Supporting Information for:

Copper-catalyzed decarboxylative cross-coupling of cinnamic acids and ACCN *via* single electron transfer

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CONTENTS

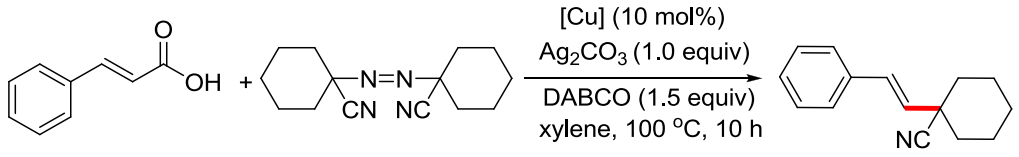
1. General experiment details and materials

Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under argon atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument(ESI). Cinnamic acids and 1,1'-azobis(cyclohexanecarbonitrile) (ACCN) used here were known compounds and purchased from Sigma-Aldrich or Alfa aesar. The subustrates **1k**-**1r** were prepared accoording to the reported methods[1-3].

2. Optimization of the reaction conditions

Cinnamic acid **1a** (0.5 mmol, 74 mg), ACCN (0.5 mmol, 122 mg), DABCO (0.75 mmol, 84 mg), silver salt, [Cu] were added to a 25 mL flame-dried Young-type tube. The tube was replaced with nitrogen atmosphere three times and 2 mL of xylene were added under nitrogen atmosphere, and then stirred at 100 °C for 24 hours. After evaporation of the solvent under reduced pressure, yields of product **3a** were determined by GC using *n*-hexadecane as an internal standard.

Table S1 Screening of catalyst[a]

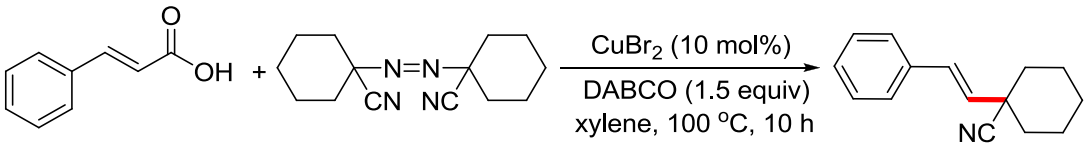


1a **2a** **3a**

Entry	[Cu]	Yield(%)[b]
1	CuTc	31
2	$Cu(OTf)_2$	20
3	CuBr	34
4	**$CuBr_2$**	**36**
5	CuF_2	31
6	$Cu(acac)_2$	6
7	Cu_2O	25
8	$CuSO_45H_2O$	15
9	$Cu(OAc)_2$	31
10	$CuCl_2$	33
11	CuCl	11
12	$Cu(BF_4)6H_2O$	30
13	Cu(2-ethylhexanoate)	18

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a** (0.5 mmol), DABCO (0.75 mmol), Ag_2CO_3 (0.5 mmol), [Cu] (10 mol%), xylene (2 mL), 100 °C, 10 h. [b] yield determined by GC using *n*-hexadecane as an internal standard.

Table S2 Screening of oxidant[a]

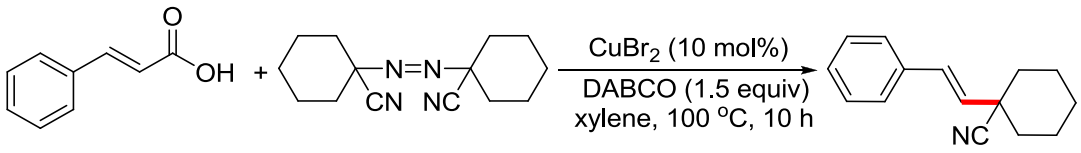


1a **2a** **3a**

Entry	Oxidant	Yield(%)[b]
1	**AgOAc**	**38**
2	AgOTf	26
3	AgF	19
4	$AgClO_4$	trace
5	$AgBrO_3$	19
6	Ag_2CO_3	36

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a**(0.5 mmol), DABCO (0.75 mmol), oxidant (1.0 mmol), $CuBr_2$ (10 mol%), xylene (2 mL), 100 °C, 10 h. [b] yield determined by GC using *n*-hexadecane as an internal standard.

Table S3 Screening of the amount of AgOAc[a]

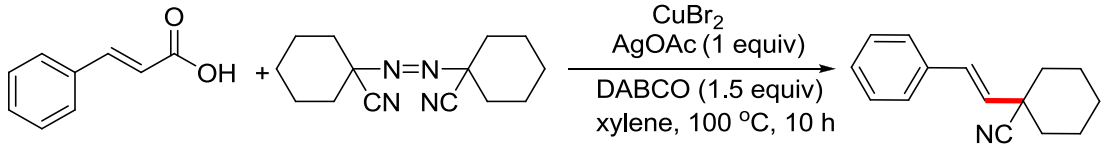


1a **2a** **3a**

Entry	The amount of AgOAc	Yield(%)[b]
1	0.5 equiv	31
2	**1.0 equiv**	**40**
3	2.0 equiv	38
4	3.0 equiv	38

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a** (0.5 mmol), DABCO (0.75 mmol), AgOAc, $CuBr_2$ (10 mol%), xylene(2 mL), 100 °C, 10 h. [b] yield determined by GC using *n*-hexadecane as an internal standard.

Table S4 Screening of the amount of $CuBr_2$[a]

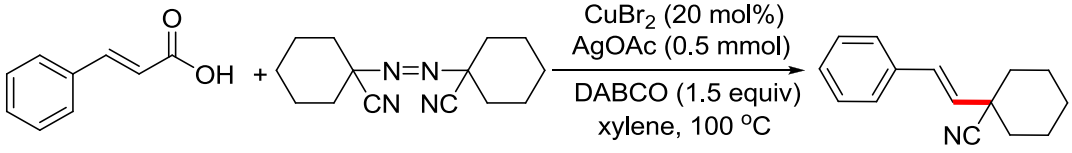


1a **2a** **3a**

Entry	The amount of $CuBr_2$	Yield(%)[b]
1	5 mol%	33
2	10 mol%	40
3	**20 mol%**	**44**
4	30 mol%	41

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a** (0.5 mmol), DABCO (0.75 mmol), AgOAc (0.5 mmol), $CuBr_2$, xylene (2 mL), 100 °C, 10 h. [b] yield determined by GC using *n*-hexadecane as an internal standard.

Table S5 The effect of reaction time[a]

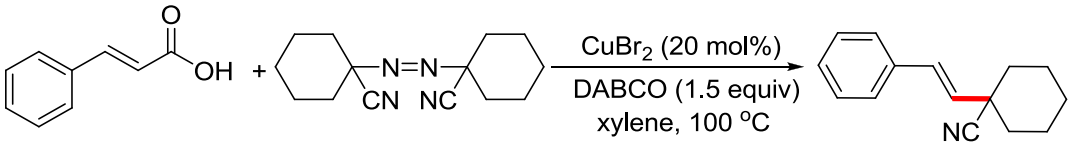


1a **2a** **3a**

Entry	t (h)	Yield(%)[b]
1	10	44
2	18	45
3	**24**	**55**

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a** (0.5 mmol), DABCO (0.75 mmol), AgOAc (0.5 mmol), $CuBr_2$ (20 mol%), xylene(2 mL), 100 °C. [b] yield determined by GC using *n*-hexadecane as an internal standard.

Table S6 The effect of other oxidant[a]

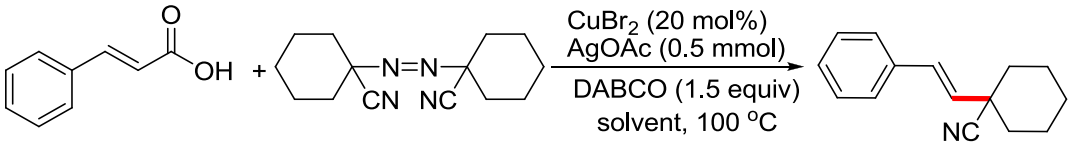


1a **2a** **3a**

Entry	Oxidant	Yield(%)[b]
1	$Na_2S_2O_8$	22
2	$K_2S_2O_8$	31
3	Oxone	24
4	BQ	trace
5	TBHP	13
6	DTBP	14

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a** (0.5 mmol), DABCO (0.75 mmol), Oxidant (0.5 mmol), $CuBr_2$ (20 mol%), xylene(2 mL), 100 °C, 24 h. [b] yield determined by GC using *n*-hexadecane as an internal standard.

Table S7 The effect of solvent [a]

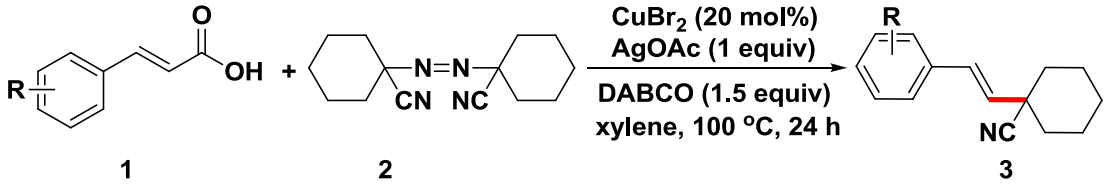


1a **2a** **3a**

Entry	solvent	Yield(%)[b]
1	THF	27
2	1,4-dioxane	49
3	CH_3NO_2	nr
4	CH_3CN	45
5	CH_3OH	19
6	DCE	11

[a]Reaction conditions: cinnamic acid **1a** (0.5 mmol), ACCN **2a** (0.5 mmol), DABCO (0.75 mmol), AgOAc (0.5 mmol), $CuBr_2$ (20 mol%), solvent (2 mL), 100 °C, 24 h. [b] yield determined by GC using *n*-hexadecane as an internal standard.

3. General procedure for the decarboxylation coupling

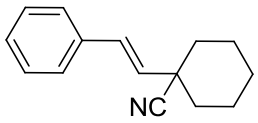


1 2 3

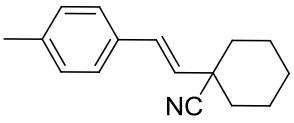
Cinnamic acid (0.5 mmol), ACCN (0.5 mmol, 122 mg), DABCO (1.5 mmol, 84 mg), AgOAc (0.5 mmol, 84 mg), $CuBr_2$ (0.1 mmol, 20 mol%) were added to a 25 mL flame-dried Young-type tube. The tube was replaced with nitrogen atmosphere three times and 2 mL of xylene were added under nitrogen atmosphere, and then stirred at 100 ^{o}C for 24 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel to give the desired product **3**.

4. Experimental characterization data for products

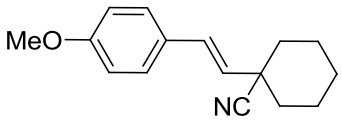
(*E*)-1-styrylcyclohexanecarbonitrile (3a): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 54.5 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.39 (m, 5H), 6.78 (d, *J* = 16 Hz, 1H), 5.99 (d, *J* = 16 Hz, 1H), 2.01 (d, *J* = 12.8 Hz, 2H), 1.66-1.81 (m, 5H), 1.47-1.55 (m, 2H), 1.19-1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 130.4, 130.2, 128.7, 128.1, 126.6, 122.1, 41.7, 36.4, 24.9, 22.9; HRMS (ESI) calcd. for $C_{15}H_{17}NNa$ [M+Na]: 234.1253, found: 234.1254.



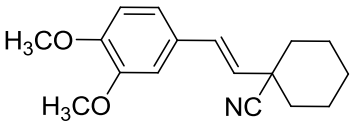
(*E*)-1-(4-methylstyryl)cyclohexanecarbonitrile (3b): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 66.4 mg, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 5.94 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 3H), 2.0 (d, *J* = 12.8 Hz, 2H), 1.66-1.80 (m, 5H), 1.47-1.54 (m, 2H), 1.18-1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 133.3, 130.1, 129.4, 129.4, 126.5, 122.2, 41.6, 36.5, 24.9, 22.9, 21.2; HRMS (ESI) calcd. for $C_{16}H_{19}NNa$ [M+Na]: 248.1410, found: 248.1411.



(*E*)-1-(4-methoxystyryl)cyclohexanecarbonitrile (3c): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 67.0 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.34 (m, 2H), 6.85-6.88 (m, 2H), 6.71 (d, *J* = 16.0 Hz, 1H), 5.86 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 2.01 (d, *J* = 12.8 Hz, 2H), 1.65-1.81 (m, 5H), 1.47-1.54 (m, 2H), 1.18-1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 129.6, 128.8, 128.2, 127.7, 122.3, 114.1, 55.3, 41.6, 36.5, 24.9, 22.9; HRMS (ESI) calcd. for $C_{16}H_{19}NONa$ [M+Na]: 264.1359, found: 264.1365.

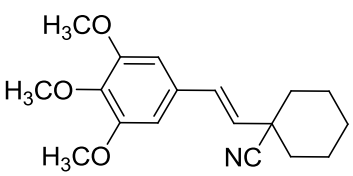


(*E*)-1-(3,4-dimethoxystyryl)cyclohexanecarbonitrile (3d): The title compound was prepared according to the general procedure and purified by flash column

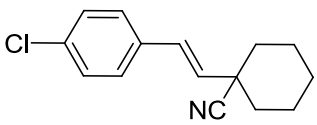


chromatography to give a white solid, 86.6 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.95 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 5.87 (d, *J* = 16.0 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.01 (d, *J* = 12.8 Hz, 2H), 1.66-1.81 (m, 5H), 1.49-1.56 (m, 2H), 1.19-1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 149.1, 129.9, 129.0, 128.4, 122.2, 119.7, 111.2, 109.0, 55.9, 55.9, 41.6, 36.5, 24.9, 22.9; HRMS (ESI) calcd. for $C_{17}H_{21}NONa$ [M+Na]: 294.1465, found: 294.1465.

(*E*)-1-(3,4,5-trimethoxystyryl)cyclohexanecarbonitrile (3e): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 85.6 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 16.0 Hz, 1H), 6.61 (s, 2H), 5.91 (d, *J* = 16.0 Hz, 1H), 3.89 (s, 6H), 3.85 (s, 3H), 2.02 (d, *J* = 13.2 Hz, 2H), 1.67-1.83 (m, 5H), 1.50-1.57 (m, 2H), 1.20-1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 138.2, 131.7, 130.2, 129.8, 122.1, 103.6, 61.0, 56.1, 41.7, 36.5, 24.9, 22.9; HRMS (ESI) calcd. for $C_{18}H_{23}NO_3Na$ [M+Na]: 324.1570, found: 324.1582.



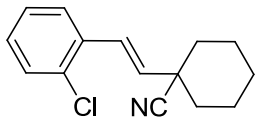
(*E*)-1-(4-chlorostyryl)cyclohexanecarbonitrile (3f): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 55.0 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.32 (m, 4H), 6.73 (d, *J* = 16.0 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 2.01 (d, *J* = 12.8 Hz, 2H), 1.66-2.00 (m, 5H), 1.48-1.55 (m, 2H), 1.21-1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 133.7, 131.0, 129.1, 128.9, 127.8, 121.9, 41.7, 36.3, 24.9, 22.9; HRMS (ESI) calcd. for $C_{15}H_{16}ClNNa$ [M+Na]: 268.0863, found: 268.0855



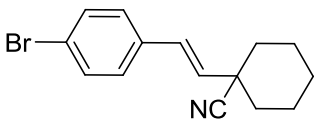
(*E*)-1-(3-chlorostyryl)cyclohexanecarbonitrile (3g): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 51mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.22-7.38 (m, 3H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.00 (d, *J* = 16.0 Hz, 1H), 2.01 (d, *J* = 12.4 Hz, 2H), 1.67-2.00 (m,

5H), 1.48-1.55 (m, 2H), 1.22-1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 134.6, 131.8, 129.9, 129.0, 128.0, 126.3, 125.0, 121.8, 41.7, 36.3, 24.9, 22.8; HRMS (ESI) calcd. for $C_{15}H_{16}ClNNa$ [M+Na]: 268.0863, found: 268.0854.

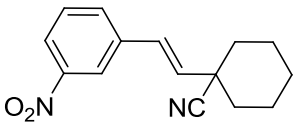
(*E*)-1-(2-chlorostyryl)cyclohexanecarbonitrile (3h): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 56.0 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.49 (m, 1H), 7.35-7.38 (m, 1H), 7.20-7.26 (m, 2H), 7.14 (d, *J* = 16.0 Hz, 1H), 6.00 (d, *J* = 16.0 Hz, 1H), 2.06 (d, *J* = 12.4 Hz, 2H), 1.68-1.83 (m, 5H), 1.51-1.60 (m, 2H), 1.21-1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 133.4, 133.2, 129.8, 129.1, 127.0, 126.9, 126.9, 121.9, 41.6, 36.2, 24.9, 22.8; HRMS (ESI) calcd. for $C_{15}H_{16}ClNNa$ [M+Na]: 268.0863, found: 268.0854.

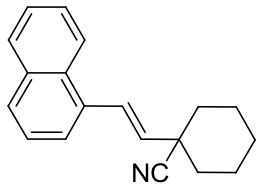


(*E*)-1-(4-bromostyryl)cyclohexanecarbonitrile (3i): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 63.0 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.46 (m, 2H), 7.23-7.26 (m, 2H), 6.71 (d, *J* = 16.0 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 2.00 (d, *J* = 12.8 Hz, 2H), 1.65-2.00 (m, 5H), 1.47-1.55 (m, 2H), 1.21-1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 131.8, 131.1, 129.1, 128.1, 121.9, 41.7, 36.3, 24.9, 22.9; HRMS (ESI) calcd. for $C_{15}H_{16}BrN$ [M]: 289.0461, found: 289.0450

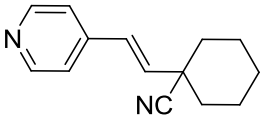


(*E*)-1-(3-nitrostyryl)cyclohexanecarbonitrile (3j): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 18.7 mg, 15% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.50-7.54 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.15 (d, *J* = 16.0 Hz, 1H), 2.03 (d, *J* = 12.8 Hz, 2H), 1.69-1.85 (m, 5H), 1.53-1.60 (m, 2H), 1.25-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 137.8, 133.6, 132.8, 129.7, 128.2, 122.6, 121.5, 120.8, 41.9, 36.2, 24.8, 22.8; HRMS (ESI) calcd. for $C_{15}H_{16}N_2O_2Na$ [M+Na]: 279.1104, found: 279.1111.

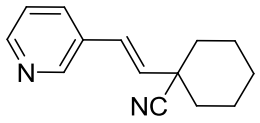


(*E*)-1-(2-(naphthalen-1-yl)vinyl)cyclohexanecarbonitrile (3k): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 68.6 mg, 53% yield. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 0.8 Hz, 1H), 7.83-7.85 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.41-7.58 (m, 5H), 6.00 (d, *J* = 15.6 Hz, 1H), 2.09 (d, *J* = 12.4 Hz, 2H), 1.69-1.83 (m, 5H), 1.53-1.60 (m, 2H), 1.21-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 133.7, 133.6, 131.2, 128.6, 128.5, 127.8, 126.3, 126.0, 125.5, 124.0, 123.8, 122.2, 42.0, 36.5, 24.9, 22.9; HRMS (ESI) calcd. for $C_{19}H_{19}NNa$ [M+Na]: 284.1410, found: 284.1419.

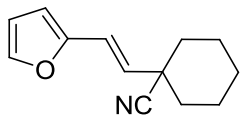
(*E*)-1-(2-(pyridin-4-yl)vinyl)cyclohexanecarbonitrile (3l): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 27.0 mg, 26% yield. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.2 Hz, 2H), 7.25-7.27 (m, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.21 (d, *J* = 16.0 Hz, 1H), 2.02 (d, *J* = 13.6 Hz, 2H), 1.68-1.84 (m, 5H), 1.50-1.58 (m, 2H), 1.23-1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 143.4, 135.0, 128.2, 121.5, 121.1, 41.9, 36.1, 24.8, 22.8; HRMS (ESI) calcd. for $C_{14}H_{17}N_2$ [M+H]: 213.1386, found: 213.1379.

(*E*)-1-(2-(pyridin-3-yl)vinyl)cyclohexanecarbonitrile (3m): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 65.1 mg, 61% yield. 

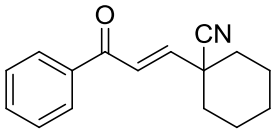
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.50 (d, *J* = 4.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.26-7.29 (m, 1H), 6.78 (d, *J* = 16.4 Hz, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 2.03 (d, *J* = 13.2 Hz, 2H), 1.68-1.84 (m, 5H), 1.51-1.58 (m, 2H), 1.24-1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.3, 133.2, 132.6, 131.7, 126.9, 123.5, 121.7, 41.9, 36.2, 24.8, 22.8; HRMS (ESI) calcd. for $C_{14}H_{17}N_2$ [M+H]: 213.1386, found: 213.1384.

(*E*)-1-(2-(furan-2-yl)vinyl)cyclohexanecarbonitrile (3n): The title compound was



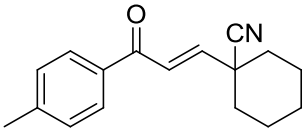
prepared according to the general procedure and purified by flash column chromatography to give a white solid, 31.2 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 1.2 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.37-6.39 (m, 1H), 6.28 (d, *J* = 3.2 Hz, 1H), 5.96 (d, *J* = 16.0 Hz, 1H), 1.98 (d, *J* = 12.4 Hz, 2H), 1.63-1.80 (m, 5H), 1.46-1.53 (m, 2H), 1.17-1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ. 151.5, 142.3, 128.7, 121.9, 118.6, 111.5, 109.1, 41.6, 36.4, 24.9, 22.9; HRMS (EI) calcd. for $C_{13}H_{15}NO$ [M]: 201.1154, found: 201.1153.

(*E*)-1-(3-oxo-3-phenylprop-1-enyl)cyclohexanecarbonitrile (3o): The title compound



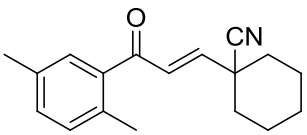
was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 53.6 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-8.00 (m, 2H), 7.58-7.63 (m, 1H), 7.48-7.52 (m, 2H), 7.34 (d, *J* = 15.2 Hz, 1H), 6.80 (d, *J* = 15.2 Hz, 1H), 2.00 (d, *J* = 12.4 Hz, 2H), 1.67-1.86 (m, 5H), 1.55-1.63 (m, 2H), 1.26-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 146.6, 137.2, 133.4, 128.8, 128.7, 124.8, 121.0, 42.3, 35.6, 24.7, 22.5; HRMS (ESI) calcd. for $C_{16}H_{17}NONa$ [M+Na]: 262.1202, found: 262.1205.

(*E*)-1-(3-oxo-3-*p*-tolylprop-1-enyl)cyclohexanecarbonitrile (3p): The title compound



was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 60.8 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 15.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 15.6 Hz, 1H), 2.43 (s, 3H), 1.99 (d, *J* = 12.4 Hz, 2H), 1.67-1.86 (m, 5H), 1.55-1.62 (m, 2H), 1.25-1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 146.2, 144.4, 134.7, 129.5, 128.8, 124.8, 121.1, 42.2, 35.6, 24.7, 22.5, 21.7; HRMS (ESI) calcd. for $C_{17}H_{19}NONa$ [M+Na]: 276.1359, found: 276.1364.

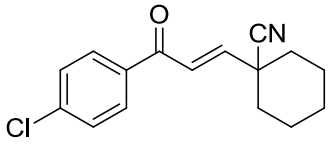
(*E*)-1-(3-(2,5-dimethylphenyl)-3-oxoprop-1-enyl)cyclohexanecarbonitrile (3q): The



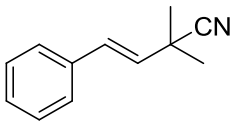
title compound was prepared according to the general procedure and purified by flash column chromatography to give a white

solid, 58.4 mg, 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 15.6 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.99 (d, *J* = 12.4 Hz, 2H), 1.66-1.84 (m, 5H), 1.51-1.58 (m, 2H), 1.23-1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 146.7, 137.9, 135.3, 134.6, 132.1, 131.6, 129.1, 128.9, 120.9, 41.9, 35.5, 24.7, 22.5, 20.9, 20.2; HRMS (ESI) calcd. for $C_{18}H_{21}NONa$ [M+Na]: 290.1515, found: 290.1517.

(*E*)-1-(3-(4-chlorophenyl)-3-oxoprop-1-enyl)cyclohexanecarbonitrile (3r): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 49 mg, 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.96 (m, 2H), 7.47-7.49 (m, 2H), 7.29 (d, *J* = 15.6 Hz, 1H), 6.81 (d, *J* = 15.2 Hz, 1H), 1.99 (d, *J* = 12.4 Hz, 2H), 1.68-1.87 (m, 5H), 1.55-1.62 (m, 2H), 1.26-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 147.2, 139.9, 135.5, 130.1, 129.1, 124.3, 120.9, 42.3, 35.5, 24.6, 22.5; HRMS (ESI) calcd. for $C_{16}H_{16}ClNONa$ [M+Na]: 296.0813, found: 296.0799.



(*E*)-2,2-dimethyl-4-phenylbut-3-enenitrile (4a): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 8 mg, 9% yield. NMR: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.40 (m, 2H), 7.32-7.35 (m, 2H), 7.25-7.29 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.01 (d, *J* = 15.6 Hz, 1H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 130.5, 130.0, 128.8, 128.3, 126.7, 123.6, 35.1, 27.8; HRMS (ESI) calcd. for $C_{12}H_{13}NNa$ [M+Na]: 194.0940, found: 194.0935.



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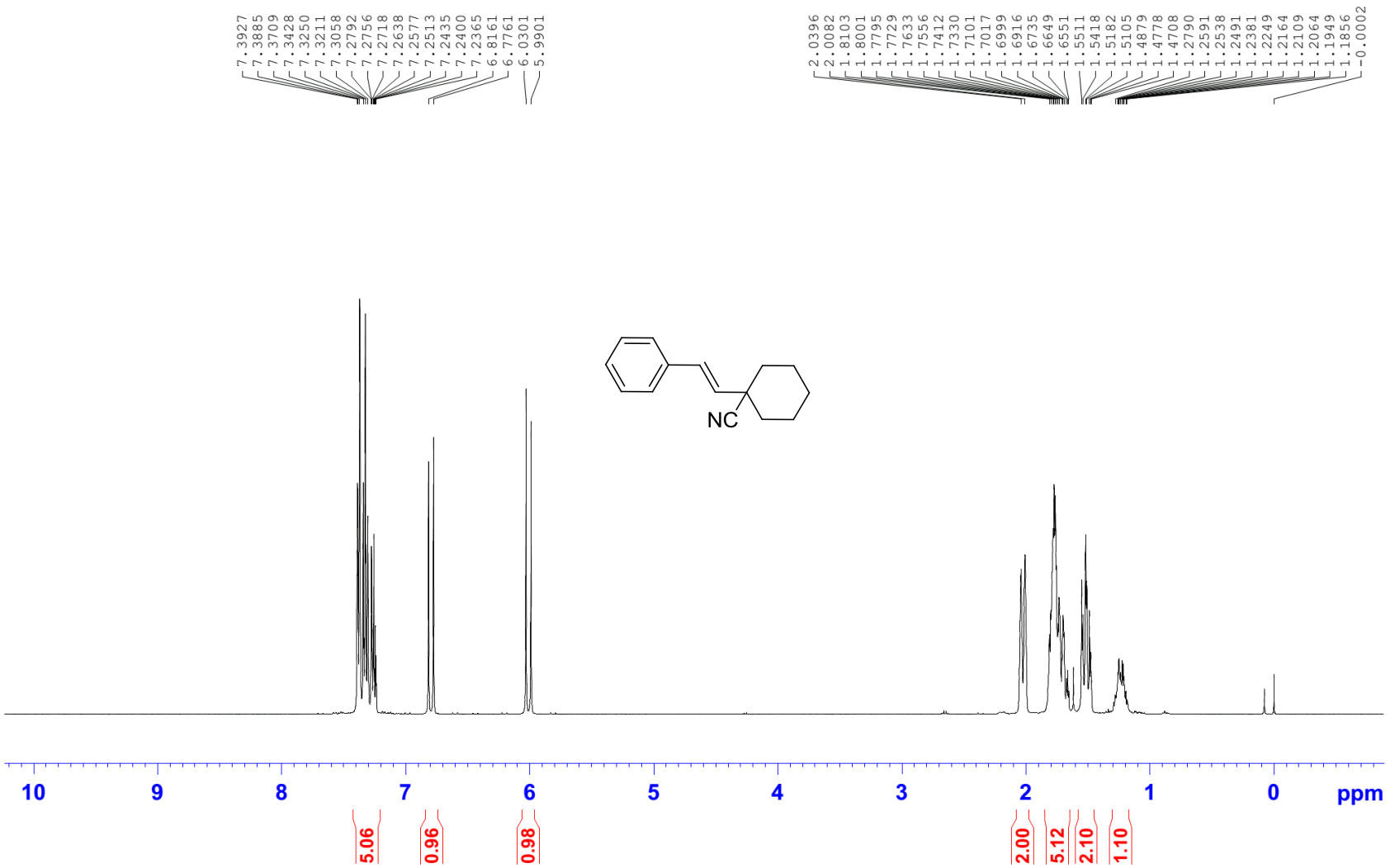
1. P. Zhang, H.-R. Hu, S.-H. Bian, Z.-H. Huang, Y. Chu, D.-Y. Ye, *Eur. J. Med. Chem.* **2013**, *61*, 95.

2. D. Papa, E. Schwenk, F. Villani, E. Klingsberg, *J. Am. Chem. Soc.* **1948,** *70*, 3356.

3. P. Jakubec, D. Berkeš, A. Kolarovič, F. Považanec, *Synthesis*. **2006**, 4032.

5. Copies for ^{1}H NMR and ^{13}C NMR of the products

GB-140317-2-HNMR



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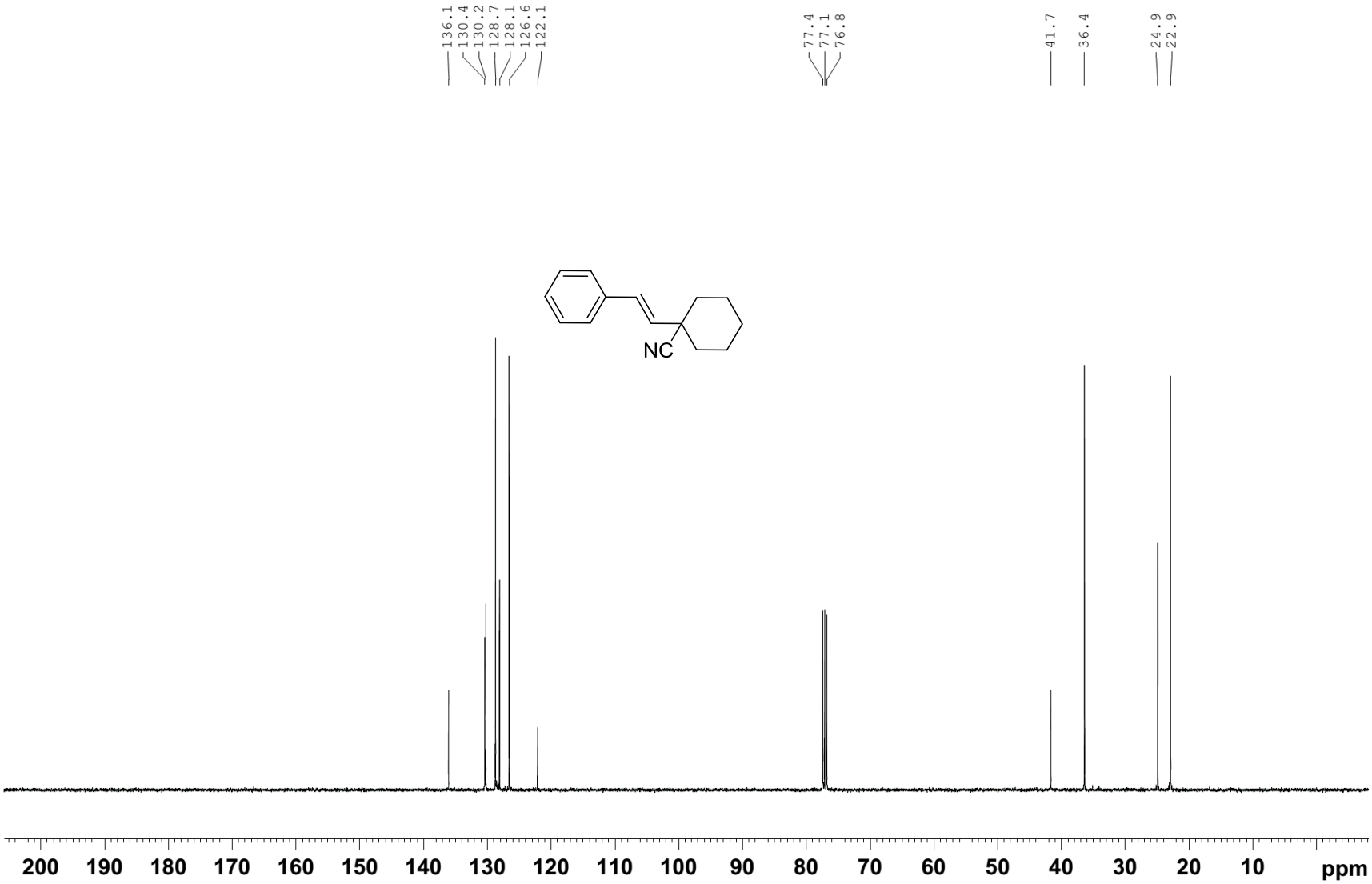

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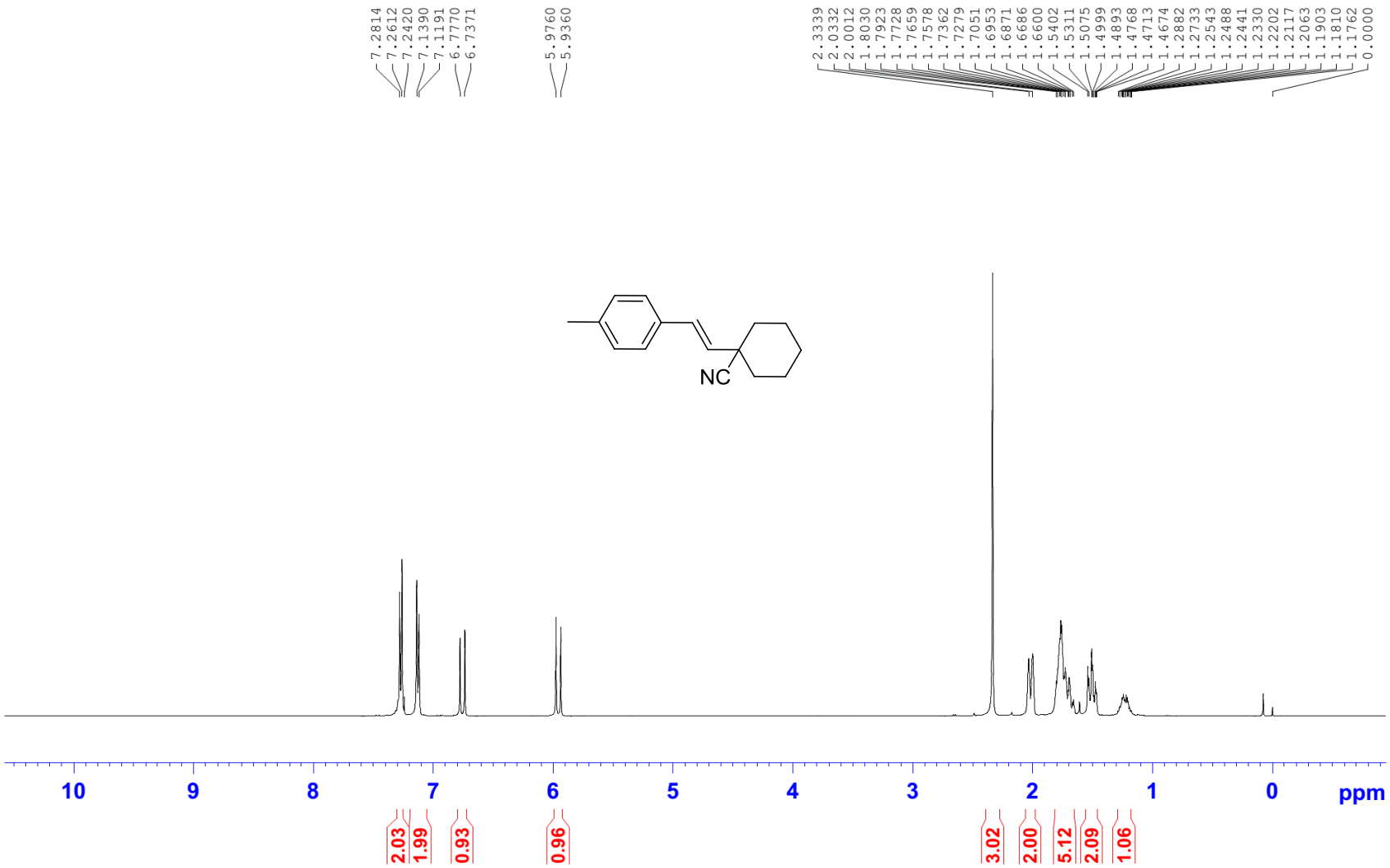

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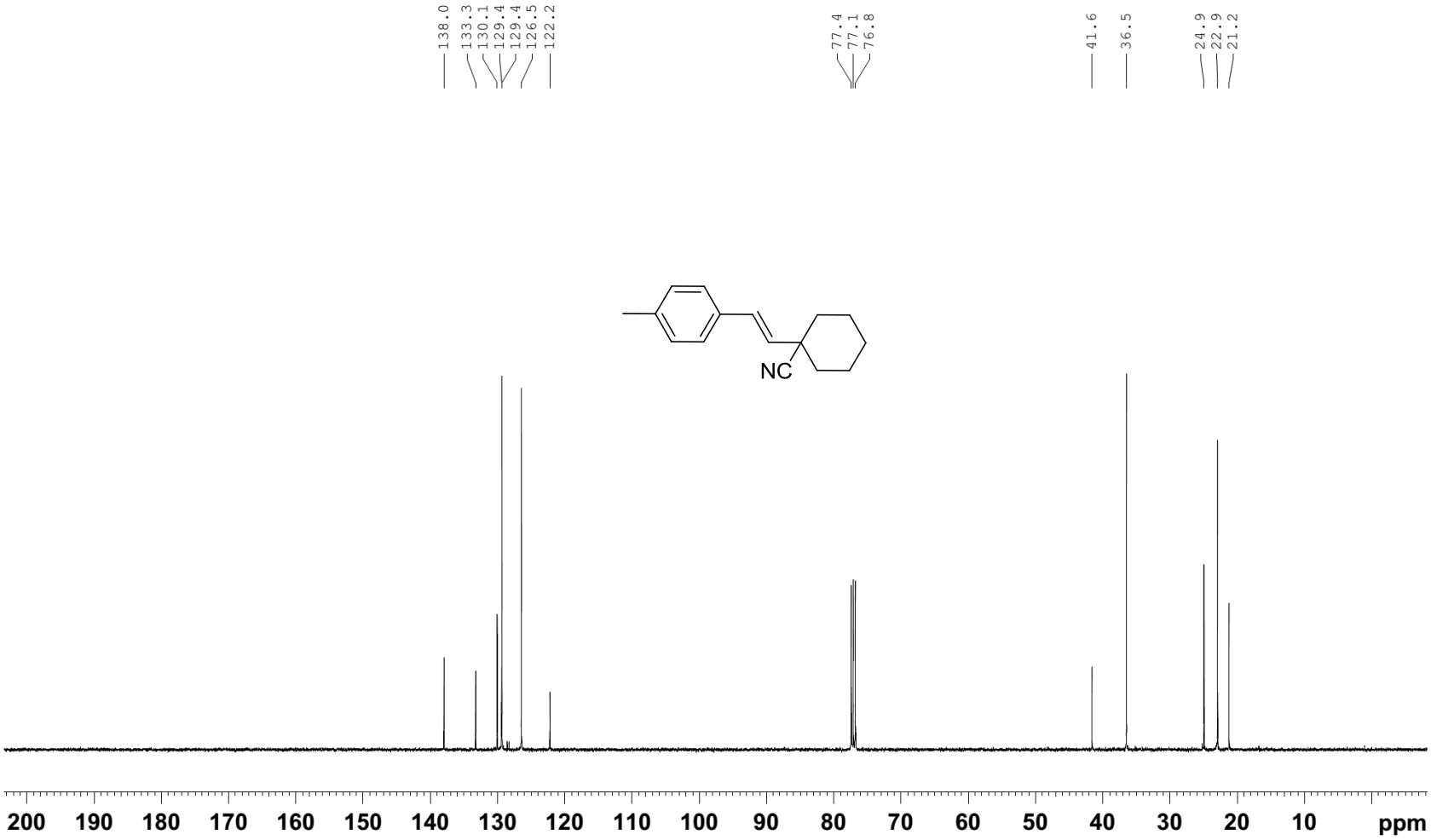

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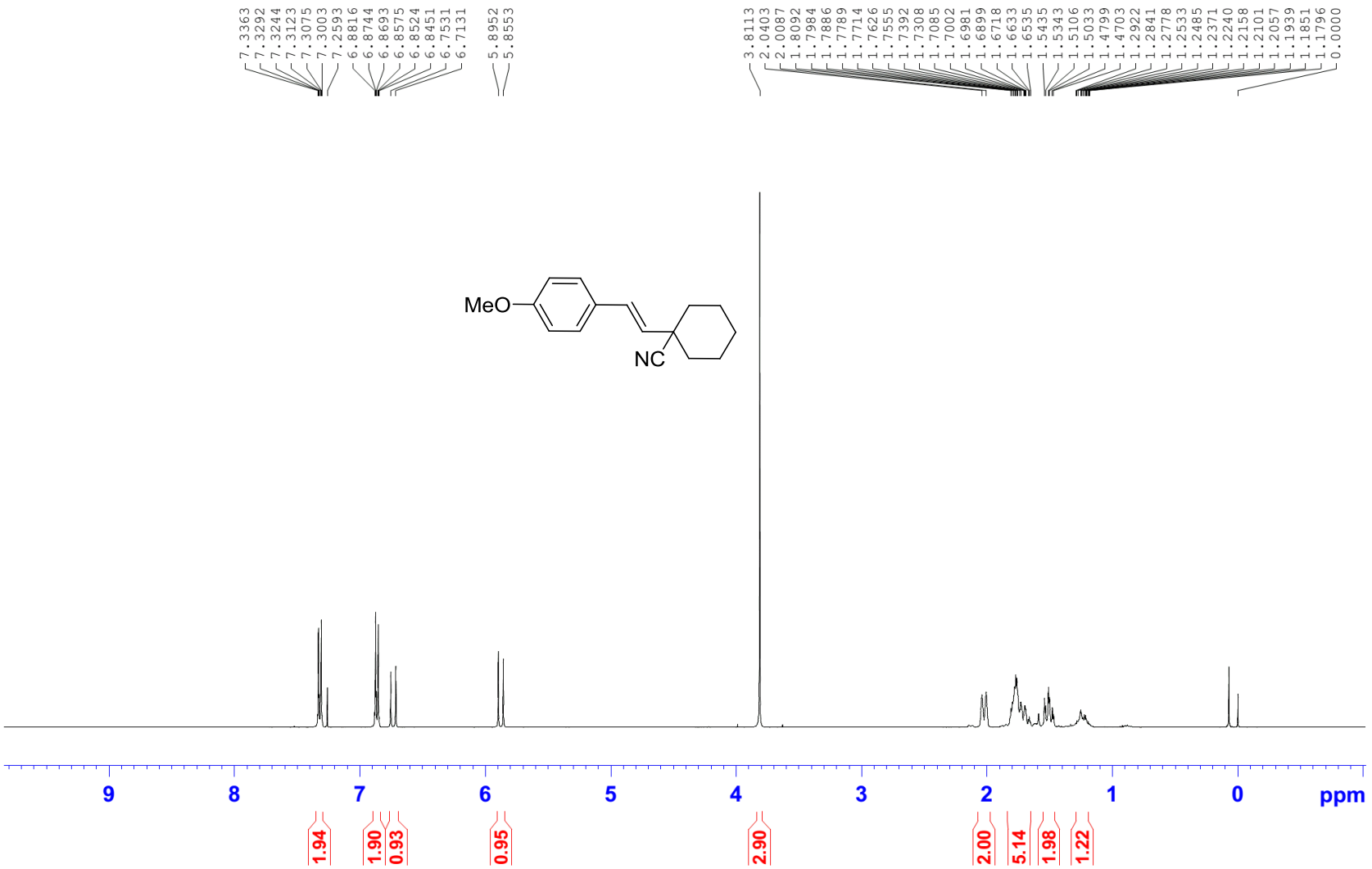

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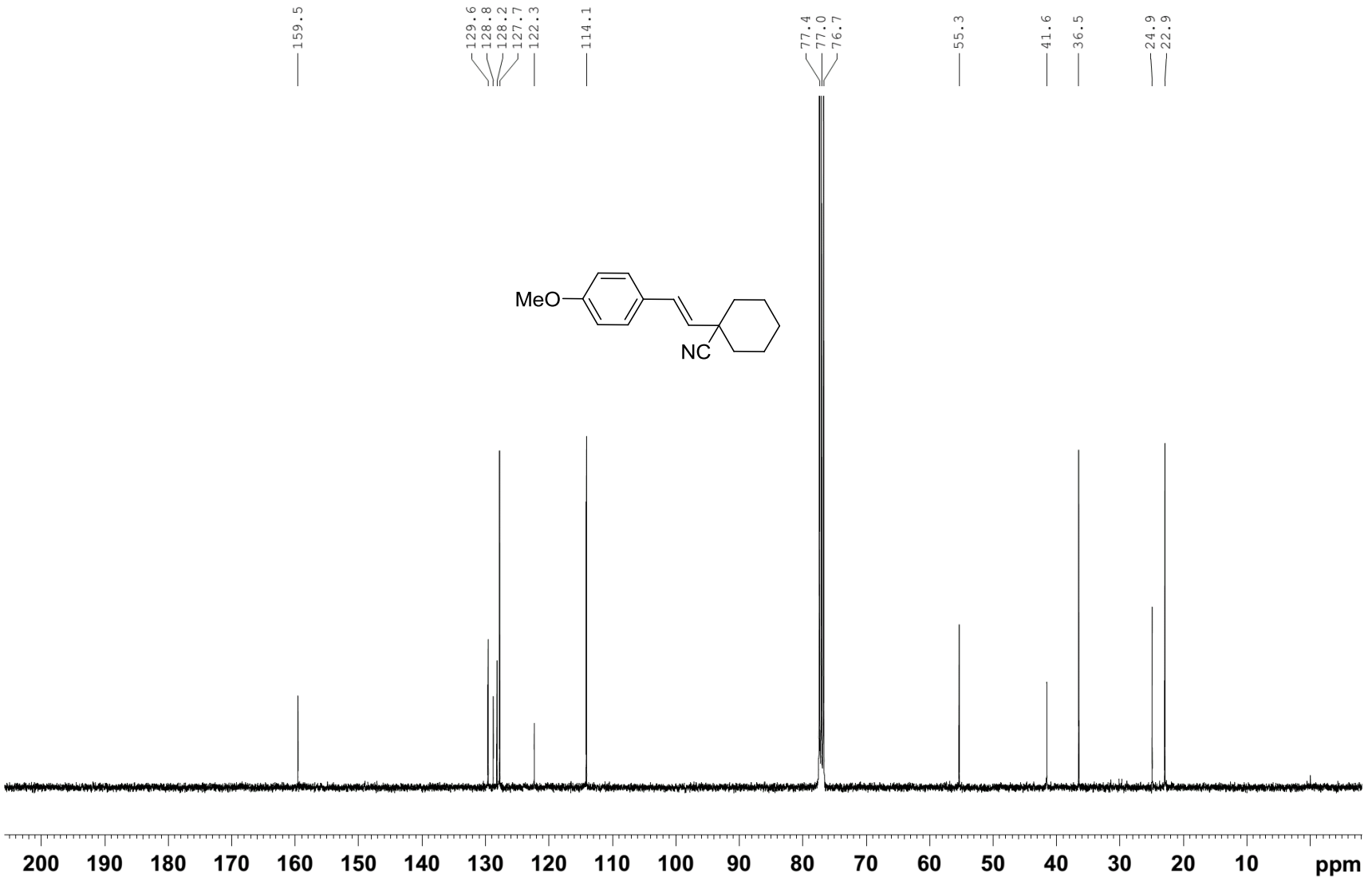

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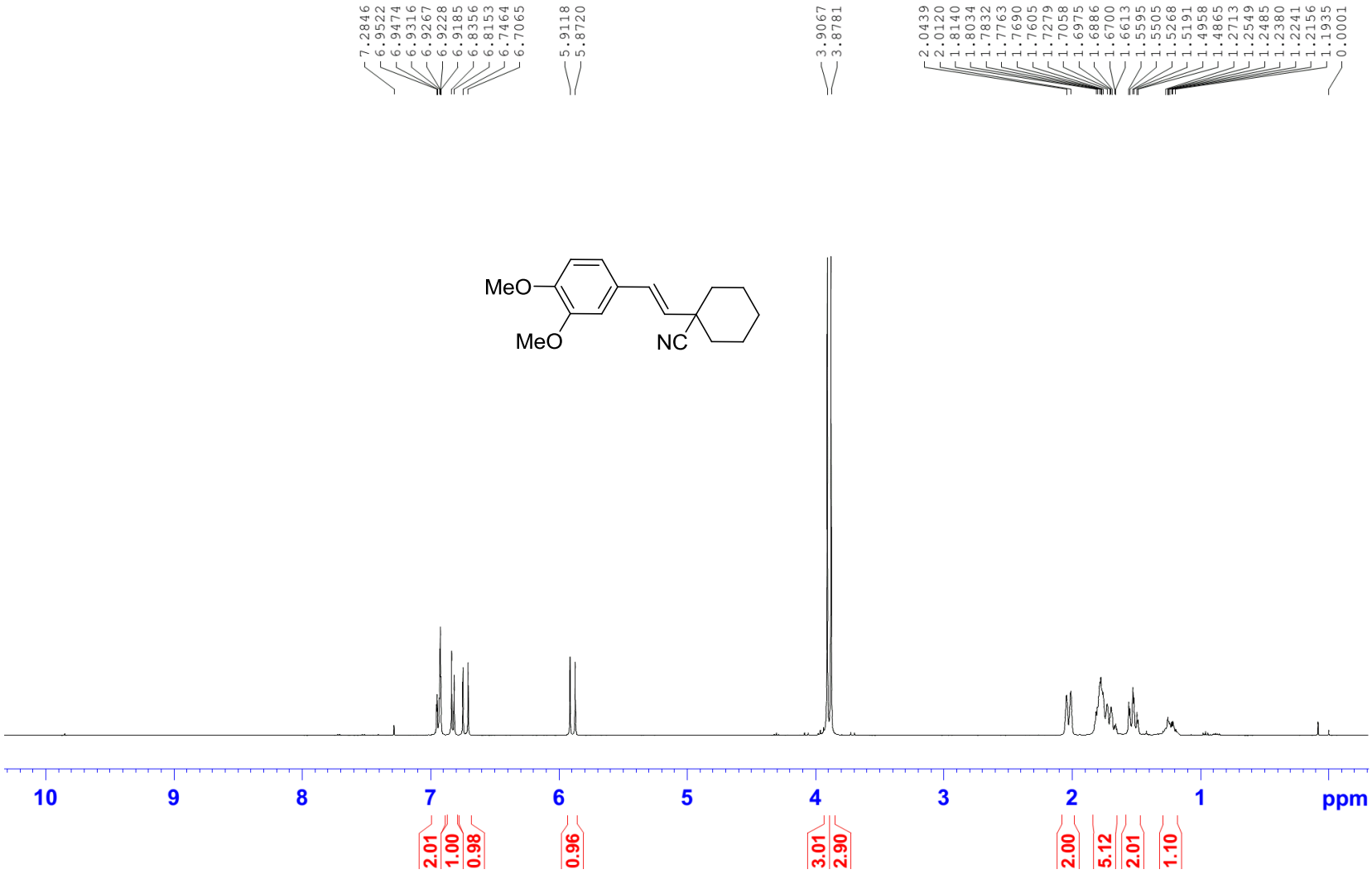

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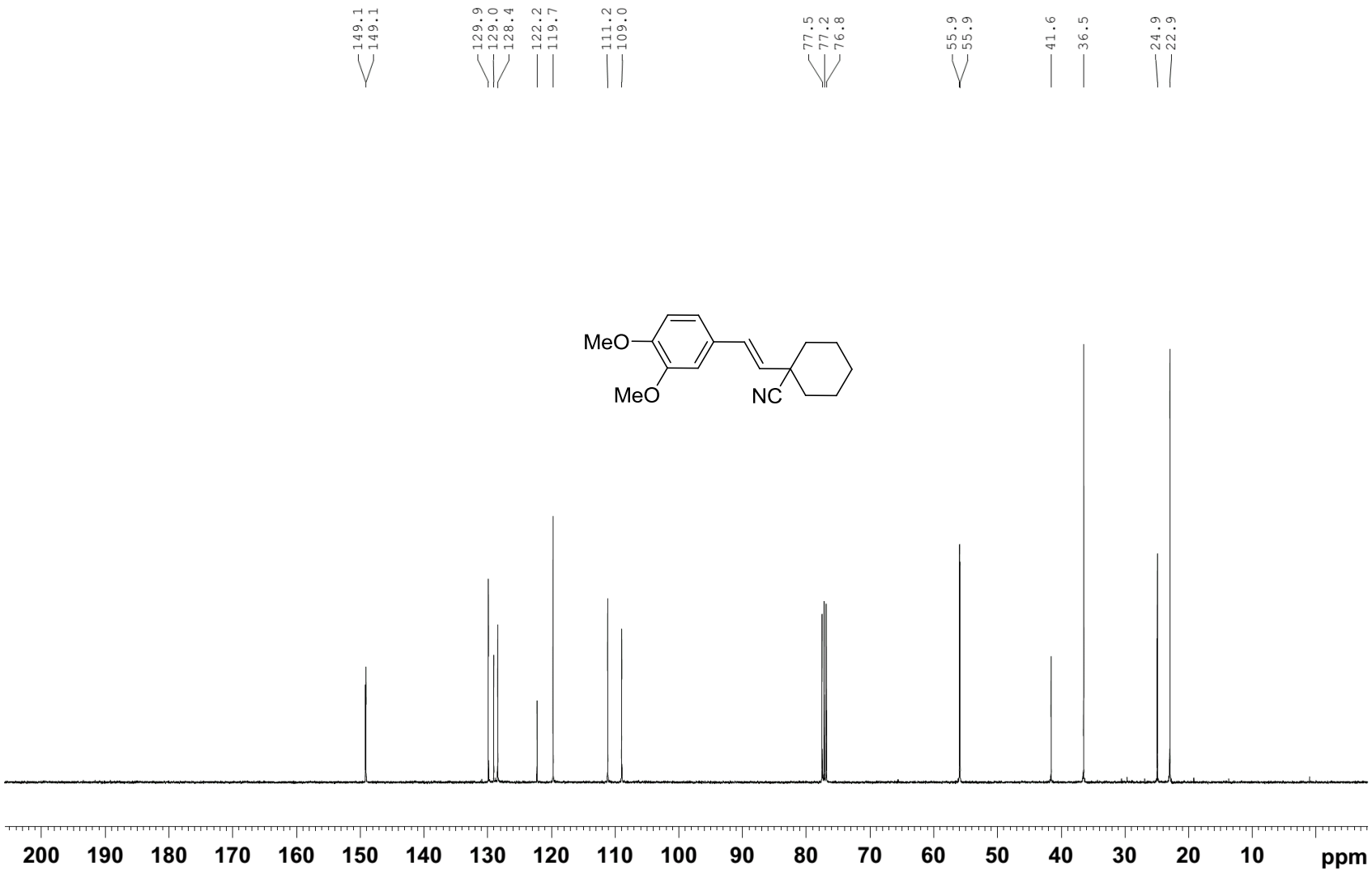

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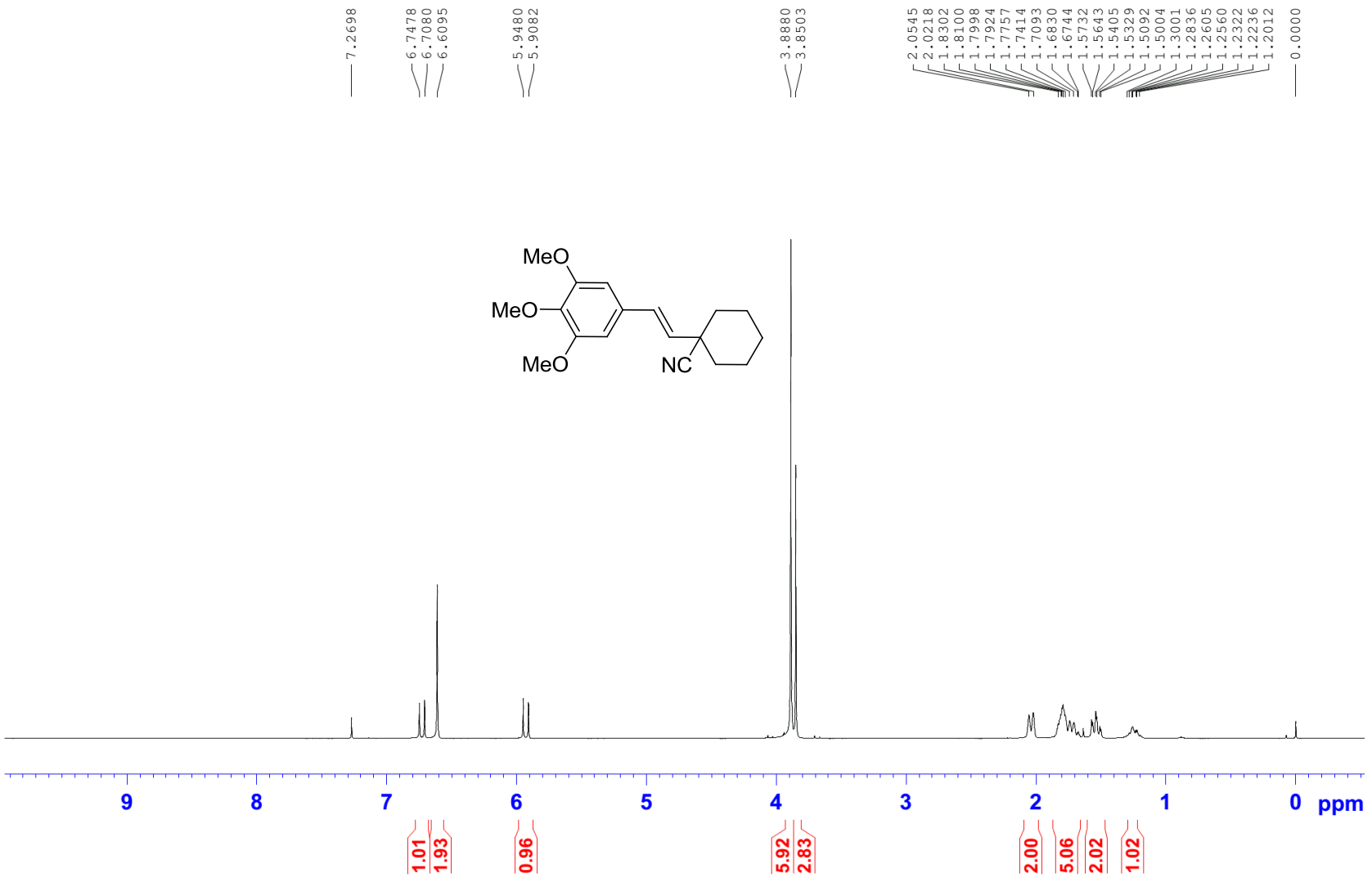

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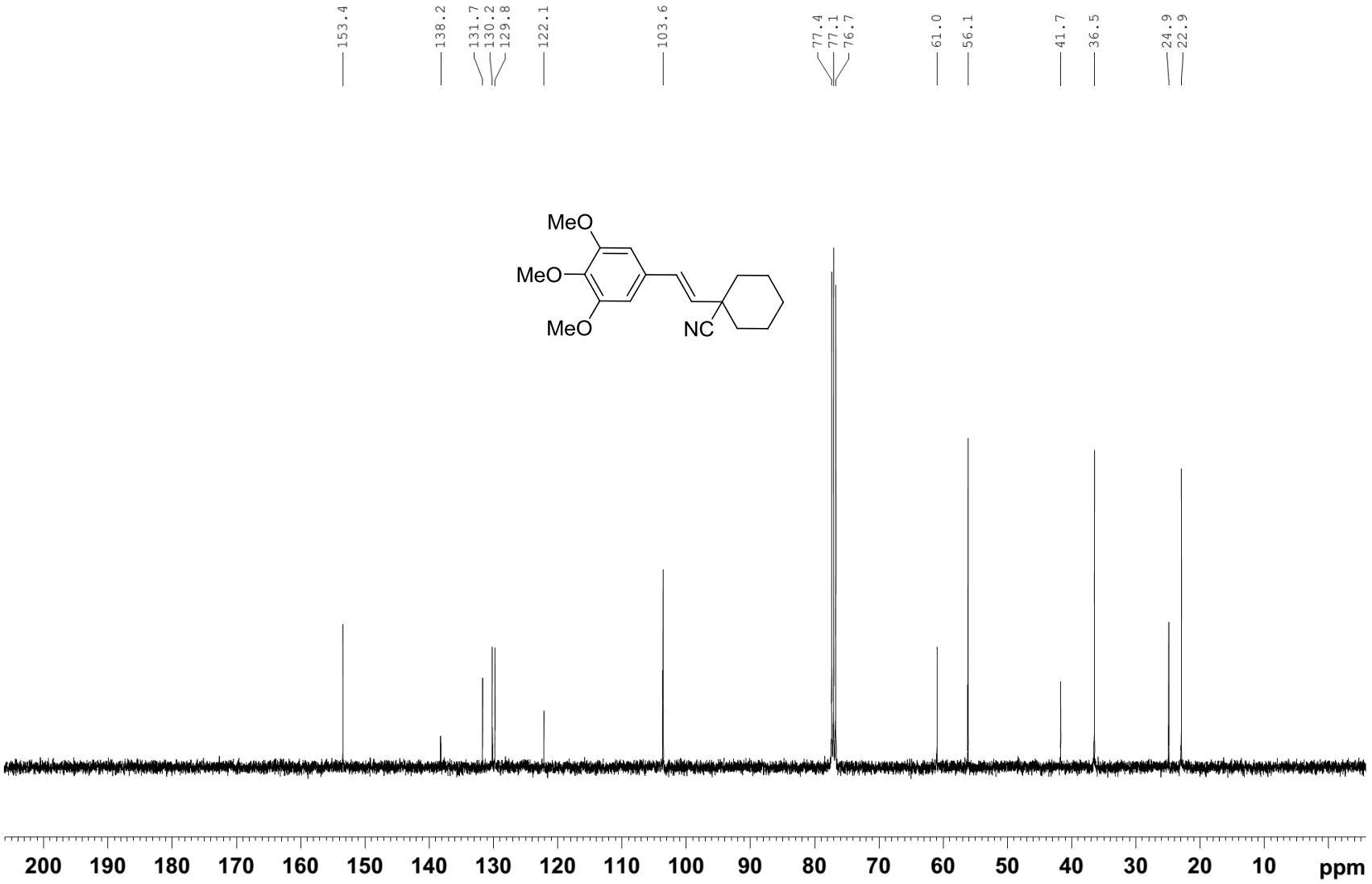

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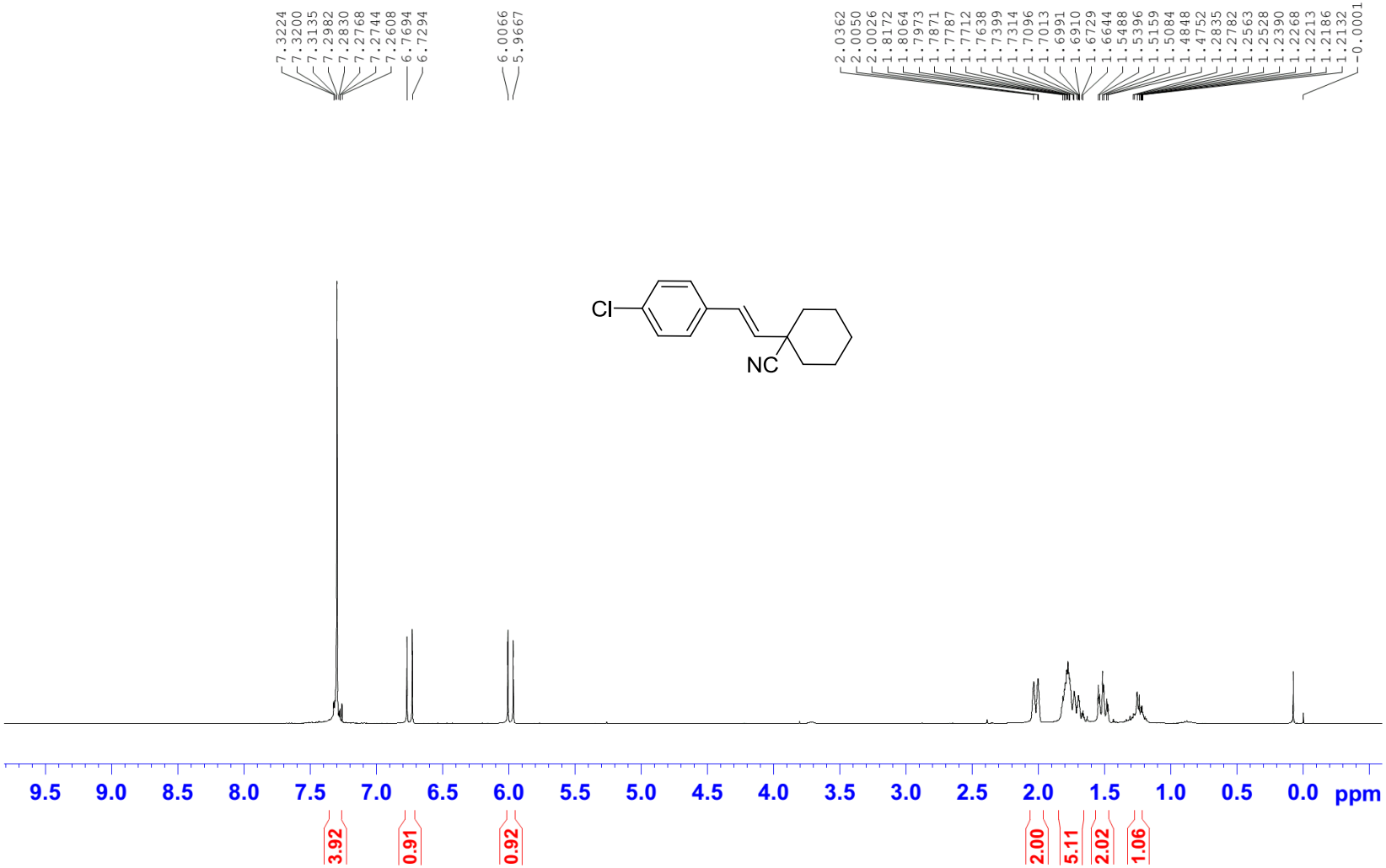

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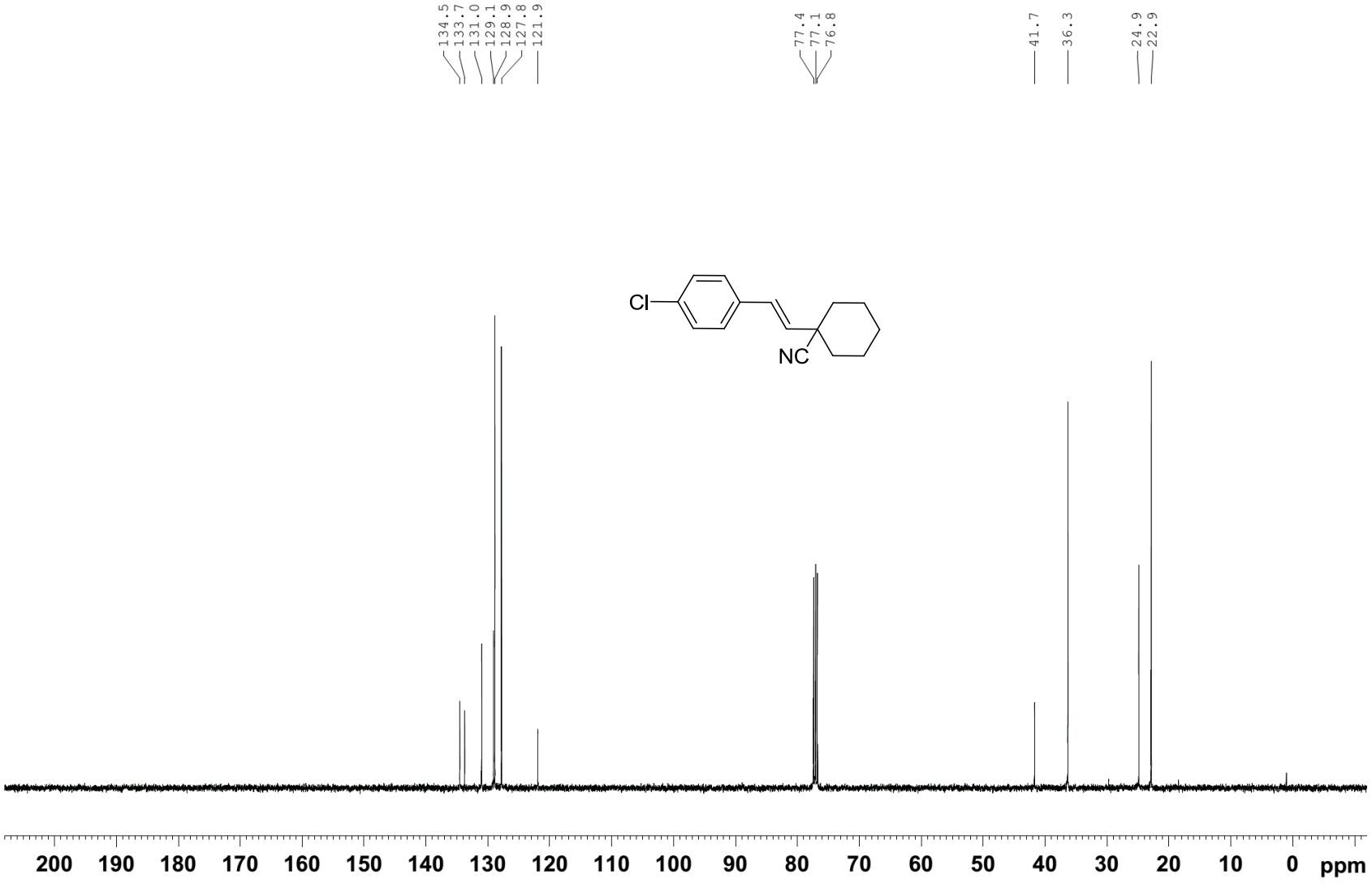

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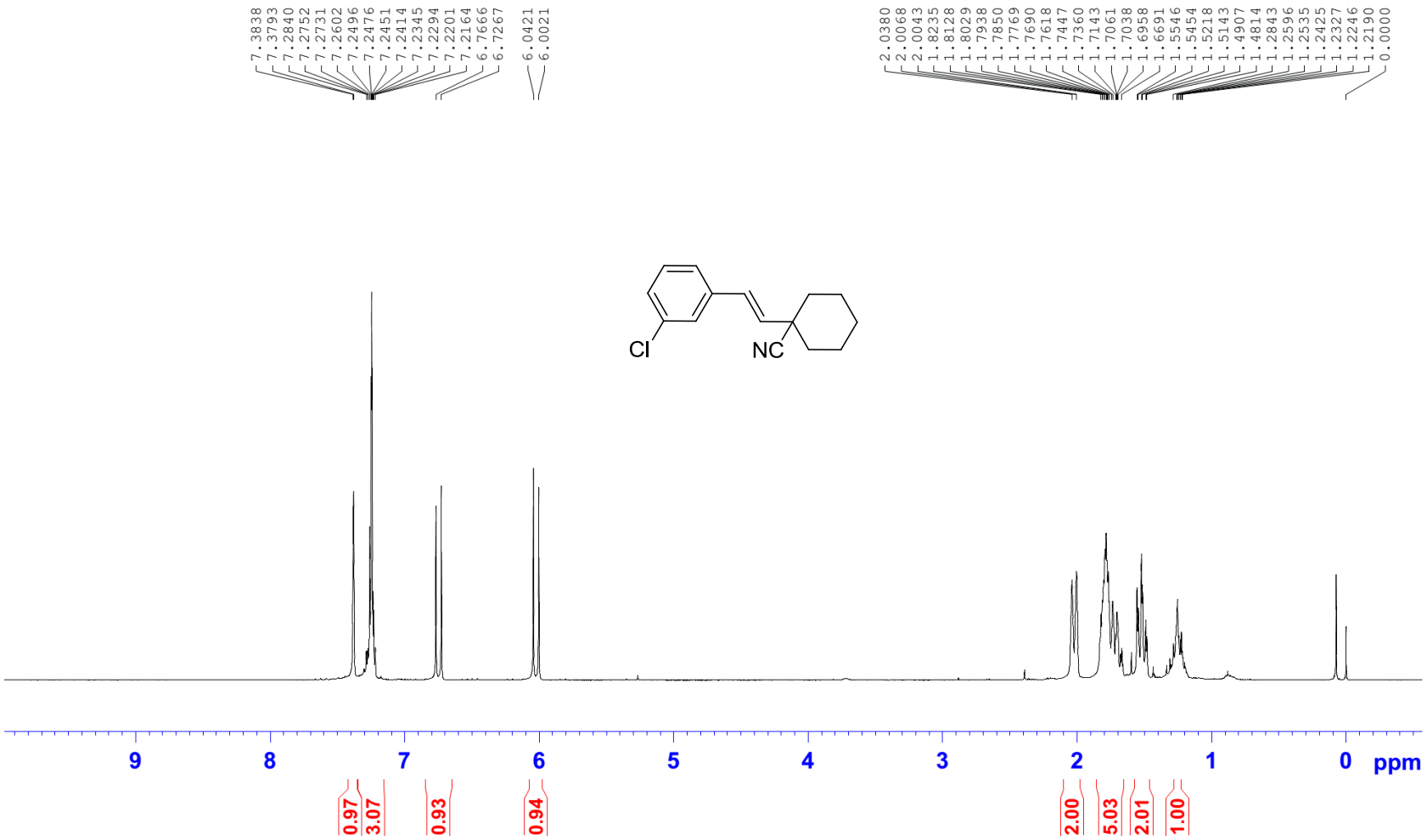

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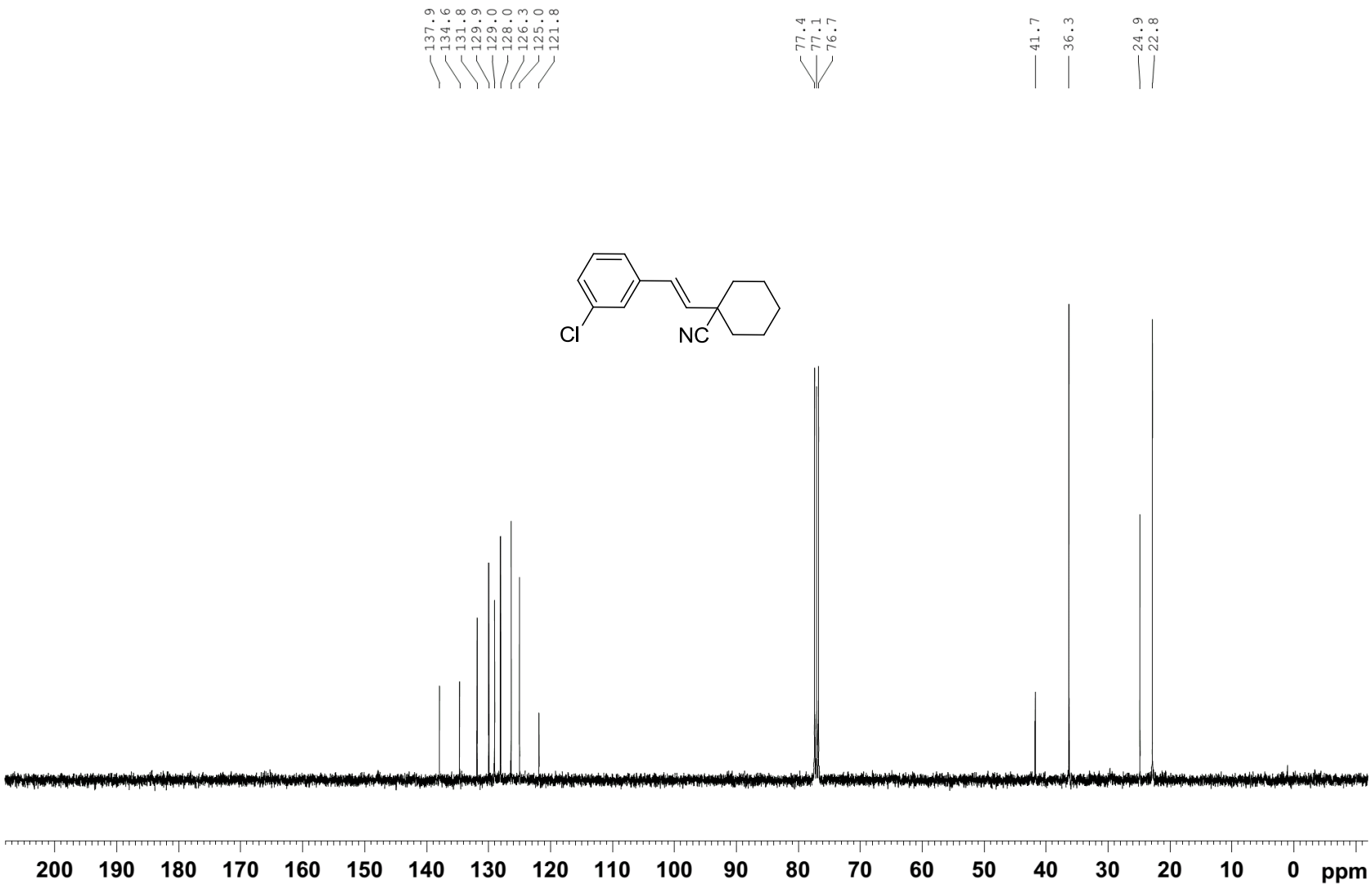

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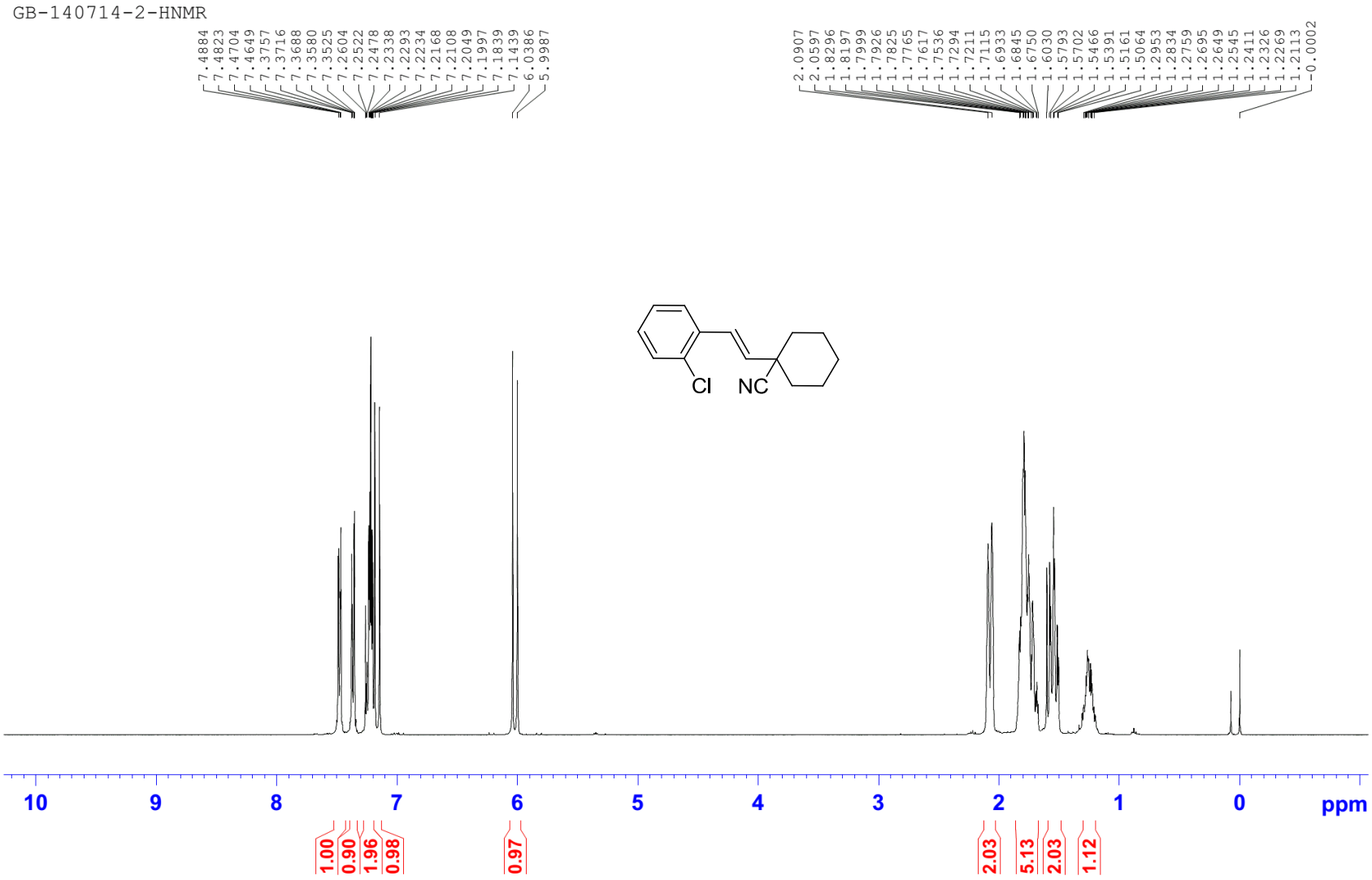

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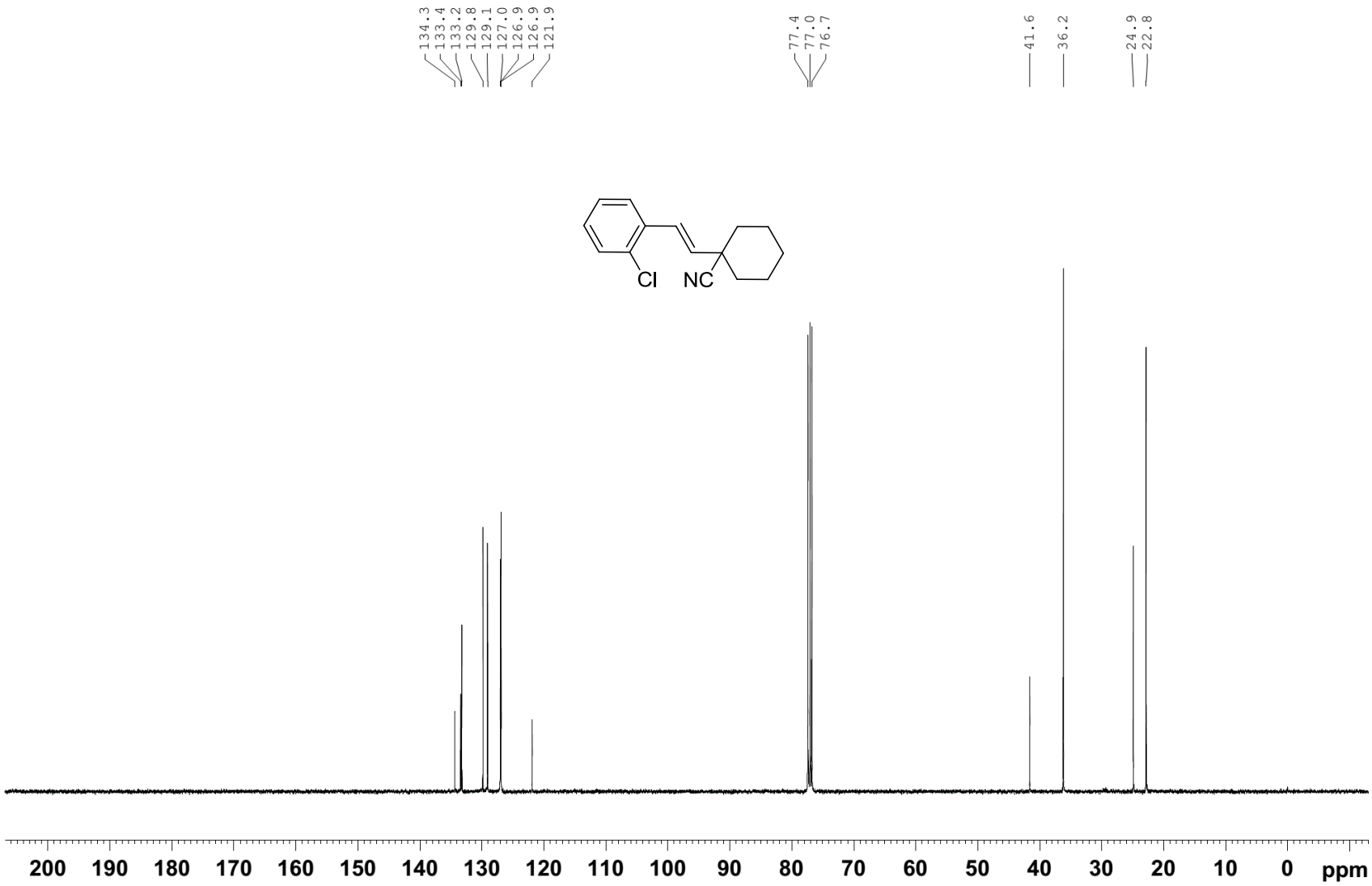

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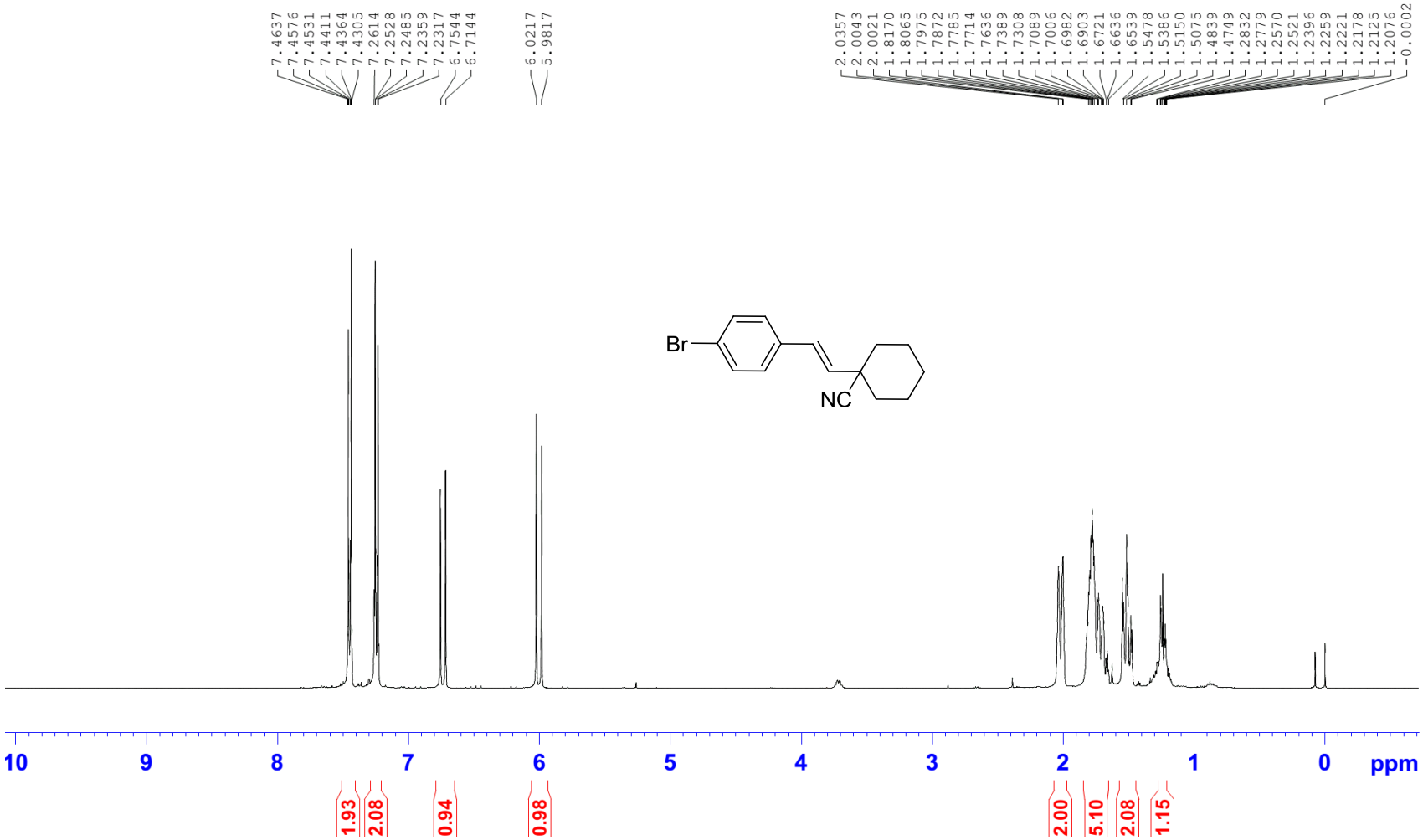

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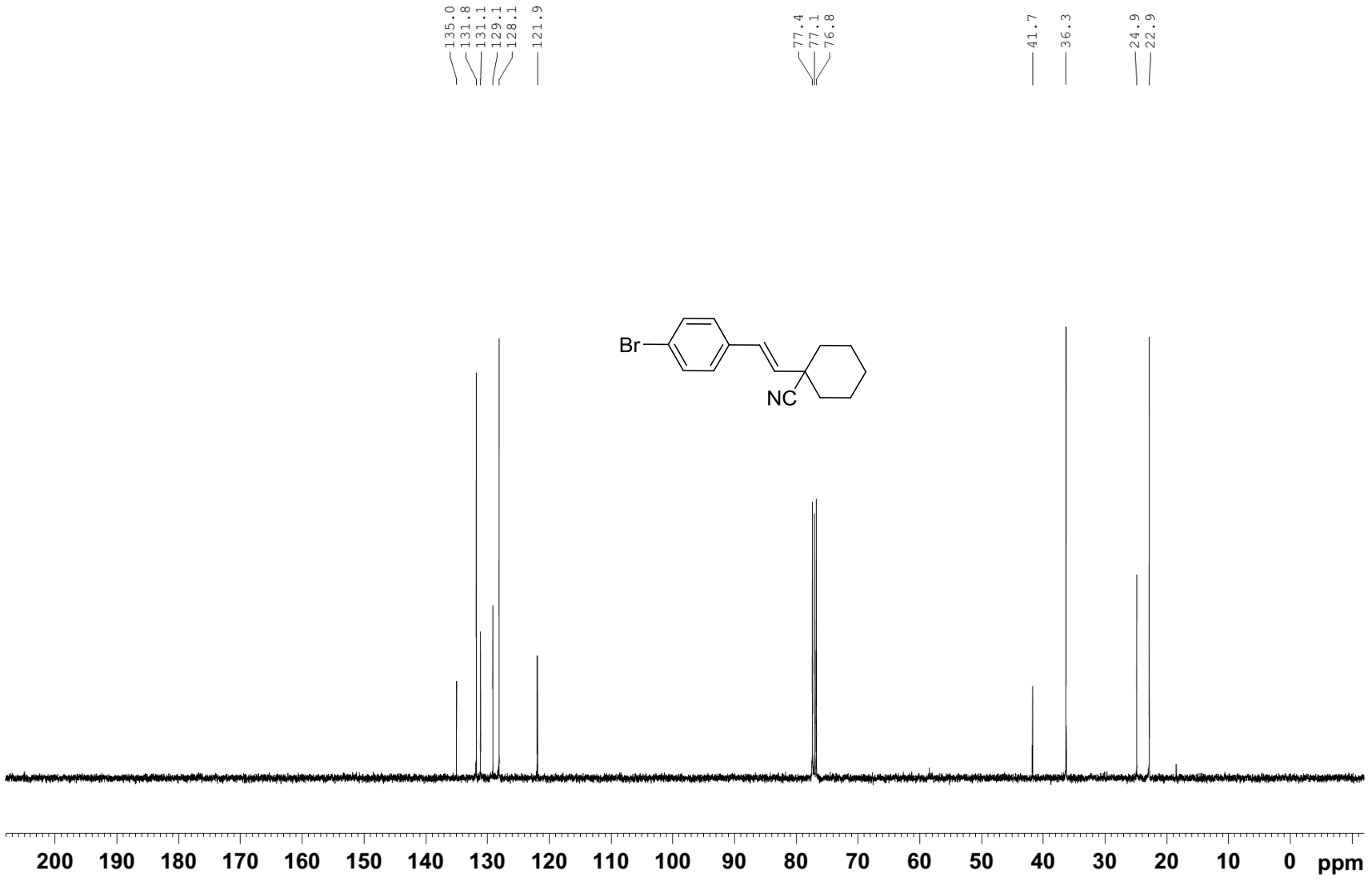

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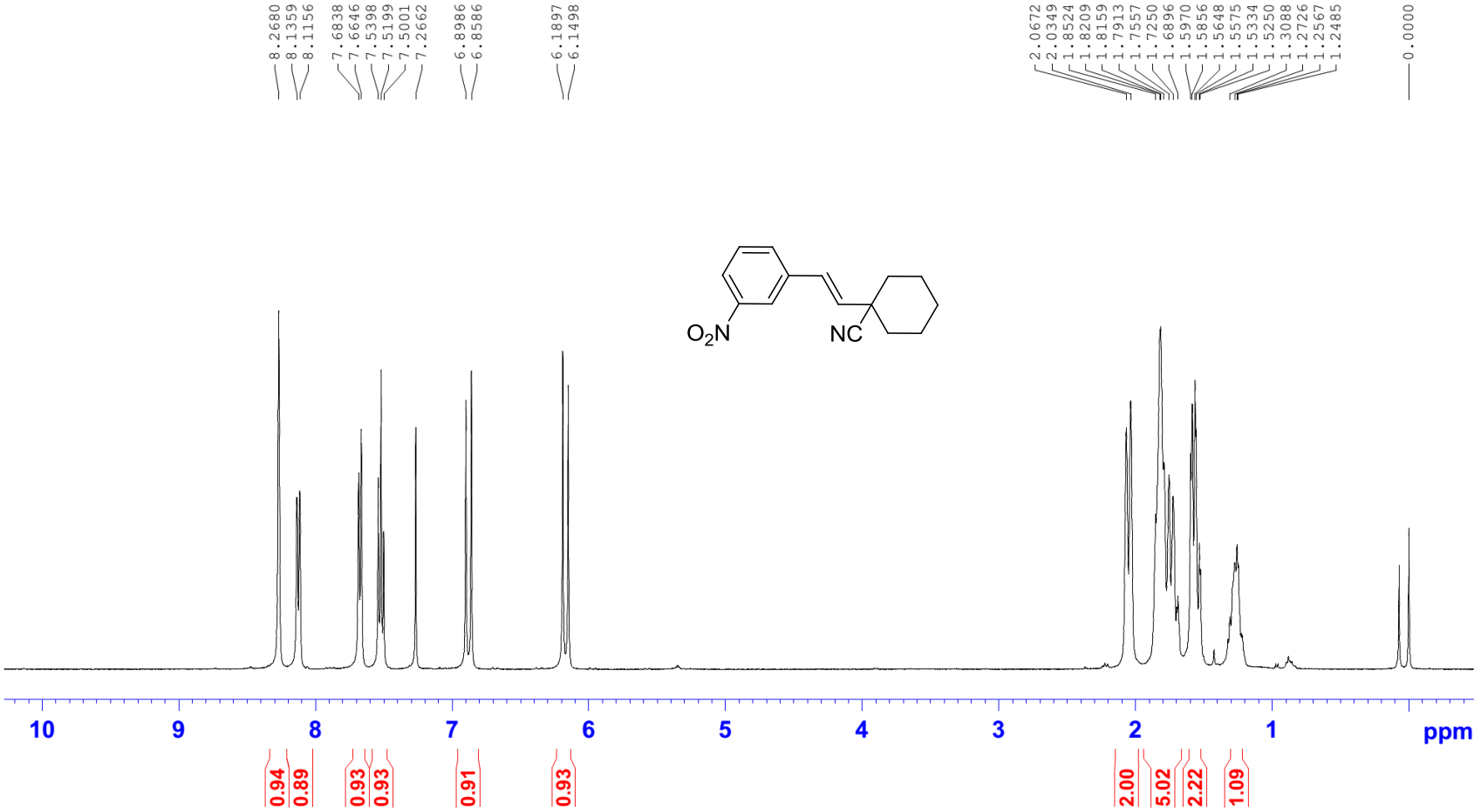

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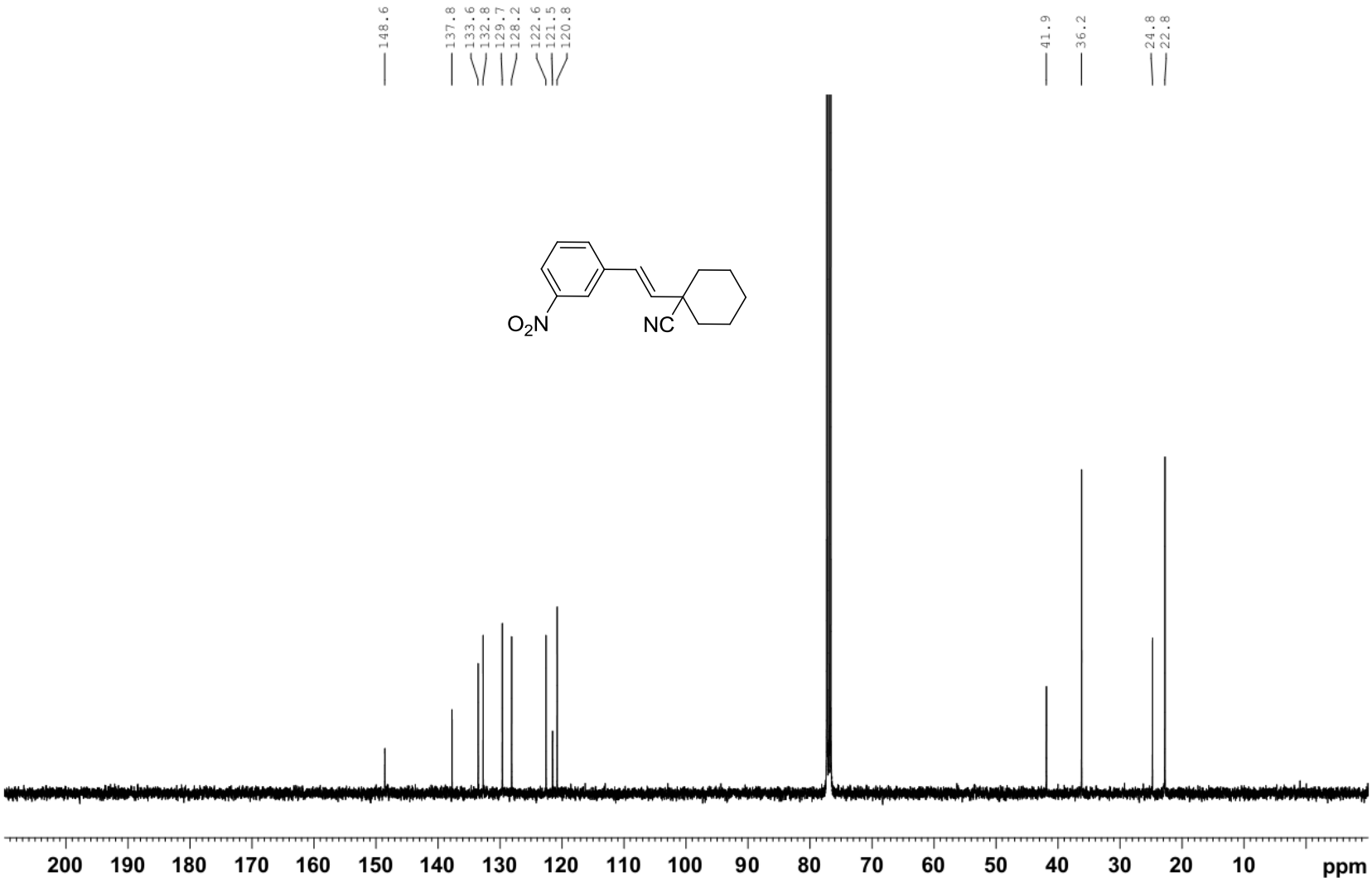

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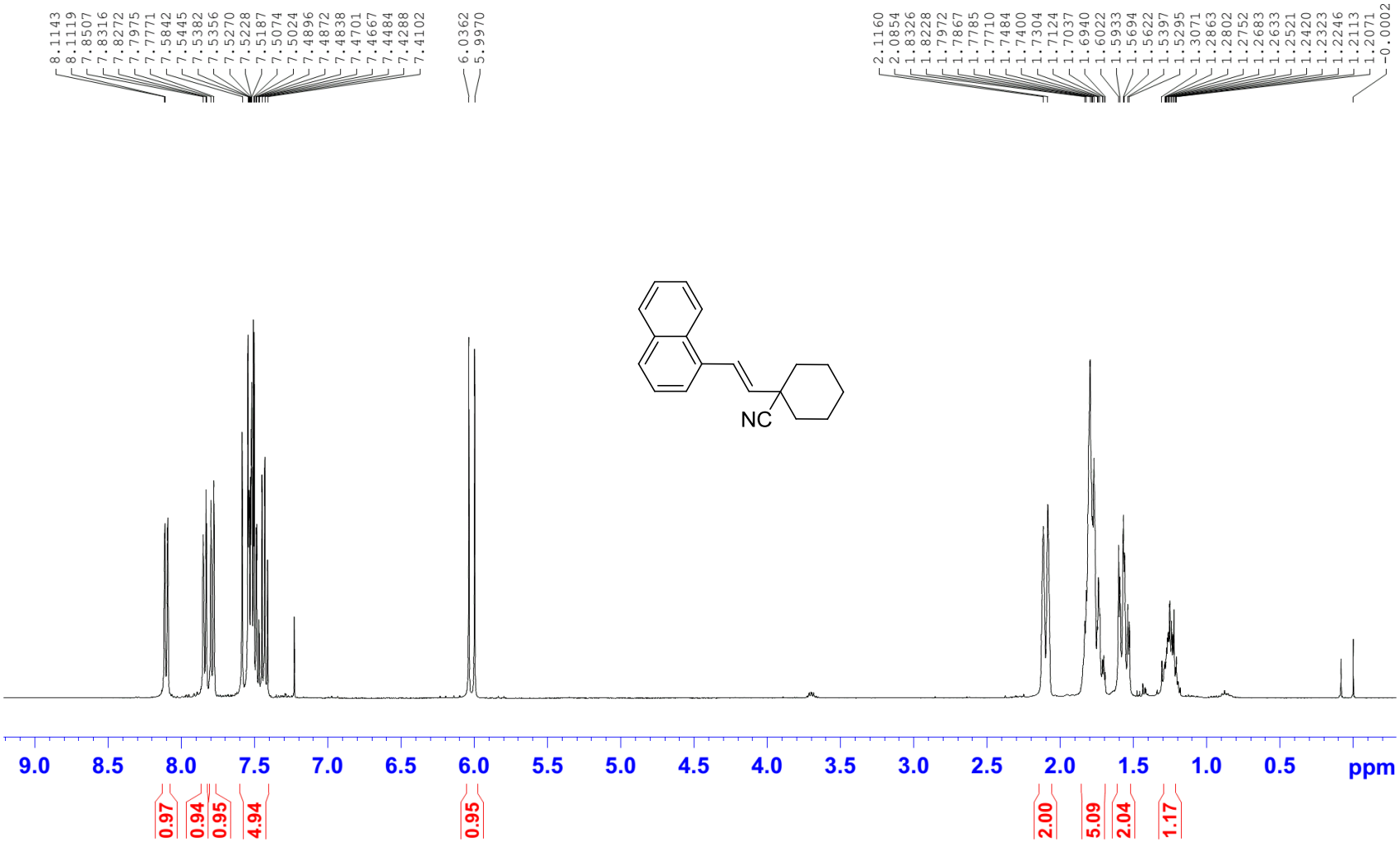

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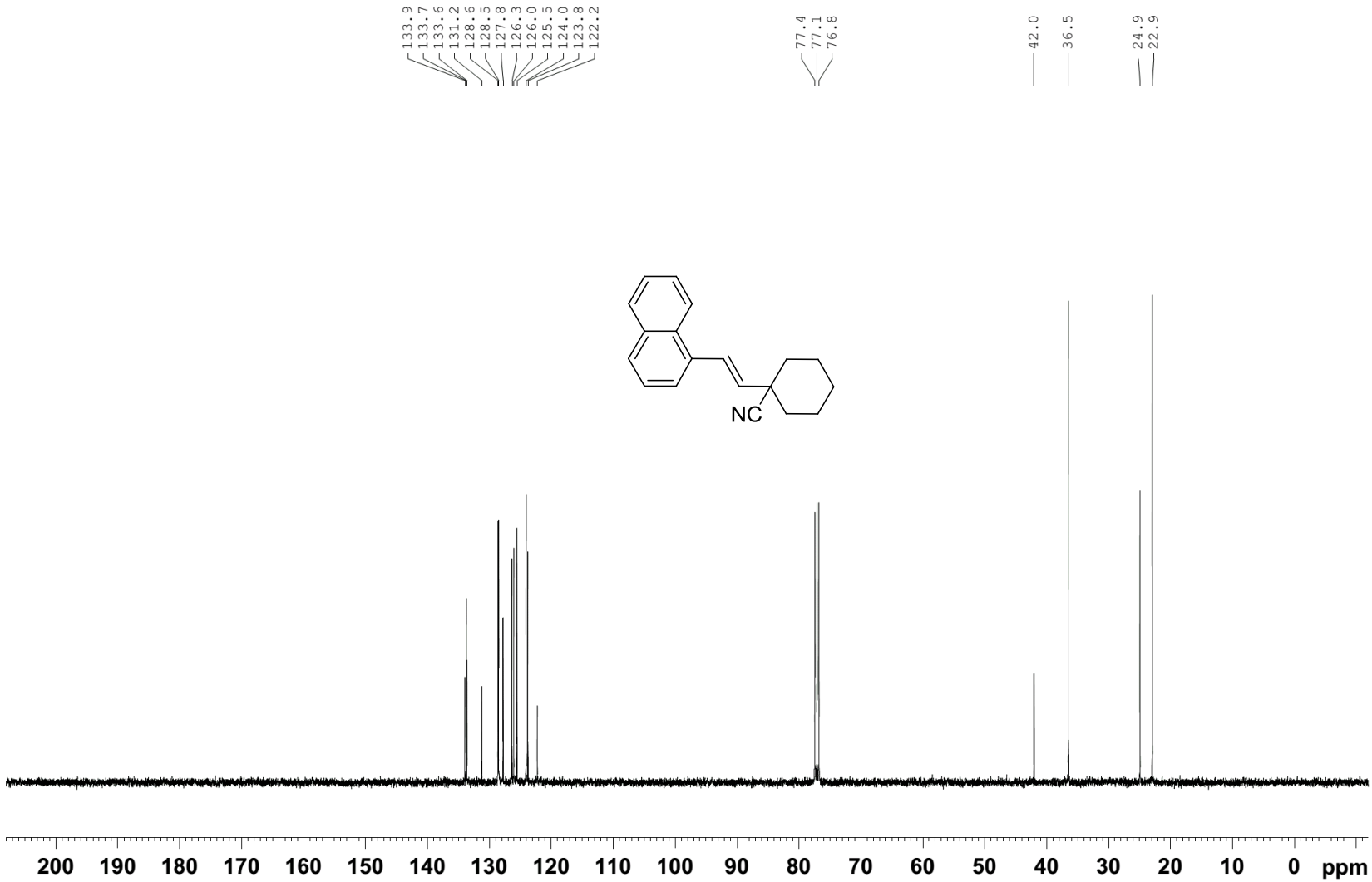

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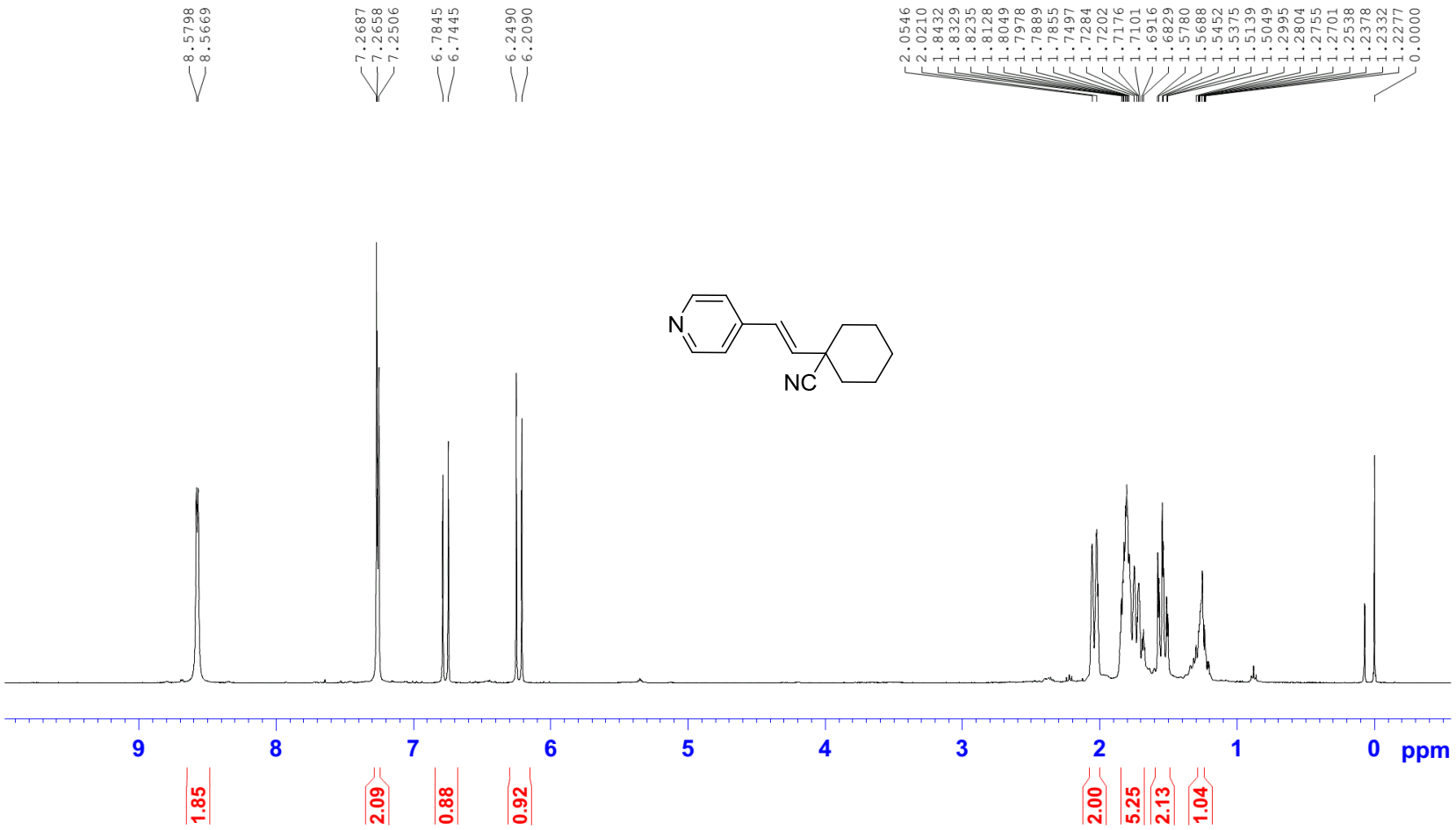

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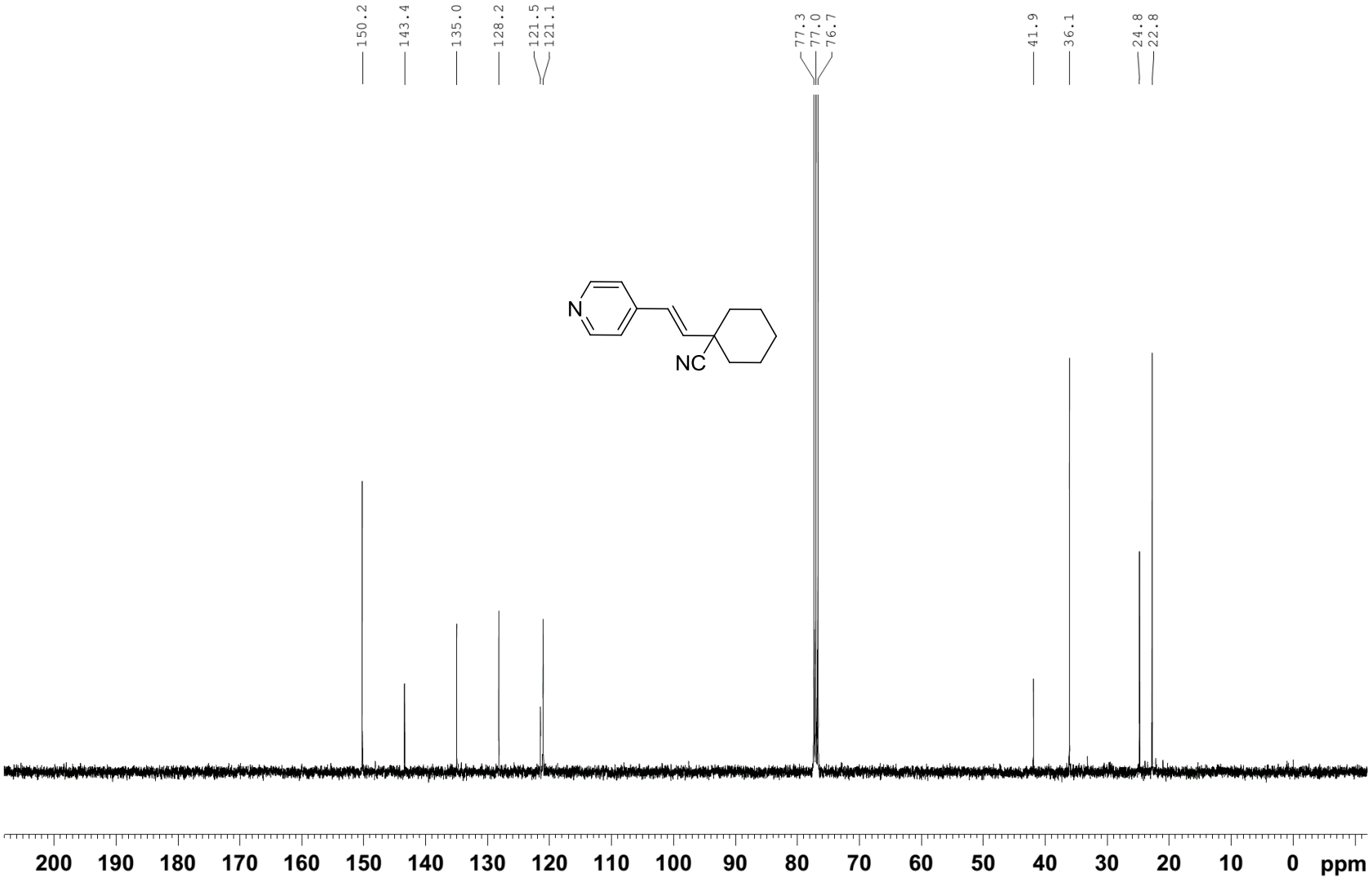

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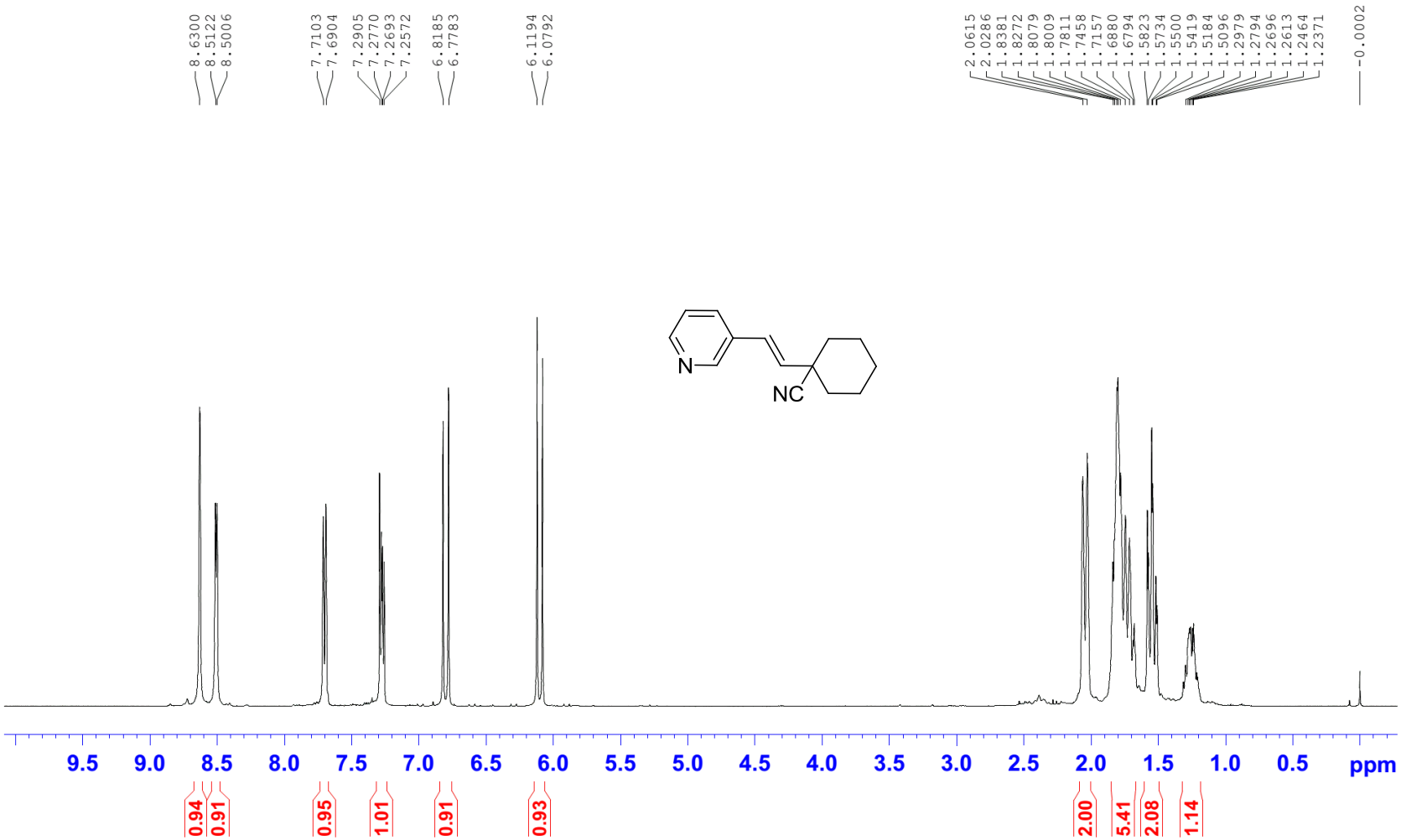

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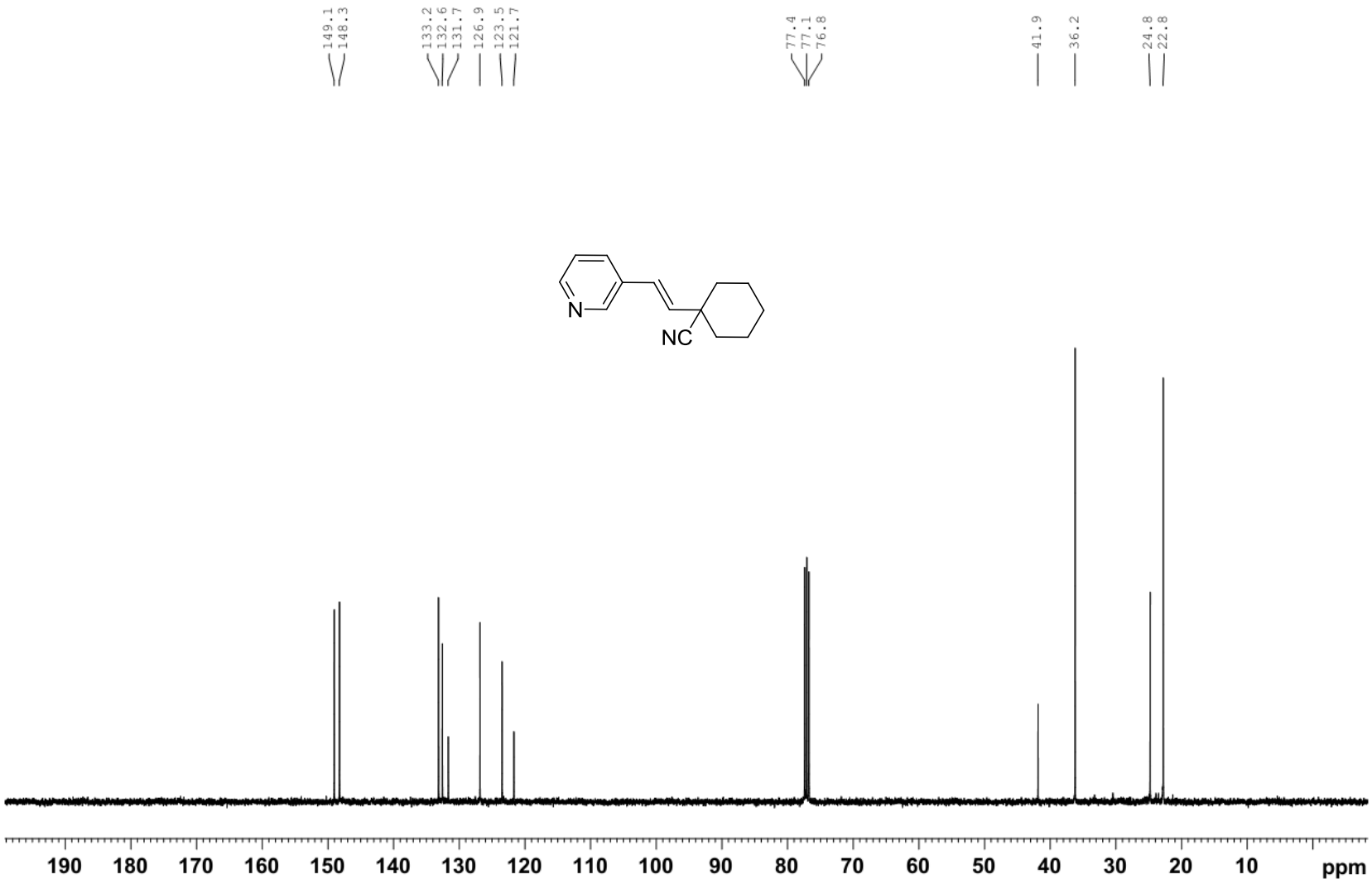

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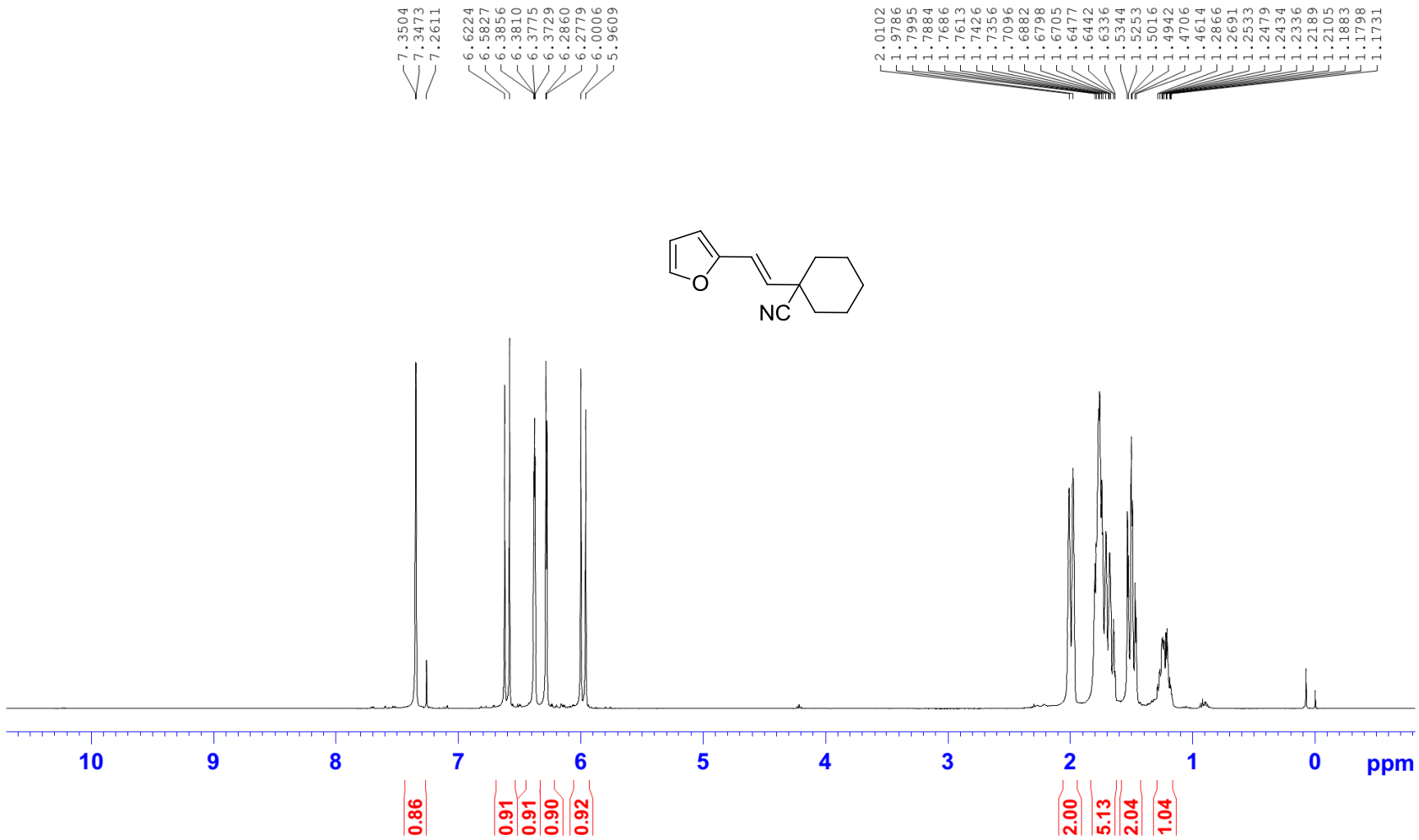

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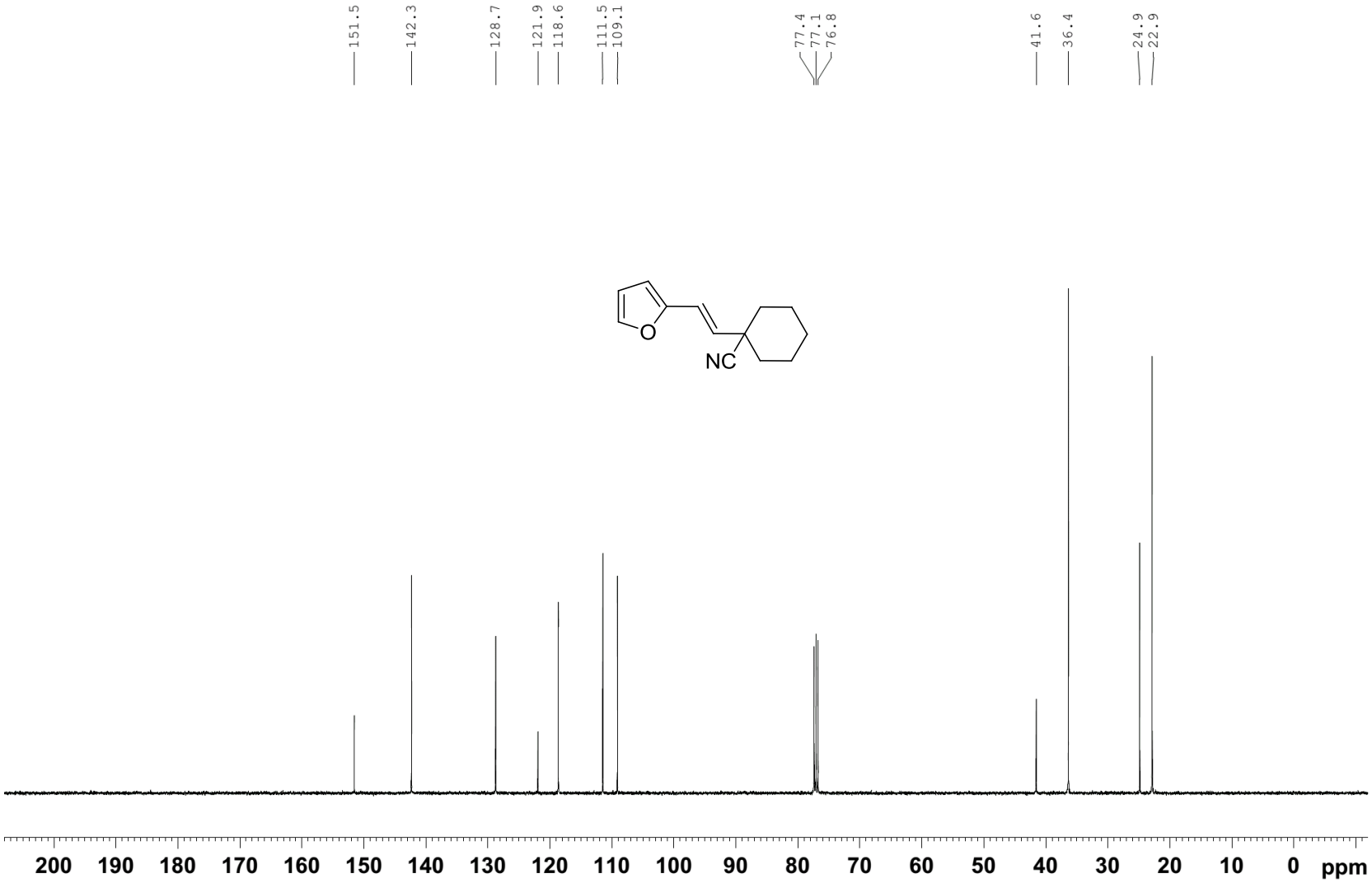
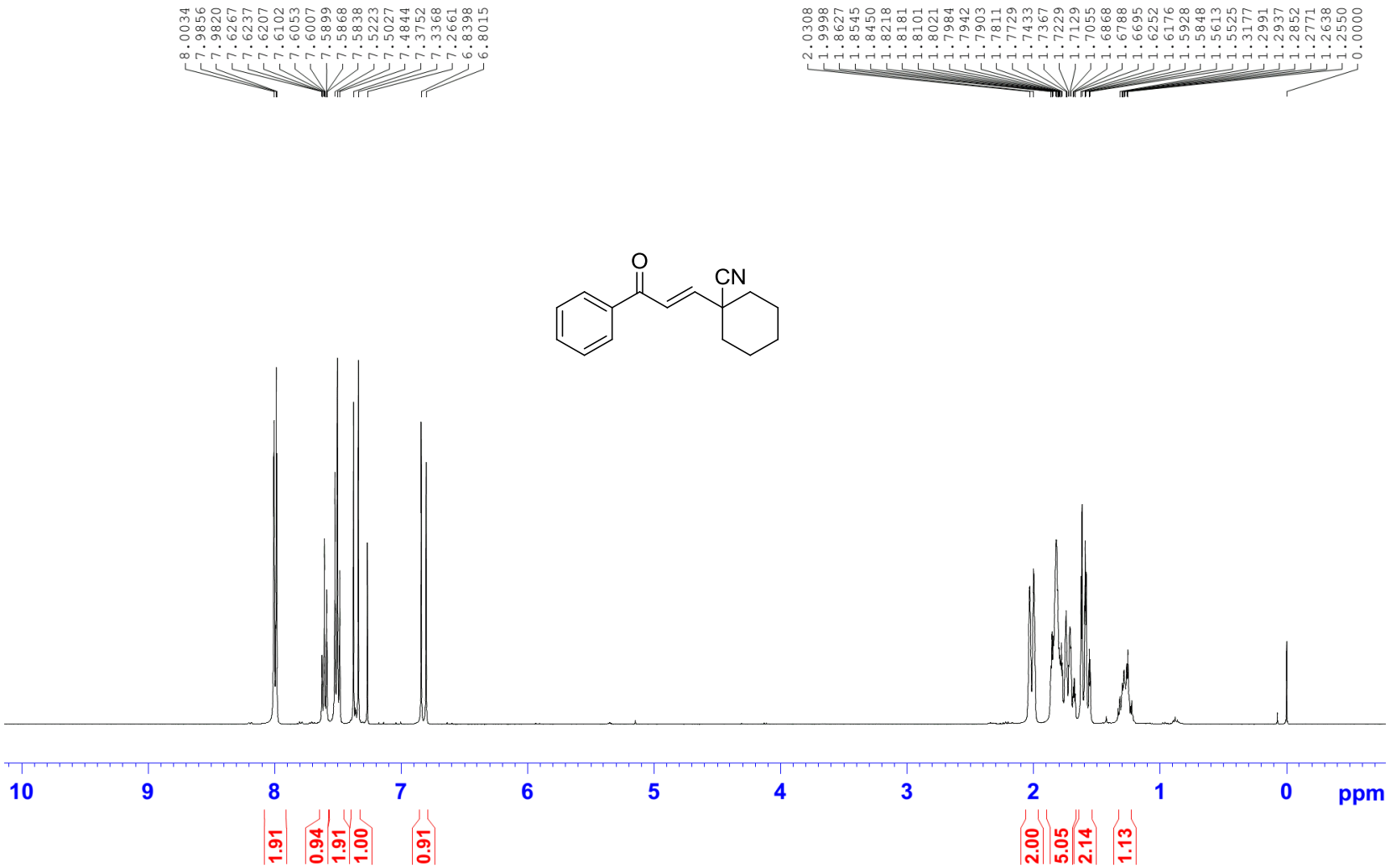
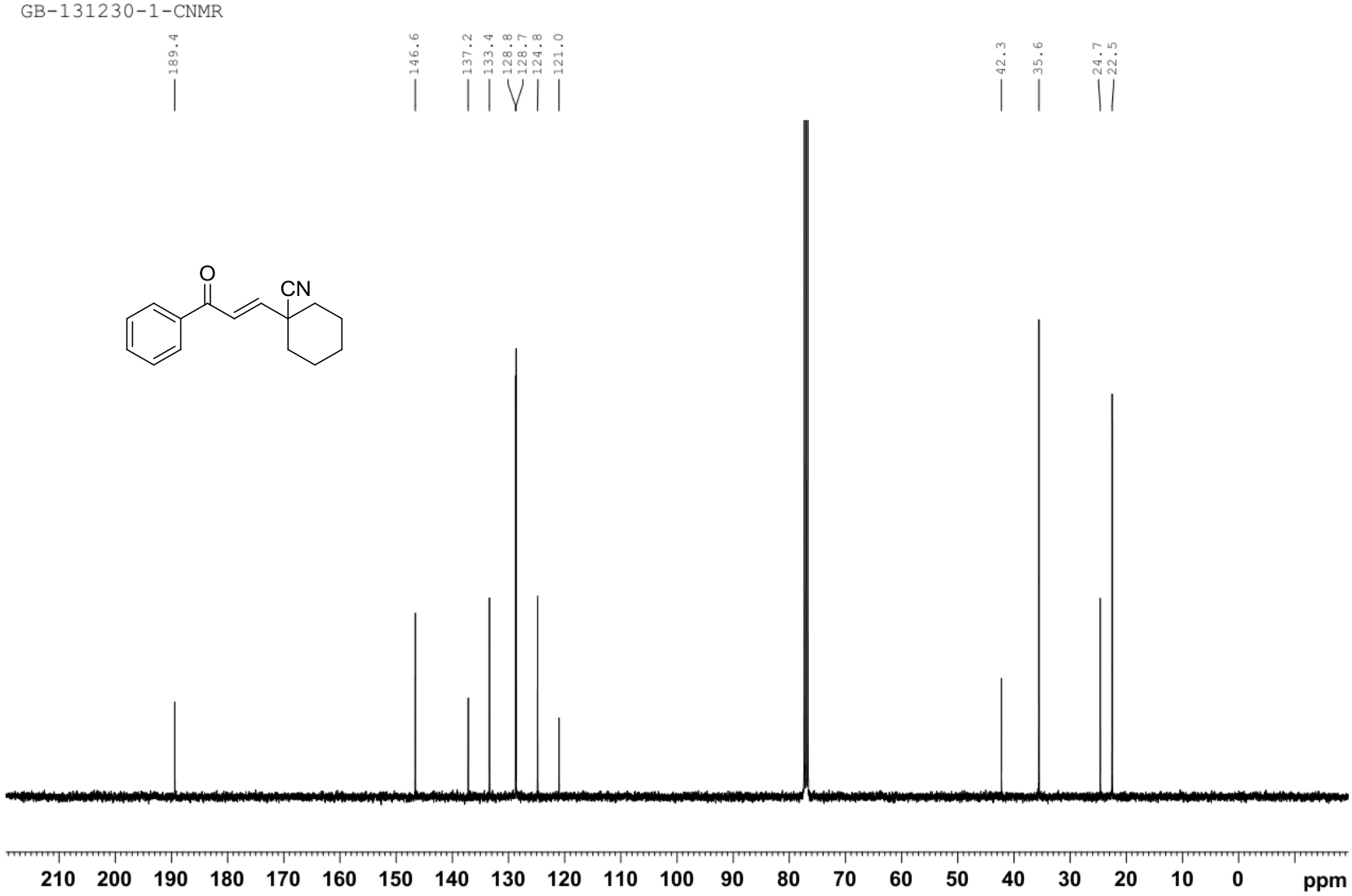
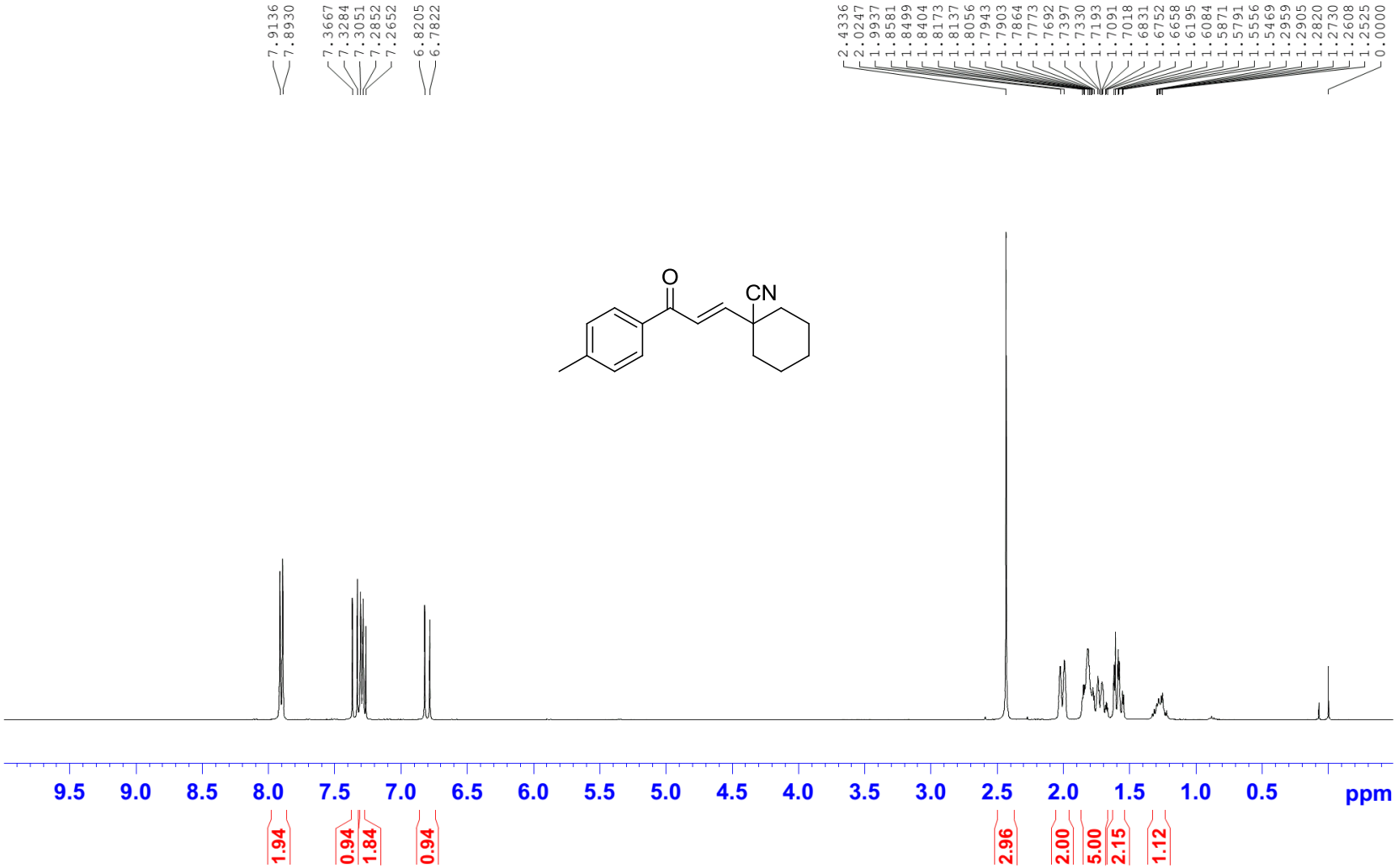


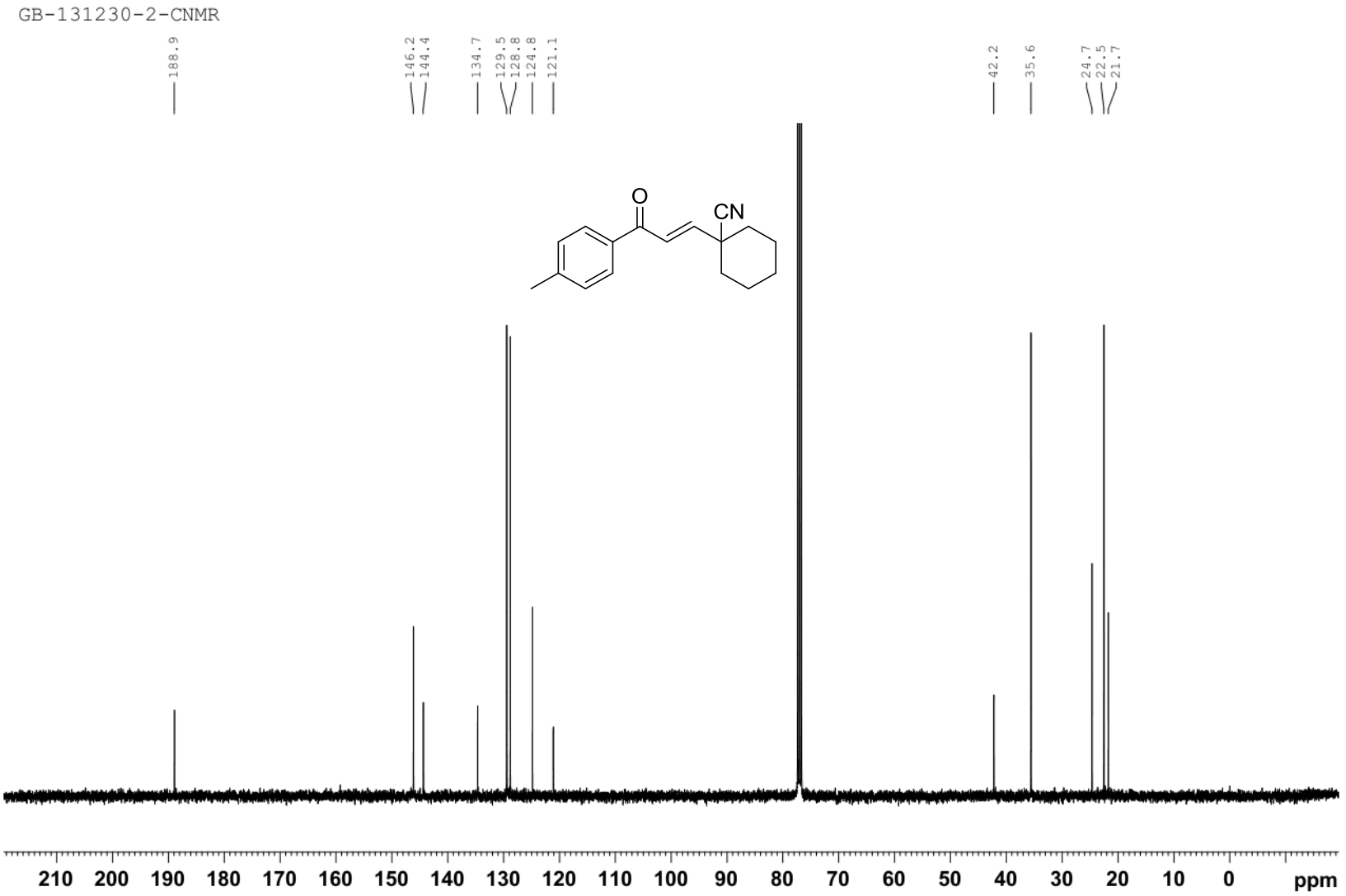
GB-131230-1-HNMR



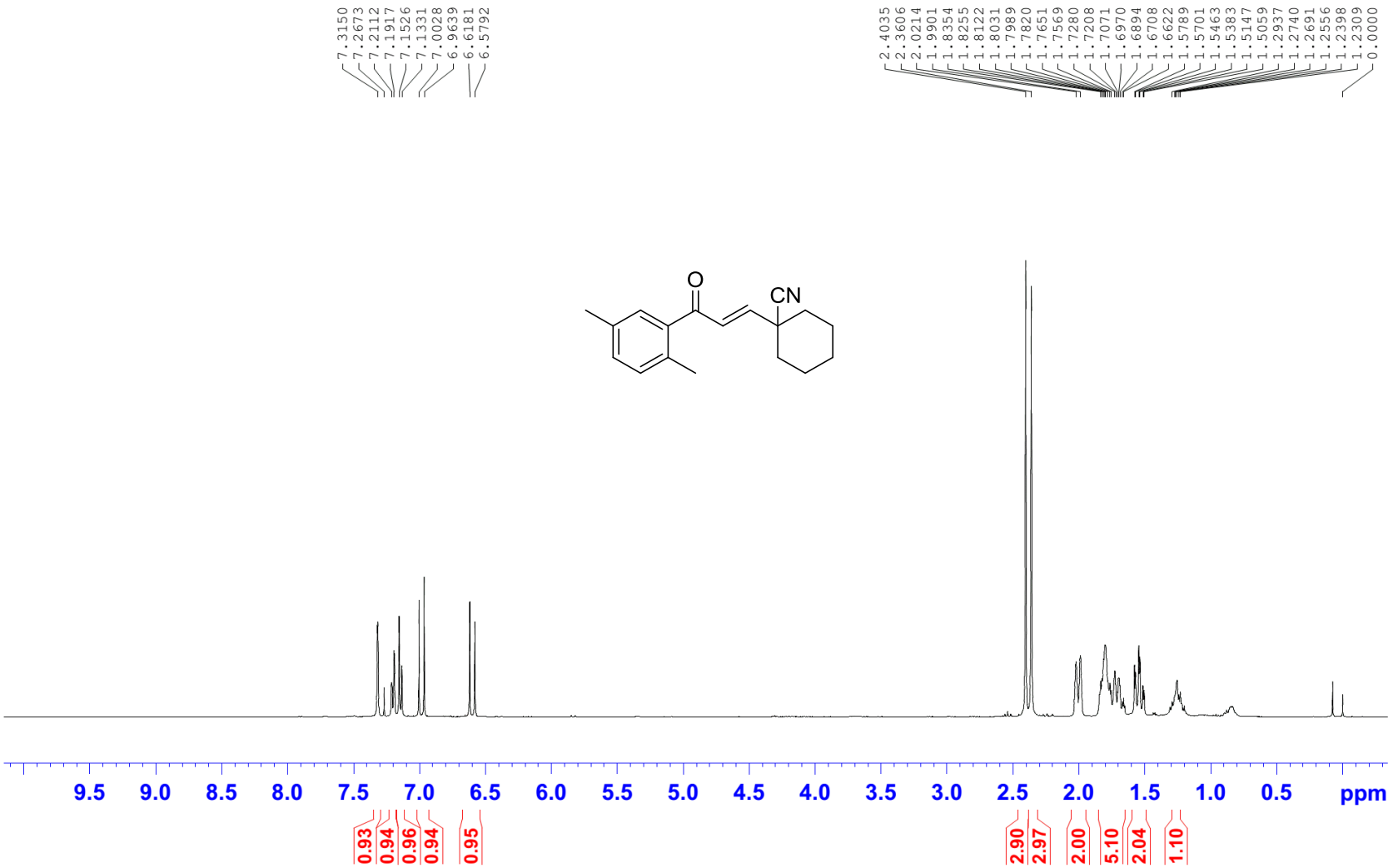

GB-131230-1-CNMR
189.4
146.6
137.2
133.4
128.8
128.7
124.8
121.0
42.3
35.6
24.7
22.5
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

GB-131230-2-HNMR




GB-131230-2-CNMR
188.9
146.2
144.4
134.7
129.5
128.8
124.8
121.1
42.2
35.6
24.7
22.5
21.7
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

GB-131230-3-HNMR



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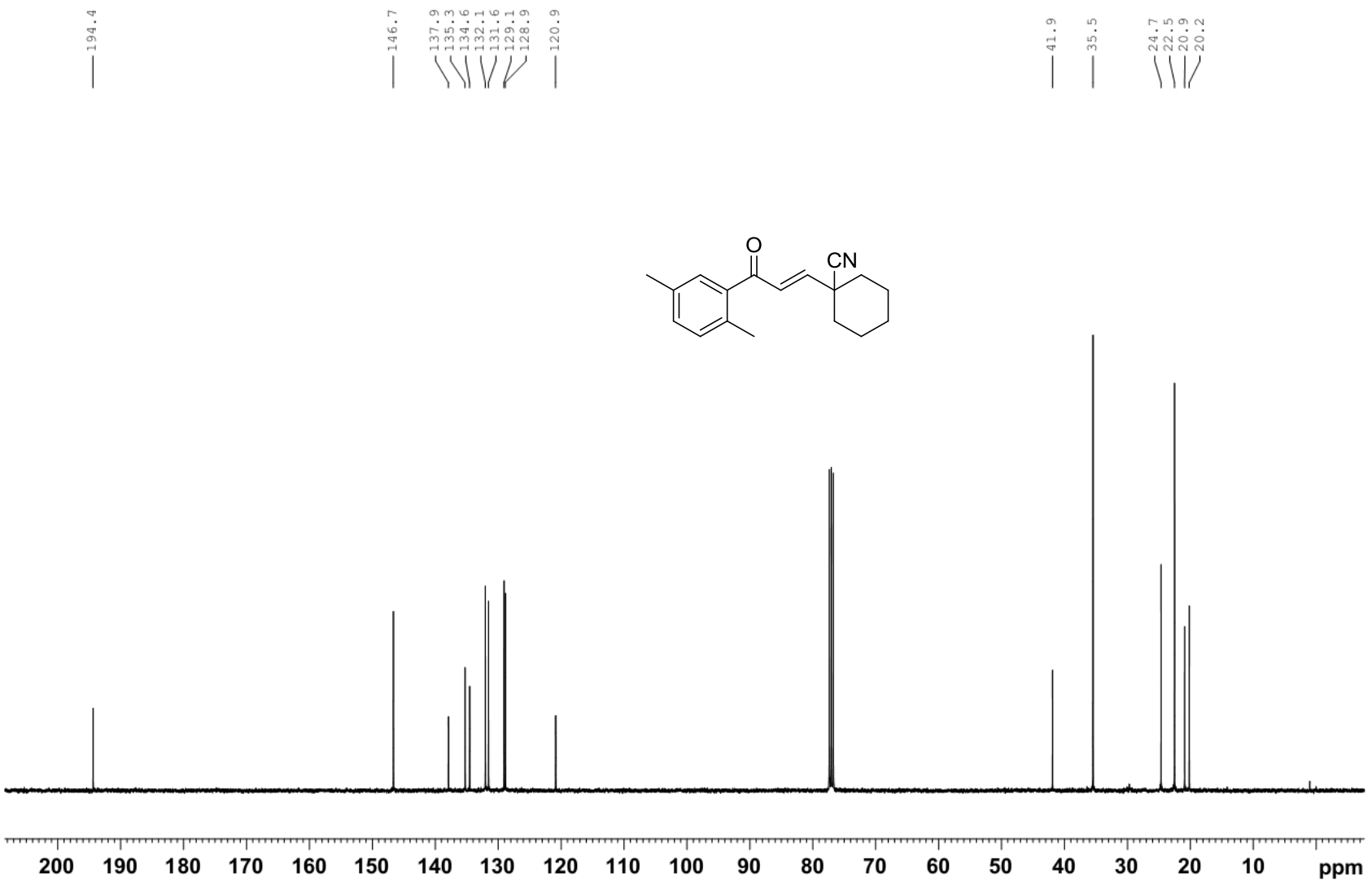
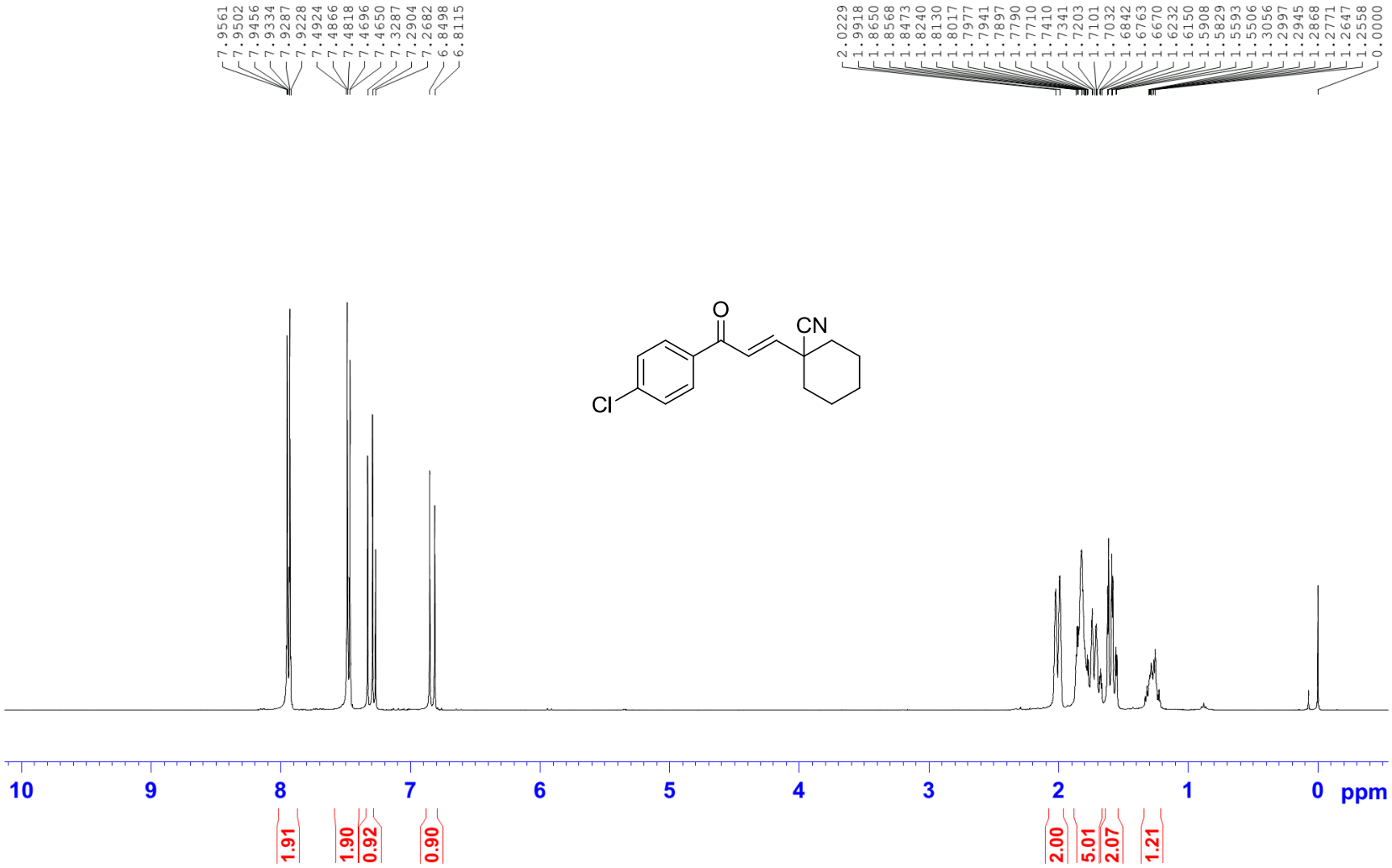
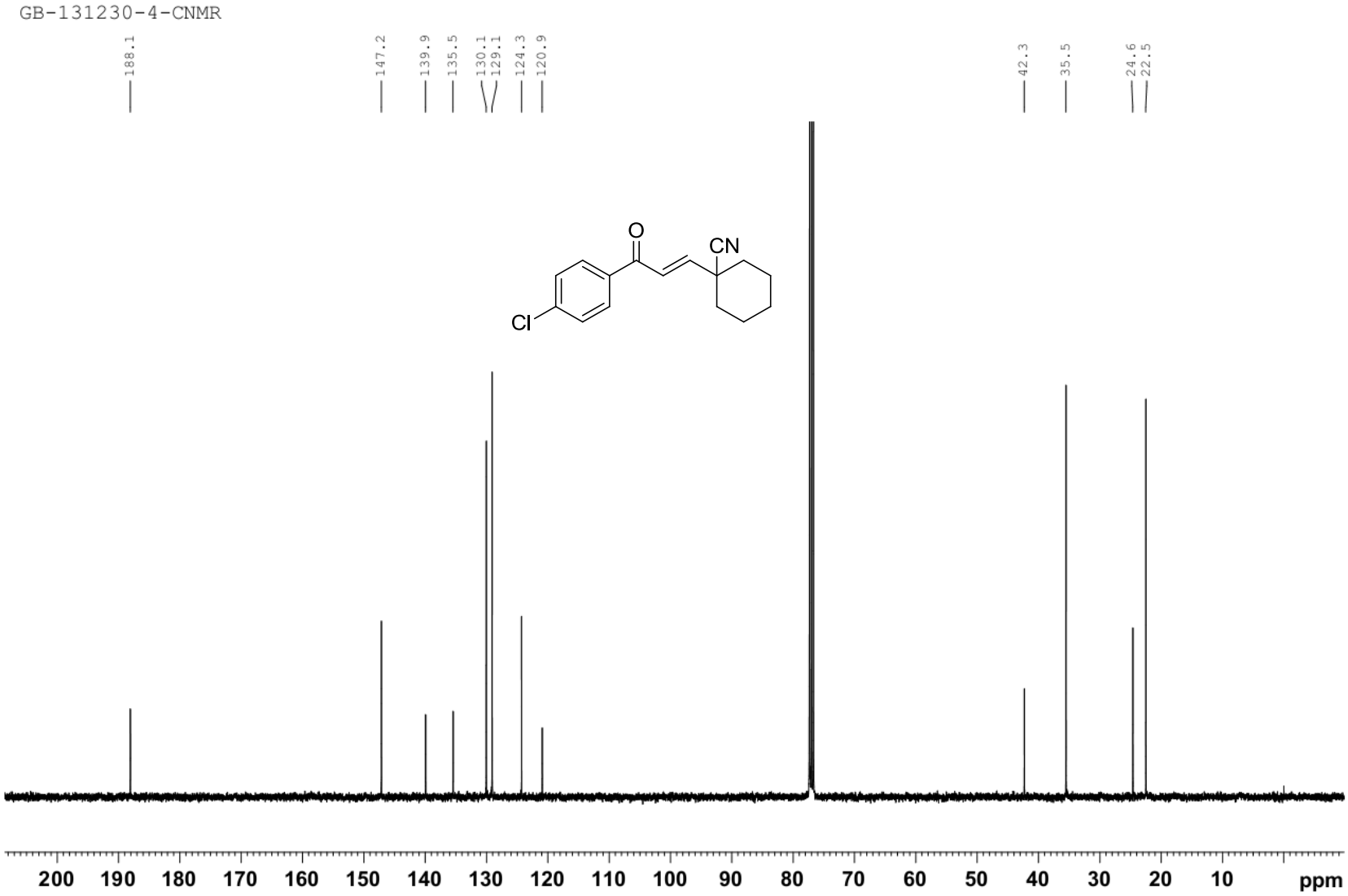
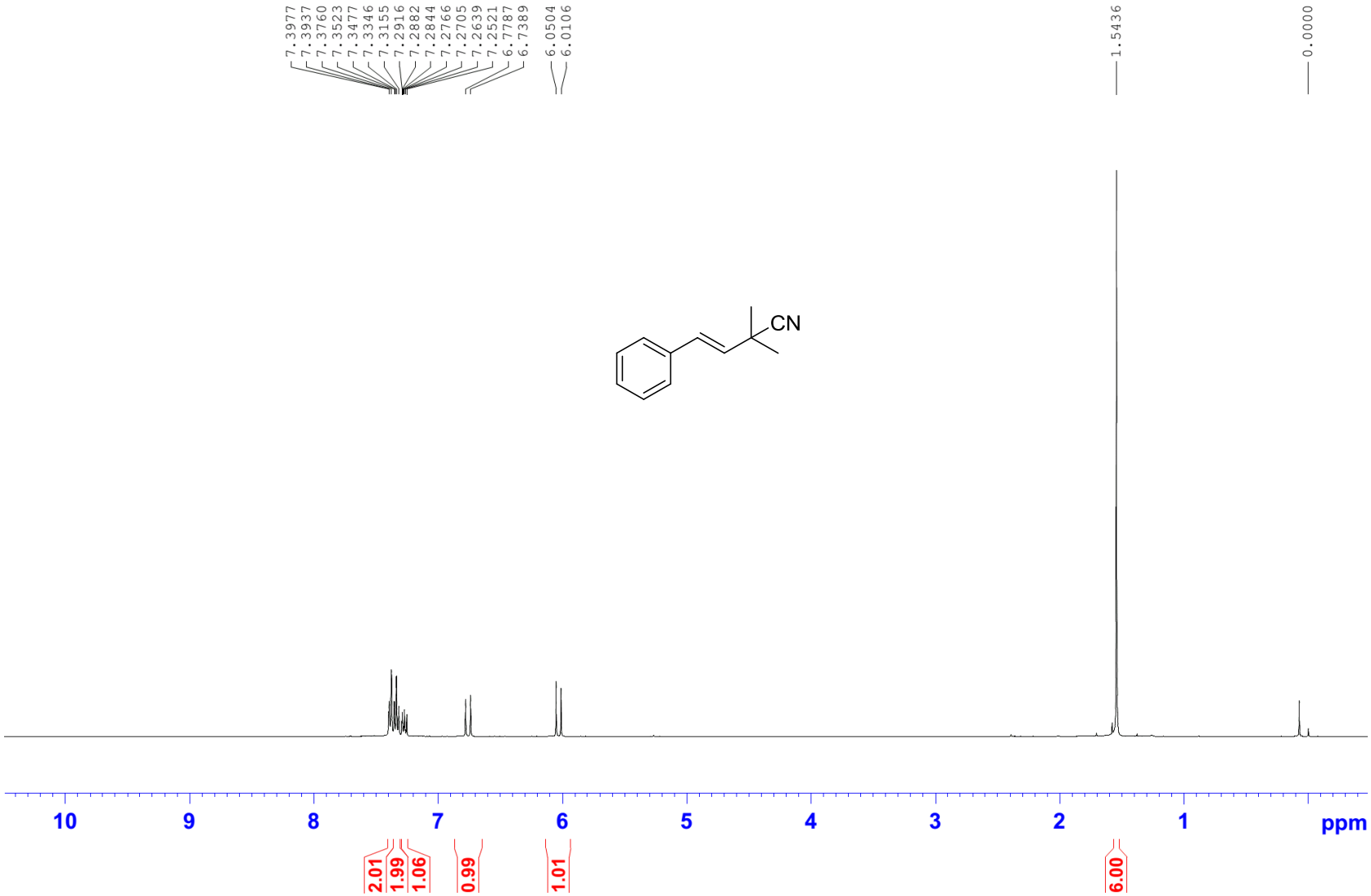


GB-131230-4-HNMR




GB-131230-4-CNMR
188.1
147.2
139.9
135.5
130.1
129.1
124.3
120.9
42.3
35.5
24.6
22.5
O
CN
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

GB-X160113-1-HNMR



GB-X160113-1-CNMR