NBS mediated nitriles synthesis through C=C double bond cleavage

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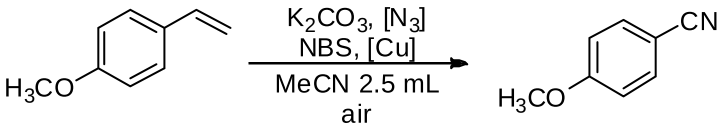
Supporting Information

Table of Contents

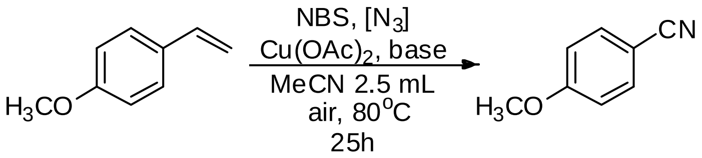
Table S1: the reactions of **1a** with different catalysts, temperature and nitrogen source.[a]



entry	[Cu]	$[N_3]$	T [°C]	yield[b]
1	$Cu(OAc)_2$	$TMSN_3$	80	47%
2	CuI	$TMSN_3$	80	25%
3	$CuCl_2$	$TMSN_3$	80	<10%
4	$Cu(NO_3)_2{\cdot}3H_2O$	$TMSN_3$	80	47%
5[c]	$Cu(OAc)_2$	$TMSN_3$	80	42%
6[c]	$Cu(NO_3)_2{\cdot}2H_2O$	$TMSN_3$	80	trace
7	$Cu(NO_3)_2{\cdot}2H_2O$	$TMSN_3$	70	55%
8	$Cu(OAc)_2$	DPPA	80	trace
9	$Cu(NO_3)_2{\cdot}2H_2O$	DPPA	80	trace
10	$Cu(OAc)_2$	TsN_3	80	trace
11	$Cu(NO_3)_2{\cdot}2H_2O$	TsN_3	80	trace

[a] 1-methoxy-4-vinylbenzene **1a** (0.4 mmol), [Cu] (0.08 mmol), NBS(0.4 mmol), $[N_3]$ (1.08 mmol), K_2CO_3 (0.4 mmol), MeCN (2.5 mL), air (1 atm), 25 h. [b] Isolated yields. [c] 0.4 mmol [Cu] was used. $TMSN_3$ was trimethylsilyl azide, DPPA was diphenylphosphoryl azide, TsN_3 was *p*-toluenesulfonyl azide.

Table S2: the effect of different base on the reactions of **1a**. [a]



entry	Base (eq.)	$[N_3]$ (eq.)	yield[b]
1	Li_2CO_3 (1.0)	$TMSN_3$ (2.7)	ND
2	Na_2CO_3 (1.0)	$TMSN_3$ (2.7)	22%
3	K_2CO_3 (1.0)	$TMSN_3$ (2.7)	47%
4	Cs_2CO_3 (1.0)	$TMSN_3$ (2.7)	53%
5	KOH (1.0)	$TMSN_3$ (2.7)	30%
6	NaOH (1.0)	$TMSN_3$ (2.7)	24%
7	$NaHCO_3$ (1.0)	$TMSN_3$ (2.7)	<10%
8	t-BuOK (1.0)	$TMSN_3$ (2.7)	52%
9	t-BuONa (1.0)	$TMSN_3$ (2.7)	<10%
10	CH_3CH_2ONa (1.0)	$TMSN_3$ (2.7)	<10%
11	CH_3ONa (1.0)	$TMSN_3$ (2.7)	ND
12	AgOAc (1.0)	$TMSN_3$ (2.7)	ND
13	Ag_2CO_3 (1.0)	$TMSN_3$ (2.7)	<10%
14	K_3PO_4•$7H_2O$ (1.0)	$TMSN_3$ (2.7)	49%
15	Et_3N (1.0)	$TMSN_3$ (2.7)	<10%
16	Pyridine (1.0)	$TMSN_3$ (2.7)	ND
17	NaH_2PO_4•$2H_2O$ (1.0)	$TMSN_3$ (2.7)	ND
18	Cs_2CO_3(1.2)	$TMSN_3$ (2.7)	45%
19	t-BuOK (1.2)	$TMSN_3$ (2.7)	<10%
20	K_3PO_4•$7H_2O$(1.2)	$TMSN_3$ (2.7)	42%
21	K_2CO_3 (2.0)	$TMSN_3$ (2.7)	50%
22	Cs_2CO_3 (2.0)	$TMSN_3$ (2.7)	45%
23	t-BuOK(2.0)	$TMSN_3$ (2.7)	41%
24	K_3PO_4•$7H_2O$(2.0)	$TMSN_3$ (2.7)	61%
25	K_3PO_4•$7H_2O$(2.0)	$TMSN_3$ (2.5)	77%
26	K_3PO_4•$7H_2O$(2.0)	$TMSN_3$ (2.0)	55%
27	K_3PO_4(2.0)	$TMSN_3$ (2.7)	49%
28	K_3PO_4•$3H_2O$(2.0)	$TMSN_3$ (2.5)	24%
29	KH_2PO_4 (2.0)	$TMSN_3$ (2.7)	ND

[a] 1-methoxy-4-vinylbenzene **1a** (0.4 mmol), NBS (0.4 mmol), $Cu(OAc)_2$ (0.08 mmol), MeCN (2.5 mL), air (1 atm), 80 °C, 25 h, ND was not detected. [b] Isolated yields.

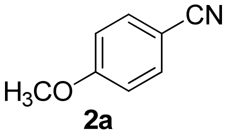
Experimental section:

General Remarks.

All manipulations were conducted with Schlenk tube. ^{1}H-NMR spectra were recorded on Bruker AVIII-400 spectrometers. 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 using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Analytical data for compounds **2** and **3**

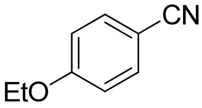
1):



2a

4-Methoxybenzonitrile.[1] **Typical procedure**: Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-methoxy-4-vinylbenzene **1a** (53.6 mg, 0.40 mmol), N-bromosuccinimide (71.2 mg, 0.40 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (115.2 mg, 1.00 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to afford 41.0 mg (77%) of **2a**. **2a**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, J = 9.2 Hz, 2H), 6.95 (d, J = 9.2 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.8, 133.9, 119.2, 114.7, 103.9, 55.5 ppm; IR (neat): ν = 2977.6, 2217.6, 1258.5, 1175.8, 829.7 cm^{-1}; MS (70 eV): m/z(%) 133.0 (M^+, 100).

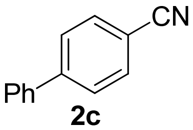
2):



2b

4-Ethoxybenzonitrile.[2] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-ethoxy-4-vinylbenzene **1b** (59.2 mg, 0.40 mmol), N-bromosuccinimide (71.2 mg, 0.40 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 41.2 mg (70%) of **2b**. **2b**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, *J* = 9.2 Hz 2H), 6.93 (d, *J* = 9.2 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.2, 133.9, 119.2, 115.1, 103.6, 63.9, 14.5 ppm; IR (neat): ν = 2981.3, 2219.7, 1258.9, 1172.5, 1039.1 cm^{-1}; MS (70 eV): m/z(%) 147.1 (M$^+$, 100).

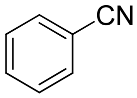
3):



2c

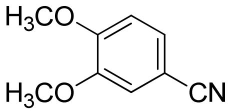
[1,1'-biphenyl]-4-carbonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 4-vinyl-1,1'-biphenyl **1c** (72.0 mg, 0.40 mmol), *N*-iodosuccinimide (90.0 mg, 0.40 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (115.2 mg, 1.00 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 118.1 mg (66%) of **2c**. **2c**: white solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.50-7.44 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 118.9, 110.9 ppm; IR (neat): ν = 3030.8, 2101.3, 1484.6, 768.0, 697.7 cm^{-1}; MW (70 eV):m/z (%) 179.1 (M$^+$,100).

4):

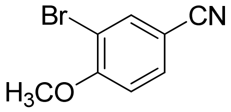


2d

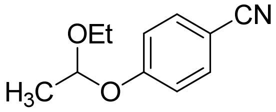
Benzonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), styrene **1d** (41.6 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (115.2 mg, 1.00 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. After cooling down to room temperature and concentrating in vacuum, This reaction was determined by GC using n-dodecane as internal standard to afford 26% of **2d**. **2d**: colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66-7.59 (m, 3H), 7.49-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.7, 132.0, 129.0, 118.7, 122.2 ppm; MS (70 eV): m/z (%) 103.0 (M$^+$, 100).

5):  **2e**

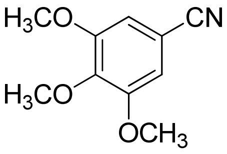
3,4-Dimethoxybenzonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1,2-dimethoxy-4-vinylbenzene **1e** (65.6 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 33.9 mg (52%) of **2e**. **2e**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.29 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 7.08 (d, J = 2 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.8, 149.1, 126.4, 119.1, 113.8, 111.2, 103.8, 56.1, 56.0 ppm;

6):  **2f**

3-Bromo-4-methoxybenzonitrile.[3] **Typical procedure**: Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 2-bromo-1-methoxy-4-vinylbenzene **1f** (84.8 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 44.7 mg(53%) of **2f**. **2f**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, J = 2.0 Hz, 1H), 7.60 (dd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.4, 136.7, 133.1, 117.7, 112.3, 111.9, 105.2, 56.5 ppm; IR (neat): ν = 2923.0, 2225.3, 1494.9, 1262.9, 1246.6 cm^{-1}; MS (70 eV): m/z(%) 211.0 ([M-1]$^+$,100), 213.0 ([M+1]$^+$, 100).

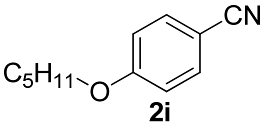
7):  **2g**

4-(1-Ethoxyethoxy)benzonitrile.[4] **Typical procedure**: Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-(1-ethoxyethoxy)-4-vinylbenzene **1g** (76.8 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction was determined by NMR using 1,1,2,2-tetrachloroethane as internal standard afforded 53% of **2g**. **2g**: colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 5.49 (q, *J* = 5.3 Hz, 1H), 3.78-3.70 (m, 1H), 3.58-3.50 (m, 1H), 1.53 (d, *J* = 5.2 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.3, 133.8, 119.1, 117.3, 104.6, 99.1, 60.9, 19.7, 15.0 ppm; IR (neat): ν = 2980.8, 2225.5, 1604.6, 1505.1, 1251.4 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{13}NNaO_2$ $(M+Na)^+$ 214.0844, found 214.0841.

8): 

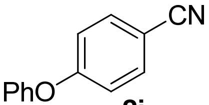
2h

3,4,5-Trimethoxybenzonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1,2,3-trimethoxy-5-vinyl-benzene **1h** (77.6 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h.. This reaction afforded 41.7 mg(54%) of **2h**. **2h**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.87 (s, 2H), 3.90 (s, 3H), 3.88 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.5, 142.2, 118.9, 109.4, 106.6, 60.9, 56.3 ppm; IR (neat): ν = 2938.6, 2225.6, 1242.1, 1131.4, 998.8 cm^{-1}; MS (70 eV): m/z (%).193.1 (M^+, 100)..

9): 

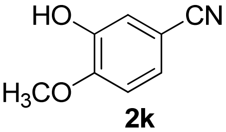
2i

4-(Pentyloxy)benzonitrile.[5] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-(pentyloxy)-4-vinylbenzene **1i** (76.0 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction was determined by NMR using 1,1,2,2-tetrachloroethane as internal standard afforded 59% of **2i**. **2i**: colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz 2H), 3.99 (t, *J* = 4.3 Hz, 2H), 1.84-1.77(m, 2H), 1.46-1.36(m, 4 H), 0.94(t, *J* = 4.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.4, 133.9, 119.3, 115.1, 103.6, 68.3, 28.6, 28.0, 22.3, 13.9 ppm; MS (70 eV): m/z(%) 119.0 (100), 189.1 (M^+, 30).

10): 

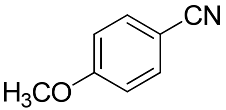
2j

4-Phenoxybenzonitrile.[6] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-phenoxy-4-vinylbenzene **1j** (78.4 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h.. This reaction was determined by NMR using 1,1,2,2-tetrachloroethane as internal standard afforded 56% of **2j**. **2j**: white solid; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.23 (q, *J* = 6.3 Hz, 1H), 7.06 (d, J = 7.6 Hz, 2H), 7.00 (d, *J* = 8.8Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.6, 154.7, 134.1, 130.2, 125.1, 120.3, 118.8, 117.8, 105.7 ppm; IR (neat): ν = 2924.8, 2226.5, 1502.7, 1485.1, 1245.6 cm^{-1}; MS (70 eV): m/z(%) 195.1 (M^+, 100).

11): 

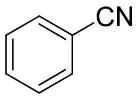
2k

3-Hydroxy-4-methoxybenzonitrile.[7] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), *tert*-butyl(2-methoxy-5-vinylphenoxy)dimethylsilane **1k** (105.6 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction was determined by NMR using 1,1,2,2-tetrachloroethane as internal standard afforded 51% of **2k**. **2k**: white solid; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.21 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 7.17 (d, *J* = 2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 5.83 (brs, 1H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.2, 145.9, 125.6, 119.0, 117.6, 110.8, 104.6, 56.1 ppm; IR (neat): ν = 3321.3, 2229.9, 1510.8, 1283.4, 1247.0 cm^{-1}; MS (70 eV): m/z(%) 149.1 (M^+, 95), 134.0 (100).

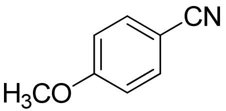
12): 

2a

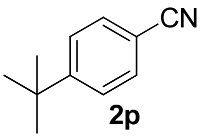
4-Methoxybenzonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), (E)-1-methoxy-4-(prop-1-en-1-yl)benzene **1l** (59.6 mg, 0.40 mmol), N-bromosuccinimide (71.2 mg, 0.40 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (115.2 mg, 1.00 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 26.6 mg (50%) of **2a**. **2a**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.8, 133.9, 119.2, 114.7, 103.9, 55.5 ppm; IR (neat): ν = 2977.6, 2217.6, 1258.5, 1175.8, 829.7 cm^{-1}; MS (70 eV): m/z(%) 133.0 (M$^+$, 100).

13): 
2d

Benzonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), (E)-1,2-diphenylethene **1m** (72.0 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (115.2 mg, 1.00 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction was determined by GC using n-dodecane as internal standard to afford 52% of **2d**. **2d**: colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66-7.59 (m, 3H), 7.49-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.7, 132.0, 129.0, 118.7, 122.2 ppm; MS (70 eV): m/z (%) 103.0 (M$^+$, 100).

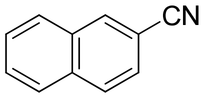
14): 
2a

4-Methoxybenzonitrile.[1] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-ethynyl-4-methoxybenzene **1n** (52.8 mg, 0.40 mmol), N-iodosuccinimide (90 mg, 0.40 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (115.2 mg, 1.00 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 26.6 mg (50%) of **2a**. **2a**: colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.8, 133.9, 119.2, 114.7, 103.9, 55.5 ppm; IR (neat): ν = 2977.6, 2217.6, 1258.5, 1175.8, 829.7 cm^{-1}; MS (70 eV): m/z(%) 133.0 (M$^+$, 100).

15): 
2p

4-(*tert*-Butyl)benzonitrile.[2] Mix Cu(OAc)$_2$ (14.5 mg, 0.08 mmol), 1-(*tert*-butyl)-4-vinylbenzene **1p** (64.0 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), K$_3$PO$_4$ • 7H$_2$O (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 50% of **2p**. **2p**: ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 156.6, 131.9, 126.1, 119.0, 109.3, 35.2, 30.9 ppm; HRMS m/z (ESI) calcd for C$_{11}$H$_{14}$N (M+H)$^+$ 160.1126, found 160.1122.

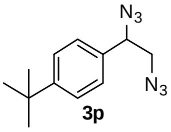
16):



2s

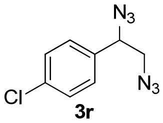
2-Naphthonitrile.[2] Mix Cu(OAc)$_2$ (14.5 mg, 0.08 mmol), 2-vinylnaphthalene **1t** (61.6 mg, 0.40 mmol), *N*-iodosuccinimide (108 mg, 0.48 mmol), K$_3$PO$_4$ • 7H$_2$O (270 mg, 0.80 mol), azidotrimethylsilane (127.0, 1.10 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 59% of **3s**. **3s**: ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.17 (s, 1H), 7.88(t, *J* = 8.0 Hz, 3H), 7.63-7.56 (m, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 134.5, 134.0, 132.1, 129.0, 128.9, 128.3, 127.9, 127.5, 126.2, 119.1, 109.2 ppm; HRMS m/z (ESI) calcd for C$_{11}$H$_8$N (M+H)$^+$ 154.0651, found 154.0654.

17):

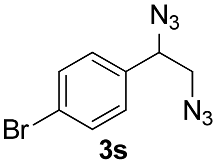


3p

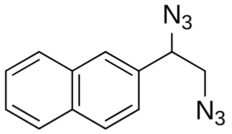
1-(*tert*-Butyl)-4-(1,2-diazidoethyl)benzene. Mix Cu(OAc)$_2$ (14.5 mg, 0.08 mmol), 1-(*tert*-butyl)-4-vinylbenzene **1p** (64.0 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.40 mmol), K$_3$PO$_4$ • 7H$_2$O (270 mg, 0.80 mol), azidotrimethylsilane (124.4 mg, 1.08 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel. The product was mixed with 4-(*tert*-Butyl)benzonitrile, and the proportion was determined by NMR spectrum. This reaction afforded 20% of **3p**. **3p**: yellow liquid; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.66-4.63 (m, 1H), 3.53-3.41(m, 2H). 1.32(s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.0, 133.2, 126.6, 125.9, 65.2, 55.9, 34.6, 31.2, 31.0 ppm; MS (70 eV): m/z(%) 160.2 (100),145.2 (40), 188.2 ($[M-N_4]^+$, 10)); HRMS m/z (ESI) calcd for $C_{12}H_{16}N_3$ $(M-N_3)^+$ 202.1339, found 202.1335.

18): 
3r

1-Chloro-4-(1,2-diazidoethyl)benzene. Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-chloro-4-vinylbenzene **1r** (59.3 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.48 mmol), K_3PO_4 • $7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (140.8 mg, 1.20 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 87% of **3r**. **3r**: pale-yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.66-4.63 (m, 1H), 3.51-3.40(m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.9, 134.8, 129.3, 128.3, 64.7, 55.8 ppm; MS (70 eV): m/z(%) 111.1(100), 138.1 (85), 166.1 ($[M-N_4]^+$, 20)).

19): 
3s

1-Bromo-4-(1,2-diazidoethyl)benzene.[8] Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 1-bromo-4-vinylbenzene **1r** (72.8 mg, 0.40 mmol), N-bromosuccinimide (85.4 mg, 0.40 mmol), K_3PO_4 •$7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (140.8 mg, 1.20 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 81.9 mg(77%) of **3s**. **3s**: pale-yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.65-4.60 (m, 1H), 3.50-3.39(m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.4, 132.2, 128.6, 123.0, 64.8, 55.7 ppm; MS (70 eV): m/z(%) 154.9 (100), 181.9 (80), 211.9 ($[M-N_4]^+$, 10)).



20): **3s**

2-(1,2-Diazidoethyl)naphthalene. Mix $Cu(OAc)_2$ (14.5 mg, 0.08 mmol), 2-vinylnaphthalene **1t** (61.6 mg, 0.40 mmol), *N*-iodosuccinimide (108 mg, 0.48 mmol), $K_3PO_4 \cdot 7H_2O$ (270 mg, 0.80 mol), azidotrimethylsilane (127.0, 1.10 mmol) in MeCN (2.5 mL) under air (1 atm). The reaction mixture was stirred at 80 °C for 25 h. This reaction afforded 59% of **3s**. **3s**: pale-yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.83-4.79 (m, 1H), 3.60-3.46 (m, 2H), 7.41-7.38 (m, 1H), 7.58-7.46 (m, 3H), 7.87-7.82 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 133.6, 133.0, 129.1, 128.0, 127.7, 126.6, 126.5, 123.9, 65.6, 55.7 ppm; MS (70 eV): m/z(%) 153.1 (100), 154.2 (70), 182.1 ($[M-N_4]^+$, 25).

Reference:

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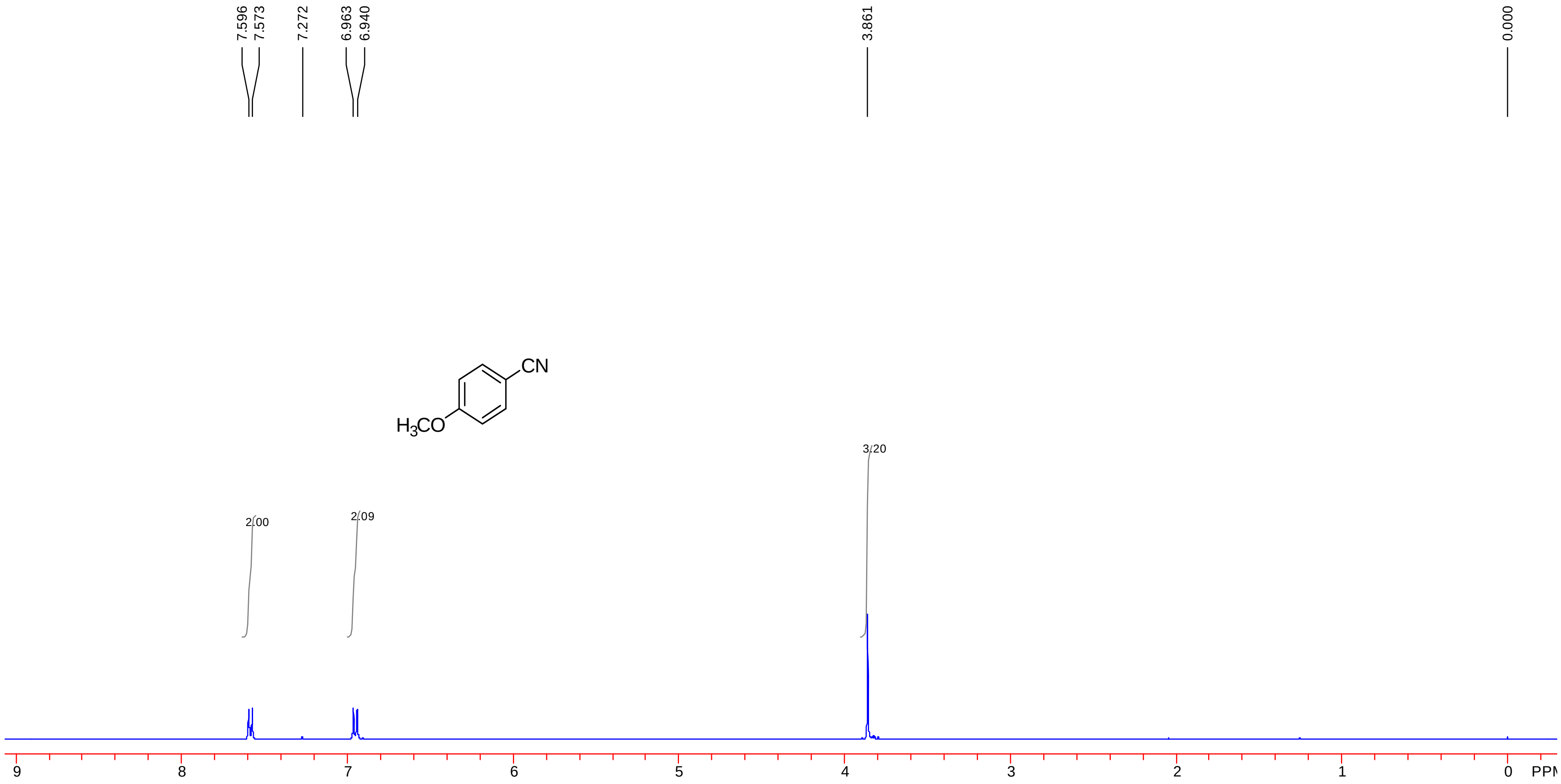
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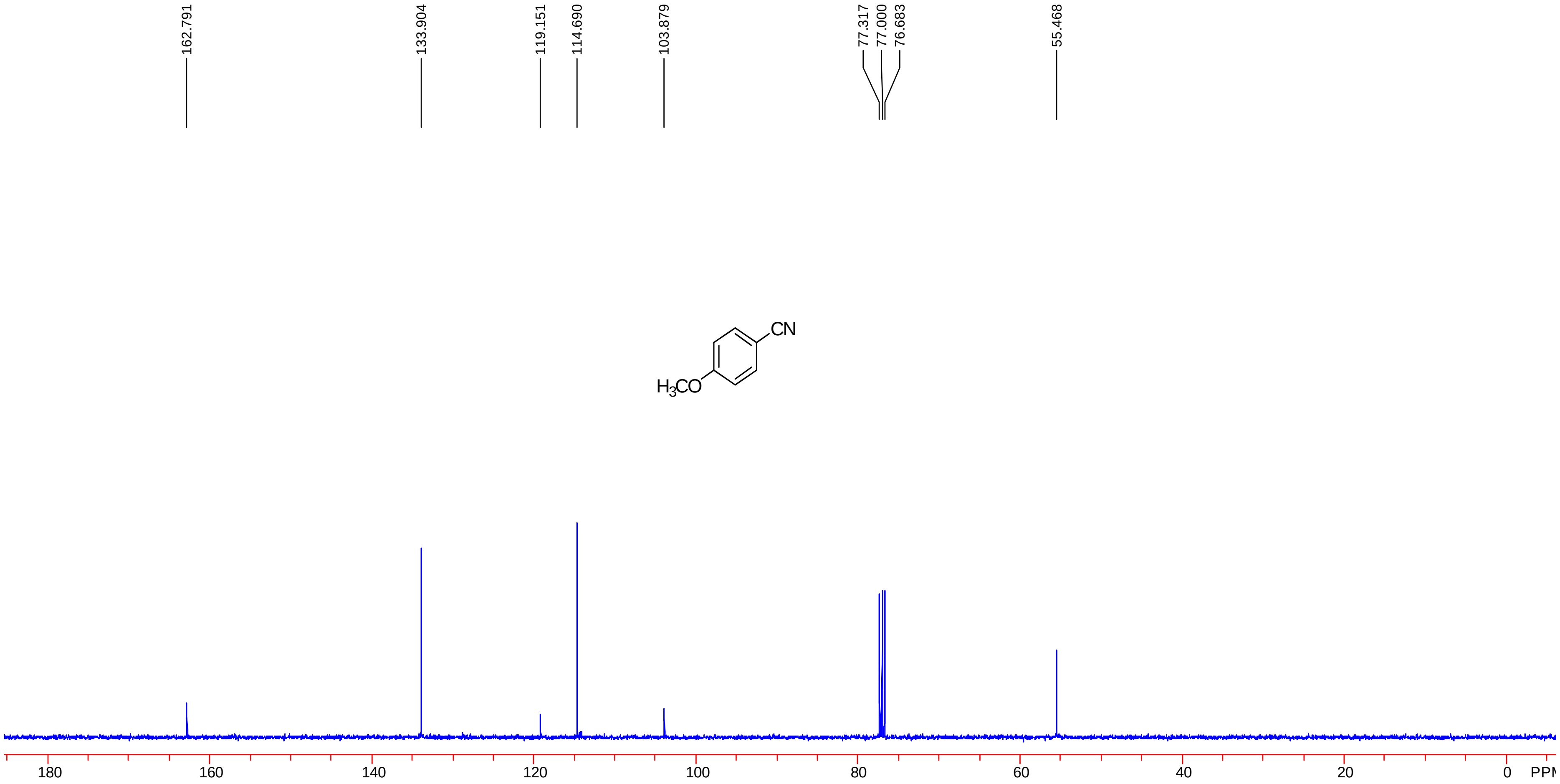
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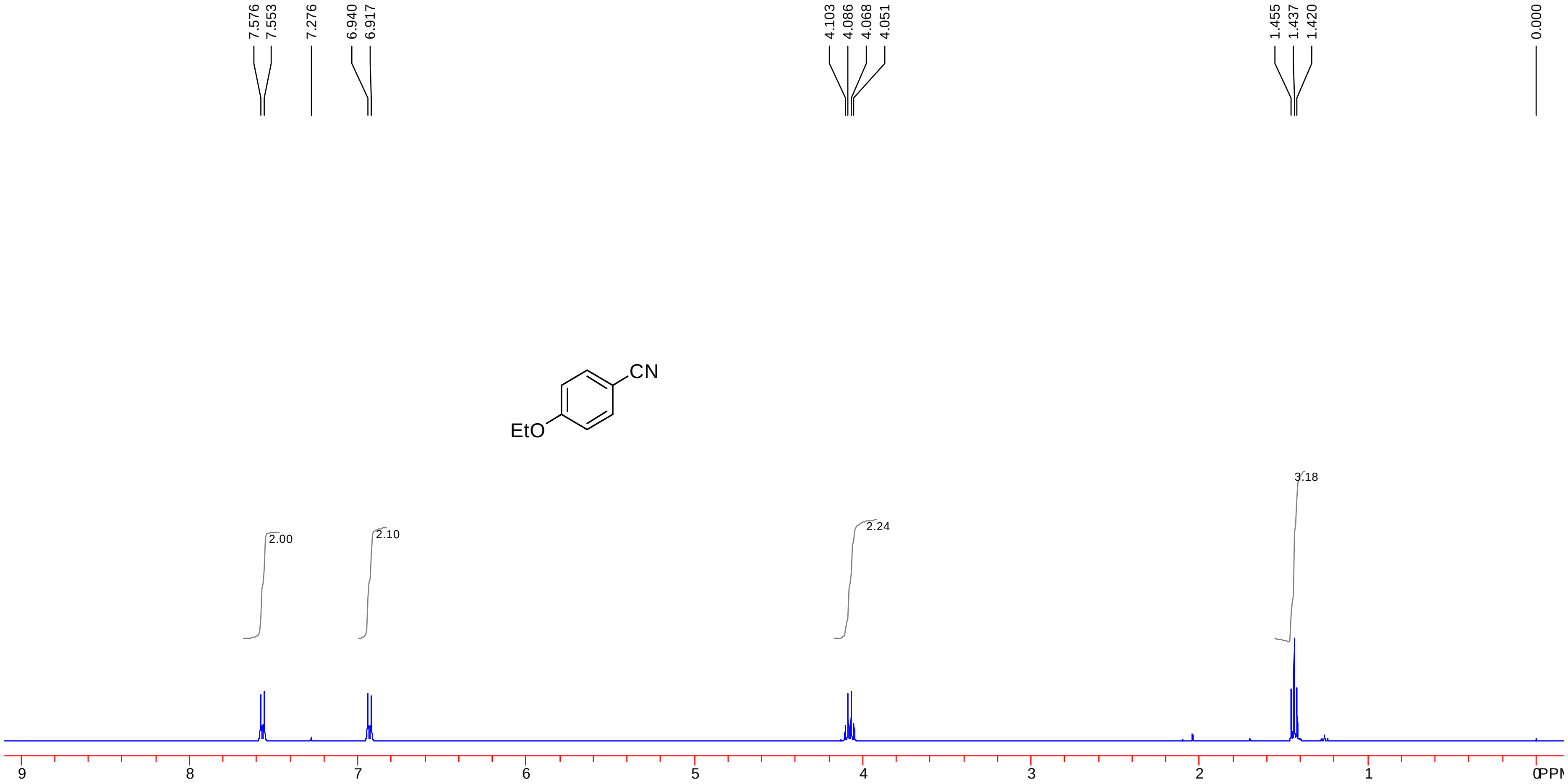
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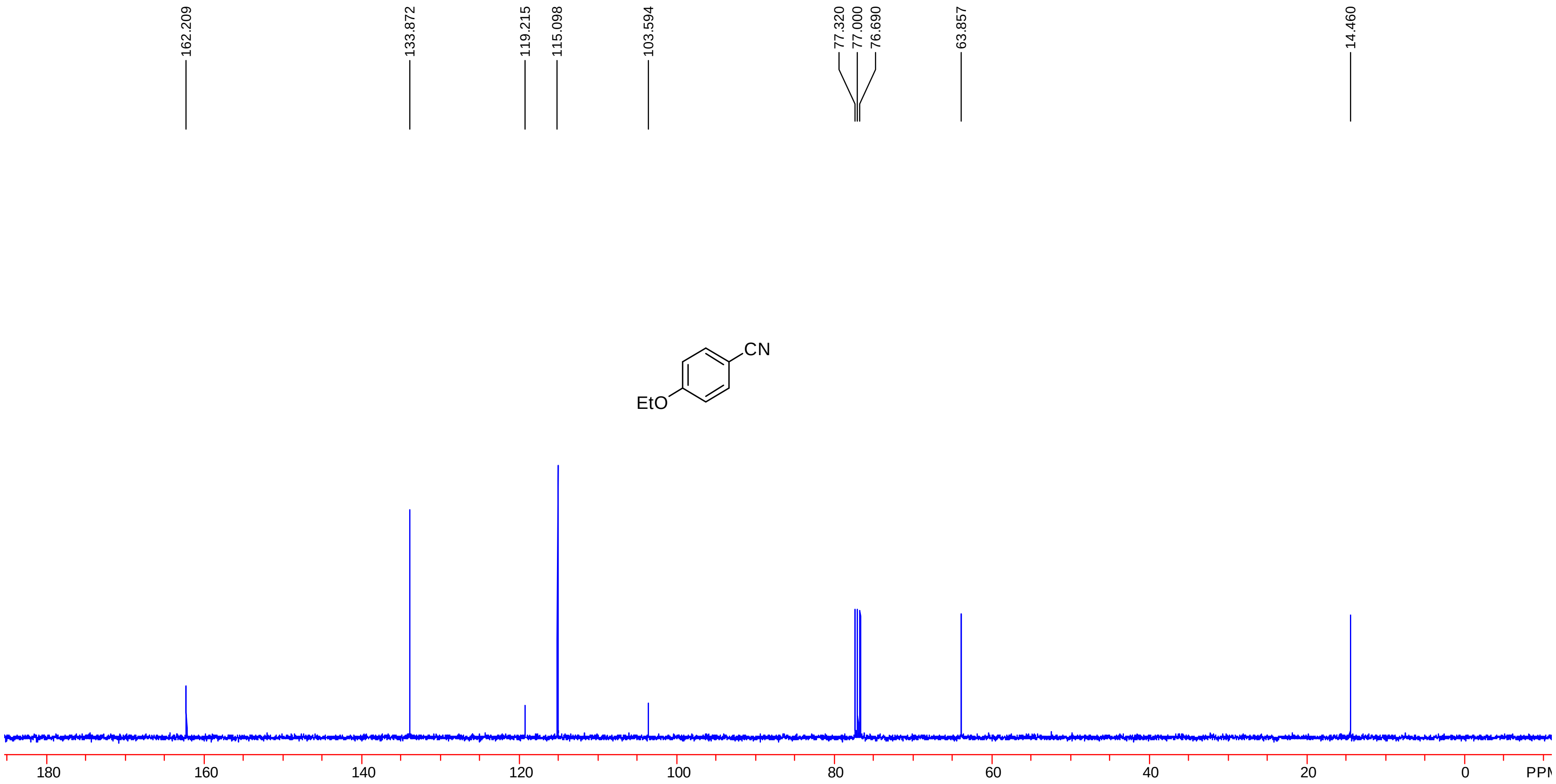
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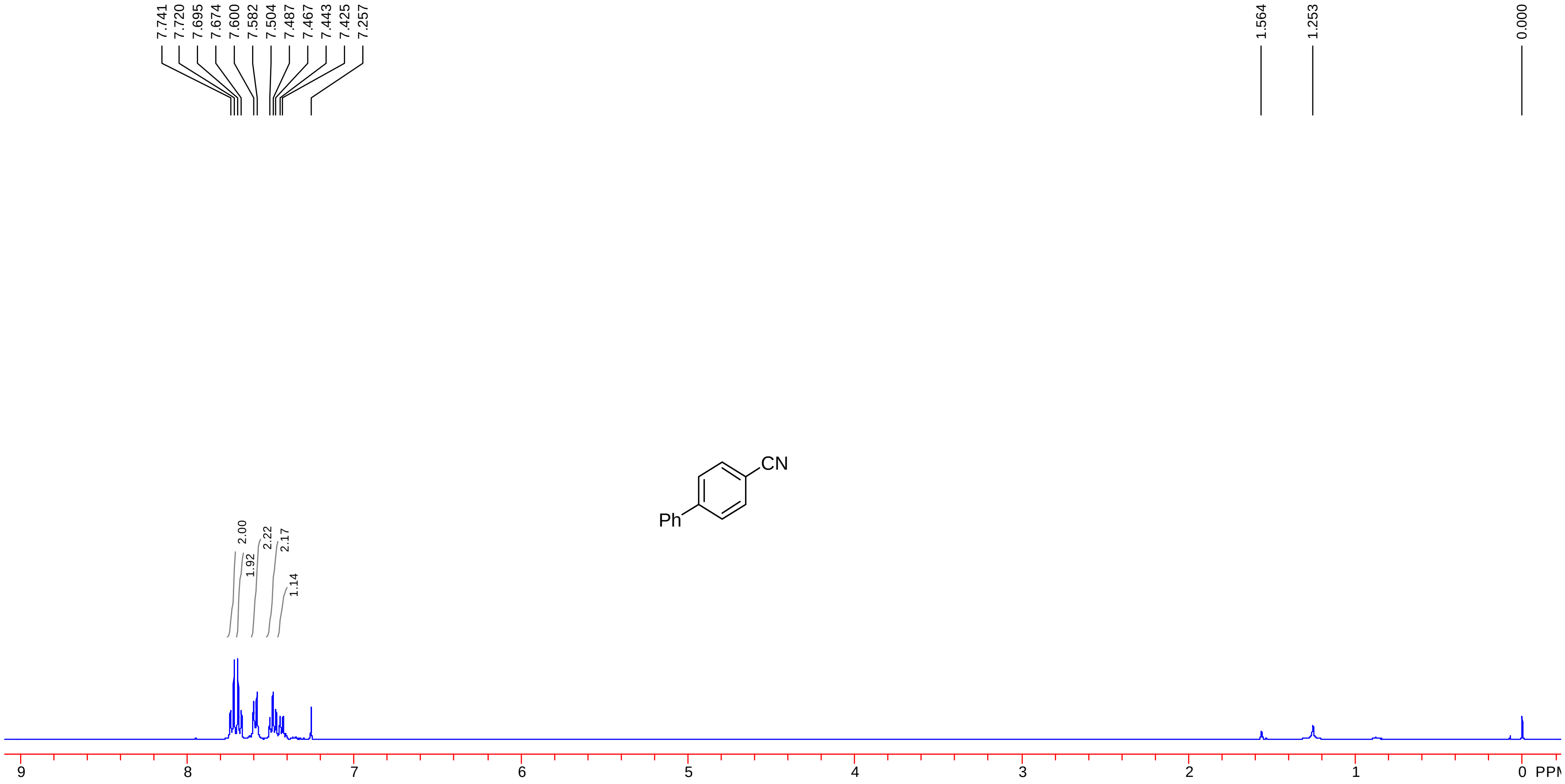
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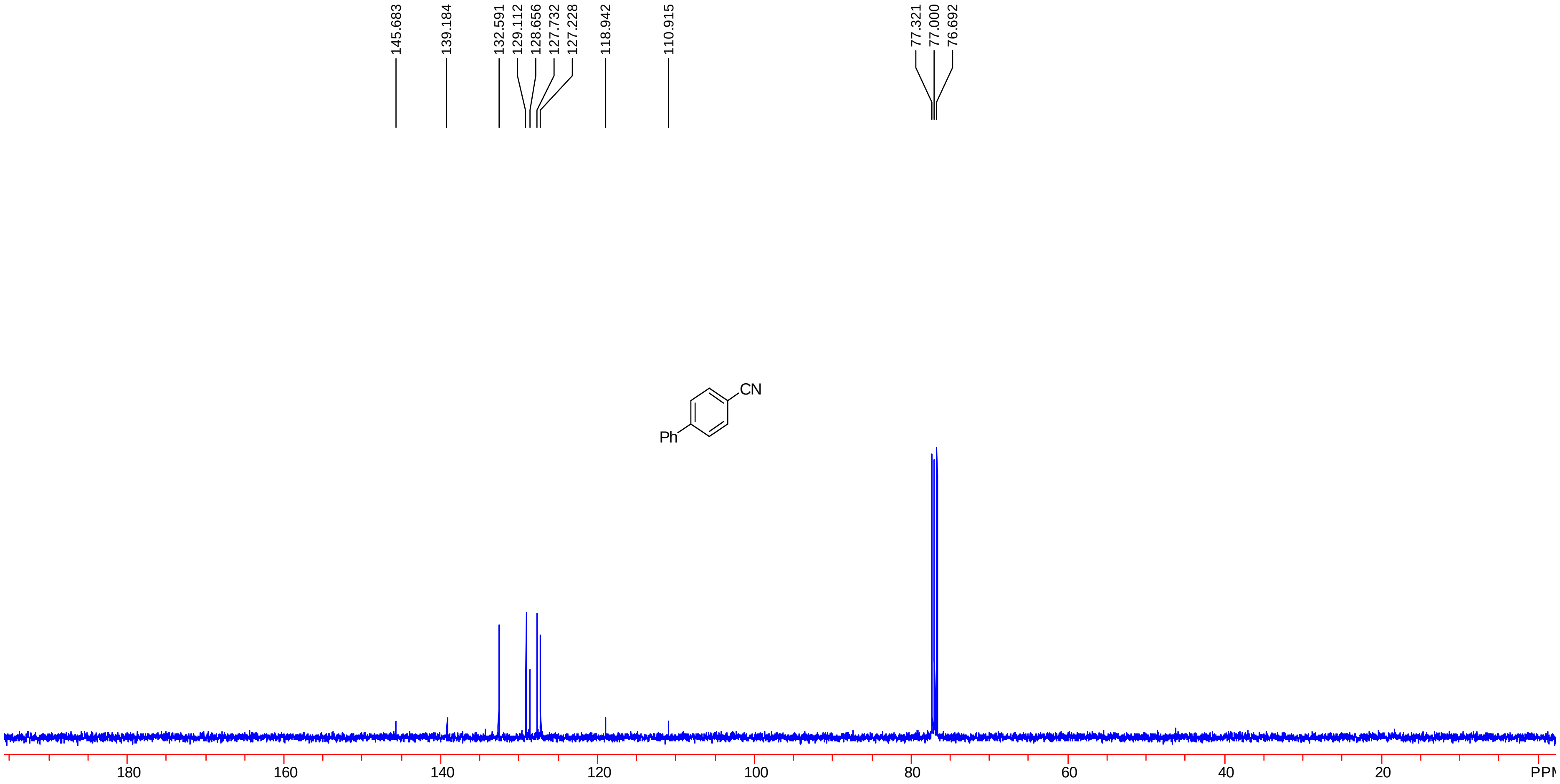
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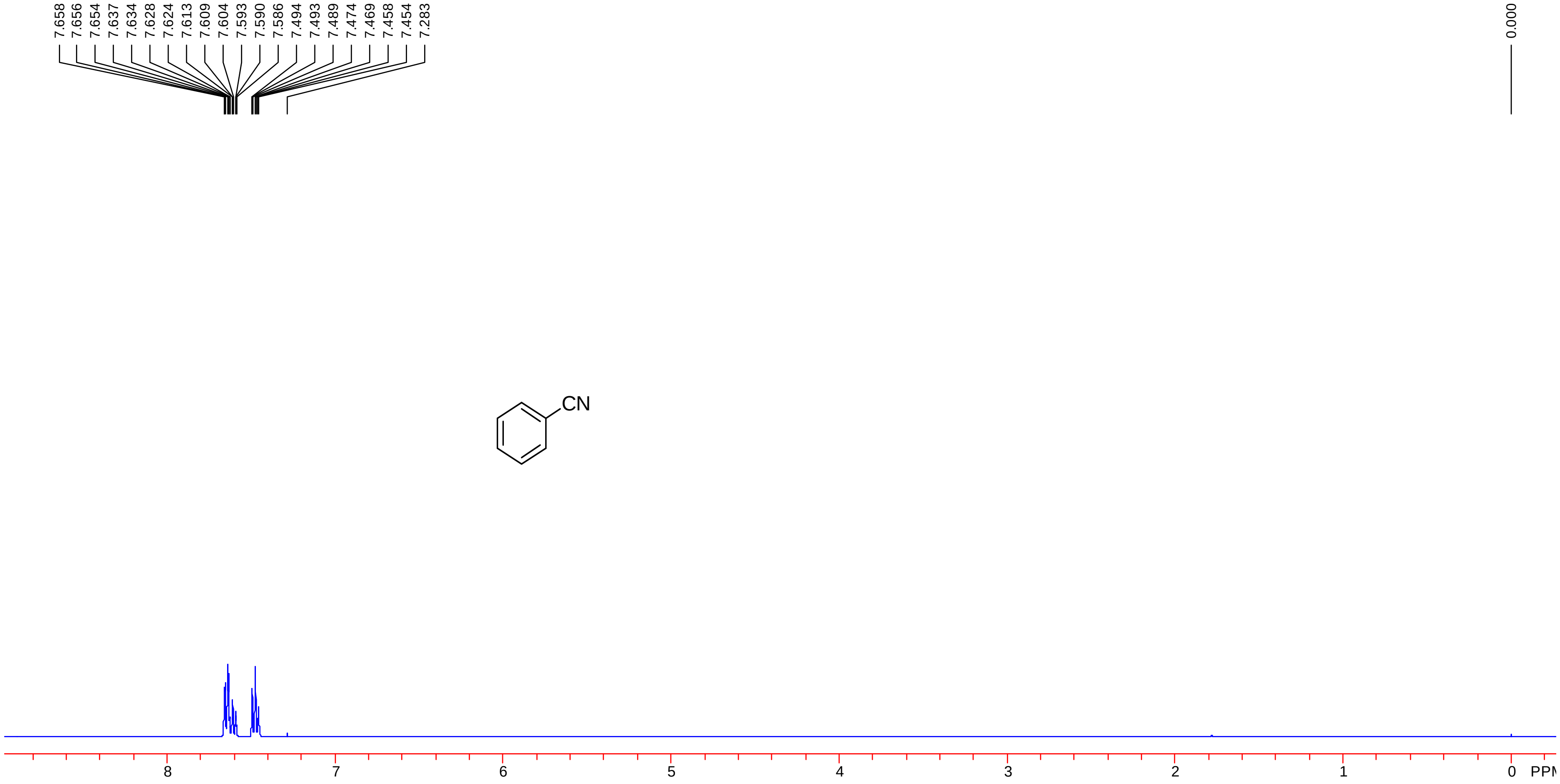
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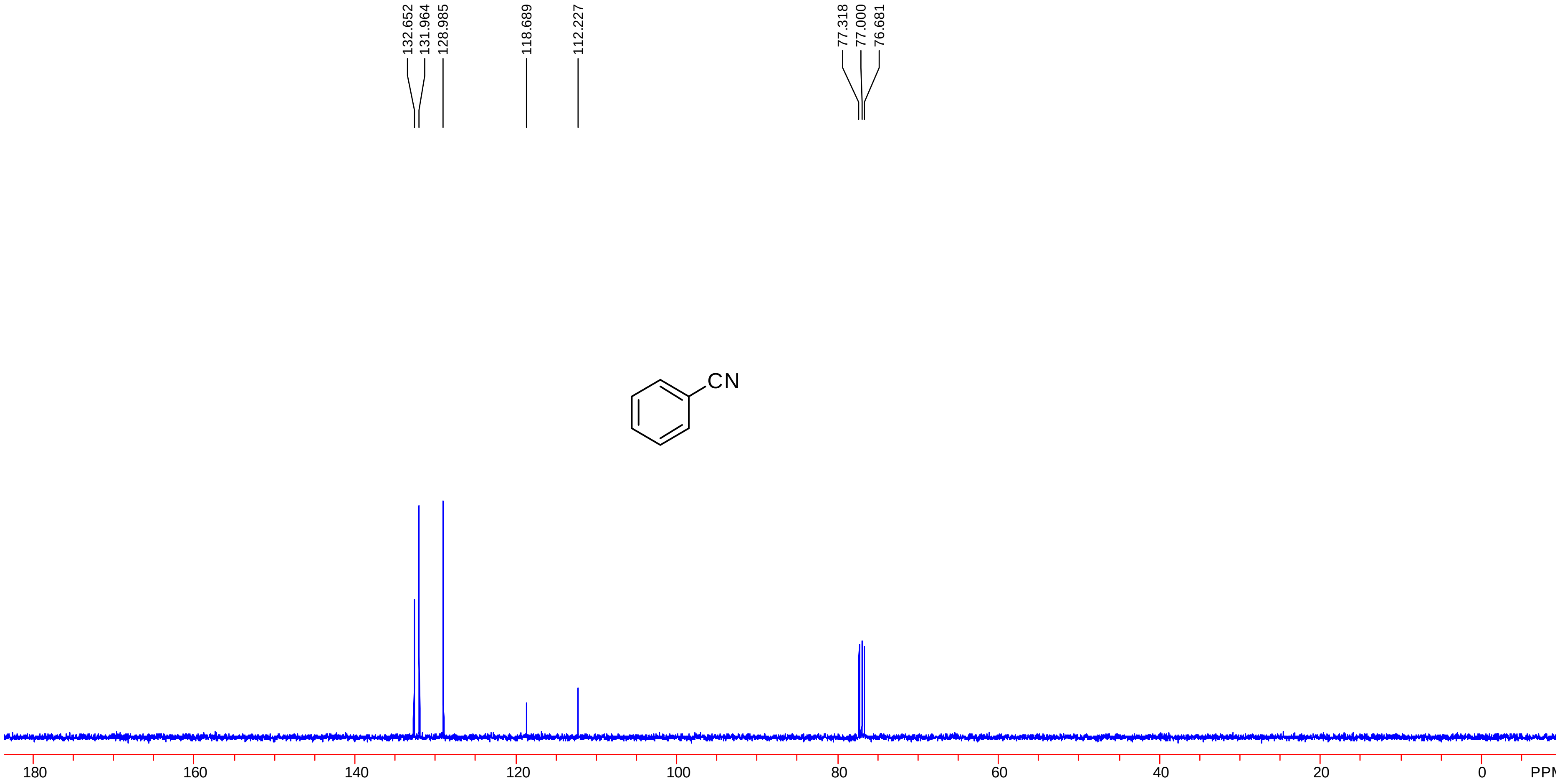
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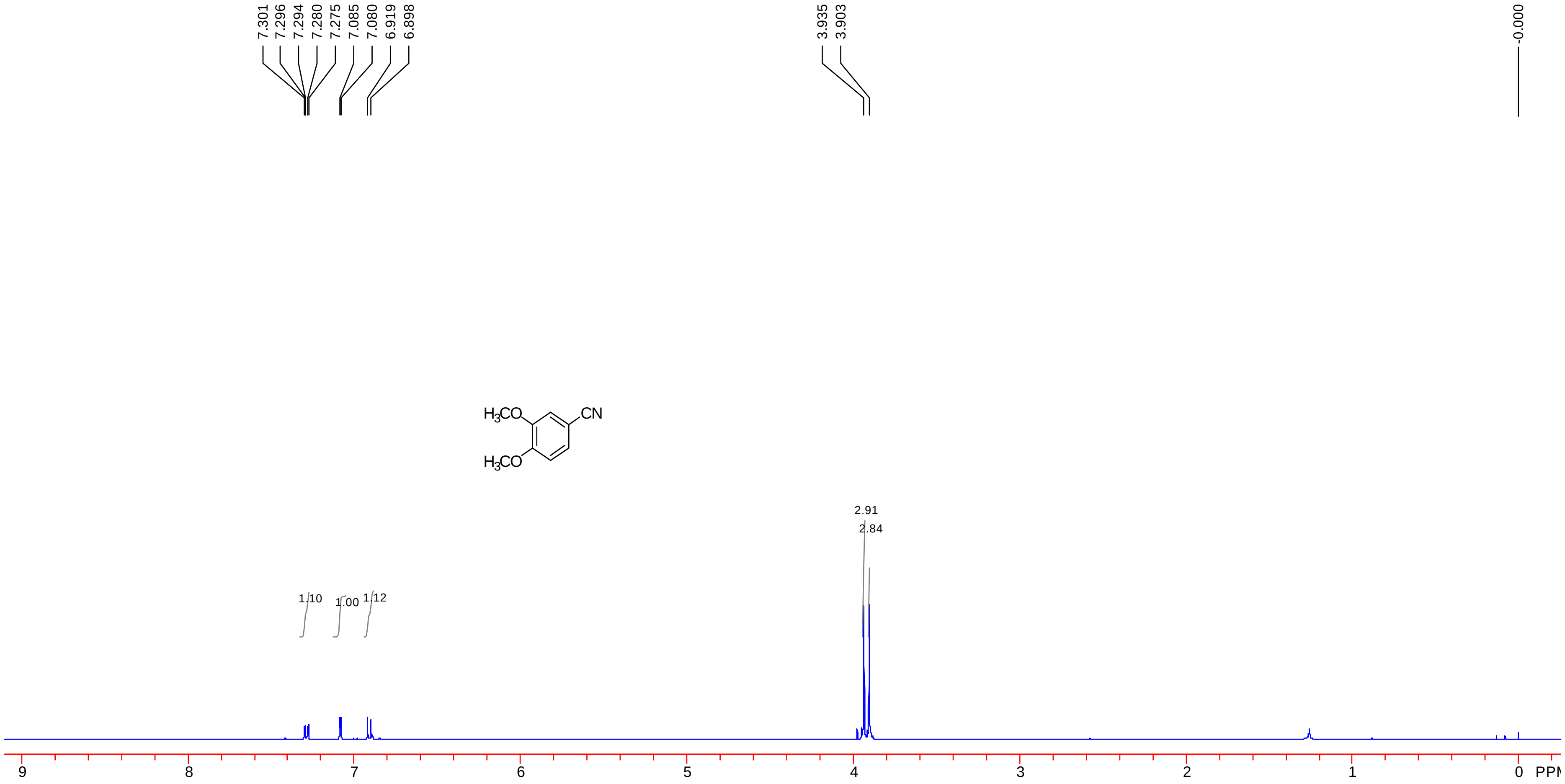
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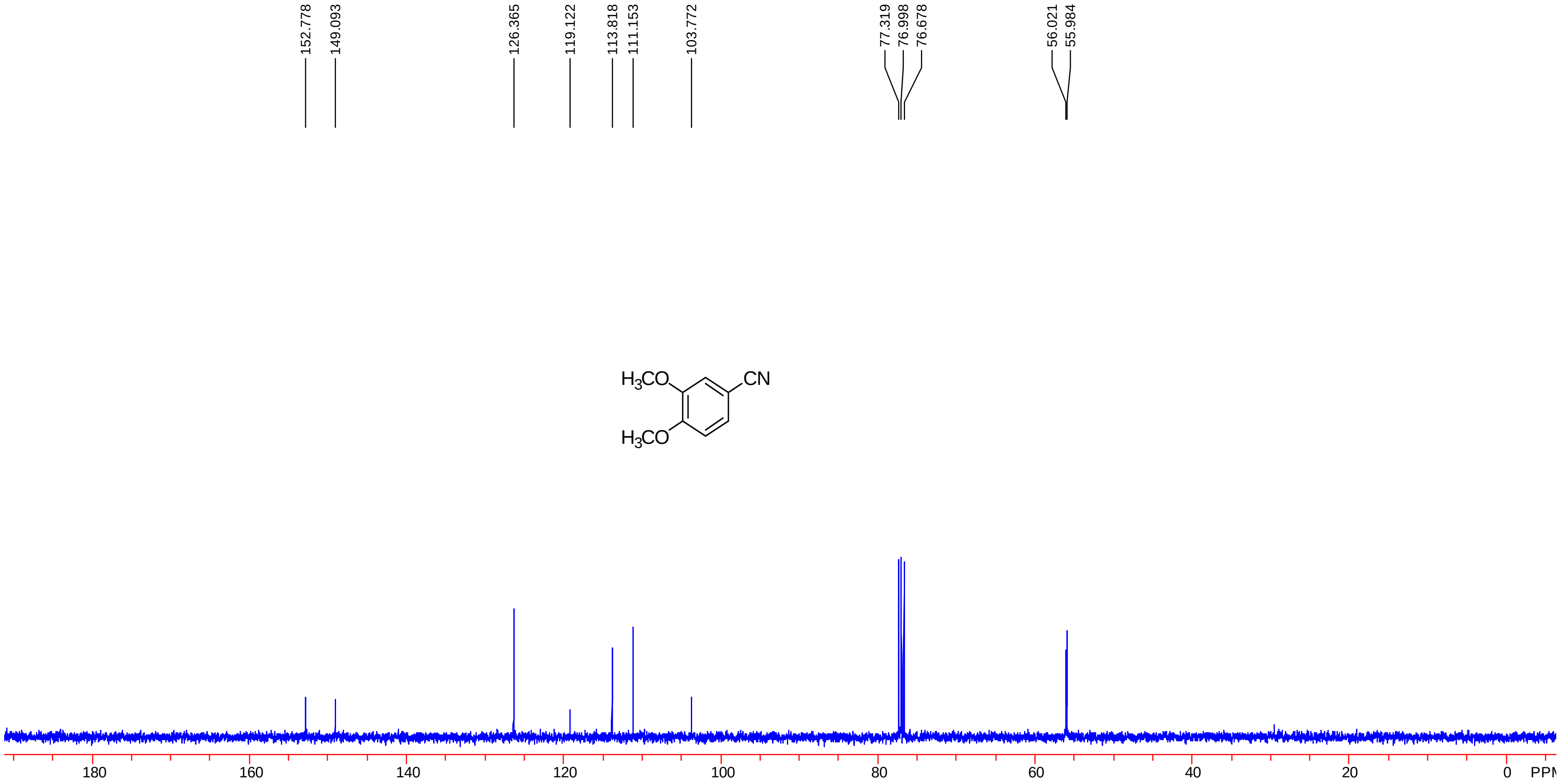
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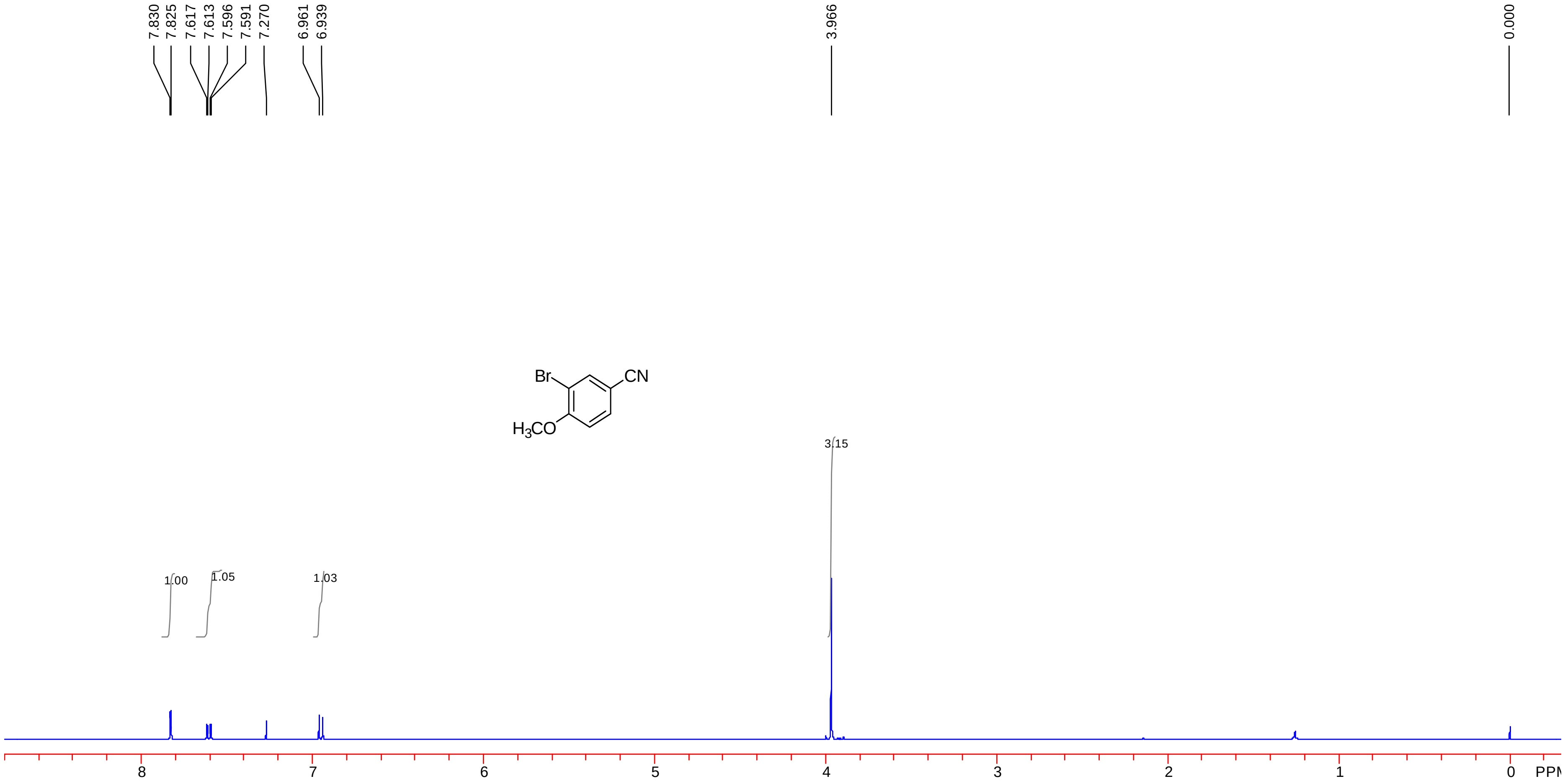
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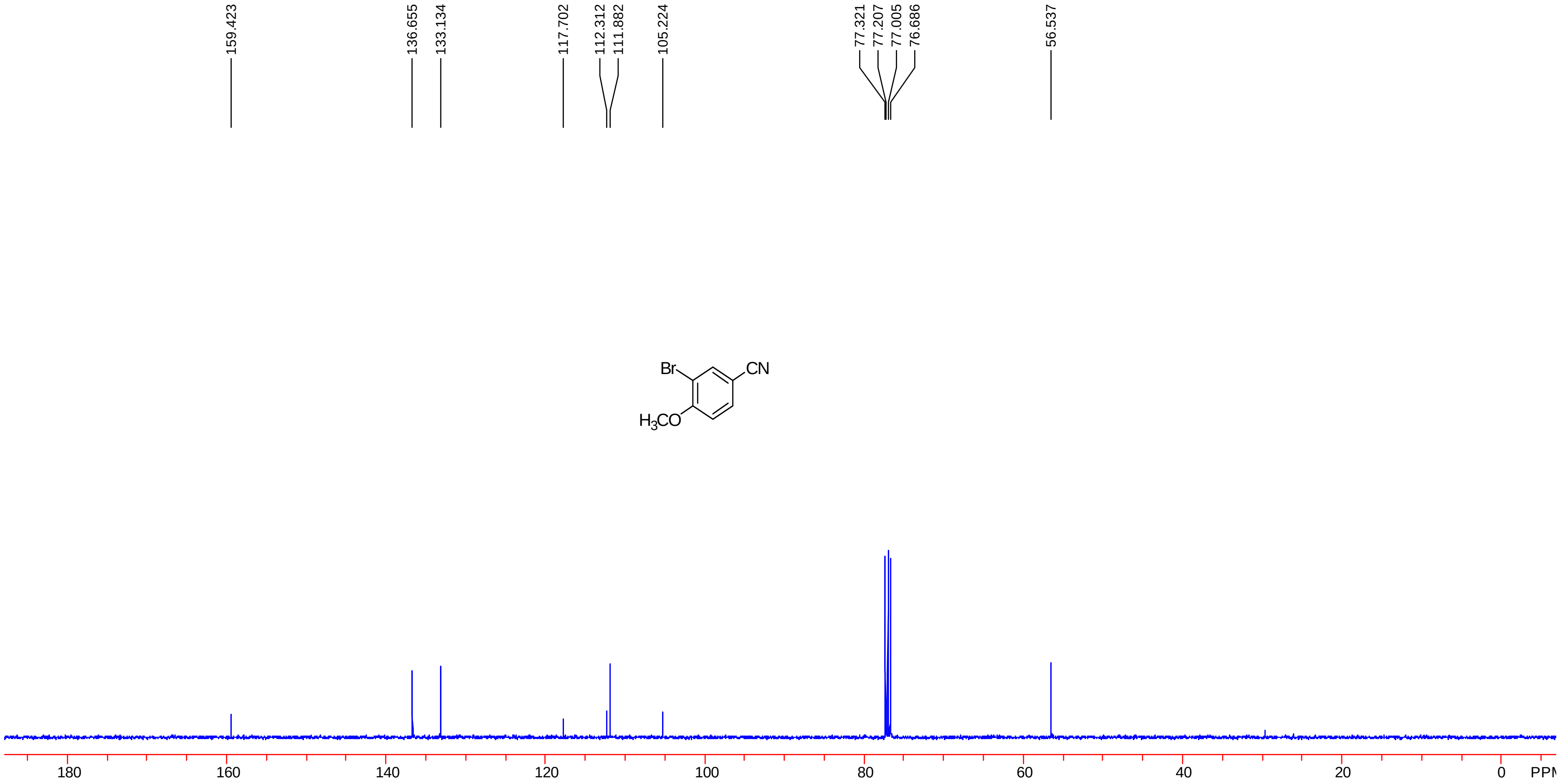
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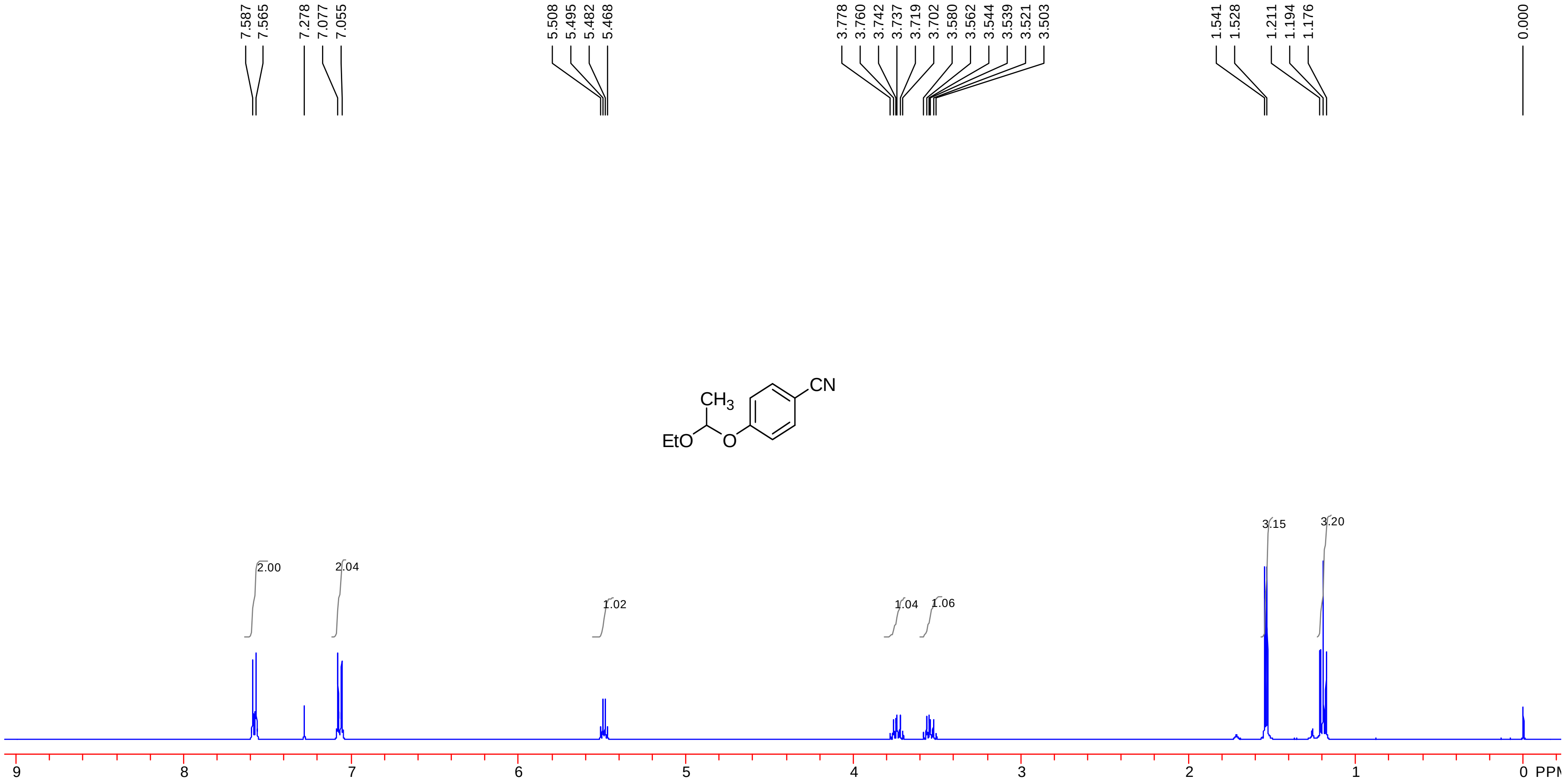
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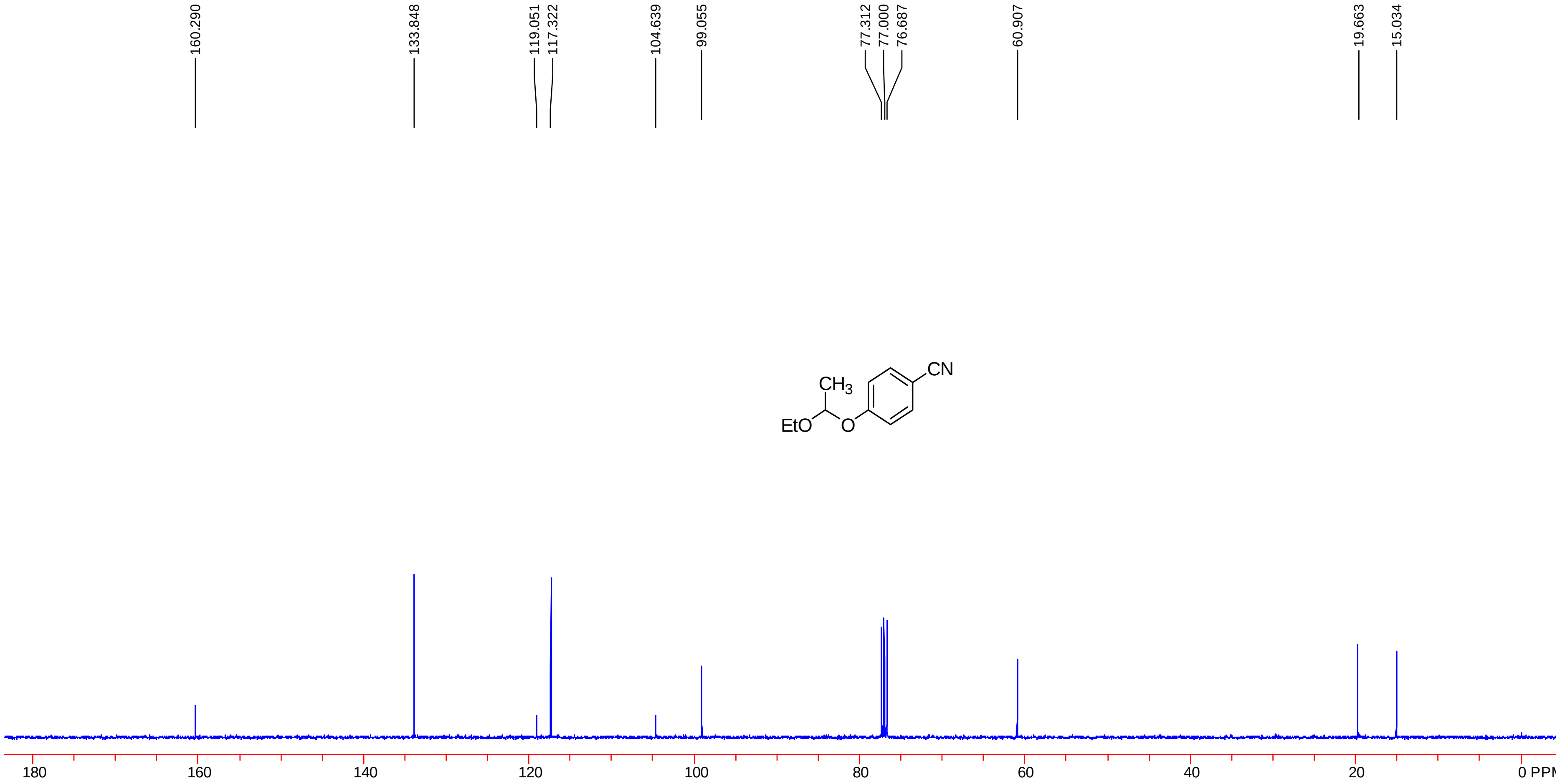
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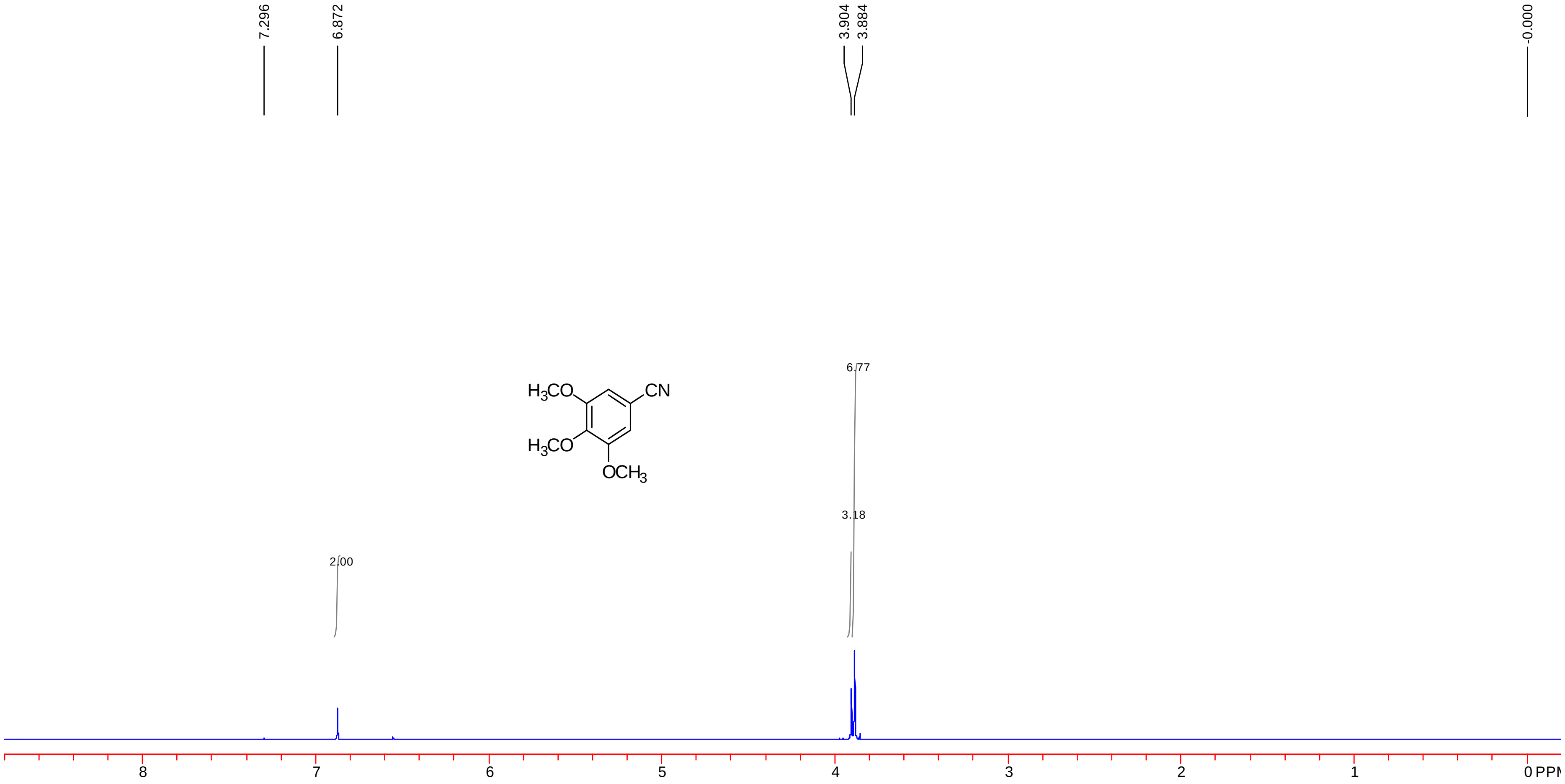
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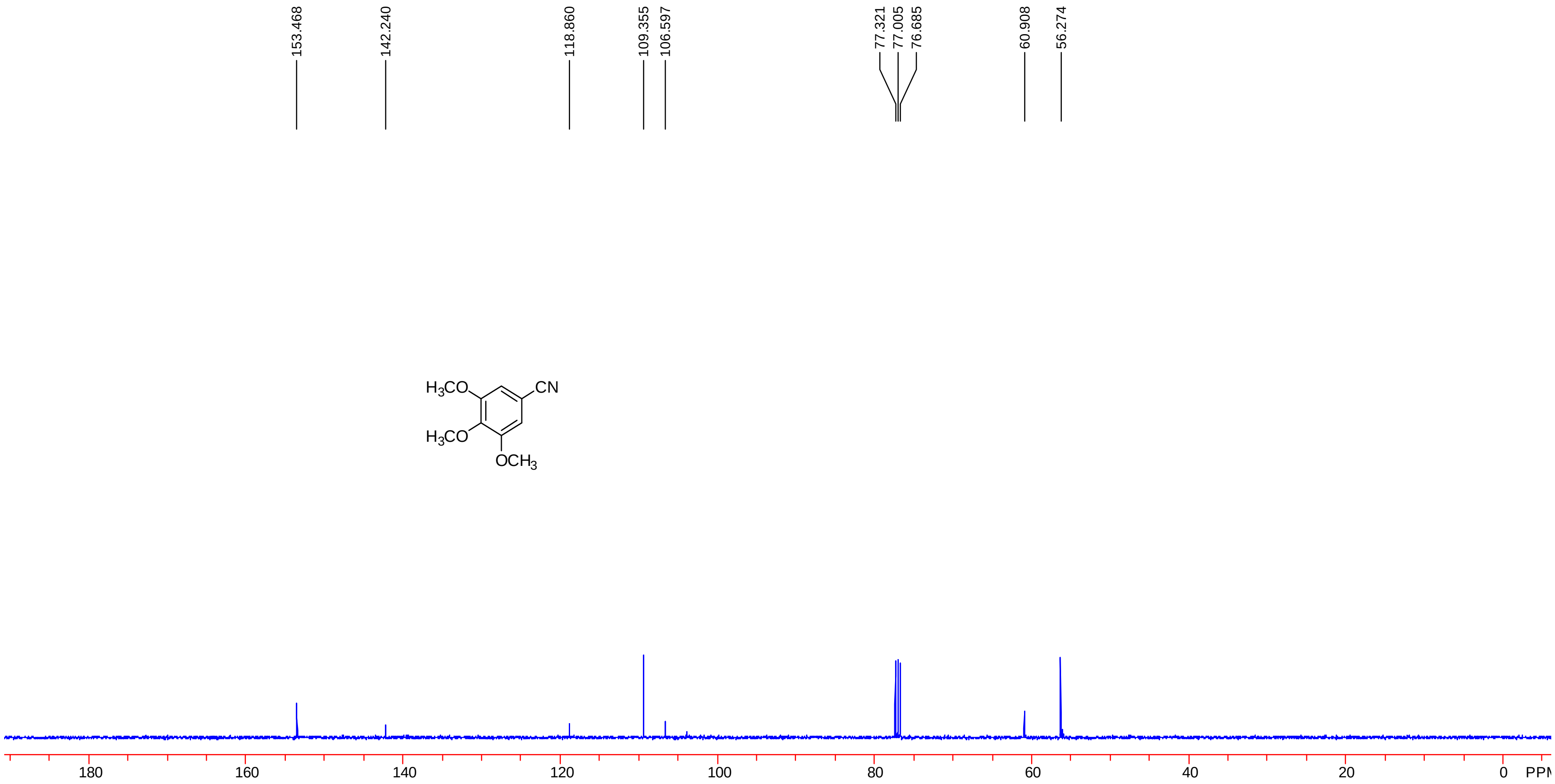
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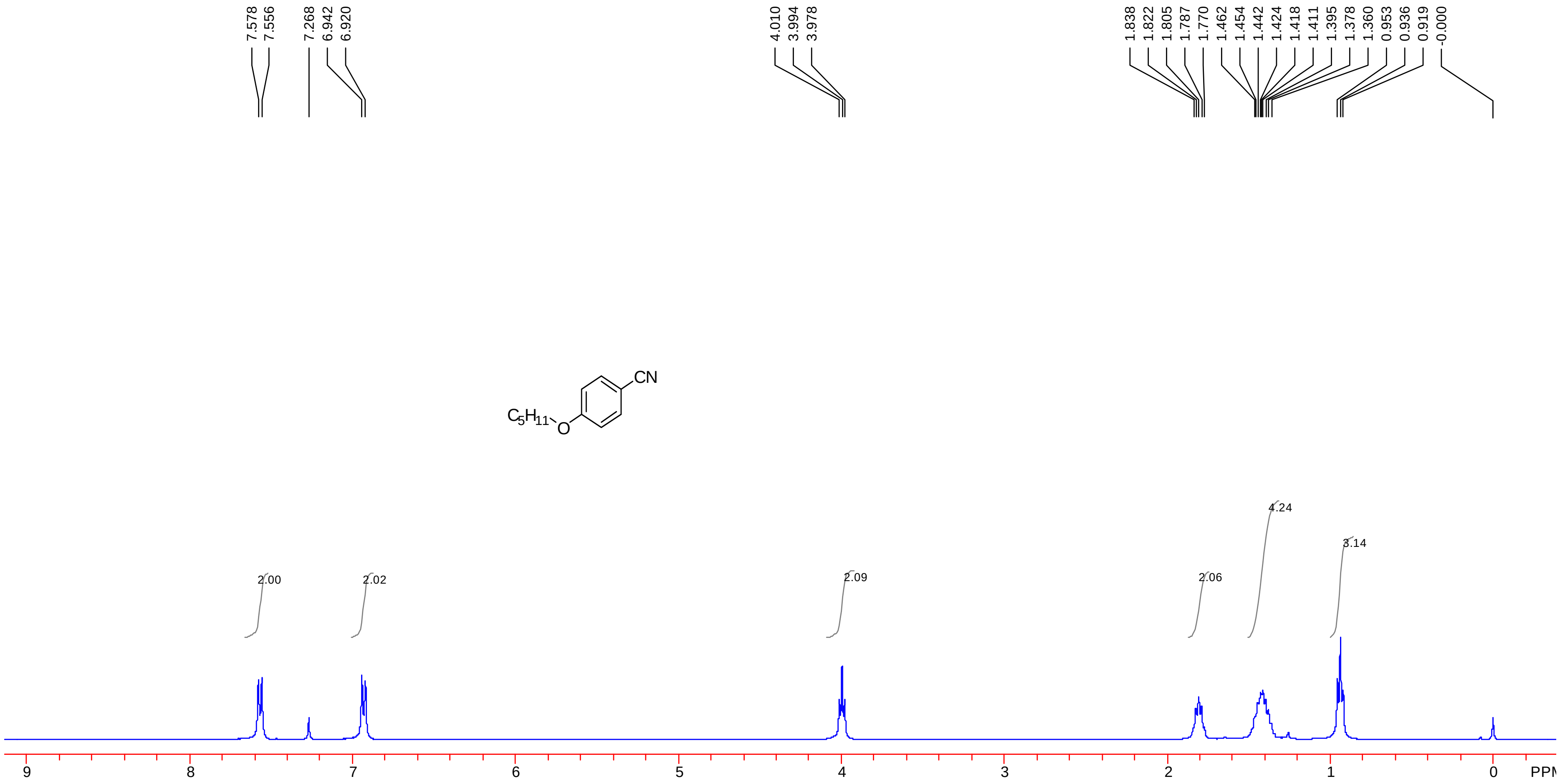
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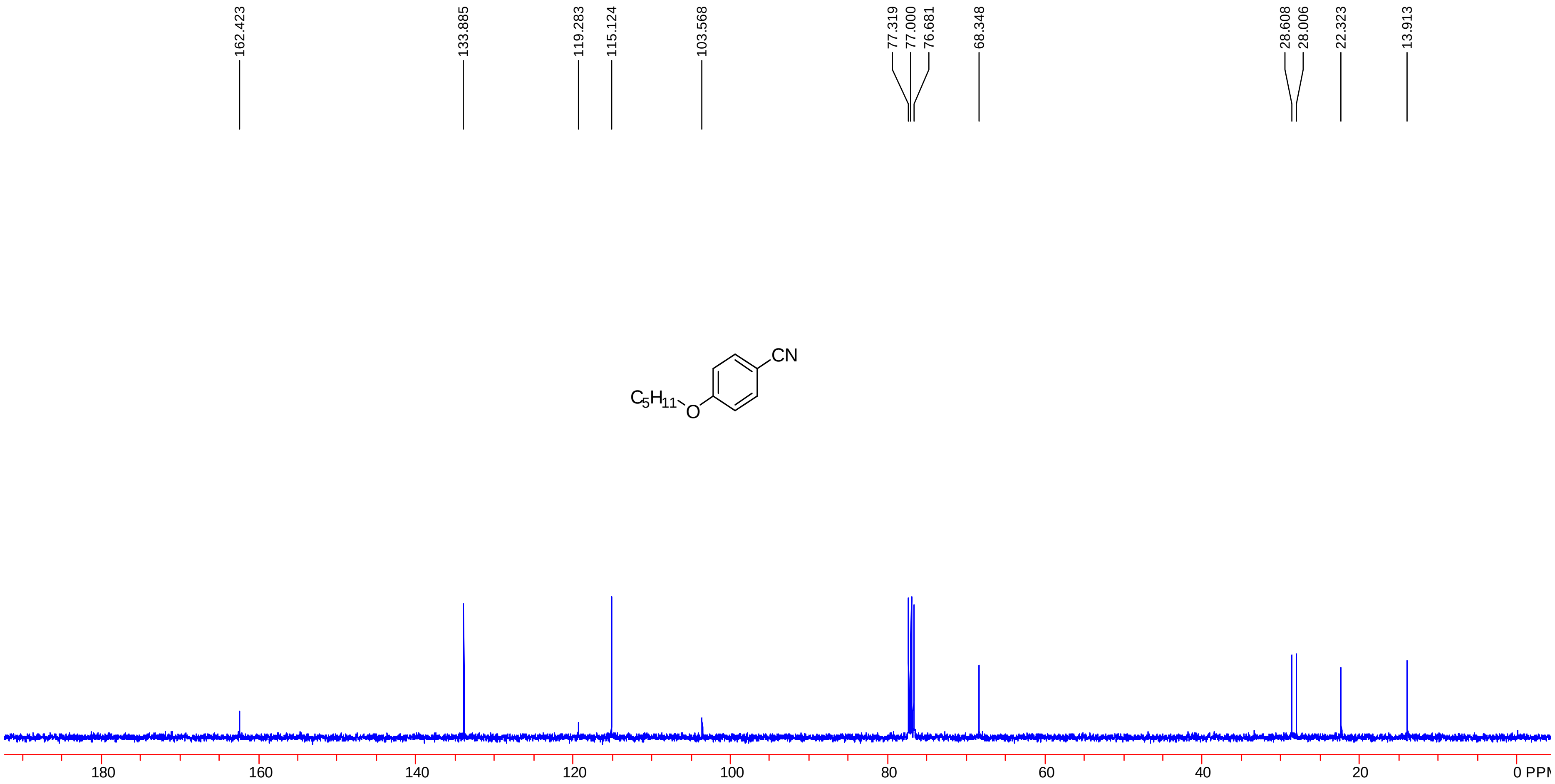
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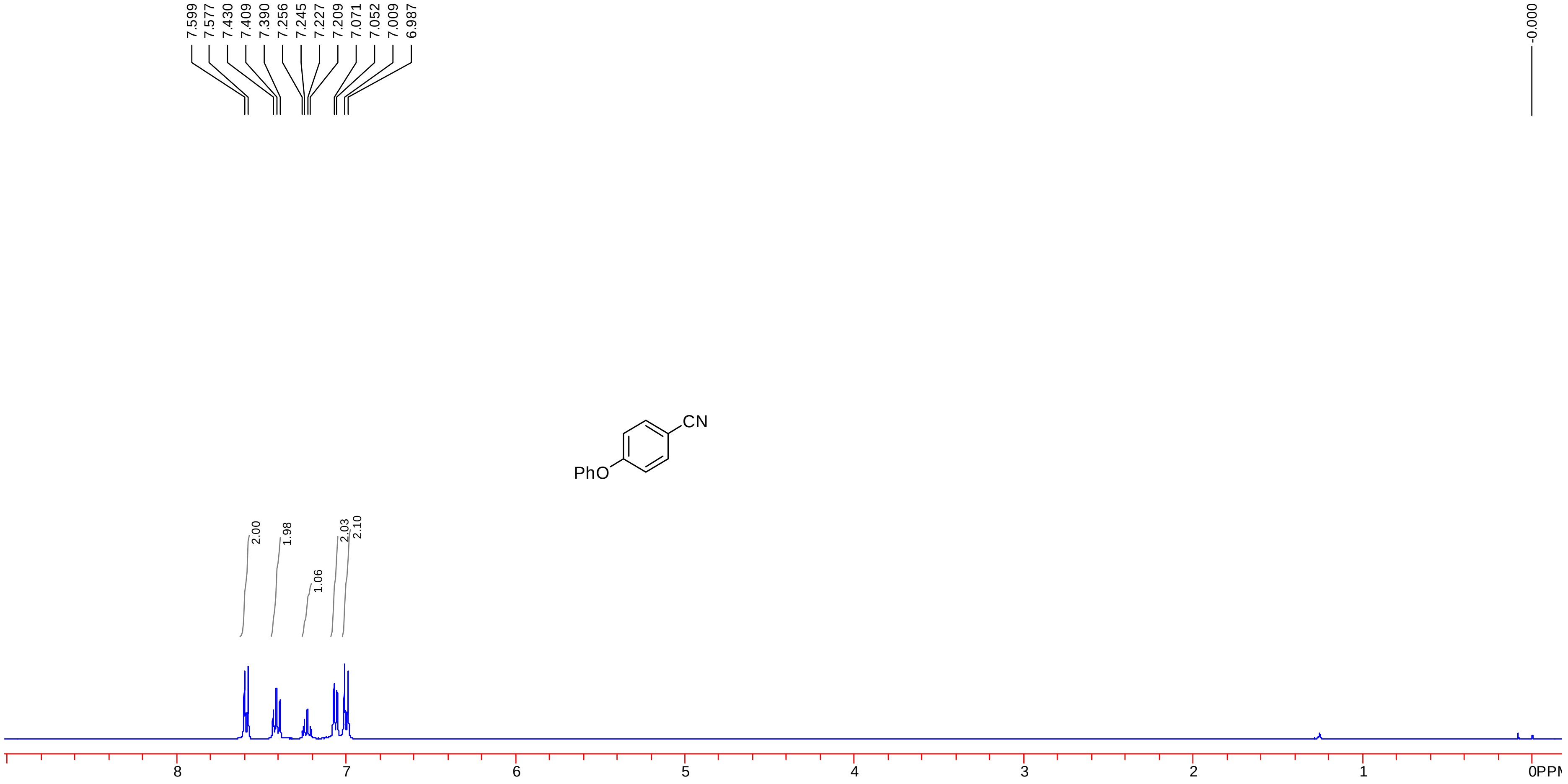
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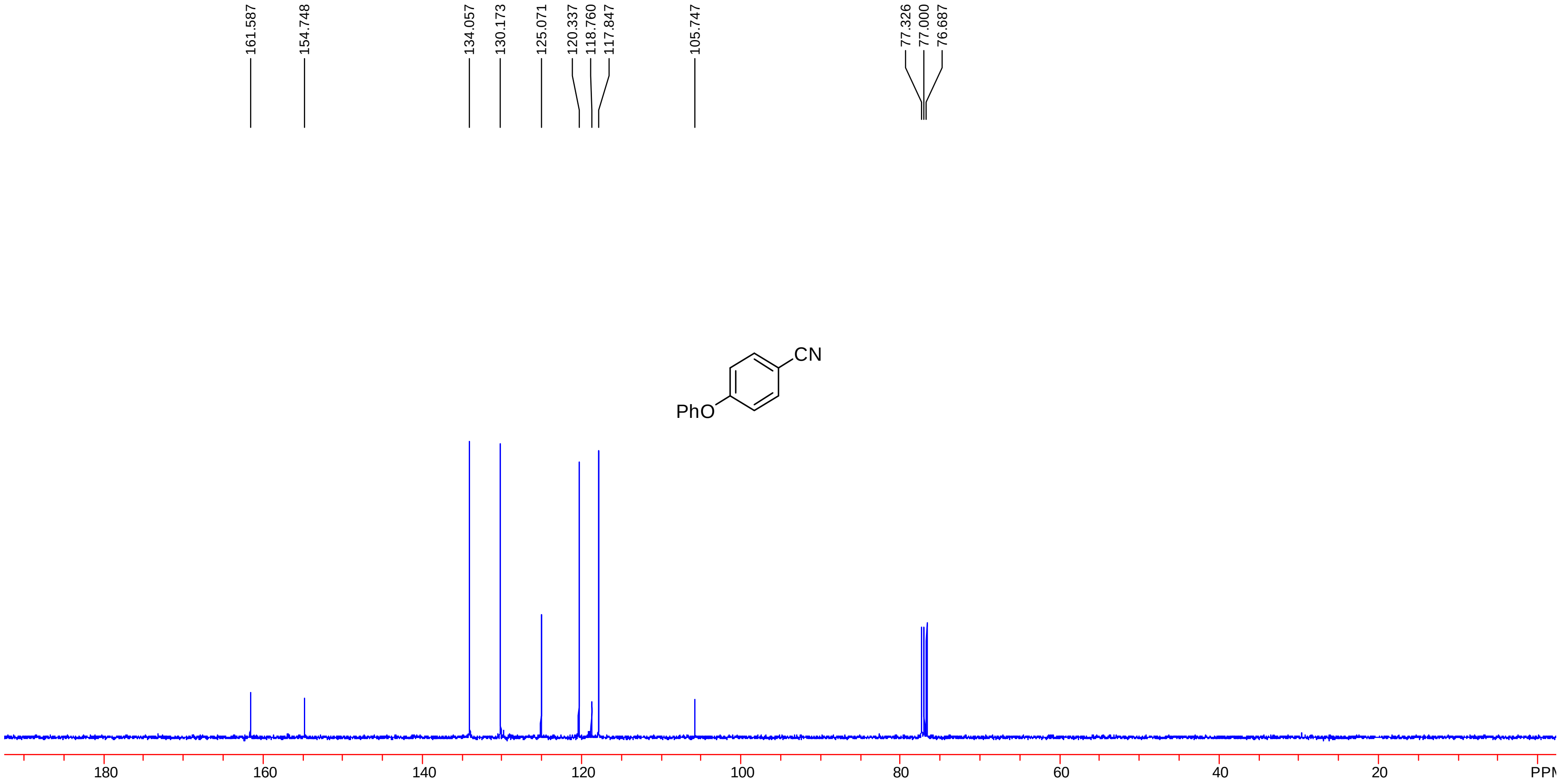
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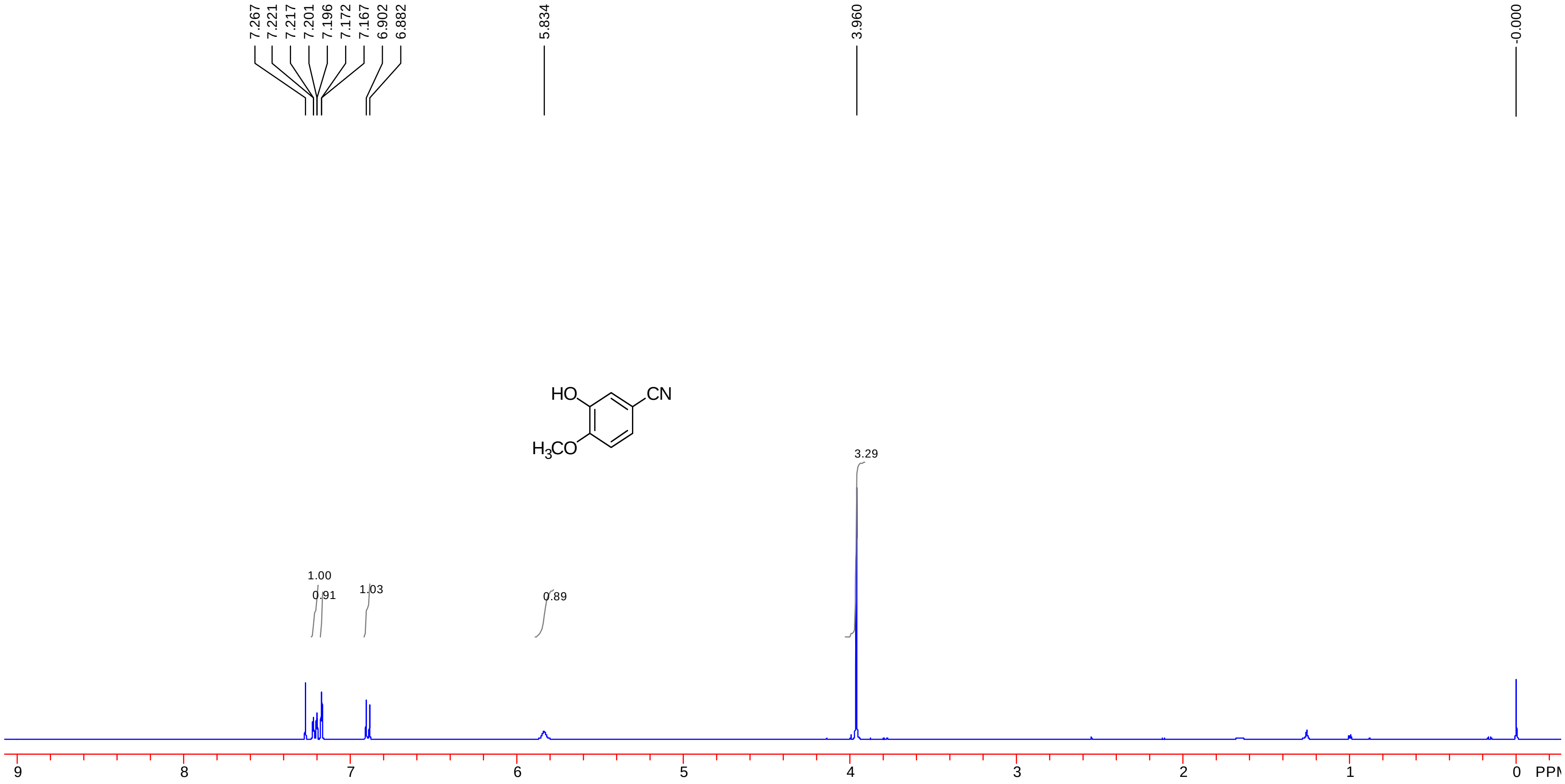
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CN
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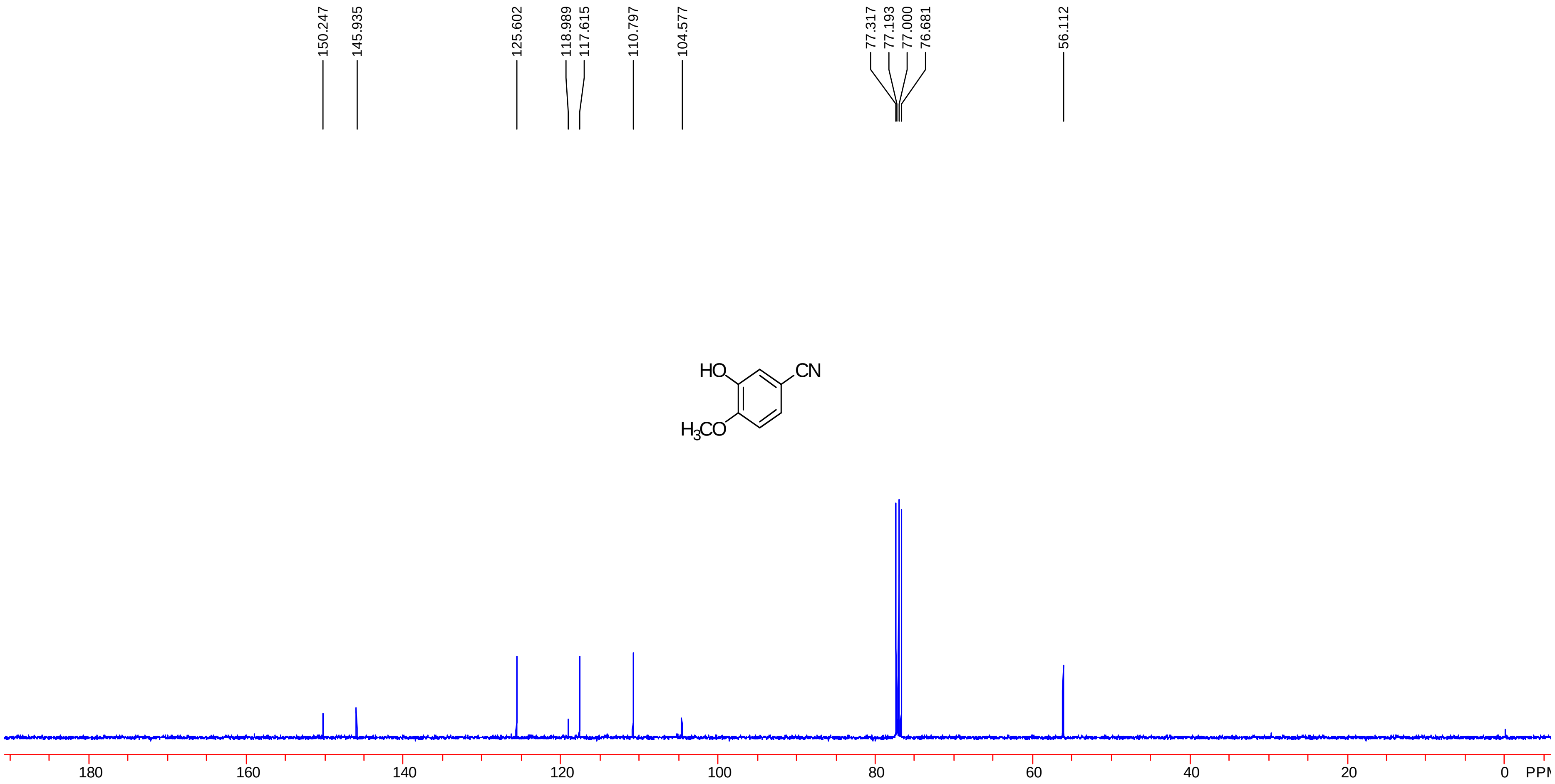
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CN
H3CO
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160
140
120
100
80
60
40
20
0
PP


7.591
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7.490
7.469
7.433
7.413
7.267
7.257
7.247
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4.652
4.643
4.631
3.504
3.493
3.473
3.451
3.439
1.329
1.321
0.000
CN
+
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N_3
2.00
2.01
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0.95
0.45
0.98
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4.11
9
8
7
6
5
4
3
2
1
0 PPM


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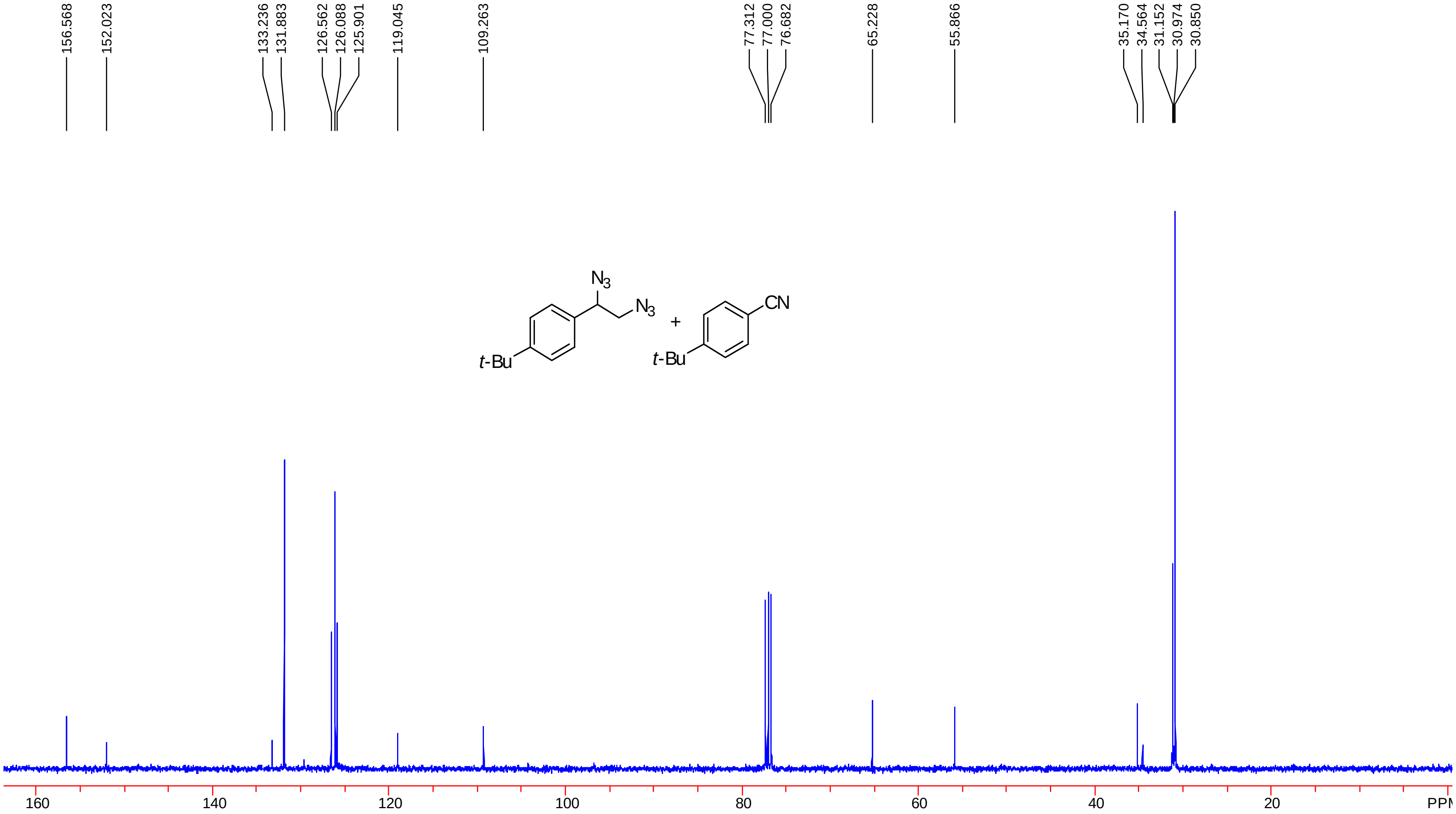
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20
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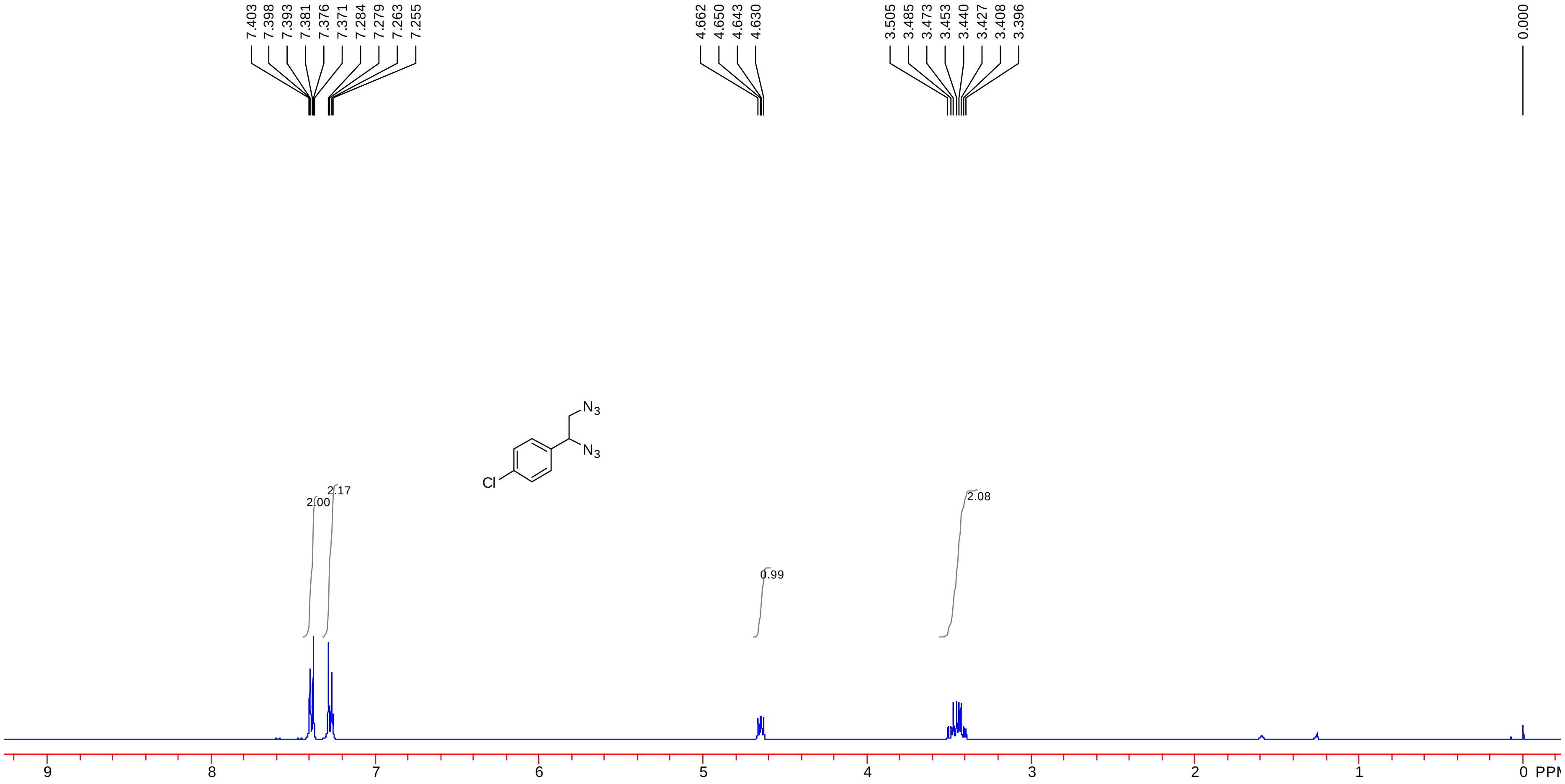
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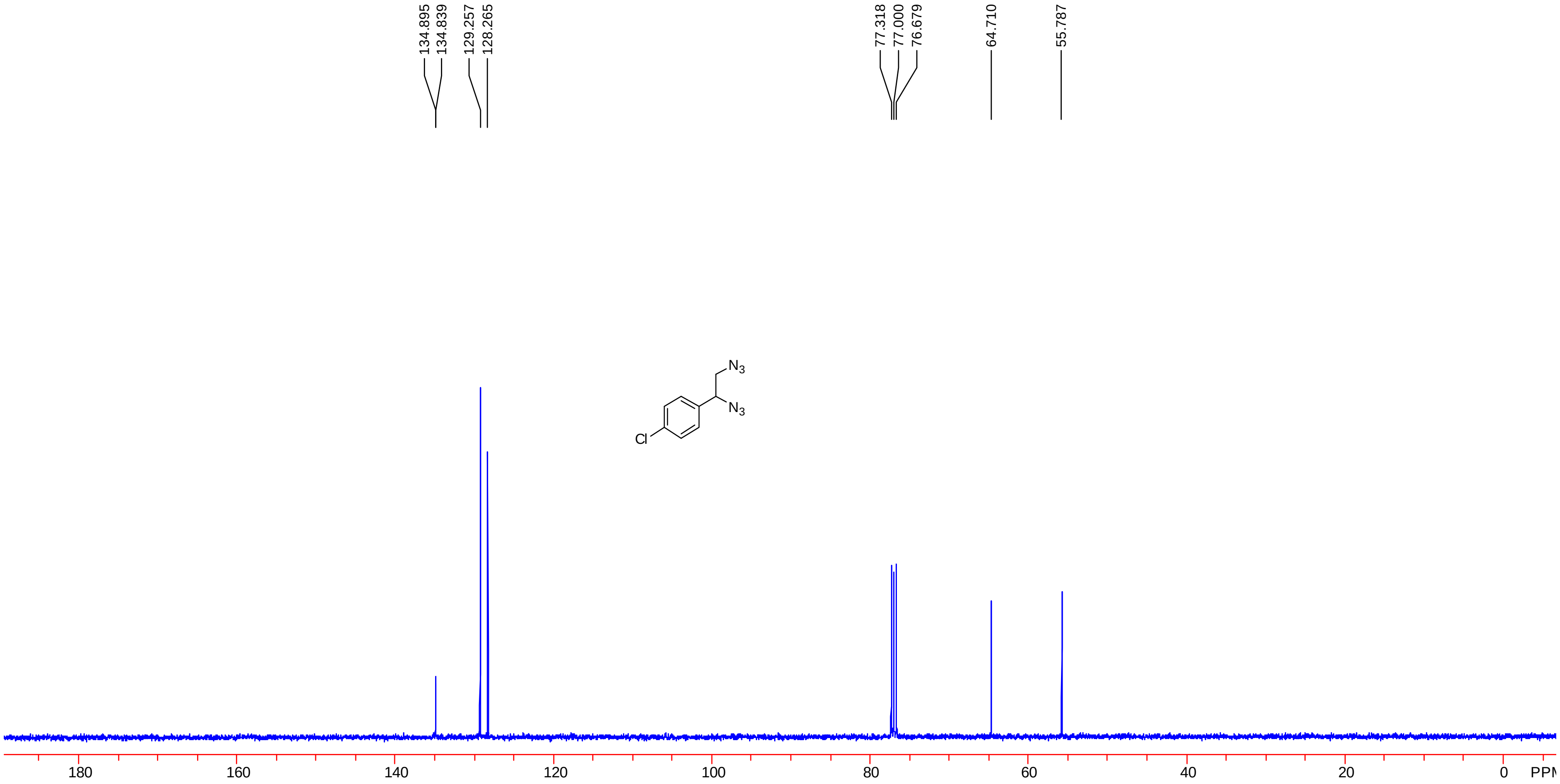
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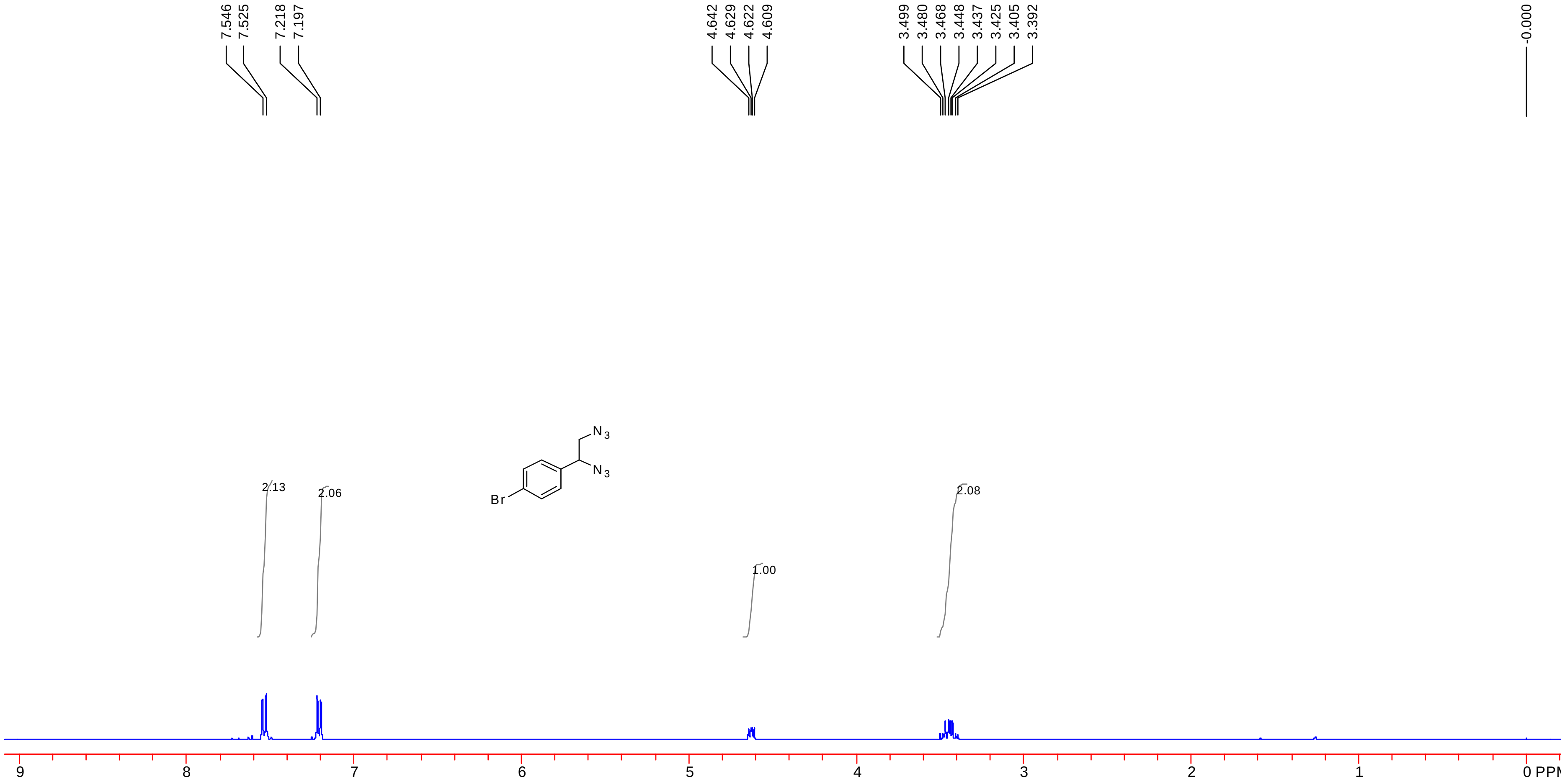
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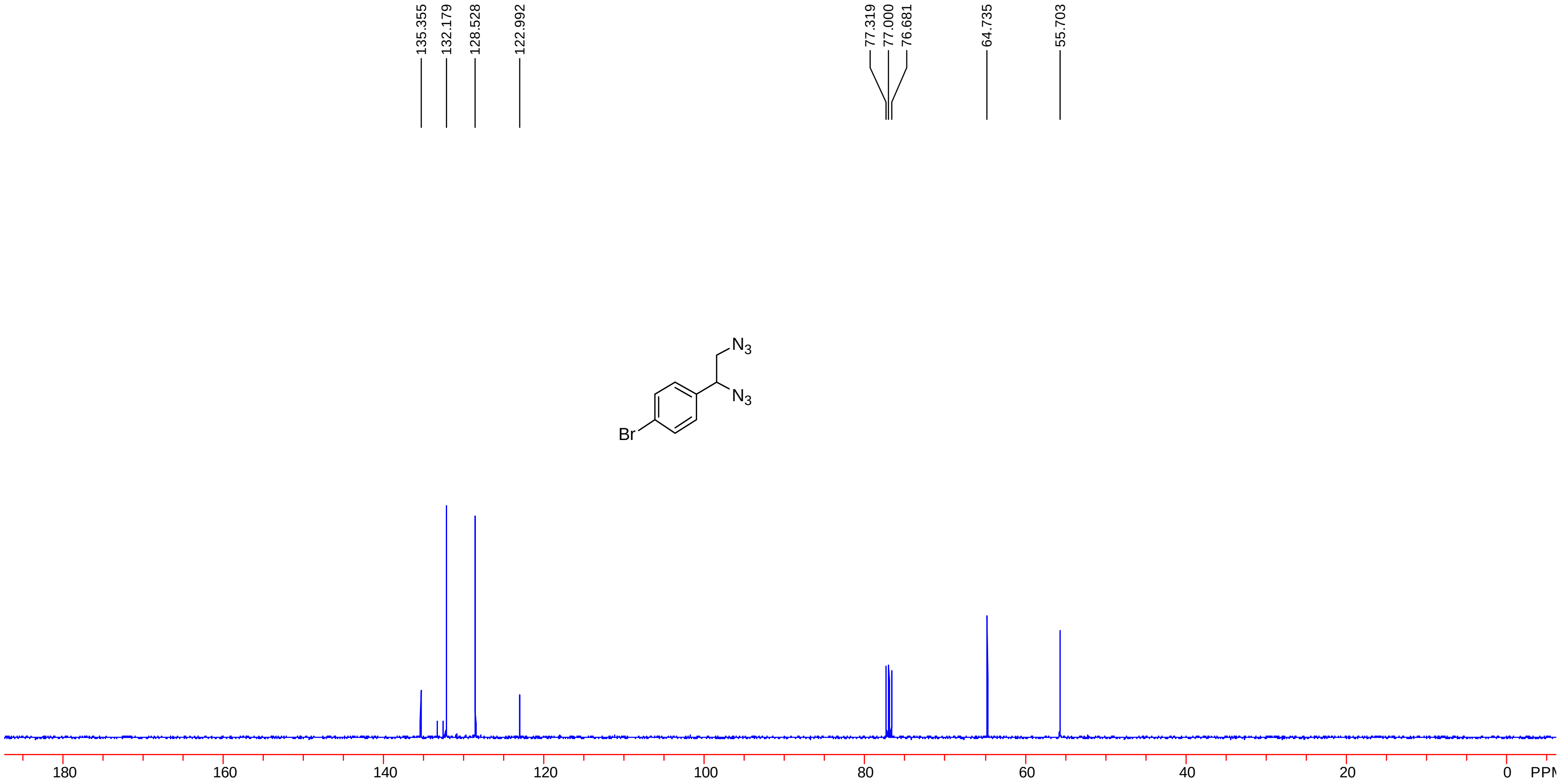
0 PPM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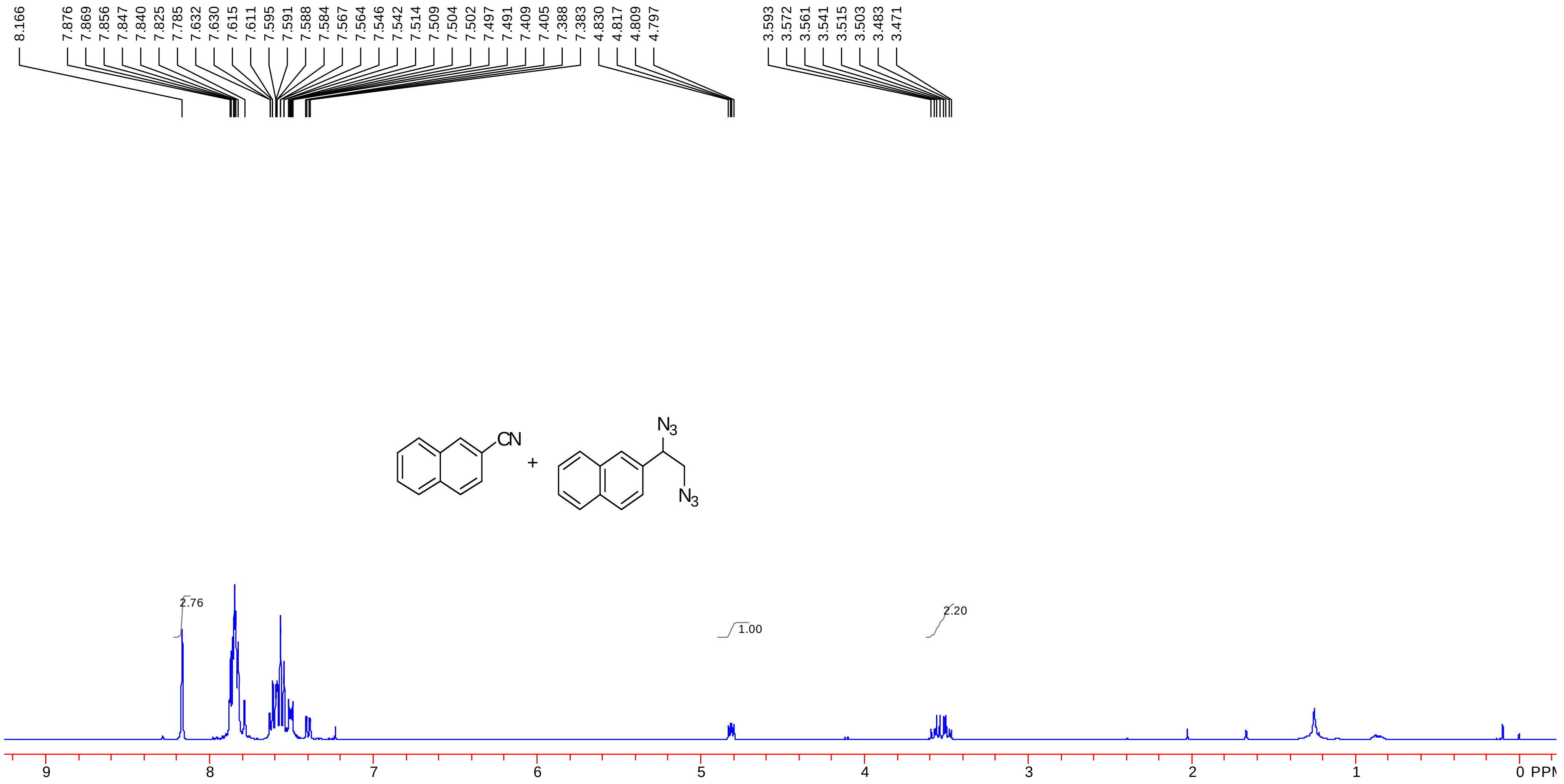
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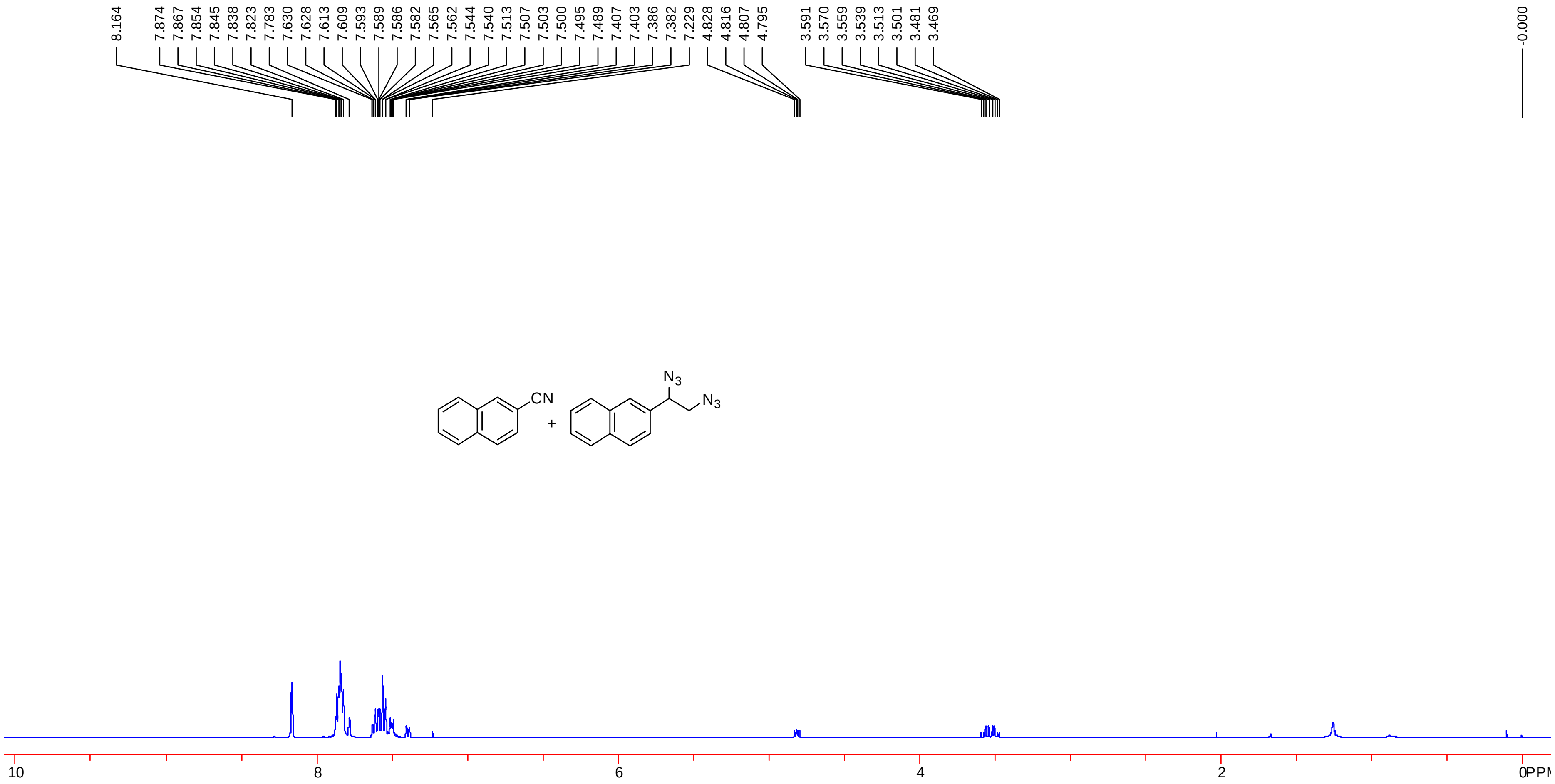
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7.565
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7.503
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7.495
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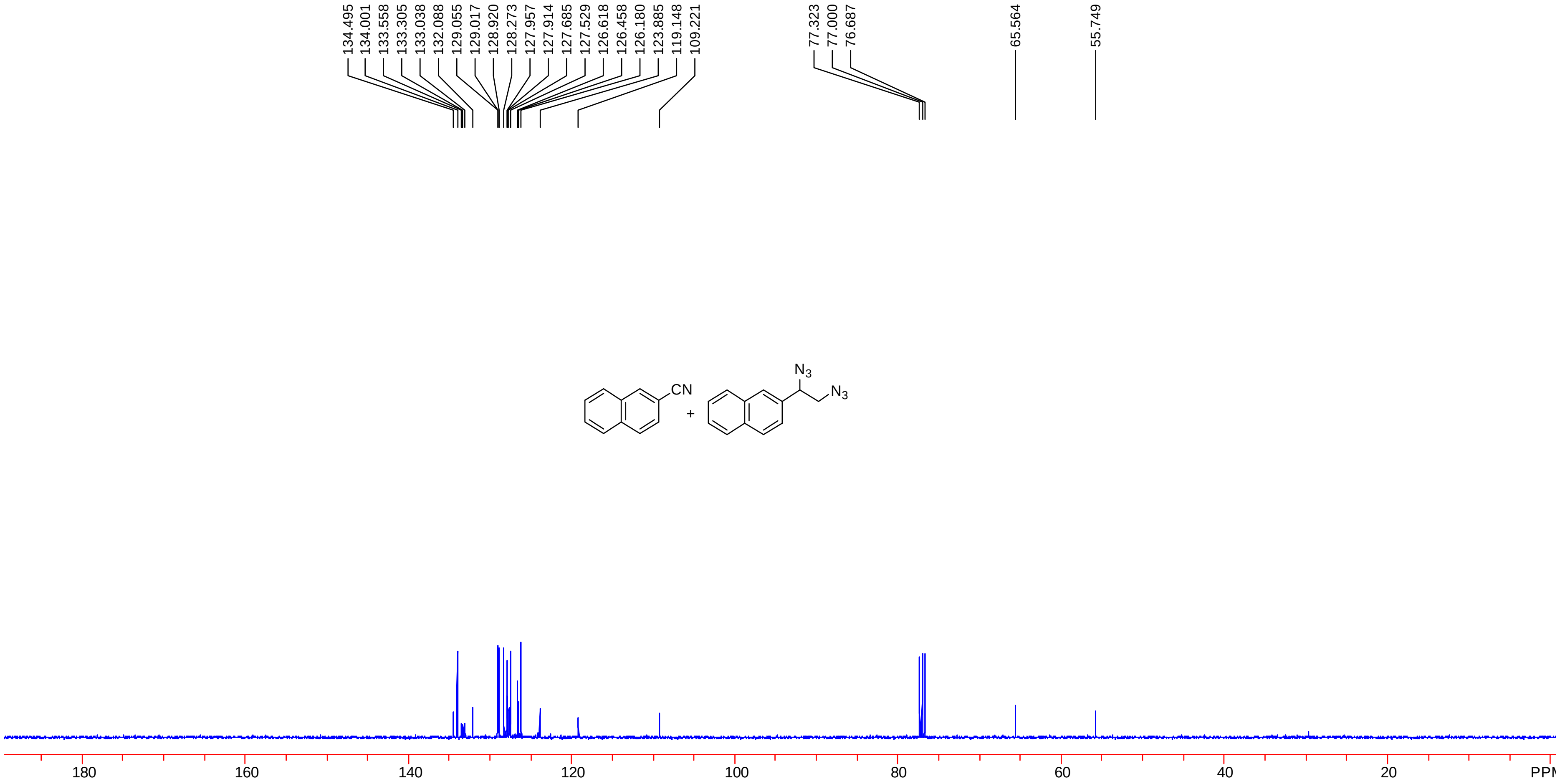
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127.529
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126.458
126.180
123.885
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77.000
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65.564
55.749
CN
+
N3
N3
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60
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PPM