Electronic Supplementary Information

Ni-catalyzed hydrocyanation of alkenes with formamide as the cyano source

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- **Caution 1:** All reactions were run in thick-wall pressure-proof glass tube (Chemglass brand microwave tube, CG-4920-01) to avoid the possible crack of the reactor.
- **Caution 2:** All work-up and purifications were done in the fume-hood. The reaction wastes were treated by 10% $FeSO_4$ aqueous solution and collected separately to avoid possible safety risk of cyanide.

Contents

I. General information

Unless otherwise noted, all commercially available compounds were used as purchased without further purification. Dry solvents (toluene, ethyl acetate, dichloromethane, acetonitrile, chlorobenzene, fluorobenzene, trifluoromethyl benzene) were used as commercially available. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

II. General experimental procedure

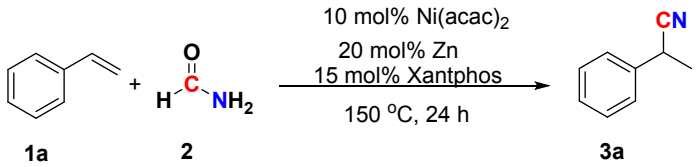
Method A: for the hydrocyanation of **alkenes (3a-3m, 3t-3v)**:

An oven-dried reaction vessel was charged with styrene (**1a**, 0.2 mmol, 20.8 mg), $Ni(acac)_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg) and formamide (1.0 mL) under argon atmosphere. The vessel was sealed, heated and stirred at 150 °C (oil bath temperature) for 24 h. After the resulting mixture was cooled to room temperature, added with 10 mL brine and extracted with ethyl acetate (3x10 mL). The organic layer was combined, washed with brine (2x10 mL), dried with anhydrous sodium sulfate and filtered. The filtrate was condensed in vacuo to remove solvent and further purified by column chromatography on silica gel with a mixture of EtOAc / petroleum ether as eluent to give the product (**3a**, 21.2 mg) in 81% yield.

Method B: for the hydrocyanation of **1,2-diarylethene** (**3n-3s**):

An oven-dried reaction vessel was charged with 1,2-diphenylethene (**1n**, 0.2 mmol, 36.0 mg), $Ni(acac)_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), and formamide (1.0 mL) under argon atmosphere. The vessel was sealed, heated and stirred at **155 °C** (oil bath temperature) for **36 h**. After the resulting mixture was cooled to room temperature, added with 10 mL brine and extracted with ethyl acetate (3x10 mL). The organic layer was combined, washed with brine (2x10 mL), dried with anhydrous sodium sulfate and filtered. The filtrate was condensed in vacuo to remove solvent and further purified by column chromatography on silica gel with a mixture of EtOAc / petroleum (1:15) ether as eluent to give the product (**3n**, 32.3 mg) in 78% yield.

III. Conditions optimization [a]



1a **2** **3a**

entry	Change from the "standard conditions"	**3a** (%) [b]	**1a** (%) [b]
1	5 mol% $Ni(acac)_2$	30	32
2	**10 mol% $Ni(acac)_2$**	**81**	**8**
3	15 mol% $Ni(acac)_2$	54	24
4	10 mol% $Ni(OAc)_2$	48	26
5	10 mol% $NiBr_2$	36	40
6	10 mol% NiF_2	37	52
7	10 mol% $Ni(OAc)_2$	66	18
8	10 mol% $NiCl_2$	53	33
9	10 mol% Xantphos	40	41
10	**15 mol% Xantphos**	**81**	**8**
11	20 mol% Xantphos	51	31
12	15 mol% PPh_3	10	60
13	15 mol% $PyPPh_2$	8	55

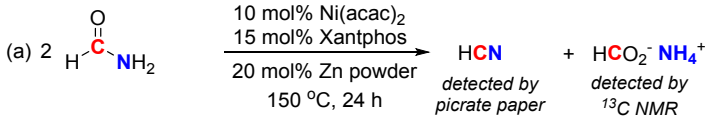
14	15 mol% Dpephos	10	51
15	10 mol% Dpephos + 10% DPPP	12	56
16	10 mol% Dpephos + 10% BINAP	18	51
17	**20 mol% Zn**	**81**	**8**
18	40 mol% Zn	41	12
19	20 mol% Mn	40	45
20	20 mol% Mg	34	48
21	20 mol% HCO_2H	54	22
22	20 mol% HCO_2NH_4	48	25
23	140 °C	44	36
24	**150 °C**	**81**	**8**
25	160 °C	28	12

[a]Conditions: Styrene (**1a**, 0.2 mmol, 20.8 mg), $Ni(acac)_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), formamide (1.0 mL) were reacted at 150 °C (oil bath temperature) for 24 h under argon atmosphere. [b]Yields and recovered **1a** were tested by GC with an internal standard.

IV. Mechanistic experiments

(1) Detection of cyanide anion by indicator paper

Picrate paper was prepared by wetting filter paper with a solution of sodium bicarbonate (5.0 g) and picric acid (0.5 g) in 100 mL of water. After drying the paper, it was cut as strips and inserted into a 10 mL reaction vessel (**A**). Another oven-dried reaction vessel (**B**) was charged with $Ni(acac)_2$ (0.01 mmol, 10 mol%), Zn powder (20 mol%, 2.6 mg, with or without), Xantphos (0.015 mmol, 15 mol%), formamide (1.0 mL) under argon. The reaction vessel was sealed, heated and stirred at 150 °C (oil bath temperature) for 12 h. Then, the reaction vessel **B** was cooled to r.t., connected to the reaction vessel (**A**) in head-to-head model and sealed the joint by rubber stopper immediately. Then, this reaction **B** was heated at 80 °C for 1 h. The test paper was changed from yellow to red, indicating the presence of cyanide anion.

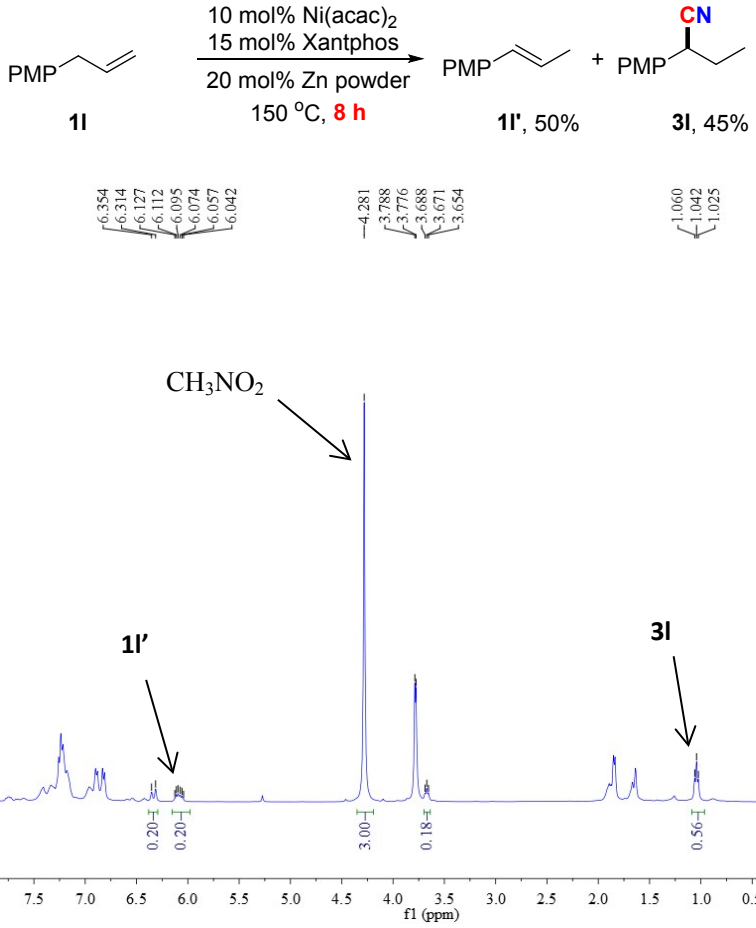


(2) Detection of ammonium formate (HCO_2^- NH_4^+) by ^{13}C NMR.

$Ni(acac)_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), and formamide (1.0 mL) were reacted at 150 °C for 12 h under argon atmosphere in the sealed reaction vessel. After cooled to room temperature, 0.1 mL of the reaction mixture was transferred into the NMR tube and 0.4 mL of DMSO-d_6 was added as an internal standard for ^{13}C NMR measurements. The ammonium formate was detected by the ^{13}C NMR at 167.36 ppm (C=O), which was identical with the literature reports. Authentic sample of ammonium formate (5 mg) was further added into the same NMR tube and recorded the ^{13}C NMR spectrum again, to find that the chemical shift of added ammonium formate was same as the signal of the previously observed one.

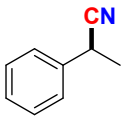
(3) Ni-catalyzed migrative isomerization

An oven-dried reaction vessel was charged with 1-methoxy-4-(prop-1-en-1-yl)benzene (**1l**, 0.21 mmol, 31.1 mg), $Ni(acac)_2$ (10 mol%, 5.2 mg), Zn powder (20 mol%, 2.6 mg), Xantphos (15 mol%, 17.4 mg), and formamide (1.0 mL) under argon atmosphere. The vessel was sealed, heated and stirred at 150 °C (oil bath temperature) for 8 h. After the resulting mixture was cooled to room temperature, added with 10 mL brine and extracted with ethyl acetate (3x10 mL). The organic layer was combined, washed with brine (2x10 mL), dried with anhydrous sodium sulfate and filtered. Then, we carefully isolated the reaction mixture, two main-products (**1l'** and **3l**) were obtained and characterized. Their yields were determined by the ^1H NMR of reaction mixture using CH_3NO_2 (0.25 mmol, 15.3 mg) as the internal standard.



V. Spectra data of products 3a-3v, 4v and 5a

(3a) 2-phenylpropanenitrile[1]

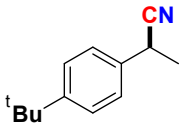


The title compound was prepared according to the general procedure described above by the reaction between styrene **(1a)** with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (20.4 mg, 78%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.31 (m, 5H), 3.91 (q, J = 7.2 Hz, 1H), 1.65 (d, J = 7.2 Hz,

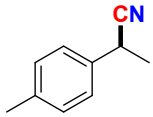
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.18, 129.28, 128.18, 126.83, 121.72, 31.39, 21.61. IR (cm^{-1}): 2984, 2935, 2241, 1495, 1453, 1403, 1232, 699.

(3b) 2-(4-butylphenyl)propanenitrile[2]



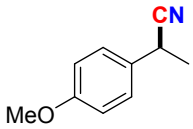
The title compound was prepared according to the general procedure described above by the reaction between 1-(tert-butyl)-4-vinylbenzene (**1b**) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (30.2 mg, 73%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 3.89 (q, J = 7.6 Hz, 1H), 1.64 (d, J = 7.6 Hz, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.66, 134.20, 129.47, 128.24, 121.24, 42.69, 30.86, 23.56, 21.50. IR (cm^{-1}): 2931, 2871, 2859, 2241, 1654, 1513, 1086, 833.

(3c) 2-(p-tolyl)propanenitrile[1]



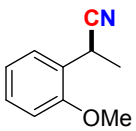
The title compound was prepared according to the general procedure described above by the reaction between 1-methyl-4-vinylbenzene (**1c**) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (21.7 mg, 75%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 3.87 (q, J = 7.2 Hz, 1H), 2.35 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.00, 134.22, 129.91, 126.71, 121.91, 31.01, 21.64, 21.18. IR (cm^{-1}): 2360, 2240, 1685, 1514, 1403.

(3d) 2-(4-methoxyphenyl)propanenitrile[1]



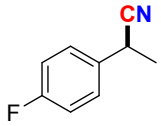
The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-vinylbenzene (**1d**) with formamide, and purified by standard extraction and concentration procedures to provide yellow oil (23.2 mg, 72%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.25 (m, 2H), 6.93 - 6.89 (m, 2H), 3.87 (q, J = 7.6 Hz, 1H), 3.81 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.41, 129.20, 127.97, 122.00, 114.60, 55.48, 30.60, 21.66. IR (cm^{-1}): 2984, 2938, 2240, 1612, 1514, 1250, 1181, 832.

(3e) 2-(2-methoxyphenyl)propanenitrile[6]



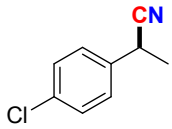
The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-2-vinylbenzene (**1e**) with formamide, and purified by standard extraction and concentration procedures to provide oil (22.5 mg, 70%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.6 Hz, 1H), 6.98 (tt, *J* = 21.6, 10.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.13, 129.44, 127.72, 125.47, 122.15, 121.10, 110.85, 55.58, 25.74, 19.64. IR (cm^{-1}): 2940, 2840, 2242, 1601, 1250, 1028, 755.

(3f) 2-(4-fluorophenyl)propanenitrile[1]



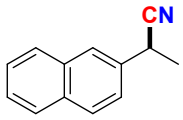
The title compound was prepared according to the general procedure described above by the reaction between 1-fluoro-4-vinylbenzene (**1f**) with formamide, and purified by standard extraction and concentration procedures to provide oil (17.3 mg, 58%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.29 (m, 4H), 3.89 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.51 (d, *J* = 245.7 Hz), 129.74 (d, *J* = 8.2 Hz), 125.77, 117.80, 116.22 (d, *J* = 21.8 Hz), 33.13, 23.03. IR (cm^{-1}): 2919, 2853, 1648, 1462, 1305, 1231, 962.

(3g) 2-(4-chlorophenyl)propanenitrile[6]



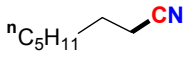
The title compound was prepared according to the general procedure described above by the reaction between 1-chloro-4-vinylbenzene (**1g**) with formamide, and purified by standard extraction and concentration procedures to provide oil (16.5 mg, 50%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.28 (m, 4H), 3.89 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.65, 134.21, 129.48, 128.24, 121.25, 30.87, 21.51. IR (cm^{-1}): 2987, 2243, 1493, 1095, 827.

(3h) 2-(naphthalen-2-yl)propanenitrile[1]



The title compound was prepared according to the general procedure described above by the reaction between 2-vinylnaphthalene (**1h**) with formamide, and purified by standard extraction and concentration procedures to provide white solid (26.2 mg, 72%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.84 (m, 4H), 7.54 - 7.50 (m, 2H), 7.43 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 1H), 1.73 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.44, 133.44, 132.90, 129.28, 127.99, 127.86, 126.87, 126.63, 125.72, 124.55, 121.74, 31.57, 21.59. IR (cm^{-1}): 3055, 2988, 2932, 2241, 1601, 1509, 1453, 1372, 1148, 821, 750.

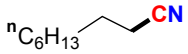
(3i) octanenitrile[3]



The title compound was prepared according to the general procedure described above by the reaction between heptane (**1i**) with formamide, and purified by standard extraction and concentration procedures to provide oil (16.8 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (t, *J* = 7.2 Hz, 2H), 1.69 - 1.62 (m, 2H), 1.46 - 1.41 (m, 2H), 1.36 - 1.30 (m, 6H), 0.91 - 0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.83, 31.44, 28.56, 28.38, 25.33, 22.47, 17.04, 13.95. IR (cm^{-1}): 2958, 2927, 2246, 1260, 1011.

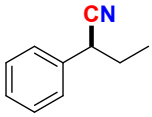
(3j) nonanenitrile[7]



The title compound was prepared according to the general procedure described above by the reaction between oct-1-ene (**1j**) with formamide, and purified by standard extraction and concentration procedures to provide oil (17.7 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (t, *J* = 7.2 Hz, 2H), 1.65 (q, *J* = 7.2 Hz, 2H), 1.46 - 1.41 (m, 2H), 1.31 - 1.28 (m, 8H), 0.90 - 0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.00, 31.81, 29.08, 28.84, 28.78, 25.48, 22.71, 17.25, 14.17. IR (cm^{-1}): 2987, 2243, 1493, 1095, 827.

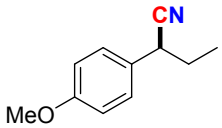
(3k) 2-phenylbutanenitrile[4]



The title compound was prepared according to the general procedure described above by the reaction between allylbenzene (**1k**) with formamide, and purified by standard extraction and concentration procedures to provide oil (18.0 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.30 (m, 5H), 3.74 (t, *J* = 7.2 Hz, 1H), 1.99 - 1.91 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.86, 129.16, 128.15, 127.43, 120.90, 39.07, 29.37, 11.64. IR (cm^{-1}): 3040, 2963, 2241, 1600, 1458, 1327, 752, 700.

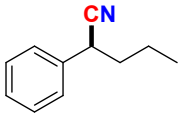
(3l) 2-(4-methoxyphenyl)butanenitrile[5]



The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-(prop-1-en-1-yl)benzene (**1l**) with formamide, and purified by standard extraction and concentration procedures to provide oil (26.6 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.68 (t, *J* = 7.2 Hz, 1H), 1.95 - 1.89 (m, 2H), 1.06(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.36, 128.40, 127.82, 121.14, 114.44, 55.42, 38.20, 29.33, 11.53. IR (cm^{-1}): 2955, 2925, 2870, 2239, 1611, 1459, 828.

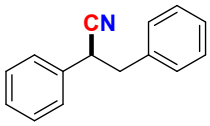
(3m) 2-phenylpentanenitrile[6]



The title compound was prepared according to the general procedure described above by the reaction between but-3-en-1-ylbenzene (**1m**) with formamide, and purified by standard extraction and concentration procedures to provide oil (24.1 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.30 (m, 5H), 3.79 (q, *J* = 7.6 Hz, 1H), 1.96 - 1.79 (m, 2H), 1.56 - 1.46 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.18, 129.18, 128.12, 127.38, 121.06, 77.48, 77.16, 76.84, 38.04, 37.32, 20.45, 13.56. IR (cm^{-1}): 3065, 3033, 2962, 2874, 2239, 1602, 1495, 1464, 1455, 1383, 1031, 757, 699.

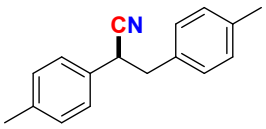
(3n) 2,3-diphenylpropanenitrile[8]



The title compound was prepared according to the general procedure described above by the reaction between 1,2-diphenylethene (**1n**) with formamide, and purified by standard extraction and concentration procedures to provide white solid (32.3 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.25 (m, 8H), 7.15-7.26 (m, 2H), 4.00 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.22 - 3.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.39, 135.34, 129.32, 129.12, 128.72, 128.30, 127.59, 127.48, 120.46, 42.29, 39.89. IR (cm^{-1}): 3087, 3063, 3031, 2241, 1497, 1455, 755, 698. Melting point: 55-56 °C.

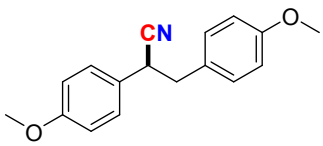
(3o) 2,3-di-p-tolylpropanenitrile[8]



The title compound was prepared according to the general procedure described above by the reaction between 1,2-di-p-tolylethene (**1o**) with formamide, and purified by standard extraction and concentration procedures to provide white solid (34.3 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.93 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.16 - 3.03 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.07, 137.07, 133.51, 132.47, 129.77, 129.42, 129.19, 127.46, 120.77, 42.00, 39.74, 21.23. IR (cm^{-1}): 3024, 2923, 2862, 2240, 1701, 1514, 1112, 813. Melting point: 65-66 °C.

(3p) 2,3-bis(4-methoxyphenyl)propanenitrile[9]

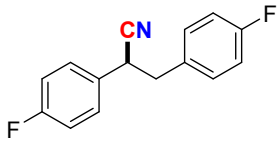


The title compound was prepared according to the general procedure described above by the

reaction between 1,2-bis(4-methoxyphenyl)ethene (**1p**) with formamide, and purified by standard extraction and concentration procedures to provide white solid (38.4 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.14 (m, 2H), 7.05 - 7.02 (m, 2H), 6.88 - 6.86 (m, 2H), 6.83 - 6.81 (m, 2H), 3.91 (dd, *J* = 8.0, 6.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.14 - 3.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.47, 158.93, 130.45, 128.78, 128.53, 127.35, 120.87, 114.43, 114.07, 55.45, 55.36, 41.59, 39.35. IR (cm^{-1}): 2938, 2839, 2241, 1611, 1510, 1457, 1178, 1027, 827. Melting point: 117-118 °C.

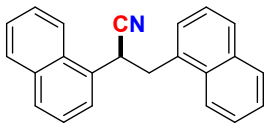
(3q) 2,3-bis(4-fluorophenyl)propanenitrile[10]



The title compound was prepared according to the general procedure described above by the reaction between 1,2-bis(4-fluorophenyl)ethene (**1q**) with formamide, and purified by standard extraction and concentration procedures to provide white solid (34.1 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 - 7.15 (m, 2H), 7.07 - 7.01 (m, 4H), 7.00 - 6.95 (m, 2H), 3.97 (t, *J* = 7.2 Hz, 1H), 3.18 - 3.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.68 (d, *J* = 29.5 Hz), 161.22 (d, *J* = 27.9 Hz), 131.67 (d, *J* = 3.3 Hz), 130.98 (d, *J* = 8.1 Hz), 130.73 (d, *J* = 3.3 Hz), 129.36 (d, *J* = 8.2 Hz), 120.13, 116.16 (d, *J* = 21.7 Hz), 115.68 (d, *J* = 21.3 Hz), 41.39, 39.11. IR (cm^{-1}): 2924, 2854, 2242, 1891, 1602, 1223, 1016, 831. Melting point: 95-96 °C..

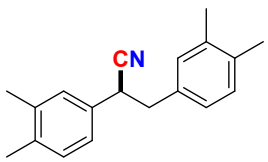
(3r) 2,3-di(naphthalen-1-yl)propanenitrile[11]



The title compound was prepared according to the general procedure described above by the reaction between 1,2-di(naphthalen-1-yl)ethene (**1r**) with formamide, and purified by standard extraction and concentration procedures to provide white solid (40.5 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.86 (m, 5H), 7.81 - 7.78 (m, 1H), 7.66 (d, *J* = 6.4 Hz, 1H), 7.57 - 7.48 (m, 5H), 7.42 - 7.38 (m, 2H), 4.91 (t, *J* = 7.4 Hz, 1H), 3.80 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.18, 134.10, 132.66, 131.67, 131.63, 130.31, 129.49, 129.34, 129.32, 128.44, 128.00, 127.09, 126.58, 126.29, 126.16, 125.93, 125.65, 125.61, 122.82, 122.21, 120.92, 38.04, 35.66. IR (cm^{-1}): 3060, 2240, 1598, 1511, 1396, 797, 776. Melting point: 134-135°C.

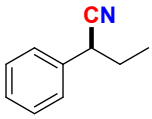
(3s) 2,3-bis(3,5-dimethylphenyl)propanenitrile



The title compound was prepared according to the general procedure described above by the reaction between 1,2-bis(3,5-dimethylphenyl)ethene (**1s**) with formamide, and purified by

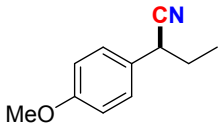
standard extraction and concentration procedures to provide white solid (34.6 mg, 66%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.92 (s, 3H), 6.82 (s, 2H), 3.88 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.03 (dd, *J* = 9.2, 5.6 Hz, 2H), 2.32 (s, 6H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.79, 138.22, 136.71, 135.64, 129.82, 129.06, 127.03, 125.26, 120.77, 42.44, 40.07, 21.34. IR (cm^{-1}): 3016, 2919, 2862, 2240, 1607, 1465, 849, 699 cm^{-1}. HRMS: calcd. for $C_{19}H_{21}NNa^+$ $[M+Na]^+$: 286.1566, Found: 286.1571. Melting point: 144-145 °C.

(3k) 2-phenylbutanenitrile[4]



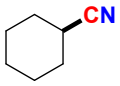
The title compound was prepared according to the general procedure described above by the reaction between prop-1-en-1-ylbenzene (**1k'**) with formamide, and purified by standard extraction and concentration procedures to provide oil (17.98 mg, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.30 (m, 5H), 3.74 (t, *J* = 7.2 Hz, 1H), 1.99 - 1.91 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.86, 129.16, 128.15, 127.43, 120.90, 39.07, 29.37, 11.64. IR (cm^{-1}): 3040, 2963, 2241, 1600, 1458, 1327, 752, 700.

(3l) 2-(4-methoxyphenyl)butanenitrile[5]



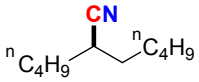
The title compound was prepared according to the general procedure described above by the reaction between 1-methoxy-4-(prop-1-en-1-yl)benzene (**1l'**) with formamide, and purified by standard extraction and concentration procedures to provide oil (26.6 mg, 76%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.68 (t, *J* = 7.2 Hz, 1H); 1.95 - 1.89 (m, 2H), 1.06(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.36, 128.40, 127.82, 121.14, 114.44, 55.42, 38.20, 29.33, 11.53. IR (cm^{-1}): 2955, 2925, 2870, 2239, 1611, 1459, 828.

(3t) cyclohexanecarbonitrile[12]



The title compound was prepared according to the general procedure described above by the reaction between cyclohexene (**1t**) with formamide, and purified by standard extraction and concentration procedures to provide oil (14.8 mg, 68%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 - 2.67 (m, 1H), 1.95 (d, *J* = 13.2 Hz, 2H), 1.85 - 1.81(m, 2H), 1.67 - 1.57 (m, 2H), 1.45 - 1.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.44, 47.08, 42.01, 31.37, 27.19, 26.13, 26.04. IR (cm^{-1}): 2928, 2853, 2245, 1450, 1423.

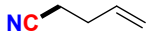
(3u) 2-butylheptanenitrile



The title compound was prepared according to the general procedure described above by the reaction between methyl dec-5-yne (**1u**) with formamide, and purified by standard extraction and concentration procedures to provide colorless oil (21.0 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 - 2.47 (m, 1H), 1.67 - 1.47 (m, 6H), 1.42 - 1.26 (m, 8H), 0.94 - 0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.64, 32.36, 32.09, 31.78, 31.41, 29.41, 26.97, 22.53, 22.36, 14.08, 13.95. IR (cm^{-1}): 2237, 1647, 1466, 669. HRMS: calcd. for $C_{11}H_{21}NNa^+$ $[M+Na]^+$: 190.1566, Found: 190.1569.

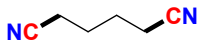
(3v) pent-4-enenitrile[13]



The title compound was prepared according to the general procedure described above by the reaction between 1,3-butadiene (**1v**) with formamide.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 - 5.78 (m, 1H), 5.21 - 5.15 (m, 2H), 2.47 - 2.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.23, 119.27, 117.78, 29.38, 17.04. IR (cm^{-1}): 2922, 2852, 2240, 1462, 1019.

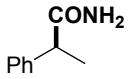
(4v) adiponitrile[14]



The title compound was prepared according to the general procedure described above by the reaction between methyl pent-4-enenitrile (**3v**) with formamide, and purified by standard extraction and concentration procedures to provide colorless oil (6.1 mg, 28%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 - 2.43 (m, 4H), 1.86 - 1.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.89, 24.07, 16.42. IR (cm^{-1}): 2947, 2245, 1425, 913, 743.

(5a) 2-phenylpropanamide[15]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.25 (m, 5H), 6.08 (s, 1H), 5.45 (s, 1H), 3.59 (q, J = 6.8 Hz, 1H), 1.51 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.09, 141.35, 129.03, 127.68, 127.43, 46.68, 18.41. IR (cm^{-1}): 3361, 3185, 2801, 1451, 1287, 1264, 1114, 656.

VI. Reference

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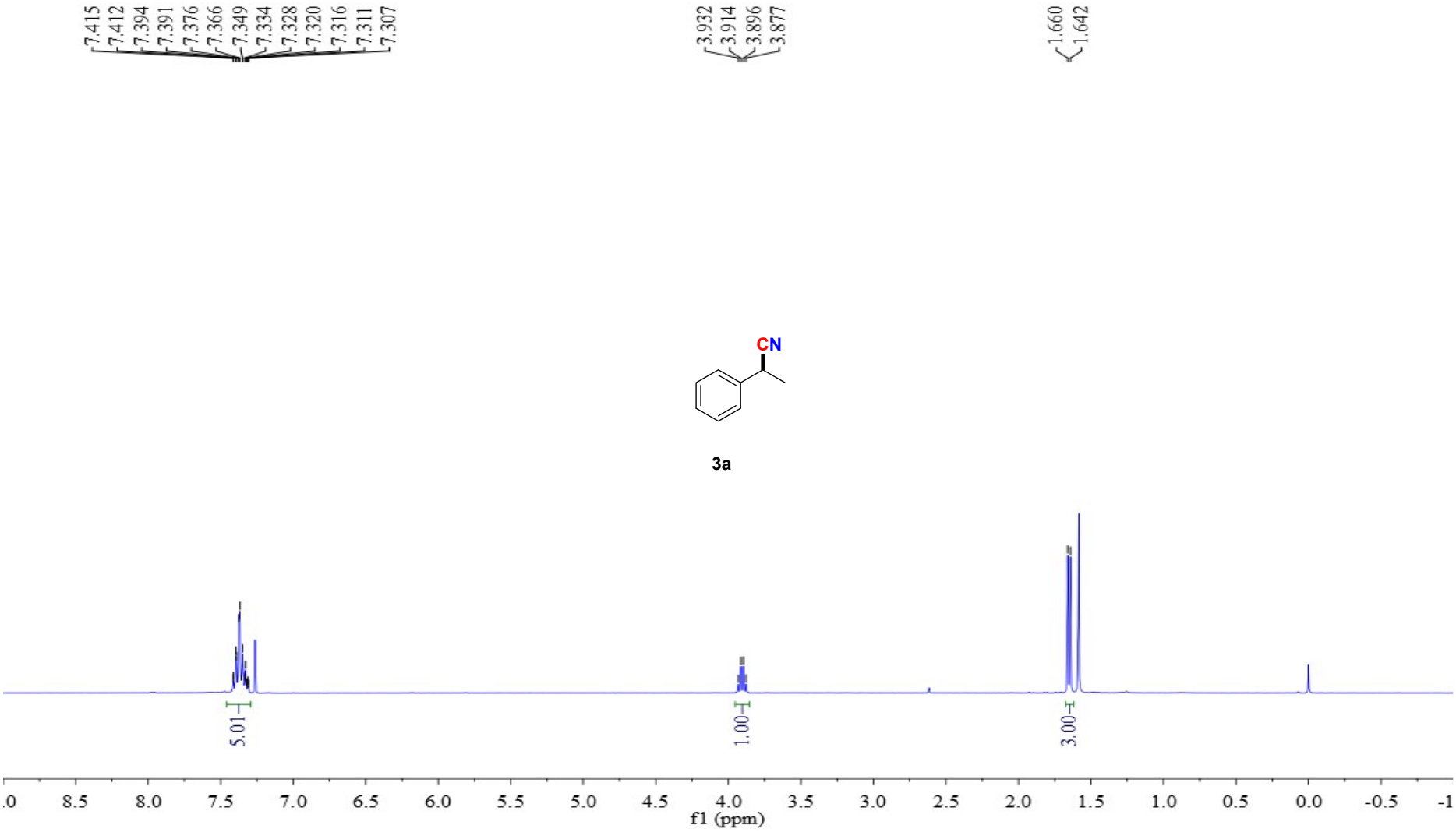
VII. Copies of ^{1}H and ^{13}C NMR spectra of products 3a-3v, 4v, and 5a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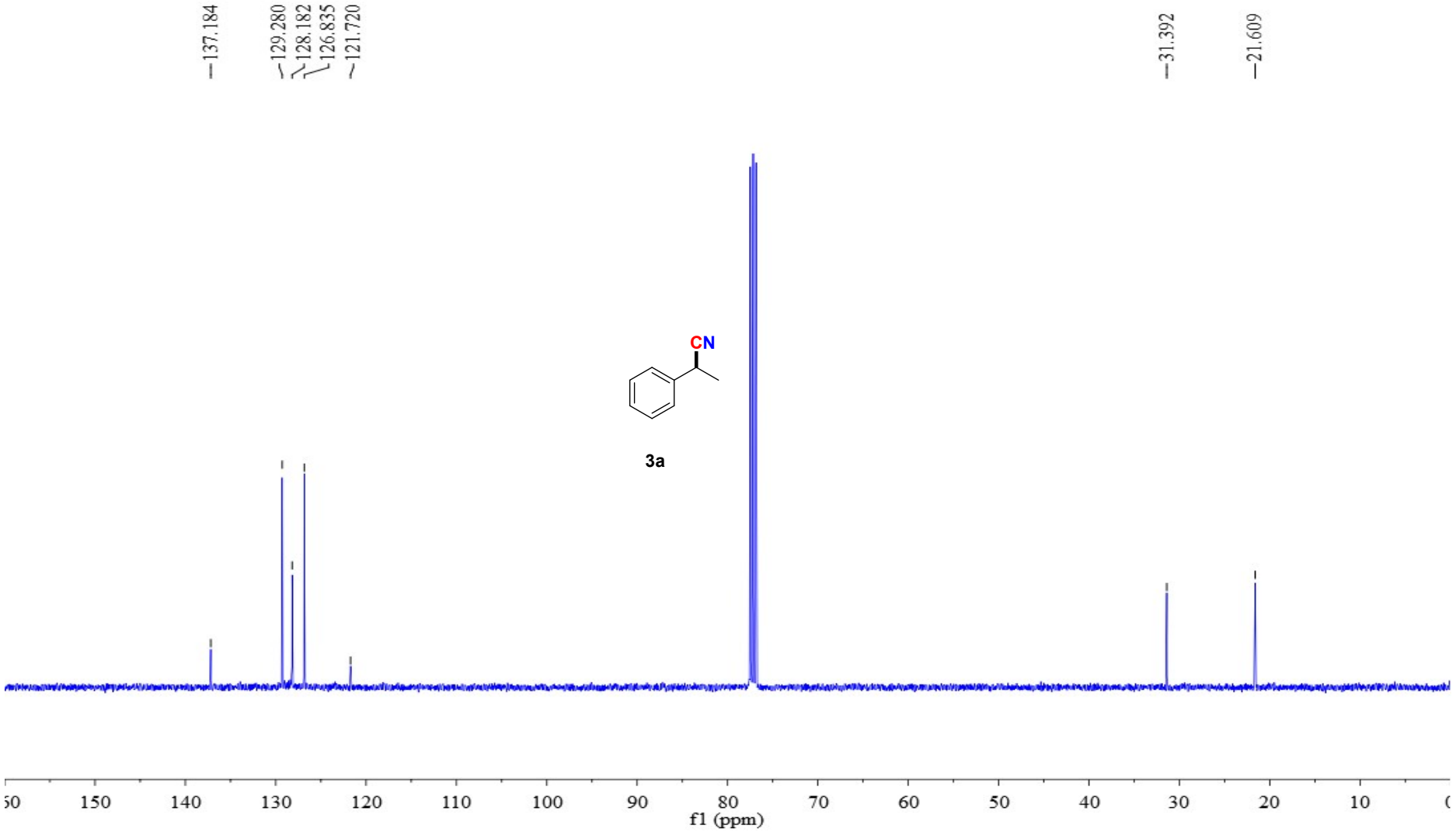
7.394
7.391
7.376
7.366
7.349
7.334
7.328
7.320
7.316
7.311
7.307
3.932
3.914
3.896
3.877
1.660
1.642
CN
5.01
1.00
3.00
f1 (ppm)

3a


137.184
129.280
128.182
126.835
121.720
31.392
21.609
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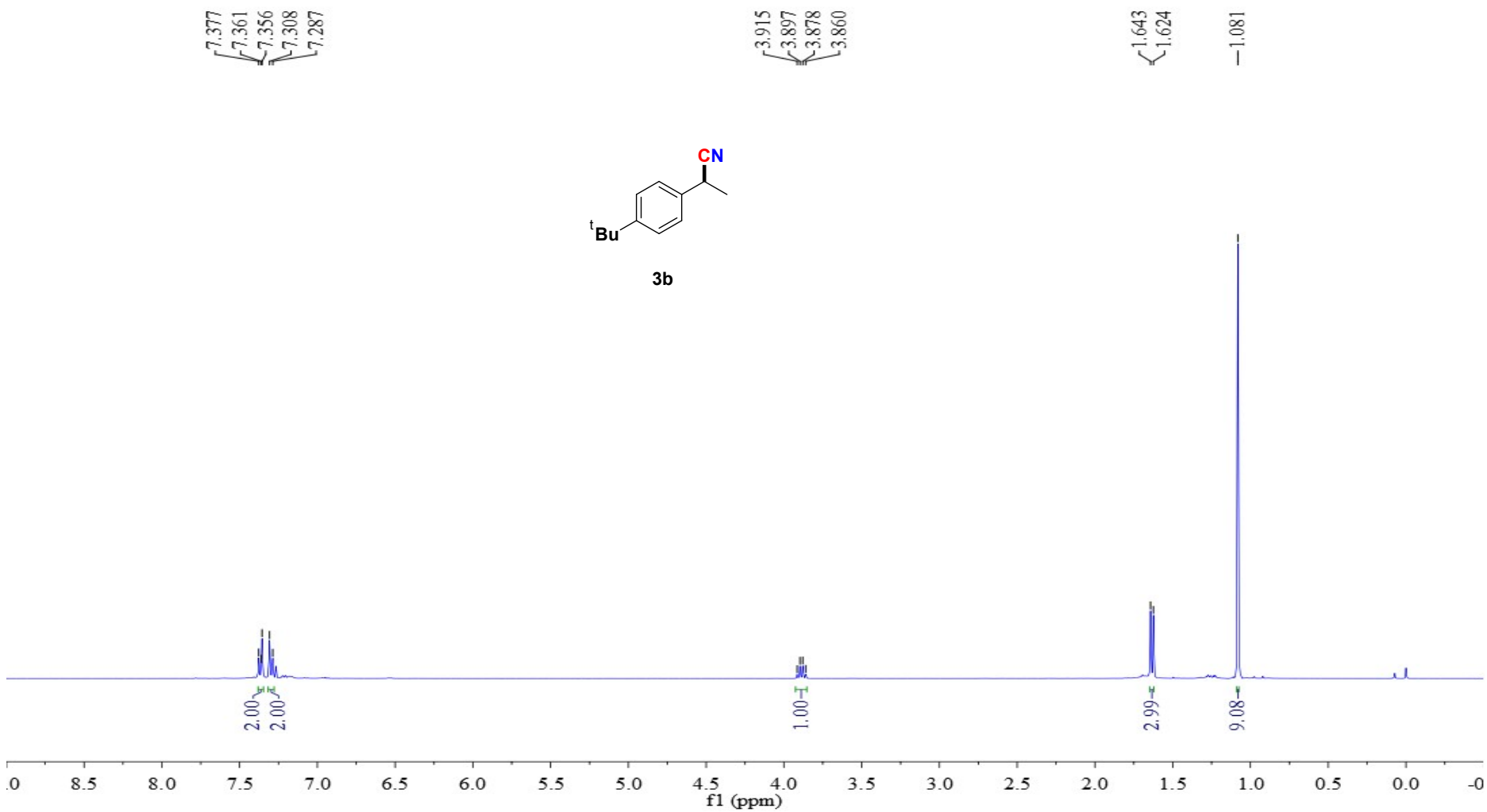
3a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.361
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7.308
7.287
3.915
3.897
3.878
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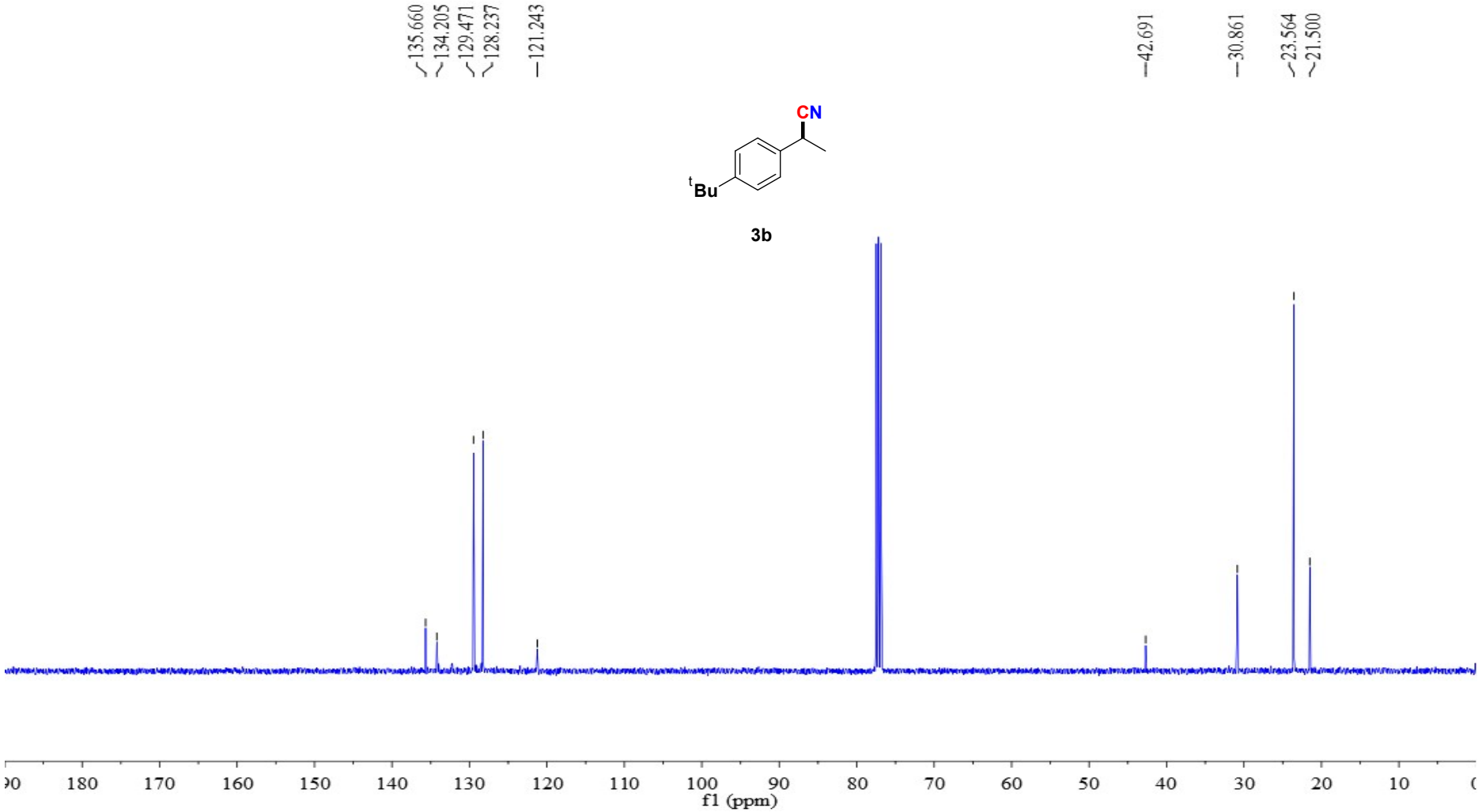
1.081
CN
tBu
3b
2.00
2.00
1.00
2.99
9.08
f1 (ppm)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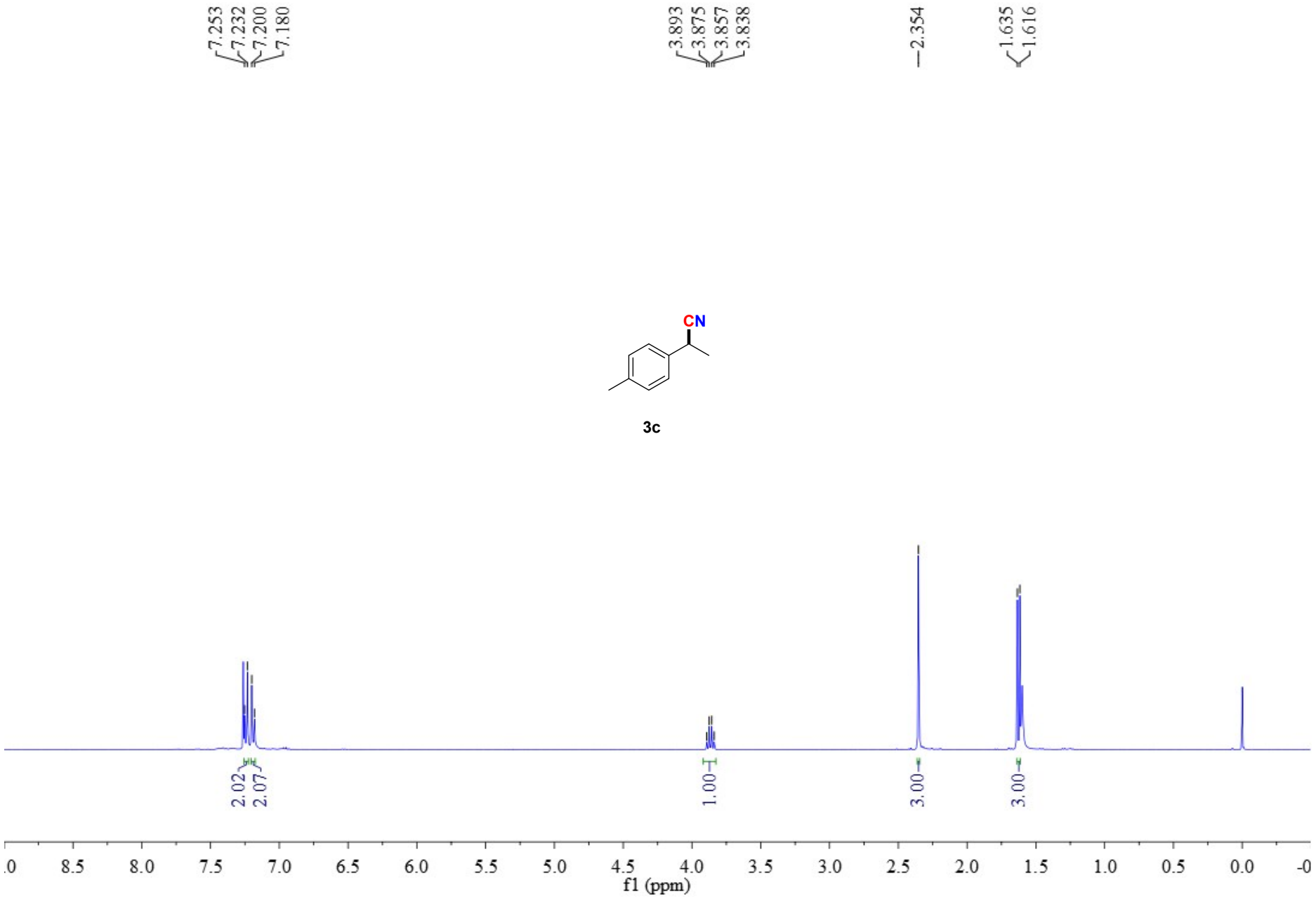
128.237
121.243
42.691
30.861
23.564
21.500
CN
tBu
3b
f1 (ppm)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7.232
7.200
7.180
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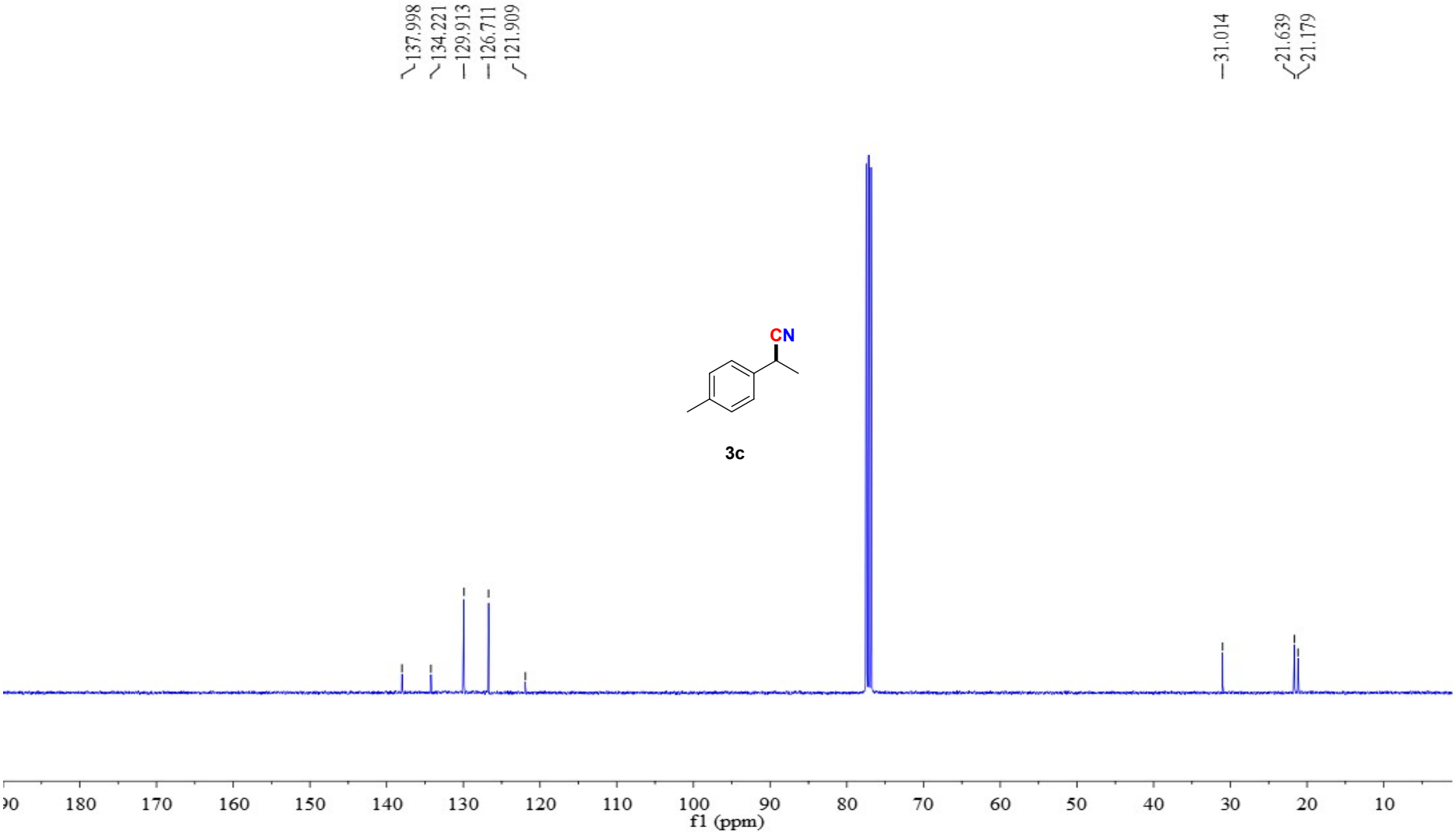
1.616
CN
2.02
2.07
1.00
3.00
3.00
f1 (ppm)

3c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21.179
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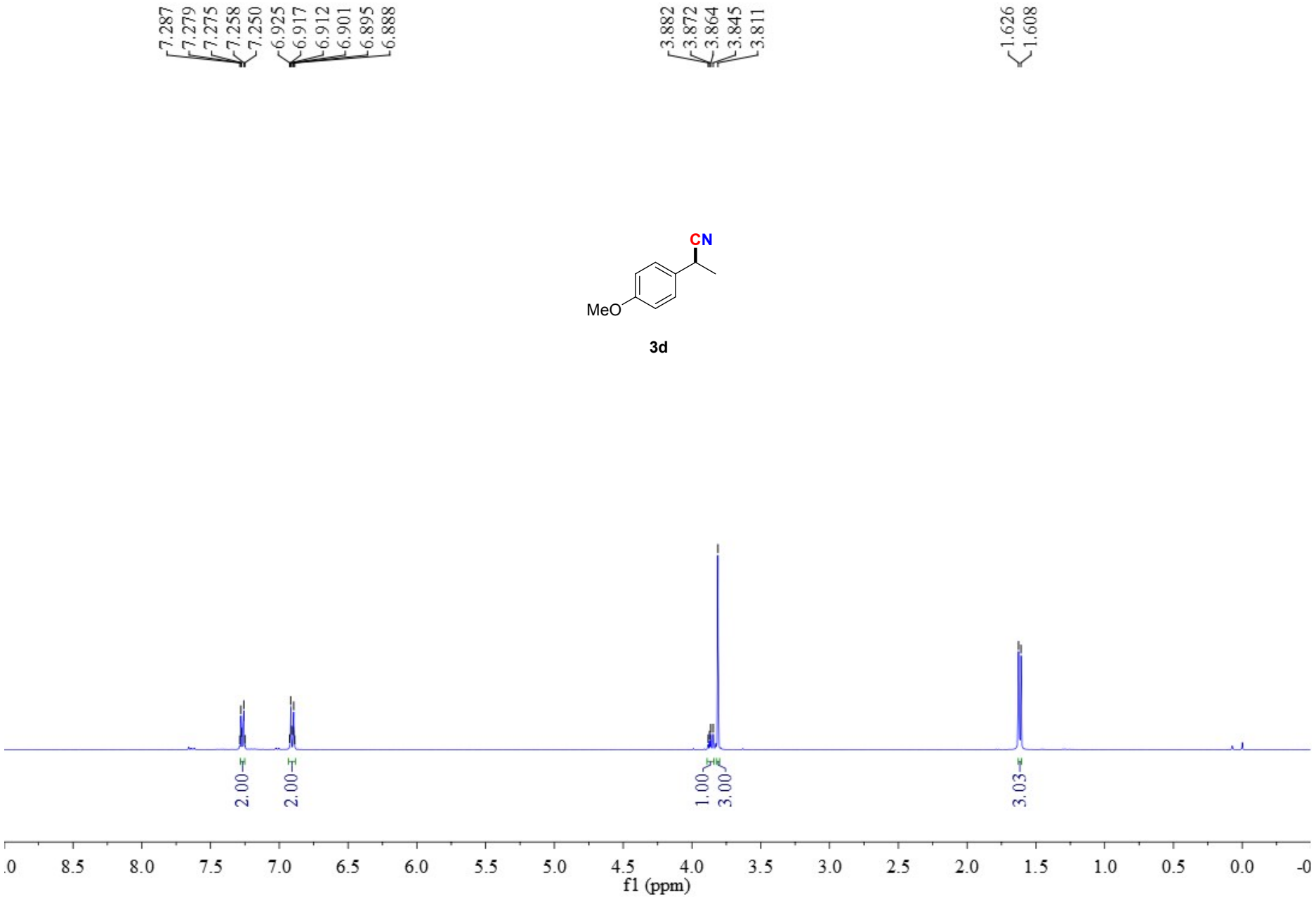
3c
f1 (ppm)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7.250
6.925
6.917
6.912
6.901
6.895
6.888
3.882
3.872
3.864
3.845
3.811
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1.608
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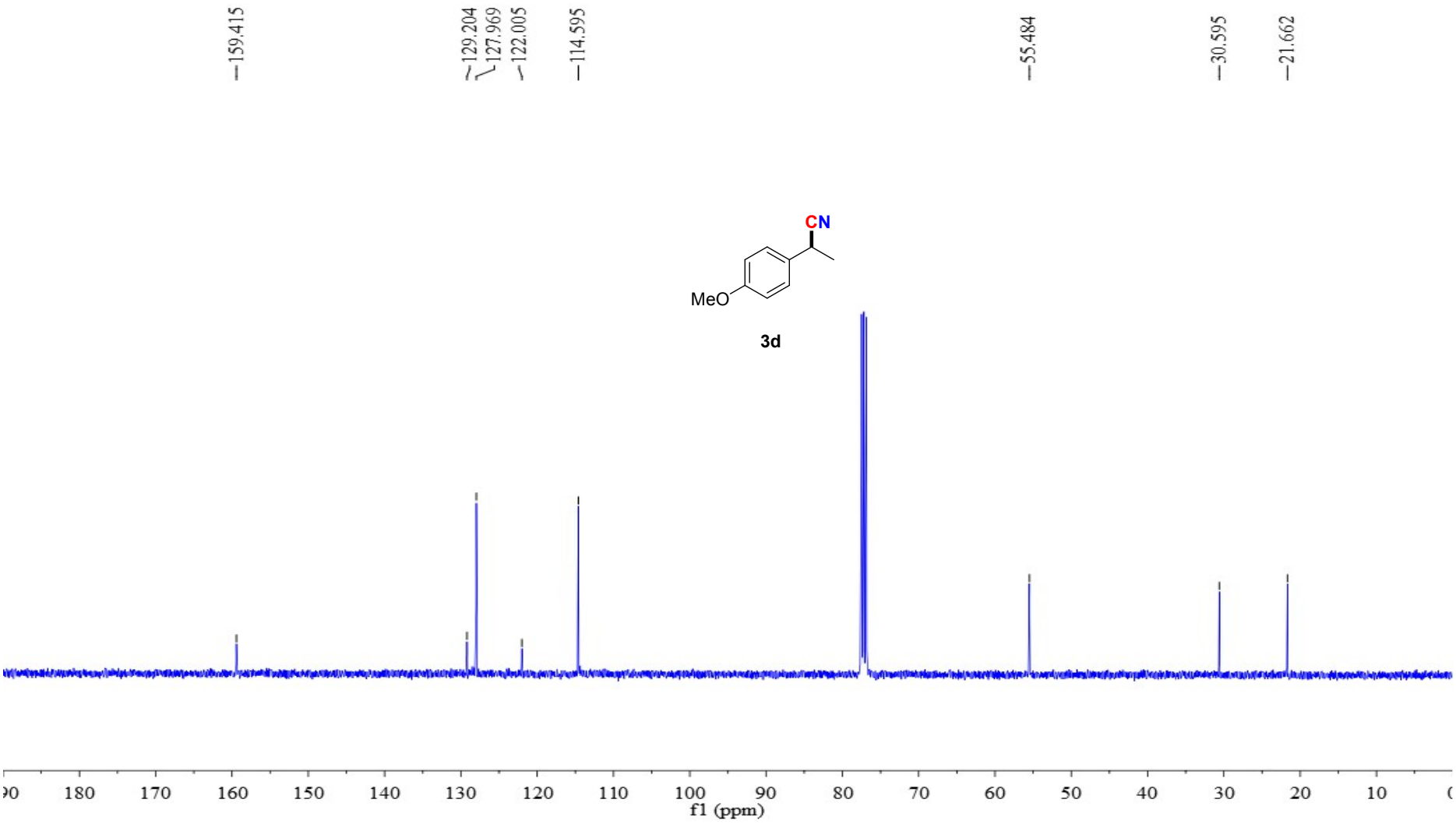
1.00
3.00
3.03
f1 (ppm)

3d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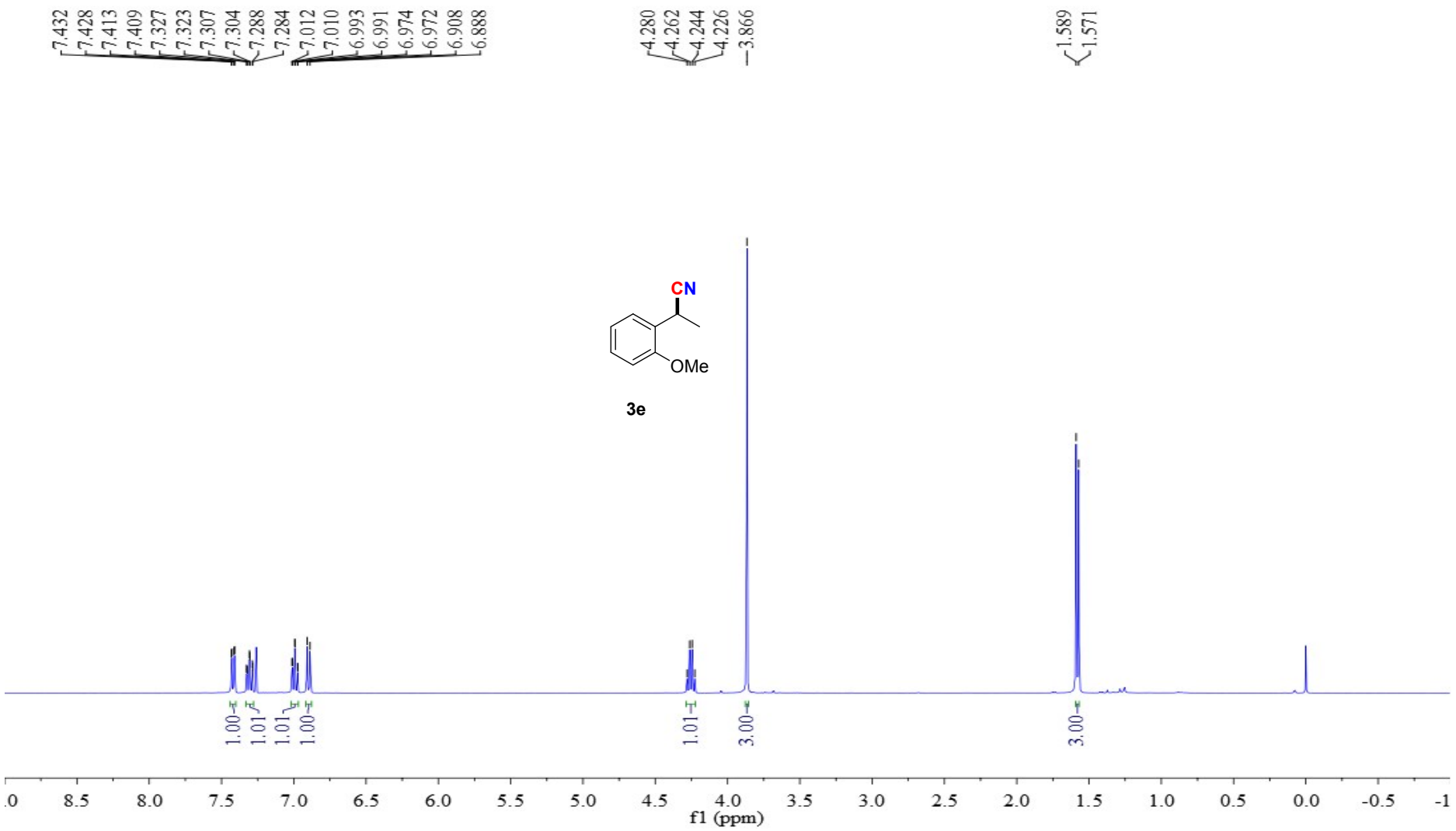
CN
MeO
3d
f1 (ppm)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7.323
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7.304
7.288
7.284
7.012
7.010
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6.991
6.974
6.972
6.908
6.888
4.280
4.262
4.244
4.226
3.866
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1.571
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OMe
3e
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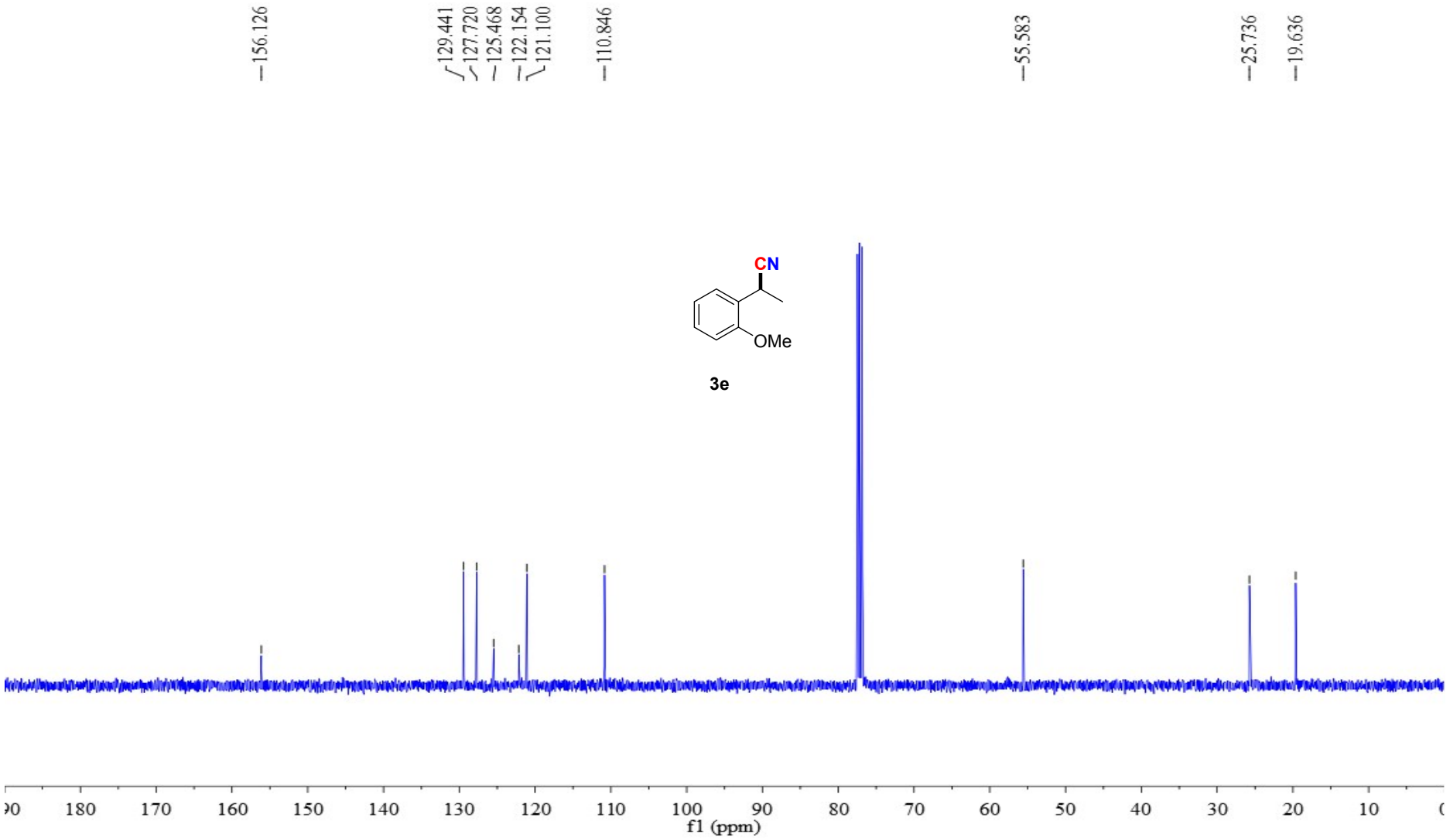
1.01
1.01
1.00
1.01
3.00
3.00
f1 (ppm)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OMe
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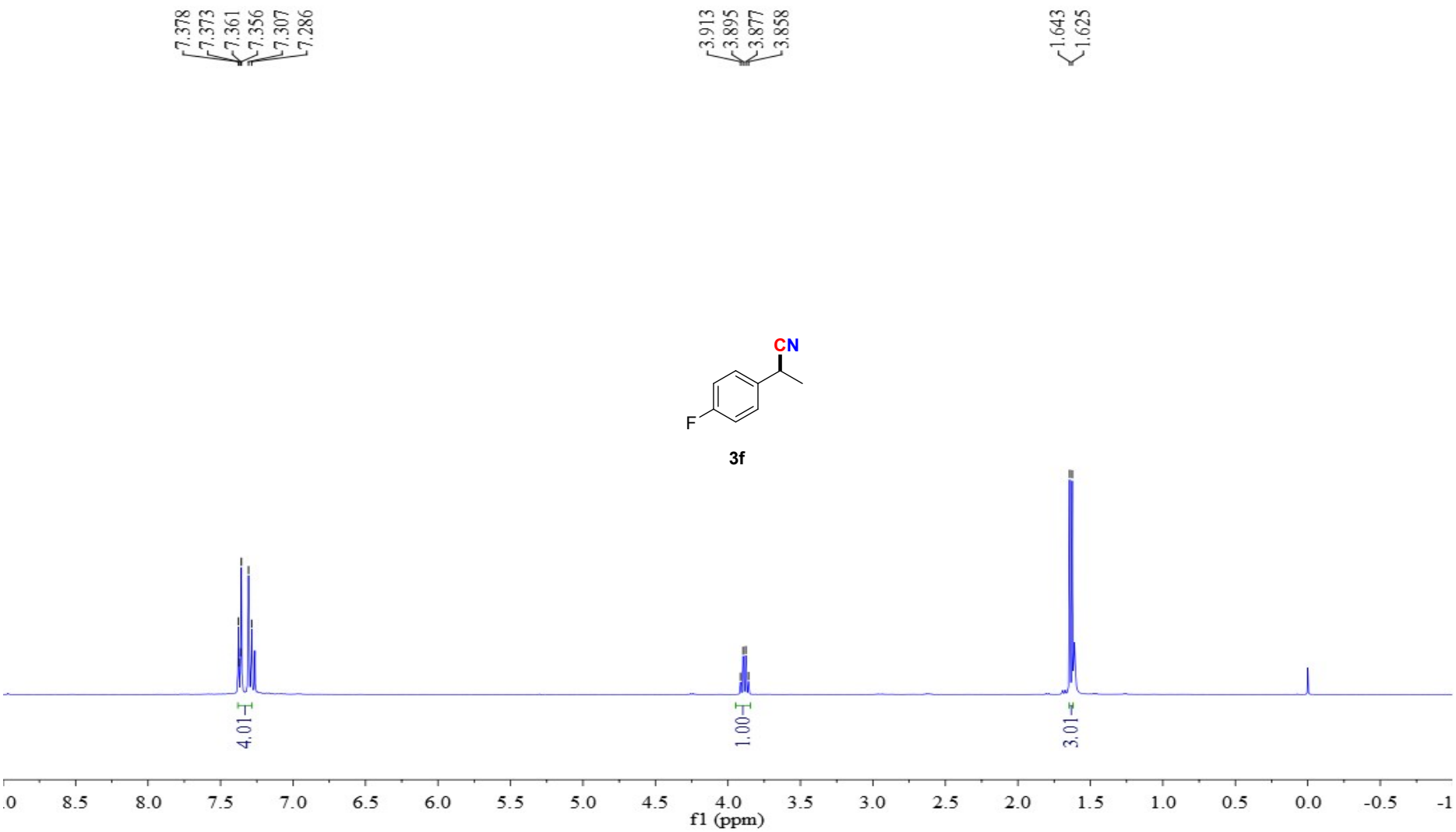
70
60
50
40
30
20
10
f1 (ppm)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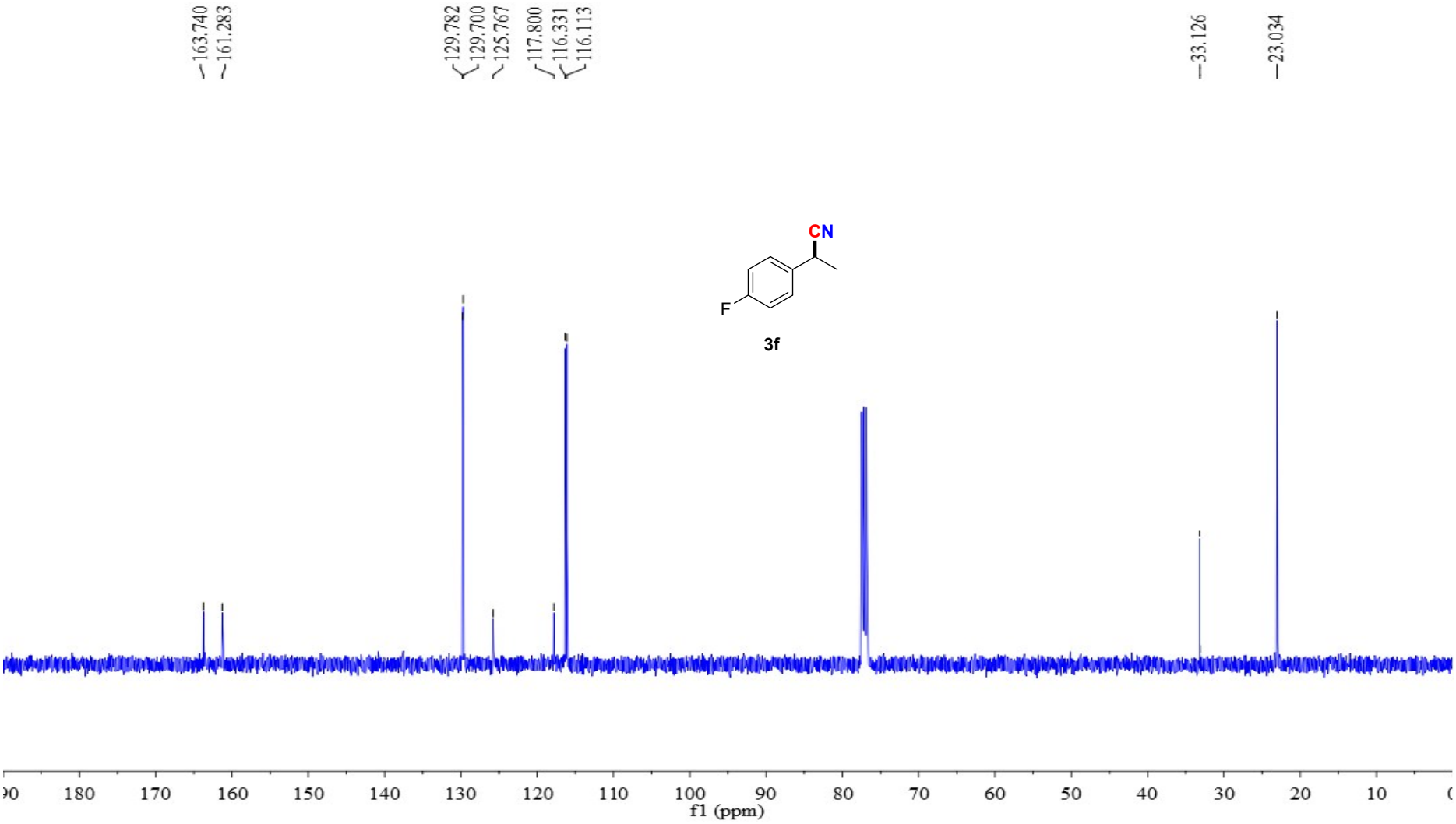
F
3f
4.01
1.00
3.01
f1 (ppm)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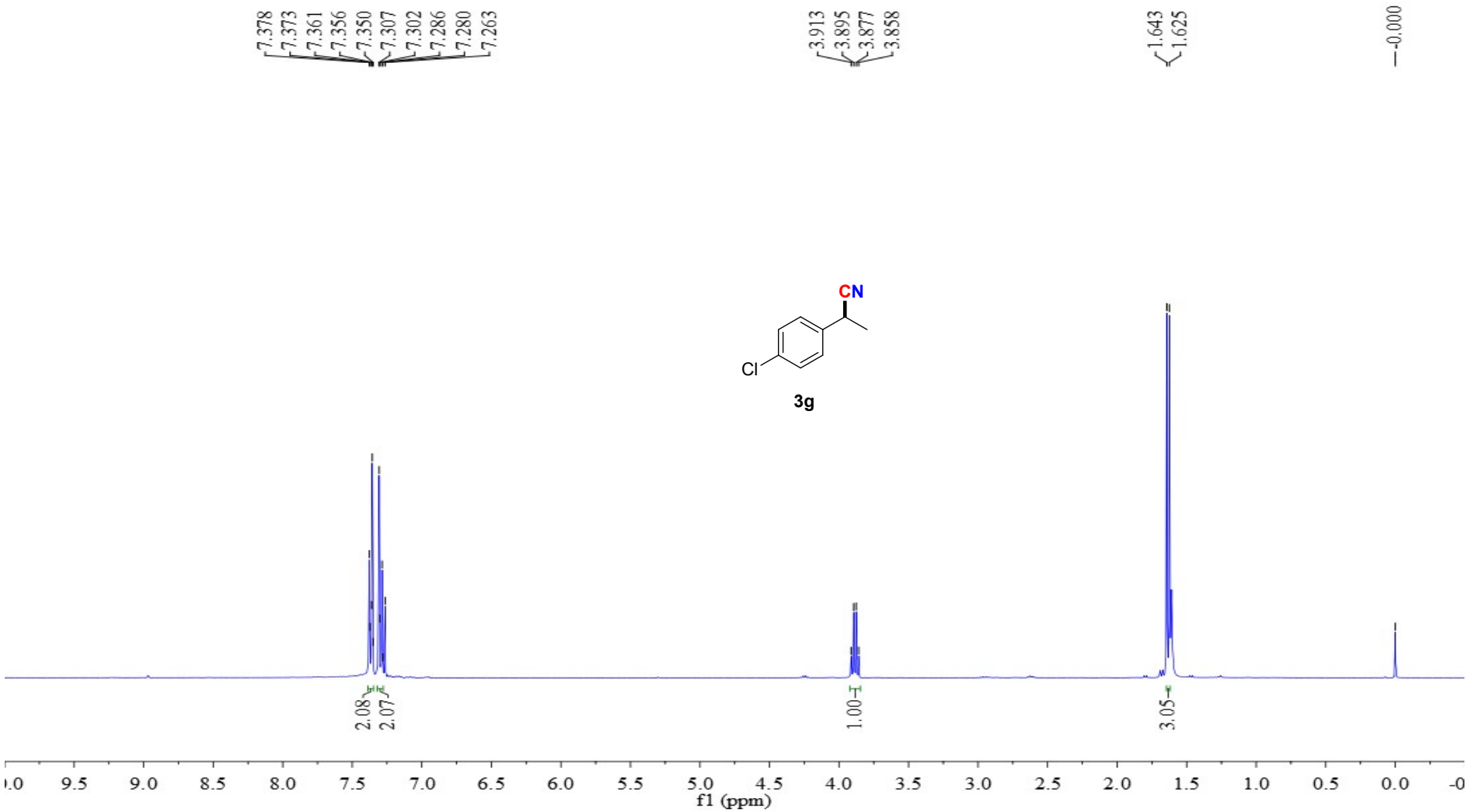
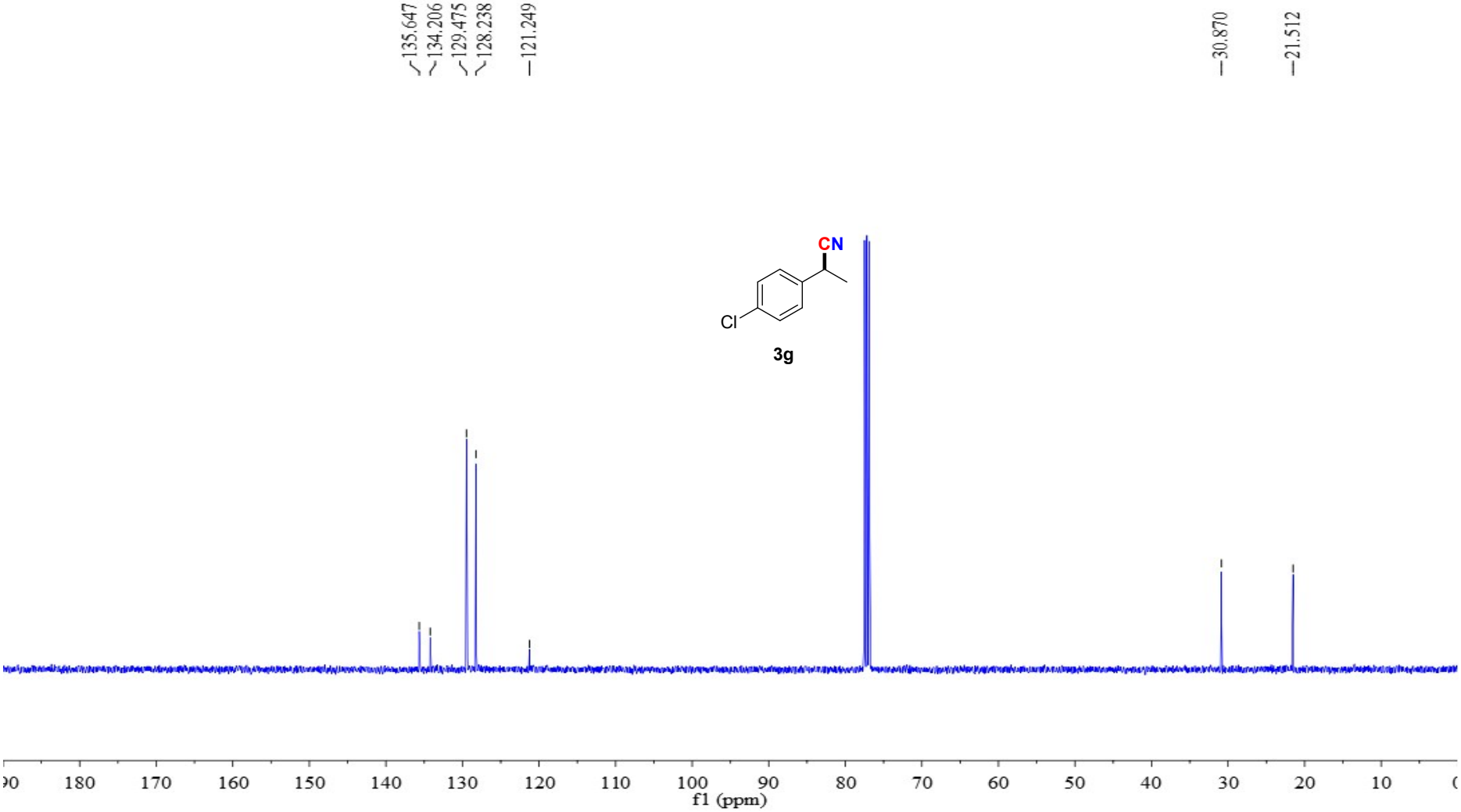
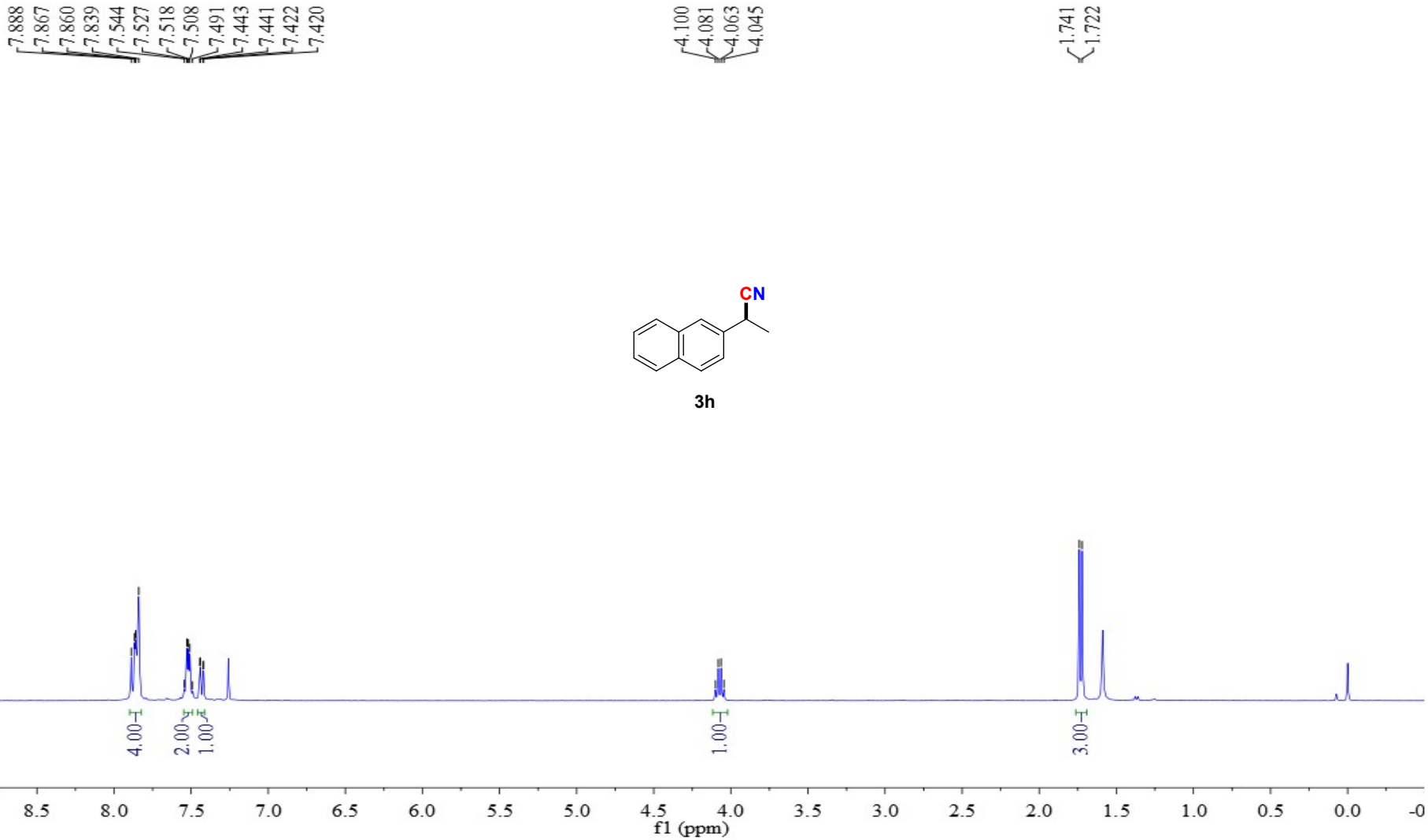
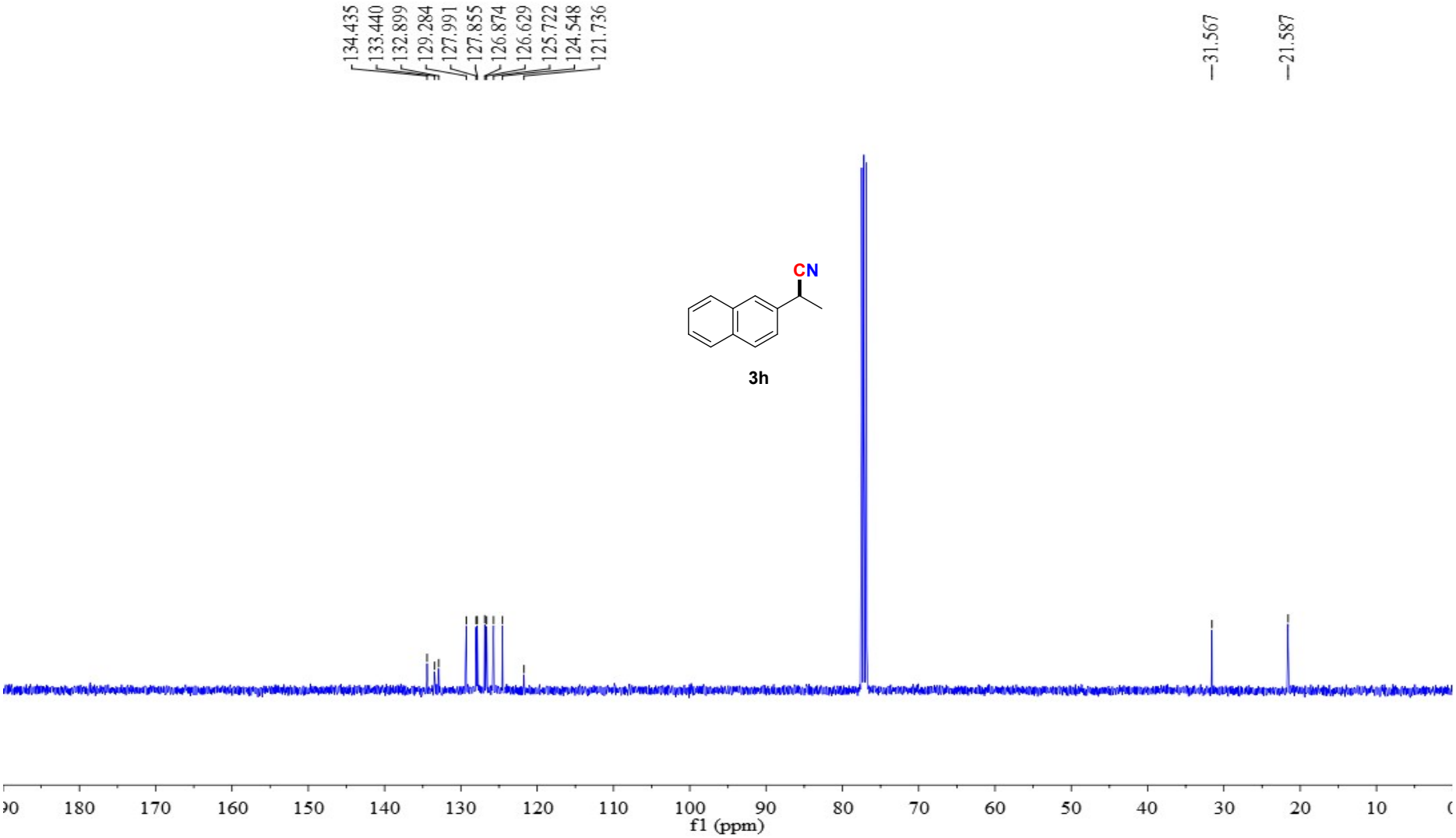
CN
F
3f
f1 (ppm)

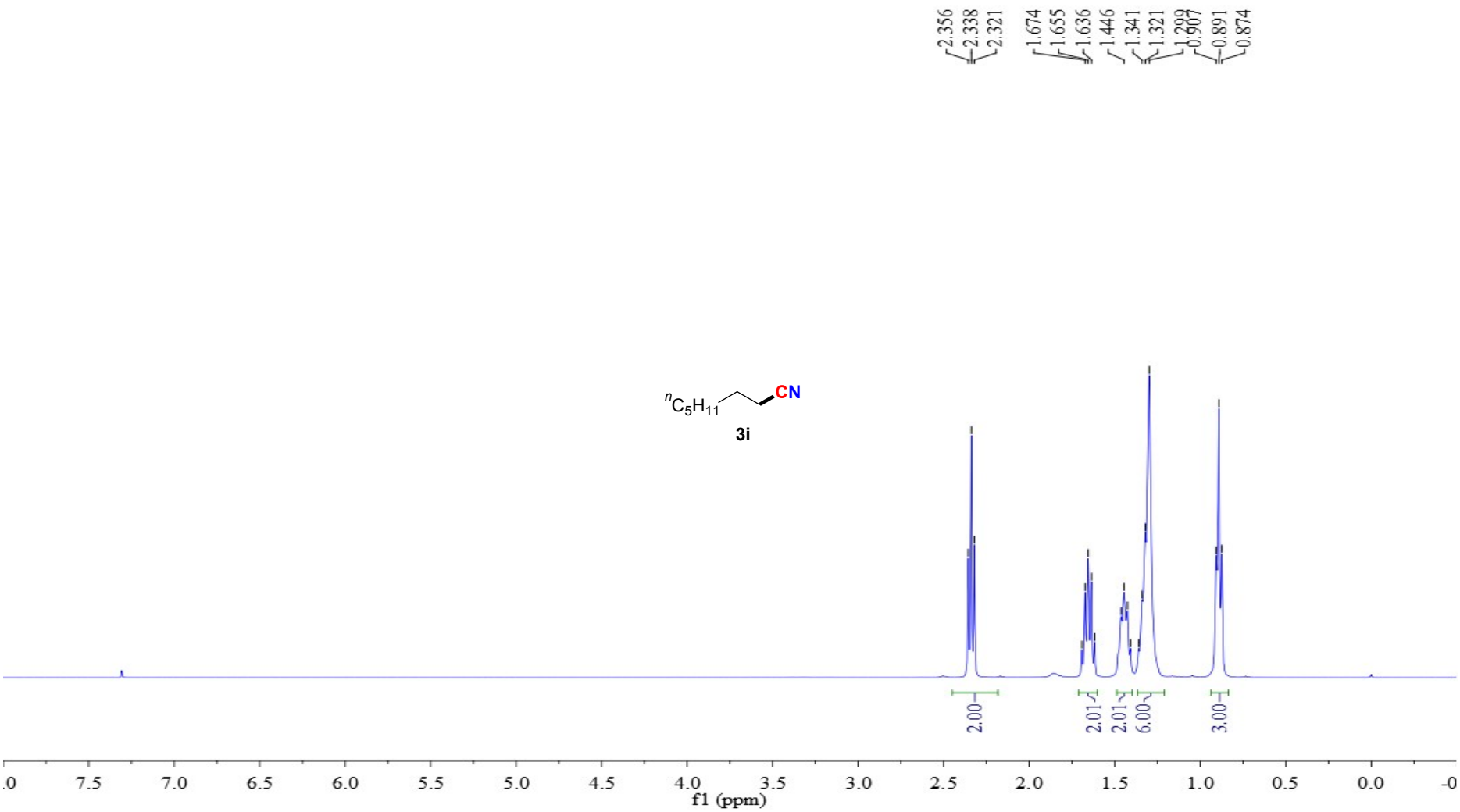

7.378
7.373
7.361
7.356
7.350
7.307
7.302
7.286
7.280
7.263
3.913
3.895
3.877
3.858
1.643
1.625
-0.000
CN
Cl
3g
2.08
2.07
1.00
3.05
f1 (ppm)

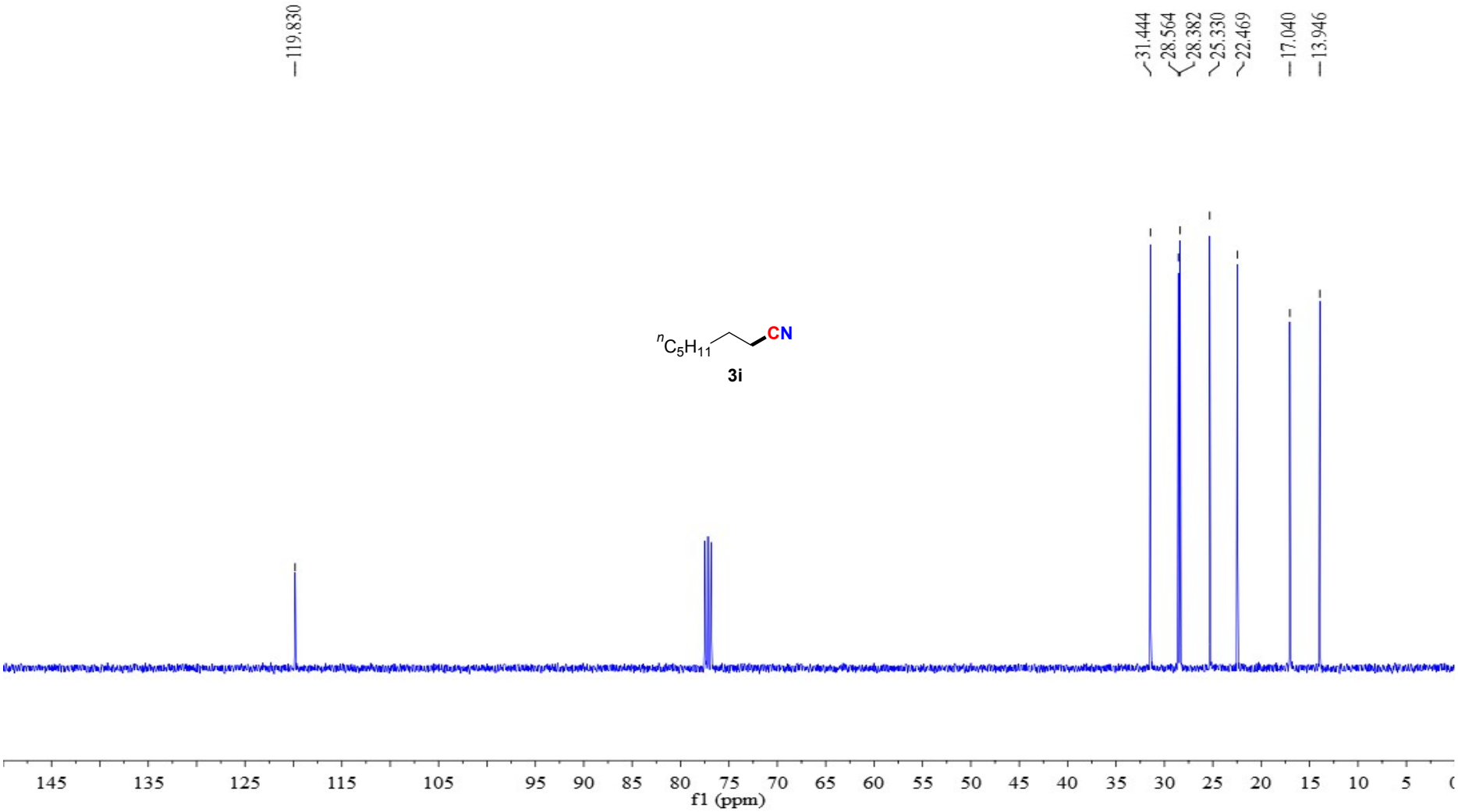

135.647
134.206
129.475
128.238
121.249
30.870
21.512
CN
Cl
3g
f1 (ppm)

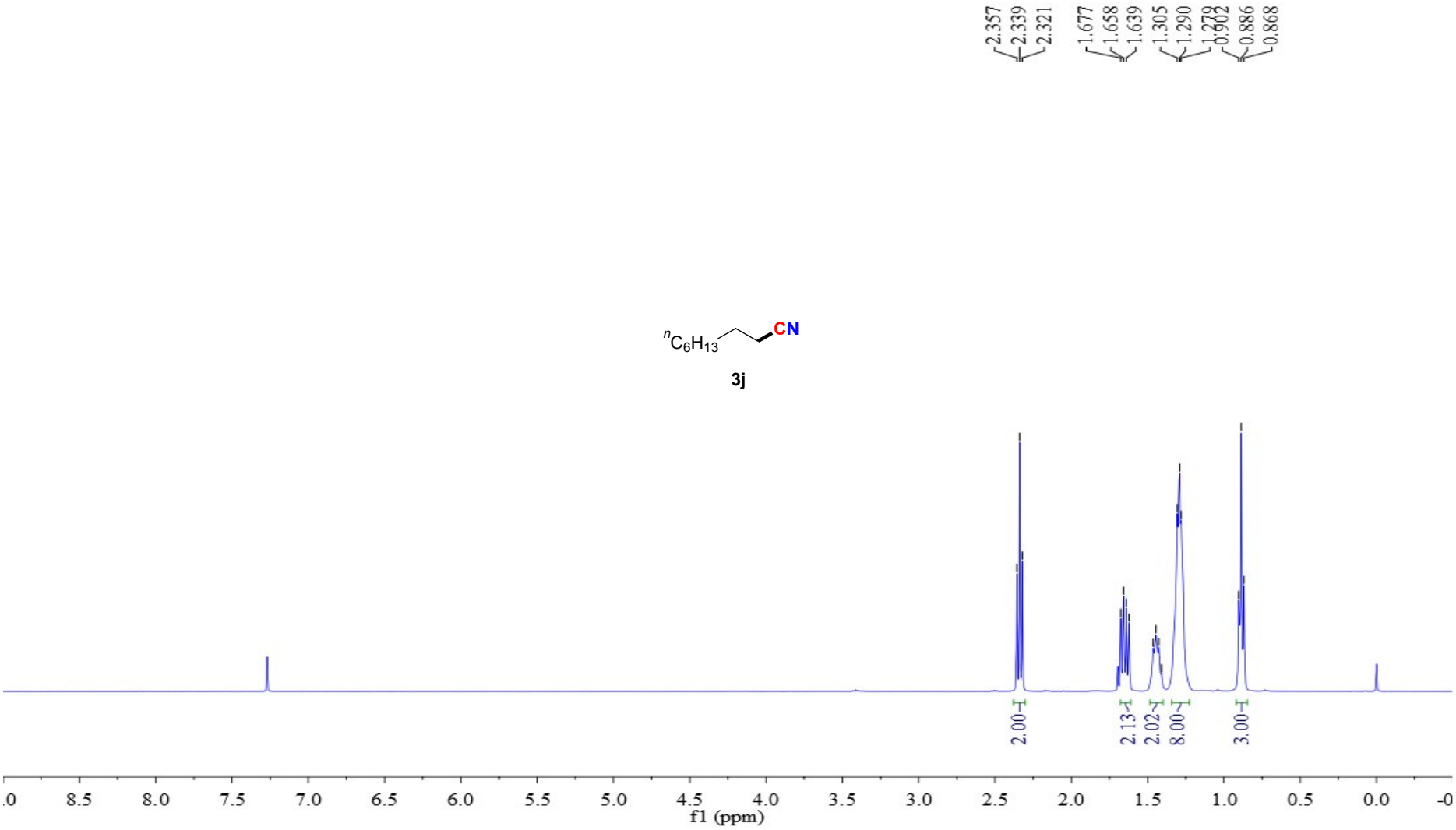

7.888
7.867
7.860
7.839
7.544
7.527
7.518
7.508
7.491
7.443
7.441
7.422
7.420
4.100
4.081
4.063
4.045
1.741
1.722
CN
4.00
2.00
1.00
1.00
3.00
f1 (ppm)

3h

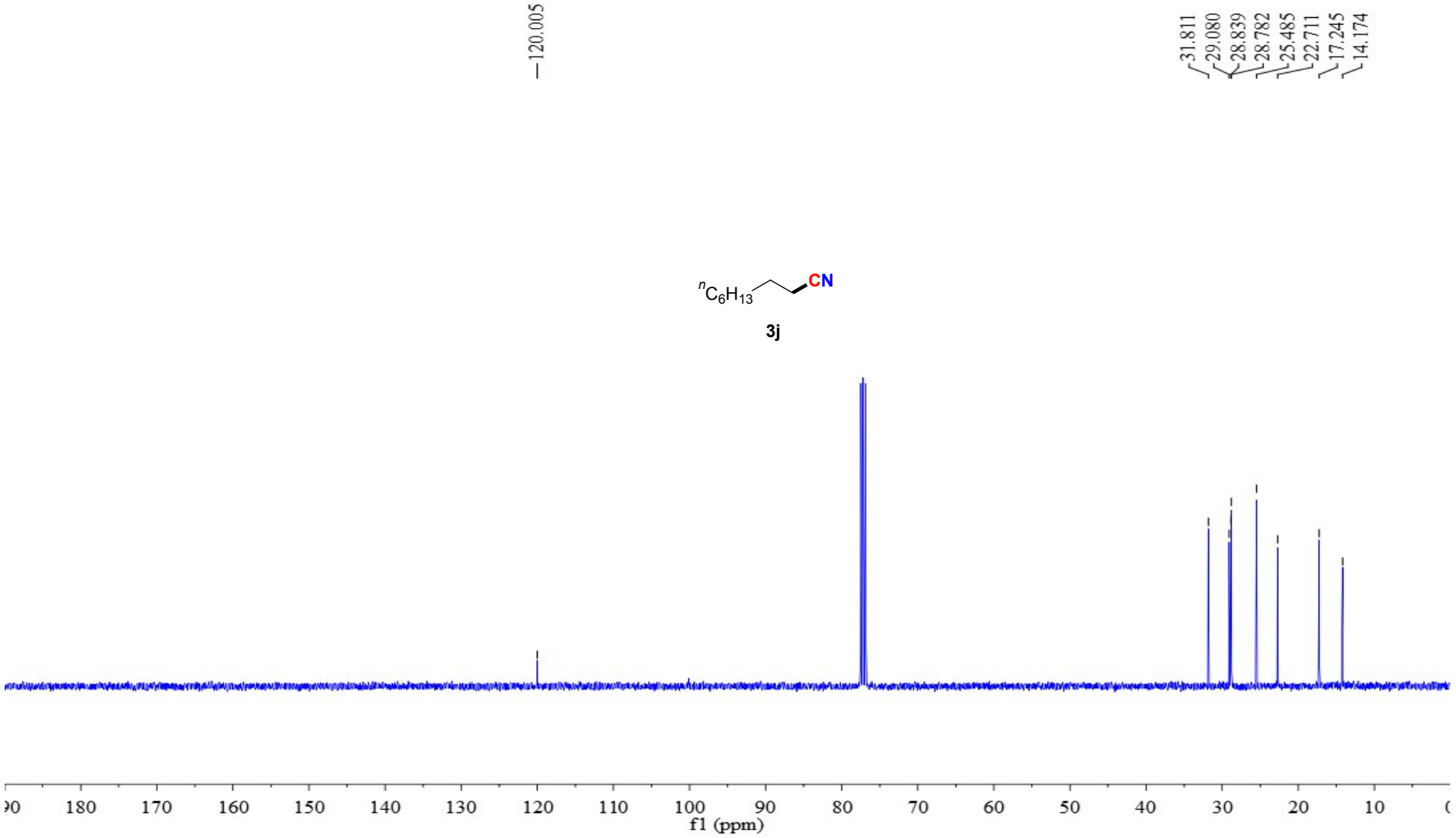

134.435
133.440
132.899
129.284
127.991
127.855
126.874
126.629
125.722
124.548
121.736
31.567
21.587
CN
3h
f1 (ppm)

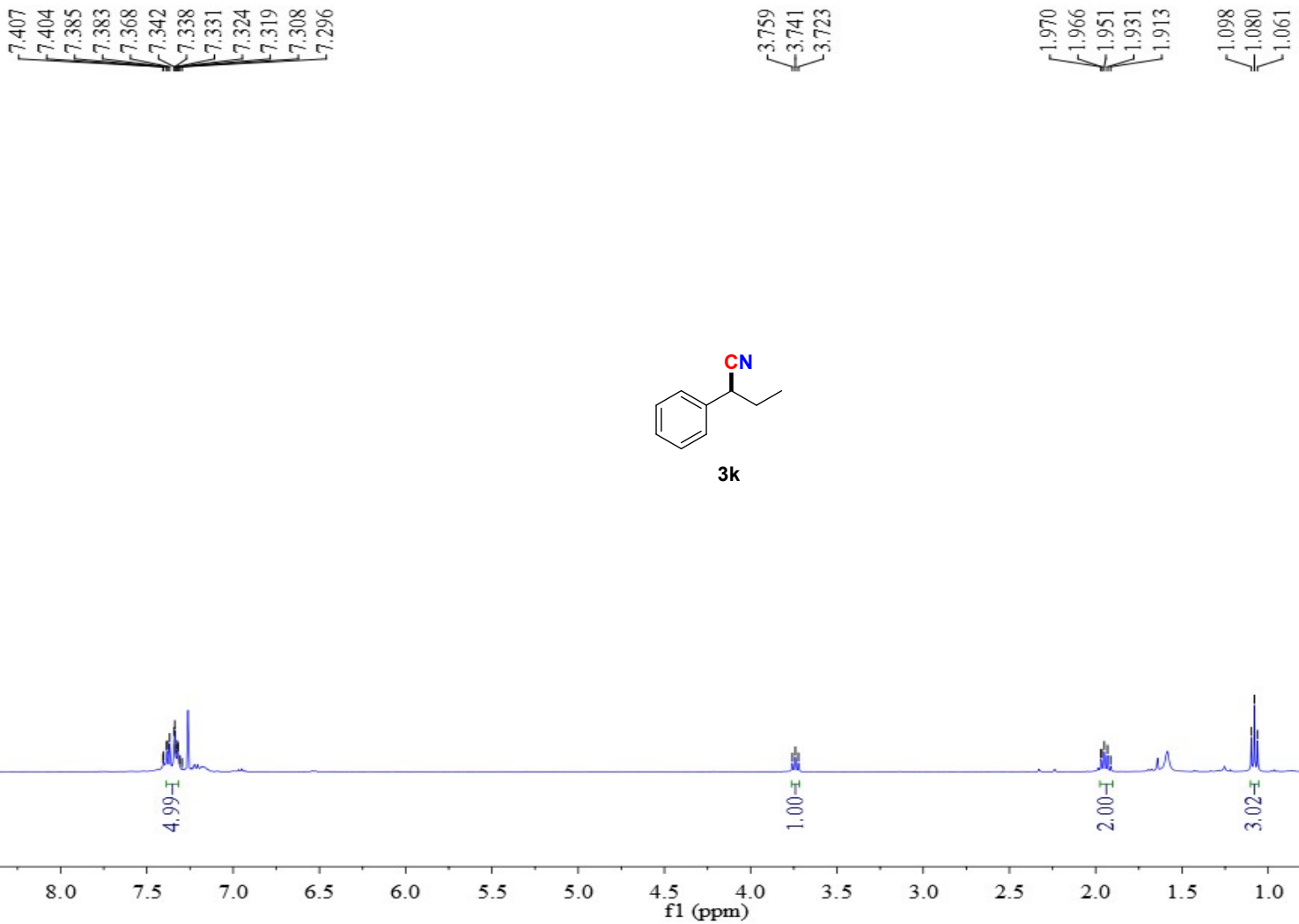

2.356
2.338
2.321
1.674
1.655
1.636
1.446
1.341
1.321
1.299
0.907
0.891
0.874
$^{n}C_5H_{11}$
CN
3i
2.00
2.01
2.01
6.00
3.00
f1 (ppm)

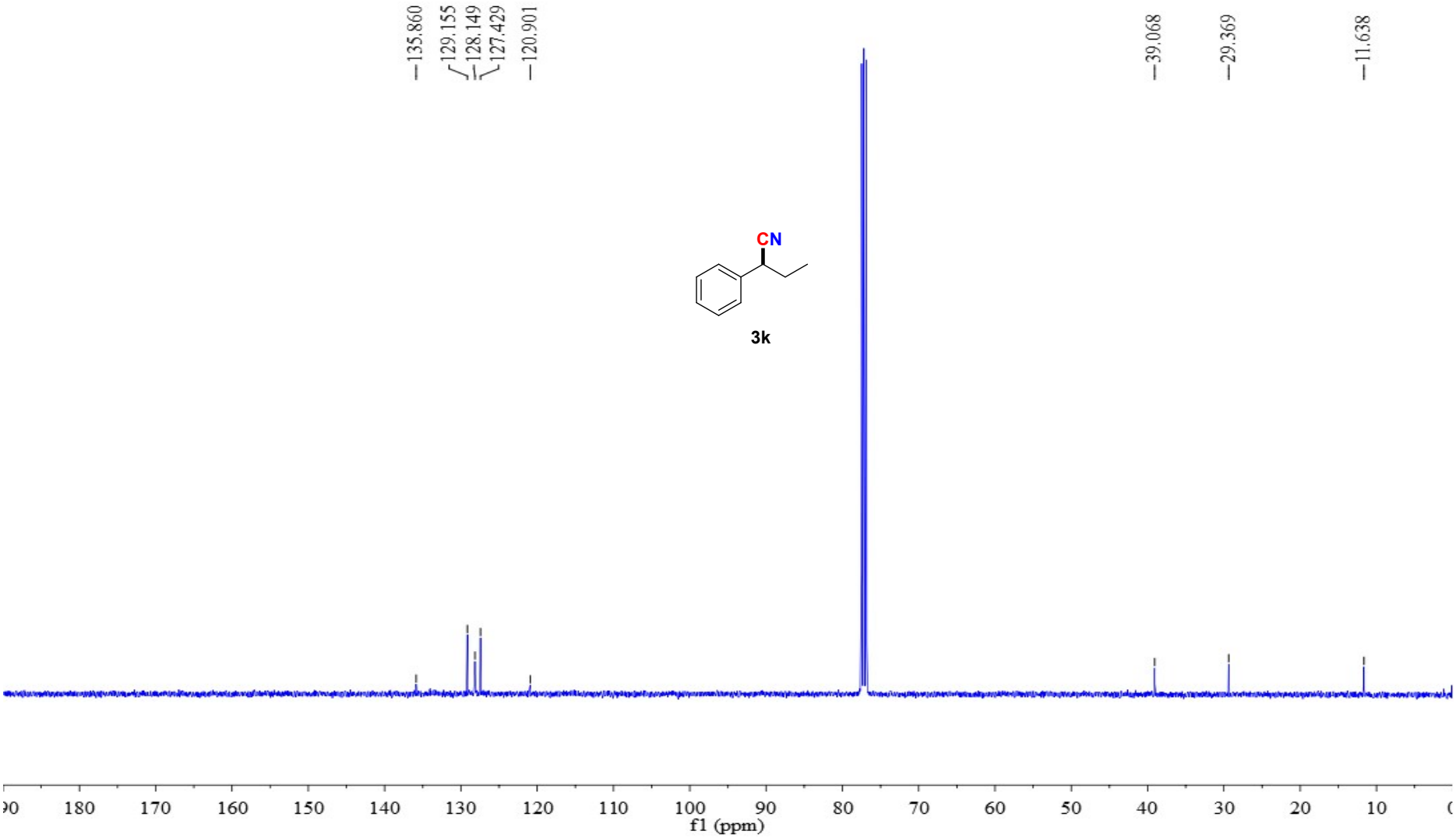

119.830
31.444
28.564
28.382
25.330
22.469
17.040
13.946
$^{n}C_5H_{11}$
CN
3i
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

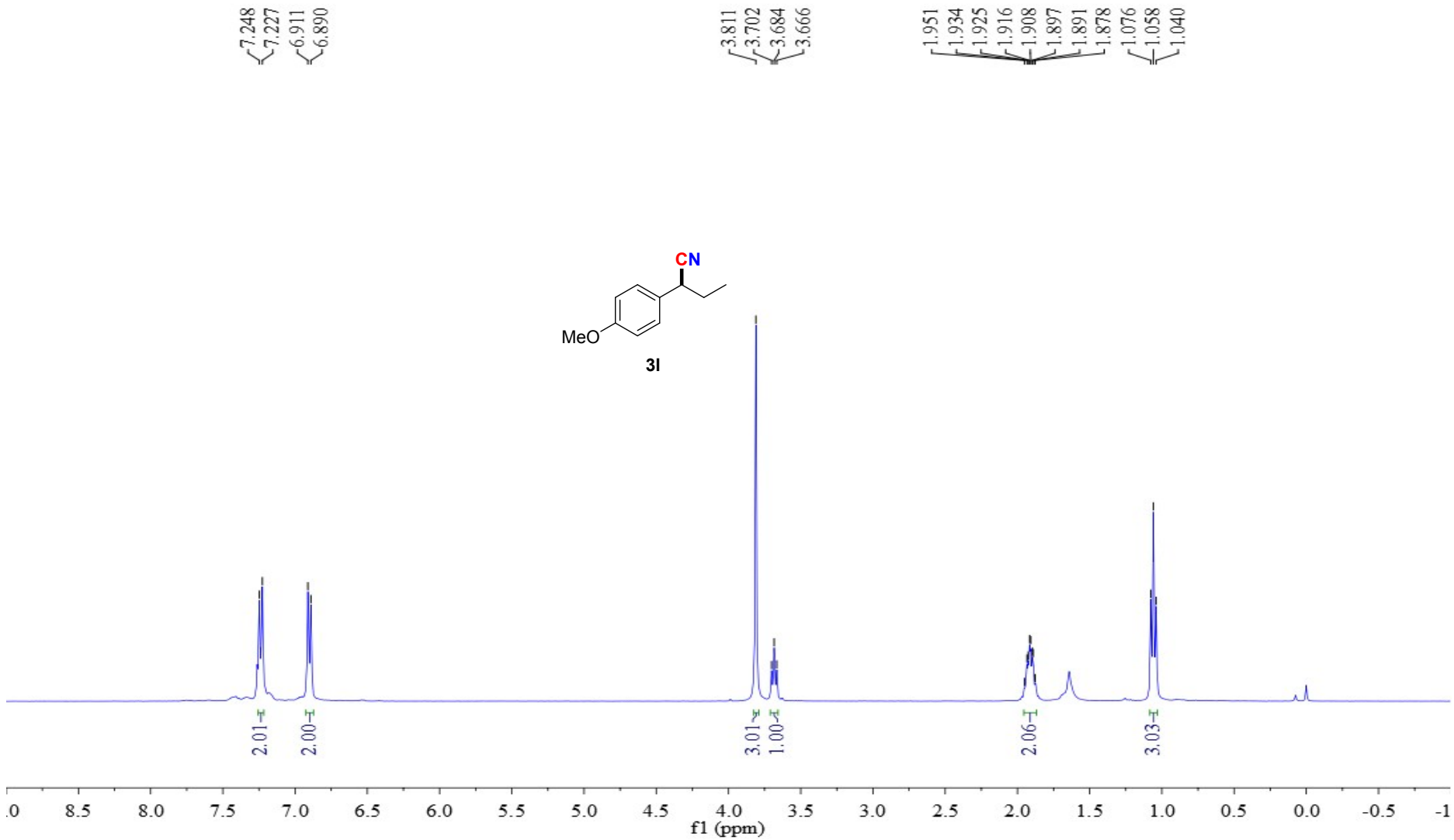

2.357
2.339
2.321
1.677
1.658
1.639
1.305
1.290
1.279
0.902
0.886
0.868
$^{n}C_6H_{13}$
CN
2.00
2.13
2.02
8.00
3.00
f1 (ppm)

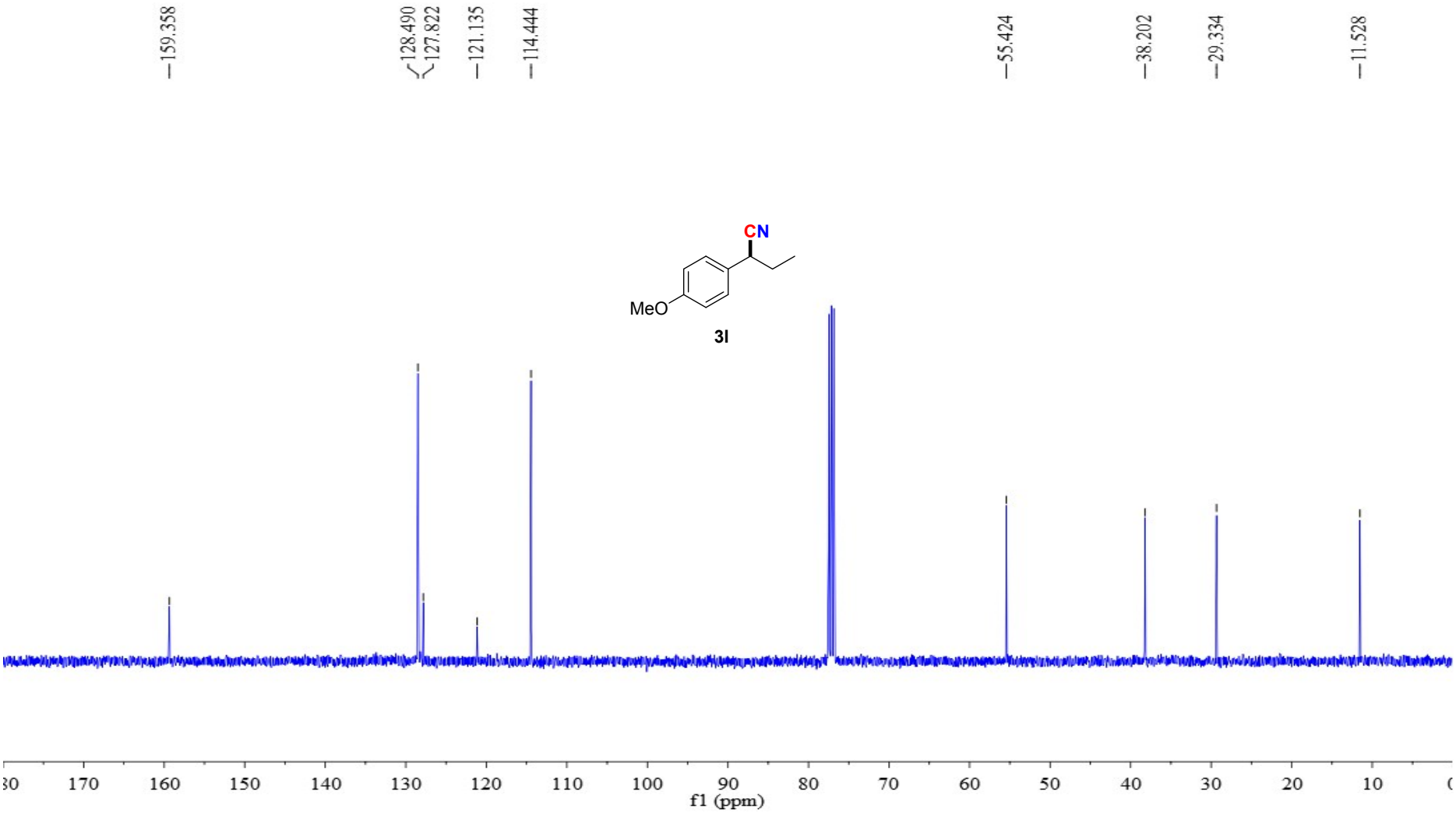
3j


120.005
31.811
29.080
28.839
28.782
25.485
22.711
17.245
14.174
nC6H13
CN
3j
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

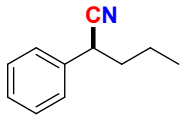

7.407
7.404
7.385
7.383
7.368
7.342
7.338
7.331
7.324
7.319
7.308
7.296
3.759
3.741
3.723
1.970
1.966
1.951
1.931
1.913
1.098
1.080
1.061
CN
3k
4.99
1.00
2.00
3.02
f1 (ppm)


135.860
129.155
128.149
127.429
120.901
39.068
29.369
11.638
CN
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

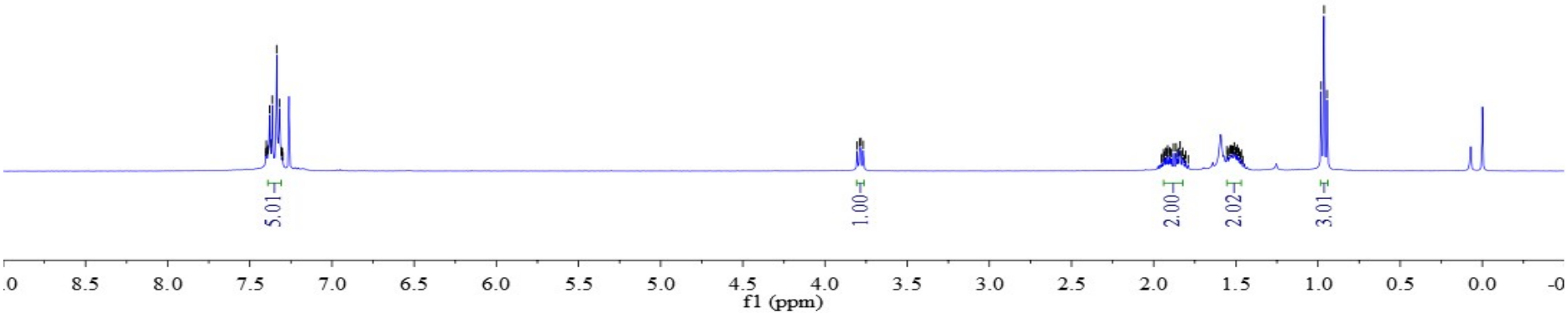

7.248
7.227
6.911
6.890
3.811
3.702
3.684
3.666
1.951
1.934
1.925
1.916
1.908
1.897
1.891
1.878
1.076
1.058
1.040
CN
MeO
3l
2.01
2.00
3.01
1.00
2.06
3.03
f1 (ppm)

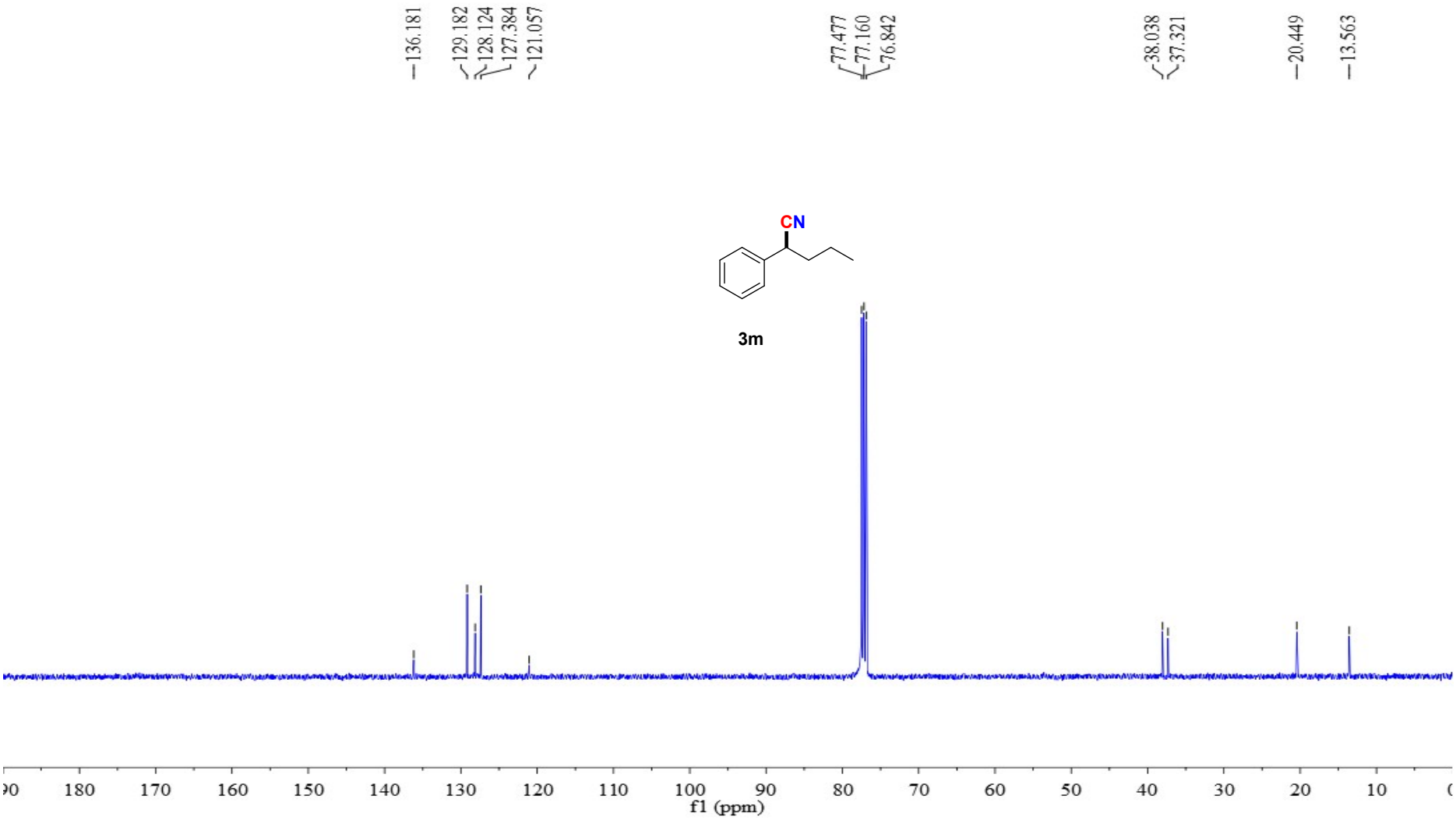

159.358
128.490
127.822
121.135
114.444
55.424
38.202
29.334
11.528
CN
MeO
3l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.403
7.400
7.396
7.390
7.379
7.372
7.364
7.337
7.319
7.309
7.302
7.299
3.805
3.789
3.784
3.768
1.915
1.879
1.863
1.839
1.555
1.536
1.530
1.525
1.522
1.517
1.510
1.500
1.482
0.982
0.963
0.945

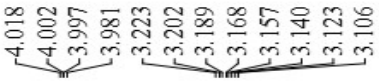

CN

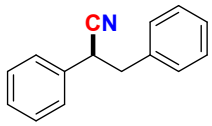
3m


5.01
1.00
2.00
2.02
3.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

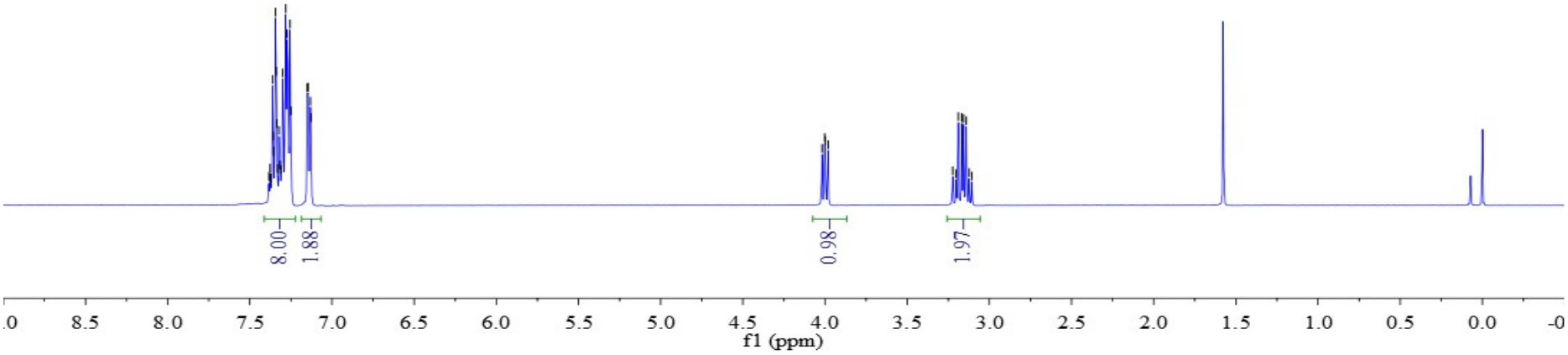

136.181
129.182
128.124
127.384
121.057
77.477
77.160
76.842
38.038
37.321
20.449
13.563
CN
3m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

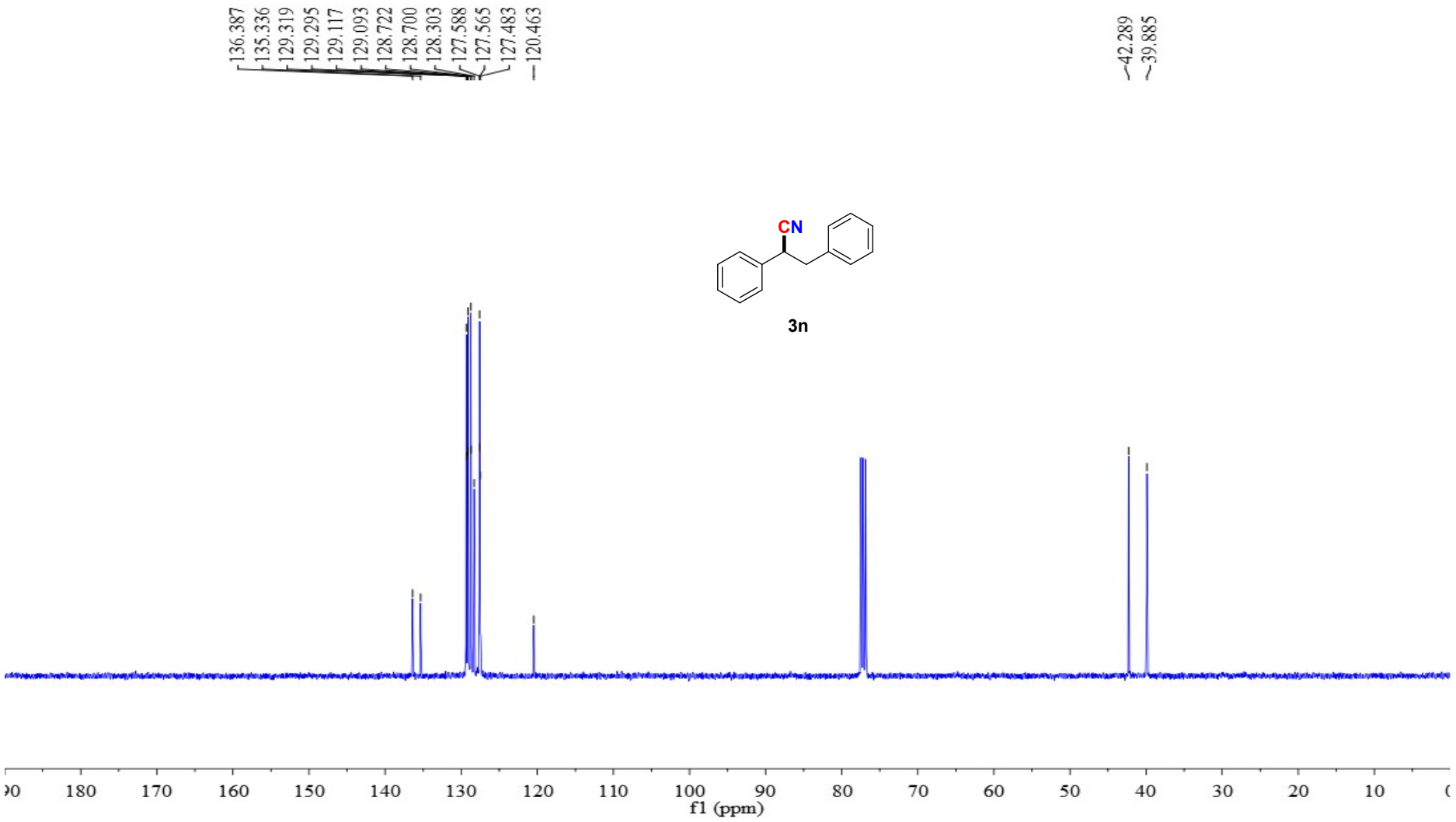

7.383
7.377
7.372
7.361
7.358
7.355
7.344
7.340
7.335
7.331
7.323
7.315
7.311
7.301
7.282
7.274
7.255
7.250
7.150
7.146
7.131
7.128

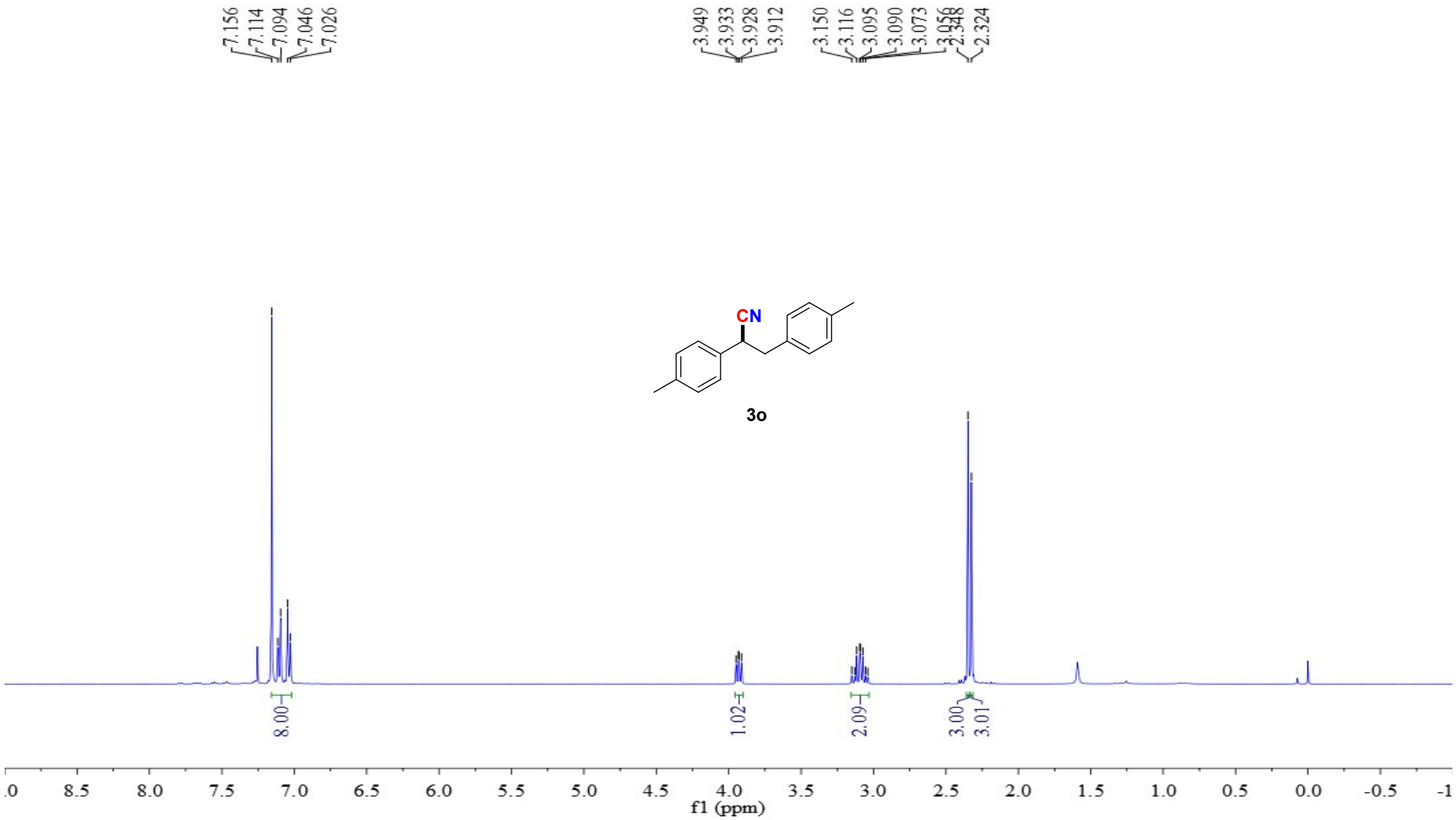

4.018
4.002
3.997
3.981
3.223
3.202
3.189
3.168
3.157
3.140
3.123
3.106

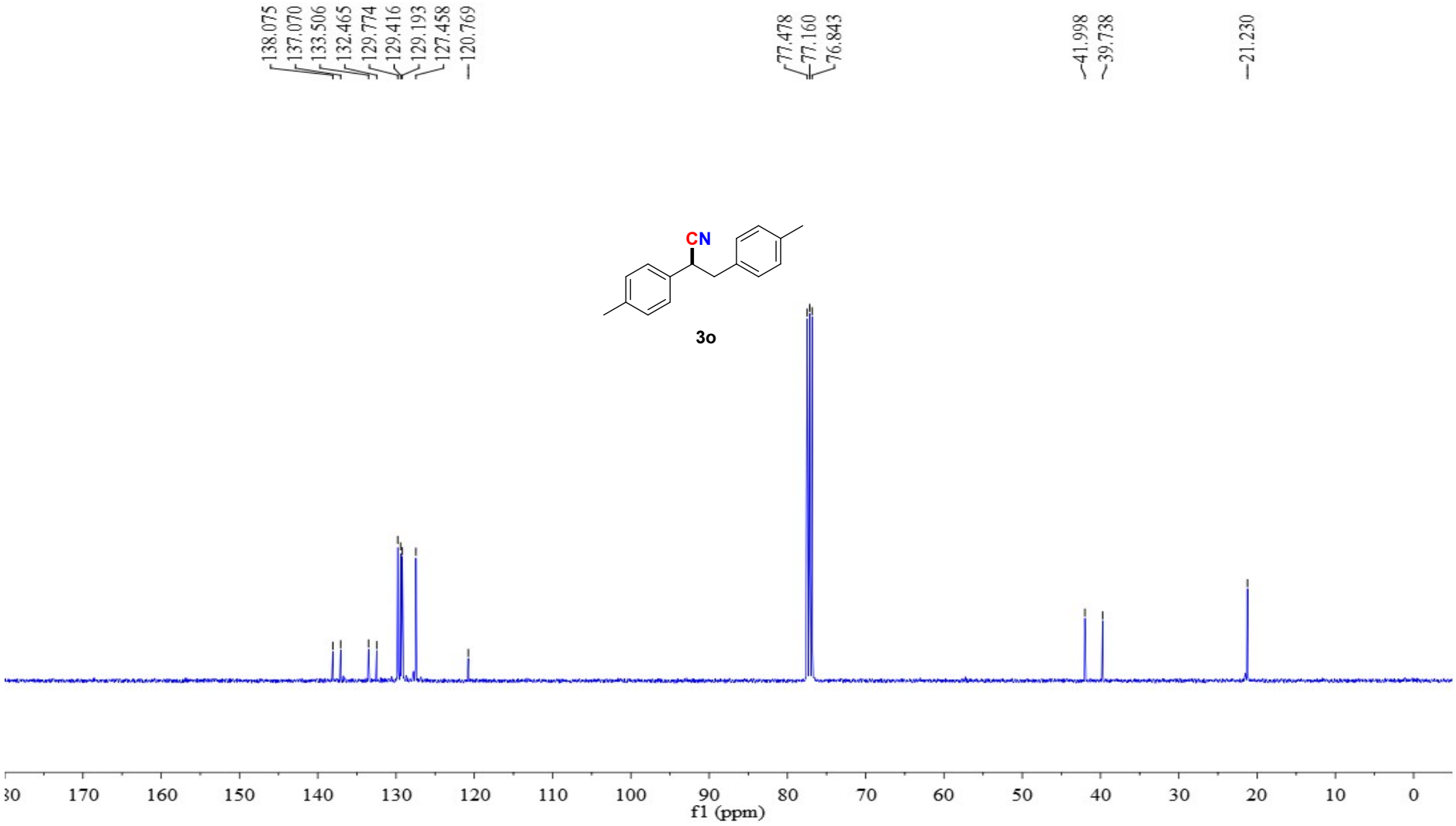

CN

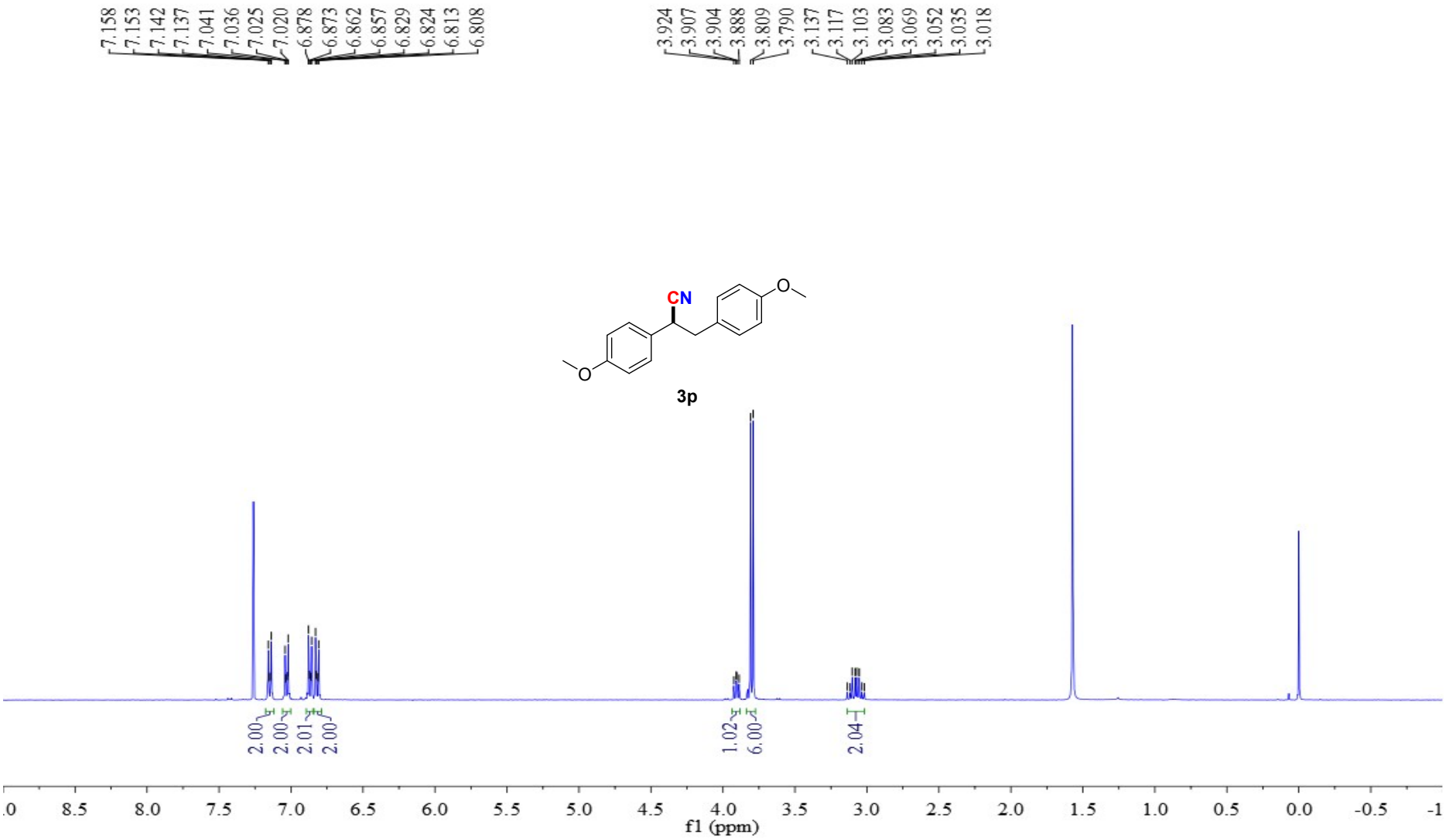
3n

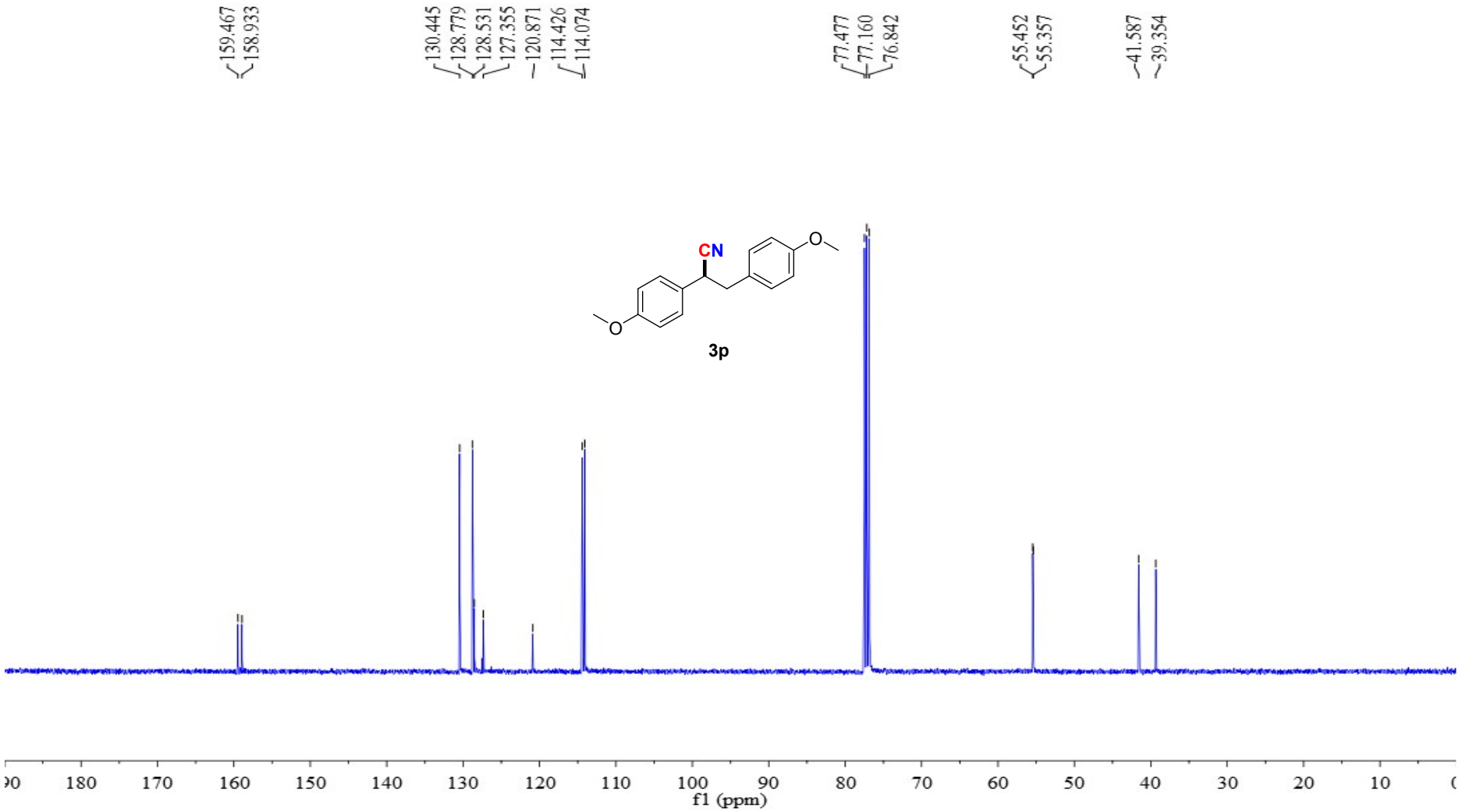

8.00
1.88
0.98
1.97
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

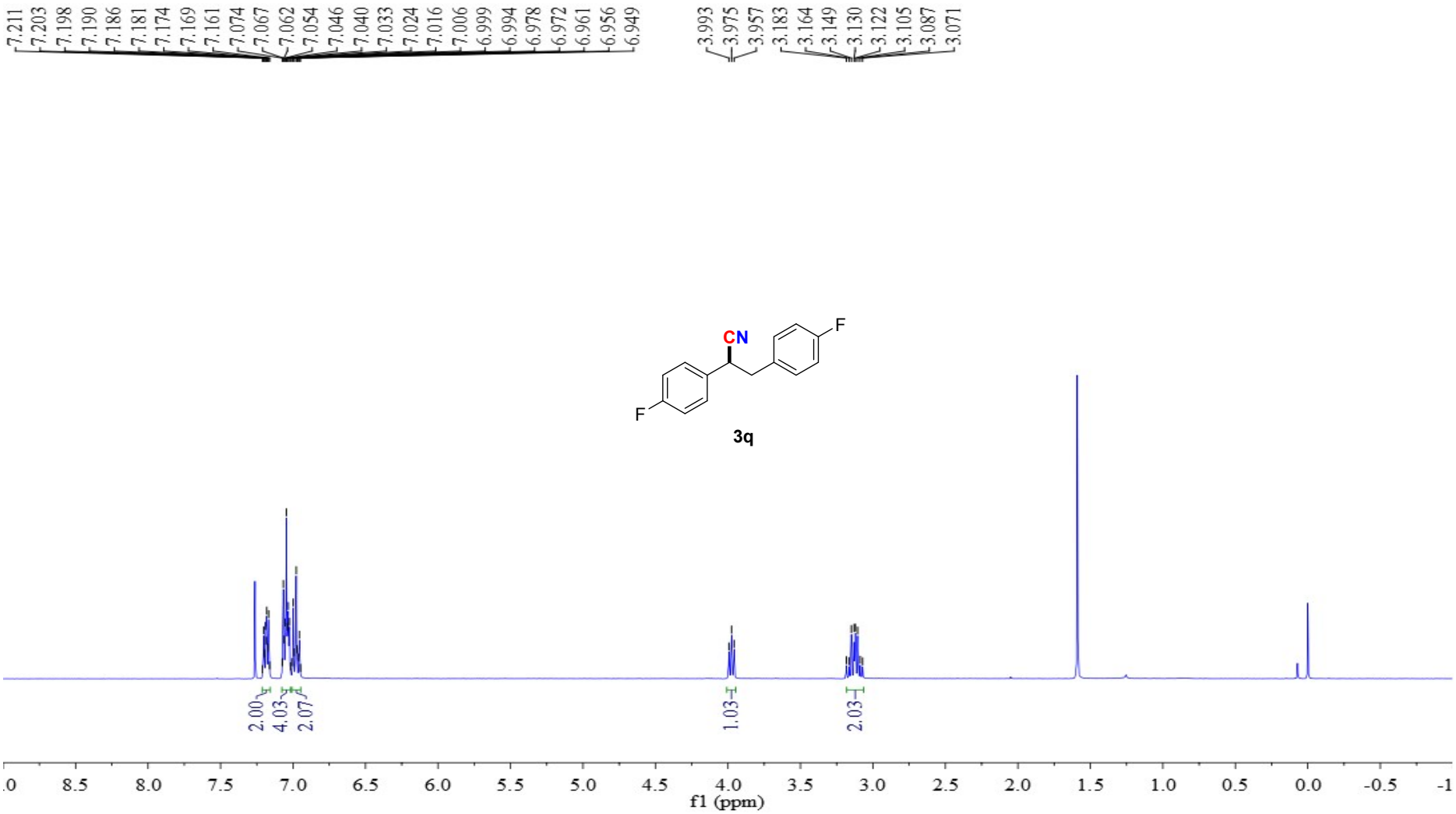

136.387
135.336
129.319
129.295
129.117
129.093
128.722
128.700
128.303
127.588
127.565
127.483
120.463
42.289
39.885
CN
3n
f1 (ppm)

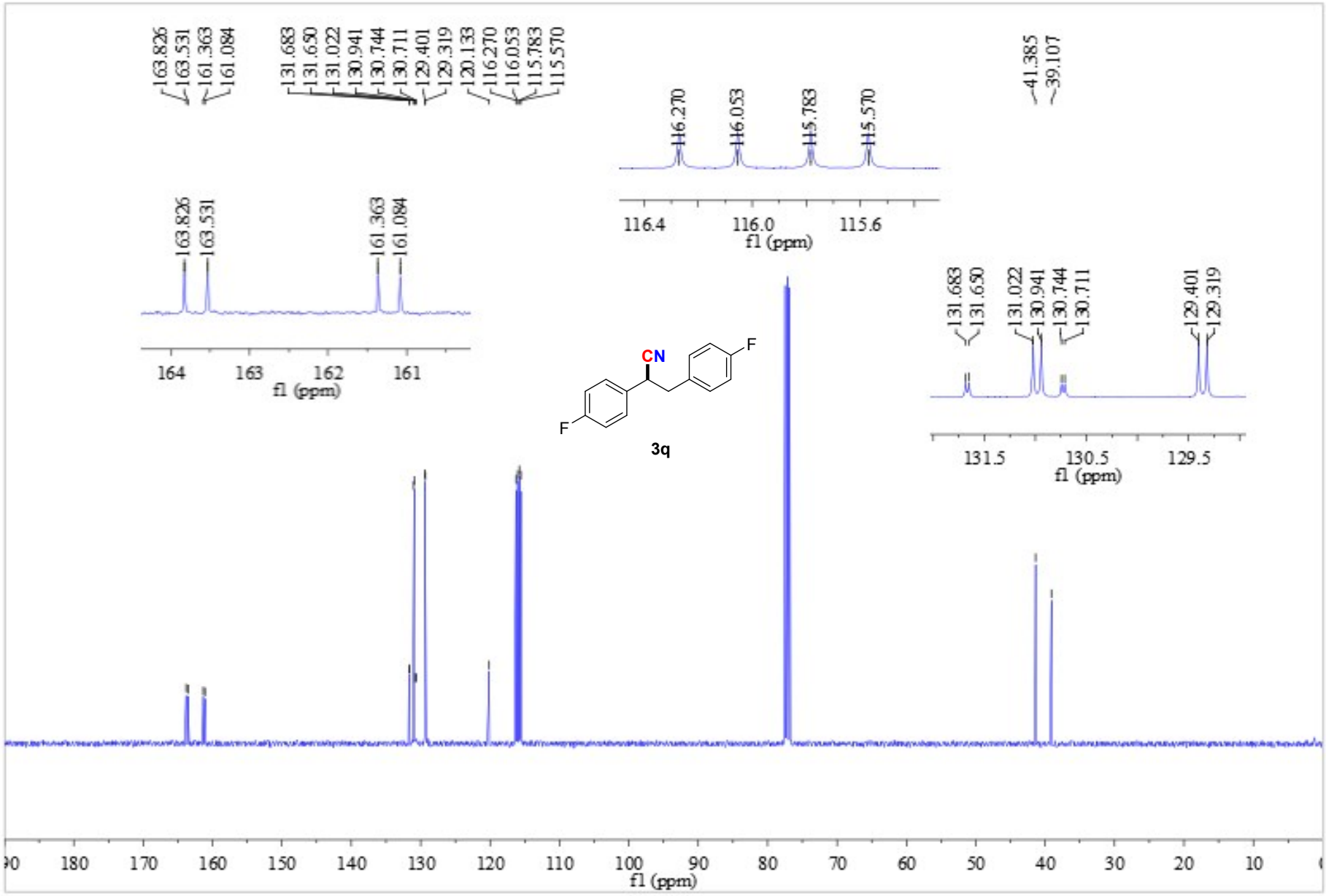

7.156
7.114
7.094
7.046
7.026
3.949
3.933
3.928
3.912
3.150
3.116
3.095
3.090
3.073
3.056
2.348
2.324
CN
3o
8.00
1.02
2.09
3.00
3.01
f1 (ppm)

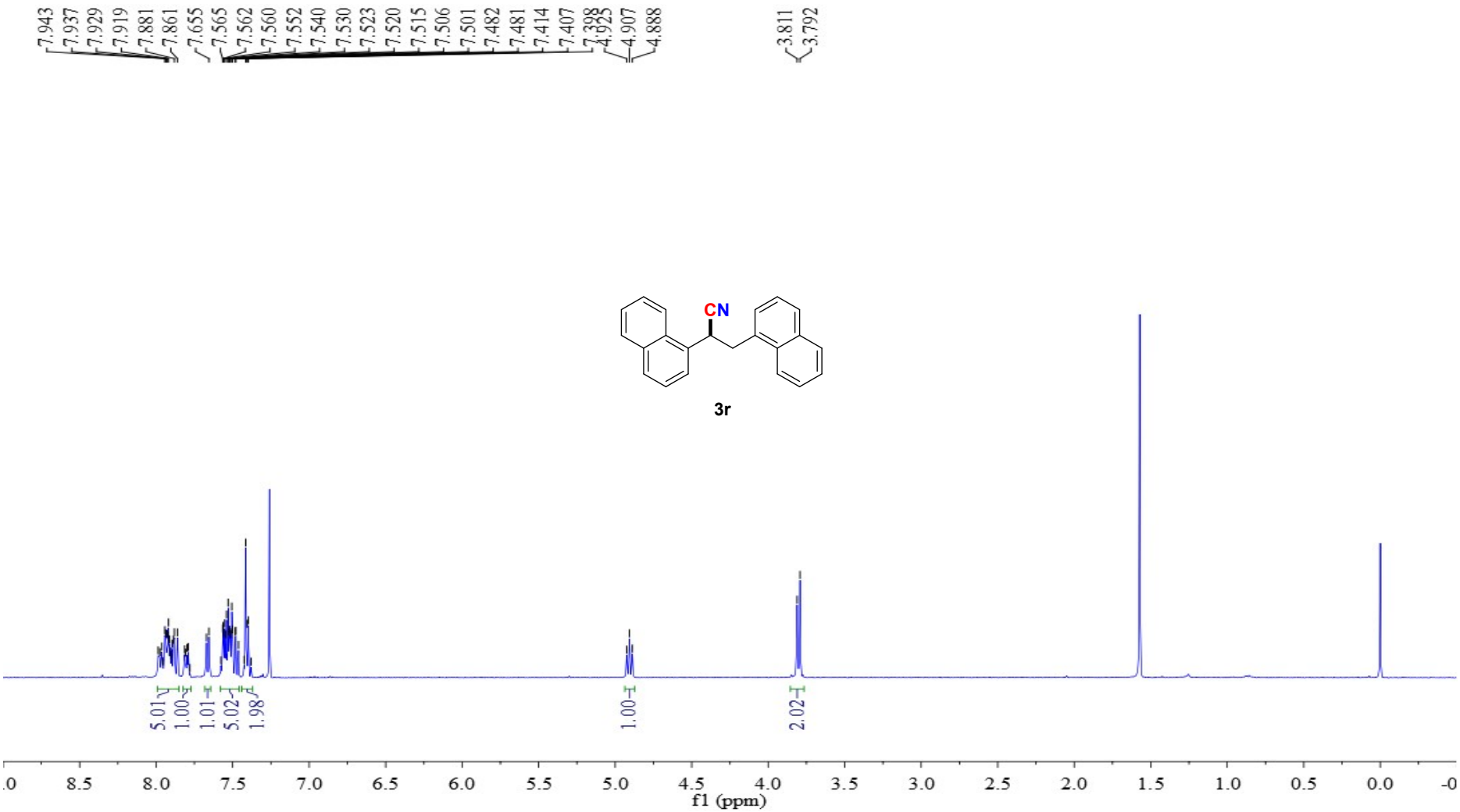

138.075
137.070
133.506
132.465
129.774
129.416
129.193
127.458
120.769
77.478
77.160
76.843
41.998
39.738
21.230
CN
3o
f1 (ppm)

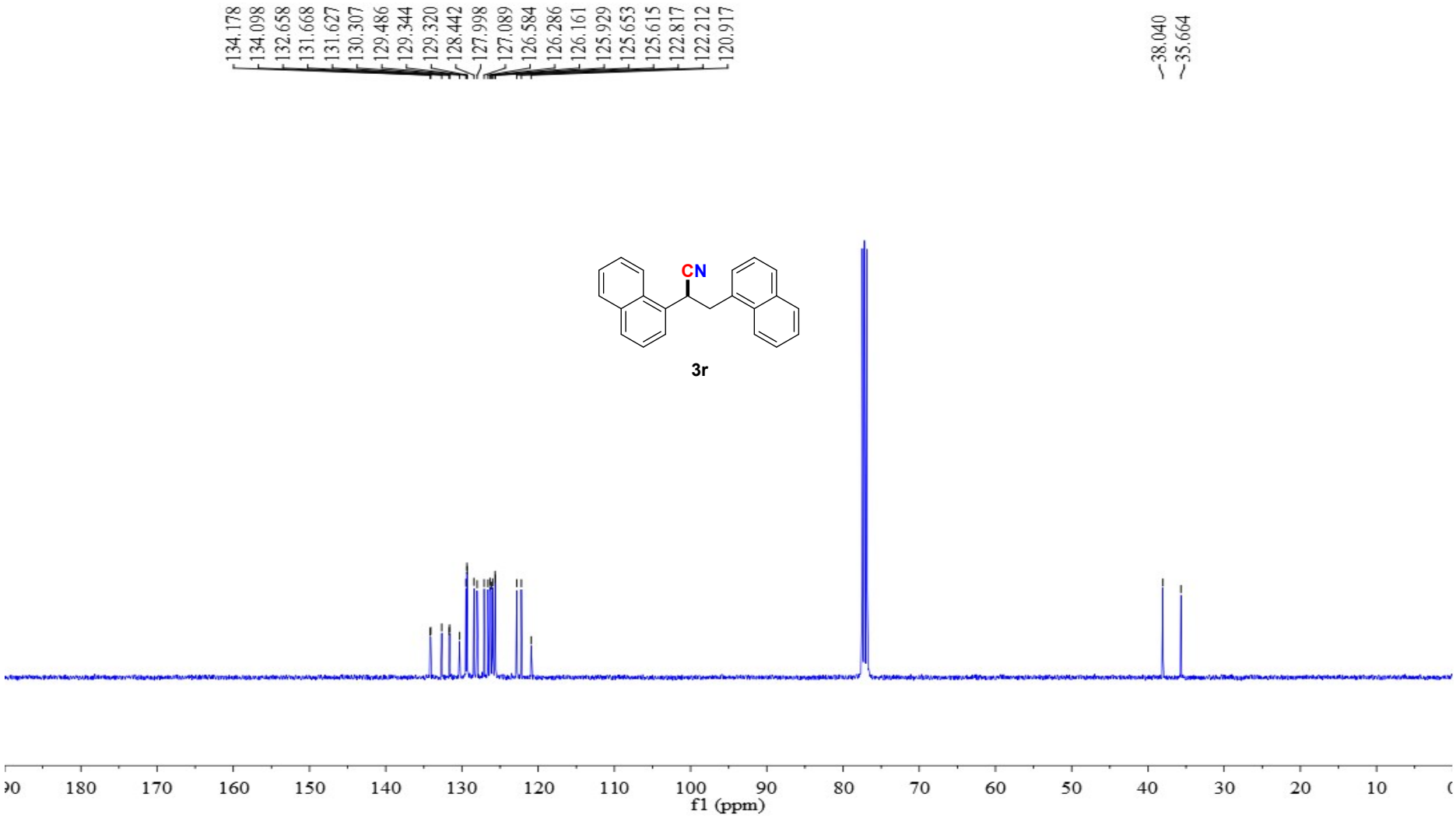

7.158
7.153
7.142
7.137
7.041
7.036
7.025
7.020
6.878
6.873
6.862
6.857
6.829
6.824
6.813
6.808
3.924
3.907
3.904
3.888
3.809
3.790
3.137
3.117
3.103
3.083
3.069
3.052
3.035
3.018
CN
O
O
3p
2.00
2.00
2.01
2.00
1.02
6.00
2.04
f1 (ppm)

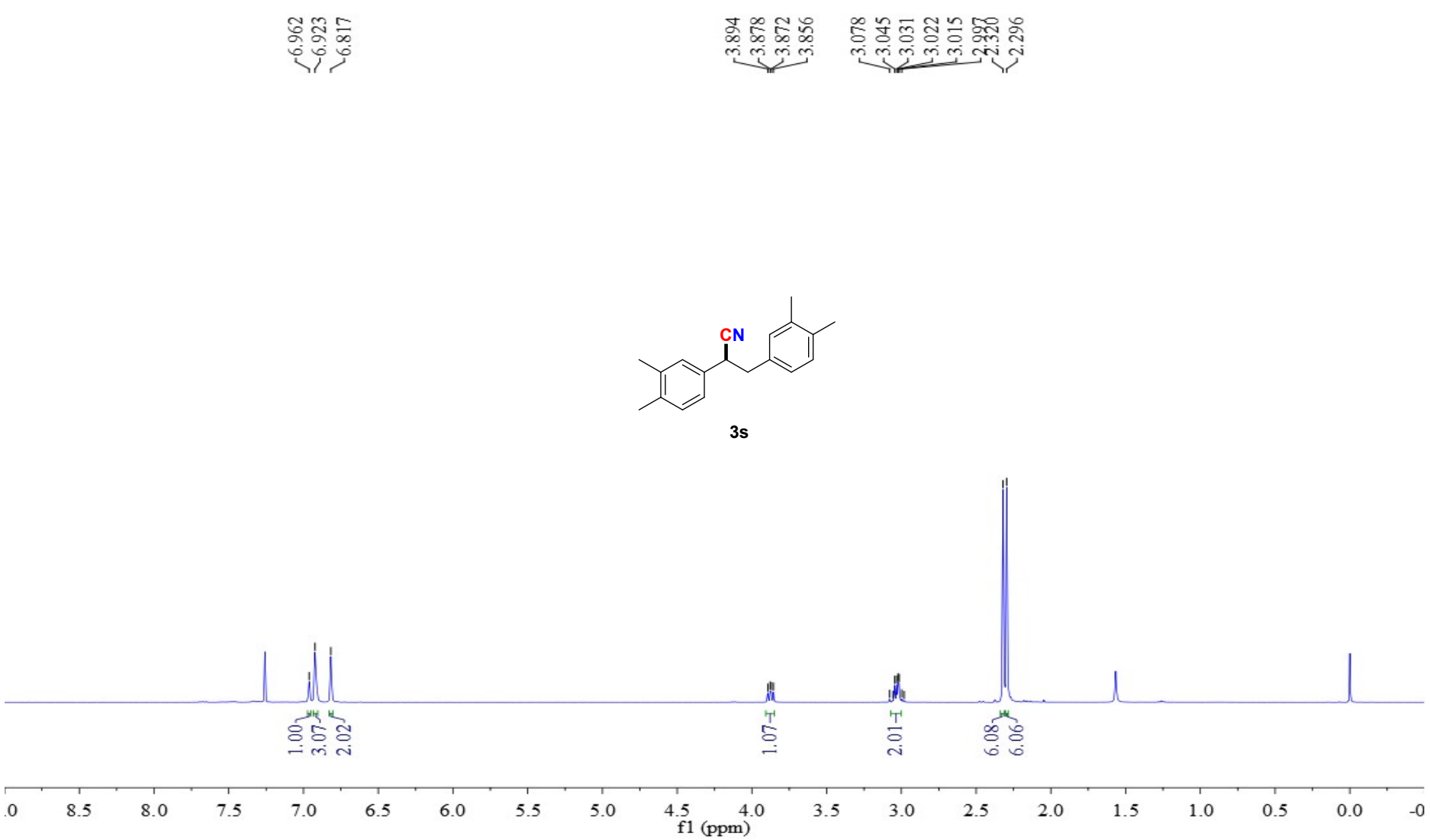

159.467
158.933
130.445
128.779
128.531
127.355
120.871
114.426
114.074
77.477
77.160
76.842
55.452
55.357
41.587
39.354
CN
O
O
3p
f1 (ppm)


7.211
7.203
7.198
7.190
7.186
7.181
7.174
7.169
7.161
7.074
7.067
7.062
7.054
7.046
7.040
7.033
7.024
7.016
7.006
6.999
6.994
6.978
6.972
6.961
6.956
6.949
3.993
3.975
3.957
3.183
3.164
3.149
3.130
3.122
3.105
3.087
3.071
CN
F
F
3q
2.00
4.03
2.07
1.03
2.03
f1 (ppm)

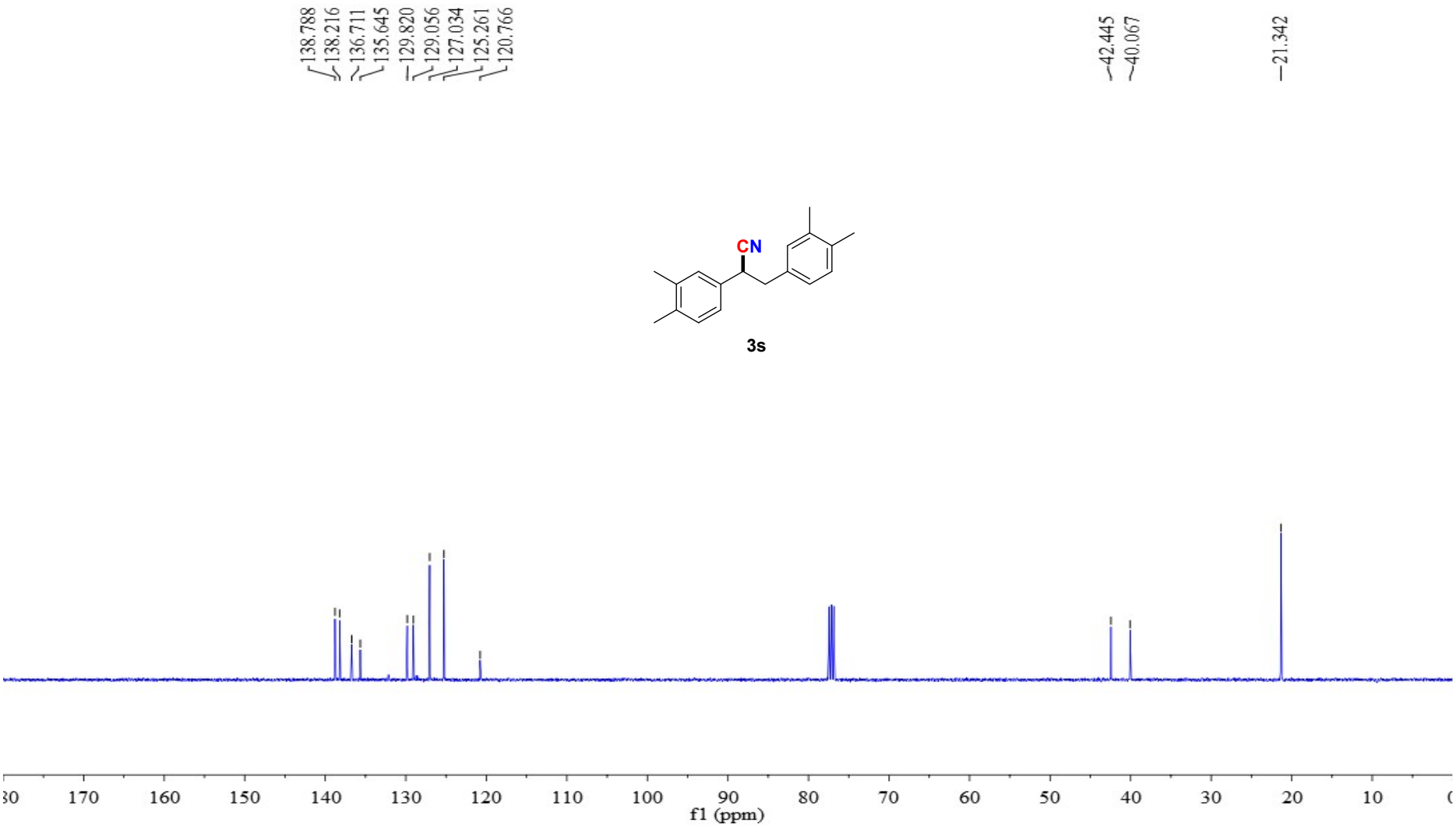

163.826
163.531
161.363
161.084
131.683
131.630
131.022
130.941
130.744
130.711
129.401
129.319
120.133
116.270
116.053
115.783
115.570
41.385
39.107
H6.270
H6.053
H5.783
H5.570
116.4
116.0
115.6
f1 (ppm)
164
163
162
161
f1 (ppm)
CN
F
F
3q
131.5
130.5
129.5
f1 (ppm)
f1 (ppm)


7.943
7.937
7.929
7.919
7.881
7.861
7.655
7.565
7.562
7.560
7.552
7.540
7.530
7.523
7.520
7.515
7.506
7.501
7.482
7.481
7.414
7.407
7.398
4.925
4.907
4.888
3.811
3.792
CN
3r
5.01
1.00
1.01
5.02
1.98
1.00
2.02
f1 (ppm)

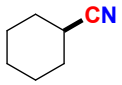

134.178
134.098
132.658
131.668
131.627
130.307
129.486
129.344
129.320
128.442
127.998
127.089
126.584
126.286
126.161
125.929
125.653
125.615
122.817
122.212
120.917
38.040
35.664
CN
3r
f1 (ppm)


6.962
6.923
6.817
3.894
3.878
3.872
3.856
3.078
3.045
3.031
3.022
3.015
2.337
2.320
2.296
CN
1.00
3.07
2.02
1.07
2.01
6.08
6.06
f1 (ppm)

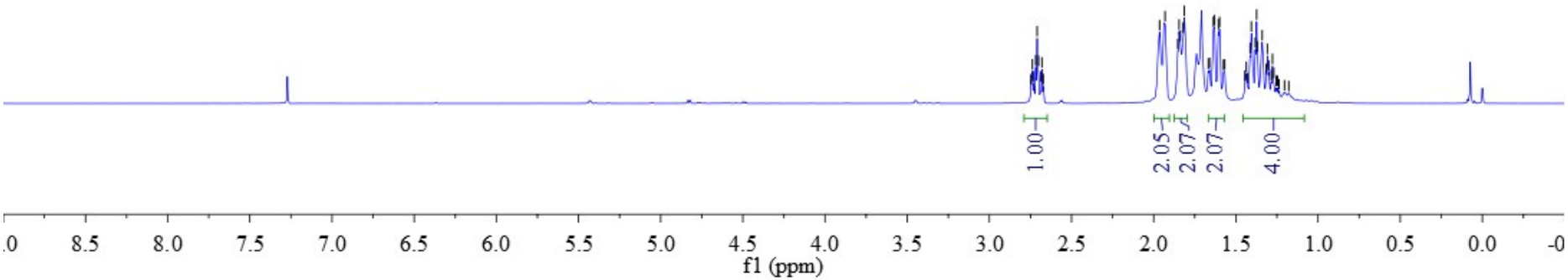
3s

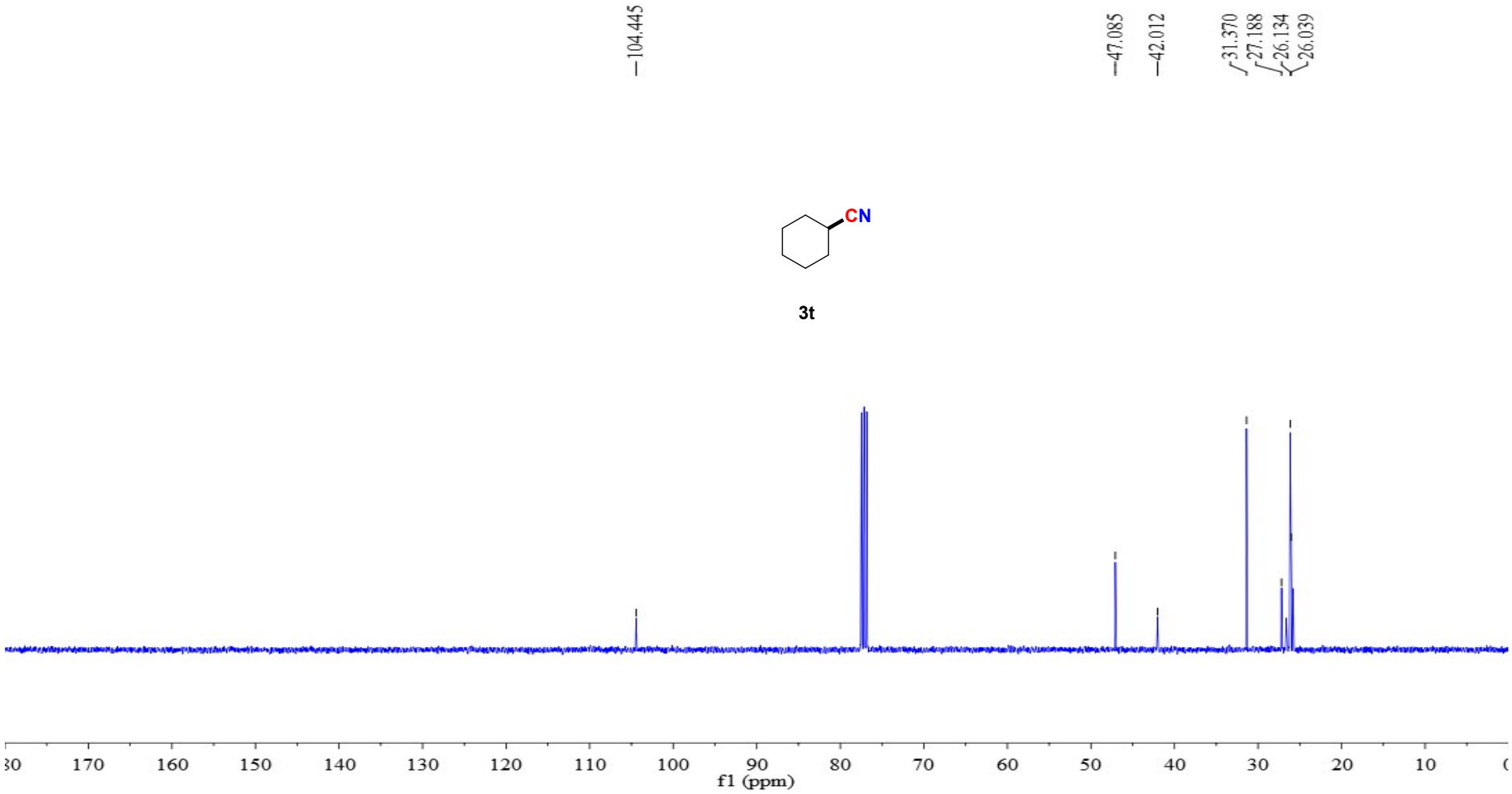

138.788
138.216
136.711
135.645
129.820
129.056
127.034
125.261
120.766
42.445
40.067
21.342
CN
3s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

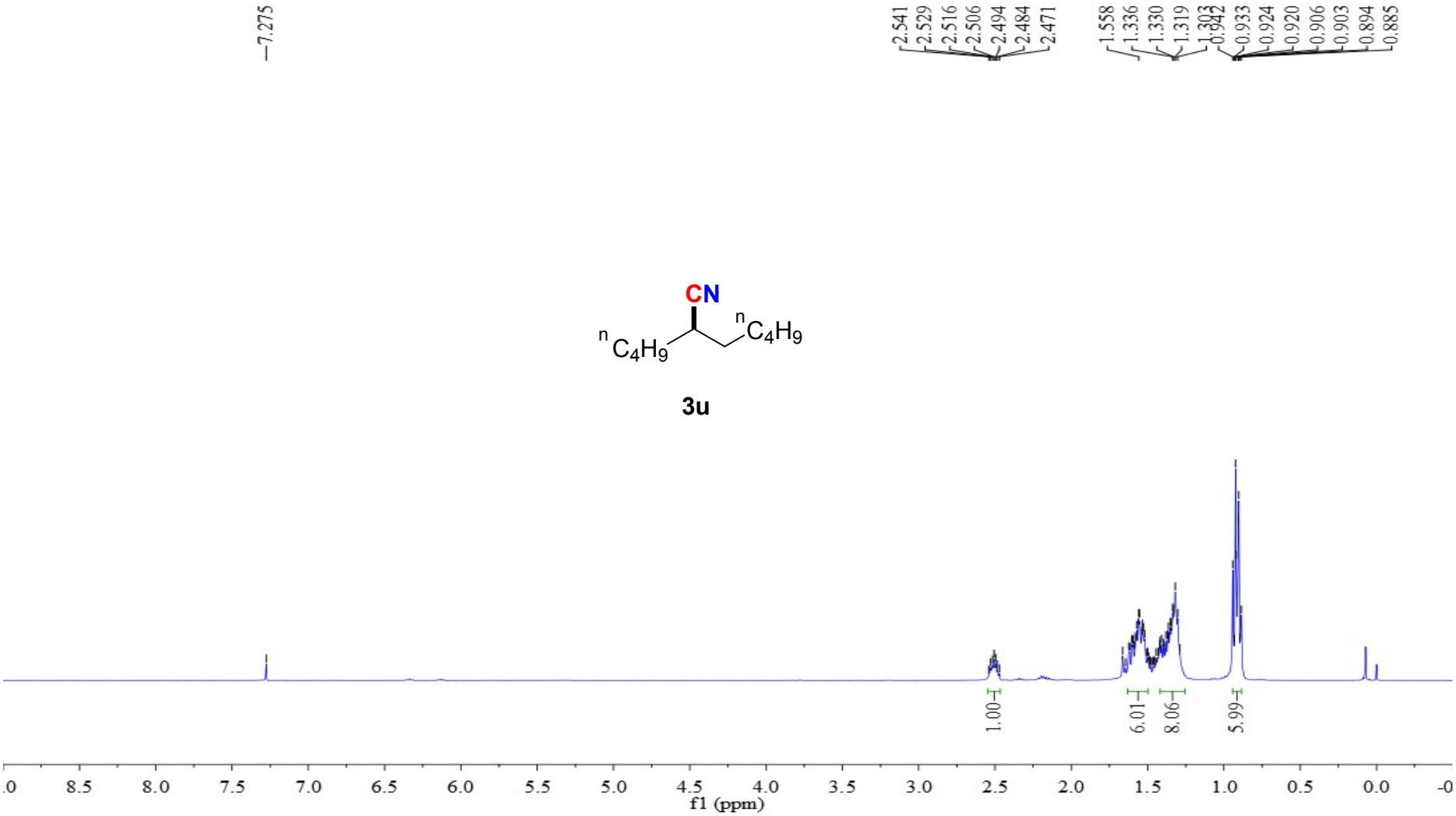

2.747
2.739
2.730
2.718
2.709
2.701
2.689
2.680
2.672
1.964
1.931
1.853
1.846
1.838
1.821
1.813
1.637
1.630
1.606
1.599
1.414
1.406
1.382
1.374
1.368


CN

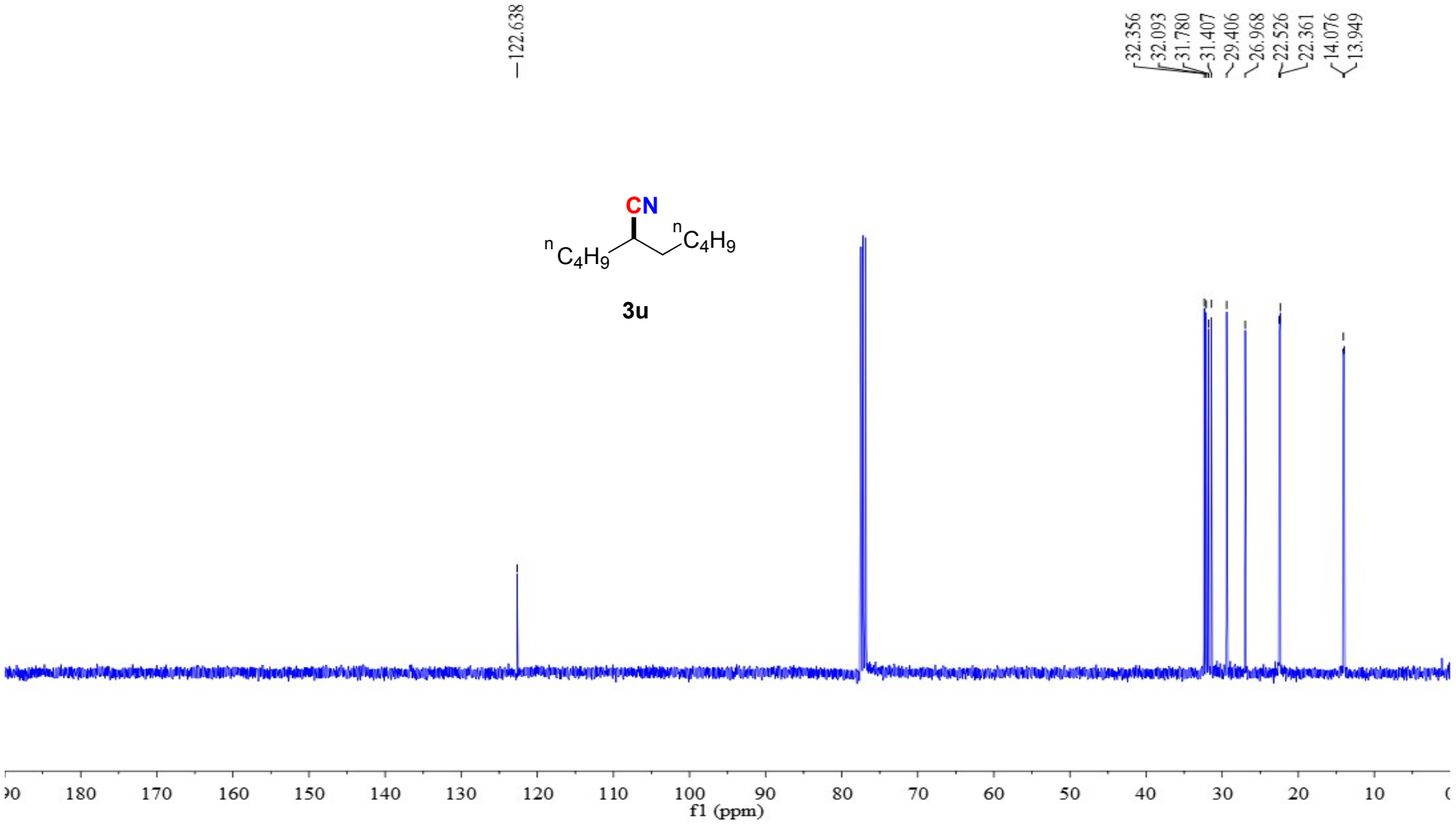
3t

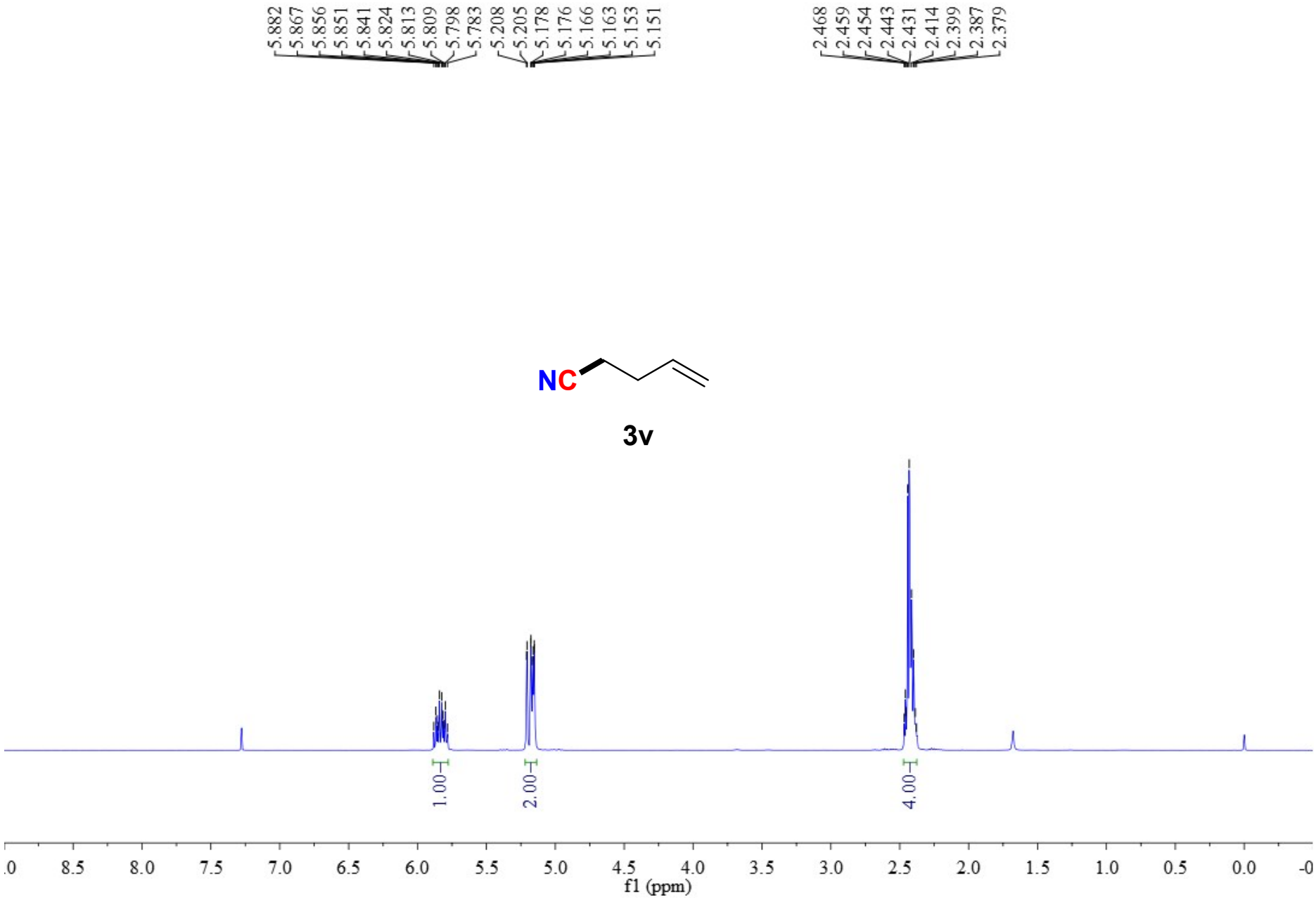

1.00
2.05
2.07
2.07
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


104.445
47.085
42.012
31.370
27.188
26.134
26.039
CN
3t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

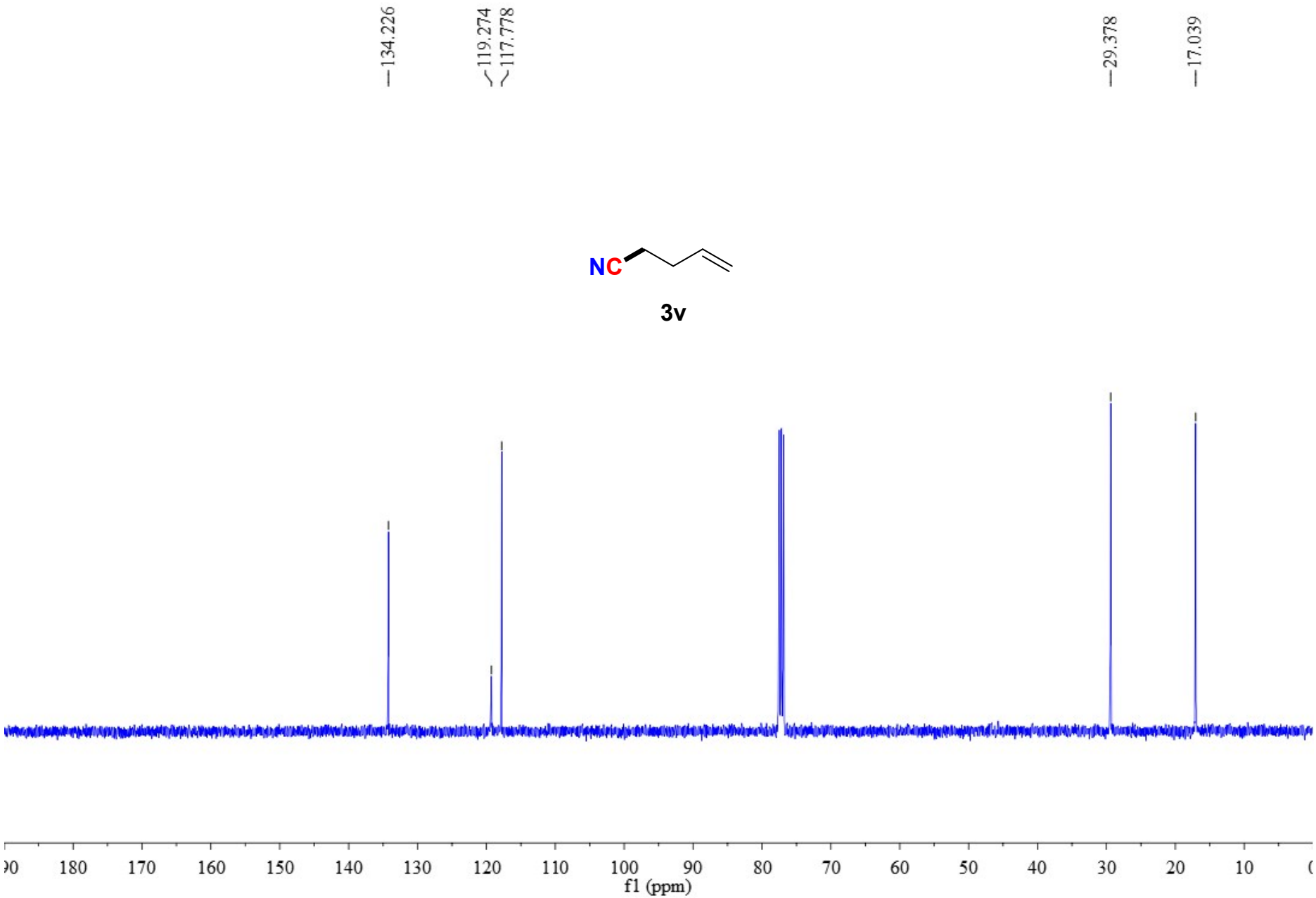

7.275
2.541
2.529
2.516
2.506
2.494
2.484
2.471
1.558
1.336
1.330
1.319
1.303
0.942
0.933
0.924
0.920
0.906
0.903
0.894
0.885
CN
nC4H9
nC4H9
1.00
6.01
8.06
5.99
f1 (ppm)

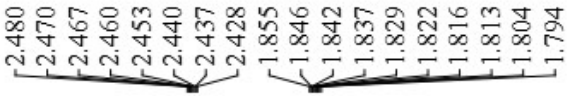
3u

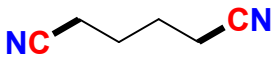

122.638
32.356
32.093
31.780
31.407
29.406
26.968
22.526
22.361
14.076
13.949
CN
nC4H9
nC4H9
3u
f1 (ppm)


5.882
5.867
5.856
5.851
5.841
5.824
5.813
5.809
5.798
5.783
5.208
5.205
5.178
5.176
5.166
5.163
5.153
5.151
2.468
2.459
2.454
2.443
2.431
2.414
2.399
2.387
2.379
NC
1.00
2.00
4.00
f1 (ppm)

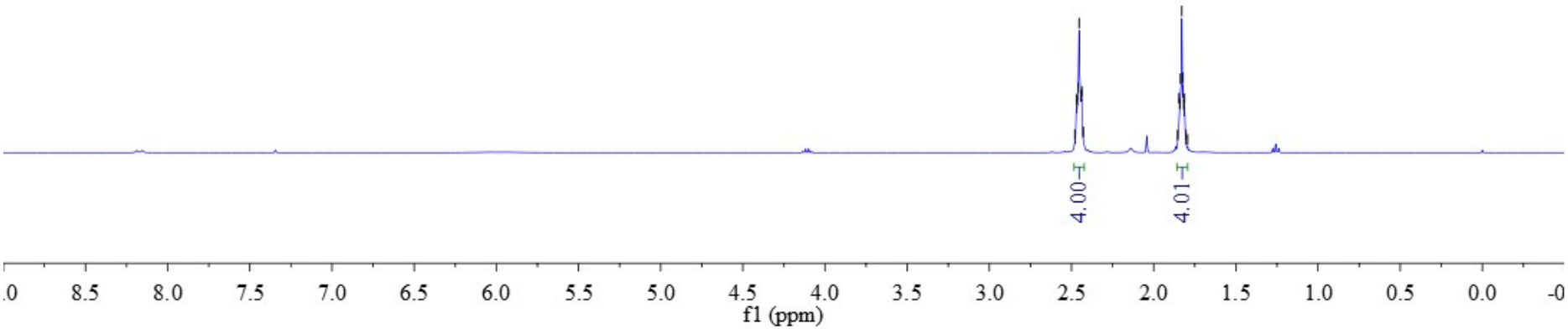
3v

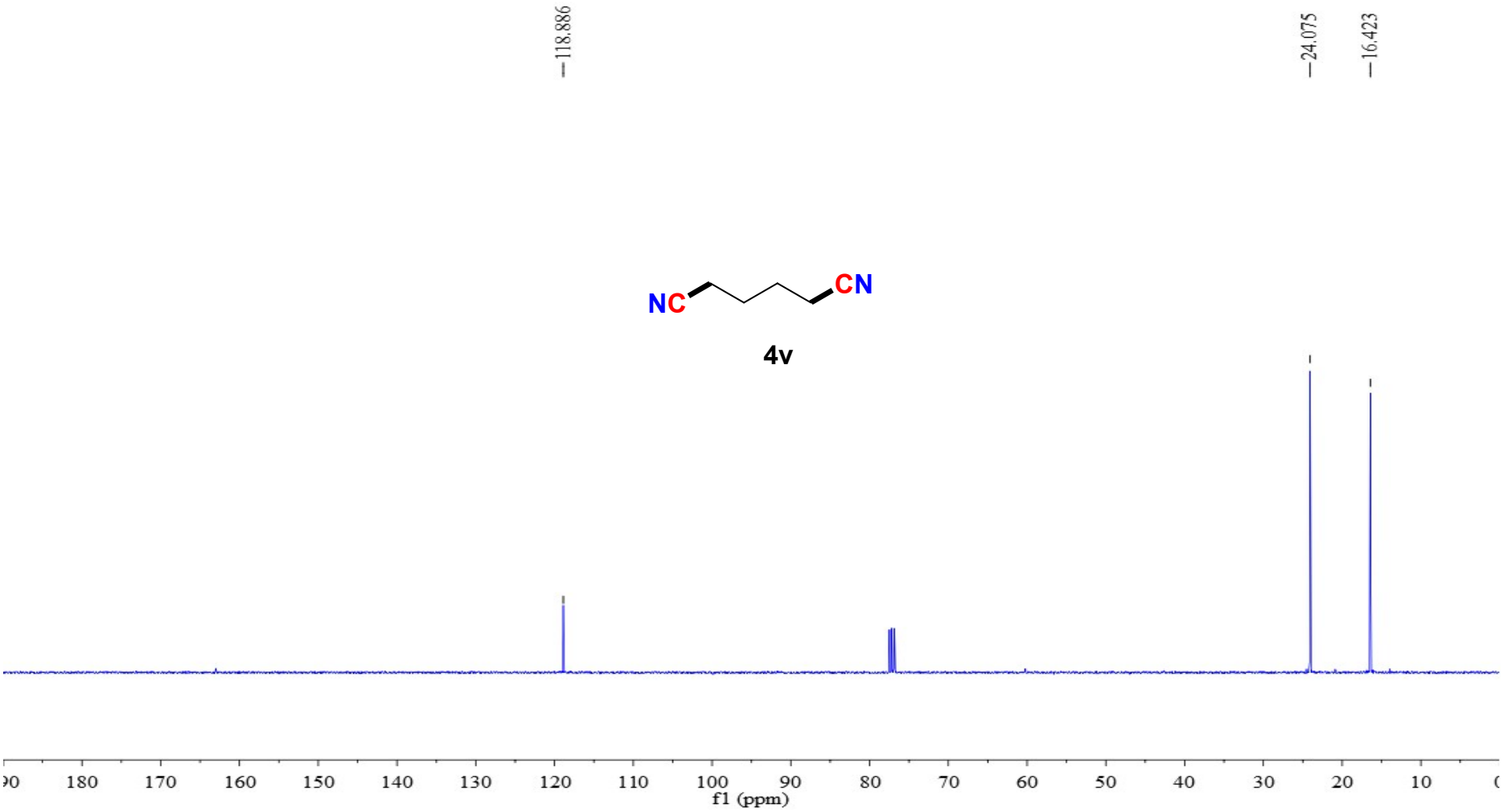

134.226
119.274
117.778
29.378
17.039
NC
3v
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

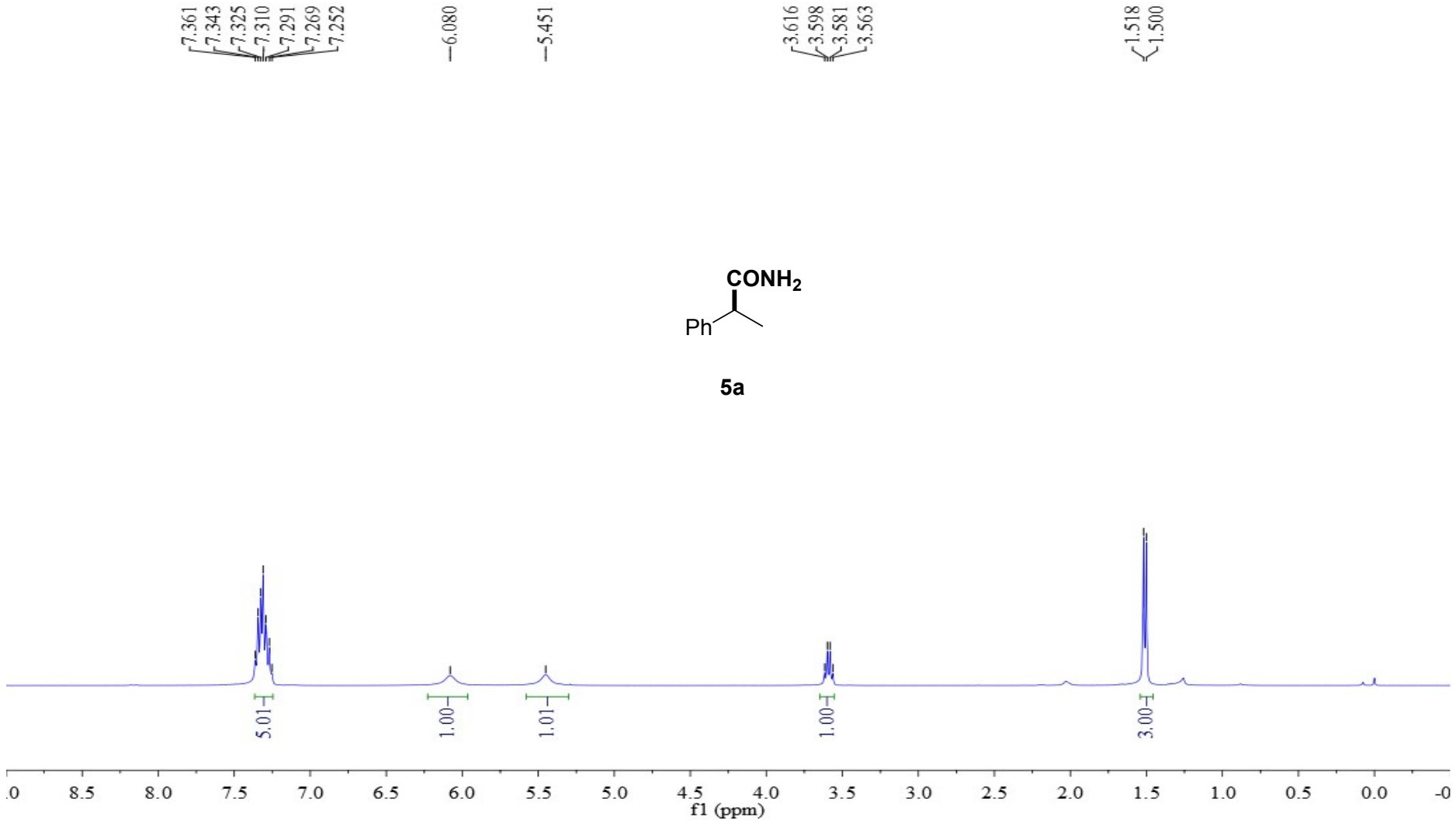

2.480
2.470
2.467
2.460
2.453
2.440
2.437
2.428
1.855
1.846
1.842
1.837
1.829
1.822
1.816
1.813
1.804
1.794


NC
CN

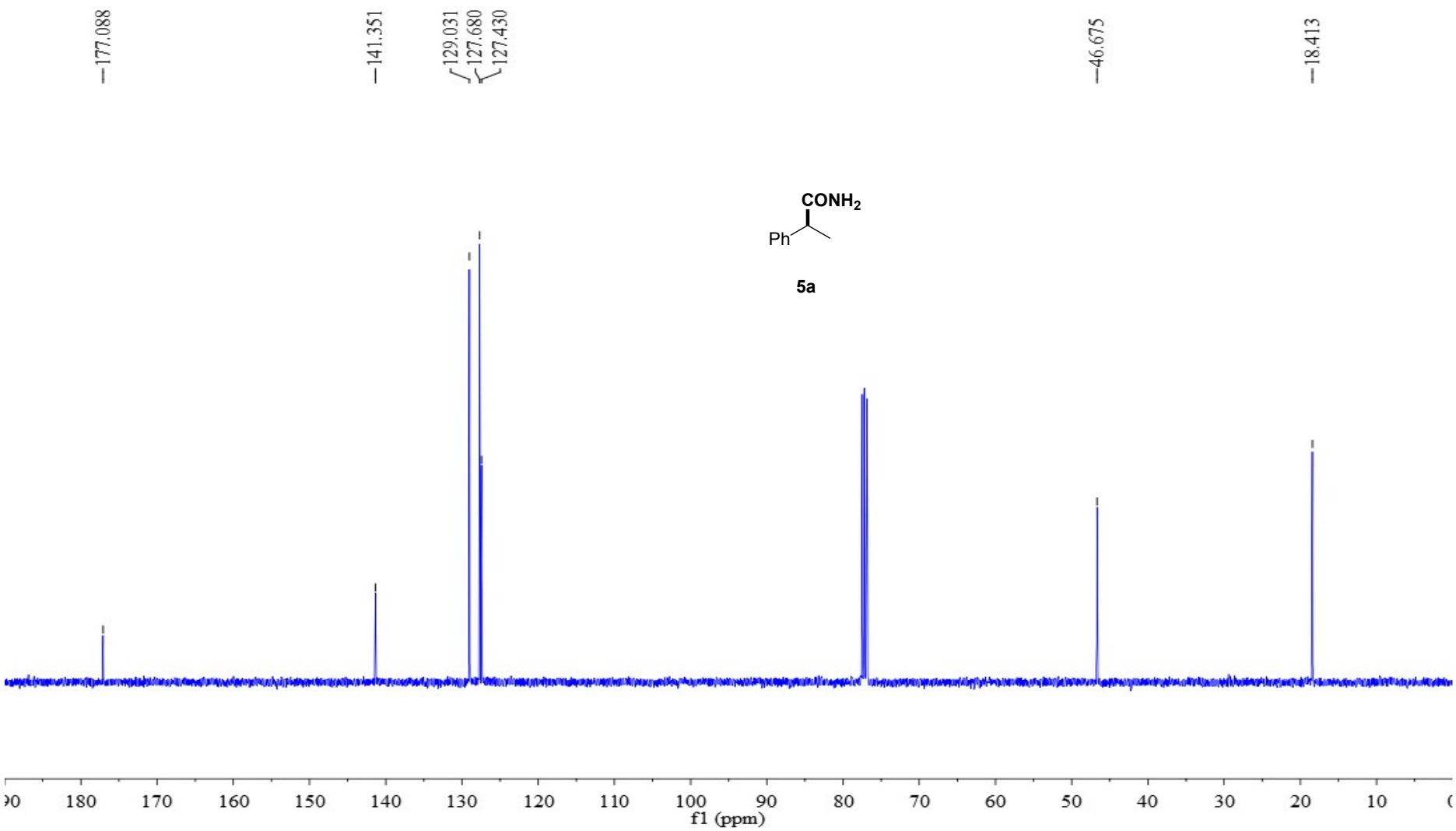
4v


4.00
4.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


118.886
24.075
16.423
NC
CN
4v
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.361
7.343
7.325
7.310
7.291
7.269
7.252
6.080
5.451
3.616
3.598
3.581
3.563
1.518
1.500
CONH2
Ph
5.01
1.00
1.01
1.00
3.00
f1 (ppm)

5a


177.088
141.351
129.031
127.680
127.430
46.675
18.413
CONH2
Ph
5a
f1 (ppm)