Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Nickel-Catalyzed Highly Regioselective Hydrocyanation of Alkenes with $Zn(CN)_2$

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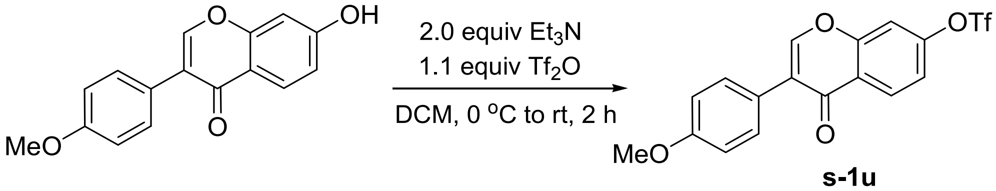
General Methods. Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran and toluene were distilled from sodium and benzophenone. 1,4-dioxane was distilled from sodium. Acetonitrile was dried using Innovative Technology Solvent Purifier. *N, N*-Dimethylformamide (Superdry), Xantphos, DPEphos, dppf, dppp, neocuproine and 2,2':6',2''-terpyridine were purchased from J&K Chemical Company. PPh_3, $P(OPh)_3$ and dppb were purchased from TCI. $Ni(COD)_2$, NiI_2, $Ni(acac)_2$ and $Ni(ClO_4)_2{\cdot}6H_2O$ were purchased from Strem Chemicals Inc. $NiCl_2(DME)$ and $NiBr_2(DME)$ were purchased from Sigma-Aldrich. $NiCl_2{\cdot}6H_2O$, $NiCl_2$, dppe, $Zn(CN)_2$, and DMAP were purchased from Alfa Aesar. Zinc powder (99.8%, -100 mesh) and Mn powder (APS<10 micron, 99.6% metals basis) were purchased from Alfa Aesar. Al powder (200 mesh) was purchased from Acros Organics. Before using, zinc powder was stirred with 1 M HCl aqueous solution, filtered and washed thoroughly with water, acetone and diethyl ether and dried under vacuum. Unless noted, all commercial reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS) on Varian or Agilent XL-400 MHz spectrometer. ^1H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) or solvent residual peak (chloroform, $\delta = 7.26$ ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ ($\delta = 77.00$ ppm) as internal reference. High-resolution mass spectra were obtained by using Waters Micromass GCT Premier mass spectrometer, Agilent Technologies 6224 TOF LC/MS or Thermo Fisher Scientific LTQ FT Ultra mass spectrometers. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer.

Note: It was noted that partial dehydration of $NiCl_2{\cdot}6H_2O$ stored in a nitrogen-filled glove box for a long time might occur. In order to obtain the accurate experimental data, $NiCl_2{\cdot}6H_2O$ used in this study was stored under air (outside of glove box), which was brought into the glove box and used immediately for every experiment.

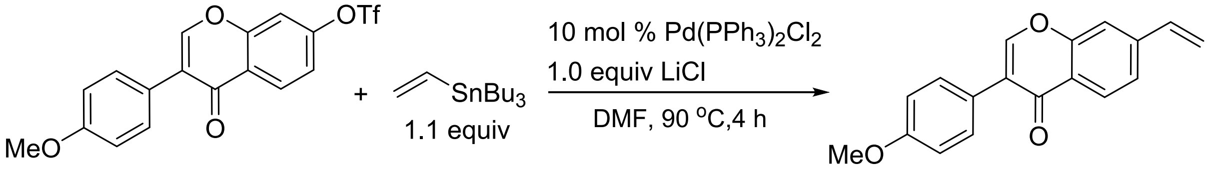
Caution! Zinc cyanide is toxic and should be handled with extra care. The crude reaction mixture or the aqueous layer should not be exposed to acidic conditions as formation of hydrogen cyanide is possible.

Alkenes were synthesized according to the published methods. For the characterization of the new alkene substrates, see the following:



s-1u

To a solution of 7-hydroxy-3-(4-methoxyphenyl)-4*H*-chromen-4-one (2.68 g, 10 mmol) and Et$_3$N (2.02 g, 20 mmol) in DCM (50 mL) was added Tf$_2$O (3.10 g, 11 mmol) at 0 °C under Argon, then the mixture was warmed up to room temperature and stirred for another 2 h. The reaction was quenched with saturated NH$_4$Cl and extracted with DCM. The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 2:1) to give 3-(4-methoxyphenyl)-4-oxo-4*H*-chromen-7-yl trifluoromethanesulfonate **(s-1u)** in 69% yield (2.76 g) as a white solid. M.p.: 125.0-126.3 °C**.** ^{1}H NMR (400 M, CDCl$_3$): δ 3.84 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 7.33 (dd, J = 8.8, 2.4 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H), 8.01 (s, 1H), 8.40 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 M, CDCl$_3$): δ 55.26, 111.39, 114.04, 118.47, 118.63 (q, $^1J_{C\text{-}F}$ = 321.3 Hz), 123.08, 124.14, 125.62, 129.12, 130.00, 152.02, 152.80, 156.27, 159.86, 175.11. IR (neat): 3097, 3076, 3058, 2954, 2907, 2836, 1644, 1612, 1568, 1516, 1424, 1400, 1292, 1250, 1212, 1182, 1168, 1132, 1095, 1029, 952, 883, 864, 824, 801, 788, 782, 689, 659 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{12}F_3O_6S[M+H]^+$: 401.0301, found 401.0298.



s-1u **1u**

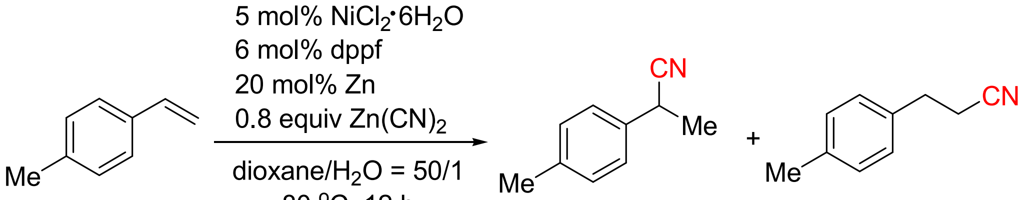
To a solution of **s-1u** (1.20 g, 3 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (210.6 mg, 0.3 mmol) and LiCl (127.2 mg, 3 mol) in DMF (18 mL) was added tributyl(vinyl)stannane (1.05 g, 3.3 mmol) dropwise under Argon. The mixture was heated at 90 °C for 4 h. After completion the reaction mixture was cooled down to room temperature and diluted with Et_2O and washed with 1 M HCl(aq.), then washed with saturated $NaHCO_3$(aq.) and brine. The combined aqueous layers were extracted once with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether /dichloromethane/ethyl acetate = 6:1:1) to give 3-(4-methoxyphenyl)-7-vinyl-4*H*-chromen-4-one **(1u)** in 76% yield (637.7 mg) as a white solid. M.p.: 154.0-155.1 °C**.** ^{1}H NMR (400 M, $CDCl_3$): δ 3.83 (s, 3H), 5.48 (d, *J* = 11.2 Hz, 1H), 5.94 (d, *J* = 17.6, Hz, 1H), 6.79 (dd, *J* = 17.6, 11.2 Hz, 1H), 6.96-6.98 (m, 2H), 7.41 (s, 1H), 7.46-7.52 (m, 3H), 7.96 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 55.26, 113.91, 115.37, 117.81, 122.83, 123.62, 124.03, 124.97, 126.49, 130.02, 135.32, 142.89, 152.49, 156.44, 159.55, 176.06. IR (neat): 3092, 3076, 3040, 3011, 2972, 2930, 2838, 1624, 1609, 1557, 1513, 1439, 1407, 1358, 1291, 1253, 1233, 1176, 1106, 1024, 985, 927, 901, 886, 878, 830, 821, 802, 791, 767, 717 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{15}O_3$ $[M+H]^+$: 279.1016, found 279.1007.

Optimization studies for Ni-catalyzed hydrocyanation of aryl alkenes.

General procedure for optimization studies.

The reaction was conducted in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiCl_2{\cdot}6H_2O$ (3.6 mg, 0.015 mmol) [or other Ni(II) salts], Xantphos (10.4 mg, 0.018 mmol) [or other ligands], Zinc powder (3.9 mg, 0.06 mmol) [or other reductants], $Zn(CN)_2$ (28.2 mg, 0.24 mmol), dioxane or other solvents (1.5 mL) and 1-methyl-4-vinylbenzene (35.5 mg, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (30 µL or x equiv) was added to the vial. After the reaction mixture was stirred at 80 °C, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^{1}H NMR analysis of the crude mixture using mesitylene (36.1 mg, 0.3 mmol) as an internal standard. In some cases, the reaction mixture was quenched by 10% $NH_3{\cdot}H_2O$ aquous solution and extracted with ethyl acetate. The combined organic layers were washed with water and saturated NaCl solution, dried over anhydrous Na_2SO_4 (for entries 1-4).

Table S1. Optimization studies for Ni-catalyzed hydrocyanation of aryl alkenes.[a]



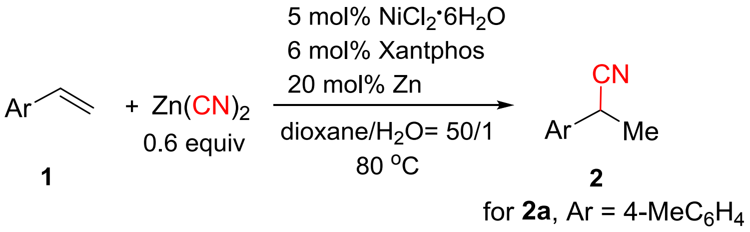
1a **2a** (branched) **3a** (linear)

entry	deviation from conditions shown in eq 1	yield (%)[b]	
		2a	**3a**
1	none	89	3
2	dioxane/H_2O = 25/1	0	0
3	1.0 equiv H_2O was used	33	9.5
4	2.0 equiv H_2O was used	75	10
5	$NiCl_2$ instead of $NiCl_2•6H_2O$	60	3
6	$NiCl_2$(DME) instead of $NiCl_2•6H_2O$	87	4
7	$NiBr_2$(DME) instead of $NiCl_2•6H_2O$	78	13
8	NiI_2 instead of $NiCl_2•6H_2O$	79	11
9	$Ni(ClO_4)_2•6H_2O$ instead of $NiCl_2•6H_2O$	5	<1
10	$Ni(acac)_2$ instead of $NiCl_2•6H_2O$	0	0
11	10 mol% PPh_3 or $P(OPh)_3$ instead of 6 mol% dppf	0	0
12	dppe instead of dppf	8	4
13	dppp instead of dppf	37	8
14	dppb instead of dppf	10	2.5
15	Xantphos instead of dppf	96	1
16	DPEPhos instead of dppf	3	0
17	neocuproine instead of dppf	0	0
18	terpyridine instead of dppf	0	0
19	Xantphos instead of dppf, toluene instead of dioxane	0	0
20	Xantphos instead of dppf, MeCN instead of dioxane	49	33
21	Xantphos instead of dppf, THF instead of dioxane	95	1
22	Xantphos instead of dppf, DMF instead of dioxane	26	0
23[c]	**Xantphos instead of dppf, 0.6 equiv $Zn(CN)_2$ was used**	**97**	**1**
24[c,d]	Xantphos instead of dppf, Mn instead of Zn	73	<1
25[c,d]	Xantphos instead of dppf, Al instead of Zn	2	0
26[c,d]	Without either of $NiCl_2•6H_2O$, Xantphos or Zn	0	0
27[c,d]	Without H_2O	25	0

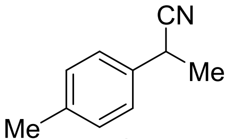
[a] **1a** (0.3 mmol), $Zn(CN)_2$ (0.24 mmol), $NiCl_2•6H_2O$ (0.015 mmol), dppf (0.018 mmol) and zinc powder (0.06 mmol) in dioxane/H_2O (1.5 mL/0.03 mL) at 80 °C for 12 h. [b] Determined by ^{1}H NMR of the crude reaction mixture using mesitylene as an internal standard. [c] The reaction time was 4 h. [d] 0.6 equiv $Zn(CN)_2$ was used.

Ni-Catalyzed hydrocyanation of aryl/heteroaryl alkenes.

Typical procedure for the synthesis of 2a.

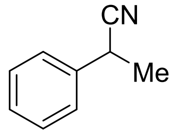


The reaction was conducted in an oven-dried screw-cap vial (8 mL) equipped with a magnetic stir bar. The vial containing $NiCl_2 \cdot 6H_2O$ was equipped with a septum cap, which was pierced by a needle and introduced into the antechamber of nitrogen-filled glovebox. Before transferring into the inside of the glovebox, it was evacuated and back-filled with nitrogen for three times (ca. 5 min). In a nitrogen-filled glove box, $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give the desired product **2a** in 93% yield (67.5 mg) as a colorless oil.



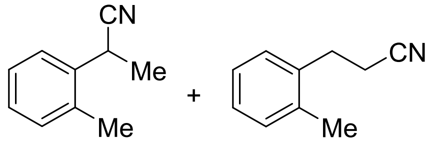
2a

2-*p*-Tolylpropanenitrile (2a). ^1H NMR (400 M, $CDCl_3$): δ 1.62 (d, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.98, 21.44, 30.80, 121.73, 126.52, 129.71, 134.05, 137.78. The spectroscopic data are in agreement with that previously reported.[1]



2b

2-Phenylpropanenitrile (2b). $NiCl_2{\cdot}6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), styrene (52.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the product **2b** in 88% yield (57.4 mg) as a colorless oil. ^{1}H NMR (400 M, $CDCl_3$): δ 1.62 (d, J = 7.2 Hz, 3H), 3.89 (q, J = 7.2 Hz, 1H), 7.29-7.40 (m, 5H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.34, 31.10, 121.51, 126.58, 127.92, 129.02, 136.96. The spectroscopic data are in agreement with that previously reported.[1]

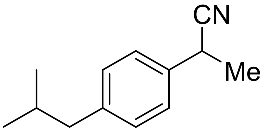


2c **3c**

$NiCl_2{\cdot}6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-methyl-2-vinylbenzene (59.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1 to 20:1) afforded the product **2c** in 63% yield (46.0 mg) as a colorless oil and **3c** in 10% yield (7.0 mg) as a colorless oil.

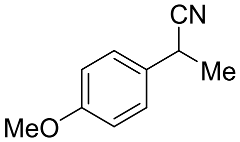
2-*o*-Tolylpropanenitrile (2c). ^{1}H NMR (400 M, $CDCl_3$): δ 1.60 (d, J = 7.2 Hz, 3H), 2.35 (s, 3H), 4.03 (q, J = 7.2 Hz, 1H), 7.17-7.27 (m, 3H), 7.43-7.45 (m, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 18.90, 19.93, 28.05, 121.72, 126.59, 126.88, 128.02, 130.90, 134.69, 135.17. The spectroscopic data are in agreement with that previously reported.[2]

3-*o*-Tolylpropanenitrile (3c). ^{1}H NMR (400 M, $CDCl_3$): δ 2.33 (s, 3H), 2.58 (t, J = 7.6 Hz, 2H), 2.98 (t, J = 7.6 Hz, 2H), 7.15-7.20 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 17.97, 19.14, 28.84, 119.19, 126.45, 127.33, 128.67, 130.61, 135.74, 136.18. The spectroscopic data are in agreement with that previously reported.[3]



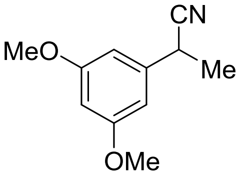
2d

2-(4-Isobutylphenyl)propanenitrile (2d). $NiCl_2\cdot6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-isobutyl-4-vinylbenzene (80.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 6 h. Purification by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the product **2d** in 75% yield (70.0 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 0.90 (d, J = 6.8 Hz, 6H), 1.62 (d, J = 7.6 Hz, 3H), 1.80-1.90 (m, 1H), 2.47 (d, J = 7.2 Hz, 2H), 3.86 (q, J = 7.2 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.34, 22.22, 30.09, 30.78, 44.85, 121.73, 126.34, 129.72, 134.22, 141.53. The spectroscopic data are in agreement with that previously reported.[4]



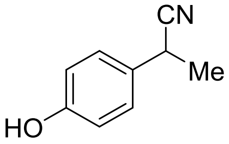
2e

2-(4-Methoxyphenyl)propanenitrile (2e). $NiCl_2\cdot6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-methoxy-4-vinylbenzene (67.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **2e** in 92% yield (73.9 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.60 (d, J = 7.6 Hz, 3H), 3.80 (s, 3H), 3.84 (q, J = 7.6 Hz, 1H), 6.89-6.92 (m, 2H), 7.25-7.27 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.39, 30.31, 55.22, 114.36, 121.79, 127.72, 128.98, 159.18. The spectroscopic data are in agreement with that previously reported.[5]



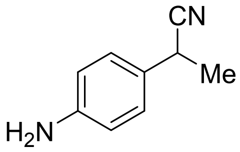
2f

2-(3,5-Dimethoxyphenyl)propanenitrile (2f). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1,3-dimethoxy-5-vinylbenzene(82.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **2f** in 95% yield (91.3mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.62 (d, J = 7.2 Hz, 3H), 3.79-3.84 (m, 7H), 6.40 (t, J = 2.0 Hz, 1H), 6.49 (d, J = 2.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.12, 31.19, 55.24, 99.52, 104.75, 121.35, 139.12, 161.14. IR (neat): 2985, 2941, 2839, 2242, 1596, 1457, 1429, 1349, 1328, 1296, 1204, 1152, 1051, 836, 735, 694 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{14}NO_2$ $[M+H]^+$: 192.1019, found 192.1017.



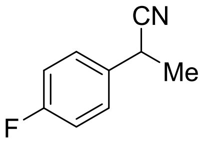
2g

2-(4-Hydroxyphenyl)propanenitrile (2g). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4-vinylphenol (60.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1 to 3:1) afforded the product **2g** in 87% yield (63.7 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.59 (d, J = 7.6 Hz, 3H), 3.84 (q, J = 7.2 Hz, 1H), 6.59 (s, 1H), 6.82-6.86 (m, 2H), 7.17 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.21, 30.30, 115.97, 121.95, 127.88, 128.44, 155.67. IR (neat): 3344, 3022, 2988, 2936, 2254, 1613, 1591, 1515, 1441, 1372, 1356, 1343, 1274, 1264, 1216, 1185, 1174, 1107, 1083, 1054, 987, 837, 818, 732 cm^{-1}. HRMS (EI) calcd for C_9H_9NO $[M]^+$: 147.0684, found 147.0679.



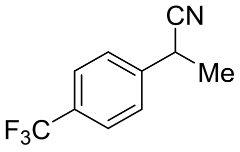
2h

2-(4-Aminophenyl)propanenitrile (2h). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4-vinylaniline (59.6 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded the product **2h** in 89% yield (64.7 mg) as a light yellow oil. ^1H NMR (400 M, $CDCl_3$): δ 1.56 (d, J = 7.2 Hz, 3H), 3.72 (s, 2H), 3.76 (q, J = 7.2 Hz, 1H), 6.64 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.25, 30.19, 115.20, 122.10, 126.39, 127.46, 146.18. IR (neat): 3460, 3369, 3225, 2983, 2924, 2853, 2238, 1623, 1516, 1452, 1378, 1285, 1183, 1130, 1084, 988, 826 cm^{-1}. HRMS (ESI) calcd for $C_9H_{11}N_2$ $[M+H]^+$: 147.0917, found 147.0914.



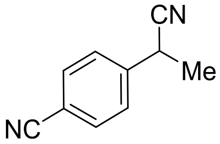
2i

2-(4-Fluorophenyl)propanenitrile (2i). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-fluoro-4-vinylbenzene (61.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) afforded the product **2i** in 81% yield (60.4 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.63 (d, J = 7.2 Hz, 3H), 3.90 (q, J = 7.2 Hz, 1H), 7.05-7.09 (m, 2H), 7.31-7.35 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.37, 30.44, 115.97 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 121.34, 128.35 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 132.77 (d, $^4J_{C\text{-}F}$ = 3.8 Hz), 162.22 (d, $^1J_{C\text{-}F}$ = 247.3 Hz). The spectroscopic data are in agreement with that previously reported.[5]



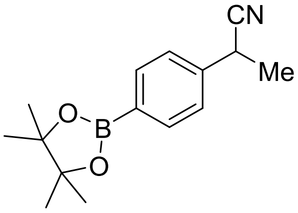
2j

2-(4-(Trifluoromethyl)phenyl)propanenitrile (2j). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-(trifluoromethyl)-4-vinylbenzene (86.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **2j** in 84% yield (84.0 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.67 (d, J = 7.2 Hz, 3H), 3.99 (q, J = 7.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.13, 31.01, 120.72, 123.75 (q, $^1J_{C-F}$ = 272.4 Hz), 126.08 (q, $^3J_{C-F}$ = 3.8 Hz), 127.15, 130.35 (q, $^2J_{C-F}$ = 32.9 Hz), 140.94 (q, $^5J_{C-F}$ = 1.5 Hz). The spectroscopic data are in agreement with that previously reported.[6]



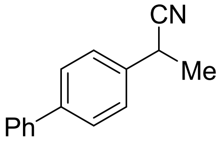
2k

4-(1-Cyanoethyl)benzonitrile (2k). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4-vinylbenzonitrile (64.6 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the product **2k** in 85% yield (66.2 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.68 (d, J = 7.6 Hz, 3H), 4.02 (q, J = 7.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.93, 31.11, 112.01, 118.01, 120.26, 127.52, 132.81, 142.00. The spectroscopic data are in agreement with that previously reported.[7]



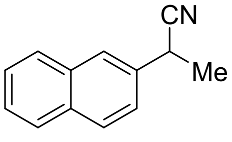
2l

2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanenitrile (2l). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (115.1 mg, 0.5 mmol)and H_2O (50 µL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1 to 10:1) afforded the product **2l** in 77% yield (98.8 mg) as a white solid. M.p.: 100.1-101.4 °C**.** ^1H NMR (400 M, $CDCl_3$): δ 1.34 (s, 12H), 1.62 (d, *J* = 7.2 Hz, 3H), 3.90 (q, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.29, 24.72, 31.23, 83.82, 121.24, 125.91, 135.47, 139.88. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. IR (neat): 2983, 2920, 2239, 1614, 1521, 1454, 1412, 1398, 1358, 1333, 1282, 1267, 1167, 1138, 1094, 1021, 963, 856, 833, 675, 656 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{24}O_2N_2{}^{10}B$ $[M+NH_4]^+$: 274.1962, found 274.1961.



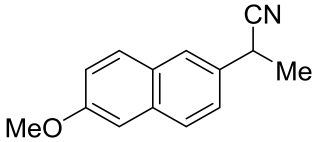
2m

2-(Biphenyl-4-yl)propanenitrile (2m). $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 4-vinyl-1,1'-biphenyl (90.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 µL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) afforded the product **2m** in 95% yield (98.3 mg) as a white solid. ^1H NMR (400 M, $CDCl_3$): δ 1.63 (d, *J* = 7.2 Hz, 3H), 3.90 (q, *J* = 7.2 Hz, 1H), 7.32-7.44 (m, 5H), 7.57 (t, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.26, 30.76, 121.47, 126.93, 127.03, 127.48, 127.67, 128.74, 135.89, 140.07, 140.88. The spectroscopic data are in agreement with that previously reported.[5]



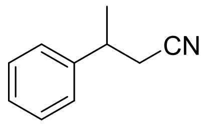
2n

2-(Naphthalen-2-yl)propanenitrile (2n). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 2-vinylnaphthalene (77.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) afforded the product **2n** in 91% yield (82.4 mg) as a white solid. ^1H NMR (400 M, $CDCl_3$): δ 1.66 (d, J = 7.2 Hz, 3H), 3.99 (q, J = 7.2 Hz, 1H), 7.37 (dd, J = 8.6, 2.0 Hz, 1H), 7.45-7.50 (m, 2H), 7.79-7.83 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.22, 31.20, 121.50, 124.26, 125.41, 126.33, 126.57, 127.57, 127.70, 128.98, 132.60, 133.14, 134.19. The spectroscopic data are in agreement with that previously reported.[1]



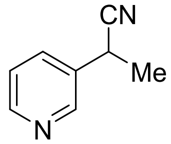
2o

2-(6-Methoxynaphthalen-2-yl)propanenitrile (2o). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 2-methoxy-6-vinylnaphthalene (82.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **2o** in 98% yield (103.7 mg) as a white solid. ^1H NMR (400 M, $CDCl_3$): δ 1.65 (d, J = 7.6 Hz, 3H), 3.87 (s, 3H), 3.95 (q, J = 7.2 Hz, 1H), 7.09 (d, J = 2.0 Hz, 1H), 7.15 (dd, J = 9.0, 2.0 Hz, 1H), 7.34 (dd, J = 8.4, 1.2 Hz, 1H), 7.67-7.72 (m, 3H). ^{13}C NMR (100 M, $CDCl_3$): δ 21.19, 30.98, 55.12, 105.49, 119.37, 121.65, 124.75, 125.18, 127.72, 128.57, 129.12, 131.85, 133.83, 157.90. The spectroscopic data are in agreement with that previously reported.[8]



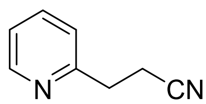
2p

3-Phenylbutanenitrile (2p). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), ZnI_2 (79.8 mg, 0.25 mmol), MeCN (2.5 mL), prop-1-en-2-ylbenzene (59.1 mg, 0.5 mmol) and H_2O (18 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **2p** in 75% yield (54.4 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.45 (d, *J* = 6.8 Hz, 3H), 2.51-2.64 (m, 2H), 3.11-3.20 (m, 1H), 7.23-7.28 (m, 3H), 7.33-7.36 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.60, 26.27, 36.44, 118.55, 126.48, 127.25, 128.79, 143.07. The spectroscopic data are in agreement with that previously reported.[9]



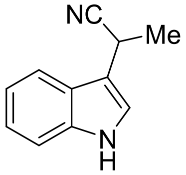
2q

2-(Pyridin-3-yl)propanenitrile (2q). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 3-vinylpyridine (52.6 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded the product **2q** in 83% yield (54.6 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.68 (d, *J* = 7.2 Hz, 3H), 3.98 (q, *J* = 7.2 Hz, 1H), 7.34-7.37 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 8.60-8.62 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.99, 28.78, 120.42, 123.74, 132.72, 134.12, 148.02, 149.34. IR (neat): 3037, 2988, 2941, 2243, 1577, 1481, 1455, 1426, 1301, 1181, 1129, 1089, 1043, 1027, 990, 810, 711 cm^{-1}. HRMS (ESI) calcd for $C_8H_9N_2$ $[M+H]^+$: 133.0760, found 133.0758.



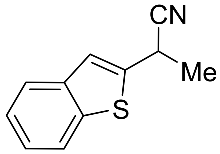
2r

3-(Pyridin-2-yl)propanenitrile (2r). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 2-vinylpyridine (52.6 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 3.5 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded the product **2r** in 91% yield (60.4 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 2.84 (t, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 7.17-7.23 (m, 2H), 7.65 (td, *J* = 7.6, 0.8 Hz, 1H), 8.55 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.37, 33.09, 119.27, 121.98, 122.90, 136.55, 149.36, 156.97. The spectroscopic data are in agreement with that previously reported.[10]



2s

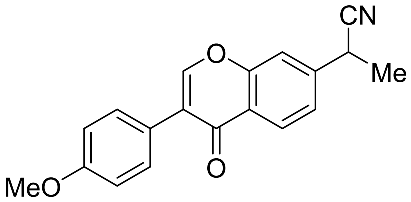
2-(1*H*-Indol-3-yl)propanenitrile (2s). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 3-vinyl-1*H*-indole (71.6 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the product **2s** in 87% yield (73.8 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.67 (d, *J* = 7.2 Hz, 3H), 4.08 (q, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 1.6 Hz, 1H), 7.12-7.22 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 19.39, 22.66, 111.36, 111.62, 118.17, 119.86, 121.66, 121.98, 122.50, 124.94, 136.33. IR (neat): 3409, 3063, 2983, 2943, 2240, 1618, 1457, 1421, 1355, 1339, 1248, 1225, 1100, 1032, 1012, 909, 819, 765, 739 cm^{-1}. HRMS (EI) calcd for $C_{11}H_{10}N_2$ $[M]^+$: 170.0844, found 170.0842.



2t

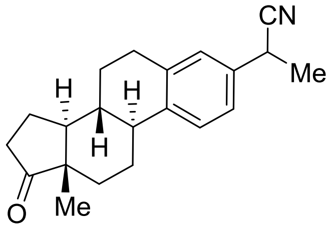
2-(Benzo[*b*]thiophen-2-yl)propanenitrile (2t). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos

(17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 2-vinylbenzo[*b*]thiophene (80.1 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 μL) were stirred at 80 °C for 8 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **2t** in 84% yield (79.0 mg) as a white solid. M.p.: 81.0-82.0 °C. ^{1}H NMR (400 M, $CDCl_3$): δ 1.73 (d, *J* = 7.2 Hz, 3H), 4.16 (q, *J* = 7.2 Hz, 1H), 7.27-7.36 (m, 3H), 7.69-7.71 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.87, 27.20, 120.09, 122.11, 122.17, 123.58, 124.63, 124.69, 138.96, 139.24, 139.66. IR (neat): 3056, 2993, 2983, 2938, 2925, 2241, 1459, 1435, 1376, 1205, 1156, 1143, 1129, 1057, 967, 943, 876, 841, 823, 728, 679, 666 cm^{-1}. HRMS (EI) calcd for $C_{11}H_9NS$ $[M]^+$: 187.0456, found 187.0459.



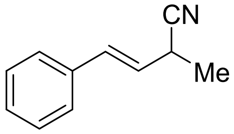
2u

2-(3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)propanenitrile (2u). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 3-(4-methoxyphenyl)-7-vinyl-4*H*-chromen-4-one (139.2 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the product **2u** in 86% yield (131.0 mg) as a white solid. M.p.: 147.8-149.1 °C**.** ^{1}H NMR (400 M, $CDCl_3$): δ 1.70 (d, *J* = 7.2 Hz, 3H), 3.82 (s, 3H), 4.05 (q, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 3H), 7.99 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.99, 31.04, 55.16, 113.83, 116.18, 120.41, 123.54, 123.84, 125.04, 127.38, 129.89, 142.81, 152.51, 156.09, 159.54, 175.66. IR (neat): 3081, 2961, 2937, 2909, 2833, 2246, 1637, 1624, 1606, 1574, 1562, 1511, 1437, 1371, 1357 1289, 1246, 1229, 1195, 1178, 1116, 1107, 1028, 902, 887, 837, 818, 805, 789, 701 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.1125, found 306.1117.



2v d.r =1:1

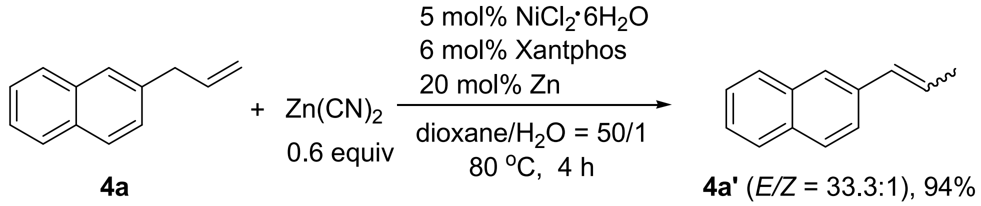
2-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)propanenitrile (2v). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (140.2 mg, 0.5 mmol), dioxane (2.5 mL) and H_2O (50 μL) were stirred at 80 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded the product **2v** (dr = 1:1 determined by HPLC) in 95% yield (146.0 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 0.91 (s, 3H), 1.40-1.67 (m, 9H), 1.95-2.19 (m, 4H), 2.26-2.31 (m, 1H), 2.39-2.44 (m, 1H), 2.50 (dd, *J* = 18.6, 8.6 Hz, 1H), 2.91-2.95 (m, 2H), 3.84 (q, *J* = 7.2 Hz, 1H), 7.10-7.13 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 M, $CDCl_3$): δ 13.62, 21.20, 21.23, 21.35, 25.46, 26.13, 29.12, 29.15, 30.50, 30.52, 31.33, 35.62, 37.78, 44.02, 47.71, 50.21, 121.57, 123.85, 125.94, 127.03, 134.29, 134.31, 137.26, 139.47, 220.51. IR (neat): 3369, 2927, 2859, 2239, 1732, 1498, 1454, 1404, 1373, 1243, 1086, 1050, 1008, 819 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{25}NO$ $[M]^+$: 307.1936, found 307.1943.



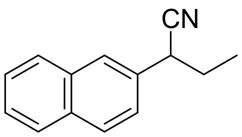
2w

(*E*)-2-Methyl-4-phenylbut-3-enenitrile (2w). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), (*E*)-buta-1,3-dien-1-ylbenzene (65.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the product **2w** in 80% yield (63.0 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.49 (d, *J* = 6.8 Hz, 3H), 3.45-3.52 (m, 1H), 6.06 (dd, *J* = 15.8, 6.4 Hz, 1H), 6.71 (d, J = 16.0 Hz, 1H), 7.24-7.38 (m, 5H). ^{13}C NMR (100 M, CDCl$_3$): δ 18.95, 28.27, 120.81, 124.23, 126.45, 128.17, 128.63, 132.41, 135.60. The spectroscopic data are in agreement with that previously reported.[5]

Isolation of 4a' at the early stage of the hydrocyanation of 4a.



NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 2-allylnaphthalene (84.1 mg, 0.5 mmol) and H$_2$O (50 μL) were stirred at 80 °C for 4 h. The mixture was filtered through a pad of silica gel and washed with ether. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: pentane) to give the product **4a'** (*E*/*Z* = 33.3:1) in 94% yield (78.9 mg) as a colorless oil. For ***E*-4a'**:^{1}H NMR (400 M, CDCl$_3$): δ 1.90 (dd, J = 6.8, 1.6 Hz, 3H), 6.28-6.37 (m, 1H), 6.52 (d, J = 16.0 Hz, 1H), 7.35-7.42 (m, 2H), 7.51-7.54 (m, 1H), 7.61 (s, 1H), 7.70-7.75 (m, 3H). ^{13}C NMR (100 M, CDCl$_3$): δ 18.60, 123.45, 125.16, 125.37, 126.05, 126.11, 127.58, 127.79, 128.01, 131.12, 132.58, 133.67, 135.33. The spectroscopic data are in agreement with that previously reported.[11] For partial ^{1}H NMR of ***Z*-4a'**: ^{1}H NMR (400 M, CDCl$_3$): δ 1.95 (dd, J = 6.8, 1.6 Hz, 3H), 5.81-5.89 (m, 1H). The spectroscopic data are in agreement with that previously reported.[12]



5

2-(Naphthalen-2-yl)butanenitrile (5). This product was synthesized following the procedure described for Ni-catalyzed hydrocyanation of aryl alkenes. NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3

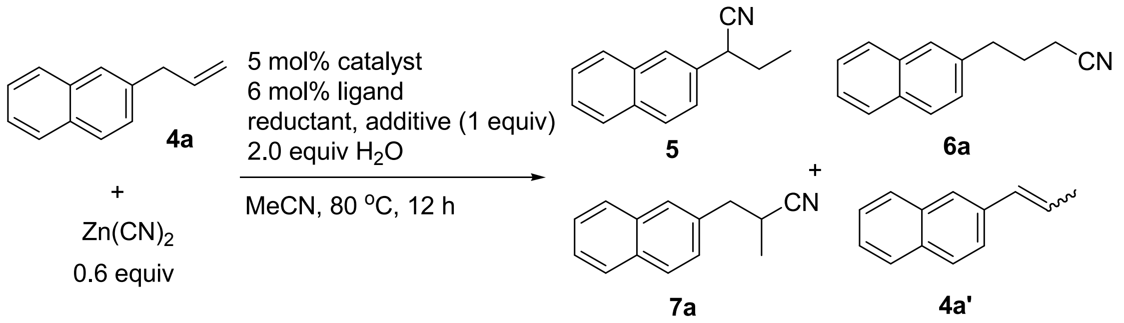
mmol), dioxane (2.5 mL), 2-allylnaphthalene (84.1 mg, 0.5 mmol) and H_2O (50 μL) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **5** in 88% yield (85.9 mg) as a colorless oil. ^{1}H NMR (400 M, $CDCl_3$): δ 1.07 (t, J = 7.2 Hz, 3H), 1.95-2.03 (m, 2H), 3.86 (t, J = 7.2 Hz, 1H), 7.36 (dd, J = 8.6, 1.6 Hz, 1H), 7.46-7.51 (m, 2H), 7.79-7.84 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 11.36, 28.93, 38.88, 120.67, 124.71, 126.24, 126.33, 126.57, 127.59, 127.73, 128.87, 132.66, 132.88, 133.14. IR (neat): 3055, 2970, 2932, 2875, 2236, 1600, 1508, 1458, 1370, 1268, 1124, 893, 857, 816, 786, 748 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{13}N$ $[M]^+$: 195.1048, found 195.1042.

Optimization studies for Ni-catalyzed hydrocyanation of aliphatic alkenes.

General procedure for optimization studies.

The reaction was conducted in an oven-dried screw-cap vial (4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $Ni(ClO_4)_2\cdot 6H_2O$ (5.5 mg, 0.015 mmol) [or other Ni(II) salts], dppp (7.4 mg, 0.018 mmol) [or other ligands], Zinc powder (19.6 mg, 0.3 mmol), $Zn(CN)_2$ (21.1 mg, 0.18 mmol), DMAP (36.7 mg, 0.3 mmol) [or other additives], acetonitrile (1.5 mL), 2-allylnaphthalene (50.5 mg, 0.3 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (10.8 μL, 0.6 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^{1}H NMR analysis of the crude mixture using mesitylene (36.1 mg, 0.3 mmol) as an internal standard.

Table S2. Optimization studies for Ni-catalyzed hydrocyanation of aliphatic alkenes.

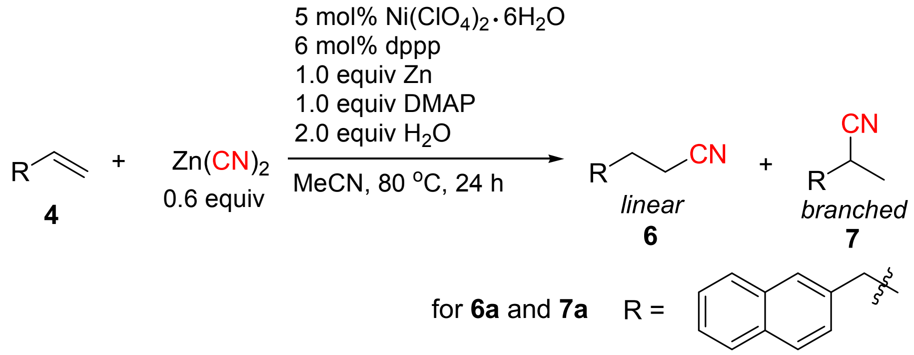


entry	catalyst	ligand	reductant (%)	additive	**4a** (%)^{a}	yield (%)^{a}			
						5	**7a**	**6a**	**4a'**^{b}
1	$NiCl_2{\cdot}6H_2O$	dppf	Zn (20)	-	0	66	2	5	22
2	$NiCl_2{\cdot}6H_2O$	dppf	Zn (20)	DMAP	0	9	2	4	67 (33:1)
3	$NiCl_2{\cdot}6H_2O$	dppp	Zn (20)	DMAP	0	2	10	76	11
4	$NiCl_2{\cdot}6H_2O$	Xantphos	Zn (20)	DMAP	0	17	1	23	53 (52:1)
5	$NiCl_2{\cdot}6H_2O$	neocuproine	Zn (20)	DMAP	20	0	2	22	56 (18:1)
6	$NiCl_2{\cdot}6H_2O$	dppp	Zn (20)	4-NH_2-pyridine	13	1	9	64	13
7	$NiCl_2{\cdot}6H_2O$	dppp	Zn (20)	TBAI	0	20	0	10	69 (22:1)
8	$NiCl_2{\cdot}6H_2O$	dppp	Zn (20)	TMEDA	47	1	1	26	25 (24:1)
9	$Ni(ClO_4)_2{\cdot}6H_2O$	dppp	Zn (20)	DMAP	16	0	7	65	9
10	$NiSO_4$	dppp	Zn (20)	DMAP	50	0	6	38	6
11	$Ni(OTf)_2$	dppp	Zn (20)	DMAP	49	0	5	40	6
12^{c}	$Ni(ClO_4)_2{\cdot}6H_2O$	dppp	Zn (100)	DMAP	0	5	10	80	0
13^{cd}	$Ni(ClO_4)_2{\cdot}6H_2O$	dppp	Zn (100)	DMAP	0	5	11	77	1
14^{c}	$Ni(ClO_4)_2{\cdot}6H_2O$	-	Zn (100)	DMAP	0	2	3	33	61 (30:1)
15^{c}	$Ni(ClO_4)_2{\cdot}6H_2O$	dppp	Zn (100)	-	0	89	0	3	4
16^{ce}	$Ni(ClO_4)_2{\cdot}6H_2O$	dppp	Zn (100)	DMAP	24	0	7	56	10
15^{c}	$NiCl_2$(dppp)	-	Zn (100)	DMAP	0	4	12	71	12
16^{ce}	$NiCl_2$(dppp)	-	Zn (100)	DMAP	80	0	2	12	6

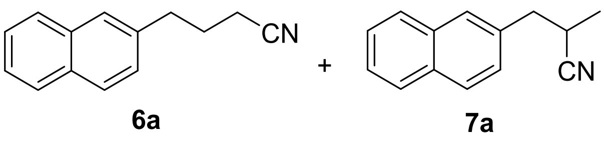
[a] Determined by ^{1}H NMR of the crude reaction mixture using mesitylene as an internal standard. [b] Overall yields of the *E*- and *Z*-isomers of **4a**' and the ratio of *E*/*Z* isomers are shown in parentheses if *Z*-isomers exist. [c] 24 h. [d] 10 mol% $Ni(ClO_4)_2{\cdot}6H_2O$ and 12 mol% dppp were used. [e] Without H_2O.

Synthesis of 6a-6m and 7a-7m.

Typical procedure for the synthesis of 6a and 7a.



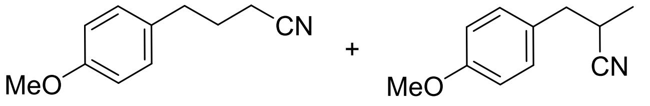
The reaction was conducted in an oven-dried screw-cap vial (8 mL) equipped with a magnetic stir bar. The vial containing $Ni(ClO_4)_2 \cdot 6H_2O$ was equipped with a septum cap, which was pierced by a needle and introduced into the antechamber of nitrogen-filled glovebox. Before transferring into the inside of the glovebox, it was evacuated and back-filled with nitrogen for three times (ca. 5 min). In a nitrogen-filled glove box, $Ni(ClO_4)_2 \cdot 6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 2-allylnaphthalene (84.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (18 μL, 1 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 24 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product **6a** in 78% yield (76.2 mg) as a white solid and **7a** in 9% yield (8.8 mg) as a white solid.



4-(Naphthalen-2-yl)butanenitrile (6a). ^{1}H NMR (400 M, $CDCl_3$): δ 1.94-2.01 (m, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 7.25 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.39-7.46 (m, 2H), 7.58 (s, 1H), 7.75-7.79 (m, 3H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.22, 26.60, 34.31, 119.47, 125.45, 126.09, 126.69, 127.35, 127.53, 128.25, 132.07, 133.38, 137.03. The spectroscopic data are in agreement with that previously reported.[13]

2-Methyl-3-(naphthalen-2-yl)propanenitrile (7a). ^{1}H NMR (400 M, $CDCl_3$): δ 1.36 (d, *J* =

6.8 Hz, 3H), 2.92-3.01 (m, 2H), 3.09-3.14 (m, 1H), 7.34 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.46-7.49 (m, 2H), 7.69 (s, 1H), 7.80-7.83 (m, 3H). ^{13}C NMR (100 M, $CDCl_3$): δ 17.62, 27.42, 40.11, 122.54, 125.88, 126.27, 126.93, 127.65, 127.84, 128.46, 132.52, 133.40, 134.27. The spectroscopic data are in agreement with that previously reported.[14]



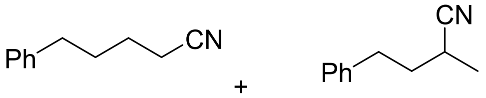
6b **7b**

(**6b**:**7b** = 8.3:1)

$Ni(ClO_4)_2·6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 1-allyl-4-methoxybenzene (74.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give the desired product **6b** and **7b** in 81% overall yield (70.6 mg) as a colorless oil (**6b**:**7b** = 8.3:1).

4-(4-Methoxyphenyl)butanenitrile (6b). ^{1}H NMR (400 M, $CDCl_3$): δ 1.89-1.96 (m, 2H), 2.28 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 6.84 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.10, 26.95, 33.29, 55.09, 113.89, 119.47, 129.25, 131.58, 158.08. The spectroscopic data are in agreement with that previously reported.[15]

3-(4-Methoxyphenyl)-2-methylpropanenitrile (7b). Partial ^{1}H NMR (400 M, $CDCl_3$): δ 1.30 (d, *J* = 6.4 Hz, 3H)，2.77-2.87 (m, 3H), 3.78 (s, 3H), 7.14 (d, *J* = 8.8 Hz, 2H), partial ^{13}C NMR (400 M, $CDCl_3$): δ 17.34, 27.61, 38.96, 113.90, 129.95. The spectroscopic data are in agreement with that previously reported.[14]



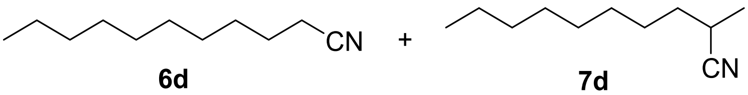
6c **7c**

$Ni(ClO_4)_2·6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), but-3-en-1-ylbenzene (66.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for

24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1 to 20:1) to give the desired product **6c** in 81% yield (64.3 mg) as a colorless oil and **7c** in 12% yield (9.2 mg) as a colorless oil.

5-Phenylpentanenitrile (6c). ^{1}H NMR (400 M, $CDCl_3$): δ 1.62-1.69 (m, 2H), 1.73-1.81 (m, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 7.15-7.21 (m, 3H), 7.26-7.30 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.92, 24.71, 30.14, 34.85, 119.54, 125.95, 128.24, 128.35, 141.12. The spectroscopic data are in agreement with that previously reported.[16]

2-Methyl-4-phenylbutanenitrile (7c). ^{1}H NMR (400 M, $CDCl_3$): δ 1.33 (d, *J* = 7.2 Hz, 3H), 1.79-1.88 (m, 1H), 1.91-2.01 (m, 1H), 2.53-2.62 (m, 1H), 2.71-2.79 (m, 1H), 2.84-2.91 (m, 1H), 7.19-7.26 (m, 3H), 7.29-7.33 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 17.97, 24.81, 33.15, 35.71, 122.74, 126.38, 128.38, 128.61, 140.11. The spectroscopic data are in agreement with that previously reported. [2]



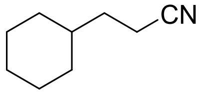
6d **7d**

(**6d**:**7d** = 12.5:1)

$Ni(ClO_4)_2·6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), dec-1-ene (70.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product **6d** and **7d** in 77% overall yield (64.7 mg) as a colorless oil (**6d**:**7d** = 12.5:1).

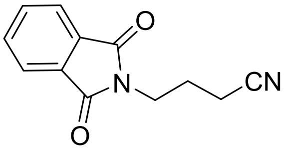
Undecanenitrile (6d). ^{1}H NMR (400 M, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.20-1.32 (m, 12H), 1.41-1.46 (m, 2H), 1.62-1.69 (m, 2H), 2.33 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 13.96, 16.98, 22.54, 25.26, 28.54, 28.64, 29.13, 29.19, 29.34, 31.73, 119.73. The spectroscopic data are in agreement with that previously reported.[17]

2-Methyldecanenitrile (7d). Partial ^{1}H NMR (400 M, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 2.55-2.64 (m, 1H), partial ^{13}C NMR (400 M, $CDCl_3$): δ 17.90, 25.38, 26.91, 28.95, 29.05, 29.20, 31.69, 33.95. The ^{1}H NMR spectroscopic data are in agreement with that previously reported.[18]



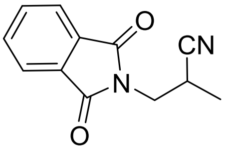
6e

3-Cyclohexylpropanenitrile (6e). $Ni(ClO_4)_2{\cdot}6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), vinylcyclohexane (55.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product **6e** in 80% yield (55.0 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 0.87-0.95 (m, 2H), 1.09-1.30 (m, 3H), 1.35-1.44 (m, 1H), 1.55 (q, *J* = 7.2 Hz, 2H), 1.65-1.74 (m, 5H), 2.35 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 14.49, 25.81, 26.17, 32.36, 32.42, 36.43, 119.96. The spectroscopic data are in agreement with that previously reported.[19]



6f

+

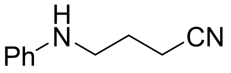


7f

$Ni(ClO_4)_2{\cdot}6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 2-allylisoindoline-1,3-dione (93.6 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Puritification by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the desired product **6f** in 78% yield (83.5 mg) as a colorless oil and **7f** in 17% yield (18.2 mg) as a white solid.

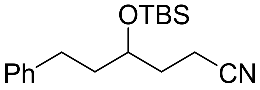
4-(1,3-Dioxoisoindolin-2-yl)butanenitrile (6f). ^1H NMR (400 M, $CDCl_3$): δ 2.05-2.12 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 3.82 (t, *J* = 6.4 Hz, 2H), 7.73-7.77 (m, 2H), 7.84-7.88 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 14.95, 24.60, 36.50, 118.70, 123.30, 131.70, 134.11, 168.10. The spectroscopic data are in agreement with that previously reported.[20]

3-(1,3-Dioxoisoindolin-2-yl)-2-methylpropanenitrile (7f). ^1H NMR (400 M, $CDCl_3$): δ 1.40 (d, *J* = 6.8 Hz, 3H), 3.19-3.28 (m, 1H), 3.77 (dd, *J* = 13.8, 6.8 Hz, 1H), 4.02 (dd, *J* = 13.6, 8.4 Hz, 1H), 7.76-7.79 (m, 2H), 7.87-7.91 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 15.54, 25.23, 40.09, 120.37, 123.68, 131.59, 134.40, 167.69. The spectroscopic data are in agreement with that previously reported.[21]



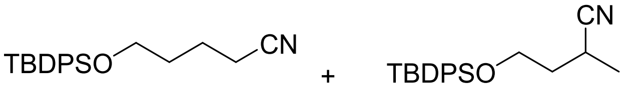
6g

4-(Phenylamino)butanenitrile (6g). $Ni(ClO_4)_2 \cdot 6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), *N*-allylaniline (66.6 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) to give the product **6g** in 81% yield (64.9 mg) as a light yellow oil. ^{1}H NMR (400 M, $CDCl_3$): δ 1.88-1.95 (m, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 3.73 (s, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 14.61, 25.00, 42.07, 112.65, 117.65, 119.39, 129.24, 147.43. The spectroscopic data are in agreement with that previously reported.[22]



6h

4-((*tert*-Butyldimethylsilyl)oxy)-6-phenylhexanenitrile (6h). $Ni(ClO_4)_2 \cdot 6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), *tert*-butyldimethyl((5-phenylpent-1-en-3-yl)oxy)silane (138.3 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to give the desired product **6h** in 80% yield (120.7 mg) as a colorless oil. ^{1}H NMR (400 M, $CDCl_3$): δ 0.12 (d, *J* = 2.0 Hz, 6H), 0.95 (s, 9H), 1.77-1.94 (m, 4H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 8.4 Hz, 2H), 3.85-3.90 (m, 1H), 7.19-7.24 (m, 3H), 7.30-7.34 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ -4.74, -4.44, 12.97, 17.92, 25.73, 31.19, 32.10, 38.52, 69.70, 119.85, 125.86, 128.15, 128.39, 141.64. IR (neat): 3084, 3060, 3026, 2952, 2929, 2857, 2246, 1603, 1495, 1469, 1453, 1362, 1254, 1092, 993, 834, 774, 746, 698, 663 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{29}NOSi$ $[M]^+$: 303.2018, found 303.2010.

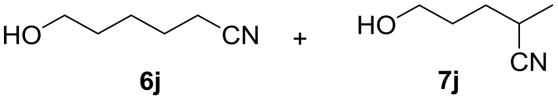


6i **7i**

$Ni(ClO_4)_2 \cdot 6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), (but-3-en-1-yloxy)(*tert*-butyl)diphenylsilane (155.3 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Puritification by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product **6i** in 74% yield (124.3 mg) as a colorless oil and **7i** in 7% yield (11.5 mg) as a colorless oil.

5-((*tert*-Butyldiphenylsilyl)oxy)pentanenitrile (6i). ^{1}H NMR (400 M, $CDCl_3$): δ 1.06 (s, 9H), 1.64-1.71 (m, 2H), 1.73-1.81 (m, 2H), 2.30 (t, J = 7.2 Hz, 2H), 3.69 (t, J = 6.0 Hz, 2H), 7.35-7.43 (m, 6H), 7.64-7.66 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.74, 19.05, 22.09, 26.73, 31.08, 62.52, 119.62, 127.60, 129.60, 133.45, 135.38. IR (neat): 3071, 3045, 2931, 2857, 2244, 1590, 1472, 1427, 1385, 1186, 1109, 1007, 974, 822, 740, 700, 686 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{31}N_2OSi$ $[M+NH_4]^+$: 355.2200, found 355.2199.

4-((*tert*-Butyldiphenylsilyl)oxy)-2-methylbutanenitrile (7i). ^{1}H NMR (400 M, $CDCl_3$): δ 1.06 (s, 9H), 1.32 (d, J = 7.2 Hz, 3H), 1.68-1.79 (m, 1H), 1.81-1.89 (m, 1H), 2.92-3.01 (m, 1H), 3.73-3.85 (m, 2H), 7.37-7.46 (m, 6H), 7.64-7.67 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 17.76, 19.18, 21.94, 26.79, 36.70, 60.53, 122.91, 127.75, 127.76, 129.78, 129.80, 133.15, 133.35, 135.45, 135.51. IR (neat): 3071, 2931, 2857, 2239, 1587, 1472, 1428, 1388, 1110, 998, 981, 902, 822, 738, 700, 687 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{31}N_2OSi$ $[M+NH_4]^+$: 355.2200, found 355.2196.



6j **7j**

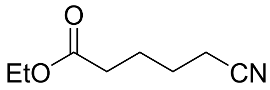
(**6j**:**7j** =9.1:1)

$Ni(ClO_4)_2 \cdot 6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), pent-4-en-1-ol (43.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h.

Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =3:2) to give the desired product **6j** and **7j** in 89% overall yield (50.4 mg) as a colorless oil (**6j**:**7j** = 9.1:1).

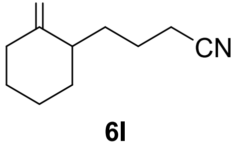
6-Hydroxyhexanenitrile (6j). ^{1}H NMR (400 M, CDCl$_3$): δ 1.49-1.64 (m, 4H), 1.67-1.74 (m, 2H), 2.27 (s, 1H), 2.38 (t, J = 7.2 Hz, 2H), 3.64 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 M, CDCl$_3$): δ 16.98, 24.85, 25.01, 31.53, 61.98, 119.68. The spectroscopic data are in agreement with that previously reported.[23]

5-Hydroxy-2-methylpentanenitrile (7j). Partial ^{1}H NMR (400 M, CDCl$_3$): δ 1.34 (d, J = 7.2 Hz, 3H), 2.64-2.73 (m, 1H), partial ^{13}C NMR (100 M, CDCl$_3$): δ 17.87, 25.24, 29.77, 30.38, 61.54.



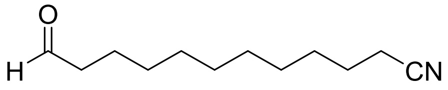
6k

Ethyl 5-cyanopentanoate (6k). Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), ethyl pent-4-enoate (64.1 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) to give the desired product **6k** in 74% yield (57.5 mg) as a colorless oil. ^{1}H NMR (400 M, CDCl$_3$): δ 1.26 (t, J = 7.2 Hz, 3H), 1.68-1.82 (m, 4H), 2.34-2.41 (m, 4H), 4.14 (q, J = 7.2 Hz, 2H). ^{13}C NMR (100 M, CDCl$_3$): δ 14.00, 16.74, 23.69, 24.61, 33.09, 60.28, 119.21, 172.58. The spectroscopic data are in agreement with that previously reported.[17]



6l

4-(2-Oxocyclohexyl)butanenitrile (6l). Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 2-allylcyclohexan-1-one (69.1 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) to give the desired product **6l** in 68% yield (56.4 mg) as a colorless oil. ^{1}H NMR (400 M, CDCl$_3$): δ 1.32-1.46 (m, 2H), 1.58-1.78 (m, 4H), 1.82-1.92 (m, 2H), 2.05-2.14 (m, 2H), 2.28-2.42 (m, 5H). ^{13}C NMR (100 M, CDCl$_3$): δ 17.17, 23.08, 24.81, 27.77, 28.60, 33.97, 41.90, 49.75, 119.50, 212.26. The spectroscopic data are in agreement with that previously reported.[24]

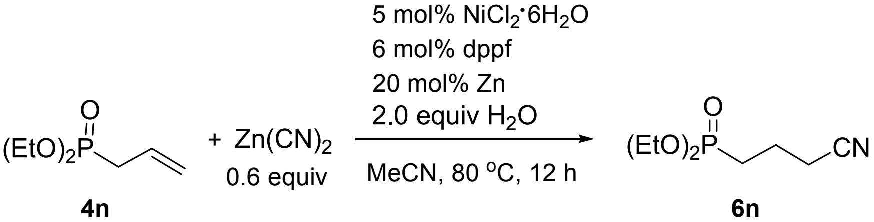


6m

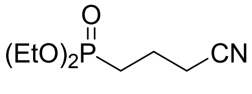
12-Oxododecanenitrile (6m). Ni(ClO$_4$)$_2$·6H$_2$O (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), undec-10-enal (84.1 mg, 0.5 mmol) and H$_2$O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give the desired product **6m** in 58% yield (57.1 mg) as a colorless oil. ^{1}H NMR (400 M, CDCl$_3$): δ 1.26-1.30 (m, 10H), 1.39-1.46 (m, 2H), 1.59-1.69 (m, 4H), 2.34 (t, J = 7.2 Hz, 2H), 2.41-2.45 (m, 2H), 9.76 (s, 1H). ^{13}C NMR (100 M, CDCl$_3$): δ 16.96, 21.88, 25.20, 28.47, 28.56, 28.95, 29.05, 29.09, 29.11, 43.73, 119.74, 202.80. The spectroscopic data are in agreement with that previously reported.[25]

Synthesis of 6n-6s.

Typical procedure for the synthesis of 6n.

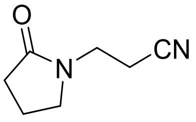


The reaction was conducted in an oven-dried screw-cap vial (8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, NiCl$_2$·6H$_2$O (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), Zn(CN)$_2$ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), diethyl allylphosphonate (89.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (18 µL, 1 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 12 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate) to give the desired product **6n** in 85% yield (86.9 mg) as a colorless oil.



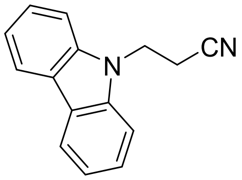
6n

Diethyl (3-cyanopropyl)phosphonate (6n). ^1H NMR (400 M, $CDCl_3$): δ 1.34 (t, J = 7.2 Hz, 6H), 1.85-2.03 (m, 4H), 2.52 (t, J = 6.8 Hz, 2H), 4.07-4.17 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.17 (d, $^3J_{C\text{-}P}$ = 5.7 Hz), 17.46 (d, $^2J_{C\text{-}P}$ = 15.4 Hz), 18.90 (d, $^3J_{C\text{-}P}$ = 4.5 Hz), 24.20 (d, $^1J_{C\text{-}P}$ = 142.6 Hz), 61.59 (d, $^2J_{C\text{-}P}$ = 6.1 Hz), 118.63. ^{31}P NMR (162 M, $CDCl_3$): δ 29.28. IR (neat): 3458, 2979, 2927, 2909, 2244, 1233, 1163, 1024, 957, 784, 733 cm^{-1}. HRMS (ESI) calcd for $C_8H_{20}N_2O_3P$ $[M+NH_4]^+$: 223.1206, found 223.1201.



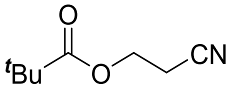
6o

3-(2-Oxopyrrolidin-1-yl)propanenitrile (6o). $NiCl_2\cdot 6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), 1-vinylpyrrolidin-2-one (55.6 mg, 0.5 mmol) and H_2O (18 µL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: ethyl acetate) to give the desired product **6o** in 80% yield (55.4 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 2.06-2.14 (m, 2H), 2.41 (t, J = 8.0 Hz, 2H), 2.64 (t, J = 6.4 Hz, 2H), 3.55-3.59 (m, 4H). ^{13}C NMR (100 M, $CDCl_3$): δ 16.39, 17.98, 30.43, 38.82, 47.87, 117.96, 175.44. The spectroscopic data are in agreement with that previously reported.[26]



6p

3-(9*H*-Carbazol-9-yl)propanenitrile (6p). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), 9-vinyl-9*H*-carbazole (96.6 mg, 0.5 mmol), acetonitrile (2.5 mL) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the product **6p** in 97% yield (106.8 mg) as a white solid. M.p.: 149.0-150.2 °C. ^{1}H NMR (400 M, $CDCl_3$): δ 2.62 (t, J = 7.2 Hz, 2H), 4.41 (t, J = 7.2 Hz, 2H), 7.20-7.28 (m, 4H), 7.41 (t, J = 7.6 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 17.02, 38.54, 108.09, 117.35, 119.75, 120.50, 123.09, 125.99, 139.34. IR (neat): 3045, 2956, 2930, 2244, 1593, 1485, 1459, 1419, 1383, 1353, 1333, 1327, 1261, 1225, 1198, 1152, 1123, 1066, 744, 724 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}N_2$ $[M]^+$: 220.1000, found 220.1005.



6q

2-Cyanoethyl pivalate (6q). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), vinyl pivalate (64.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the product **6q** in 53% yield (41.1mg) as a colorless oil. ^{1}H NMR (400 M, $CDCl_3$): δ 1.24 (s, 9H), 2.72 (t, J = 6.4 Hz, 2H), 4.27 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 17.89, 26.95, 38.69, 58.43, 116.68, 177.91. The spectroscopic data are in agreement with that previously reported.[27]

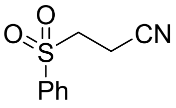
6r **7r**

(**6r**:**7r** = 16.7:1)

$NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), acetonitrile (2.5 mL), dimethyl(phenyl)(vinyl)silane (81.2 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the product **6r** and **7r** in 86% overall yield (81.3 mg) as a colorless oil (**6r**:**7r** = 16.7:1).

3-(Dimethyl(phenyl)silyl)propanenitrile (6r). ^1H NMR (400 M, $CDCl_3$): δ 0.34 (s, 6H), 1.11-1.15 (m, 2H), 2.22-2.26 (m, 2H), 7.35-7.38 (m, 3H), 7.47-7.49 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ -3.67, 11.77, 11.95, 121.02, 127.95, 129.41, 133.34, 136.46. The spectroscopic data are in agreement with that previously reported.[28]

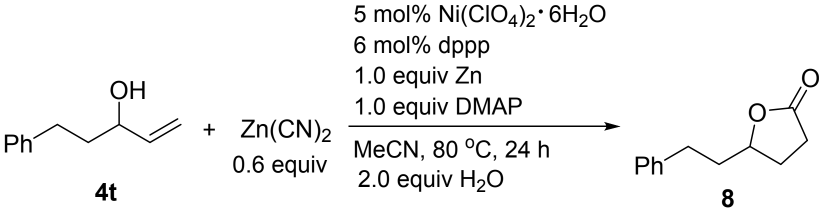
2-(Dimethyl(phenyl)silyl)propanenitrile (7r). Partial ^1H NMR (400 M, $CDCl_3$): δ 0.48 (d, *J* = 0.8 Hz, 6H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.98 (q, *J* = 7.2 Hz, 1H), 7.54-7.57 (m, 2H). Partial ^{13}C NMR (100 M, $CDCl_3$): δ -5.69, -5.09, 11.43, 11.86, 128.02, 130.04, 133.76. The ^1H NMR spectroscopic data are in agreement with that previously reported.[29]



6s

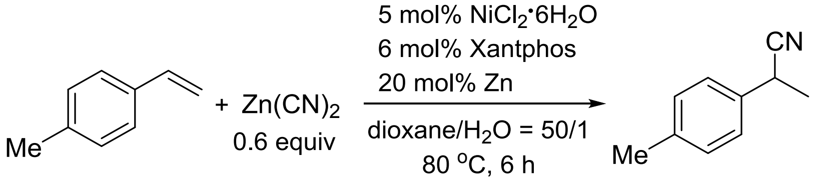
3-(Phenylsulfonyl)propanenitrile (6s). $NiCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), (vinylsulfonyl)benzene (84.1 mg, 0.5 mmol), acetonitrile (2.5 mL) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 12 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2:1) afforded the product **6s** in 86% yield (84.0 mg) as a white solid. ^1H NMR (400 M, $CDCl_3$): δ 2.81 (t, *J* = 7.6 Hz, 2H), 3.41 (t, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 11.79, 50.75, 116.09, 128.04, 129.57, 134.51, 137.27. The spectroscopic data are in agreement with that previously reported.[30]

Synthesis of 8.



5-Phenethyldihydrofuran-2(3*H*)-one (8). $Ni(ClO_4)_2·6H_2O$ (9.1 mg, 0.025 mmol), dppp (12.4 mg, 0.03 mmol), Zinc powder (32.7 mg, 0.5 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), DMAP (61.1 mg, 0.5 mmol), acetonitrile (2.5 mL), 5-phenylpent-1-en-3-ol (81.1 mg, 0.5 mmol) and H_2O (18 μL, 1 mmol) were stirred at 80 °C for 24 h. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the product **8** in 67% yield (63.5 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.80-1.94 (m, 2H), 1.99-2.08 (m, 1H), 2.24-2.33 (m, 1H), 2.49-2.53 (m, 2H), 2.68-2.85 (m, 2H), 4.41-4.48 (m, 1H), 7.18-7.21 (m, 3H), 7.27-7.30 (m, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 27.77, 28.63, 31.44, 37.13, 79.76, 125.99, 128.26, 128.35, 140.58, 177.03. The spectroscopic data are in agreement with that previously reported.[31]

Gram scale study:

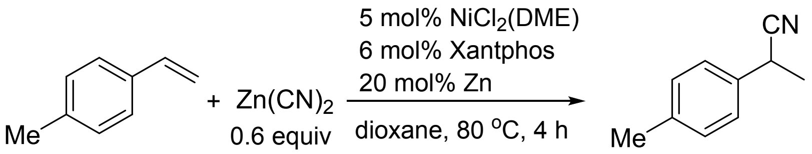


1a **2a,** 1.25 g, 86%

To an oven-dried sealable Schlenk tube were added $NiCl_2·6H_2O$ (0.5 mmol, 118.8 mg), Xantphos (0.6 mmol, 347.2 mg), Zn (2 mmol, 130.8 mg) and $Zn(CN)_2$ (6 mmol, 704.5 mg). The tube was evacuated and back-filled with argon for three times, then dioxane (50 mL), **1a** (10 mmol, 1.18 g) and water (1 mL) were added sequentially under argon. The tube was sealed and the mixture was stirred at 80 °C for 6 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and dissolved in 20 mL ethyl acetate, then 3 mL 30% H_2O_2 was added to the solution and the mixture was stirred at room temperature for 10 min. The reaction was quenched by saturated $Na_2S_2O_3$ and extracted with ethyl acetate, the organic layers was combined, washed by saturated NaCl and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to give the desired product **2a** in 86% yield (1.25 g) as a colorless oil.

Control experiments.

(1) Reaction of 1a in the absence of water.

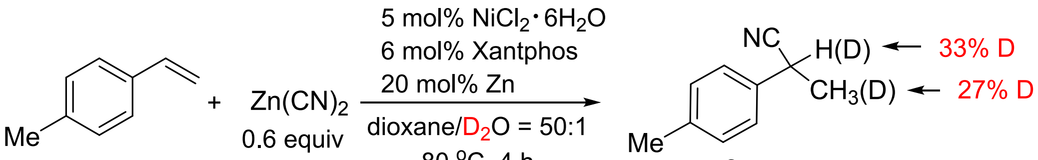


1a **2a**, 0%

In a nitrogen-filled glove box, $NiCl_2(DME)$ (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. The disired product **2a** was not detected.

(2) Deuterium labeling experiments.

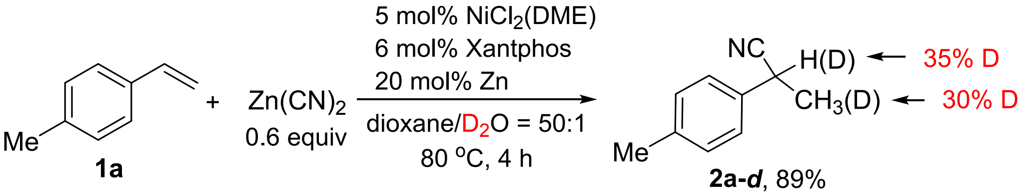
a) $NiCl_2·6H_2O$-catalyzed deuterium labeling experiment of 1a with D_2O.



1a **2a-*d***, 91%

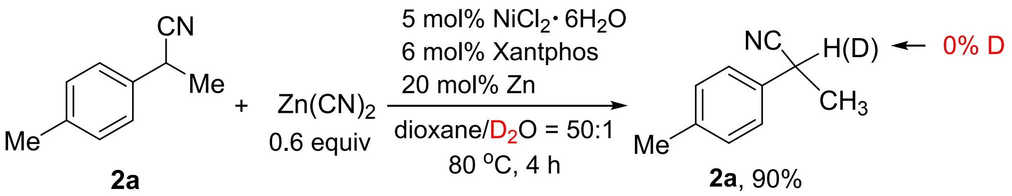
In a nitrogen-filled glove box, $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then D_2O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to give the desired product **2a-*d*** in 91% yield (66.8mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.57-1.60 (m, 2.19H), 2.33 (s, 3H), 3.81-3.87 (m, 0.67H), 7.17 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.87, 21.06 (t, J = 19.4 Hz), 21.22, 21.31, 30.51, 30.59, 30.66, 121.65, 126.42, 129.61, 133.97, 137.64.

b) $NiCl_2$(DME)-catalyzed deuterium labeling experiment of 1a with D_2O.



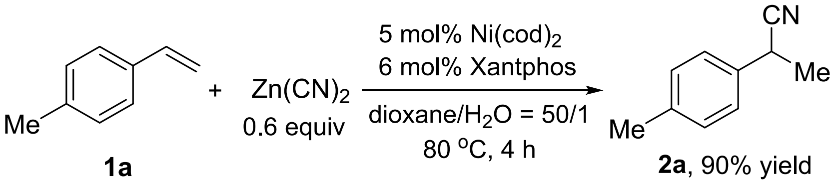
In a nitrogen-filled glove box, $NiCl_2$(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then D_2O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give the desired product **2a-*d*** in 89% yield (65.0 mg) as a colorless oil. ^1H NMR (400 M, $CDCl_3$): δ 1.57-1.61 (m, 2.11H), 2.34 (s, 3H), 3.82-3.87 (m, 0.65H), 7.17 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 M, $CDCl_3$): δ 20.89, 21.06 (t, J = 20.1 Hz), 21.24, 21.34, 30.45, 30.54, 30.61, 30.69, 121.67, 126.43, 129.63, 133.99, 137.67. IR (neat): 3053, 3027, 2984, 2923, 2873, 2240, 1514, 1453, 1379, 1284, 1116, 1083, 1051, 1021, 814, 720 cm^{-1}.

c) $NiCl_2·6H_2O$-catalyzed deuterium labeling experiment of 2a with D_2O.



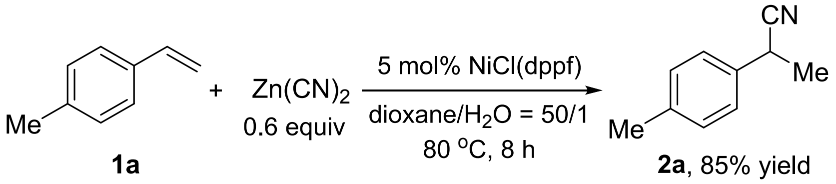
In a nitrogen-filled glove box, $NiCl_2{\cdot}6H_2O$ (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and **2a** (72.6 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then D_2O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give product **2a** in 90% yield (65.3 mg) as a colorless oil.

(3) Ni(cod)$_2$-catalyzed hydrocyanation of 1a.



In a nitrogen-filled glove box, $Ni(cod)_2$ (6.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol) and dioxane (2.5 mL) were stirred for at room temperature10 min. Then $Zn(CN)_2$ (35.2 mg, 0.3 mmol) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to the mixture. The vial cap was then securely fitted and taken outside the glove box, then H_2O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) to give the desired product **2a** in 90% yield (65.3 mg) as a colorless oil.

(4) NiCl(dppf)[32]-catalyzed hydrocyanation of 1a.

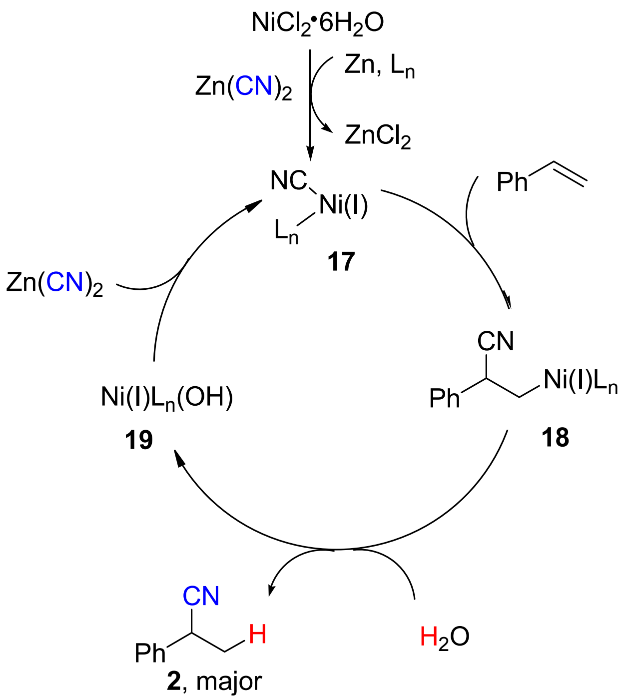


1a

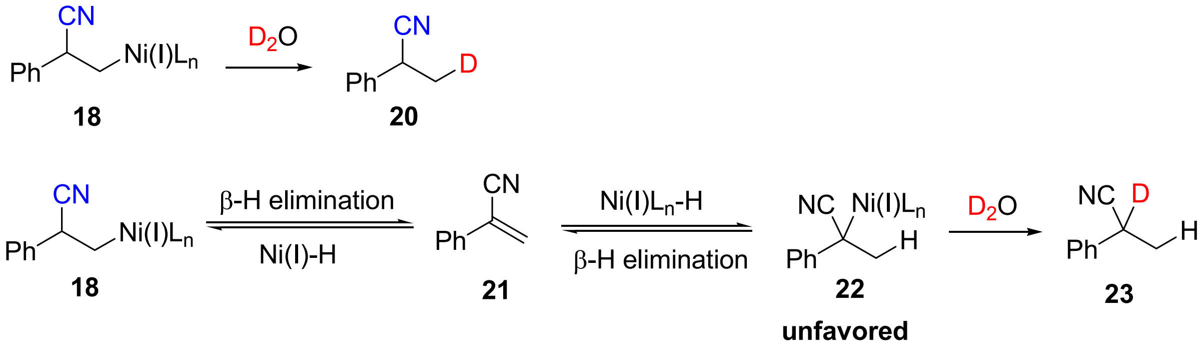
2a, 85% yield

In a nitrogen-filled glove box, NiCl(dppf) (9.7 mg, 0.015 mmol), $Zn(CN)_2$ (21.1 mg, 0.18 mmol), dioxane (1.5 mL), 1-methyl-4-vinylbenzene (35.5 mg, 0.3 mmol) were added sequentially to the vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (30 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 8 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to give the desired product **2a** in 85% yield (37.0 mg) as a colorless oil.

It is unlikely that the reaction goes through Ni(I) species involving transmetalation of Ni-Cl with $Zn(CN)_2$ to form a Ni(I)-CN species followed by addition of Ni(I)-CN to the alkene and protonation (Scheme S1), since it is hard to explain the observed regioselectivity and deuterium labeling results. For regioselectivity, the formation of intermediate **18** would lead to the branched isomer. However, it is not stable compared to η^3-benzyl nickel species. Deuterium labeling experiment indicated that deuterium was found in both benzylic position and methyl group. To explain the formation of the product bearing a D atom at the benzylic position, intermediate **21** should be formed (Scheme S2). However, **21** was not observed during the reaction. In addition, the intermediate **22** was also unfavored due to the steric effect.

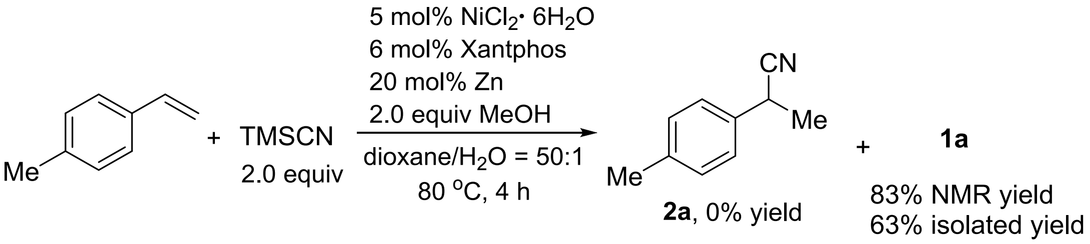


Scheme S1. Unfavored reaction pathway for Ni(I)-catalyzed hydrocyanation reaction



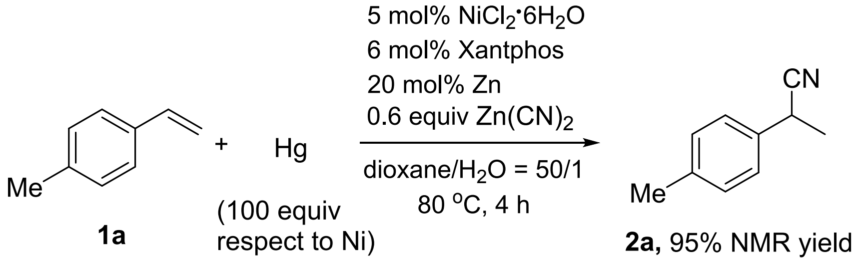
Scheme S2

(5) Reaction of 1a in the presence of TMSCN/MeOH.



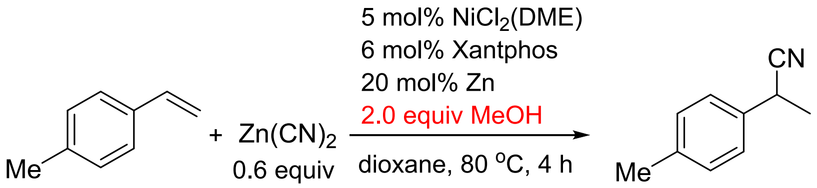
In a nitrogen-filled glove box, $NiCl_2{\cdot}6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), dioxane (2.5 mL), 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) and TMSCN (99.2 mg, 1 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (50 μL) and MeOH (32 mg, 1 mmol) were added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. The disired product **2a** was not formed and 83% of starting material **1a** was observed. Column chromatography on silica gel (eluent: pentane) afforded the **1a** in 63% yield (37.0 mg) as a colorless liquid.

(6) Mercury poisoning experiment.



In a nitrogen-filled glove box, $NiCl_2·6H_2O$ (5.9 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL), 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) and Hg (501.5 mg, 2.5 mmol, 100 equiv respect to Ni) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then H_2O (50 μL) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. 95% NMR yield of the desired product **2a** was observed.

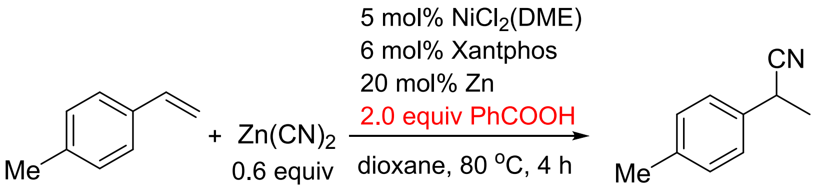
(7) Ni-catalyzed hydrocyanation of 1a using MeOH or PhCOOH as the hydrogen source.



1a

2a, 11% NMR yield

In a nitrogen-filled glove box, $NiCl_2$(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box, then MeOH (32 mg, 1.0 mmol) was added to the vial. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. 11% NMR yield of the desired product **2a** was observed.



1a

2a, 6% NMR yield

In a nitrogen-filled glove box, $NiCl_2$(DME) (5.5 mg, 0.025 mmol), Xantphos (17.4 mg, 0.03 mmol), Zinc powder (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (35.2 mg, 0.3 mmol), PhCOOH (122.1 mg, 1.0 mmol), dioxane (2.5 mL) and 1-methyl-4-vinylbenzene (59.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 80 °C for 4 h, the mixture was filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was dissolved in $CDCl_3$. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using mesitylene (60.1 mg, 0.5 mmol) as an internal standard. 6% NMR yield of the desired product **2a** was observed.

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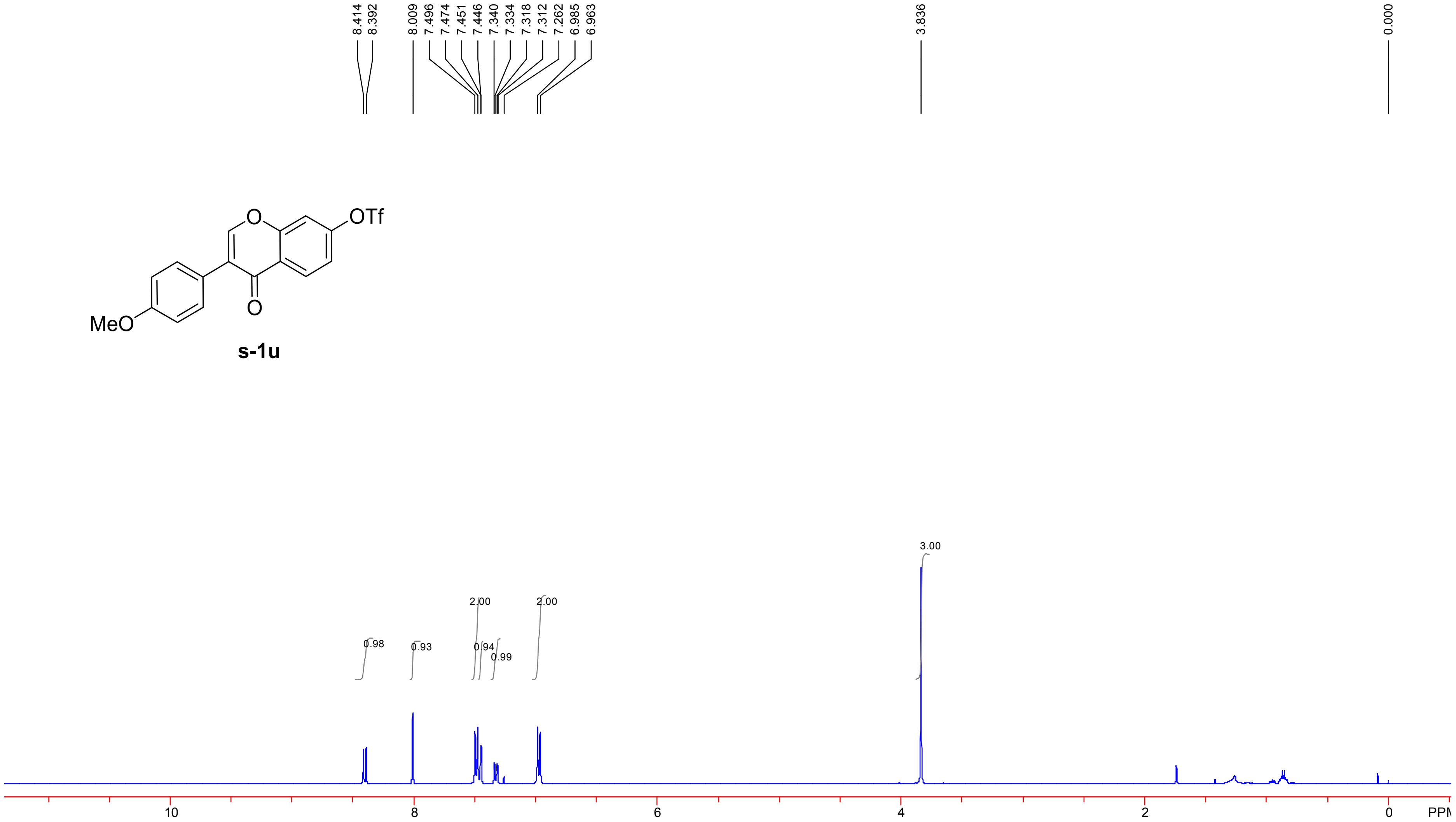

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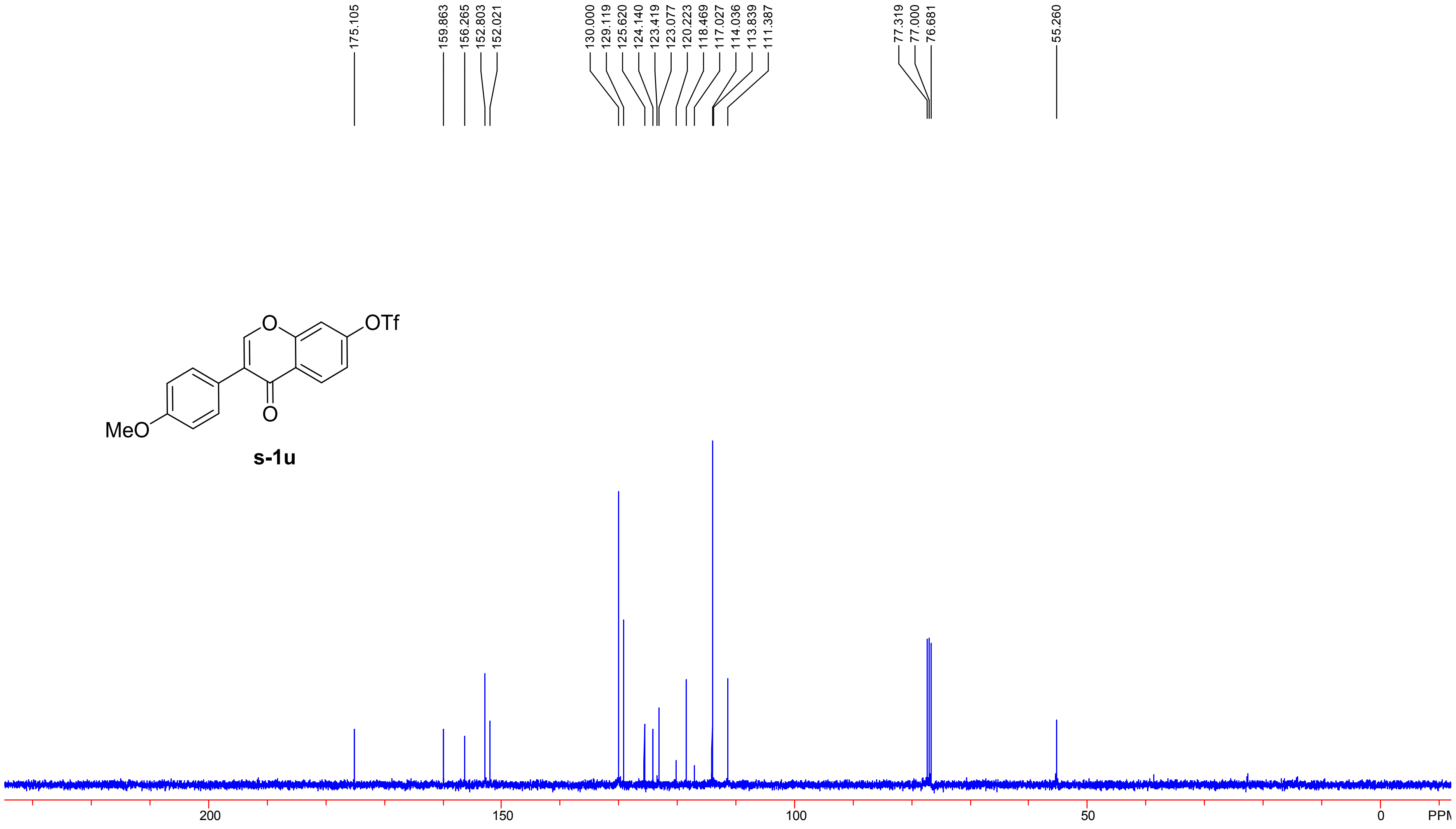
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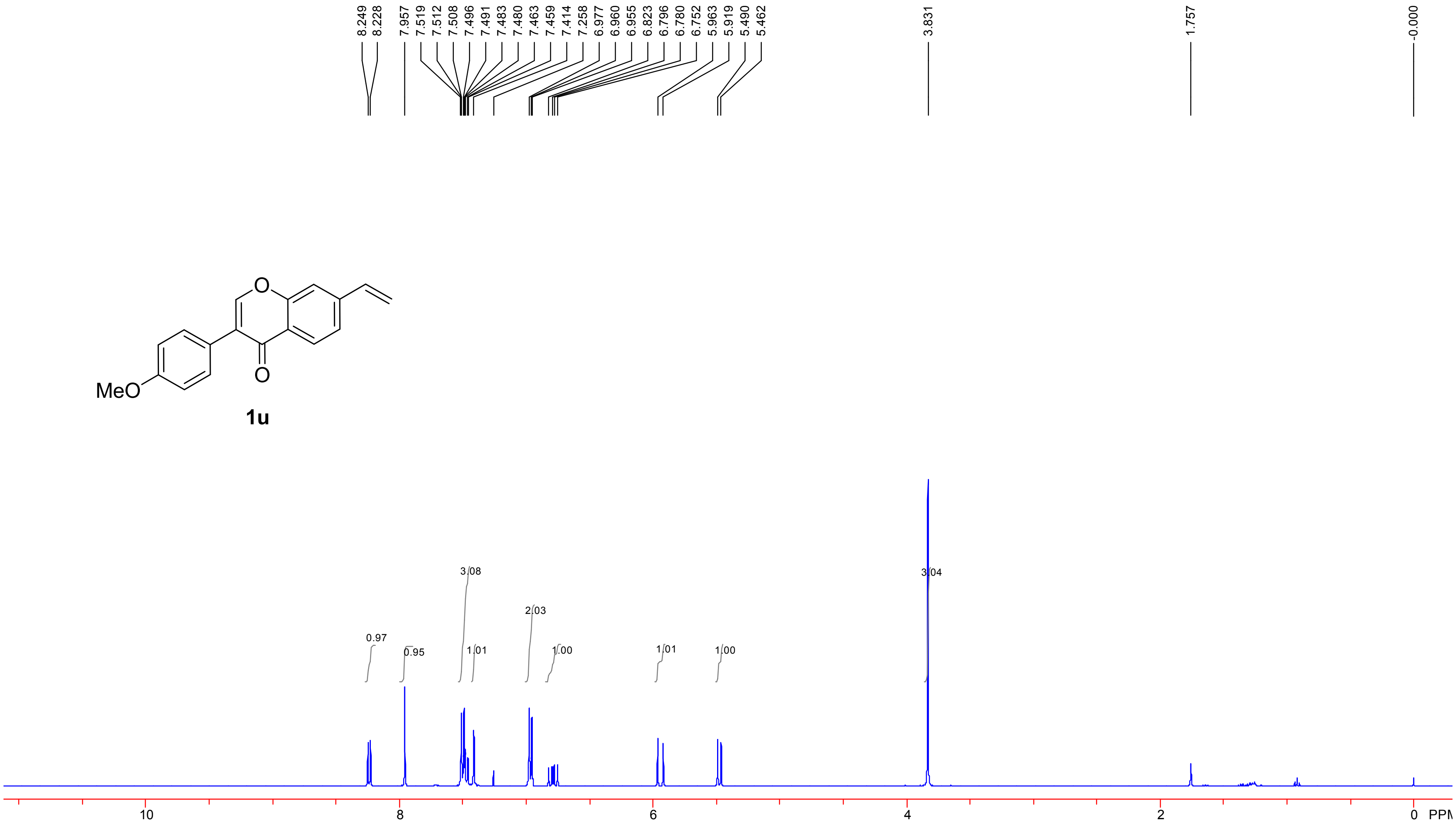
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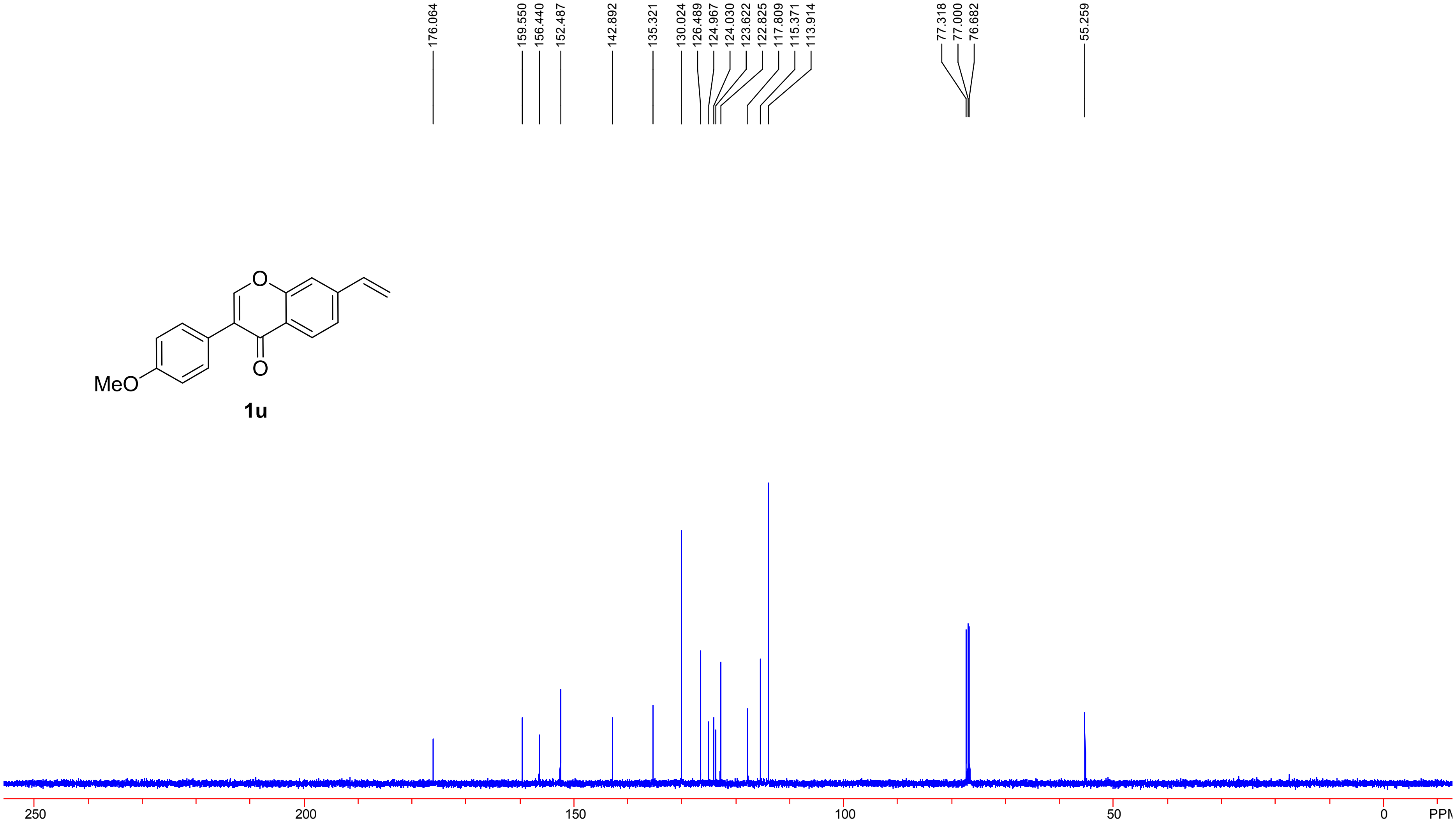
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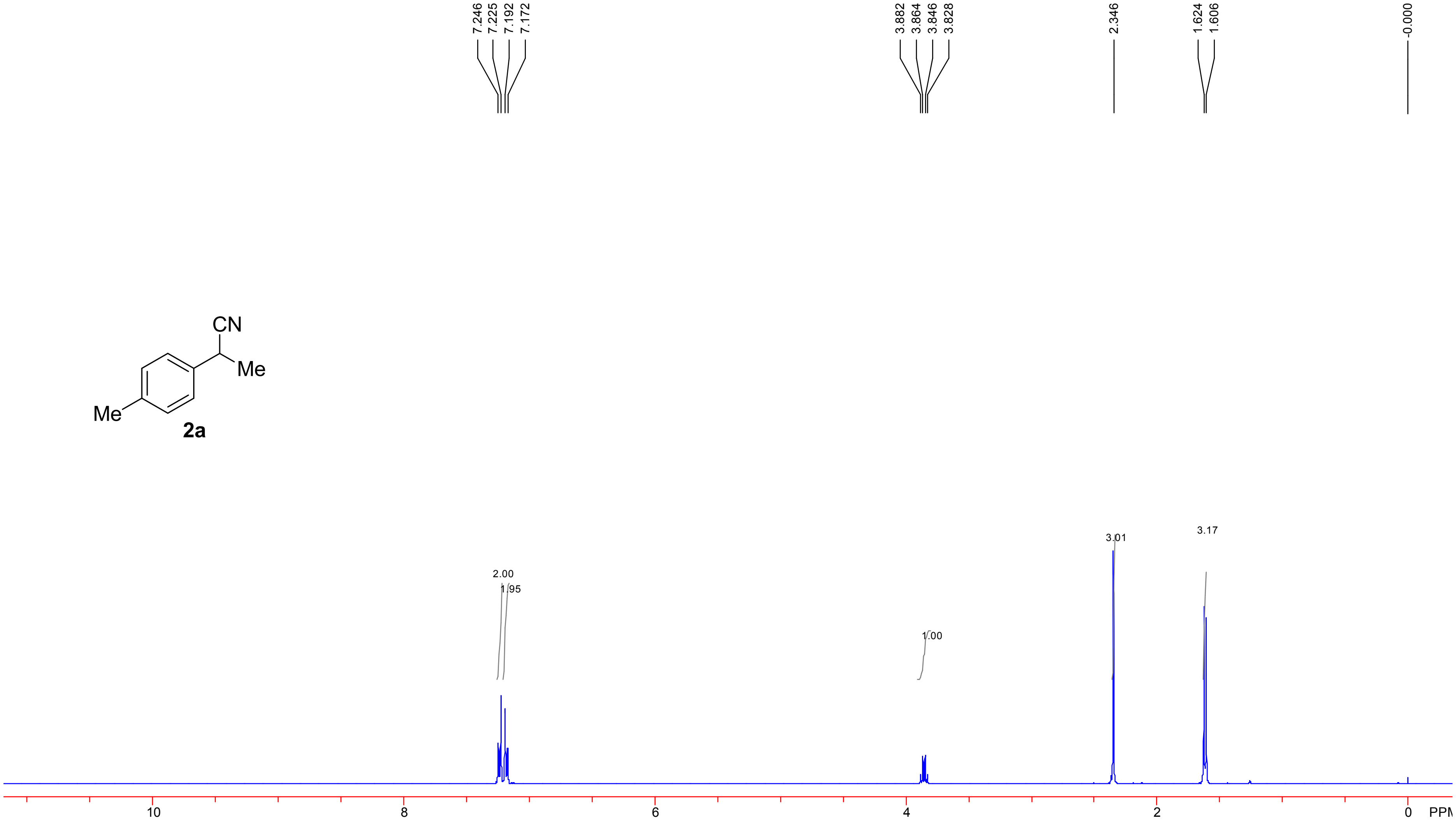
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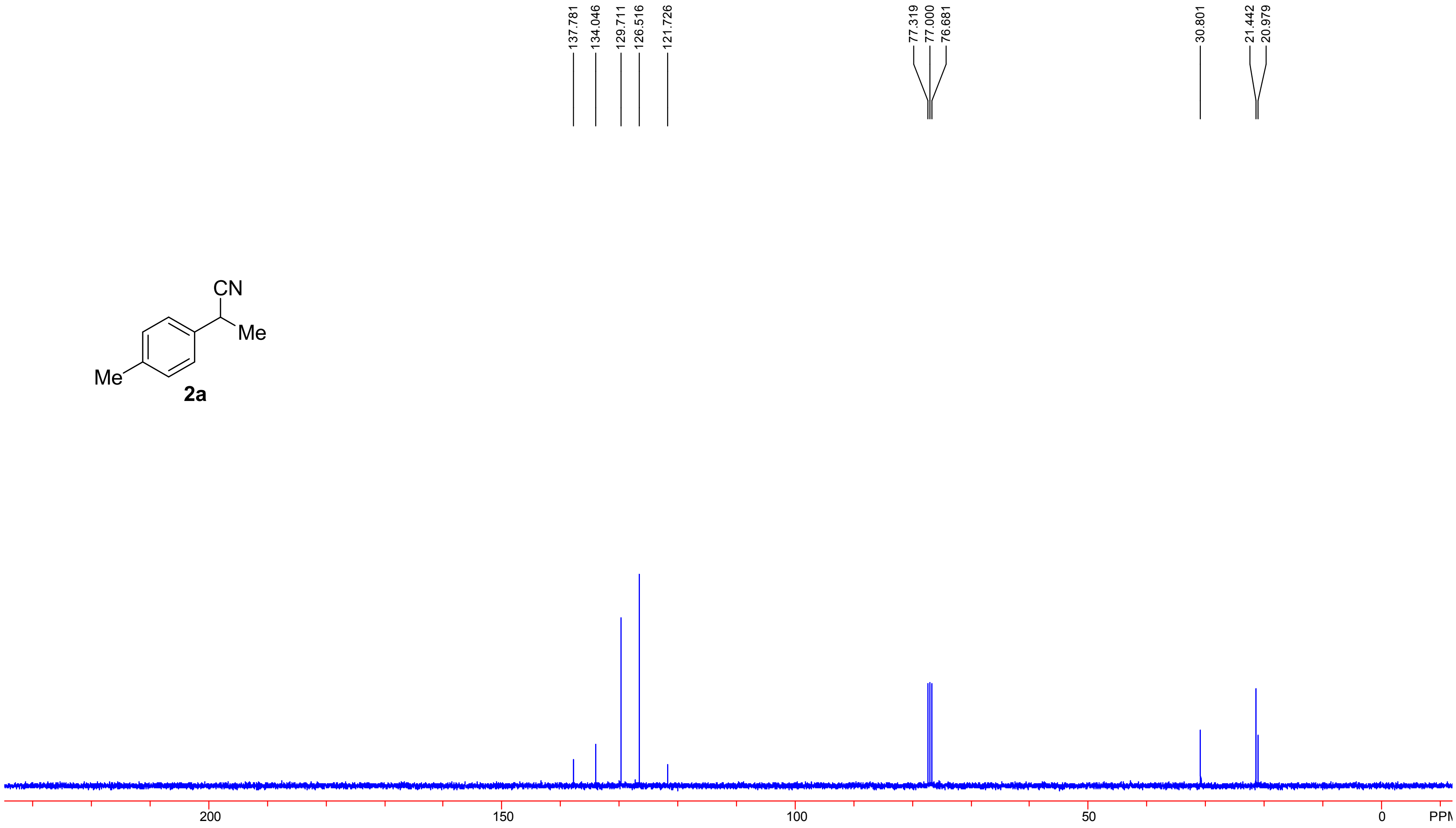
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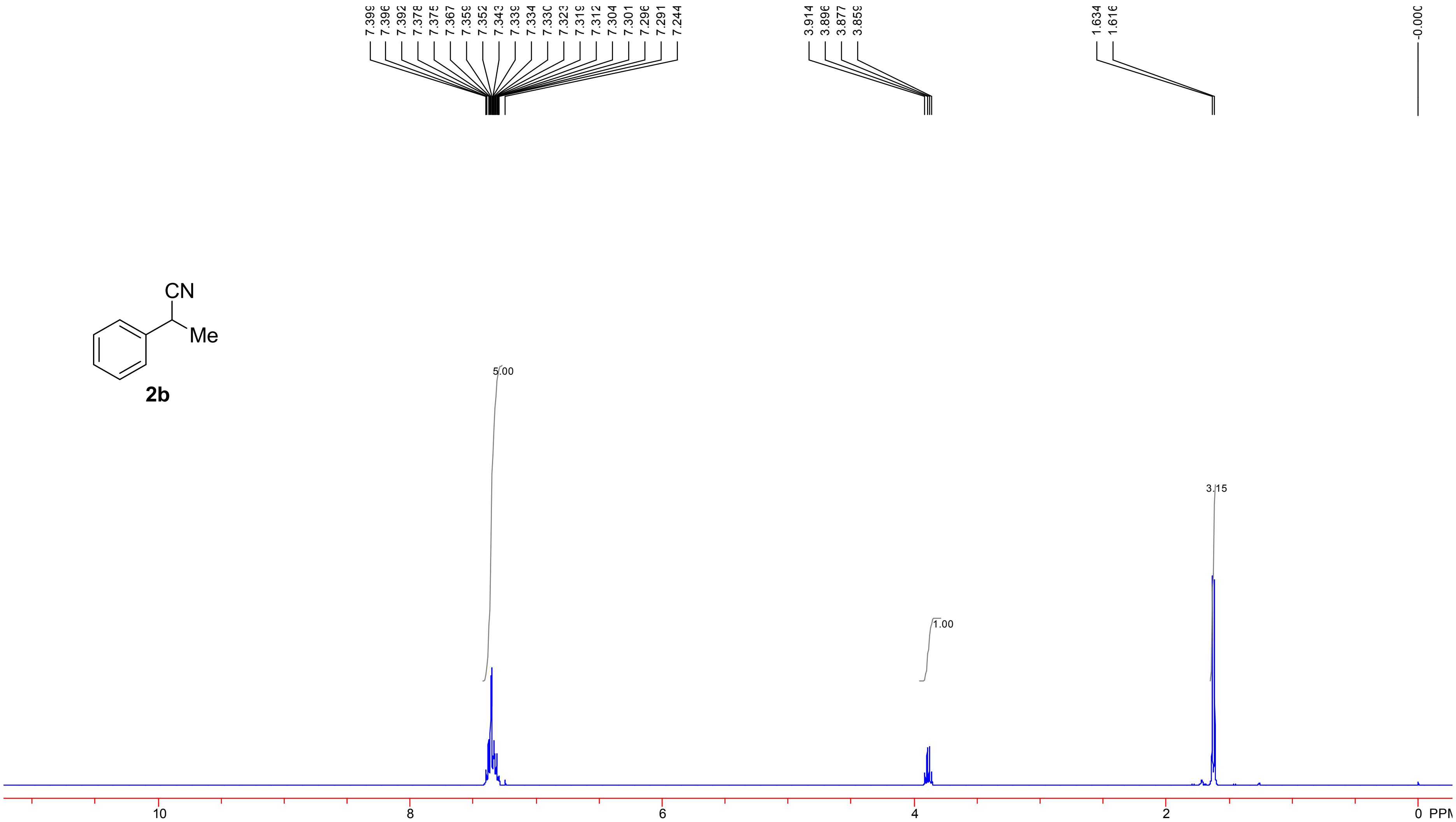

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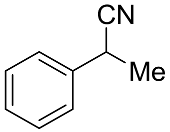
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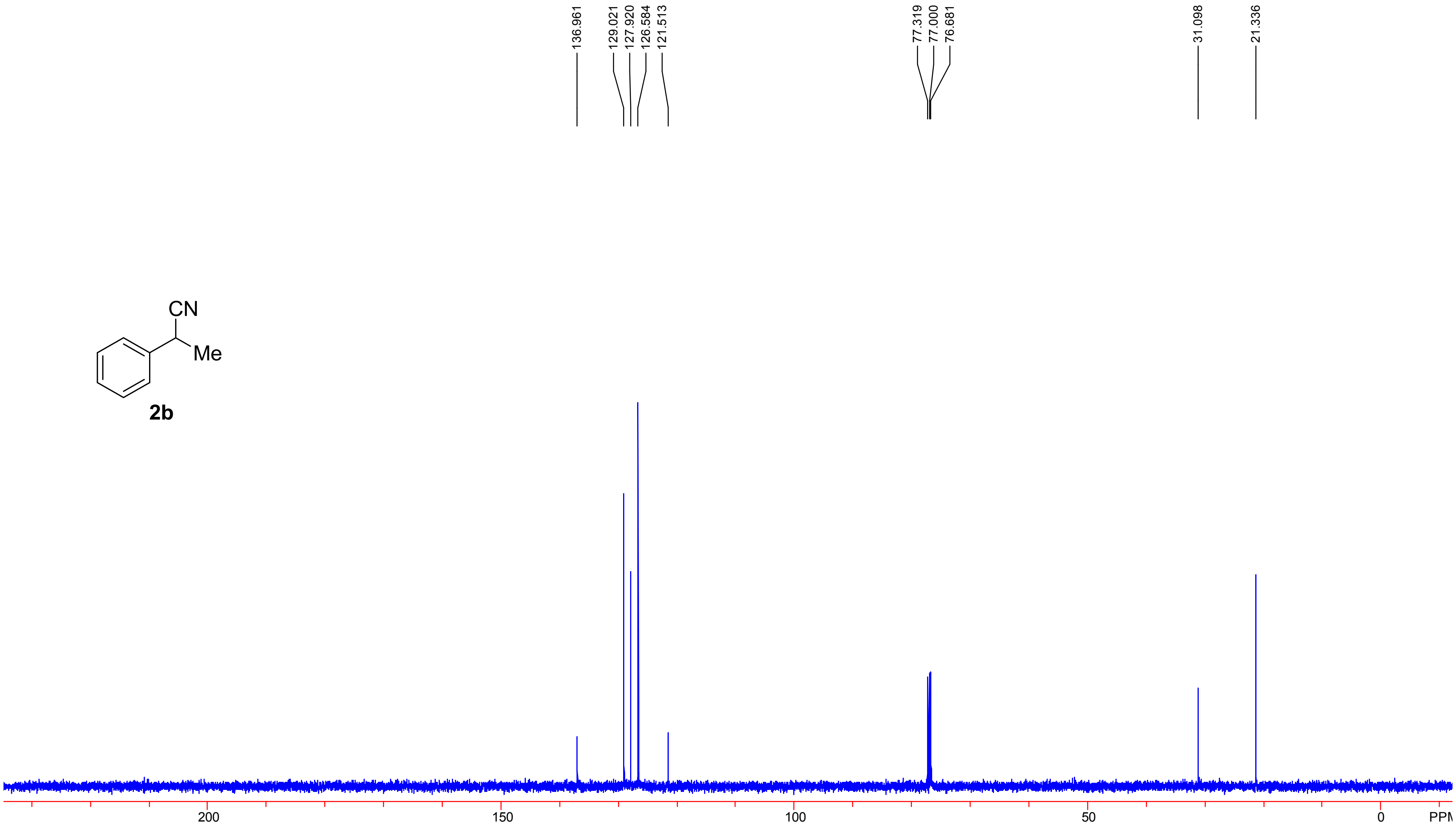
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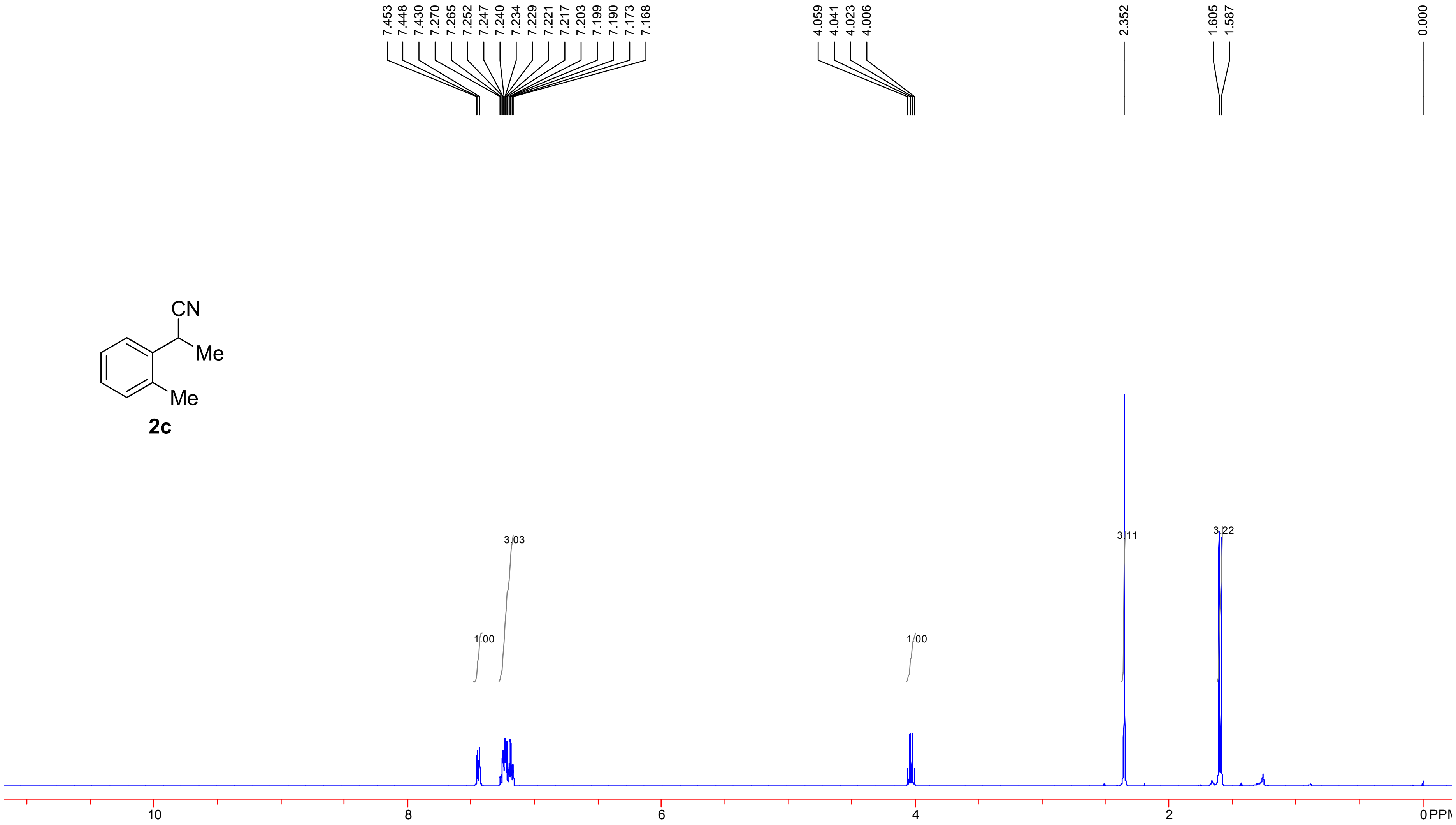
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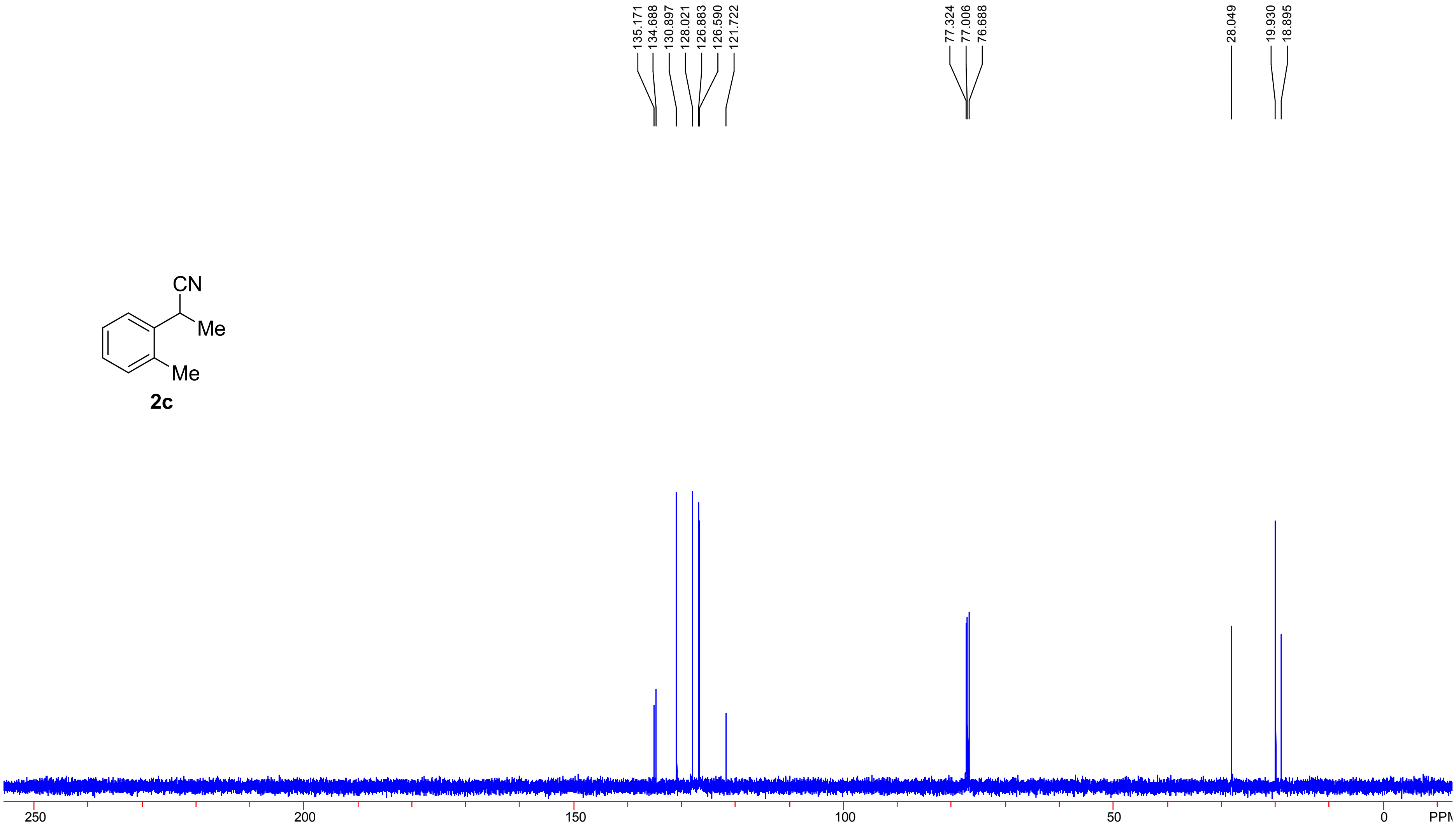

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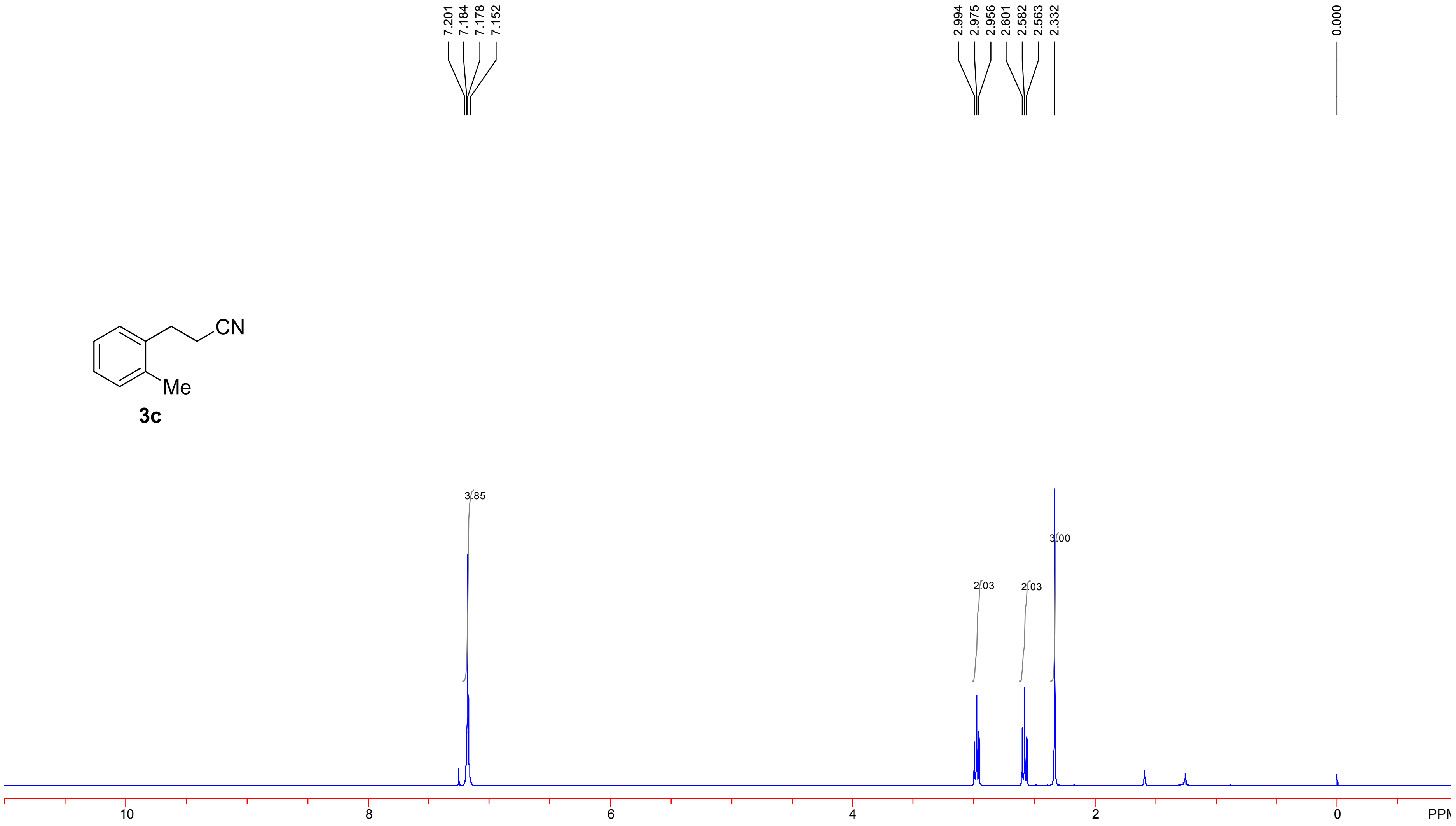
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2.563
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Me
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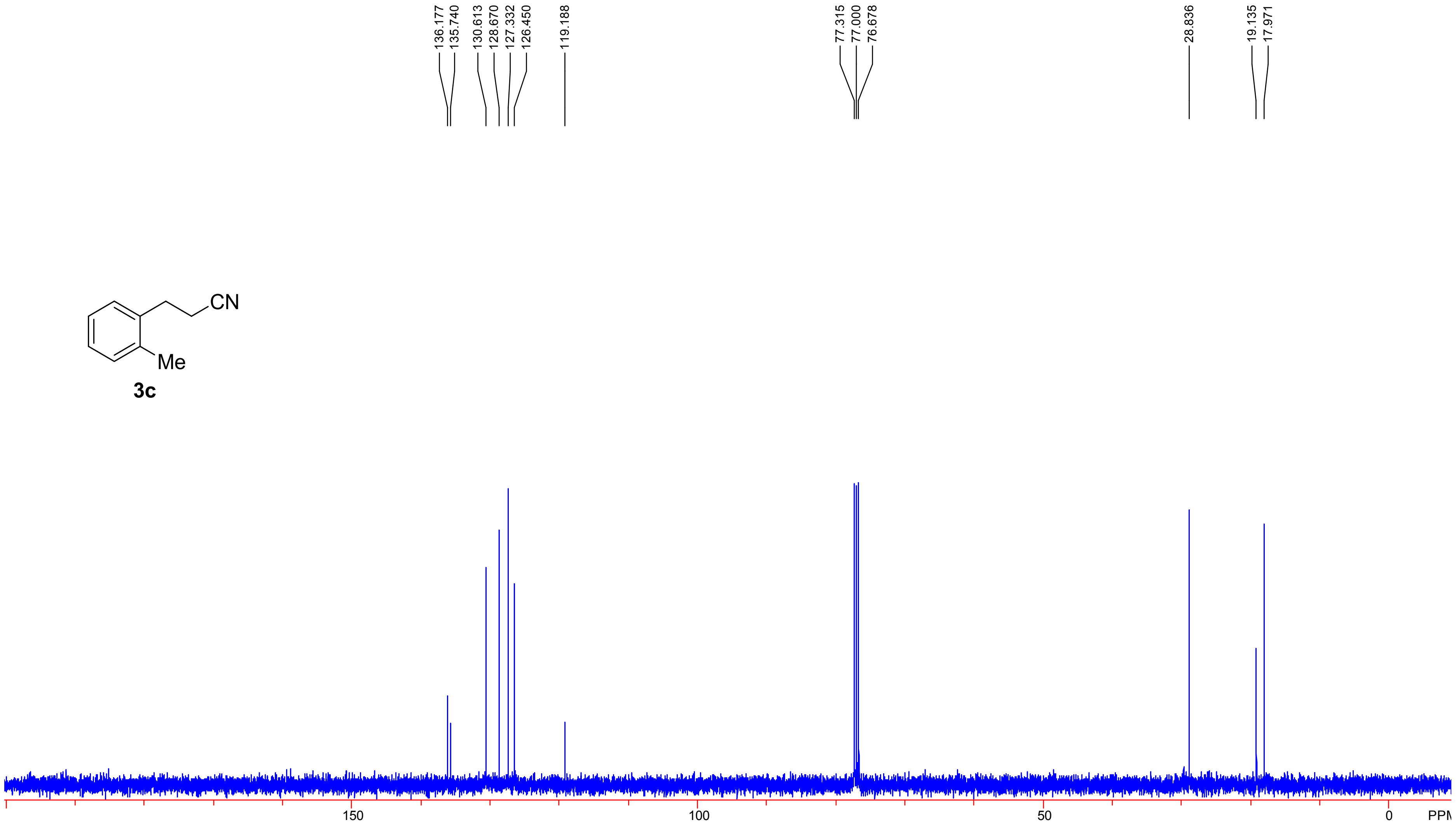
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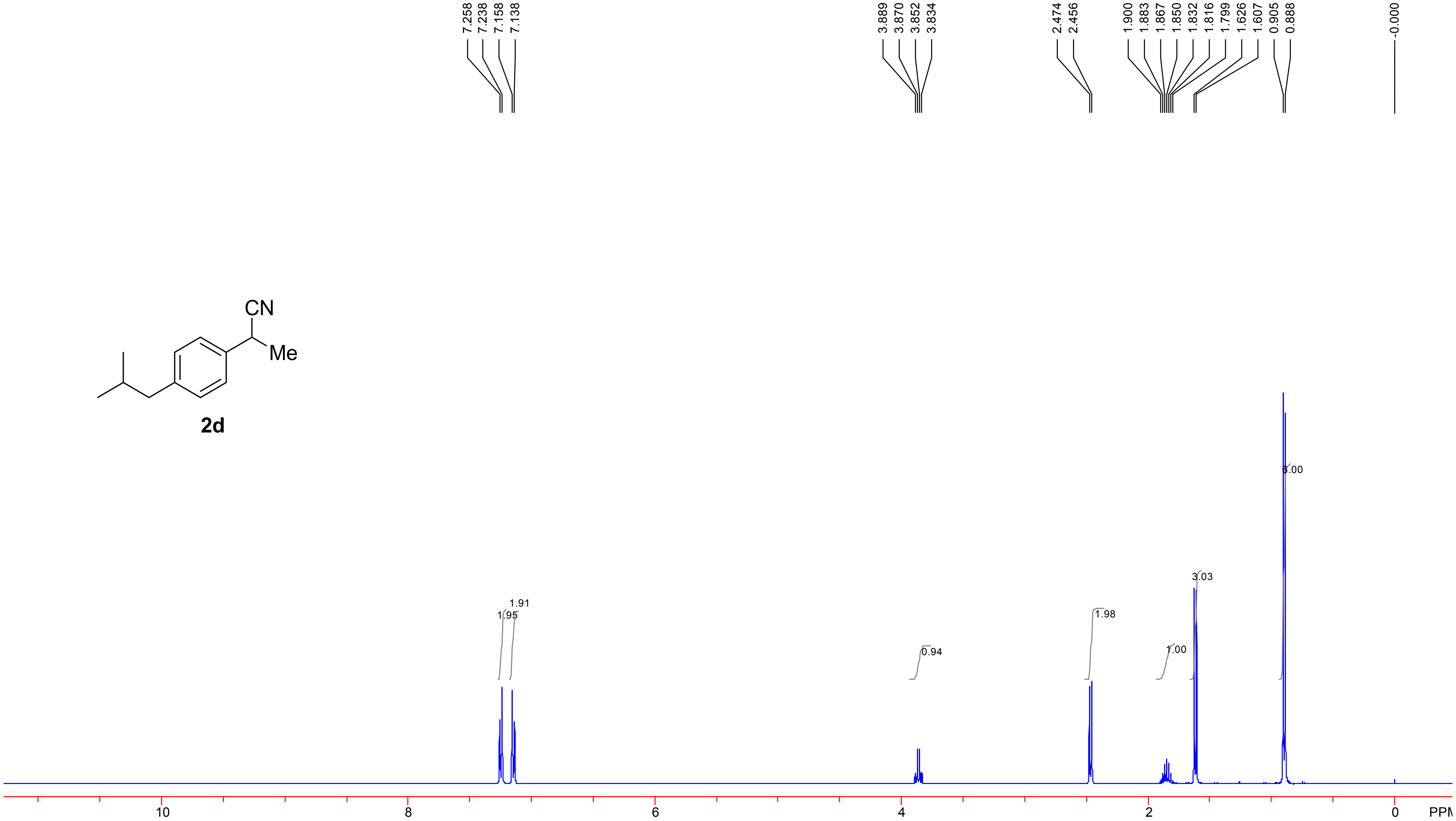
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1.867
1.850
1.832
1.816
1.799
1.626
1.607
0.905
0.888
-0.000
CN
Me
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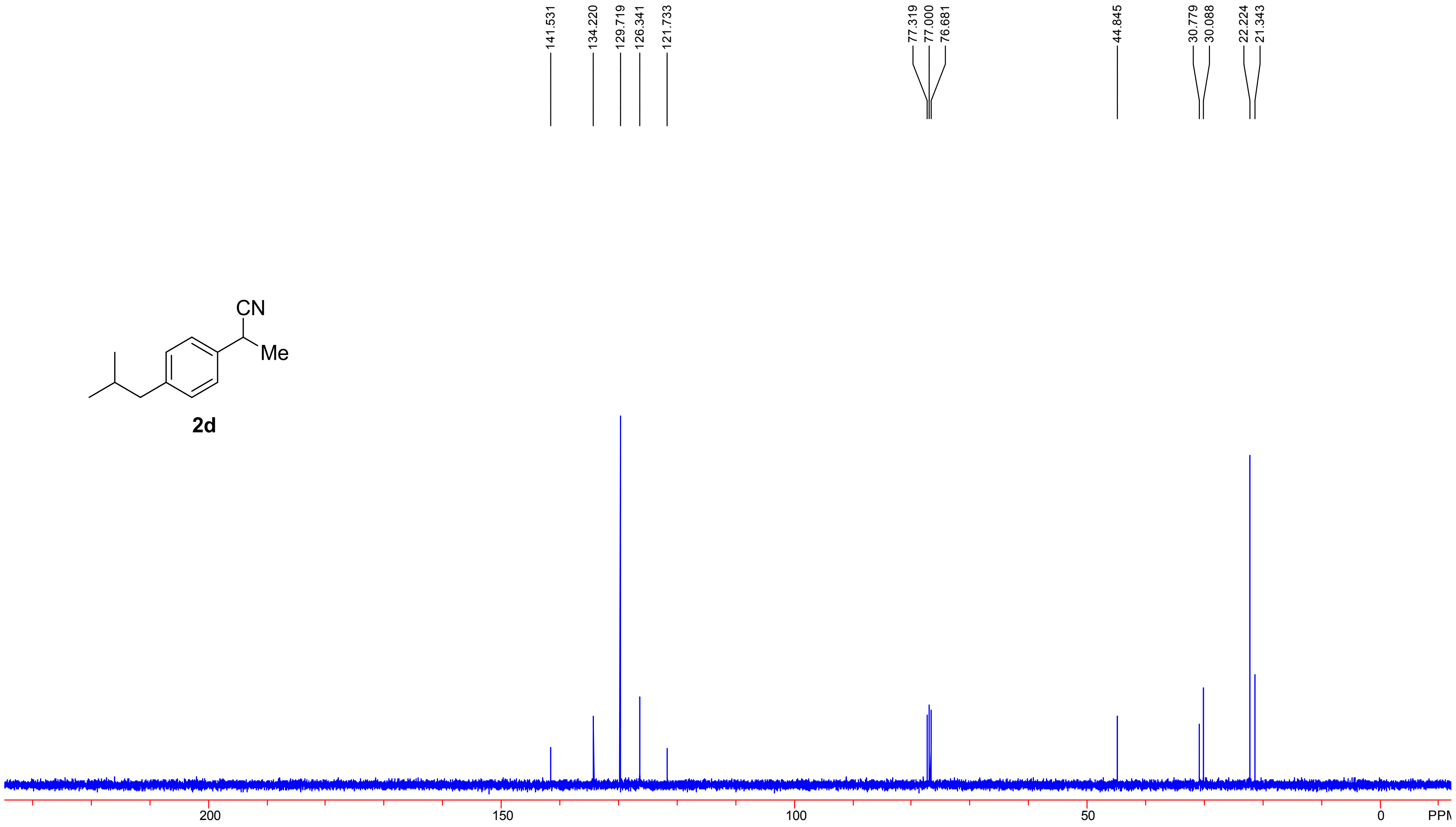
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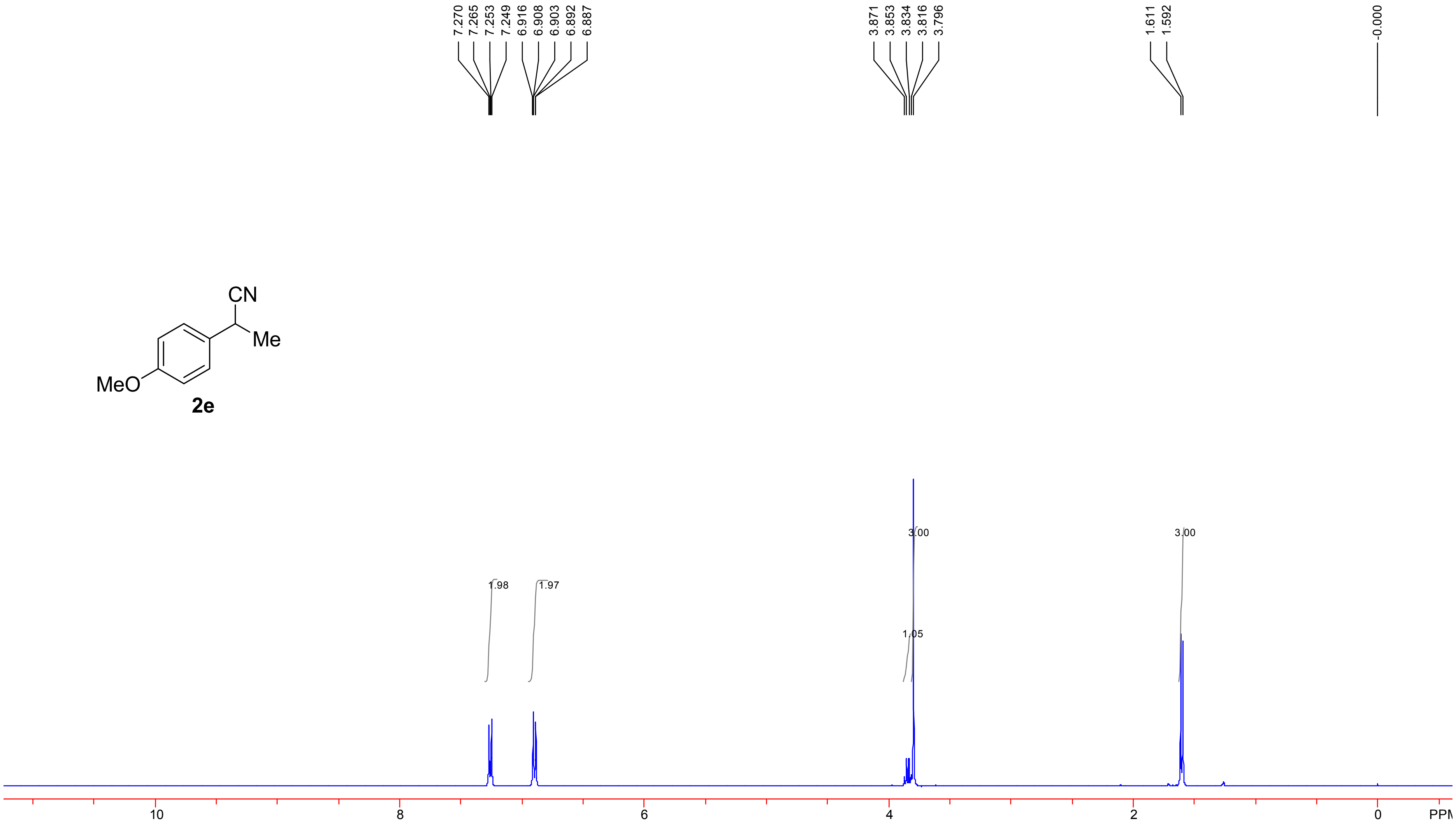
PPM

2d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3.816
3.796
1.611
1.592
-0.000
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1.05
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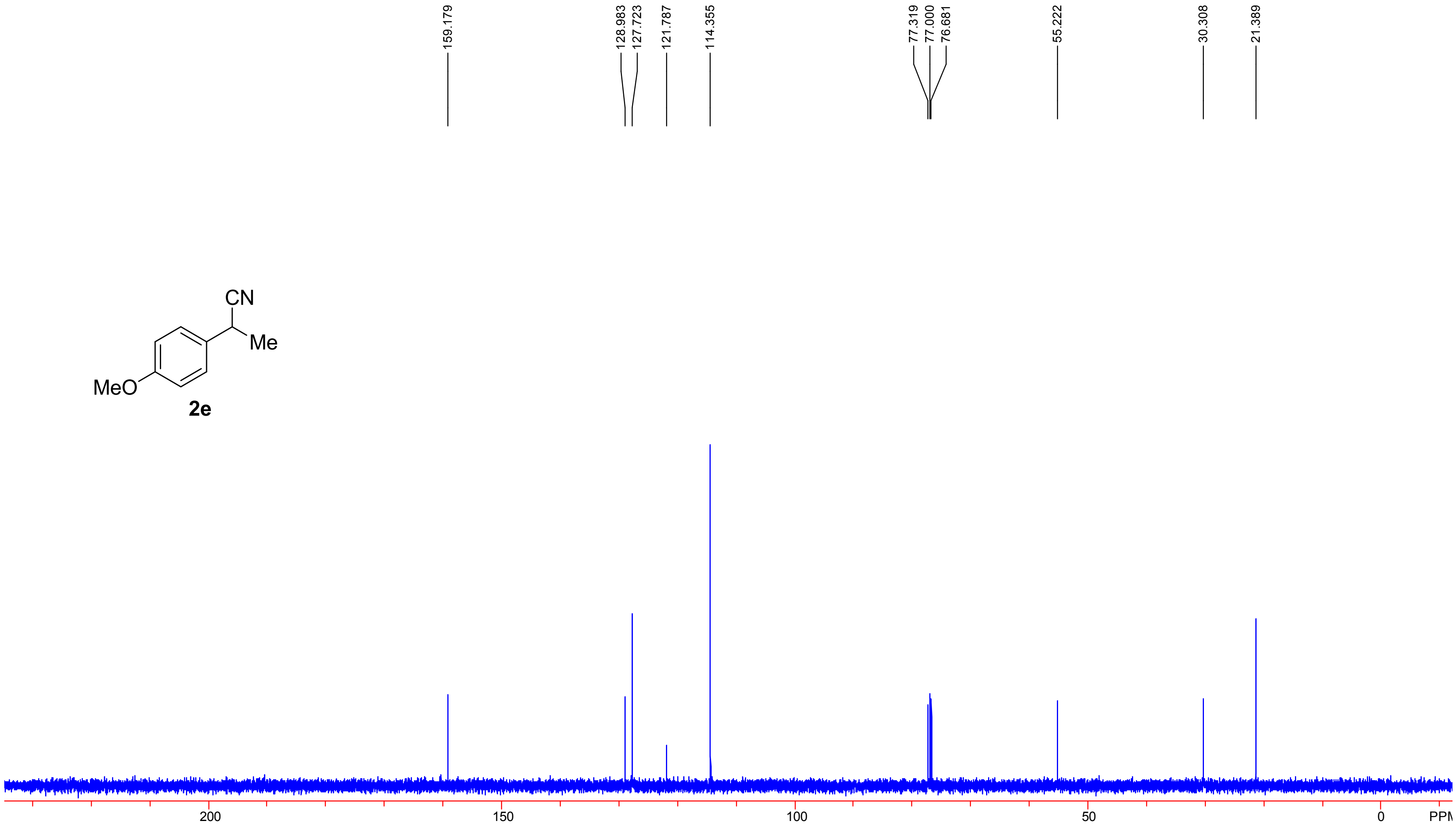
2e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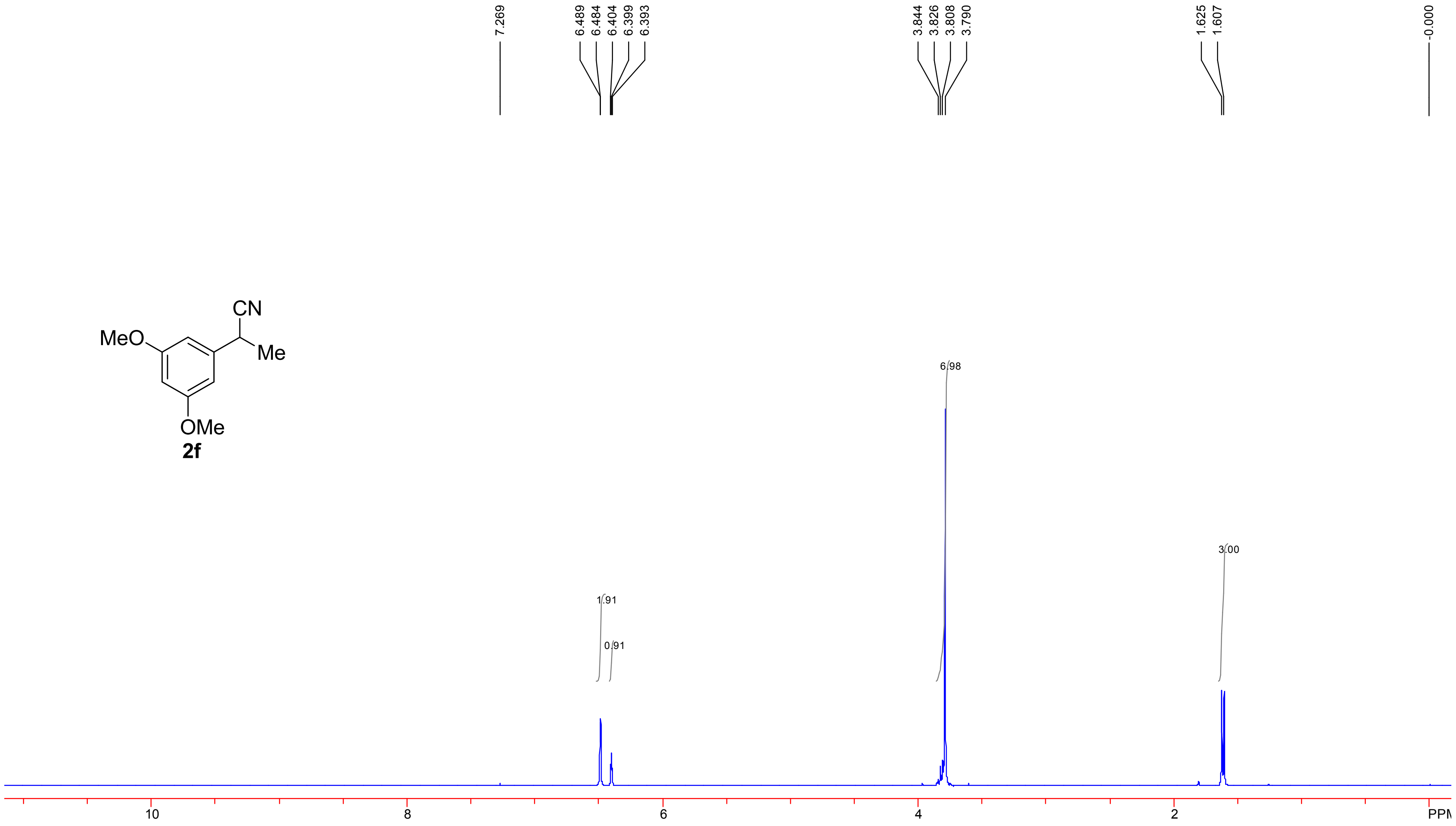
2e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6.399
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3.790
1.625
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MeO
CN
Me
OMe
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10
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2
PPM

CN
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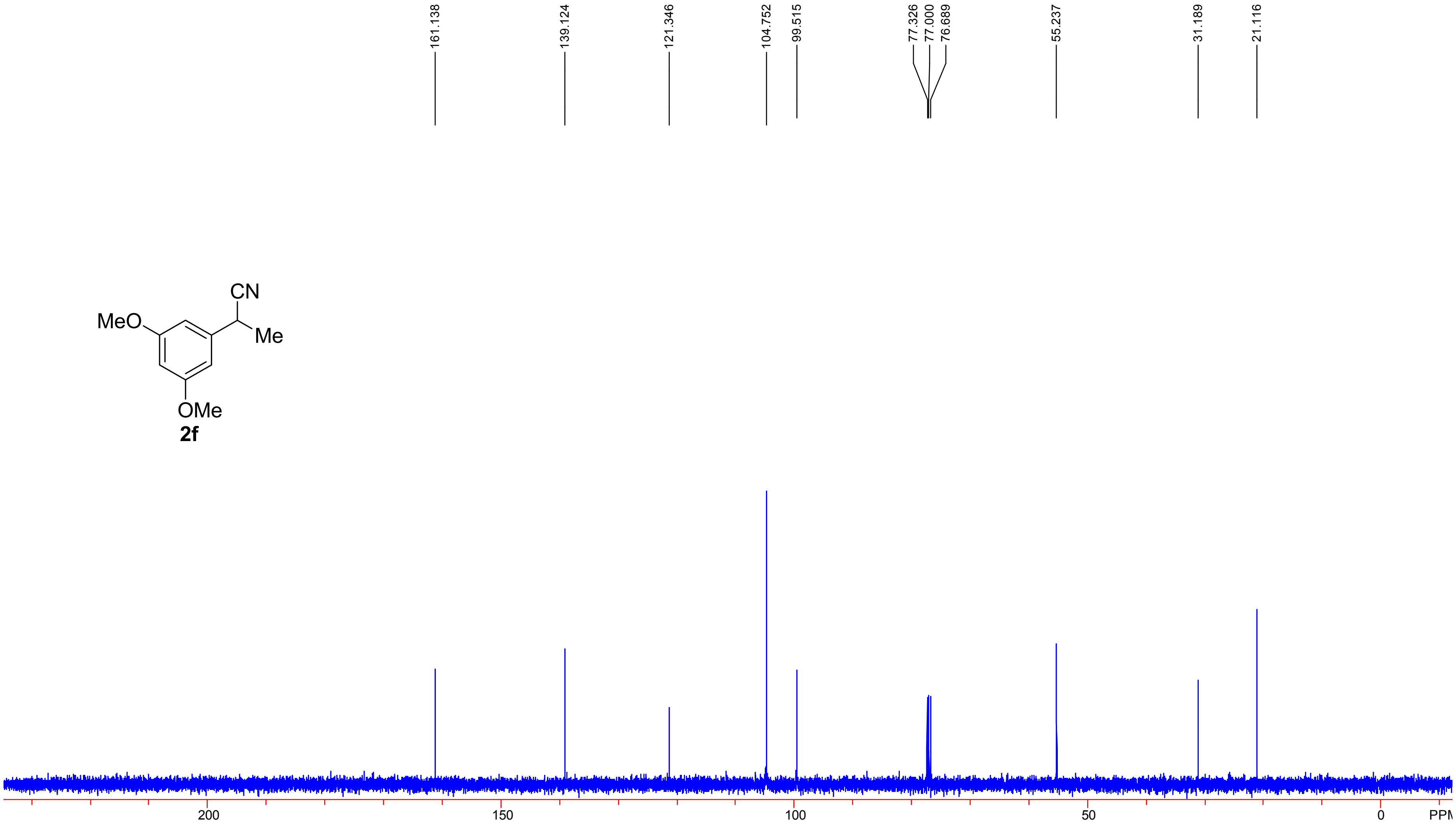
Me
OMe

2f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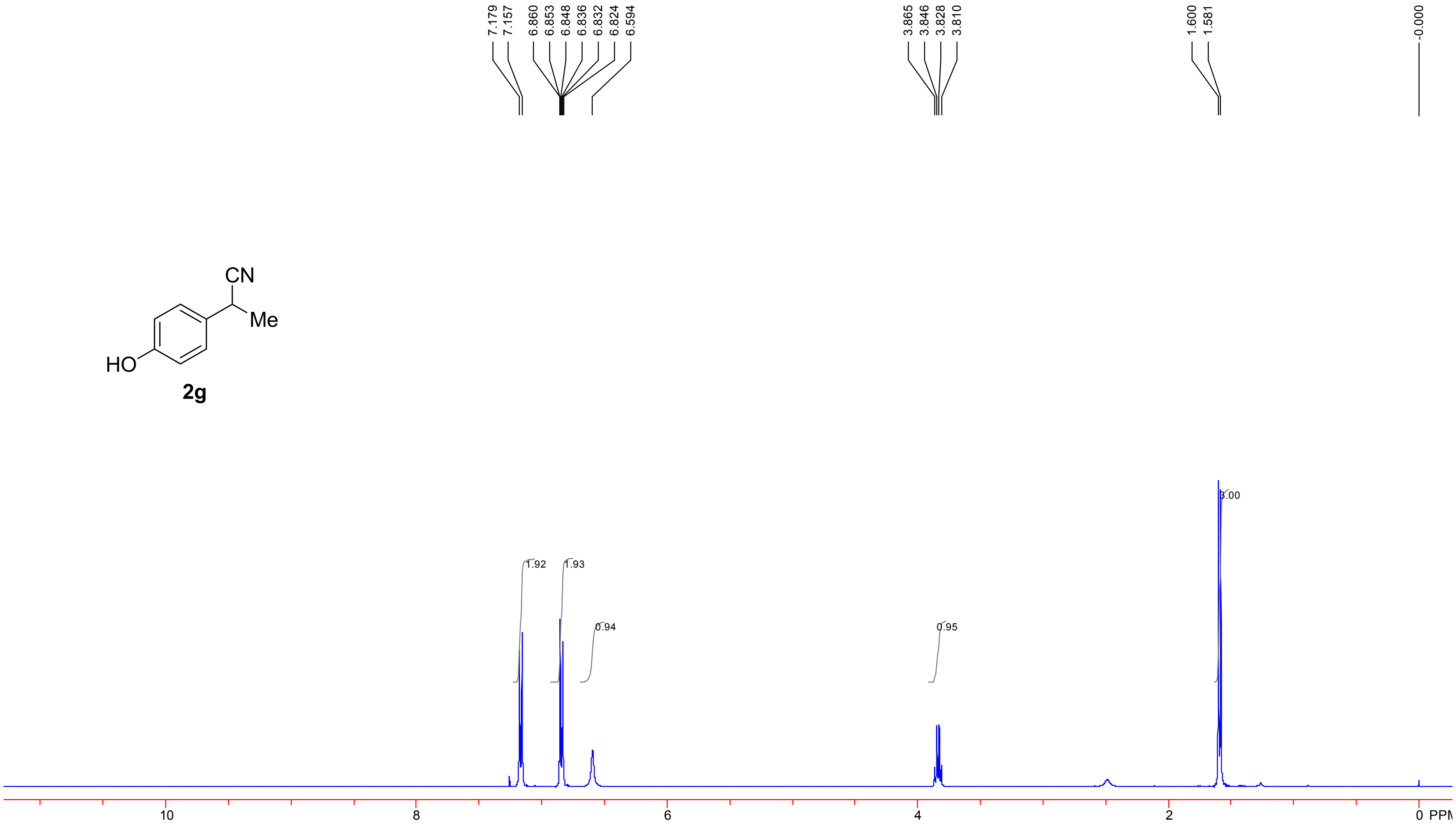
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HO

2g

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3.865
3.846
3.828
3.810
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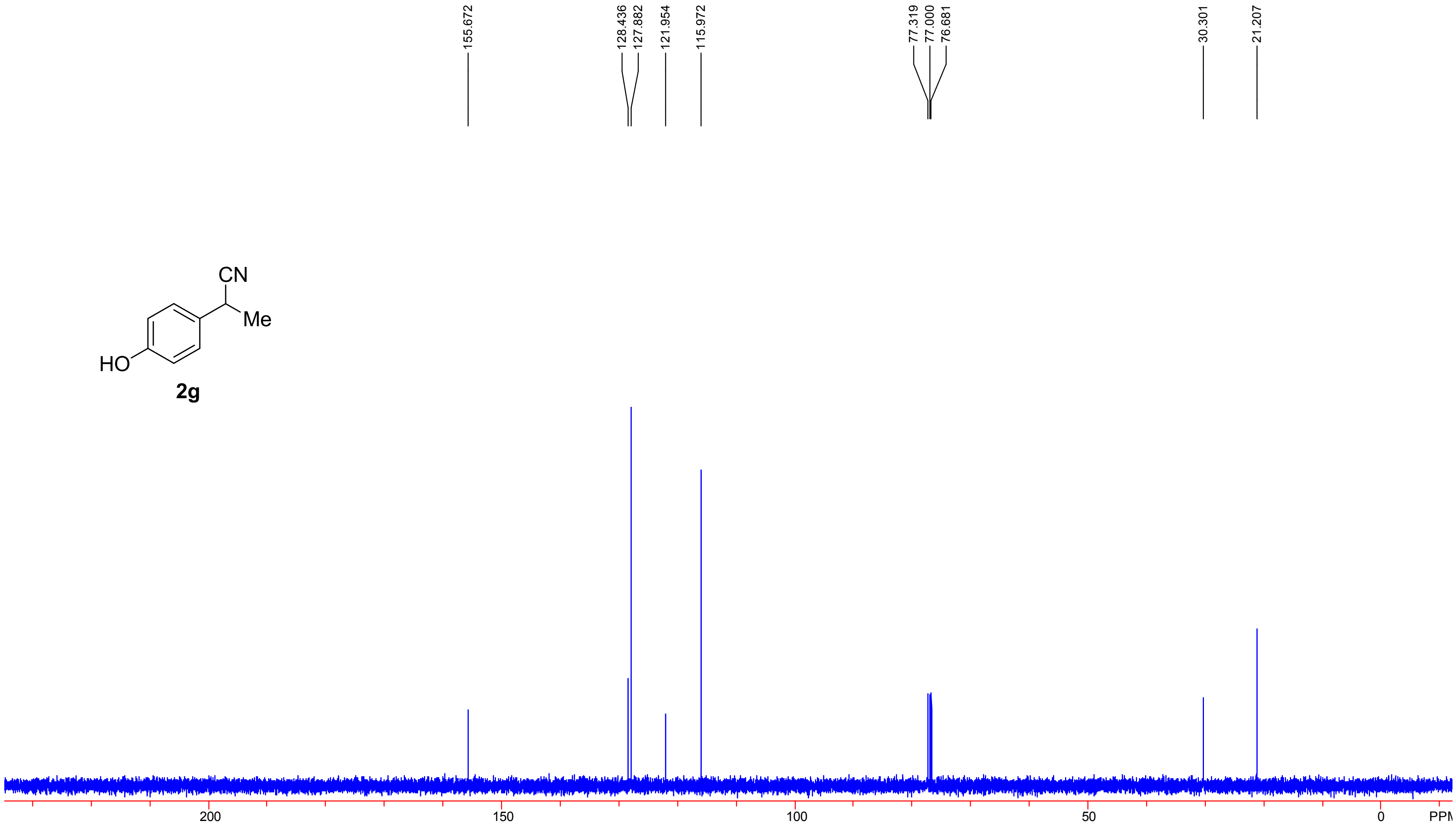
6
4
2
0 PPM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HO
2g
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100
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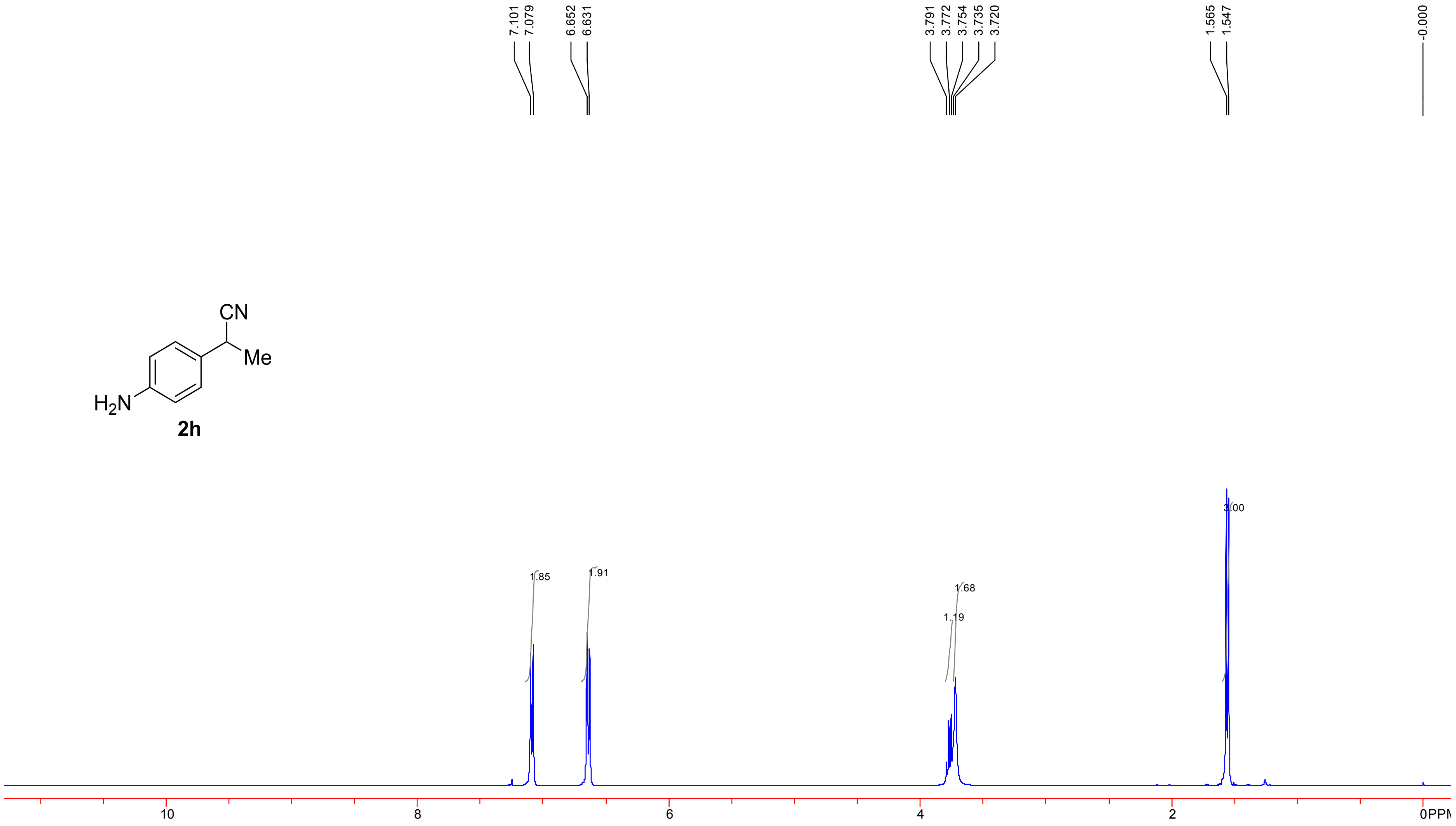
PPM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1.547
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1.91
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10
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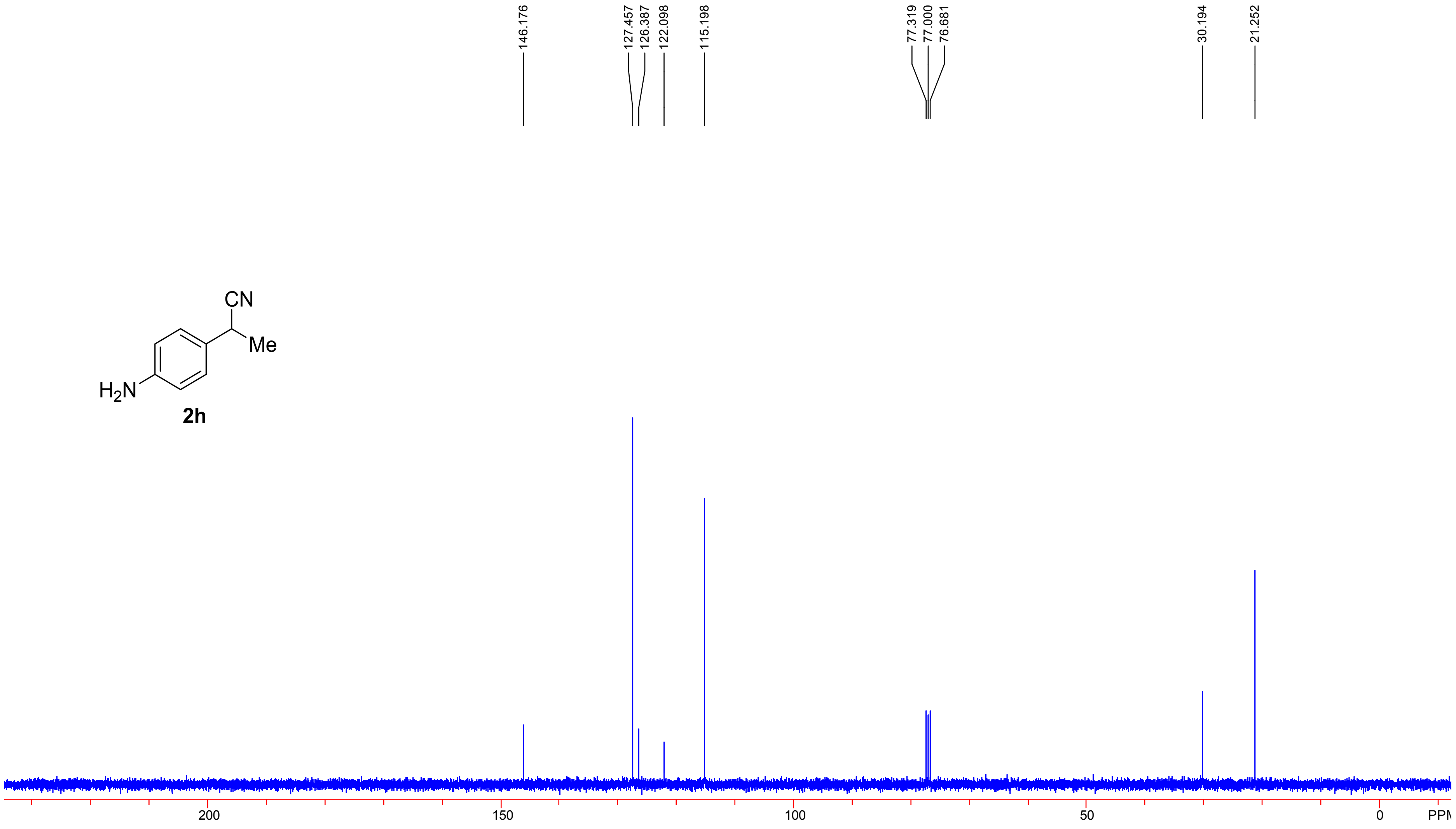
6
4
2
0PPM

2h



2h

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H_2N
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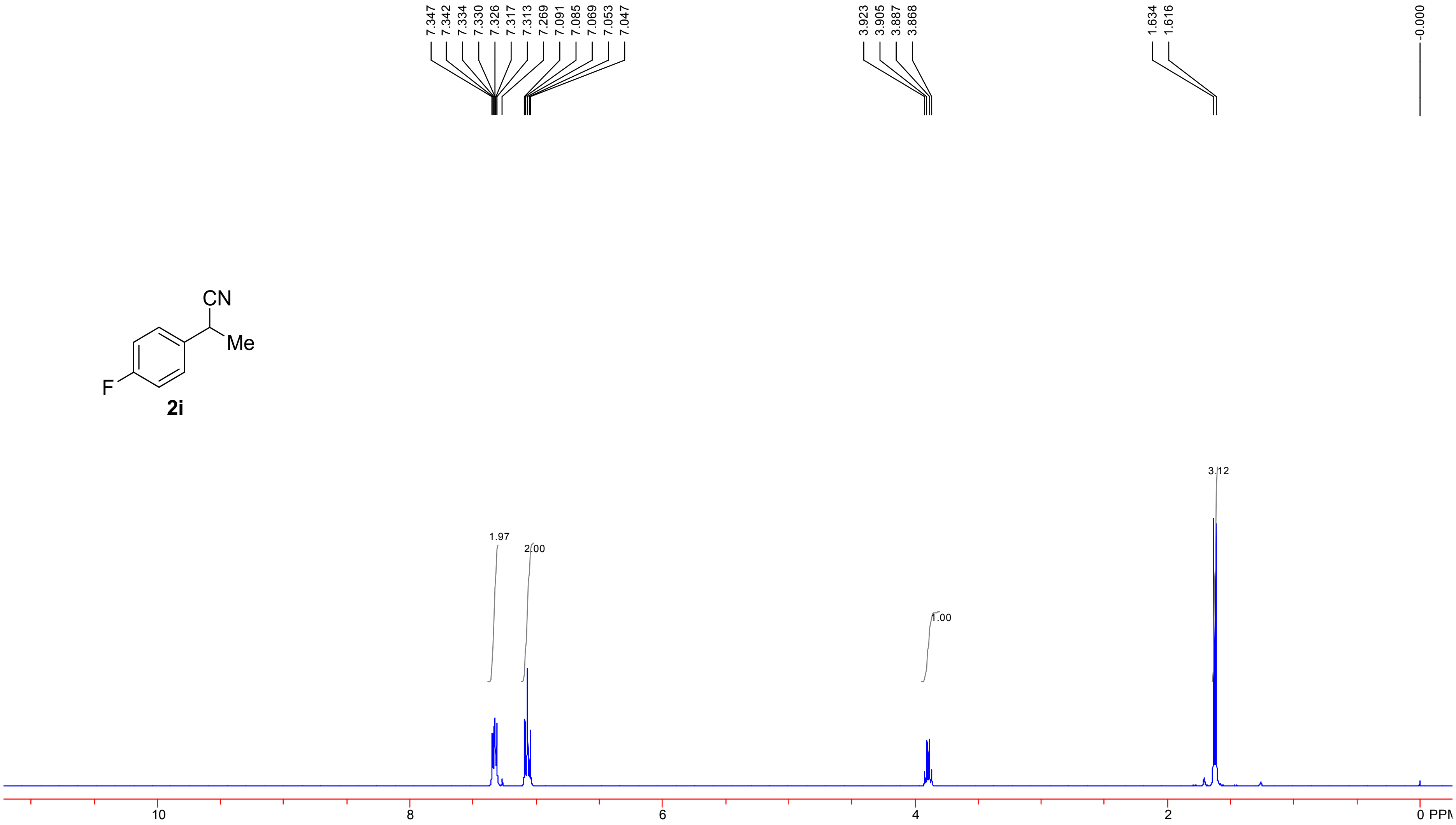
50
0
PPM

CN
Me
F

2i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7.085
7.069
7.053
7.047
3.923
3.905
3.887
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-0.000
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3.12
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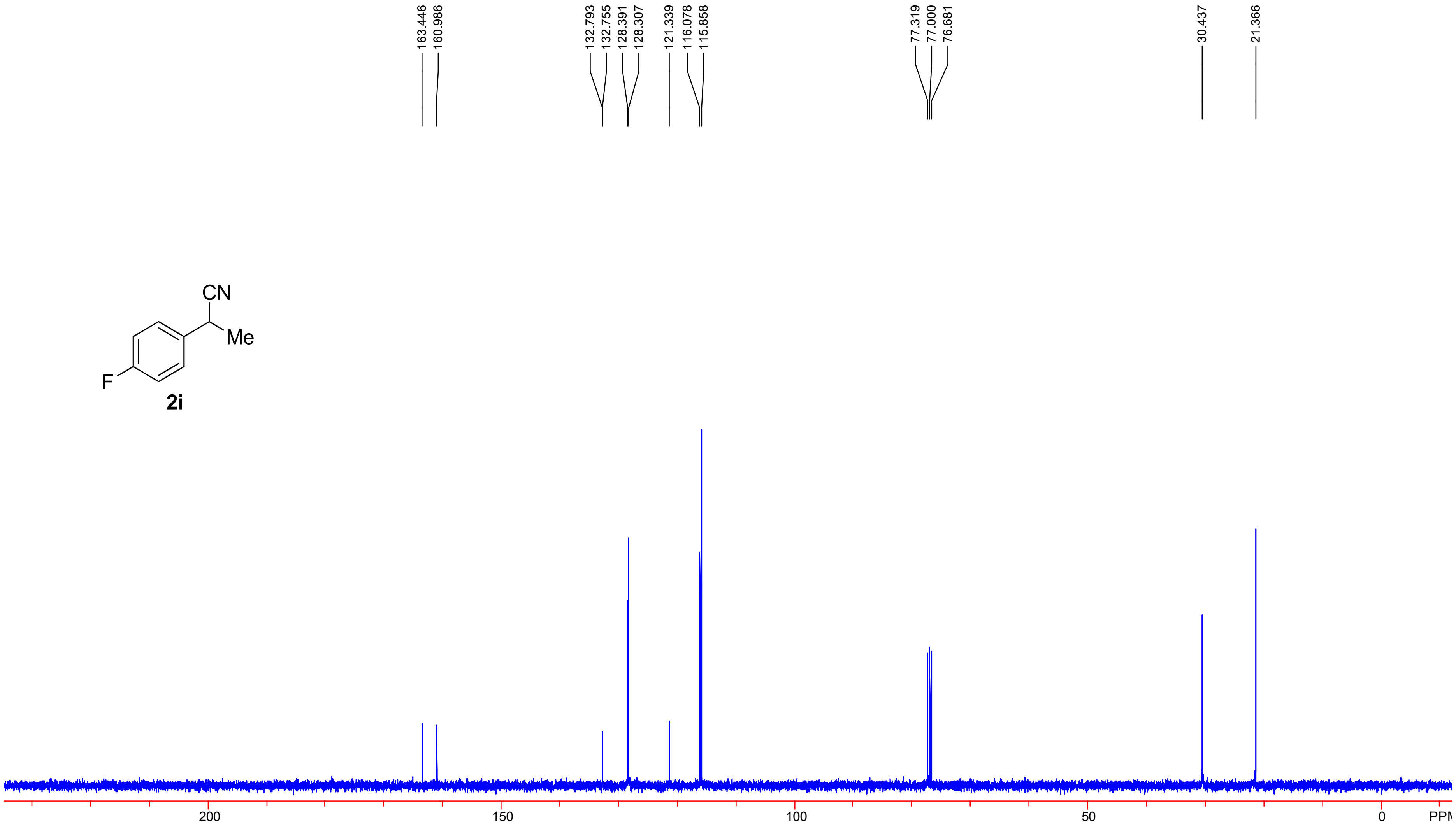
8
6
4
2
0 PPM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116.078
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77.000
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CN
Me
F
2i
200
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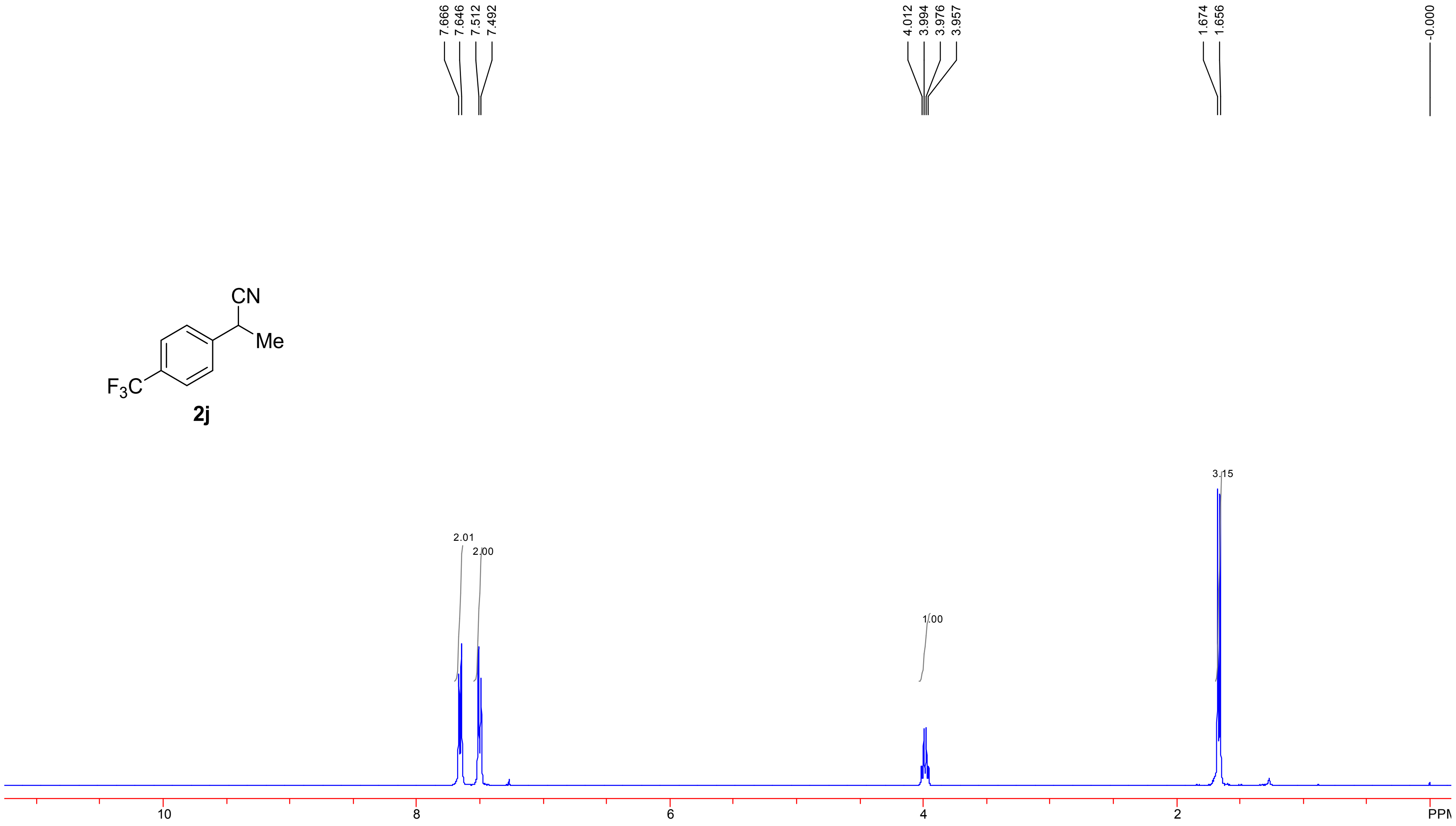
100
50
0
PPM

CN
Me
F3C

2j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1.00
3.15
10
8
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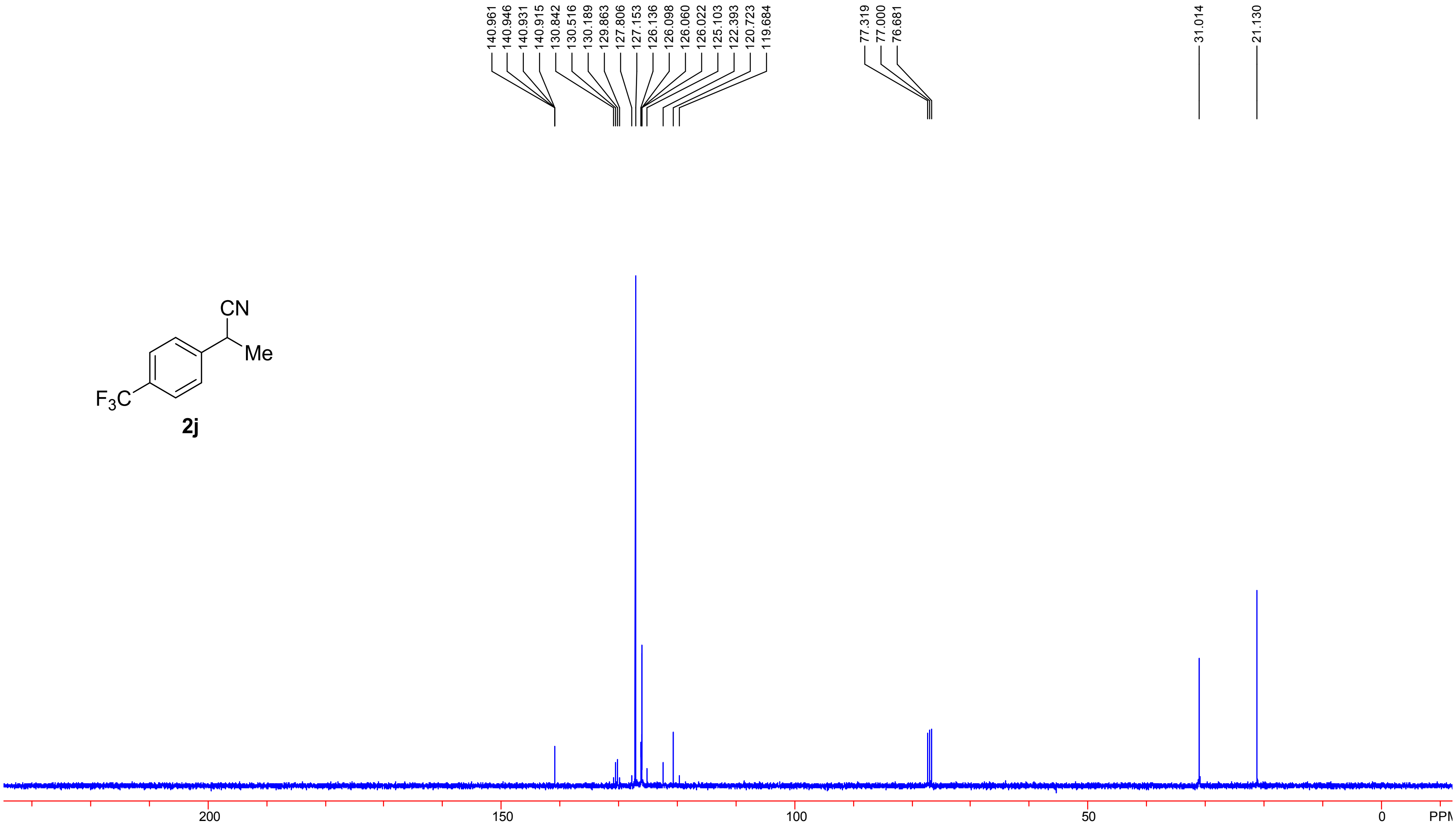
4
2
PPM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126.098
126.060
126.022
125.103
122.393
120.723
119.684
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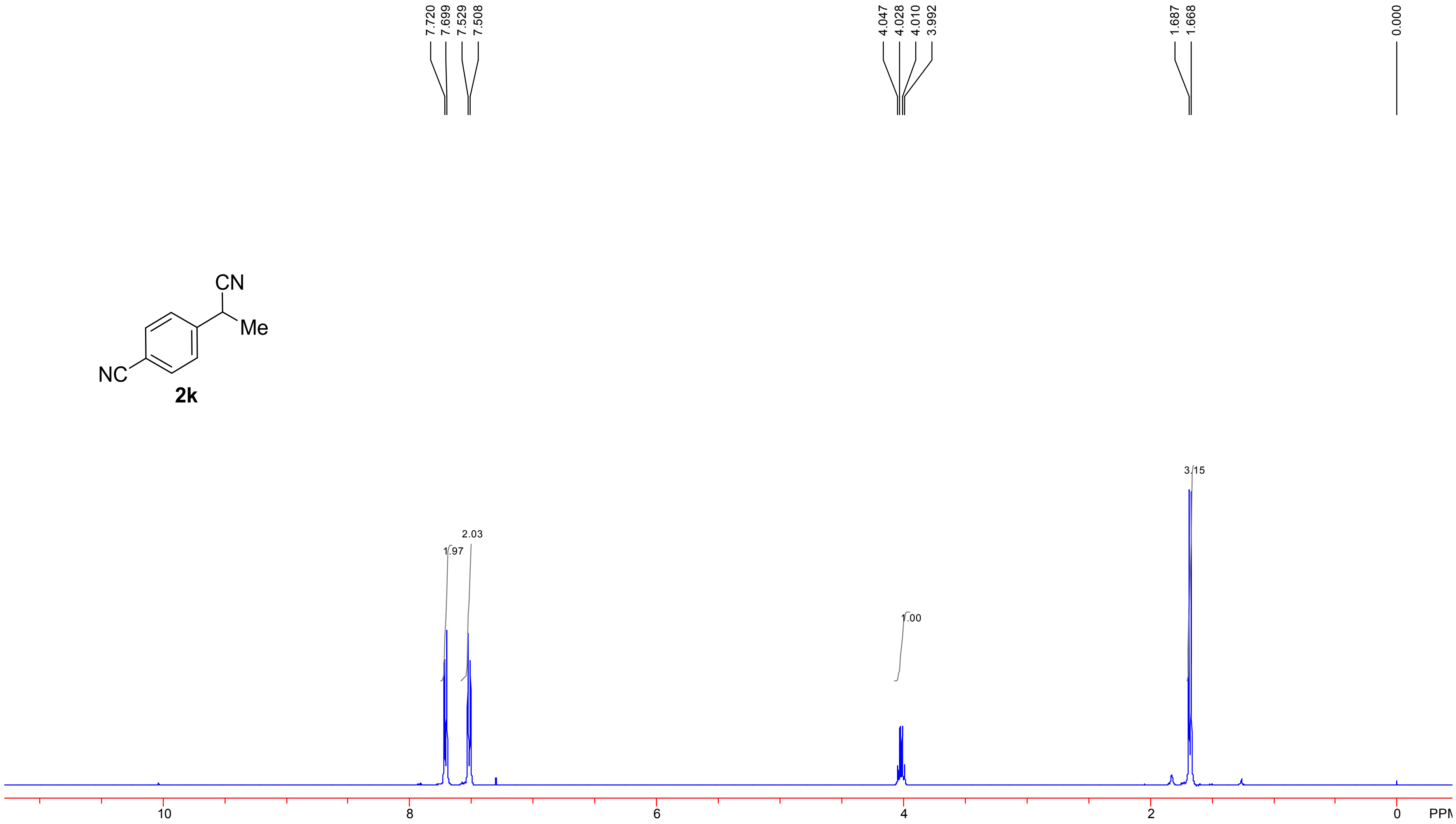
PPM

2j



2k

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4.010
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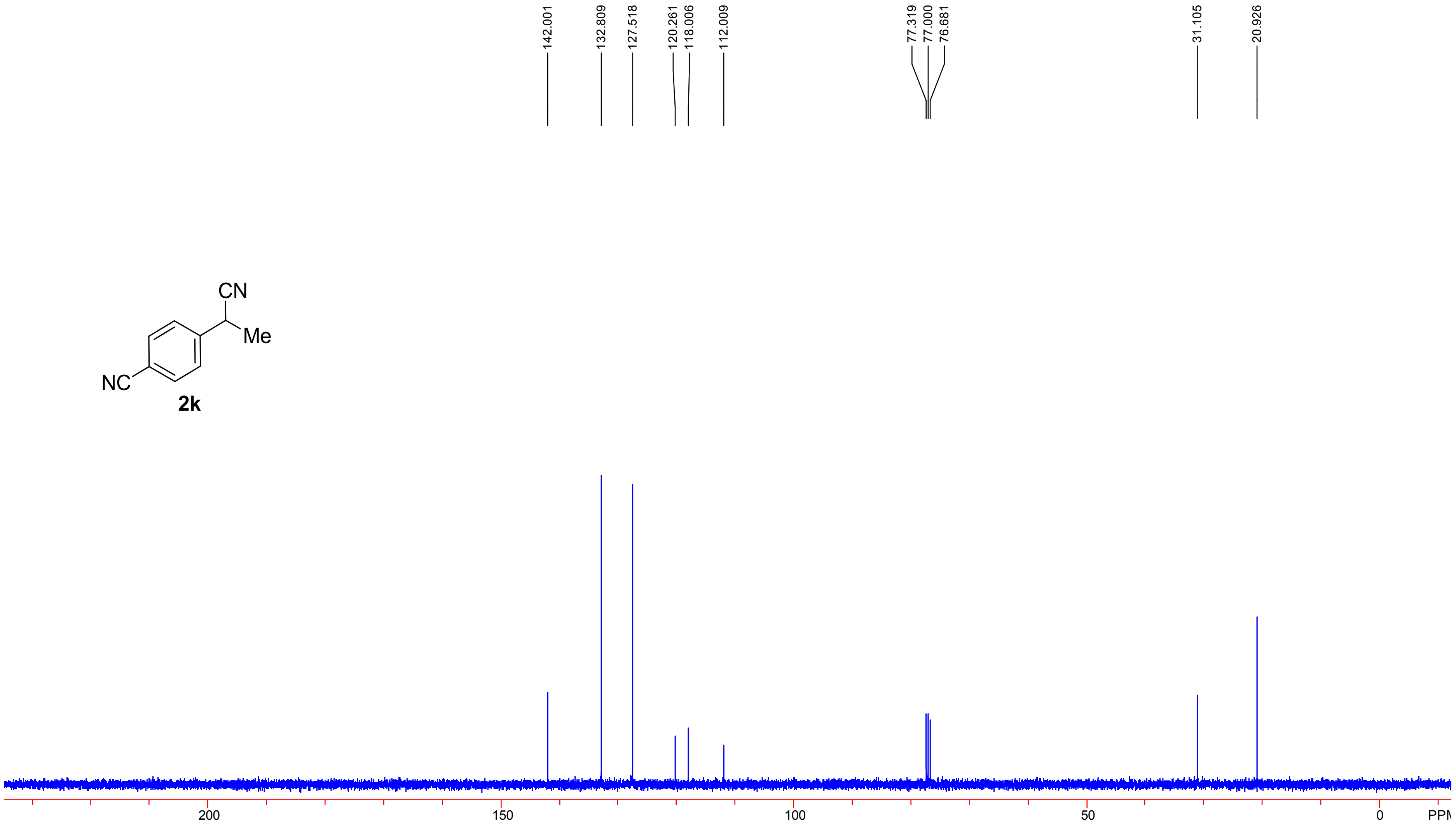
PPM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2k
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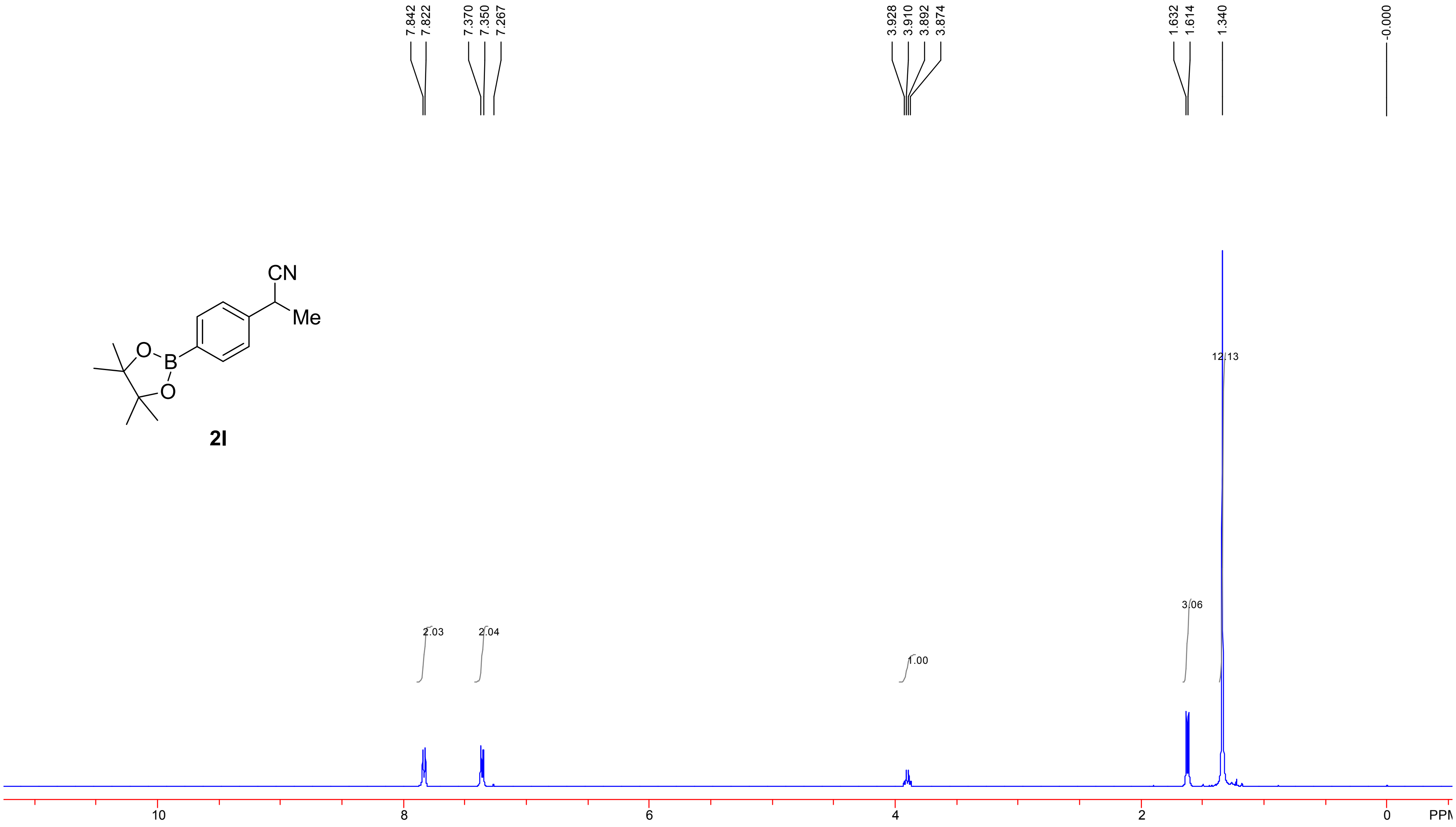
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3.892
3.874
1.632
1.614
1.340
-0.000
CN
Me
O
B
O
2.03
2.04
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2l

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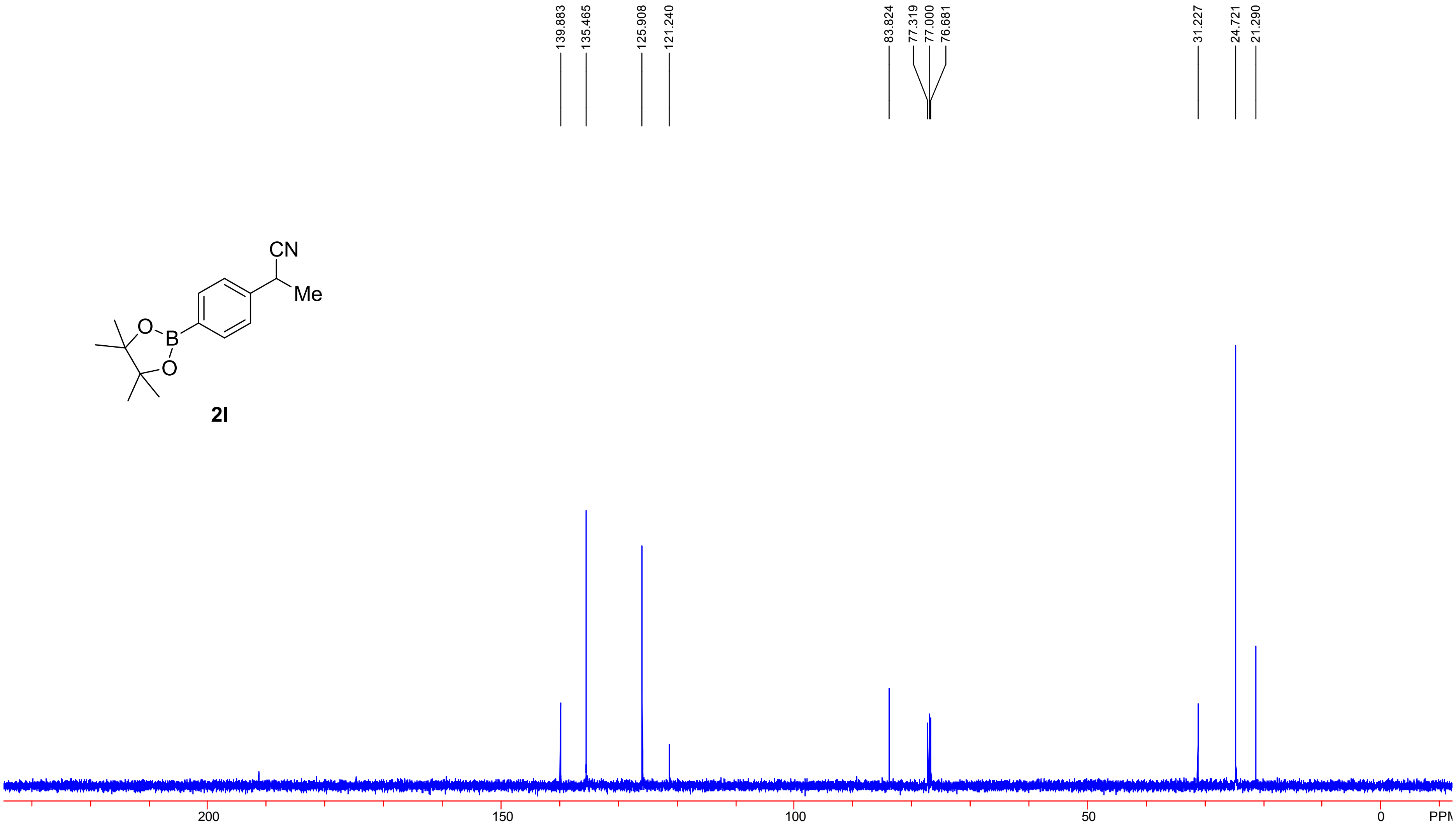
O
B
O

2l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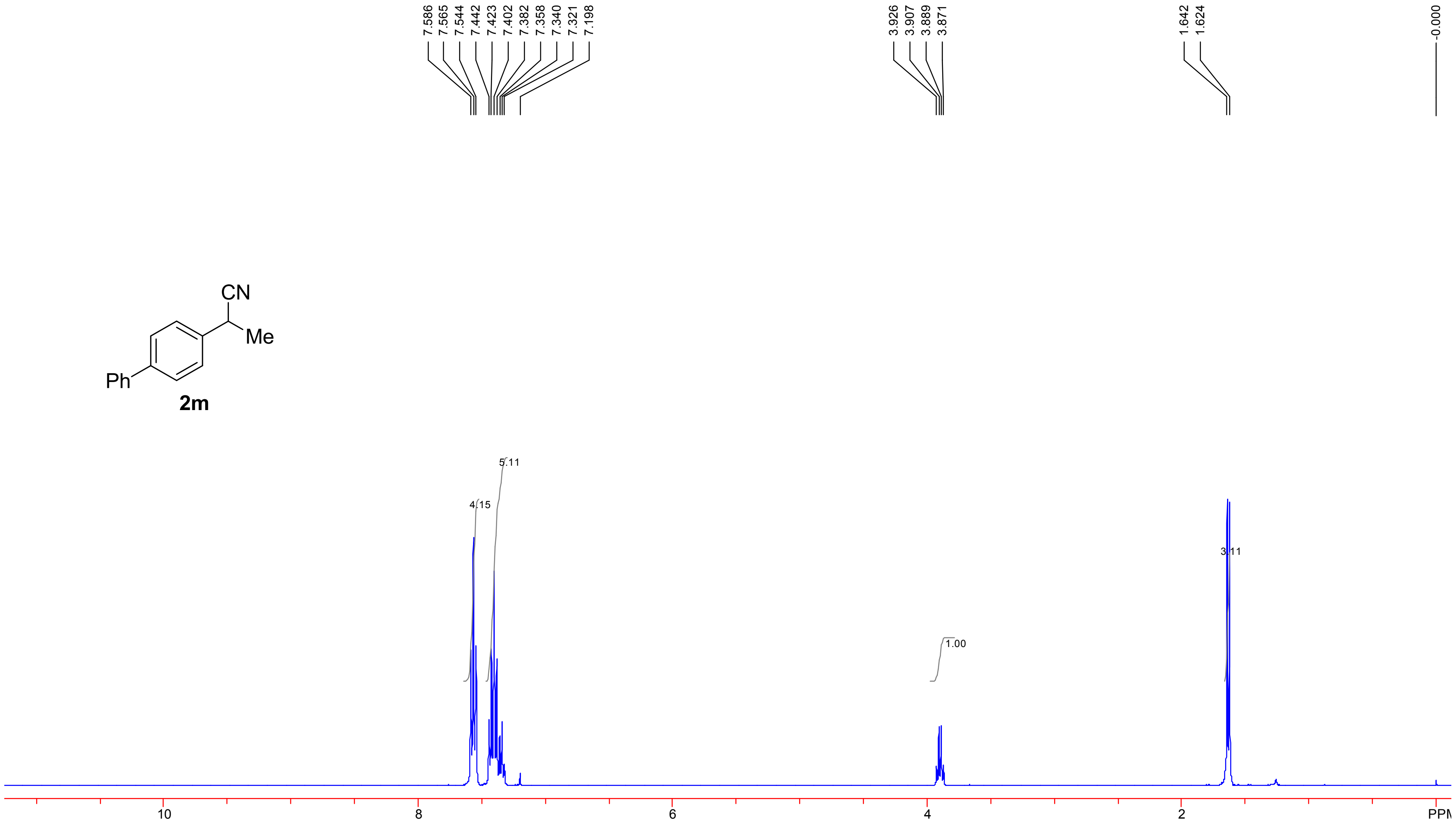
CN
Me
Ph

2m

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3.871
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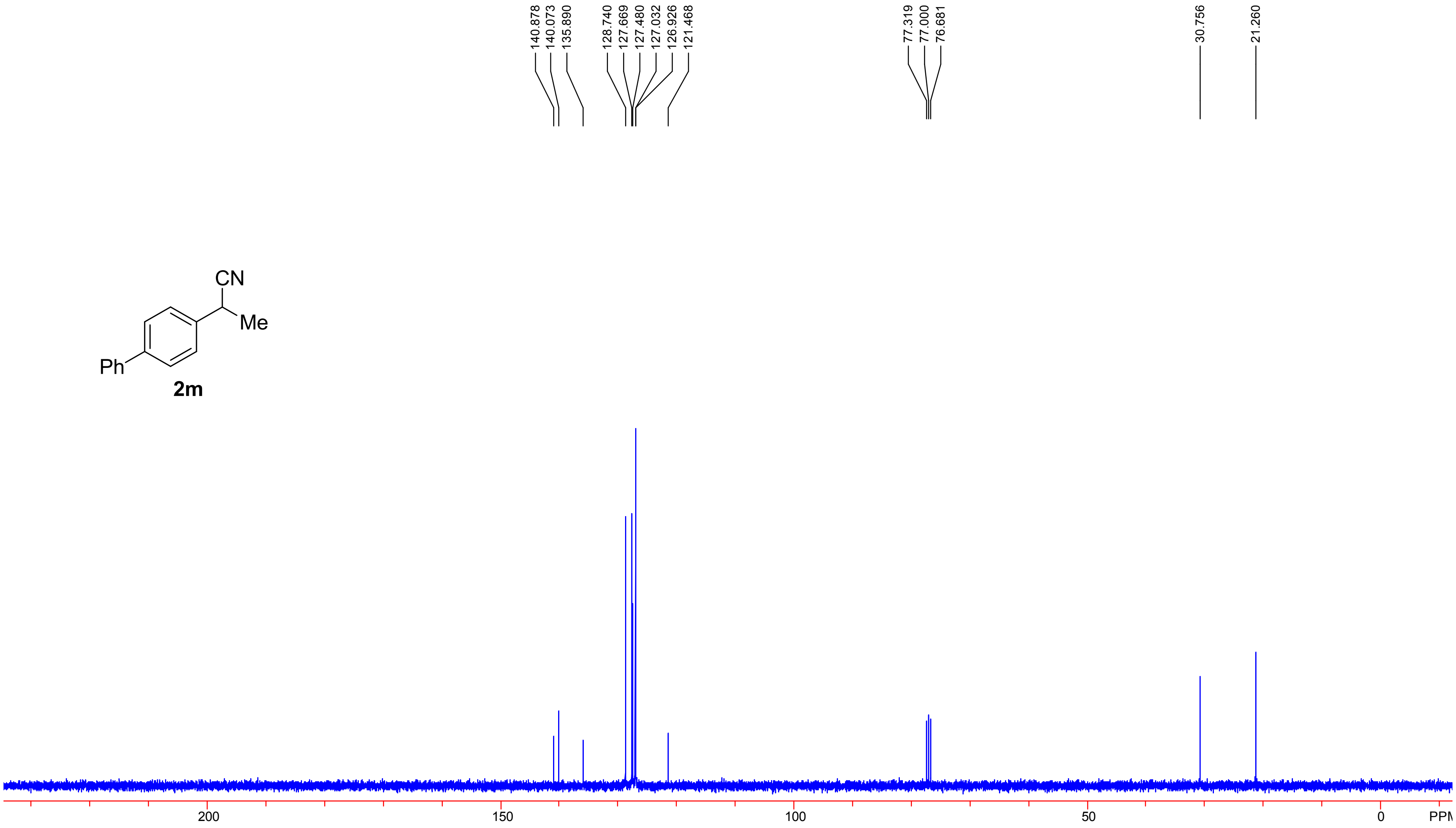
PPM

CN
Me
Ph

2m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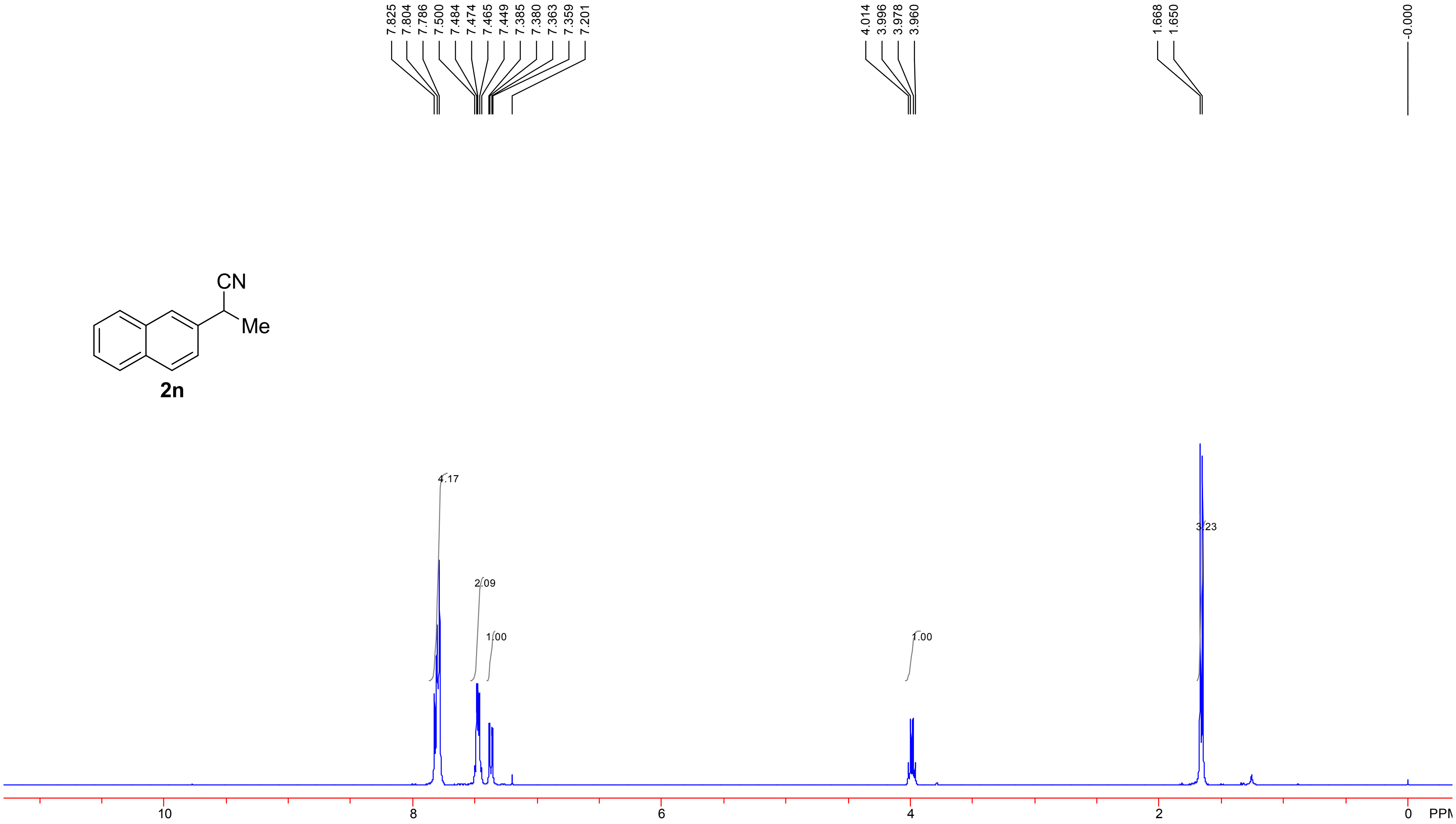
CN
Me

2n

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7.359
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3.978
3.960
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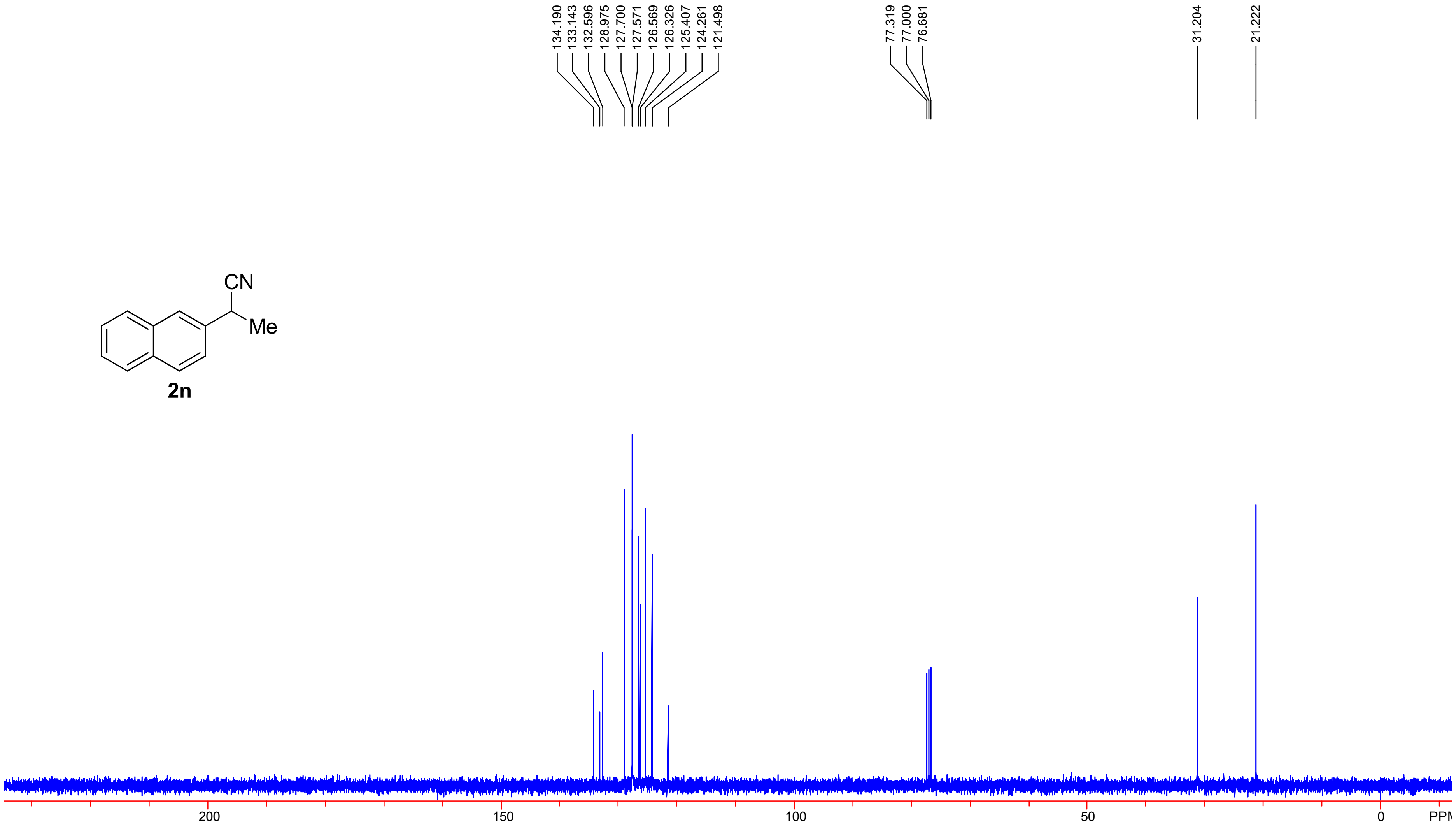
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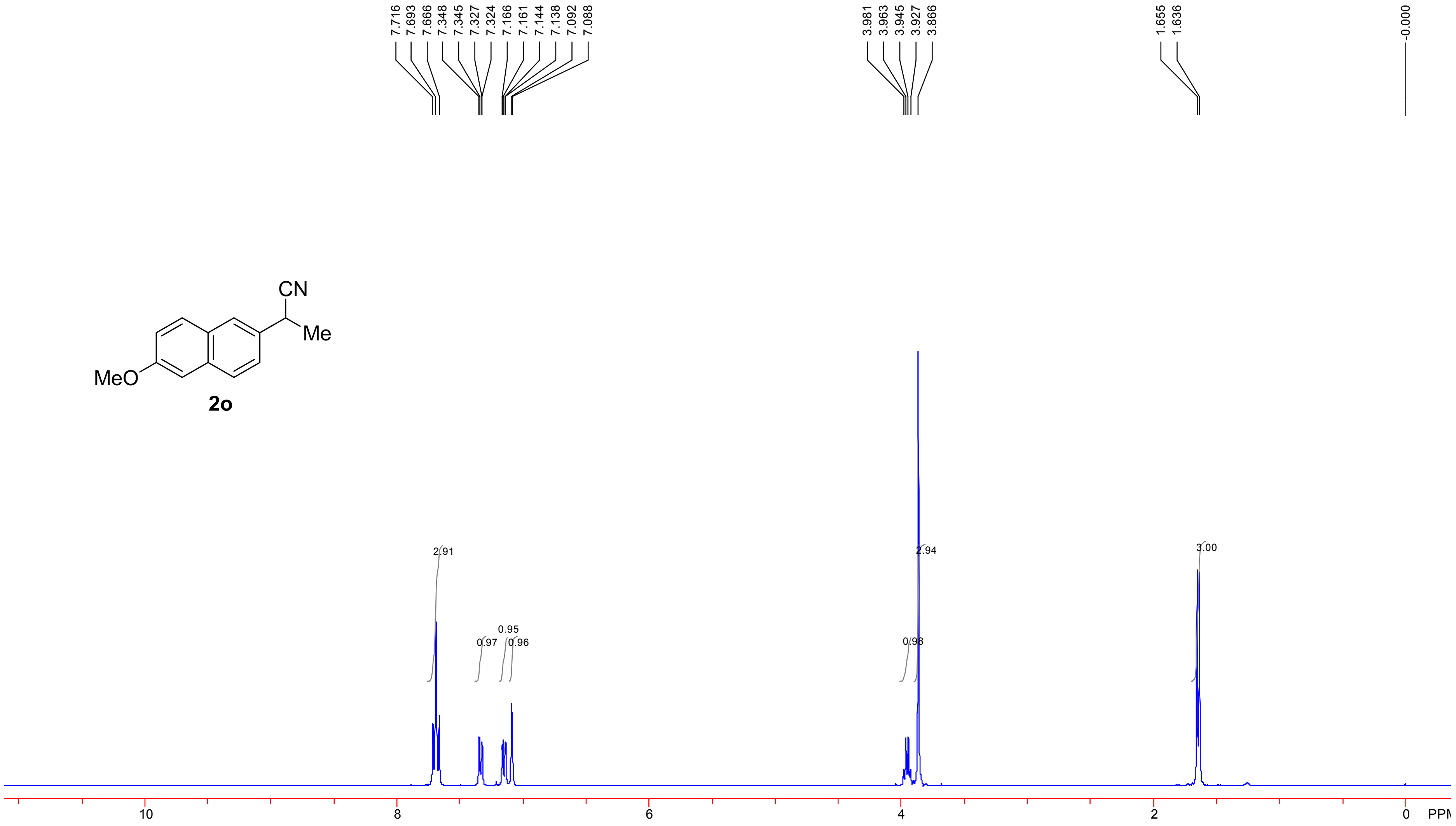
PPM

2n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3.963
3.945
3.927
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1.655
1.636
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CN
Me
MeO
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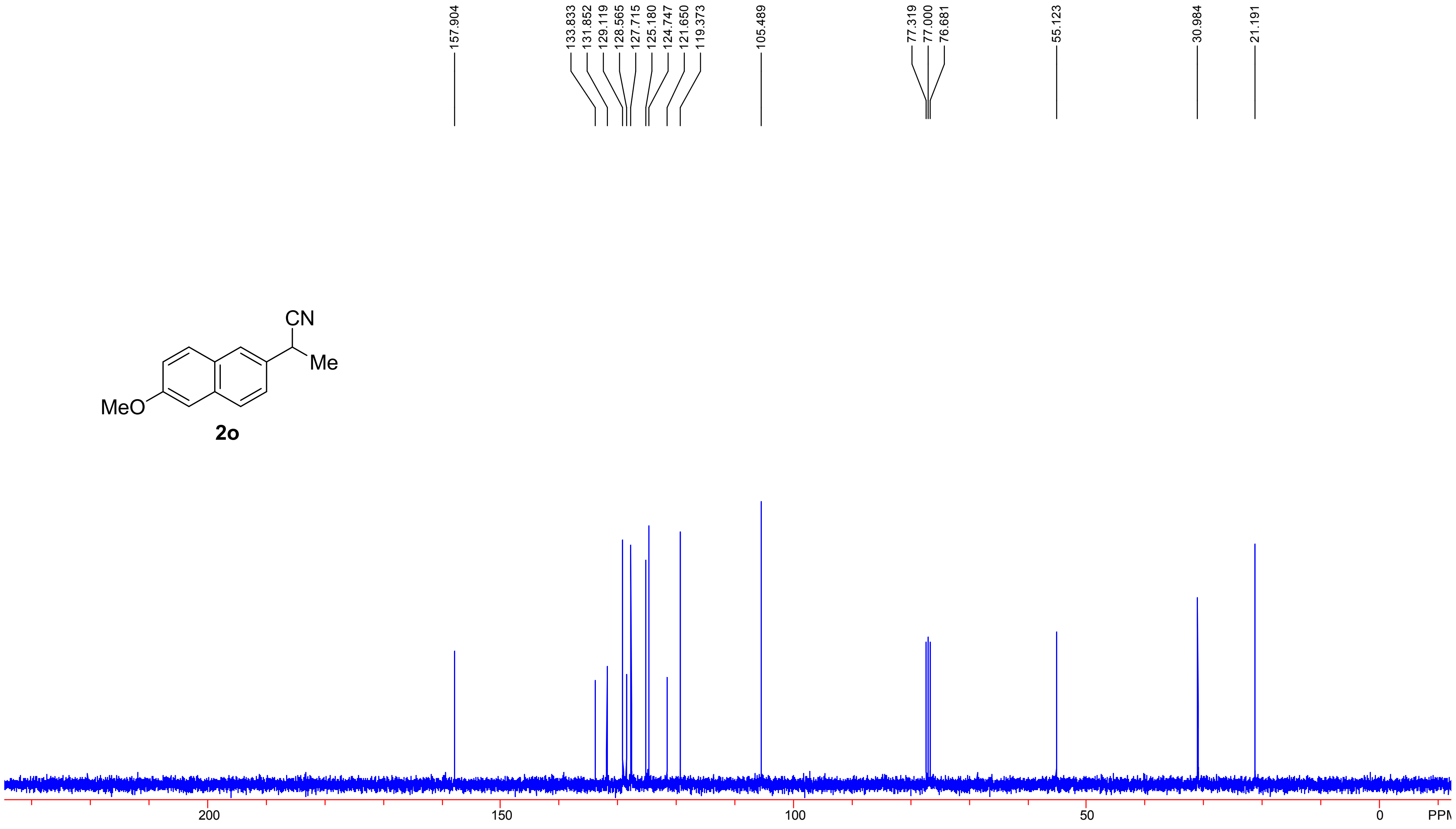

2o

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121.650
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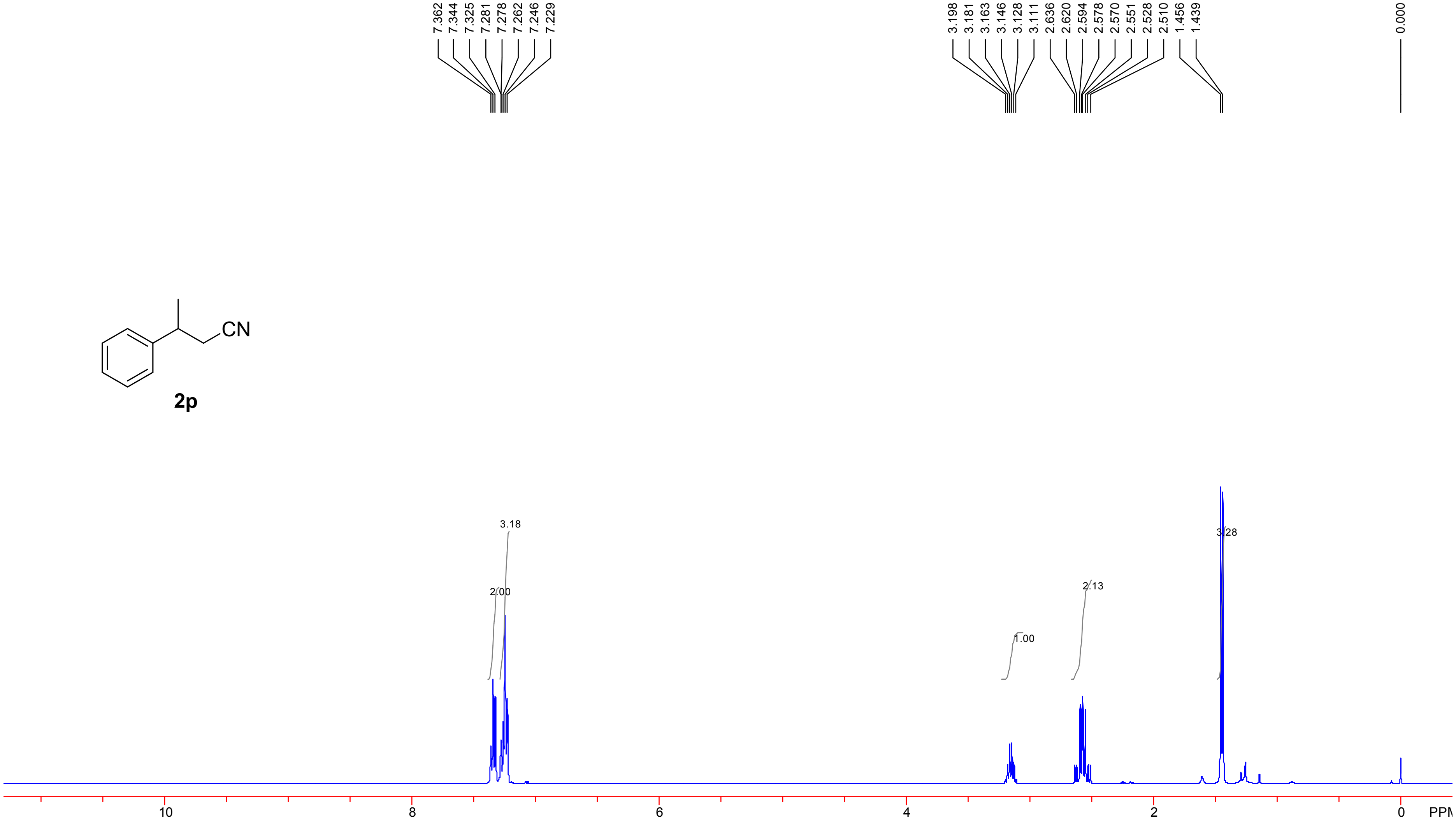
CN

2p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3.128
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2.594
2.578
2.570
2.551
2.528
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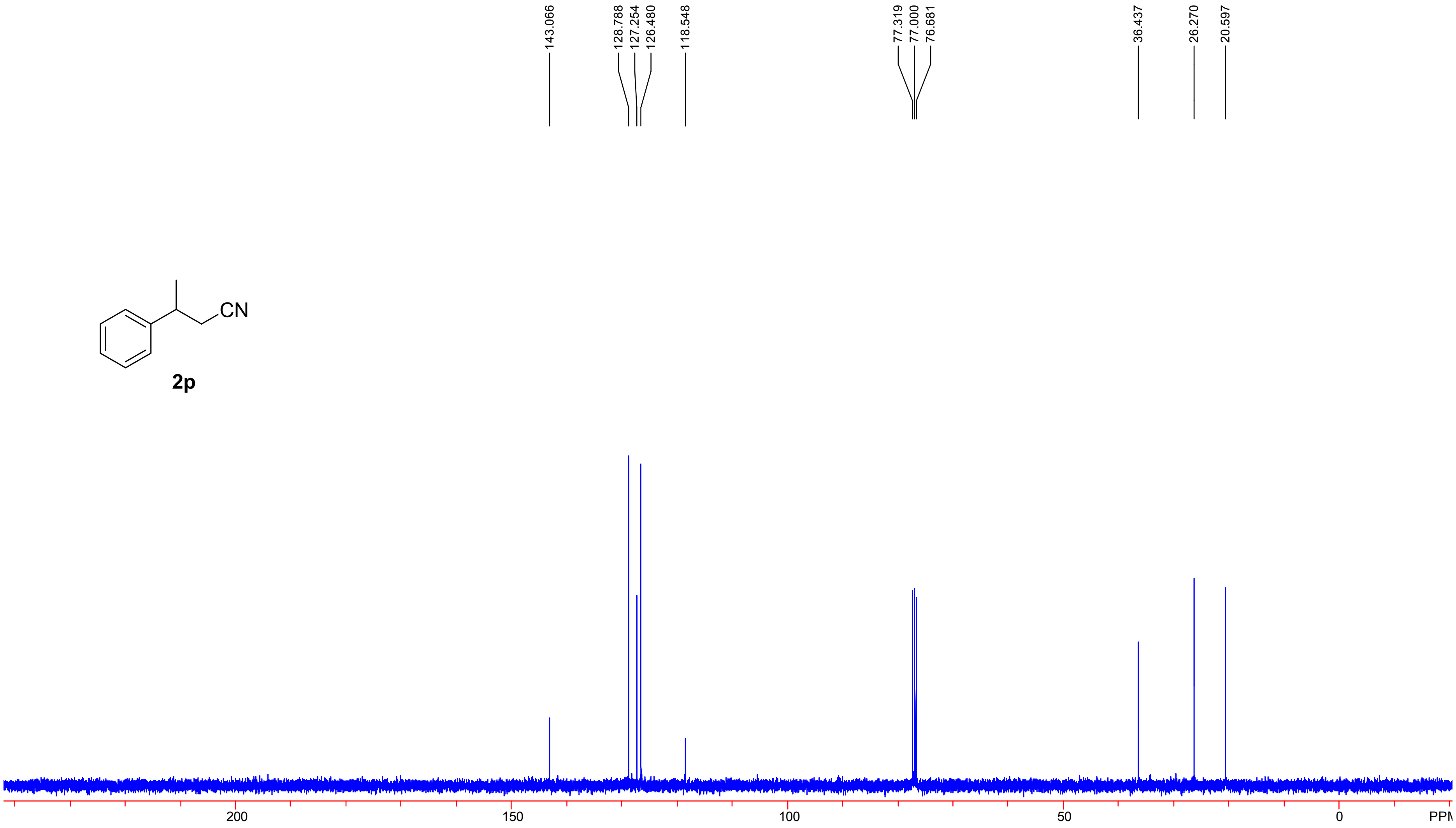
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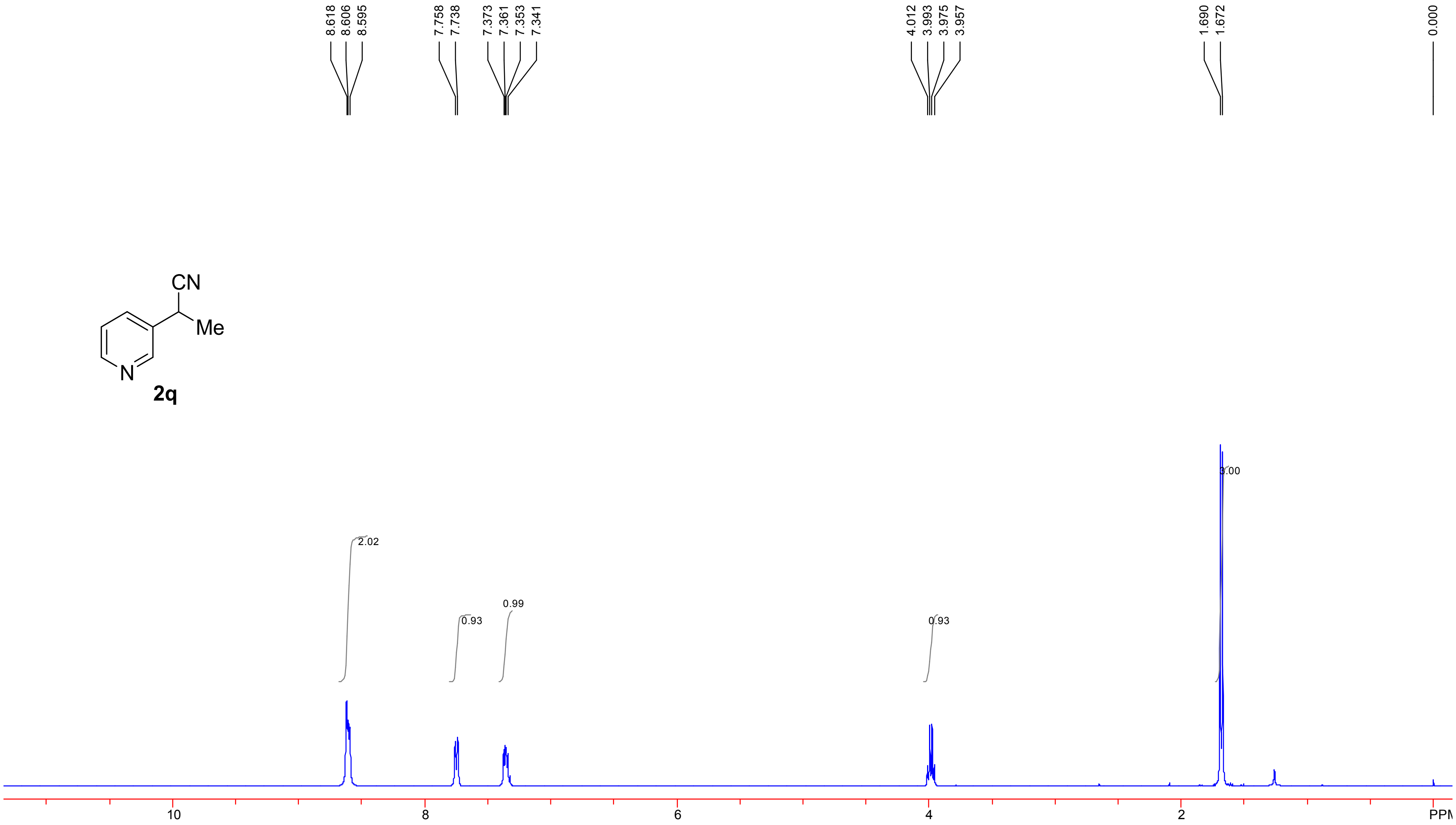
PPM

CN

2p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1.672
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10
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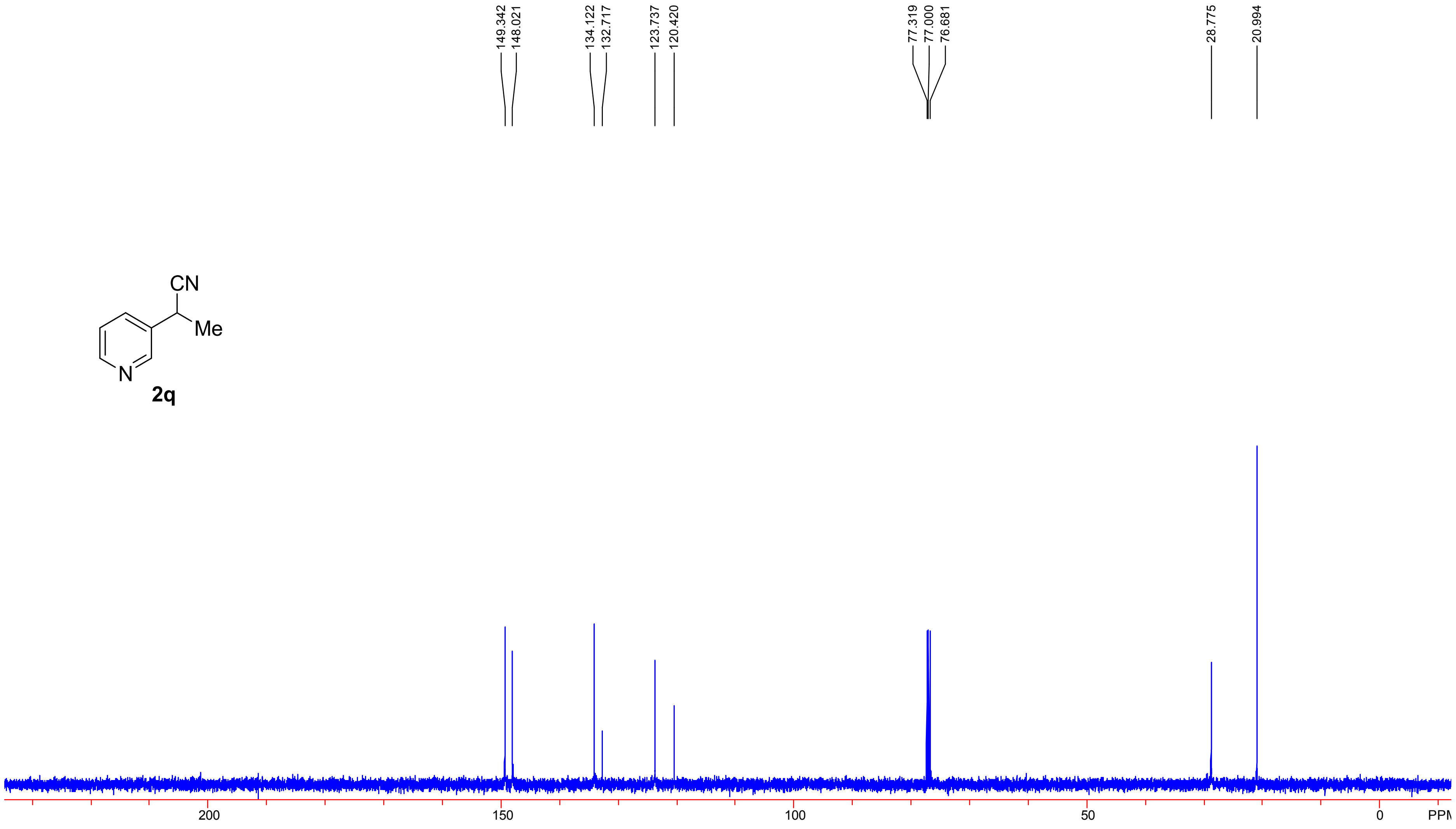
6
4
2
PPM

2q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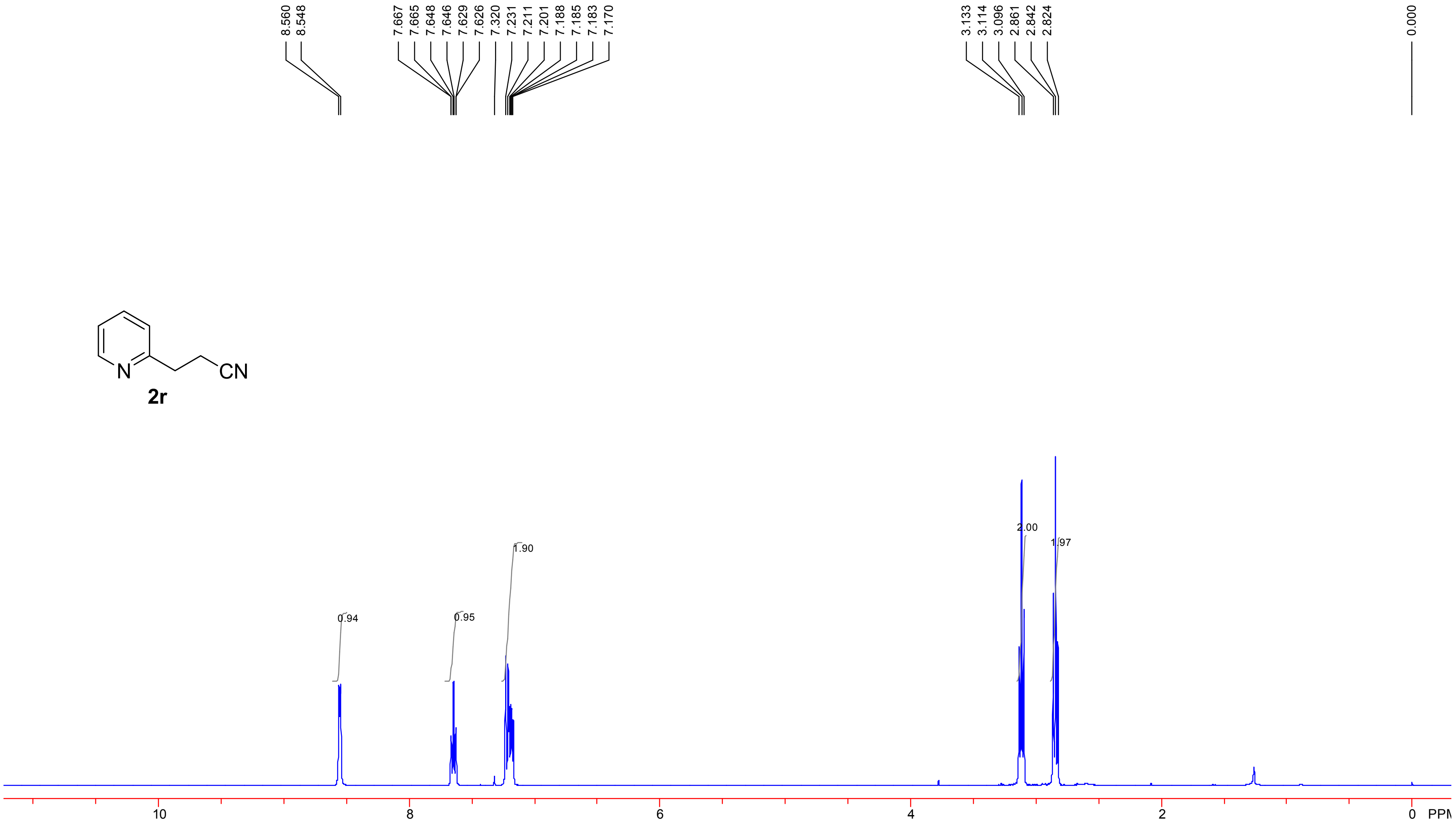
150
100
50
0
PPM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7.231
7.211
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7.188
7.185
7.183
7.170
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3.114
3.096
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2.824
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6
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2
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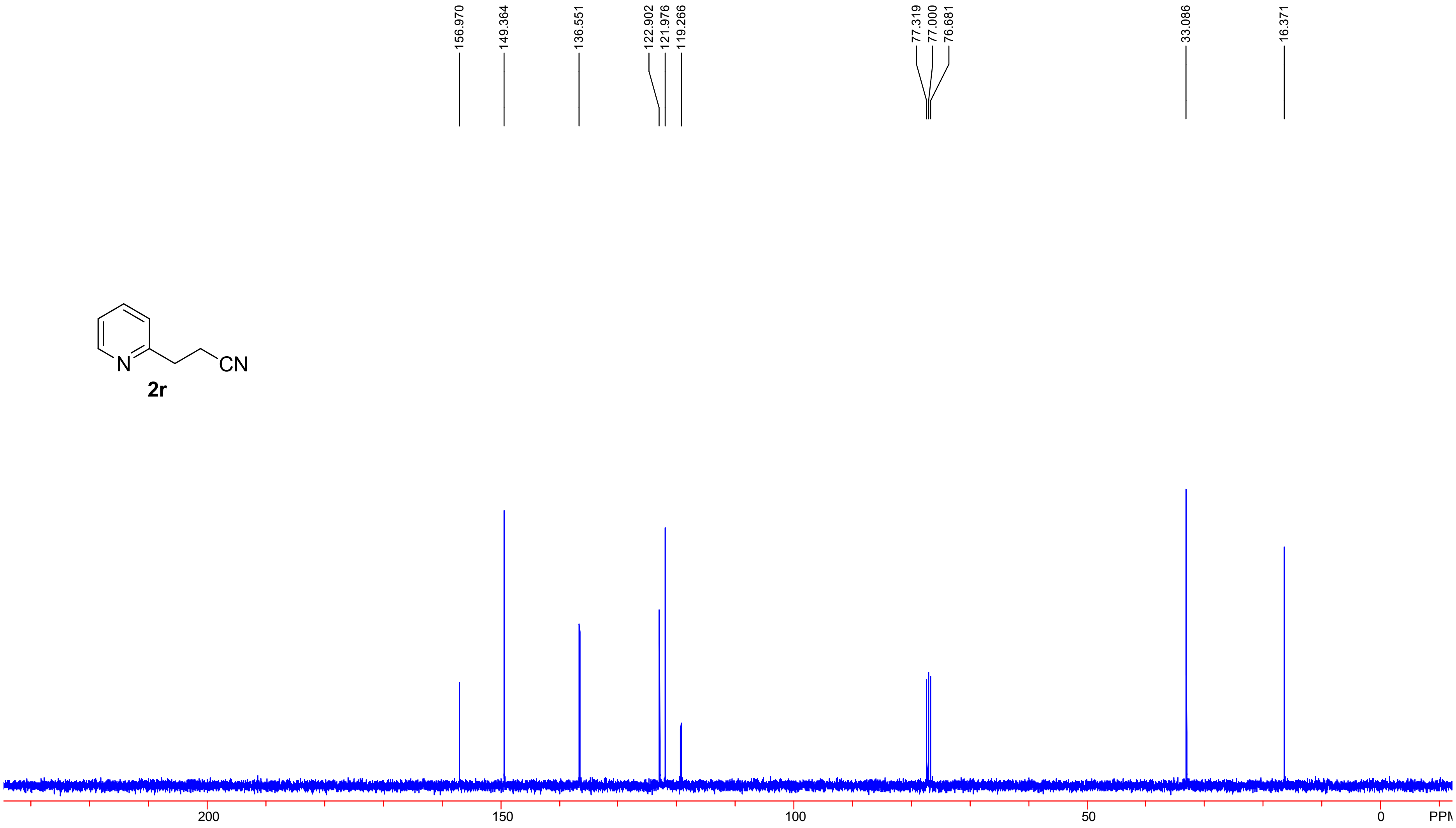
PPM

2r

2r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50
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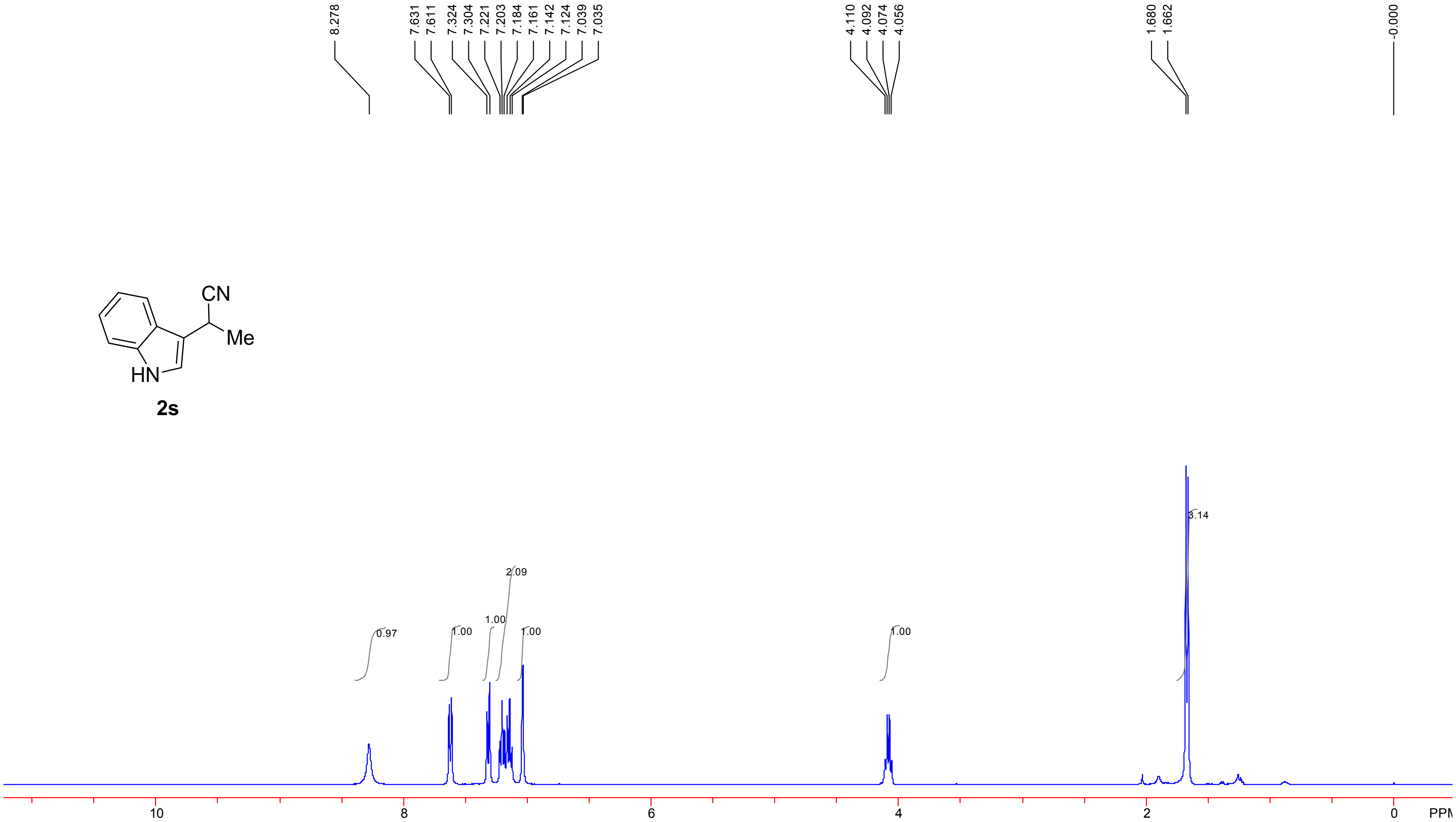
PPM

CN
Me
HN

2s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7.142
7.124
7.039
7.035
4.110
4.092
4.074
4.056
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1.662
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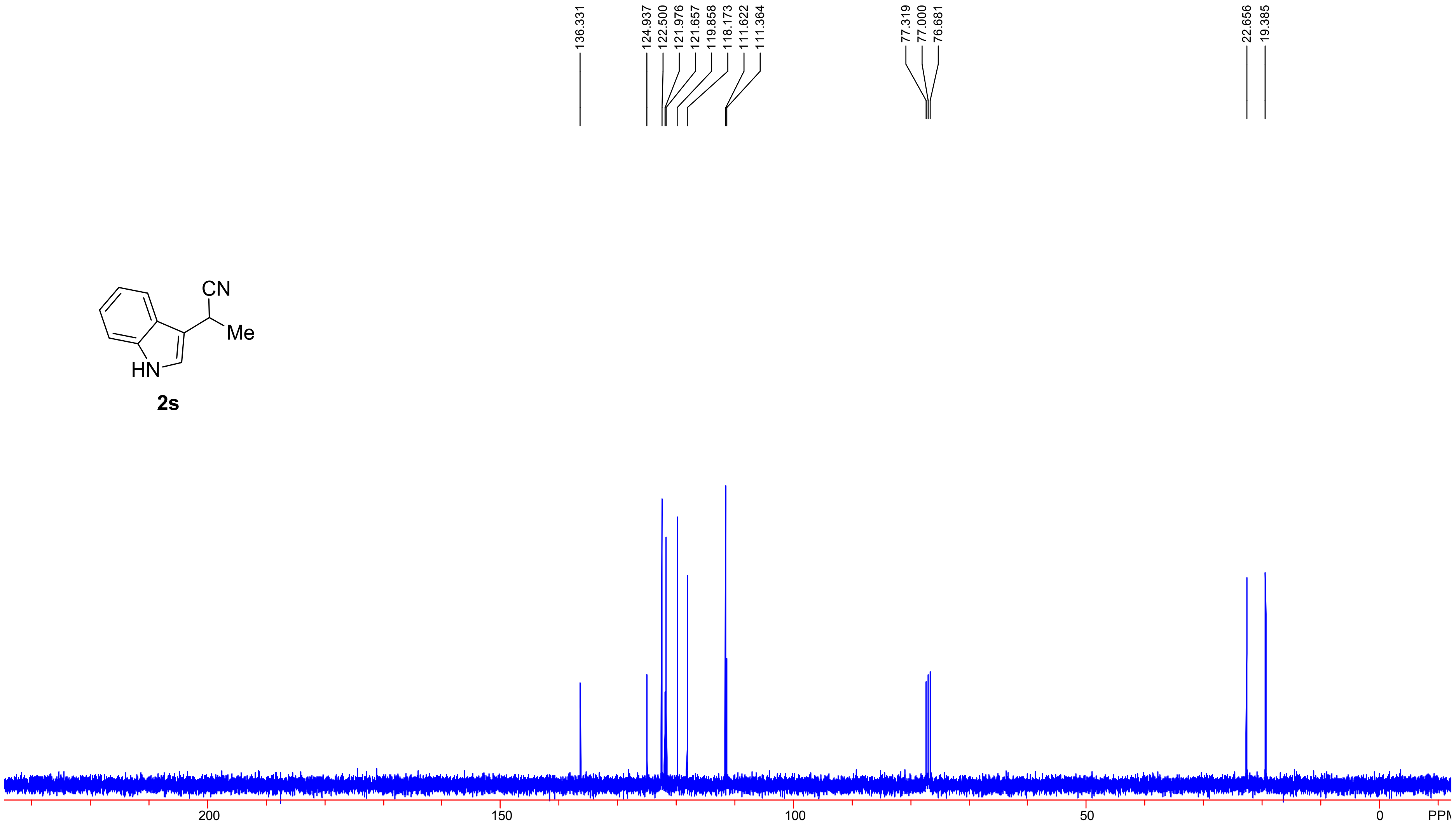

2s

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PPM

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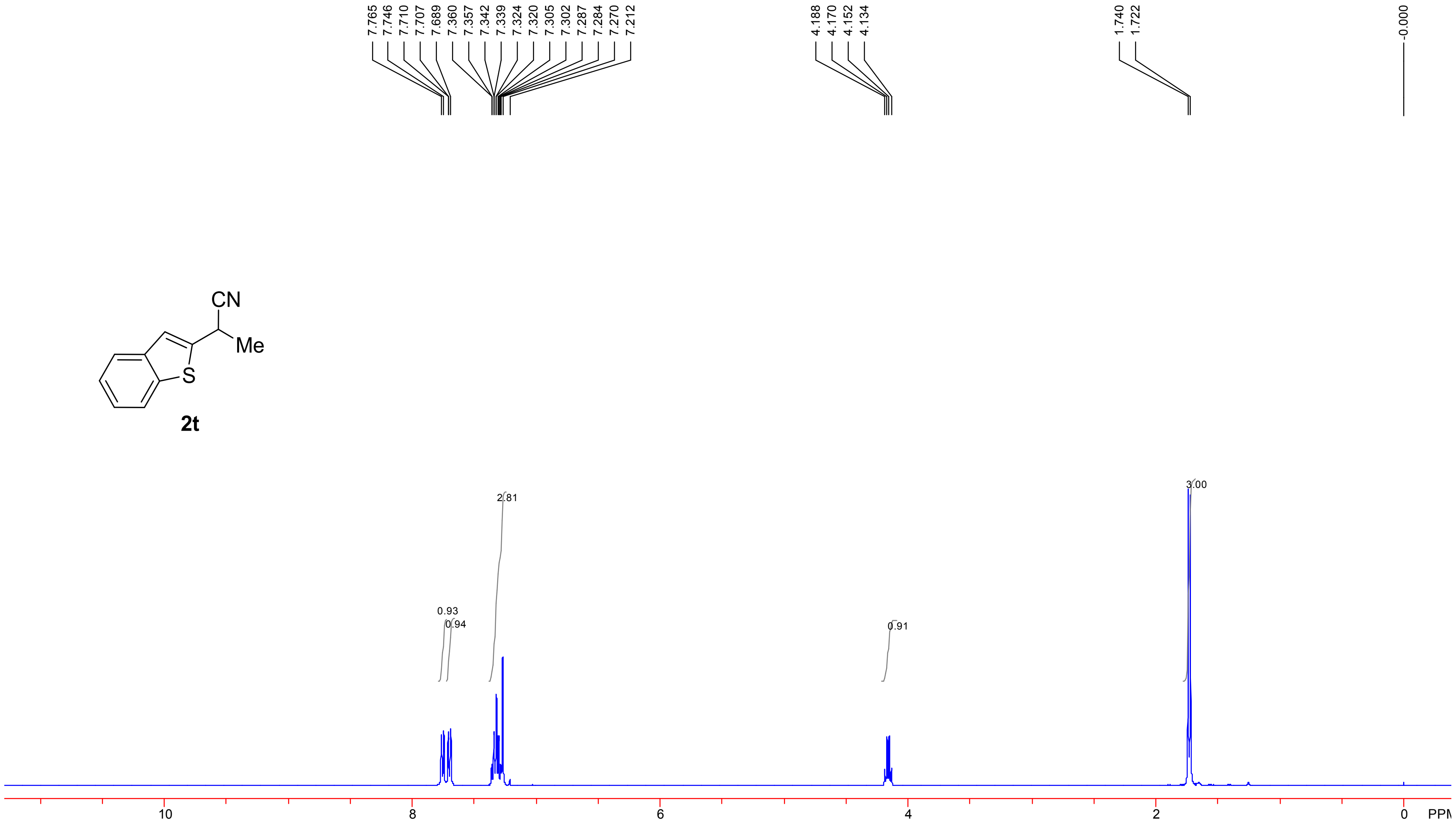
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7.302
7.287
7.284
7.270
7.212
4.188
4.170
4.152
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1.722
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0.94
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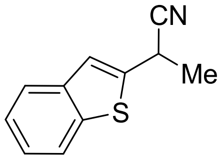
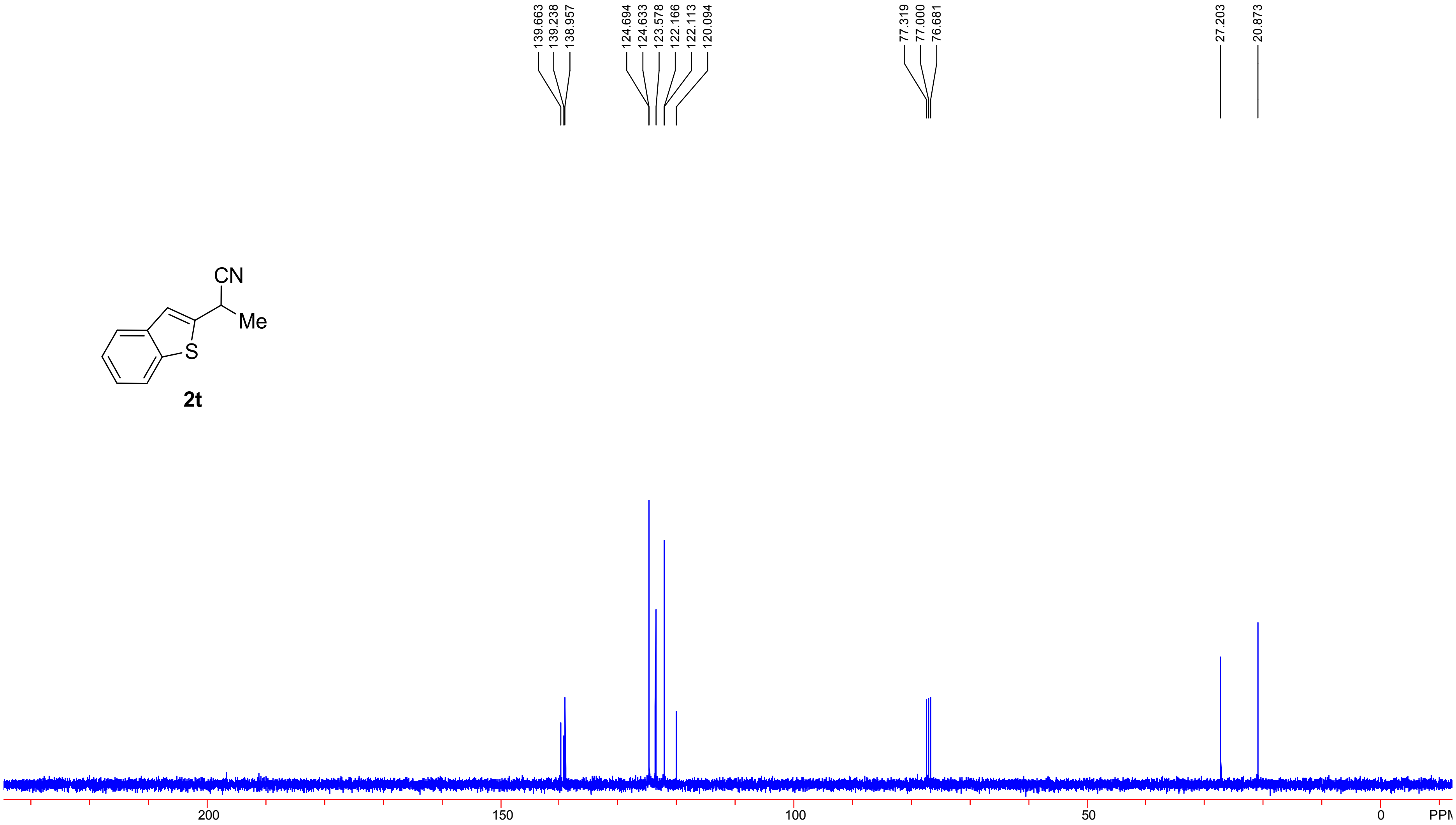
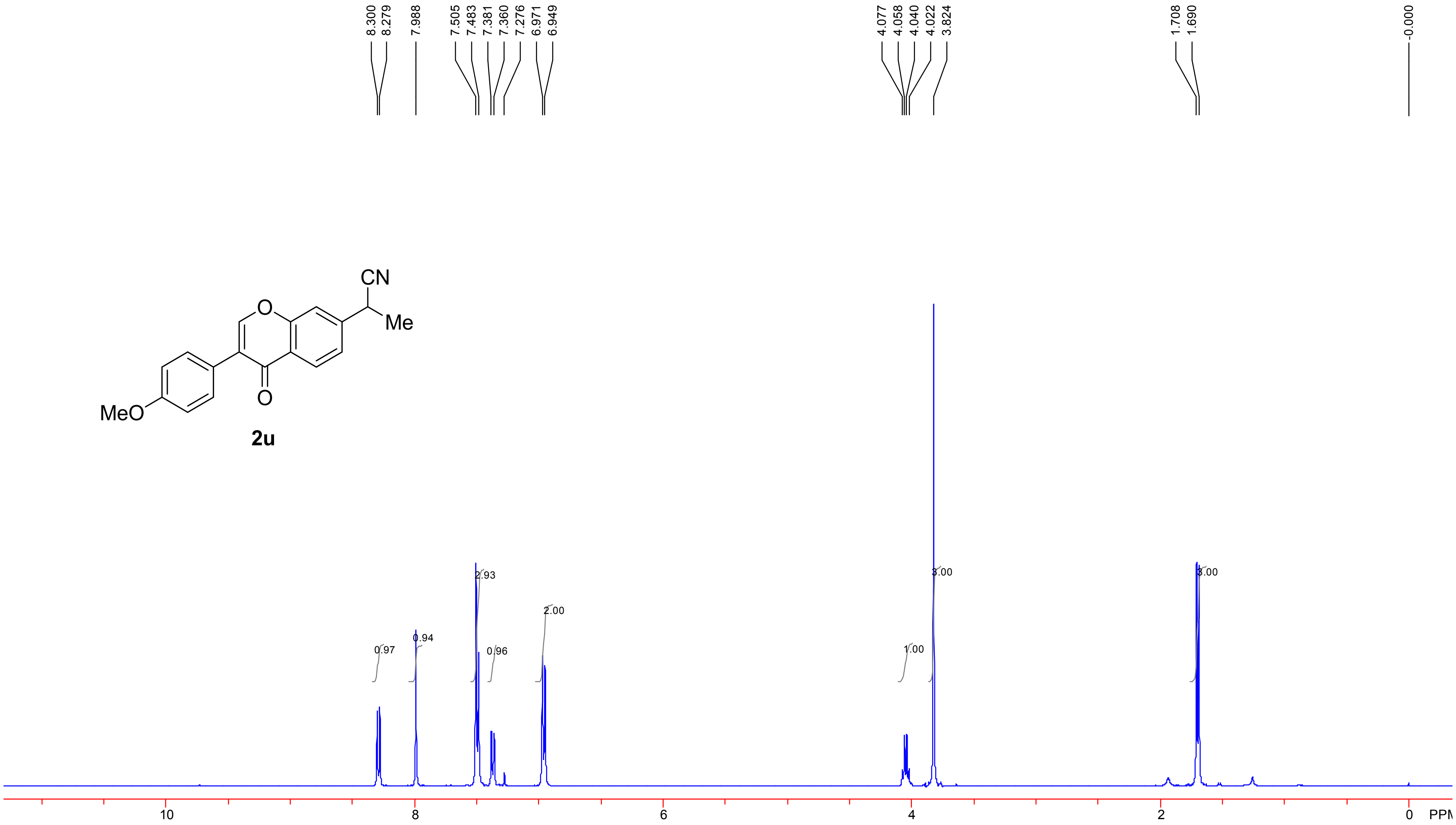
0.91
3.00
10
8
6
4
2
0
PPM


CN
Me
S

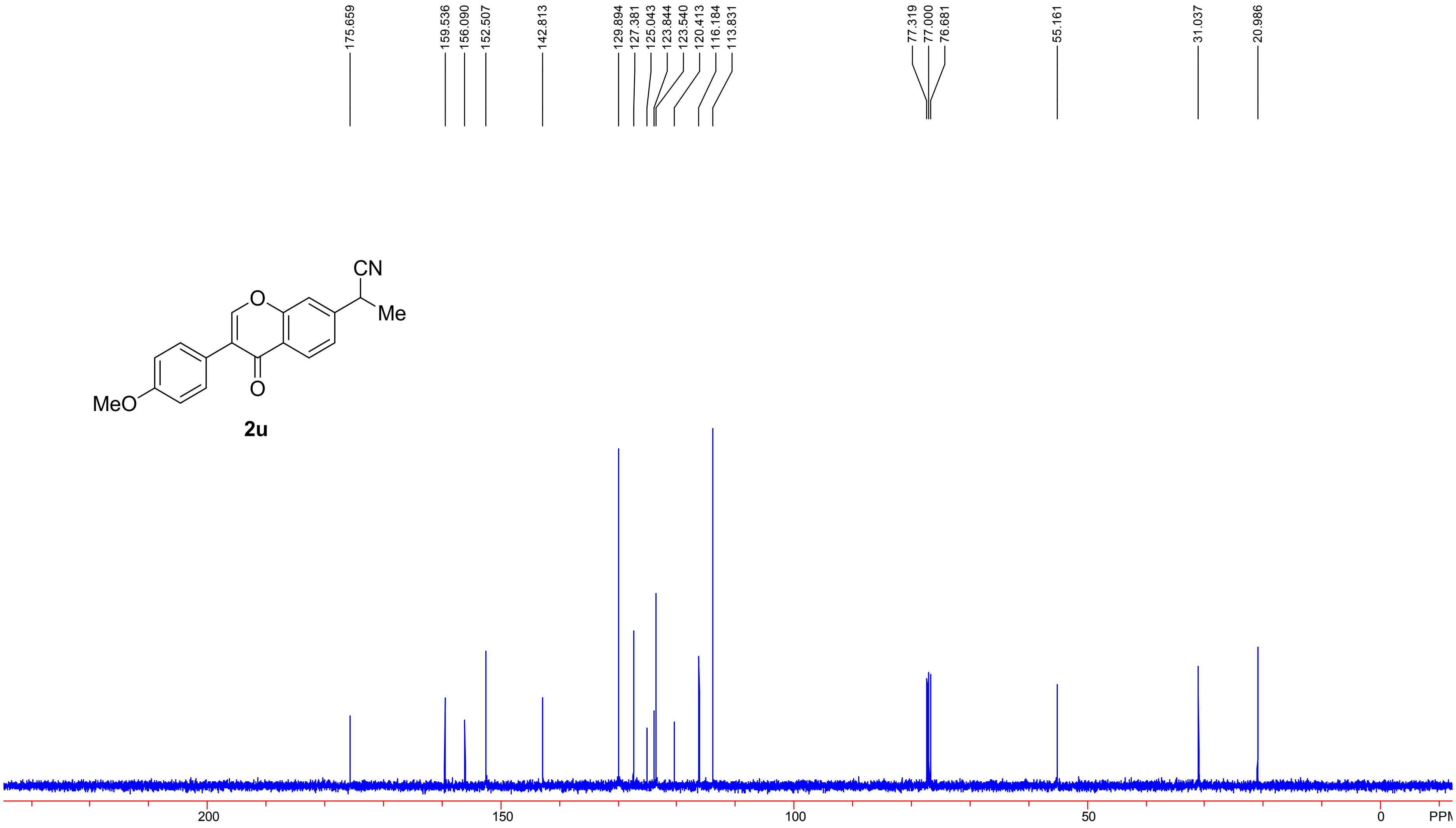
2t


139.663
139.238
138.957
124.694
124.633
123.578
122.166
122.113
120.094
77.319
77.000
76.681
27.203
20.873
200
150
100
50
0
PPM



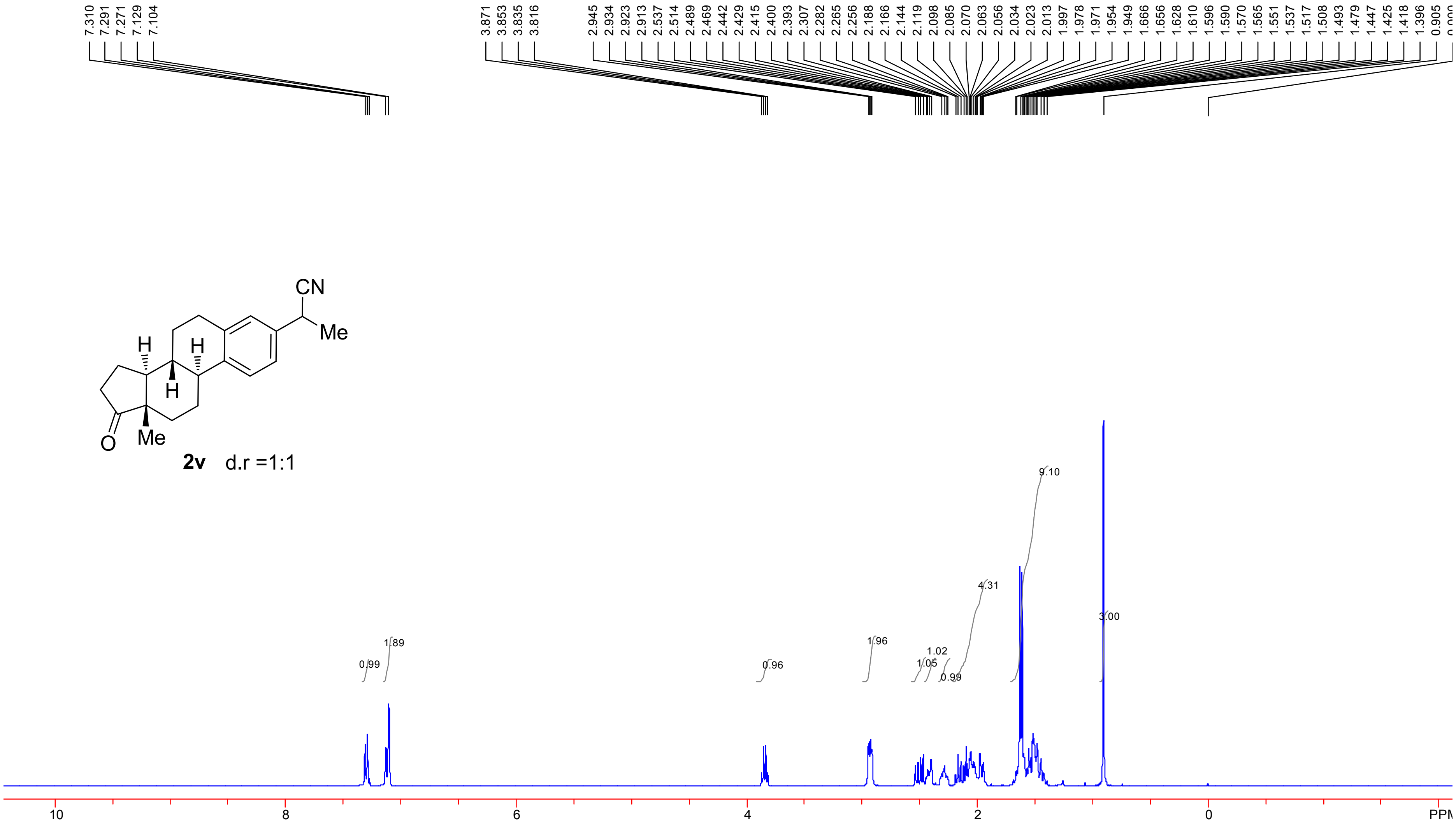
2u

8.300
8.279
7.988
7.505
7.483
7.381
7.360
7.276
6.971
6.949
4.077
4.058
4.040
4.022
3.824
1.708
1.690
-0.000
0.97
0.94
2.93
0.96
2.00
1.00
3.00
3.00
10
8
6
4
2
0
PPM

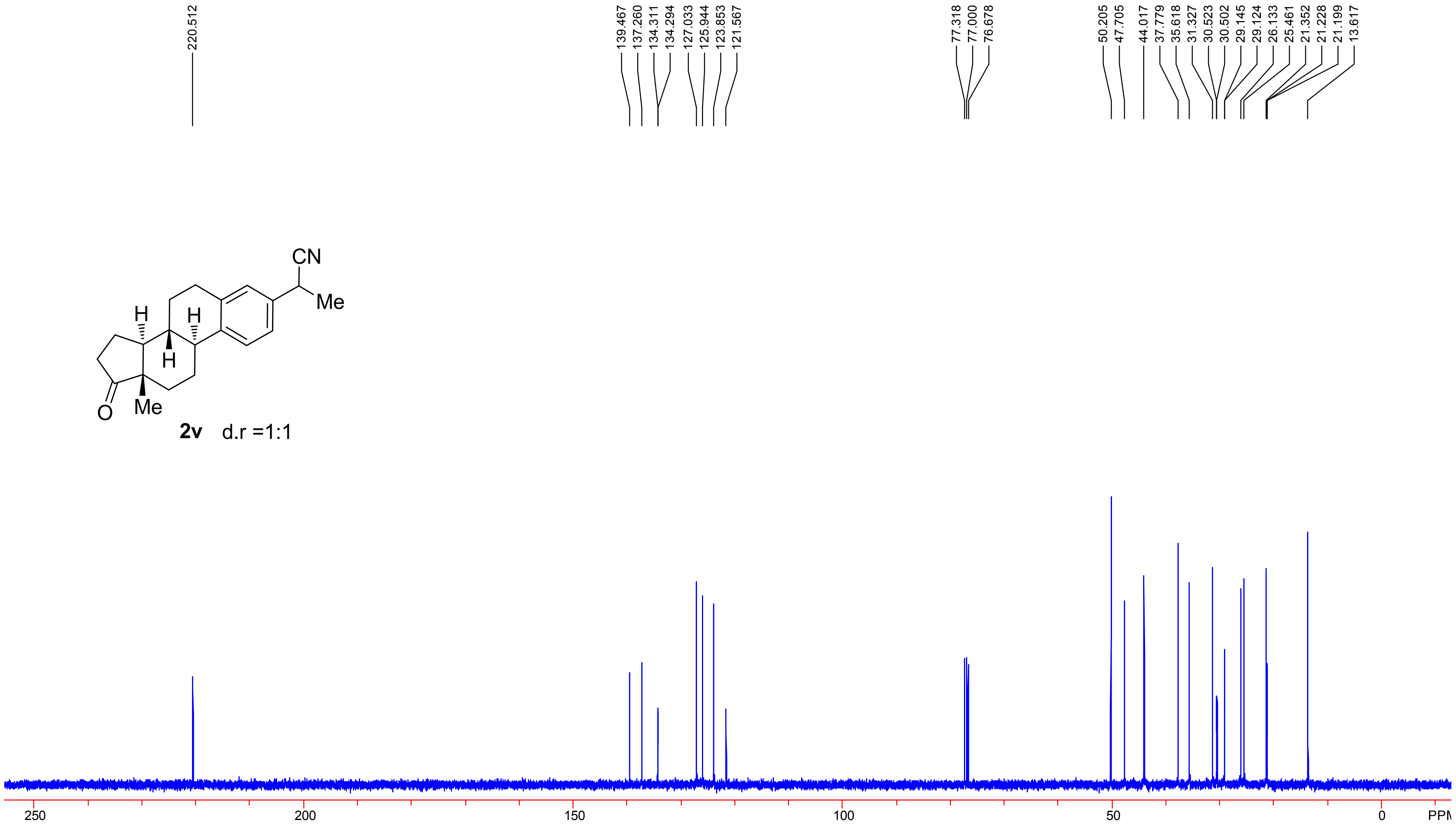

175.659
159.536
156.090
152.507
142.813
129.894
127.381
125.043
123.844
123.540
120.413
116.184
113.831
77.319
77.000
76.681
55.161
31.037
20.986
200
150
100
50
0
PPM

CN
O
Me
MeO
O

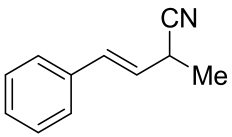
2u


7.310
7.291
7.271
7.129
7.104
3.871
3.853
3.835
3.816
2.945
2.934
2.923
2.913
2.537
2.514
2.489
2.469
2.442
2.429
2.415
2.400
2.393
2.307
2.282
2.265
2.256
2.188
2.166
2.144
2.119
2.098
2.085
2.070
2.063
2.056
2.034
2.023
2.013
1.997
1.978
1.971
1.954
1.949
1.666
1.656
1.628
1.610
1.596
1.590
1.570
1.565
1.551
1.537
1.517
1.508
1.493
1.479
1.447
1.425
1.418
1.396
0.905
CN
Me
H
H
H
O
Me
0.99
1.89
0.96
1.96
1.05
1.02
0.99
4.31
9.10
3.00
10
8
6
4
2
0
PP

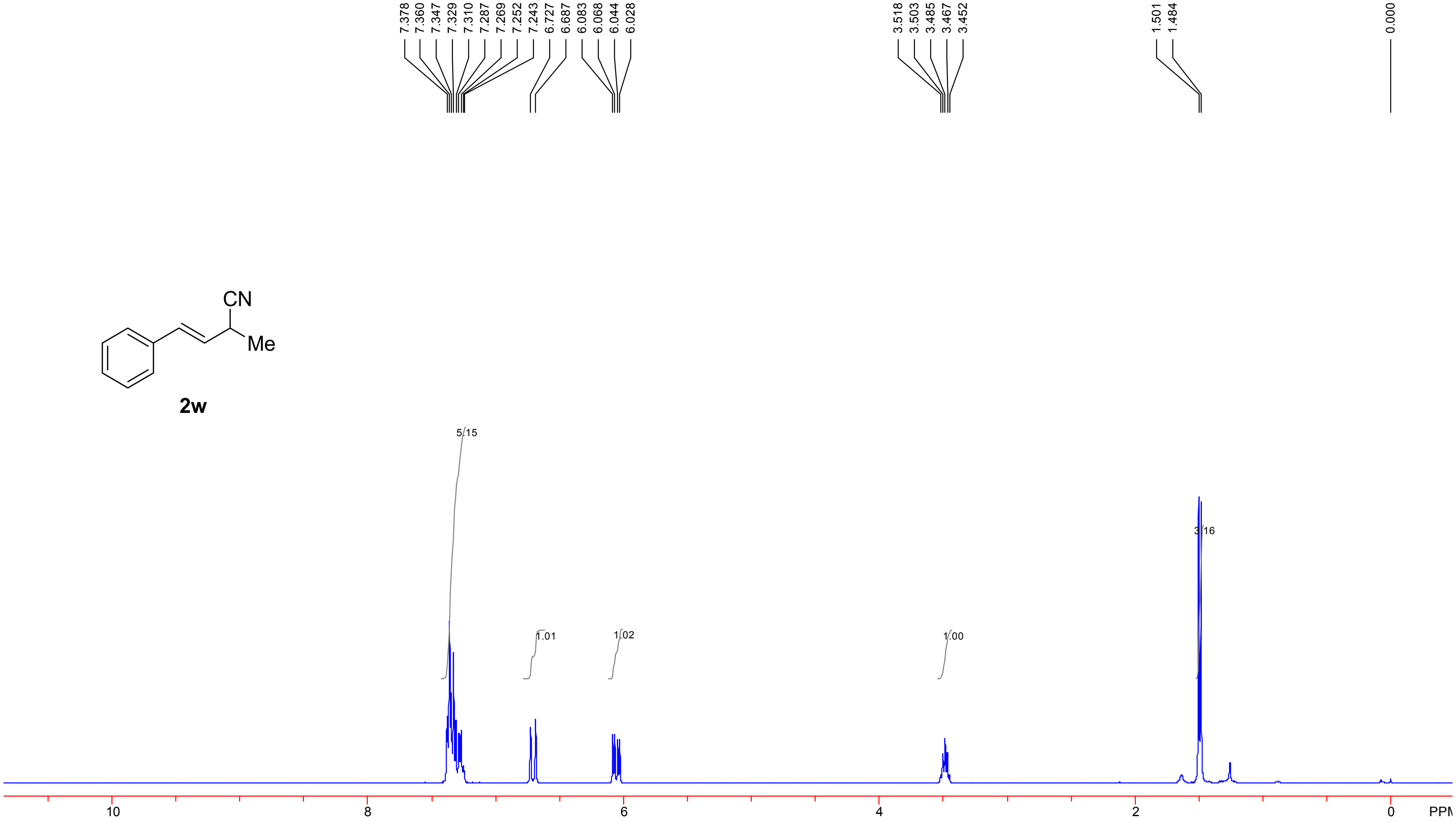
2v d.r =1:1

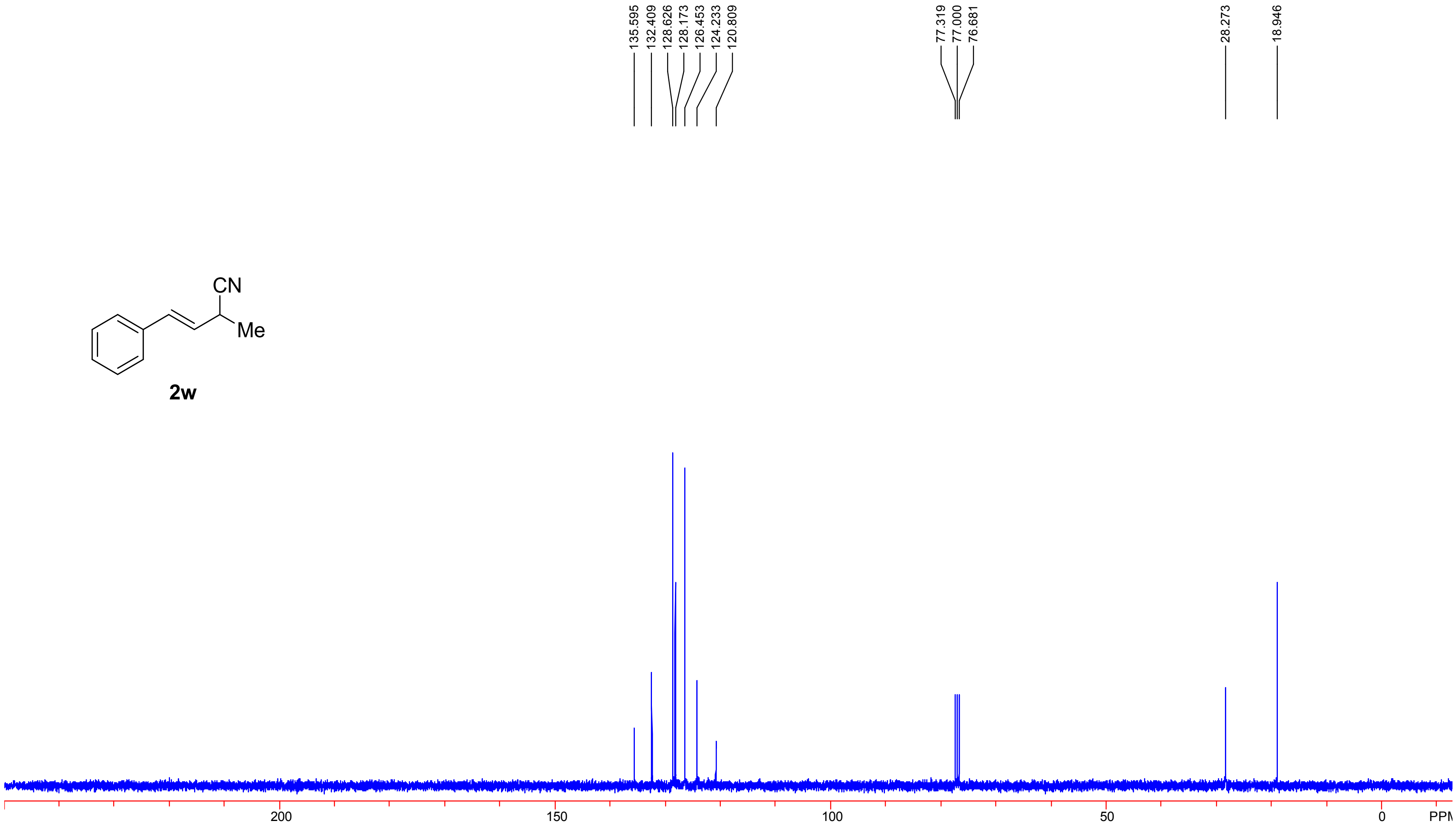

220.512
139.467
137.260
134.311
134.294
127.033
125.944
123.853
121.567
77.318
77.000
76.678
50.205
47.705
44.017
37.779
35.618
31.327
30.523
30.502
29.145
29.124
26.133
25.461
21.352
21.228
21.199
13.617
250
200
150
100
50
0
PPM
CN
Me
H
H
H
O
Me

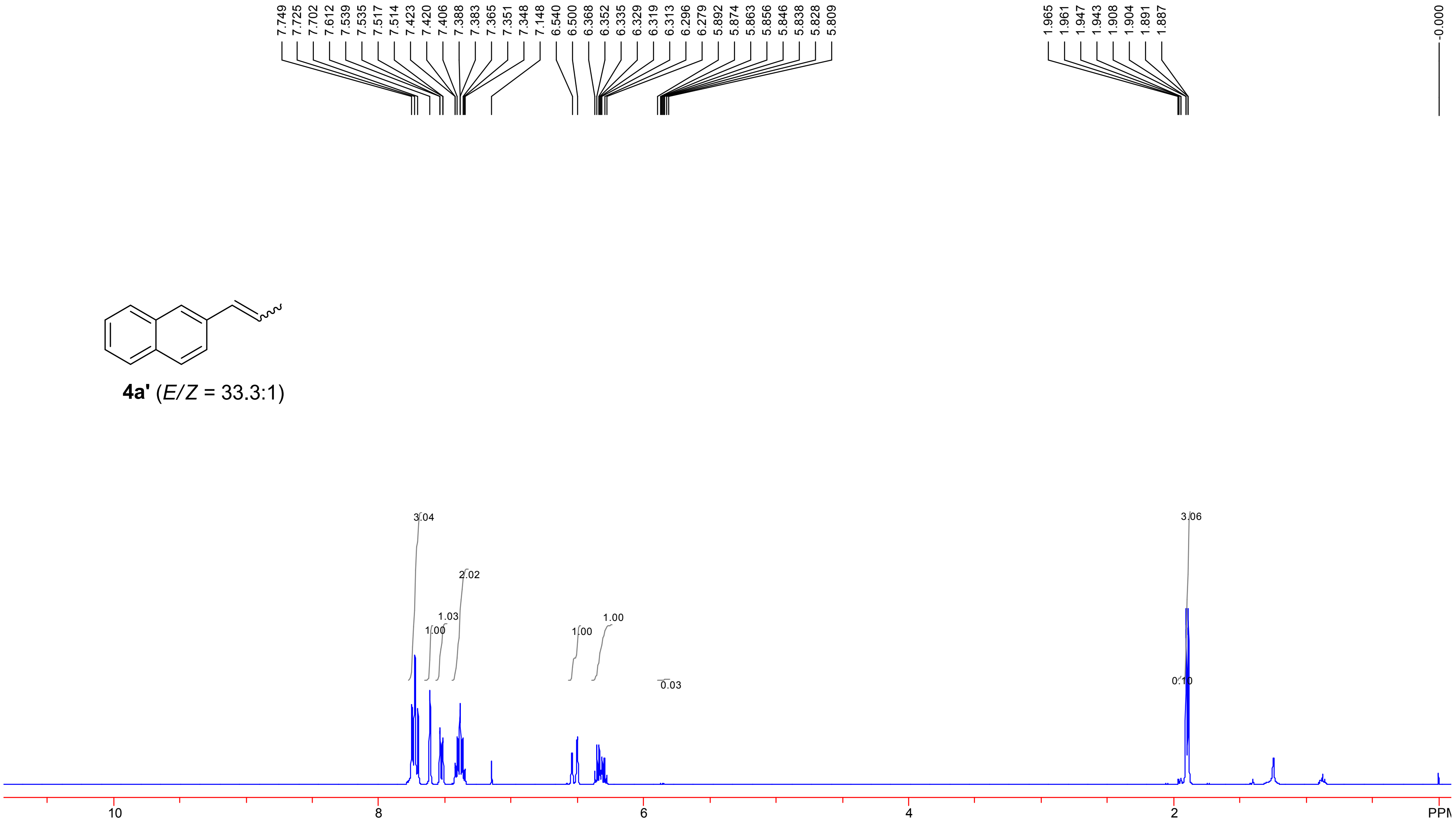
2v d.r =1:1


CN
Me

2w

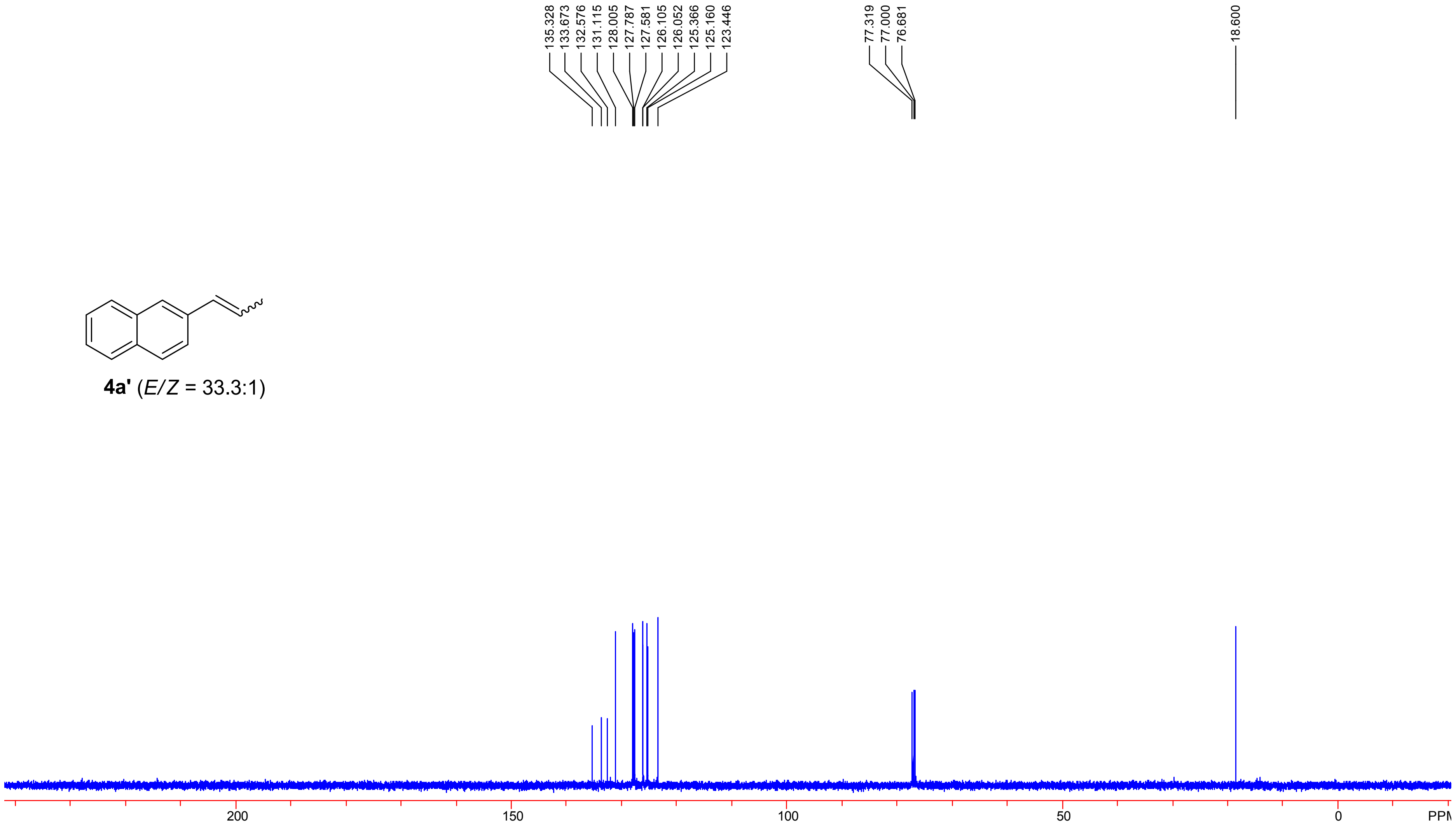

7.378
7.360
7.347
7.329
7.310
7.287
7.269
7.252
7.243
6.727
6.687
6.083
6.068
6.044
6.028
3.518
3.503
3.485
3.467
3.452
1.501
1.484
0.000
5.15
1.01
1.02
1.00
3.16
10
8
6
4
2
0
PPM


2w
135.595
132.409
128.626
128.173
126.453
124.233
120.809
77.319
77.000
76.681
28.273
18.946
CN
Me
200
150
100
50
0
PPM

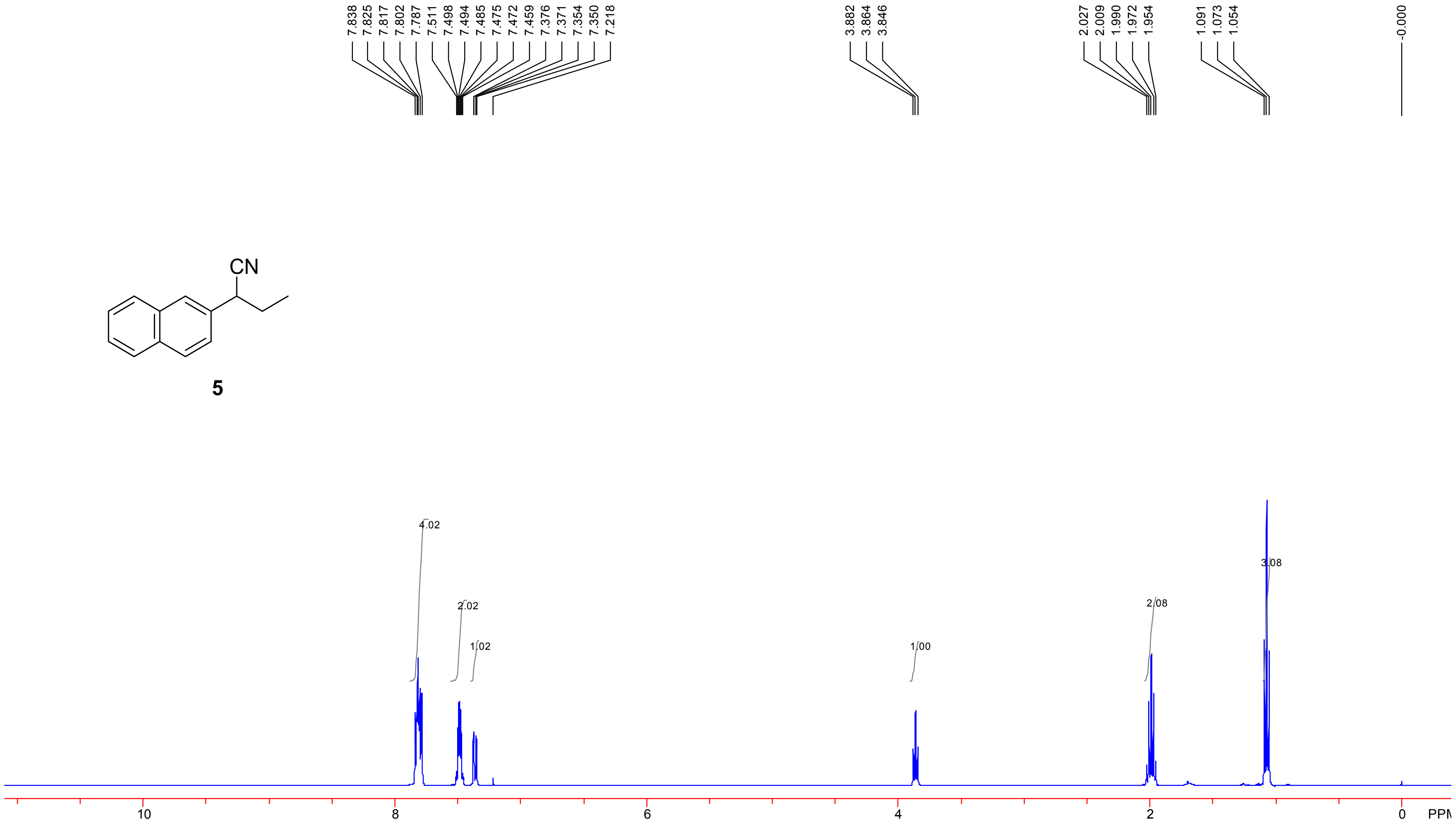


4a' (*E*/*Z* = 33.3:1)

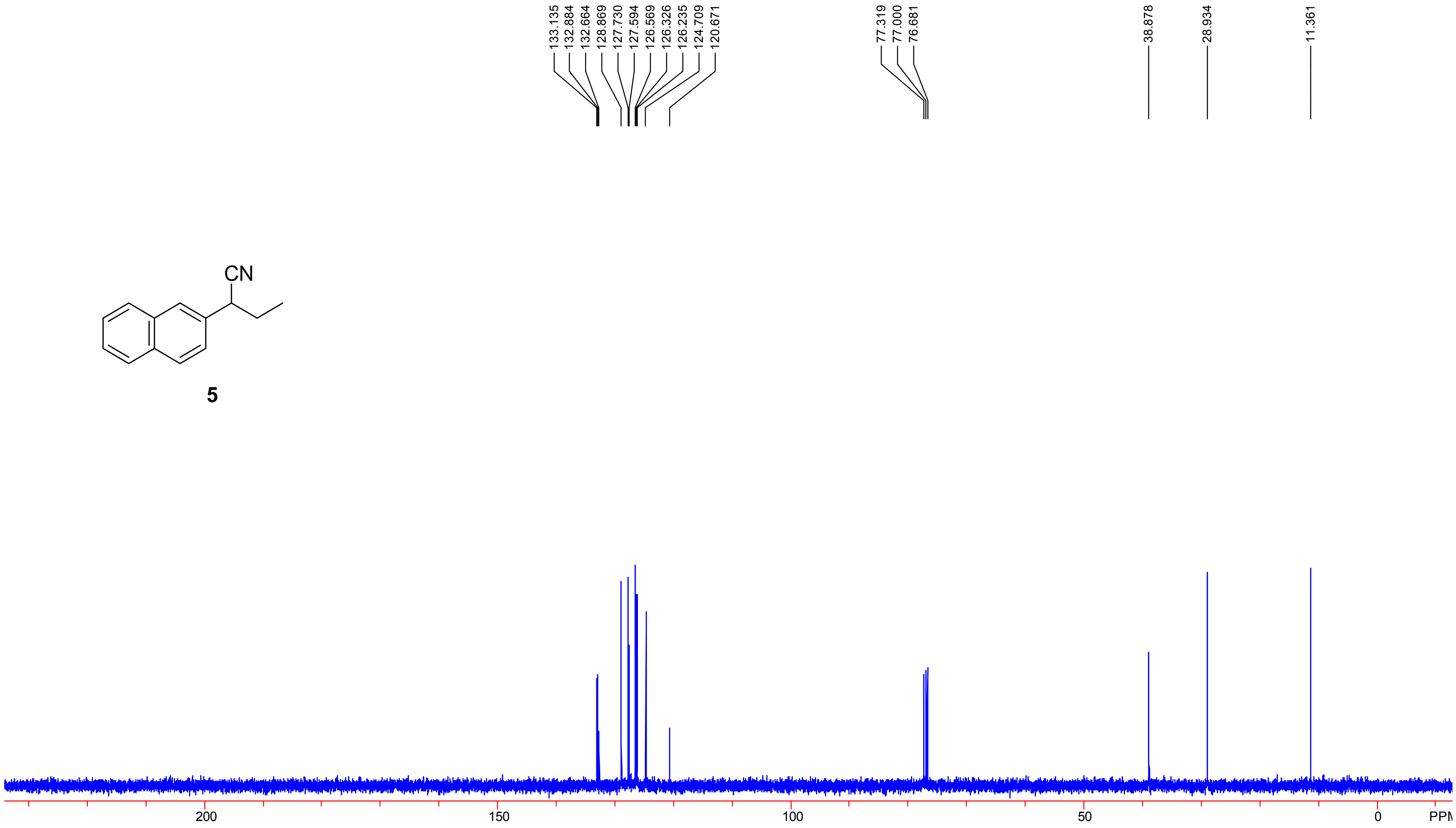
7.749
7.725
7.702
7.612
7.539
7.535
7.517
7.514
7.423
7.420
7.406
7.388
7.383
7.365
7.351
7.348
7.148
6.540
6.500
6.368
6.352
6.335
6.329
6.319
6.313
6.296
6.279
5.892
5.874
5.863
5.856
5.846
5.838
5.828
5.809
1.965
1.961
1.947
1.943
1.908
1.904
1.891
1.887
-0.000
3.04
2.02
1.03
1.00
1.00
1.00
0.03
3.06
0.10
10
8
6
4
2
PPM


135.328
133.673
132.576
131.115
128.005
127.787
127.581
126.105
126.052
125.366
125.160
123.446
77.319
77.000
76.681
18.600
200
150
100
50
0
PPM

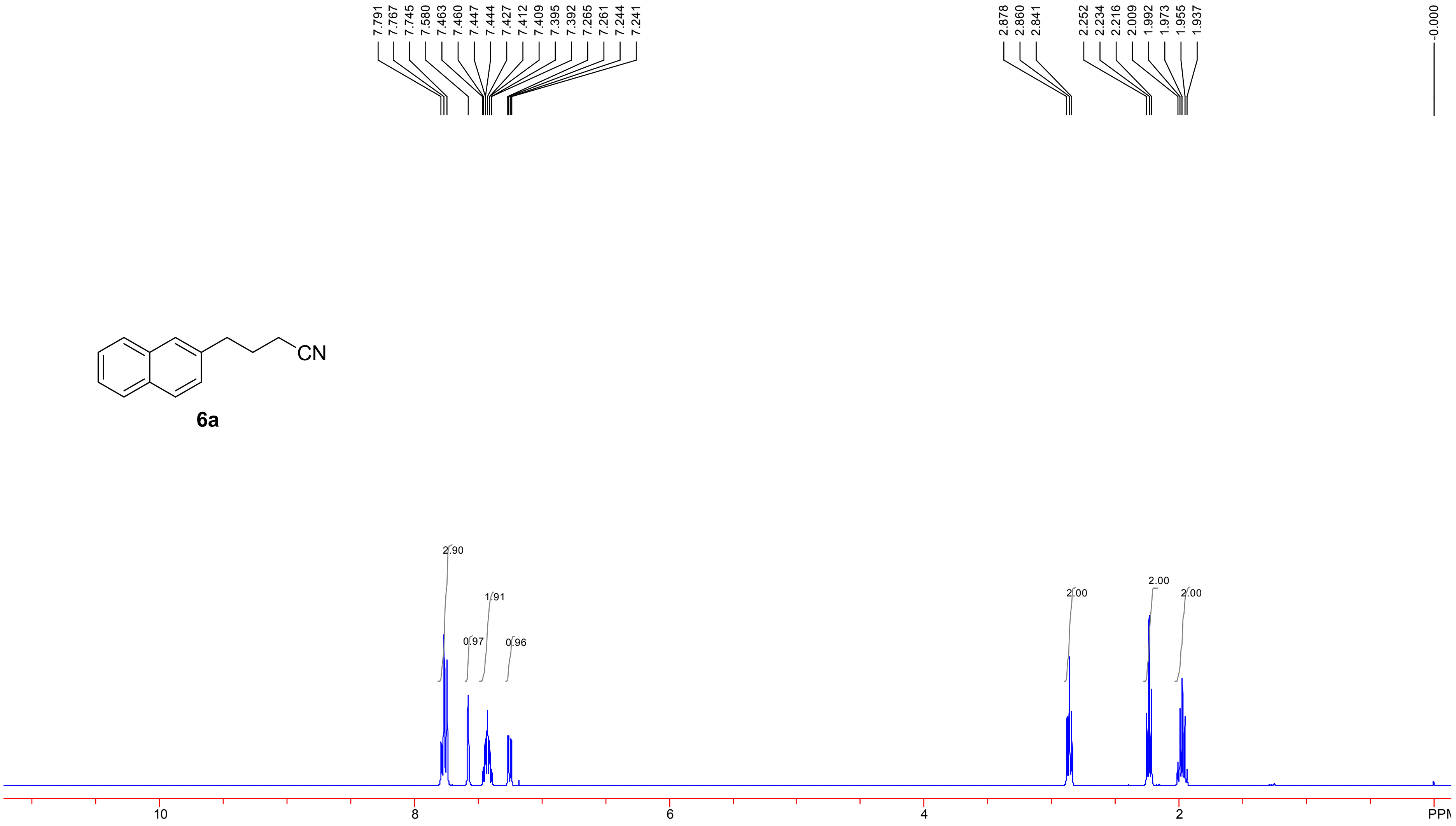
4a' (*E*/*Z* = 33.3:1)


7.838
7.825
7.817
7.802
7.787
7.511
7.498
7.494
7.485
7.475
7.472
7.459
7.376
7.371
7.354
7.350
7.218
3.882
3.864
3.846
2.027
2.009
1.990
1.972
1.954
1.091
1.073
1.054
-0.000
CN
4.02
2.02
1.02
1.00
2.08
3.08
10
8
6
4
2
0
PPM

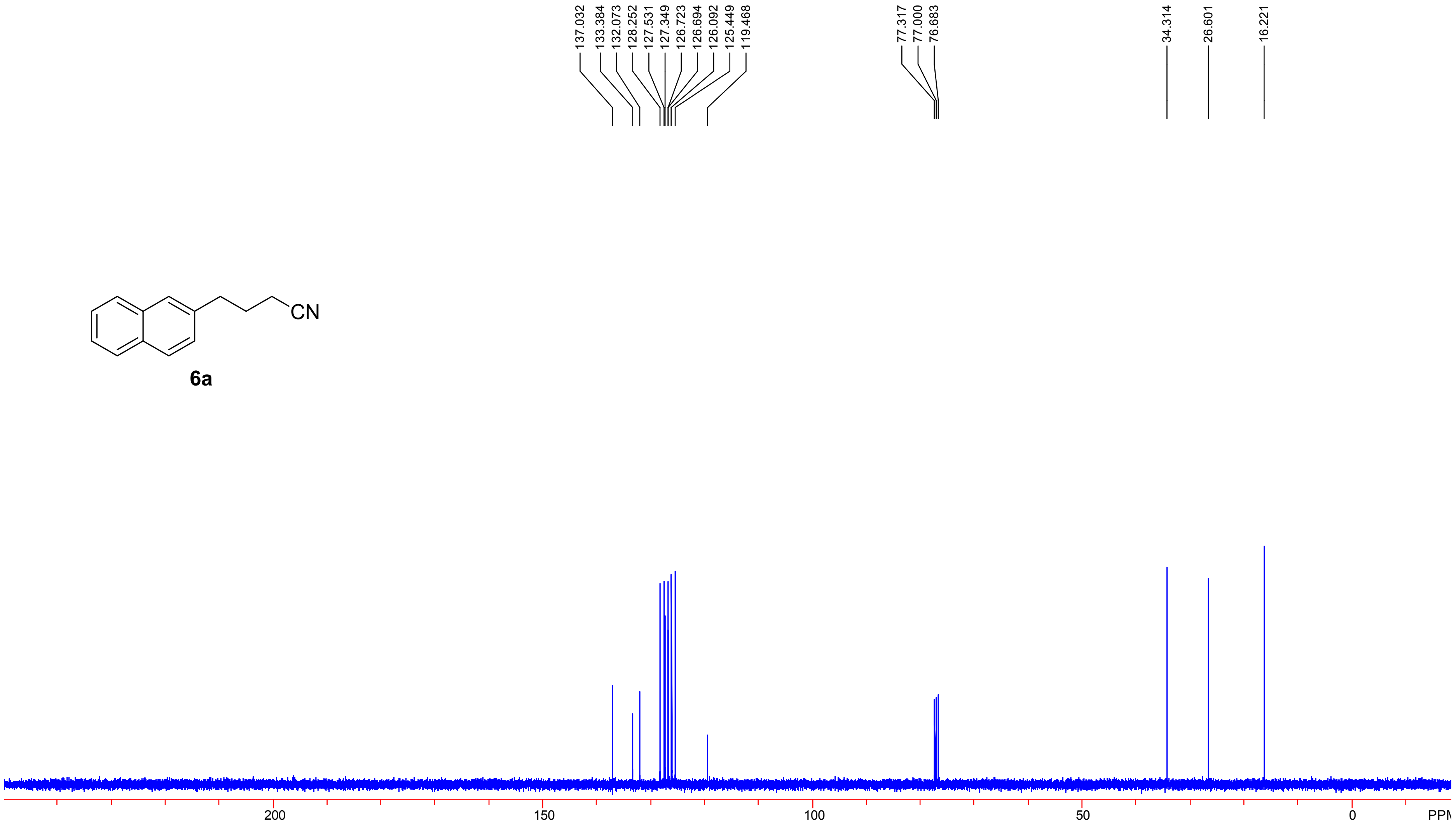
5


133.135
132.884
132.664
128.869
127.730
127.594
126.569
126.326
126.235
124.709
120.671
77.319
77.000
76.681
38.878
28.934
11.361
CN
200
150
100
50
0
PPM

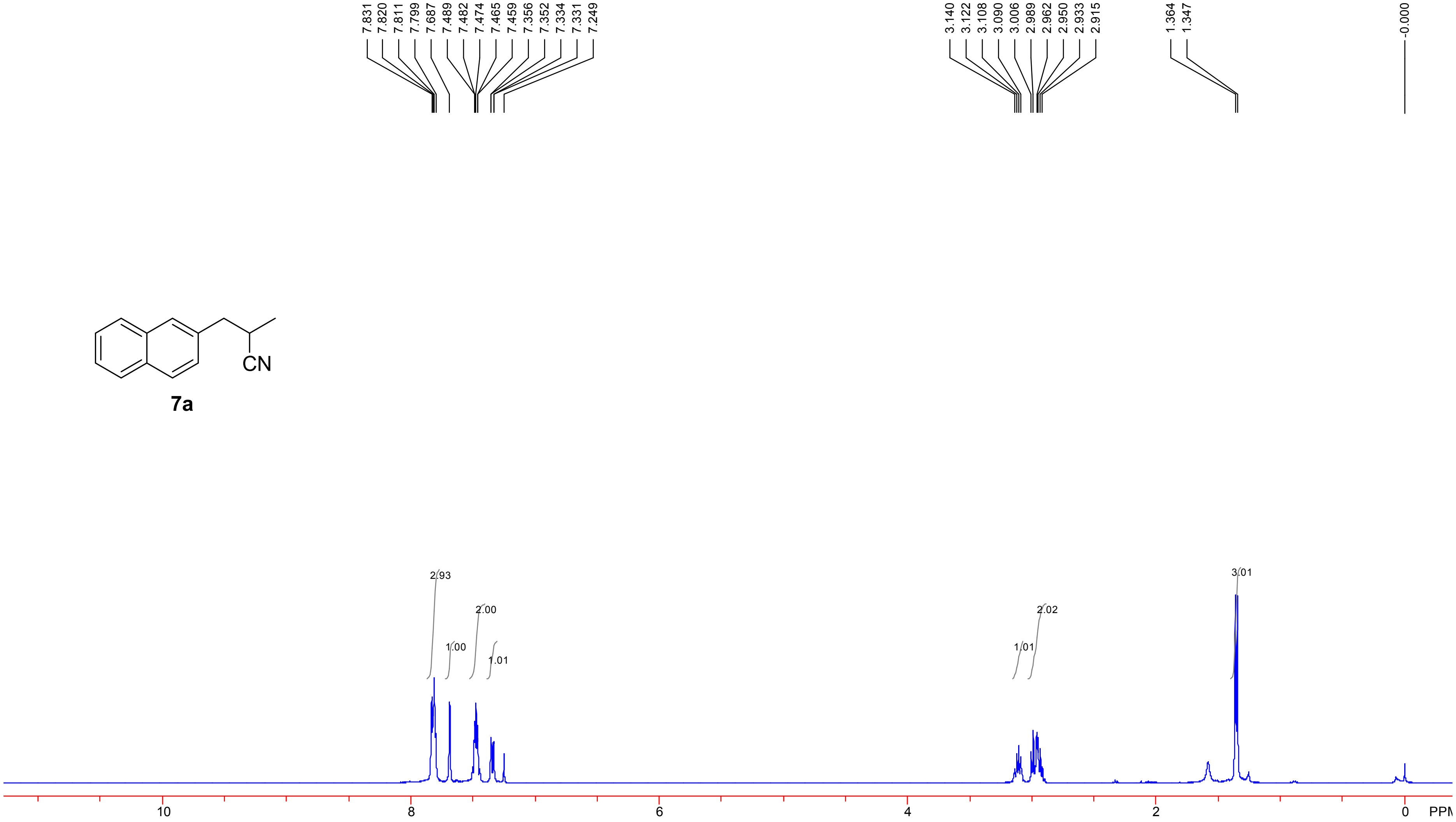
5

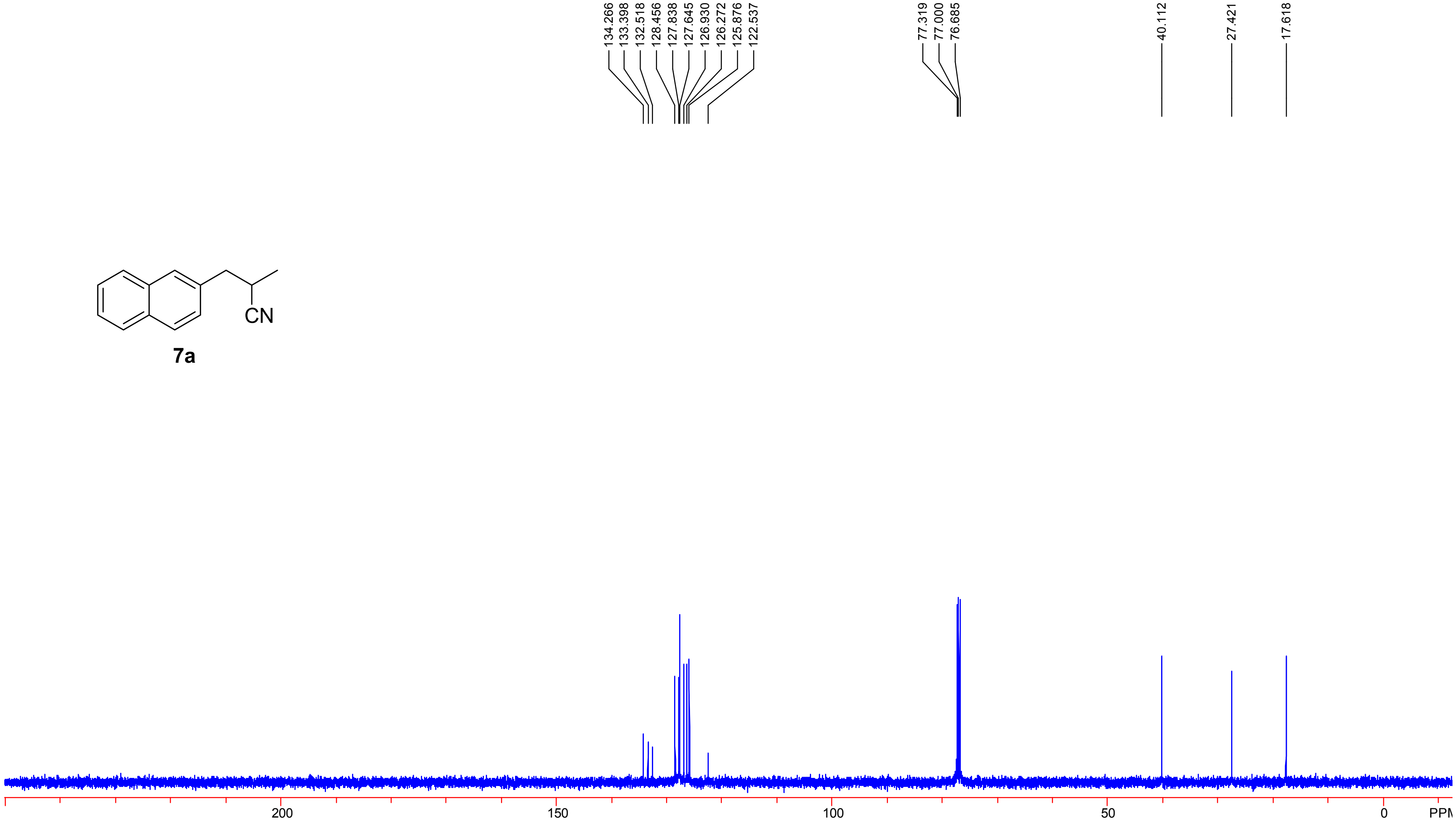

7.791
7.767
7.745
7.580
7.463
7.460
7.447
7.444
7.427
7.412
7.409
7.395
7.392
7.265
7.261
7.244
7.241
2.878
2.860
2.841
2.252
2.234
2.216
2.009
1.992
1.973
1.955
1.937
-0.000
CN
2.90
0.97
1.91
0.96
2.00
2.00
2.00
10
8
6
4
2
PPM

6a


137.032
133.384
132.073
128.252
127.531
127.349
126.723
126.694
126.092
125.449
119.468
77.317
77.000
76.683
34.314
26.601
16.221
CN
6a
200
150
100
50
0
PP

7a


7.831
7.820
7.811
7.799
7.687
7.489
7.482
7.474
7.465
7.459
7.356
7.352
7.334
7.331
7.249
3.140
3.122
3.108
3.090
3.006
2.989
2.962
2.950
2.933
2.915
1.364
1.347
-0.000
2.93
1.00
2.00
1.01
1.01
2.02
3.01
10
8
6
4
2
0
PPM



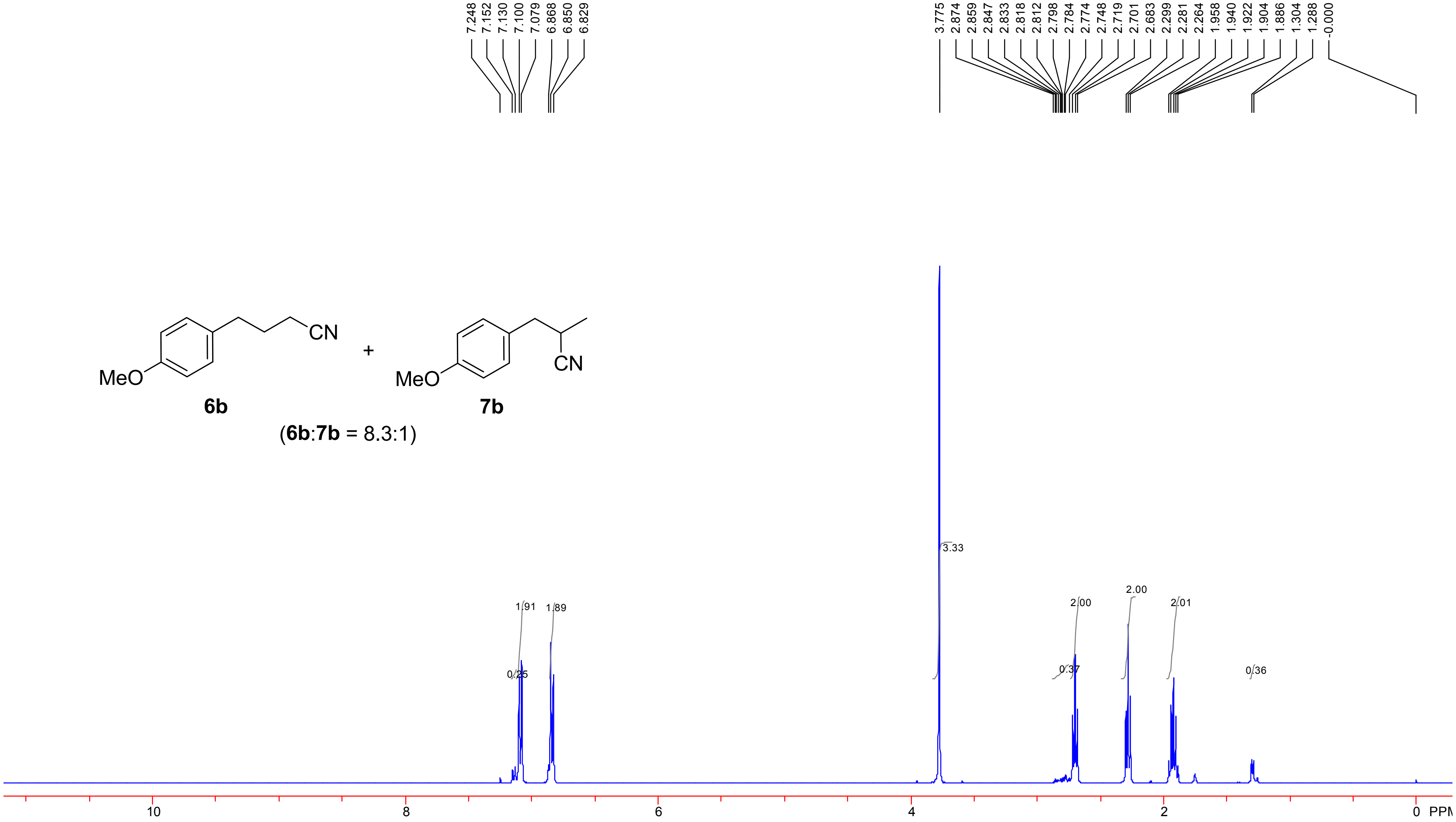
7a
134.266
133.398
132.518
128.456
127.838
127.645
126.930
126.272
125.876
122.537
77.319
77.000
76.685
40.112
27.421
17.618
200
150
100
50
0
PPM

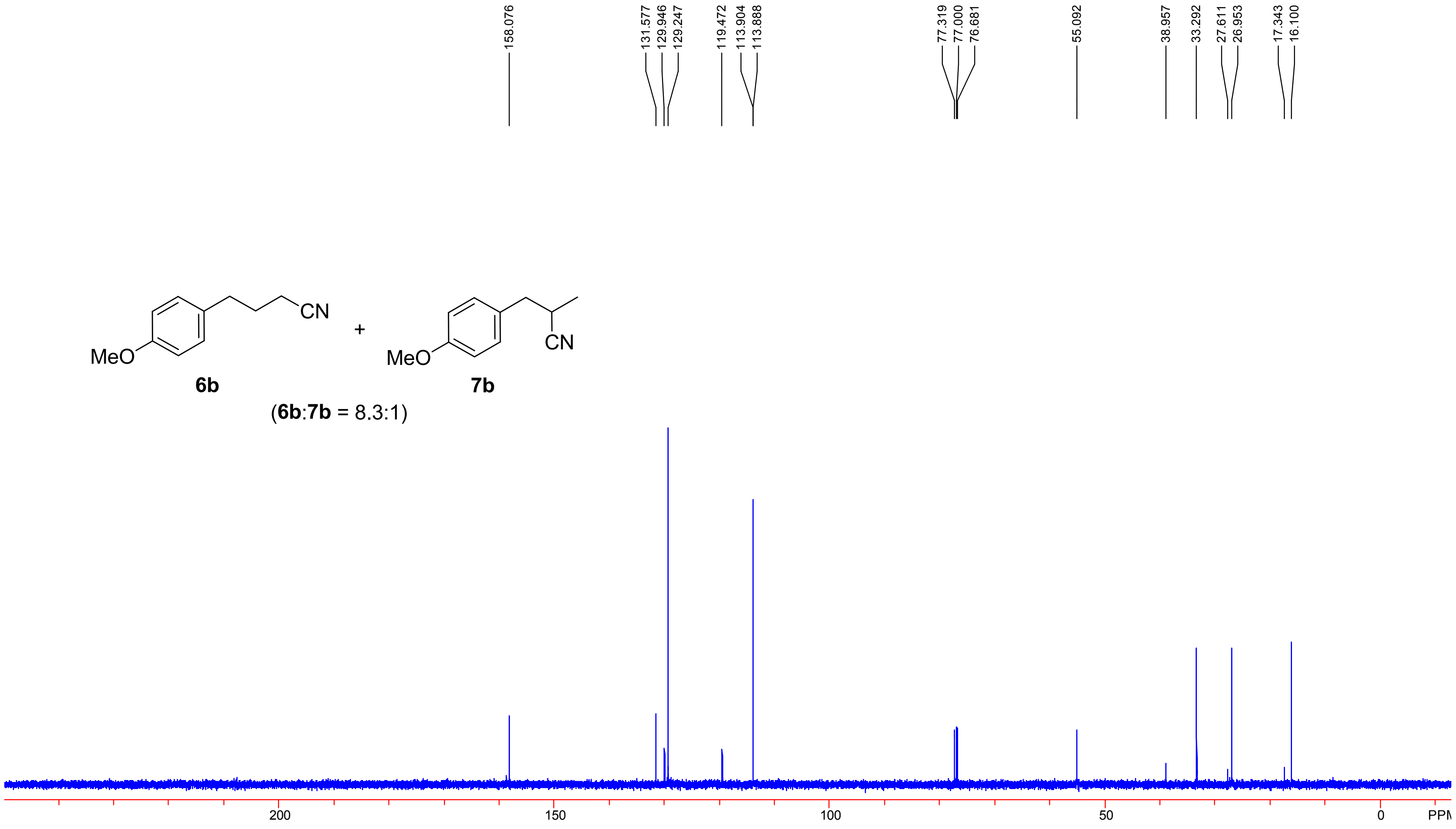
6b

+

7b

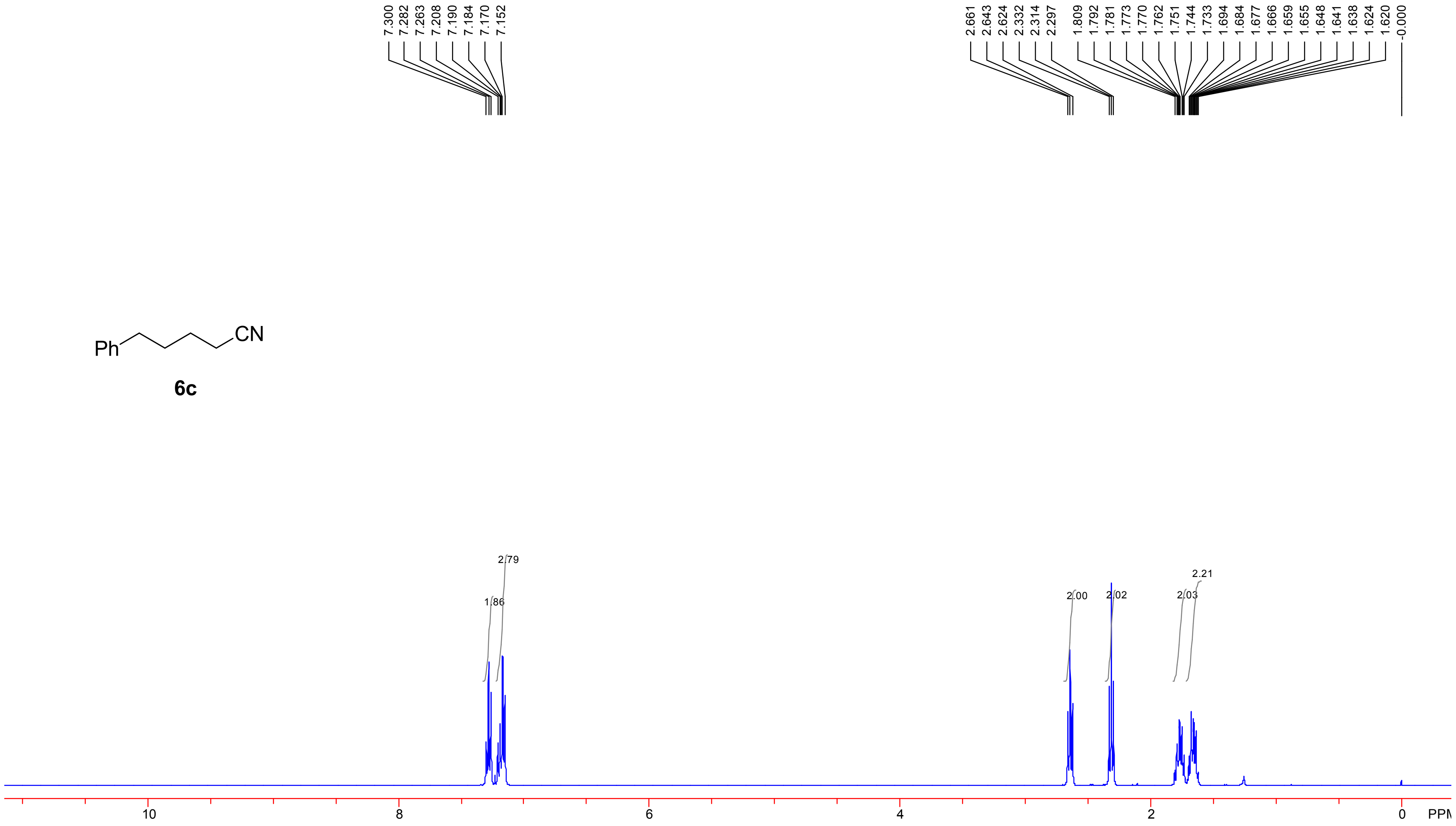
(**6b**:**7b** = 8.3:1)





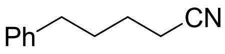
6b **7b**

(**6b**:**7b** = 8.3:1)

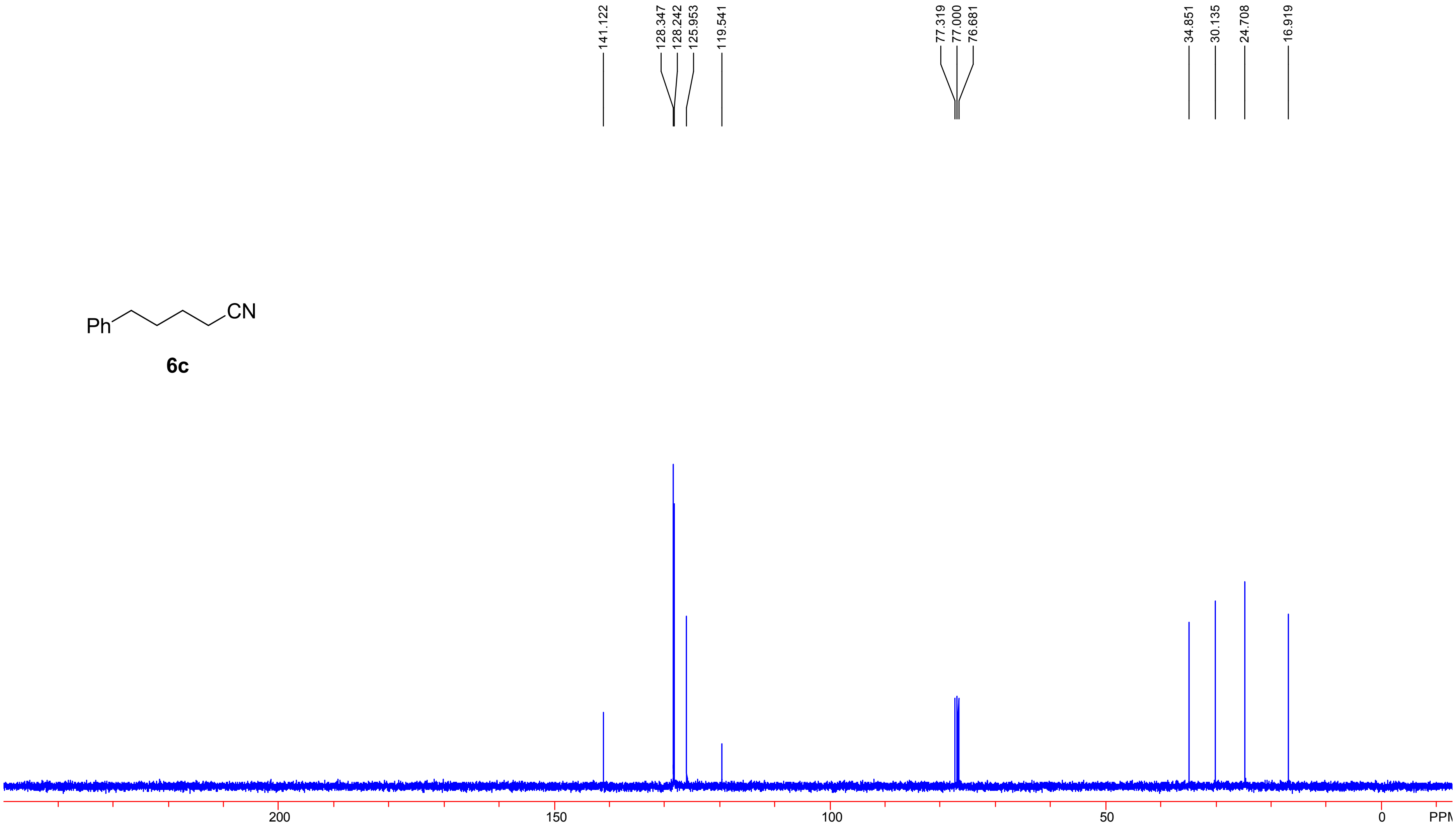


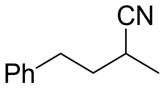
6c

7.300
7.282
7.263
7.208
7.190
7.184
7.170
7.152
2.661
2.643
2.624
2.332
2.314
2.297
1.809
1.792
1.781
1.773
1.770
1.762
1.751
1.744
1.733
1.694
1.684
1.677
1.666
1.659
1.655
1.648
1.641
1.638
1.624
1.620
-0.000
1.86
2.79
2.00
2.02
2.03
2.21
10
8
6
4
2
0
PPM


Ph
CN

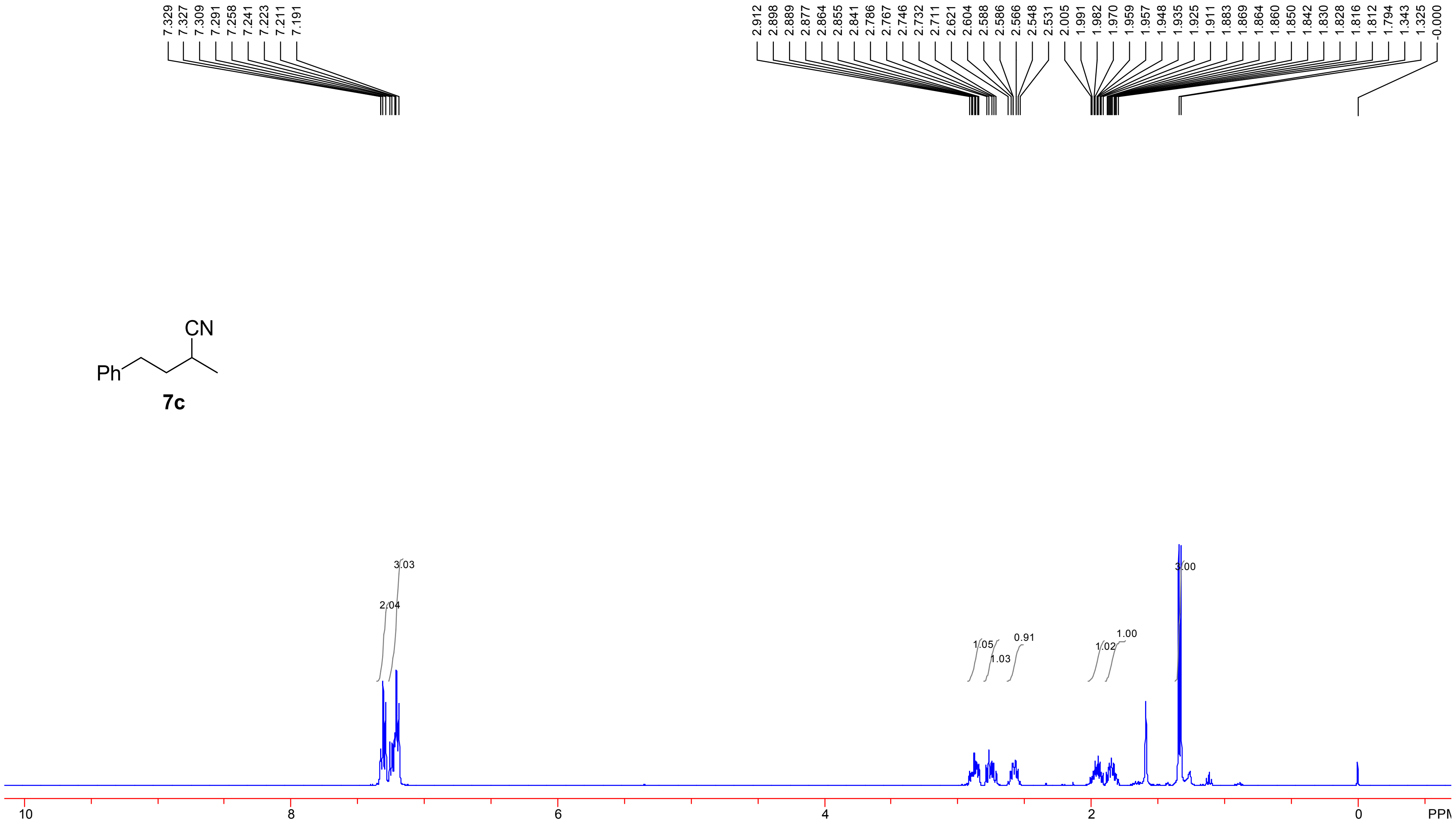
6c


141.122
128.347
128.242
125.953
119.541
77.319
77.000
76.681
34.851
30.135
24.708
16.919
200
150
100
50
0
PPM

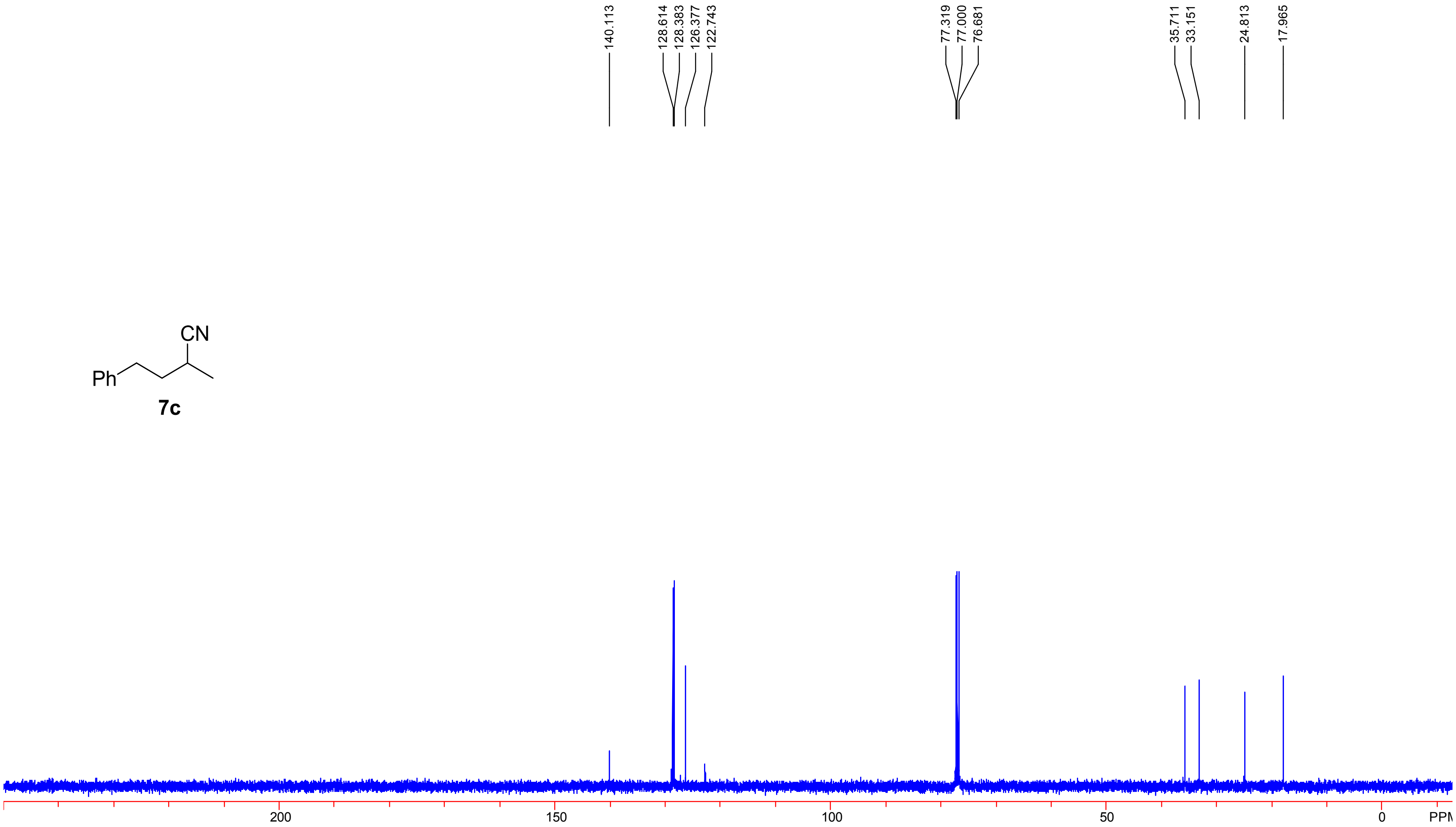


CN
Ph

7c

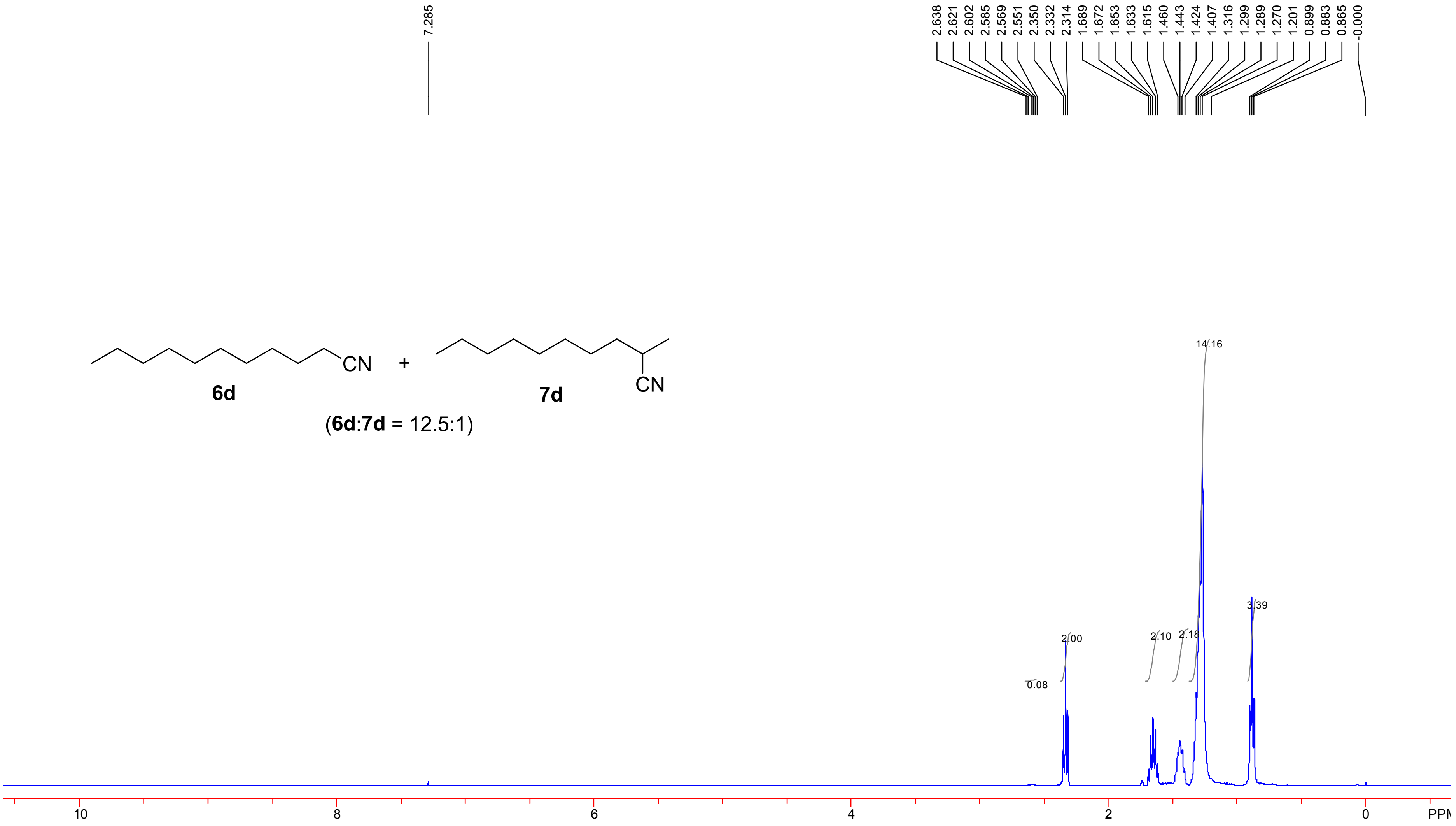


7.329
7.327
7.309
7.291
7.258
7.241
7.223
7.211
7.191
2.912
2.898
2.889
2.877
2.864
2.855
2.841
2.786
2.767
2.746
2.732
2.711
2.621
2.604
2.588
2.586
2.566
2.548
2.531
2.005
1.991
1.982
1.970
1.959
1.957
1.948
1.935
1.925
1.911
1.883
1.869
1.864
1.860
1.850
1.842
1.830
1.828
1.816
1.812
1.794
1.343
1.325
-0.000
3.03
2.04
1.05
1.03
0.91
1.02
1.00
3.00
10
8
6
4
2
0
PPM


CN
Ph

7c

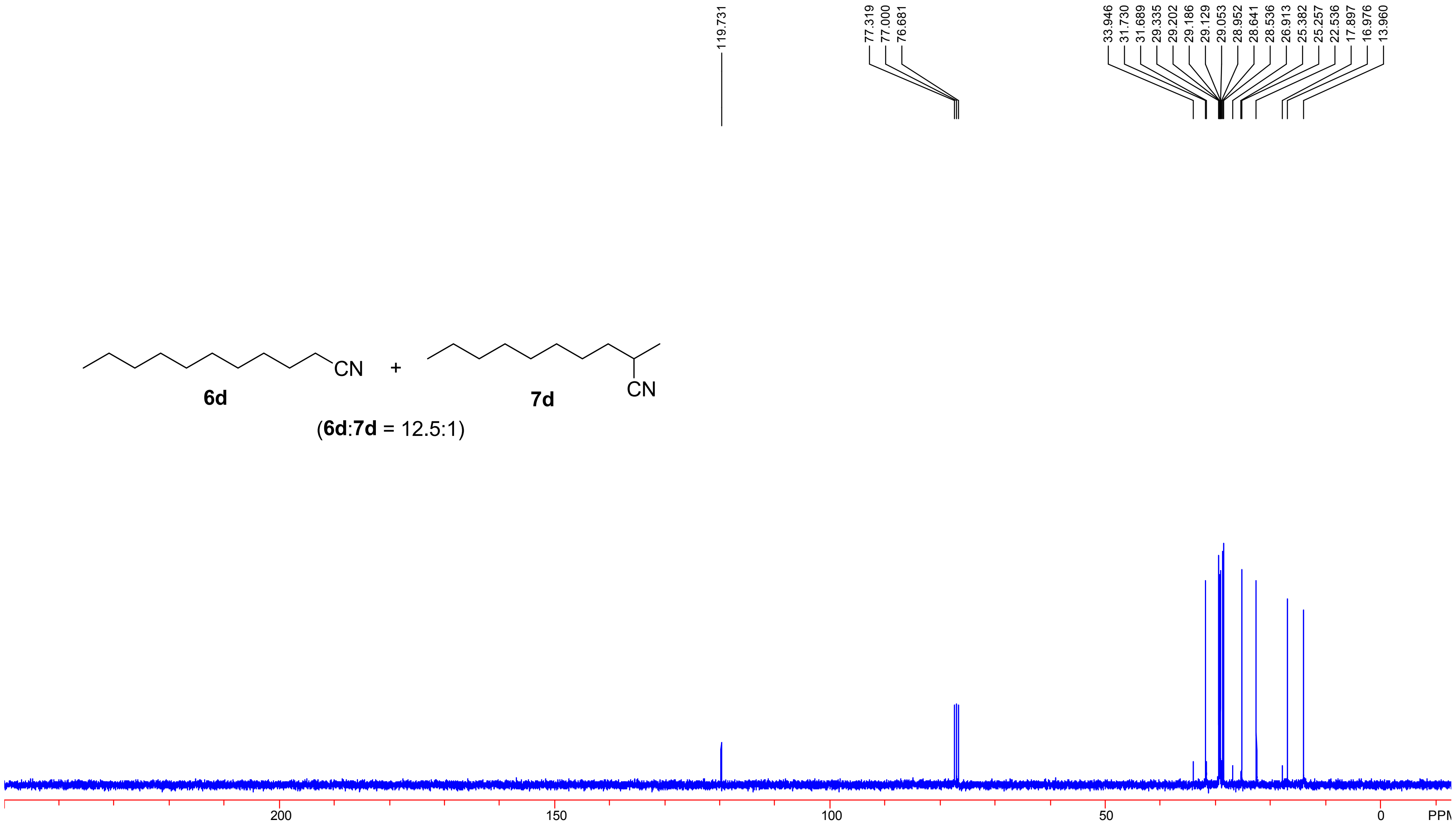
140.113
128.614
128.383
126.377
122.743
77.319
77.000
76.681
35.711
33.151
24.813
17.965
200
150
100
50
0
PPM



6d

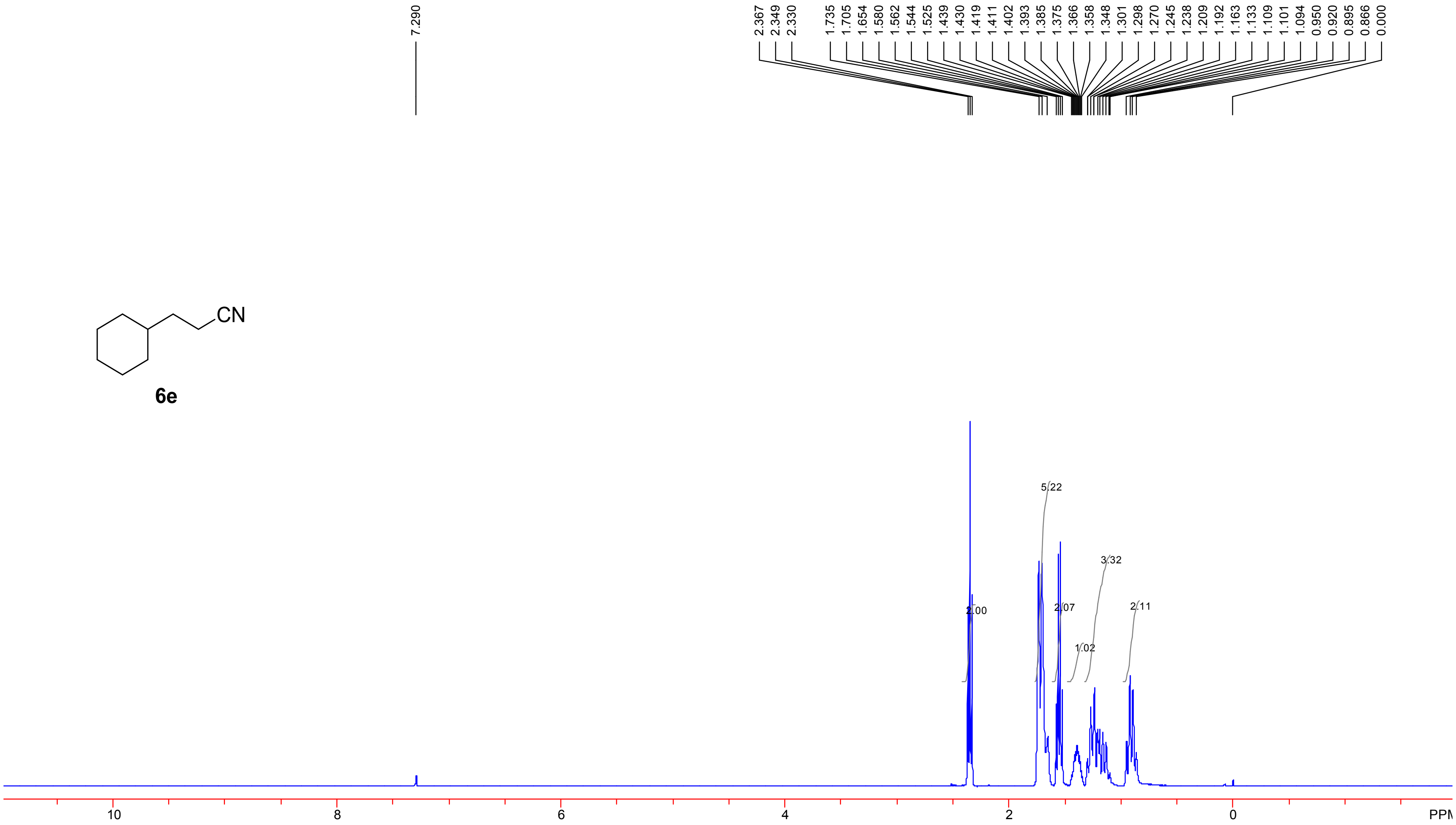
7d

(**6d**:**7d** = 12.5:1)



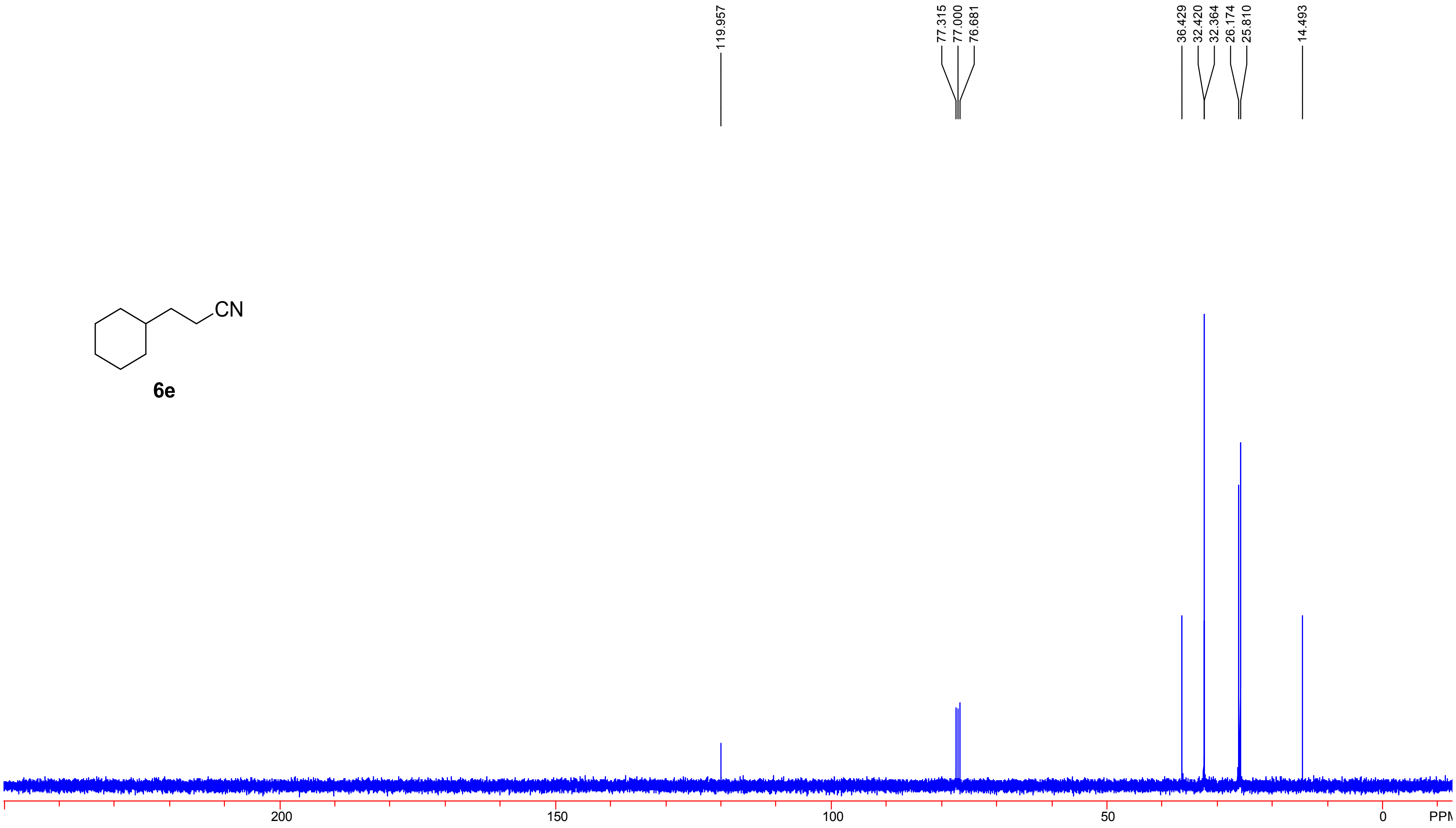
6d **7d**

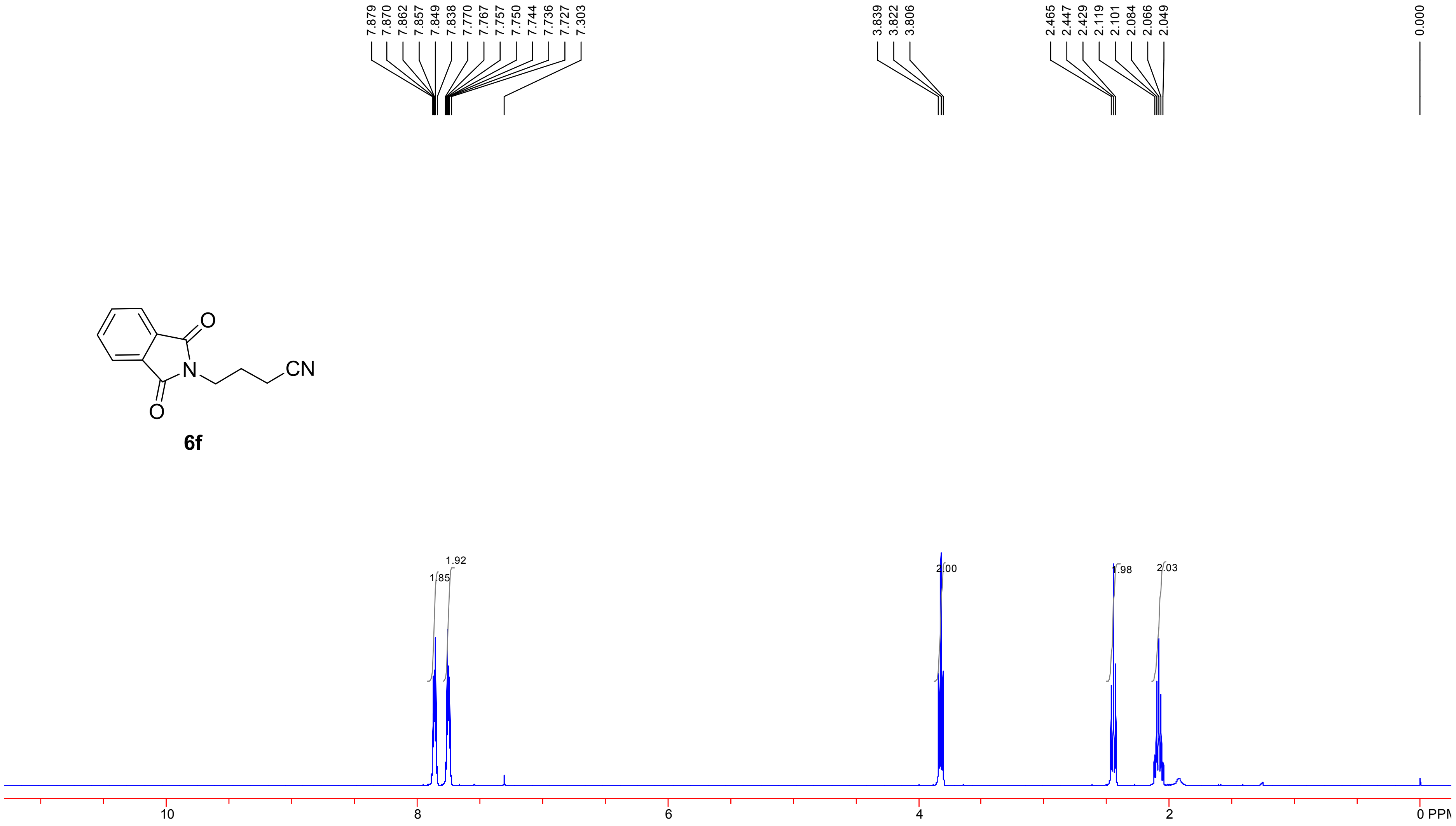
(**6d**:**7d** = 12.5:1)



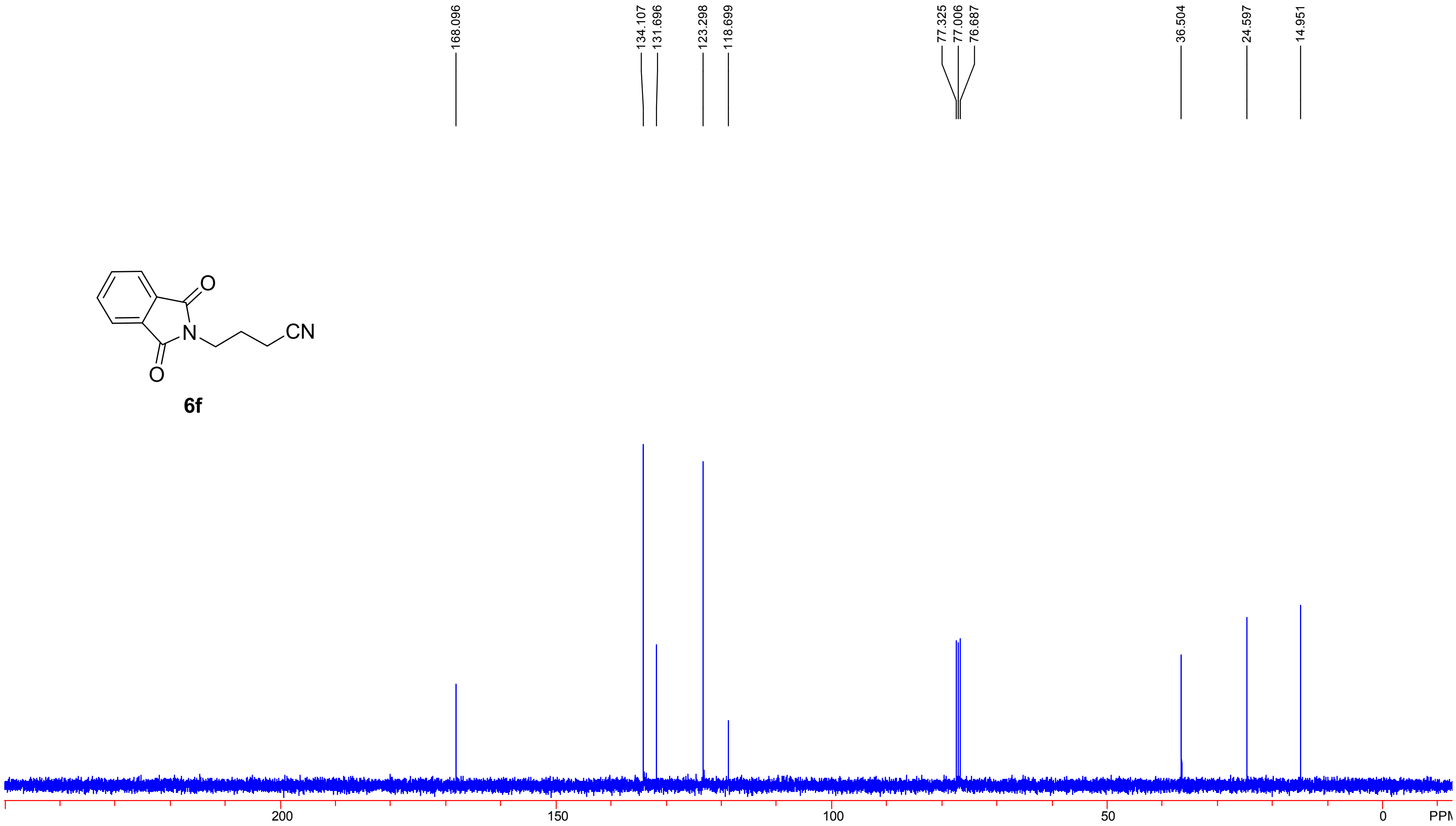
6e

7.290
2.367
2.349
2.330
1.735
1.705
1.654
1.580
1.562
1.544
1.525
1.439
1.430
1.419
1.411
1.402
1.393
1.385
1.375
1.366
1.358
1.348
1.301
1.298
1.270
1.245
1.238
1.209
1.192
1.163
1.133
1.109
1.101
1.094
0.950
0.920
0.895
0.866
0.000
2.00
5.22
2.07
1.02
3.32
2.11
10
8
6
4
2
0
PPM


119.957
77.315
77.000
76.681
36.429
32.420
32.364
26.174
25.810
14.493
CN
6e
200
150
100
50
0
PPM


7.879
7.870
7.862
7.857
7.849
7.838
7.770
7.767
7.757
7.750
7.744
7.736
7.727
7.303
3.839
3.822
3.806
2.465
2.447
2.429
2.119
2.101
2.084
2.066
2.049
0.000
O
N
CN
O
1.85
1.92
2.00
1.98
2.03
10
8
6
4
2
0 PPM

6f

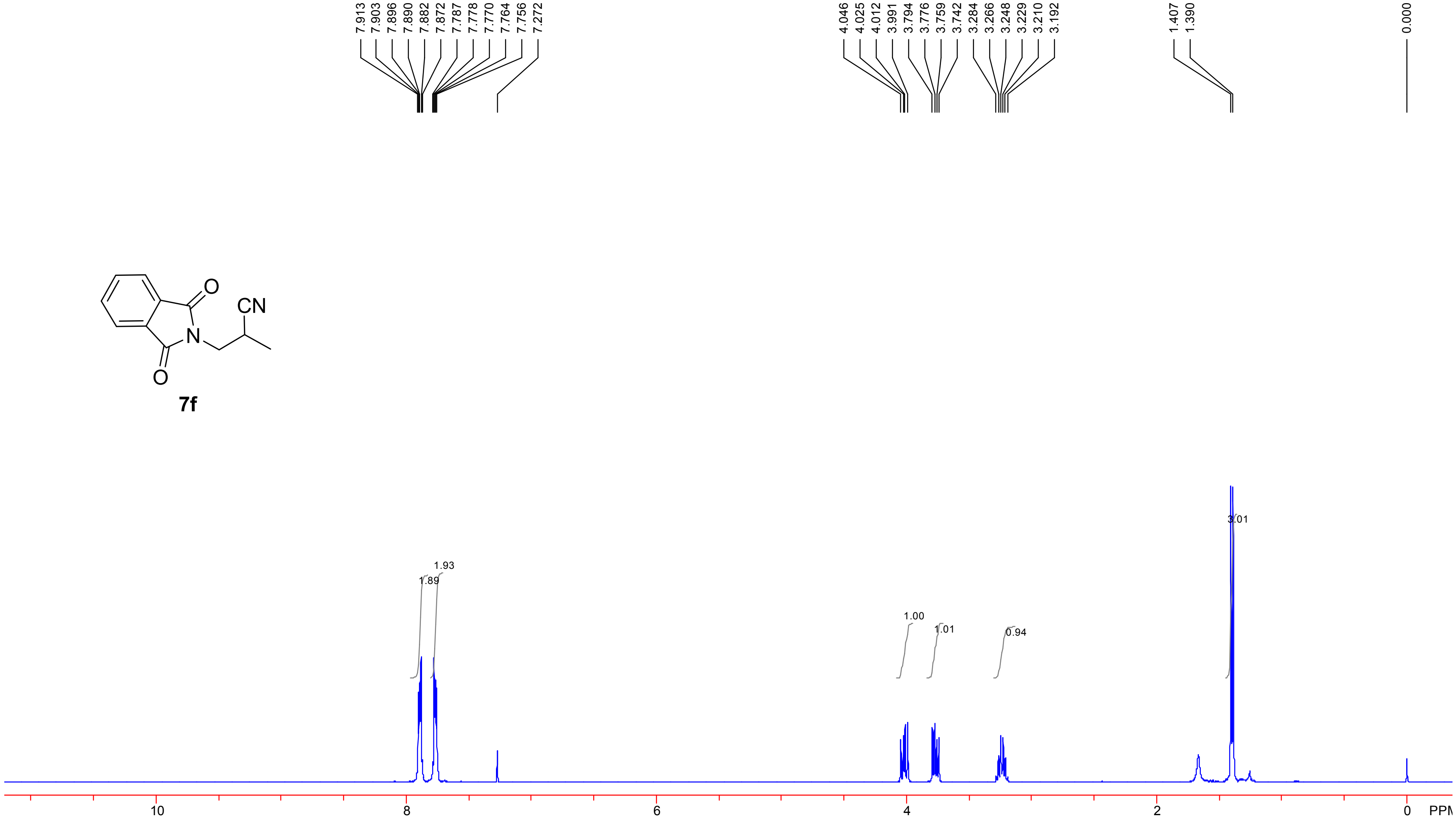

O
N
CN
O

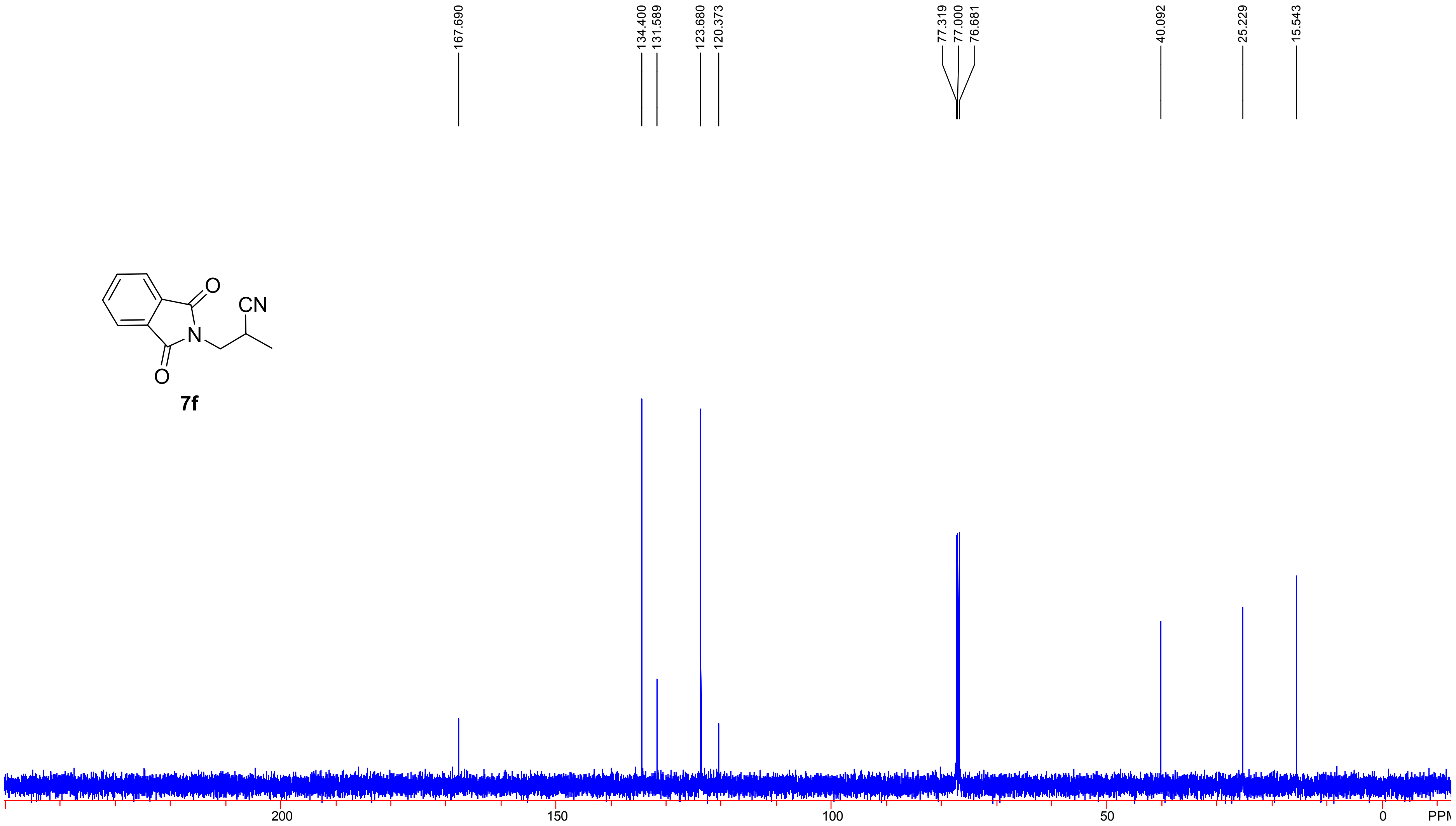
6f

168.096
134.107
131.696
123.298
118.699
77.325
77.006
76.687
36.504
24.597
14.951
200
150
100
50
0
PPM

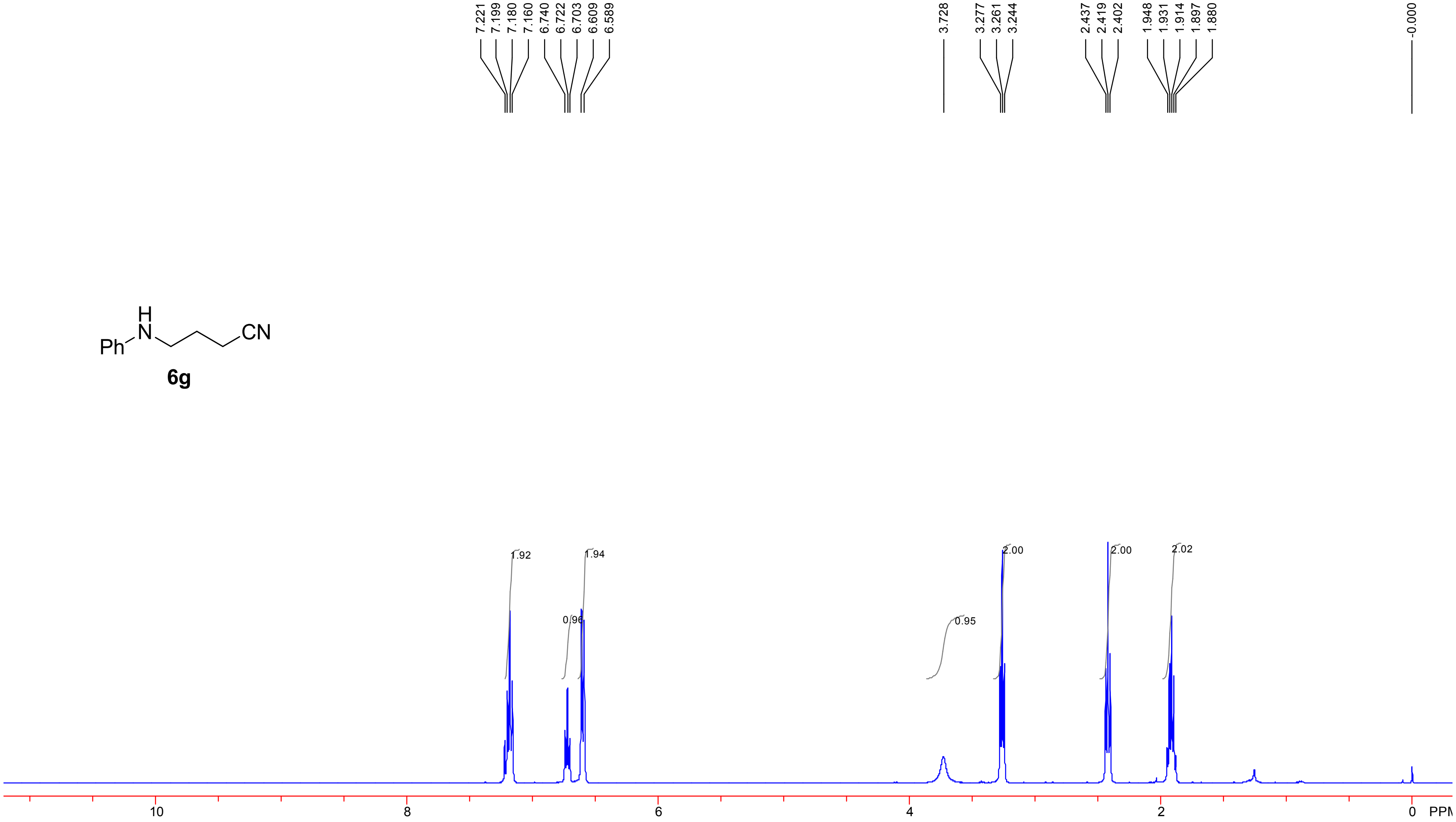
O
CN
N
O

7f

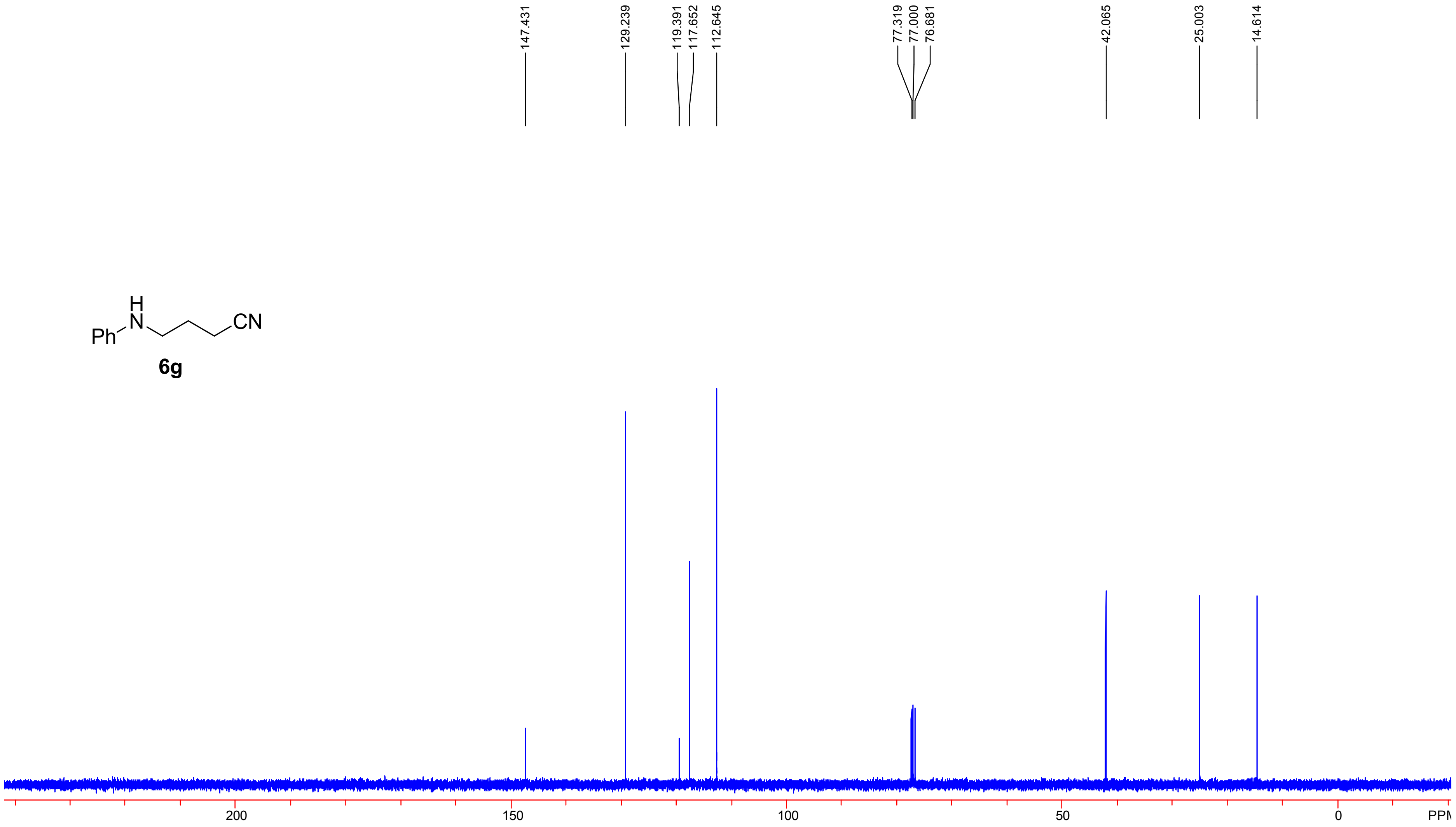

7.913
7.903
7.896
7.890
7.882
7.872
7.787
7.778
7.770
7.764
7.756
7.272
4.046
4.025
4.012
3.991
3.794
3.776
3.759
3.742
3.284
3.266
3.248
3.229
3.210
3.192
1.407
1.390
0.000
1.89
1.93
1.00
1.01
0.94
3.01
10
8
6
4
2
0
PPM



7f
167.690
134.400
131.589
123.680
120.373
77.319
77.000
76.681
40.092
25.229
15.543
200
150
100
50
0
PPM



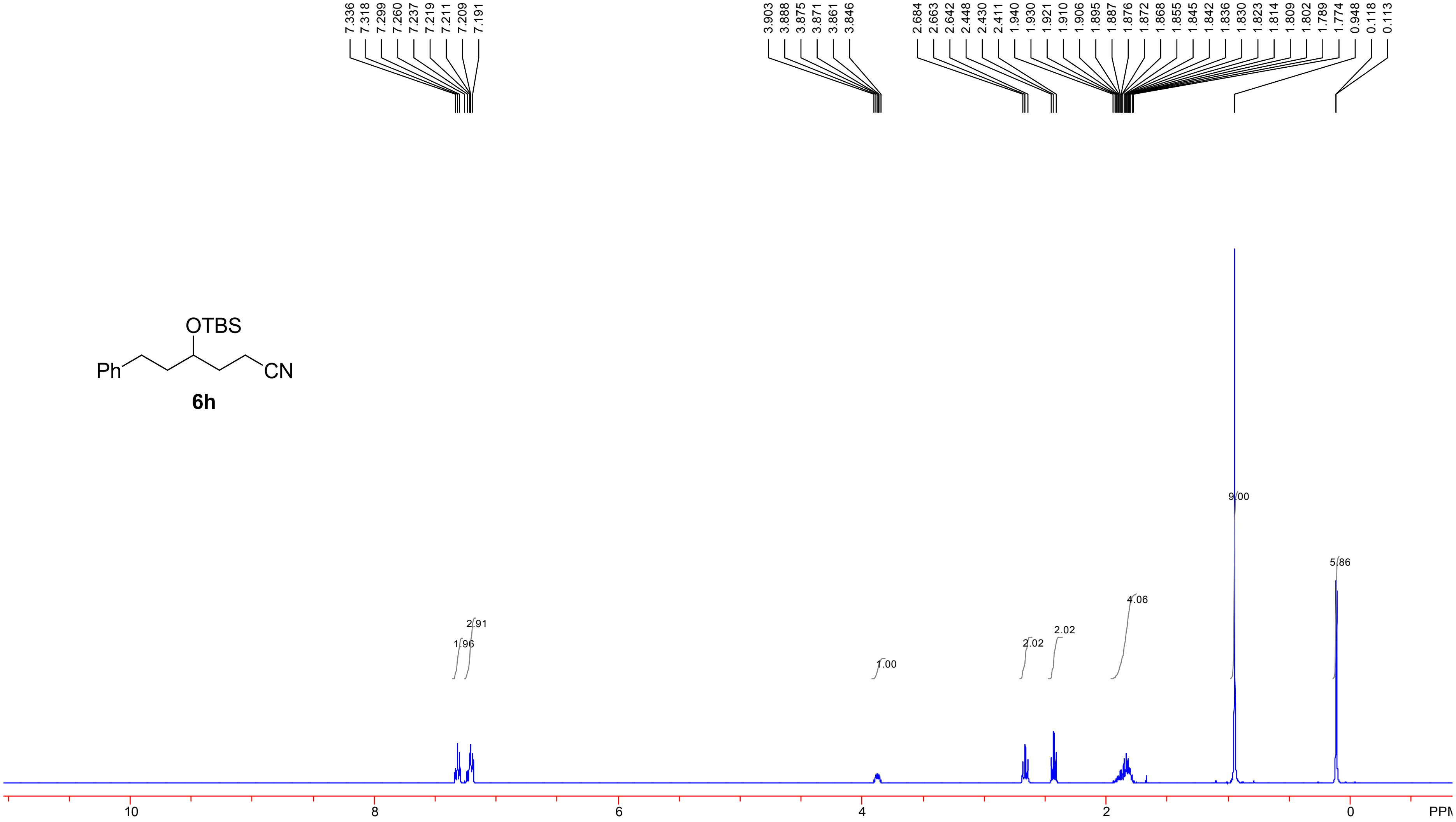
6g
7.221
7.199
7.180
7.160
6.740
6.722
6.703
6.609
6.589
3.728
3.277
3.261
3.244
2.437
2.419
2.402
1.948
1.931
1.914
1.897
1.880
-0.000
1.92
0.96
1.94
0.95
2.00
2.00
2.02
10
8
6
4
2
0
PPM


6g

147.431
129.239
119.391
117.652
112.645
77.319
77.000
76.681
42.065
25.003
14.614
H
N
Ph
CN
200
150
100
50
0
PPM

OTBS
Ph
CN

6h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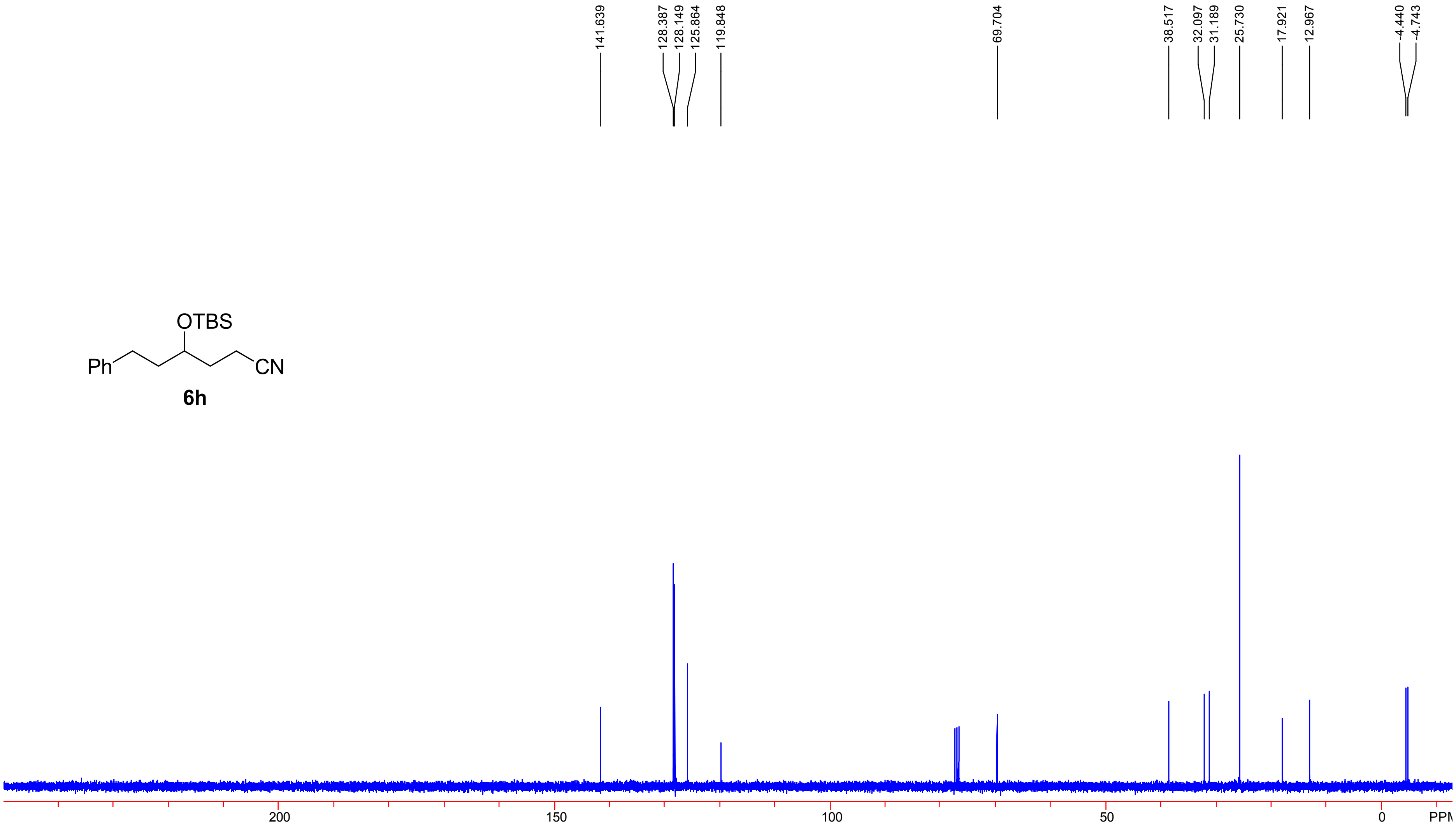
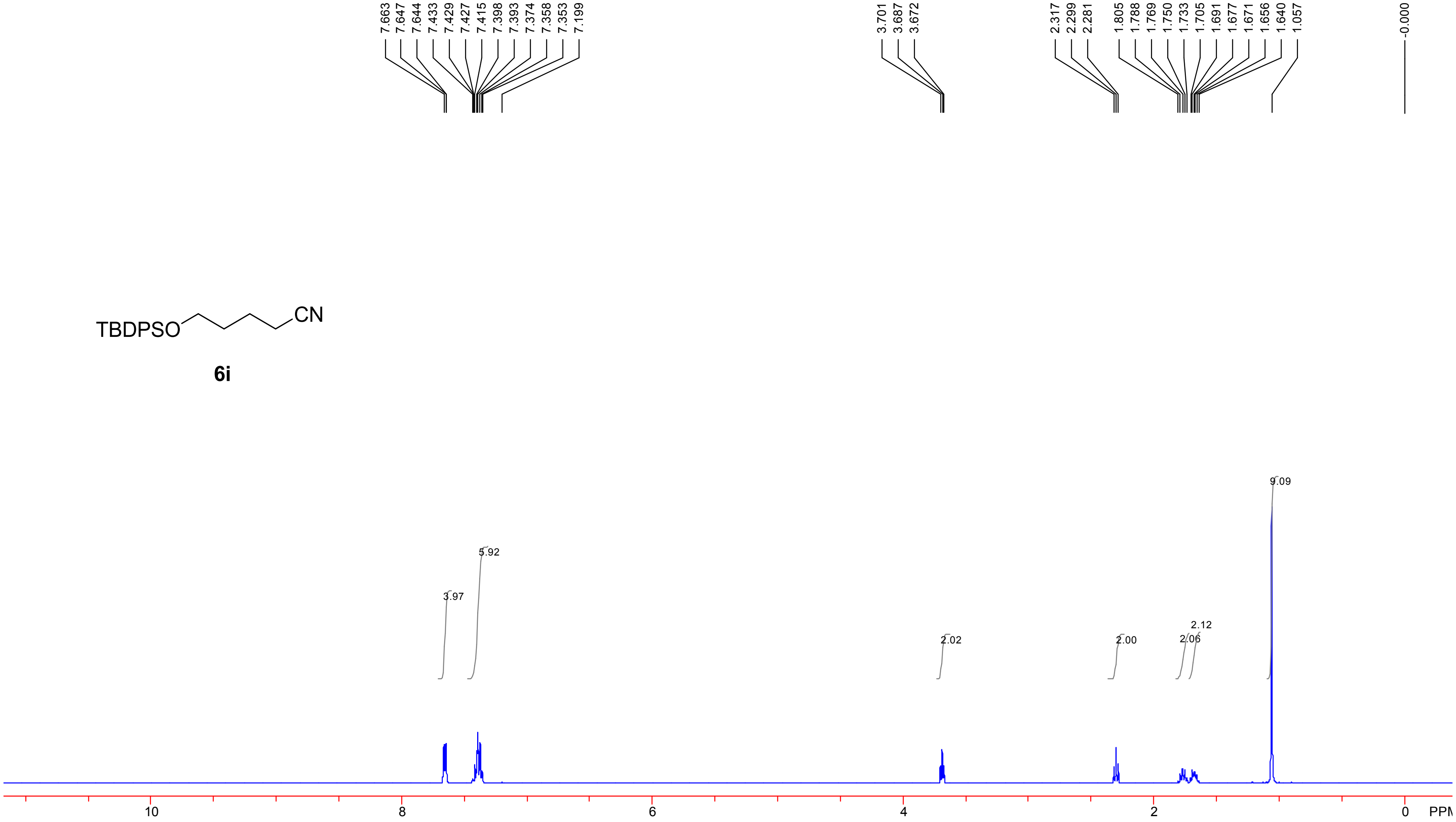
7.318
7.299
7.260
7.237
7.219
7.211
7.209
7.191
3.903
3.888
3.875
3.871
3.861
3.846
2.684
2.663
2.642
2.448
2.430
2.411
1.940
1.930
1.921
1.910
1.906
1.895
1.887
1.876
1.872
1.868
1.855
1.845
1.842
1.836
1.830
1.823
1.814
1.809
1.802
1.789
1.774
0.948
0.118
0.113
1.96
2.91
1.00
2.02
2.02
4.06
9.00
5.86
10
8
6
4
2
0
PPM

OTBS
Ph
CN

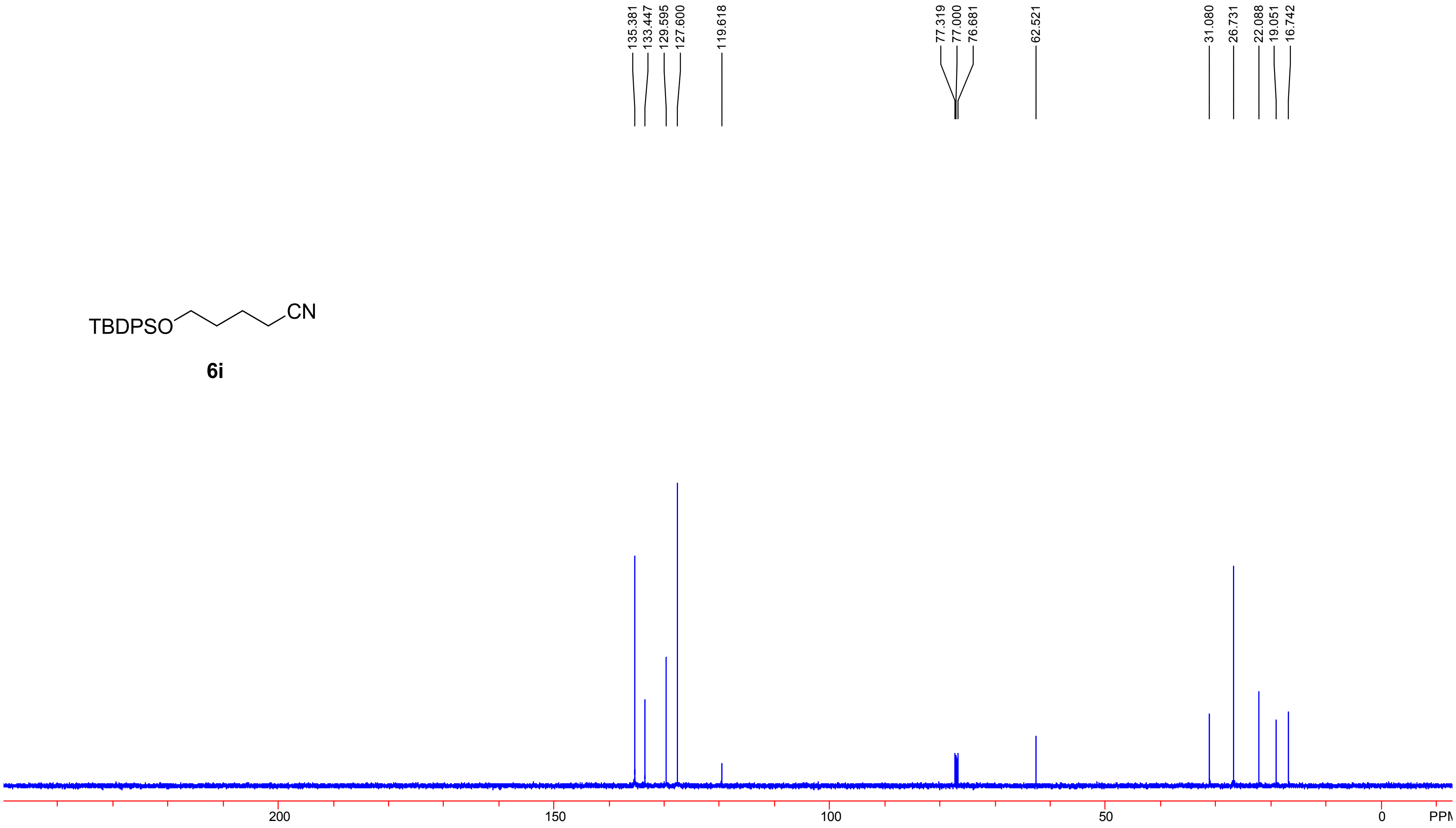
6h


141.639
128.387
128.149
125.864
119.848
69.704
38.517
32.097
31.189
25.730
17.921
12.967
-4.440
-4.743
200
150
100
50
0
PPM


TBDPSO
CN

6i

7.663
7.647
7.644
7.433
7.429
7.427
7.415
7.398
7.393
7.374
7.358
7.353
7.199
3.701
3.687
3.672
2.317
2.299
2.281
1.805
1.788
1.769
1.750
1.733
1.705
1.691
1.677
1.671
1.656
1.640
1.057
-0.000
3.97
5.92
2.02
2.00
2.06
2.12
9.09
10
8
6
4
2
0
PPM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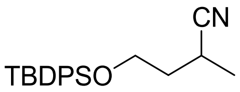
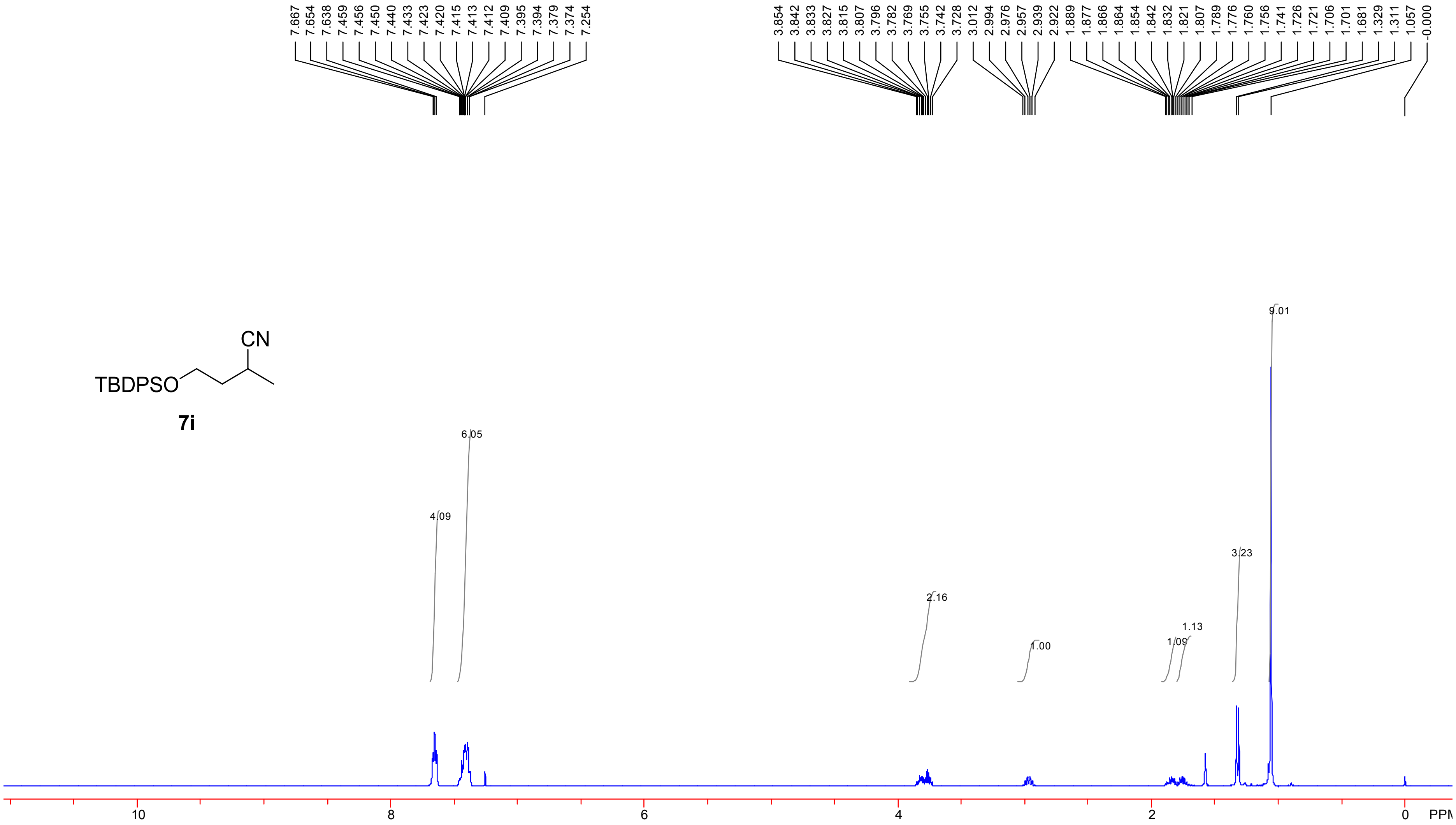
133.447
129.595
127.600
119.618
77.319
77.000
76.681
62.521
31.080
26.731
22.088
19.051
16.742
TBDPSO
CN
200
150
100
50
0
PPM

6i

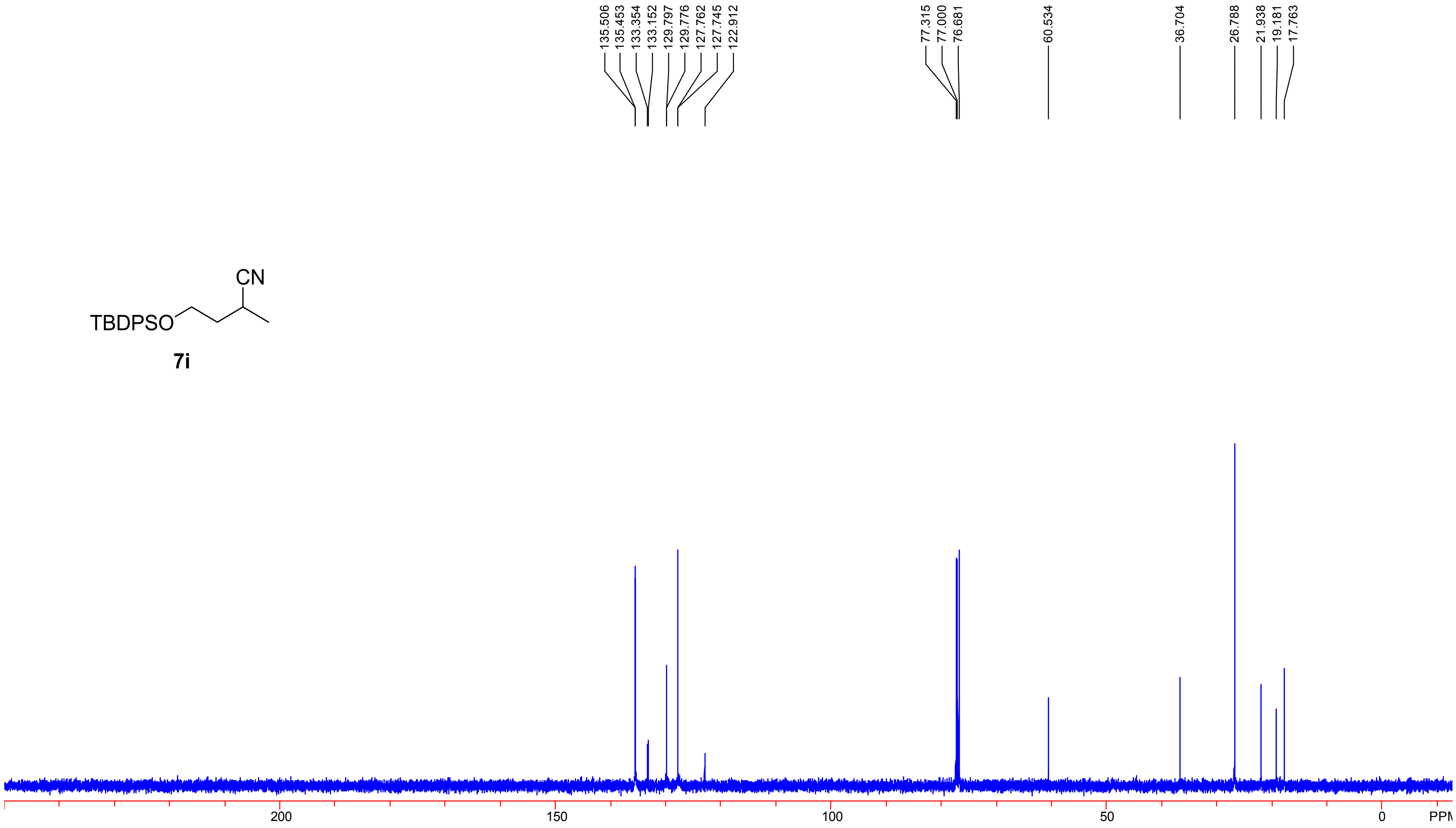

CN
TBDPSO

7i


7.667
7.654
7.638
7.459
7.456
7.450
7.440
7.433
7.423
7.420
7.415
7.413
7.412
7.409
7.395
7.394
7.379
7.374
7.254
3.854
3.842
3.833
3.827
3.815
3.807
3.796
3.782
3.769
3.755
3.742
3.728
3.012
2.994
2.976
2.957
2.939
2.922
1.889
1.877
1.866
1.864
1.854
1.842
1.832
1.821
1.807
1.789
1.776
1.760
1.756
1.741
1.726
1.721
1.706
1.701
1.681
1.329
1.311
1.057
-0.000
4.09
6.05
2.16
1.00
1.09
1.13
3.23
9.01
10
8
6
4
2
0
PPM

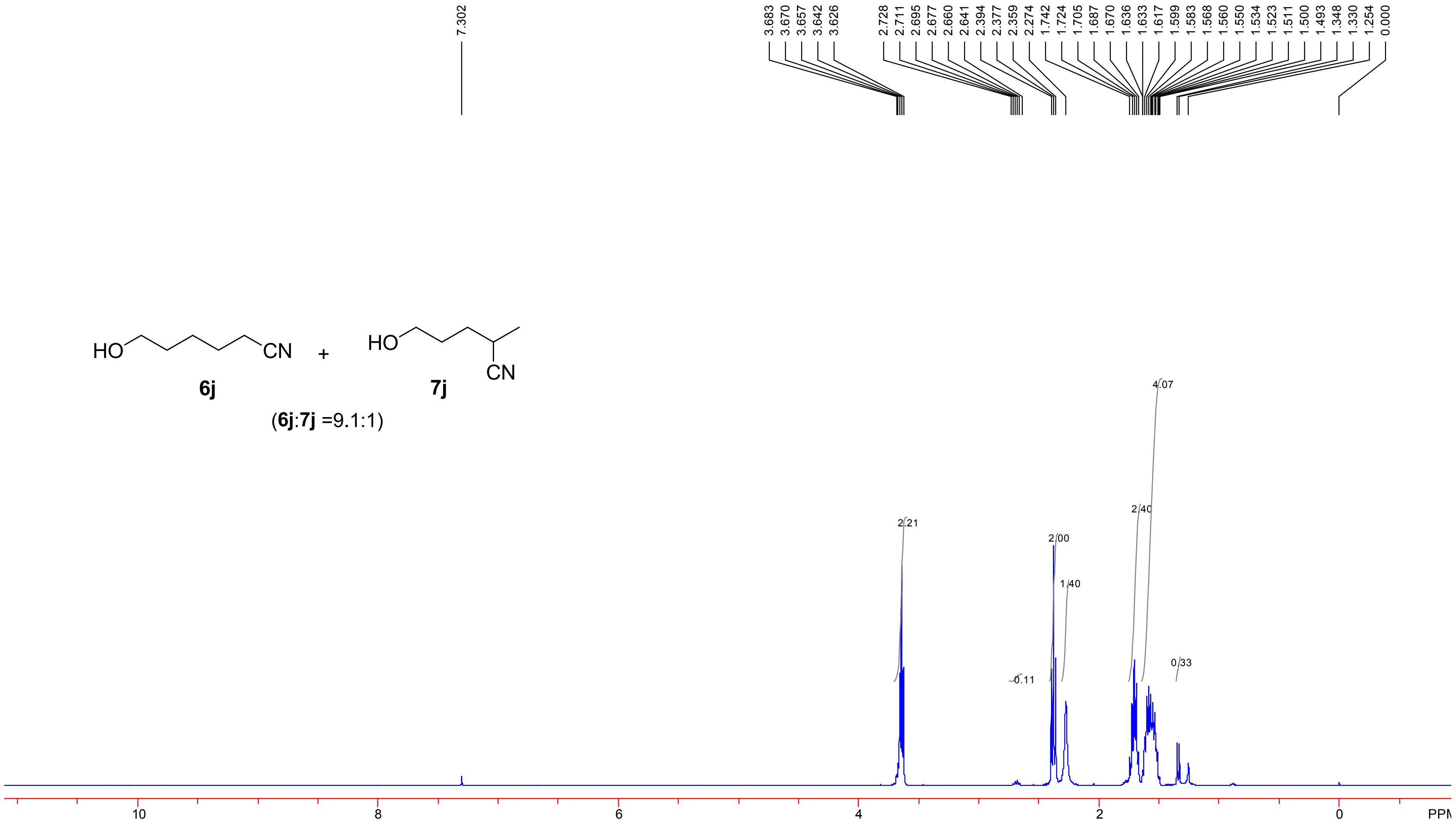
CN
TBDPSO

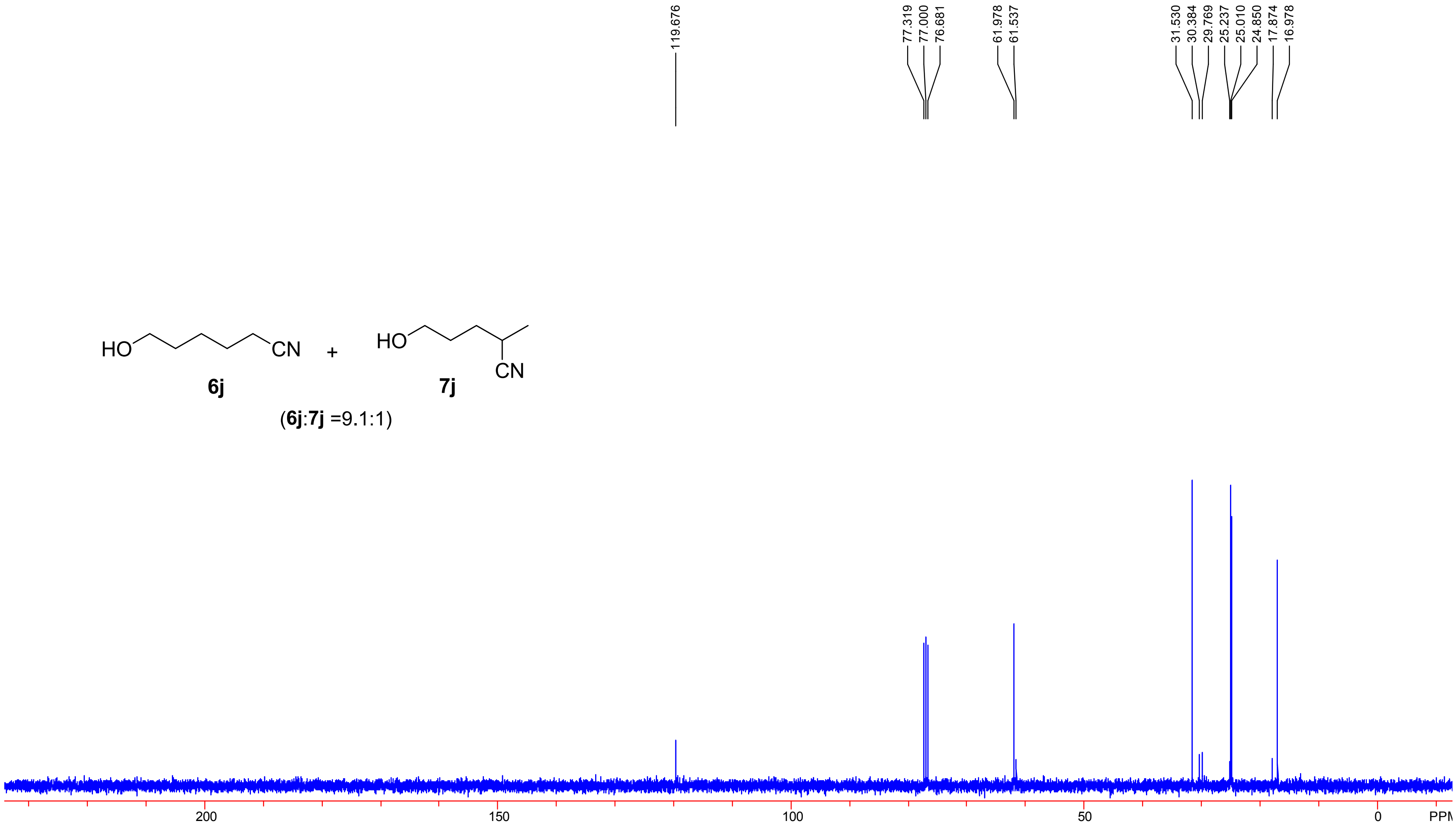
7i


135.506
135.453
133.354
133.152
129.797
129.776
127.762
127.745
122.912
77.315
77.000
76.681
60.534
36.704
26.788
21.938
19.181
17.763
200
150
100
50
0
PP

6j **7j**

(**6j**:**7j** =9.1:1)



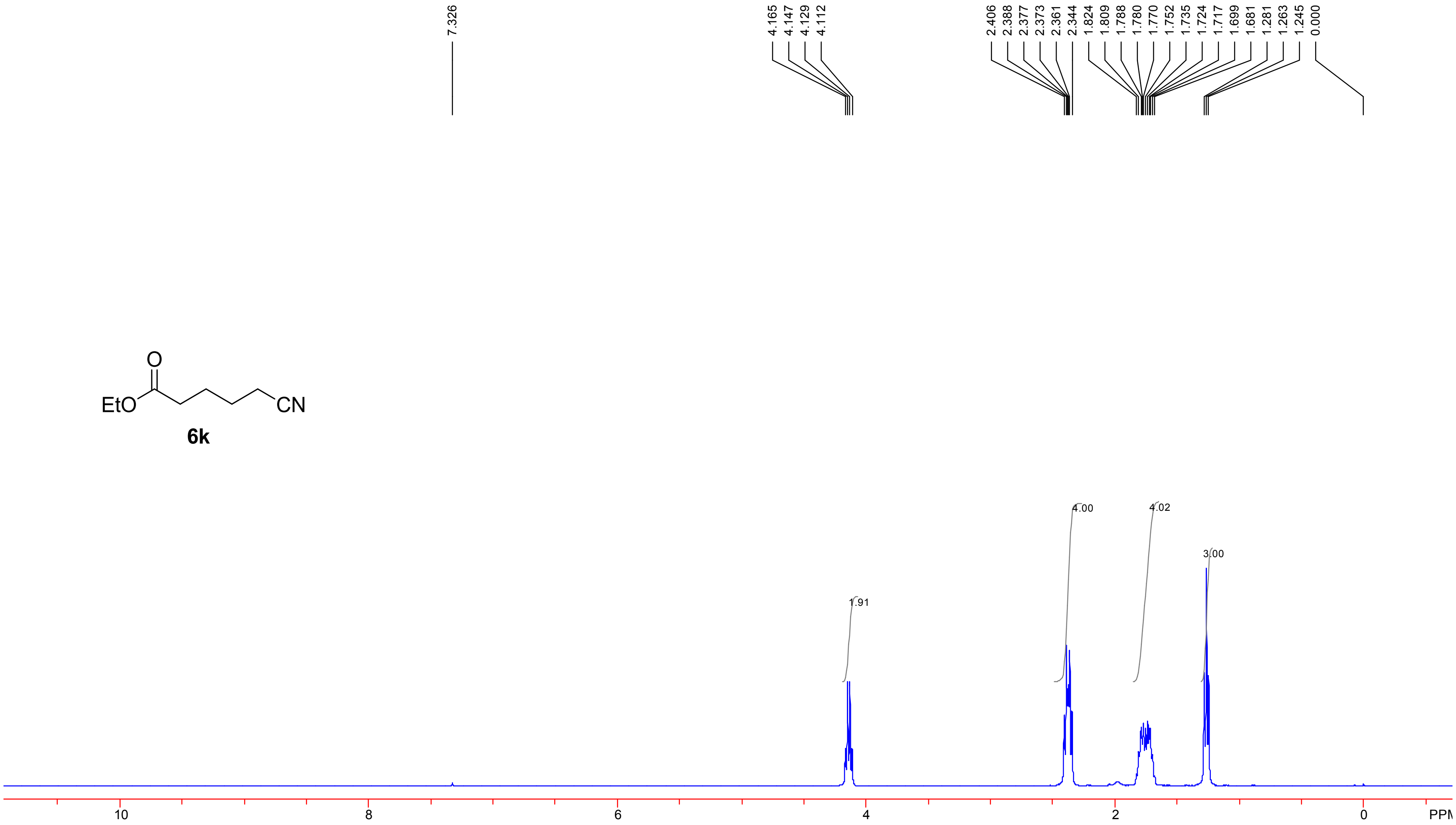


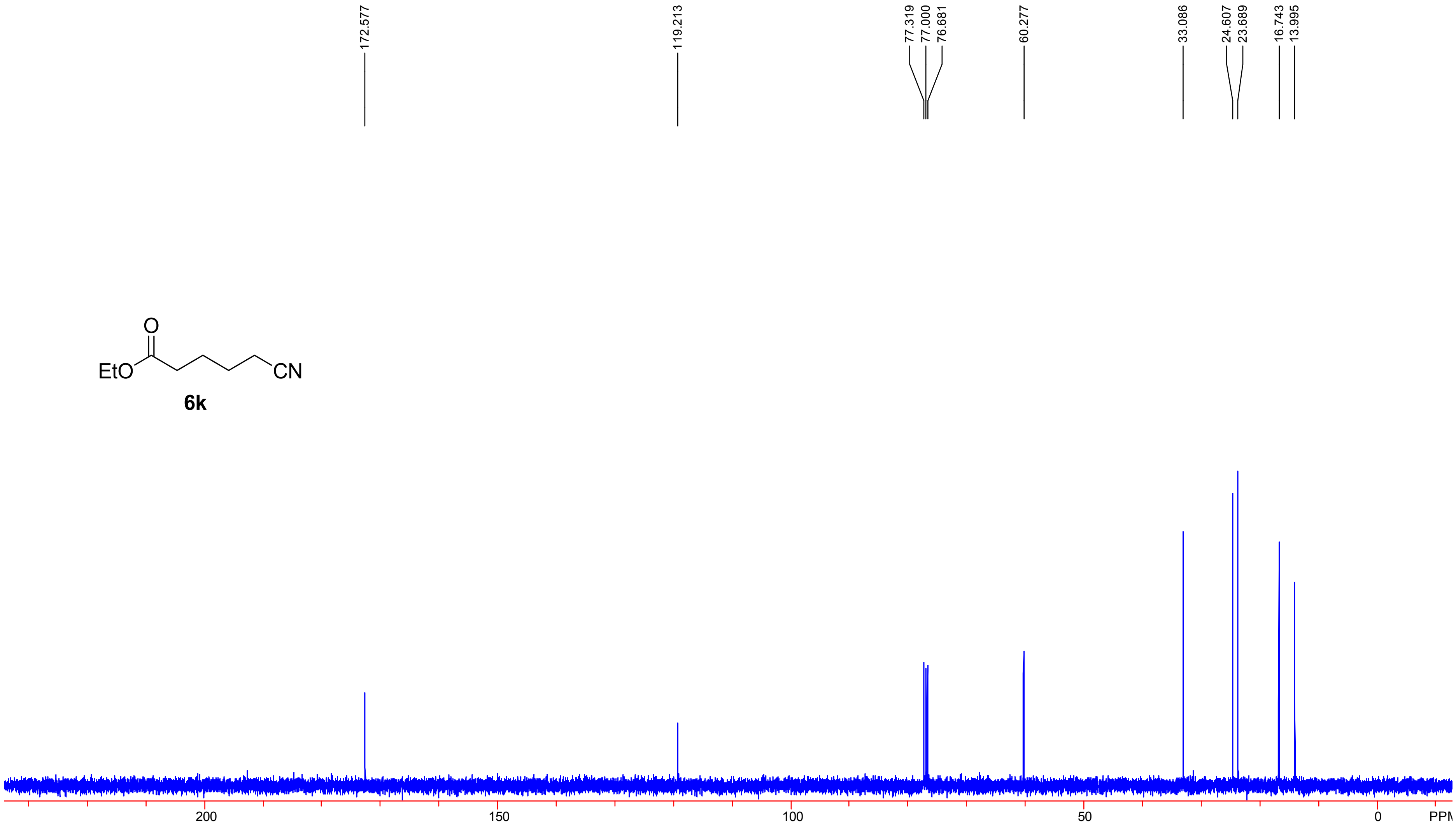
6j **7j**

(**6j**:**7j** =9.1:1)

O
EtO
CN

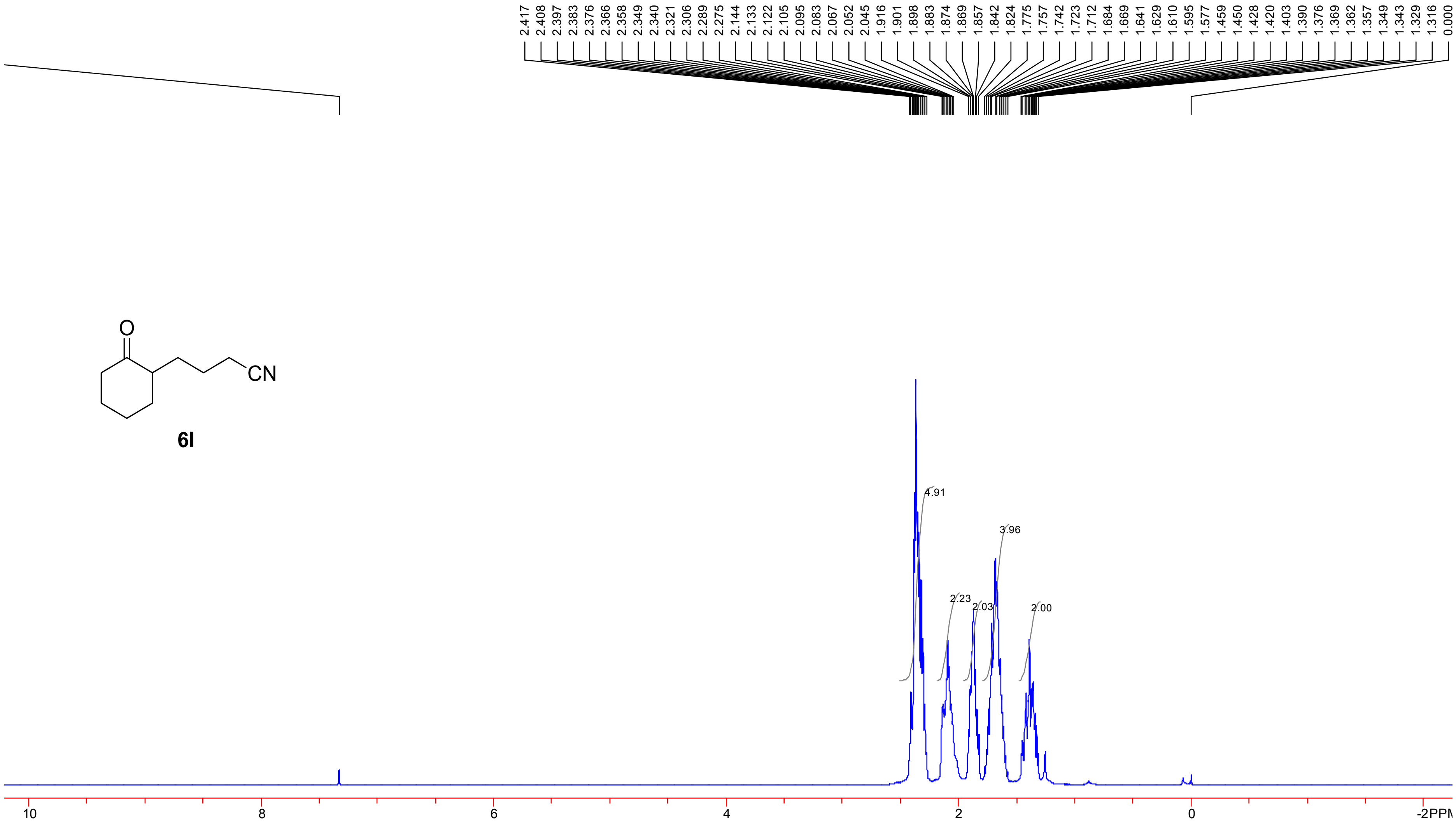
6k


7.326
4.165
4.147
4.129
4.112
2.406
2.388
2.377
2.373
2.361
2.344
1.824
1.809
1.788
1.780
1.770
1.752
1.735
1.724
1.717
1.699
1.681
1.281
1.263
1.245
0.000
1.91
4.00
4.02
3.00
10
8
6
4
2
0
PPM



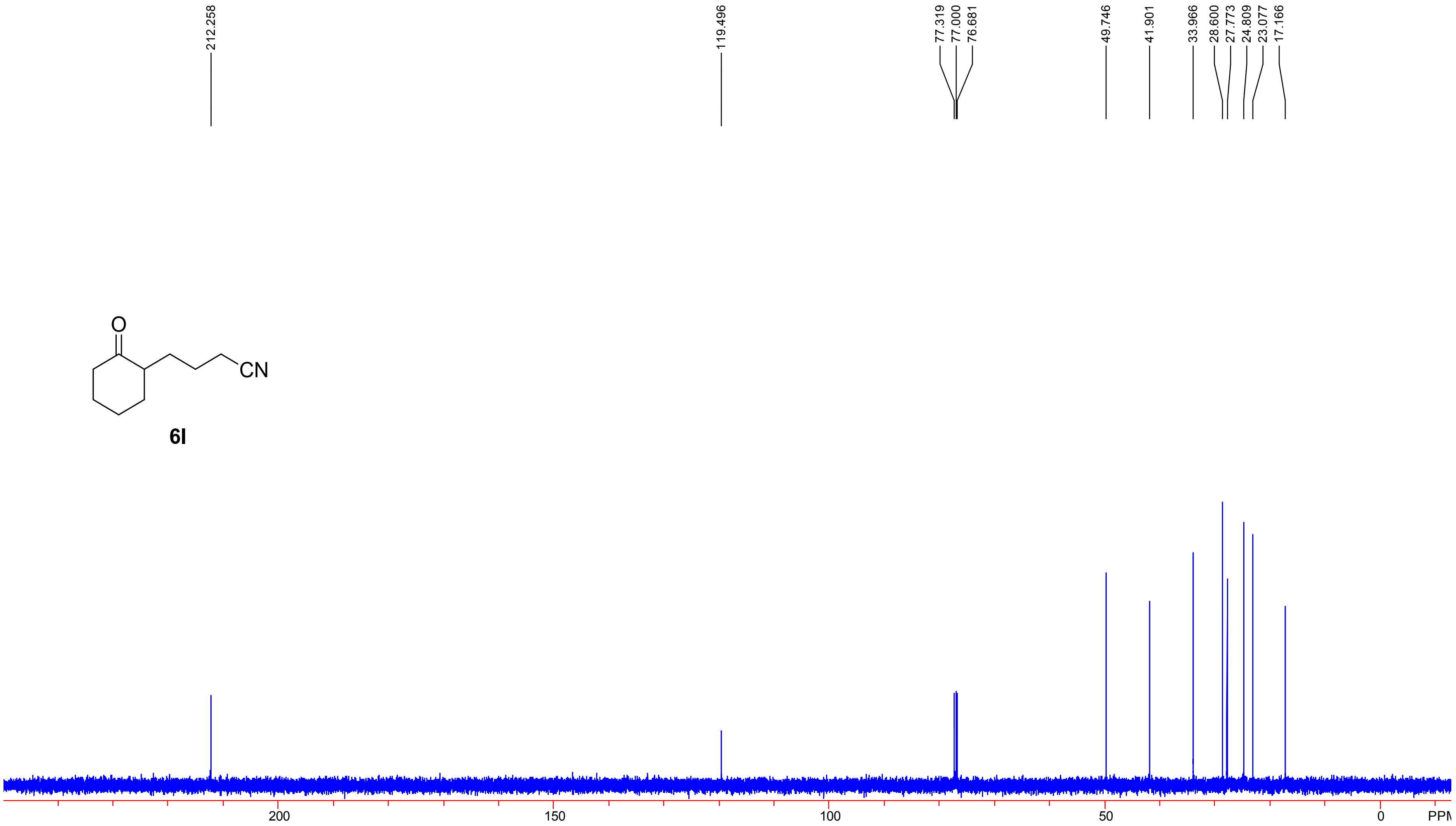
6k

172.577
119.213
77.319
77.000
76.681
60.277
33.086
24.607
23.689
16.743
13.995
O
EtO
CN
200
150
100
50
0
PPM


O
CN

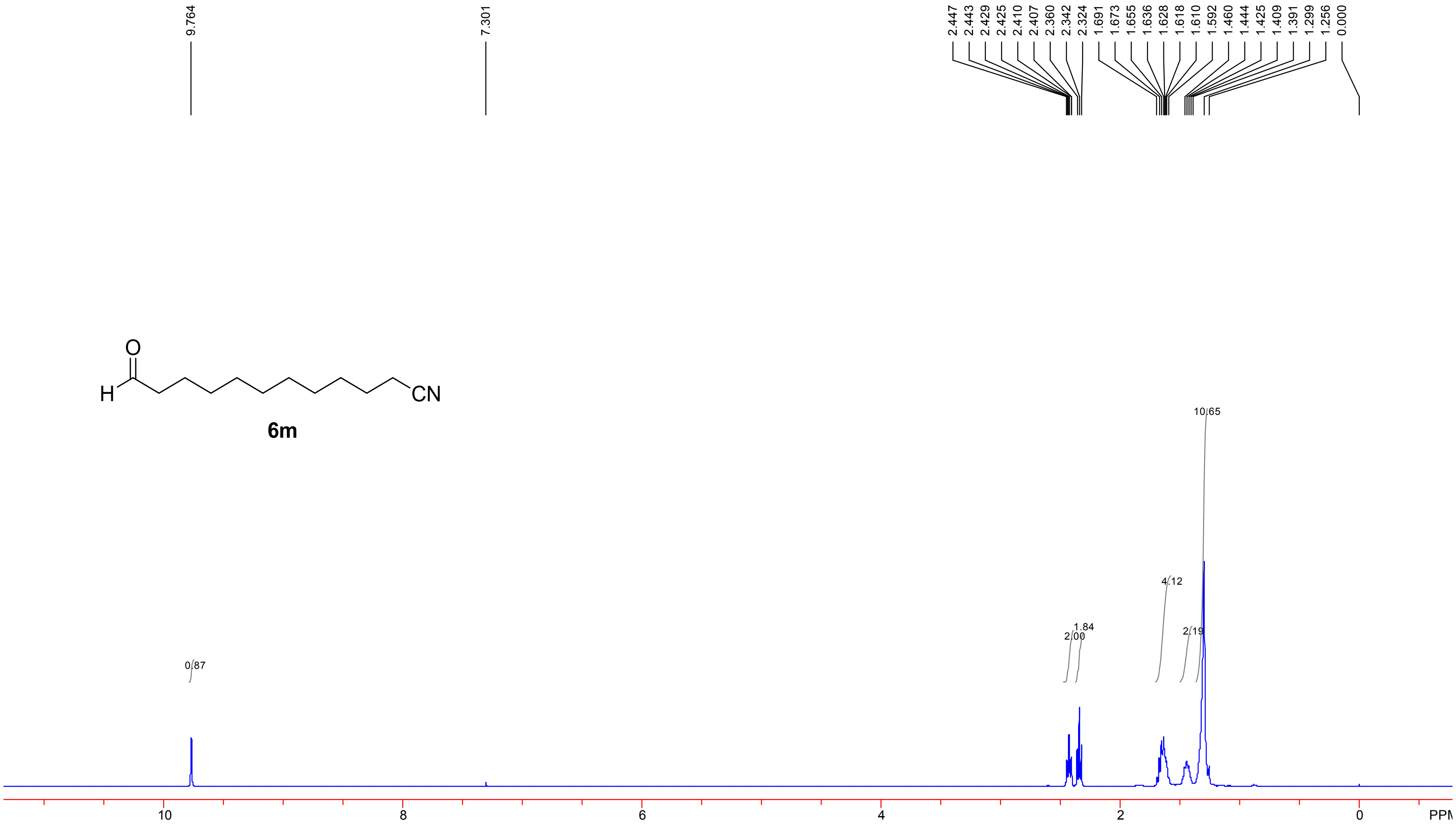
6l

2.417
2.408
2.397
2.383
2.376
2.366
2.358
2.349
2.340
2.321
2.306
2.289
2.275
2.144
2.133
2.122
2.105
2.095
2.083
2.067
2.052
2.045
1.916
1.901
1.898
1.883
1.874
1.869
1.857
1.842
1.824
1.775
1.757
1.742
1.723
1.712
1.684
1.669
1.641
1.629
1.610
1.595
1.577
1.459
1.450
1.428
1.420
1.403
1.390
1.376
1.369
1.362
1.357
1.349
1.343
1.329
1.316
0.000
4.91
3.96
2.23
2.03
2.00
10
8
6
4
2
0
-2PP

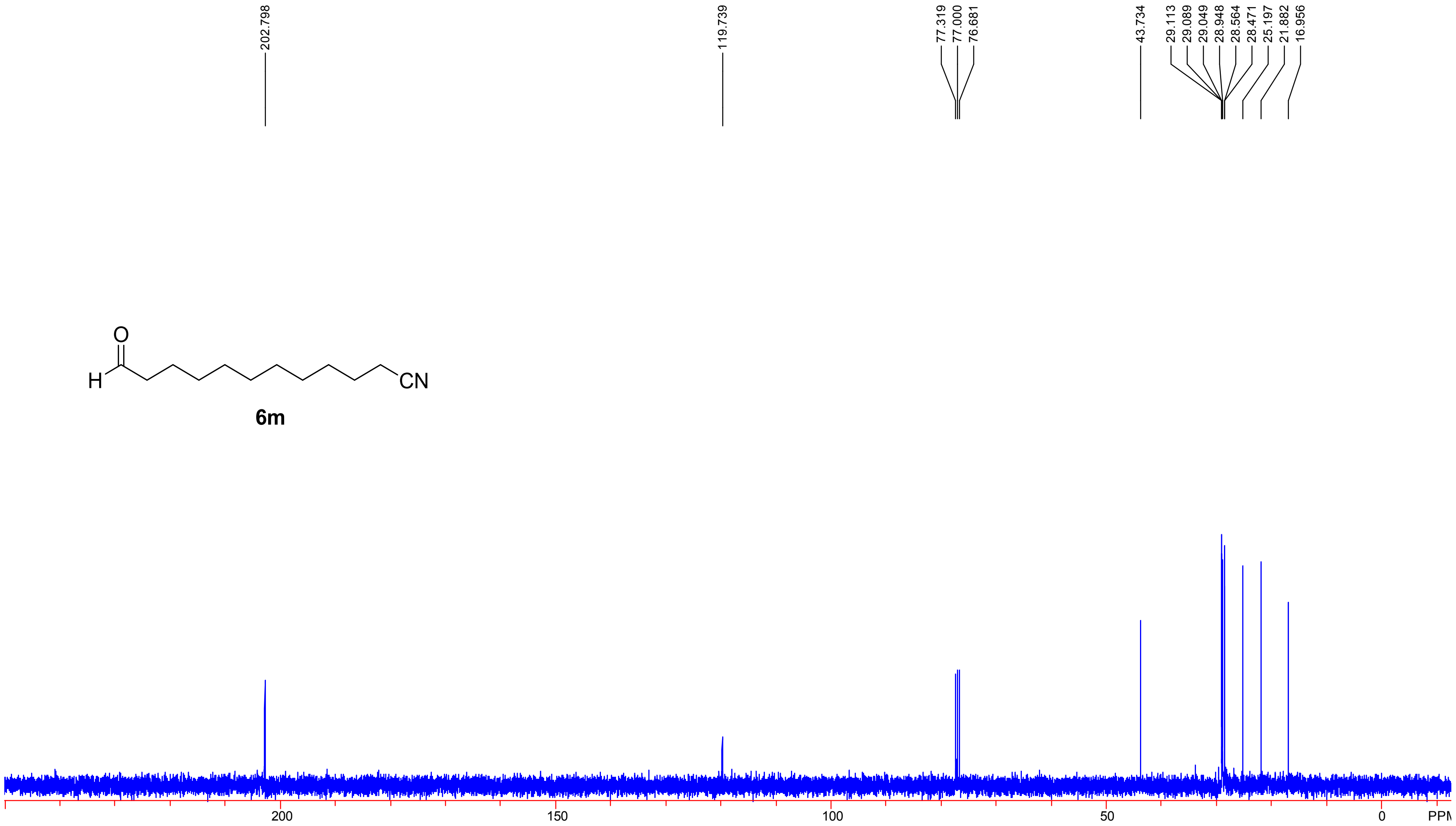

O
CN

6l

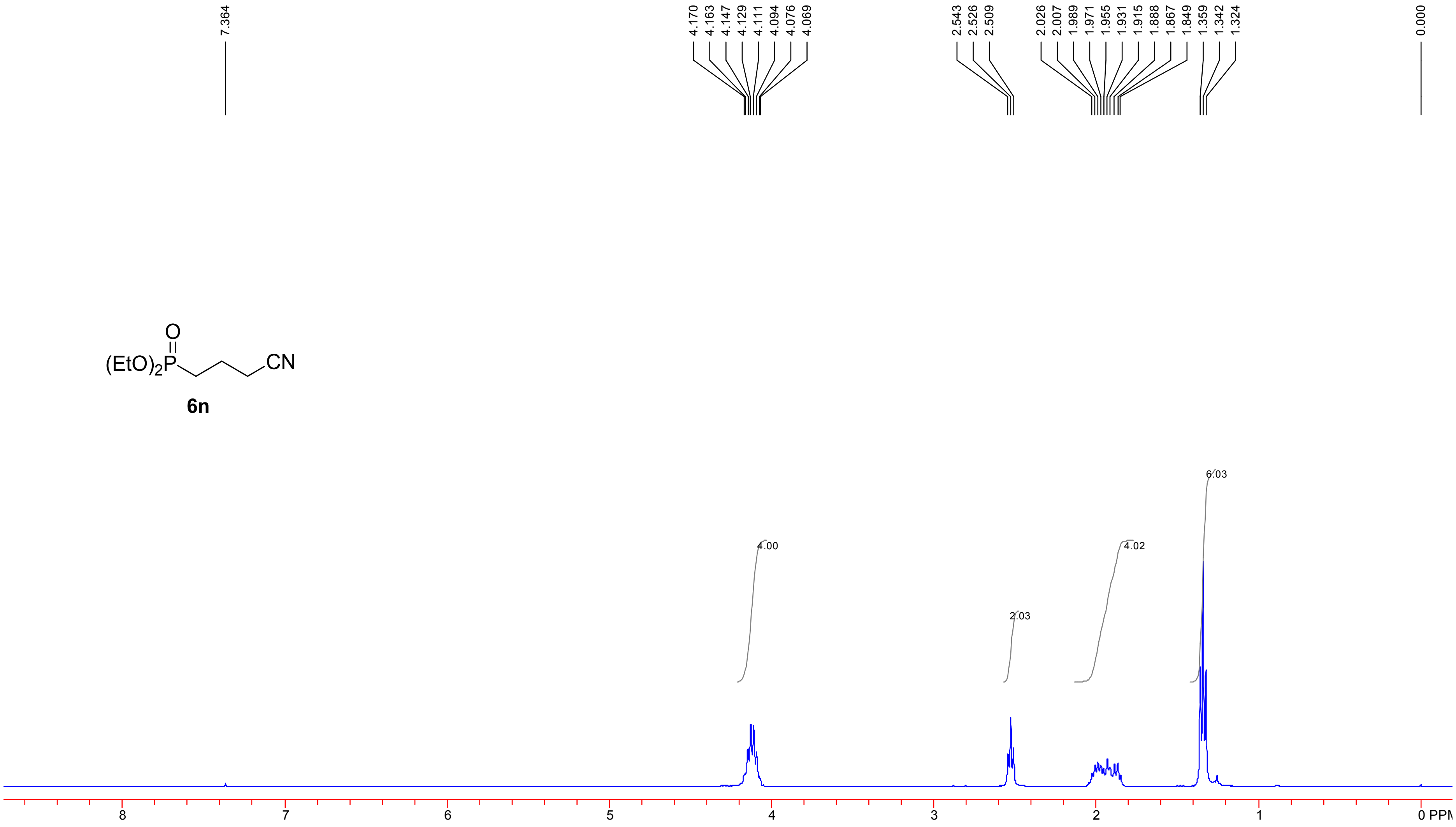
212.258
119.496
77.319
77.000
76.681
49.746
41.901
33.966
28.600
27.773
24.809
23.077
17.166
200
150
100
50
0
PPM

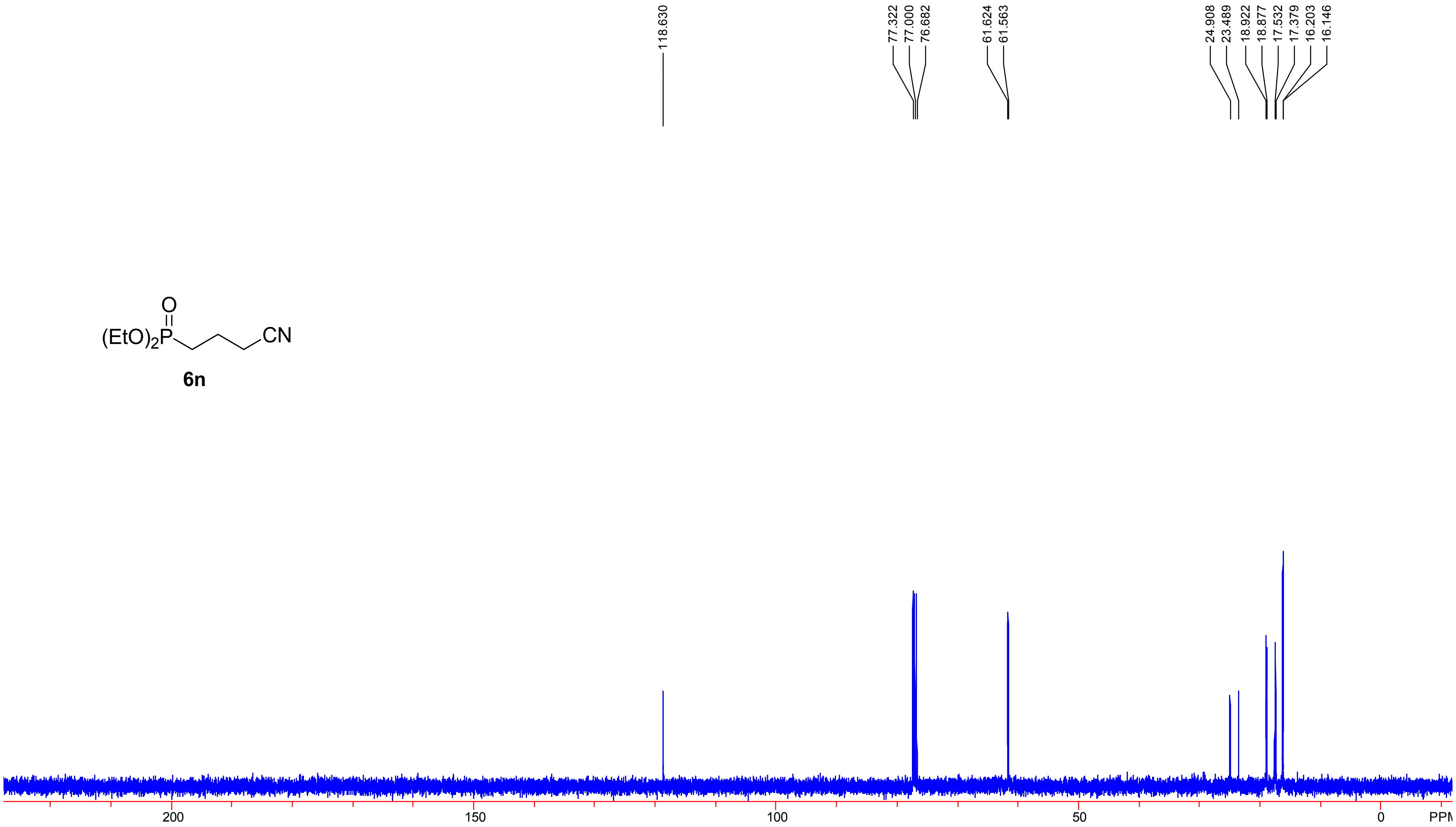

9.764
7.301
2.447
2.443
2.429
2.425
2.410
2.407
2.360
2.342
2.324
1.691
1.673
1.655
1.636
1.628
1.618
1.610
1.592
1.460
1.444
1.425
1.409
1.391
1.299
1.256
0.000
O
H
CN
0.87
2.00
1.84
4.12
2.19
10.65
10
8
6
4
2
0
PPM

6m


202.798
119.739
77.319
77.000
76.681
43.734
29.113
29.089
29.049
28.948
28.564
28.471
25.197
21.882
16.956
O
H
CN
6m
200
150
100
50
0
PP

6n


7.364
4.170
4.163
4.147
4.129
4.111
4.094
4.076
4.069
2.543
2.526
2.509
2.026
2.007
1.989
1.971
1.955
1.931
1.915
1.888
1.867
1.849
1.359
1.342
1.324
0.000
4.00
2.03
4.02
6.03
8
7
6
5
4
3
2
1
0 PP

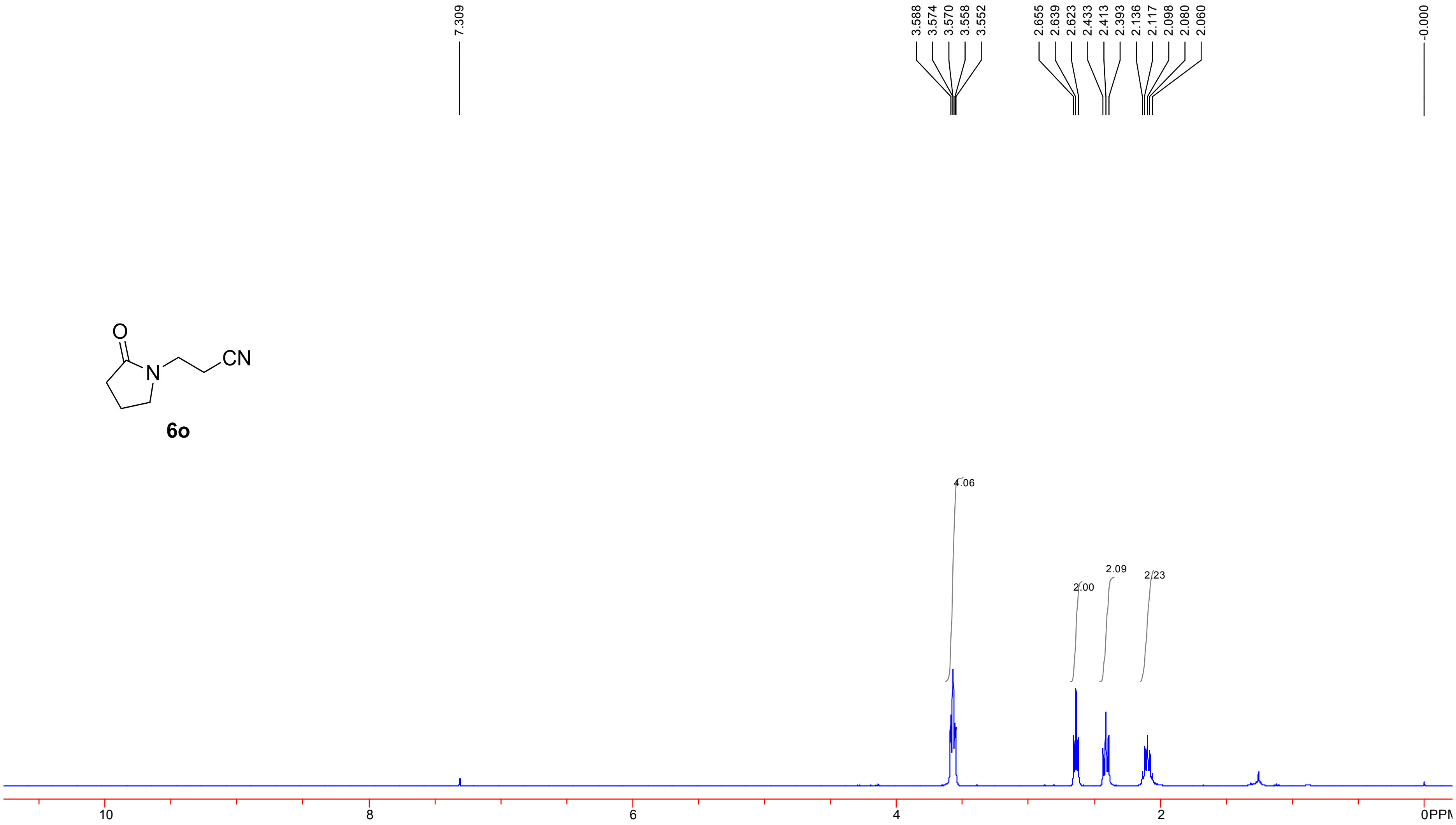


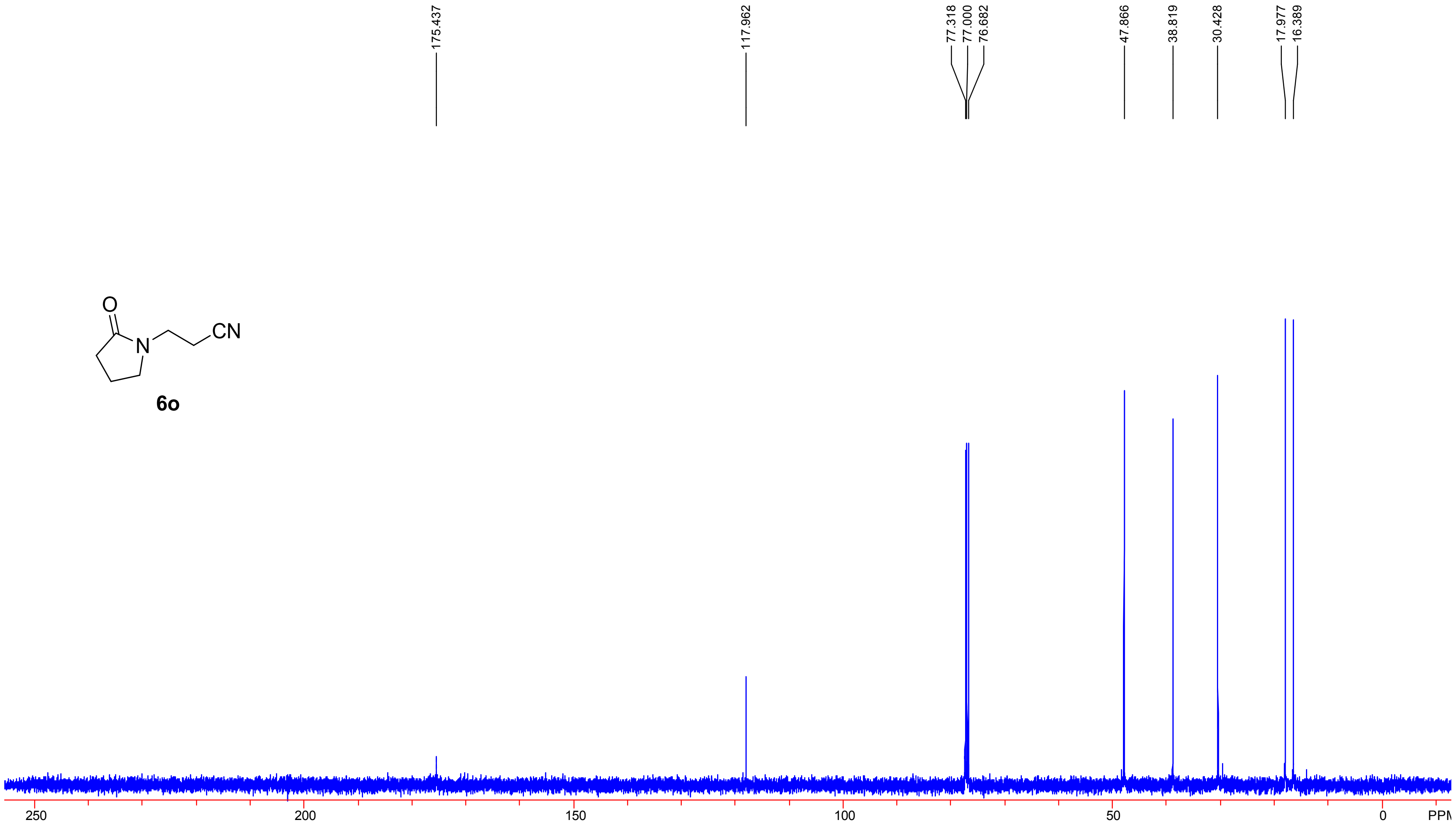
6n

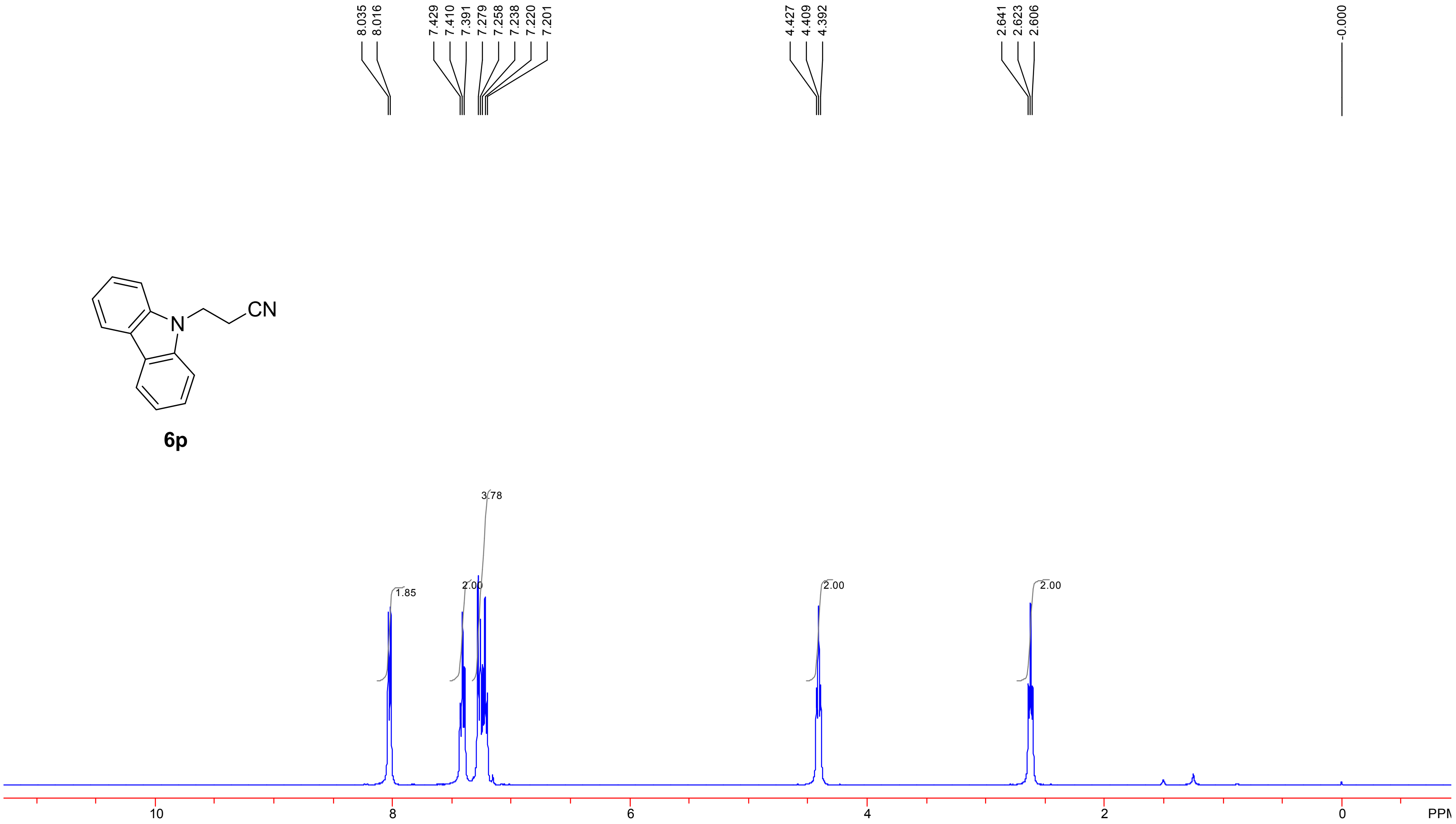
118.630
77.322
77.000
76.682
61.624
61.563
24.908
23.489
18.922
18.877
17.532
17.379
16.203
16.146
200
150
100
50
0
PPM

O
N
CN

6o


7.309
3.588
3.574
3.570
3.558
3.552
2.655
2.639
2.623
2.433
2.413
2.393
2.136
2.117
2.098
2.080
2.060
-0.000
4.06
2.00
2.09
2.23
10
8
6
4
2
0PPM

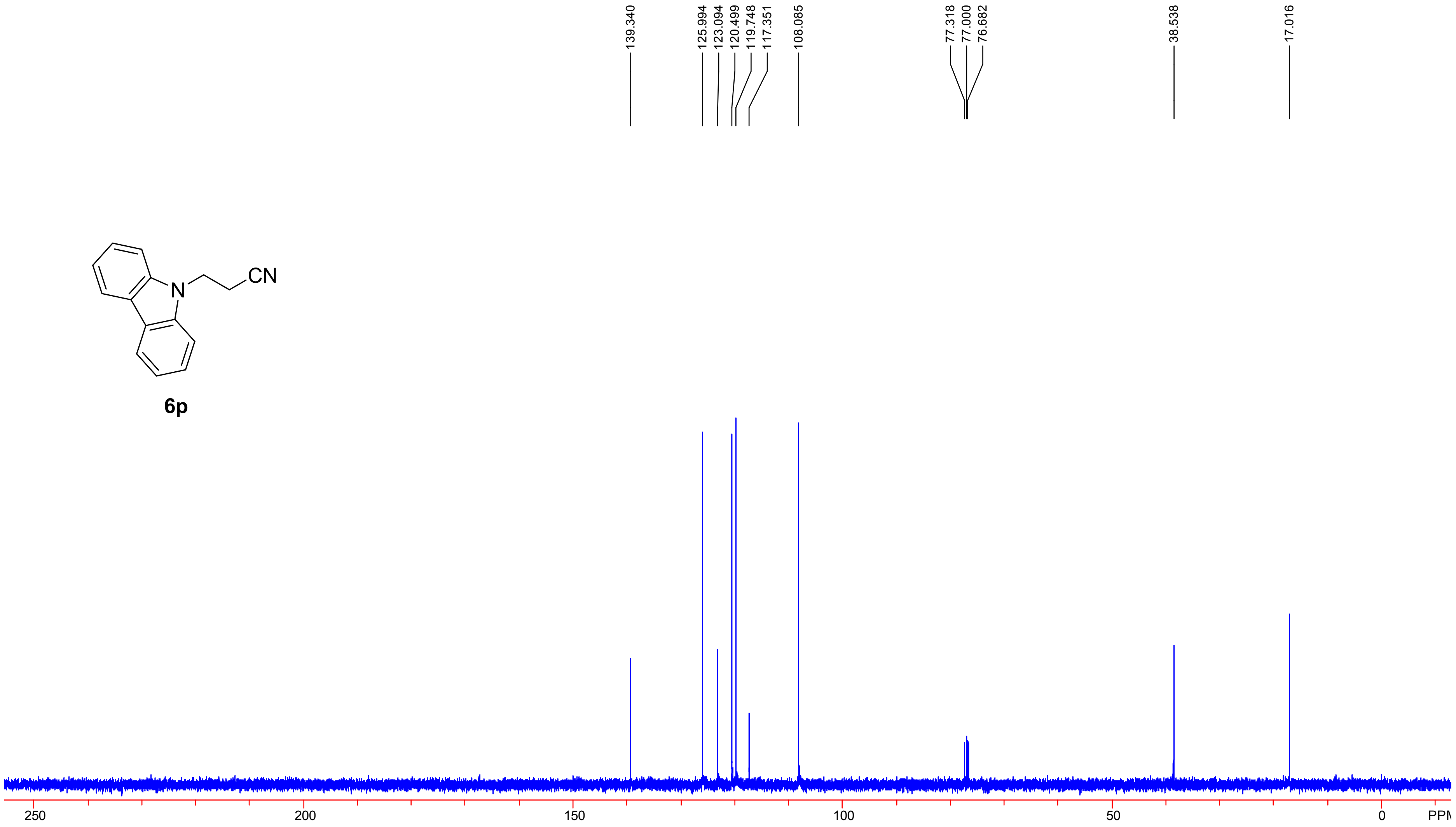

175.437
117.962
77.318
77.000
76.682
47.866
38.819
30.428
17.977
16.389
O
N
CN
6o
250
200
150
100
50
0
PPM

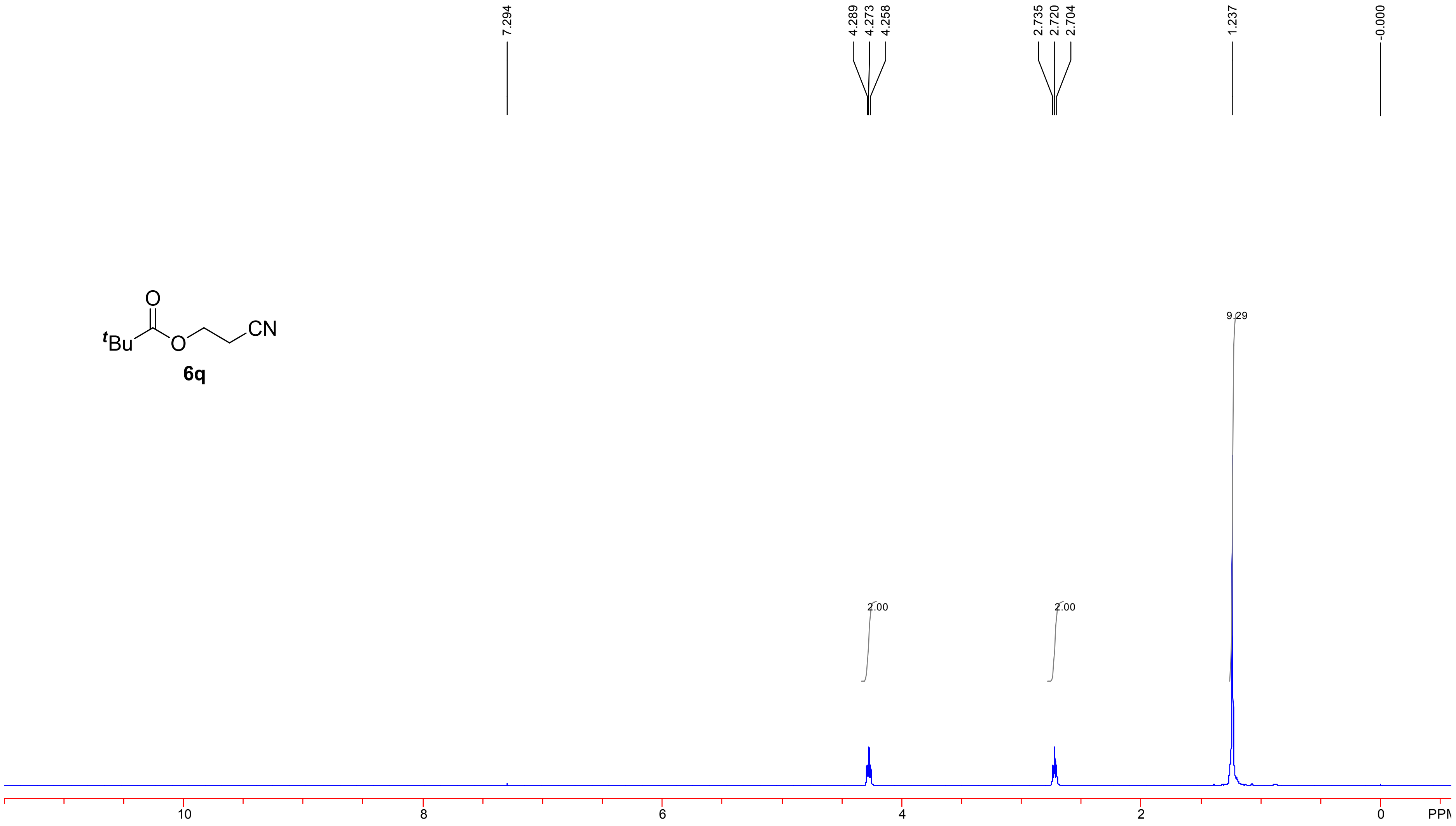


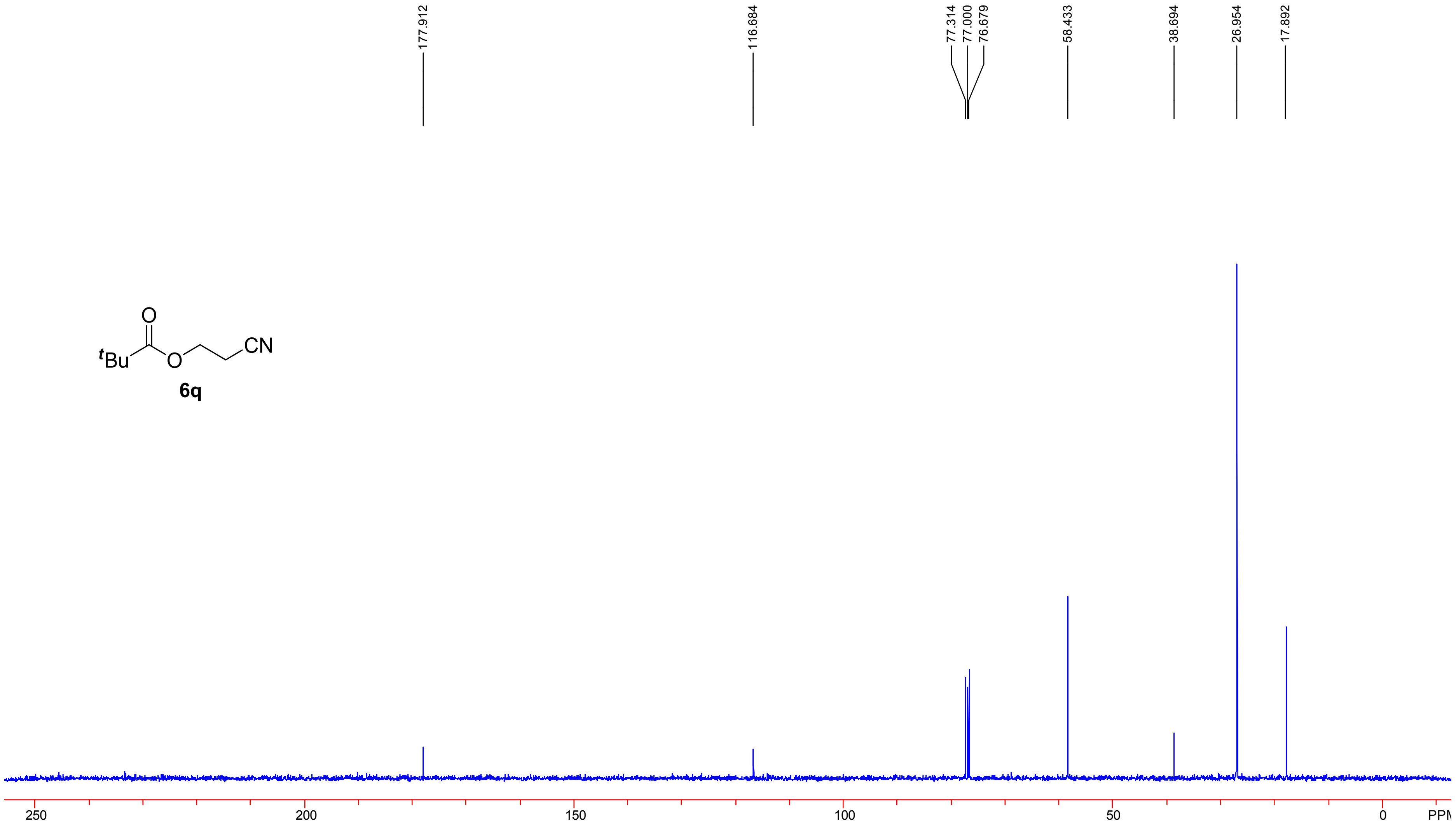
6p
8.035
8.016
7.429
7.410
7.391
7.279
7.258
7.238
7.220
7.201
4.427
4.409
4.392
2.641
2.623
2.606
-0.000
1.85
2.00
3.78
2.00
2.00
10
8
6
4
2
0
PPM

N
CN

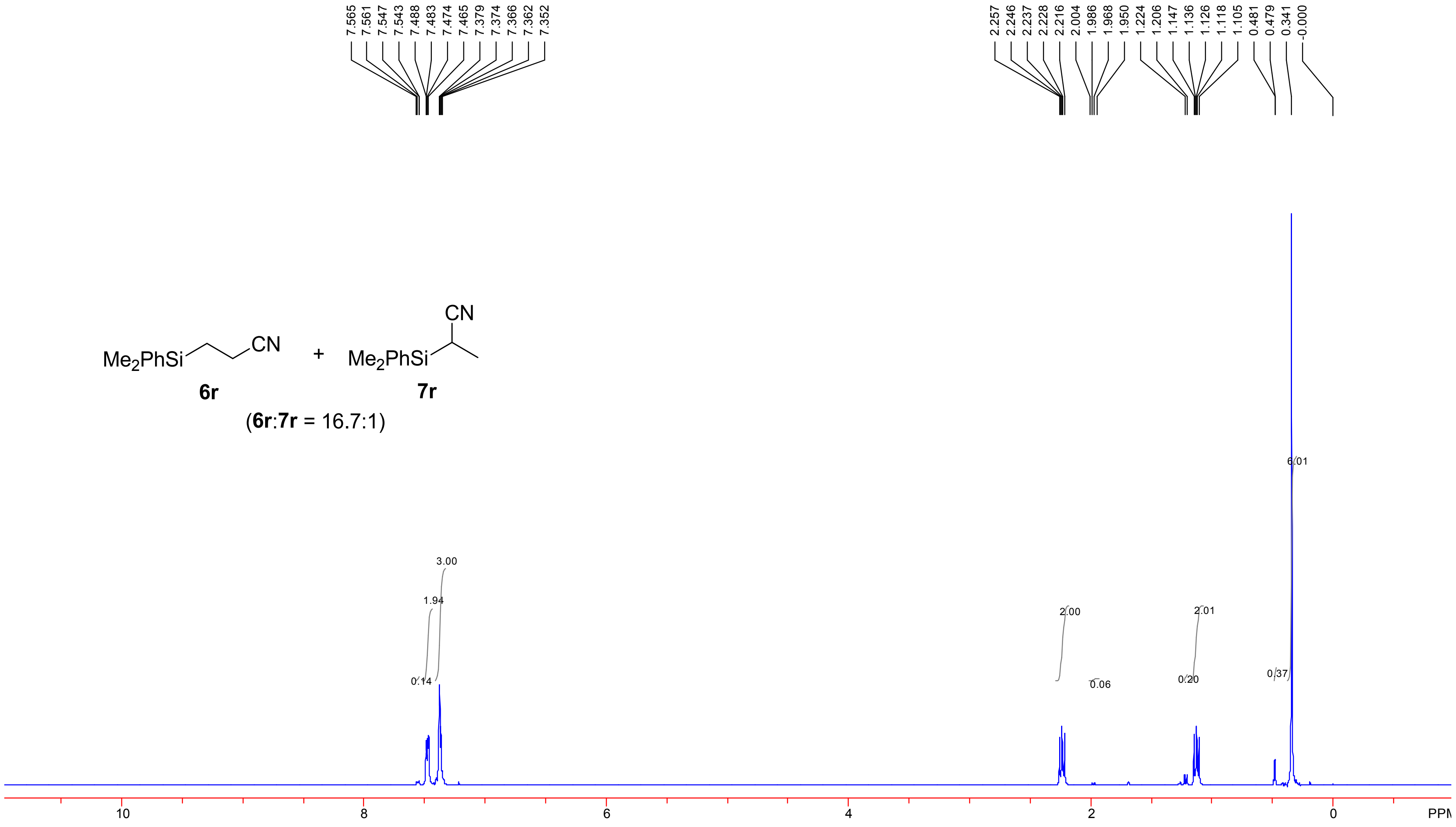
6p


139.340
125.994
123.094
120.499
119.748
117.351
108.085
77.318
77.000
76.682
38.538
17.016
250
200
150
100
50
0
PPM


7.294
4.289
4.273
4.258
2.735
2.720
2.704
1.237
-0.000
tBu
O
O
CN
6q
9.29
2.00
2.00
10
8
6
4
2
0
PPM


177.912
116.684
77.314
77.000
76.679
58.433
38.694
26.954
17.892
O
tBu
O
CN
250
200
150
100
50
0
PPM

6q



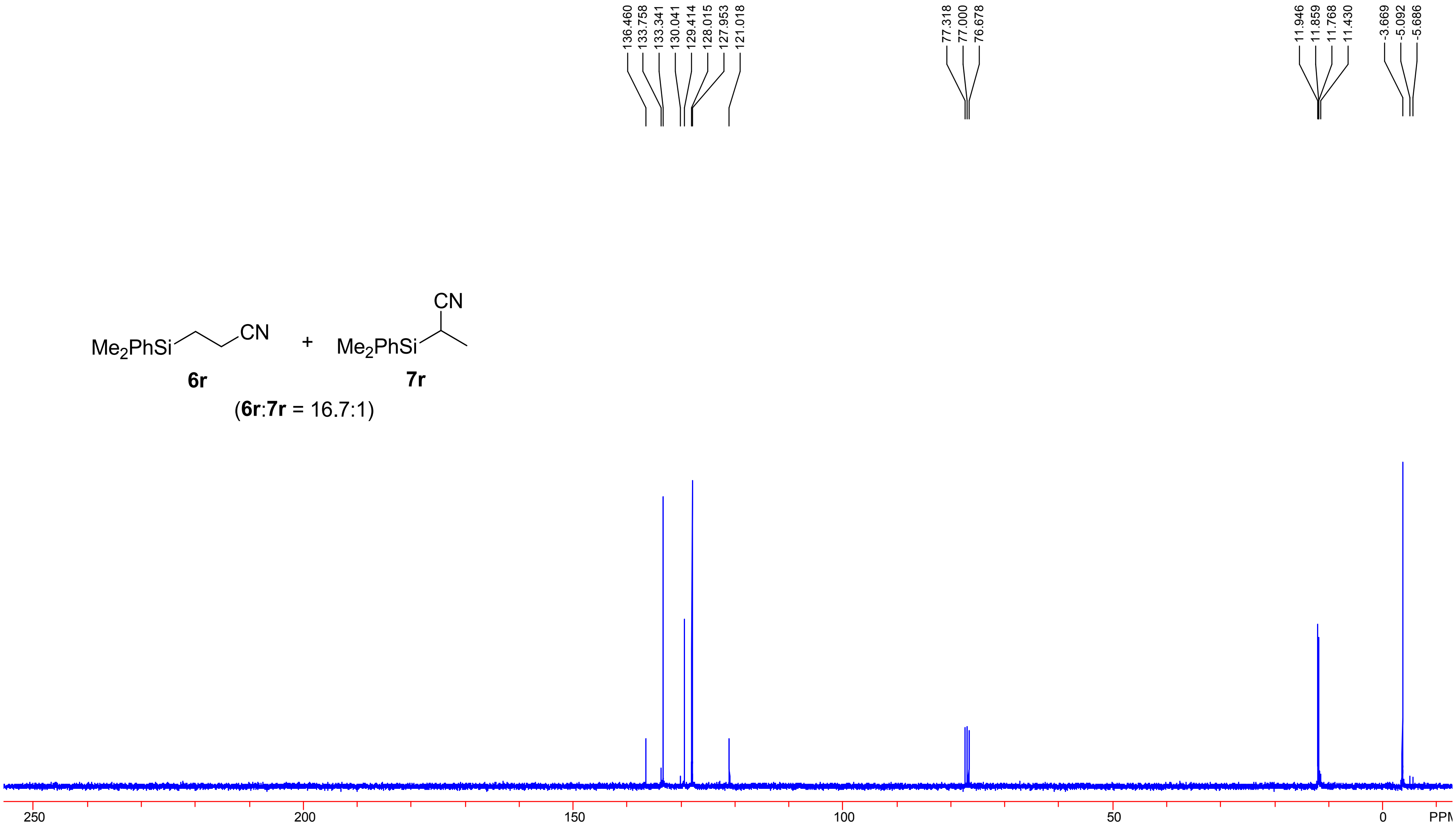
6r

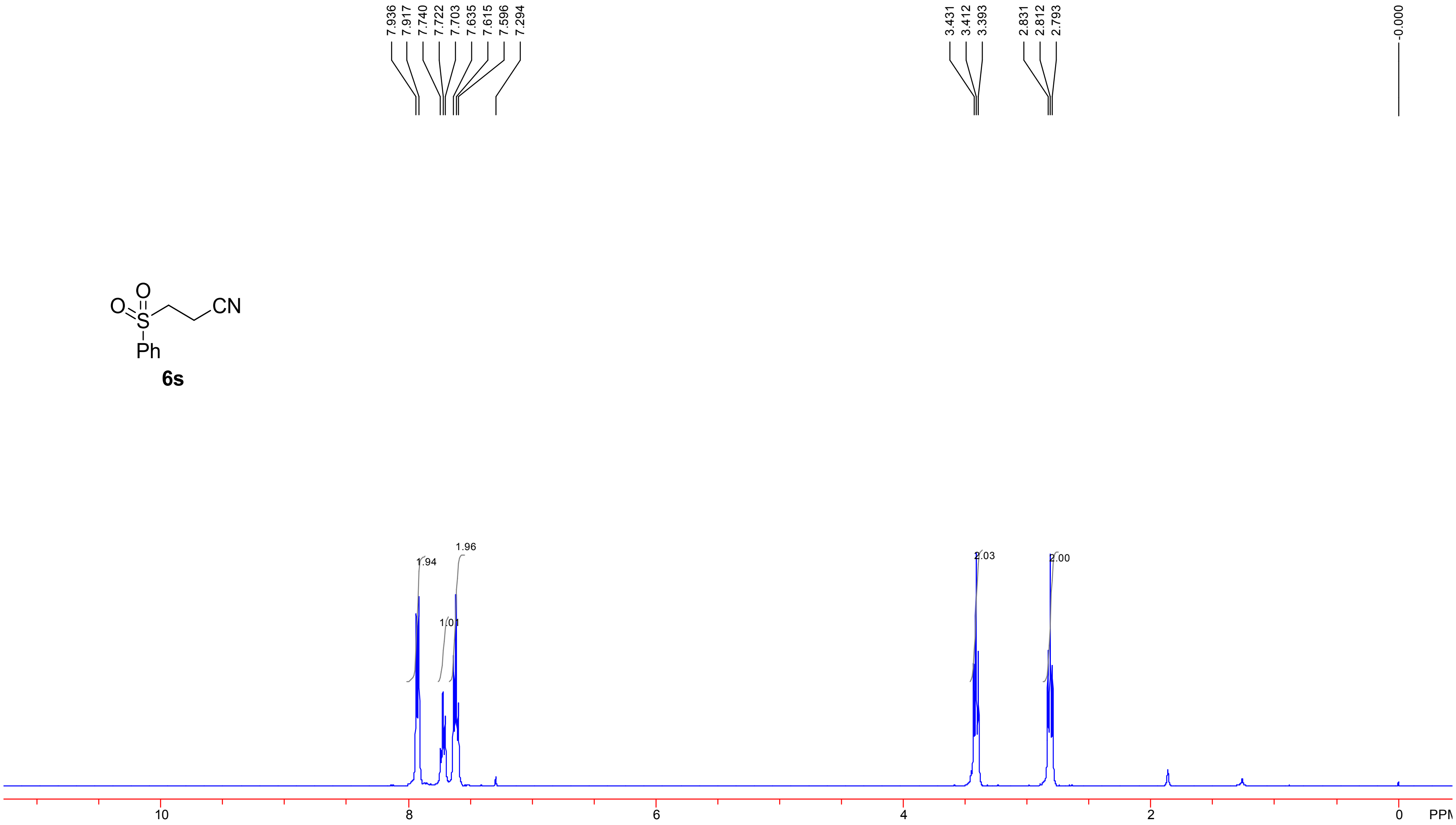
7r

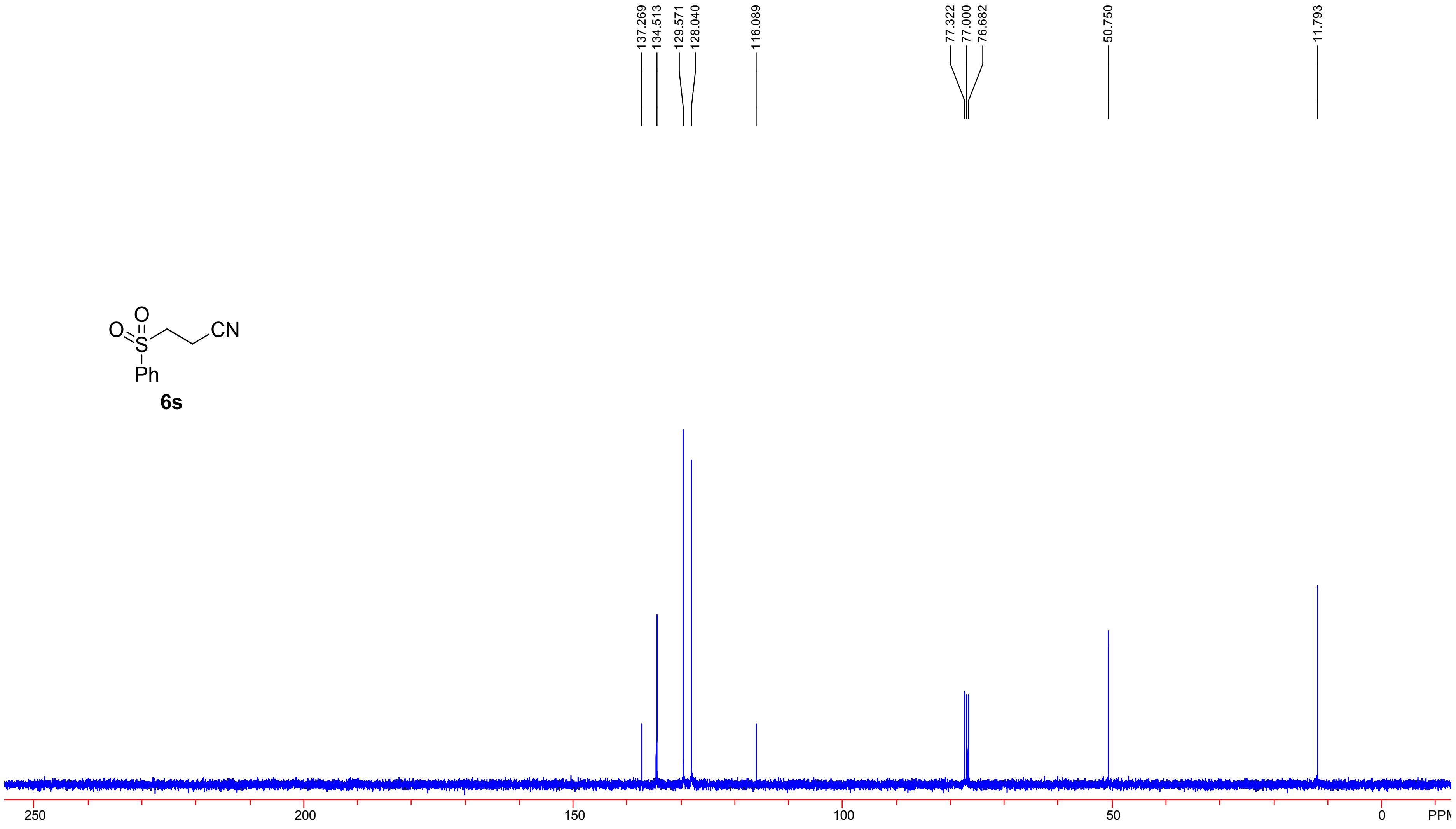
(**6r**:**7r** = 16.7:1)

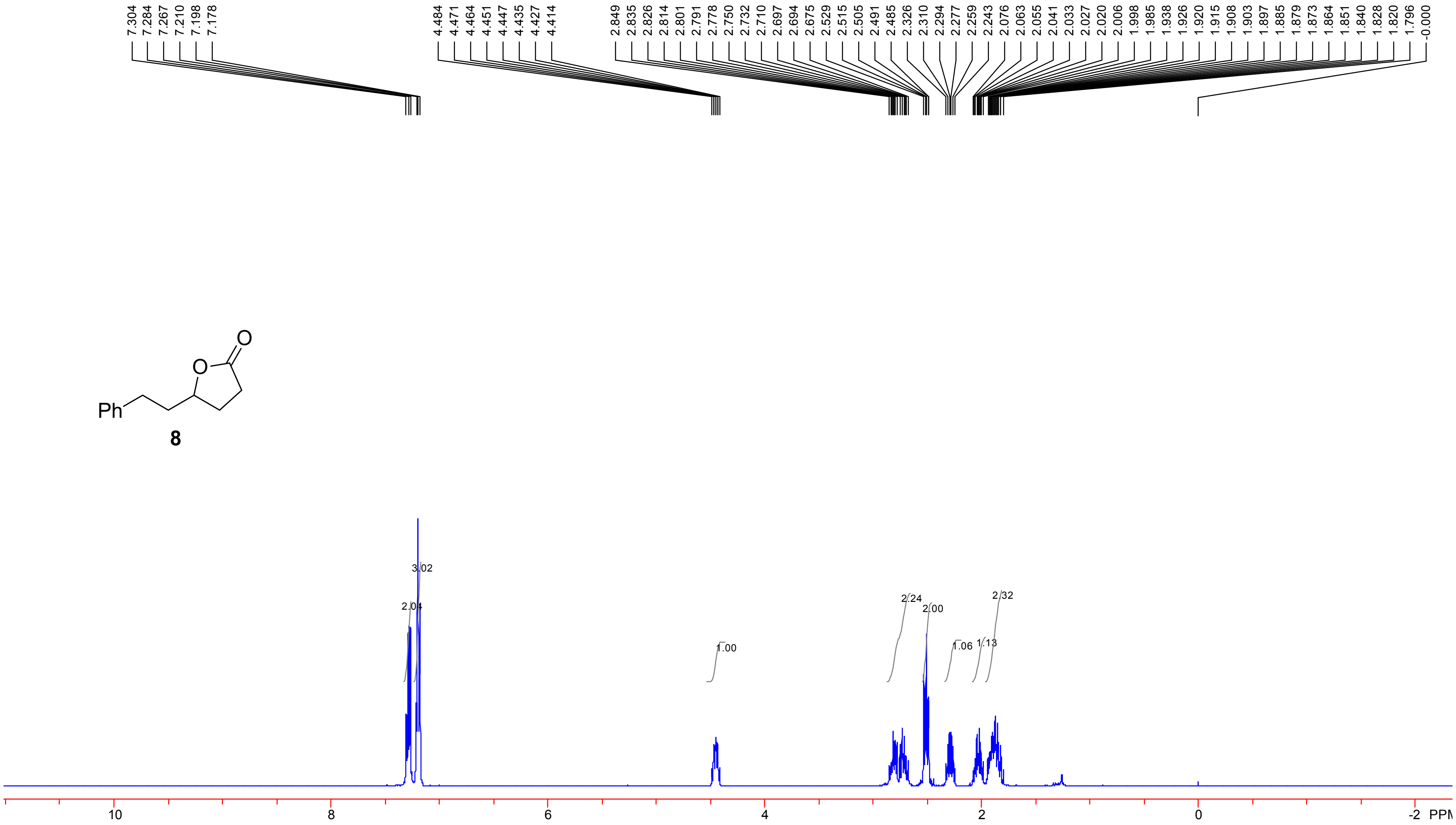
6r **7r**

(**6r**:**7r** = 16.7:1)




7.936
7.917
7.740
7.722
7.703
7.635
7.615
7.596
7.294
3.431
3.412
3.393
2.831
2.812
2.793
-0.000
O
O
S
CN
Ph
6s
1.94
1.01
1.96
2.03
2.00
10
8
6
4
2
0
PPM


6s
137.269
134.513
129.571
128.040
116.089
77.322
77.000
76.682
50.750
11.793
O
O
S
CN
Ph
250
200
150
100
50
0
PPM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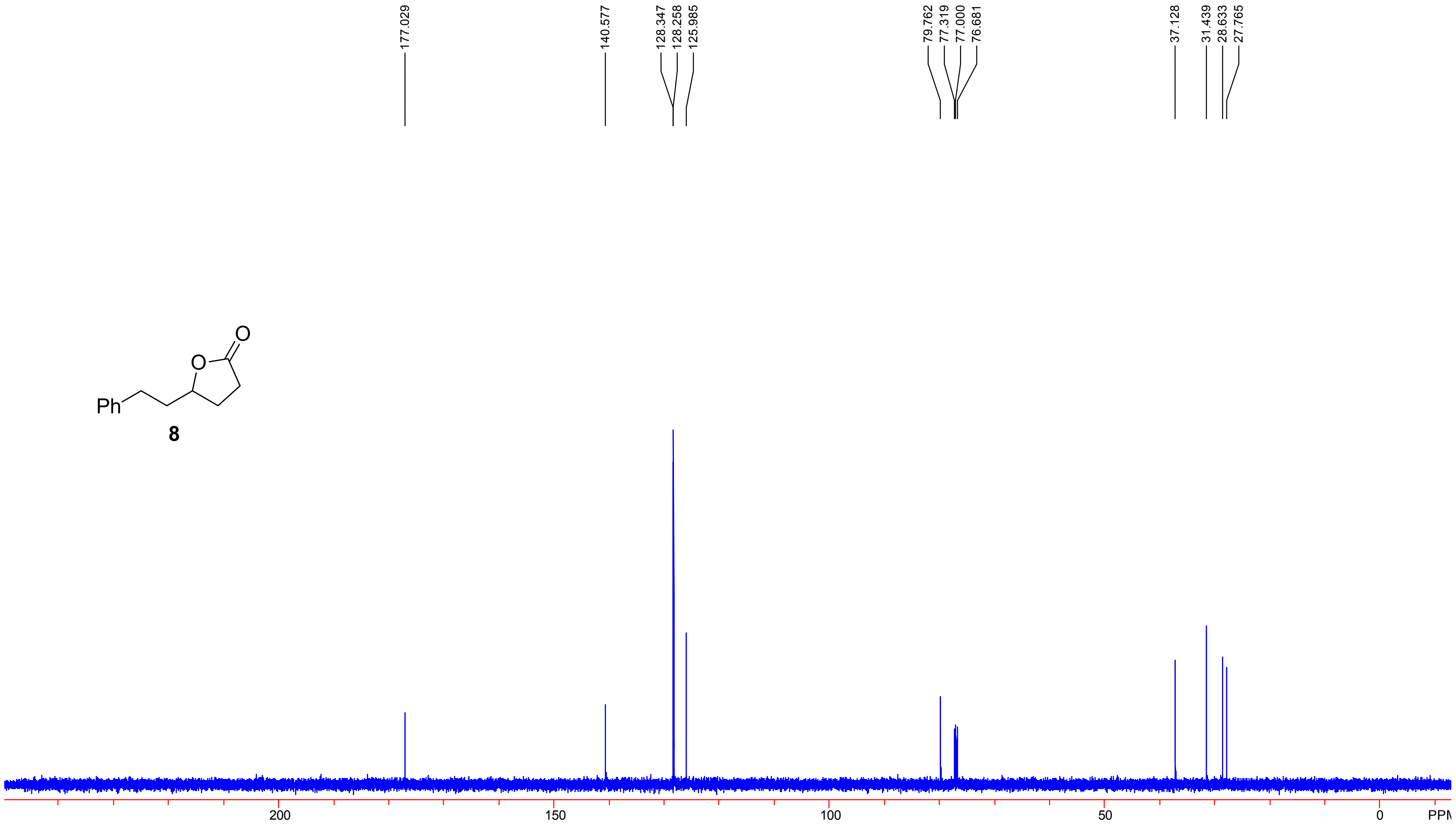
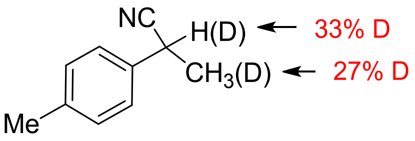
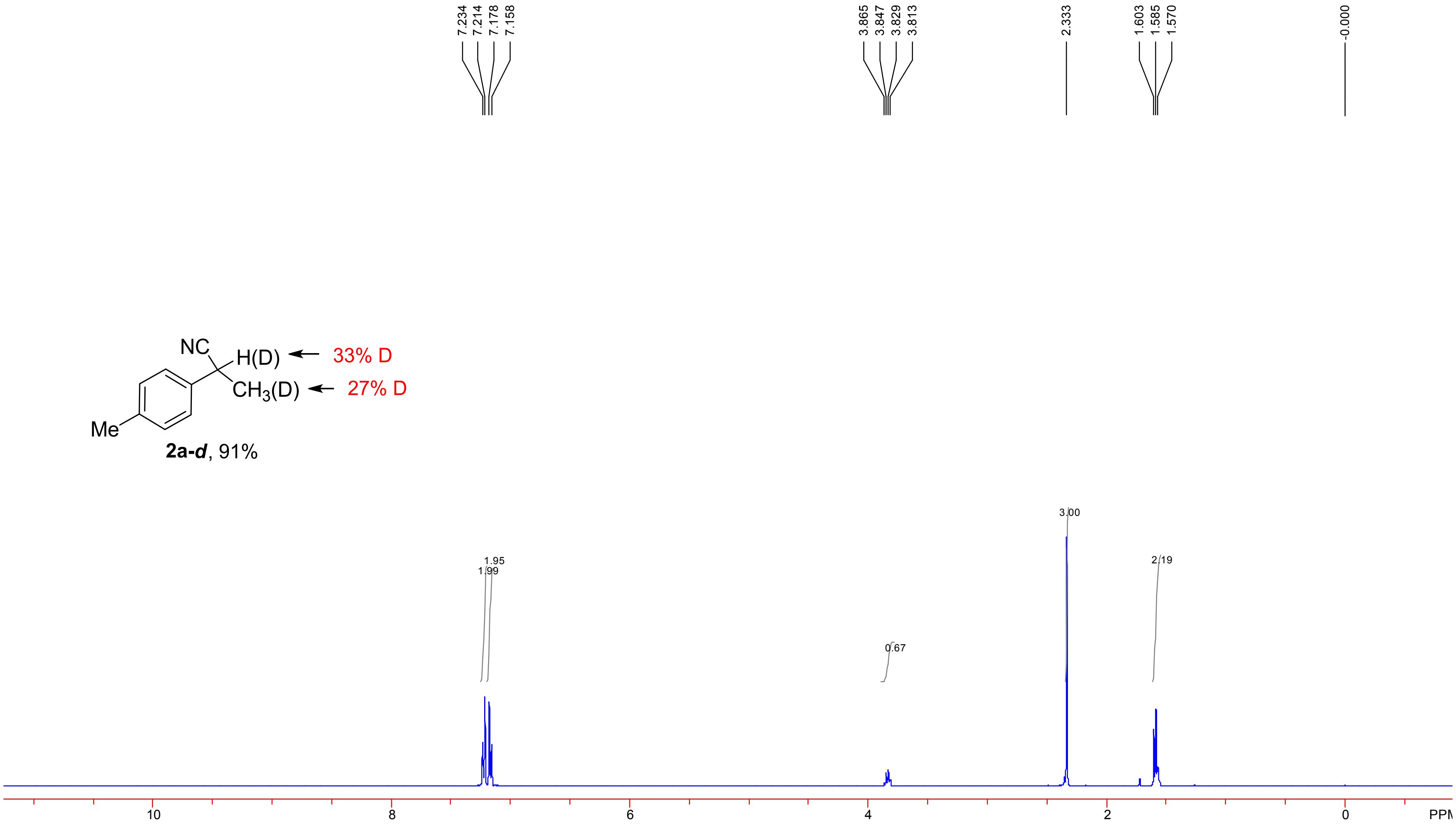
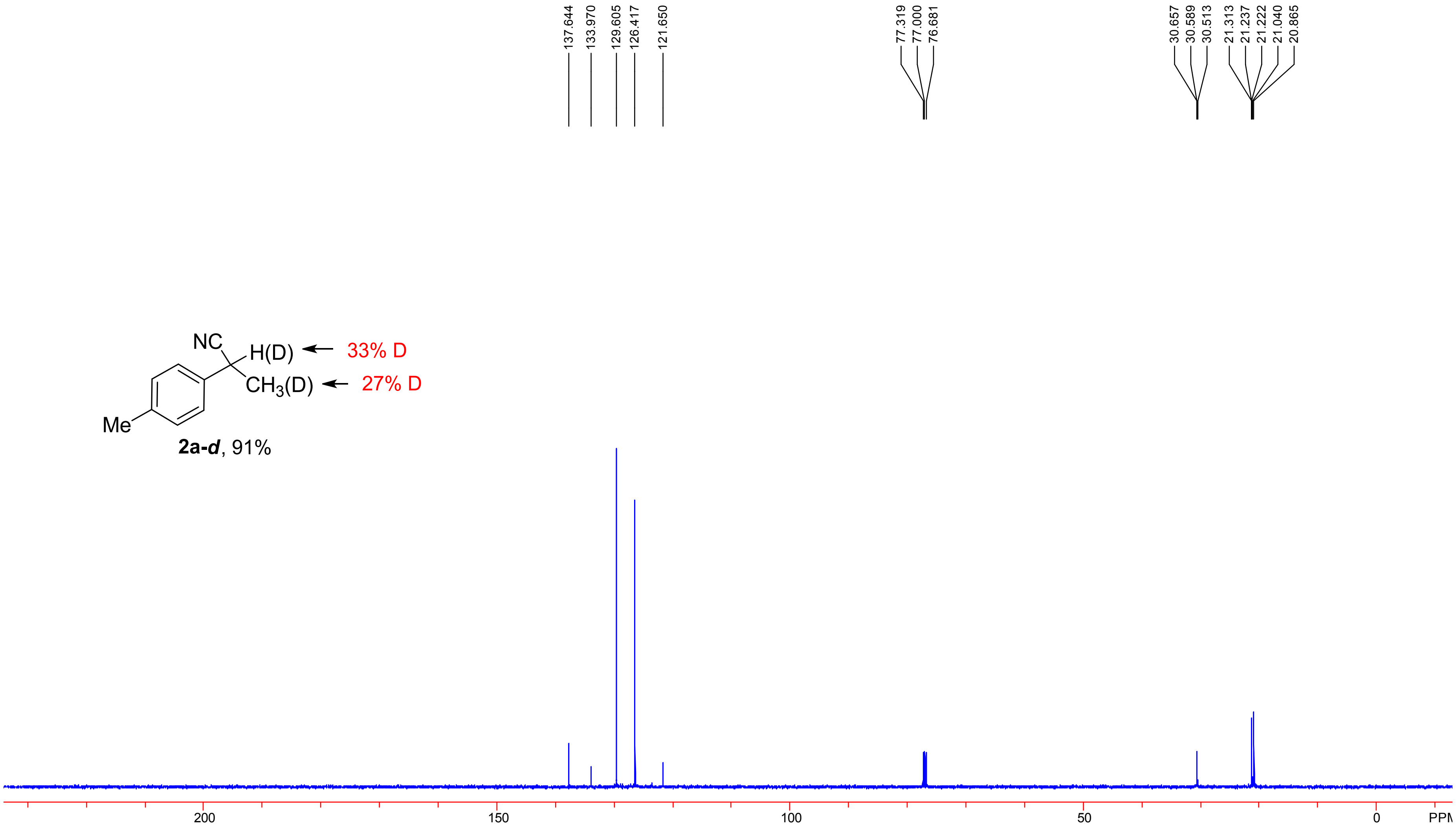
7.284
7.267
7.210
7.198
7.178
4.484
4.471
4.464
4.451
4.447
4.435
4.427
4.414
2.849
2.835
2.826
2.814
2.801
2.791
2.778
2.750
2.732
2.710
2.697
2.694
2.675
2.529
2.515
2.505
2.491
2.485
2.326
2.310
2.294
2.277
2.259
2.243
2.076
2.063
2.055
2.041
2.033
2.027
2.020
2.006
1.998
1.985
1.938
1.926
1.920
1.915
1.908
1.903
1.897
1.885
1.879
1.873
1.864
1.851
1.840
1.828
1.820
1.796
-0.000
O
O
Ph
8
3.02
2.04
1.00
2.24
2.00
1.06
1.13
2.32
10
8
6
4
2
0
-2
PPM


177.029
140.577
128.347
128.258
125.985
79.762
77.319
77.000
76.681
37.128
31.439
28.633
27.765
Ph
O
O
8
200
150
100
50
0
PPM


NC
H(D)
33% D
CH3(D)
27% D
Me

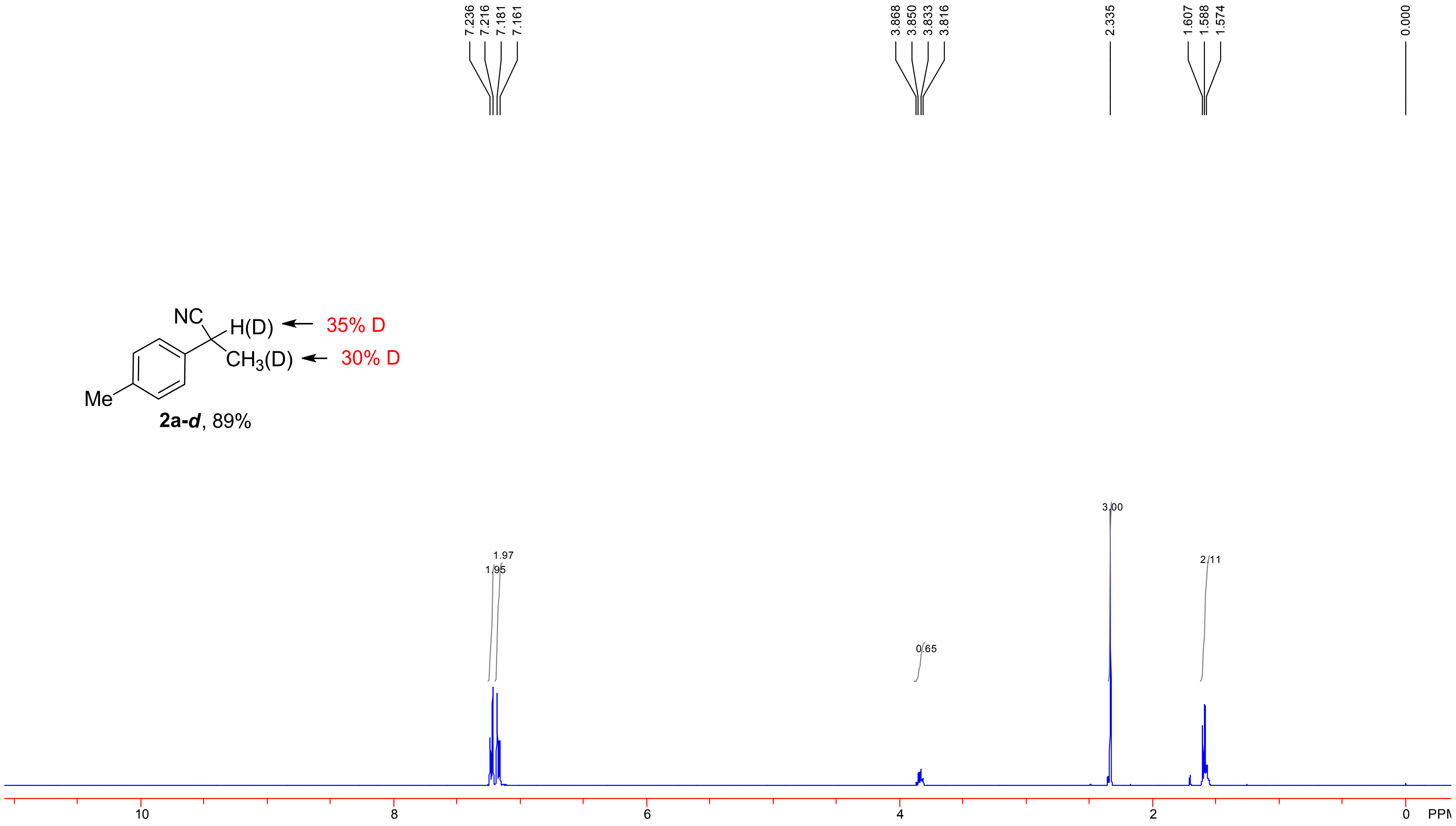
2a-*d*, 91%


7.234
7.214
7.178
7.158
3.865
3.847
3.829
3.813
2.333
1.603
1.585
1.570
-0.000
1.95
1.99
0.67
3.00
2.19
10
8
6
4
2
0
PPM

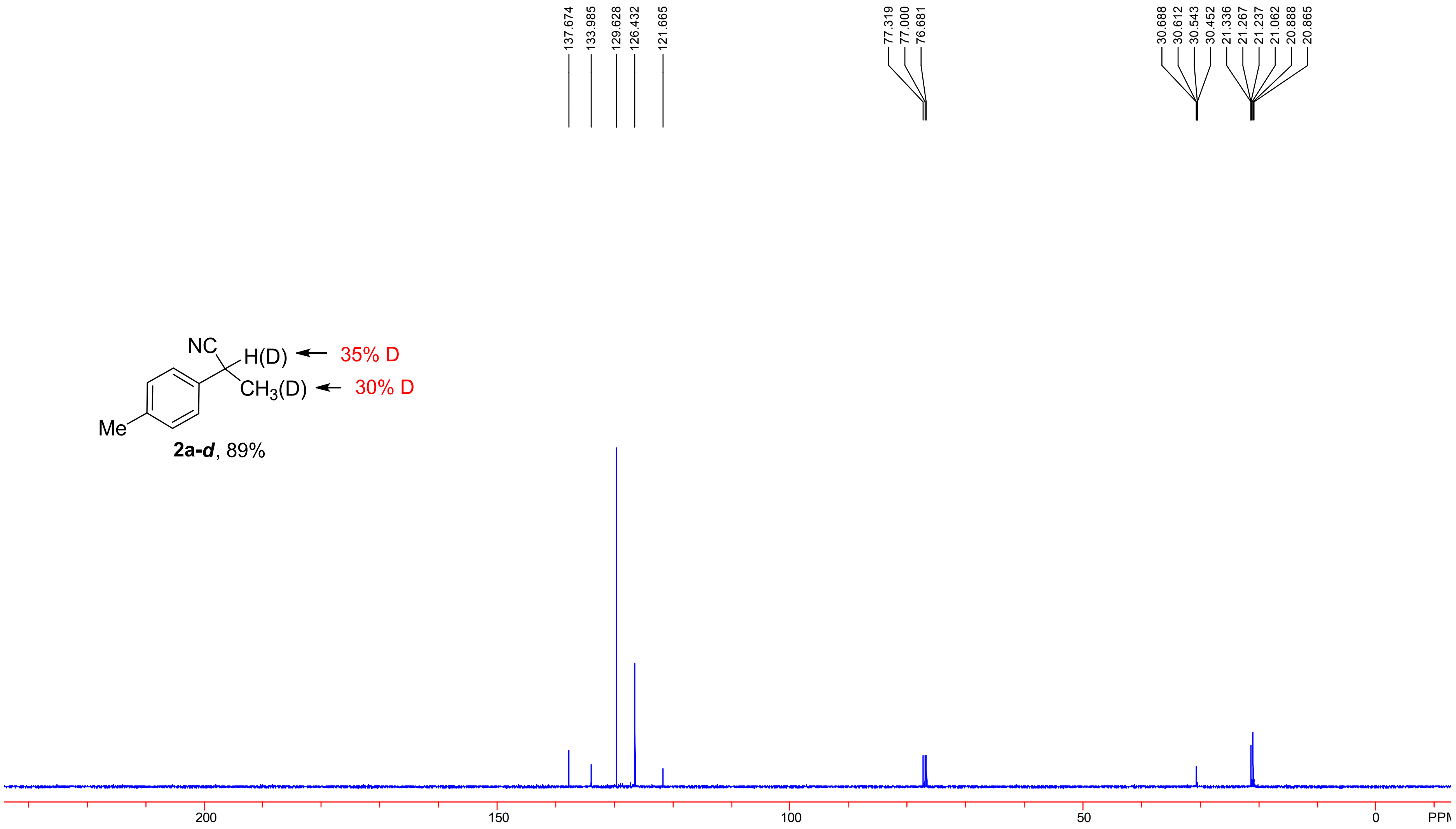

137.644
133.970
129.605
126.417
121.650
77.319
77.000
76.681
30.657
30.589
30.513
21.313
21.237
21.222
21.040
20.865
200
150
100
50
0
PPM

NC
H(D)
CH3(D)
Me
33% D
27% D

2a-*d*, 91%


7.236
7.216
7.181
7.161
3.868
3.850
3.833
3.816
2.335
1.607
1.588
1.574
0.000
NC
H(D)
35% D
CH3(D)
30% D
Me
1.97
1.95
0.65
3.00
2.11
10
8
6
4
2
0
PPM

2a-*d*, 89%


137.674
133.985
129.628
126.432
121.665
77.319
77.000
76.681
30.688
30.612
30.543
30.452
21.336
21.267
21.237
21.062
20.888
20.865
NC
H(D)
35% D
CH3(D)
30% D
Me
2a-d, 89%
200
150
100
50
0
PPM