Supporting Information

Lewis Acid-Mediated Formamidation Employing Carbohydrates as Synthons

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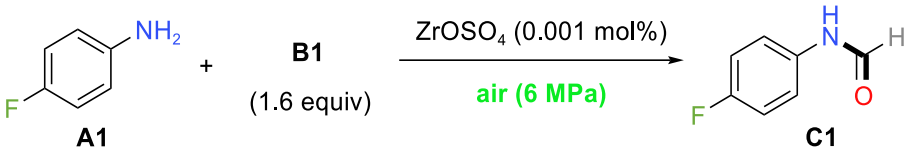
Table of contents

1. General

Experimental: Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signal. Coupling constants (J) are given in Hz (coupling patterns: s: singlet, s_br: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Machinery-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC-MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography.

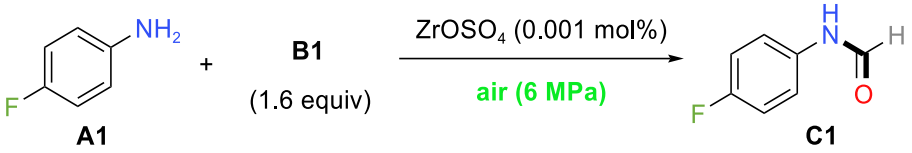
2. Screening of reaction parameters



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, 4-Fluorobenzenamine (**A1**), carbon sources (**B1**), $ZrOSO_4$ and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C1**.

Entry	Parameter
Table S1	The difference of catalyst screening
Table S2	The loading catalyst screening
Table S3	The difference of solvent screening
Table S4	Reaction temperature screening
Table S5	Reaction time screening
Table S6	Reaction pressure screening
Table S7	The loading of **B1** screening
Table S8	Screening studies on carbon sources

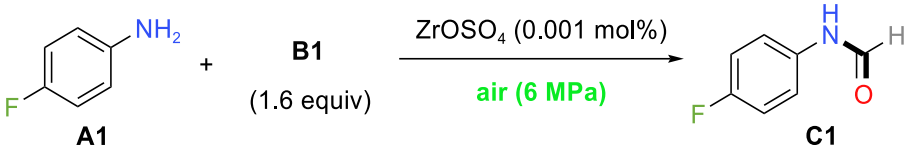
Table S1: The difference of catalyst screening [a]



Entry	Catalyst (0.001 mol%)	**C1** (%)
1	$FeCl_3$	<5
2	**$ZrOSO_4$**	**81**
3	$ZrCl_4$	<5
4	ZrO_2	<5
5	$CuCl_2$	11
6	$CuSO_4$	<5
7	$AlCl_3$	16
8	MnO_2	<5
9	$BF_3{\cdot}Et_2O$	<5

[a] Reaction condition: **A1** (0.5 mmol), Glucose (0.8 mmol), 1,4-dioxane (2.0 mL), air (6.0 MPa), 130 °C, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

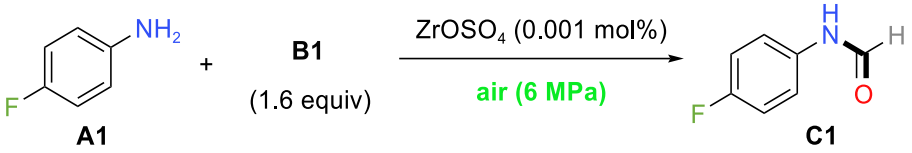
Table S2: The loading catalyst screening [a]



Entry	**Cat.** (mol%)	**C1**(%)
1	0.0001	5
2	0.00025	13
3	0.0005	47
4	**0.001**	**81**
6	0.0015	75
7	0.002	62

[a] Reaction condition: **A1** (0.5 mmol), Glucose (0.8 mmol), 1,4-dioxane (2.0 mL), air (6.0 MPa), 130 ℃, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

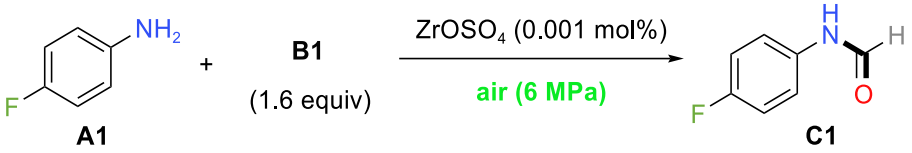
Table S3: The difference of solvent screening [a]



Entry	Solvent (2 mL)	**C1** (%)
1	DMSO	0
2	DMF	23
3	H_2O	0
4	**1,4-dioxane**	**81**
5	THF	65
6	Et_2O	53
7	MeOH	12
8	DMAC	10
9	Toluene	13
10	MeCN	25
11	IPA	48
12	DMAC	13
13	DGME	64
14	NMP	16
15	DCE	18
16	*n*-Hexane	0
17	DGME	65
18	Propylene Carbonate	56
19	Ethylene Carbonate	52
20	Butylene Carbonate	48

[a] Reaction condition: **A1** (0.5 mmol), Glucose (0.8 mmol), $ZrOSO_4$ (0.001 mol%), air (6.0 Mpa), 130 °C, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

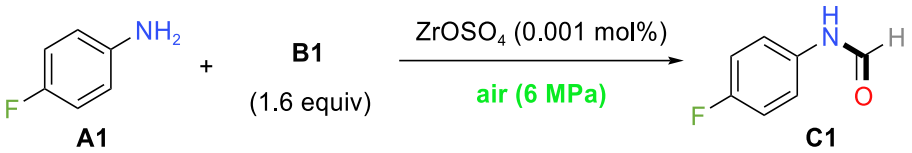
Table S4: Reaction temperature screening [a]



Entry	T [°C]	**C1** (%)
1	25	0
2	50	0
3	80	0
4	100	74
5	120	76
6	**130**	**82**
7	140	78

[a] Reaction condition: **A1** (0.5 mmol), Glucose (0.8 mmol), $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (2.0 mL), air (6.0 MPa), x °C, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

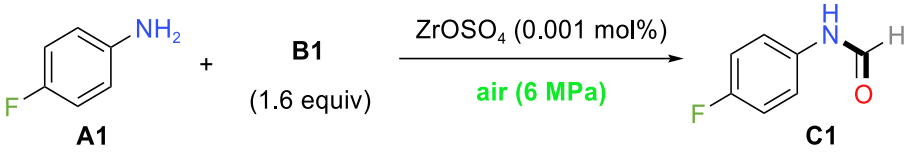
Table S5: Reaction time screening [a]



Entry	t [h]	**C1** (%)
1	3	0
2	6	39
3	9	67
4	**12**	**82**
5	18	81
6	24	80
7	30	79

[a] Reaction condition: **A1** (0.5 mmol), Glucose (0.8 mmol), $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (2.0 mL), air (6.0 MPa), 130 °C, x hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

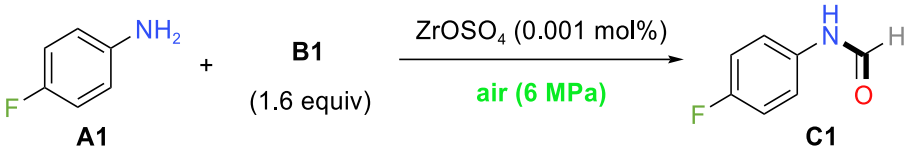
Table S6: Reaction pressure screening [a]



Entry	P [MPa]	**C** 1(%)
1	0.1	23
2	0.5	41
3	1.0	55
4	2.0	63
5	4.0	71
6	5.0	75
7	**6.0**	**82**
8	8.0	78

[a] Reaction condition: **A1** (0.5 mmol), Glucose (0.8 mmol), $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (2.0 mL), air (x MPa), 130 °C, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

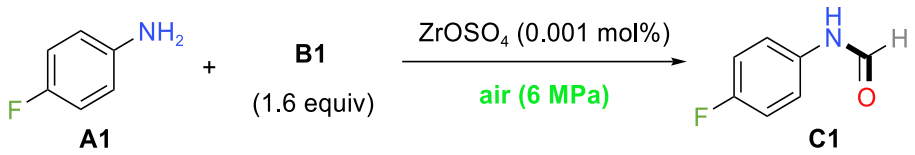
Table S7: The loading of B1 screening [a]



Entry	**B1** (mmol)	**C1** (%)
1	0	0
2	0.2	14
3	0.5	22
4	0.6	59
5	**0.8**	**81**
6	1	72

[a] Reaction condition: **A1** (0.5 mmol), $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (2.0 mL), air (6.0 MPa), 130 °C, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

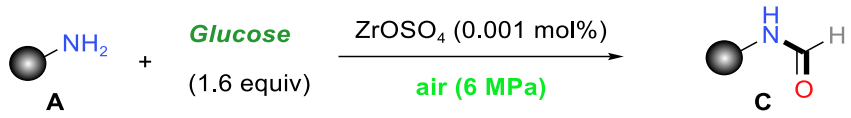
Table S8 Screening studies on carbon sources [a]



Entry	B	Loading	C1 (%)
1	**B1**	Formaldehyde (0.8 mmol)	<5
2	**B2**	Butyraldehyde (0.8mmol)	9
3	**B3**	1,1-Dimethoxybutane (0.8 mmol)	<5
4	**B4**	Butyric acid (0.8 mmol)	<5
5	**B5**	*(E)*-3,6-dimethylhepta-2,5-dienal (0.8 mmol)	15
6	**B6**	*(E)*-1,1-dimethoxy-3,6-dimethylhepta-2,5-diene (0.8 mmol)	<5
7	**B7**	*(E)*-3,6-dimethylhepta-2,5-dienoic acid (0.8 mmol)	<5
8	**B8**	Furfural (0.8 mmol)	7
9	**B9**	5-Hydroxymethyl furfural (0.8 mmol)	<5
10	**B10**	D-arabinose (0.8 mmol)	53
11	**B11**	D-Glucurono-6,3-lactone (0.8 mmol)	31
12	**B12**	**Glucose (0.8 mmol)**	**83**
13	**B13**	Pentahydroxy hexanoic acid (0.8 mmol)	<5
14	**B14**	D-sorbitol (0.8 mmol)	<5
15	**B15**	Anhydrous lactose (0.8 mmol)	<5
16	**B16**	Sucrose (0.8 mmol)	<5
17	**B17**	Hydroxyethyl cellulose (0.10 g)	<5
18	**B18**	Microcrystalline cellulose (0.10 g)	<5

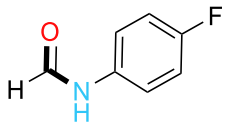
[a] Reaction condition: **A1** (0.5 mmol), $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (2.0 mL), air (6.0 MPa), 130 °C, 12 hr. Yields of **C1** was determined by GC analysis using *n*-cetane as the internal standard.

3. Experimental characterization data for products



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was loaded with a magnetic stirring bar, amines (**A**, 10 mmol), glucose (16 mmol), and $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (30 mL) while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C**.

4. Characterization data



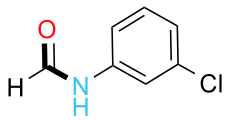
***N*-(4-fluorophenyl)formamide (C1)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.16 g, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$)**)** δ 8.59 – 8.49 (m, 1H, -CHO), 8.34 (d, *J* = 1.2 Hz, 0.58 H), 7.60 (s, 0.42 H), 7.51 (m, 1H), 7.09 – 6.98 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 161.8, 160.9, 159.4, 159.2, 158.5, 133.0, 132.9, 132.8, 132.81, 122.0, 121.9, 121.4, 121.3, 117.2, 116.6, 116.0, 115.8 ppm.

HRMS (ESI) calcd. for $C_7H_7FNO[M+H]^+$: 140.0512, found: 140.0507.



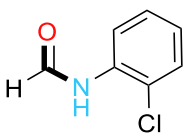
***N*-(3-chlorophenyl)formamide (C2)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.26 g, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 – 8.64 (m, 1H, -CHO), 8.37 (d, *J*=2.0 Hz, 0.58H), 7.67 (m, ,1H), 7.41 – 7.38 (m, 0.60H), 7.31 – 7.23 (m, 1H), 7.18 – 7.16 (m, 0.45H), 7.13 – 7.10 (m, 1H), 7.01 – 6.98 (m, 0.46H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 159.3, 138.1, 138.05, 135.6, 134.9, 131.0, 130.3, 125.5, 125.0, 120.2, 118.9, 118.0, 116.8 ppm.

HRMS (ESI) calcd. for $C_7H_7ClNO[M+H]^+$: 156.0216, found: 156.0221.



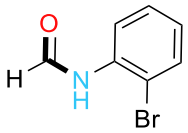
***N*-(2-chlorophenyl)formamide (C3)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.09 g, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 (d, *J*=11.6 Hz, 0.32H, -CHO), 8.50 (d, *J*=1.2 Hz, 0.70H, -CHO), 8.42 (dd, *J*=8.4 Hz, 2.1, 0.70H), 7.76 (s, 1H), 7.45 – 7.37 (m, 1H), 7.28 (dd, *J*=8.8, 2.2 Hz, 1.43H), 7.14 (m, 0.31H), 7.07 (m, 0.71H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.66, 159.1, 159.0, 133.9, 130.4, 129.3, 129.2, 128.1, 128., 127.9, 126.1, 126.07, 125.33, 125.3, 125.26, 124.4, 122.8, 122.7, 122.2, 122.1, 119.1, 118.8 ppm.

HRMS (ESI) calcd. for $C_7H_7ClNO[M+H]^+$: 156.0216, found: 156.0211.



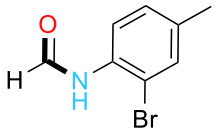
***N*-(2-bromophenyl)formamide (C4)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.35 g, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (d, *J*=11.6 Hz, 0.31H, -CHO), 8.51 (s, 0.62H, -CHO), 8.40 (dd, *J*=8.4 Hz, 1.3, 0.62H), 7.73 (s, 0.80H), 7.58 (m, 1H), 7.38 – 7.24 (m, 1.45H), 7.13 – 6.95 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.5, 137.6, 134.9, 133.6, 132.5, 129.8, 128.6, 126.9, 125.8, 121.8, 118.4, 114.6, 113.1 ppm.

HRMS (ESI) calcd. for C_7H_7BrNO $[M+H]^+$: 199.9711, found: 199.9715.



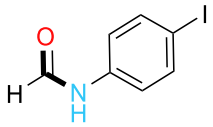
***N*-(2-bromo-4-methylphenyl)formamide (C5)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.51 g,71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.61 (d, *J*=11.6 Hz, 0.31H, -CHO), 8.43 (d, *J*=1.2 Hz, 0.61H, -CHO), 8.21 (d, *J*=8.8 Hz, 0.65H), 7.74 (s, 1H), 7.41 – 7.35 (m, 1H), 7.11 (m, 1.35H), 2.30 (d, *J*=8.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.0, 136.9, 135.9, 133.8, 132.7, 132.5, 132.3, 129.4, 129.1, 122.3, 119.6, 114.4, 113.1, 20.65, 20.59 ppm.

HRMS (ESI) calcd. for C_8H_9BrNO $[M+H]^+$: 213.9868, found: 213.9863.



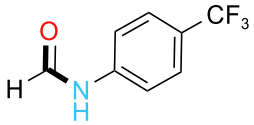
***N*-(4-iodophenyl)formamide (C6)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.81 g, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, *J*=11.6 Hz, 0.41H, -CHO), 8.35 (d, *J*=1.2 Hz, 0.60H, -CHO), 8.19 (s, 0.41H), 7.67 – 7.62 (m, 2H), 7.35 – 7.26 (m, 1.61H), 6.86 (dd, *J*=8.8, 2.2 Hz, 0.80H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 159.0, 140.1 138.2, 135.0, 121.3, 120.6, 91.3, 88.3 ppm.

HRMS (ESI) calcd. for C_7H_7INO $[M+H]^+$: 247.9572, found: 247.9568.



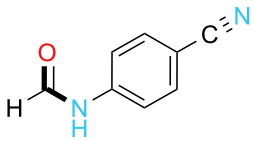
***N*-(4-(trifluoromethyl)phenyl)formamide (C7)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.18 g, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J*=11.6 Hz, 0.25H), 8.41 (d, *J*=1.2 Hz, 1H, -CHO), 7.68 (s, 1.20H), 7.61 (dd, *J*=13.6 Hz, 8.5, 2H), 7.49 (d, *J*=6.4 Hz, 0.57H), 7.20 (d, *J*=8.8 Hz, 0.81H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.2, 139.9, 127.4, 127.3, 127.28, 127.2, 127.0, 126.7, 126.6, 126.59, 125.55, 126.5, 119.7, 118.8.

HRMS (ESI) calcd. for $C_8H_7NOF_3$ $[M+H]^+$: 190.0480, found: 190.0485.



***N*-(4-cyanophenyl)formamide (C8)**

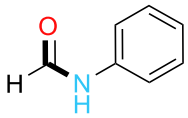
The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.04 g, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83 (d, *J*=10.8 Hz, 0.32H, -CHO), 8.41 (d, *J*=1.2 Hz, 0.66H, -CHO), 7.88 (s, 0.4H), 7.70 – 7.63 (m, 3.18H), 7.42 (d, *J*=10.4 Hz, 0.63H), 7.17 (d, *J*=8.8 Hz, 0.6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 158.5, 139.6, 134.2, 133.1, 119.9, 119.1, 118.0,

107.7 ppm.

HRMS (ESI) calcd. for $C_8H_7N_2O$ $[M+H]^+$: 147.0558, found: 147.0553.



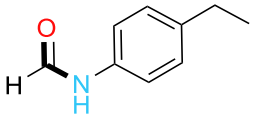
***N*-phenylformamide (C9)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.09 g, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (d, *J*=11.6 Hz, 0.51H, -CHO), 8.37 (d, *J*=2.4 Hz, 0.51H, -CHO), 8.31 (s, 0.40H), 7.53 (d, *J*=8.0 Hz, 1H), 7.46 (s, 0.30H), 7.34 (m, 2H), 7.21 – 7.08 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 158.4, 138.0, 137.6, 131.0, 129.3, 125.5, 124.4, 121.37, 118.6 ppm.

HRMS (ESI) calcd. for C_7H_8NO $[M+H]^+$: 122.0606, found: 122.0602.



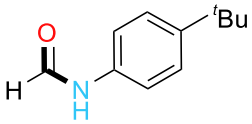
***N*-(4-ethylphenyl)formamide (C10)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.36 g, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.64 (d, *J*=10.8 Hz, 0.53H), 8.35 (d, *J*=2.4 Hz, 1H, -CHO), 7.51 (s, 0.36H), 7.46 – 7.43 (m, 1H), 7.16 (dd, *J*=10.8 Hz, 8.4, 2H), 7.02 – 7..00 (m, 1H), 2.63 (m, 2H), 1.23 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 159.1, 141.7, 140.7, 135.3, 134.4, 129.2, 128.5, 121.4, 119.3, 28.4, 28.3, 15.8, 15.7 ppm.

HRMS (ESI) calcd. for $C_9H_{12}NO$ $[M+H]^+$: 150.0919, found: 150.0916.



***N*-(4-(tert-butyl)phenyl)formamide (C11)**

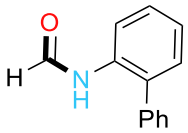
The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.05 g, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65 (d, *J*=12.4 Hz, 0.51H, -CHO), 8.47 (s, 0.50H, -CHO), 8.34 (d, *J*=1.6 Hz, 0.45H), 7.63 (s, 0.45H), 7.50 – 7.46 (m, 1H), 7.35 (m, 2H), 7.05 – 7.03 (m, 1H), 1.31 (d, *J*=6.0 Hz, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 159.7, 148.6, 147.9, 134.8, 134.2, 126.7, 126.0,

119.97, 118.9, 34.54, 34.5, 31.4, 31.3 ppm.

HRMS (ESI) calcd. for $C_{11}H_{16}NO$ $[M+H]^+$: 178.1232, found: 178.1230.



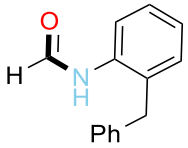
***N*-([1,1'-biphenyl]-2-yl)formamide (C12)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.44 g, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (m, 0.42H, -CHO), 8.31 (d, *J*=8.4 Hz, 0.50H, -CHO), 8.19 (s, 0.50H), 7.47 – 7.15 (m, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 162.1, 159.2, 159.1, 137.8, 137.4, 133.9, 133.8, 133.1 133.09, 132.14, 132.11, 131.2, 130.2, 129.4, 129.2, 129.16, 128.8, 128.5, 128.1, 128.09, 125.4, 124.7, 121.7, 121.68, 118.6, 118.57 ppm.

HRMS (ESI) calcd. for $C_{13}H_{12}NO$ $[M+H]^+$: 198.0918, found: 198.0920.



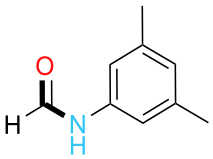
***N*-(2-benzylphenyl)formamide (C13)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.57 g, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (d, *J*=11.6 Hz, 0.54H, -CHO), 8.29 (s, 0.36H, -CHO), 7.96 (d, *J*=8.4, 0.36H), 7.48 (s, 0.64H), 7.35 – 7.00 (m, 9H), 4.04 (s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 159.2, 138.8, 138.6, 135.2, 134.8, 132.8, 131.6, 131.2, 131.14, 129.1, 128.5, 128.48, 128.1, 127.8, 126.9, 126.6, 125.9, 124.2, 122.0, 38.2, 38.0 ppm.

HRMS (ESI) calcd. for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1075, found: 212.1070.



***N*-(3,5-dimethylphenyl)formamide (C14)**

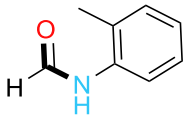
The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.25 g, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (s, 0.54H, -CHO), 8.34 (m, 0.45H, -CHO), 8.07

(m, 0.55H) , 7.34 (m, 0.41 H), 6.77 (s, 1H), 6.27– 6.21 (m, 2H), 3.78 (d, *J*=8.8 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.8, 161.2, 158.6, 138.7, 138.5, 98.4, 97.4, 97.2, 96.9, 55.6, 55.56 ppm.

HRMS (ESI) calcd. for $C_9H_{12}NO$ $[M+H]^+$: 150.0919, found: 150.0920.



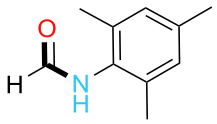
***N*-*o*-tolylformamide (C15)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 0.94 g, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, *J*=11.6 Hz, 0.61H, -CHO), 8.42 (d, *J*=2.4 Hz, 0.35H, -CHO), 8.23 (d, *J*=10.8 Hz, 0.60H), 7.88 (m, 0.35H), 7.24 – 7.07 (m, 4H), 2.29 (d, *J*=14.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.8, 135.2, 134.7, 131.7, 130.7, 129.9, 128.8, 127.2, 126.9, 126.2, 125.6, 124.0, 121.3, 17.9, 17.8 ppm.

HRMS (ESI) calcd. for $C_8H_{10}NO$ $[M+H]^+$: 136.0762, found: 136.0760.



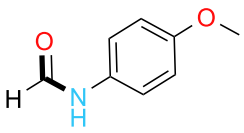
***N*-mesitylformamide (C16)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 1.11 g, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, *J*=1.2 Hz, 0.40H, -CHO), 8.03 (d, *J*=12.4 Hz, 0.45H, -CHO), 7.18 – 6.99 (m, 0.75H), 6.91 (d, *J*=14.8 Hz, 2H), 2.29 – 2.20 (m, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 159.8, 137.7, 137.6, 135.3, 135.1, 130.6, 129.8, 129.5, 129.1, 21.03, 21.0, 18.7, 18.6 ppm.

HRMS (ESI) calcd. for $C_9H_{11}NO$ $[M+H]^+$: 164.1075, found: 164.1070.



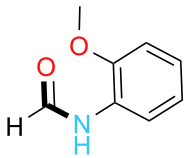
***N*-(4-methoxyphenyl)formamide (C17)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.32 g, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (d, *J*=11.2 Hz, 0.50H, -CHO), 8.31 (d, *J*=2.4 Hz, 0.50H, -CHO), 8.04 (s, 0.50H), 7.46 – 7.42 (m, 1H), 7.38 (s, 0.50H), 7.05 – 7.01 (m, 1H), 6.89 – 6.83 (m, 2H), 3.78 (d, *J*=5.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 160.1, 158.3, 157.3, 130.6, 129.2, 121.9, 121.8, 115.6, 114.4, 55.7, 55.6 ppm.

HRMS (ESI) calcd. for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0711, found: 152.0706.



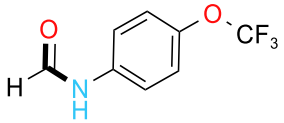
***N*-(2-methoxyphenyl)formamide (C18)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale white solid, 1.11 g, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (d, *J*=11.2 Hz, 0.25H, -CHO), 8.45 (d, *J*=2.4 Hz, 0.57H, -CHO), 8.35 (m, 0.75H), 7.88 (s, 0.48H), 7.81 (s, 0.45H), 7.20 – 6.85 (m, 3.32H), 3.86 (d, *J*=6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 161.6, 159.8, 148.8, 147.9, 147.8, 128.6, 127.8, 126.8, 126.2, 125.3, 124.4, 123.7, 121.1, 120.5, 119.9, 116.0, 112.0, 110.1, 110.0, 55.8, 55.7 ppm.

HRMS (ESI) calcd. for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0711, found: 152.0716.



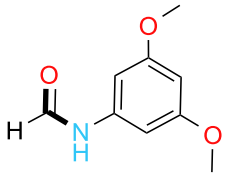
***N*-(4-(trifluoromethoxy)phenyl)formamidee (C19)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow oil, 1.64 g, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 – 8.64 (m, 0.80H, -CHO), 8.37 (d, *J*=1.2 Hz, 0.60H, -CHO), 7.79 (s, 0.55H), 7.59 – 7.56 (m, 1.22H), 7.23 – 7.08 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 159.3, 146.53, 146.51, 145.76, 145.74, 135.6, 135.55, 123.1, 122.0, 121.3, 120.2, 119.5, 119.3 ppm.

HRMS (ESI) calcd. for $C_8H_7F_3NO_2$ $[M+H]^+$: 206.0429, found: 206.0426.



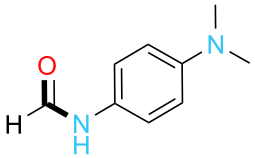
N-(3,5-dimethoxyphenyl)formamide (C20)

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.47 g, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, *J*=11.6 Hz,0.52H, -CHO), 8.33 (d, *J*=2.4 Hz, 0.43H, -CHO), 8.10 (d, *J*=10.8 Hz, 0.51H), 7.38 (s, 0.40H), 6.76 (d, *J*=2.0 Hz, 1H), 6.27 – 6.19 (m, 2H), 3.76 (d, *J*=4.8 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 161.8, 161.2, 159.6, 138.7, 138.6, 98.4, 97.4, 97.2, 96.9, 55.6, 55.55 ppm.

HRMS (ESI) calcd. for $C_9H_{12}NO_3$ $[M+H]^+$: 182.0817, found: 182.0812.



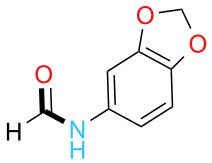
N-(4-(dimethylamino)phenyl)formamide (C21)

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale yellow solid, 1.48 g, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (d, *J*=11.2 Hz, 0.52H, -CHO), 8.27 (d, *J*=2.4 Hz, 0.45H, -CHO), 7.92 (d, *J*=11.6 Hz, 0.52H), 7.38 – 7.36 (m, 1.35H), 6.99 – 6.97 (m, 1H), 6.69 – 6.68 (m, 2H), 2.92 (d, *J*=8.4 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 159.0, 149.1, 148.3, 126.8, 125.9, 122.3, 121.9, 113.4, 113.1, 41.0, 40.9 ppm.

HRMS (ESI) calcd. for $C_9H_{13}N_2O$ $[M+H]^+$: 165.1027, found: 165.1032.



***N*-(benzo[d][1,3]dioxol-5-yl)formamide (C22)**

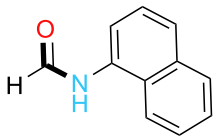
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 1.34 g, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J*=11.6 Hz, 0.45H, -CHO), 8.30 (d, *J*=1.2 Hz,

0.52H, -CHO), 7.94 (s, 0.47H), 7.27 – 7.23 (m, 1.20H), 6.85 – 6.73 (m, 1.53H), 6.62 – 6.52 (m, 1H), 5.97 (d, *J*=12.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 159.0, 148.7, 148.0, 145.8, 144.8, 131.1, 130.8, 113.4, 113.3, 108.8, 108.3, 103.0, 102.3, 101.8, 101.5 ppm.

HRMS (ESI) calcd. for $C_8H_8NO_3$ $[M+H]^+$: 166.0504, found: 166.0509.



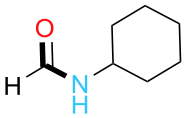
***N*-(naphthalen-1-yl)formamide (C23)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a pale brown solid, 1.27 g, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.78 (d, J=11.6 Hz, 0.51H), 8.45 – 8.37 (m, 1H, -CHO), 8.15 (d, J=2.0 Hz, 0.50H), 7.77 – 7.69 (m, 3H), 7.51 (s, 0.45H), 7.44 – 7.31 (m, 3H), 7.17 – 7.15 (m, 0.64H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.3, 134.3, 133.9, 133.8, 133.4, 131.2, 130.9, 130.1, 129.1, 127.9, 127.8, 127.7, 127.4, 127.3, 126.9, 125.6, 125.4, 119.7, 118.9, 117.2, 115.9 ppm.

HRMS (ESI) calcd. for $C_{11}H_{10}NO$ $[M+H]^+$: 172.0762, found: 172.0767.



***N*-cyclohexylformamide (C24)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 0.80 g, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 – 8.03 (m, 1H, -CHO), 6.10(m, 1H), 3.78 (m, 0.74H), 3.29 – 3.20 (m, 0.26H), 1.85 (m, 2H), 1.71 – 1.63 (m, 2H), 1.55 (m, 1H), 1.36 – 1.21 (m, 2.41H), 1.12 (m, 2.59H) ppm.

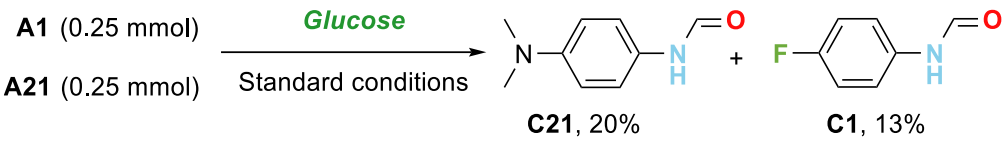
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.5, 51.1, 48.0, 34.7, 33.0, 27.0, 25.4, 25.0, 24.8 ppm.

HRMS (ESI) calcd. for $C_7H_{14}NO$ $[M+H]^+$: 128.1075, found: 128.1080.

5. Mechanism investigations

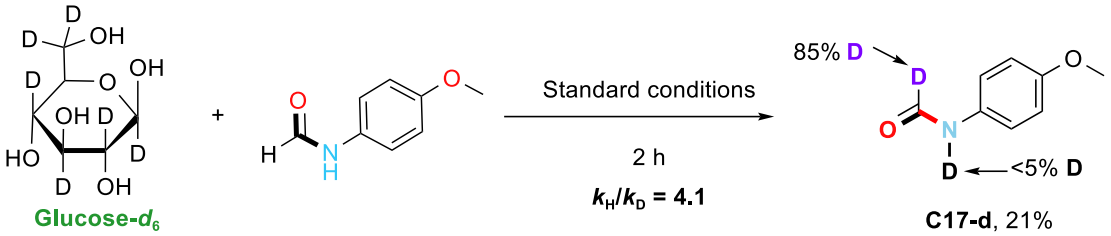
5.1 Competition experiments

5.1.1 Substrate Competition Experiments

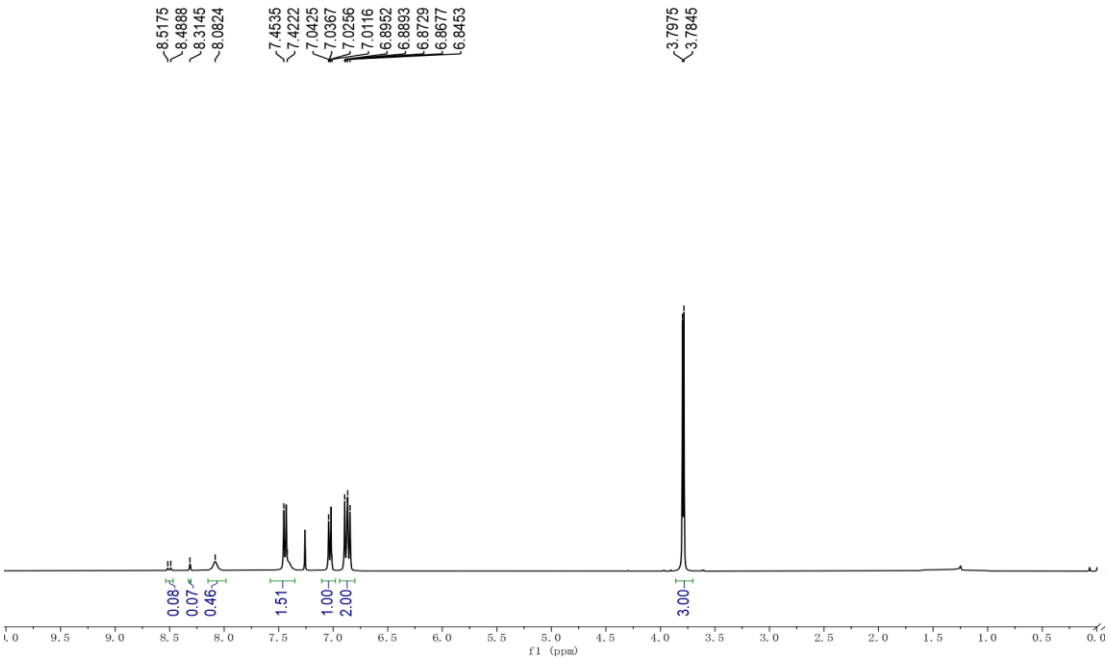


Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (25.0 mL) was loaded with a magnetic stirring bar, 4-Fluorobenzenamine (**A1**, 0.25 mmol), *N,N*-dimethyl-*p*-phenylenediamine (**A21**, 0.25 mmol), glucose (0.4 mmol), $ZrOSO_4$ (0.001 mol%), 1,4-dioxane (10 mL) while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for 2 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding products **C21** (yield: 20%), **C1** (yield: 13%).

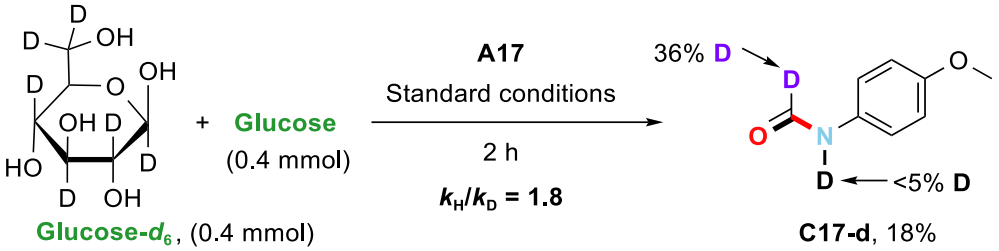
5.1.2 Experimental detail for determination of the intramolecular KIE



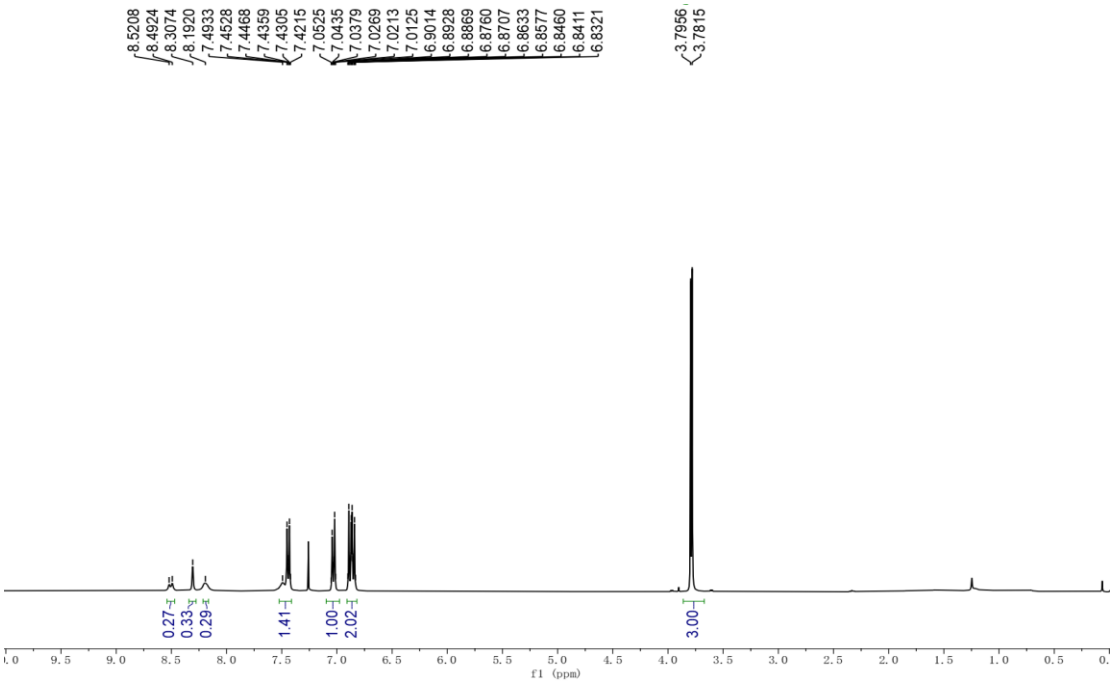
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (5.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), glucose-d_6 (0.8 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-d** (yield: 21%).



5.1.3 Experimental detail for determination of the intermolecular KIE

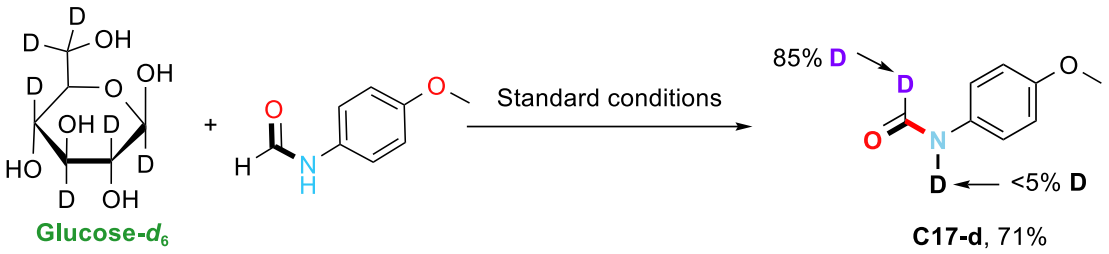


Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (5.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.25 mmol), glucose-d_6 (0.4 mmol), glucose (0.4 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-d** (yield: 18%).



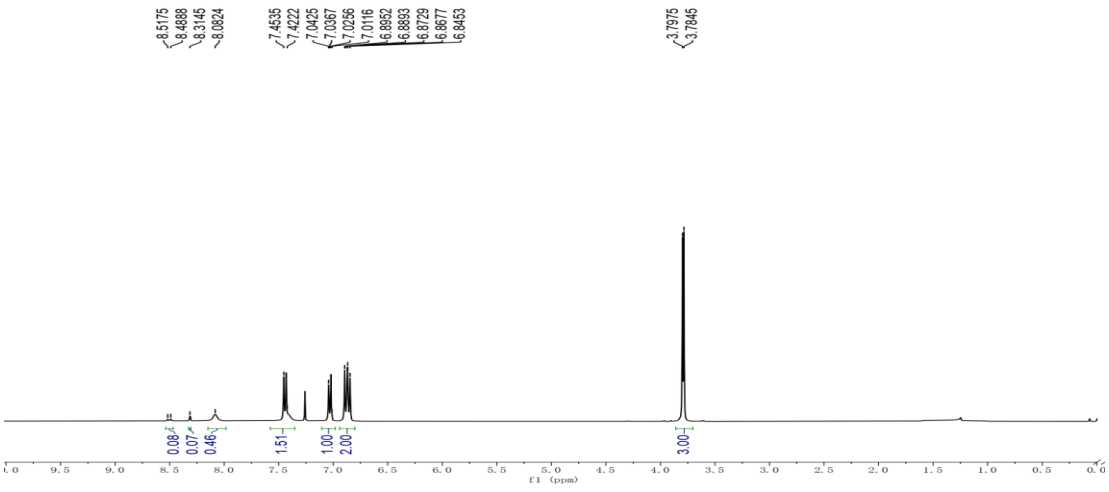
5.2 Labelled investigations

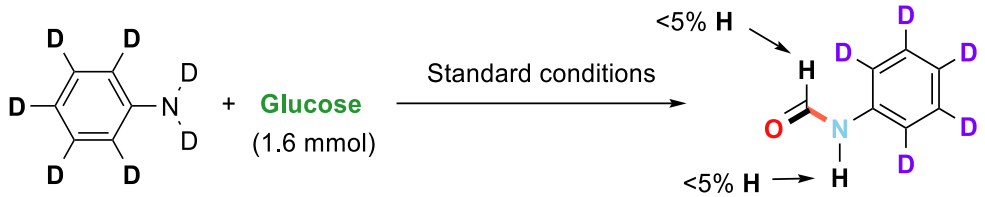
5.2.1 D-labelled experiments



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), glucose-d_6 (0.8 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-d** (yield: 71%).

HRMS (ESI) calcd. for $C_8H_9DNO_2$ $[M+H]^+$: 153.0711, found: 153.0712.

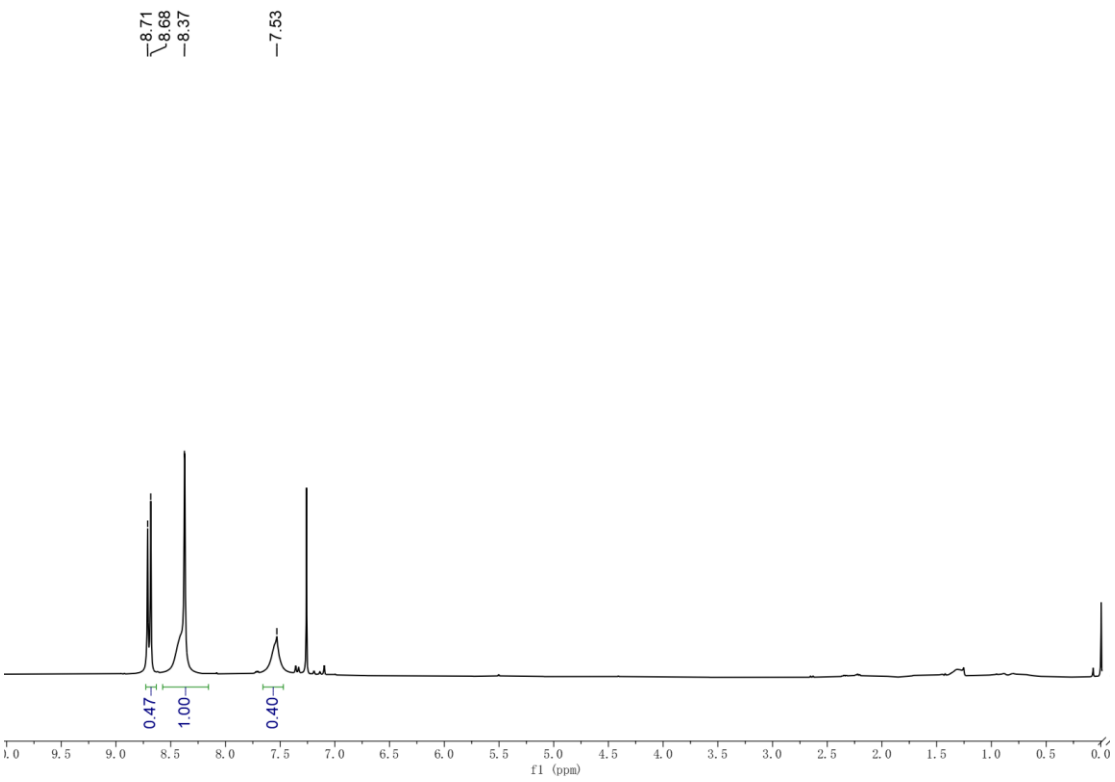


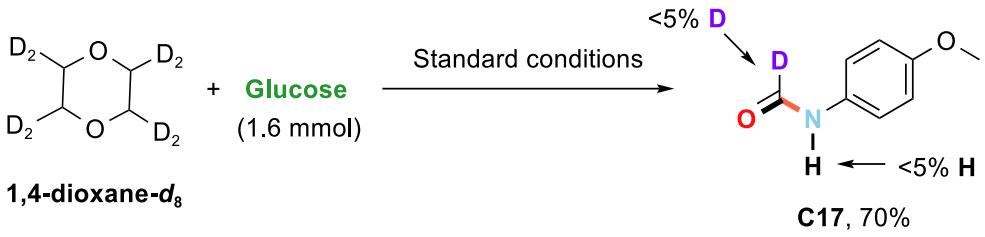


C9-*d*, 75%

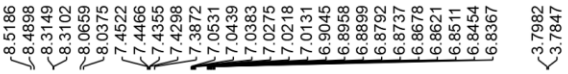
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, aniline-d_7 (1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C9-d** (yield: 75%).

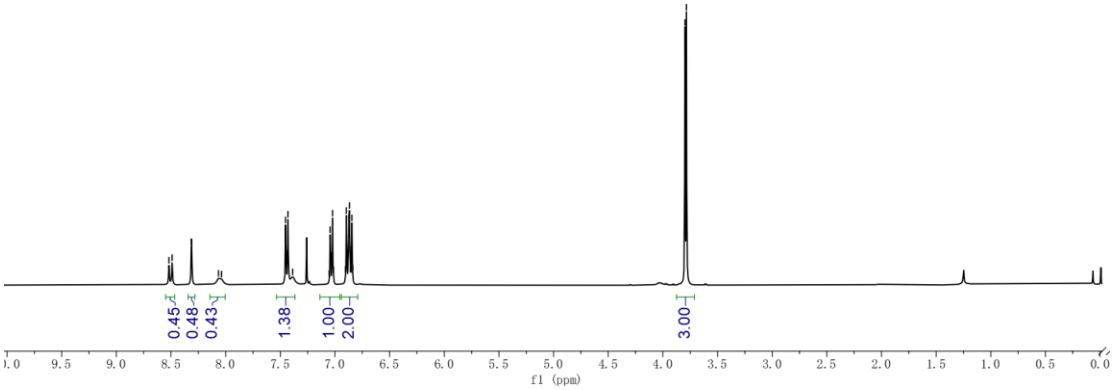
HRMS (ESI) calcd. for $C_7H_3D_5NO$ $[M+H]^+$: 127.0605, found: 127.0610.

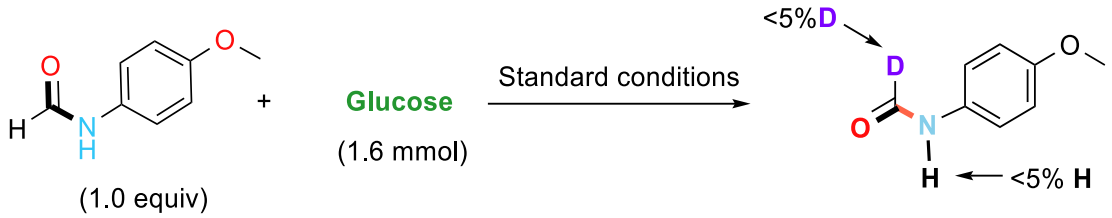




Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%) and 1,4-dioxane-d_8 (4.0 mL) while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield: 70%).



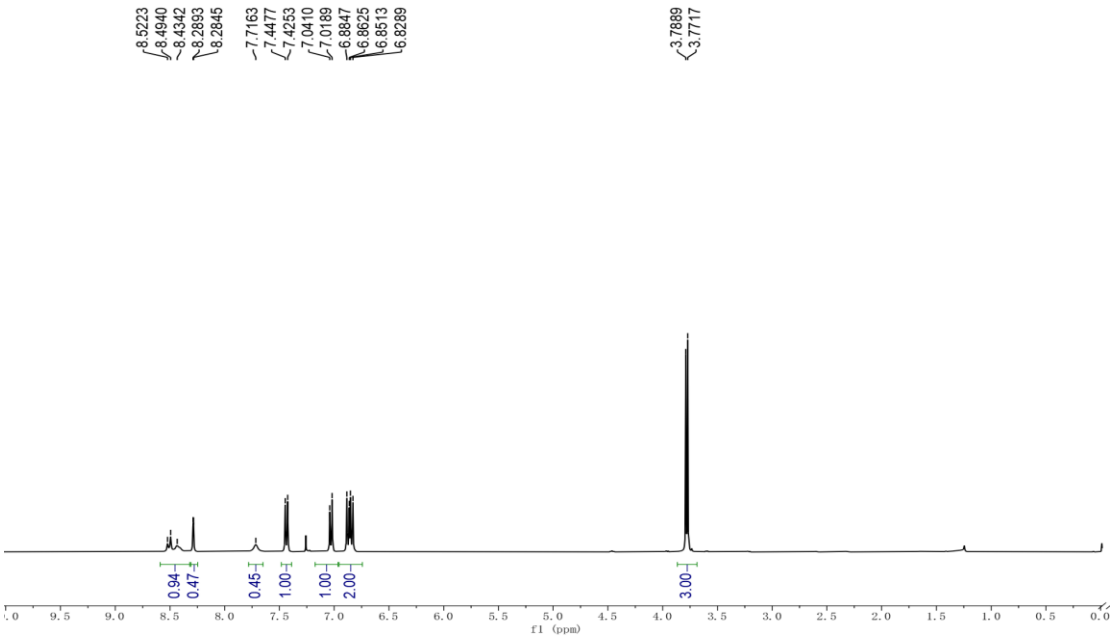




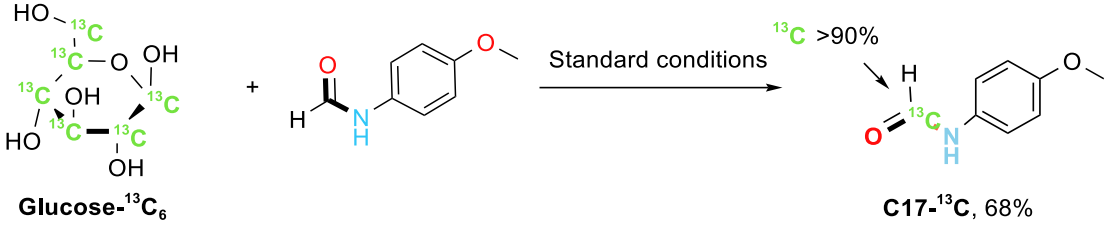
with additive D_2O (10 equiv): **C17**, 61%

Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%), D_2O (10 mmol, 10.0 equiv) and solvent while being stirred for 30 minutes.Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield: 61%).

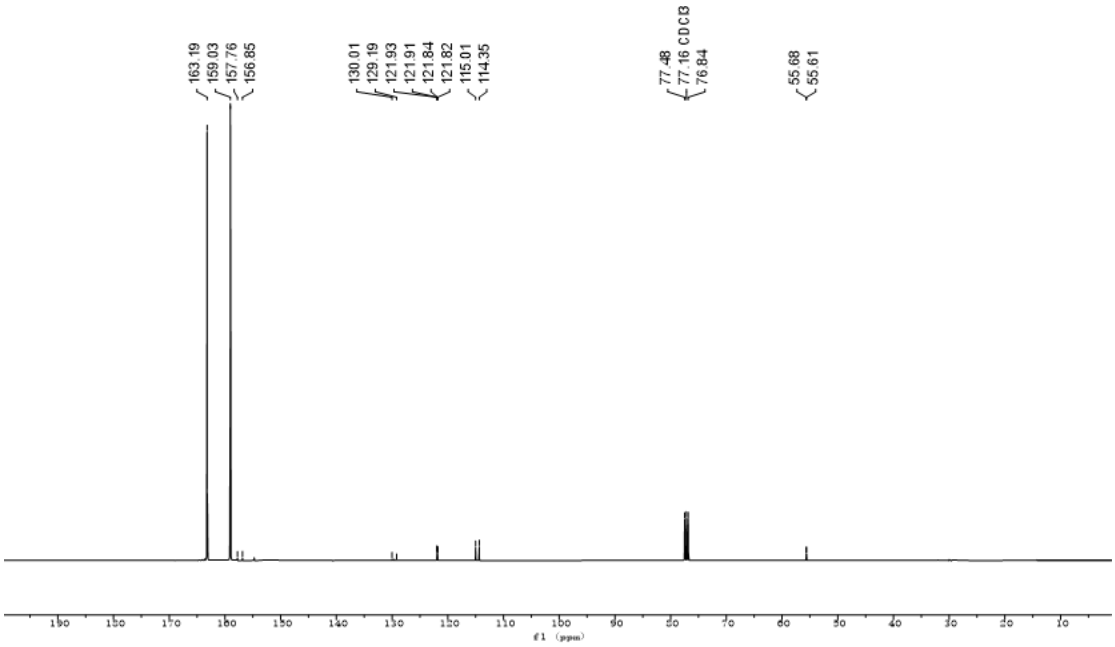
HRMS (ESI) calcd. for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0712, found: 152.0717.

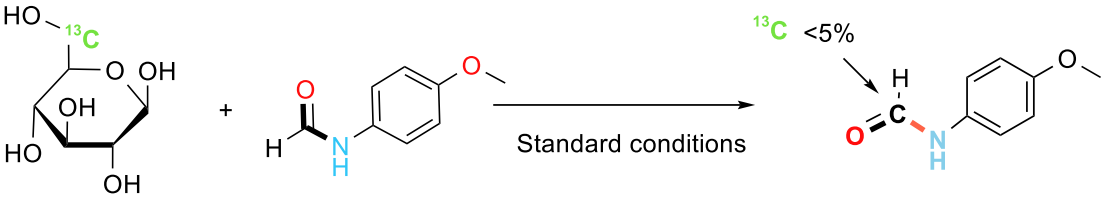


5.2.2 ^{13}C-labelled experiments



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), glucose-$^{13}C_6$ (0.8 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-^{13}C** (yield: 68%).
HRMS (ESI) calcd. for $C_7{}^{13}CH_{10}NO_2$ $[M+H]^+$: 153.0712, found: 153.0717.

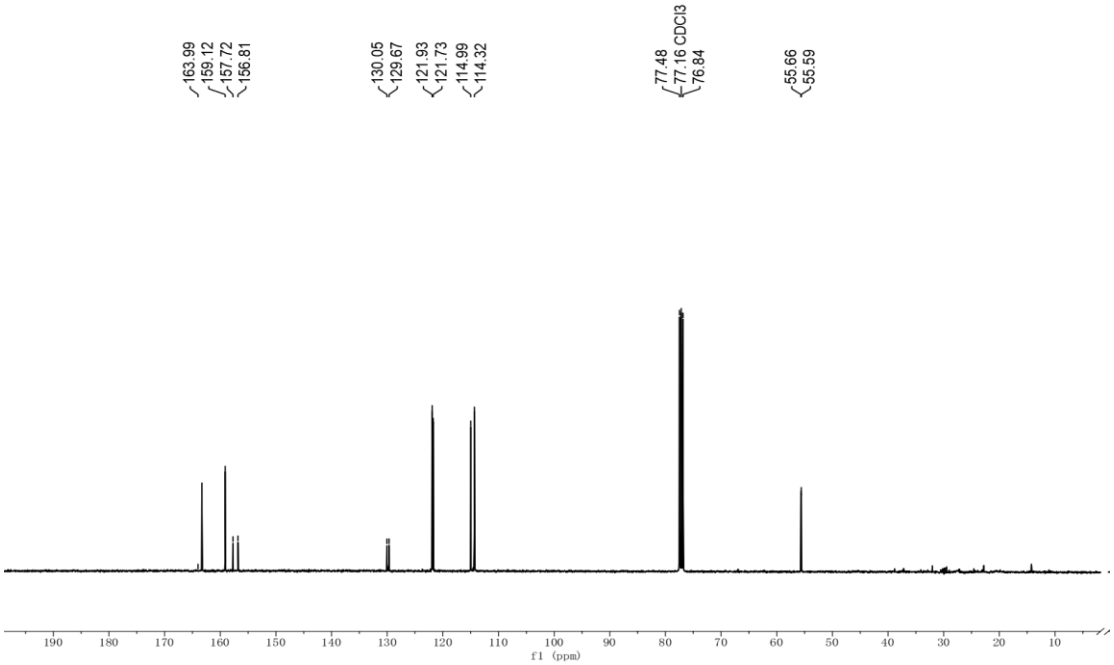


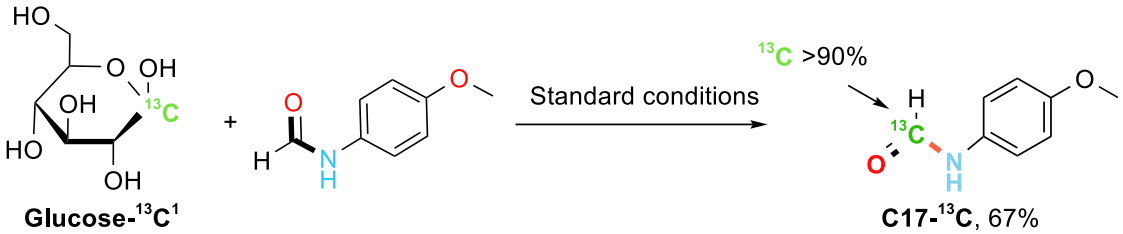


Glucose-$^{13}C^{6}$ **C17**, 69%

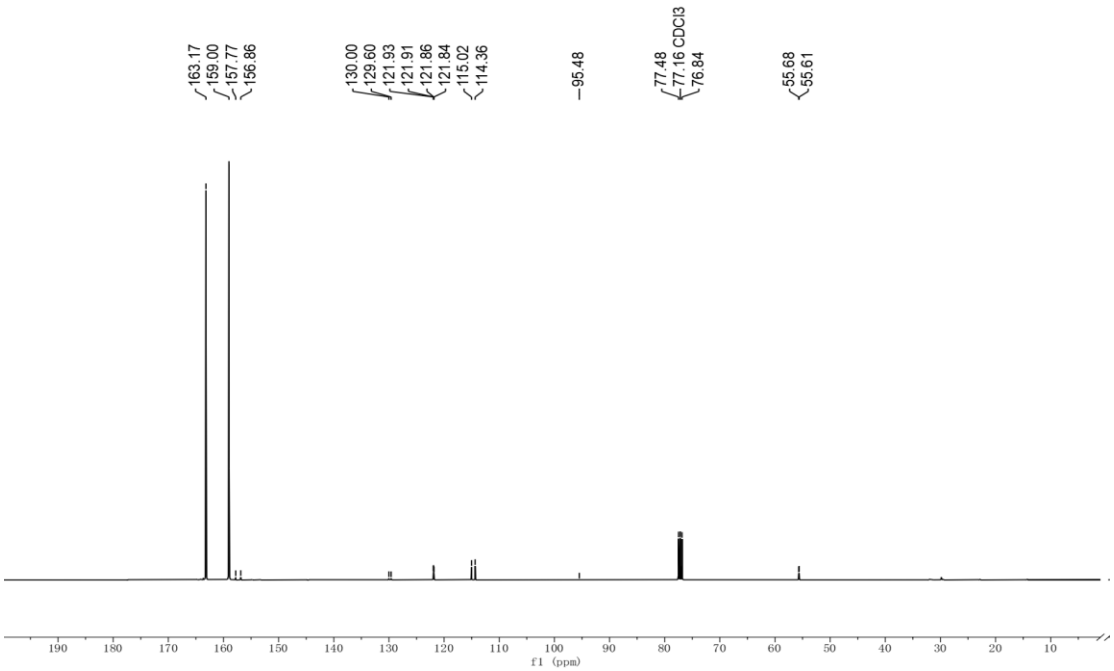
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), glucose-$^{13}C^{6}$ (0.8 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield: 69%).

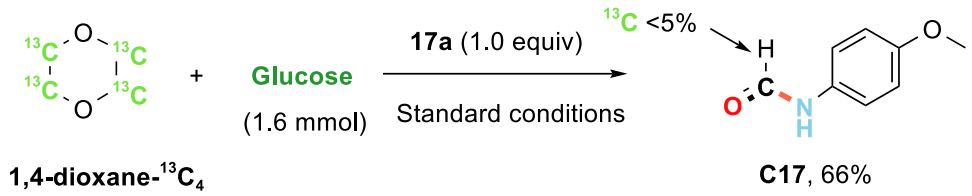
HRMS (ESI) calcd. for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0712, found: 152.0717.





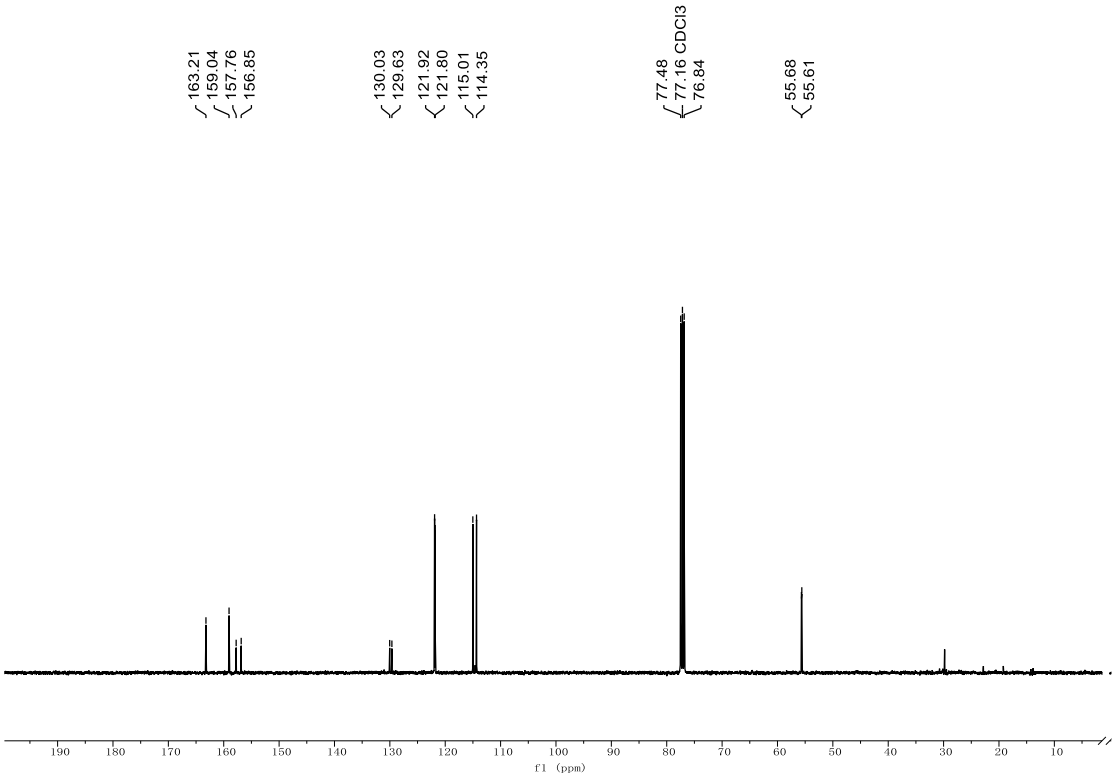
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), glucose-$^{13}C^{1}$ (0.8 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-^{13}C** (yield: 67%).
HRMS (ESI) calcd. for $C_7{}^{13}CH_{10}NO2$ $[M+H]^+$: 153.0712, found: 153.0707.



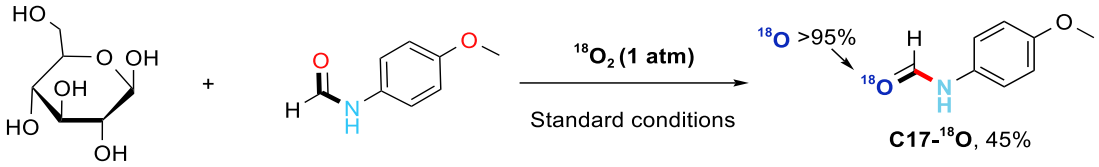


Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%), and 1,4-dioxane-$^{13}C_4$ (4.0 mL) while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield: 66%).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 159.4, 158.1, 157.1, 130.3, 129.9, 122.2, 122.1, 115.3, 114.7, 56.0, 55.9 ppm.

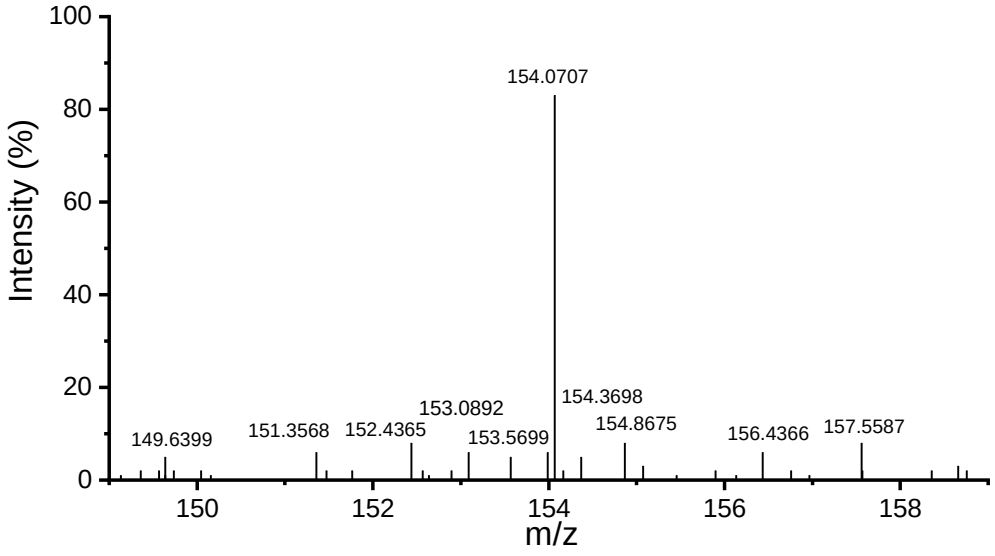


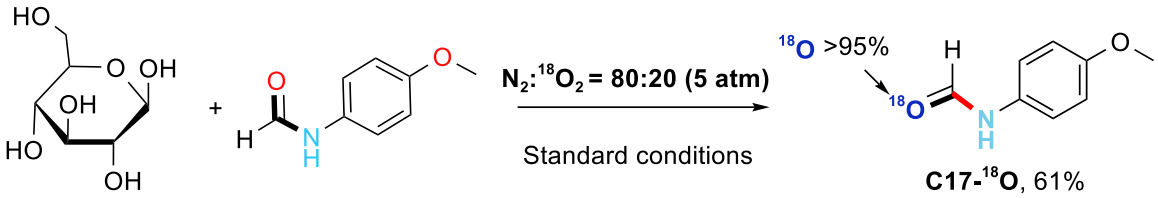
5.2.3 ^{18}O-labelled experiments



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with $^{18}O_2$ (1 atm) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-^{18}O** (yield: 45%).

HRMS (ESI) calcd. for $C_8H_{10}N^{18}OO$ $[M+H]^+$: 154.0712, found: 154.0707.

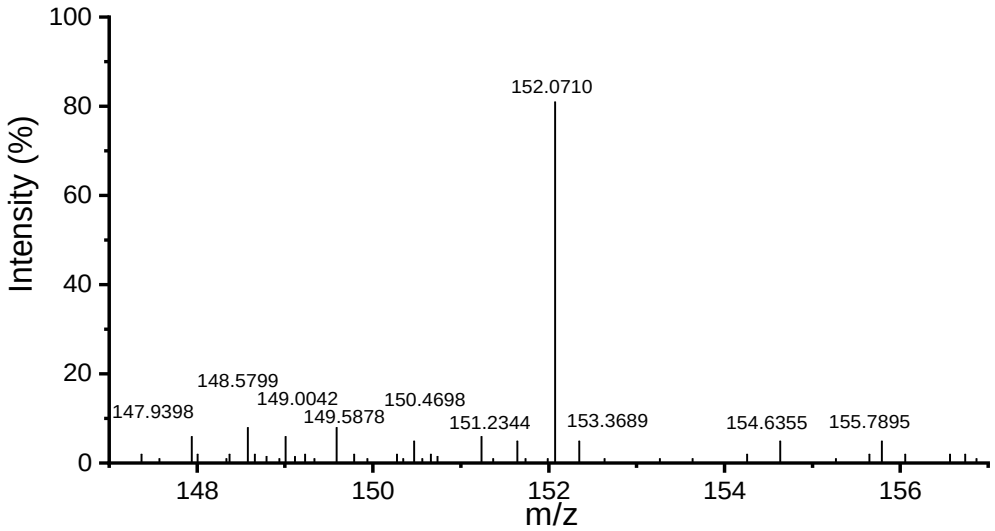


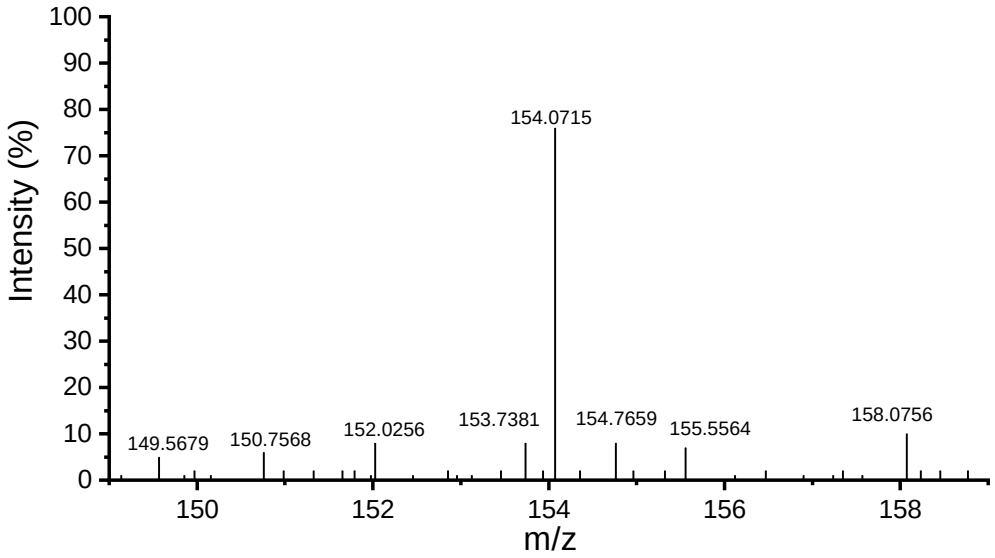


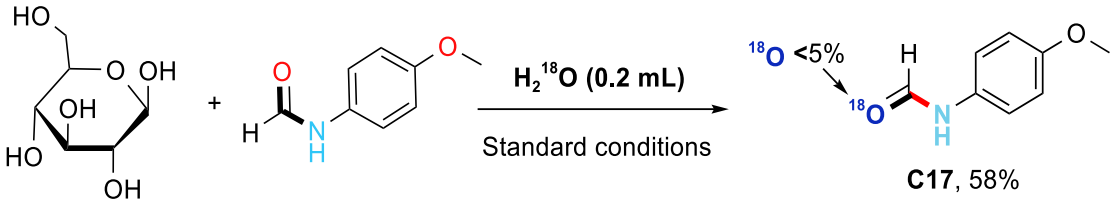
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged illed with 4 atm N_2 and 1 atm $^{18}O_2$ (N_2:$^{18}O_2$=80:20) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17-^{18}O** (yield: 61%).

HRMS (ESI) calcd. for $C_8H_{10}NO_2$ $[M+H]^+$: 152.0712, found: 152.0710.

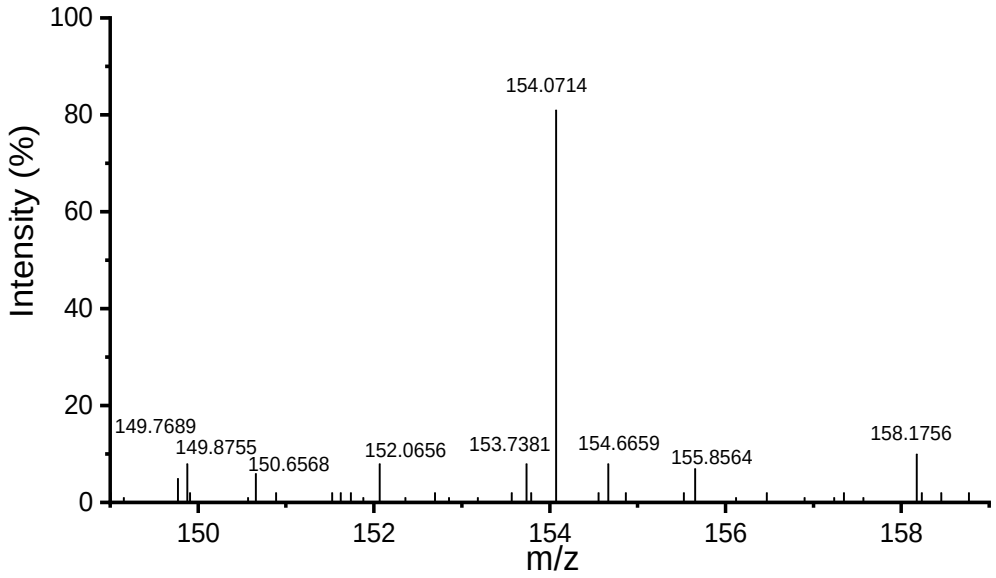
HRMS (ESI) calcd. for $C_8H_{10}N^{18}OO$ $[M+H]^+$: 154.0712, found: 154.0715.



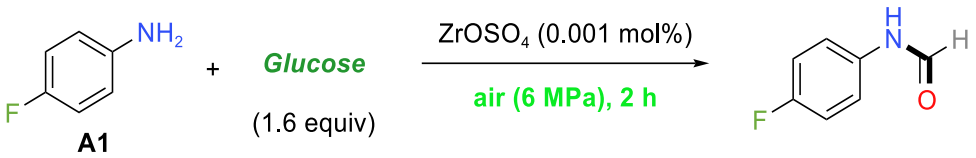

Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
154.0715
149.5679
150.7568
152.0256
153.7381
154.7659
155.5564
158.0756
150
152
154
156
158
m/z



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (1 mmol), glucose (1.6 mmol), $ZrOSO_4$ (0.001 mol%), $H_2{}^{18}O$ (0.2 ml) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged illed with air (6 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield: 58%). **HRMS** (ESI) calcd. for $C_8H_{10}N^{18}OO$ $[M+H]^+$: 154.0712, found: 154.0714.



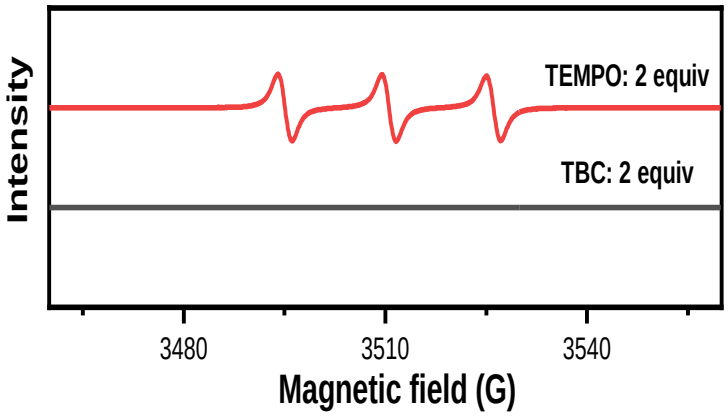
5.3 Control experiments for radical scavenger



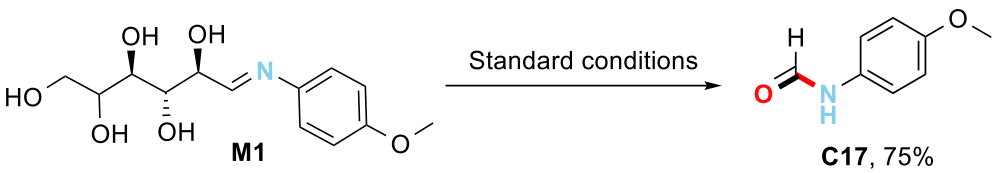
with TBC (2.0 equiv): **C1**, 78%

with TEMPO (2.0 equiv): **C1**, 65%

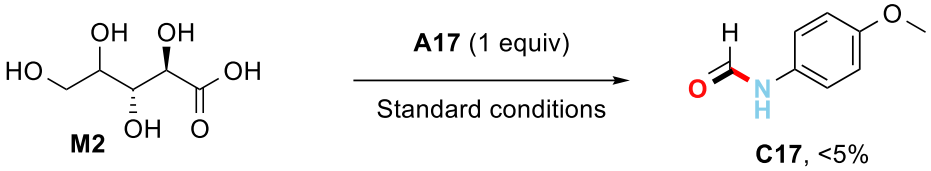
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (5.0 mL) was loaded with a magnetic stirring bar, 4-Fluorobenzenamine (**A1**, 0.5 mmol), glucose (0.8 mmol), $ZrOSO_4$ (0.001 mol%), TEMPO or TBC (0.4 mmol, 2.0 equiv) and solvent while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C1** (with TEMPO: yield: 78%; with TBC: yield: 65%).



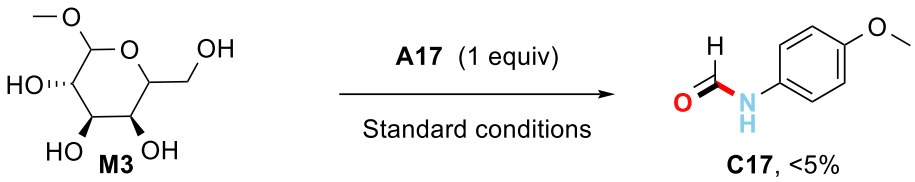
5.4 Intermediator investigation



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), **M1 (**0.8 mmol), $ZrOSO_4$ (0.001 mol%), and solvent. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield: 75%).

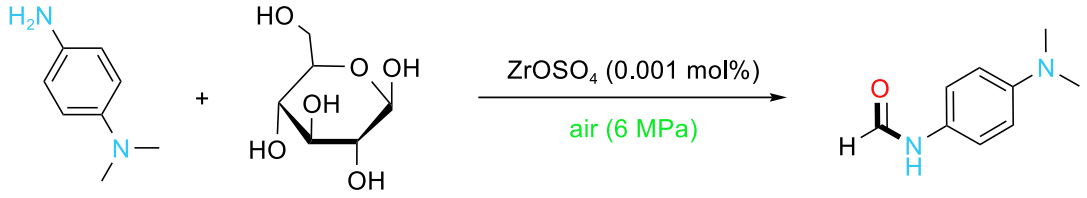


Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), **M2 (**0.8 mmol), $ZrOSO_4$ (0.001 mol%), and solvent. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield<5%).



Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was loaded with a magnetic stirring bar, *p*-methoxyaniline (**A17**, 0.5 mmol), **M3 (**0.8 mmol), $ZrOSO_4$ (0.001 mol%), and solvent. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C17** (yield<5%).

6. Gram-scale experiment



50 mmol 80 mmol **C21** 83%

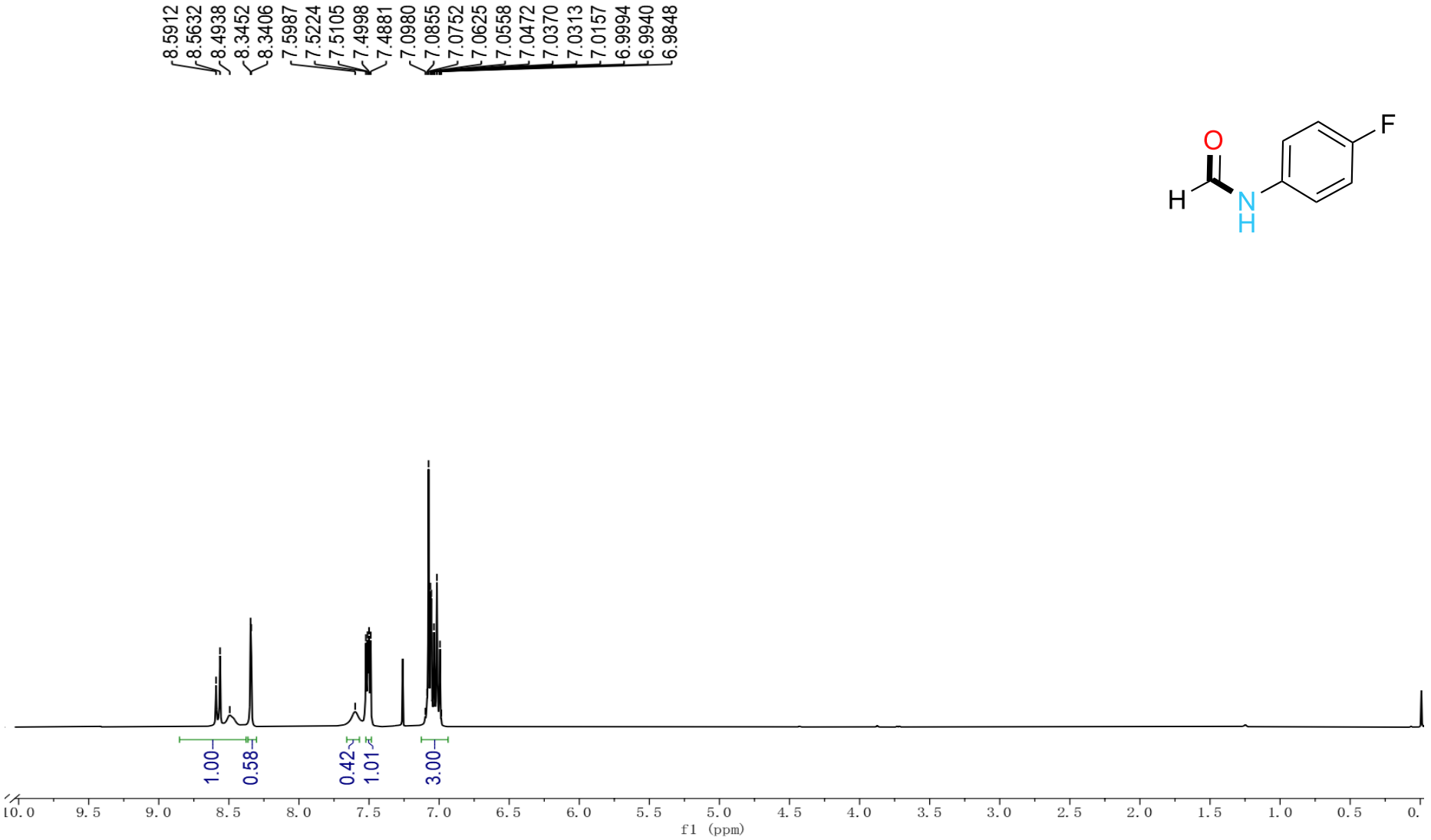
Utilizing a nitrogen-filled glove box, an oven-dried pressure tube (500.0 mL) was loaded with a magnetic stirring bar, *N,N*-Dimethyl-*p*-Phenylenediamine (**A21**, 50 mmol), glucose (80 mmol), $ZrOSO_4$ (0.001 mol%) and 1,4-dioxane (150 mL) while being stirred for 30 minutes. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with air (6.0 MPa) and immersed into a pre-heated metal bath for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 1:1) on silica gel to give the corresponding product **C21** in 83% yield (6.83 g).

7. Comparison Table of Formamidation Reactions

Table S9 Comparison Table of Formamidation Reactions

Entry	catalyst	loading	Carbonyl source	Substrate Scope	number of substrates types	Yield
1	KOH	40 mol%	CO	aliphatic secondary amines, aliphatic primary amines, benzyl-type amines, heterocyclic amines,	4	70%-99%
2	Co $(ClO_4)_2$	5 mol%	CO_2+H_2	aliphatic secondary amines, aliphatic primary amines, benzyl-substituted amines	3	82%-95%
3	CuI bpy NMI TEMPO	CuI (5 mol%) bpy (5 mol%) NMI (10 mol%) TEMPO (10 mol%)	MeOH	aliphatic secondary amines, benzyl-type primary amines heterocyclic amines	3	40%-96%
4	$HClO_4$-SiO_2	2.5 mol%	HCOOH	aromatic amines aliphatic amines	2	70%-96%
5	**$ZrOSO_4$**	**0.001 mol%**	**Glucose**	**aromatic primary amines, polycyclic aromatic amines, aliphatic amines, halogen-containing aromatic amines**	**4**	**63%-91%**

8. NMR Spectra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7.0855
7.0752
7.0625
7.0558
7.0472
7.0370
7.0313
7.0157
6.9994
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H
N
H
F
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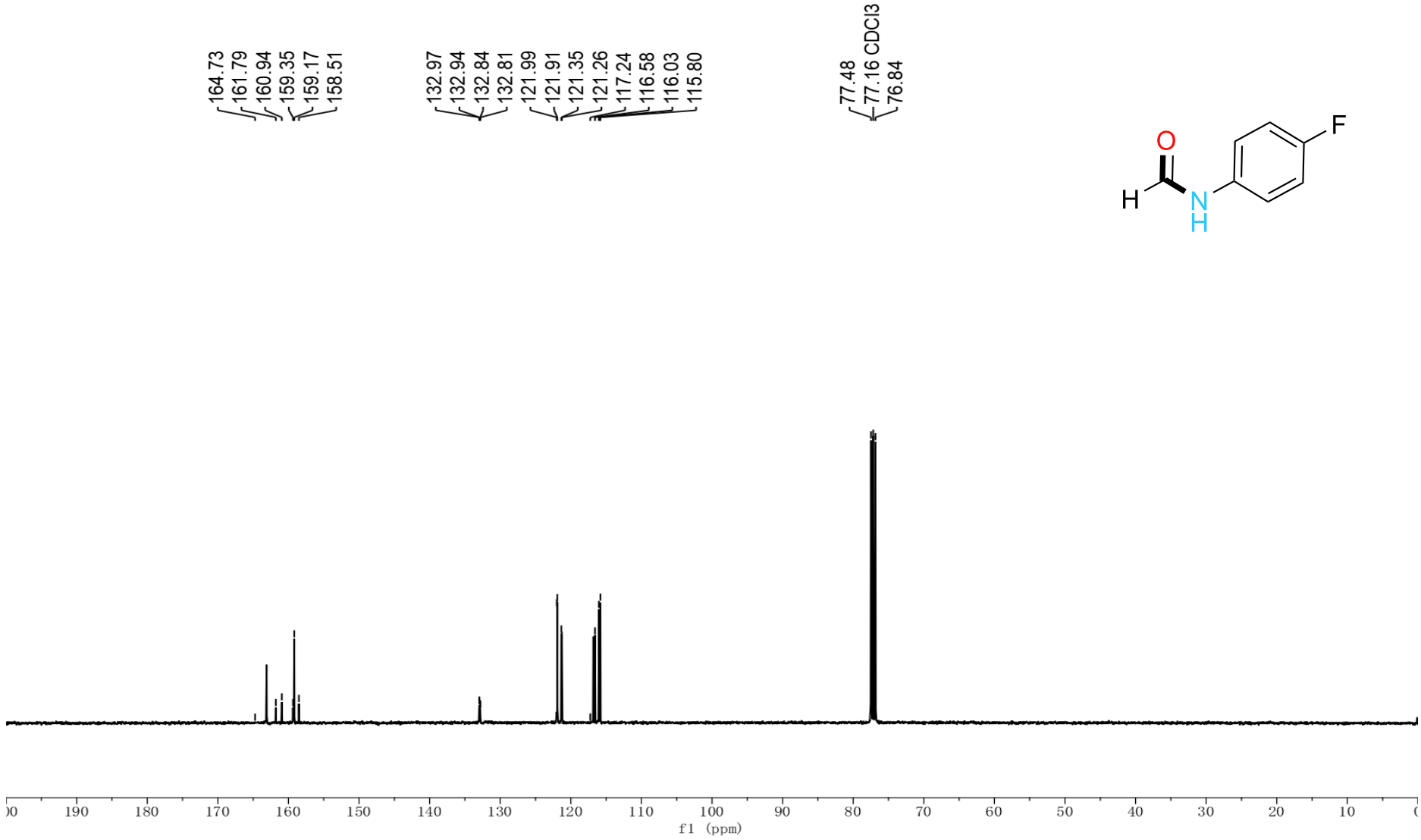
0.42
1.01
3.00
f1 (ppm)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132.81
121.99
121.91
121.35
121.26
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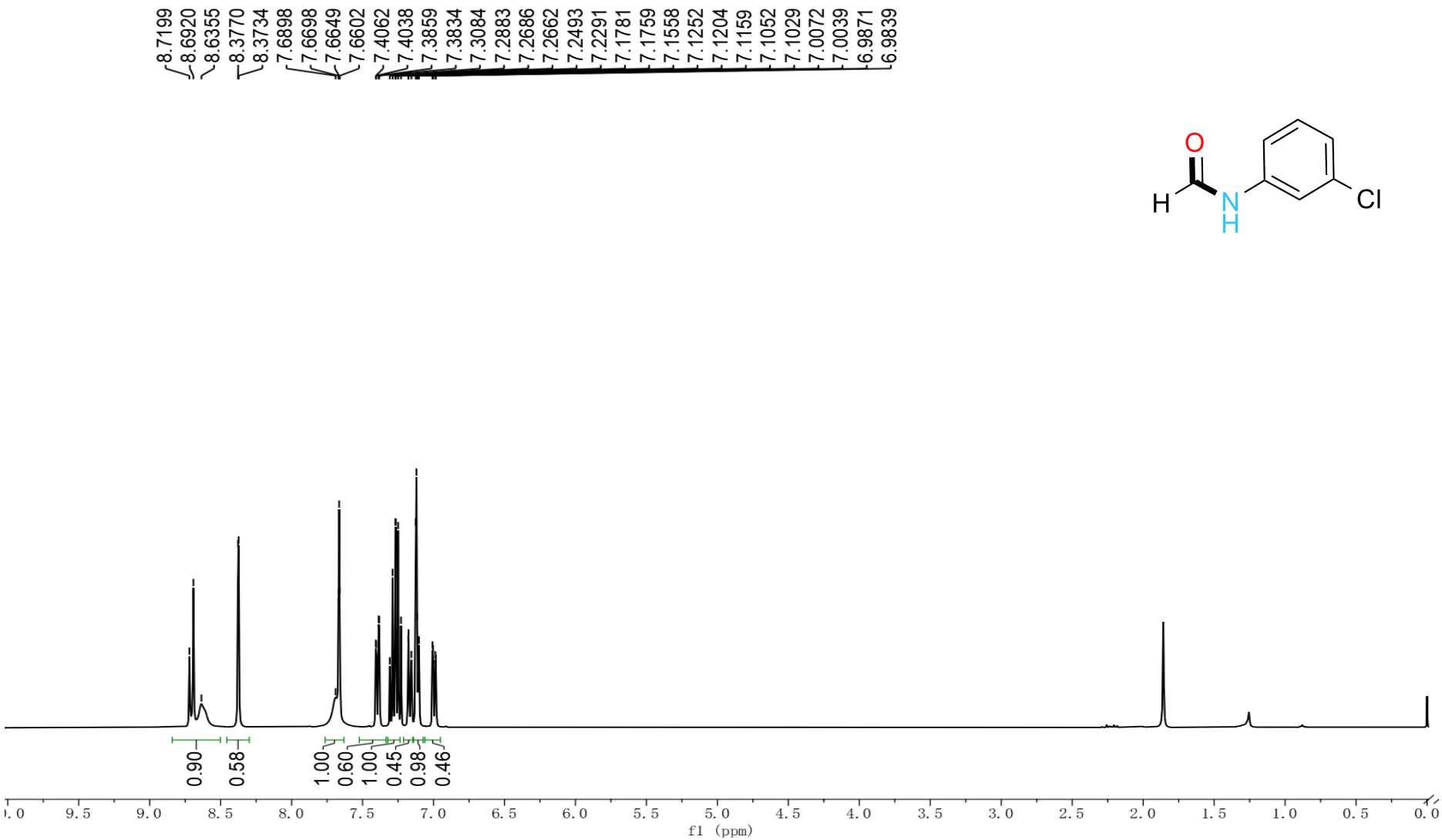
116.03
115.80
77.48
77.16 CDCl3
76.84
O
H
N
H
F
f1 (ppm)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7.3834
7.3084
7.2883
7.2686
7.2662
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7.1759
7.1558
7.1252
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7.1052
7.1029
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7.0039
6.9871
6.9839
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N
H
Cl
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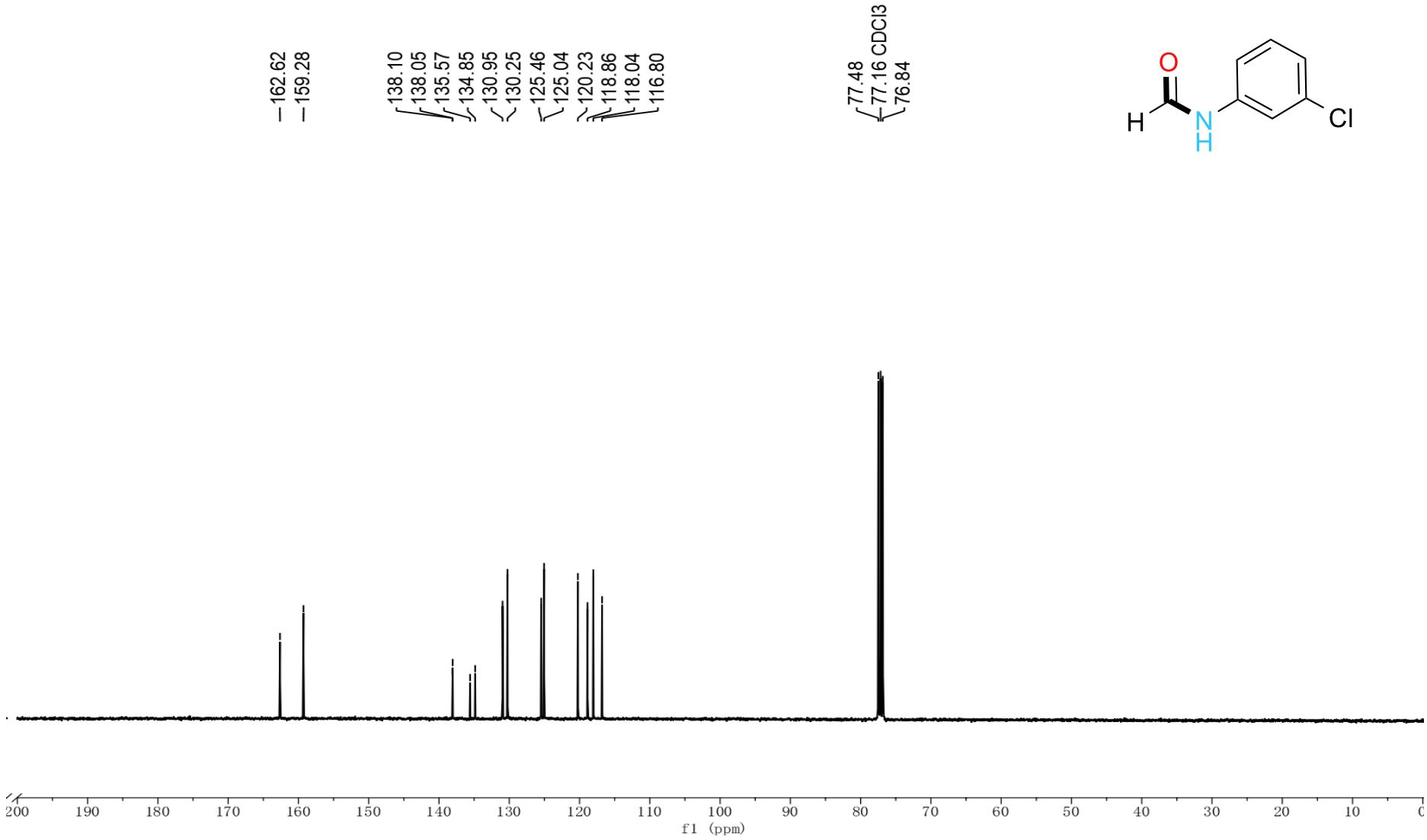
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125.04
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118.04
116.80
77.48
77.16 CDCl3
76.84
O
H
N
H
Cl
200
190
180
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110
100
90
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70
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50
40
30
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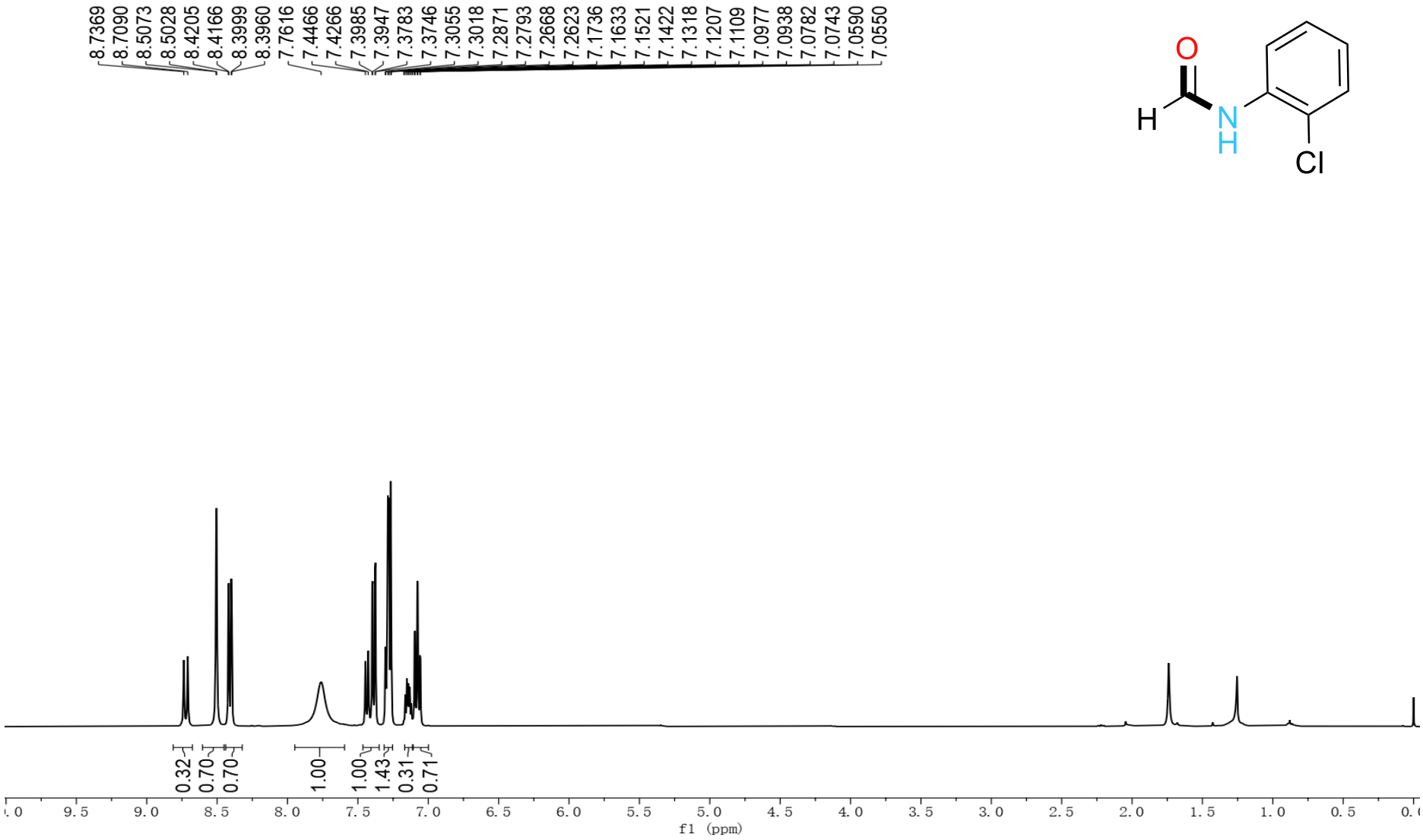
10
0
f1 (ppm)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7.3985
7.3947
7.3783
7.3746
7.3055
7.3018
7.2871
7.2793
7.2668
7.2623
7.1736
7.1633
7.1521
7.1422
7.1318
7.1207
7.1109
7.0977
7.0938
7.0782
7.0743
7.0590
7.0550
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N
H
Cl
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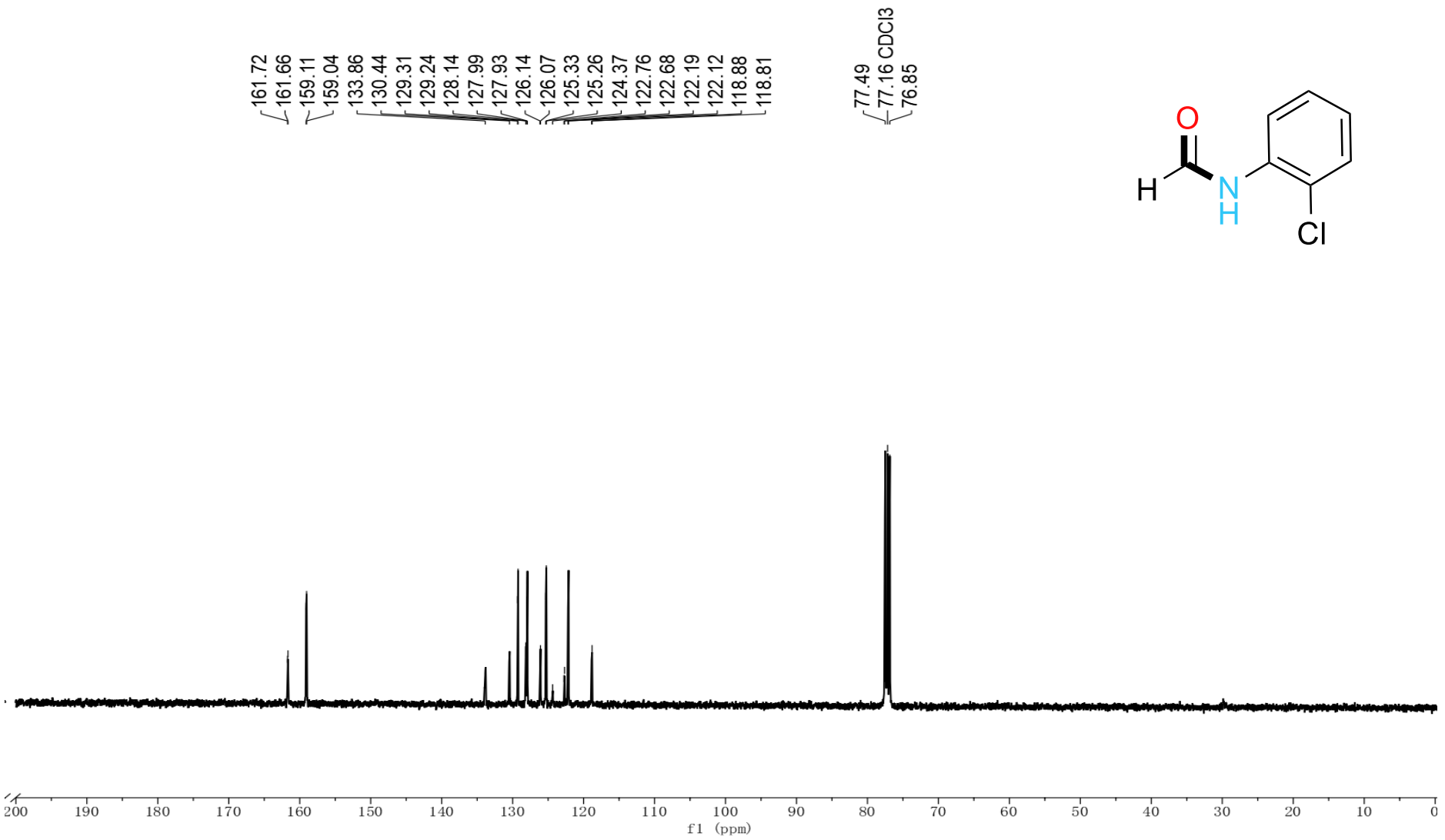
0.71
f1 (ppm)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127.93
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126.07
125.33
125.26
124.37
122.76
122.68
122.19
122.12
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118.81
77.49
77.16 CDCl3
76.85
O
H
N
H
Cl
200
190
180
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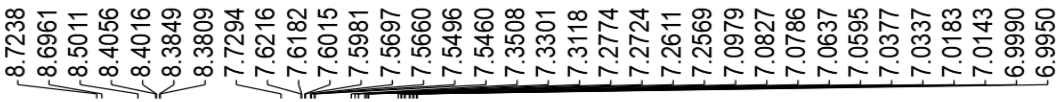
50
40
30
20
10
0
f1 (ppm)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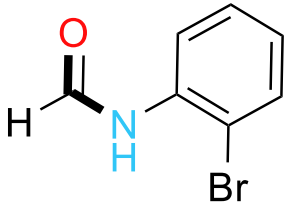
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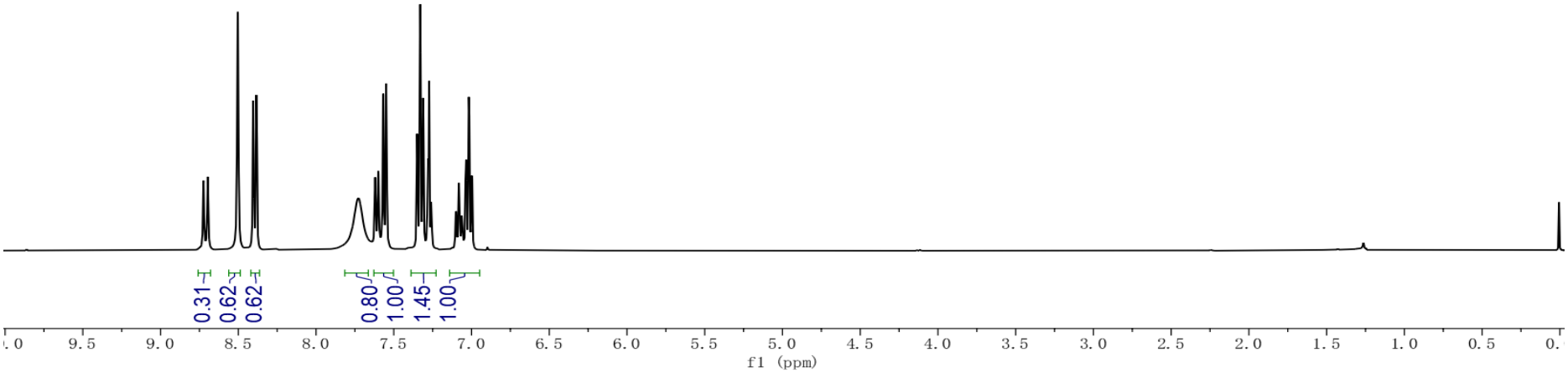
H
N
H
Br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1.00
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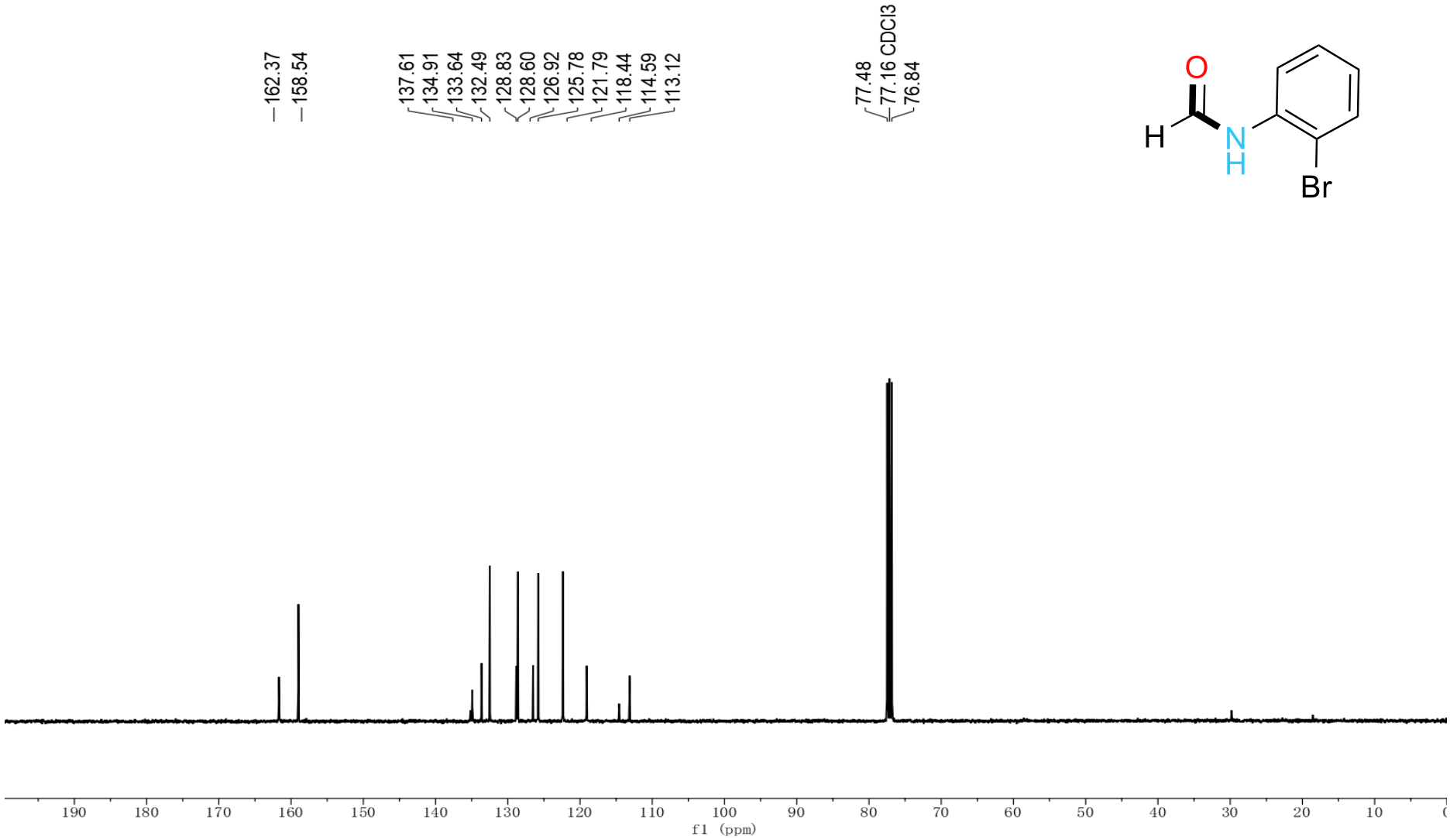
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125.78
121.79
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114.59
113.12
77.48
77.16 CDCl3
76.84
O
H
N
H
Br
190
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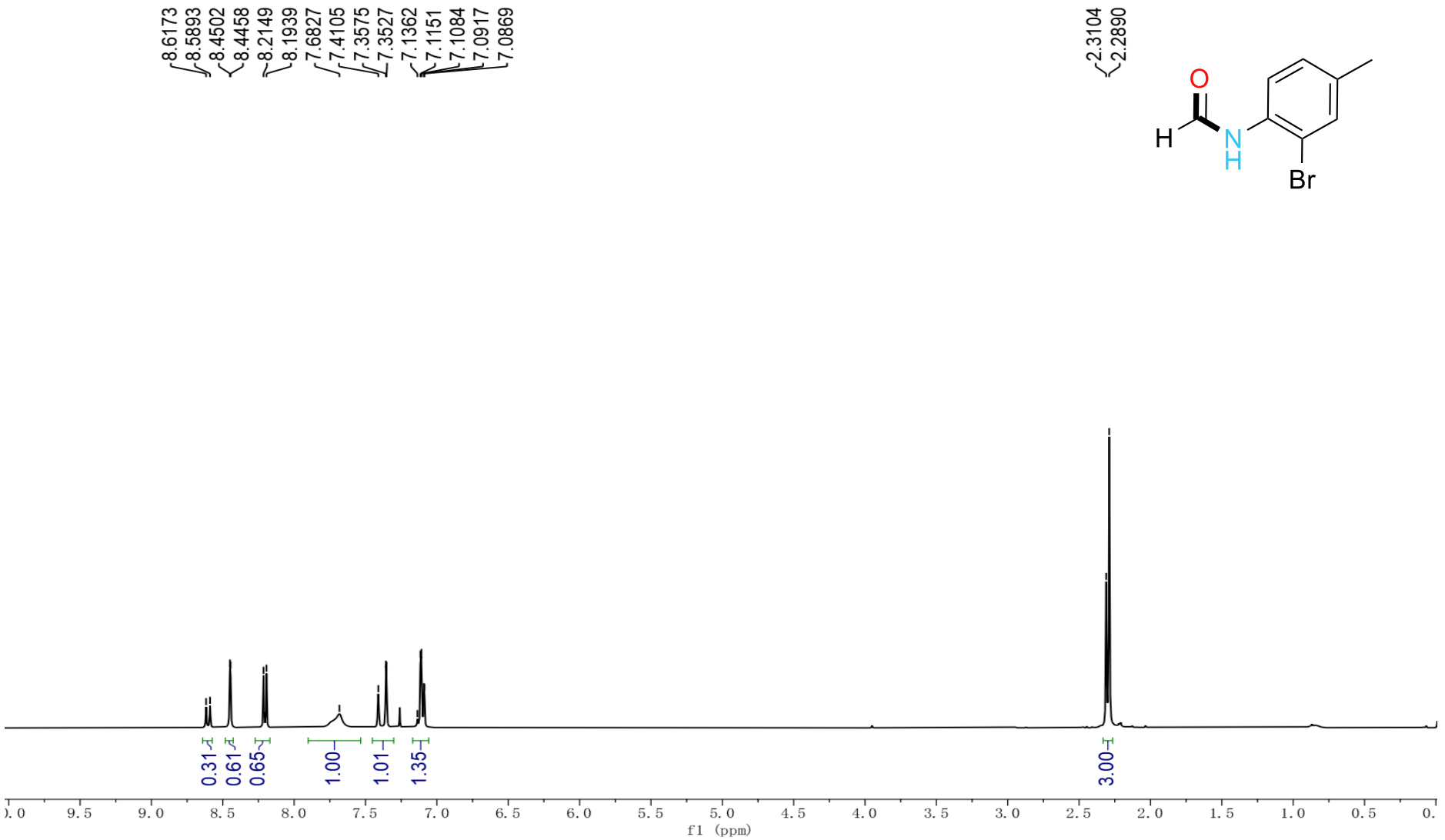
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.1362
7.1151
7.1084
7.0917
7.0869
2.3104
2.2890
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H
N
H
Br
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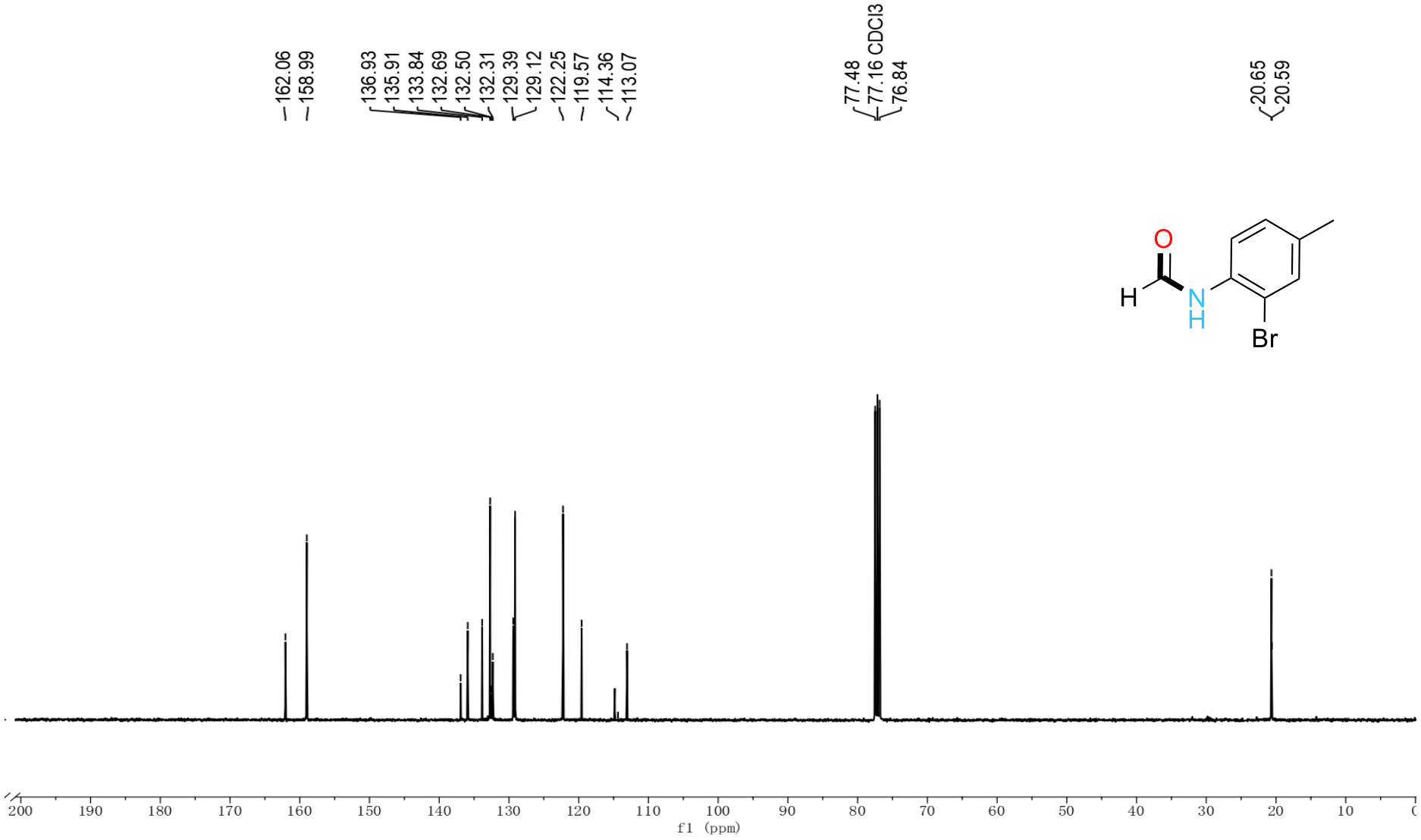
1.01
1.35
3.00
f1 (ppm)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132.31
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129.12
122.25
119.57
114.36
113.07
77.48
77.16 CDCl3
76.84
20.65
20.59
O
H
N
H
Br
200
190
180
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150
140
130
120
110
100
90
80
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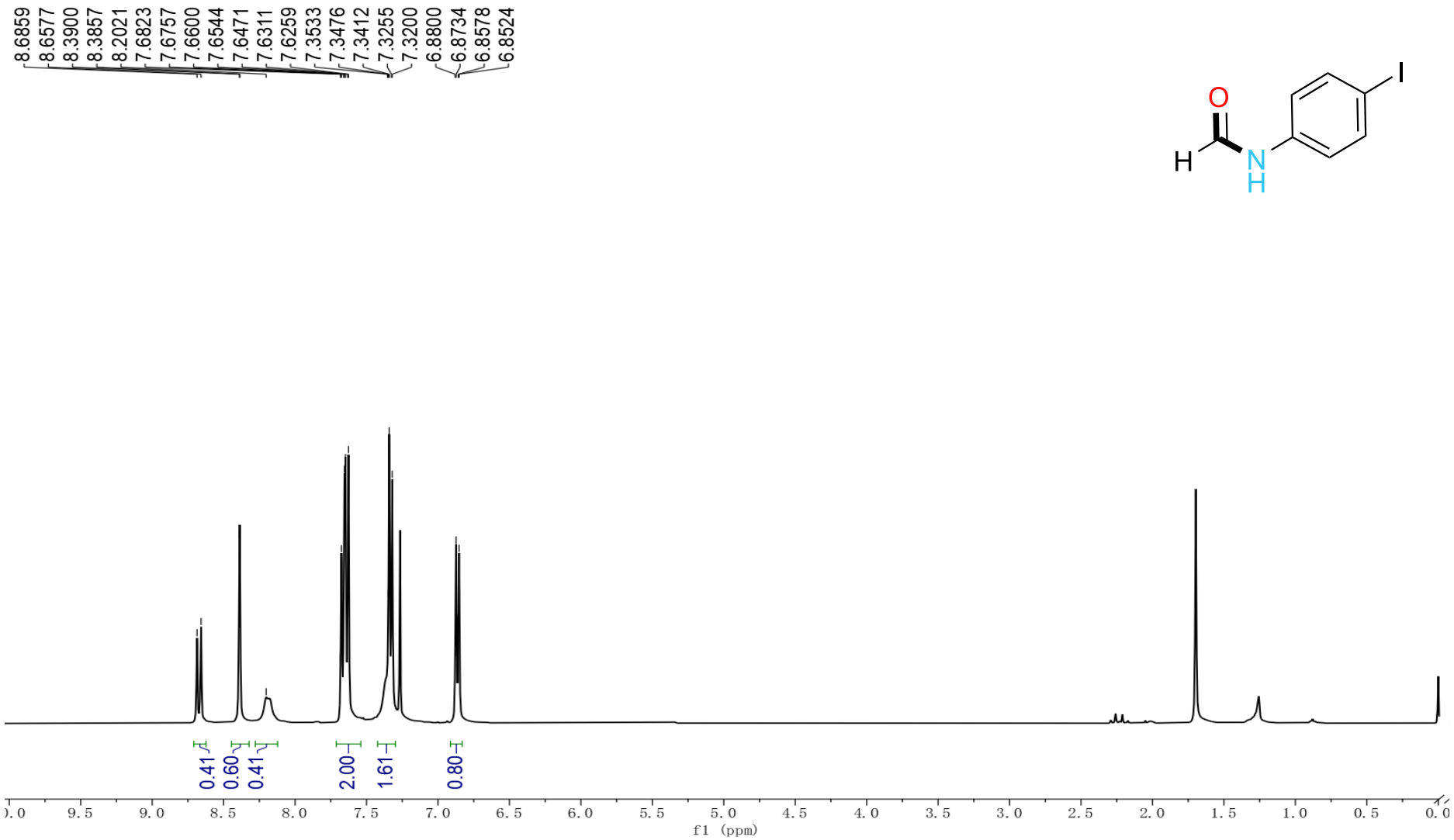
60
50
40
30
20
10
f1 (ppm)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7.6259
7.3533
7.3476
7.3412
7.3255
7.3200
6.8800
6.8734
6.8578
6.8524
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H
N
H
I
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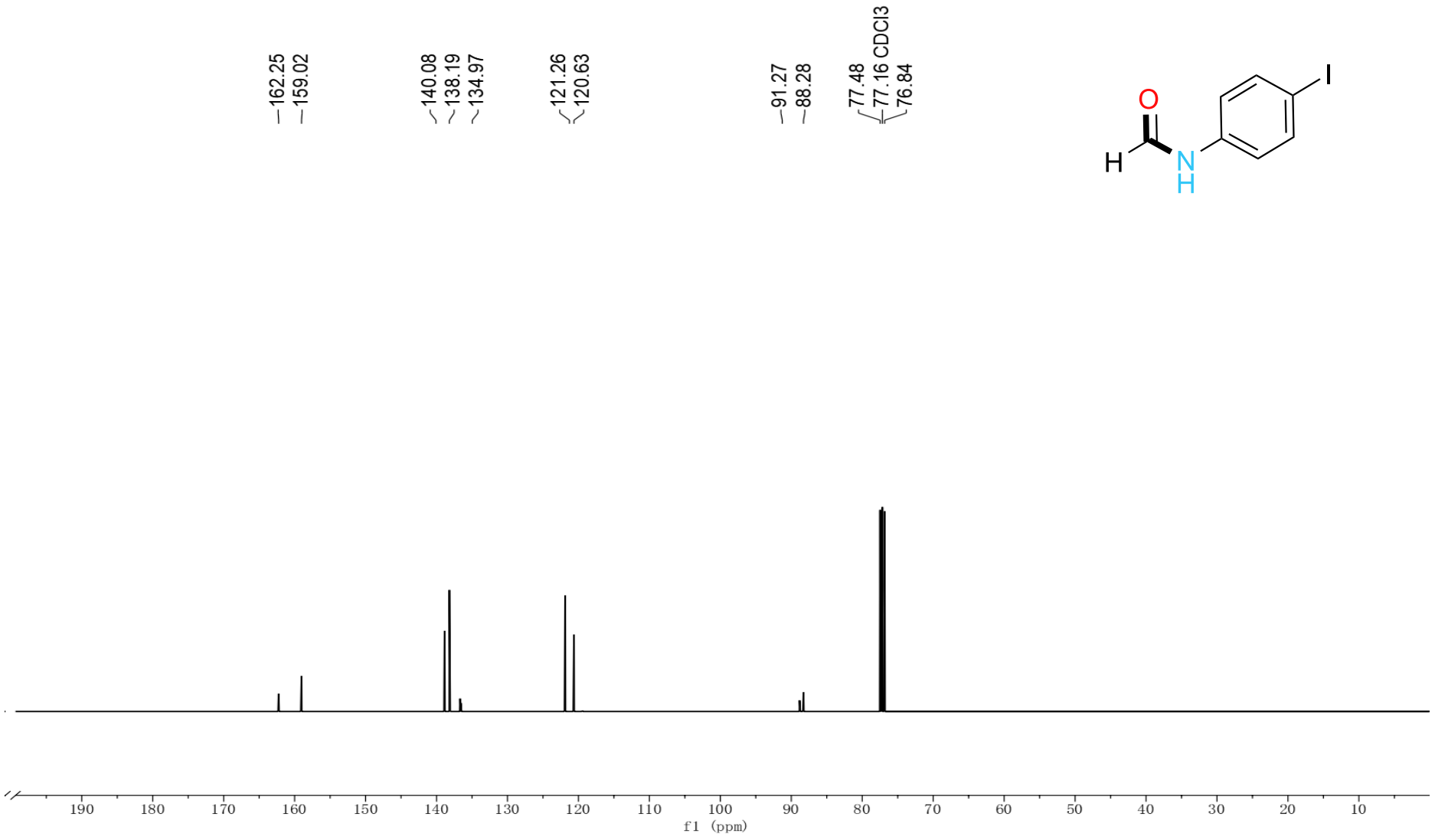
f1 (ppm)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77.48
77.16 CDCl3
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N
H
I
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


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8.4350
8.4132
8.4130
8.3855
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7.6897
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7.6167
7.6046
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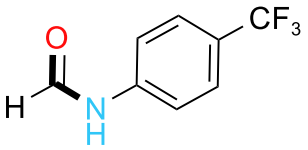
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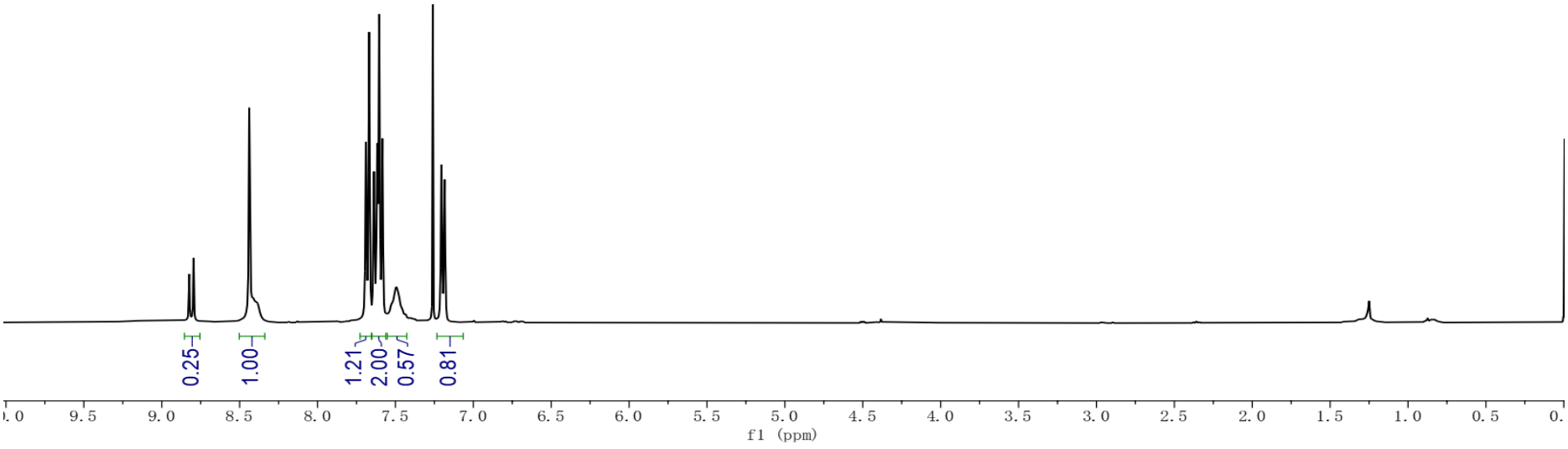
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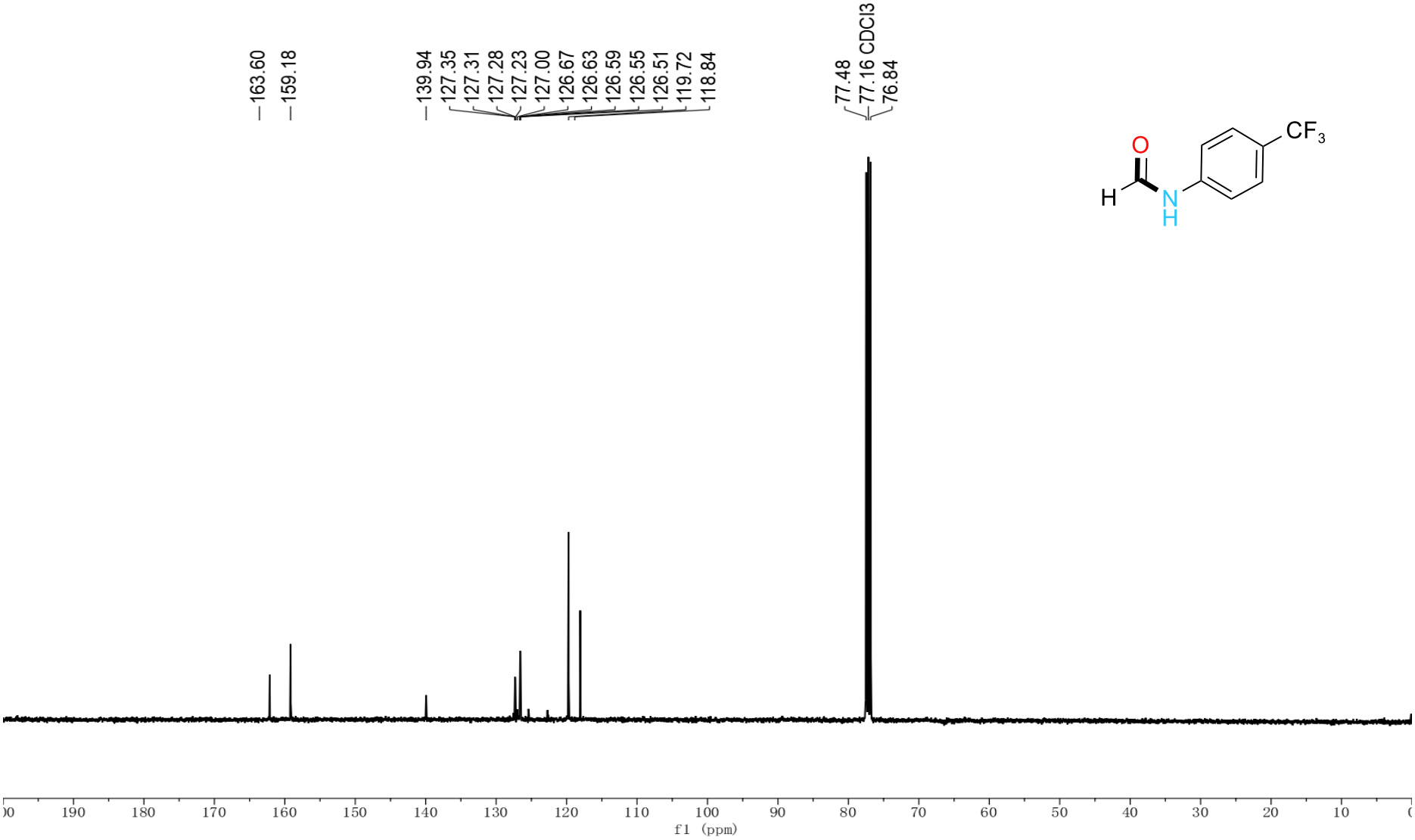
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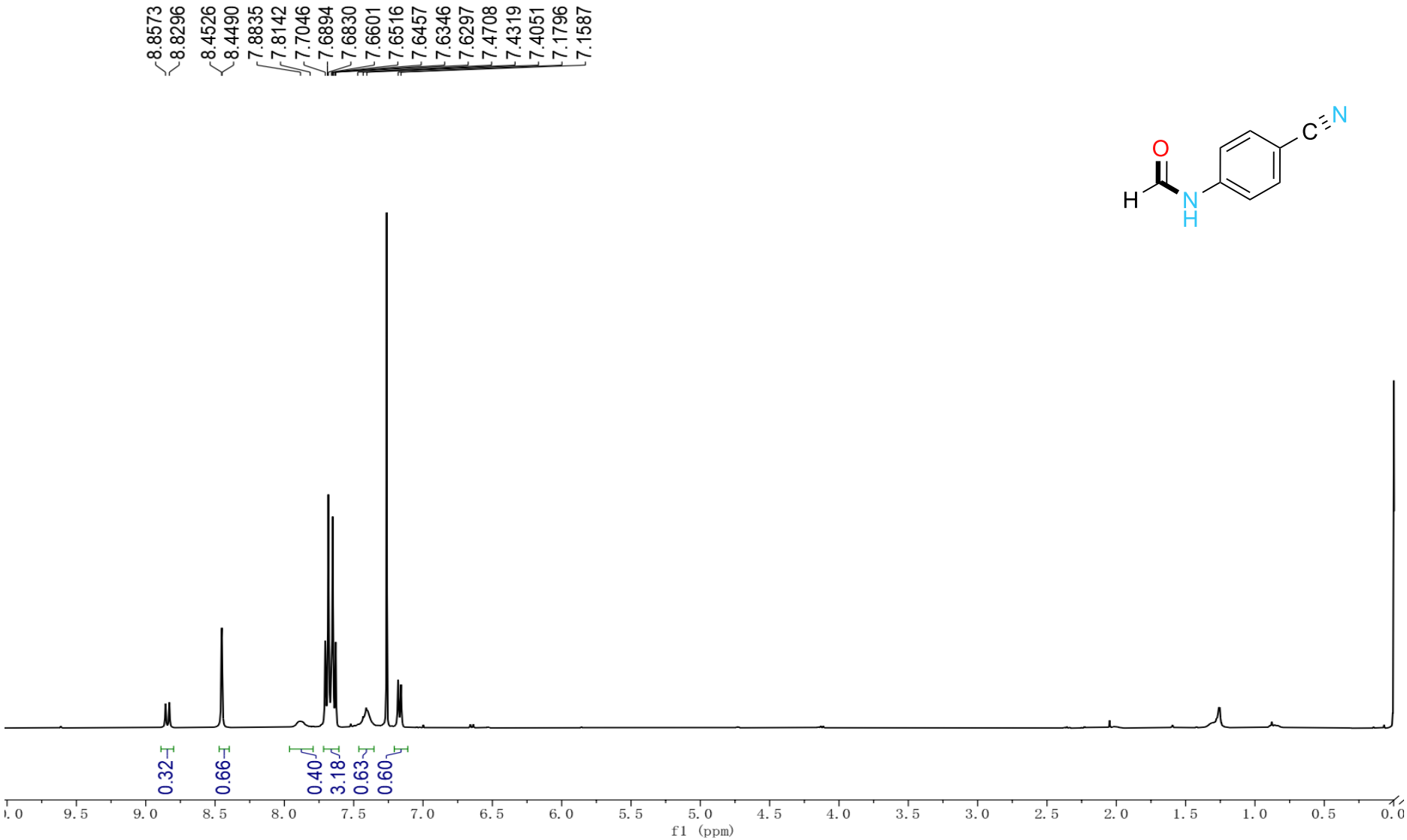
76.84
O
H
N
H
CF3
f1 (ppm)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7.4051
7.1796
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H
C
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3.18
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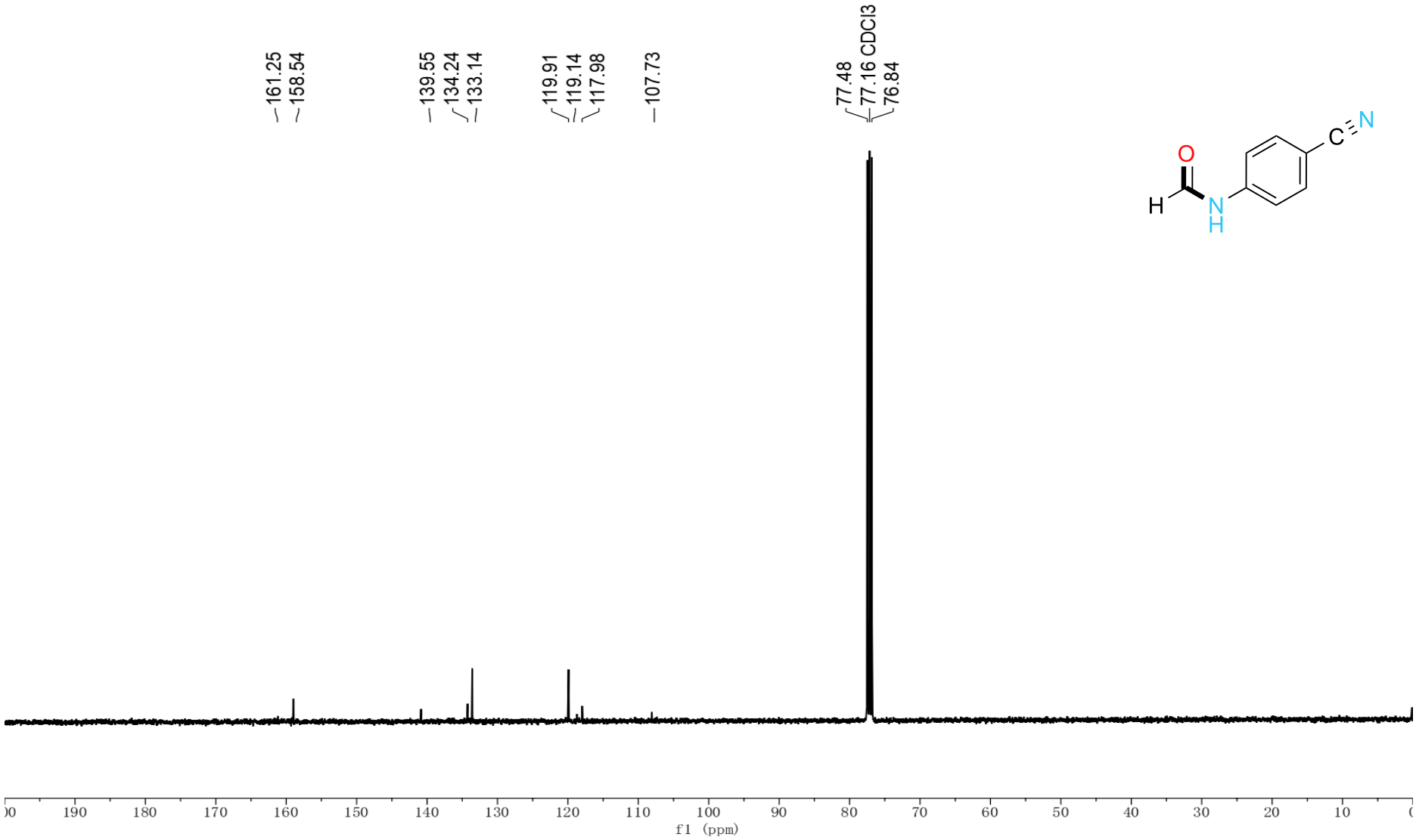
0.60
f1 (ppm)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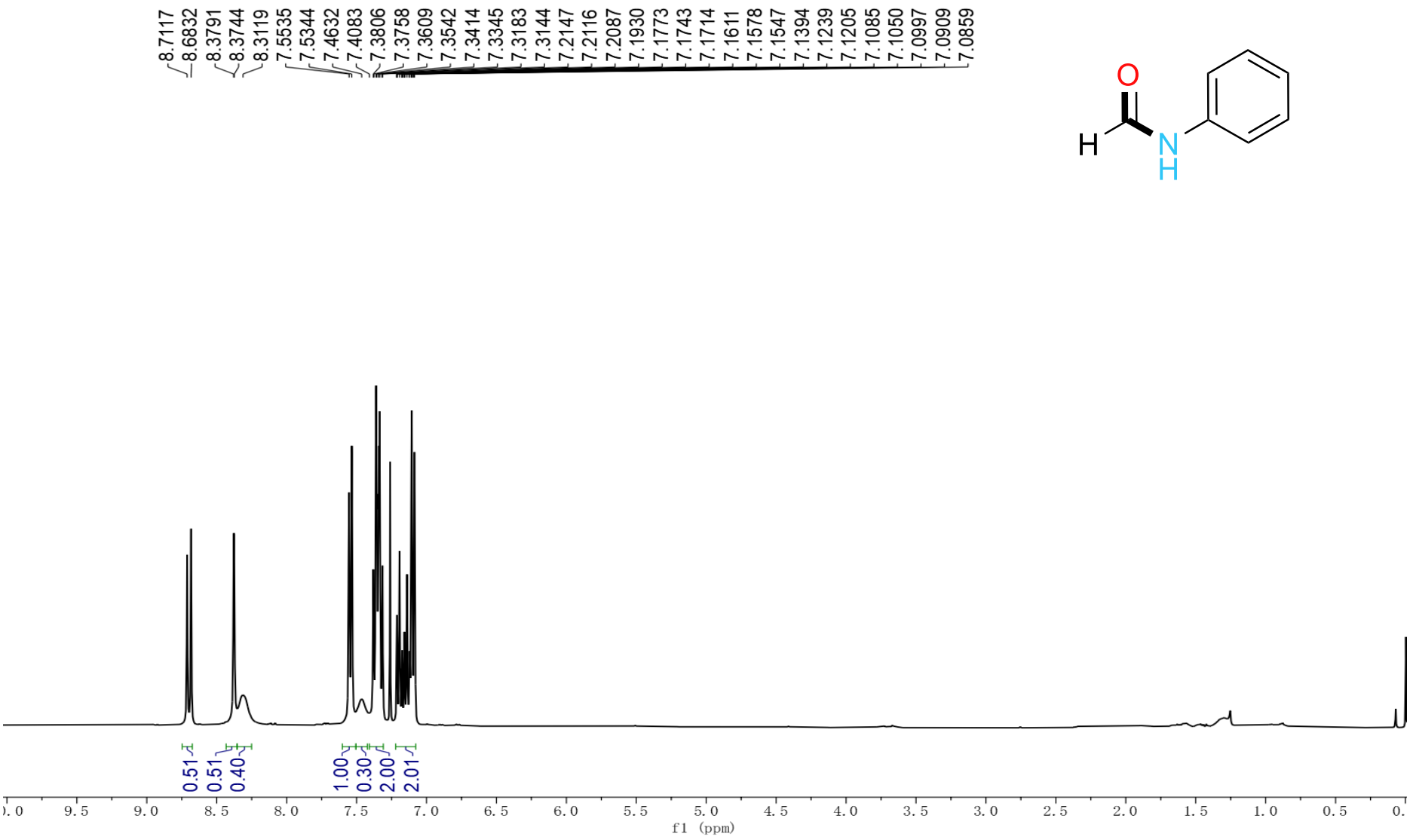
H
N
H
C
N
f1 (ppm)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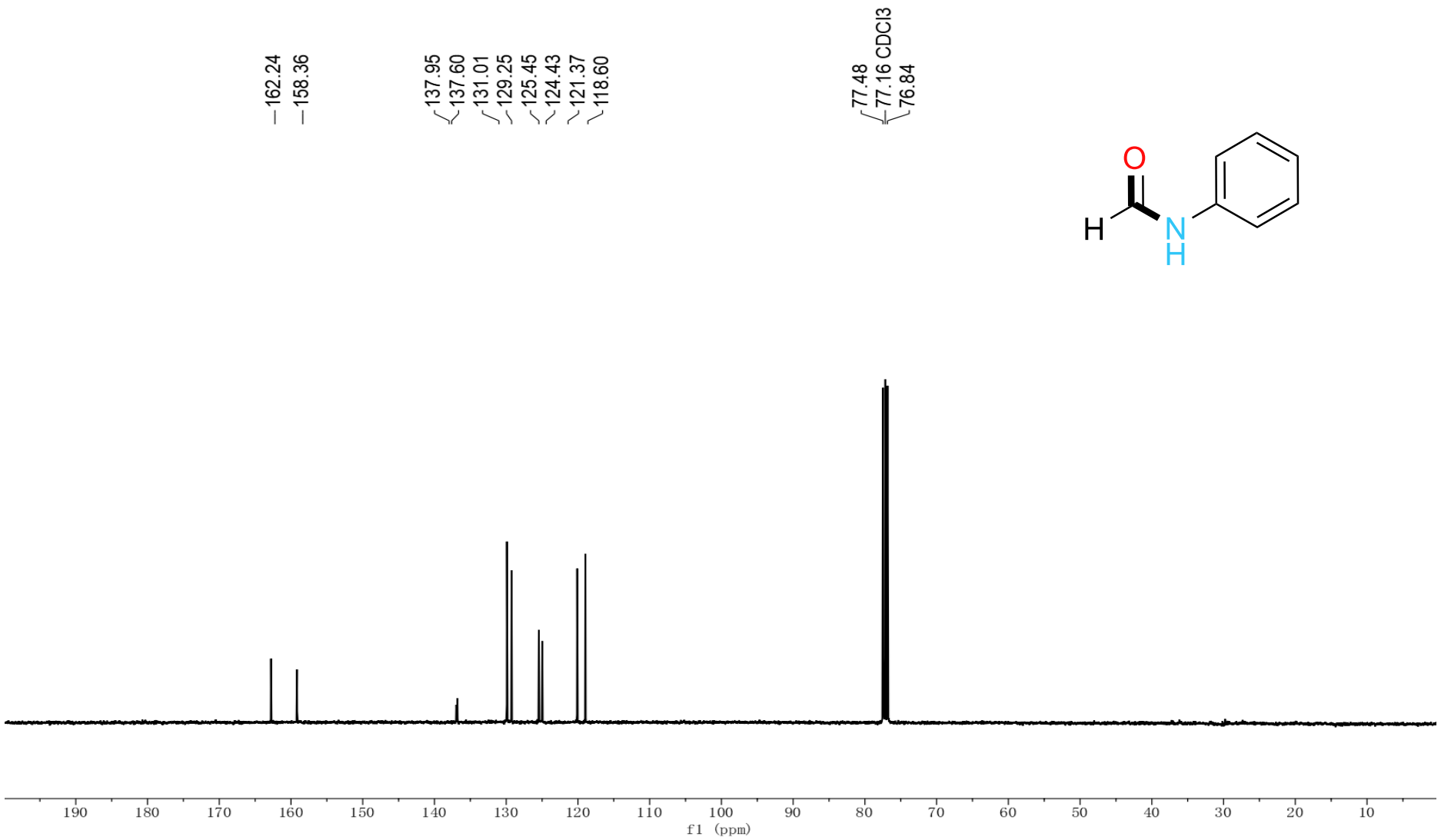
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H
N
H
190
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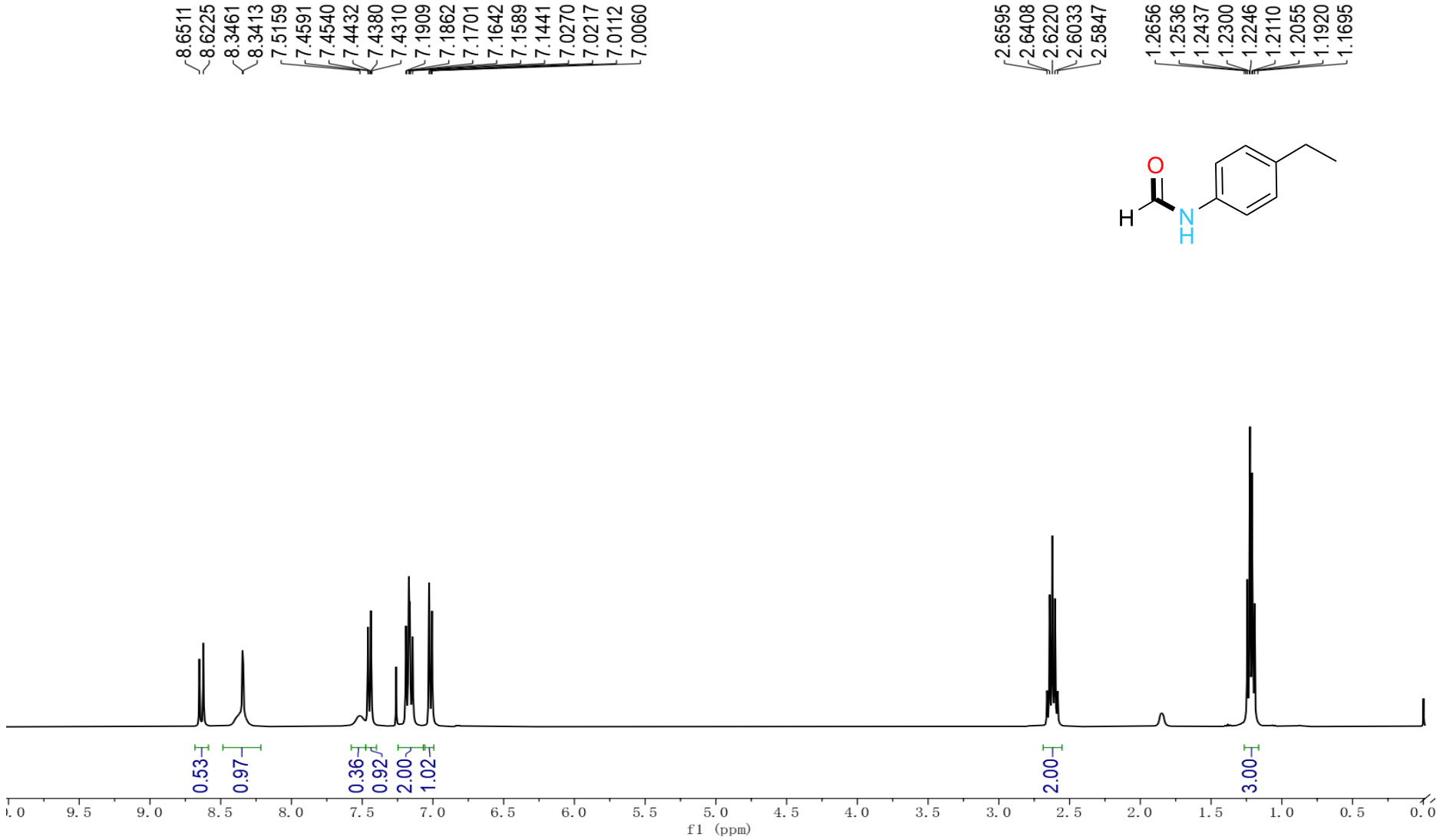
60
50
40
30
20
10
f1 (ppm)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1.2656
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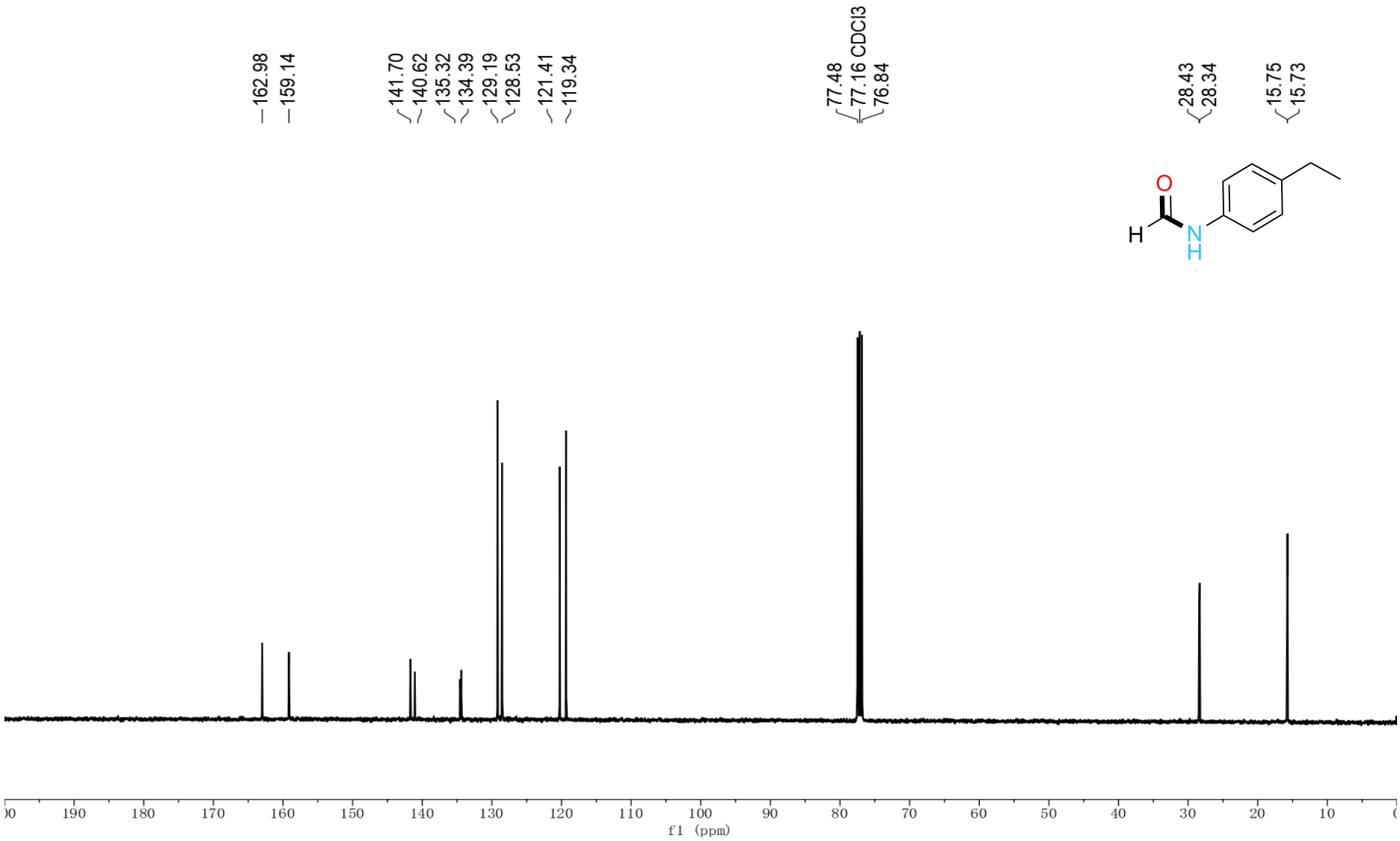
3.00
f1 (ppm)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121.41
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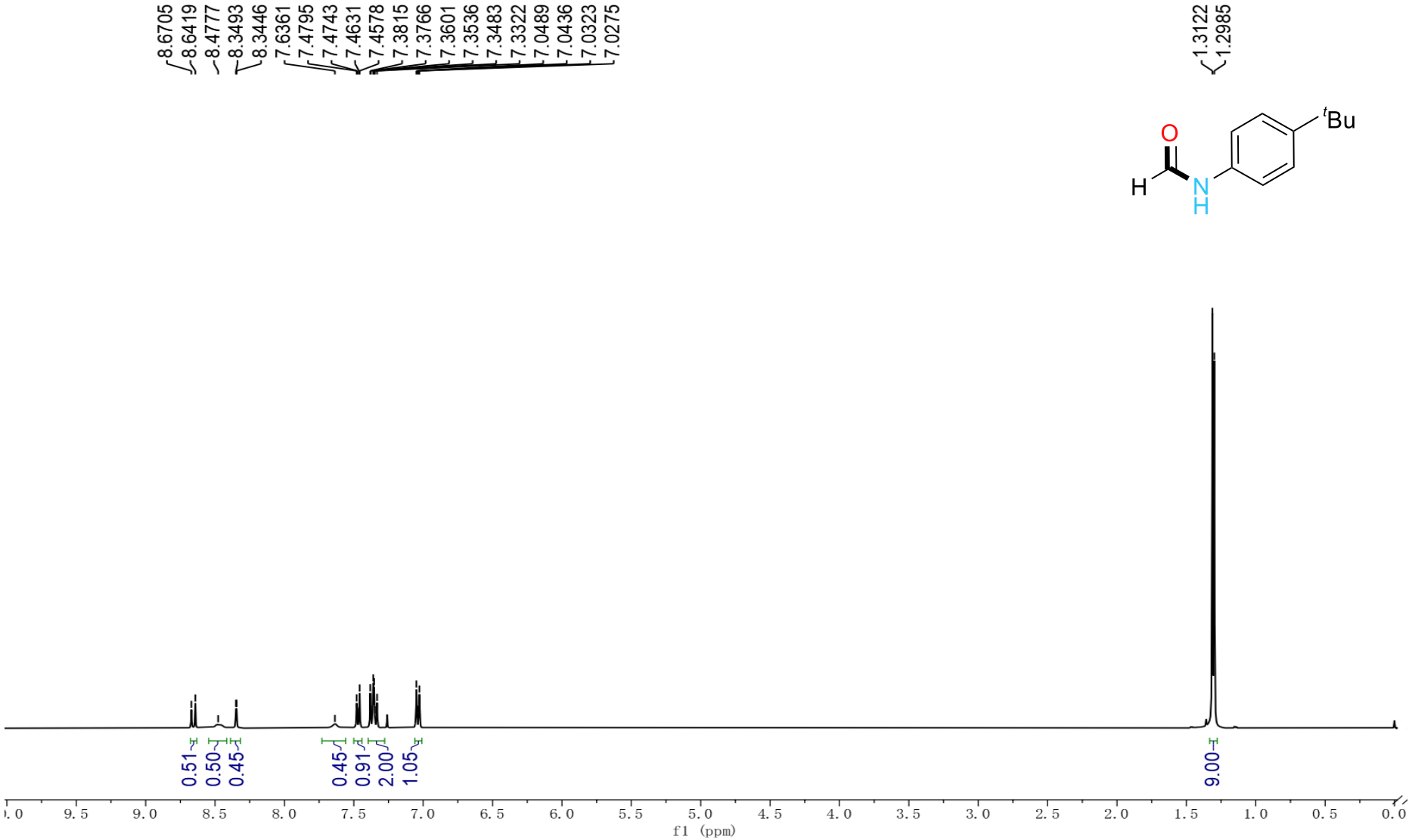
15.73
O
H
N
H
f1 (ppm)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7.0323
7.0275
1.3122
1.2985
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H
N
H
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2.00
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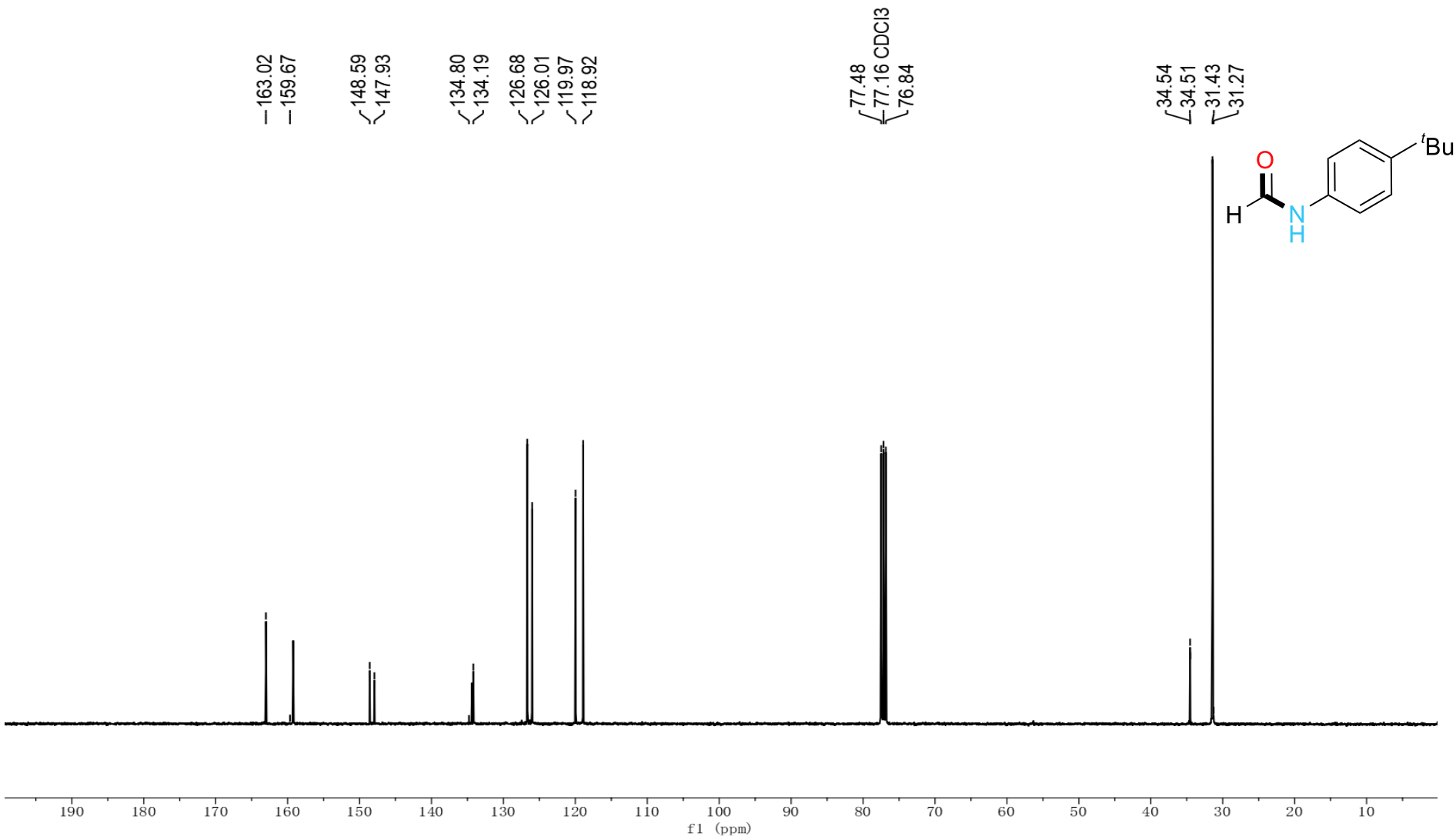
9.00
f1 (ppm)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34.51
31.43
31.27
O
H
N
H
tBu
190
180
170
160
150
140
130
120
110
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90
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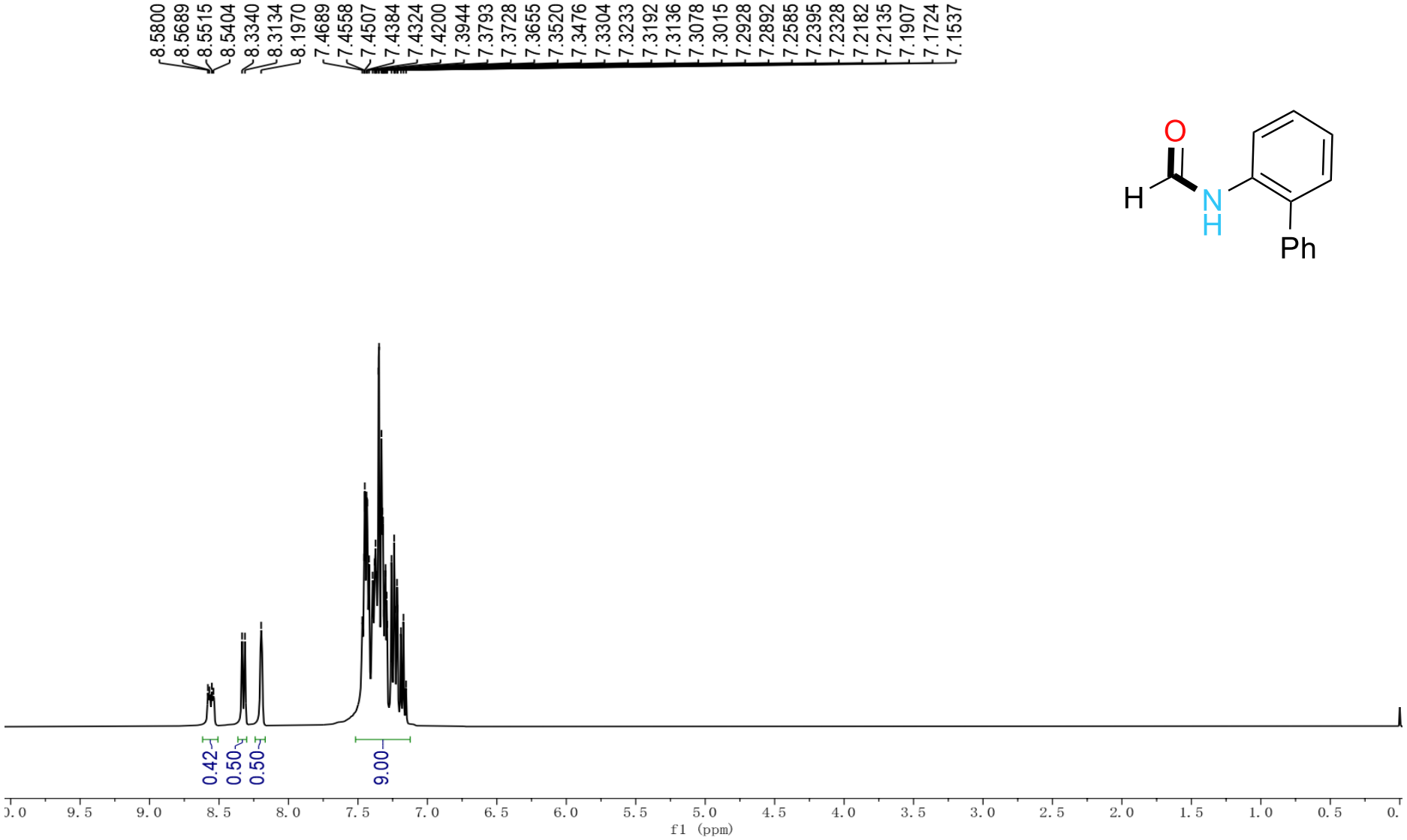
f1 (ppm)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7.4324
7.4200
7.3944
7.3793
7.3728
7.3655
7.3520
7.3476
7.3304
7.3233
7.3192
7.3136
7.3078
7.3015
7.2928
7.2892
7.2585
7.2395
7.2328
7.2182
7.2135
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O
H
N
H
Ph
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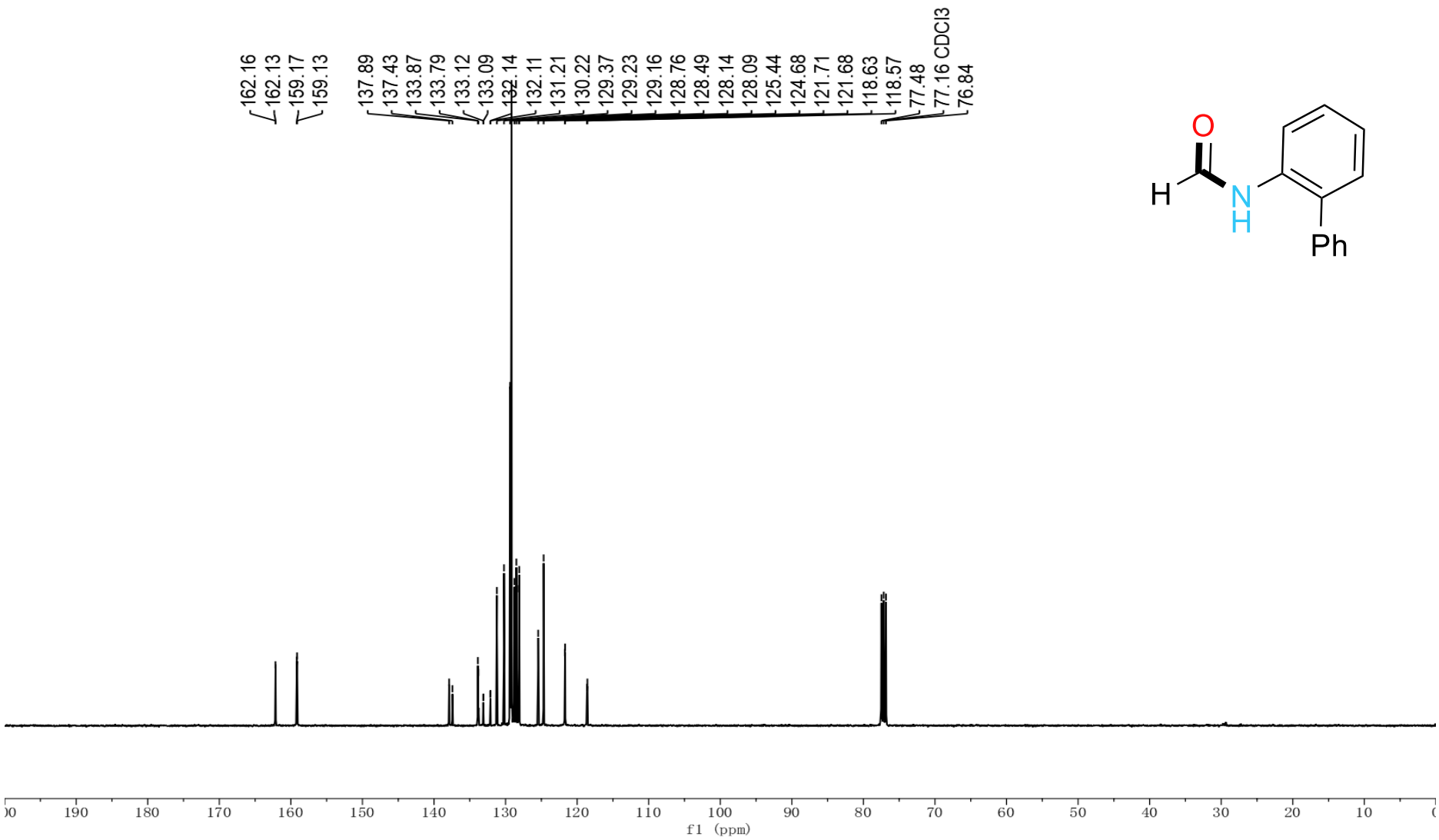
f1 (ppm)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130.22
129.37
129.23
129.16
128.76
128.49
128.14
128.09
125.44
124.68
121.71
121.68
118.63
118.57
77.48
77.16 CDCl3
76.84
O
H
N
H
Ph
190
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140
130
120
110
100
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80
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60
50
40
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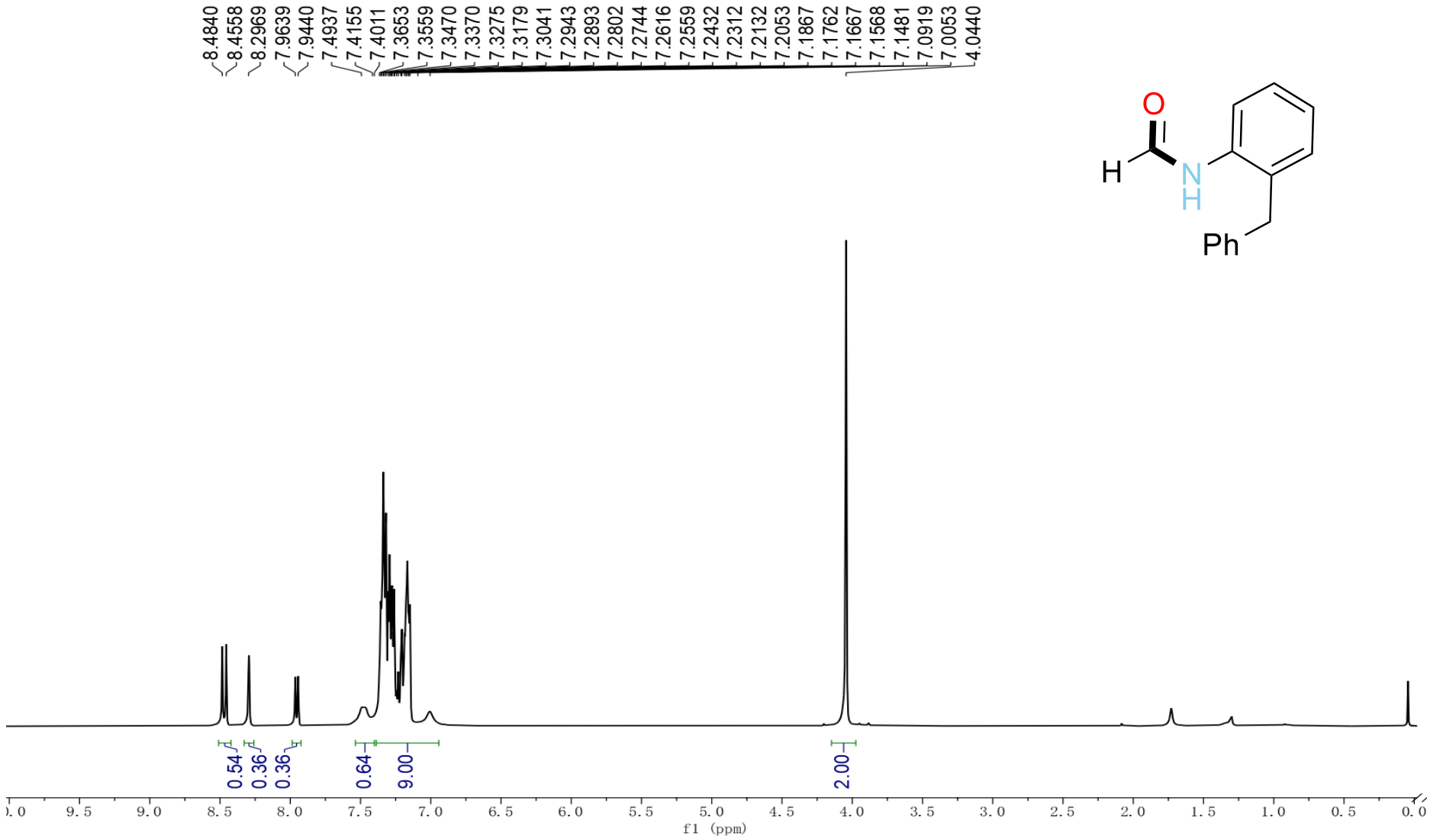
20
10
f1 (ppm)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7.3470
7.3370
7.3275
7.3179
7.3041
7.2943
7.2893
7.2802
7.2744
7.2616
7.2559
7.2432
7.2312
7.2132
7.2053
7.1867
7.1762
7.1667
7.1568
7.1481
7.0919
7.0053
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N
H
Ph
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2.00
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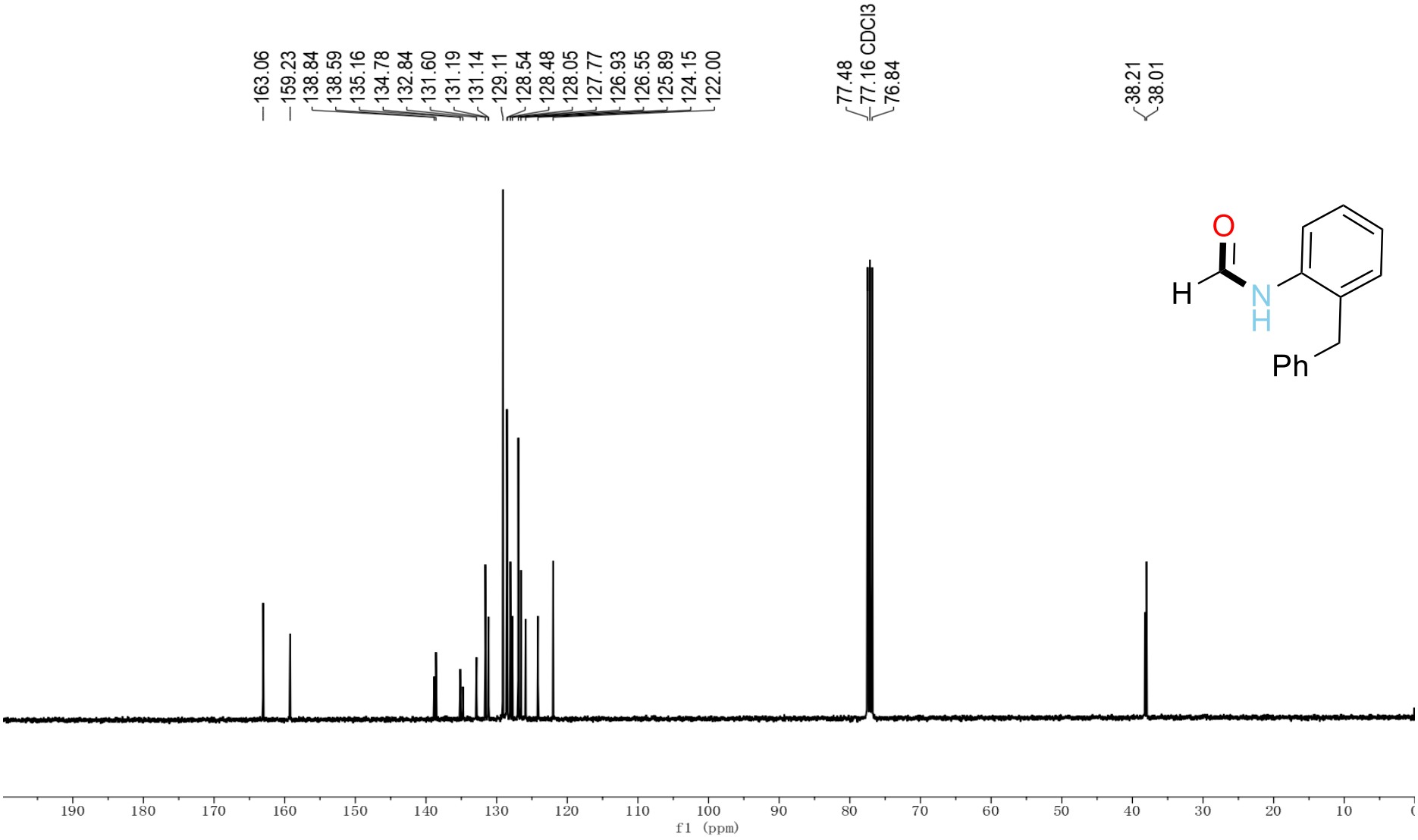
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127.77
126.93
126.55
125.89
124.15
122.00
77.48
77.16 CDCl3
76.84
38.21
38.01
O
H
N
H
Ph
190
180
170
160
150
140
130
120
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100
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80
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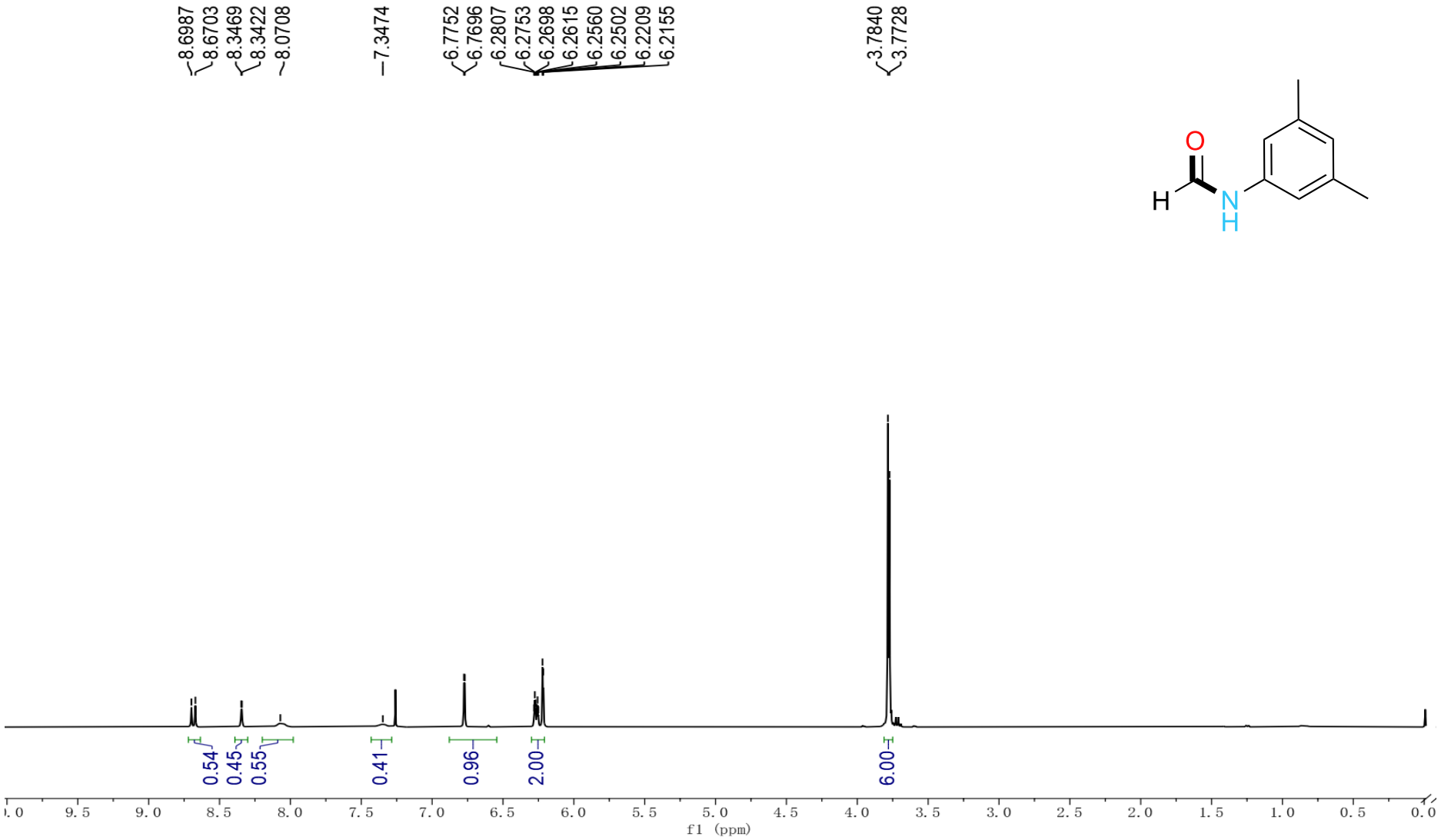
60
50
40
30
20
10
f1 (ppm)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6.2615
6.2560
6.2502
6.2209
6.2155
3.7840
3.7728
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H
N
H
0.54
0.45
0.55
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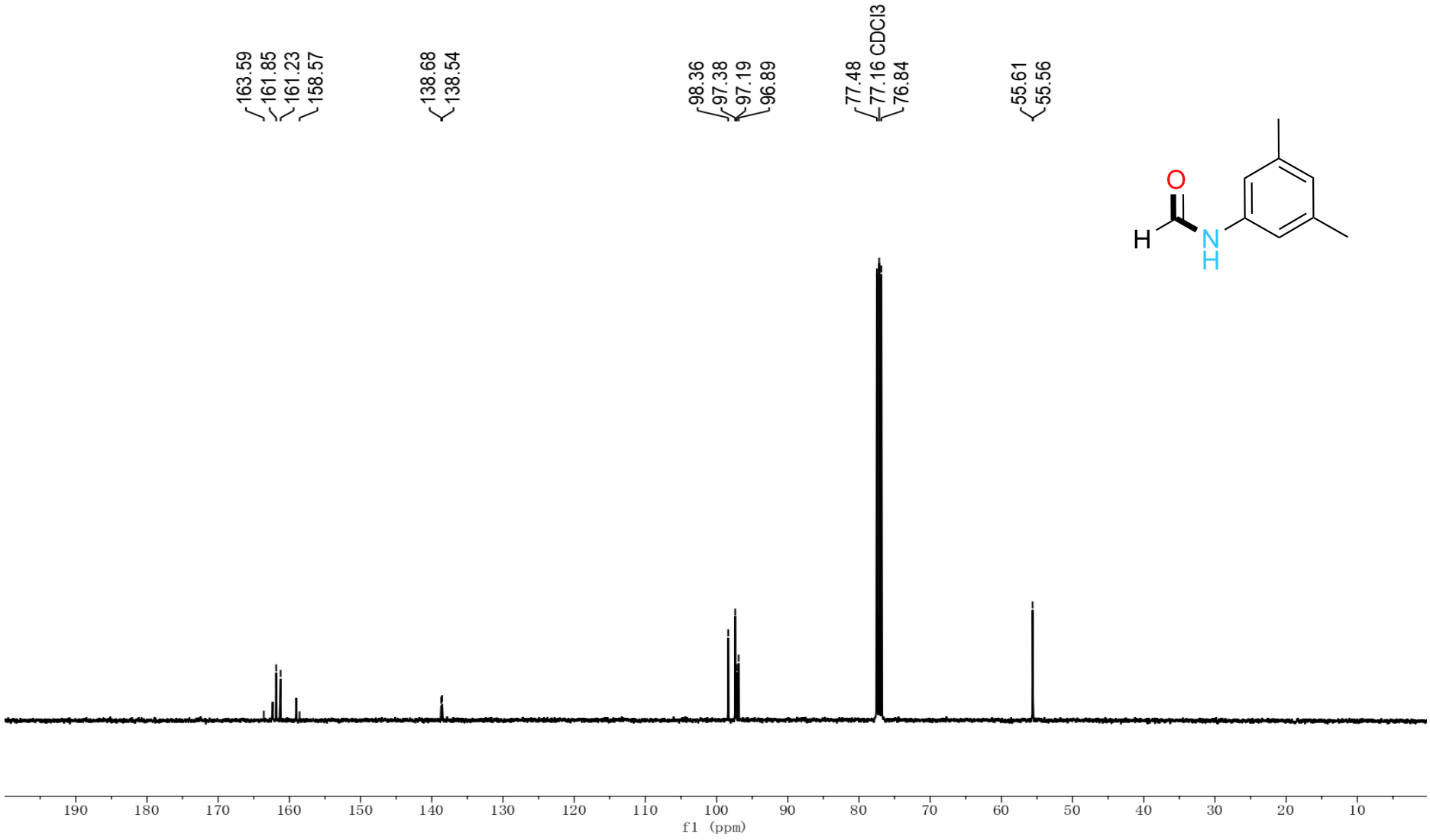
0.96
2.00
6.00
f1 (ppm)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97.38
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96.89
77.48
77.16 CDCl3
76.84
55.61
55.56
O
H
N
H
190
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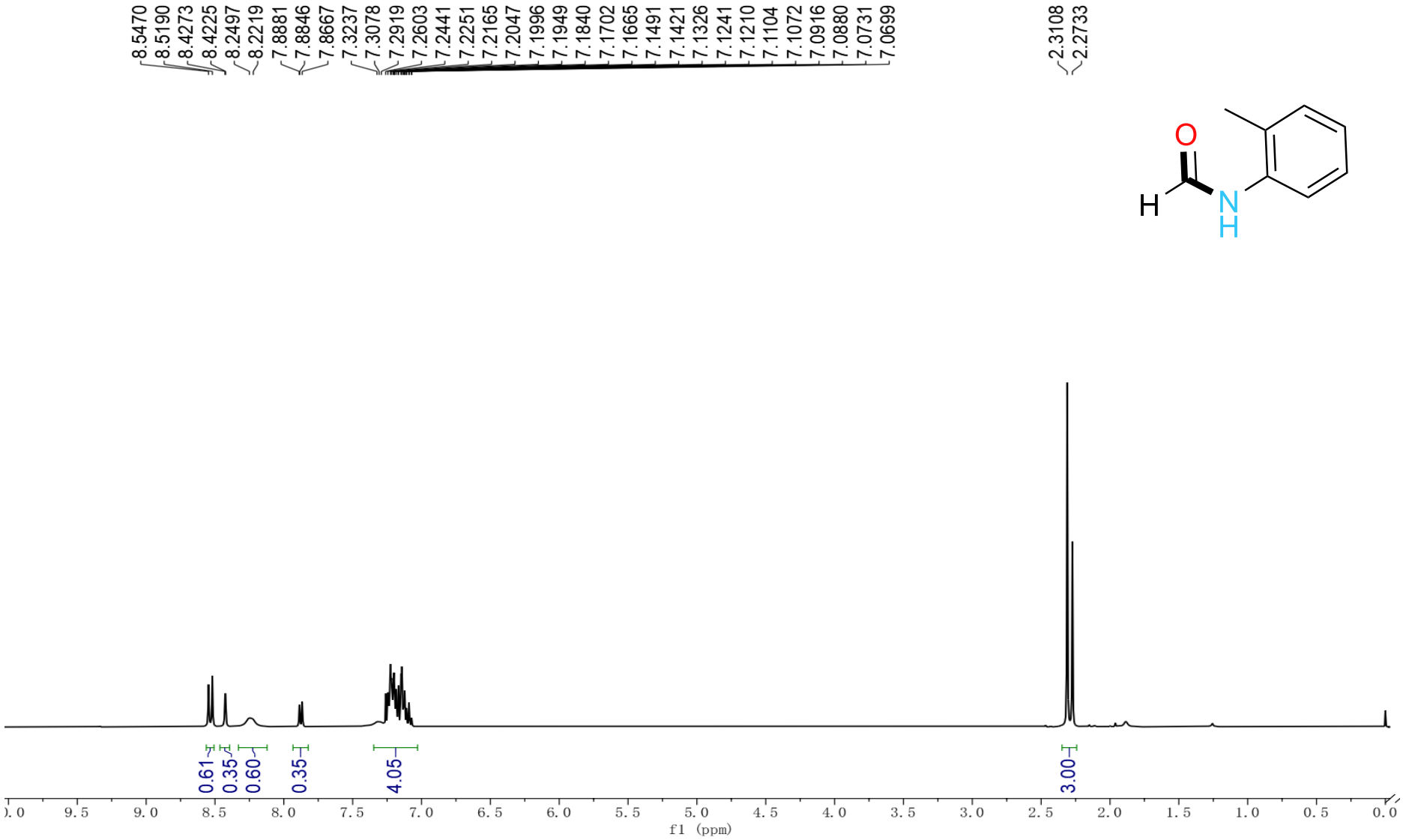
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.3237
7.3078
7.2919
7.2603
7.2441
7.2251
7.2165
7.2047
7.1996
7.1949
7.1840
7.1702
7.1665
7.1491
7.1421
7.1326
7.1241
7.1210
7.1104
7.1072
7.0916
7.0880
7.0731
7.0699
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2.2733
O
H
N
H
0.61
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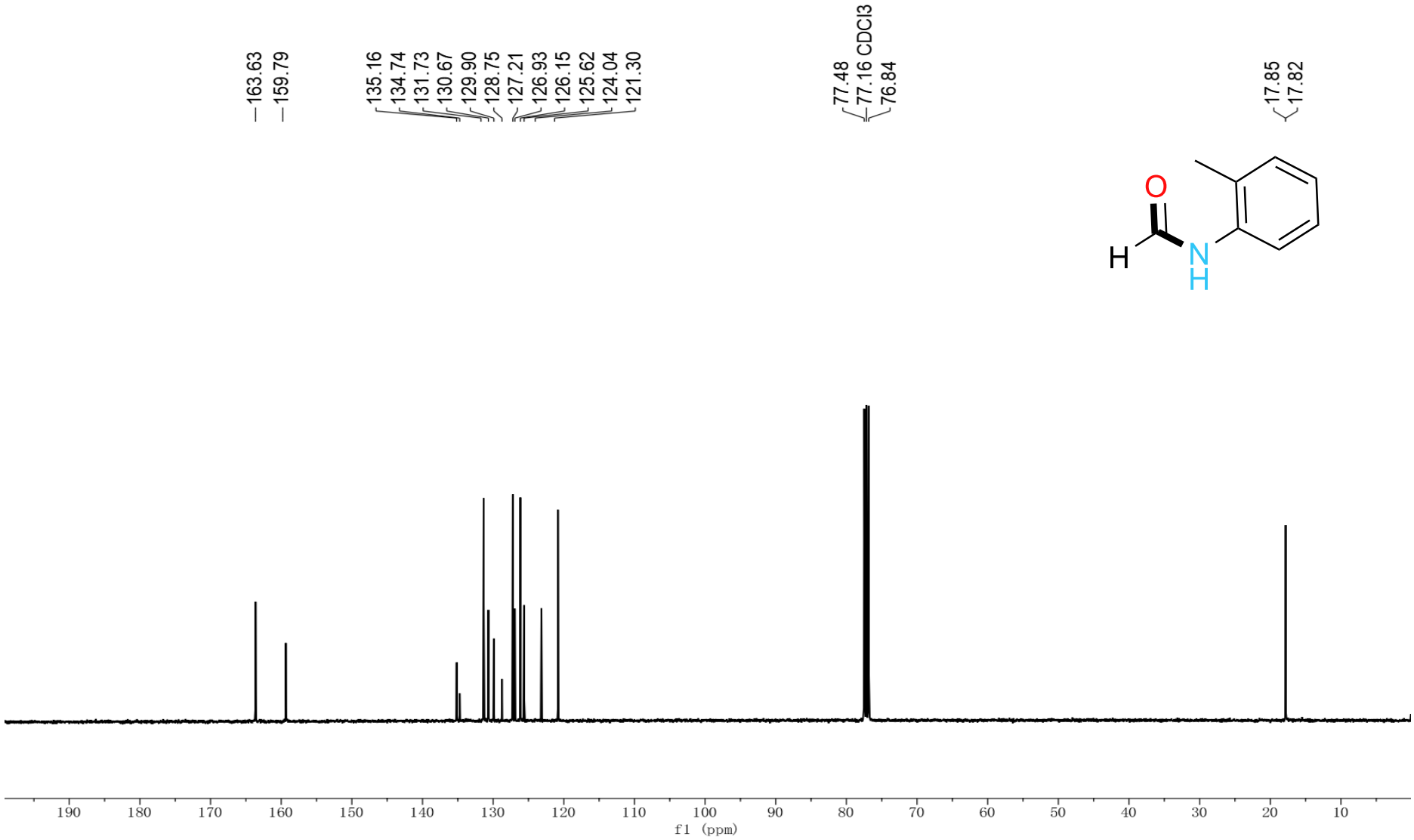
3.00
f1 (ppm)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130.67
129.90
128.75
127.21
126.93
126.15
125.62
124.04
121.30
77.48
77.16 CDCl3
76.84
17.85
17.82
O
H
N
H
190
180
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140
130
120
110
100
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80
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60
50
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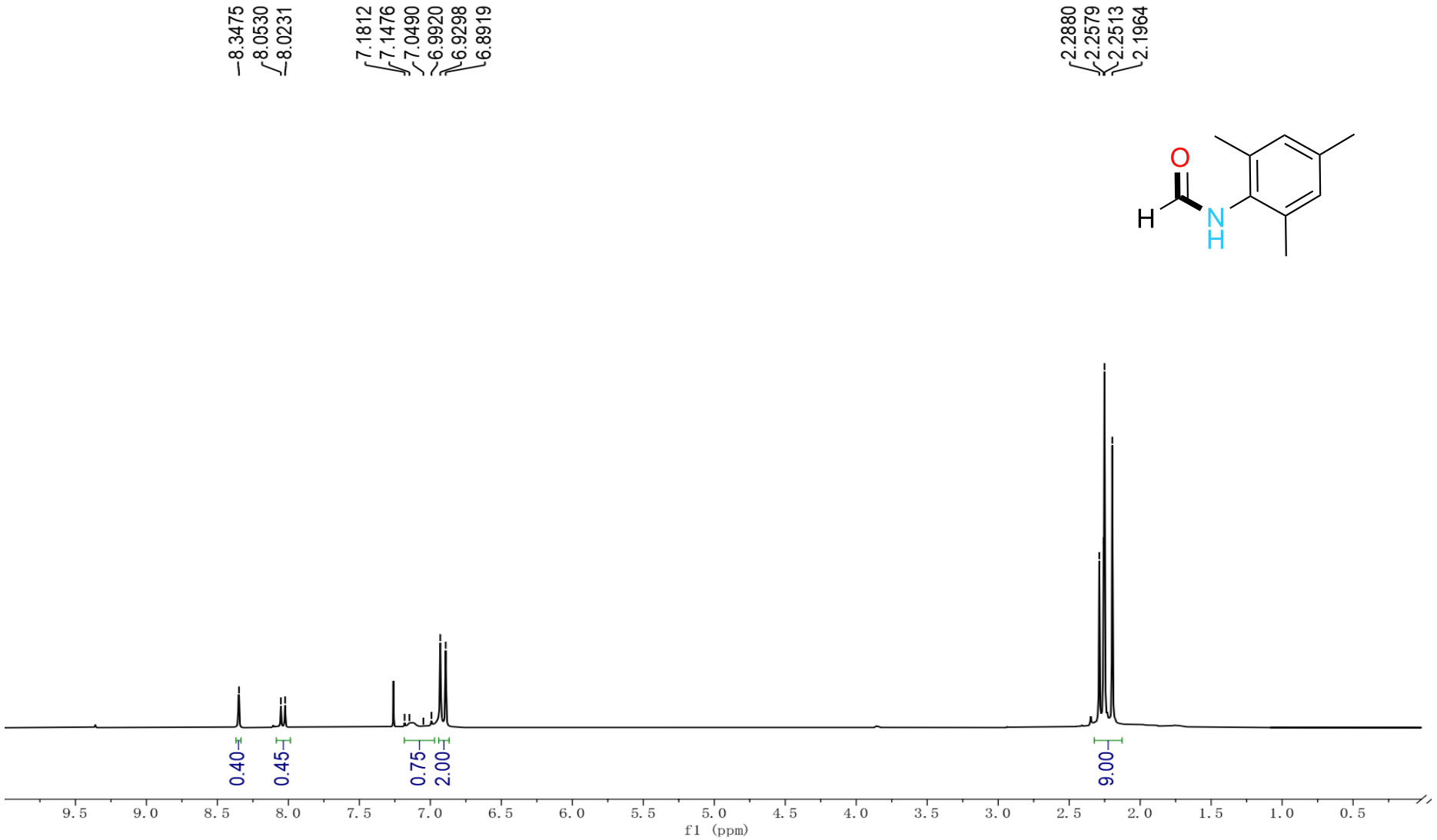
20
10
f1 (ppm)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6.9920
6.9298
6.8919
2.2880
2.2579
2.2513
2.1964
O
H
N
H
0.40
0.45
0.75
2.00
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
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1.5
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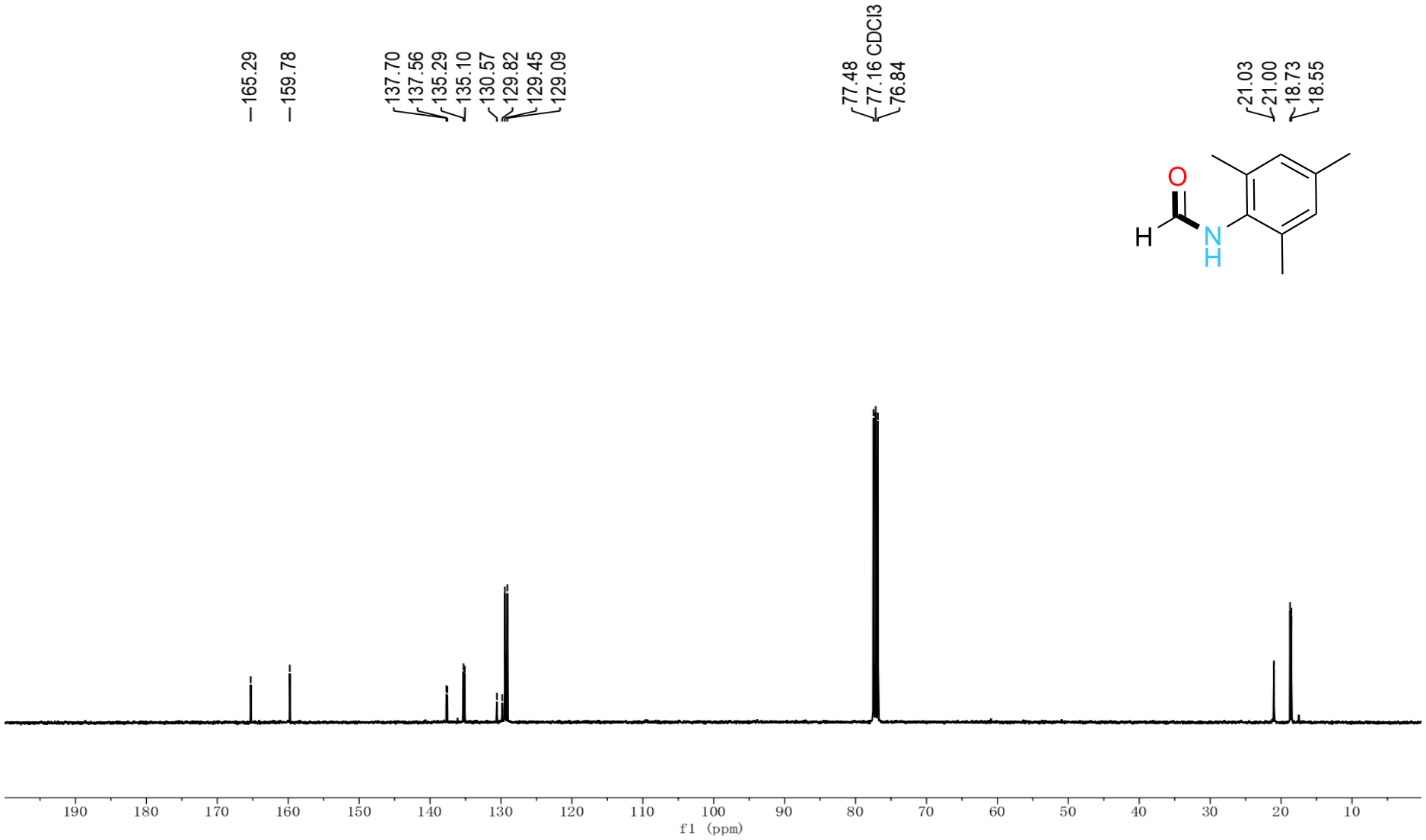
0.5
f1 (ppm)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130.57
129.82
129.45
129.09
77.48
77.16 CDCl3
76.84
21.03
21.00
18.73
18.55
O
H
N
H
190
180
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160
150
140
130
120
110
100
90
80
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60
50
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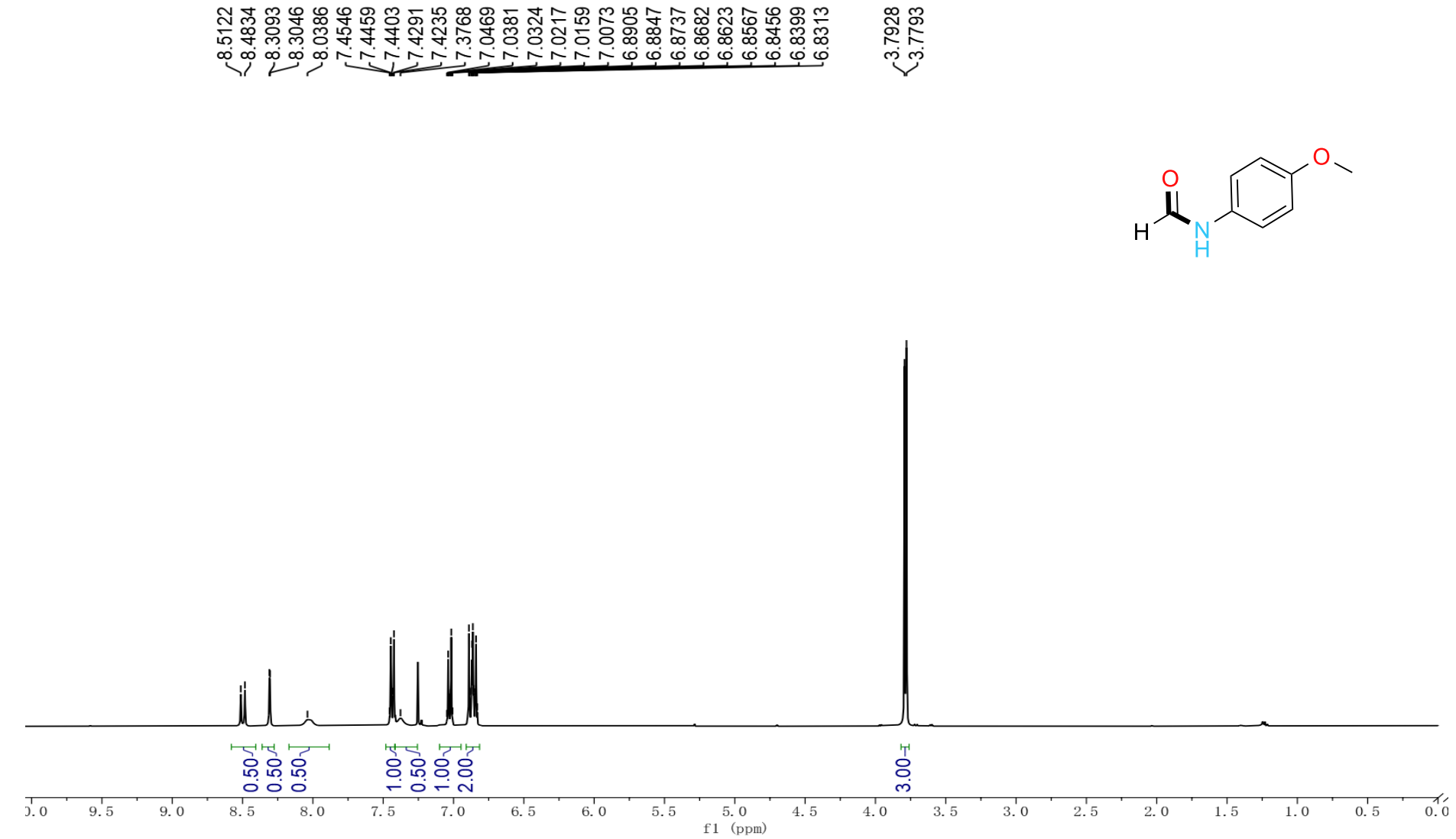
30
20
10
f1 (ppm)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7.0381
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7.0217
7.0159
7.0073
6.8905
6.8847
6.8737
6.8682
6.8623
6.8567
6.8456
6.8399
6.8313
3.7928
3.7793
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O
H
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H
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0.50
0.50
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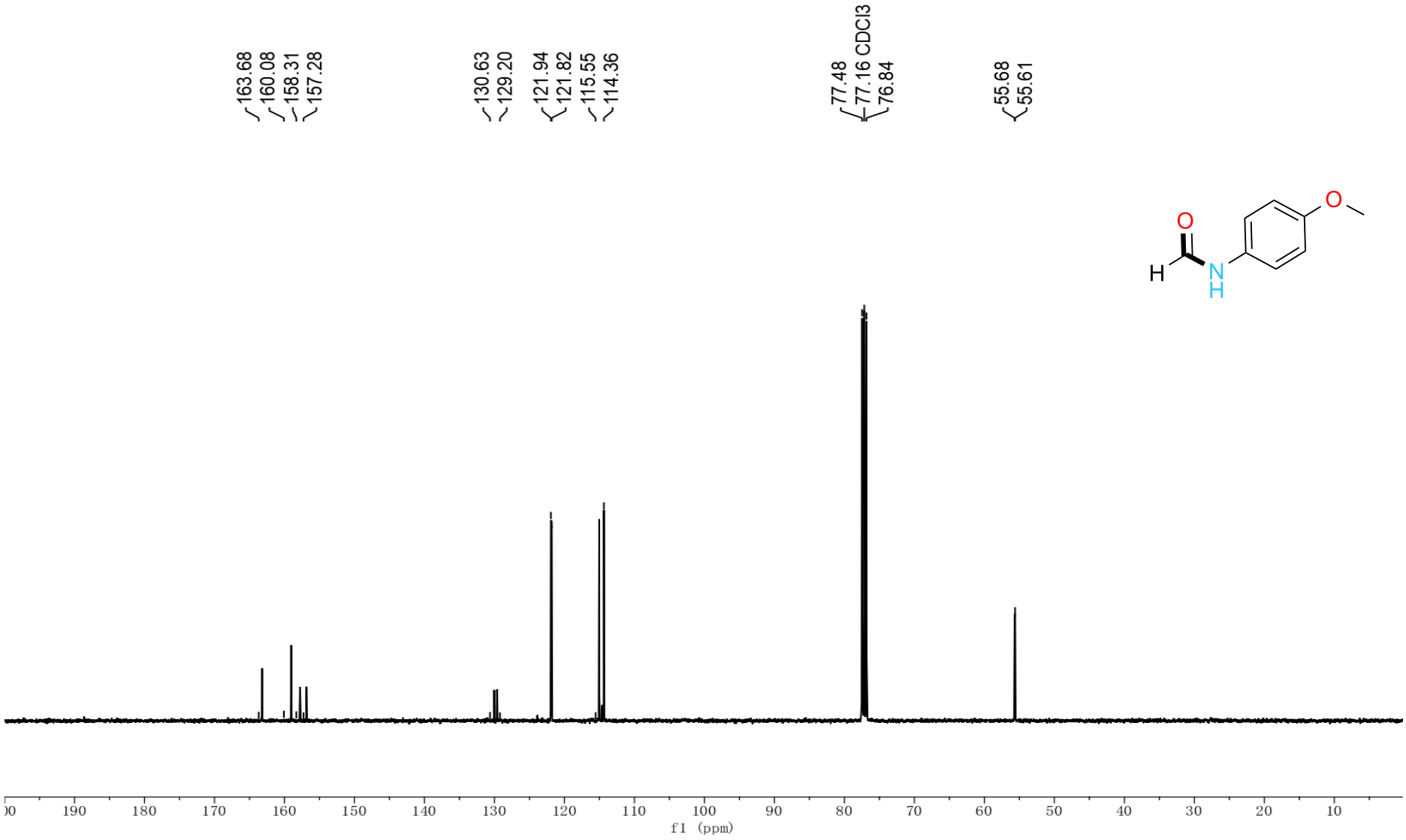
1.00
2.00
3.00
f1 (ppm)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121.82
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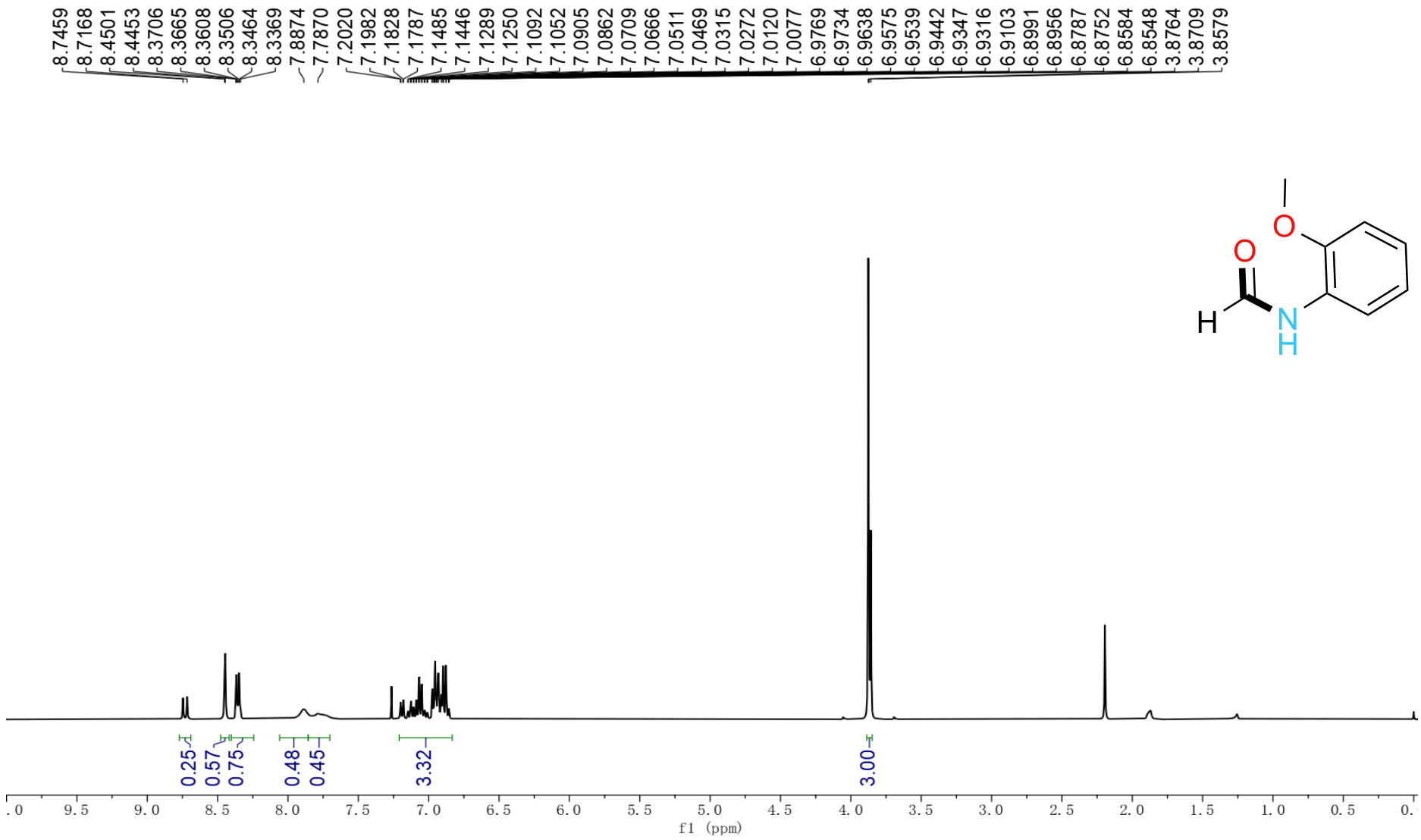
114.36
77.48
77.16 CDCl3
76.84
55.68
55.61
O
H
N
H
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.1982
7.1828
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7.1485
7.1446
7.1289
7.1250
7.1092
7.1052
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7.0511
7.0469
7.0315
7.0272
7.0120
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6.9734
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6.8991
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6.8752
6.8584
6.8548
3.8764
3.8709
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N
H
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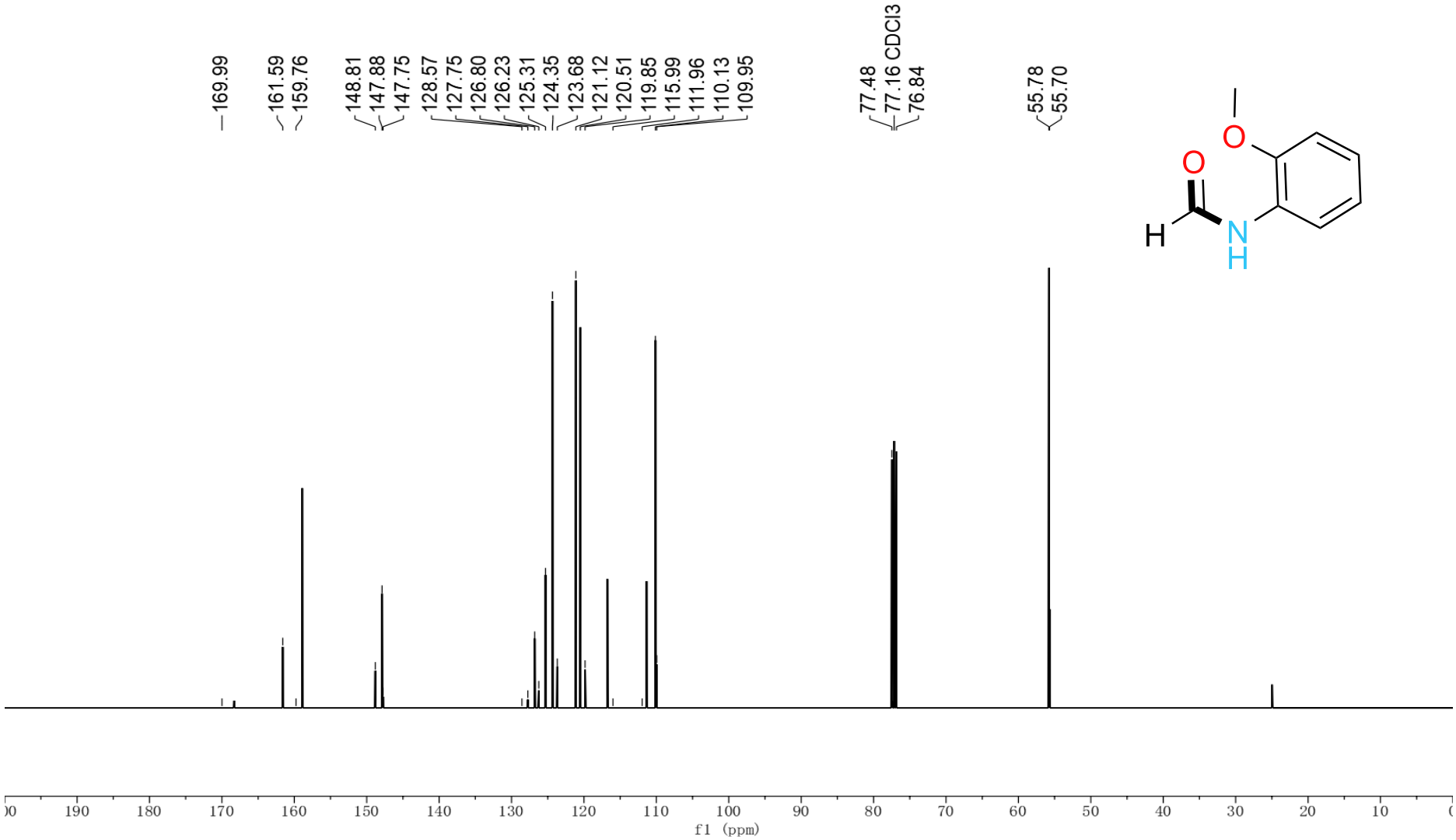
0.45
3.32
3.00
f1 (ppm)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125.31
124.35
123.68
121.12
120.51
119.85
115.99
111.96
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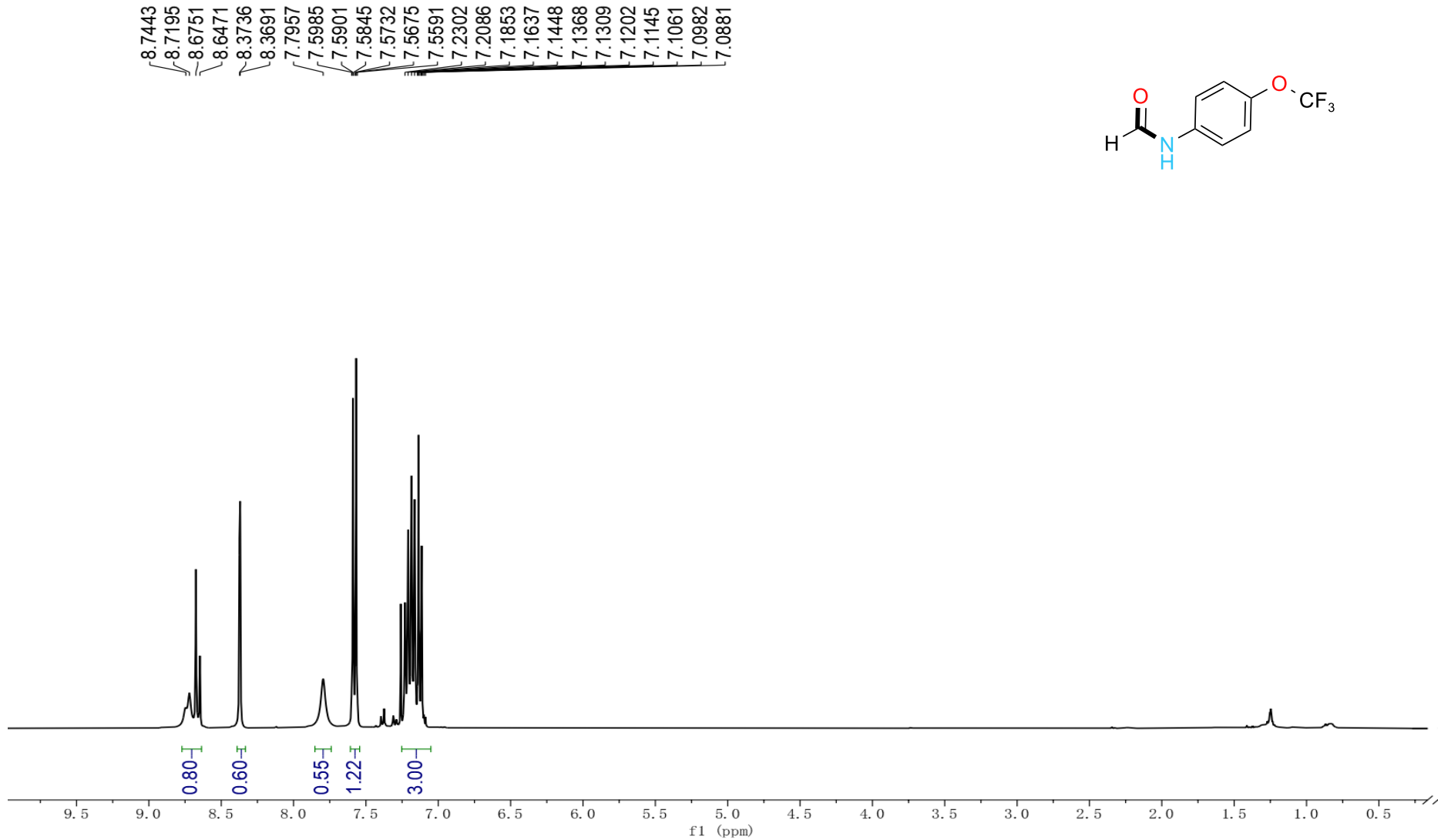
77.48
77.16 CDCl3
76.84
55.78
55.70
O
O
H
N
H
f1 (ppm)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7.5732
7.5675
7.5591
7.2302
7.2086
7.1853
7.1637
7.1448
7.1368
7.1309
7.1202
7.1145
7.1061
7.0982
7.0881
O
O
CF3
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N
H
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3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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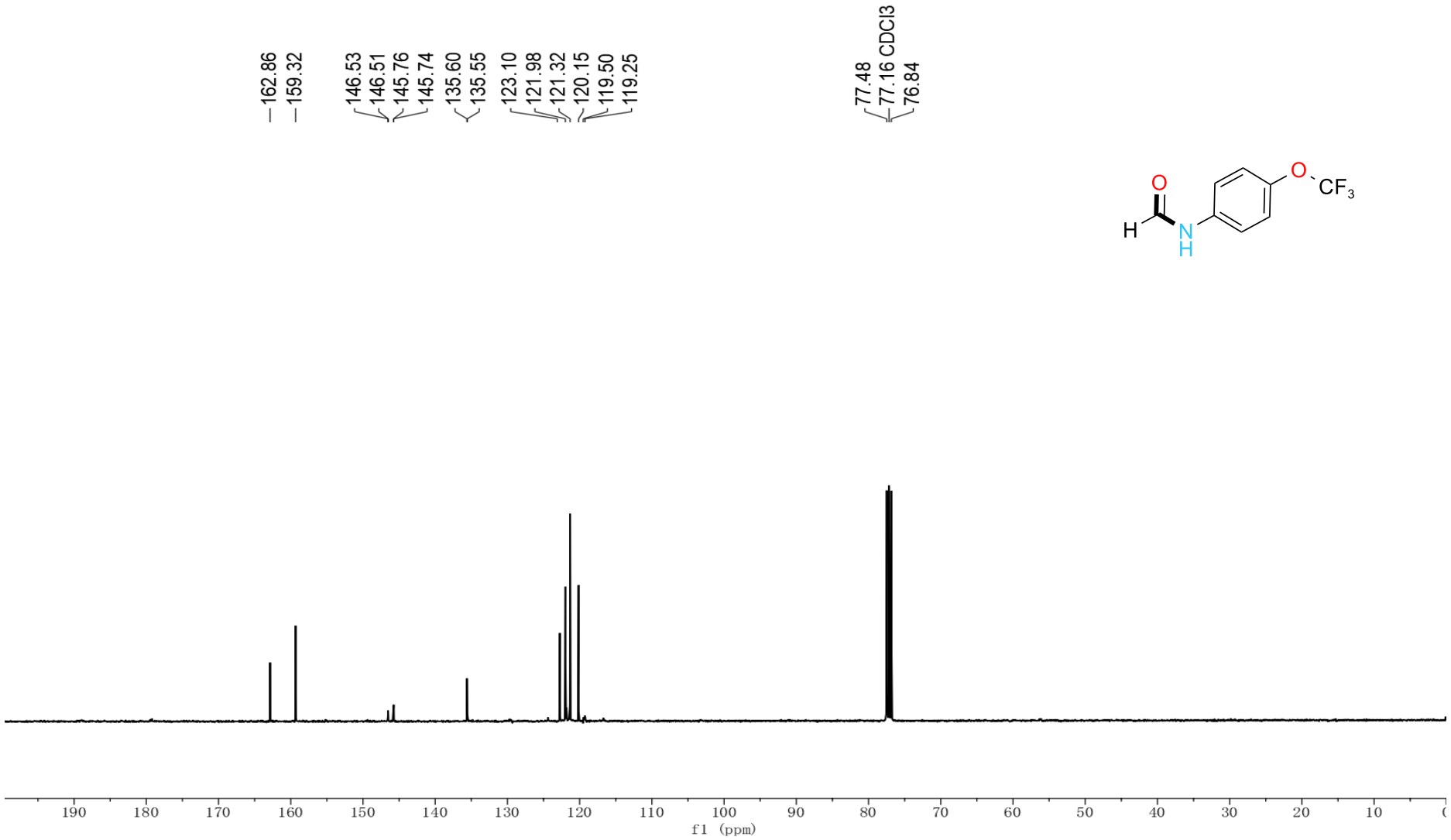
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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135.55
123.10
121.98
121.32
120.15
119.50
119.25
77.48
77.16 CDCl3
76.84
O
H
N
H
O
CF3
190
180
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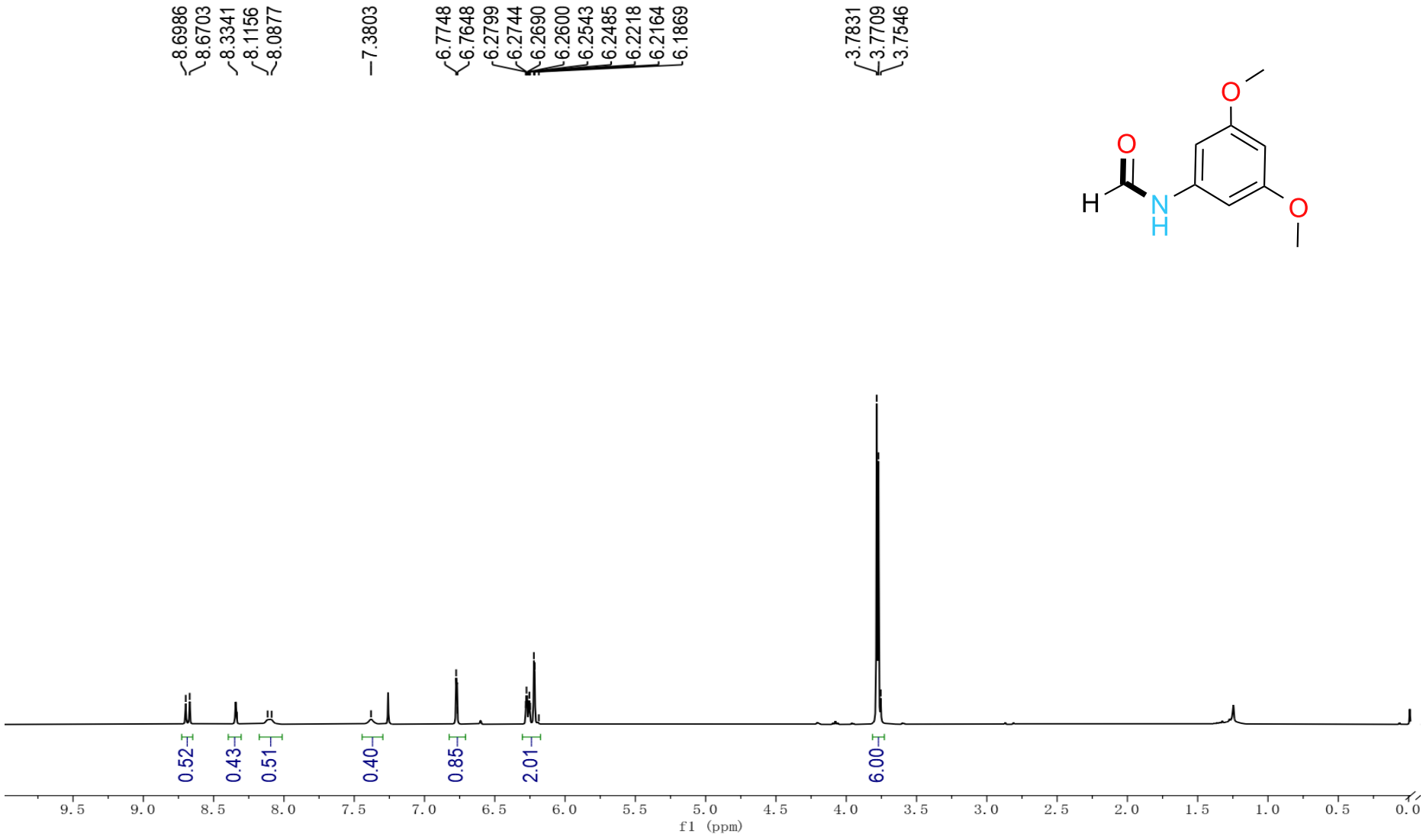
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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6.2690
6.2600
6.2543
6.2485
6.2218
6.2164
6.1869
3.7831
3.7709
3.7546
O
O
H
N
H
O
0.52
0.43
0.51
0.40
0.85
2.01
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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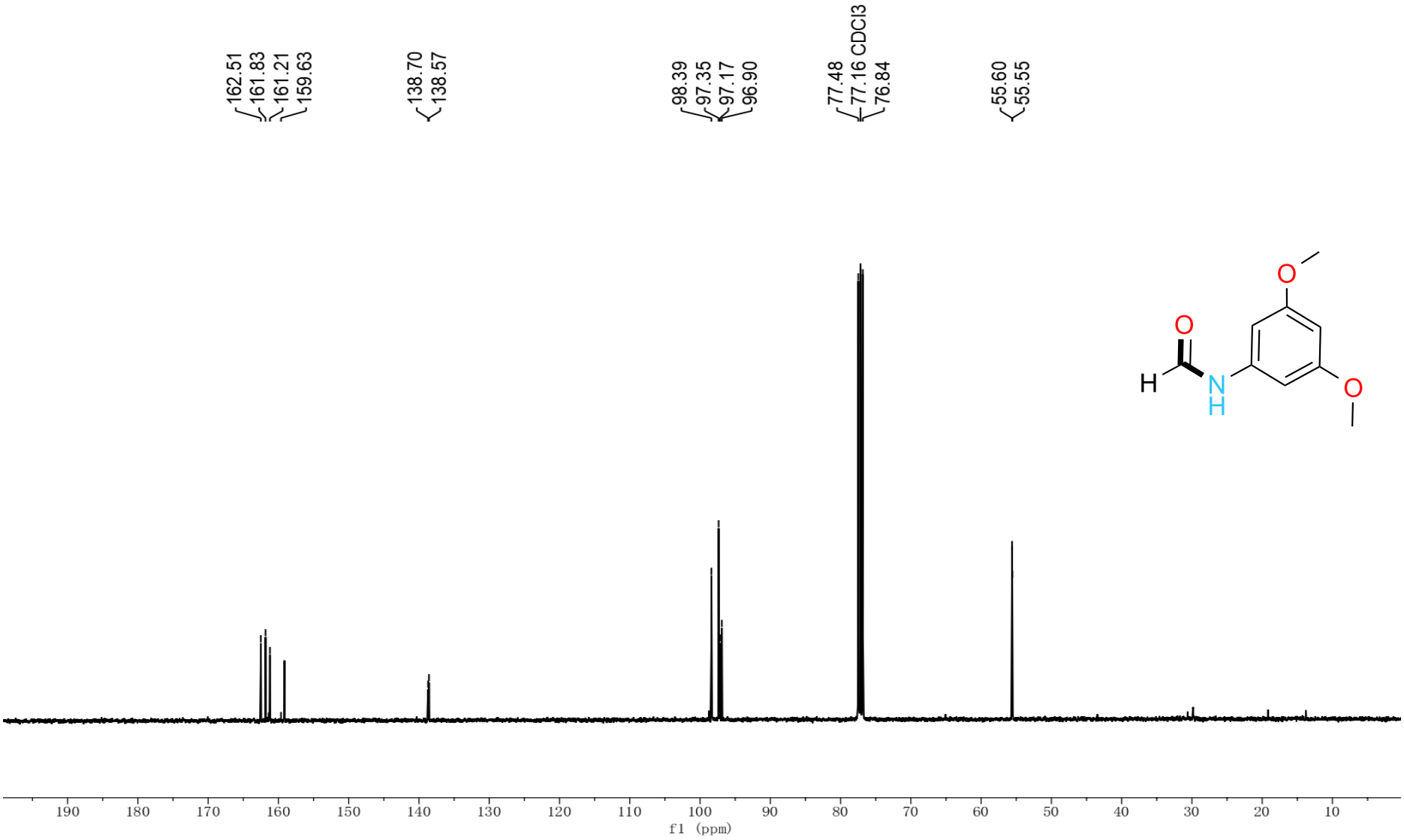
0.0
f1 (ppm)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96.90
77.48
77.16 CDCl3
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55.55
O
O
H
N
H
O
190
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140
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120
110
100
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80
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60
50
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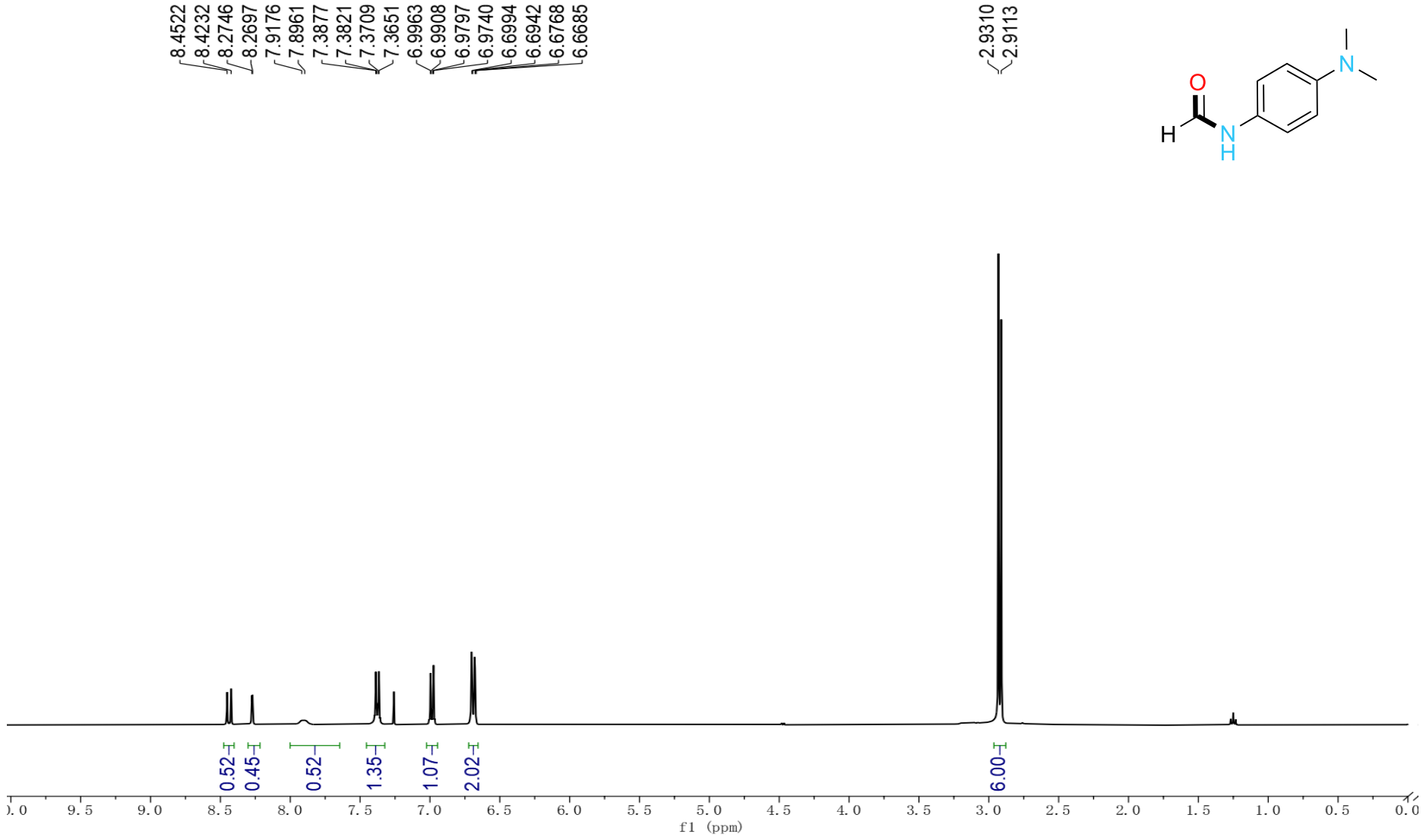
30
20
10
f1 (ppm)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6.9908
6.9797
6.9740
6.6994
6.6942
6.6768
6.6685
2.9310
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N
H
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0.52
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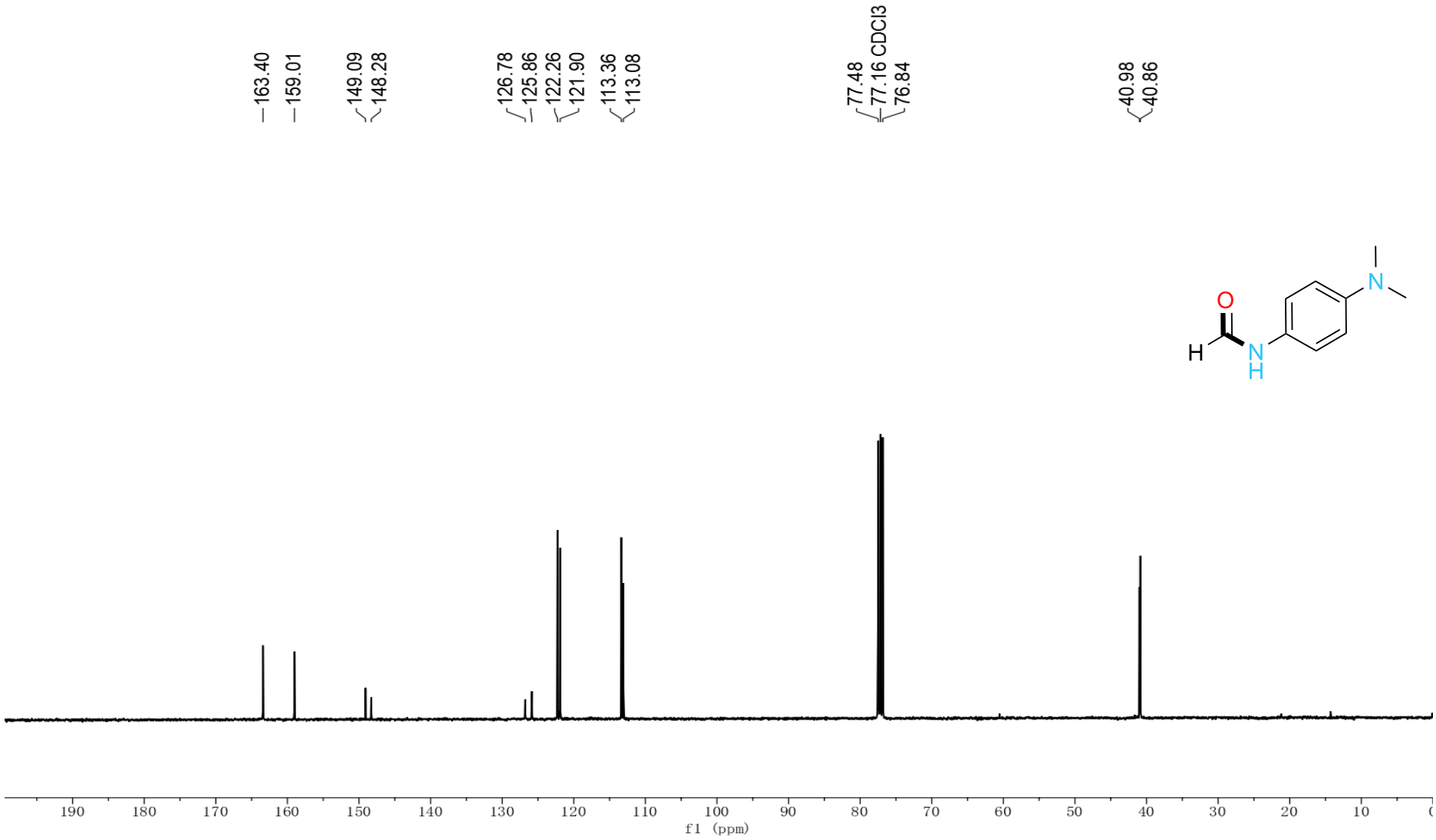
1.07
2.02
6.00
f1 (ppm)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121.90
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113.08
77.48
77.16 CDCl3
76.84
40.98
40.86
O
H
N
H
N
190
180
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150
140
130
120
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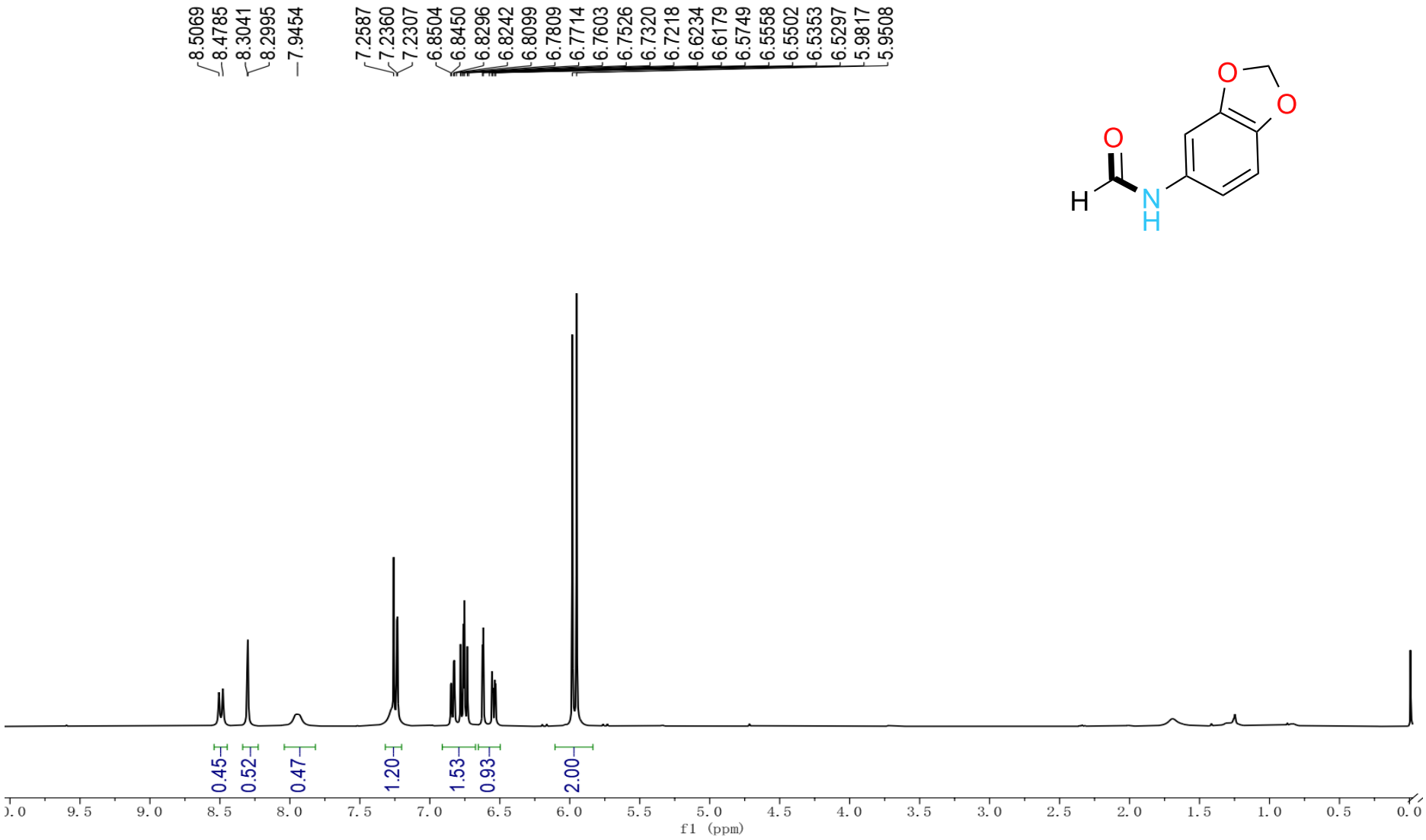
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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6.8242
6.8099
6.7809
6.7714
6.7603
6.7526
6.7320
6.7218
6.6234
6.6179
6.5749
6.5558
6.5502
6.5353
6.5297
5.9817
5.9508
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O
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N
H
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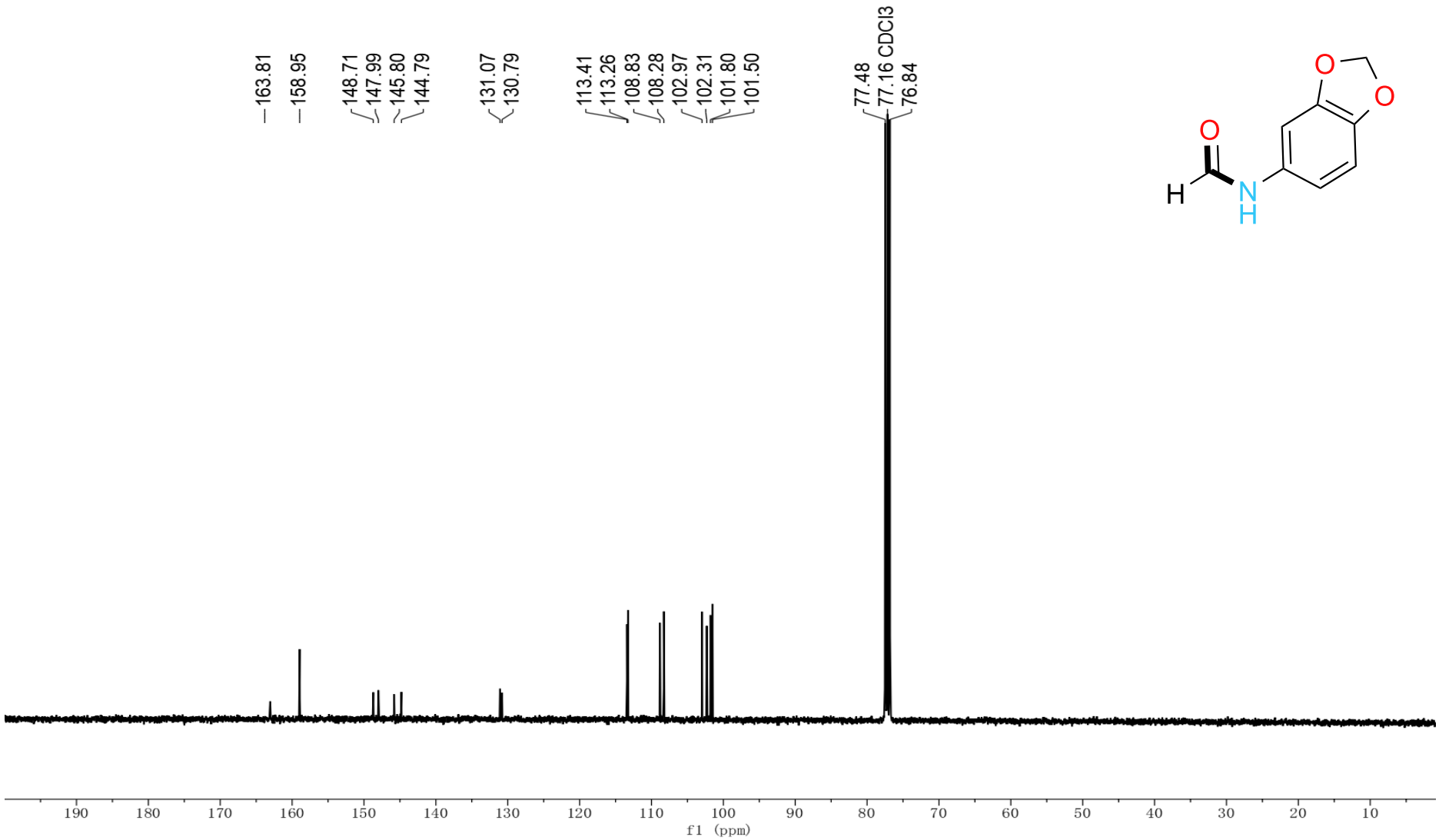
1.53
0.93
2.00
f1 (ppm)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113.26
108.83
108.28
102.97
102.31
101.80
101.50
77.48
77.16 CDCl3
76.84
O
O
O
H
N
H
190
180
170
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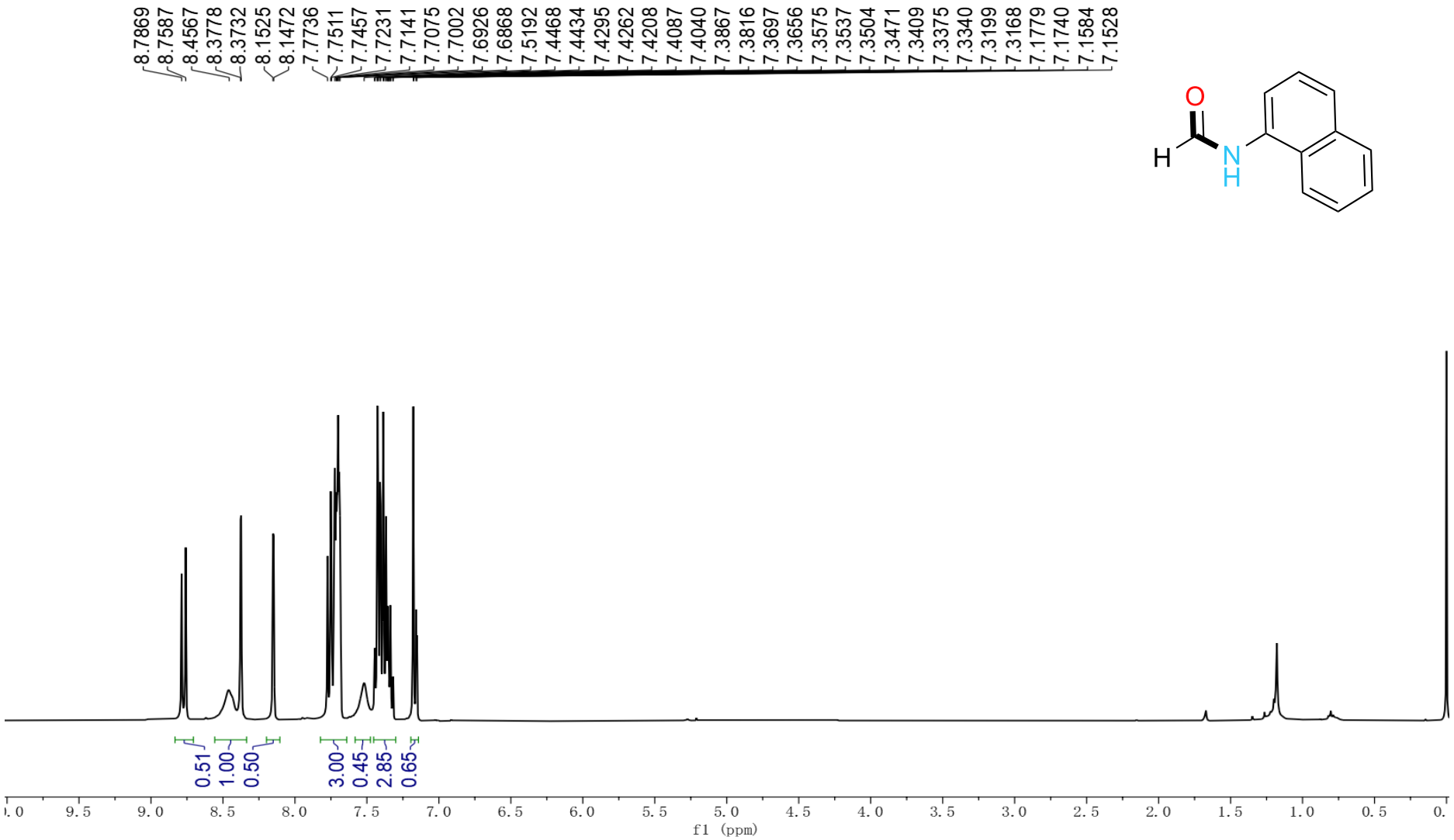
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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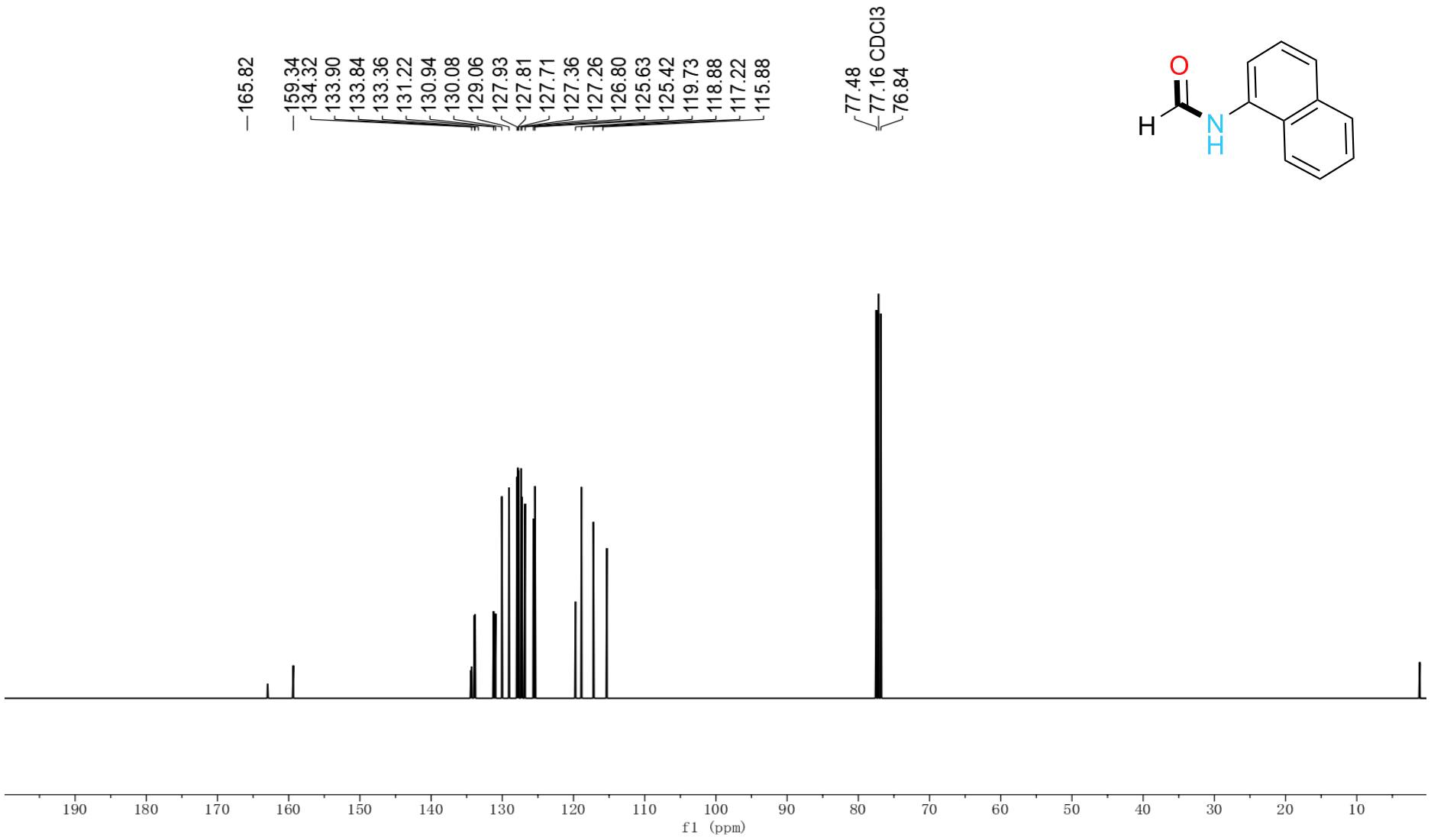
0.65
f1 (ppm)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127.36
127.26
126.80
125.63
125.42
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118.88
117.22
115.88
77.48
77.16 CDCl3
76.84
O
H
N
H
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
30
20
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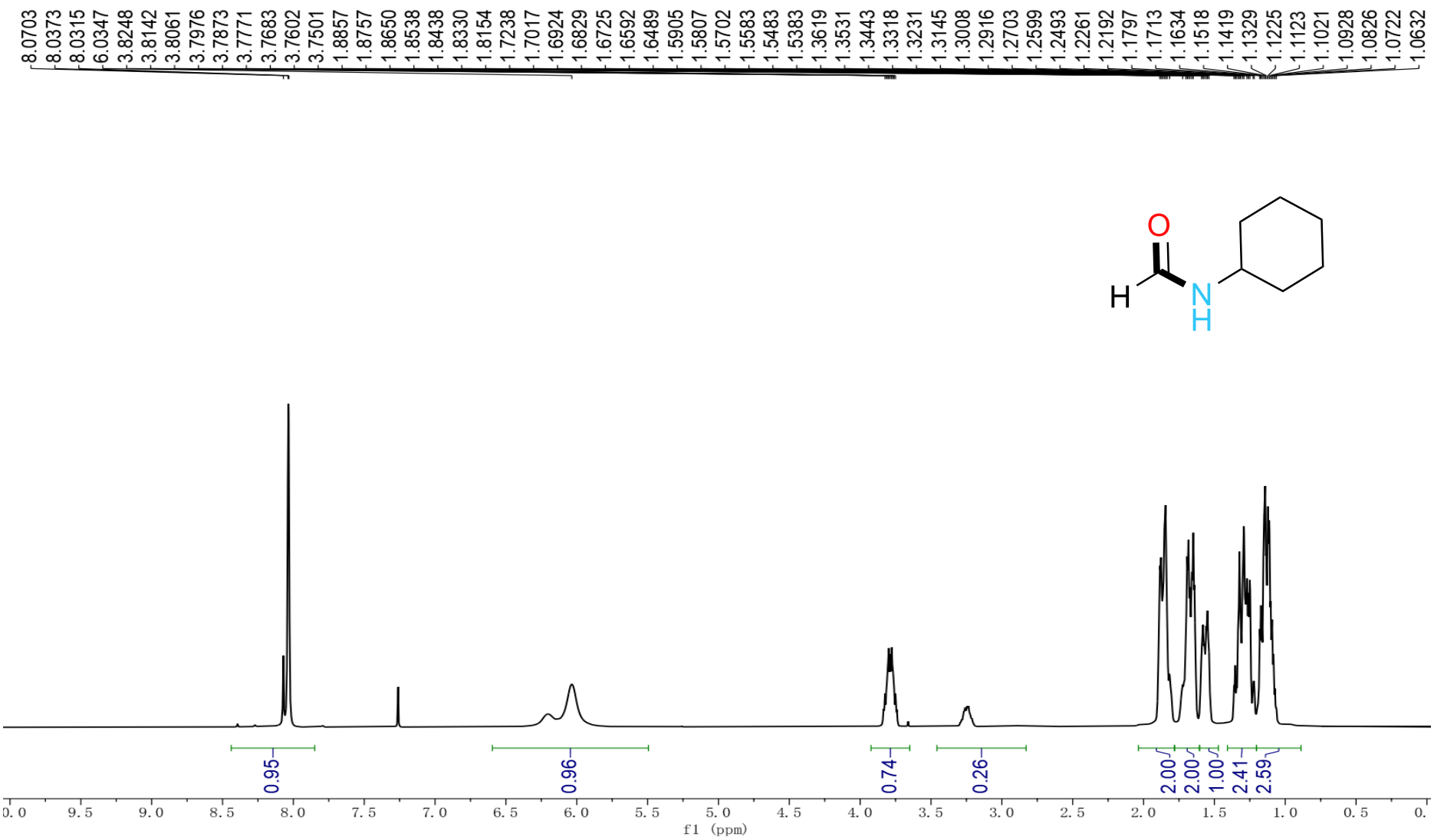
f1 (ppm)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8.0373
8.0315
6.0347
3.8248
3.8142
3.8061
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3.7771
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1.8857
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1.8650
1.8538
1.8438
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1.7238
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1.6924
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1.6725
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1.5483
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1.3619
1.3531
1.3443
1.3318
1.3231
1.3145
1.3008
1.2916
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1.2599
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1.2261
1.2192
1.1797
1.1713
1.1634
1.1518
1.1419
1.1329
1.1225
1.1123
1.1021
1.0928
1.0826
1.0722
1.0632
O
H
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2.00
1.00
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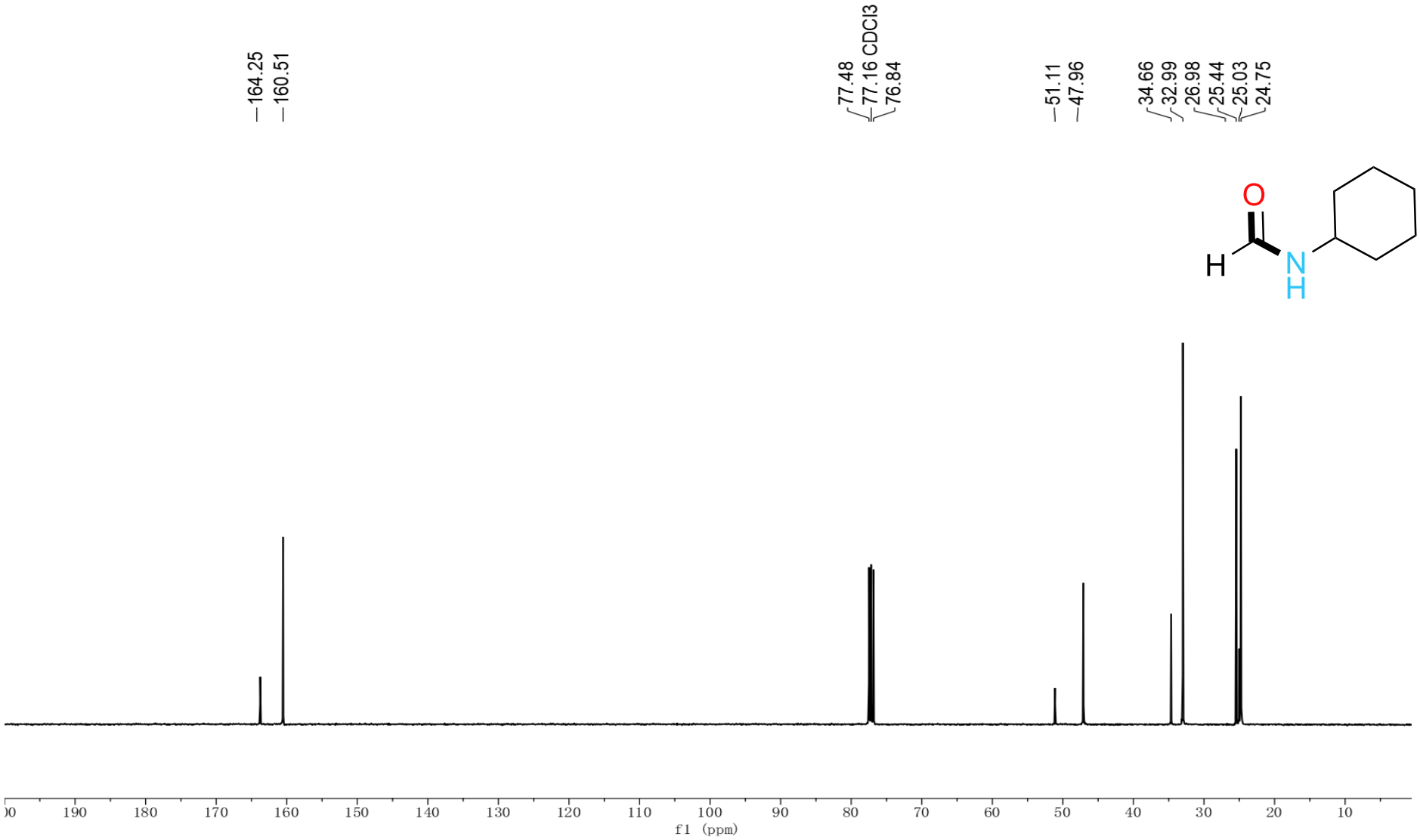
f1 (ppm)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77.16 CDCl3
76.84
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25.03
24.75
O
H
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)