Electronic Supplementary Information

A Novel OxidativeTransformation of Alcohols to Nitriles: An Efficient Utility of Azide as a Nitrogen Source

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Contents

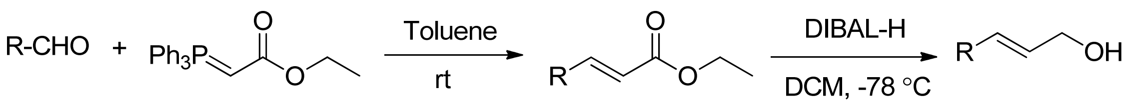
General experimental

NMR spectra were recorded in $CDCl_3$, Tetramethylsilane (TMS; δ = 0.00 ppm) served as internal standards for ^{1}H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$: δ = 77.00 ppm) was used as internal standards for ^{13}C NMR. Column chromatography were conducted on silica gel 230-400 mesh or 100-200 mesh (Merck). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Note: ***Although we have not encountered disastrous results during our experiments, while using azides proper safety precautions should be followed!!!***

Starting material preparation:

The starting materials, cinnamyl alcohols were prepared from the corresponding aldehydes using general procedure shown in the following scheme and spectral data are in agreement with the literature.



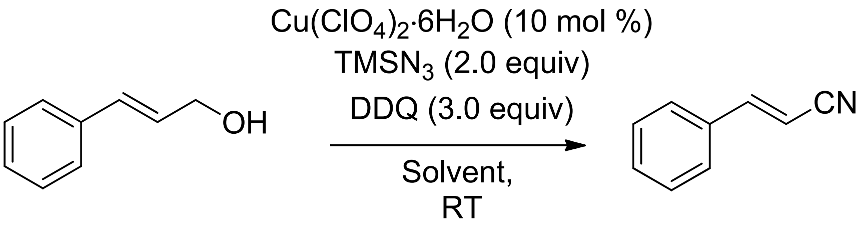
Benzylic alcohols were prepared from the corresponding aldehydes using sodium borohydride reduction and spectral data are in agreement with the literature.

Typical experimental procedure: synthesis of aryl and alkenyl nitriles from benzyl and allyl alcohols :

Trimethylsilylazide (0.75 mmol) was added dropwise to a well-stirred mixture of alcohol (0.5 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (1.1 mmol) in 1,2-dichloroethane (2 ml) and stirred at 60 °C till the reaction is completed (monitored by TLC). After removal of the solvent under reduced pressure, the reaction mixture was cooled to room temperature, the residue was dissolved in small amount of CH_2Cl_2 (2 mL), passed through alumina, and purified by column chromatography on silica gel.

Optimization studies: Screening of different solvents

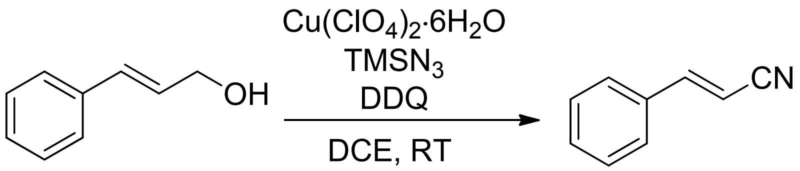
SI Table 1. Solvent Screening



Entry	Solvent	Yield (%)[a]
1	H_2O	nd
2	MeOH	nd
3	THF	55
4	Toluene	95
5	CH_3CN	98
6	DCE	100

[a] Yields were determined by ^{1}H NMR analyses w.r.t starting material. nd = not detected (<1%).

SI Table 2. Screening for amount of $Cu(ClO_4)_2{\cdot}6H_2O$,$TMSN_3$ and DDQ



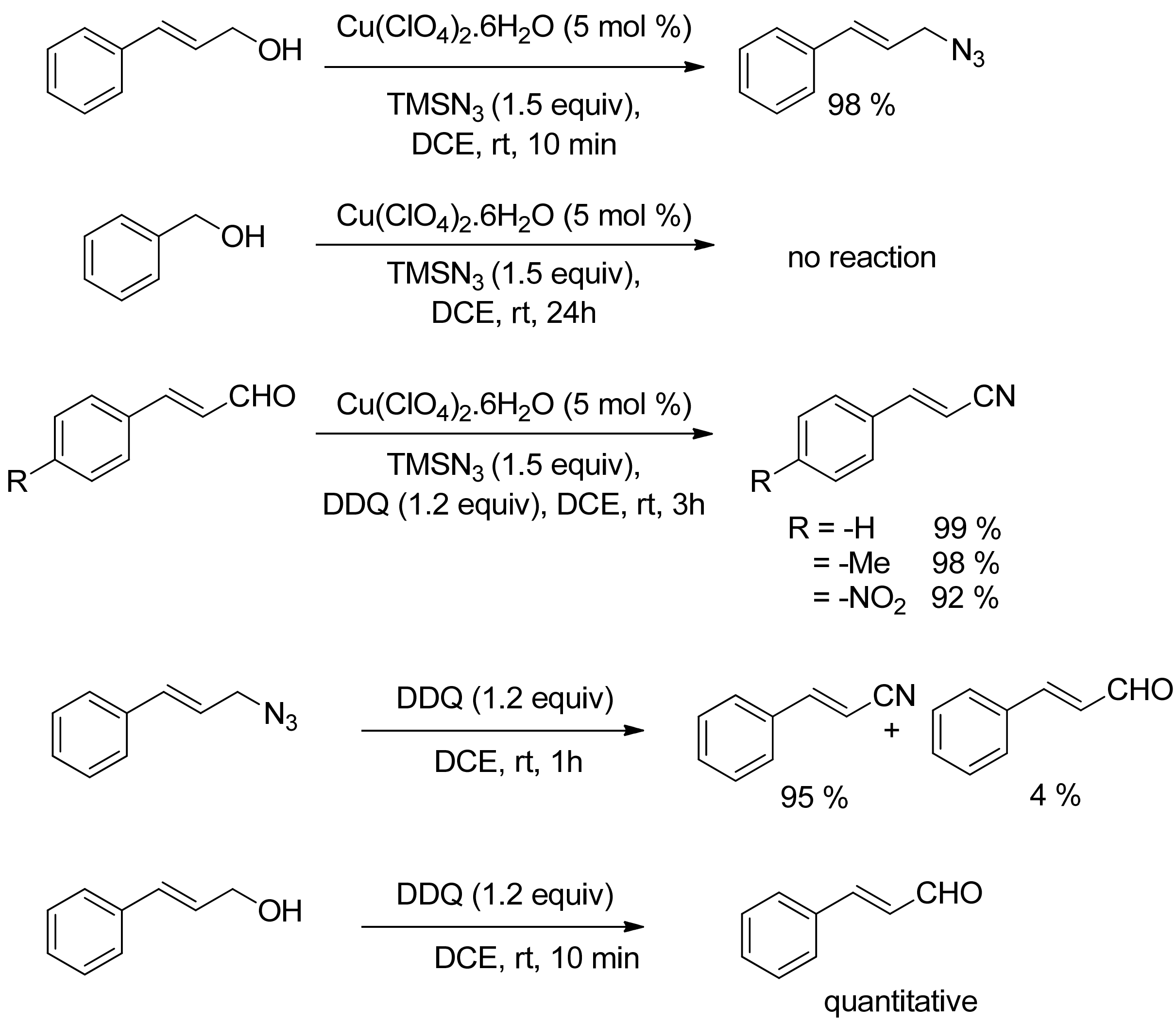
Entry	$Cu(ClO_4)_2{\cdot}6H_2O$ (equiv)	$TMSN_3$ (equiv)	DDQ (equiv)	Yield (%)[a]
1	0.05	2.0	3.0	98
2	0.01	2.0	3.0	82
3	0.05	1.5	3.0	98
4	0.05	1.1	3.0	78
5	0.05	1.5	2.2	98

[a] Yields were determined by ^{1}H NMR analyses with respect to starting material.

Electronic Supplementary Material (ESI) for Chemical Communications

Control Experiments:

SI Scheme 1. Control experiments

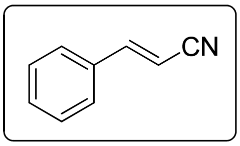


Mechanistic studies:

It is known that cinnamyl azide is oxidized in the presence of DDQ to the corresponding nitrile.[1] Similarly, benzaldehyde is known to react with $TMSN_3$ to form corresponding α-silyloxy azido derivatives in the presence of Lewis acids.[2] We have also observed that aldehyde and azides were formed as by-products in few control experiments (Table 1 and 2). In light of these observations, we carried out few more control experiments (ESI Scheme 1). The reaction of cinnamyl alcohol with $TMSN_3$ in the presence of $Cu(ClO_4)_2{\cdot}6H_2O$ (5 mol %) furnished the corresponding azide in almost quantitative yield. However, under the similar reaction condition, benzyl alcohol failed to furnish the corresponding azide even under forcing conditions. Further, it was observed that the reaction of cinnamaldehyde with $Cu(ClO_4)_2{\cdot}6H_2O$ (5 mol %), $TMSN_3$ and DDQ furnished the corresponding cinnamonitrile in almost quantitative yield. These experiments indicate that the benzyl alcohol and cinnamyl alcohol are following different route to furnish their corresponding nitriles.

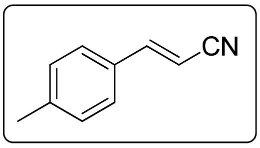
Characterization data for Nitriles:

(E)-Cinnamonitrile (2a):



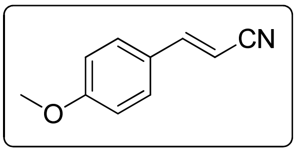
Colorless liquid; Yield = 98 %; R_f (15% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (Neat, cm^{-1}): 2218; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.36 (m, 6H), 5.87 (d, J = 16.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.5, 133.4, 131.1, 129.0, 127.3, 118.1, 96.2; **HRESI-MS** *(m/z)*: Calculated for C_9H_7N (M+H): 130.0657, found (M+H): 130.0656.

(E)-4-Methylcinnamonitrile (2b):



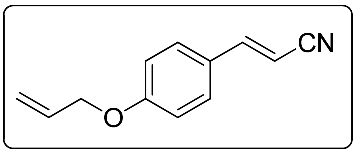
White solid; Yield = 92 %; ***mp***: 72 - 73 °C (lit.[3] 72 - 73 °C); R_f (15% EtOAc/Hexane) 0.75; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2215; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.33 (m, 3H), 7.20 (d, J = 8 Hz, 2H), 5.81 (d, J = 16.8 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.5, 141.8, 130.8, 129.8, 127.3, 118.4, 95.0, 21.5; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_9N$ (M+Na): 166.0633, found (M+Na): 166.0635.

(E)-4-Methoxycinnamonitrile (2c):



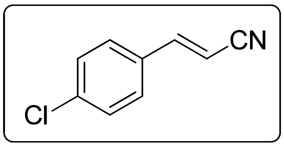
White solid; Yield = 86 %; ***mp***: 63 - 65 °C (lit.[4] 62 - 65 °C); R_f (25% EtOAc/Hexane) 0.65; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2214; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8 Hz, 2H), 7.32 (d, *J* = 16.8 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.71 (d, *J* = 16.4 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.0, 150.0, 129.0, 126.3, 118.7, 114.4, 93.3, 55.4; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_9NO$ (M+H): 160.0762, found (M+H): 160.0765.

(E)-4-Allyloxycinnamonitrile (2d):



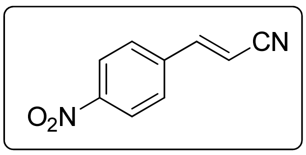
White solid; Yield = 73%; ***mp***: 50 - 52 °C; R_f (25% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2211; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.30 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.09-5.99 (m, 1H), 5.71 (d, *J* = 16.8 Hz, 1H), 5.44-5.30 (dd, 2H), 4.58-4.56 (d, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.1, 150.0, 132.5, 129.0, 126.4, 118.7, 118.2, 115.2, 93.4, 68.9; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{11}NO$ (M+Na): 208.0738, found (M+Na): 208.0736.

(E)-4-Chlorocinnamonitrile (2e):



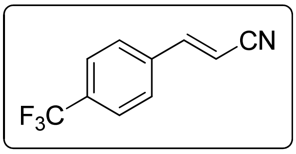
White solid; Yield = 97 %; ***mp***: 78 - 80 °C (lit.[5] 83 - 84 °C); R_f (25% EtOAc/Hexane) 0.8; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2225; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.33 (m, 5H), 5.86 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.1, 137.2, 131.9, 129.4, 128.5, 117.8, 96.9; **HRESI-MS** *(m/z)*: Calculated for C_9H_6ClN (M+Na): 186.0086, found (M+Na): 186.0087.

(E)-4-Nitrocinnamonitrile (2f):



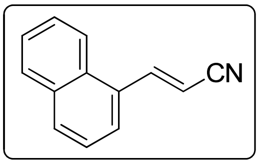
Yellow Solid; Yield = 83 %; ***mp:*** 198 - 200 °C (lit.[6] 200 - 201 °C); R_f (25% EtOAc/Hexane) 0.56; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2217; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.47 (d, *J* = 16.8 Hz, 1H), 6.06 (d, J = 16.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.0, 147.7, 139.1, 128.1, 124.4, 116.9, 101.0; Anal.Calcd for $C_9H_6N_2O_2$ C, 62.07; H, 3.47; N, 16.09; Found: C, 62.25; H, 4.06; N, 15.12.

(E)-3-(4-(Trifluoromethyl)phenyl)-2-propenenitrile (2g):



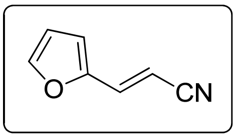
White solid; Yield = 90%; ***mp:*** 92 – 94 °C; R_f (15% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2226; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8Hz, 2H), 7.44 (d, *J* = 16.8 Hz, 1H), 6.00 (d, *J* = 16.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.7, 136.7, 132.7 (q, *J* = 32.7 Hz), 127.6, 126.1 (q, *J* = 3.3 Hz), 123.6 (q, *J* = 270.7 Hz), 117.3, 99.2; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_6F_3N$ (M+H): 198.0531, found (M+H): 198.0530.

(E)-1-Napthylcinnamonitrile (2h):



White solid; Yield = 72 %; ***mp:*** 73 - 76 °C (lit.[7] 72 - 75 °C); R_f (15% EtOAc/Hexane) 0.45; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2217; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 16 Hz, 1H), 8.03-7.87 (m, 3H), 7.65-7.46 (m, 4H), 5.95 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.8, 133.6, 131.5, 130.8, 130.6, 128.8, 127.3, 126.5, 125.3, 124.6, 122.7, 118.2, 98.7; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_9N$ (M+Na): 202.0633, found (M+Na): 202.0631.

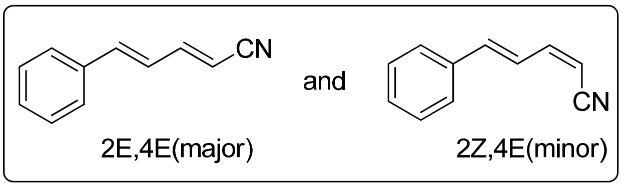
(E)-3-(2-furyl)propenonitrile (2i):



White solid; Yield = 72 %; ***mp:*** 35 - 36 °C (lit.[8] 36 °C); R_f (25% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2226; **^{1}H NMR** (400 MHz, $CDCl_3$):

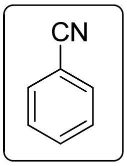
δ 7.49 (s, 1H), 7.11 (d, *J* = 16.4 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 6.50 (dd, J_1 = 1.6 Hz, J_2 = 3.2 Hz, 1H), 5.76 (d, *J* = 16.4 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 149.8, 145.4, 136.1, 118.2, 115.4, 112.6, 93.4; **HRESI-MS** *(m/z)*: Calculated for C_7H_5NO (M+H):120.0449, found (M+H): 120.0449.

2E,4E/ 2Z,4E5 - Phenylpenta-2,4-dienenitrile (2j): 2E,4E : 2Z,4E = 8.9 : 1.1



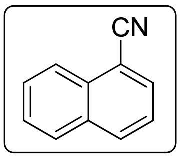
Yellow oil; Yield = 60 %; R_f (15% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure. **IR** (Neat, cm^{-1}): 2217; **2E,4E(major isomer):** ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.52-7.35 (m, 5H), 7.18-7.12 (m, 1H), 6.91-6.78 (m, 2H), 5.44 (d, *J* = 16 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 150.3, 141.4, 135.2, 129.6, 128.9, 127.6, 125.4, 118.3, 98.2; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_9N$ (M+Na):178.0633, found (M+Na):178.0632.

Benzonitrile[1] (6a):



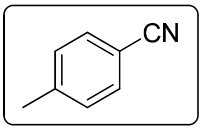
Colorless liquid; Yield = 80 %, *Rf* (10 % EtOAc/Hexane) 0.80; Prepared as shown in general experimental procedure. **IR** (Neat, cm^{-1}): 2225; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.59 (m, 3H), 7.49-7.45 (m, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 132.7, 132.0, 129.0, 118.8, 112.3.

1-Naphthonitrile (6b):



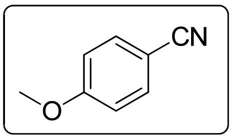
White solid; Yield = 72 %; ***mp***: 55 - 57 °C (lit.[9] 56 - 58 °C); R_f (10 % EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}); 2222; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.93 - 7.90 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 133.2, 132.9, 132.6, 132.3, 128.6, 128.5, 127.5, 125.1, 124.9, 117.8, 110.1; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_7N$ (M+): 153.0578, found (M+): 153.0578.

4-Methylbenzonitrile (6c):



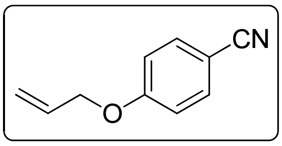
White solid; Yield = 78 %; ***mp***: 27 – 29 °C (lit.[10] 26 – 28 °C); R_f (15 % EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}); 2228; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.6, 132.0, 129.8, 119.1, 109.2, 21.8; **HRESI-MS** *(m/z)*: Calculated for C_8H_7N (M+H): 118.0657, found (M+H): 118.0649

4-Methoxybenzonitrile (6d):



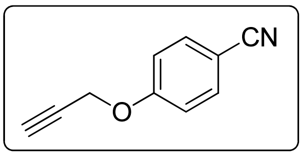
White solid; Yield = 82 %, ***mp***: 55 – 57 °C (lit.[1] 56 - 57 ºC); *Rf* (10 % EtOAc/Hexane) 0.40; Prepared as shown in general experimental procedure. **IR** (KBr, cm-1): 2222; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8Hz, 2H), 3.86 (s, 3H); **^{13} C NMR** (100 MHz, $CDCl_3$): δ 162.8, 133.9, 119.2, 114.7, 103.9, 55.5; **HRESI-MS** *(m/z)*: Calculated for C_8H_7NO (M + Na): 156.0425, found (M + Na): 156.0422.

4-(allyloxy)benzonitrile (6e):



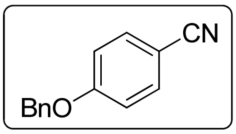
Brown solid; Yield = 82 %; ***mp***: 41 - 43 °C (lit.[11] 43 - 44 °C); R_f (10% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2218 ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.08 – 5.98 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 5.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.8, 133.9, 132.0, 119.1, 118.4, 115.4, 104.0, 68.9; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_9NO$ (M+Na): 182.0582, found (M+Na): 182.0583.

4-(2-propynyloxy)benzonitrile (6f):



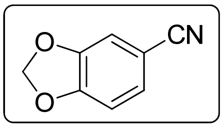
White solid; Yield = 74 %; ***mp***: 109 - 111 °C (lit.[12] 113 - 114 °C); R_f (15% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2223; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.75 (d, *J* = 2.4 Hz, 2H), 2.57 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.6, 133.9, 118.9, 115.6, 104.9, 76.7, 76.5, 55.9; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_7NO$ (M+Na): 180.0425, found (M+Na): 180.0422.

4-(Benzyloxy)benzonitrile (6g) :



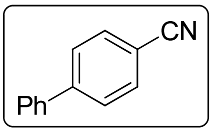
White solid; Yield = 96 %; ***mp***: 92 - 94 °C (lit.[13a] 91 - 94 °C); R_f (10% EtOAc/Hexane) 0.45; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2217; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.41 - 7.35 (m, 5H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.11 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.9, 135.6, 134.0, 128.7, 128.4, 127.4, 119.1, 115.5, 104.2, 70.2; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{11}NO$ (M+Na): 232.0738, found (M+Na): 232.0735.

Piperonylnitrile (6h):



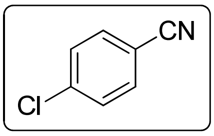
White solid; Yield = 82 %; ***mp***: 83 – 85 °C (lit.[11] 90 - 93 °C); R_f (15 % EtOAc/Hexane) 0.8; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2223; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8 Hz, 1H), 7.03 (s, 1H), 6.86 (d, *J* = 8 Hz, 1H), 6.07 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.5, 148.0, 128.2, 118.8, 111.3, 109.1, 104.9, 102.2; **HRESI-MS** *(m/z)*: Calculated for $C_8H_5NO_2$ (M+Na): 170.0218, found (M+Na): 170.0218.

4-(Phenyl)benzonitrile (6i):



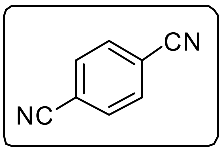
White solid; Yield = 79 %; ***mp***: 82 - 83 °C (lit.[14] 83 - 84 °C); R_f (15% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2225; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73-7.67 (m, 4H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.50-7.42 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.7, 127.2, 118.9, 110.8; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_9N$ (M+Na): 202.0633, found (M+Na): 202.0630.

4-chlorobenzonitrile (6j):



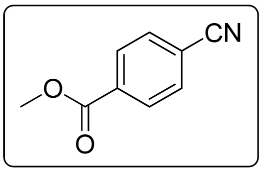
White solid; Yield = 98 %; ***mp***: 91 – 92 °C (lit.[15a] 90 - 92 °C); R_f (15% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2226 ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.5, 133.3, 129.6, 117.9, 110.7; Anal.Calcd for C_7H_4ClN C, 61.12; H, 2.93; N,10.18; Found: C, 61.26; H, 3.28; N,10.22.

Terephthalonitrile1 (6k):



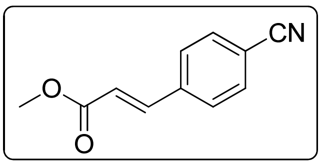
White solid; Yield = 77 %; ***mp***: 225 – 227 °C (lit.[9] 226 - 228 °C); R_f (15% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2233 ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.7, 116.9, 116.6; **MS** *(m/z)*: 128(M^+).

4-carbomethoxybenzonitrile (6l):



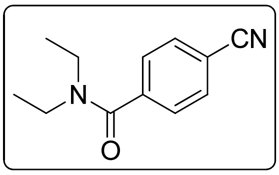
White solid; Yield = 82 %; ***mp***: 67 - 68 °C(lit.[15c] 67 - 69 °C); R_f (15% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2233; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.4, 133.8, 132.2, 130.0, 117.9, 116.3, 52.7; **HRESI-MS** *(m/z)*: Calculated for $C_9H_7NO_2$ (M+H): 162.0555, found (M+H): 162.0552.

(E)-methyl 3-(4-cyanophenyl)acrylate (6m):



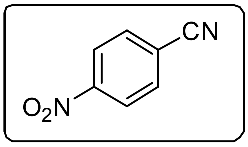
White solid; Yield = 99 %; ***mp***: 111 - 114 °C (lit.[16] 118 - 121 °C); R_f (25% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2225; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 – 7.60 (m, 5H), 6.52 (d, J = 16 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 142.4, 138.6, 132.6, 128.4, 121.3, 118.3, 113.4, 52.0; Anal.Calcd for $C_{11}H_9NO_2$ C, 70.58; H, 4.85; N, 7.48; Found: C, 71.80; H, 5.58; N, 6.84.

4-cyano-N,N-diethylbenzamide (6n):



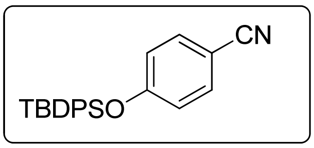
White solid; Yield = 73 %; ***mp***: 77 - 78 °C (lit.[15b] 79 - 80 °C); R_f (50 % EtOAc/Hexane) 0.35; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2231; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8 Hz, 2H), 7.48 (d, J = 8Hz, 2H), 3.55 (br, 2H), 3.20 (br, 2H), 1.26 (br, 3H), 1.11 (br, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.2, 141.4, 132.4, 127.0, 118.1, 113.0, 43.2, 39.4, 14.2, 12.8; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{14}N_2O$ (M+Na): 225.1004 found (M+Na): 225.1003.

4-Nitrobenzonitrile (6o):



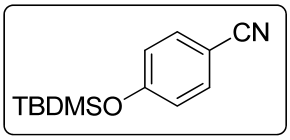
White solid; Yield = 76 %; ***mp***: 148 - 149 °C (lit.[11] 148 - 149 °C); R_f (25% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2222; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (d, J = 8.96 Hz, 2H), 7.90 (d, J = 8.92 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.0, 133.4, 124.2, 118.3, 116.8; Anal.Calcd for $C_7H_4N_2O_2$ C, 56.76; H, 2.72; N, 18.91; Found: C, 56.67; H, 3.26; N, 19.14.

4-((tert-butyldiphenylsilyl)oxy)benzonitrile (6p):



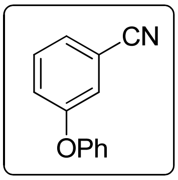
White solid; Yield = 98 %; ***mp***: 100 – 103 °C (lit.[13b] 106 -108 °C); R_f (15% EtOAc/Hexane) 0.55; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2226; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 – 7.66 (m, 4H), 7.47 - 7.37 (m, 8H), 6.80 – 6.78 (m, 2H), 1.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.4, 135.3, 133.8, 131.6, 130.3, 128.0, 120.6, 119.1, 104.4, 26.3, 19.4; **HRESI-MS** *(m/z)*: Calculated for $C_{23}H_{23}NOSi$ (M+Na): 380.1447, found (M+Na): 380.1446.

4-((tert-butyldimethylsilyl)oxy)benzonitrile (6q):



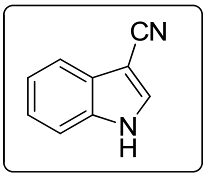
White solid; Yield = 90 %; ***mp***: 56 - 58 °C; R_f (10% EtOAc/Hexane) 0.8; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2227; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 0.98 (s, 9H), 0.23 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.6, 133.9, 120.8, 119.2, 104.5, 25.4, 18.1, -04.5; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{19}NOSi$ (M+Na): 256.1134, found (M+Na): 256.1130.

3-Cyanophenyl(phenyl) ether (6r):



Light yellow oil; Yield = 95 %; R_f (15 % EtOAc/Hexane) 0.75; Prepared as shown in general experimental procedure. **IR** (Neat, cm^{-1}): 2233 ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 - 7.34 (m, 4H), 7.25 – 7.18 (m, 3h), 7.03 (d, *J* = 8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.1, 155.4, 130.6, 130.1, 126.3, 124.7, 122.7, 121.0, 119.7, 118.2, 113.5; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_9NO$ (M+Na): 218.0582, found (M+Na): 218.0586.

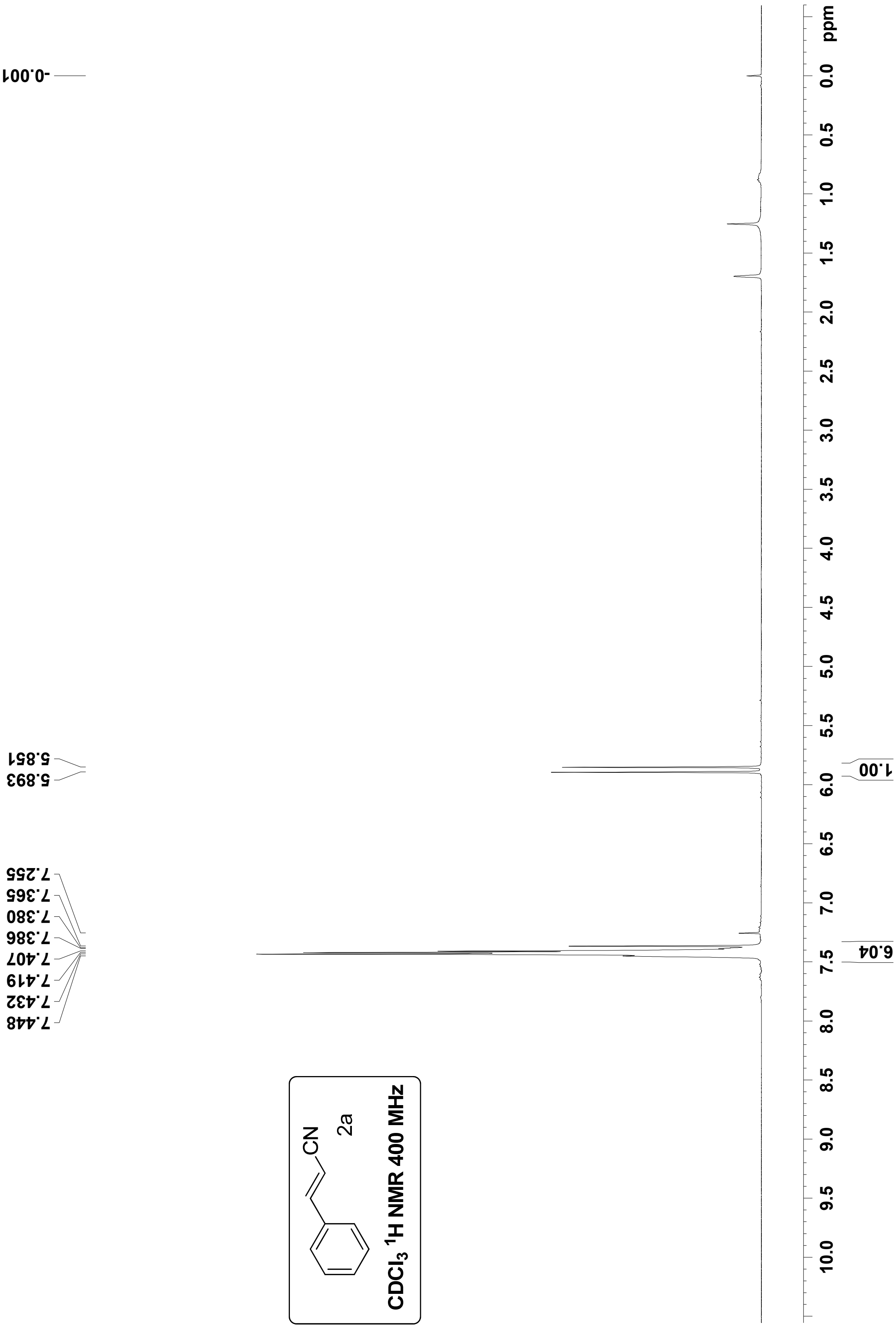
3-Cyanoindole (6s):



White solid; Yield = 72 %; ***mp***: 174 - 176 °C (lit.[17] 175 - 177 °C); R_f (20 % EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. **IR** (KBr, cm^{-1}): 2222; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.8 (br, 1H), 7.79 - 7.74 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.36 - 7.28 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.8, 131.8, 126.9, 124.3, 122.4, 119.7, 115.8, 112.0, 87.5; **HRESI-MS** *(m/z)*: Calculated for $C_9H_6N_2$ (M+Na): 165.0429, found (M+Na): 165.0428.

References:

1. Zhou, W.; Xu, J.; Zhang, L.; Jiao, N. *Org. Lett.* **2010**, *12*, 2888.
2. Nishiyama, K.; Oba, M.; Watanabe, A. Tetrahedron 1987, 43, 693.
3. L. Wang, H. Li, P. Li, *Tetrahedron,* 2009, **65**, 364.
4. Gokel et al *Tetrahedron Lett.,* 1976, 3495.
5. J. Zheng, Y. Yu, Y. Shen, *Synth. Commun.,* 1990, **20**, 3277.
6. T. Fumagalli, G. Sello, F. Orsini, *Synth. Commun.,* 2009, **39**, 2178.
7. K. Masuda, Y. Ito, M. Horiguchi, H. Fujita, *Tetrahedron,* 2005, **61**, 213.
8. R. Reitz, *Chemische Berichte*, 1956, **89**, 2570.
9. Z. Zhang, L.S. Liebeskind, *Org. Lett.,* 2006, **8**, 4331.
10. (*a*) S. Ushijima, K. Moriyama, H. Togo, *Tetrahedron,* 2011, **67**, 958. (*b*) G. Ishii, K. Moriyama, H. Togo, *Tetrahedron Lett.,* 2011, **52**, 2404.
11. X. L. Wang, K. Wan, C.H. Zhou, *Eur. J. Med. Chem.,* 2010, **45**, 4631.
12. T. Harfenist, *J. Org. Chem*., 1972, **37,** 841.
13. (*a*) H. Wagner, *Pharmazie,* 1975, **30**, 353. (*b*) W. Zhou, L. Zhang, N. Jiao, *Angew. Chem. Int. Ed.,* 2009, **48**, 7094.
14. X. -H. Fan, L. -M. Yang, *Euro. J. Org. Chem.,* 2011, **8**, 1467.
15. (*a*) M. E. Moon, *Tetrahedron Lett*., 2010, **51**, 6769. (*b*) G. Ecanow, *J. Am. Pharm. Asso.,* 1957, **46**, 315. (*c*) Y. Yamamoto, *Adv. Synth. Catal*., 2010, **352,** 478.
16. A. R. Hajipour, K. Karami, G. Tavakoli, *Appl. Organomet. Chem.,* 2010, **24**, 798.
17. B. V. Subba Reddy, Z. Begum, Y. Jayasudhan Reddy, J. S. Yadav, *Tetrahedron Lett.,* 2010, **51**, 3334.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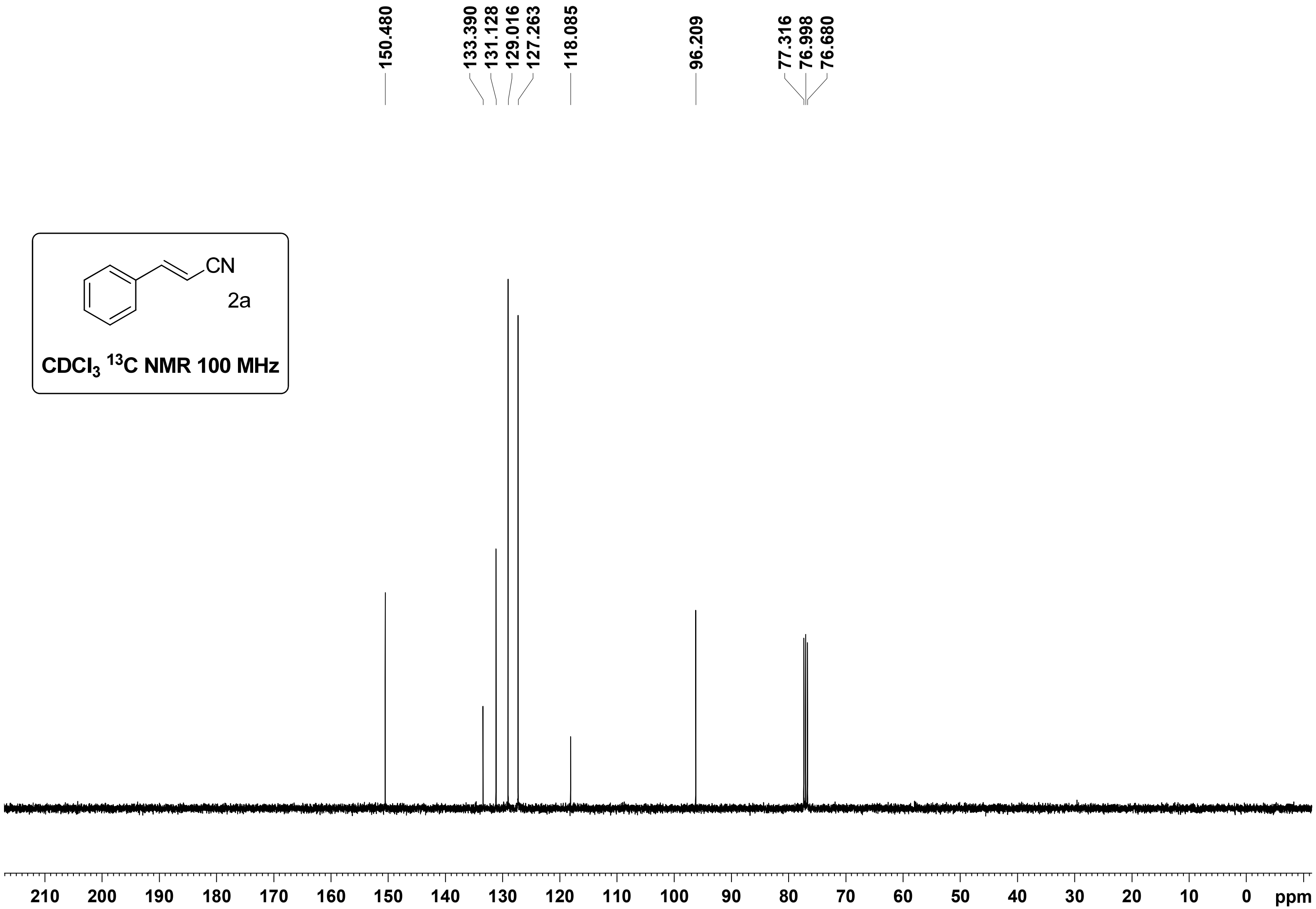
6.04
ppm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200
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140
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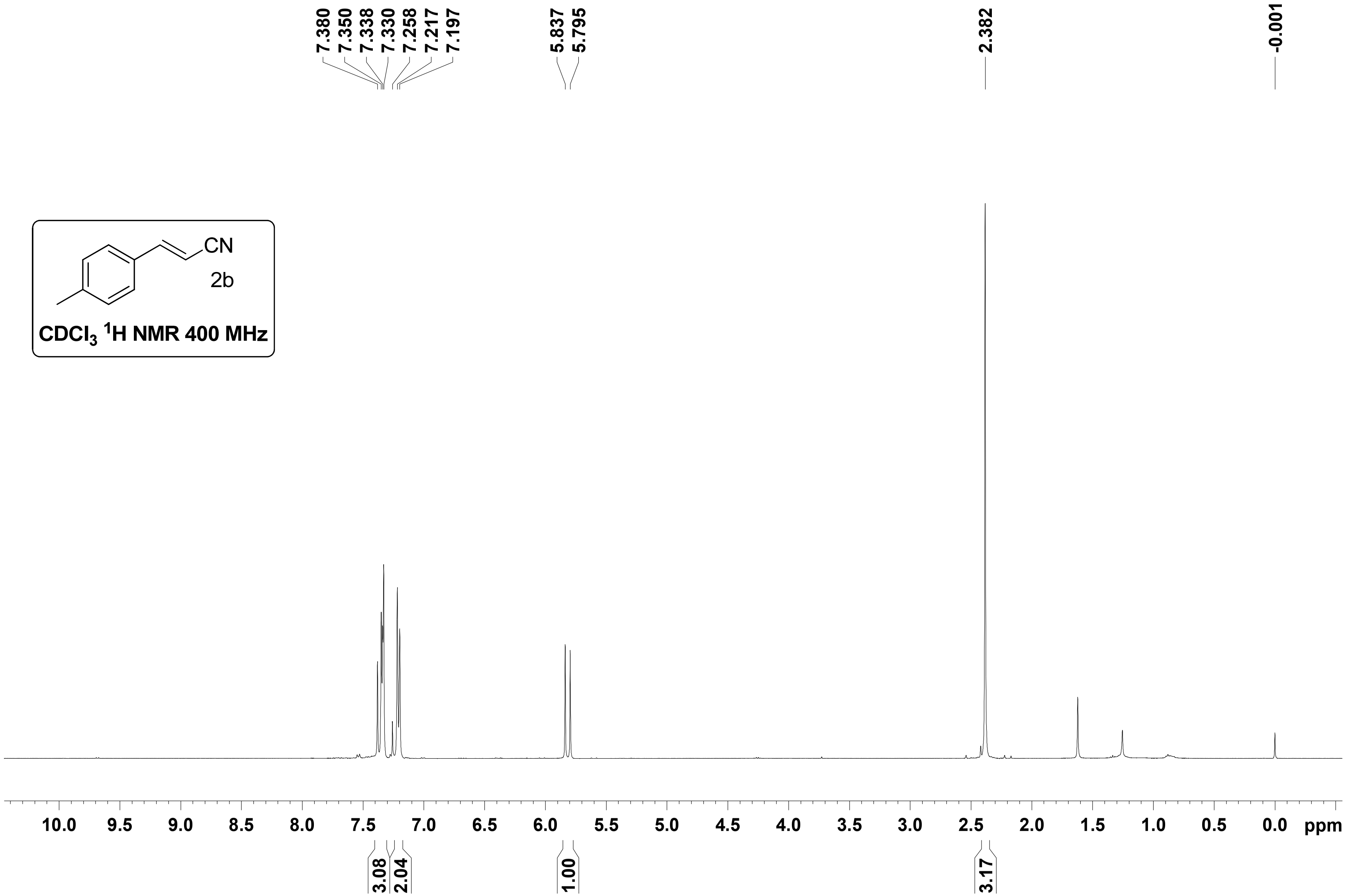
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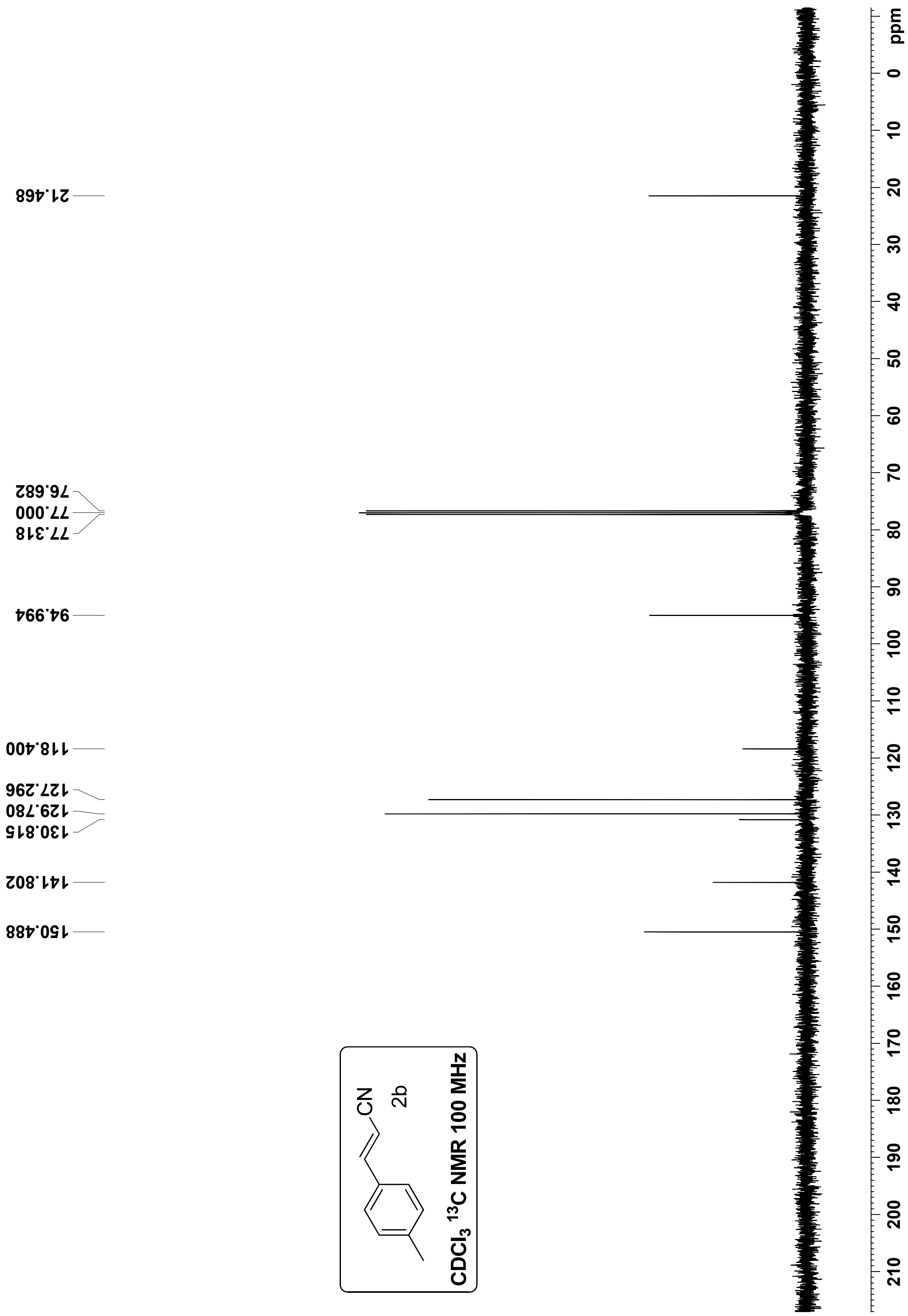
1.00
3.17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0
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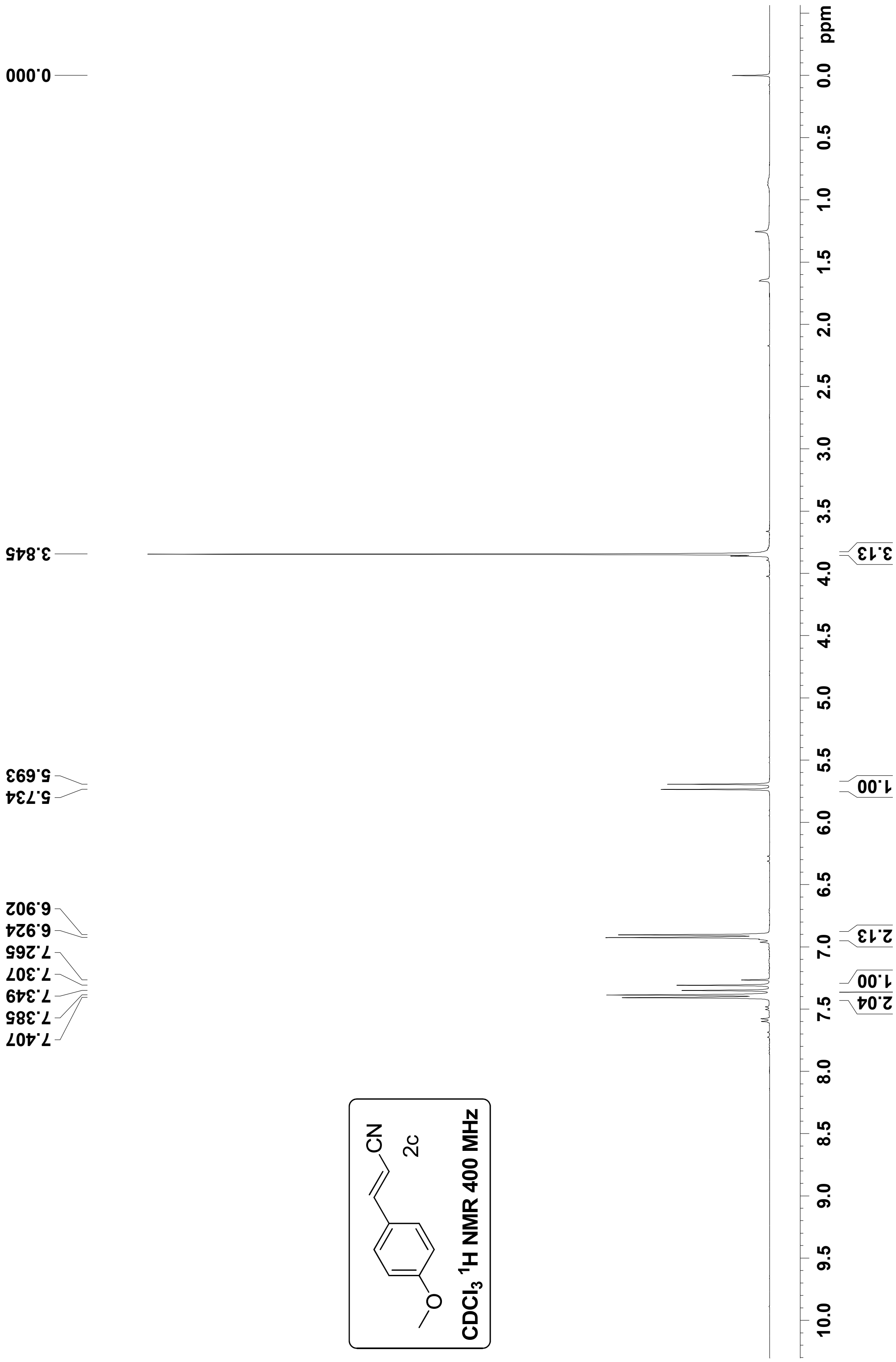
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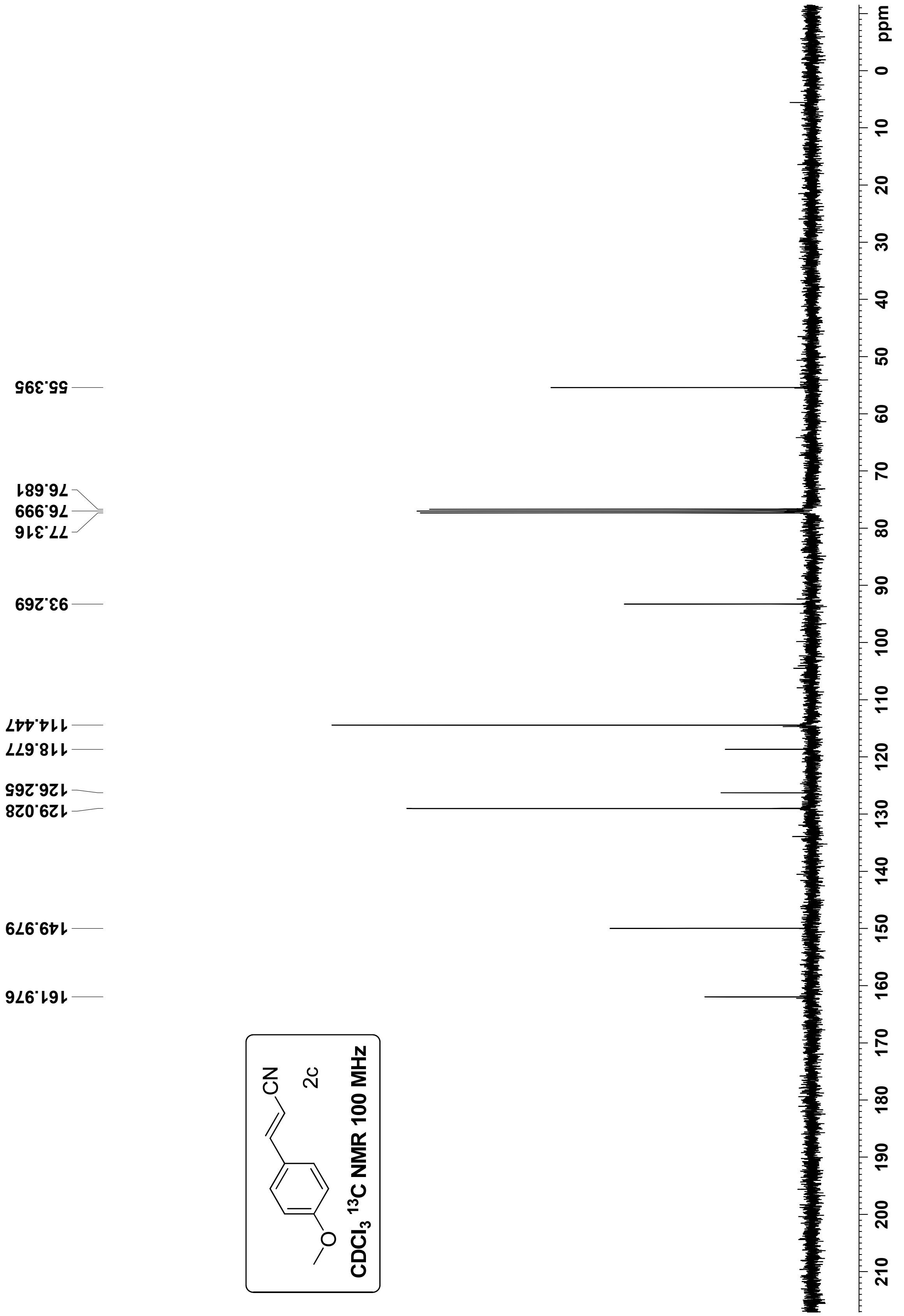
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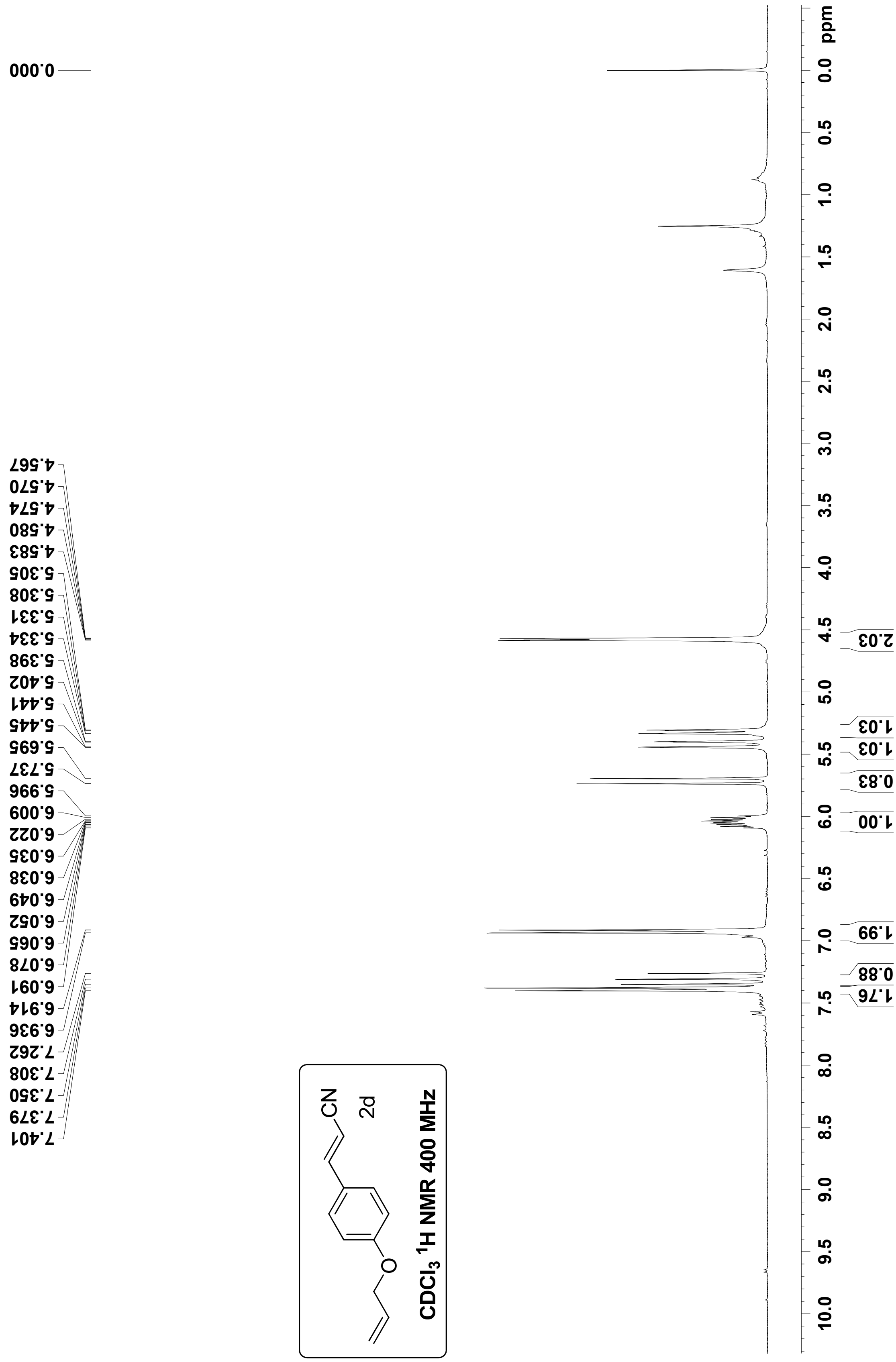
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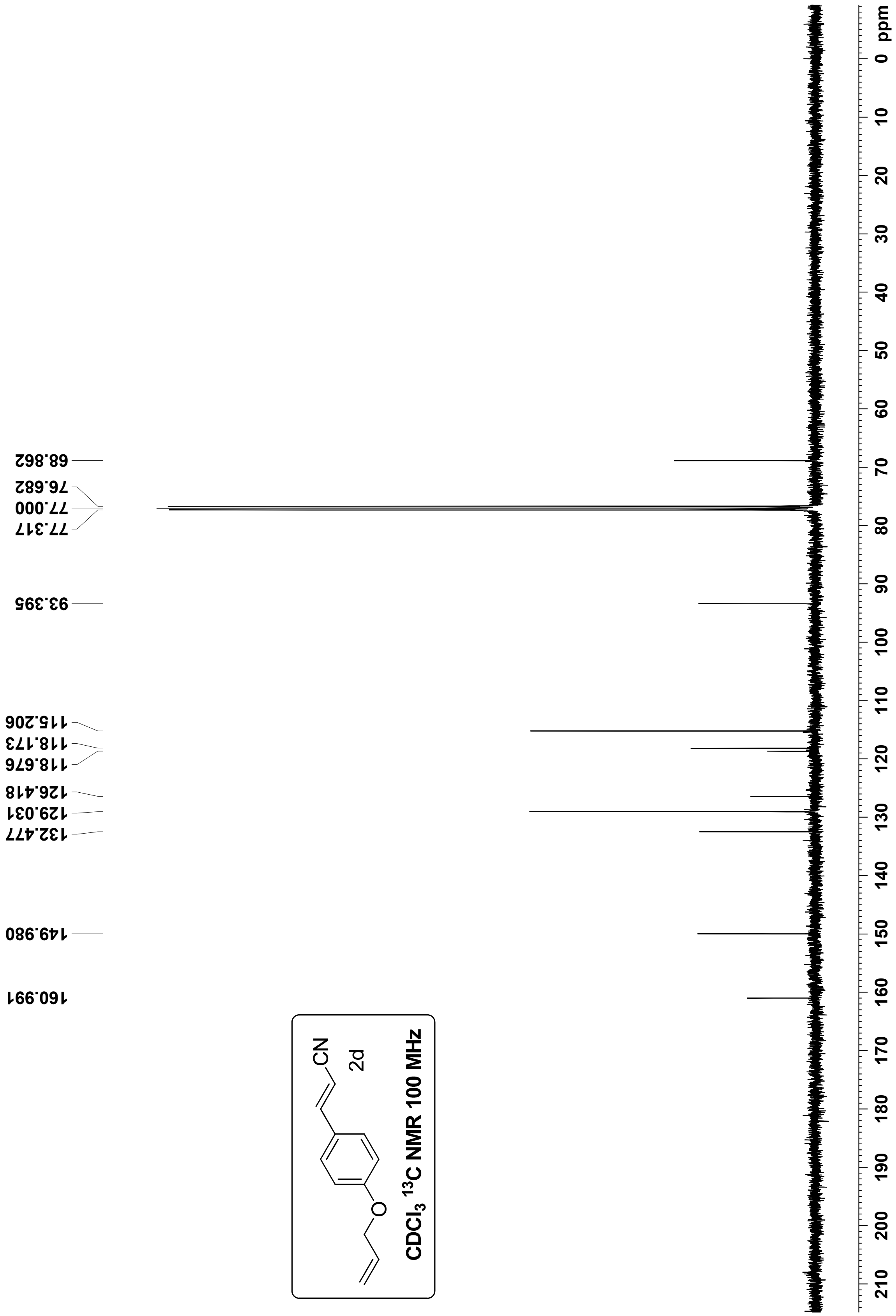
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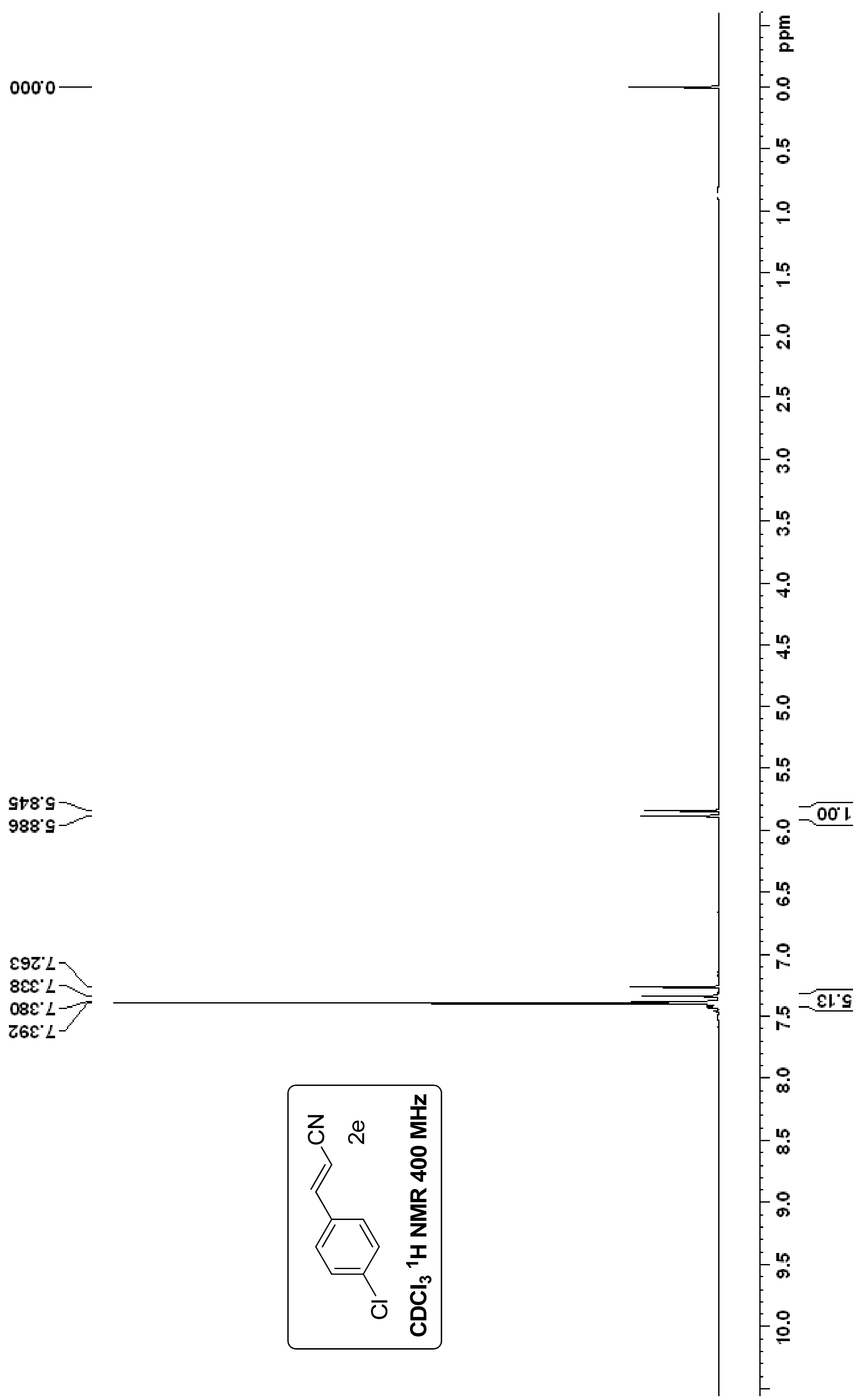
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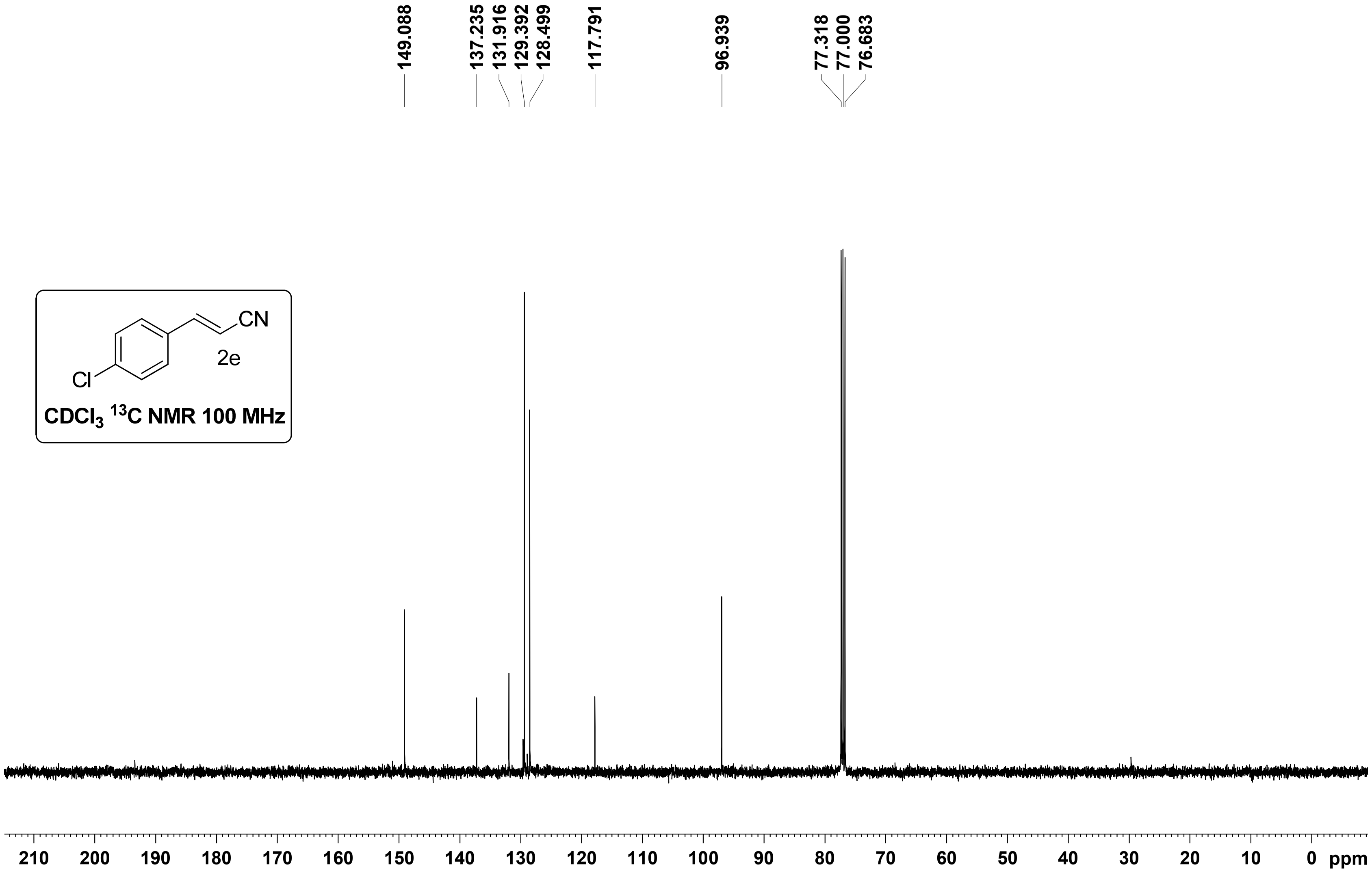
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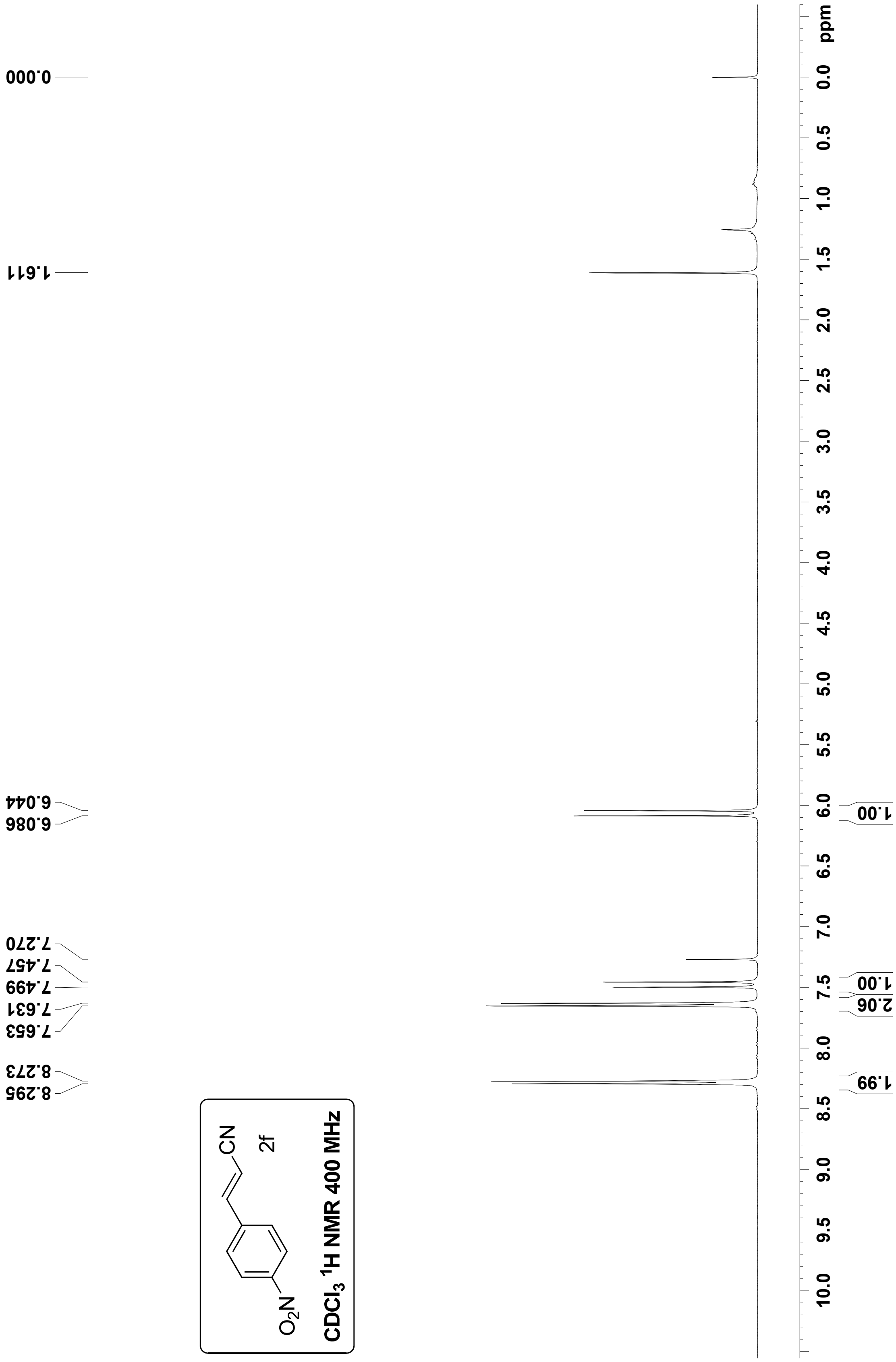
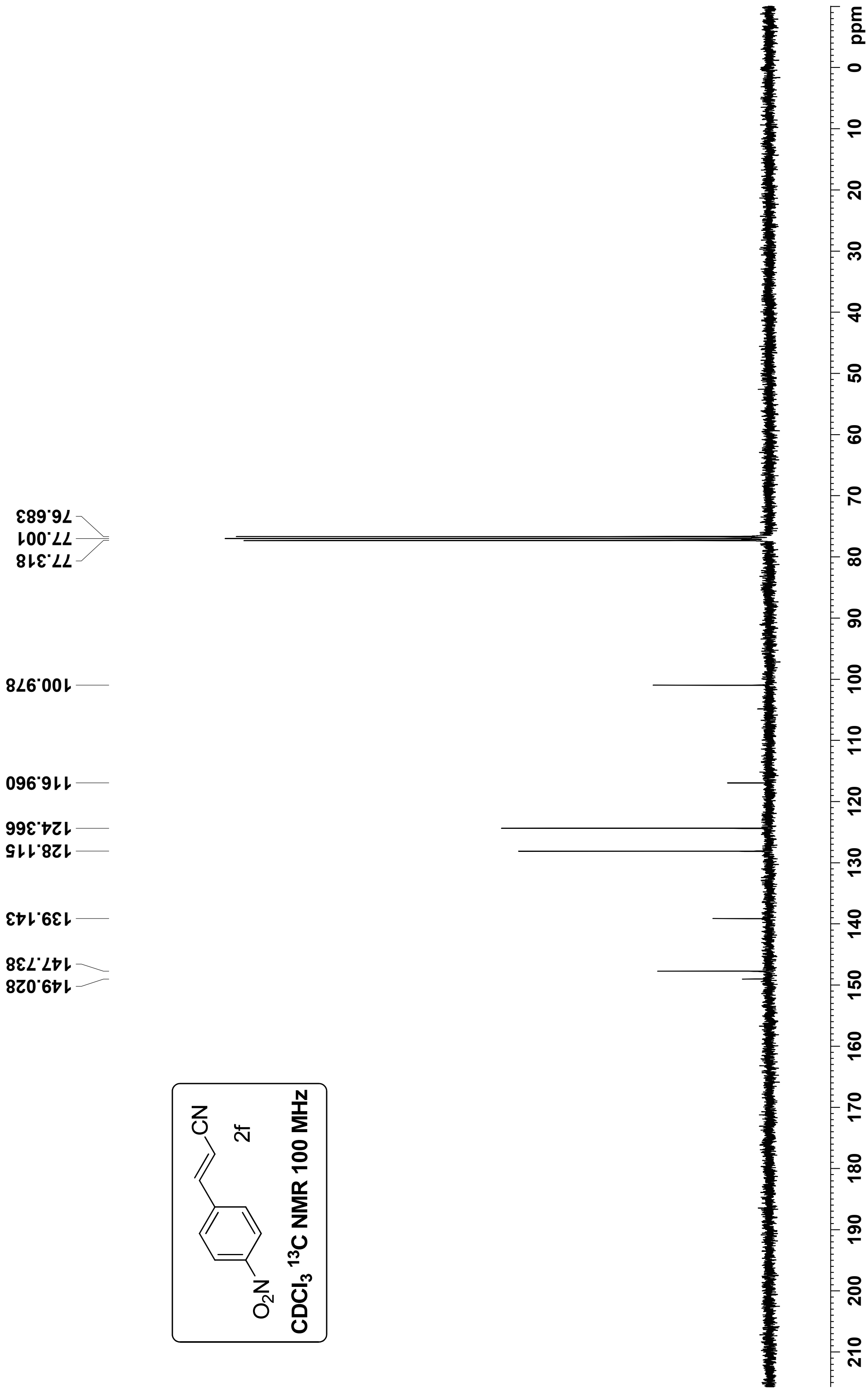
Electronic Supplementary Material (ESI) for Chemical Communications

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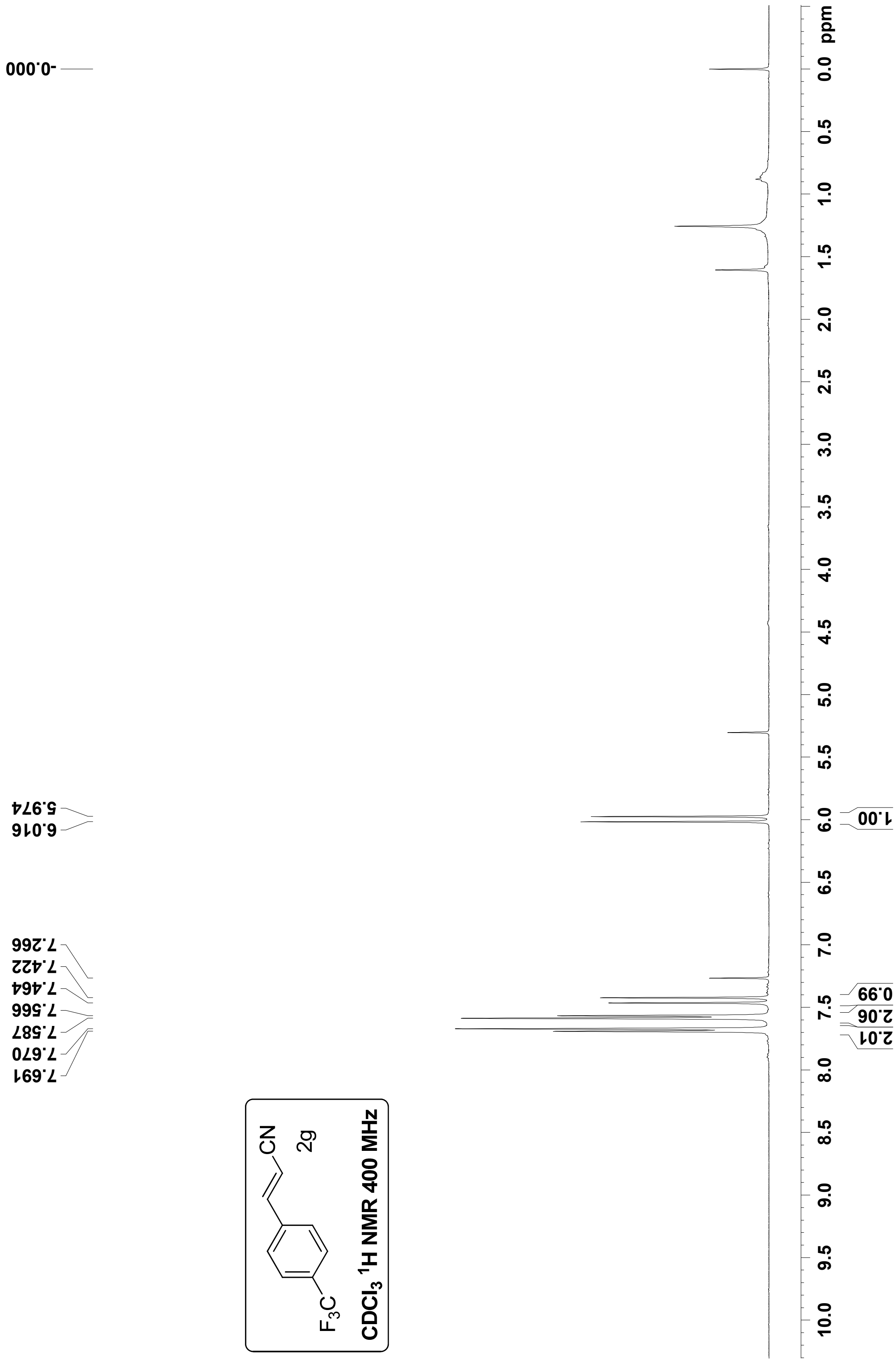
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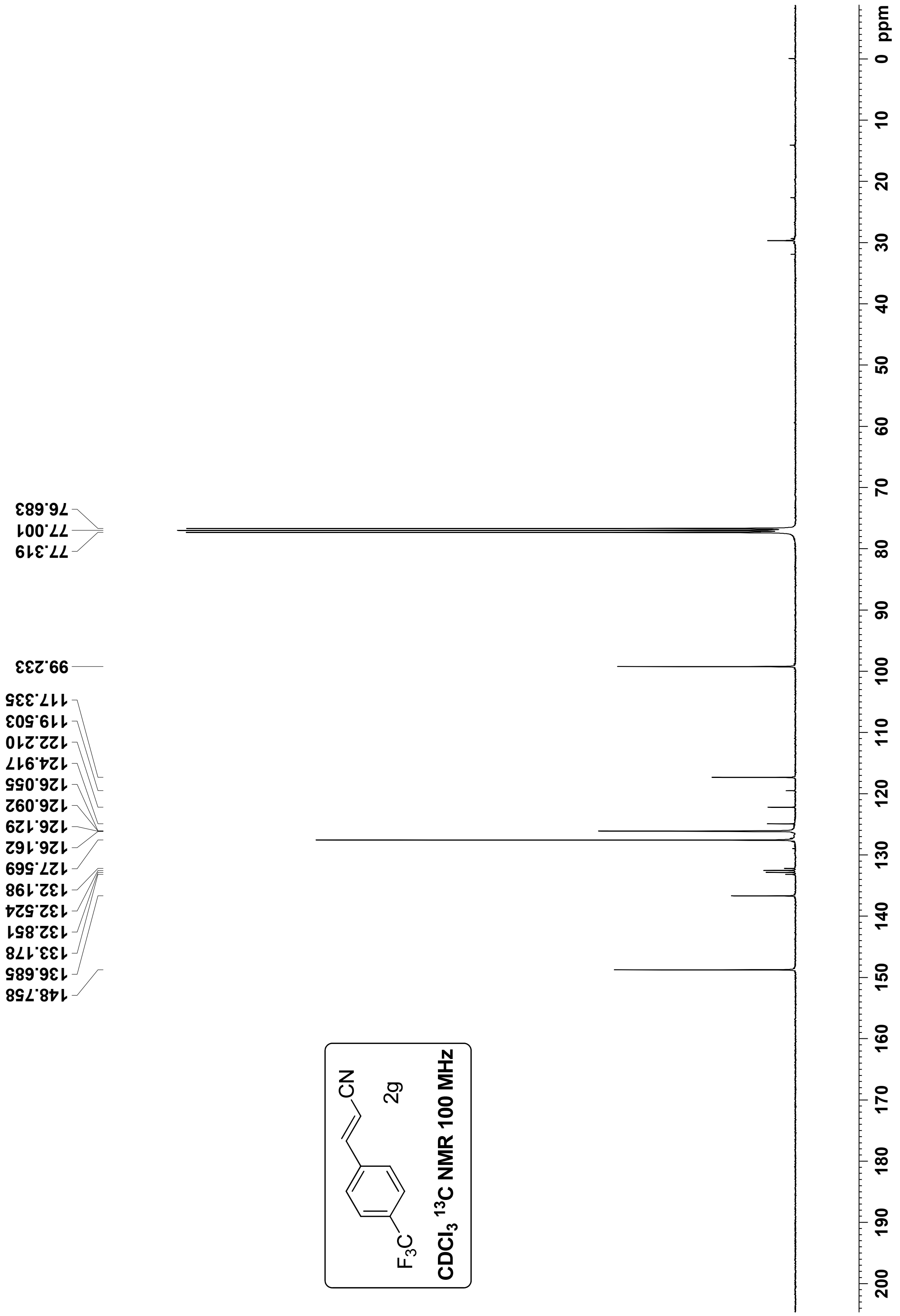
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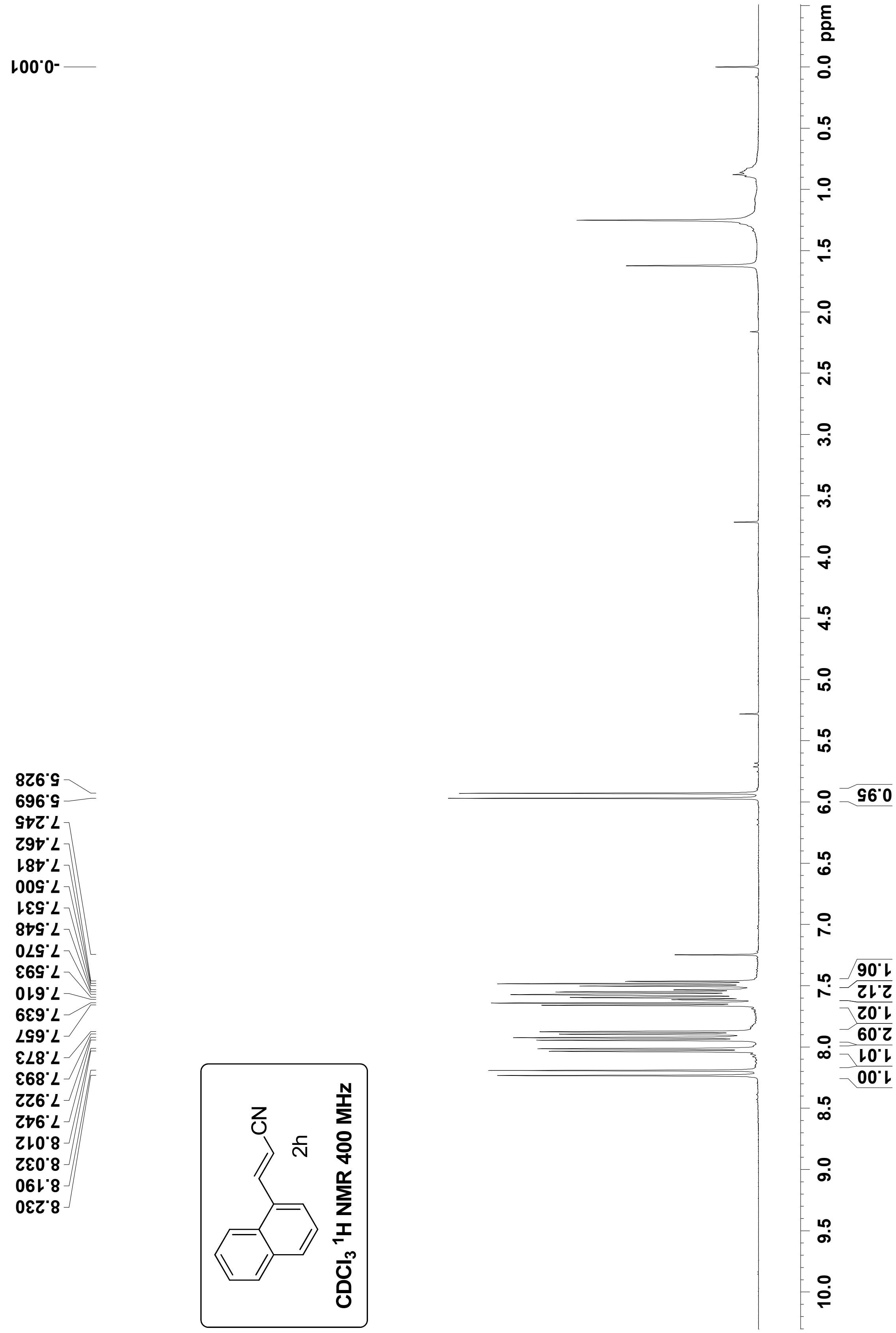
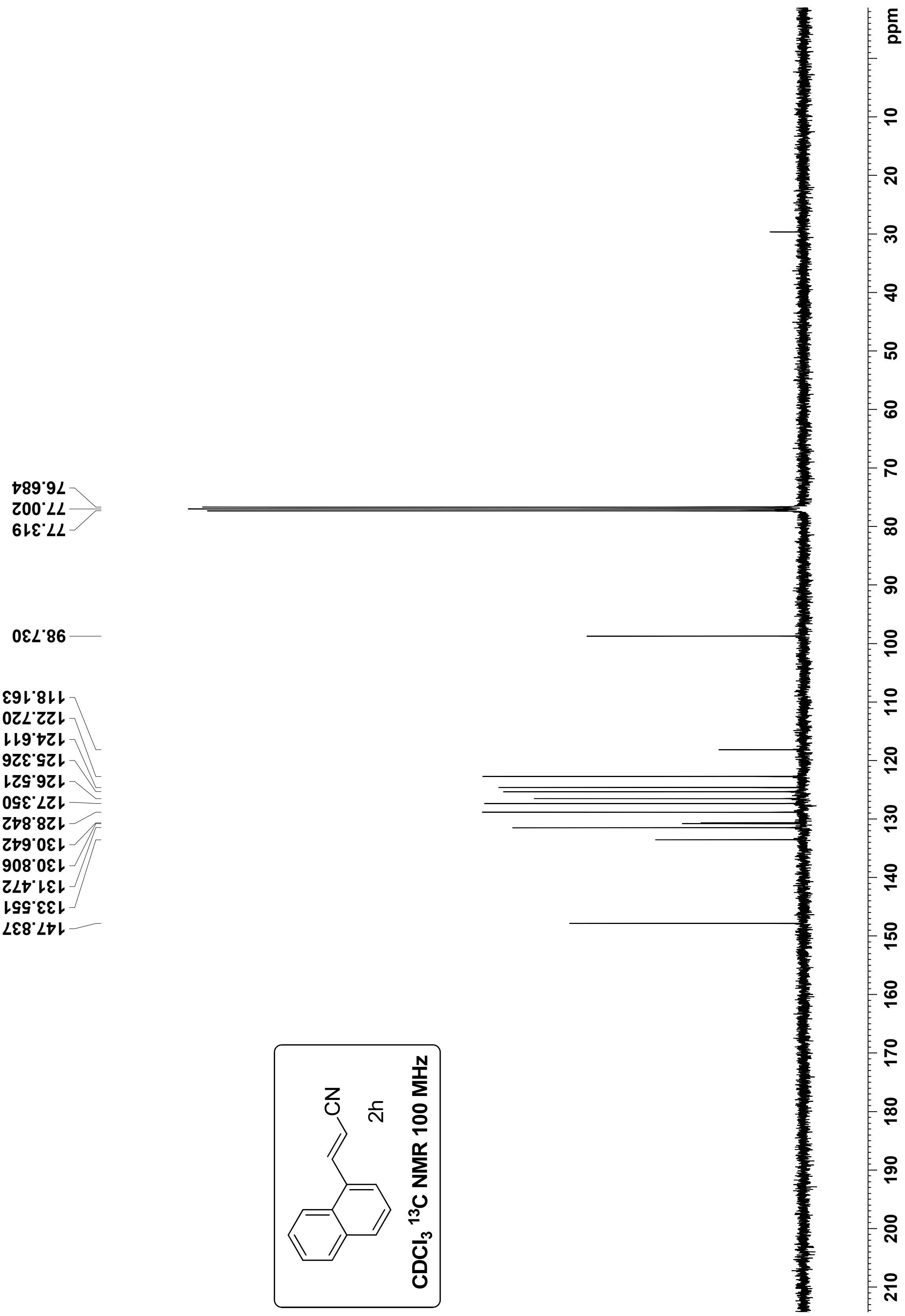
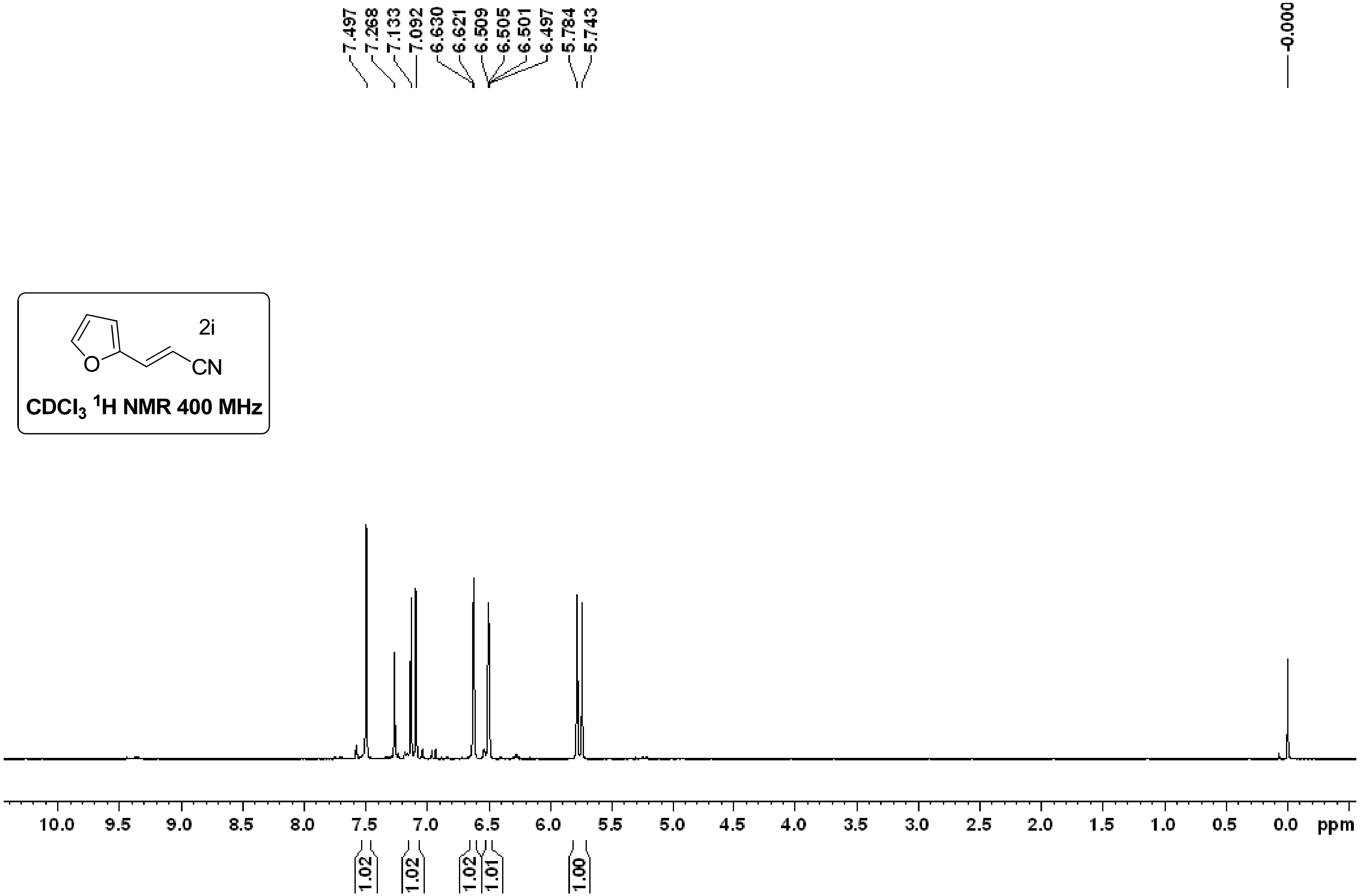
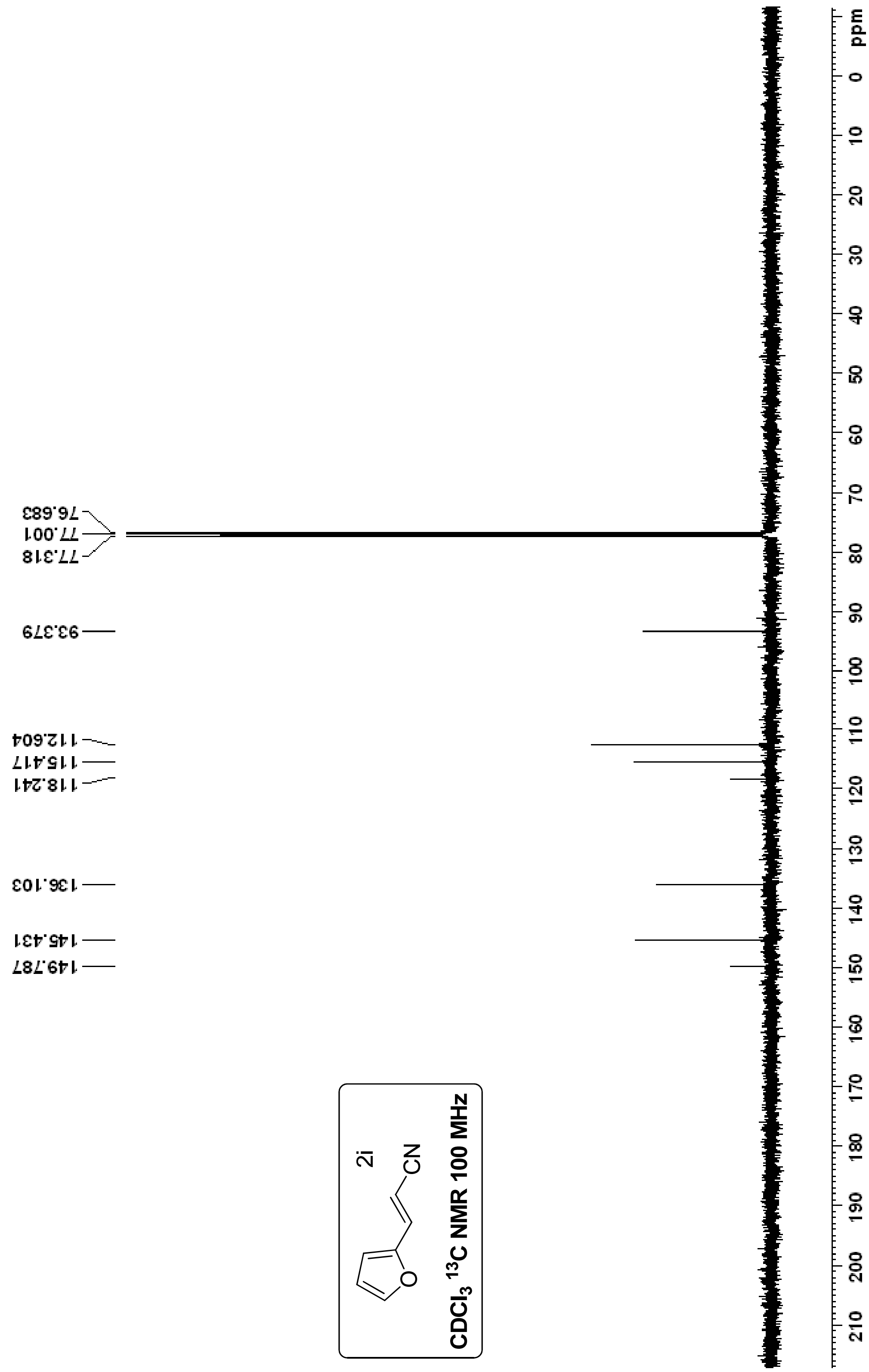
CDCl3 13C NMR 100 MHz
ppm

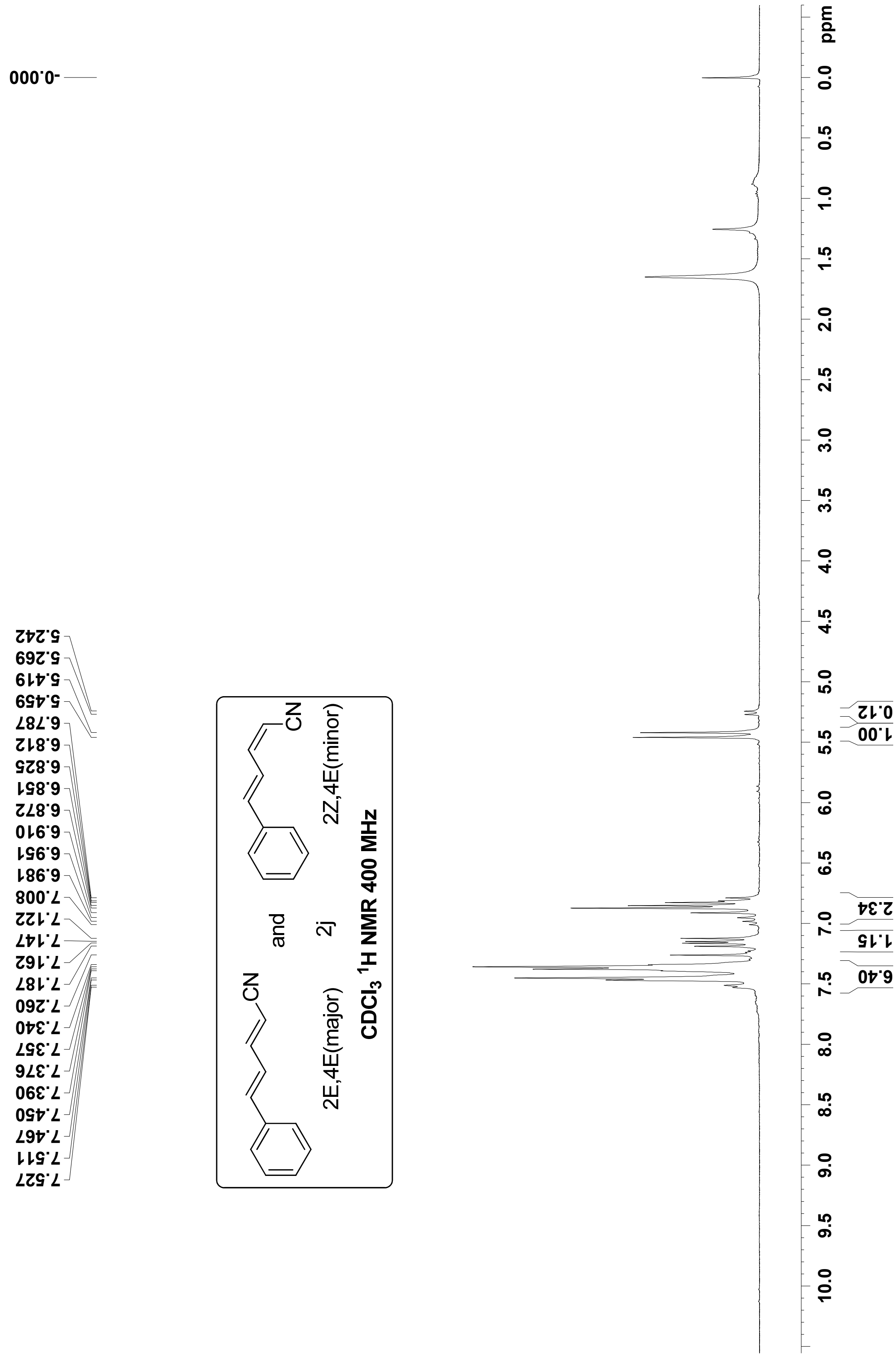

-0.001
5.928
5.969
7.245
7.462
7.481
7.500
7.531
7.548
7.570
7.593
7.610
7.639
7.657
7.873
7.893
7.922
7.942
8.012
8.032
8.190
8.230
CN
2h
CDCl3 1H NMR 400 MHz
0.95
1.06
2.12
1.02
2.09
1.01
1.00
ppm

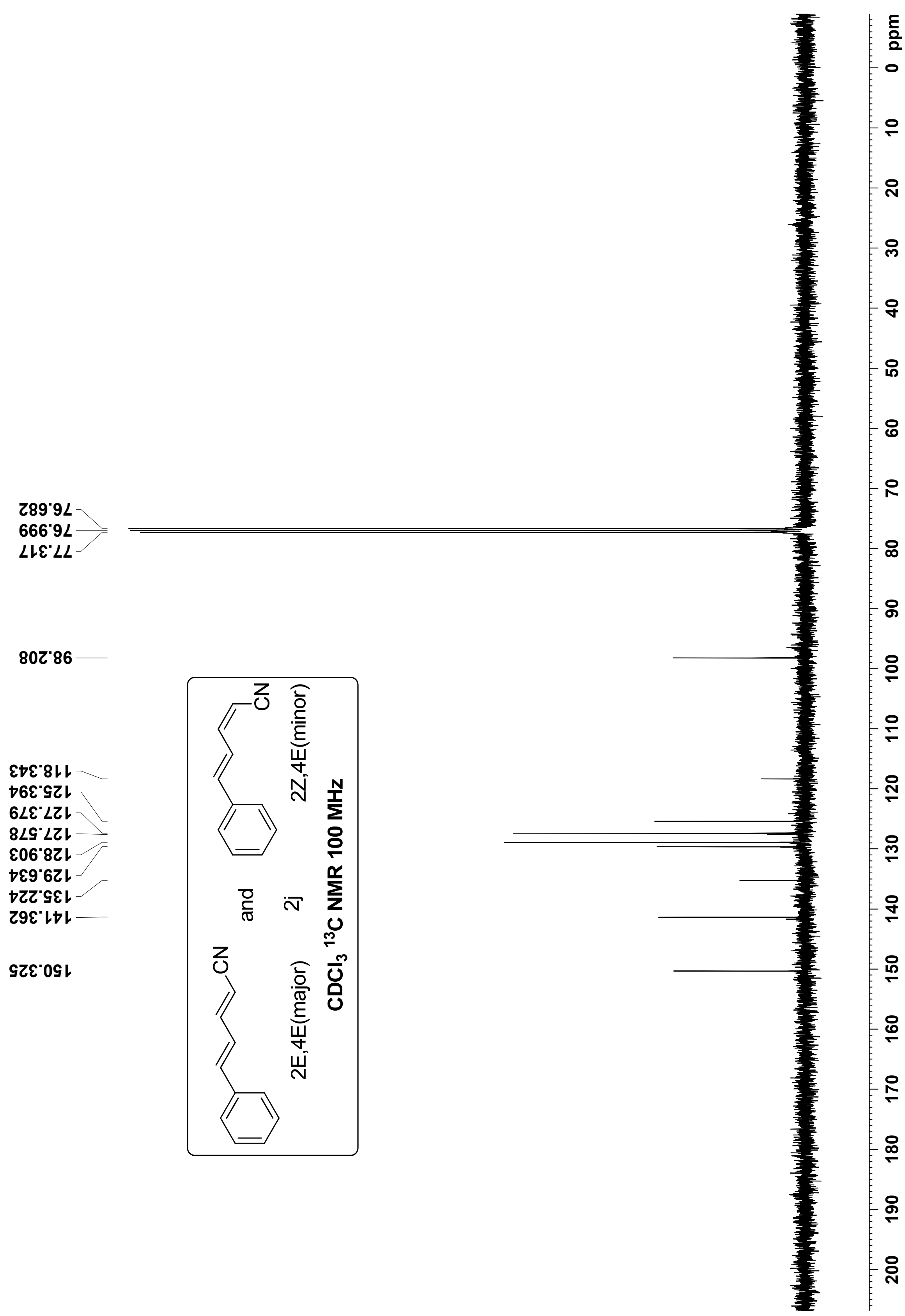

76.684
77.002
77.319
98.730
118.163
122.720
124.611
125.326
126.521
127.350
128.842
130.642
130.806
131.472
133.551
147.837
CN
2h
CDCl3 13C NMR 100 MHz
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

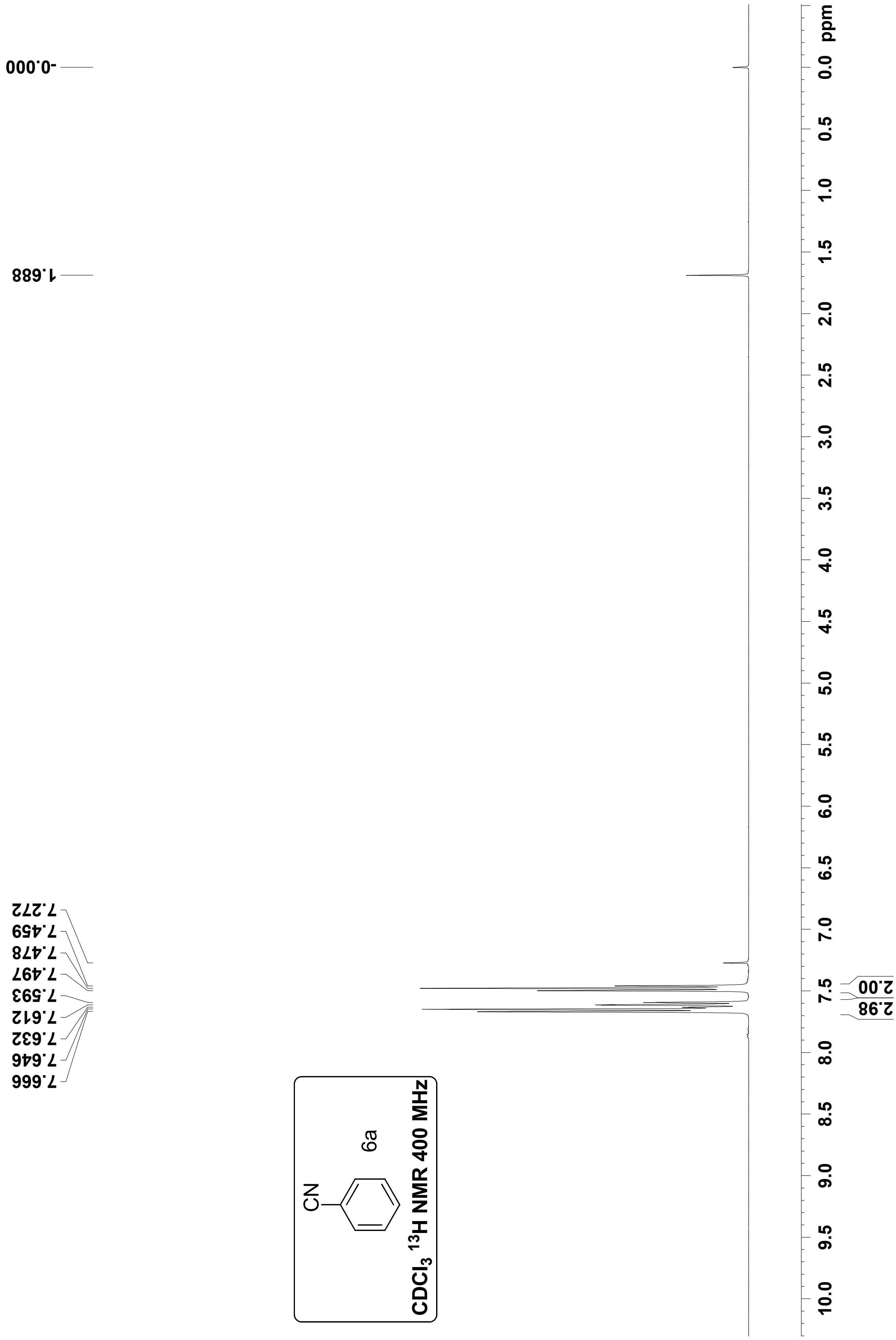

7.497
7.268
7.133
7.092
6.630
6.621
6.509
6.505
6.501
6.497
5.784
5.743
-0.000
2i
O
CN
CDCl3 1H NMR 400 MHz
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.02
1.02
1.02
1.01
1.00

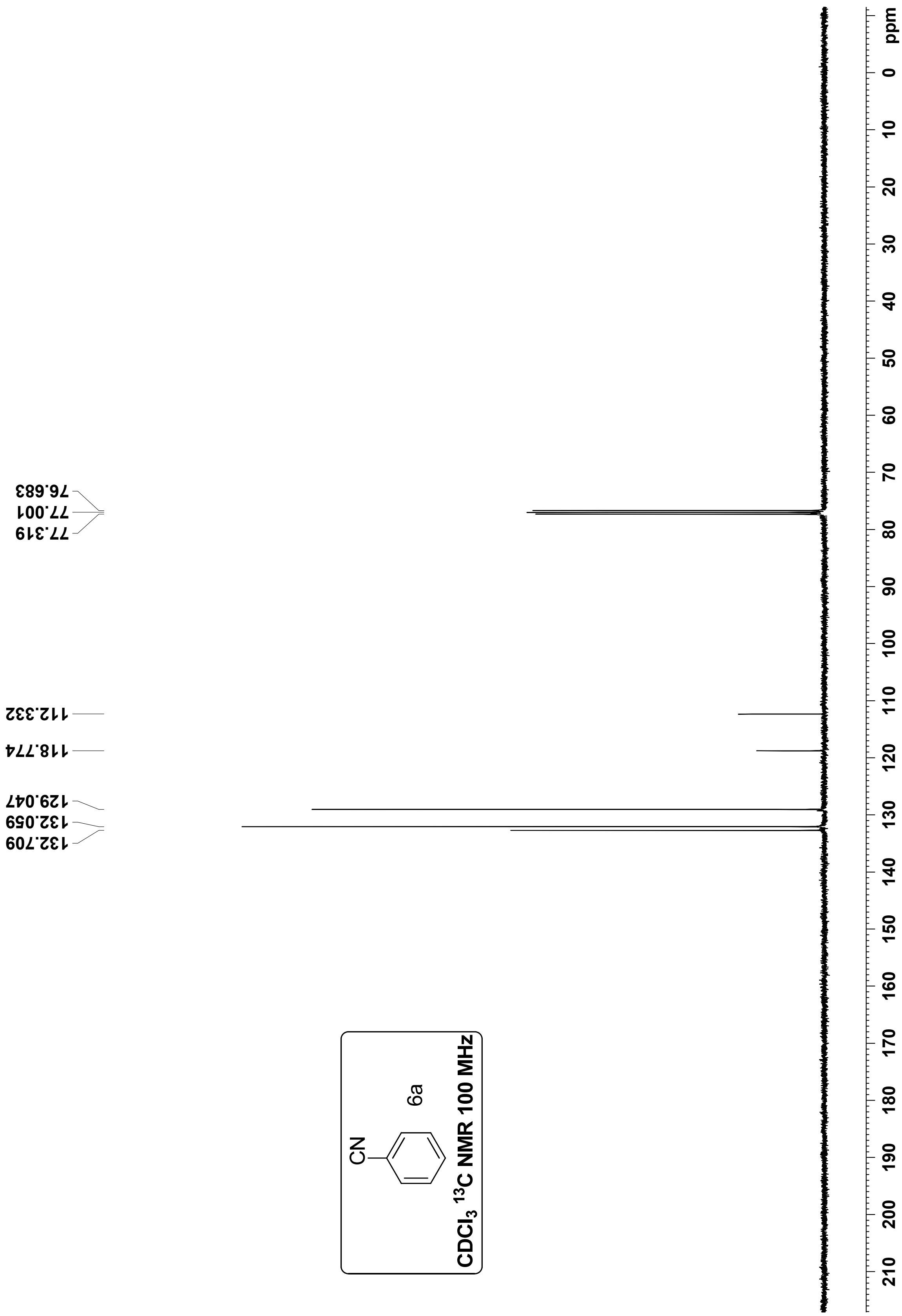

76.683
77.001
77.318
93.379
112.604
115.417
118.241
136.103
145.431
149.787
O
CN
2i
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

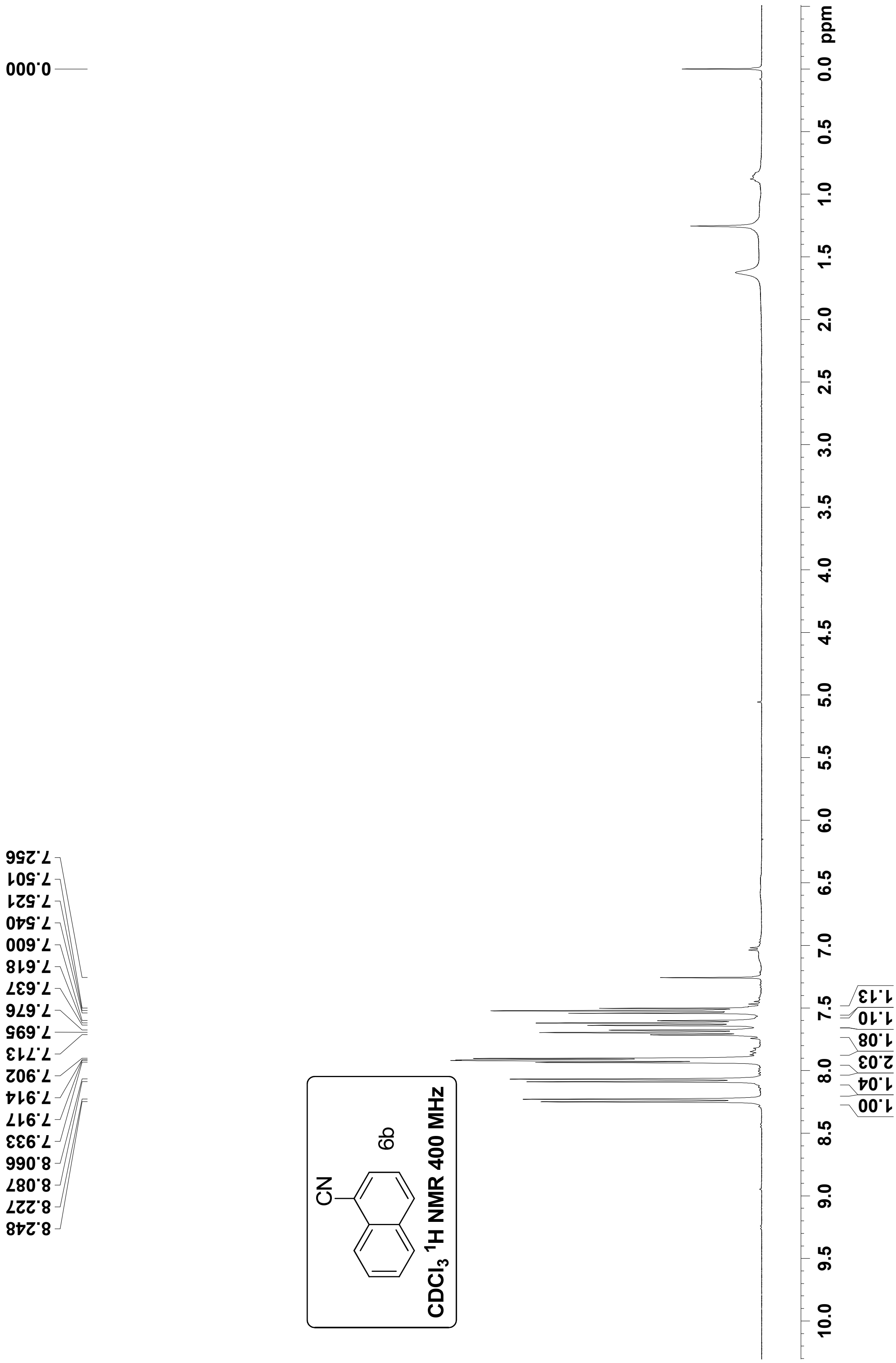
Electronic Supplementary Material (ESI) for Chemical Communications

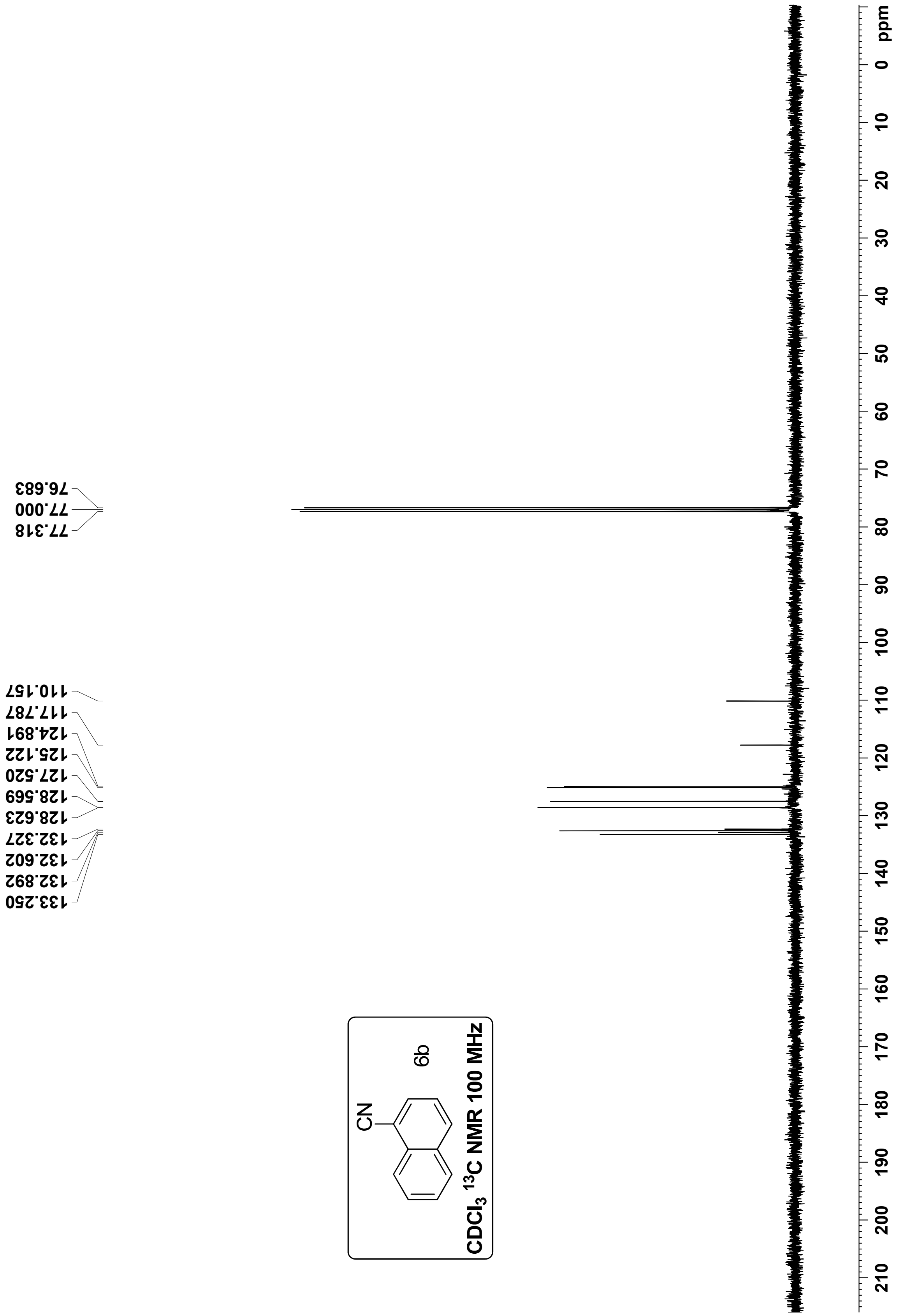


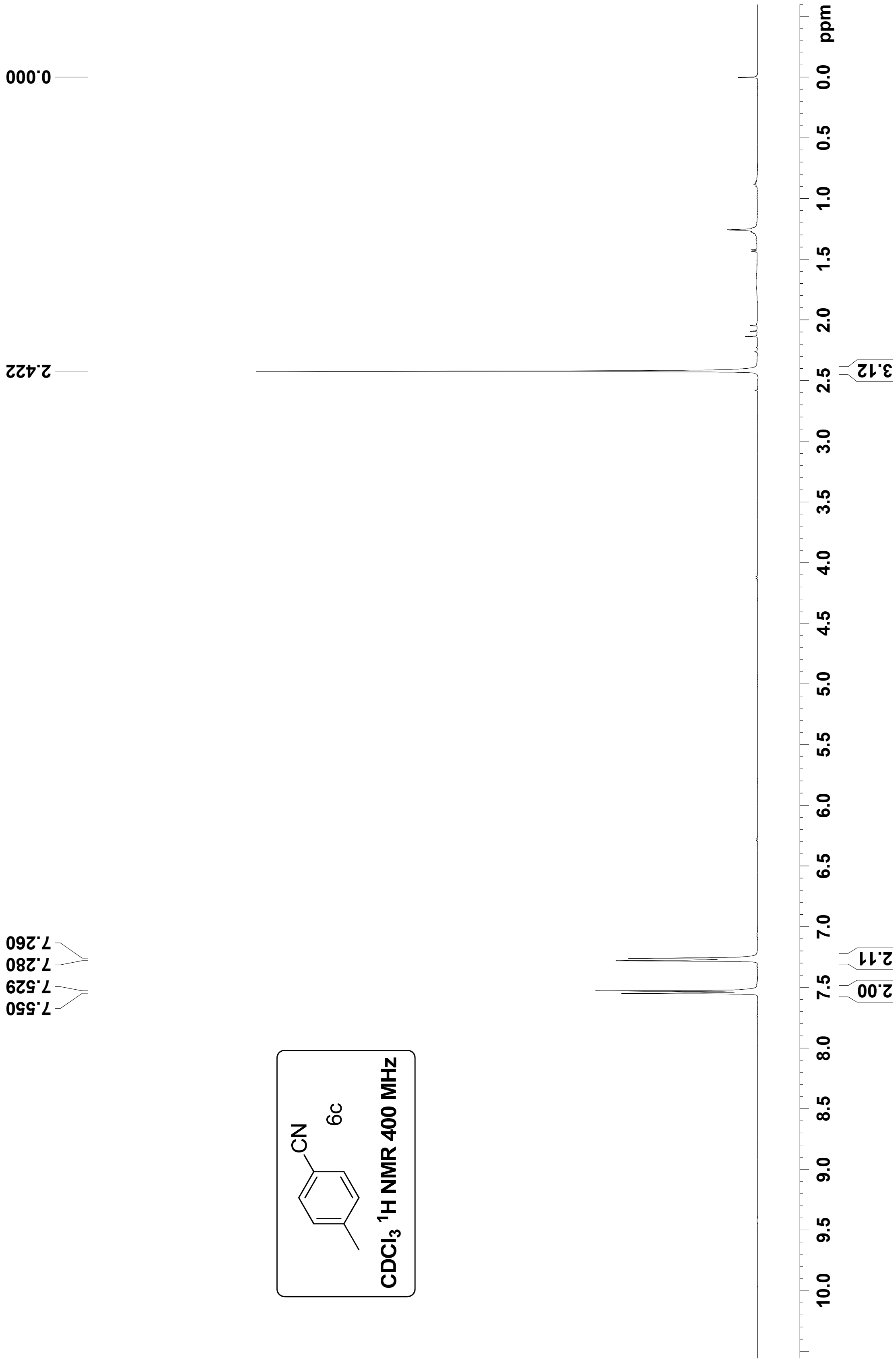

76.682
76.999
77.317
98.208
118.343
125.394
127.379
127.578
128.903
129.634
135.224
141.362
150.325
CN
CN
and
2E,4E(major)
2j
2Z,4E(minor)
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

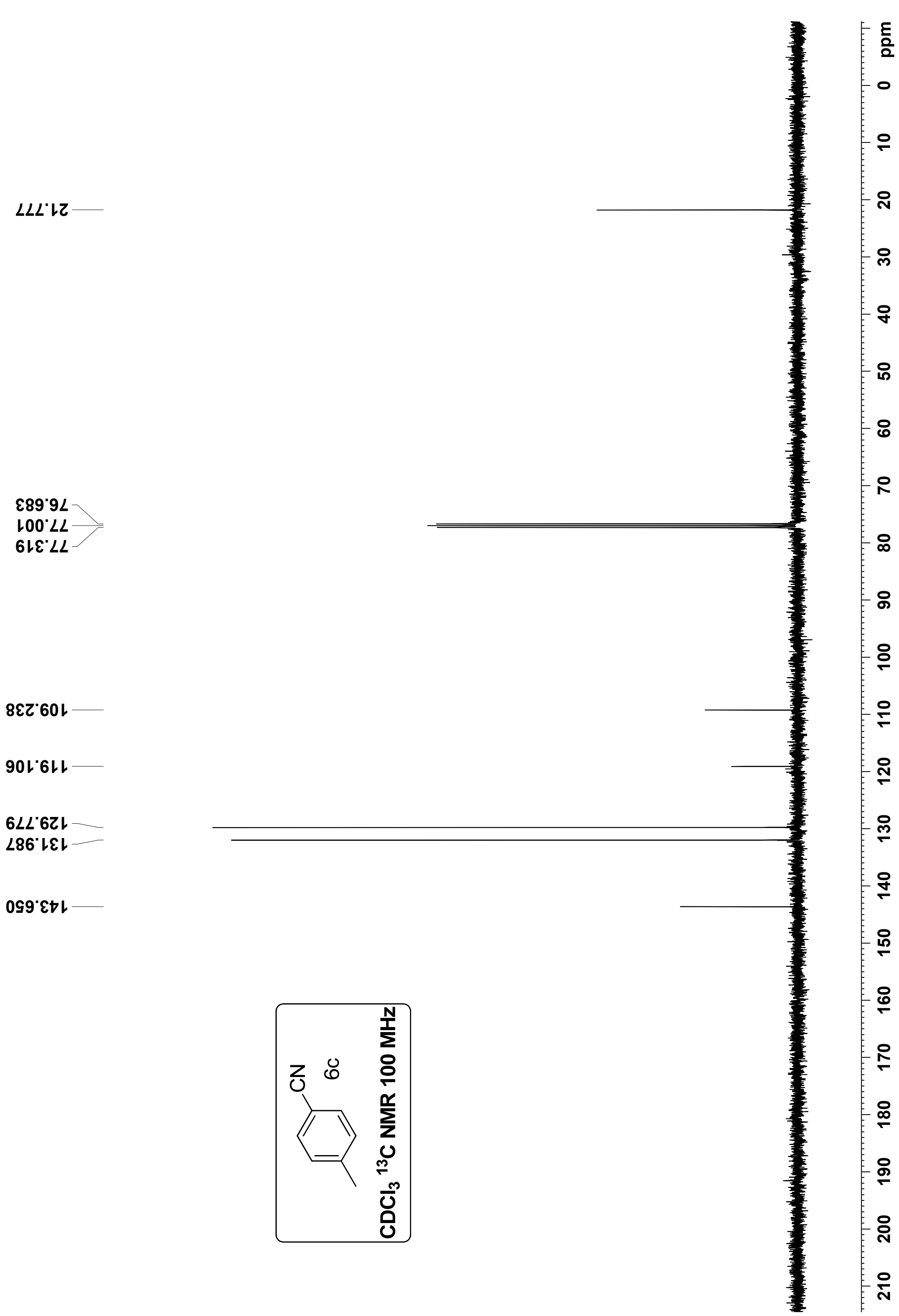

-0.000
1.688
7.272
7.459
7.478
7.497
7.593
7.612
7.632
7.646
7.666
2.00
2.98
ppm
CN
6a
$CDCl_3$ ^{13}H NMR 400 MHz

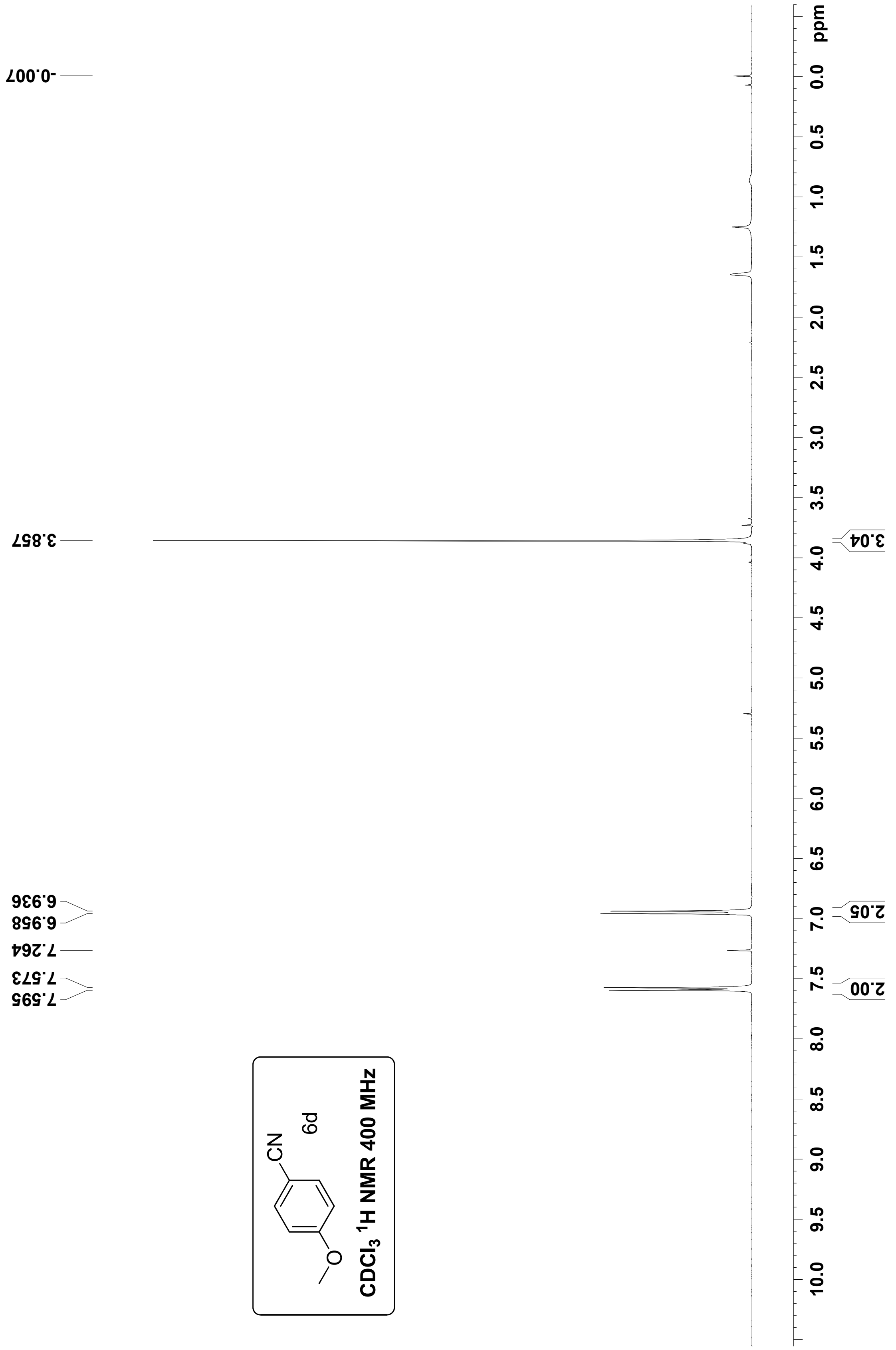

76.683
77.001
77.319
112.332
118.774
129.047
132.059
132.709
CN
6a
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

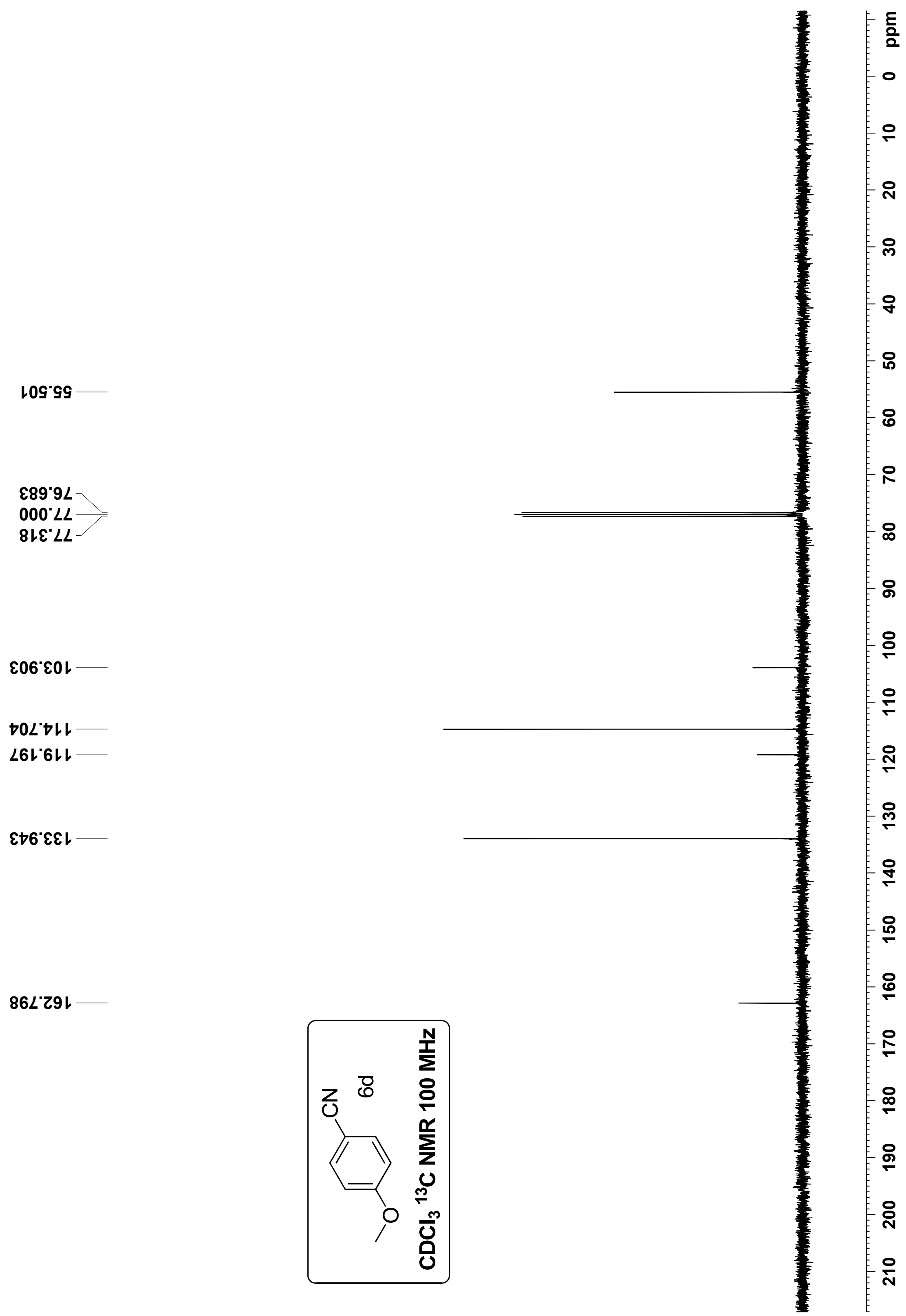

0.000
7.256
7.501
7.521
7.540
7.600
7.618
7.637
7.676
7.695
7.713
7.902
7.914
7.917
7.933
8.066
8.087
8.227
8.248
CN
6b
CDCl3 1H NMR 400 MHz
1.13
1.10
1.08
2.03
1.04
1.00
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

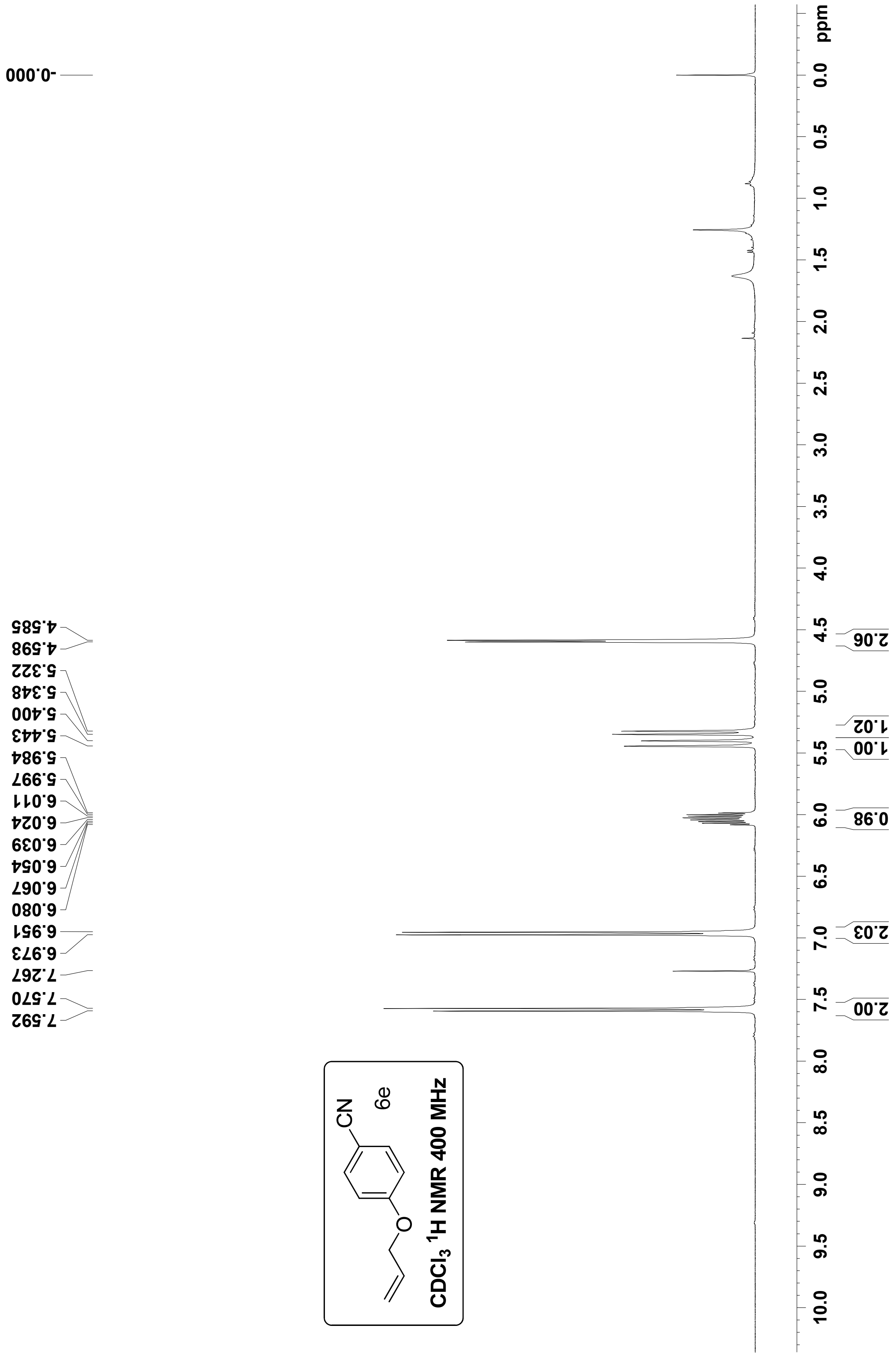

76.683
77.000
77.318
110.157
117.787
124.891
125.122
127.520
128.569
128.623
132.327
132.602
132.892
133.250
CN
6b
CDCl$_3$ ^{13}C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

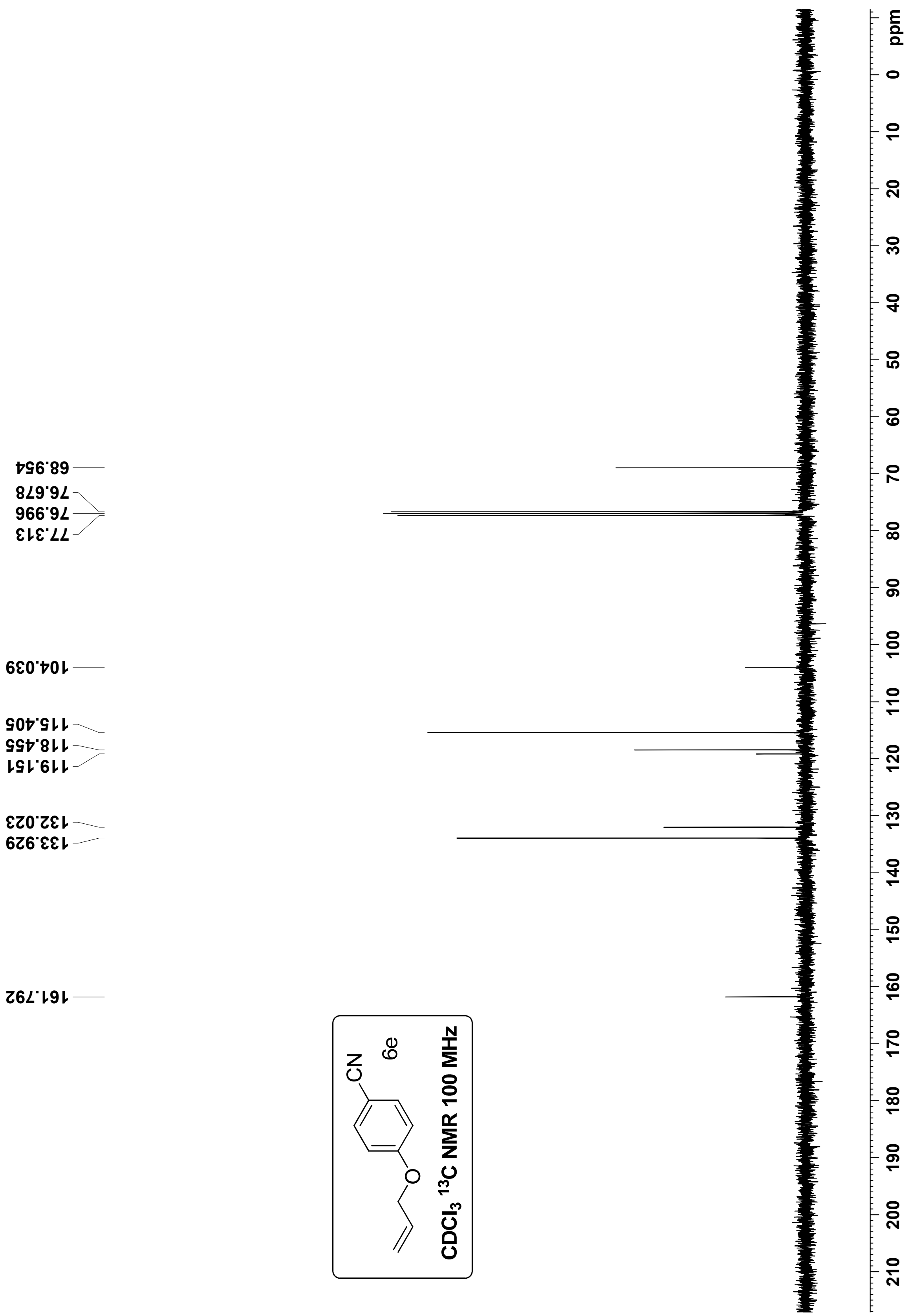

0.000
2.422
7.260
7.280
7.529
7.550
3.12
2.11
2.00
ppm
CN
6c
CDCl3 1H NMR 400 MHz

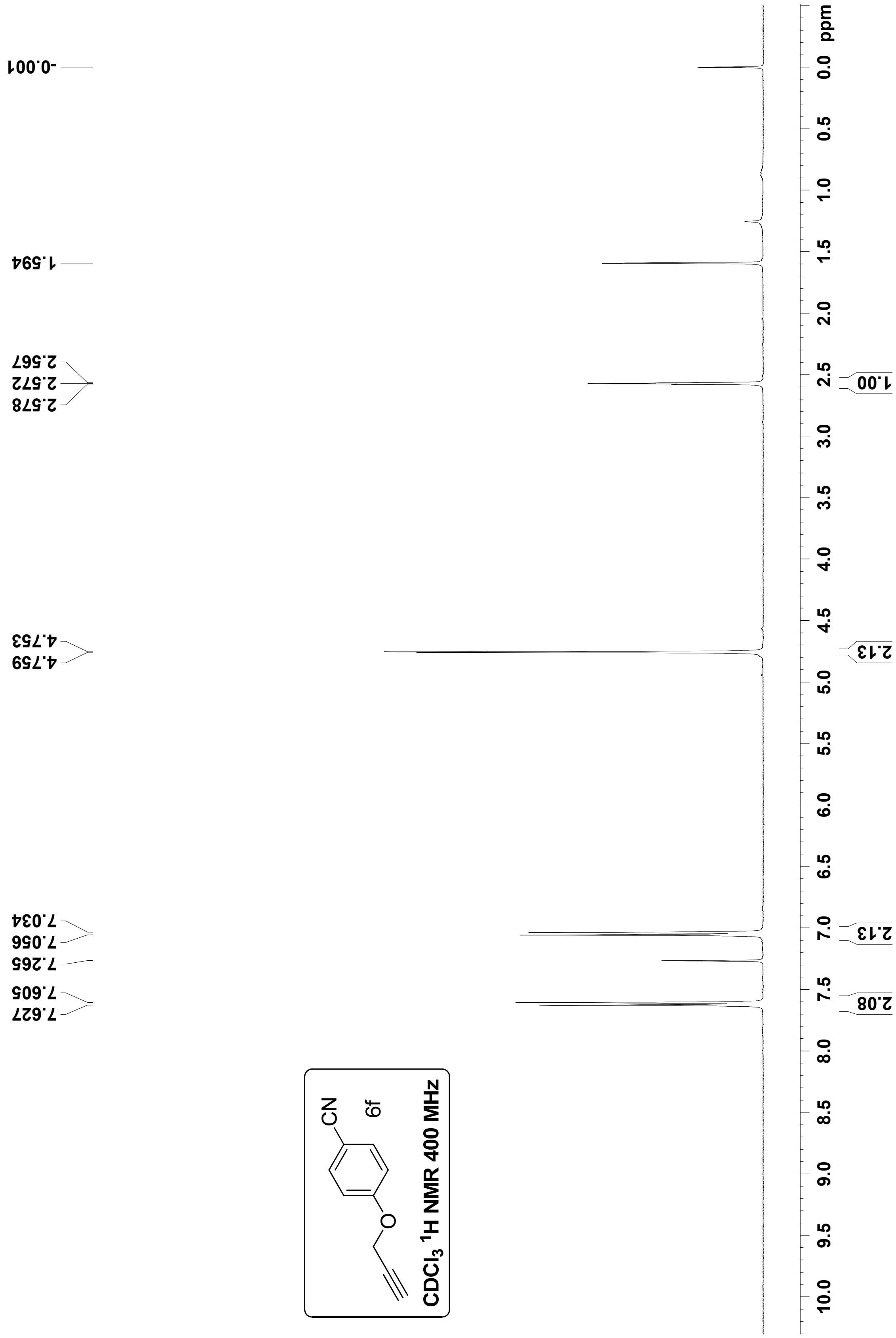

21.777
76.683
77.001
77.319
109.238
119.106
129.779
131.987
143.650
CN
6c
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

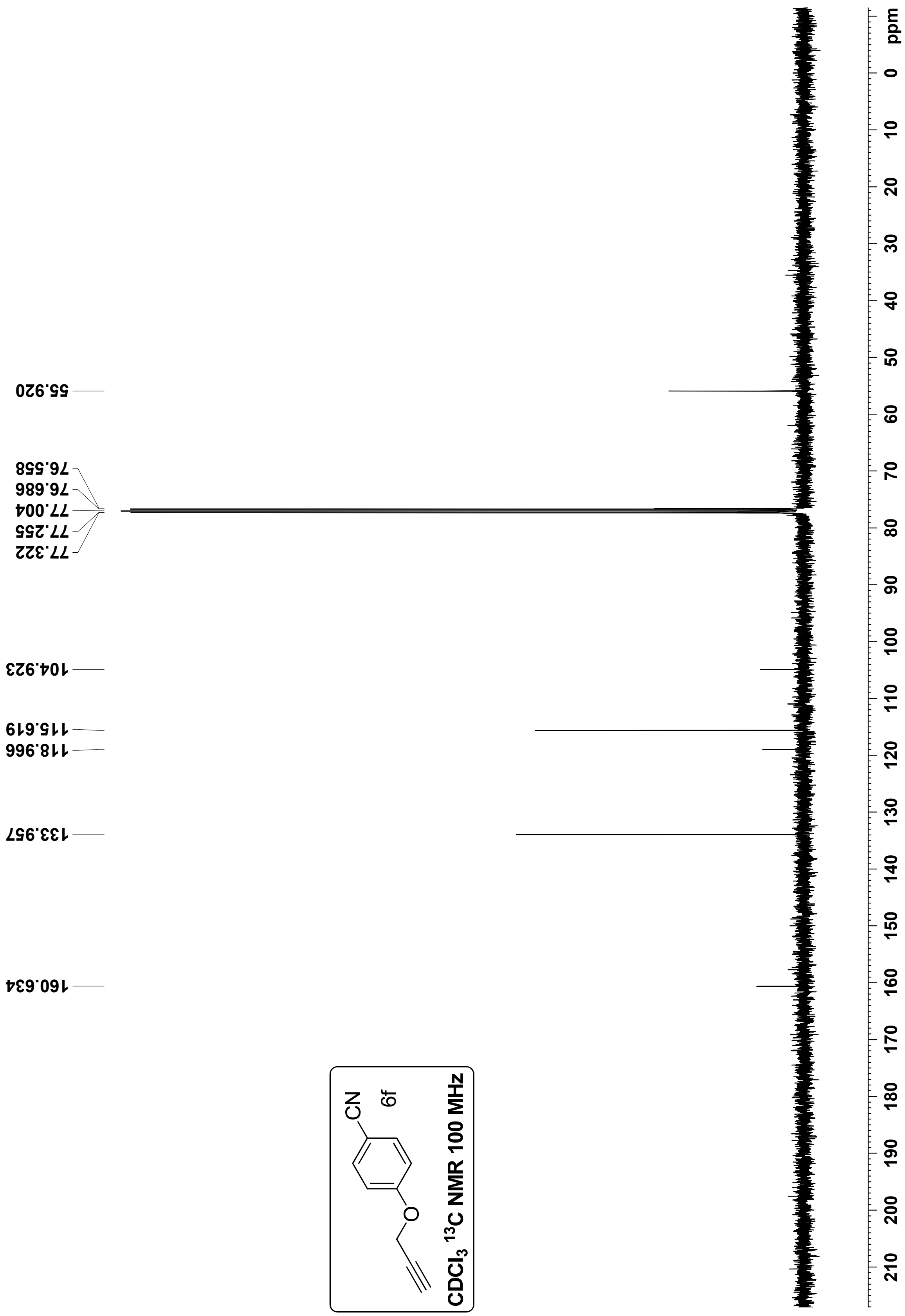

-0.007
3.857
6.936
6.958
7.264
7.573
7.595
3.04
2.05
2.00
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
CN
O
6d
CDCl3 1H NMR 400 MHz

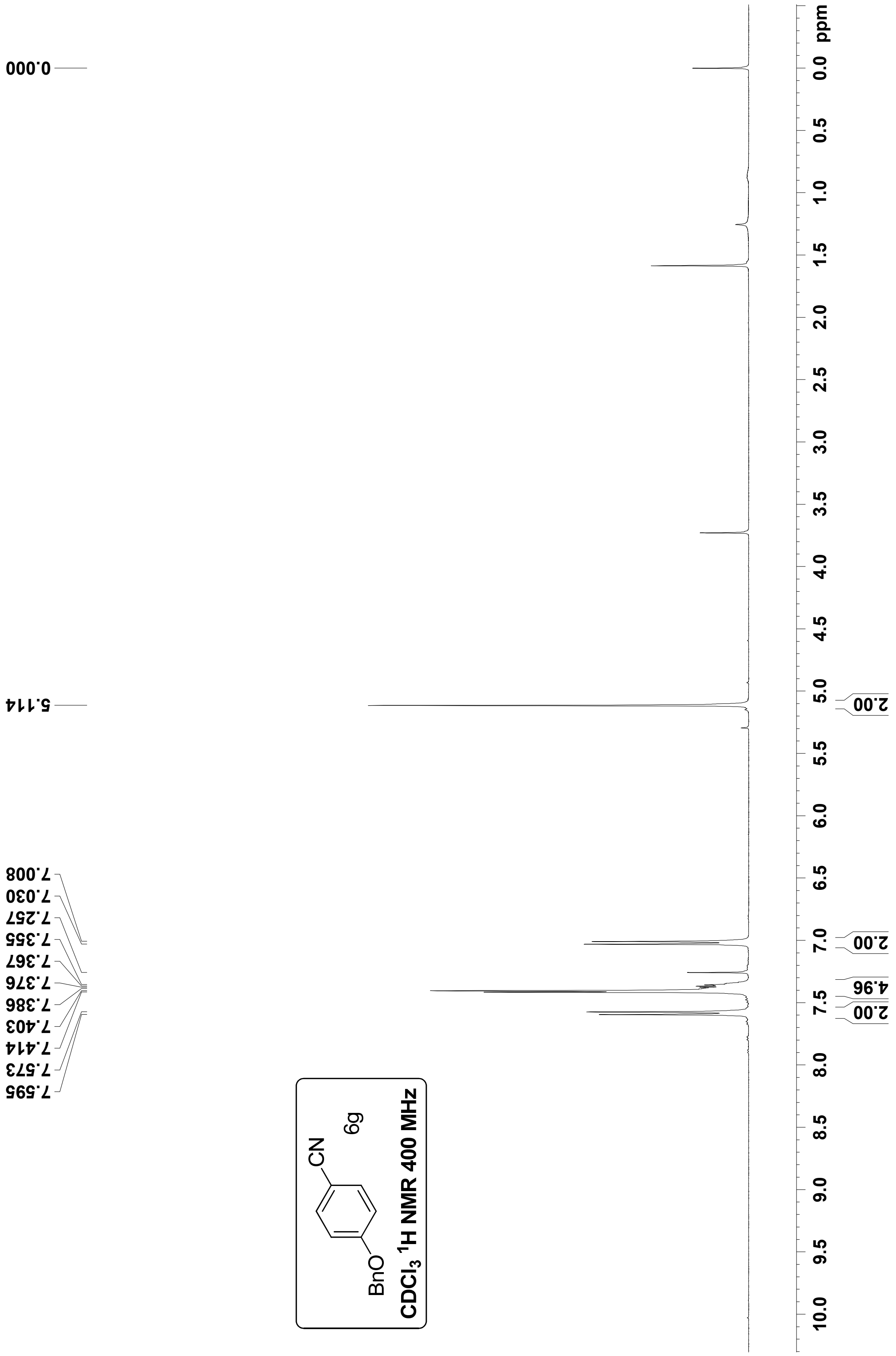

55.501
76.683
77.000
77.318
103.903
114.704
119.197
133.943
162.798
CN
O
6d
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


-0.000
4.585
4.598
5.322
5.348
5.400
5.443
5.984
5.997
6.011
6.024
6.039
6.054
6.067
6.080
6.951
6.973
7.267
7.570
7.592
2.06
1.02
1.00
0.98
2.03
2.00
ppm
CN
6e
O
CDCl3 1H NMR 400 MHz

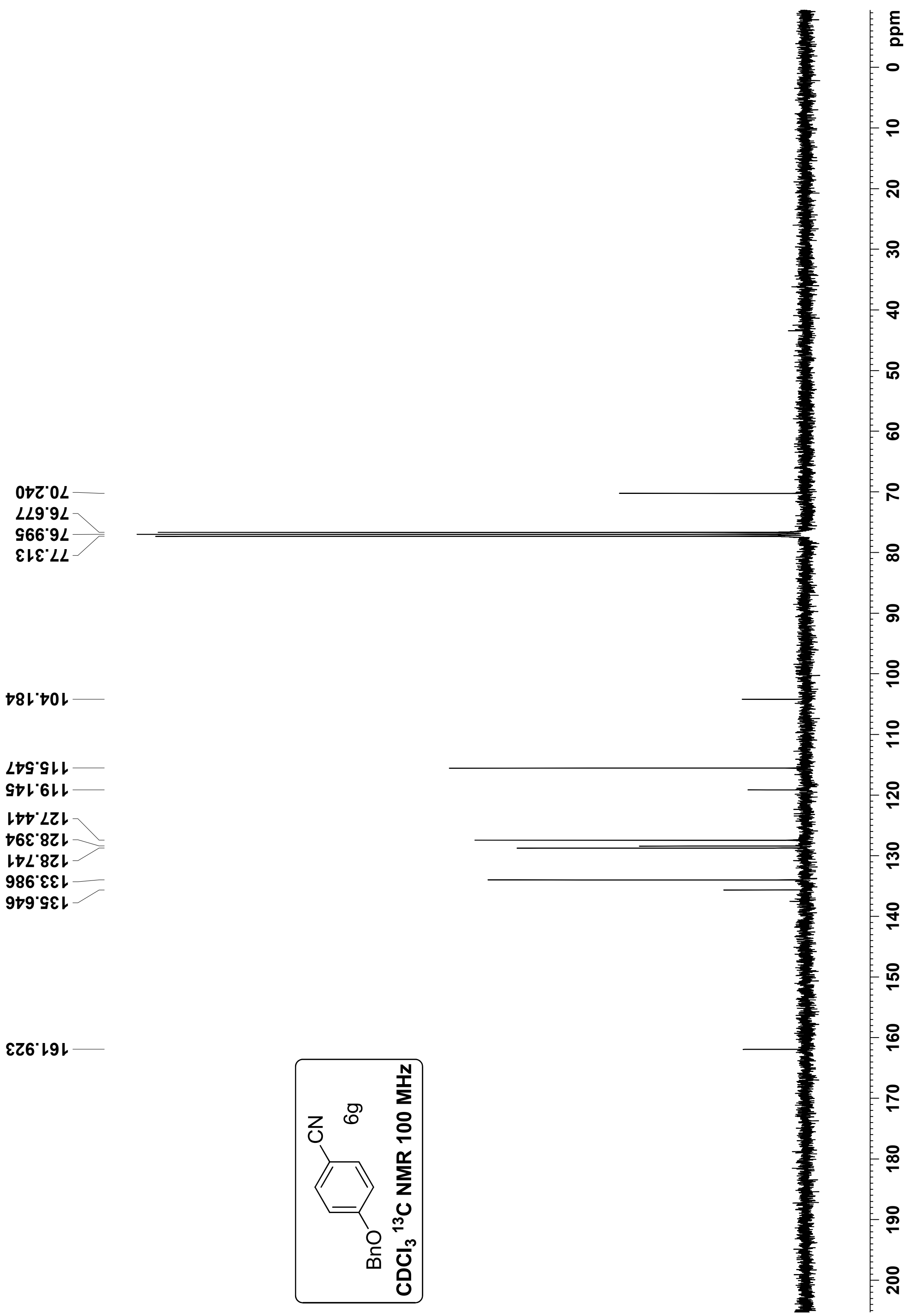

68.954
76.678
76.996
77.313
104.039
115.405
118.455
119.151
132.023
133.929
161.792
CN
O
6e
$CDCl_3$, ^{13}C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

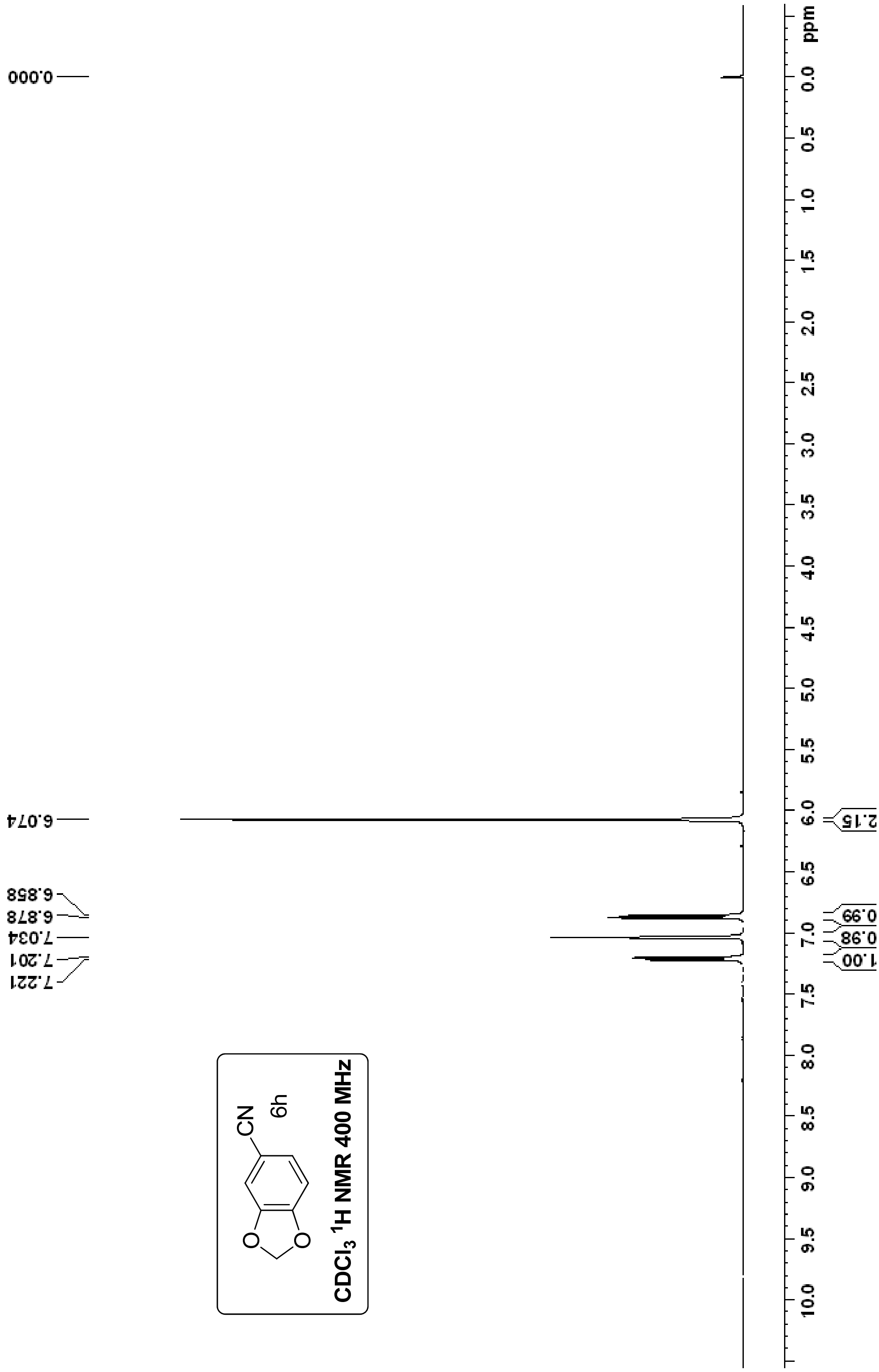

-0.001
1.594
2.567
2.572
2.578
4.753
4.759
7.034
7.056
7.265
7.605
7.627
1.00
2.13
2.13
2.08
ppm
CN
O
6f
CDCl$_3$ ^{1}H NMR 400 MHz

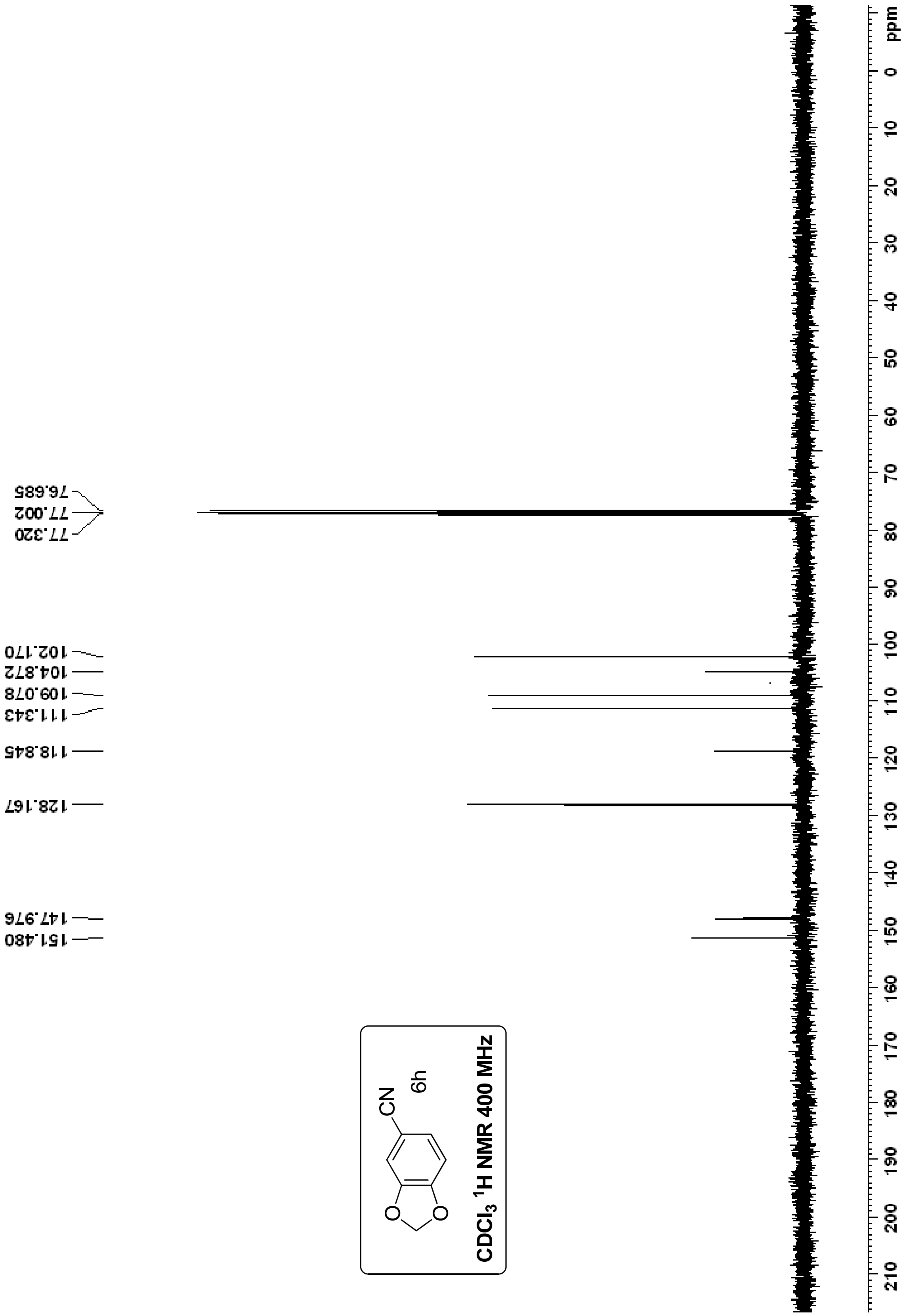

55.920
76.558
76.686
77.004
77.255
77.322
104.923
115.619
118.966
133.957
160.634
CN
O
6f
$CDCl_3$ ^{13}C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


0.000
5.114
7.008
7.030
7.257
7.355
7.367
7.376
7.386
7.403
7.414
7.573
7.595
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
2.00
2.00
4.96
2.00
CN
BnO
6g
CDCl3 1H NMR 400 MHz

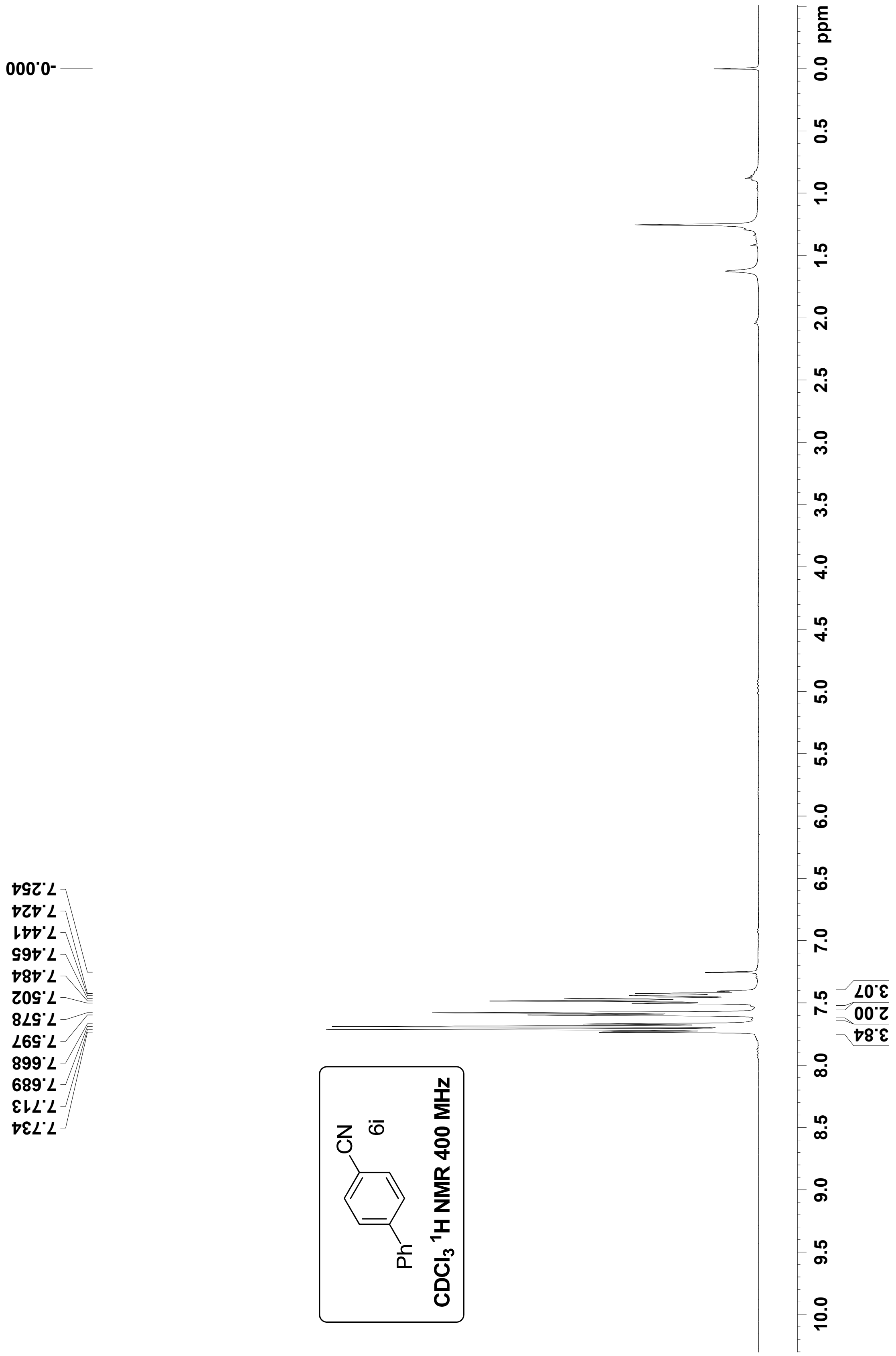
Electronic Supplementary Material (ESI) for Chemical Communications

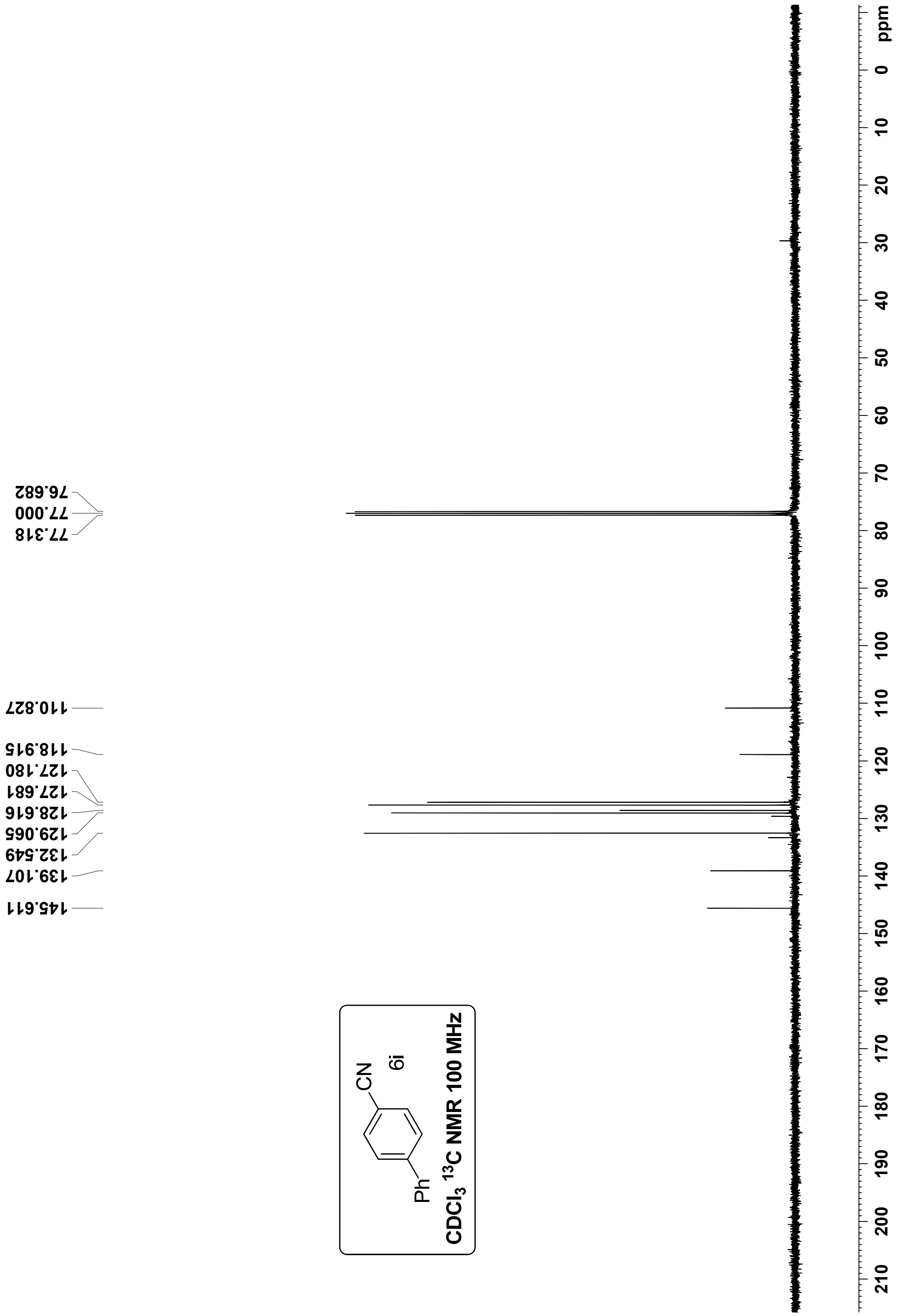


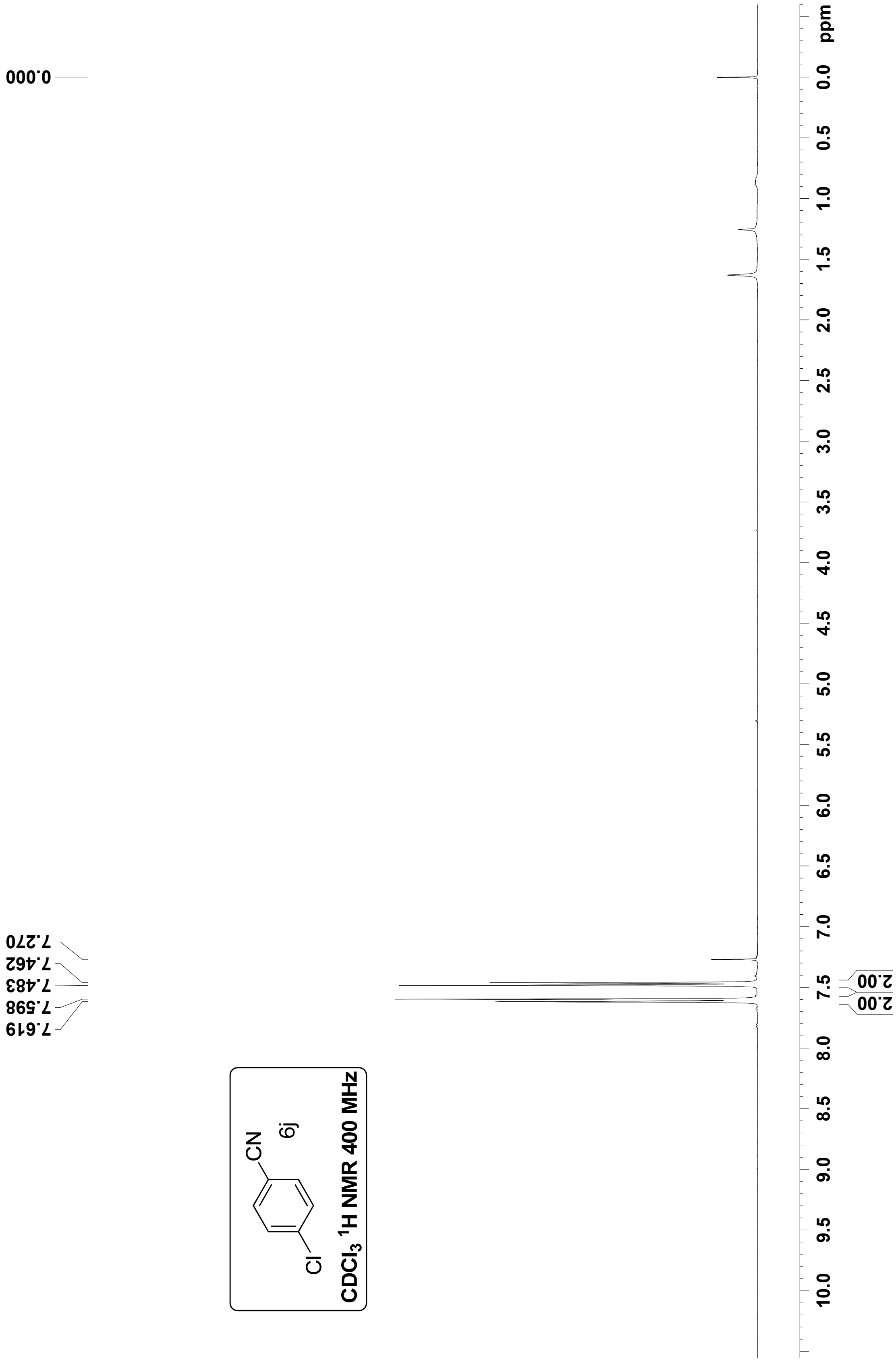

0.000
6.074
6.858
6.878
7.034
7.201
7.221
2.15
0.99
0.98
1.00
ppm
CN
6h
$CDCl_3$ ^1H NMR 400 MHz

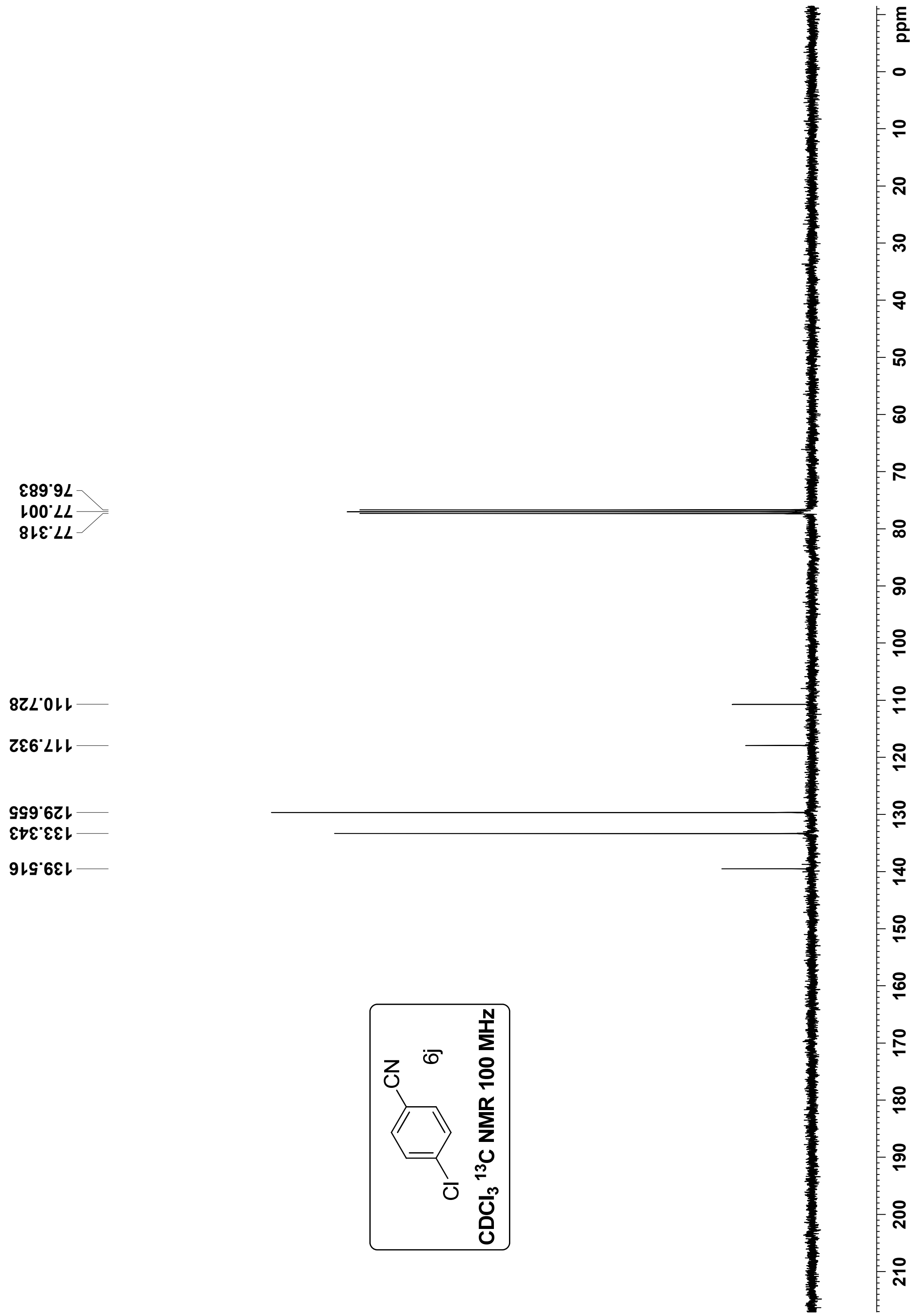


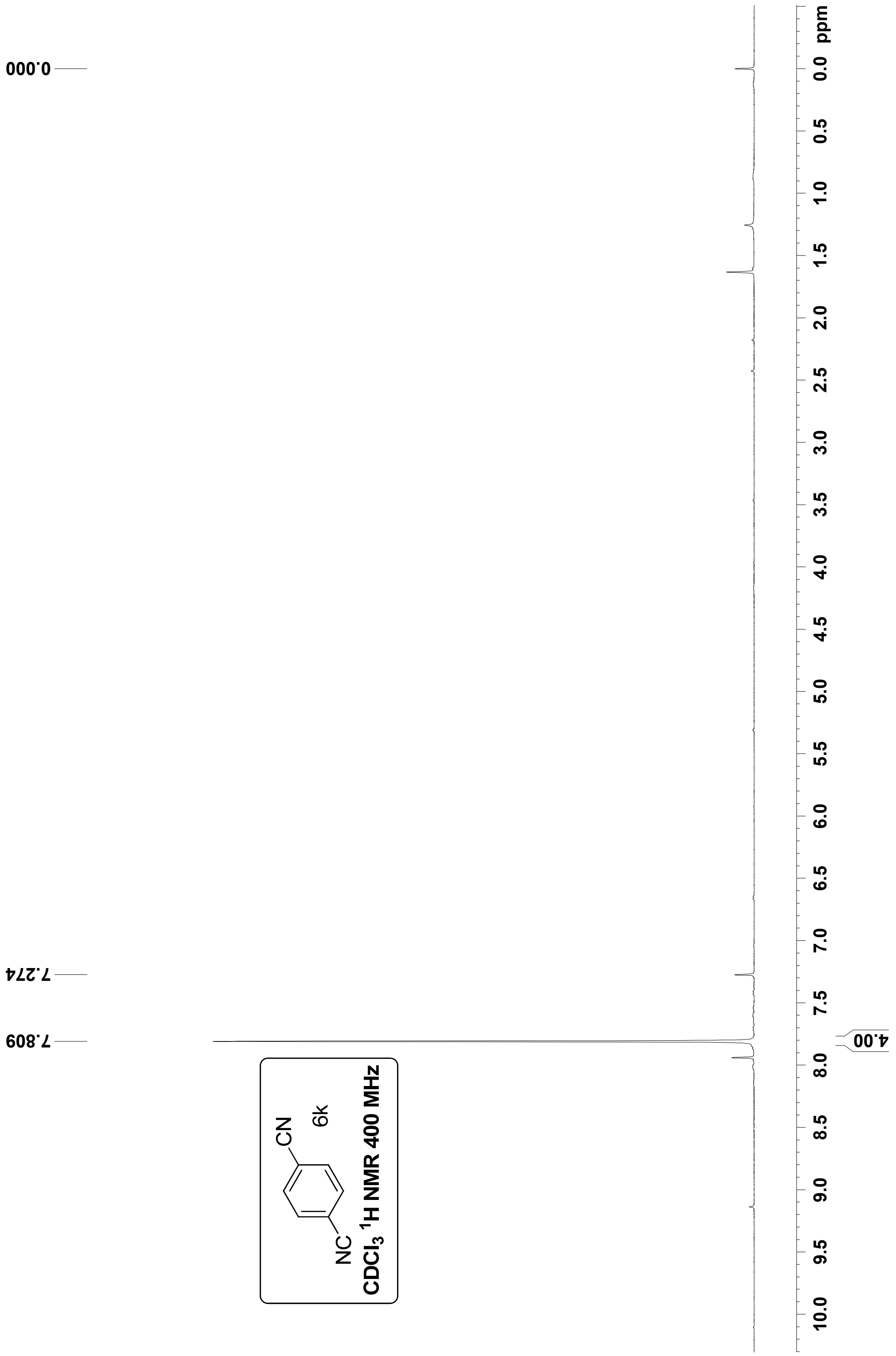
76.685
77.002
77.320
102.170
104.872
109.078
111.343
118.845
128.167
147.976
151.480
CN
6h
O
O
CDCl3 1H NMR 400 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

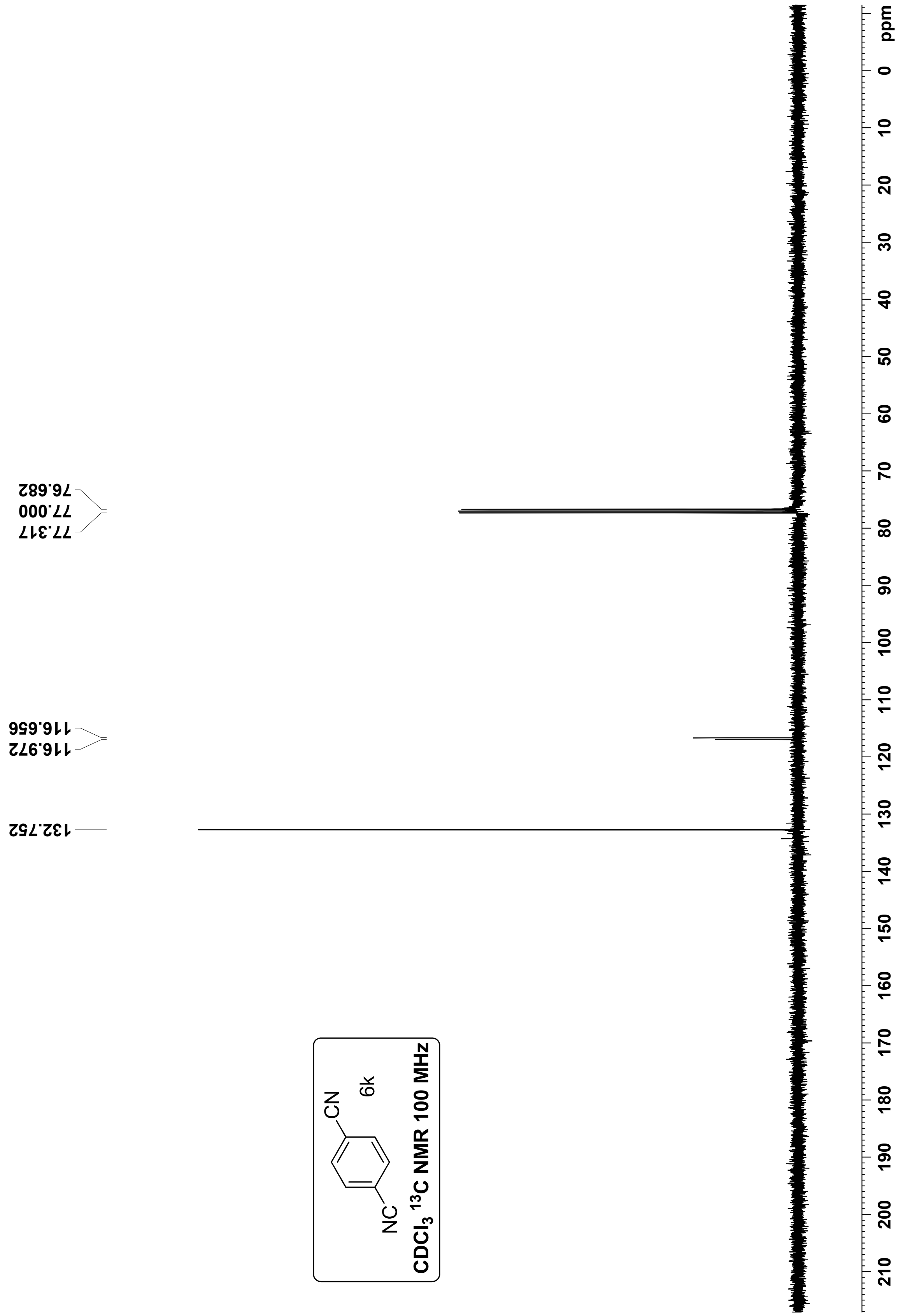

-0.000
7.254
7.424
7.441
7.465
7.484
7.502
7.578
7.597
7.668
7.689
7.713
7.734
CN
Ph
6i
CDCl3 1H NMR 400 MHz
3.07
2.00
3.84
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

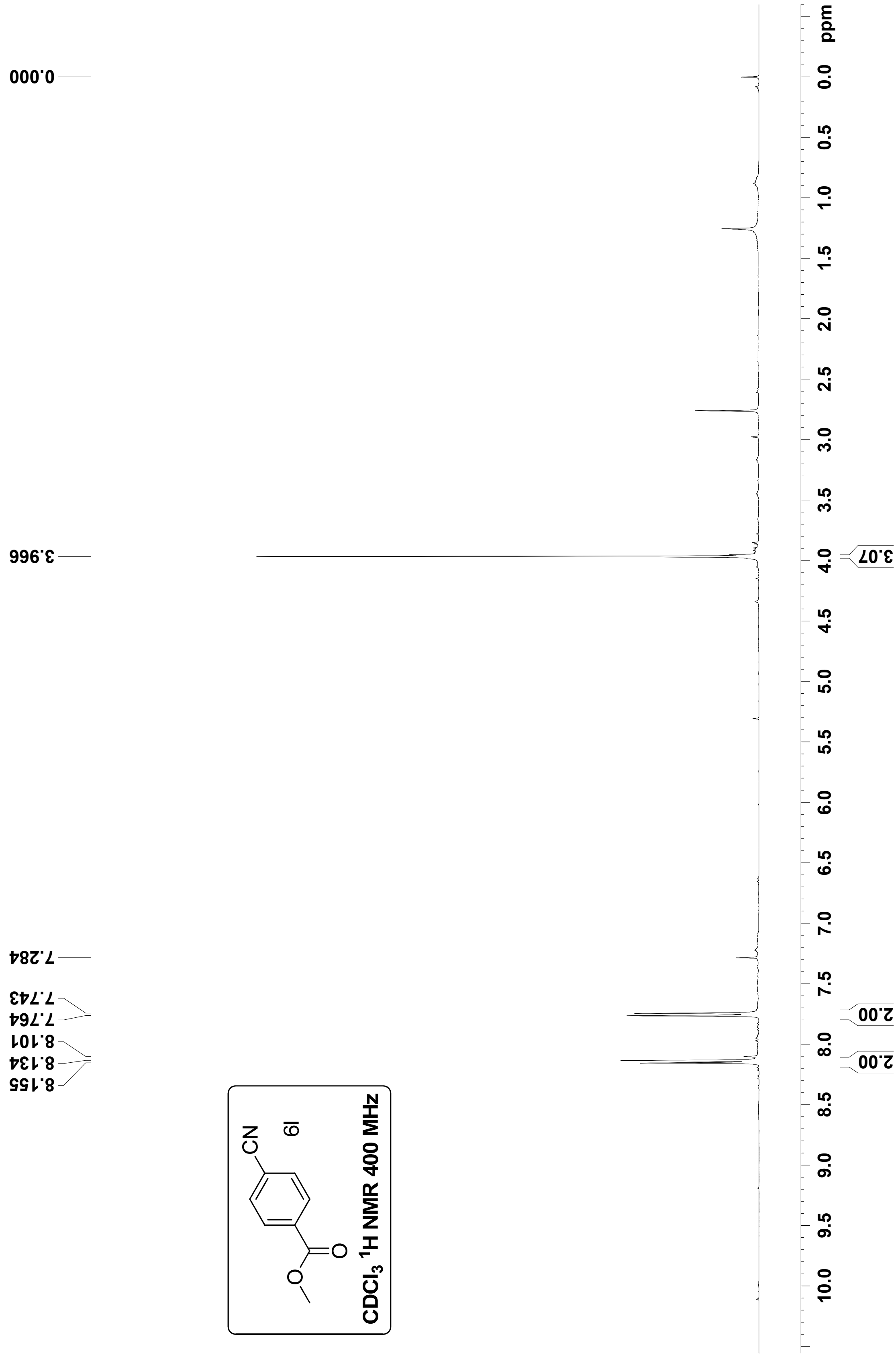

76.682
77.000
77.318
110.827
118.915
127.180
127.681
128.616
129.065
132.549
139.107
145.611
CN
6i
Ph
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

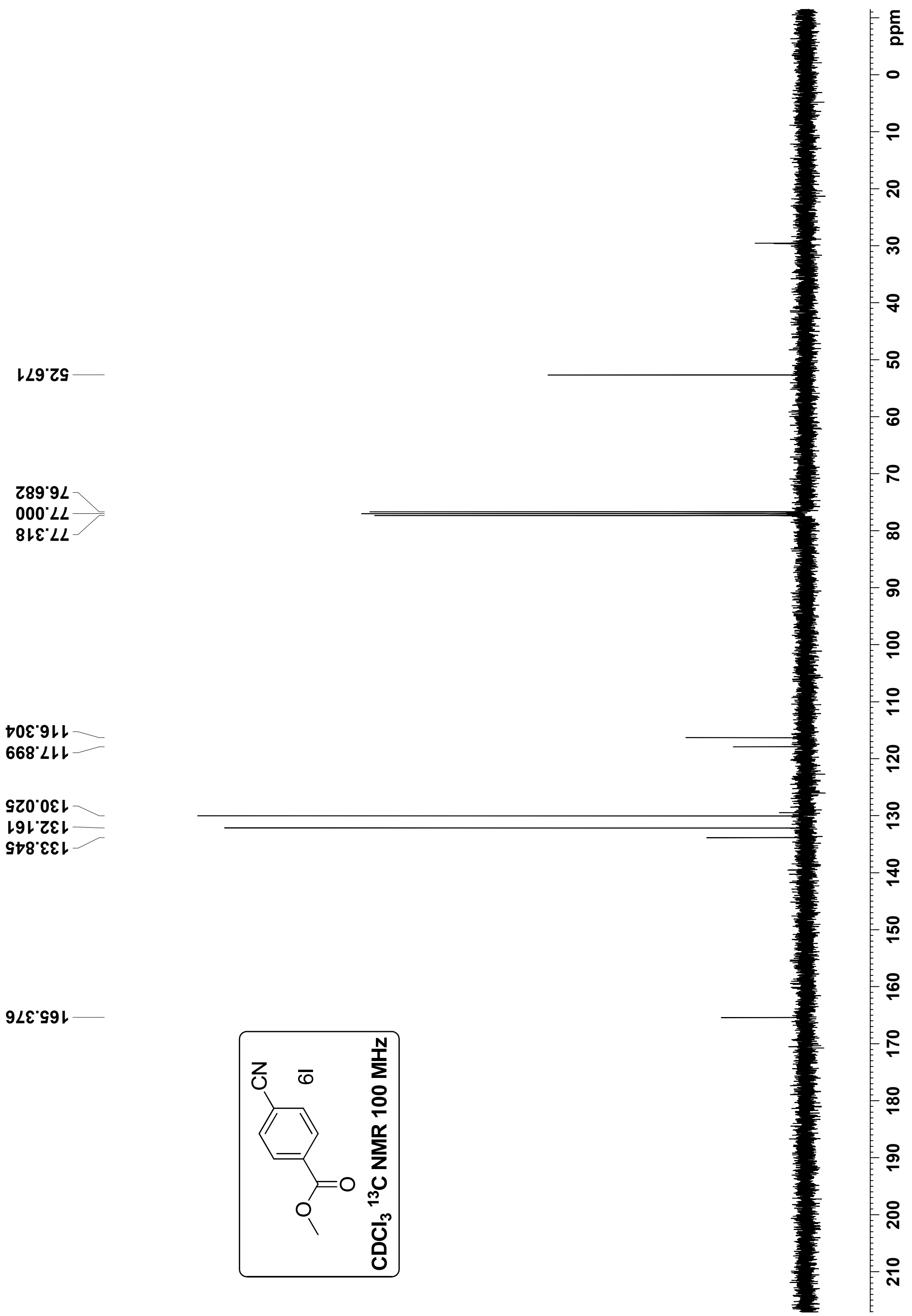

0.000
7.270
7.462
7.483
7.598
7.619
2.00
2.00
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
CN
Cl
6j
CDCl3 1H NMR 400 MHz

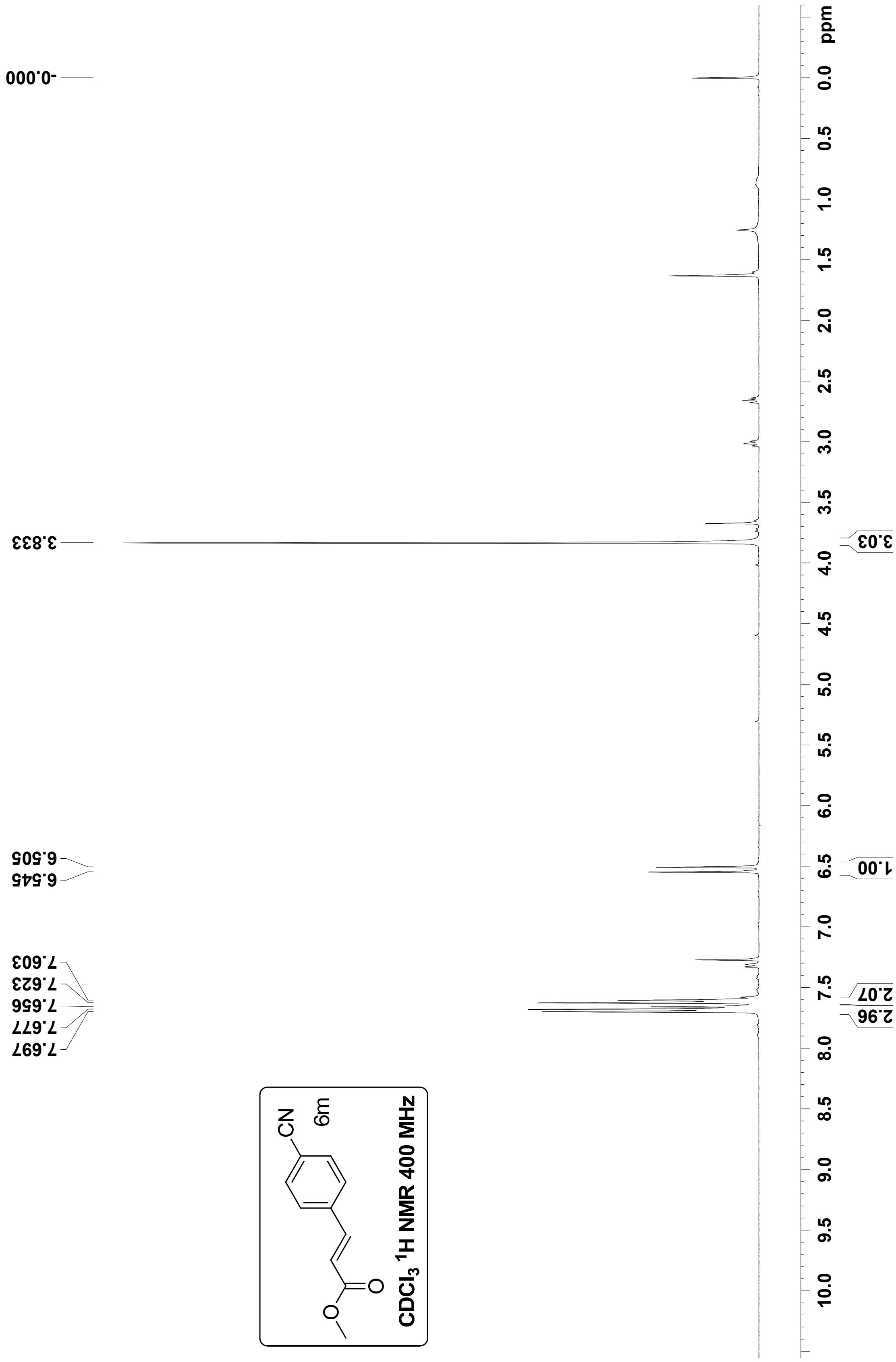

76.683
77.001
77.318
110.728
117.932
129.655
133.343
139.516
CN
Cl
6j
$CDCl_3$ ^{13}C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

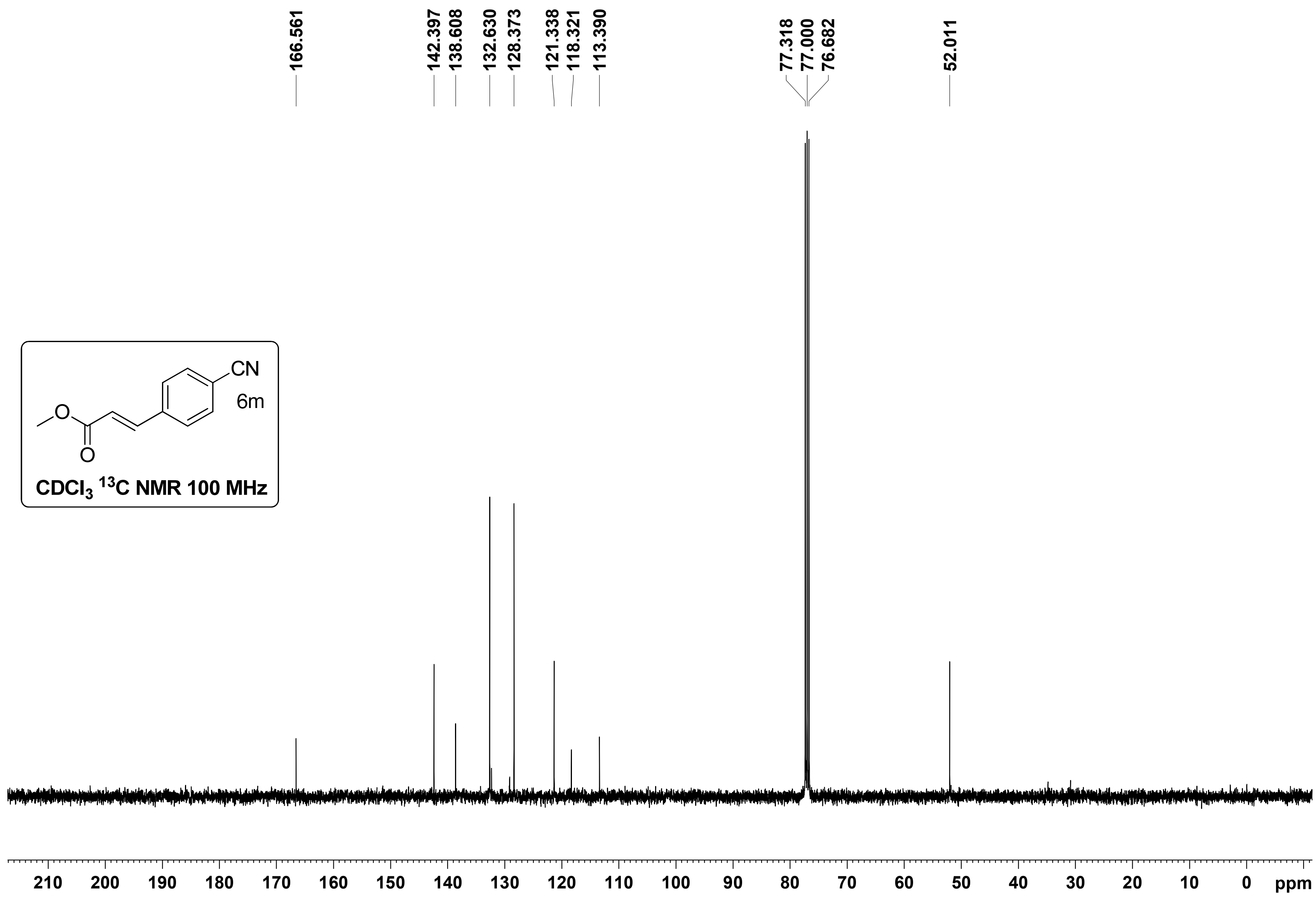

0.000
7.274
7.809
4.00
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
NC
CN
6k
CDCl3 1H NMR 400 MHz

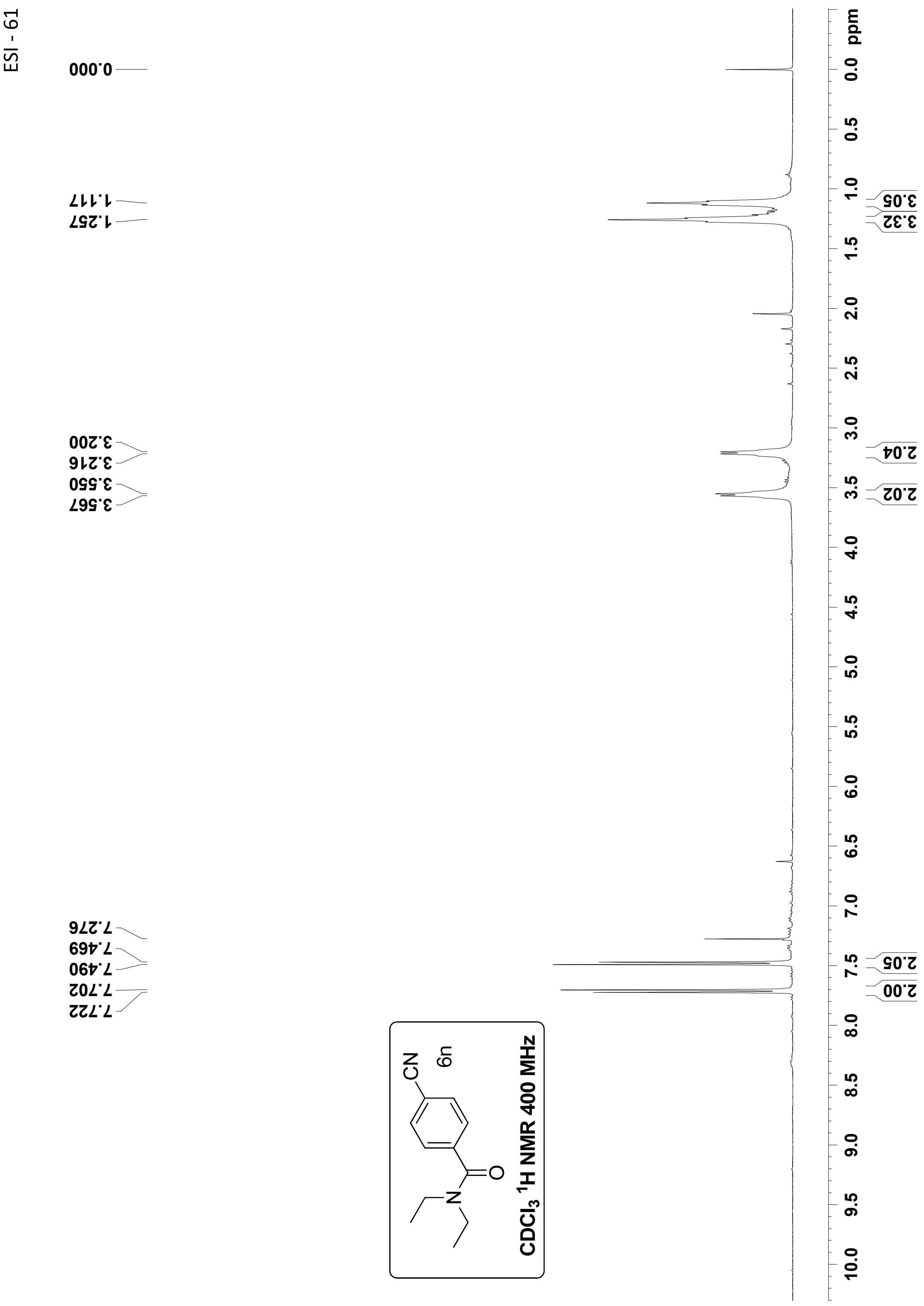

76.682
77.000
77.317
116.656
116.972
132.752
CN
NC
6k
$CDCl_3$ ^{13}C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

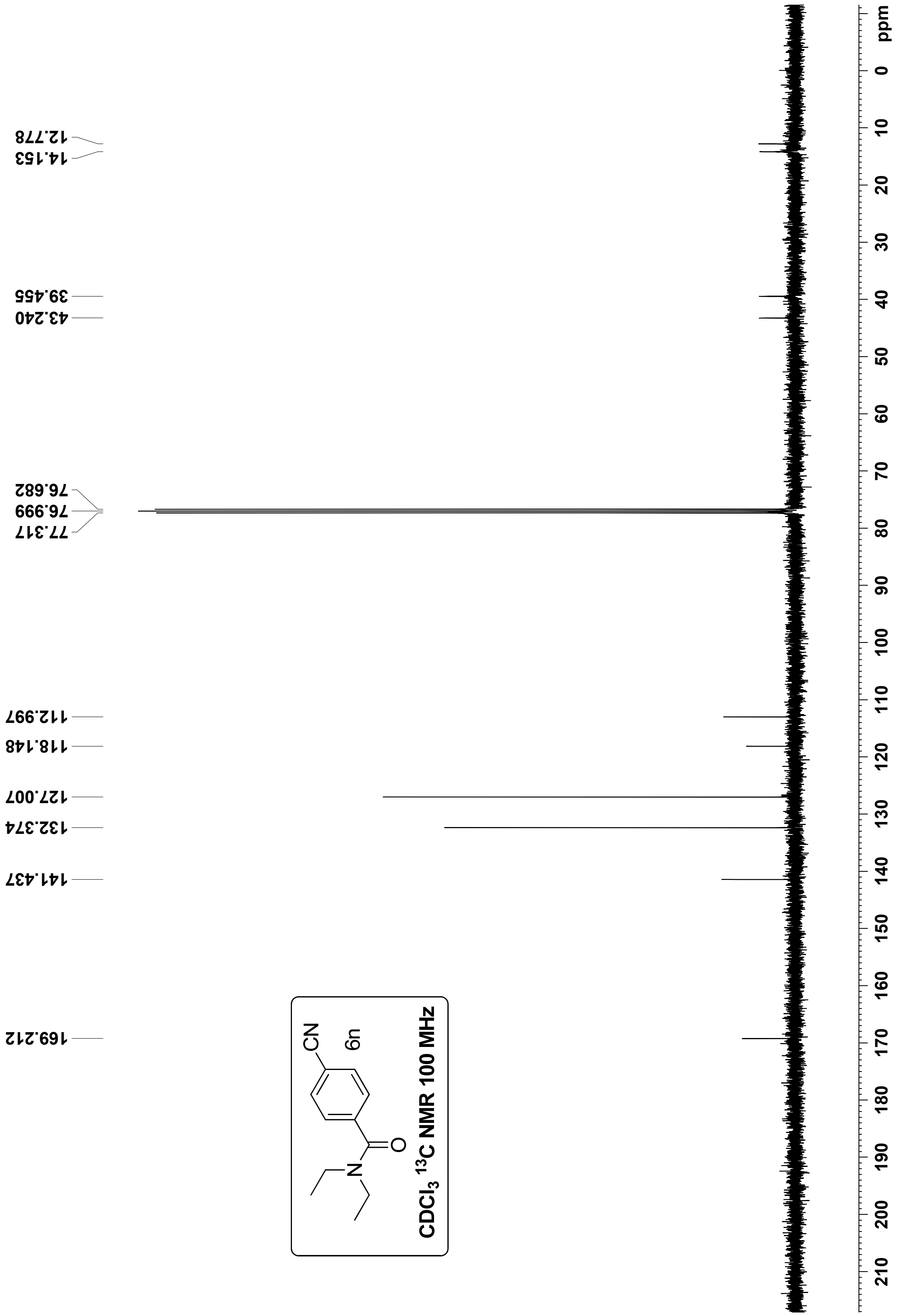

0.000
3.966
7.284
7.743
7.764
8.101
8.134
8.155
3.07
2.00
2.00
ppm
CN
O
O
6l
CDCl3 1H NMR 400 MHz

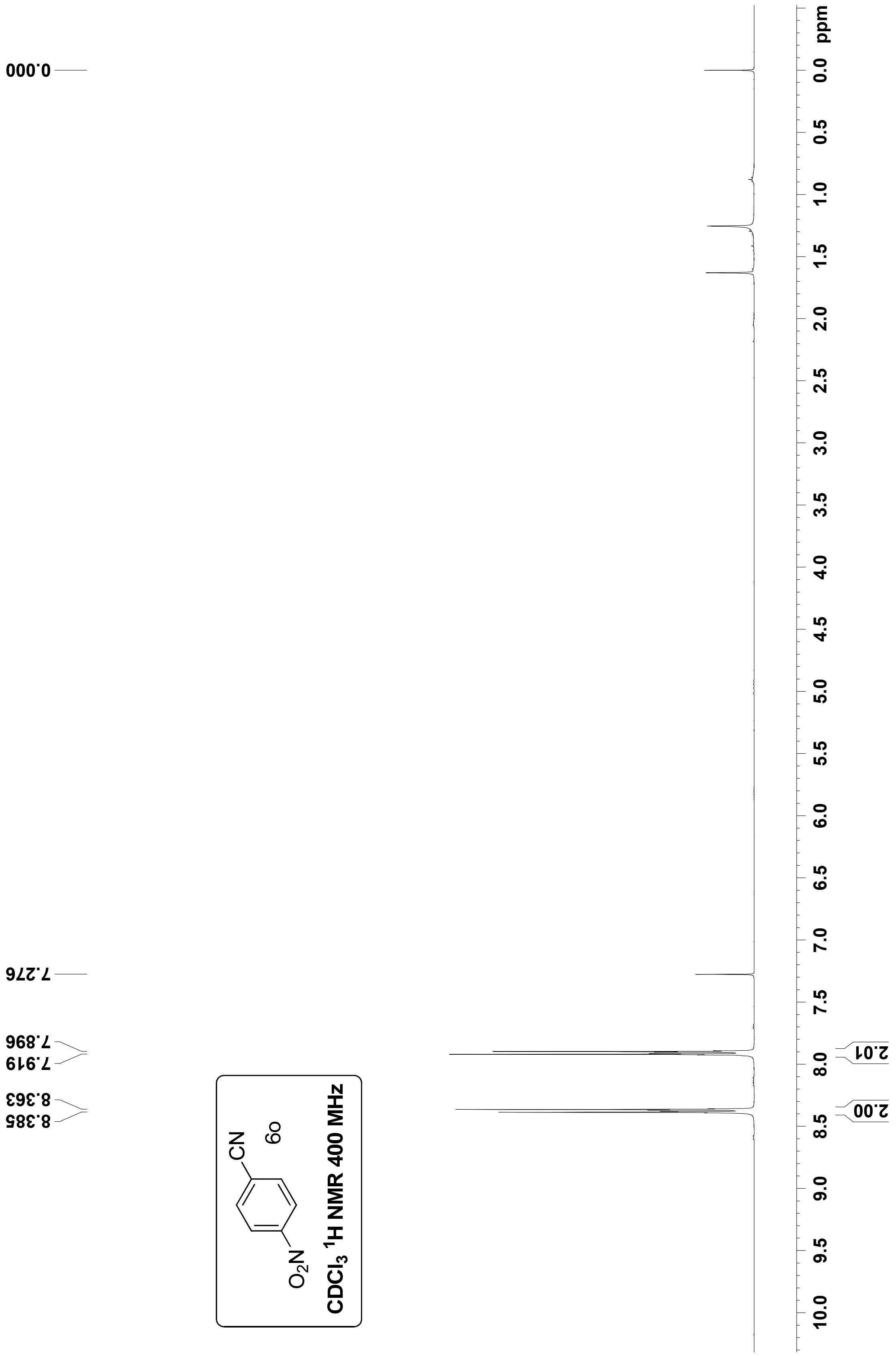

52.671
76.682
77.000
77.318
116.304
117.899
130.025
132.161
133.845
165.376
CN
O
O
6l
CDCl$_3$ ^{13}C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

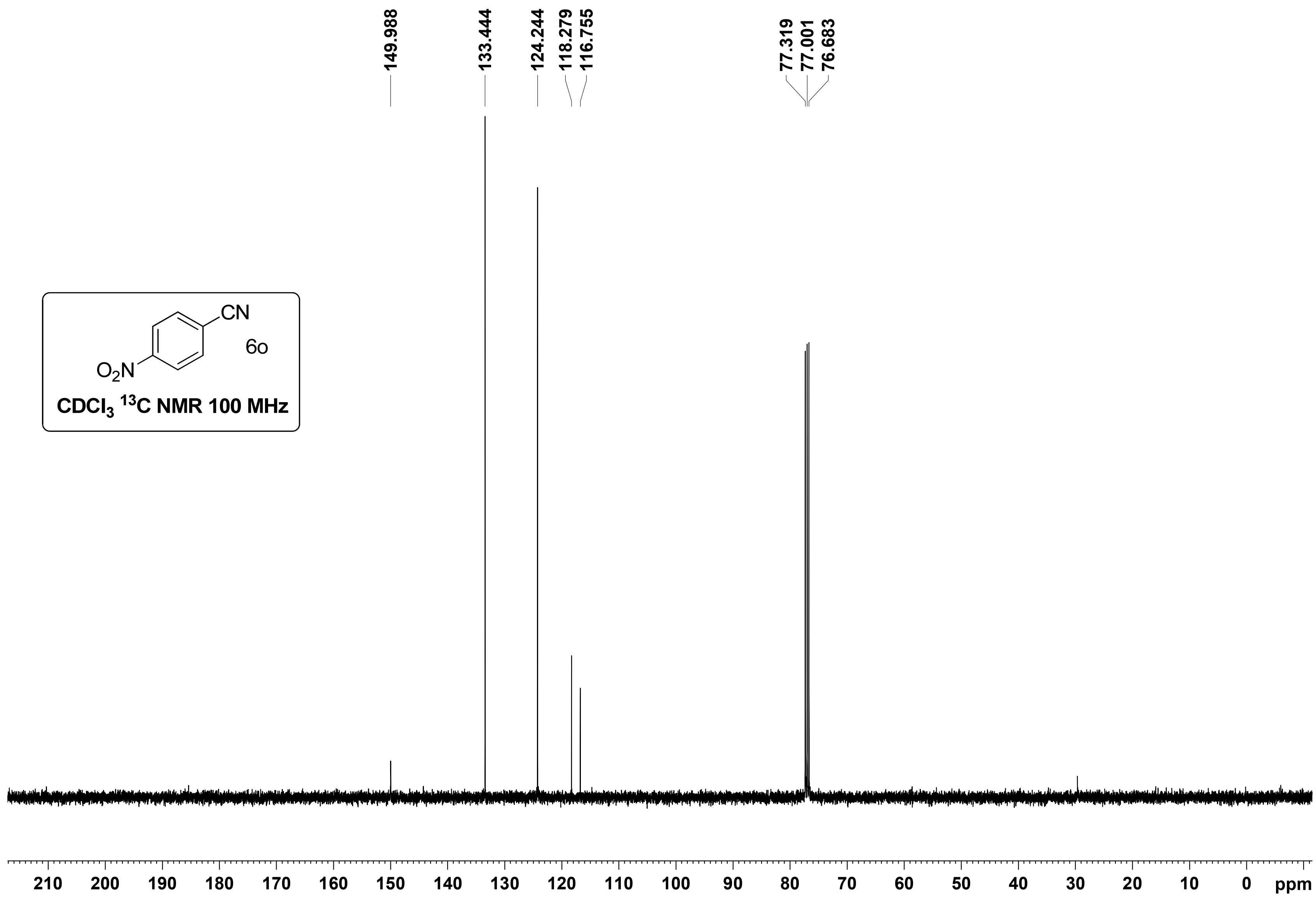

-0.000
3.833
6.505
6.545
7.603
7.623
7.656
7.677
7.697
3.03
1.00
2.07
2.96
ppm
CN
6m
CDCl3 1H NMR 400 MHz

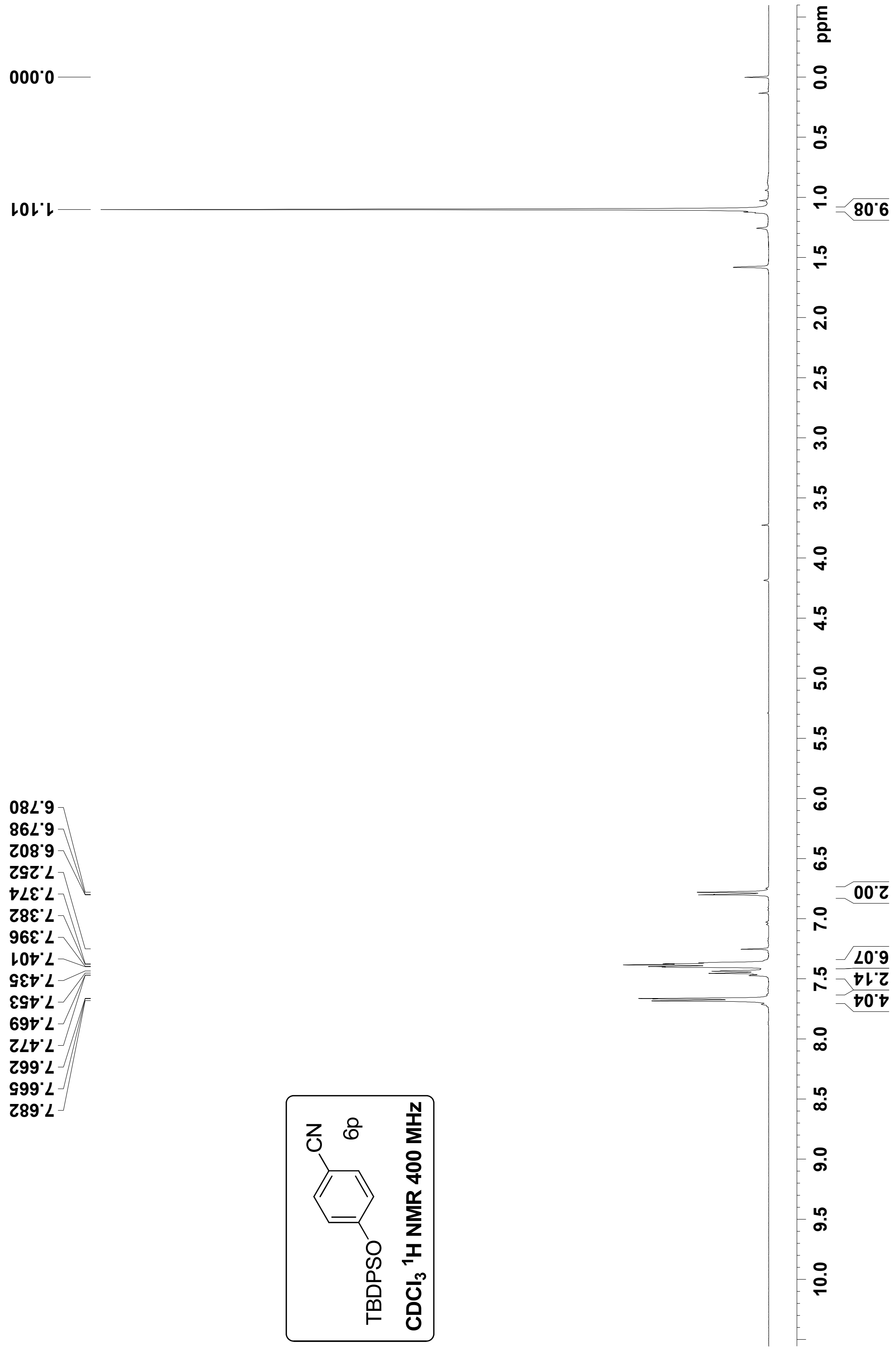

166.561
142.397
138.608
132.630
128.373
121.338
118.321
113.390
77.318
77.000
76.682
52.011
CN
6m
O
O
CDCl3 13C NMR 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

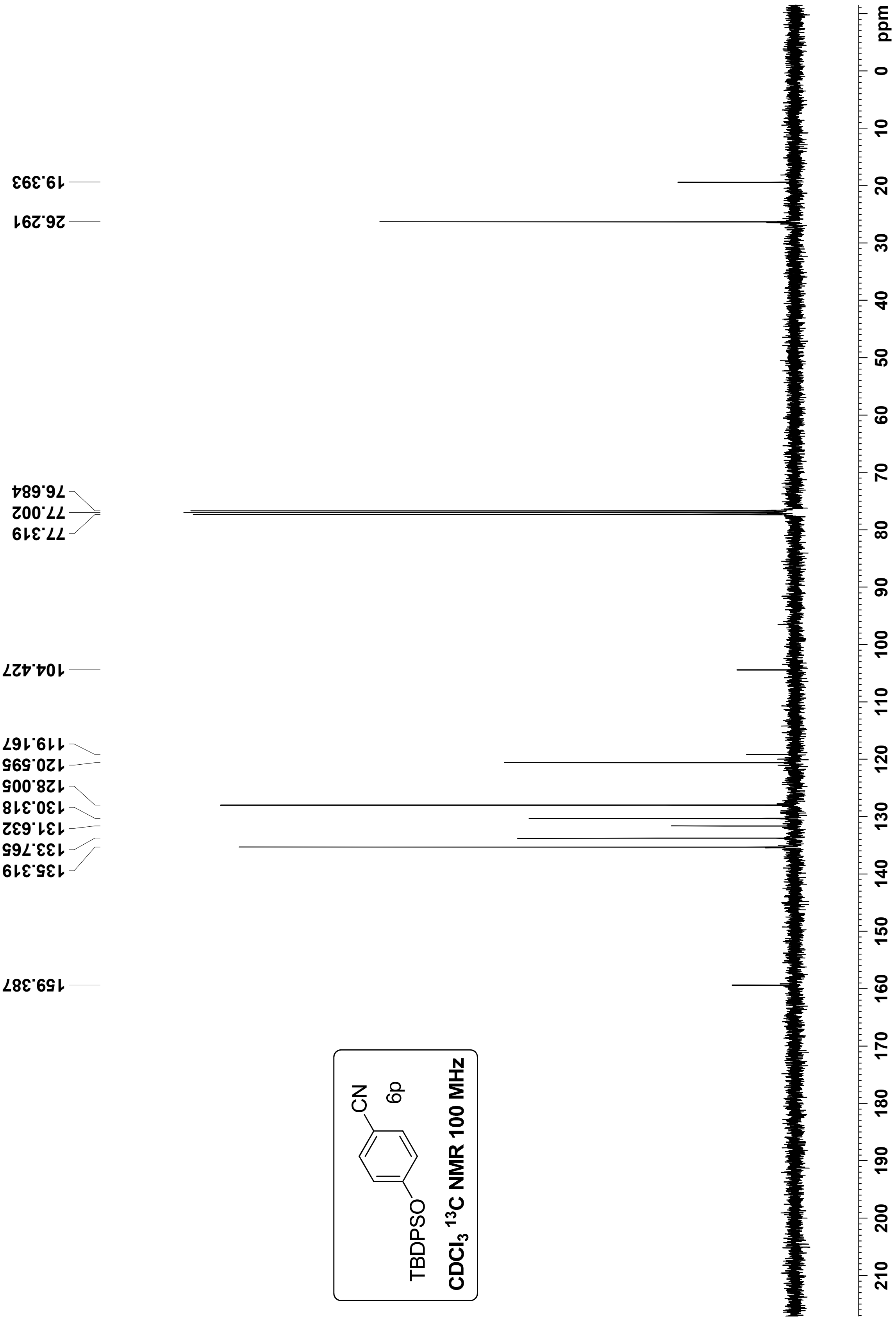

ESI - 61
0.000
1.117
1.257
3.200
3.216
3.550
3.567
7.276
7.469
7.490
7.702
7.722
3.05
3.32
2.04
2.02
2.05
2.00
ppm
CN
6n
O
N
CDCl$_3$ ^{1}H NMR 400 MHz

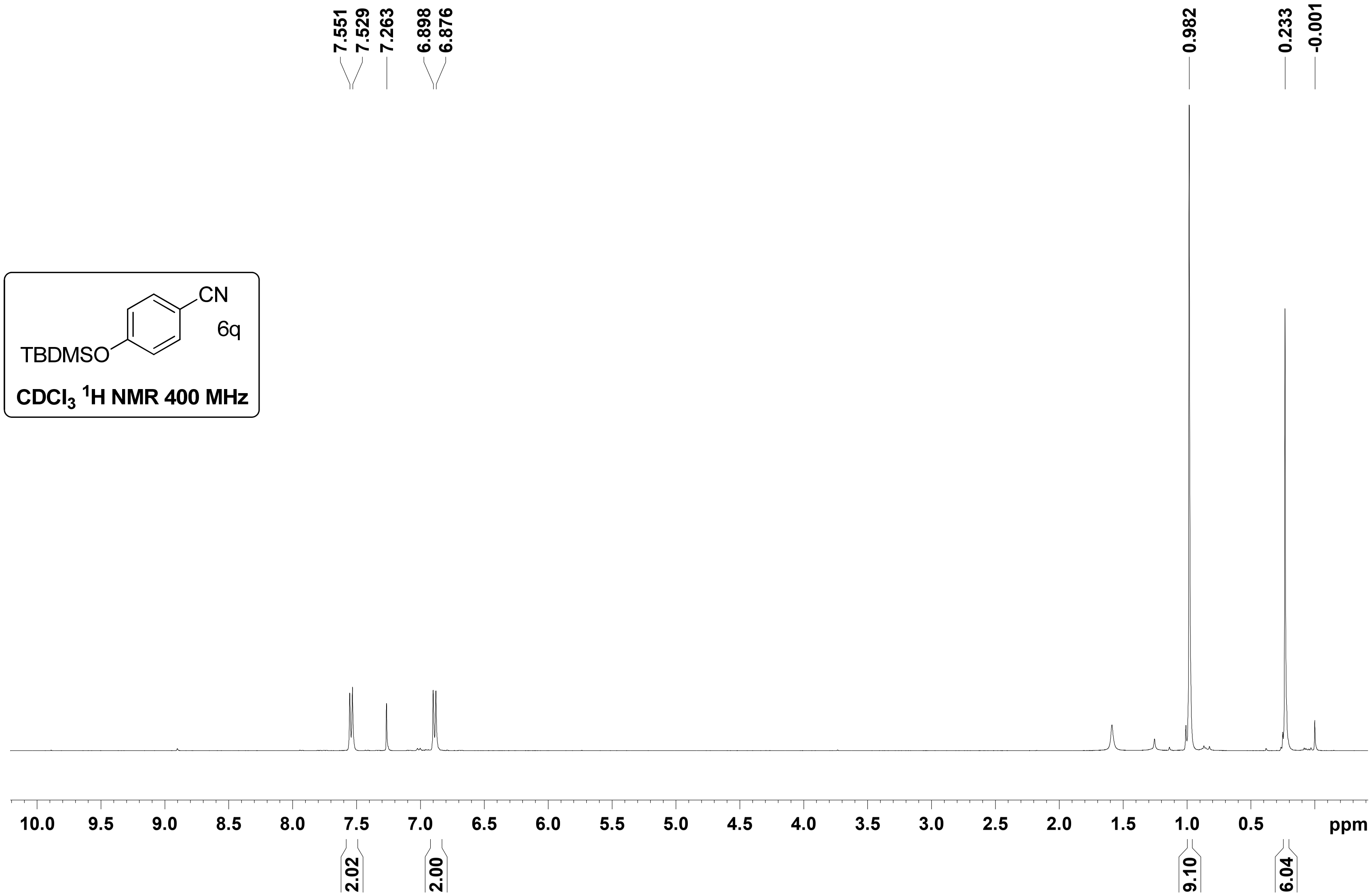

12.778
14.153
39.455
43.240
76.682
76.999
77.317
112.997
118.148
127.007
132.374
141.437
169.212
CN
6n
N
O
CDCl3 13C NMR 100 MHz
ppm


0.000
7.276
7.896
7.919
8.363
8.385
CN
O_2N
6o
$CDCl_3$ ^1H NMR 400 MHz
2.01
2.00
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

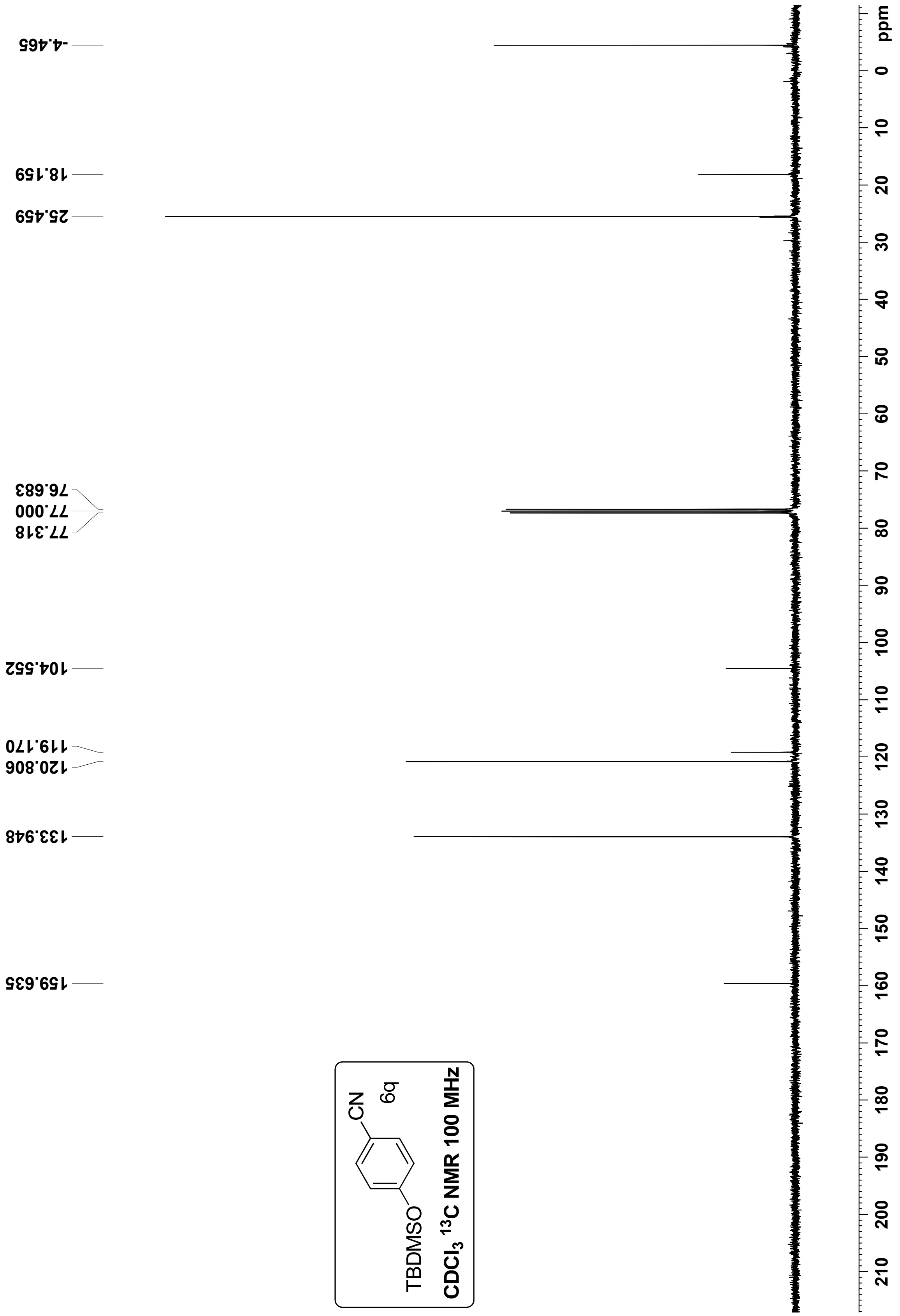

149.988
133.444
124.244
118.279
116.755
77.319
77.001
76.683
CN
6o
O2N
CDCl3 13C NMR 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

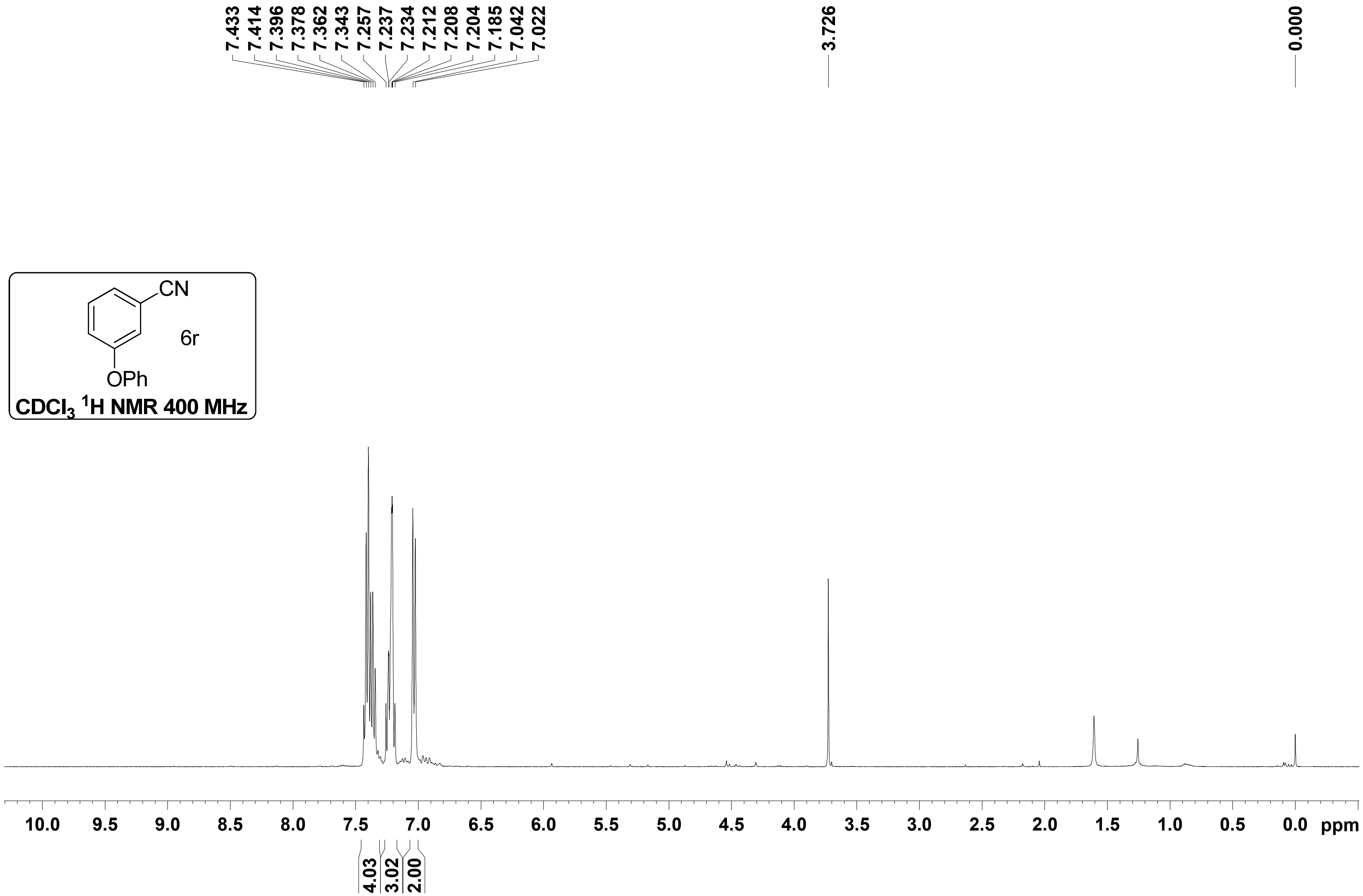

0.000
1.101
6.780
6.798
6.802
7.252
7.374
7.382
7.396
7.401
7.435
7.453
7.469
7.472
7.662
7.665
7.682
9.08
2.00
6.07
2.14
4.04
ppm
TBDPSO
CN
6p
CDCl3 1H NMR 400 MHz


19.393
26.291
76.684
77.002
77.319
104.427
119.167
120.595
128.005
130.318
131.632
133.765
135.319
159.387
TBDPSO
CN
6p
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

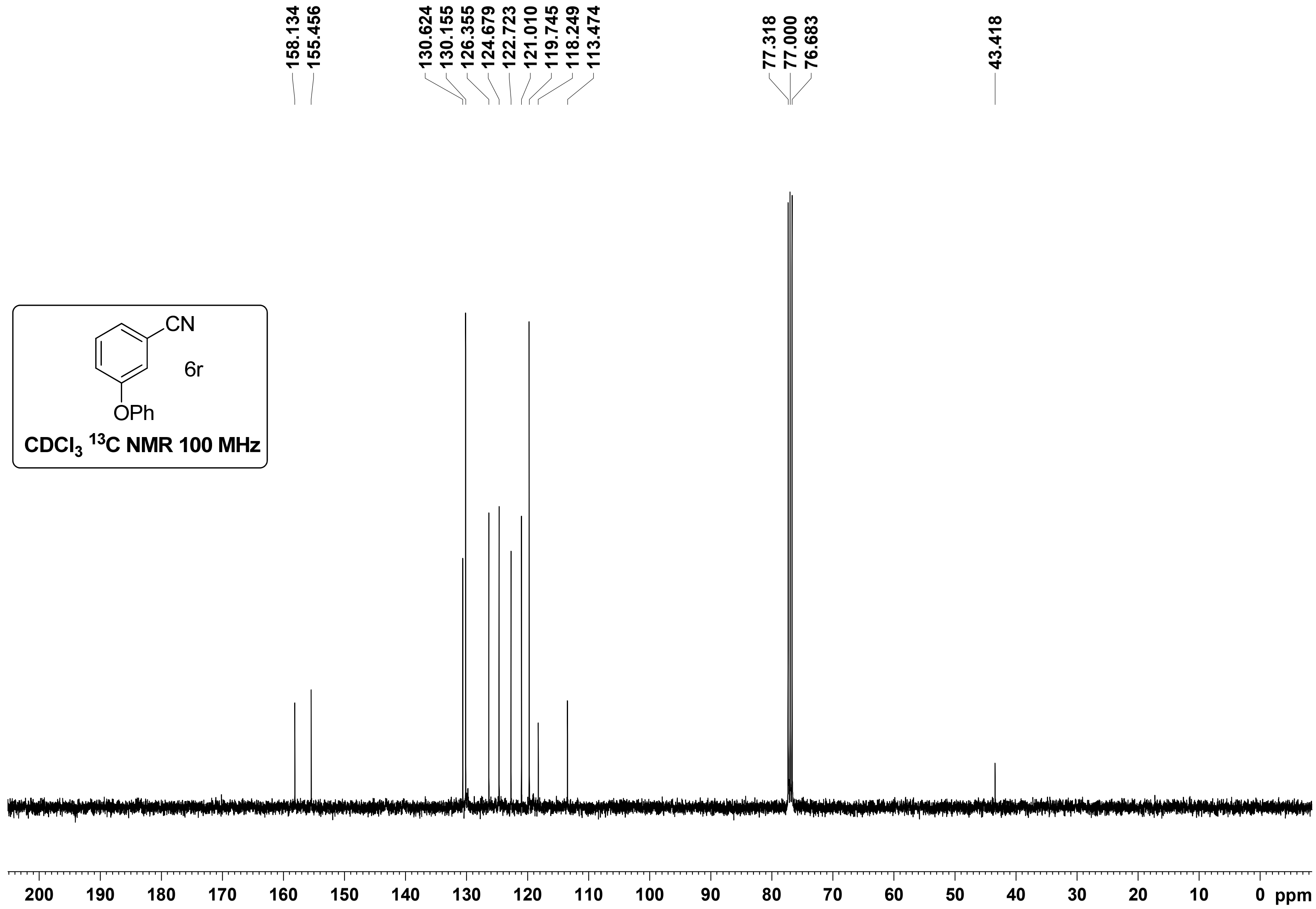

7.551
7.529
7.263
6.898
6.876
0.982
0.233
-0.001
CN
6q
TBDMSO
CDCl3 1H NMR 400 MHz
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
2.00
9.10
6.04

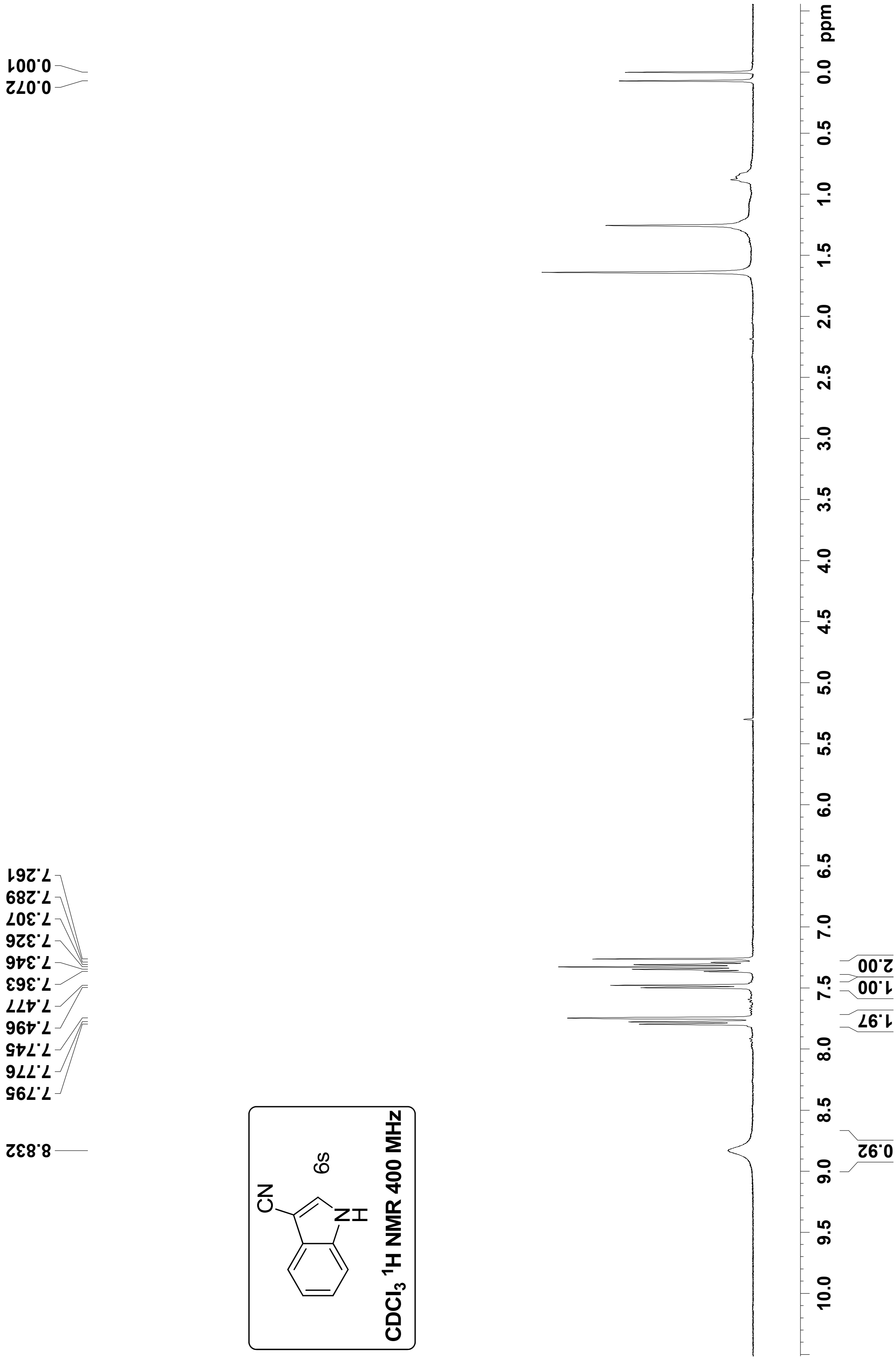
Electronic Supplementary Material (ESI) for Chemical Communications

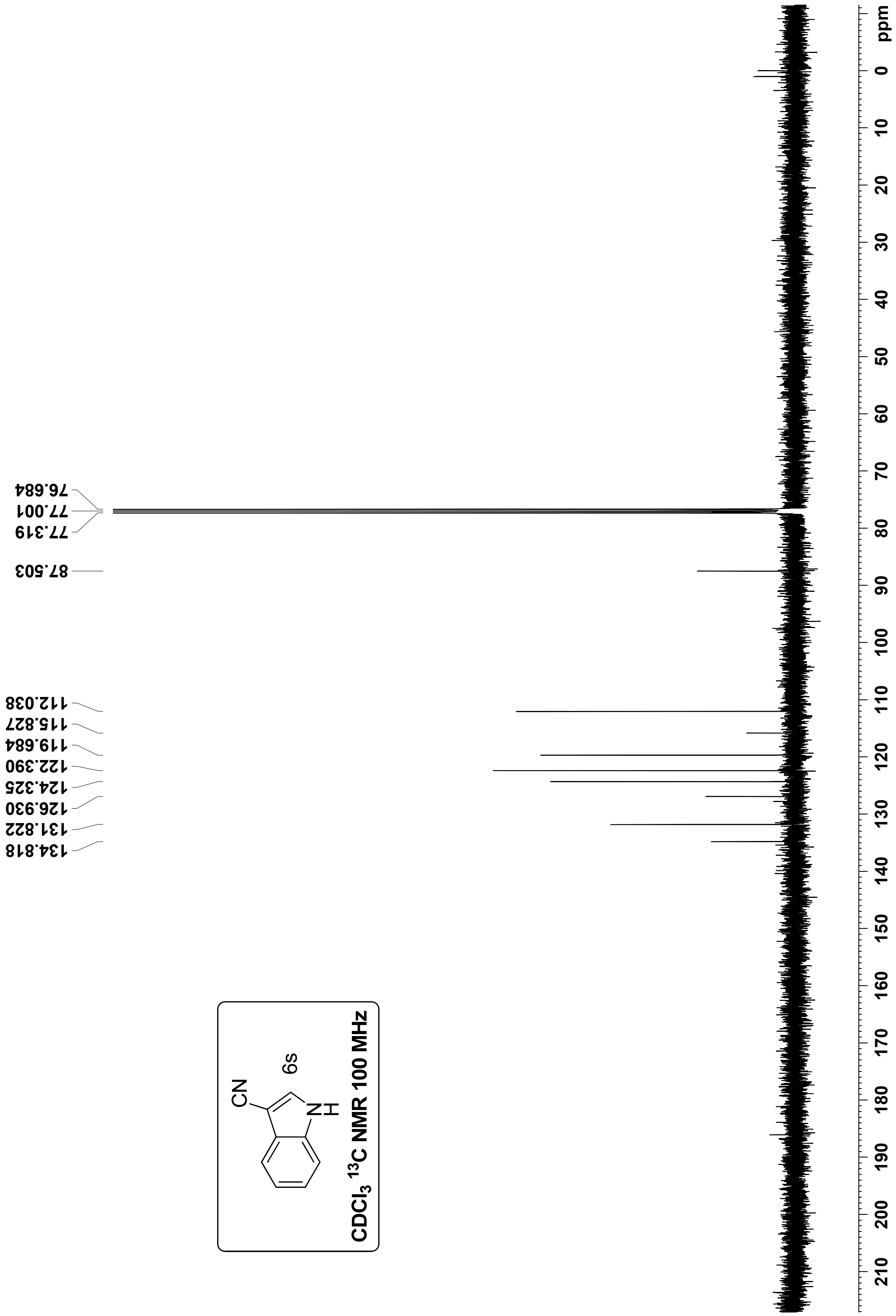



7.433
7.414
7.396
7.378
7.362
7.343
7.257
7.237
7.234
7.212
7.208
7.204
7.185
7.042
7.022
3.726
0.000
CN
6r
OPh
CDCl3 1H NMR 400 MHz
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.03
3.02
2.00

Electronic Supplementary Material (ESI) for Chemical Communications




0.001
0.072
7.261
7.289
7.307
7.326
7.346
7.363
7.477
7.496
7.745
7.776
7.795
8.832
CN
N
H
6s
CDCl3 1H NMR 400 MHz
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
2.00
1.00
1.97
0.92


76.684
77.001
77.319
87.503
112.038
115.827
119.684
122.390
124.325
126.930
131.822
134.818
CN
6s
N
H
CDCl3 13C NMR 100 MHz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210