

Supporting Information

Department of Pharmacology and Pharmaceutical Sciences, School of life sciences and School of Medicine, Tsinghua University, Beijing 100084, China
yrao@mail.tsinghua.edu.cn

SUPPORTING INFORMATION

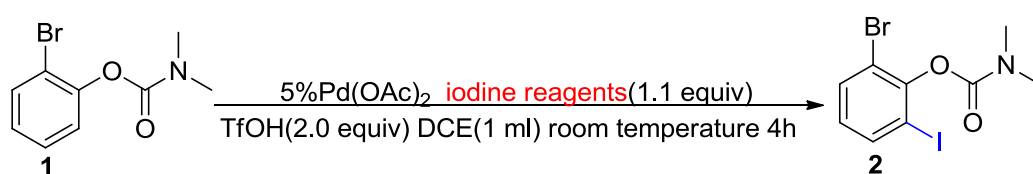
Table of Contents	Page
Materials and Methods	S2
Optimization of the reaction conditions.	S2
General procedure for synthesis of carbamates	S4
General procedure for palladium-catalyzed the synthesis of Ortho-iodinated carbamates	S4
Mechanistic study	S5
Applications	S9
References	S11
Data of products	S12

Materials and Methods

All commercial materials (Alfa Aesar, Aladdin, J&K Chemical LTD.) were used without further purification. All solvents were analytical grade. The ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl_3 using TMS or solvent peak as a standard. All ^{13}C -NMR spectra were recorded with complete proton decoupling. Low-resolution mass spectral analyses were performed with a Waters AQUITY UPLCTM/MS. All reactions were carried out in oven-dried sealed tube. Analytical TLC was performed on Yantai Chemical Industry Research Institute silica gel 60 F254 plates and flash column chromatography was performed on Qingdao Haiyang Chemical Co. Ltd silica gel 60 (200-300 mesh). The rotavapor was BUCHI's Rotavapor R-3.

Optimization of the reaction conditions.

I Effects of various hypervalent iodine reagents



entry	catalyst	iodine reagents	conditions	yield(%) ^a
1	Pd(OAc) ₂	Togni's reagents II	TfOH, DCE, rt	20
2	Pd(OAc) ₂	Togni's reagents	TfOH, DCE, rt	NR
3	Pd(OAc) ₂	PhI(OAc) ₂	TfOH, DCE, rt	NR
4	Pd(OAc) ₂	I(III)-OMe	TfOH, DCE, rt	70 ^b
5	Pd(OAc) ₂	I(III)-OAc	TfOH, DCE, rt	32
6	Pd(OAc) ₂	I(III)-OH	TfOH, DCE, rt	47
7	Pd(OAc) ₂	I(III)-OTs	TfOH, DCE, rt	37
8	Pd(OAc) ₂	DMP	TfOH, DCE, rt	43
9	Pd(OAc) ₂	NaIO ₃	TfOH, DCE, rt	32
10	Pd(OAc) ₂	KIO ₃	TfOH, DCE, rt	26
11	Pd(OAc) ₂	NaIO ₄	TfOH, DCE, rt	26
12	Pd(OAc) ₂	KIO ₄	TfOH, DCE, rt	30
13	Pd(OAc) ₂	NIS	TfOH, DCE, rt	10%+62%SP
14	Pd(OAc) ₂	I ₂ +PhI(OAc) ₂	TfOH, DCE, rt	78%SP
15	Pd(OAc) ₂	I ₂	TfOH, DCE, rt	NR
16	Pd(OAc) ₂	[Hydroxy(tosyloxy)iodo]benzene	TfOH, DCE, rt	n.t.
17	Pd(OAc) ₂	Diphenyliodonium iodide	TfOH, DCE, rt	NR
18	Pd(OAc) ₂	Diphenyliodonium chloride	TfOH, DCE, rt	NR

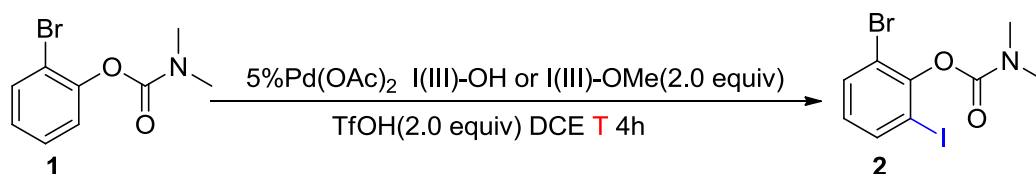
^aNMR yield using 4-Nitrobenzaldehyde as internal standard. ^bIsolated yield.

DCE=1,2-dichloroethane. TfOH=trifluoromethanesulfonic acid.

n.t. meant no target product.

SP was para-iodinated product of **1**

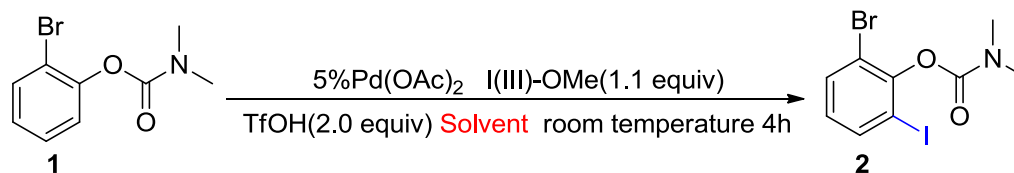
II Effects of reaction temperature



entry	catalyst	iodine reagents	conditions	yield(%) ^a
1	Pd(OAc) ₂	I(III)-OH	TfOH, DCE, 40°C	60
2	Pd(OAc) ₂	I(III)-OH	TfOH, DCE, 60°C	37
3	Pd(OAc) ₂	I(III)-OH	TfOH, DCE, 80°C	<10%
4	Pd(OAc) ₂	I(III)-OMe	TfOH, DCE, 40°C	68
5	Pd(OAc) ₂	I(III)-OMe	TfOH, DCE, 60°C	45
6	Pd(OAc) ₂	I(III)-OMe	TfOH, DCE, 80°C	30

^aConversion ratio determined by ¹H NMR using 4-Nitrobenzaldehyde as internal standard.

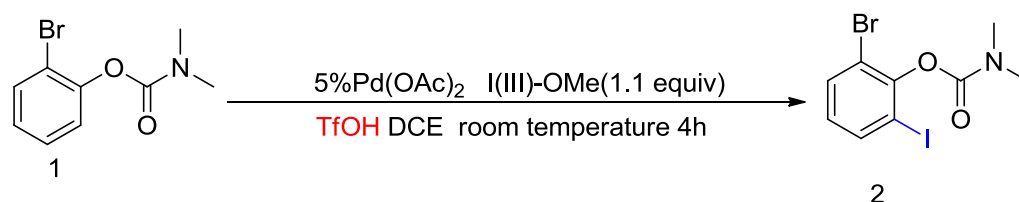
III Effects of solvents



entry	catalyst	iodine reagents	conditions	yield(%) ^a
1	Pd(OAc) ₂	I(III)-OMe	TfOH, Toluene, rt	NR
2	Pd(OAc) ₂	I(III)-OMe	TfOH, MeOH, rt	NR
3	Pd(OAc) ₂	I(III)-OMe	TfOH, EtOH, rt	NR
4	Pd(OAc) ₂	I(III)-OMe	TfOH, DMSO, rt	NR
5	Pd(OAc) ₂	I(III)-OMe	TfOH, TFEA, rt	30
6	Pd(OAc) ₂	I(III)-OMe	TfOH, TFEA:DCE=0.2:0.8, rt	50
7	Pd(OAc) ₂	I(III)-OMe	TfOH, TFEA:DCE=0.4:0.6, rt	60

^aConversion ratio determined by ¹H NMR using 4-Nitroaldehyde as internal standard.

IV Effects of TfOH

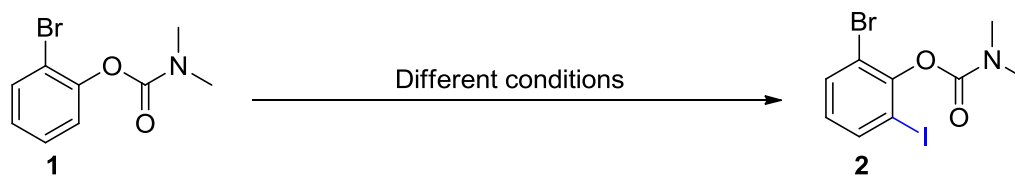


entry	catalyst	iodine reagents	conditions	yield(%) ^a
1	Pd(OAc) ₂	I(III)-OMe	no TfOH, DCE, rt	NR
2	Pd(OAc) ₂	I(III)-OMe	0.5 eq TfOH, DCE, rt	NR
3	Pd(OAc) ₂	I(III)-OMe	1.0 eq TfOH, DCE, rt	66
4	Pd(OAc) ₂	I(III)-OMe	1.5 eq TfOH, DCE, rt	68
5	Pd(OAc) ₂	I(III)-OMe	2.0 eq TfOH, DCE, rt	70 ^b
6	Pd(OAc) ₂	I(III)-OMe	3.0 eq TfOH, DCE, rt	62

^aConversion ratio determined by ¹H NMR using 4-Nitrobenzaldehyde as internal standard.

^bIsolated yield

V Effects of other factors



entry	catalyst	iodine reagents	conditions	yield(%) ^a
1	Pd(OAc) ₂	I ₂ + PhI(OAc) ₂	K ₂ CO ₃ , DMF, 100°C	NR ^c
2	Pd(OAc) ₂	I ₂	CsOAc, NaHCO ₃ , 65°C	NR ^d
3	[Rh(Cp*Cl ₂) ₂]	NIS	AgSbF ₆ , PivOH, 120°C	8
4	Pd(OAc) ₂	NIS	AcOH, 100°C	NR ^e
5	[Rh(Cp*Cl ₂) ₂]	I(III)-OMe	TfOH, DCE, rt	NR
6	PdCl ₂	I(III)-OMe	TfOH, DCE, rt	NR
7	no Pd(OAc) ₂	I(III)-OMe	TfOH, DCE, rt	NR
8	[Ru(p-cymene) ₂ Cl ₂] ₂	I(III)-OMe	TfOH, DCE, rt	trace

^aConversion ratio determined by ¹H NMR using 4-Nitrobenzaldehyde as internal standard.

^cDMF as the solvent, 36h. ^dt-AmOH/DMF, 20h. ^eAcOH as the solvent, 12h.

General procedure

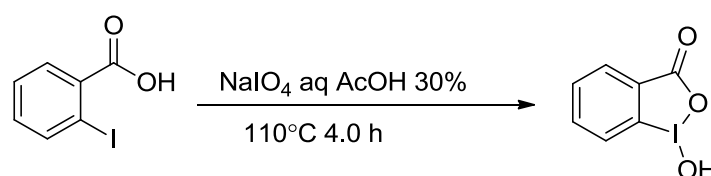
I Synthesis of carbamates^[1]

A mixture of the phenol (1.0 equiv) and Me₂NCOCl (1.5 equiv) and K₂CO₃ (1.5 equiv) in MeCN was refluxed for 6 h. The reaction mixture was cooled to room temperature and concentrated under a vacuum. The residue was dissolved in H₂O and extracted with dichloroethane. The organic fractions were combined and then washed successively with 1 N NaOH and water. Finally the organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated under a vacuum to yield the corresponding carbamates.

II Synthesis of iodinated carbamates

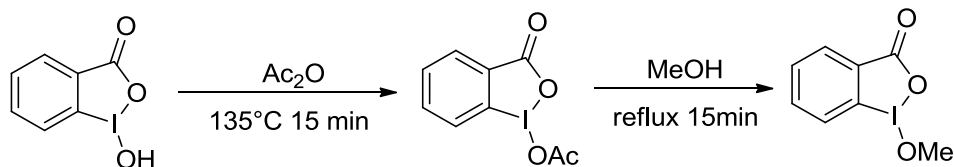
Substituted carbamates (1.0 equiv), I-OMe or I-OTs (1.1-2.0 equiv), Pd(OAc)₂ (0.05 equiv) were dissolved in commercial dichloroethane in a 15 mL sealed tube. Following that, TfOH (0.5~3.0 equiv) was added into the reaction solution. Then the reaction mixture was stirred at room temperature for 1.5-18.5 h. The reaction was monitored by TLC. After completion of the reaction, saturated NaHCO₃ was added to quench the reaction. The reaction mixture was diluted with dichloromethane and washed once with saturated aqueous NaHCO₃. Then organic layer was dried over anhydrous Na₂SO₄ and concentrated on rotavapor under reduced pressure. Finally the residue was purified by silical gel column chromatography to give corresponding iodinated products.

III Synthesis of 1-Methoxy-1,2-benziodoxol-3-(1H)-one^[2,3]



Step 1: Following the literature's method, in a 100mL round-bottom flask, 2-iodobenzoic acid (5 g, 20 mmol) and NaIO₄ (4.53 g, 21 mmol, as oxidant) were

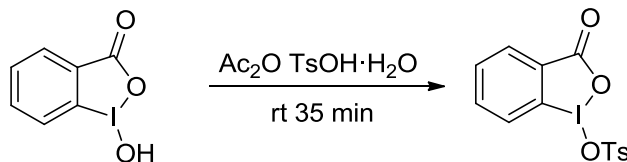
added into 30% HOAc/H₂O solution (30 mL). Then the reaction was heated up to 110 °C and stirred for 4 h under reflux. After that, the flask was cooled down to room temperature and ice water (ca. 50 mL) was purged into the bottle. The mixture was kept stirring until the crystal precipitated (about 10min). The crystals were filtered, washed with ice water, and dried in vacuo.



Step 2: In a 100 mL round-bottom flask, 1-hydroxy-1,2-benziodoxol-3-(1H)-one was subjected into Ac₂O (14 mL) and the system was quickly heated up to 135° C until the solid is completely dissolved. Then, the flask was cooled down to room temperature and put into a refrigerator under -20° C until the crystals precipitated from the solution. Subsequently, the solid was filtered and washed with water for 3 times. Finally, the product was dried in vacuo to afford a white solid. After heating the above-obtained solid in MeOH (35 mL) to reflux for 15 min until a clear, colorless solution was obtained and cooling to ambient temperature followed by crystallization at -20° C, filtration, washing with a minimal amount of MeOH, and drying under vacuum, the desired product was obtained as white crystals.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.26 (s, 3H), 7.64 – 7.76 (m, 2H), 7.88 (t, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 1H)

IV Synthesis of 1-(p-Toluenesulfonyloxy)-1,2-benziodoxol-3(1H)-one^[4]

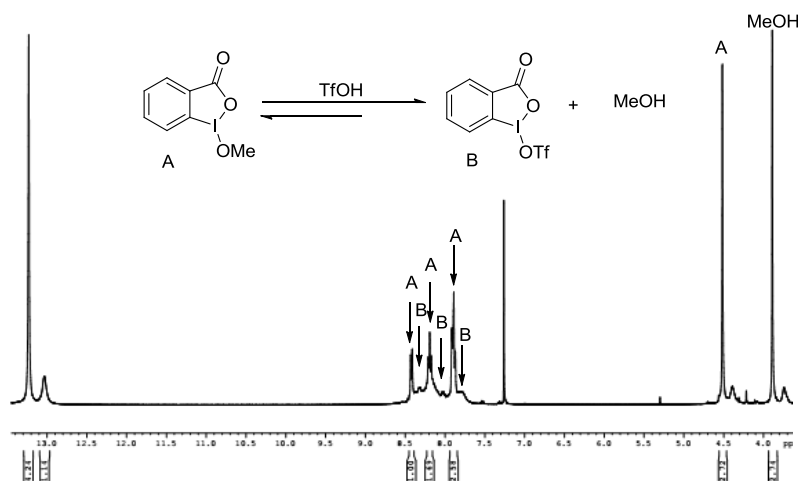


To a stirred mixture of 2-iodosylbenzoic acid (3.17 g, 12 mmol) in acetic anhydride (6 mL), TsOH·H₂O (4.56 g, 24 mmol) was added at room temperature. After 5 min stirring a slightly exothermic reaction began, and the mixture turned into a clear solution. The solution was additionally stirred for 30 min until a white microcrystalline precipitate formed. Then the reaction mixture was diluted with dry ether (20 mL), the precipitate was filtered, washed with anhydrous ether (3x20 mL), and dried in vacuo to afford analytically pure product yield 3.90 g (79%).

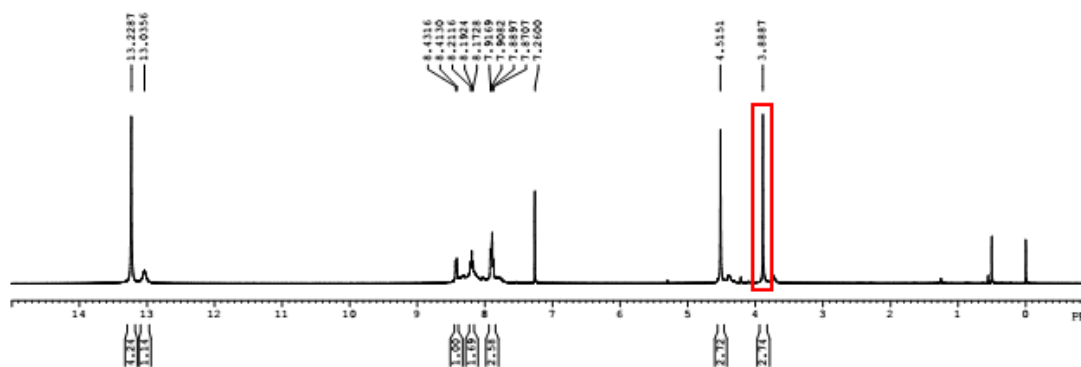
¹H NMR (CDCl₃/CF₃COOH, 20:1): δ (ppm) 8.30 (d, 1H, *J* = 8 Hz), 8.09 (t, 1H, *J* = 8 Hz), 7.94 (d, 1H, *J* = 8 Hz), 7.80 (t, 1H, *J* = 8 Hz), 7.71 (d, 2H, *J* = 8 Hz), 7.29 (d, 2H, *J* = 8 Hz), 2.40 (s, 3H).

V Mechanism studies

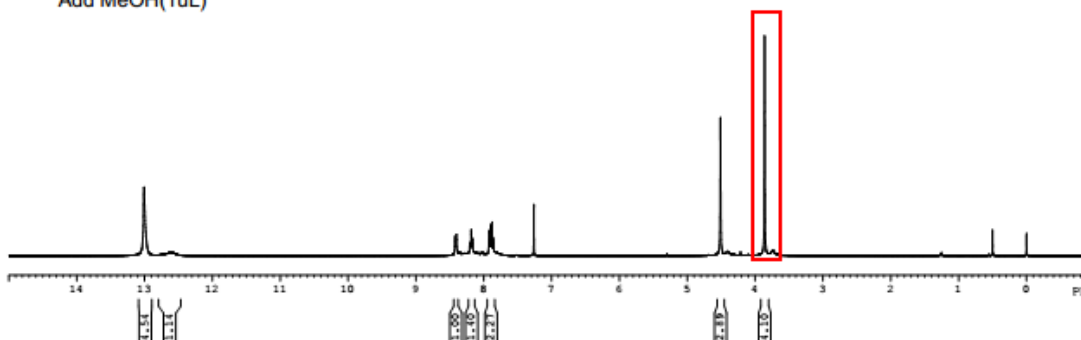
In NMR tube, I(III)-OMe (0.055 mmol, 15 mg) was dissolved in CDCl₃ (0.4 mL), then TfOH (0.1 mmol, 9 μL) was added. After 1.0 h, the reaction mixture directly monitored by ¹H NMR.



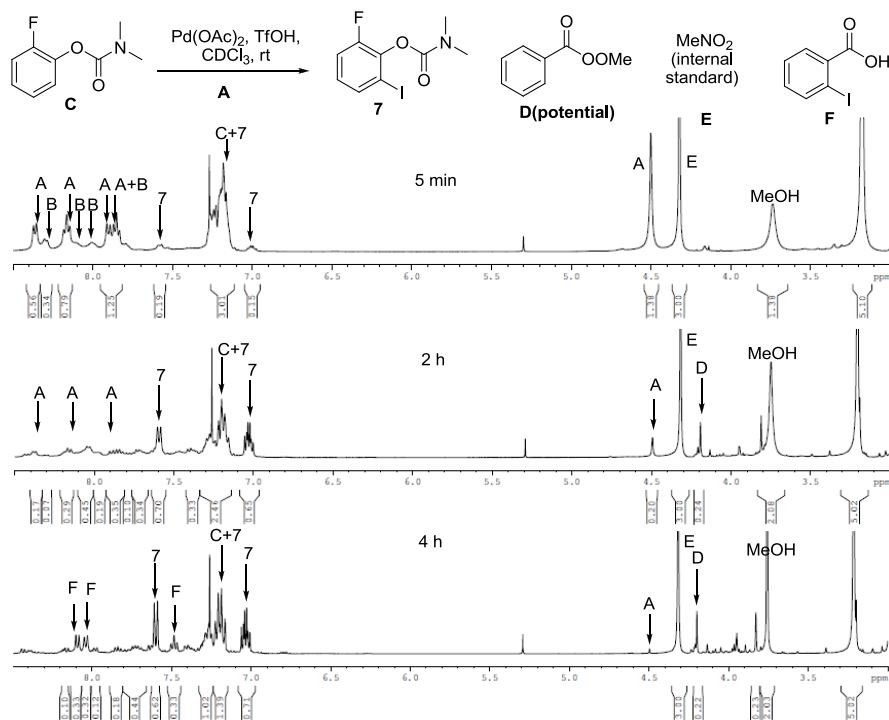
Then 1 uL of MeOH was added to confirm the peak of methanol.



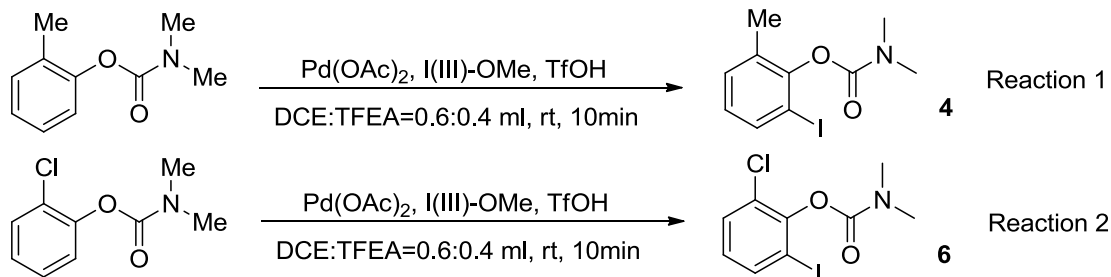
Add MeOH(1uL)



In NMR tube, 2-fluorophenyl dimethylcarbamate (0.05 mmol, 9 mg), I-OMe (1.1 equiv, 15 mg) and Pd(OAc)₂ (0.05 equiv, 0.6 mg) were dissolved in CDCl₃. Following that, TfOH (2.0 equiv, 9 uL) was added into the reaction solution. The reaction mixtures was monitored by ¹H NMR at different time points.



VI Intermolecular Competition Experiments



To two separated sealed tubes, following the general procedure **I**, o-tolyl dimethylcarbamate (36 mg, 0.20 mmol) or 2-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol), I-OMe (61 mg, 0.22 mmol), TfOH (1.0 equiv, 18 μL) and DCE:TFEA = 0.6:0.4 ml was added. The mixture was stirred at room temperature. After 10 min, two reactions were quenched and added 4-nitrobenzaldehyde as internal standard. Then, the mixture was washed once with saturated aqueous NaHCO_3 and extracted with dichloromethane and concentrated on rotavapor under reduced pressure. The conversion ratio was determined by crude ¹H-NMR. The ratio of (**4**) to (**6**) was 10.3.

VII Procedure for preliminary mechanistic study

1. Preparation of 2-deuterio phenyl dimethylcarbamate^[5, 6,7].

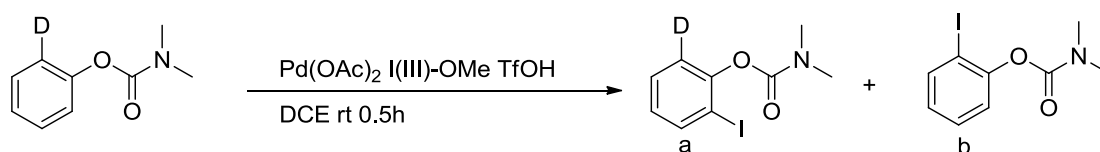
In an oven-dried 100-mL round-bottomed flask, a solution of 2-bromophenol (1g, 5.78 mmol) and Et_2O (15 mL) were cooled to 0 °C. After 5 min, t-BuLi (1.6 M, 8 mL, 12.7 mmol) was added dropwise over 10 min. The mixture was stirred for 3.5 h at 0 °C. Then, D_2O (500 mg, 24.9 mmol) was added via syringe. The mixture was then warmed to room temperature slowly overnight. The cloudy, white mixture was diluted

with H₂O (20 mL). The layers were separated. The organic layer was washed with H₂O (20 mL x 3), dried (Na₂SO₄), filtered and concentrated.

Following the general procedure I, the above compounds without further purification (5.78 mmol, 1.0 equiv), K₂CO₃ (1.2 g, 8.68 mmol), dimethylcarbamoyl chloride (6.4 mL, 6.94 mmol) and MeCN (15 mL) was added. The reaction mixture was refluxed for 4h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 10:1). Finally, desired product (670 mg) was isolated in 70% yield.

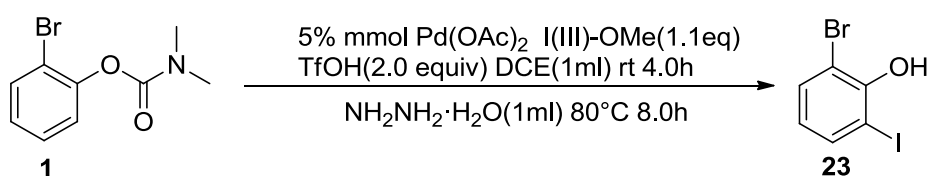
¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.37-7.34 (m, 2H), 7.19 (t, *J* = 7.40 Hz, 1H), 7.11 (d, *J* = 8.40 Hz, 1H), 3.10 (s, 3H), 3.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 155.0, 151.6, 129.3, 129.2, 125.2, 121.8, 121.6 (*J*_{C-D} = 24.5 Hz), 36.8, 36.5; LRMS (ESI) calcd for C₉H₁₁DNO₂ [M+H]⁺: 167.09, found 167.12

2. Intramolecular experiments



Following the general procedure I, to a 15 mL sealed tube, 2-deuterio phenyl dimethylcarbamate (33 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (0.5 equiv, 9 uL) in DCE (1 ml) was stirred at room temperature for 0.5 h. Then the mixture was quenched, washed once with saturated aqueous NaHCO₃, extracted by dichloromethane and concentrated on rotavapor under reduced pressure. The conversion ratio was determined by crude ¹H-NMR. ¹H-NMR showed *k*_H/*k*_D = 1.0.

VIII Deprotection of products in one pot.

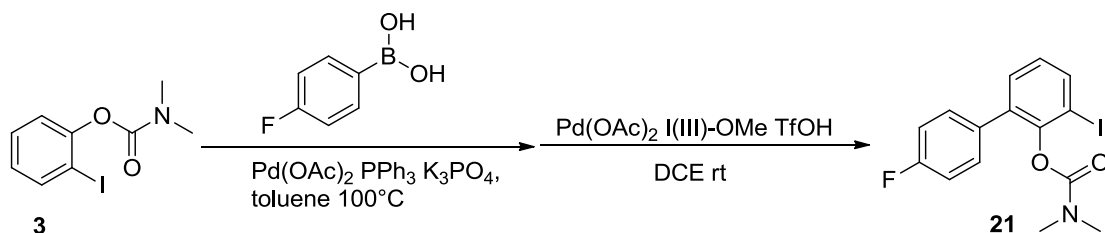


After the completion of the first step, without purification, hydrazine hydride (1.0 mL) was added to the mixture as solvent and stirred at 80°C until the reaction finished. When the deprotection was finished, the mixture was acidified by conc. HCl, washed by water and extracted by dichloromethane. Then organic layer was dried over anhydrous Na₂SO₄ and concentrated on rotavapor under reduced pressure. Finally the residue was purified by silical gel column chromatography to give corresponding deprotected products. The yield was 50%.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.65 (d, *J* = 7.88 Hz, 1H), 7.46 (d, *J* = 7.96 Hz, 1H), 6.56 (t, *J* = 7.92 Hz, 1H), 5.90 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 151.6, 138.7, 132.9, 123.5, 108.8, 83.4; LRMS (ESI) calcd for C₆H₄BrIO [M-H]⁻: 297.90, found 296.92

IX Applications

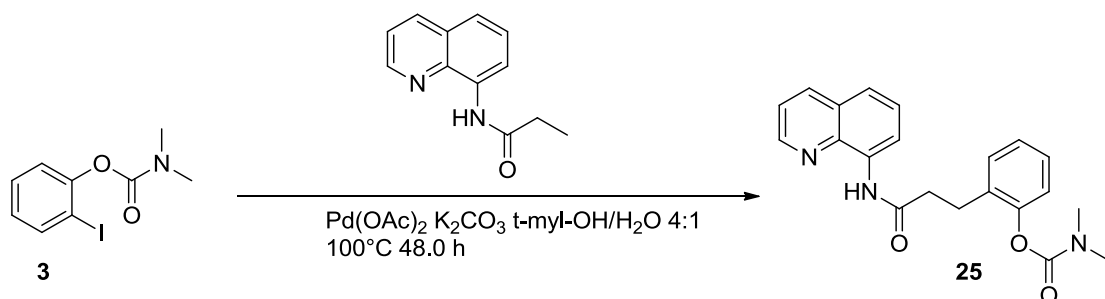
1. Sequential Suzuki coupling and C-H iodination reactions



In an oven-dried 25-mL round-bottom flask, a mixture of compound **3** (150 mg, 0.5 mmol), (4-fluorophenyl)boronic acid (139 mg, 1.0 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol), PPh₃ (6 mg, 0.02 mmol), K₃PO₄ (213 mg, 1.0 mmol) was dissolved in toluene (1 ml) under argon. The mixture was stirred overnight at 100 °C. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 10:1). The Suzuki coupling product was isolated in 67% yield as white solid.

Then Following the general procedure **II**, a mixture of 4'-fluoro-[1,1'-biphenyl]-2-yl dimethylcarbamate (26 mg, 0.10 mmol), I-OMe (31 mg, 0.22 mmol), Pd(OAc)₂ (1.2 mg, 0.01 mmol) and TfOH (1.5 equiv, 14 uL) in DCE (1 ml) was stirred at room temperature for 2.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **21** (25 mg) was isolated in 65% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.80 (d, *J* = 8.00 Hz, 1H), 7.38 (dd, *J* = 7.20, 6.00 Hz, 2H), 7.30 (d, *J* = 7.60 Hz, 1H), 7.08 (t, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 8.00 Hz, 1H), 3.00 (s, 3H), 2.88 (s, 3H); ¹⁹F-NMR (400 MHz, CDCl₃) -114.66 (s, 3F); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 162.5 (d, *J*_{C-F} = 239 Hz, 1C), 153.1, 149.0, 138.7, 136.2, 133.7 (d, *J*_{C-F} = 3 Hz, 1C), 131.0, 130.7 (d, *J*_{C-F} = 8 Hz, 2C), 127.6, 115.2 (d, *J*_{C-F} = 22 Hz, 2C), 93.2, 37.0, 36.7; LRMS (ESI) calcd for C₁₅H₁₃FINO₂ [M+H]⁺: 386.18, found 385.90

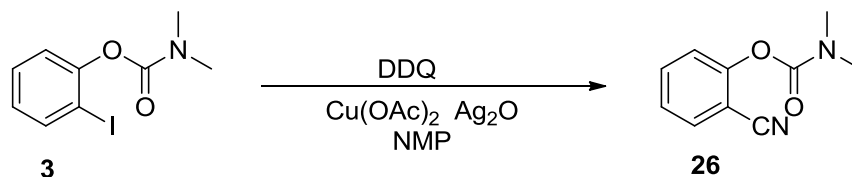
2. sp³ C-H arylation reaction^[8]



In an oven-dried 25-mL round-bottom flask, a mixture of compound **3** (87 mg, 0.3 mmol), N-(quinolin-8-yl)propionamide (20 mg, 0.1 mmol), K₂CO₃ (7 mg, 0.25 mmol) were dissolved in 2-Methyl-2-butanol:H₂O=0.8:0.2 ml. The mixture was stirred for 48 h at 100 °C. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 4:1). Finally, compound **25** (22 mg) was isolated in 60% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.80-8.75 (m, 2H), 8.13 (d, *J* = 8.20 Hz, 1H), 7.55-7.48 (m, 2H), 7.44-7.41 (m, 1H), 7.32 (d, *J* = 7.36 Hz, 1H), 7.25-7.21 (m, 1H), 7.16-7.10 (m, 2H), 3.16 (s, 3H), 3.10 (t, *J* = 8.32 Hz, 2H), 3.02 (s, 3H), 2.84 (t, *J* = 7.44 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.8, 154.9, 149.8, 148.2, 138.3, 136.4, 134.5, 132.9, 130.0, 128.0,

127.5, 127.4, 125.8, 122.9, 121.7, 121.5, 116.6, 38.5, 36.9, 36.6, 26.2; LRMS (ESI) calcd for C₂₁H₂₁N₃O₃ [M+H]⁺: 364.42, found 363.38

3. Cyanation reaction^[9]

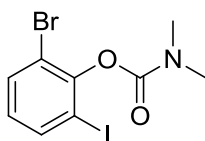


Under air, a reaction tube was charged with compound **3** (58 mg, 0.2 mmol), DDQ (45.2mg, 0.2 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mol), Ag₂O (46.3 mg, 0.3 mmol) and NMP (2mL). The mixture was stirred at 120 °C for 22 h. After the completion of the reaction, the reaction mixture was diluted with dichloromethane and washed once with saturated aqueous NaHCO₃. Then organic layer was dried over anhydrous Na₂SO₄ and concentrated on rotavapor under reduced pressure. Finally the residue was purified by silical gel column chromatography to give compound **26** (32 mg) in 85% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.65-7.58 (m, 2H), 7.40 (d, *J* = 8.32 Hz, 1H), 6.89 (d, *J* = 7.76 Hz, 1H), 3.18 (s, 3H), 3.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.4, 153.3, 134.0, 133.1, 125.6, 123.5, 115.7, 106.9, 37.1, 36.8; LRMS (ESI) calcd for C₁₀H₁₀N₂O₂ [M+H]⁺: 191.21, found 191.66

References

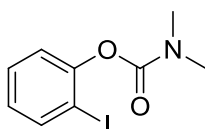
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Date of products



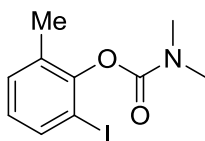
6-bromo-2-iodophenyl dimethylcarbamate (2)

Following the general procedure **II**, a mixture of 2-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (2.0 equiv, 36 uL) in DCE (1 ml) was stirred at room temperature for 4 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **2** (52 mg) was isolated in 70% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.74 (d, *J* = 7.92 Hz, 1H), 7.56 (d, *J* = 8.00 Hz, 1H), 6.81 (t, *J* = 7.92 Hz, 1H), 3.20 (s, 3H), 3.06 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 152.4, 149.4, 138.4, 133.5, 128.4, 117.4, 92.8, 37.2, 36.9; LRMS (ESI) calcd for C₉H₉BrINO₂ [M+H]⁺: 370.99, found 371.71.



2-iodophenyl dimethylcarbamate (3)

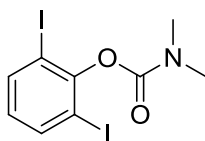
Following the general procedure **II**, a mixture of phenyl dimethylcarbamate (33 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (0.5 equiv, 9 uL) in TFEA:DCE=0.2:0.8 ml was stirred at room temperature for 9.5 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **3** (37 mg) was isolated in 64% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.80 (d, *J* = 7.88 Hz, 1H), 7.34 (t, *J* = 7.56 Hz, 1H), 7.19 (d, *J* = 8.00 Hz, 1H), 6.94 (t, *J* = 7.48 Hz, 1H), 3.19 (s, 3H), 3.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.8, 151.8, 139.2, 129.4, 127.1, 123.5, 90.9, 37.0, 36.9; LRMS (ESI) calcd for C₉H₁₀INO₂ [M+H]⁺: 292.09, found 292.20.



2-iodo-6-methylphenyl dimethylcarbamate (4)

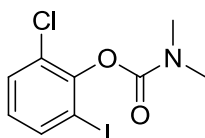
Following the general procedure **II**, a mixture of o-tolyl dimethylcarbamate (36 mg, 0.20 mmol), I-OMe (61.0 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (0.5 equiv, 9 uL) in TFEA (1 ml) was stirred at room temperature for 4.5 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **4** (39 mg) was isolated in 64% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.62 (d, *J* = 7.92 Hz, 1H), 7.17 (d, *J* = 7.56 Hz, 1H), 6.85 (t, *J* = 7.72 Hz, 1H), 3.20 (s, 3H), 3.05 (s, 3H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.2, 150.3, 136.8,

132.9, 131.2, 127.3, 92.1, 37.0, 36.8, 17.4; LRMS (ESI) calcd for C₁₀H₁₂I₂NO₂ [M+H]⁺: 306.12, found 306.29.



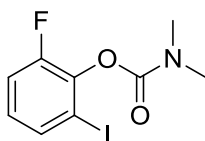
2,6-diiodophenyl dimethylcarbamate (5)

Following the general procedure **II**, a mixture of 2-iodophenyl dimethylcarbamate (29 mg, 0.10 mmol), I-OMe (31 mg, 0.11 mmol), Pd(OAc)₂ (1.2 mg, 0.005 mmol) and TfOH (2.0 equiv, 18 uL) in DCE (1 ml) was stirred at room temperature for 2 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **5** (25 mg) was isolated in 60% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.78 (d, *J* = 7.88 Hz, 2H), 6.65 (t, *J* = 7.88 Hz, 1H), 3.21 (s, 3H), 3.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 152.3, 151.9, 139.5, 128.9, 91.5, 37.2, 37.0; LRMS (ESI) calcd for C₉H₉I₂NO₂ [M+H]⁺: 417.99, found 417.68.



2-chloro-6-iodophenyl dimethylcarbamate (6)

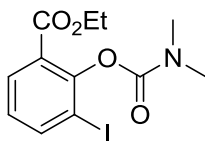
Following the general procedure **II**, a mixture of 2-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (2.0 equiv, 36 uL) in DCE (1 ml) was stirred at room temperature for 4 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **6** (39 mg) was isolated in 60% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.70 (d, *J* = 7.92 Hz, 1H), 7.40 (d, *J* = 7.92 Hz, 1H), 6.89 (t, *J* = 8.00 Hz, 1H), 3.20 (s, 3H), 3.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 152.5, 148.4, 137.6, 130.4, 128.4, 128.0, 93.0, 37.2, 36.9; LRMS (ESI) calcd for C₉H₉ClINO₂ [M+H]⁺: 326.54, found 325.81.



6-fluoro-2-iodophenyl dimethylcarbamate (7)

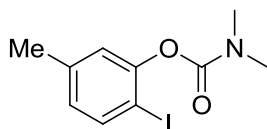
Following the general procedure **II**, a mixture of 2-fluorophenyl dimethylcarbamate (58 mg, 0.20 mmol), I-OMe (111 mg, 0.40 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (3.0 equiv, 54 uL) in DCE (1 ml) was stirred at room temperature for 12.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **7** (62 mg) was isolated in 62% yield as a colorless solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.56 (d, *J* = 8.04 Hz, 1H), 7.15-7.11 (m, 1H), 6.93 (td, *J*₁ = 8.20 Hz, *J*₂ = 5.20 Hz, 1H), 3.19 (s, 3H), 3.05 (s, 3H); ¹⁹F-NMR (400 MHz, CDCl₃) -123.80 (s, 1F); ¹³C NMR

(100 MHz, CDCl₃) δ (ppm) 154.9 (d, J_{C-F} = 252 Hz, 1C), 152.7, 140.4 (d, J_{C-F} = 14 Hz, 1C), 134.1 (d, J_{C-F} = 3 Hz, 1C), 128.0 (d, J_{C-F} = 7 Hz, 1C), 116.9 (d, J_{C-F} = 19 Hz, 1C), 92.7, 37.2, 36.9; LRMS (ESI) calcd for C₉H₉FINO₂ [M+H]⁺: 310.08, found 309.97.



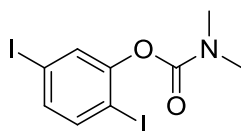
Ethyl 2-((dimethylcarbamoyl)oxy)-3-iodobenzoate (**8**)

Following the general procedure **II**, a mixture of ethyl 2-((dimethylcarbamoyl)oxy)benzoate (52 mg, 0.20 mmol), I-OTs (92.0 mg, 0.22 mmol), Pd(OAc)₂ (13.8 mg, 0.06 mmol) and TfOH (0.5 equiv, 9 μ L) in DCE (1 ml) was stirred at 60 °C for 3.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **8** (32 mg) was isolated in 45% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.98-7.95 (m, 2H), 7.01 (t, J = 7.84 Hz, 1H), 4.31 (q, J = 7.16 Hz, 2H), 3.20 (s, 3H), 3.05 (s, 3H), 1.34 (t, J = 7.12 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 164.2, 153.3, 151.1, 143.2, 131.9, 127.0, 125.8, 94.1, 61.4, 37.0, 36.9, 14.2; LRMS (ESI) calcd for C₁₂H₁₄INO₄ [M+H]⁺: 364.16, found 364.25.



2-iodo-5-methylphenyl dimethylcarbamate (**9**)

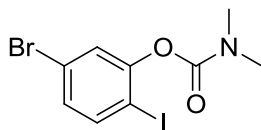
Following the general procedure **II**, a mixture of m-tolyl dimethylcarbamate (36 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) in TFEA:DCE=0.4:0.6 ml was stirred at room temperature for 5.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **9** (40 mg) was isolated in 66% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.64 (d, J = 8.04 Hz, 1H), 7.01 (s, 1H), 6.76 (d, J = 7.96 Hz, 1H), 3.17 (s, 3H), 3.03 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 154.0, 151.6, 139.9, 138.7, 128.2, 124.2, 86.6, 37.0, 36.8, 21.1; LRMS (ESI) calcd for C₁₀H₁₂INO₂ [M+H]⁺: 306.12, found 306.19.



2,5-diiodophenyl dimethylcarbamate (**10**)

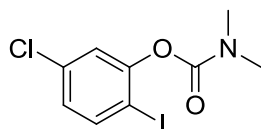
Following the general procedure **II**, a mixture of 3-iodophenyl dimethylcarbamate (58 mg, 0.20 mmol), I-OTs (92 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (1.0 equiv, 18 μ L) in TFEA (1 ml) was stirred at room temperature for 3.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **10** (61 mg) was isolated in 73% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm)

7.53(d, $J = 1.92$ Hz, 1H), 7.49 (d, $J = 8.32$ Hz, 1H), 7.25 (dd, $J_1 = 8.32$ Hz, $J_2 = 1.96$ Hz, 1H), 3.16 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 153.4, 152.3, 140.3, 136.2, 132.6, 93.2, 90.6, 37.0, 36.9; LRMS (ESI) calcd for $\text{C}_9\text{H}_{10}\text{BrClINO}_2$ $[\text{M}+\text{H}]^+$: 417.98, found 418.17.



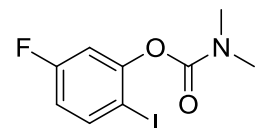
5-bromo-2-iodophenyl dimethylcarbamate (11)

Following the general procedure **II**, a mixture of 3-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), I-OMe (84 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol) and TfOH (2.5 equiv, 45 μL) in DCE (1 ml) was stirred at room temperature for 6.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **11** (55 mg) was isolated in 74% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.63 (d, $J = 8.44$ Hz, 1H), 7.37 (d, $J = 2.04$ Hz, 1H), 7.08 (dd, $J_1 = 8.44$ Hz, $J_2 = 2.00$ Hz, 1H), 3.17 (s, 3H), 3.04 (s, 3H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm) 153.3, 152.4, 139.9, 130.3, 126.9, 122.5, 89.2, 37.1, 36.9; LRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{BrINO}_2$ $[\text{M}+\text{H}]^+$: 370.99, found 371.86.



5-chloro-2-iodophenyl dimethylcarbamate (12)

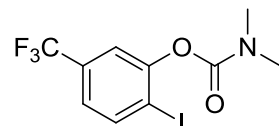
Following the general procedure **II**, a mixture of 3-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol) and TfOH (2.0 equiv, 36 μL) in DCE (1 ml) was stirred at room temperature for 2.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **12** (48 mg) was isolated in 74% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.70(d, $J = 8.48$ Hz, 1H), 7.23 (d, $J = 2.20$ Hz, 1H), 6.94 (dd, $J_1 = 8.48$ Hz, $J_2 = 2.16$ Hz, 1H), 3.17 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 153.3, 152.4, 139.6, 135.0, 127.4, 124.0, 88.3, 37.0, 36.9; LRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{ClINO}_2$ $[\text{M}+\text{H}]^+$: 326.54, found 325.71.



5-fluoro-2-iodophenyl dimethylcarbamate (13)

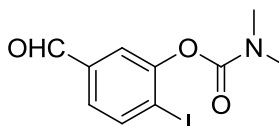
Following the general procedure **II**, a mixture of 3-fluorophenyl dimethylcarbamate (58 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol) and TfOH (1.0 equiv, 18 μL) in TFEA:DCE=0.4:0.6 (1 ml) was stirred at room temperature for 11.5 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally,

compound **13** (38 mg) was isolated in 62% yield as a colorless solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.72 (dd, $J = 8.76, 6.20$ Hz, 1H), 7.01 (dd, $J_1 = 9.36$ Hz, $J_2 = 2.80$ Hz, 1H), 6.73 (dd, $J_1 = 8.56$ Hz, $J_2 = 2.80$ Hz, 1H), 3.18 (s, 3H), 3.04 (s, 3H); ^{19}F -NMR (400 MHz, CDCl_3) -111.60 (s, 1F); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 163.2 (d, $J_{\text{C-F}} = 247$ Hz, 1C), 153.3, 152.6 (d, $J_{\text{C-F}} = 11$ Hz, 1C), 139.3 (d, $J_{\text{C-F}} = 9$ Hz, 1C), 114.6 (d, $J_{\text{C-F}} = 22$ Hz, 1C), 111.7 (d, $J_{\text{C-F}} = 25$ Hz, 1C), 83.9 (d, $J_{\text{C-F}} = 4$ Hz, 1C), 37.0, 36.9; LRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{FINO}_2$ $[\text{M}+\text{H}]^+$: 310.08, found 309.45.



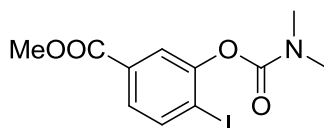
2-iodo-5-(trifluoromethyl)phenyl dimethylcarbamate (**14**)

Following the general procedure **II**, a mixture of 3-(trifluoromethyl)phenyl dimethylcarbamate (47 mg, 0.20 mmol), I-OMe (84 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (9.2 mg, 0.04 mmol) and TfOH (3.0 equiv, 54 μL) in DCE (1 ml) was stirred at rt for 4.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **14** (42 mg) was isolated in 58% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.93 (d, $J = 8.24$ Hz, 1H), 7.46 (d, $J = 1.24$ Hz, 1H), 7.19 (dd, $J_1 = 8.20$ Hz, $J_2 = 1.24$ Hz, 1H), 3.19 (s, 3H), 3.05 (s, 3H); ^{19}F -NMR (400 MHz, CDCl_3) -62.85 (s, 3F); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 153.2, 152.2, 139.9, 132.1 (q, $J_{\text{C-F}} = 33$ Hz, 1C), 123.6 (q, $J_{\text{C-F}} = 4$ Hz, 1C), 123.5 (q, $J_{\text{C-F}} = 271$ Hz, 1C), 120.5 (q, $J_{\text{C-F}} = 4$ Hz, 1C), 95.5, 37.1, 36.9; LRMS (ESI) calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{INO}_2$ $[\text{M}+\text{H}]^+$: 360.09, found 359.52.



5-formyl-2-iodophenyl dimethylcarbamate (**15**)

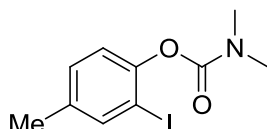
Following the general procedure **II**, a mixture of 3-formylphenyl dimethylcarbamate (39 mg, 0.20 mmol), I-OTs (92 mg, 0.22 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol) and TfOH (3.0 equiv, 54 μL) in TFEA (1 ml) was stirred at room temperature for 12.5h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **15** (19 mg) was isolated in 30% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.94 (s, 1H), 8.00 (d, $J = 8.08$ Hz, 1H), 7.67 (d, $J = 1.72$ Hz, 1H), 7.44 (dd, $J_1 = 8.08$ Hz, $J_2 = 1.72$ Hz, 1H), 3.20 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 190.7, 153.4, 152.6, 140.2, 137.8, 127.1, 124.0, 99.6, 37.1, 36.9; LRMS (ESI) calcd for $\text{C}_{10}\text{H}_9\text{INO}_3$ $[\text{M}+\text{H}]^+$: 320.10, found 320.28.



Methyl 3-((dimethylcarbamoyl)oxy)-4-iodobenzoate (**16**)

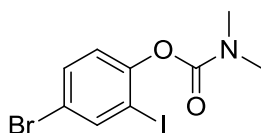
Following the general procedure **II**, a mixture of methyl 3-((dimethylcarbamoyl)-

oxy)benzoate (45 mg, 0.20 mmol), I-OMe (84 mg, 0.30 mmol), Pd(OAc)₂ (4.6 mg, 0.02 mmol) and TfOH (2.5 equiv, 33 uL) in DCE (1 ml) was stirred at room temperature for 6.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **16** (50 mg) was isolated in 71% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.89 (d, *J* = 8.24Hz, 1H), 7.81 (d, *J* = 1.76Hz, 1H), 7.59 (dd, *J*₁ = 8.20 Hz, *J*₂ = 1.76 Hz, 1H), 3.89 (s, 1H), 3.19 (s, 3H), 3.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 166.0, 153.5, 152.0, 139.4, 131.8, 127.8, 124.2, 97.5, 52.5, 37.1, 36.9; LRMS (ESI) calcd for C₁₁H₁₂INO₄ [M+H]⁺: 350.13, found 350.21.



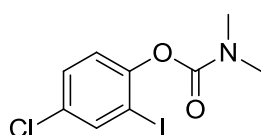
2-iodo-4-methylphenyl dimethylcarbamate (**17**)

Following the general procedure **II**, a mixture of p-tolyl dimethylcarbamate (36 mg, 0.20 mmol), I-OMe (61.0 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (1.0 equiv, 18 uL) in TFEA (1 ml) was stirred at room temperature for 4.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **17** (39 mg) was isolated in 64% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.61 (s, 1H), 7.13 (d, *J* = 8.24 Hz, 1H), 7.05(d, *J* = 8.20 Hz, 1H), 3.17 (s, 3H), 3.03 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 154.1, 149.6, 139.4, 137.1, 130.1, 122.9, 90.6, 37.0, 36.8, 20.5; LRMS (ESI) calcd for C₁₀H₁₂INO₂ [M+H]⁺: 306.12, found 305.98.



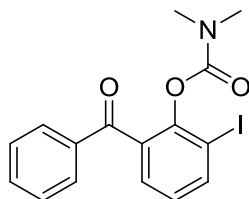
4-bromo-2-iodophenyl dimethylcarbamate (**18**)

Following the general procedure **II**, a mixture of 4-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (1.0 equiv, 18 uL) in TFEA (1 ml) was stirred at room temperature for 8.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **18** (41 mg) was isolated in 55% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.92 (d, *J* = 1.24 Hz, 1H), 7.45 (d, *J* = 8.64 Hz, 1H), 7.06 (d, *J* = 8.60 Hz, 1H), 3.17 (s, 3H), 3.02 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 153.4, 151.1, 141.0, 132.4, 124.5, 119.0, 91.7, 37.0, 36.9; LRMS (ESI) calcd for C₉H₉BrINO₂ [M+H]⁺: 370.99, found 371.71.

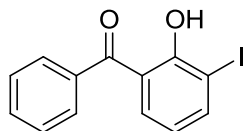


4-chloro-2-iodophenyl dimethylcarbamate (**19**)

Following the general procedure **II**, a mixture of 4-chlorophenyl dimethylcarbamate (40mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (1.5 equiv, 27 uL) in TFEA (1 ml) was stirred at room temperature for 4.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **19** (35 mg) was isolated in 55% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.77 (s, 1H), 7.31 (d, *J* = 8.64 Hz, 1H), 7.11 (d, *J* = 8.68 Hz, 1H), 3.17 (s, 3H), 3.03 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 153.5, 150.6, 138.3, 131.4, 129.4, 124.0, 91.1, 37.0, 36.8; LRMS (ESI) calcd for C₉H₉ClINO₂ [M+H]⁺: 326.54, found 325.47.



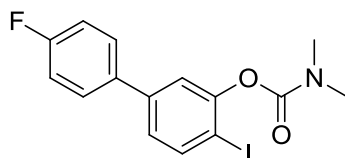
2-benzoyl-6-iodophenyl dimethylcarbamate **20a**



(2-hydroxy-3-iodophenyl)(phenyl)methanone **20b**

Following the general procedure **II**, a mixture of 2-benzoylphenyl dimethylcarbamate (54 mg, 0.20 mmol), I-OMe (84 mg, 0.30 mmol), Pd(OAc)₂ (9.6 mg, 0.04 mmol) and TfOH (3.0 equiv, 54 uL) in DCE (1 ml) was stirred at room temperature for 4.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **20a** (32 mg) was isolated in 41% yield and compound **20b** (15 mg) was isolated in 23% yield. **20a** ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.98 (dd, *J*₁ = 7.88 Hz, *J*₂ = 1.04 Hz, 1H), 7.79 (d, *J* = 7.40 Hz, 2H), 7.57 (t, *J* = 7.36 Hz), 7.47-7.43 (m, 3H), 7.04 (t, *J* = 7.76 Hz), 2.88 (s, 3H), 2.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 194.1, 152.8, 149.6, 142.0, 137.3, 133.7, 133.1, 130.6, 130.1, 128.4, 126.8, 93.2, 36.9, 36.5; LRMS (ESI) calcd for C₁₆H₁₄INO₃ [M+H]⁺: 396.20, found 396.28.

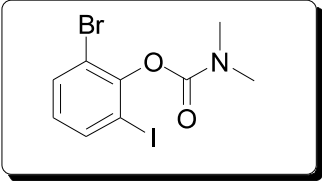
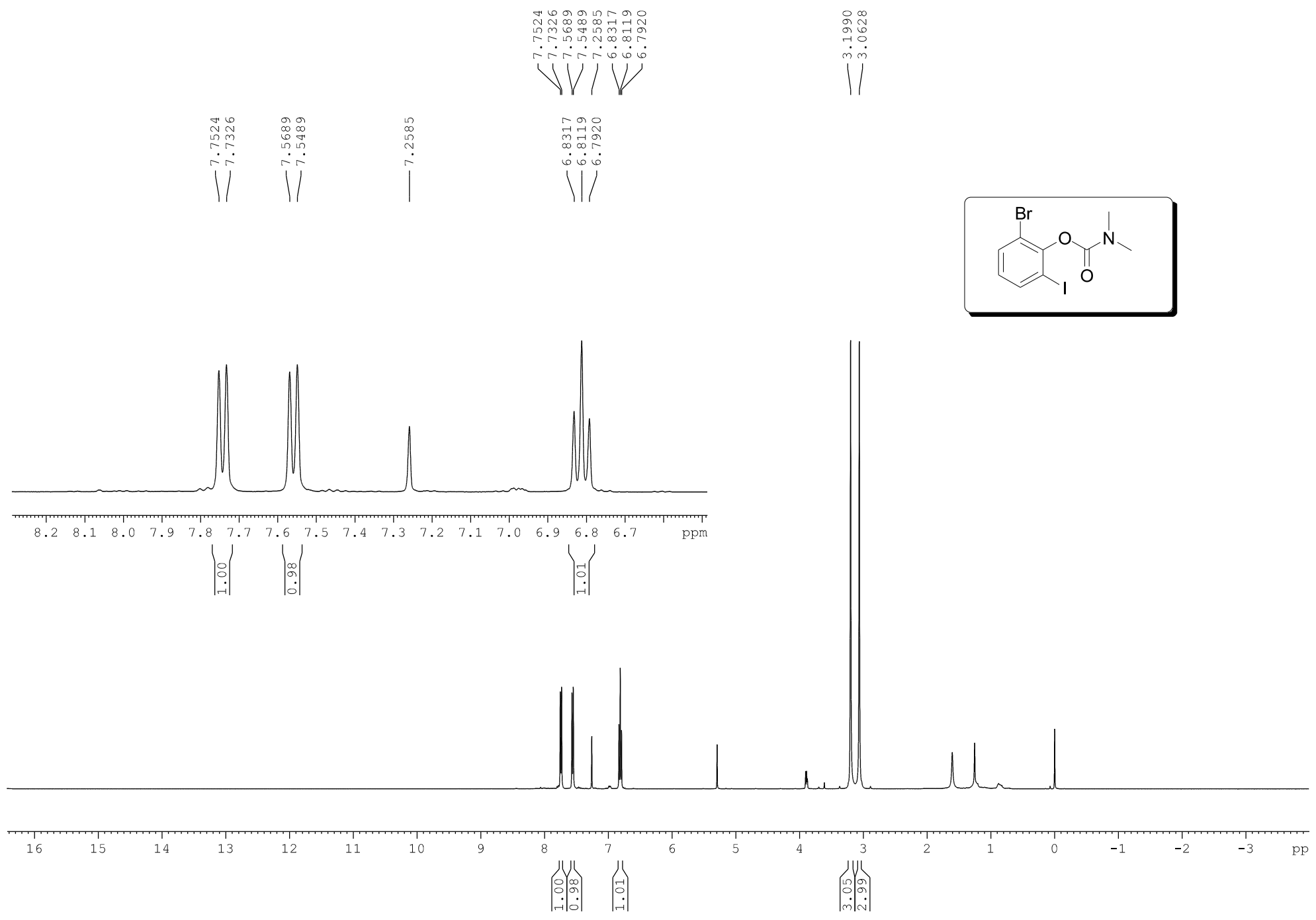
20b ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.00 (d, *J* = 7.68 Hz, 1H), 7.67 (d, *J* = 7.52 Hz, 2H), 7.63-7.60 (m, 2H), 7.52 (t, *J* = 7.36 Hz, 2H), 6.69 (t, *J* = 7.80 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 201.3, 161.9, 145.8, 137.3, 134.0, 132.5, 129.4, 128.6, 120.5, 118.4, 86.6; LRMS (ESI) calcd for C₁₃H₉IO₂ [M-H]⁻: 323.11, found 322.89.

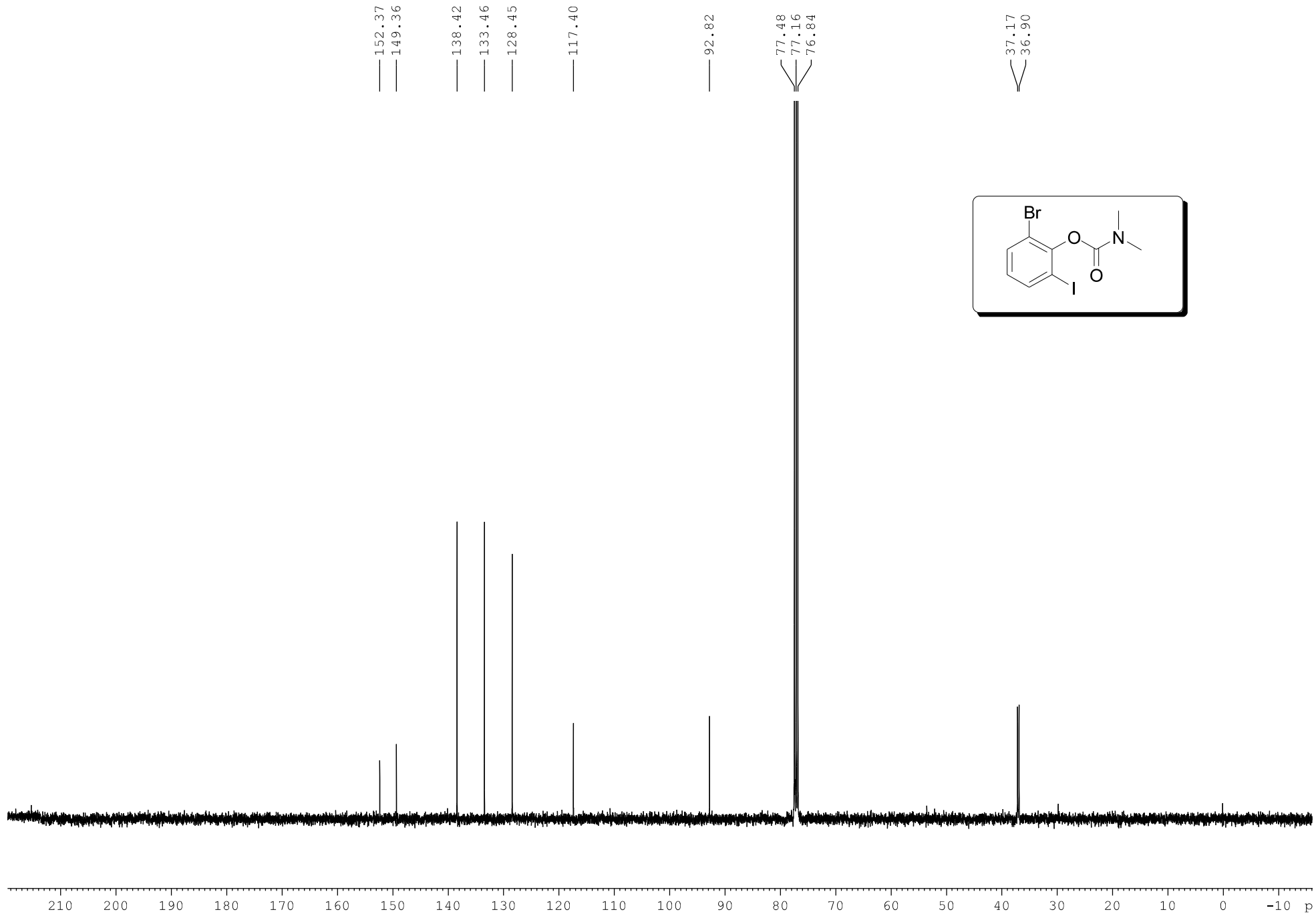


4'-fluoro-4-iodo-[1,1'-biphenyl]-3-yl dimethylcarbamate (**22**)

Following the general procedure **II**, a mixture of 4'-fluoro-[1,1'-biphenyl]-3-yl dimethylcarbamate (52 mg, 0.20 mmol), I-OMe (61 mg, 0.22 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol) and TfOH (1.0 equiv, 18 uL) in TFEA:DCE=0.2:0.8 ml was stirred at

room temperature for 2.0 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 9:1). Finally, compound **22** (46 mg) was isolated in 60% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.83 (d, $J = 8.20$ Hz, 1H), 7.51 (dd, $J_1 = 8.56$ Hz, $J_2 = 5.36$ Hz, 2H), 7.37 (d, $J = 1.96$ Hz, 1H), 7.13-7.08 (m, 3H), 3.21 (s, 3H), 3.06 (s, 3H); ^{19}F -NMR (400 MHz, CDCl_3) -114.6 (s, 1F); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 162.9 (d, $J_{\text{C-F}} = 245$ Hz, 1C), 153.8, 152.2, 142.0, 139.4, 135.6 (d, $J_{\text{C-F}} = 3$ Hz, 1C), 128.8 (d, $J_{\text{C-F}} = 8$ Hz, 2C), 125.7, 122.1, 115.9 (d, $J_{\text{C-F}} = 22$ Hz, 2C), 89.3, 37.0, 36.9; LRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{FINO}_2$ $[\text{M}+\text{H}]^+$: 386.18, found 386.29.





152.37
149.36

138.42
133.46
128.45

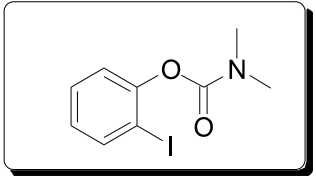
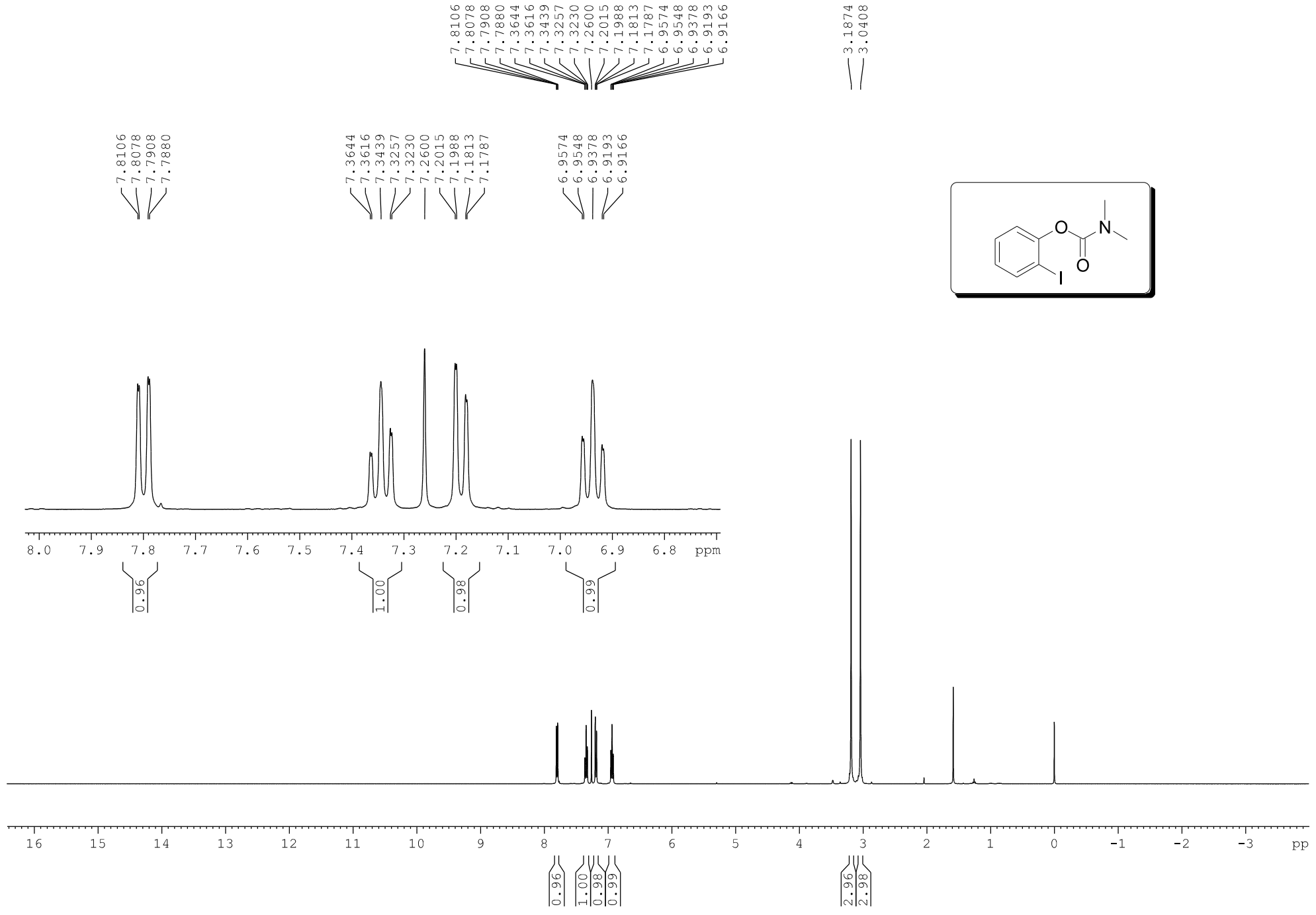
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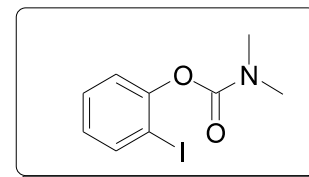
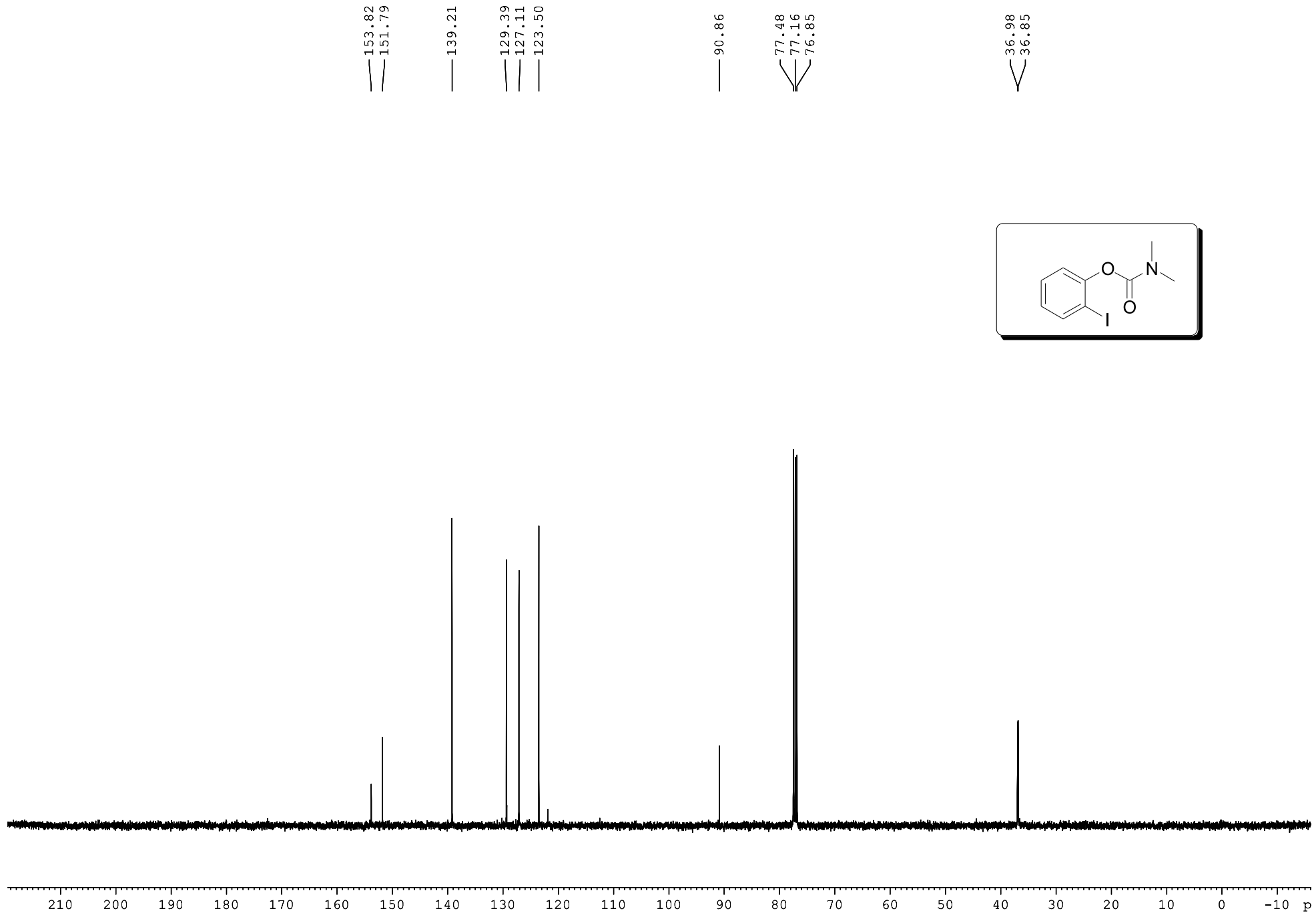
92.82

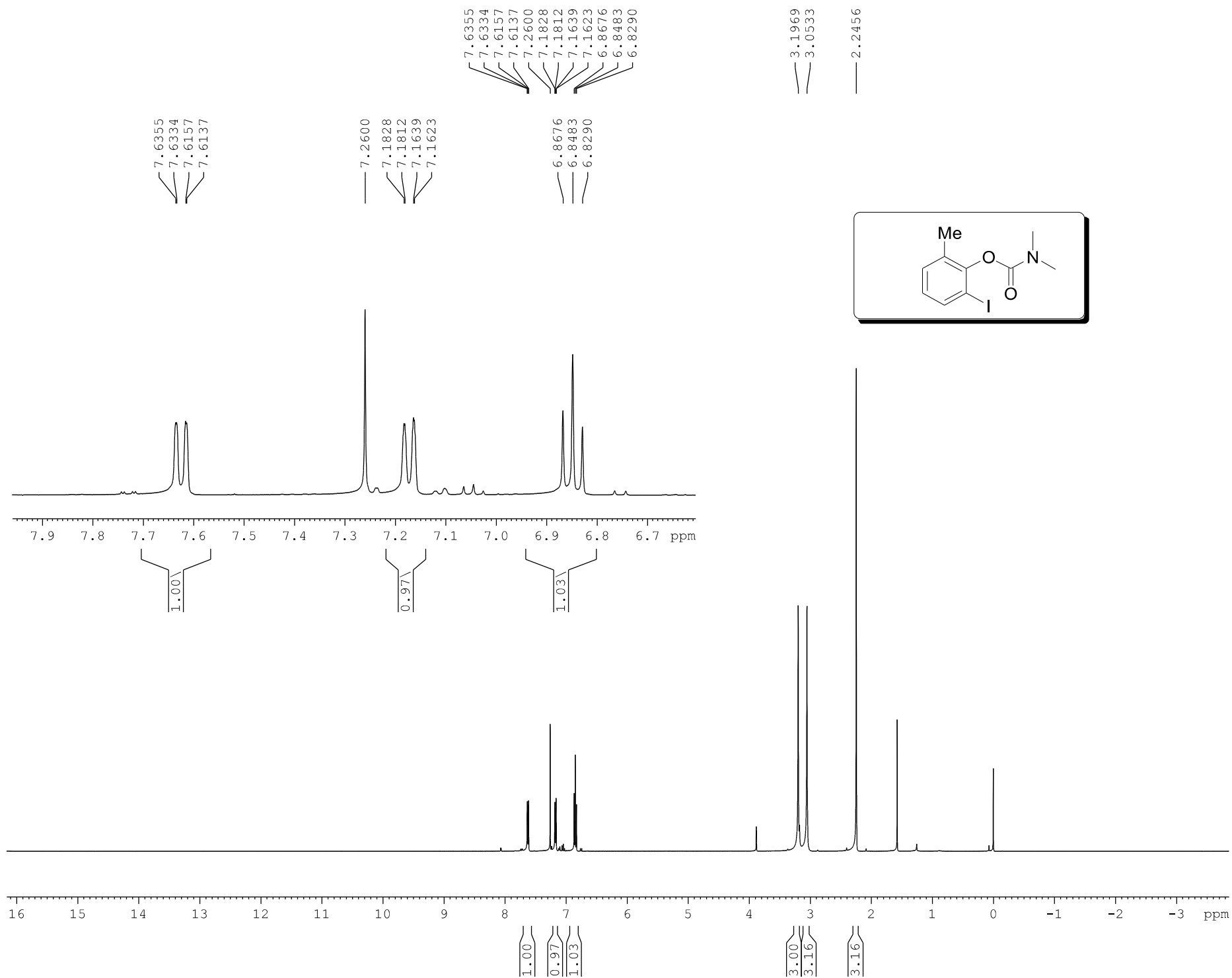
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77.16
76.84

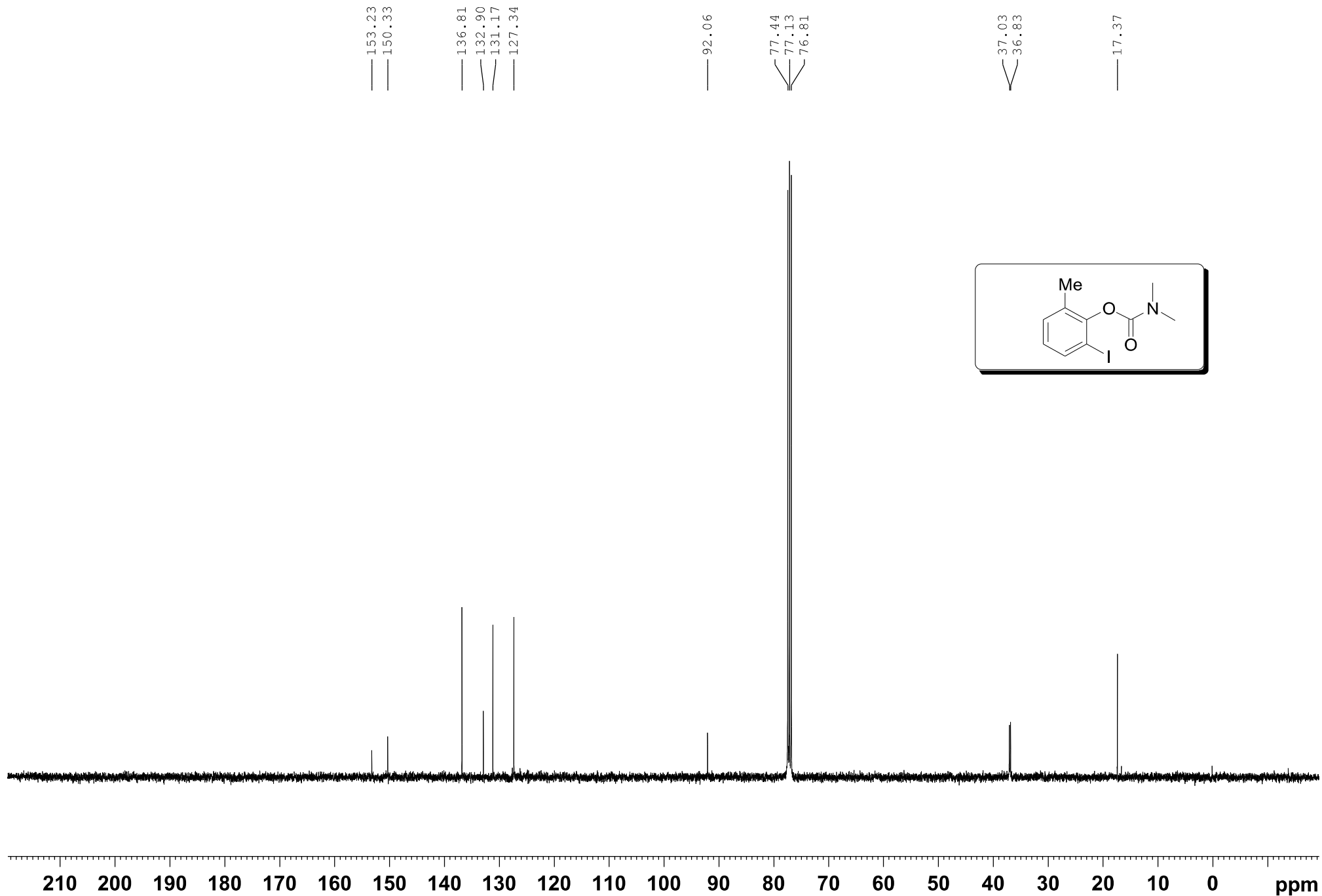
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36.90

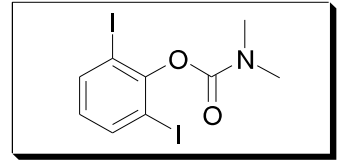
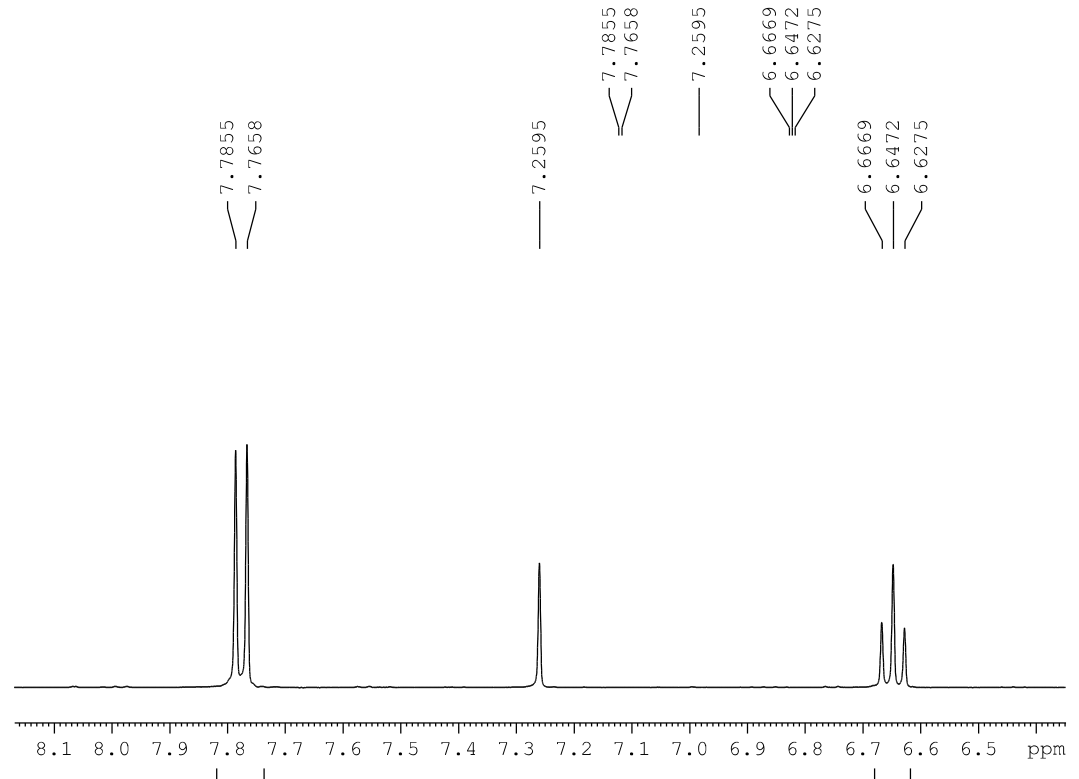
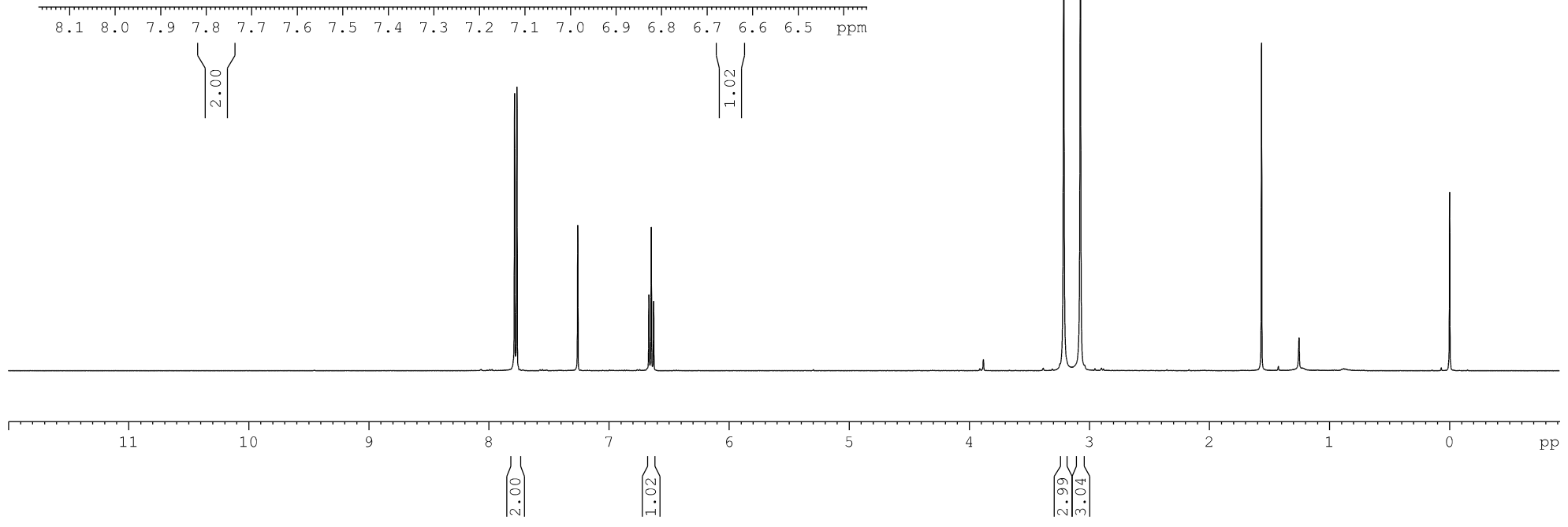
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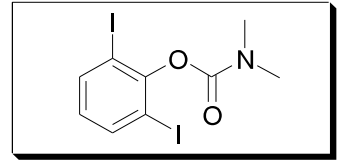
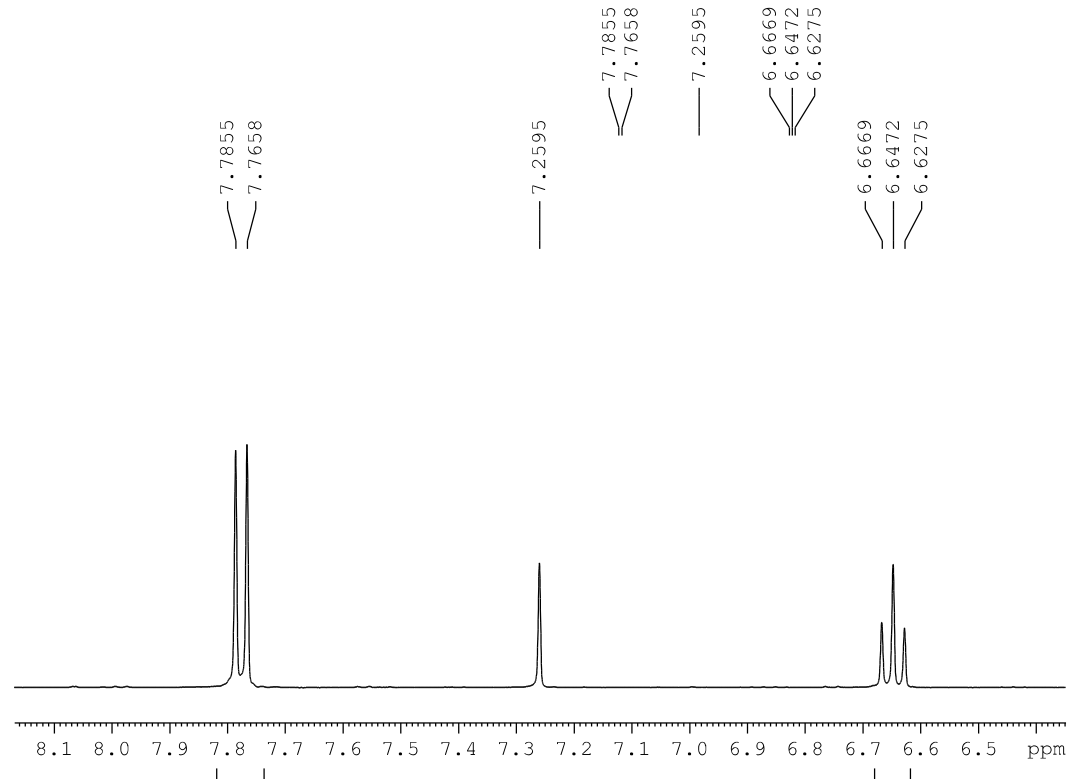
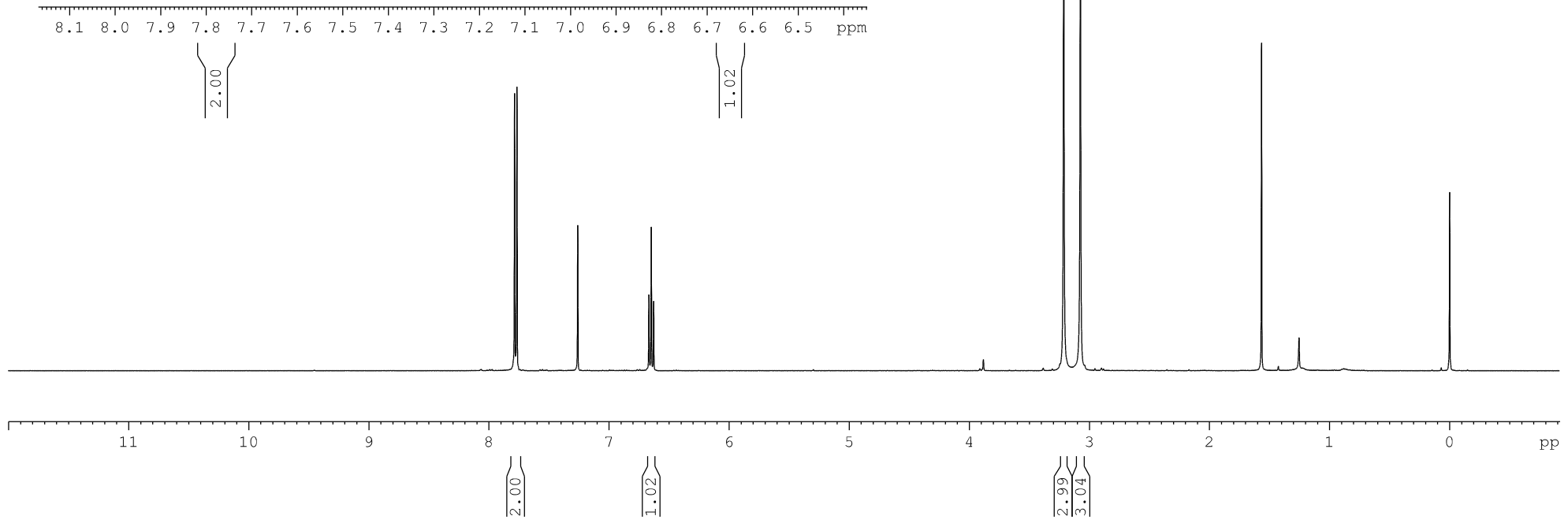


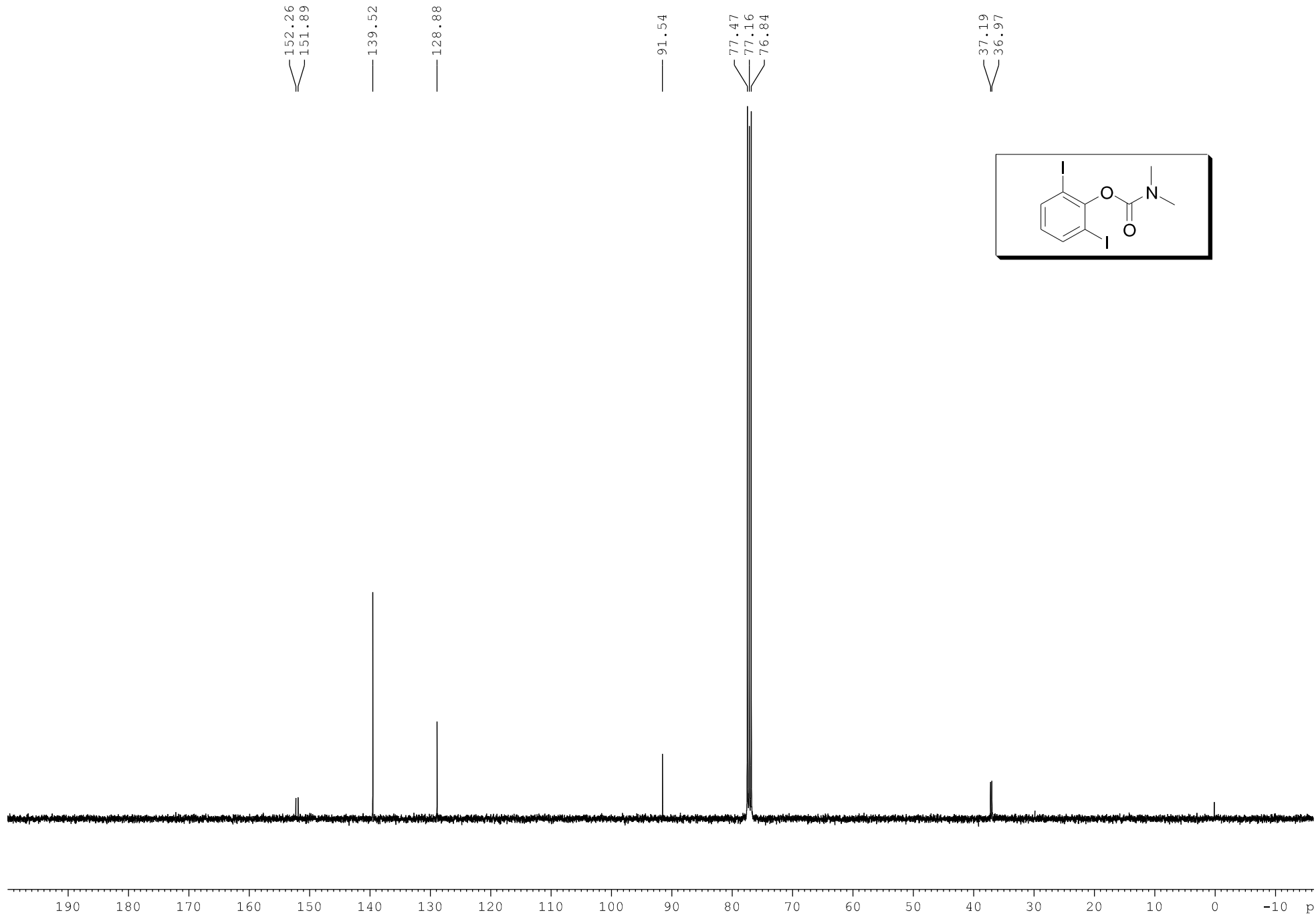


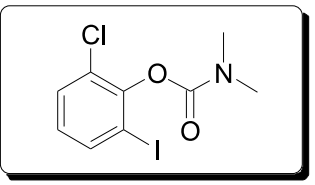
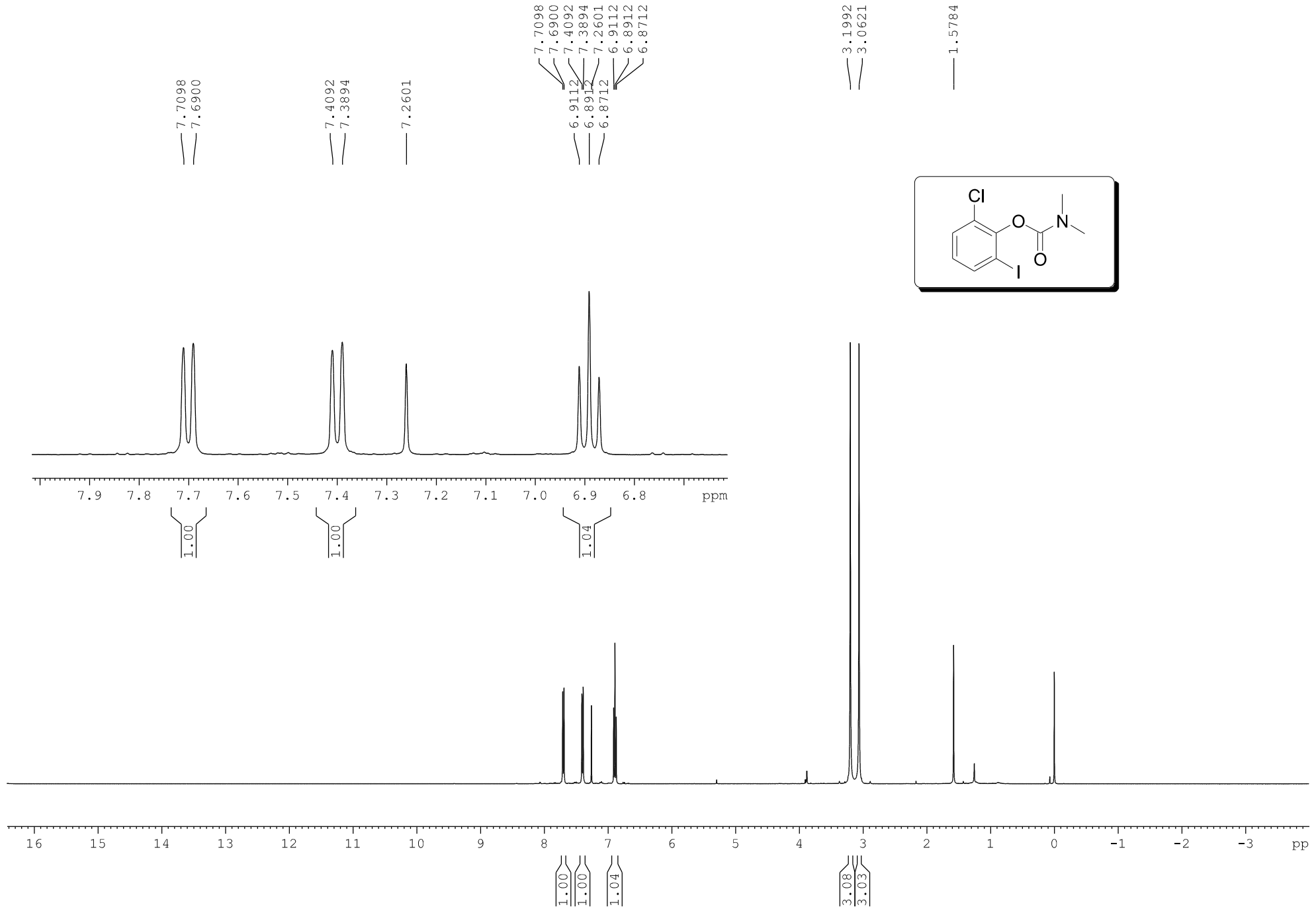


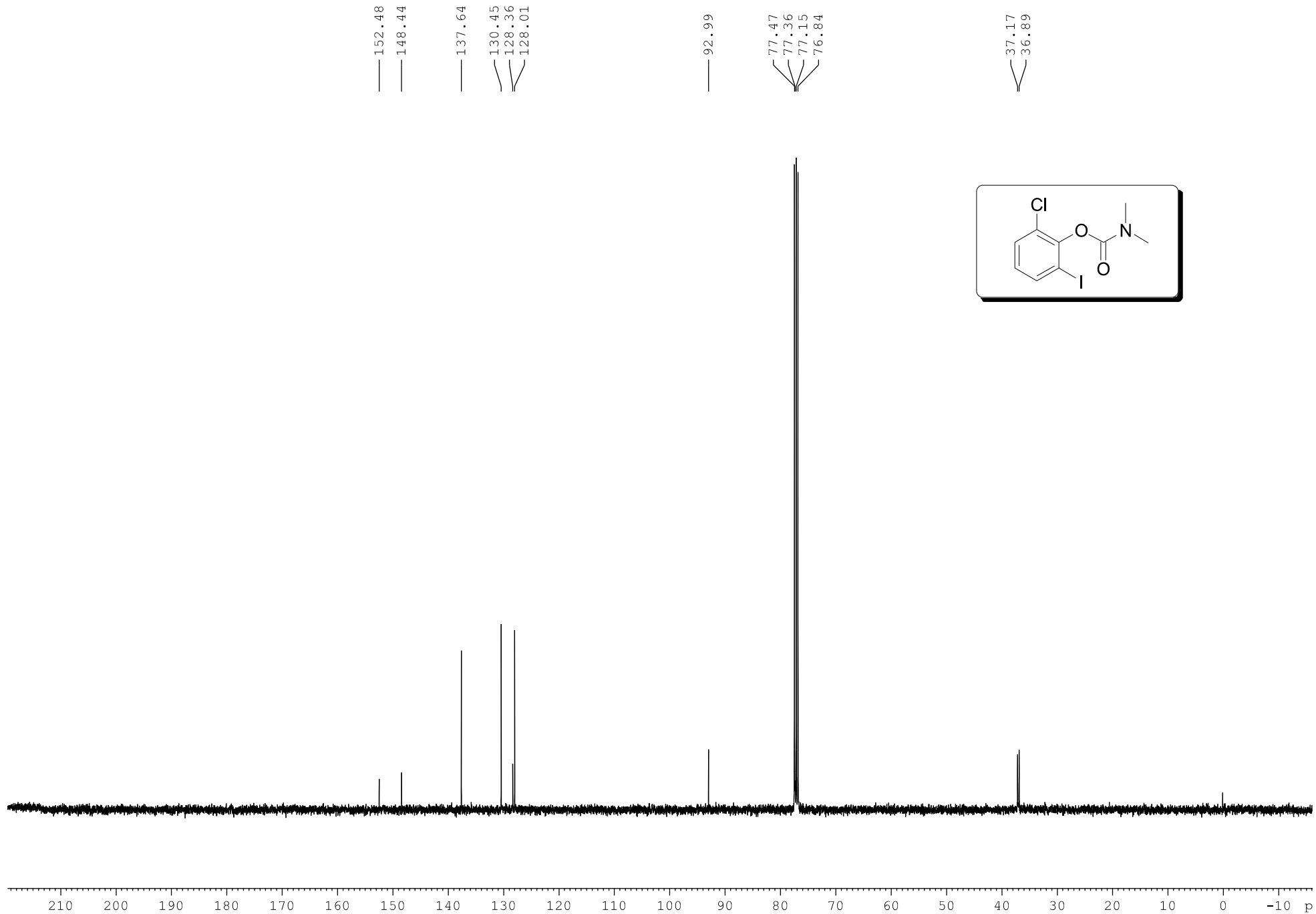


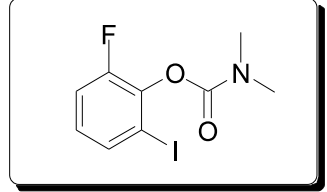
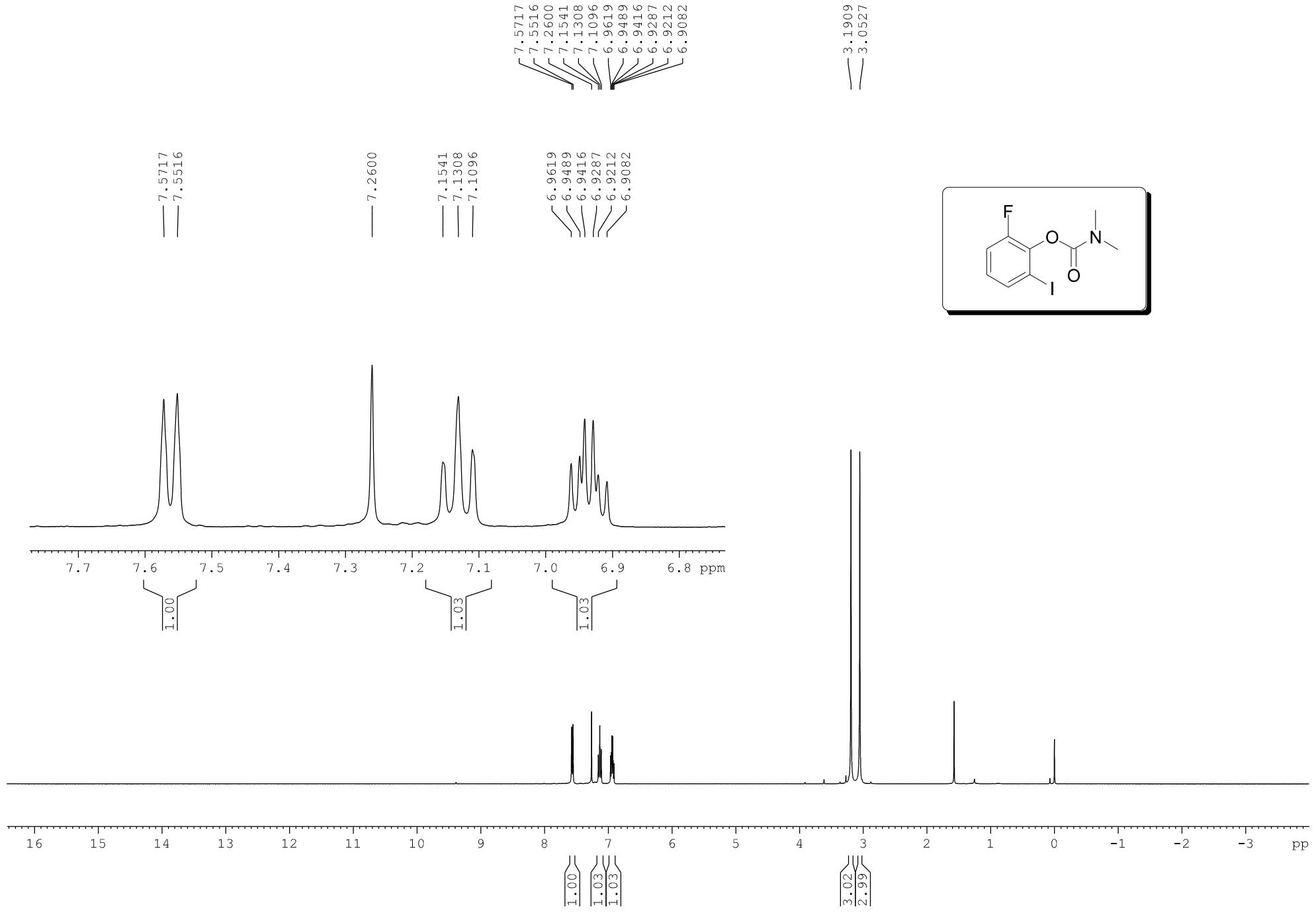


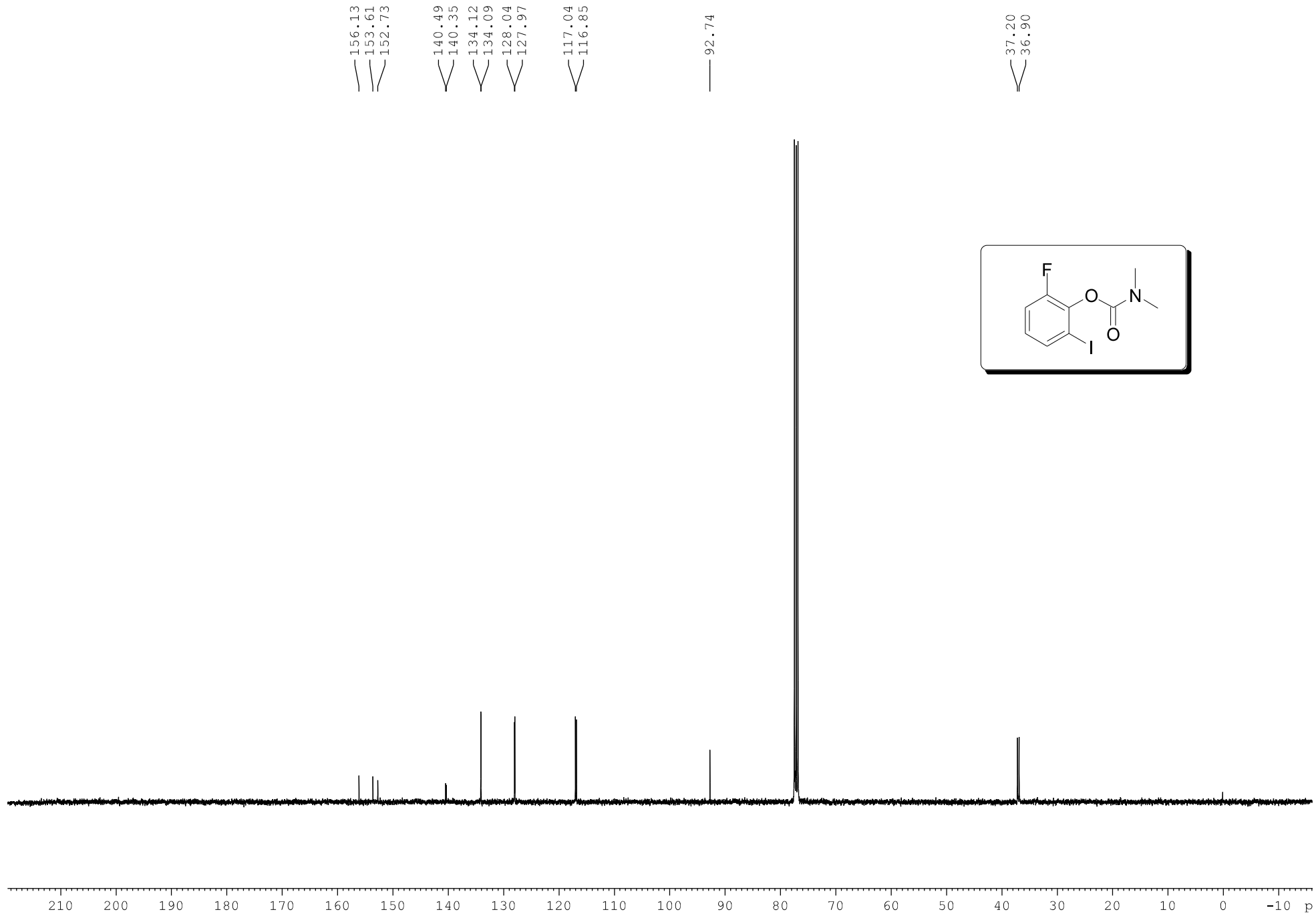


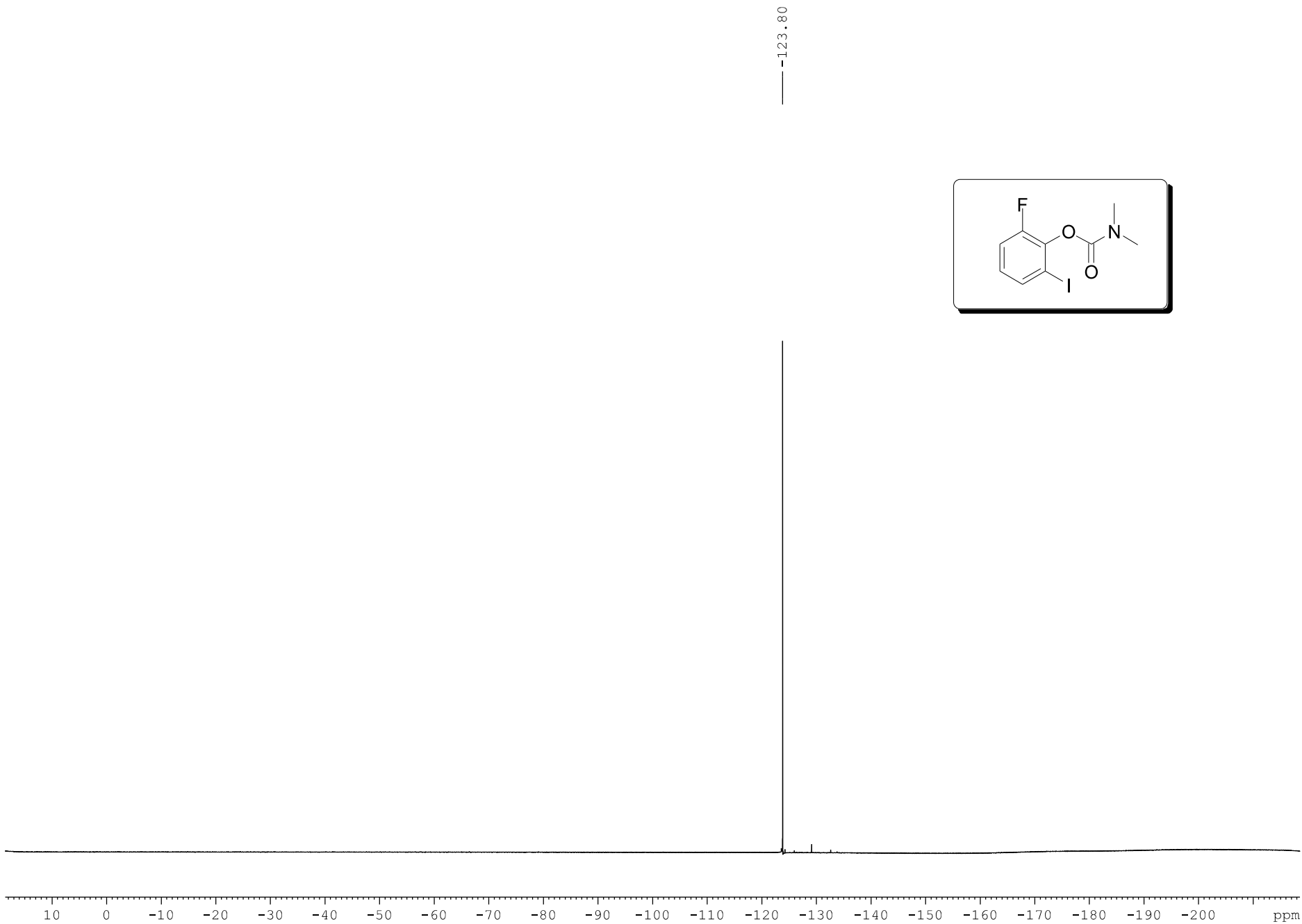


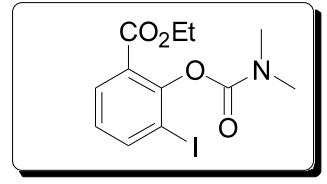
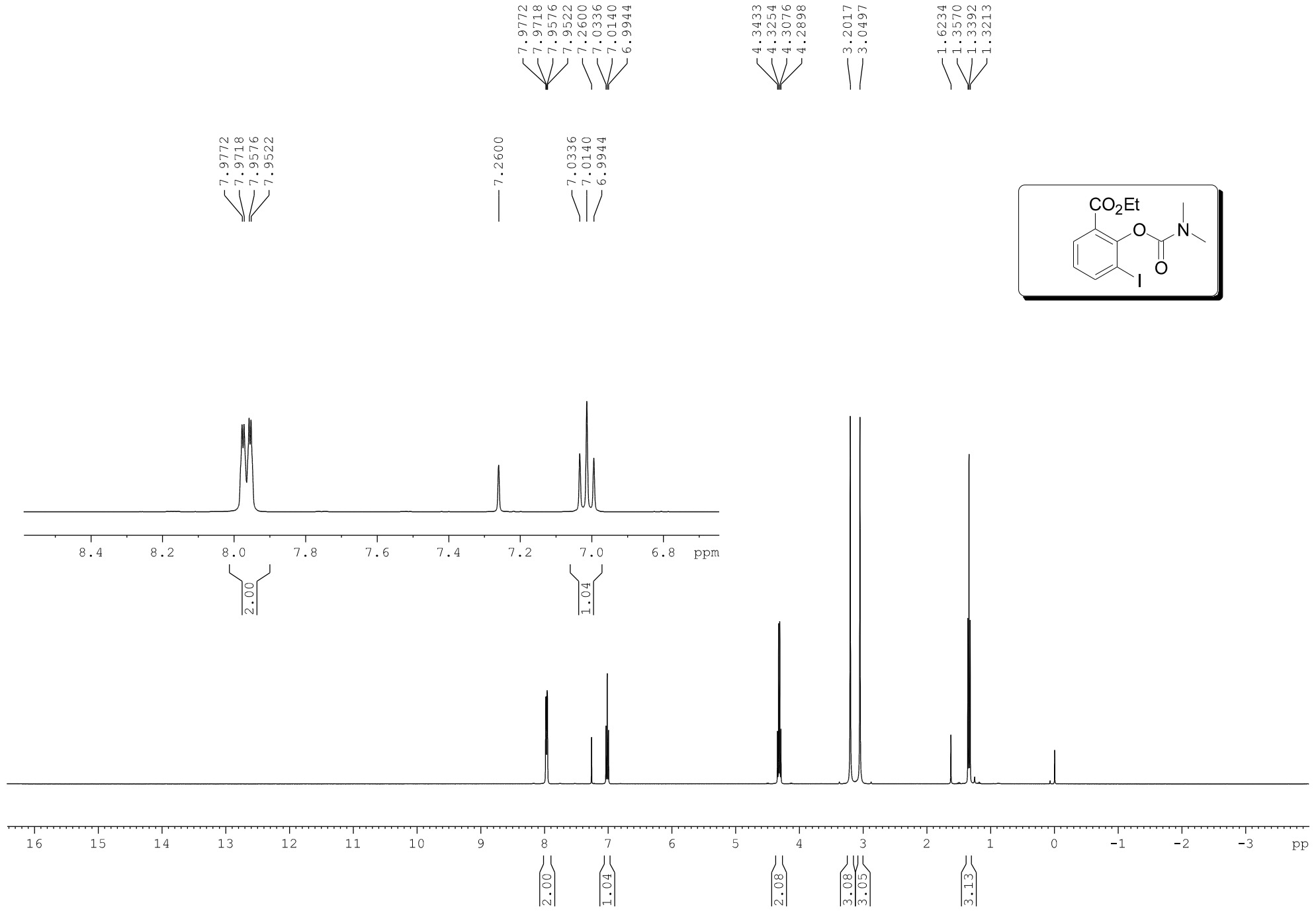


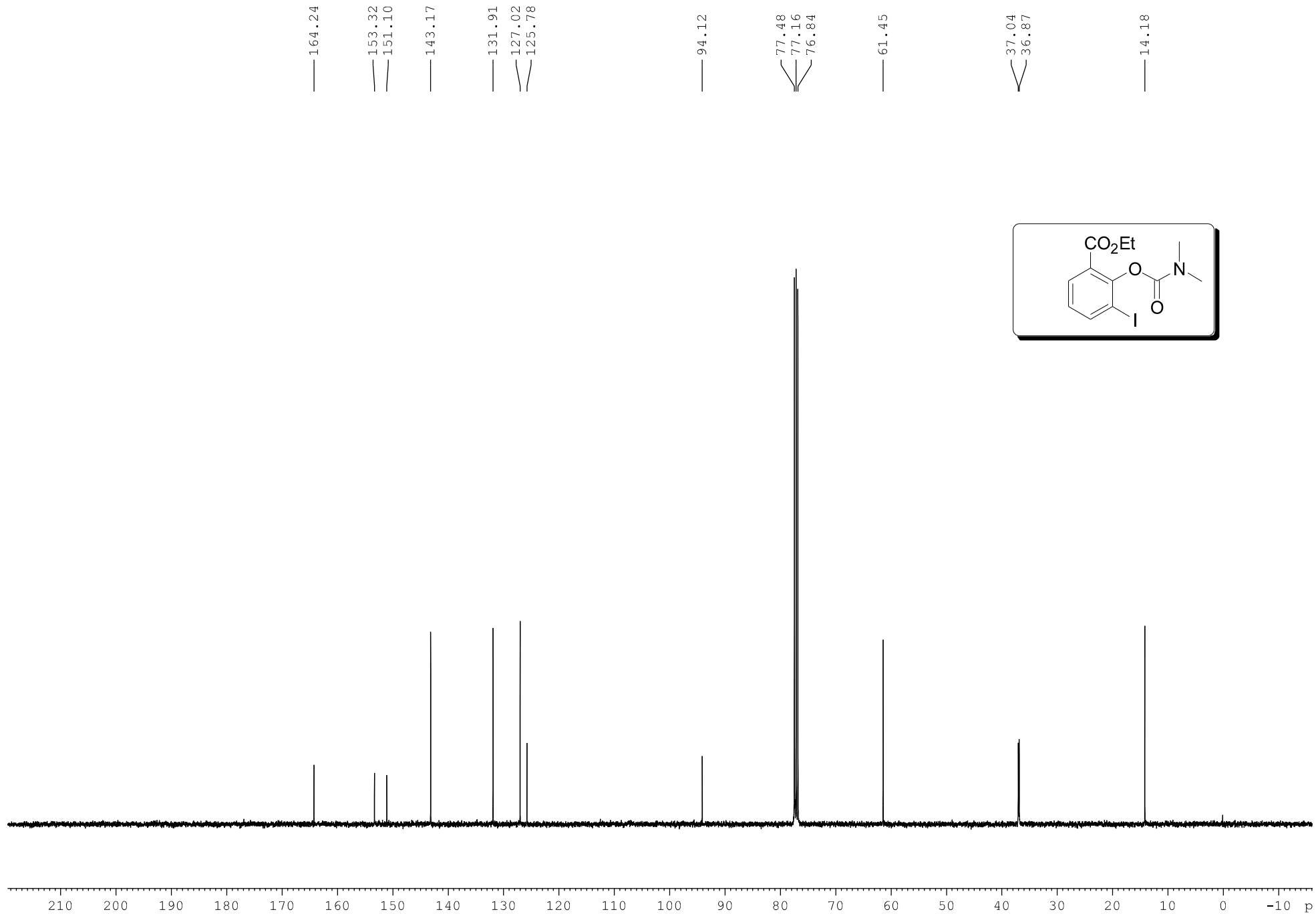


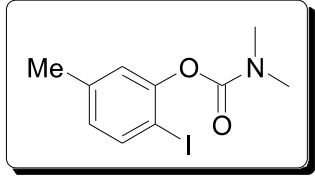
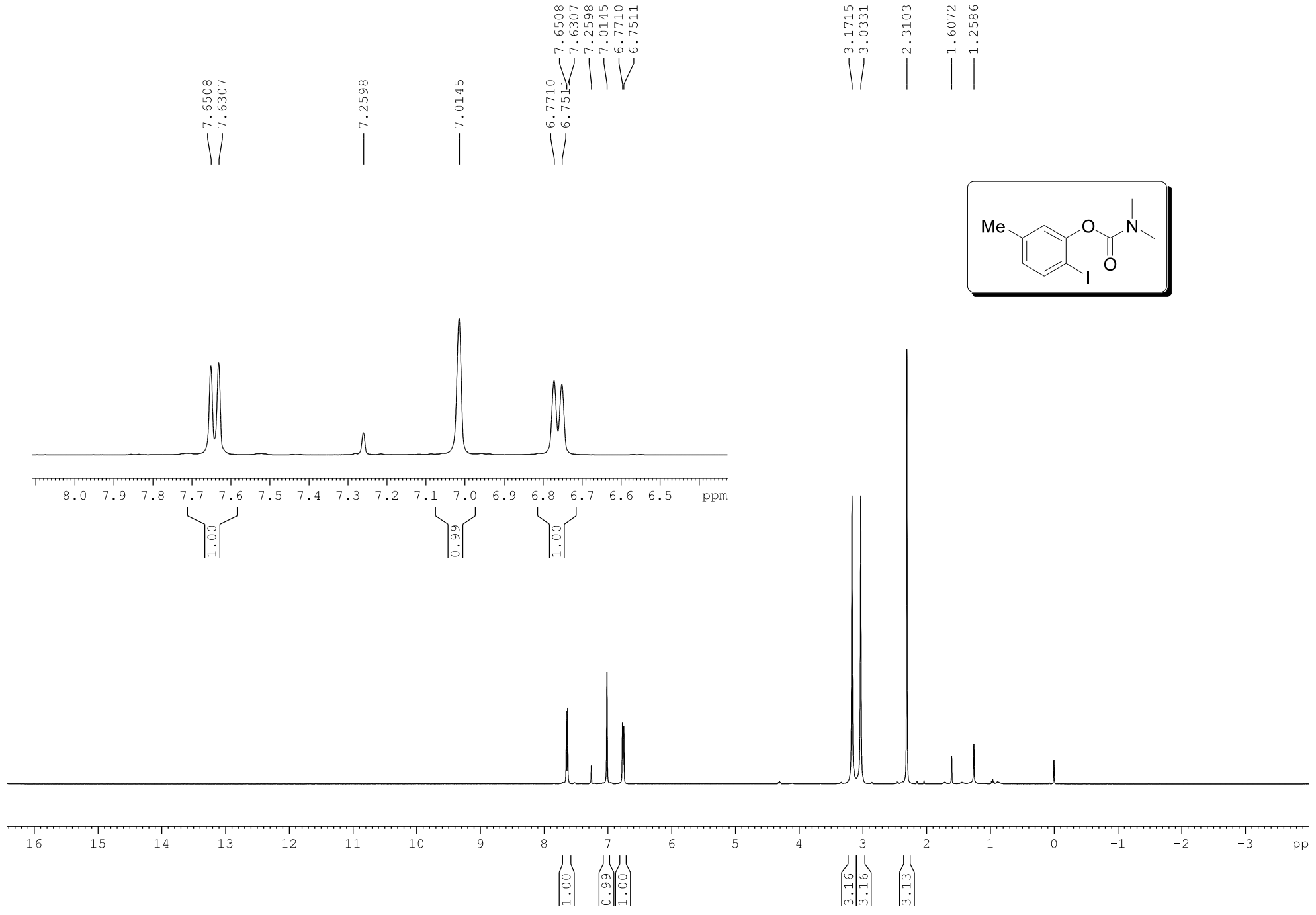


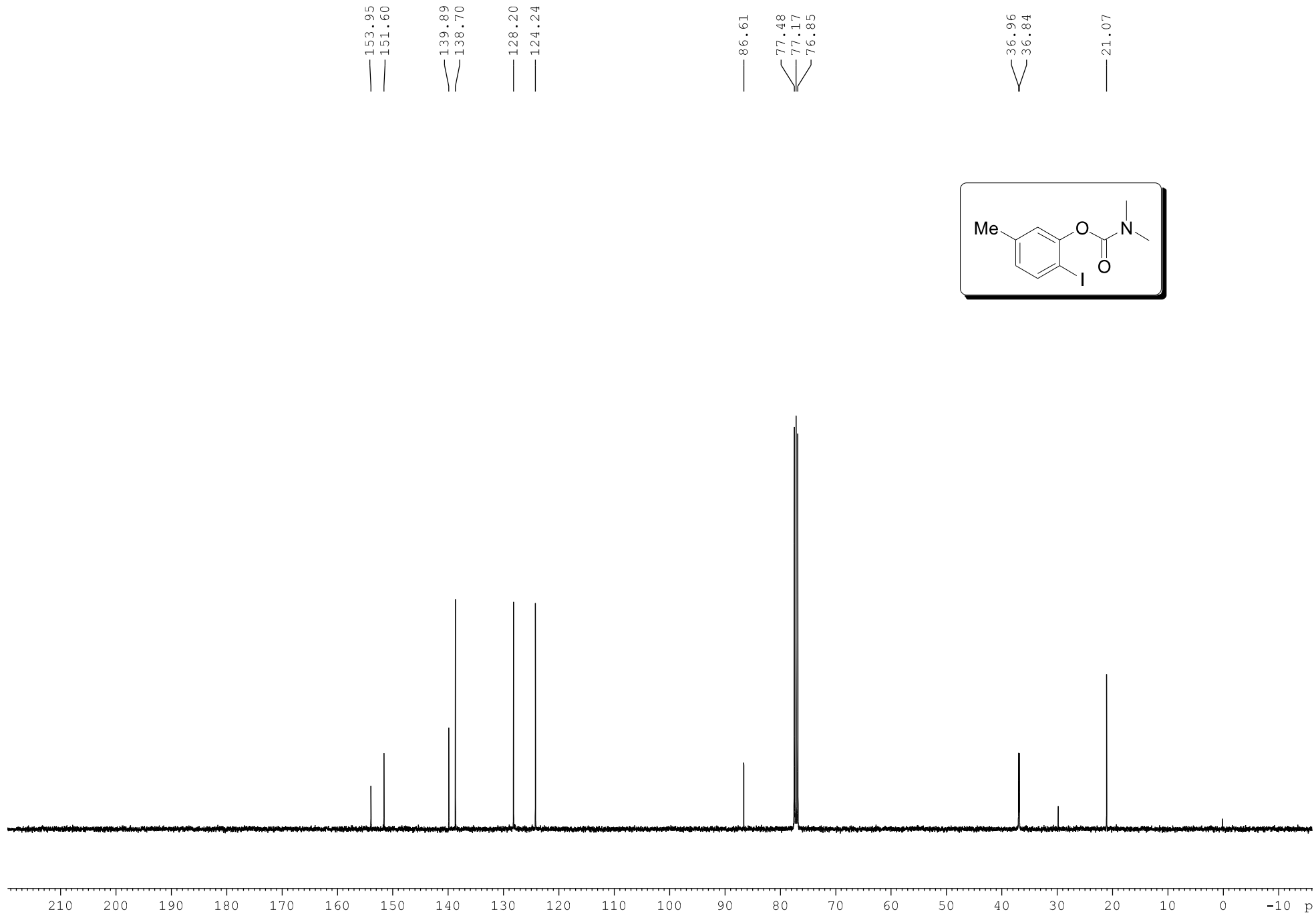


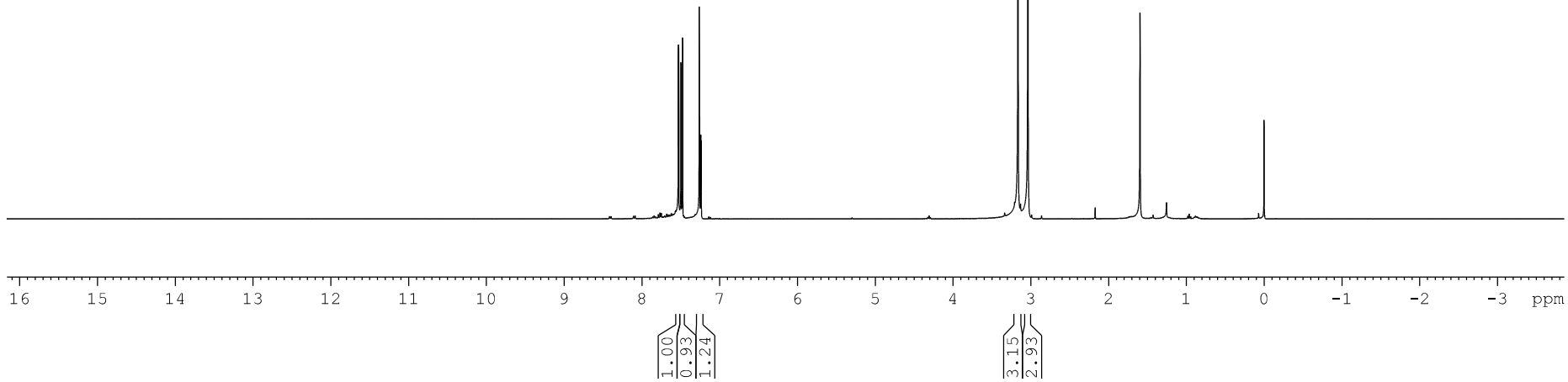
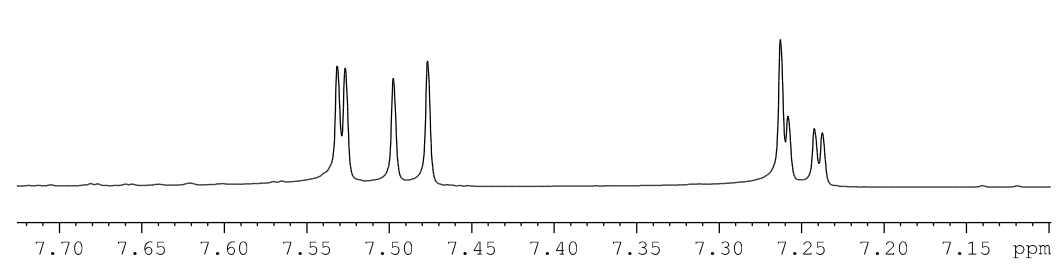








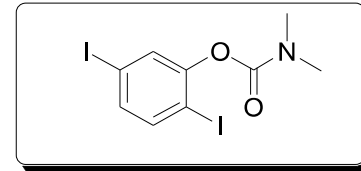


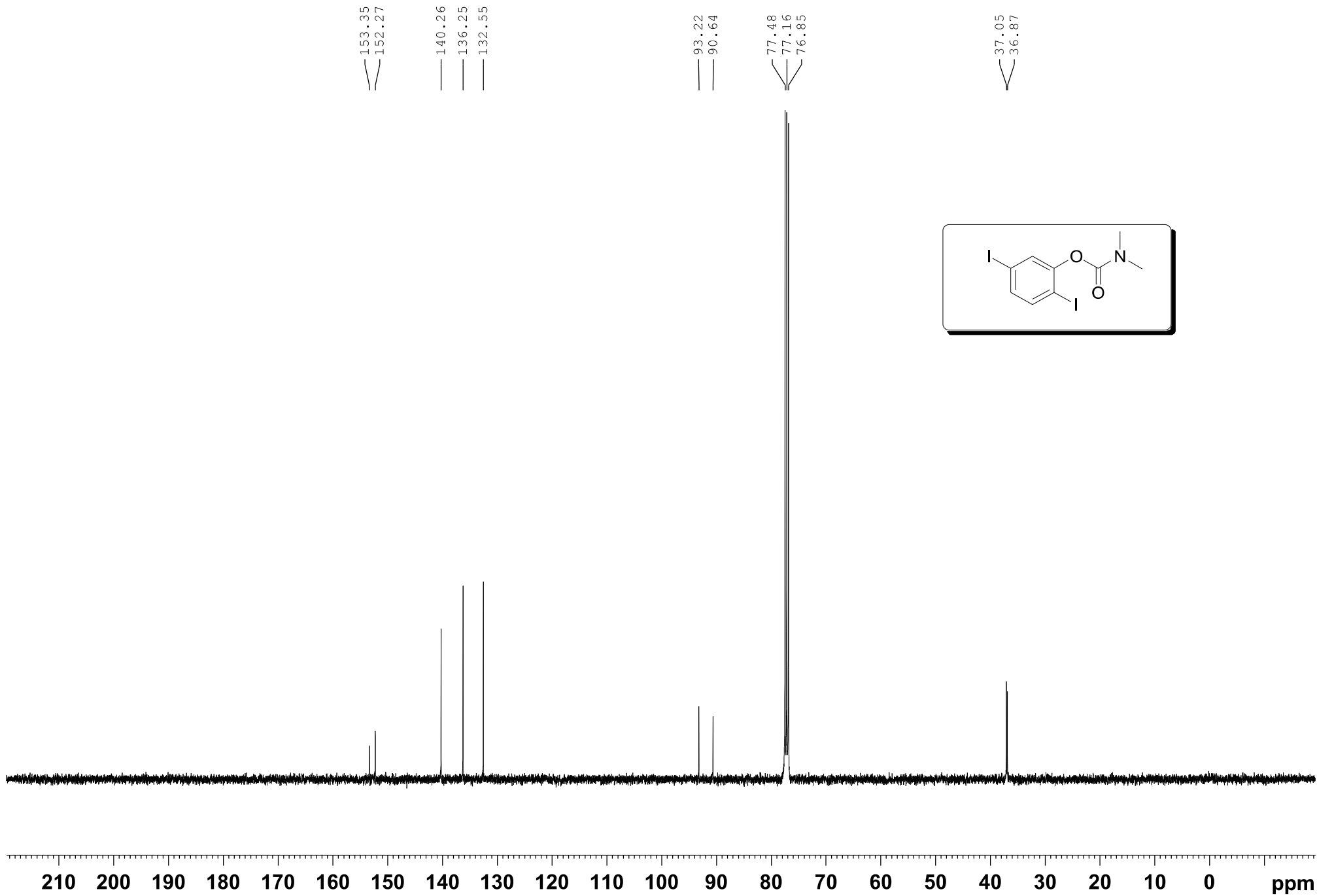


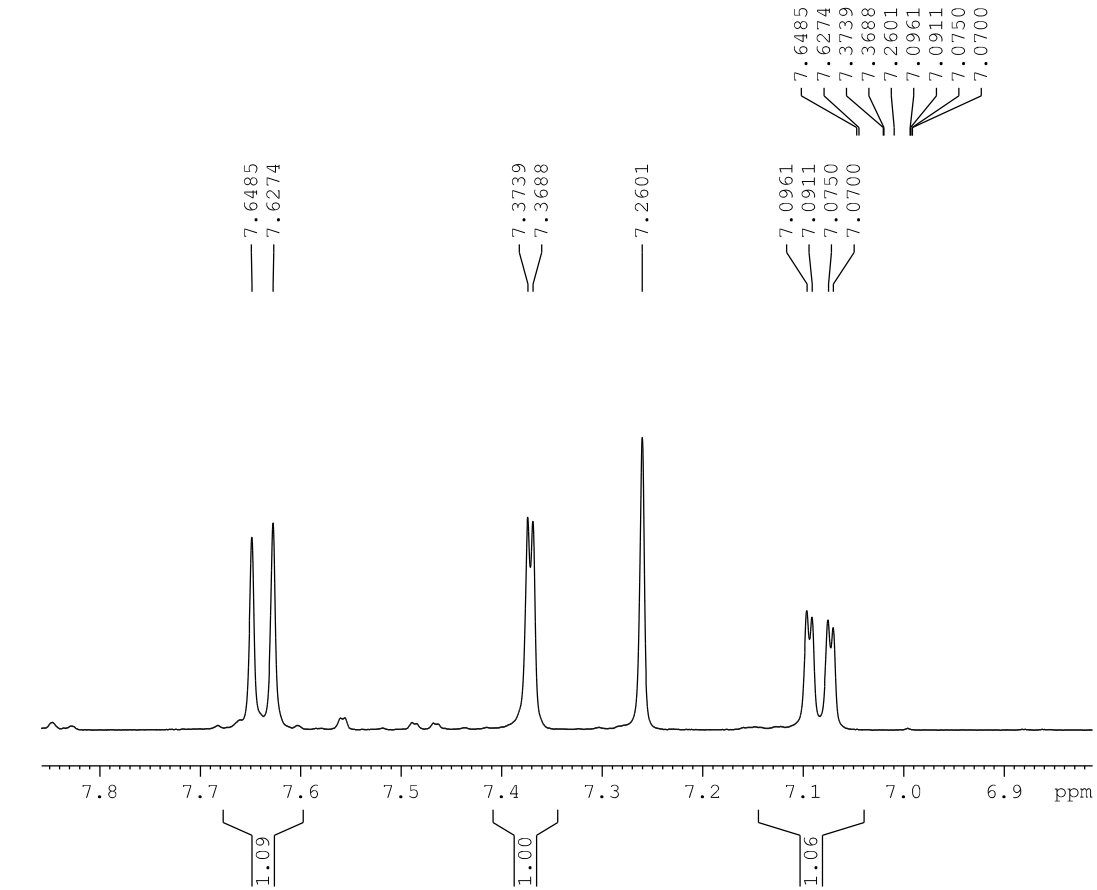
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7.2628
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7.2423
7.2374

3.1639
3.0362

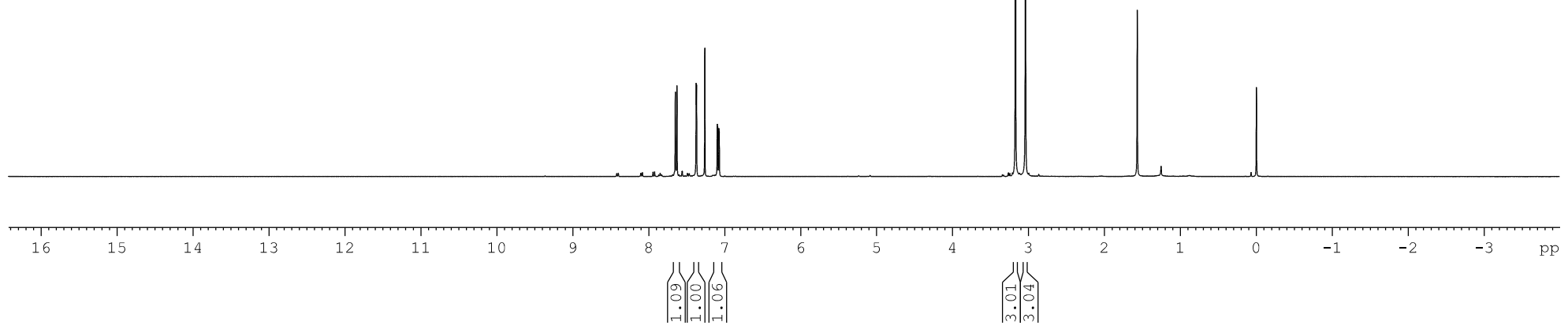
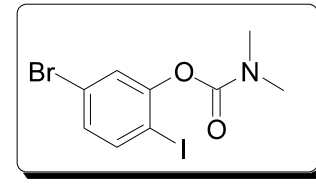
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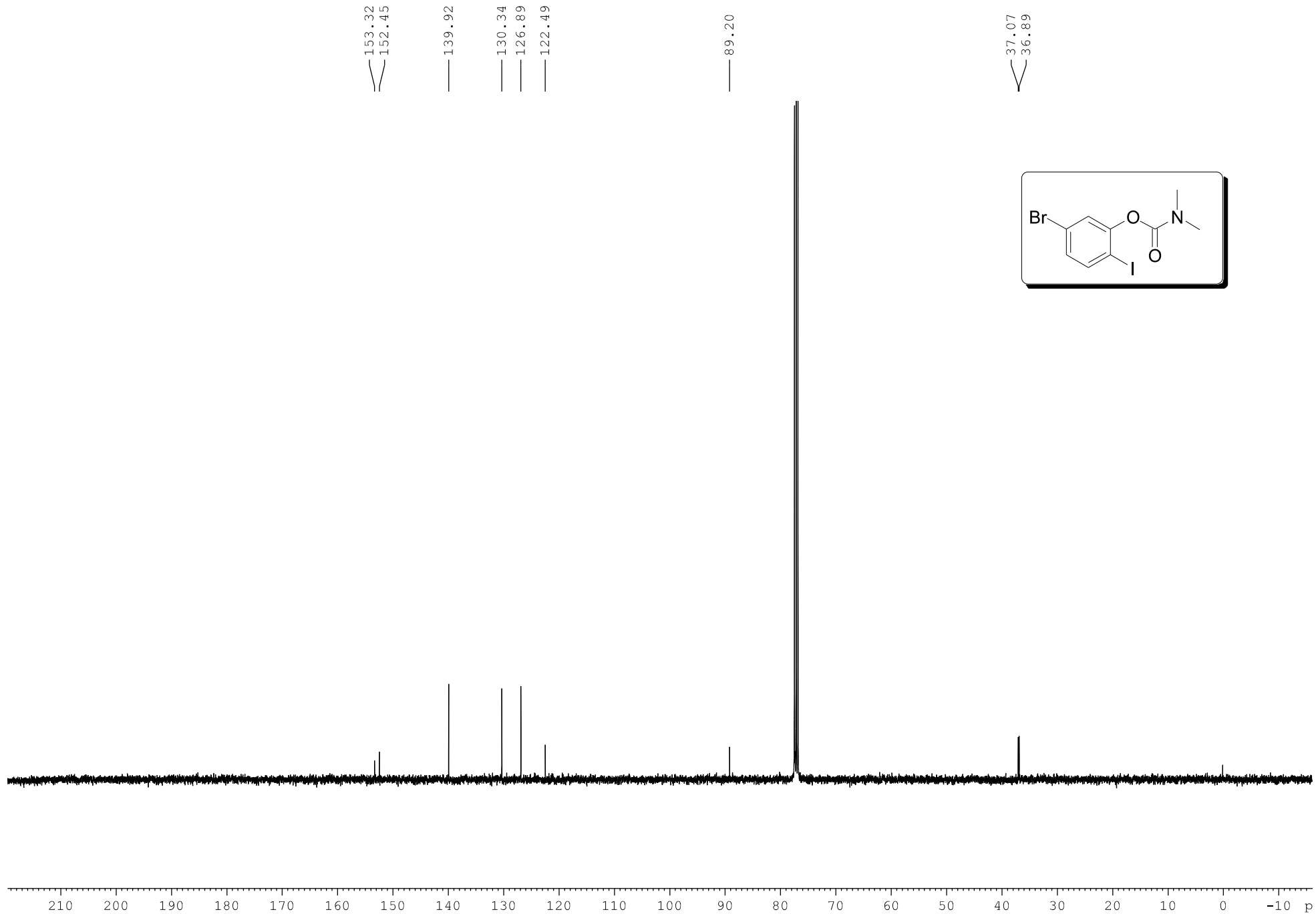


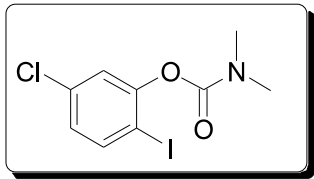
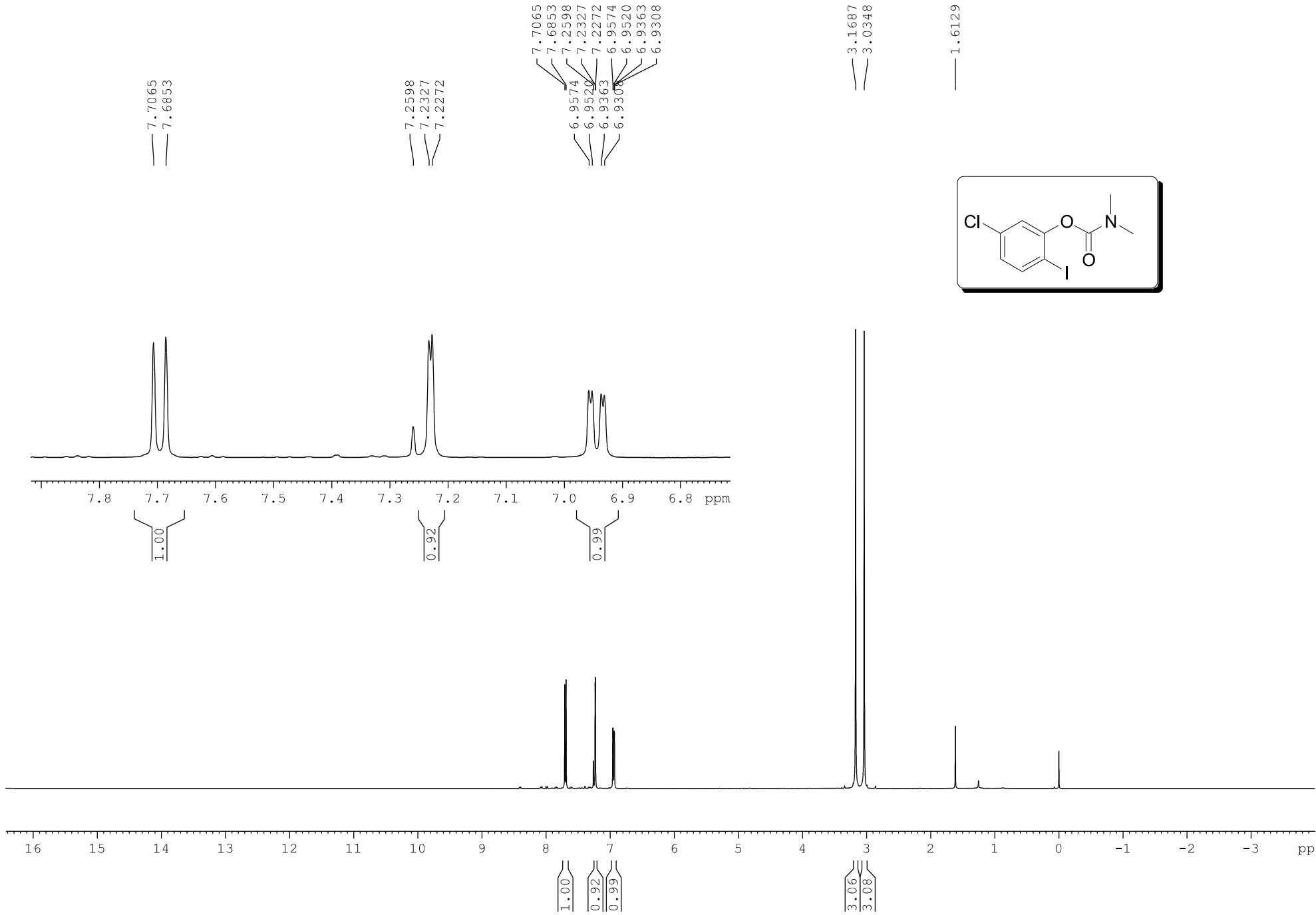


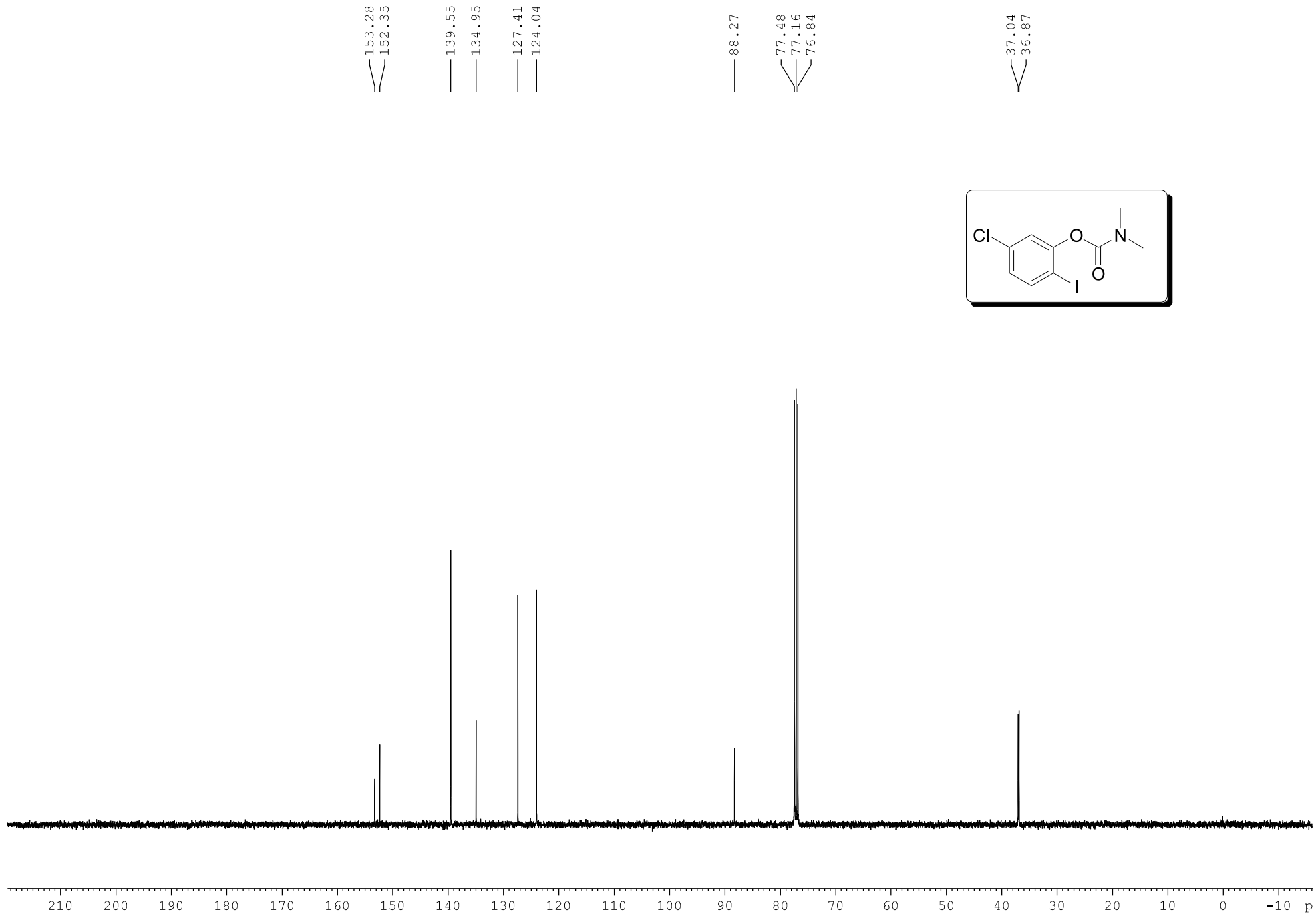


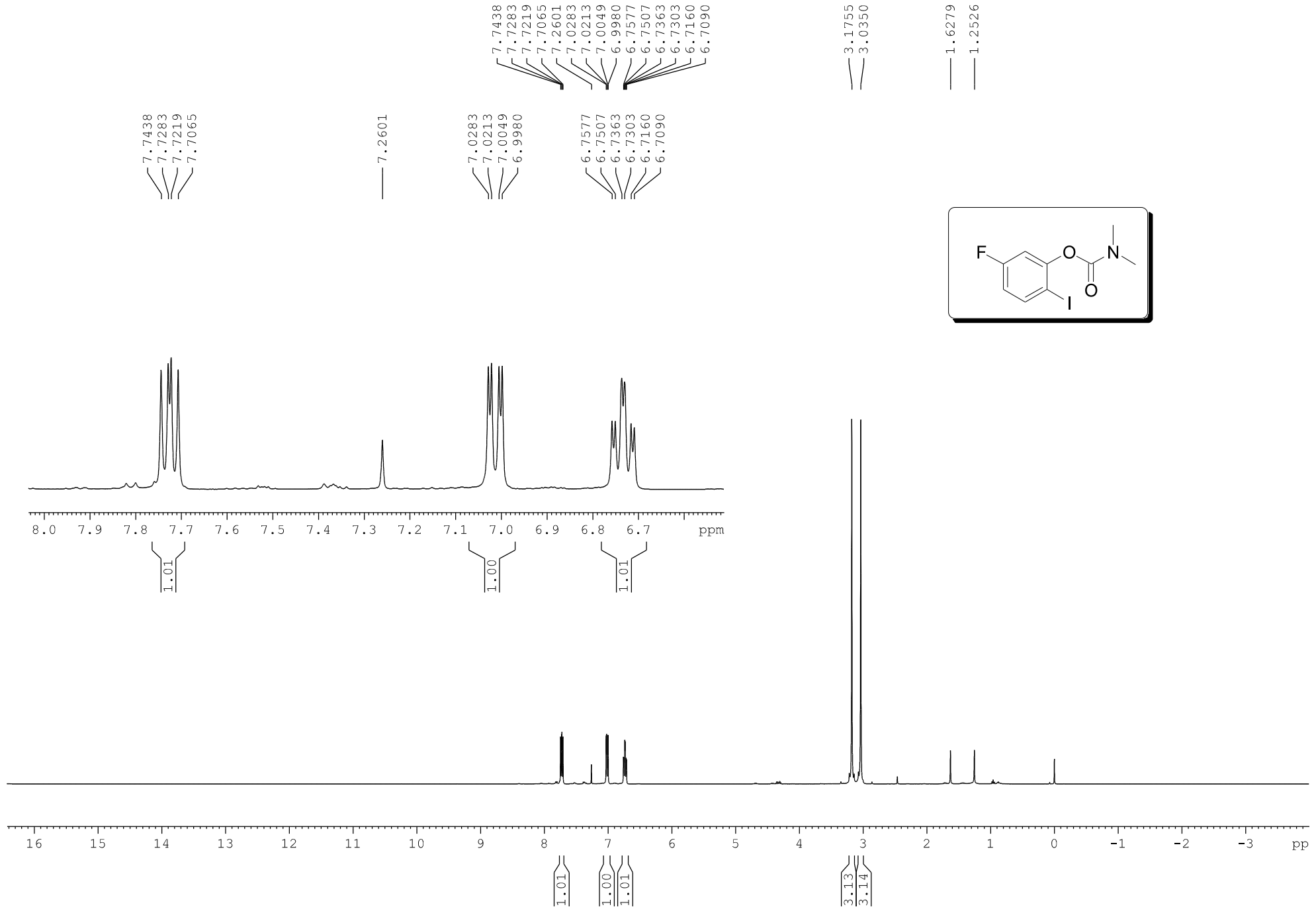
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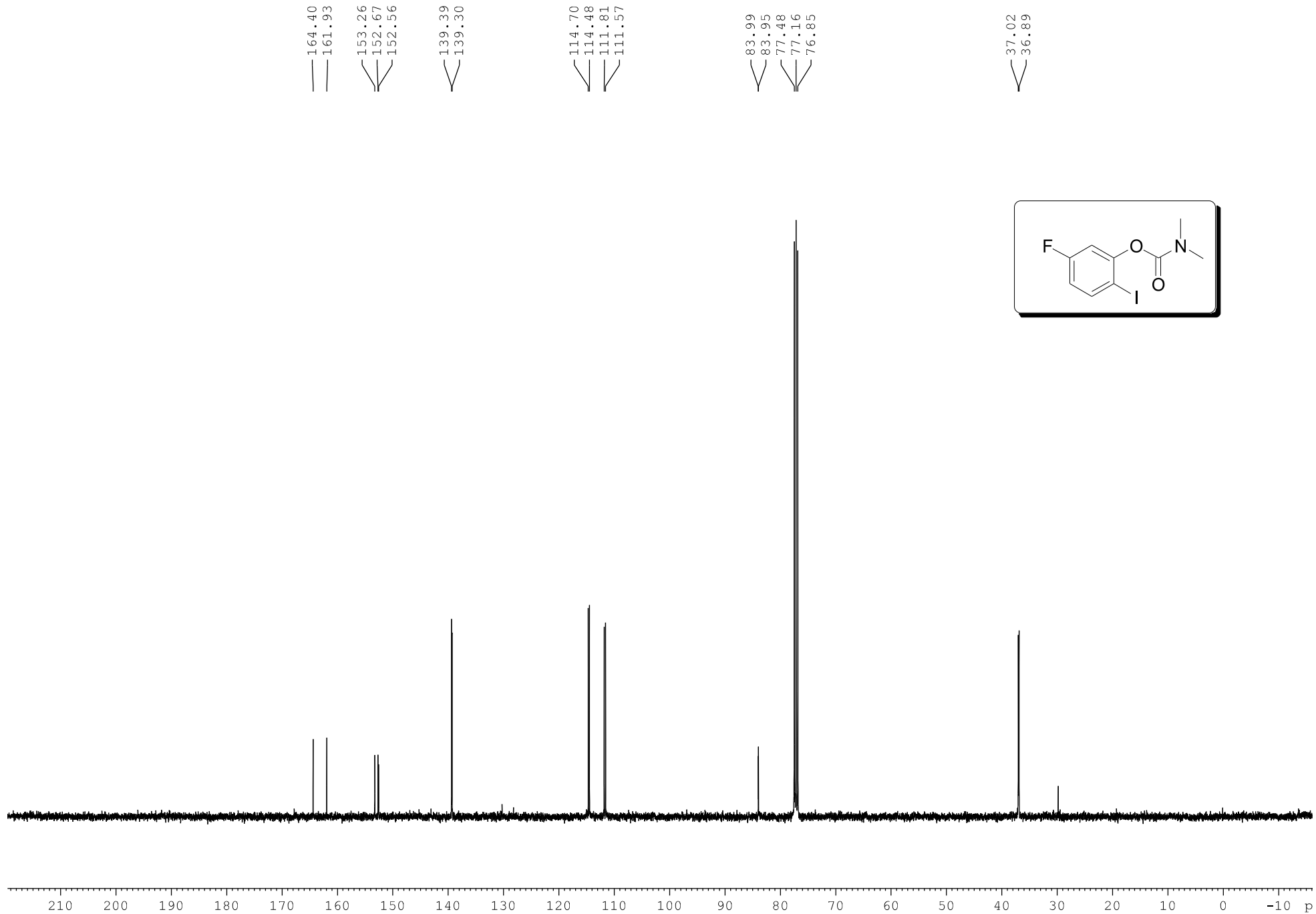


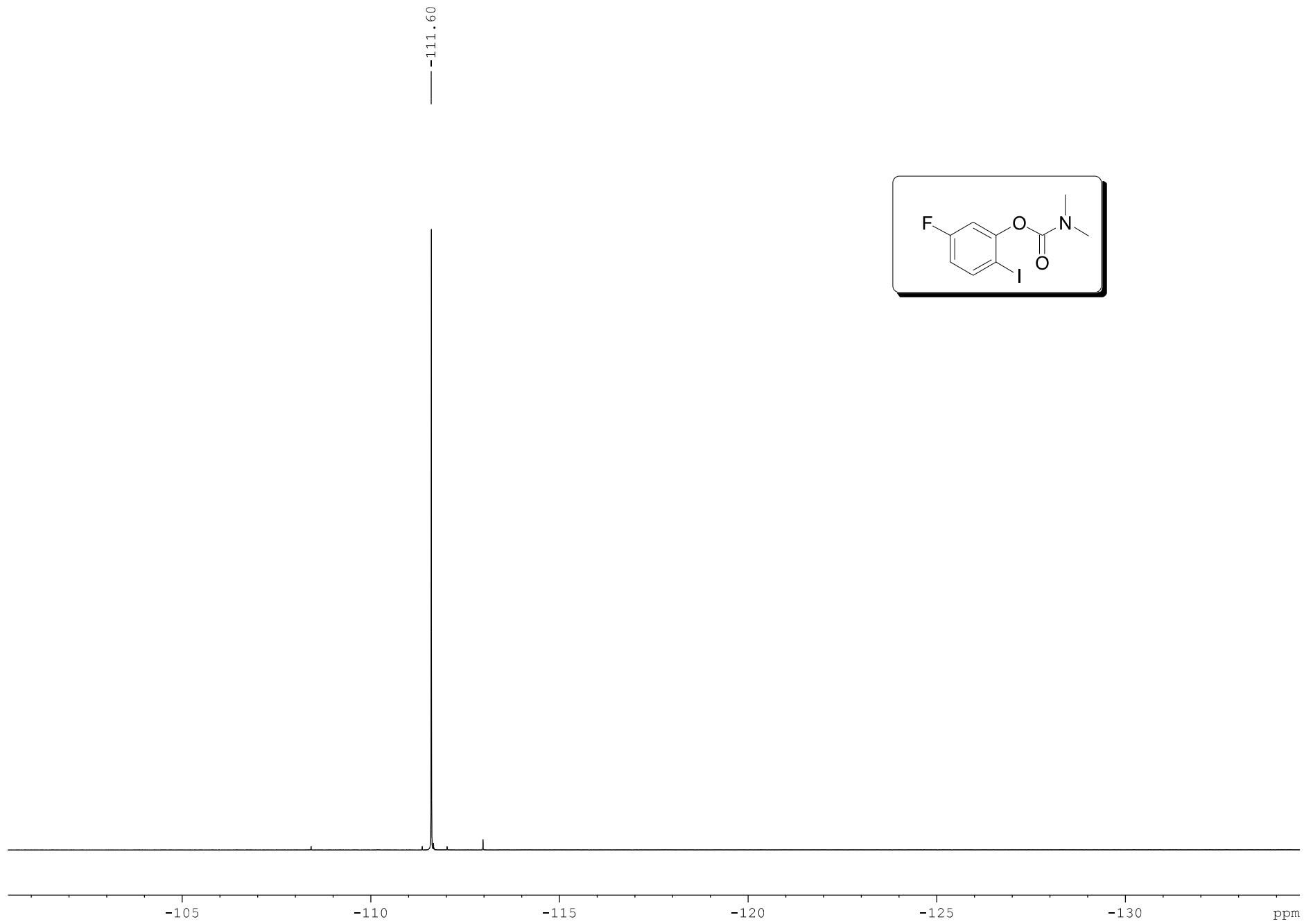
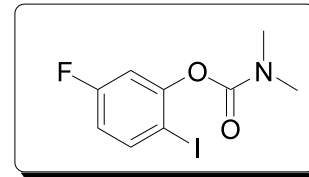


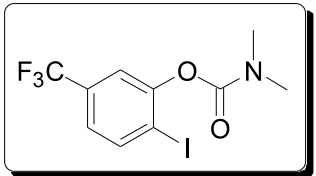
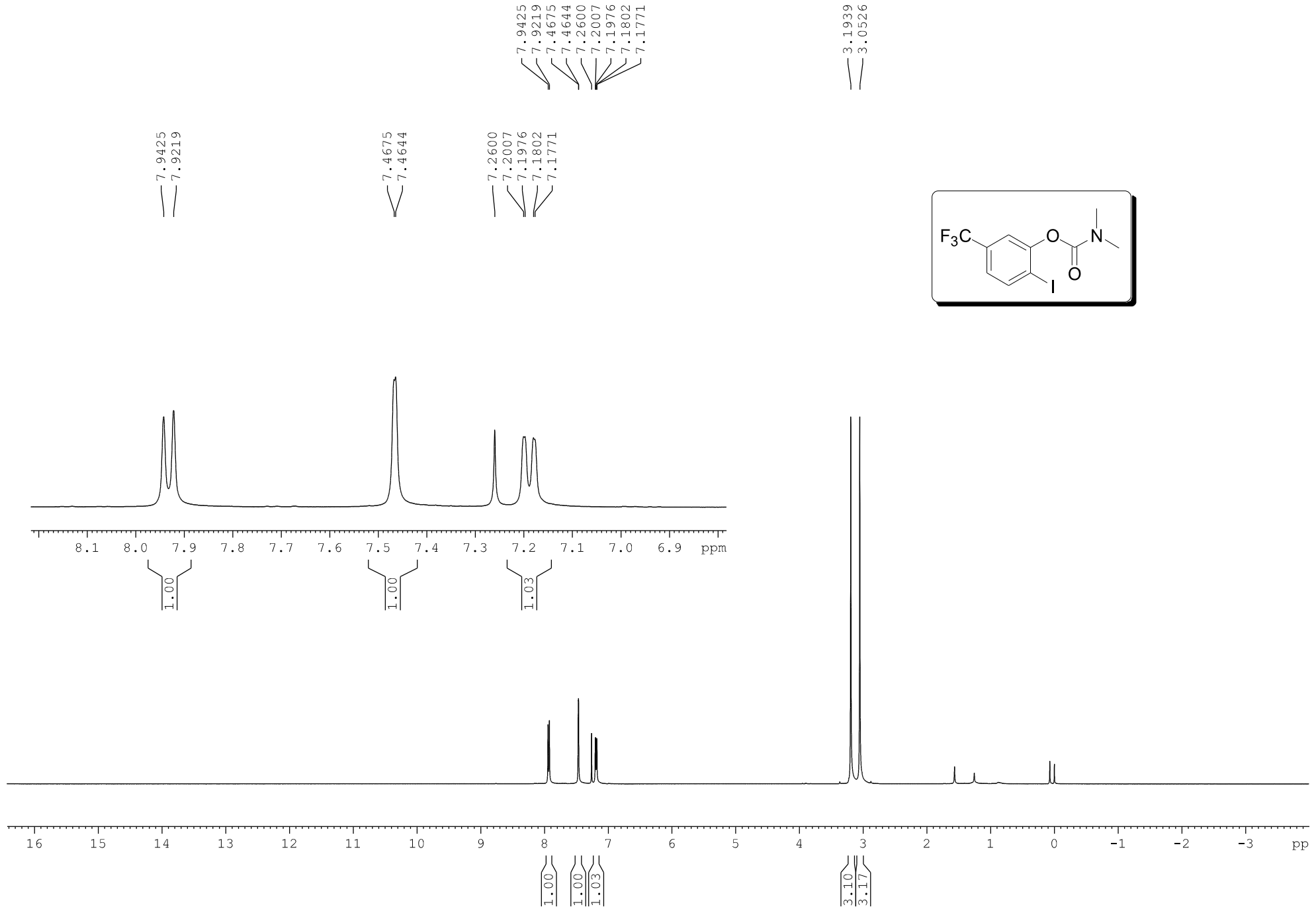


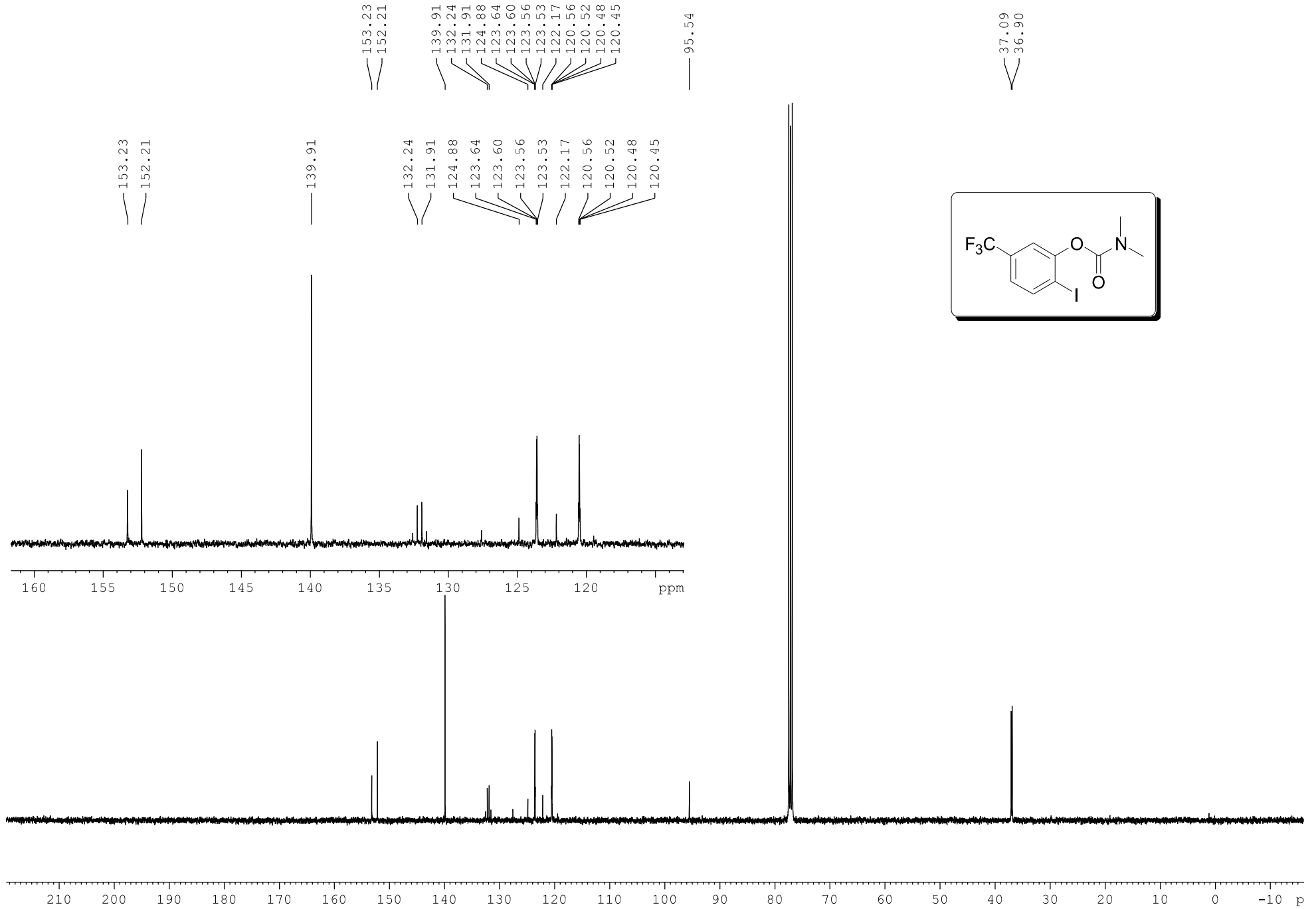


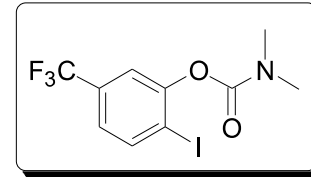




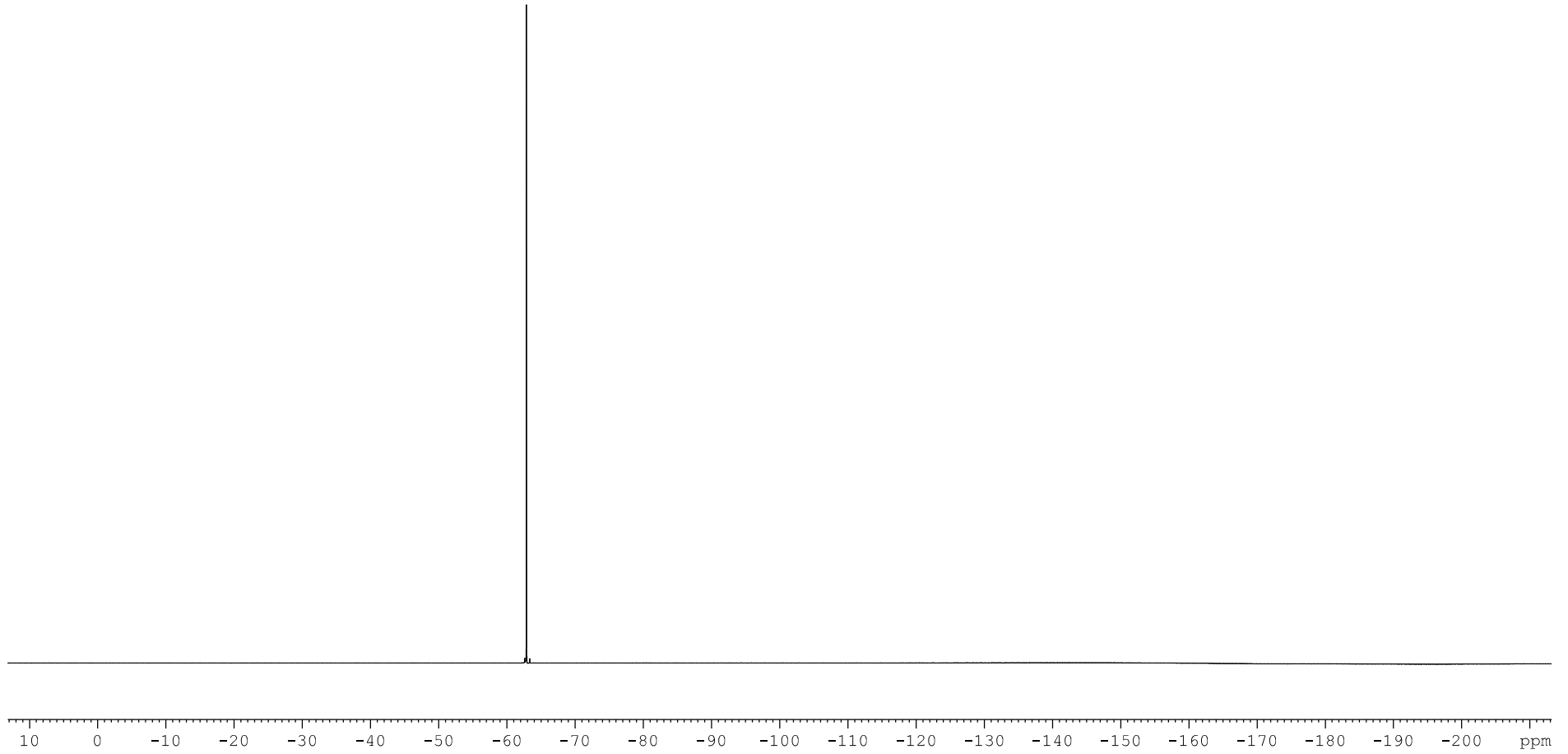


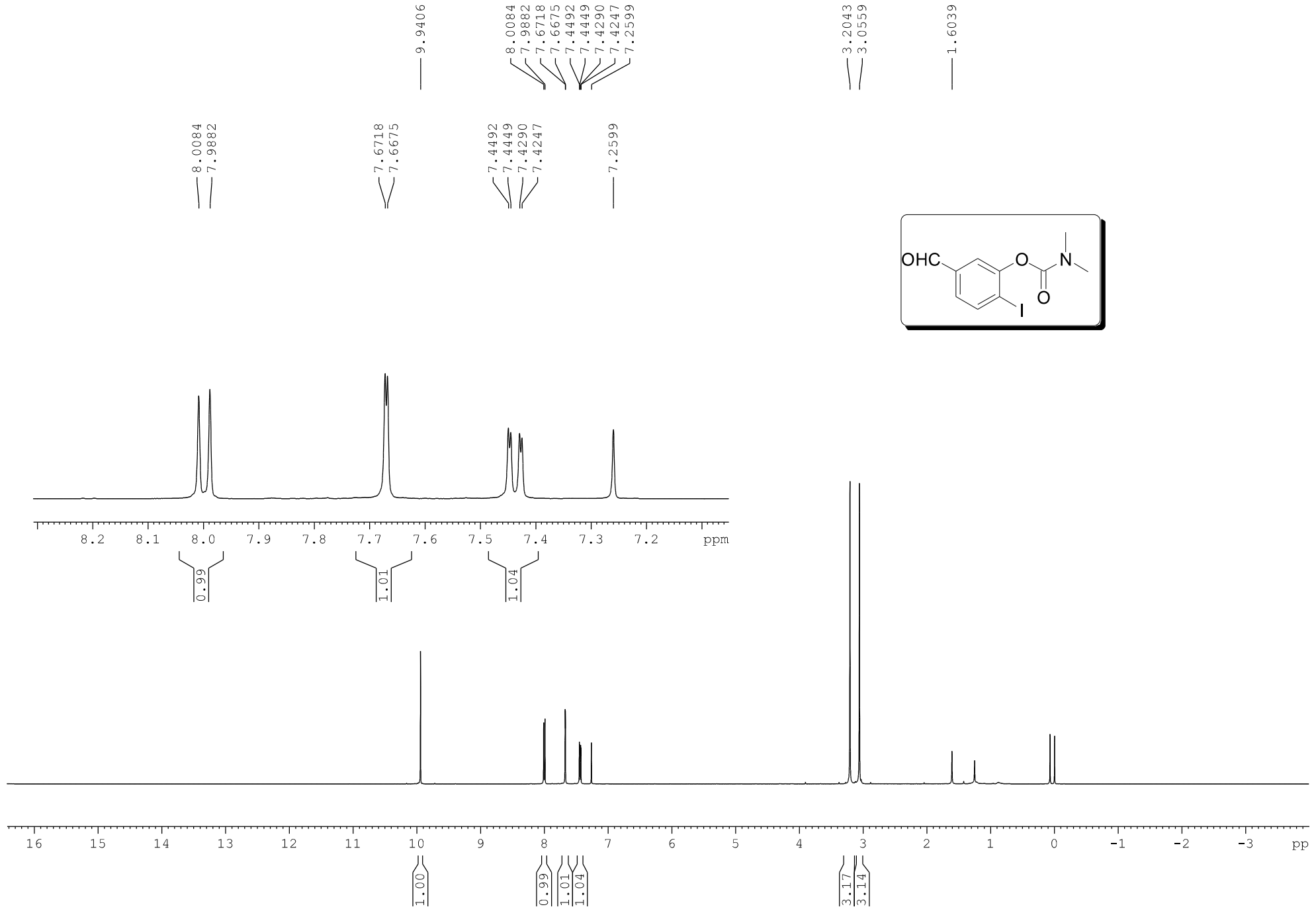


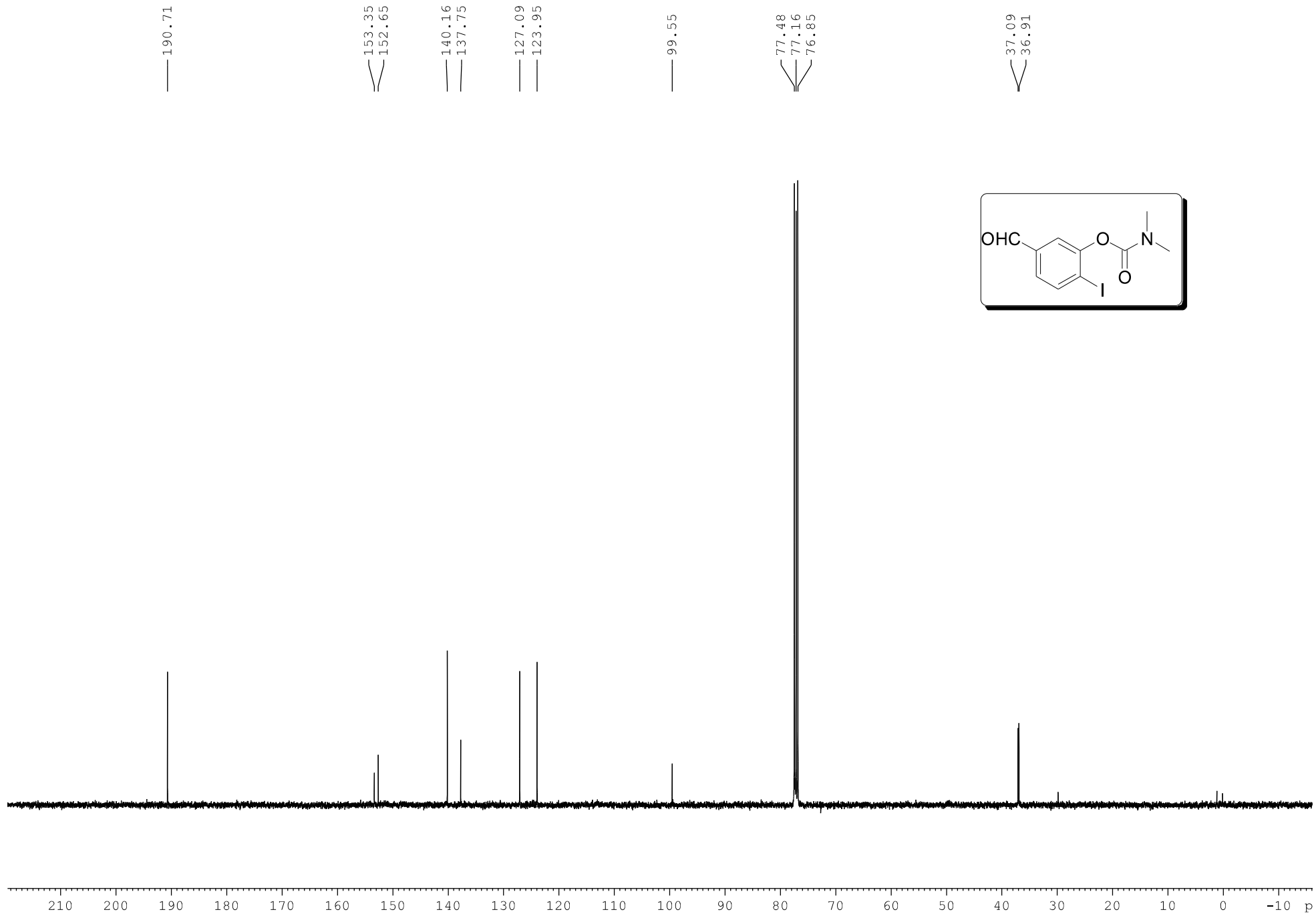


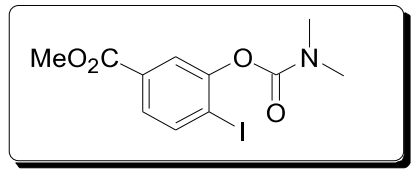
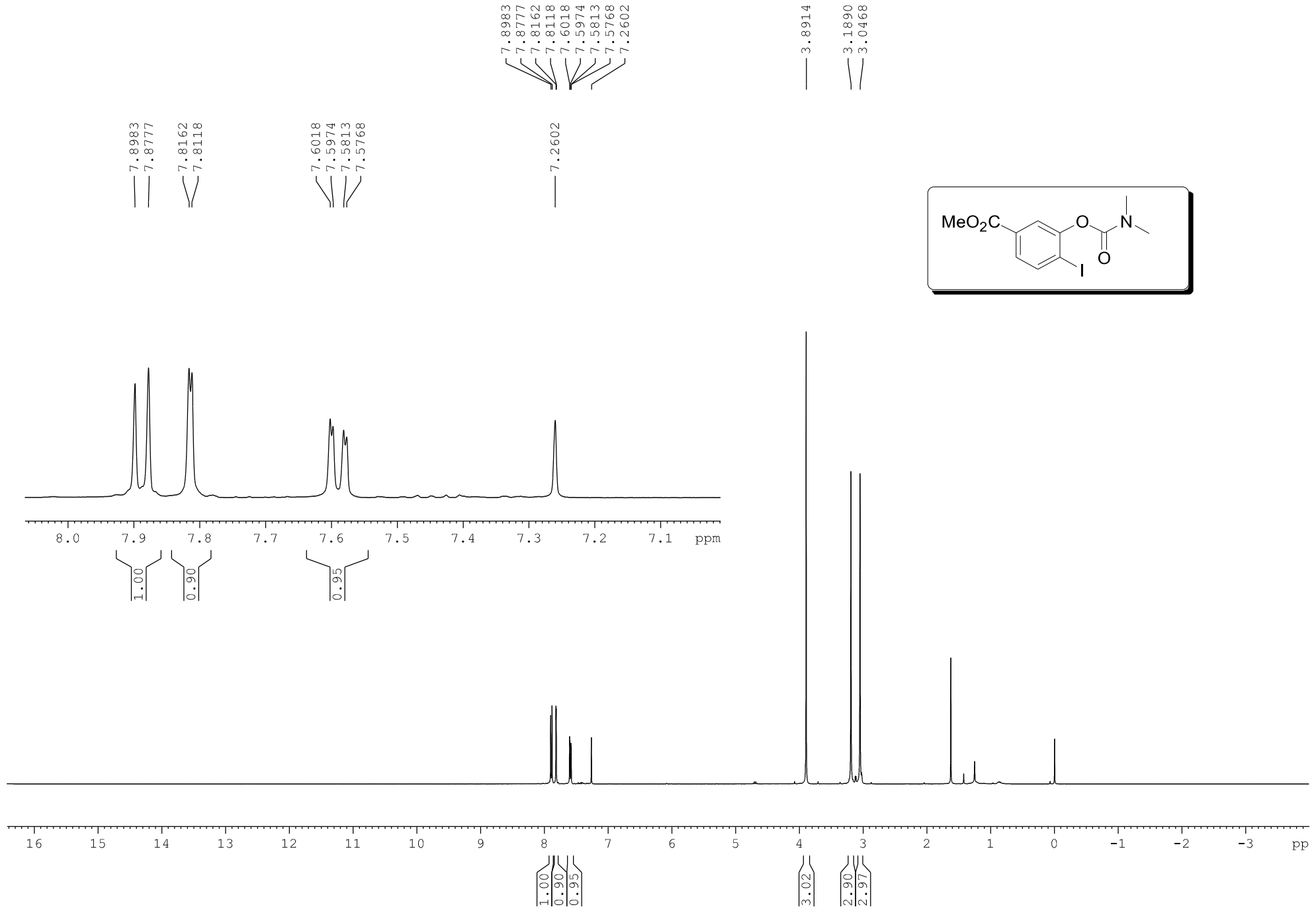


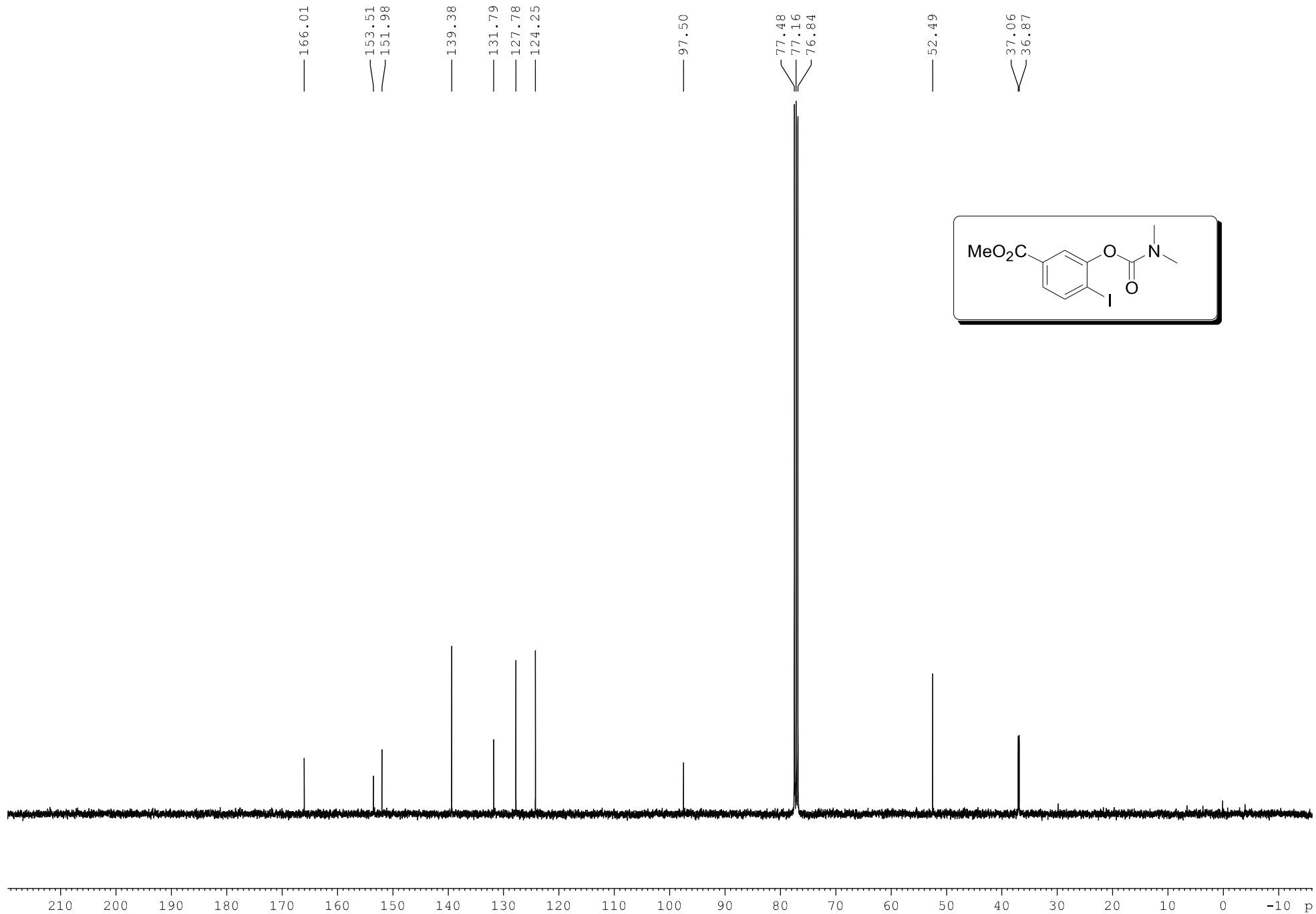
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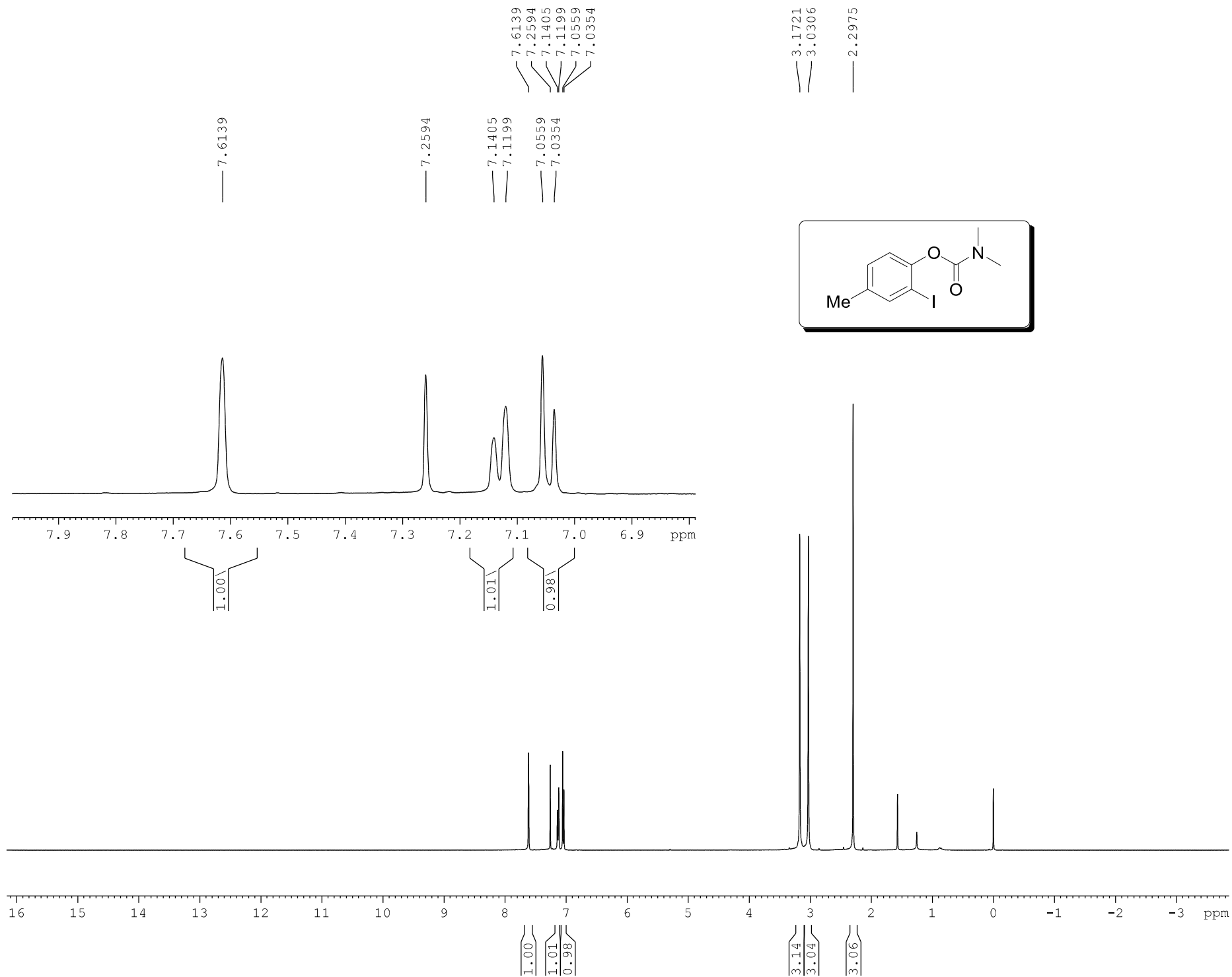


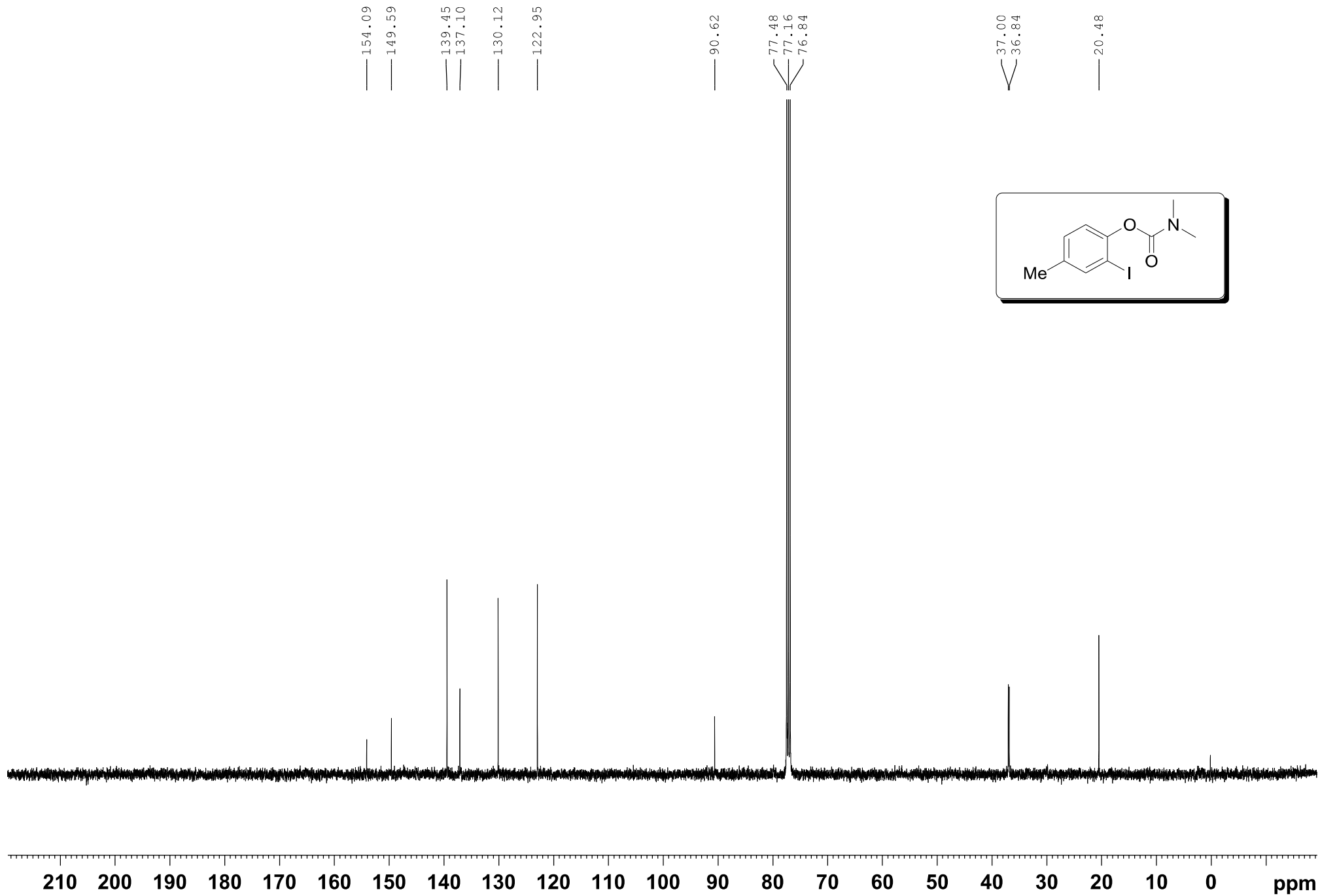


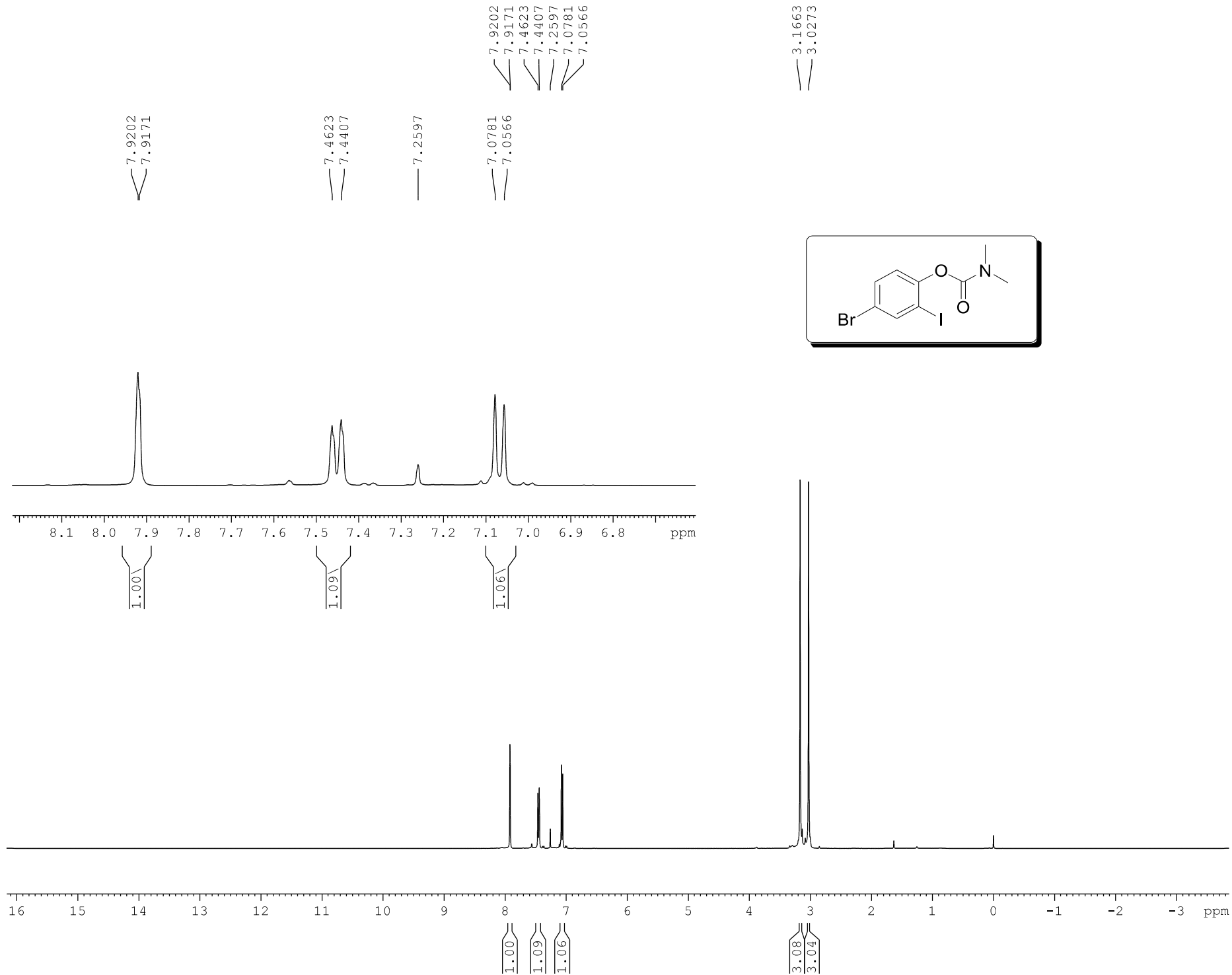


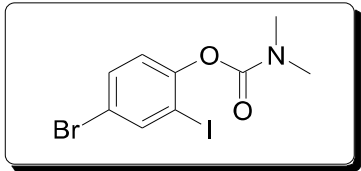
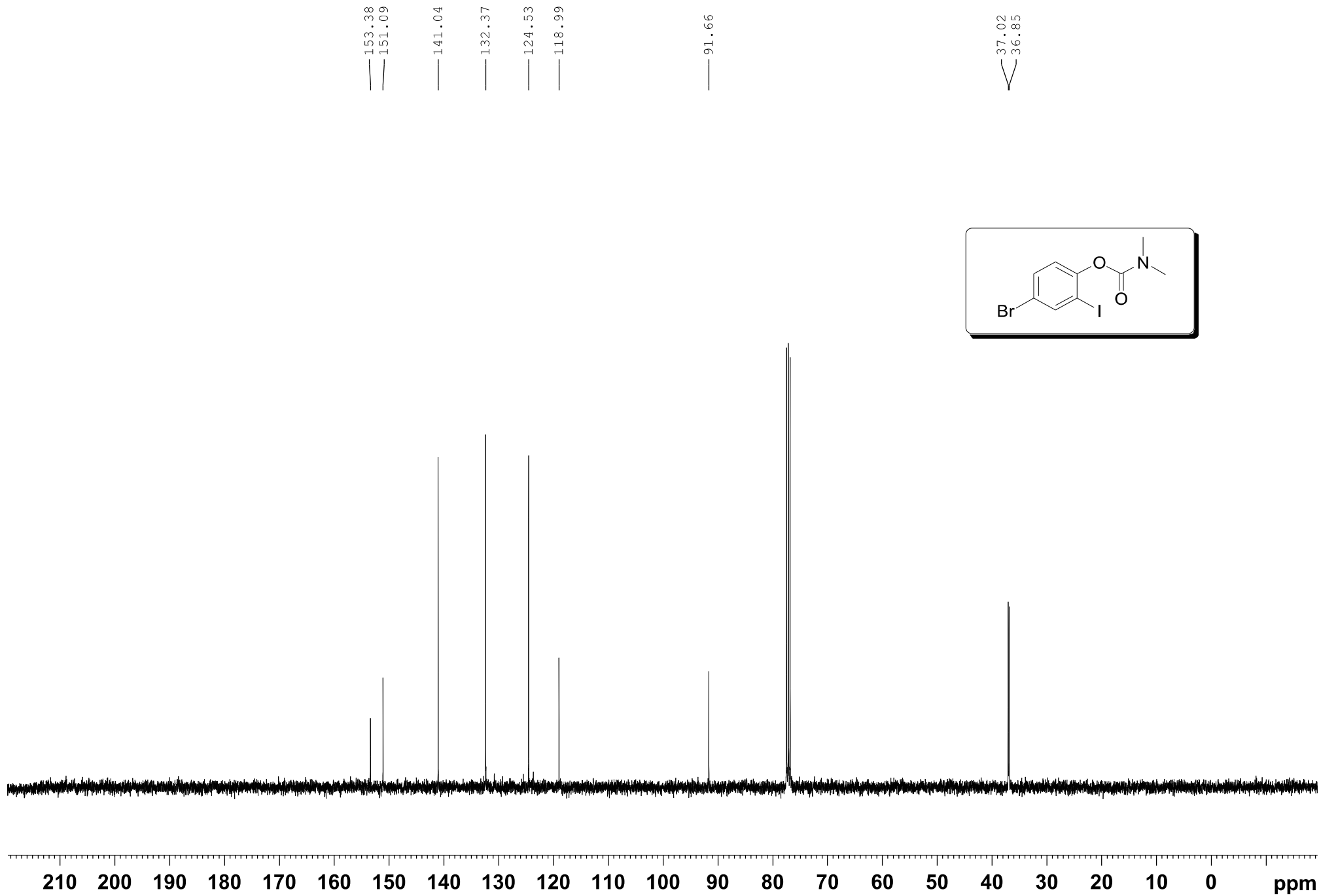


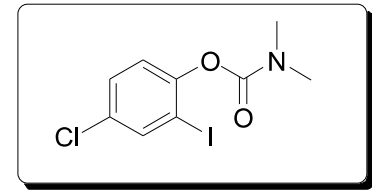
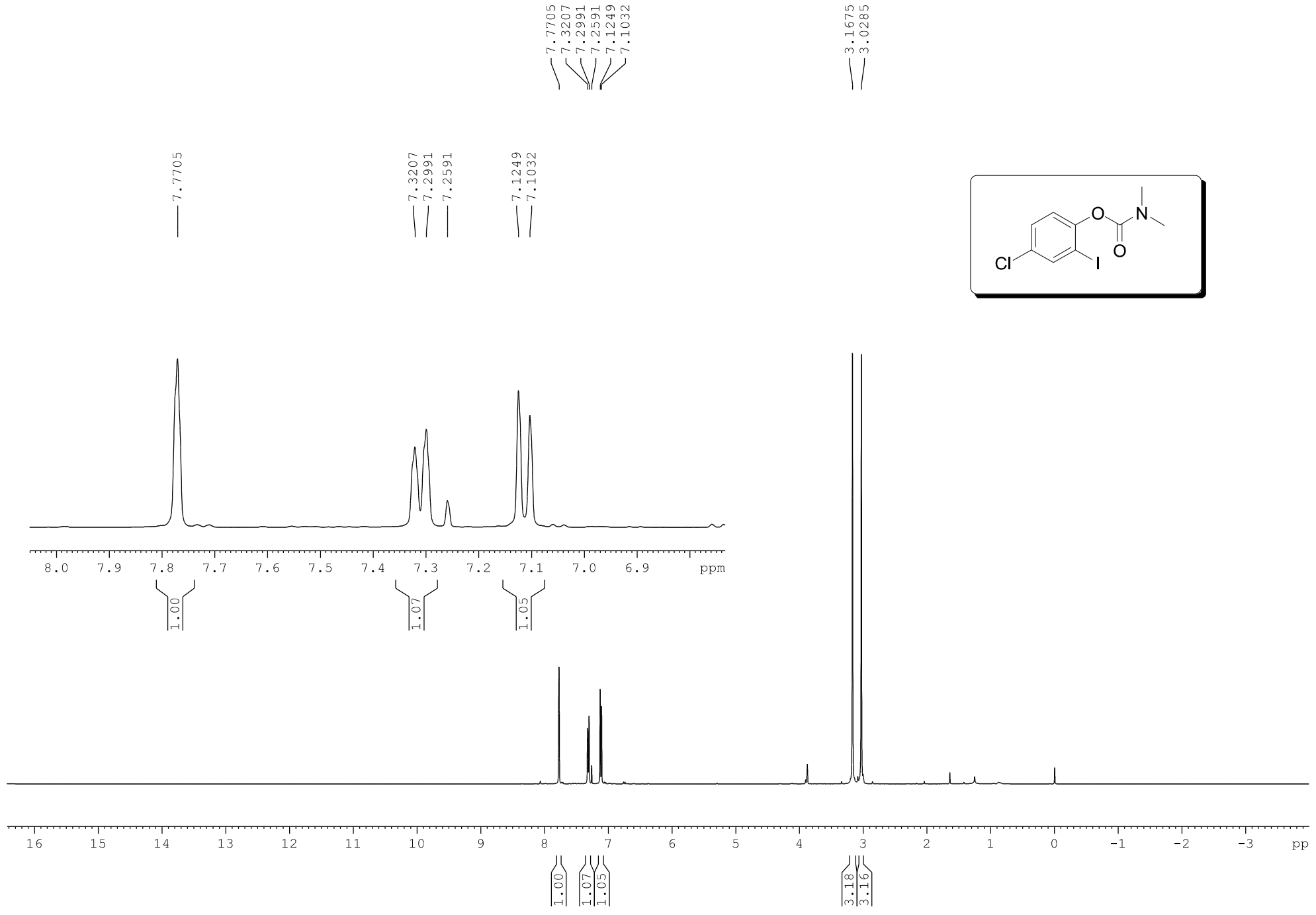


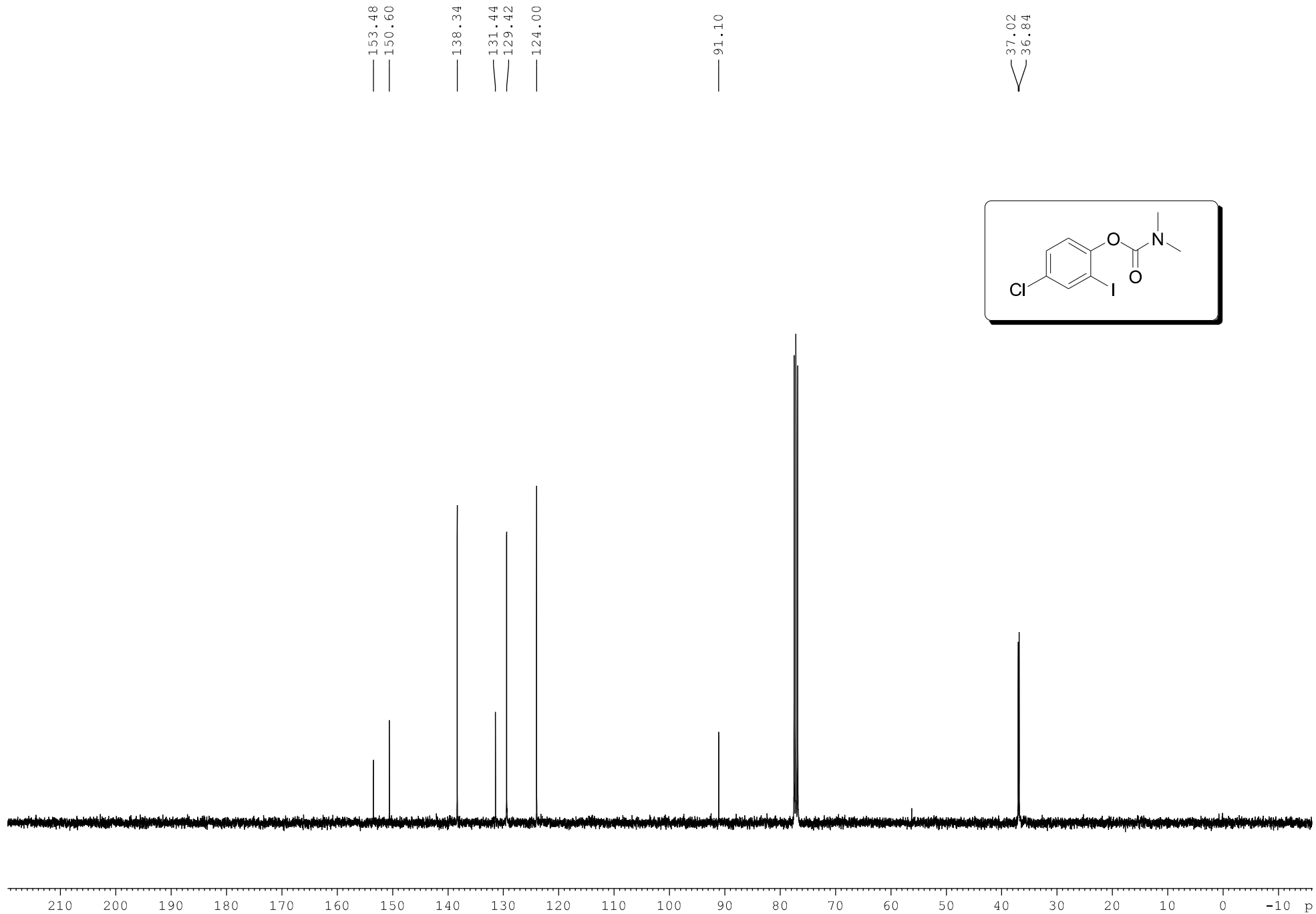












153.48
150.60

138.34

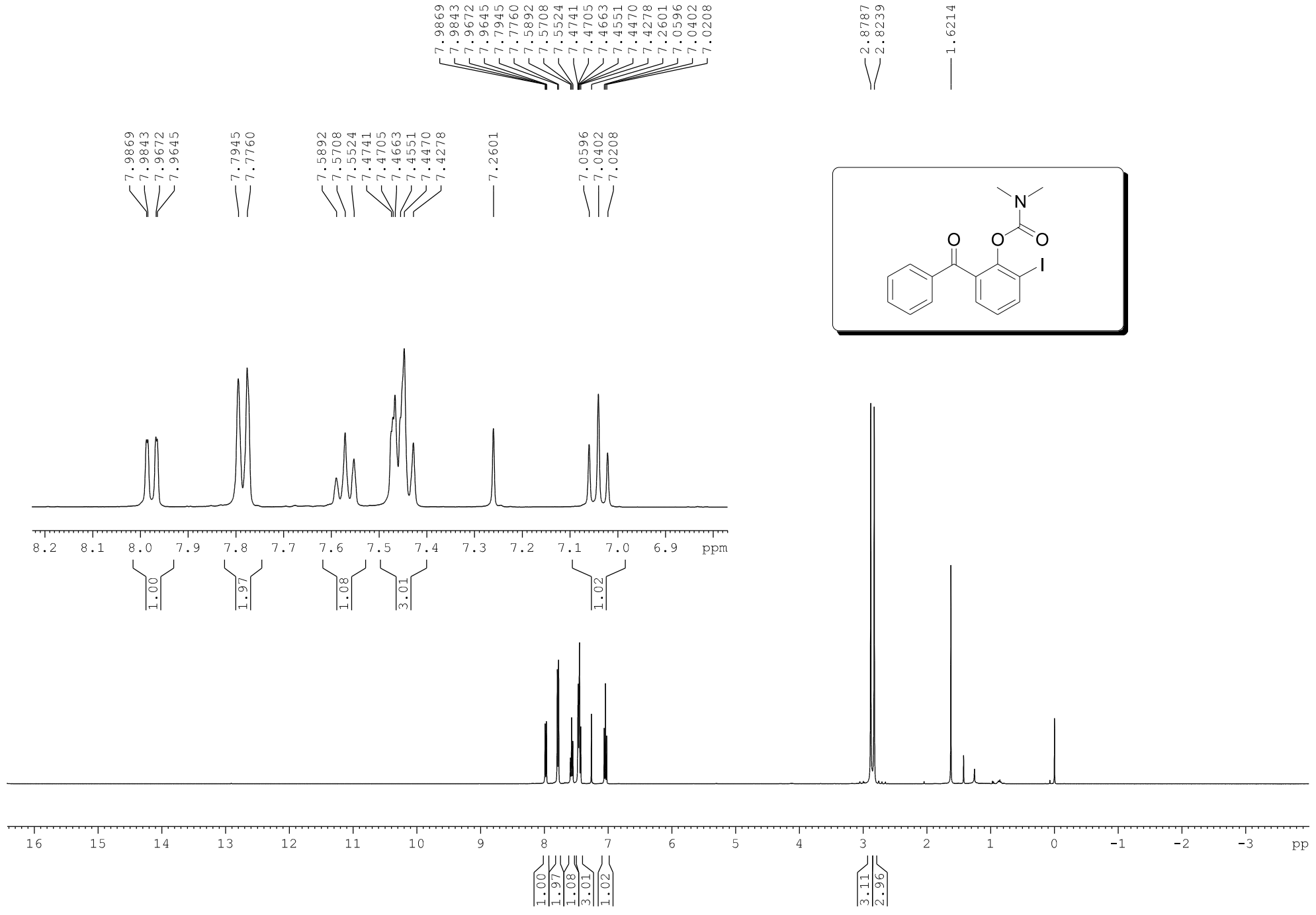
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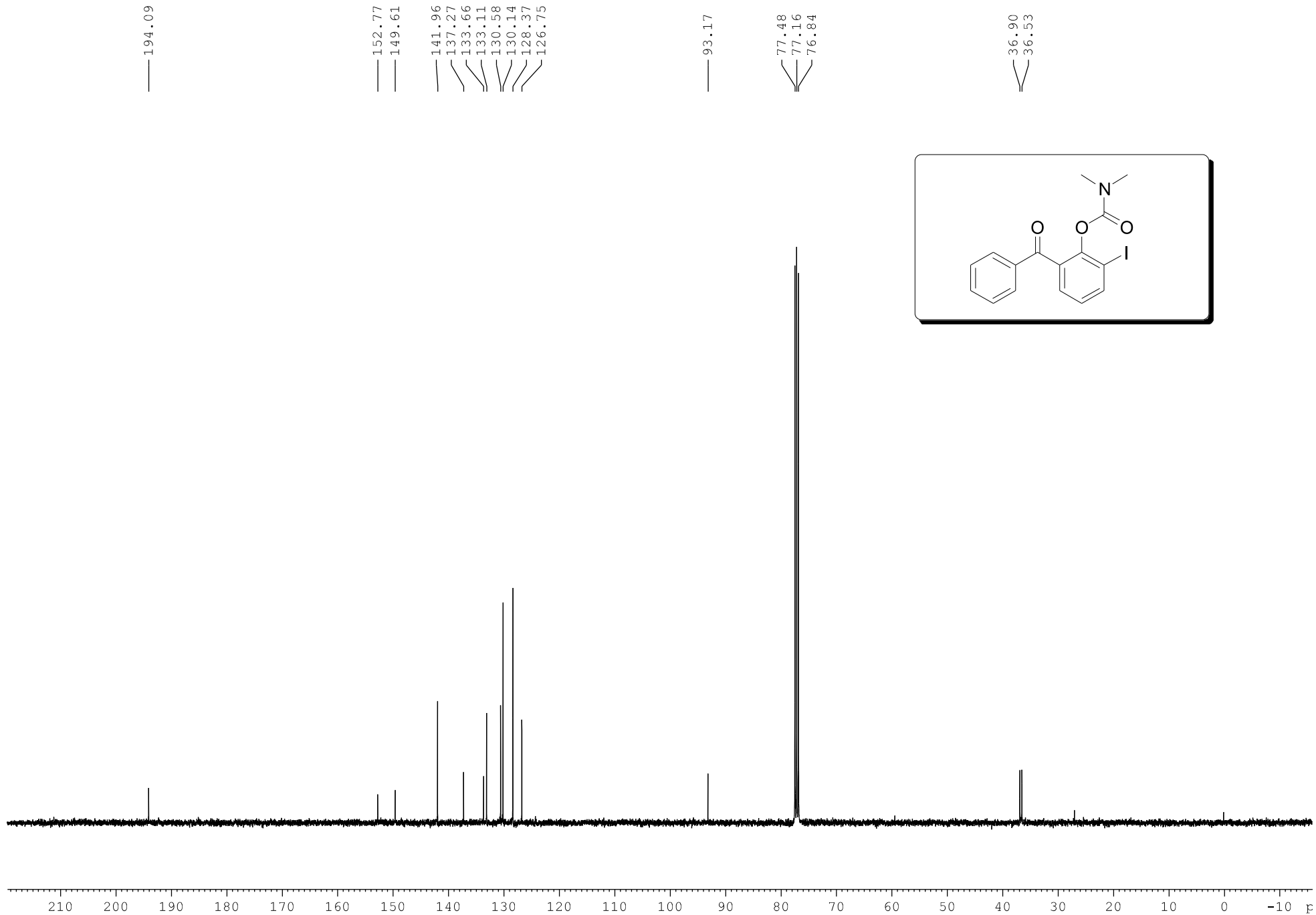
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37.02
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194.09

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133.66

133.11

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93.17

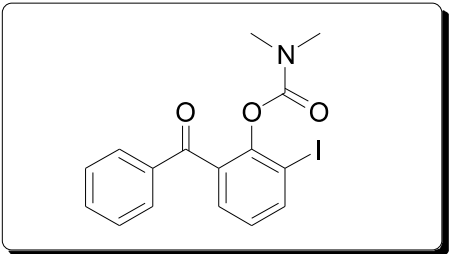
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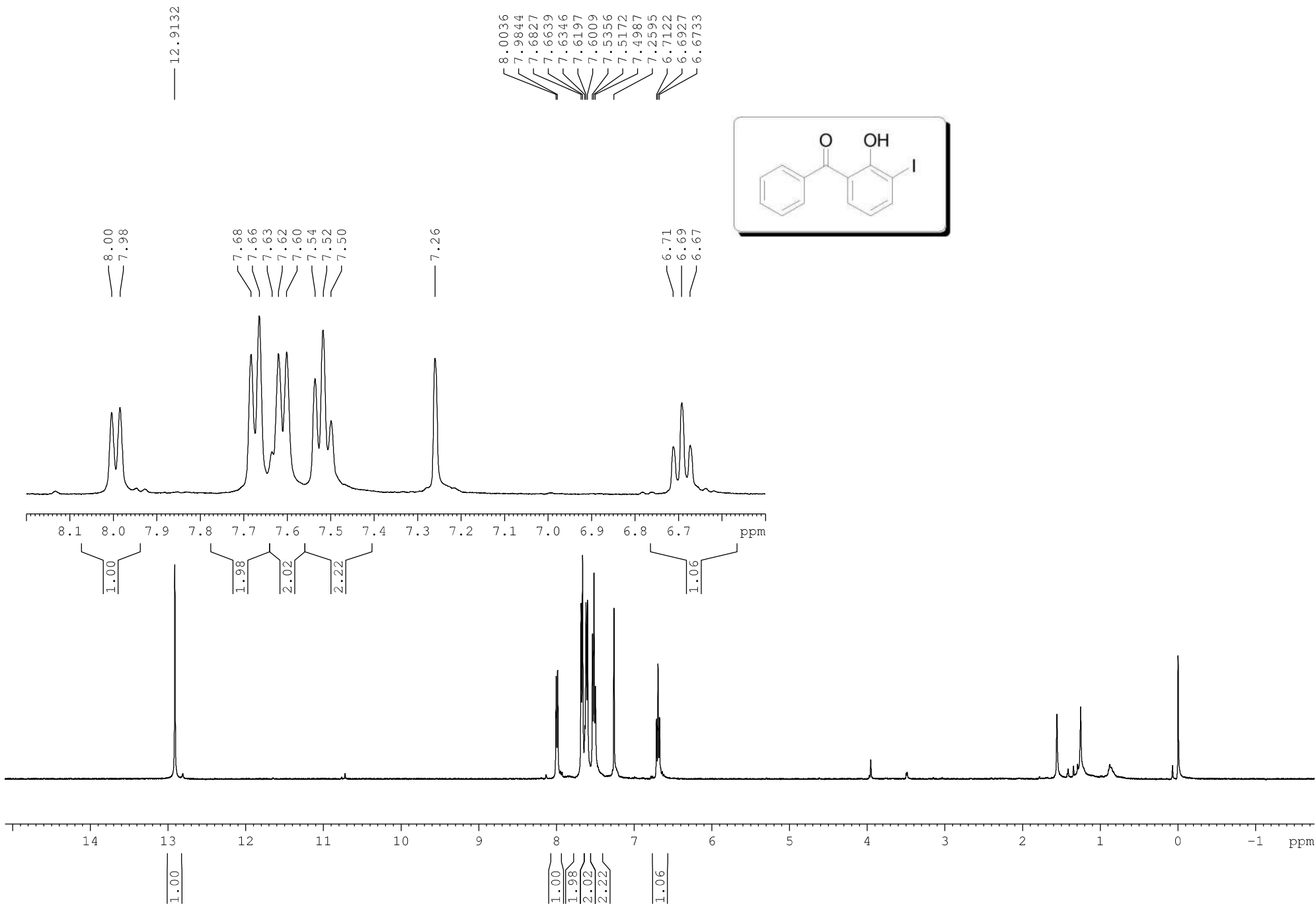
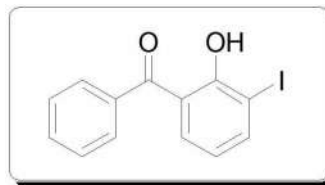
77.16

76.84

36.90

36.53





— 201.29

— 161.94

— 145.80

— 137.32

— 134.01

— 132.47

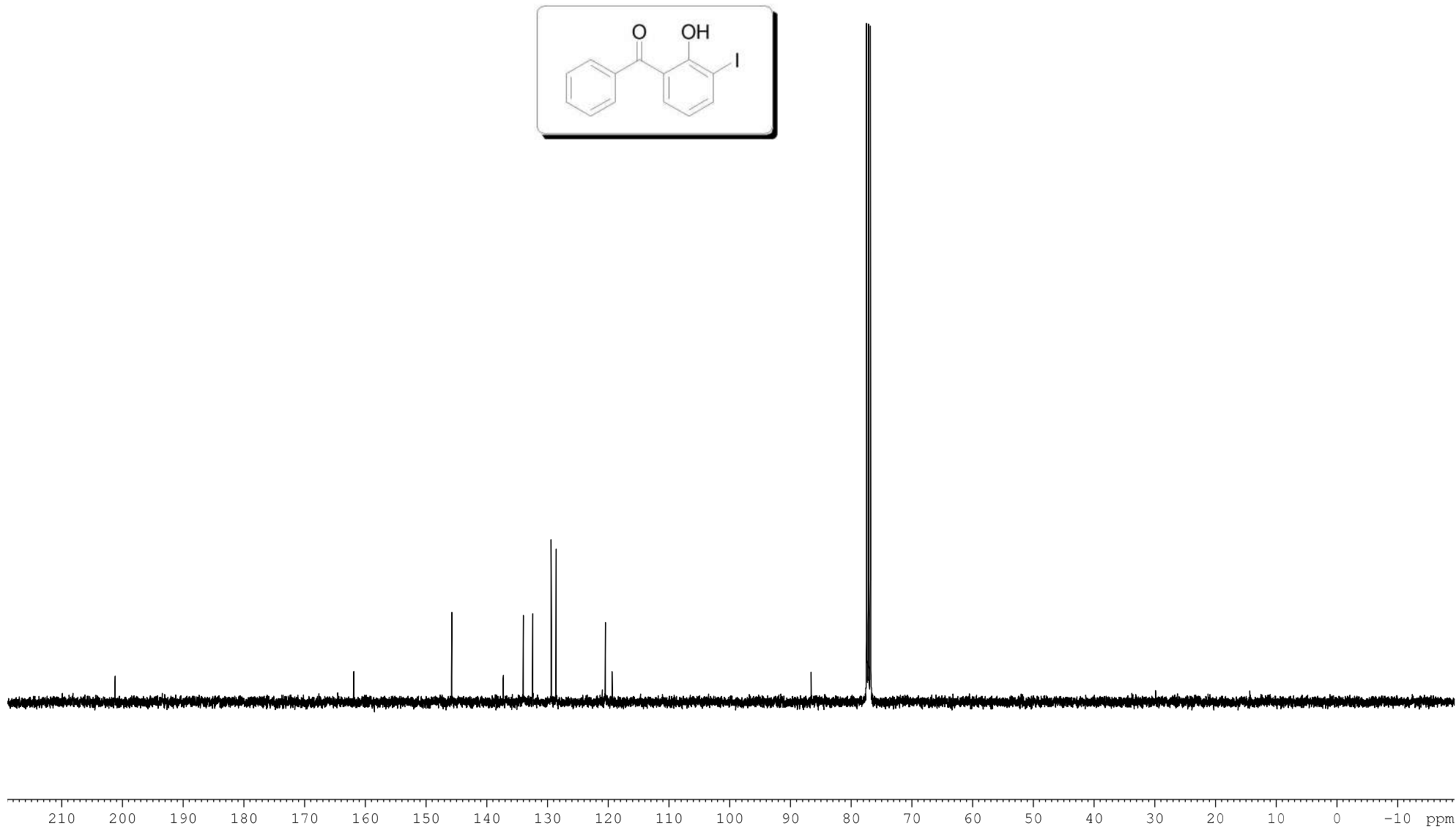
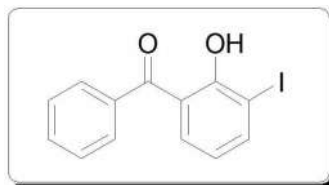
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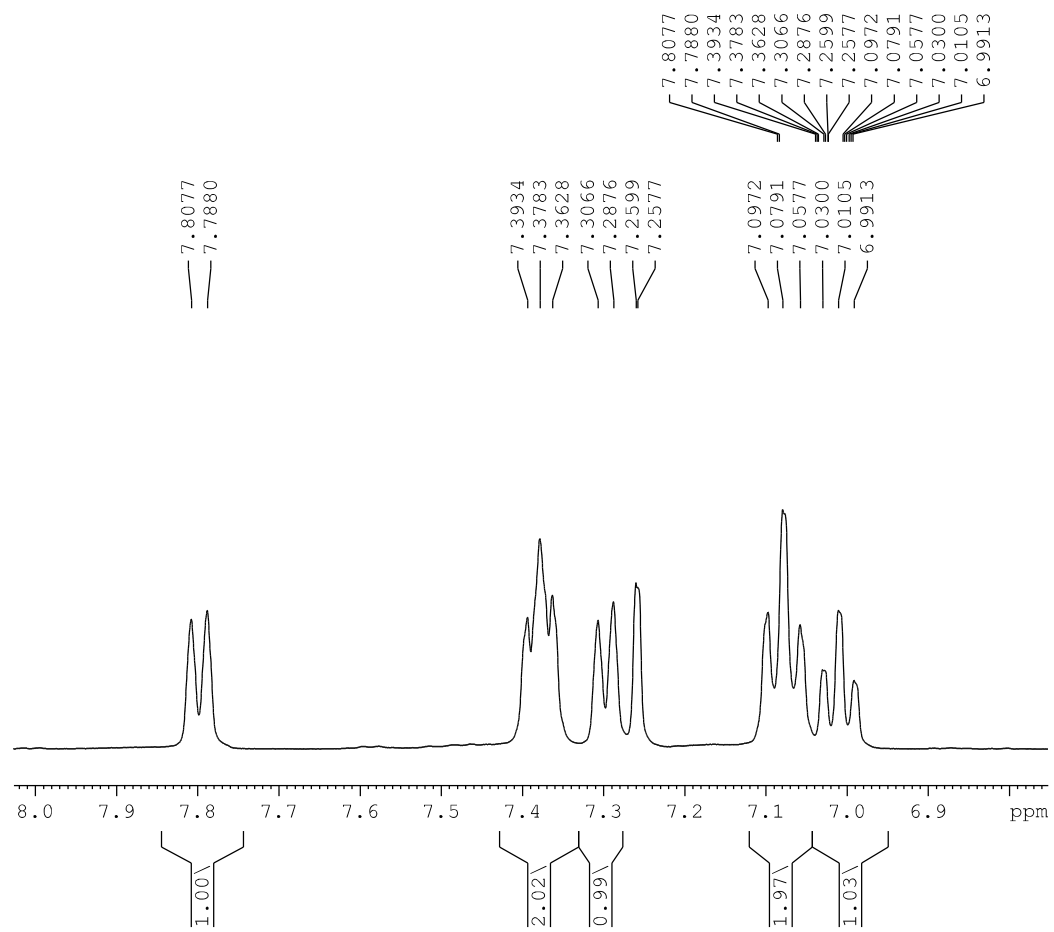
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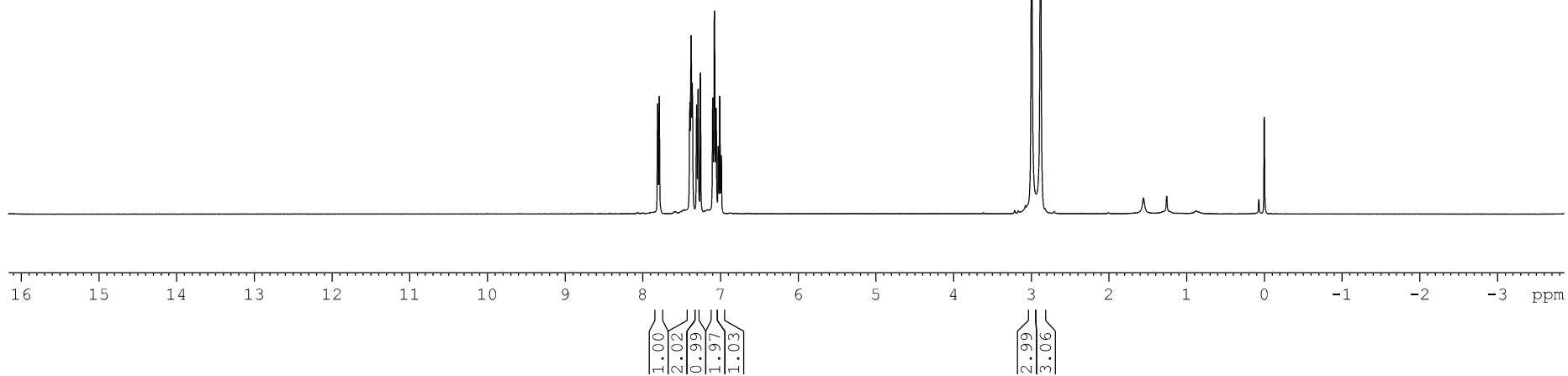
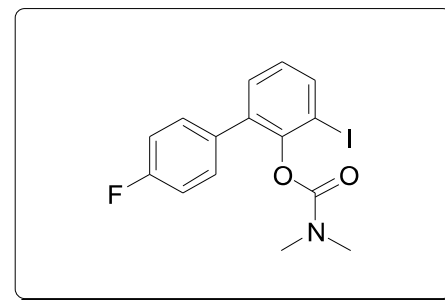
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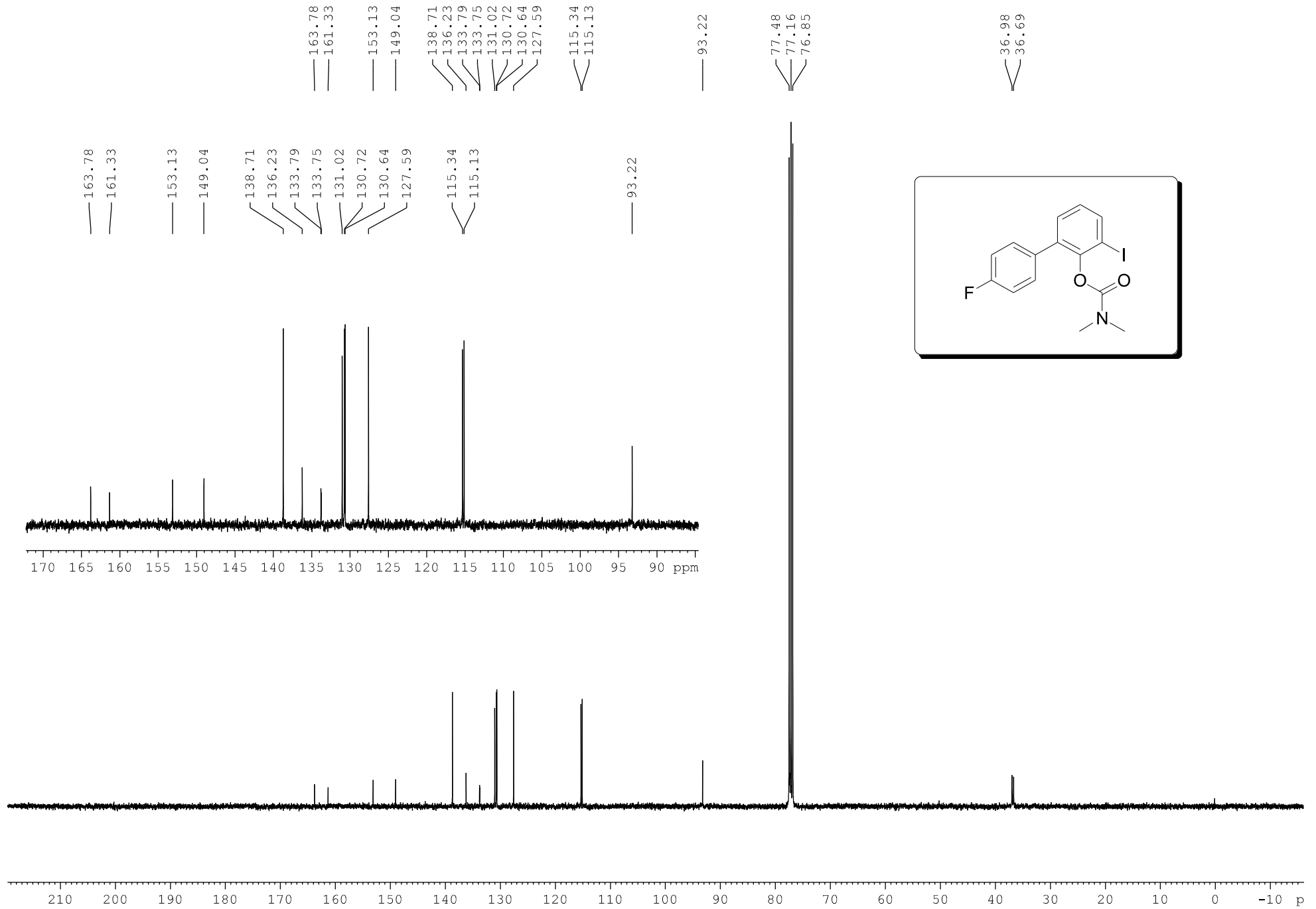
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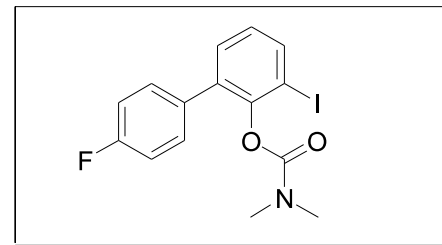




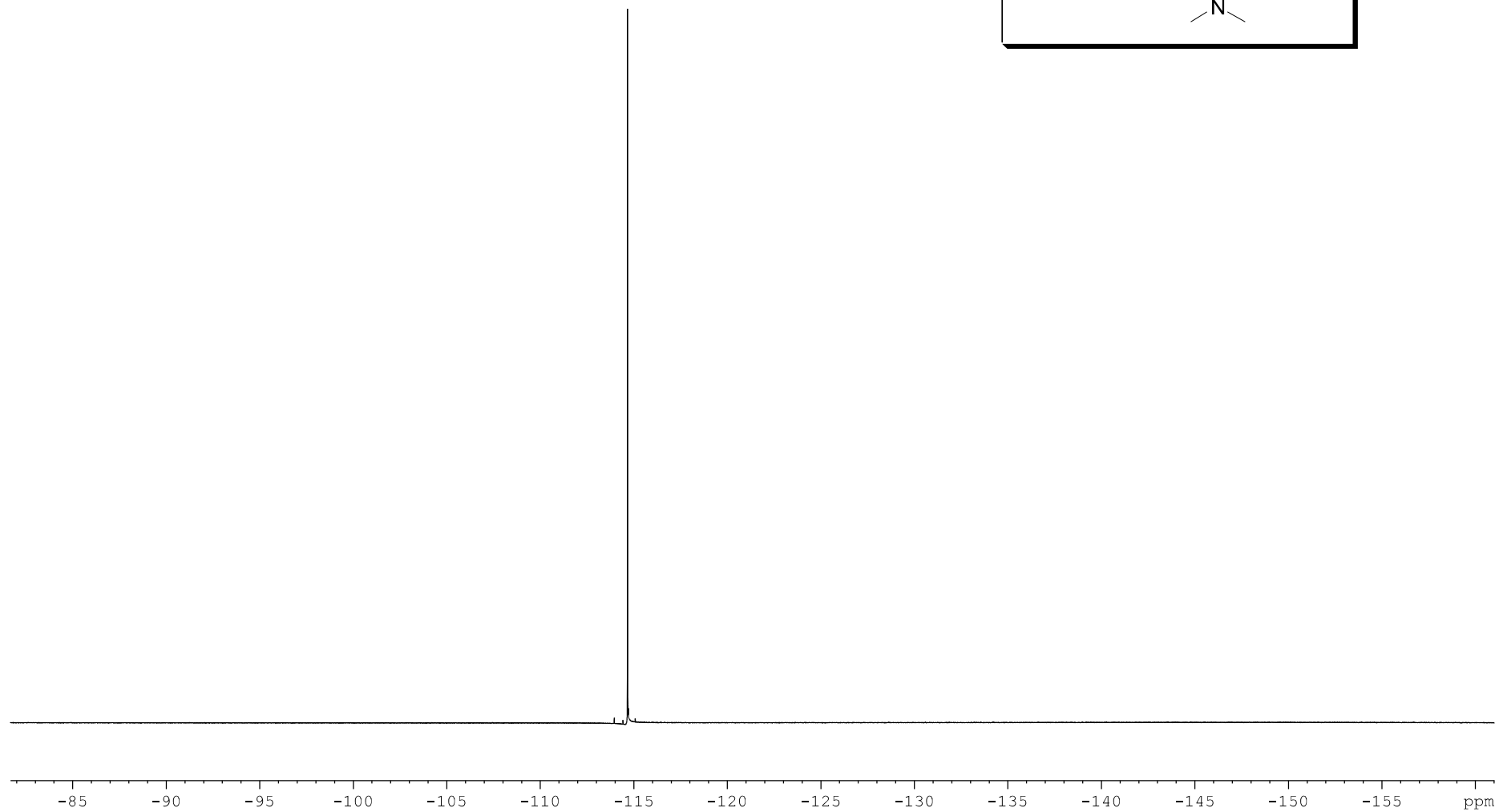
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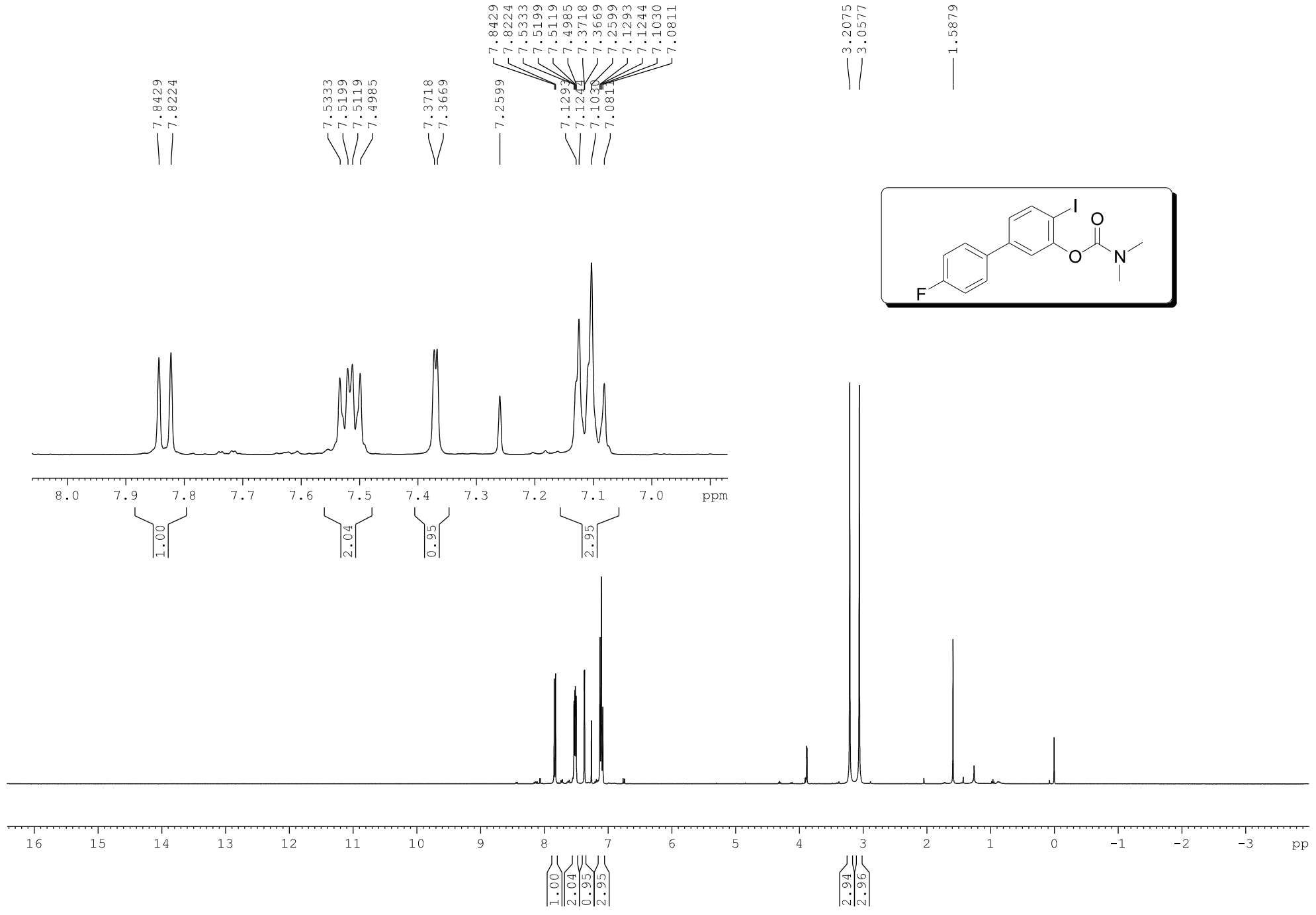


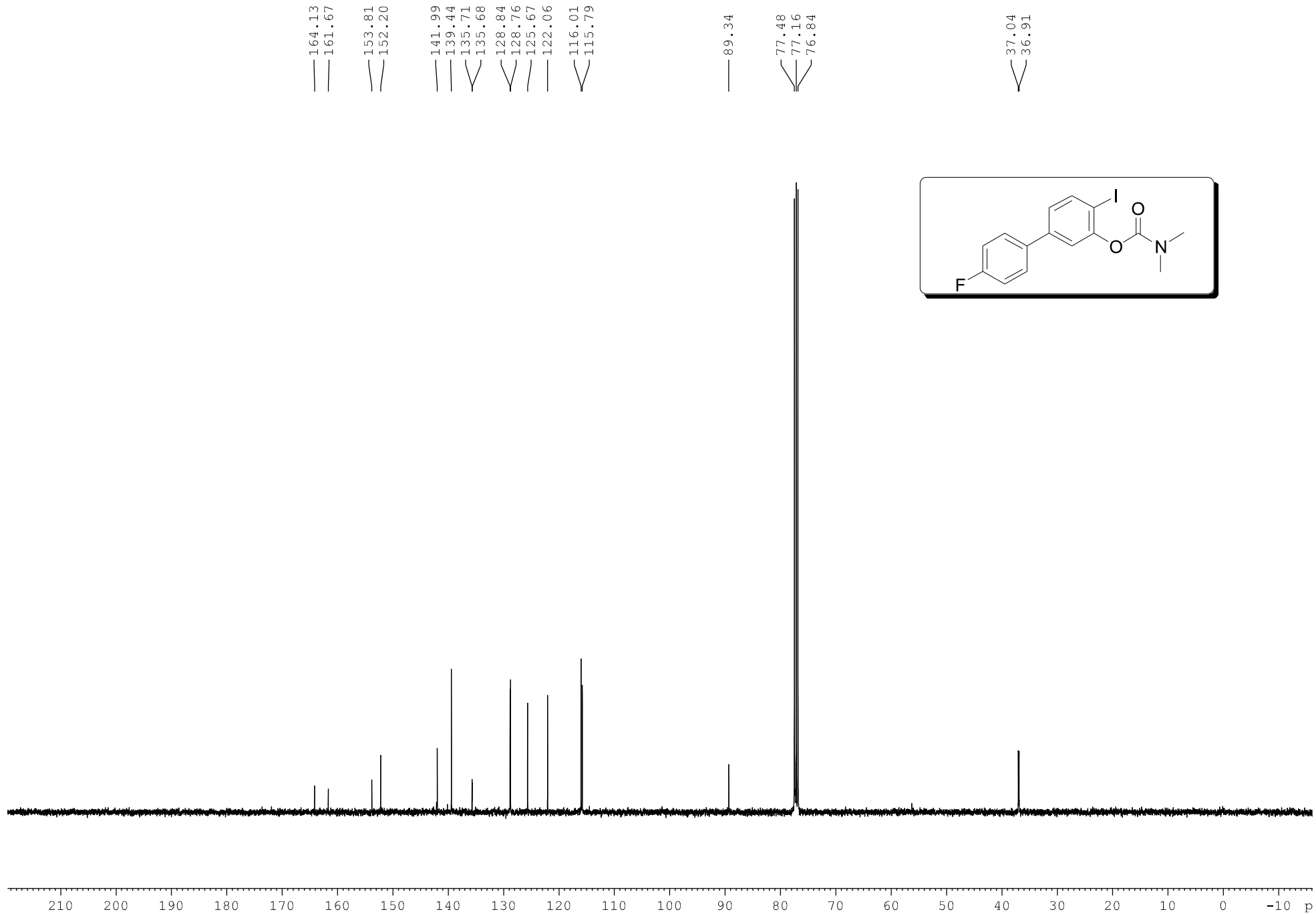


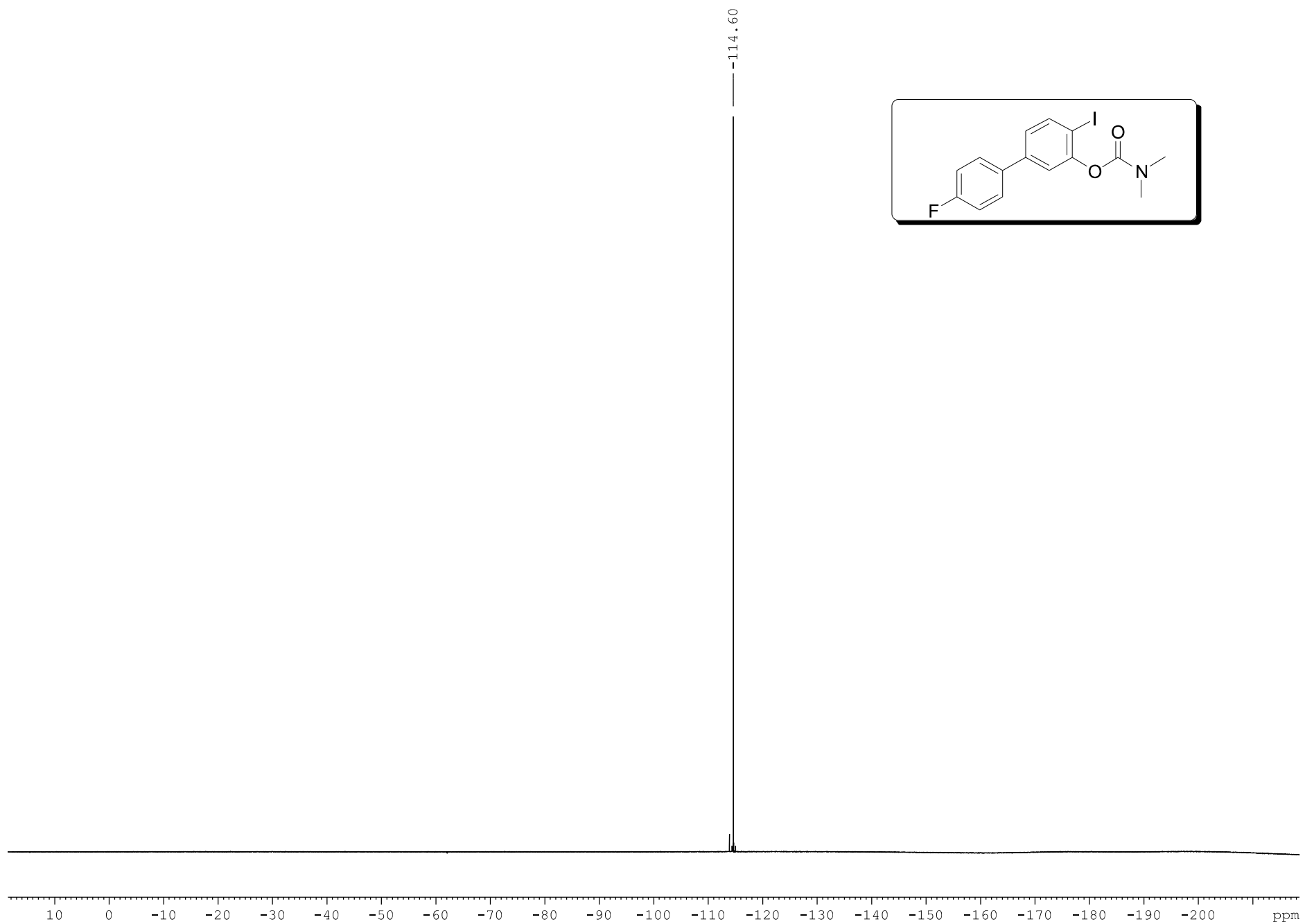


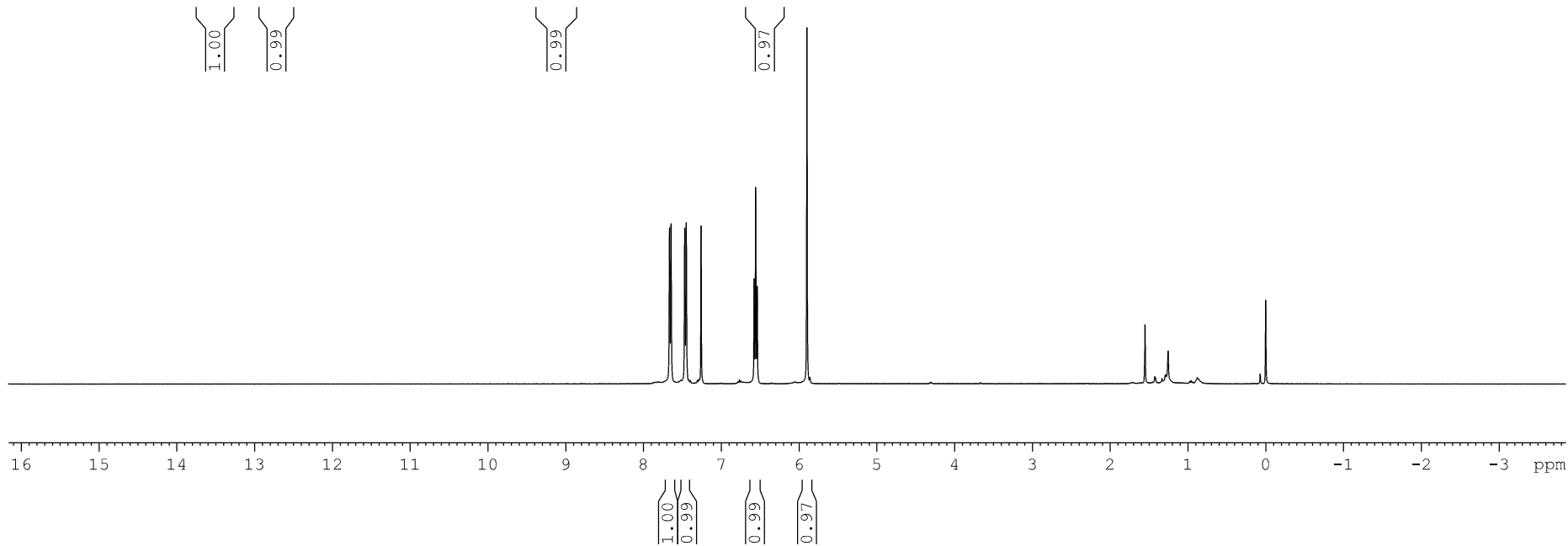
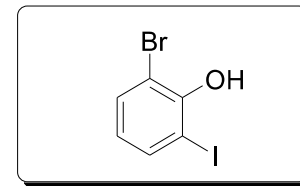
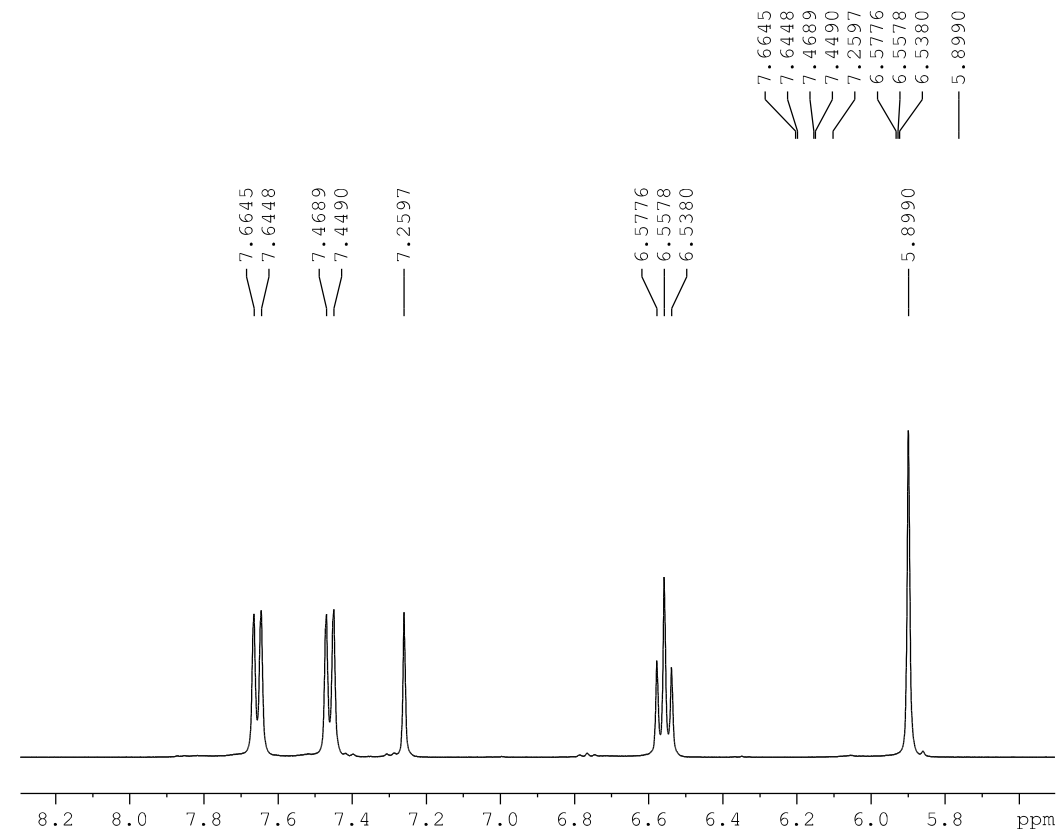
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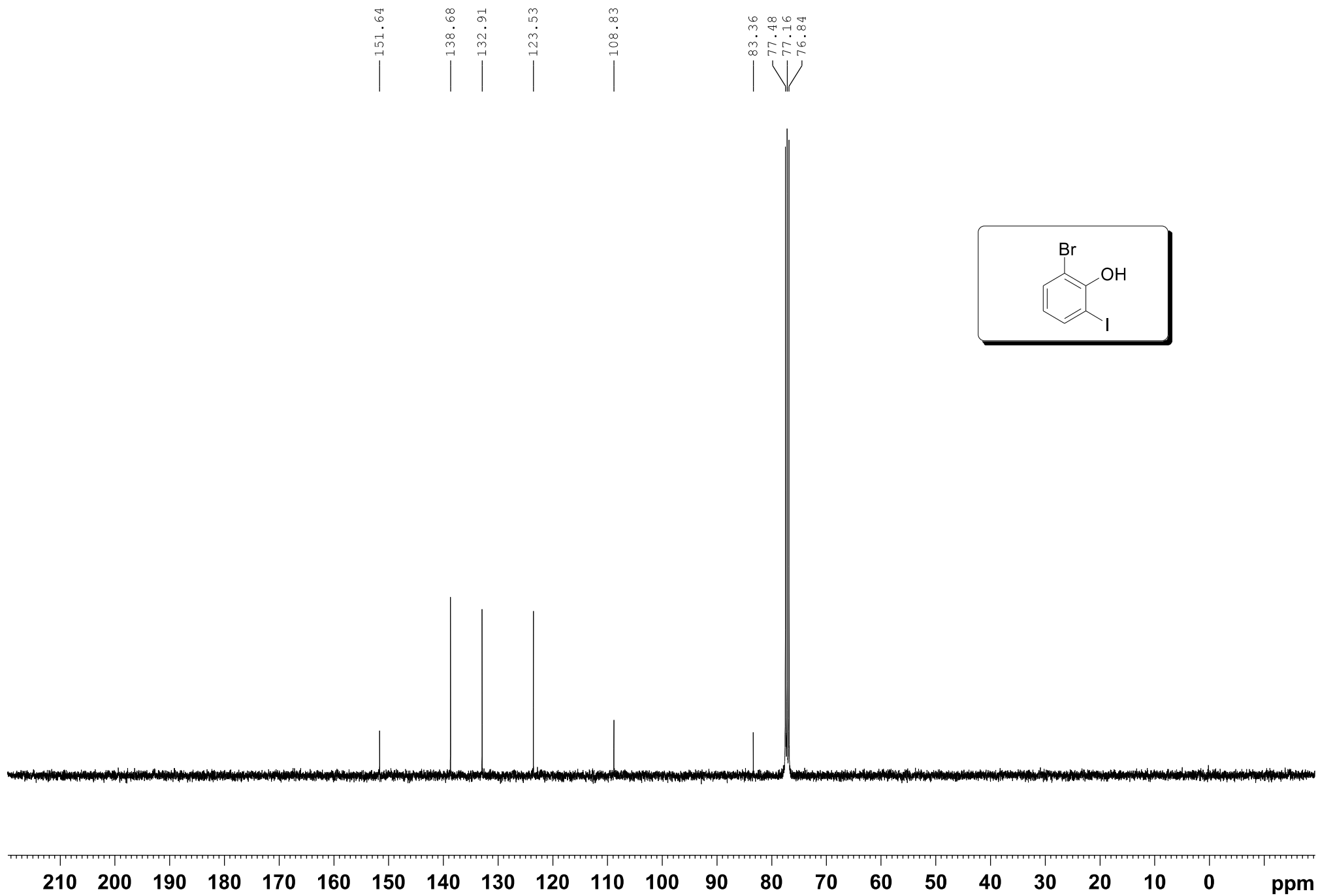


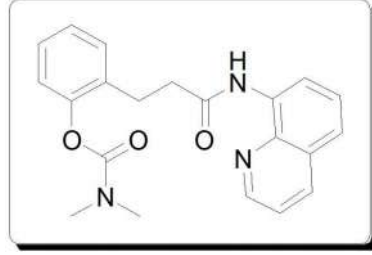
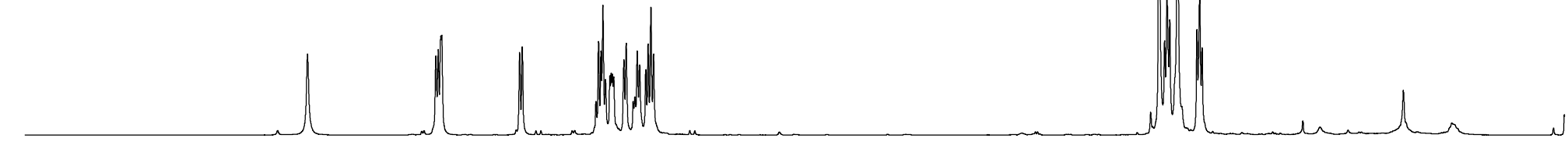
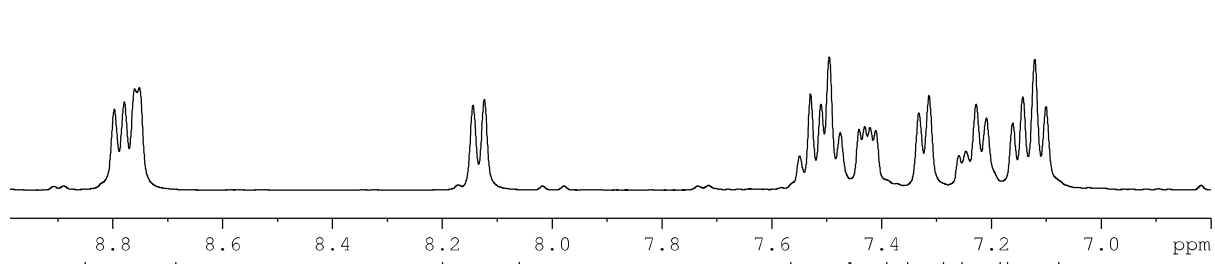












9.7971

8.7971
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7.5297
7.5106
7.4956
7.4754
7.4412
7.4310
7.4211
7.4109
7.3323
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7.1007

2.08

1.07

2.17
1.11
1.04
1.22
2.12

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

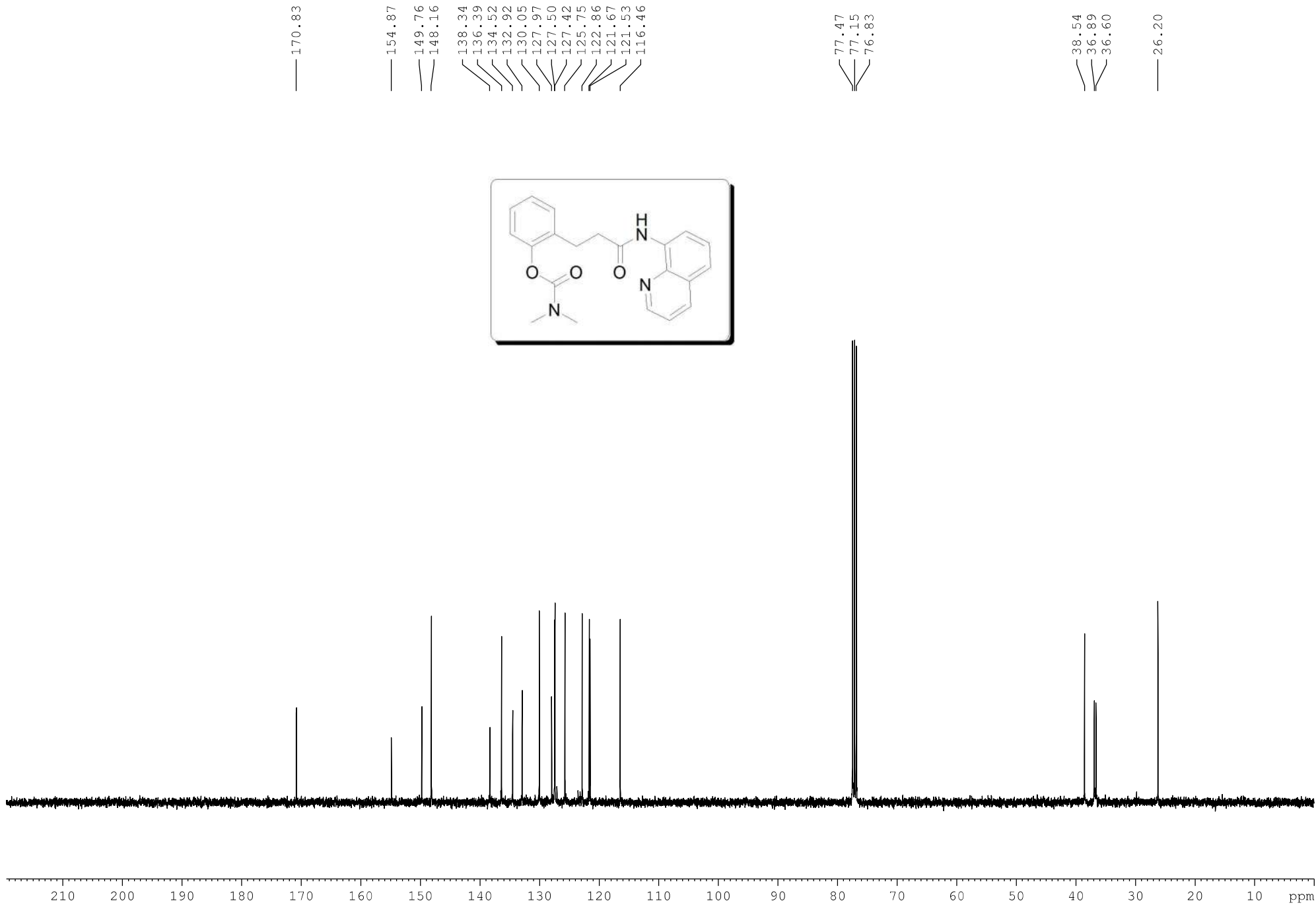
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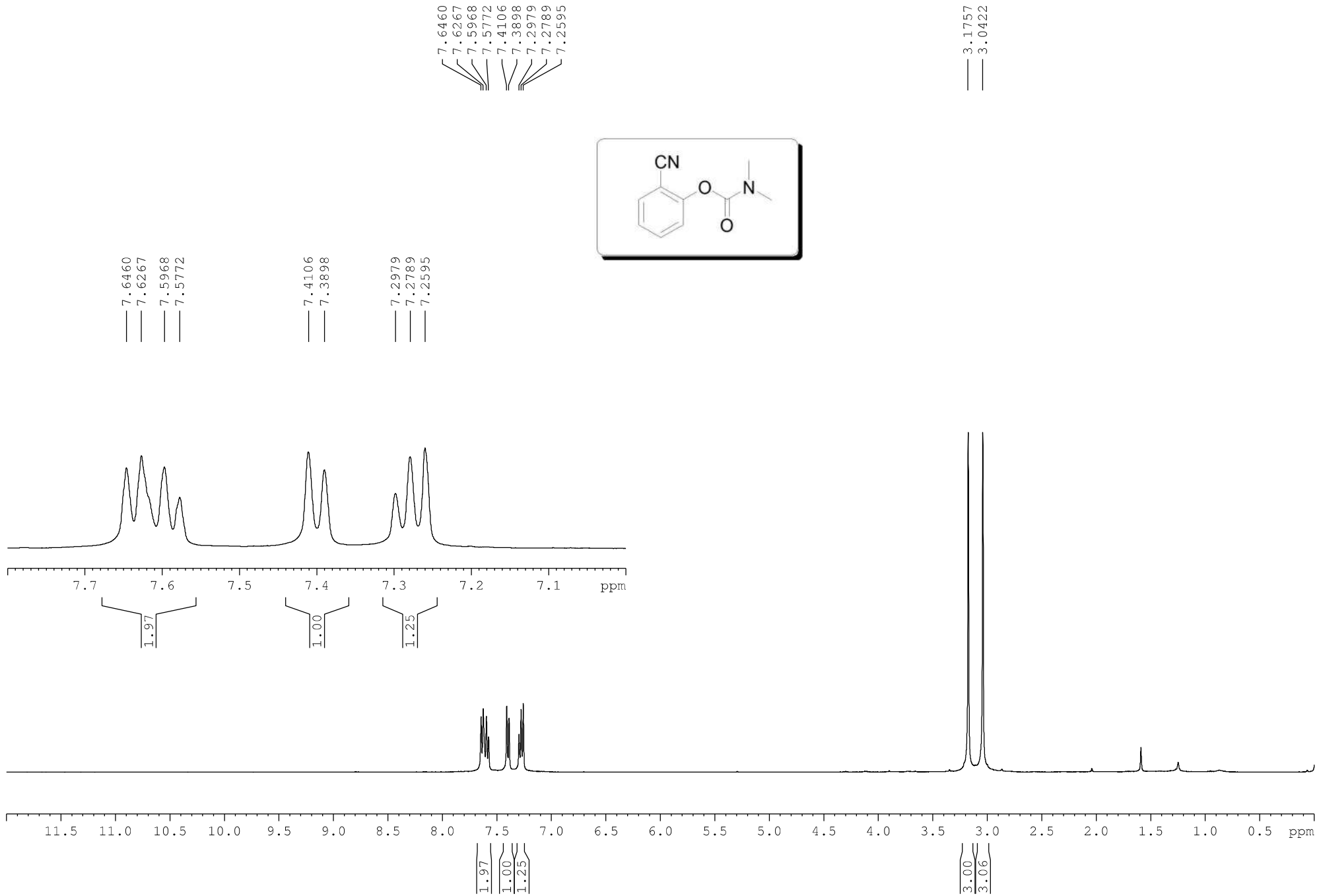
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2.12

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2.97
2.14





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153.24

133.95
133.07

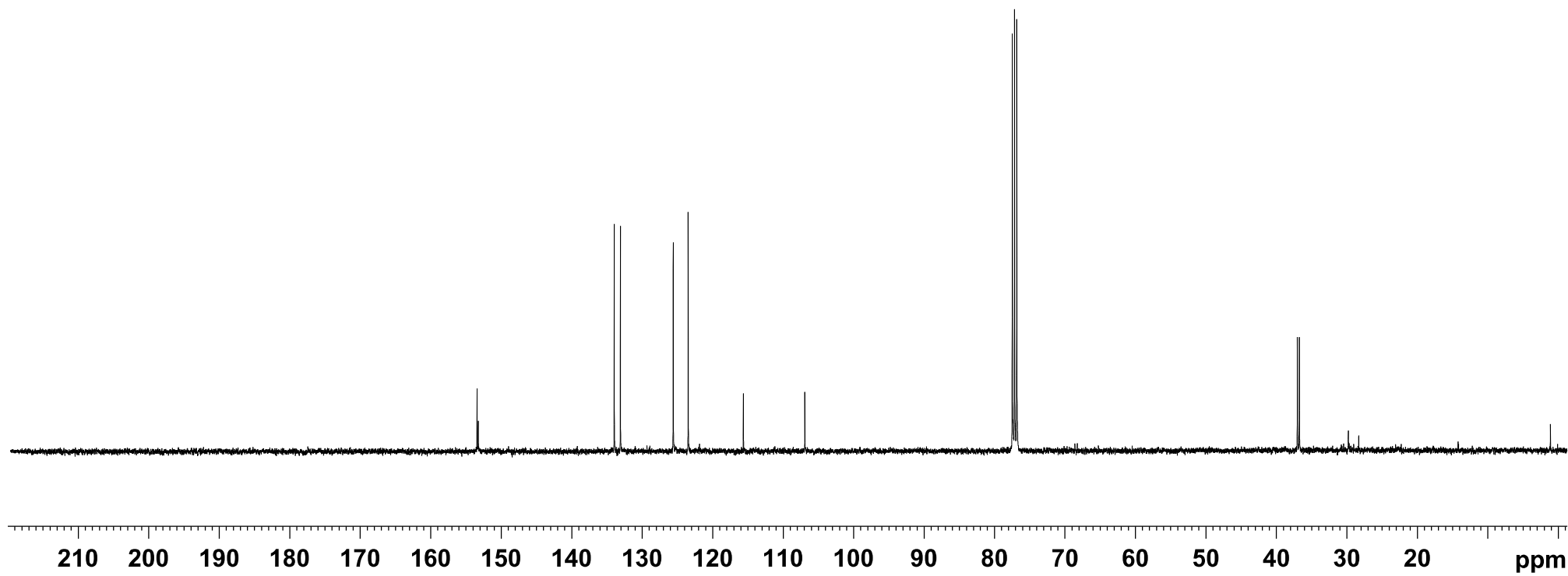
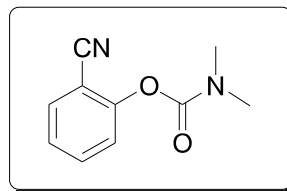
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123.46

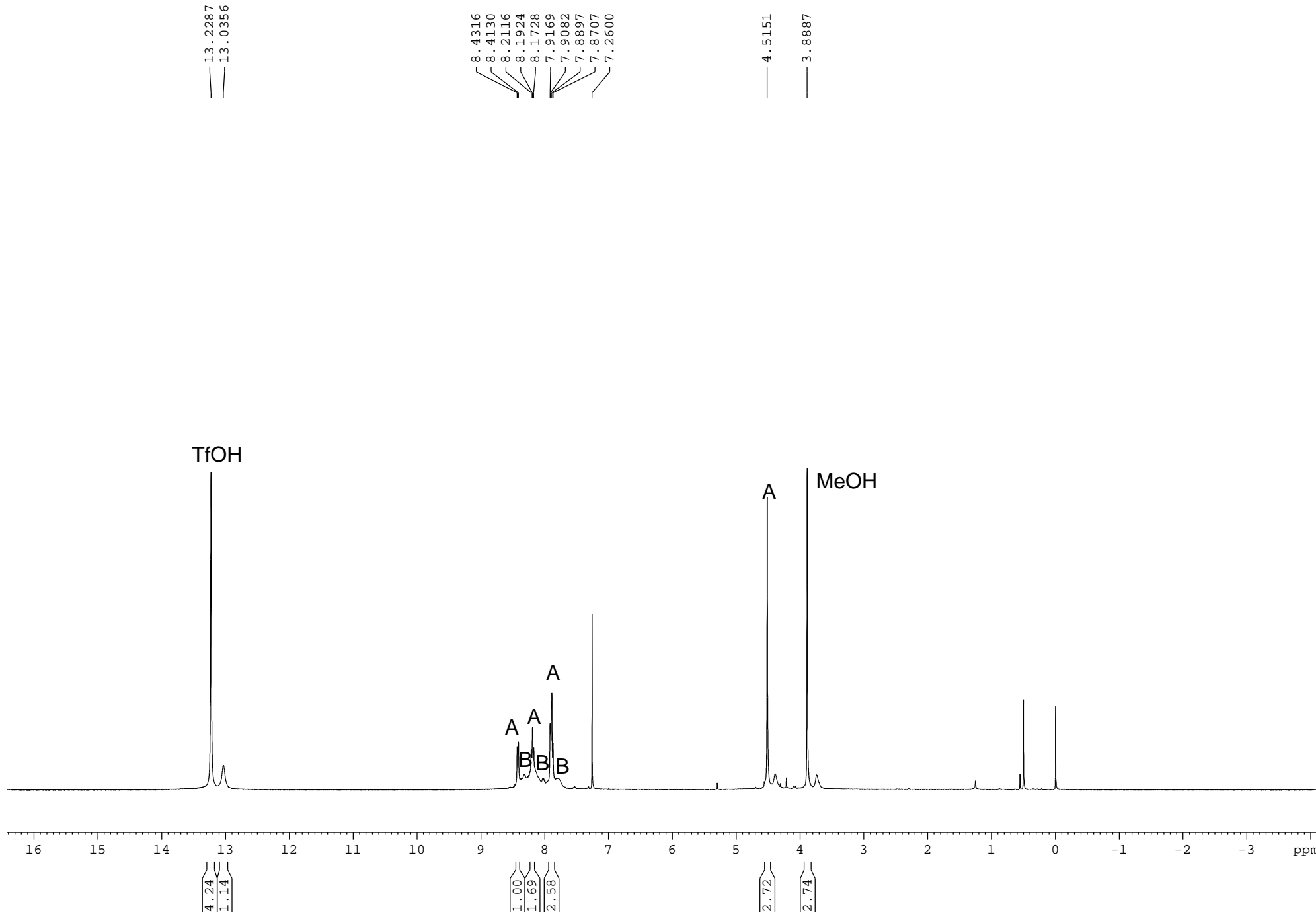
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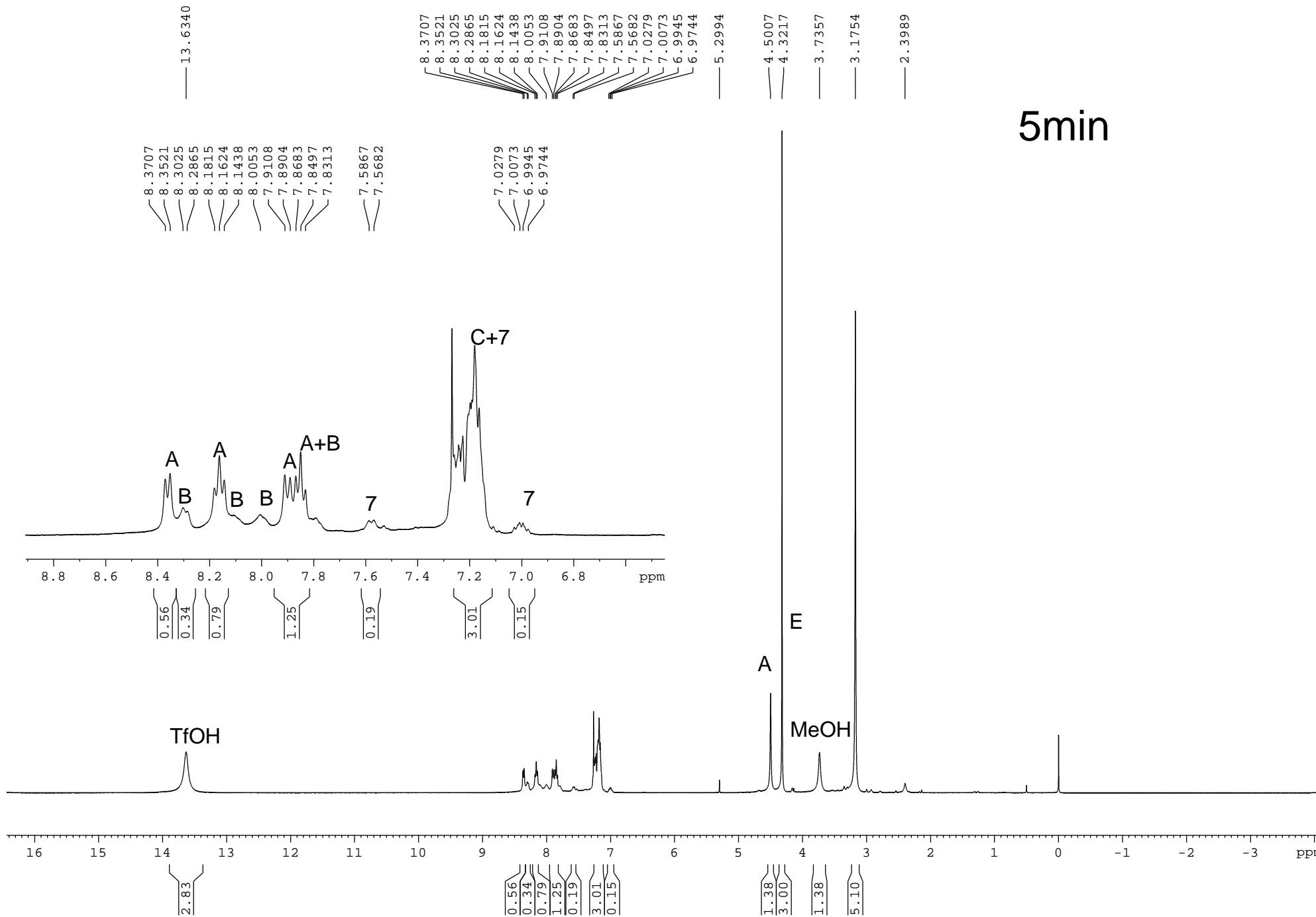
106.91

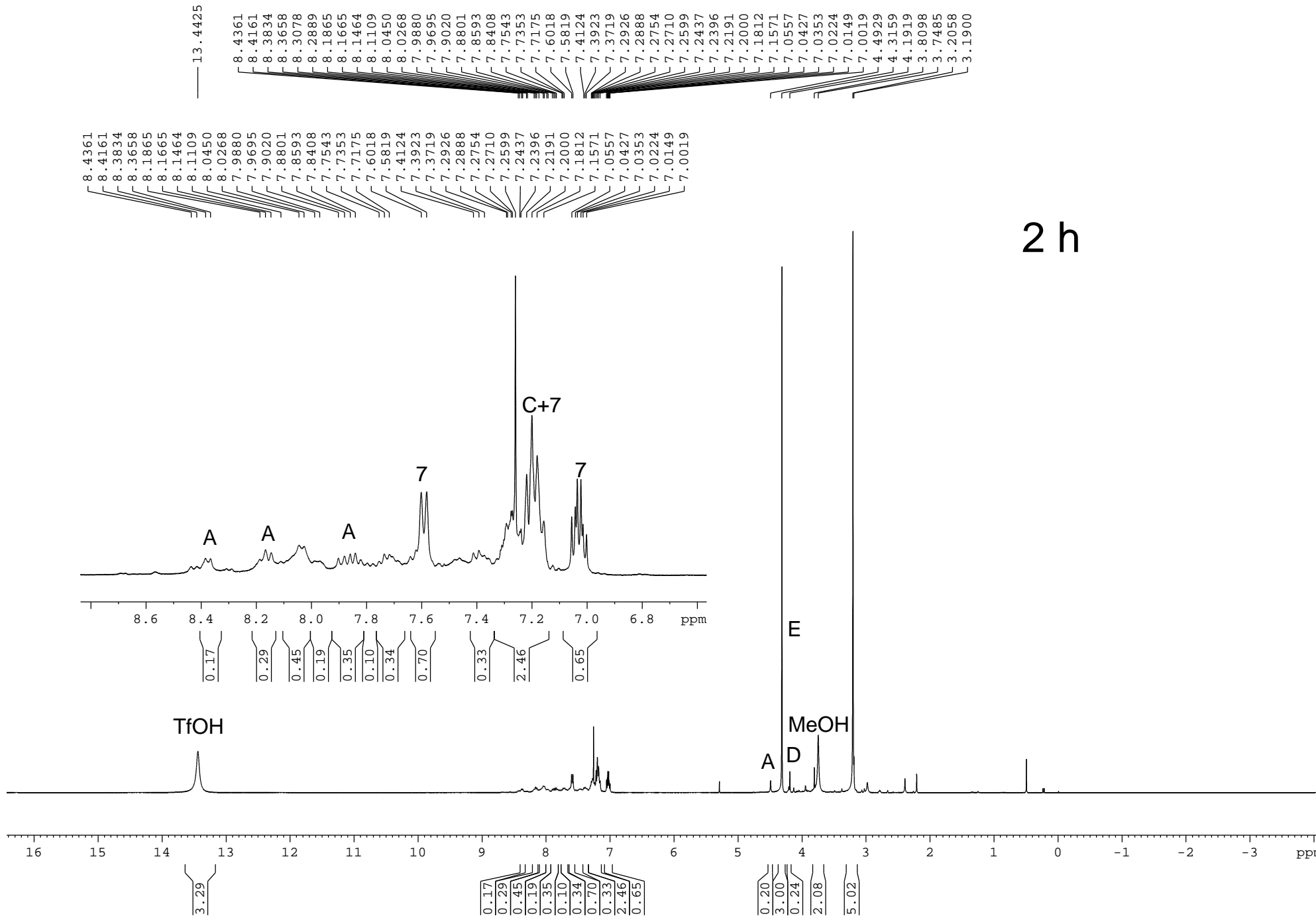
77.47
77.16
76.84

37.03
36.75









4 h

