Electronic Supplementary Material (ESI) for Chemical Communications


# Room-Temperature Pd-Catalyzed C-H Chlorination by Weak Coordination: One-Pot Synthesis of 2-Chlorophenols with Excellent Regioselectivity

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## SUPPORTING INFORMATION

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## Materials and Methods

All commercial materials (Alfa Aesar, Aladdin, J&K Chemical LTD.) were used without further purification. All solvents were analytical grade. The $^{1}$H-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 UPLC$^{TM}$/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. Benzoates were commercially available or easily synthesized from benzoic acid.

## General procedure

### I Synthesis of carbamates[1]

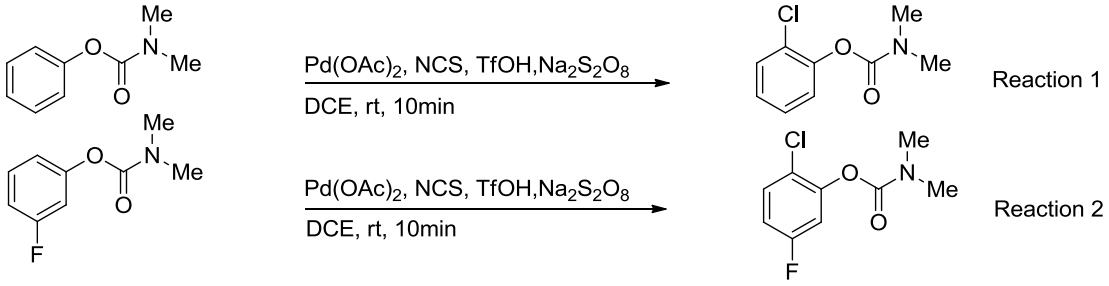
A mixture of the phenol (1.0 equivl) and $Me_2NCOCl$ (1.2 equiv) and $K_2CO_3$ (1.5 equiv) in MeCN was refluxed for 2h. The reaction mixture was cooled to room temperature and concentrated under a vacuum. The residue was dissolved in $H_2O$ and extracted with dichloroethane. The organic fractions were combined and then washed successively with 1 M KOH and water. Finally the organic layer was separated, dried over anhydrous $Na_2SO_4$, and concentrated under a vacuum to yield the corresponding carbamates.

### II Synthesis of halogenated carbamates

Substituted carbamates (1.0 equiv), NCS or NBS (1.1 equiv), $Pd(OAc)_2$ (0.05 – 0.10 equiv) and oxidant (1.2 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 3-24 h. The reaction was monitored by TLC and LC-MS. After completion of the reaction, the mixture was cooled to room temperature and then saturated $NaHCO_3$ was added to quench the reaction. The reaction mixture was diluted with dichloromethane and washed once with saturated aqueous $NaHCO_3$. Then organic layer was dried over $Na_2SO_4$ and concentrated on rotavapor under reduced pressure. Finally the residue was purified by silical gel column chromatography to give corresponding halogenated products.

In some cases, NCS or NBS was 1.0 equiv and starting material was from 1.5 equiv to 2.0 equiv. For this reaction, the cooxidant could drive the reaction faster generally, but in some cases, the yields were higher than the conditions without cooxidants.

### III Intermolecular Competition Experiments




To two separated sealed tubes, following the general procedure **I,** phenyl dimethylcarbamate (33 mg, 0.20 mmol) or 3-fluorophenyl dimethylcarbamate (37 mg, 0.20 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), NCS (30 mg, 0.22 mmol), $Na_2S_2O_8$ (57 mg, 0.22 mmol), TfOH (1.8 equiv, 32 uL) and DCE was added. The mixture was stirred at room temperature. After 10min, two reactions were quenched and added 4-nitrobenzaldyhyde 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 $^1$H-NMR. The ratio of (**2a**) to (**5a**) was 2.13.

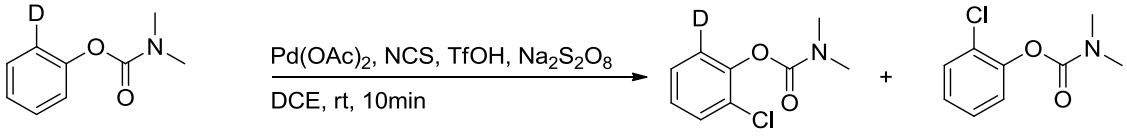
**IV Procedure for preliminary mechanistic study**

1. Preparation of 2-deuterio phenyl dimethylcarbamate[2,3,4].

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 ℃. 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 ℃. 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 $H_2O$ (20 mL). The layers were separated. The organic layer was washed with $H_2O$ (20 mL x 3), dried ($Na_2SO_4$), filtered and concentrated.

Following the general procedure I, the above compounds without further purification (5.78 mmol, 1.0 equiv), $K_2CO_3$ (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 (Petrom ether: Ethyl acetate = 10:1). Finally, compound 5b (670 mg) was isolated in 70% yield.

2. Intramolecular experiments




Following the general procedure **I**, to a 15 mL sealed tube, 2-deuterio phenyl dimethylcarbamate (33 mg, 0.20 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), NCS (30 mg, 0.22 mmol) and TfOH (1.5 equiv, 27 uL) were added and dissolved in 1.0 mL DCE. The mixture was stirred at room temperature for 10min. Then the mixture was quenched, washed once with saturated aqueous $NaHCO_3$, extracted by dichloromethane and concentrated on rotavapor under reduced pressure. The conversion ratio was determined by crude $^1$H-NMR. $^1$H-NMR showed $k_H/k_D = 3.00$.

**V Gram Scale Reactions**

1. **2-Chloro-5-methylphenyl dimethylcarbamate 10**

To a 50 mL round bottom flask, following the general procedure **II**, m-tolyl dimethylcarbamate (1.15 g, 6.42 mmol), NCS (0.90 g, 6.74 mmol), $Pd(OAc)_2$ (15 mg, 1% mmol) and TfOH (1.0 equiv, 570 uL) were used. The reaction mixture was stirred at room temperature for 8h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 6:1). Finally, compound **10** (1.03 g) was isolated in 75% yield.

2. **2-Chloro-6-methylphenyl dimethylcarbamate 2**

To a 100 mL round bottom flask, following the general procedure **II**, o-tolyl dimethylcarbamate (2.00 g, 11.17 mmol), NCS (1.57 g, 11.7 mmol), $Pd(OAc)_2$ (25 mg, 1% mmol) and TfOH (1.05 equiv, 1.08 mL) were used. The reaction mixture was stirred at room temperature for 8h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether: Ethyl acetate = 6:1). Finally, compound **2** (1.14 g) was isolated in 48% yield. Starting material remained 43%. The yield based on recovered materials was 84%.

**VI Deprotection of products in one pot.**

After the completion of the first step, DCE was removed by rotavapor under reduced pressure directly. Then hydrazine hydride (1.0 mL) was added to the mixture as solvent and stirred at room temperature or 60$^{o}$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 $Na_2SO_4$ and concentrated on rotavapor under reduced pressure. Finally the residue was purified by silical gel column chromatography to give corresponding deprotected products.

**References**

1. Alex, J.; Kenneth, M. N. *J. Org. Chem.* **2012**, *77*, 5600
2. John, J. T.; Irene, Q. E.; *J. Org. Chem.* **1984**, *49*(26), 5267
3. Cong, Y. W.; Isabel, P.; Frank, G. *J. Am. Chem. Soc.* **2009**, *131*, 4194
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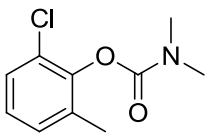
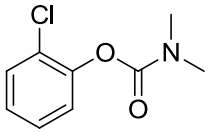
## Date of products




**2-Chloro-6-methylphenyl dimethylcarbamate 2**

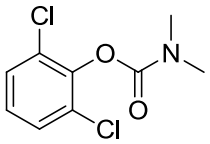
Following the general procedure **II**, o-tolyl dimethylcarbamate (36 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (1.5 equiv, 27 uL) were used. The reaction mixture was stirred at room temperature for 11h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **2** (32 mg) was isolated in 75% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm)

7.25 (d, *J* = 8.76 Hz, 1H), 7.11 (d, *J* = 7.44 Hz, 1H), 7.04 (t, *J* = 7.72 Hz, 1H), 3.17 (s, 3H), 3.04 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 146.5, 133.5, 129.4, 127.8, 127.7, 126.3, 37.1, 36.7, 16.7; LRMS (ESI) calcd for $C_{10}H_{13}ClNO_2$ $[M+H]^+$: 214.06, found 214.14



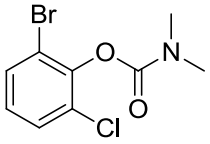

**2-chlorophenyl dimethylcarbamate 3**

Following the general procedure **II**, phenyl dimethylcarbamate (33 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.5 equiv, 27 uL) were used. The reaction mixture was stirred at room temperature for 11h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **3** (30 mg) was isolated in 75% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 (d, *J* = 7.96 Hz, 1H), 7.24-7.14 (m, 2H), 7.14 (t, *J* = 7.72 Hz, 1H), 3.13 (s, 3H), 3.01 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.0, 147.8, 130.2, 127.7, 127.2, 126.5, 124.3, 37.0, 36.7; LRMS (ESI) calcd for $C_9H_{11}ClNO_2$ $[M+H]^+$: 200.05, found 200.14




**2,6-Dichlorophenyl dimethylcarbamate 4**

Following the general procedure **II**, 2-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and TfOH (2.0 equiv, 36 uL) were used. The reaction mixture was stirred at room temperature for 10h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **4** (25 mg) was isolated in 54% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33 (d, *J* = 8.12 Hz, 2H), 7.09 (t, *J* = 8.20 Hz, 1H), 3.18 (s, 3H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.7, 144.8, 129.7, 128.6, 126.8, 37.2, 36.8; LRMS (ESI) calcd for $C_9H_{10}ClNO_2$ $[M+H]^+$: 234.01, found 234.05



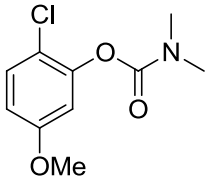

**2-Bromo-6-chlorophenyl dimethylcarbamate 5**

Following the general procedure **II**, 2-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), NCS (29 mg, 0.22 mmol), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol) and TfOH (1.8 equiv, 32 uL) were used. The reaction mixture was stirred at room temperature for 14h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 6:1). Finally, compound **5** (40 mg) was isolated in 72% yield.

Following the general procedure **I**, 2-chlorophenyl dimethylcarbamate (40 mg, 0.20

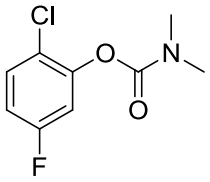
mmol), NBS (35 mg, 0.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and TfOH (2.5 equiv, 45 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 6:1). Finally, compound **5** (42 mg) was isolated in 75% yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (d, $J$ = 8.08 Hz, 1H), 7.38 (d, $J$ = 8.04 Hz, 1H), 7.03 (t, $J$ = 8.00 Hz, 1H), 3.19 (s, 3H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.6, 145.8, 131.6, 129.5, 129.4, 127.3, 118.8, 37.2, 36.8; LRMS (ESI) calcd for $C_9H_{10}BrClNO_2$ $[M+H]^+$: 277.96, found 278.05; HRMS (ESI) calcd for $C_9H_{10}BrClNO_2$ $[M+H]^+$: 277.9578, found 277.9589




**2-Chloro-5-methoxyphenyl dimethylcarbamate 6**

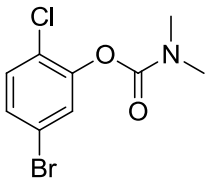
Following the general procedure **II**, 3-methoxyphenyl dimethylcarbamate (39 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.2 equiv, 21 uL) were used. The reaction mixture was stirred at room temperature for 8h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **6** (30 mg) was isolated in 66% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (d, J = 8.88 Hz, 1H), 6.78 (d, $J$ = 2.72 Hz, 1H), 6.71 (dd, $J_1$ = 2.76 Hz, $J_2$ = 8.84 Hz, 1H), 3.78 (s, 3H), 3.14 (s, 3H), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.0, 153.9, 130.1, 118.5, 112.8, 109.9, 55.8, 37.0, 36.7; LRMS (ESI) calcd for $C_{10}H_{13}ClNO_3$ $[M+H]^+$: 230.06, found 230.12; HRMS (ESI) calcd for $C_{10}H_{13}ClNO_3$ $[M+H]^+$: 230.0578, found 230.0590




**2-Chloro-5-fluorophenyl dimethylcarbamate 7**

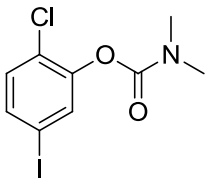
Following the general procedure **II**, 3-fluorophenyl dimethylcarbamate (37 mg, 0.20 mmol), NCS (30 mg, 0.25 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (2.5 equiv, 44 uL) were used. The reaction mixture was stirred at room temperature for 12h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **7** (23 mg) was isolated in 52% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36 (dd, $J_1$ = 5.72 Hz, $J_2$ = 8.80 Hz, 1H), 7.02 (dd, $J_1$ = 2.68 Hz, $J_2$ = 8.88 Hz, 1H), 6.90 (t*d, $J_1$ = 2.72 Hz, $J_2$ = 8.12 Hz, 1H), 3.14 (s, 3H), 3.03 (s, 3H); $^{19}$F-NMR (400 MHz, $CDCl_3$) -112.99 (s, 1F); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm) 161.3 (d, $J_{C\text{-}F}$ = 246 Hz, 1C), 153.4, 148.4 (d, $J_{C\text{-}F}$ = 11 Hz, 1C), 130.5 (d, $J_{C\text{-}F}$ = 9 Hz,

1C), 122.5 (d, $J_{C-F}$ = 4 Hz, 1C), 113.6 (d, $J_{C-F}$ = 22 Hz, 1C), 112.3 (d, $J_{C-F}$ = 25 Hz, 1C), 37.0, 36.7; LRMS (ESI) calcd for $C_9H_{10}ClFNO_2$ $[M+H]^+$: 218.04, found 218.10



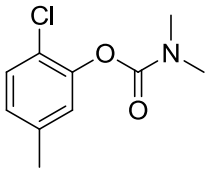

**5-Bromo-2-chlorophenyl dimethylcarbamate 8**

Following the general procedure **II**, 3-bromophenyl dimethylcarbamate (40 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and TfOH (1.85equiv, 27 uL) were used. The reaction mixture was stirred at room temperature for 13h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **8** (38 mg) was isolated in 69% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 1H), 7.27 (s, 2H), 3.13 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 148.3, 131.0, 129.6, 127.6, 126.5, 120.2, 37.0, 36.7; LRMS (ESI) calcd for $C_9H_{10}BrClNO_2$ $[M+H]^+$: 277.96, found 278.01




**2-Chloro-5-iodophenyl dimethylcarbamate 9**

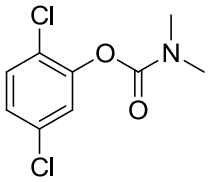
Following the general procedure **II**, 3-iodophenyl dimethylcarbamate (58 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 24h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **9** (44 mg) was isolated in 68% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (d, $J$ = 1.36 Hz, 1H), 7.46 (d, $J$ = 8.40 Hz, 1H), 7.12 (d, $J$ = 8.44 Hz, 1H), 3.12 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 148.2, 135.6, 133.3, 131.4, 127.6, 90.7, 37.0, 36.7; LRMS (ESI) calcd for $C_9H_{10}ClINO_2$ $[M+H]^+$: 325.94, found 326.04




**2-Chloro-5-methylphenyl dimethylcarbamate 10**

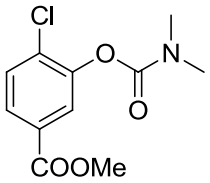
Following the general procedure **II**, m-tolyl dimethylcarbamate (36 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally,

compound **10** (37 mg) was isolated in 86% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 (d, *J* = 8.32 Hz, 1H), 7.02 (s, 1H), 6.95 (d, *J* = 8.08 Hz, 1H), 3.14 (s, 3H), 3.02 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.1, 147.4, 138.0, 129.7, 124.8, 124.0, 36.9, 36.6, 21.0; LRMS (ESI) calcd for $C_{10}H_{13}ClNO_2$ $[M+H]^+$: 214.06, found 214.16



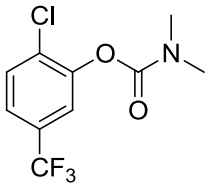

**2,5-Dichlorophenyl dimethylcarbamate 11**

Following the general procedure **II**, 3-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.8 equiv, 32 uL) were used. The reaction mixture was stirred at room temperature for 5h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **11** (34 mg) was isolated in 72% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (d, *J* = 8.56 Hz, 1H), 7.19 (s, 1H), 7.06 (d, *J* = 8.56 Hz, 1H), 3.06 (s, 3H), 2.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 148.2, 132.9, 130.7, 126.7, 125.8, 124.8, 37.0, 36.7; LRMS (ESI) calcd for $C_9H_{10}Cl_2NO_2$ $[M+H]^+$: 234.01, found 234.08




**Methyl 4-chloro-3-((dimethylcarbamoyl)oxy)benzoate 12**

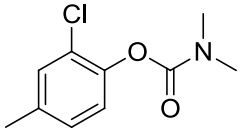
Following the general procedure **II**, methyl 3-((dimethylcarbamoyl)oxy)benzoate (45 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and TfOH (2.5 equiv, 45 uL) were used. The reaction mixture was stirred at room temperature for 5h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **12** (29 mg) was isolated in 56% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (s, 1H), 7.83 (d, *J* = 8.36 Hz, 1H), 7.48 (d, *J* = 8.32 Hz), 3.90 (s, 3H), 3.16 (s, 3H), 3.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 153.6, 147.8, 132.6, 130.2, 130.0, 127.6, 125.5, 52.5, 37.1, 36.7; LRMS (ESI) calcd for $C_{11}H_{13}ClNO_4$ $[M+H]^+$: 258.05, found 258.14; HRMS (ESI) calcd for $C_{11}H_{13}ClNO_4$ $[M+H]^+$: 258.0528, found 258.0540




**2-Chloro-5-(trifluoromethyl)phenyl dimethylcarbamate 13**

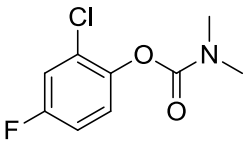
Following the general procedure **II**, 3-(trifluoromethyl)phenyl dimethylcarbamate (47 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH

(3.0 equiv, 53 uL) were used. The reaction mixture was stirred at room temperature for 5h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **13** (12 mg) was isolated in 23% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, $J$ = 8.52 Hz, 1H), 7.52 (s, 1H), 7.41 (d, $J$ = 7.80 Hz), 3.16 (s, 3H), 3.04 (s, 3H); $^{19}$F-NMR (400 MHz, $CDCl_3$) -62.60 (s, 3F); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.3, 148.1, 130.9 (q, $J_{C-F}$ = 88 Hz, 1C), 130.0 (q, $J_{C-F}$ = 40 Hz, 1C), 130.8, 123.4 (q, $J_{C-F}$ = 271 Hz, 1C), 123.3 (q, $J_{C-F}$ = 4 Hz, 1C), 121.7 (q, $J_{C-F}$ = 4 Hz, 1C), 37.1, 36.7; LRMS (ESI) calcd for $C_{10}H_{10}ClF_3NO_2$ $[M+H]^+$: 268.03, found 268.11; HRMS (ESI) calcd for $C_{10}H_{10}ClF_3NO_2$ $[M+H]^+$: 268.0347, found 268.0360



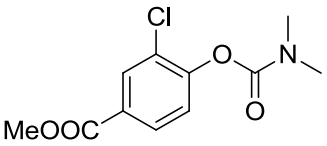

**2-Chloro-4-methylphenyl dimethylcarbamate 14**

Following the general procedure **II**, p-tolyl dimethylcarbamate (36 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.5 equiv, 27 uL) were used. The reaction mixture was stirred at room temperature for 12h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **14** (35 mg) was isolated in 73% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 (s, 1H), 7.08 (d, $J$ = 8.00 Hz, 1H), 7.04 (d, $J$ = 8.28 Hz), 3.14 (s, 3H), 3.02 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 145.5, 136.6, 130.5, 128.3, 126.6, 123.8, 37.0, 36.6, 20.8; LRMS (ESI) calcd for $C_{10}H_{13}ClNO_2$ $[M+H]^+$: 214.06, found 214.14



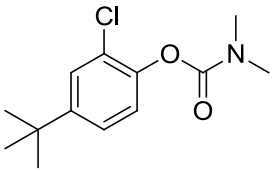

**2-Chloro-4-fluorophenyl dimethylcarbamate 15**

Following the general procedure **II**, 4-fluorophenyl dimethylcarbamate (37 mg, 0.20 mmol), NCS (30 mg, 0.25 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), N-Fluoropyridium trifluorormethylsulfonate (66 mg, 0.24 mmol) and TfOH (2.0 equiv, 36 uL) were used. The reaction mixture was stirred at room temperature for 5h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **15** (31 mg) was isolated in 77% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.19-7.14 (m, 2H), 6.99-6.95 (m, 1H), 3.14 (s, 3H), 3.02 (s, 3H); $^{19}$F-NMR (400 MHz, $CDCl_3$) -115.34 (s, 1F); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm) 159.7 (d, $J_{C-F}$ = 246 Hz, 1C), 153.9, 144.1 (d, $J_{C-F}$ = 3 Hz, 1C), 128.0 (d, $J_{C-F}$ = 11 Hz, 1C), 125.0 (d, $J_{C-F}$ = 9 Hz, 1C), 117.3 (d, $J_{C-F}$ = 26 Hz, 1C), 114.6 (d, $J_{C-F}$ = 22 Hz, 1C), 37.0, 36.6; LRMS (ESI) calcd for $C_9H_{10}ClFNO_2$ $[M+H]^+$: 218.04, found 218.10; HRMS (ESI) calcd for $C_9H_{10}ClFNO_2$ $[M+H]^+$: 218.0379, found 218.0391;



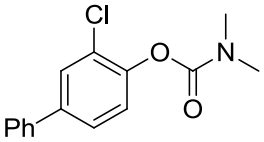

**Methyl 3-chloro-4-((dimethylcarbamoyl)oxy)benzoate 16**

Following the general procedure **II**, methyl 4-((dimethylcarbamoyl)oxy)benzoate (45 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (2.0 equiv, 35 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **16** (33 mg) was isolated in 63% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, $J$ = 1.96 Hz, 1H), 7.93 (dd, $J_1$ = 2.04 Hz, $J_2$ = 8.48 Hz, 1H), 7.31 (d, $J$ = 8.48 Hz, 1H), 3.90 (s, 3H), 3.15 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.6, 153.2, 151.5, 131.6, 129.2, 128.5, 127.4, 124.1, 52.5, 37.0, 36.7; LRMS (ESI) calcd for $C_{11}H_{13}ClNO_4$ $[M+H]^+$: 258.05, found 258.14




**4-(Tert-butyl)-2-chlorophenyl dimethylcarbamate 17**

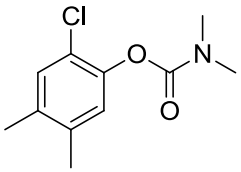
Following the general procedure **II**, 4-(tert-butyl)phenyl dimethylcarbamate (45 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (1.0 equiv, 18 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **17** (48 mg) was isolated in 93% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (d, $J$ = 2.20 Hz, 1H), 7.25 (dd, $J_1$ = 2.24 Hz, $J_2$ = 8.48 Hz, 1H), 7.12 (d, $J$ = 8.52 Hz, 1H), 3.14 (s, 3H), 3.02 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 149.9, 145.3, 127.2, 126.4, 124.8, 123.5, 36.9, 36.6, 31.4; LRMS (ESI) calcd for $C_{13}H_{19}ClNO_2$ $[M+H]^+$: 256.11, found 256.20




**3-Chloro-[1,1'-biphenyl]-4-yl dimethylcarbamate 18**

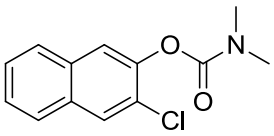
Following the general procedure **II**, [1,1'-biphenyl]-4-yl dimethylcarbamate (73 mg, 0.30 mmol), NCS (27 mg, 0.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and TfOH (1.8 equiv, 32 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **18** (44 mg) was isolated in 80% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (d, $J$ = 2.08 Hz, 1H), 7.53 (d, $J$ = 8.76 Hz, 2H), 7.47-7.41 (m, 3H), 7.35 (t, $J$ = 7.02 Hz, 1H), 7.28 (d, $J$

= 8.40 Hz, 1H), 3.17 (s, 3H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.0, 147.1, 140.3, 139.5, 129.0, 128.8, 127.9, 127.2, 126.4, 124.4, 37.0, 36.7; LRMS (ESI) calcd for $C_{15}H_{15}ClNO_2$ $[M+H]^+$: 276.08, found 276.16



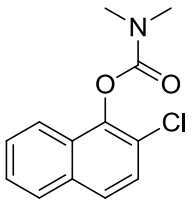

**2-Chloro-4,5-dimethylphenyl dimethylcarbamate 19**

Following the general procedure **II**, 3,4-dimethylphenyl dimethylcarbamate (39 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (0.6 equiv, 11 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **19** (44 mg) was isolated in 96% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16 (s, 1H), 6.97 (s, 1H), 3.13 (s, 3H), 3.02 (s, 3H), 2.21 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 145.3, 136.4, 135.2, 130.7, 125.0, 123.6, 37.0, 36.6, 19.5, 19.2; LRMS (ESI) calcd for $C_{11}H_{15}ClNO_2$ $[M+H]^+$: 228.08, found 228.14




**3-Chloronaphthalen-2-yl dimethylcarbamate 20**

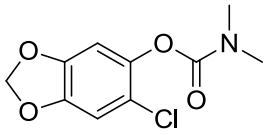
Following the general procedure **II**, naphthalen-2-yl dimethylcarbamate (43 mg, 0.20 mmol), NCS (14 mg, 0.10 mmol), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol), $Na_2S_2O_8$(28 mg, 0.12 mmol) and TfOH (0.8 equiv, 10 uL) were used. The reaction mixture was stirred at room temperature for 4.5h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **20** 12 mg) was isolated in 51% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87-7.84 (m, 3H), 7.80 (s, 1H), 7.53-7.45 (m, 2H), 2.78 (s, 3H), 2.67 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 147.4, 133.5, 131.0, 130.8, 130.5, 127.8, 127.5, 126.4, 125.6, 119.2, 36.6, 36.1; LRMS (ESI) calcd for $C_{13}H_{13}ClNO_2$ $[M+H]^+$: 250.06, found 250.12




**8-Chloronaphthalen-1-yl dimethylcarbamate 21**

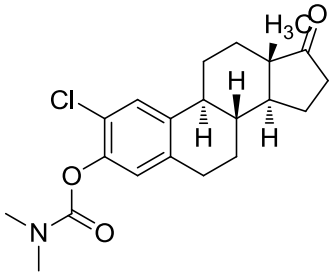
Following the general procedure **II**, naphthalen-1-yl dimethylcarbamate (21 mg, 0.10 mmol), NCS (15 mg, 0.11 mmol), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol) and TfOH (1.2 equiv, 11 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column

chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **21** (25 mg) was isolated in 98% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 (d, *J* = 8.32 Hz, 1H), 7.95 (d, *J* = 8.12 Hz, 1H), 7.64-7.54 (m, 3H), 7.22 (d, *J* = 8.12 Hz, 1H), 3.27 (s, 3H), 3.08 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.7, 146.4, 131.7, 128.8, 128.6, 127.5, 127.1, 125.8, 125.0, 121.9, 118.4, 37.1, 36.8; LRMS (ESI) calcd for $C_{13}H_{13}ClNO_2$ $[M+H]^+$: 250.06, found 250.15



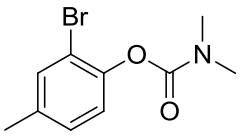

**6-Chlorobenzo[d][1,3]dioxol-5-yl dimethylcarbamate 22**

Following the general procedure **II**, benzo[d][1,3]dioxol-5-yl dimethylcarbamate (42 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 20h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **22** (41 mg) was isolated in 86% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.85 (s, 1H), 6.71 (s, 1H), 5.98 (s, 2H), 3.12 (s, 3H), 3.01 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.1, 146.8, 145.6, 141.9, 118.8, 109.3, 105.5, 102.3, 37.0, 36.6; LRMS (ESI) calcd for $C_{10}H_{11}ClNO_4$ $[M+H]^+$: 244.04, found 244.12; HRMS (ESI) calcd for $C_{10}H_{11}ClNO_4$ $[M+H]^+$: 244.0371, found 244.0385



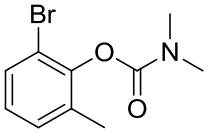

**(8R,9S,13S,14S)-2-chloro-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl dimethylcarbamate 23**

Following the general procedure **II**, estrone dimethylcarbamate (68 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 12h. After completion of the reaction, the residue was purified by silical gel column chromatography (Toluene: Ethyl acetate = 6:1). Finally, compound **23** (35 mg) was isolated in 47% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30 (s, 1H), 6.92 (s, 1H), 3.13 (s, 3H), 3.02 (s, 3H), 2.88-2.85 (m, 1H), 2.54-2.47 (m, 1H), 2.36-2.32 (m, 1H), 2.28-1.94 (m, 6H), 1.65-1.39 (m, 7H), 0.90-0.87 (m, 4H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 145.4, 138.6, 136.5, 127.1, 124.1, 124.0, 50.5, 48.0, 44.1, 37.8, 37.0, 36.6, 36.0, 31.6, 29.0, 26.3, 25.8, 21.7, 13.9; LRMS (ESI) calcd for $C_{21}H_{27}ClNO_3$ $[M+H]^+$: 376.17, found 376.29; HRMS (ESI) calcd for $C_{21}H_{27}ClNO_3$ $[M+H]^+$: 376.1674, found 376.1694



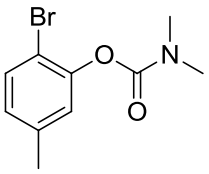

**2-Bromo-4-methylphenyl dimethylcarbamate 24**

Following the general procedure **II**, p-tolyl dimethylcarbamate (36 mg, 0.20 mmol), NBS (40 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.5 equiv, 27 uL) were used. The reaction mixture was stirred at room temperature for 11h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 8:1). Finally, compound **24** (37 mg) was isolated in 71% yield. Without cooxidant 65%. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 (s, 1H), 7.08 (s, 2H), 3.15 (s, 3H), 3.02 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.1, 146.6, 136.9, 133.5, 129.1, 123.8, 116.0, 37.0, 36.7, 20.7; LRMS (ESI) calcd for $C_{10}H_{13}BrNO_2$ $[M+H]^+$: 258.01, found 258.08




**2-Bromo-6-methylphenyl dimethylcarbamate 25**

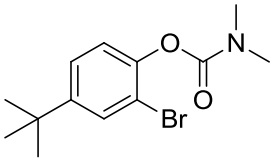
Following the general procedure **II**, o-tolyl dimethylcarbamate (36 mg, 0.20 mmol), NBS (39 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$ (57 mg, 0.24 mmol) and TfOH (1.5 equiv, 27 uL) were used. The reaction mixture was stirred at room temperature for 20h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **25** (41 mg) was isolated in 80% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 7.92 Hz, 1H), 7.15 (d, *J* = 7.52 Hz, 1H), 6.98 (t, *J* = 7.76 Hz, 1H), 3.18 (s, 3H), 3.04 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 147.6, 133.6, 130.7, 130.1, 126.7, 117.3, 37.0, 36.7, 16.9; LRMS (ESI) calcd for $C_{10}H_{13}BrNO_2$ $[M+H]^+$: 258.01, found 258.13; HRMS (ESI) calcd for $C_{10}H_{13}BrNO_2$ $[M+H]^+$: 258.0124, found 258.0139




**2-Bromo-5-methylphenyl dimethylcarbamate 26**

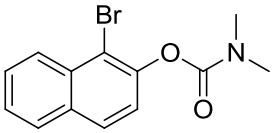
Following the general procedure **II**, m-tolyl dimethylcarbamate (36 mg, 0.20 mmol), NBS (39 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 4h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **26** (42 mg) was isolated in 82% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)

7.43 (d, *J* = 8.16 Hz, 1H), 7.03 (s, 1H), 6.89 (d, *J* = 8.12 Hz, 1H), 3.15 (s, 3H), 3.03 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 148.6, 138.8, 132.7, 127.7, 124.9, 113.0, 37.0, 36.7, 21.1; LRMS (ESI) calcd for $C_{10}H_{13}BrNO_2$ $[M+H]^+$: 258.01, found 258.12



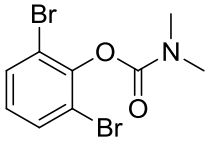

**2-Bromo-4-(tert-butyl)phenyl dimethylcarbamate 27**

Following the general procedure **II**, 4-(tert-butyl)phenyl dimethylcarbamate (45 mg, 0.20 mmol), NBS (40 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$(57 mg, 0.24 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 12h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 9:1). Finally, compound **27** (52 mg) was isolated in 87% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (s, 1H), 7.31 (d, *J* = 8.48 Hz, 1H), 7.12 (d, *J* = 8.48 Hz, 1H), 3.15 (s, 3H), 3.03 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.1, 150.2, 146.5, 130.2, 125.5, 123.5, 115.9, 37.0, 36.7, 34.7, 31.4; LRMS (ESI) calcd for $C_{13}H_{19}BrNO_2$ $[M+H]^+$: 300.06, found 300.18




**1-Bromonaphthalen-2-yl dimethylcarbamate 28**

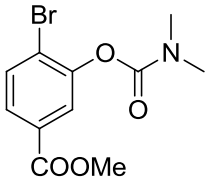
Following the general procedure **II**, naphthalen-2-yl dimethylcarbamate (43 mg, 0.20 mmol), NBS (40 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $Na_2S_2O_8$ (57 mg, 0.24 mmol) and TfOH (0.8 equiv, 14 uL) were used. The reaction mixture was stirred at room temperature for 12h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 6:1). Finally, compound **28** (34 mg) was isolated in 59% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, *J* = 8.48 Hz, 1H), 7.81 (t, *J* = 7.20 Hz, 2H), 7.56 (t, *J* = 7.32 Hz, 1H), 7.48 (t, *J* = 7.48 Hz, 1H), 7.35 (d, *J* = 8.80 Hz, 1H), 3.22 (s, 3H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.1, 147.1, 132.8, 132.4, 128.6, 128.3, 127.7, 127.0, 126.2, 122.7, 115.2, 37.0, 36.8; LRMS (ESI) calcd for $C_{13}H_{13}BrNO_2$ $[M+H]^+$: 294.01, found 294.05; HRMS (ESI) calcd for $C_{13}H_{13}BrNO_2$ $[M+H]^+$: 294.0124, found 294.0138




**2,6-Dibromophenyl dimethylcarbamate 29**

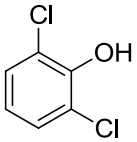
Following the general procedure **II**, 2-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), NBS (40 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.8 equiv, 32 uL) were used. The reaction mixture was stirred at room temperature for 6h.

After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 6:1). Finally, compound **29** (40 mg) was isolated in 70% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, $J$ = 8.08 Hz, 2H), 6.94 (d, $J$ = 8.04 Hz, 1H), 3.17 (s, 3H), 3.03 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm) 152.5, 146.8, 132.4, 127.8, 118.6, 37.2, 36.8; LRMS (ESI) calcd for $C_9H_{10}Br_2NO_2$ $[M+H]^+$: 321.91, found 322.01




**Methyl 4-bromo-3-((dimethylcarbamoyl)oxy)benzoate 30**

Following the general procedure **II**, methyl 3-((dimethylcarbamoyl)oxy)benzoate (44 mg, 0.20 mmol), NBS (35 mg, 0.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and TfOH (2.5 equiv, 45 uL) were used. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 6:1). Finally, compound **30** (43 mg) was isolated in 72% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (s, 1H), 7.74 (dd, $J_1$ = 8.32 Hz, $J_2$ = 1.00 Hz, 1H), 7.64 (d, $J$ = 8.32 Hz, 1H), 3.88 (s, 3H), 3.16 (s, 3H), 3.03 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 153.5, 149.0, 133.3, 130.7, 127.7, 125.3, 122.3, 52.5, 37.0, 36.7; LRMS (ESI) calcd for $C_{11}H_{13}BrNO_4$ $[M+H]^+$: 302.00, found 302.09; HRMS (ESI) calcd for $C_{11}H_{13}BrNO_4$ $[M+H]^+$: 302.0022, found 302.0037




**2,6-Dichlorophenol 31**

Following the general procedure **VI**, 2-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (2.0 equiv, 36 uL) were used. The reaction mixture was stirred at room temperature for 6h. Then DCE was removed. $NH_2NH_2.H_2O$ (1.0 mL) was added to the reaction mixture and the mixture was stirred at 60$^{o}$C for 2h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 30:1). Finally, compound **31** (16 mg) was isolated in 50% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (d, $J$ = 8.12 Hz, 2H), 6.82 (t, $J$ = 8.04 Hz, 1H), 5.87 (bs, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm) 148.0, 128.4, 121.3


**2-Bromo-6-chlorophenol 32**

Following the general procedure **VI**, 2-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), NCS (30 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (1.8

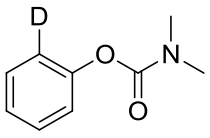
equiv, 32 uL) were used. The reaction mixture was stirred at room temperature for 6h. Then DCE was removed. $NH_2NH_2.H_2O$ (1.0 mL) was added to the reaction mixture and the mixture was stirred at room temperature for 12h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 30:1). Finally, compound **32** (23 mg) was isolated in 56% yield.

Following the general procedure **VI**, 2-chlorophenyl dimethylcarbamate (40 mg, 0.20 mmol), NBS (40 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (2.5 equiv, 45 uL) were used. The reaction mixture was stirred at room temperature for 5h. Then DCE was removed. $NH_2NH_2.H_2O$ (1.0 mL) was added to the reaction mixture and the mixture was stirred at 60$^oC$ for 2h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 30:1). Finally, compound **35** (21 mg) was isolated in 51% yield.

$^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 8.08 Hz, 1H), 7.29 (d, *J* = 8.04 Hz, 1H), 6.76 (t, *J* = 8.04 Hz, 1H), 5.88 (bs, 1H); $^{13}C$-NMR (100 MHz, $CDCl_3$) δ (ppm) 148.83, 131.5, 129.1, 122.0, 121.0, 110.4; LRMS (ESI) calcd for $C_6H_3BrClO$ $[M-H]^-$: 204.91, found 204.88

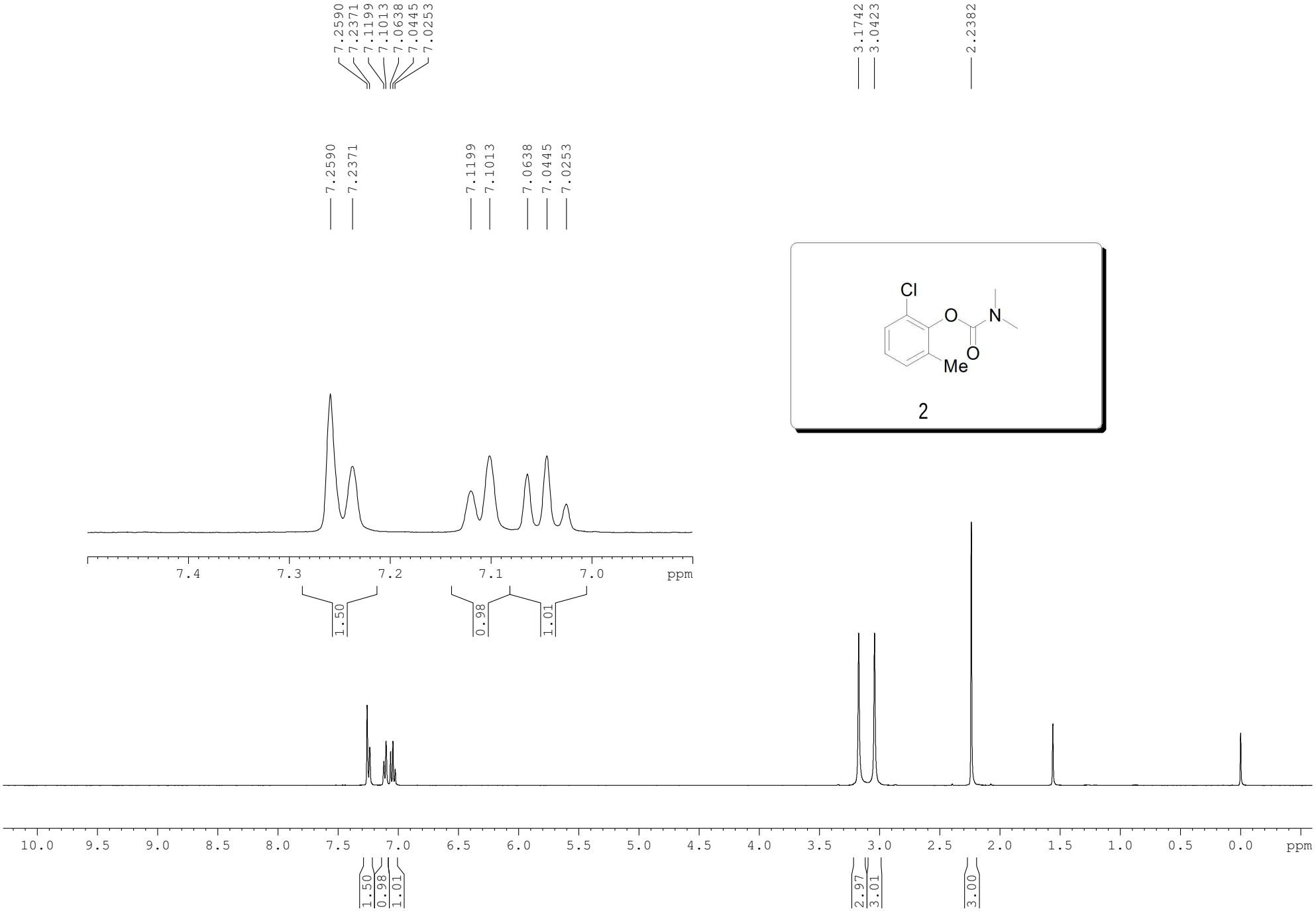

**2,6-Dibromophenol 33**

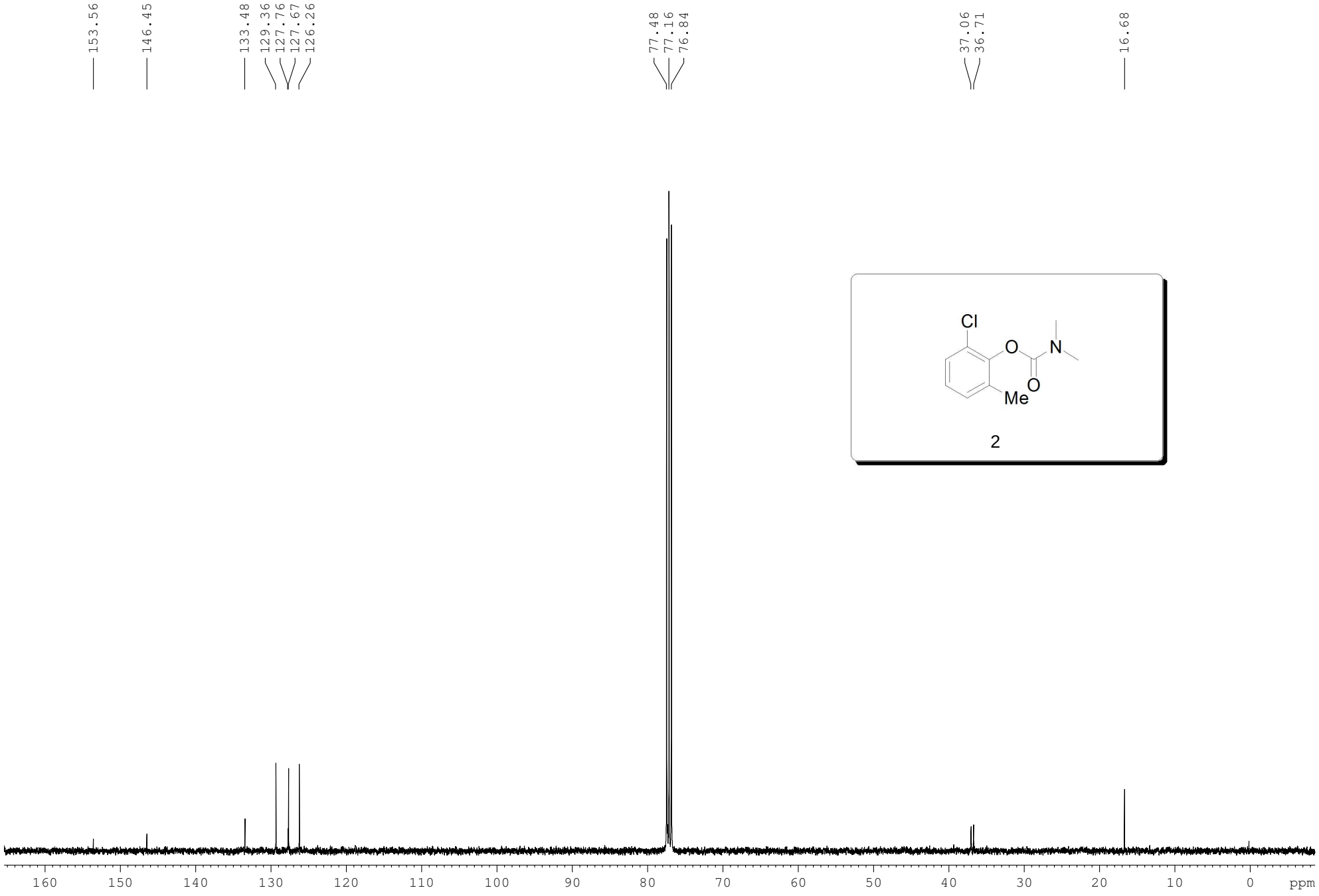
Following the general procedure **VI**, 2-bromophenyl dimethylcarbamate (49 mg, 0.20 mmol), NBS (40 mg, 0.22 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol) and TfOH (2.5 equiv, 45 uL) were used. The reaction mixture was stirred at room temperature for 5h. Then DCE was removed. $NH_2NH_2.H_2O$ (1.0 mL) was added to the reaction mixture and the mixture was stirred at 60$^oC$ for 2h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petrom ether: Ethyl acetate = 30:1). Finally, compound **33** (40 mg) was isolated in 80% yield. $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, *J* = 8.00 Hz, 2H), 6.70 (t, *J* = 8.00 Hz, 1H); $^{13}C$-NMR (100 MHz, $CDCl_3$) δ (ppm) 149.6, 132.2, 122.6, 110.1; LRMS (ESI) calcd for $C_6H_3Br_2O$ $[M-H]^-$: 248.86, found 248.86

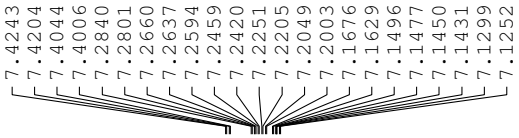



**2-Deuterio-phenyl dimethylcarbamate**

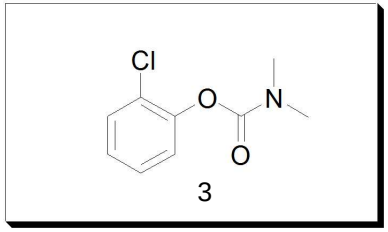
$^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.34 (m, 2H), 7.19 (t, *J* = 7.40 Hz, 1H), 7.11 (d, *J* = 8.40 Hz, 1H), 3.10 (s, 3H), 3.01 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 155.0, 151.6, 129.3, 129.2, 125.2, 121.8, 121.6 ($J_{C-D}$ = 24.5 Hz), 36.8, 36.5; LRMS (ESI) calcd for $C_9H_{11}DNO_2$ $[M+H]^+$: 167.09, found 167.12

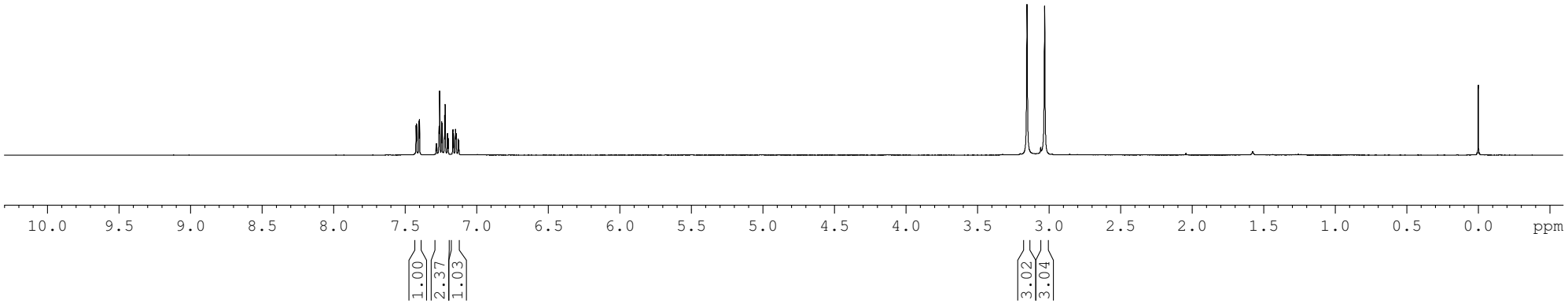


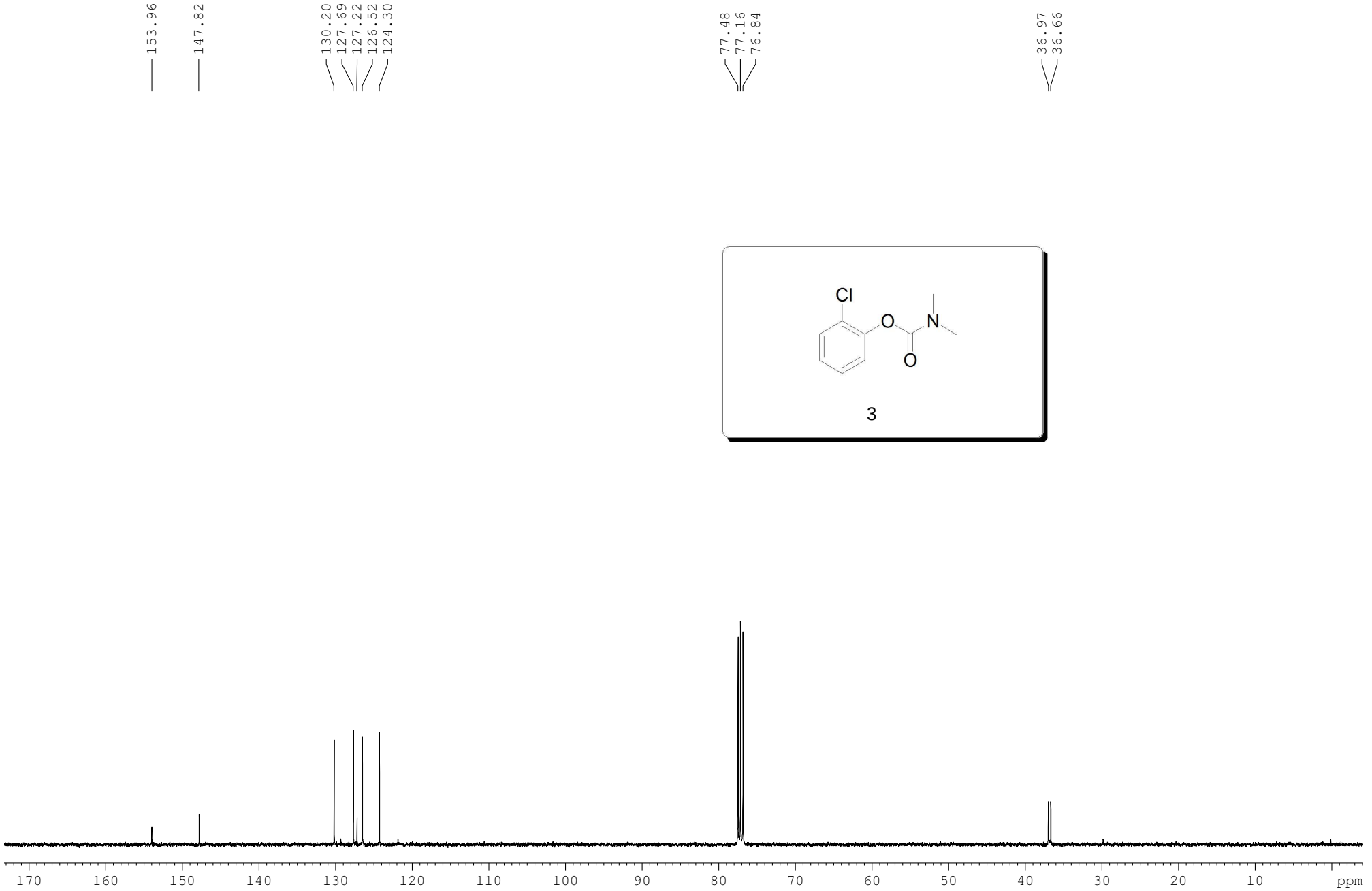


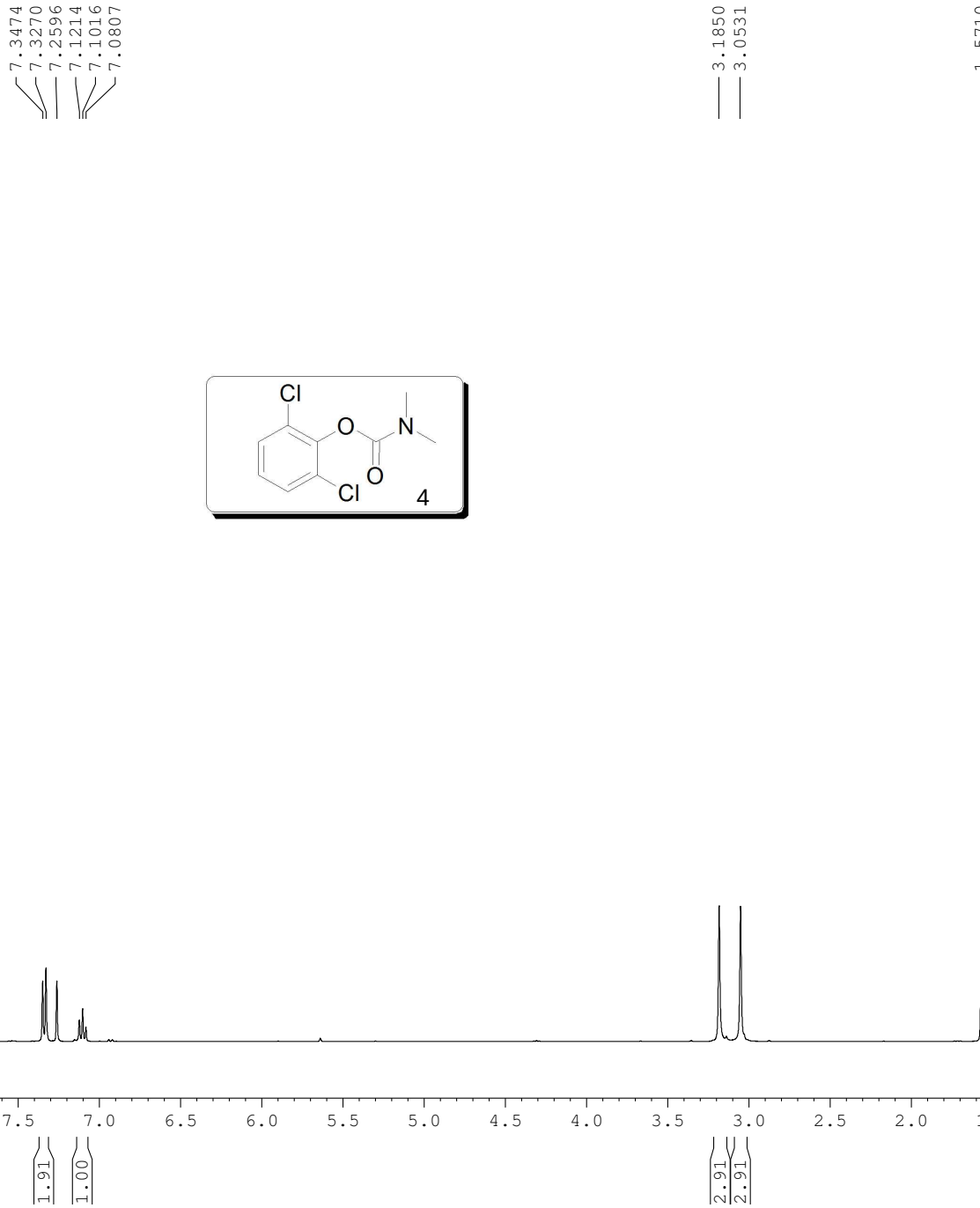


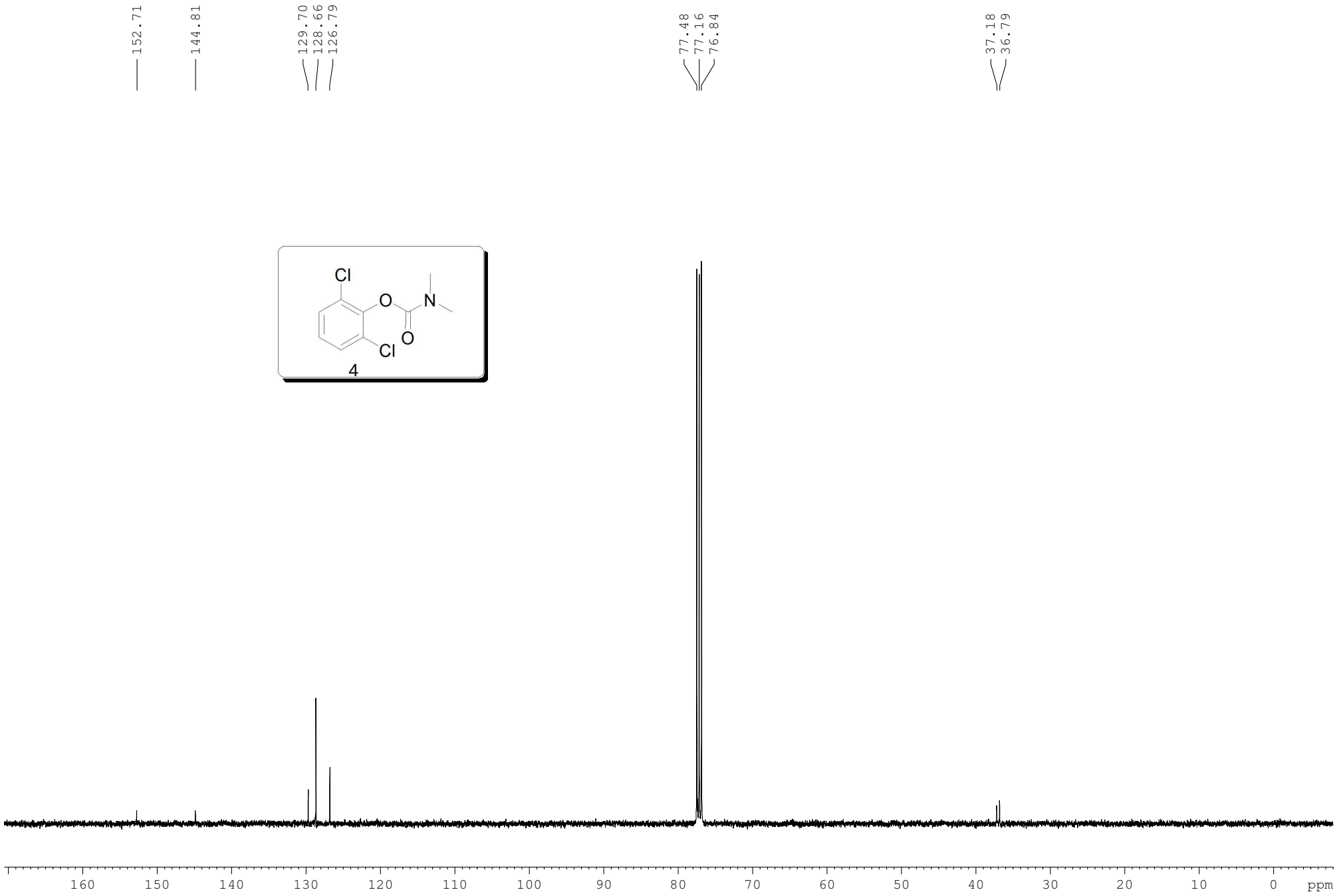


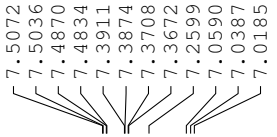


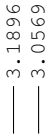



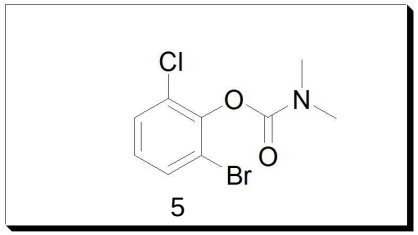


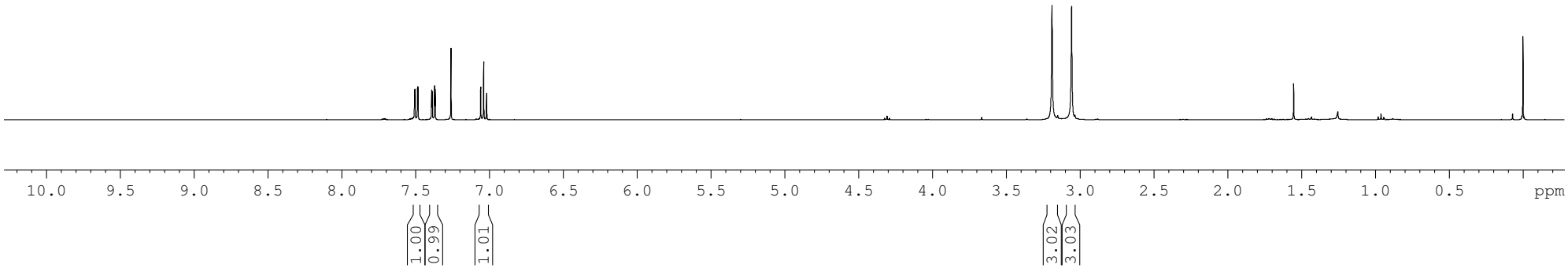


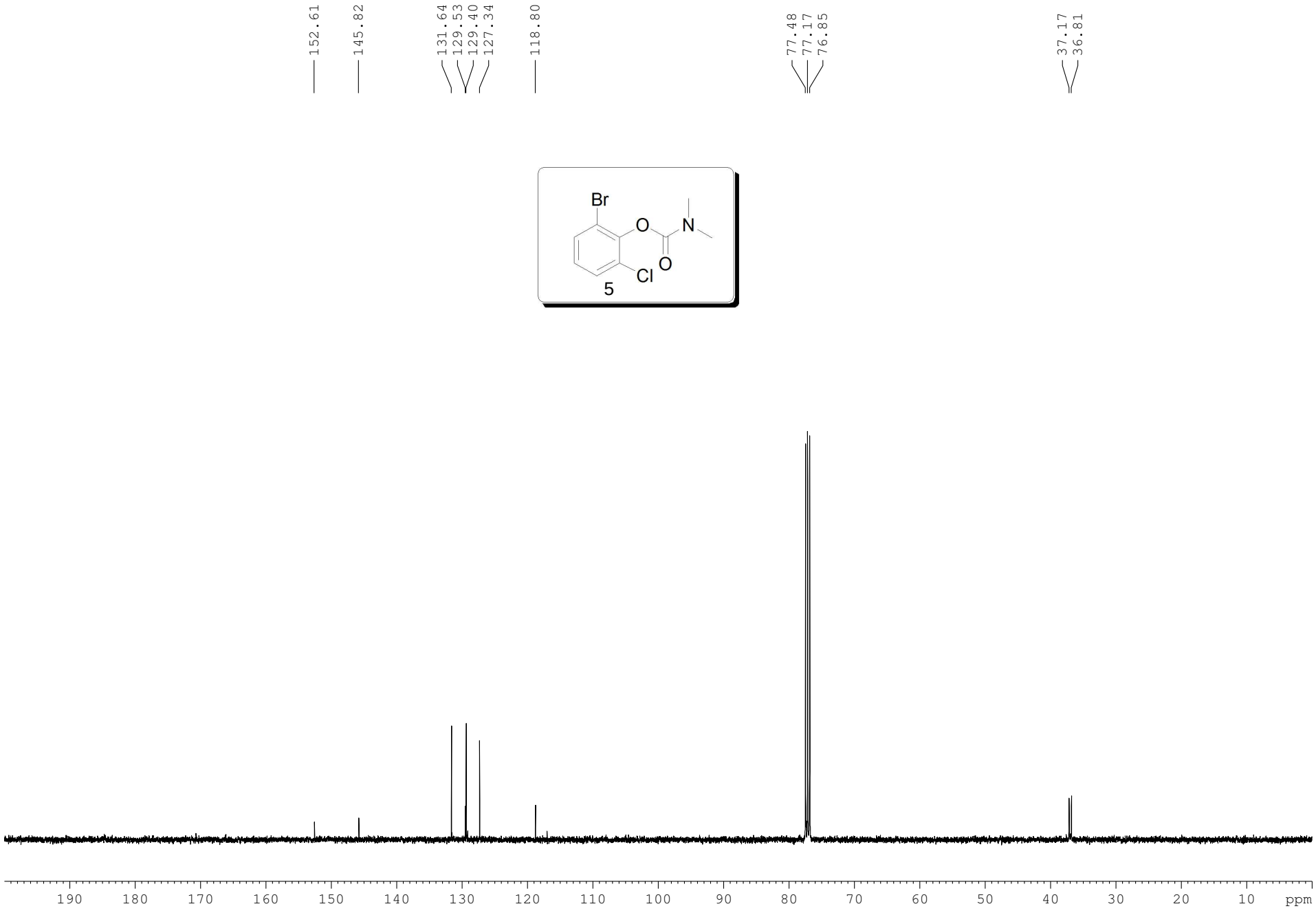


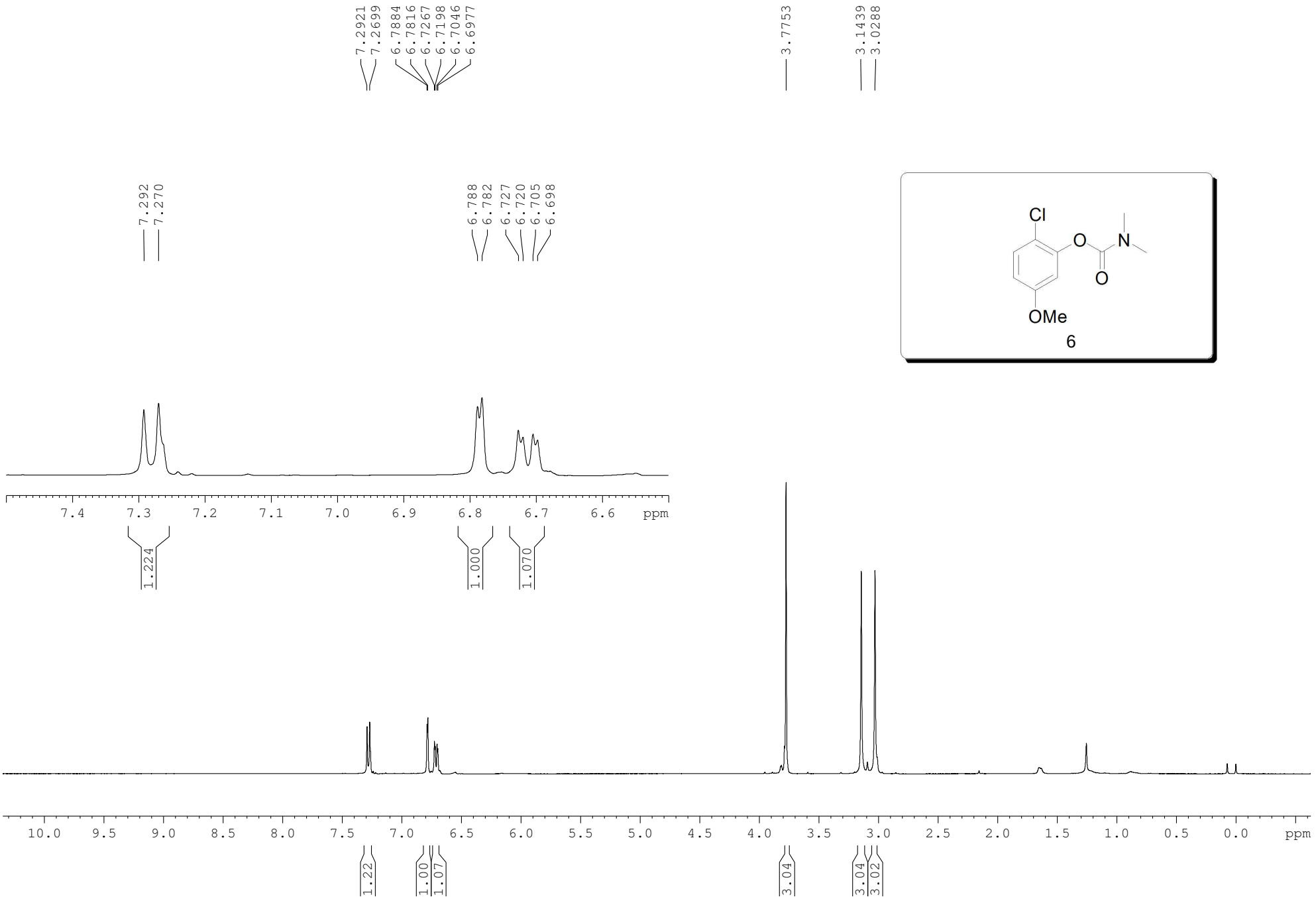


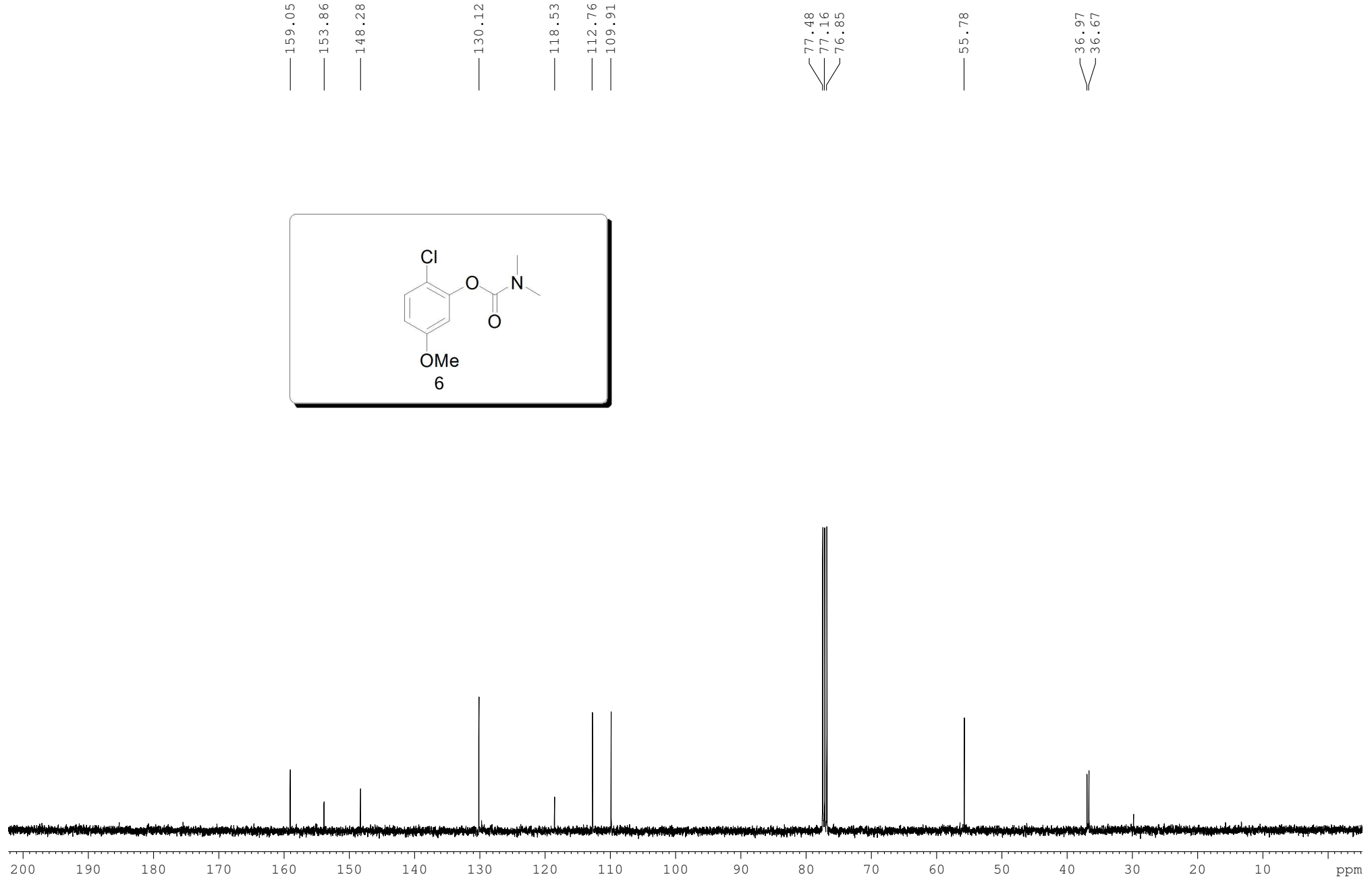



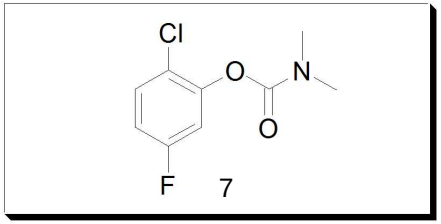







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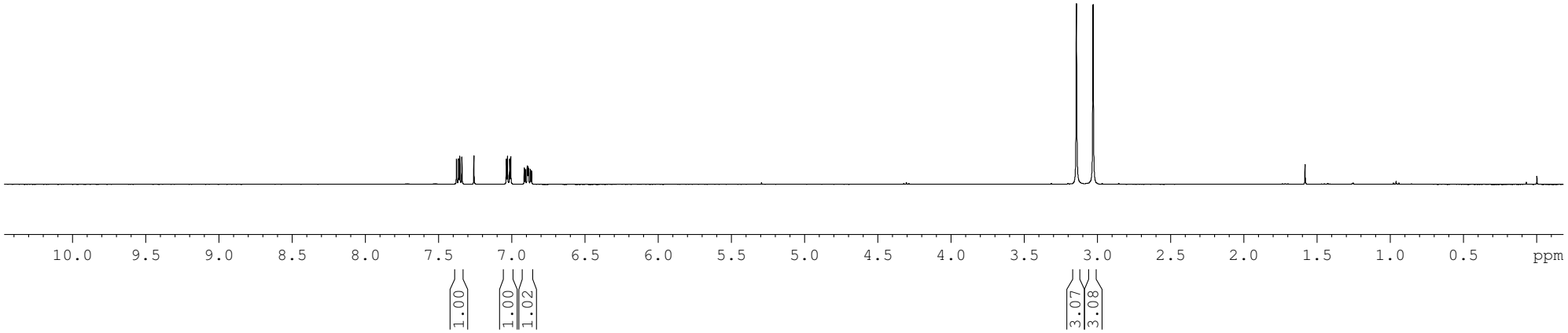

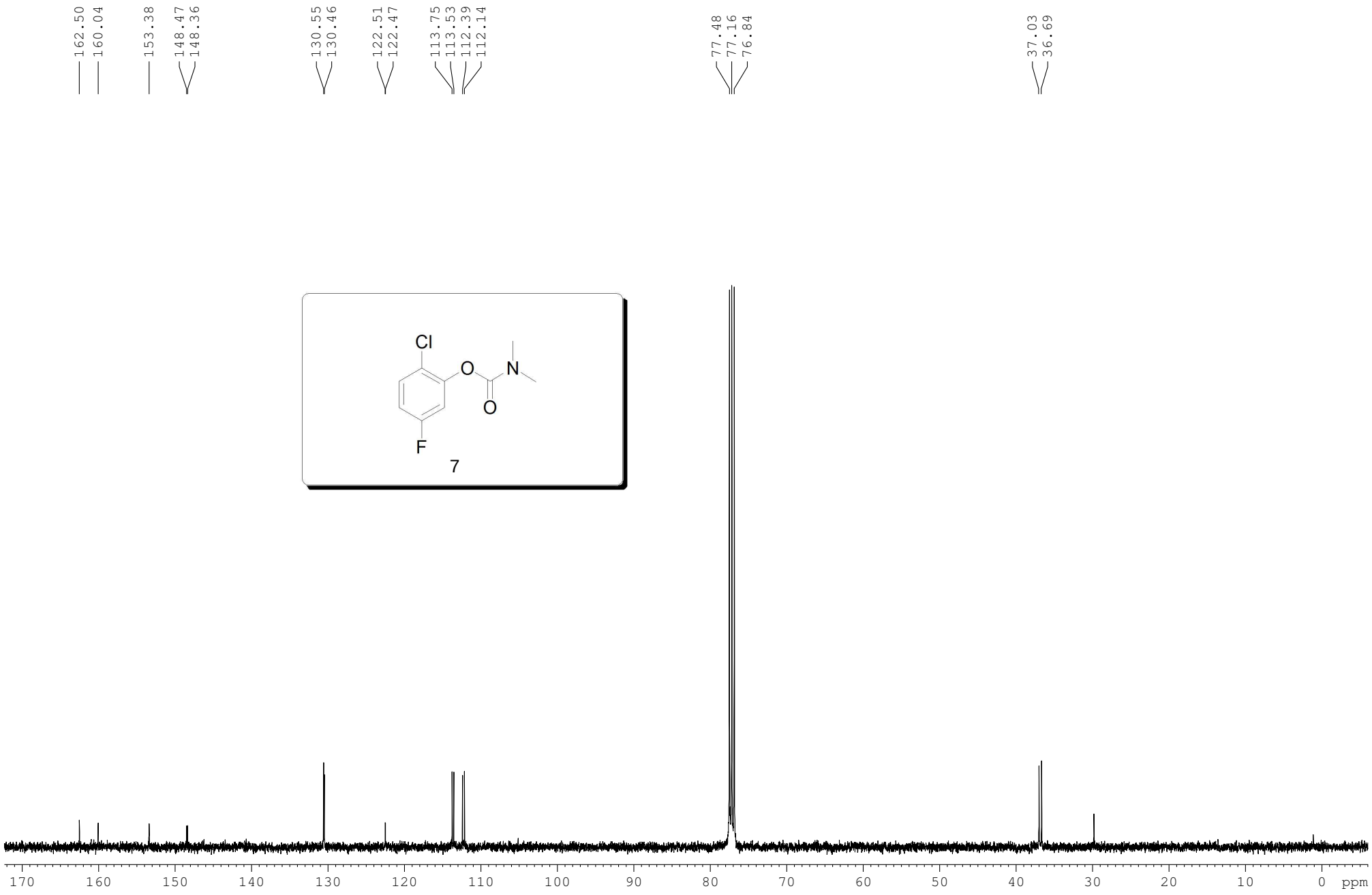

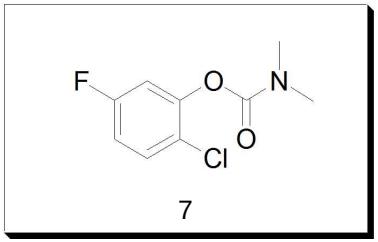


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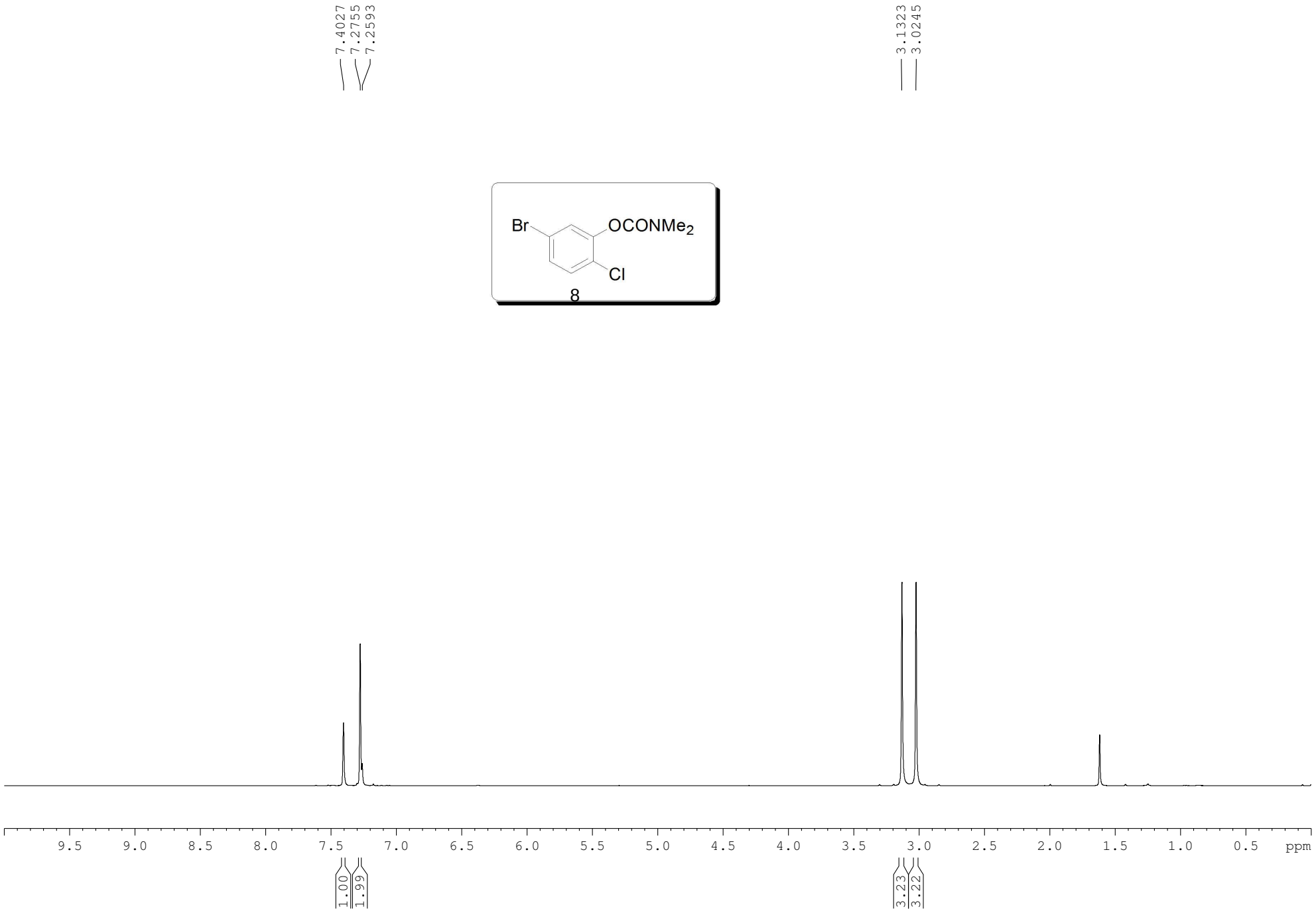

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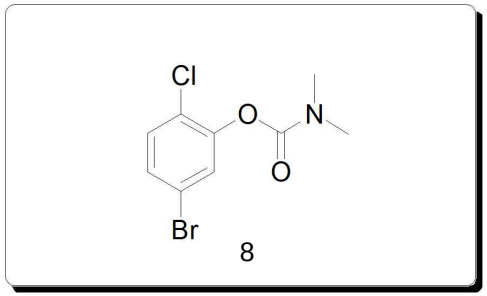


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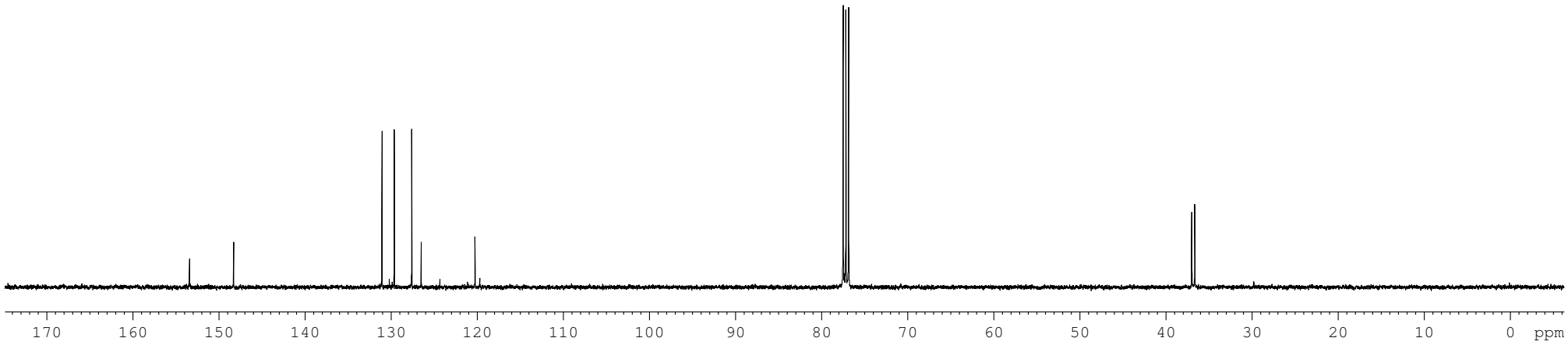

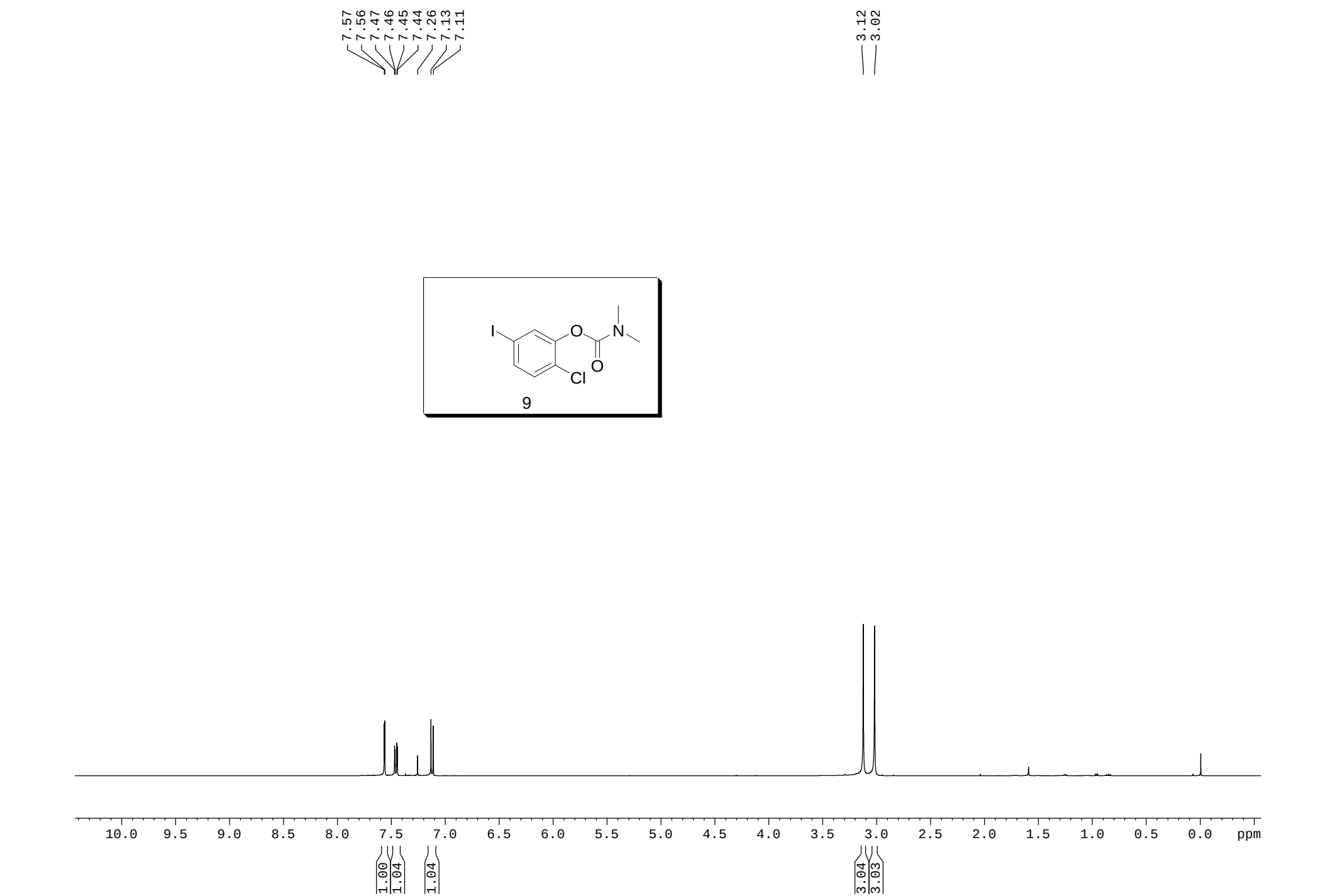

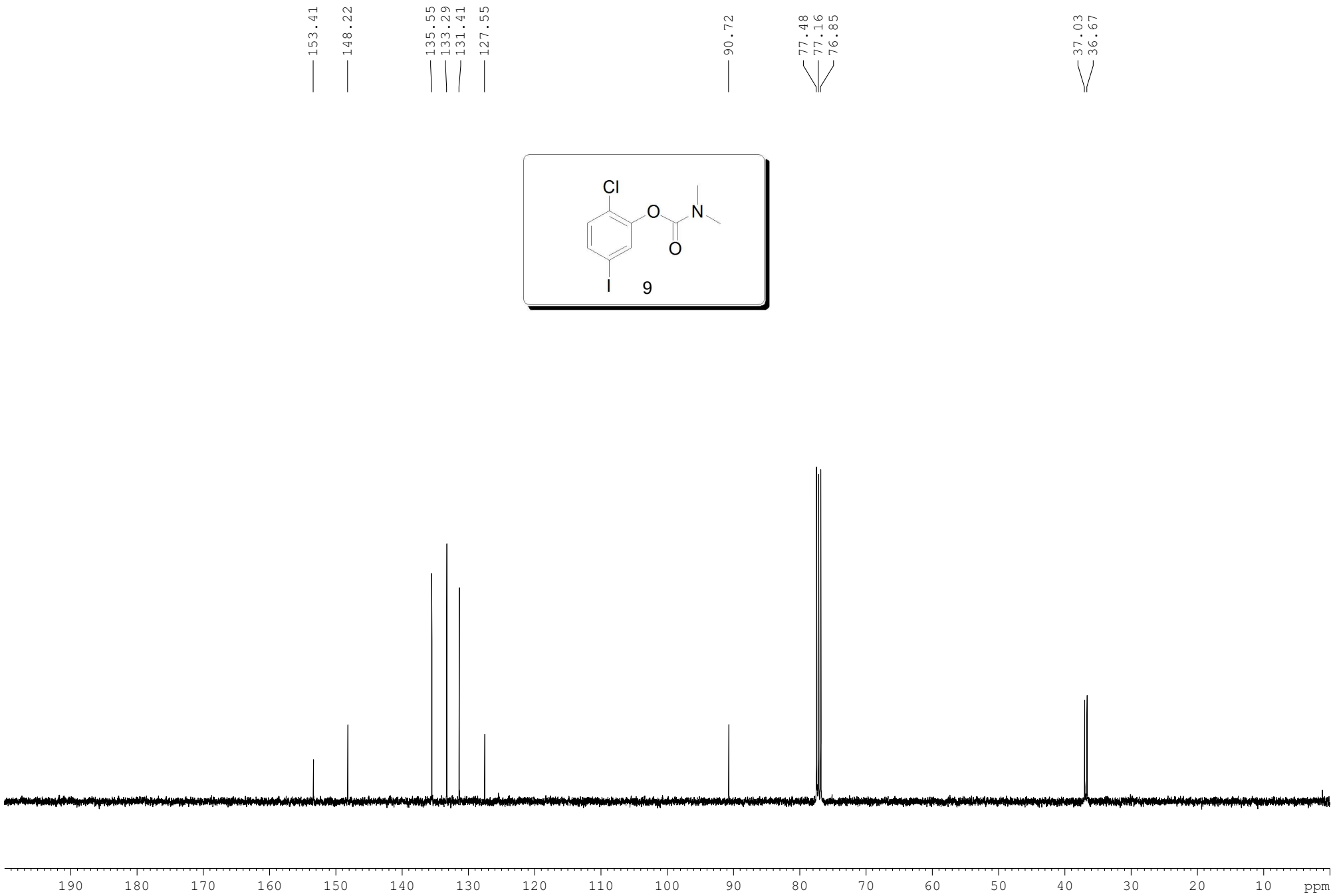

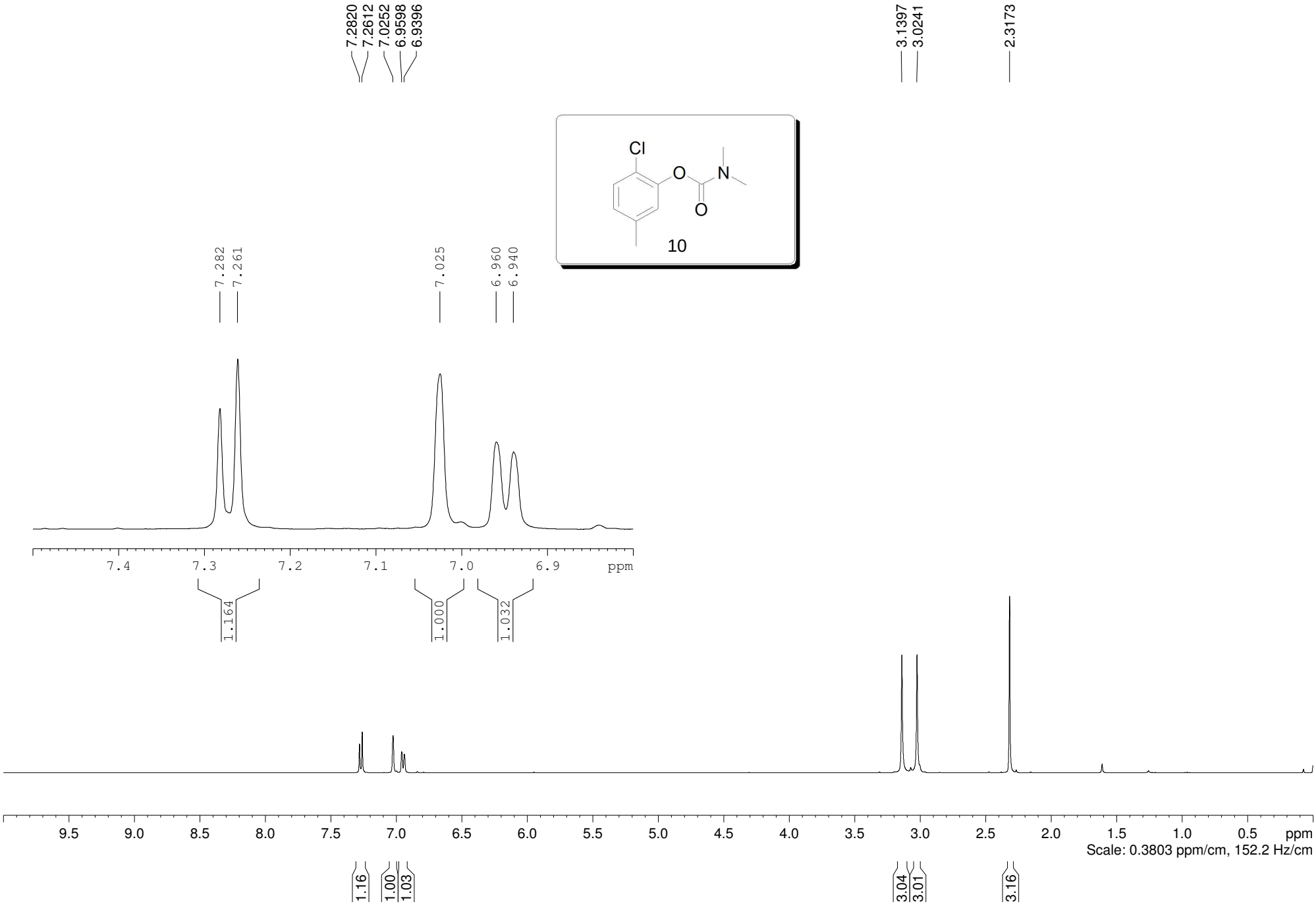

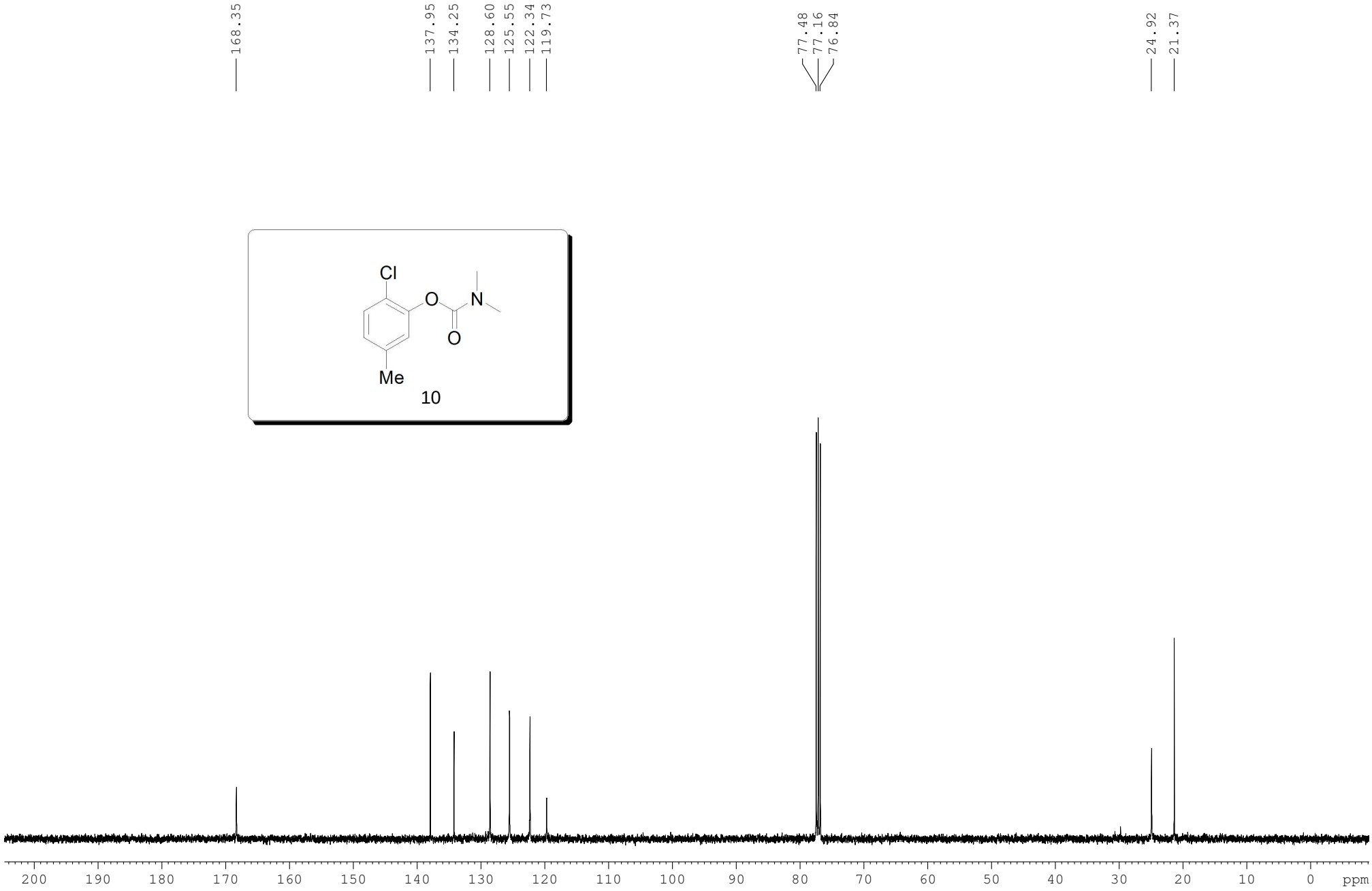

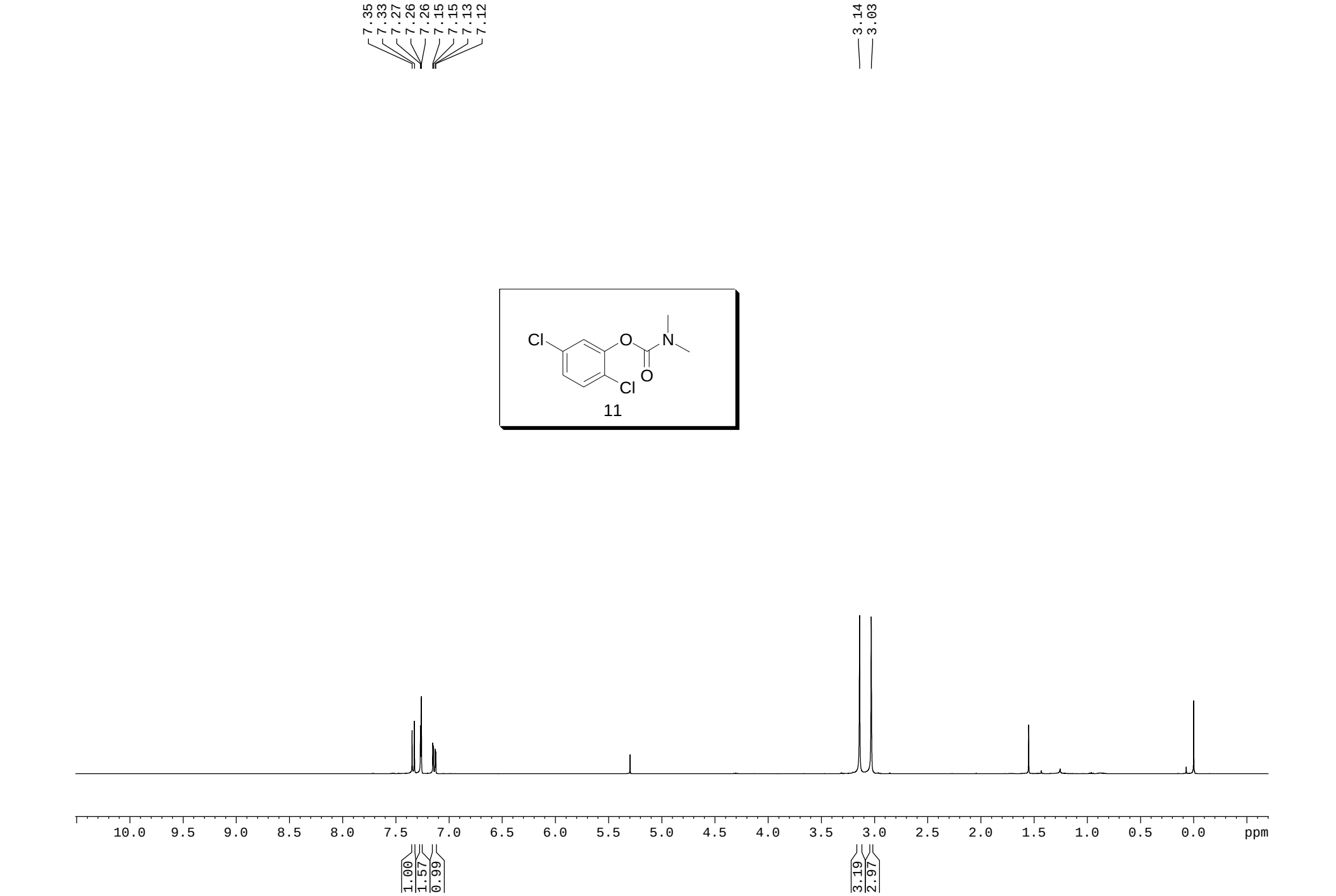

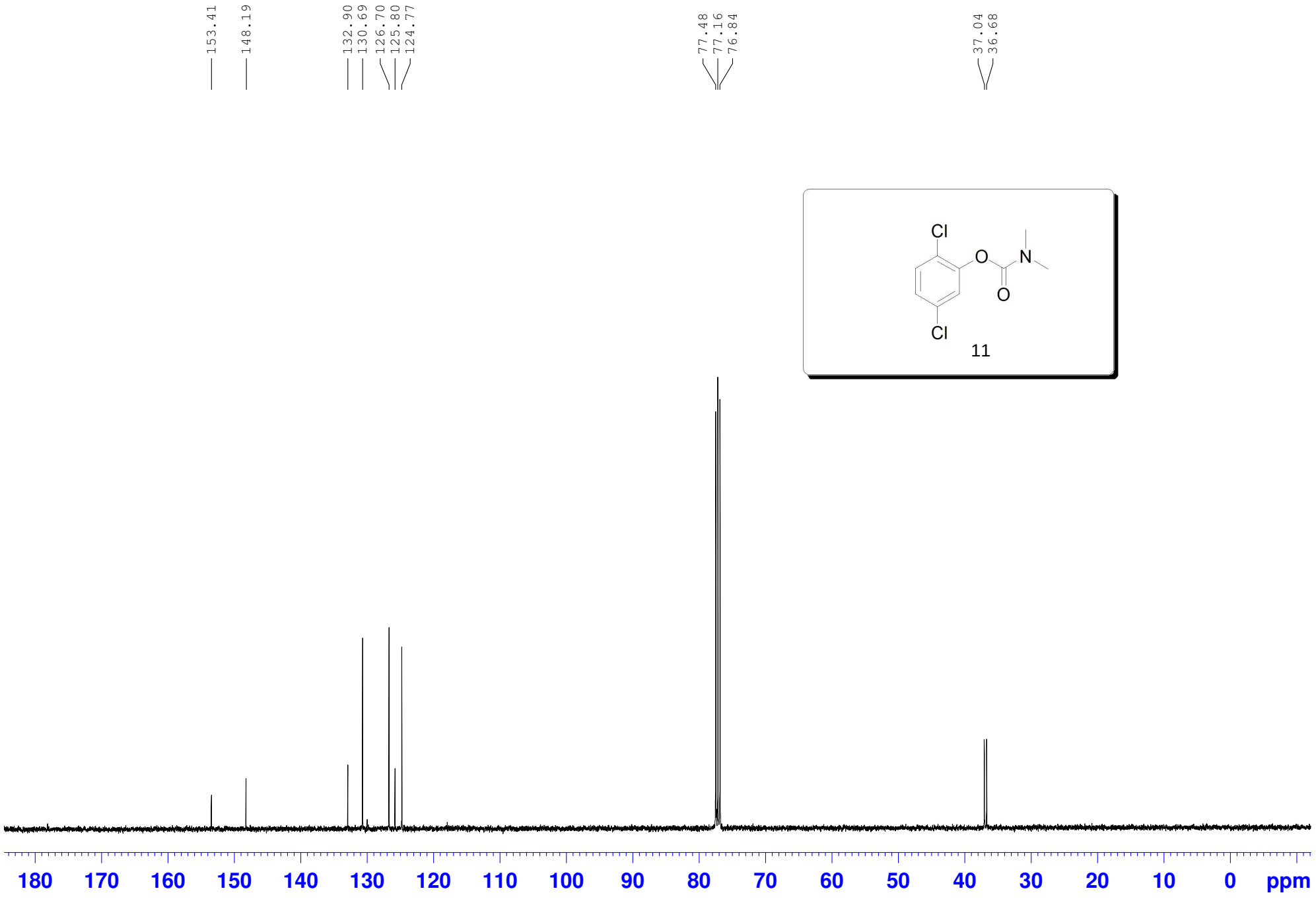

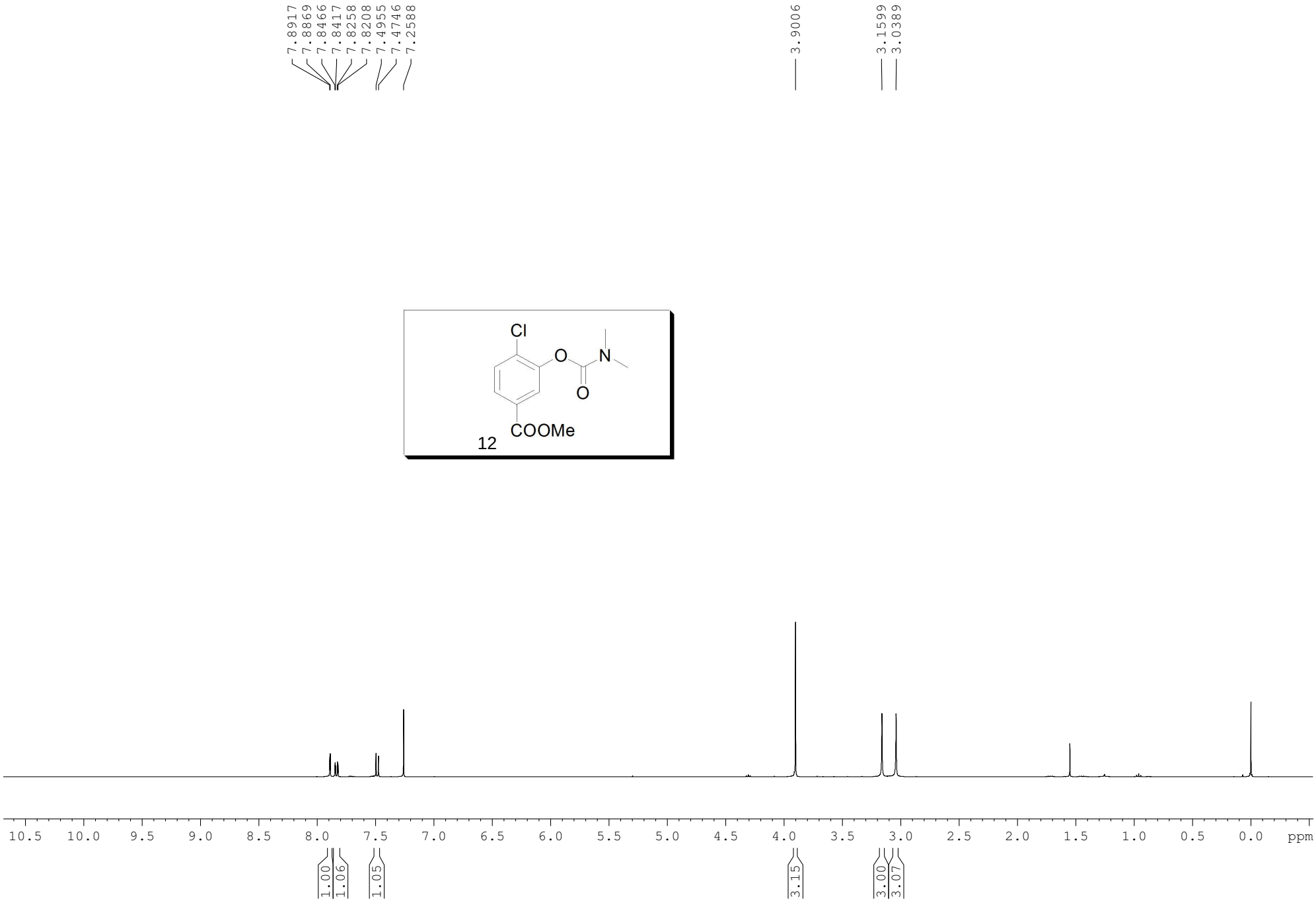

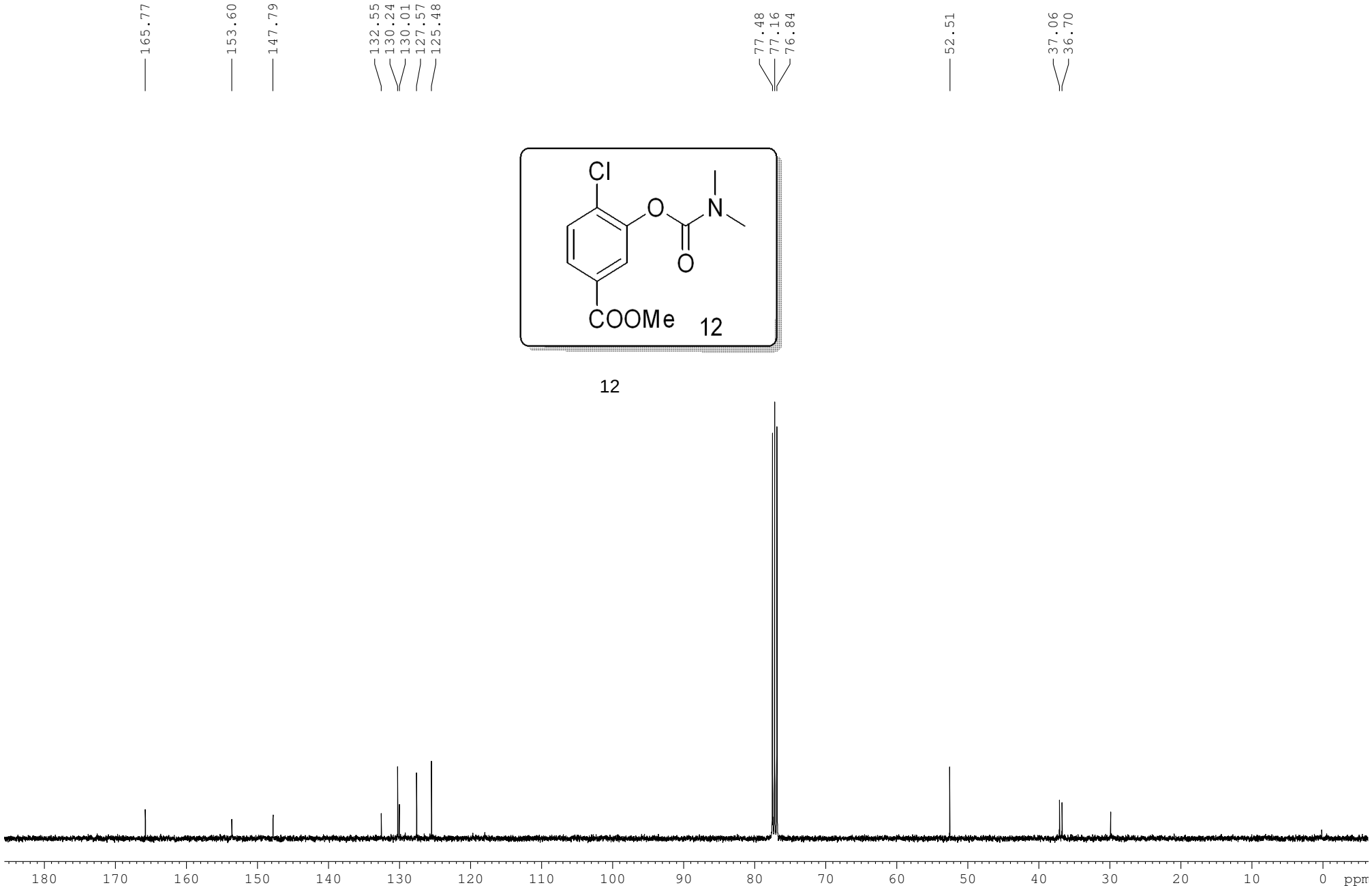


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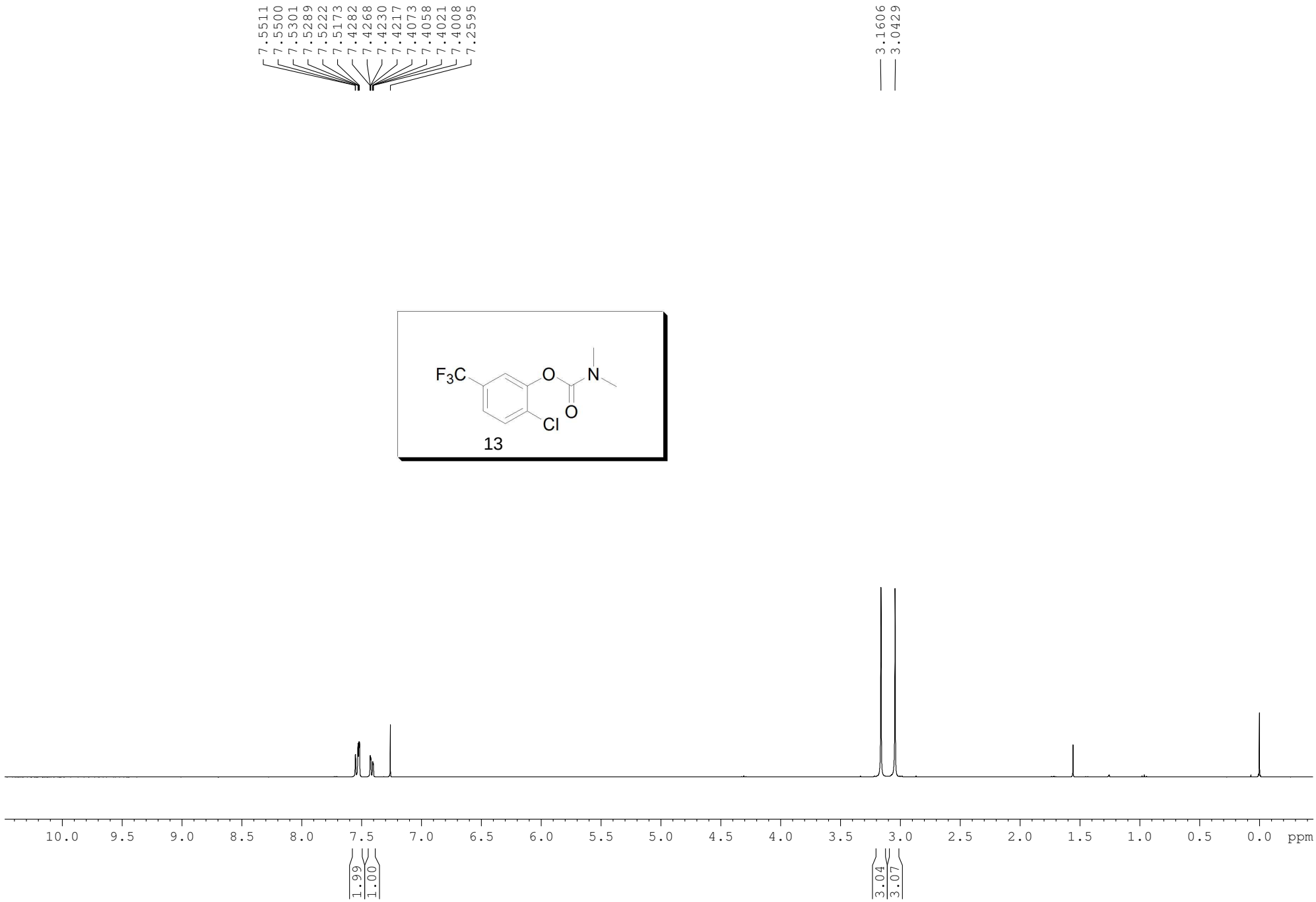

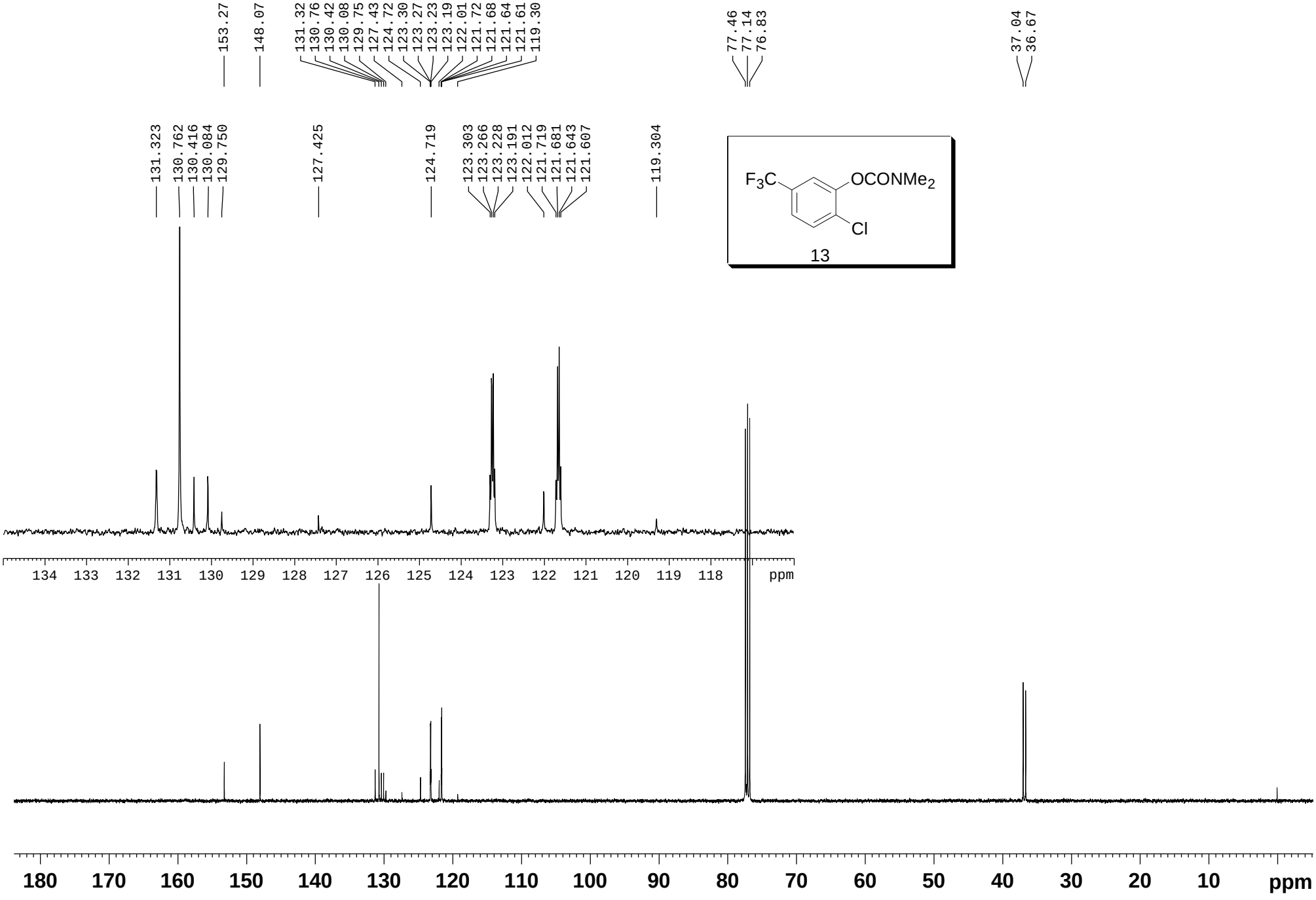

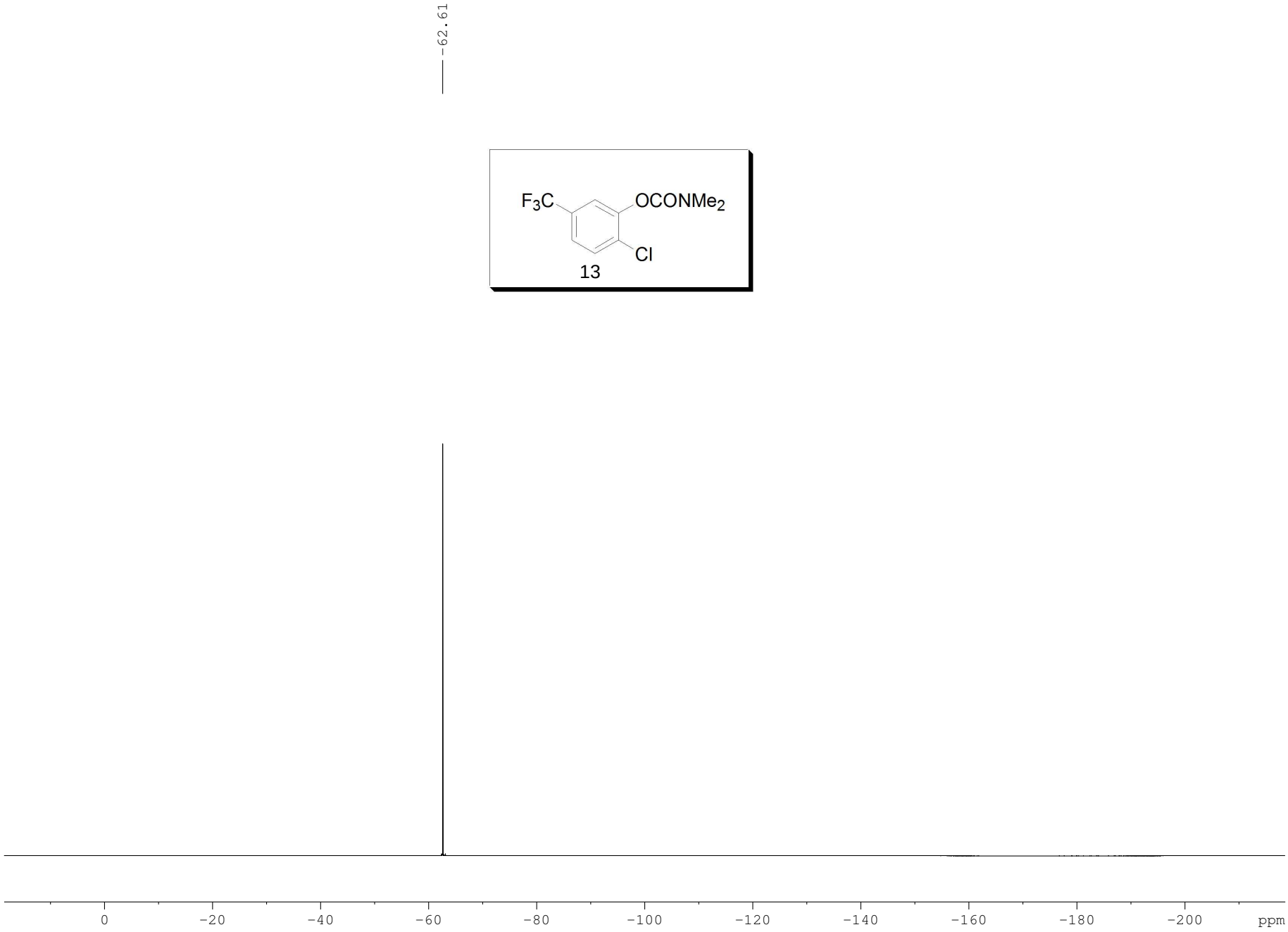

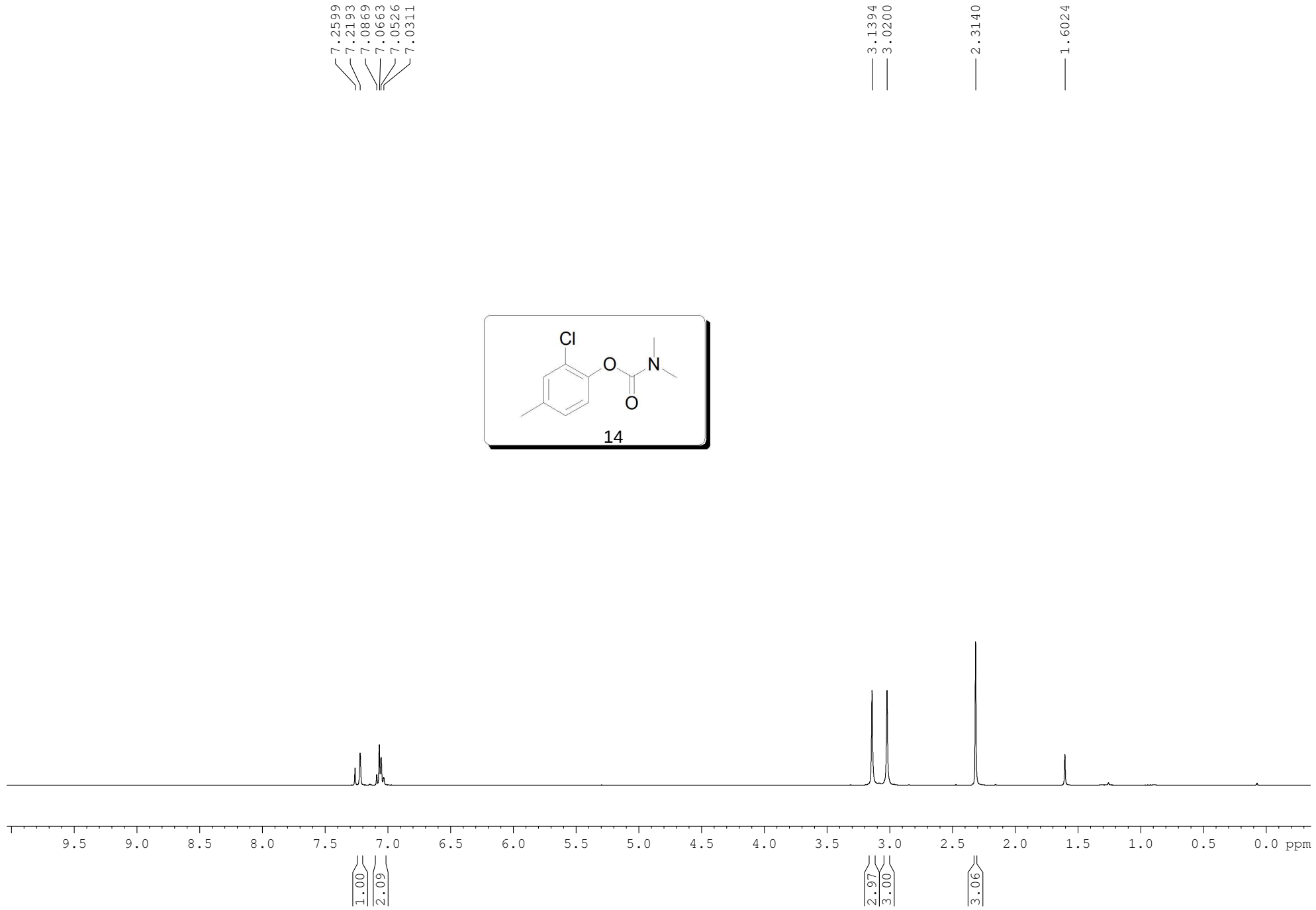

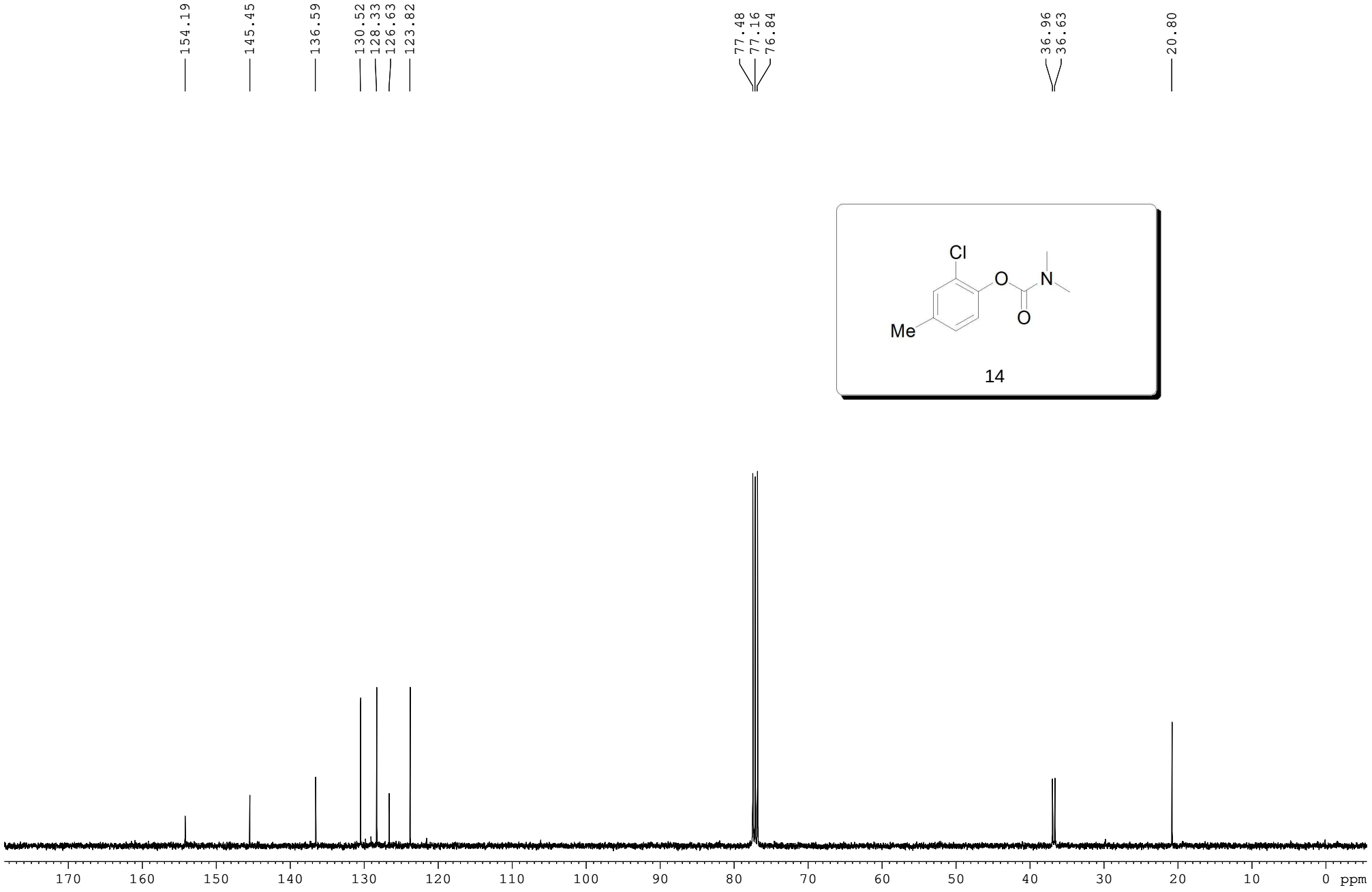

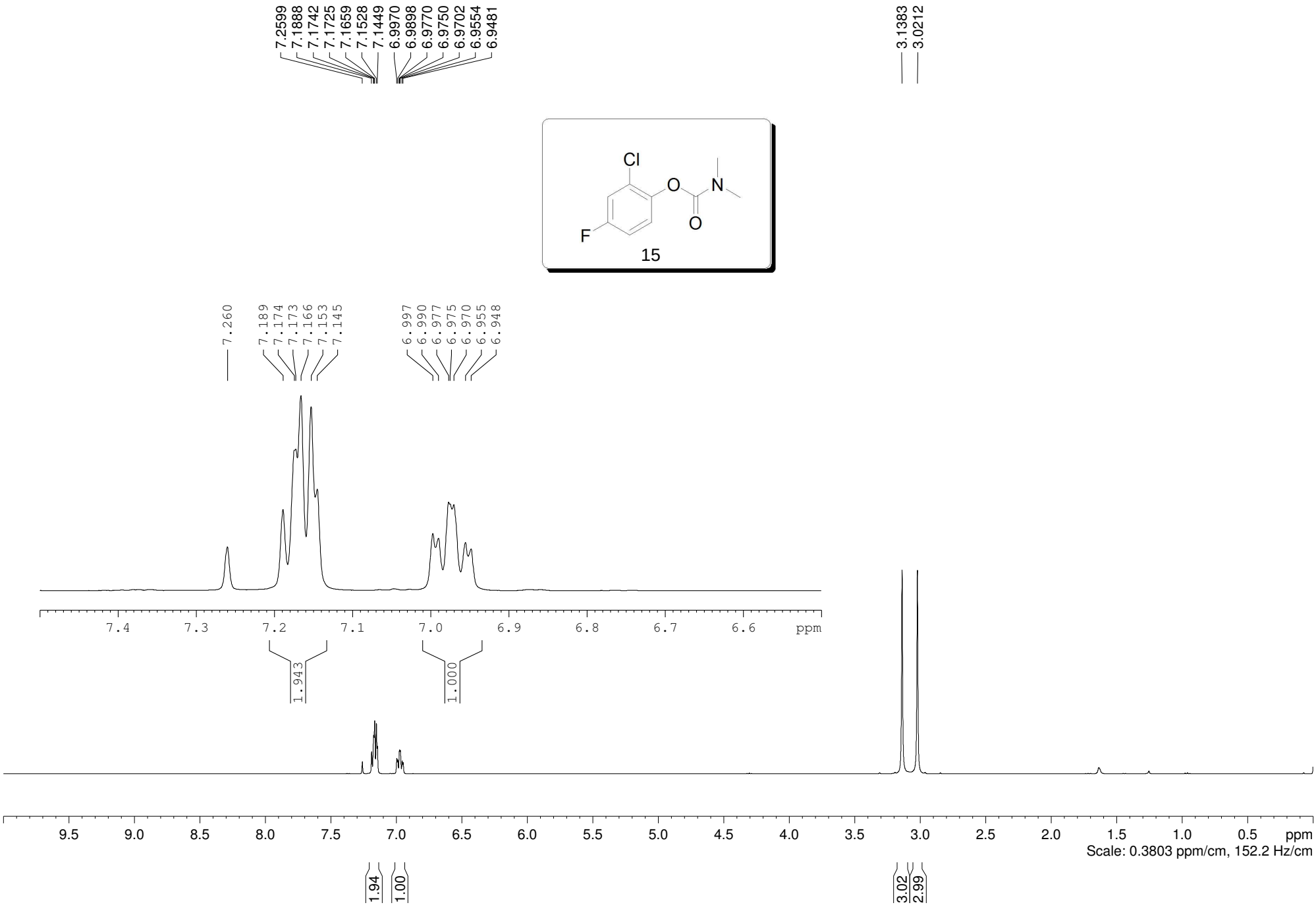

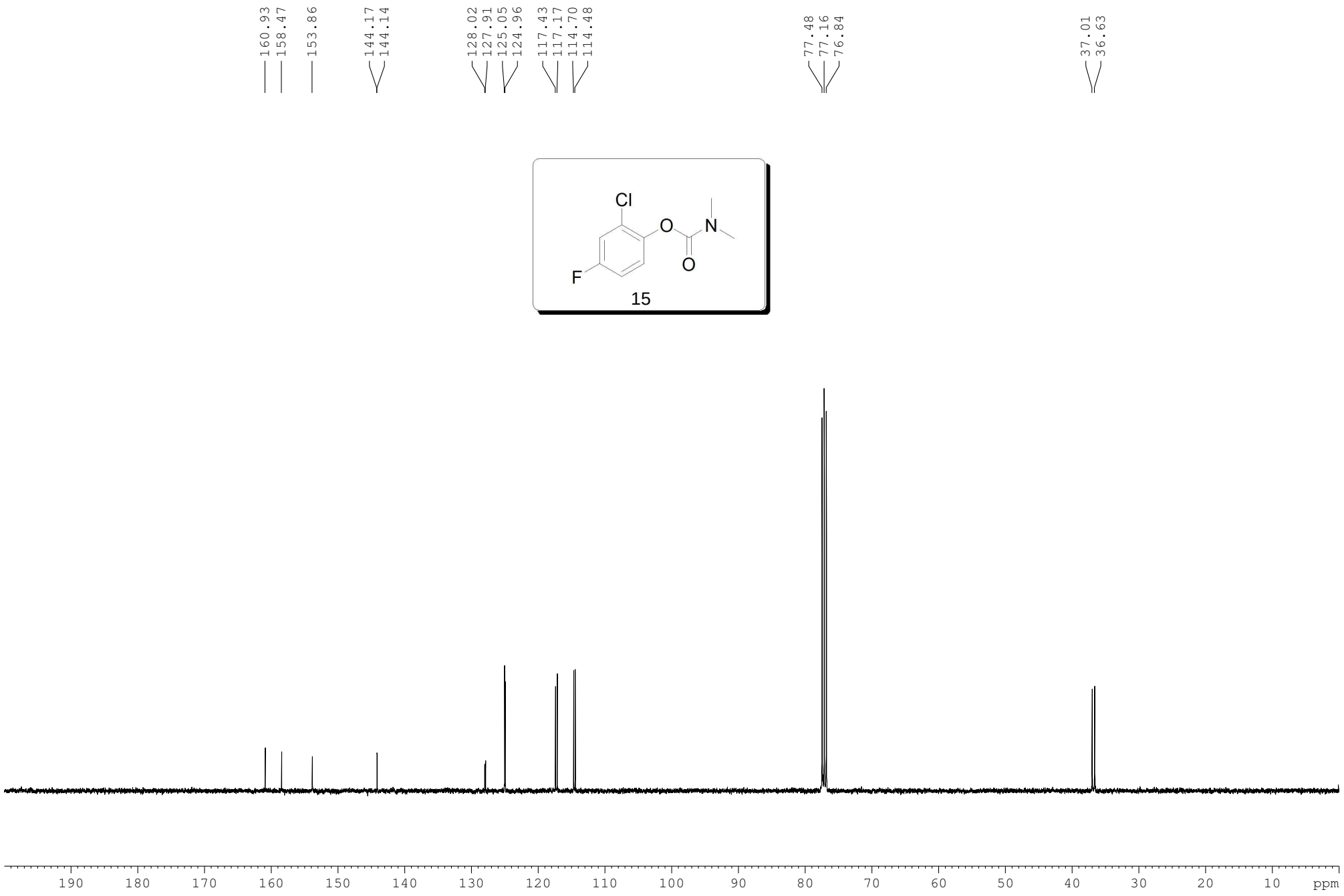

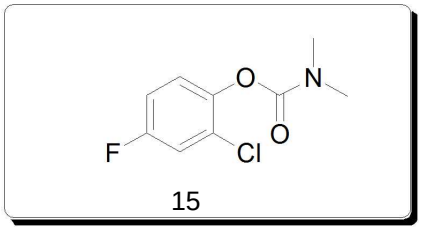


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