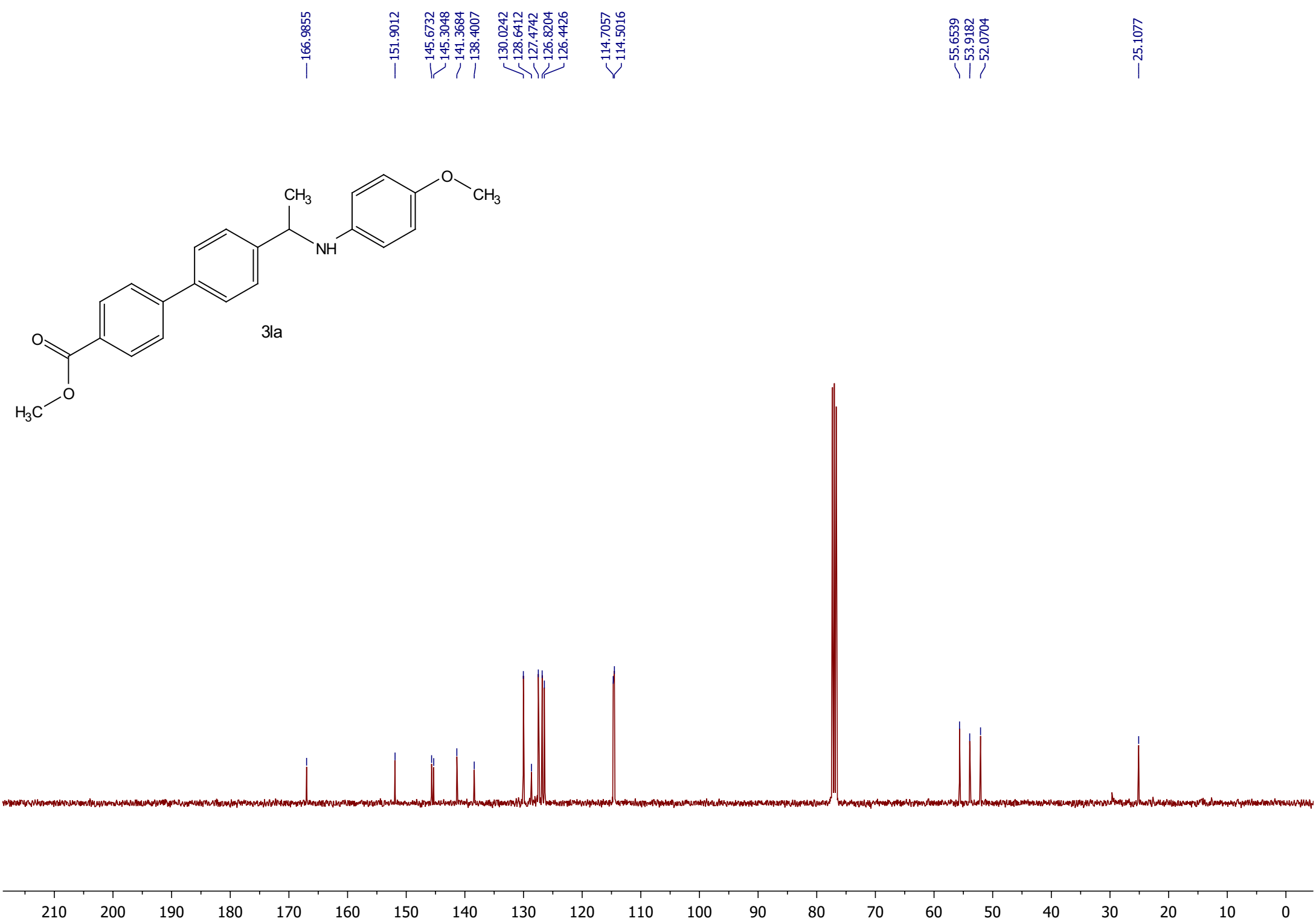
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126.8204
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114.7057
114.5016
55.6539
53.9182
52.0704
25.1077
CH3
O
CH3
NH
O
O
H3C
3la
210
200
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180
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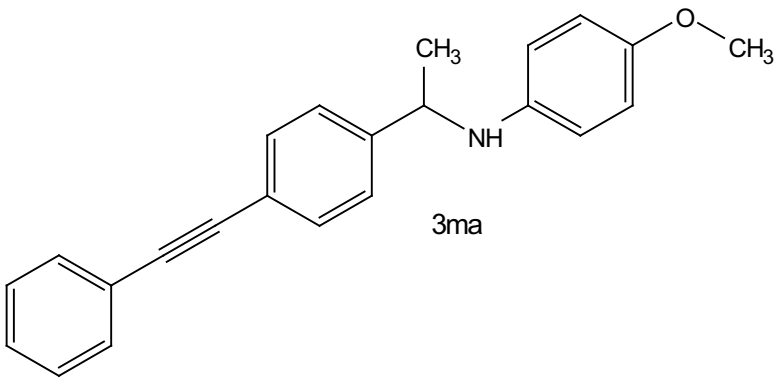
CH3
O
CH3
NH

3ma

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6.4461
4.4401
4.4234
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3.7000
1.5094
1.4926
3.64
4.70
1.83
1.95
1.00
2.91
3.04
12.5
12.0
11.5
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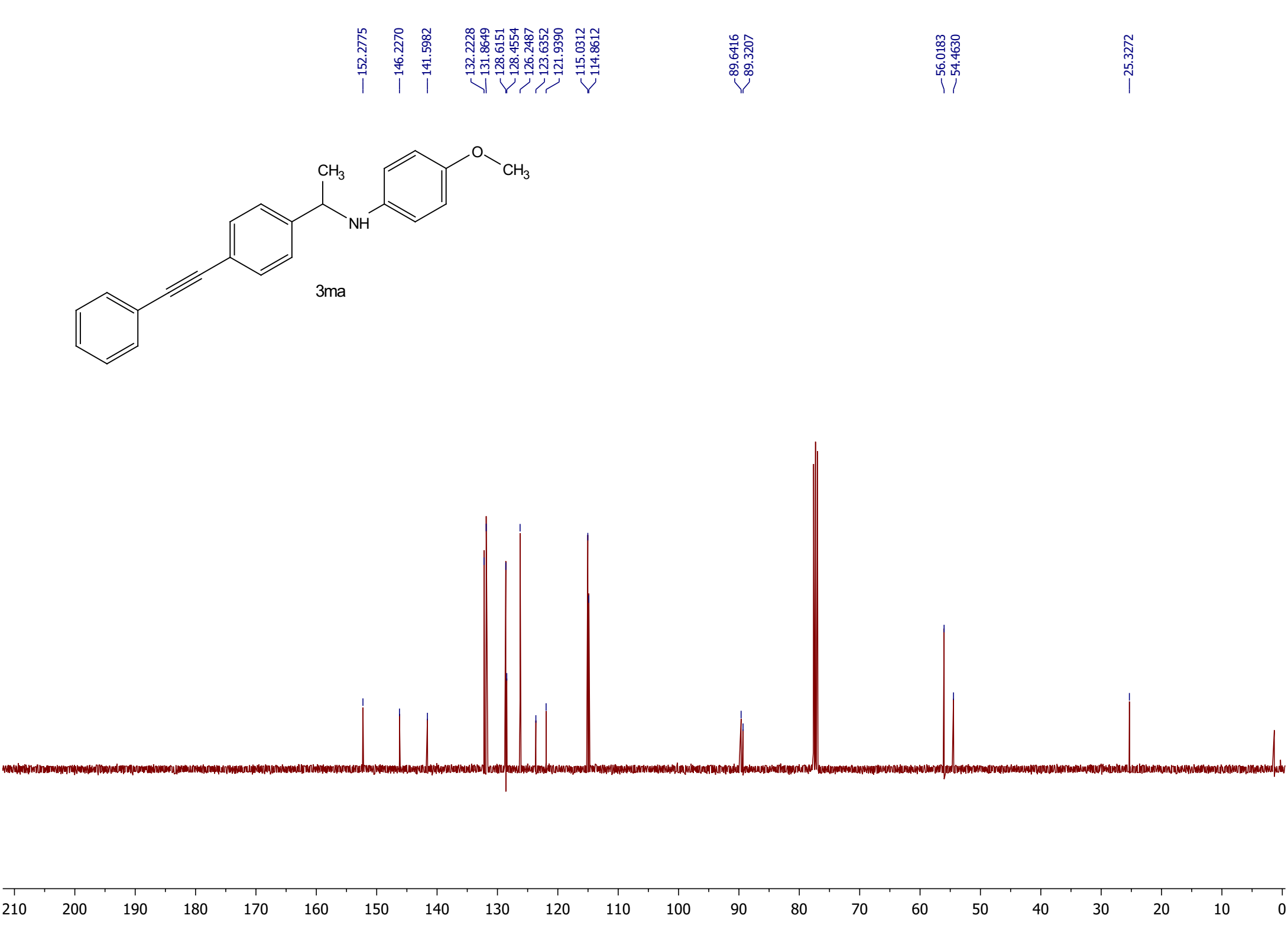
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114.8612
89.6416
89.3207
56.0183
54.4630
25.3272
CH3
NH
O
CH3
3ma
210
200
190
180
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150
140
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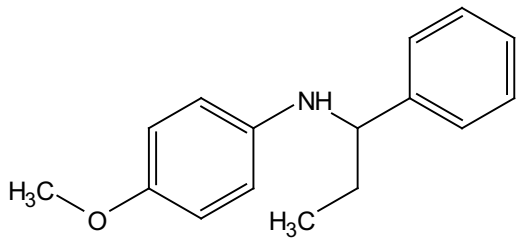
NH
H3C
O
H3C

3na

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7.2190
6.7158
6.6935
6.5052
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4.1741
4.1574
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1.8607
1.8191
1.8023
1.7843
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0.9653
0.9467
3.65
0.94
1.80
1.88
1.00
2.82
2.16
3.06
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8.5
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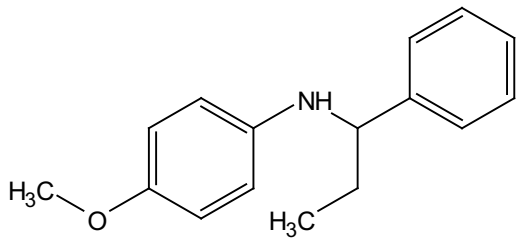
NH
H3C
O
H3C

3na

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55.6845
31.6322
10.7757
220
210
200
190
180
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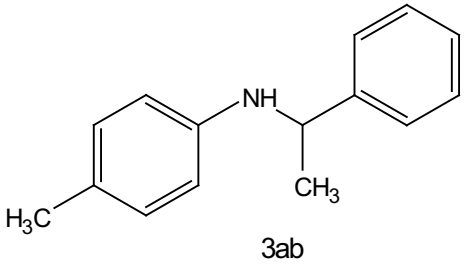
-10
-20


NH
CH3
H3C

3ab

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6.45
4.50
4.49
4.47
4.45
2.21
1.53
1.52
1.90
1.96
1.01
1.88
1.94
1.05
3.08
3.18
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10.5
10.0
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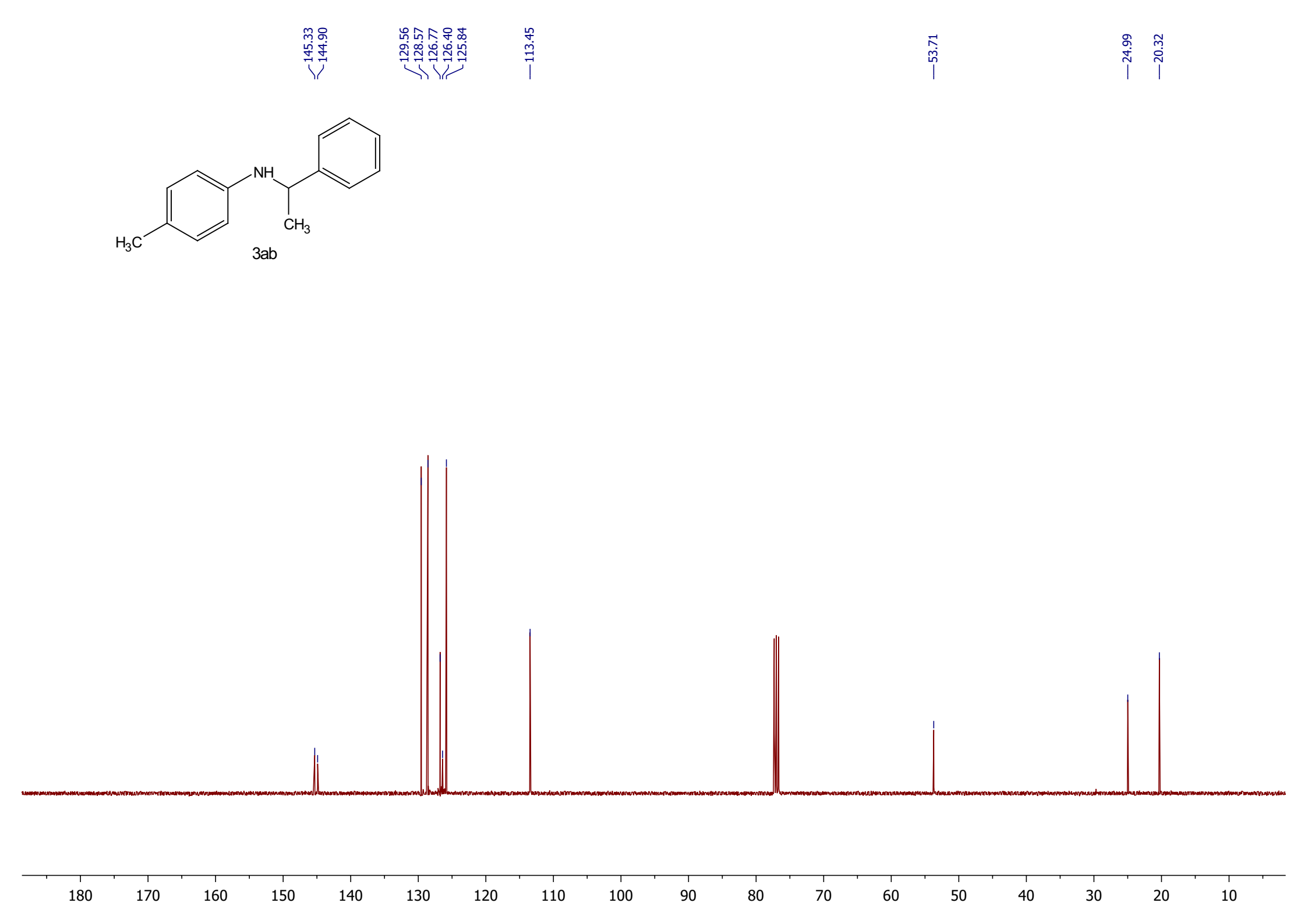
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20.32
NH
CH3
H3C
3ab
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160
150
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120
110
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20
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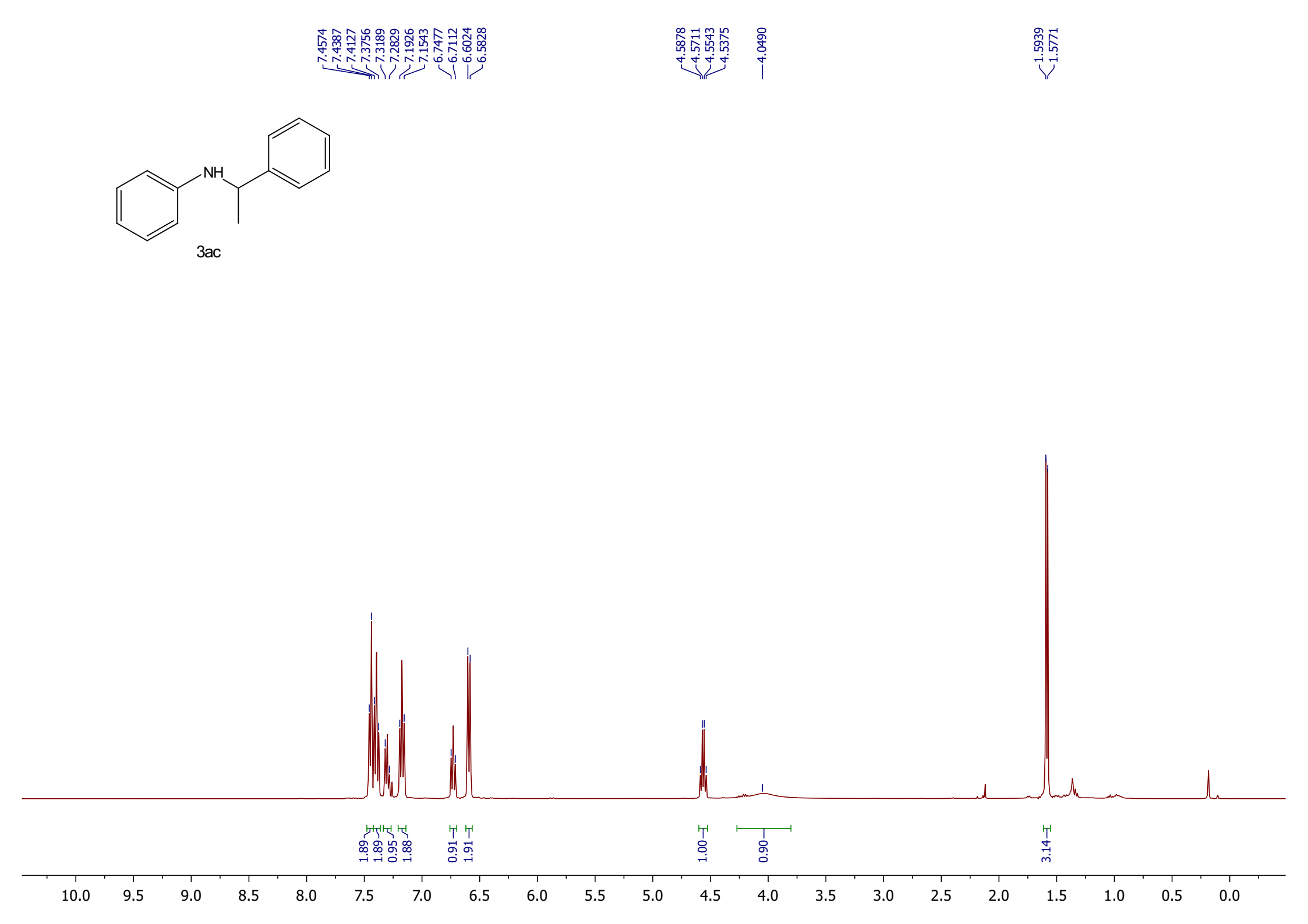
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4.5375
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1.5939
1.5771
NH
3ac
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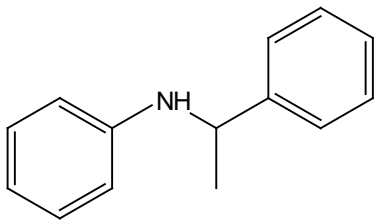

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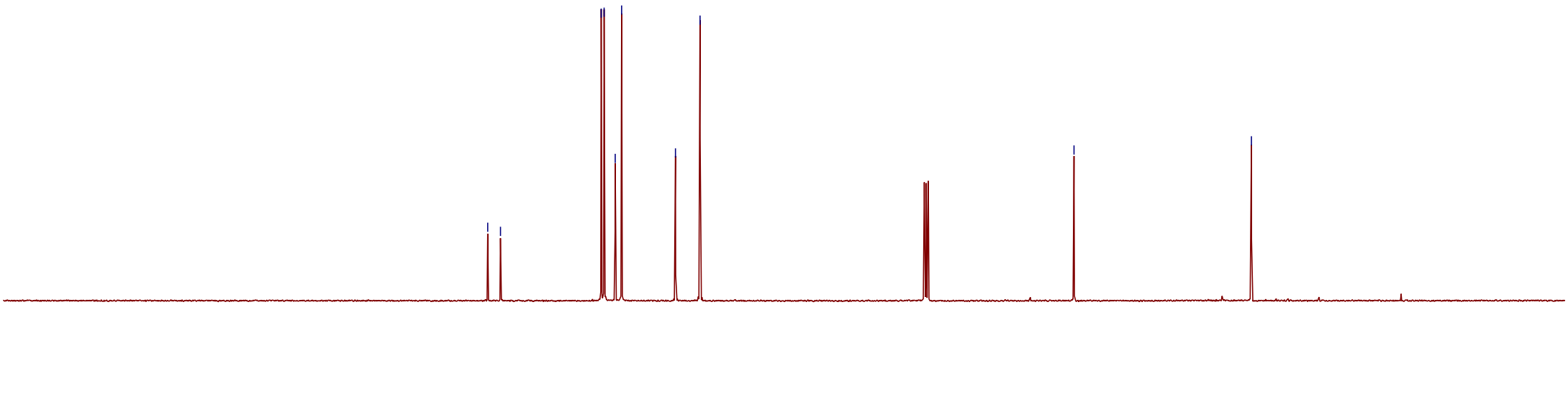

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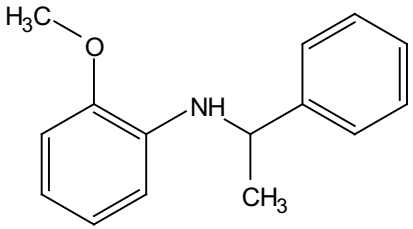
H3C
O
NH
CH3

3ad

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6.72
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6.62
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6.38
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4.54
4.52
4.51
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1.60
1.58
1.99
2.06
1.46
0.88
0.88
0.99
0.87
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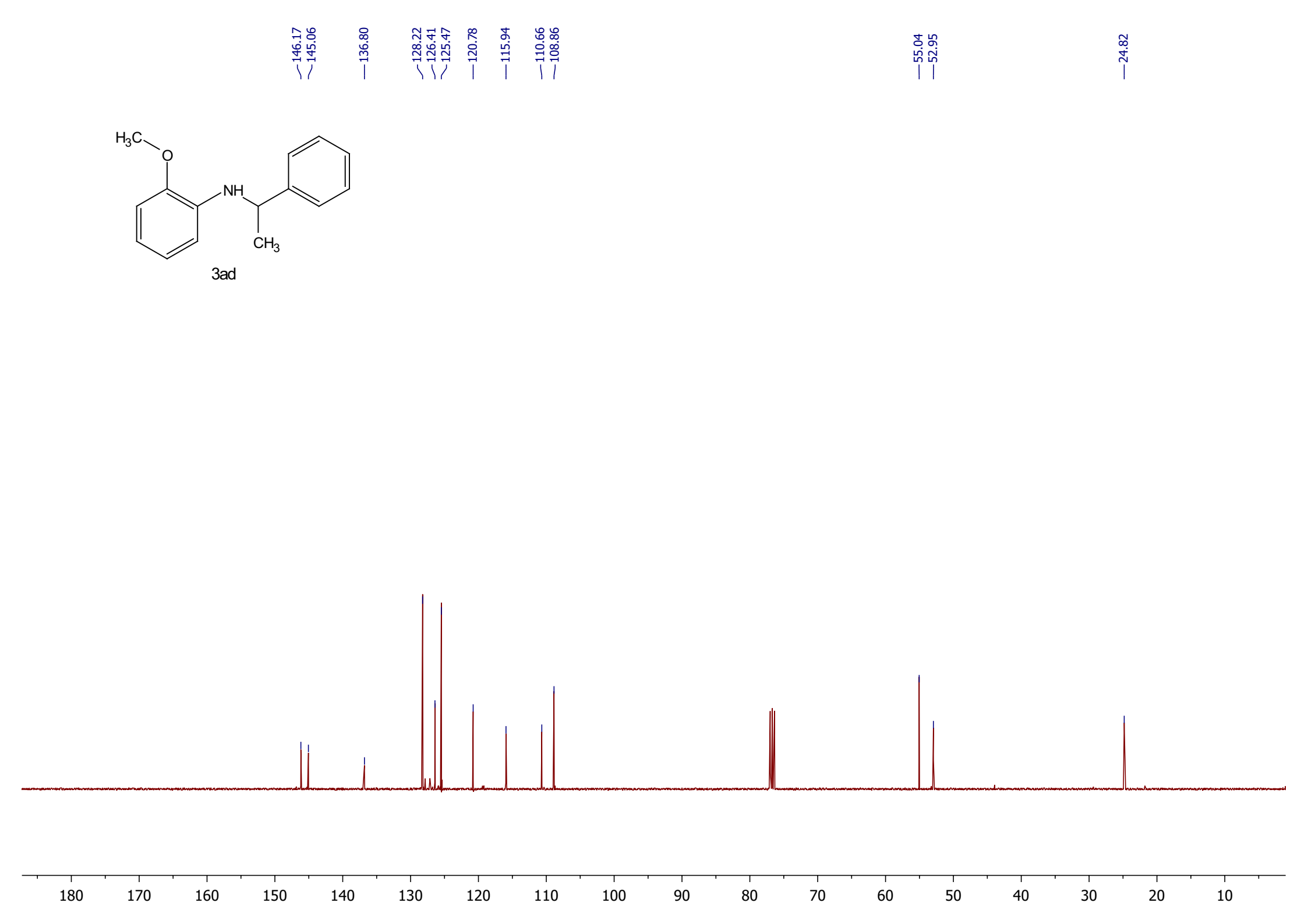
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52.95
24.82
H3C
O
NH
CH3
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20
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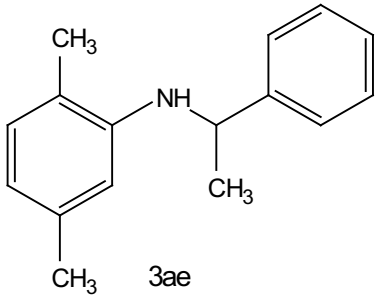
CH3
NH
CH3
CH3

3ae

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6.00
1.13
1.04
1.13
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3.29
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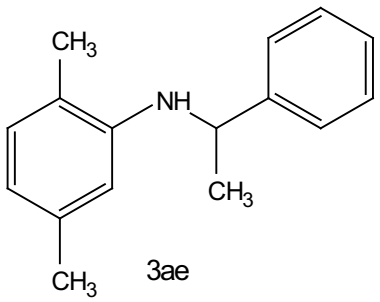
CH3
NH
CH3
CH3

3ae

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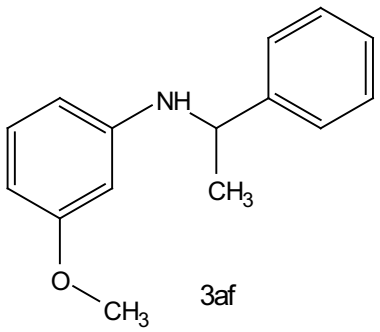
NH
CH3
O
CH3

3af

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6.50
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6.35
6.33
4.54
4.50
4.49
2.24
1.54
1.53
2.04
2.36
1.11
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0.96
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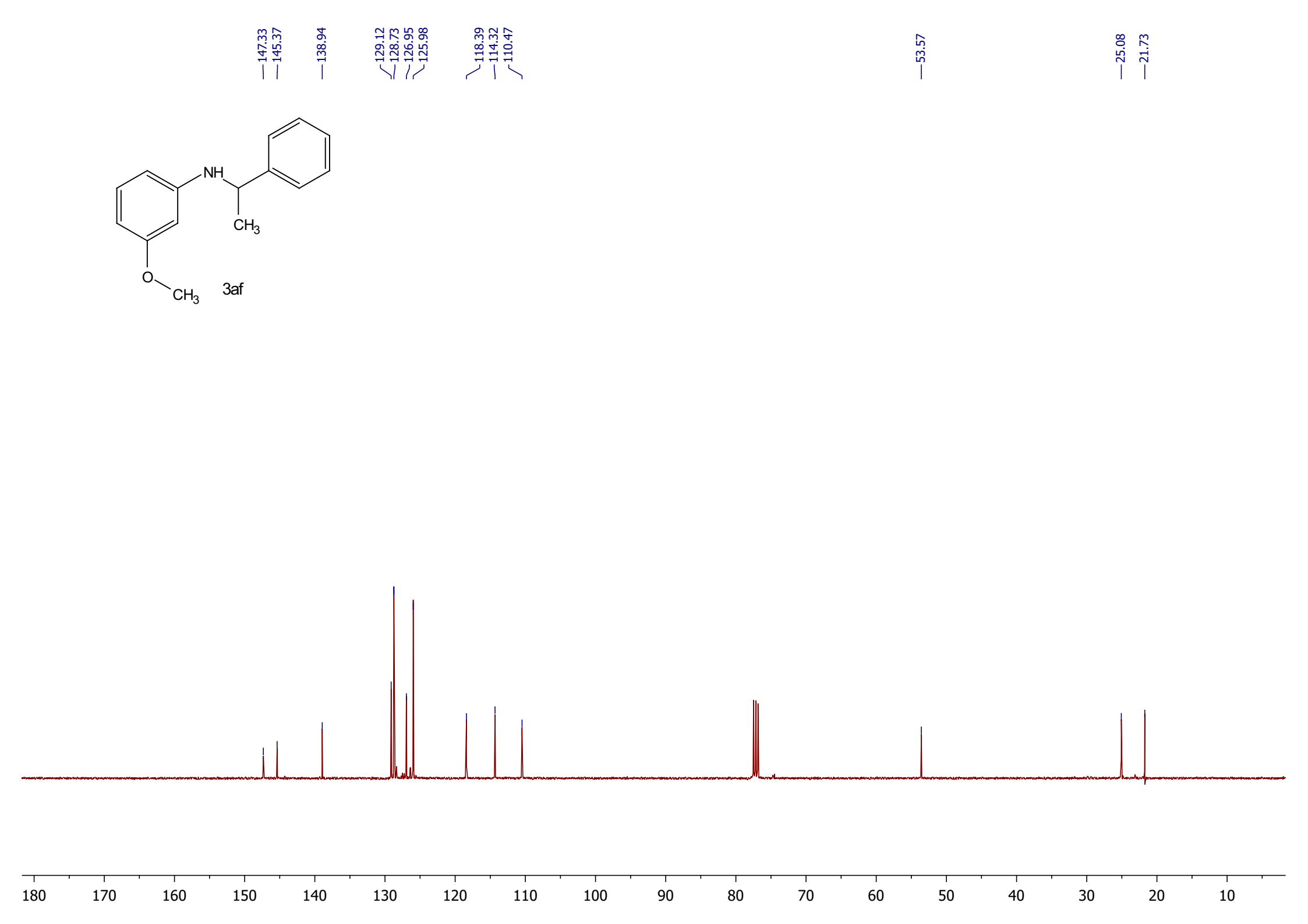
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25.08
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NH
CH3
O
CH3
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120
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100
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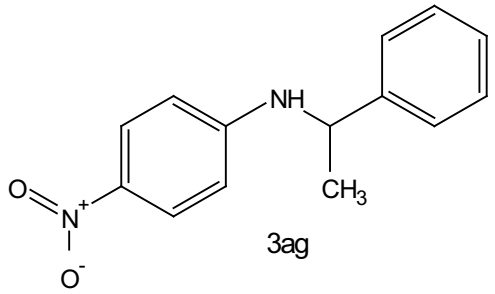
20
10


NH
CH3
O
N+
O-

3ag

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7.2836
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6.4508
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4.6086
4.5796
1.5917
1.5749
1.76
4.52
1.87
0.92
0.96
3.00
10.5
10.0
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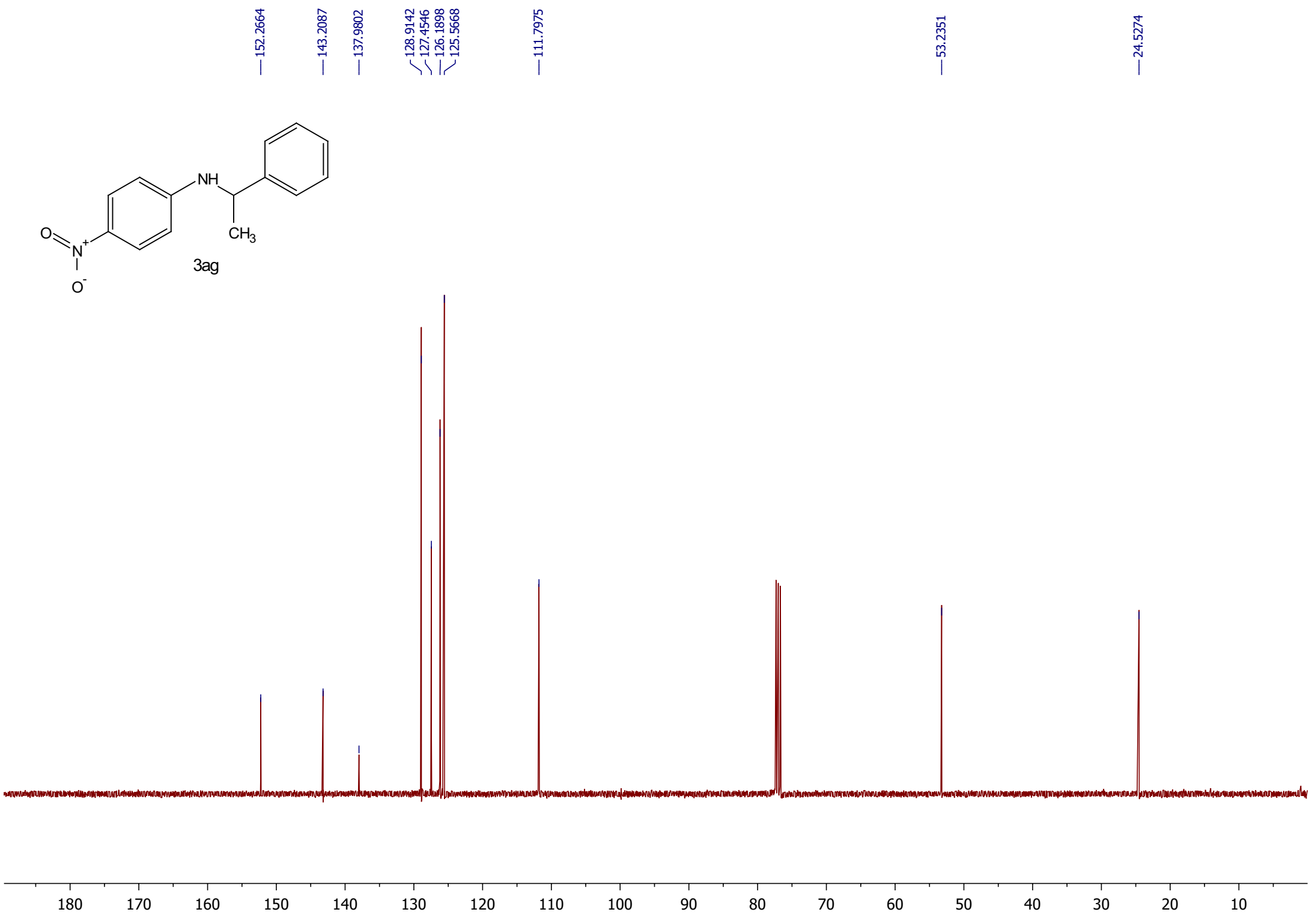
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24.5274
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CH3
O
N+
O-
3ag
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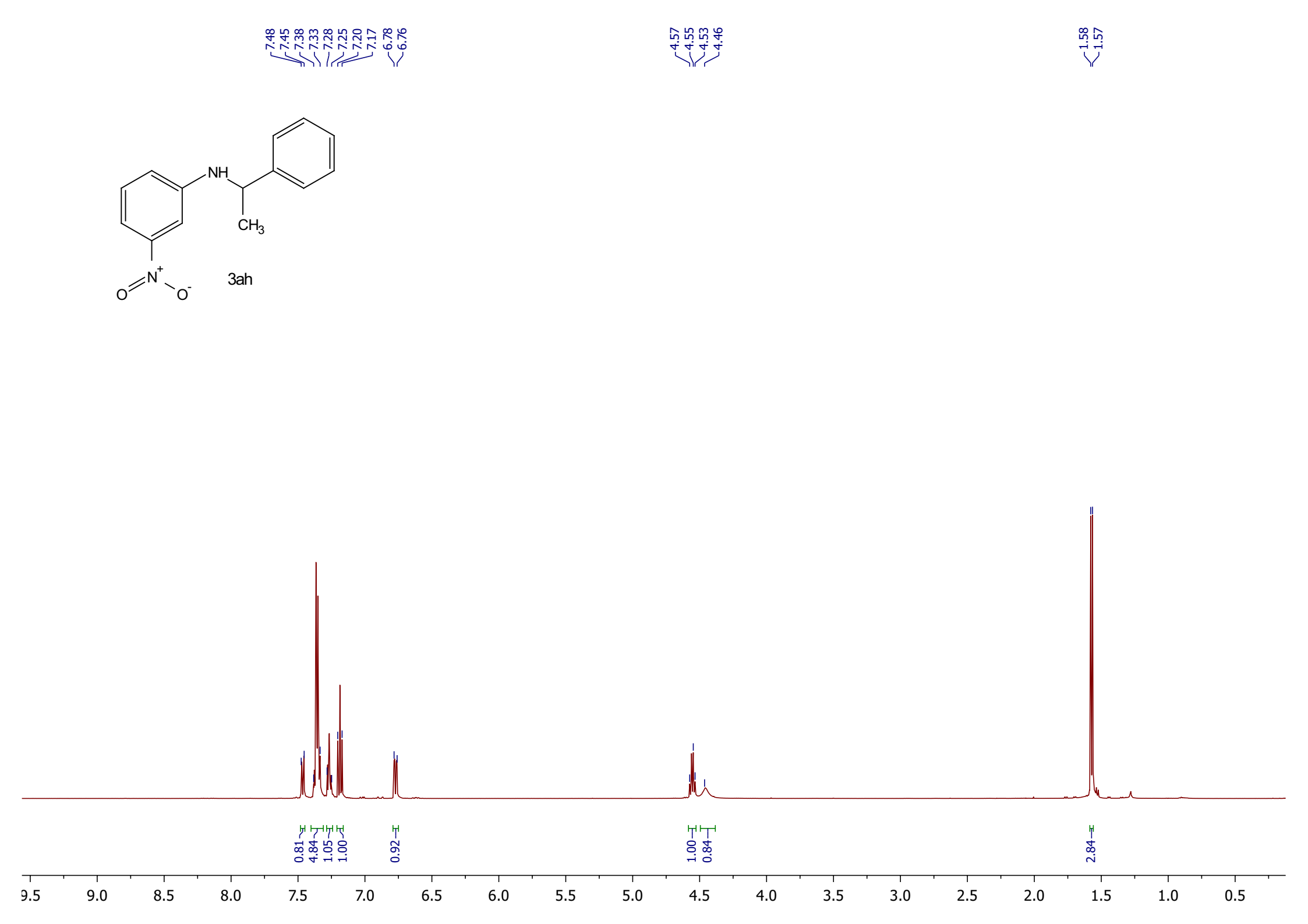
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6.76
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4.53
4.46
1.58
1.57
NH
CH3
N+
O
O-
3ah
0.81
4.84
1.05
1.00
0.92
1.00
0.84
2.84
9.5
9.0
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8.0
7.5
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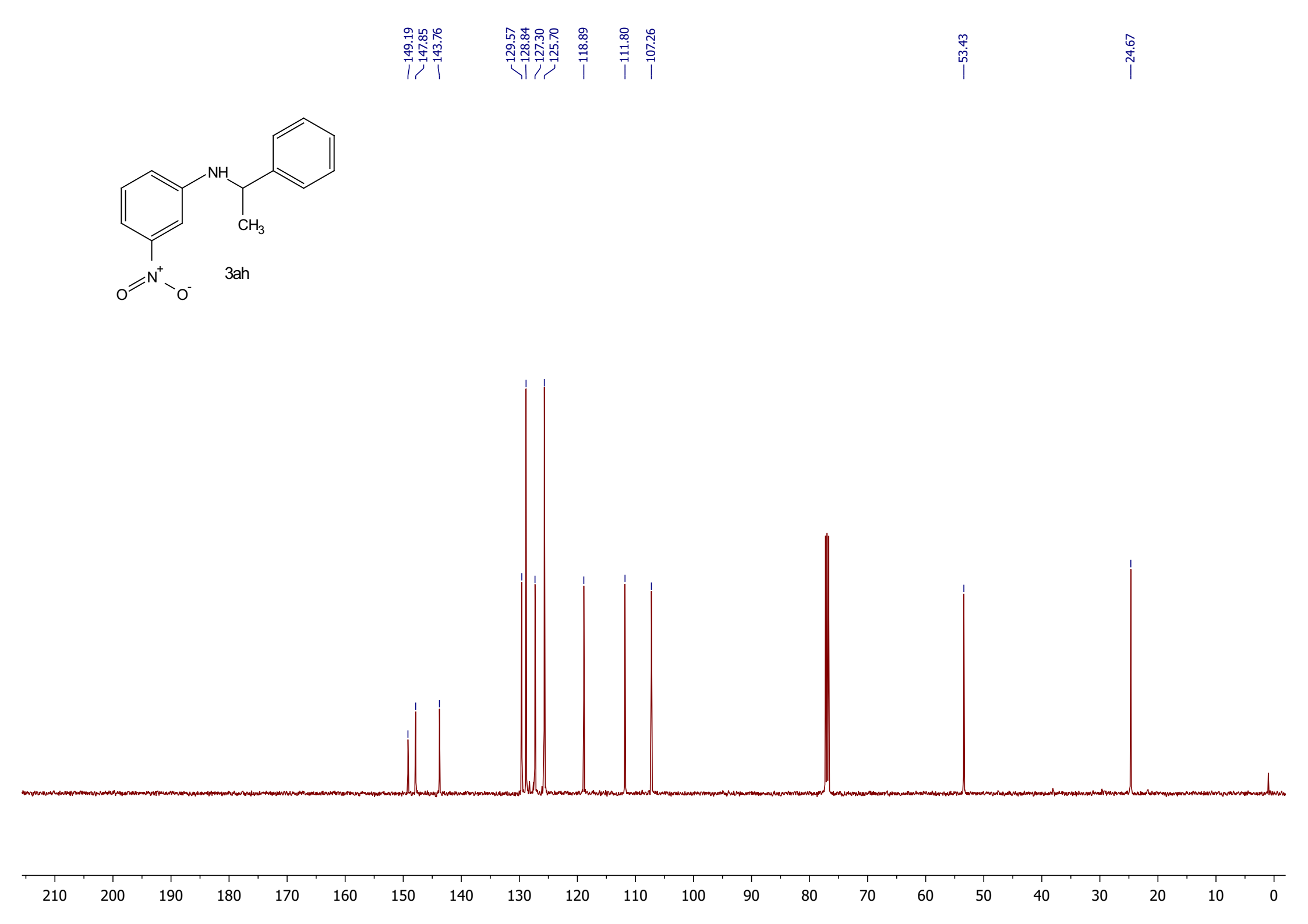
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107.26
53.43
24.67
NH
CH3
N+
O
O-
3ah
210
200
190
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150
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10
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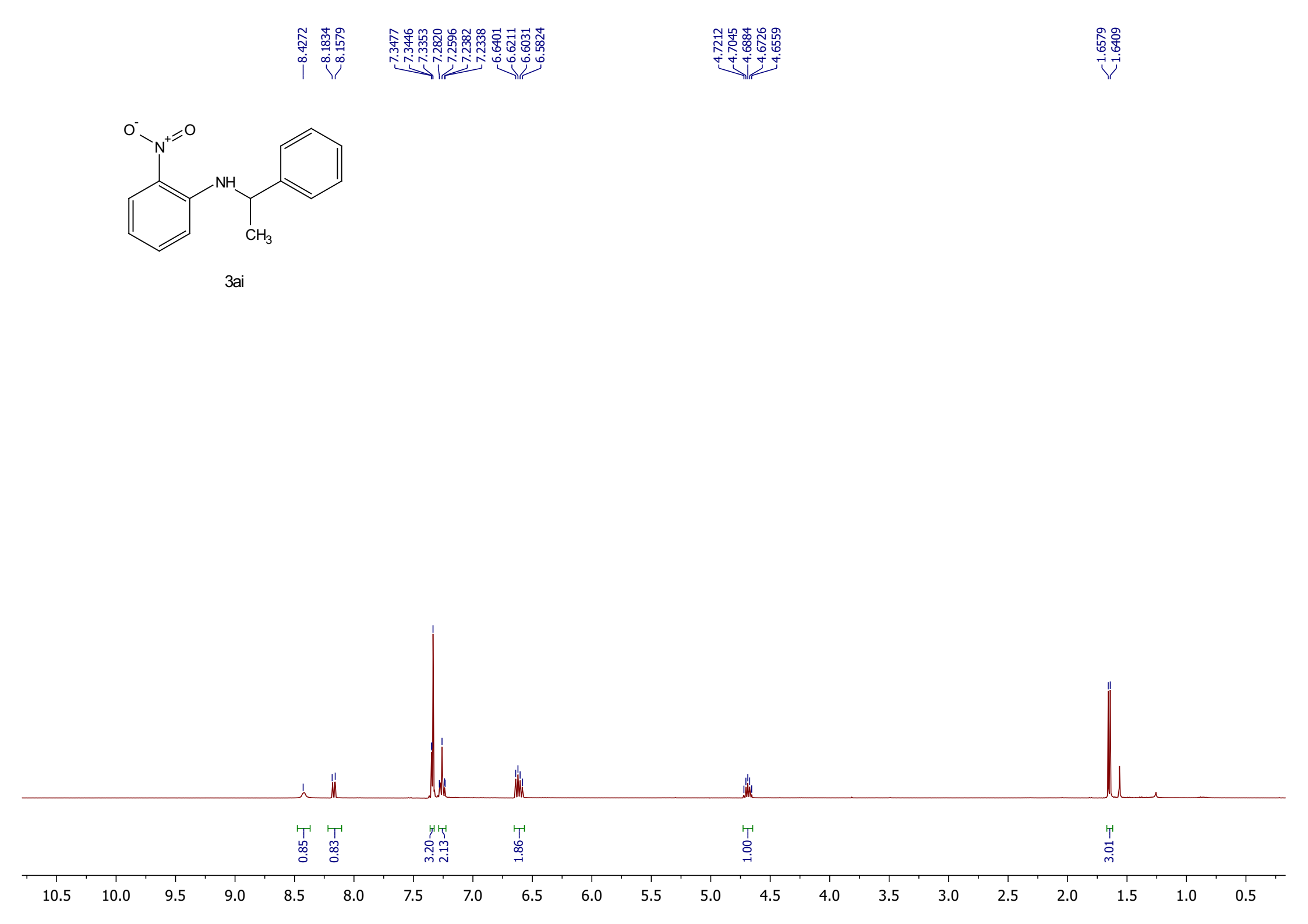
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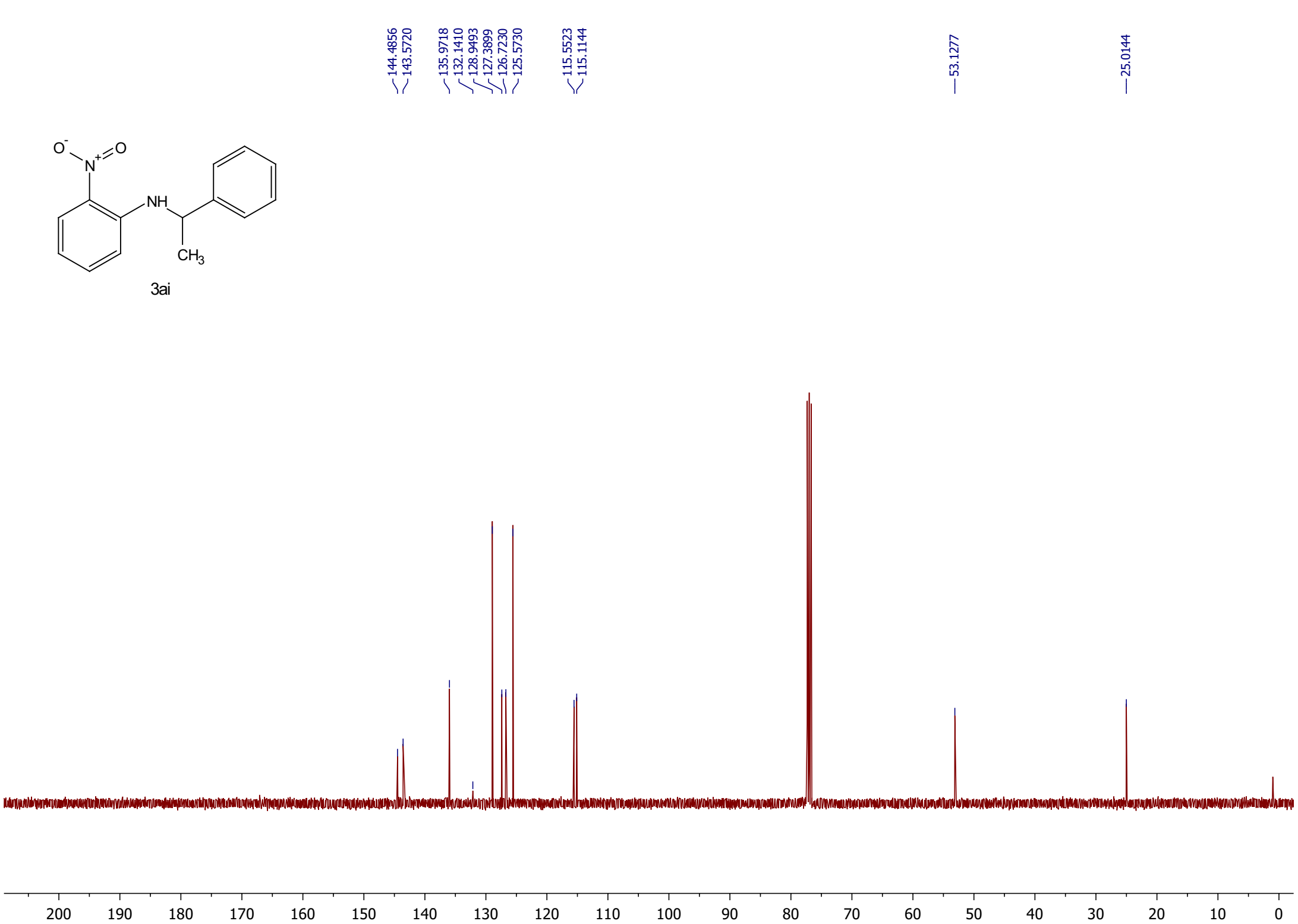
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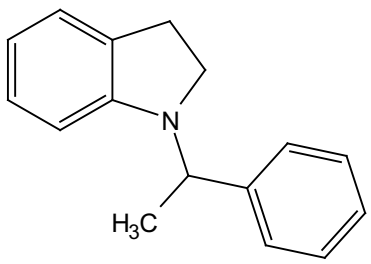
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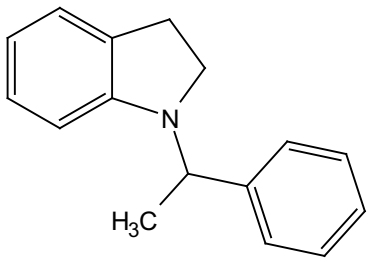
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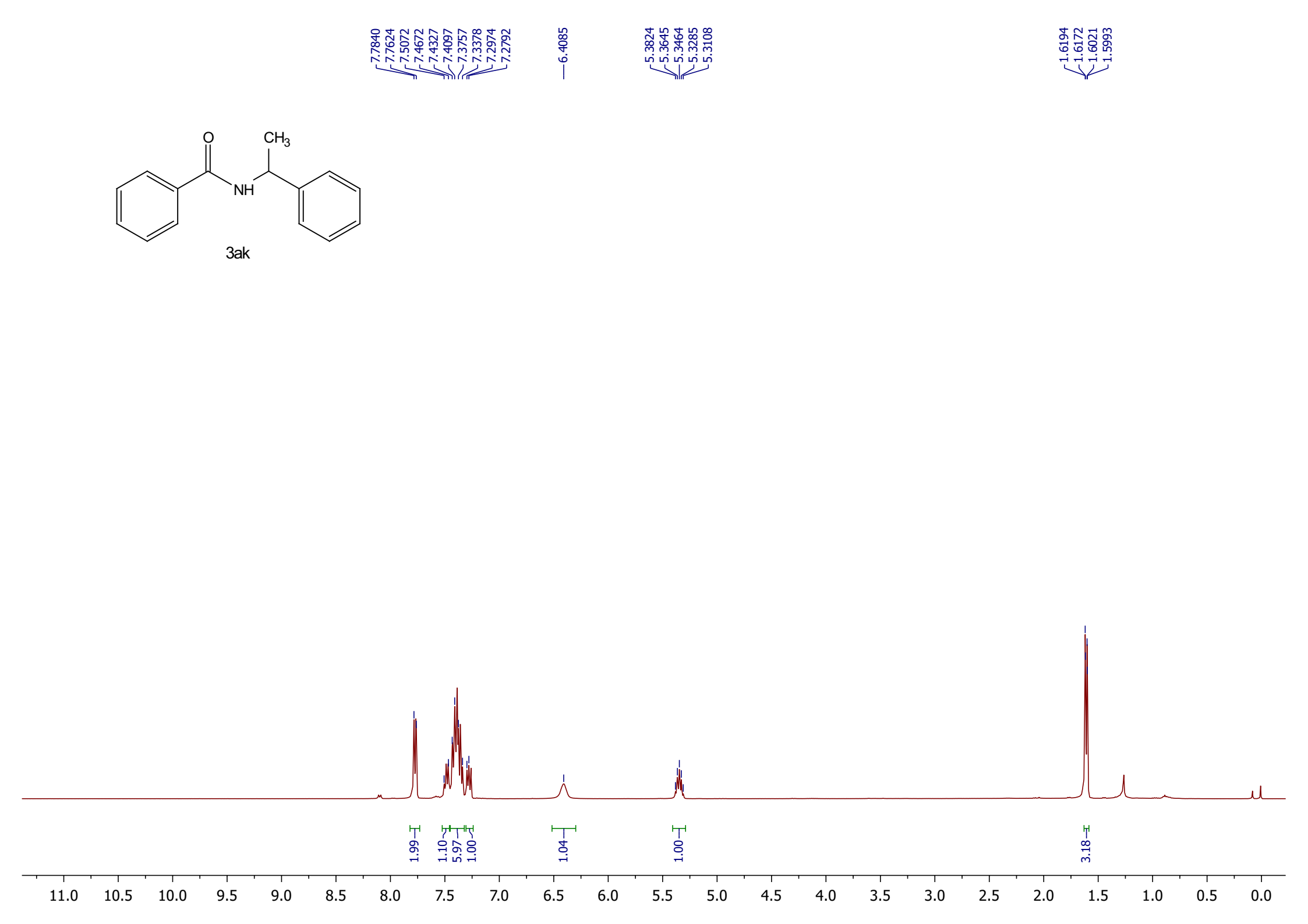
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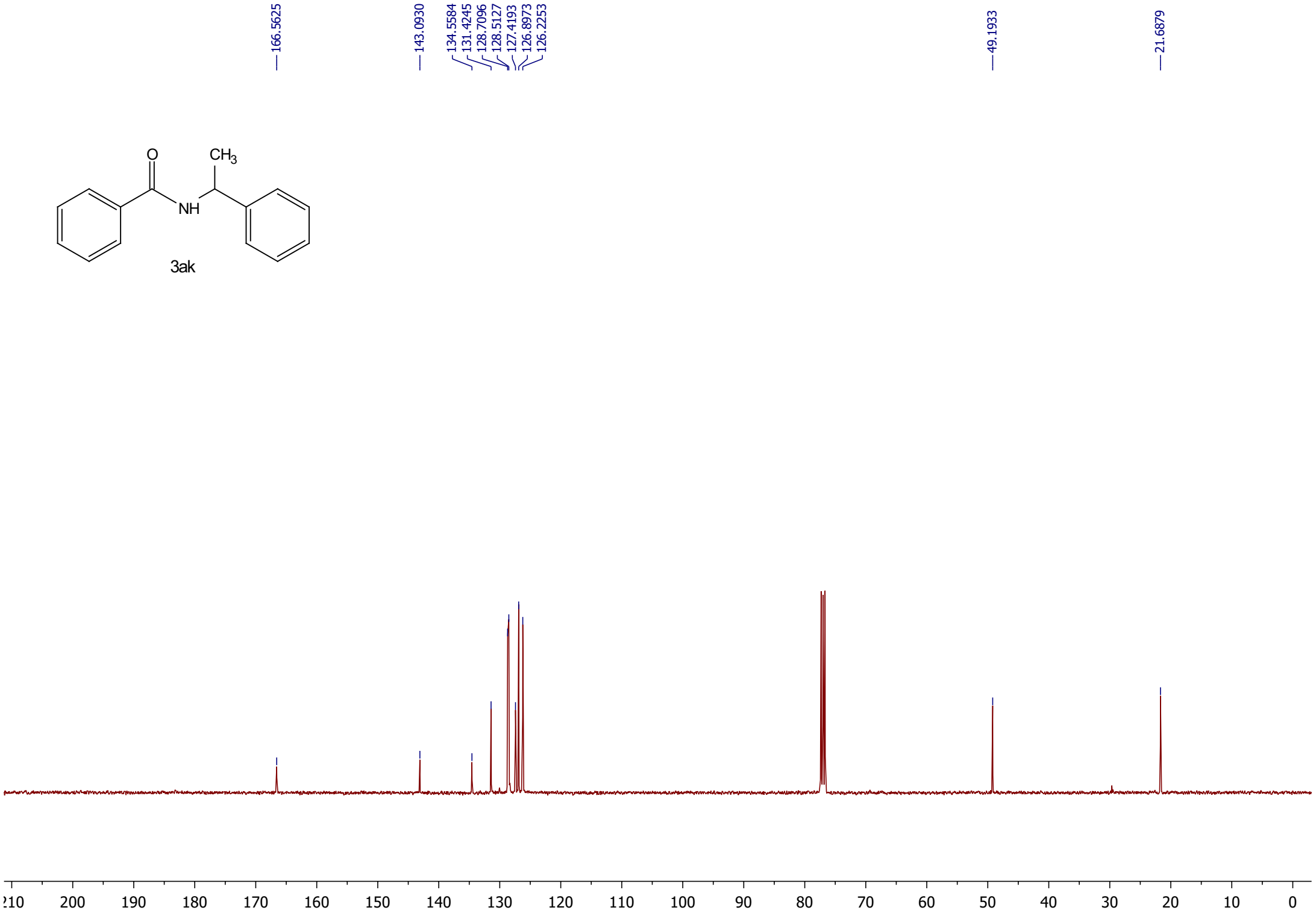
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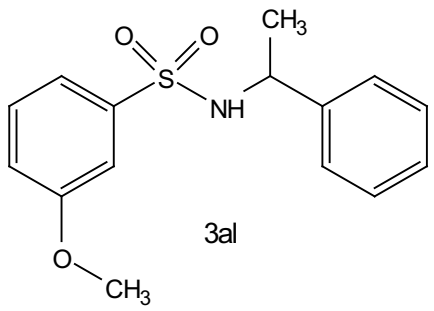
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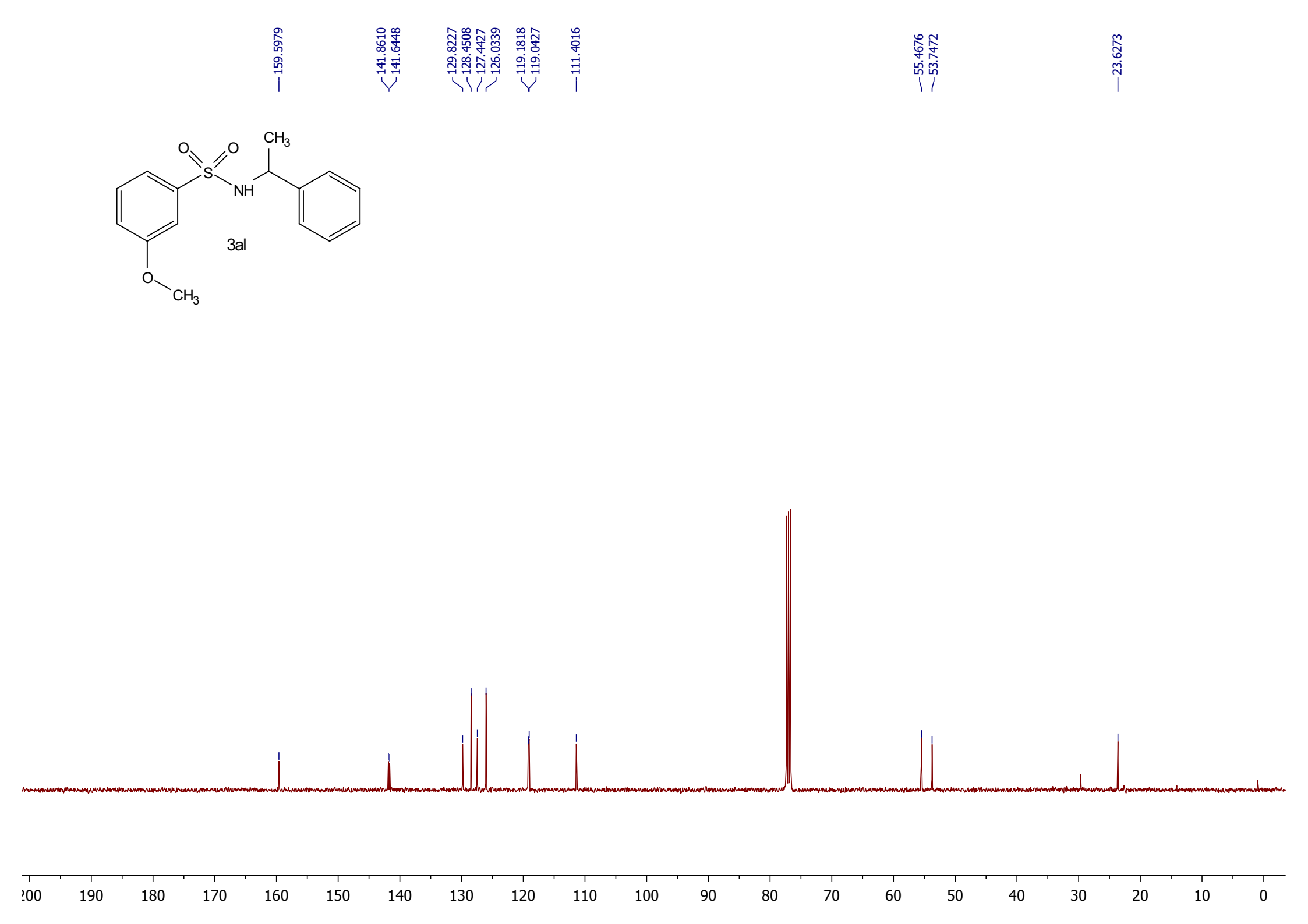
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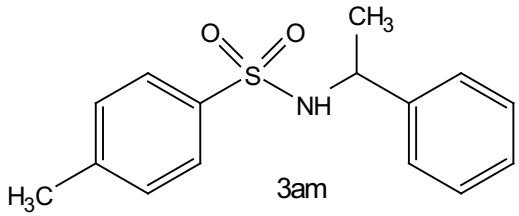
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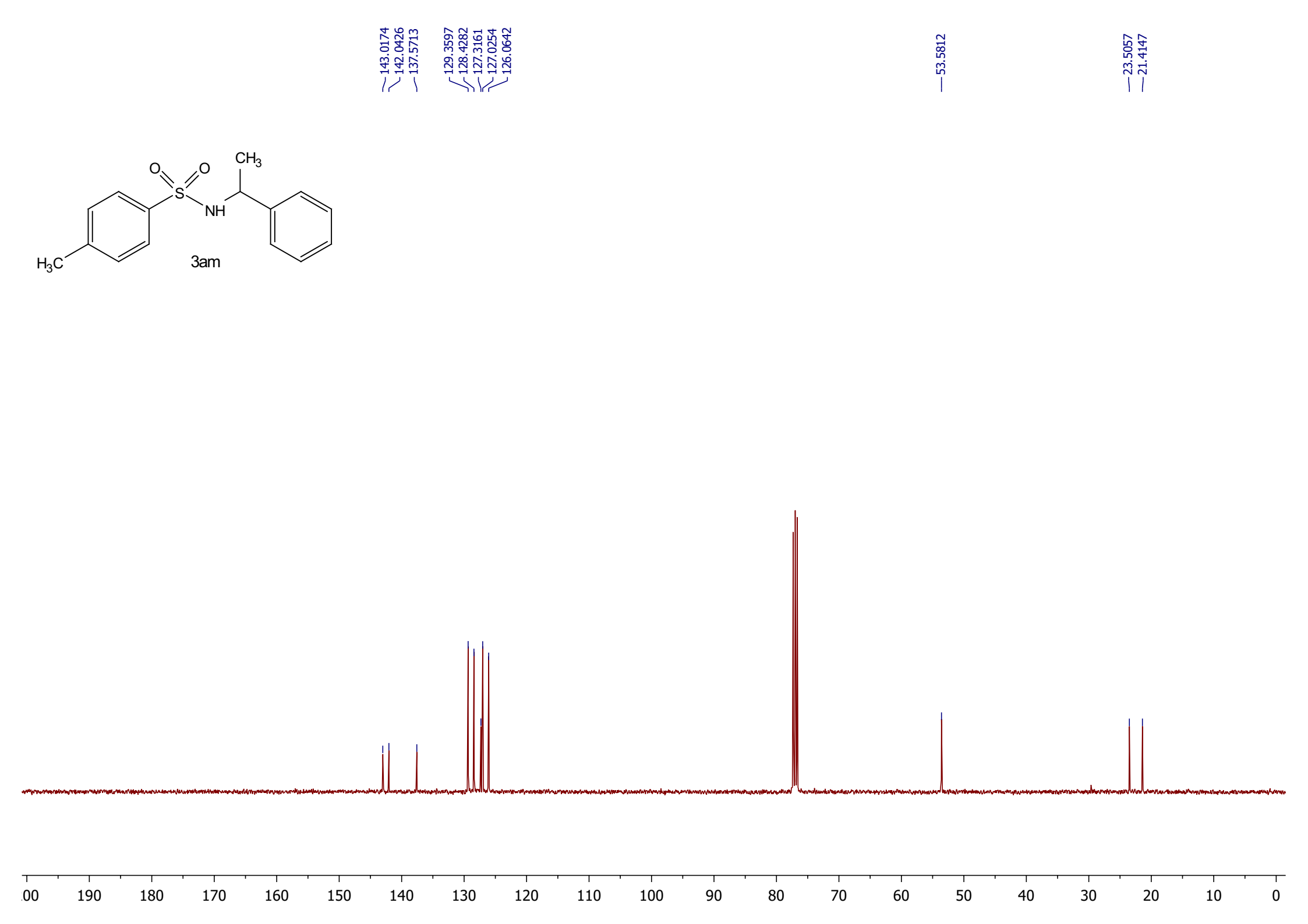
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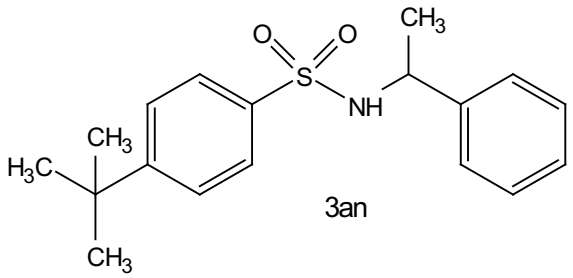
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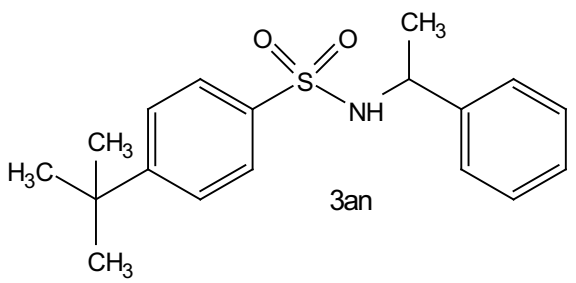
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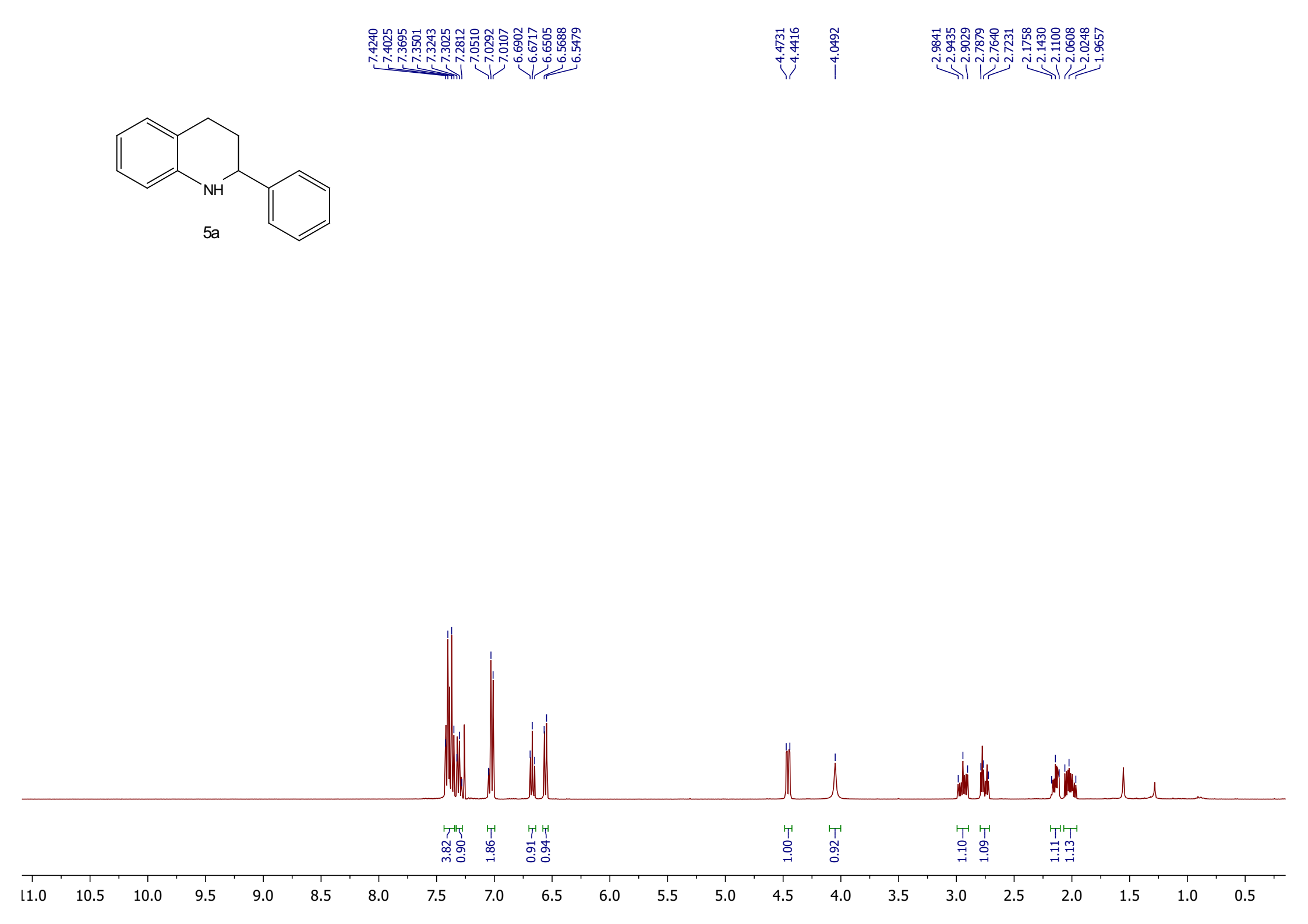
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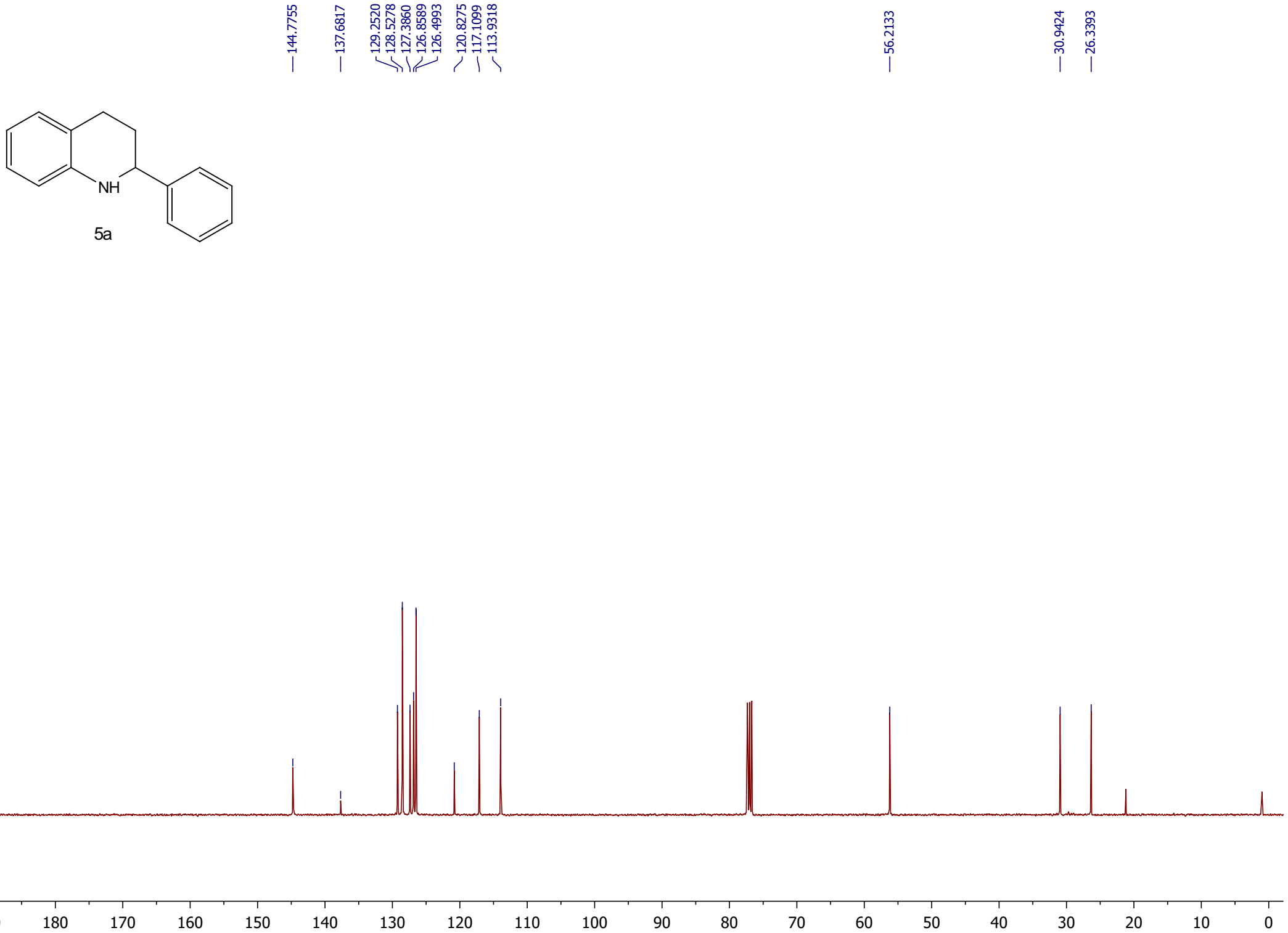
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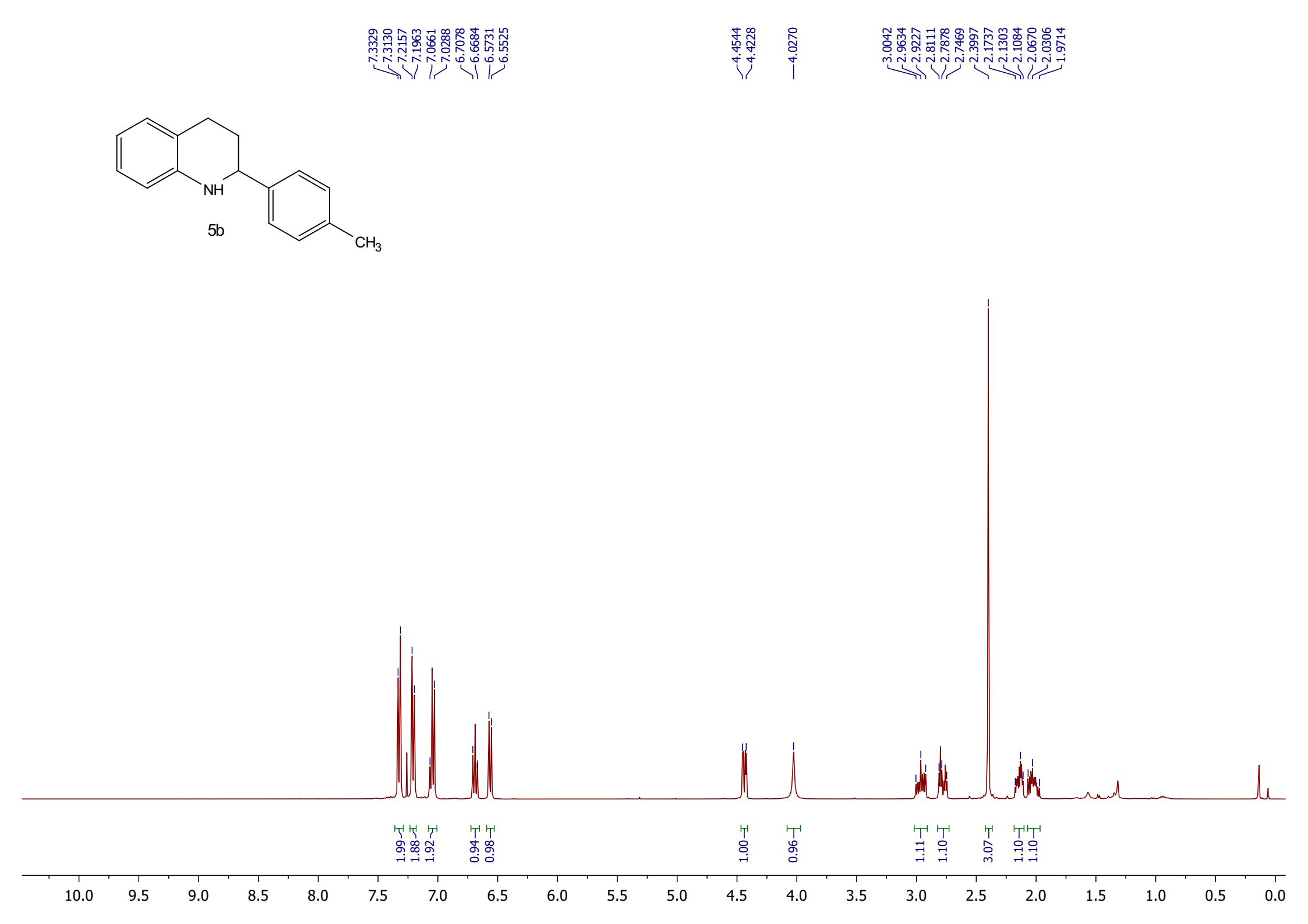
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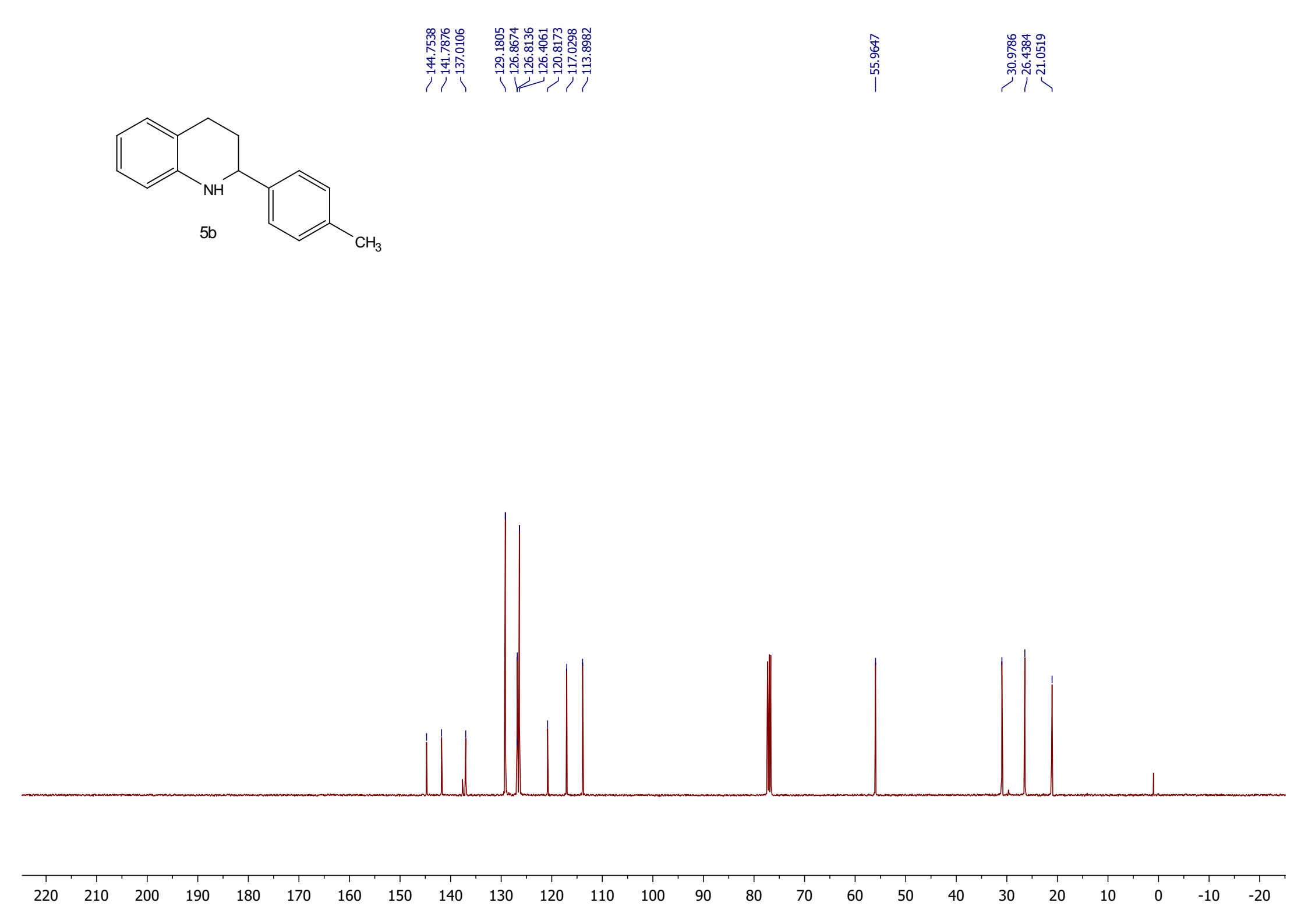
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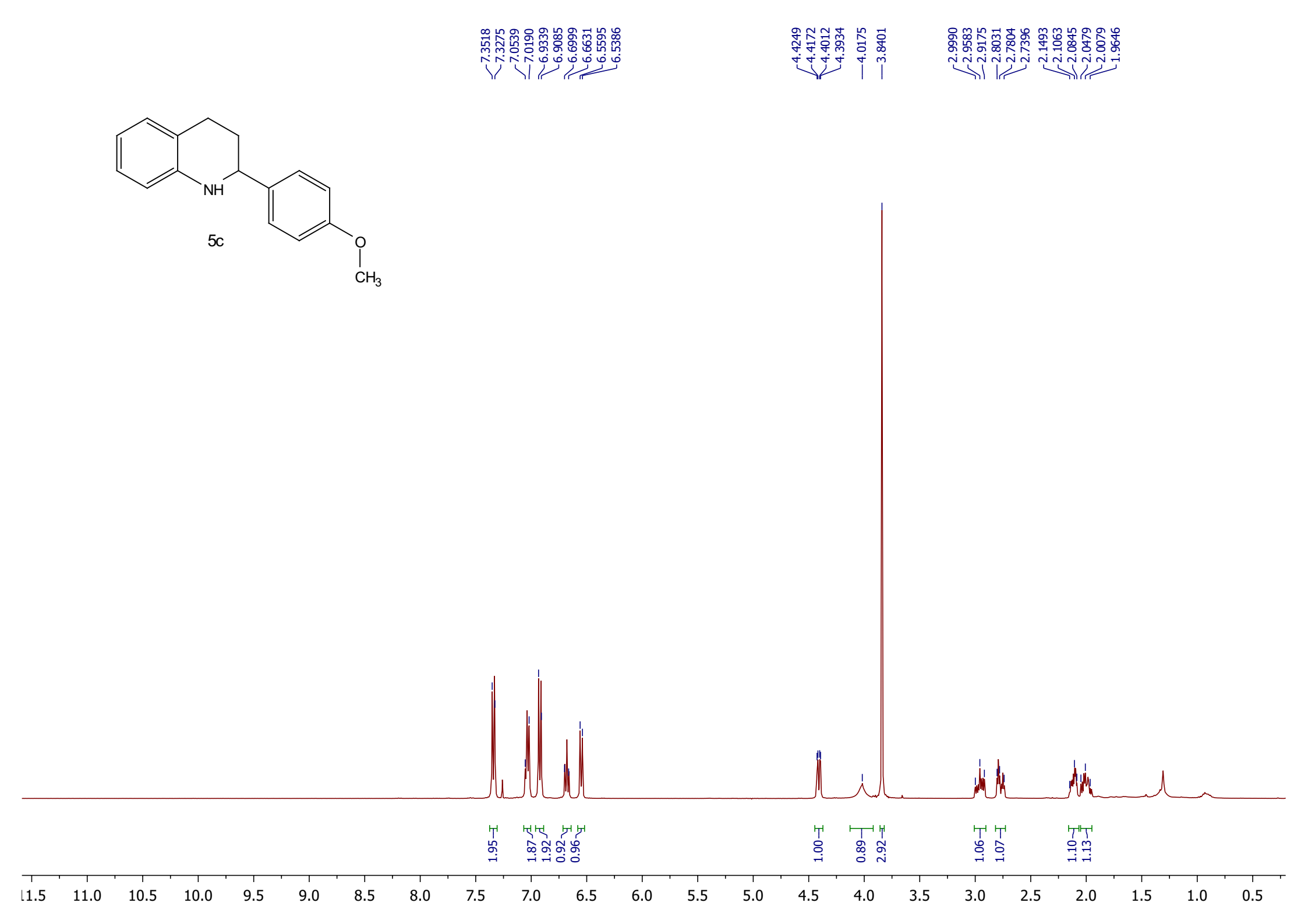
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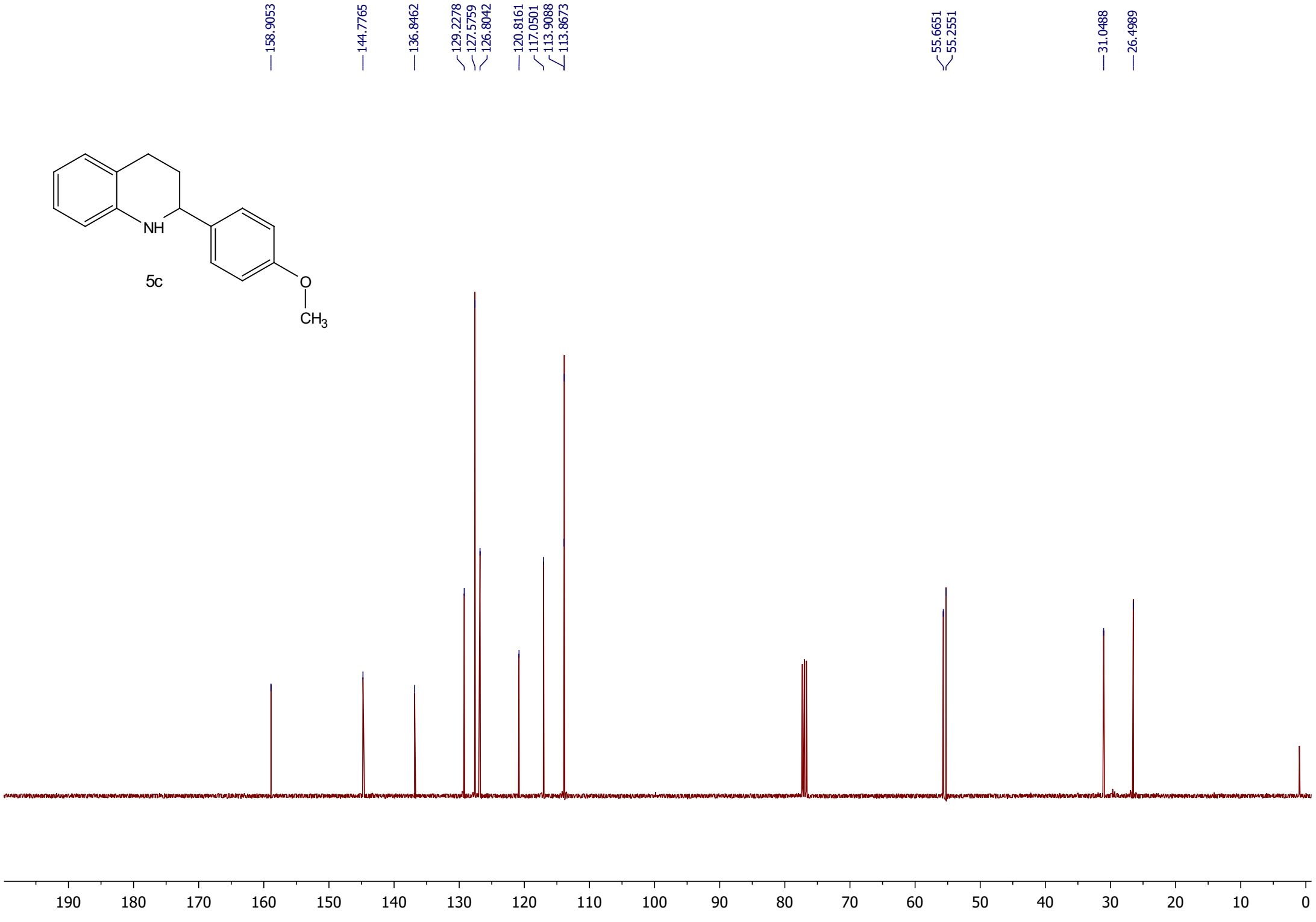
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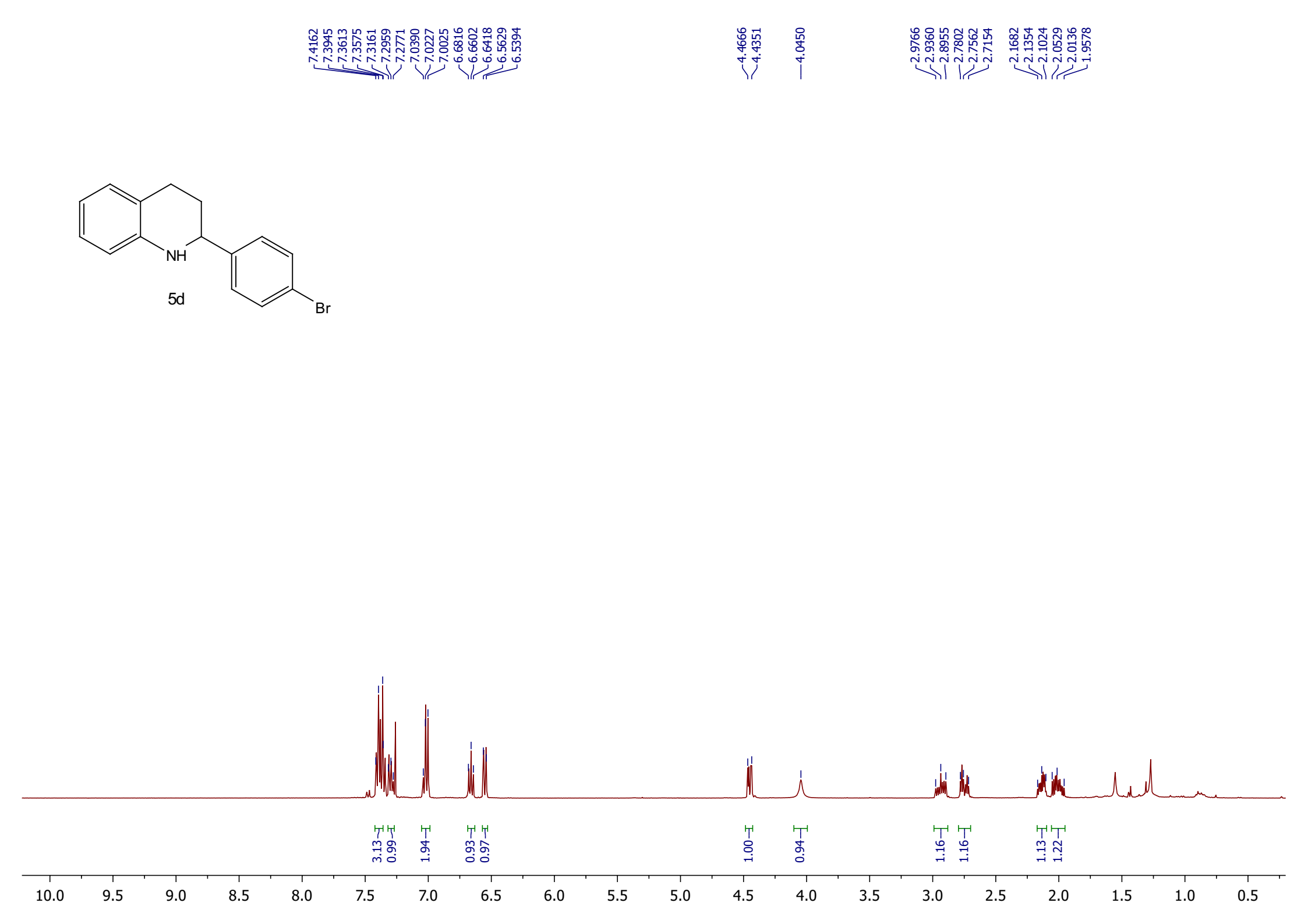
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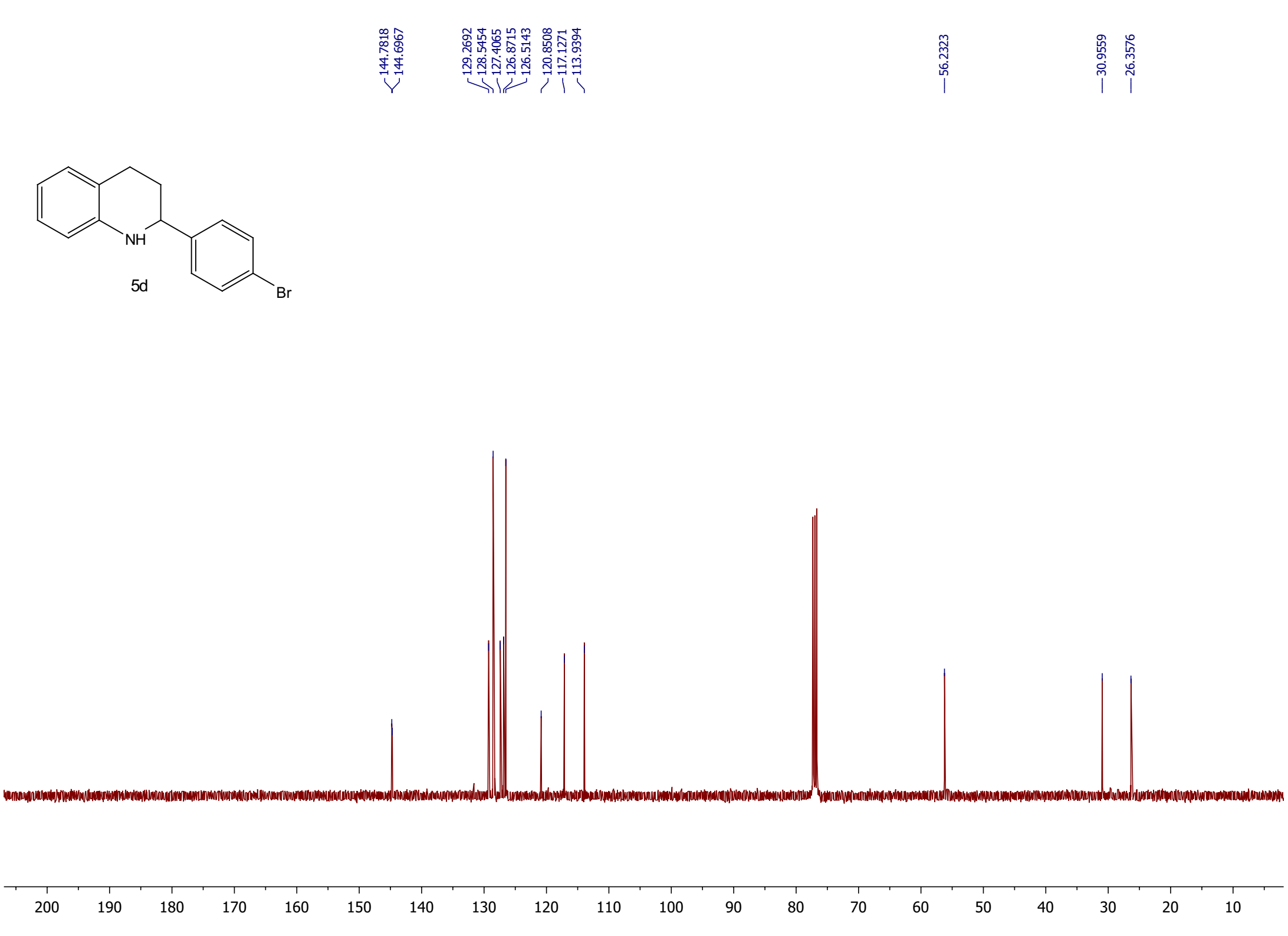
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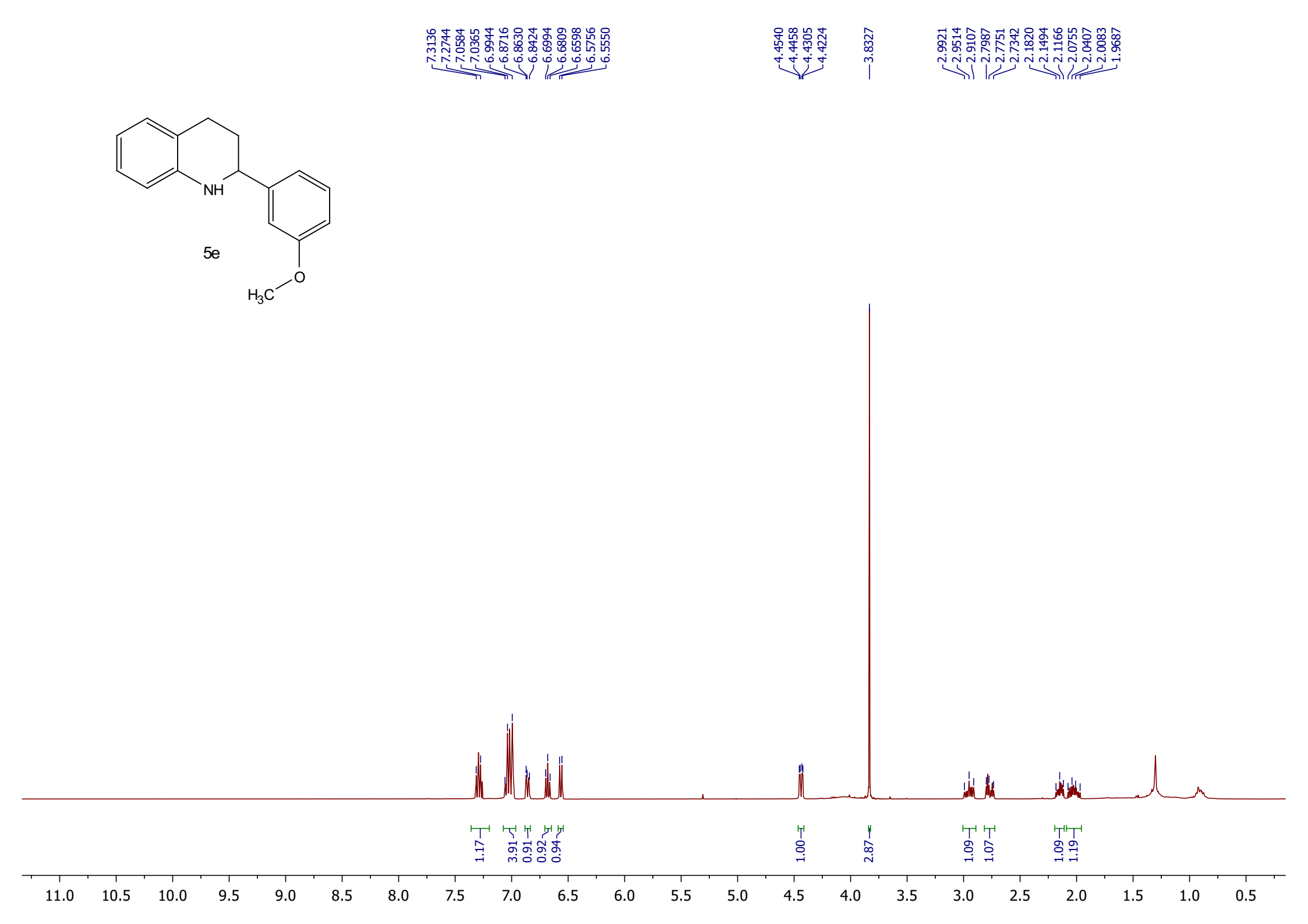
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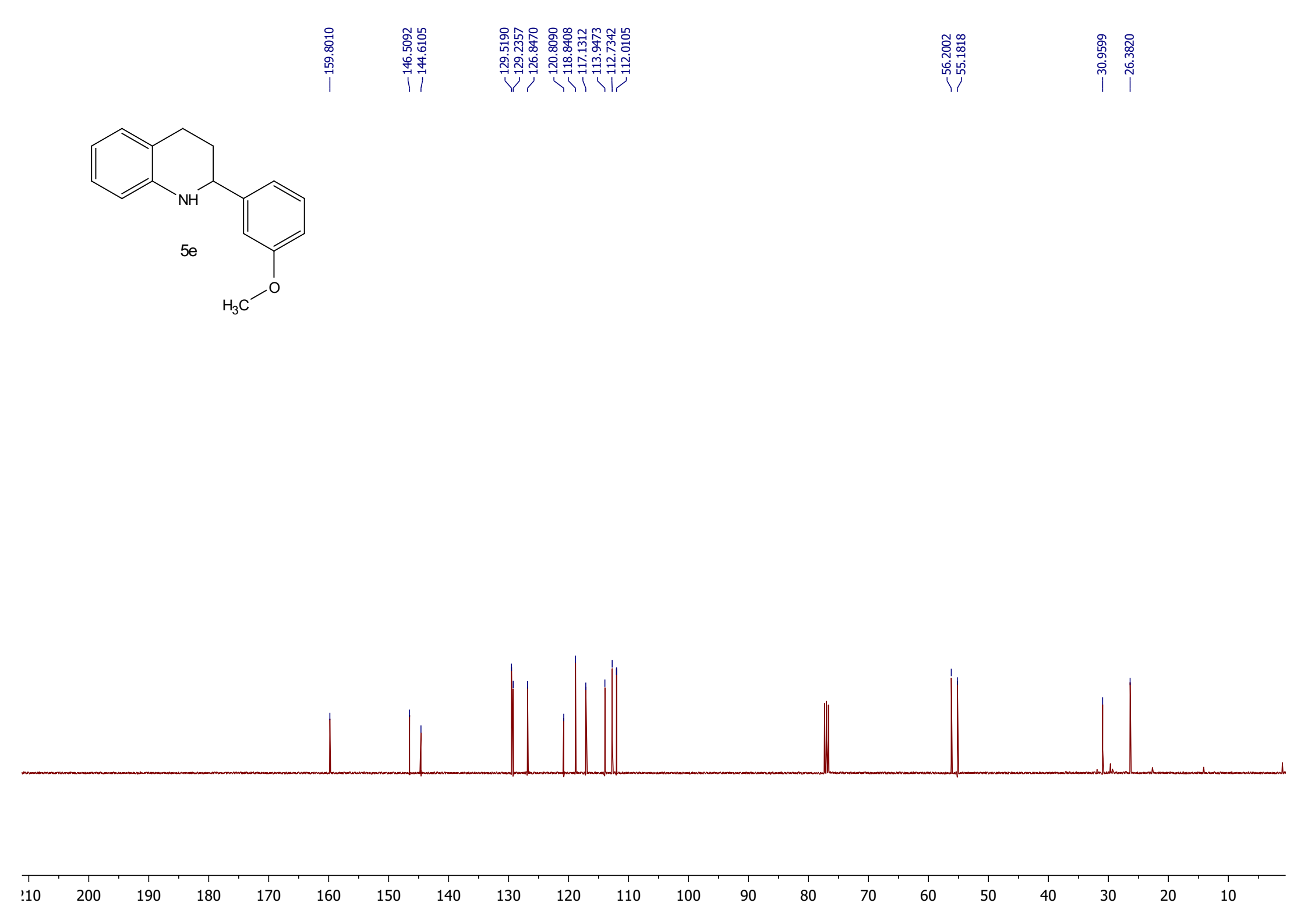
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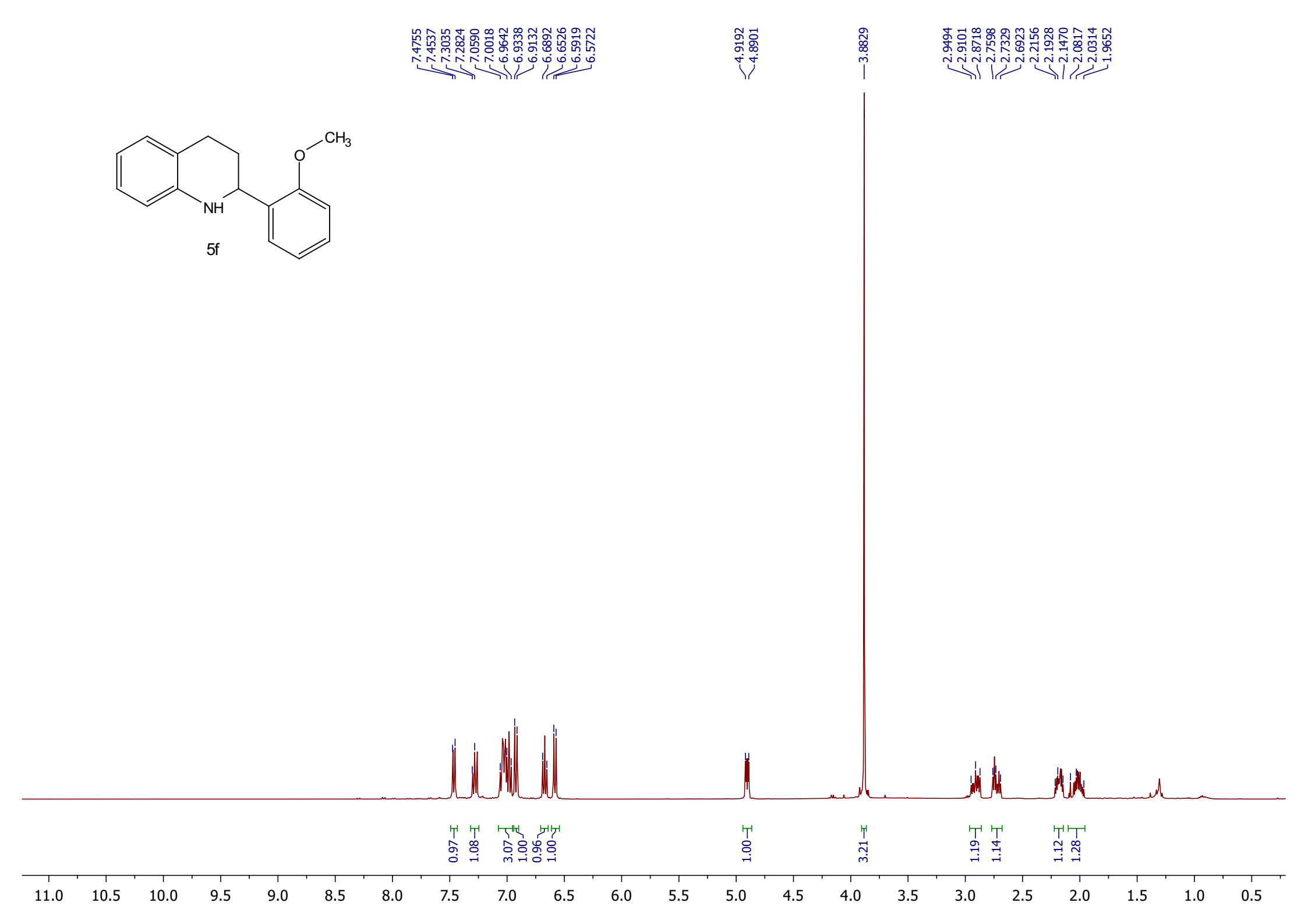
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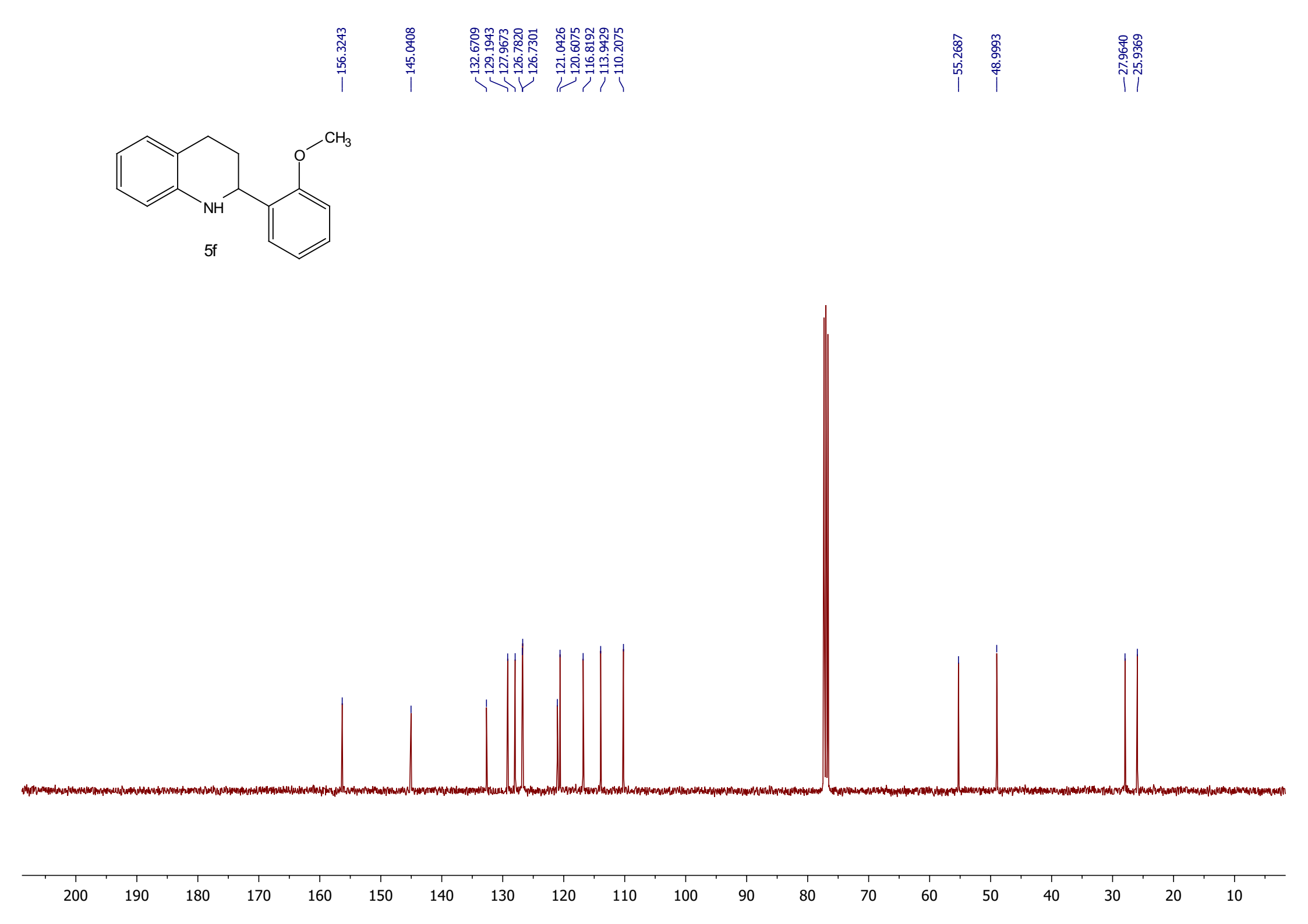
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CH3
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5f
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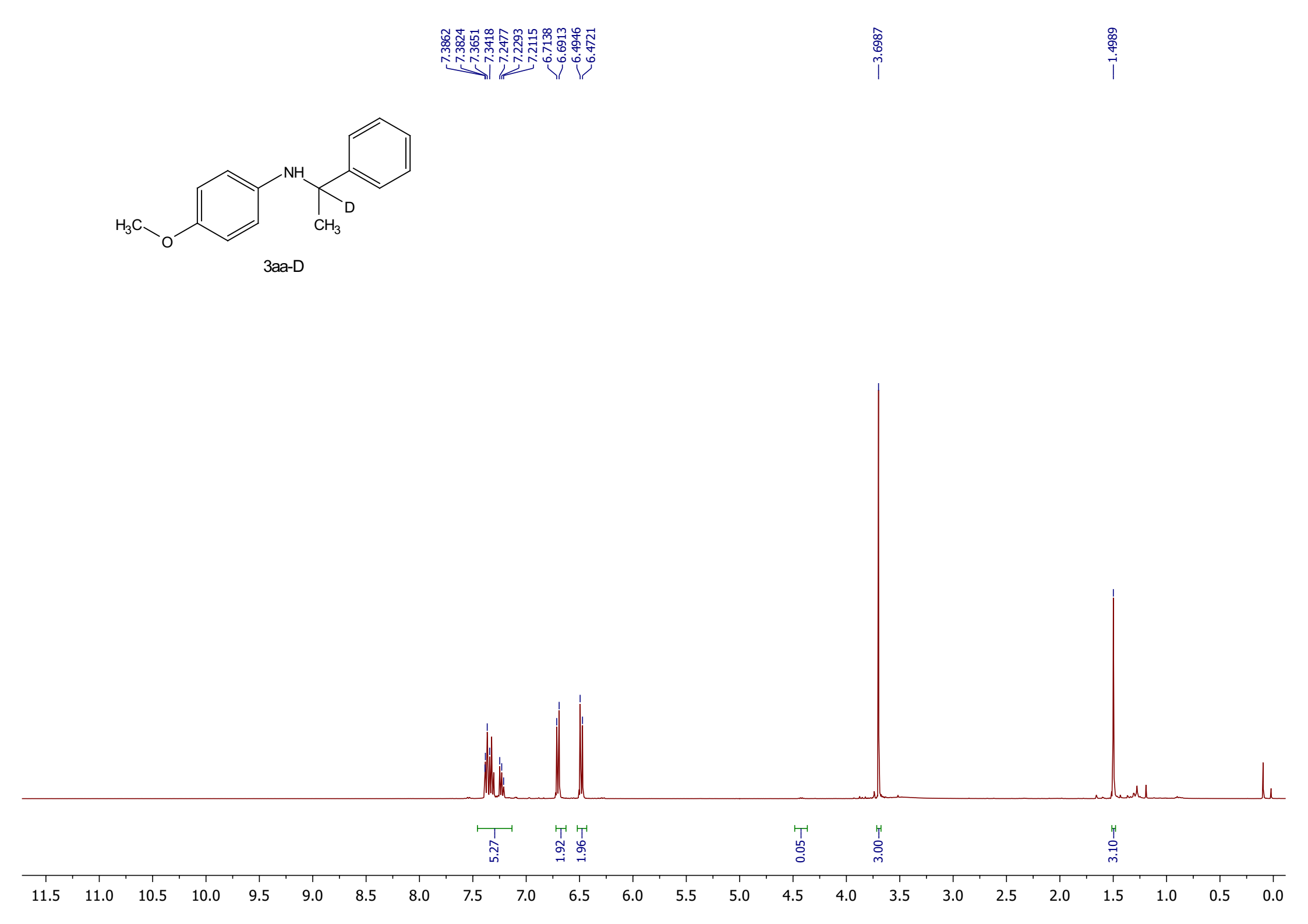
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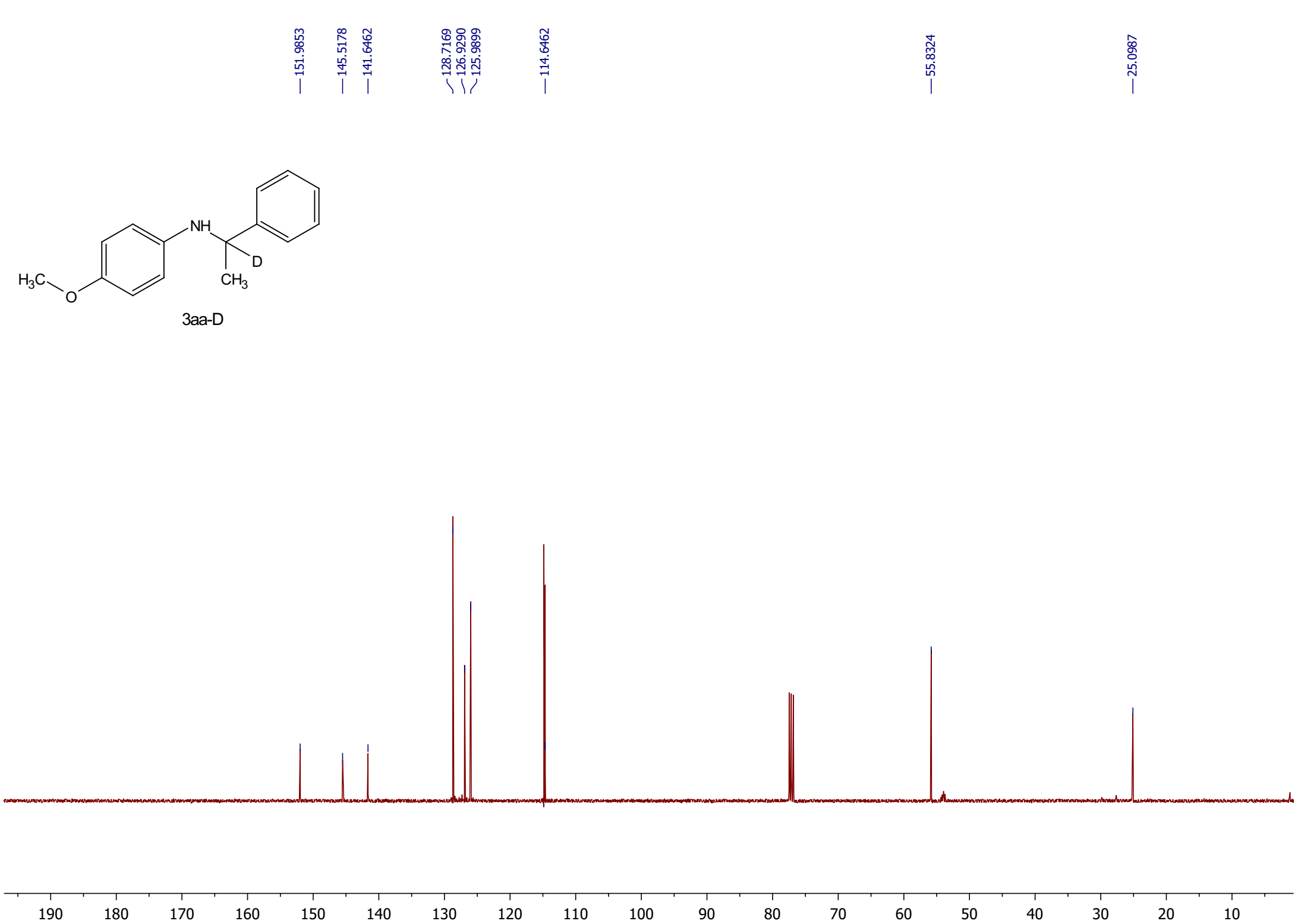
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