Electronic Supplementary Information for:

Copper-catalyzed direct transformation of simple alkynes to alkenyl nitriles via aerobic oxidative N-incorporation

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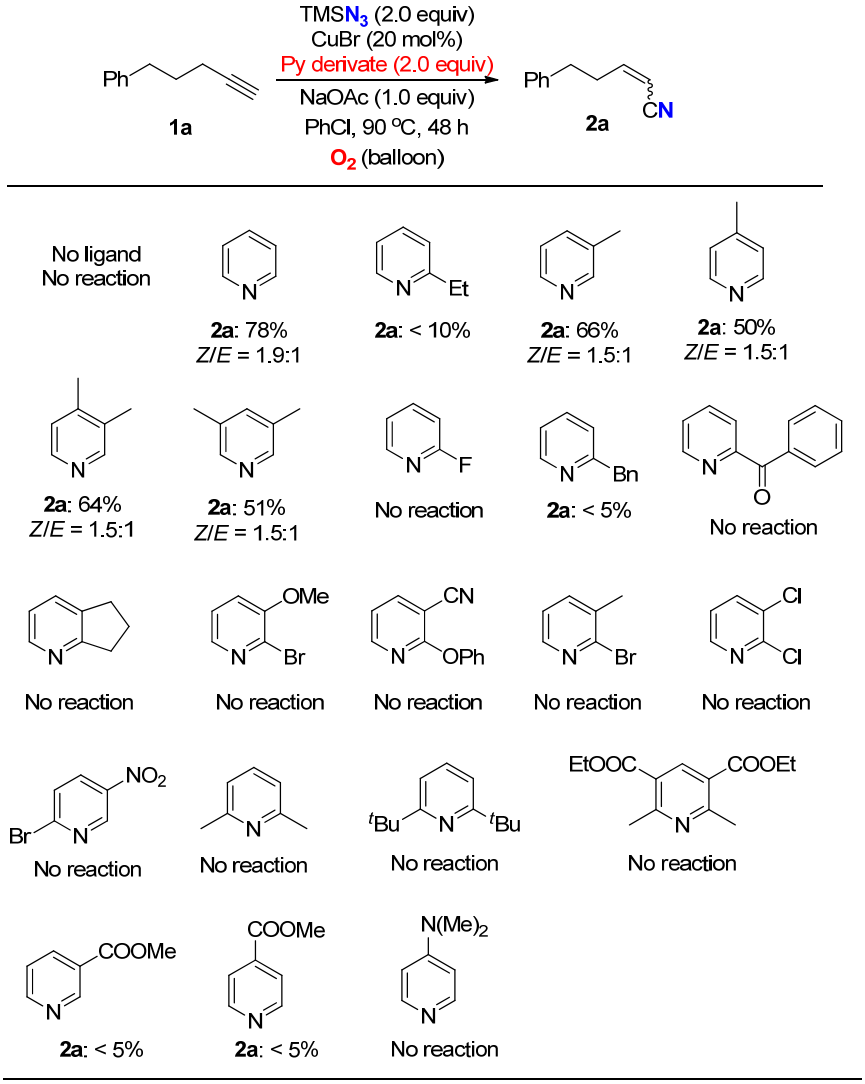
General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Beijing Ouhe and Beijing Chemical Works, Ltd. 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 on silica gel. ^{1}H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced 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). 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 spectrometer. Infrared spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm^{-1}).

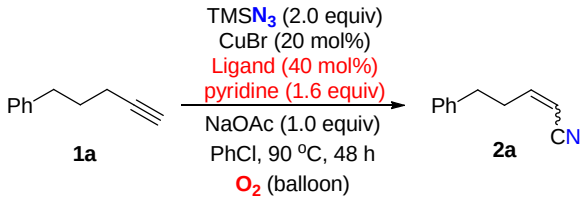
Screening of Different Reaction Parameters

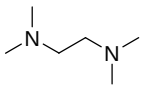
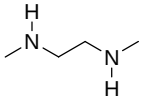
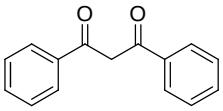
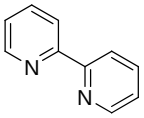
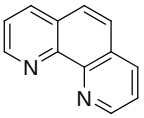
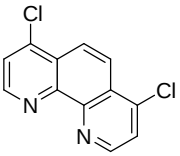
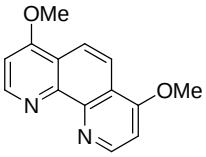
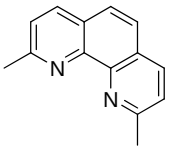
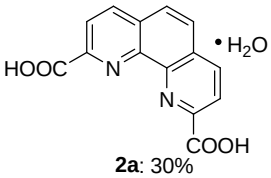
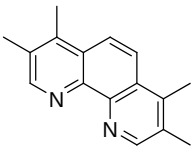
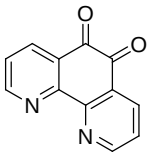
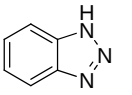
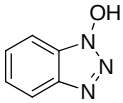
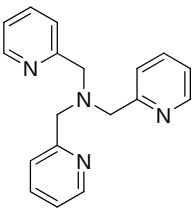
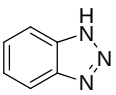
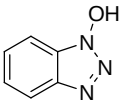
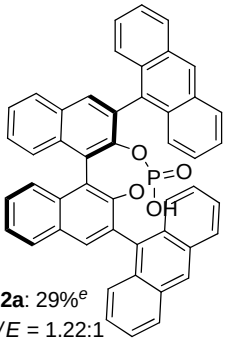
Table S1 Screening of pyridine derivates[a]



[a]Reaction conditions: **1a** (0.20 mmol), $TMSN_3$ (0.40 mmol), CuBr (0.04 mmol), **pyridine derivates** (0.40 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and *Z*/*E* ratio were determined by ^{1}H NMR measurement of the crude mixture.

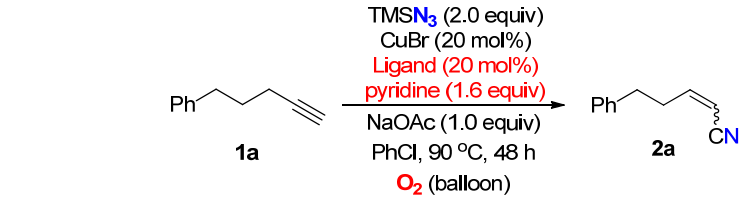
Table S2 Screening of ligands-1[a]

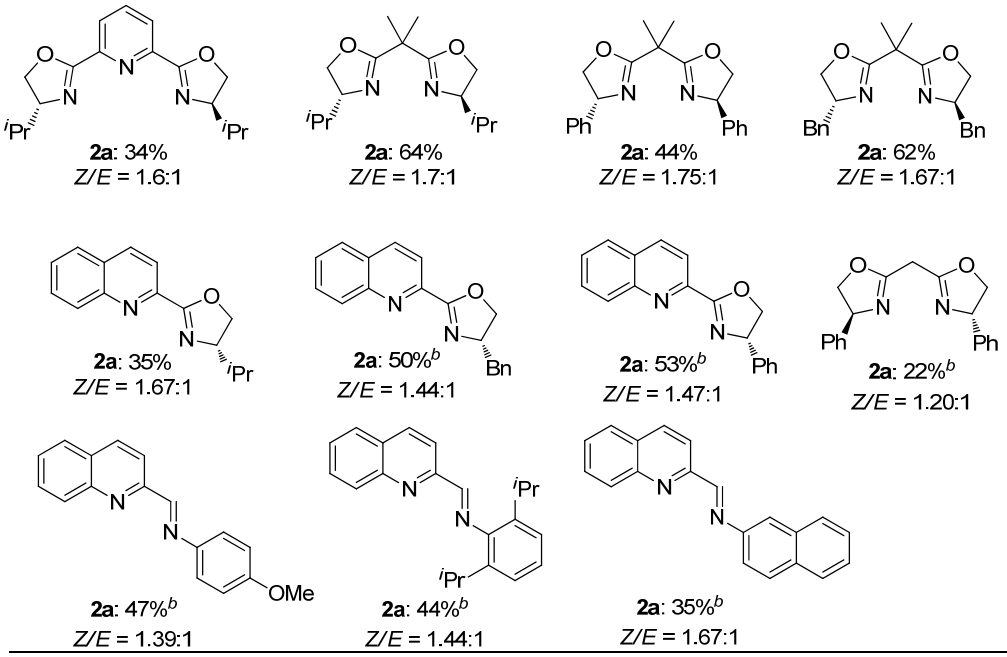


 **2a**: 31% *Z*/*E* = 1.7:1	 **2a**: 14% *Z*/*E* = 1.5:1	 **2a**: < 5%	IPr•HCl Not detected[b]
 Not detected	 Not detected	 Not detected	 Not detected
 Not detected	 **2a**: 30% *Z*/*E* = 1.7:1	 Not detected	 Not detected
 Not detected	 Not detected	 Not detected	 Not detected[d]
 Not detected[c]	 Not detected[c]	 Not detected[c]	
PPh_3 **2a**: 14%[e]	$P(O)Ph_3$ **2a**: 33%[e] *Z*/*E* = 1.55:1	Xantphos **2a**: < 5%[e]	**2a**: 29%[e] *Z*/*E* = 1.22:1

[a]Reaction conditions: **1a** (0.20 mmol), $TMSN_3$ (0.40 mmol), CuBr (0.04 mmol), **Ligand (40 mmol%), Pyridine** (0.32 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and *Z*/*E* ratio were determined by ^{1}H NMR measurement of the crude mixture. [b]**Pyridine** (0.40 mmol) was employed. [c]**Ligand** (0.40 mmol) was employed without **Pyridine**. [d]**Ligand** (0.10 mmol) was employed without **Pyridine**. [e]**Ligand (20 mmol%), Pyridine** (0.40 mmol) was employed without NaOAc.

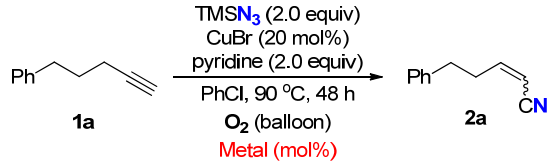
Table S3 Screening of ligands-2[a]





[a]Reaction conditions: **1a** (0.20 mmol), $TMSN_3$ (0.40 mmol), CuBr (0.04 mmol), **Ligand (20 mmol%), Pyridine** (0.32 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and *Z*/*E* ratio were determined by ^{1}H NMR measurement of the crude mixture. [b]without **NaOAc.**

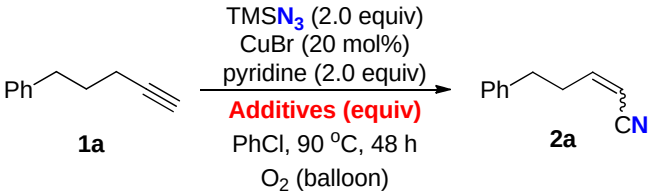
Table S4 Screening of metal[a]



Entry	Metal (mol%)	Yield of **2a**[b]	*E*/*Z*[c]
1	$Rh_2(OAc)_4$ (2 mol%)	41%	1.47:1
2	$Rh_2(Oct)_4$ (2 mol%)	34%	1.39:1
3	$Rh(PPh_3)_3Cl$ (5 mol%)	37%	~ 2:1
4	$[Cp^*RhCl_2]_2$ (2.5 mol%)	25%	1.5:1
5	$Pd(OAc)_2$ (5 mol%)	< 20%	
6	$Fe(OAc)_2$ (10 mol%)	43%	1.44:1
7	$[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%)	34%	1.39:1

[a]Reaction conditions: **1a** (0.20 mmol), $TMSN_3$ (0.40 mmol), CuBr (0.04 mmol), pyridine (0.40 mmol), and **Metal (2-10 mol%)** in PhCl (2.0 mL) was stirred at 90 °C for 48 h. [b]NMR yield. [c]Determined by ^1H NMR measurement of the crude mixture.

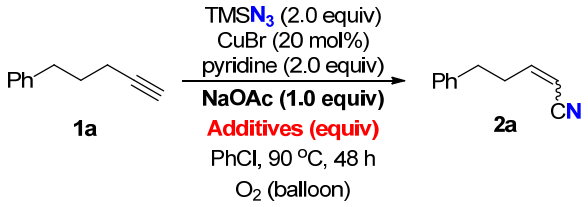
Table S5 Screening of the additives[a]



Entry	**Additives (equiv)**	Yield of **2a** (%)[b]	*Z*/*E*[c]
1	none	48	64:36
2	**NaOAc (1.0)**	**78**	**65:35**
3	LiOAc (1.0)	50	64:36
4	NaOMe (1.0)	47	67:33
5[d]	mCPBA (0.15)	50	63:37
6[d]	$FeCl_2$ (0.1)	43	64:36
7[d]	$Yb(OTf)_3{\bullet}H_2O$ (0.1)	50	63:37
8[d]	CsOPiv (0.1)	41	63:37
9[d]	NHPI (0.1)	46	62:38
10[d]	NH_4F (1.0)	43	63:37
11[e]	PhCOONa (1.0)	48	58:42
12[e]	Na_2CO_3 (1.0)	38	61:39
13[e]	NaOPiv (1.0)	24	63:37
14[e]	NaOTf (1.0)	32	57:43
15[e]	NaOTFA (1.0)	40	63:37
16[e]	NaOPO (1.0)	35	61:39
17[e]	KPF_4 (1.0)	44	60:40
18[e]	dppp (0.2)	< 5	\
19[e]	$P(OEt)_3$ (1.0)	12	\

[a]Reaction conditions: **1a** (0.40 mmol), $TMSN_3$ (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), and **Additives** in PhCl (2.0 mL) was stirred at 90 °C for 48 h. [b]Isolated yield. [c]Determined by ^1H NMR measurement of the crude mixture. [d]PhCl : 1,4-dioxane (10 : 1) was used instead of PhCl. [e]0.2 mmol scale, NMR yield.

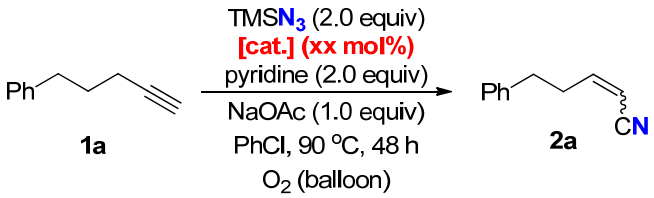
Table S6 Screening of the additives with addition of NaOAc[a]



Entry	Additives (equiv)	Yield of **2a** (%)[b]	*Z*/*E*[c]
1[d]	NH_4I (1.0) or NaI (1.0)	0	/
2[d]	KBr (1.0)	66	62:38
3[d]	NaBr (1.0)	69	61:39
4	$NaBO_3$ H_2O (0.1)	71	65:35
5	dppf (0.1)	58	63:37
6	$FeCl_2$ (0.1)	56	65:35
7	$NaClO_4$ (1)	50	66:34
8	NH_4F (2)	47	62:38
9	DMF (10)	82	65:35
10	MS 4A (200 mg)	63	66:34
11	$Sc(OTf)_3$ (0.1)	56	65:35
12	$Mg(OTf)_2$ (0.1)	70	67:33
13	$InCl_3$ (0.1)	60	64:36
14	NH_4Br (0.5)	66	63:37
15	H_2O (10)	44	69:31
16	TBAB (0.1)	37	67:33
17	$NaHSO_3$ (0.1)	73	64:36
18	PhCOOK (0.1)	76	64:36
19	KPF_6 (0.1)	77	65:35
20	NH_4SCN (0.1)	23	60:40

[a]Reaction conditions: **1a** (0.40 mmol), $TMSN_3$ (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), NaOAc (0.4 mmol) and **Additives** in PhCl (2.0 mL) was stirred at 90 °C for 48 h. [b]Isolated yield. [c]Determined by ^1H NMR measurement of the crude mixture. [d]0.2 mmol scale, NMR yield.

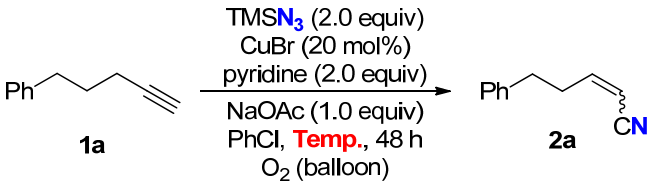
Table S7 Screening of the catalysts[a]



Entry	[Cat.] (xx mol%)	Yield of **2a** (%)[b]	*Z*/*E*[c]
1	none	0	-
2	**CuBr (20 mol%)**	**78**	**65:35**
3	CuOTf (20 mol%)	70	64:36
4	Cu_2O (20 mol%)	51	65:35
5	$Cu(OAc)_2$ (20 mol%)	49	69:31
6	$CuBr_2$ (20 mol%)	62	67:33
7	$Cu(ClO_4)_2 \cdot 6H_2O$ (20 mol%)	42	71:29
8	CuBr (10 mol%)	41	63:37
9	CuOAc	60	67:33
10[d]	$FeCl_2$ (10 mol%)	0	-
11[d]	$FeCl_3$ (10 mol%)	0	-
12[d]	$CoCl_2$	0	-
13[d]	$Co(acac)_2$	0	-
14[d]	$Mn(OAc) \cdot 2H_2O$ (10 mol%)	0	-
15[d]	MnO_2	0	-
16[d]	$AgNO_3$	0	-

[a]Reaction conditions: **1a** (0.40 mmol), $TMSN_3$ (0.80 mmol), **catalyst**, pyridine (0.80 mmol), and NaOAc (0.40 mmol) in PhCl (2.0 mL) was stirred at 90 °C for 48 h. [b]Isolated yield. [c]Determined by ^1H NMR measurement of the crude mixture. [d]without NaOAc.

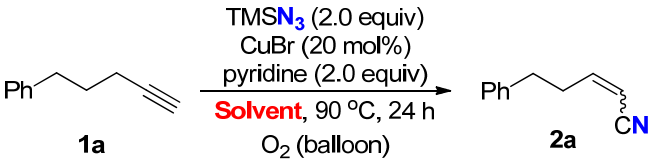
Table S8 Screening of the reaction temperatures[a]



Entry	Temp.	Yield of **2a** (%)[b]	*Z*/*E*[c]
1	70 °C	67	63:37
2	**90 °C**	**78**	**65:35**
3	120 °C	31	69:31

[a]Reaction conditions: **1a** (0.40 mmol), $TMSN_3$ (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), and NaOAc (0.40 mmol) in PhCl (2.0 mL) was stirred at **Temp.** °C for 48 h. [b]Isolated yield. [c]Determined by ^1H NMR measurement of the crude mixture.

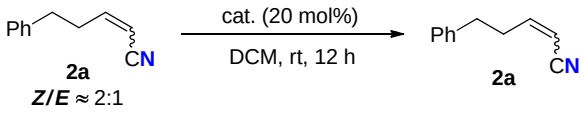
Table S9 Screening of the solvents[a]



Entry	Solvent	Yield of **2a** (%)[b]	*Z*/*E*[c]
1	PhCl	45	/
2	$PhCH_3$	30	/
3	1,1,2-trichloroethane	43	/
4	1,2-dichlorobenzene	39	/
5	DMF	40	/
6	PhOMe	40	/
7	DMAc	37	/
8	DMSO	15	/
9	cumene	25	/
10[d]	THF	0	/
11[e]	$PhCH_3$	68	1.73:1
12[e]	1,1,2,2-tetrachloroethane	60	1.63:1
13[e]	PhOMe	65	1.60:1
14[e]	MeCN	< 10	/
15[e]	dioxane	0	/
16[e]	AcOPr	68	1.71:1
17[e]	PhCl	78	1.86:1

[a]Reaction conditions: **1a** (0.40 mmol), $TMSN_3$ (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), and NaOAc (0.40 mmol) in solvent (2.0 mL) was stirred at 90 °C for 24 h. [b]Isolated yield. [c]Not Determined. [d]Under reflux conditions. [e]0.2 mmol scale, NMR yield.

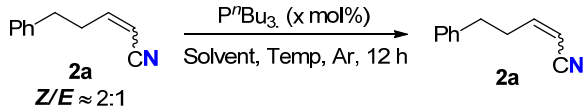
Table S10 Evaluation of isomerization reaction-1[a]



Entry	Cat. (20 mol%)	Recovery of **2a** (%)	*Z/E* Selectivity
1	PPh_3	> 95	NO improvement
2	P^nBu_3	> 95	**from 2.1:1 to 1:1.14**
3	PCy_3	> 95	NO improvement
4[b]	PMe_3 (THF)	> 95	**form 2.1:1 to 1:1.06**
5	DABCO	> 85	NO improvement
6	DBU	> 70	**from 2.1:1 to 1:1.18**
7	P^tBu_3	> 95	NO improvement
8	HMPA	> 99	NO improvement
9	R-(+)-Binap	> 80	NO improvement
10	IPr	> 50	NO improvement
11[b]	$ClRuH(CO)(PPh_3)_3$	> 95	NO improvement
12[c]	$ClRuH(PPh_3)_3$	> 95	NO improvement
13[c]	$Pd(TFA)_2$/^{i}PrOH	> 95	No improvement

[a]Reaction conditions: 2**a** (0.20 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) was stirred at rt for 12 h. recovery and *Z/E* ratio was determined by NMR measurement. [b]PhCH3, rt, 60 °C or 80 °C [c] MeCN, 80 °C.

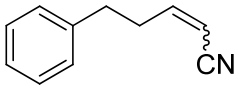
Table S11 Evaluation of isomerization reaction-2[a]



Entry	P^nBu_3 (x mol%)	Temp	Solvent	Additive	Recovery of **2a** (%)	*Z/E* Selectivity
1	20 mol%	rt	DCM	/	> 95	**from 2.1:1 to 1:1.14**
2	20 mol%	80 °C	$PhCH_3$	/	> 95	**from 1.23:1 to 1:19**
3	20 mol%	100 °C	$PhCH_3$	/	> 95	**from 1.23:1 to 1:1.22**
4	20 mol%	140 °C	MeCN	/	> 95	**from 1.23:1 to 1:1.20**
5	50 mol%	80 °C	MeCN	/	> 95	**from 1.09:1 to 1:1.14**
6	100 mol%	80 °C	MeCN	/	> 95	**from 1.09:1 to 1:1.07**
7	20 mol%	rt	DCM	HOAc	> 95	NO improvement
8	20 mol%	rt	DCM	NaOAc	> 99	**from 1.37:1 to 1:1.14**
9	20 mol%	rt	DCM	BF_3 Et_2O	> 95	NO improvement
10	20 mol%	rt	EA	/	> 95	**from 2.10:1 to 1.48:1**
11	20 mol%	rt	MeCN	/	> 95	**from 2.10:1 to 1:1**
12	20 mol%	rt	MeOH	/	> 50	**from 2.10:1 to 1:1**
13	20 mol%	rt	hexane	/	> 95	**from 2.10:1 to 1.43:1**
14	20 mol%	rt	PhCl	/	> 95	**from 2.10:1 to 1.64:1**
15	20 mol%	rt	DMF	/	> 95	**from 2.10:1 to 1.05:1**

[a]Reaction conditions: 2**a** (0.20 mmol), P^nBu_3 (0.04 mmol) in solvent (1.0 mL) was stirred under Ar for 12 h. Recovery and *Z/E* ratio was determined by NMR measurement.

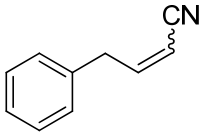
Experimental Procedure and Characterization Data for Products

01) 

5-Phenylpent-2-enenitrile (2a):[1]

Typical procedure: Mix pent-4-yn-1-ylbenzene **1a** (57.7 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. 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 = 50:1) to afford 49.3mg (78%) of **2a**. **2a**: obtained as a 65:35 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35-7.25 (m, 2H), 7.24-7.12 (m, 3H), 6.70 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.46 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.33-5.26 (m, 1H), 2.83-2.70 (m, 2H), 2.83-2.70 (m, 2H, *Z*-isomer), 2.57-2.49 (m, 2H, *E*-isomer); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 154.6, 153.7, 139.8, 139.7, 128.6, 128.5, 128.3, 128.2, 126.40, 126.35, 117.3, 115.7, 100.4, 100.1, 34.8, 34.2, 33.8, 33.2 ppm; **MS (70 eV) m/z (%)**: found 157.1 (M^+)

02) 

4-Phenylbut-2-enenitrile (2b):[2]

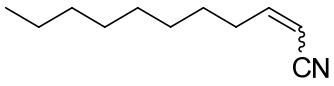
The reaction of but-3-yn-1-ylbenzene **1b** (52.1 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 25.0 mg (44%) of **2b**. **2b**: obtained as a 67:33 mixture of *Z/E* isomers. Colorless liquid.

***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.36-7.30 (m, 2H), 7.29-7.23 (m, 1H), 7.23-7.18 (m, 2H), 6.61 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H), 5.41 (dt, J_1 = 10.8 Hz, J_2 = 1.4 Hz, 1H), 3.75 (d, J = 7.6 Hz, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 152.8,

136.8, 128.9, 128.5, 127.0, 115.9, 99.9, 38.0 ppm;

^{1}H NMR for the minor *E*-isomer: 7.37-7.30 (m, 2H), 7.29-7.22 (m, 1H), 7.16-7.12 (m, 2H), 6.87 (dt, J_1 = 16.0 Hz, J_2 = 6.6 Hz, 1H), 5.27 (dt, J_1 = 16.4 Hz, J_2 = 1.8 Hz, 1H), 3.53 (dd, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 1H).

MS (70 eV) m/z (%): found 143.1 (M^+).

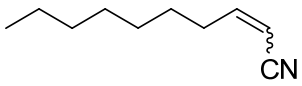
03) 

Undec-2-enenitrile (2c):[3]

The reaction of undec-1-yne **1c** (60.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 50.0 mg (76%) of **2c**. **2c**: obtained as a 61:39 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.72 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.49 (dt, J_1 = 10.8 Hz, J_2 = 5.6 Hz, 1H, *Z*-isomer), 5.37-5.27 (m, 1H), 2.42 (td, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2H, *Z*-isomer), 2.26-2.15 (m, 2H, *E*-isomer), 1.53-1.40 (m, 2H), 1.35-1.21 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 156.2, 155.3, 117.6, 116.0, 99.5, 99.3, 33.3, 31.8, 31.7, 29.2, 29.08, 29.06, 29.0, 28.9, 28.2, 27.5, 22.6, 14.0 ppm;

MS (70 eV) m/z (%): found 150.1 ($[M\text{-}CH_3]^+$).

04) 

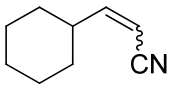
Dec-2-enenitrile (2d):[4]

The reaction of dec-1-yne **1d** (55.3 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 37.7 mg (62%) of **2d**. **2d**: obtained as a 66:34 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.72 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer),

6.48 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.35-5.28 (m, 1H), 2.46-2.39 (m, 2H, *Z*-isomer), 2.26-2.19 (m, 2H, *E*-isomer), 1.52-1.40 (m, 2H), 1.35-1.23 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 156.2, 155.3, 117.6, 116.1, 99.6, 99.4, 33.3, 31.9, 31.7, 31.6, 29.0, 28.92, 28.88, 28.2, 27.6, 22.6, 14.0 ppm;

MS (70 eV) m/z (%): found 136.1 ($[M\text{-}CH_3]^+$).

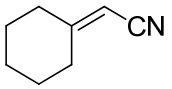
05) 

3-Cyclohexylacrylonitrile (2e):[5]

The reaction of prop-2-yn-1-ylcyclohexane **1e** (48.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 34.3 mg (63%) of **2e**. **2e**: obtained as a 60:40 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.67 (dd, J_1 = 16.4 Hz, J_2 = 6.4 Hz, 1H, *E*-isomer), 6.32 (dd, J_1 = 10.8 Hz, J_2 = 10.4 Hz, 1H, *Z*-isomer), 5.27 (dd, J_1 = 16.4 Hz, J_2 = 1.6 Hz, 1H, *E*-isomer), 5.21 (dd, J_1 = 10.8 Hz, J_2 = 0.4 Hz, 1H, *Z*-isomer), 2.68-2.55 (m, 1H, *Z*-isomer), 2.20-2.09 (m, 1H, *E*-isomer), 1.80-1.65 (m, 5H), 1.42-1.08 (m, 5H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 160.8, 160.1, 117.9, 116.1, 97.5, 97.1, 41.4, 41.0, 31.7, 31.1, 25.6, 25.5, 25.4, 25.1 ppm;

MS (70 eV) m/z (%): found 135.1 (M^+)

06) 

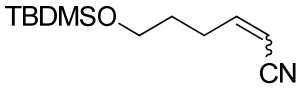
2-Cyclohexylideneacetonitrile (2f):[6]

The reaction of ethynylcyclohexane **1f** (43.3 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 29.8 mg (61%) of **2f**. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.04 (s, 1H), 2.49 (t, *J* = 6.0 Hz, 2H), 2.25 (t, *J* =

5.6 Hz, 2H), 1.71-1.58 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 168.7, 117.0, 91.9, 35.9, 33.1, 27.9, 27.5, 25.6 ppm;

MS (70 eV) m/z (%): found 121.1 (M^+)

07) 

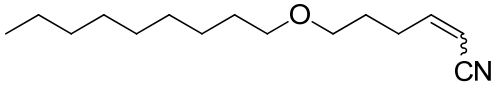
6-((*tert*-Butyldimethylsilyl)oxy)hex-2-enenitrile (2g):

The reaction of *tert*-butyl(hex-5-yn-1-yloxy)dimethylsilane **1g** (85.0 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 61.0 mg (68%) of **2g**. **2g**: obtained as a 69:31 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.74 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.52 (dt, J_1 = 10.8 Hz, J_2 = 5.6 Hz, 1H, *Z*-isomer), 5.33 (dt, J_1 = 16.4 Hz, J_2 = 1.6 Hz, 1H, *E*-isomer), 5.31 (dt, J_1 = 10.8 Hz, J_2 = 1.4 Hz, 1H, *Z*-isomer), 3.66-3.58 (m, 2H), 2.49 (tdd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, J_3 = 1.2 Hz, 2H, *Z*-isomer), 2.30 (tdd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, J_3 = 1.2 Hz, 2H, *E*-isomer), 1.72-1.61 (m, 2H), 0.879 (s, 9H, *Z*-isomer), 0.875 (s, 9H, *E*-isomer), 0.04 (s, 6H, *Z*-isomer), 0.03 (m, 6H, *E*-isomer); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 155.8, 155.0, 117.4, 115.9, 99.8, 99.4, 62.0, 61.7, 31.3, 30.6, 29.9, 28.6, 25.83, 25.80, 18.2, -5.5 ppm;

HRMS *m/z* (ESI) calcd for $C_{12}H_{23}NNaOSi$ $(M + Na)^+$ 248.1441, found 248.1440.

IR (neat): ν_{max} = 2953, 2933, 2859, 2222, 1628, 1105, 839.

08) 

6-(Nonyloxy)hex-2-enenitrile (2h):

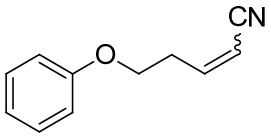
The reaction of 1-(hex-5-yn-1-yloxy)nonane **1h** (89.8 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc

(32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 55.9 mg (59%) of **2h**. **2h**: obtained as a 69:31 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.74 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.53 (dt, J_1 = 10.8 Hz, J_2 = 5.6 Hz, 1H, *Z*-isomer), 5.35 (dt, J_1 = 16.4 Hz, J_2 = 1.8 Hz, 1H, *E*-isomer), 5.32 (dt, J_1 = 10.8 Hz, J_2 = 1.4 Hz, 1H, *Z*-isomer), 3.46-3.56 (m, 4H), 2.49 (tdd, J_1 = 7.4 Hz, J_2 = 7.4 Hz, J_3 = 1.2 Hz, 2H, *Z*-isomer), 2.30 (tdd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, J_3 = 1.2 Hz, 2H, *E*-isomer), 1.80-1.70 (m, 2H), 1.60-1.50 (m, 2H), 1.38-1.21 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 155.5, 154.8, 117.4, 115.9, 99.9, 99.6, 71.13, 71.08, 69.6, 69.2, 31.8, 30.2, 29.6, 29.5, 29.4, 29.2, 28.9, 28.3, 27.8, 26.1, 22.6, 14.0 ppm;

HRMS *m/z* (ESI) calcd for $C_{15}H_{27}NNaO$ $(M + Na)^+$ 260.1985, found 260.1982.

IR (neat): ν_{max} = 2927, 2856, 2222, 1632, 1465, 1117, 739.

09) 

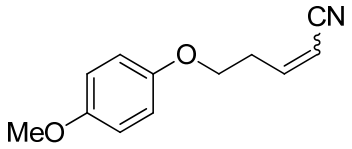
Methyl 10-cyanodec-9-enoate (2i):

The reaction of (pent-4-yn-1-yloxy)benzene **1i** (64.1 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 41.6 mg (60%) of **2i**. **2i**: obtained as a 68:32 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33-7.25 (m, 2H), 7.00-6.91 (m, 1H), 6.91-6.85 (m, 2H), 6.79 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H, *E*-isomer), 6.66 (dt, J_1 = 11.2 Hz, J_2 = 5.6 Hz, 1H, *Z*-isomer), 5.47 (dt, J_1 = 16.4 Hz, J_2 = 1.6 Hz, 1H, *E*-isomer), 5.43 (dt, J_1 = 11.2 Hz, J_2 = 1.4 Hz, 1H, *Z*-isomer), 4.10-4.02 (m, 2H), 2.93-2.85 (m, 2H, *Z*-isomer), 2.67 (tdd, J_1 = 6.4 Hz, J_2 = 6.4 Hz, J_3 = 1.6 Hz, 2H, *E*-isomer); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 158.5, 158.3, 151.9, 151.1, 129.62, 129.59, 121.3, 121.2, 117.2, 115.8, 114.6, 102.0, 101.6, 65.6, 65.2, 33.1, 31.8 ppm;

HRMS *m/z* (EI) calcd for $C_{12}H_{13}NNaO_2$ $(M + Na)^+$ 226.0839, found 226.0835.

IR (neat): ν_{max} = 3070, 2925, 2879, 2222, 1634, 1600, 1496, 1244, 1042, 755.

10) 

5-(4-Methoxyphenoxy)pent-2-enenitrile (2j):

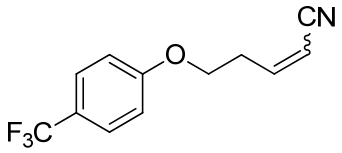
The reaction of 1-methoxy-4-(pent-4-yn-1-yloxy)benzene **1j** (76.1 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 41.0 mg (50%) of **2j**. **2j**: obtained as a 69:31 mixture of *Z/E* isomers. Colorless liquid.

***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 6.85-6.82 (m, 4H), 6.67 (dt, J_1 = 10.8 Hz, J_2 = 5.6 Hz, 1H), 5.45 (dt, J_1 = 11.2 Hz, J_2 = 1.4 Hz, 1H), 4.04 (t, J = 6.0 Hz, 2H), 3.77 (s, 3H), 2.91-2.84 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 154.1, 152.5, 151.2, 115.7, 115.5, 114.7, 101.5, 66.3, 55.7, 31.9 ppm;

^{1}H NMR for the minor *E*-isomer: 6.85-6.76 (m, 5H), 5.48 (dt, J_1 = 16.4 Hz, J_2 = 1.6 Hz, 1H), 4.05-3.89 (m, 2H), 3.77 (s, 3H), 2.70-2.62 (m, 2H).

HRMS *m/z* (ESI) calcd for $C_{12}H_{13}NNaO_2$ $(M + Na)^+$ 226.0839, found 226.0835.

IR (neat): ν_{max} = 3070, 2953, 2220, 1624, 1509, 1232, 1042, 828.

11) 

6-(4-(Trifluoromethyl)phenoxy)hex-2-enenitrile (2k):

The reaction of 1-(hex-5-yn-1-yloxy)-4-(trifluoromethyl)benzene **1k** (91.3 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 63.8 mg (66%) of **2k**. **2k**: obtained as a 63:37 mixture of *Z/E* isomers. Colorless liquid.

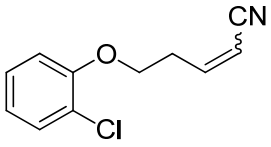
***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.55 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.66 (dt, J_1 = 10.8 Hz, J_2 = 5.6 Hz, 1H), 5.49 (dt, J_1 = 10.8 Hz, J_2 = 1.2 Hz, 1H), 4.14 (t, J = 6.0 Hz, 2H), 2.93 (tdd, J_1 = 6.0 Hz, J_2 = 6.0 Hz, J_3 = 1.2 Hz, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 160.8, 150.4, 126.9 (q, J = 3.7 Hz), 124.3 (q, J = 269.5

Hz), 123.3 (q, J = 32.4 Hz), 115.6, 114.4, 102.1, 65.8, 31.5 ppm;

^{1}H NMR for the minor *E*-isomer: 7.58-7.54 (m, 2H), 6.98-6.92 (m, 2H), 6.81 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H). 5.54-5.46 (m, 1H), 4.17-4.07 (m, 2H), 2.77-2.70 (m, 2H).

HRMS *m/z* (ESI) calcd for $C_{12}H_{10}F_3NNaO$ $(M + Na)^+$ 264.0607, found 264.0601.

IR (neat): ν_{max} = 3075, 2938, 2225, 1617, 1331, 1258, 1113, 839.

12) 

5-(2-Chlorophenoxy)pent-2-enenitrile (2l):

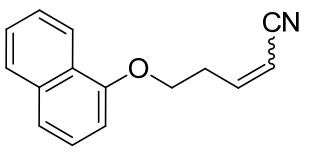
The reaction of 1-chloro-2-(pent-4-yn-1-yloxy)benzene **1l** (77.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 58.6 mg (71%) of **2l**. **2l**: obtained as a 36:34 mixture of *Z/E* isomers. Colorless liquid.

***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.39-7.35 (m, 1H), 7.21 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.96-6.88 (m, 2H), 6.76 (dt, J_1 = 11.2 Hz, J_2 = 5.4 Hz, 1H), 5.48 (d, J = 11.2 Hz, 1H), 4.15 (t, J = 5.8 Hz, 2H), 2.99-2.92 (tdd, J_1 = 6.4 Hz, J_2 = 6.4 Hz, J_3 = 1.2 Hz, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 153.8, 150.7, 130.3, 127.7, 123.1, 121.9, 115.6, 113.6, 101.7, 66.8, 31.6 ppm;

^{1}H NMR for the minor *E*-isomer: 7.37 (dd, J_1 = 8.0 Hz, J_1 = 1.2 Hz, 1H), 7.22 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.96-6.86 (m, 2H), 6.86 (dt, J_1 = 11.2 Hz, J_2 = 7.0 Hz, 1H), 5.55 (d, J = 16.4 Hz, 1H), 4.13 (t, J = 6.0 Hz, 2H), 2.75 (tdd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, J_3 = 1.6 Hz, 2H).

HRMS *m/z* (ESI) calcd for $C_{11}H_{10}ClNNaO$ $(M + Na)^+$ 230.0343, found 230.0339.

IR (neat): ν_{max} = 3066, 2934, 2225, 1636, 1250, 1063, 751.

13) 

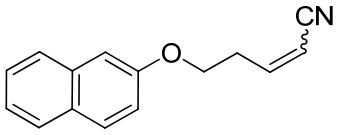
5-(Naphthalen-2-yloxy)pent-2-enenitrile (2m):

The reaction of 1-(pent-4-yn-1-yloxy)naphthalene **1m** (84.1 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 54.0 mg (60%) of **2m**. **2m**: obtained as a 64:36 mixture of *Z/E* isomers. Colorless liquid. ***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 8.27-8.21 (m, 1H), 7.82-7.76 (m, 1H), 7.53-7.42 (m, 3H), 7.36 (t, J = 8.0 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.74 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H), 5.49 (dt, J_1 = 10.8 Hz, J_2 = 1.2 Hz, 1H), 4.25 (t, J = 6.0 Hz, 2H), 3.04 (tdd, J_1 = 6.4 Hz, J_2 = 6.4 Hz, J_3 = 1.2 Hz, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 154.1, 151.1, 134.4, 127.5, 126.5, 125.7, 125.40, 125.35, 121.8, 120.7, 115.8, 104.6, 101.8, 65.7, 31.9 ppm;

^{1}H NMR for the minor *E*-isomer: 8.20-8.15 (m, 1H), 7.82-7.76 (m, 1H), 7.52-7.41 (m, 3H), 7.35 (t, J = 7.8 Hz, 1H), 6.87 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H), 6.78-6.72 (m, 1H), 5.56-5.44 (m, 1H), 4.25-4.17 (m, 2H), 2.79 (tdd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, J_3 = 1.6 Hz, 2H);

HRMS *m/z* (ESI) calcd for $C_{15}H_{13}NNaO$ $(M + Na)^+$ 246.0889, found 246.0885.

IR (neat): ν_{max} = 3056, 2931, 2880, 2220, 1626, 1508, 1270, 1101, 773.

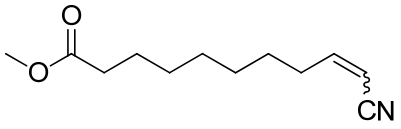
14) 

5-(Naphthalen-2-yloxy)pent-2-enenitrile (2n):

The reaction of 2-(pent-4-yn-1-yloxy)naphthalene **1n** (84.1 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 51.3 mg (57%) of **2n**. **2n**: obtained as a 64:36 mixture of *Z/E* isomers. Colorless liquid. ***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.80-7.70 (m, 3H), 7.48-7.41 (m, 1H), 7.38-7.31 (m, 1H), 7.17-7.11 (m, 2H), 6.71 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H), 5.47 (dt, J_1 = 10.8 Hz, J_2 = 1.4 Hz, 1H), 4.20 (t, J = 6.2 Hz, 2H), 2.99-2.93 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 156.4, 151.0, 134.4, 129.5, 129.1, 127.7, 126.7, 126.5, 123.8, 118.7, 115.7, 106.7, 101.7, 65.6, 31.7 ppm;

^{1}H NMR for the minor *E*-isomer: 7.80-7.70 (m, 3H), 7.48-7.41 (m, 1H), 7.38-7.31 (m, 1H), 7.17-7.08 (m, 2H), 6.82 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H), 5.52 (dt, J_1 = 16.4 Hz, J_2 = 1.6 Hz, 1H), 4.20-4.12 (m, 2H), 2.75-2.68 (m, 2H).

HRMS *m/z* (ESI) calcd for $C_{15}H_{13}NNaO$ $(M + Na)^+$ 246.0889, found 246.0884.
IR (neat): ν_{max} = 3059, 2945, 2220, 1628, 1508, 1250, 1144, 837, 753.

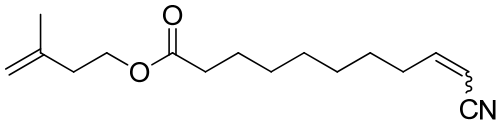
15) 

Methyl 10-cyanodec-9-enoate (2o):

The reaction of methyl undec-10-ynoate **1o** (78.5 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 58.0 mg (69%) of **2o**. **2o**: obtained as a 69:31 mixture of *Z*/*E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.72 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.49 (dt, J_1 = 11.2 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.37-5.29 (m, 1H), 3.67 (s, 3H), 2.42 (td, J_1 = 7.4 Hz, J_2 = 7.4 Hz, 2H, *Z*-isomer), 2.31 (t, J = 7.4 Hz, 2H), 2.26-2.18 (m, 2H, *E*-isomer), 1.66-1.58 (m, 2H), 1.52-1.42 (m, 2H), 1.37-1.28 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 174.1, 174.0, 155.9, 155.0, 117.4, 115.9, 99.6, 99.4, 51.3, 33.9, 33.8, 33.1, 31.7, 28.79, 18.78, 28.75, 28.63, 28.60, 28.0, 27.4, 24.69, 24.67, 24.67 ppm;

HRMS *m/z* (ESI) calcd for $C_{12}H_{19}NNaO_2$ $(M + Na)^+$ 232.1308, found 232.1305.
IR (neat): ν_{max} = 2933, 2858, 2221, 1738, 1631, 1249, 1173, 743.

16) 

3-Methylbut-3-en-1-yl 10-cyanodec-9-enoate (2p):

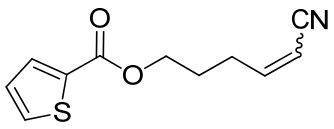
Mix 3-methylbut-3-en-1-yl undec-10-ynoate **1p** (100.2 mg, 0.40 mmol), $TMSN_3$ (69.2 mg, 0.60 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2. After stirring at 90 °C for 24 hours, another portion of $TMSN_3$ (69.2 mg, 0.60 mmol) was added. Then the mixture was

stirred for another 24 hours. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford 41.7 mg (40%) of **2p**. **2p**: obtained as a 64:36 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.72 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H, *E*-isomer), 6.48 (dt, J_1 = 11.2 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.38-5.29 (m, 1H), 4.80 (s, 1H), 4.73 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.46-2.39 (m, 2H, *Z*-isomer), 2.34 (t, *J* = 6.8 Hz, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 2.25-2.18 (m, 2H, *E*-isomer), 1.76 (s, 3H), 1.65-1.58 (m, 2H), 1.52-1.42 (m, 2H), 1.38-1.28 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.73, 173.68, 156.0, 155.1, 141.7, 117.5, 116.0, 112.2, 99.7, 99.5, 62.4, 36.7, 34.21, 34.18, 33.2, 31.8, 28.87, 28.86, 28.8, 28.7, 28.1, 27.5, 24.81, 24.79, 22.4 ppm;

HRMS *m/z* (ESI) calcd for $C_{16}H_{25}NNaO_2$ $(M + Na)^+$ 286.1778, found 286.1778.

IR (neat): ν_{max} = 3077, 2933, 2858, 2221, 1735, 1651, 1632, 1457, 1176, 836.

17) 

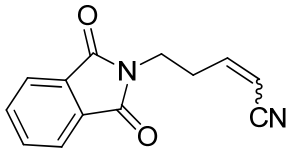
5-Cyanopent-4-en-1-yl thiophene-2-carboxylate (2q):

The reaction of hex-5-yn-1-yl thiophene-2-carboxylate **1q** (83.3 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (ballon) at 90 ^{o}C for 60 hours, afforded 65.0 mg (73%) of **2q**. **2q**: obtained as a 34:66 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76-7.71 (m, 1H), 7.52-7.47 (m, 1H), 7.06-7.01 (m, 1H), 6.68 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H, *E*-isomer), 6.46 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.36-5.28 (m, 1H), 4.29-4.22 (m, 2H), 2.56-2.48 (m, 2H, *Z*-isomer), 2.36-2.28 (m, 2H, *E*-isomer), 192-1.80 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 162.0, 161.9, 154.3, 153.4, 133.5, 133.4, 133.3, 132.53, 133.47, 127.8, 127.7, 117.1, 115.6, 100.6, 100.5, 63.72, 63.67, 29.9, 28.4, 27.3, 26.8 ppm;

HRMS *m/z* (ESI) calcd for $C_{11}H_{11}NNaO_2S$ $(M + Na)^+$ 244.0403, found 244.0398.

IR (neat): ν_{max} = 3104, 2958, 2222, 1709, 1633, 1262, 1098, 751.

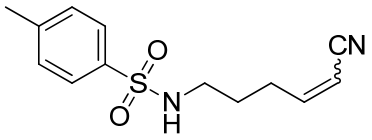
18) 

5-(1,3-Dioxoisoindolin-2-yl)pent-2-enenitrile (2r):

The reaction of 2-(pent-4-yn-1-yl)isoindoline-1,3-dione **1r** (87.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (ballon) at 90 ºC for 72 hours, afforded 58.9 mg (65%) of **2r**. **2r**: obtained as a 69:31 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89-7.84 (m, 2H), 7.78-7.72 (m, 2H), 6.70 (dt, J_1 = 16.4 Hz, J_2 = 7.2 Hz, 1H, *E*-isomer), 6.53 (dt, J_1 = 11.2 Hz, J_2 = 5.6 Hz, 1H, *Z*-isomer), 5.46-5.36 (m, 1H), 3.92-3.81 (m, 2H), 2.88-2.80 (m, 2H, *Z*-isomer), 2.69-2.61 (m, 2H, *E*-isomer); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 168.0, 167.9, 151.1, 150.4, 134.14, 134.08, 131.72, 131.65, 123.32, 123.30, 116.7, 115.2, 102.3, 102.0, 35.8, 35.7, 32.2, 31.1 ppm;

HRMS *m/z* (ESI) calcd for $C_{13}H_{10}N_2NaO_2$ $(M + Na)^+$ 249.0635, found 249.0630.
IR (neat): ν_{max} = 3064, 2939, 2220, 1773, 1708, 1619, 1397, 722.

19) 

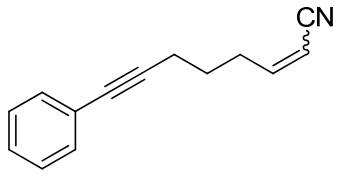
***N*-(5-Cyanopent-4-en-1-yl)-4-methylbenzenesulfonamide (2s):**

The reaction of N-(hex-5-yn-1-yl)-4-methylbenzenesulfonamide **1s** (100.5 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (ballon) at 90 ºC for 48 hours, afforded 64.5 mg (61%) of **2s**. **2s**: obtained as a 70:30 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77-7.73 (m, 2H), 7.34-7.30 (m, 2H), 6.60 (dt, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.44 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H,

Z-isomer), 5.36-5.26 (m, 1H), 5.12-4.96 (m, 1H), 3.00-2.90 (m, 2H), 2.46-2.39 (s, 2H, *Z*-isomer), 2.44 (s, 3H), 2.30-2.22 (m, 2H, *E*-isomer), 1.72-1.58 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 154.2, 153.5, 143.7, 143.6, 136.7, 129.8, 127.0, 117.2, 115.7, 100.7, 100.5, 42.3, 42.0, 29.9, 28.8, 28.2, 27.6, 21.5 ppm;

HRMS *m/z* (ESI) calcd for $C_{13}H_{16}N_2NaO_2S$ $(M + Na)^+$, 287.0825, found 287.0818.
IR (neat): ν_{max} = 3280, 3068, 2929, 2872, 2222, 1624, 1326, 1159.

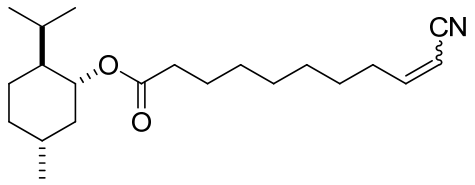
20) 

8-Phenyloct-2-en-7-ynenitrile (2t):

The reaction of octa-1,7-diyn-1-ylbenzene **1t** (72.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 72 hours, afforded 35.6 mg (46%) of **2t**. **2t**: obtained as a 66:34 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44-7.35 (m, 2H), 7.31-7.26 (m, 3H), 6.75 (dt, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.53 (dt, J_1 = 11.2 Hz, J_2 = 5.6 Hz, 1H, *Z*-isomer), 5.39 (dt, J_1 = 16.0 Hz, J_2 = 1.6 Hz, 1H, *E*-isomer), 5.36 (dt, J_1 = 11.2 Hz, J_2 = 1.2 Hz, 1H, *Z*-isomer), 2.62 (tdd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, J_3 = 1.2 Hz, 2H, *Z*-isomer), 2.50-2.43 (m, 2H), 2.45-2.38 (m, 2H, *E*-isomer), 1.84-1.71 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 154.8, 153.9, 131.52, 131.49, 128.23, 128.19, 127.8, 127.7, 123.6, 123.5, 117.3, 115.8, 100.5, 100.3, 88.6, 88.4, 81.7, 81.6, 32.2, 30.9, 27.3, 26.5, 18.9, 18.7 ppm;

HRMS *m/z* (ESI) calcd for $C_{14}H_{13}KN$ $(M + K)^+$, 234.0680, found 234.0679.
IR (neat): ν_{max} = 3057, 2931, 2863, 2237, 2222, 1626, 1490, 758, 693.

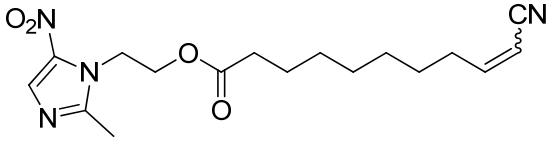
21) 

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 10-cyanodec-9-enoate (4a):

The reaction of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl undec-10-ynoate **3a** (128.2 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 65.3 mg (49%) of **4a**. **4a**: obtained as a 65:35 mixture of *Z*/*E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.71 (dt, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.48 (dt, J_1 = 11.2 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.35-5.28 (m, 1H), 4.68 (td, J_1 = 11.0 Hz, J_2 = 4.4 Hz, 1H), 2.46-2.38 (m, 2H, *Z*-isomer), 2.28 (t, *J* = 7.4 Hz, 2H), 2.25-2.18 (m, 2H, *E*-isomer), 2.01-1.94 (m, 1H), 1.91-1.82 (m, 1H), 1.72-1.57 (m, 4H), 1.52-1.28 (m, 10H), 1.12-0.83 (m, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.76 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.31, 173.27, 156.0, 155.1, 117.5, 116.0, 99.7, 99.5, 73.91, 73.89, 47.0, 40.9, 34.9, 34.63, 34.59, 34.2, 33.2, 31.8, 31.3, 28.89, 28.88, 28.86, 28.8, 28.7, 28.1, 27.5, 26.2, 25.0, 24.9, 23.4, 22.0, 20.7, 16.3 ppm;

HRMS *m/z* (ESI) calcd for $C_{21}H_{35}NNaO_2$ $(M + Na)^+$, 356.2560, found 356.2557.
IR (neat): ν_{max} = 2930, 2861, 2222, 1729, 1629, 1459, 1181.

22) 

2-(2-Methyl-5-nitro-1*H*-imidazol-1-yl)ethyl 10-cyanodec-9-enoate (4b):

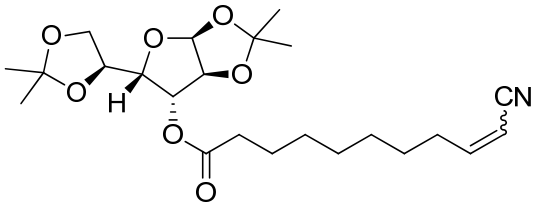
The reaction of 2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethyl undec-10-ynoate **3b** (134.2 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 ºC for 48 hours, afforded 84.1 mg (60%) of **4b**. **4b**: obtained as a 68:32 mixture of *Z*/*E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (s, 1H), 6.72 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.48 (dt, J_1 = 11.2 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.36-5.29 (m, 1H), 4.60 (t, *J* = 5.2 Hz, 2H), 4.41 (t, *J* = 5.2 Hz, 2H), 2.52 (s, 3H), 2.46-2.38 (m, 2H, *Z*-isomer), 2.29-2.24 (m, 2H), 2.24-2.18 (m, 2H, *E*-isomer), 1.60-1.51 (m, 2H), 1.50-1.40 (m, 2H), 1.36-1.23 (m, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.93, 172.89, 155.9,

155.0, 150.8, 150.7, 138.5, 133.03, 133.01, 117.5, 115.0, 99.7, 99.5, 62.2, 45.0, 44.9, 33.7, 33.2, 31.7, 28.8, 28.73, 28.71, 28.6, 28.0, 27.4, 24.5, 14.3 ppm;

HRMS *m/z* (ESI) calcd for $C_{17}H_{25}N_4O_4$ $(M + H)^+$ 349.1870, found 349.1868.

IR (neat): ν_{max} = 2932, 2858, 2220, 1740, 1630, 1468, 1190.

23) 

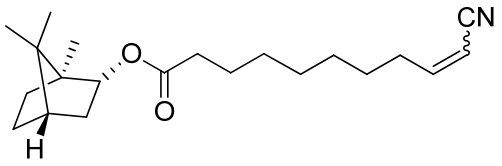
(3*aS*,5*S*,6*R*,6*aS*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 10-cyanodec-9-enoate (4c):

The reaction of (3*aS*,5*S*,6*R*,6*aS*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl undec-10-ynoate **3c** (169.8 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 116.9 mg (67%) of **4c**. **4c**: obtained as a 67:33 mixture of *Z/E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.71 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.48 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.89-5.86 (m, 1H), 5.36-5.30 (m, 1H), 5.27 (d, J_1 = 1.6 Hz, 1H), 4.49-4.46 (m, 1H), 4.21-4.19 (m, 2H), 4.11-3.98 (m, 2H), 2.46-2.38 (m, 2H, *Z*-isomer), 2.35 (td, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 2H), 2.25-2.18 (m, 2H, *E*-isomer), 1.67-1.59 (m, 2H), 1.52 (s, 3H), 1.50-1.41 (m, 2H), 1.41 (s, 3H), 1.36-1.28 (m, 12H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.19, 172.16, 155.9, 155.0, 117.5, 116.0, 112.22, 112.20, 109.2, 105.0, 99.7, 99.6, 83.3, 79.8, 75.80, 75.78, 72.4, 67.2, 34.1, 33.2, 31.7, 28.84, 28.80, 28.76, 28.7, 28.0, 27.5, 26.74, 26.66, 26.1, 25.2, 24.7 ppm;

HRMS *m/z* (ESI) calcd for $C_{23}H_{35}NNaO_7$ $(M + Na)^+$, 460.2306, found 460.2295.

IR (neat): ν_{max} = 2988, 2935, 2859, 2221, 1745, 1631, 1377, 1077, 847.

24) 

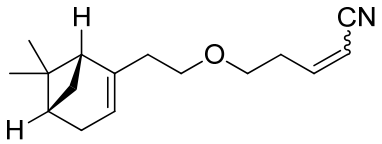
(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 10-cyanodec-9-enoate (4d):

The reaction of (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl undec-10-ynoate **3d** (127.4 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 97.3 mg (73%) of **4d**. **4d**: obtained as a 65:35 mixture of *Z*/*E* isomers. Colorless liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.71 (dt, J_1 = 16.4 Hz, J_2 = 7.0 Hz, 1H, *E*-isomer), 6.48 (dt, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.36-5.28 (m, 1H), 4.92-4.85 (m, 1H), 2.46-2.39 (m, 2H, *Z*-isomer), 2.38-2.28 (m, 3H), 2.25-2.18 (m, 2H, *E*-isomer), 1.98-1.90 (m, 1H), 1.80-1.70 (m, 1H), 1.69-1.60 (m, 3H), 1.52-1.41 (m, 2H), 1.38-1.18 (m, 8H), 0.95 (dd, J_1 = 13.6 Hz, J_2 = 3.6 Hz, 1H), 0.91 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 174.1, 174.0, 156.0, 155.1, 117.5, 116.0, 99.7, 99.5, 79.60, 79.57, 48.7, 47.7, 44.8, 36.8, 34.60, 34.56, 33.2, 31.8, 28.90, 28.88, 28.80, 28.7, 28.1, 28.0, 27.5, 27.1, 25.0, 19.7, 18.8, 13.5 ppm;

HRMS *m/z* (ESI) calcd for $C_{21}H_{33}NNaO_2$ $(M + Na)^+$ 354.2404, found 354.2403.

IR (neat): ν_{max} = 2933, 2860, 2221, 1731, 1631, 1455, 1186.

25) 

5-(2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethoxy)pent-2-enenitrile (4e):

The reaction of (1*R*,5*S*)-6,6-dimethyl-2-(2-(pent-4-yn-1-yloxy)ethyl)bicyclo[3.1.1]hept-2-ene **3e** (92.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 at 90 °C for 48 hours, afforded 50.2 mg (52%) of **4e**. **4e**: obtained as a 63:37 mixture of

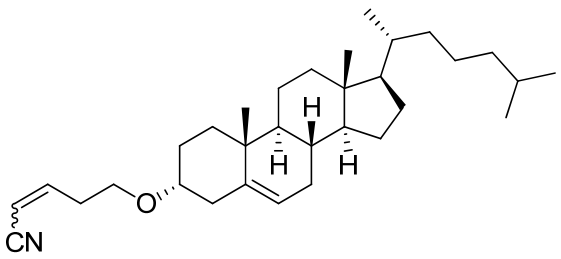
Z/E isomers. Colorless liquid.

***Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 6.59 (dt, J_1 = 10.8 Hz, J_2 = 5.6 Hz, 1H), 5.38 (dt, J_1 = 10.8 Hz, J_2 = 1.4 Hz, 1H), 5.28-5.23 (m, 1H), 3.54 (t, J = 6.2 Hz, 2H), 3.47-3.40 (m, 2H), 2.72-2.64 (m, 2H), 2.35 (dt, J_1 = 8.4 Hz, J_2 = 4.2 Hz, 1H), 2.29-2.13 (m, 4H), 2.10-2.05 (m, 1H), 2.03 (td, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 1.27 (s, 3H), 1.14 (d, J = 8.4 Hz, 1H), 0.82 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 152.2, 144.9, 118.0, 115.9, 100.8, 69.4, 68.3, 45.8, 40.7, 38.0, 37.0, 32.3, 31.6, 31.3, 26.3, 21.1 ppm;

^{1}H NMR for the minor *E*-isomer: 6.75 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H), 5.46-5.38 (m, 1H), 5.28-5.23 (m, 1H), 3.56-3.48 (m, 2H), 3.47-3.38 (m, 2H), 2.50-2.48 (m, 2H), 2.40-2.32 (m, 1H), 2.29-2.13 (m, 4H), 2.10-2.00 (m, 2H), 1.27 (s, 3H), 1.14 (d, J = 8.4 Hz, 1H), 0.82 (s, 3H).

HRMS *m/z* (ESI) calcd for $C_{16}H_{24}NO$ $(M + H)^+$ 246.1852, found 246.1845.

IR (neat): ν_{max} = 2918, 2873, 2223, 1726, 1632, 1367, 1114.

26) 

5-(((3*R*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)pent-2-enenitrile (4f):

The reaction of (3*R*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(pent-4-yn-1-yloxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene **3f** (90.6 mg, 0.20 mmol), $TMSN_3$ (46.1 mg, 0.40 mmol), CuBr (5.8 mg, 0.04 mmol), Py (31.6 mg, 0.40 mmol) and NaOAc (16.4 mg, 0.20 mmol) in PhCl (1.0 mL) under O_2 at 90 ºC for 48 hours, afforded 46.7 mg (50%) of **4f**. **4f**: obtained as a 68:32 mixture of *Z/E* isomers. White solid.

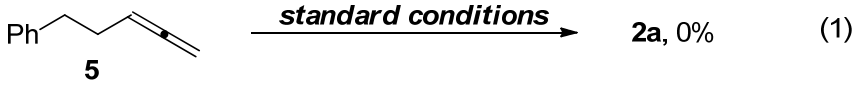
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.75 (dt, J_1 = 16.4 Hz, J_2 = 6.8 Hz, 1H, *E*-isomer), 6.48 (dt, J_1 = 11.2 Hz, J_2 = 5.4 Hz, 1H, *Z*-isomer), 5.46-5.36 (m, 1H), 5.36-5.32 (m, 1H), 3.61-3.54 (m, 2H), 3.20-3.08 (m, 1H), 2.70-2.63 (m, 2H, *Z*-isomer), 2.50-2.43 (m, 2H, *E*-isomer), 2.36-2.29 (m, 1H), 2.22-2.13 (m, 1H), 2.04-1.92 (m, 2H), 1.91-1.77 (m, 3H), 1.61-1.04 (m, 20H), 1.04-0.96 (m, 1H), 0.99 (s, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.860 (d, J = 6.4 Hz, 3H), 0.855 (d, J_1 = 6.8 Hz, 3H), 0.67 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 153.0, 152.3, 140.7, 140.6, 121.8, 121.7, 117.4, 115.8, 101.2, 100.7, 79.4, 79.2, 65.7, 65.3, 56.7, 56.1, 50.2, 42.3, 39.7, 39.5, 39.02, 38.99, 37.2, 36.8, 36.2, 35.7, 34.0, 32.7, 31.91, 31.86, 28.35, 28.31, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8 ppm;

HRMS *m/z* (ESI) calcd for $C_{32}H_{51}NNaO$ $(M + Na)^+$ 488.3863, found 488.3858.

IR (neat): ν_{max} = 2936, 2868, 2222, 1733, 1672, 1632, 1466, 1380, 1107.

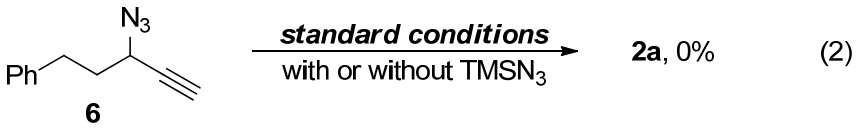
Mechanistic Studies

(1) Control experiment with allene



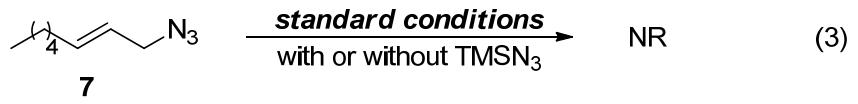
Allene **5** was prepared according to Ma's report.[7] Mix **5** (57.7 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. **NO 2a** was detected.

(2) Control experiment with propargylic azide



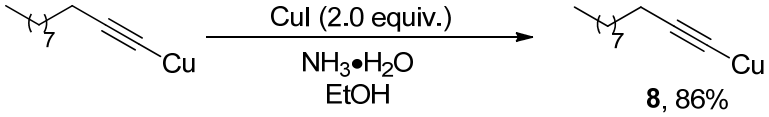
Propargylic azide **6** was prepared according to literature report.[8] Mix **6** (74.1 mg, 0.40 mmol), $TMSN_3$ (**0.80 mmol or 0 mmol**, **for two independent reactions**), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. **NO 2a** was detected.

(3) Control experiment with allyl azide



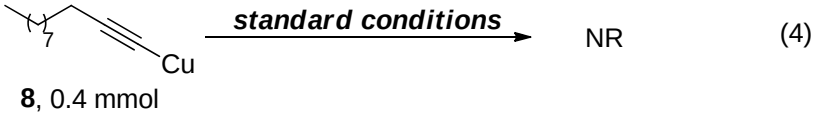
Allyl azide **7** was prepared according to literature report.[9] Mix **7** (61.3 mg, 0.40 mmol), $TMSN_3$ (**0.80 mmol or 0 mmol**, **for two independent reactions**), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. **NO 2a** was detected. And **7** remained.

(4) Preparation of copper(I)-acetylide



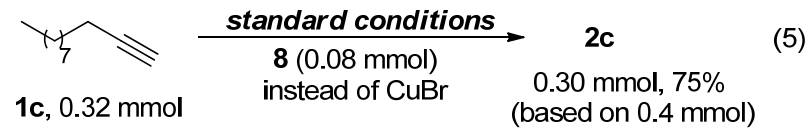
Copper(I)-acetylide **8** was prepared according to the reported procedure.[10] Add **undec-1-yne** (0.46 g, 3 mmol) to a solution of copper iodide (1.15 g, 6.0 mmol) in a mixture of ammonium hydroxide (28% NH_3 solution, 28 mL) and ethanol (9 mL) by dropwise under Ar atmosphere. The deep blue reaction mixture was stirred overnight at room temperature and the yellow precipitate was collected by filtration and successively washed with ammonium hydroxide (10% NH_3 solution, 3 x 15 mL), water (3 x 15 mL), ethanol (3 x 15 mL), and diethyl ether (3 x 15 mL). The bright yellow solid was then dried under high vacuum overnight to afford the desired Copper(I)-acetylide **8** (0.56 g, 86%).

(5) Control experiment with copper(I)-acetylide



Mix **8** (85.9 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. **NO 2a** was detected.

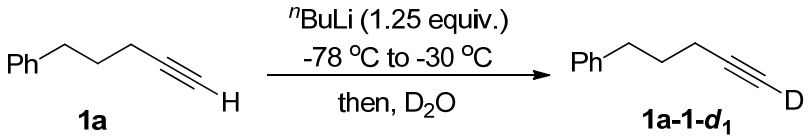
(6) Reaction catalyzed by copper(I)-acetylide



Mix **1c** (48.7 mg, 0.32 mmol), copper(I)-acetylide **8** (used as a **catalyst**, 17.2 mg, 0.08 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), **NO** CuBr (0 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room

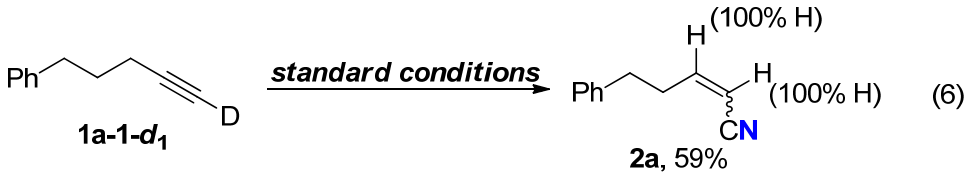
temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford 49.4 mg (75%, *Z/E* = 63:37) of **2c**. The yield is competent with the reaction employing CuBr (20 mol%) as a catalyst (entry 3 of Table 2 in Text).

(7) Preparation of **1a-1-*d*$_1$**



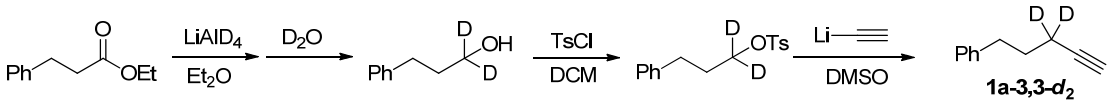
According to the literature[11], **1a** (0.58 g, 4 mmol) and dry THF (5 mL) was added to a sealed flask via a syringe under argon. ^{n}BuLi (2.5 M hexane solution; 2.0 mL, 1.25 equiv.) was added dropwise at -78 ˚C, and the reaction mixture was stirred at for 1 h at -30 ˚C. D_2O (99.9%-d; 10 mL) was carefully added to the lithium acetylide solution at -78 ˚C, and the reaction mixture was stirred for 30 min at the same temperature. After dilution with diethyl ether (15 mL), the mixture was washed with HCl (2 M, 10 mL) and extracted with diethyl ether (10 mL x 3). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. **1a-1-*d*$_1$** was obtained by flash chromatography on a short silica gel (0.47g, 81%, > 99% D).

(8) Deuterium labelling experiments with **1a-1-*d*$_1$**



Mix **1a-1-*d*$_1$** (58.1 mg, 0.40 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. 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 = 50:1) to afford 43.2 mg (69%, *Z/E* = 65:35) of **2a**. **NO** deuterium was detected in the product.

(9) Preparation of **1a-3,3-d_2**



According to the reported procedure,[12] $LiAlD_4$ (0.42 g, 10 mmol) was added to a solution of **ethyl 3-phenylpropanoate** (1.78 g, 10 mmol, in 12 mL dry Et_2O) by dropwise under argon at room temperature. The mixture was stirred until the reaction was completed (TLC monitoring). After careful addition of D_2O to the reaction mixture, the white solid was filtered off and the solvent carefully evaporated to dryness and then the residue obtained was purified by flash chromatography on silica gel to give 1.32 g of the pure dideuterated alcohol (96% for the first step).

Next, pyridine (1.58 g, 20 mmol) was added dropwise to the dideuterated alcohol (1.32 g, 9.6 mmol) and tosyl chloride (2.86 g, 15 mmol) in CH_2Cl_2 at room temperature. After being stirred for 24 h at room temperature, the reaction mixture was poured into saturated NH_4Cl. Usual work up and column purification afforded 1,1-dideuterio hydrocinnamyl tosylate (2.39 g, 85% yield for the second step).

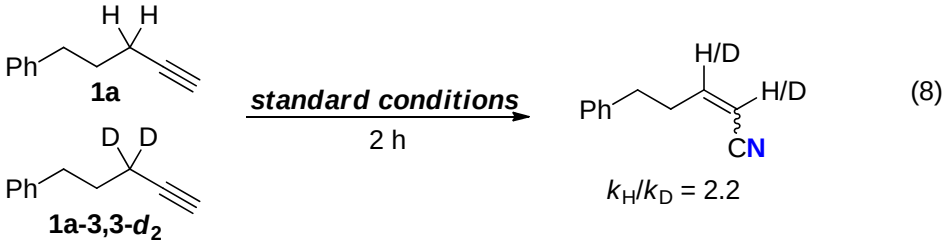
Then, a solution of 1,1-dideuterio hydrocinnamyl tosylate (1.96 g, 6.7 mmol) in DMSO (6 mL) was added dropwise to a solution of lithium acetylide ethylenediamine complex (0.78 g, 8.7 mmol) in DMSO (6 mL) at room temperature. The resulting dark brown solution was stirred for 3 h and then 30 mL of ice-water was added. After adjusting pH to 1 by HCl (1 M) and extracting with diethyl ether (10 mL x 3), The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. **1a-3,3-d_2** was obtained by flash chromatography on a short silica gel (0.10 g, 7% for three steps, > 99% D).

(10) Deuterium labelling experiments with **1a-3,3-d_2**

Mix **1a-3,3-d_2** (14.6 mg, 0.10 mmol), $TMSN_3$ (23.1 mg, 0.20 mmol), CuBr (2.9

mg, 0.02 mmol), Py (15.8 mg, 0.20 mmol) and NaOAc (8.2 mg, 0.10 mmol) in PhCl (0.5 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for 48 hours. 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 = 50:1) to afford 7.3 mg (46%, *Z*/*E* = 64:36) of **2a-*d*$_2$**. To our surprise, nearly 100% incorporation of deuterium at the both α and β positions of the nitrile was observed.

(11) Intermolecular kinetic isotopic experiment



(8)

Mix **1a** (28.8 mg, 0.20 mmol), **1a-3,3-*d*$_2$** (29.2 mg, 0.20 mmol), $TMSN_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O_2 (balloon). The reaction mixture was stirred at 90 °C for **2 hours**. After cooling down to room temperature and concentrating in vacuum, the residue was analyzed by ^{1}H-NMR. The calulated k_H/k_D is 2.2.

Computational Methods

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs.[13] Density functional theory B3LYP[14] with a standard 6-31G(d) basis set (SDD basis set for Cu atom)[15] was used for geometry optimizations (keyword 5D was used in the calculations). The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. IRC calculations[16] were used to confirm that the transition states found from the optimization calculations connect the related reactants and products. Single-point energies were obtained at the B3LYP level using 6-311+G(d,p) basic set (SDD basis set for Cu atom) based on the structures obtained on the gas-phase. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the CPCM model,[17] where UFF radii were used. The reported energies are Gibbs free energies in PhCl solution (ΔG_{sol}).

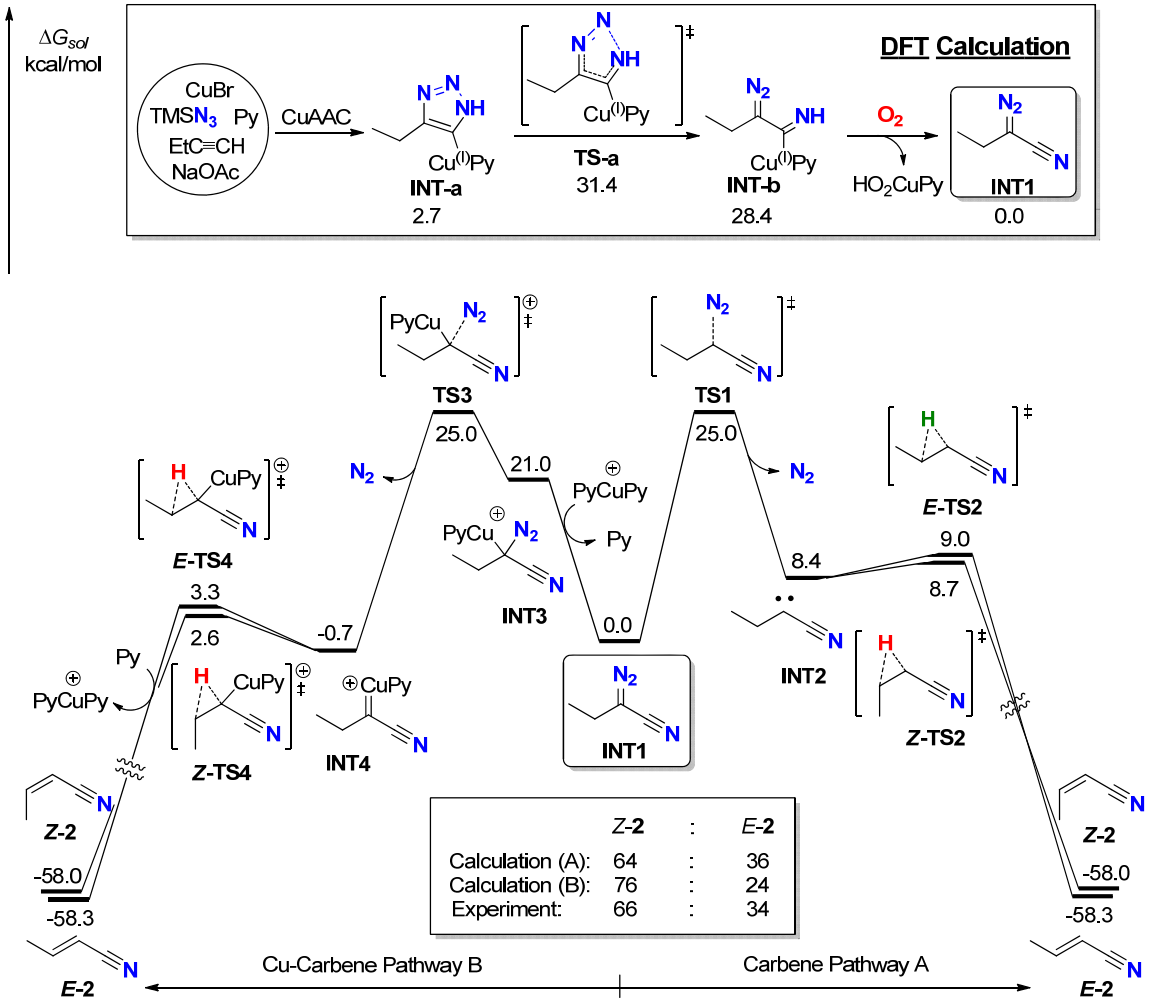


Figure S1 DFT-computed energy profiles.

To further unravel the mechanism, the density functional theory (DFT) calculation investigation was carried out (Figure S1). After the reasonable Cu-catalyzed azide-alkyne cycloaddition (CuAAC), the formed triazole intermediate **INT-a** undergoes ring-opening reaction through transition state **TS-a** with an activation free energy of 28.7 kcal/mol to afford **INT-b**. Although this is an endergonic process by 25.7 kcal/mol, the following oxidation of imine motif by molecular oxygen exergonic by 28.4 kcal/mol, delivering the stable α-diazonitrile **INT1**. See text for the details of the following processes.

Computed Energies of All Stationary Points

Table S12 Sum of electronic and zero-point energies (E, in a.u.), sum of electronic and thermal enthalpies (H, in a.u.), sum of electronic and thermal free energies (G, in a.u.), thermal correction to Gibbs free energy (TCGFE, in Hartree), and total free energy in solution (Es, in Hartree, solvent = PhCl).

Structure	$E^{[a]}$	$H^{[a]}$	$G^{[a]}$	TCGFE[a]	E_S[b]
INT-a	-765.733472	-765.718742	-765.778674	0.151388	-766.112663
TS-a	-765.685777	-765.670555	-765.731488	0.146553	-766.062095
INT-b	-765.688477	-765.672390	-765.735482	0.145851	-766.066212
O_2	-150.312830	-150.309523	-150.332809	-0.016204	-150.370488
HO_2CuPy	-596.517148	-596.506550	-596.554771	0.069743	-596.771284
INT1	-319.515380	-319.507790	-319.546183	0.058613	-319.709329
TS1	-319.469962	-319.460992	-319.502777	0.051775	-319.662595
INT2	-209.962268	-209.955363	-209.991022	0.047277	-210.111887
N_2	-109.515118	-109.511814	-109.533568	-0.012849	-109.559840
***E*-TS2**	-209.955495	-209.949091	-209.983590	0.045818	-210.109496
***Z*-TS2**	-209.956470	-209.950060	-209.984948	0.045645	-210.109881
***E*-2**	-210.069473	-210.062946	-210.097708	0.051125	-210.222077
***Z*-2**	-210.069383	-210.062979	-210.097777	0.051181	-210.221684
Cu^+Py_2	-693.614497	-693.601906	-693.655731	0.141739	-693.981660
Py	-248.190580	-248.185368	-248.217980	0.061690	-248.355795
INT3	-764.894836	-764.878742	-764.940606	0.135644	-765.298793
TS3	-764.889112	-764.872889	-764.934696	0.133422	-765.290183
INT4	-655.395055	-655.380968	-655.437847	0.127563	-655.752457
***E*-TS4**	-655.383954	-655.370368	-655.425750	0.125755	-655.744288
***Z*-TS4**	-655.386037	-655.372337	-655.428405	0.125175	-655.744857

[a] Computed at the B3LYP(gas)/SDD-6-31G(d) level.

[b] Computed at the B3LYP (CPCM)/SDD-6-311+G(d,p)// B3LYP(gas)/SDD-6-31G(d) level.

Coordinates of All Stationary Points

INT-a

C	-1.70946600	-0.62748500	-0.02954500
C	-2.76594200	0.22225700	0.31060100
N	-2.39372800	-1.75904500	-0.38873700
H	-2.01441200	-2.64170400	-0.69896300
N	-3.73630800	-1.63922200	-0.28445800
N	-3.95950000	-0.42545500	0.14161000
C	-2.73335600	1.65265500	0.76842800
H	-3.37384800	1.76119300	1.65373000
H	-1.71270700	1.90652600	1.08309600
Cu	0.15134200	-0.39446700	-0.03328600
C	2.72106300	0.33309500	-1.12028000
C	2.79984800	-0.31588100	1.10250400
C	4.09223300	0.56552000	-1.14456600
H	2.10529300	0.49498200	-1.99866200
C	4.17383100	-0.10661400	1.15850600
H	2.24595800	-0.66357200	1.96811900
C	4.83448200	0.34219000	0.01501700
H	4.56145800	0.91527100	-2.05803500
H	4.70819600	-0.29362600	2.08392600
H	5.90662200	0.51487400	0.02740400
N	2.07722900	-0.10174900	-0.01688400
C	-3.20467200	2.64319500	-0.31028400
H	-4.22056700	2.39559800	-0.63501500
H	-3.20447000	3.67319700	0.06784600
H	-2.55240200	2.60150800	-1.19114100

TS-a

C	-1.78703700	-0.77929200	-0.05207100
C	-2.73453900	0.27298500	0.29536500
N	-2.27525700	-1.93588300	-0.37889100
H	-1.56894000	-2.63918700	-0.59063900
N	-4.58698500	-1.15754700	-0.05246400
N	-3.97417700	-0.20591300	0.19648800
C	-2.46685800	1.70667000	0.64859100
H	-3.21126200	2.05272000	1.37812900
H	-1.49526200	1.75378900	1.15970000
Cu	0.08332100	-0.42134600	-0.01135000
C	2.70596600	0.03216400	-1.14766700
C	2.71052500	-0.13528800	1.16259600
C	4.08195000	0.23444300	-1.17803400
H	2.11778100	0.01247900	-2.05932700
C	4.08660500	0.06094400	1.21631900
H	2.12586900	-0.28661600	2.06411400
C	4.78738500	0.24977300	0.02516000
H	4.58332000	0.37635900	-2.12962600
H	4.59183500	0.06430100	2.17641300
H	5.86214700	0.40567000	0.03438600
N	2.02388600	-0.15044800	0.00163500
C	-2.44981300	2.67205000	-0.55201900
H	-3.41796400	2.67116800	-1.06579100
H	-2.23301500	3.70023900	-0.23412100
H	-1.68817300	2.36994200	-1.28088900

INT-b

C	-1.75234300	-0.85510200	-0.20414800
C	-2.74721600	0.12723000	0.27136000
N	-2.18587100	-1.97939800	-0.68506600
H	-1.40277900	-2.57410100	-0.96062600
N	-5.05883900	-0.65986300	0.08803600
N	-4.00296300	-0.23006500	0.19322500
C	-2.43276700	1.51329700	0.78401300
H	-3.15994800	1.80475300	1.55348400
H	-1.45708100	1.45883500	1.28604300
Cu	0.10660500	-0.43832600	-0.08045600
C	2.71151100	0.36741600	-1.06997700
C	2.75443200	-0.43546800	1.10163500
C	4.08379900	0.59557100	-1.05809200
H	2.10882800	0.59073600	-1.94439200
C	4.12835500	-0.23690500	1.19326400
H	2.18530300	-0.84218400	1.93135500
C	4.80761400	0.28847800	0.09405700
H	4.56841800	1.00559300	-1.93796200
H	4.64853600	-0.49163900	2.11068600
H	5.88007600	0.45511900	0.13440800
N	2.05041500	-0.14007000	-0.00988700
C	-2.38227500	2.59599700	-0.30843300
H	-3.35239000	2.69434400	-0.80899400
H	-2.11730600	3.57318300	0.11536300
H	-1.63905000	2.33951400	-1.07237600

O_2

O	0.00000000	0.00000000	0.60710800

O	0.00000000	0.00000000	-0.60710800

HO_2CuPy

C	1.27678400	1.15775000	-0.01231400
C	1.54845400	-1.14479300	0.01477300
C	2.65212300	1.36063600	-0.00728000
H	0.58233800	1.99070800	-0.02716100
C	2.93317900	-1.02162900	0.01983200
H	1.06711700	-2.11642100	0.02320400
C	3.49992000	0.25302200	0.00929100
H	3.04327100	2.37255300	-0.01711400
H	3.54945900	-1.91447200	0.03193500
H	4.57838700	0.38030100	0.01341100
N	0.72322500	-0.07515700	-0.00072600
Cu	-1.16887400	-0.27971800	-0.00914100
O	-2.95660100	-0.48316700	-0.03711200
O	-3.47375100	0.91047000	-0.04618800
H	-4.00575900	0.87692300	0.76649100

INT1

C	1.66355500	-0.30549800	-0.00006100
N	2.80555900	-0.54435900	0.00007700
C	0.26566700	-0.08241600	-0.00007100
C	-0.74323300	-1.22485800	-0.00002100
H	-0.54756800	-1.85215000	0.87910400
H	-0.54764600	-1.85216100	-0.87915600
C	-2.20587600	-0.77105100	0.00004100
H	-2.44590800	-0.17523900	-0.88746200
H	-2.86150200	-1.64689600	0.00007600
H	-2.44582900	-0.17522700	0.88755600
N	-0.14127300	1.16337500	-0.00002200
N	-0.52603400	2.23878500	0.00002400

TS1

C	1.55943200	-0.57067900	-0.08364500
N	2.70869600	-0.74142400	0.08037100
C	0.21857400	-0.36717400	-0.46546500
C	-0.81840900	-1.18697000	0.22602100
H	-0.65052400	-1.34259000	1.30186300
H	-0.61348300	-2.17324100	-0.23631400
C	-2.26482400	-0.78270900	-0.06680400
H	-2.42993800	-0.68250600	-1.14384900
H	-2.96290600	-1.52733300	0.32921700
H	-2.50226700	0.17827000	0.40359200
N	-0.06549600	1.47820100	0.21016200
N	-0.21598900	2.54787900	-0.04984000

INT2

C	-1.49388700	-0.10524200	-0.00306500
N	-2.64841400	0.10883800	0.11820000
C	-0.19081100	-0.54788700	-0.16561700
C	0.89612000	0.44041400	-0.09059300
H	0.69720000	1.31717100	0.54703300
H	0.82147200	0.84254800	-1.12970300
C	2.29975300	-0.13394500	0.12564600
H	2.48859900	-0.95908400	-0.56714900
H	3.06319600	0.63715900	-0.02114800
H	2.40138300	-0.51970000	1.14534200

N_2

N	0.00000000	0.00000000	0.55265300
N	0.00000000	0.00000000	-0.55265300

***E*-TS2**

C	1.49259500	-0.09256700	-0.01481300
N	2.63208000	0.17288200	-0.04602400
C	0.16405300	-0.58798200	-0.03380100
C	-0.86947100	0.36136200	0.04603800
H	-0.67511800	1.44339900	0.01640400
H	-0.46478700	-0.19585900	1.10468700
C	-2.32357300	-0.03019000	-0.06890400
H	-2.44523500	-1.10795100	0.06684900
H	-2.95388300	0.51620000	0.64107200
H	-2.66715700	0.23029200	-1.07795700

***Z*-TS2**

C	1.24533000	0.09475800	-0.01759700
N	2.20015800	-0.58248400	0.02442200
C	0.20661800	1.05212100	-0.12793200
C	-1.11607900	0.58312900	-0.01098800
H	-1.89548100	1.34050000	-0.13870800
H	-0.58237400	1.05024800	1.01658300
C	-1.61445200	-0.84648900	-0.00528500
H	-0.82147100	-1.55025700	0.26075700
H	-2.46229300	-0.97199400	0.67613000
H	-1.96799000	-1.09221900	-1.01490500

***E*-2**

C	1.50211500	0.09189200	-0.00006900
N	2.62510300	-0.21441700	0.00022300
C	0.13044100	0.49228400	-0.00025700
C	-0.88530900	-0.38650300	-0.00033400
H	-0.05638500	1.56433000	0.00021600
H	-0.65529200	-1.45097100	-0.00003400
C	-2.33242700	-0.00621800	0.00020500
H	-2.84226700	-0.42034500	-0.87969100

H	-2.84170800	-0.42038000	0.88039300
H	-2.46899100	1.07955900	0.00028100
Z-2			
C	-1.24825900	0.07645800	-0.00028200
N	-2.16216000	-0.64471500	0.00016000
C	-0.13899200	0.97891200	0.00001800
C	1.14351100	0.57528400	-0.00011300
H	-0.38809600	2.03676300	0.00040300
H	1.90663500	1.35223300	0.00044600
C	1.62754800	-0.84039000	0.00000600
H	2.25621000	-1.03022200	-0.87991200
H	2.25560700	-1.03033400	0.88037500
H	0.80191000	-1.55701900	-0.00020600
$Cu^{+}Py_2$			
C	-2.59374500	-0.58111600	1.00790700
C	-2.59377700	0.58110700	-1.00791100
C	-3.98224900	-0.60033900	1.04087100
H	-2.00707900	-1.03685700	1.79805500
C	-3.98228500	0.60036400	-1.04081200
H	-2.00713900	1.03683300	-1.79808900
C	-4.69176600	0.00002200	0.00004500
H	-4.49102200	-1.07921900	1.87032200
H	-4.49108000	1.07925500	-1.87024200
H	-5.77741900	0.00003300	0.00007200
N	-1.90166200	-0.00001000	-0.00002000
Cu	-0.00026700	-0.00003000	-0.00003800
C	2.59379800	1.00805500	0.58098900
C	2.59387800	-1.00804300	-0.58100400
C	3.98242500	1.04116200	0.60032200
H	2.00693700	1.79827600	1.03651000
C	3.98253600	-1.04109500	-0.60025300
H	2.00711800	-1.79829300	-1.03661200
C	4.69181400	0.00003800	0.00006400
H	4.49123600	1.87063300	1.07901800
H	4.49137500	-1.87054200	-1.07896000
H	5.77748600	0.00009000	0.00011300
N	1.90217200	-0.00002800	-0.00003700
Py			
C	-1.14277700	-0.72193400	-0.00021700
C	-1.19895300	0.67332800	-0.00012000
C	0.00024400	1.38569300	0.00009400
C	1.19919000	0.67292200	0.00021600
C	1.14252300	-0.72232100	0.00012500
N	-0.00024900	-1.42075700	-0.00009900
H	0.00040800	2.47254800	0.00016200
H	-2.06016500	-1.30893500	-0.00037300
H	-2.15797400	1.18298700	-0.00023100
H	2.15840900	1.18221300	0.00035900
H	2.05970200	-1.30964500	0.00018600
INT3			
C	-2.20077600	1.66158300	-0.32628300
N	-2.17206000	2.79843000	-0.57200700
C	-2.83005500	-0.66507700	-1.17435500
H	-2.36912200	-0.36017800	-2.11910200
H	-3.89086100	-0.39404800	-1.23639500
C	-2.66174800	-2.16863600	-0.95269100
H	-3.11717700	-2.50549100	-0.01440100
H	-3.15775800	-2.71074400	-1.76293300
H	-1.60586700	-2.46297900	-0.94989400
N	-2.66035800	-0.05355200	1.18670000
N	-3.03291400	-0.35158900	2.19697200
C	-2.14822700	0.22849300	-0.09316200
Cu	-0.16148800	0.01303900	0.02646700
C	2.42795700	-1.21928700	0.13908300
C	2.46330300	1.09791600	-0.08760300
C	3.81540000	-1.27912400	0.13504100
H	1.82815500	-2.11820200	0.23151200
C	3.85224100	1.11323200	-0.09898800
H	1.89110400	2.01543700	-0.17386200
C	4.54277000	-0.09406700	0.01394300
H	4.31019000	-2.23994900	0.22567800
H	4.37559900	2.05820100	-0.19543300
H	5.62825200	-0.11146200	0.00774100
N	1.75468100	-0.05027300	0.02971300
TS3			
C	-2.40254100	1.58660800	-0.45348300
N	-2.59718900	2.71609300	-0.66035900
C	-2.87545200	-0.78814000	-1.09037900
H	-2.55748800	-0.55367300	-2.11878100
H	-3.94411500	-0.54776500	-1.04639700
C	-2.61865000	-2.26529800	-0.79000500
H	-2.93790500	-2.53519500	0.22327300
H	-3.18724300	-2.88793200	-1.48614200
H	-1.55830800	-2.52021100	-0.89765400
N	-2.62104800	-0.05338600	1.37528400
N	-2.78697500	-0.23411300	2.45497000
C	-2.05555400	0.19854200	-0.27018100
Cu	-0.14033300	0.03276200	-0.07926700

C	2.45819900	-1.18606800	0.04583300
C	2.48500500	1.13991300	-0.03411900
C	3.84542300	-1.23926800	0.08469500
H	1.86176900	-2.09198100	0.06072000
C	3.87335800	1.16329100	0.00183300
H	1.90950800	2.05822600	-0.08270000
C	4.56814200	-0.04542200	0.06230100
H	4.34373500	-2.20141400	0.13118600
H	4.39331400	2.11482100	-0.01817100
H	5.65334800	-0.05707000	0.09116300
N	1.78027900	-0.01614400	-0.01228400

INT4

C	-2.85469600	-1.47185100	-0.03179600
N	-3.20591500	-2.58850000	-0.09450400
C	-3.32211800	0.93146900	0.13382400
H	-3.64221500	0.83904900	1.19934600
H	-4.24441500	0.68941600	-0.41719500
C	-2.81929500	2.34880900	-0.14045000
H	-2.52515700	2.46039800	-1.18897100
H	-3.61170900	3.07362400	0.06444100
H	-1.96196800	2.59750200	0.49465500
C	-2.33819500	-0.16456900	0.03018400
Cu	-0.47513100	-0.05298500	0.02410300
C	2.15509600	-1.16903600	0.00195100
C	2.13151700	1.16067300	0.00355100
C	3.54323100	-1.19287000	-0.00981200
H	1.57802900	-2.08772900	0.00606600
C	3.51871200	1.21273200	-0.00827300
H	1.53600200	2.06739800	0.00862900
C	4.23937900	0.01703400	-0.01497600
H	4.06270100	-2.14481100	-0.01492800
H	4.01922800	2.17479100	-0.01221900
H	5.32495000	0.02811000	-0.02419500
N	1.45185300	-0.01086000	0.00881100

***E*-TS4**

C	-2.79112200	1.53780200	-0.02608200
N	-3.02733400	2.67427200	-0.11319500
C	-3.37630800	-0.81573300	-0.04925400
H	-4.41446000	-0.48372300	-0.14157900
H	-2.83544200	-0.34986800	1.11292900
C	-3.13691400	-2.28698000	-0.09471100
H	-2.10130200	-2.55005300	0.13575900
H	-3.82639300	-2.82951400	0.56006400
H	-3.35568300	-2.61136400	-1.12274600
C	-2.36540900	0.16309400	0.03602200
Cu	-0.45439000	-0.01432100	0.05885400
C	2.16972900	-1.19446500	-0.00016100
C	2.15041100	1.13199400	0.00560900
C	3.55780500	-1.22181400	-0.03531300
H	1.59169100	-2.11219400	0.01196900
C	3.53813800	1.18188200	-0.02986900
H	1.55715400	2.04012400	0.02237500
C	4.25690800	-0.01392800	-0.05064200
H	4.07505100	-2.17492000	-0.05060400
H	4.03893400	2.14376700	-0.04100800
H	5.34216600	-0.00498400	-0.07845400
N	1.46821600	-0.03756600	0.02047100

***Z*-TS4**

C	2.74228400	1.26662000	-0.02817000
N	3.06003100	2.38161500	-0.13831400
C	3.14968900	-1.13209700	0.04456200
H	2.72574400	-2.13523000	0.10372900
H	2.64954700	-0.63221300	1.17150600
C	4.62672200	-1.03424500	-0.16391600
H	4.99823400	-0.00951200	-0.09424600
H	5.16808200	-1.68329100	0.53153300
H	4.83431900	-1.41125100	-1.17599800
C	2.21922400	-0.07048500	0.06254900
Cu	0.30448700	-0.13272700	0.07563400
C	-2.35201200	-1.21715000	-0.05714800
C	-2.26174300	1.10553200	0.04967500
C	-3.73977400	-1.19972800	-0.10892700
H	-1.80203700	-2.15182100	-0.07871400
C	-3.64669300	1.19987200	0.00103300
H	-1.64119200	1.99317100	0.11219400
C	-4.40129100	0.02887200	-0.07968600
H	-4.28561900	-2.13476200	-0.17156900
H	-4.11777800	2.17639400	0.02611200
H	-5.48533400	0.07281300	-0.11932200
N	-1.61610400	-	

References

(1) P. J. Black, M. G. Edwards and J. M. J. Williams, *Eur. J. Org. Chem.,* 2006, 4367.

(2) (a) C. Hayashi, T. Hayashi, S. Kikuchi and T. Yamada, *Chem. Lett.,* 2014, **43**, 565; (b) Z. Zhang and L. S. Liebeskind, *Org. Lett.,* 2006, **8**, 4331.

(3) S. T. Kemme, T. Šmejkal and B. Breit, *Chem. Eur. J.,* 2010, **16**, 3423.

(4) T. Kochi, S. Noda, K. Yoshimura and K. Nozaki, *J. Am. Chem. Soc.,* 2007, **129**, 8948.

(5) C. M. McMahon and E. J. Alexanian, *Angew. Chem., Int. Ed.,* 2014, **53**, 5974.

(6) M. Tobisu, H. Kinuta, Y. Kita, E. Rémond and N. Chatani, *J. Am. Chem. Soc.,* 2011, **134**, 115.

(7) H. Luo and S. Ma, *Eur. J. Org. Chem.*, 2013, 3041.

(8) P. Wipf, Y. Aoyama and T. E. Benedum, *Org. Lett.*, 2004, **6**, 3593.

(9) A. Jaganathan, A. Garzan, D. C. Whitehead, R. J. Staples and B. Borhan, *Angew. Chem., Int. Ed.*, 2011, **50**, 2593.

(10) K. Jouvin, R. Veillard, C. Theunissen, C. Alayrac, A.-C. Gaumont and G. Evano, *Org. Lett.*, 2013, **15**, 4592.

(11) M. Fukushima, D. Takushima, H. Satomura, G. Onodera and M. Kimura, *Chem.-Eur. J.*, 2012, **18**, 8019.

(12) (a) K. Fujita, H. Yorimitsu, H. Shinokubo and K. Oshima, *J. Am. Chem. Soc.*, 2004, **126**, 6776; (b) S. E. Tully and B. F. Cravatt, *J. Am. Chem. Soc.*, 2010, **132**, 3264.

(13) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, Revision A.01,

Gaussian, Inc., Wallingford CT, 2009.

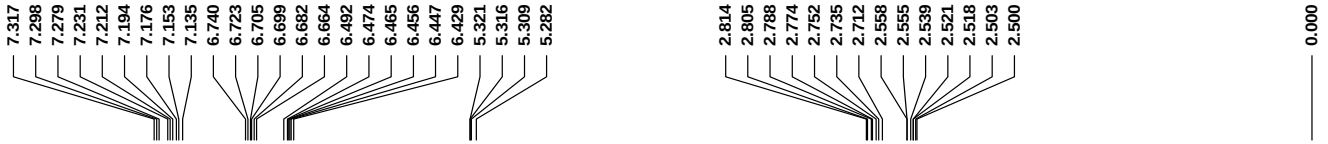
(14) (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

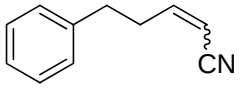
(15) W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(16) (a) K. Fukui, *J. Phys. Chem.,* 1970, **74**, 4161; (b) C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.,* 1989, **90**, 2154; (c) C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.,* 1990, **94**, 5523.

(17) (a) V. Barone and M. Cossi, *J. Phys. Chem. A,* 1998, **102**, 1995; (b) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.,* 2003, **24**, 669.

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





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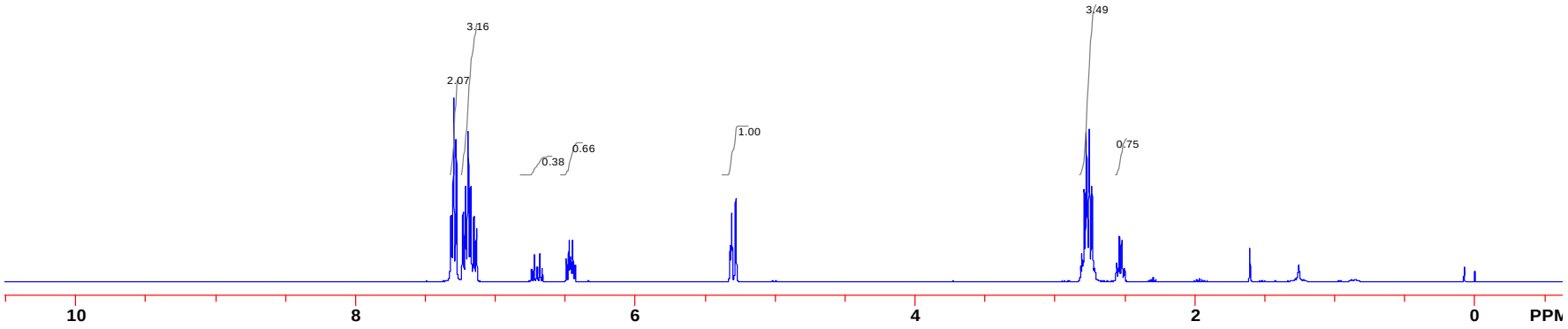

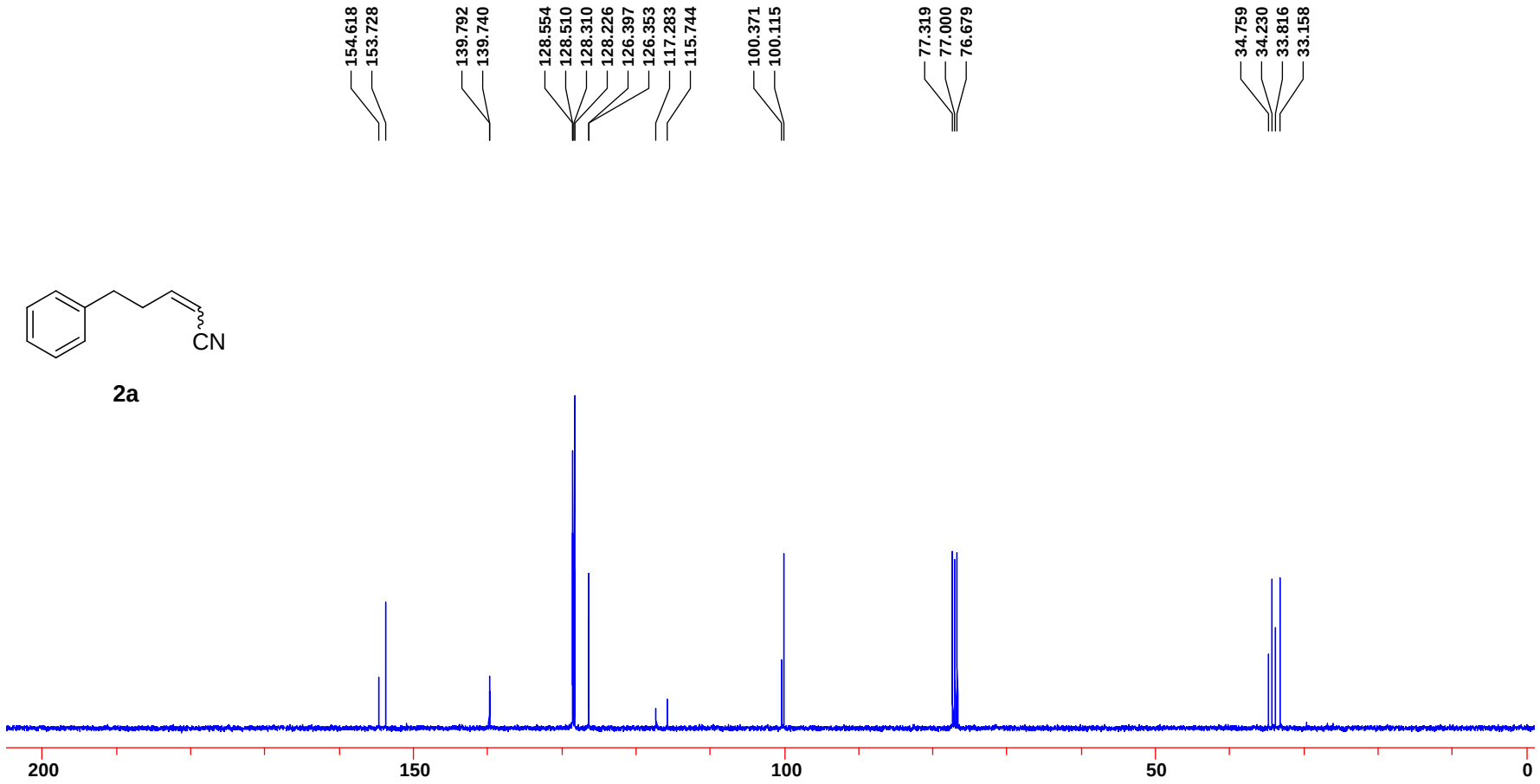
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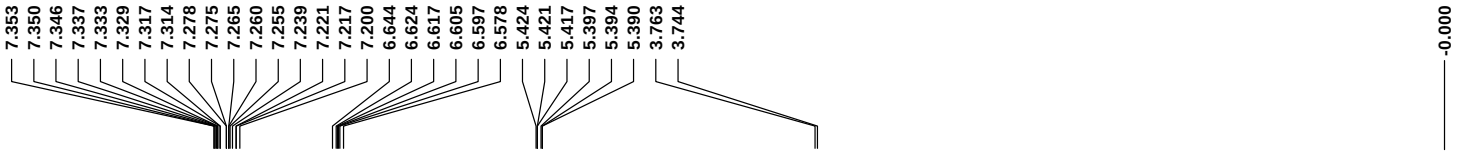
100
50
0

2a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7.217
7.200
6.644
6.624
6.617
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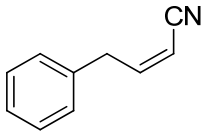
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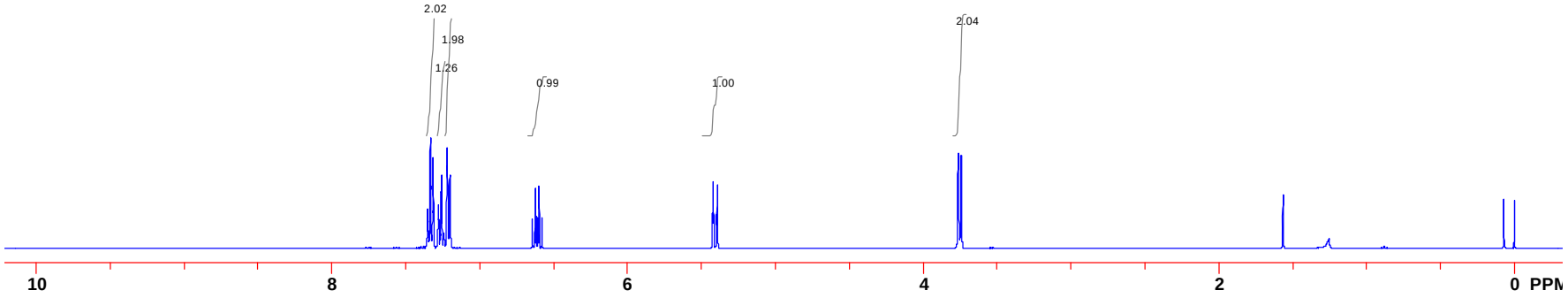
***Z*-2b**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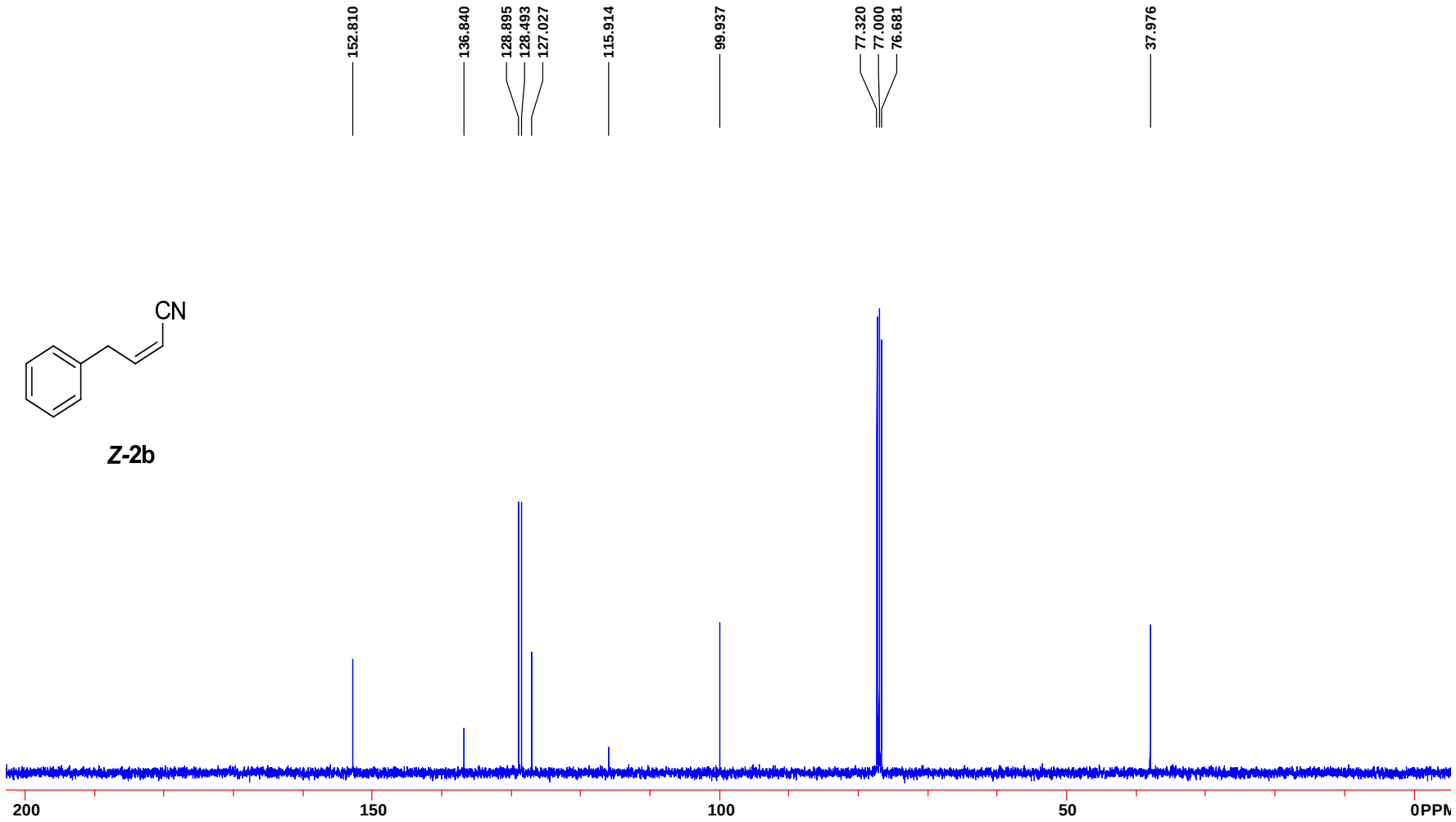
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Z-2b
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150
100
50
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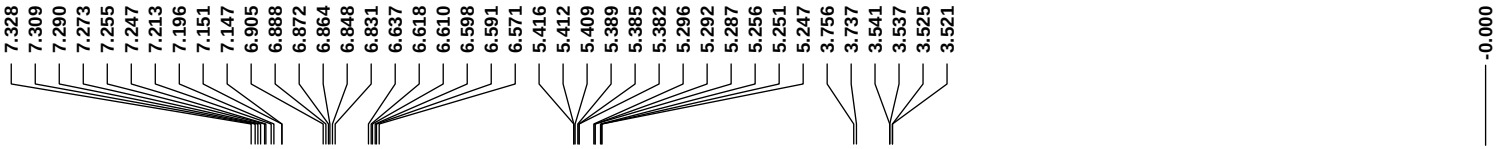
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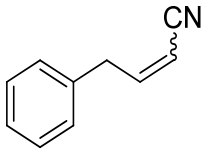
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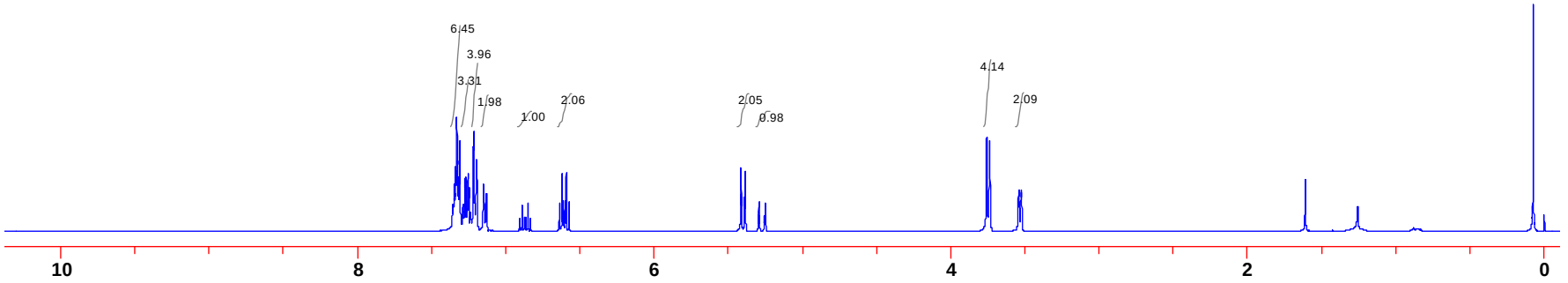
***(Z/E)*-2b**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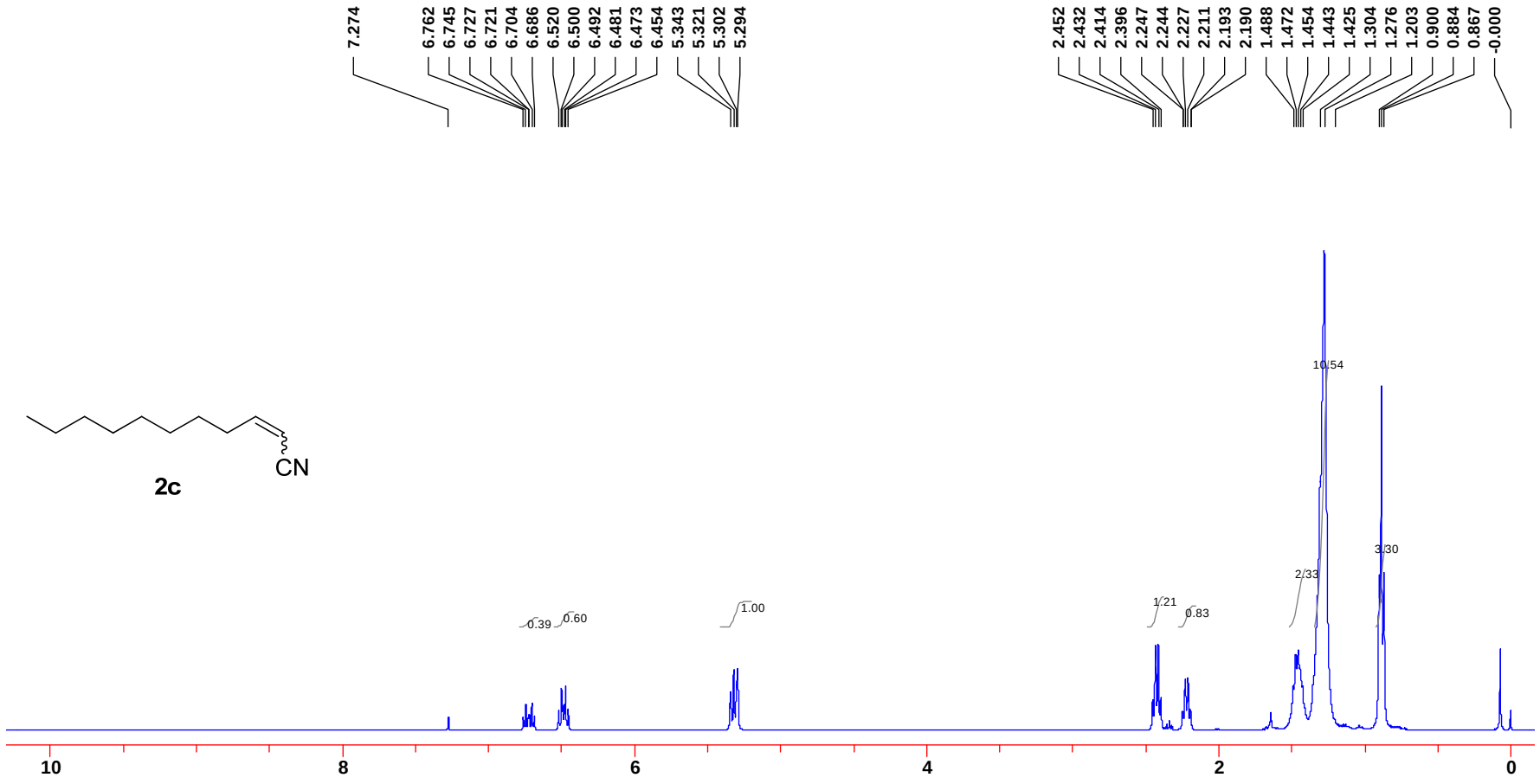
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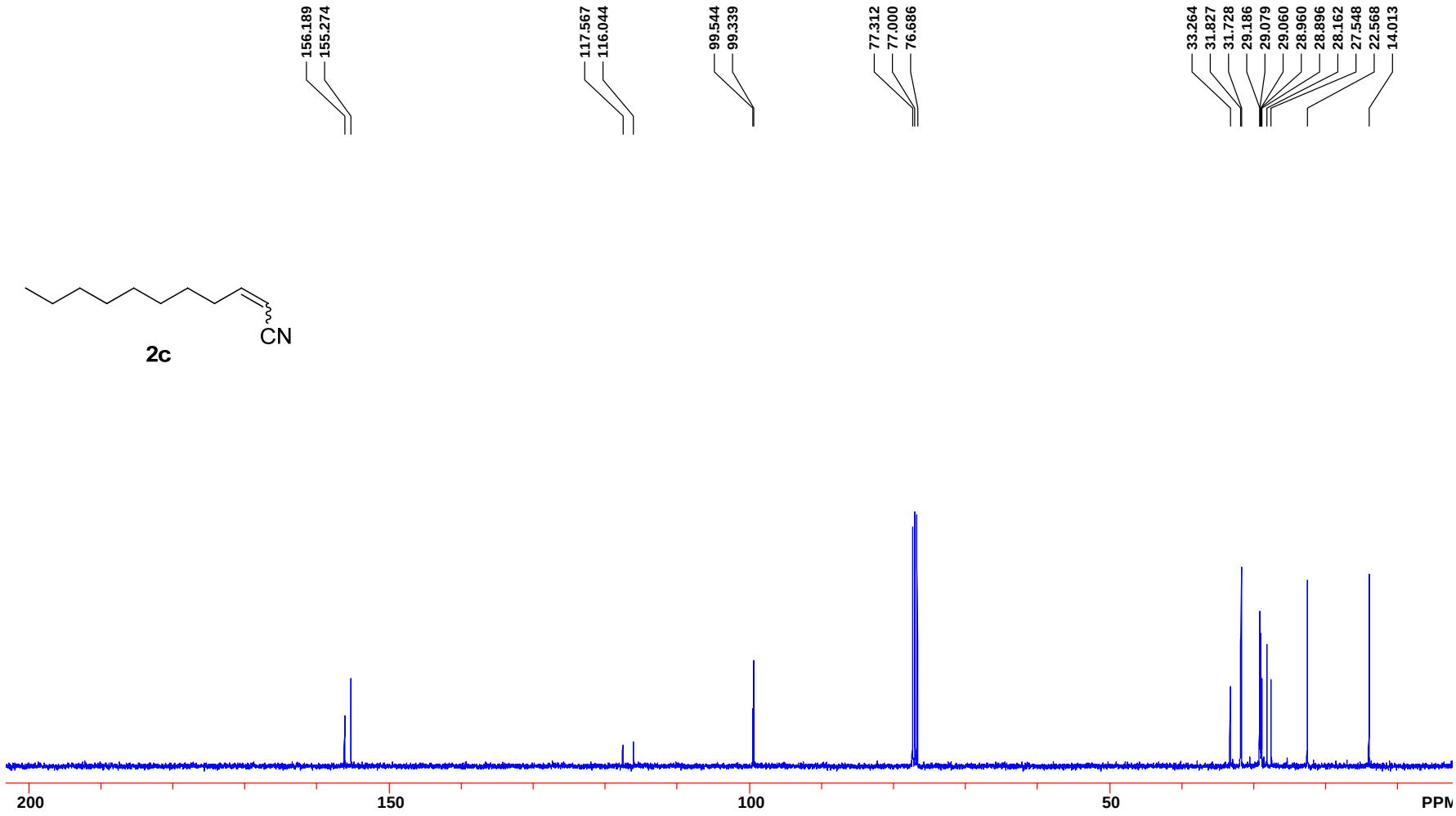
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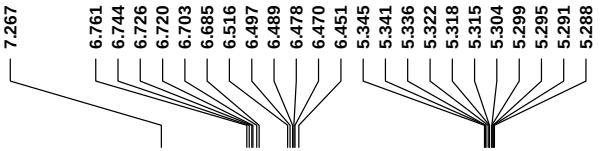
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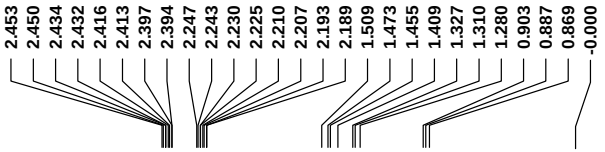
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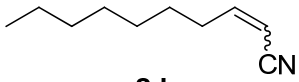
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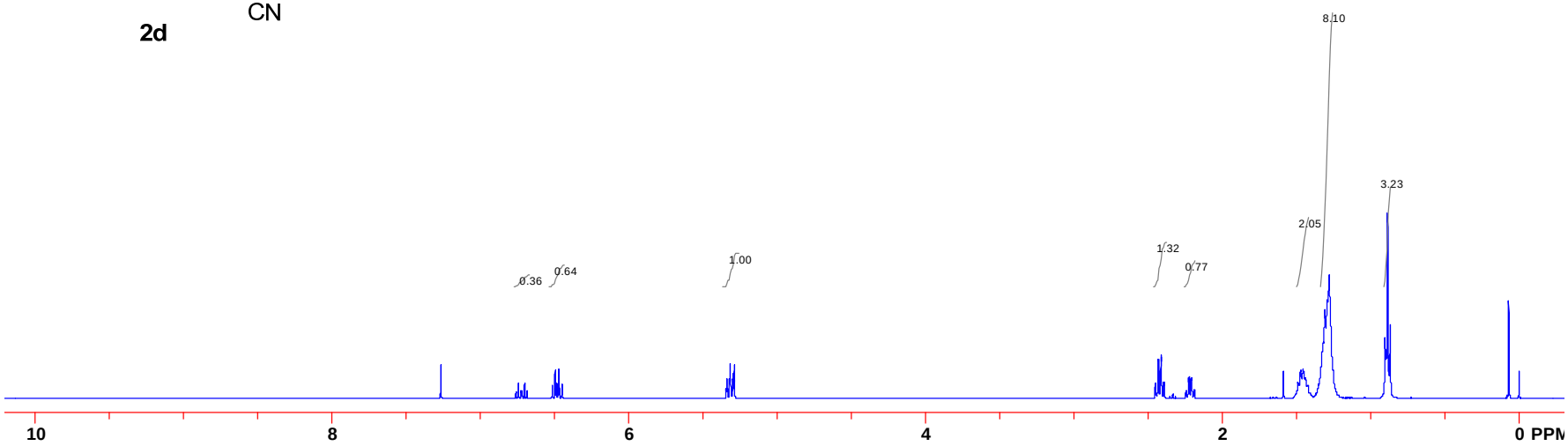
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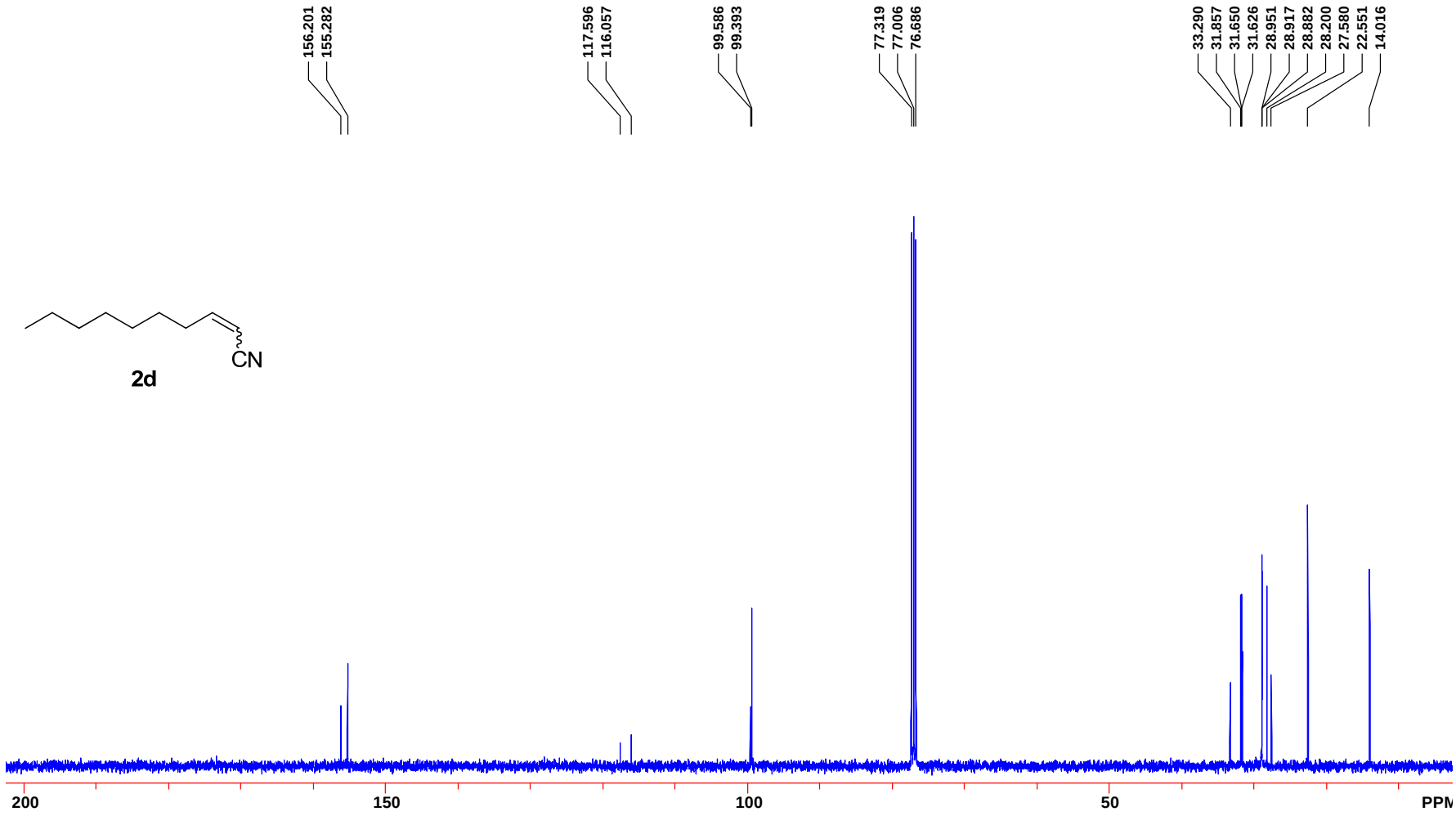
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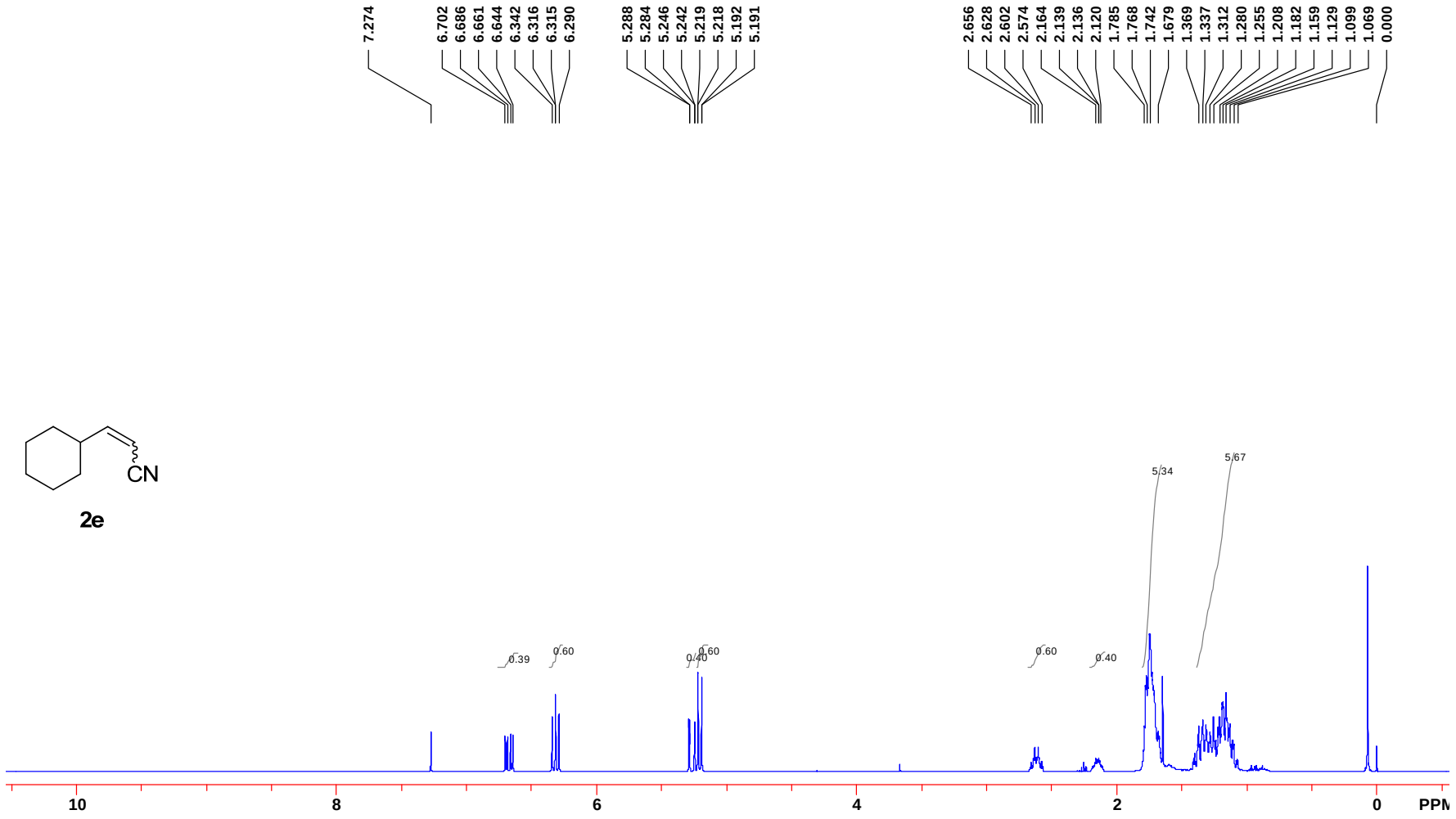
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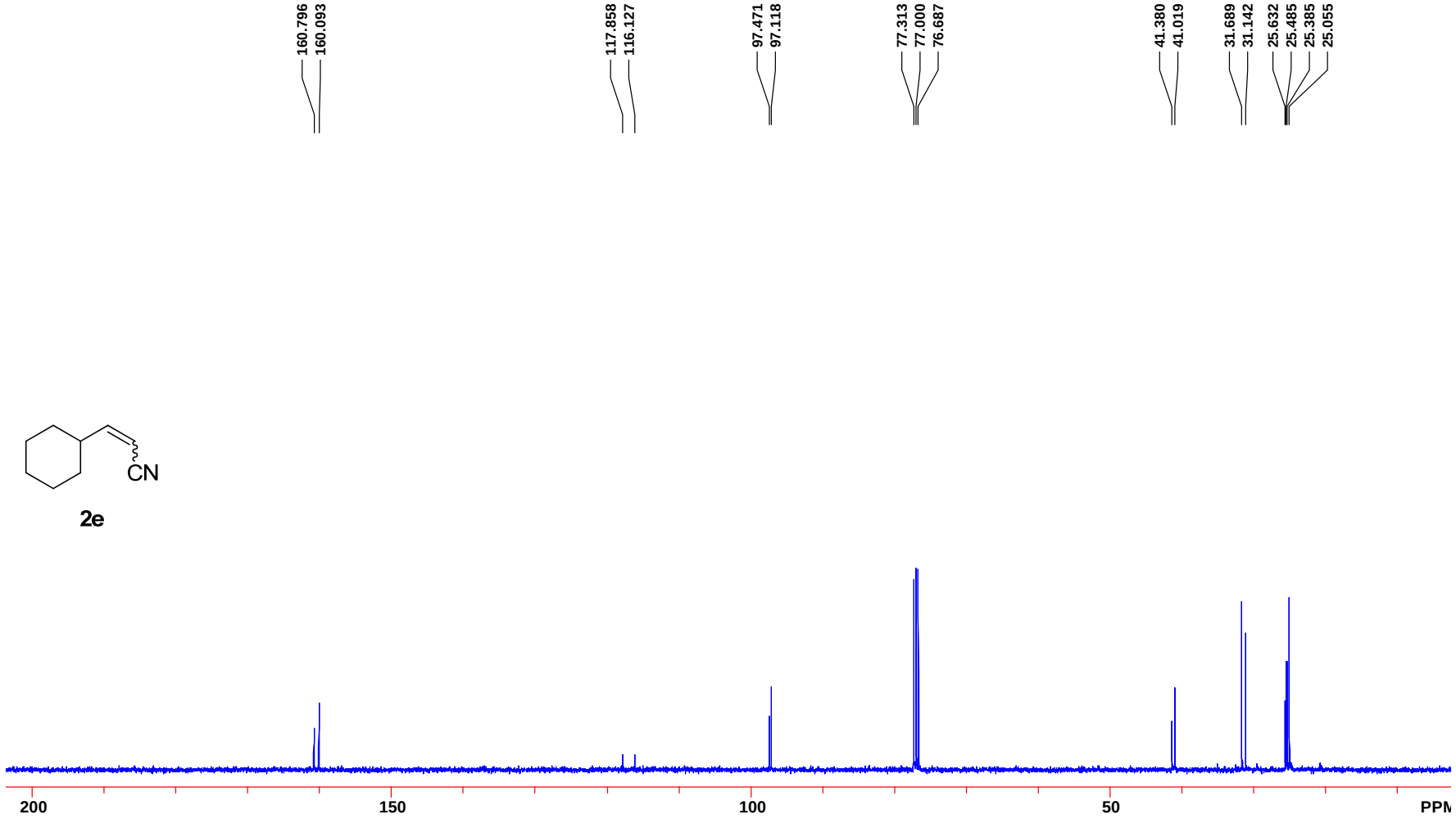
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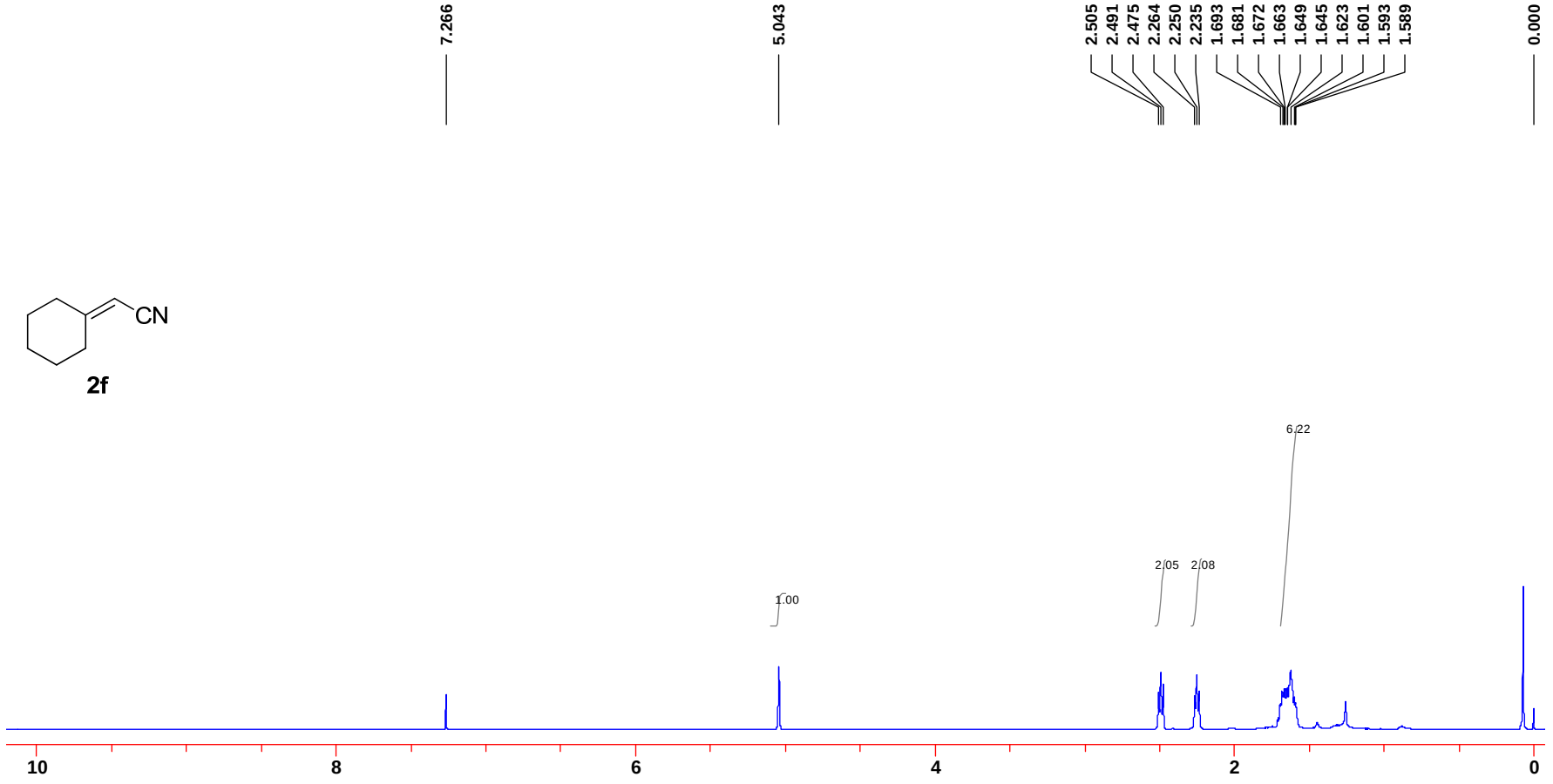
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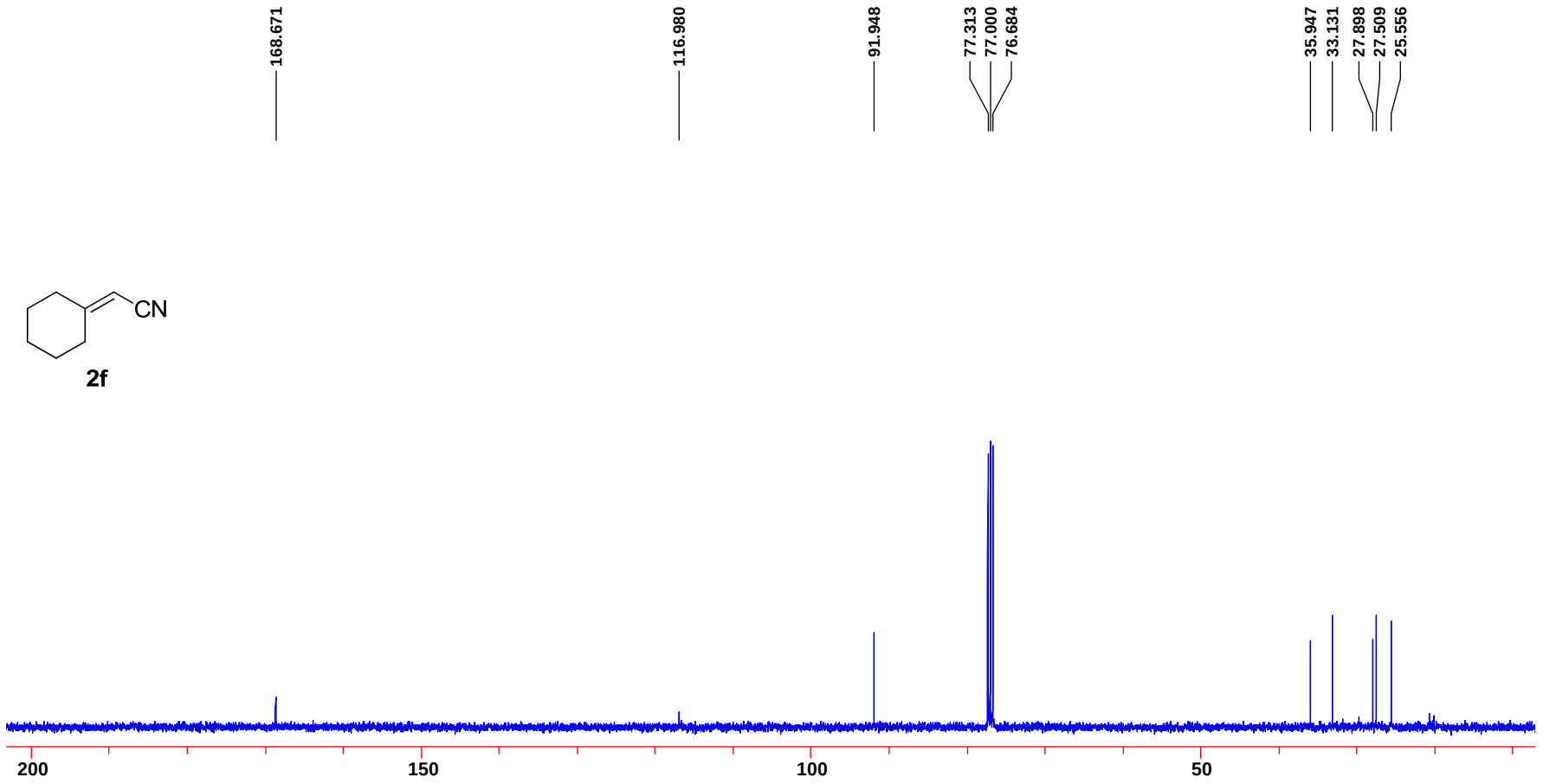
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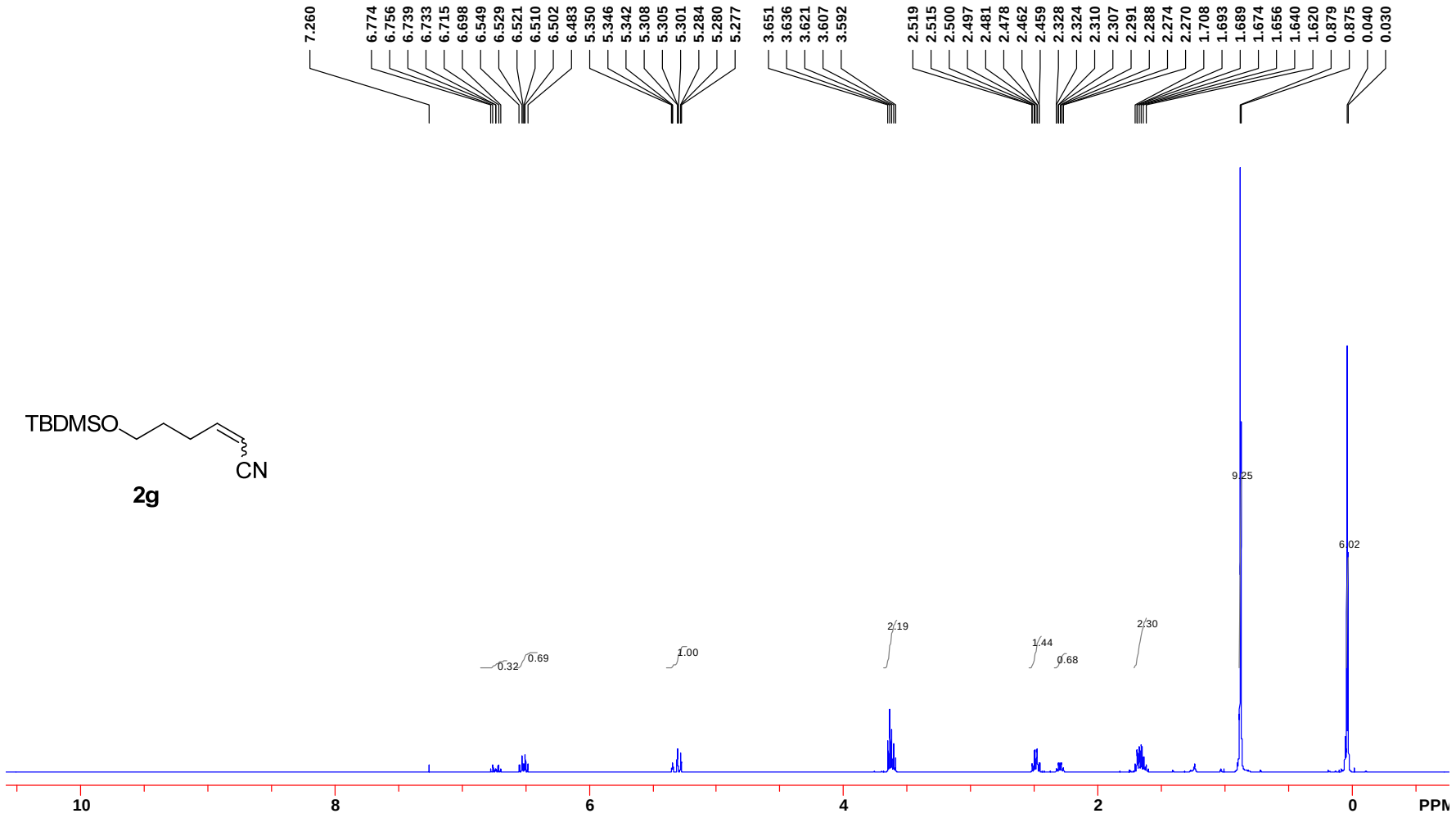
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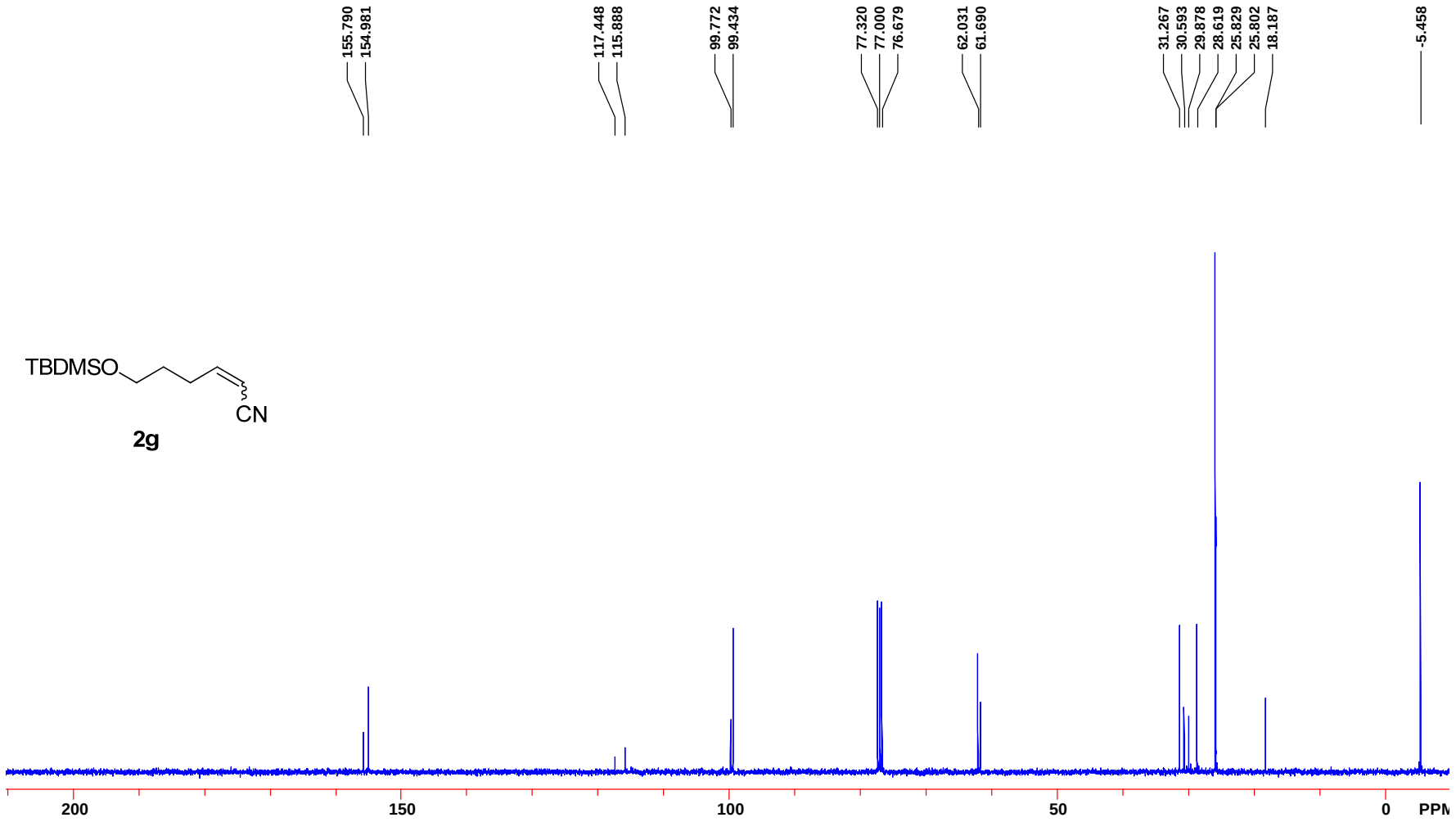
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-5.458
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2g
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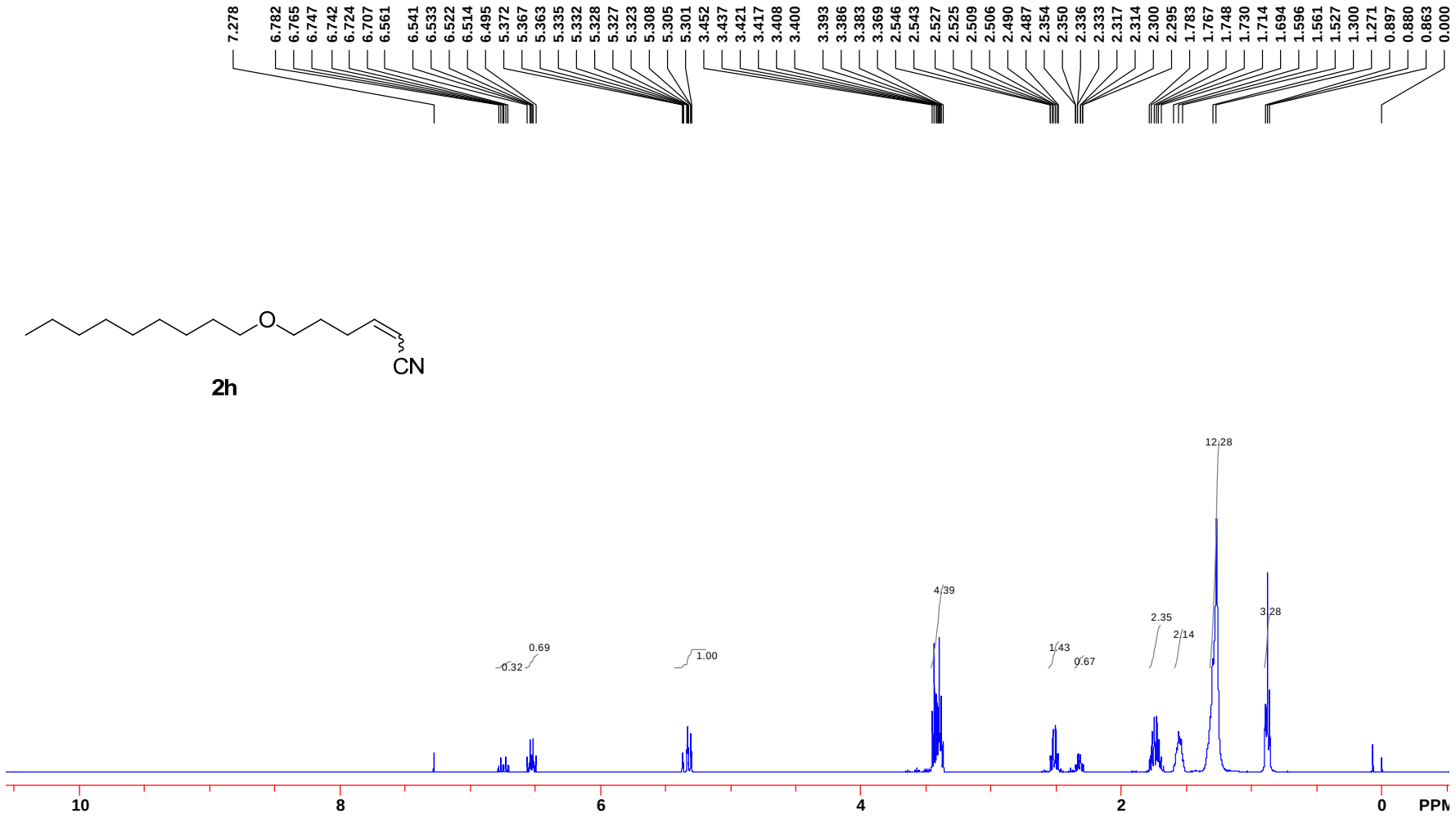
PPM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5.363
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5.332
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5.327
5.323
5.308
5.305
5.301
3.452
3.437
3.421
3.417
3.408
3.400
3.393
3.386
3.383
3.369
2.546
2.543
2.527
2.525
2.509
2.506
2.490
2.487
2.354
2.350
2.336
2.333
2.317
2.314
2.300
2.295
1.783
1.767
1.748
1.730
1.714
1.694
1.596
1.561
1.527
1.300
1.271
0.897
0.880
0.863
0.000
O
CN
2h
0.32
0.69
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10
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6
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0
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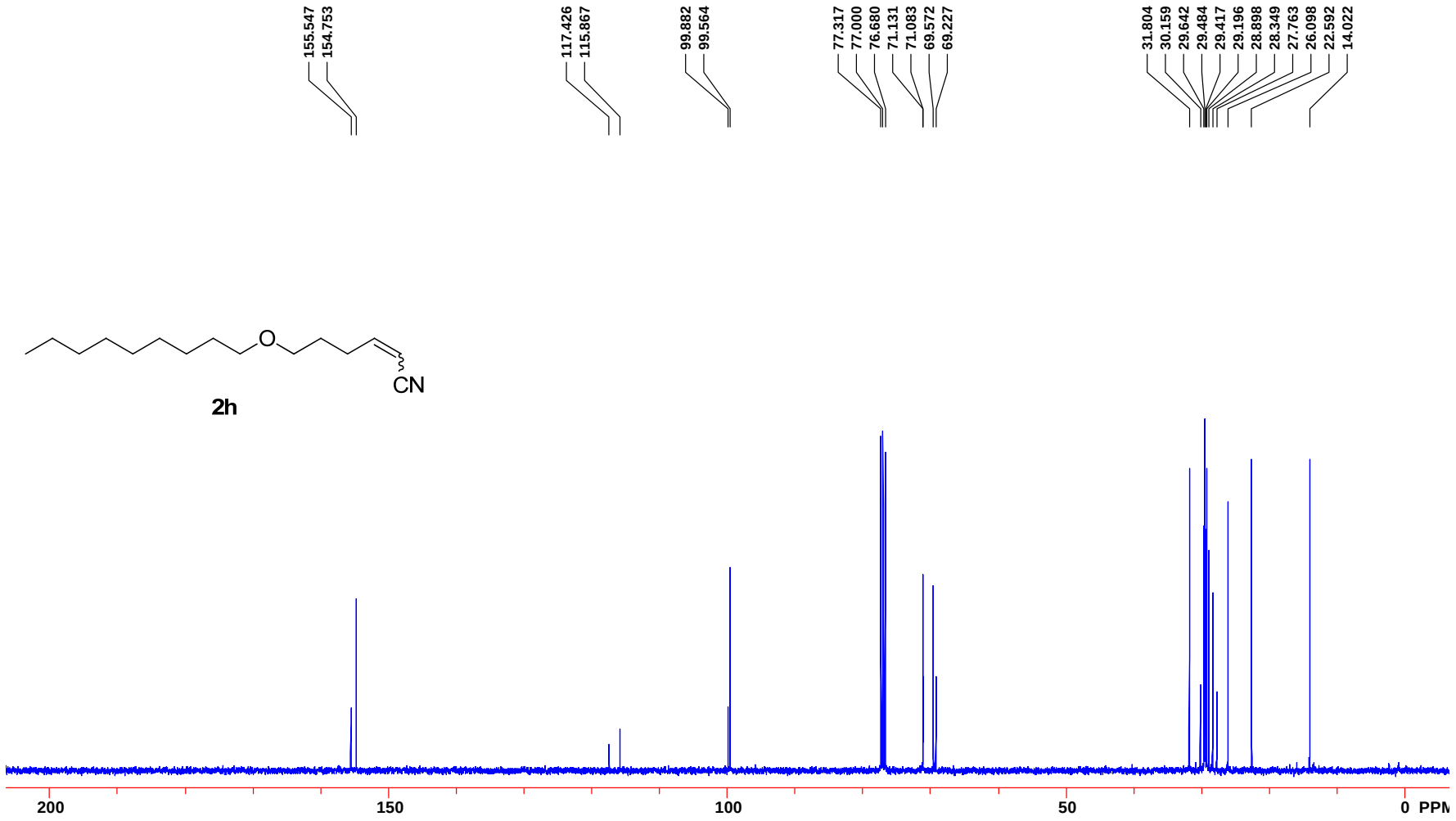
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69.227
31.804
30.159
29.642
29.484
29.417
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22.592
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CN
2h
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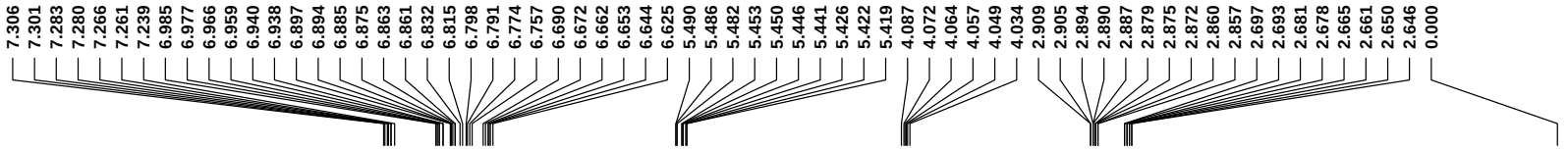
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6.966
6.959
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6.875
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6.861
6.832
6.815
6.798
6.791
6.774
6.757
6.690
6.672
6.662
6.653
6.644
6.625
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5.486
5.482
5.453
5.450
5.446
5.441
5.426
5.422
5.419
4.087
4.072
4.064
4.057
4.049
4.034
2.909
2.905
2.894
2.890
2.887
2.879
2.875
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2.681
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2.650
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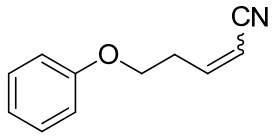
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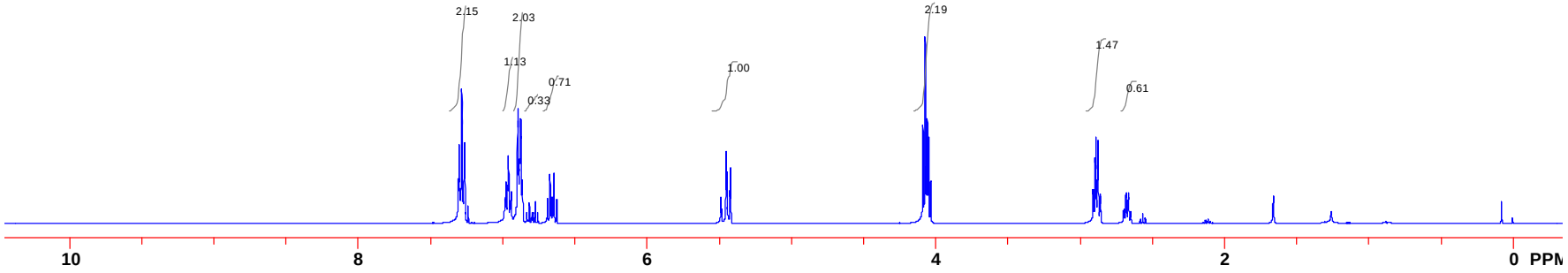
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10
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6
4
2
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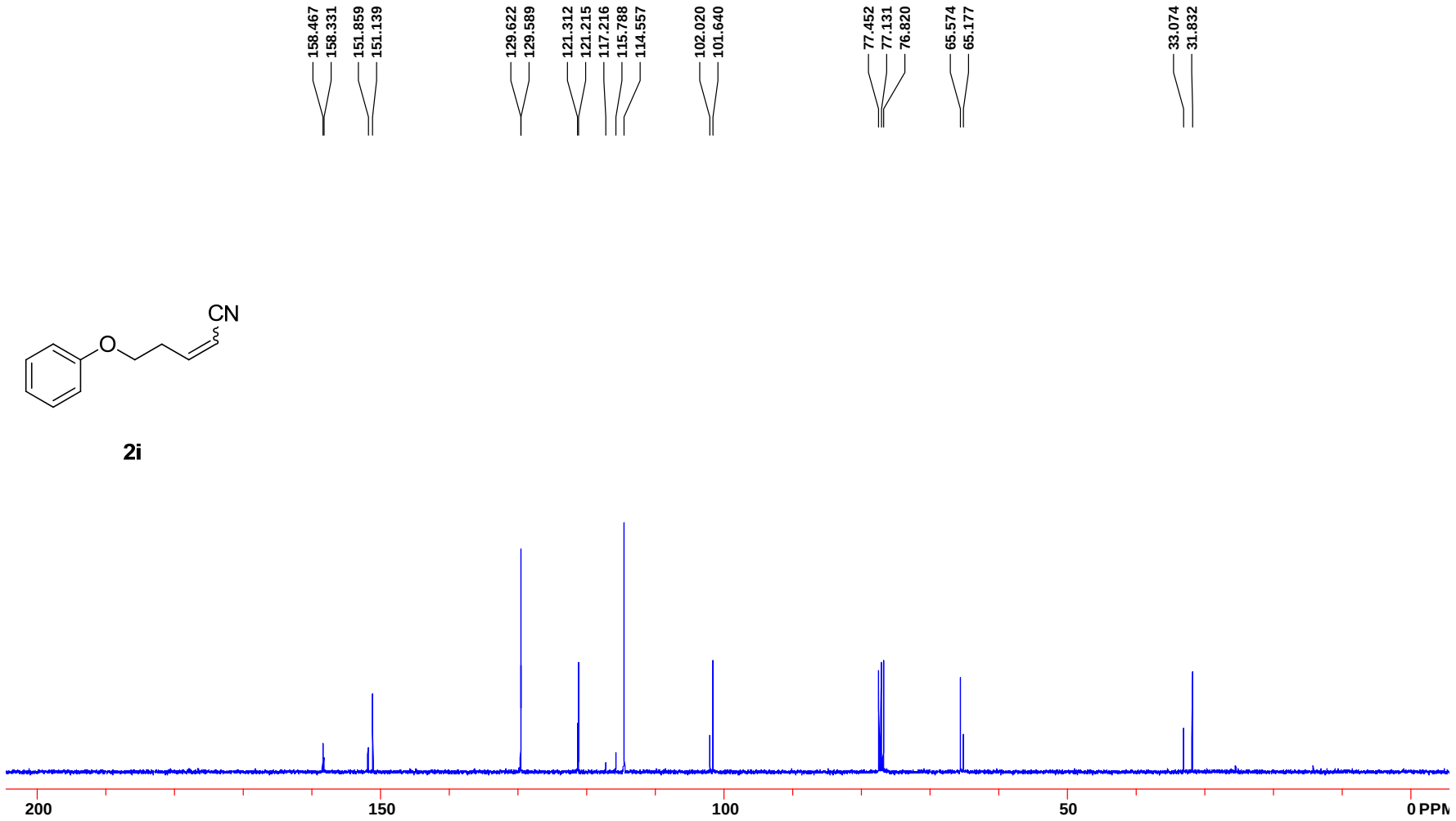
PPM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121.215
117.216
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114.557
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101.640
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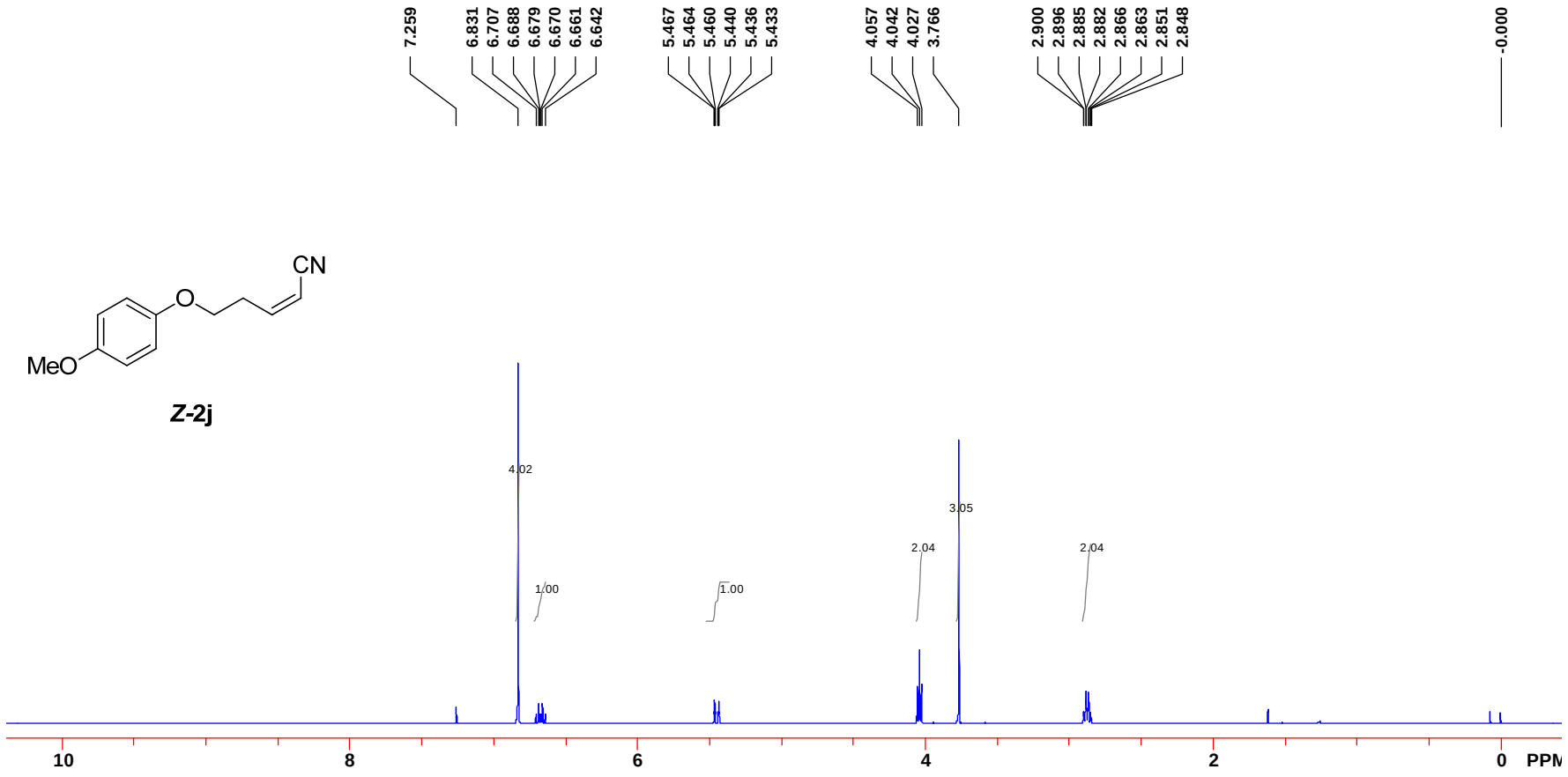
77.131
76.820
65.574
65.177
33.074
31.832
CN
O
200
150
100
50
0 PPM

2i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6.707
6.688
6.679
6.670
6.661
6.642
5.467
5.464
5.460
5.440
5.436
5.433
4.057
4.042
4.027
3.766
2.900
2.896
2.885
2.882
2.866
2.863
2.851
2.848
-0.000
CN
O
MeO
Z-2j
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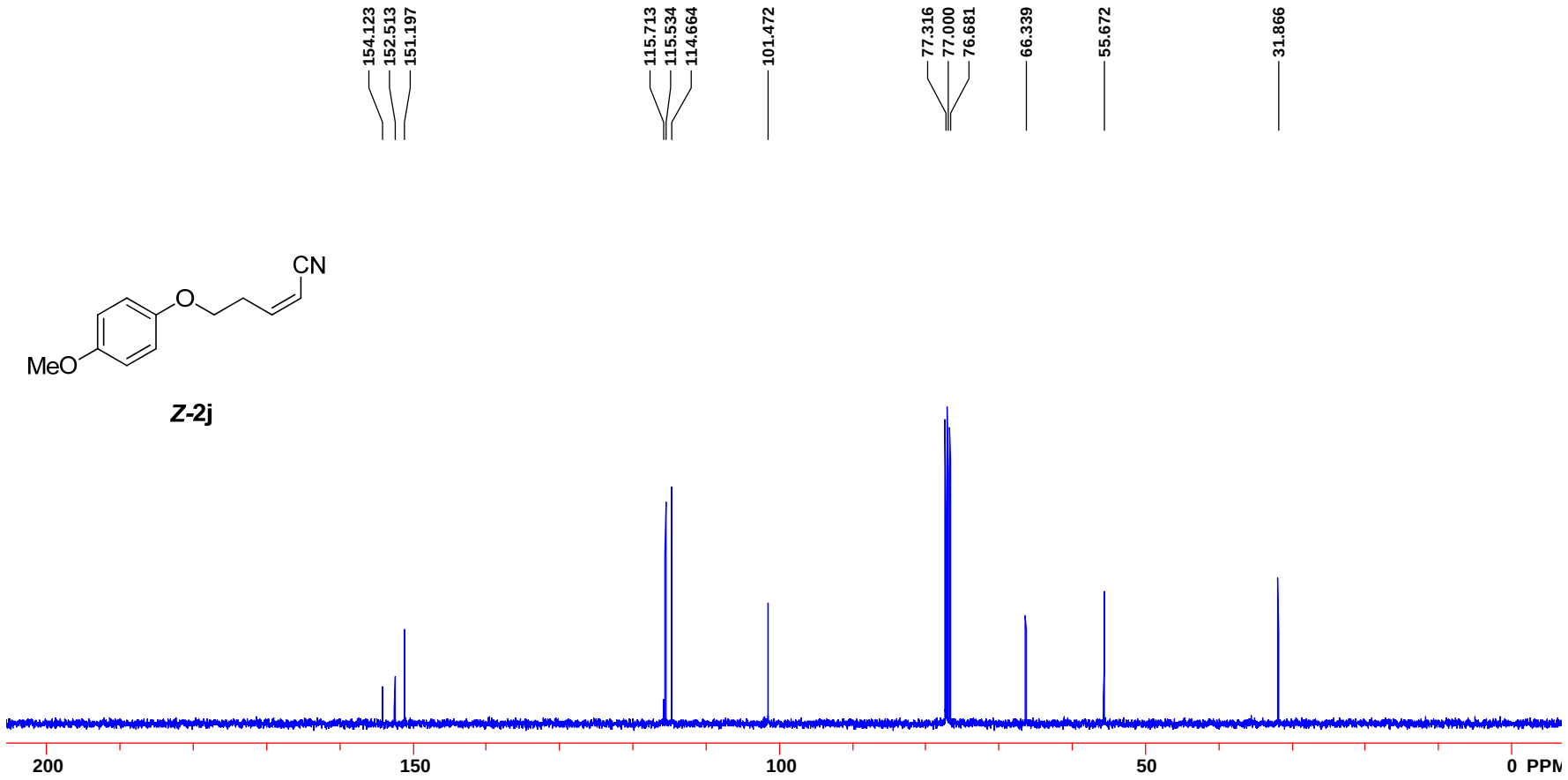
1.00
1.00
2.04
3.05
2.04
10
8
6
4
2
0
PPM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114.664
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77.316
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55.672
31.866
CN
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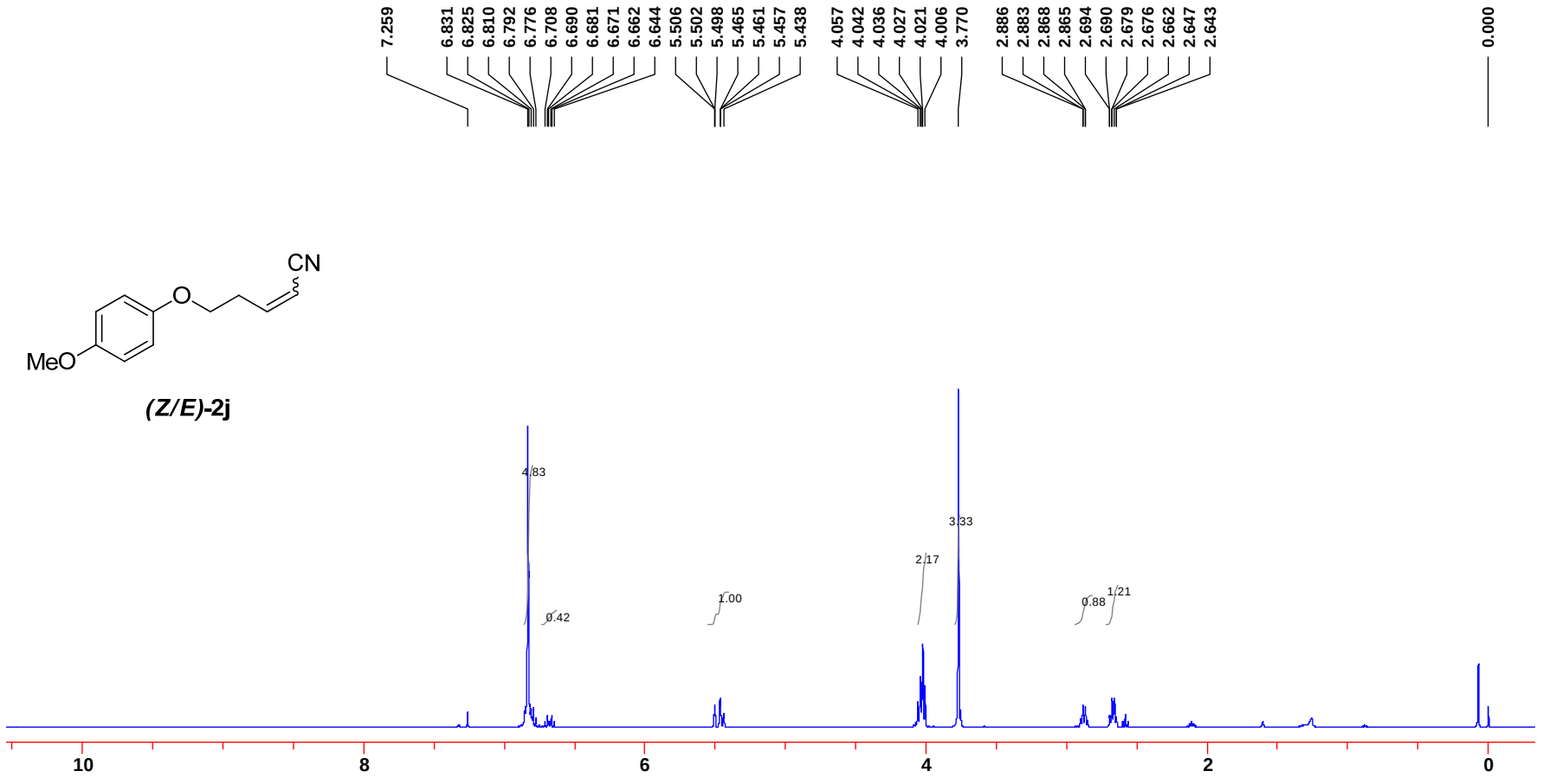
MeO
200
150
100
50
0 PPM

***Z*-2j**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6.776
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6.690
6.681
6.671
6.662
6.644
5.506
5.502
5.498
5.465
5.461
5.457
5.438
4.057
4.042
4.036
4.027
4.021
4.006
3.770
2.886
2.883
2.868
2.865
2.694
2.690
2.679
2.676
2.662
2.647
2.643
0.000
CN
O
MeO
(Z/E)-2j
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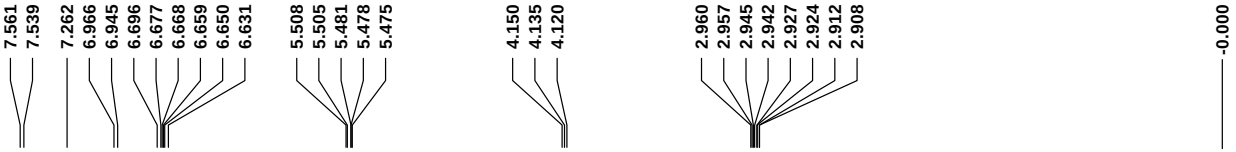
6
4
2
0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7.262
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6.945
6.696
6.677
6.668
6.659
6.650
6.631
5.508
5.505
5.481
5.478
5.475
4.150
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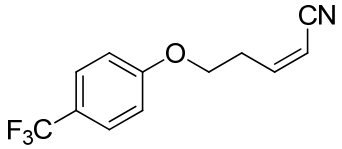
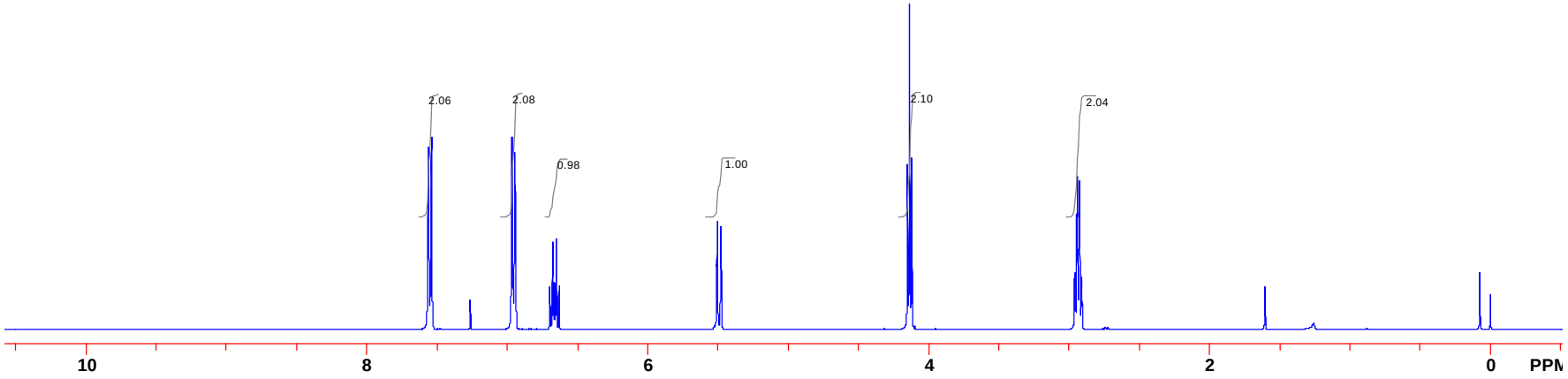
2.957
2.945
2.942
2.927
2.924
2.912
2.908
-0.000


CN
O
F3C

***Z*-2k**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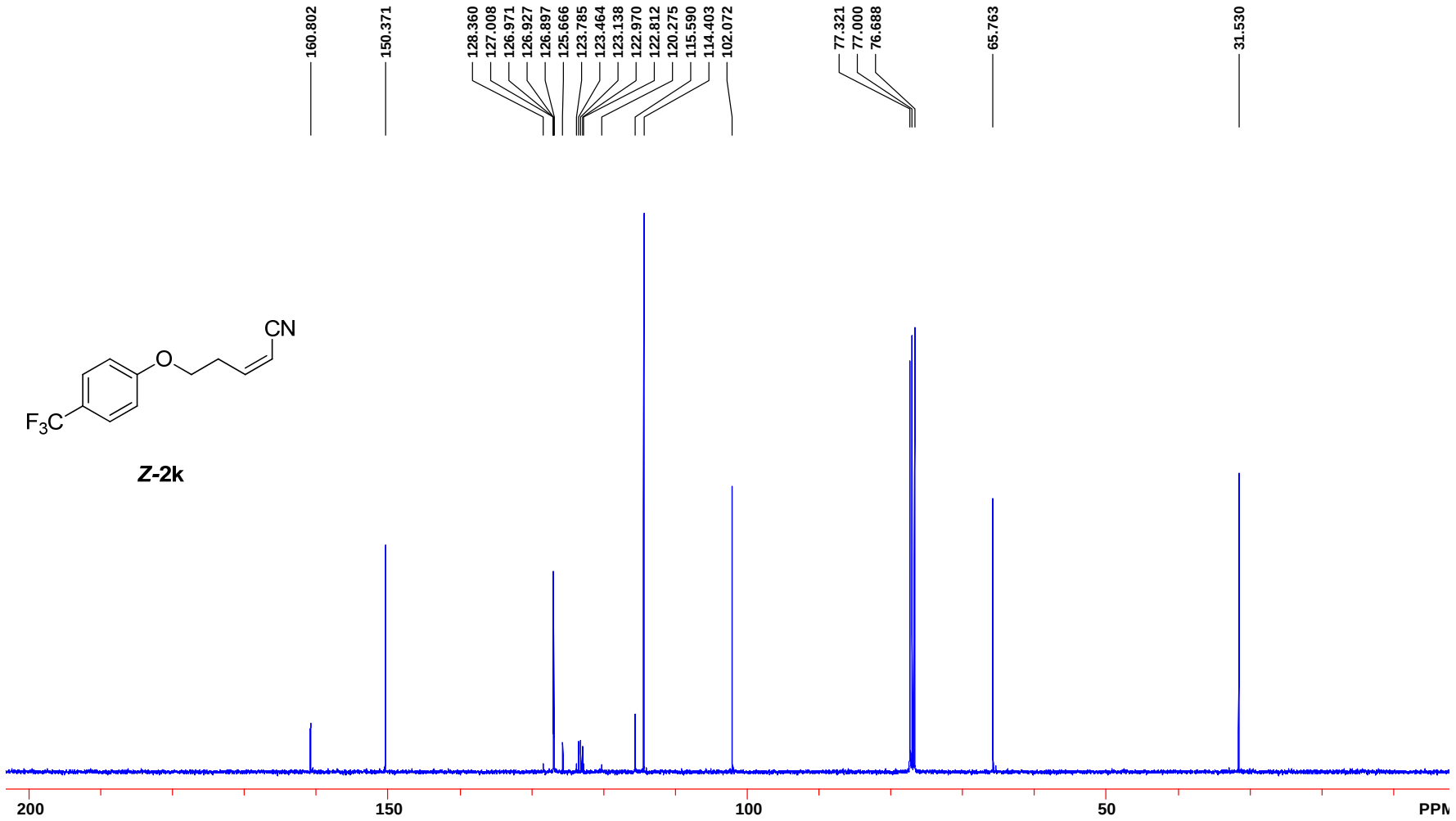
2.10
2.04
10
8
6
4
2
0
PPM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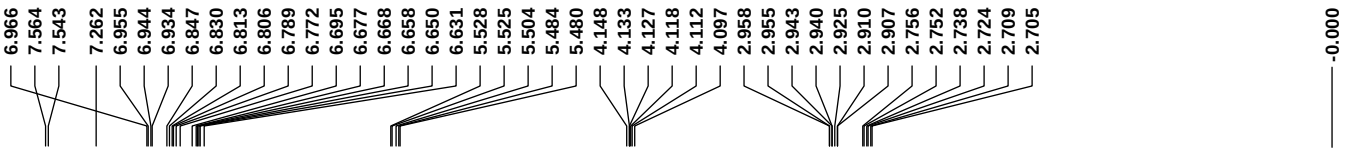
128.360
127.008
126.971
126.927
126.897
125.666
123.785
123.464
123.138
122.970
122.812
120.275
115.590
114.403
102.072
77.321
77.000
76.688
65.763
31.530
CN
O
F3C
Z-2k
200
150
100
50
PPM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6.944
6.934
6.847
6.830
6.813
6.806
6.789
6.772
6.695
6.677
6.668
6.658
6.650
6.631
5.528
5.525
5.504
5.484
5.480
4.148
4.133
4.127
4.118
4.112
4.097
2.958
2.955
2.943
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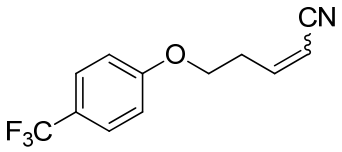
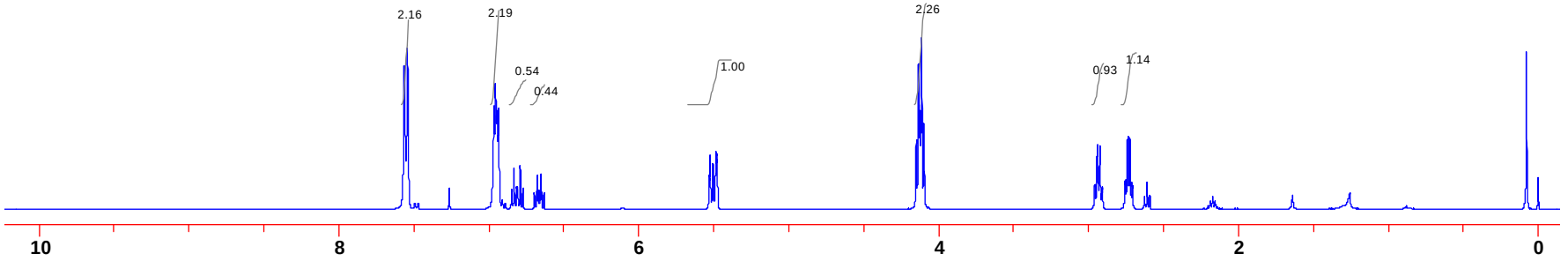
2.907
2.756
2.752
2.738
2.724
2.709
2.705
-0.000


CN
O
F3C

***(Z/E)*-2k**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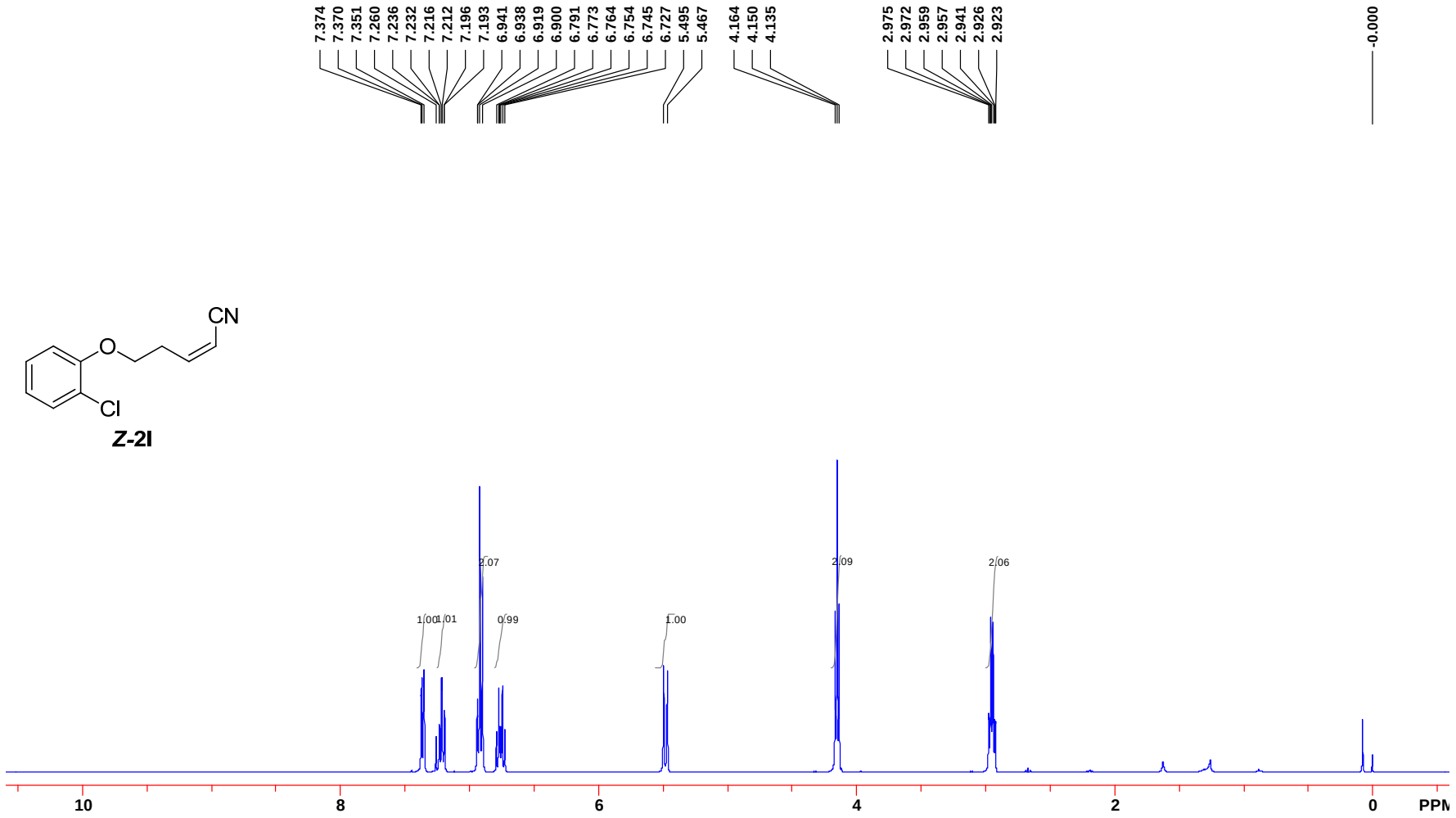
1.14
10
8
6
4
2
0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7.236
7.232
7.216
7.212
7.196
7.193
6.941
6.938
6.919
6.900
6.791
6.773
6.764
6.754
6.745
6.727
5.495
5.467
4.164
4.150
4.135
2.975
2.972
2.959
2.957
2.941
2.926
2.923
-0.000
CN
O
Cl
Z-2l
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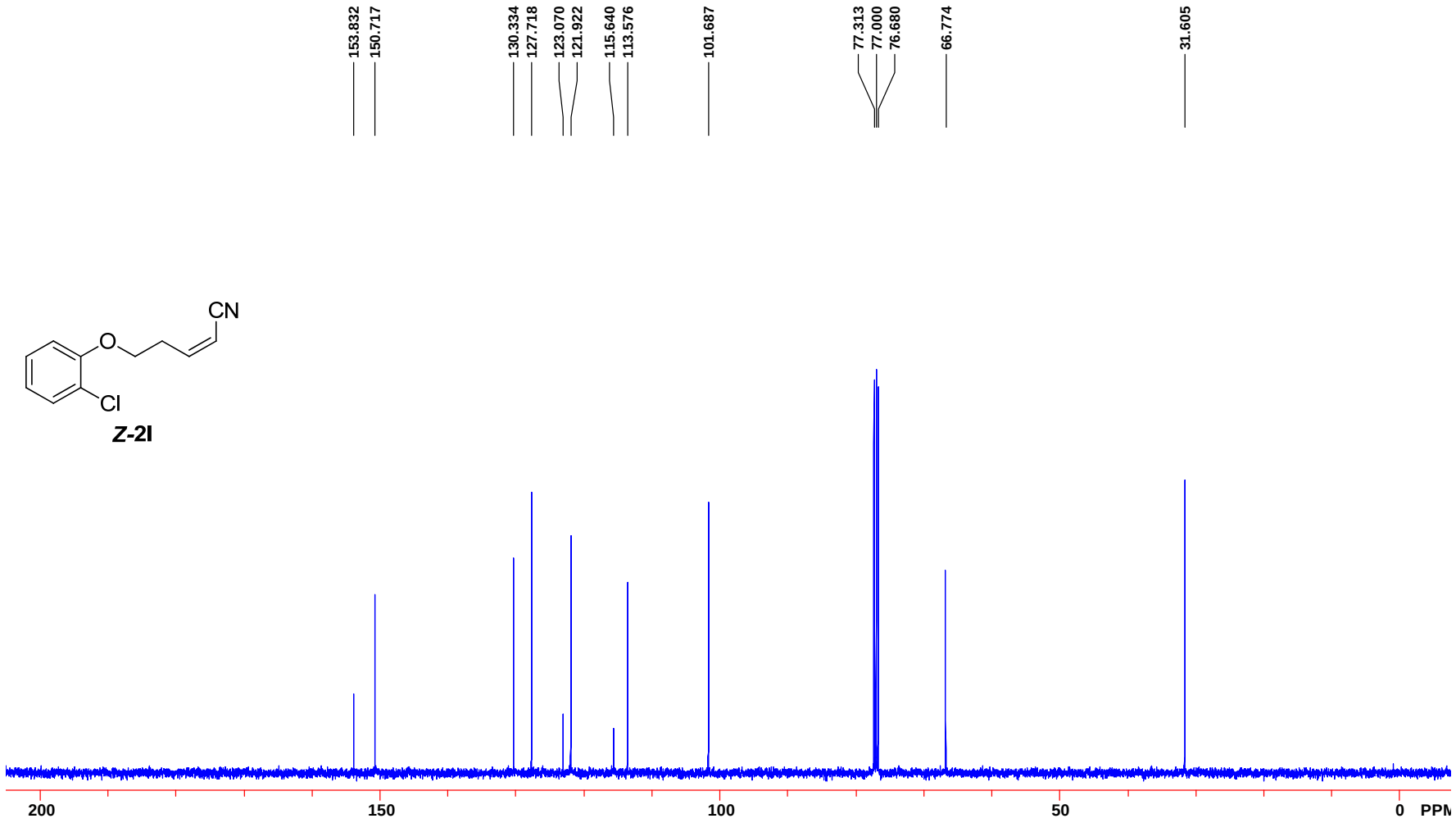
2.07
0.99
1.00
2.09
2.06
10
8
6
4
2
0
PPM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113.576
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77.000
76.680
66.774
31.605
CN
O
Cl
Z-2l
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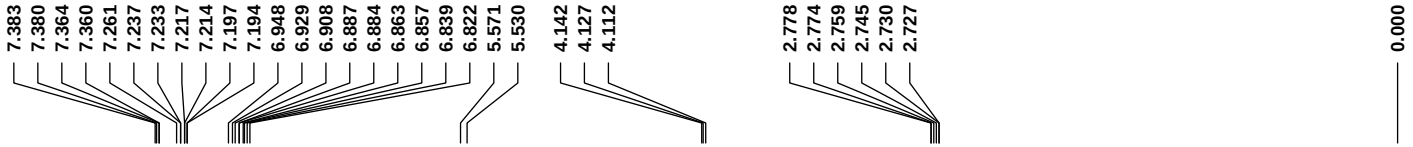
150
100
50
0
PPM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7.233
7.217
7.214
7.197
7.194
6.948
6.929
6.908
6.887
6.884
6.863
6.857
6.839
6.822
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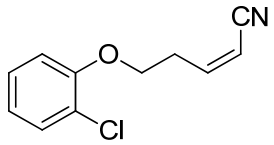
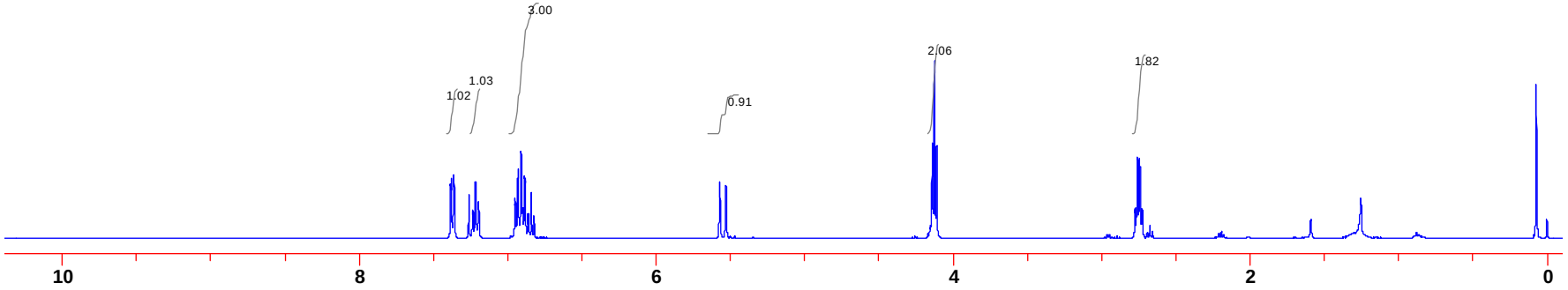
2.774
2.759
2.745
2.730
2.727
0.000


CN
O
Cl

***(Z/E)*-2l**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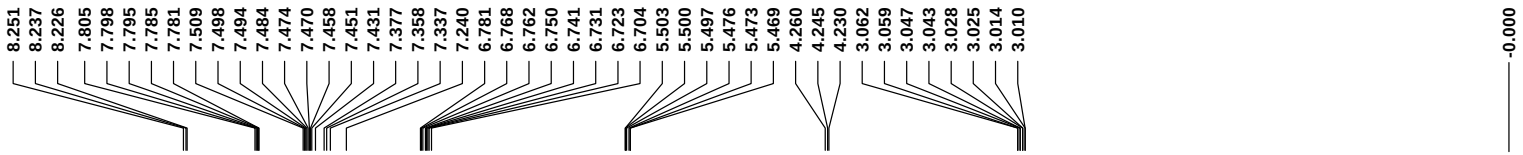
1.82
1.03
1.02
0.91
10
8
6
4
2
0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8.237
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7.798
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7.785
7.781
7.509
7.498
7.494
7.484
7.474
7.470
7.458
7.451
7.431
7.377
7.358
7.337
7.240
6.781
6.768
6.762
6.750
6.741
6.731
6.723
6.704
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5.500
5.497
5.476
5.473
5.469
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4.245
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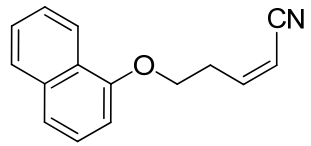
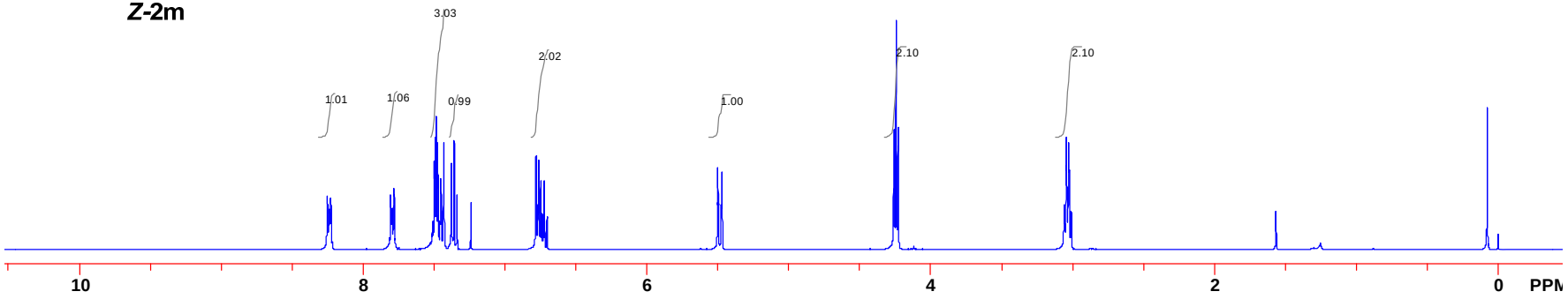
3.059
3.047
3.043
3.028
3.025
3.014
3.010
-0.000


CN
O

***Z*-2m**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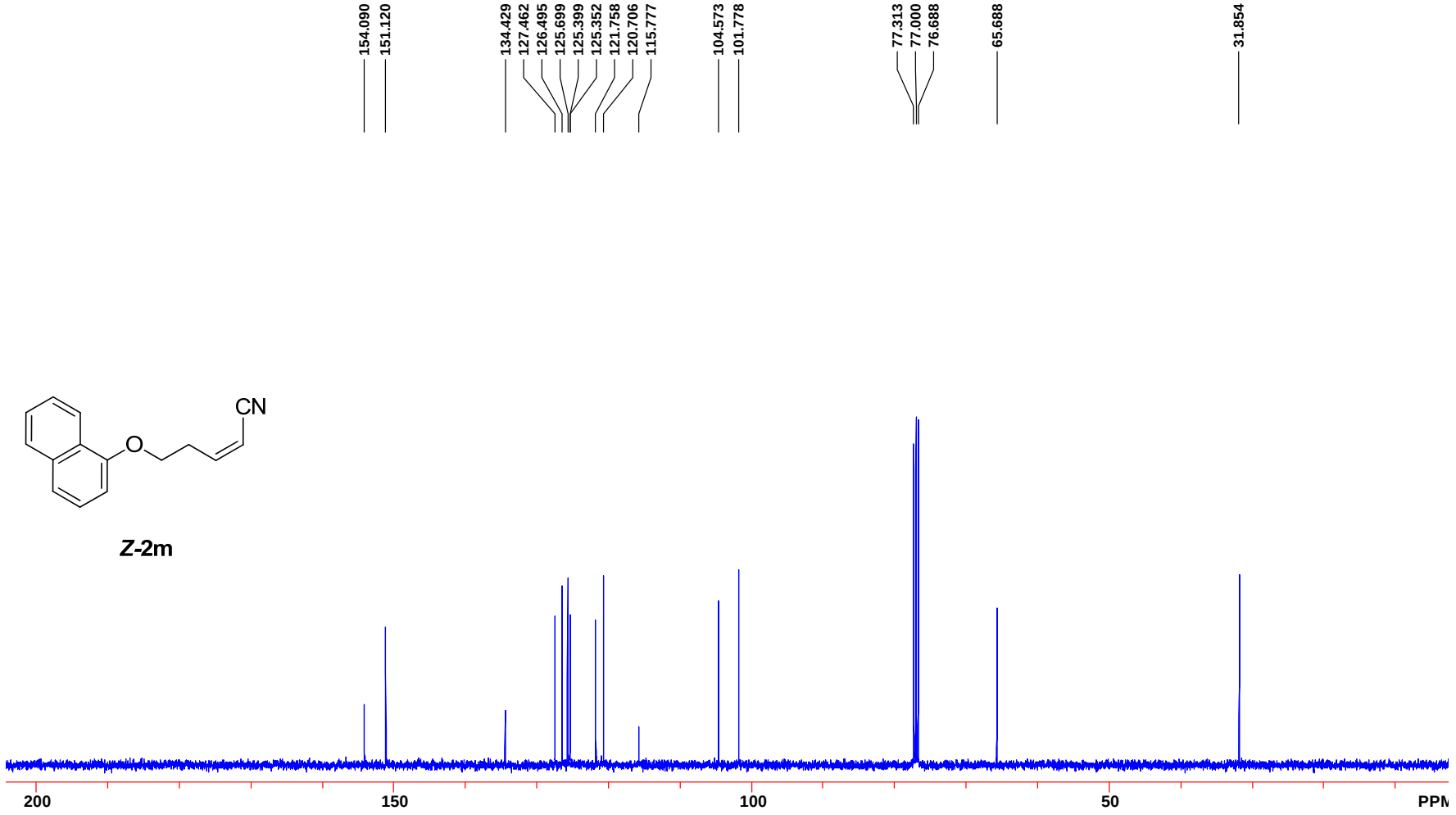
2.10
2.10
1.01
1.06
0.99
1.00
10
8
6
4
2
0
PPM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127.462
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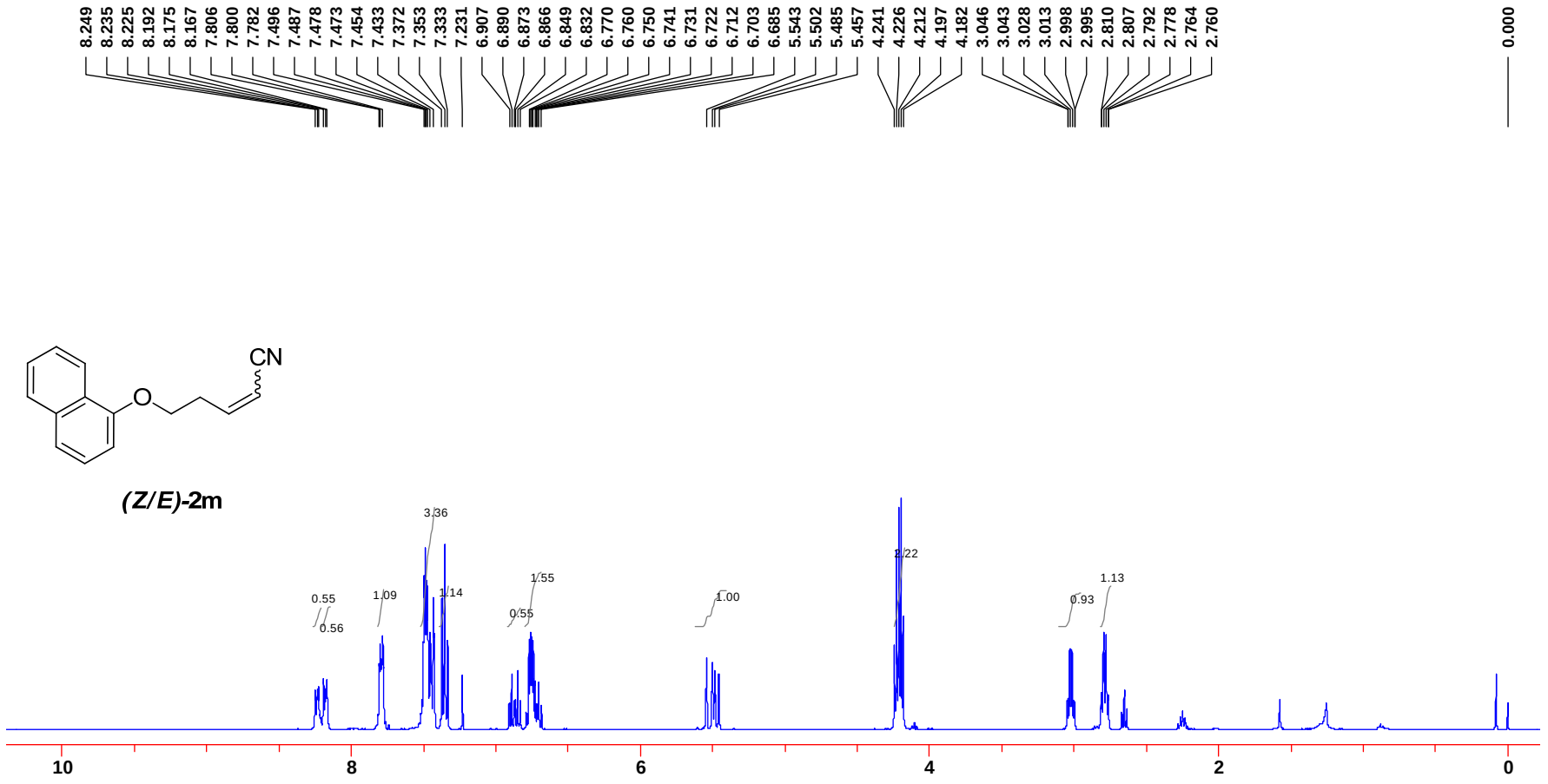
125.699
125.399
125.352
121.758
120.706
115.777
104.573
101.778
77.313
77.000
76.688
65.688
31.854
CN
O
Z-2m
200
150
100
50
PPM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8.192
8.175
8.167
7.806
7.800
7.782
7.496
7.487
7.478
7.473
7.454
7.433
7.372
7.353
7.333
7.231
6.907
6.890
6.873
6.866
6.849
6.832
6.770
6.760
6.750
6.741
6.731
6.722
6.712
6.703
6.685
5.543
5.502
5.485
5.457
4.241
4.226
4.212
4.197
4.182
3.046
3.043
3.028
3.013
2.998
2.995
2.810
2.807
2.792
2.778
2.764
2.760
0.000
CN
O
(Z/E)-2m
0.55
0.56
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0.55
1.55
1.00
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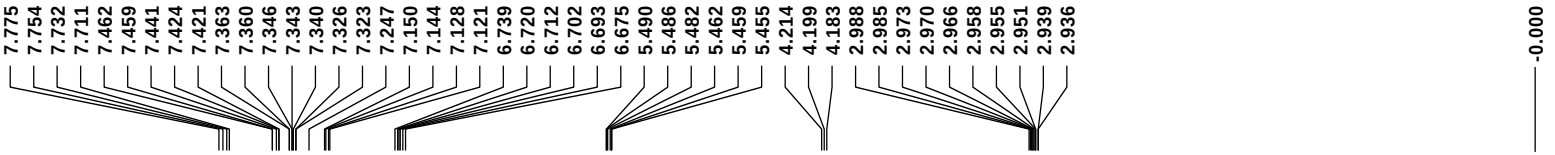
0.93
1.13
10
8
6
4
2
0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7.441
7.424
7.421
7.363
7.360
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7.343
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7.326
7.323
7.247
7.150
7.144
7.128
7.121
6.739
6.720
6.712
6.702
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5.459
5.455
4.214
4.199
4.183
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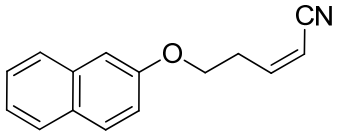
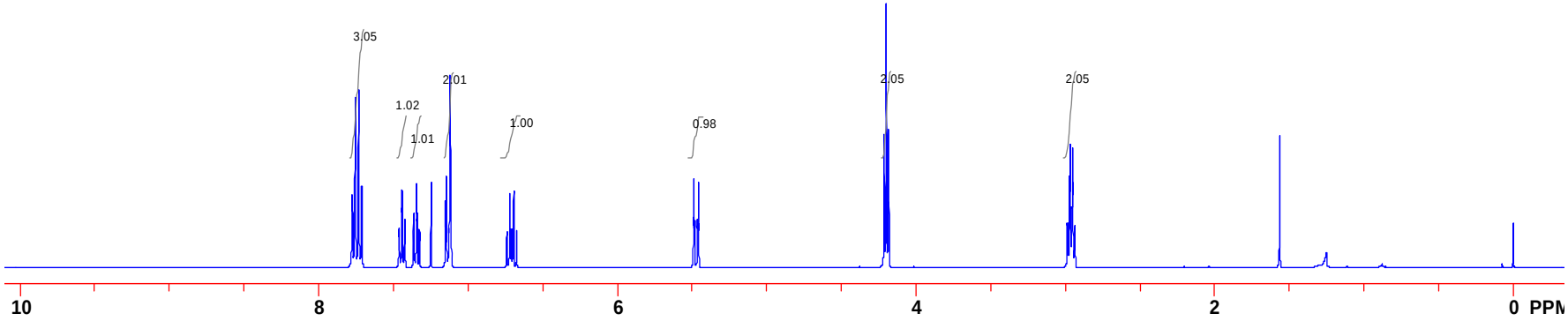

CN
O

***Z*-2n**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1.02
1.01
2.01
1.00
0.98
2.05
2.05
10
8
6
4
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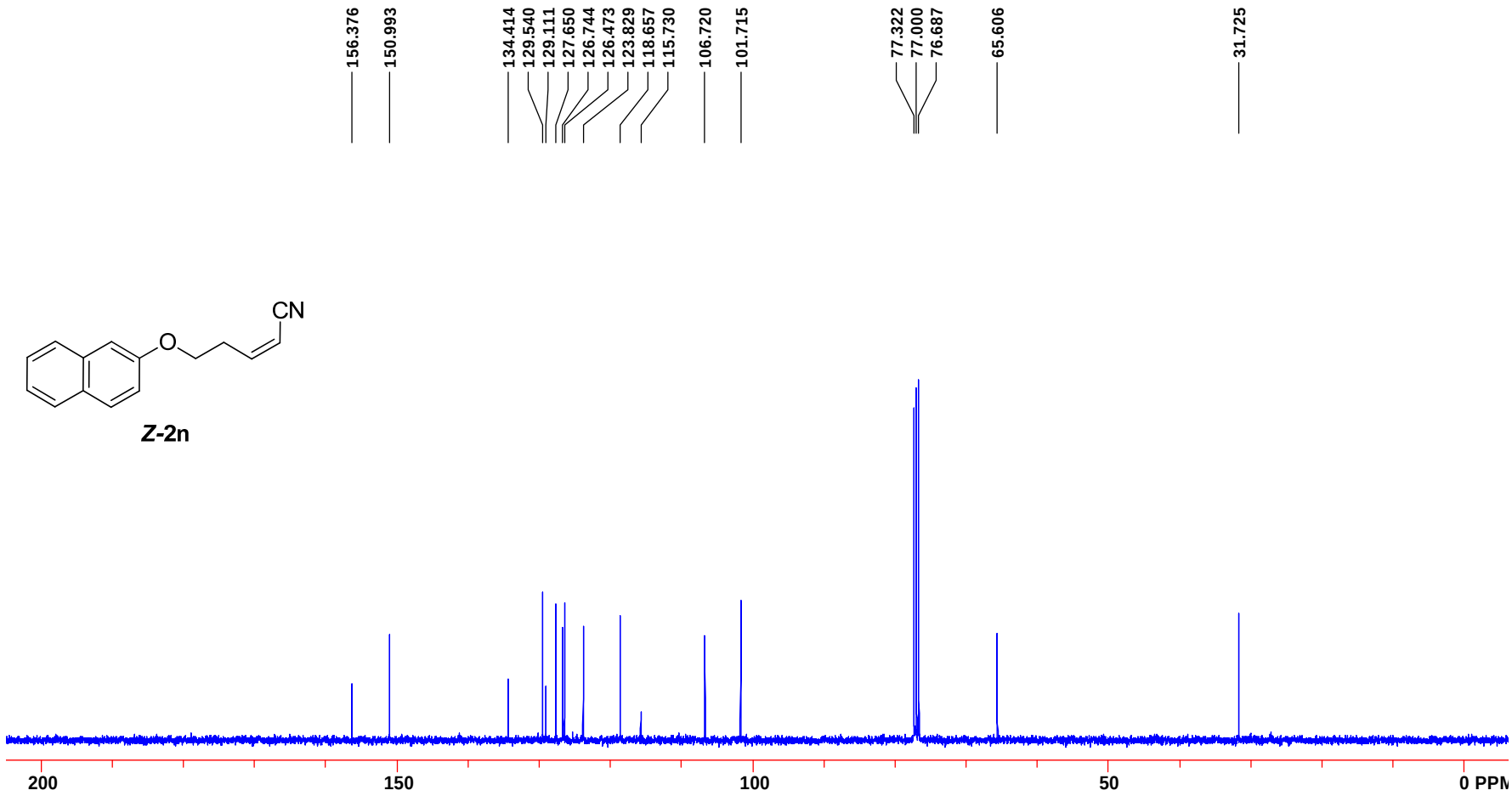
0 PPM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Z-2n
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100
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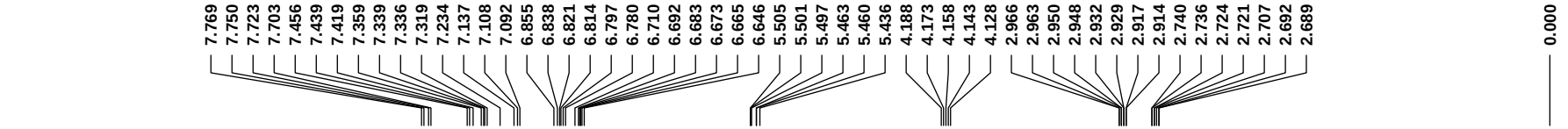
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6.692
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6.665
6.646
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5.501
5.497
5.463
5.460
5.436
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4.173
4.158
4.143
4.128
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2.963
2.950
2.948
2.932
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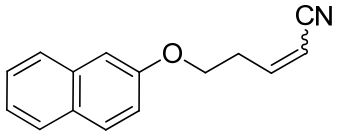
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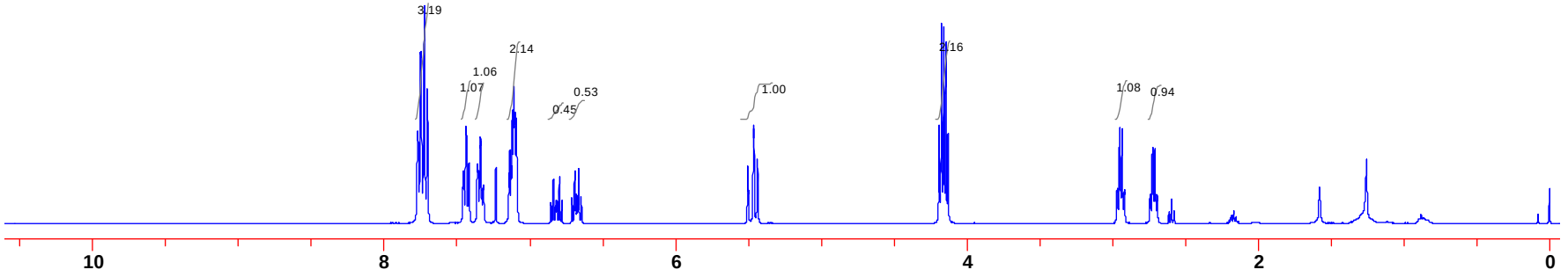
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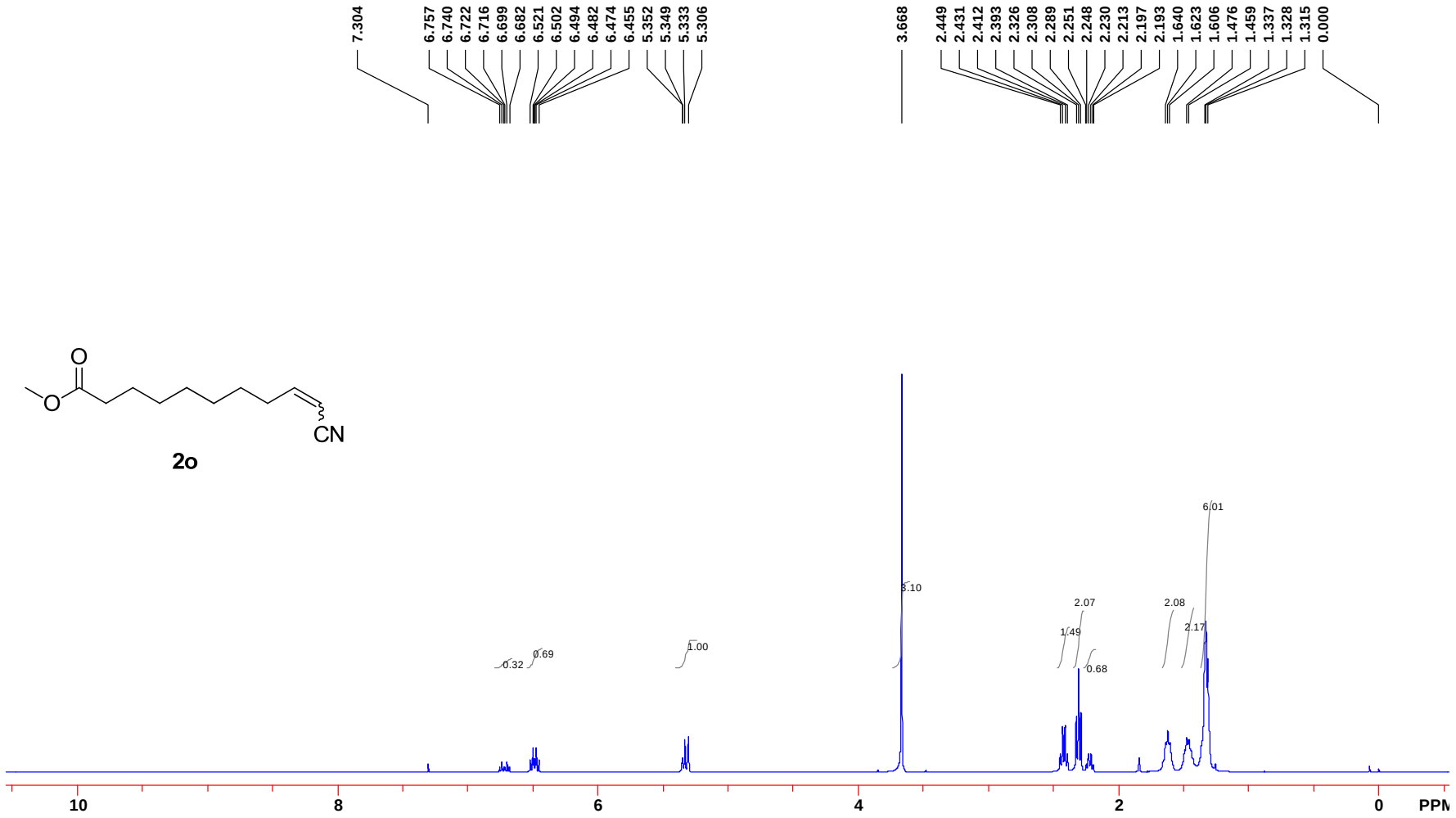
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6.474
6.455
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5.349
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2.431
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2.193
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1.623
1.606
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1.337
1.328
1.315
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O
O
CN
2o
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0.69
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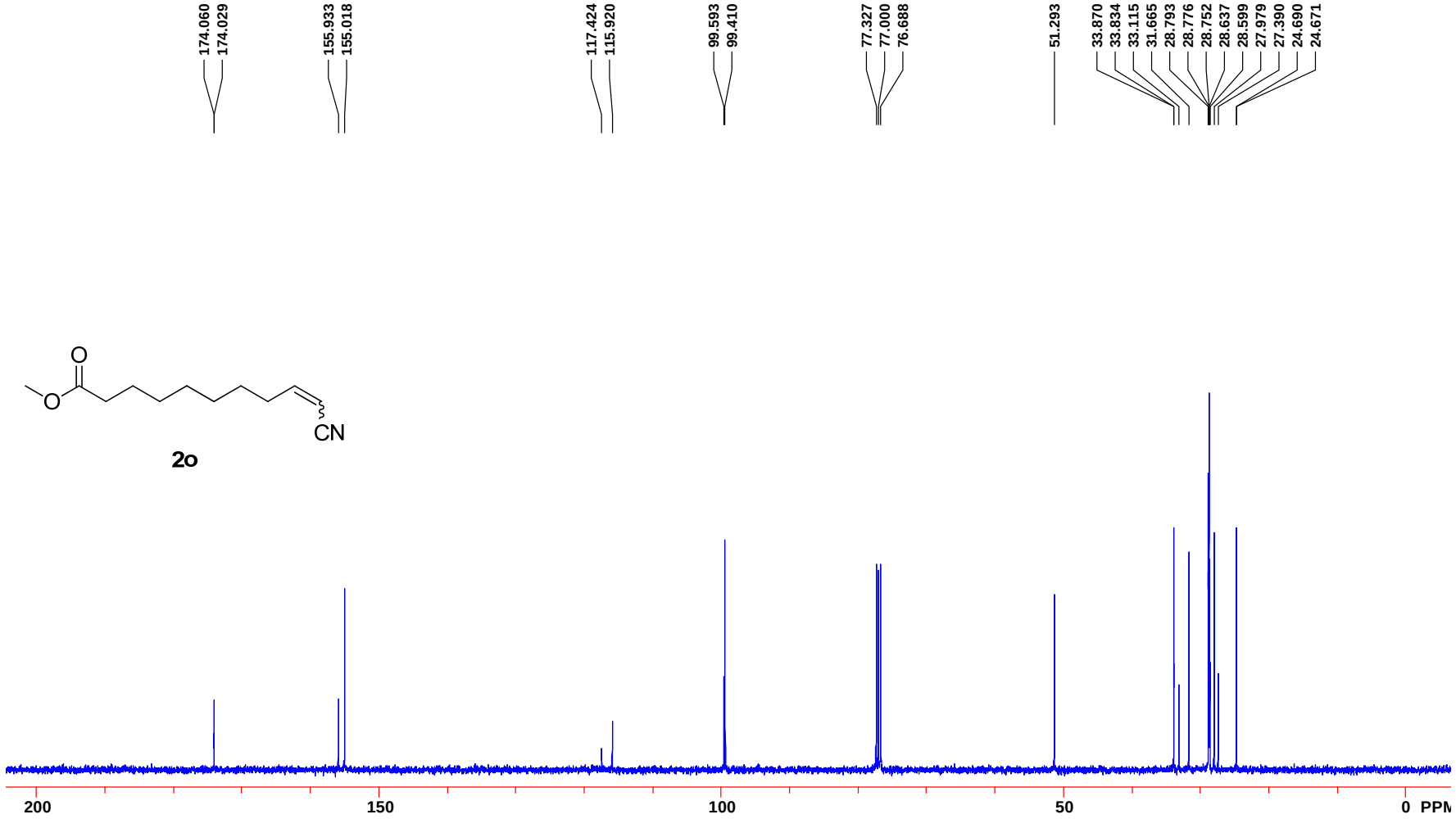
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O
CN
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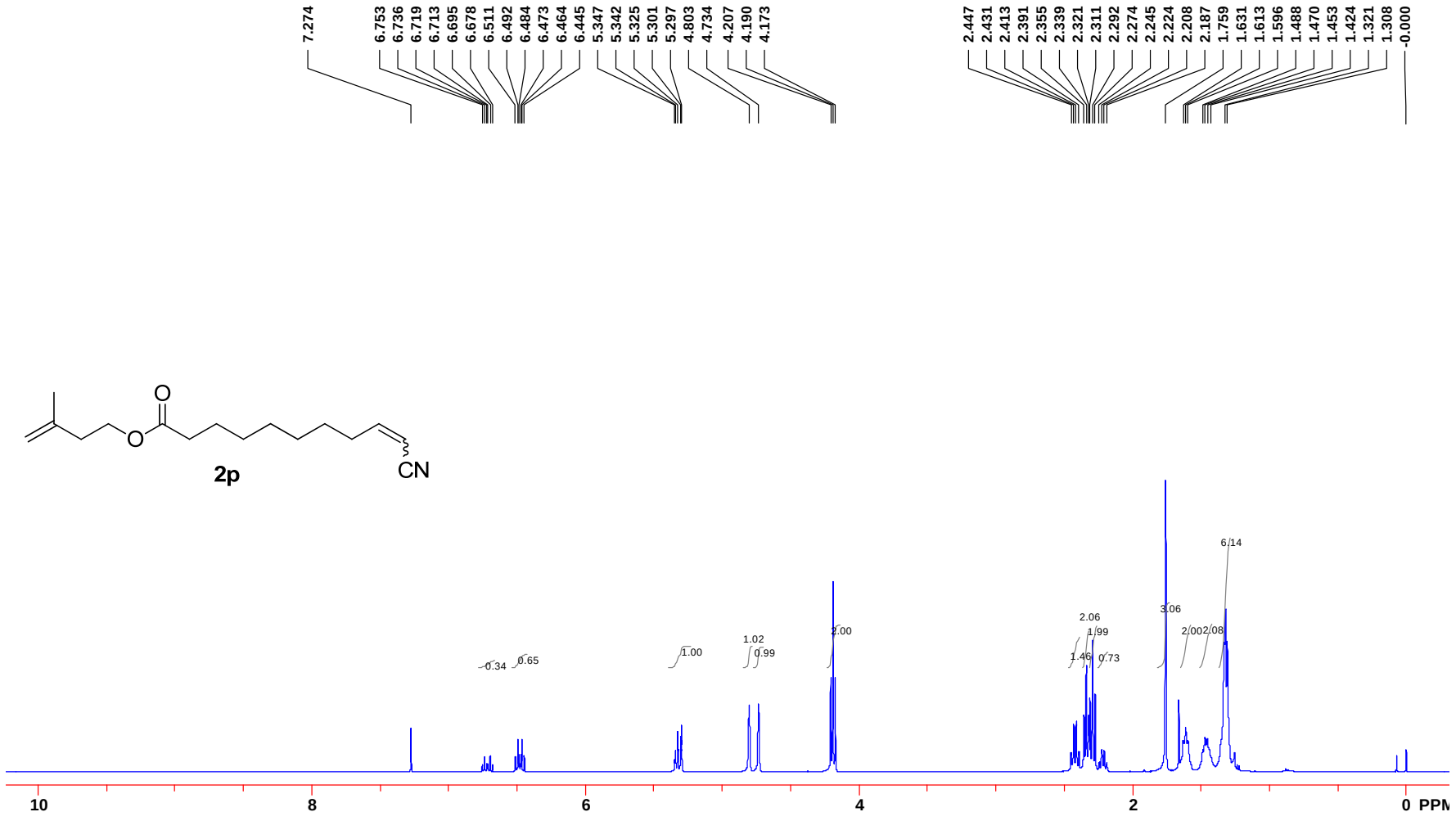
50
0 PPM

2o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2.431
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2.391
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1.613
1.596
1.488
1.470
1.453
1.424
1.321
1.308
-0.000
O
O
CN
2p
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0.99
2.00
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4
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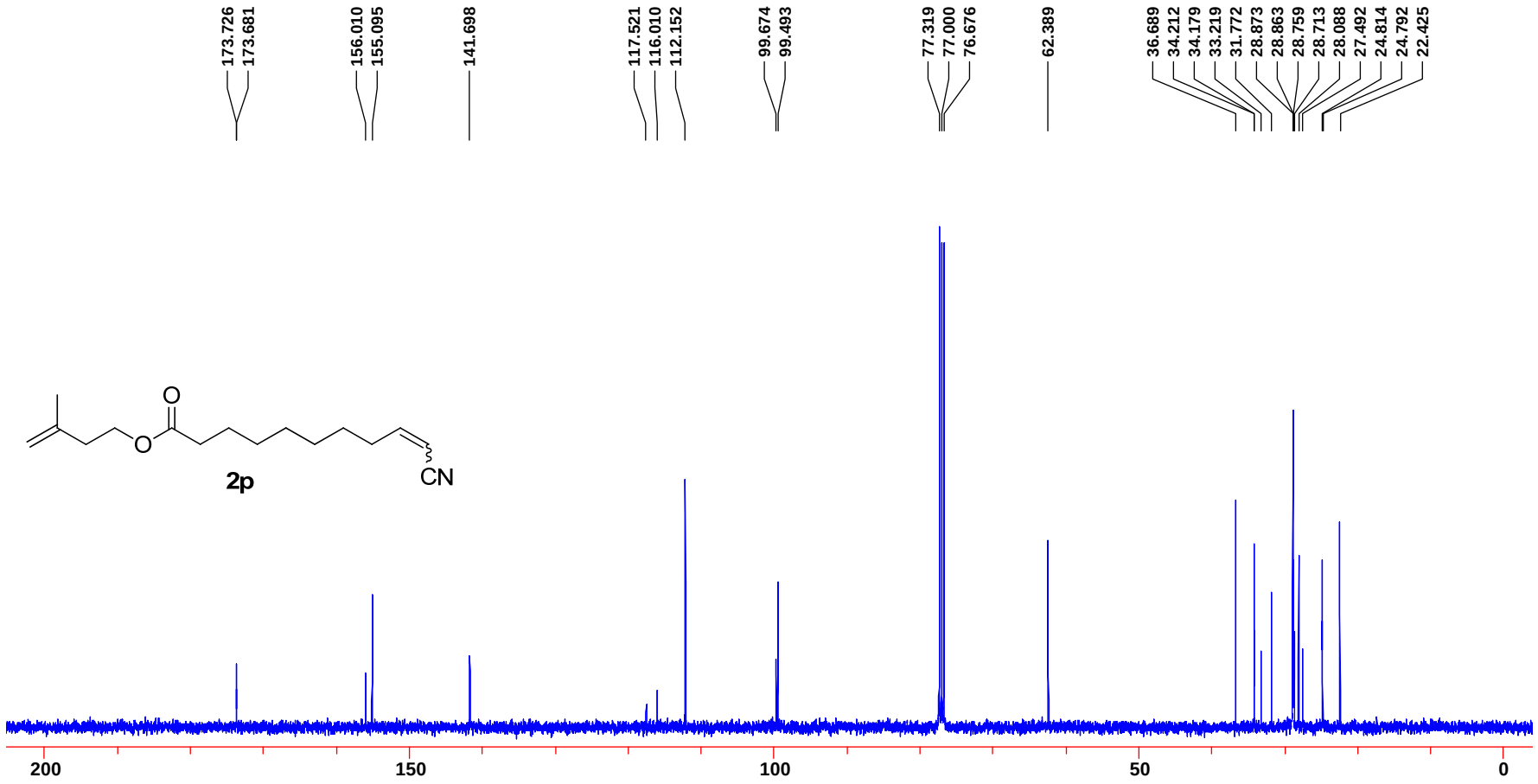
0 PPM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O
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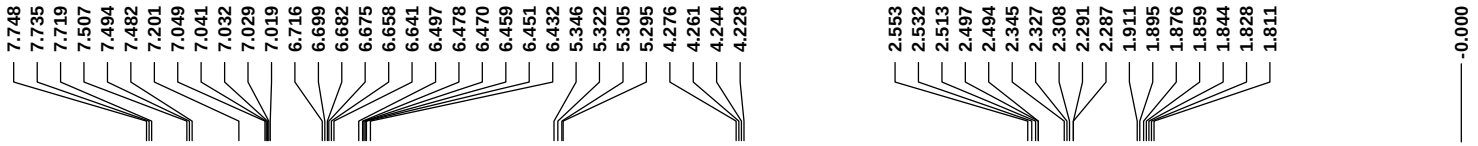
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6.470
6.459
6.451
6.432
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5.322
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5.295
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4.244
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1.811
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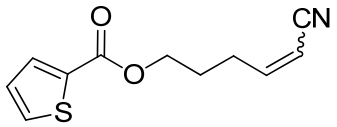
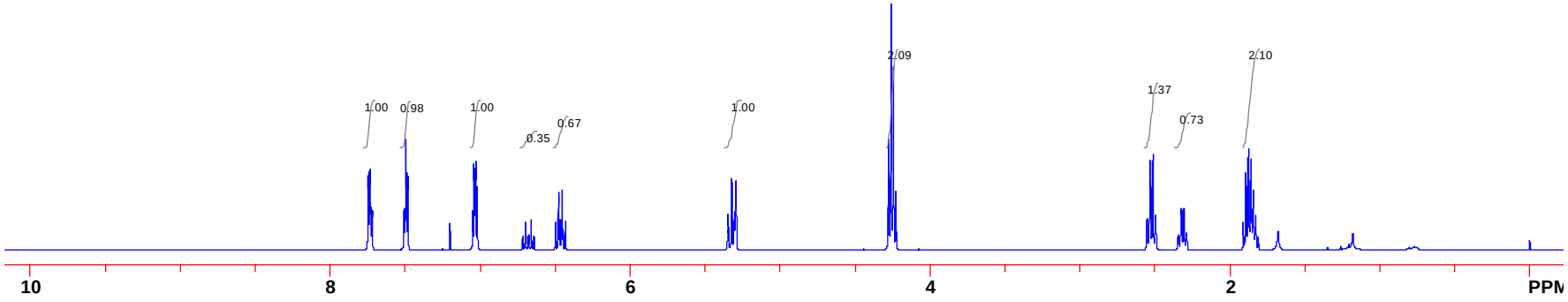

O
CN
O
S

2q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8
6
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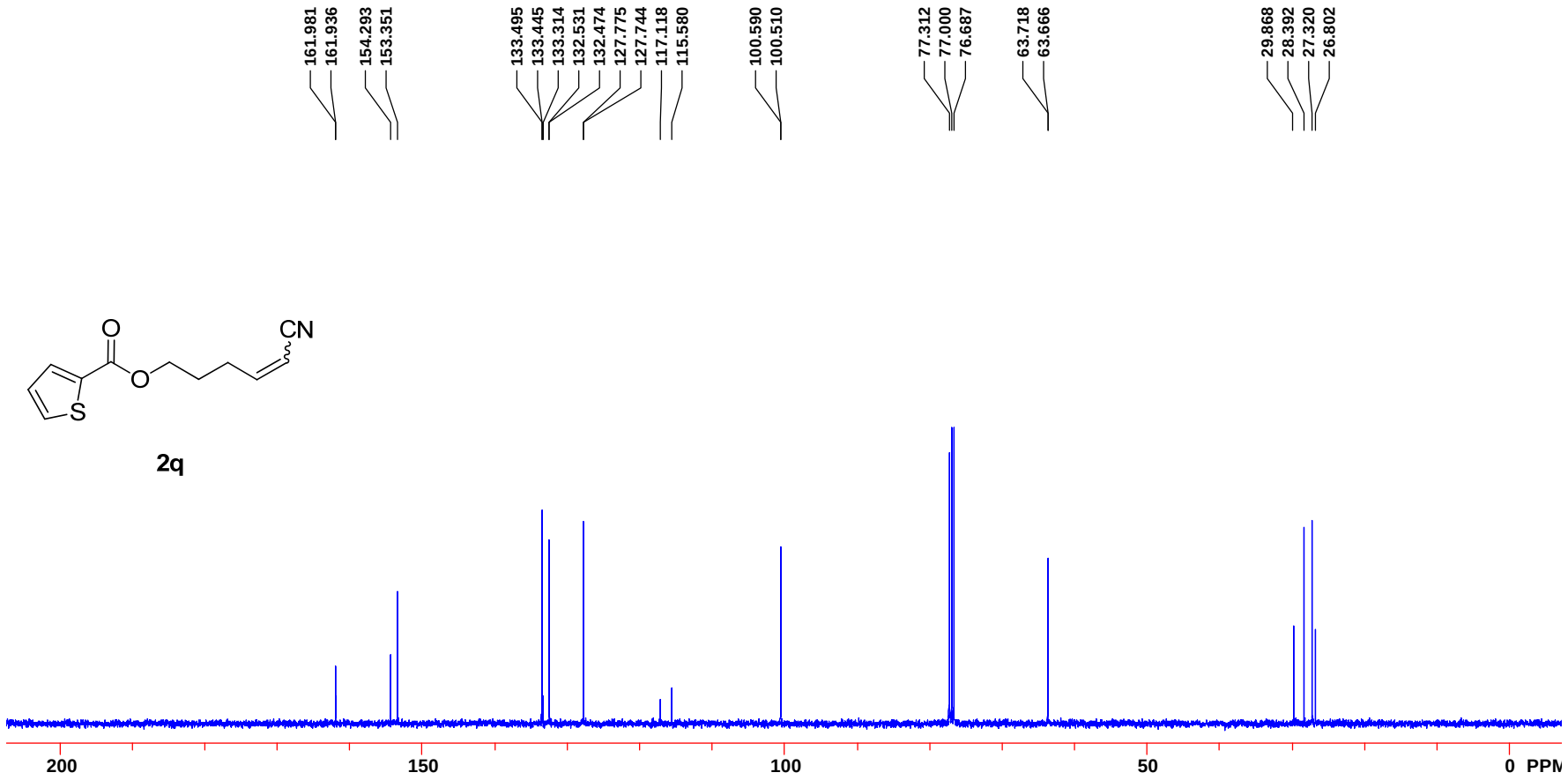
2
PPM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100.590
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77.000
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26.802
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CN
O
S
2q
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100
50
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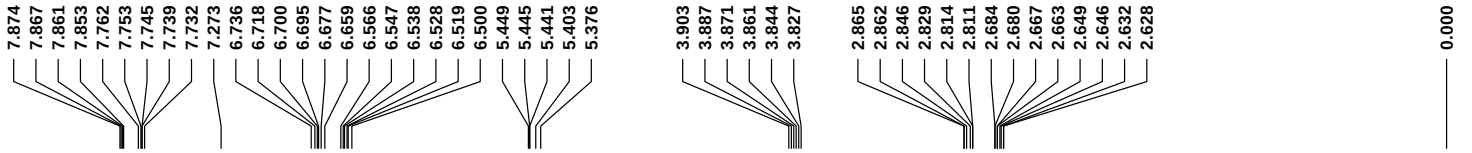
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6.695
6.677
6.659
6.566
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6.538
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6.519
6.500
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5.445
5.441
5.403
5.376
3.903
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3.844
3.827
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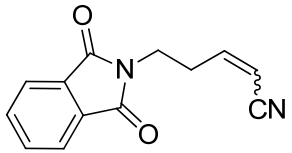
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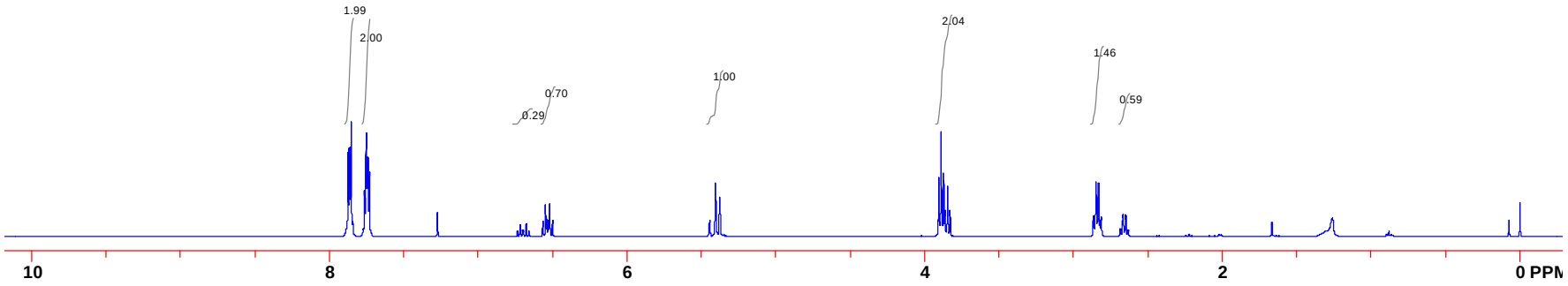
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4
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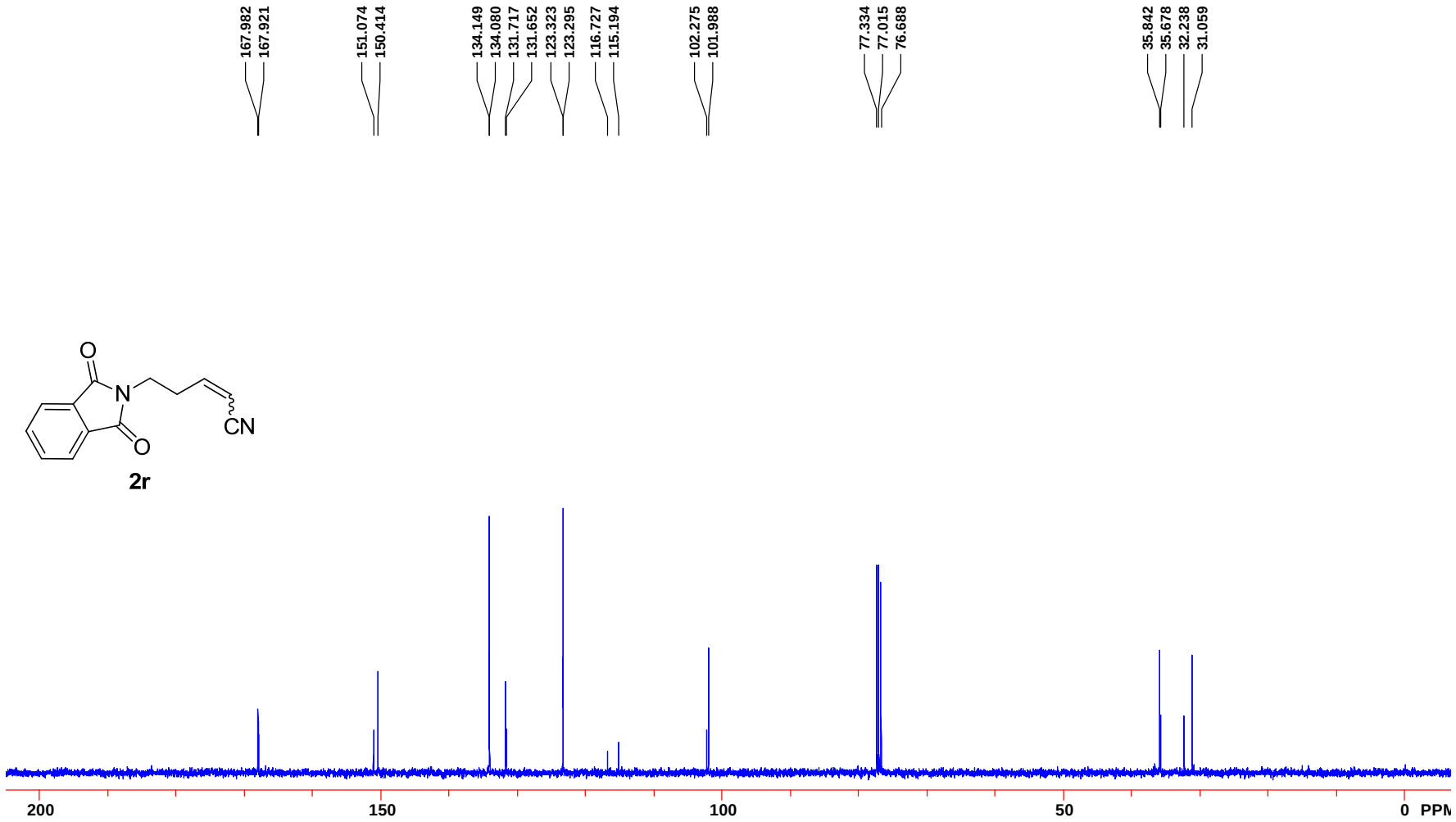
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35.678
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O
N
O
CN
2r
200
150
100
50
0
PPM


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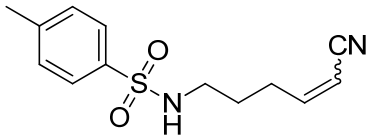
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N
H
CN

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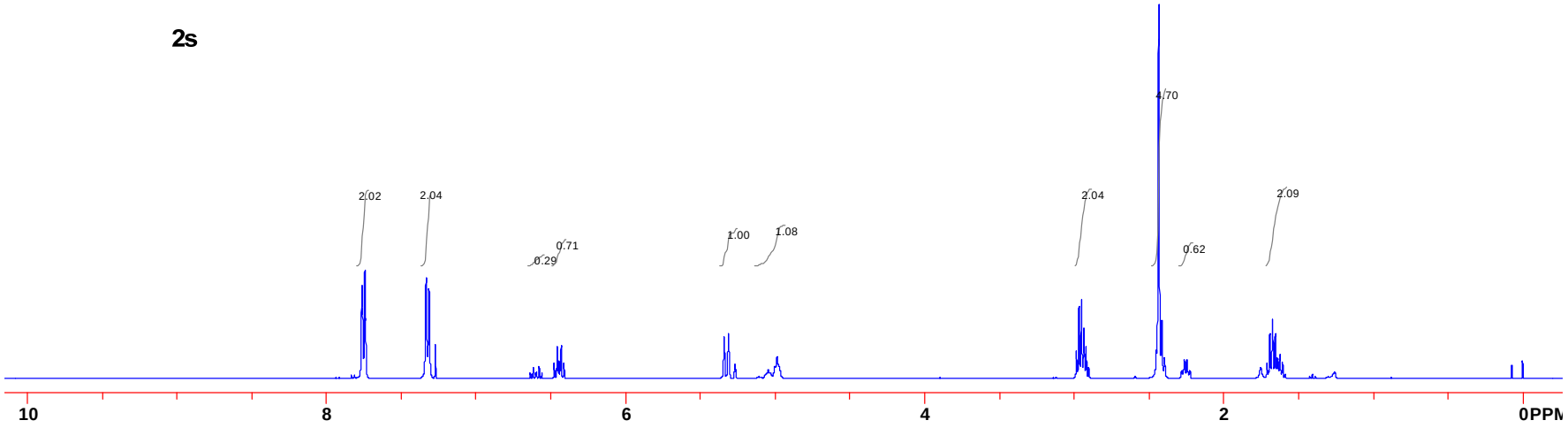
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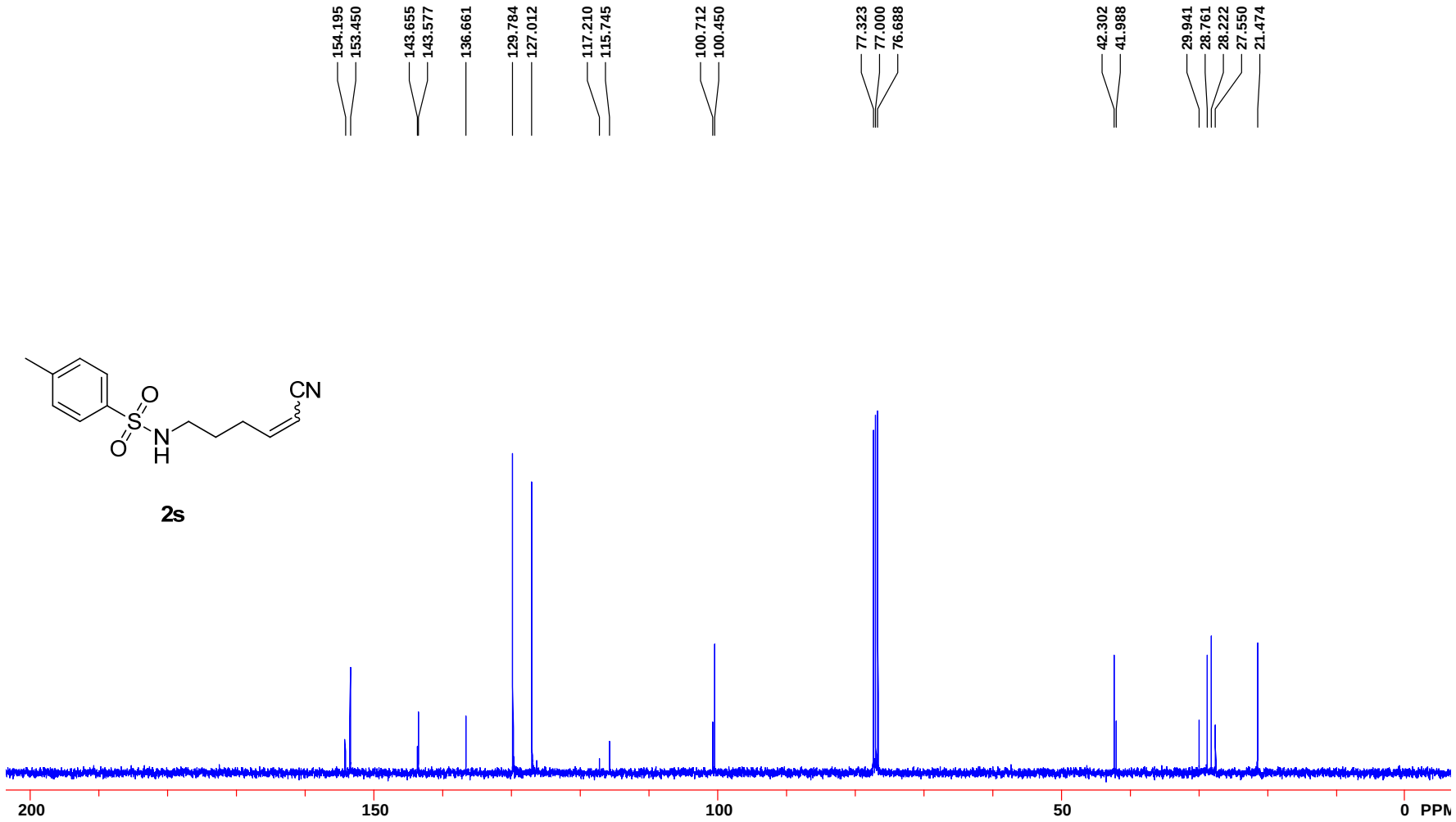
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O
S
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CN
2s
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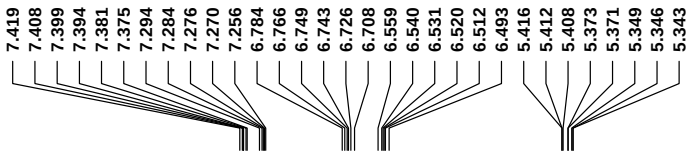
PPM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6.766
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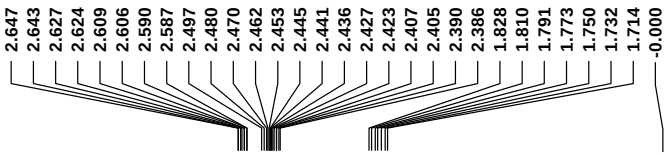
5.343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2.441
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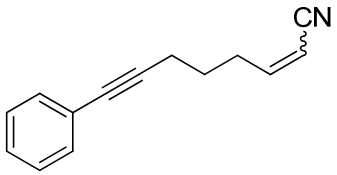
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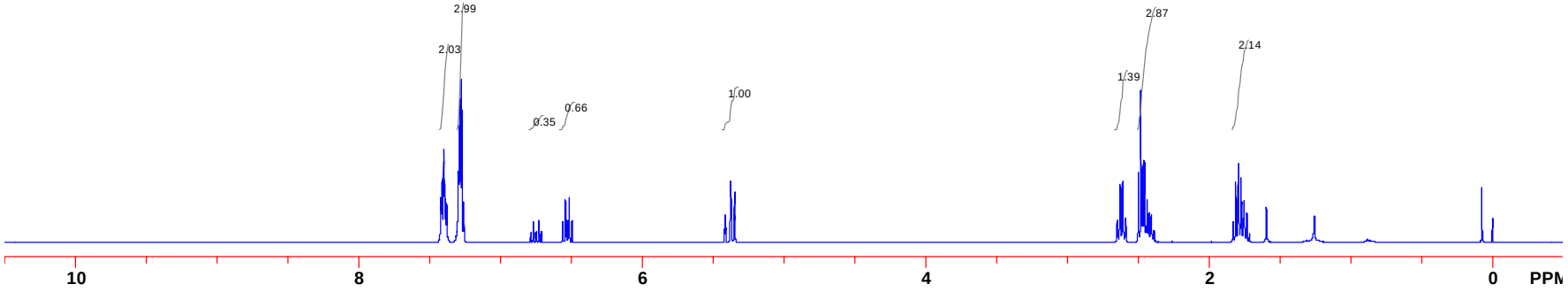
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4
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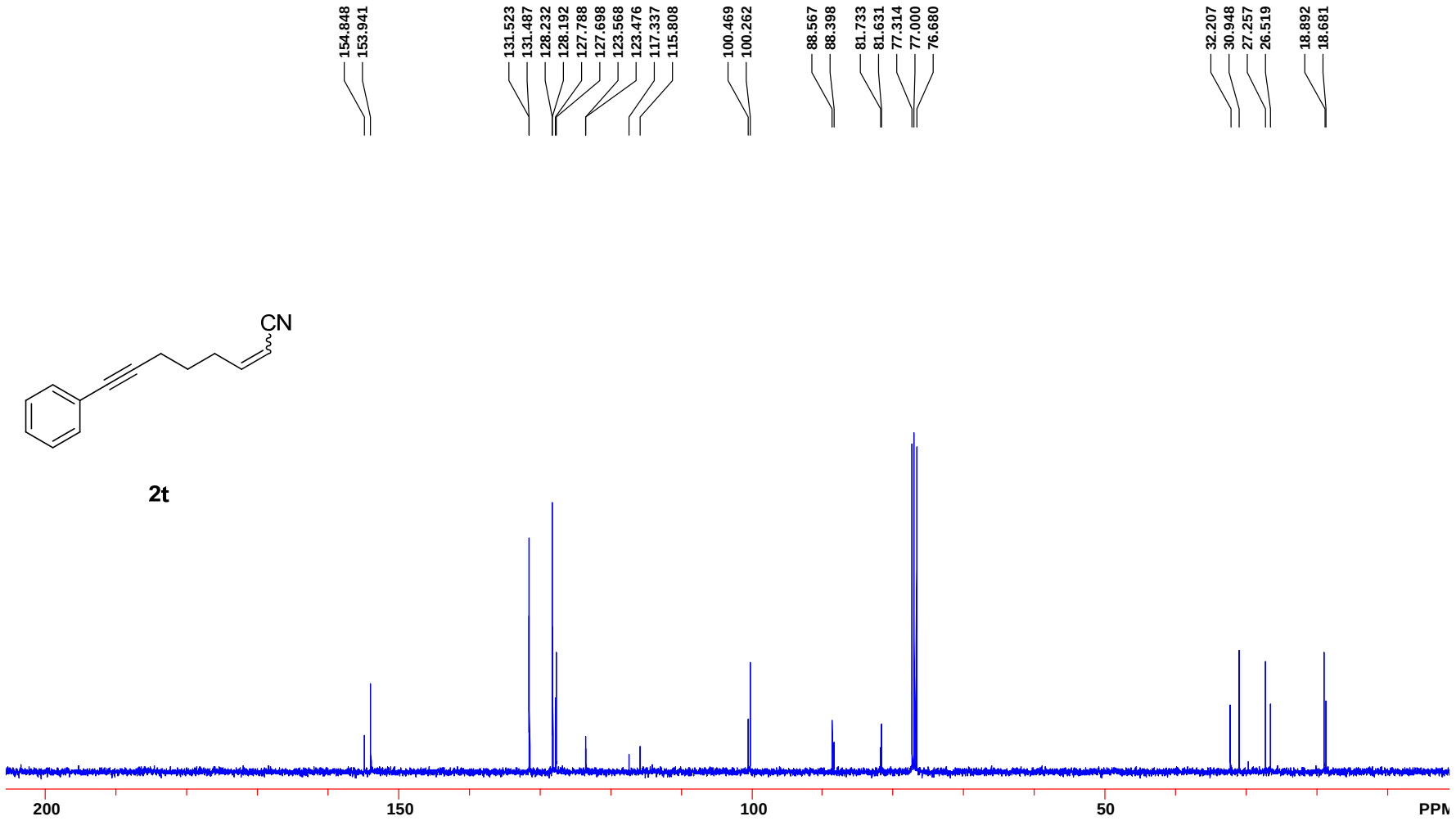
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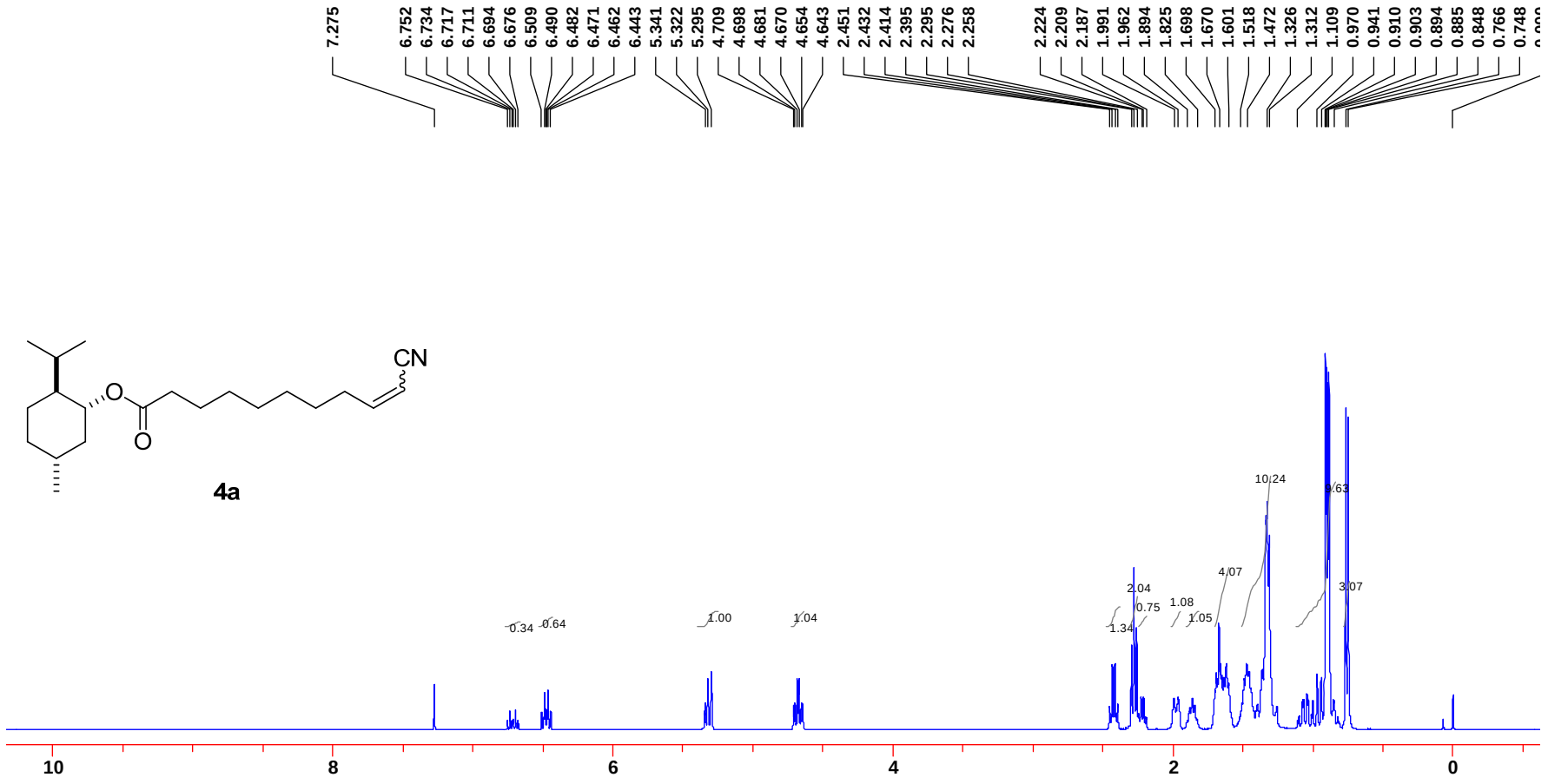
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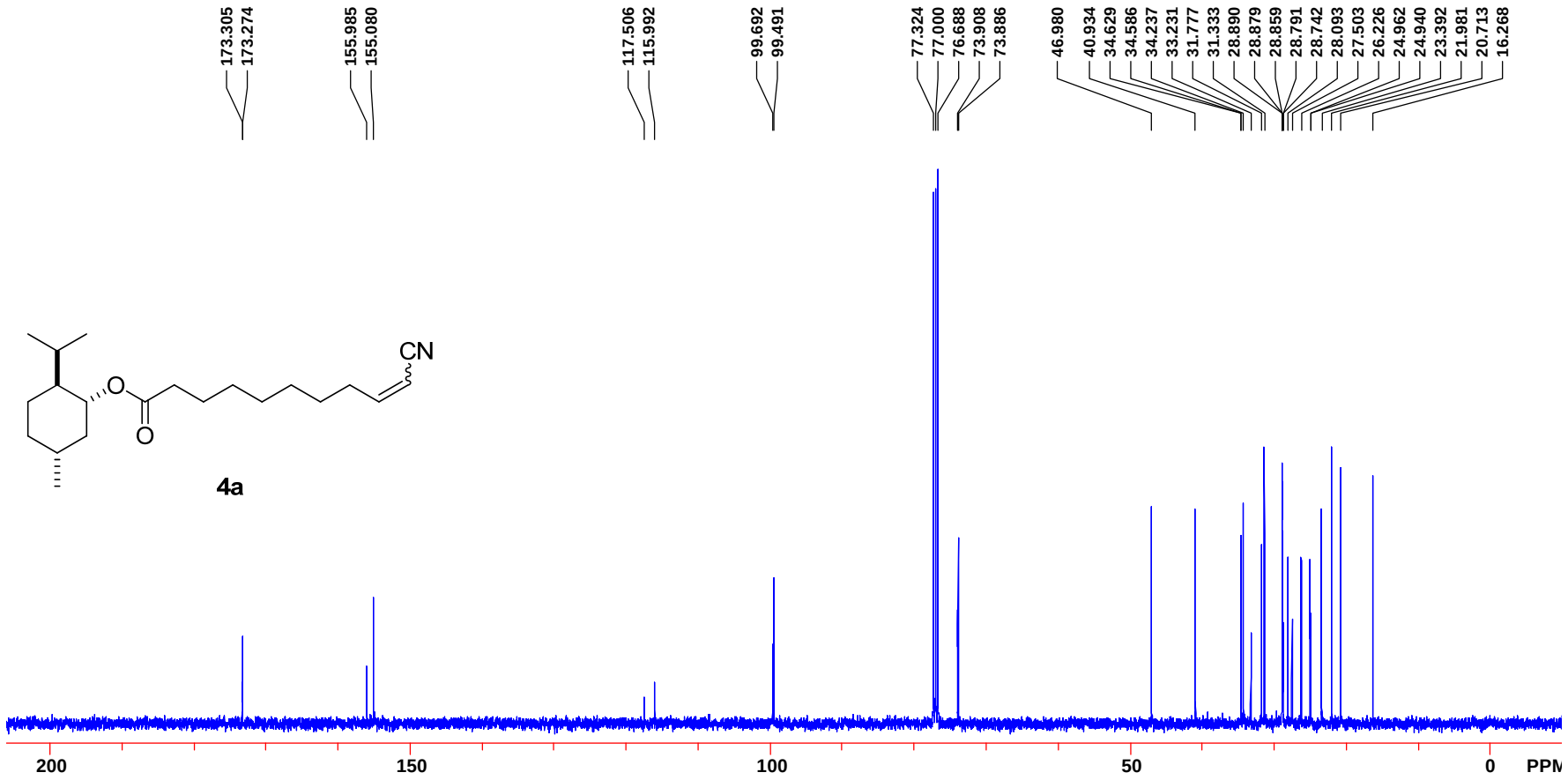
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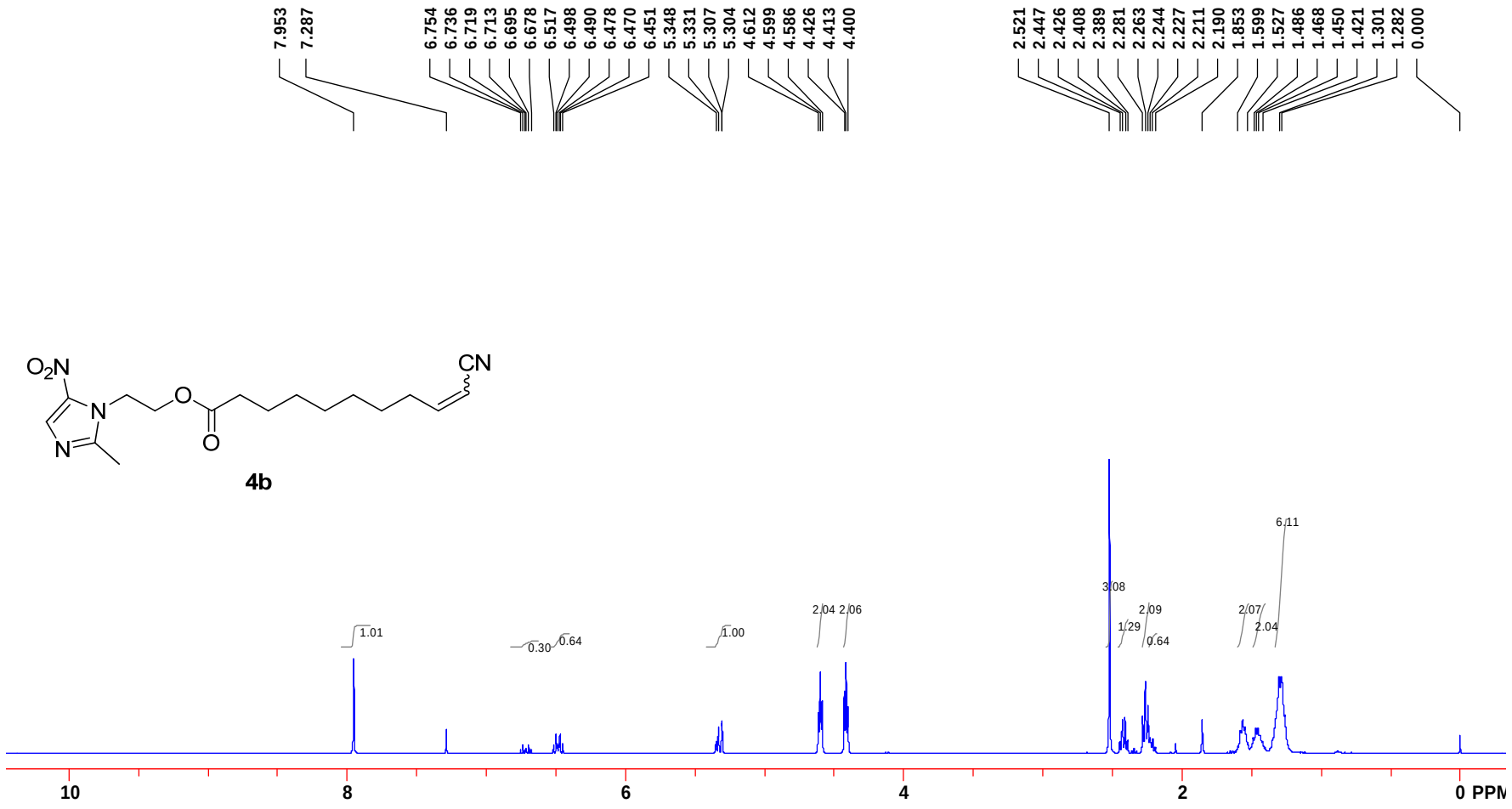
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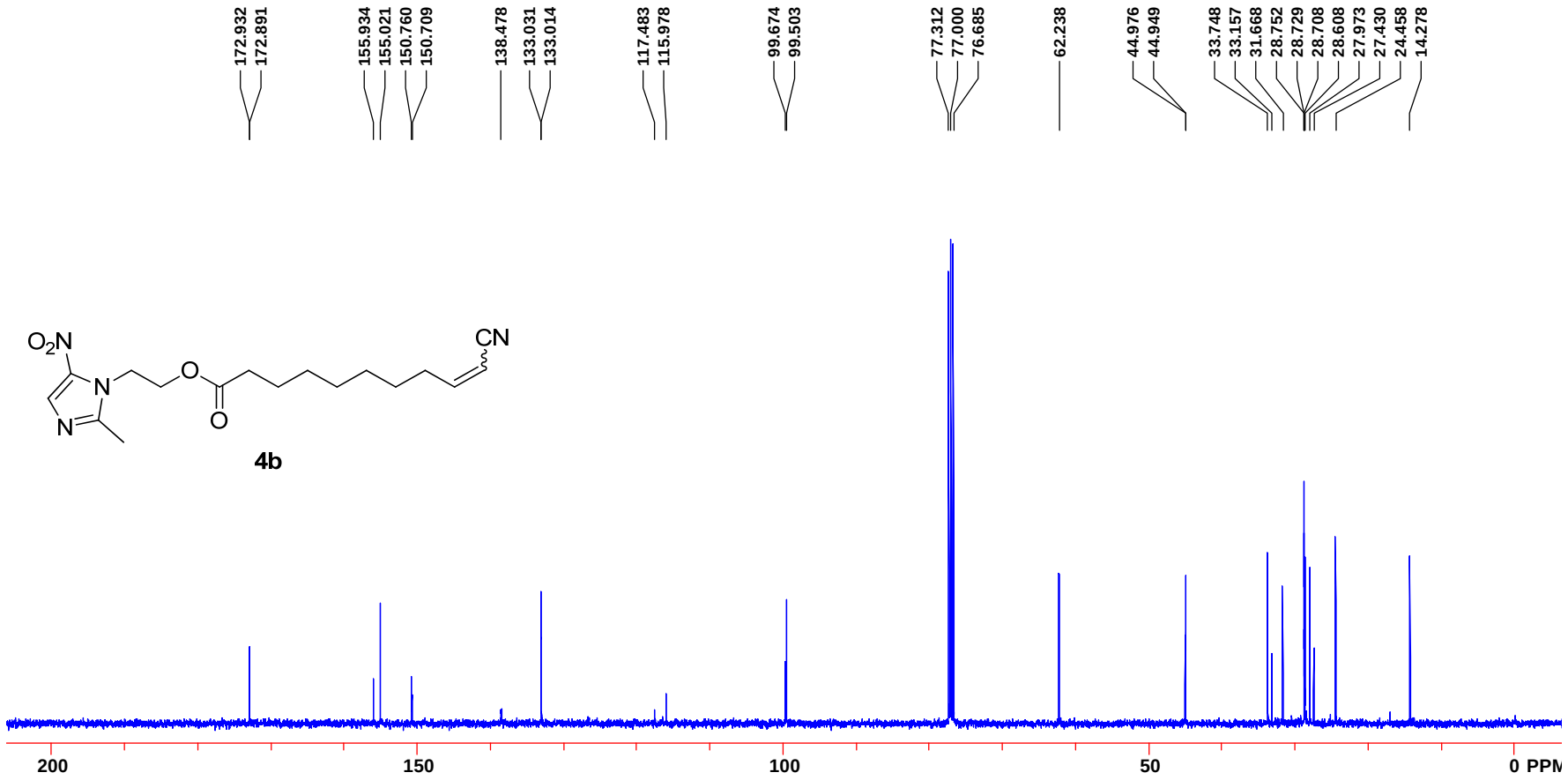
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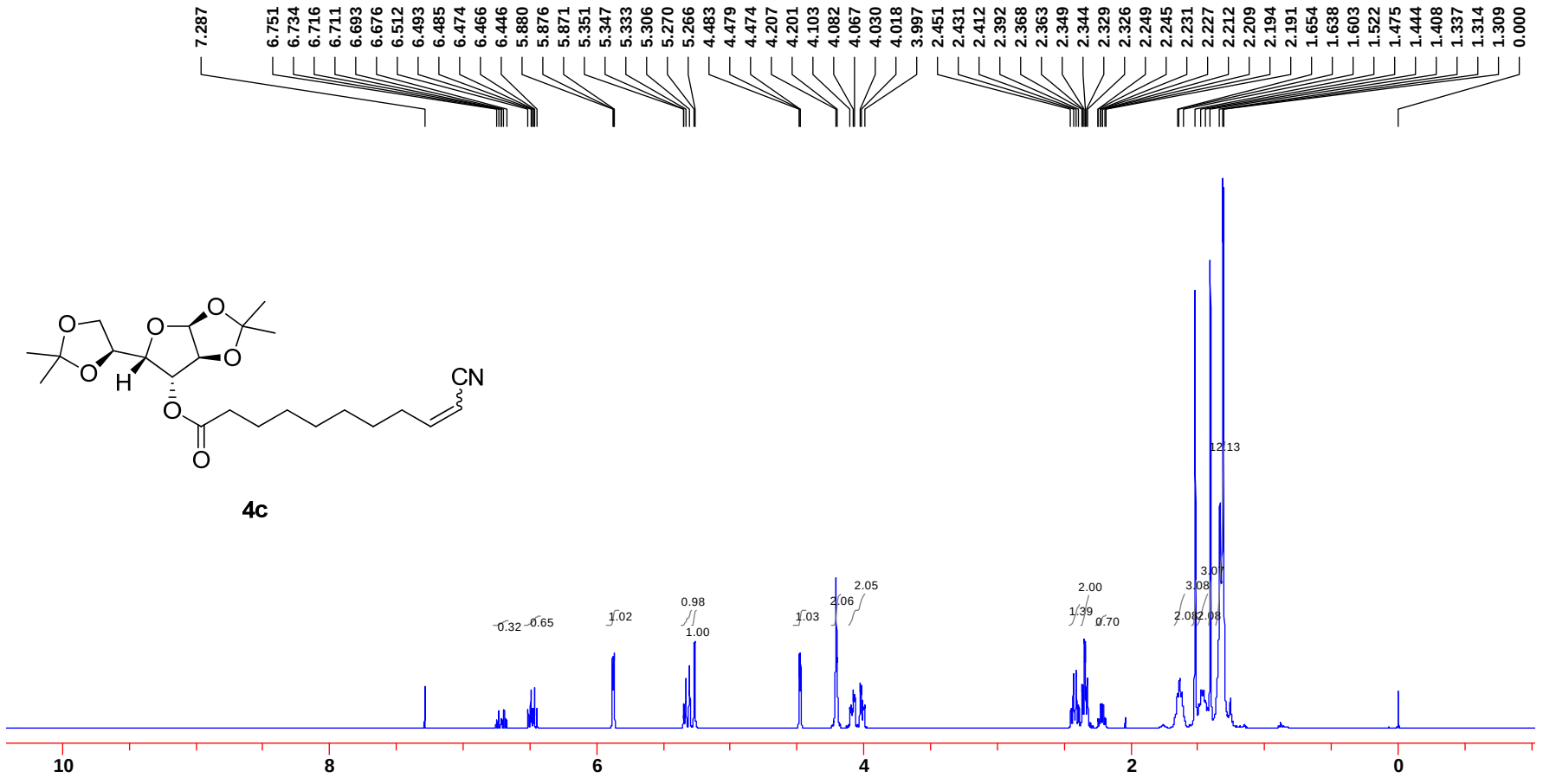
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1.314
1.309
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O
O
O
O
H
O
O
CN
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2.06
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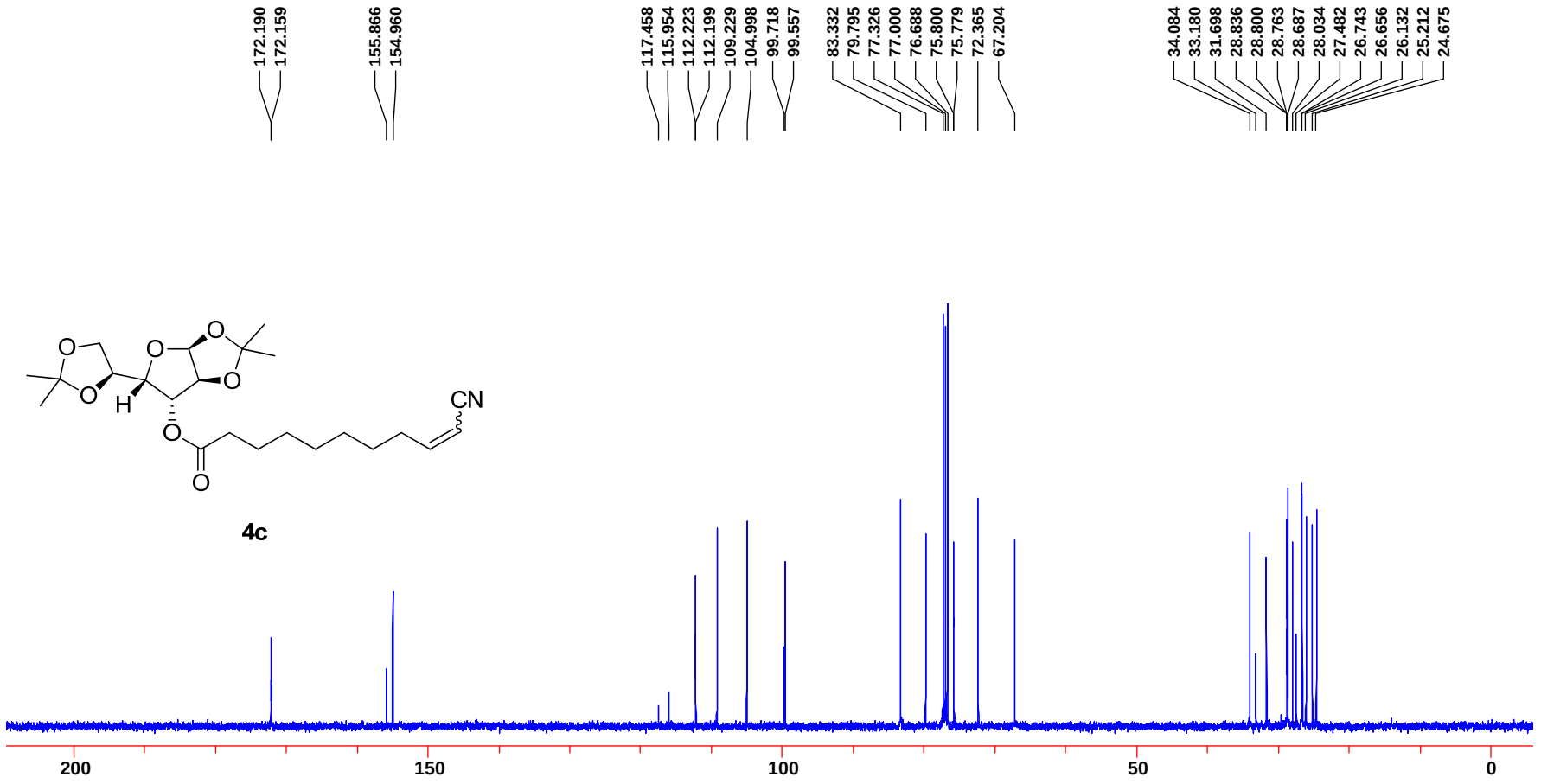
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76.688
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75.779
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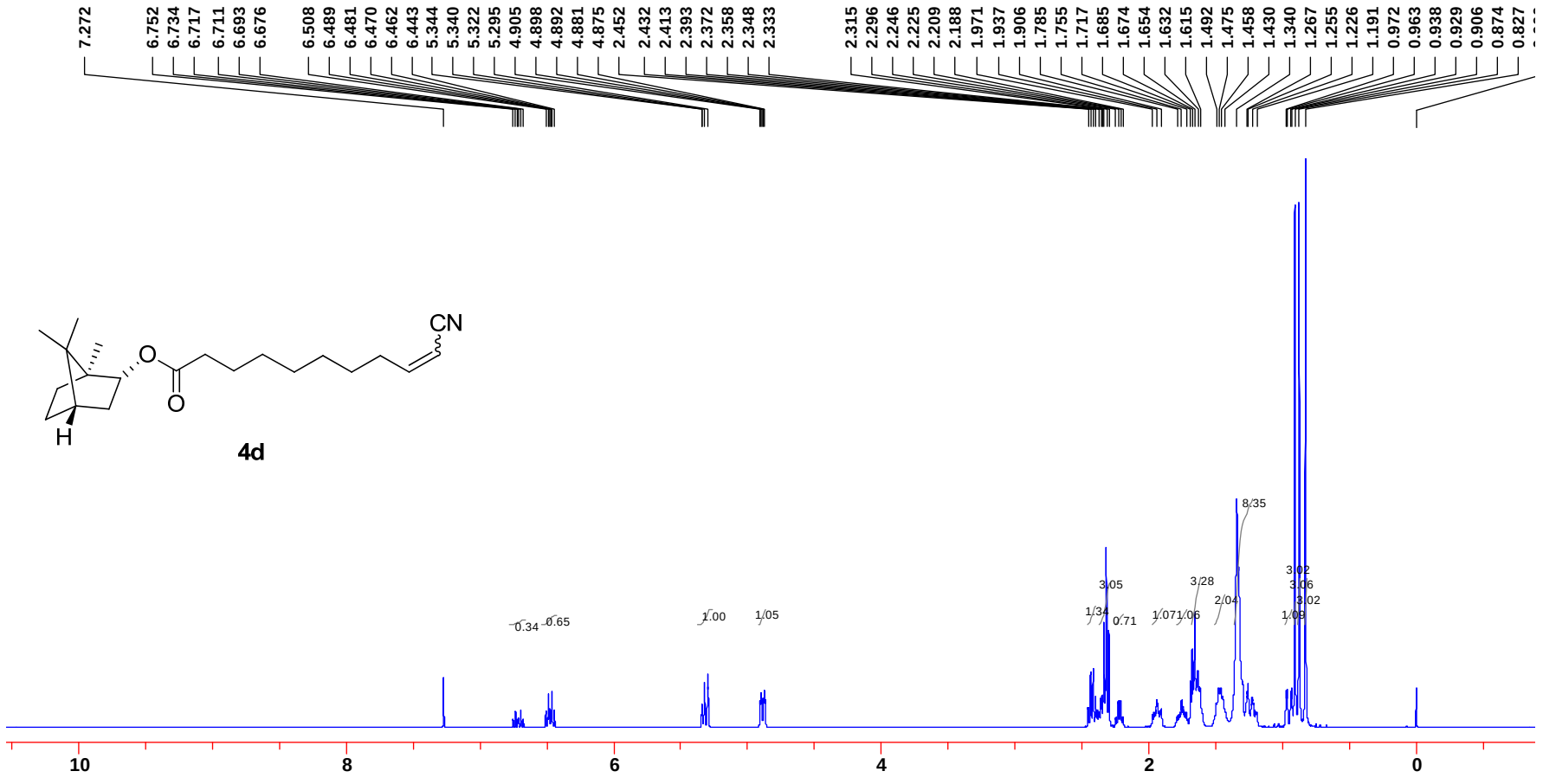
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1.475
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0.929
0.906
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CN
O
O
H
4d
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1.34
3.05
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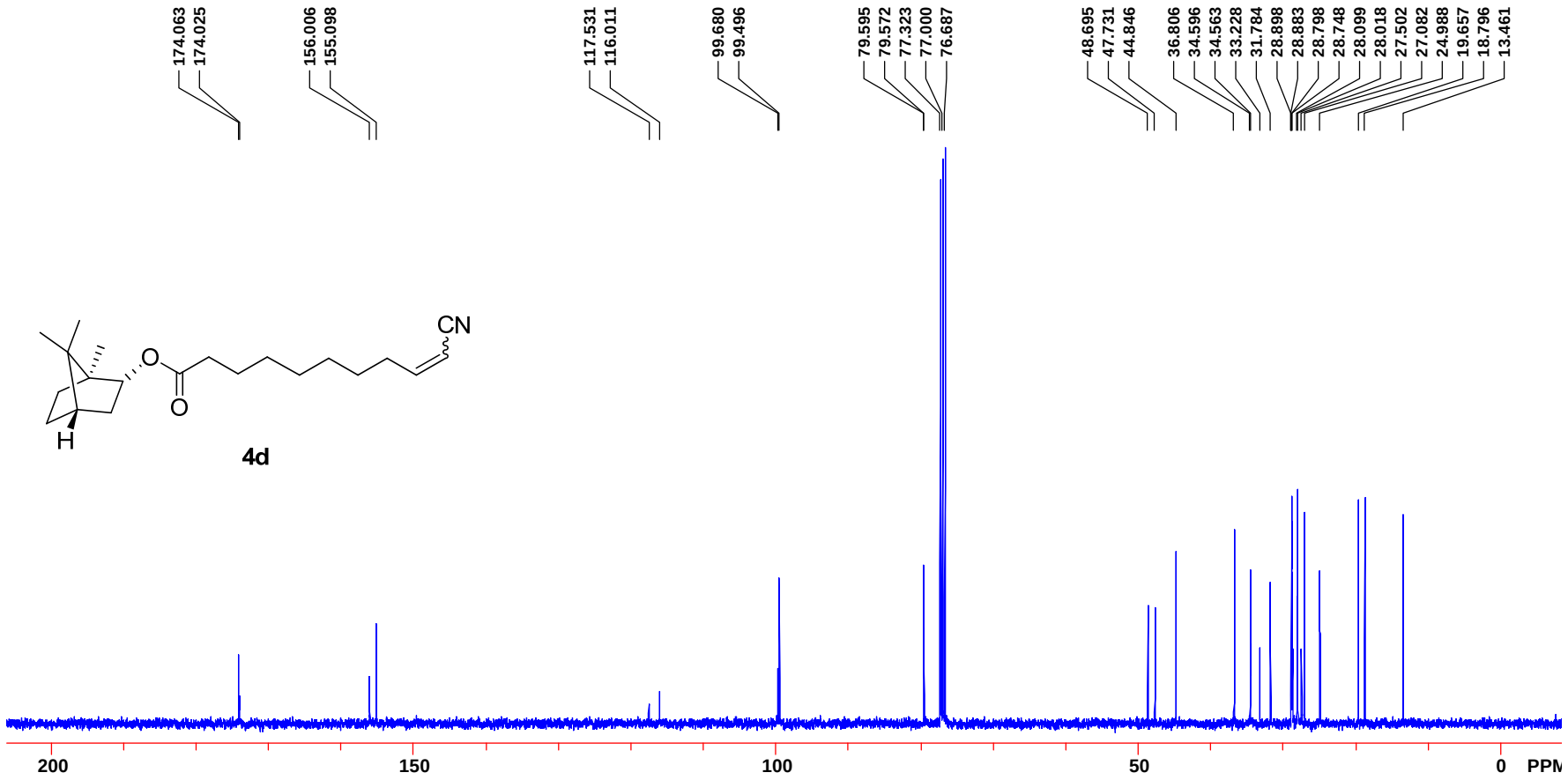
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28.018
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O
H
4d
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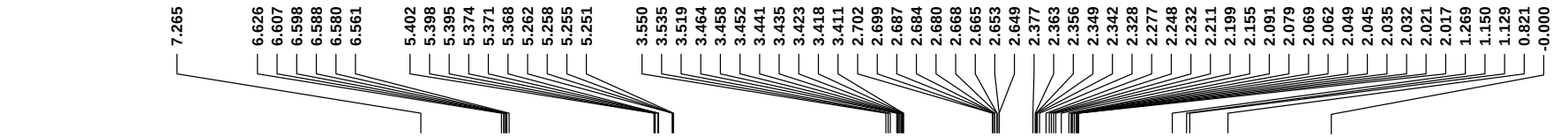
PPM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5.258
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3.535
3.519
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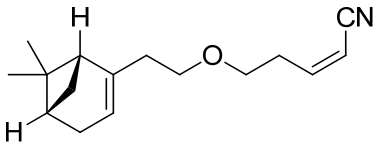
H
CN
O
H

***Z*-4e**

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1.02
2.04
2.05
2.04
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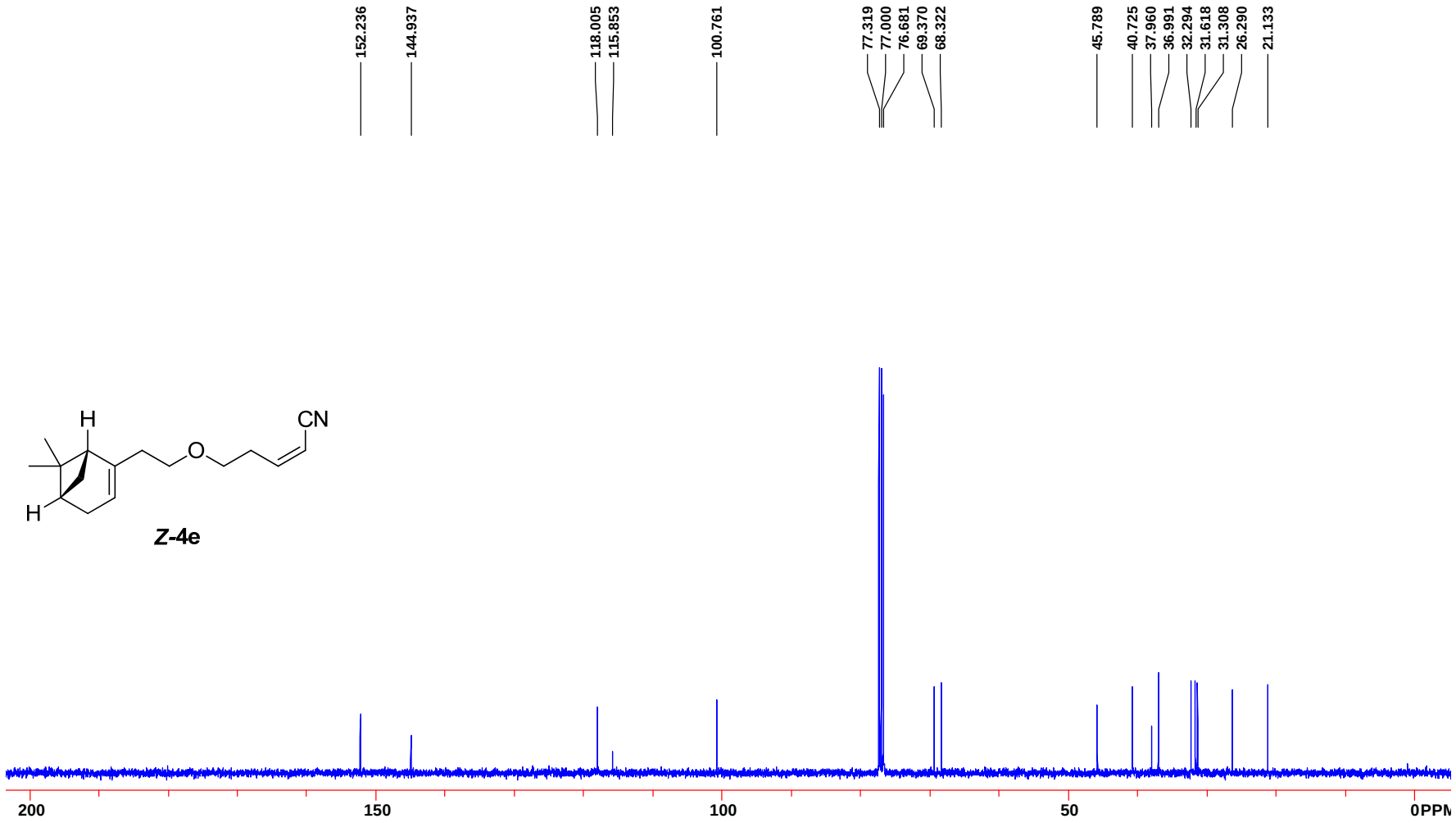
1.00
1.11
3.14
1.03
3.04
10
8
6
4
2
0
PPM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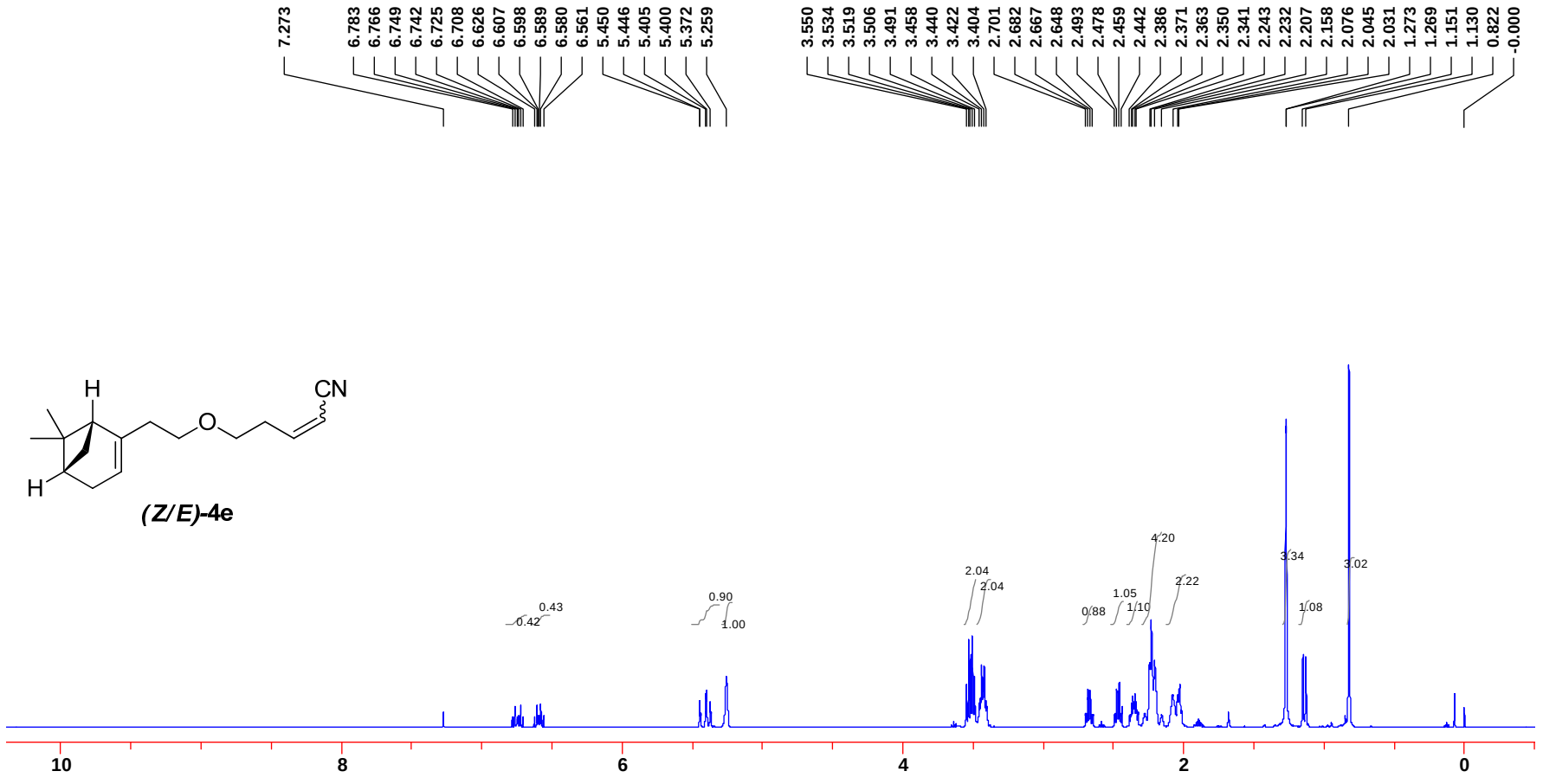
H
CN
O
H
200
150
100
50
0PPM

***Z*-4e**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3.534
3.519
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3.440
3.422
3.404
2.701
2.682
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2.341
2.243
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2.207
2.158
2.076
2.045
2.031
1.273
1.269
1.151
1.130
0.822
-0.000
H
CN
O
H
(Z/E)-4e
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0.42
0.90
1.00
2.04
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1.10
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3.02
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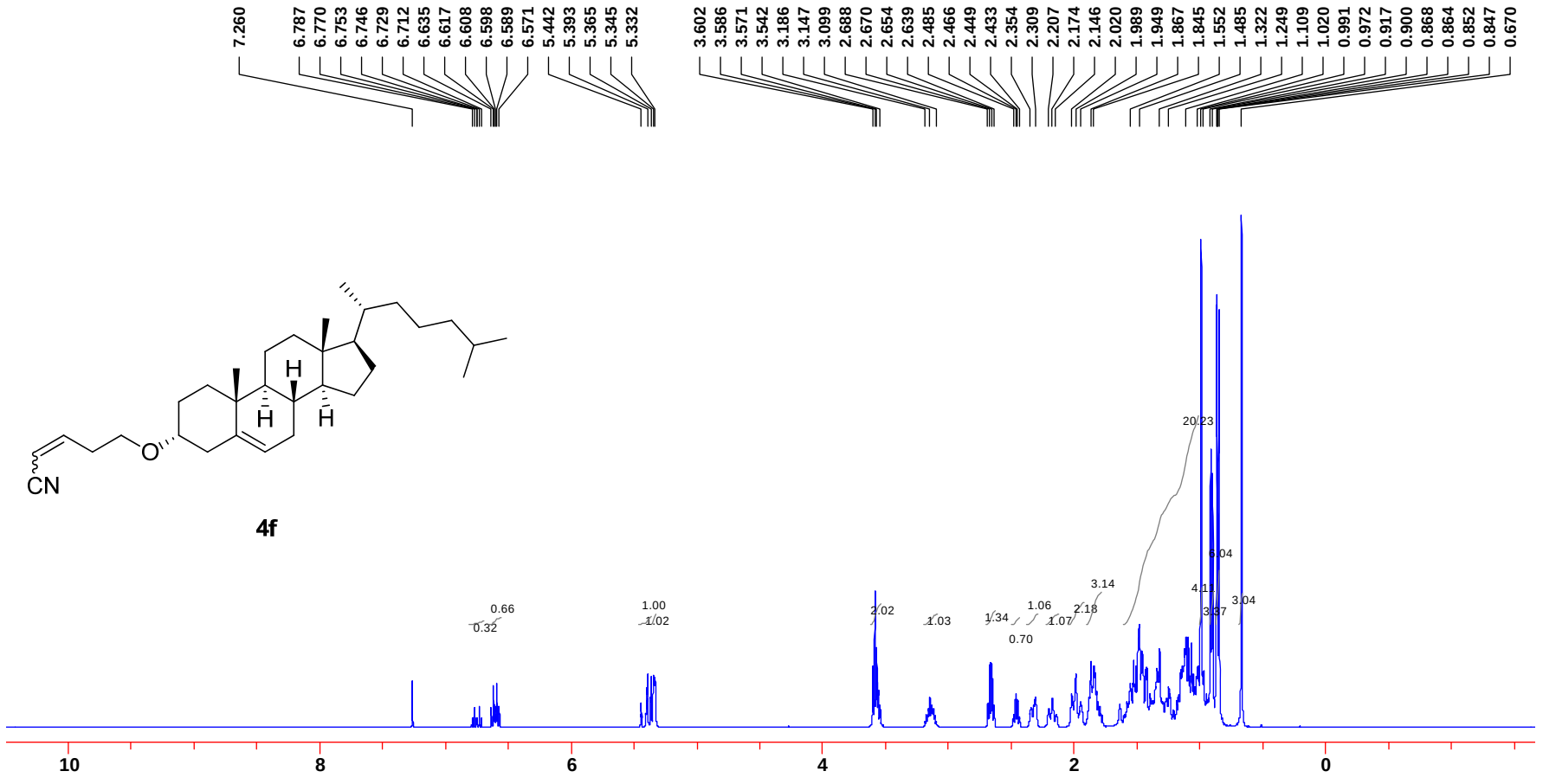
4
2
0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0.847
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H
H
H
O
CN
4f
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0.32
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1.02
2.02
1.03
1.34
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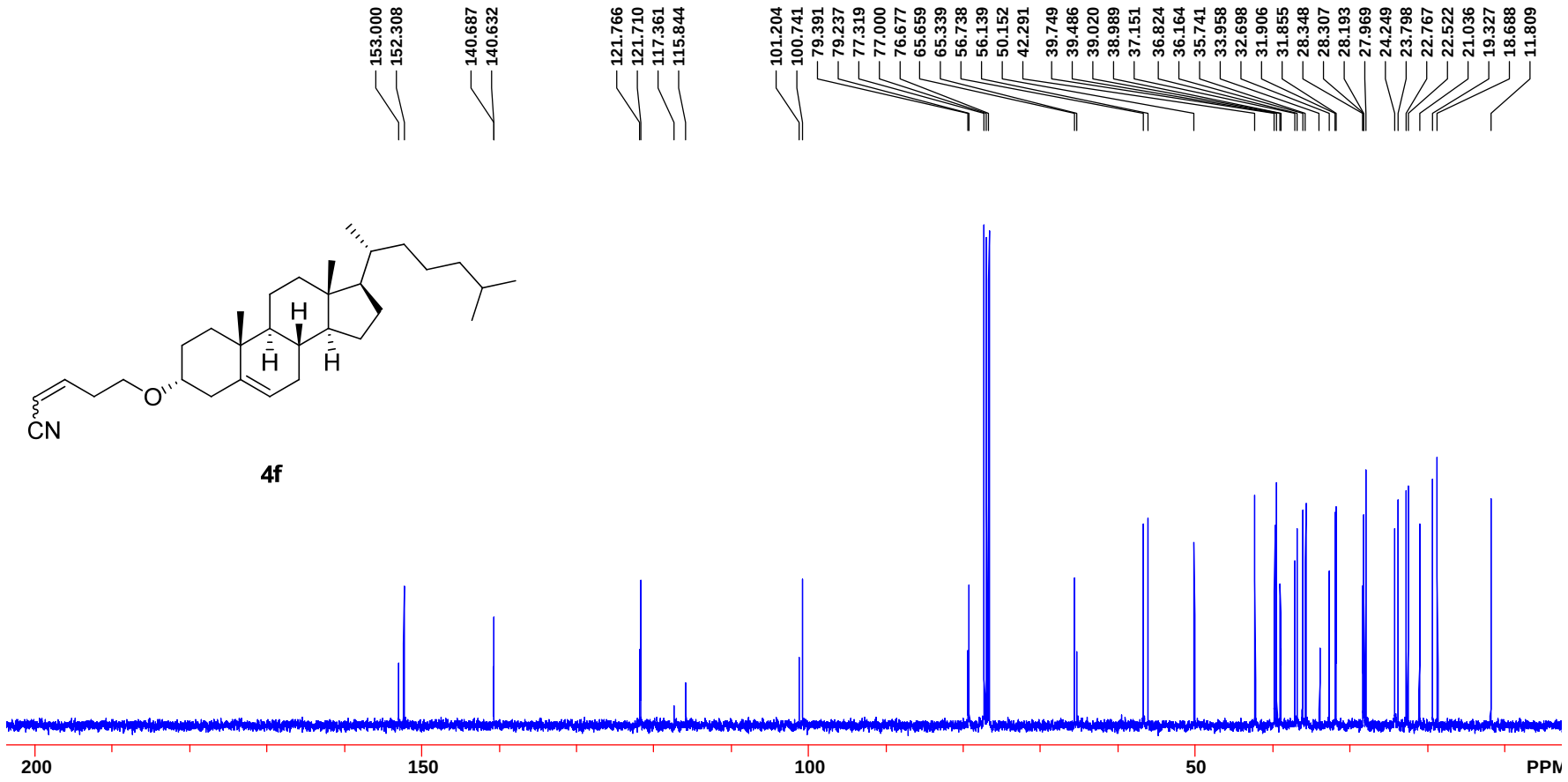
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37.151
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36.164
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32.698
31.906
31.855
28.348
28.307
28.193
27.969
24.249
23.798
22.767
22.522
21.036
19.327
18.688
11.809
H
H
H
O
CN
200
150
100
50
PPM

4f