Copper-catalyzed C-H Azidation of Anilines under Mild Conditions

(Supporting Information)

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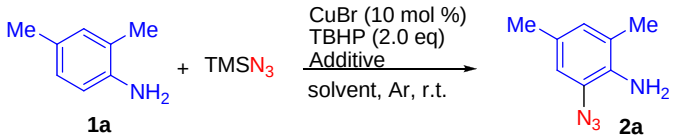
1. General Information

All manipulations were conducted with a standard Schlenk technique under argon atmosphere (1 atm). ^{1}H-NMR spectra were recorded with a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C-NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were recorded by PE SCLEX QSTAR spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. CuBr was purchased from Alfa Aesar, TBHP (5.5 M in decane) was purchased from Sigma Aldrich. Compounds **1j-1t** were synthesized according to related literatures. [1]

Table S1 Screening with different reaction conditions.[a]

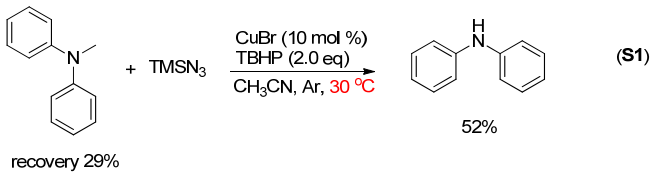


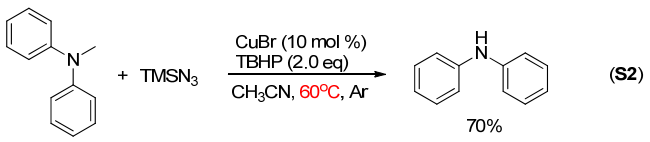
1a **2a**

entry	additive (eq)	solvent	yield (%)[b]
1	none	Toluene	52
2	none	EA	61
3	none	Benzene	58
4	none	CH_3CN	68
5	none	DCE	0
6	none	CH_3NO_2	0
7	none	DMF	0
8[c]	none	CH_3CN	57
9	pyridine (1.0)	CH_3CN	63
10	AcOH (1.0)	CH_3CN	50
11	Et_3N (1.0)	CH_3CN	0
12	1,10-Phenanthroline (1.0)	CH_3CN	0
13	bipyridine (1.0)	CH_3CN	0

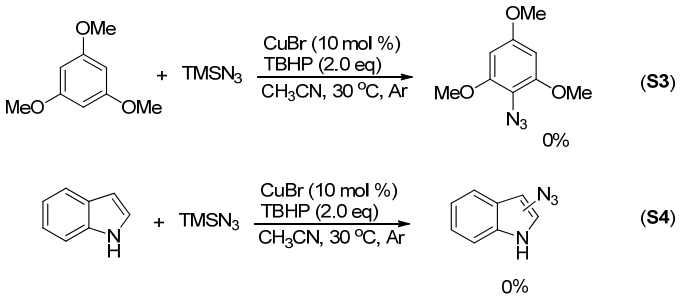
[a] Reaction conditions: **1a** (0.5 mmol), $TMSN_3$ (1.0 mmol), CuBr (0.05mmol), TBHP (1.0 mmol), solvent (2 mL), stirred at 30 °C under Ar. TMS=trimethylsilyl. [b] Yield of the isolated product. [c] Carried out in O_2 (1 atm).

The reaction of arylamines with a tertiary amino group did not work under the standard conditions. Azidation product of N-methyl-N-phenylaniline under the optimized conditions was not observed. However, the demethylation process occurred to afford diphenylamine in 52% and 70% yields respectively at different temperatures (Eq. S1-S2). These results indicate that a free N-H bond is required for this transformation.



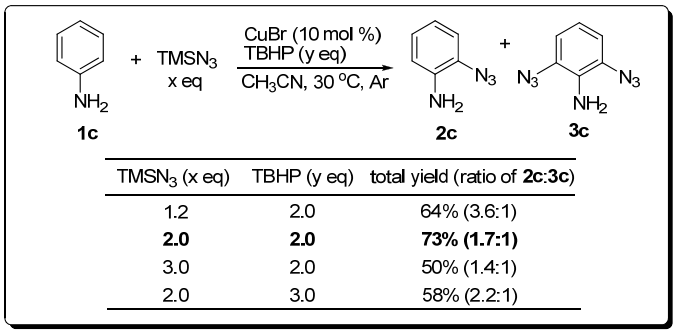


When employing 1,3,5-trimethoxybenzene or indole as the substrate, no desired azidation products were obtained (Eq. S3-S4), which indicates that this transformation is not a simple Friedel–Crafts reaction process.



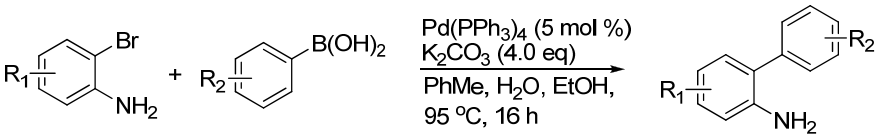
The ratio of mono- and di-azidation product of aniline was also investigated. Different loading of $TMSN_3$ and TBHP was tested (table S2).

Table S2 Screening the ratio of mono to di-azidated product



$TMSN_3$ (x eq)	TBHP (y eq)	total yield (ratio of **2c**:**3c**)
1.2	2.0	64% (3.6:1)
2.0	**2.0**	**73% (1.7:1)**
3.0	2.0	50% (1.4:1)
2.0	3.0	58% (2.2:1)

General Procedure for the Preparation of 2-Aminobiaryls[1]

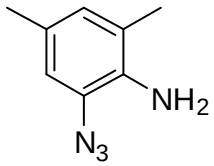


The 2-aminobiaryls were synthesized from substituted 2-bromoanilines using a Suzuki reaction. In a dry 100 mL round bottom flask, phenylboronic acid (1.00 g, 8.20 mmol, 1.3 equiv), K_2CO_3 (3.48 g, 25.2 mmol, 4.0 equiv), and $Pd(PPh_3)_4$ (0.365 g, 0.32 mmol, 0.05 equiv) were then dissolved in 30 mL of toluene, 20 mL of H_2O, and

10 mL of EtOH. 2-Bromoaniline (1.08 g, 0.715 mL, 6.31 mmol, 1.0 equiv) was added, and the resulting mixture was heated to 95 °C for 16 hours. After cooling, the biphasic solution was diluted with 100 mL of saturated aqueous NH_4Cl and 100 mL of CH_2Cl_2 and separated. The aqueous phase was extracted with an additional 2 × 100 mL of CH_2Cl_2, and the combined organic phases were washed 1 × 100 mL of water and 1 × 100 mL of saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford a brown oil. Purification by column chromatography on silica gel afforded the product.

2. Experimental Procedures and Characterization of Products

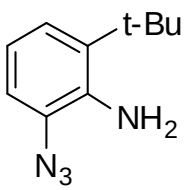
2-Azido-4,6-dimethylaniline (2a)



2a

Typical procedure: Substrate **1a** (60.5 mg, 0.5 mmol) and CuBr (7.2 mg, 0.05 mmol) were added to a 20 mL Schlenk tube under Ar, followed by addition of $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), CH_3CN (2.0 mL). The formed mixture was stirred at 30 ºC under Ar (1 atm) for 2 h as monitored by TLC. The solution was then diluted with ethyl acetate (15 mL), and evaporated under vaccum. The crude product was purified by column chromatography on silica gel to afford 55.1 mg (68%) of product **2a** (petroleum ether : ethyl acetate = 60:1, Rf = 0.3). **2a**: brown solid; IR: (KBr) ν_{max} 3421, 3322, 2108, 1632, 1498, 1318, 1265, 833 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.74 (s, 1 H), 6.69 (s, 1 H), 3.62 (br s, 2 H), 2.25 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 133.8, 128.0, 127.6 124.7, 123.6, 116.3, 20.5, 17.2; HRMS *m/z* (ESI) calcd. for $C_8H_{11}N_4$ $(M + H)^+$ 163.0978, found 163.0979.

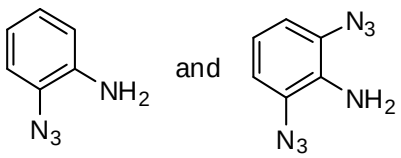
2-Azido-6-*tert*-butylaniline (2b)



2b

The reaction of 2-*tert*-butylaniline **1b** (74.5 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 4 h as monitored by TLC afforded 64.9 mg (68%) of **2b** (petroleum ether : ethyl acetate = 60:1, Rf = 0.4). **2b**: brown liquid; IR: (KBr) ν_{max} 3503, 3395, 2115, 1614, 1470, 1446, 1294, 732 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 1 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 6.79 (t, *J* = 8.0 Hz, 1 H), 4.10 (br s, 2 H), 1.44 (s, 9 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 136.3, 134.7, 126.0, 123.0, 118.1, 116.0, 34.4, 29.3; HRMS *m/z* (ESI) calcd. for $C_{10}H_{15}N_4$ $(M + H)^+$ 191.1291, found 191.1292.

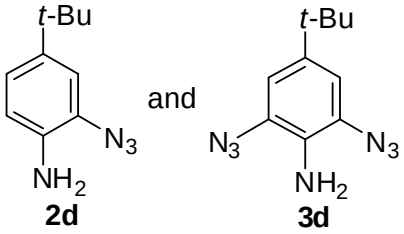
2-Azidoaniline (2c)[2] and 2,6-diazidoaniline (3c)



2c **3c**

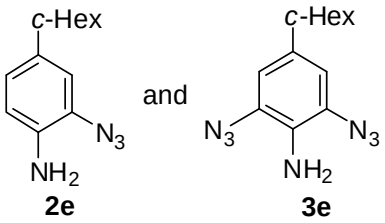
The reaction of aniline **1c** (46.5 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 4 h as monitored by TLC afforded 31.0 mg (46%) of **2c** (petroleum ether : ethyl acetate = 30:1, Rf = 0.3) and 23.6 mg (27%) of **3c** (petroleum ether : ethyl acetate = 60:1, Rf = 0.3). **2c**: brown solid; IR: (KBr) ν_{max} 3734, 3669, 2117, 1618, 1447, 1388, 872 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.6 Hz, 1 H), 6.97 (t, *J* = 7.2 Hz, 1 H), 6.80 (t, *J* = 7.6 Hz, 1 H), 6.70 (d, *J* = 7.6 Hz, 1 H), 3.81 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.1, 125.6, 125.2, 119.1, 118.4, 115.9; MS (EI) *m/z* (relative intensity) 134.1 (100) $[M]^+$. **3c**: brown solid; IR: (KBr) ν_{max} 3445, 3335, 2126, 1587, 1486, 1465, 1286, 764 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.86-6.78 (m, 3 H), 3.94 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 130.1, 126.0, 118.4, 114.5; HRMS *m/z* (ESI) calcd. for $C_6H_6N_7$ $(M + H)^+$ 176.0679, found 176.0681.

2-Azido-4-*tert*-butylaniline (2d) and 2, 6-diazido-4-*tert*-butylaniline (3d)



The reaction of 4-*tert*-butylaniline **1d** (74.5 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 2 h as monitored by TLC afforded 28.4 mg (30%) of **2d** (petroleum ether : ethyl acetate = 60:1, Rf = 0.1) and 63.2 mg (55%) of **3d** (petroleum ether : ethyl acetate = 60:1, Rf = 0.3). **2d**: brown liquid; IR: (KBr) ν_{max} 3469, 3373, 2111, 1620, 1515, 1304, 815 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.04 (s, 1 H), 6.99 (dd, *J* = 8.2 Hz, 1 H), 6.65 (d, *J* = 8.2 Hz, 1 H), 3.69 (br s, 2 H), 1.30 (s, 9 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 142.5, 135.6, 124.6, 122.6, 115.7, 115.2, 34.2, 31.4; HRMS *m/z* (ESI) calcd. for $C_{10}H_{15}N_4$ $(M + H)^+$ 191.1291, found 191.1291. **3d**: brown liquid; IR: (KBr) ν_{max} 3484, 3381, 2110, 1580, 1512, 1279 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.85 (s, 2 H), 3.82 (br s, 2 H), 1.32 (s, 9 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 142.2, 127.8, 125.4, 111.6, 34.5, 31.3; HRMS *m/z* (ESI) calcd. for $C_{10}H_{14}N_7$ $(M + H)^+$ 232.1305, found 232.1308.

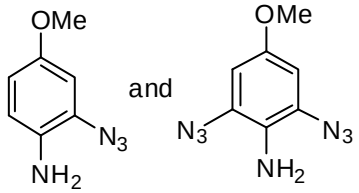
2-Azido-4-cyclohexylaniline (2e) and 2, 6-diazido-4-cyclohexylaniline (3e)



The reaction of 4-cyclohexylaniline **1e** (70.0 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 4 h as monitored by TLC afforded 26.4 mg (31%) of **2e** (petroleum ether : ethyl acetate = 60:1, Rf = 0.1) and 45.0 mg (44%) of **3e** (petroleum ether : ethyl acetate = 60:1, Rf = 0.3). **2e**: brown liquid; IR: (KBr) ν_{max} 3480, 3371, 2112, 1514, 1302, 814 cm^{-1}; ^1H

NMR: (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 1.6 Hz, 1 H), 6.81 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 6.64 (d, *J* = 8.0 Hz, 1 H), 3.67 (br s, 2 H), 2.45-2.39 (m, 1 H), 1.86-1.84 (m, 4 H), 1.76-1.73 (m, 1 H), 1.43-1.33 (m, 4 H), 1.29-1.22 (m, 1 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.5, 135.9, 124.9, 123.9, 116.6, 116.0, 43.8, 34.6, 26.9, 26.1; HRMS *m/z* (ESI) calcd. for $C_{12}H_{17}N_4$ $(M + H)^+$ 217.1448, found 217.1444. **3e**: brown liquid; IR: (KBr) ν_{max} 3413, 3326, 2132, 1591, 1508, 1433, 1276, 834 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.68 (s, 2 H), 3.80 (br s, 2 H), 2.46-2.41 (m, 1 H), 1.86 (d, *J* = 8.0 Hz, 4 H), 1.77-1.74 (m, 1 H), 1.44-1.33 (m, 4 H), 1.30-1.24 (m, 1 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.1, 128.0, 125.8, 112.9, 44.0, 34.5, 26.8, 26.0; HRMS *m/z* (ESI) calcd. for $C_{12}H_{16}N_7$ $(M + H)^+$ 258.1462, found 258.1459.

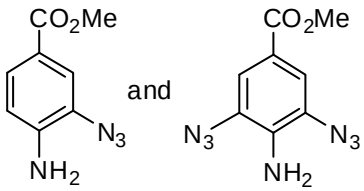
2-Azido-4-methoxyaniline (2f) and 2,6-diazido-4-methoxyaniline (3f)



2f **3f**

The reaction of 4-methoxyaniline **1f** (61.5 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 3 h as monitored by TLC afforded 19.0 mg (23%) of **2f** (petroleum ether : ethyl acetate = 10:1, Rf = 0.2) and 38.9 mg (38%) of **3f** (petroleum ether : ethyl acetate = 10:1, Rf = 0.4). **2f**: brown solid; IR: (KBr) ν_{max} 3739, 3289, 2107, 1589, 1514, 1451, 1251, 1235,1042, 825 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.66-6.62 (m, 2 H), 6.57-6.54 (m, 1 H), 3.76 (s, 3 H), 3.53 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.2, 131.8, 126.1, 117.0, 111.2, 104.6, 55.9; HRMS *m/z* (ESI) calcd. for $C_7H_9N_4O$ $(M + H)^+$ 165.0771, found 165.0773. **3f**: brown solid; IR: (KBr) ν_{max} 3431, 3318, 2117, 1587, 1509, 1280, 1062, 802 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.42 (s, 2 H), 3.77 (s, 3 H), 3.61 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.6, 126.8, 124.0, 100.8, 55.9; HRMS *m/z* (ESI) calcd. for $C_7H_8N_7O$ $(M + H)^+$ 206.0785, found 206.0788.

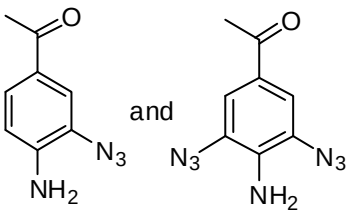
Methyl 4-amino-3-azidobenzoate (2g) and methyl 4-amino-3,5-diazidobenzoate (3g)



2g **3g**

The reaction of methyl 4-aminobenzoate **1g** (75.5 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 50 ºC for 36 h as monitored by TLC afforded 40.0 mg (42%) of **2g** (petroleum ether : ethyl acetate = 10:1, Rf = 0.2) and 24.4 mg (21%) of **3g** (petroleum ether : ethyl acetate = 10:1, Rf = 0.4). **2g**: brown solid; IR: (KBr) ν_{max} 3473, 3366, 2116, 1685, 1617, 1265, 764 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.70 (s, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 6.64 (d, *J* = 8.4 Hz, 1 H), 4.27 (br s, 2 H), 3.87 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 166.4, 142.5, 127.8, 124.5, 120.1, 119.8, 114.2, 51.8; HRMS *m/z* (ESI) calcd. for $C_8H_9N_4O_2$ $(M + H)^+$ 193.0720, found 193.0723. **3g**: brown solid; IR: (KBr) ν_{max} 3487, 3385, 2112, 1606, 1587, 1437, 1267, 1010, 759 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.53 (s, 2 H), 4.38 (br s, 2 H), 3.90 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.8, 134.2, 125.1, 119.6, 116.1, 52.1; HRMS *m/z* (ESI) calcd. for $C_8H_7N_7NaO_2$ $(M + Na)^+$ 256.0553, found 256.0559.

1-(4-Amino-3-azidophenyl)ethanone (2h) and 1-(4-amino-3,5-diazidophenyl) ethanone (3h)

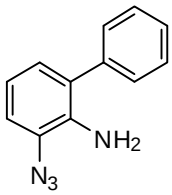


2h **3h**

The reaction of 1-(4-aminophenyl)ethanone **1h** (67.6 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 16 h as monitored by TLC afforded 41.7 mg (45%) of **2h** (petroleum ether :

ethyl acetate = 10:1, Rf = 0.2) and 9.6 mg (9%) of **3h** (petroleum ether : ethyl acetate = 10:1, Rf = 0.3). **2h**: brown solid; IR: (KBr) ν_{max} 3447, 3334, 2133, 1654, 1630, 1587, 1321, 1247, 886, 814 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.69 (s, 1 H), 7.58 (d, *J* = 7.2 Hz, 1 H), 6.66 (d, *J* = 8.0 Hz, 1 H), 4.32 (br s, 2 H), 2.52 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 195.7, 142.8, 128.2, 127.4, 125.0, 118.4, 113.9, 26.0; HRMS *m/z* (ESI) calcd. for $C_8H_9N_4O$ $(M + H)^+$ 177.0771, found 177.0772. **3h**: brown solid; IR: (KBr) ν_{max} 3475, 3324, 2115, 1611, 1514, 1248, 743, 708 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.47 (s, 2 H), 4.45 (br s, 2 H), 2.55 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 195.0, 134.6, 127.4, 125.2, 115.1, 26.1; HRMS *m/z* (ESI) calcd. for $C_8H_8N_7O$ $(M + H)^+$ 218.0785, found 218.0787.

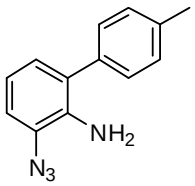
3-Azidobiphenyl-2-amine (2i)



2i

The reaction of biphenyl-2-amine **1i** (85.0 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 3 h as monitored by TLC afforded 71.4 mg (68%) of **2i** (petroleum ether : ethyl acetate = 60:1, Rf = 0.4). **2i**: brown solid; IR: (KBr) ν_{max} 3471, 3380, 2103, 1612, 1467, 757, 702 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 4 H), 7.38-7.35 (m, 1 H), 7.06 (d, *J* = 7.6 Hz, 1 H), 6.95 (d, *J* = 6.8 Hz, 1 H), 6.85 (t, *J* = 8.0 Hz, 1 H), 3.94 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.8, 135.6, 128.95, 128.90, 128.5, 127.5, 126.8, 125.3, 118.3, 117.3; HRMS *m/z* (ESI) calcd. for $C_{12}H_{11}N_4$ $(M + H)^+$ 211.0978, found 211.0975.

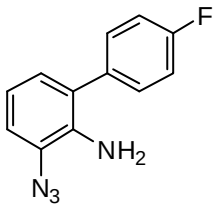
3-Azido-4'-methylbiphenyl-2-amine (2j)



2j

The reaction of 4'-methylbiphenyl-2-amine **1j** (73.2 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 5 h as monitored by TLC afforded 46.9 mg (53%) of **2j** (petroleum ether : ethyl acetate = 60:1, Rf = 0.6). **2j**: brown liquid; IR: (KBr) ν_{max} 3480, 3380, 2107, 1610, 1467, 1297, 821, 775, 732 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.06 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 6.95 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 6.86 (t, *J* = 8.0 Hz, 1 H), 3.96 (br s, 2 H), 2.43 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.2, 135.7, 135.6, 129.5, 128.7, 128.4, 126.7, 125.1, 118.3, 117.1, 21.1; HRMS *m/z* (ESI) calcd. for $C_{13}H_{13}N_4$ $(M + H)^+$ 225.1135, found 225.1136.

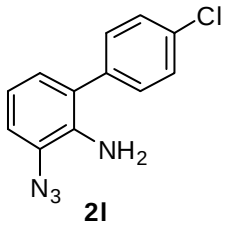
3-Azido-4'-fluorobiphenyl-2-amine (2k)



2k

The reaction of 4'-fluorobiphenyl-2-amine **1k** (74.8 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 10 h as monitored by TLC afforded 60.9 mg (67%) of **2k** (petroleum ether : ethyl acetate = 60:1, Rf = 0.2). **2k**: brown liquid; IR: (KBr) ν_{max} 3475, 3378, 2109, 1604, 1509, 1467, 1231, 839, 777, 733 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2 H), 7.16-7.12 (m, 2 H), 7.05 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 6.91 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 6.84 (t, *J* = 8.0 Hz, 1 H), 3.90 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.9 Hz), 135.6, 134.6 (d, *J* = 3.4 Hz), 130.6 (d, *J* = 8.4 Hz), 127.4, 126.7, 125.4, 118.4, 117.4, 115.8 (d, *J* = 21.1 Hz); HRMS *m/z* (ESI) calcd. for $C_{12}H_{10}FN_4$ $(M + H)^+$ 229.0884, found 229.0884.

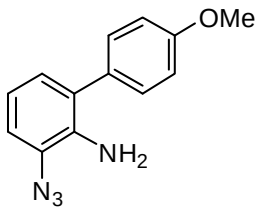
3-Azido-4'-chlorobiphenyl-2-amine (2l)



2l

The reaction of 4'-chlorobiphenyl-2-amine **1l** (81.2 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 10 h as monitored by TLC afforded 62.0 mg (64%) of **2l** (petroleum ether : ethyl acetate = 60:1, Rf = 0.2). **2l**: brown liquid; IR: (KBr) ν_{max} 3478, 3382, 2110, 1613, 1466, 1299, 1236, 1090, 829, 733 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 4 H), 7.06 (d, *J* = 7.2 Hz, 1 H), 6.90 (d, *J* = 6.4 Hz, 1 H), 6.84 (t, *J* = 7.2 Hz, 1 H), 3.90 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.1, 135.5, 133.5, 130.3, 129.1, 127.1, 126.6, 125.5, 118.5, 117.6; HRMS *m/z* (ESI) calcd. for $C_{12}H_{10}ClN_4$ $(M + H)^+$ 245.0589, found 245.0590.

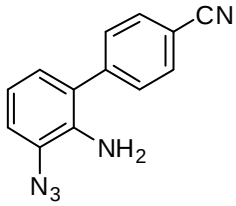
3-Azido-4'-methoxybiphenyl-2-amine (2m)



2m

The reaction of 4'-methoxybiphenyl-2-amine **1m** (79.6 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 5 h as monitored by TLC afforded 41.0 mg (43%) of **2m** (petroleum ether : ethyl acetate = 40:1, Rf = 0.3). **2m**: brown liquid; IR: (KBr) ν_{max} 3478, 3371, 2106, 1609, 1512, 1466, 832, 777, 734 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2 H), 7.03 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 7.00-6.98 (m, 2 H), 6.92 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 6.83 (t, *J* = 8.0 Hz, 1 H), 3.92 (br s, 2 H), 3.86 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.0, 135.7, 131.0, 130.1, 128.2, 126.8, 125.2, 118.3, 117.0, 114.3, 55.3; HRMS *m/z* (ESI) calcd. for $C_{13}H_{13}N_4O$ $(M + H)^+$ 241.1084, found 241.1084.

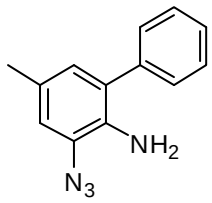
2'-Amino-3'-azidobiphenyl-4-carbonitrile (2n)



2n

The reaction of 2'-aminobiphenyl-4-carbonitrile **1n** (77.6 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 10 h as monitored by TLC afforded 51.7 mg (55%) of **2n** (petroleum ether : ethyl acetate = 10:1, Rf = 0.4). **2n**: brown solid; IR: (KBr) ν_{max} 3467, 3369, 2227, 2111, 1610, 1466, 844, 777, 734 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.09 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 6.92-6.85 (m, 2 H), 3.93 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.7, 132.7, 129.7, 126.4, 126.2, 118.72, 118.67, 118.3, 111.3; HRMS *m/z* (ESI) calcd. for $C_{13}H_{10}N_5$ $(M + H)^+$ 236.0931, found 236.0931.

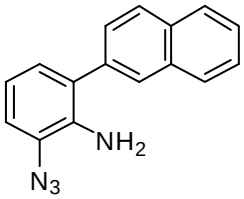
3-Azido-5-methylbiphenyl-2-amine (2o)



2o

The reaction of 5-methylbiphenyl-2-amine **1o** (73.2 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 5 h as monitored by TLC afforded 46.3 mg (52%) of **2o** (petroleum ether : ethyl acetate = 60:1, Rf = 0.4). **2o**: brown liquid; IR: (KBr) ν_{max} 3474, 3380, 2103, 1589, 1484, 1444, 1263, 845, 770, 704 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 4 H), 7.39-7.30 (m, 1 H), 6.87 (s, 1 H), 6.77 (s, 1 H), 3.79 (br s, 2 H), 2.31 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.9, 133.1, 128.9, 128.8, 128.6, 127.9, 127.5, 127.4, 125.2, 117.8, 20.5; HRMS *m/z* (ESI) calcd. for $C_{13}H_{13}N_4$ $(M + H)^+$ 225.1134, found 225.1130.

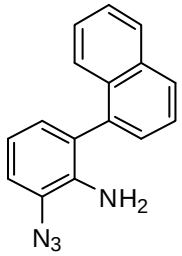
2-Azido-6-(naphthalen-2-yl)aniline (2p)



2p

The reaction of 2-(naphthalen-2-yl)aniline **1p** (87.6 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 5 h as monitored by TLC afforded 70.7 mg (68%) of **2p** (petroleum ether : ethyl acetate = 40:1, Rf = 0.5). **2p**: brown solid; IR: (KBr) ν_{max} 3479, 3377, 2117, 1610, 1465, 1297, 732 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.95-7.89 (m, 4 H), 7.59-7.54 (m, 3 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 6.91 (t, *J* = 7.2 Hz, 1 H), 4.01 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 136.1, 135.7, 133.6, 132.6, 128.5, 128.3, 128.0, 127.8, 127.7, 127.01, 126.95, 126.4, 126.2, 125.3, 118.4, 117.4; HRMS *m/z* (ESI) calcd. for $C_{16}H_{13}N_4$ $(M + H)^+$ 261.1135, found 261.1136.

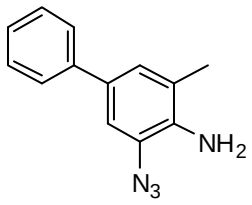
2-Azido-6-(naphthalen-1-yl)aniline (2q)



2q

The reaction of 2-(naphthalen-1-yl)aniline **1q** (87.6 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 5 h as monitored by TLC afforded 55.9 mg (54%) of **2q** (petroleum ether : ethyl acetate = 60:1, Rf = 0.6). **2q**: brown solid; IR: (KBr) ν_{max} 3478, 3380, 2112, 1609, 1465, 1297, 801, 778, 733 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 8.0 Hz, 2 H), 7.63-7.43 (m, 5 H), 7.16 (d, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 8.0 Hz, 1 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 3.67 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 136.4, 136.0, 133.8, 131.4, 128.3, 128.2, 127.6, 127.5, 126.7, 126.4, 126.1, 125.76, 125.74, 125.0, 118.1, 117.6; HRMS *m/z* (ESI) calcd. for $C_{16}H_{13}N_4$ $(M + H)^+$ 261.1135, found 261.1136.

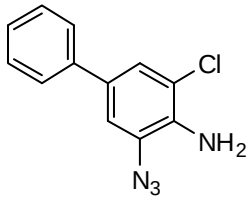
3-Azido-5-methylbiphenyl-4-amine (2r)



2r

The reaction of 3-methylbiphenyl-4-amine **1r** (73.2 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 5 h as monitored by TLC afforded 51.1 mg (57%) of **2r** (petroleum ether : ethyl acetate = 20:1, Rf = 0.3). **2r**: brown liquid; IR: (KBr) ν_{max} 3491, 3395, 2108, 1619, 1595, 1483, 1255, 852, 761, 701 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2 H), 7.44-7.42 (m, 2 H), 7.33-7.31 (m, 1 H), 7.18-7.12 (m, 2 H), 3.83 (br s, 2 H), 2.24 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.6, 135.8, 131.7, 128.7, 126.7, 126.5, 125.7, 125.2, 123.6, 114.5, 17.5; HRMS *m/z* (ESI) calcd. for $C_{13}H_{13}N_4$ $(M + H)^+$ 225.1134, found 225.1130.

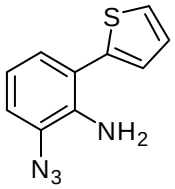
3-Azido-5-chlorobiphenyl-4-amine (2s)



2s

The reaction of 3-chlorobiphenyl-4-amine **1s** (81.2 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 10 h as monitored by TLC afforded 60.9 mg (63%) of **2s** (petroleum ether : ethyl acetate = 60:1, Rf = 0.4). **2s**: brown solid; IR: (KBr) ν_{max} 3469, 3380, 2107, 1613, 1564, 1480, 758, 697 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2 H), 7.44-7.41 (m, 2 H), 7.35-7.30 (m, 2 H), 7.16 (s, 1 H), 4.25 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.4, 134.5, 131.9, 128.9, 127.2, 126.4, 126.3, 124.2, 120.0, 115.2; HRMS *m/z* (ESI) calcd. for $C_{12}H_{10}ClN_4$ $(M + H)^+$ 245.0589, found 245.0590.

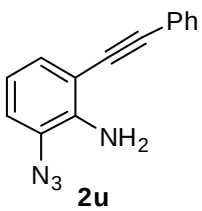
2-Azido-6-(thiophen-2-yl)aniline (2t)



2t

The reaction of 2-(thiophen-2-yl)aniline **1t** (70.0 mg, 0.4 mmol), CuBr (5.6 mg, 0.04 mmol), $TMSN_3$ (105.0 μL, 0.8 mmol), TBHP (146.0 μL, 5.5 M, 0.8 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 8 h as monitored by TLC afforded 58.3 mg (67%) of **2t** (petroleum ether : ethyl acetate = 60:1, Rf = 0.4). **2t**: brown liquid; IR: (KBr) ν_{max} 3469, 3365, 2117, 1608, 1464, 1057, 700 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 5.2 Hz, 1 H), 7.22 (d, *J* = 3.2 Hz, 1 H), 7.13 (dd, *J* = 8.4 Hz, 3.6 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.82 (t, *J* = 8.0 Hz, 1 H), 4.21 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.1, 136.1, 127.6, 127.2, 126.0, 125.6, 125.5, 120.8, 118.2, 117.7; HRMS *m/z* (ESI) calcd. for $C_{10}H_9N_4S$ $(M + H)^+$ 217.0542, found 217.0544.

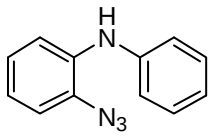
2-Azido-6-(phenylethynyl)aniline (2u)



2u

The reaction of 2-(phenylethynyl)aniline **1u** (96.5 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol), $TMSN_3$ (131.5 μL, 1.0 mmol), TBHP (182.5 μL, 5.5 M, 1 mmol), in CH_3CN (2.0 mL) under Ar (1 atm) at 30 ºC for 8 h as monitored by TLC afforded 67.0 mg (57%) of **2u** (petroleum ether : ethyl acetate = 20:1, Rf = 0.4). **2u**: brown liquid; IR: (KBr) ν_{max} 3481, 3380, 2116, 1605, 1468, 1295, 1239, 755, 727, 689 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 2 H), 7.35-7.30 (m, 3 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 6.98 (d, *J* = 7.6 Hz, 1 H), 6.71 (t, *J* = 8.0 Hz, 1 H), 4.42 (br s, 2 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.8, 131.5, 128.44, 128.41, 128.36, 124.8, 123.0, 118.4, 117.8, 108.8, 95.4, 85.1; HRMS *m/z* (ESI) calcd. for $C_{14}H_{11}N_4$ $(M + H)^+$ 235.0978, found 235.0979.

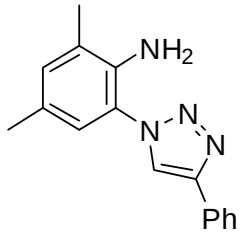
2-Azido-*N*-phenylaniline (2v)



2v

The reaction of diphenylamine **1v** (42.5 mg, 0.25 mmol), CuBr (3.6 mg, 0.025 mmol), $TMSN_3$ (65.5 μL, 0.5 mmol), TBHP (91.3 μL, 5.5 M, 0.5 mmol), in CH_3CN (1.0 mL) under Ar (1 atm) at 30 ºC for 6 h as monitored by TLC afforded 25.9 mg (49%) of **2v** (petroleum ether : ethyl acetate = 60:1, Rf = 0.5). **2v**: brown liquid; IR: (KBr) ν_{max} 3400, 2123, 1592, 1461, 1380, 743 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3 H), 7.15-7.11 (m, 3 H), 7.06-6.98 (m, 2 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 5.94 (br s, 1 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.9, 135.1, 129.4, 127.1, 125.3, 122.0, 120.5, 119.2, 118.5, 115.6; MS (EI) *m/z* (relative intensity) 210.2 (100) $[M]^+$; HRMS *m/z* (ESI) calcd. for $C_{12}H_{11}N_2$ $(M - N_2 + H)^+$ 183.0917, found 183.0914.

2,4-Dimethyl-6-(4-phenyl-1H-1,2,3-triazol-1-yl)aniline (4)

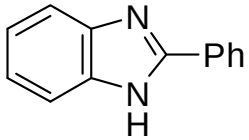


4

2-Azido-4,6-dimethylaniline (**2a**) (0.25 mmol, 40.5 mg, 1.0 equiv) and then phenylacetylene (0.3 mmol, 1.2 equiv) were suspended in a 1:1 mixture of water and *t*-BuOH (0.5 mL each) in a 10-mL one-neck round bottle equipped with a small magnetic stirring bar. To this was added copper sulfate (0.005 mmol, 1.25 mg) and sodium ascorbate solution (0.025 mmol, 4.95 mg). The mixture was stirred for 12 h at room temperature, after which time TLC analysis indicated complete consumption of starting materials. The solvent was distilled, water (20 mL) was added, and the mixture was extracted with dichloromethane. The organic layer was separated, washed with brine (20 mL) and saturation $NaHCO_3$ (20 ml), anhydrous $MgSO_4$ dried. The solvent was evaporated to afford crude product, which was further purified by alumina column chromatography to offer 56.3 mg (85 %) product **4** as a yellow solid. ^1H NMR: (400 MHz, $CDCl_3$) δ 8.02 (s, 1 H), 7.92-7.88 (m, 2 H), 7.47-

7.42 (m, 2 H), 7.38-7.33 (m, 1 H), 6.99 (s ,1 H), 6.95 (s, 1 H), 4.33 (br s, 2 H), 2.27 (s, 3 H), 2.23 (s, 3 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 147.5, 136.7, 132.0, 130.2, 128.8, 128.3, 127.0, 125.7, 124.7, 122.8, 122.6, 120.6, 20.1, 17.6. HRMS *m/z* (ESI) calcd. for $C_{16}H_{17}N_4$ $(M + H)^+$ 265.1448, found 265.1446.

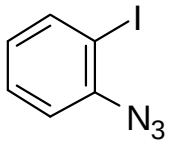
2-Phenyl-1H-benzo[d]imidazole (5) [2]



5

To a solution of 0.067 g of 2-azidoaniline (**2c)** (0.50 mmol) and 0.056 mL of benzaldehyde (0.60 mmol) in 0.5 mL of CH_2Cl_2 was added 0.20 g of anhydrous $MgSO_4$. The mixture was stirred at room temperature. After 36 h, the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. To the unpurified product, 0.032 g of $FeBr_2$ (0.15 mmol), 0.167 g of crushed 4Å molecular sieves, and 0.50 mL of CH_2Cl_2 was added. The resulting mixture was heated to 40 °C. After 12 h, the reaction mixture was cooled to room temperature, and the heterogenous mixture was filtered through SiO_2. The filtrate was concentrated *in vacuo*. Purification by column chromatography on silica gel provided the benzimidazole **5** as a white solid (0.068 g, 70%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.88 (br s, 1H), 8.18 (d, J = 8.0 Hz, 2H), 7.60–7.47 (m, 5H), 7.21–7.19 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 151.2, 143.8, 135.0, 130.2, 129.8, 128.9, 126.4, 122.5, 121.6, 118.9, 111.3; MS (EI) *m/z* (relative intensity) 194.1 (100) $[M]^+$.

1-Azido-2-iodobenzene (6) [3]

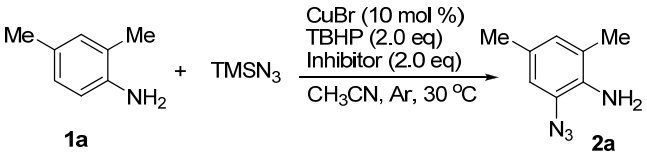


To a solution of *p*-TsOH·H_2O (286.5 mg, 1.5 mmol) in MeCN (2 mL) was added 2-azidoaniline **(2c)** (67 mg, 0.5 mmol). The resulting suspension of amine salt was cooled to 5-10 °C and to this was added,

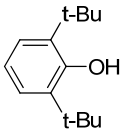
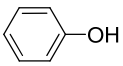
gradually, a solution of $NaNO_2$ (69 mg, 1 mmol) and KI (207.5 mg, 1.25 mmol) in H_2O (0.3 mL). The reaction mixture was stirred for 10 min then allowed to come to 20 °C and stirred for 30 min. To the reaction mixture was then added H_2O (10 mL), $NaHCO_3$ (1 M; until pH = 9-10) and $Na_2S_2O_3$ (2 M, 1 mL). The crude product was extracted EtOAc and purified by flash chromatography (hexane) to offer 90 mg (73%) product **6** as a colorless oil. IR: (KBr) ν_{max} 2131, 2109, 2092, 1577, 1466, 1305, 1289 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.0 Hz, 1.0 Hz, 1 H), 7.38 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.0 Hz, 1 H), 7.13 (dd, *J* = 8.0 Hz, 1.0 Hz, 1 H), 6.86 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.0 Hz, 1 H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.6, 140.0, 129.5, 126.2, 118.4, 87.8. MS (EI) *m/z* (relative intensity) 245.1 (100) $[M]^+$.

3. Mechanistic Study

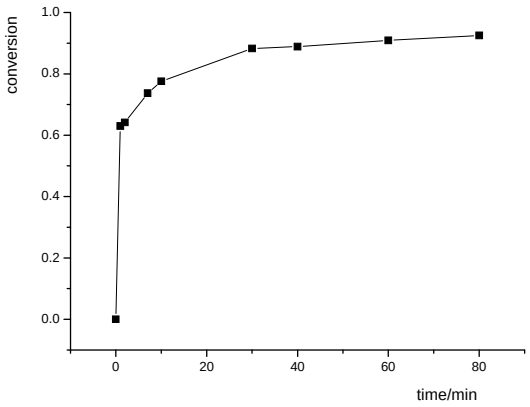
Radical Inhibition Experiments



1a **2a**

Inhibitor (2.0 eq)	result
	trace
	trace

The reaction rate order has been determined. The azidation of substrate **1a** under the standard conditions at different reaction time was tested. The conversion was measured by GC.

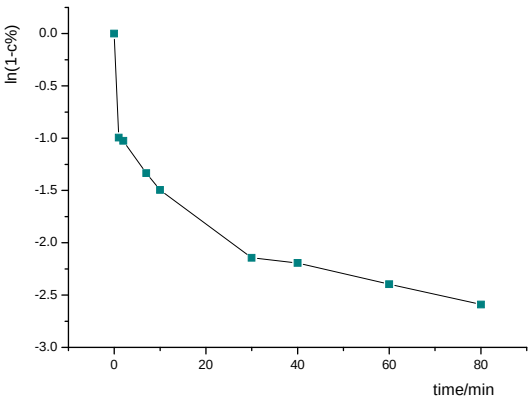


Plot of conversion versus reaction time.

According to the equation of a first order reaction, the plot of ln(1-c%) versus time gives a straight line. The plot obtained under standard conditions was not in good agreement with equation S5, which indicates that the reaction is not a first order reaction.

$$\ln(1-c\%) = -kt \qquad \textbf{(equation S5)}$$

c%: conversion



Moreover, the electronic effects show that electron-withdrawing group decelerates the reaction, because anilines bearing electron-withdrawing groups always need longer reaction time and higher reaction temperature.

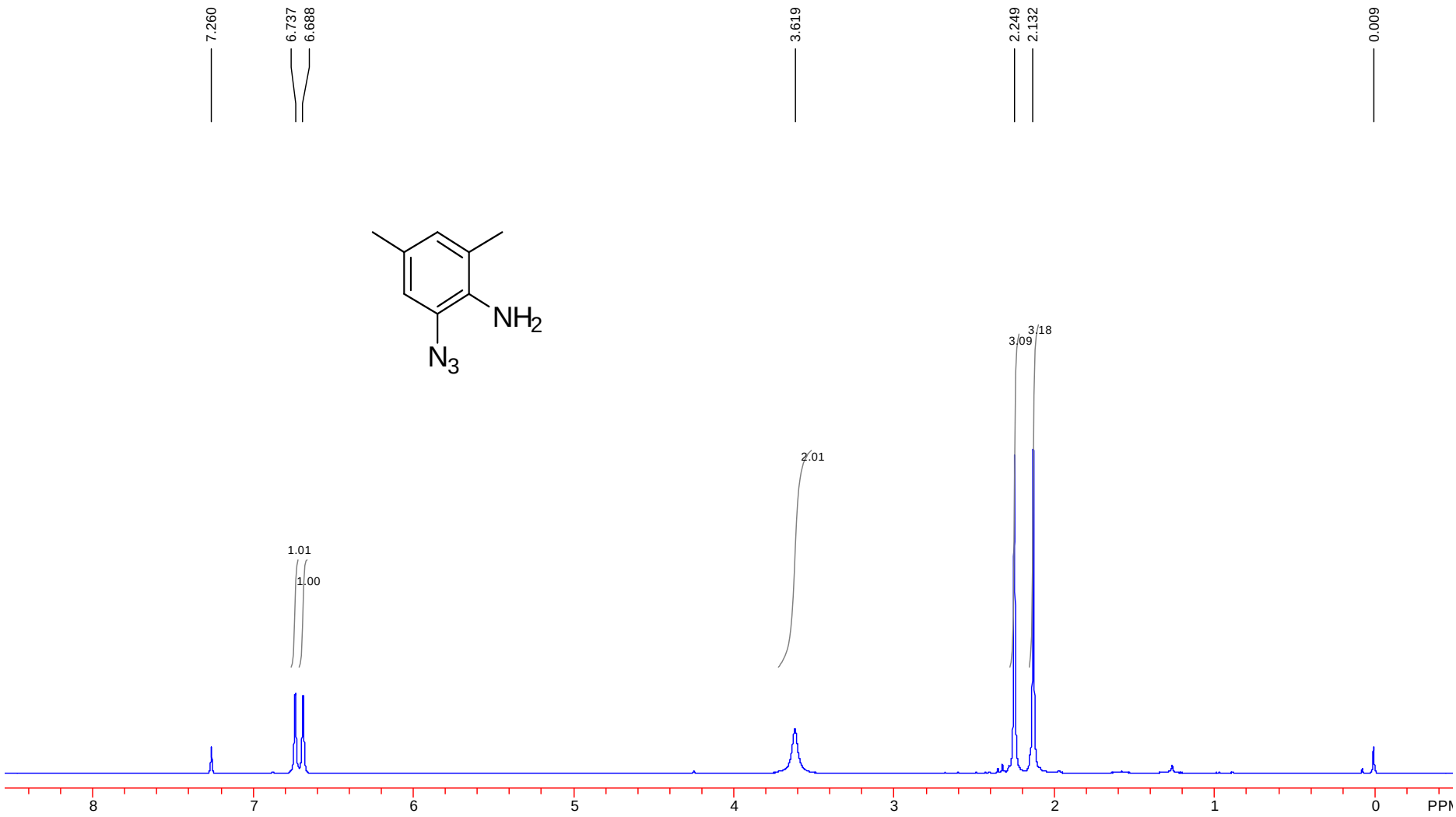
4. References

1. For recent examples of anilines employed as substrates in the Suzuki reaction, see: (a) Miura, Y.; Nishi, T.; Teki, Y. *J. Org. Chem.* **2003**, *68*, 10158. (b) Camacho, D. H.; Salo, E. V.; Guan, Z. *Org. Lett.* **2004**, *6*, 865. (c) Wu, Y.; Li, J.; Fu, Y.; Bo, Z. *Org. Lett.* **2004**, *6*, 3485. (d) Miura, Y.; Muranaka, Y.; Teki, Y. *J. Org. Chem.* **2006**, *71*, 4786. (e) Arnold, L. A.; Kiplin Guy, R. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5360.

2. Shen, M.; Driver, T. G. *Org. Lett.* **2008**, *10*, 3367.

3. Smith, C. J.; Smith, C. D.; Nikbin, N.; Ley, S. V.; Baxendale, I. R. *Org. Biomol. Chem.* **2011**, *9*, 1927.

4. Pinto, A; Neuville, L; Retailleau, P; Zhu, J. *Org. Lett.* **2006**, *8*, 4927.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3.18
8
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6
5
4
3
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1
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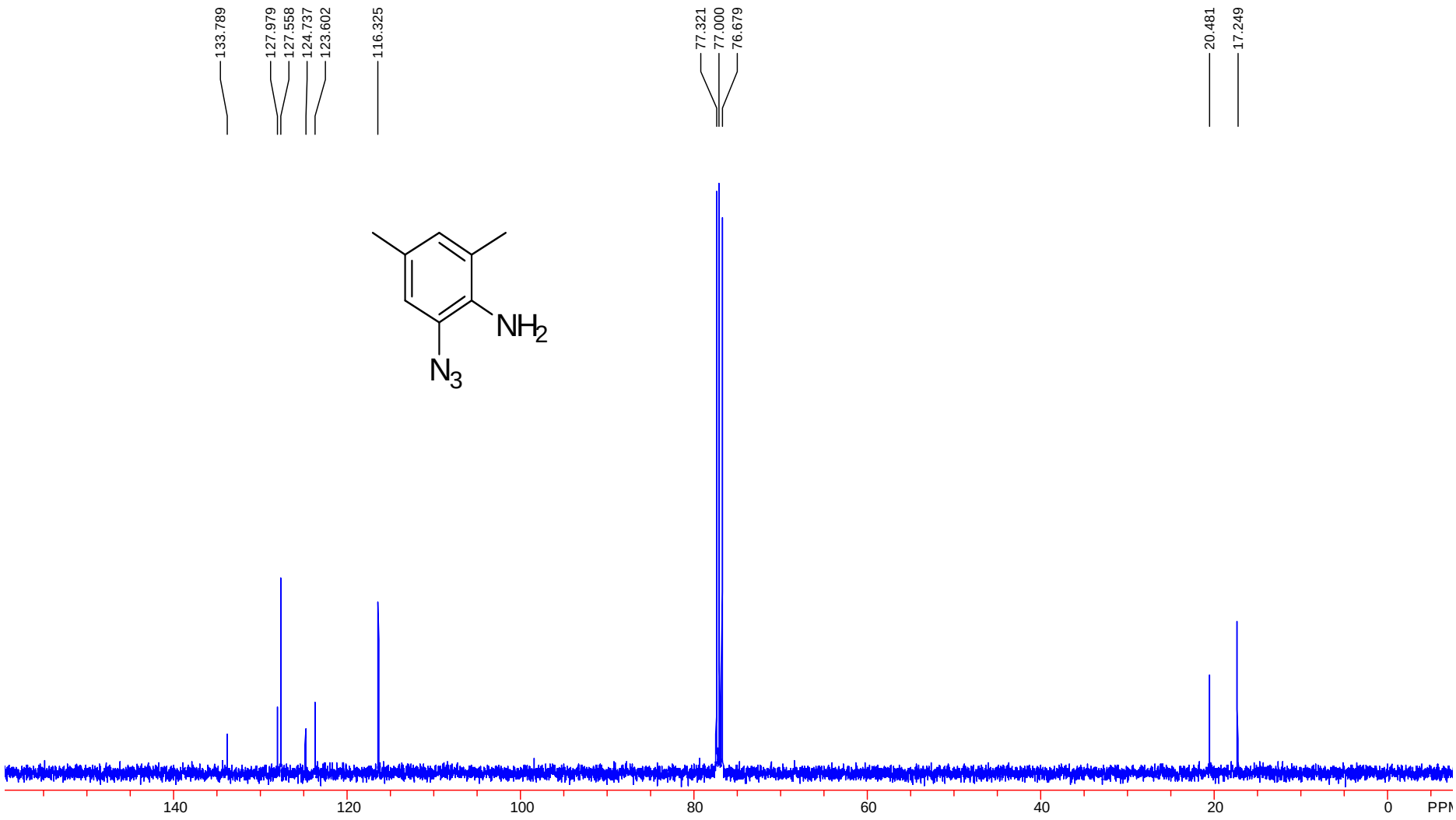
PPM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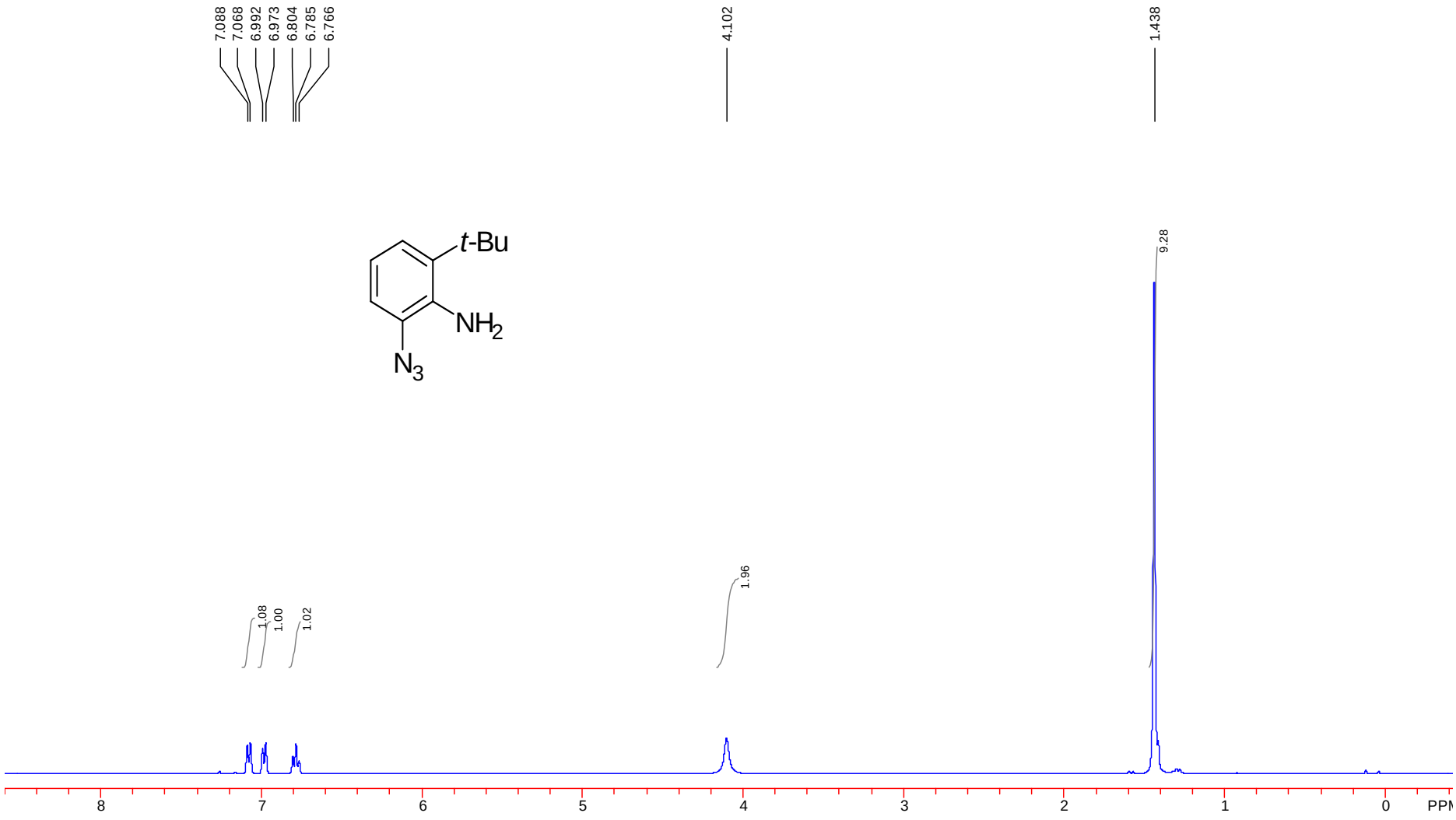
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1.08
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1.02
8
7
6
5
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1
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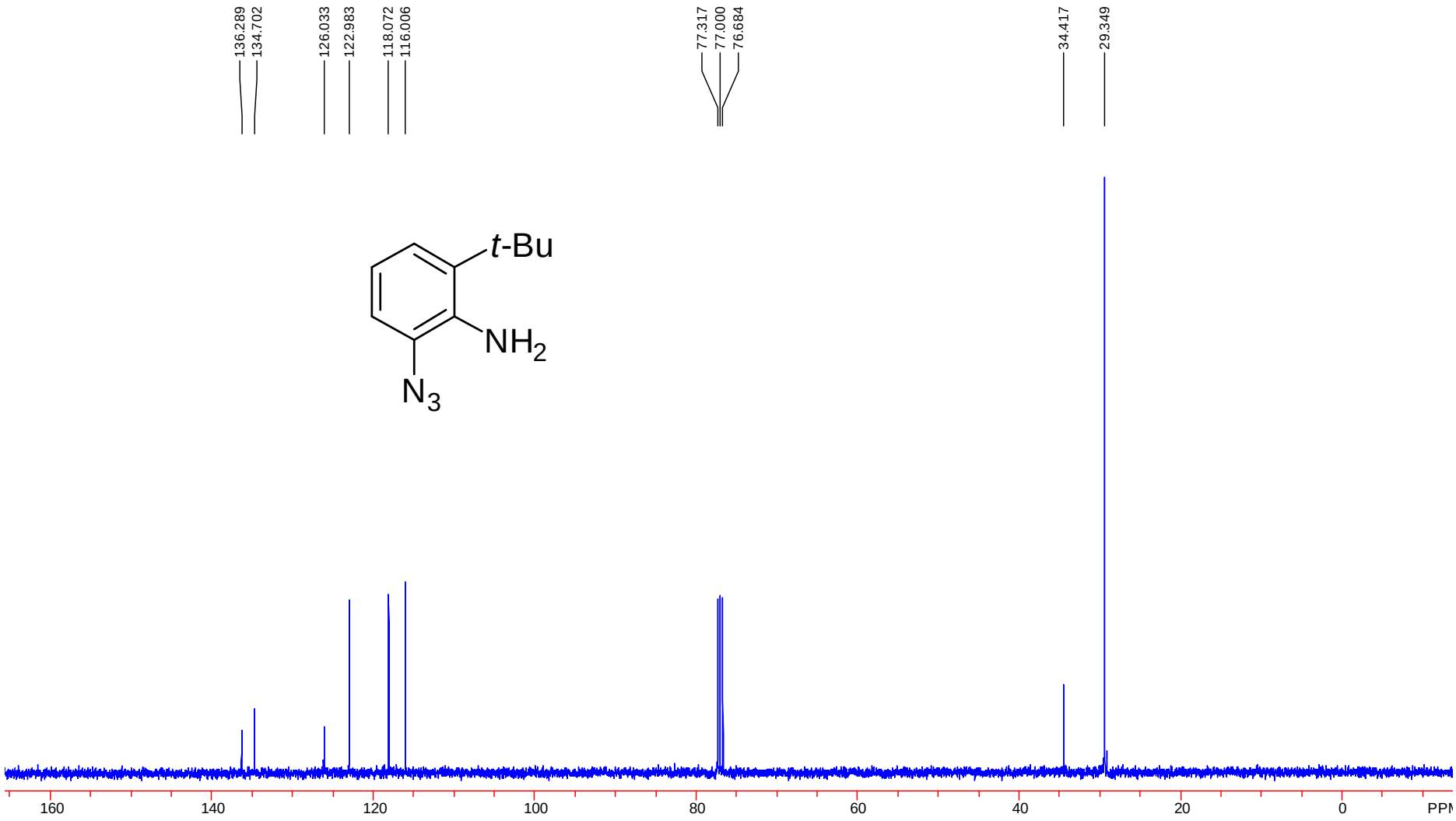
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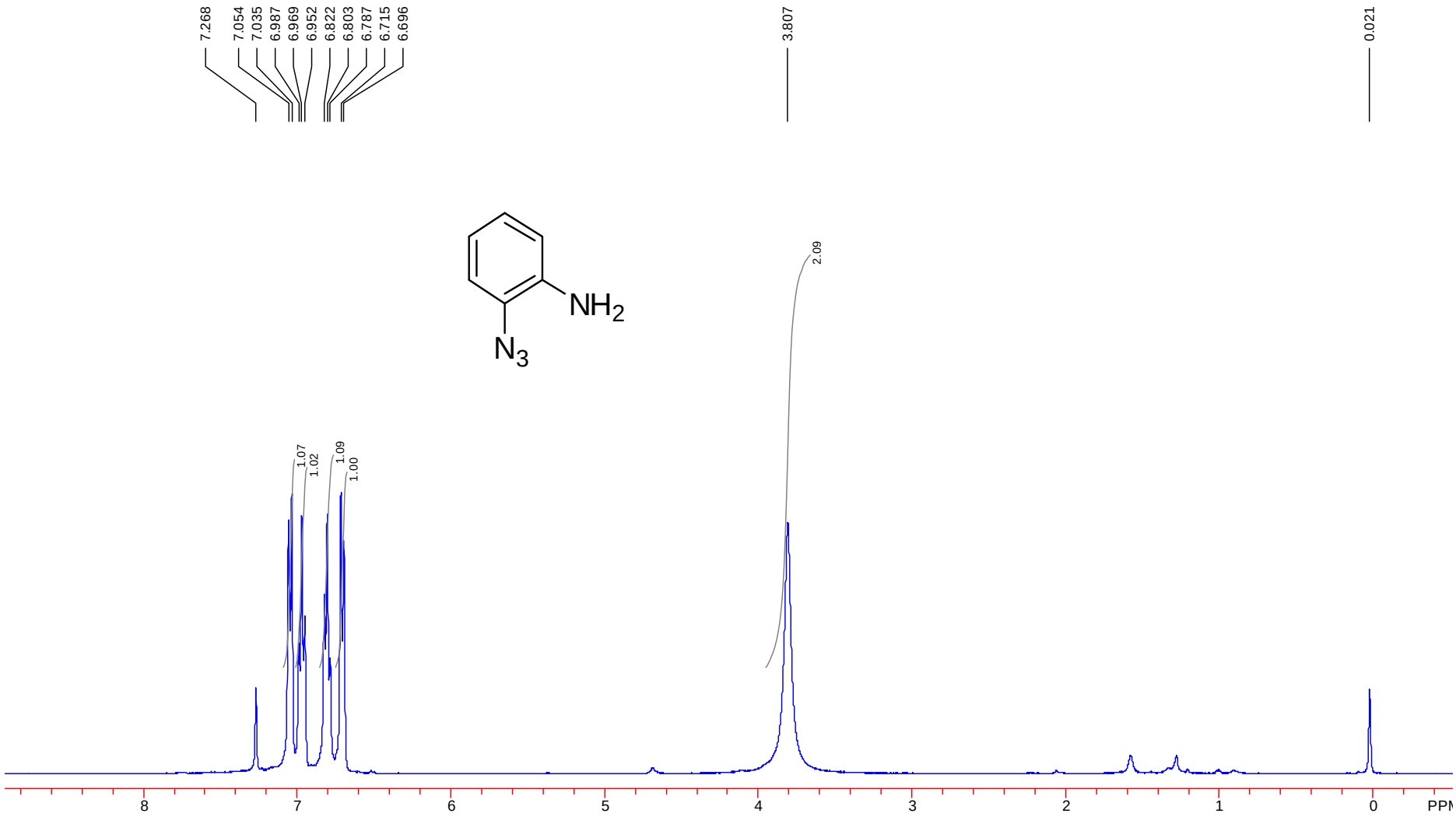
PPM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1.07
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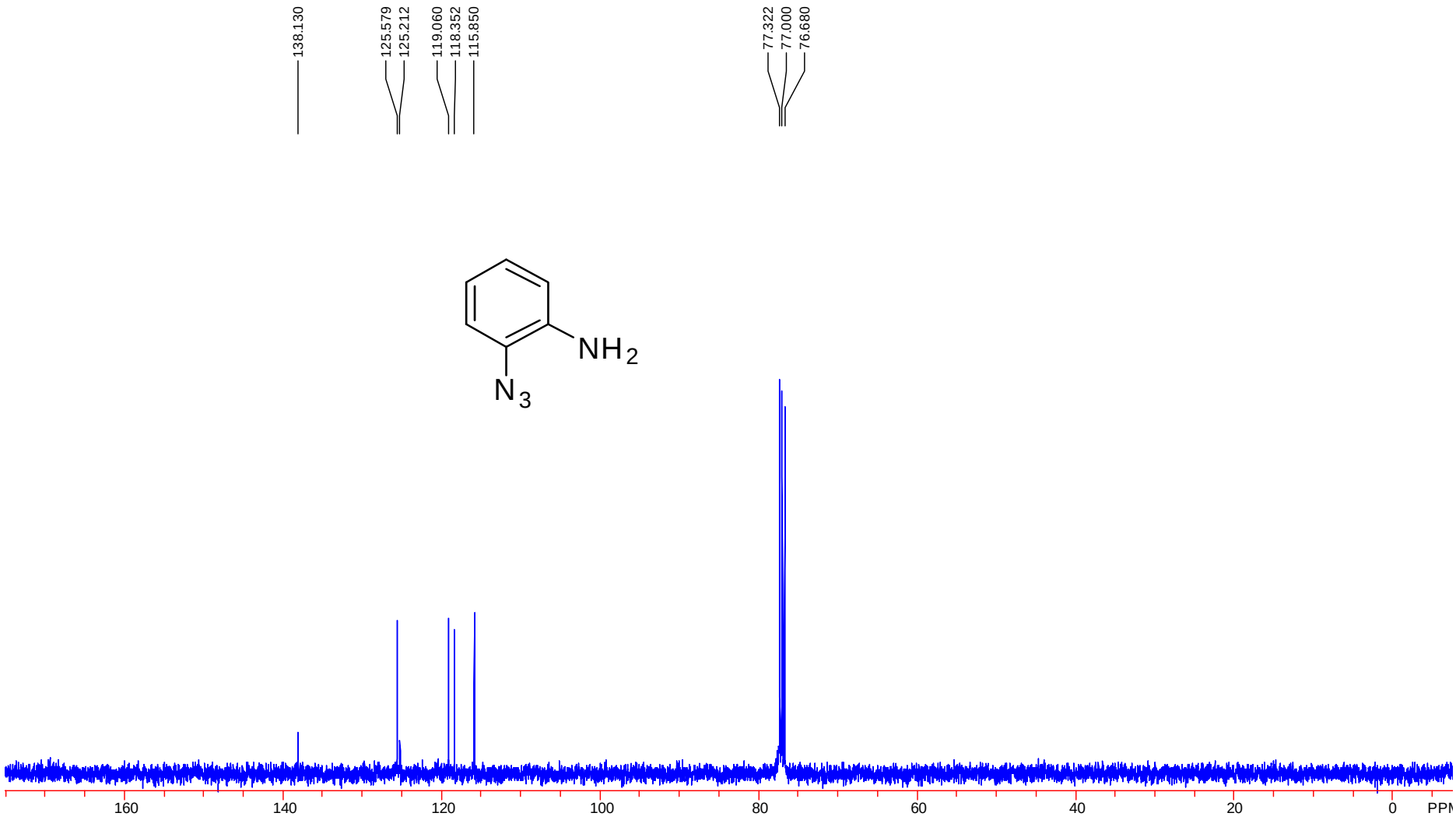
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40
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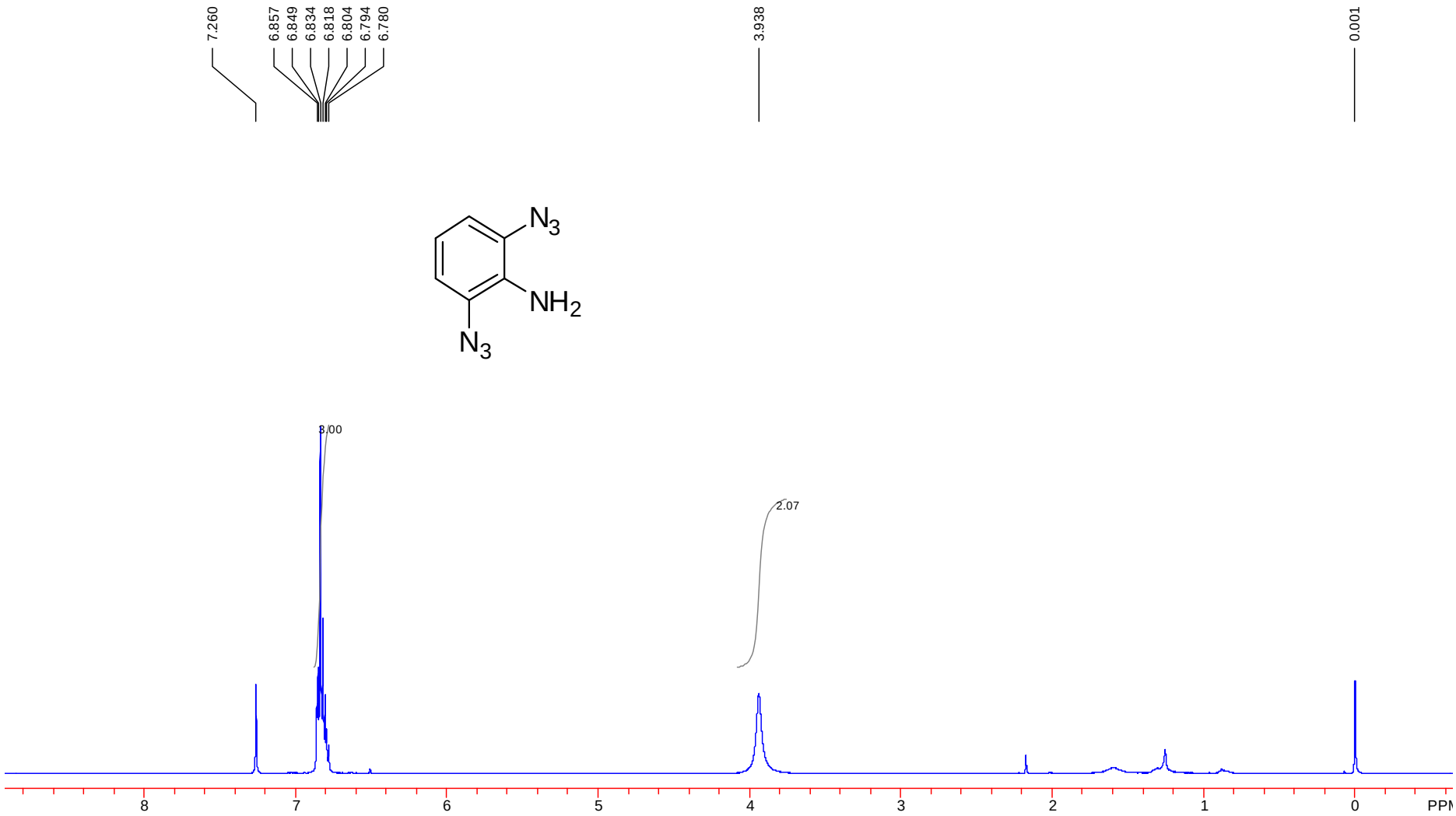
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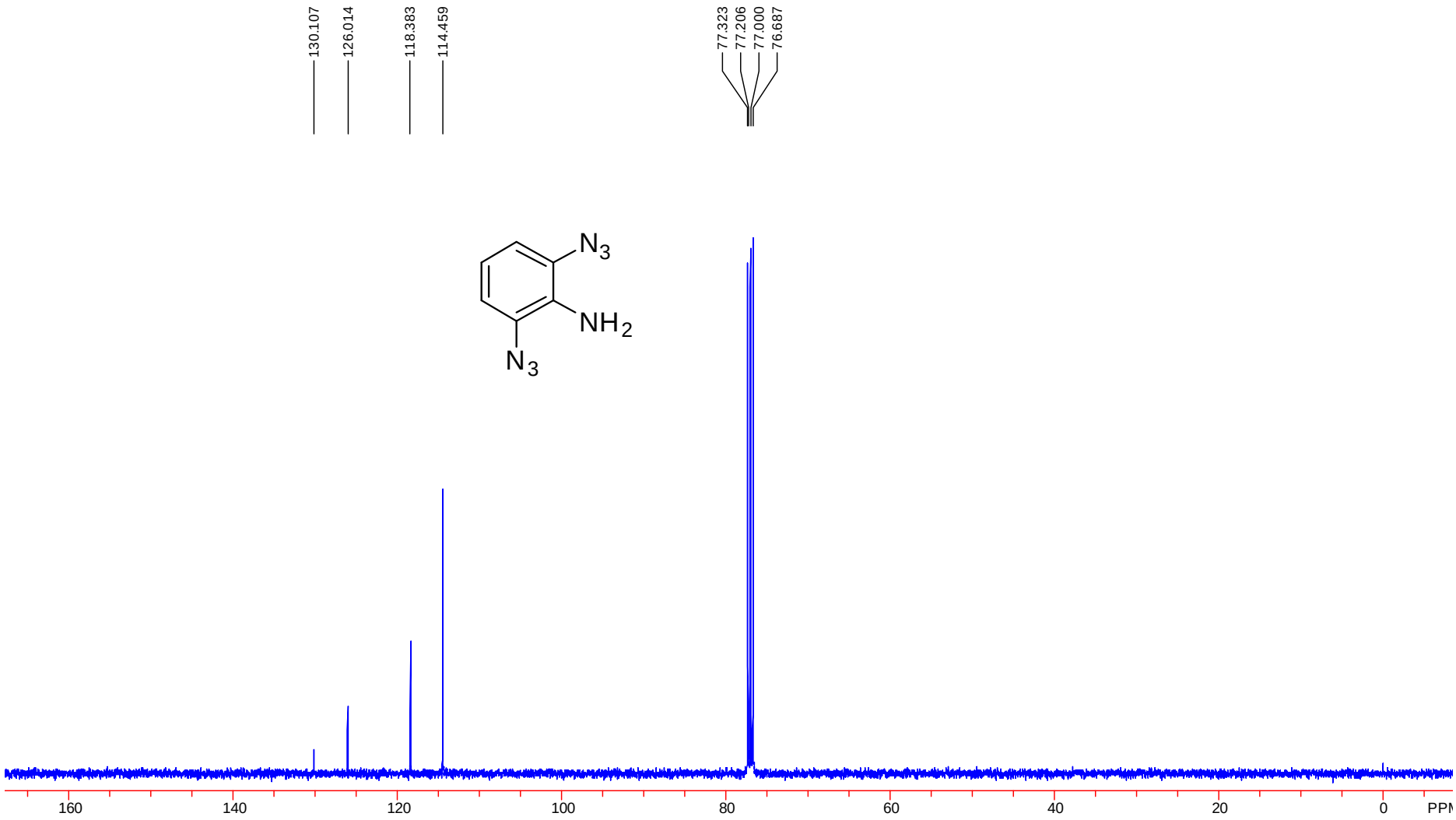
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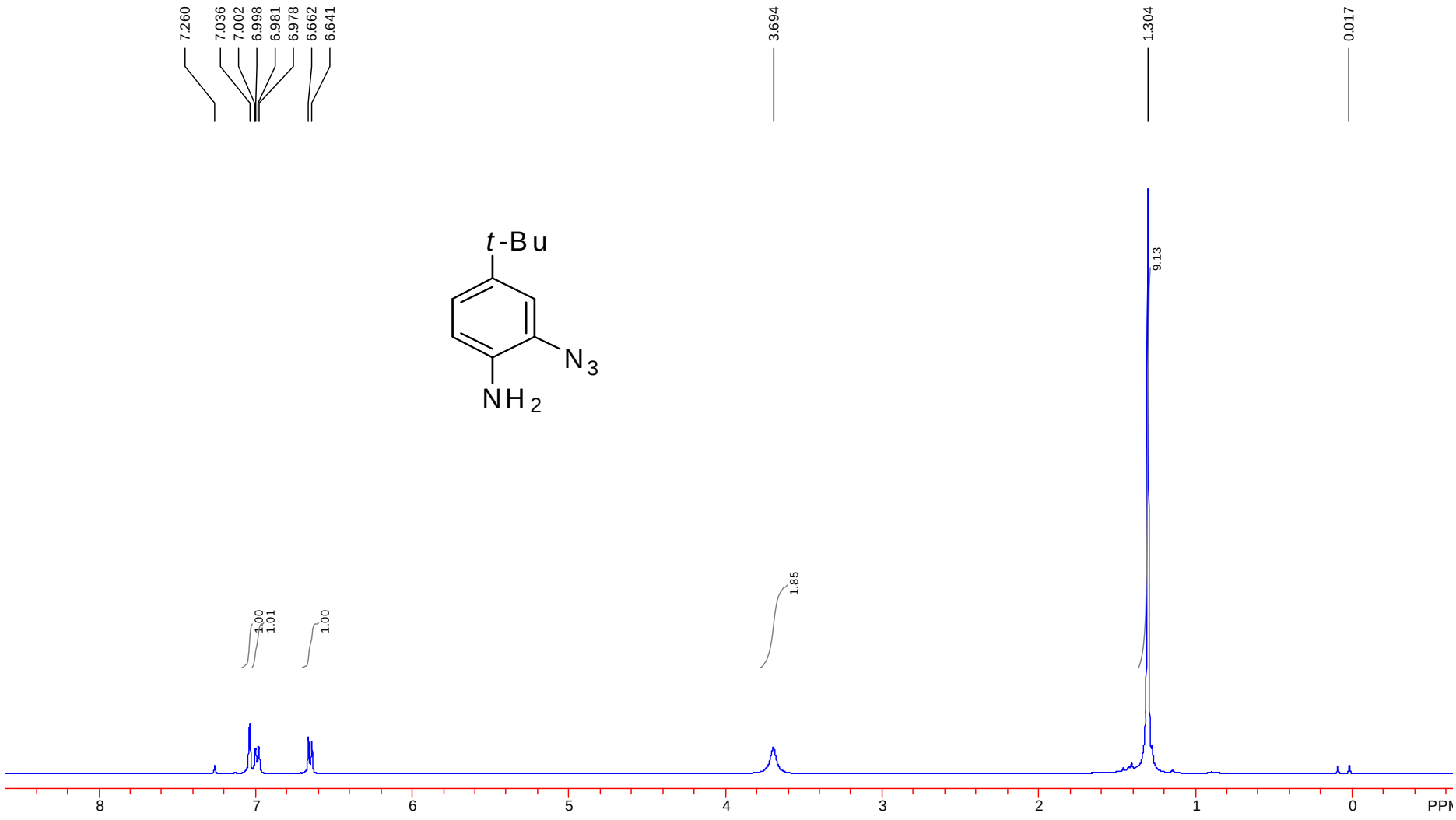
PPM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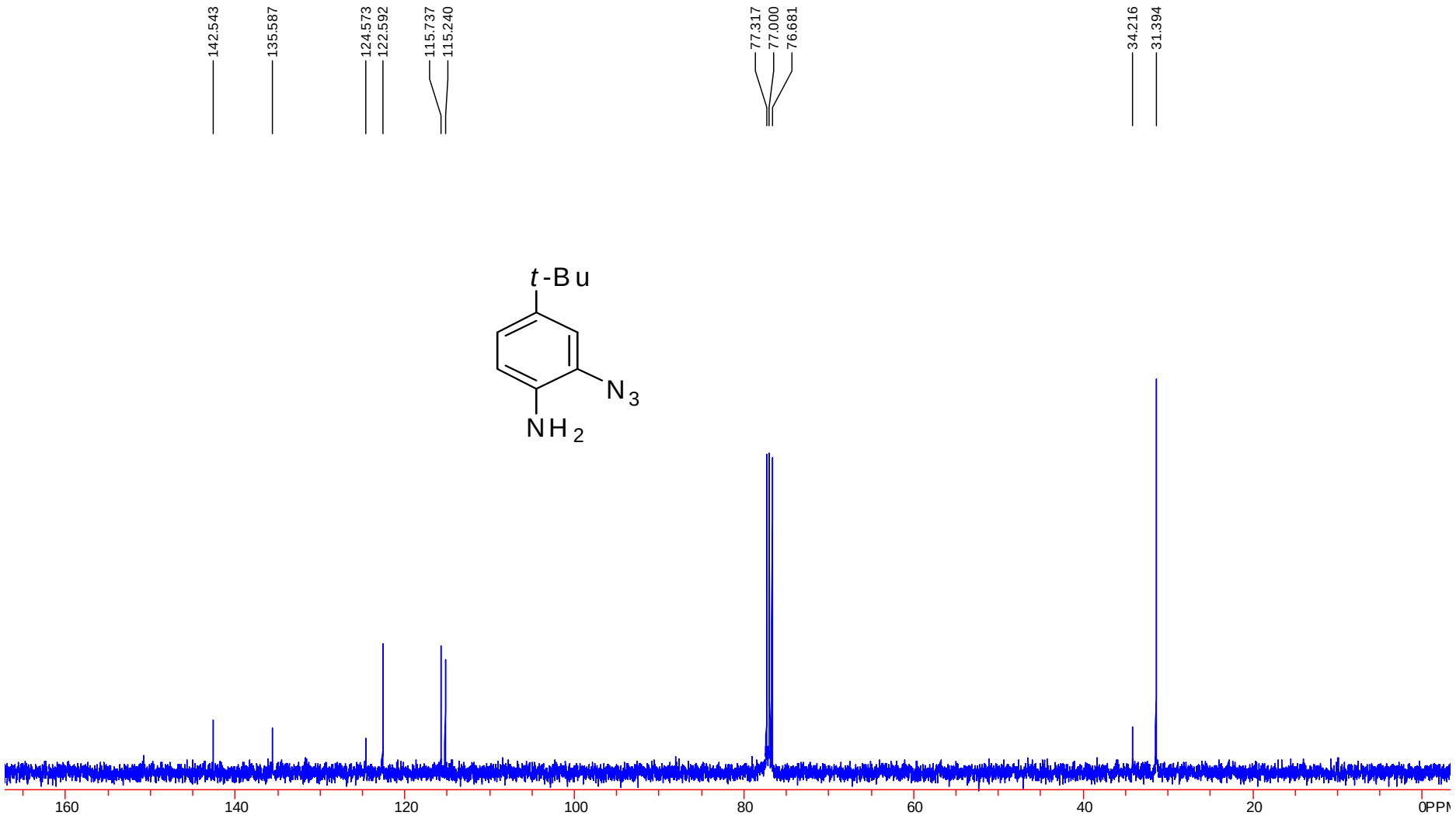
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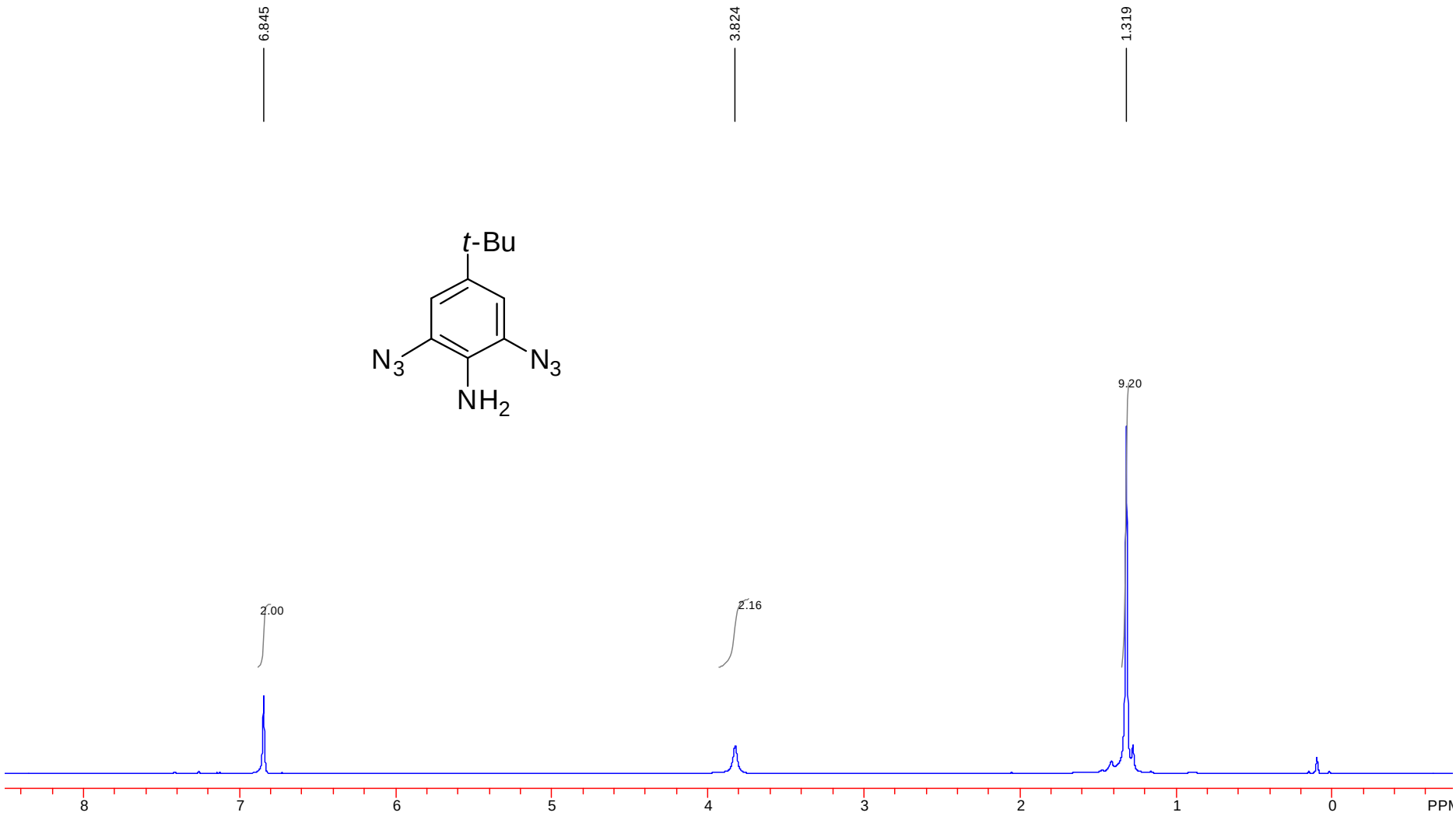
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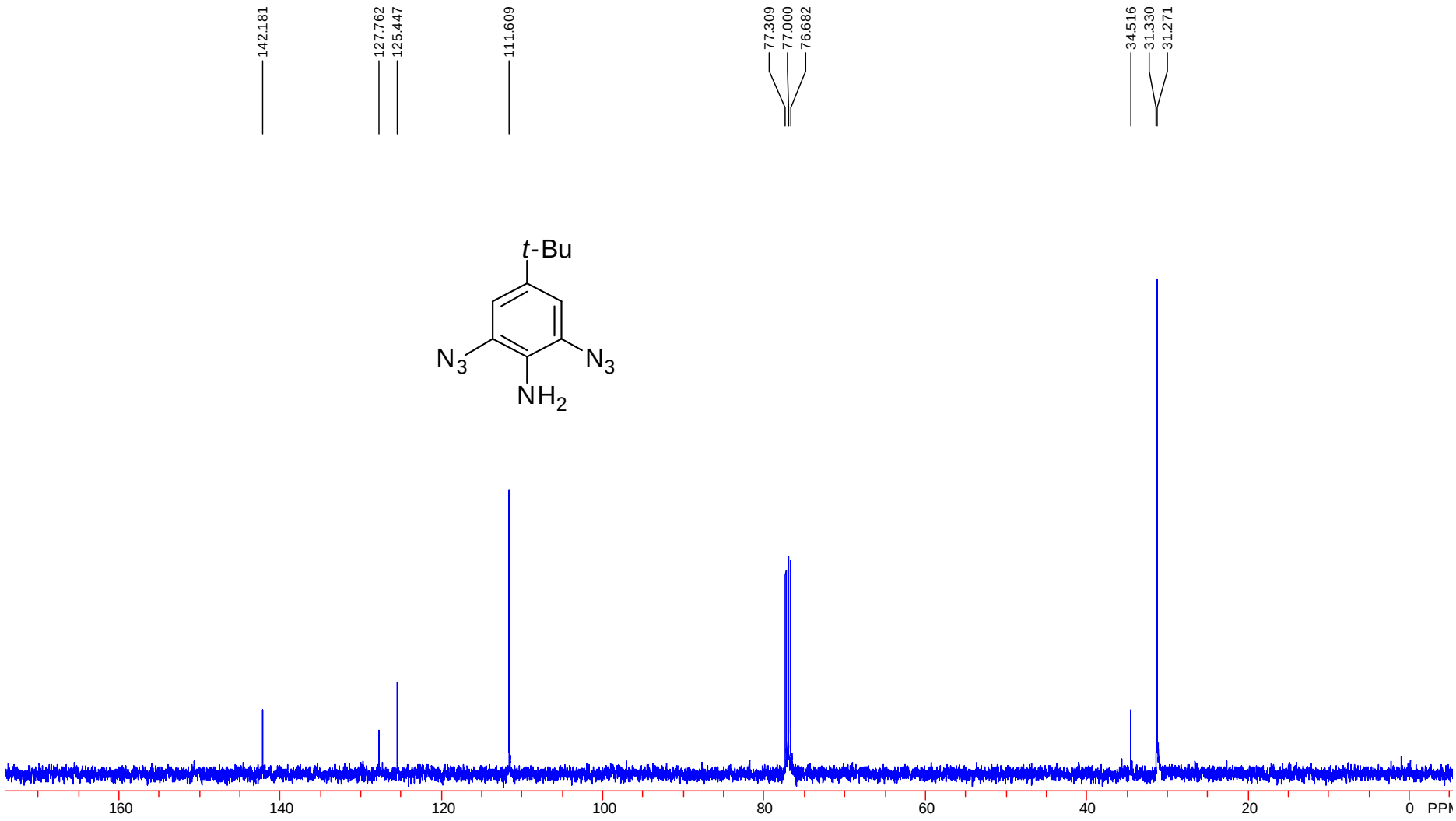
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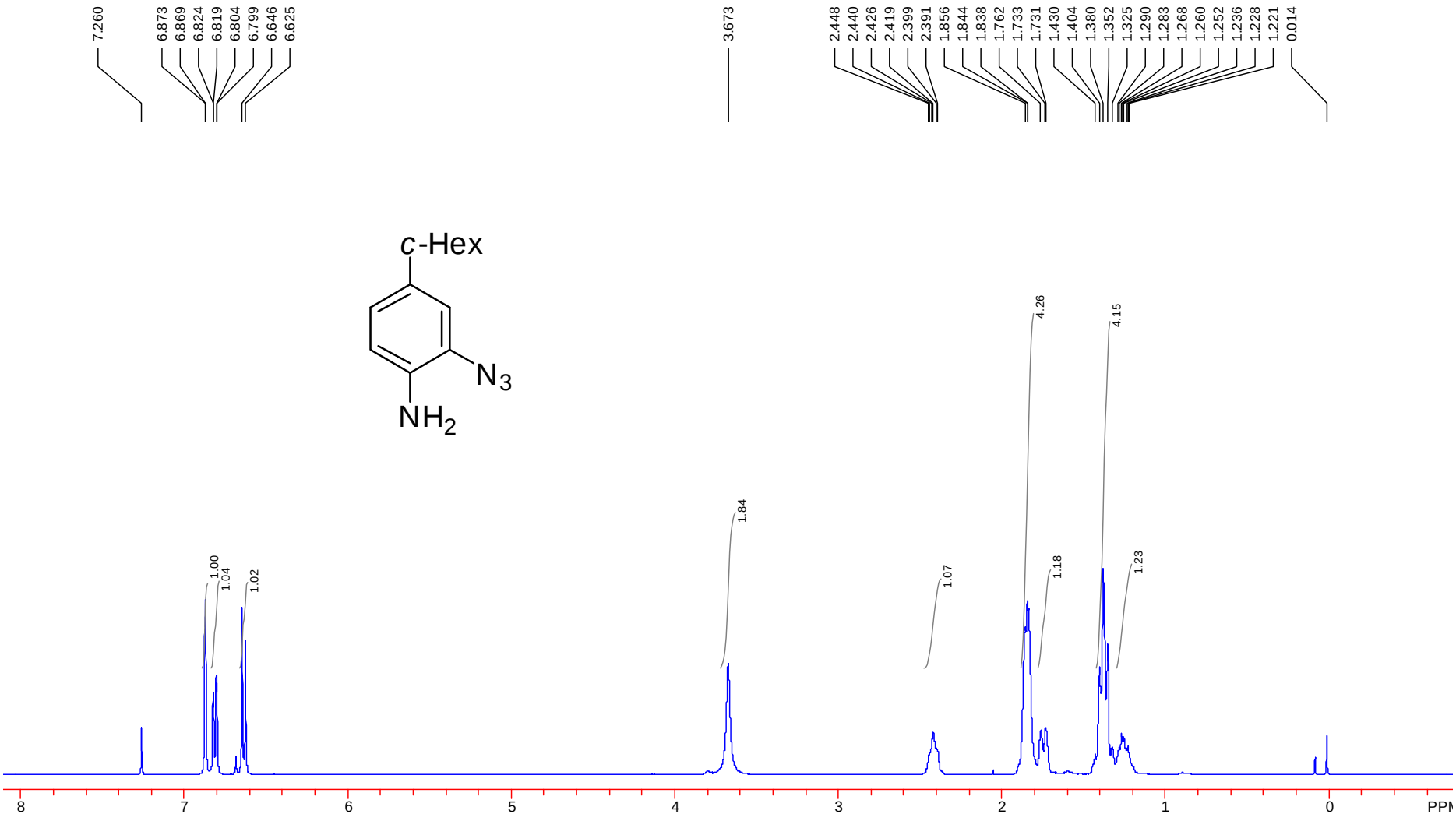
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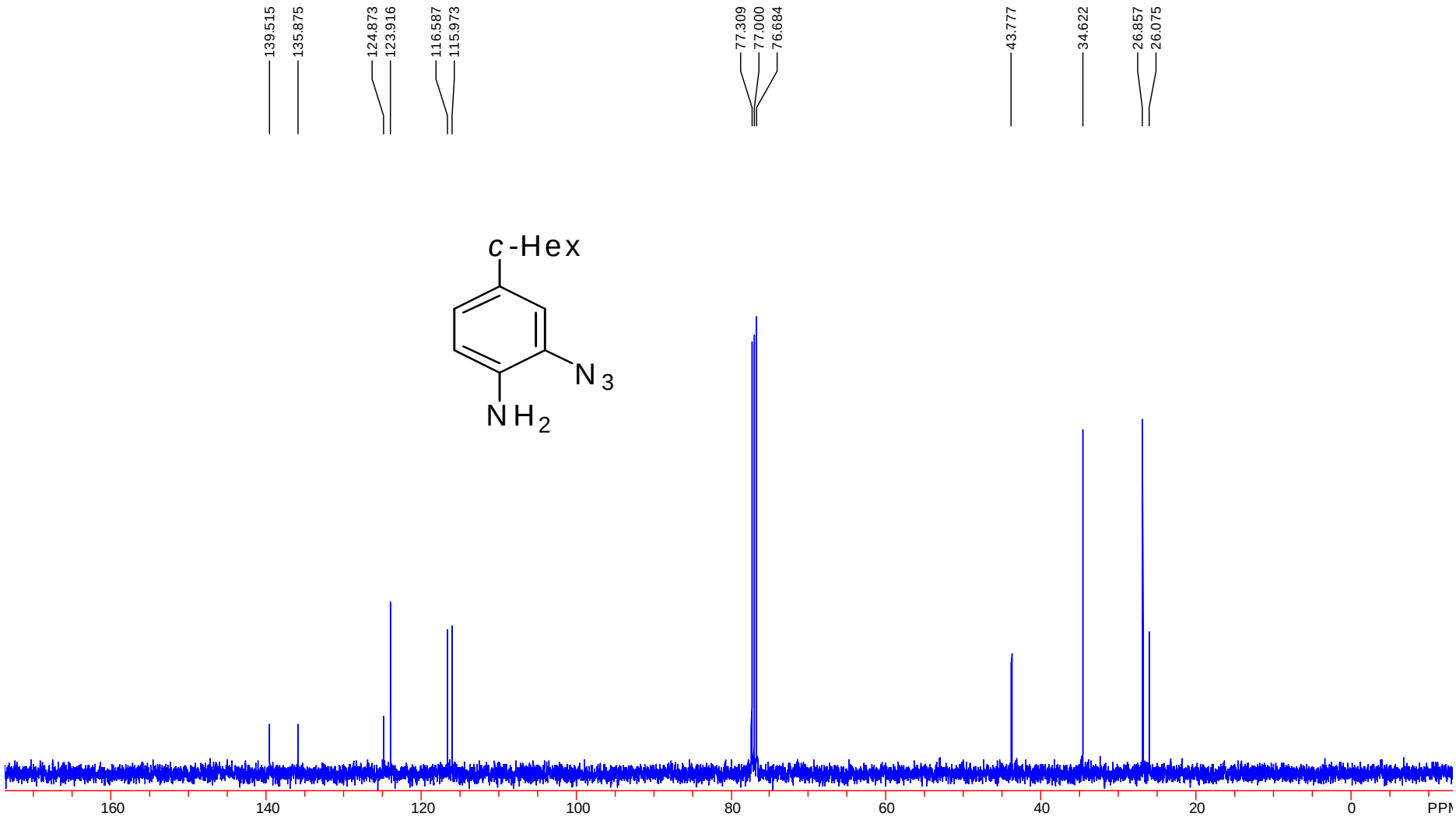
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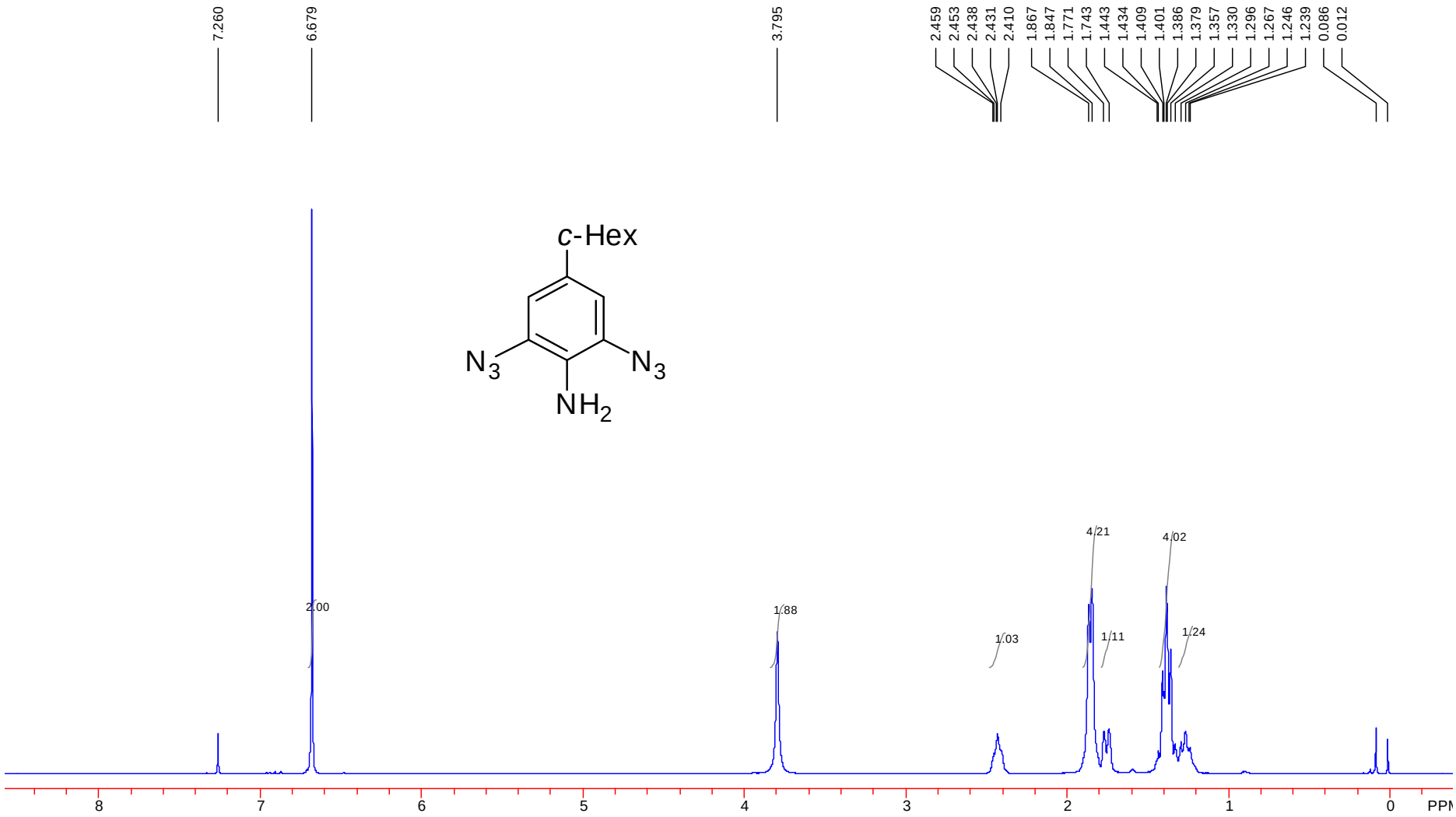
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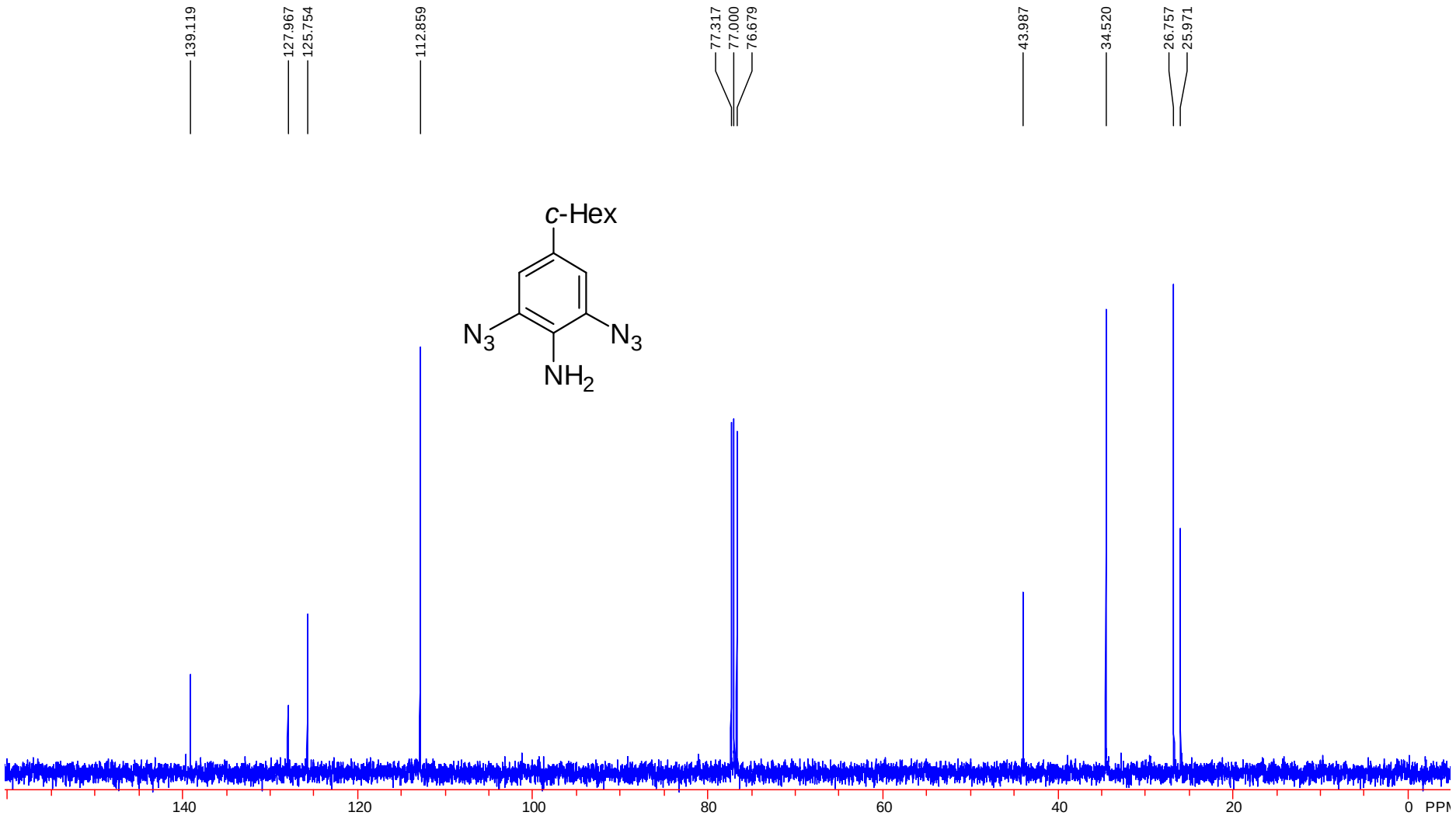
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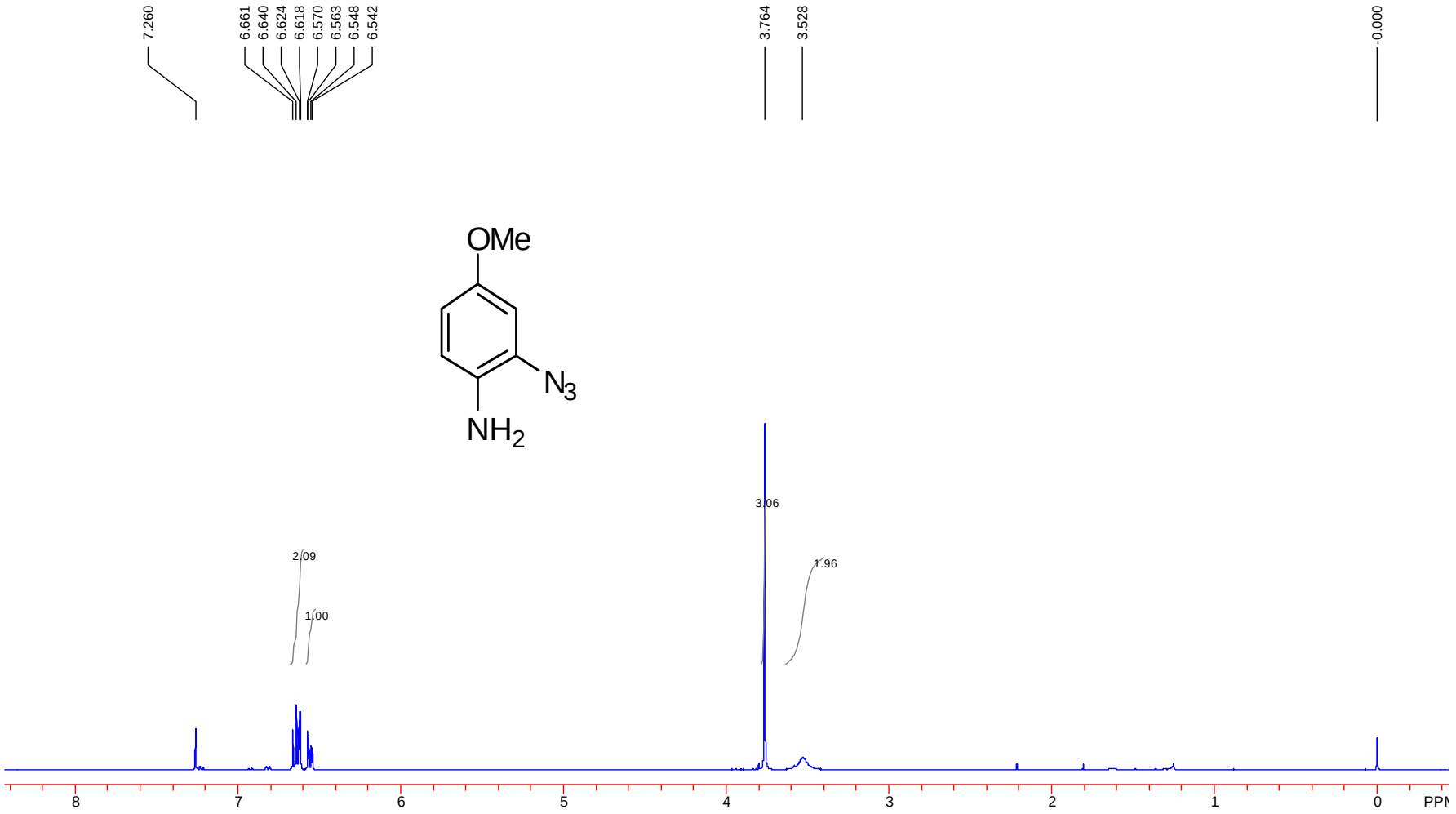
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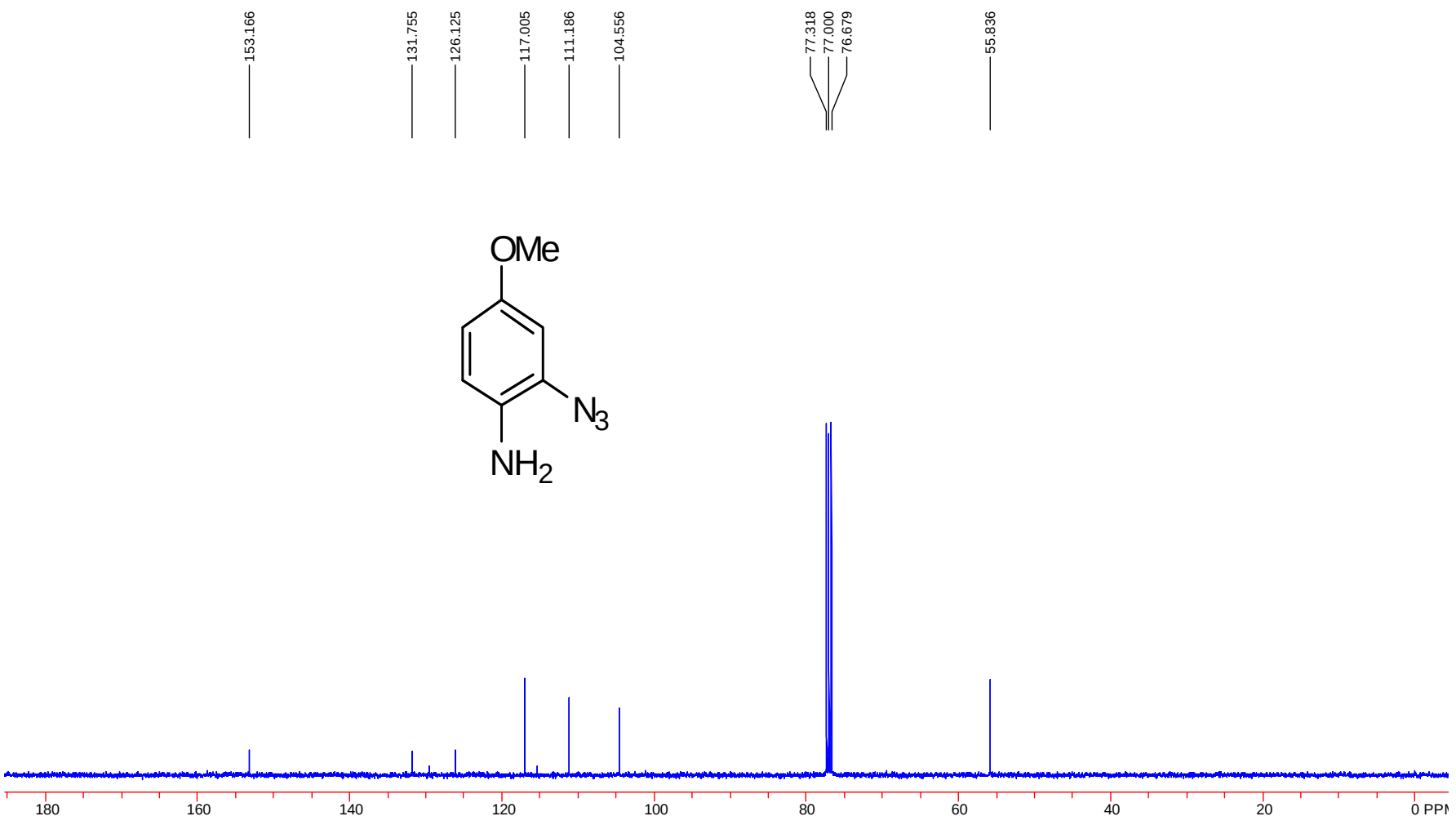
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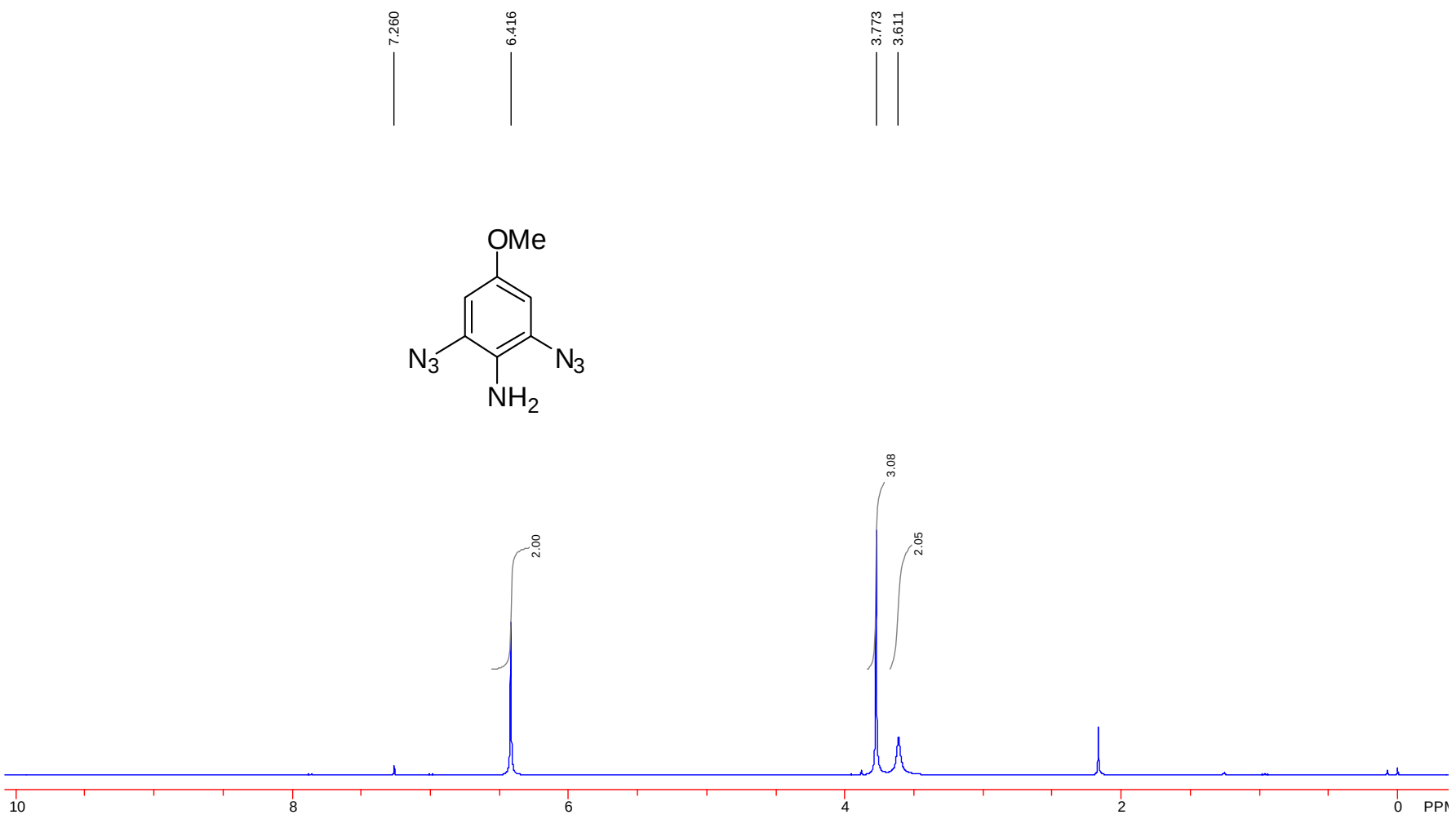
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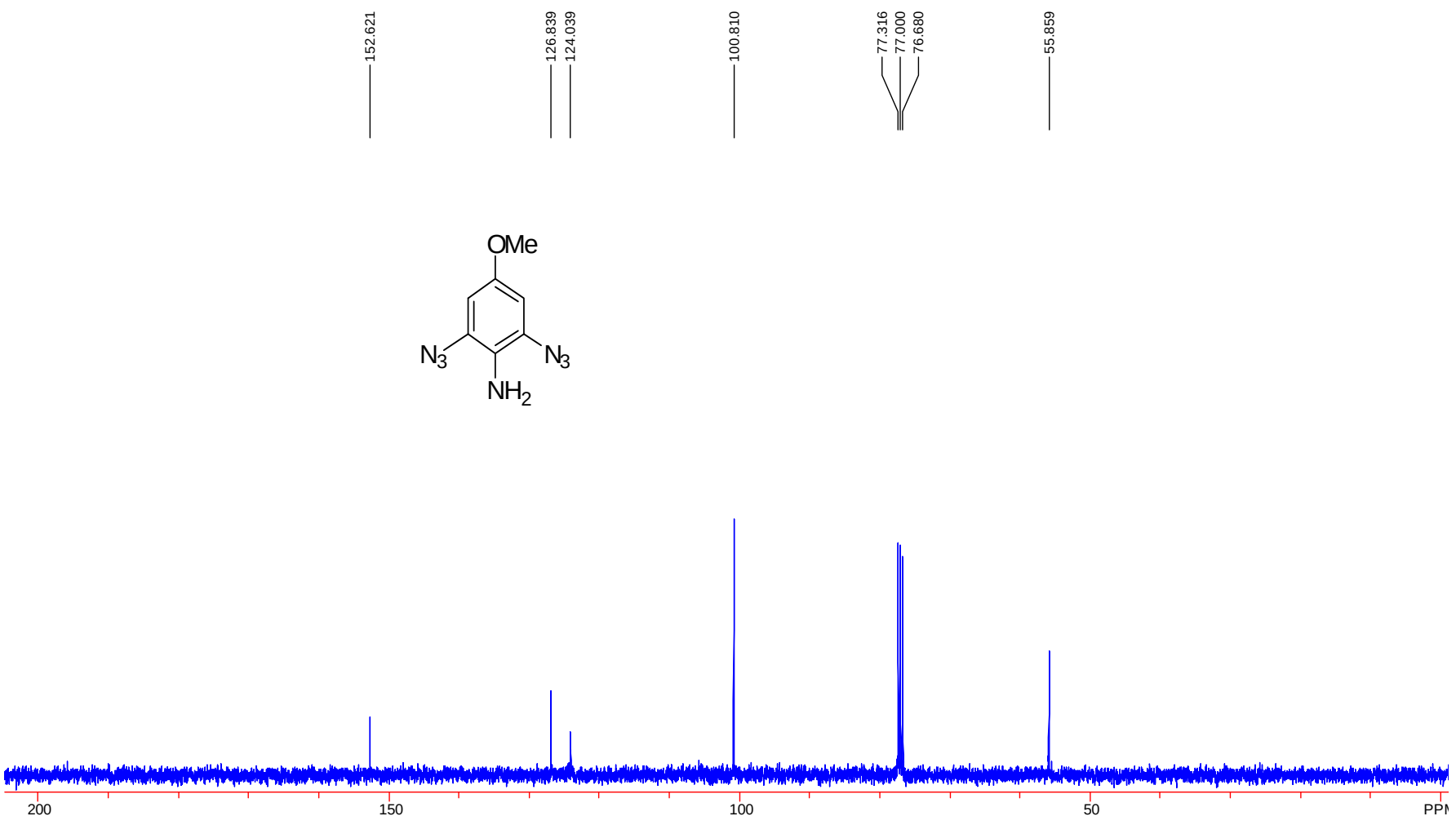
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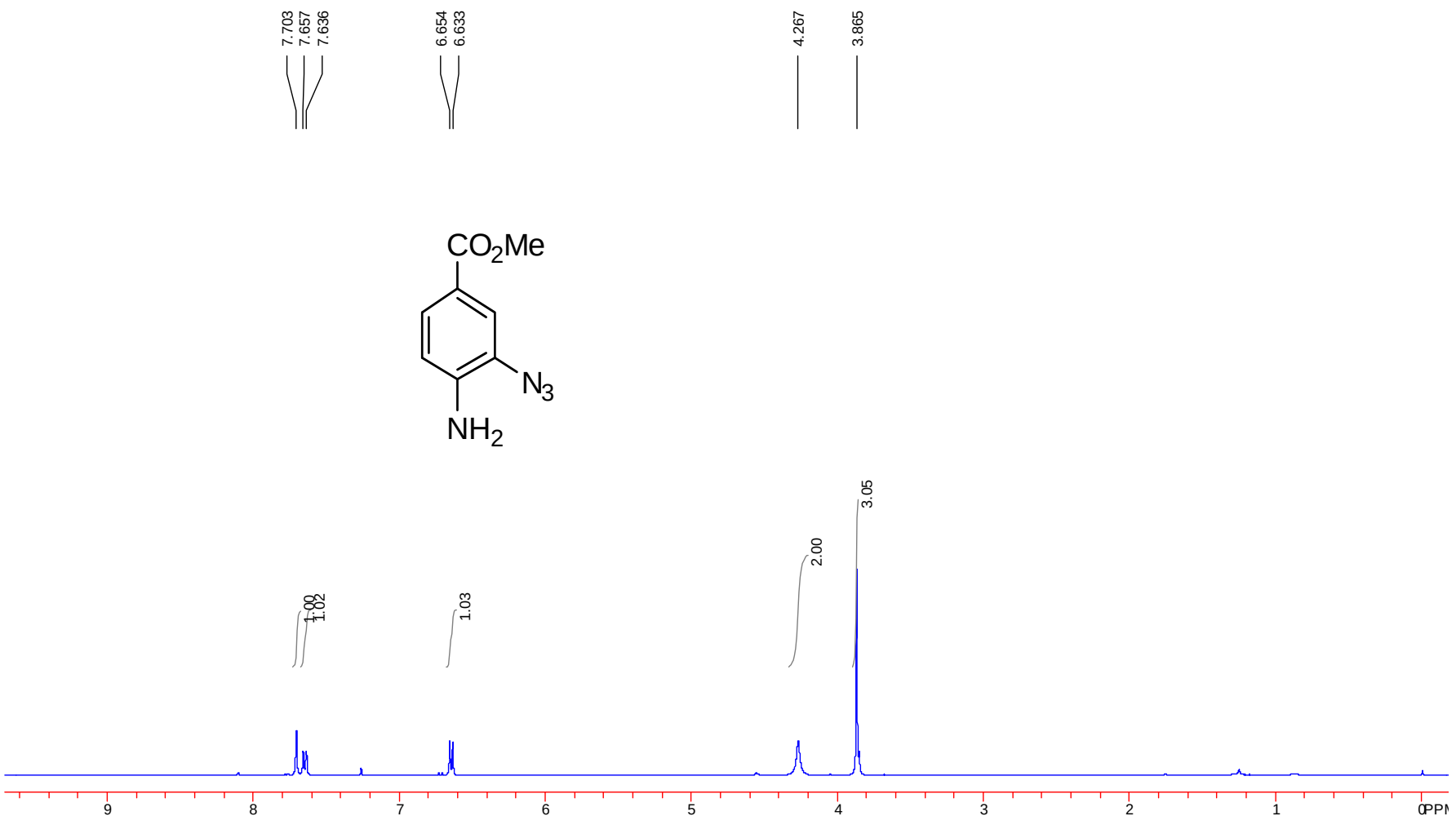
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5
4
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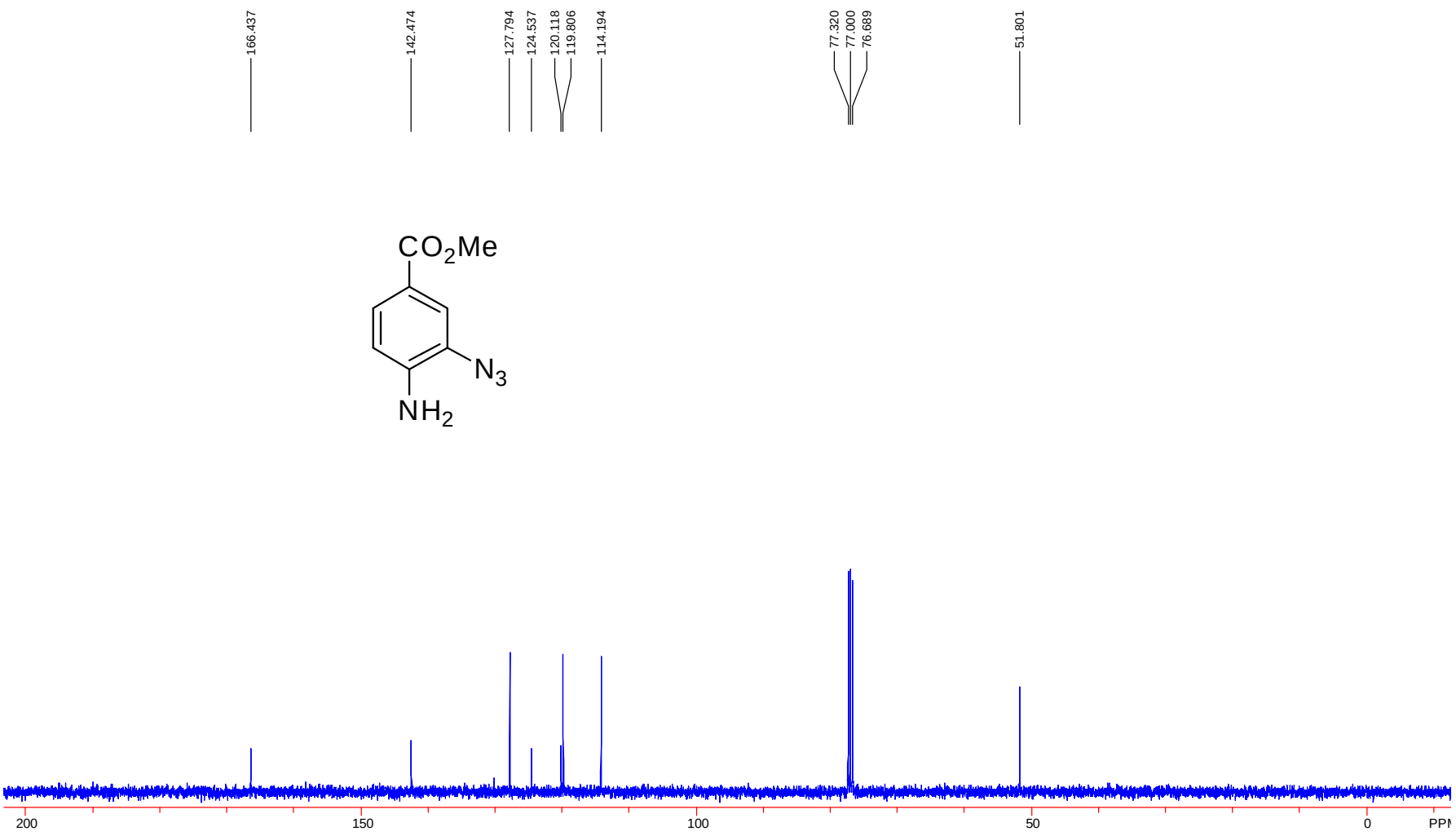
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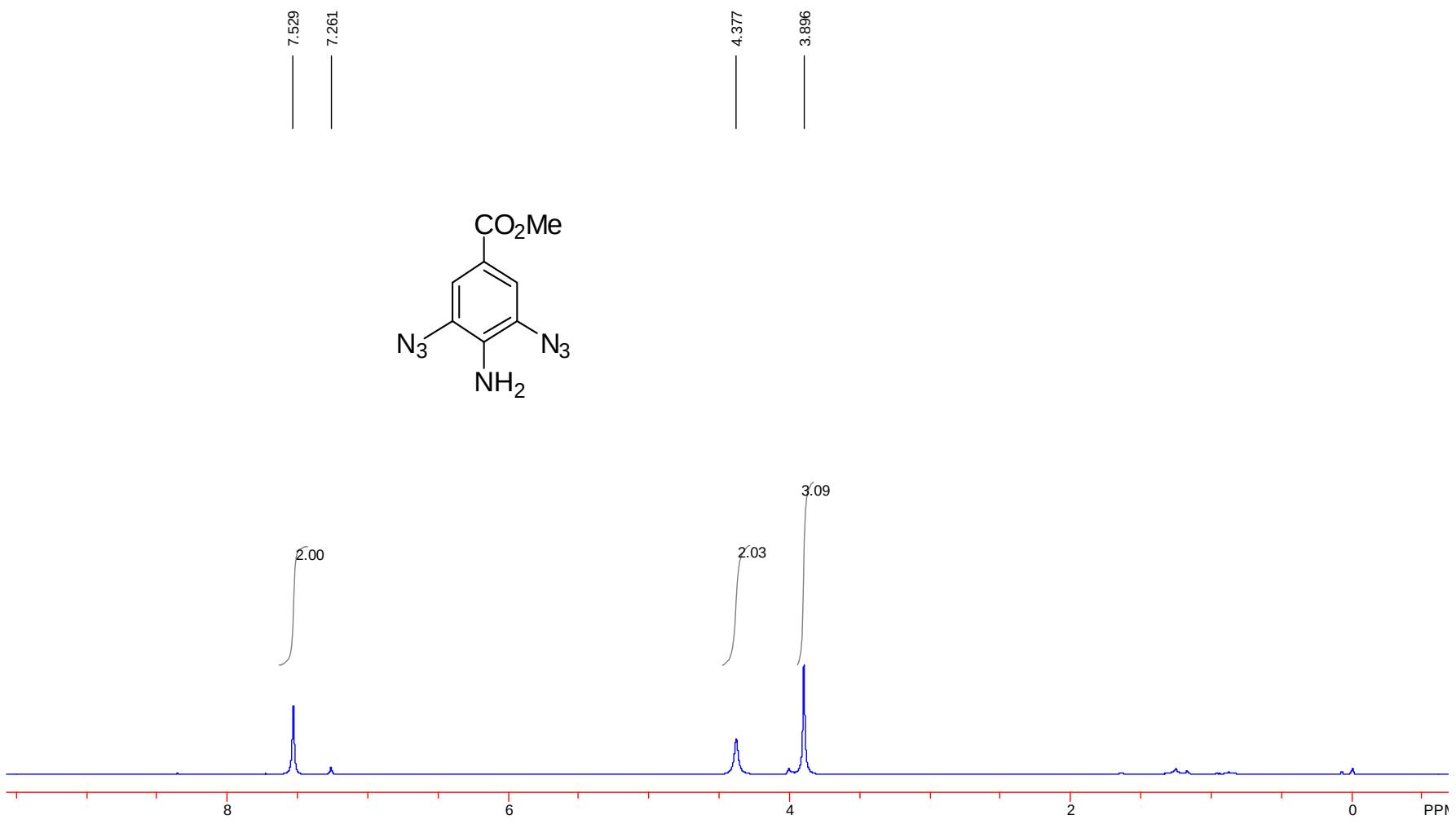
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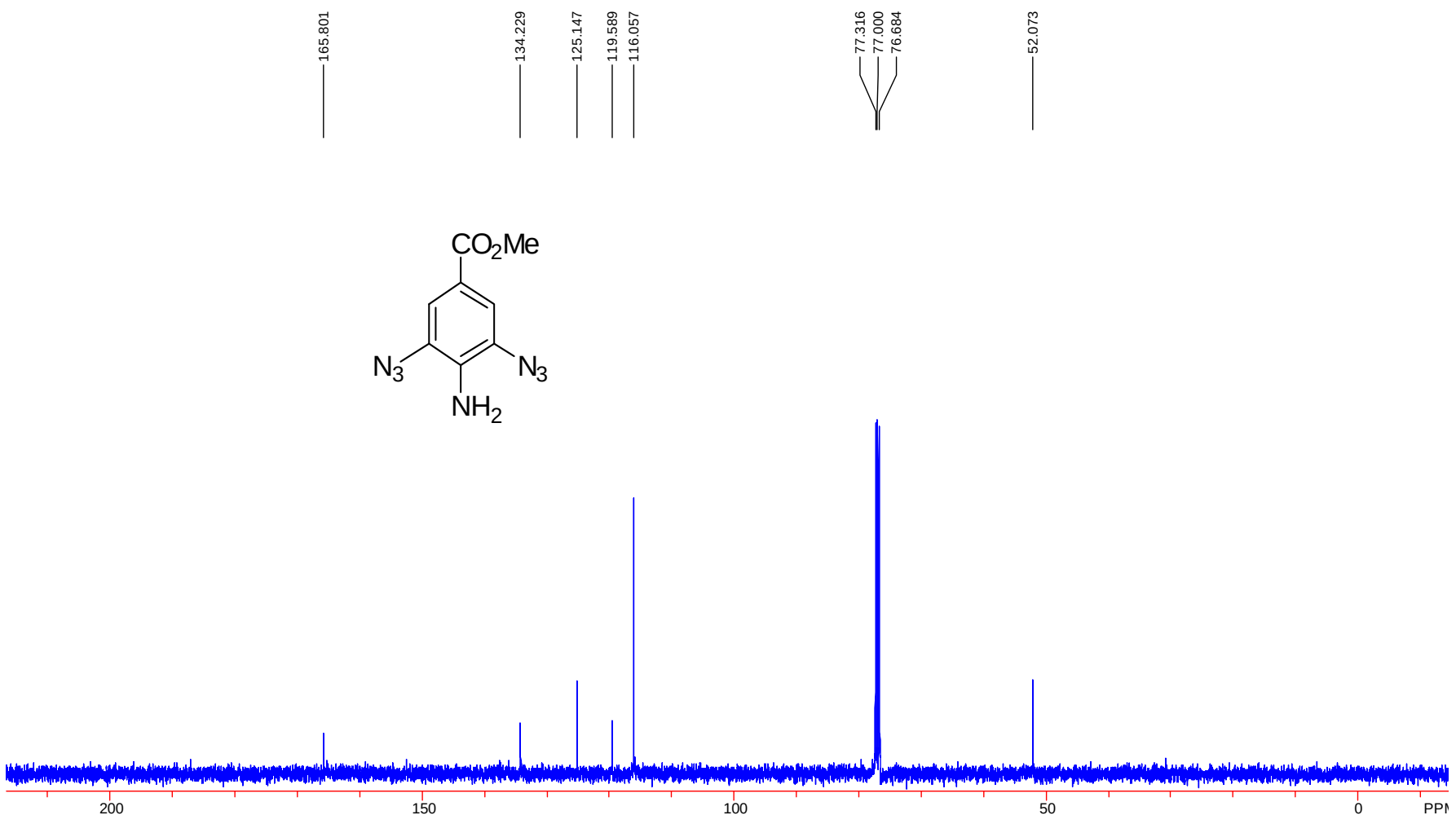
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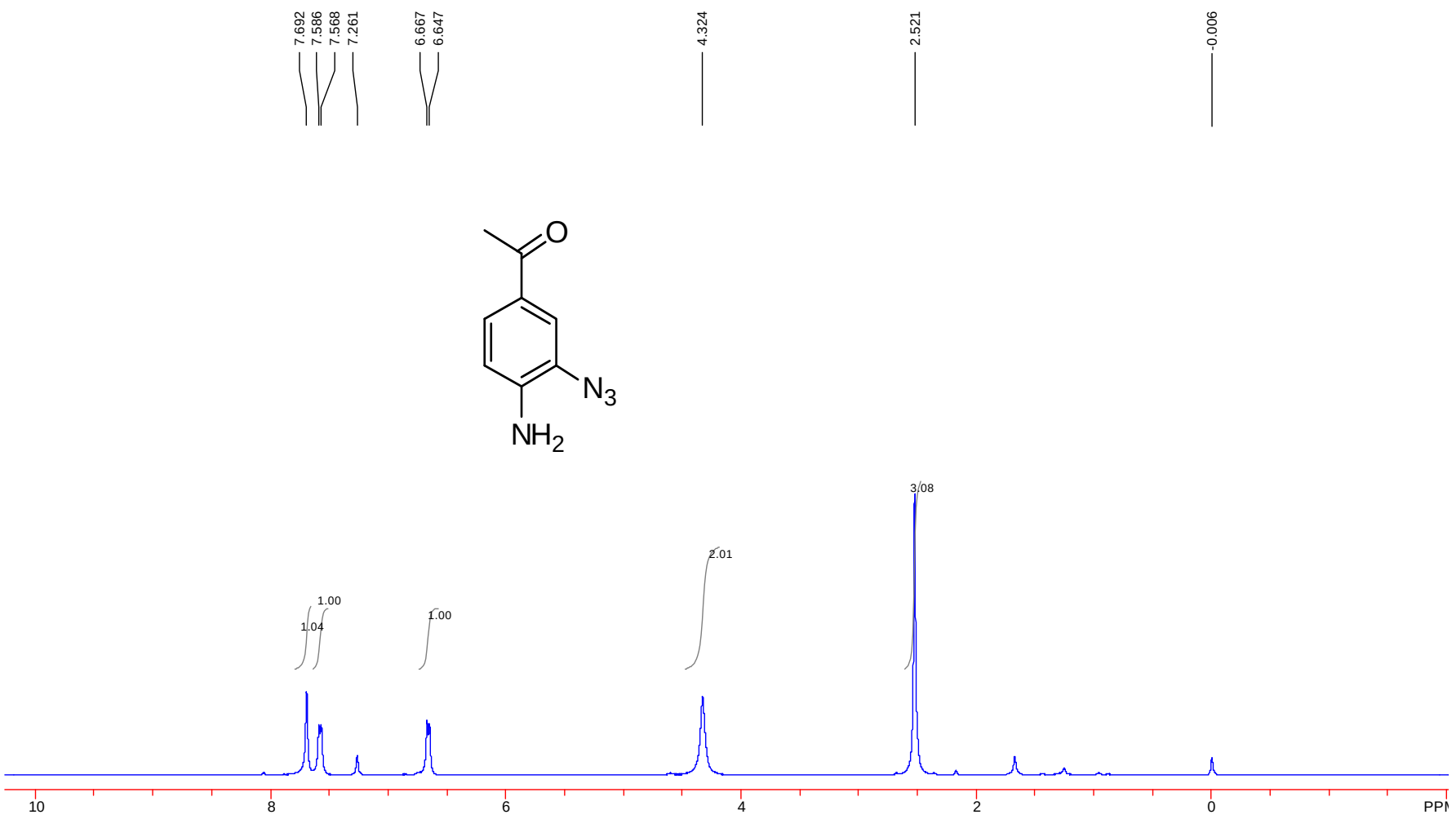
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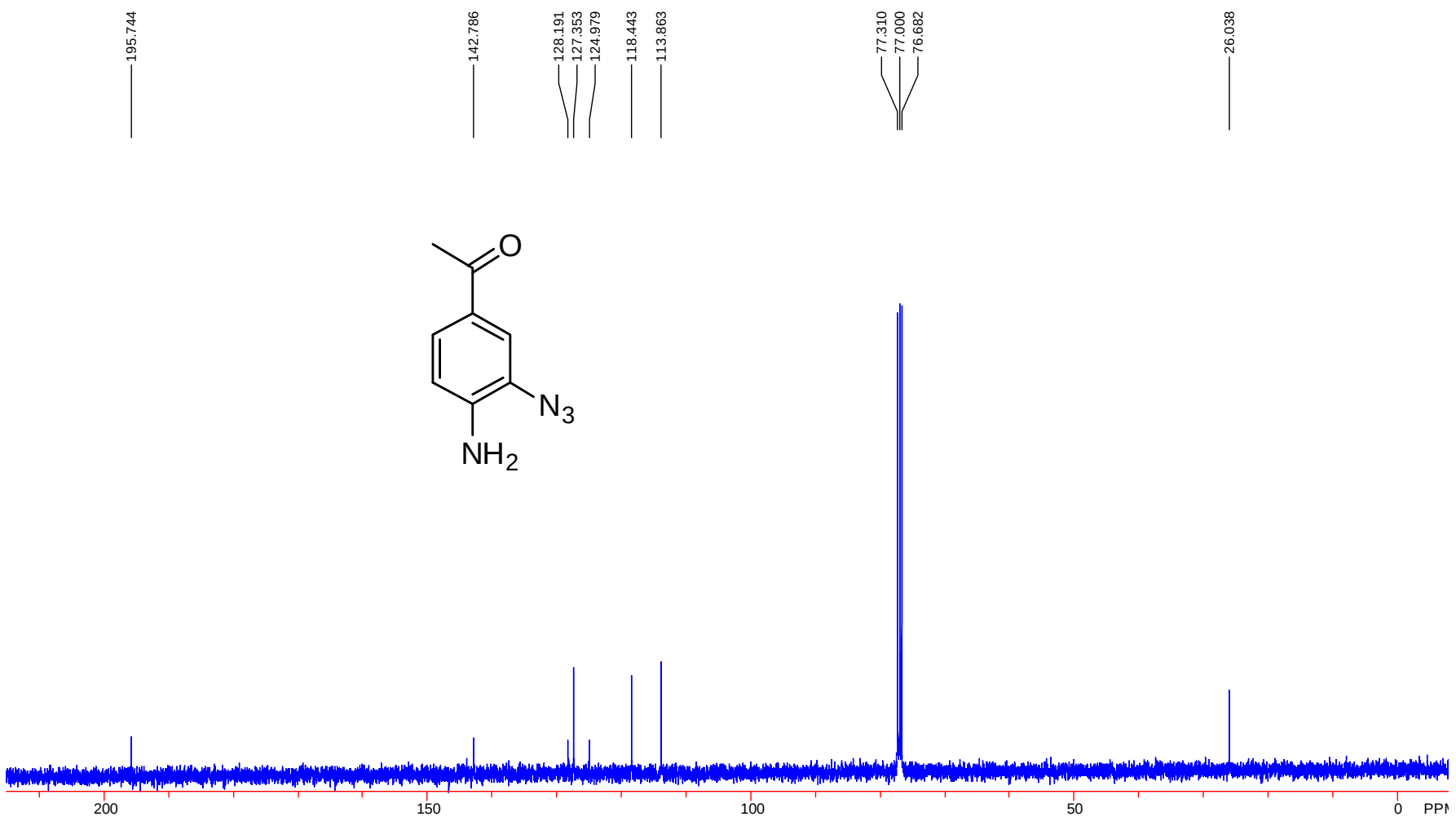
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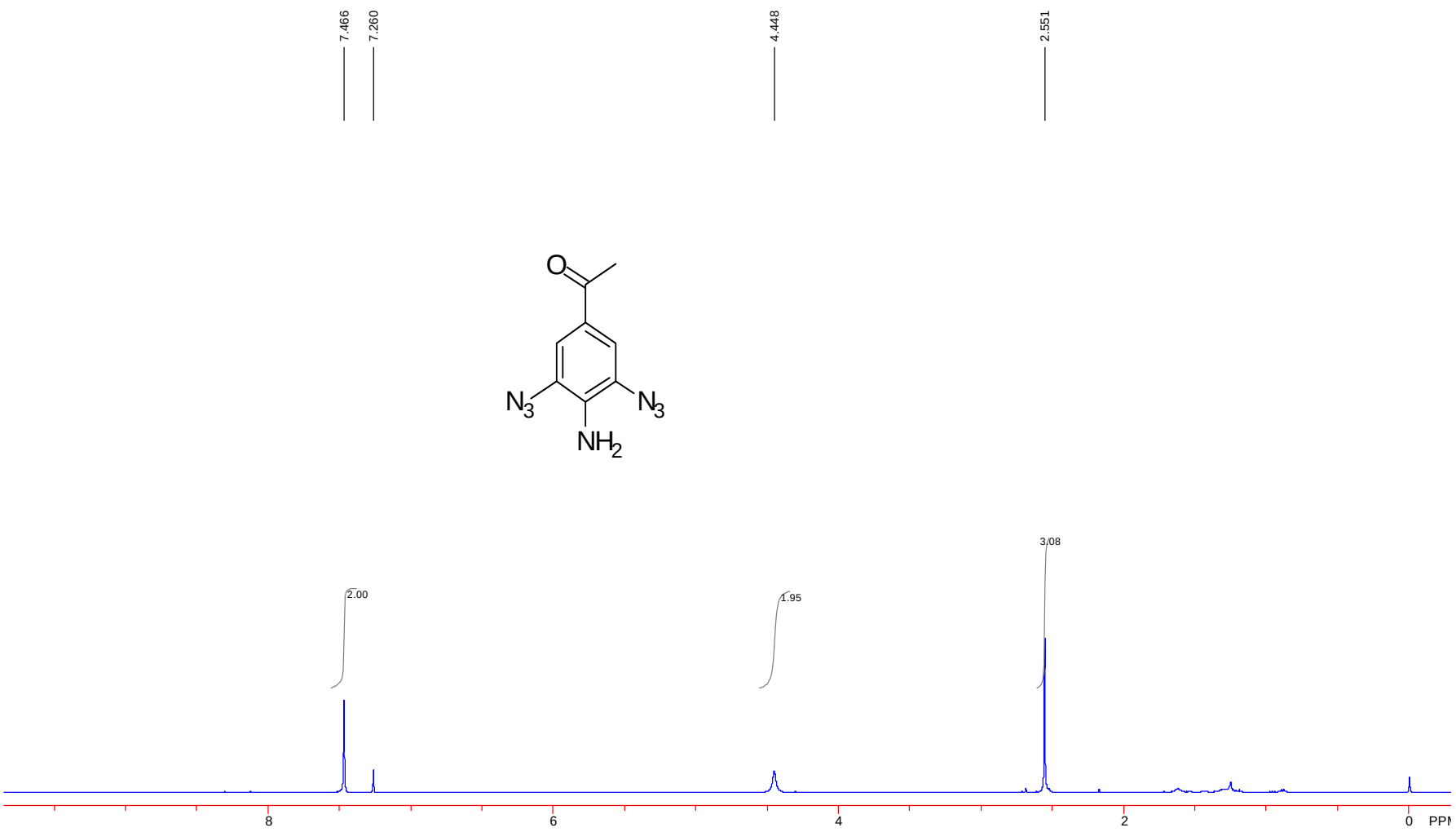
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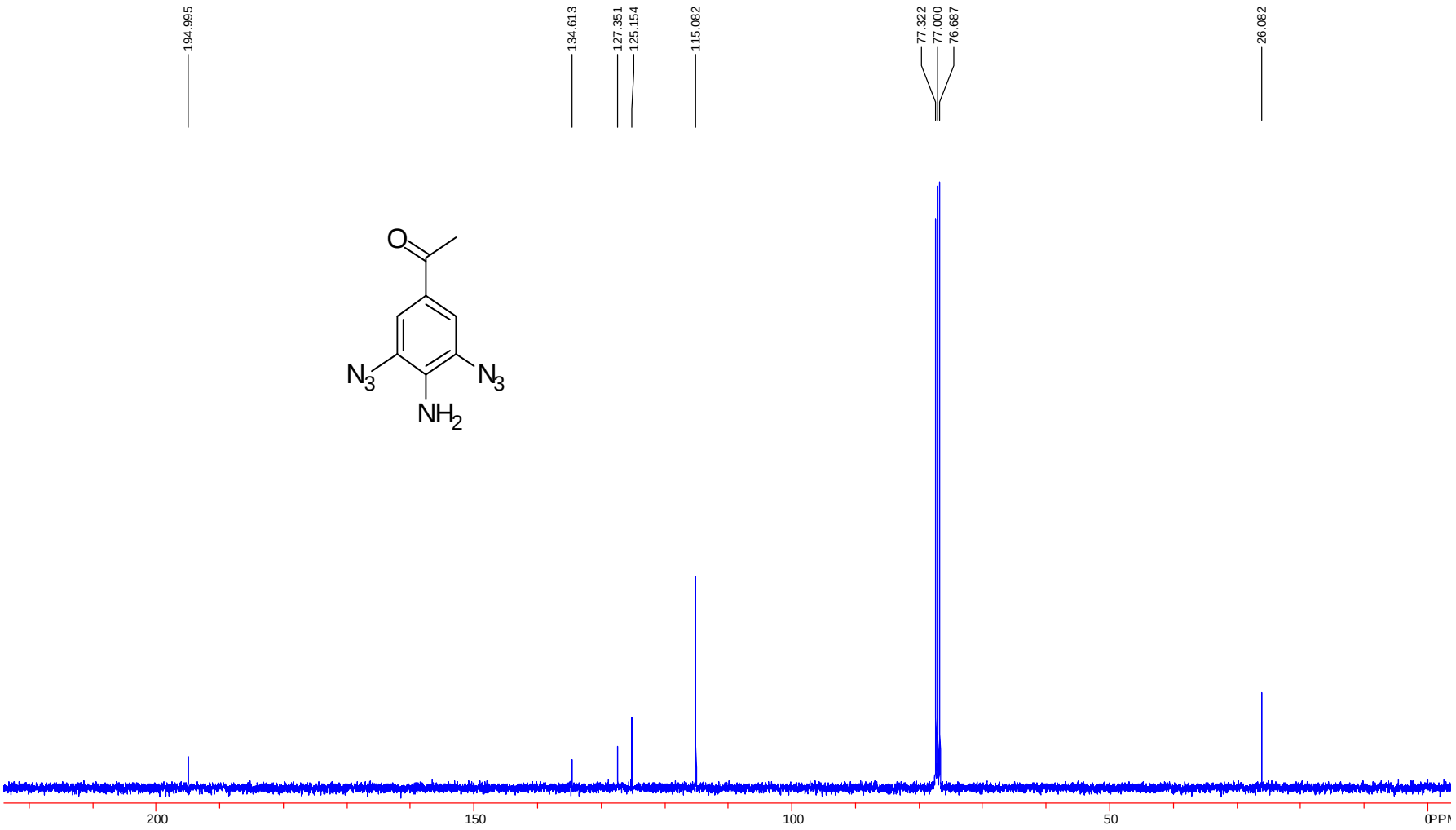
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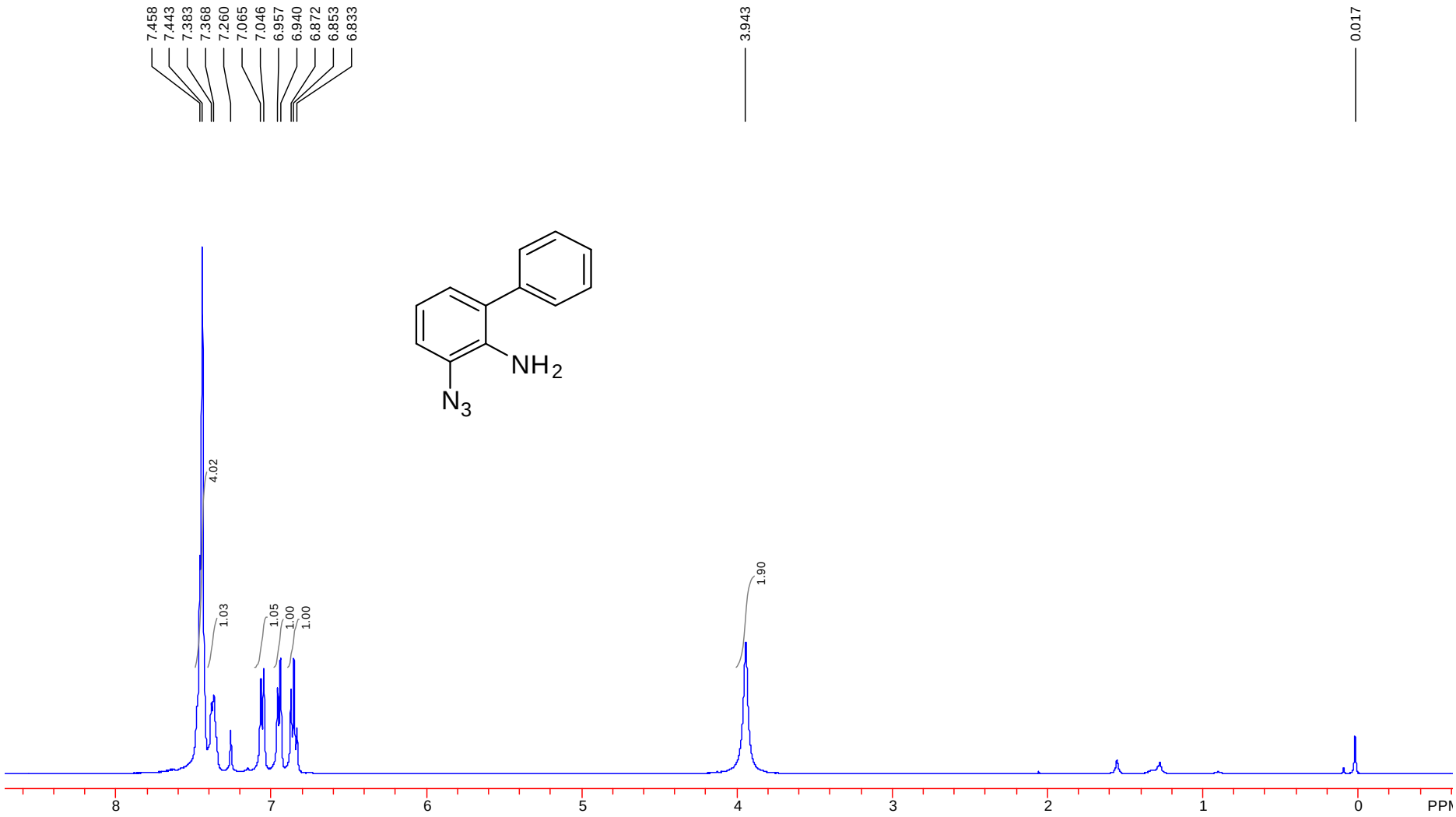
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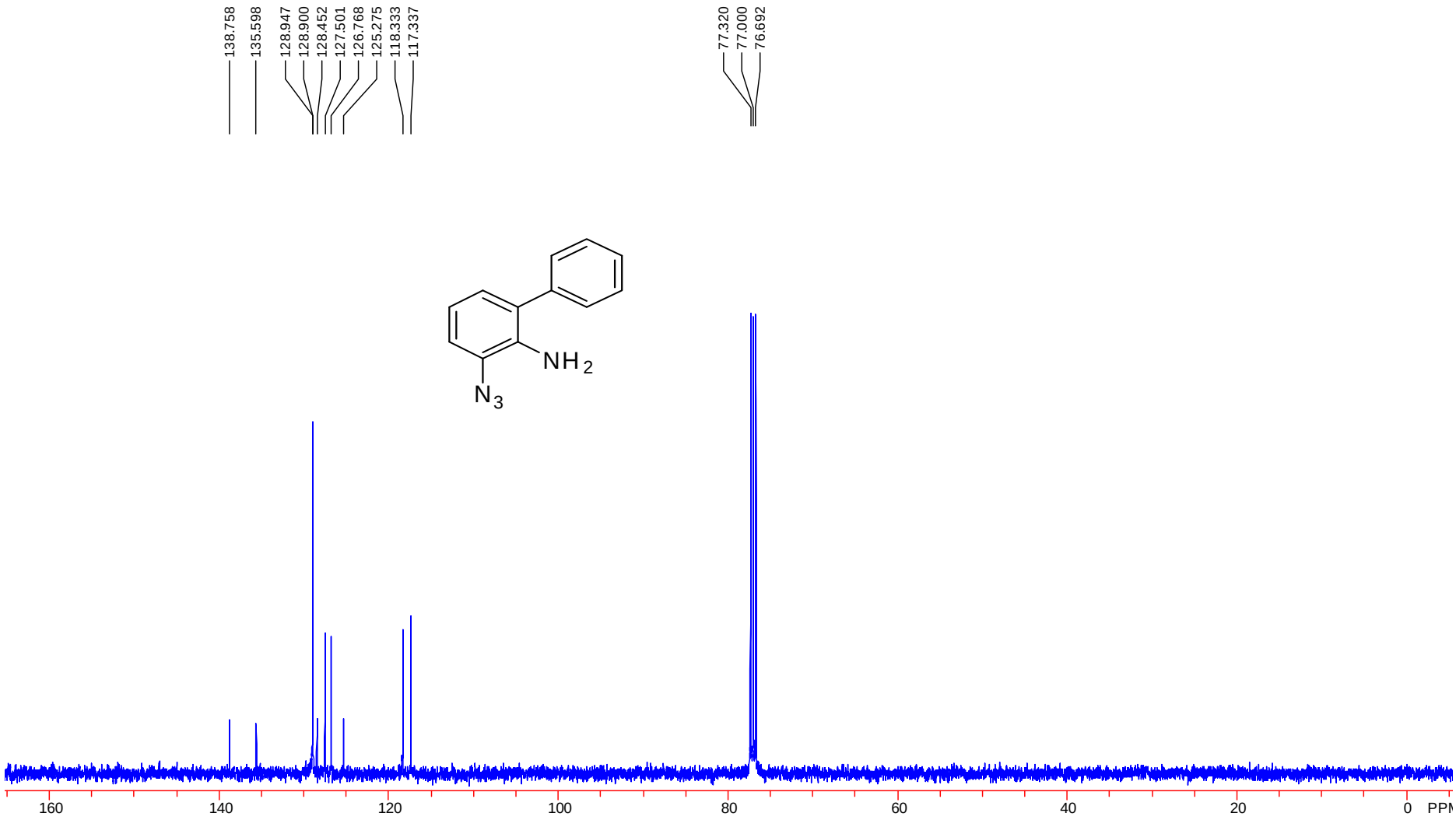
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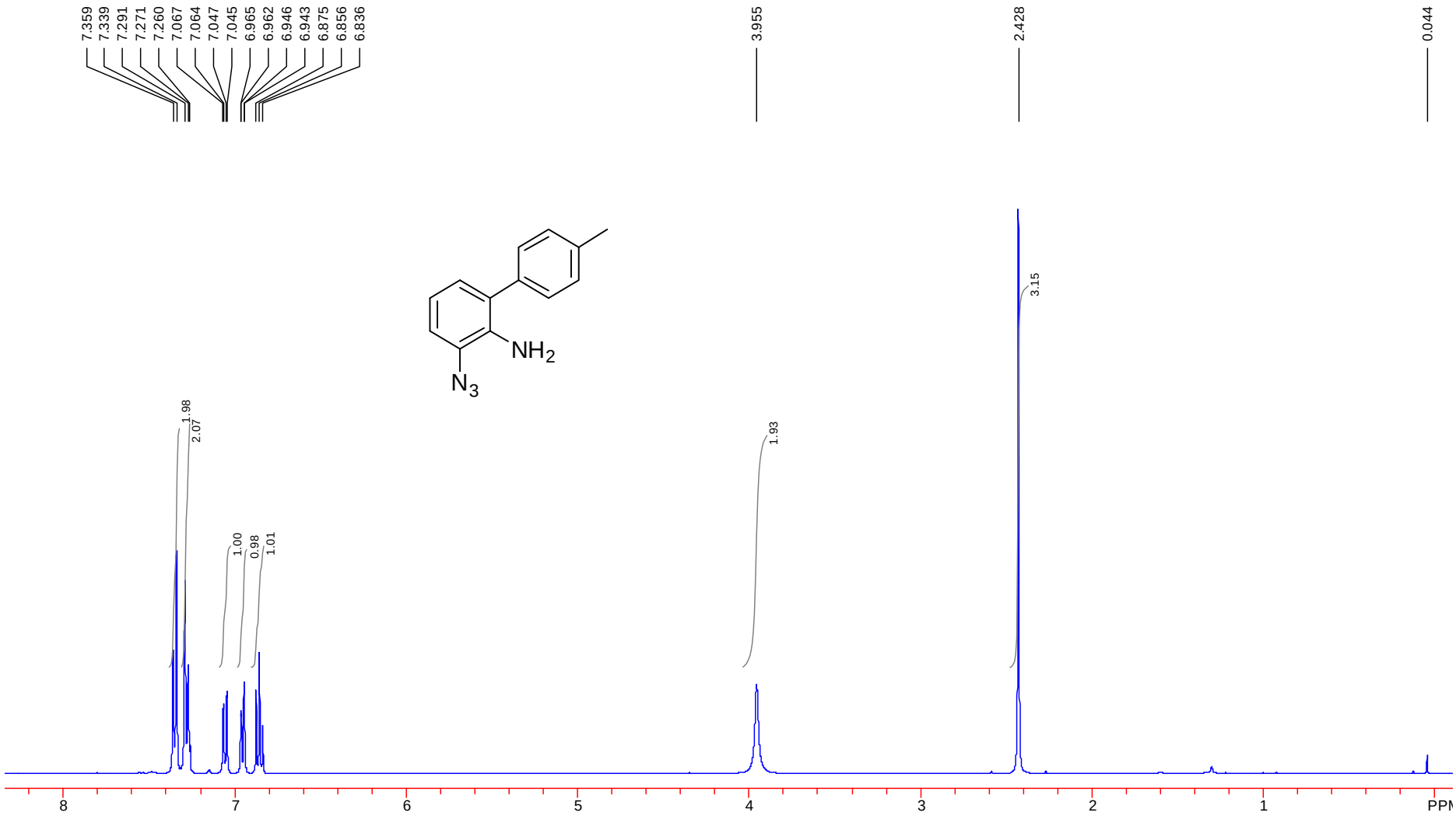
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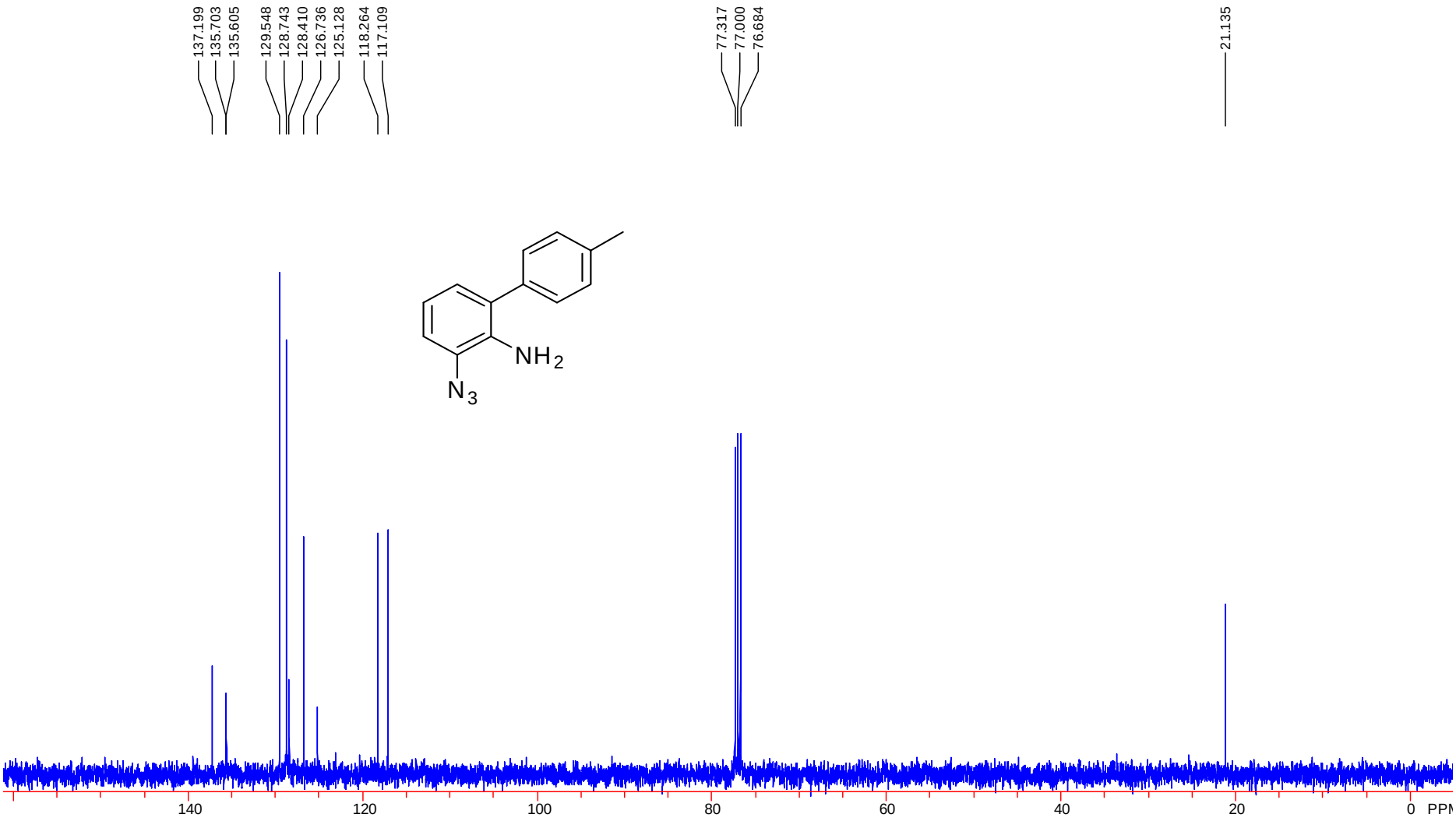
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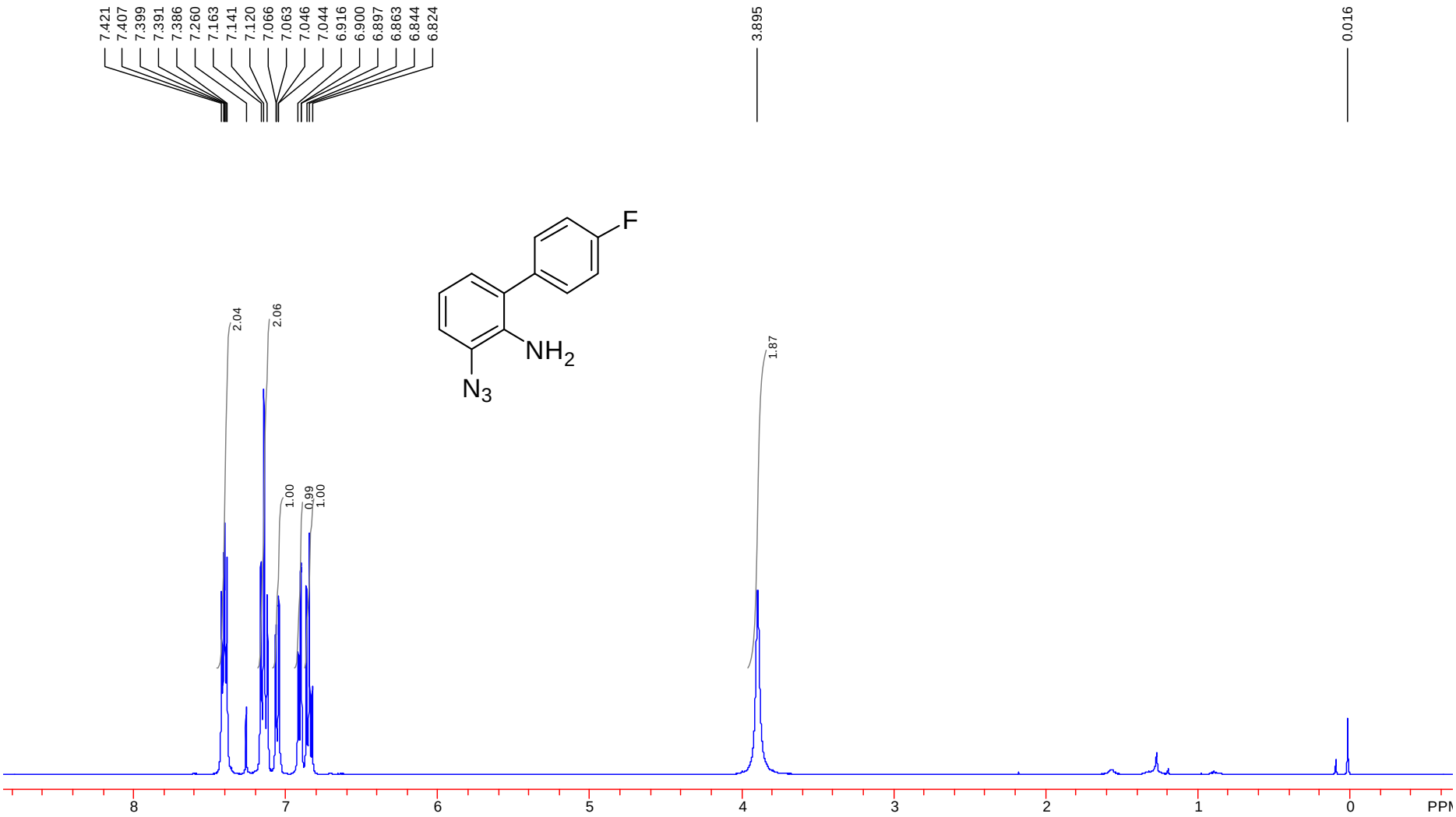
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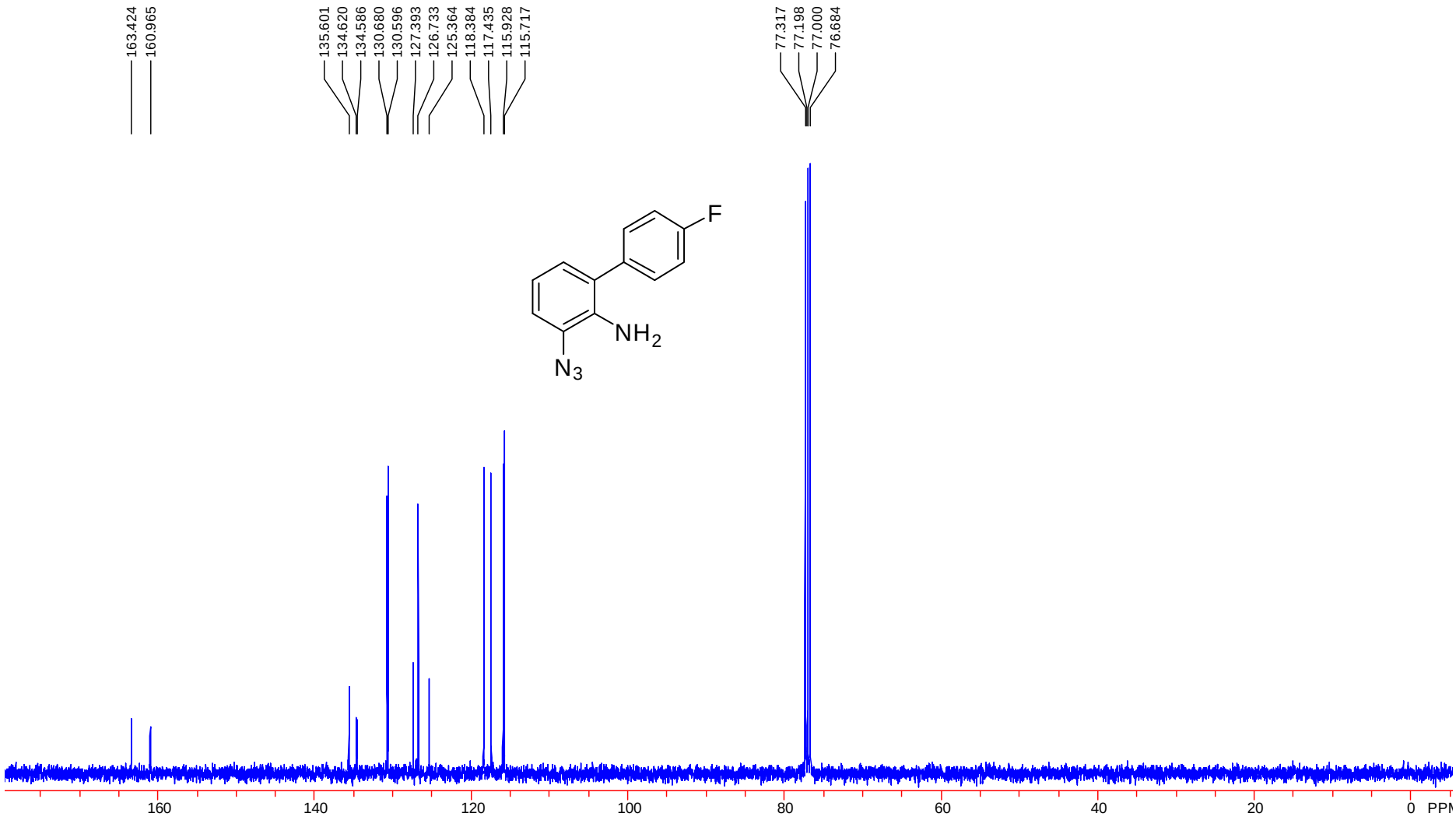
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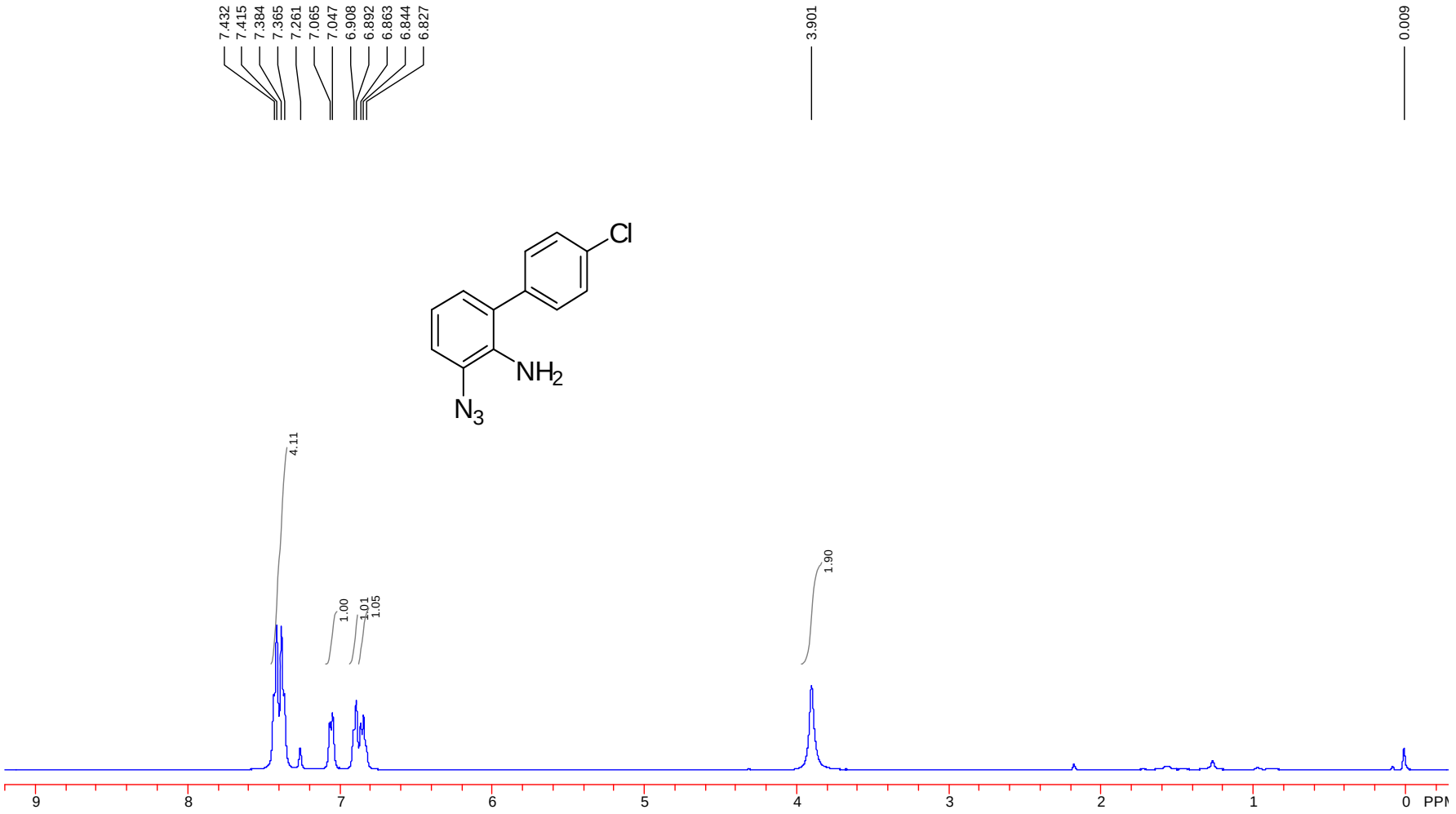
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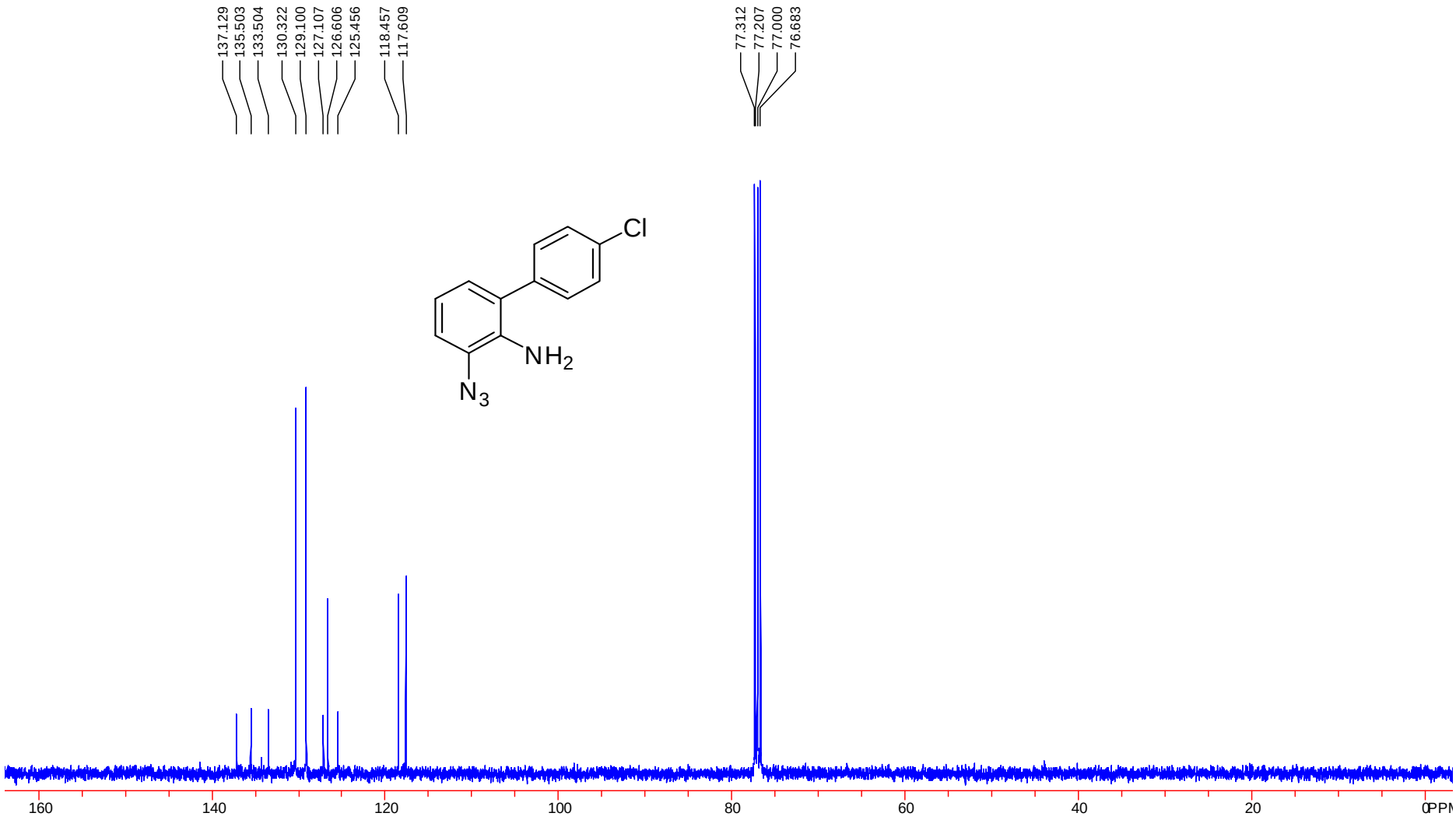
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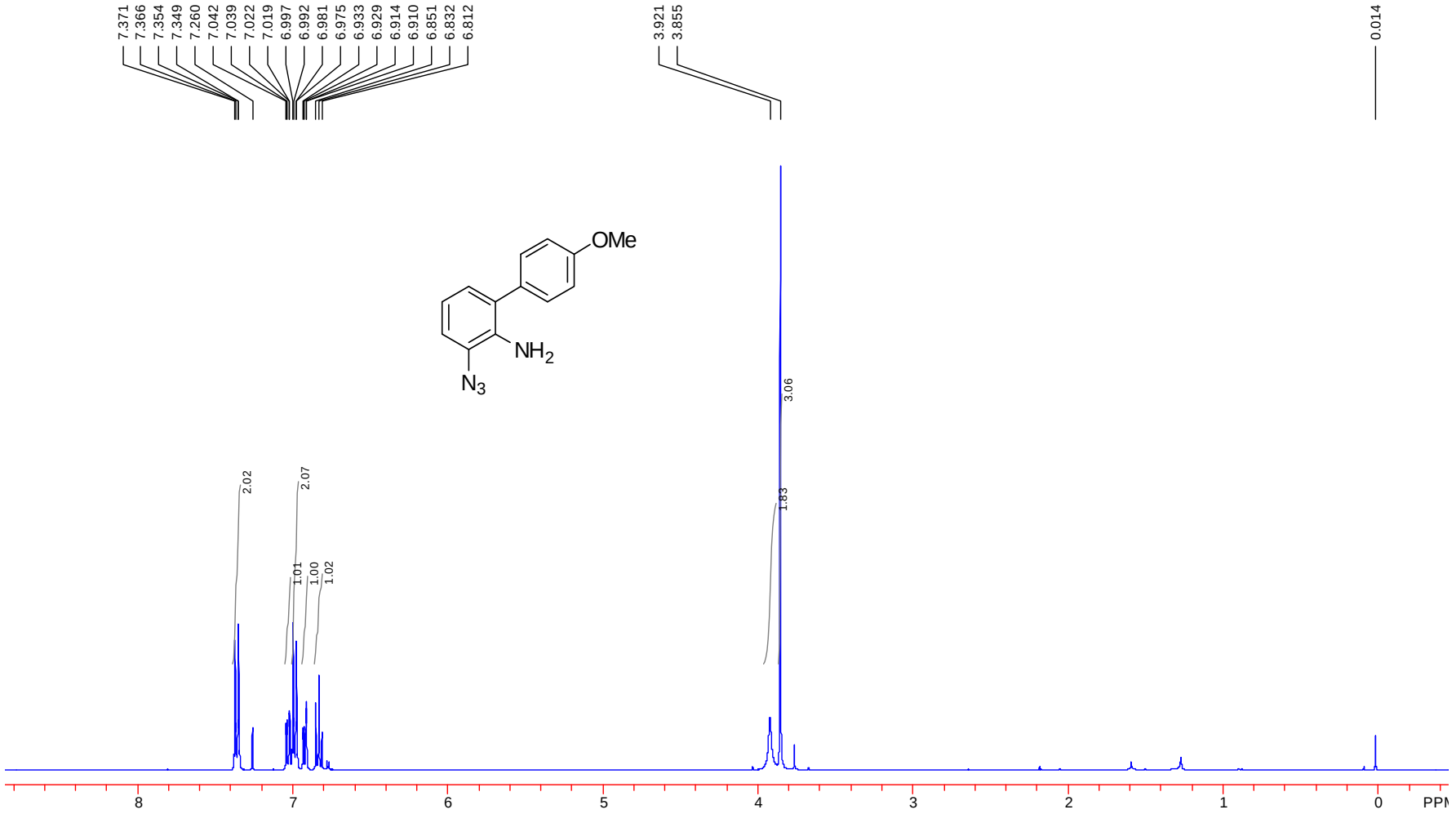
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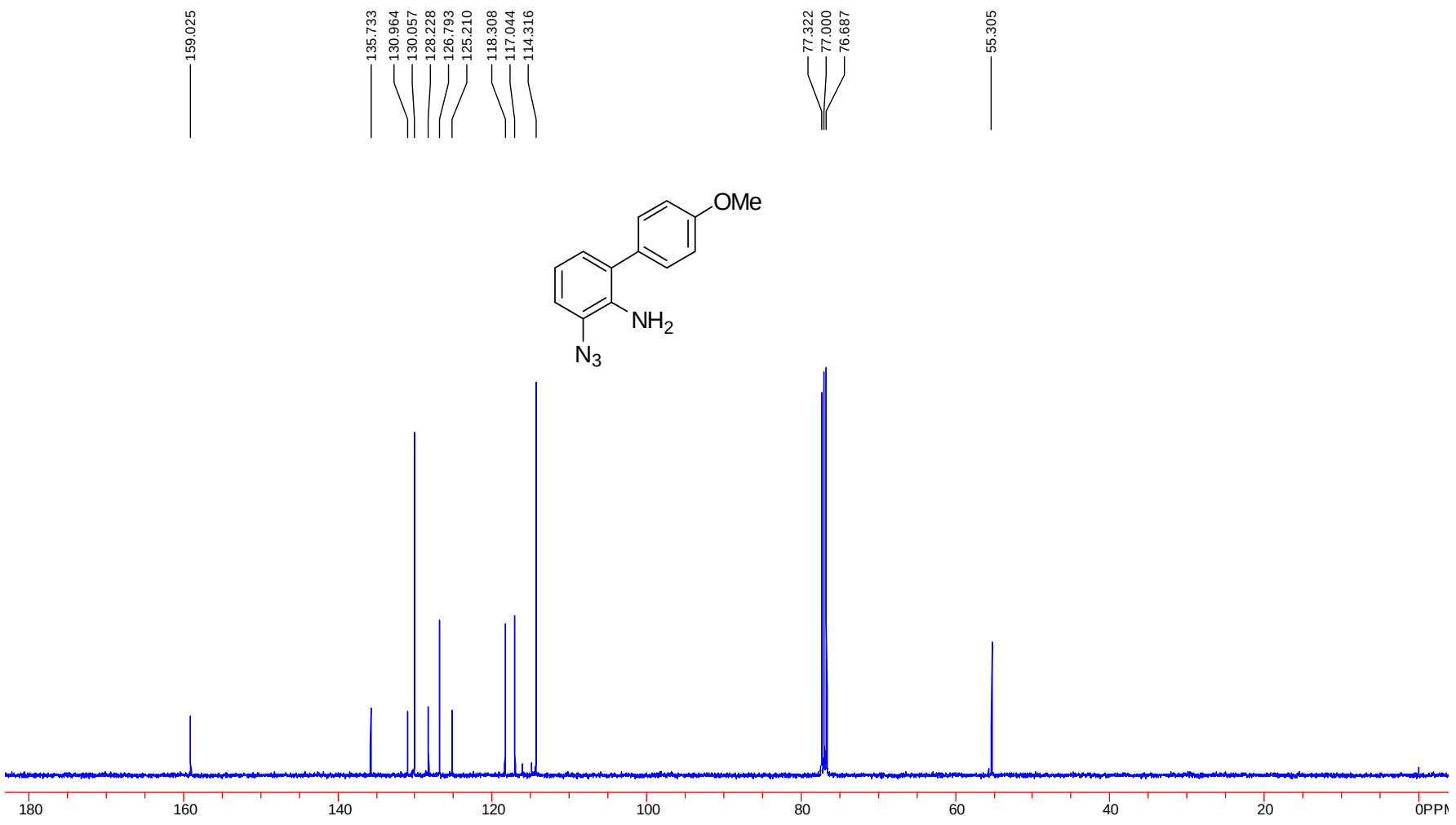
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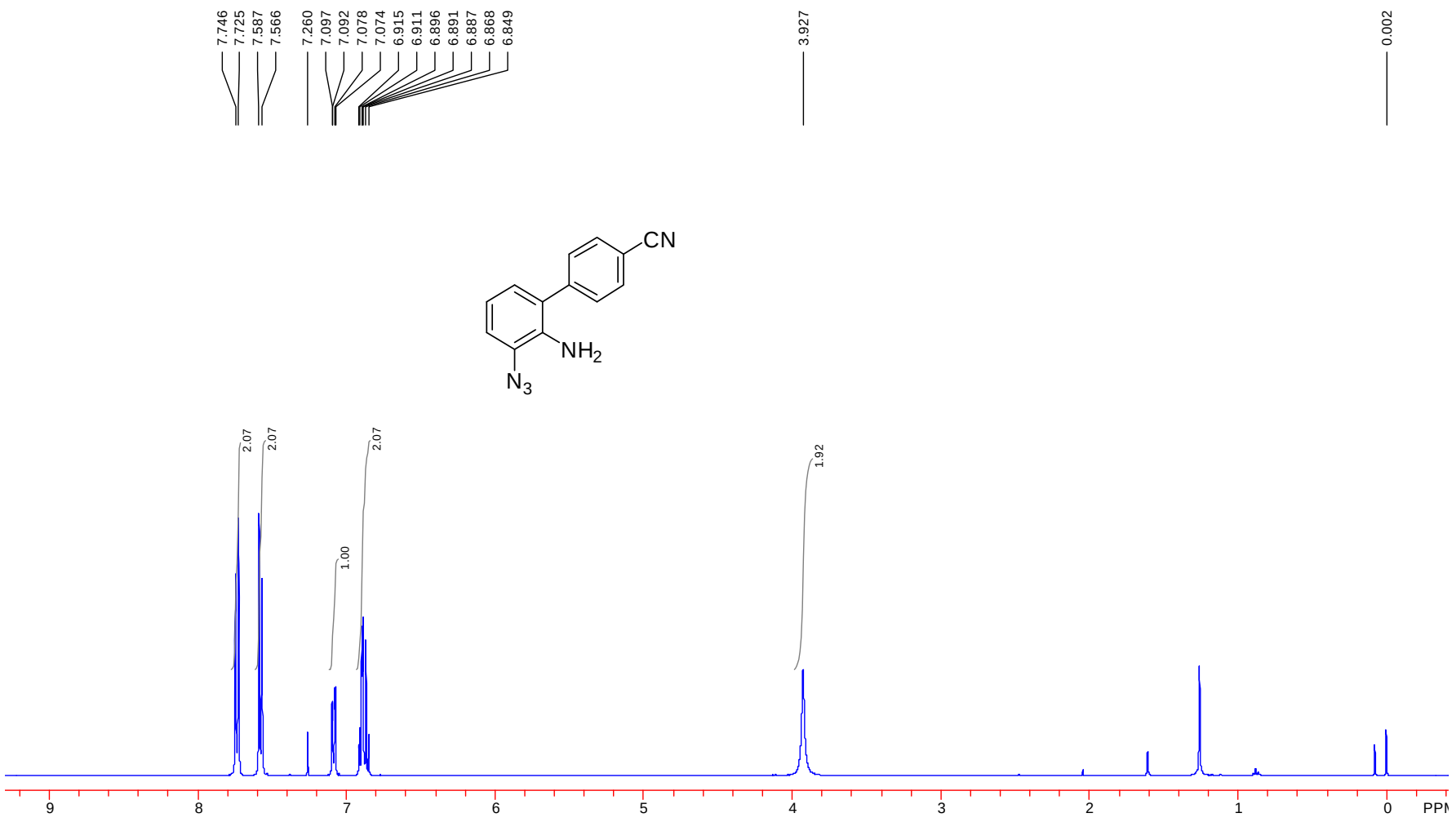
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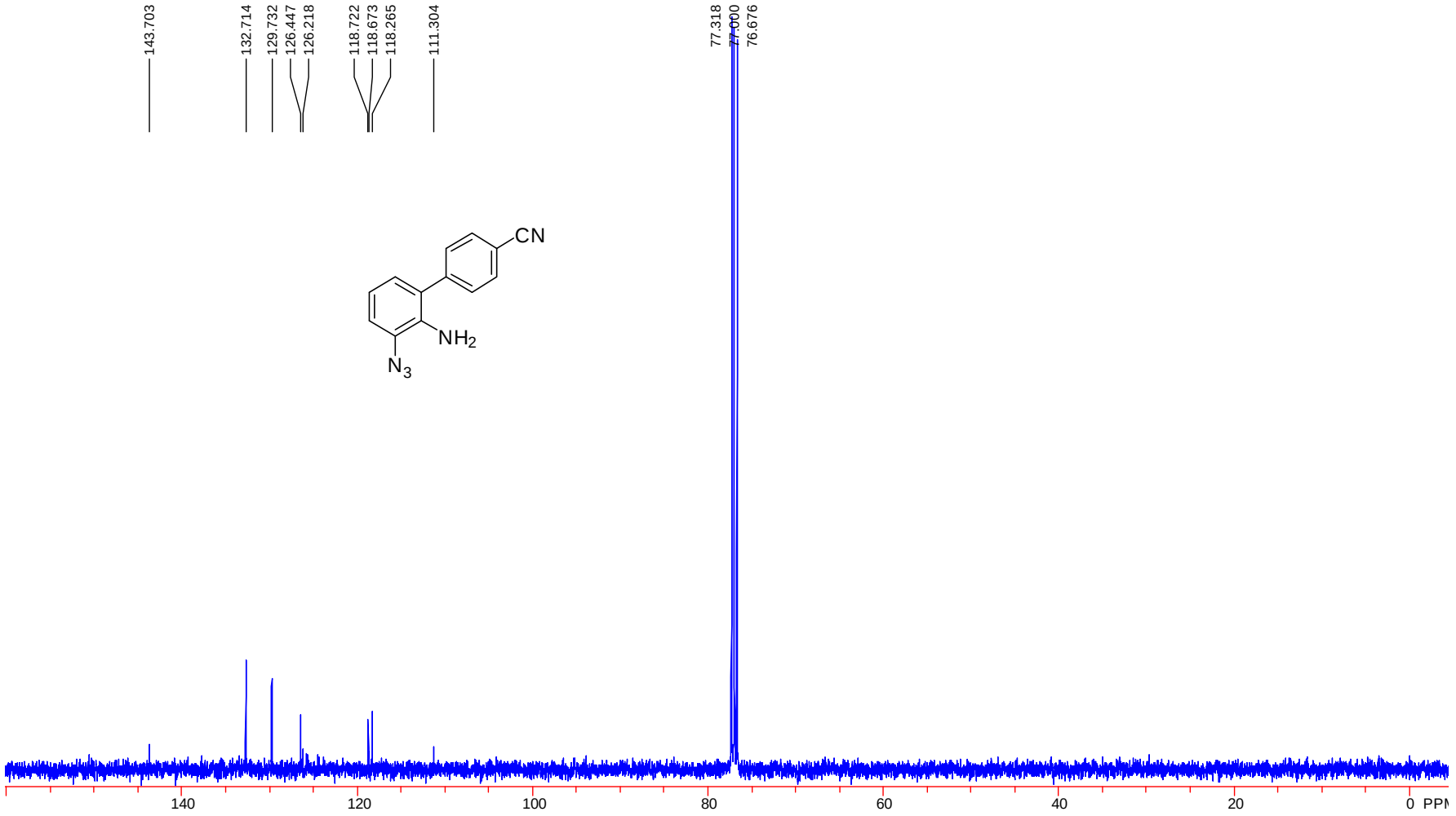
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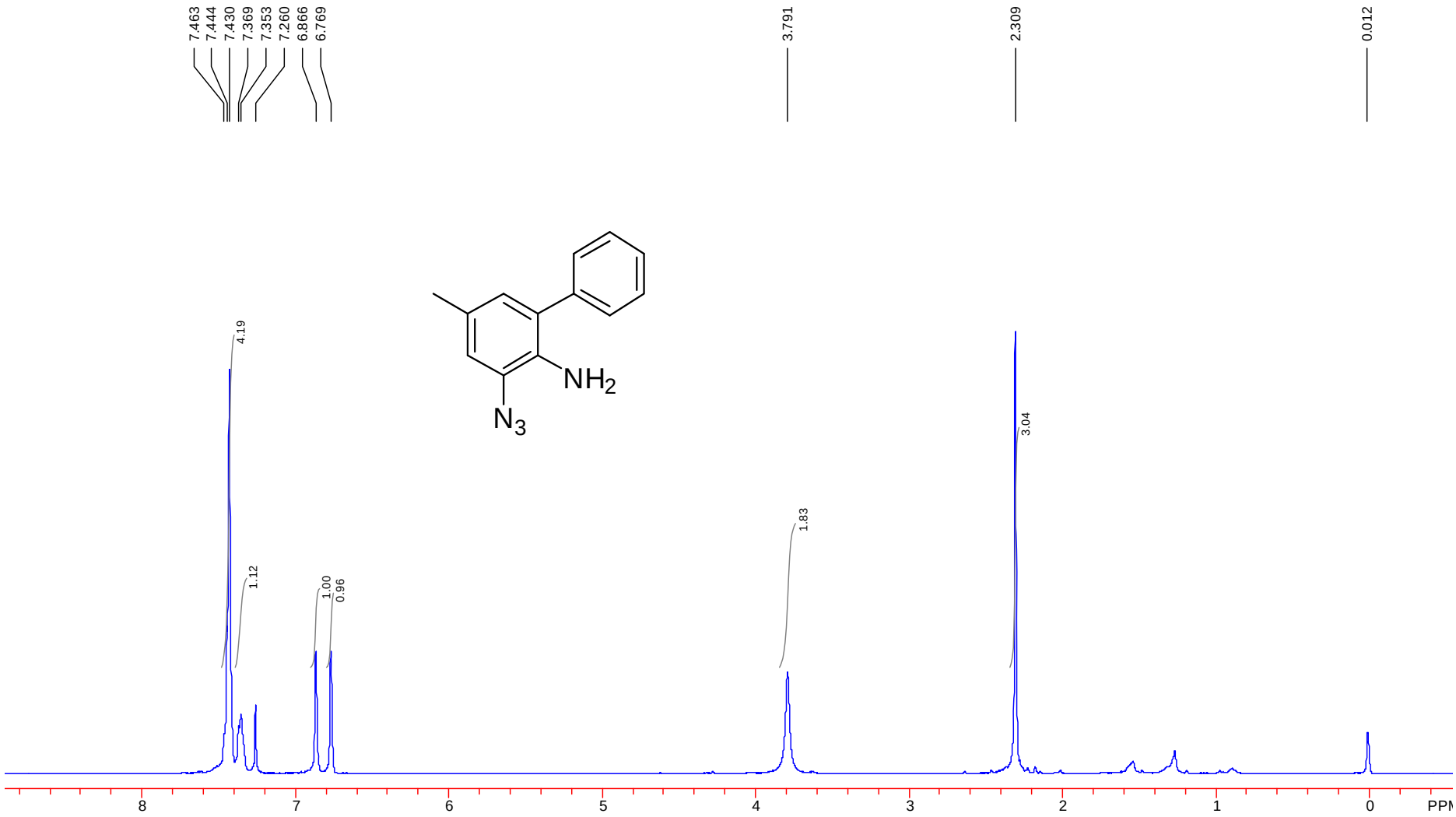
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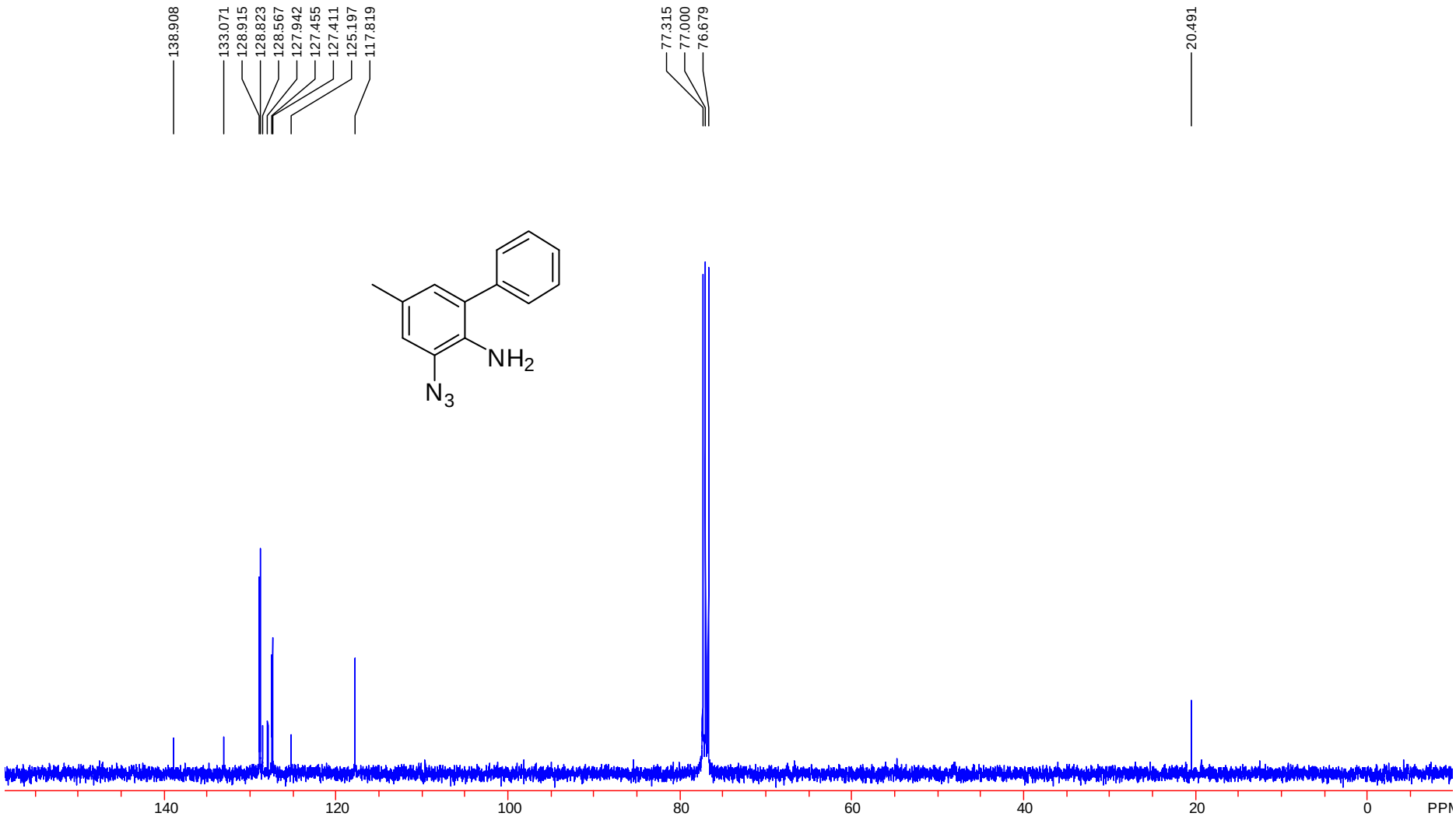
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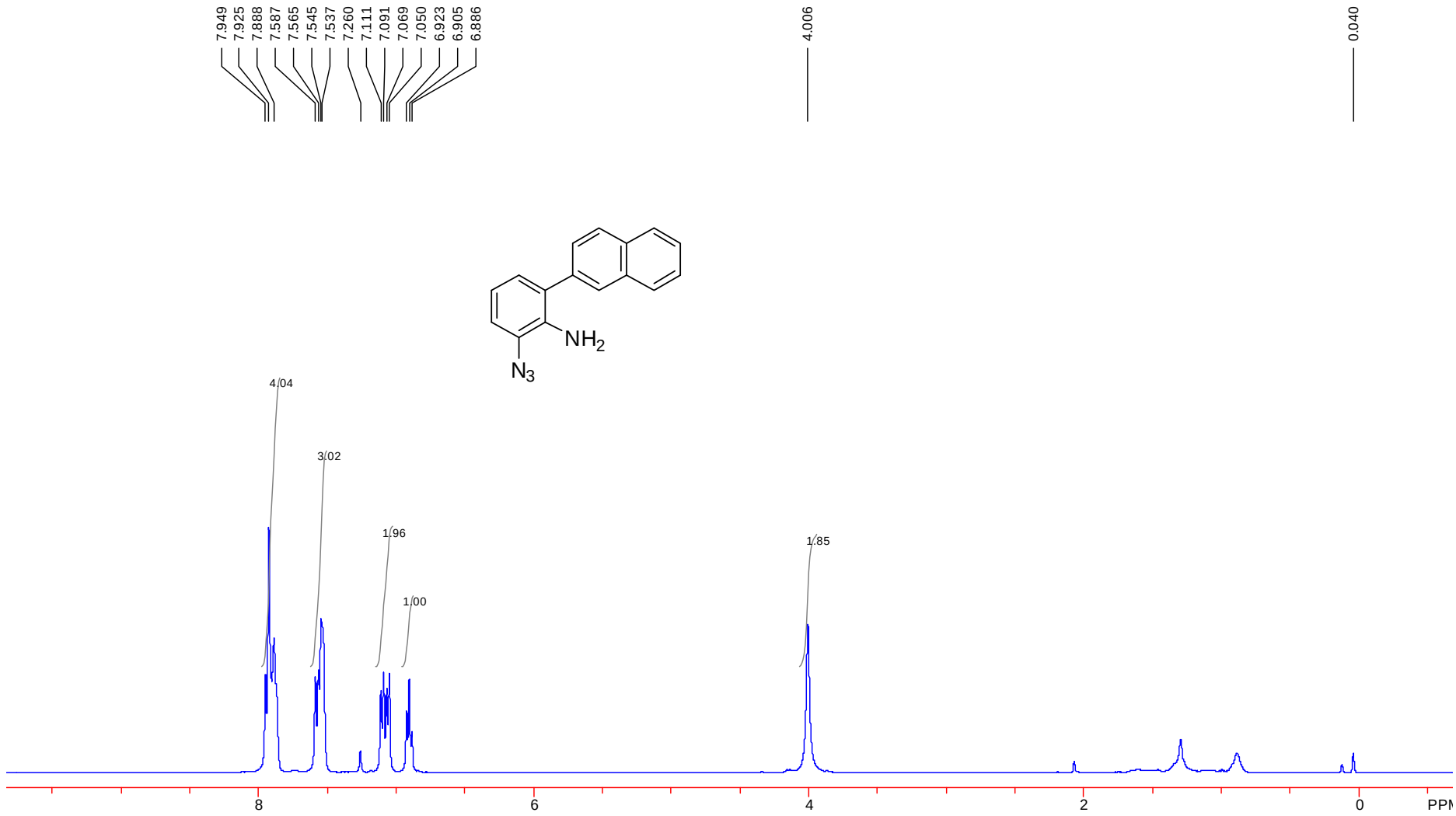
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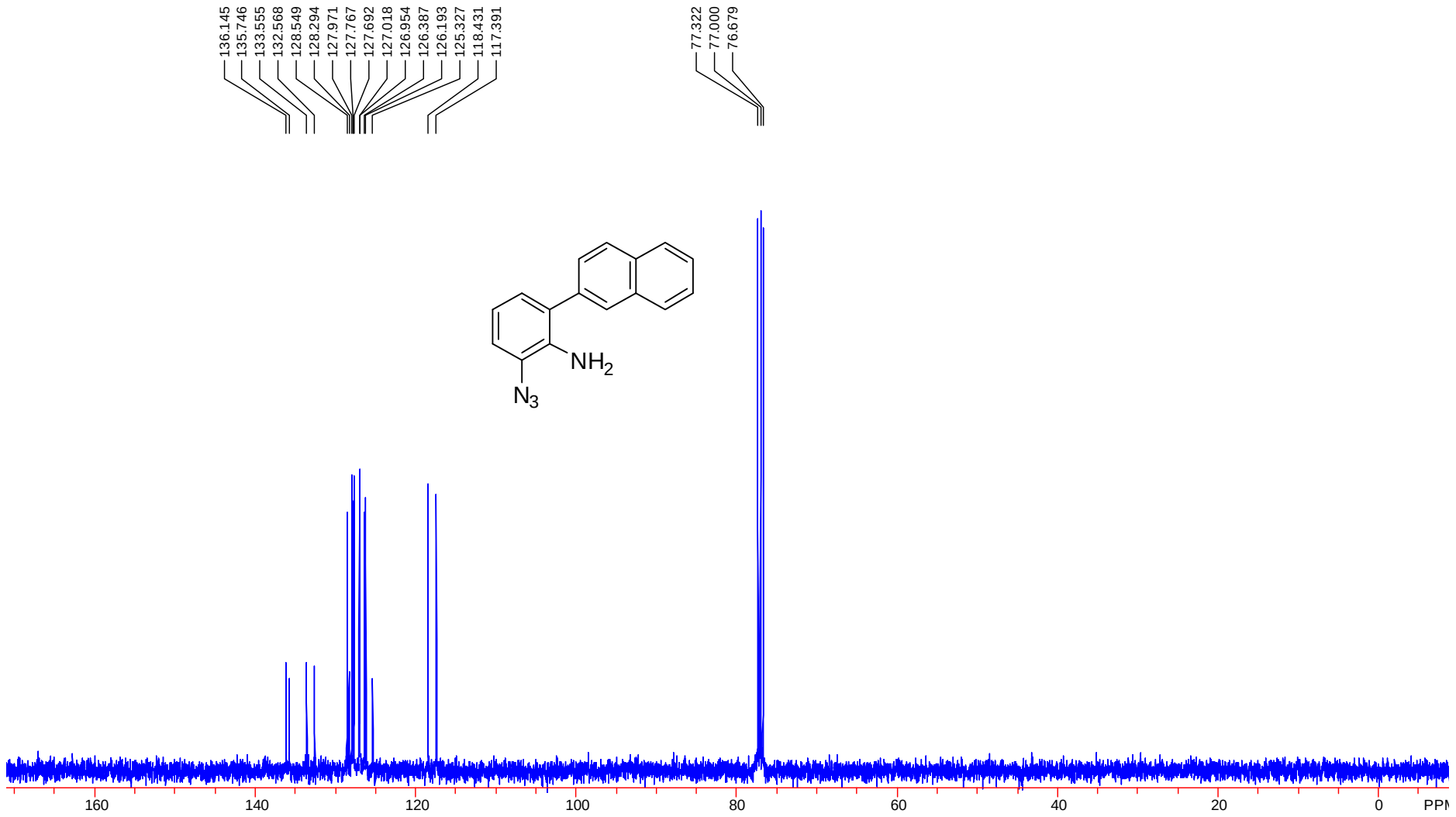
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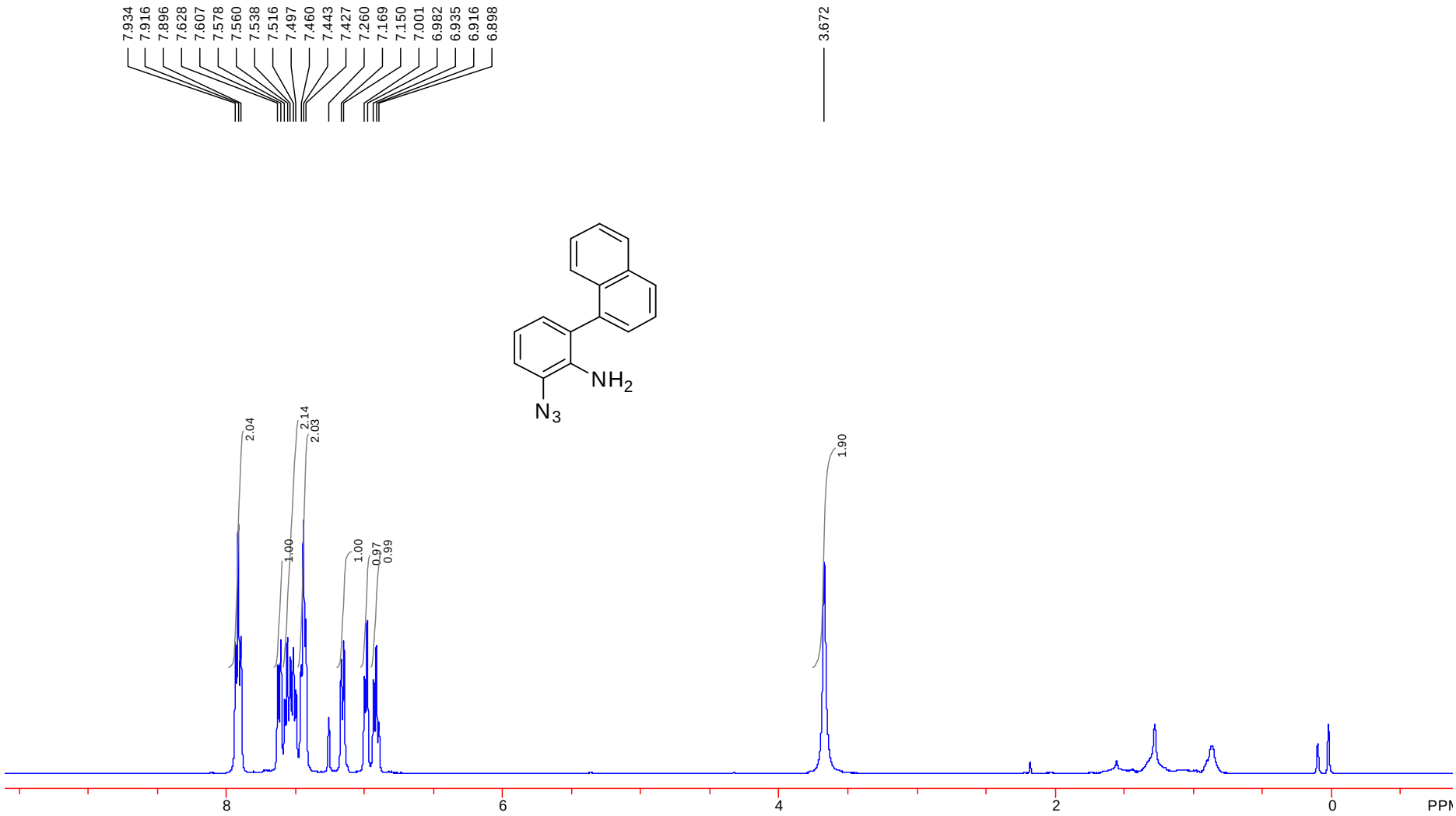
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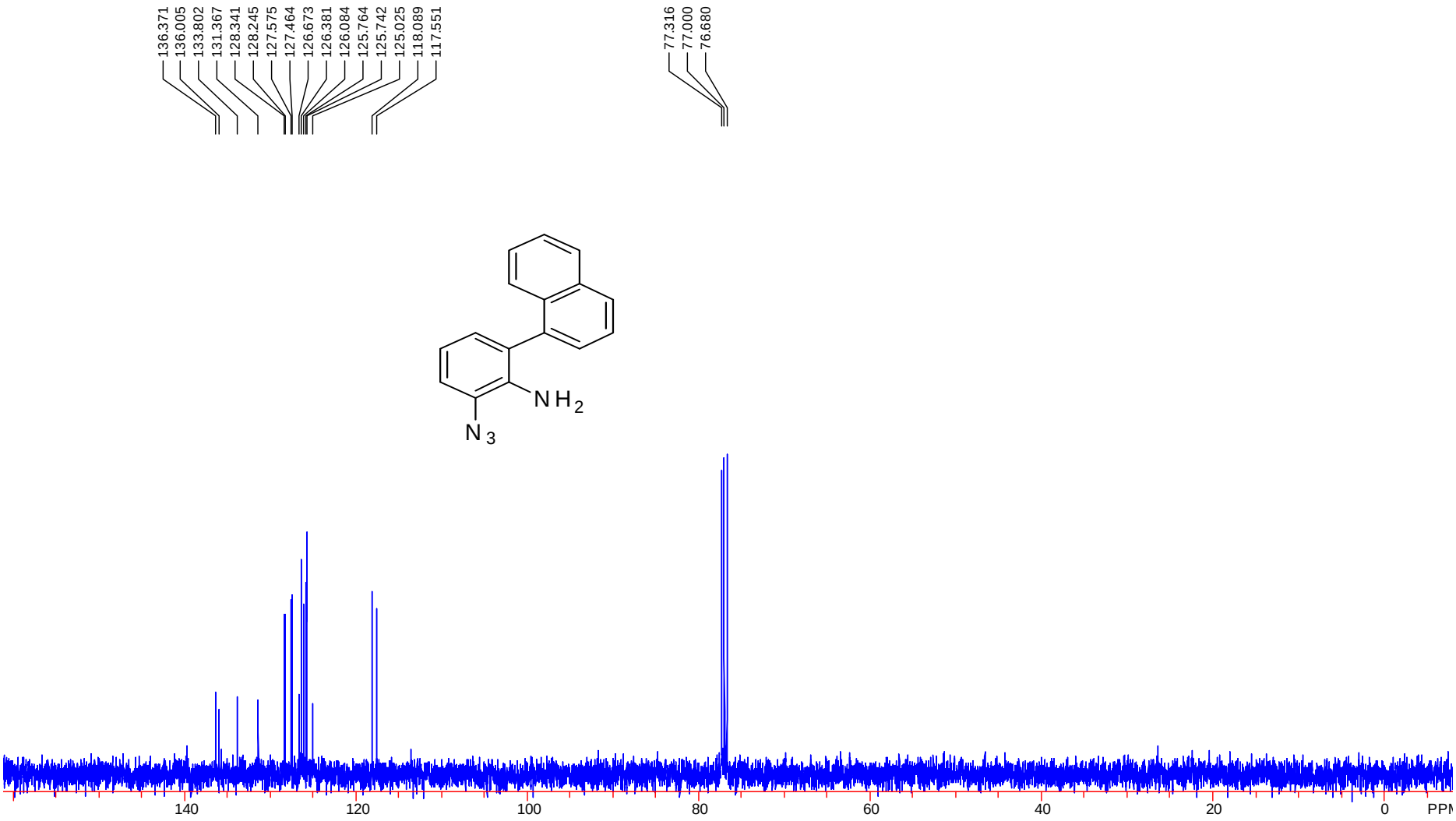
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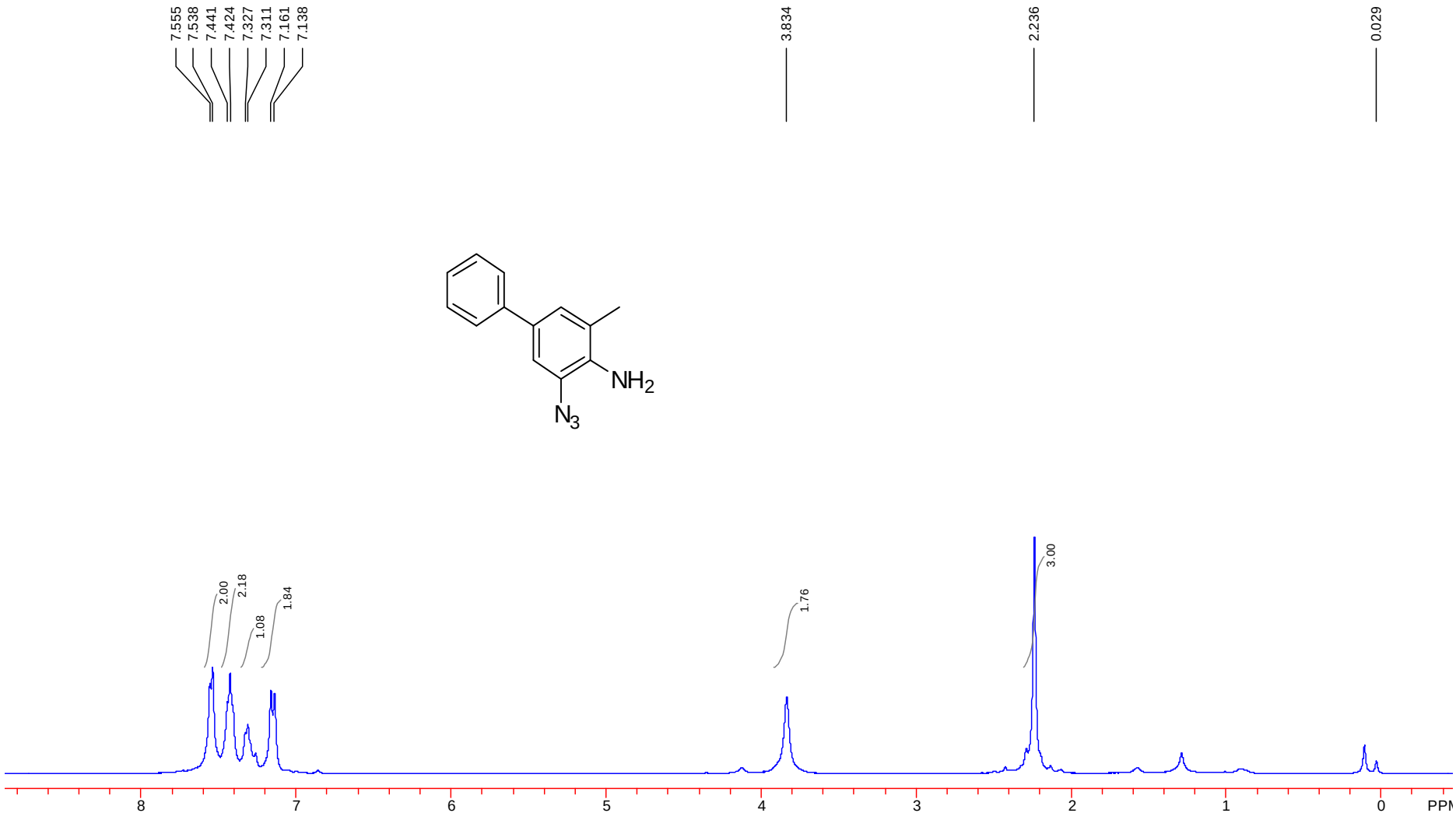
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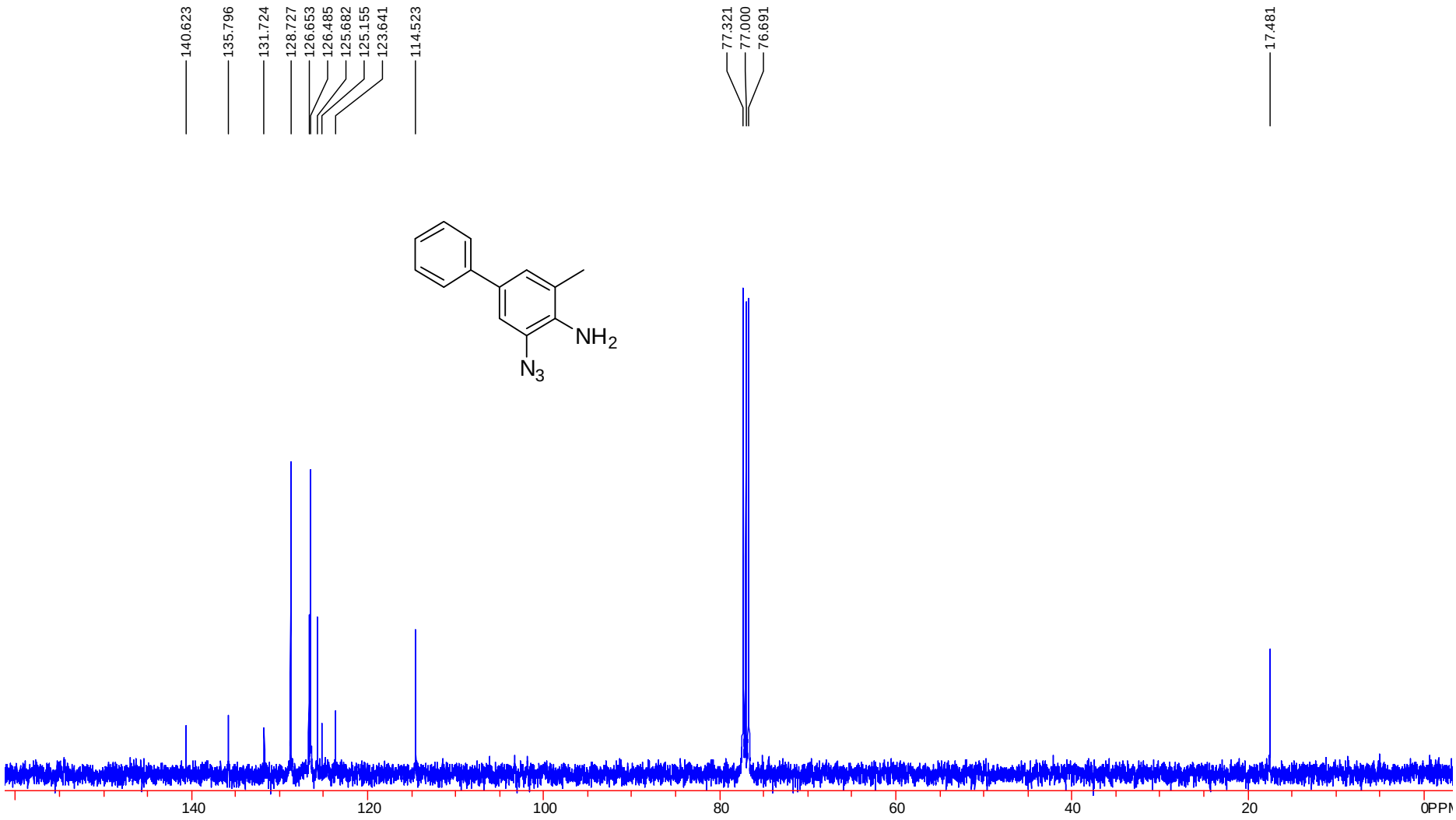
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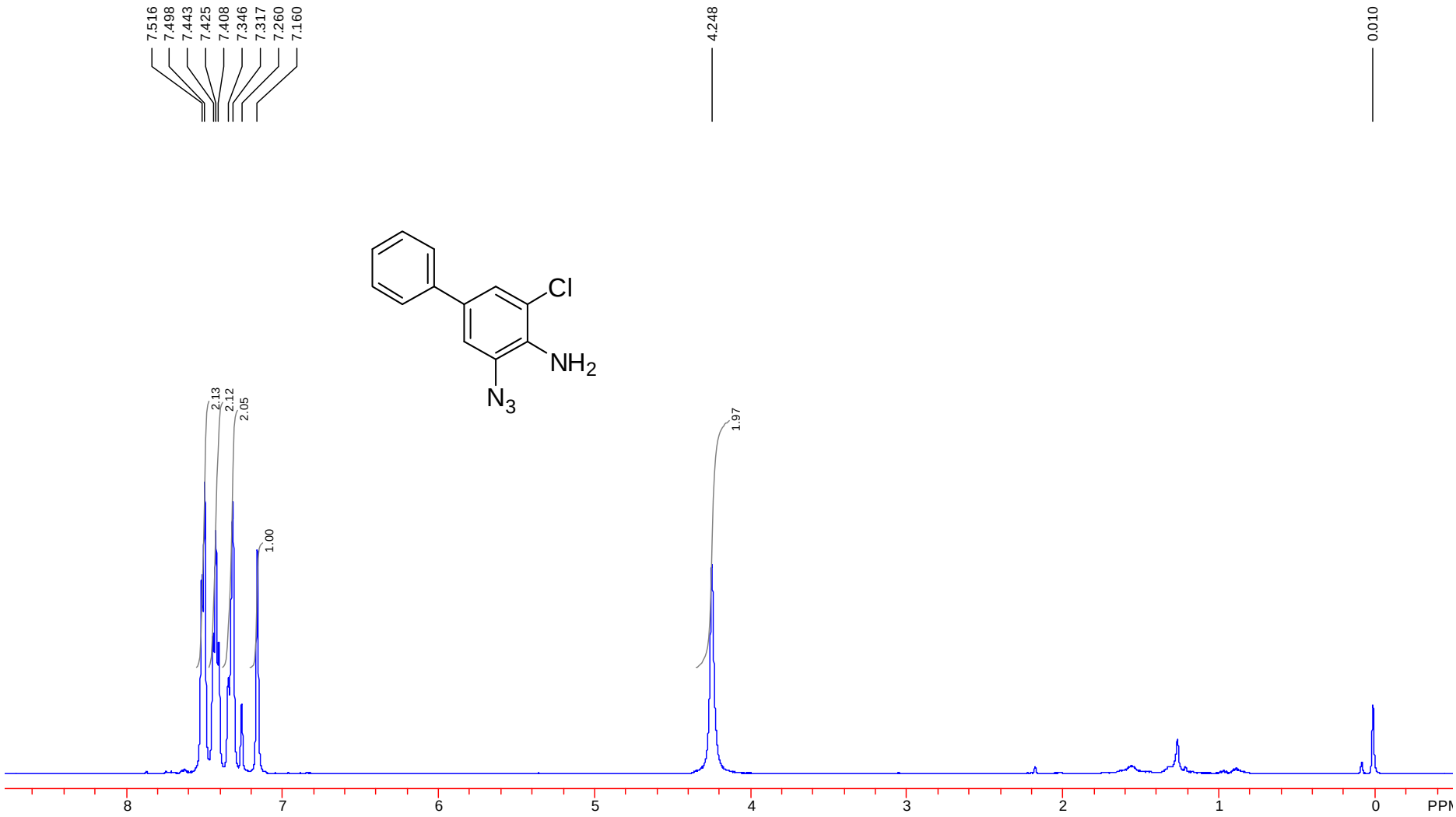
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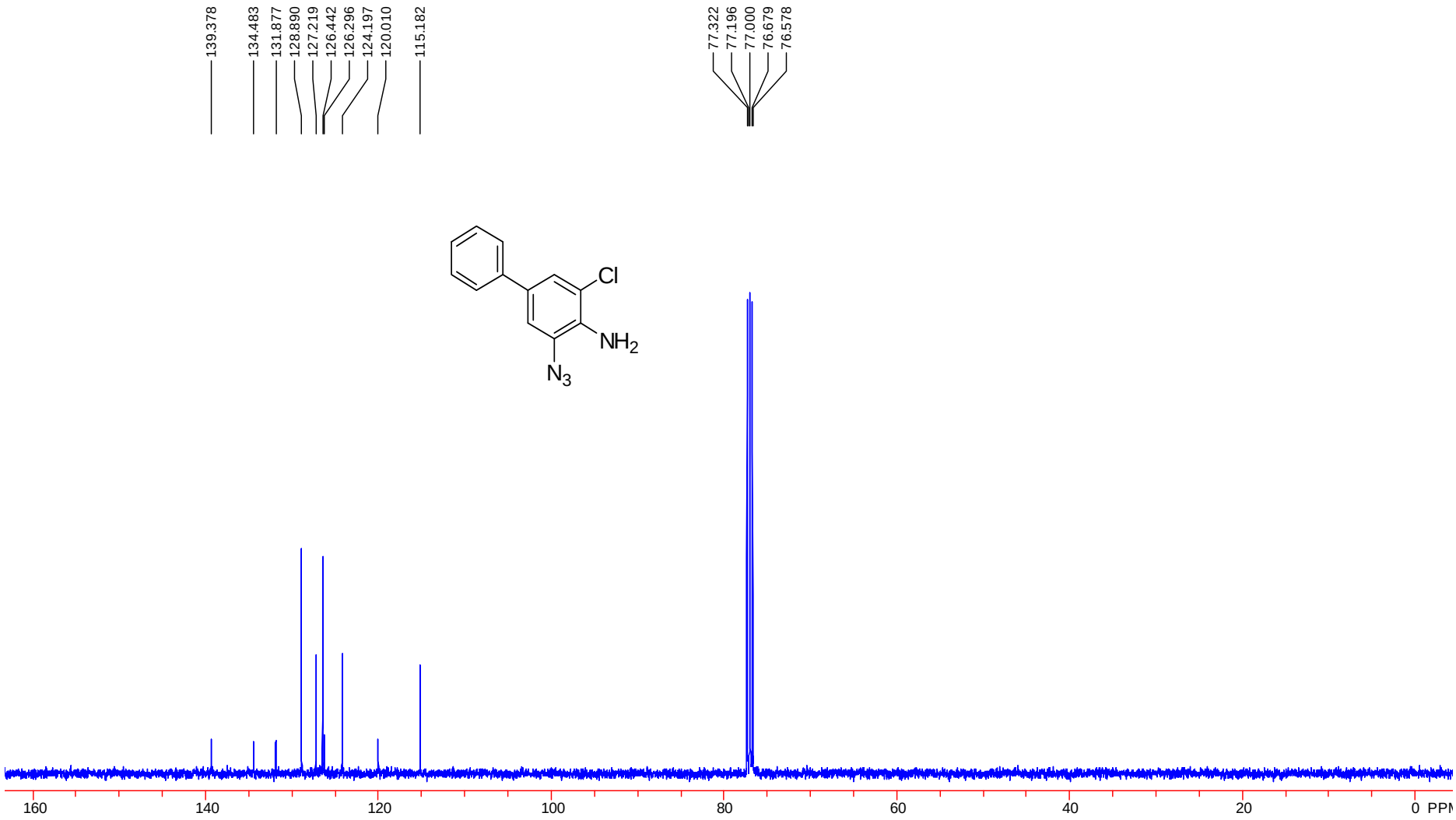
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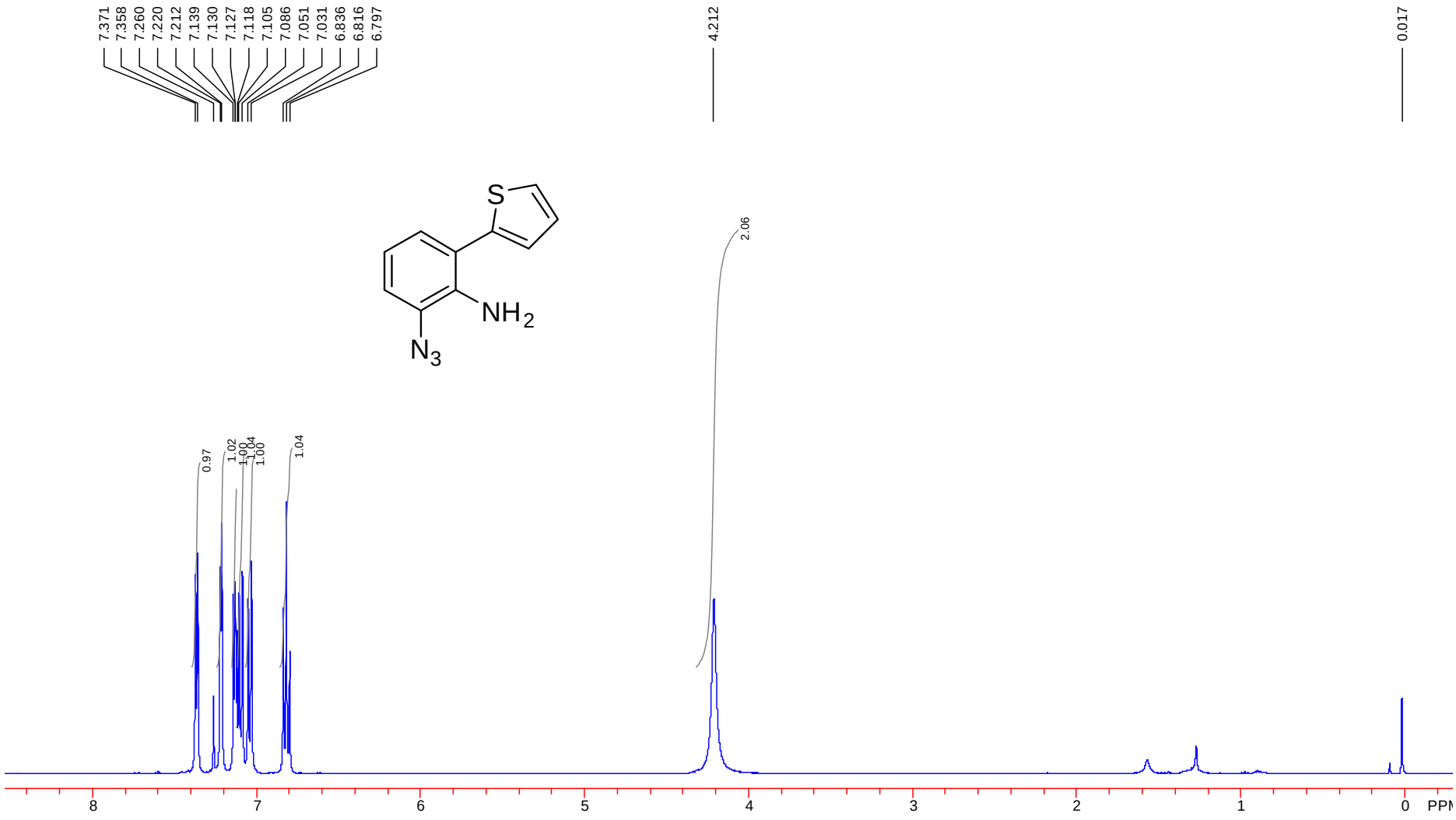
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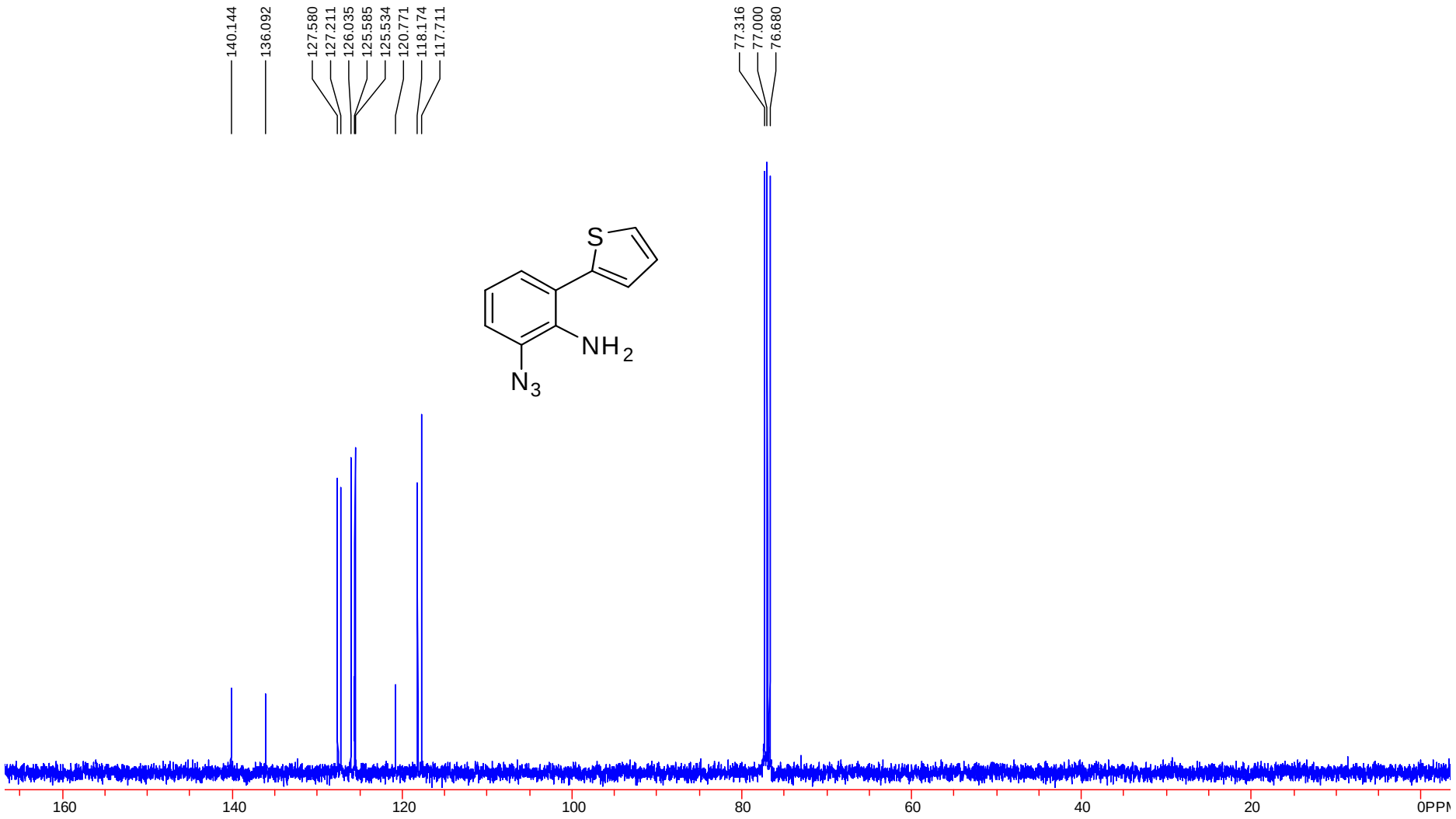
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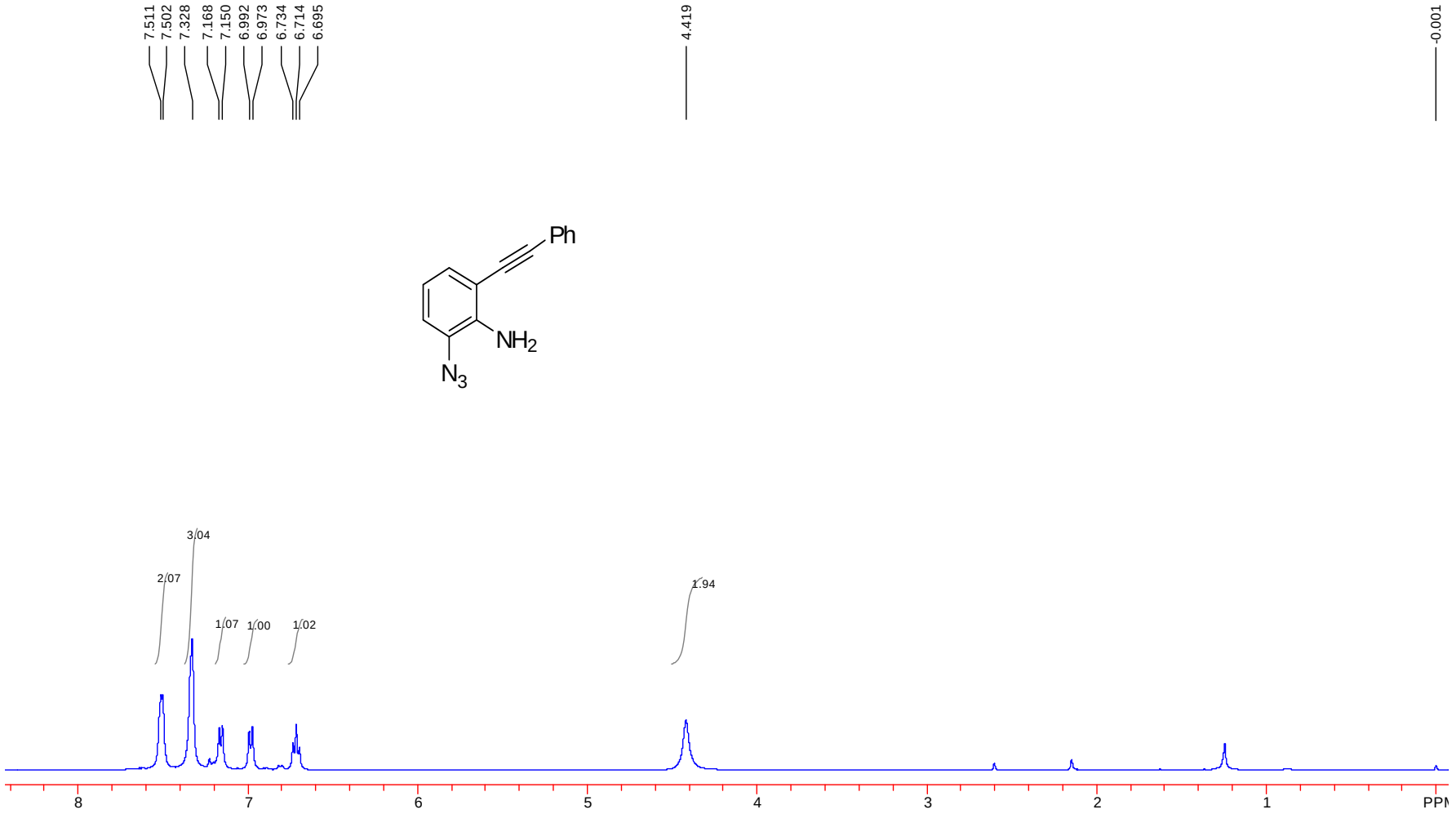
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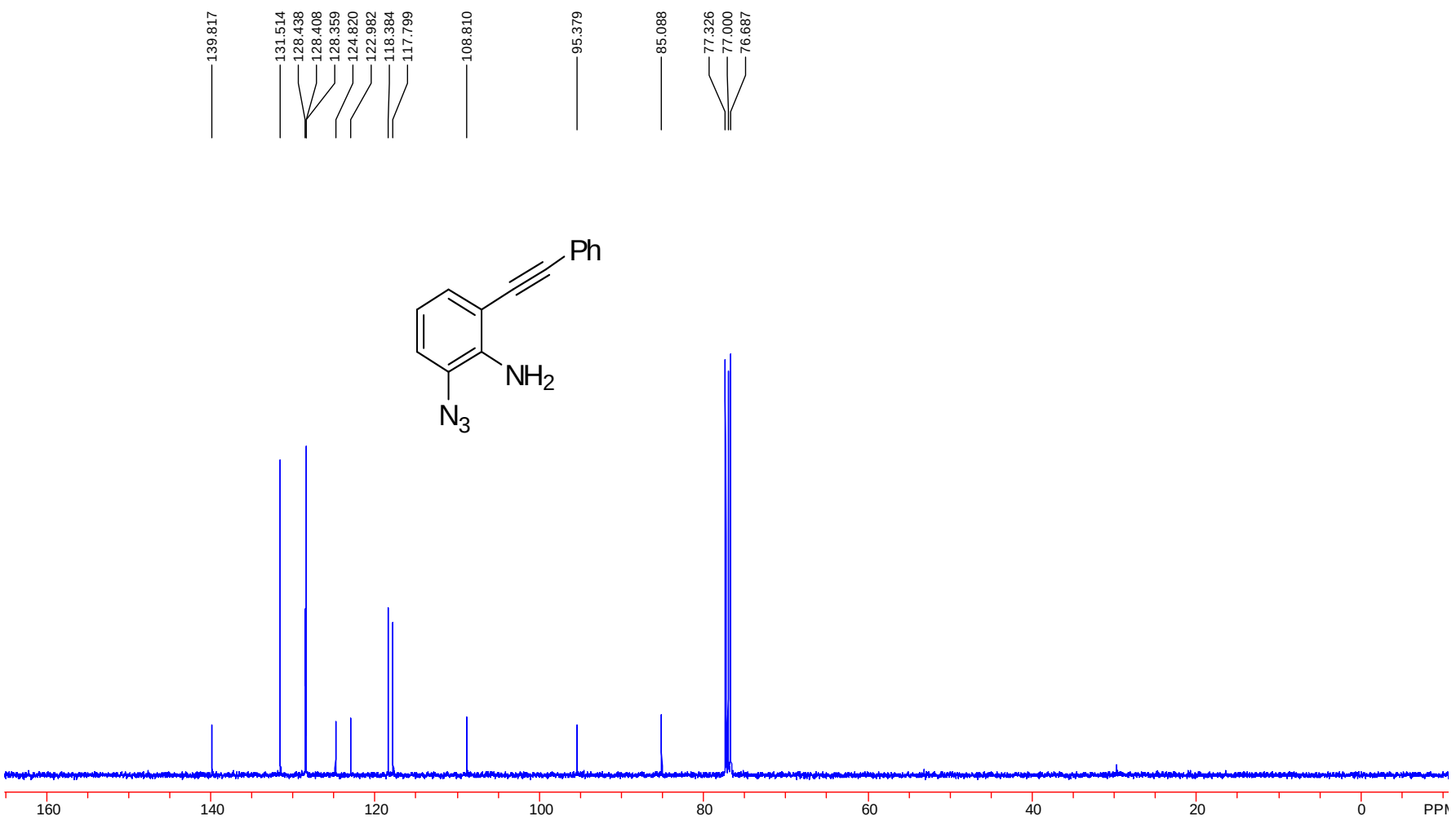
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76.687
Ph
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N3
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120
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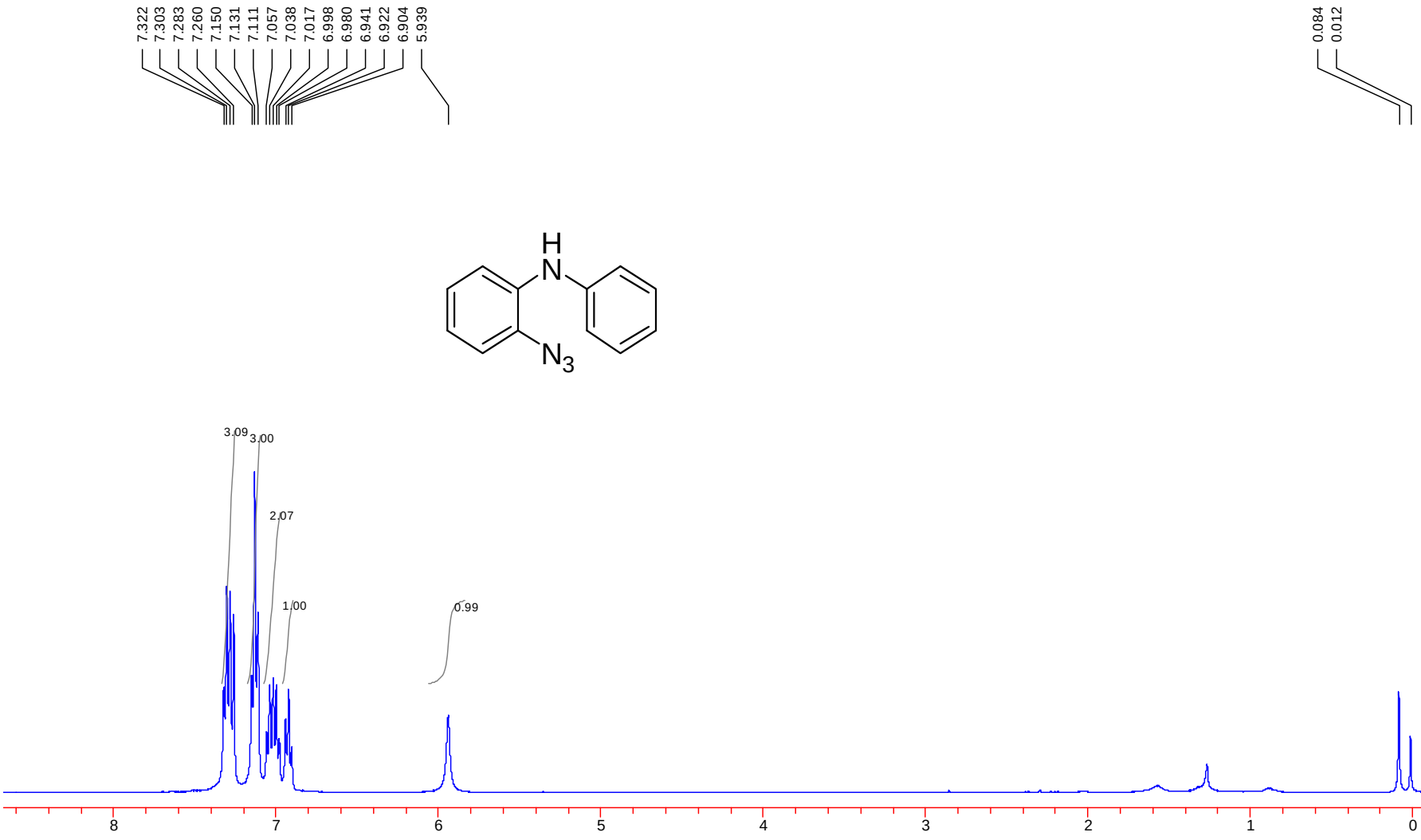
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7.057
7.038
7.017
6.998
6.980
6.941
6.922
6.904
5.939
0.084
0.012
H
N
N3
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3.00
2.07
1.00
0.99
8
7
6
5
4
3
2
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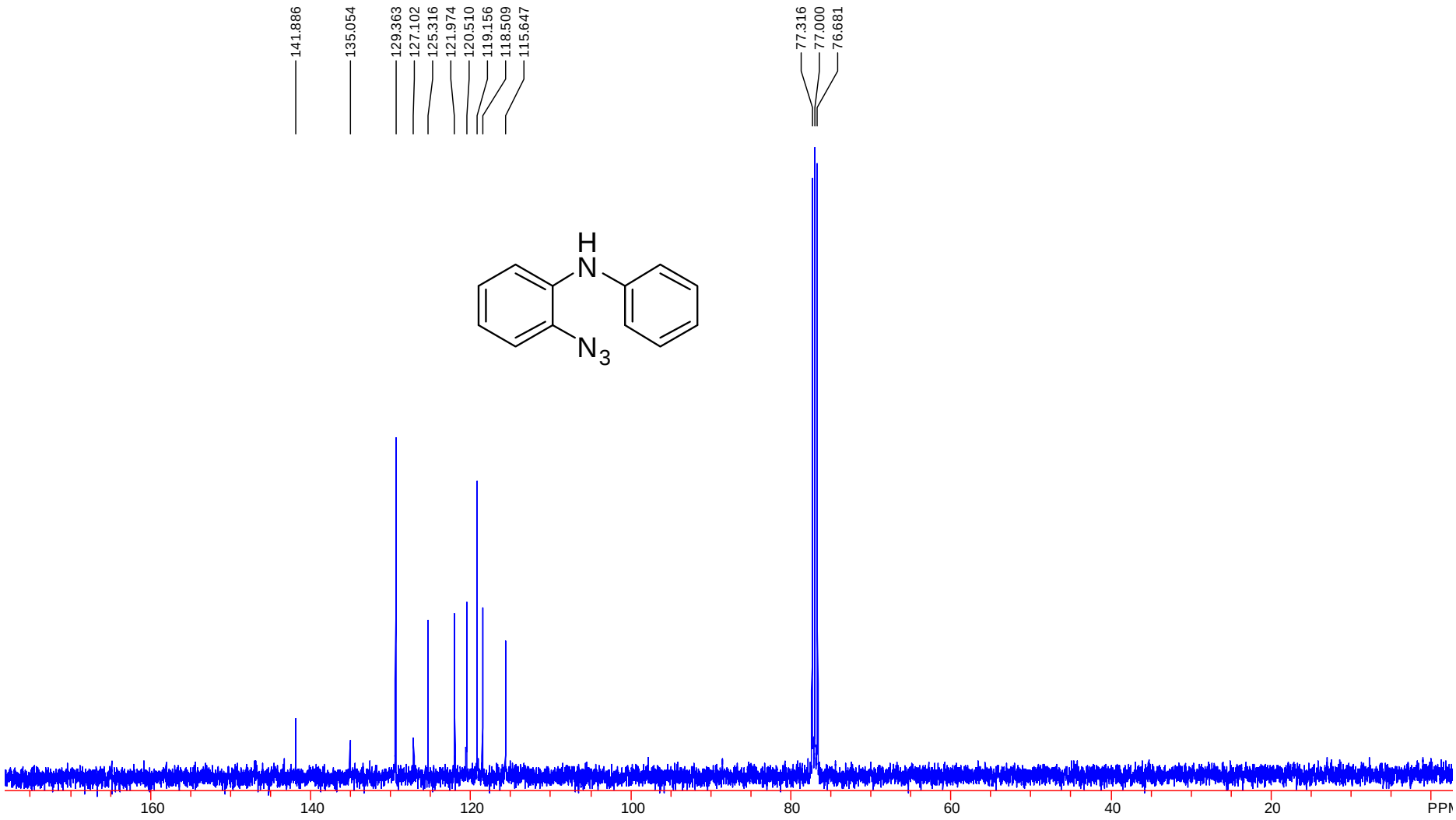
0
PPM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119.156
118.509
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76.681
H
N
N3
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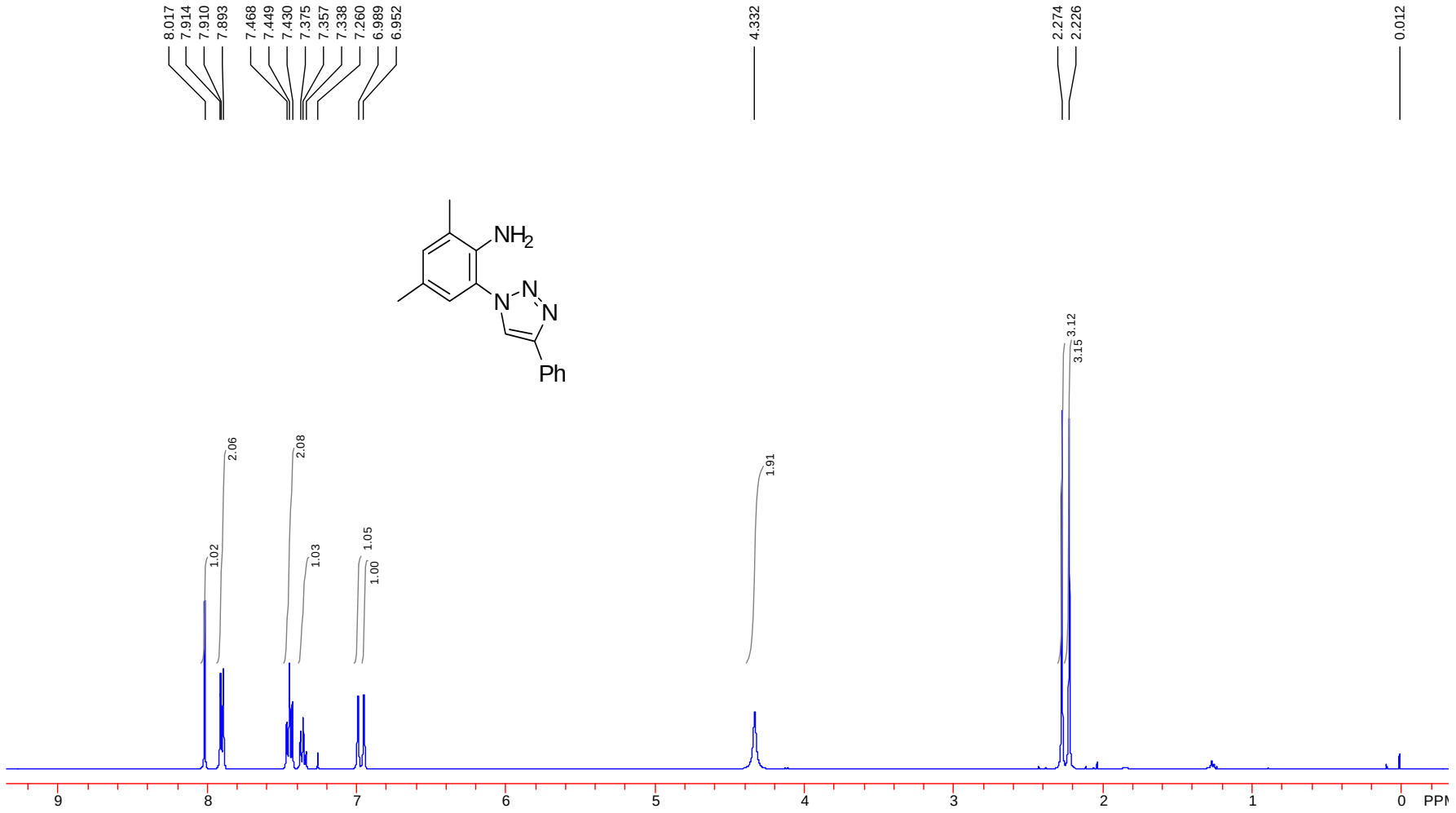
140
120
100
80
60
40
20
PPM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7.910
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6.989
6.952
4.332
2.274
2.226
0.012
NH2
N
N
N
Ph
2.06
2.08
1.91
3.12
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1.03
1.05
1.00
9
8
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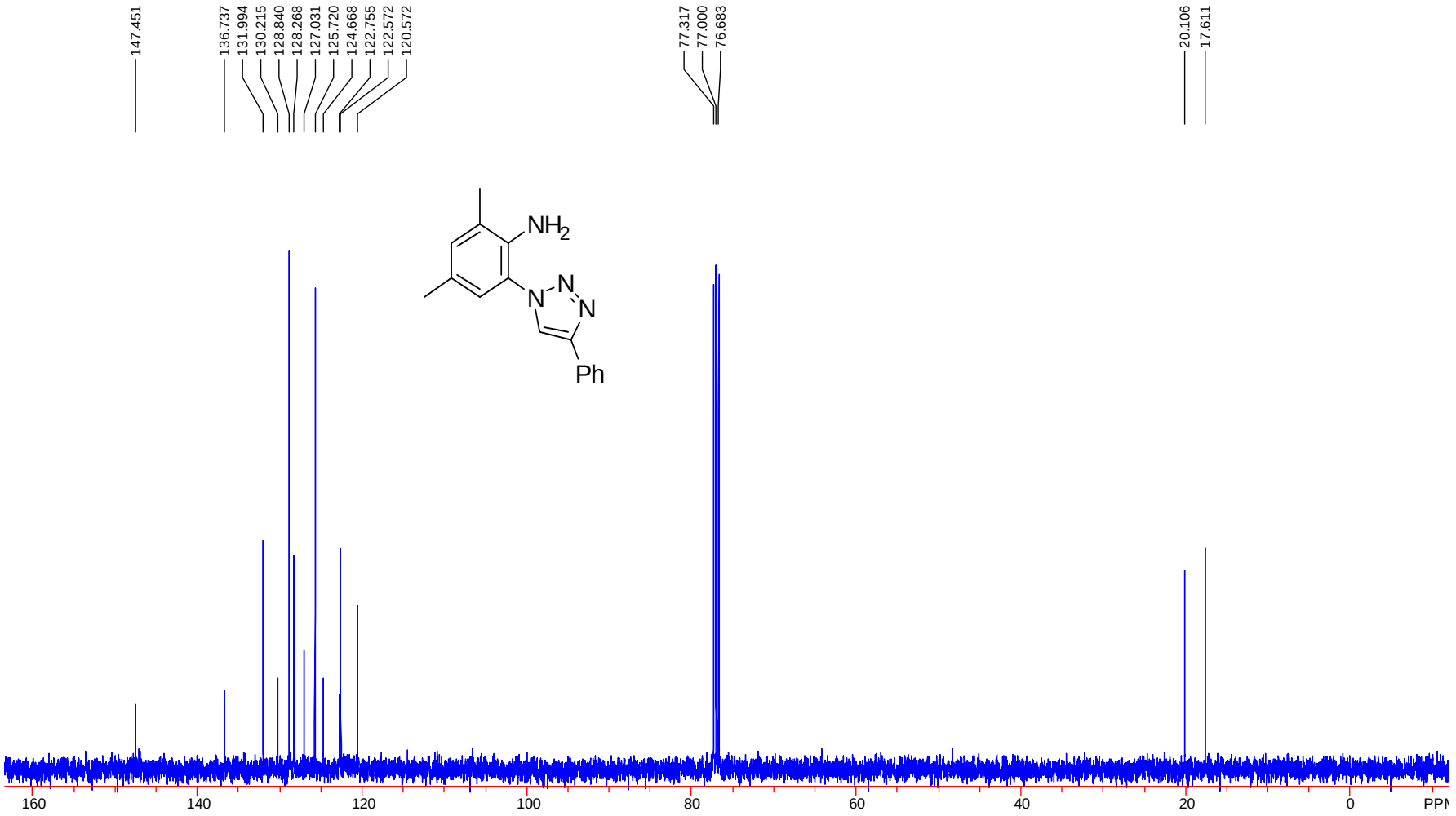
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128.268
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122.755
122.572
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77.000
76.683
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17.611
NH2
N
N
N
Ph
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140
120
100
80
60
40
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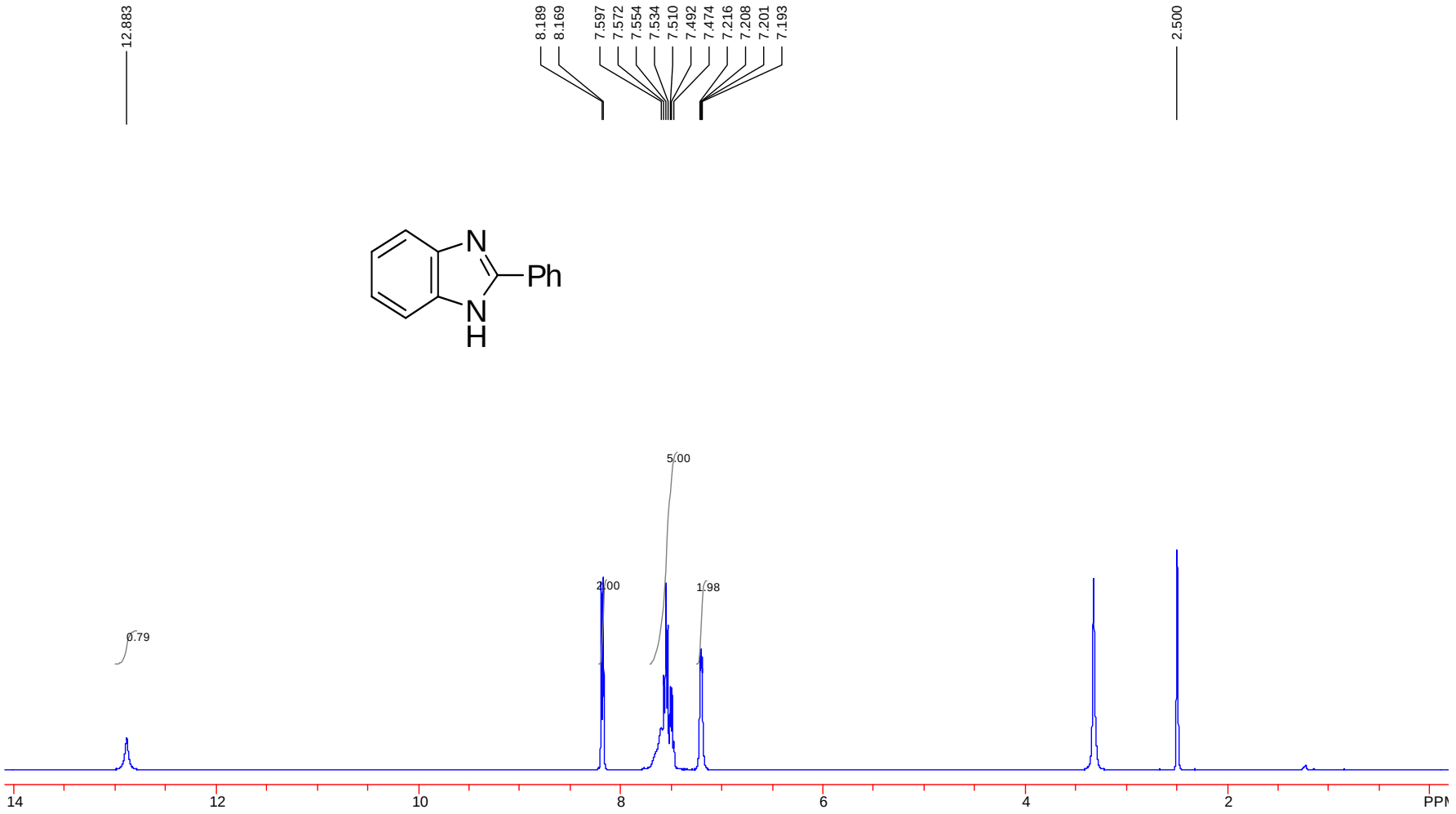
0
PPM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8.169
7.597
7.572
7.554
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7.510
7.492
7.474
7.216
7.208
7.201
7.193
2.500
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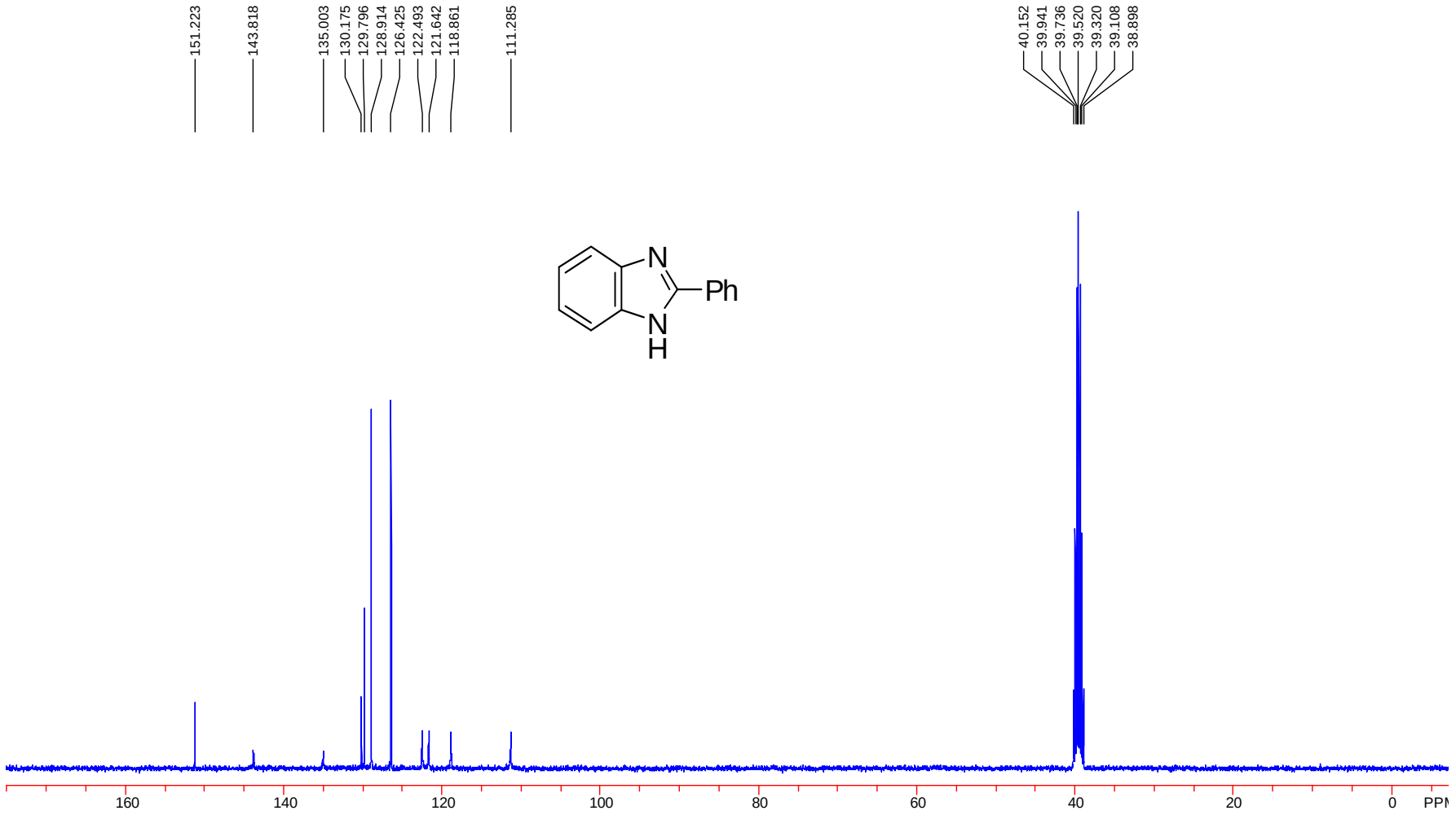
Ph
N
H
5.00
2.00
1.98
0.79
14
12
10
8
6
4
2
PPM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135.003
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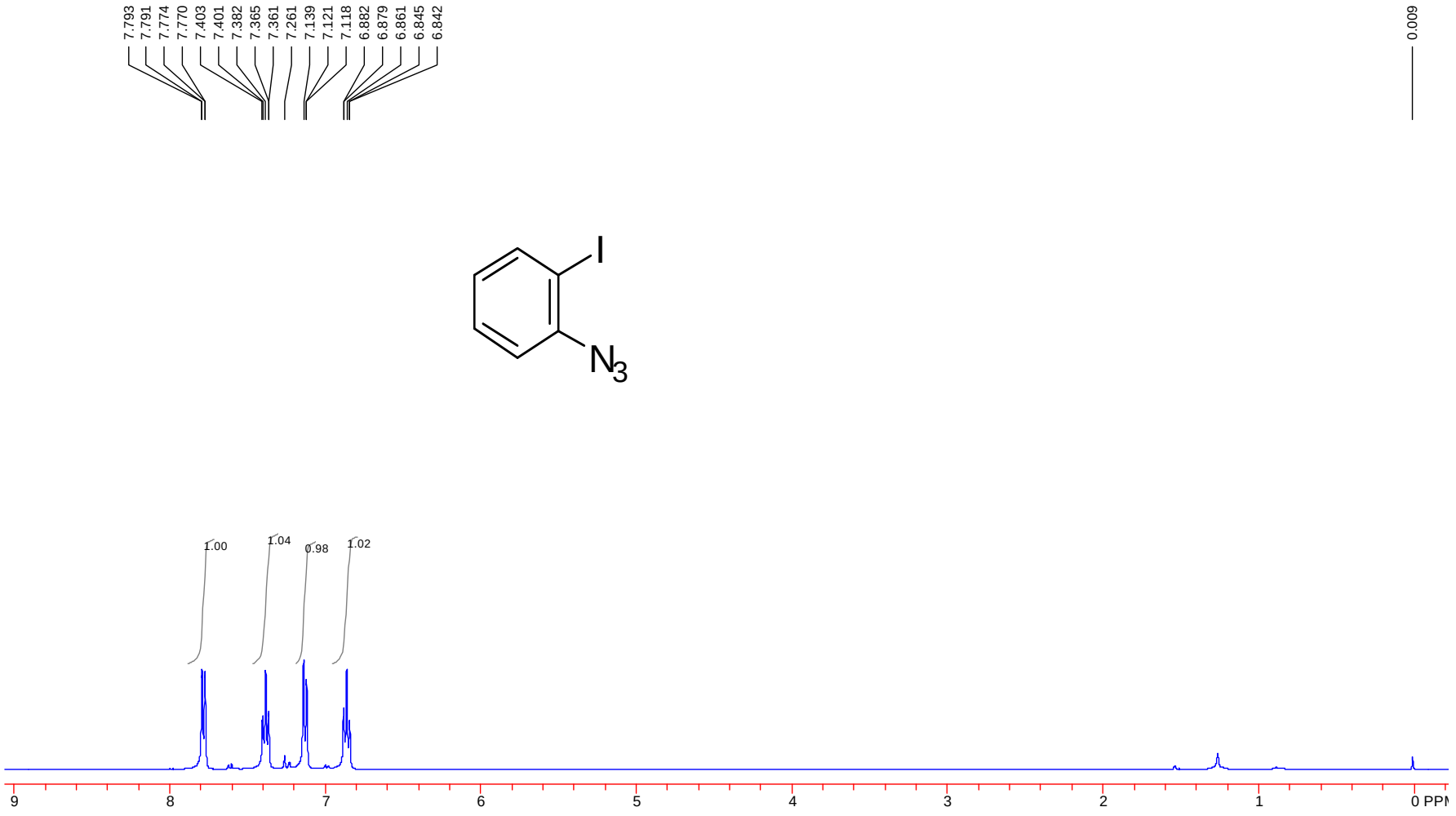
128.914
126.425
122.493
121.642
118.861
111.285
40.152
39.941
39.736
39.520
39.320
39.108
38.898
N
Ph
N
H
160
140
120
100
80
60
40
20
0
PPM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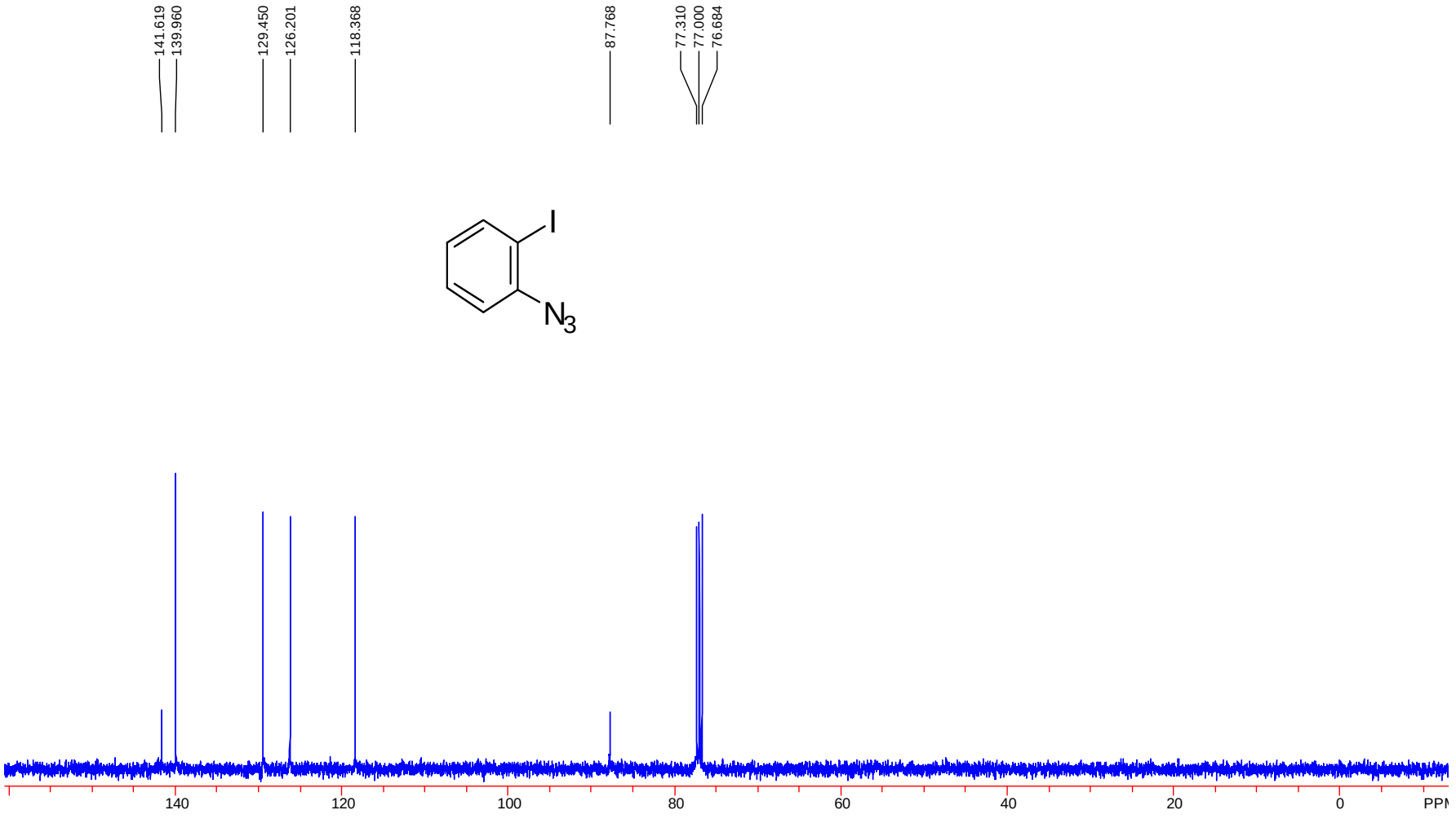
7.791
7.774
7.770
7.403
7.401
7.382
7.365
7.361
7.261
7.139
7.121
7.118
6.882
6.879
6.861
6.845
6.842
0.009
I
N3
1.00
1.04
0.98
1.02
9
8
7
6
5
4
3
2
1
0 PPM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129.450
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N3
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100
80
60
40
20
0
PPM