Supporting Information for:

Brønsted Acid Mediated Nitrogenation of Propargylic Alcohols: An Efficient Approach to Alkenyl Nitriles

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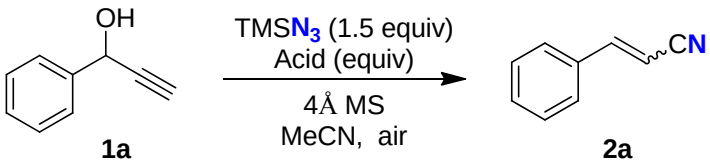
General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Beijing Ouhe and Beijing Chemical Works, Ltd. MeCN was used after distillation. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography or by preparative thin-layer chromatography on silica gel. ^{1}H-NMR spectra were recorded on a Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced to the residual solvent peak (7.26 in $CDCl_3$, 2.50 in DMSO-*d6*) or TMS in $CDCl_3$ (0 ppm) ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) or DMSO-d_6 (39.51). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometerusing electrospray ionisation (ESI). Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Nexus 470 Fourier transform infrared spectrometer.

Screening with Different Reaction Conditions

Table S1. Screening with Different Acids. [a]

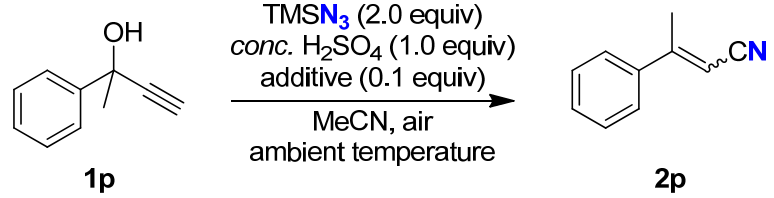


1a **2a**

entry	acid (equiv)	temperature	yield of **2a**
1	*conc.* H_2SO_4 (0.1)	60 °C	trace
2	p-TSA•H_2O (0.1)	60 °C	NR
3	HCOOH (0.1)	60 °C	NR
4	HPA (0.02)	60 °C	NR
5	TFA (0.1)	60 °C	NR
6	$AlCl_3$ (0.1)	60 °C	NR
7	BF_3•Et_2O (0.1)	60 °C	NR
8	$FeCl_3$ (0.1)	60 °C	NR
9	$Cu(OTf)_2$ (0.1)	60 °C	trace
10	$Sc(OTf)_3$ (0.1)	60 °C	trace
11[b]	$HClO_4$ (1.0)	A. T.	21%[c]
12[b]	TFA (1.0)	A. T.	NR
13[b]	HCOOH (1.0)	A. T.	NR
14[b]	$MeSO_3H$ (1.0)	A. T.	trace
15[b]	CH_3COOH (1.0)	A. T.	NR
16[b]	*conc.* HCl (1.0)	A. T.	NR
17[b]	$Cu(OTf)_2$ (1.0)	A. T.	NR
18[b]	$FeCl_3$ (1.0)	A. T.	NR

[a] Reaction conditions: **1a** (0.50 mmol), $TMSN_3$ (2.0 equiv), 4Å MS (200 mg), Acid and MeCN (2.0 mL), stirred at ambient temperature under air for 12 hours. TMS = trimethylsilyl, NR = no reaction, HPA = phosphomolybdic acid hydrate (CAS number: 51429-74-4), A. T. = ambient temperature; [b] without 4Å MS; [c] isolated yield.

Table S2. Screening with Different Additives.[a]

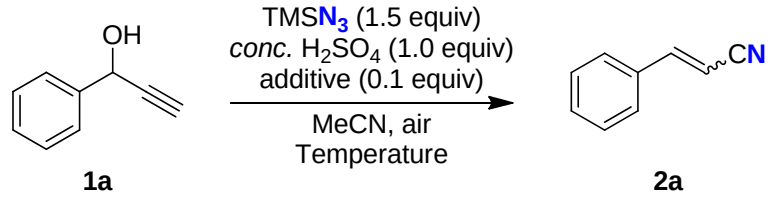


1p **2p**

entry	additive (0.1 equiv)	yield (%)[b]	*E*:*Z*[c]
1	None	58	32:68
2	NaBr	96	79:21
3	NH_4Br	97	80:20
4	KCl	74	40:60
5	$MgSO_4$	52	66:34
6	KH_2PO_4	58	>1
7	$NaClO_4$	40	68:32
8	$NaBF_4$	41	64:36
9[d,e]	NH_4Br	94	81:19
10[d]	NH_4Br	92	78:22
11[d,f]	NH_4Br	61	60:40

[a] Reaction conditions: **1p** (0.5 mmol), $TMSN_3$ (2.0 equiv), *conc.* H_2SO_4 (1.0 equiv), additive (0.1 equiv) and MeCN (2.0 mL), stirred at ambient temperature under air for 12 hours. [b] isolated yields. [c] Determined by ^1H NMR measurement of the mixture. [d] 1.5 equiv of $TMSN_3$. [e] -20 °C. [f] 60 °C.

Table S3. Screening with Different Temperatures.[a]



1a **2a**

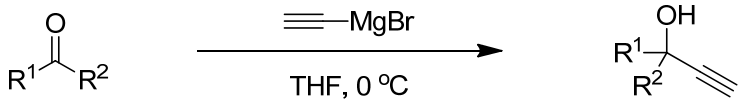
entry	temperature	additive	yield (%)[b]	*E*:*Z*[c]
1	-20 °C	None	trace[d]	/
2	A. T.	None	71	66:34
3	40 °C	None	64	59:41
4	60 °C	None	55	55:45
5	80 °C	None	52	54:46
6	-20 °C	NH_4Br	trace[d]	/
7	A. T.	NH_4Br	82	>99:1
8	40 °C	NH_4Br	75	93:7
9	60 °C	NH_4Br	66	85:15
10	80 °C	NH_4Br	56	84:16

[a] Reaction conditions: **1a** (0.5 mmol), $TMSN_3$ (1.5 equiv), *conc.* H_2SO_4 (1.0 equiv), additive (0.1 equiv) and MeCN (2.0 mL), stirred at ambient temperature under air for 12 hours. A. T. = ambient temperature. [b] NMR yields using 1,1,2,2-tetrachloroethane as internal standard. [c] Determined by ^1H NMR measurement of the crude mixture. [d] **2a** could be obtained aftertreatment.

Experimental Procedure and Characterization Data for Products

The Synthesis of Substrates:

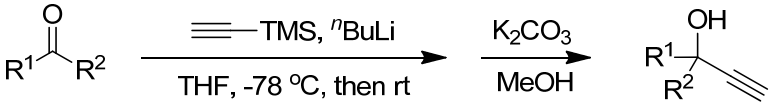
Method A:



1'b-1'j, 1'l-1n, 1'q, 1'u, 1'v **1b-1j, 1l-1n, 1q, 1u, 1v**

According to the literature procedure[S1], a solution of **1'** (3 mmol) in anhydrous THF (7 mL) in a three-necked round bottom flask under an argon atmosphere was cooled down to 0 °C. And ethynylmagnesium bromide (7.2 mL, 0.5 M in THF, 3.6 mmol) was added dropwise over 10 minutes with stirring. Then the reaction mixture was warmed to room temperature and continued stirring overnight. Quenched with saturated NH_4Cl aqueous solution (20 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed by water (50 mL) and saturated NH_4Cl aqueous solution (50 mL). After the organic layer was dried over anhydrous $MgSO_4$, the solvent was evaporated. Finally substrate **1** was obtained by flash column chromatography.

Method B:



1'k, 1'o, 1'r, 1's, 1't, **1k, 1o, 1r, 1s, 1t**

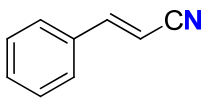
According to the literature procedure[S2], to a stirred solution of trimethylsilylacetylene (0.68 mL, 3.6 mmol) in THF (8 mL) under argon atmosphere at -78 °C, n-Butyllithium (2.3 mL, 1.6 M in THF, 3.6 mmol) was added over 20 minutes. The reaction mixture was stirred for an additional 1 hour. Then a solution of **1'** (3 mmol) in THF (10 mL) was added dropwise. And the reaction was warmed to room temperature slowly. After stirring overnight the reaction mixture was quenched with saturated NH_4Cl aqueous solution (20 mL) and extracted with diethyl ether (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated giving the crude residue.

The crude residue was dissolved by methanol (5 mL) and K_2CO_3 (11.2 g, 60 mmol) was added. The heterogeneous mixture was stirred for 2 hours at room temperature. After the solid was filtered, the solution was concentrated. Then the mixture was diluted by diethyl ether (20 mL), added with saturated NH_4Cl aqueous solution (20 mL). The water layer was extracted by diethyl ether (20 mL × 3). The combined ether layer was washed by water (50 mL) and saturated NH_4Cl aqueous solution (50 mL), dried over anhydrous $MgSO_4$. After the solvent was evaporated, the substrate **1** was obtained by flash column chromatography.

Analytical Data for Compounds 2:

Typical procedure:

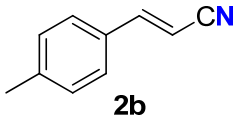
1) **cinnamonitrile (2a)**[S3]**:**



2a

Typical procedure: $TMSN_3$ (86 mg, 0.75 mmol) was added to a solution of 1-phenylprop-2-yn-1-ol **1a** (66 mg, 0.50 mmol) and NH_4Br (5 mg, 0.05 mmol) in MeCN (1.0 mL) under air at ambient temperature. A solution of *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) was added dropwise in one minute with stirring. Continue stirring for 12 hours. The solvent was evaporated and the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford 51 mg (79%) of **2a**. **2a**: yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48-7.30 (m, 6H), 5.87 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.4, 133.3, 131.1, 129.0, 127.2, 118.0, 96.2 ppm; IR (KBr): ν_{max} = 2217, 1619, 967, 749, 690 cm^{-1}; MS (70 eV): m/z (%): 129.2 (M^+, 100).

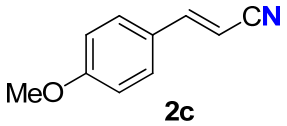
2) **(*E*)-3-(*p*-tolyl)acrylonitrile (2b)**[S3]**:**



2b

The reaction of 1-(*p*-tolyl)prop-2-yn-1-ol **1b** (73 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 70 mg (98%) of **2b**. **2b**: yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.30 (m, 3H), 7.25-7.18 (m, 2H), 5.81 (d, *J* = 16.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.4, 141.8, 130.8, 129.8, 127.3, 118.4, 95.0, 21.4 ppm; IR (KBr): ν_{max} = 2215, 1604, 1181, 978, 802 cm^{-1}; MS (70 eV): m/z (%): 143.2 (M^+, 100).

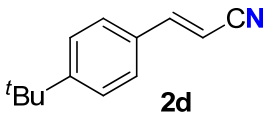
3) **(*E*)-3-(4-methoxyphenyl)acrylonitrile (2c)** [S3]**:**



2c

The reaction of 1-(4-methoxyphenyl)prop-2-yn-1-ol **1c** (81 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 46 mg (58%) of **2c**. **2c**: yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 16.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.71 (d, *J* = 16.4 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.0, 150.0, 129.0, 126.3, 118.7, 114.5, 93.3, 55.4 ppm; IR (KBr): ν_{max} = 2213, 1601, 1510, 1251, 1175, 806 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}NO$ $[M+H]^+$, 160.0757, found: 160.0755.

4) **(*E*)-3-(4-(*tert*-butyl)phenyl)acrylonitrile (2d)**[S4]**:**

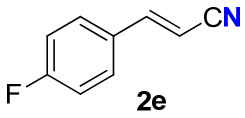


2d

The reaction of 1-(4-(*tert*-butyl)phenyl)prop-2-yn-1-ol **1d** (94 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 86 mg (93%) of **2d**. **2d**: yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45-7.35 (m, 5H), 5.84 (d, *J* = 16.8 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.9, 150.4, 130.8, 127.2, 126.1, 118.4, 95.2, 35.0, 31.1 ppm; IR (KBr): ν_{max} = 2964, 2216, 1619, 1272, 970, 810 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{16}N$ $[M+H]^+$, 186.1277, found: 186.1272.

5) **(*E*)-3-(4-fluorophenyl)acrylonitrile (2e)**[S4]**:**

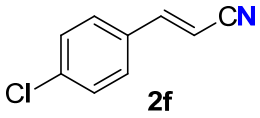
The reaction of 1-(4-fluorophenyl)prop-2-yn-1-ol **1e** (75 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75



2e

mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 55 mg (75%) of **2e**. **2e**: yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48-7.42 (m, 2H), 7.36 (d, *J* = 16.4 Hz, 1H), 7.14-7.06 (m, 2H), 5.81 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.3 (d, *J* = 252.1), 149.2, 129.8 (d, *J* = 2.6), 129.3 (d, *J* = 8.6), 117.9, 116.3 (d, *J* = 22.3), 96.1 (d, *J* = 2.1) ppm; IR (KBr): ν_{max} = 2211, 1604, 1512, 1243, 971, 808 cm^{-1}; MS (70 eV): m/z (%): 147.1 (M^+, 100).

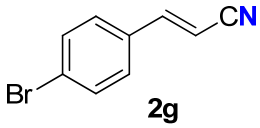
6) **(*E*)-3-(4-chlorophenyl)acrylonitrile (2f)**[S3]**:**



2f

The reaction of 1-(4-chlorophenyl)prop-2-yn-1-ol **1f** (83 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 56 mg (69%) of **2f**. **2f**: white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41-7.30 (m, 5H), 5.86 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.0, 137.1, 131.9, 129.3, 128.5, 117.7, 96.9 ppm; IR (KBr): ν_{max} = 2217, 1623, 1488, 1090, 965, 801 cm^{-1}; MS (70 eV): m/z (%): 163.1 (M^+, 67), 128.1 (100).

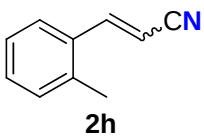
7) **(*E*)-3-(4-bromophenyl)acrylonitrile (2g)**[S5]**:**



2g

The reaction of **1f** (106 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at 30 °C for 12 hours, afford 73 mg (70%) of **2f**. **2f**: white solid. ^{1}HNMR ($CDCl_3$, 400 MHz): δ = 7.54 (d, *J* = 8.4 Hz, 2H), 7.37-7.27 (m, 3H), 5.88 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.2, 132.4, 128.7, 125.6, 117.8, 97.1 ppm; IR (KBr): ν_{max} = 2216, 1621, 1484, 1070, 965, 796 cm^{-1}; MS (70 eV): m/z (%): 207.1 ($[M-1]^+$, 52), 209.1 ($[M+1]^+$, 49), 128.2 (100).

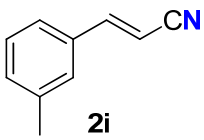
8) **3-(*o*-tolyl)acrylonitrile (2h)**[S3]**:**



2h

The reaction of 1-(*o*-tolyl)prop-2-yn-1-ol **1h** (73 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 62 mg (87%) of **2h**. **2h**: obtained as a 96:4 mixture of *E/Z* isomers. Yellow solid. ***E*-2h:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (d, *J* = 16.8 Hz, 1H), 7.49-7.43 (m, 1H), 7.36-7.30 (m, 1H), 7.26-7.20 (m, 2H), 5.80 (d, *J* = 16.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.4, 137.2, 132.5, 131.0, 130.9, 126.6, 125.5, 118.3, 97.2, 19.5 ppm; IR (KBr): ν_{max} = 2214, 1615, 1601, 967, 755, 743 cm^{-1}; MS (70 eV): m/z (%): 143.2 (M^+, 40), 116.2 (100). Partial ^{1}H NMR for the minor *Z*-isomer: 5.52 (d, *J* = 11.6 Hz, 1H), 2.36 (s, 3H).

9) **(*E*)-3-(*m*-tolyl)acrylonitrile (2i)**[S3]**:**

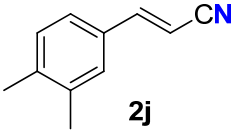


2i

The reaction of 1-(*m*-tolyl)prop-2-yn-1-ol **1i** (73 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 60 mg (84%) of **2i**. **2i**: yellow liquid. ^{1}H NMR ($CDCl_3$, 400

MHz): δ = 7.34 (d, *J* = 16.8 Hz, 1H), 7.31-7.20 (m, 4H), 5.84 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.7, 138.8, 133.4, 132.0, 128.9, 127.9, 124.5, 118.2, 96.0, 21.2 ppm; IR (KBr): ν_{max} = 2213, 1618, 1603, 964, 783, 691 cm^{-1}; MS (70 eV): m/z (%): 143.2 (M^+, 40), 115.1 (100).

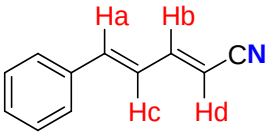
10) **(*E*)-3-(3,4-dimethylphenyl)acrylonitrile (2j):**



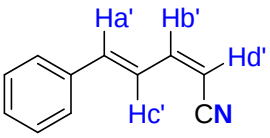
2j

The reaction of 1-(3,4-dimethylphenyl)prop-2-yn-1-ol **1j** (80 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 65 mg (83%) of **2j**. **2j**: white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (d, *J* = 16.8 Hz, 1H), 7.23-7.13 (m, 3H), 5.80 (d, *J* = 16.4 Hz, 1H), 2.294 (s, 3H), 2.286 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.6, 140.5, 137.4, 131.2, 130.3, 128.4, 124.9, 118.5, 94.7, 19.8, 19.6 ppm; IR (KBr): ν_{max} = 2209, 1621, 1606, 1501, 980, 803 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}N$ $[M+H]^+$, 158.0964, found: 158.0964.

11) **5-phenylpenta-2,4-dienenitrile (2k)**[S3]**:**



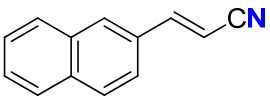
2*E*,4*E*-2k



2*Z*,4*E*-2k

The reaction of (*E*)-1-phenylpent-1-en-4-yn-3-ol **1k** (79 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 34 mg (44%) of **2k**. **2k**: obtained as a 93:7 mixture of **2*E*,4*E*-2k**/**2*Z*,4*E*-2k** isomers. Brown oil. **2*E*,4*E*-2k:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49-7.43 (m, 2H), 7.42-7.34 (m, 3H), 7.14 (Hb, dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 6.88 (Ha, d, *J* = 15.6 Hz, 1H), 6.81 (Hc, dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 5.43 (Hd, d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.2, 141.3, 135.2, 129.6, 128.9, 127.3, 125.4, 118.3, 98.2 ppm; IR (KBr): ν_{max} = 2212, 1623, 991, 737, 690 cm^{-1}; MS (70 eV): m/z (%): 155.2 (M^+, 100). Partial ^{1}H NMR for the minor **2*Z*,4*E*-2k**: 5.25 (Hd', d, *J* = 10.4 Hz, 1H).

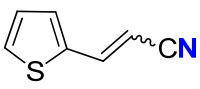
12) **(*E*)-3-(naphthalen-2-yl)acrylonitrile (2l)**[S3]**:**



2l

The reaction of 1-(naphthalen-2-yl)prop-2-yn-1-ol **1l** (91 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 46 mg (51%) of **2l**. **2l**: brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89-7.80 (m, 4H), 7.60-7.48 (m, 4H), 5.96 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.5, 134.4, 133.0, 130.9, 129.6, 129.0, 128.7, 127.79, 127.76, 127.0, 122.1, 118.3, 96.2 ppm; IR (KBr): ν_{max} = 2214, 1617, 967, 814, 751 cm^{-1}; MS (70 eV): m/z (%): 179.2 (M^+, 100).

13) **3-(thiophen-2-yl)acrylonitrile (2m)**[S3]**:**

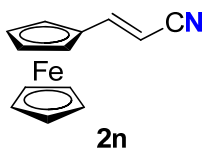


2m

The reaction of 1-(thiophen-2-yl)prop-2-yn-1-ol **1m** (69 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 28 mg (42%) of **2m**. **2m**: obtained as a 98:2

mixture of *E/Z* isomers. Brown oil. ***E*-2m:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 4.8 Hz, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 7.08 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz 1H), 5.65 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.7, 138.4, 131.2, 129.3, 128.3, 118.0, 94.4 ppm; IR (KBr): ν_{max} = 2214, 1606, 1420, 954, 711 cm^{-1}; MS (70 eV): m/z (%): 135.1 (M^+, 100). Partial ^{1}H NMR for the minor ***Z*-2m**: 5.26 (d, *J* = 11.6 Hz, 1H).

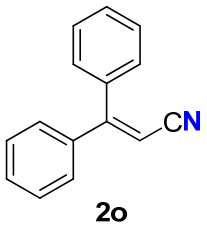
14) **(*E*)-3-(ferrocenyl)acrylonitrile (2n):**



2n

The reaction of 1-(ferrocenyl)prop-2-yn-1-ol **1n** (120 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 28 mg (24%) of **2n**. **2n**: brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (d, *J* = 16.4 Hz, 1H), 5.43 (d, *J* = 16.4 Hz, 1H), 4.45 (s, 4H), 4.19 (s, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.6, 119.0, 91.8, 78.0, 71.4, 69.8, 68.1 ppm; IR (KBr): ν_{max}= 2924, 2209, 1612, 1459, 818, 475 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{13}H_{12}FeN$ $(M + H)^+$, 238.0314, found 238.0311.

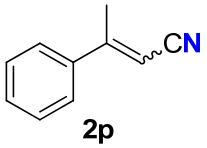
15) **3,3-diphenylacrylonitrile (2o)**[S6]**:**



2o

The reaction of 1,1-diphenylprop-2-yn-1-ol **1o** (104 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 40 mg (39%) of **2o**. **2o**: yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50-7.42 (m, 6H), 7.41-7.36 (m, 2H), 7.34-7.29 (m, 2H), 5.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.1, 138.9, 137.0, 130.4, 130.0, 129.5, 128.6, 128.5, 128.4, 117.8, 94.8 ppm; IR (KBr): ν_{max} = 2212, 1569, 1444, 762, 696 cm^{-1}; MS (70 eV): m/z (%): 205.2 (M^+, 100).

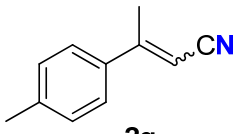
16) **3-phenylbut-2-enenitrile (2p)**[S7]**:**



2p

The reaction of 2-phenylbut-3-yn-2-ol **1p** (73 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 66 mg (92%) of **2p**. **2p**: obtained as a 78:22 mixture of *E/Z* isomers. Yellow oil. ***E*-2p:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52-7.35 (m, 5H), 5.62 (s, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.7, 138.1, 130.2, 128.8, 125.8, 117.5, 95.5 ppm, 20.1; ***Z*-2p:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.57-7.51 (m, 2H), 7.47-7.39 (m, 3H), 5.40 (q, *J* = 1.5 Hz, 1H), 2.28 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.9, 137.9, 129.8, 128.6, 127.0, 117.5, 95.4, 24.6 ppm; IR (KBr): ν_{max} = 2215, 1612, 1440, 806, 767, 697 cm^{-1}; MS (70 eV): m/z (%): 143.2 (M^+, 100).

17) **3-(*p*-tolyl)but-2-enenitrile (2q)**[S7]**:**

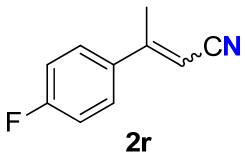


2q

The reaction of 2-(*p*-tolyl)but-3-yn-2-ol **1q** (80 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 51 mg (65%) of **2q**. **2q**: obtained as a 76:24 mixture of

E/Z isomers. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): ***E*-2q:** δ = 7.38-7.34 (m, 2H), 7.23-7.28 (m, 2H), 5.59 (s, 1H), 2.44 (s, 3H), 2.38 (s, 3H); ***Z*-2q:** δ = 7.48-7.44 (m, 2H), 7.26-7.23 (m, 2H), 5.35-5.33 (m, 1H), 2.38 (s, 3H), 2.26 (q, *J* = 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.7, 159.5, 140.6, 140.1, 135.2, 134.9, 129.5, 129.2, 127.0, 125.7, 117.8, 94.6, 94.4, 24.5, 21.3, 21.2, 20.0 ppm; IR (KBr): ν_{max} = 2212, 1604, 1513, 1440, 825, 804 cm^{-1}; MS (70 eV): m/z (%): 157.2 (M^+, 72), 143.2 (100).

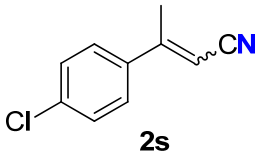
18) **3-(4-fluorophenyl)but-2-enenitrile (2r):**



2r

The reaction of 2-(4-fluorophenyl)but-3-yn-2-ol **1r** (82 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 70 mg (87%) of **2r**. **2r**: obtained as a 84:16 mixture of *E/Z* isomers. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): ***E*-2r:** δ = 7.49-7.42 (m, 2H), 7.16-7.04 (m, 2H), 5.57 (s, 1H), 2.45 (d, *J* = 0.4 Hz, 3H); ***Z*-2r:** δ = 7.59-7.51 (m, 2H), 7.16-7.04 (m, 2H), 5.42-5.38 (m, 1H), 2.27 (d, *J* =1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.1, 162.6, 158.4, 134.33, 134.29, 129.2, 129.1, 127.9, 127.8, 117.4, 116.0, 115.81, 115.76, 115.6, 95.5, 95.4, 24.6, 20.2 ppm; IR (KBr): ν_{max} = 2214, 1601, 1510, 1235, 1164, 842, 815 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_9FN$ $[M+H]^+$ 162.0714, found: 162.0713.

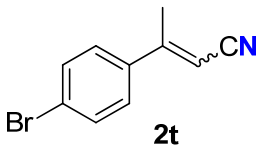
19) **3-(4-chlorophenyl)but-2-enenitrile (2s)**[S7]**:**



2s

The reaction of 2-(4-chlorophenyl)but-3-yn-2-ol **1s** (90 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 73 mg (82%) of **2s**. **2s**: obtained as a 77:23 mixture of *E/Z* isomers. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): ***E*-2s:** δ = 7.42-7.35 (m, 4H), 5.62-5.58 (m, 1H), 2.45 (d, *J* = 0.8 Hz, 3H); ***Z*-2s:** δ = 7.51-7.46 (m, 2H), 7.42-7.35 (m, 2H), 5.41 (q, *J* = 1.6 Hz, 1H), 2.26 (d, *J* =1.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.5, 158.3, 136.5, 136.4, 136.2, 135.8, 129.0, 128.9, 128.4, 127.1, 117.3, 117.2, 96.02, 95.99, 24.5, 20.1 ppm; IR (KBr): ν_{max} = 2215, 1609, 1491, 1096, 1012, 811 cm^{-1}; MS (70 eV): m/z (%): 177.1 (M^+, 100).

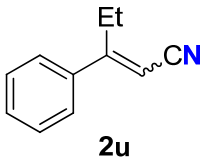
20) **3-(4-bromophenyl)but-2-enenitrile (2t):**



2t

The reaction of 2-(4-bromophenyl)but-3-yn-2-ol **1t** (113 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 94 mg (85%) of **2t**. **2t**: obtained as a 78:22 mixture of *E/Z* isomers. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): ***E*-2t:** δ = 7.57-7.50 (m, 2H), 7.35-7.30 (m, 2H), 5.63-5.59 (m, 1H), 2.44 (d, *J* = 0.8 Hz, 3H); ***Z*-2t:** δ = 7.57-7.52 (m, 2H), 7.43-7.39 (m, 2H), 5.41 (q, *J* = 1.6 Hz, 1H), 2.26 (d, *J* =1.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.6, 158.4, 137.0, 136.6, 131.9, 131.8, 128.6, 127.3, 124.6, 124.1, 117.21, 117.16, 96.02, 95.98, 24.4, 20.0 ppm; IR (KBr): ν_{max} = 2215, 1608, 1488, 1401, 1008, 808 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{10}H_9BrN$ $(M + H)^+$, 221.9913, found 221.9917.

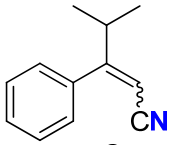
21) **3-phenylpent-2-enenitrile (2u)**[S7]**:**



2u

The reaction of 3-phenylpent-1-yn-3-ol **1u** (80 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 52 mg (66%) of **2u**. **2u**: obtained as a 54:46 mixture of *E/Z* isomers. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): ***E*-2u:** δ = 7.46-7.35 (m, 5H), 5.49 (s, 1H), 2.91 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H); ***Z*-2u:** δ = 7.46-7.35 (m, 5H), 5.27 (t, *J* = 1.4 Hz, 1H), 2.60 (qd, J_1 = 7.6 Hz, J_2 = 1. 6 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.3, 166.4, 137.6, 137.3, 130.0, 129.5, 129.1, 128.9, 128.6, 127.2, 126.3, 117.6, 117.3, 95.0, 94.5, 31.1, 27.2, 13.3, 12.2 ppm; IR (KBr): ν_{max}= 2974, 2214, 1604, 1444, 761, 697 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{11}H_{12}N$ $(M + H)^+$, 158.0964, found 158.0967.

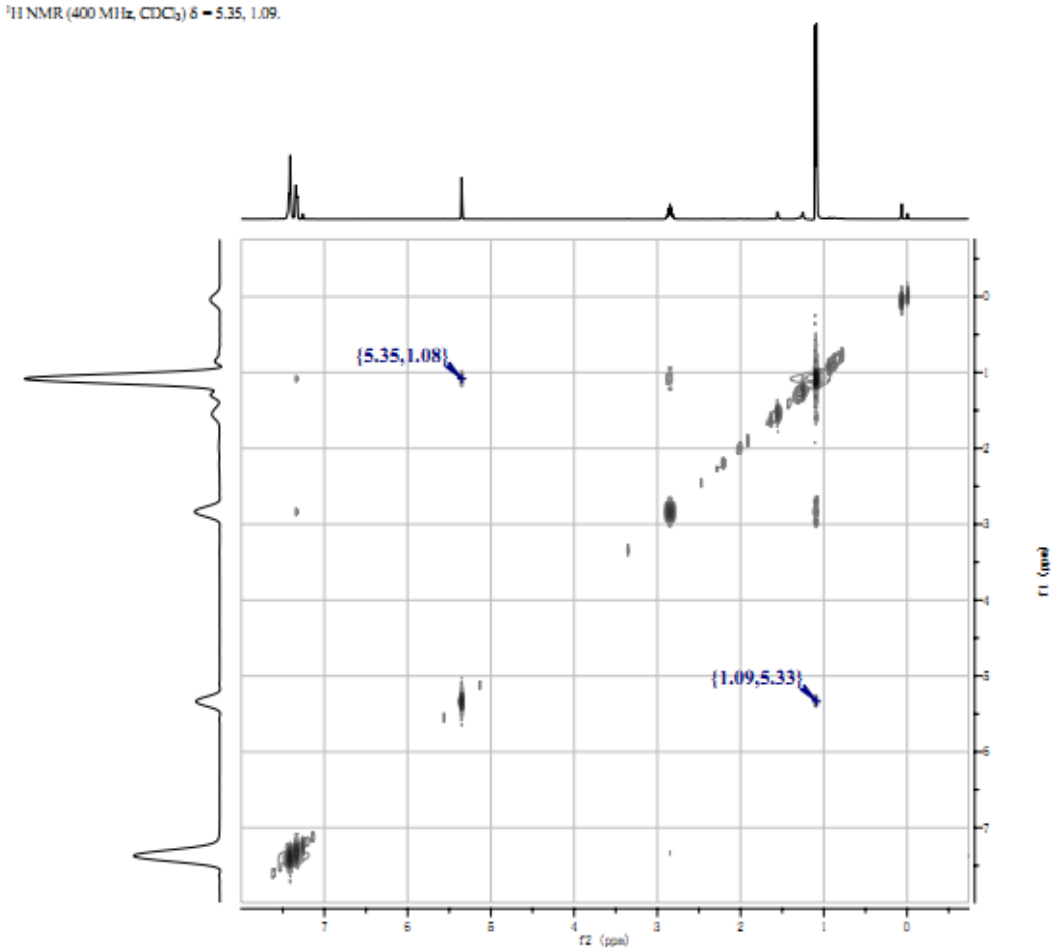
22) **4-methyl-3-phenylpent-2-enenitrile (2v)**[S7]**:**



2v

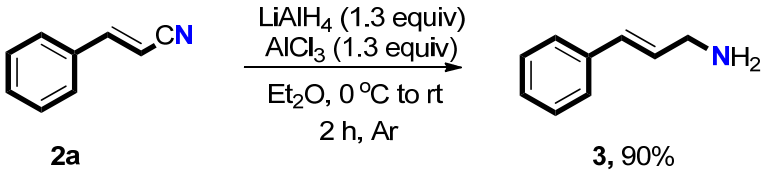
The reaction of 4-methyl-3-phenylpent-1-yn-3-ol **1v** (87 mg, 0.50 mmol), $TMSN_3$ (86 mg, 0.75 mmol), NH_4Br (5 mg, 0.05 mmol) and *conc.* H_2SO_4 (1.0 mL, 0.5M in MeCN) in MeCN (1.0 mL) under air at ambient temperature for 12 hours, afford 35 mg (41%) of **2v**. **2v**: obtained as a 21:79 mixture of *E/Z* isomers. The double bond geometry was determined by NOE experiment. Colorless oil. ***E*-2v:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.43-7.33 (m, 3H), 7.25-7.20 (m, 2H), 5.27 (s, 1H), 3.34 (sept, *J* = 7.0 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 127.1, 138.8, 128.9, 128.3, 127.1, 116.8, 96.5, 34.5, 21.2 ppm; IR (KBr): ν_{max}= 2962, 2215, 1461, 1019, 800, 700 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{12}H_{14}N$ $(M + H)^+$, 172.1121, found 172.1124. ***Z*-2v**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.46-7.38 (m, 3H), 7.36-7.31 (m, 2H), 5.35 (d, *J* = 1.6 Hz, 1H), 2.85 (septd, *J* = 6.8, 1.2 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz):δ = 172.4, 138.2, 129.2, 128.6, 127.3, 117.6, 94.3, 35.7, 21.1 ppm; IR (KBr): ν_{max}= 2965, 2217, 1464, 1015, 774, 700 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{12}H_{14}N$ $(M + H)^+$ 172.1121, found 172.1123.

NOE Spectrum of **Z-2v:**



Transformations:

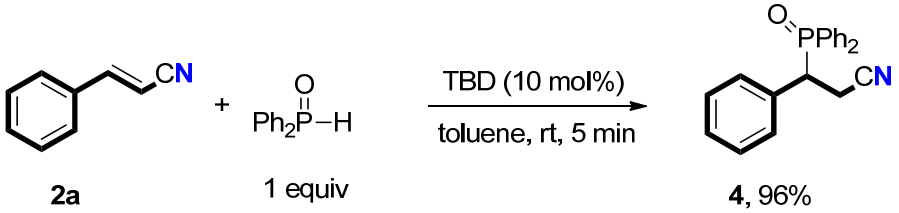
Reduction reaction of 2a:



2a **3,** 90%

According to the literature procedure[S8], $AlCl_3$ (1.3 mmol, 176.7 mg) in dry Et_2O (1.7 mL) was added to a suspension of $LiAlH_4$ (1.3 mmol, 50.5 mg) in dry Et_2O (1.7 mL) at 0 °C under Ar. After stirred for 10 minutes, a solution of **2a** (1.0 mmol, 129 mg) in 1.7 mL dry Et_2O was added dropwise. The reaction mixture was stirred at room temperature for 2 hours. When the starting material disappeared, 2 mL ice water was added. The pH was adjusted to 9~10 with NaOH. The mixture was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$, the solvent was evaporated. Finally, compound (*E*)-3-phenylprop-2-en-1-amine **5** was obtained by flash chromatography on silica gel (eluent: DCM/MeOH = 10:1) in 90% yield (102 mg) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.35 (m, 2H), 7.34-7.27 (m, 2H), 7.25-7.19 (m, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.32 (dt, J_1 = 16.0 Hz, J_2 = 5.8 Hz, 1H), 3.48 (dd, J_1 = 5.8 Hz, J_2 = 1.0 Hz, 2H), 1.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.1, 131.0, 129.5, 128.5, 127.3, 126.2, 44.2 ppm; IR (KBr): ν_{max}= 3357, 1662, 1459, 1377, 967, 695 cm^{-1}; MS (70 eV): m/z (%): 133.1 (M^+, 91).

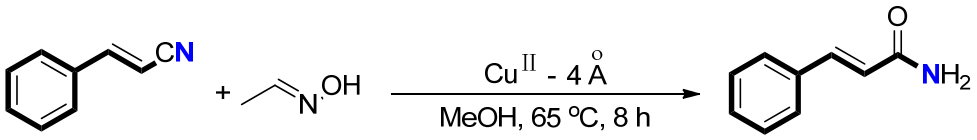
Conjugate Addition of P(O)—H:



2a 1 equiv **4**, 96%

According to the literature procedure[S9], diphenylphosphine oxide (0.3 mmol, 61 mg) was added to a tube, followed by cinnamonitrile **2a** (0.3 mmol, 39 mg), toluene (1 mL) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 0.03 mmol, 4 mg). The reaction mixture was stirred at room temperature for 5 minutes. When the starting material disappeared, the solvent was evaporated and compound (3-(diphenylphosphoryl)-3-phenylpropanenitrile) **6** was obtained by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) in 96% yield (95 mg) as white solid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 8.13-8.03 (m, 2H), 7.72-7.56 (m, 5H), 7.46-7.28 (m, 5H), 7.26-7.13 (m, 3H), 4.69-4.59 (m, 1H), 3.30-3.15 (m, 1H), 2.82-2.70 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 134.6, 134.5, 132.2, 132.14, 132.11, 132.0, 131.60, 131.58, 131.2, 131.0, 130.9, 130.8, 130.6, 130.5, 129.6, 129.5, 129.1, 128.9, 128.3, 128.2, 127.5, 118.6, 118.4, 40.4, 18.6 ppm; IR (KBr): ν_{max} = 2254, 1436, 1175, 752, 693, 545 cm^{-1}; MS (70 eV): m/z (%): 331.2 (M^+, 24), 201.0 (100).

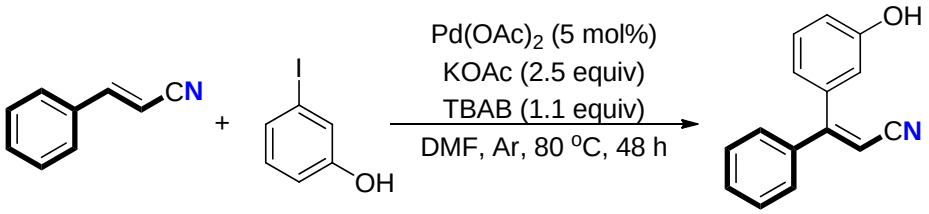
Hydration Reaction:



2a 3.0 equiv **5**, 99%

According to the literature procedure[S10], cinnamonitrile **2a** (0.5 mmol, 65 mg), acetaldoxime (1.5 mmol, 89 mg), catalyst (50 mg, 0.85 mmol $CuCl_2$/g support, preparation of the catalyst, see: Ref. S10) in MeOH (1 mL) were stirred at 65 °C for 8 hours. When the starting material disappeared, the solvent was evaporated and compound cinnamamide **7** was obtained by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) in 99% yield (73 mg) as white solid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.62 (s, 1H), 7.59-7.53 (m, 2H), 7.47 (d, J = 16.0 Hz, 1H), 7.42-7.30 (m, 3H), 7.21 (s, 1H), 6.66 (d, J = 15.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 166.9, 139.4, 134.9, 129.5, 129.0, 127.6, 122.3 ppm; IR (KBr): ν_{max} = 3423, 1672, 1026, 1003, 764, 631 cm^{-1}; MS (70 eV): m/z (%): 147.2 (M^+, 18), 84.1 (100).

Heck Reaction:



2a 2.0 equiv **6**, 94%

According to the literature procedure[S11], cinnamonitrile **2a** (0.3 mmol, 39 mg) was added to a mixture of 3-iodophenol (0.6 mmol, 132 mg), KOAc (0.75 mmol, 74 mg), TBAB (0.33 mmol, 106 mg), $Pd(OAc)_2$ (0.015 mmol, 3.4 mg) and DMF (2 mL) under Ar. The mixture was stirred at 80 °C for 48 hours. When the starting material disappeared, the reaction was quenched with saturated NH_4Cl aqueous solution (10 mL) and extracted with ethyl acetate (20 mL × 3). After the organic layer was dried over anhydrous $MgSO_4$, the solvent was evaporated and compound (*Z*)-3-(3-hydroxyphenyl)-3-phenylacrylonitrile **8** was obtained by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) in 94% yield (62 mg) as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50-7.39 (m, 5H), 7.23 (t, J = 7.8 Hz, 1H), 6.92-6.87 (m, 1H), 6.88-6.83 (m, 1H), 6.74 (t, J = 2.0 Hz, 1H), 5.71 (s, 1H), 5.56 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.3, 155.9, 140.3, 136.8, 130.1, 129.9, 129.5, 128.5, 120.9, 117.8, 117.6, 115.4, 94.7 ppm; IR (KBr): ν_{max} = 3310, 2226, 1579, 1358, 1284, 789, 697 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{15}H_{12}NO$ $(M + H)^+$, 222.0913, found 220.0918.

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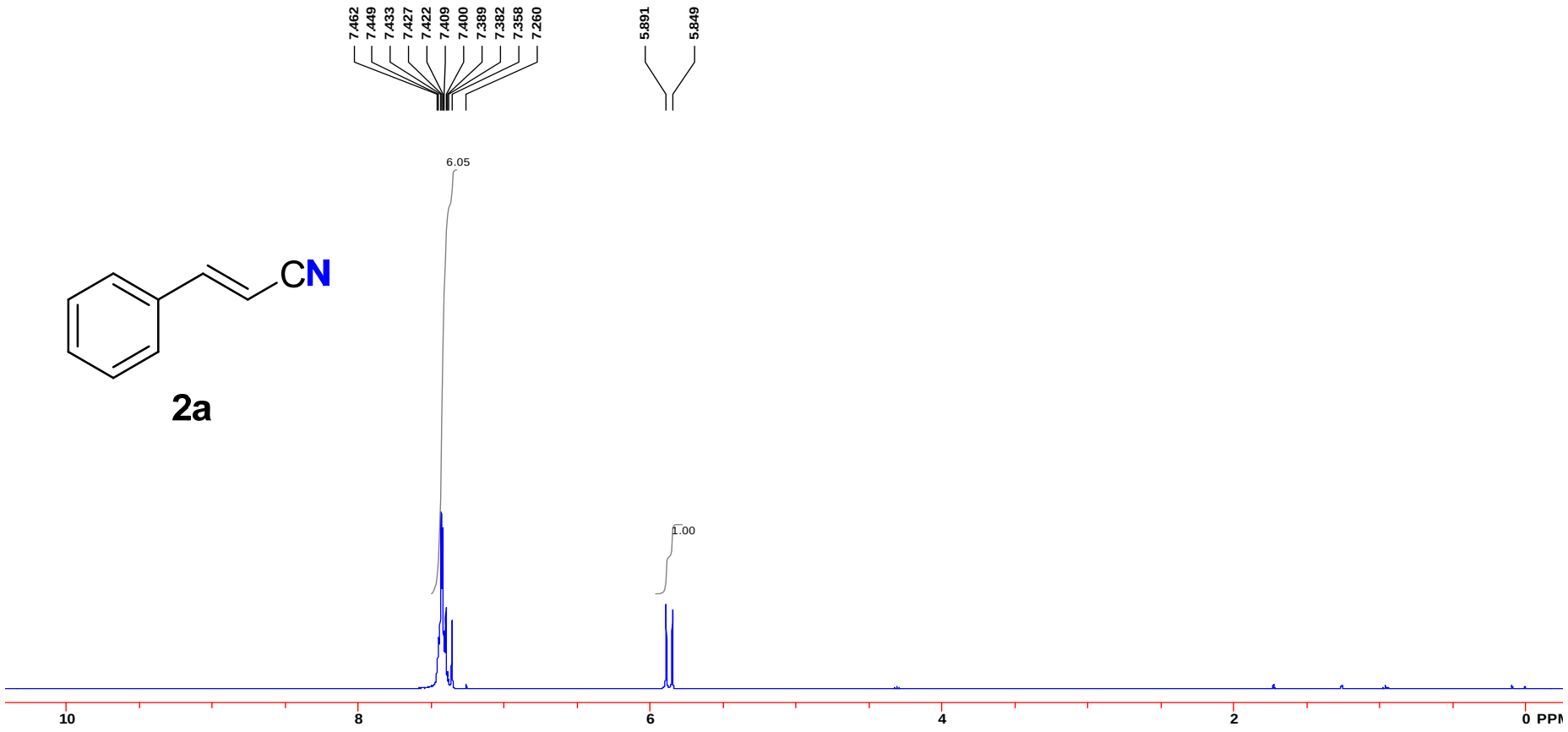
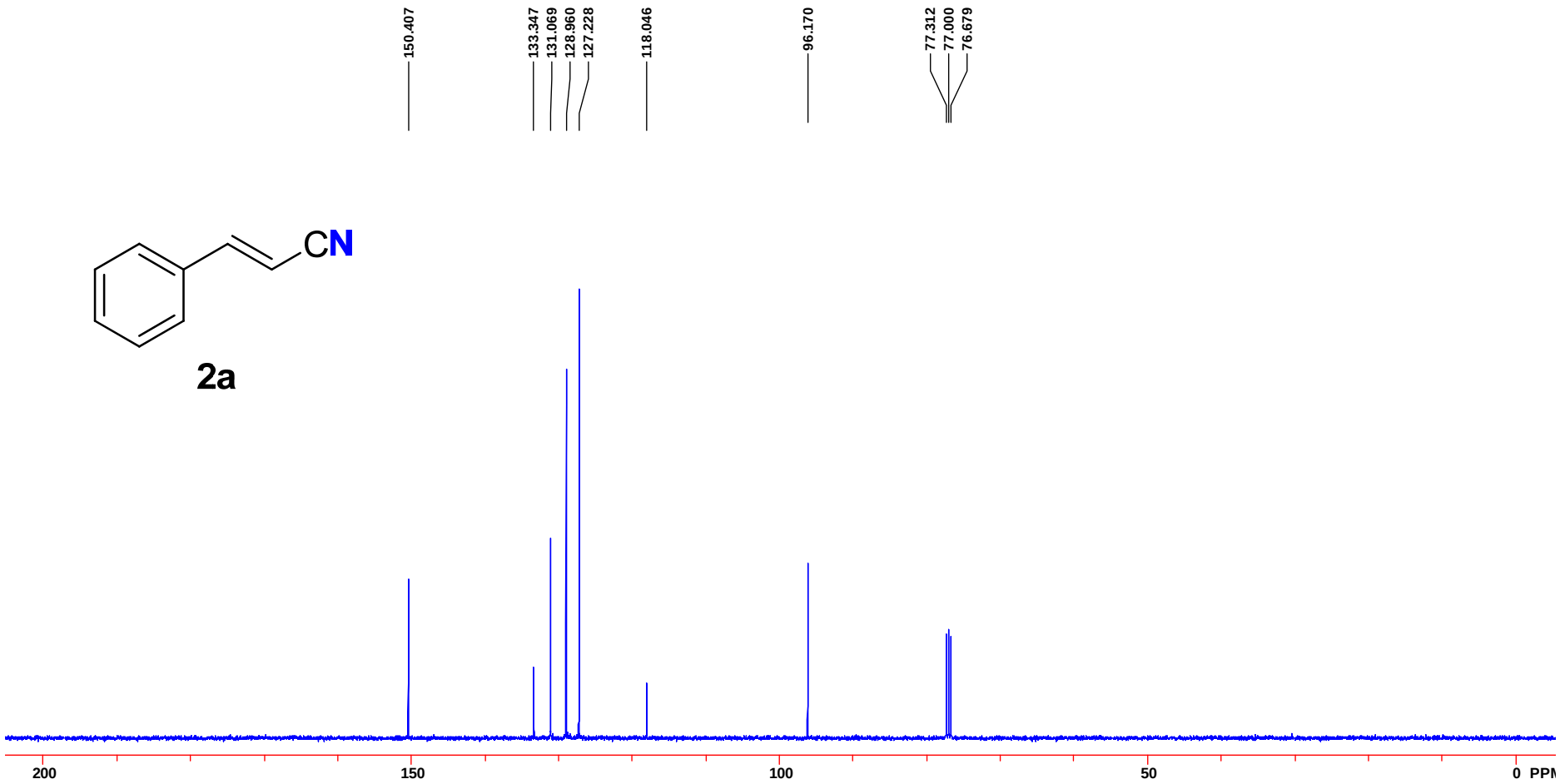
^{1}H NMR and ^{13}C NMR Spectra of Products

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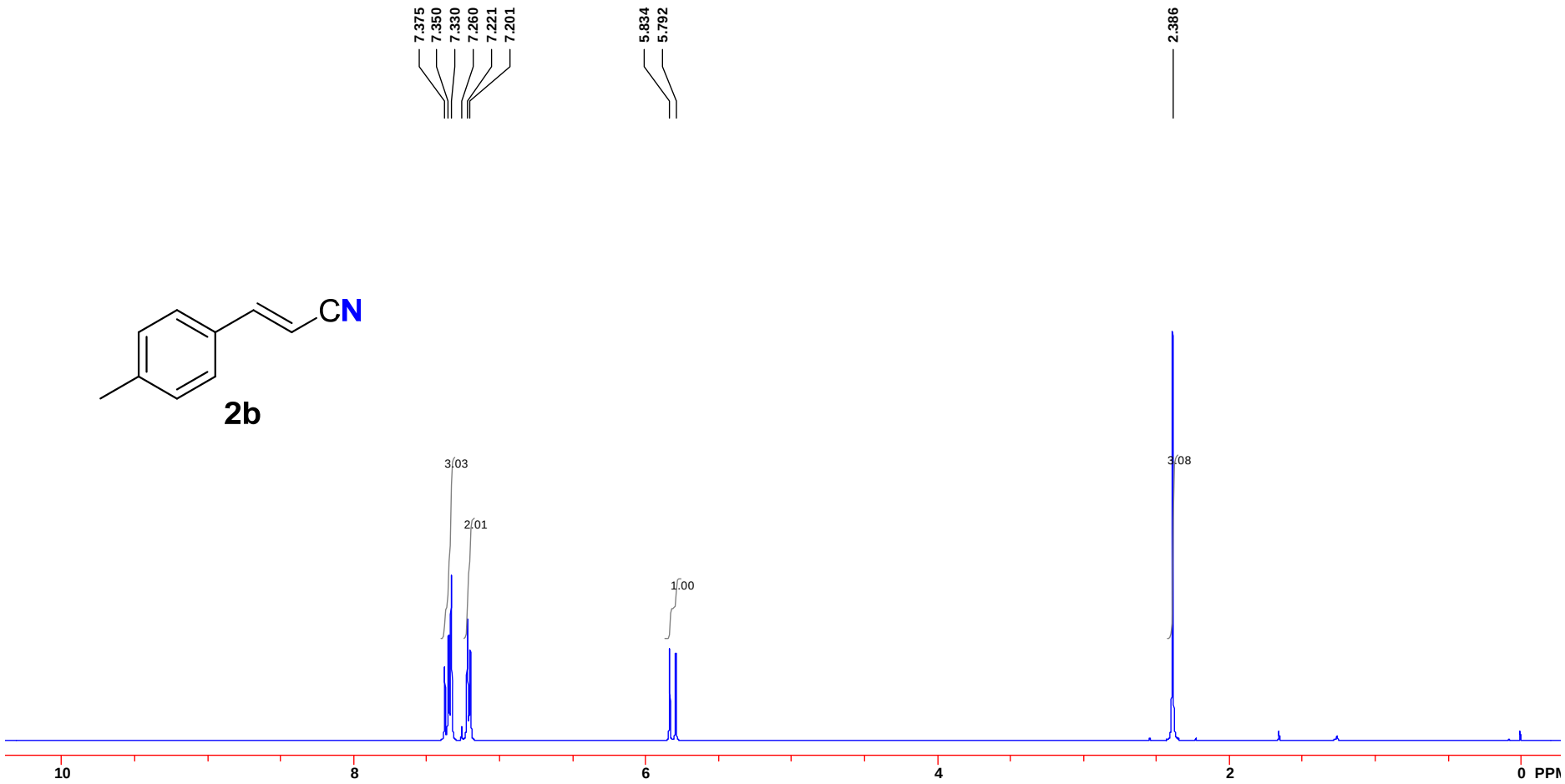
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6
4
2
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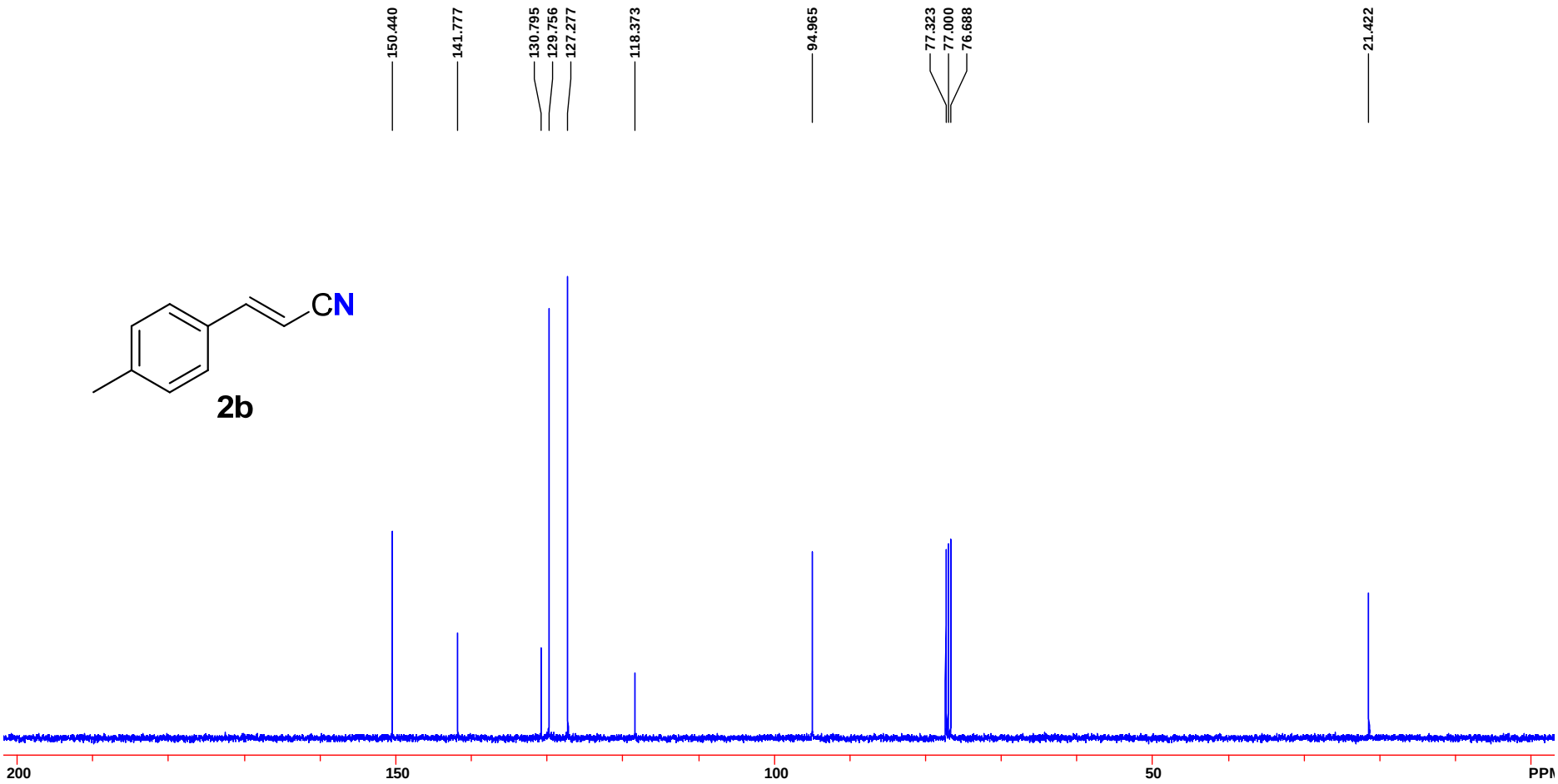
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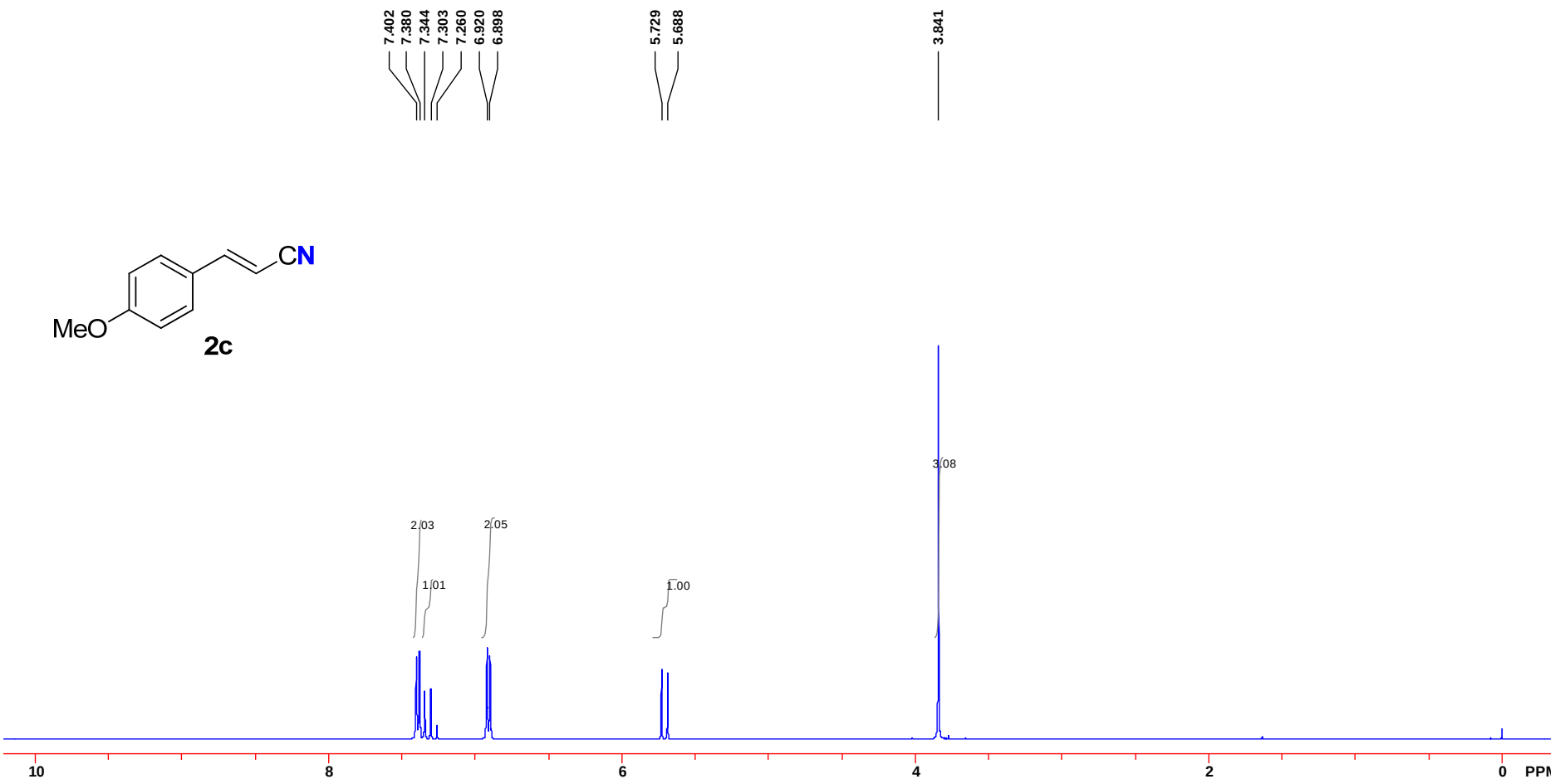
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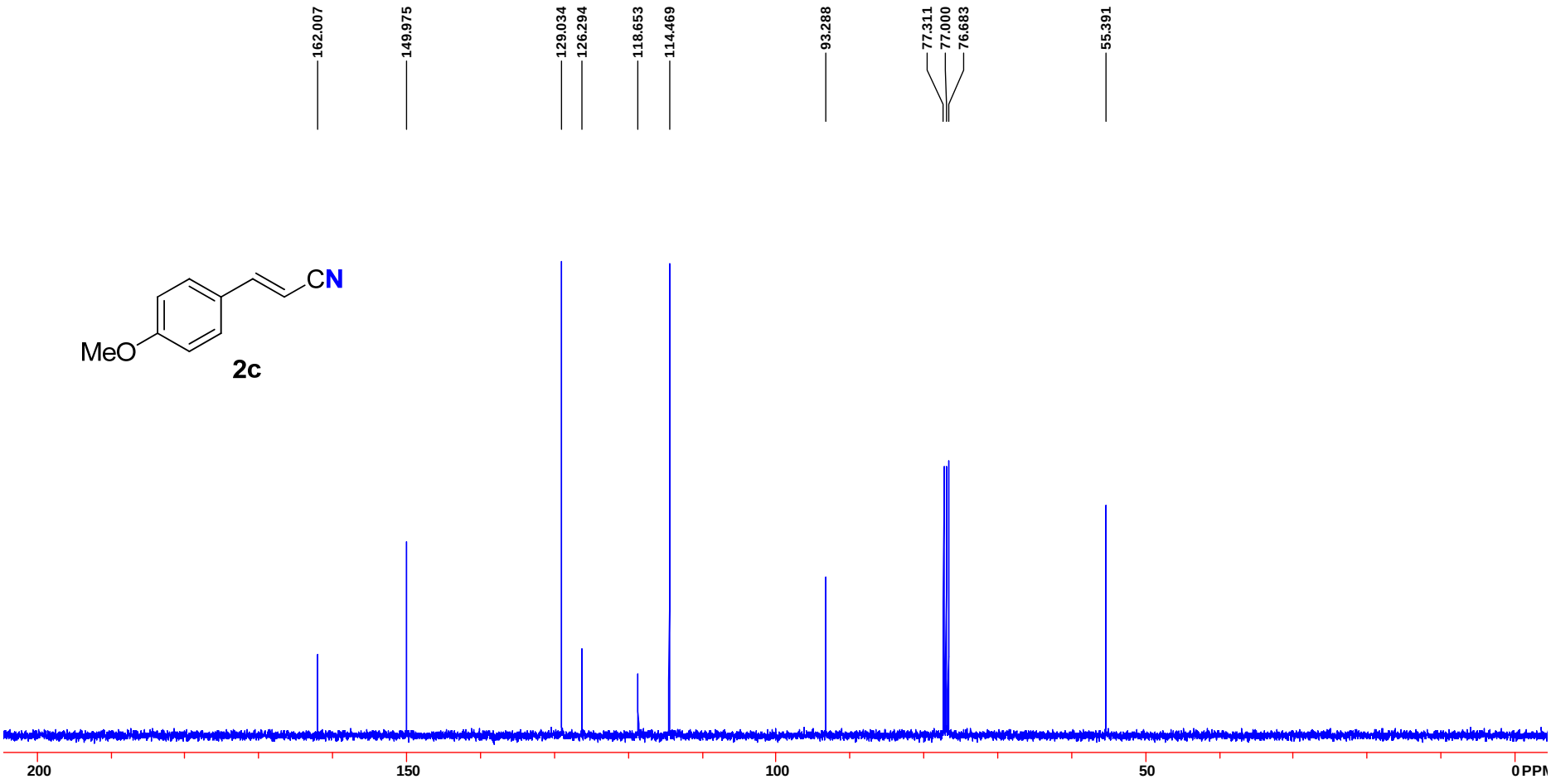
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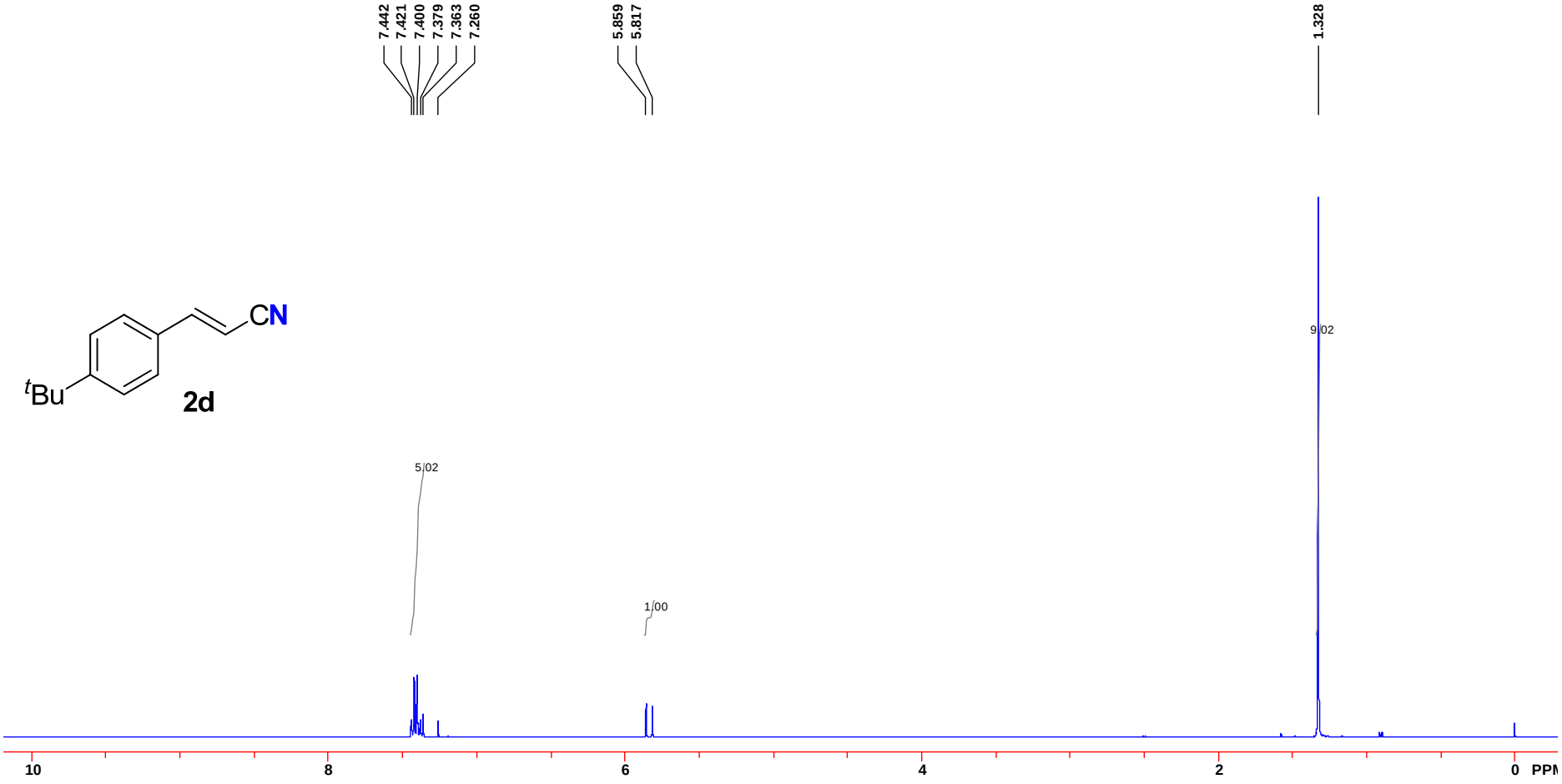
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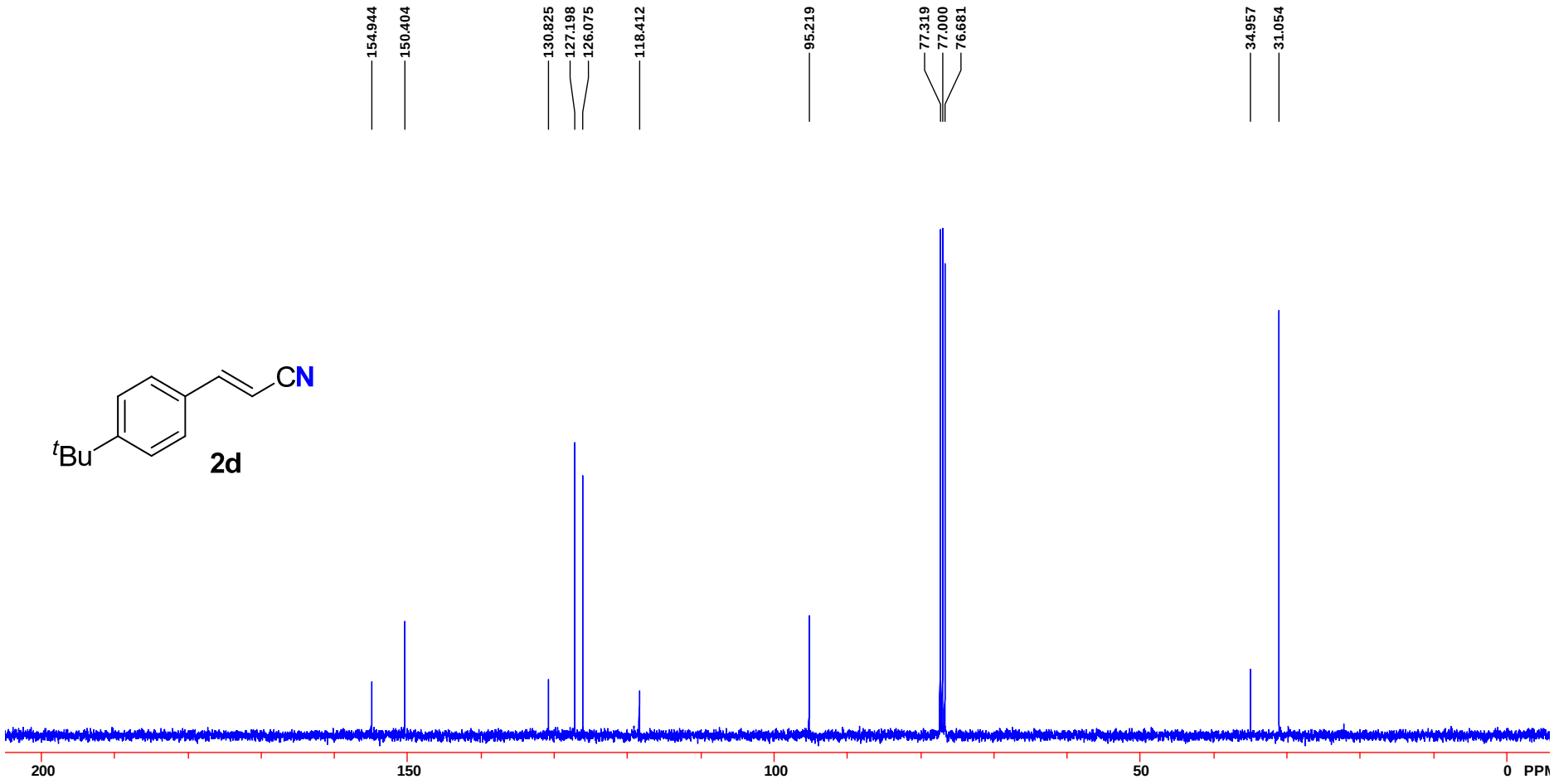
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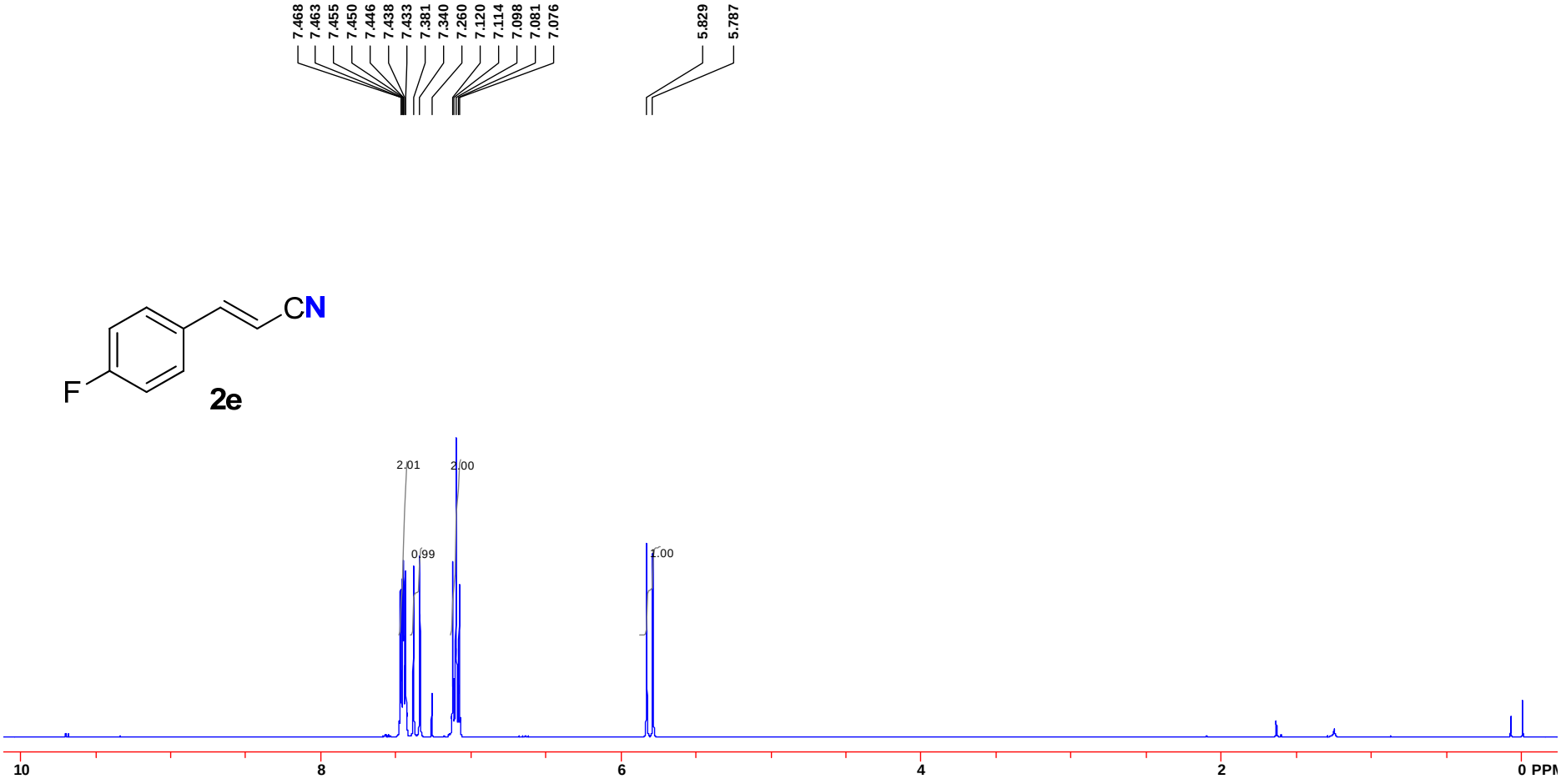
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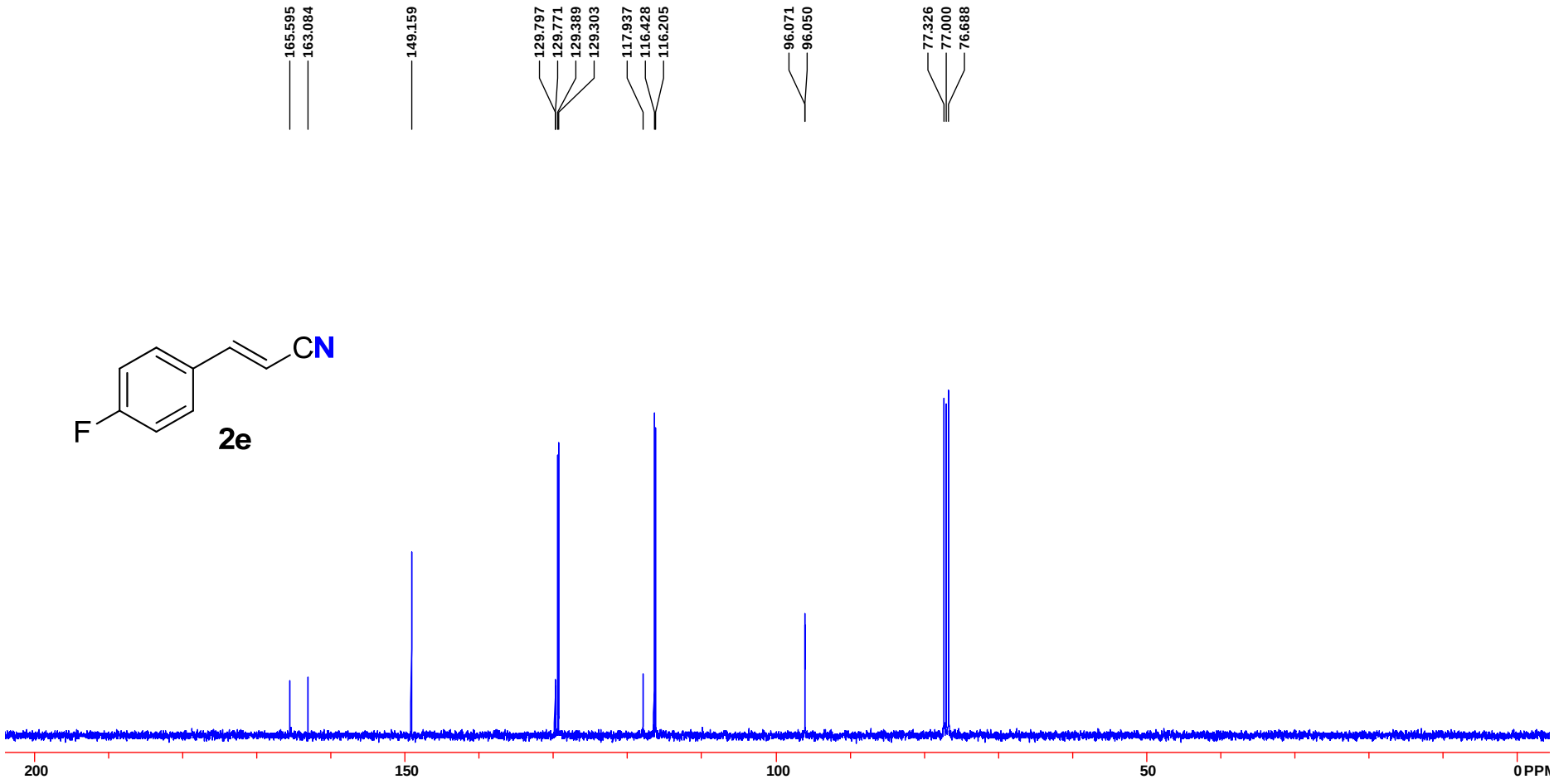
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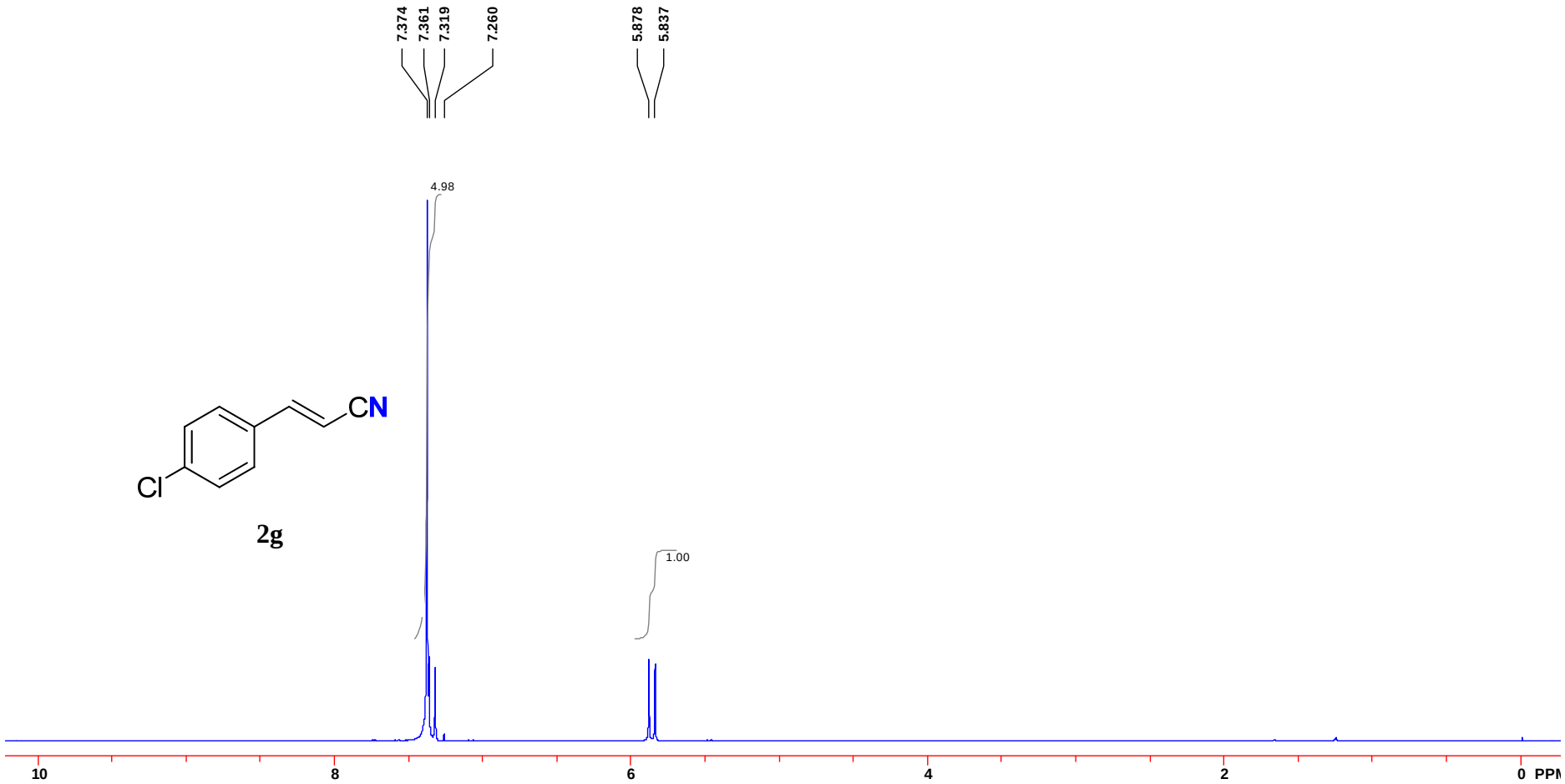

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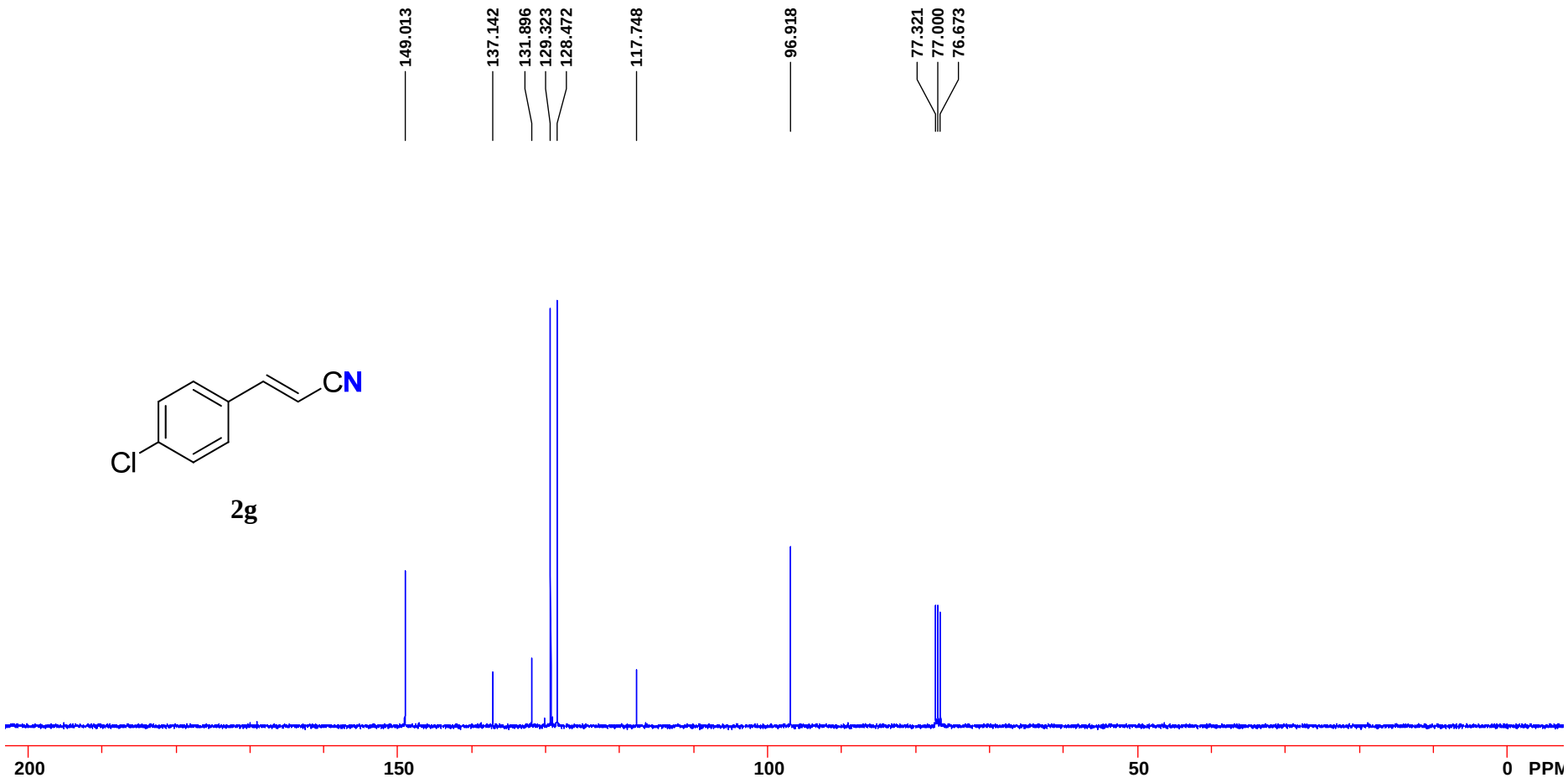
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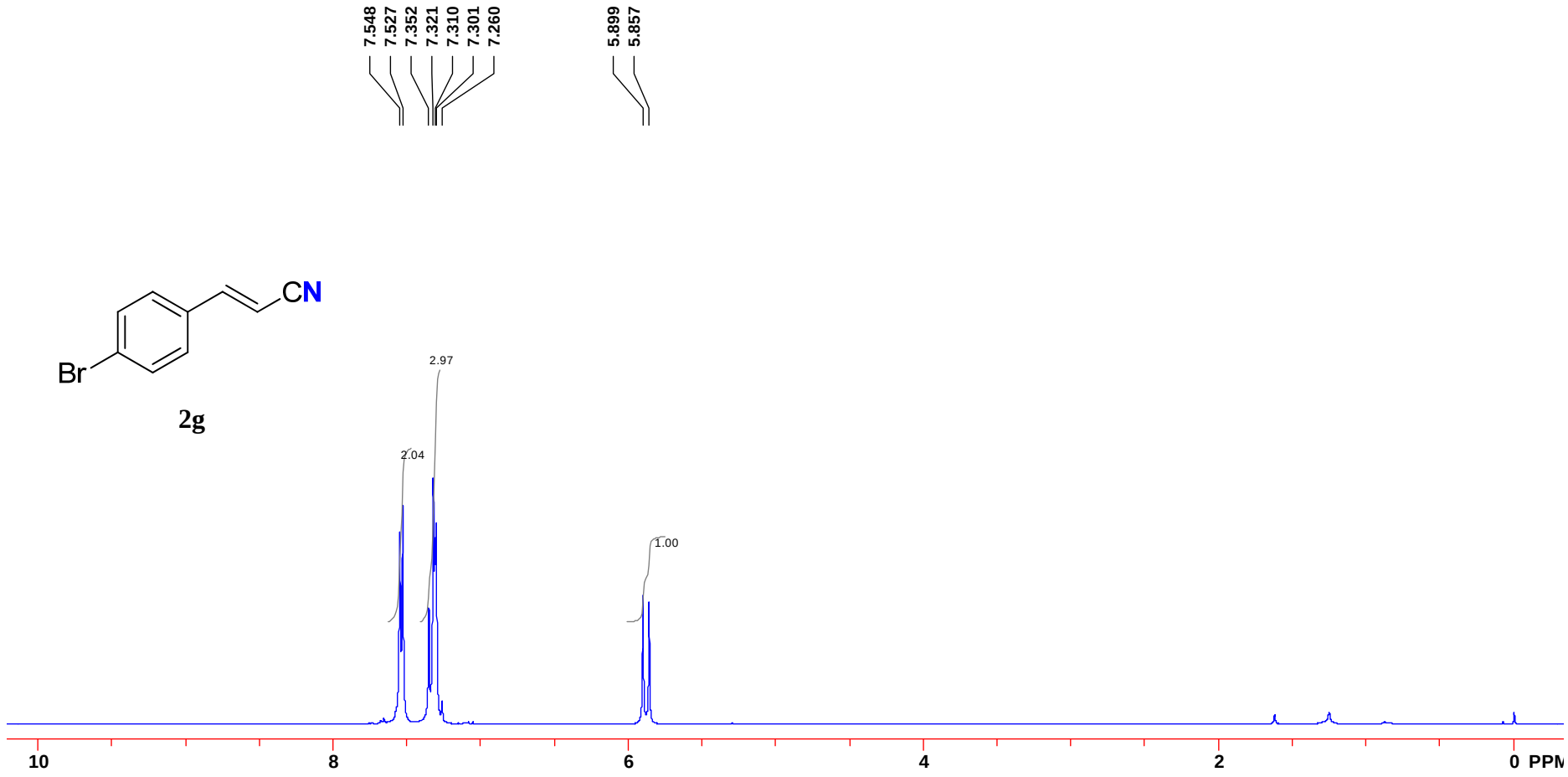
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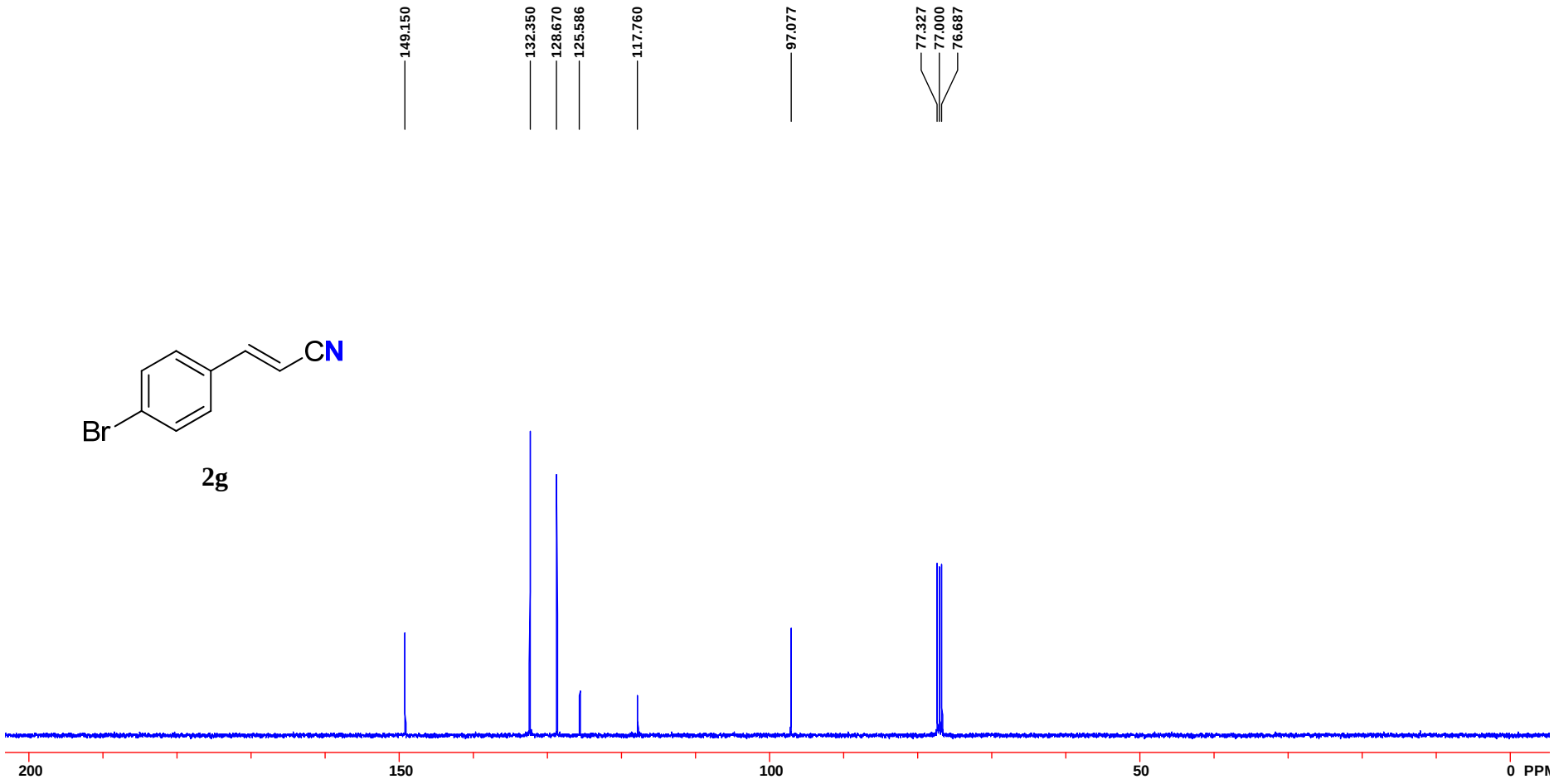
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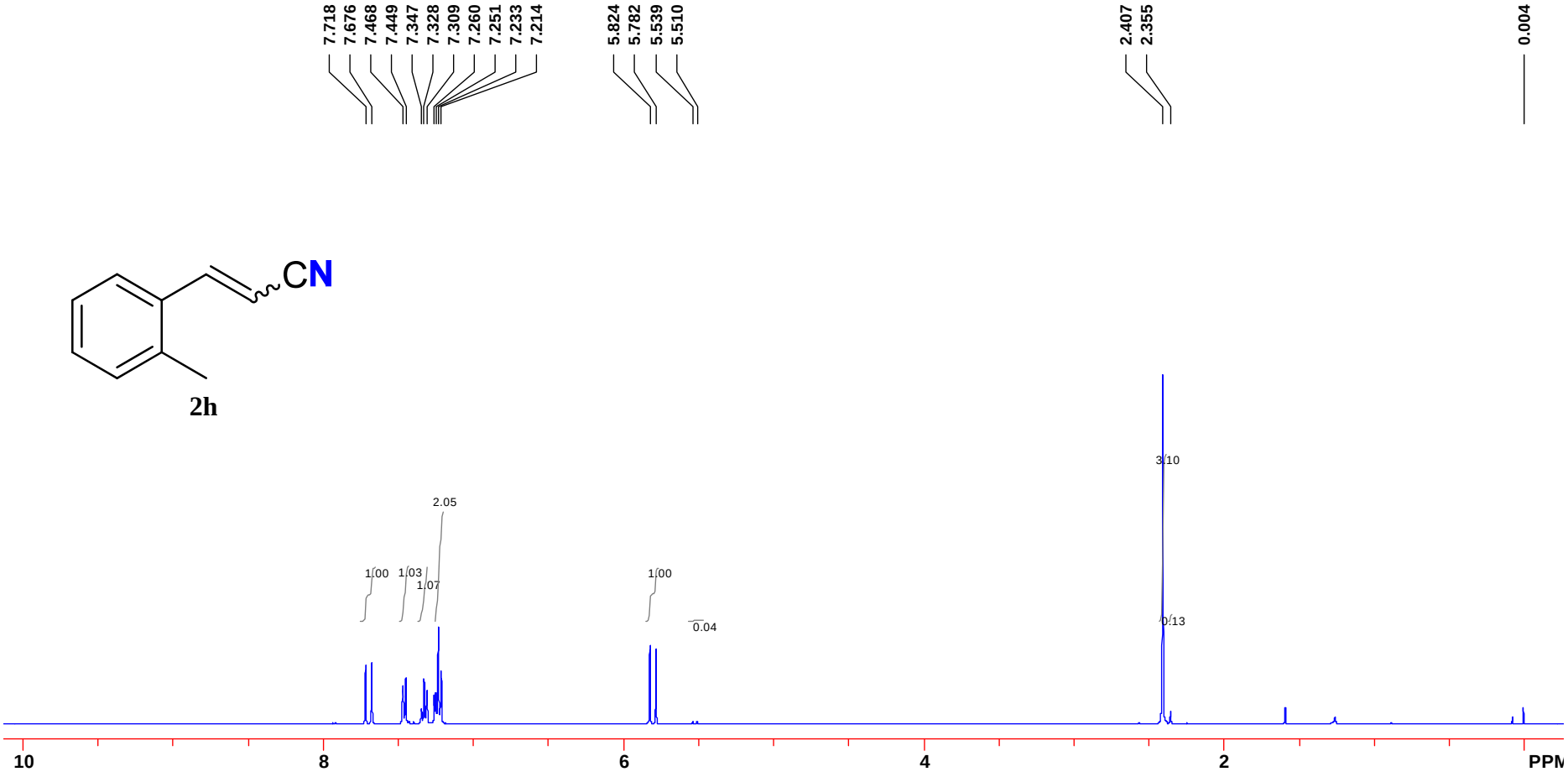
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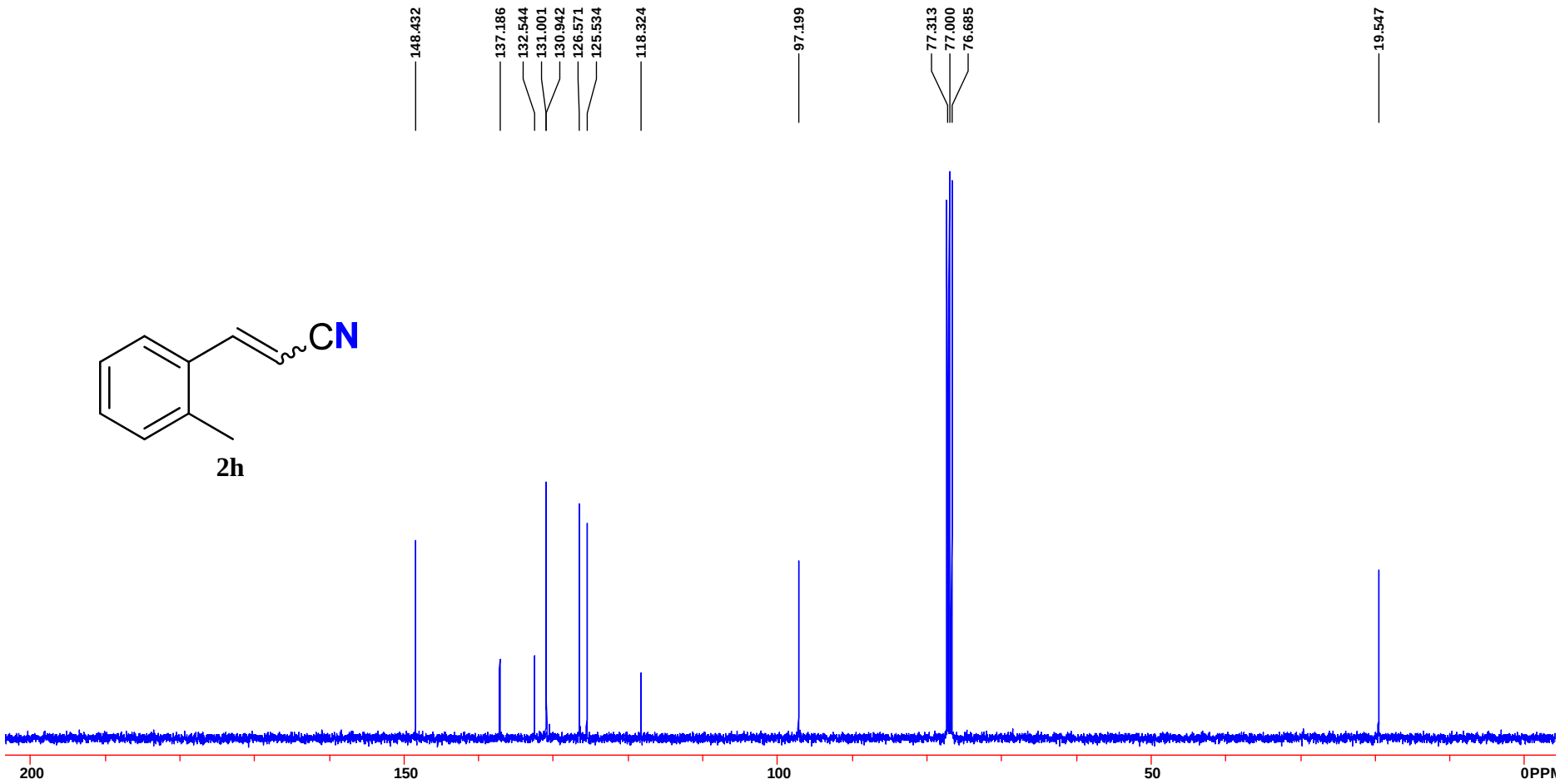
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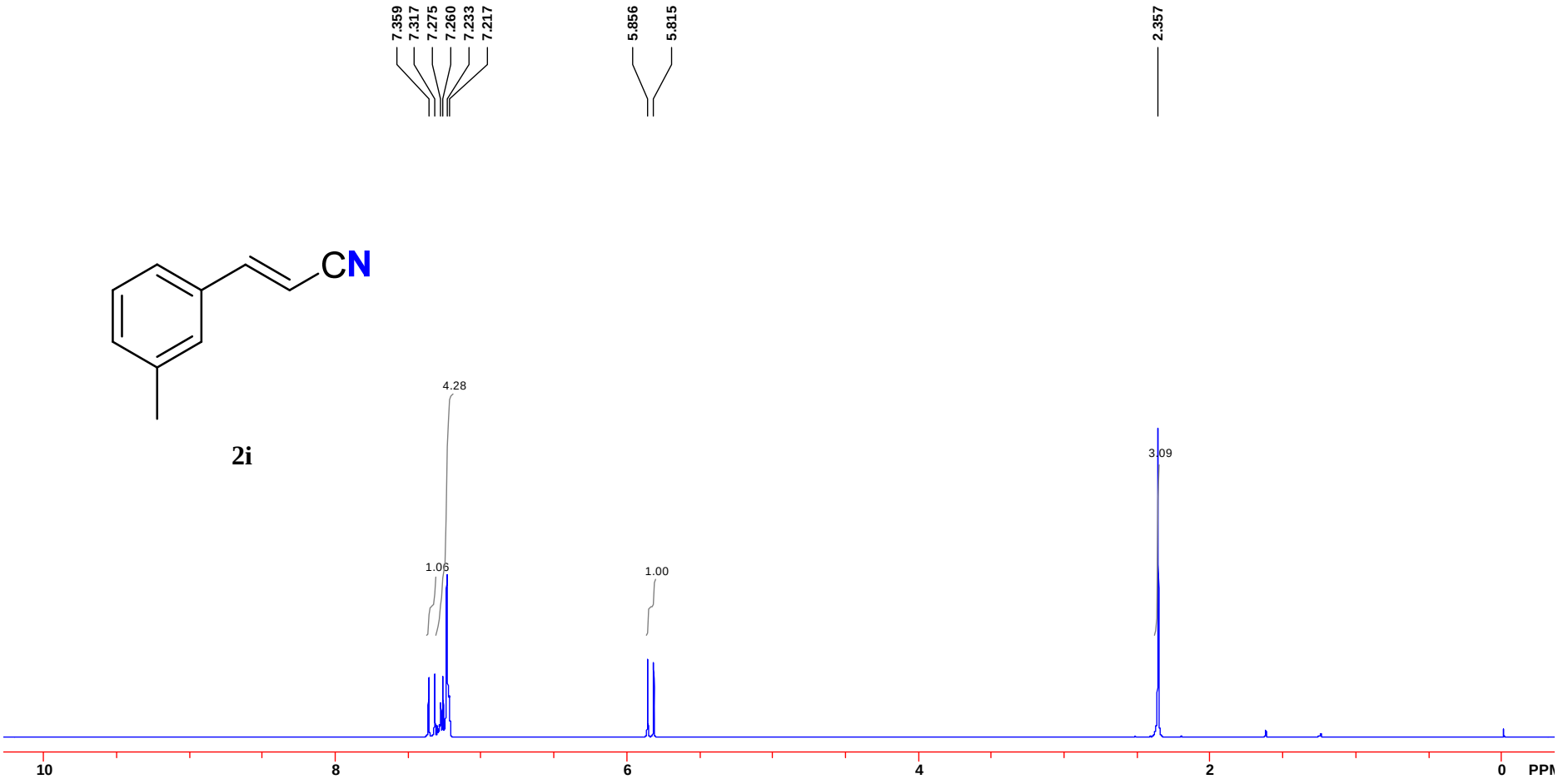
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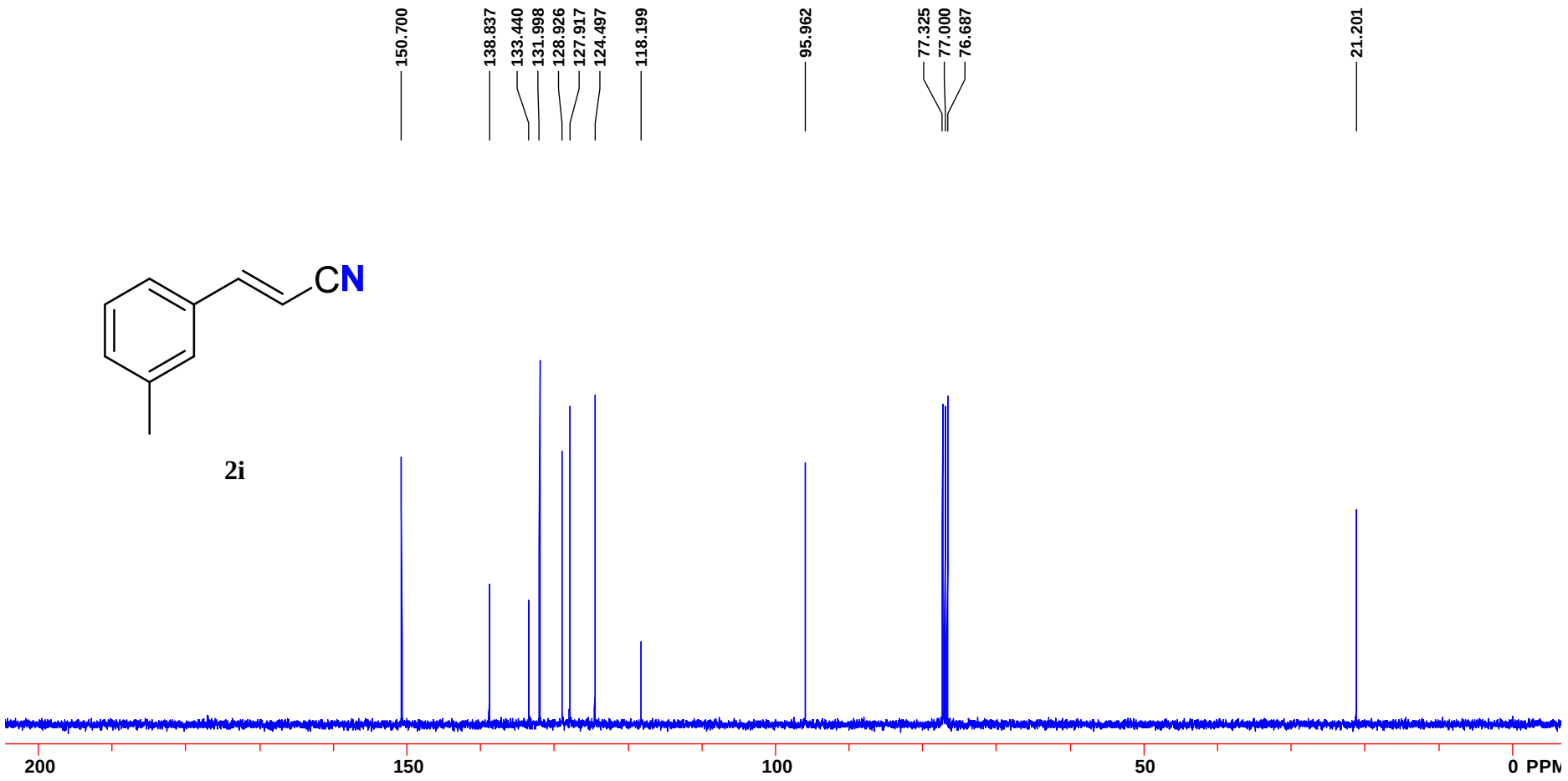
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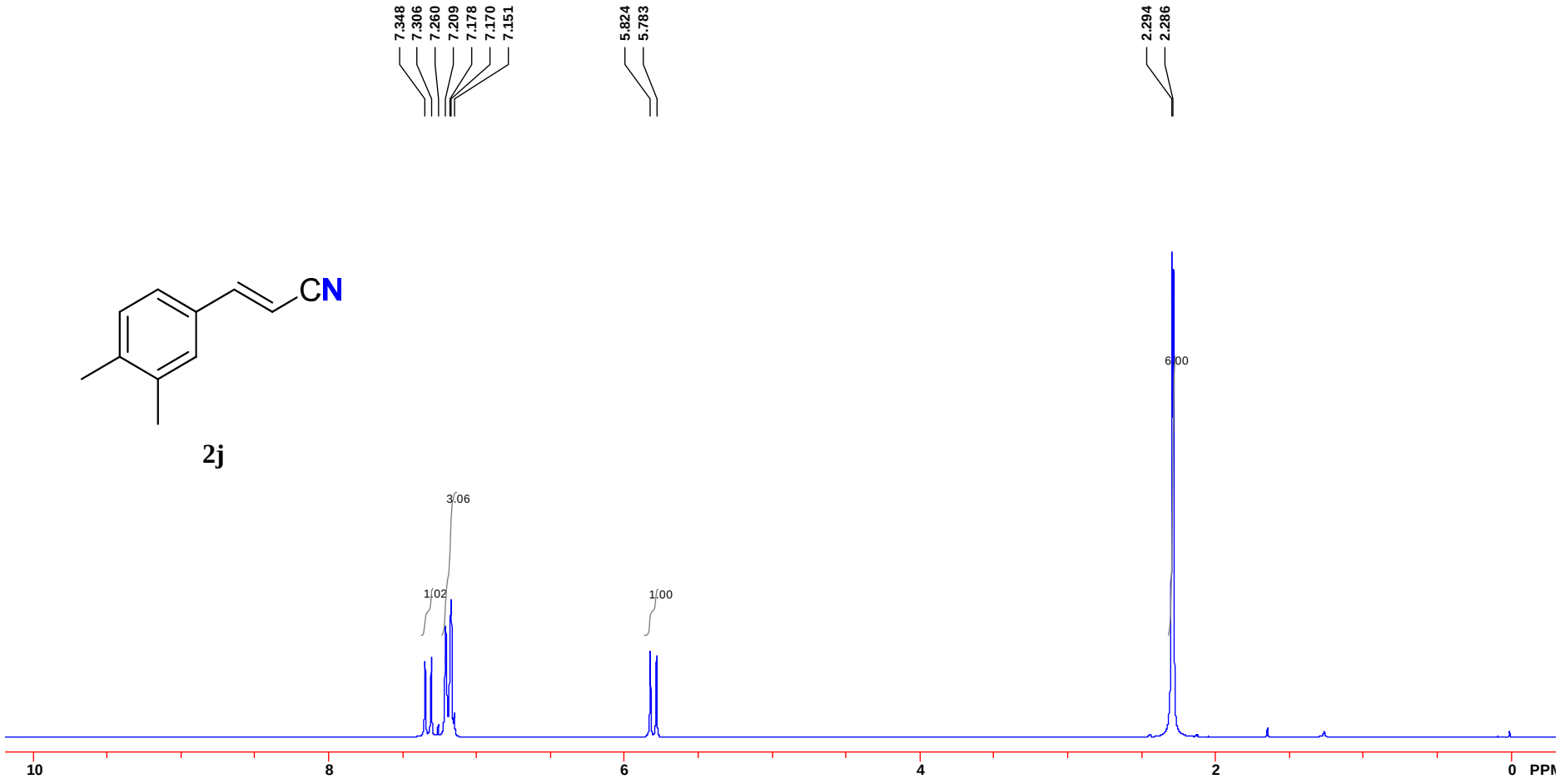
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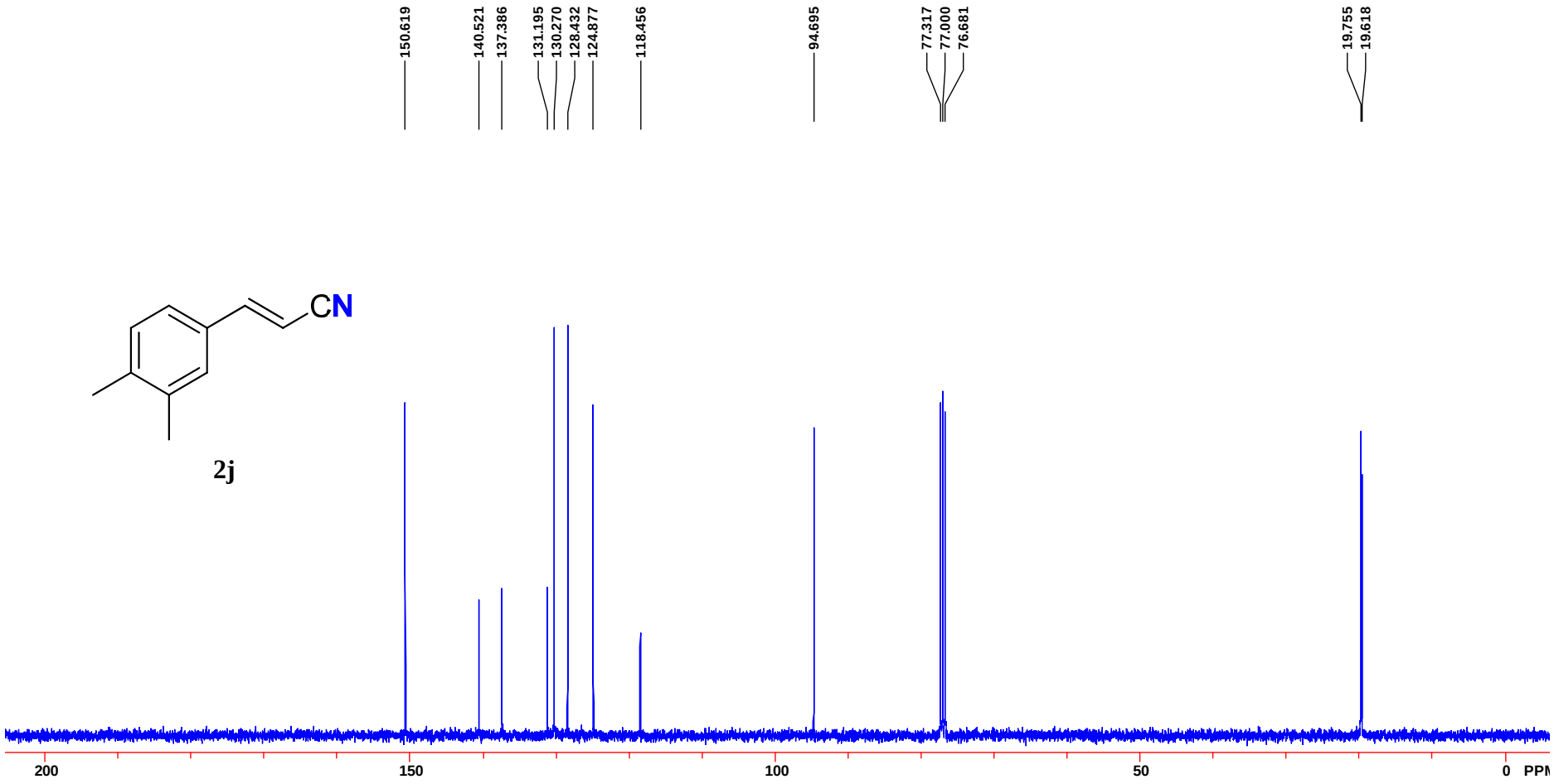
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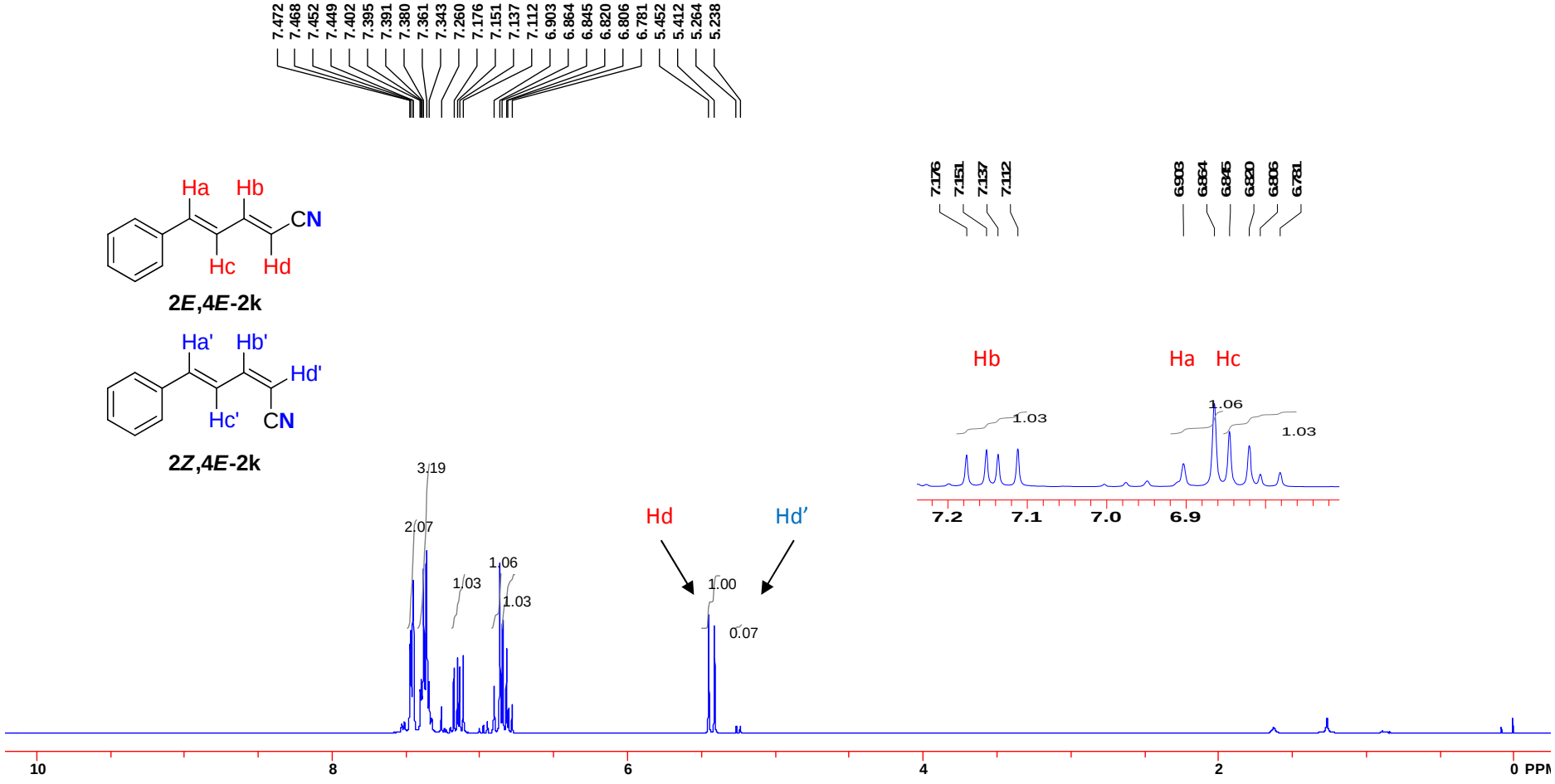
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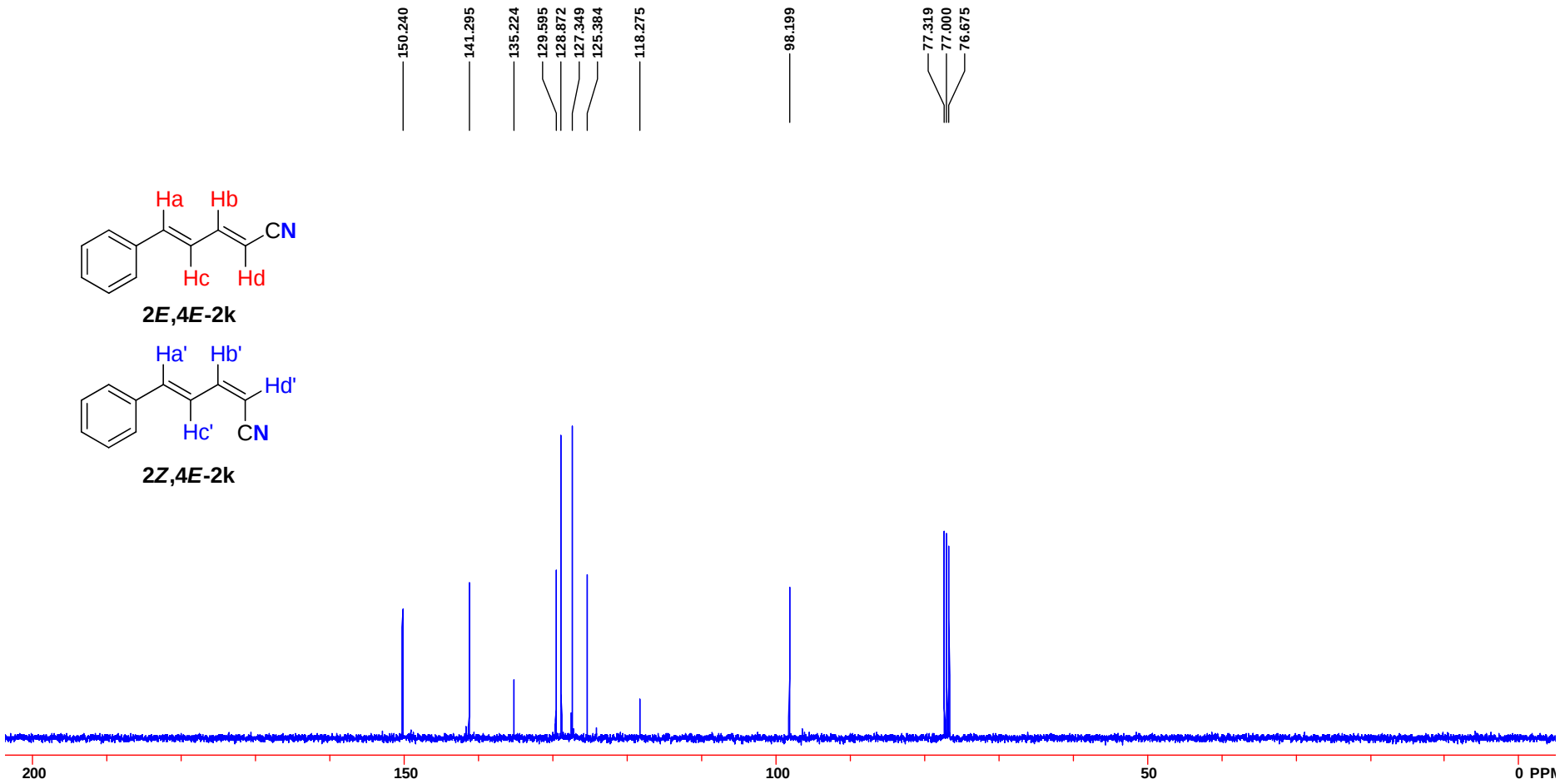
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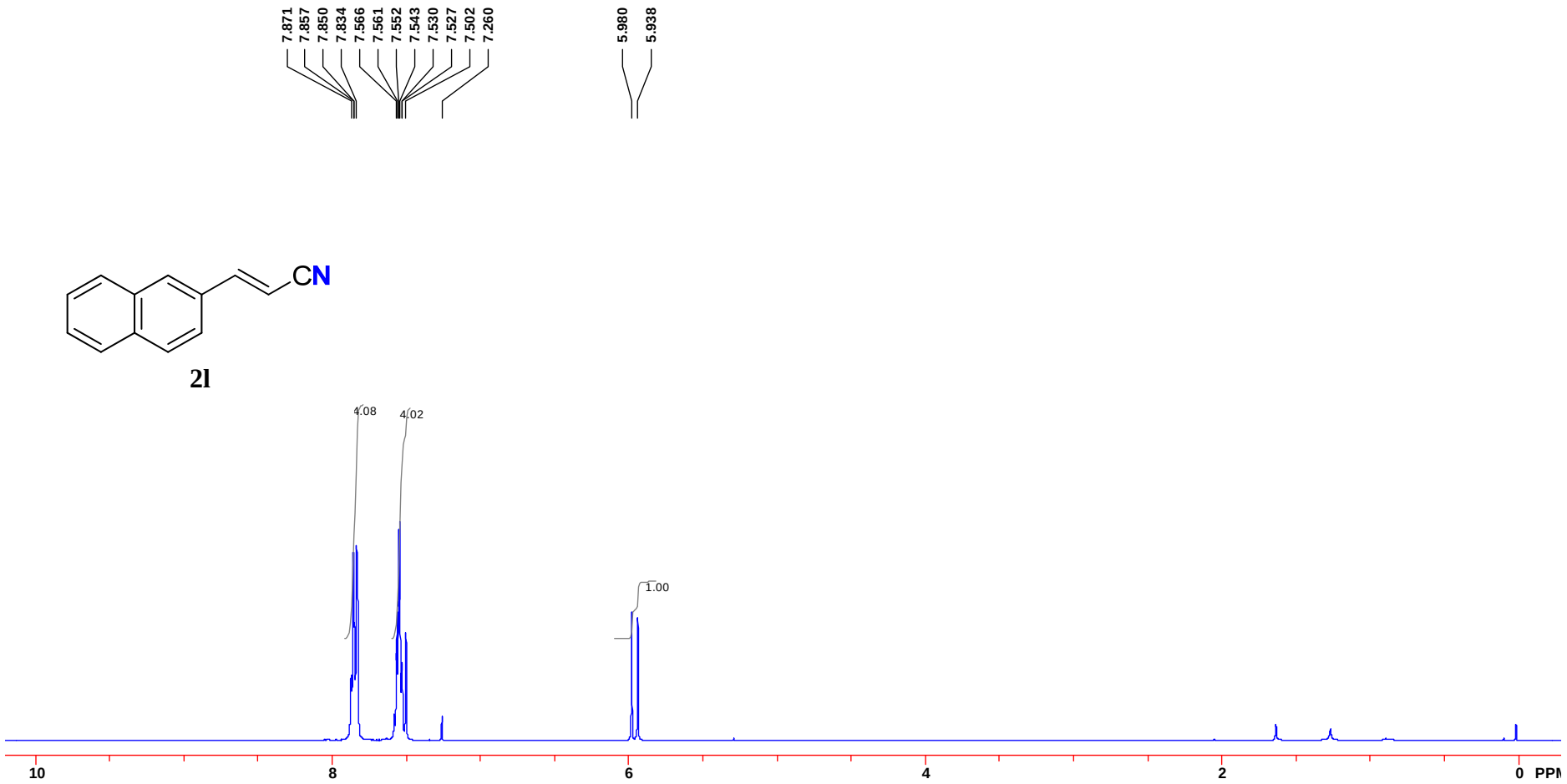
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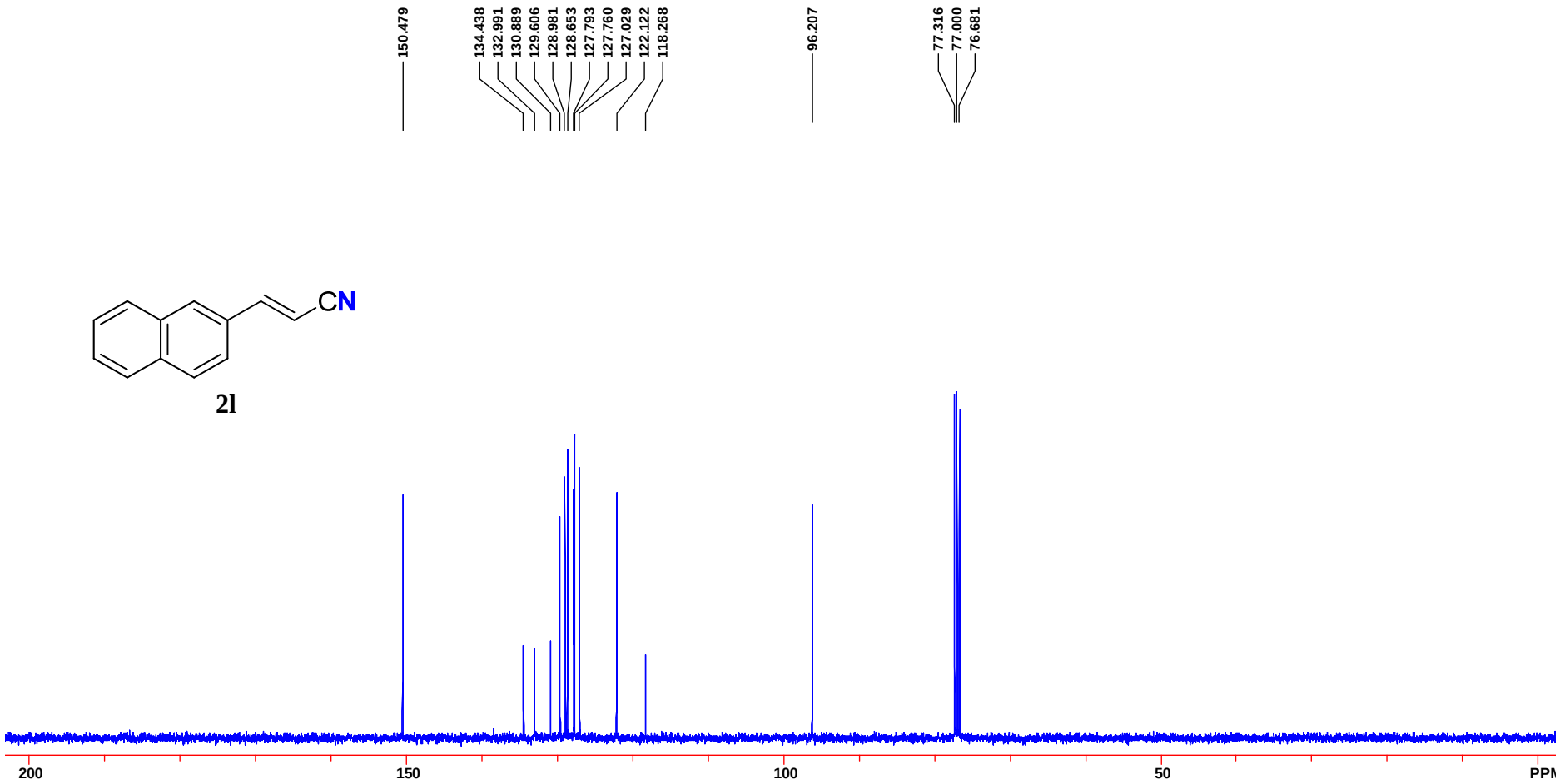
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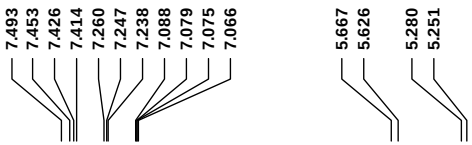
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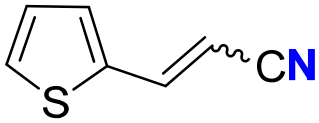
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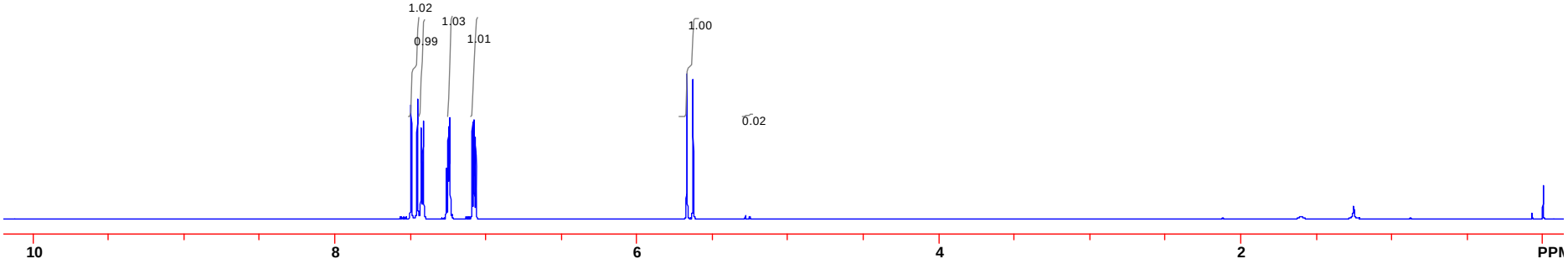
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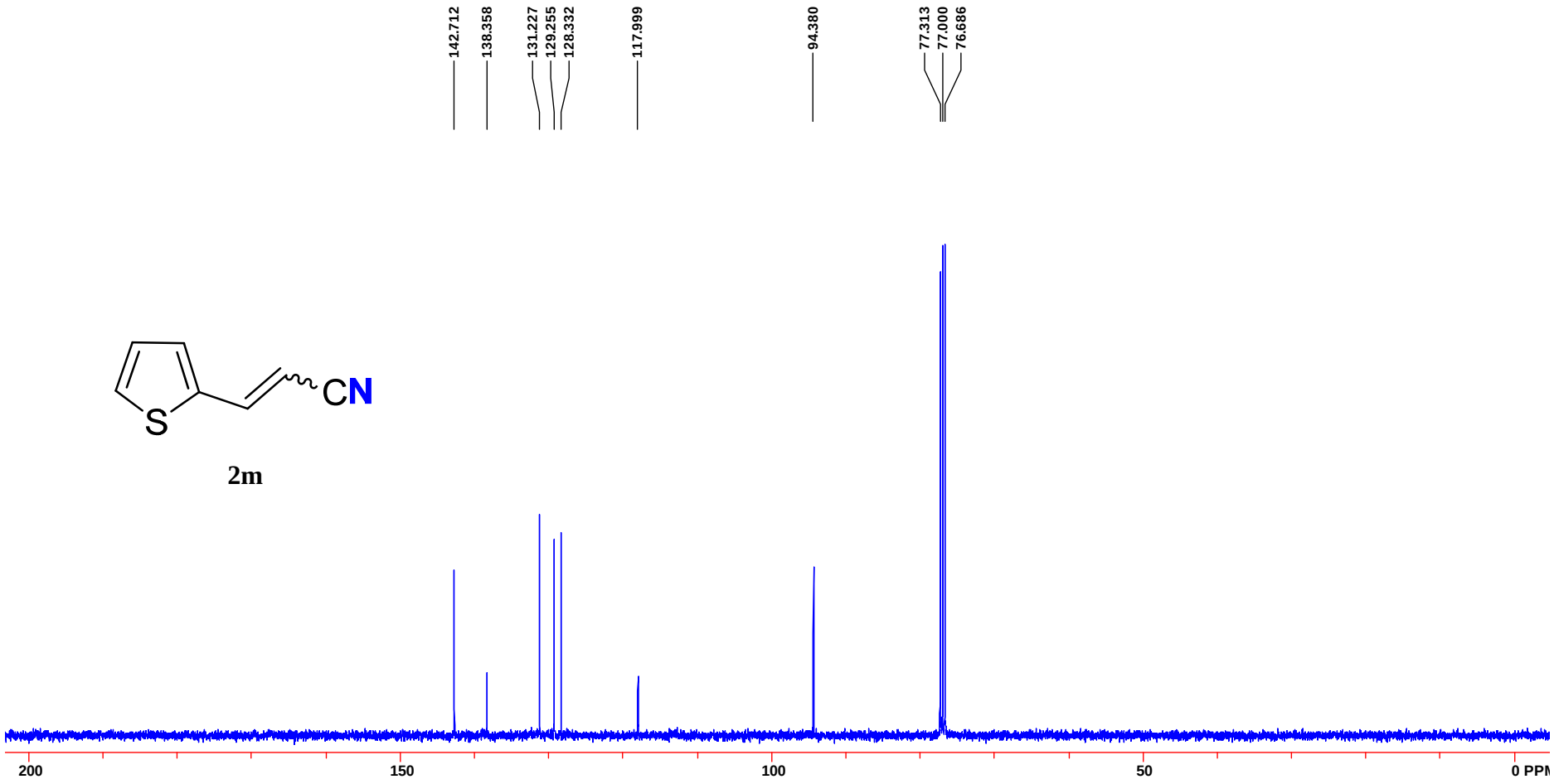
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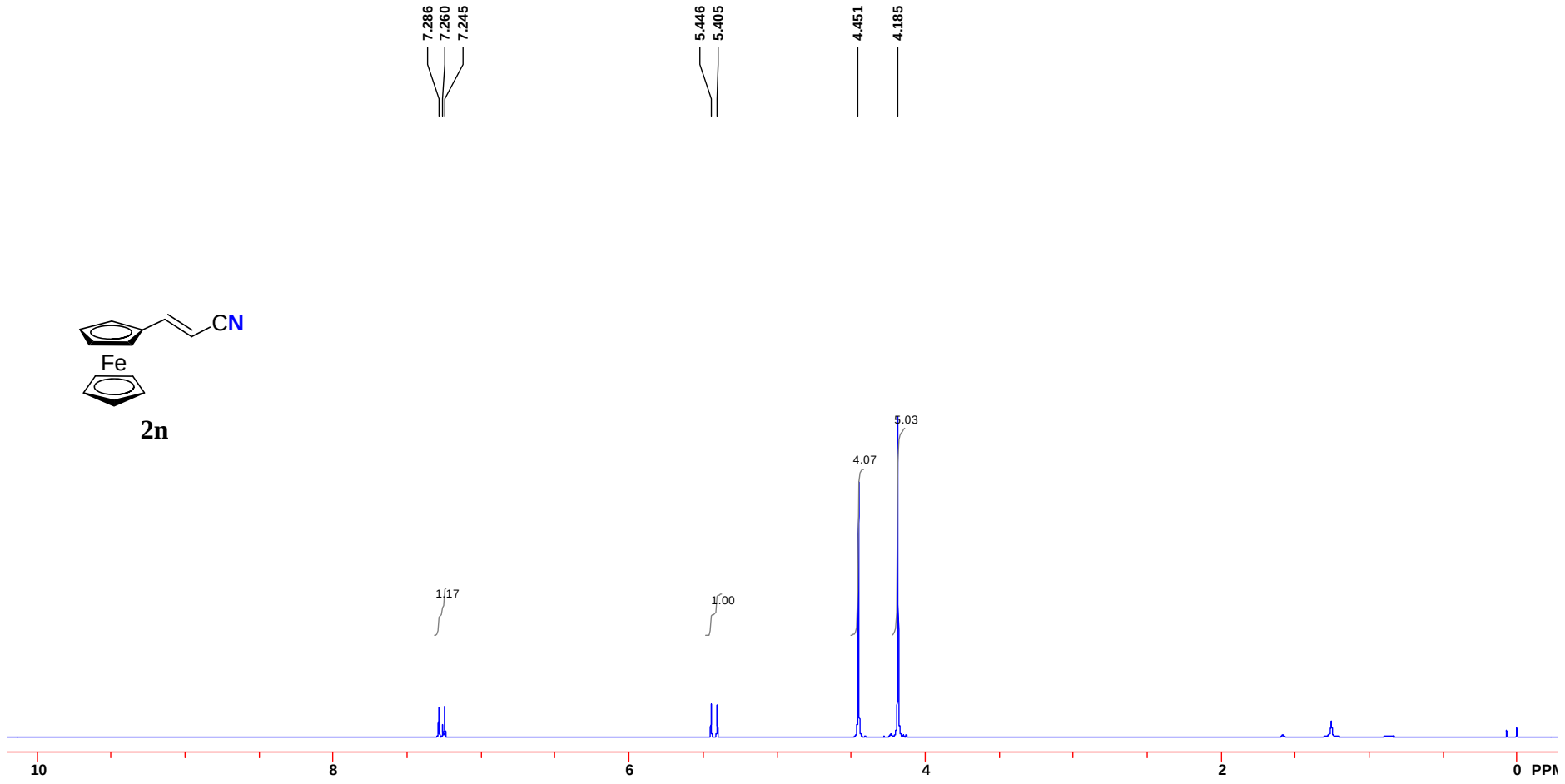
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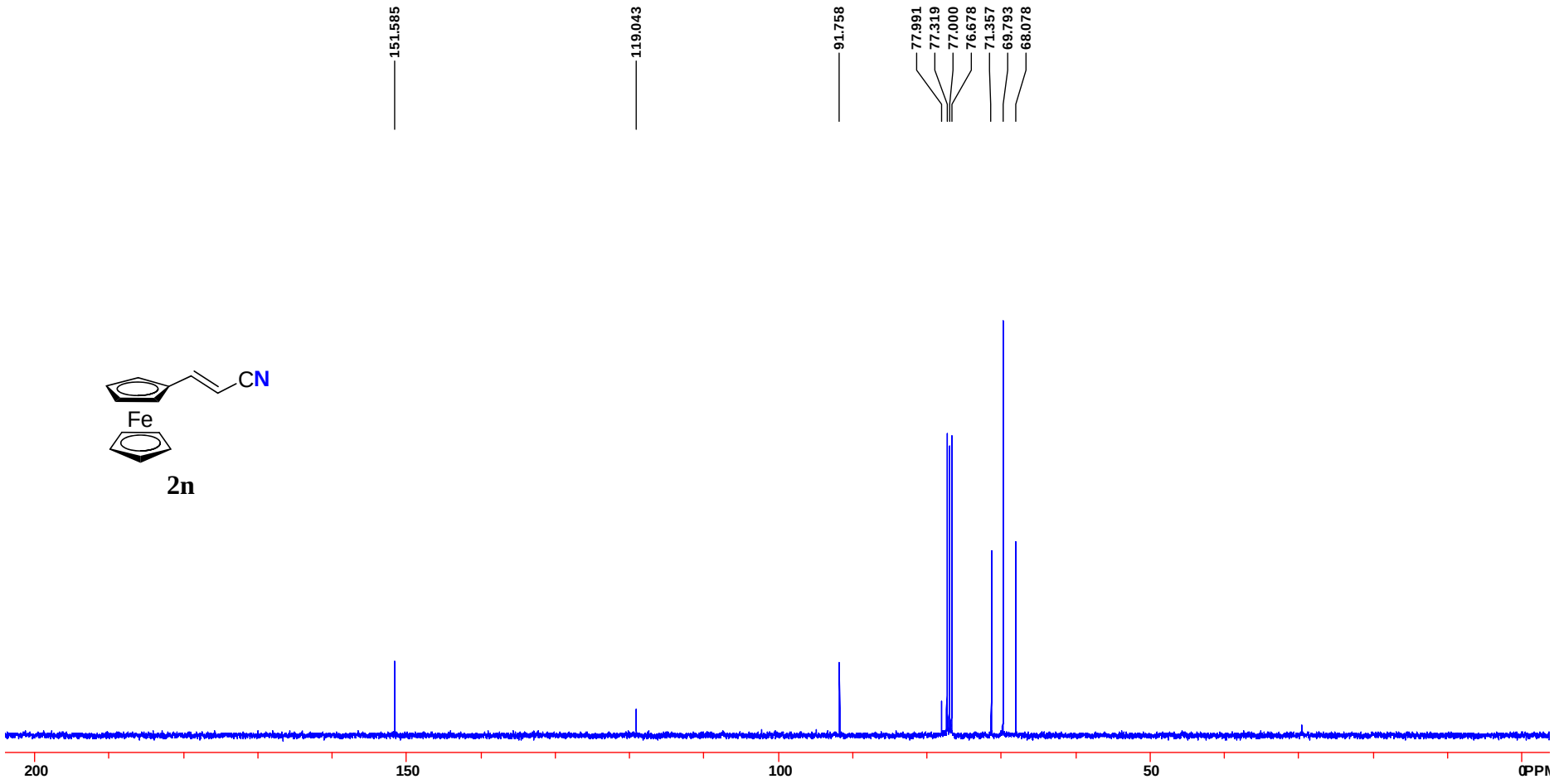
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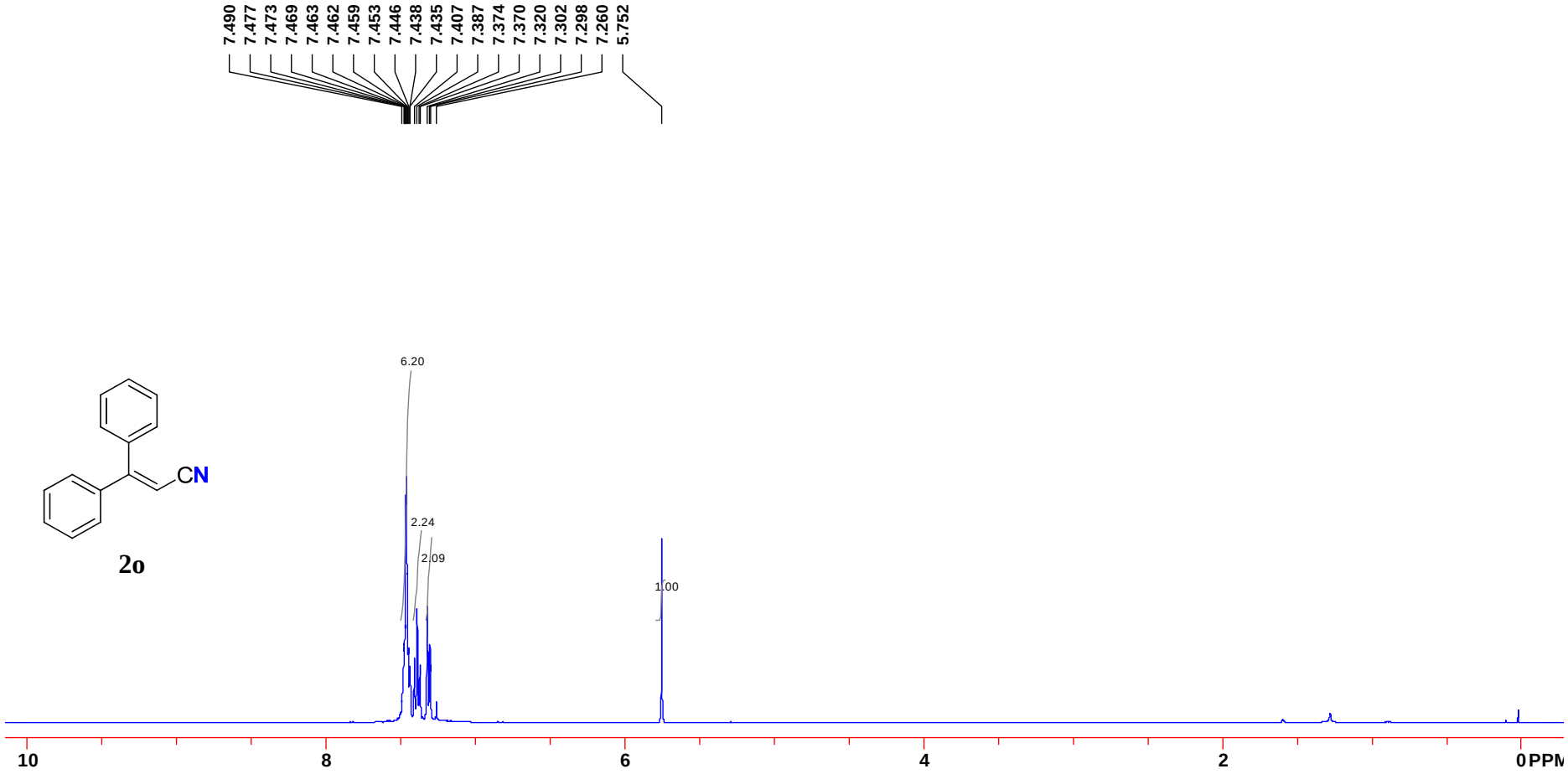
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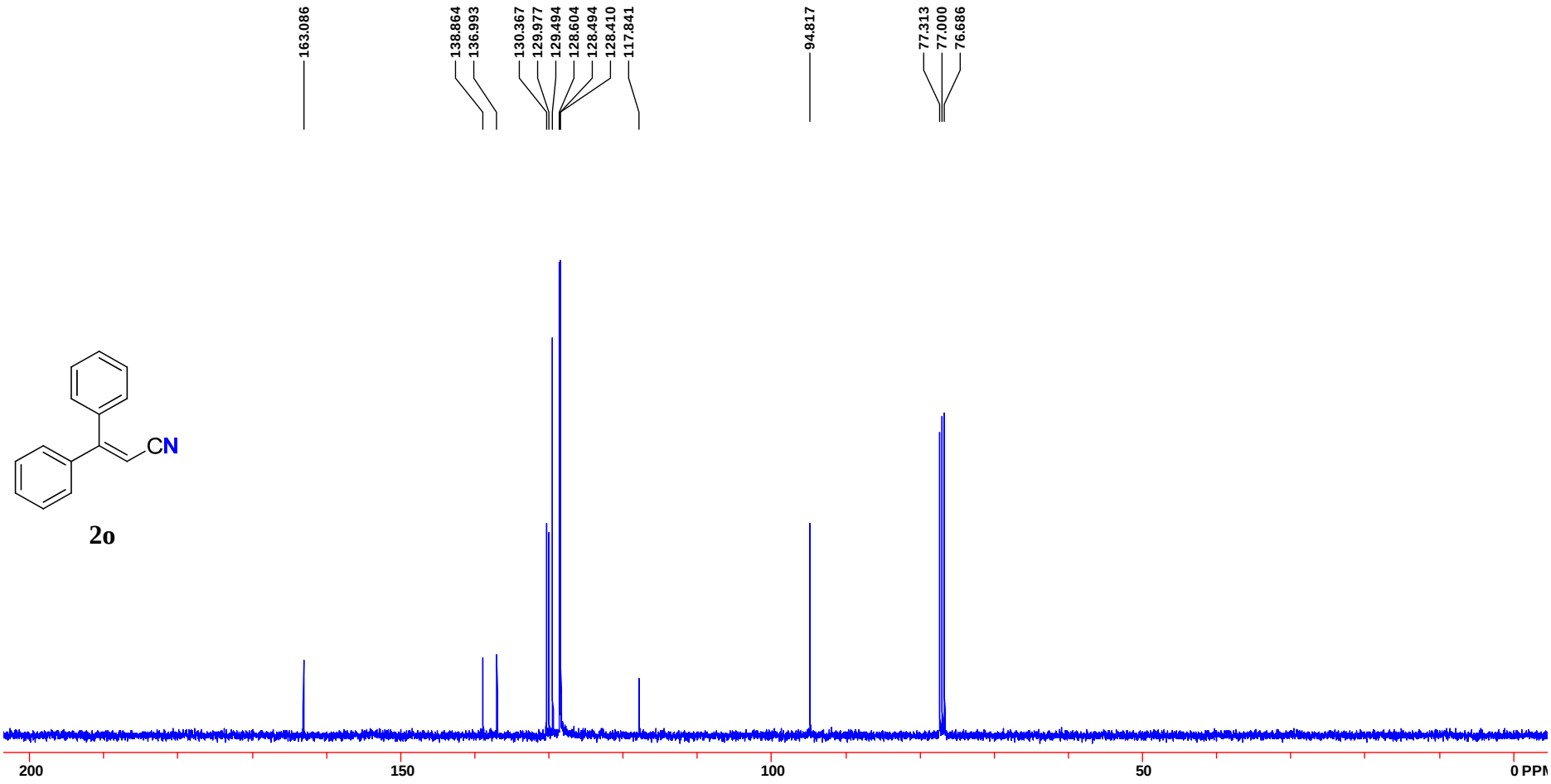
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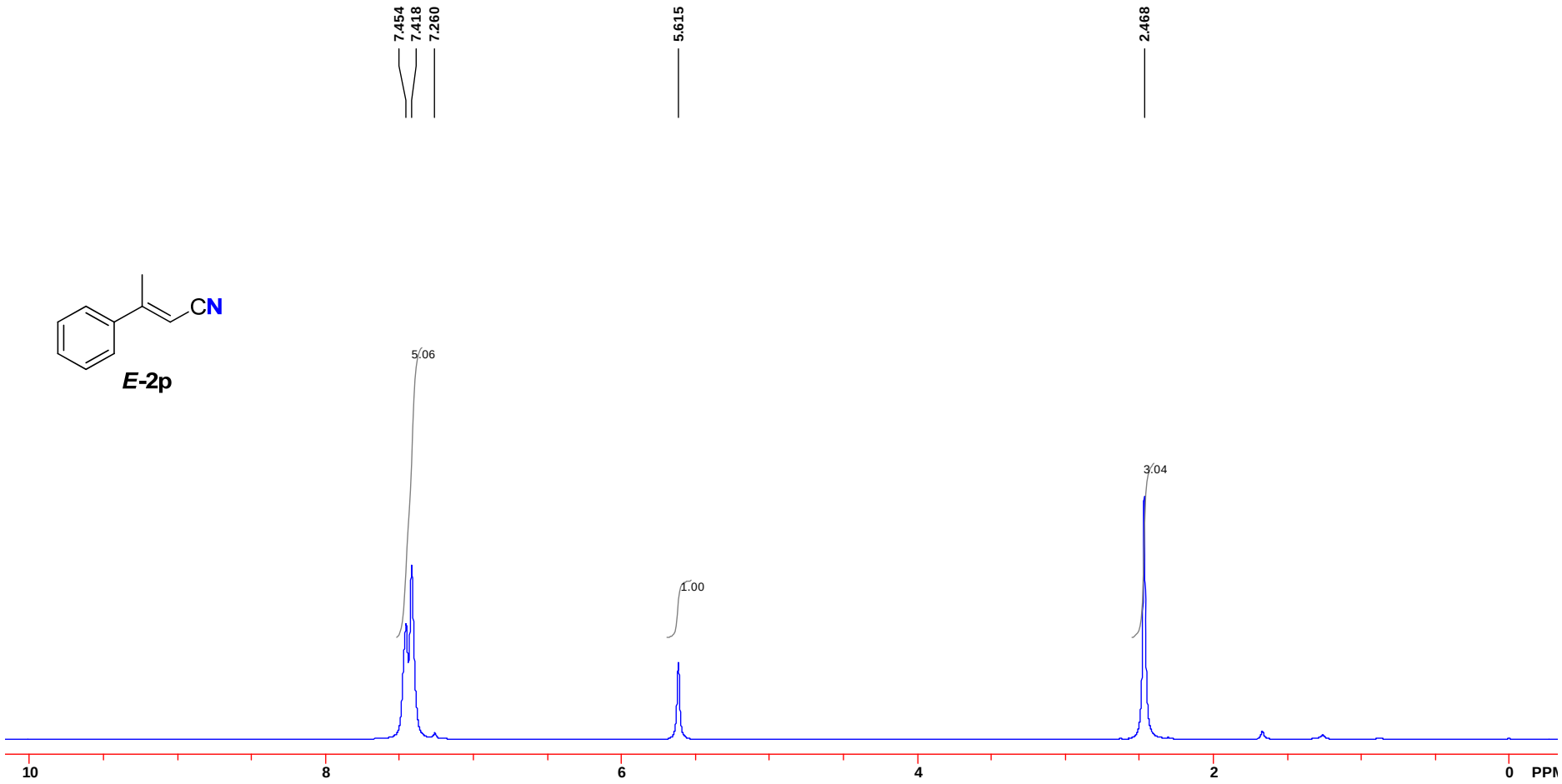
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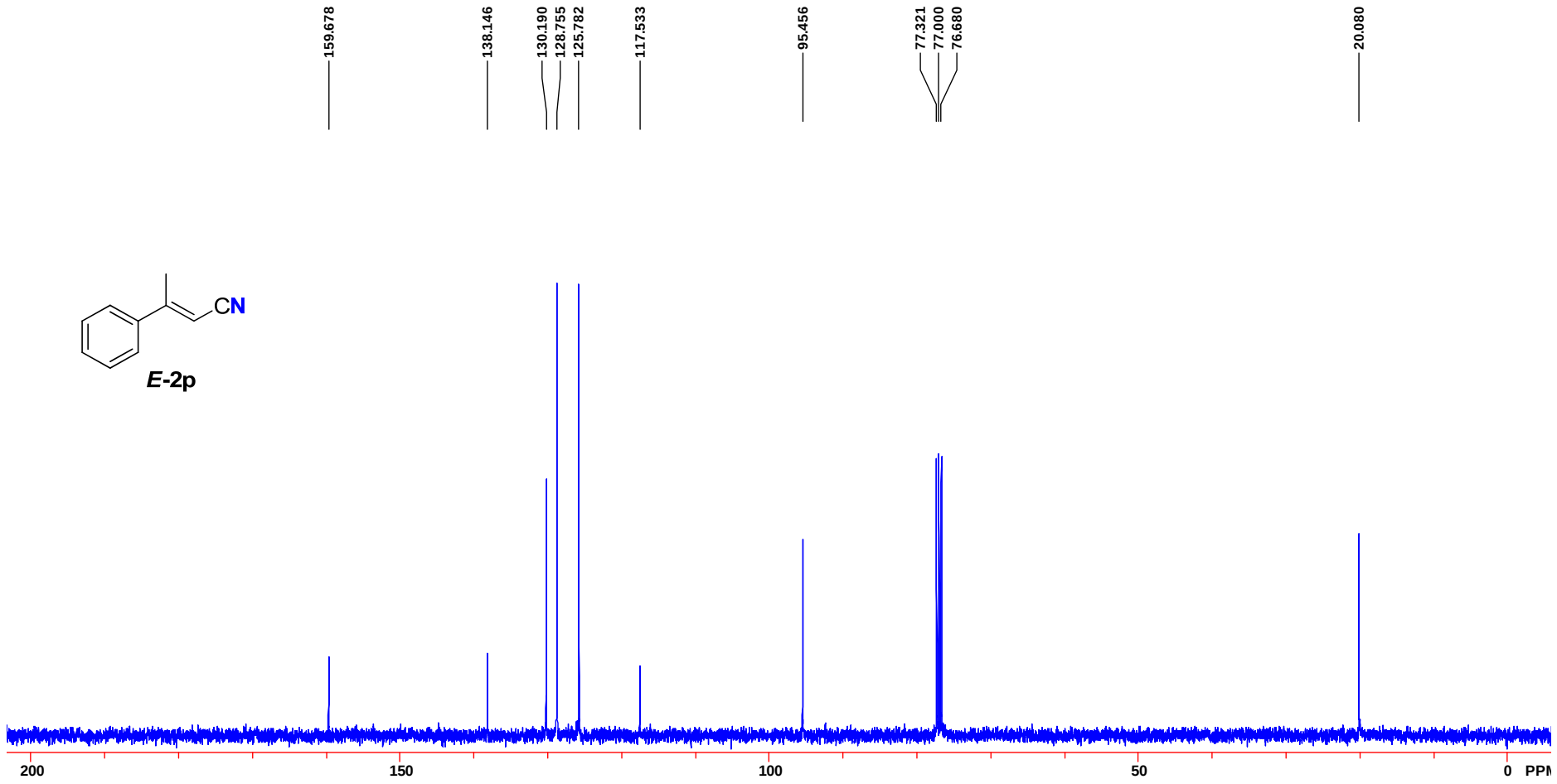
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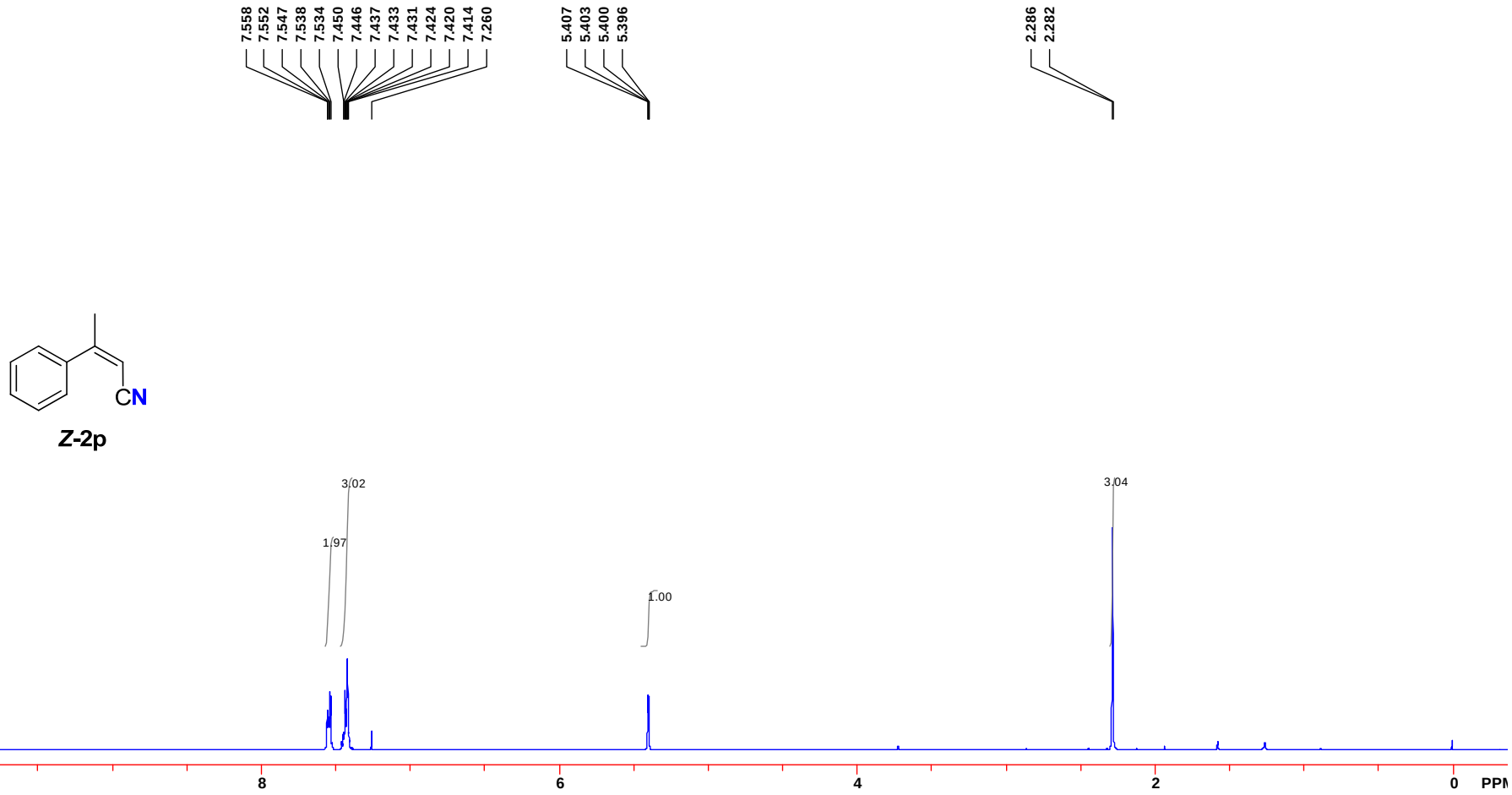
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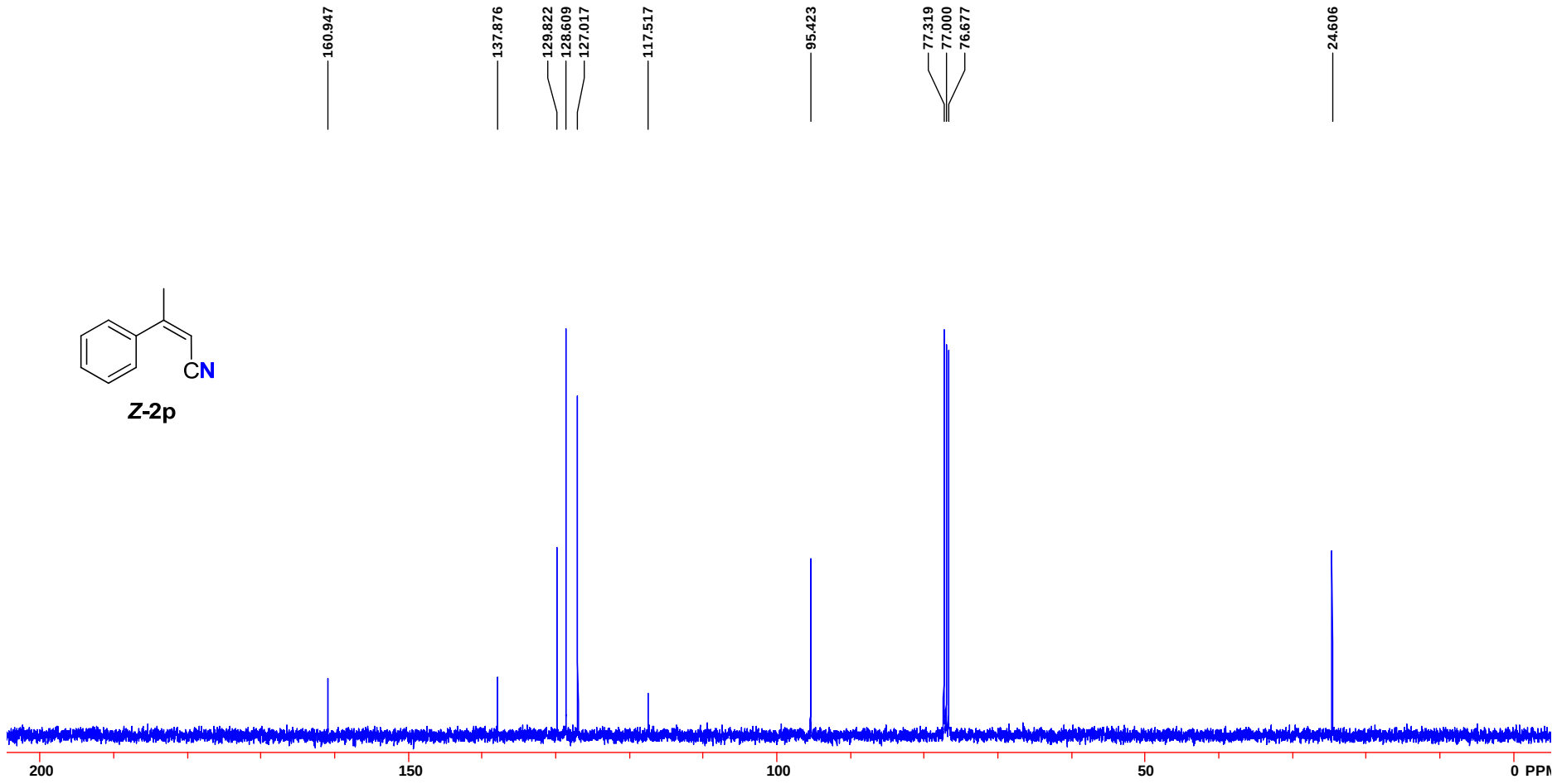
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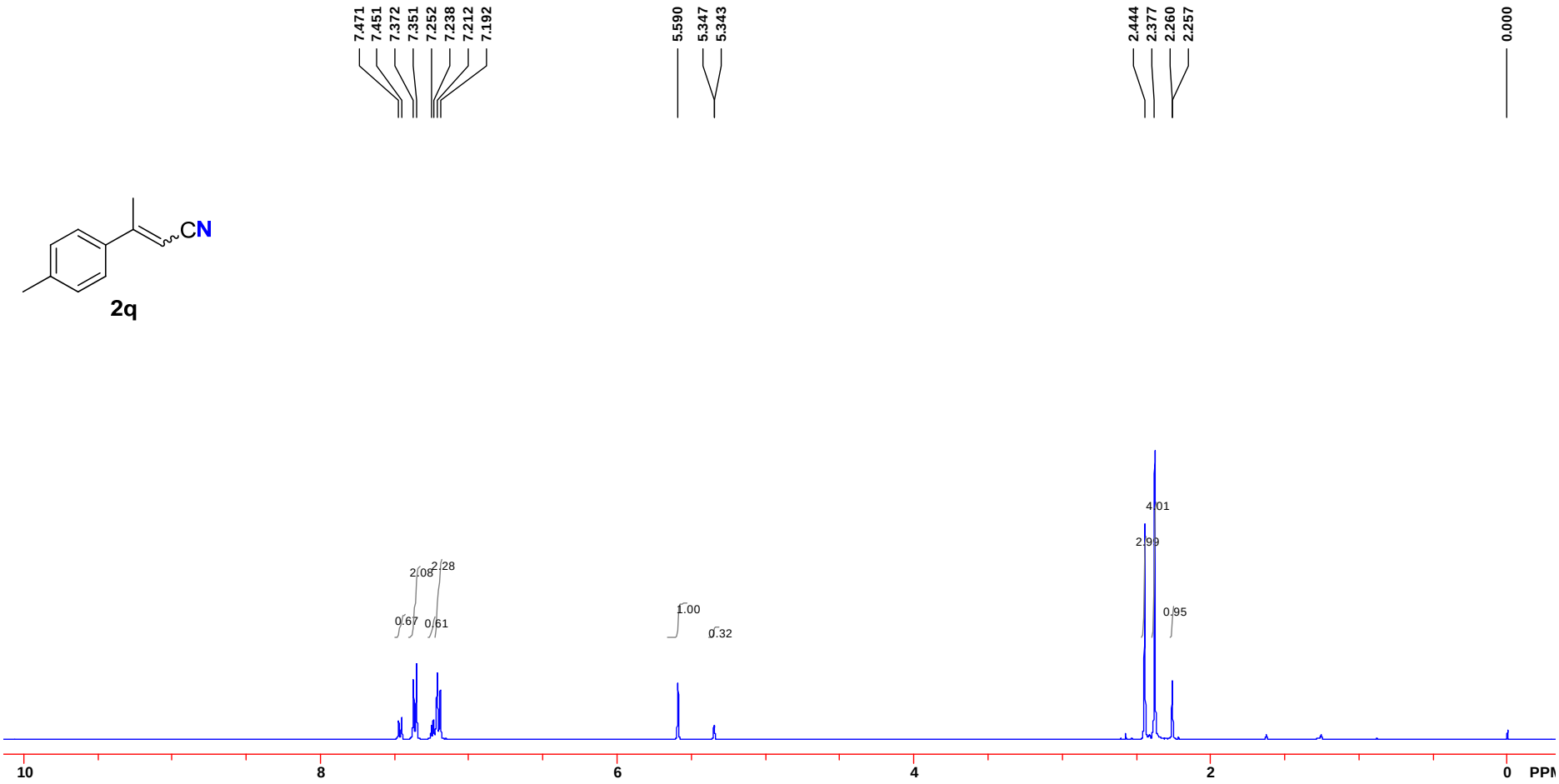
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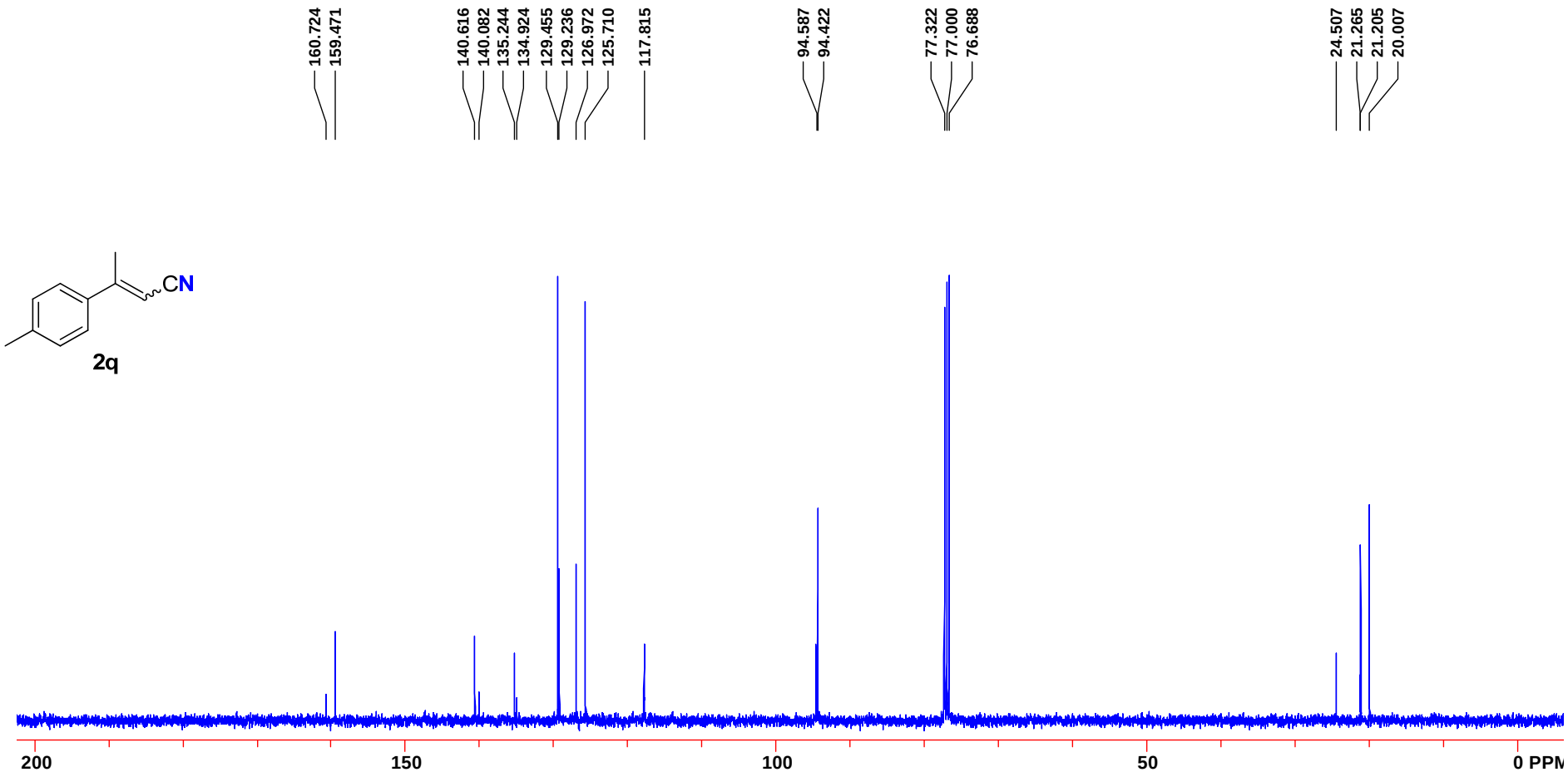
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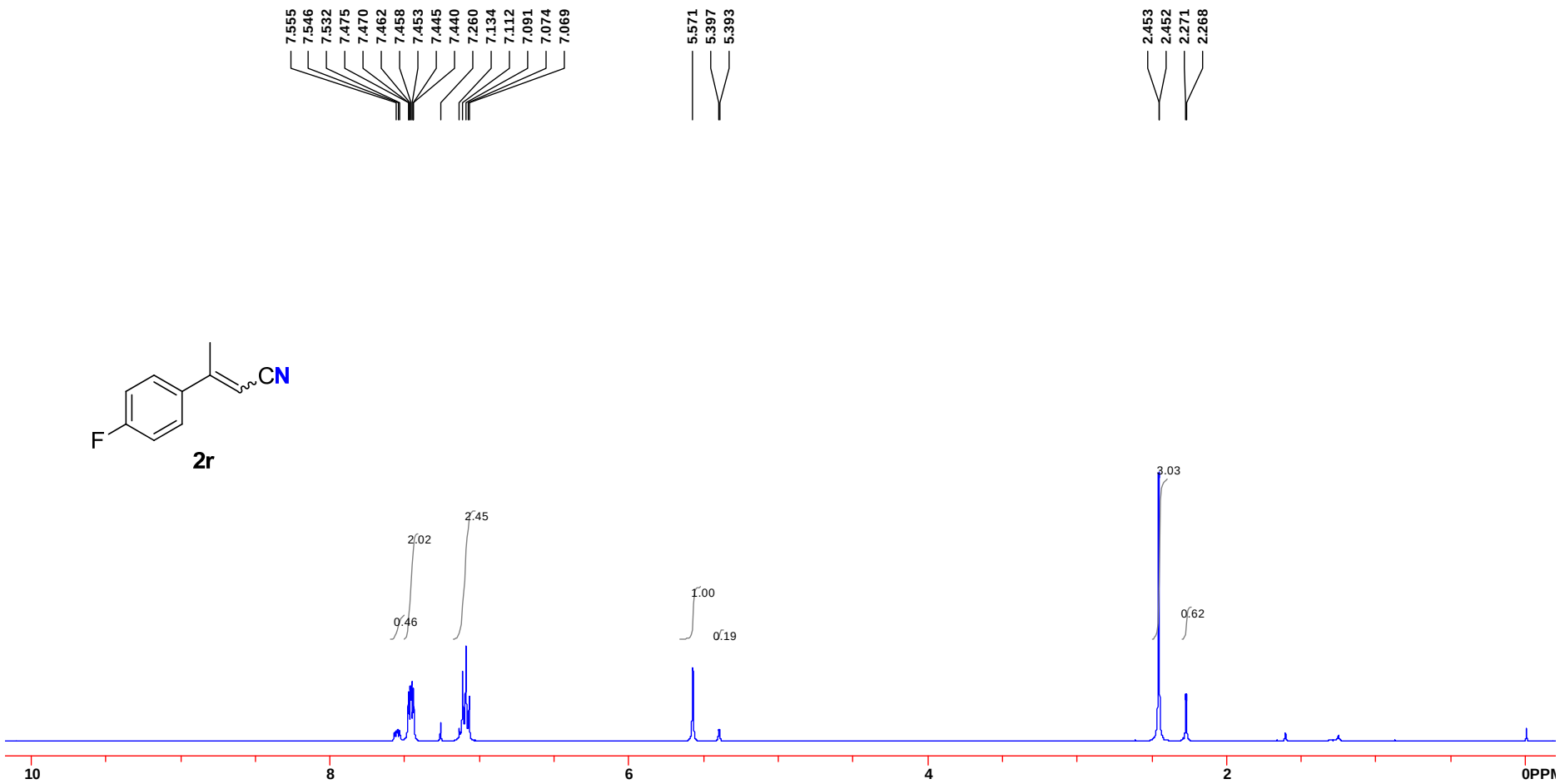
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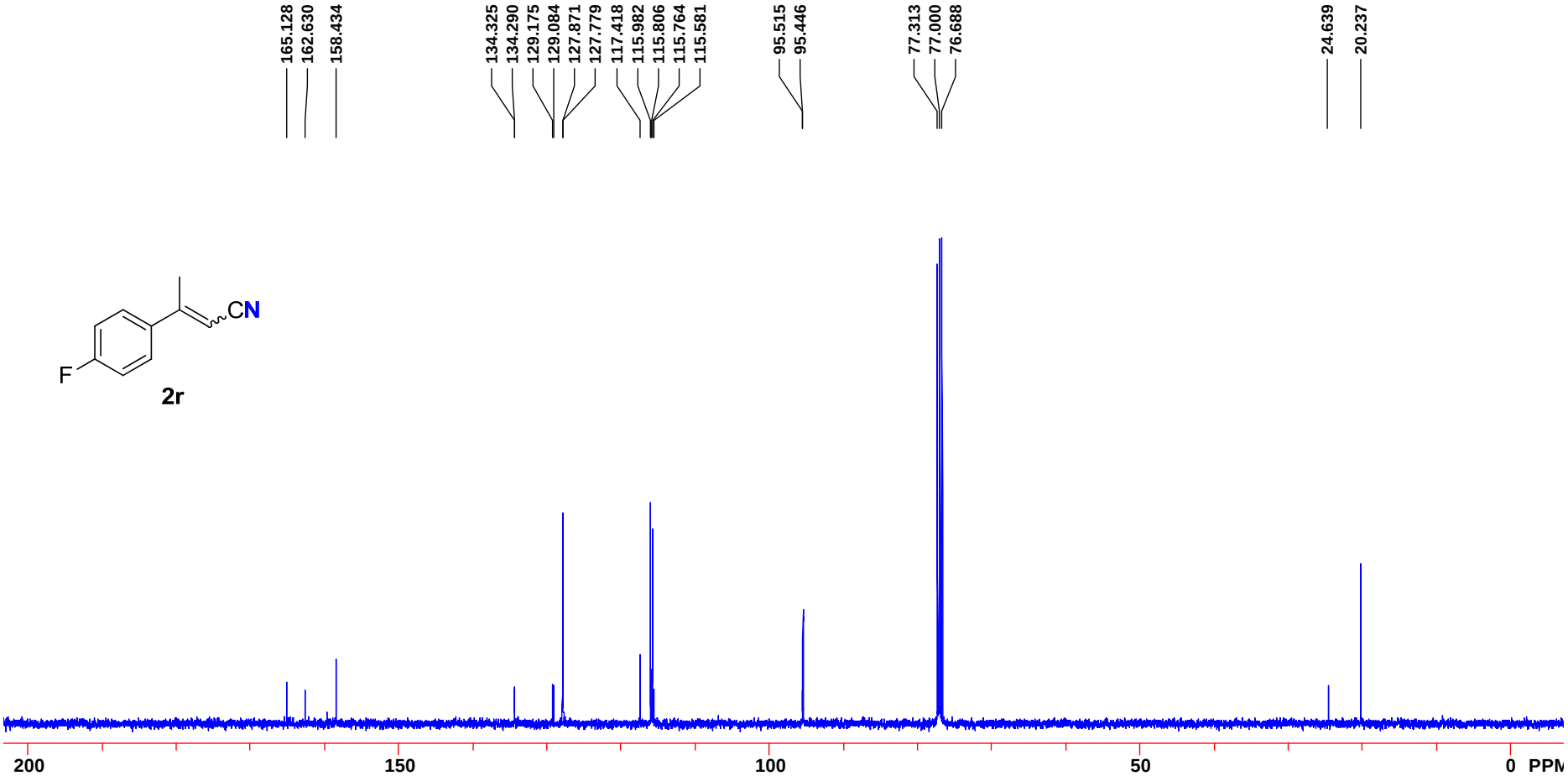
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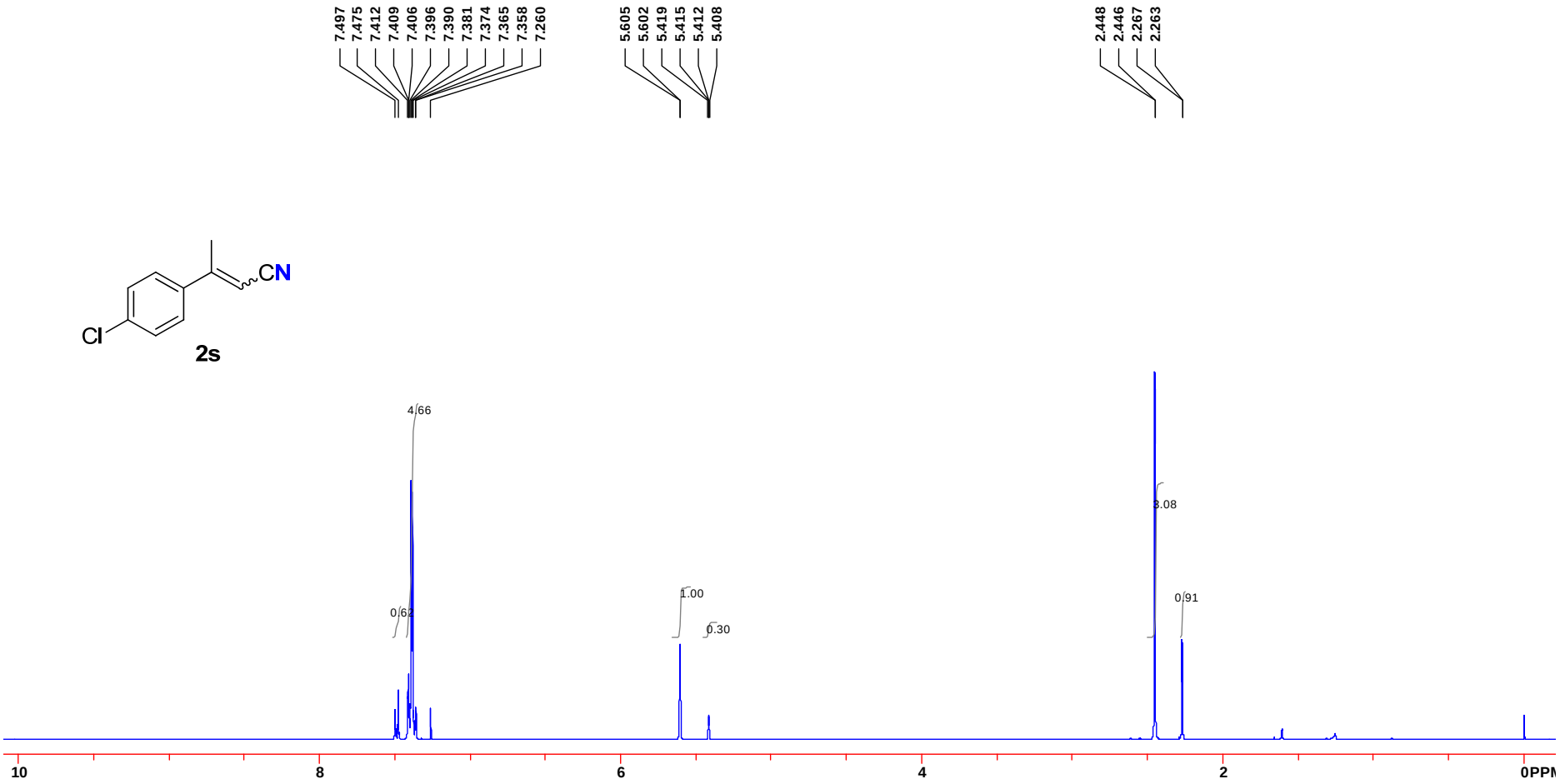
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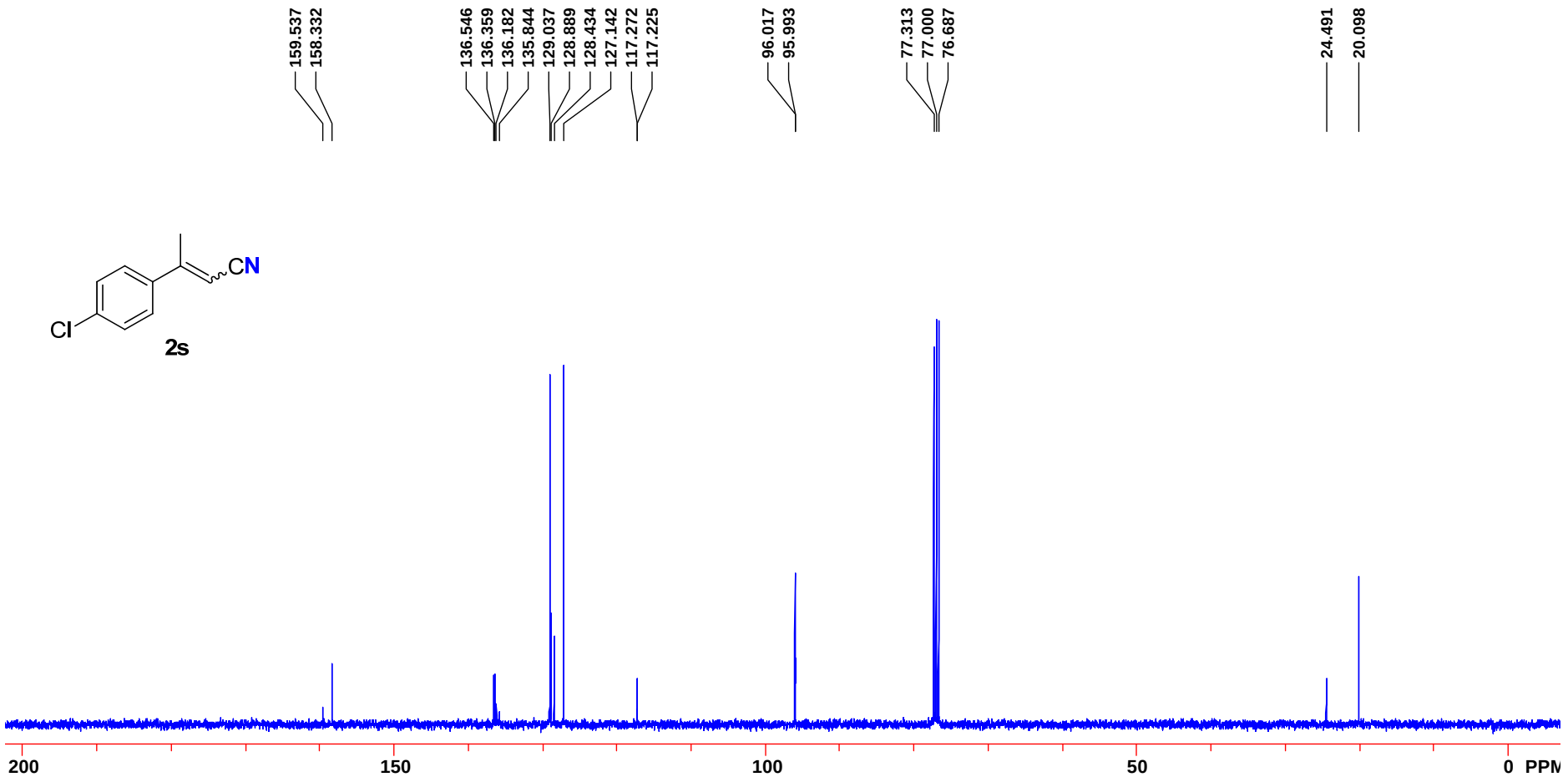
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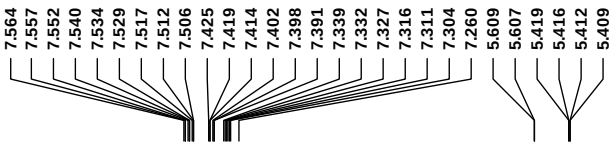
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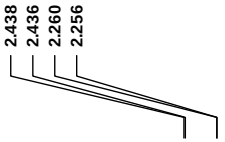
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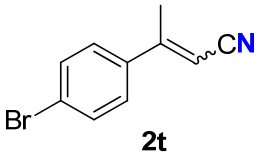
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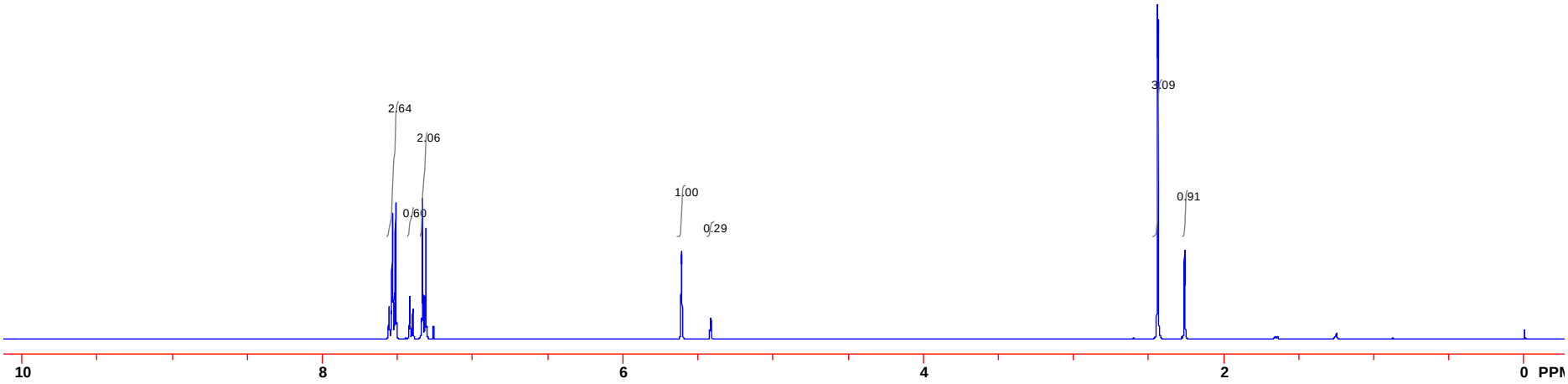
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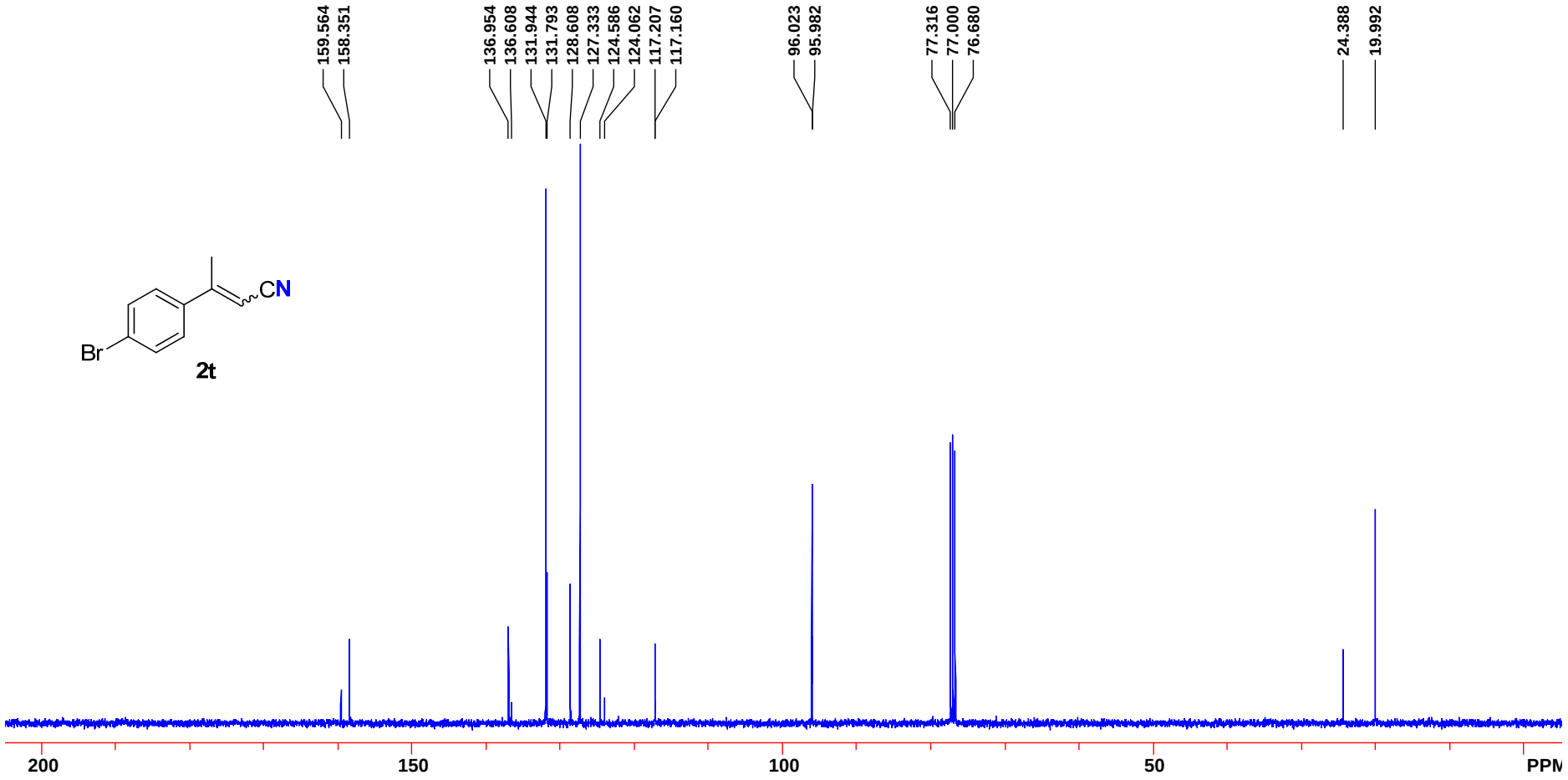
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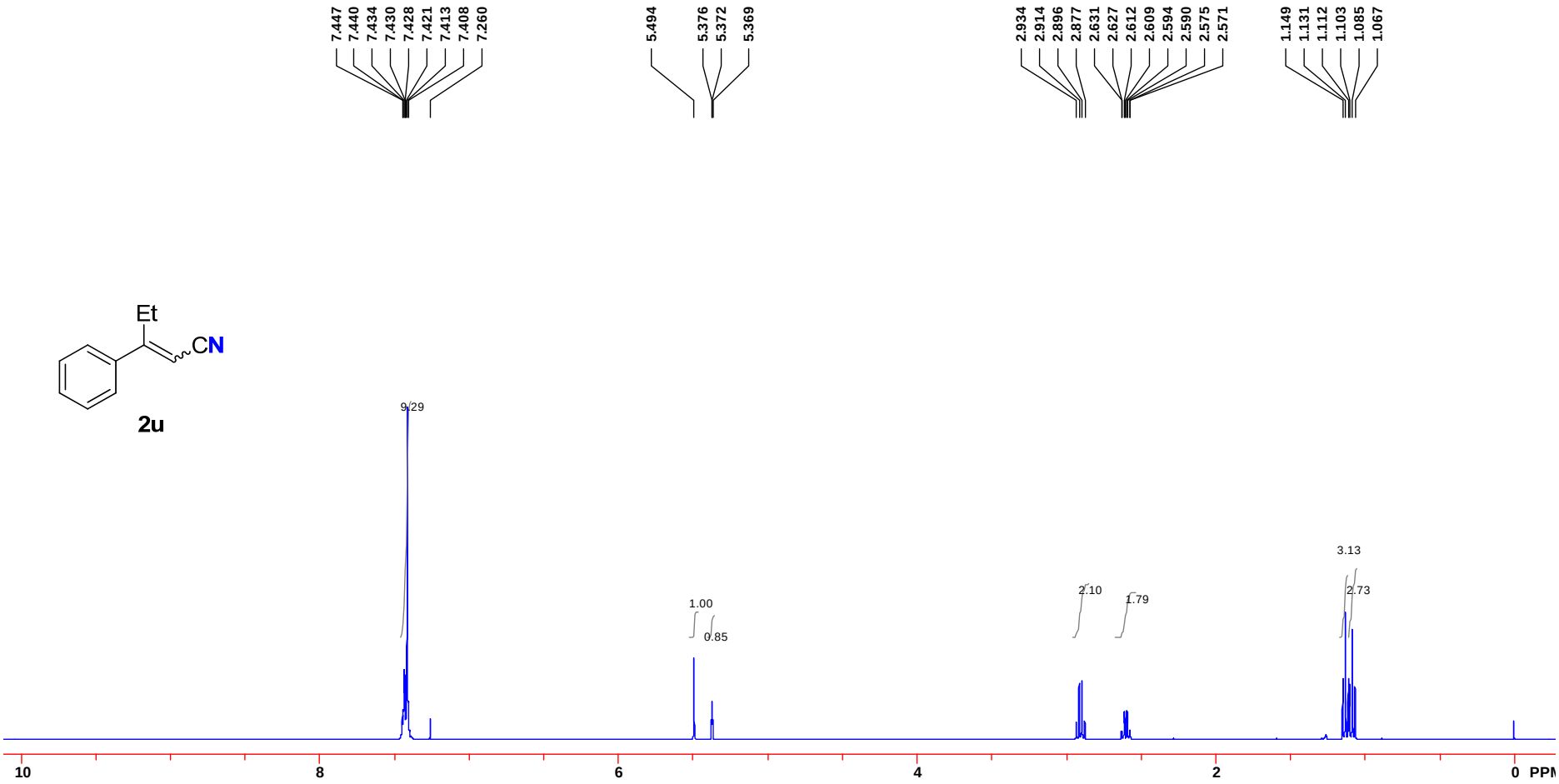
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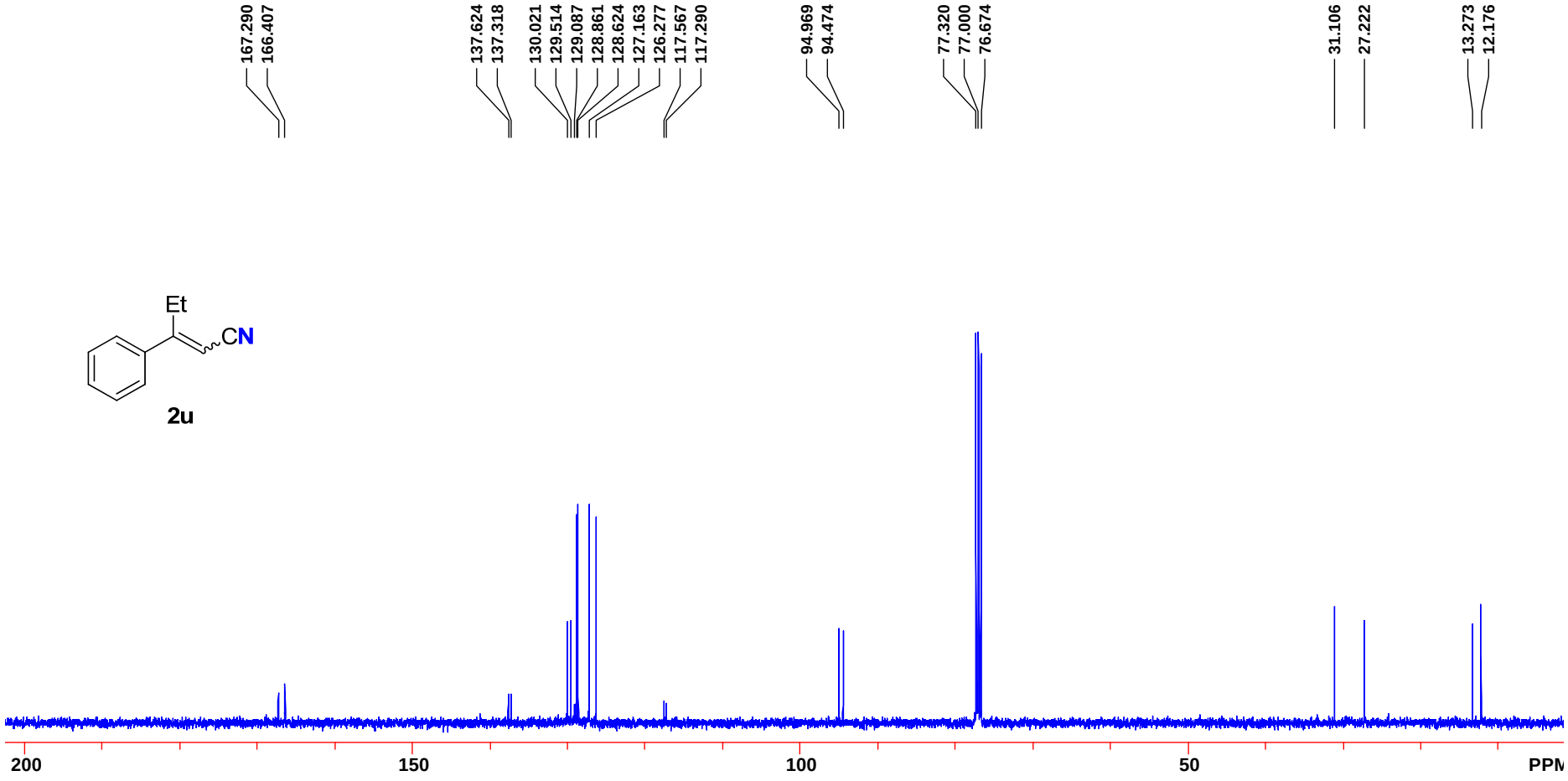
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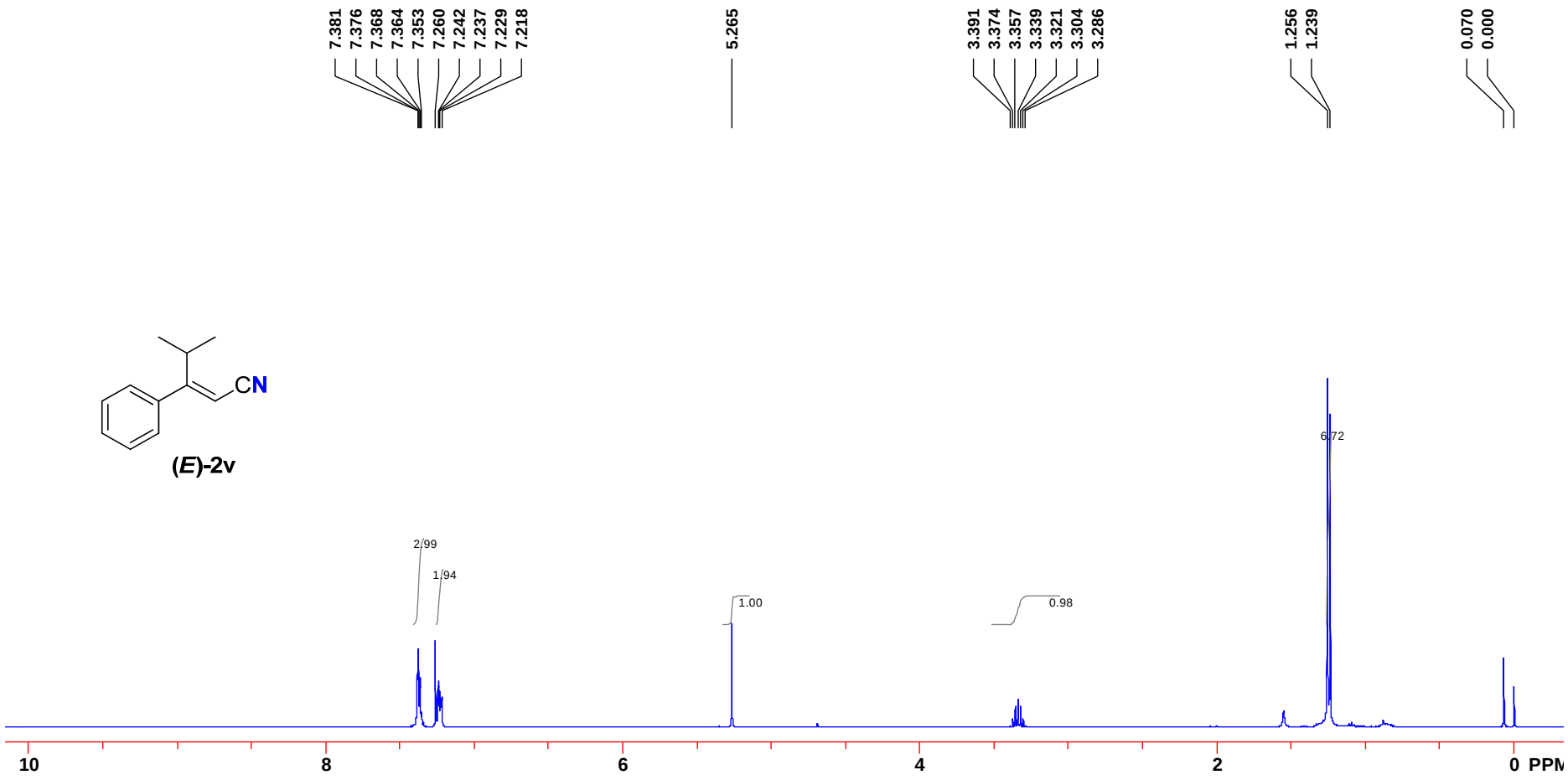
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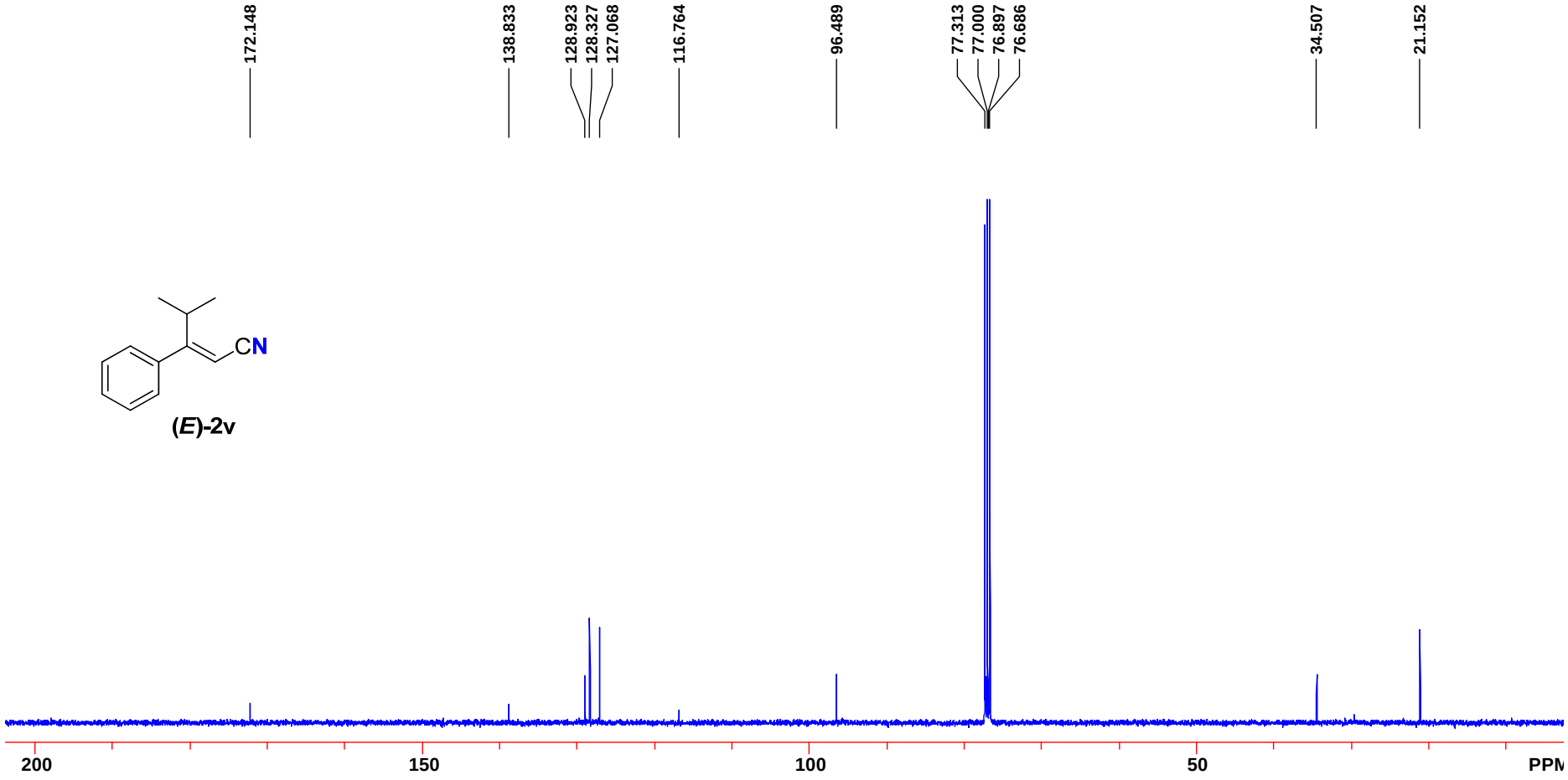
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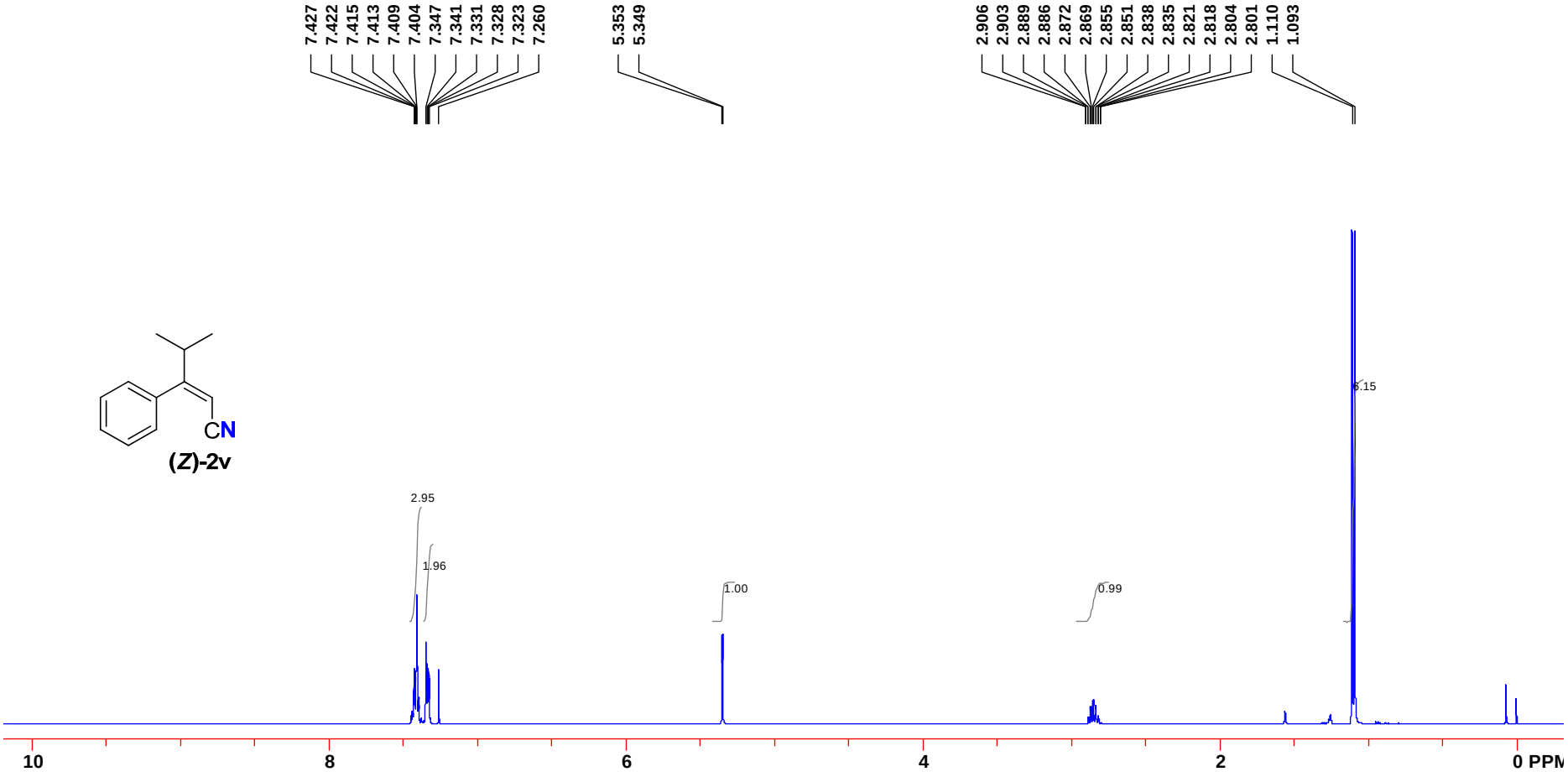
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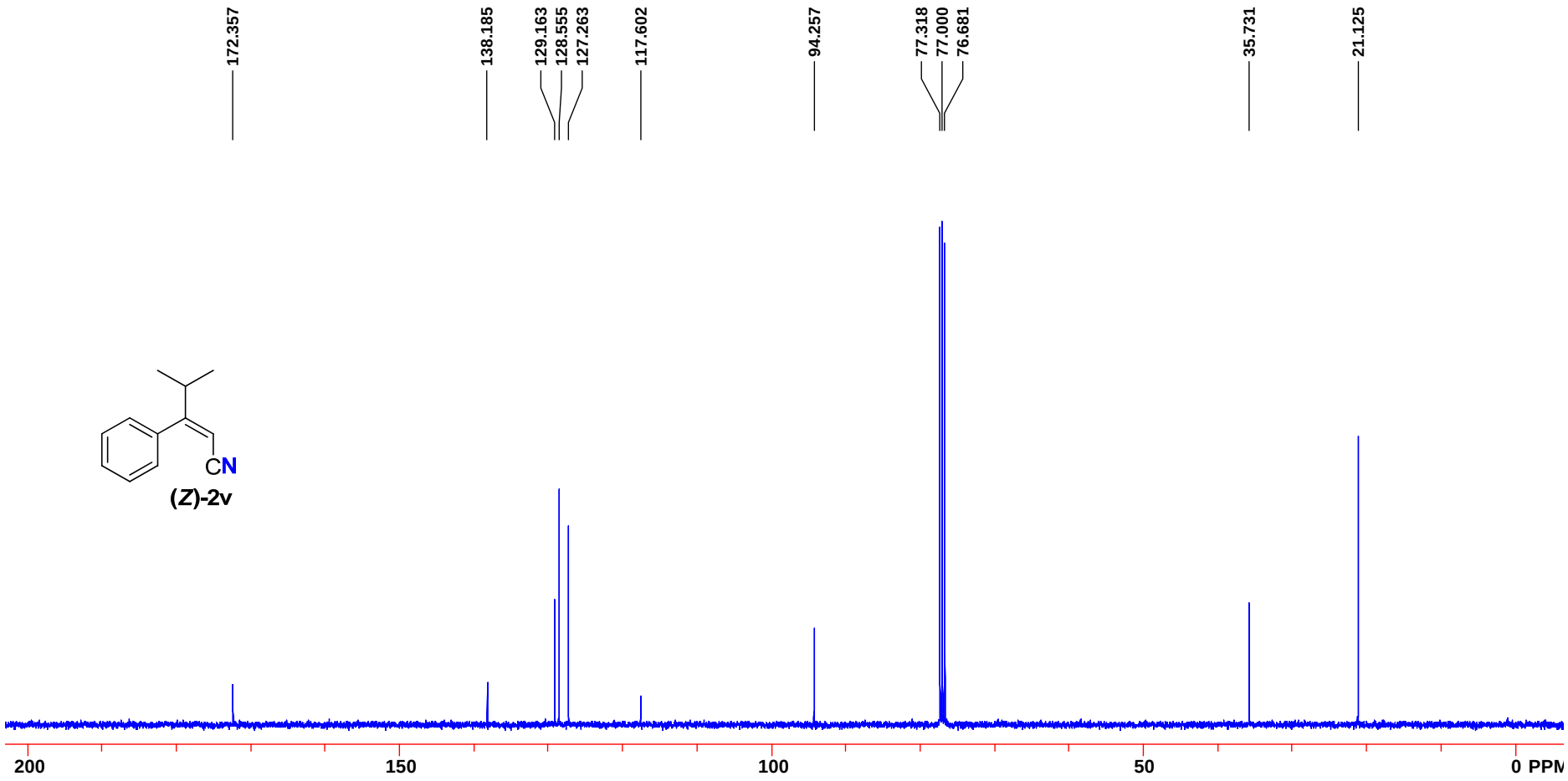
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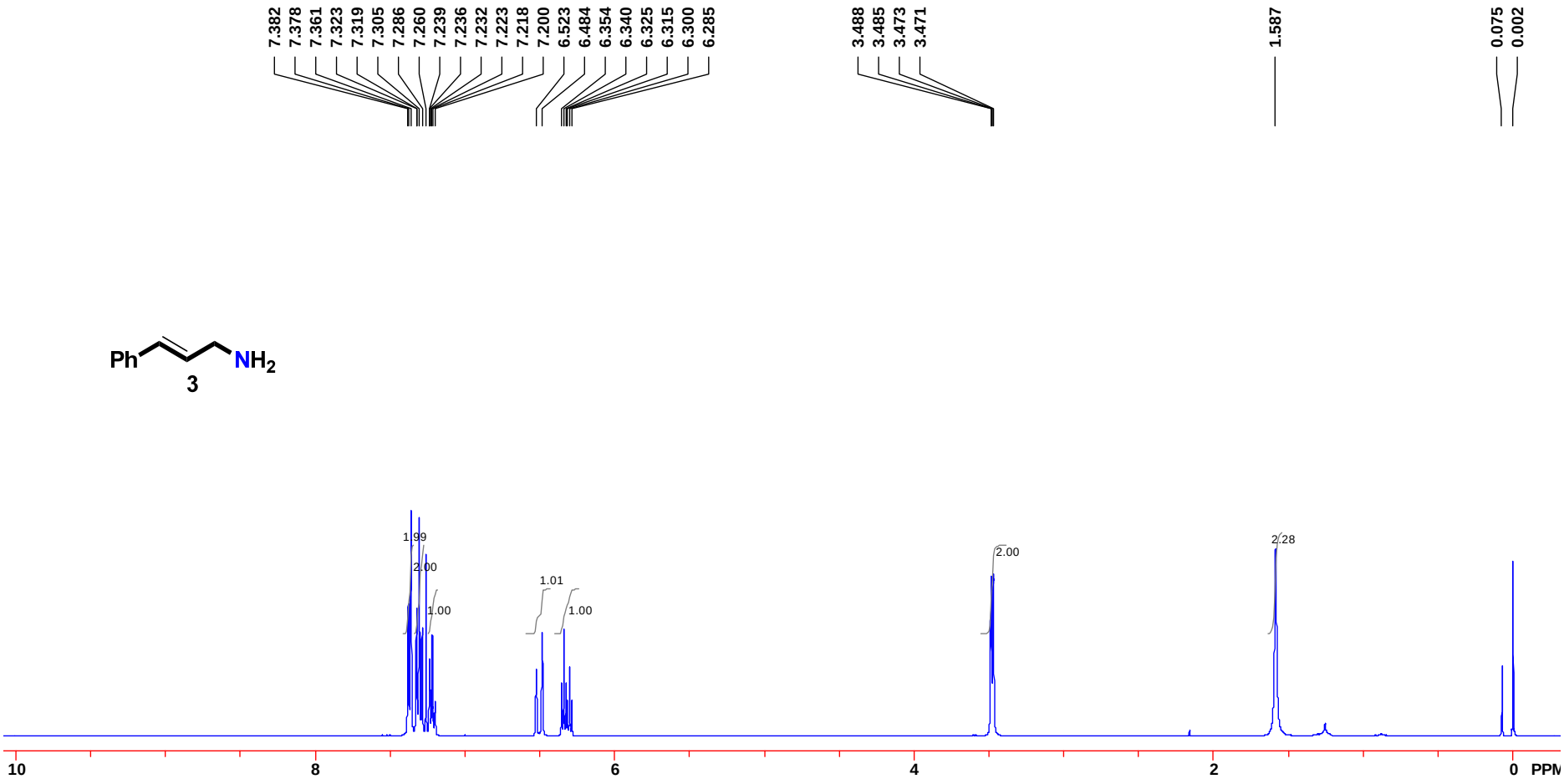
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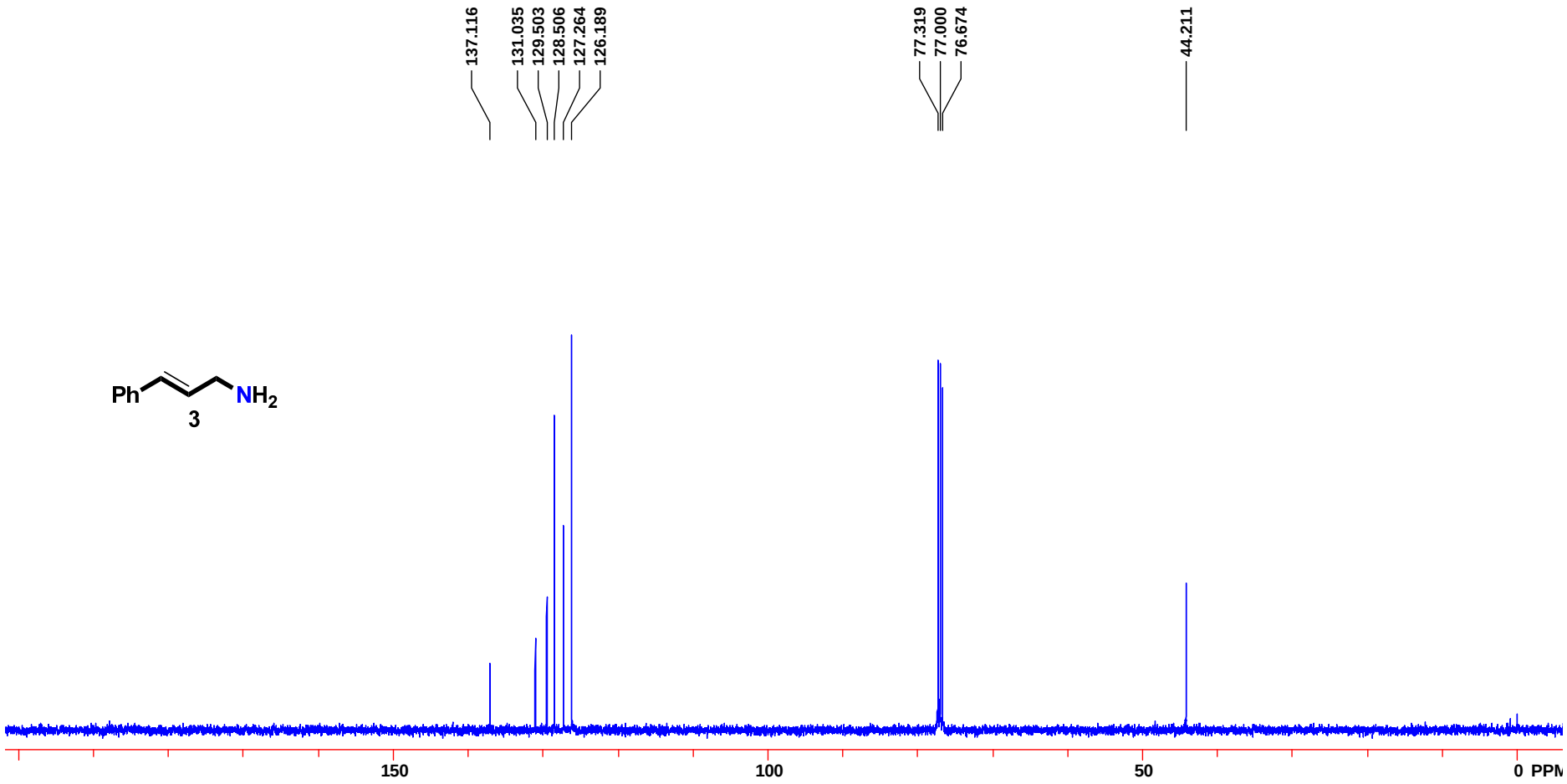
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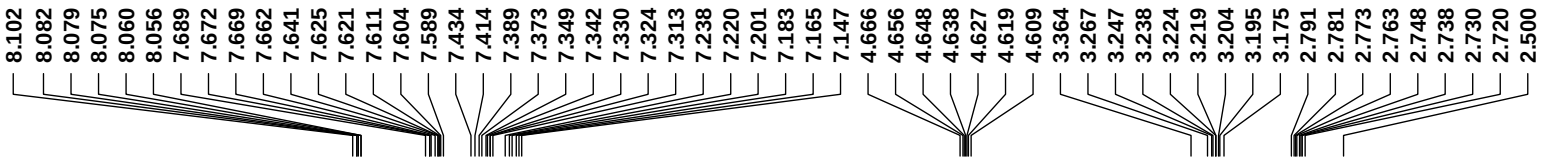
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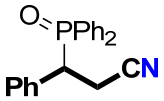
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Ph
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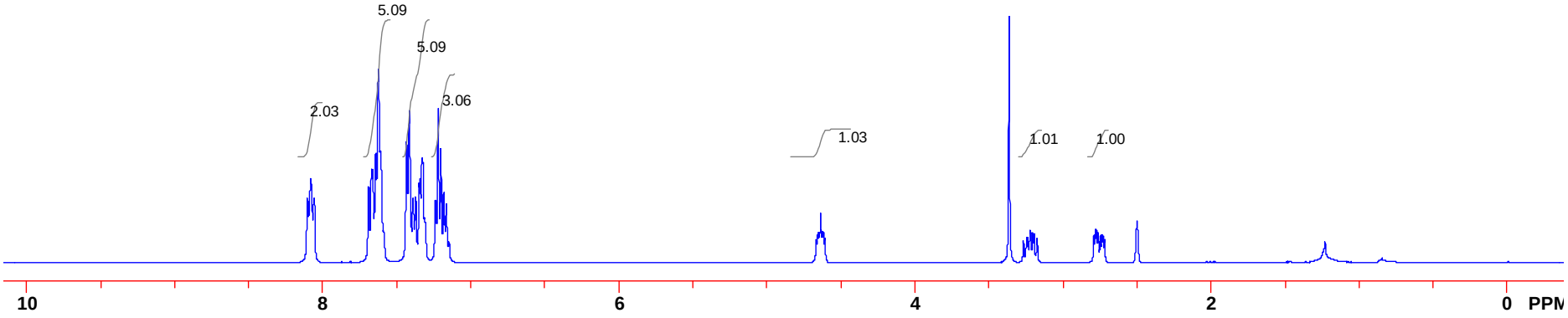
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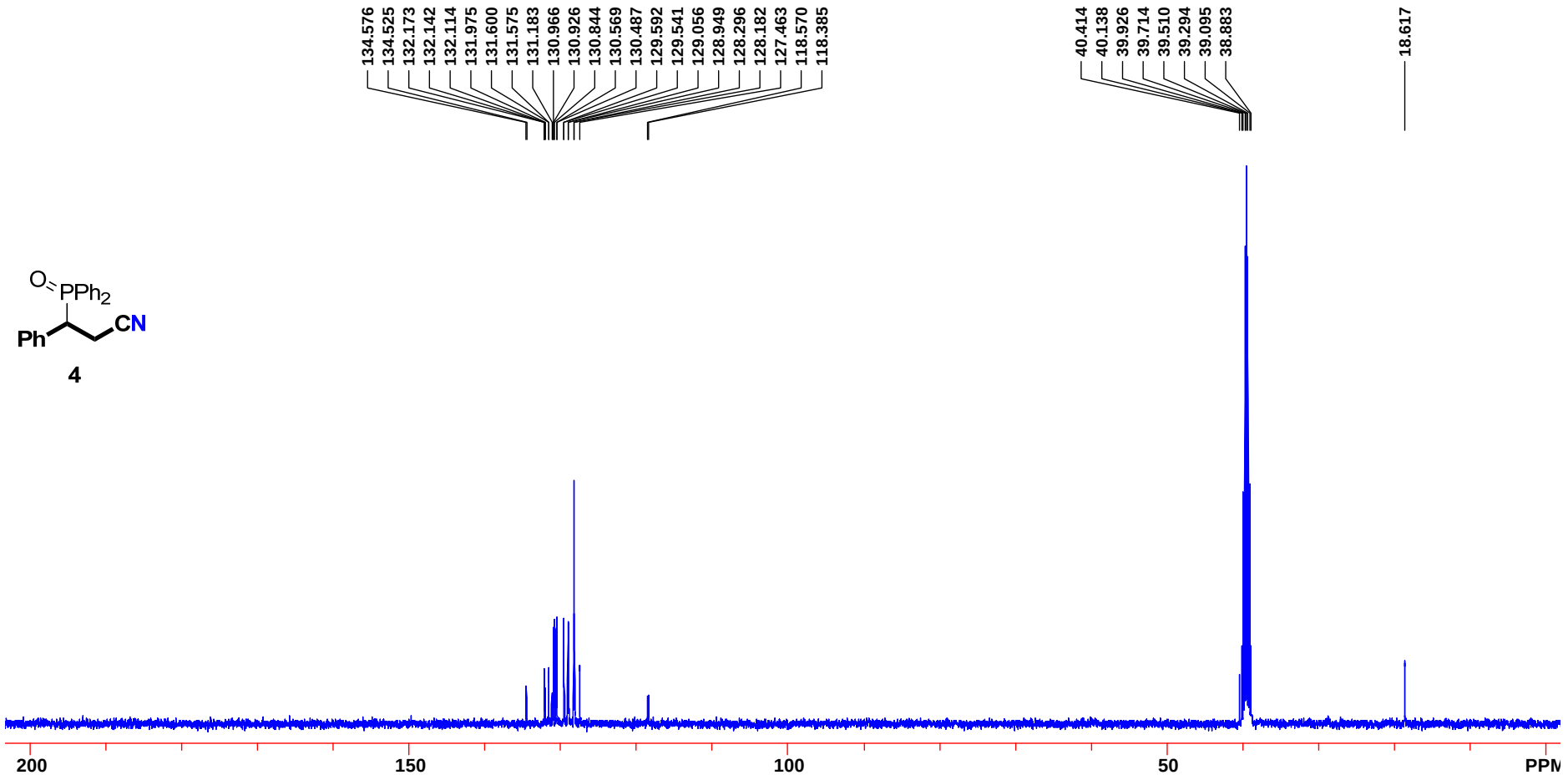
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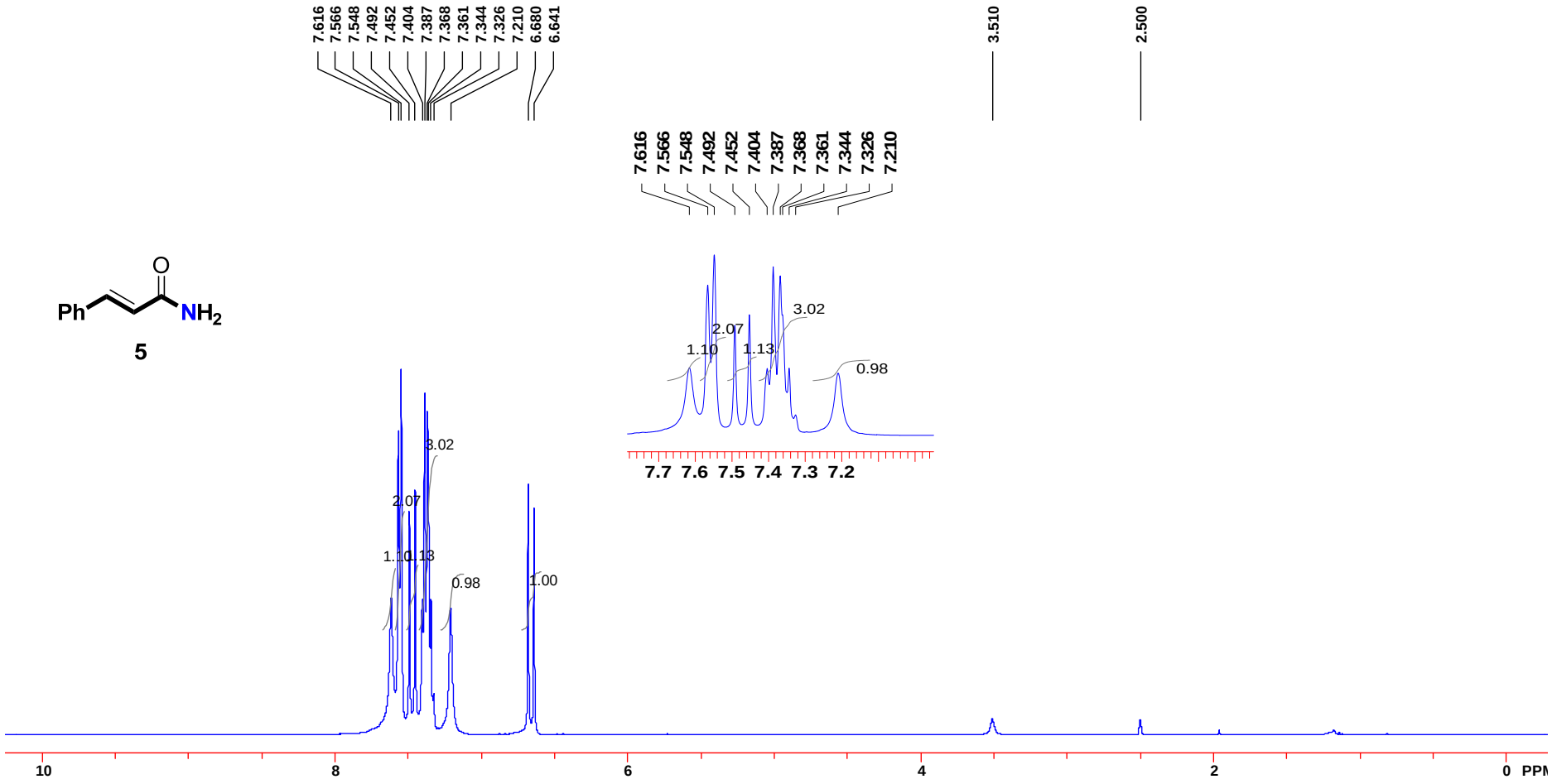
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Ph
NH2
O
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2.07
1.13
3.02
0.98
7.7 7.6 7.5 7.4 7.3 7.2
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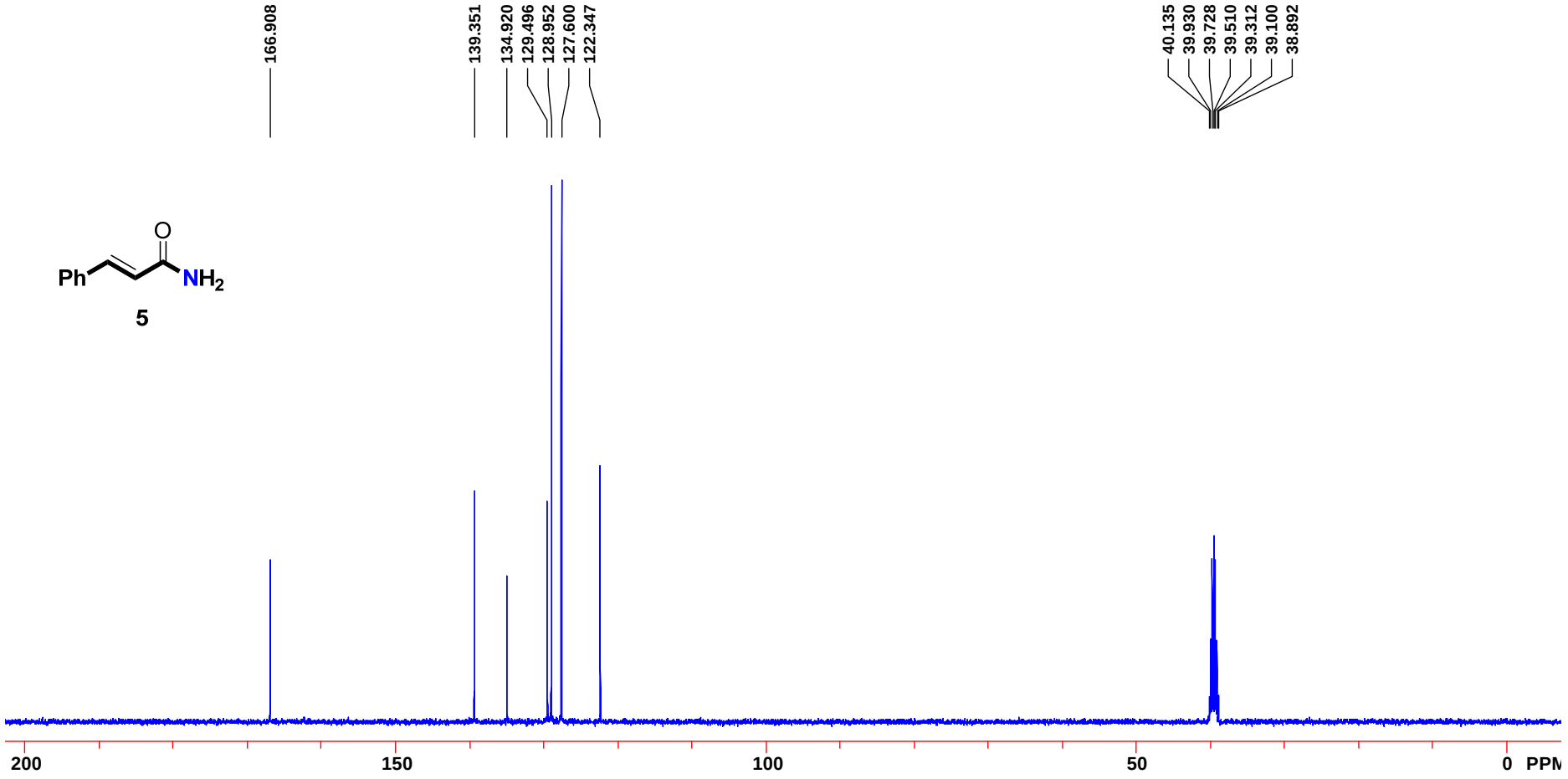
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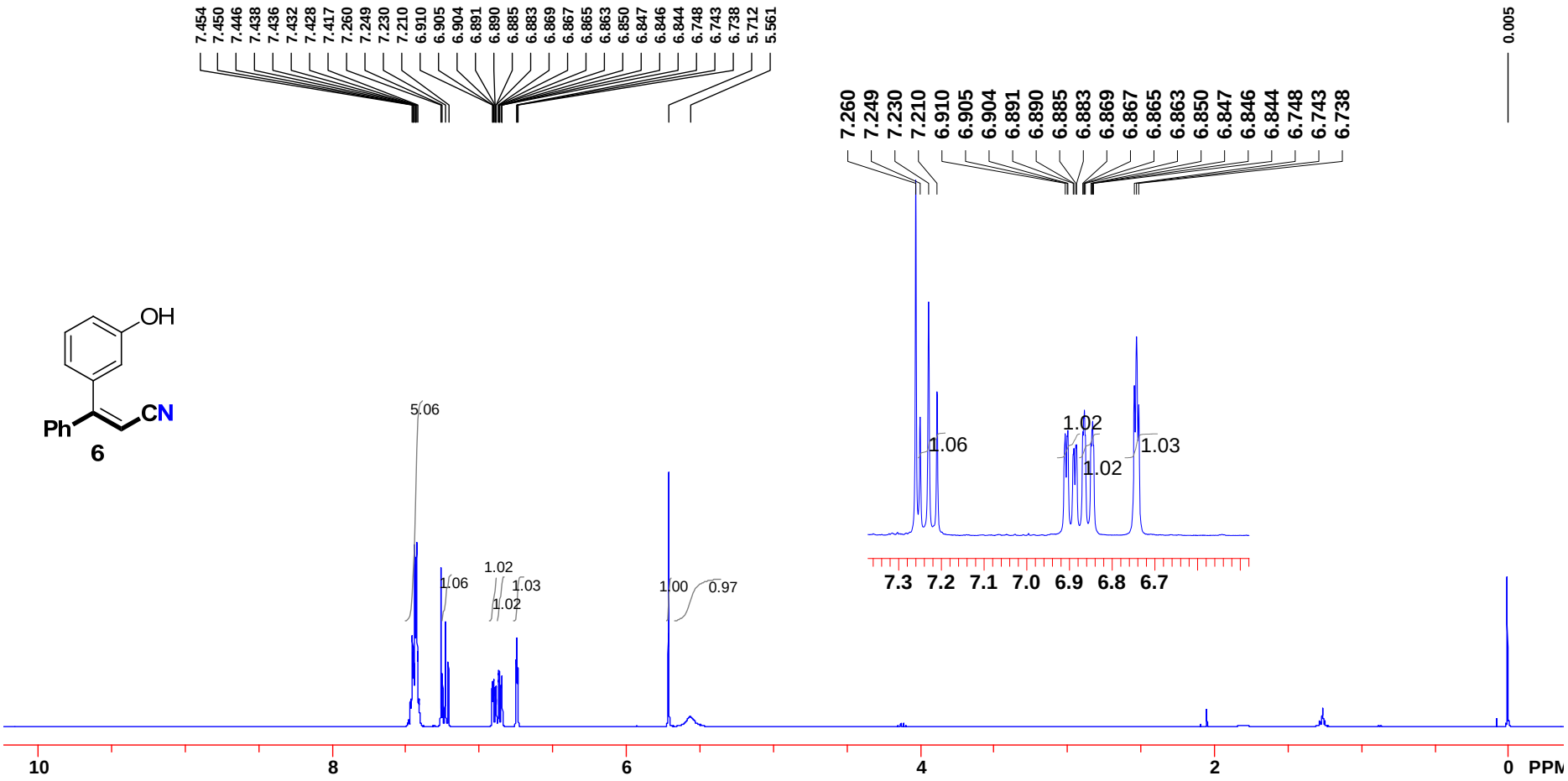
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6.905
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6.867
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6.743
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OH
CN
Ph
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5.06
1.06
1.02
1.03
1.02
1.00
0.97
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1.02
1.02
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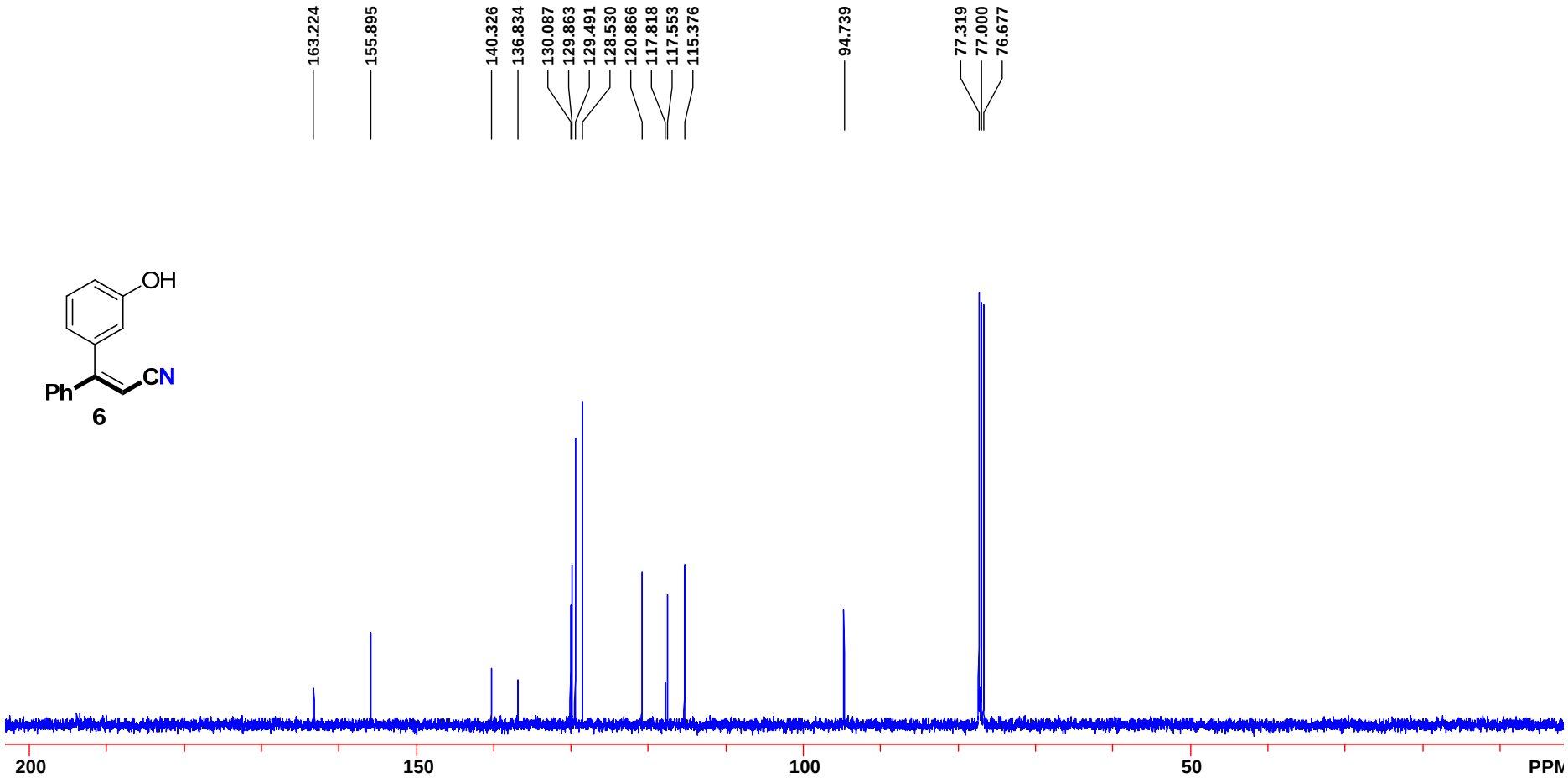
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50
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