

Supporting Information

For

Regioselective Synthesis of 3-Nitroindole under Non-acidic and Non-metallic Conditions

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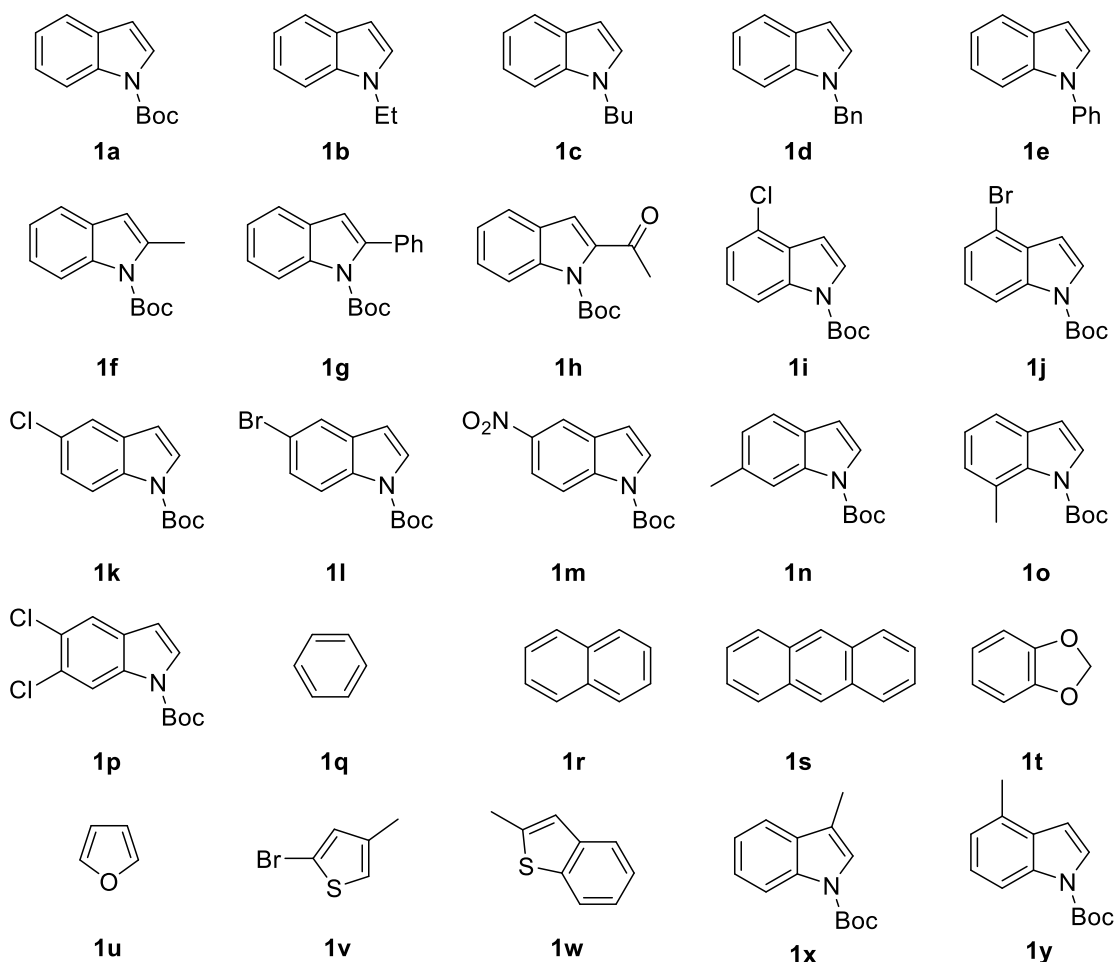
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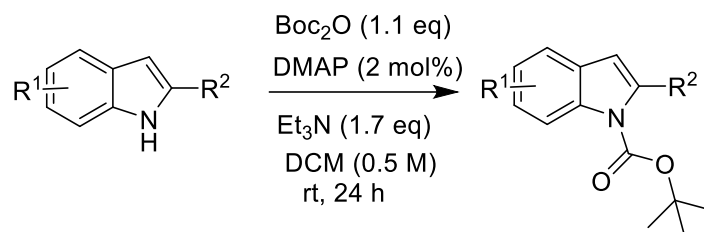
1. General Information:

All template reaction experiments were carried out under atmospheric conditions. Thin layer chromatography was carried out in the ultraviolet light using a GF-254 silica gel plate. Column chromatography was carried out using 200-300 mesh silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 600MHz on an Agilent spectrometer. CDCl_3 and DMSO-d_6 were used as solvent. Chemical shifts were referenced relative to residual solvent. Coupling constants (J) were reported in Hertz (Hz). HRMS were performed on a Thermo Scientific LTQ Orbitrap XL instrument. Melting points were measured with micro melting point apparatus. NMe_4NO_3 (Adamas, 99%), $(\text{CF}_3\text{CO})_2\text{O}$ (Adamas, 99%), CH_3CN (Adamas, 99%), 1-phenyl-1*H*-indole (**1e**, Adamas, 99%), benzene (**1q**, Adamas, 97%), naphthalene (**1r**, 97%), anthracene (**1s**, Adamas, 98%), benzo[*d*][1,3]dioxole (**1t**, Adamas, 98%), furan (**1u**, Adamas, 98%), 2-bromo-4-methylthiophene (**1v**, Adamas, 99%), 2-methylbenzo[*b*]thiophene (**1w**, Adamas, 97%) were commercial available, and the naphthoquinone derivatives (**1a-1d**, **1f-1p**) were prepared according to literature.^[1, 2]



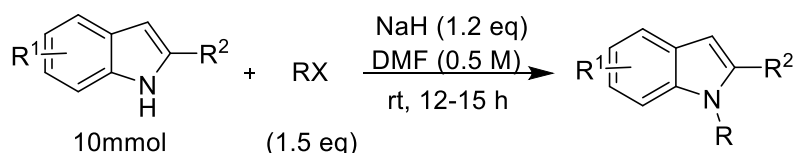
2. Substrate synthesis:

(a) Synthesis of compounds **1a**, **1f-1p**, **1x-1y**^[1]



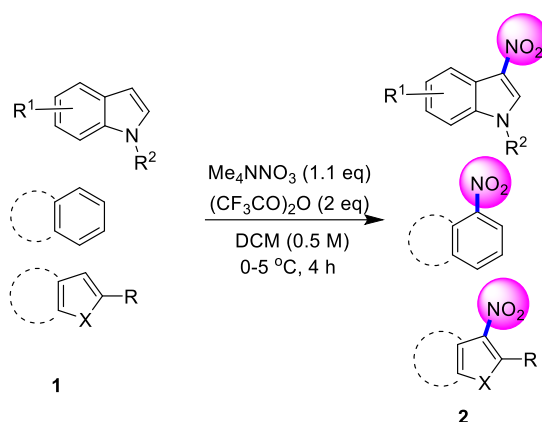
Indole (10 mmol), DMAP (25 mg, 0.2 mmol), $(\text{Et})_3\text{N}$ (1720 mg, 17 mol) were sequentially weighed into the reaction flask, then 10 mL of DCM was added, and the reaction was reduced to 0-5 °C for 10min. Boc_2O (2400 mg dissolved in 20mL DCM, 11 mol) was added to the reaction system and incubated for 24 hours at room temperature. After the reaction was completed, saturated ammonium chloride solution was added to extract with DCM. The organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated to dryness under reduced pressure, and the product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to obtain **1a**, **1f-1m**, **1x-1y**.

(b) Synthesis of compounds **1b-1d**^[2]



To a stirred suspension of NaH (60% dispersion in mineral oil; 480 mg, 12.0 mmol) in DMF (10 mL) was added dropwise a solution of an indole (10.0 mmol) in DMF (10 mL) at 0 °C, and the mixture was stirred at room temperature for 30 min. To the mixture was added dropwise halogenated hydrocarbons (15.0 mmol) at 0 °C, and the resulting mixture was stirred at room temperature overnight. The reaction was quenched with water and the aqueous layer was extracted with ethyl acetate. The organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated to dryness under reduced pressure, and the product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to obtain **1b-1d**.

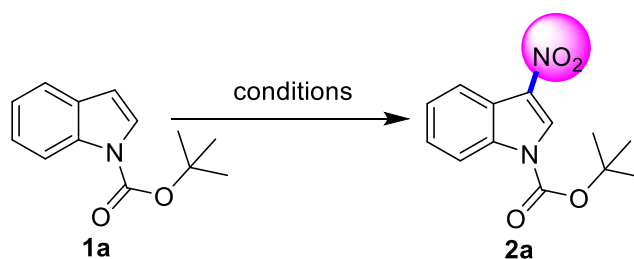
3. Typical Procedure for Synthesis of 2:



Add aromatic or heteroaromatic hydrocarbons (1 mmol) and NMe₄NO₃ (150 mg, 1.1 mmol) to the reaction tube and immediately dissolve it with CH₃CN (1 mL). The reaction system was then cooled to 0-5 °C and the trifluoroacetic anhydride solution (420mg dissolved in 1mL CH₃CN) was added. The reaction system was incubated at 0-5 °C for 4 hours. At the same time, the reaction was monitored by TLC. When the reaction was completed, the reaction was quenched by saturated sodium carbonate. Extract with EA and transfer to a round bottom flask. Silica gel was added to the flask, and the solvent was evaporated under vacuum. Purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain compound **2**.

4. Optimization of the Reaction Conditions.

Table 1. Optimization of the Reaction Conditions ^{a, b}



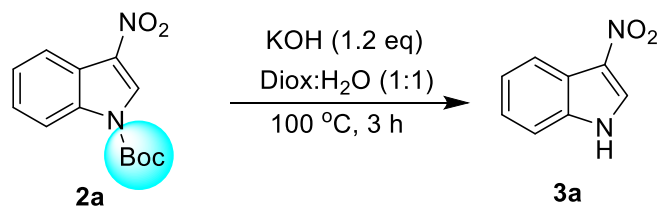
entry	Ammonium salts	Anhydride	solvent	T (°C)	Yield(%) 2a
1	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DCM	0-5	78
2	NBu ₄ NO ₃	(CF ₃ CO) ₂ O	DCM	0-5	56
3	KNO ₃	(CF ₃ CO) ₂ O	DCM	0-5	trace
4	BiNO ₃	(CF ₃ CO) ₂ O	DCM	0-5	trace
5	NMe ₄ NO ₃	(Ac) ₂ O	DCM	0-5	NR
6	NMe ₄ NO ₃	(CF ₃ SO ₂) ₂ O	DCM	0-5	trace
7 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DCM	0-5	85
8 ^d	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DCM	0-5	72
9 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	HFIP	0-5	87

10 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	THF	0-5	41
12 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	MeOH	0-5	NR
13 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DMF	0-5	33
14 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DMSO	0-5	trace
15 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	EA	0-5	92
16 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	CH ₃ CN	0-5	97
17 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DCM	-20	trace
18 ^c	NMe ₄ NO ₃	(CF ₃ CO) ₂ O	DCM	25	trace

^{a)} Reaction conditions: **1a** (0.5 mmol), Ammonium salts (0.55 mmol), Anhydride (1 mL), solvent (1 mL), 4h; ^{b)}yield refers to isolated product. ^{c)} 1 mmol of anhydride was used. ^{d)}0.5 mmol of anhydride was used.

The reaction conditions were optimized by using *tert*-butyl 1*H*-indole-1-carboxylate (**1a**) as substrate (**Table 1**). Gratifyingly, when trifluoroacetic anhydride and tetramethylammonium nitrate were used as reaction reagents, *tert*-butyl 3-nitro-1*H*-indole-1-carboxylate (**2a**) was obtained in medium yield (entry 1). Then we investigated other ammonium salts, which only got trace product except tetrabutylammonium nitrate which could get the target product in medium yield (entries 2-4). We tried to improve the yield of the reaction by changing the type of anhydride. It was regrettable that acetic anhydride was not capable of performing this reaction (entry 5). The triflic anhydride could only get trace amounts of the product (entry 6). The exciting thing was that the yield was unexpectedly increased to 85% when the amount of trifluoroacetic anhydride was two equivalent (entry 7). However, the yield of decreased with the decrease of the amount of anhydride (entry 8). We also investigated the effects of different solvents on the reaction, most of which could not get ideal results (entries 10-15). Interestingly, when acetonitrile was used as a solvent, the yield of the reaction could be dramatically increased to 97% (entry 16). What's more, the reaction was almost impossible when the temperature was reduced to -20 °C (entry 17). Finally, Only trace amounts are produced when the temperature increased to 25 °C (entry 18).

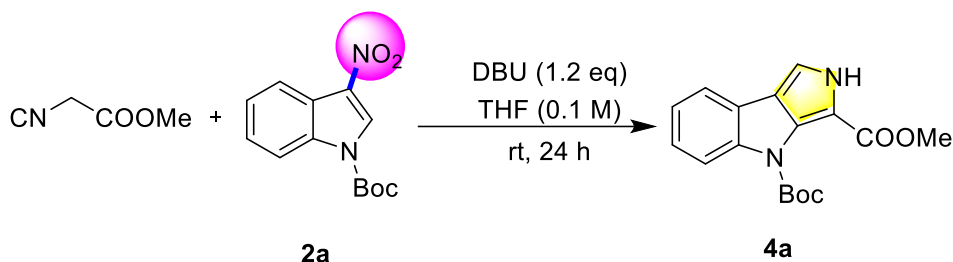
5. Typical Procedure for Synthesis of **3a**.



2a (262 mg, 1 mmol), KOH (1.2 mmol), 1,4-dioxane (1 mL) and water (1 mL) were added to the reaction tube in turn. The reaction system was incubated at 100 °C for 3 hours. At the same time, the reaction was monitored by TLC. The solution was then diluted with water. Extract with ethyl acetate and transfer to a round bottom flask. Silica gel was added to the flask, and the solvent was evaporated under vacuum. Purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain compound **3a** (3-nitro-1*H*-indole) as a yellow solid (154 mg, 95%

yield).

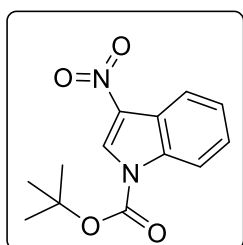
6. Typical Procedure for Synthesis of 4a.



To a stirred solution of *tert*-butyl 3-nitro-1*H*-indole-1-carboxylate **2a** (262 mg, 1.00 mmol) and Methyl isocyanoacetate (119 mg, 1.20 mmol) in THF (10 mL) was added DBU (182 mg, 1.20 mmol) at r.t. The mixture was stirred at r.t. for 20-24 h. Removal of the solvent in vacuo gave a crude oil. Purify by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain compound **4a** (4-(*tert*-butyl) 3-methyl pyrrolo[3,4-*b*]indole-3,4(2*H*)-dicarboxylate) as a yellow solid (289 mg, 92% yield).

7. Characterization of 2, 3a, 4a:

tert-butyl 3-nitro-1*H*-indole-1-carboxylate (**2a**)^[3]



2a

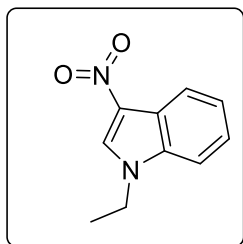
Pale yellow solid, m.p. 134-135°C, 254 mg, yield: 97%; $R_f = 0.46$ (EtOAc/Petroleum ether 1:10).

¹H NMR (400 MHz, CDCl₃): δ 8.57 (s, 1H), 8.28 (m, 2H), 7.51-7.45 (m, 2H), 1.73 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 148.2, 134.3, 132.5, 127.9, 126.6, 125.5, 121.5, 120.7, 115.5, 86.7, 28.0.

HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for C₁₃H₁₄N₂O₄Na 285.0850; found 285.0851.

1-ethyl-3-nitro-1*H*-indole (**2b**)



2b

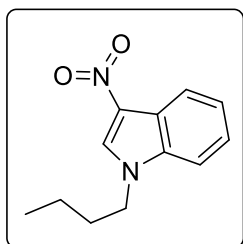
Pale yellow solid, m.p. 100-101°C, 112 mg, yield: 59%; $R_f = 0.12$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 8.33-8.24 (m, 1H), 8.14 (s, 1H), 7.41 (m, 3H), 4.26 (q, $J = 7.3$ Hz, 2H), 1.58 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 135.0, 129.8, 124.4, 124.2, 121.1, 120.9, 110.6, 42.2, 14.9.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2\text{Na}$ 213.0636; found 213.0634.

1-butyl-3-nitro-1H-indole (2c)



2c

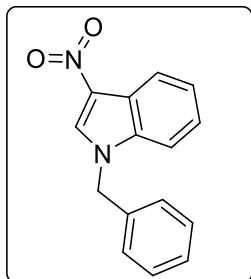
Pale yellow solid, m.p. 150-151°C, 146 mg, yield: 67%; $R_f = 0.15$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 8.33-8.28 (m, 1H), 8.12 (s, 1H), 7.48-7.34 (m, 3H), 4.20 (t, $J = 7.2$ Hz, 2H), 1.97-1.84 (m, 2H), 1.47-1.36 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 135.2, 130.4, 124.4, 124.2, 121.1, 121.0, 110.7, 47.3, 31.7, 20.0, 13.6.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}$ 241.0953; found 241.0948.

1-benzyl-3-nitro-1H-indole (2d) ^[3]



2d

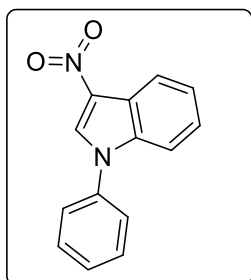
Pale yellow solid, m.p. 119-120°C, 141 mg, yield: 56%; $R_f = 0.11$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 8.33 (m, 1H), 8.10 (s, 1H), 7.45-7.33 (m, 6H), 7.27-7.19 (m, 2H), 5.38 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3): δ 135.4, 134.4, 130.6, 129.3, 129.1, 128.8, 127.5, 124.7, 124.4, 121.1, 121.0, 111.0, 51.3.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{Na}$ 275.0796; found 275.0798.

3-nitro-1-phenyl-1H-indole (2e)



2e

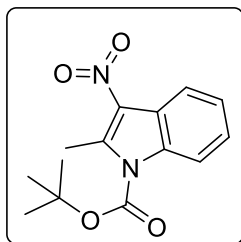
Pale yellow solid, m.p. 109-110°C, 164 mg, yield: 69%; $R_f = 0.21$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 8.40 (m, 1H), 8.32 (s, 1H), 7.68-7.59 (m, 2H), 7.61-7.44 (m, 5H), 7.40 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 137.3, 135.6, 130.6, 130.2, 130.1, 129.0, 125.1, 124.7, 121.0, 121.0, 111.7.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Na}$ 261.0640; found 261.0638.

tert-butyl 2-methyl-3-nitro-1H-indole-1-carboxylate (2f)^[4]



2f

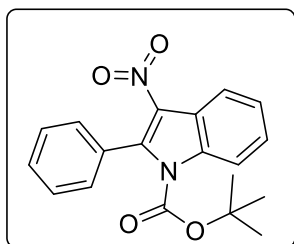
Pale yellow solid, m.p. 130-131°C, 210 mg, yield: 88%; $R_f = 0.35$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.29-8.21 (m, 1H), 8.12-8.05 (m, 1H), 7.47-7.36 (m, 2H), 3.09 (s, 3H), 1.75 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.2, 142.3, 133.6, 131.4, 125.8, 125.1, 121.7, 120.4, 115.0, 86.7, 28.1, 15.1.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4\text{Na}$ 299.1008; found 299.1009.

***tert*-butyl 3-nitro-2-phenyl-1H-indole-1-carboxylate (2g)**



2g

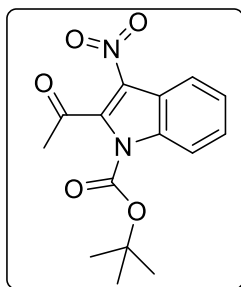
Pale yellow solid, m.p. 166-167°C, 318 mg, yield: 94%; $R_f = 0.36$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.38-8.30 (m, 1H), 8.30-8.21 (m, 1H), 7.56-7.48 (m, 5H), 7.46 (m, 2H), 1.25 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 148.7, 140.4, 134.3, 131.0, 130.8, 129.4, 129.4, 128.2, 126.6, 125.4, 121.3, 120.9, 114.9, 86.0, 27.2.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4\text{Na}$ 361.1164; found 361.1166.

***tert*-butyl 2-acetyl-3-nitro-1H-indole-1-carboxylate (2h)**



2h

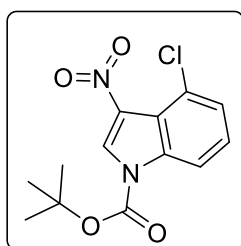
Pale yellow solid, m.p. 104-105°C, 250 mg, yield: 82%; $R_f = 0.44$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 8.59-8.54 (m, 1H), 8.31 (dd, $J = 9.2, 2.3$ Hz, 1H), 8.15 (dt, $J = 9.2, 0.7$ Hz, 1H), 7.17 (d, $J = 0.8$ Hz, 1H), 2.61 (s, 3H), 1.64 (s, 9H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 190.9, 148.7, 144.1, 141.1, 140.7, 127.1, 122.0, 118.9, 115.1, 113.5, 86.4, 29.0, 27.7.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_5\text{Na}$ 327.0957; found 327.0956.

***tert*-butyl 4-chloro-3-nitro-1*H*-indole-1-carboxylate (2i)**



2i

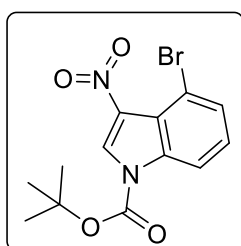
Pale yellow solid, m.p. 130-131°C, 199 mg, yield: 67%; $R_f = 0.32$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.43 (s, 1H), 8.21 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.39-7.31 (m, 2H), 1.72 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.7, 135.8, 128.6, 127.1, 126.9, 125.9, 118.7, 114.2, 87.1, 28.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_4\text{NaCl}$ 319.0462; found 319.0458.

***tert*-butyl 4-bromo-3-nitro-1*H*-indole-1-carboxylate (2j)^[5]**



2j

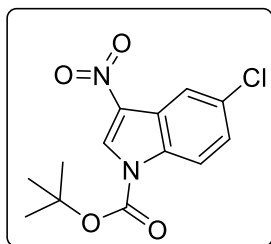
Pale yellow solid, m.p. 105-106°C, 201 mg, yield: 59%; $R_f = 0.35$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.43 (s, 1H), 8.21 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.39-7.31 (m, 2H), 1.72 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.7, 135.7, 133.5, 130.7, 128.4, 127.2, 120.4, 114.7, 113.1, 87.1, 28.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_4\text{NaBr}$ 362.9956; found 362.9957.

***tert*-butyl 5-chloro-3-nitro-1*H*-indole-1-carboxylate (2k)** ^[5]



2k

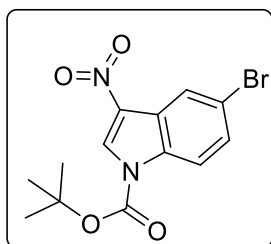
Pale yellow solid, m.p. 249-250°C, 279 mg, yield: 94%; $R_f = 0.23$ (EtOAc/Petroleum ether 1:10).

¹H NMR (400 MHz, CDCl₃): δ 8.54 (s, 1H), 8.24 (d, $J = 2.1$ Hz, 1H), 8.17 (d, $J = 9.0$ Hz, 1H), 7.42 (dd, $J = 9.0, 2.2$ Hz, 1H), 1.73 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 132.6, 131.6, 128.7, 127.0, 122.5, 120.3, 116.7, 87.3, 28.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for C₁₃H₁₃N₂O₄NaCl 319.0462; found 319.0461.

***tert*-butyl 5-bromo-3-nitro-1*H*-indole-1-carboxylate (2l)** ^[5]



2l

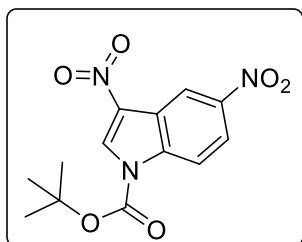
Pale yellow solid, m.p. 237-238°C, 290 mg, yield: 85%; $R_f = 0.24$ (EtOAc/Petroleum ether 1:10).

¹H NMR (600 MHz, CDCl₃): δ 8.51 (s, 1H), 8.42 (d, $J = 2.0$ Hz, 1H), 8.11 (d, $J = 8.9$ Hz, 1H), 7.56 (dd, $J = 8.9, 2.0$ Hz, 1H), 1.71 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 147.8, 133.0, 131.4, 129.7, 128.5, 123.3, 122.9, 119.3, 117.0, 87.3, 28.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for C₁₃H₁₃N₂O₄NaBr 362.9956; found 362.9955.

***tert*-butyl 3,5-dinitro-1*H*-indole-1-carboxylate (2m)** ^[5]



2m

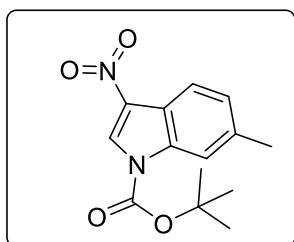
Pale yellow solid, m.p. 293-294°C, 246 mg, yield: 80%; $R_f = 0.14$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 9.16 (d, $J = 2.3$ Hz, 1H), 8.68 (s, 1H), 8.44-8.34 (m, 2H), 1.76 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.3, 145.6, 136.9, 132.5, 130.3, 121.7, 121.6, 117.2, 116.3, 88.3, 28.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_6\text{Na}$ 330.0702; found 330.0700.

***tert*-butyl 6-methyl-3-nitro-1*H*-indole-1-carboxylate (2n)** ^[5]



2n

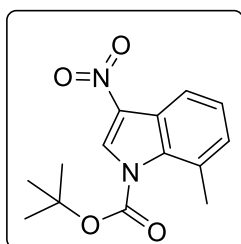
Pale yellow solid, m.p. 136-138°C, 199 mg, yield: 72%; $R_f = 0.35$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 8.47 (s, 1H), 8.15-8.07 (m, 2H), 7.28 (s, 1H), 2.53 (s, 3H), 1.74 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3): δ 148.3, 137.1, 134.8, 132.5, 127.3, 127.0, 120.2, 119.2, 115.6, 86.5, 28.0, 22.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4\text{Na}$ 299.1008; found 299.1009.

***tert*-butyl 7-methyl-3-nitro-1*H*-indole-1-carboxylate (2o)** ^[6]



2o

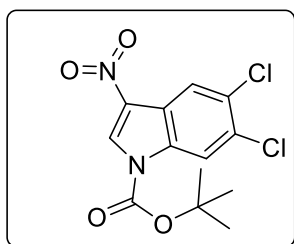
Pale yellow solid, m.p. 136-137°C, 224 mg, yield: 81%; $R_f = 0.32$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.5$ Hz, 1H), 7.73 (d, $J = 3.7$ Hz, 1H), 7.47 (d, $J = 8.5$ Hz, 1H), 6.62 (d, $J = 3.7$ Hz, 1H), 2.66 (s, 3H), 1.67 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.0, 148.2, 135.2, 135.0, 133.0, 122.4, 120.0, 118.6, 107.2, 84.8, 28.0, 18.5.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4\text{Na}$ 299.1008; found 299.1007.

***tert*-butyl 5,6-dichloro-3-nitro-1*H*-indole-1-carboxylate (2p)**



2p

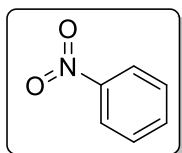
White solid, m.p. 340-341°C, 272 mg, yield: 82%; $R_f = 0.23$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.53 (s, 1H), 8.40 (s, 1H), 8.35 (s, 1H), 1.73 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 147.5, 132.7, 131.4, 131.2, 130.3, 128.9, 121.8, 120.9, 117.4, 87.8, 28.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_4\text{Cl}_2\text{Na}$ 353.0072; found 353.0075.

nitrobenzene (2q)^[7]



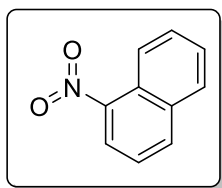
2q

Colorless liquid, 108 mg, yield: 88%; $R_f = 0.51$ (EtOAc/Petroleum ether 1:10).

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 8.23 (d, $J = 8.2$ Hz, 2H), 7.71 (t, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 2H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 148.1, 134.7, 129.3, 129.3, 123.5, 123.3.

1-nitronaphthalene (2r)^[8]



2r

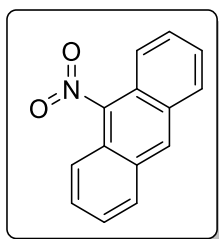
White solid, m.p. 59-60°C, 165 mg, yield: 95%; $R_f = 0.55$ (EtOAc/Petroleum ether 1:10).

^1H NMR (400 MHz, CDCl_3): δ 8.59 (dd, $J = 8.7, 1.0$ Hz, 1H), 8.26 (dd, $J = 7.7, 1.2$ Hz, 1H), 8.14 (d, $J = 8.3$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.74 (ddd, $J = 8.6, 6.9, 1.4$ Hz, 1H), 7.65 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 7.57 (t, $J = 7.9$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 146.6, 134.7, 134.3, 129.5, 128.6, 127.4, 125.1, 124.2, 124.1, 123.1.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{NO}_2$ 174.0555; found 174.0551.

9-nitroanthracene (2s) ^[9]



2s

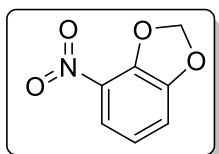
White solid, m.p. 139-140°C, 196 mg, yield: 88%; $R_f = 0.53$ (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3): δ 8.60 (s, 1H), 8.06 (d, $J = 8.5$ Hz, 2H), 7.94 (dd, $J = 8.9, 1.1$ Hz, 2H), 7.68-7.62 (m, 2H), 7.56 (td, $J = 7.6, 7.1, 1.6$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 144.2, 130.8, 130.8, 130.4, 128.9, 128.4, 126.2, 126.2, 122.7, 122.6, 121.4, 121.4.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{NO}_2$ 224.0712; found 224.0708.

4-nitrobenzo[*d*][1,3]dioxole (2t) ^[10]



2t

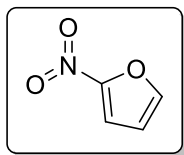
White solid, m.p. 118-119°C, 139 mg, yield: 83%; $R_f = 0.31$ (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3): δ 7.90 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.67 (d, $J = 2.3$ Hz, 1H), 6.87 (d, $J = 8.6$ Hz, 1H), 6.15 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 153.2, 148.2, 142.9, 119.9, 107.6, 104.5, 103.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_5NO_4Na$ 190.0116; found 190.0114.

2-nitrofuran (2u) ^[11]



2u

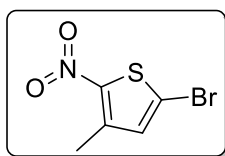
Colorless liquid, 96 mg, yield: 85%; $R_f = 0.52$ (EtOAc/Petroleum ether 1:10).

1H NMR (400 MHz, DMSO-*d*₆): δ 8.08-8.01 (m, 1H), 7.64 (dd, $J = 3.7, 1.1$ Hz, 1H), 6.86 (dd, $J = 3.8, 1.9$ Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d*₆): δ 147.5, 145.1, 114.4, 113.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_4H_3NO_3Na$ 136.0011; found 136.0009.

5-bromo-3-methyl-2-nitrothiophene (2v) ^[12]



2v

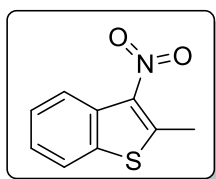
White solid, m.p. 84-85°C, 193 mg, yield: 87%; $R_f = 0.48$ (EtOAc/Petroleum ether 1:10).

1H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 1H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1, 143.8, 131.0, 113.0, 16.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_5H_5NO_2SBr$ 221.9224; found 221.9217.

2-methyl-3-nitrobenzo[*b*]thiophene (2w) ^[13]



2w

White solid, m.p. 94-95°C, 172 mg, yield: 89%; $R_f = 0.54$ (EtOAc/Petroleum ether 1:10).

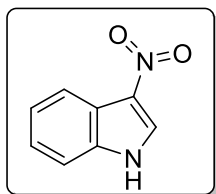
1H NMR (600 MHz, $CDCl_3$): δ 8.45 (dd, $J = 9.2, 4.8$ Hz, 1H), 7.78-7.72 (m, 1H), 7.57-7.50 (m, 1H), 7.43 (td, $J = 7.1, 6.6, 1.6$ Hz, 1H), 2.92 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.3, 138.6, 134.4, 132.1, 126.7, 125.9, 123.6, 121.9, 17.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_9H_7NO_2NaS$ 216.0095; found

216.0090.

3-nitro-1*H*-indole (3a)^[14]



3a

Yellow solid, m.p. 209-210°C, 154 mg, yield: 95%; $R_f = 0.23$ (EtOAc/Petroleum ether 1:10).

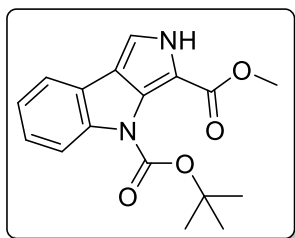
¹H NMR (400 MHz, CDCl₃): δ 12.68 (s, 1H), 8.66 (d, $J = 3.0$ Hz, 1H), 8.14-8.02 (m, 1H), 7.58 (dd, $J = 6.5, 2.8$ Hz, 1H), 7.40-7.30 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 135.5, 131.0, 128.9, 124.6, 124.2, 120.3, 119.9, 113.8.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₈H₇N₂O₂ 163.0508; found 163.0507.

4-(*tert*-butyl) 3-methyl pyrrolo[3,4-*b*]indole-3,4(2*H*)-dicarboxylate

(4a)



4a

Pale yellow solid, m.p. 168-169°C, 289 mg, yield: 92%; $R_f = 0.11$ (EtOAc/Petroleum ether 1:10).

¹H NMR (400 MHz, CDCl₃): δ 9.46 (s, 1H), 8.15 (d, $J = 8.3$ Hz, 1H), 7.68 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.35 (ddd, $J = 8.4, 7.4, 1.4$ Hz, 1H), 7.29-7.26 (m, 1H), 7.20 (d, $J = 3.2$ Hz, 1H), 3.93 (s, 3H), 1.69 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 160.6, 150.4, 143.9, 133.2, 125.2, 123.1, 122.9, 120.0, 119.4, 116.0, 111.0, 106.1, 83.4, 51.5, 28.0.

HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for C₁₇H₁₈N₂O₄Na 337.1159; found 337.1167.

8. X-Ray Analysis

Compound **2g** X-Ray crystal diffraction data: Crystals were grown in slow diffusion with EA as clusters of colorless prisms. The ellipsoids are shown at 30% probability levels. Compounds **2g** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu K α radiation. The data were collected and processed using CrysAlisPro. The structure was solved by direct methods using Olex2 software, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2 . The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2 . The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2251492 for compounds **2g**.

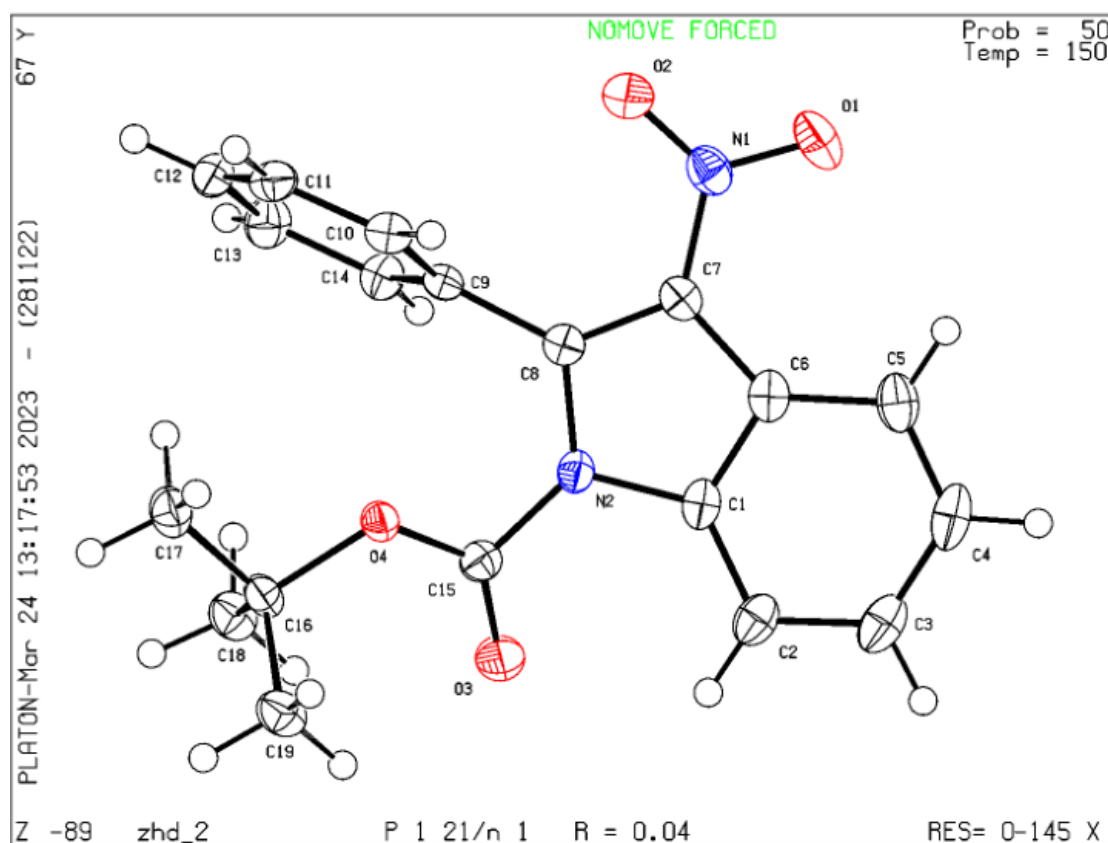


Figure S1. ORTEP Drawing of **2g** (The ellipsoids are shown at 30% probability levels)

Table 2 Crystal data and structure refinement for 2g.

Identification code	2g
Empirical formula	C ₁₉ H ₁₈ N ₂ O ₄
Formula weight	338.35
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.0316(9)
b/Å	11.9364(11)
c/Å	13.9690(14)
α/°	90
β/°	101.674(9)
γ/°	90
Volume/Å ³	1638.1(3)
Z	4
ρ _{calc} /cm ³	1.372
μ/mm ⁻¹	0.097
F(000)	712.0
Crystal size/mm ³	0.15 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.528 to 49.998
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -16 ≤ l ≤ 13
Reflections collected	6991
Independent reflections	2880 [R _{int} = 0.0308, R _{sigma} = 0.0421]
Data/restraints/parameters	2880/0/229
Goodness-of-fit on F ²	1.044
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0434, wR ₂ = 0.0979
Final R indexes [all data]	R ₁ = 0.0554, wR ₂ = 0.1075
Largest diff. peak/hole / e Å ⁻³	0.24/-0.23

Crystal structure determination of [2g]

Crystal Data for C₁₉H₁₈N₂O₄ (*M* = 338.35 g/mol): monoclinic, space group P2₁/n (no. 14), *a* = 10.0316(9) Å, *b* = 11.9364(11) Å, *c* = 13.9690(14) Å, β = 101.674(9)°, *V* = 1638.1(3) Å³, *Z* = 4, *T* = 150.00(10) K, μ(Mo Kα) = 0.097 mm⁻¹, *D*_{calc} = 1.372 g/cm³, 6991 reflections measured (4.528° ≤ 2θ ≤ 49.998°), 2880 unique (*R*_{int} = 0.0308, *R*_{sigma} = 0.0421) which were used in all calculations. The final *R*₁ was 0.0434 (*I* > 2σ(*I*)) and *wR*₂ was 0.1075 (all data).

Refinement model description

Table 3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 2g. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	4736.9(14)	5791.8(12)	8109.2(10)	39.8(4)
O2	5073.3(14)	4240.9(11)	7398.6(10)	40.0(4)
O3	539.4(13)	5825.3(11)	3752.0(10)	34.0(4)
O4	2111.0(11)	4468.5(9)	3749.0(8)	21.4(3)
N1	4549.8(15)	5166.3(13)	7387.7(11)	26.7(4)
N2	2294.2(14)	5591.6(11)	5060.8(11)	20.2(3)
C1	2304.0(17)	6688.2(14)	5442.2(13)	21.4(4)
C2	1649.8(18)	7650.5(14)	5021.9(15)	26.9(4)
C3	1874.0(19)	8623.7(15)	5564.5(16)	32.5(5)
C4	2732.1(19)	8639.2(16)	6482.2(16)	33.6(5)
C5	3395.7(19)	7694.9(15)	6893.9(15)	28.7(4)
C6	3170.7(17)	6689.4(14)	6360.1(13)	22.8(4)
C7	3678.7(17)	5566.4(14)	6515.8(12)	20.8(4)
C8	3147.3(16)	4906.7(14)	5724.5(12)	19.1(4)
C9	3281.7(17)	3690.0(14)	5554.1(12)	19.1(4)
C10	4464.8(17)	3257.2(15)	5325.4(13)	22.5(4)
C11	4544.1(18)	2133.3(15)	5114.9(13)	24.5(4)
C12	3461.7(19)	1429.6(15)	5157.9(13)	26.3(4)
C13	2295.0(18)	1853.1(15)	5398.1(14)	27.8(4)
C14	2195.0(17)	2984.2(14)	5589.6(13)	23.4(4)
C15	1536.8(17)	5304.0(14)	4114.3(13)	21.7(4)
C16	1418.8(17)	3950.6(14)	2794.3(12)	22.2(4)
C17	2341.2(19)	2972.0(15)	2704.2(14)	29.5(4)
C18	12.8(18)	3547.4(15)	2875.8(14)	28.3(4)
C19	1412.0(19)	4807.0(15)	1992.9(13)	28.9(4)

Table 4 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 2g. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*^2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	47.4(9)	46.6(9)	23.2(8)	-10.9(7)	1.6(7)	-4.3(7)
O2	45.7(9)	33.0(8)	34.6(9)	-1.1(6)	-7.6(7)	7.2(7)
O3	29.0(7)	34.0(8)	34.3(8)	-4.8(6)	-4.9(6)	12.0(6)
O4	21.3(6)	22.3(6)	19.3(7)	-3.3(5)	1.1(5)	3.9(5)
N1	26.4(8)	29.8(9)	23.7(9)	-2.4(7)	4.5(7)	-6.7(7)
N2	21.1(7)	17.8(7)	21.8(8)	-3.2(6)	4.8(6)	0.5(6)
C1	19.3(9)	19.8(9)	27.7(10)	-4.4(8)	10.7(8)	-3.9(7)
C2	23.6(9)	21.1(9)	37.8(11)	-0.3(8)	10.2(9)	-1.2(8)
C3	26.9(10)	21.6(10)	51.6(14)	-2.0(9)	14.4(10)	1.2(8)
C4	33.6(11)	23.0(10)	48.8(14)	-13.2(9)	19.2(10)	-4.1(8)
C5	26.8(10)	30.2(10)	31.6(11)	-9.5(9)	11.7(9)	-8.4(8)
C6	20.4(9)	23.7(9)	27.3(10)	-4.1(8)	11.6(8)	-4.9(7)
C7	18.5(9)	24.8(9)	19.7(9)	-0.5(7)	5.2(7)	-3.5(7)
C8	17.1(8)	21.6(9)	19.9(9)	0.8(7)	6.8(7)	-1.1(7)
C9	21.5(9)	20.4(9)	14.8(9)	1.7(7)	2.6(7)	0.6(7)
C10	18.9(9)	27.0(10)	22.1(10)	3.6(8)	5.0(7)	-0.1(7)
C11	26.5(10)	27.7(10)	21.3(10)	3.3(8)	9.0(8)	8.4(8)
C12	35.5(11)	20.1(9)	23.2(10)	-0.3(8)	5.4(8)	2.2(8)
C13	27.9(10)	24.4(10)	31.8(11)	-0.2(8)	7.5(9)	-6.0(8)
C14	21.1(9)	24.6(10)	25.9(10)	-0.7(8)	7.8(8)	0.6(8)
C15	20.6(9)	20.9(9)	23.4(10)	0.8(8)	3.9(8)	-0.1(8)
C16	24.5(9)	24.1(9)	16.9(9)	-2.7(7)	1.4(8)	-3.7(8)
C17	33.0(10)	30.3(10)	24.9(10)	-6.5(8)	5.1(8)	0.6(8)
C18	28.4(10)	30.3(10)	25.8(10)	0.4(8)	4.4(8)	-6.1(8)
C19	30.9(10)	31.6(10)	23.0(10)	2.2(8)	2.9(8)	-5.9(8)

Table 5 Bond Lengths for 2g.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.2378(19)	C5	C6	1.407(2)
O2	N1	1.2218(19)	C6	C7	1.435(2)
O3	C15	1.200(2)	C7	C8	1.374(2)
O4	C15	1.306(2)	C8	C9	1.482(2)
O4	C16	1.506(2)	C9	C10	1.390(2)
N1	C7	1.430(2)	C9	C14	1.387(2)
N2	C1	1.412(2)	C10	C11	1.379(2)
N2	C8	1.393(2)	C11	C12	1.384(3)
N2	C15	1.427(2)	C12	C13	1.377(3)
C1	C2	1.392(2)	C13	C14	1.384(2)
C1	C6	1.396(3)	C16	C17	1.511(3)
C2	C3	1.380(3)	C16	C18	1.516(2)
C3	C4	1.392(3)	C16	C19	1.515(2)
C4	C5	1.375(3)			

Table 6 Bond Angles for 2g.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C15	O4	C16	119.91(13)	N2	C8	C9	122.14(15)
O1	N1	C7	117.26(15)	C7	C8	N2	106.58(15)
O2	N1	O1	122.76(16)	C7	C8	C9	131.12(16)
O2	N1	C7	119.98(15)	C10	C9	C8	120.72(14)
C1	N2	C15	122.28(14)	C14	C9	C8	119.46(14)
C8	N2	C1	109.66(14)	C14	C9	C10	119.78(16)
C8	N2	C15	128.01(14)	C11	C10	C9	119.96(16)
C2	C1	N2	129.69(17)	C10	C11	C12	120.11(16)
C2	C1	C6	122.63(16)	C13	C12	C11	120.05(16)
C6	C1	N2	107.63(14)	C12	C13	C14	120.24(16)
C3	C2	C1	116.88(18)	C9	C14	C13	119.84(16)
C2	C3	C4	121.24(18)	O3	C15	O4	128.86(17)
C5	C4	C3	122.08(18)	O3	C15	N2	120.55(16)
C4	C5	C6	117.75(19)	O4	C15	N2	110.57(14)
C1	C6	C5	119.40(17)	O4	C16	C17	102.16(13)
C1	C6	C7	105.92(14)	O4	C16	C18	109.46(14)
C5	C6	C7	134.64(18)	O4	C16	C19	108.04(13)
N1	C7	C6	125.33(15)	C17	C16	C18	110.82(15)
C8	C7	N1	124.38(16)	C17	C16	C19	111.79(15)
C8	C7	C6	110.20(16)	C18	C16	C19	113.86(15)

Table 7 Torsion Angles for 2g.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N1	C7	C6	10.0(2)	C6	C1	C2	C3	-1.2(3)
O1	N1	C7	C8	-166.20(16)	C6	C7	C8	N2	-0.33(18)
O2	N1	C7	C6	-170.03(16)	C6	C7	C8	C9	-175.62(15)
O2	N1	C7	C8	13.8(2)	C7	C8	C9	C10	-76.8(2)
N1	C7	C8	N2	176.38(14)	C7	C8	C9	C14	105.6(2)
N1	C7	C8	C9	1.1(3)	C8	N2	C1	C2	177.36(17)
N2	C1	C2	C3	-178.48(16)	C8	N2	C1	C6	-0.27(18)
N2	C1	C6	C5	178.27(15)	C8	N2	C15	O3	156.02(17)
N2	C1	C6	C7	0.07(17)	C8	N2	C15	O4	-25.7(2)
N2	C8	C9	C10	108.57(19)	C8	C9	C10	C11	-176.34(16)
N2	C8	C9	C14	-69.1(2)	C8	C9	C14	C13	177.77(16)
C1	N2	C8	C7	0.37(18)	C9	C10	C11	C12	-1.8(3)
C1	N2	C8	C9	176.18(14)	C10	C9	C14	C13	0.1(3)
C1	N2	C15	O3	-26.5(2)	C10	C11	C12	C13	0.9(3)
C1	N2	C15	O4	151.77(14)	C11	C12	C13	C14	0.5(3)
C1	C2	C3	C4	1.0(3)	C12	C13	C14	C9	-1.0(3)
C1	C6	C7	N1	-176.51(15)	C14	C9	C10	C11	1.3(3)
C1	C6	C7	C8	0.16(19)	C15	O4	C16	C17	-174.64(14)
C2	C1	C6	C5	0.4(2)	C15	O4	C16	C18	-57.14(19)
C2	C1	C6	C7	-177.77(15)	C15	O4	C16	C19	67.35(18)
C2	C3	C4	C5	0.0(3)	C15	N2	C1	C2	-0.5(3)
C3	C4	C5	C6	-0.7(3)	C15	N2	C1	C6	-178.13(14)
C4	C5	C6	C1	0.5(2)	C15	N2	C8	C7	178.07(15)
C4	C5	C6	C7	178.09(18)	C15	N2	C8	C9	-6.1(2)
C5	C6	C7	N1	5.7(3)	C16	O4	C15	O3	-7.6(3)
C5	C6	C7	C8	-177.64(18)	C16	O4	C15	N2	174.32(12)

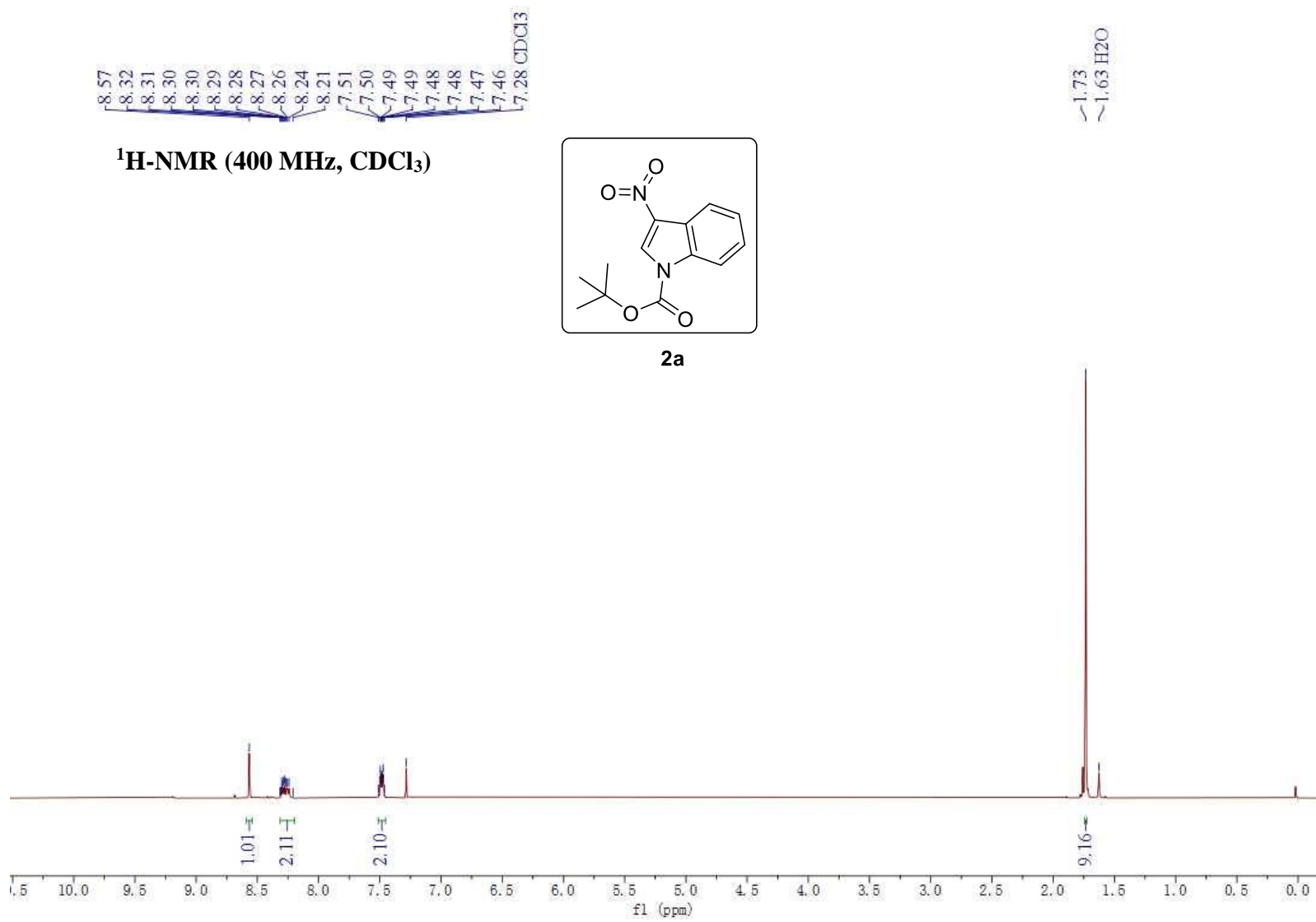
Table 8 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for 2g.

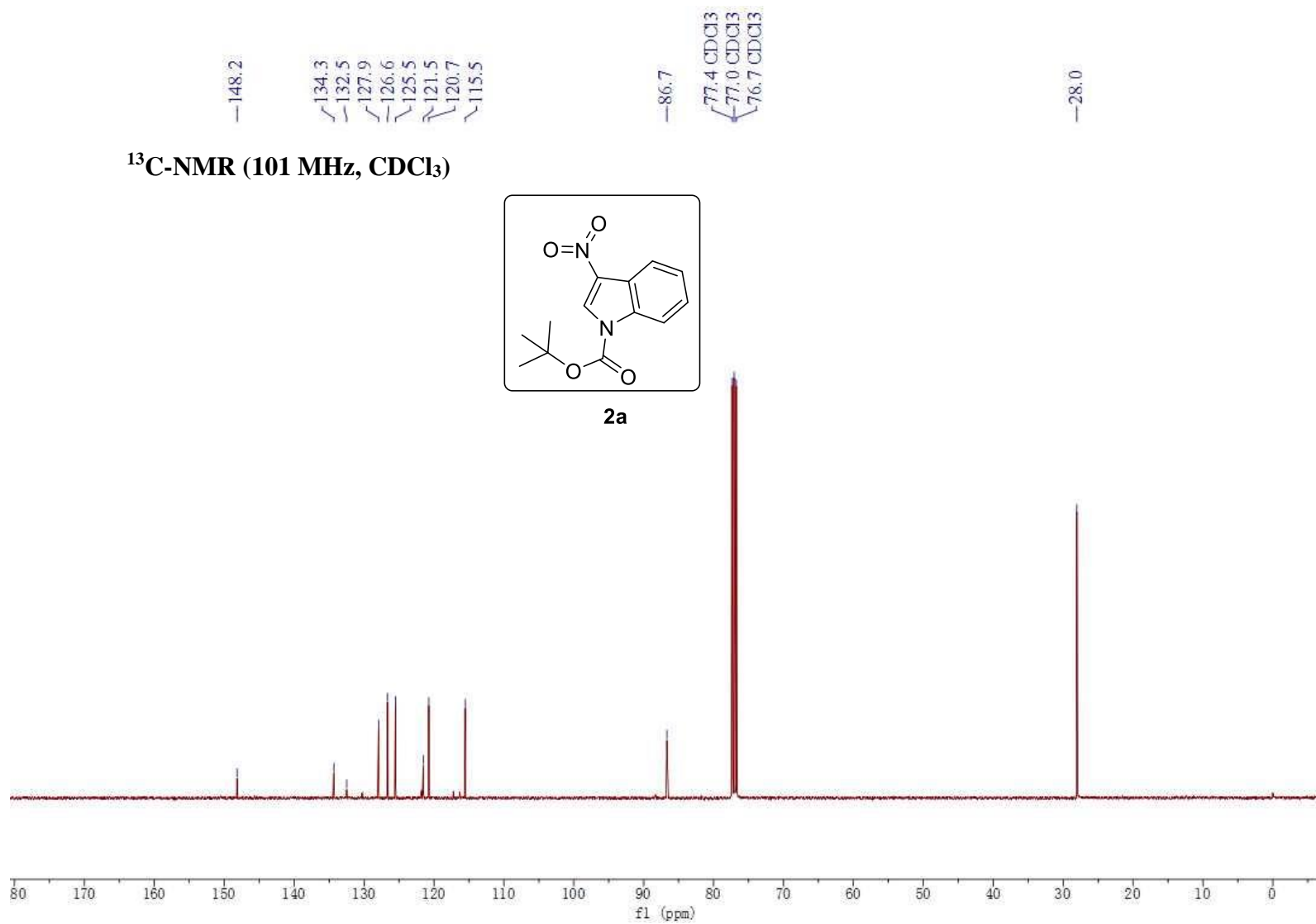
Atom	x	y	z	U(eq)
H2	1075.99	7637.96	4391.18	32
H3	1434.55	9295.4	5306.96	39
H4	2863.29	9324.2	6835.06	40
H5	3986.21	7720.39	7517.76	34
H10	5218.6	3735.26	5314.02	27
H11	5343.19	1841.8	4940.03	29
H12	3523.41	653.73	5021.69	32
H13	1556.19	1367.07	5432.34	33
H14	1383.73	3276.34	5745.02	28
H17A	3264.36	3246.51	2713.44	44
H17B	1999.91	2577.84	2087.86	44
H17C	2357.36	2456.9	3252.73	44
H18A	83.06	3072.89	3456.34	42
H18B	-385.28	3114.64	2291.6	42
H18C	-568.17	4194.23	2932.05	42
H19A	809.22	5429.44	2077.24	43
H19B	1084.83	4454.85	1354.81	43
H19C	2337.42	5090.55	2028.13	43

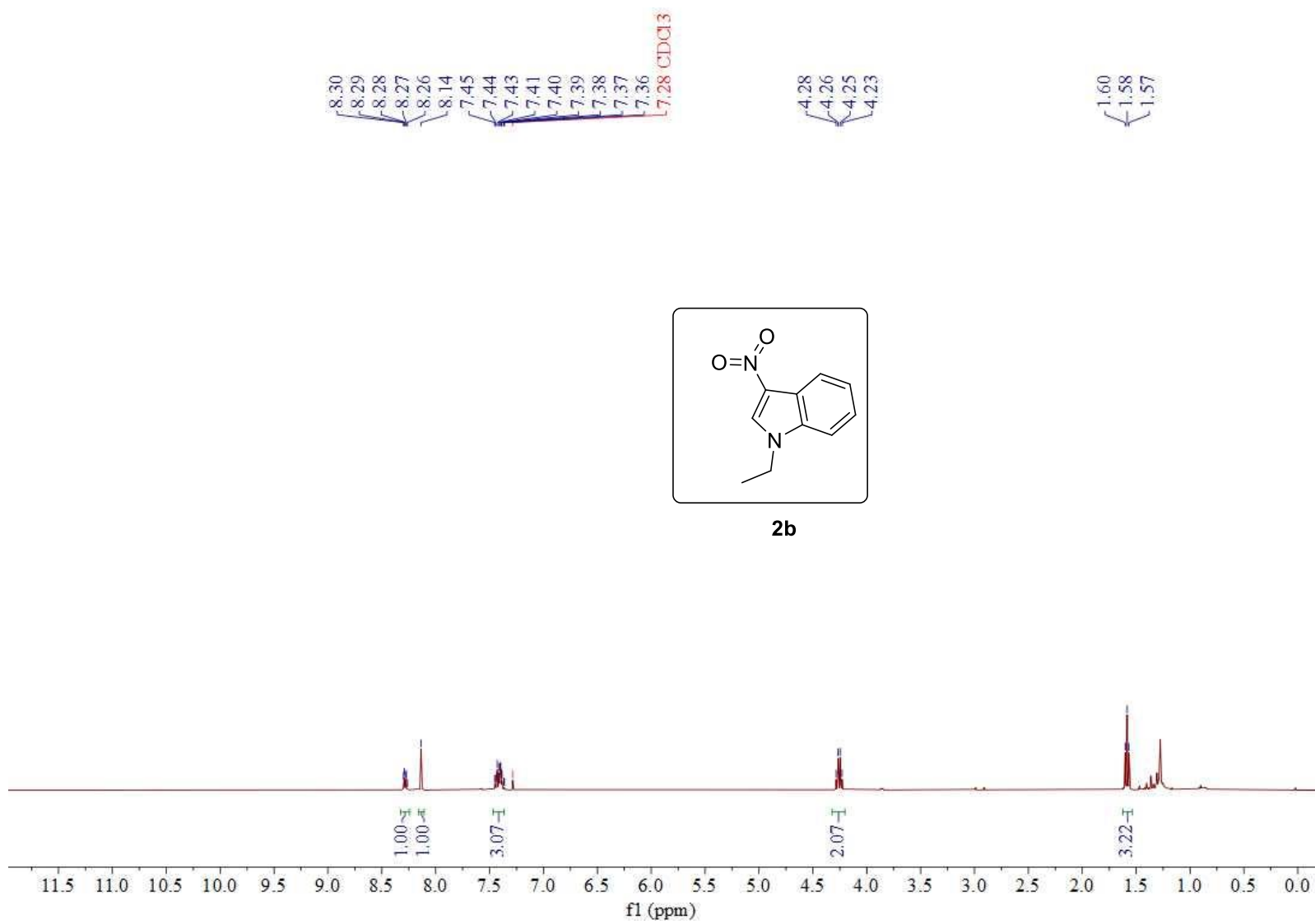
8. References

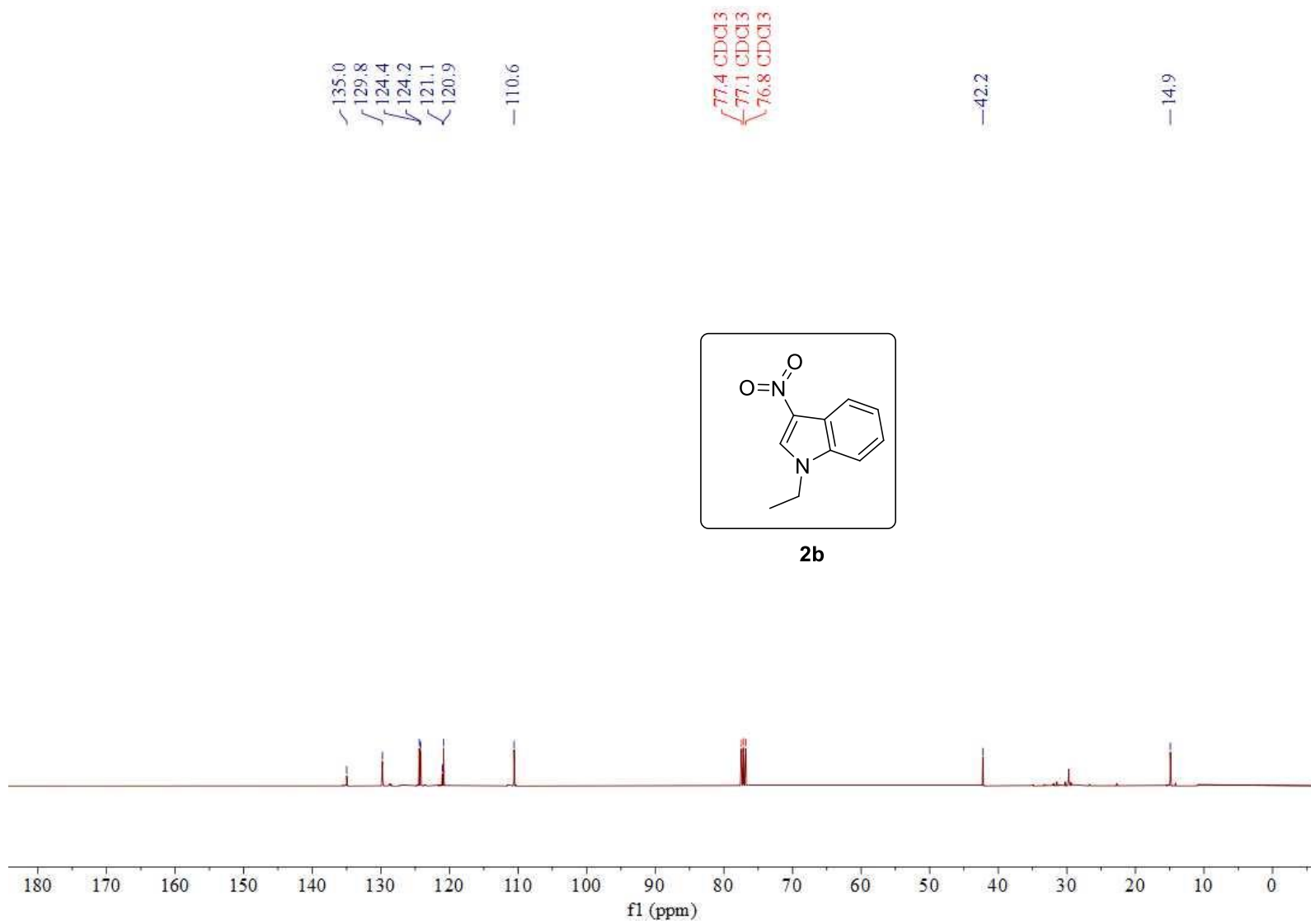
1. J. M. Fraile, K. L. Jeune, J. A. Mayoral, N. Ravasiob and F. Zaccheria, CuO/SiO₂ as a simple, effective and recoverable catalyst for alkylation of indole derivatives with diazo compounds, *Org. Biomol. Chem.*, 2013, **11**, 4327-4332.
2. K. Nemoto, S. Tanaka, M. Konno, S. Onozawa, M. Chiba, Y. Tanaka, Y. Sasaki, R. Okubo and T. Hattori, *Tetrahedron*, 2016, **72**, 734-745.
3. E. T. Pelkey, G. W. Gribble, Synthesis and Reactions of N-Protected 3-Nitroindoles, *Synthesis* 1999, **7**, 1117-1122.
4. X.-F. Ding, W.-L. Yang, J. Mao, C.-X. Cao and W.-P. Deng, Enantioselective Construction of Dihydropyrido[1,2-a]indoles via Organocatalytic Arylmethylation of 2-Enals with Inert Aryl Methane Nucleophiles, *Org. Lett.* 2019, **21**, 5514-5518.

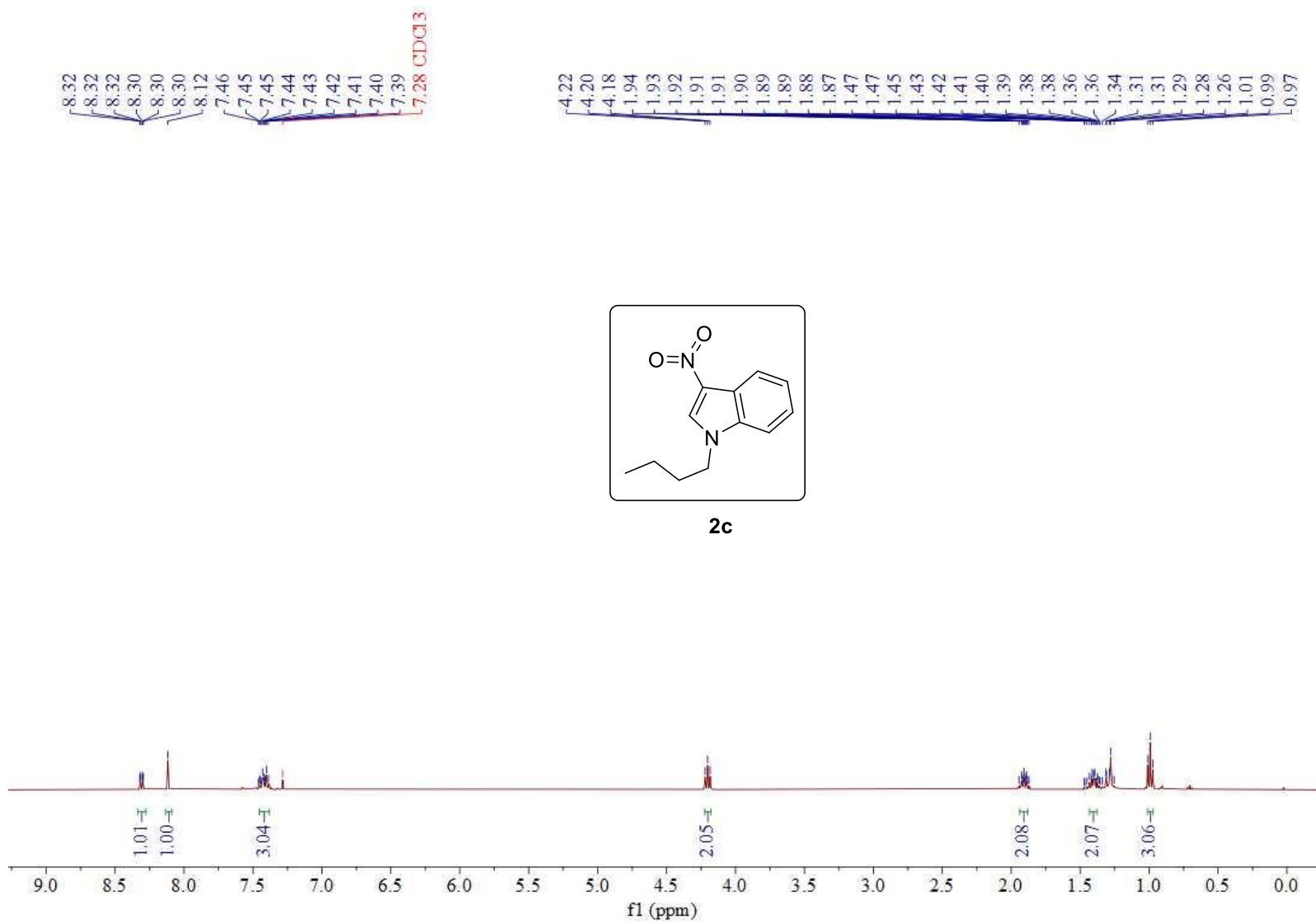
5. S. Pandit, V. K. Pandey, A. S. Adhikari, S. Kumar, A. K. Maurya, R. Kant and N. Majumda, Palladium-Catalyzed Dearomative [4+2]-Cycloaddition toward Hydrocarbazoles, *J. Org. Chem.* 2023, **88**, 97-105.
6. J.-H. Xie, C. Zheng and S.-L. You, Palladium-Catalyzed Dearomative Methoxyallylation of 3-Nitroindoles with Allyl Carbonates, *Angew. Chem. Int. Ed.*, 2021, **60**, 22184 – 22188.
7. Y. Liu, B. Liu , A. Guo, Z. Dong , S. Jin and Y. Lu, Reduction of Nitroarenes to Azoxybenzenes by Potassium Borohydride in Water, *Molecules* 2011, **16**, 3563-3568.
8. Z. Bazyar and M. Hosseini-Sarvari, On/Off O₂ Switchable Photocatalytic Oxidative and Protodecarboxylation of Carboxylic Acids, *J. Org. Chem.* 2019, **84**, 13503-13515.
9. A. R. Moosavi-Zare, M. A. Zolfigol, M. Zarei, E. noroozadeh and M. H. Beyzavi, Nitration of arenes by 1-sulfonylpyridinium nitrate as an ionic liquid and reagent by in situ generation of NO₂, *RSC Adv.*, 2016, **6**, 89572-89577.
10. L. Orús, S. Pérez-Silanes, A.-M. Oficialdegui, J. Martínez-Esparza, J.-C Del Castillo, M. Mourelle, T. Langer, S. Guccione, G. Donzella, E. M. Krovat, K. Poptodorov, B. Lasheras, S. Ballaz, I.I Hervías, R. Tordera, J. Del Río and A. Monge, Synthesis and Molecular Modeling of New 1-Aryl-3-[4-arylpiperazin-1-yl]-1-propane Derivatives with High Affinity at the Serotonin Transporter and at 5-HT_{1A} Receptors, *J. Med. Chem.* 2002, **45**, 4128-4139.
11. S. Gronowitz and B. Holm, Inverted Reactivity of Aryllithium Derivatives III. Convenient Syntheses of Isomer-Free 3-Nitrofurans and 2- and 3-Nitroselenophene, *Synthetic Commun*, 1974, **4**, 63-69.
12. G. Consiglio, D. Spinelli, S. Gronowitz, A.-B. Hörnfeld, B. Maltesson and R. Noto, Kinetics of the reactions of some 5-bromo-2-nitro-3-R-thiophenes, 3,4-dibromo-2-nitro-5-R-thiophenes, 3-bromo-2-nitro-5-R-thiophenes, and 2-bromo-3-nitro-5-R-thiophenes with nucleophiles in methanol, *J. Chem. Soc., Perkin Trans. 2*, 1982, 625-630.
13. D. S. Ashton, H. Singh, J. M. Tedder, J. C. Walton and E. A. Watt, Free-radical substitution in aliphatic compounds. Part XXVII. Chlorination and bromination of 1-cyanobutane and cyanocyclobutane, *J. Chem. Soc., Perkin Trans. 2*, 1973, 125-128.
14. J.-P Zou, A. Shoberu, C.-K. Li, Z.-K. Tao, and G.-Y. Zhang, NaNO₂/K₂S₂O₈-mediated Selective Radical Nitration/Nitrosation of Indoles: Efficient Approach to 3-Nitro- and 3-Nitrosoindoles, *Adv. Synth. Catal.* 2019, **361**, 2255-2261.

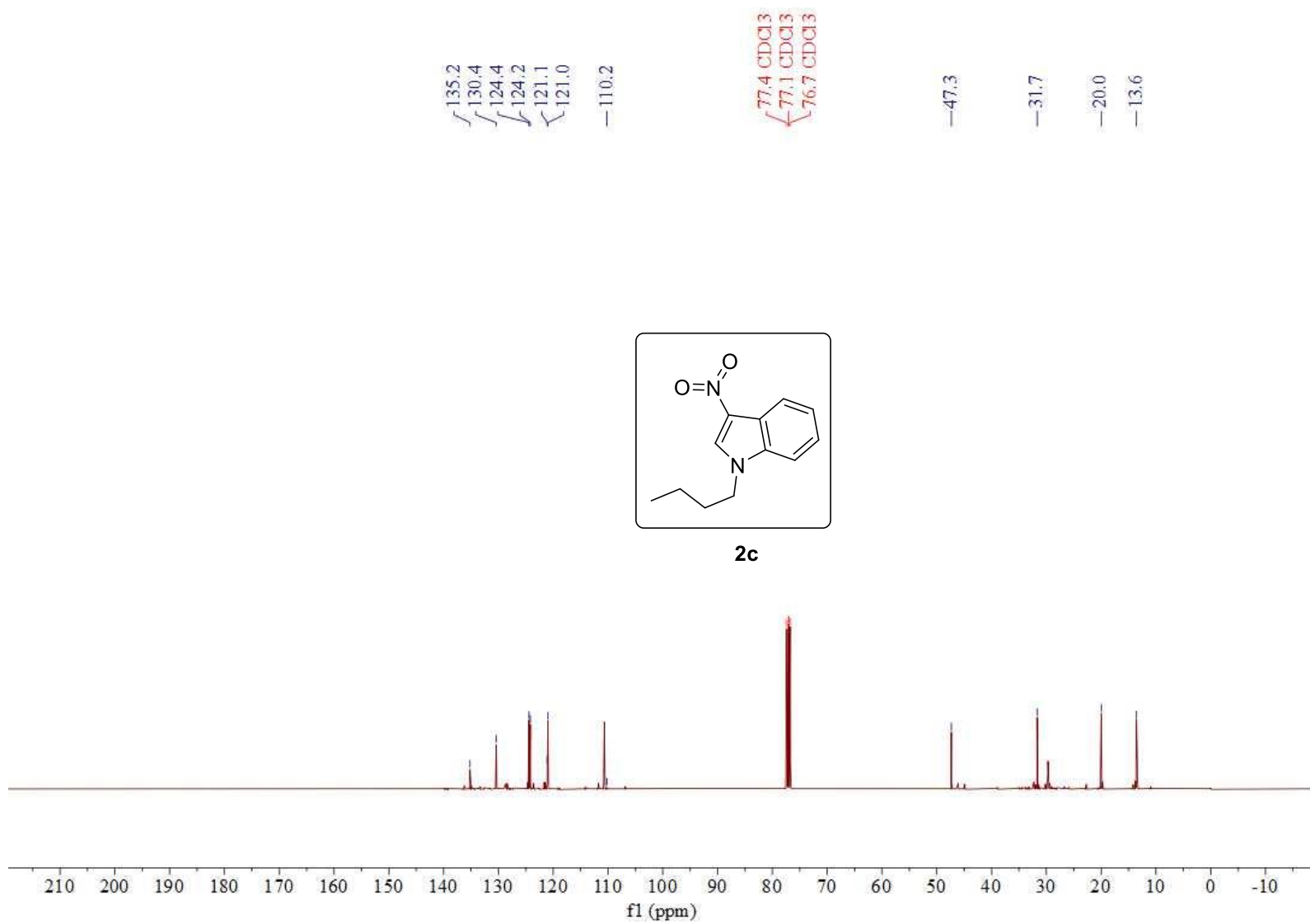


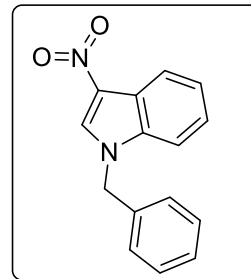
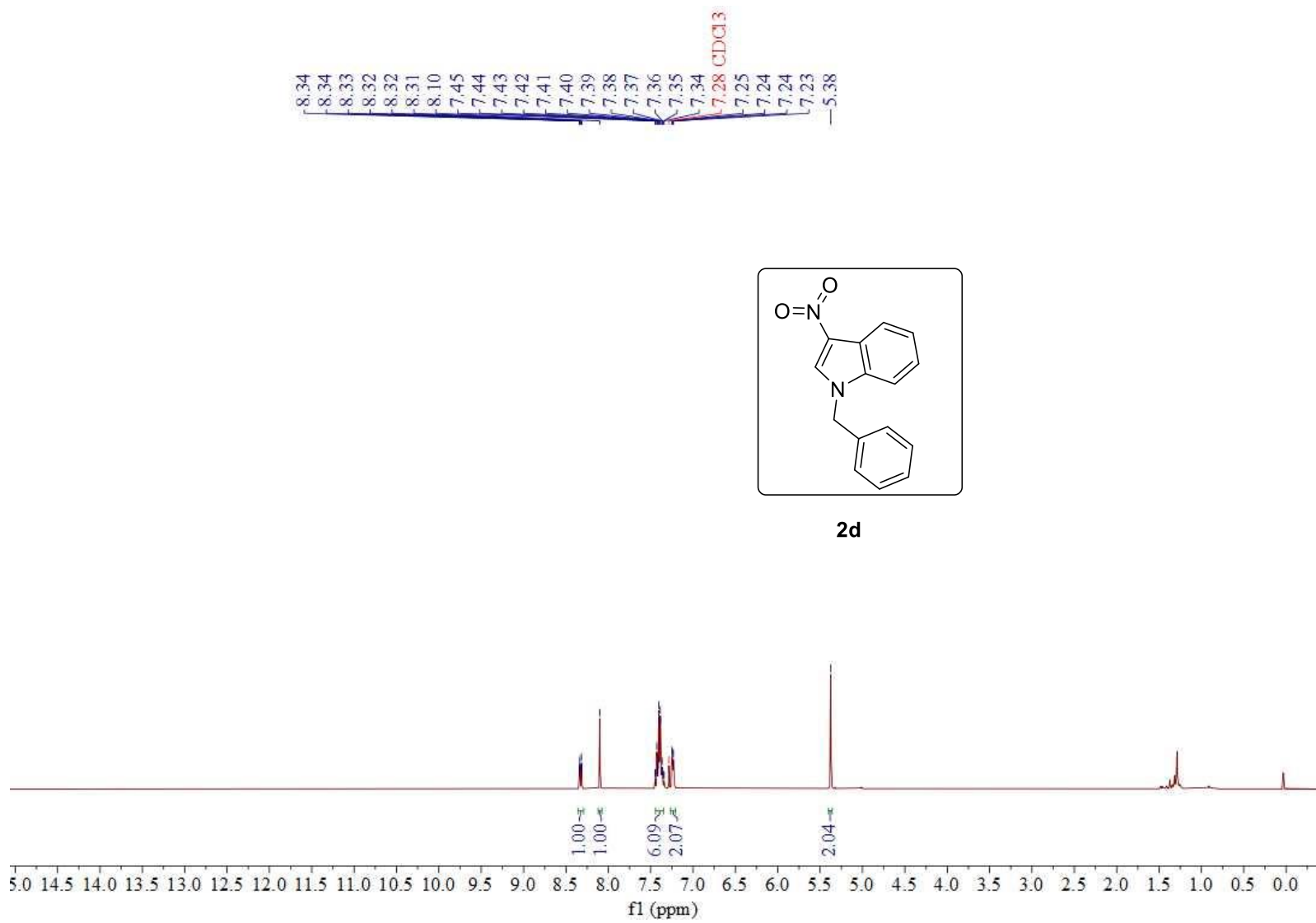




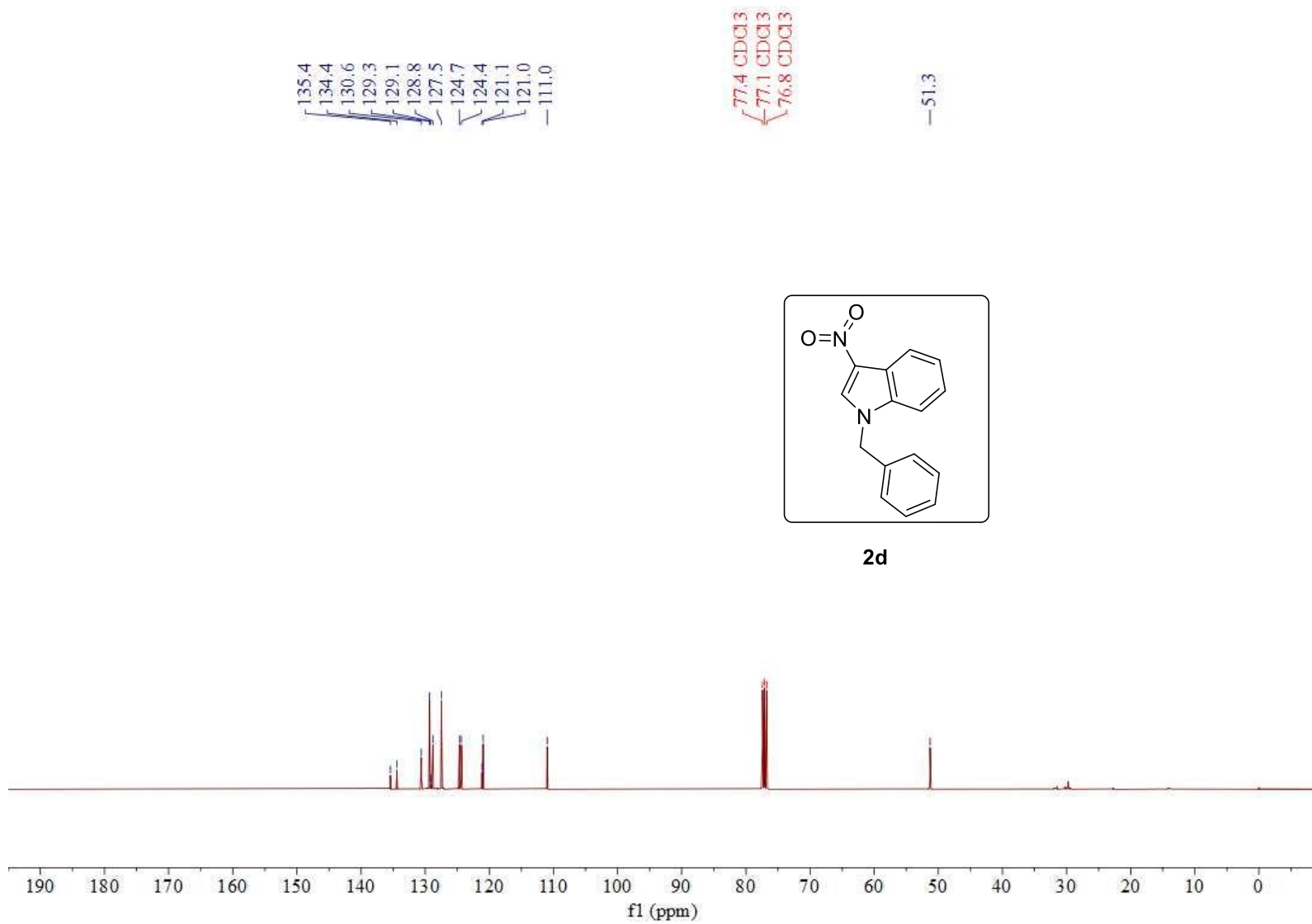


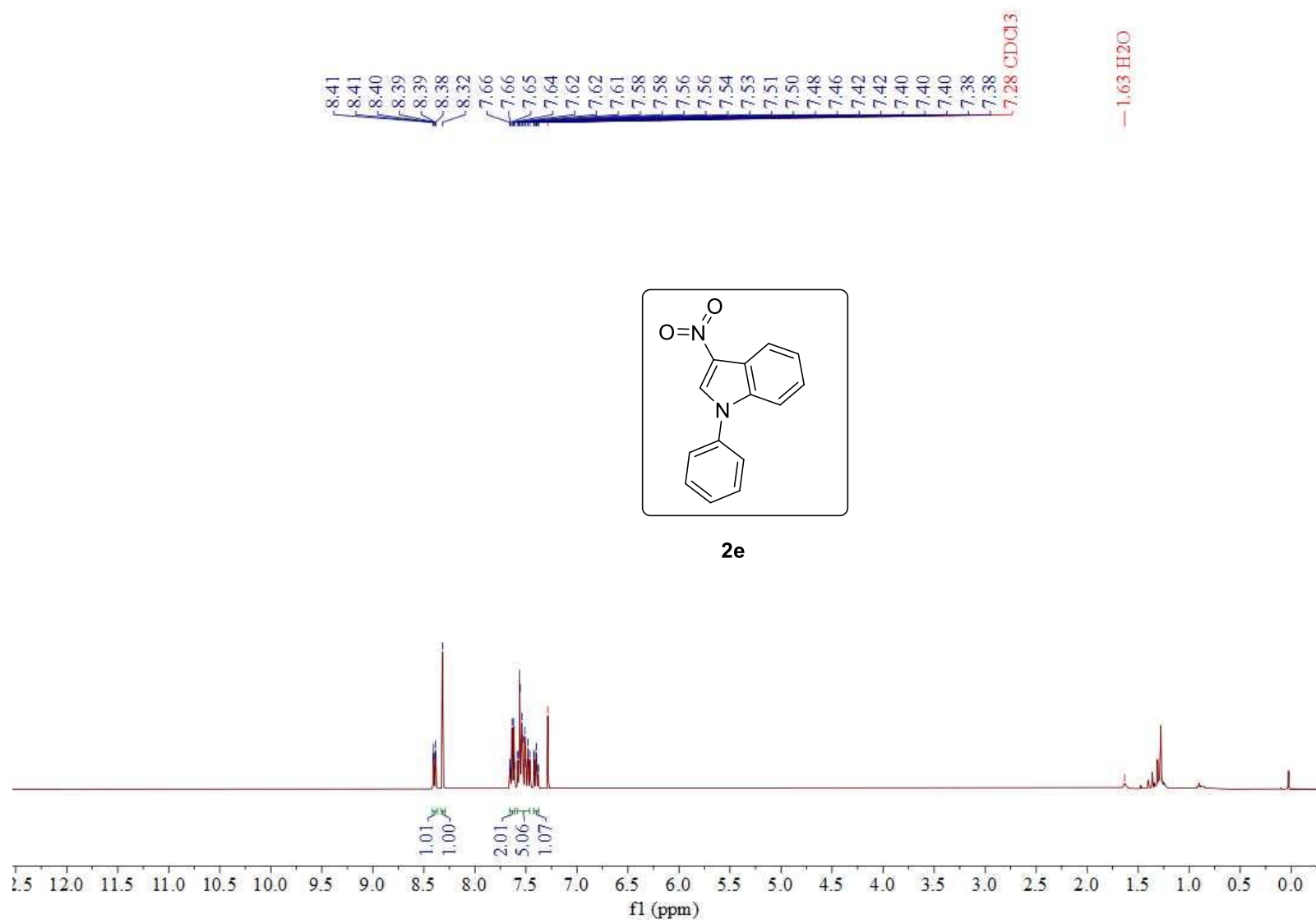


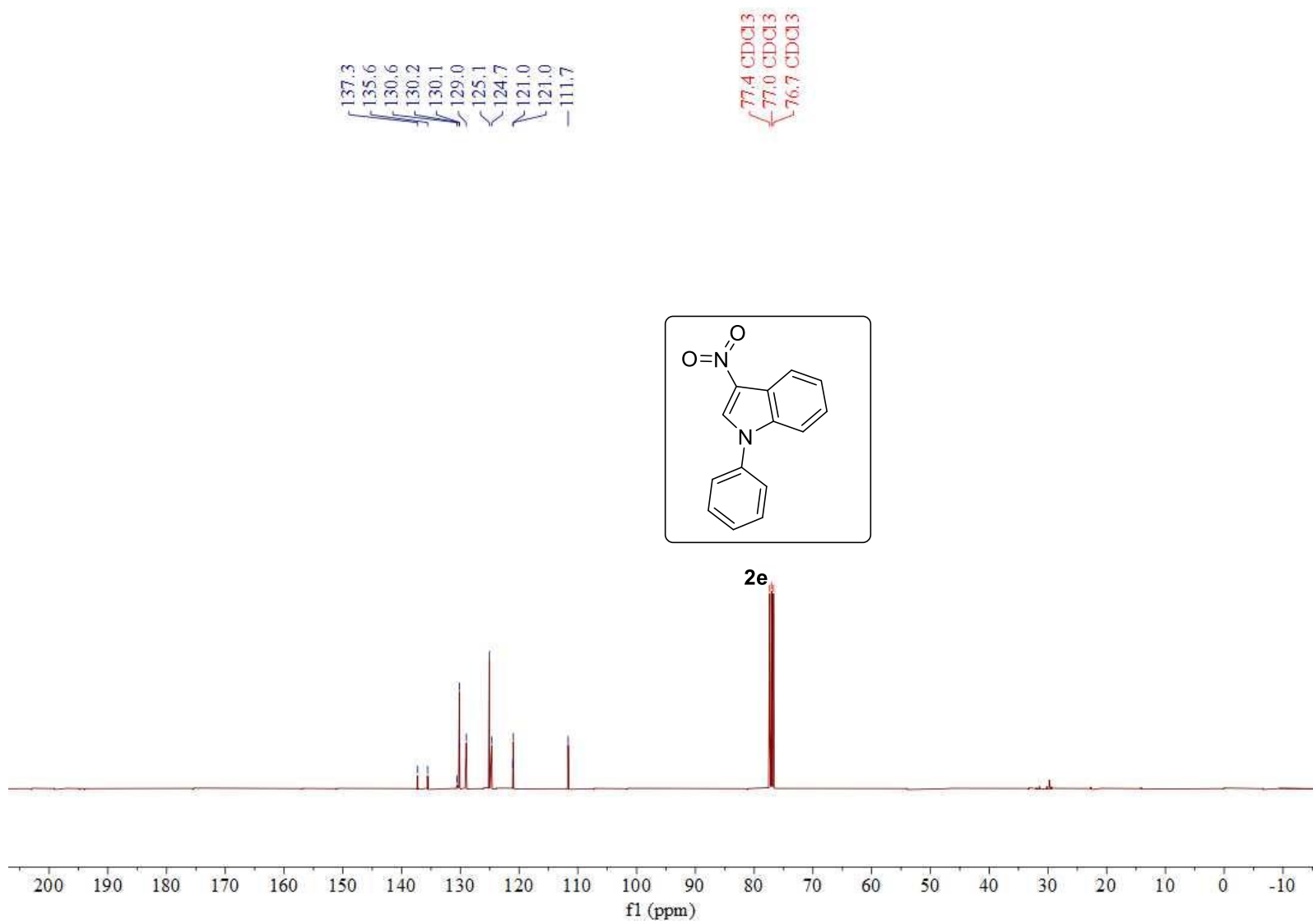


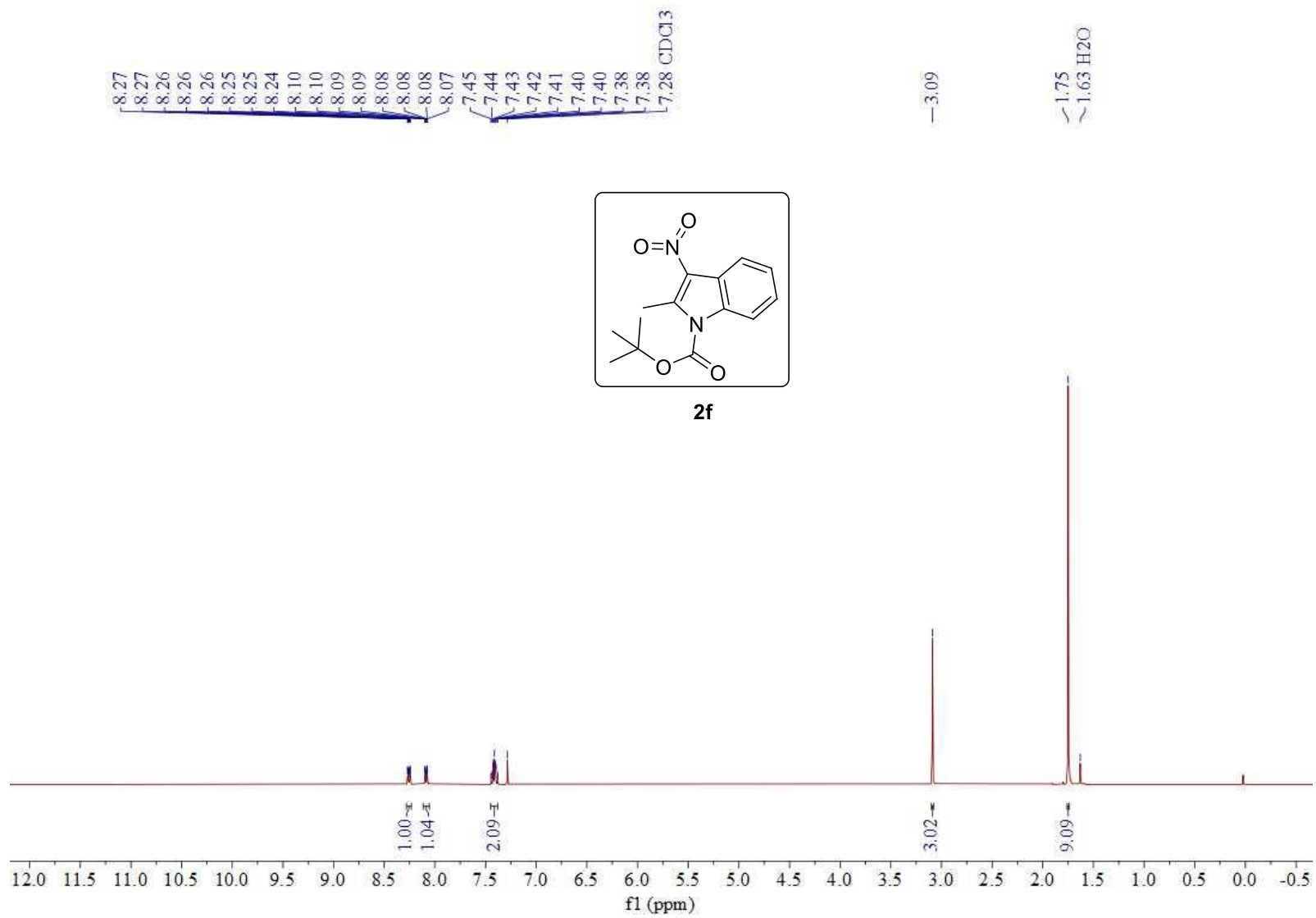


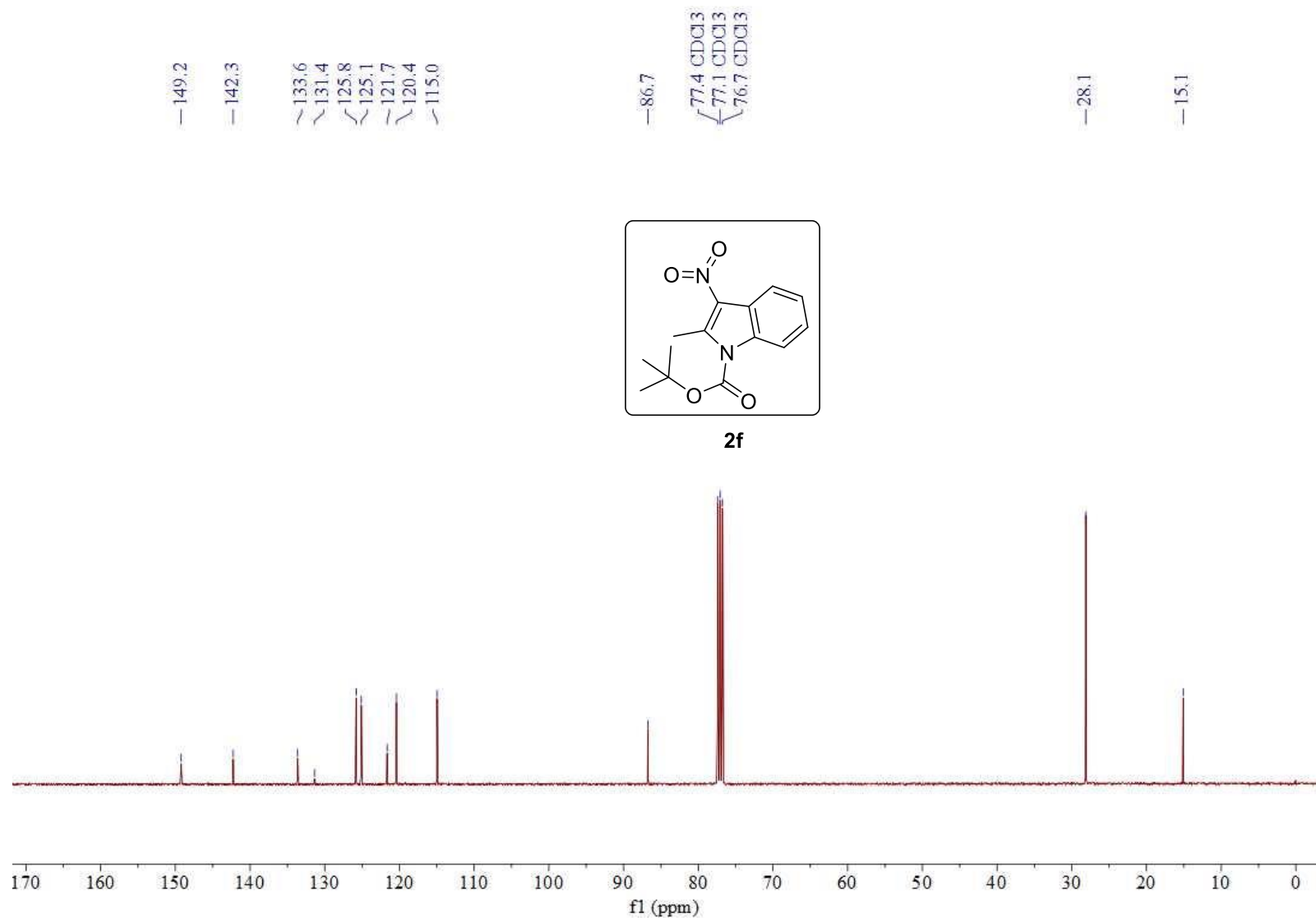
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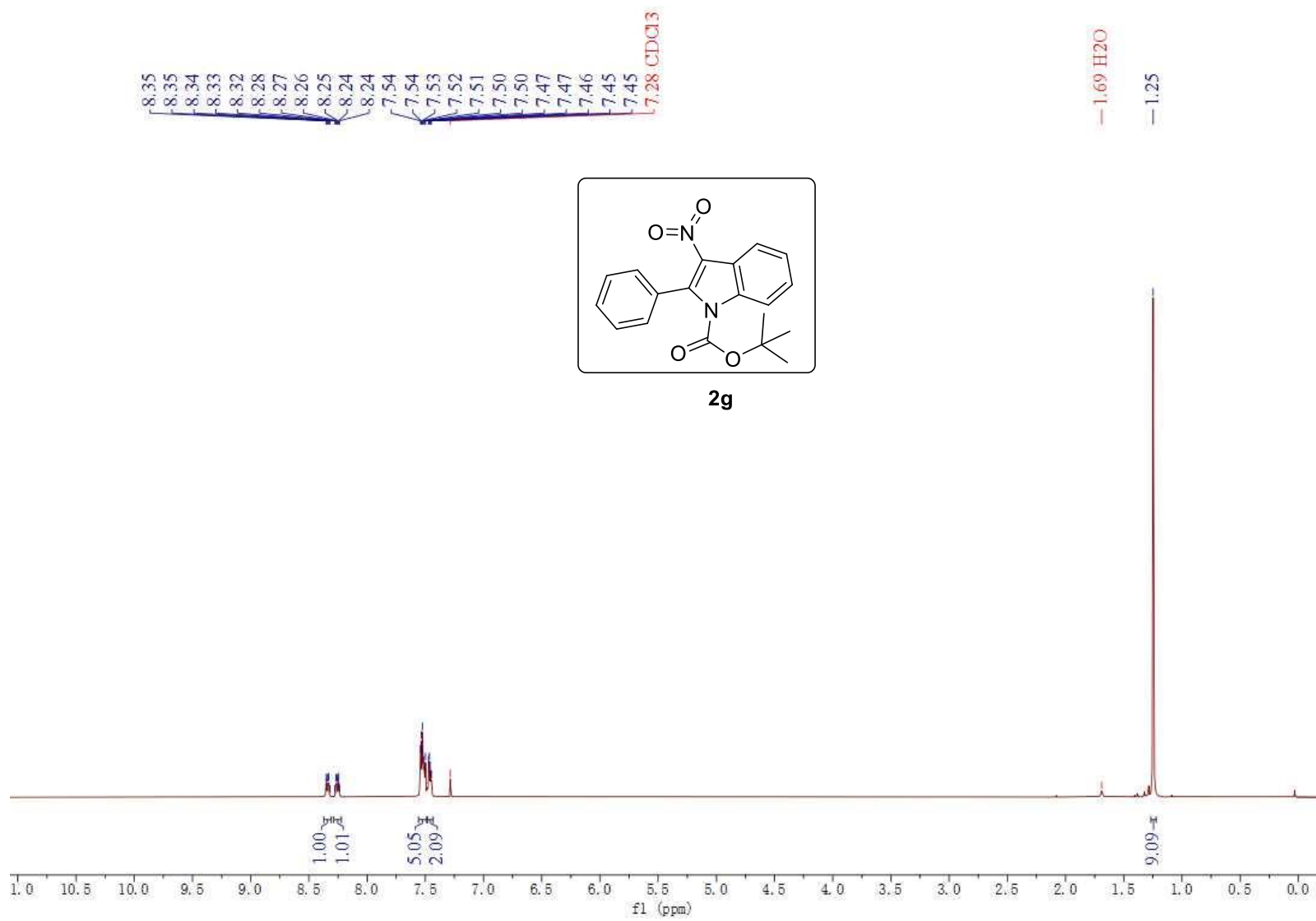


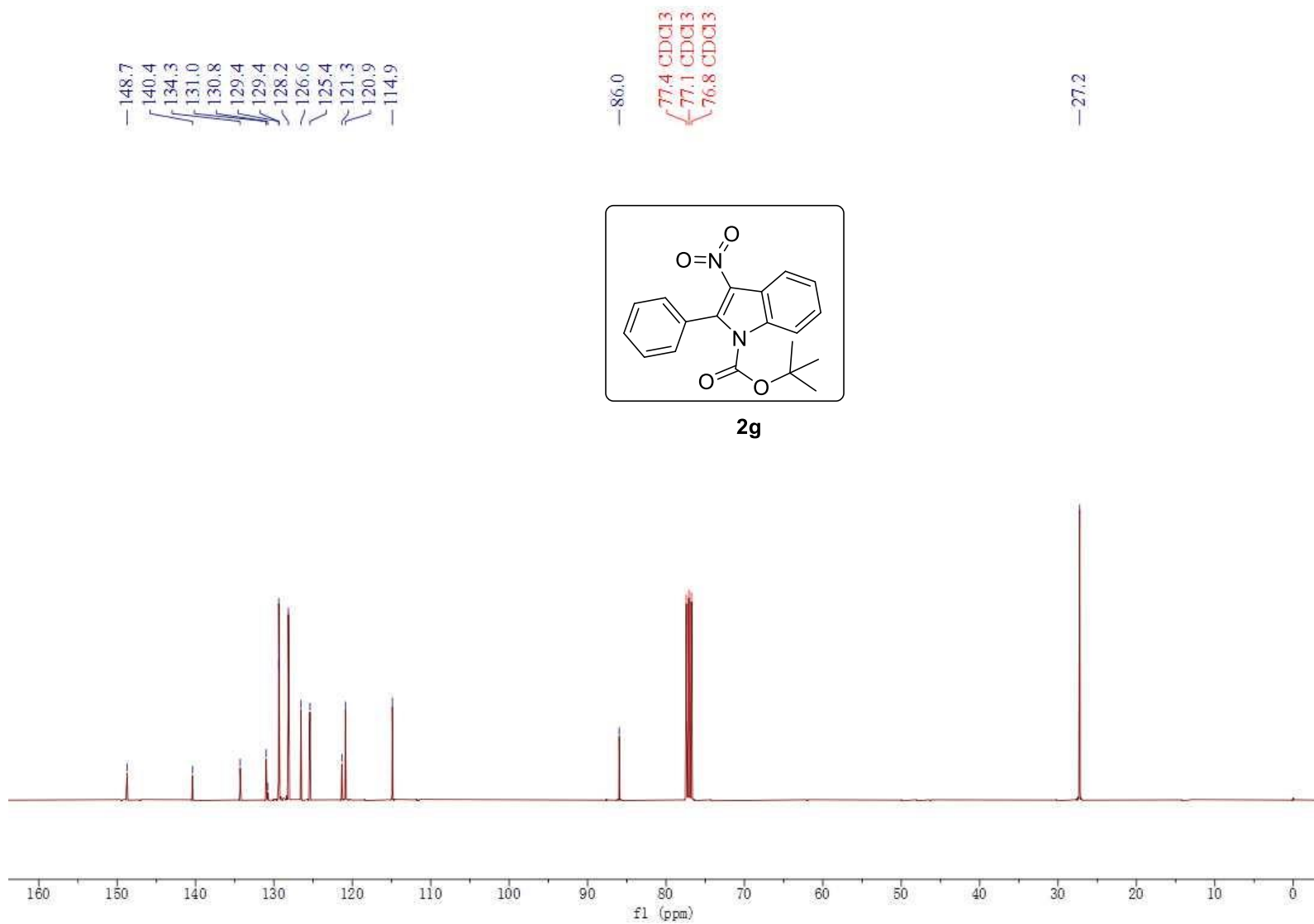


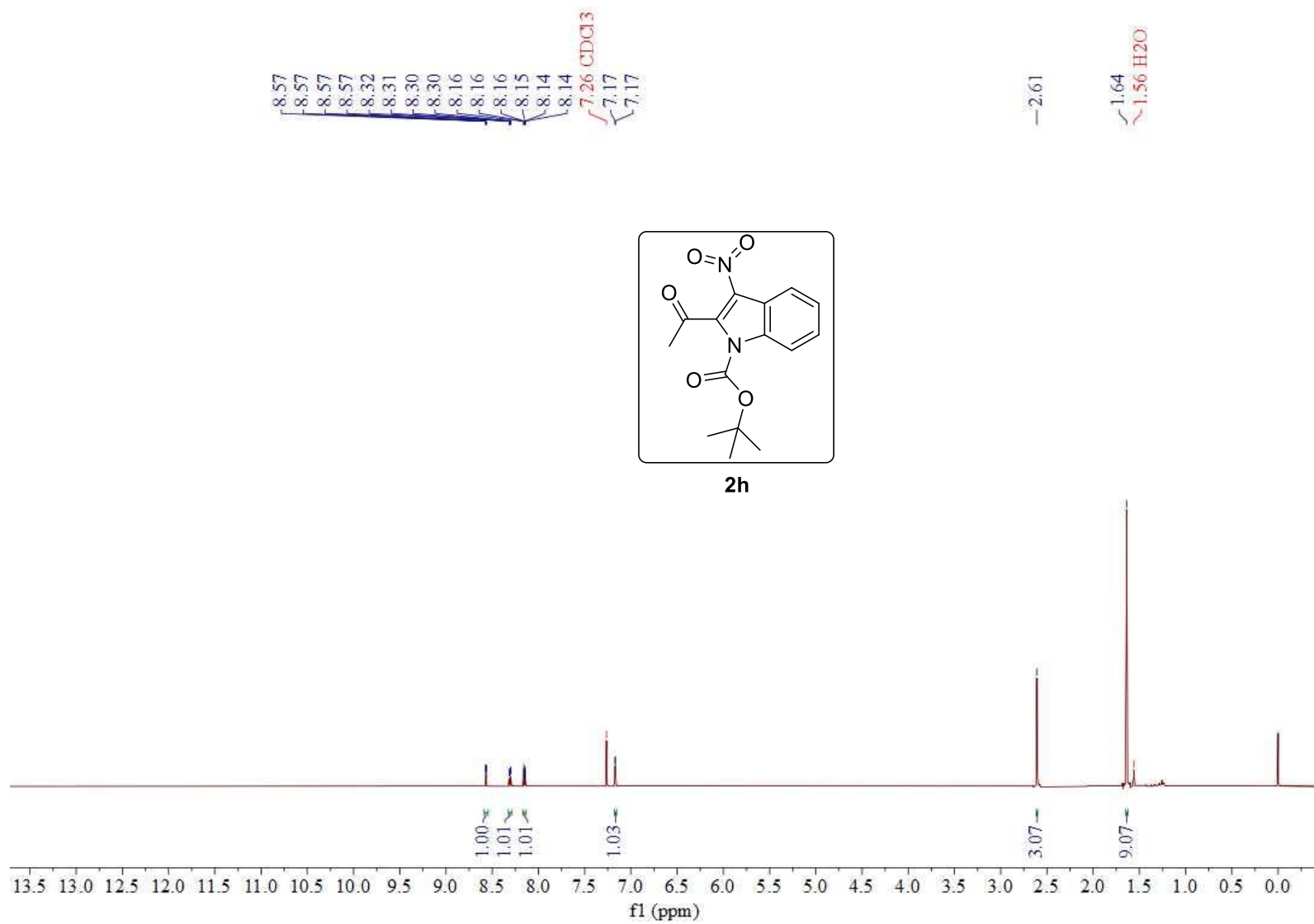


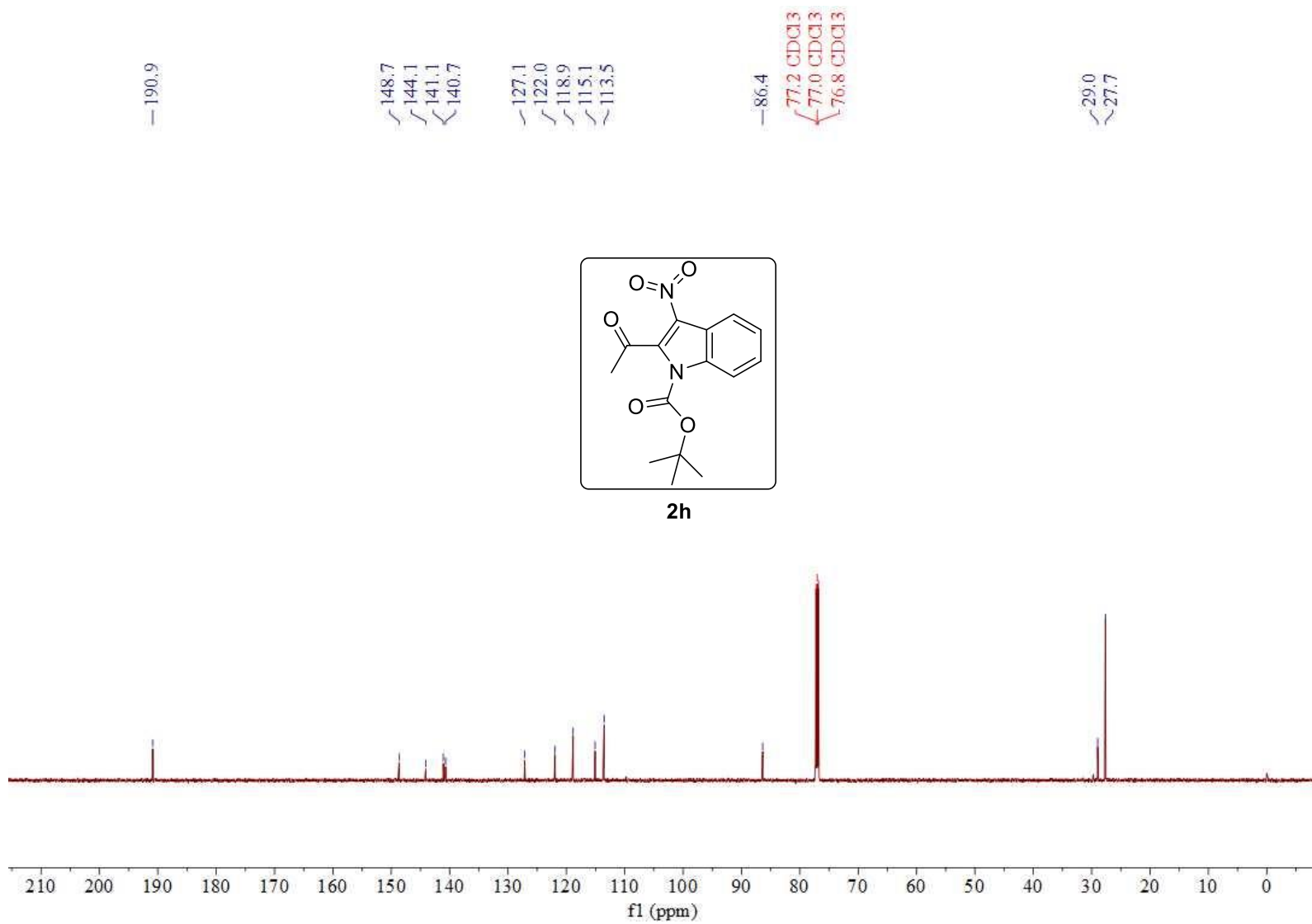


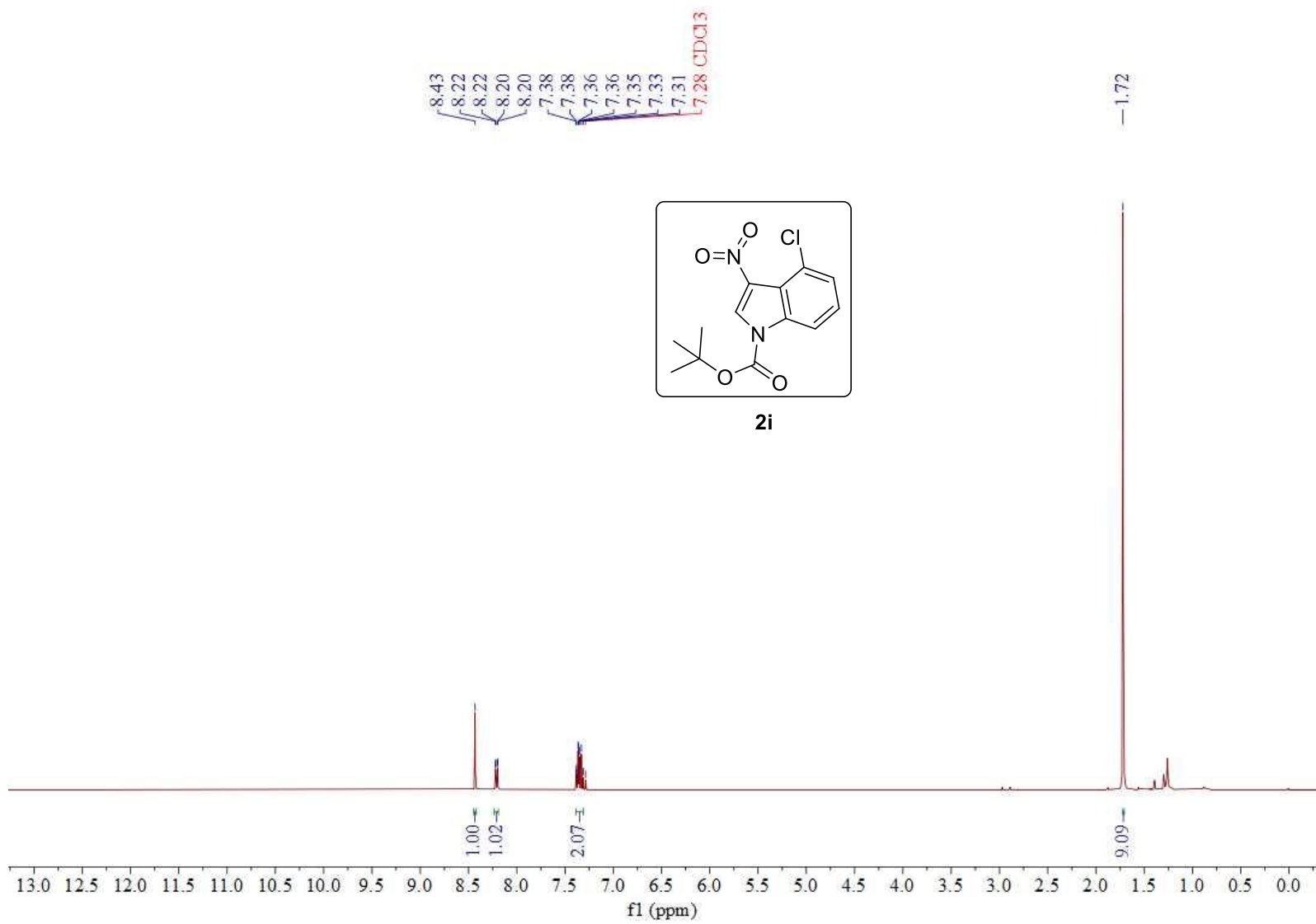


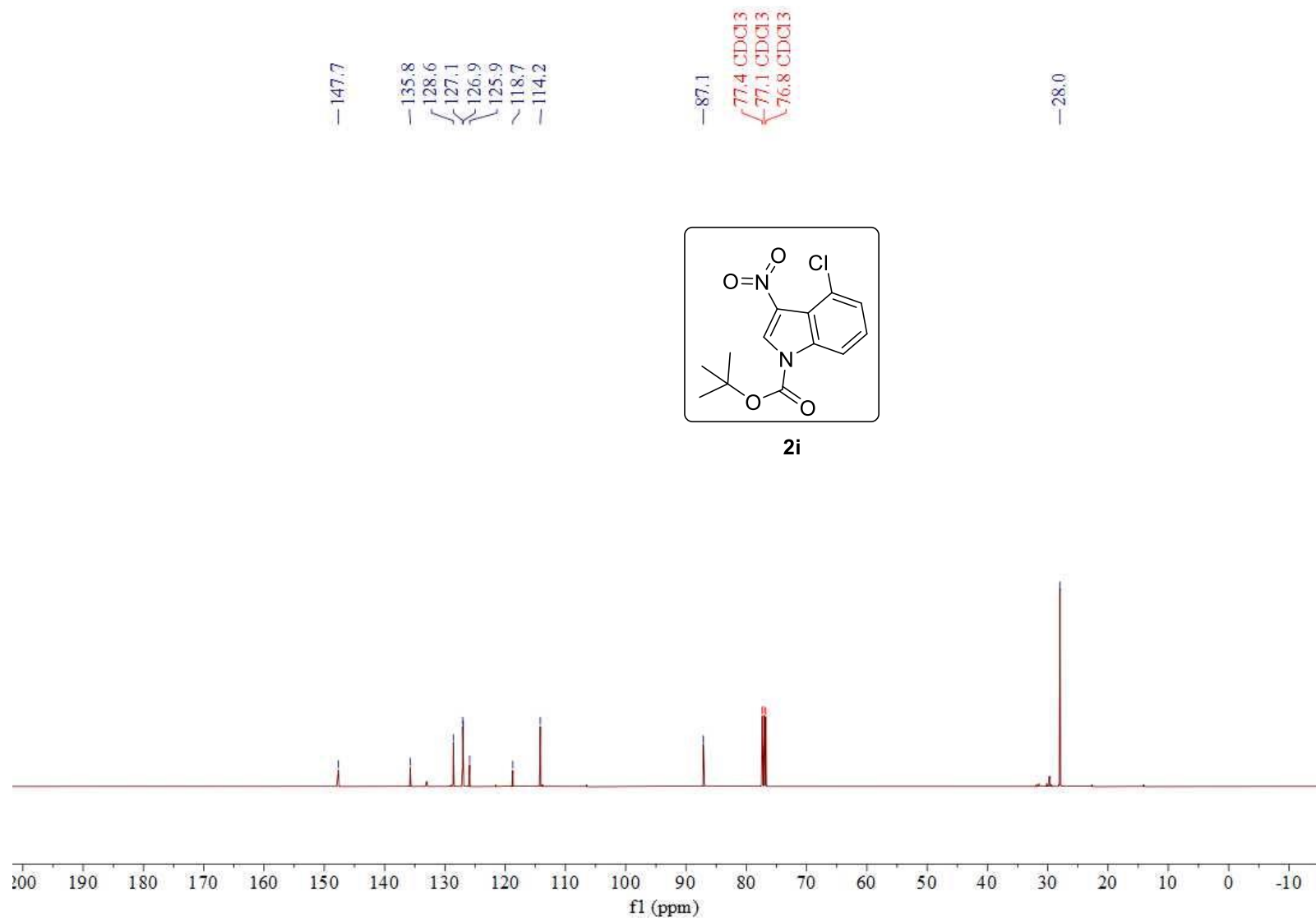


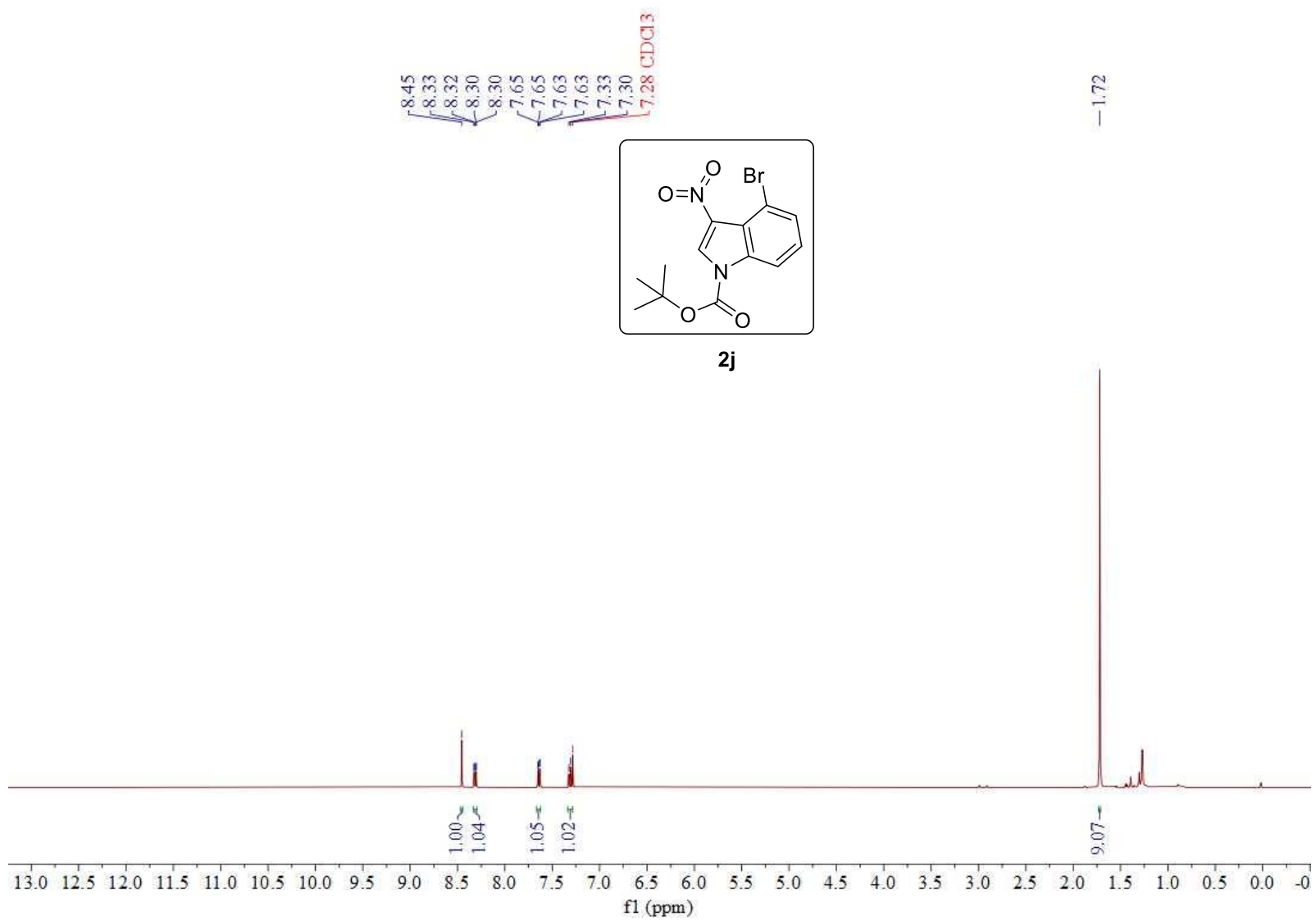


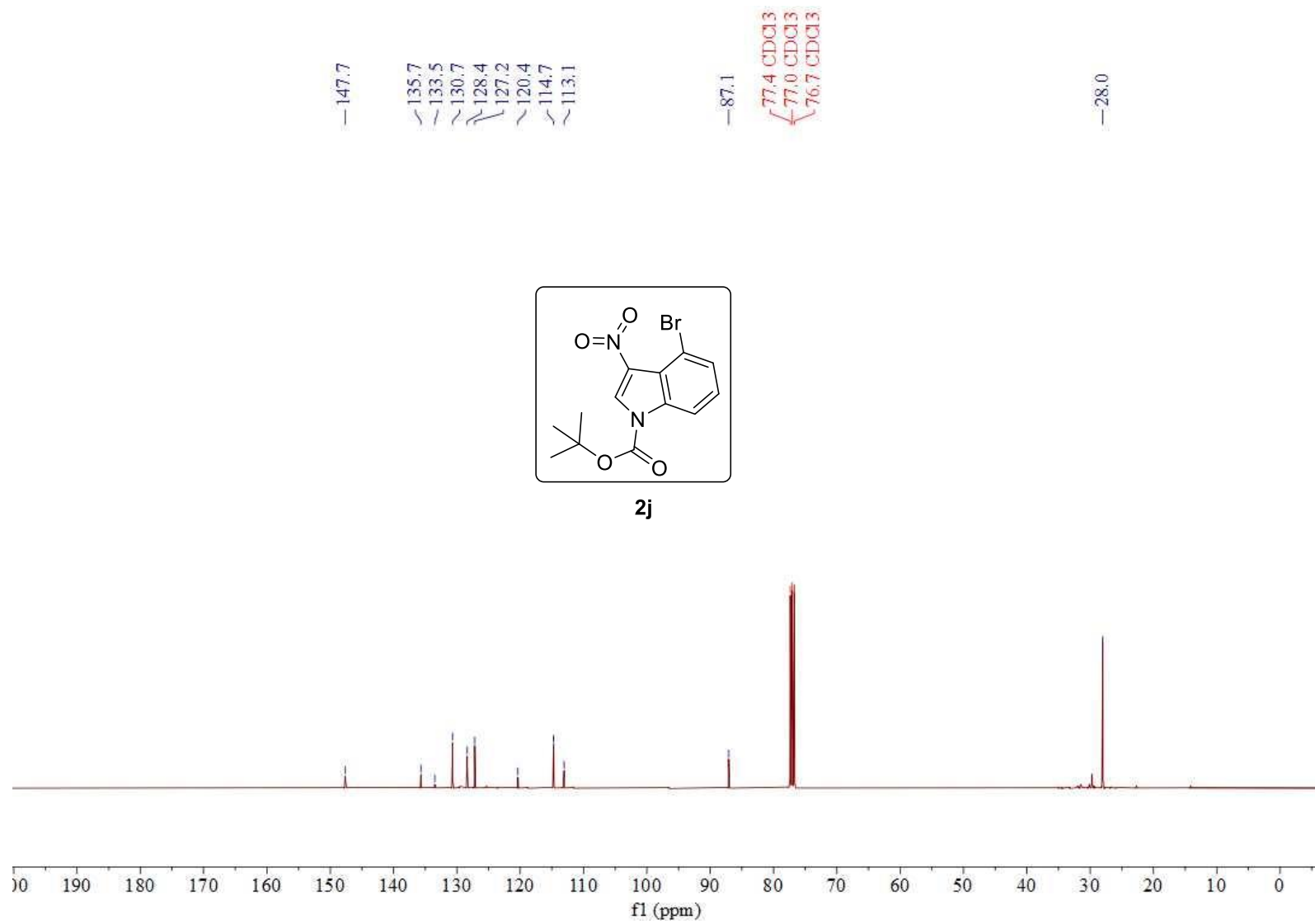


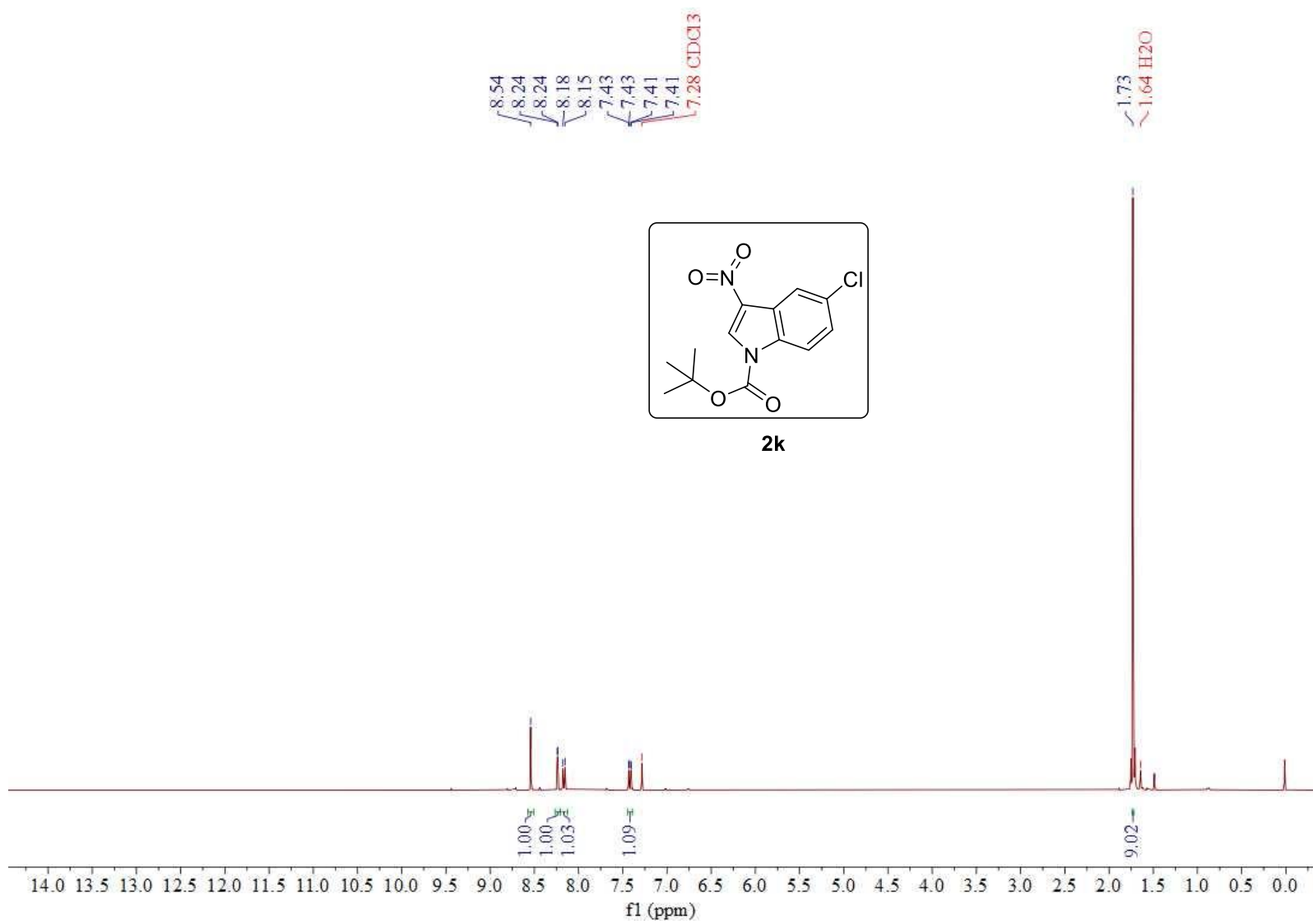


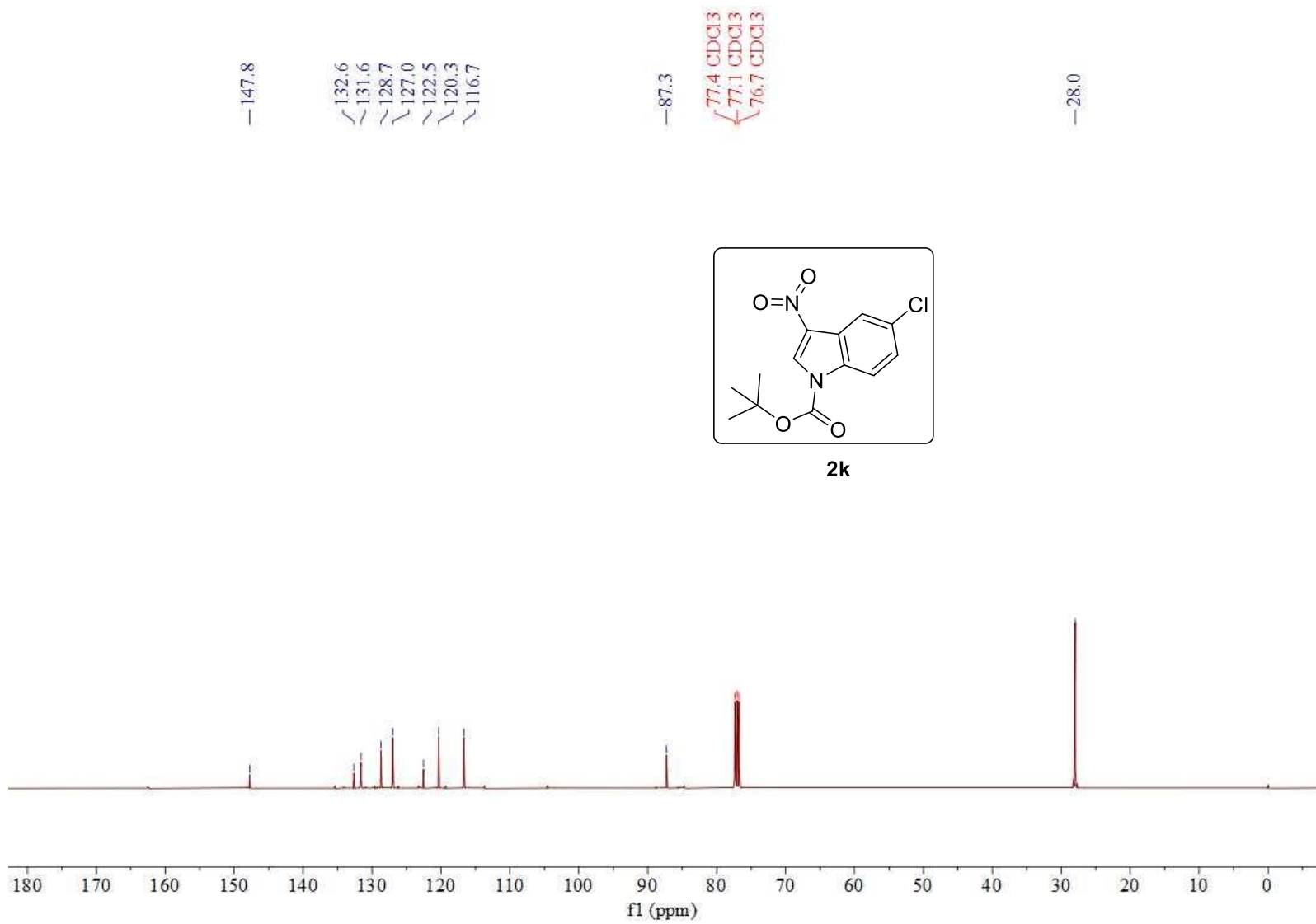


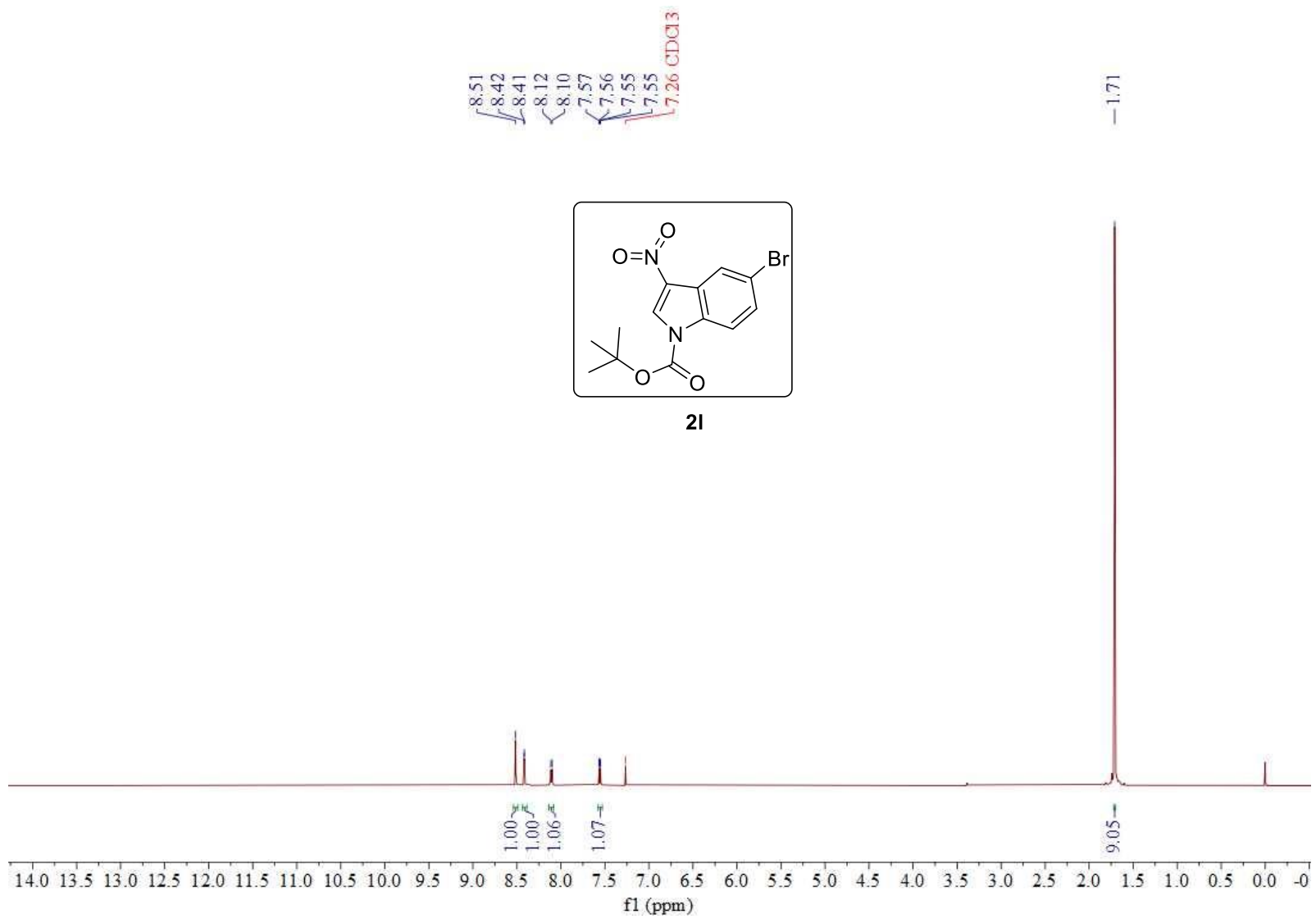


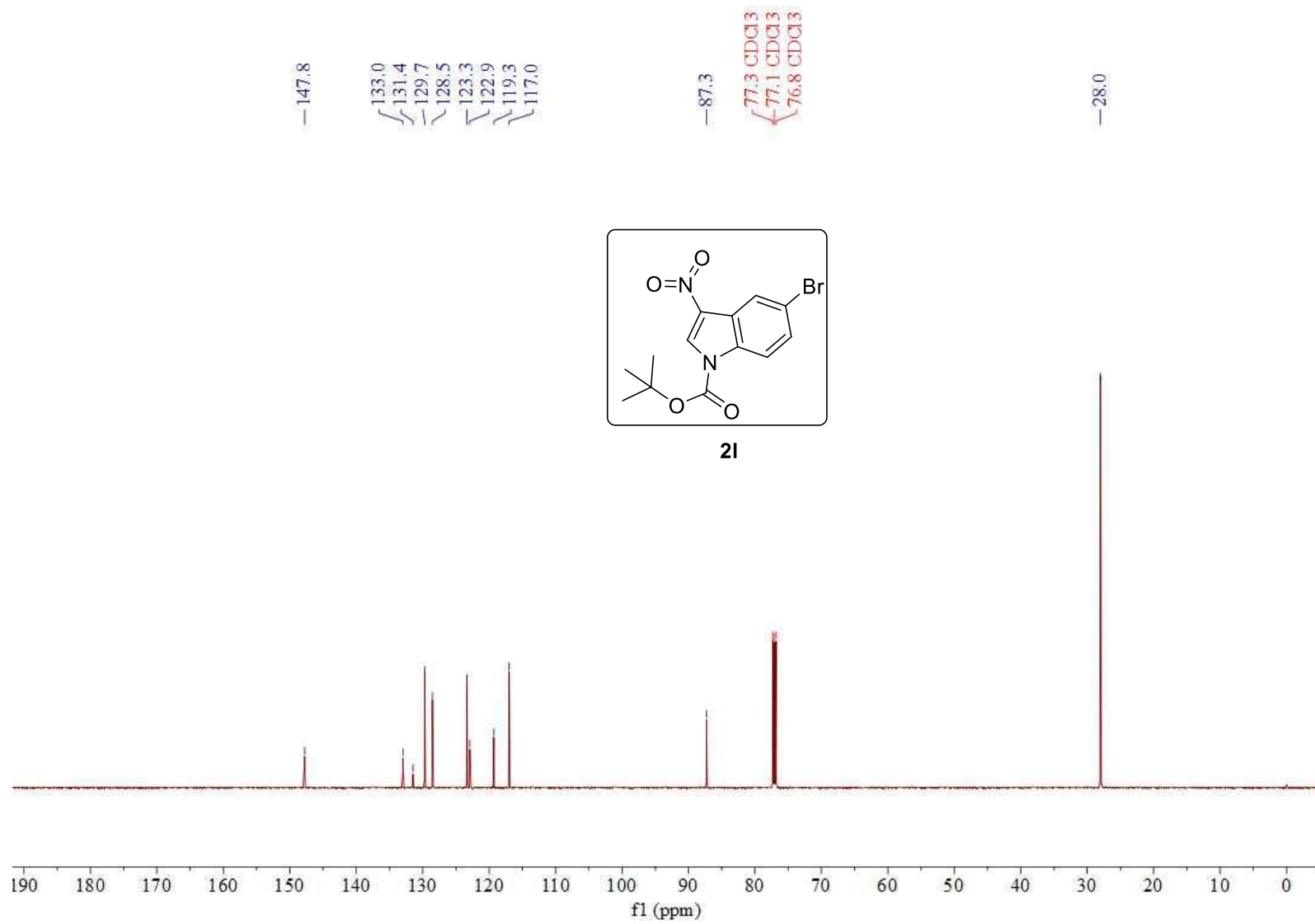


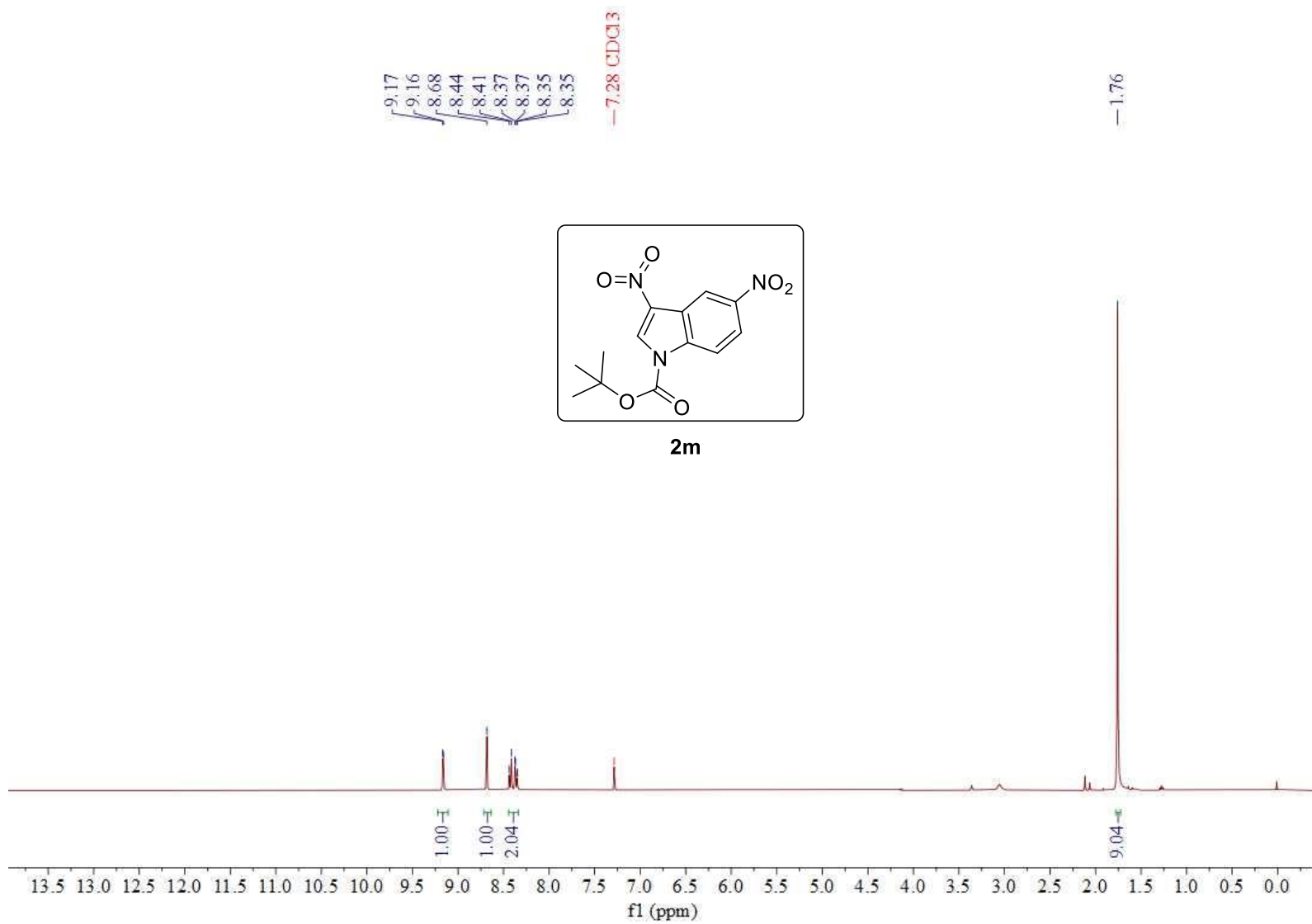


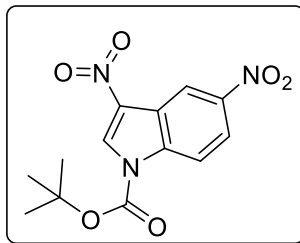
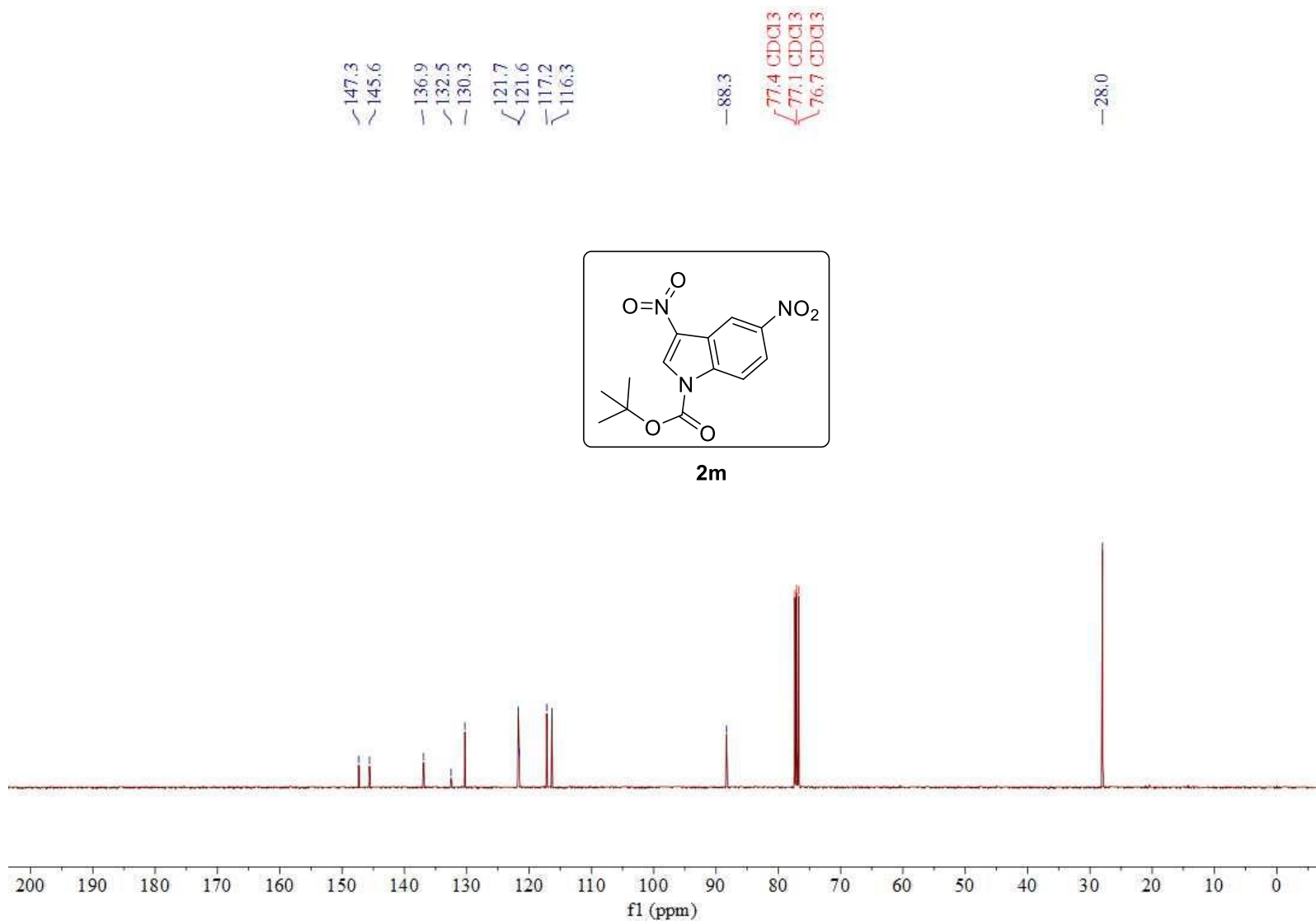




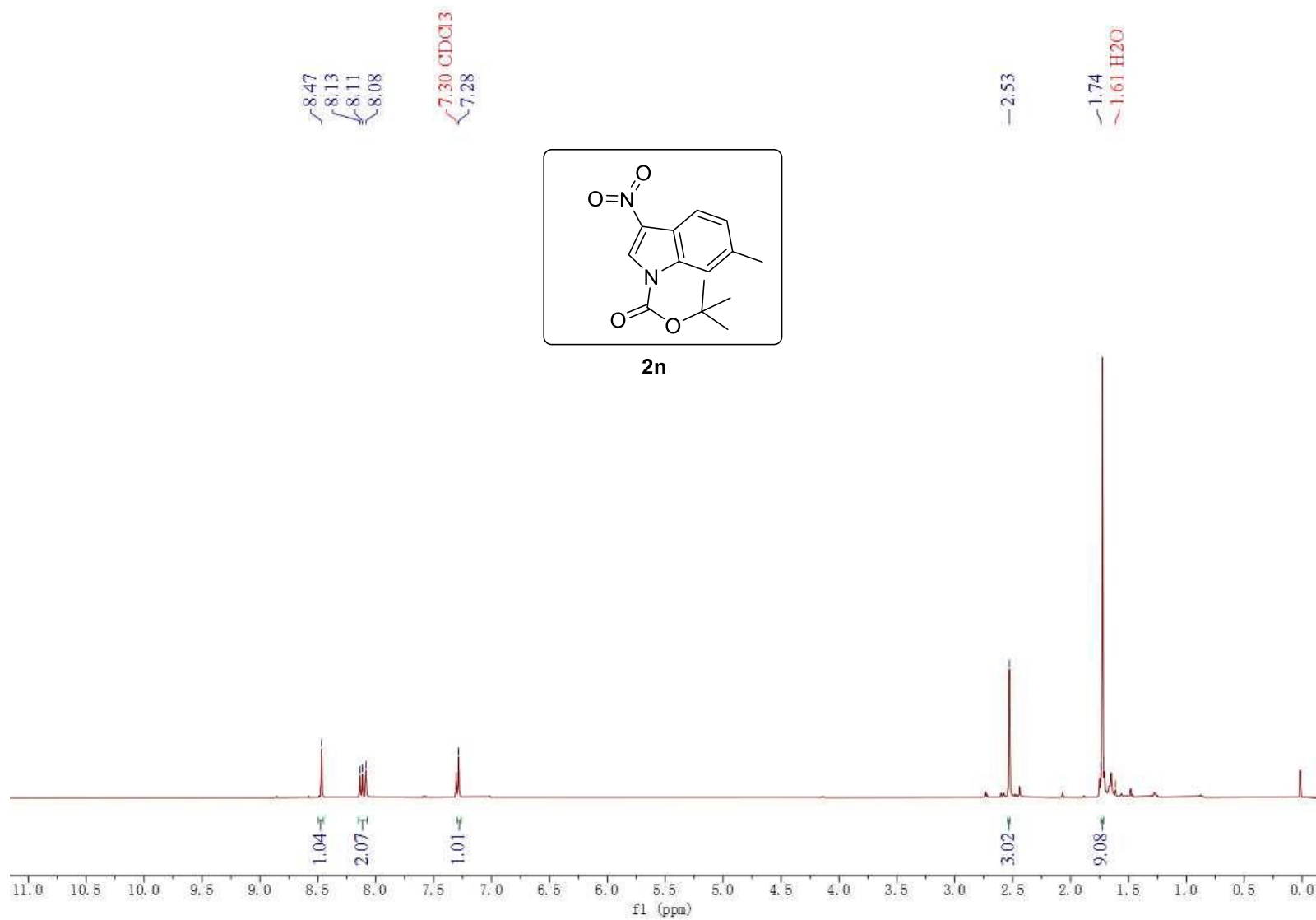


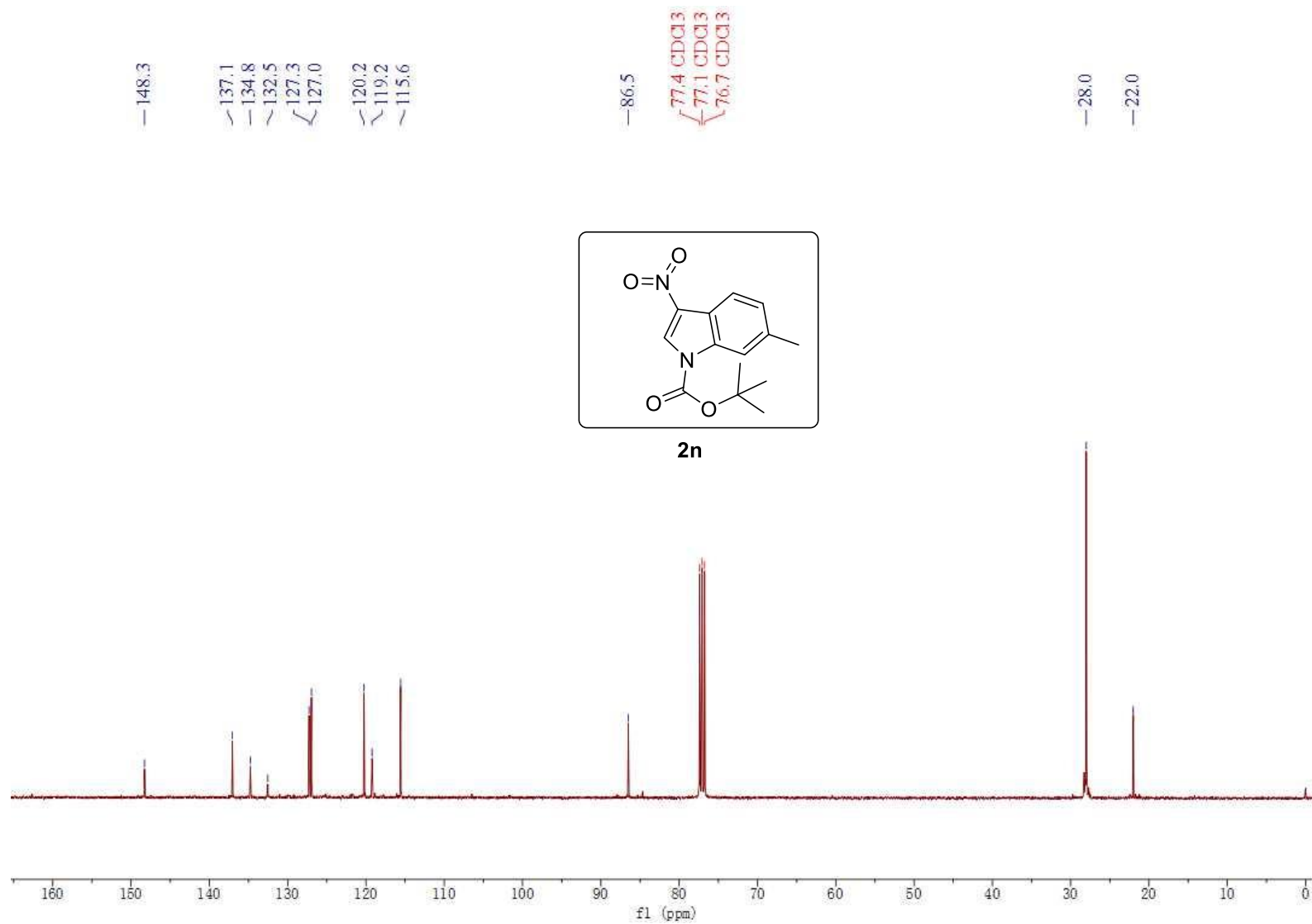


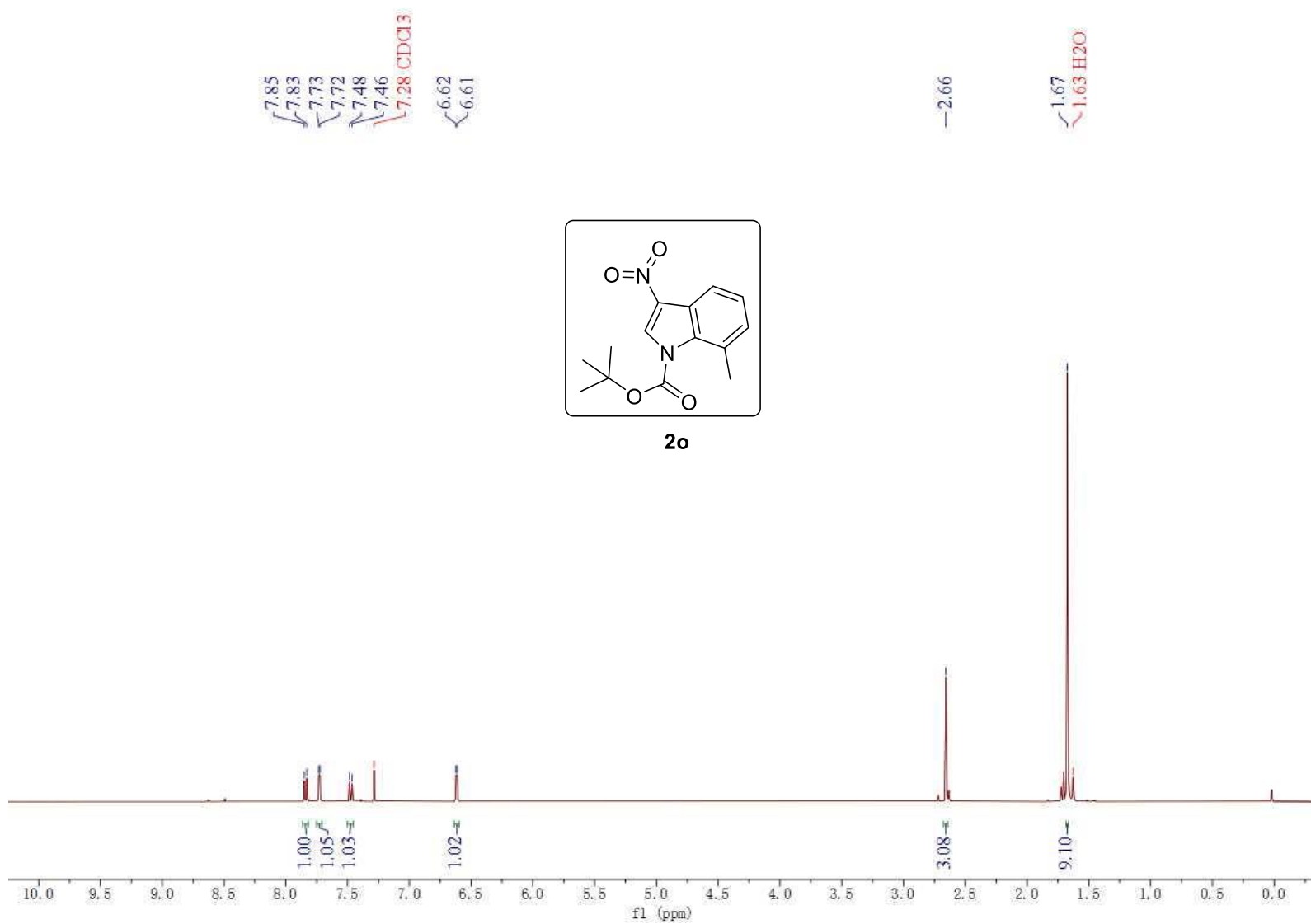


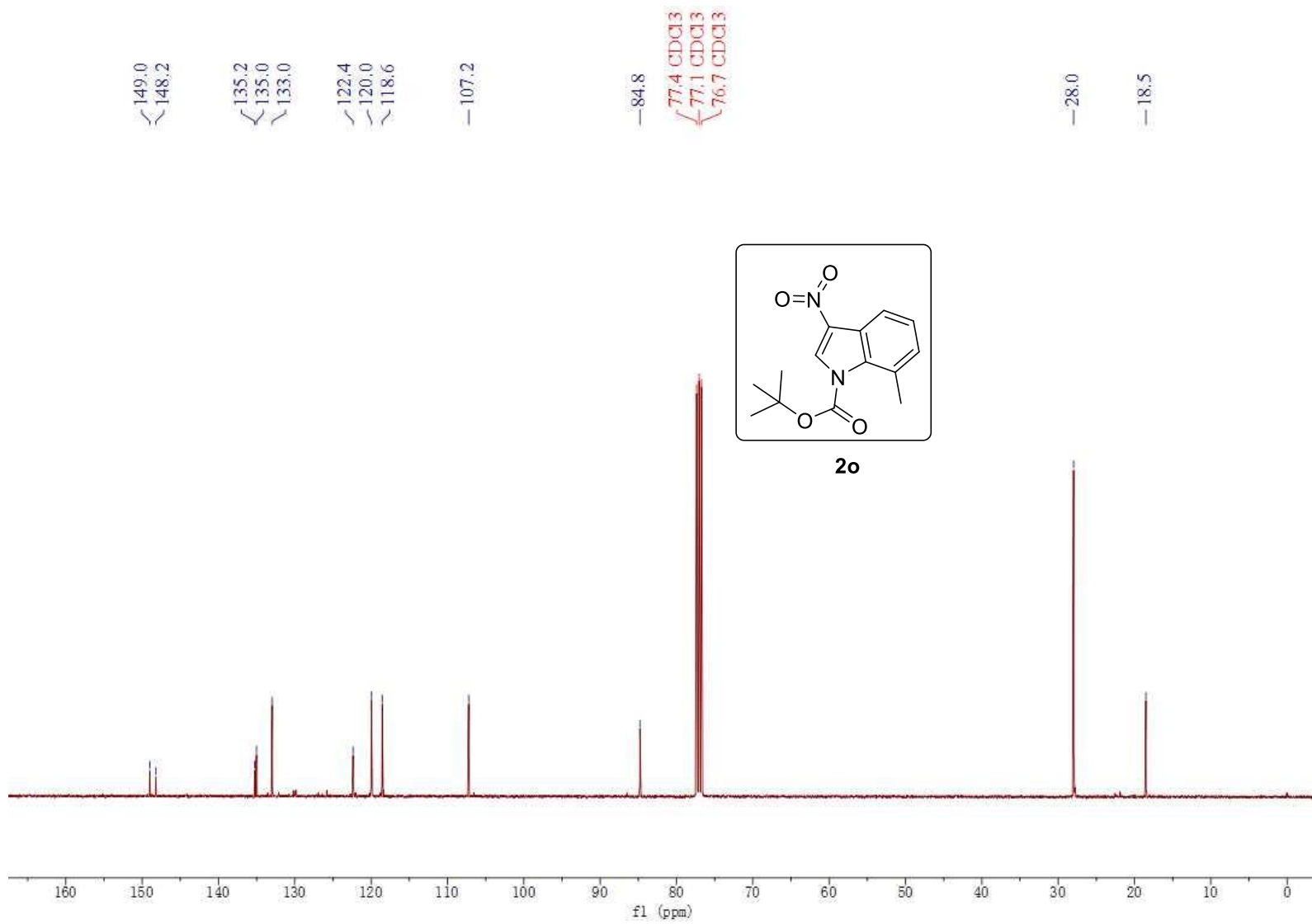


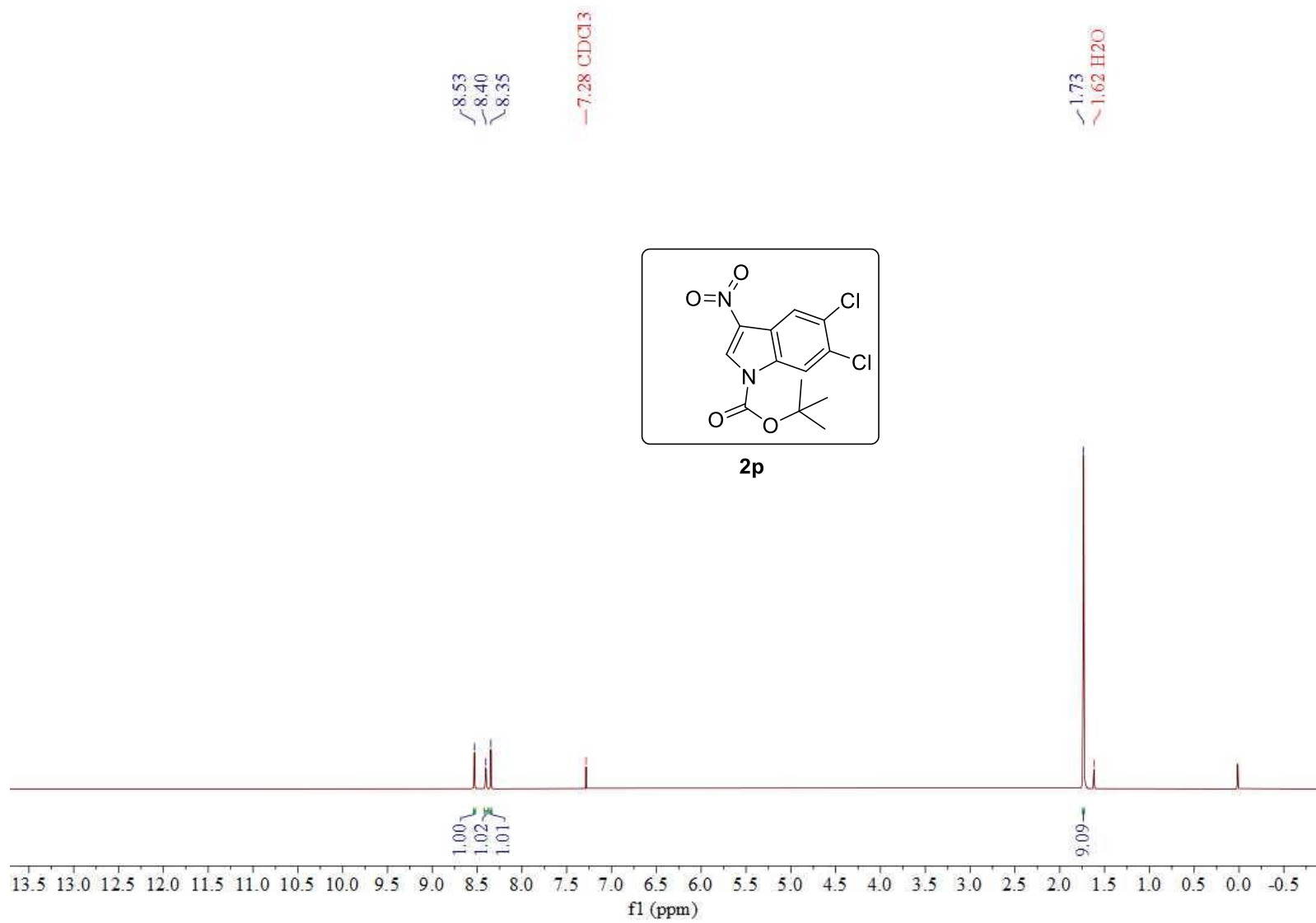
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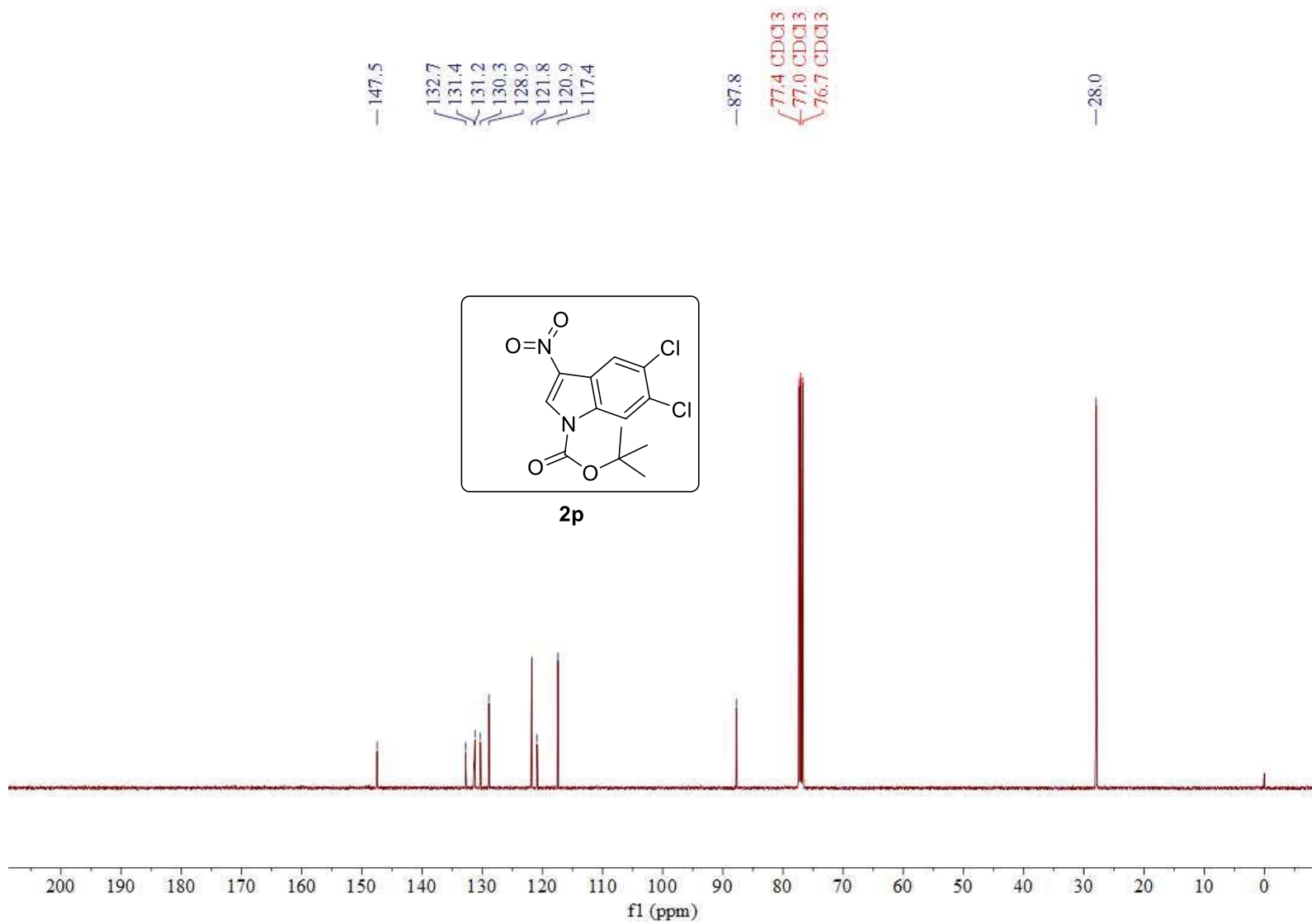


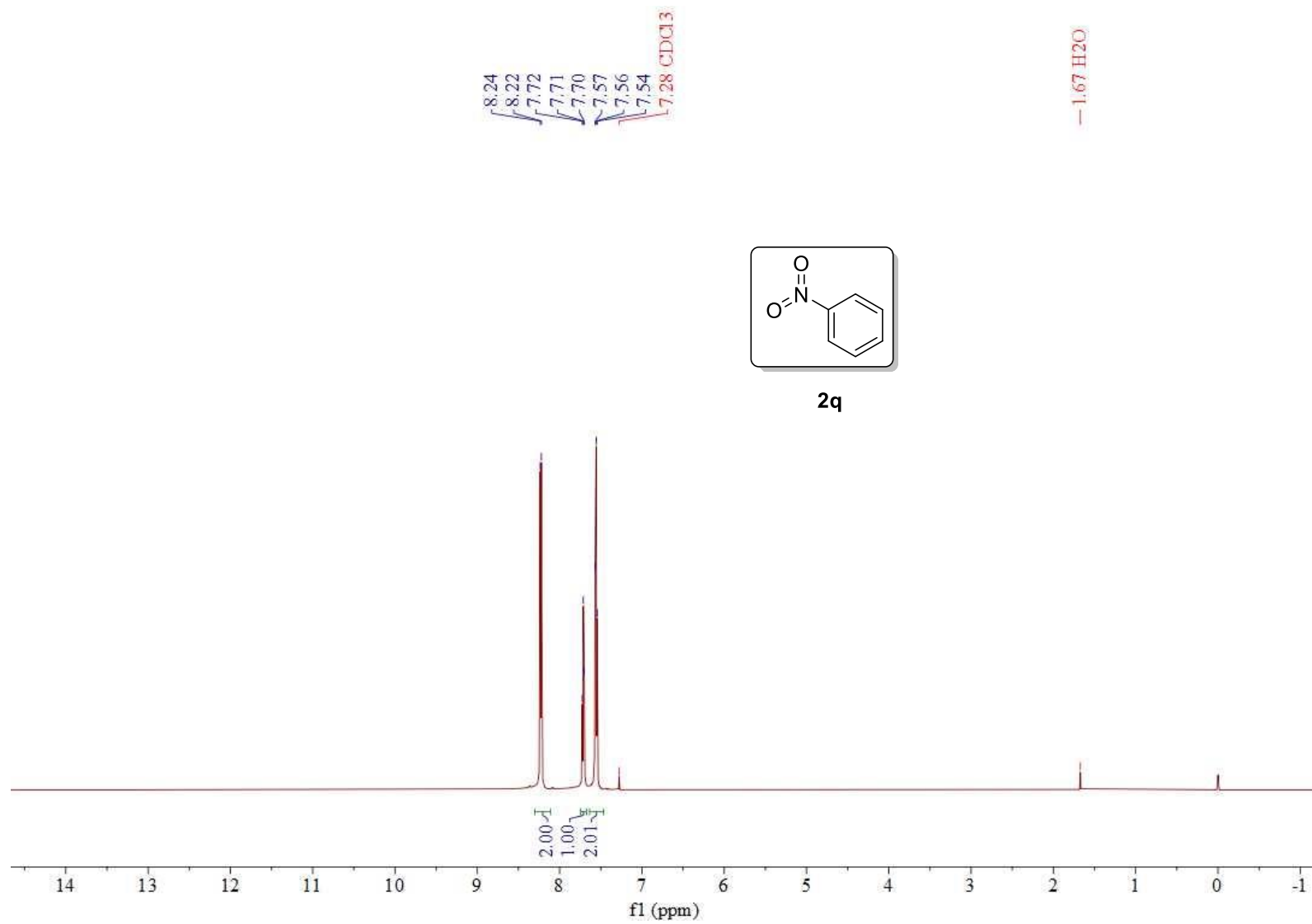


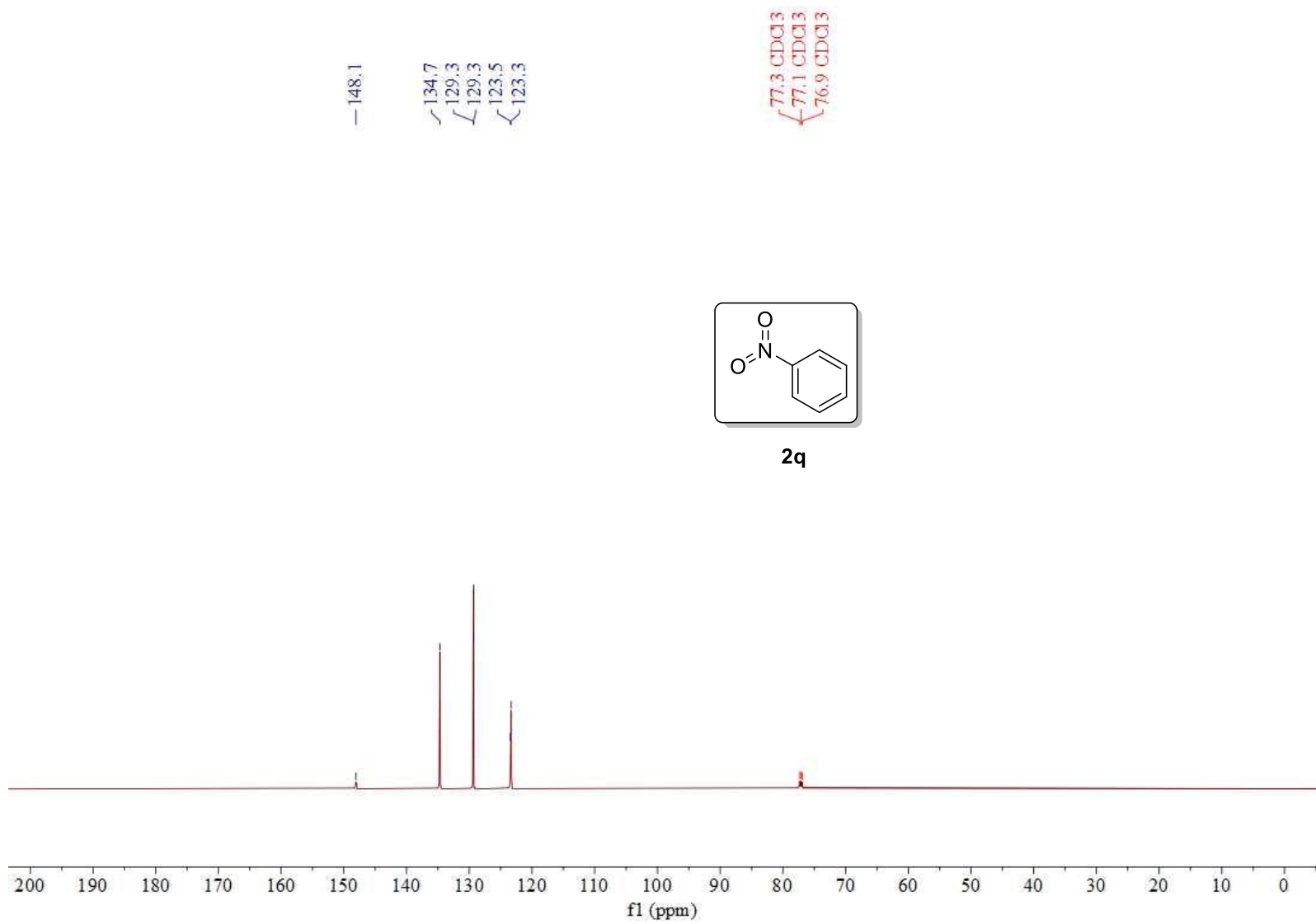


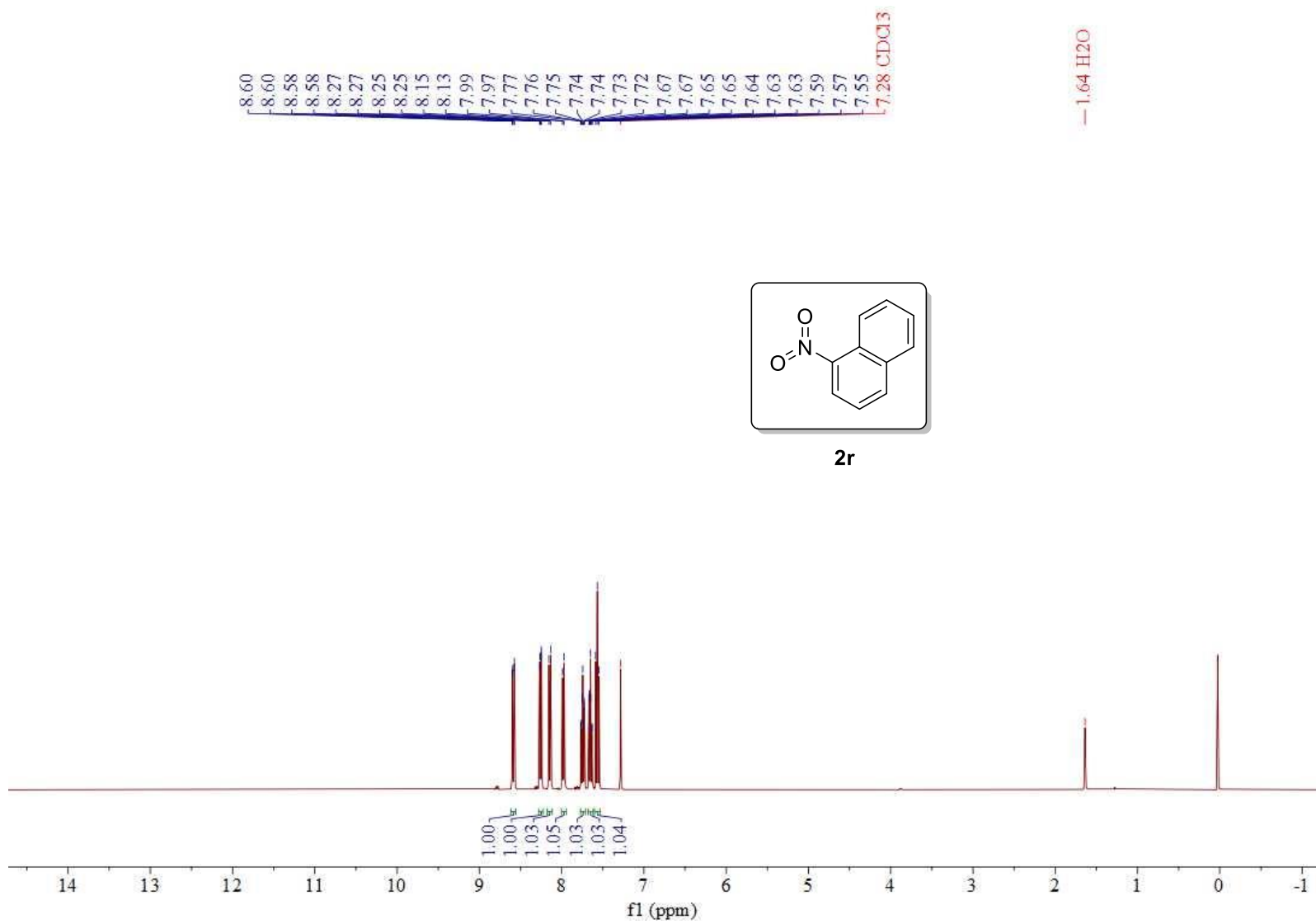


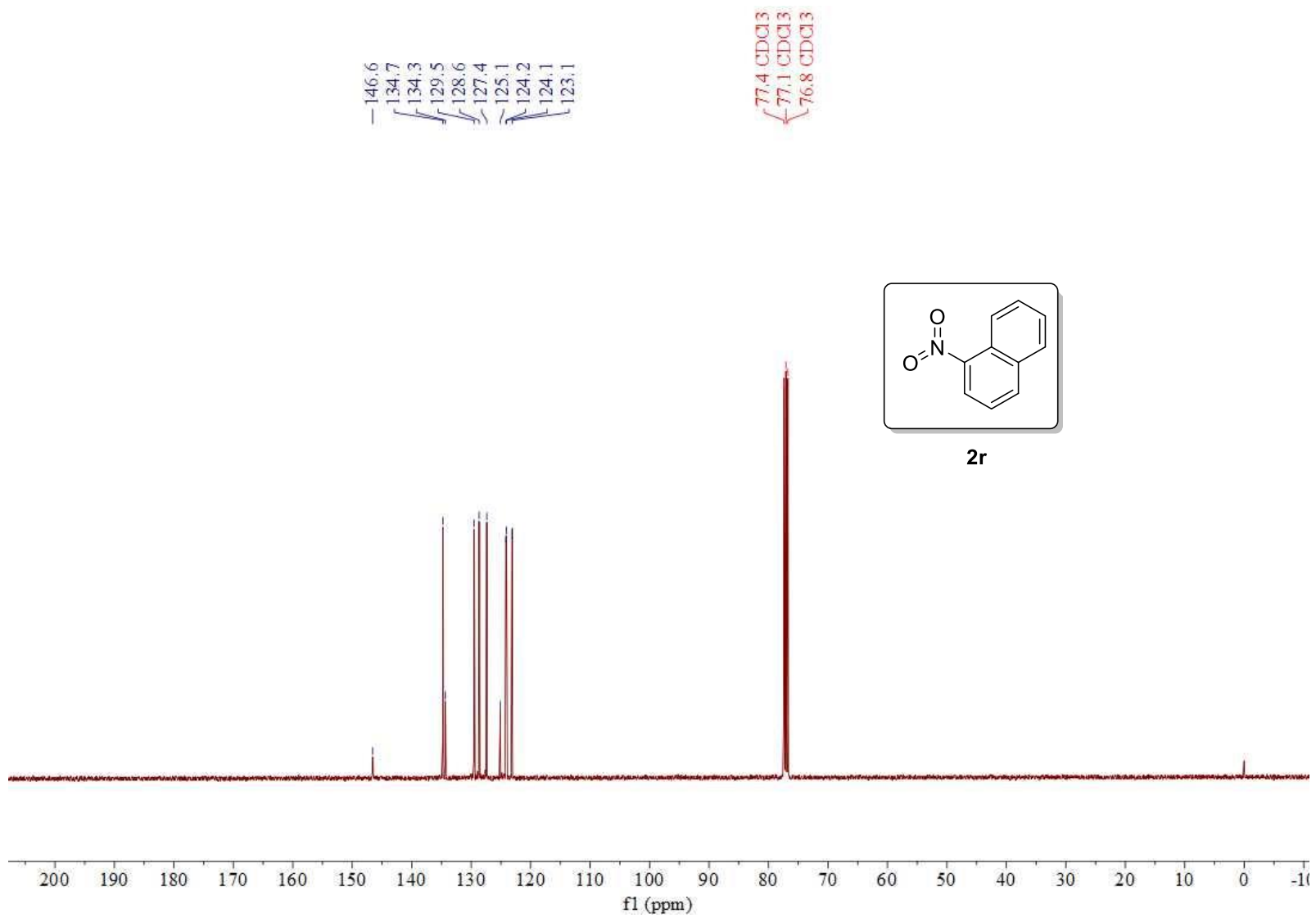


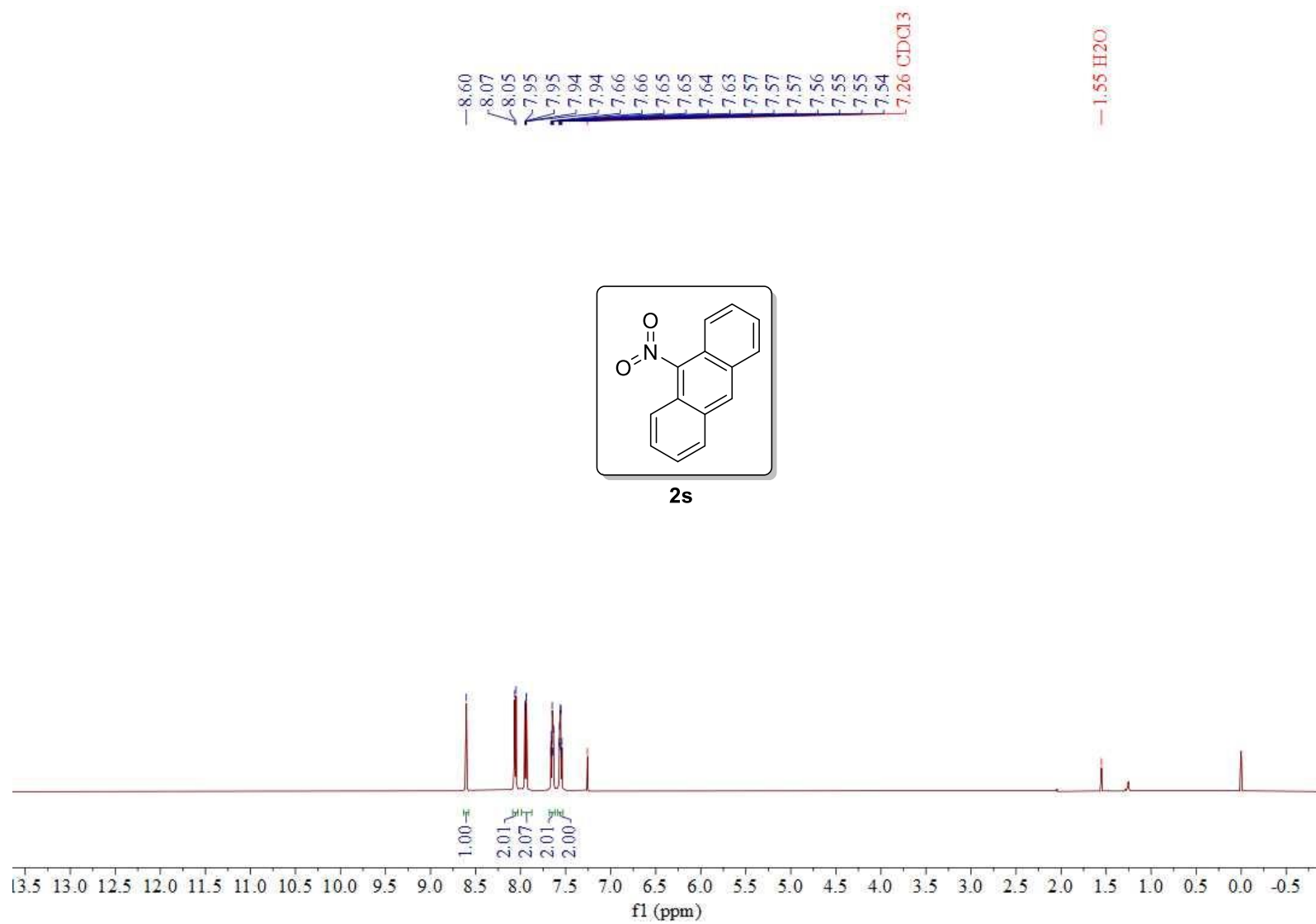


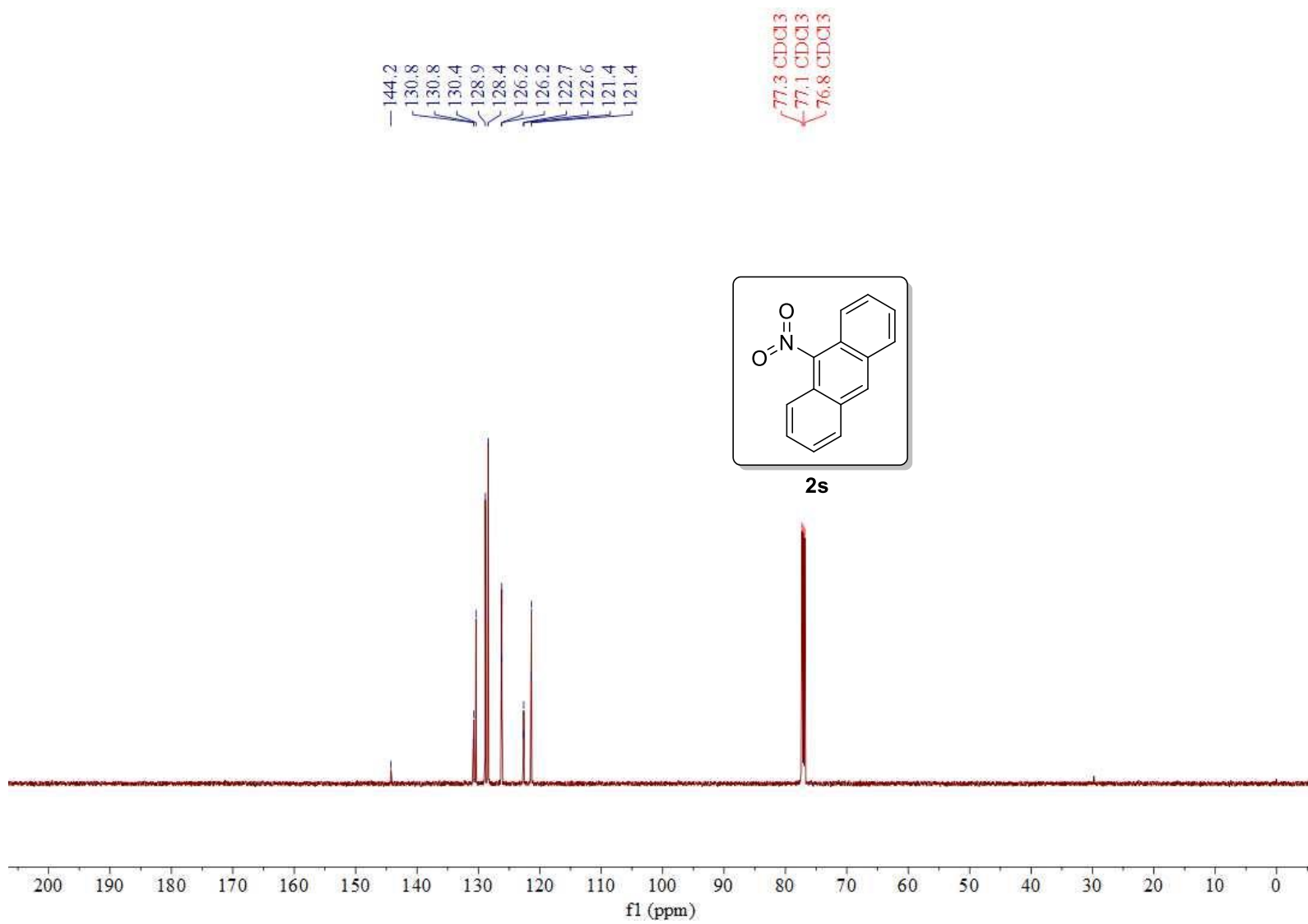




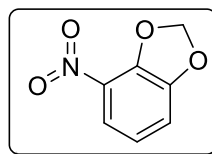




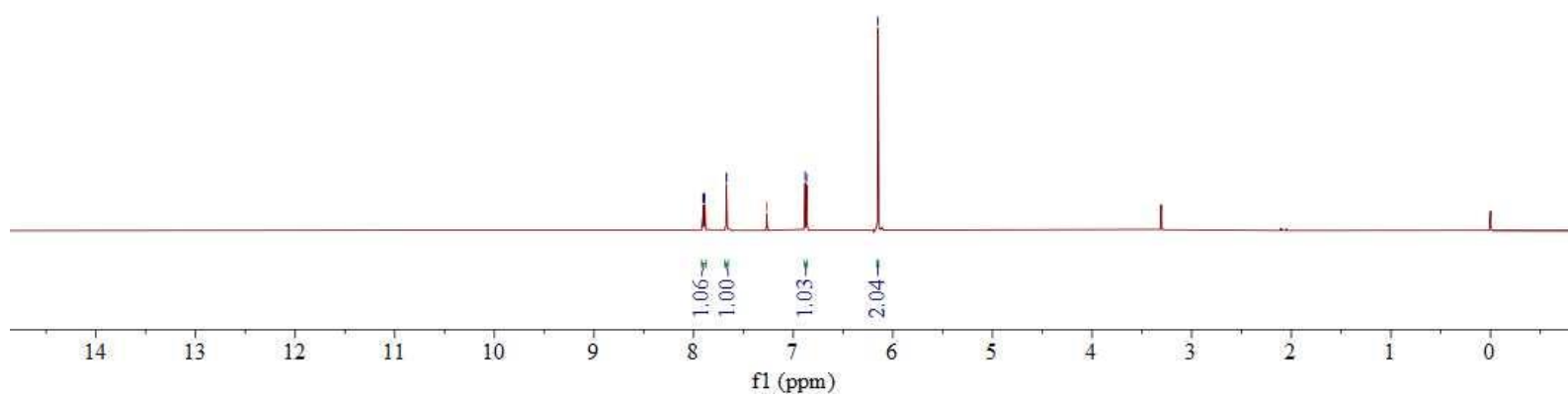




7.91
7.90
7.89
7.89
7.67
7.67
7.27 CDCl₃
6.88
6.87
-6.15



2t

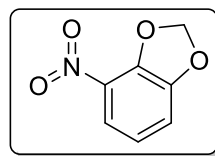


153.2
148.2
142.9

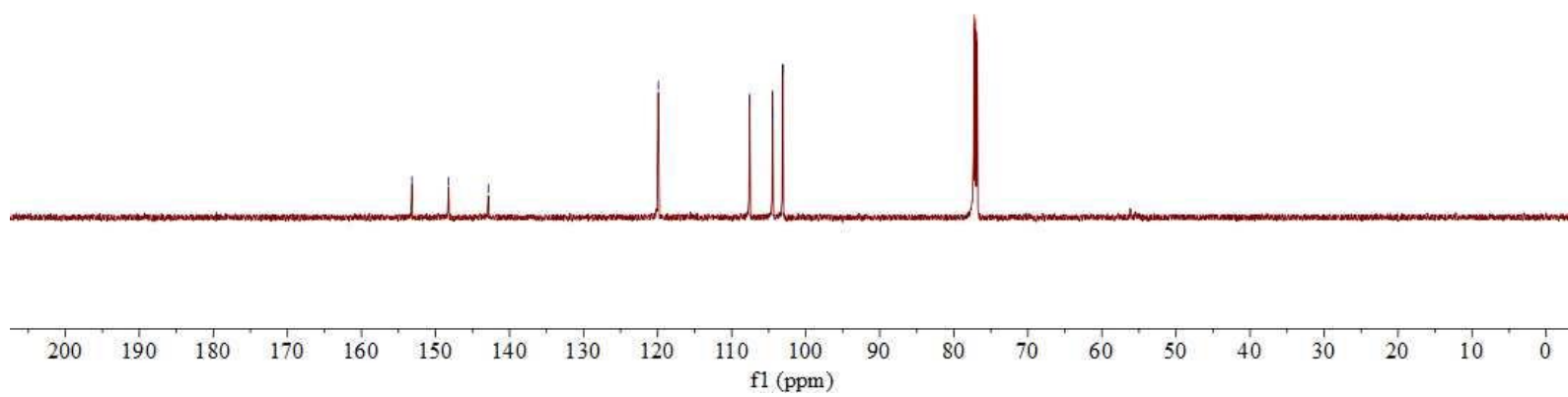
119.9

107.6
104.5
103.1

77.3 CDCl3
77.1 CDCl3
76.8 CDCl3

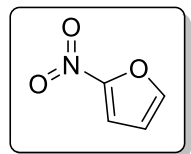


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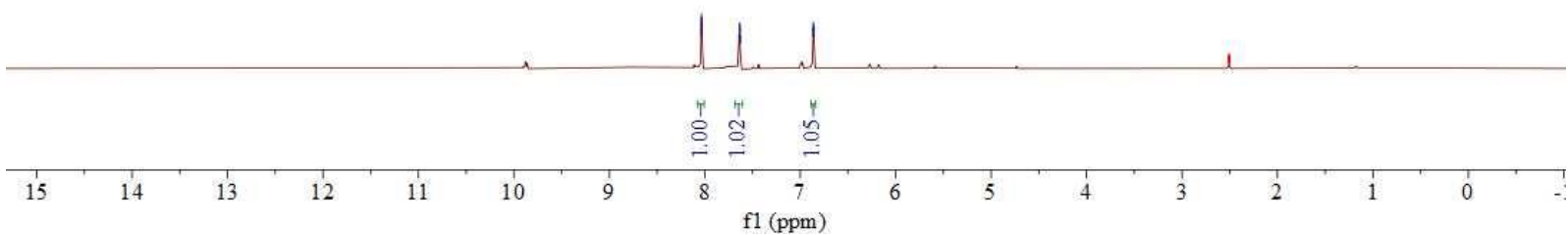


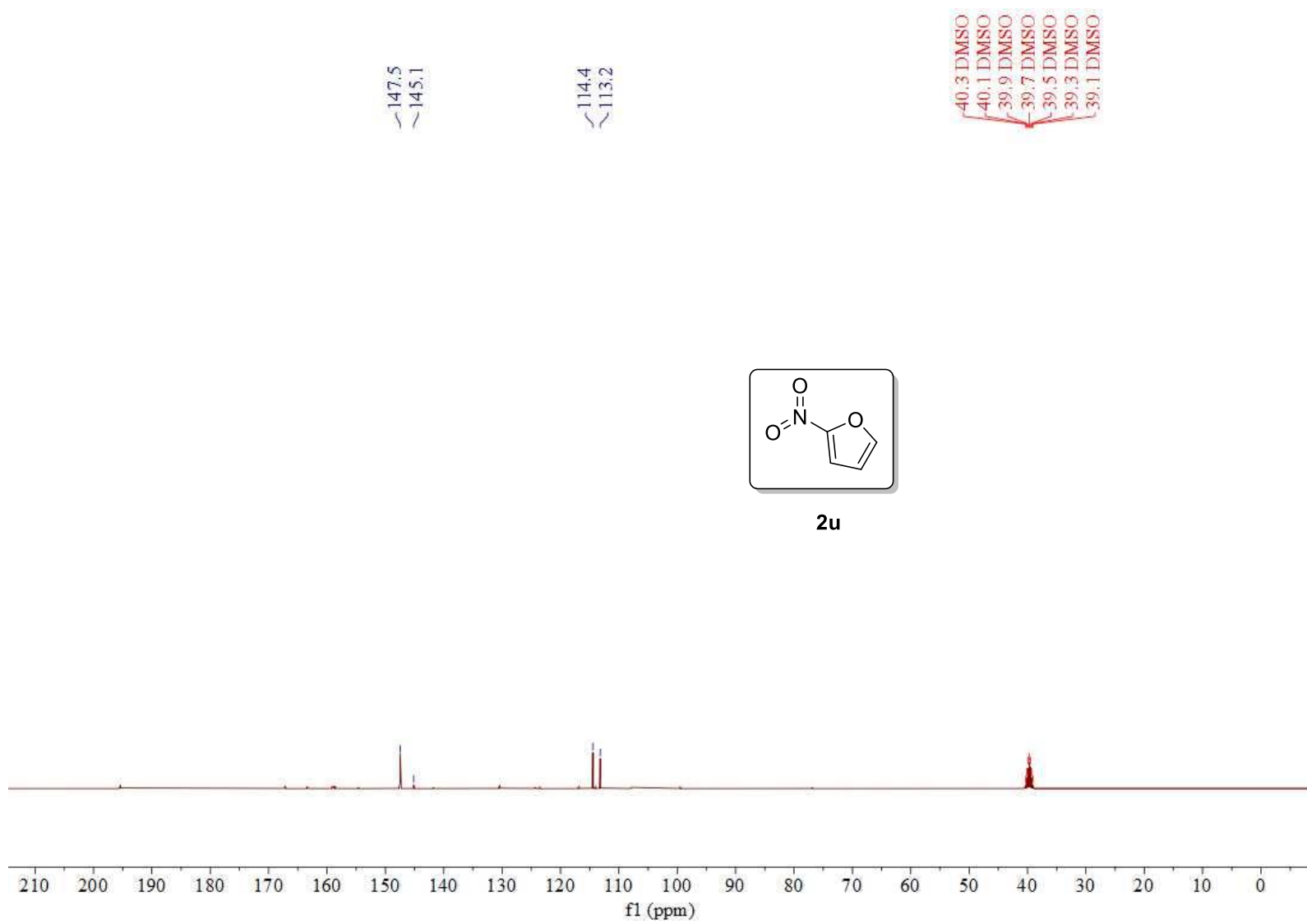
8.04
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8.03
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6.87
6.86
6.85

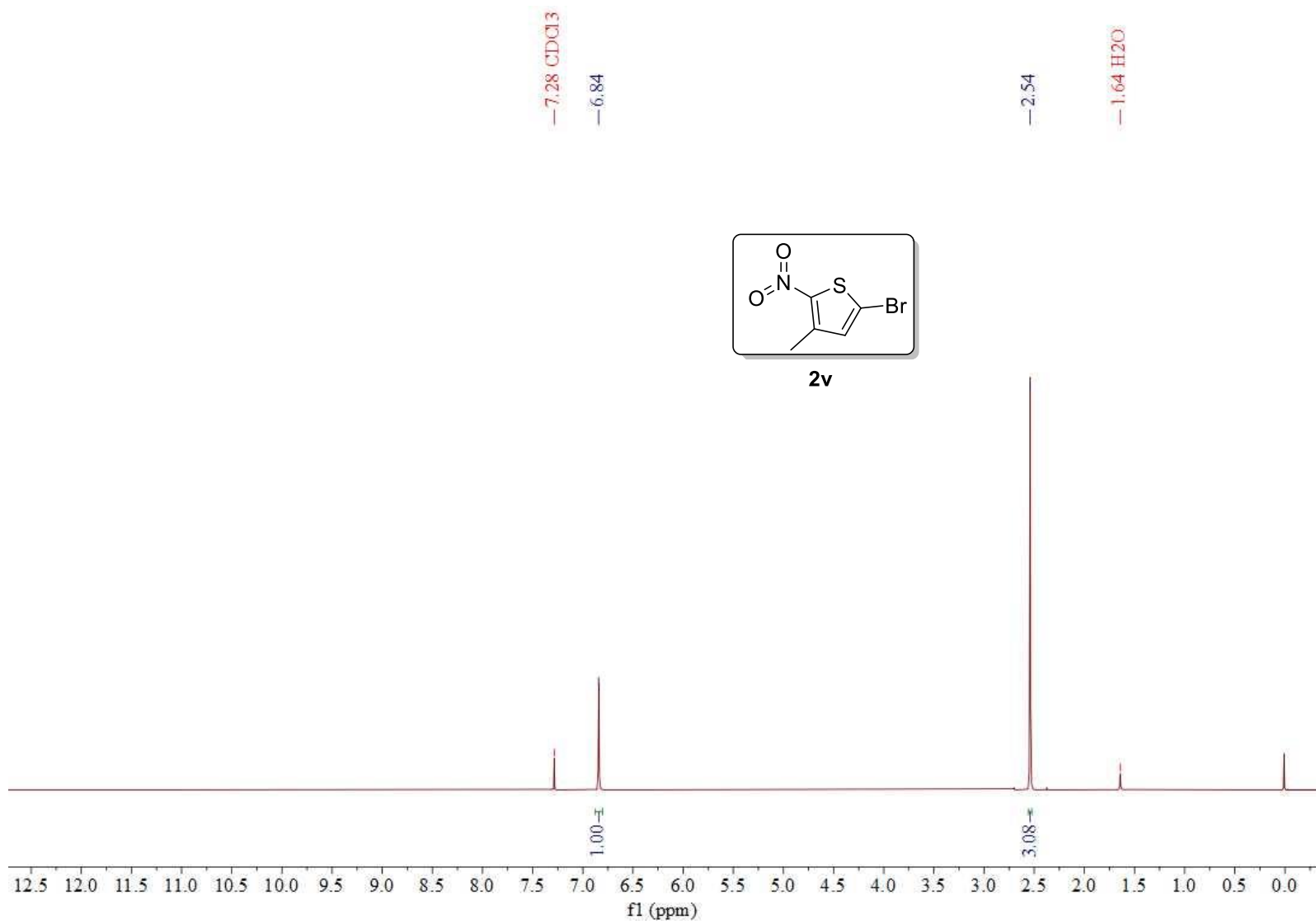
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2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO

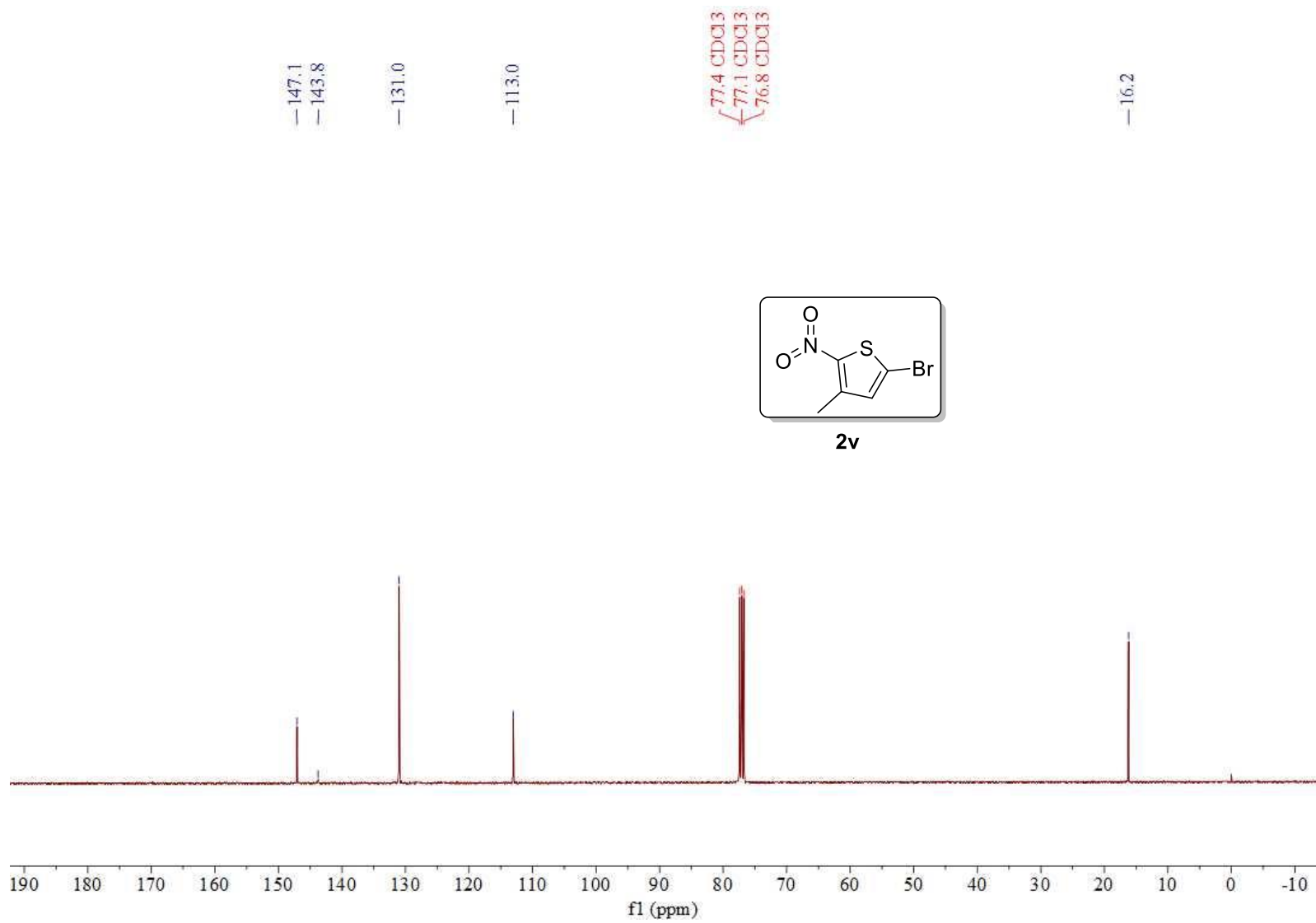


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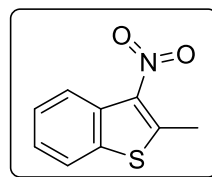




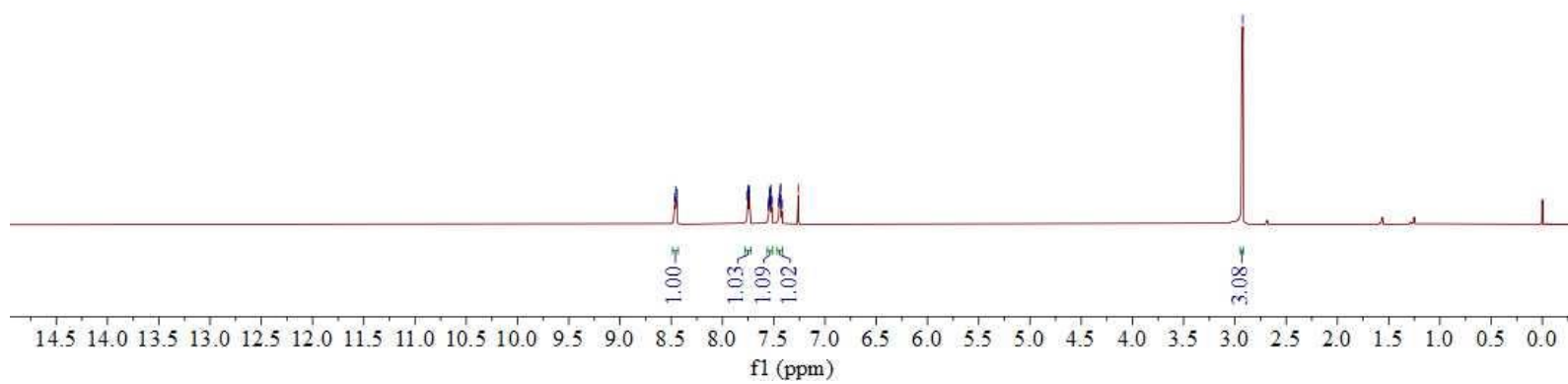


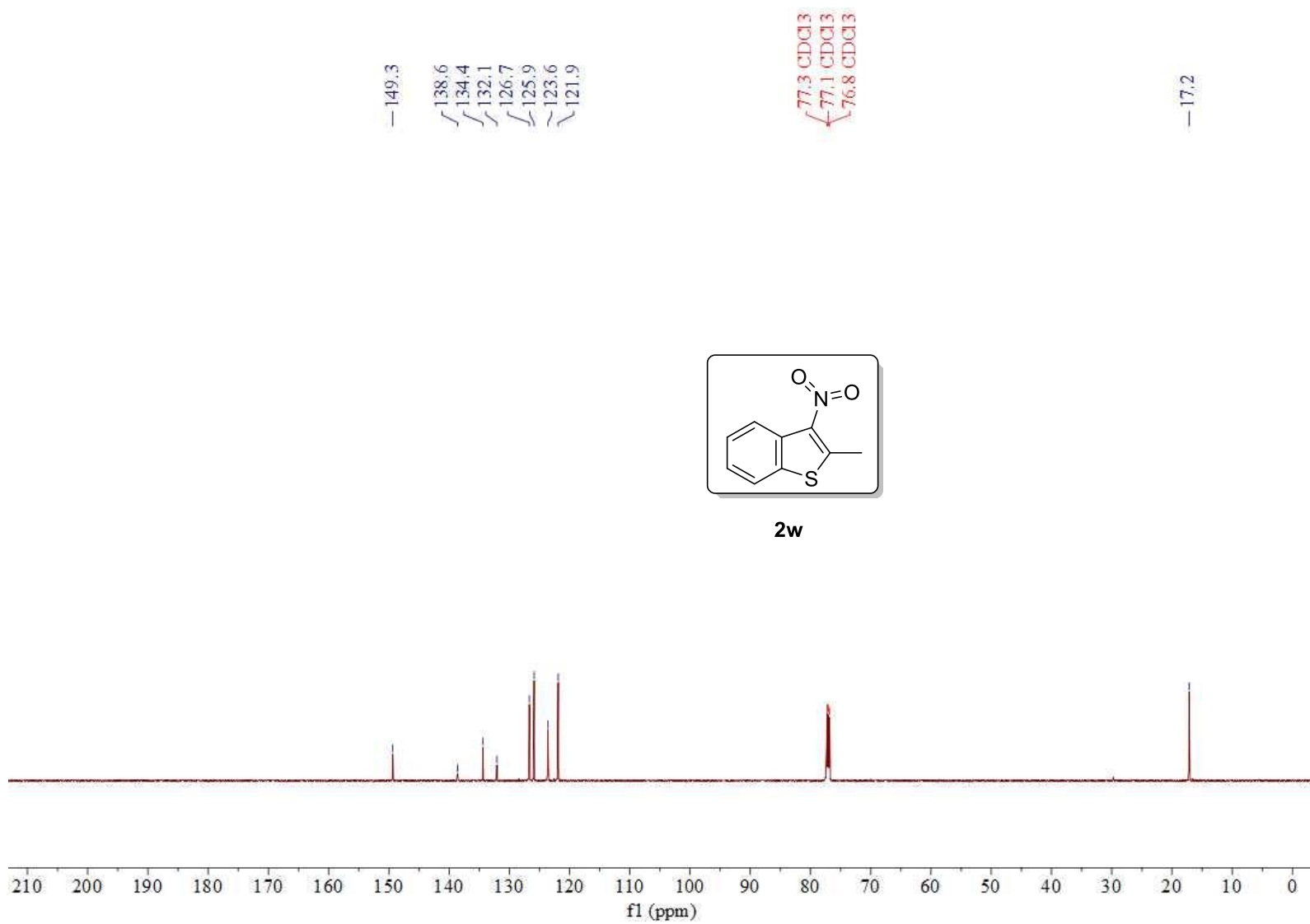


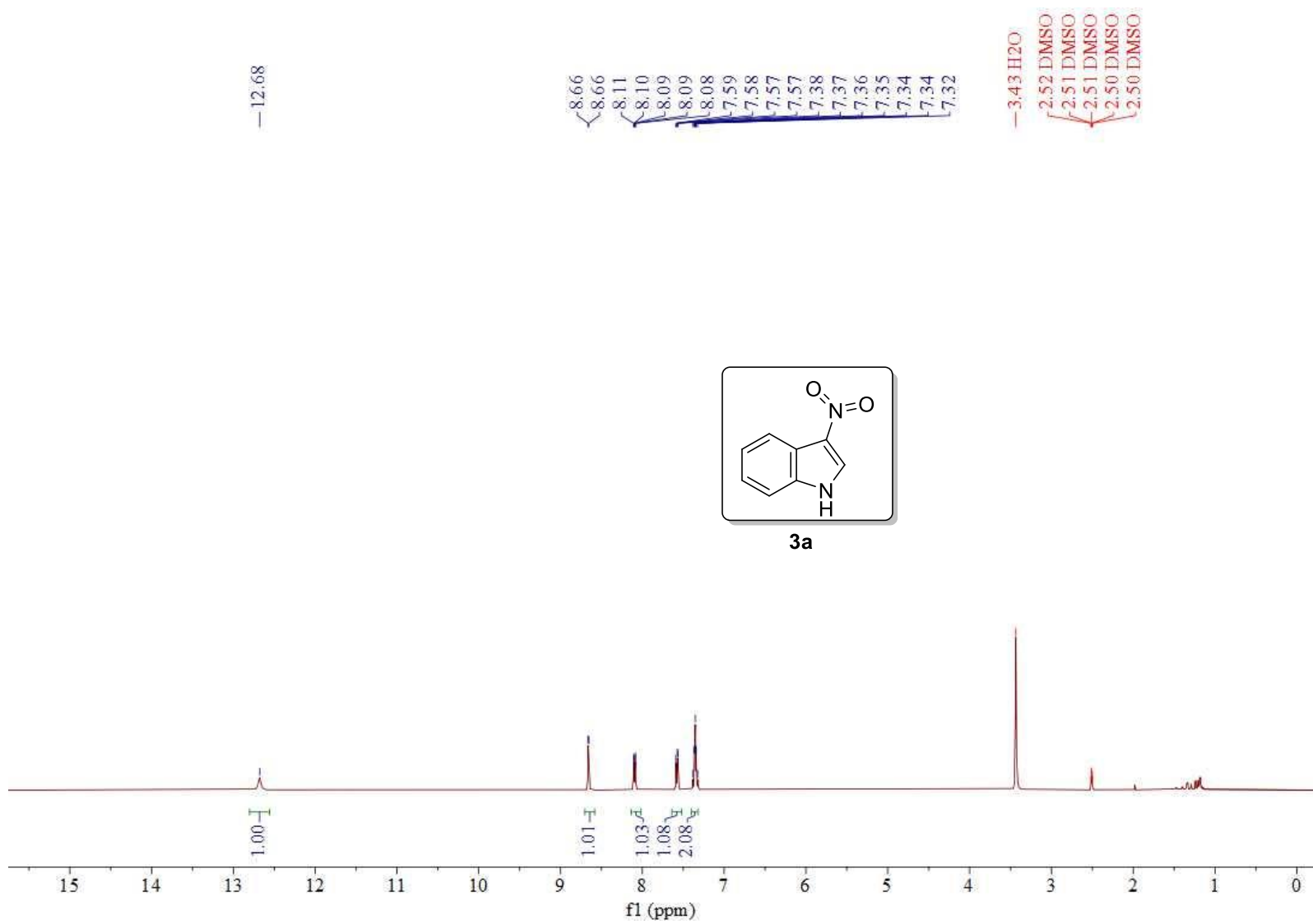
8.47
8.46
8.45
8.44
7.76
7.76
7.75
7.74
7.74
7.74
7.55
7.55
7.54
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.45
7.45
7.44
7.44
7.43
7.42
7.42
7.26 CDCl₃
2.92

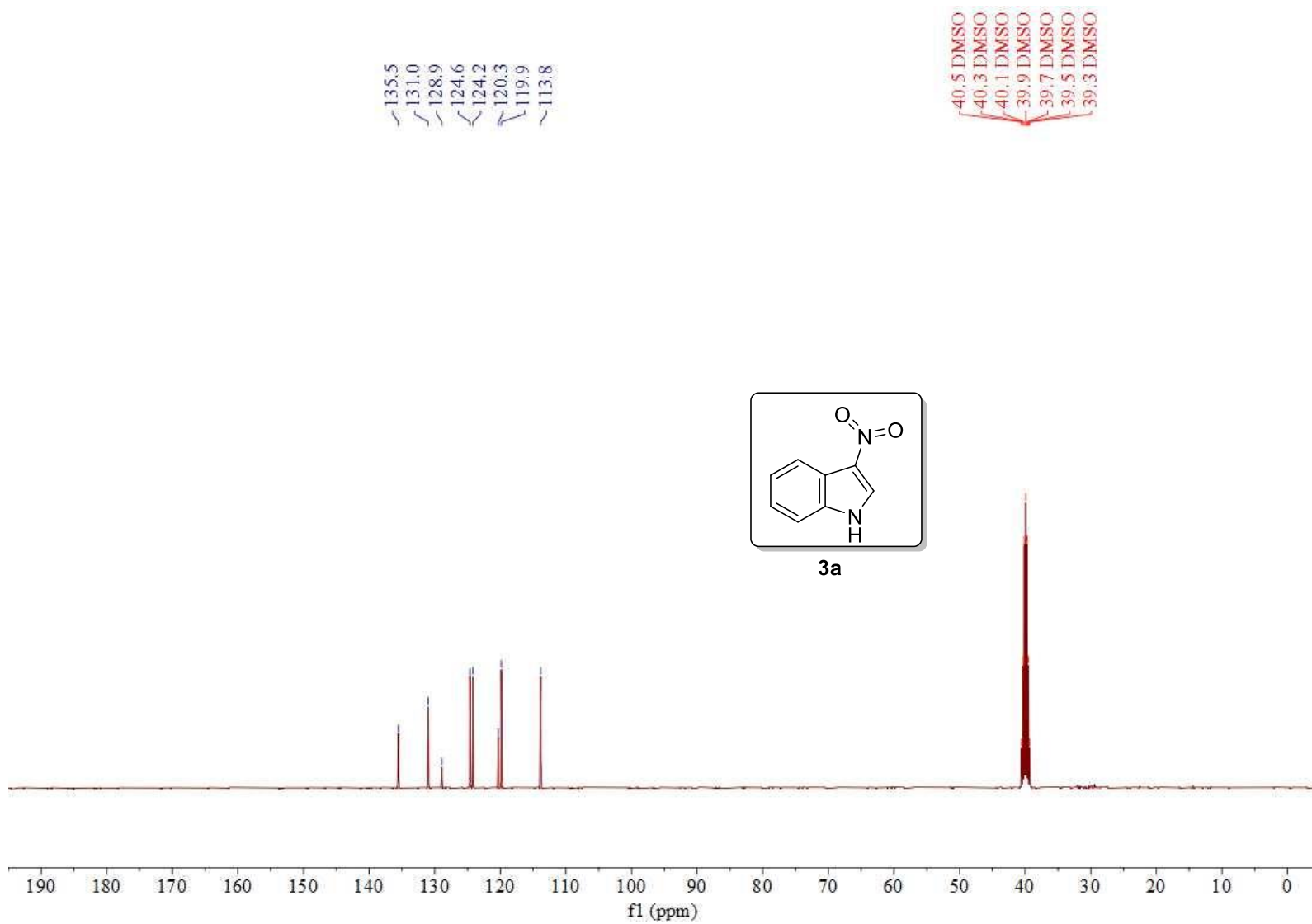


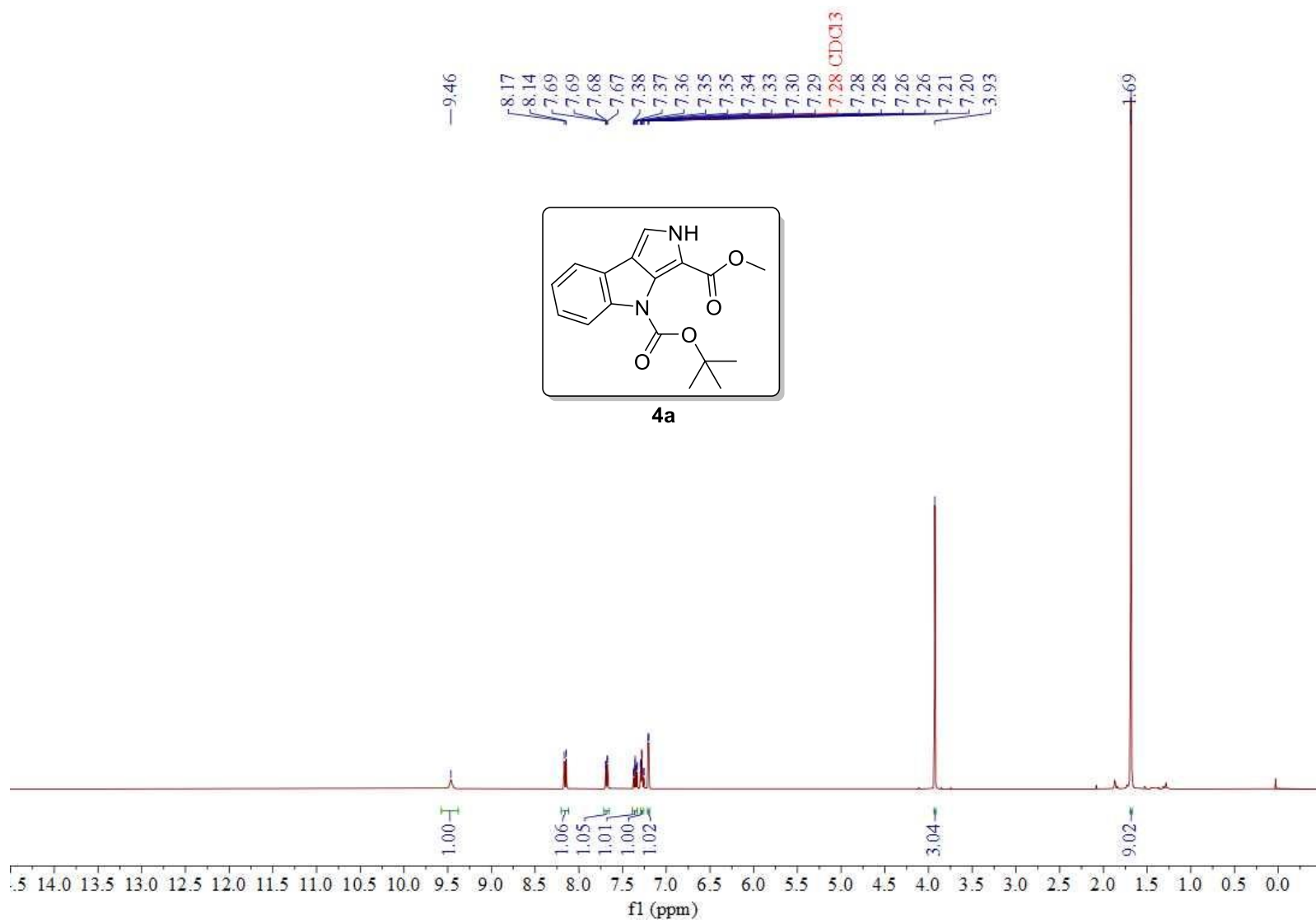
2w

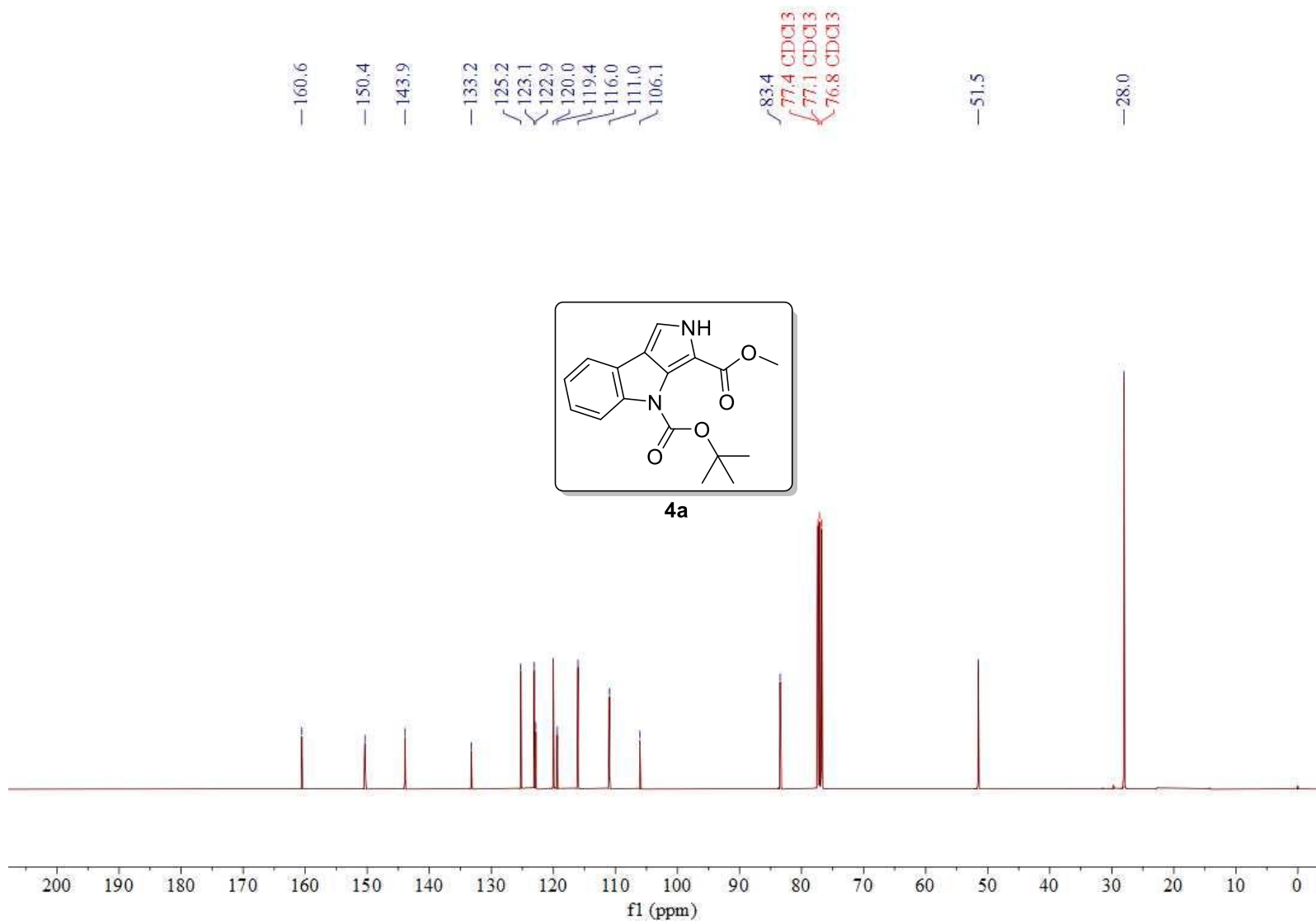


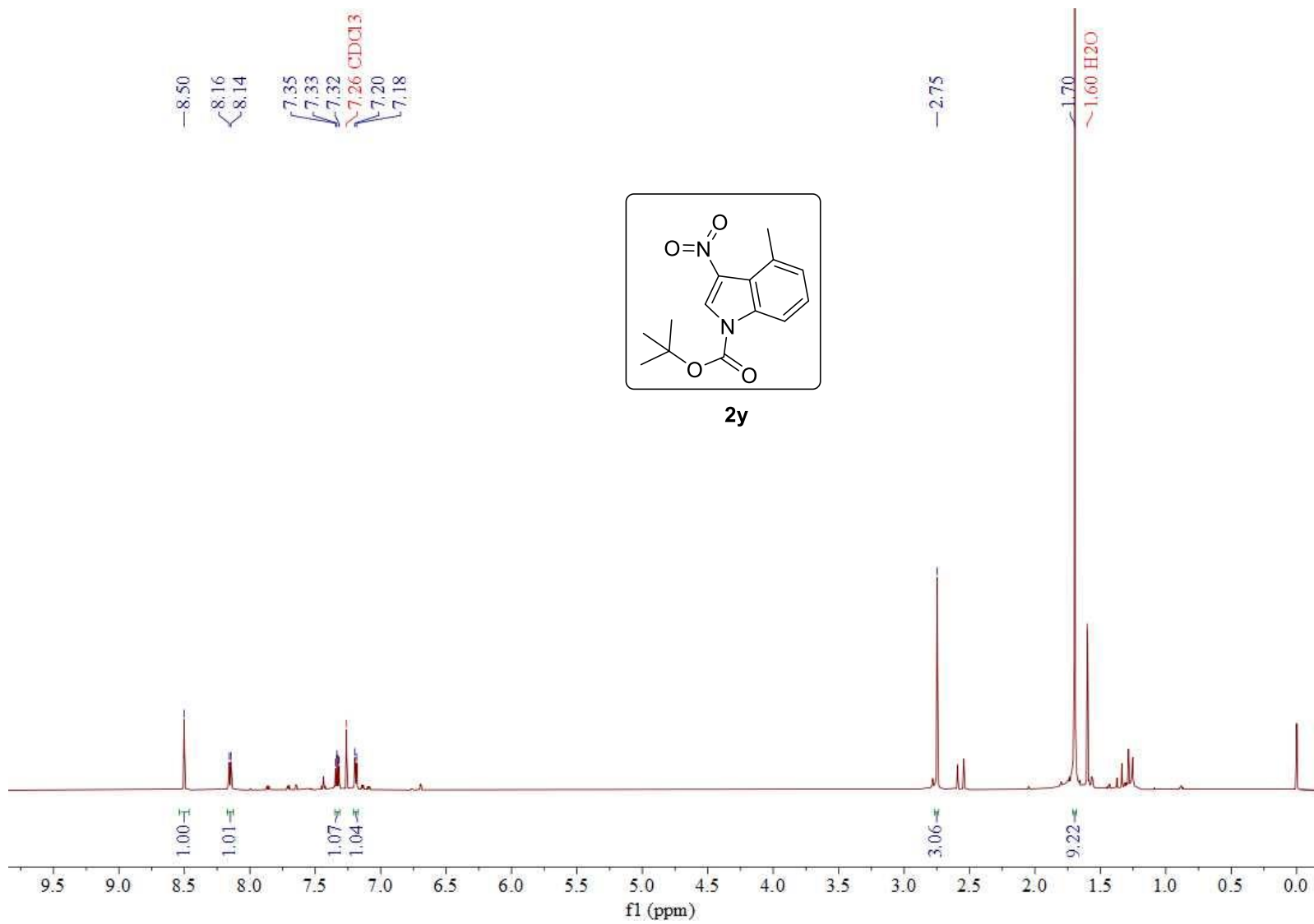












Monoisotopic Mass, Even Electron Ions

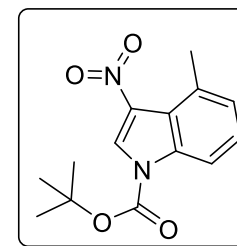
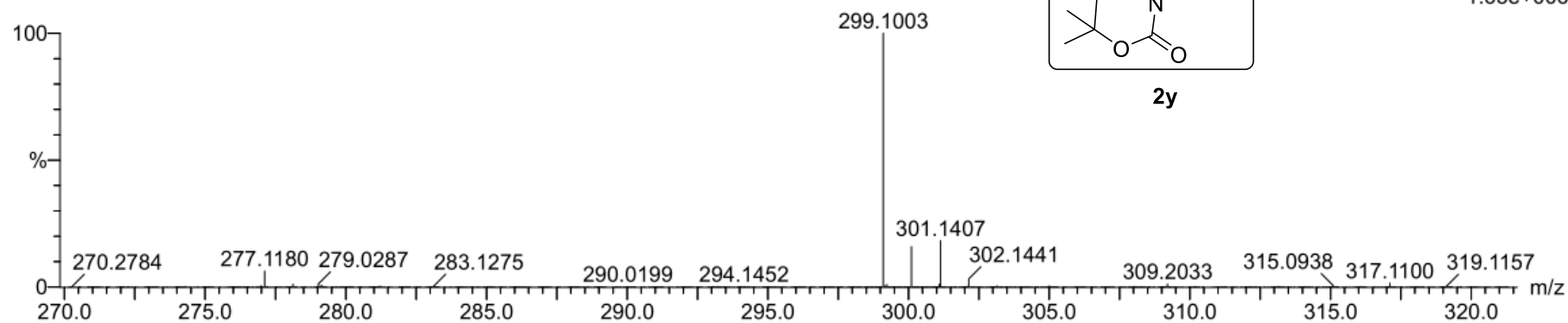
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-15 H: 0-20 N: 1-2 O: 2-6 Na: 0-1

0116-XYZH-19 80 (0.359)

1: TOF MS ES+



2y

Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
299.1003	299.1008	-0.5	-1.7	7.5	1041.2	n/a	n/a	C14 H16 N2 O4 Na