Supplementary Information for

Silver-Catalyzed Chemodivergent Assembly of Aminomethylated Isochromenes and Naphthols

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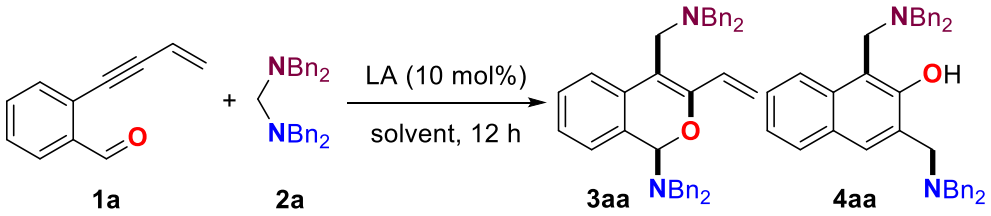
1. General Information

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before using were dried by standard methods and stored under N_2 atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Micro TOF-QII mass instrument (ESI). Single crystal X-ray diffraction analyses were recorded on Bruker SMART APEX II. All commercially available compounds were purchased from Adamas or Energy Chemical. Aminals used here were known compounds and synthesized according to the reported methods.[1-2] Enynals used here were synthesized according to the reported methods.[3] Flash column chromatography was performed using 200-300 mesh silica gels.

2. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions[a]

The mixture of *N*,*N*,*N*',*N*'-tetrabenzylmethanediamine **2a** (146.2 mg, 0.36 mmol), Lewis acid (0.03 mmol, 10 mol %), 2-(but-3-en-1-yn-1-yl)benzaldehyde **1a** (46.8 mg, 0.30 mmol) and solvent (1.0 mL) was added to a 25 mL flame-dried Young-type tube under nitrogen atmosphere. The reaction mixture was stirred at designed temperature for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the crude product was purified by flash chromatography on basic alumina (petroleum ether/ethyl acetate = 100/1 to 50/1) directly to give the desired products **3aa** and **4aa**.

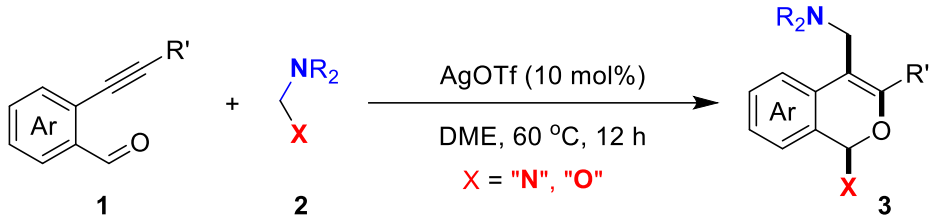


1a **2a** **3aa** **4aa**

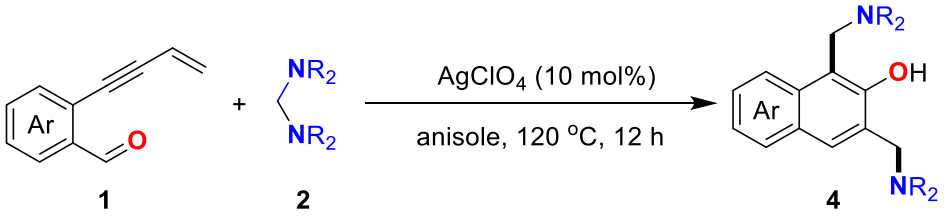
Entry	LA	solvent	T/°C	yield/%	
				3aa	**4aa**
1	$Sc(OTf)_3$	DME	100	N.D.	N.D.
2	$AuCl_3$	DME	100	73	trace
3	AgOTf	DME	100	78	15
4	$AgClO_4$	DME	100	60	29
5	$AgSbF_6$	DME	100	64	26
6	**AgOTf**	**DME**	**60**	**87**	**N.D.**
7	AgOTf	CH_3CN	100	39	48
8	AgOTf	anisole	100	32	52
9	$AgClO_4$	anisole	100	22	63
10	$AgClO_4$ (20 mol%)	anisole	100	23	59
11	AgOTf	anisole	120	25	58
12	**$AgClO_4$**	**anisole**	**120**	**7**	**71**

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), LA (10 mol%), solvent (1.0 mL), 12 h. [b]Isolated yield.

3. General Procedure for the Catalytic Reaction



The mixture of aminal **2** (0.36 mmol), AgOTf (7.7 mg, 10 mol %), alkyne-tethered aldehyde **1** (0.30 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C in an oil bath for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography on basic alumina (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3** as colorless oil.

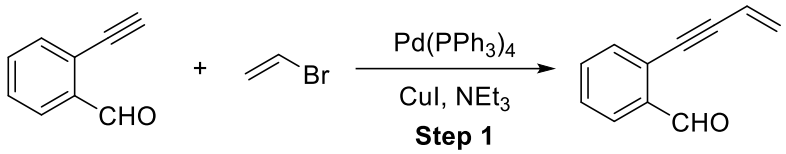


The mixture of aminal **2** (0.36 mmol), $AgClO_4$ (6.2 mg, 10 mol %), enyne-tethered aldehyde **1** (0.30 mmol) and anisole (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 120 °C in an oil bath for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 50/1 to 20/1) to give the desired product **4** as colorless oil.

4. Preparation and Spectral Data of Substrates

4.1. Preparation of Enynal Derivatives

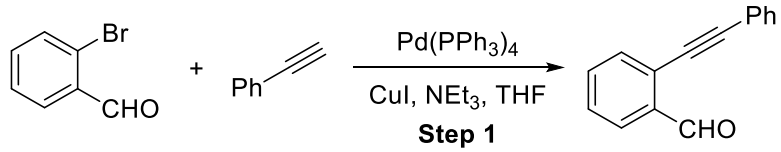
General Procedure A. Synthesis of enynal substrate **1a**



Enynals **1a-1q** were synthesized by using 2-ethynylaromatic aldehyde[3] as starting materials according to the **General Procedure A**.

Step 1. The mixture of copper (I) iodide (285 mg, 1.5 mmol) and tetrakis(triphenylphosphine)palladium (346 mg, 0.3 mmol) were dissolved in triethylamine (30 mL) under N_2 atmosphere at 0 ℃. 2-Ethynylbenzaldehyde (3.9 g, 30 mmol) and vinyl bromide (1.0 M in THF, 36 mL, 36 mmol) were added and the resulting mixture was stirred at 45 ^{o}C in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 20/1) to afford 2-(but-3-en-1-yn-1-yl)benzaldehyde (4.02 g, 86% yield).

General Procedure B. Synthesis of alkyne-tethered aldehyde substrate **1r**

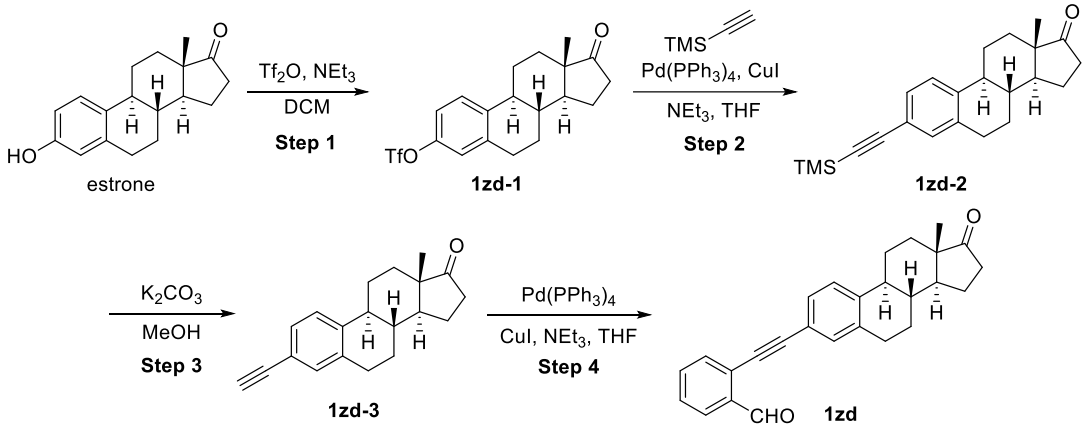


Alkyne-tethered aldehydes **1r-1zc** were synthesized by using 2-bromobenzaldehyde as starting materials according to the **General Procedure B**.

Step 1. The mixture of copper (I) iodide (95 mg, 0.5 mmol) and tetrakis(triphenylphosphine)palladium (116 mg, 0.1 mmol) were dissolved in triethylamine (10 mL) under N_2 atmosphere at 0 ℃. 2-Bromobenzaldehyde (1.85 g, 10 mmol) and ethynylbenzene (1.53 g, 15 mmol) were added and the resulting

mixture was stirred at 45 °C in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 20/1) to afford 2-(phenylethynyl)benzaldehyde (1.7 g, 83% yield).

General Procedure C. Synthesis of alkyne-tethered aldehyde substrate **1zd**[4]



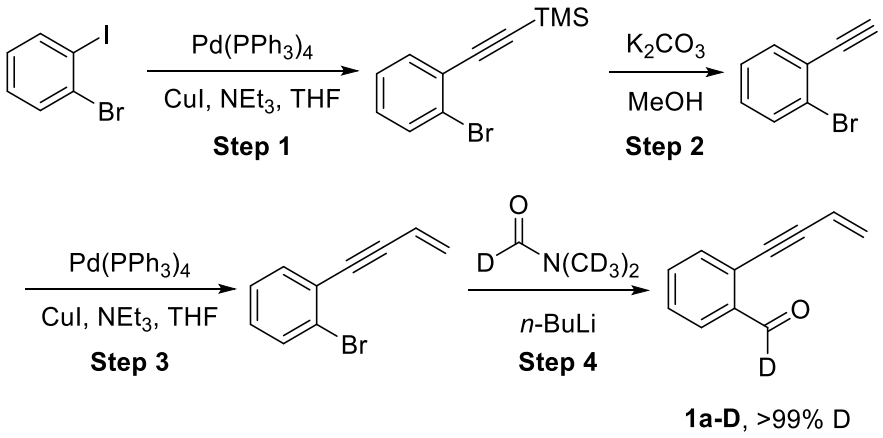
Step 1. Tf_2O (24 mmol, 4.0 mL) was added dropwise to a solution of estrone (20 mmol, 5.4 g) and NEt_3 (30 mmol, 4.2 mL) in dry CH_2Cl_2 (30 mL) at 0 ℃ under N_2 atmosphere. After that, the mixture was stirred at room temperature until estrone had been consumed (monitored by TLC). The reaction was quenched by water and extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1) to afford substrate **1zd-1** (7.08 g, 88% yield).

Step 2. The mixture of copper (I) iodide (95 mg, 0.5 mmol) and tetrakis(triphenylphosphine)palladium (116 mg, 0.1 mmol) were dissolved in triethylamine (10 mL) under N_2 atmosphere at 0 ℃. **1zd-1** (4.02 g, 10 mmol) and ethynyltrimethylsilane (2 mL, 15 mmol) were added and the resulting mixture was stirred at 45 °C in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1) to afford **1zd-2** (2.7 g, 78% yield).

Step 3. 1zd-2 (1.75 g, 5 mmol) was dissolved in anhydrous MeOH (20 mL) under N_2 atmosphere at room temperature. K_2CO_3 (138 mg, 1 mmol) was added and stirred at room temperature until complete conversion of the starting material. The reaction was quenched by H_2O and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product **1zd-3** was used for the next step directly without further purification.

Step 4. The mixture of copper (I) iodide (190 mg, 1 mmol) and tetrakis(triphenylphosphine)palladium (230 mg, 0.2 mmol) were dissolved in triethylamine (30 mL) under N_2 atmosphere at 0 ℃. The crude **1zd-3** (1.11 g, 4 mmol) and 2-bromobenzaldehyde (0.7 mL, 6 mmol) were added and the resulting mixture was stirred at 45 ^oC in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 20/1) to afford **1zd** (1.04 g, 68% yield).

General Procedure D. Synthesis of 2-(but-3-en-1-yn-1-yl)benzaldehyde-D **1a-D**



Step 1. The mixture of copper (I) iodide (190 mg, 1.0 mmol) and tetrakis(triphenylphosphine)palladium (232 mg, 0.2 mmol) were dissolved in triethylamine (10 mL) under N_2 atmosphere at 0 ℃. 1-Bromo-2-iodobenzene (4.02 g, 20 mmol) and ethynyltrimethylsilane (3.2 mL, 24 mmol) were added and the resulting mixture was stirred at 45 ^oC in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After

evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1) to afford ((2-bromophenyl)ethynyl)trimethylsilane (4.1 g, 81% yield).

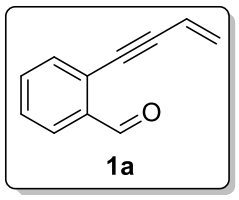
Step 2. ((2-Bromophenyl)ethynyl)trimethylsilane (3.8 g, 15 mmol) was dissolved in anhydrous MeOH (20 mL) under N_2 atmosphere at room temperature. K_2CO_3 (207 mg, 1.5 mmol) was added and stirred at room temperature until complete conversion of the starting material. The reaction was quenched by H_2O and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product 1-bromo-2-ethynylbenzene was used for the next step directly without further purification.

Step 3. The mixture of copper (I) iodide (95 mg, 0.5 mmol) and tetrakis(triphenylphosphine)palladium (116 mg, 0.1 mmol) were dissolved in triethylamine (10 mL) under N_2 atmosphere at 0 ℃. The crude 1-bromo-2-ethynylbenzene (1.8 g, 10 mmol) and vinyl bromide (1.0 M in THF, 12 mL, 12 mmol) were added and the resulting mixture was stirred at 45 ^oC in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 20/1) to afford 1-bromo-2-(but-3-en-1-yn-1-yl)benzene (1.6 g, 78% yield).

Step 4. The *n*-butyllithium (2.5 M in hexane, 2.4 mL, 6 mmol) was added dropwise to a solution of 1-bromo-2-(but-3-en-1-yn-1-yl)benzene (1.0 g, 5 mmol) in THF (20 ml) at -78 ^oC. After one hour, the *N*,*N*-dimethylformamide-d_7 (0.6 mL, 8 mmol) was added dropwise to the solution and stirred at -78 ^oC for additional 30 minutes. The reaction mixture was quenched by saturated ammonium chloride solution (10 mL) extracted with EtOAc (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4.After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 20/1) to afford **1a-D** (573 mg, 73% yield).

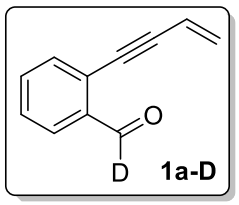
4.2. Substrates Characterization

2-(but-3-en-1-yn-1-yl)benzaldehyde (1a)



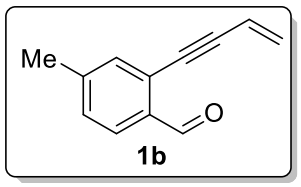
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 4.02 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (d, *J* = 0.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 3.6 Hz, 2H), 7.41-7.45 (m, 1H), 6.03 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.80 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.64 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 135.9, 133.8, 133.3, 128.8, 128.6, 127.3, 126.8, 116.7, 95.0, 85.5; HRMS (ESI) calcd for $C_{11}H_9O$ $[M+H]^+$: 157.0653, found: 157.0649.

2-(but-3-en-1-yn-1-yl)benzaldehyde-D (1a-D)



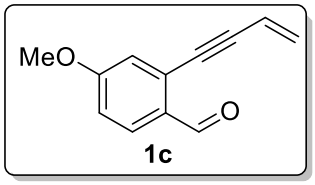
The title compound was prepared according to the general procedure D and purified by column chromatography to give yellow oil, 573 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 4.4 Hz, 2H), 7.41-7.46 (m, 1H), 6.03-6.11 (m, 1H), 5.81 (d, *J* = 17.6 Hz, 1H), 5.64 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 191.5, 191.2, 135.8, 133.9, 133.3, 128.8, 128.6, 127.3, 126.8, 116.7, 94.9, 85.5; HRMS (ESI) calcd for $C_{11}H_8DO$ $[M+H]^+$: 158.0716, found: 158.0712.

2-(but-3-en-1-yn-1-yl)-4-methylbenzaldehyde (1b)



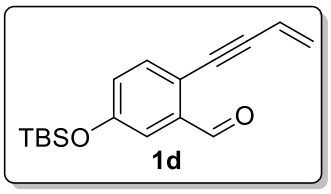
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 6.1 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.19 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.95 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.79 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 144.6, 133.6, 133.5, 129.6, 128.2, 127.1, 126.5, 116.6, 94.3, 85.6, 21.4; HRMS (ESI) calcd for $C_{12}H_{11}O$ $[M+H]^+$: 171.0810, found: 171.0812.

2-(but-3-en-1-yn-1-yl)-4-methoxybenzaldehyde (1c)



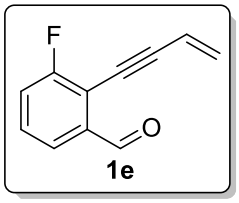
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 5.6 g, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.93 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.03 (dd, *J* = 17.5 Hz, 11.0 Hz, 1H), 5.81 (dd, *J* = 17.5 Hz, 2.0 Hz, 1H), 5.65 (dd, *J* = 11.0 Hz, 2.0 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 163.8, 129.7, 129.5, 128.9, 128.8, 117.1, 116.6, 115.7, 94.7, 85.4, 55.8; HRMS (ESI) calcd for $C_{12}H_{11}O_2$ $[M+H]^+$: 187.0759, found: 187.0758.

2-(but-3-en-1-yn-1-yl)-5-((*tert*-butyldimethylsilyl)oxy)benzaldehyde (1d)



The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 0.62 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.01 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.75 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.59 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H), 0.98 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 156.4, 137.4, 134.8, 127.8, 126.3, 119.9, 117.7, 116.9, 93.6, 85.5, 25.7, 18.3, -4.3; HRMS (ESI) calcd for $C_{17}H_{23}O_2Si$ $[M+H]^+$: 287.1467, found: 287.1472.

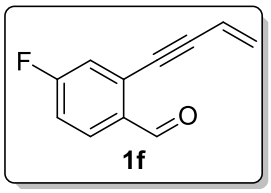
2-(but-3-en-1-yn-1-yl)-3-fluorobenzaldehyde (1e)



The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 4.5 g, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.39-7.45 (m, 1H), 7.31-7.36 (m, 1H), 6.07 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.86 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.69 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5 (d, $J_{C\text{-}F}$ = 3 Hz), 164.3 (d, $J_{C\text{-}F}$ = 252 Hz), 137.4, 129.8 (d, $J_{C\text{-}F}$ = 7 Hz), 129.4, 123.1 (d, $J_{C\text{-}F}$ =

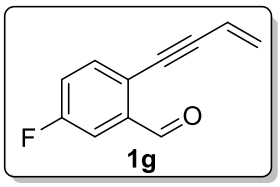
3 Hz), 121.0 (d, J_{C-F} = 22 Hz), 116.5, 115.3 (d, J_{C-F} = 16 Hz), 100.1 (d, J_{C-F} = 4 Hz), 78.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.2; HRMS (ESI) calcd for $C_{11}H_8FO$ $[M+H]^+$: 175.0559, found: 175.0557.

2-(but-3-en-1-yn-1-yl)-4-fluorobenzaldehyde (1f)



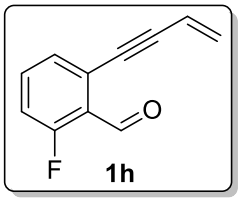
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 3.2 g, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.93 (dd, *J* = 9.0 Hz, 6.0 Hz, 1H), 7.21 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 7.11-7.15 (m, 1H), 6.03 (dd, *J* = 18.0 Hz, 11.5 Hz, 1H), 5.84-5.88 (m, 1H), 5.69-5.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 166.8 (d, J_{C-F} = 255 Hz), 132.7 (d, J_{C-F} = 3 Hz), 130.2 (d, J_{C-F} = 9 Hz), 129.5, 129.4 (d, J_{C-F} = 9 Hz), 119.9 (d, J_{C-F} = 19 Hz), 116.8 (d, J_{C-F} = 17 Hz), 116.3, 96.0, 84.3 (d, J_{C-F} = 3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -103.3; HRMS (ESI) calcd for $C_{11}H_8FO$ $[M+H]^+$: 175.0559, found: 175.0558.

2-(but-3-en-1-yn-1-yl)-5-fluorobenzaldehyde (1g)



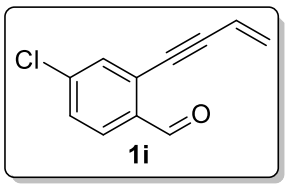
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 7.1 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (d, *J* = 3.2 Hz, 1H), 7.53-7.59 (m, 2H), 7.24-7.29 (m, 1H), 6.02 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.80 (dd, *J* = 17.6 Hz, 1.6 Hz, 1H), 5.64 (dd, *J* = 11.2 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5 (d, J_{C-F} = 1 Hz), 163.7 (d, J_{C-F} = 251 Hz), 137.9 (d, J_{C-F} = 7 Hz), 135.4 (d, J_{C-F} = 7 Hz), 128.8, 122.9 (d, J_{C-F} = 3 Hz), 121.5 (d, J_{C-F} = 22 Hz), 116.5, 113.8 (d, J_{C-F} = 23 Hz), 94.7 (d, J_{C-F} = 2 Hz), 84.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.9; HRMS (ESI) calcd for $C_{11}H_8FO$ $[M+H]^+$: 175.0559, found: 175.0559.

2-(but-3-en-1-yn-1-yl)-6-fluorobenzaldehyde (1h)



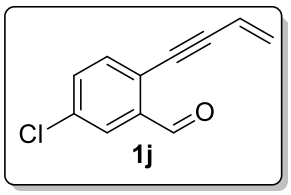
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 4.2 g, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.48-7.53 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 10.0 Hz, 9.5 Hz, 1H), 6.03 (dd, *J* = 17.5 Hz, 11.5 Hz, 1H), 5.82 (dd, *J* = 18.0 Hz, 2.0 Hz, 1H), 5.66 (dd, *J* = 11.0 Hz, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2 (d, J_{C-F} = 3 Hz), 163.5 (d, J_{C-F} = 261 Hz), 134.9 (d, J_{C-F} = 10 Hz), 129.6 (d, J_{C-F} = 4 Hz), 129.1, 127.0 (d, J_{C-F} = 4 Hz), 124.2 (d, J_{C-F} = 8 Hz), 116.9 (d, J_{C-F} = 21 Hz), 116.5, 95.4, 85.4 (d, J_{C-F} = 5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -116.1; HRMS (ESI) calcd for $C_{11}H_8FO$ $[M+H]^+$: 175.0559, found: 175.0554.

2-(but-3-en-1-yn-1-yl)-4-chlorobenzaldehyde (1i)



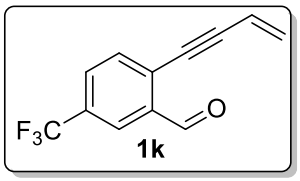
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 4.8 g, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (d, *J* = 0.8 Hz, 1H), 7.99 (dd, *J* = 8.4 Hz, 0.4 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.54-7.57 (m, 1H), 6.18 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.98 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.83 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 140.4, 134.3, 133.0, 129.5, 129.3, 128.7, 128.3, 116.4, 96.1, 84.2; HRMS (ESI) calcd for $C_{11}H_8ClO$ $[M+H]^+$: 191.0264, found: 191.0263.

2-(but-3-en-1-yn-1-yl)-5-chlorobenzaldehyde (1j)



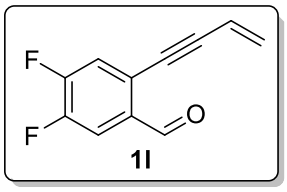
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 6.3 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.83-7.84 (m, 1H), 7.45-7.50 (m, 2H), 6.02 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.81 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.66-5.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 136.9, 135.2, 134.5, 133.7, 129.0, 127.1, 125.0, 116.4, 95.8, 84.4; HRMS (ESI) calcd for $C_{11}H_8ClO$ $[M+H]^+$: 191.0264, found: 191.0257.

2-(but-3-en-1-yn-1-yl)-5-(trifluoromethyl)benzaldehyde (1k)



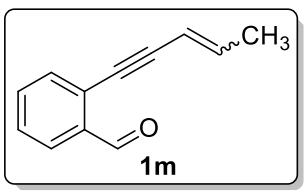
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 5.4 g, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.53 (d, *J* = 0.5 Hz, 1H), 8.17 (d, *J* = 0.5 Hz, 1H), 7.78-7.79 (m, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 6.06 (dd, *J* = 17.5 Hz, 11.0 Hz, 1H), 5.87 (dd, *J* = 17.5 Hz, 2.0 Hz, 1H), 5.72 (dd, *J* = 11.5 Hz, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 136.1, 133.9, 132.9, 131.2 (q, J_{C-F} = 34 Hz), 130.1 (q, J_{C-F} = 4 Hz), 130.0, 126.7 (q, J_{C-F} = 271 Hz), 124.5 (q, J_{C-F} = 5 Hz), 116.2, 97.5, 84.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.2; HRMS (ESI) calcd for $C_{12}H_8F_3O$ $[M+H]^+$: 225.0527, found: 225.0525.

2-(but-3-en-1-yn-1-yl)-4,5-difluorobenzaldehyde (1l)



The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 1.29 g, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.93 (dd, *J* = 9.0 Hz, 6.0 Hz, 1H), 7.21 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 7.11-7.15 (m, 1H), 6.03 (dd, *J* = 17.5 Hz, 11.5 Hz, 1H), 5.84 (dd, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.69 (dd, *J* = 11.0 Hz, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 166.8 (d, J_{C-F} = 256 Hz), 132.7 (d, J_{C-F} = 4 Hz), 130.2 (d, J_{C-F} = 10 Hz), 129.5, 129.4 (d, J_{C-F} = 11 Hz), 119.9 (d, J_{C-F} = 24 Hz), 116.8 (d, J_{C-F} = 23 Hz), 116.3, 96.0, 84.3 (d, J_{C-F} = 4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -103.3; HRMS (ESI) calcd for $C_{11}H_7F_2O$ $[M+H]^+$: 193.0465, found: 193.0460.

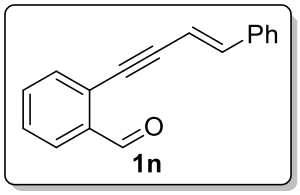
2-(pent-3-en-1-yn-1-yl)benzaldehyde (1m)



The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 3.9 g, 66% yield (*Z* : *E* = 59:41). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.74 (s, 0.38H), 10.70 (s, 0.62H), 8.06-8.09 (m, 1H), 7.68-7.72 (m, 2H), 7.54-7.60 (m, 1H), 6.48-6.55 (m, 0.62H),

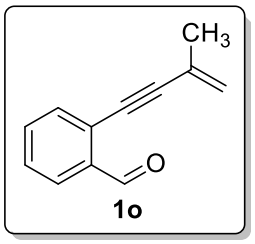
6.29-6.36 (m, 0.39H), 5.92-5.95 (m, 1H), 2.16-2.18 (m, 1.24H), 2.04-2.06 (m, 1.78H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 191.7, 141.7, 140.5, 135.7, 135.6, 133.7, 133.7, 133.2, 133.1, 128.3, 128.2, 127.3, 127.3, 127.2, 127.1, 110.3, 109.6, 95.4, 93.3, 89.5, 83.3, 18.9, 16.5; HRMS (ESI) calcd for $C_{12}H_{11}O$ $[M+H]^+$: 171.0810, found: 171.0813.

(*E*)-2-(4-phenylbut-3-en-1-yn-1-yl)benzaldehyde (1n)



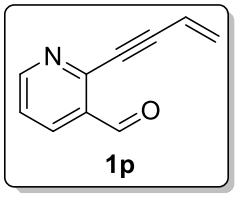
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 1.92 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 0.4 Hz, 1H), 7.90-7.92 (m, 1H), 7.51-7.58 (m, 2H), 7.38-7.44 (m, 3H), 7.28-7.37 (m, 3H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.39 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 142.9, 136.0, 135.8, 133.8, 133.2, 129.2, 128.9, 128.6, 127.4, 127.1, 126.6, 107.3, 96.0, 87.2; HRMS (ESI) calcd for $C_{17}H_{13}O$ $[M+H]^+$: 233.0966, found: 233.0964.

2-(3-methylbut-3-en-1-yn-1-yl)benzaldehyde (1o)



The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 1.37 g, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 4.0 Hz, 2H), 7.40-7.44 (m, 1H), 5.48 (s, 1H), 5.39 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 135.9, 133.8, 133.3, 128.6, 127.2, 127.0, 126.4, 123.5, 97.6, 83.9, 23.3; HRMS (ESI) calcd for $C_{12}H_{11}O$ $[M+H]^+$: 171.0810, found: 171.0809.

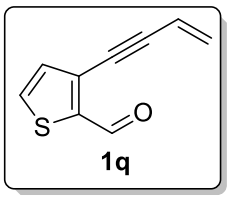
3-(but-3-en-1-yn-1-yl)picolinaldehyde (1p)



The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 372 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ

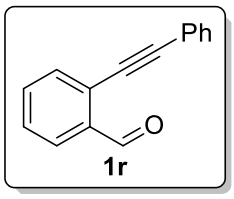
10.55 (s, 1H), 8.79-8.80 (m, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 6.07 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.95 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.76 (dd, *J* = 11.2 Hz, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 154.6, 146.0, 134.8, 131.9, 130.8, 123.4, 116.0, 94.5, 85.1; HRMS (ESI) calcd for $C_{10}H_8NO$ $[M+H]^+$: 158.0606, found: 158.0605.

3-(but-3-en-1-yn-1-yl)thiophene-2-carbaldehyde (1q)



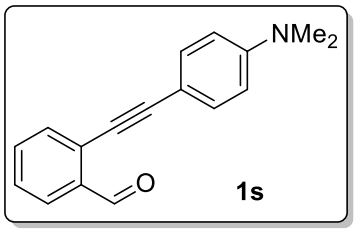
The title compound was prepared according to the general procedure A and purified by column chromatography to give yellow oil, 1.3 g, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (d, *J* = 1.5 Hz, 1H), 7.67 (dd, *J* = 5.0 Hz, 1.5 Hz, 1H), 7.17 (d, *J* = 5.0 Hz, 1H), 6.02 (dd, *J* = 17.5 Hz, 11.0 Hz, 1H), 5.82 (dd, *J* = 17.5 Hz, 2.0 Hz, 1H), 5.67 (dd, *J* = 11.0 Hz, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1, 143.7, 134.0, 131.6, 130.8, 129.2, 116.4, 94.7, 82.1; HRMS (ESI) calcd for C_9H_7OS $[M+H]^+$: 163.0218, found: 163.0215.

2-(phenylethynyl)benzaldehyde (1r)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 1.7 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.56-7.60 (m, 3H), 7.43-7.47 (m, 1H), 7.38-7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 135.9, 133.9, 133.3, 131.8, 129.2, 128.7, 128.6, 127.4, 127.0, 122.4, 96.4, 85.0; HRMS (ESI) calcd for $C_{15}H_{11}O$ $[M+H]^+$: 207.0810, found: 207.0809.

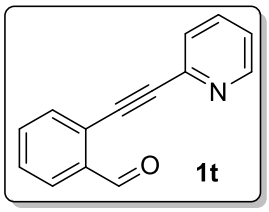
2-((4-(dimethylamino)phenyl)ethynyl)benzaldehyde (1s)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow solid, 1.02 g, 82% yield.

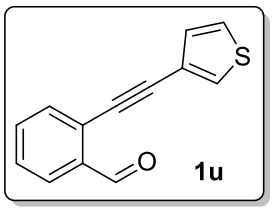
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.50-7.59 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.34-7.38 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 2.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 150.6, 135.4, 133.8, 133.0, 132.9, 128.2, 127.7, 127.1, 111.8, 108.8, 98.4, 83.3, 40.2; HRMS (ESI) calcd for $C_{17}H_{15}NONa^+$ $[M+Na]^+$: 272.1046, found: 272.1054.

2-(pyridin-2-ylethynyl)benzaldehyde (1t)



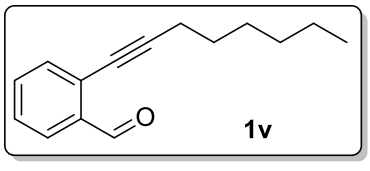
The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 515 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (d, *J* = 0.4 Hz, 1H), 8.64-8.66 (m, 1H), 7.95 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.70-7.74 (m, 2H), 7.57-7.62 (m, 2H), 7.47-7.51 (m, 1H), 7.28-7.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 150.2, 142.5, 136.3, 136.2, 133.7, 133.6, 129.3, 127.4, 127.3, 125.5, 123.4, 95.0, 84.4; HRMS (ESI) calcd for $C_{14}H_{10}NO$ $[M+H]^+$: 208.0762, found: 208.0766.

2-(thiophen-3-ylethynyl)benzaldehyde (1u)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 859 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.91-7.93 (m, 1H), 7.52-7.61 (m, 3H), 7.39-7.43 (m, 1H), 7.30 (dd, *J* = 4.8 Hz, 2.8 Hz, 1H), 7.20 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 135.8, 133.8, 133.1, 129.7, 129.7, 128.6, 127.3, 126.8, 125.8, 121.4, 91.6, 84.6; HRMS (ESI) calcd for $C_{13}H_9OS$ $[M+H]^+$: 213.0374, found: 213.0377.

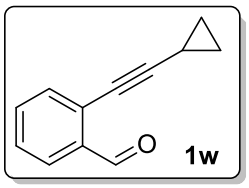
2-(oct-1-yn-1-yl)benzaldehyde (1v)



The title compound was prepared according to the general procedure B and purified by column

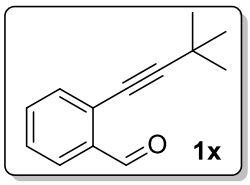
chromatography to give yellow oil, 1.82 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.87-7.89 (m, 1H), 7.48-7.53 (m, 2H), 7.34-7.39 (m, 1H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.60-1.67 (m, 2H), 1.43-1.50 (m, 2H), 1.31-1.36 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 136.1, 133.7, 133.4, 128.1, 127.9, 127.0, 98.3, 76.4, 31.4, 28.7, 28.6, 22.6, 19.7, 14.1; HRMS (ESI) calcd for $C_{15}H_{19}O$ $[M+H]^+$: 215.1436, found: 215.1437.

2-(cyclopropylethynyl)benzaldehyde (1w)



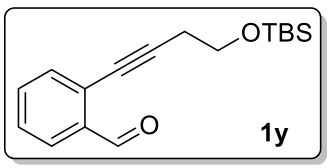
The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 1.39 g, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.46-7.51 (m, 2H), 7.34-7.37 (m, 1H), 1.49-1.54 (m, 1H), 0.92-0.96 (m, 2H), 0.85-0.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 136.2, 133.7, 133.4, 127.9, 127.8, 127.0, 101.3, 71.6, 9.0, 0.4; HRMS (ESI) calcd for $C_{12}H_{11}O$ $[M+H]^+$: 171.0810, found: 171.0808.

2-(3,3-dimethylbut-1-yn-1-yl)benzaldehyde (1x)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 1.51 g, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.54 (d, *J* = 0.4 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.47-7.50 (m, 2H), 7.35-7.38 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 135.9, 133.7, 133.3, 128.0, 127.9, 126.9, 106.2, 75.0, 30.9, 28.4; HRMS (ESI) calcd for $C_{13}H_{15}O$ $[M+H]^+$: 187.1123, found: 187.1126.

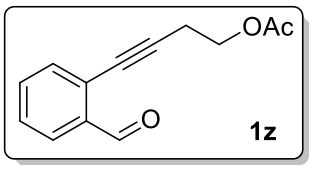
2-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)benzaldehyde (1y)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 1.0 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (d, *J* = 0.8 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.54-7.59 (m, 2H),

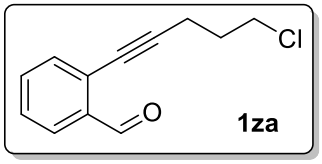
7.41-7.45 (m, 1H), 3.90 (t, *J* = 6.8 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 2H), 0.97 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 136.1, 133.8, 133.4, 128.1, 127.7, 127.0, 95.1, 77.4, 61.7, 26.0, 24.1, 18.4, -5.2; HRMS (ESI) calcd for $C_{17}H_{24}O_2SiNa^+$ $[M+Na]^+$: 311.1438, found: 311.1438.

4-(2-formylphenyl)but-3-yn-1-yl acetate (1z)



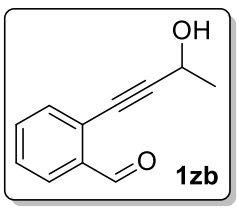
The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 766 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51-10.51 (m, 1H), 7.87 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.50-7.55 (m, 2H), 7.39-7.43 (m, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 170.7, 136.0, 133.6, 133.3, 128.3, 126.9, 126.9, 93.2, 77.7, 61.9, 20.7, 20.0; HRMS (ESI) calcd for $C_{13}H_{13}O_3$ $[M+H]^+$: 217.0865, found: 217.0855.

2-(5-chloropent-1-yn-1-yl)benzaldehyde (1za)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 854 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.50-7.55 (m, 2H), 7.38-7.42 (m, 1H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.07-2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 136.1, 133.8, 133.5, 128.3, 127.3, 127.2, 95.8, 77.5, 43.7, 31.2, 17.1; HRMS (ESI) calcd for $C_{12}H_{12}OCl$ $[M+H]^+$: 207.0577, found: 207.0572.

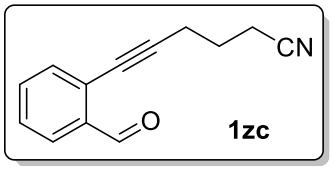
2-(3-hydroxybut-1-yn-1-yl)benzaldehyde (1zb)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 705 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.51-7.52 (m, 2H), 7.39-7.43 (m, 1H), 4.82 (q, *J* = 6.5 Hz, 1H), 3.24 (s, 1H), 1.59 (d, *J* = 6.5 Hz, 3H); ^{13}C

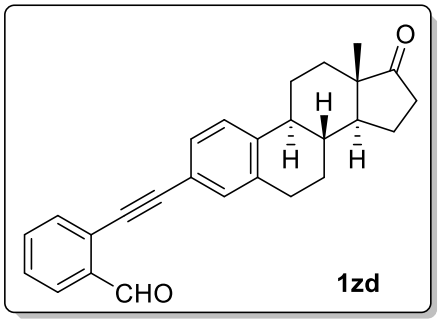
NMR (125 MHz, $CDCl_3$) δ 192.0, 135.9, 133.9, 133.4, 128.8, 127.5, 126.2, 98.4, 79.6, 58.7, 24.2; HRMS (ESI) calcd for $C_{11}H_{11}O_2$ $[M+H]^+$: 175.0759, found: 175.0751.

6-(2-formylphenyl)hex-5-ynenitrile (1zc)



The title compound was prepared according to the general procedure B and purified by column chromatography to give yellow oil, 615 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (d, *J* = 0.8 Hz, 1H), 7.87-7.89 (m, 1H), 7.51-7.56 (m, 2H), 7.40-7.44 (m, 1H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.00-2.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 136.0, 133.7, 133.5, 128.4, 127.4, 126.6, 119.0, 94.5, 78.1, 24.4, 18.7, 16.3; HRMS (ESI) calcd for $C_{13}H_{12}NO$ $[M+H]^+$: 198.0919, found: 198.0916.

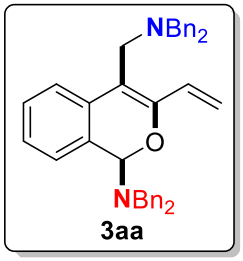
2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethynyl)benzaldehyde (1zd)



The title compound was prepared according to the general procedure C and purified by column chromatography to give yellow solid, 1.04 g, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (d, *J* = 0.8 Hz, 1H), 7.93 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.55-7.59 (m, 1H), 7.42-7.46 (m, 1H), 7.29-7.36 (m, 3H), 2.91-2.94 (m, 2H), 2.48 (dd, *J* = 18.8 Hz, 11.0 Hz, 1H), 2.41-2.46 (m, 1H), 2.29-2.36 (m, 1H), 1.96-2.20 (m, 4H), 1.44-1.67 (m, 6H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.7, 191.9, 141.4, 137.0, 135.9, 133.9, 133.2, 132.3, 129.1, 128.6, 127.3, 127.3, 125.7, 119.7, 96.7, 84.4, 50.6, 48.0, 44.6, 38.0, 35.9, 31.7, 29.2, 26.4, 25.7, 21.7, 13.9; HRMS (ESI) calcd for $C_{27}H_{27}O_2$ $[M+H]^+$: 383.2011, found: 383.2018.

5. Products Characterization

N,*N*-dibenzyl-4-((dibenzylamino)methyl)-3-vinyl-1*H*-isochromen-1-amine (3aa)



3aa

The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 142 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08-7.28 (m, 24H), 6.80 (dd, *J* = 17.0 Hz, 11.0 Hz, 1H), 5.99 (d, *J* = 16.5 Hz, 1H), 5.80 (s, 1H), 5.36 (d, *J* = 11.0 Hz, 1H), 3.86 (d, *J* = 14.0 Hz, 2H), 3.69 (d, *J* = 14.0 Hz, 2H), 3.57 (d, *J* = 13.0 Hz, 2H), 3.41-3.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 139.5, 139.3, 133.6, 129.8, 129.4, 128.8, 128.40, 128.38, 128.2, 127.9, 127.0, 126.6, 125.5, 123.2, 116.6, 109.3, 86.9, 58.4, 52.2, 49.7; HRMS (ESI) calcd for $C_{40}H_{39}N_2O$ $[M+H]^+$: 563.3062, found: 563.3053.

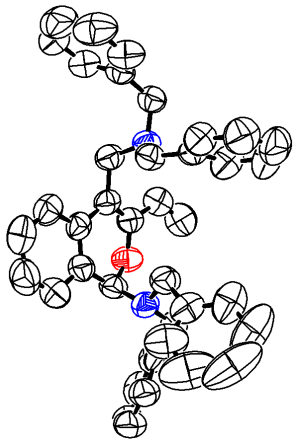
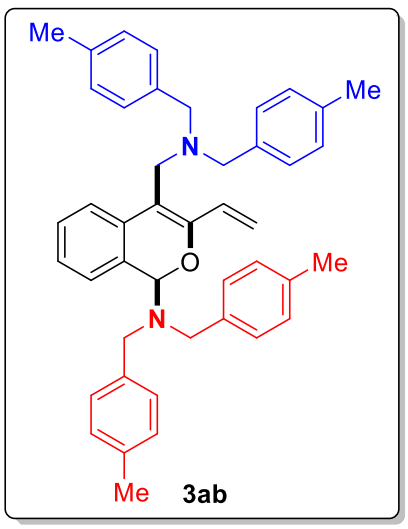


Figure S1. The ORTEP drawing of product **3aa**

4-((bis(4-methylbenzyl)amino)methyl)-*N*,*N*-bis(4-methylbenzyl)-3-vinyl-1*H*-isochromen-1-amine (3ab)

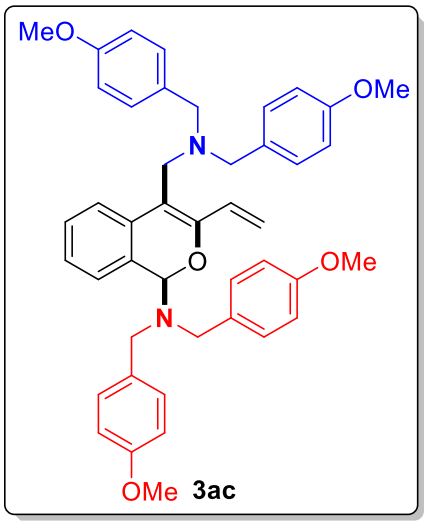


3ab

The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 144 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-7.22 (m, 20H), 6.79 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.97 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.80 (s, 1H), 5.34 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.81 (d, *J* = 13.6 Hz, 2H),

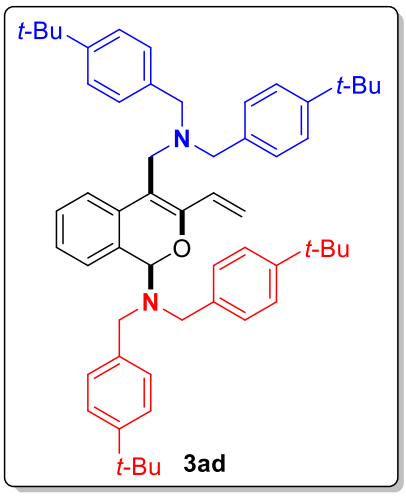
3.63 (d, *J* = 14.0 Hz, 2H), 3.37-3.53 (m, 6H), 2.28 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 136.5, 136.4, 136.4, 136.3, 133.7, 130.0, 129.4, 129.0, 128.8, 128.7, 128.5, 127.8, 126.5, 125.5, 123.3, 116.4, 109.5, 86.9, 57.9, 51.8, 49.5, 21.2, 21.2; HRMS (ESI) calcd for $C_{44}H_{47}N_2O$ $[M+H]^+$: 619.3688, found: 619.3691.

4-((bis(4-methoxybenzyl)amino)methyl)-*N*,*N*-bis(4-methoxybenzyl)-3-vinyl-1*H*-isochromen-1-amine (3ac)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 178 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.17 (m, 12H), 6.75-6.85 (m, 9H), 5.97 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.80 (s, 1H), 5.35 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.75-3.79 (m, 14H), 3.57-3.62 (m, 2H), 3.48-3.52 (m, 3H), 3.37 (d, *J* = 13.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.7, 149.8, 133.6, 131.7, 131.4, 130.5, 130.0, 129.9, 128.5, 127.8, 126.5, 125.6, 123.2, 116.4, 113.7, 113.5, 109.4, 86.6, 57.4, 55.3, 55.3, 51.3, 49.3; HRMS (ESI) calcd for $C_{44}H_{47}N_2O_5$ $[M+H]^+$: 683.3485, found: 683.3494.

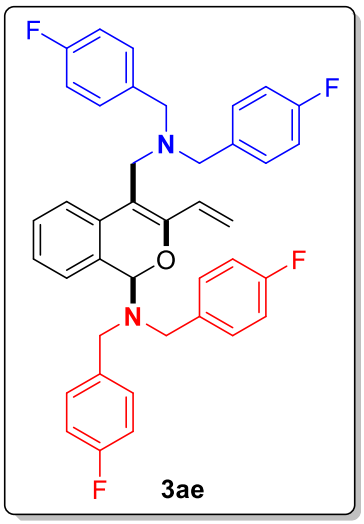
4-((bis(4-(*tert*-butyl)benzyl)amino)methyl)-*N*,*N*-bis(4-(*tert*-butyl)benzyl)-3-vinyl-1*H*-isochromen-1-amine (3ad)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 200 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.32 (m, 1H), 7.23-7.29 (m, 11H), 7.12-7.20 (m, 6H), 7.03-7.09 (m, 2H), 6.79 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.95 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.87 (s,

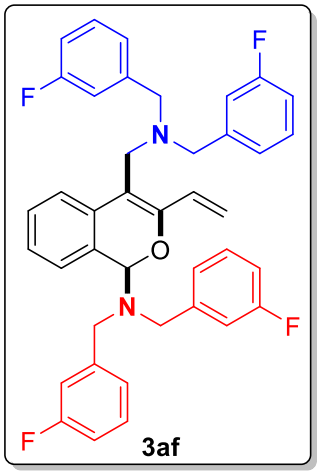
1H), 5.32 (dd, *J* = 10.8 Hz, 2.4 Hz, 1H), 3.87 (d, *J* = 14.4 Hz, 2H), 3.69-3.79 (m, 2H), 3.40-3.60 (m, 6H), 1.28 (s, 18H), 1.27 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 149.8, 136.6, 136.4, 133.8, 130.0, 129.2, 128.6, 128.5, 128.4, 127.8, 126.5, 125.5, 125.3, 125.3, 125.0, 123.3, 116.4, 109.5, 87.1, 58.0, 51.7, 49.5, 34.6, 31.6, 31.6; HRMS (ESI) calcd for $C_{56}H_{71}N_2O$ $[M+H]^+$: 787.5566, found: 787.5577.

4-((bis(4-fluorobenzyl)amino)methyl)-*N*,*N*-bis(4-fluorobenzyl)-3-vinyl-1*H*-isochromen-1-amine (3ae)



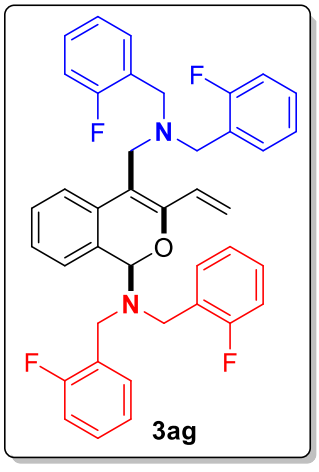
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 146 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.21 (m, 11H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.88-6.95 (m, 8H), 6.76 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.97 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.78 (s, 1H), 5.38 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.73 (d, *J* = 13.6 Hz, 2H), 3.61 (d, *J* = 13.6 Hz, 2H), 3.50-3.55 (m, 3H), 3.38-3.42 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 244 Hz), 161.1, 149.8, 135.0 (d, $J_{C\text{-}F}$ = 3 Hz), 134.7 (d, $J_{C\text{-}F}$ = 3 Hz), 133.3, 130.8 (d, $J_{C\text{-}F}$ = 9 Hz), 130.3 (d, $J_{C\text{-}F}$ = 8 Hz), 129.5, 128.1, 128.1, 126.8, 125.7, 123.0, 116.9, 115.3 (d, $J_{C\text{-}F}$ = 21 Hz), 115.1 (d, $J_{C\text{-}F}$ = 20 Hz), 109.0, 86.7, 57.4, 51.3, 49.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6, -115.7; HRMS (ESI) calcd for $C_{40}H_{35}F_4N_2O$ $[M+H]^+$: 635.2686, found: 635.2687.

4-((bis(3-fluorobenzyl)amino)methyl)-*N*,*N*-bis(3-fluorobenzyl)-3-vinyl-1*H*-isochromen-1-amine (3af)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 150 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.23 (m, 8H), 6.83-7.01 (m, 12H), 6.75 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.97 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.77 (s, 1H), 5.39 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 2H), 3.66 (d, *J* = 14.0 Hz, 2H), 3.42-3.59 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (d, J_{C-F} = 244 Hz), 163.9 (d, J_{C-F} = 245 Hz), 149.8, 142.0 (d, J_{C-F} = 6 Hz), 141.7 (d, J_{C-F} = 8 Hz), 133.2, 129.9 (d, J_{C-F} = 9 Hz), 129.7 (d, J_{C-F} = 9 Hz), 129.3, 128.3, 128.0, 127.1, 125.6, 124.8 (d, J_{C-F} = 3 Hz), 124.3 (d, J_{C-F} = 3 Hz), 123.0, 117.2, 116.1 (d, J_{C-F} = 21 Hz), 115.5 (d, J_{C-F} = 21 Hz), 114.2 (d, J_{C-F} = 8 Hz), 114.1 (d, J_{C-F} = 8 Hz), 109.0, 87.0, 58.0, 51.9, 49.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3, -113.6; HRMS (ESI) calcd for $C_{40}H_{35}F_4N_2O$ $[M+H]^+$: 635.2686, found: 635.2687.

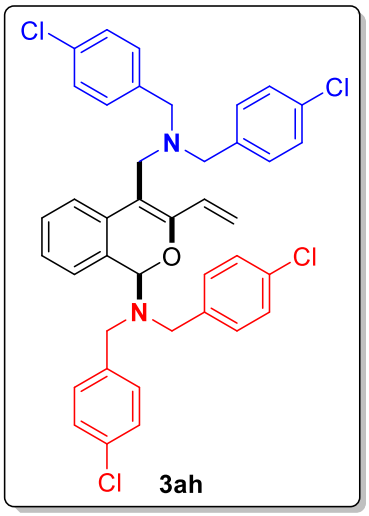
4-((bis(2-fluorobenzyl)amino)methyl)-*N*,*N*-bis(2-fluorobenzyl)-3-vinyl-1*H*-isochromen-1-amine (3ag)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 151 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.39 (m, 2H), 7.22-7.26 (m, 3H), 7.07-7.20 (m, 7H), 7.01-7.05 (m, 2H), 6.88-6.97 (m, 6H), 6.78 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.97 (dd, *J* = 16.8 Hz, 1.6 Hz, 1H), 5.82 (s, 1H), 5.36 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.98 (d, *J* = 14.4 Hz, 2H), 3.76 (d, *J* = 14.0 Hz, 2H), 3.51-3.63 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{C-F} = 244 Hz), 162.8 (d, J_{C-F} = 245 Hz), 149.9, 133.6, 131.8 (d, J_{C-F} = 4 Hz), 130.9 (d, J_{C-F} = 4 Hz), 129.6, 128.7 (d, J_{C-F} = 3 Hz), 128.6 (d, J_{C-F} = 3 Hz), 128.0 (d, J_{C-F} = 13 Hz), 126.6, 126.0, 125.9, 125.8, 125.5, 124.0 (d, J_{C-F} = 4 Hz), 123.8 (d, J_{C-F} = 4 Hz), 123.2, 117.3, 115.4 (d, J_{C-F} = 16 Hz), 115.2 (d, J_{C-F} = 16 Hz), 109.1, 87.9, 50.6, 49.9, 45.6; ^{19}F NMR (376 MHz,

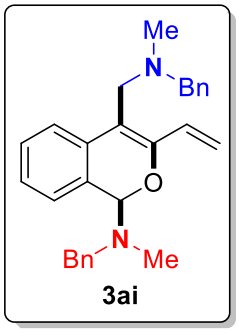
$CDCl_3$) δ -118.1, -118.4; HRMS (ESI) calcd for $C_{40}H_{35}F_4N_2O$ $[M+H]^+$: 635.2686, found: 635.2703.

4-((bis(4-chlorobenzyl)amino)methyl)-*N*,*N*-bis(4-chlorobenzyl)-3-vinyl-1*H*-isochromen-1-amine (3ah)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 172 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.23 (m, 9H), 7.12-7.16 (m, 10H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.75 (dd, *J* = 17.0 Hz, 11.0 Hz, 1H), 5.96 (dd, *J* = 16.5 Hz, 1.5 Hz, 1H), 5.76 (s, 1H), 5.38 (dd, *J* = 10.5 Hz, 1.5 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 2H), 3.60 (d, *J* = 14.0 Hz, 2H), 3.50-3.54 (m, 3H), 3.39-3.43 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 137.7, 137.4, 133.2, 133.0, 132.9, 130.6, 130.0, 129.4, 128.6, 128.4, 128.2, 128.0, 126.9, 125.7, 123.0, 117.1, 108.9, 86.8, 57.5, 51.5, 49.4; HRMS (ESI) calcd for $C_{42}H_{37}N_2Cl_4$ $[M+H]^+$: 709.1705, found: 709.1700.

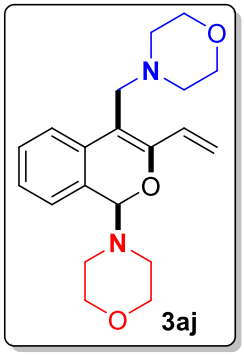
***N*-benzyl-4-((benzyl(methyl)amino)methyl)-*N*-methyl-3-vinyl-1*H*-isochromen-1-amine (3ai)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 79 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.19-7.33 (m, 13H), 6.82 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.94-5.99 (m, 2H), 5.33 (dd, *J* = 10.8 Hz, 2.4 Hz, 1H), 3.93 (d, *J* = 13.6 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.50 (ABq, *J* = 12.8 Hz, 2H), 3.44 (ABq, *J* = 13.2 Hz, 2H), 2.34 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 139.5, 139.4, 133.5, 129.9, 129.3, 128.7, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 127.1, 126.7, 125.9, 123.1, 116.6, 109.4,

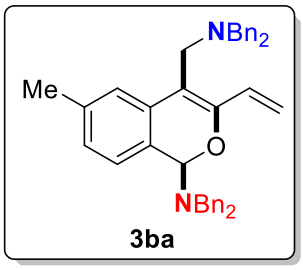
91.5, 62.0, 56.2, 53.3, 42.0, 36.1; HRMS (ESI) calcd for $C_{28}H_{31}N_2O$ $[M+H]^+$: 411.2436, found: 411.2442.

4-((1-morpholino-3-vinyl-1*H*-isochromen-4-yl)methyl)morpholine (3aj)



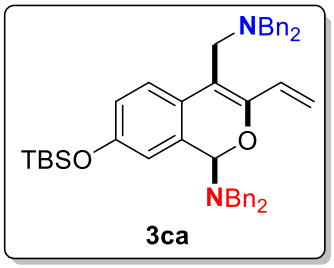
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 91 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.28-7.33 (m, 1H), 7.20-7.25 (m, 2H), 6.75 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.90 (dd, *J* = 16.8 Hz, 1.6 Hz, 1H), 5.77 (s, 1H), 5.31 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.64-3.67 (m, 8H), 3.38 (ABq, *J* = 13.2 Hz, 2H), 2.91-2.94 (m, 2H), 2.68-2.73 (m, 2H), 2.50 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 133.6, 128.5, 128.4, 127.6, 126.7, 126.0, 123.0, 117.1, 108.2, 91.8, 67.4, 67.2, 54.3, 53.5, 47.6; HRMS (ESI) calcd for $C_{20}H_{27}N_2O_3$ $[M+H]^+$: 343.2022, found: 343.2031.

***N*,*N*-dibenzyl-4-((dibenzylamino)methyl)-6-methyl-3-vinyl-1*H*-isochromen-1-amine (3ba)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 140 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.28 (m, 20H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 5.2 Hz, 2H), 6.82 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.98 (dd, *J* = 16.8 Hz, 2.4 Hz, 1H), 5.80 (s, 1H), 5.35 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 2H), 3.67 (d, *J* = 14.0 Hz, 2H), 3.39-3.60 (m, 6H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.7, 139.4, 137.5, 133.3, 129.5, 128.7, 128.4, 128.3, 128.2, 127.5, 126.99, 126.98, 126.95, 125.4, 123.6, 116.5, 109.2, 86.9, 58.6, 52.0, 49.6, 21.5; HRMS (ESI) calcd for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3219, found: 577.3229.

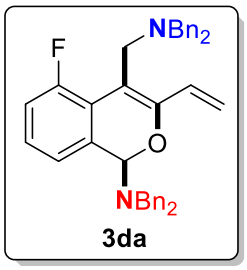
_N,N_-dibenzyl-7-((_tert_-butyldimethylsilyl)oxy)-4-((dibenzylamino)methyl)-3-vinyl-1_H_-isochromen-1-amine (3ca)



3ca

The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 158 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.30 (m, 20H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.74-6.84 (m, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 5.91 (d, *J* = 16.8 Hz, 1H), 5.68 (s, 1H), 5.30 (d, *J* = 11.2 Hz, 1H), 3.87 (d, *J* = 13.6 Hz, 2H), 3.70 (d, *J* = 14.0 Hz, 2H), 3.40-3.57 (m, 6H), 0.98 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 148.2, 139.6, 139.3, 131.6, 129.4, 128.7, 128.4, 128.3, 128.1, 127.2, 127.0, 124.9, 119.9, 116.5, 115.6, 109.5, 86.9, 58.4, 52.2, 49.9, 25.9, 18.4, -4.2; HRMS (ESI) calcd for $C_{46}H_{53}N_2O_2Si$ $[M+H]^+$: 693.3876, found: 693.3853.

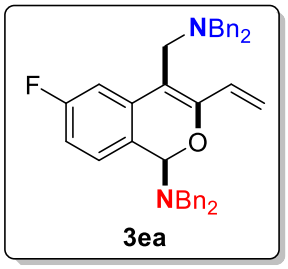
_N,N_-dibenzyl-4-((dibenzylamino)methyl)-5-fluoro-3-vinyl-1_H_-isochromen-1-amine (3da)



3da

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 137 mg, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 4H), 7.10-7.28 (m, 18H), 6.93-6.97 (m, 1H), 6.72 (dd, *J* = 17.0 Hz, 10.5 Hz, 1H), 5.94 (dd, *J* = 16.5 Hz, 2.0 Hz, 1H), 5.47 (s, 1H), 5.33 (dd, *J* = 10.5 Hz, 2.0 Hz, 1H), 3.92 (d, *J* = 13.5 Hz, 2H), 3.70-3.76 (m, 4H), 3.59 (d, *J* = 13.5 Hz, 2H), 3.46 (d, *J* = 13.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5 (d, $J_{C\text{-}F}$ = 250 Hz), 150.9, 139.7, 139.1, 134.0 (d, $J_{C\text{-}F}$ = 5 Hz), 129.2, 128.9, 128.7, 128.5, 128.0, 127.6 (d, $J_{C\text{-}F}$ = 9 Hz), 126.8, 122.64, 122.56, 121.2 (d, $J_{C\text{-}F}$ = 3 Hz), 116.8, 116.4 (d, $J_{C\text{-}F}$ = 25 Hz), 109.2 (d, $J_{C\text{-}F}$ = 5 Hz), 87.4, 57.8, 52.7, 51.1 (d, $J_{C\text{-}F}$ = 10 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.2; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2978.

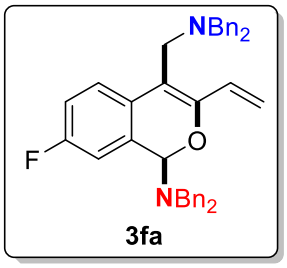
_N_,_N_-dibenzyl-4-((dibenzylamino)methyl)-6-fluoro-3-vinyl-1_H_-isochromen-1-amine (3ea)



3ea

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 136 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.25 (m, 21H), 6.88 (dd, J = 11.0 Hz, 2.0 Hz, 1H), 6.79-6.85 (m, 2H), 6.01 (d, J = 16.5 Hz, 1H), 5.78 (s, 1H), 5.40 (d, J = 11.5 Hz, 1H), 3.83 (d, J = 14.0 Hz, 2H), 3.66 (d, J = 14.0 Hz, 2H), 3.54 (d, J = 13.0 Hz, 2H), 3.36-3.48 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8 (d, J_{C-F} = 243 Hz), 150.6, 139.3, 139.0, 136.0 (d, J_{C-F} = 9 Hz), 129.4, 128.7, 128.4, 128.3, 128.0, 127.1, 127.1, 127.1, 125.4 (d, J_{C-F} = 3 Hz), 117.6, 113.5 (d, J_{C-F} = 23 Hz), 110.0 (d, J_{C-F} = 24 Hz), 108.5 (d, J_{C-F} = 3 Hz), 86.7, 58.5, 52.1, 49.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.1; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2981.

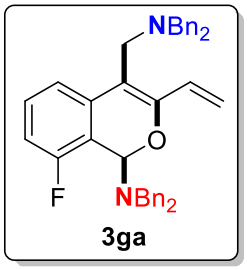
_N_,_N_-dibenzyl-4-((dibenzylamino)methyl)-7-fluoro-3-vinyl-1_H_-isochromen-1-amine (3fa)



3fa

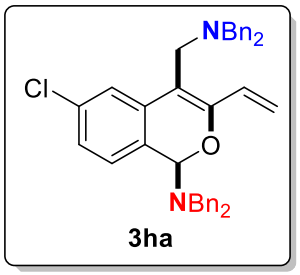
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 149 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.24 (m, 20H), 7.03 (dd, J = 8.8 Hz, 5.6 Hz, 1H), 6.93 (dd, J = 9.2 Hz, 2.8 Hz, 1H), 6.75-6.85 (m, 2H), 5.96 (dd, J = 16.8 Hz, 2.0 Hz, 1H), 5.72 (s, 1H), 5.36 (dd, J = 10.8 Hz, 2.4 Hz, 1H), 3.84 (d, J = 14.0 Hz, 2H), 3.67 (d, J = 13.6 Hz, 2H), 3.55 (d, J = 13.2 Hz, 2H), 3.39-3.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 245 Hz), 149.1, 149.1, 139.4, 139.0, 132.2 (d, J_{C-F} = 7 Hz), 129.8 (d, J_{C-F} = 2 Hz), 129.4, 128.7, 128.5, 128.2, 128.0, 127.2 (d, J_{C-F} = 7 Hz), 125.4 (d, J_{C-F} = 8 Hz), 116.7, 115.0 (d, J_{C-F} = 21 Hz), 112.2 (d, J_{C-F} = 23 Hz), 108.8, 86.5, 58.4, 52.2, 49.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2964.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-8-fluoro-3-vinyl-1_H_-isochromen-1-amine (3ga)



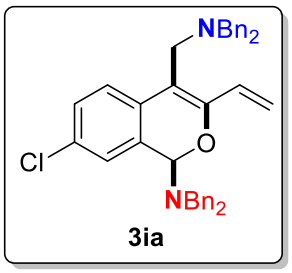
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 166 mg, 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.24 (m, 20H), 7.02 (dd, *J* = 14.0 Hz, 8.0 Hz, 1H), 6.79-6.87 (m, 3H), 6.15 (s, 1H), 6.03 (dd, *J* = 17.0 Hz, 1.5 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 3.78 (d, *J* = 13.5 Hz, 2H), 3.55-3.65 (m, 5H), 3.37-3.46 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (d, J_{C-F} = 246 Hz), 150.7, 139.3, 138.9, 135.5 (d, J_{C-F} = 3 Hz), 129.5, 129.2, 129.1, 128.8, 128.2, 128.2, 128.1, 127.1 (d, J_{C-F} = 13 Hz), 118.7 (d, J_{C-F} = 3 Hz), 117.6, 116.0 (d, J_{C-F} = 15 Hz), 113.4 (d, J_{C-F} = 21 Hz), 108.7 (d, J_{C-F} = 4 Hz), 81.3, 58.4, 52.0, 49.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.5; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2961.

_N,N_-dibenzyl-6-chloro-4-((dibenzylamino)methyl)-3-vinyl-1_H_-isochromen-1-amine (3ha)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 146 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10-7.28 (m, 23H), 6.80 (dd, *J* = 16.5 Hz, 10.5 Hz, 1H), 6.01 (dd, *J* = 17.0 Hz, 1.0 Hz, 1H), 5.75 (s, 1H), 5.41-5.43 (m, 1H), 3.82 (d, *J* = 13.5 Hz, 2H), 3.66 (d, *J* = 14.0 Hz, 2H), 3.36-3.56 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 139.3, 139.0, 135.4, 134.1, 129.3, 128.7, 128.4, 128.4, 128.0, 128.0, 127.2, 127.1, 126.8, 126.5, 123.2, 117.7, 108.2, 86.7, 58.6, 52.1, 49.8; HRMS (ESI) calcd for $C_{40}H_{38}ClN_2O$ $[M+H]^+$: 597.2673, found: 597.2665.

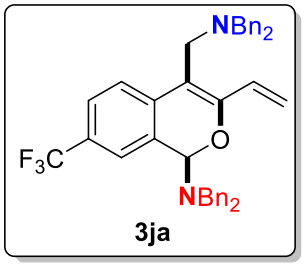
_N,N_-dibenzyl-7-chloro-4-((dibenzylamino)methyl)-3-vinyl-1_H_-isochromen-1-amine (3ia)



3ia

The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 160 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.28 (m, 21H), 6.97-7.04 (m, 2H), 6.78 (dd, *J* = 16.4 Hz, 10.8 Hz, 1H), 5.98 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.72 (s, 1H), 5.39 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.83 (d, *J* = 14.0 Hz, 2H), 3.66 (d, *J* = 14.0 Hz, 2H), 3.55 (d, *J* = 13.2 Hz, 2H), 3.38-3.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.3, 138.9, 132.2, 131.9, 131.5, 129.4, 128.8, 128.5, 128.2, 128.1, 127.9, 127.2, 127.1, 125.4, 124.8, 117.3, 108.6, 86.4, 58.4, 52.2, 49.6; HRMS (ESI) calcd for $C_{40}H_{38}ClN_2O$ $[M+H]^+$: 597.2673, found: 597.2648.

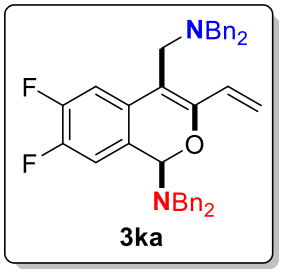
_N,N_-dibenzyl-4-((dibenzylamino)methyl)-7-(trifluoromethyl)-3-vinyl-1_H_-isochromen-1-amine (3ja)



3ja

The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 155 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.13-7.31 (m, 22H), 6.80 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 6.03 (dd, *J* = 16.8 Hz, 1.6 Hz, 1H), 5.81 (s, 1H), 5.44 (dd, *J* = 10.8 Hz, 1.6 Hz, 1H), 3.82 (d, *J* = 13.6 Hz, 2H), 3.67 (d, *J* = 13.6 Hz, 2H), 3.42-3.58 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 139.3, 138.7, 137.1, 130.1, 129.4, 128.8, 128.5, 128.3, 128.0, 127.9, 127.3, 127.2, 125.5 (q, J_{C-F} = 270 Hz), 124.7, 123.5, 122.5, 118.3, 108.3, 86.8, 58.5, 52.3, 49.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.2; HRMS (ESI) calcd for $C_{41}H_{38}F_3N_2O$ $[M+H]^+$: 631.2936, found: 631.2945.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-6,7-difluoro-3-vinyl-1_H_-isochromen-1-amine (3ka)

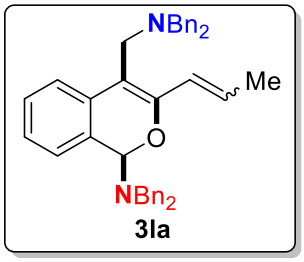


3ka

The title compound was prepared according to the general procedure and purified by column chromatography to give

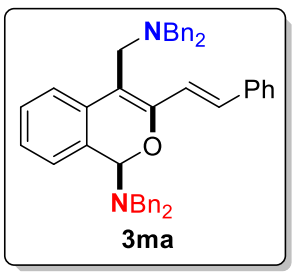
colorless oil, 168 mg, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.26 (m, 20H), 6.93-7.01 (m, 2H), 6.78 (dd, *J* = 17.0 Hz, 11.0 Hz, 1H), 5.99-6.03 (m, 1H), 5.69 (s, 1H), 5.40 (d, *J* = 11.5 Hz, 1H), 3.82 (d, *J* = 13.5 Hz, 2H), 3.65 (d, *J* = 13.5 Hz, 2H), 3.53 (d, *J* = 13.0 Hz, 2H), 3.33-3.47 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3 (dd, J_{C-F} = 244 Hz, 13 Hz), 151.0 (dd, J_{C-F} = 246 Hz, 13 Hz), 149.9, 139.2, 138.8, 131.0 (dd, J_{C-F} = 6 Hz, 4 Hz), 129.4, 128.7, 128.6, 128.5, 128.4, 127.7, 127.3 (d, J_{C-F} = 4 Hz), 126.4 (dd, J_{C-F} = 5 Hz, 3 Hz), 117.6, 114.2 (d, J_{C-F} = 19 Hz), 112.5 (d, J_{C-F} = 20 Hz), 107.9, 86.2, 58.5, 52.2, 49.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ -138.8, -138.9, -139.6, -139.6; HRMS (ESI) calcd for $C_{40}H_{37}F_2N_2O$ $[M+H]^+$: 599.2874, found: 599.2873.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-(prop-1-en-1-yl)-1_H_-isochromen-1-amine (3la)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 140 mg, 81% yield (*Z* / *E* = 65:35). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.28 (m, 25H), 6.49-6.49 (m, 1H), 5.76-5.77 (m, 1H), 3.86-3.97 (m, 2H), 3.67-3.73 (m, 2H), 3.39-3.59 (m, 6H), 2.14 (d, *J* = 7.2 Hz, 1.04H), 1.95 (d, *J* = 4.0 Hz, 1.96H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 150.2, 139.7, 139.4, 134.1, 133.9, 130.6, 129.5, 129.4, 129.2, 128.8, 128.7, 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.0, 127.0, 127.0, 126.9, 126.2, 126.0, 125.4, 125.2, 123.3, 122.9, 122.7, 121.9, 108.6, 107.0, 87.6, 87.1, 58.5, 52.7, 52.2, 50.4, 49.7, 18.8, 16.6; HRMS (ESI) calcd for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3219, found: 577.3238.

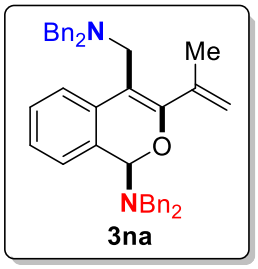
_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-styryl-1_H_-isochromen-1-amine (3ma)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 162 mg, 85% yield. ^{1}H NMR (400 MHz,

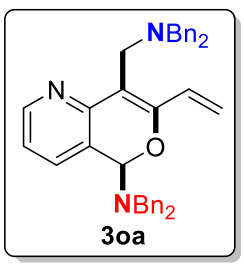
$CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30-7.35 (m, 7H), 7.23-7.28 (m, 12H), 7.14-7.21 (m, 8H), 5.85 (s, 1H), 3.91 (d, *J* = 13.6 Hz, 2H), 3.76 (d, *J* = 12.8 Hz, 2H), 3.51-3.64 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 139.6, 139.2, 137.4, 134.0, 130.8, 129.8, 129.4, 128.9, 128.8, 128.4, 128.3, 128.2, 128.2, 128.0, 127.3, 127.1, 127.0, 126.5 125.6, 122.8, 120.2, 110.1, 87.2, 58.6, 52.3, 49.8; HRMS (ESI) calcd for $C_{46}H_{43}N_2O$ $[M+H]^+$: 639.3375, found: 639.3365.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-(prop-1-en-2-yl)-1_H_-isochromen-1-amine (3na)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 145 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.27 (m, 9H), 7.08-7.18 (m, 14H), 7.02 (d, *J* = 7.6 Hz, 1H), 5.77 (s, 1H), 5.30 (s, 1H), 5.10 (s, 1H), 3.91 (d, *J* = 14.0 Hz, 2H), 3.69 (d, *J* = 13.6 Hz, 2H), 3.50-3.57 (m, 4H), 3.38 (d, *J* = 12.8 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 139.7, 139.3, 139.1, 133.2, 129.4, 128.7, 128.7, 128.3, 128.1, 127.6, 127.0, 126.9, 126.2, 125.2, 123.7, 118.8, 106.2, 87.8, 58.5, 52.4, 51.0, 22.4; HRMS (ESI) calcd for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3219, found: 577.3214.

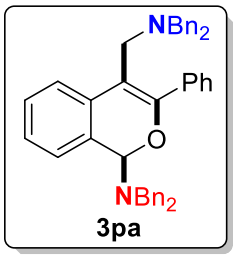
_N,N_-dibenzyl-5-((dibenzylamino)methyl)-6-vinyl-8_H_-pyrano[3,4-_b_]pyridin-8-amine (3oa)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 122 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.8 Hz, 1.6 Hz, 1H), 7.44 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.15-7.33 (m, 20H), 7.00 (dd, *J* = 7.6 Hz, 4.8 Hz, 1H), 6.64 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 5.93 (dd, *J* = 17.2 Hz, 2.4 Hz, 1H), 5.82 (s, 1H), 5.31 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.84 (d, *J* = 14.0 Hz, 2H), 3.67-3.80 (m, 4H), 3.53 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 152.6, 149.1, 140.3, 138.8, 133.2, 129.8,

129.3, 128.7, 128.5, 128.1, 127.3, 126.9, 124.8, 121.1, 116.7, 111.2, 87.4, 58.6, 52.2, 46.7; HRMS (ESI) calcd for $C_{39}H_{38}N_3O$ $[M+H]^+$: 564.3015, found: 564.3019.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-phenyl-1_H_-isochromen-1-amine (3pa)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 165 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.52 (m, 5H), 7.22-7.32 (m, 9H), 7.09-7.20 (m, 14H), 7.01 (d, J = 7.6 Hz, 1H), 5.88 (s, 1H), 4.01 (d, J = 14.0 Hz, 2H), 3.80 (d, J = 14.0 Hz, 2H), 3.42-3.55 (m, 4H), 3.23 (d, J = 13.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 139.5, 139.3, 136.1, 133.4, 130.0, 129.4, 128.9, 128.8, 128.7, 128.4, 128.2, 128.0, 127.7, 127.0, 126.9, 126.4, 125.2, 123.7, 107.5, 88.7, 58.3, 52.5, 50.9; HRMS (ESI) calcd for $C_{40}H_{41}N_2O$ $[M+H]^+$: 613.3219, found: 613.3209.

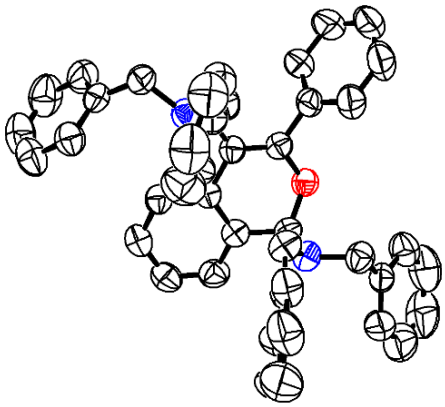
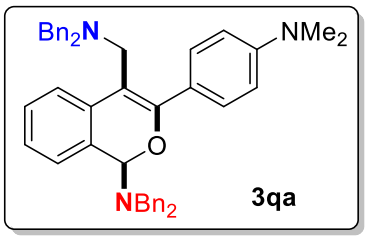


Figure S2. The ORTEP drawing of product **3pa**

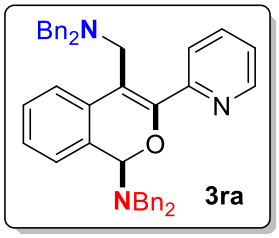
_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-(4-(dimethylamino)phenyl)-1_H_-isochromen-1-amine (3qa)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 137 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 7.2 Hz, 5H), 7.24 (t, J = 7.2 Hz, 4H), 7.10-7.19 (m, 14H), 6.99

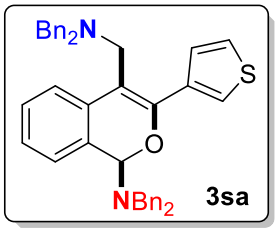
(d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.80 (s, 1H), 4.01 (d, *J* = 14.0 Hz, 2H), 3.82 (d, *J* = 14.0 Hz, 2H), 3.58 (s, 2H), 3.41 (d, *J* = 13.2 Hz, 2H), 3.30 (d, *J* = 13.2 Hz, 2H), 3.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 150.7, 139.7, 139.5, 134.1, 131.1, 129.4, 129.0, 128.7, 128.4, 128.0, 127.5, 126.9, 126.8, 125.9, 124.9, 123.7, 123.6, 111.6, 106.4, 88.5, 58.2, 52.7, 51.0, 40.5; HRMS (ESI) calcd for $C_{46}H_{46}N_3O$ $[M+H]^+$: 656.3641, found: 656.3637.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-(pyridin-2-yl)-1_H_-isochromen-1-amine (3ra)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 134 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.13-7.29 (m, 25H), 5.92 (s, 1H), 4.00 (d, *J* = 14.0 Hz, 2H), 3.79-3.90 (m, 4H), 3.49 (d, *J* = 13.0 Hz, 2H), 3.33 (d, *J* = 13.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 151.0, 148.7, 139.8, 139.2, 136.5, 133.5, 129.4, 129.2, 128.7, 128.4, 128.0, 127.8, 127.0, 126.8, 126.8, 125.2, 124.4, 124.3, 123.1, 110.3, 88.7, 58.5, 52.5, 49.7; HRMS (ESI) calcd for $C_{43}H_{40}N_3O$ $[M+H]^+$: 614.3171, found: 614.3170.

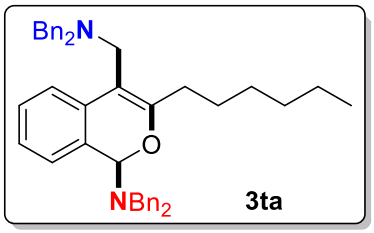
_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-(thiophen-3-yl)-1_H_-isochromen-1-amine (3sa)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 141 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 2.8 Hz, 1.2 Hz, 1H), 7.21-7.37 (m, 12H), 7.09-7.19 (m, 14H), 5.86 (s, 1H), 3.98 (d, *J* = 14.0 Hz, 2H), 3.76 (d, *J* = 14.0 Hz, 2H), 3.58 (ABq, *J* = 13.6 Hz, 2H), 3.50 (d, *J* = 13.2 Hz, 2H), 3.38 (d, *J* = 13.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 139.4, 139.2, 136.8, 133.6, 129.4, 129.0, 128.8, 128.7, 128.4, 128.1, 127.8, 127.1, 126.9, 126.4, 126.3, 125.3, 125.0, 123.5, 107.8,

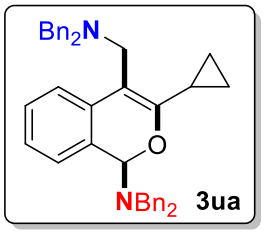
88.4, 58.2, 52.6, 50.8; HRMS (ESI) calcd for $C_{42}H_{38}N_2OSNa^+$ $[M+Na]^+$: 641.2597, found: 641.2598.

_N,N_-dibenzyl-4-((dibenzylamino)methyl)-3-hexyl-1_H_-isochromen-1-amine (3ta)



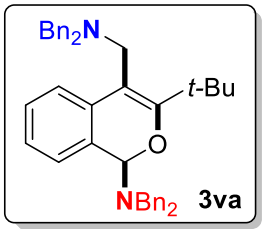
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 145 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.29 (m, 24H), 5.76 (s, 1H), 3.88 (d, *J* = 13.6 Hz, 2H), 3.67 (d, *J* = 14.0 Hz, 2H), 3.54 (d, *J* = 13.2 Hz, 2H), 3.46 (d, *J* = 13.2 Hz, 2H), 3.30 (ABq, *J* = 13.6 Hz, 2H), 2.37-2.49 (m, 2H), 1.63-1.67 (m, 2H), 1.36-1.42 (m, 6H), 0.95 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 139.8, 139.5, 134.0, 129.4, 128.8, 128.4, 128.3, 128.1, 127.8, 127.0, 126.9, 125.6, 125.3, 122.2, 104.8, 87.5, 58.4, 52.4, 50.8, 32.0, 31.2, 29.5, 28.3, 22.9, 14.3; HRMS (ESI) calcd for $C_{44}H_{49}N_2O$ $[M+H]^+$: 621.3845, found: 621.3848.

_N,N_-dibenzyl-3-cyclopropyl-4-((dibenzylamino)methyl)-1_H_-isochromen-1-amine (3ua)



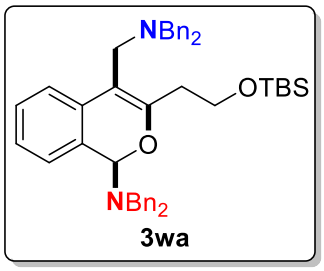
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 138 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.26 (m, 21H), 7.03-7.09 (m, 3H), 5.64 (s, 1H), 3.87 (d, *J* = 14.0 Hz, 2H), 3.43-3.65 (m, 8H), 1.99-2.04 (m, 1H), 1.00-1.10 (m, 2H), 0.73-0.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 139.9, 139.3, 134.3, 129.5, 128.7, 128.4, 128.1, 128.1, 127.9, 127.0, 126.9, 125.2, 125.2, 121.6, 104.9, 87.4, 58.4, 52.4, 50.3, 11.4, 6.2, 6.0; HRMS (ESI) calcd for $C_{41}H_{40}N_2ONa^+$ $[M+Na]^+$: 599.3033, found: 599.3020.

_N,N_-dibenzyl-3-(*tert*-butyl)-4-((dibenzylamino)methyl)-1_H_-isochromen-1-amine (3va)



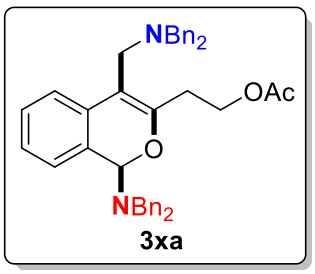
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 131 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.34 (m, 10H), 7.10-7.18 (m, 14H), 5.50-5.52 (m, 1H), 4.01 (d, *J* = 13.6 Hz, 2H), 3.55-3.77 (m, 6H), 3.42-3.45 (m, 2H), 1.37-1.39 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 139.7, 139.4, 134.8, 129.4, 129.2, 128.6, 128.4, 128.0, 127.2, 127.0, 126.9, 125.7, 124.1, 123.8, 106.5, 88.4, 58.2, 53.1, 50.1, 38.5, 30.9; HRMS (ESI) calcd for $C_{42}H_{44}N_2ONa^+$ $[M+Na]^+$: 615.3346, found: 615.3348.

_N,N_-dibenzyl-3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-((dibenzylamino)methyl)-1*H*-isochromen-1-amine (3wa)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 170 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.32 (m, 24H), 5.82 (s, 1H), 3.91-4.03 (m, 4H), 3.62-3.73 (m, 4H), 3.39-3.56 (m, 4H), 2.74-2.85 (m, 2H), 0.99 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 139.7, 139.4, 133.6, 129.5, 128.7, 128.4, 128.3, 128.2, 127.8, 127.0, 127.0, 125.8, 125.4, 122.5, 106.3, 87.4, 61.7, 58.3, 52.3, 50.9, 35.2, 26.2, 18.6, -5.0, -5.0; HRMS (ESI) calcd for $C_{46}H_{55}N_2O_2Si$ $[M+H]^+$: 695.4033, found: 695.4047.

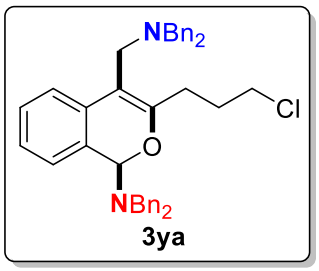
2-(1-(dibenzylamino)-4-((dibenzylamino)methyl)-1*H*-isochromen-3-yl)ethyl acetate (3xa)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 156 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.25 (m, 24H), 5.80 (s, 1H), 4.37-4.42 (m, 2H), 3.87 (d, *J* = 14.0 Hz, 2H), 3.56-3.67 (m, 4H), 3.30-3.49 (m, 4H), 2.75-2.87 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 151.7, 139.6, 139.2, 133.3, 129.4, 128.7, 128.4, 128.3, 128.1, 127.9, 127.0,

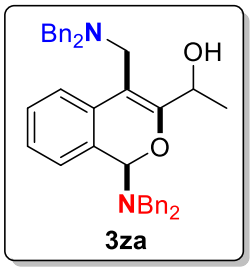
127.0, 126.1, 125.5, 122.4, 106.8, 87.7, 62.3, 58.4, 52.2, 50.4, 30.4, 21.1; HRMS (ESI) calcd for $C_{42}H_{42}N_2O_3Na^+$ $[M+Na]^+$: 645.3088, found: 645.3100.

_N,N_-dibenzyl-3-(3-chloropropyl)-4-((dibenzylamino)methyl)-1_H_-isochromen-1-amine (3ya)



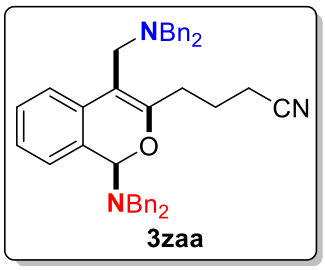
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 130 mg, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.28 (m, 24H), 5.76 (s, 1H), 3.89 (d, *J* = 14.0 Hz, 2H), 3.45-3.67 (m, 8H), 3.32 (ABq, *J* = 13.5 Hz, 2H), 2.53-2.66 (m, 2H), 2.05-2.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 139.7, 139.2, 133.6, 129.4, 128.7, 128.4, 128.2, 127.9, 127.1, 127.0, 125.9, 125.4, 122.3, 105.8, 87.8, 58.5, 52.4, 50.6, 44.9, 30.9, 28.3; HRMS (ESI) calcd for $C_{41}H_{42}N_2OCl$ $[M+H]^+$: 613.2986, found: 613.2993.

1-(1-(dibenzylamino)-4-((dibenzylamino)methyl)-1_H_-isochromen-3-yl)ethan-1-ol (3za)



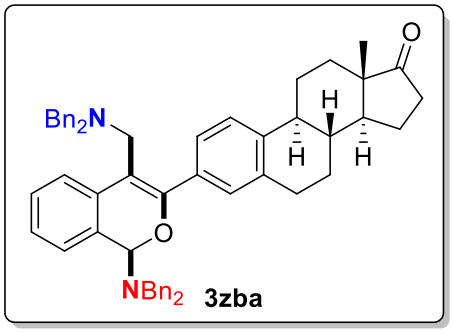
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 97 mg, 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.28 (m, 24H), 5.87-5.92 (m, 1H), 4.55-4.56 (m, 1H), 3.29-3.92 (m, 10H), 1.38-1.45 (m, 3H), 1.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 157.4, 139.2, 138.3, 138.2, 133.7, 133.6, 129.7, 129.7, 129.6, 128.9, 128.8, 128.6, 128.4, 128.4, 128.3, 128.2, 128.2, 127.4, 127.2, 127.1, 126.3, 126.0, 121.1, 121.1, 105.1, 104.6, 88.0, 88.0, 65.7, 65.4, 58.7, 58.6, 52.3, 52.0, 49.6, 49.3, 19.5, 19.4; HRMS (ESI) calcd for $C_{40}H_{40}N_2O_2Na^+$ $[M+Na]^+$: 603.2982, found: 603.2987.

4-(1-(dibenzylamino)-4-((dibenzylamino)methyl)-1_H_-isochromen-3-yl)butanenitrile (3zaa)



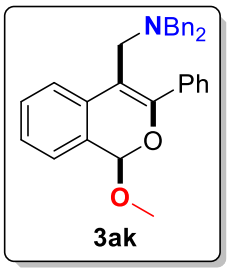
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 137 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.35 (m, 24H), 5.78 (s, 1H), 3.90 (d, *J* = 12.0 Hz, 2H), 3.30-3.72 (m, 8H), 2.51-2.62 (m, 2H), 2.28-2.37 (m, 2H), 1.93-1.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 139.6, 139.1, 133.3, 129.4, 128.7, 128.4, 128.3, 128.2, 128.0, 127.1, 127.1, 126.1, 125.5, 122.2, 119.8, 106.2, 88.0, 58.5, 52.3, 50.3, 29.7, 23.8, 17.0; HRMS (ESI) calcd for $C_{42}H_{42}N_3O$ $[M+H]^+$: 604.3328, found: 604.3330.

(8*R*,9*S*,13*S*,14*S*)-3-(1-(dibenzylamino)-4-((dibenzylamino)methyl)-1*H*-isochromen-3-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3zba)



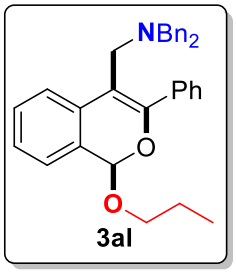
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 173 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.29-7.33 (m, 6H), 7.18-7.26 (m, 10H), 7.09-7.15 (m, 9H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.84 (s, 1H), 4.01 (d, *J* = 14.0 Hz, 2H), 3.80 (d, *J* = 14.0 Hz, 2H), 3.54 (s, 2H), 3.43 (dd, *J* = 13.6 Hz, 4.0 Hz, 2H), 3.30 (dd, *J* = 13.6 Hz, 3.6 Hz, 2H), 2.99-3.01 (m, 2H), 2.49-2.56 (m, 2H), 2.41 (t, *J* = 10.4 Hz, 1H), 2.01-2.21 (m, 4H), 1.63-1.75 (m, 3H), 1.51-1.60 (m, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 153.8, 153.8, 140.5, 139.6, 139.3, 136.3, 133.6, 130.5, 130.4, 129.3, 129.0, 128.9, 128.7, 128.4, 128.0, 127.6, 127.5, 127.4, 127.0, 126.8, 126.3, 125.2, 125.1, 125.1, 123.7, 107.4, 107.3, 88.8, 88.7, 77.4, 58.2, 52.6, 51.0, 50.7, 48.1, 44.7, 38.2, 36.0, 31.8, 29.7, 26.7, 25.8, 21.8, 14.0; HRMS (ESI) calcd for $C_{56}H_{57}N_2O_2$ $[M+H]^+$: 789.4420, found: 789.4409.

***N*,*N*-dibenzyl-1-(1-methoxy-3-phenyl-1*H*-isochromen-4-yl)methanamine (3ak)**



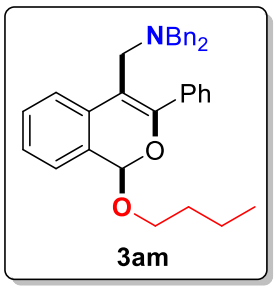
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 102 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.46 (m, 5H), 7.13-7.30 (m, 14H), 5.92 (s, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 12.8 Hz, 2H), 3.59 (s, 3H), 3.35 (d, *J* = 13.2 Hz, 1H), 3.08 (d, *J* = 13.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 139.7, 135.6, 130.6, 130.1, 129.6, 128.9, 128.7, 128.3, 128.1, 128.0, 126.9, 126.6, 125.3, 124.5, 110.1, 99.8, 57.7, 55.8, 50.7; HRMS (ESI) calcd for $C_{31}H_{30}NO_2$ $[M+H]^+$: 448.2277, found: 448.2281.

_N,N_-dibenzyl-1-(3-phenyl-1-propoxy-1_H_-isochromen-4-yl)methanamine (3al)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 106 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.46 (m, 5H), 7.13-7.28 (m, 14H), 6.00 (s, 1H), 3.90-3.96 (m, 1H), 3.62-3.73 (m, 4H), 3.37 (d, *J* = 13.2 Hz, 1H), 3.09 (d, *J* = 12.8 Hz, 2H), 1.49-1.57 (m, 2H), 0.80 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 139.7, 135.7, 130.8, 130.1, 129.6, 128.8, 128.5, 128.4, 128.2, 128.0, 126.9, 126.5, 125.1, 124.4, 110.2, 98.6, 69.9, 57.7, 50.6, 23.0, 10.7; HRMS (ESI) calcd for $C_{33}H_{34}NO_2$ $[M+H]^+$: 476.2590, found: 476.2593.

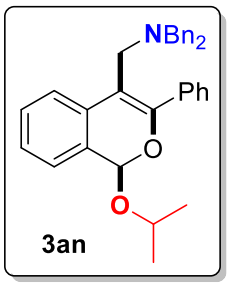
_N,N_-dibenzyl-1-(1-butoxy-3-phenyl-1_H_-isochromen-4-yl)methanamine (3am)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 99.7 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.48 (m, 5H), 7.13-7.30 (m, 14H), 5.99 (s, 1H), 3.95-4.01 (m, 1H), 3.63-3.73 (m, 4H), 3.36 (d, *J* = 13.2 Hz, 1H), 3.08 (d, *J* = 13.2 Hz, 2H), 1.44-1.52 (m, 2H), 1.19-1.28 (m, 2H), 0.74 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 139.8, 135.7, 130.8, 130.1, 129.5, 128.8, 128.5, 128.4, 128.2, 128.0, 126.9, 126.5, 125.1, 124.4, 110.2, 98.7, 68.0, 57.7,

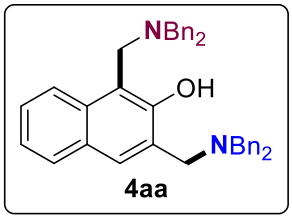
50.6, 31.8, 19.4, 13.9; HRMS (ESI) calcd for $C_{34}H_{36}NO_2$ $[M+H]^+$: 490.2746, found: 490.2757.

_N,N_-dibenzyl-1-(1-isopropoxy-3-phenyl-1H-isochromen-4-yl)methanamine (3an)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 87 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.47 (m, 5H), 7.13-7.27 (m, 14H), 6.08 (s, 1H), 4.29-4.36 (m, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.60 (d, *J* = 13.2 Hz, 2H), 3.40 (d, *J* = 13.2 Hz, 1H), 3.13 (d, *J* = 13.2 Hz, 2H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.11 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 139.7, 135.8, 130.9, 130.1, 129.6, 128.8, 128.6, 128.4, 128.2, 128.0, 126.8, 126.5, 124.8, 124.4, 110.3, 96.1, 68.8, 57.6, 50.6, 23.5, 21.6; HRMS (ESI) calcd for $C_{33}H_{34}NO_2$ $[M+H]^+$: 476.2590, found: 476.2595.

1,3-bis((dibenzylamino)methyl)naphthalen-2-ol (4aa)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 120 mg, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.35-7.38 (m, 4H), 7.31-7.33 (m, 8H), 7.19-7.28 (m, 9H), 4.07 (s, 2H), 3.84 (s, 2H), 3.64 (s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 139.0, 138.1, 133.3, 129.6, 129.4, 128.6, 128.4, 128.3, 128.2, 128.1, 127.5, 127.2, 125.9, 125.7, 123.4, 122.7, 114.9, 58.5, 58.1, 55.5, 49.6; HRMS (ESI) calcd for $C_{40}H_{39}N_2O$ $[M+H]^+$: 563.3062, found: 563.3059.

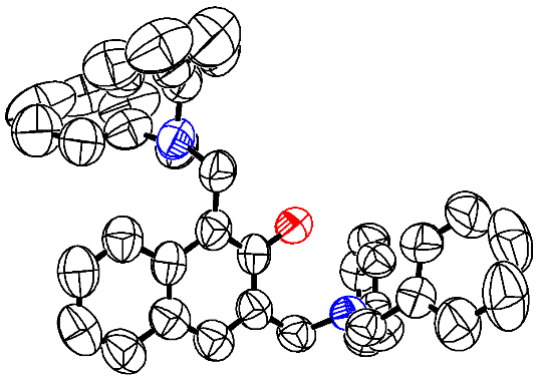
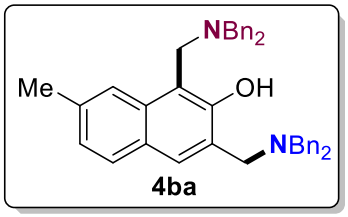


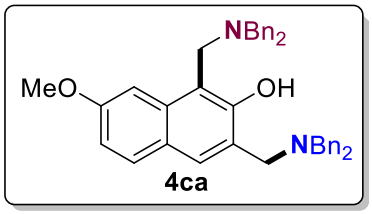
Figure S3. The ORTEP drawing of product **4aa**

1,3-bis((dibenzylamino)methyl)-7-methylnaphthalen-2-ol (4ba)



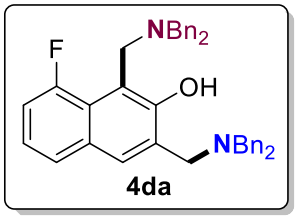
The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 121 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 0.88H), 7.64 (s, 1H), 7.54-7.56 (m, 2H), 7.19-7.37 (m, 20H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.04 (s, 2H), 3.81 (s, 2H), 3.62-3.63 (m, 8H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 139.4, 137.9, 135.3, 133.6, 129.6, 129.4, 128.6, 128.3, 128.0, 127.8, 127.5, 127.1, 126.6, 125.0, 124.5, 122.9, 114.6, 58.5, 58.0, 55.8, 49.3, 22.1; HRMS (ESI) calcd for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3219, found: 577.3223.

1,3-bis((dibenzylamino)methyl)-7-methoxynaphthalen-2-ol (4ca)



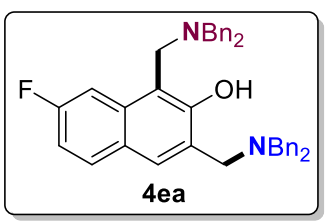
The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 117 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 0.87H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.46 (s, 1H), 7.32-7.36 (m, 12H), 7.18-7.29 (m, 9H), 6.89 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 4.05 (s, 2H), 3.82 (s, 2H), 3.75 (s, 3H), 3.62 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.4, 139.7, 137.6, 134.9, 129.5, 129.5, 129.4, 128.7, 128.3, 128.0, 127.6, 127.0, 123.7, 122.3, 115.5, 114.8, 102.7, 58.6, 58.0, 56.3, 55.7, 49.3; HRMS (ESI) calcd for $C_{41}H_{41}N_2O_2$ $[M+H]^+$: 593.3168, found: 593.3177.

1,3-bis((dibenzylamino)methyl)-8-fluoronaphthalen-2-ol (4da)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 85 mg, 49% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.65 (s, 0.63H), 7.92 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 4H), 7.27-7.33 (m, 12H), 7.20-7.23 (m, 4H), 7.11 (dd, *J* = 12.5 Hz, 8.0 Hz, 1H), 7.01 (dd, *J* = 15 Hz, 7.5 Hz, 1H), 4.42 (s, 2H), 3.80 (s, 2H), 3.66-3.68 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (d, $J_{C\text{-}F}$ = 249 Hz), 156.7, 139.5, 137.5, 131.0 (d, $J_{C\text{-}F}$ = 5 Hz), 129.6, 129.3, 128.8, 128.6, 128.4, 127.9, 127.6, 127.0, 125.0 (d, $J_{C\text{-}F}$ = 4 Hz), 122.5 (d, $J_{C\text{-}F}$ = 10 Hz), 122.1 (d, $J_{C\text{-}F}$ = 9 Hz), 111.5 (d, $J_{C\text{-}F}$ = 24 Hz), 111.4, 58.5, 58.3, 53.5 (d, $J_{C\text{-}F}$ = 16 Hz), 52.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.0; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2976.

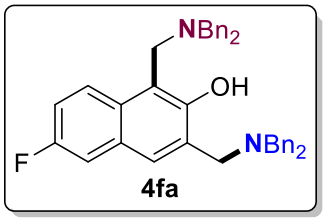
1,3-bis((dibenzylamino)methyl)-7-fluoronaphthalen-2-ol (4ea)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 115 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 7.58 (dd, *J* = 8.8 Hz, 6.0 Hz, 1H), 7.50-7.53 (m, 2H), 7.02-7.36 (m, 20H), 6.98 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 3.97 (s, 2H),

3.80 (s, 2H), 3.61-3.61 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (d, J_{C-F} = 243 Hz), 155.6, 139.1, 137.7, 134.7 (d, J_{C-F} = 10 Hz), 130.1 (d, J_{C-F} = 9 Hz), 129.5, 129.4, 128.6, 128.4, 128.0, 127.6, 127.2, 125.3, 124.6 (d, J_{C-F} = 3 Hz), 115.0 (d, J_{C-F} = 6 Hz), 112.9 (d, J_{C-F} = 25 Hz), 107.6 (d, J_{C-F} = 23 Hz), 58.6, 58.1, 55.8, 49.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.6; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2970.

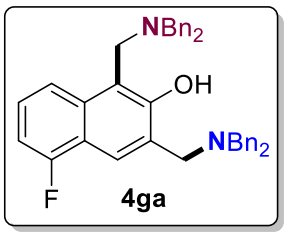
1,3-bis((dibenzylamino)methyl)-6-fluoronaphthalen-2-ol (4fa)



4fa

The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 118 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 0.94H), 7.80 (dd, J = 9.2 Hz, 5.6 Hz, 1H), 7.50 (s, 1H), 7.18-7.36 (m, 21H), 7.08-7.13 (m, 1H), 4.03 (s, 2H), 3.82 (s, 2H), 3.61 (s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (d, J_{C-F} = 240 Hz), 154.0, 139.2, 137.6, 130.4, 129.5, 129.4, 128.9 (d, J_{C-F} = 8 Hz), 128.7, 128.3, 127.6, 127.2, 127.2, 126.9, 126.2 (d, J_{C-F} = 9 Hz), 115.8, 115.6 (d, J_{C-F} = 25 Hz), 110.9 (d, J_{C-F} = 20 Hz), 58.5, 58.1, 55.9, 49.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2972.

1,3-bis((dibenzylamino)methyl)-5-fluoronaphthalen-2-ol (4ga)

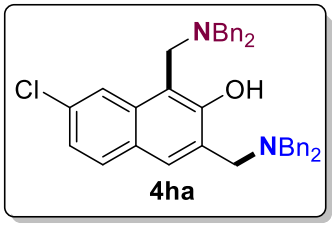


4ga

The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 104 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 0.90H), 7.92 (s, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.28-7.38 (m, 12H), 7.20-7.24 (m, 9H), 6.88 (dd, d, J = 10.4 Hz, 7.6 Hz, 1H), 4.04 (s, 2H), 3.84 (s, 2H), 3.62 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, J_{C-F} = 248 Hz), 155.6, 139.0, 137.8, 135.2 (d, J_{C-F} = 4 Hz), 129.5, 129.4, 128.6, 128.3, 127.6, 126.1, 125.5 (d, J_{C-F} = 9 Hz), 120.6 (d, J_{C-F} = 6 Hz), 119.5, 119.5, 118.5 (d, J_{C-F} = 15 Hz), 115.3, 106.5 (d, J_{C-F} = 20 Hz), 58.5, 58.1, 55.8, 49.6; ^{19}F NMR (376 MHz,

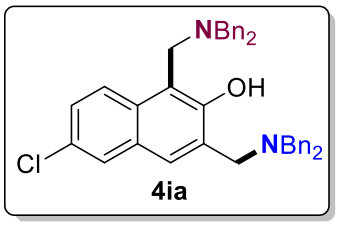
$CDCl_3$) δ -123.5; HRMS (ESI) calcd for $C_{40}H_{38}FN_2O$ $[M+H]^+$: 581.2968, found: 581.2970.

7-chloro-1,3-bis((dibenzylamino)methyl)naphthalen-2-ol (4ha)



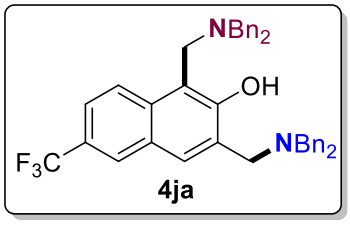
The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 114 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 0.95H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.31-7.33 (m, 10H), 7.23-7.29 (m, 7H), 7.15-7.21 (m, 4H), 3.97 (s, 2H), 3.78 (s, 2H), 3.58-3.60 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 139.1, 137.6, 134.3, 131.8, 129.4, 129.4, 128.7, 128.5, 127.9, 127.6, 127.2, 126.6, 125.7, 123.6, 123.0, 114.8, 58.6, 58.1, 55.9, 49.1; HRMS (ESI) calcd for $C_{40}H_{38}ClN_2O$ $[M+H]^+$: 597.2673, found: 597.2667.

6-chloro-1,3-bis((dibenzylamino)methyl)naphthalen-2-ol (4ia)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 111 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 0.91H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.49 (s, 1H), 7.19-7.37 (m, 21H), 4.01 (s, 2H), 3.81 (s, 2H), 3.61-3.61 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 139.0, 137.6, 131.7, 129.5, 129.4, 129.1, 128.7, 128.3, 127.6, 127.2, 127.1, 126.9, 126.5, 126.3, 125.5, 115.5, 58.5, 58.1, 55.8, 49.2; HRMS (ESI) calcd for $C_{40}H_{38}ClN_2O$ $[M+H]^+$: 597.2673, found: 597.2672.

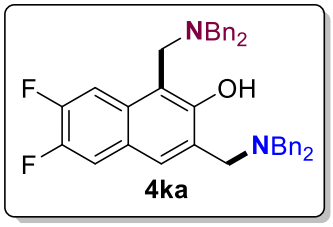
6-chloro-1,3-bis((dibenzylamino)methyl)naphthalen-2-ol (4ja)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 109 mg, 58% yield.

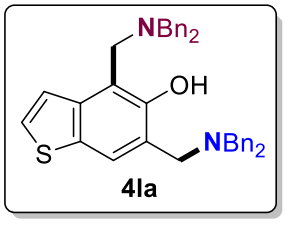
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.81 (s, 0.85H), 8.43 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.59 (s, 1H), 7.41-7.43 (m, 1H), 7.18-7.36 (m, 20H), 4.05 (s, 2H), 3.86 (s, 2H), 3.61-3.63 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 139.1, 137.3, 132.5, 129.5, 129.3, 128.7, 128.7, 128.4, 127.8, 127.8, 127.7, 127.5, 127.2, 126.1 (q, J_{C-F} = 271 Hz), 122.2 (q, J_{C-F} = 4 Hz), 118.5, 118.4, 116.6, 58.7, 58.2, 56.2, 49.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.4; HRMS (ESI) calcd for $C_{41}H_{38}F_3N_2O$ $[M+H]^+$: 631.2936, found: 631.2941.

1,3-bis((dibenzylamino)methyl)-6,7-difluoronaphthalen-2-ol (4ka)



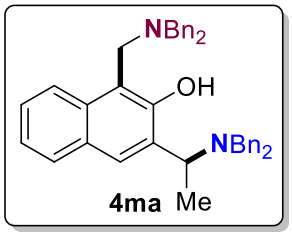
The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 113 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 0.73H), 7.60 (dd, J = 13.2 Hz, 8.0 Hz, 1H), 7.42 (s, 1H), 7.21-7.35 (m, 21H), 3.94 (s, 2H), 3.80 (s, 2H), 3.60-3.61 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8 (d, J_{C-F} = 3 Hz), 151.0 (dd, J_{C-F} = 246 Hz, 15 Hz), 149.0 (dd, J_{C-F} = 240 Hz, 11 Hz), 139.2, 137.3, 130.8 (d, J_{C-F} = 8 Hz), 129.5, 129.4, 128.7, 128.4, 127.7, 127.2, 127.1 (d, J_{C-F} = 4 Hz), 125.6, 124.9 (d, J_{C-F} = 6 Hz), 115.7, 113.3 (d, J_{C-F} = 15 Hz), 110.7 (d, J_{C-F} = 19 Hz), 58.6, 58.1, 56.2, 49.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.7, -137.8, -142.5, -142.5; HRMS (ESI) calcd for $C_{40}H_{36}F_2N_2ONa$ $[M+Na]^+$: 621.2688, found: 621.2678.

4,6-bis((dibenzylamino)methyl)benzo[*b*]thiophen-5-ol (4la)



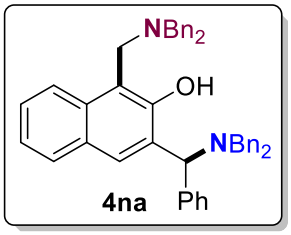
The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 80 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 0.85H), 7.67 (s, 1H), 7.36 (d, J = 7.2 Hz, 4H), 7.22-7.34 (m, 18H), 3.96 (s, 2H), 3.78 (s, 2H), 3.61-3.62 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 139.5, 138.7, 138.3, 131.2, 129.5, 129.3, 128.6, 128.4, 127.4, 127.3, 126.2, 123.1, 122.3, 121.7, 116.5, 58.4, 58.1, 54.9, 51.4; HRMS (ESI) calcd for $C_{38}H_{37}N_2OS$ $[M+H]^+$: 569.2627, found: 569.2625.

3-(1-(dibenzylamino)ethyl)-1-((dibenzylamino)methyl)naphthalen-2-ol (4ma)



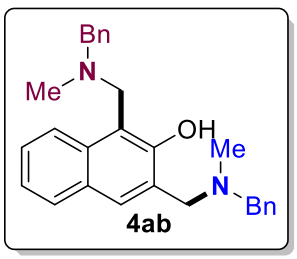
The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 112 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.17-7.34 (m, 22H), 4.26 (q, *J* = 6.4 Hz, 1H), 4.00 (ABq, *J* = 12.4 Hz, 2H), 3.67-3.78 (m, 4H), 3.46-3.59 (m, 4H), 1.54 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 139.9, 137.9, 133.8, 129.6, 129.5, 129.4, 128.6, 128.2, 128.2, 128.0, 127.6, 126.9, 126.8, 125.6, 124.2, 122.7, 116.2, 58.5, 55.5, 54.0, 48.8, 10.9; HRMS (ESI) calcd for $C_{41}H_{41}N_2O$ $[M+H]^+$: 577.3219, found: 577.3224.

3-((dibenzylamino)(phenyl)methyl)-1-((dibenzylamino)methyl)naphthalen-2-ol (4na)



The title compound was prepared according to the general procedure and purified by column chromatography to give white solid, 111 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.34 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.62-7.65 (m, 2H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.27-7.36 (m, 20H), 7.21-7.25 (m, 5H), 5.44 (s, 1H), 4.14 (s, 2H), 3.85 (d, *J* = 14.0 Hz, 2H), 3.72 (d, *J* = 13.0 Hz, 2H), 3.56-3.60 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 139.4, 138.4, 133.0, 129.8, 129.7, 129.5, 129.0, 128.6, 128.5, 128.4, 128.1, 127.5, 127.3, 127.2, 125.9, 122.7, 122.6, 114.4, 65.0, 58.3, 54.1, 50.3; HRMS (ESI) calcd for $C_{46}H_{43}N_2O$ $[M+H]^+$: 639.3375, found: 639.3380.

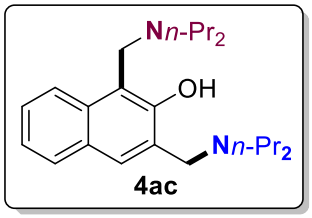
1,3-bis((benzyl(methyl)amino)methyl)naphthalen-2-ol (4ab)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 77 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.61 (s, 1H), 7.39-7.42 (m, 1H), 7.24-7.35 (m, 11H), 4.09 (s, 2H), 3.86 (s, 2H), 3.66 (s, 2H), 3.63 (s, 2H), 2.26-2.27 (m, 6H); ^{13}C NMR (125 MHz,

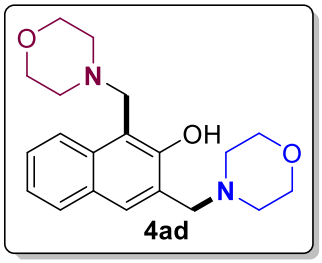
$CDCl_3$) δ 155.1, 138.8, 137.8, 133.4, 129.5, 129.4, 128.6, 128.4, 128.3, 128.2, 128.2, 127.5, 127.2, 126.0, 125.7, 123.1, 122.8, 114.9, 62.0, 61.7, 59.5, 53.1, 41.9, 41.7; HRMS (ESI) calcd for $C_{28}H_{31}N_2O$ $[M+H]^+$: 411.2436, found: 411.2426.

1,3-bis((dipropylamino)methyl)naphthalen-2-ol (4ac)



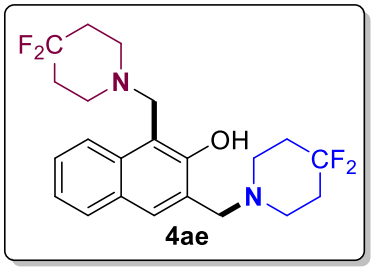
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 67 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.37-7.40 (m, 1H), 7.24-7.27 (m, 1H), 4.09 (s, 2H), 3.82 (s, 2H), 2.48-2.52 (m, 8H), 1.53-1.61 (m, 8H), 0.83-0.90 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 132.9, 128.2, 128.2, 127.6, 127.5, 125.6, 122.6, 122.4, 114.1, 56.1, 56.0, 55.6, 51.2, 20.1, 19.9, 12.1, 12.1; HRMS (ESI) calcd for $C_{24}H_{39}N_2O$ $[M+H]^+$: 371.3062, found: 371.3058.

1,3-bis(morpholinomethyl)naphthalen-2-ol (4ad)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 62 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.41-7.45 (m, 1H), 7.24-7.31 (m, 1H), 4.03-4.04 (m, 2H), 3.71-3.79 (m, 10H), 2.59-2.60 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 133.4, 128.8, 128.2, 128.1, 126.2, 124.5, 122.9, 122.7, 113.5, 67.0, 66.9, 60.3, 54.2, 53.4, 53.3; HRMS (ESI) calcd for $C_{20}H_{27}N_2O_3$ $[M+H]^+$: 343.2022, found: 343.2018.

1,3-bis((4,4-difluoropiperidin-1-yl)methyl)naphthalen-2-ol (4ae)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 71 mg, 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 4.07 (s, 2H), 3.84 (s, 2H), 2.71-2.72 (m, 8H), 1.96-2.10 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 133.4, 128.8, 128.3, 128.2, 126.4, 124.7, 124.5, 124.1, 123.1, 122.8, 122.1, 121.7, 119.7, 119.3, 114.2, 59.2, 52.9, 50.0, 49.9, 49.9, 49.8, 34.2, 34.2, 34.0, 33.9, 33.8, 33.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.9, -98.0, -98.1, -98.3; HRMS (ESI) calcd for $C_{22}H_{27}F_4N_2O$ $[M+H]^+$: 411.2060, found: 411.2058.

6. Mechanistic Experiments

To gain insights into the possible mechanism of this reaction, some mechanism experiments were conducted.

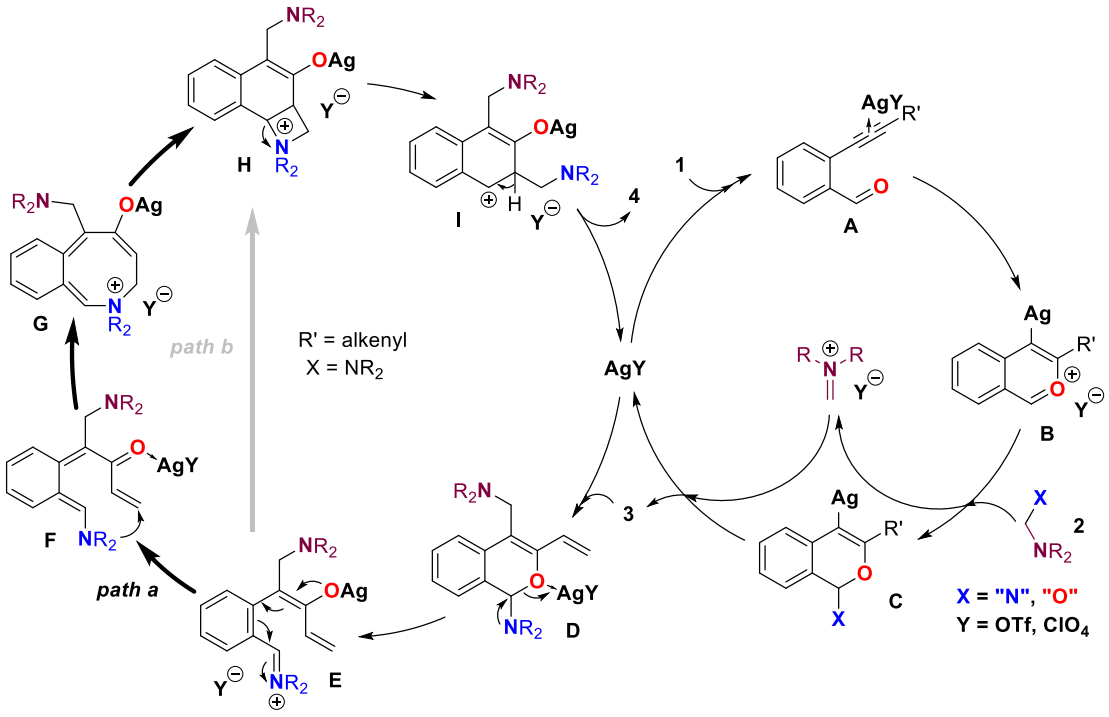
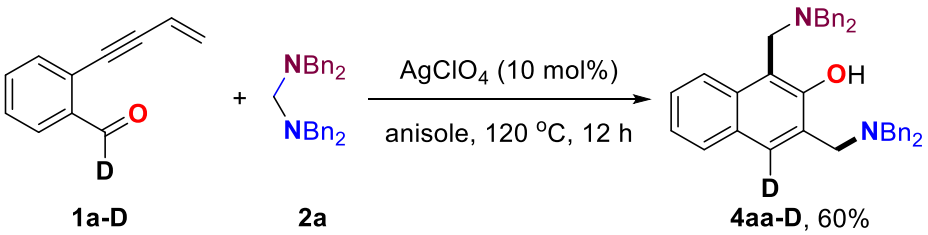


Figure S4. The proposed reaction mechanism.

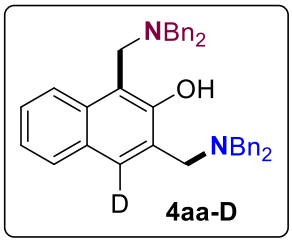
Control experiments



The mixture of aminal **2a** (146 mg, 0.36 4mmol), $AgClO_4$ (6.2 mg, 10 mol %), 2-(but-3-en-1-yn-1-yl)benzaldehyde **1a-D** (47 mg, 0.30 mmol) and anisole (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 120 °C in an oil bath for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was

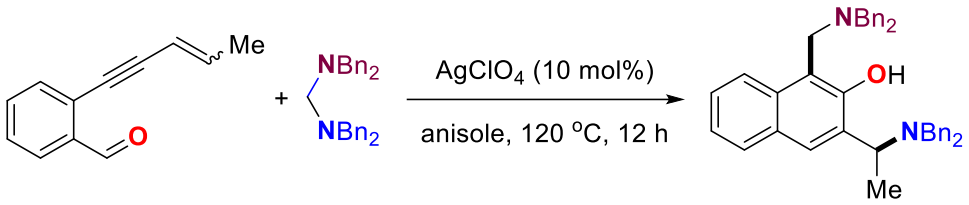
purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 50/1 to 20/1) to give the desired product **4aa-D** (101 mg, 60%) as white solid.

1,3-bis((dibenzylamino)methyl)naphthalen-4-*d*-2-ol (4aa-D)



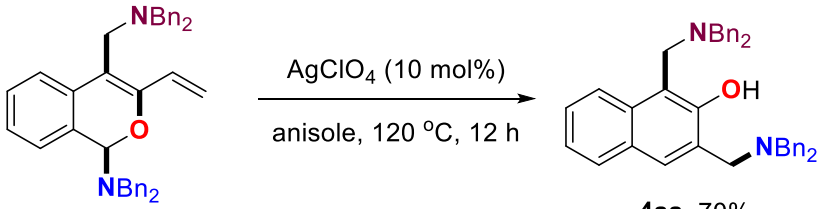
4aa-D

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 4H), 7.17-7.33 (m, 18H), 4.07 (s, 2H), 3.82 (s, 2H), 3.62-3.63 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 139.0, 138.0, 133.3, 129.5, 129.3, 128.6, 128.3, 128.0, 127.5, 127.2, 125.8, 125.6, 123.4, 122.7, 114.8, 58.4, 58.1, 55.4, 49.6; HRMS (ESI) calcd for $C_{40}H_{38}DN_2O$ $[M+H]^+$: 564.3125, found: 564.3123.



1m **2a** **4ma**, 65%

The mixture of aminal **2a** (146 mg, 0.36 mmol), $AgClO_4$ (6.2 mg, 10 mol %), 2-(pent-3-en-1-yn-1-yl)benzaldehyde **1m** (51 mg, 0.30 mmol) and anisole (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 120 °C in an oil bath for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 50/1 to 20/1) to give the desired product **4ma** (112 mg, 65%) as white solid.



3aa **4aa**, 70%

The mixture of 1*H*-isochromen **3aa** (112 mg, 0.2 mmol), $AgClO_4$ (4.2 mg, 10 mol %) and anisole (1.0 mL) were added to a 25 mL flame-dried Young-type tube

under N_2 atmosphere. The reaction mixture was stirred at 120 °C in an oil bath for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 50/1 to 20/1) to give the desired product **4aa** (78 mg, 70%) as white solid.

Reaction profile

Parallel experiments: The mixture of *N*,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (97 mg, 0.24 mmol), $AgClO_4$ (4.2 mg, 10 mol %), 2-(but-3-en-1-yn-1-yl)benzaldehyde **1a** (47 mg, 0.20 mmol) and anisole (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 120 °C for designed time and then cooled to room temperature. The yields of **3aa** and **4aa** were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as internal standard.

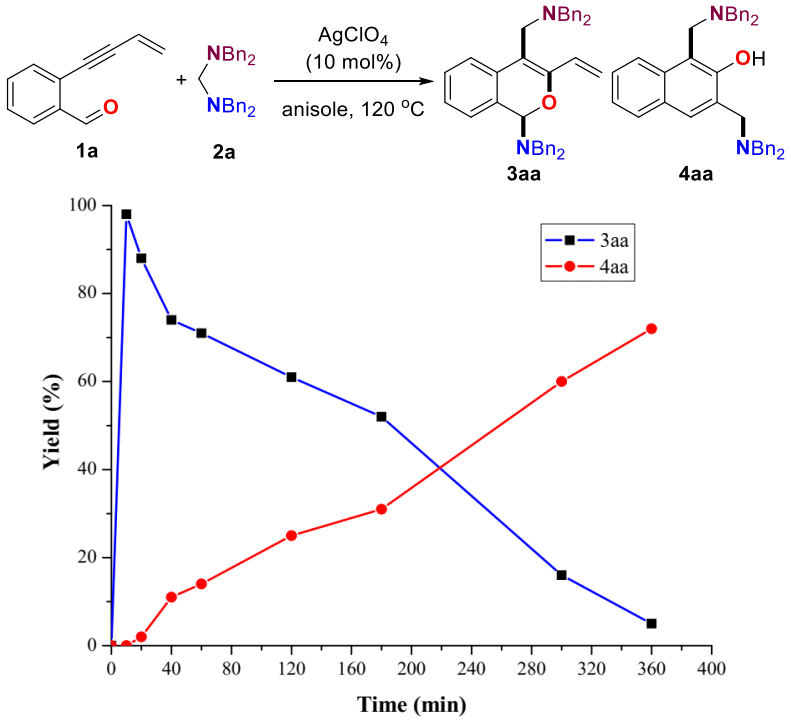
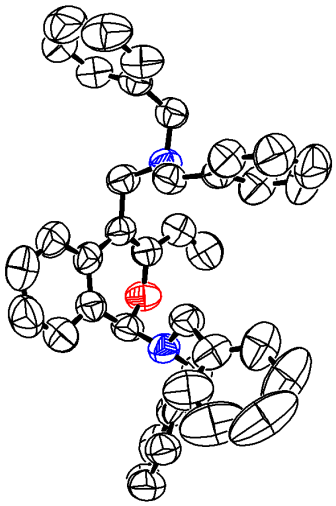


Figure S5. Reaction profile of the catalytic reaction.

7. X-ray Single Crystal Data for Compound 3aa, 3pa, and 4aa

Sample preparation: Compound **3aa** (20 mg) was dissolved in anhydrous CH_2Cl_2 (1.0 mL) in a 10 mL sample vial, and then Et_2O (3.0 mL) were added carefully to form a two-phase interface. The resulting mixture was left at room temperature under airtight conditions until the white crystals precipitated.



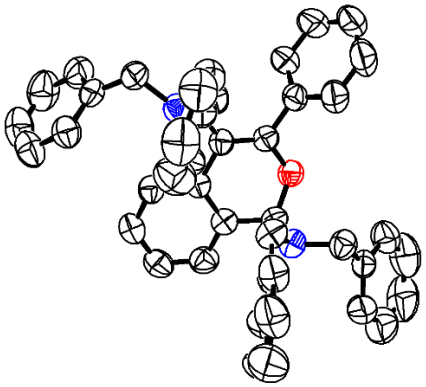
3aa

The ellipsoid contour percent probability level is 75%.

Crystal data and structure refinement for **3aa**

Identification code	**3aa**
Empirical formula	$C_{40}H_{38}N_2O$
Formula weight	562.72
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.3021(8)
b/Å	11.3449(7)
c/Å	15.1031(10)
α/°	89.431(5)
β/°	68.393(7)
γ/°	64.454(7)
Volume/Å3	1598.7(2)
Z	2

ρcalcg/cm3	1.169
μ/mm-1	0.069
F(000)	600.0
Crystal size/mm3	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.764 to 59.092
Index ranges	-14 ≤ h ≤ 9, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	11798
Independent reflections	7408 [Rint = 0.0245, Rsigma = 0.0506]
Data/restraints/parameters	7408/0/388
Goodness-of-fit on F2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0625, wR2 = 0.1284
Final R indexes [all data]	R1 = 0.1091, wR2 = 0.1527
Largest diff. peak/hole / e Å-3	0.17/-0.23



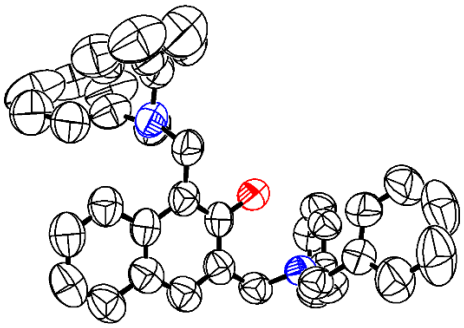
3pa

The ellipsoid contour percent probability level is 60%.

Crystal data and structure refinement for **3pa**

Identification code	YBK-0817_auto
Empirical formula	$C_{44}H_{40}N_2O$
Formula weight	612.821
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8246(2)
b/Å	16.0677(3)
c/Å	21.9664(5)
α/°	90
β/°	91.832(2)
γ/°	90
Volume/Å^3	3465.82(12)
Z	4
ρ_{calc}g/cm^3	1.174
μ/mm^{-1}	0.535
F(000)	1307.7
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.06 to 146.04
Index ranges	$-11 \le h \le 12$, $-13 \le k \le 19$, $-26 \le l \le 27$

Reflections collected	13959
Independent reflections	6743 [R_{int} = 0.0207, R_{sigma} = 0.0270]
Data/restraints/parameters	6743/0/424
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1190
Final R indexes [all data]	R_1 = 0.0623, wR_2 = 0.1331
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.21



4aa

The ellipsoid contour percent probability level is 75%.

Crystal data and structure refinement for **4aa**

Identification code **4aa**	
Empirical formula	$C_{40}H_{38}N_2O$
Formula weight	562.72
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.1191(4)
b/Å	12.6465(4)
c/Å	12.9053(4)
α/°	96.455(3)
β/°	115.408(3)
γ/°	109.434(3)
Volume/Å3	1607.44(10)
Z	2
ρcalcg/cm3	1.163
μ/mm-1	0.531
F(000)	600.0
Crystal size/mm3	0.21 × 0.15 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.77 to 146.092
Index ranges	-13 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	11050
Independent reflections	6212 [Rint = 0.0185, Rsigma = 0.0234]

Data/restraints/parameters	6212/1/389
Goodness-of-fit on F2	0.996
Final R indexes [I>=2σ (I)]	R1 = 0.0882, wR2 = 0.2846
Final R indexes [all data]	R1 = 0.0956, wR2 = 0.2960
Largest diff. peak/hole / e Å-3	0.74/-0.30

8. References

1. Heaney, H.; Papageorgiou, G.; Wilkins, R. F. The generation of iminium ions using chlorosilanes and their reactions with electron rich aromatic heterocycles. *Tetrahedron* **1997**, *53*, 2941-2958.

2. Rosenau, T.; Potthast, A.; Kosma, P. Studies on the carbenium-iminium ions derived from *N*-methylmorpholine-*N*-oxide (NMMO). *Tetrahedron* **2004**, *60*, 301-306.

3. Yu, B.; Yu, H.; Huang, H. Palladium-catalyzed chemoselective aminomethylative cyclization and aromatizing allylic amination: access to functionalized naphthalenes. *Org. Lett.* **2020**, *22*, 8962-8966.

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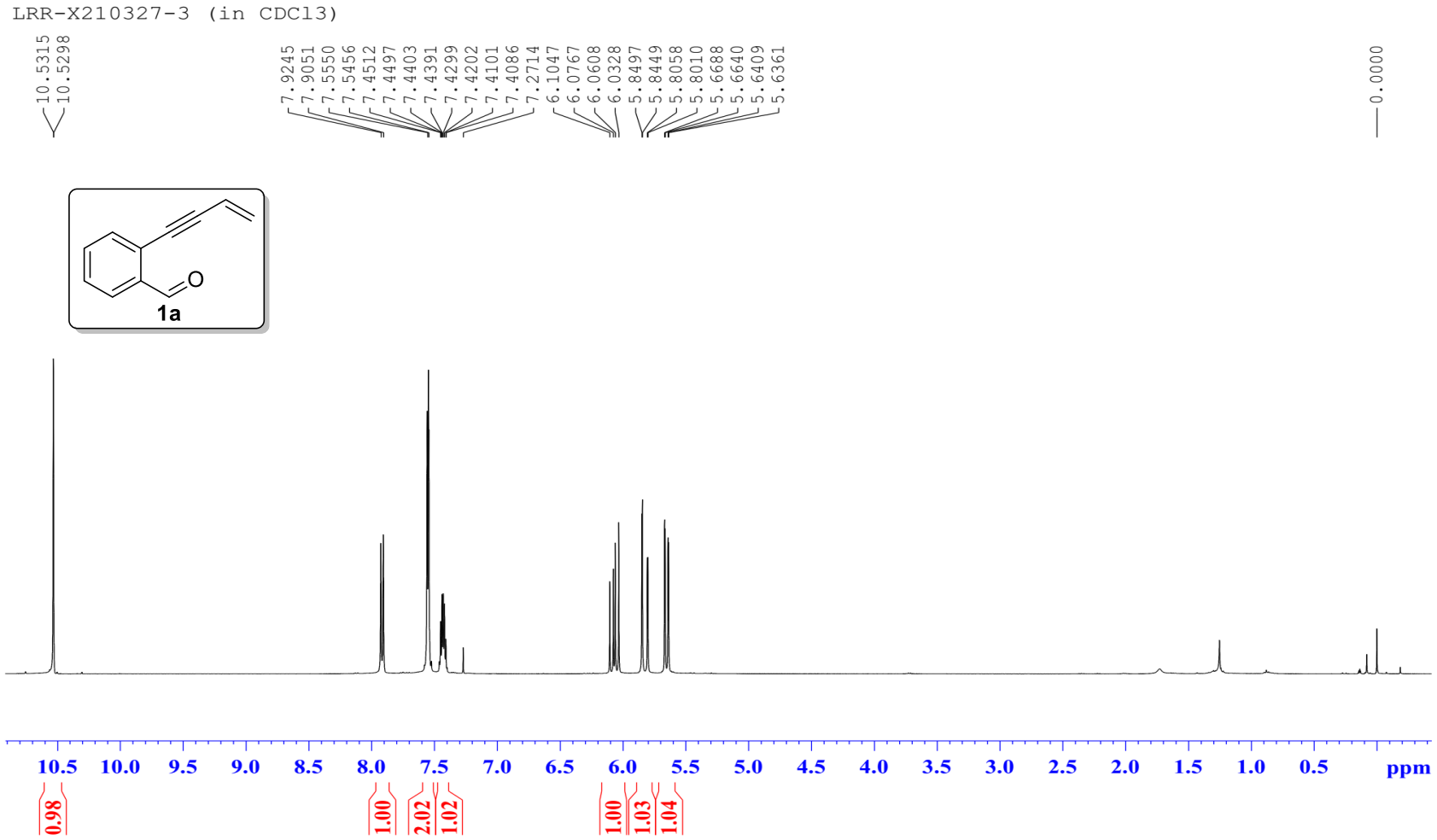
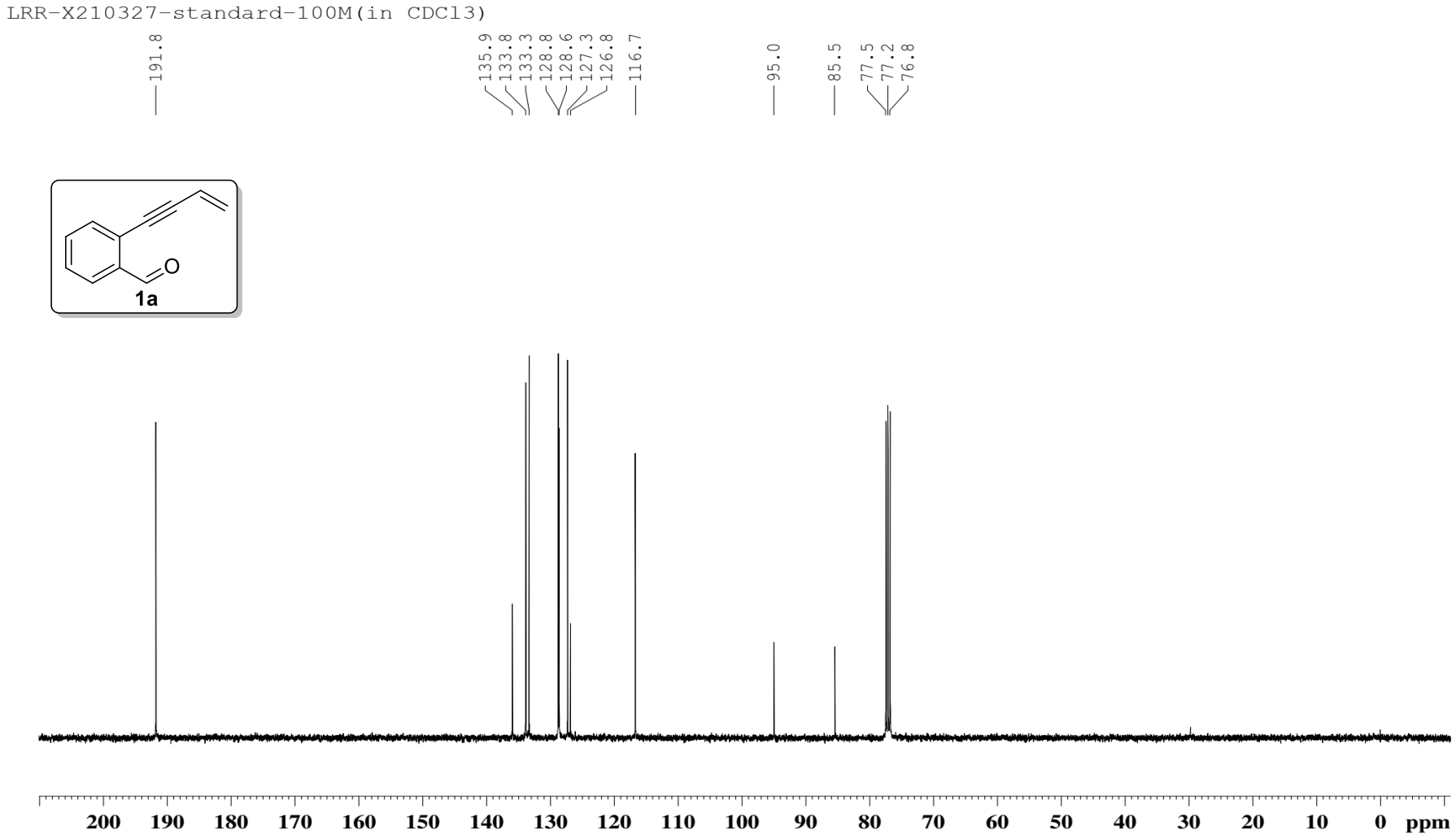
9. NMR Spectra of Materials and Products

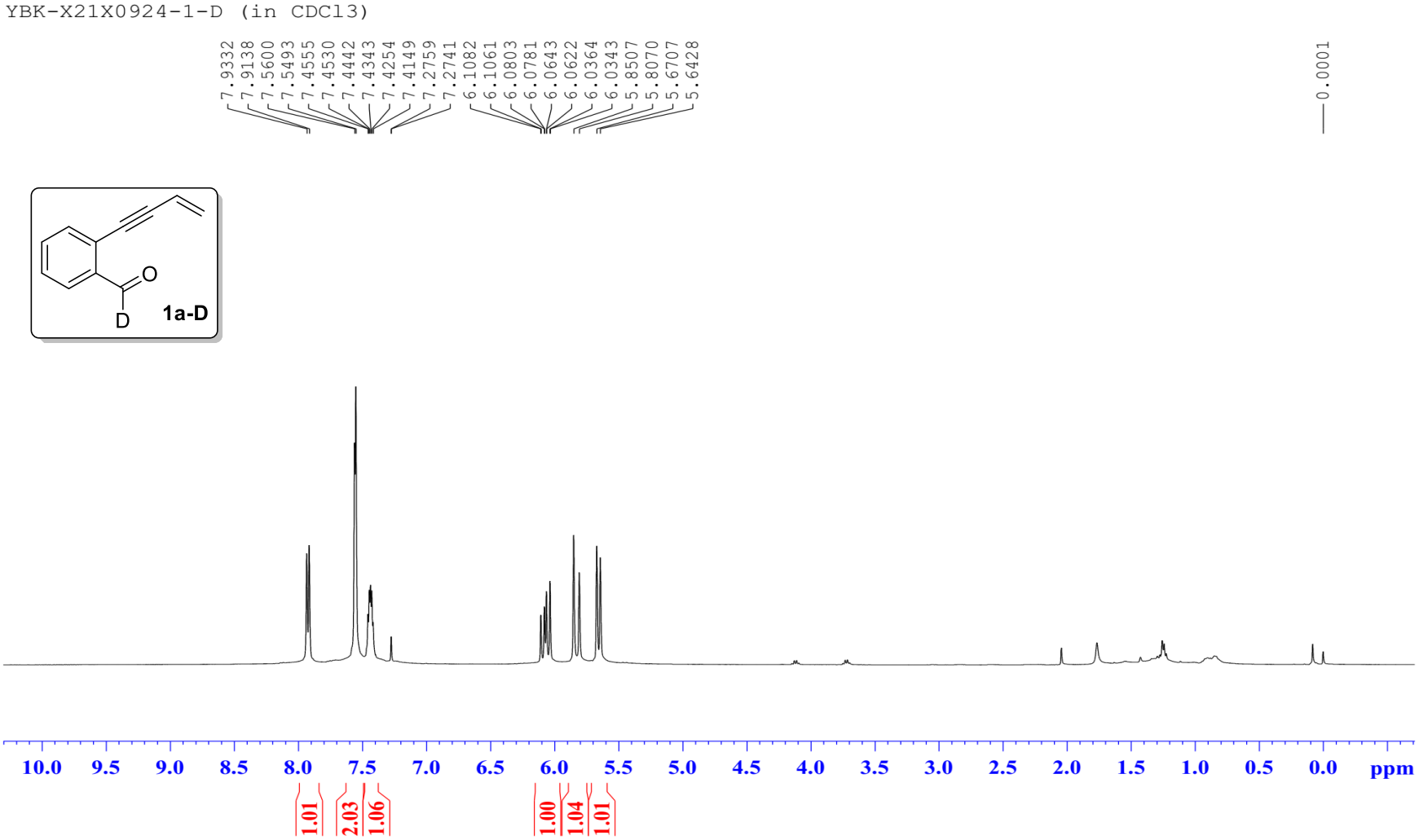
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1a



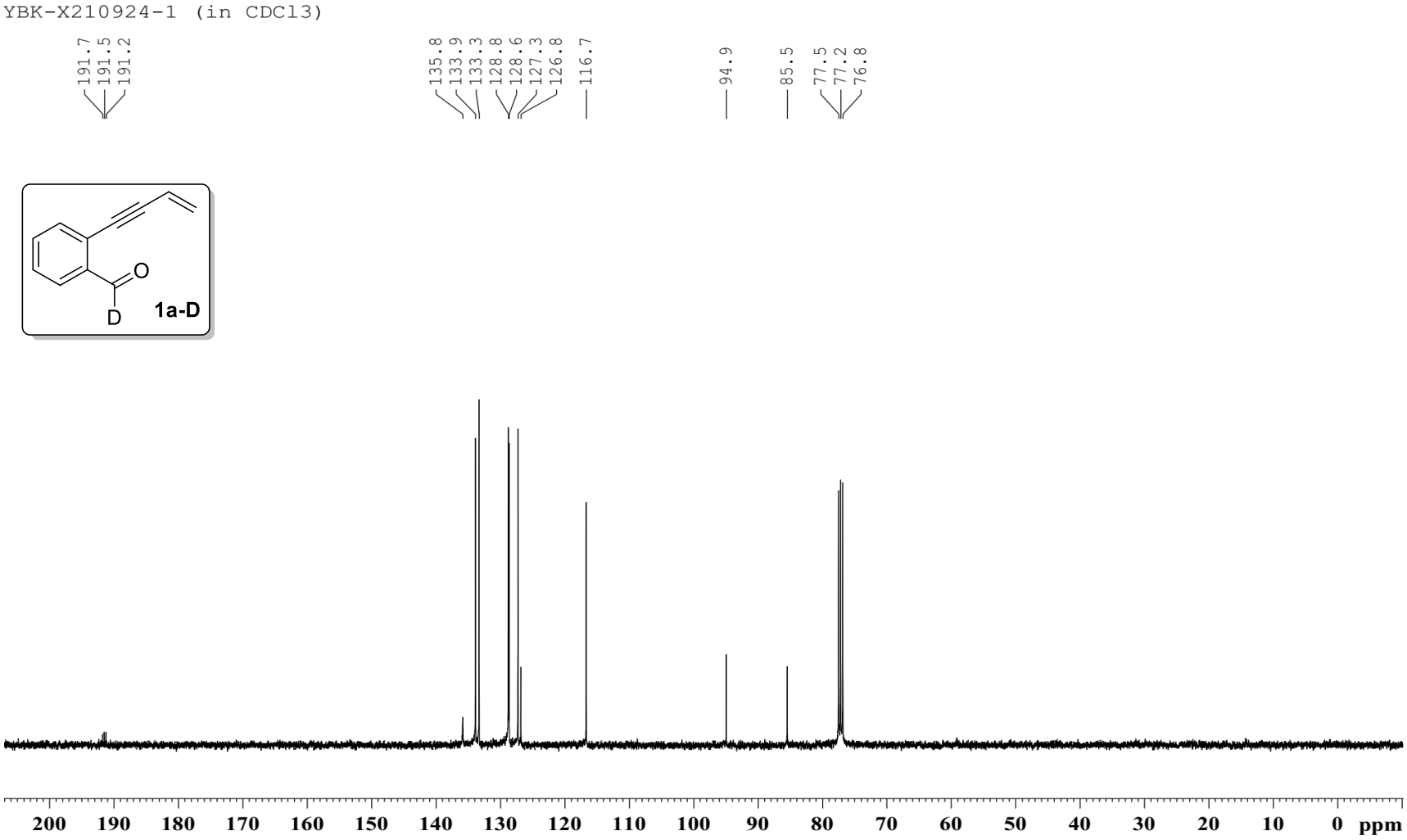
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1a



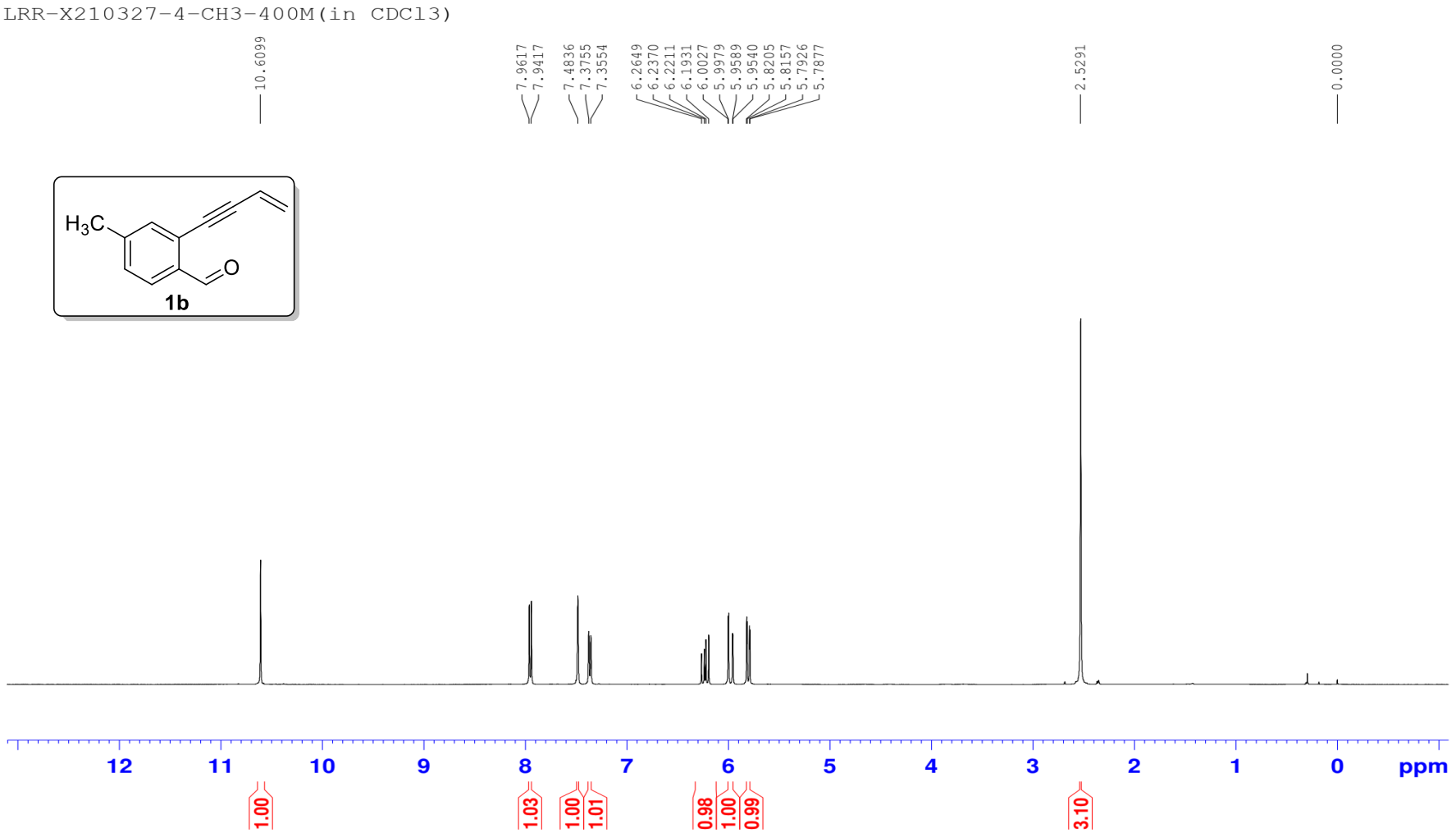
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1a-D



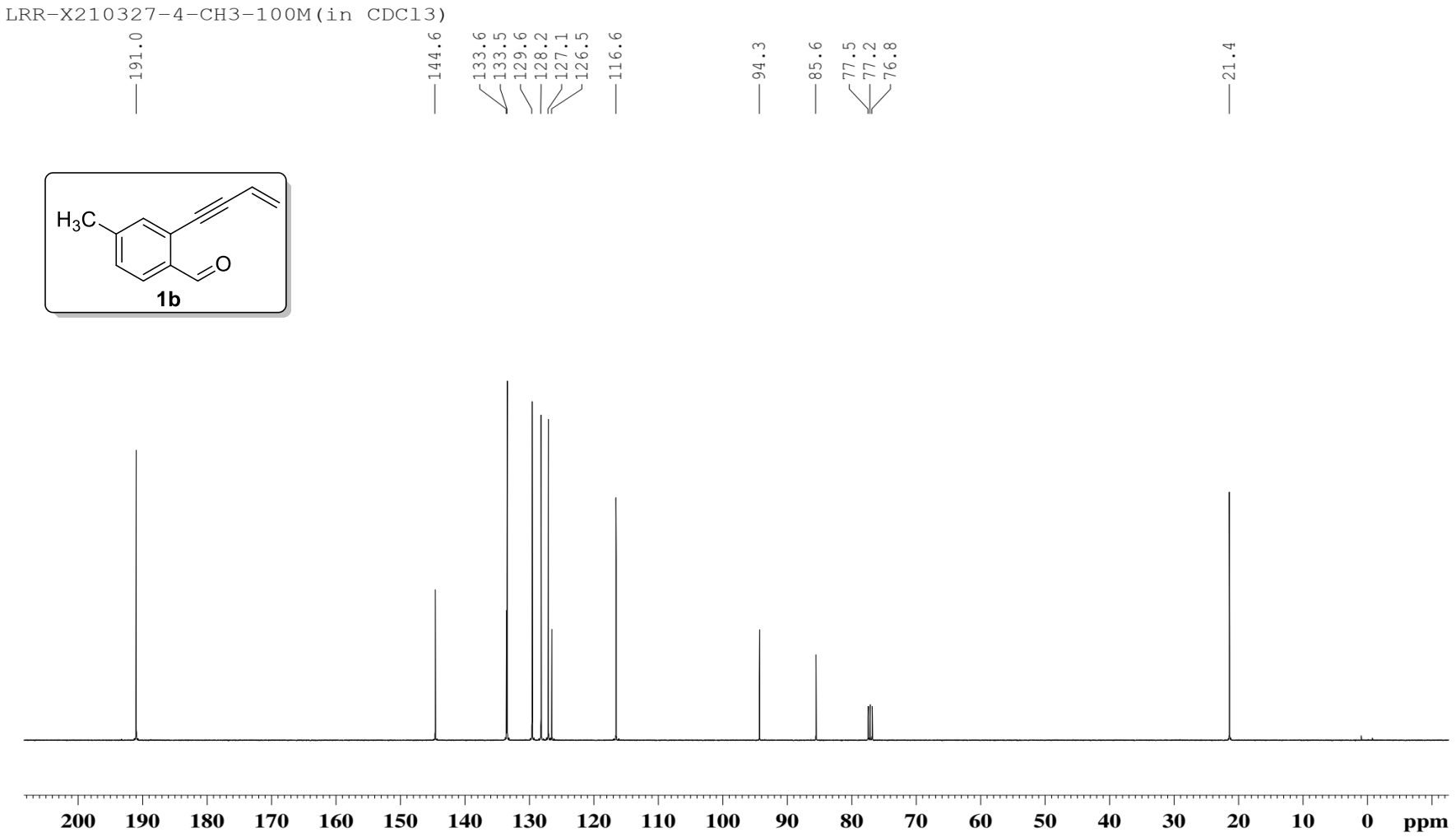
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1a-D



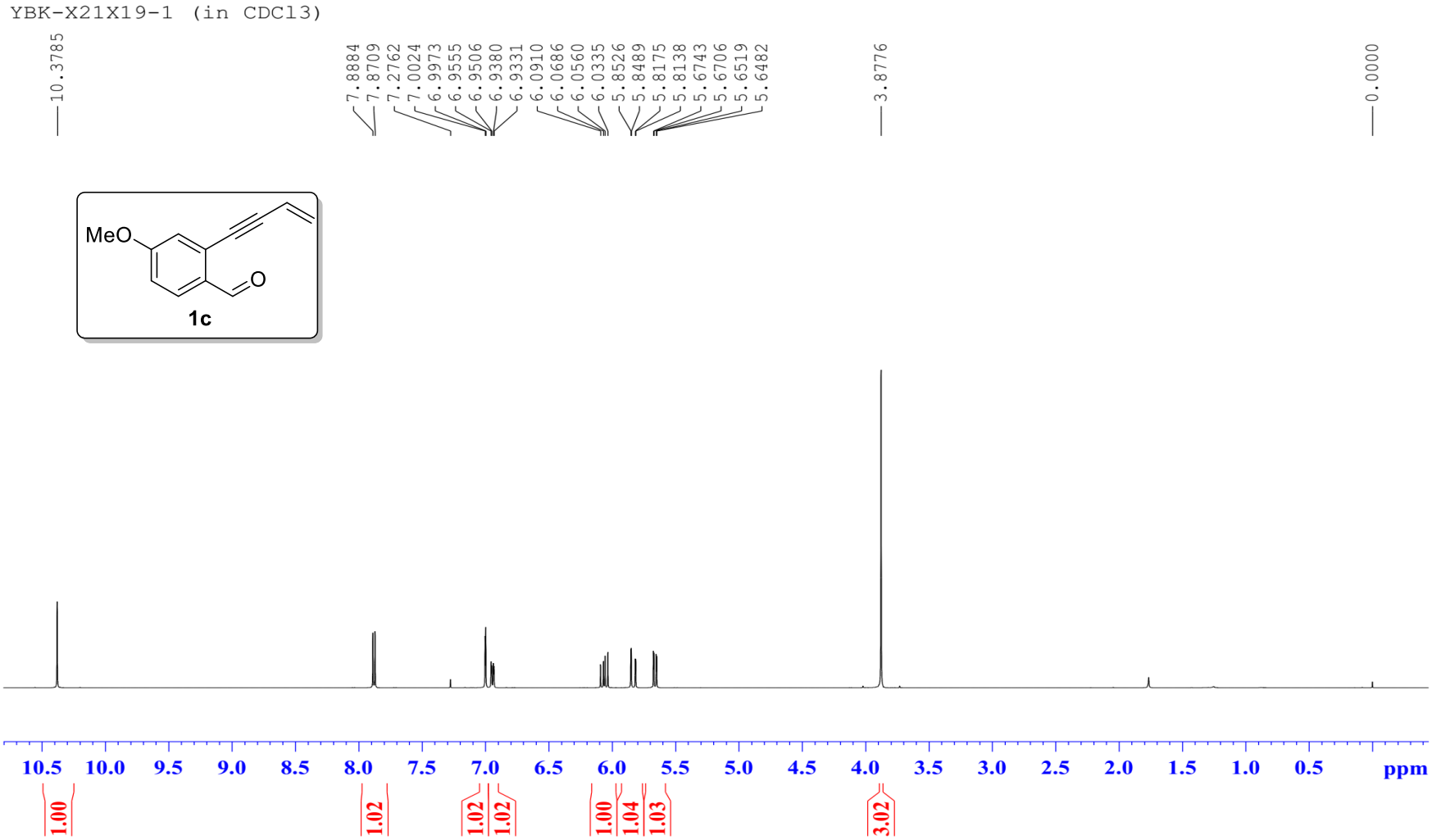
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1b



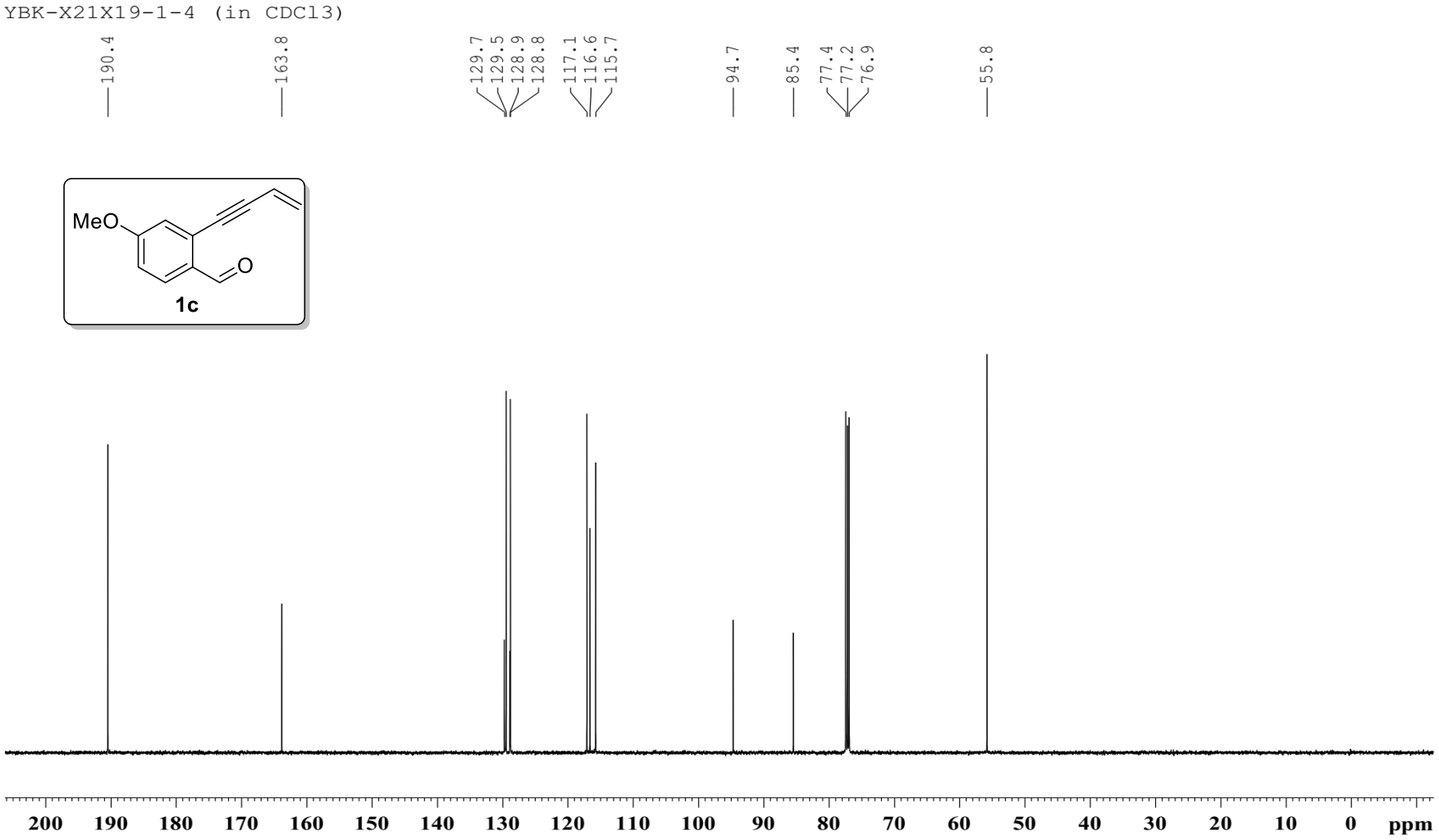
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1b



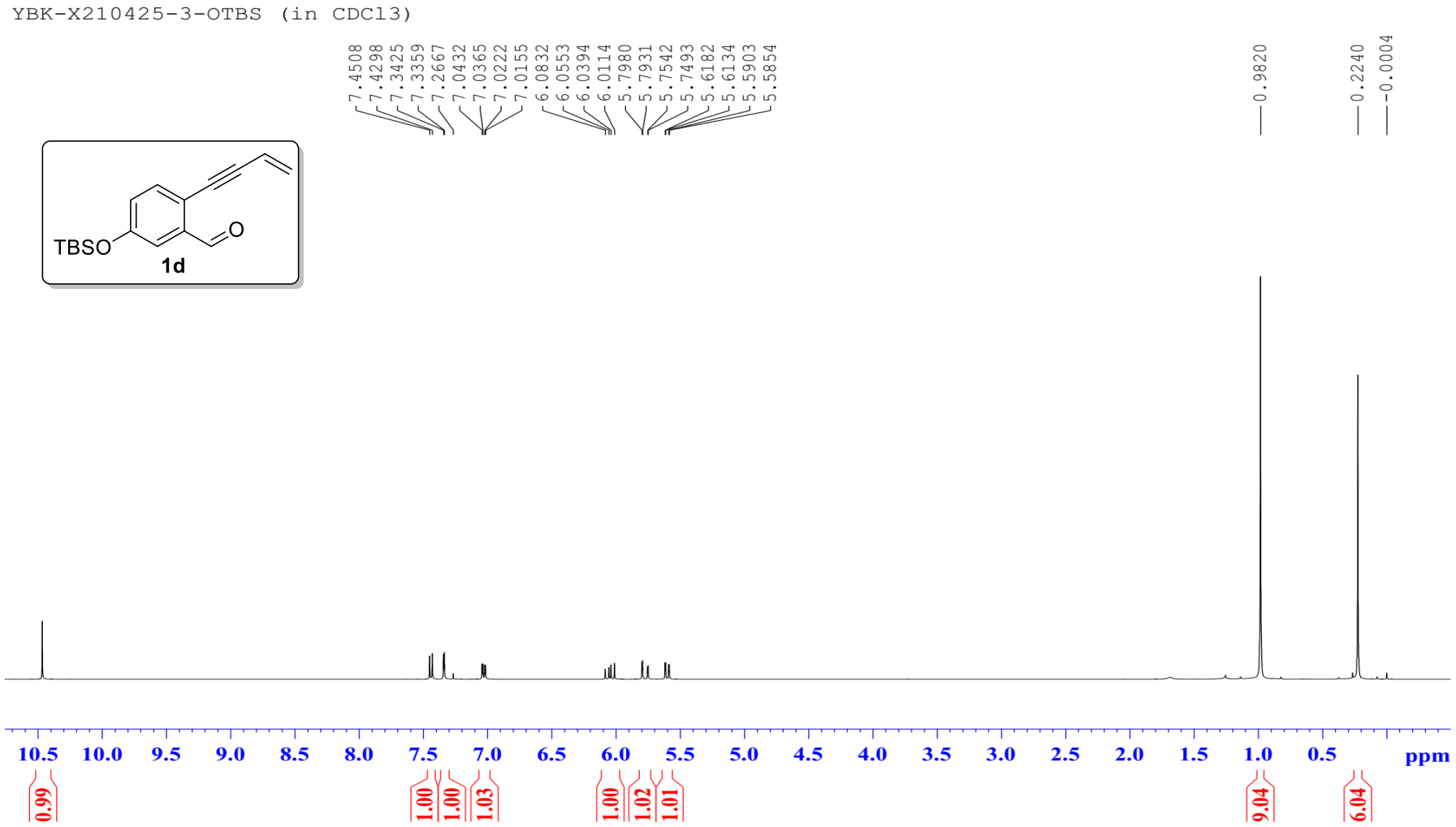
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1c



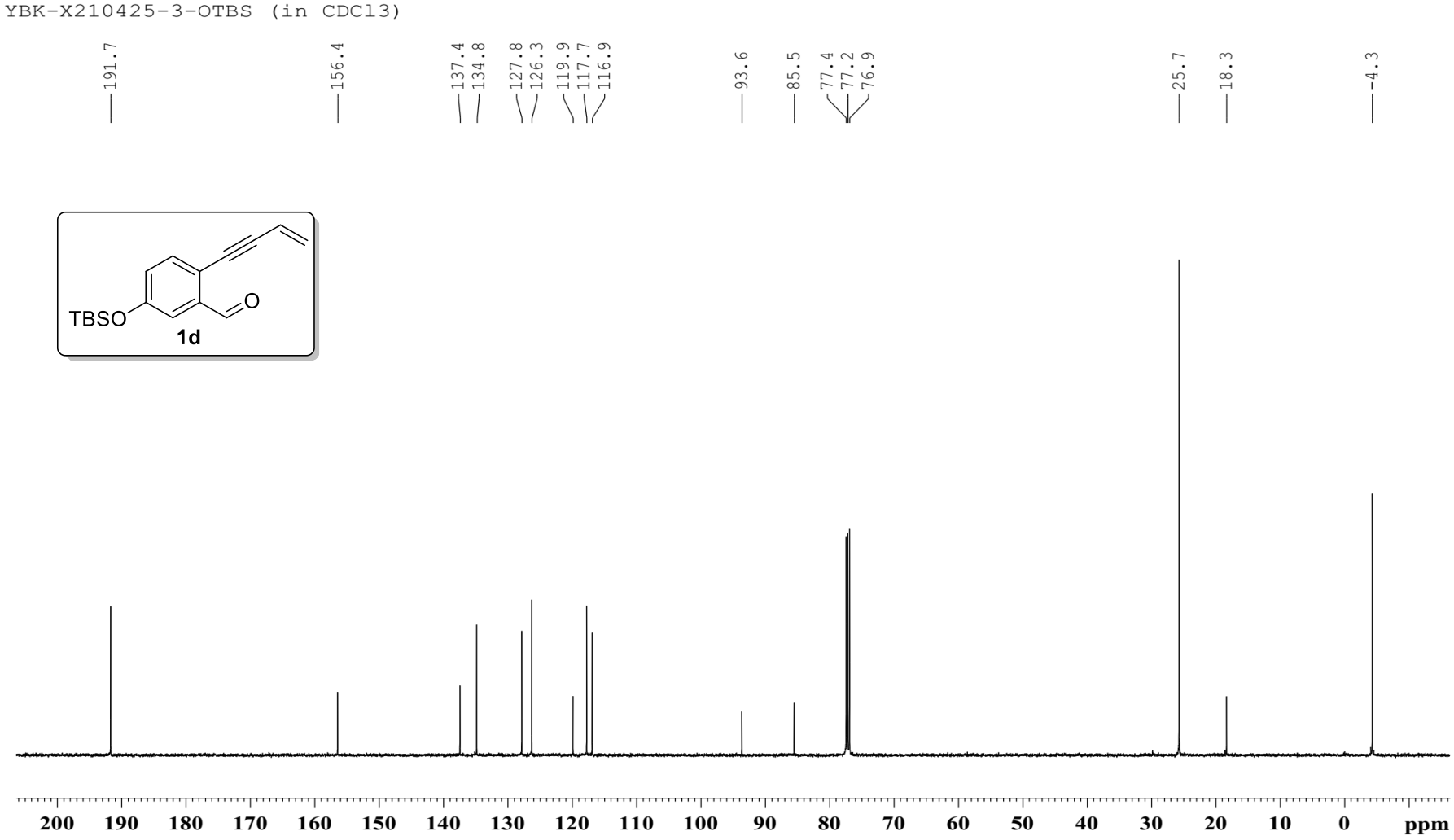
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1c



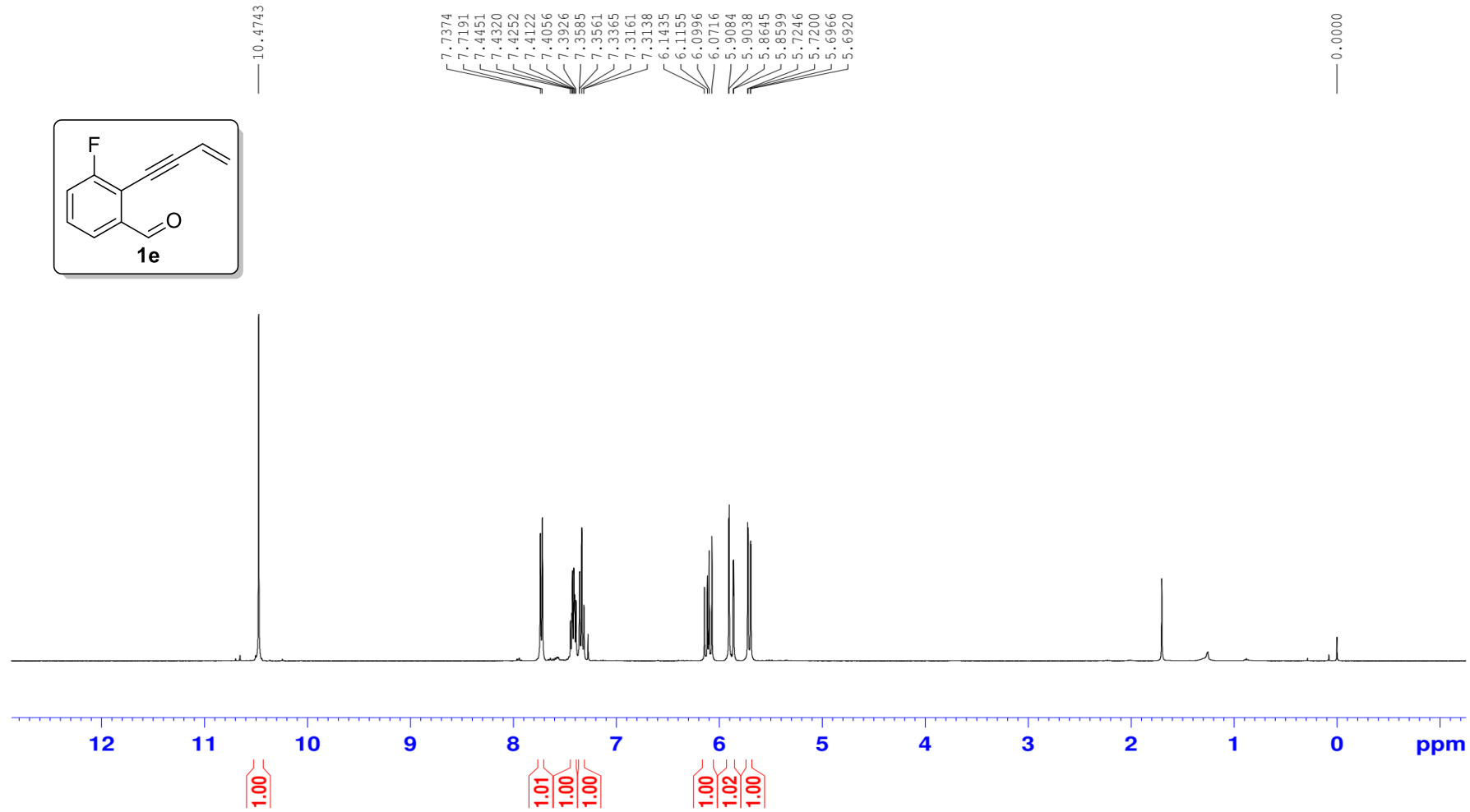
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1d



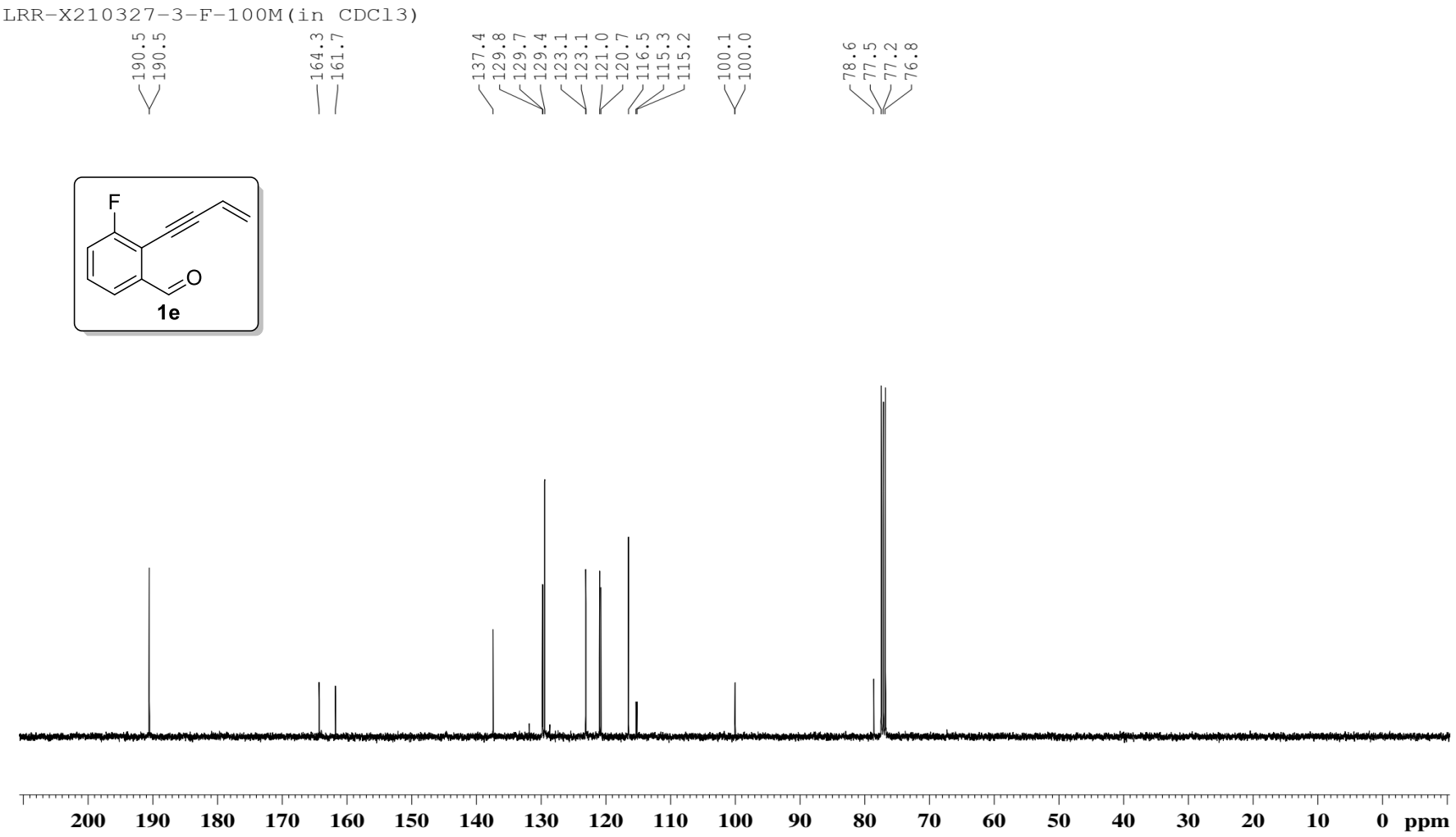
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1d



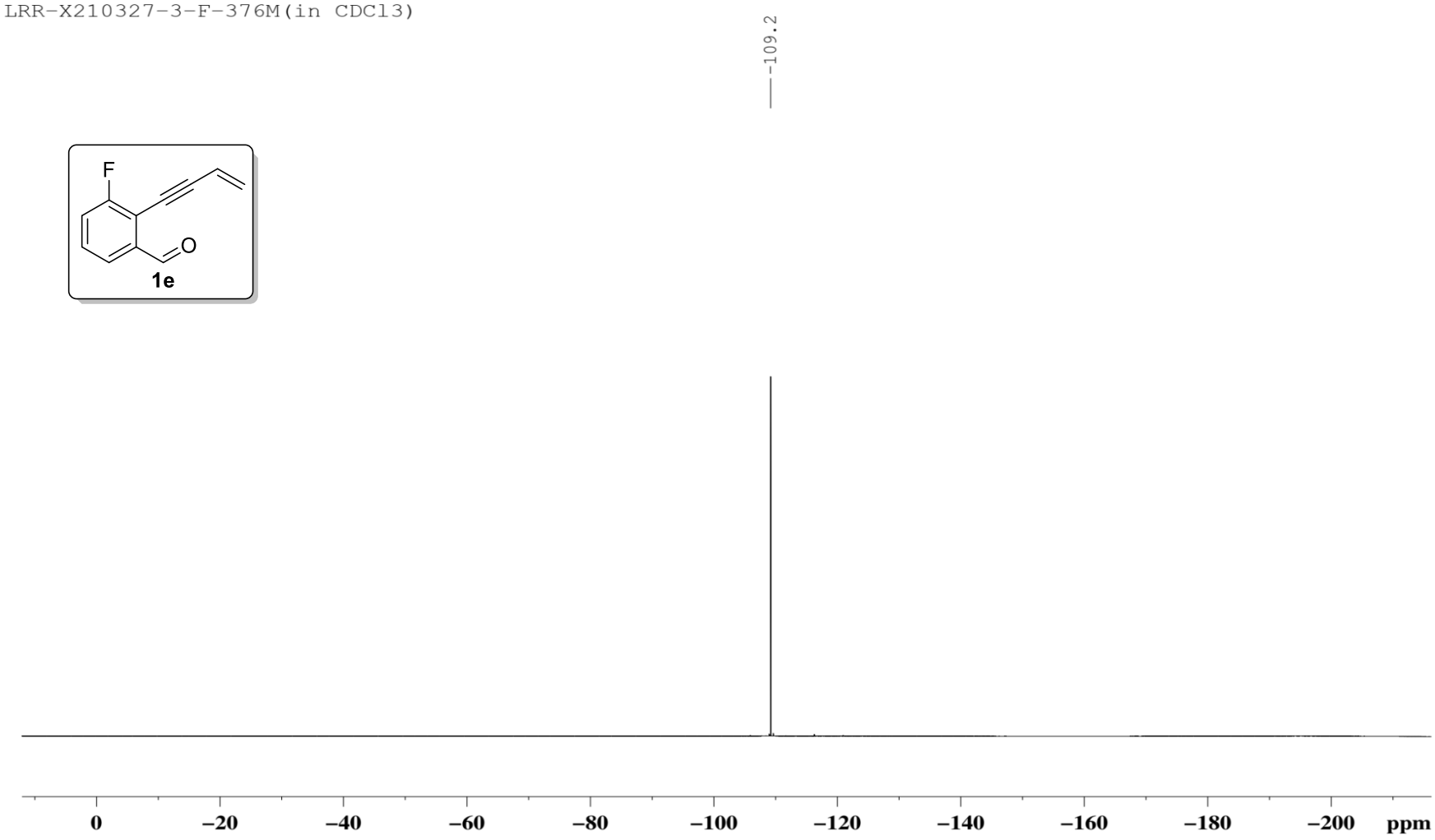
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1e



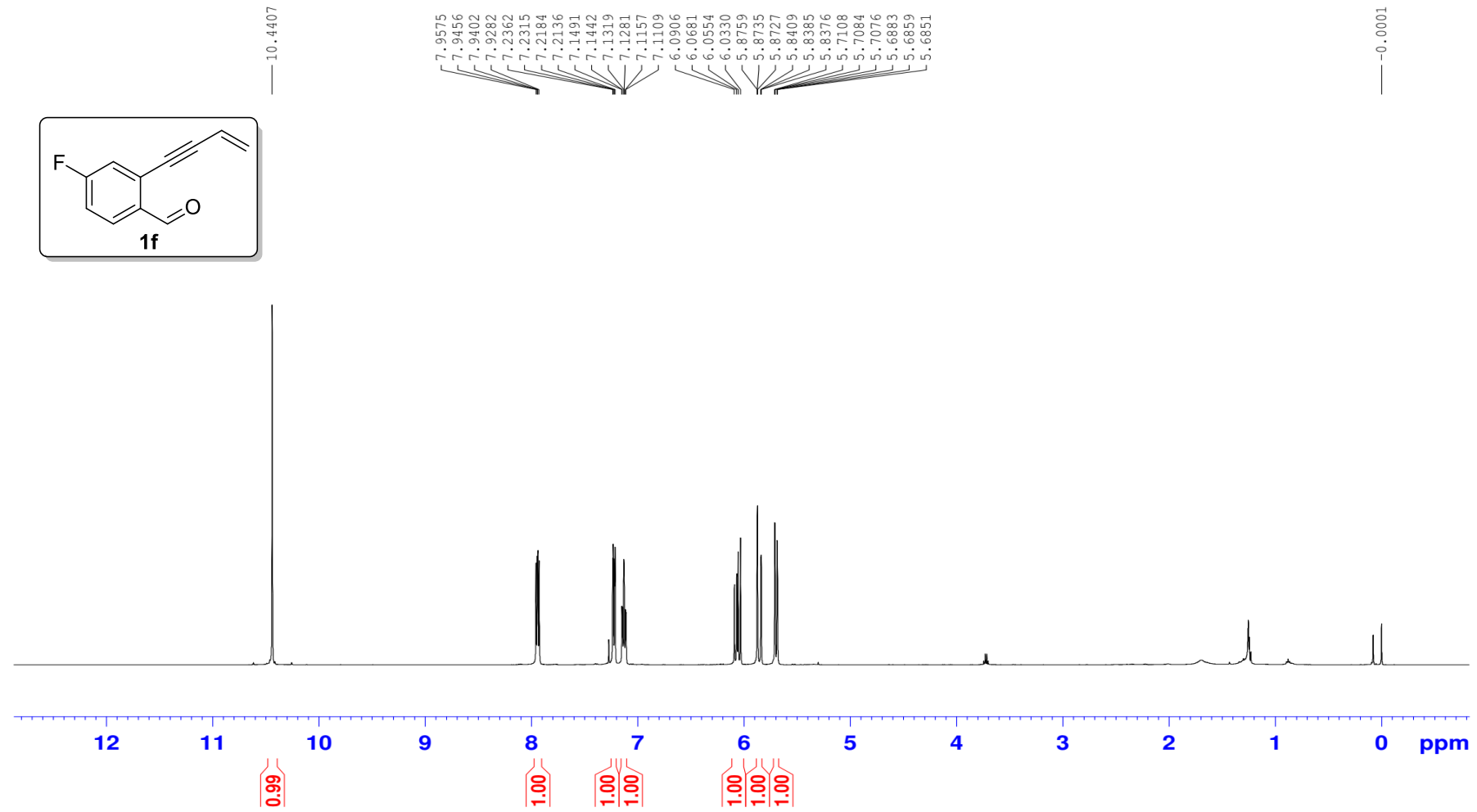
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1e



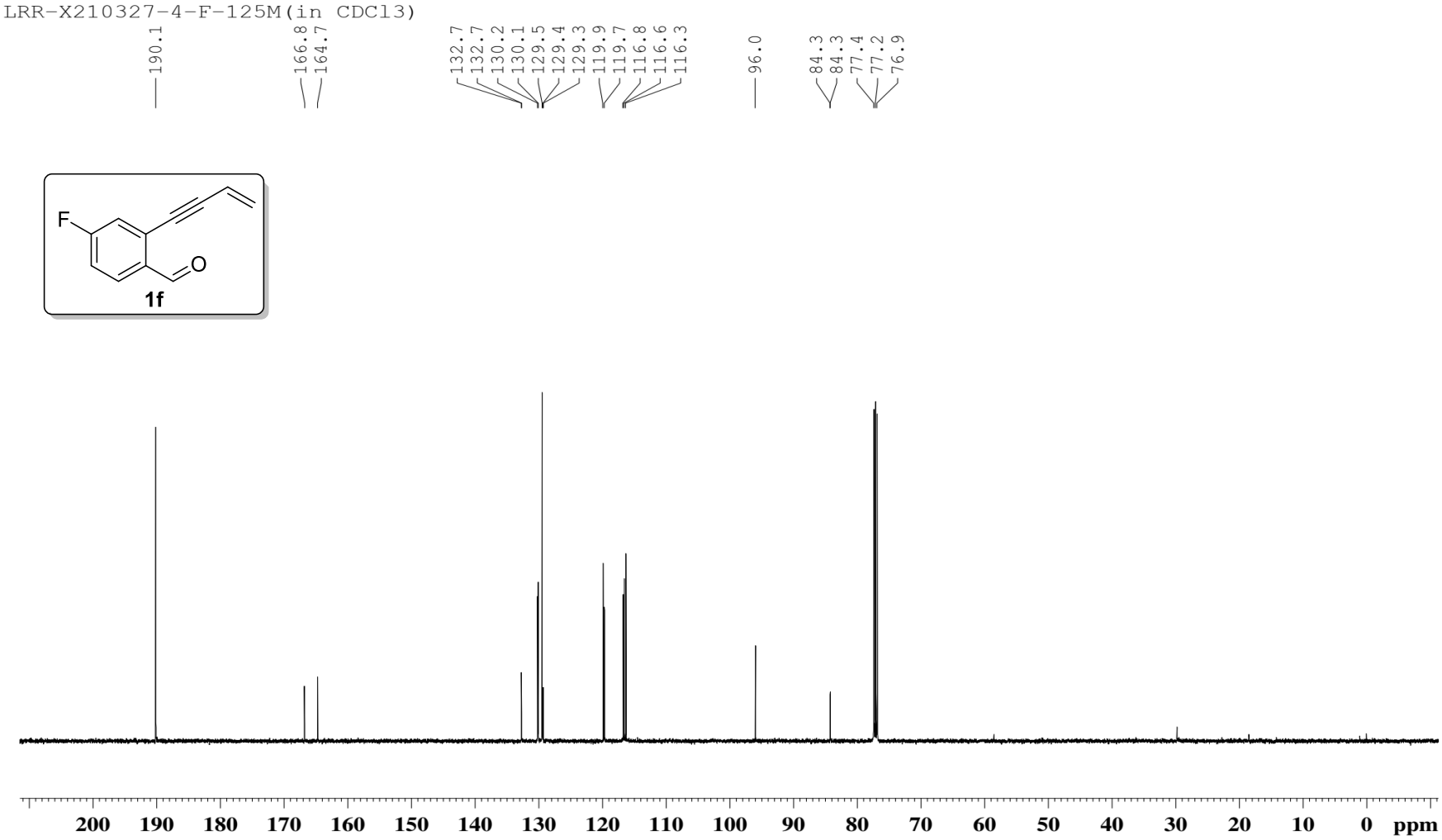
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1e



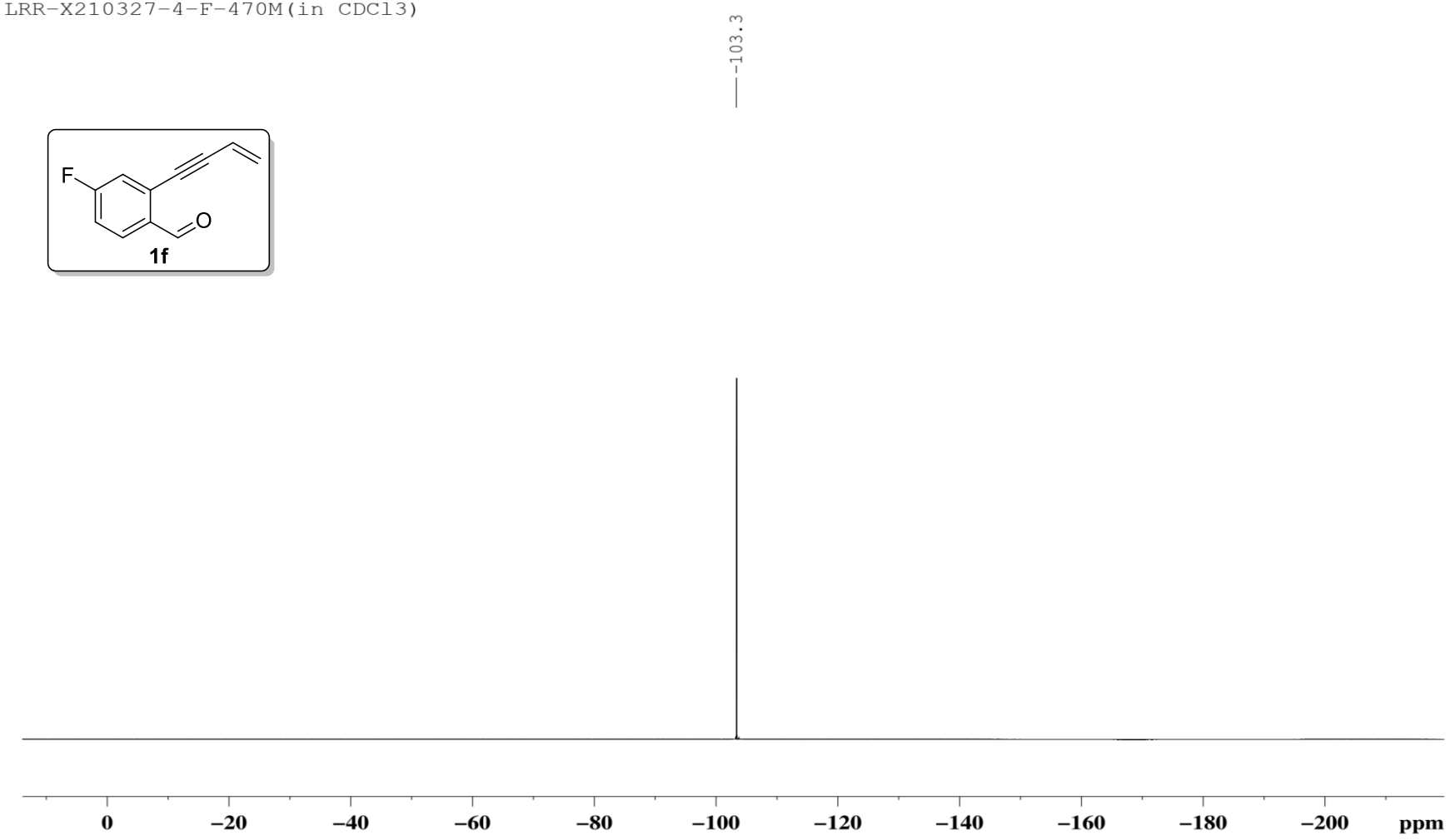
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1f



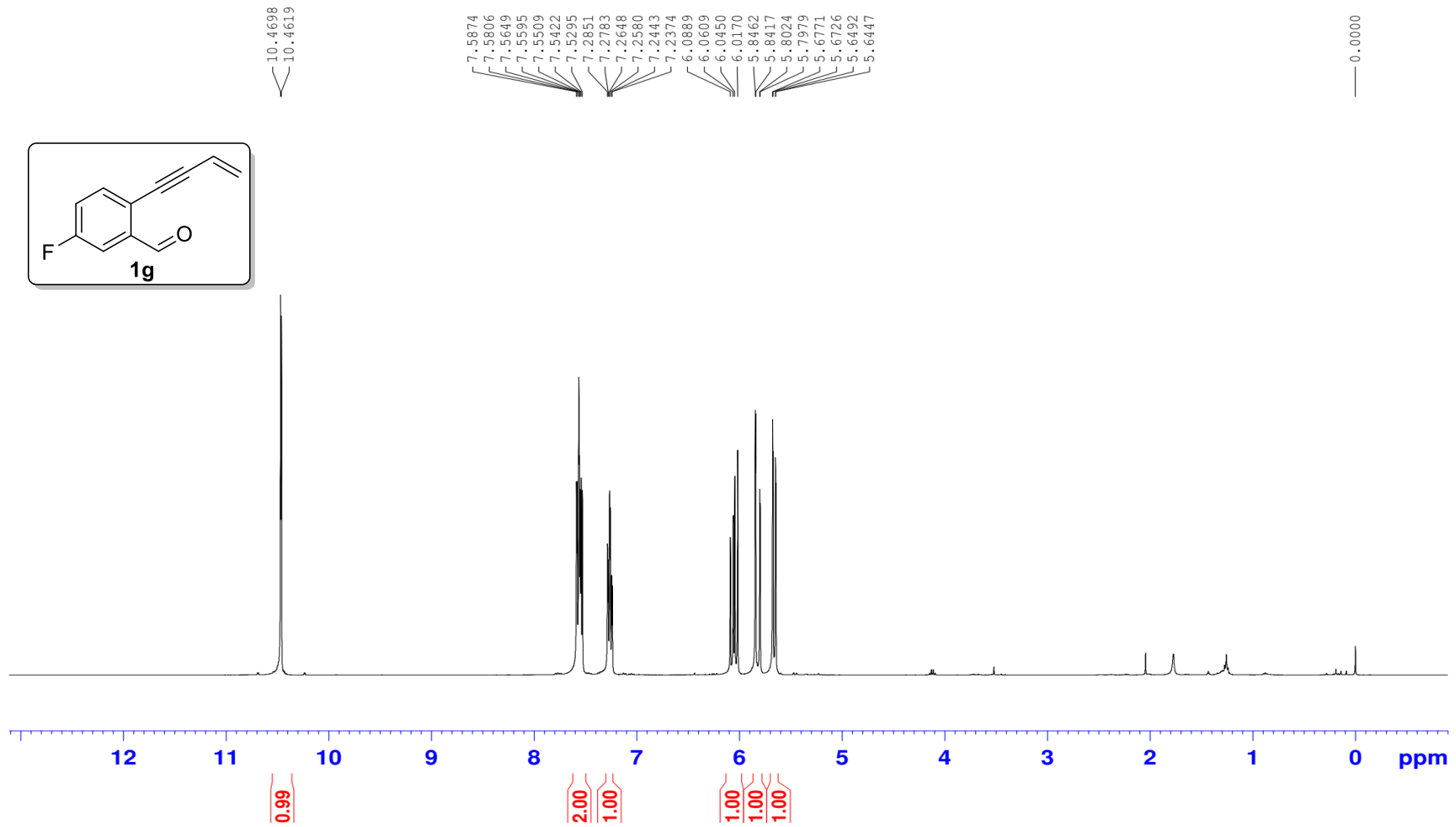
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1f



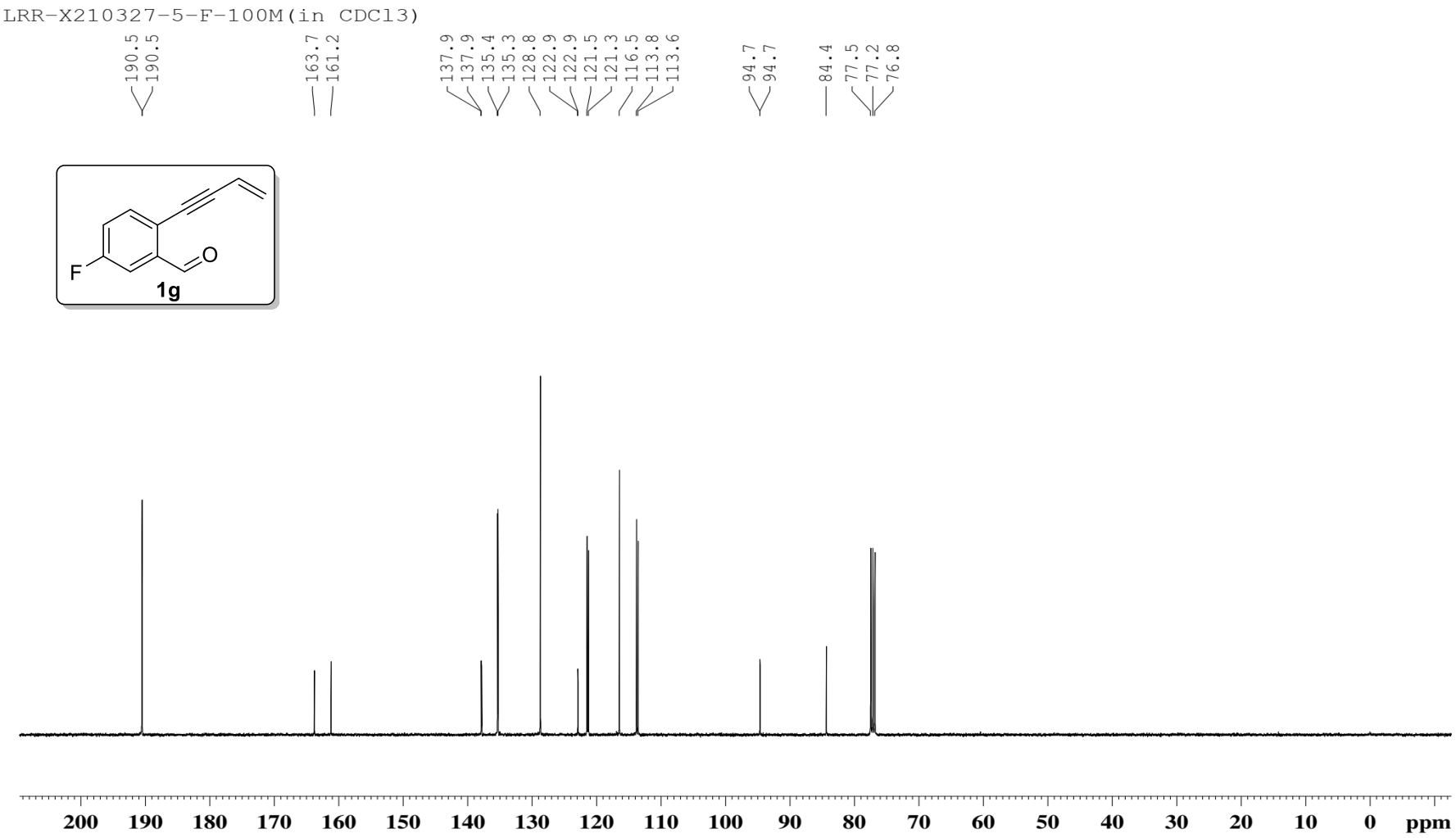
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 1f



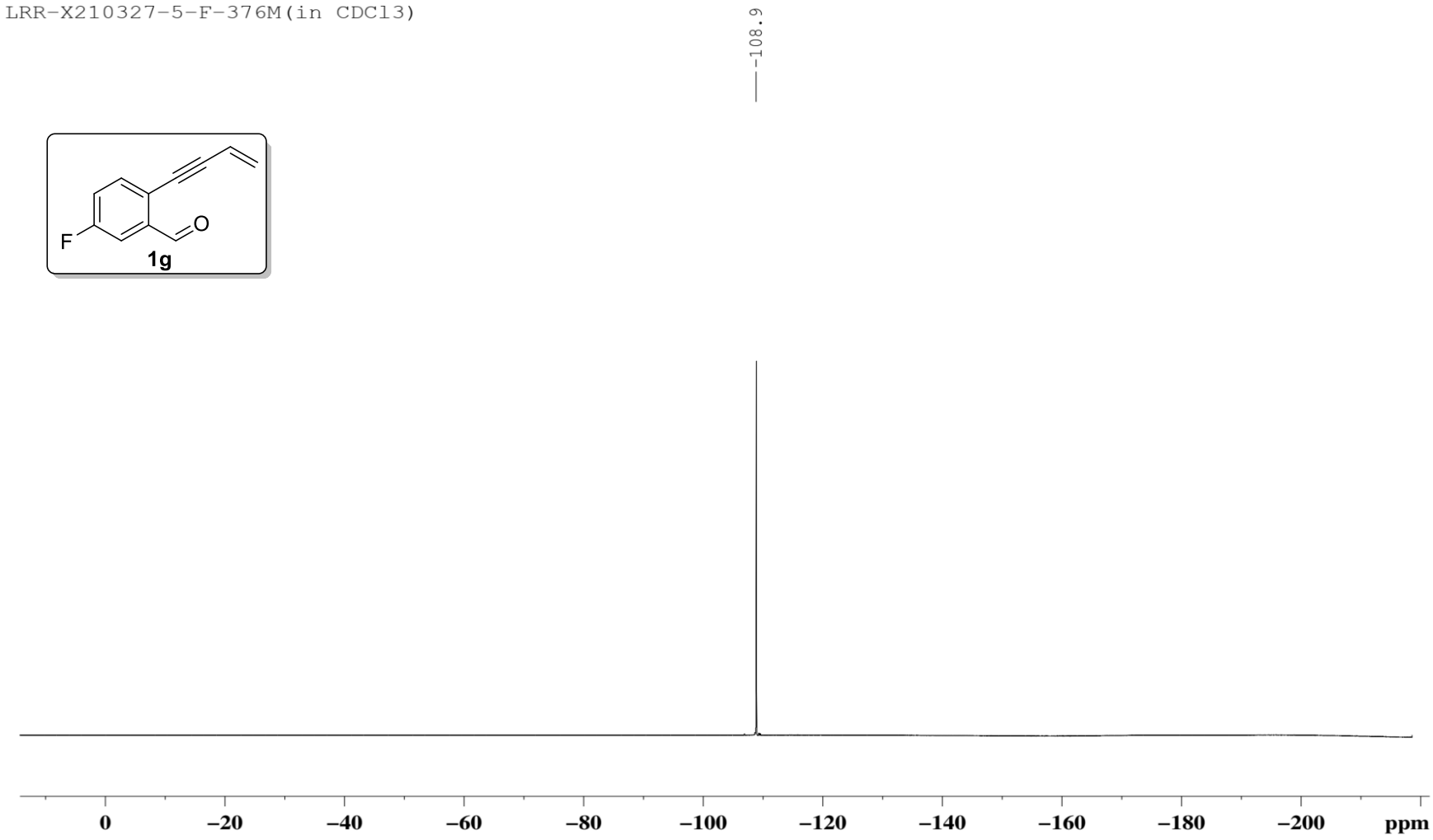
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1g



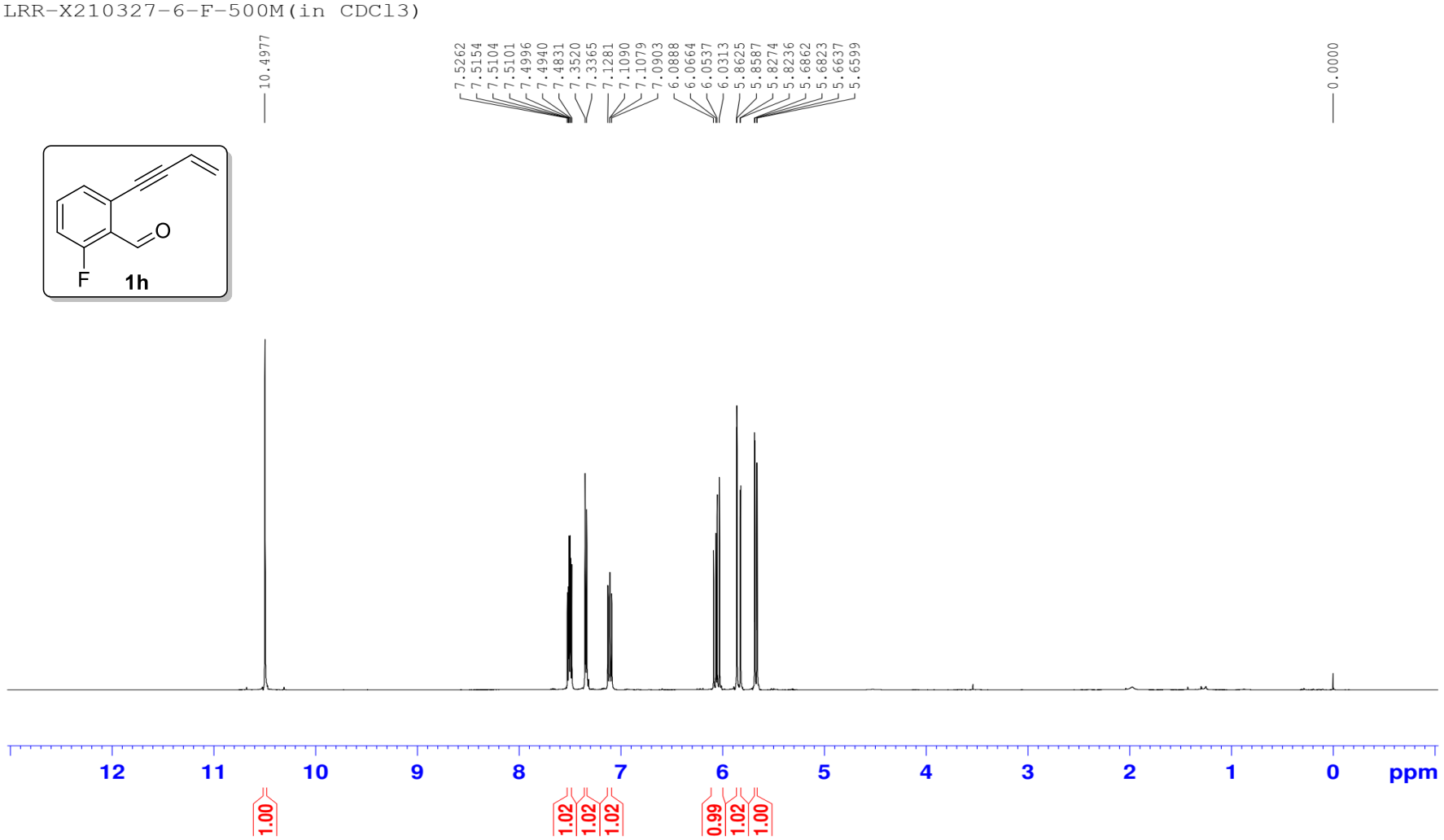
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1g



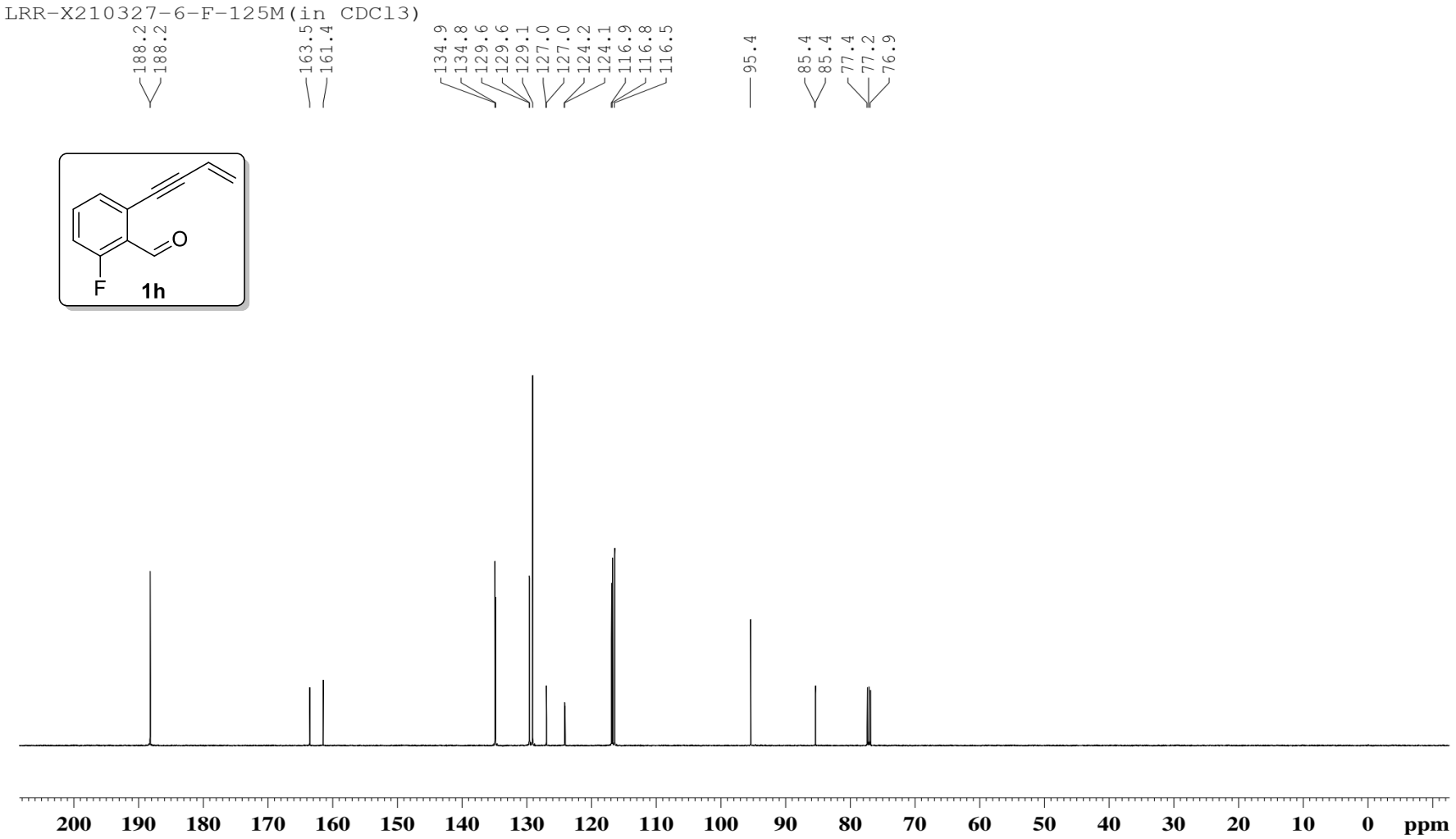
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1g



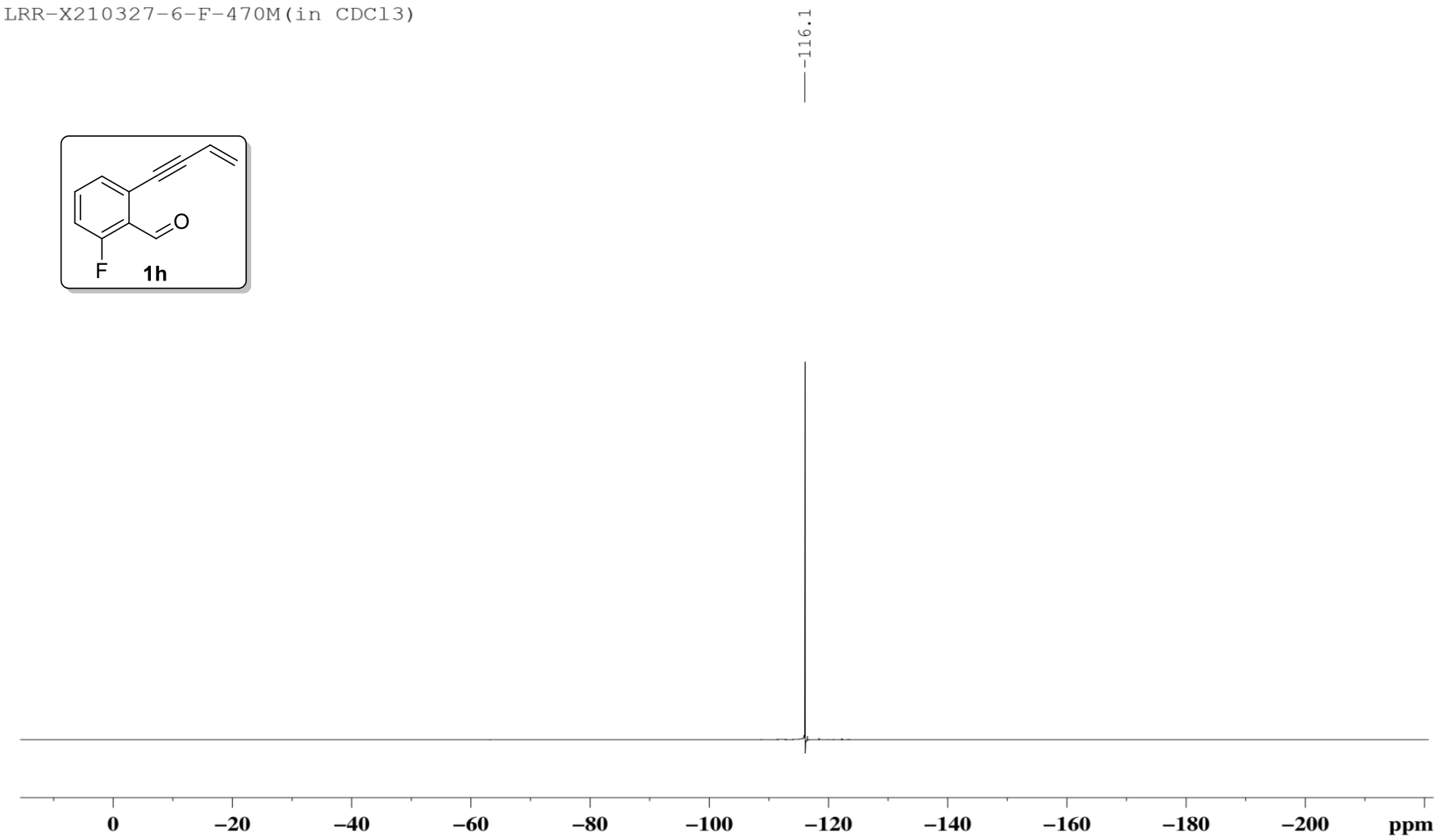
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1h



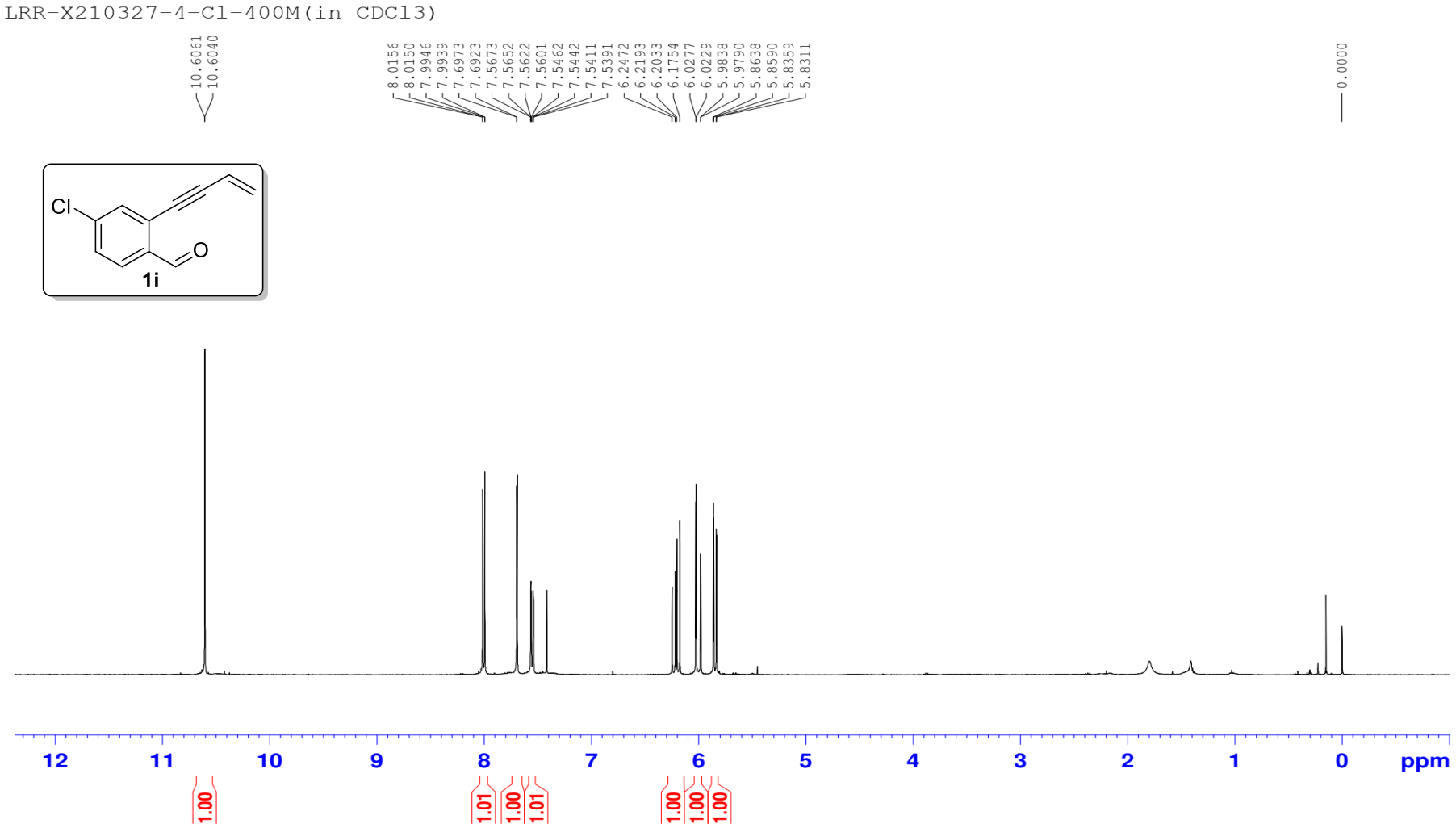
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1h



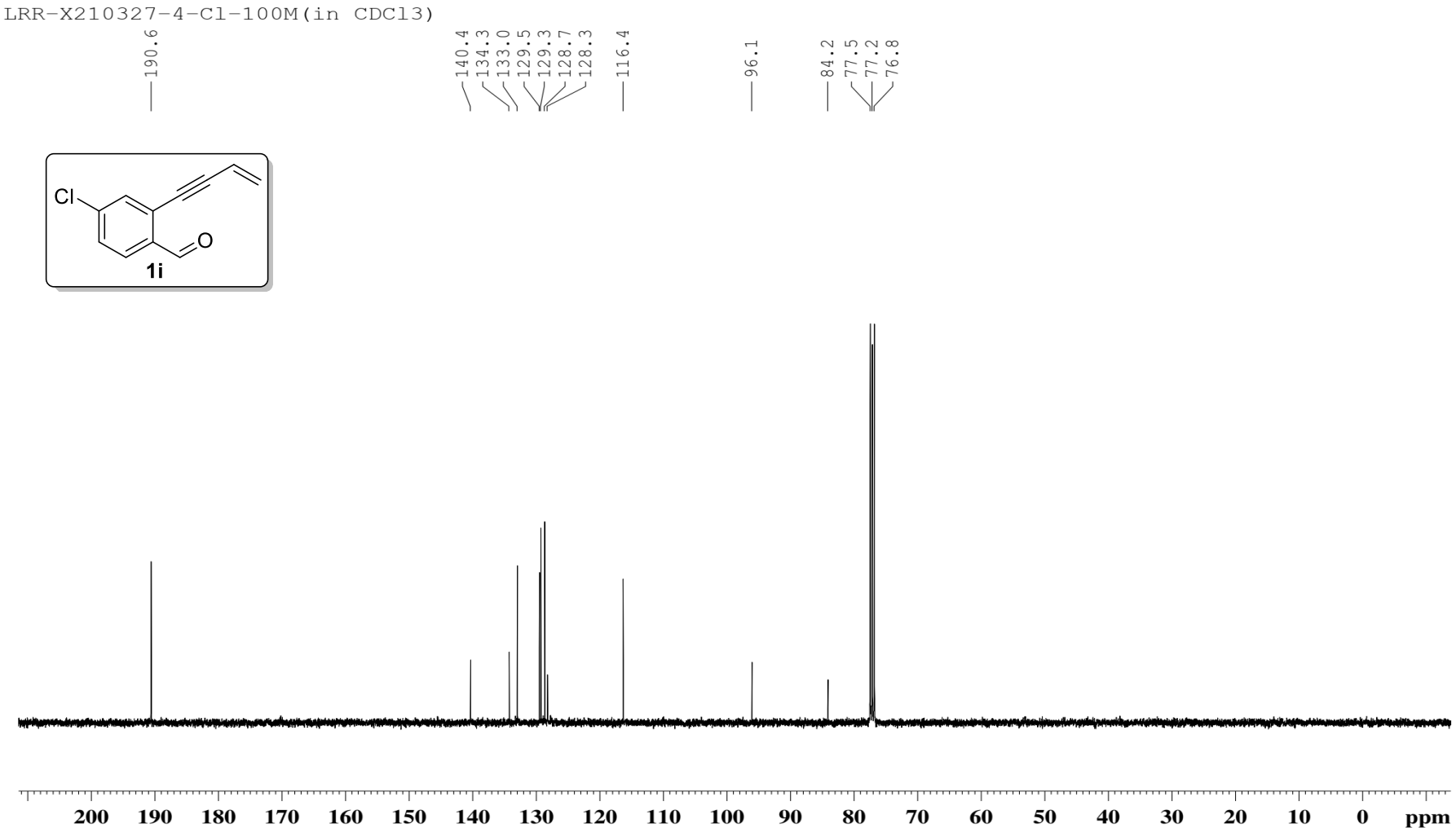
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 1h



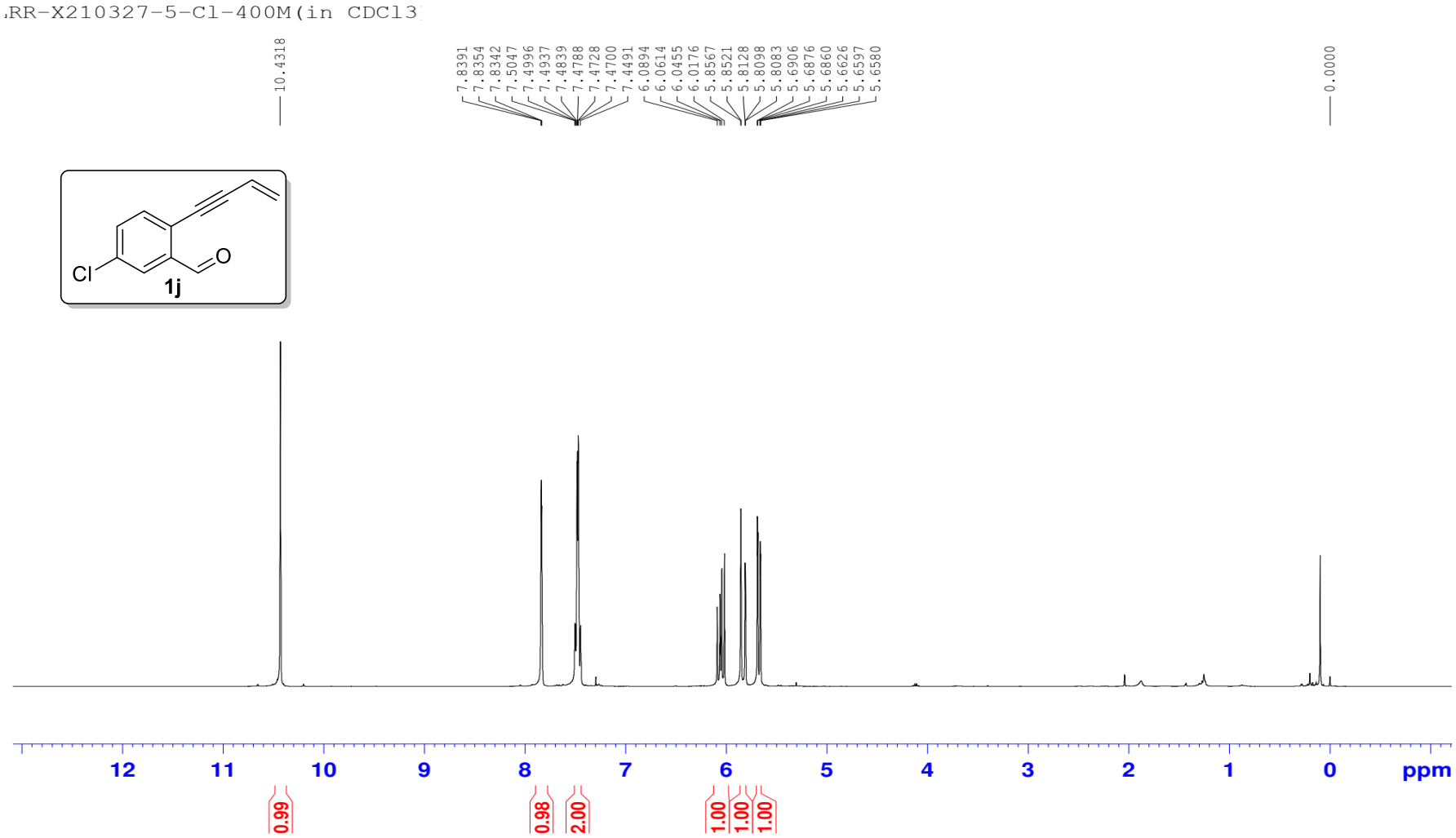
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1i



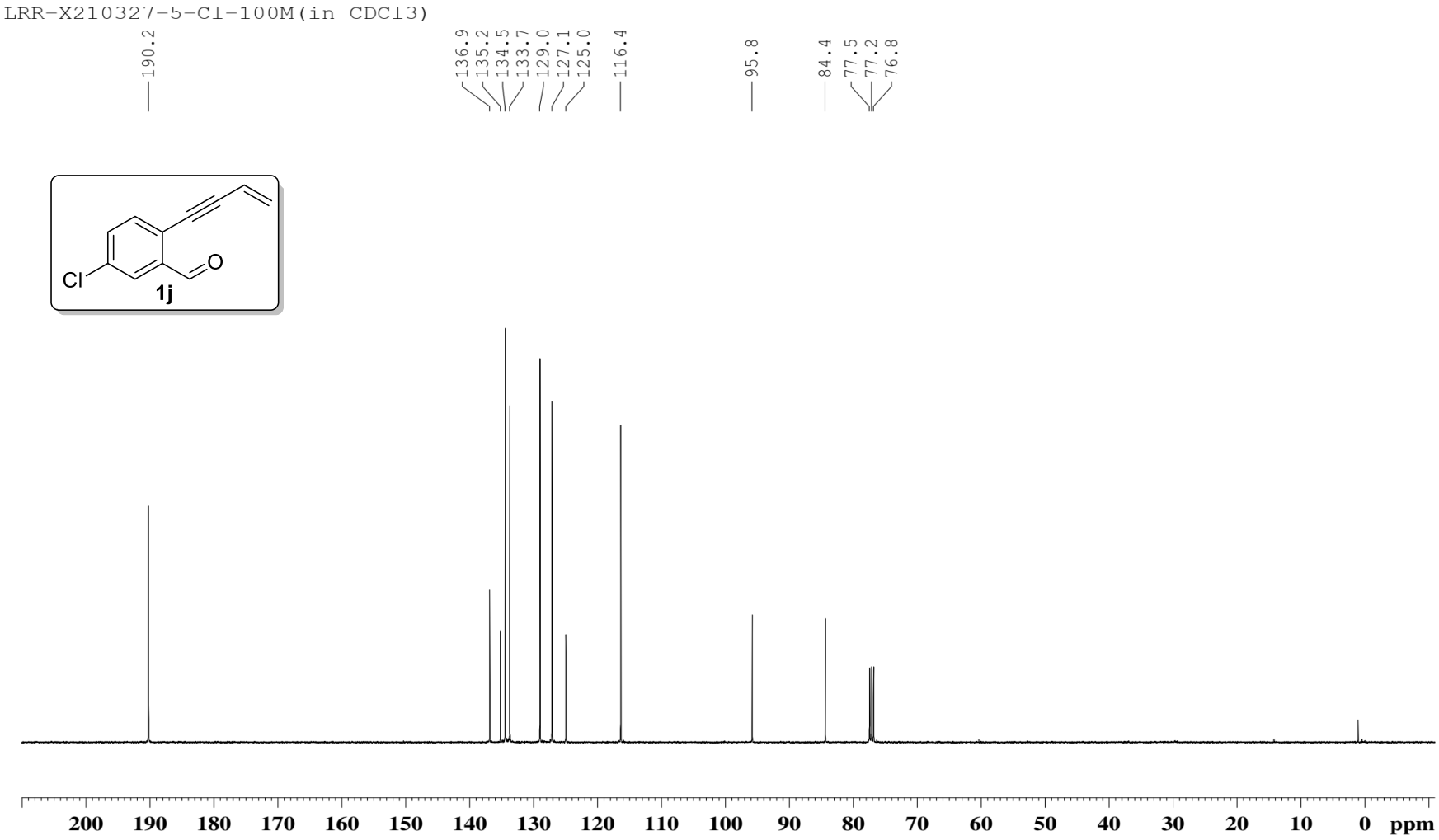
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1i



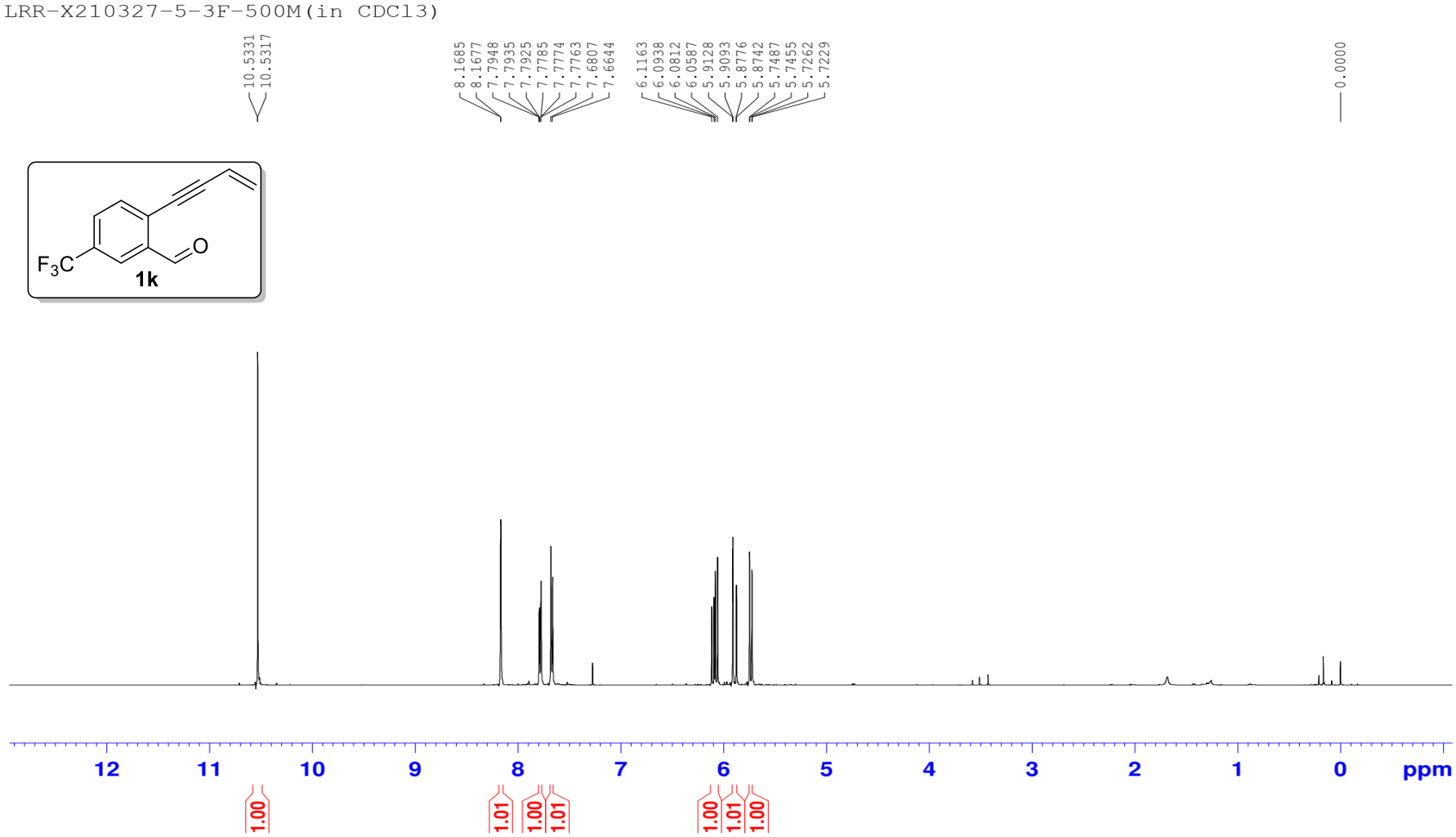
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1j



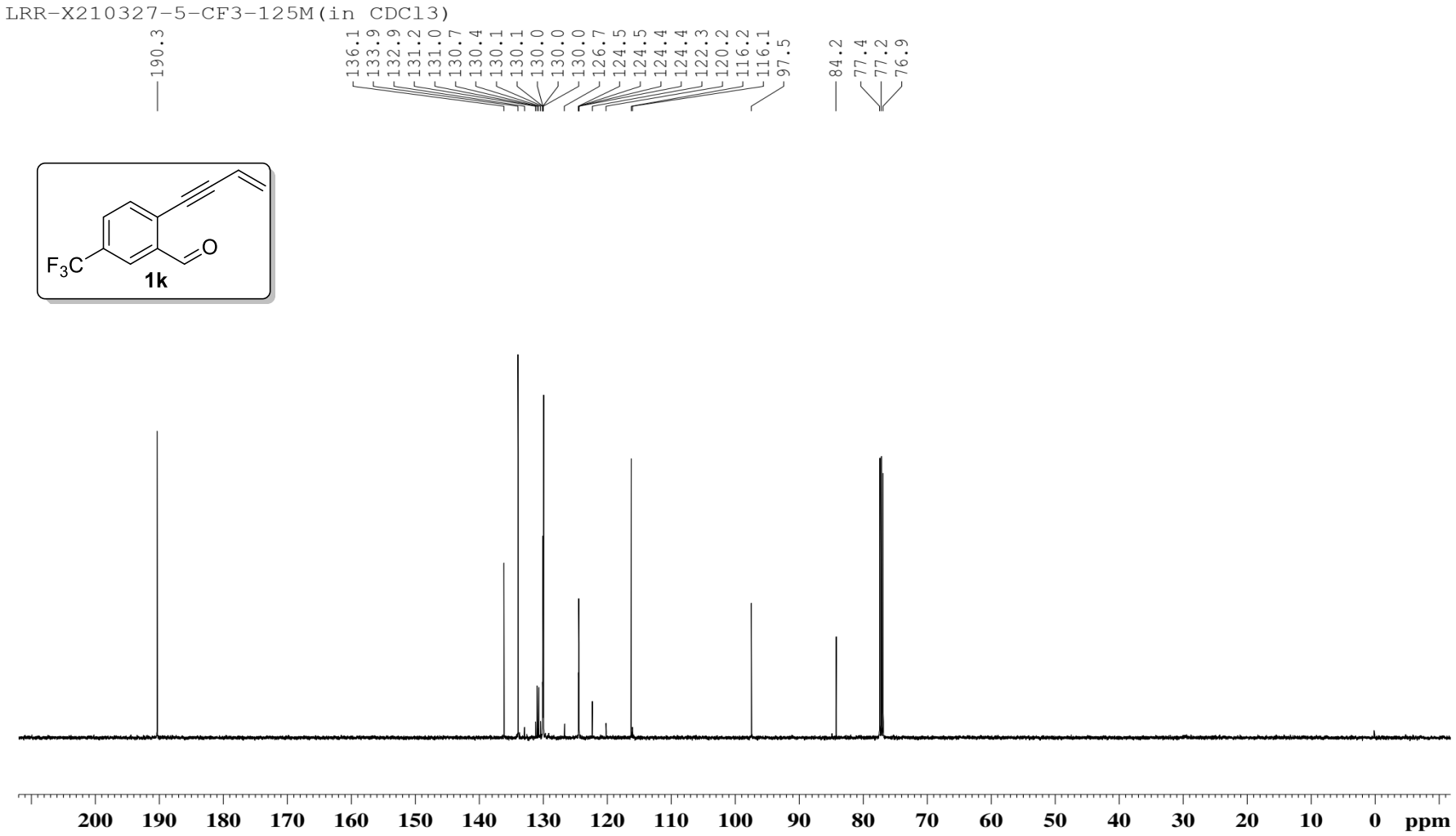
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1j



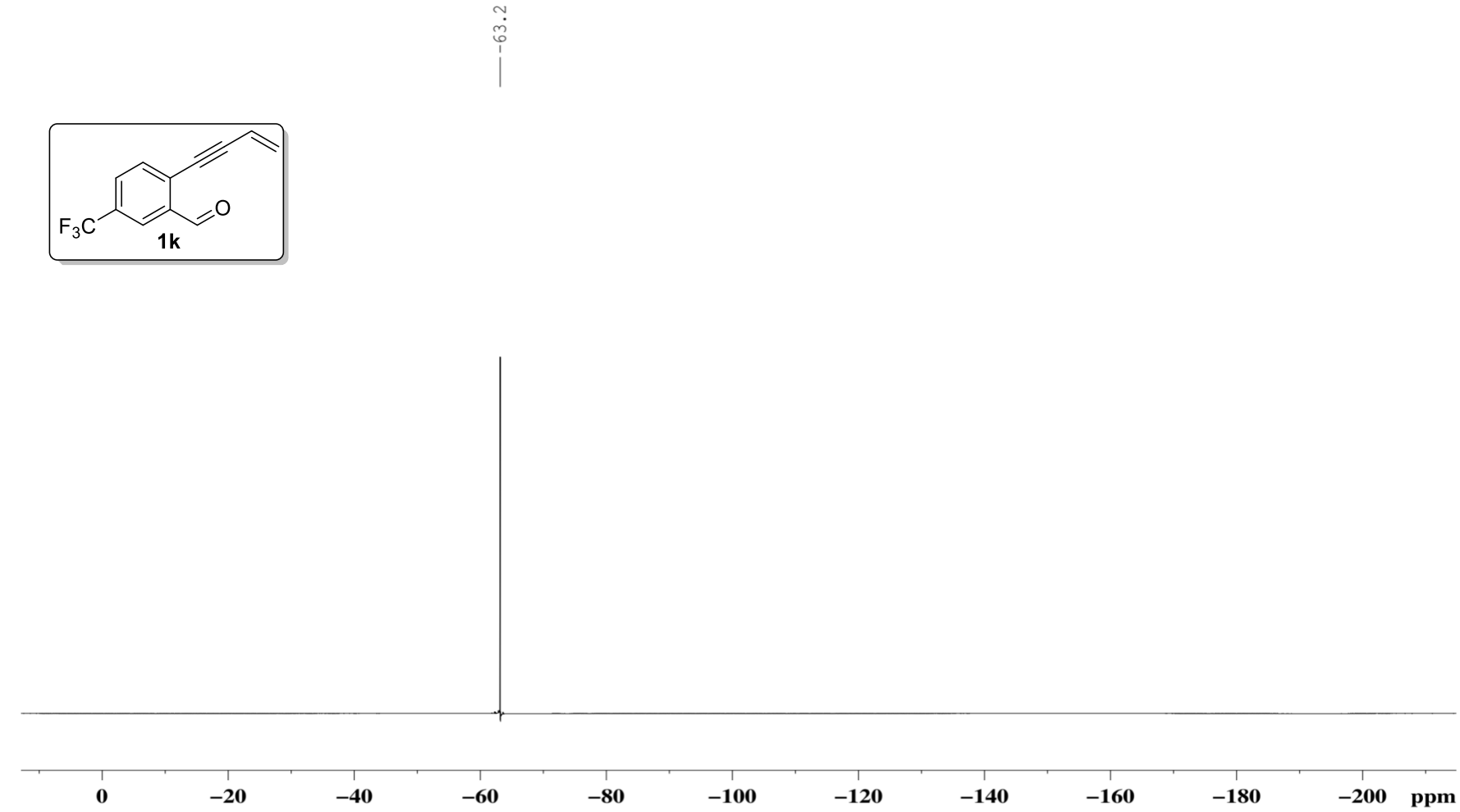
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1k



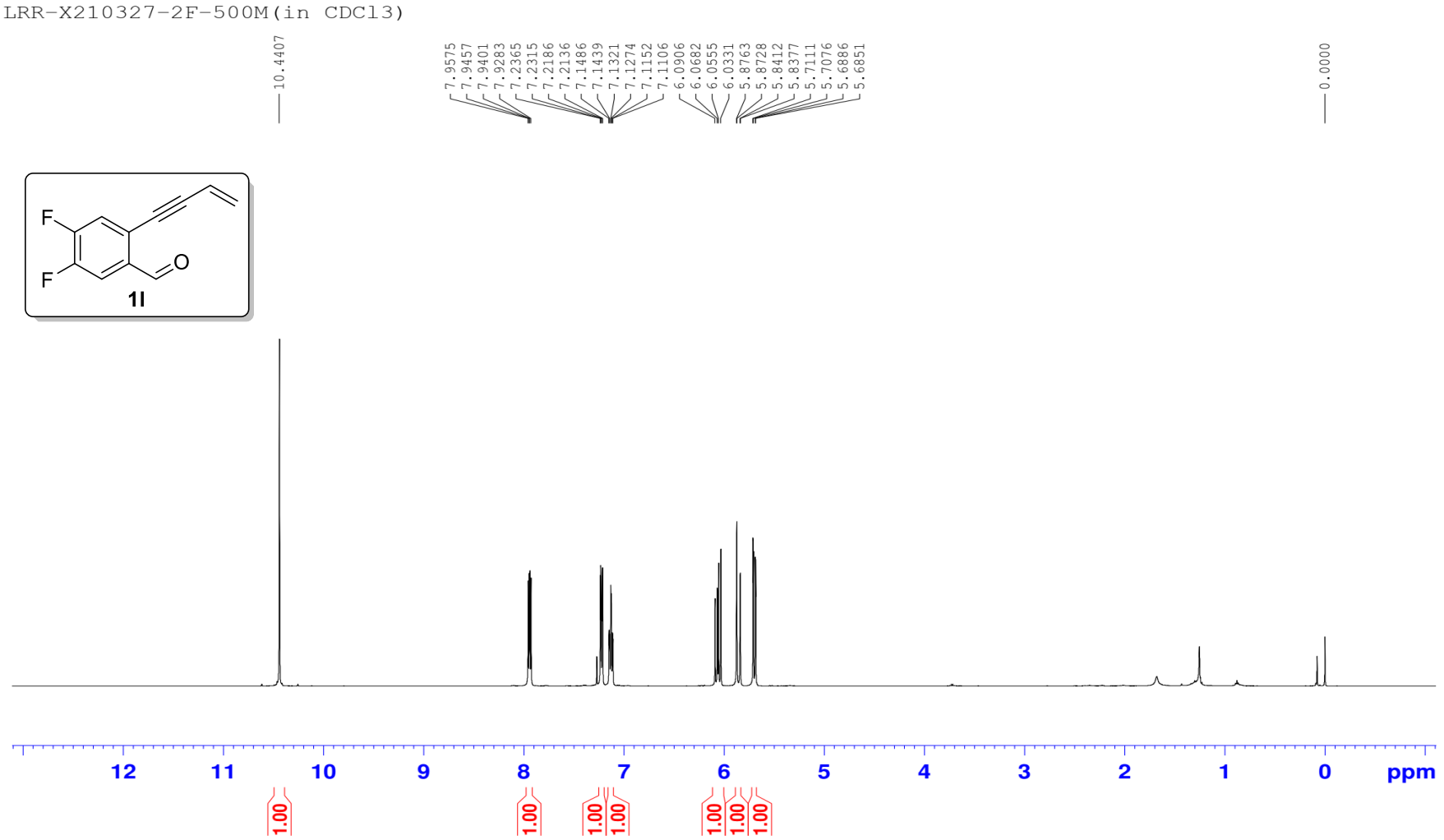
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1k



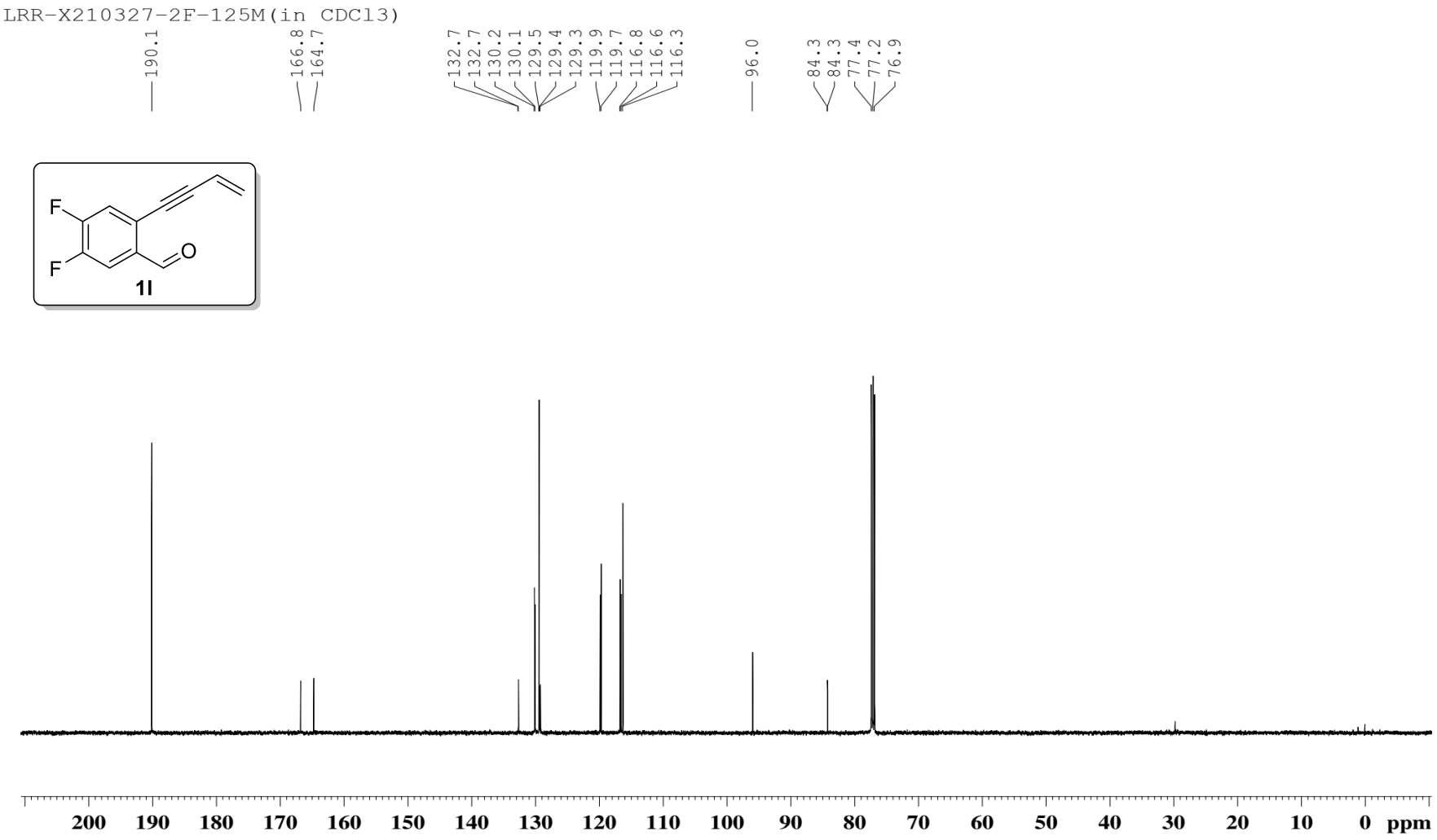
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 1k



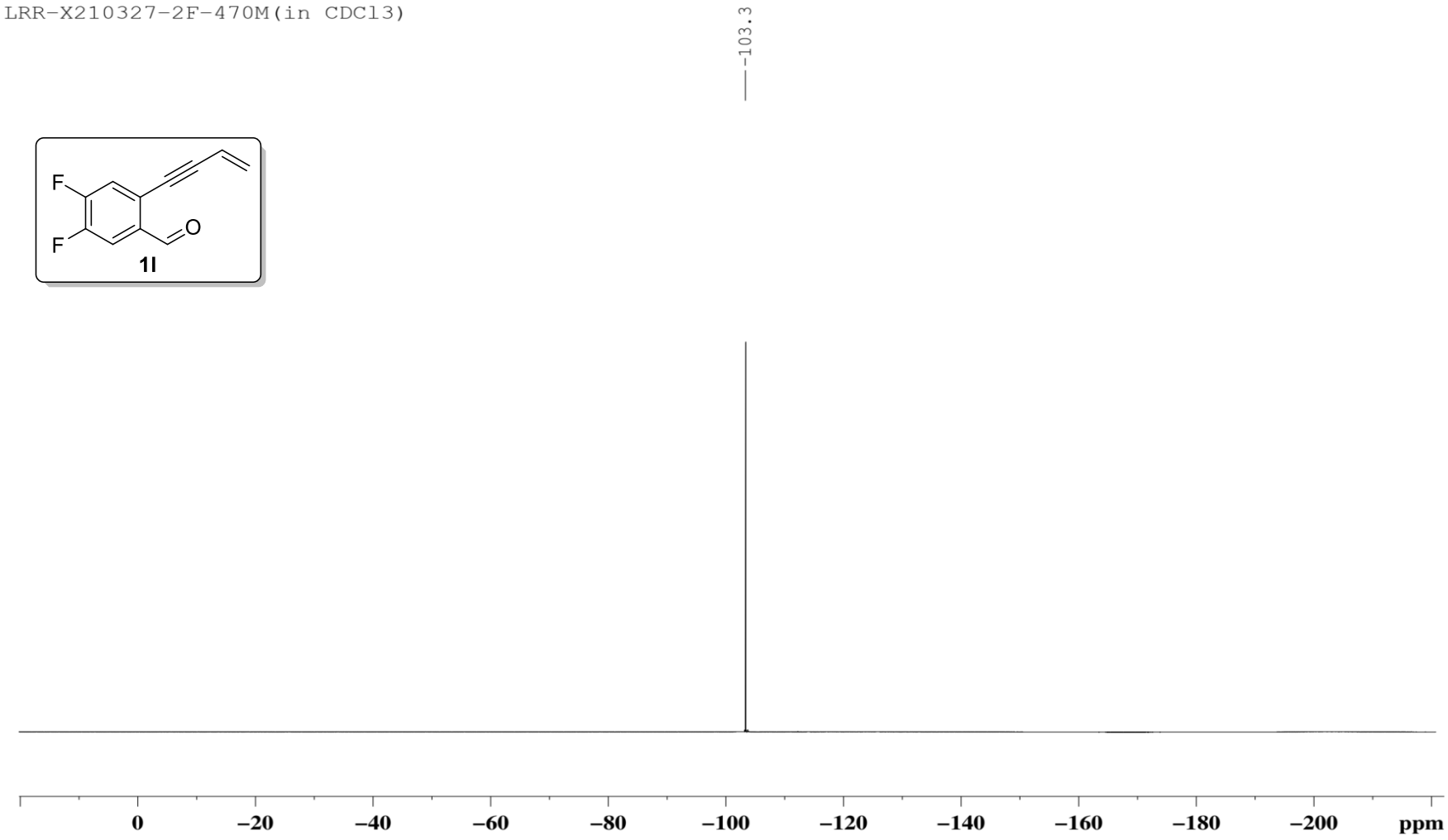
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1l



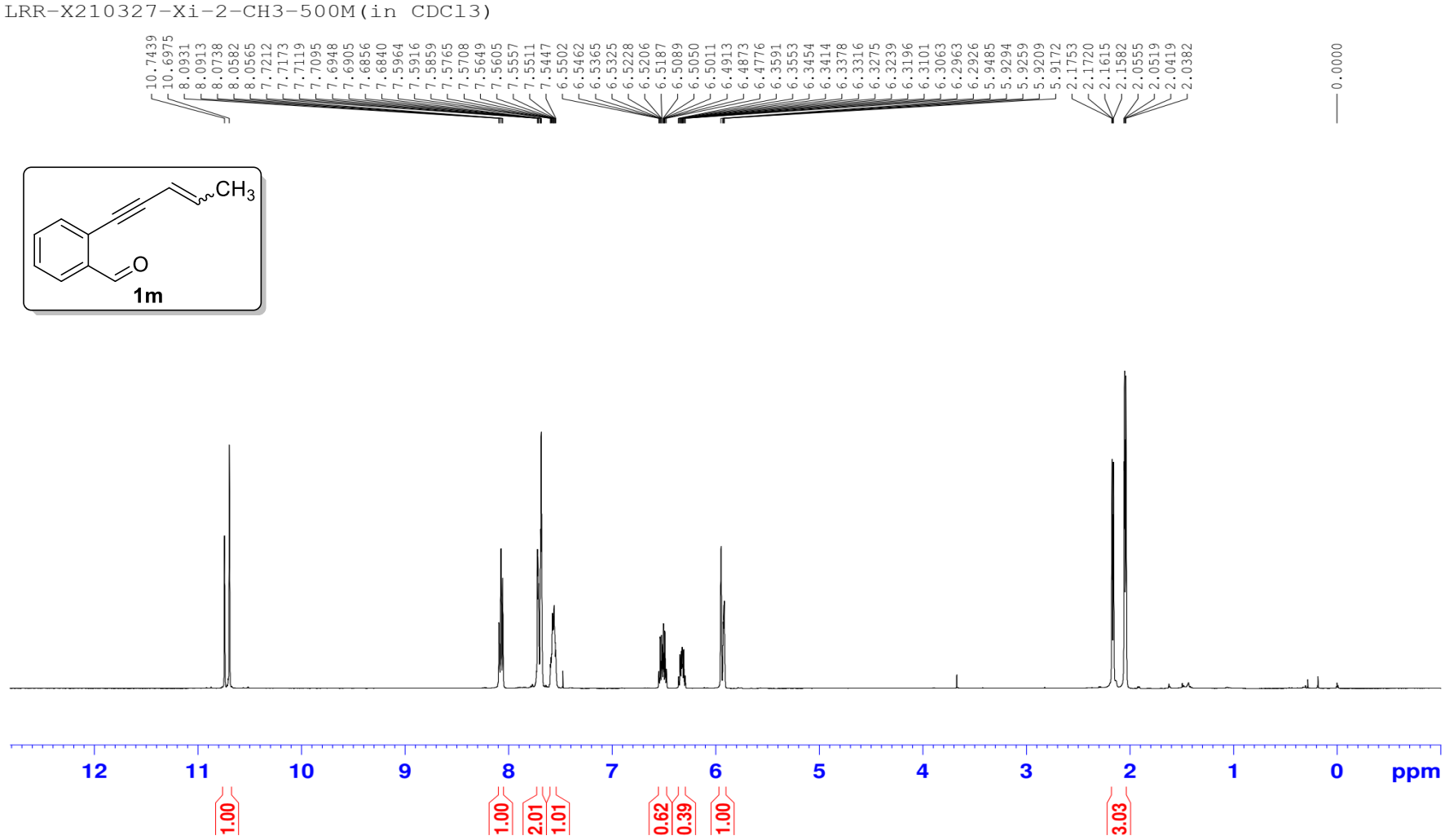
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1l



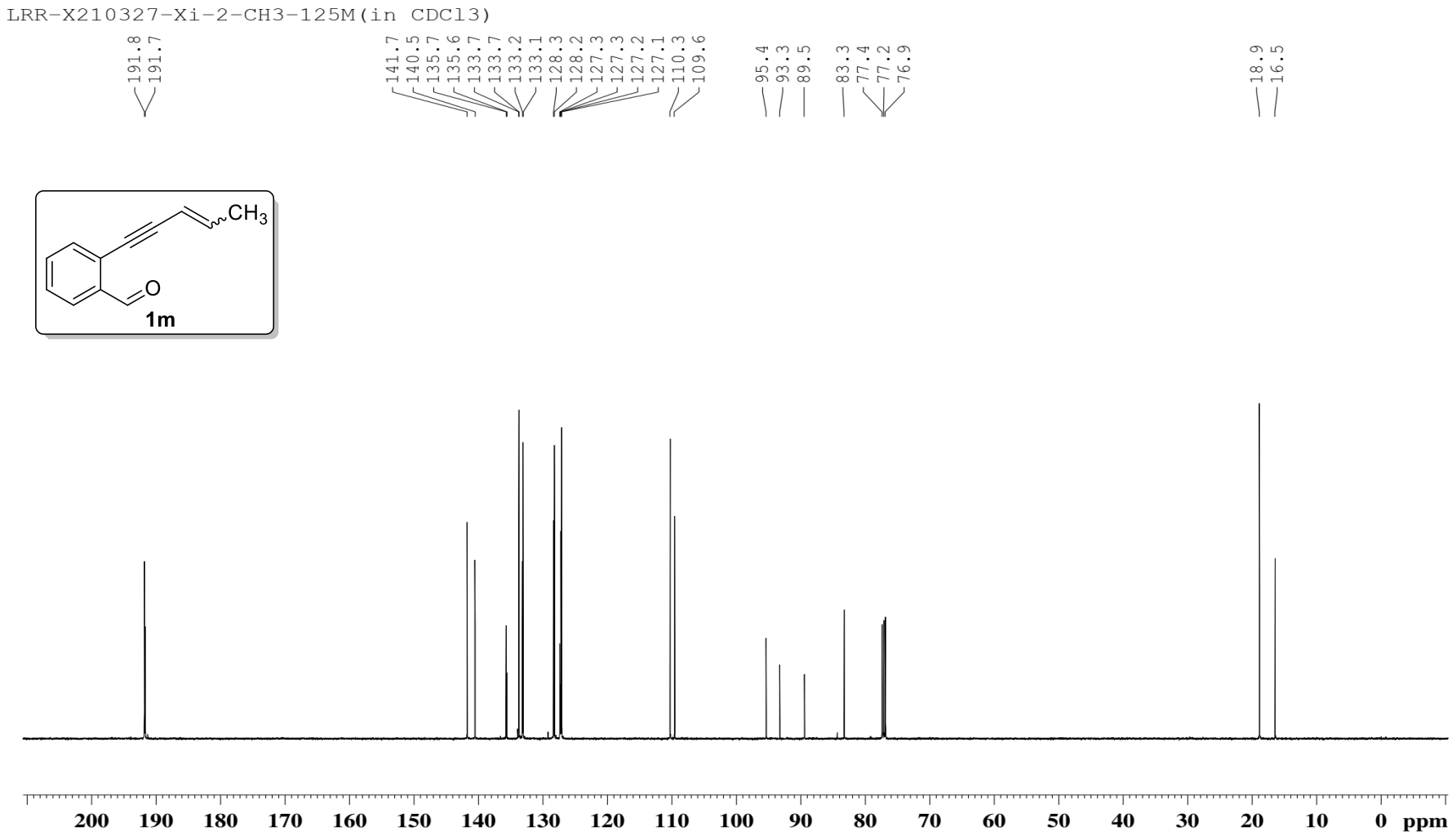
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 1l



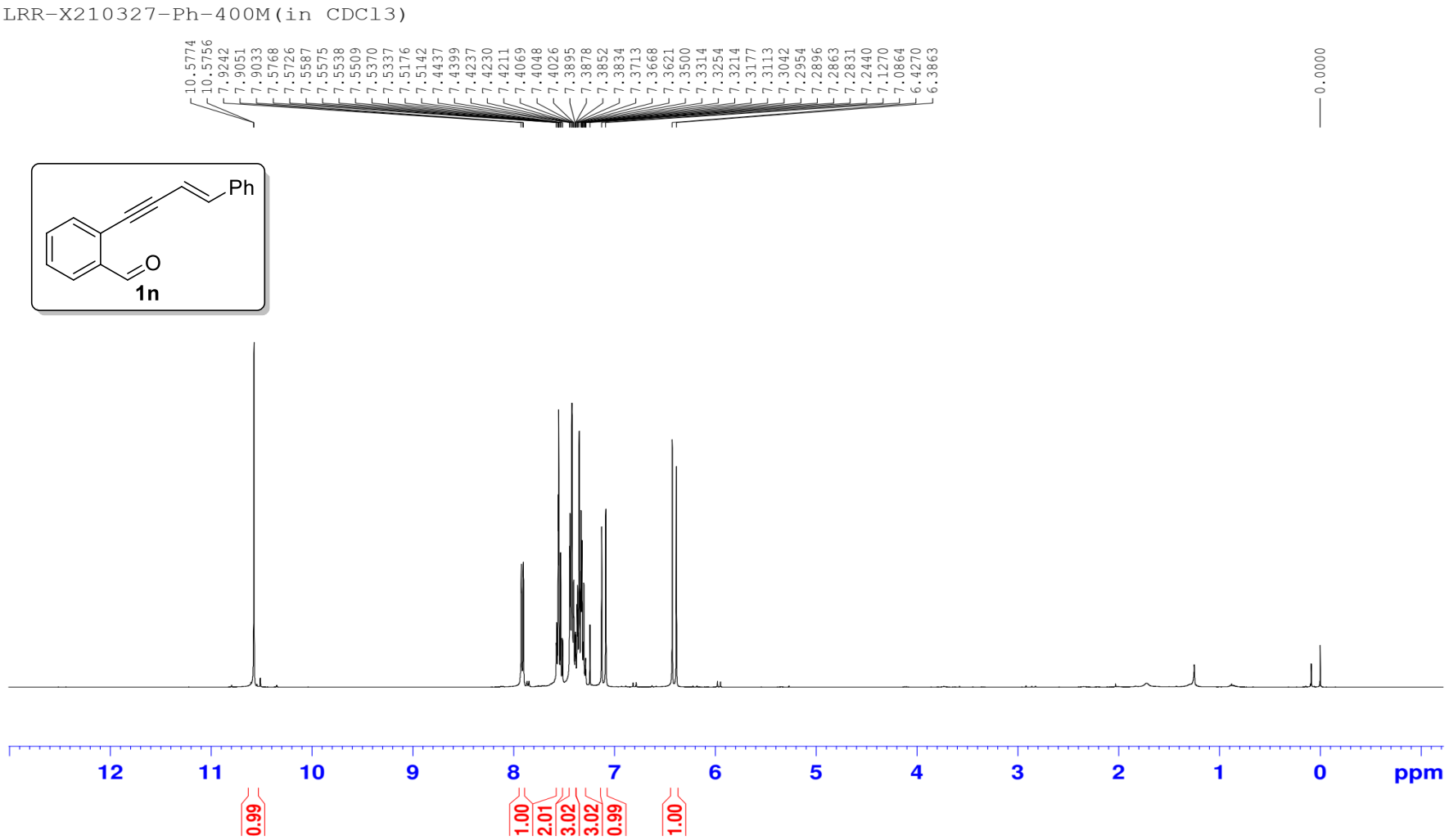
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1m



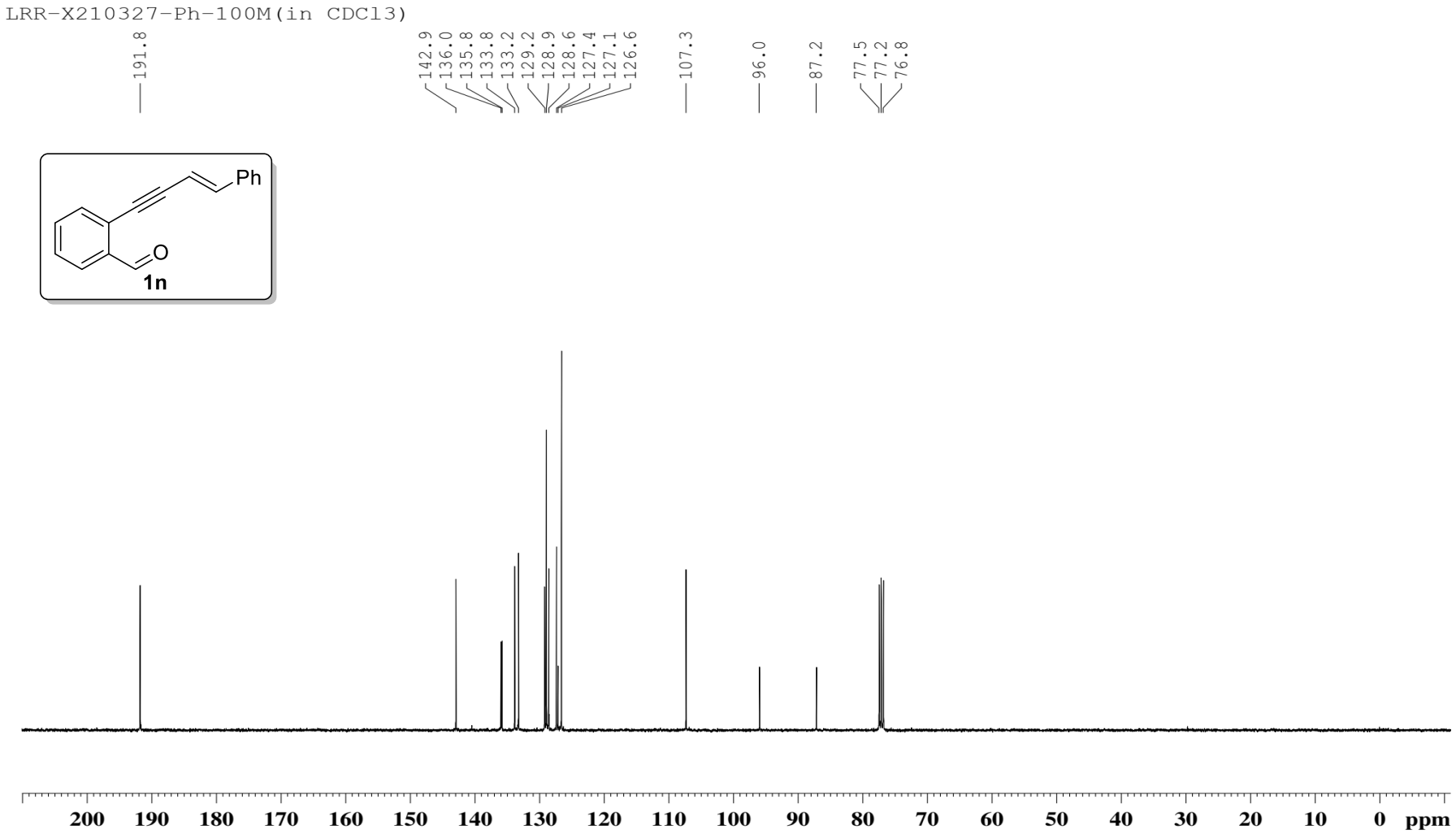
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1m



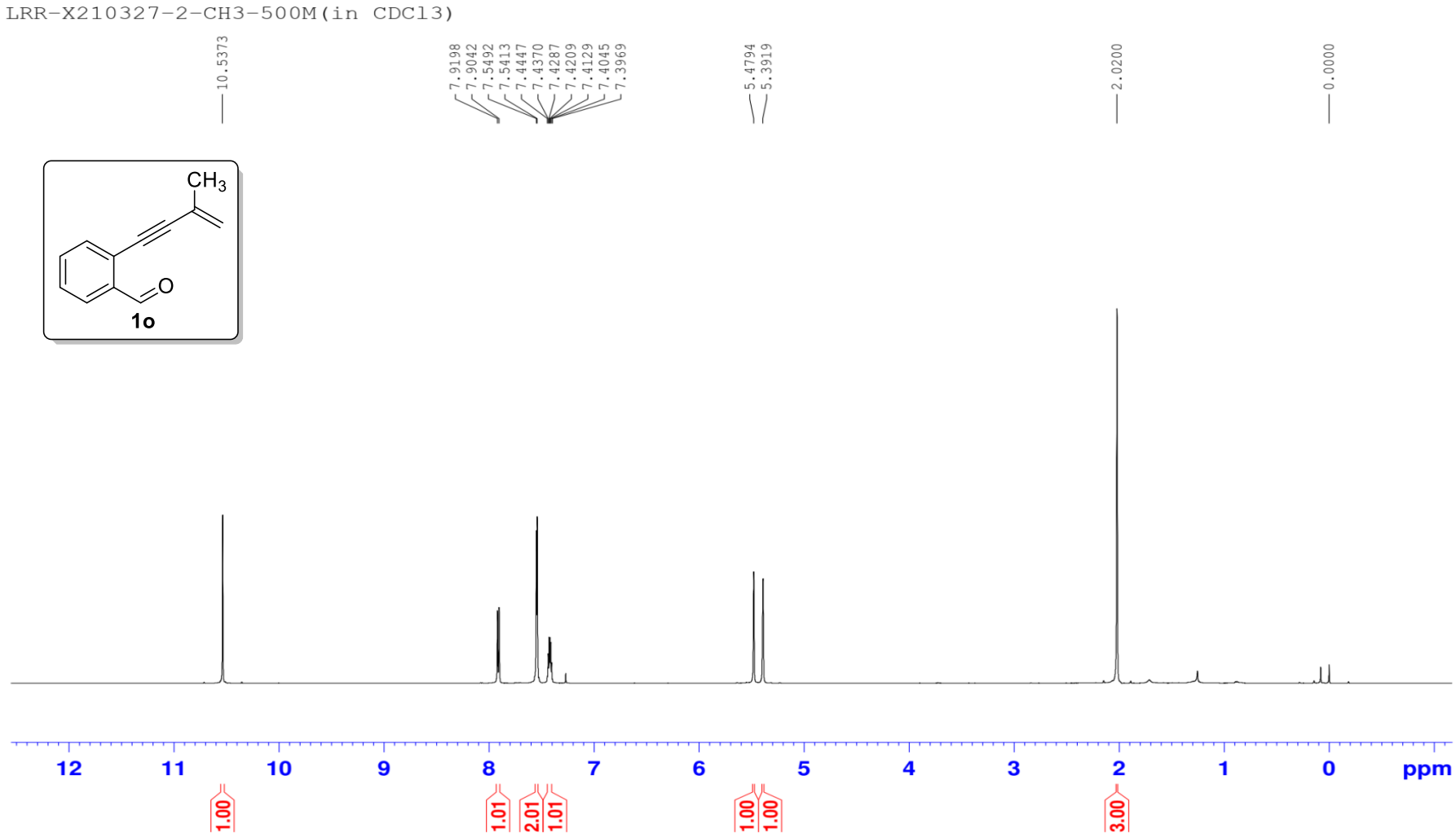
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1n



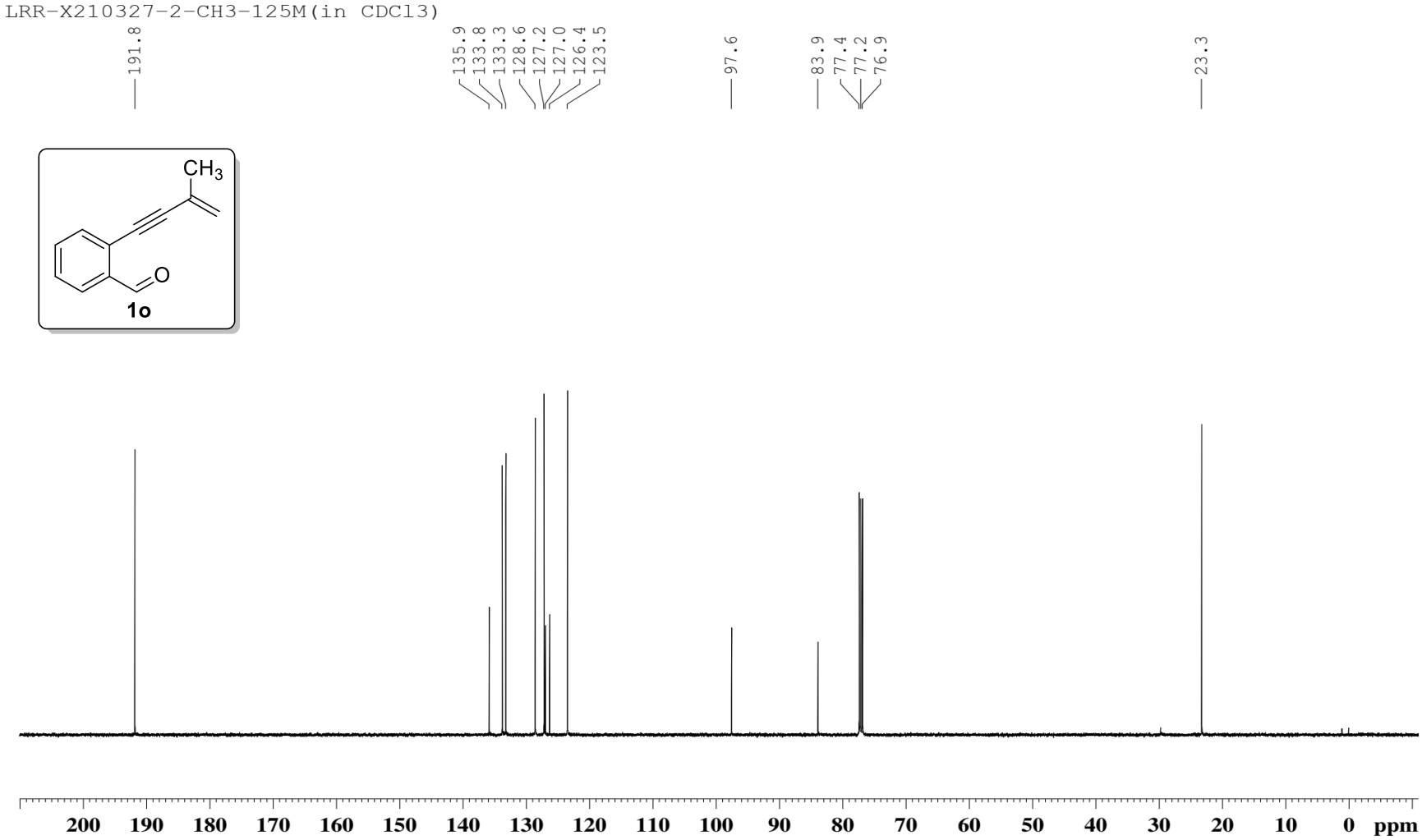
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1n



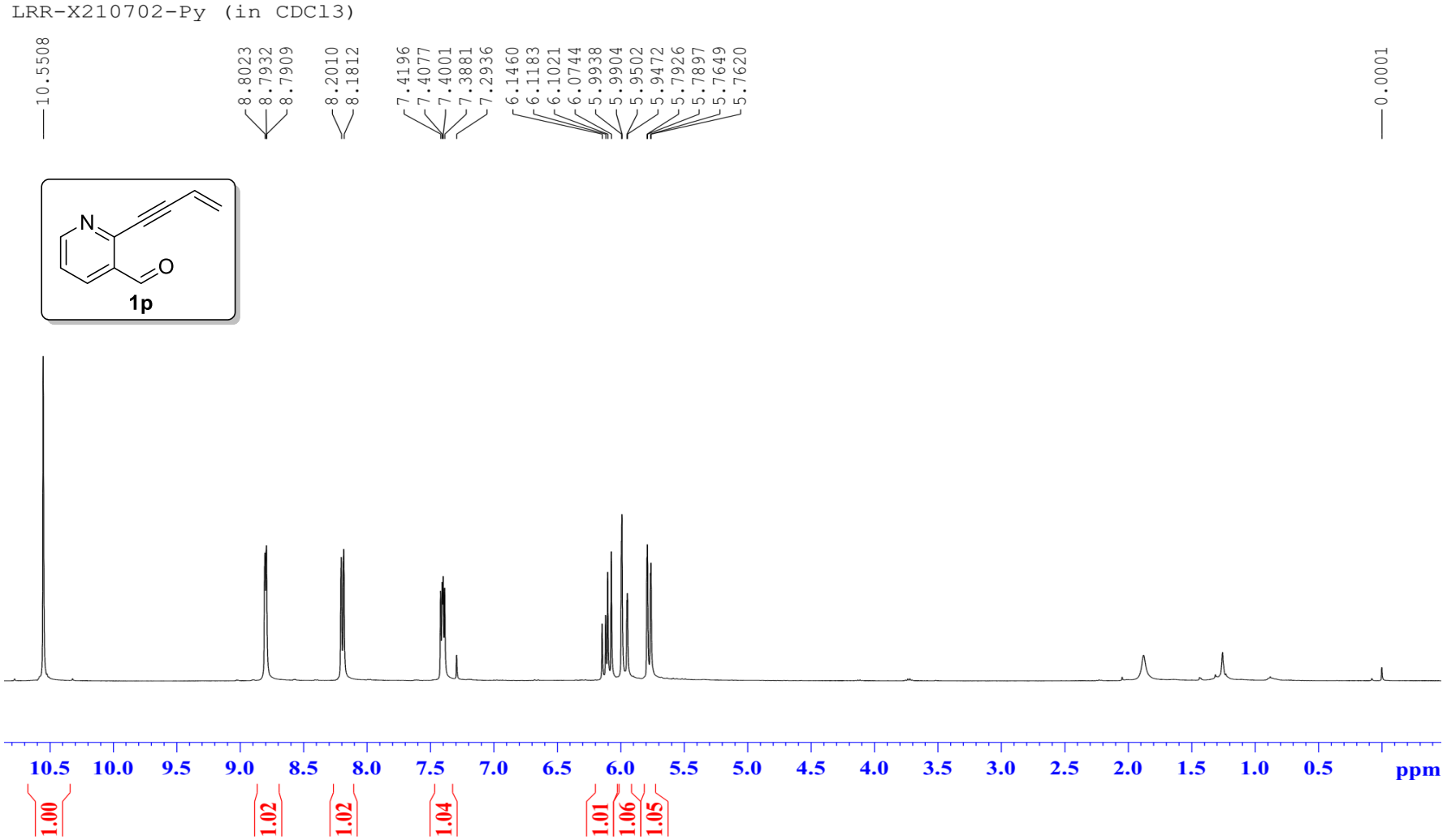
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1o



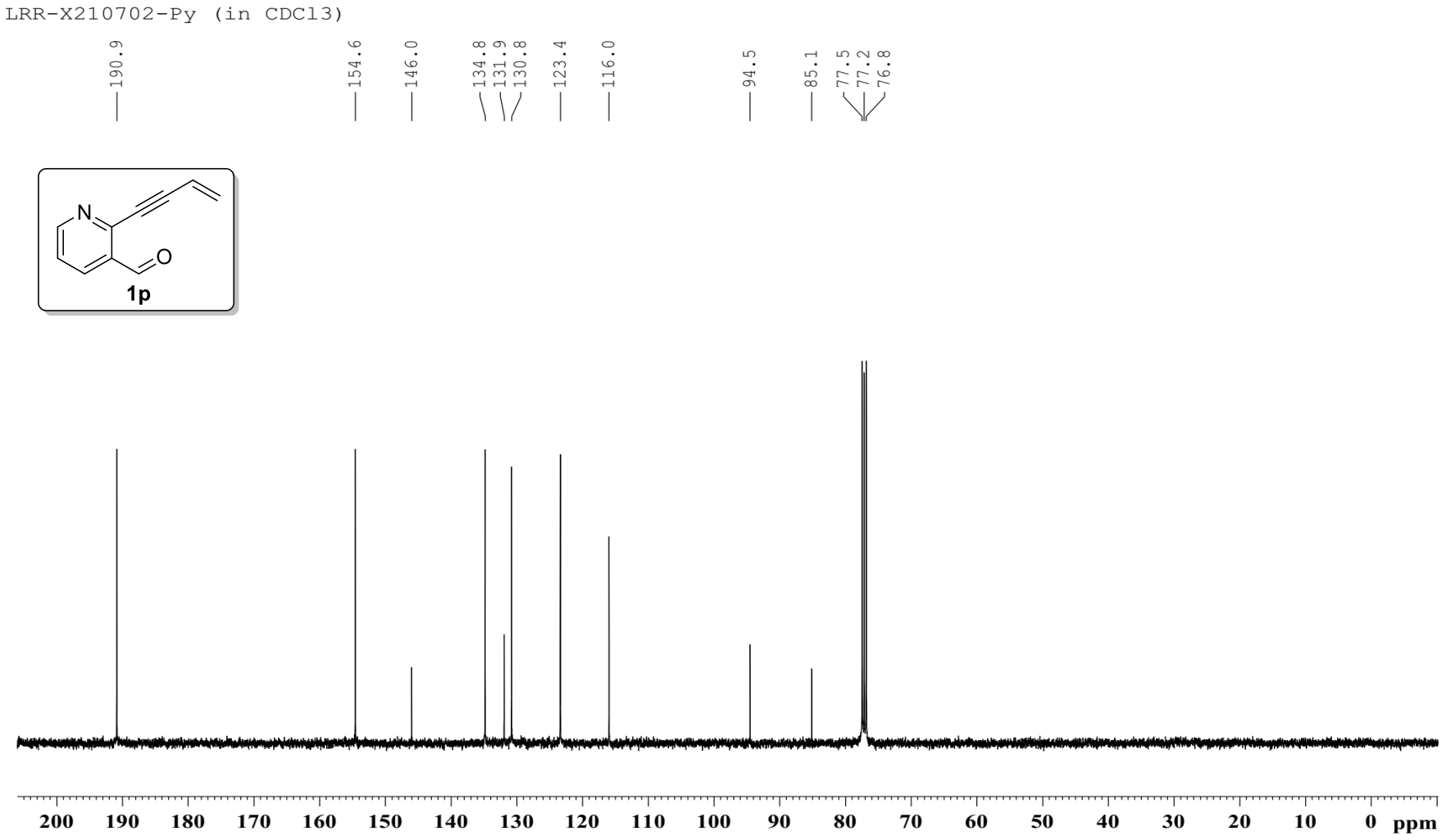
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1o



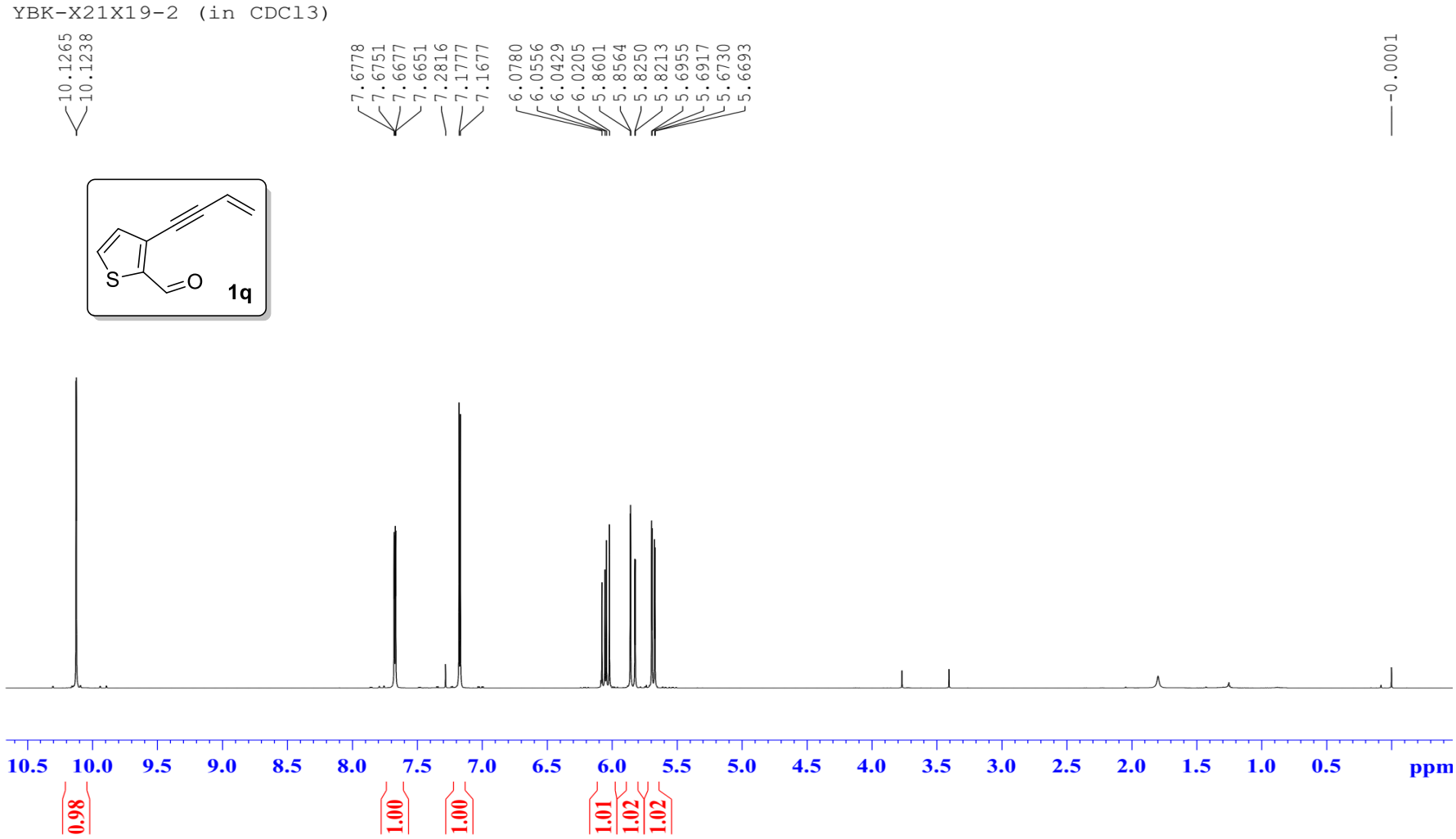
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1p



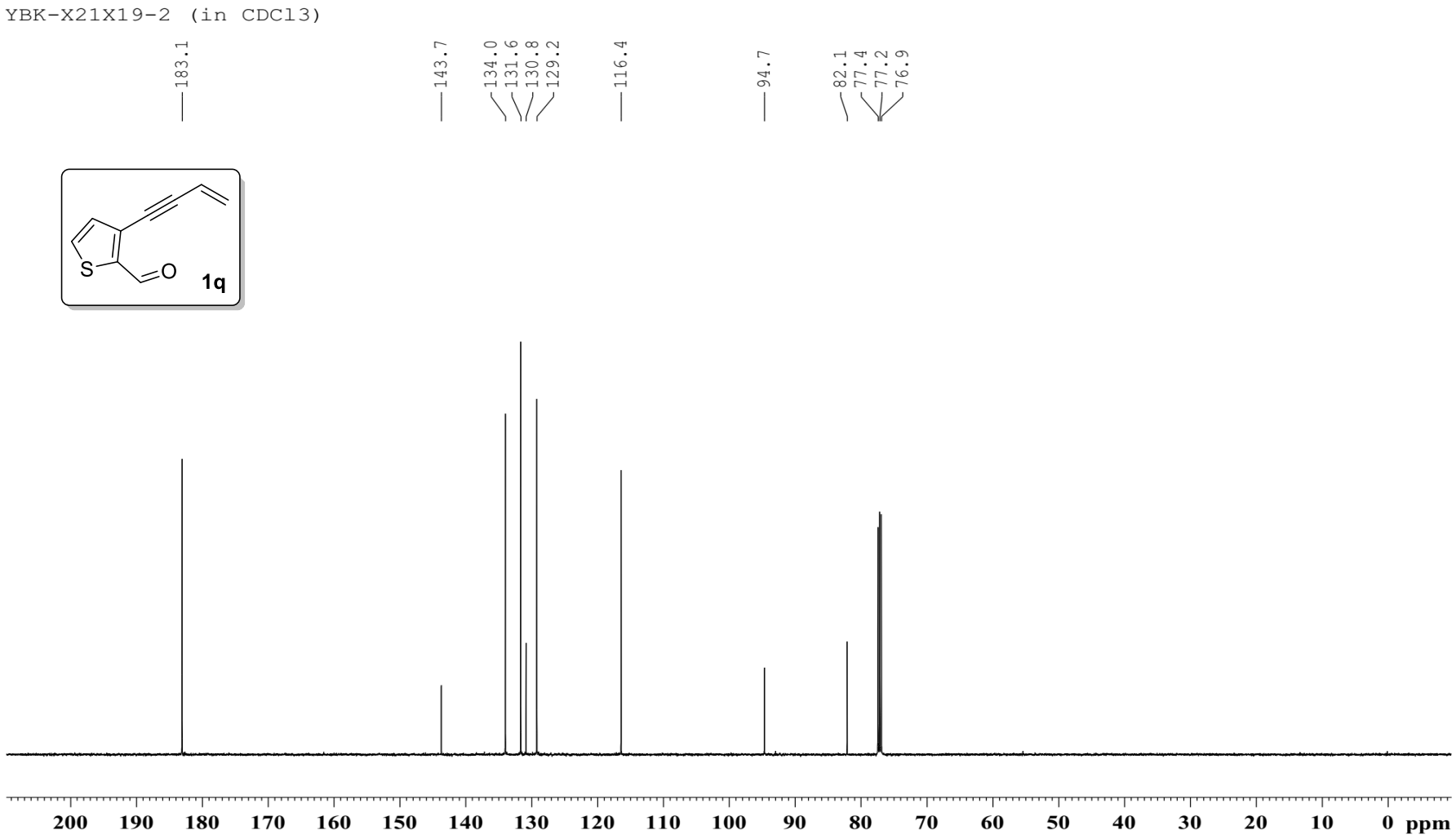
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1p



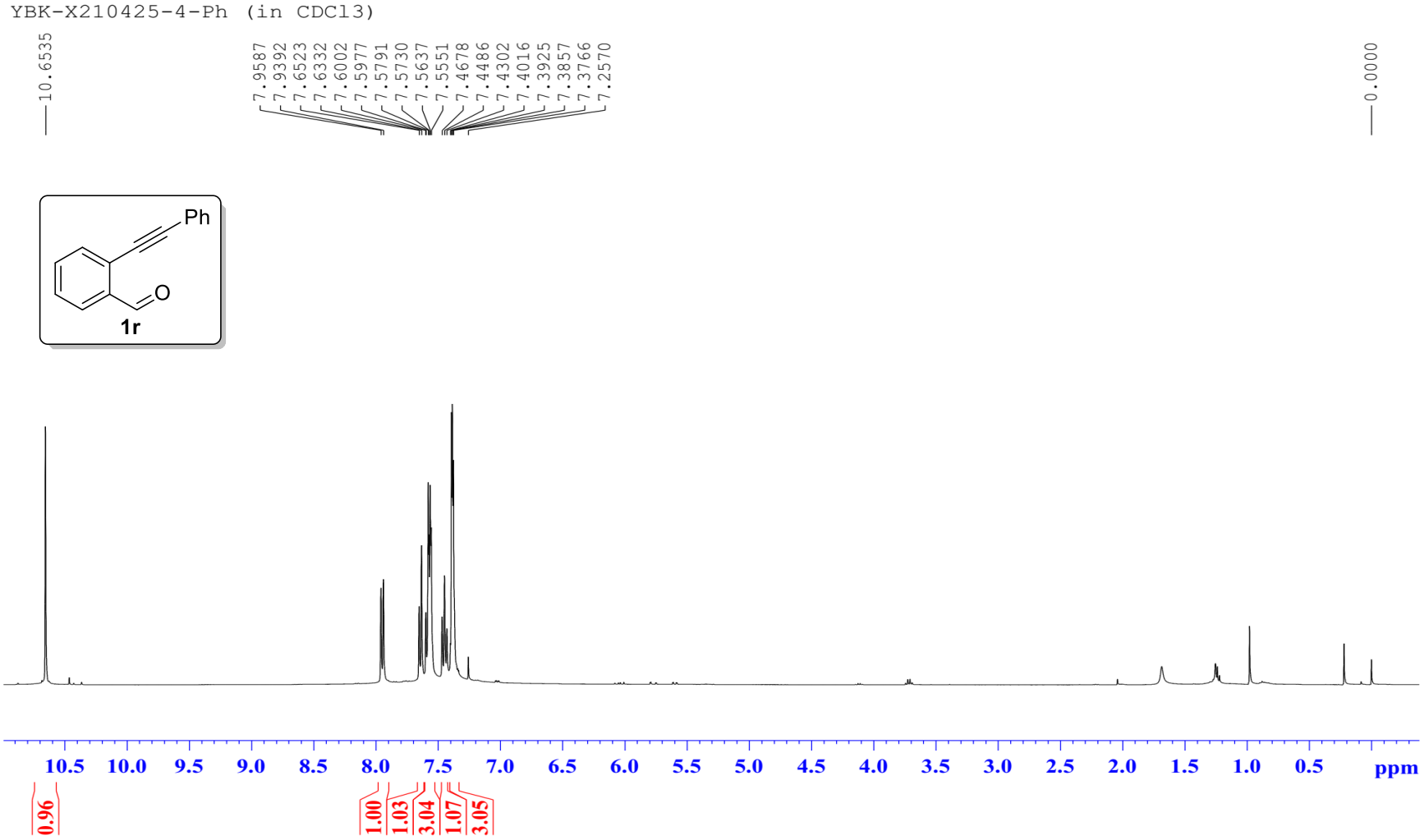
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1q



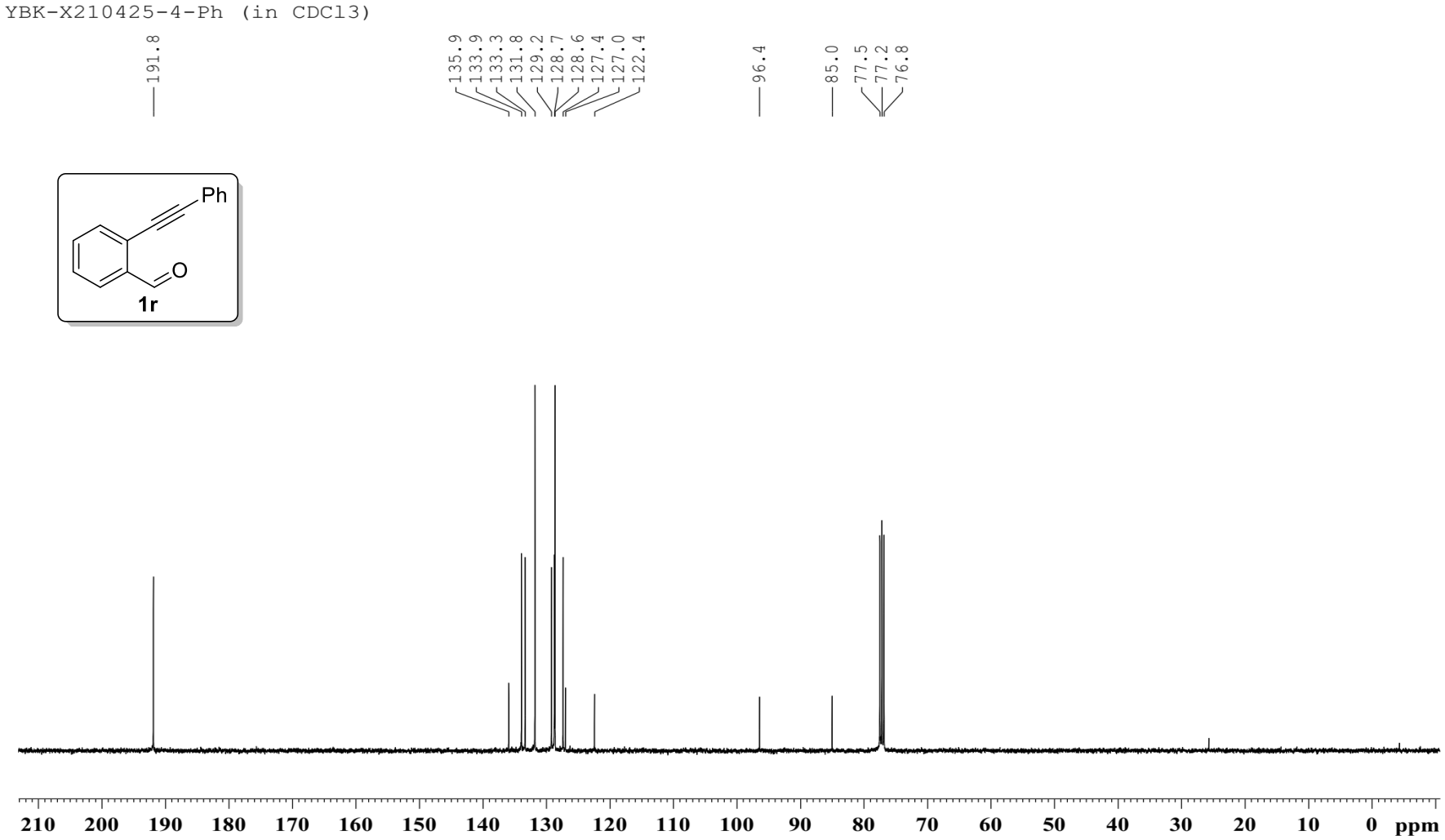
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1q



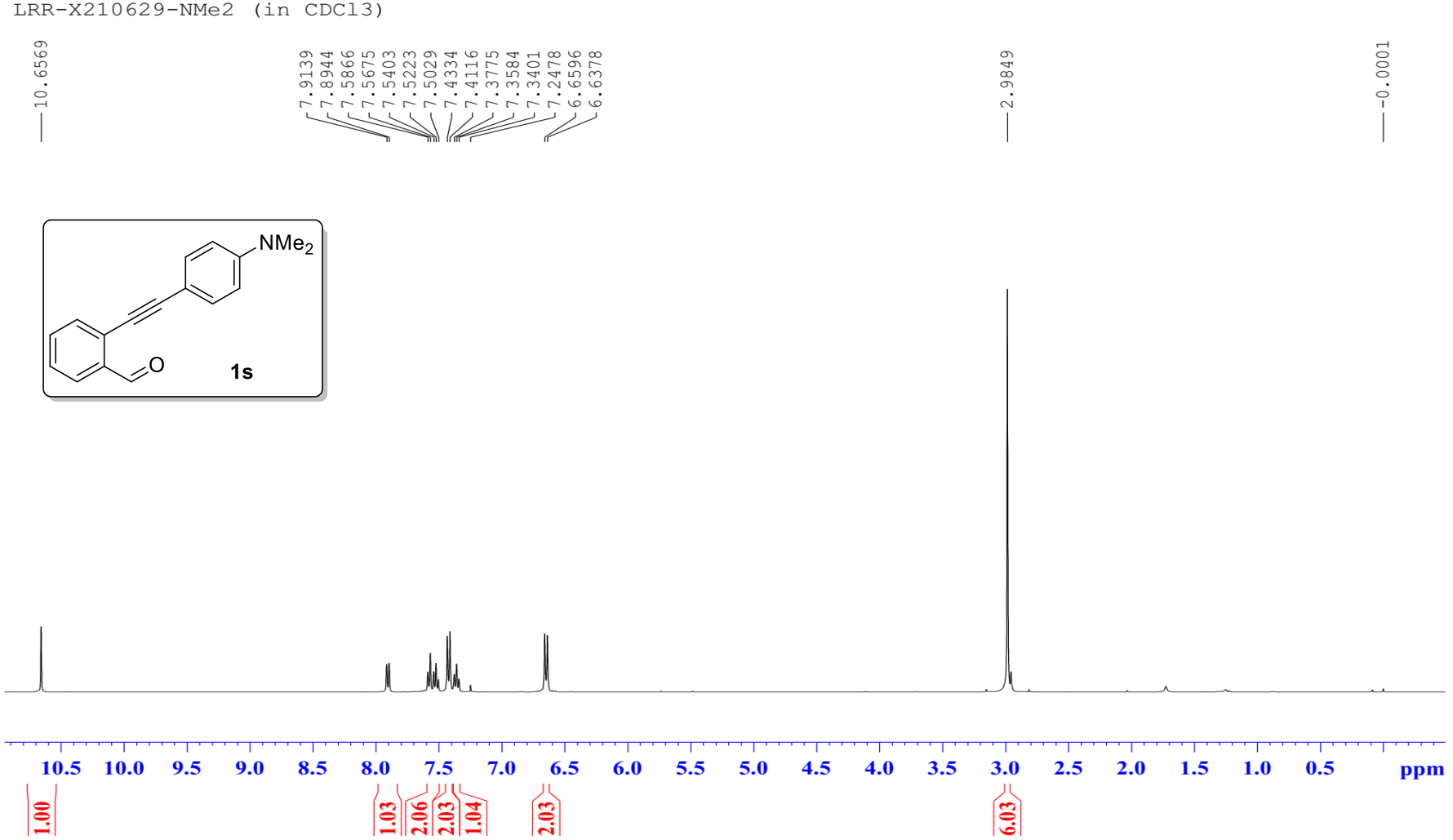
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1r



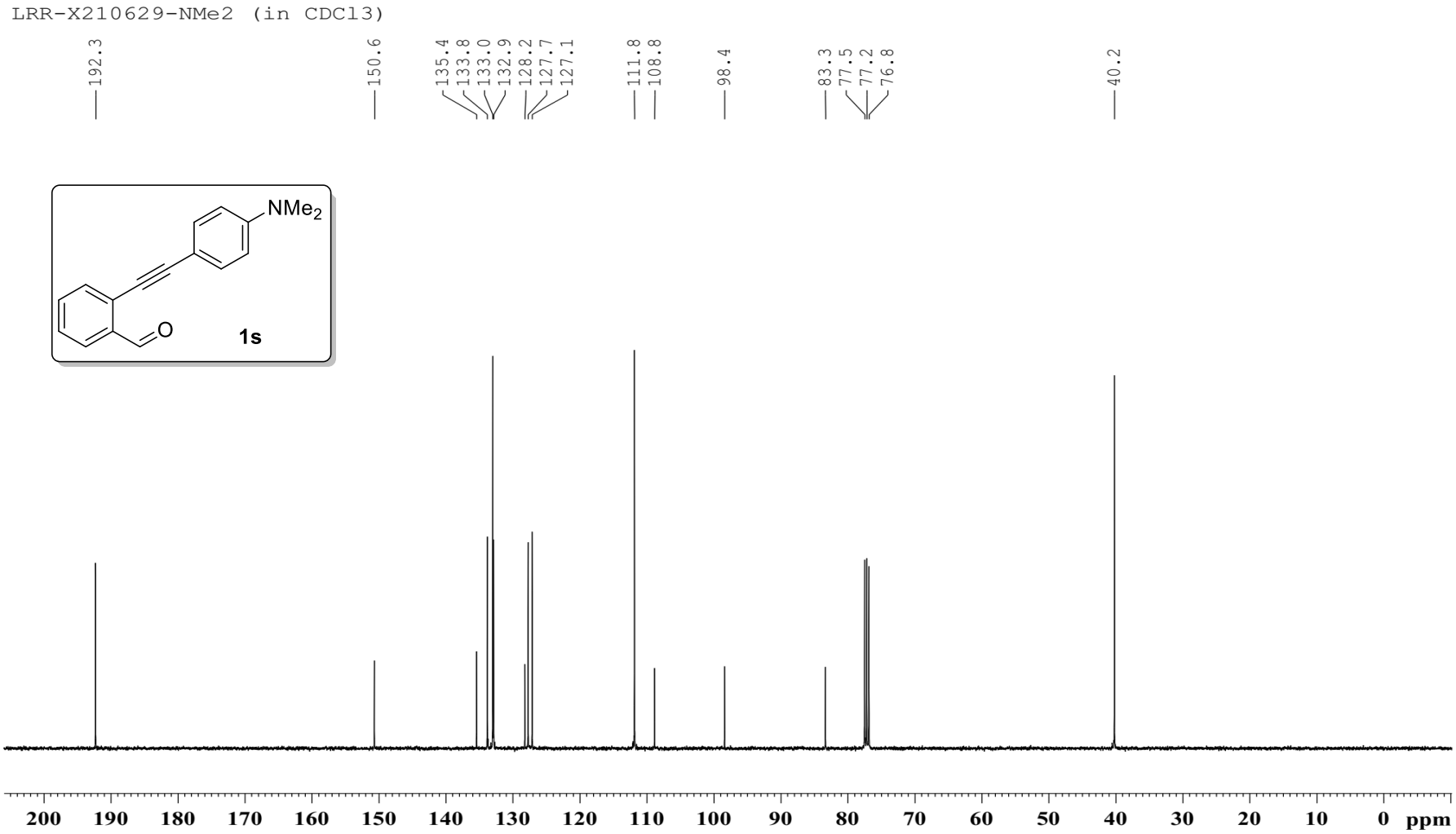
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1r



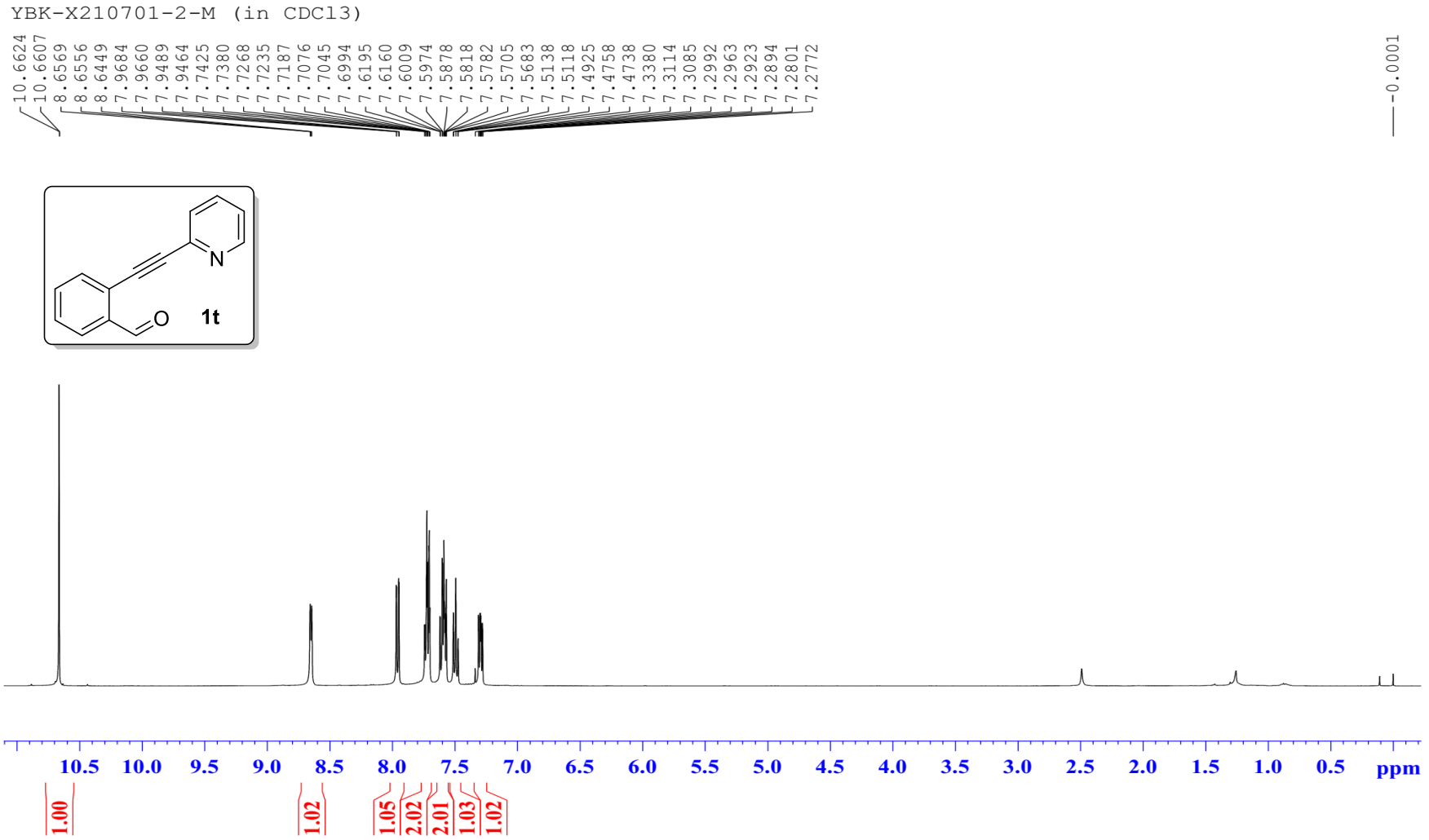
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1s



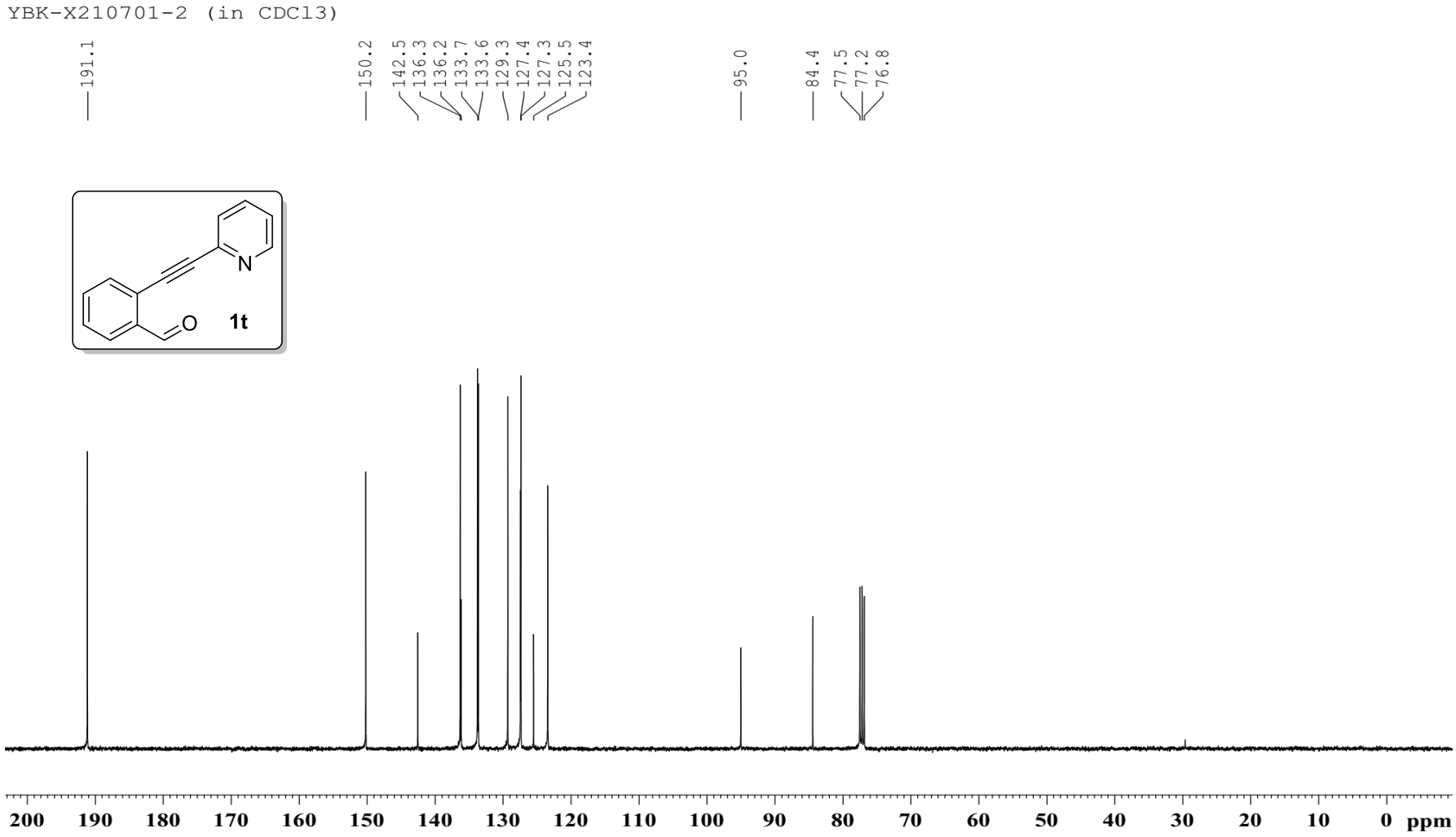
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1s



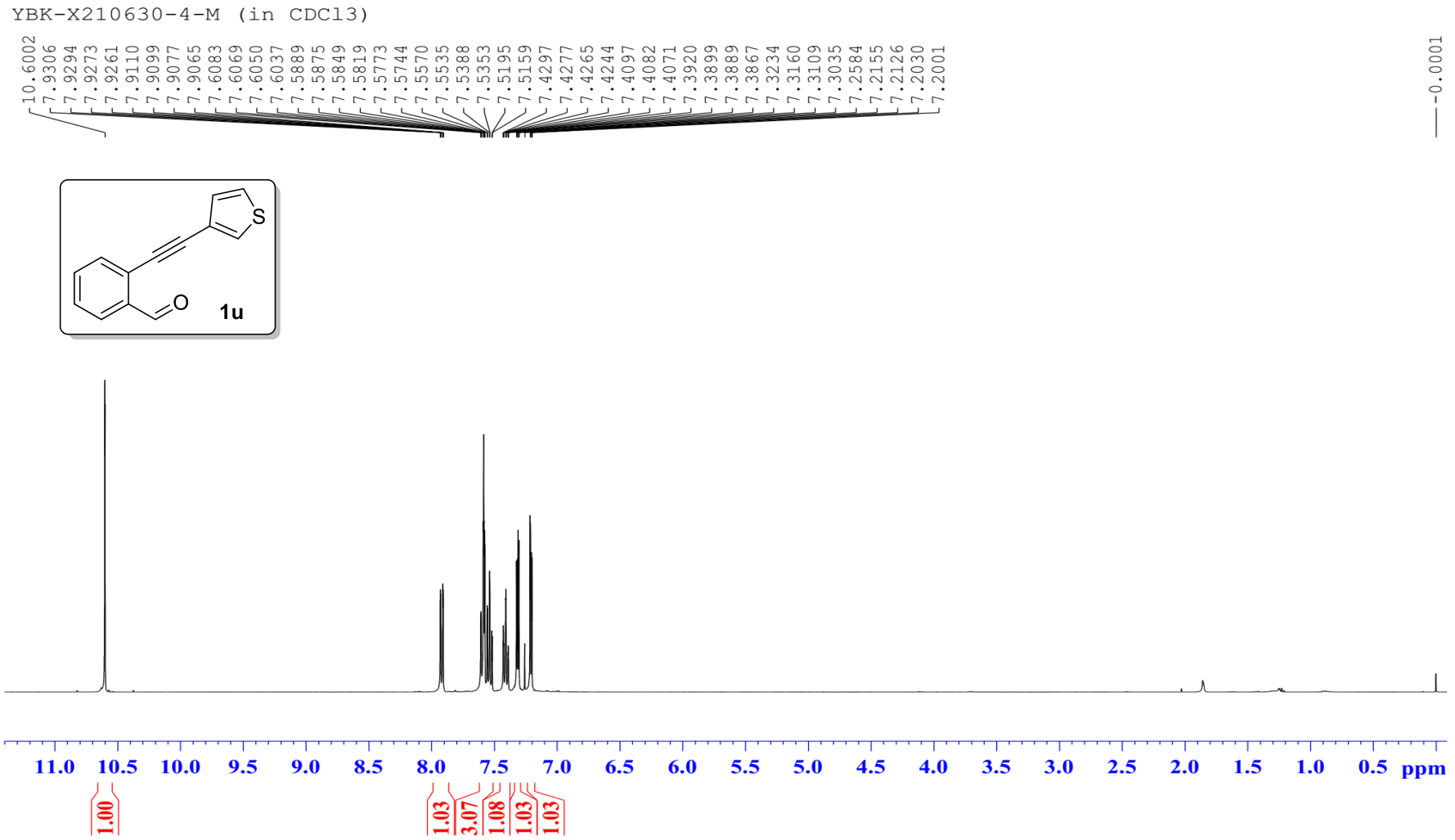
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1t



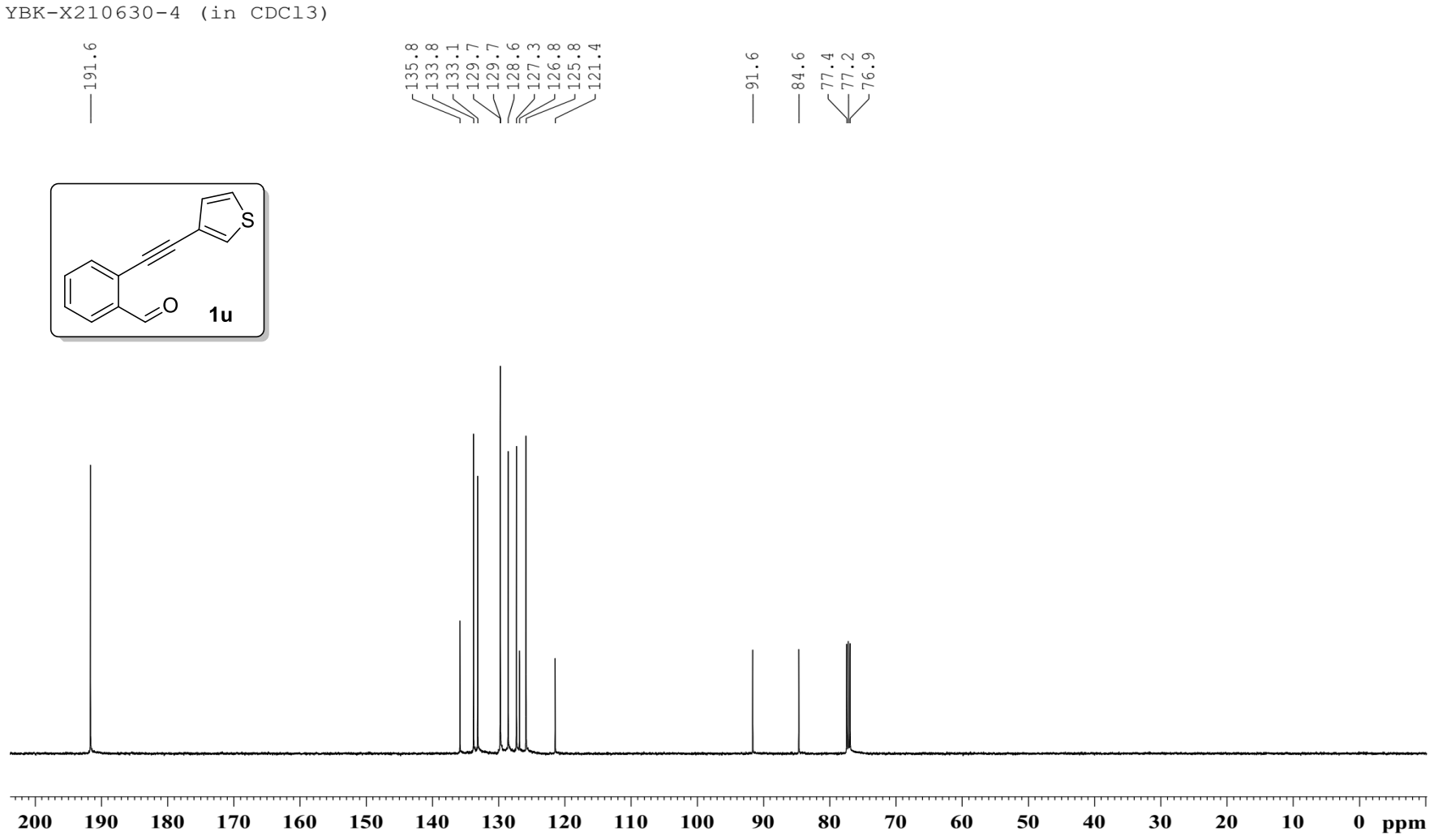
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1t



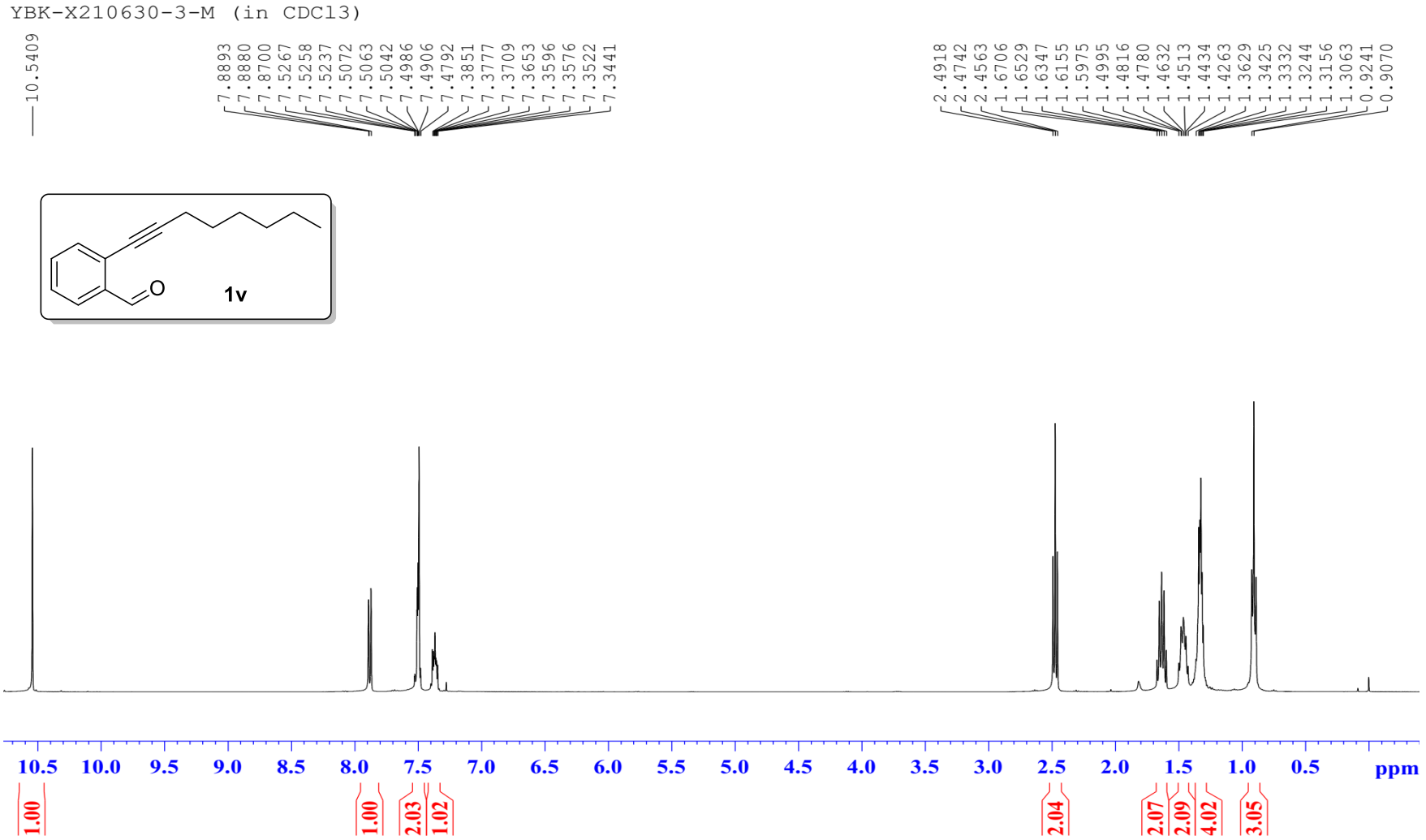
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1u



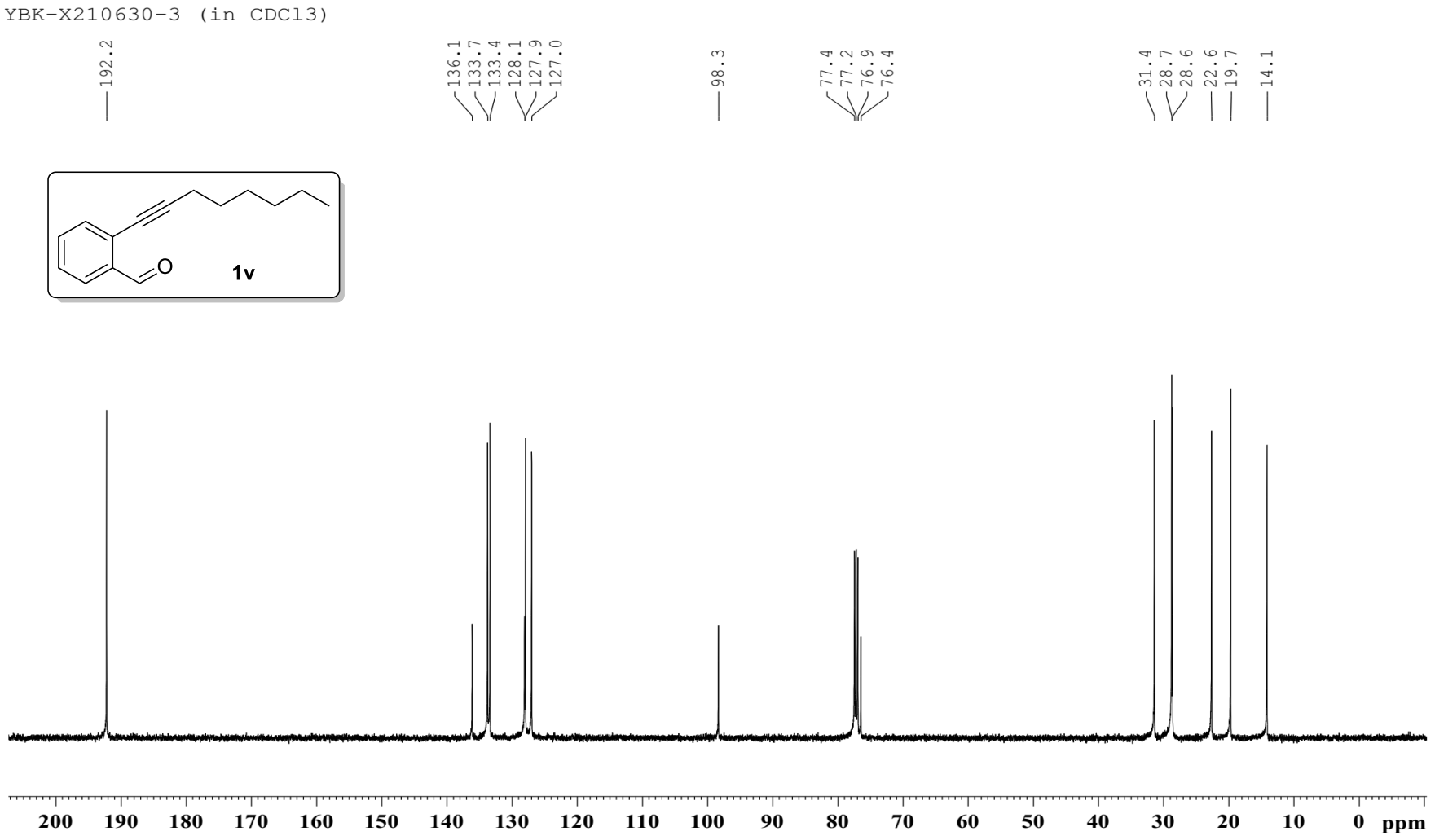
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1u



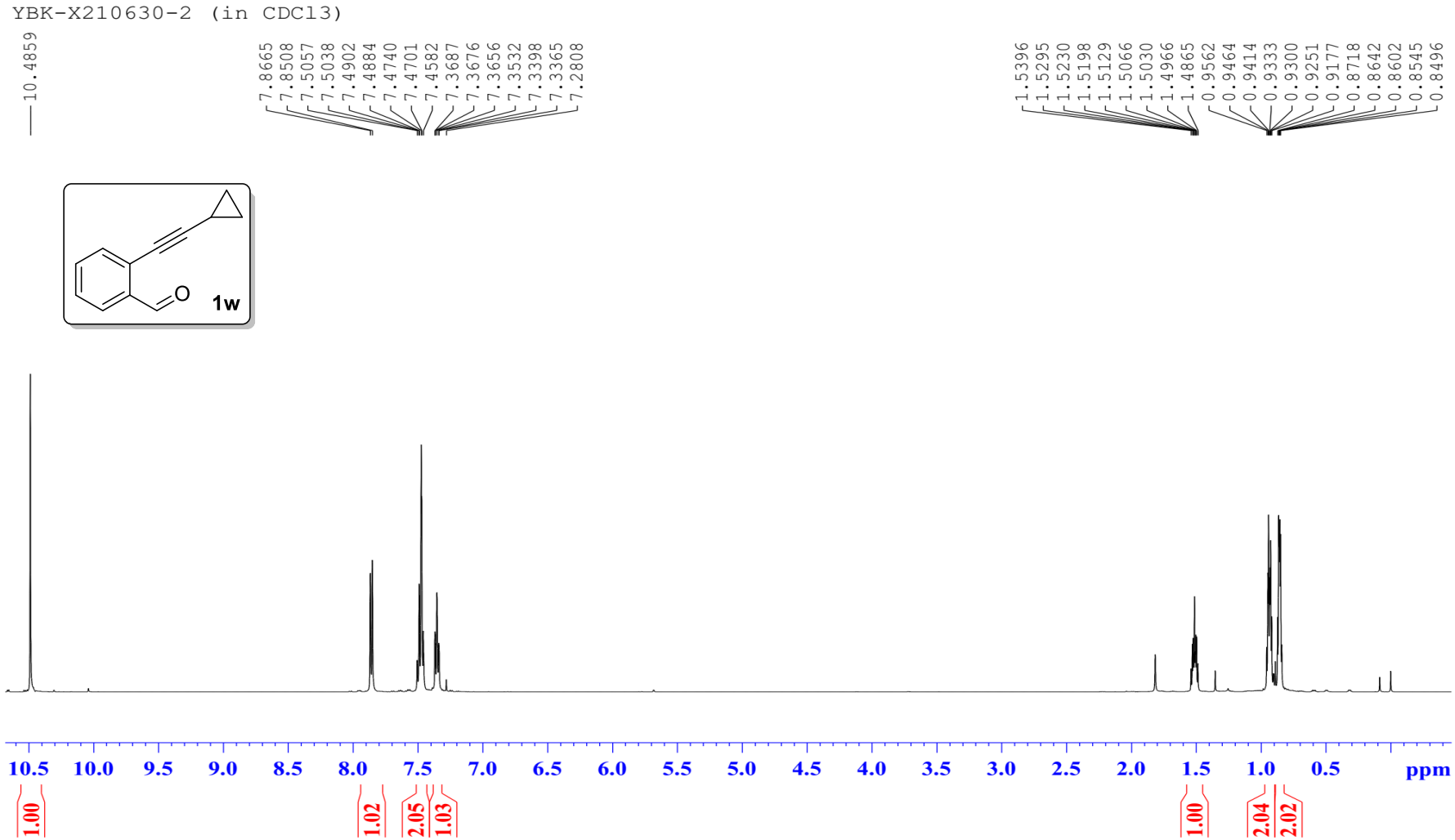
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1v



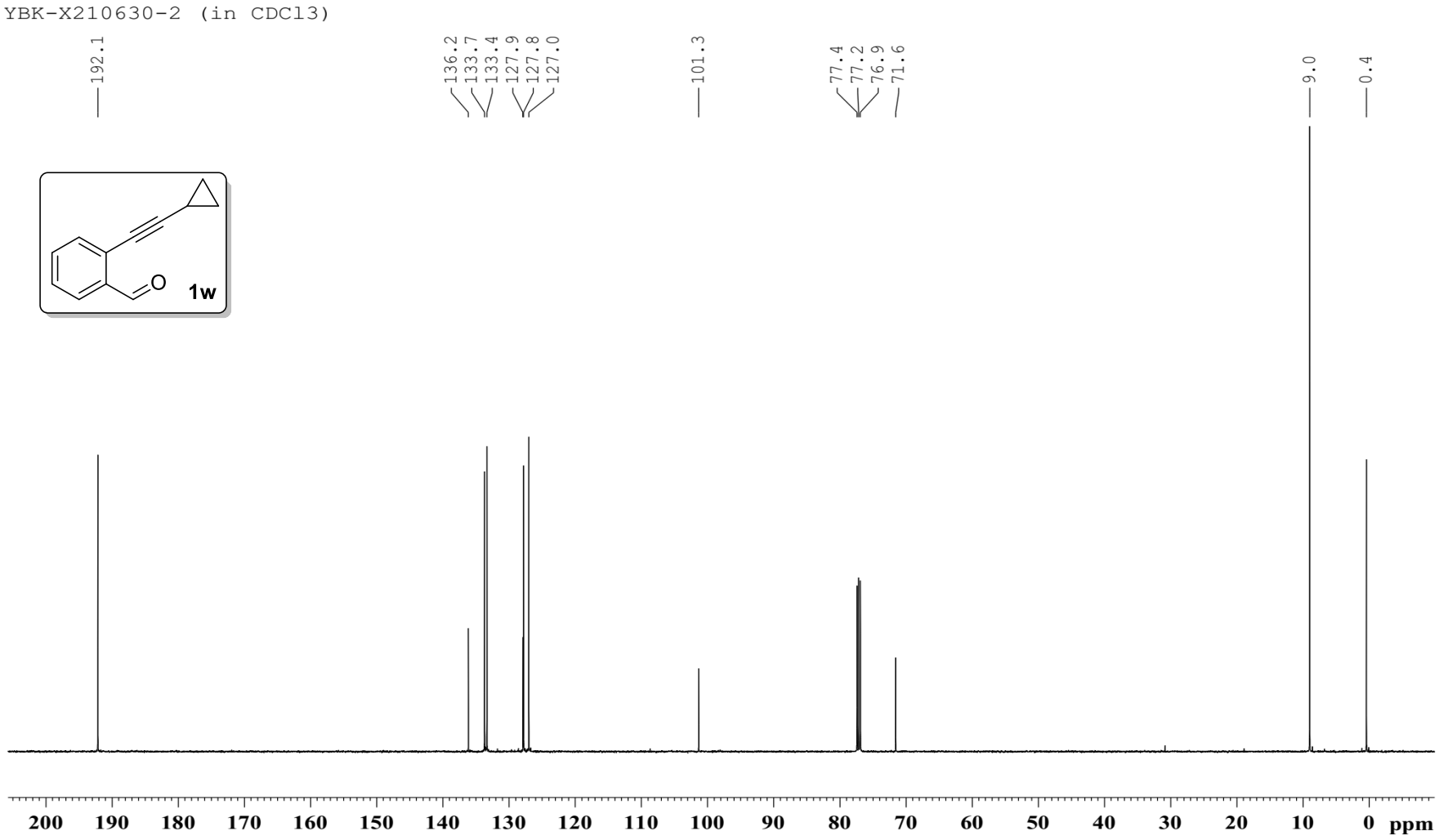
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1v



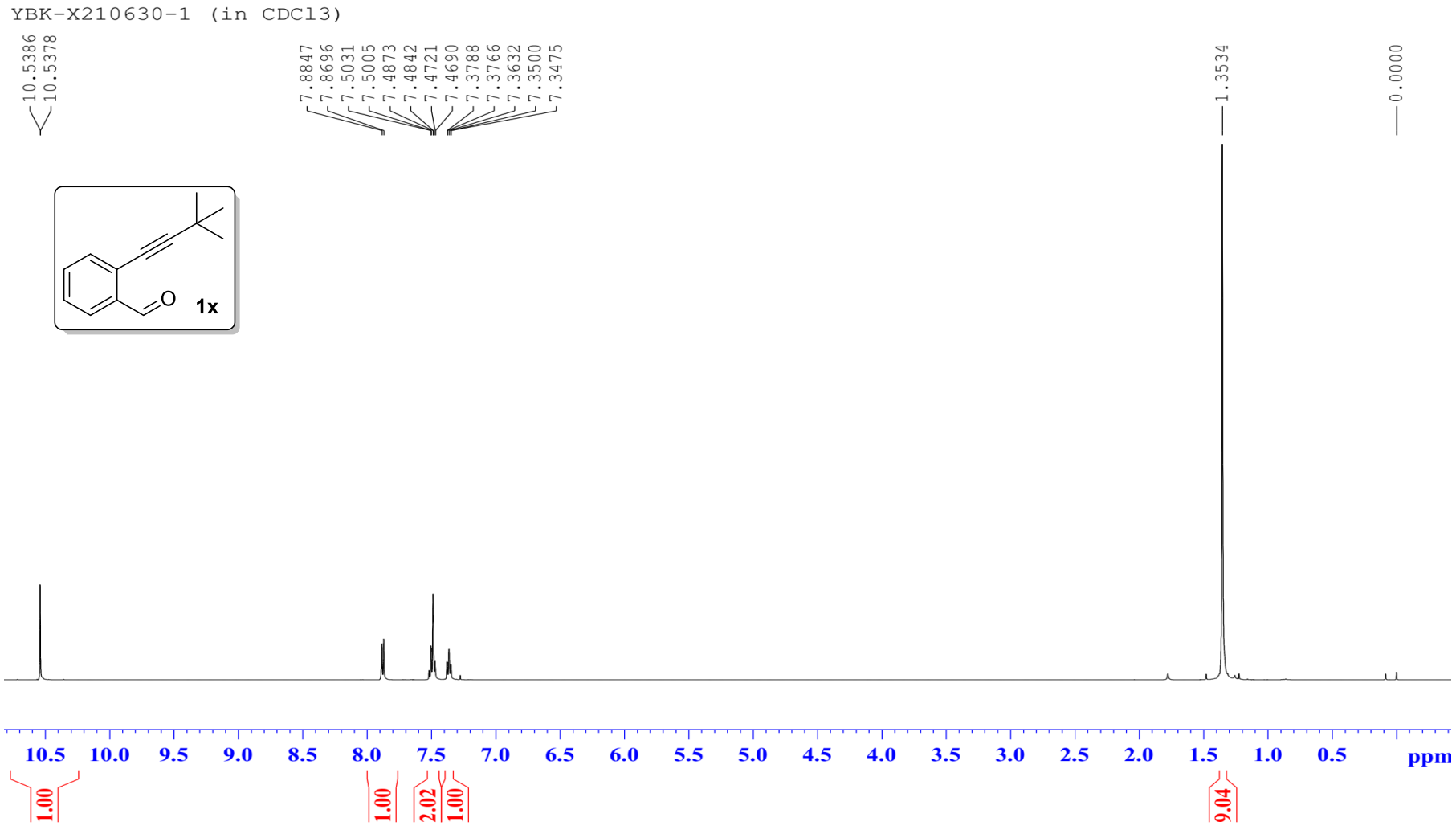
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1w



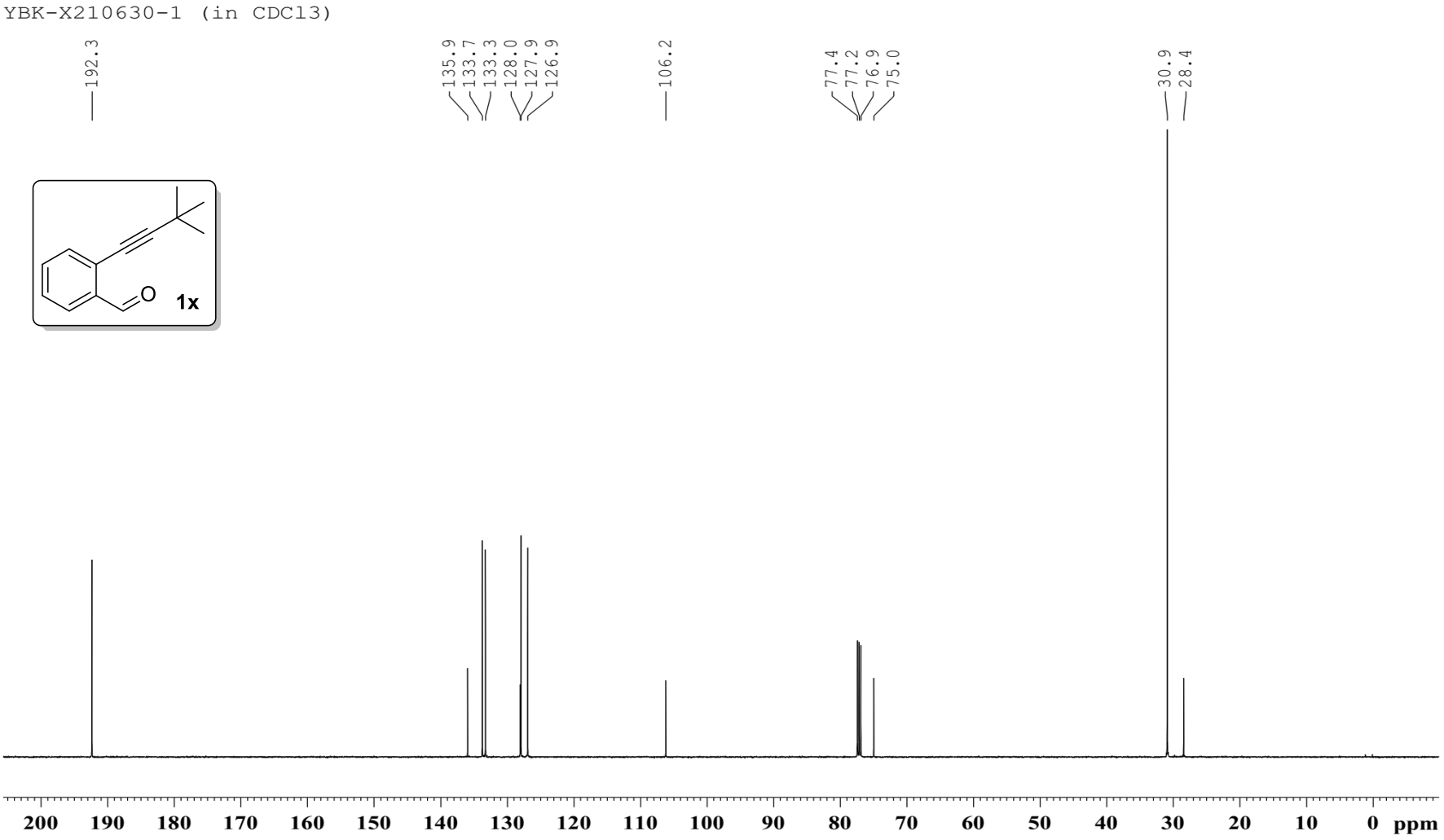
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1w



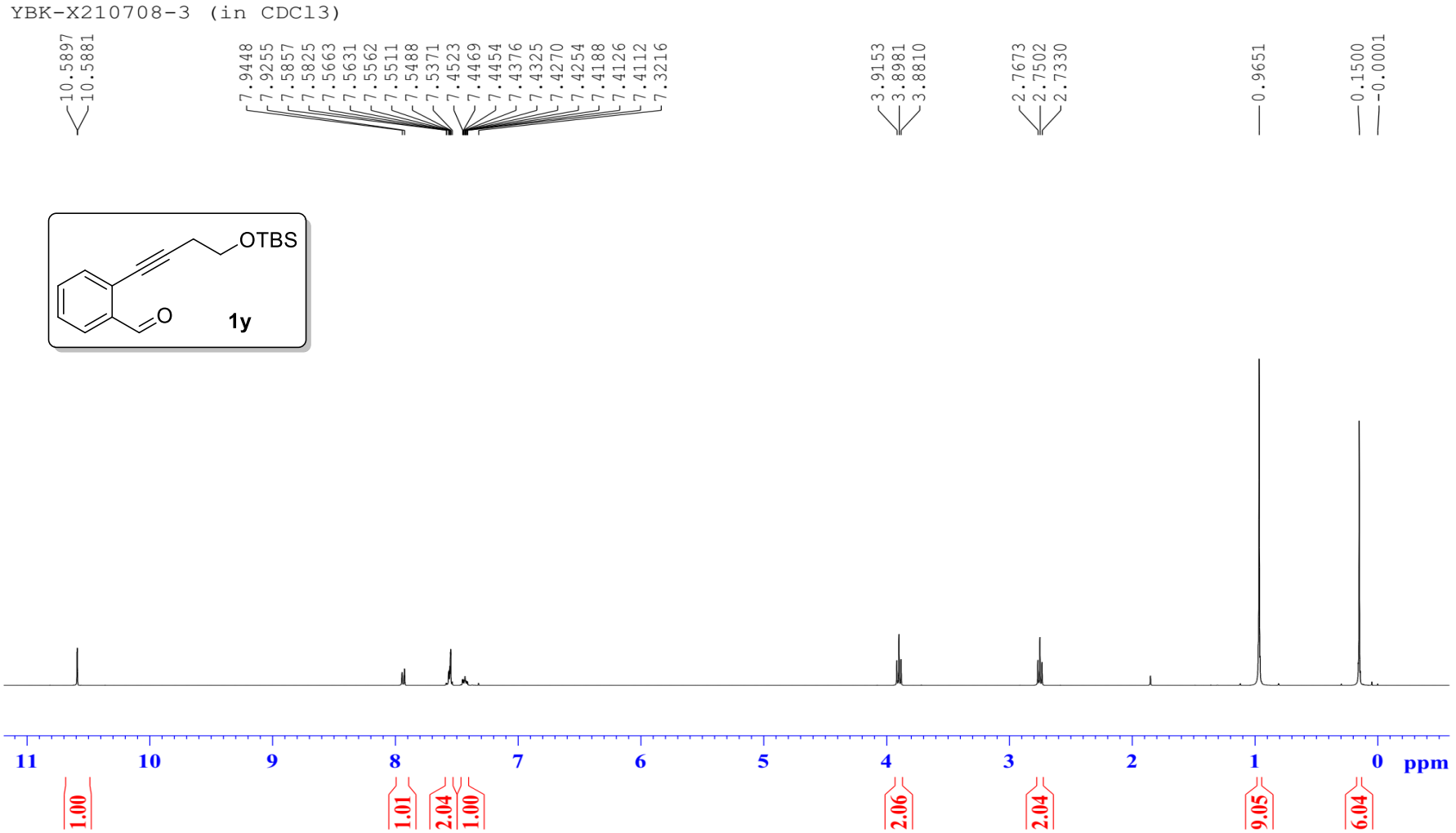
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1x



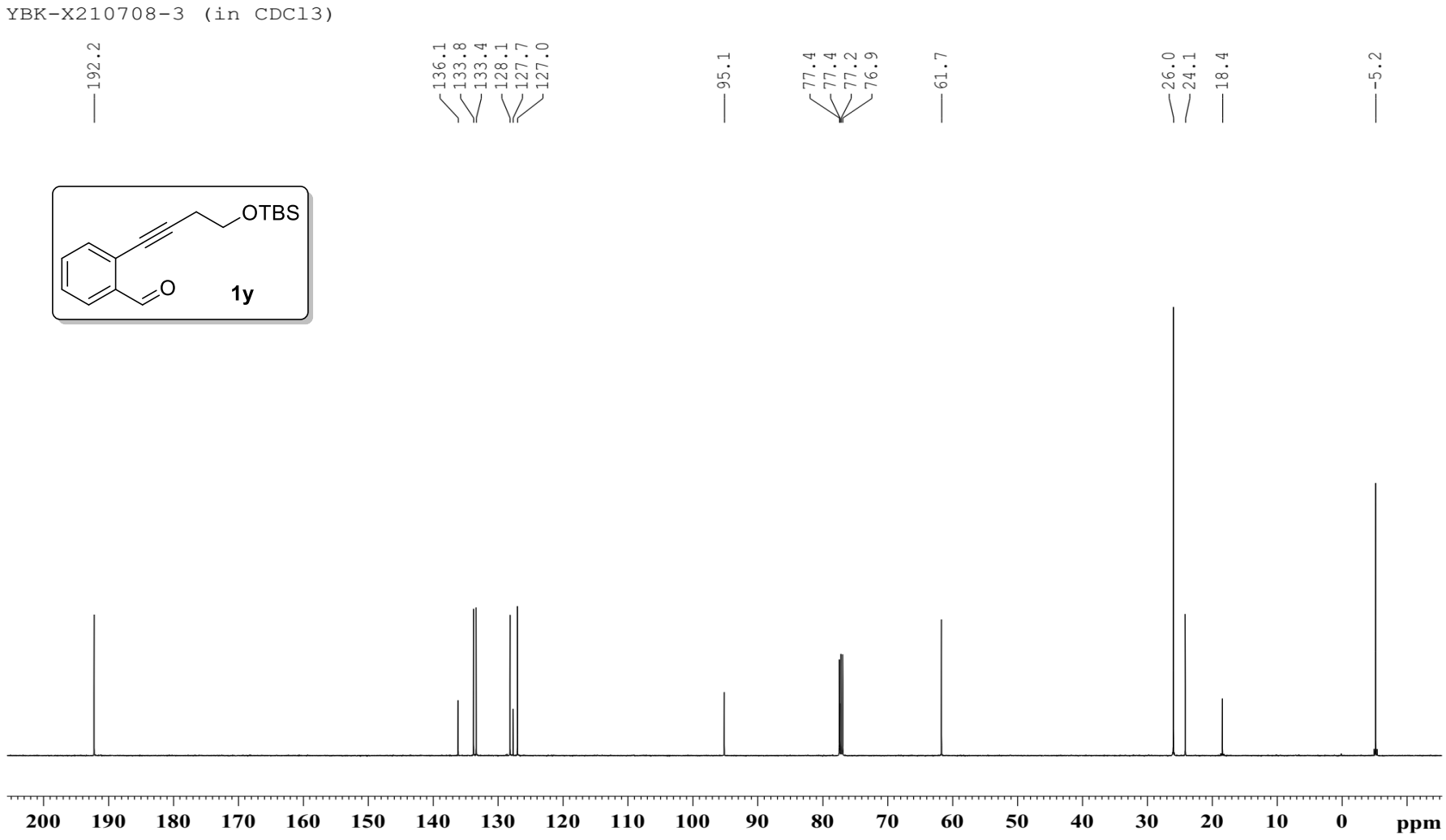
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1x



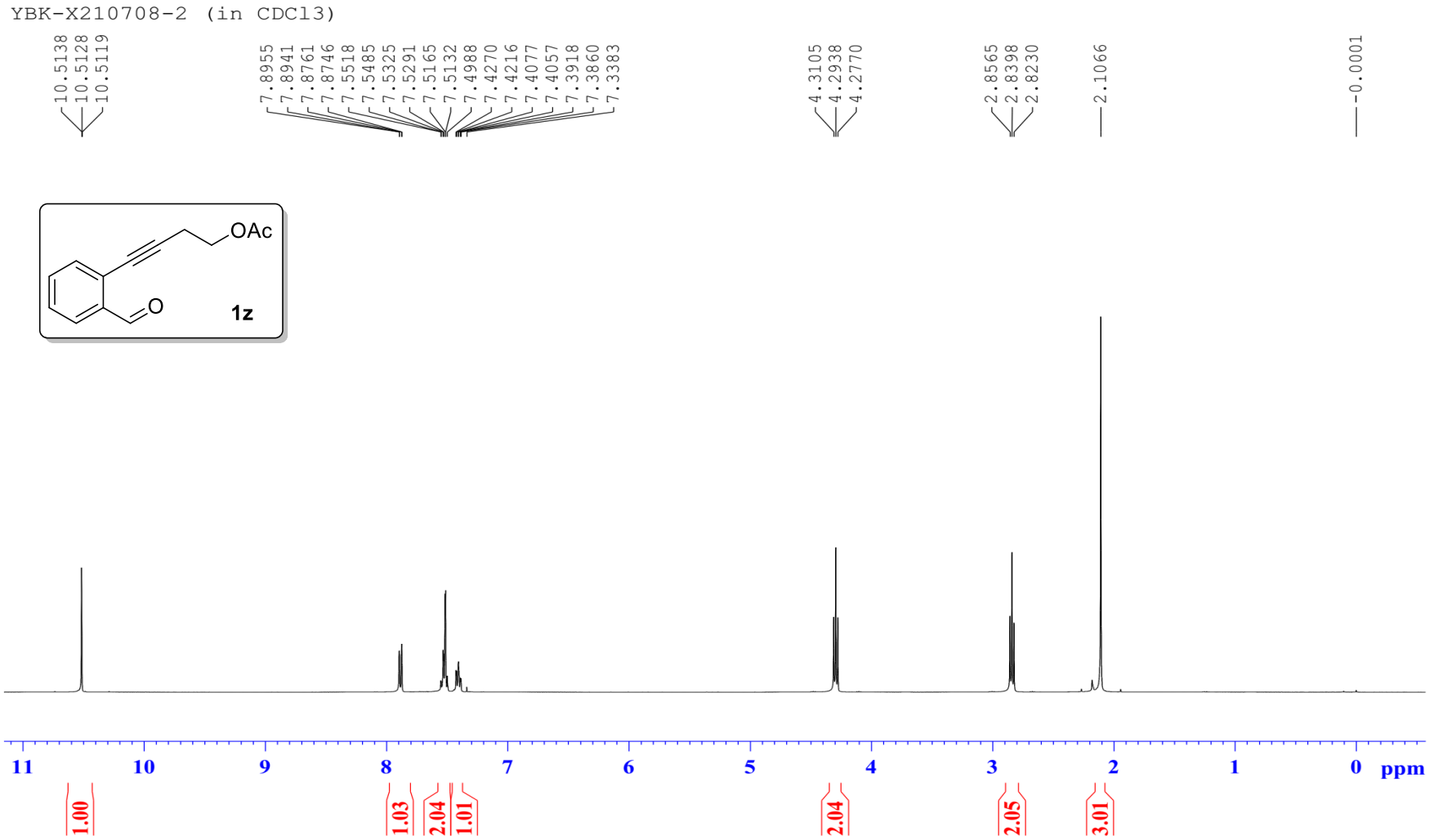
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1y



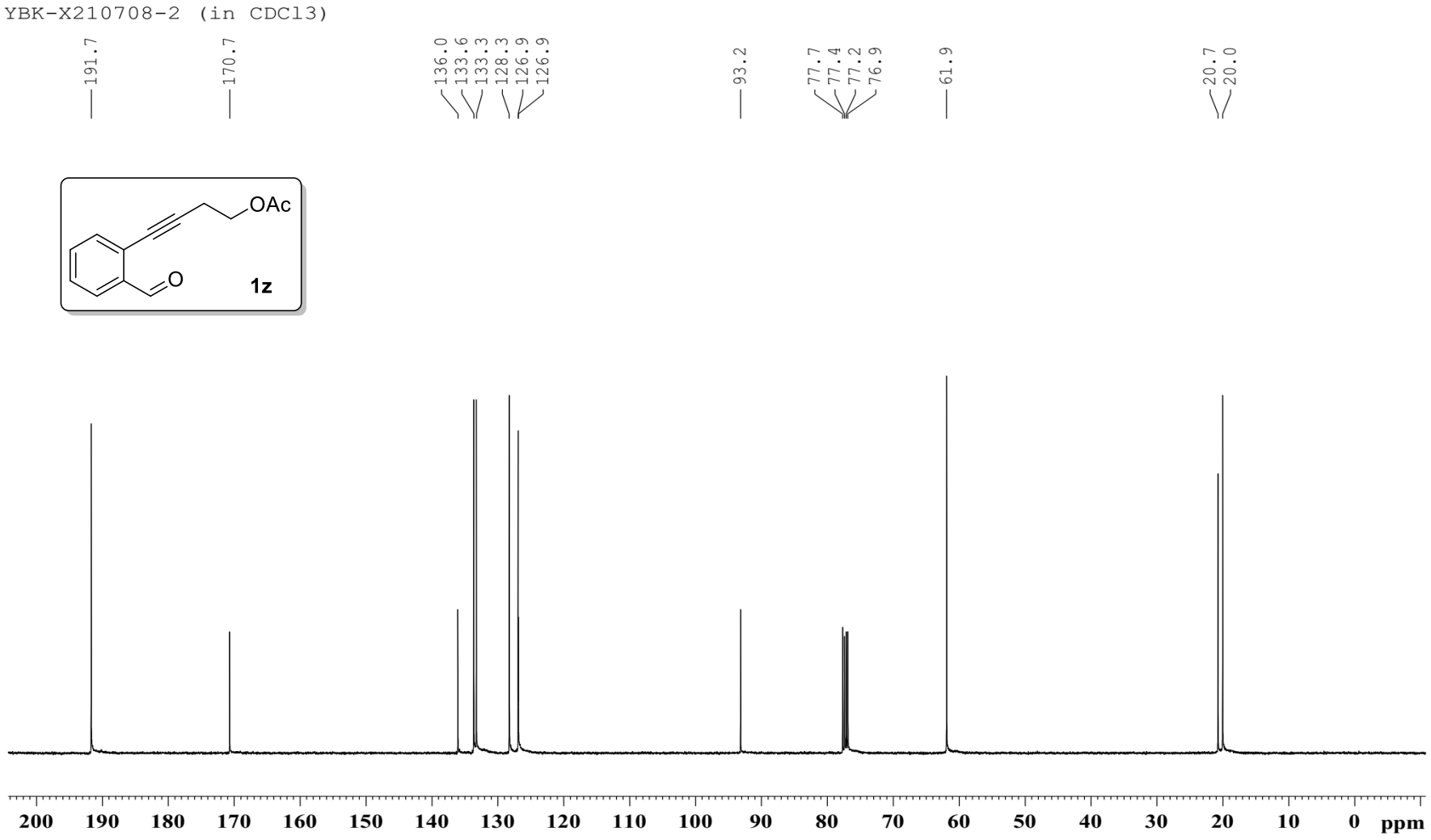
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1y



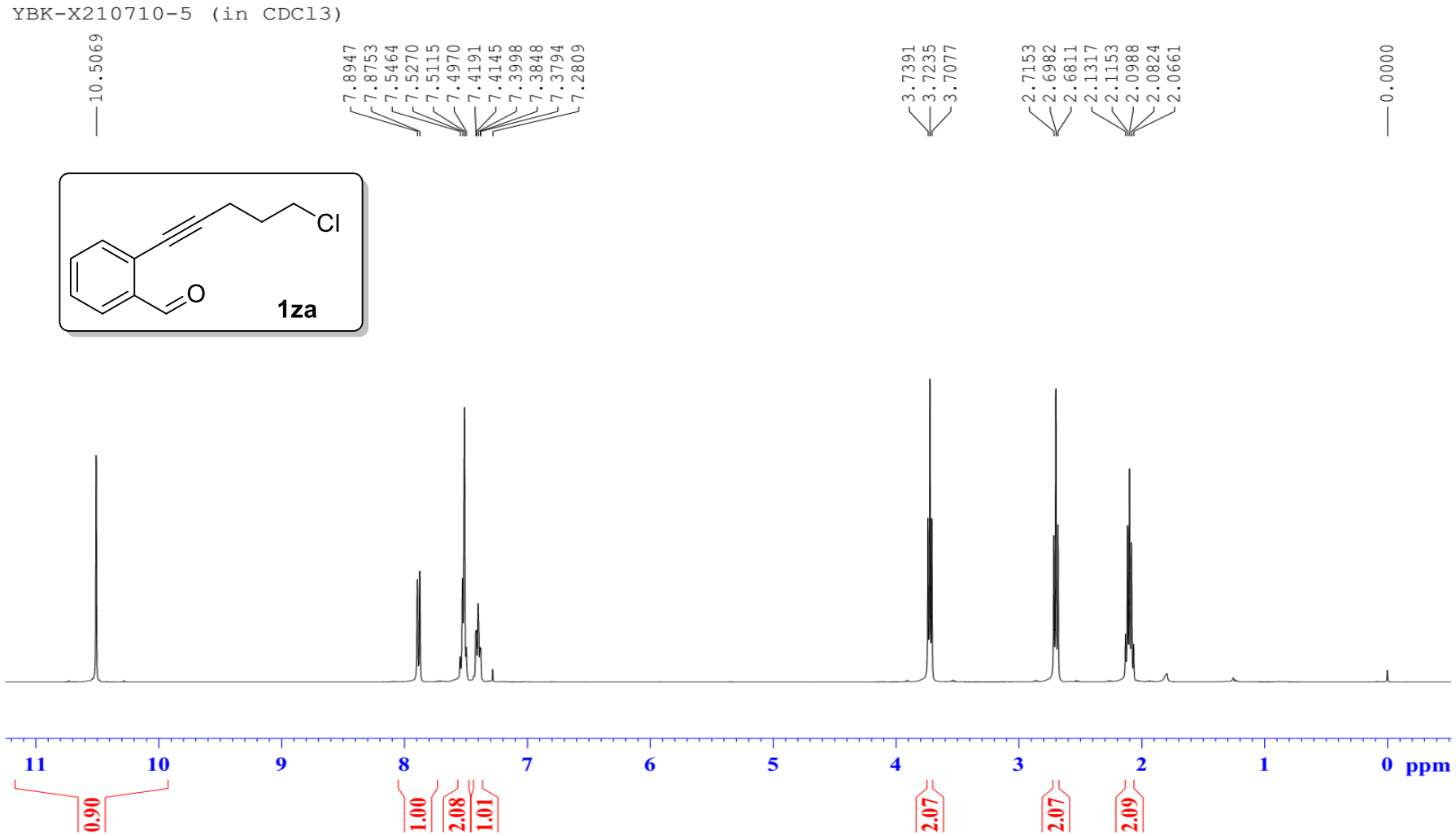
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1z



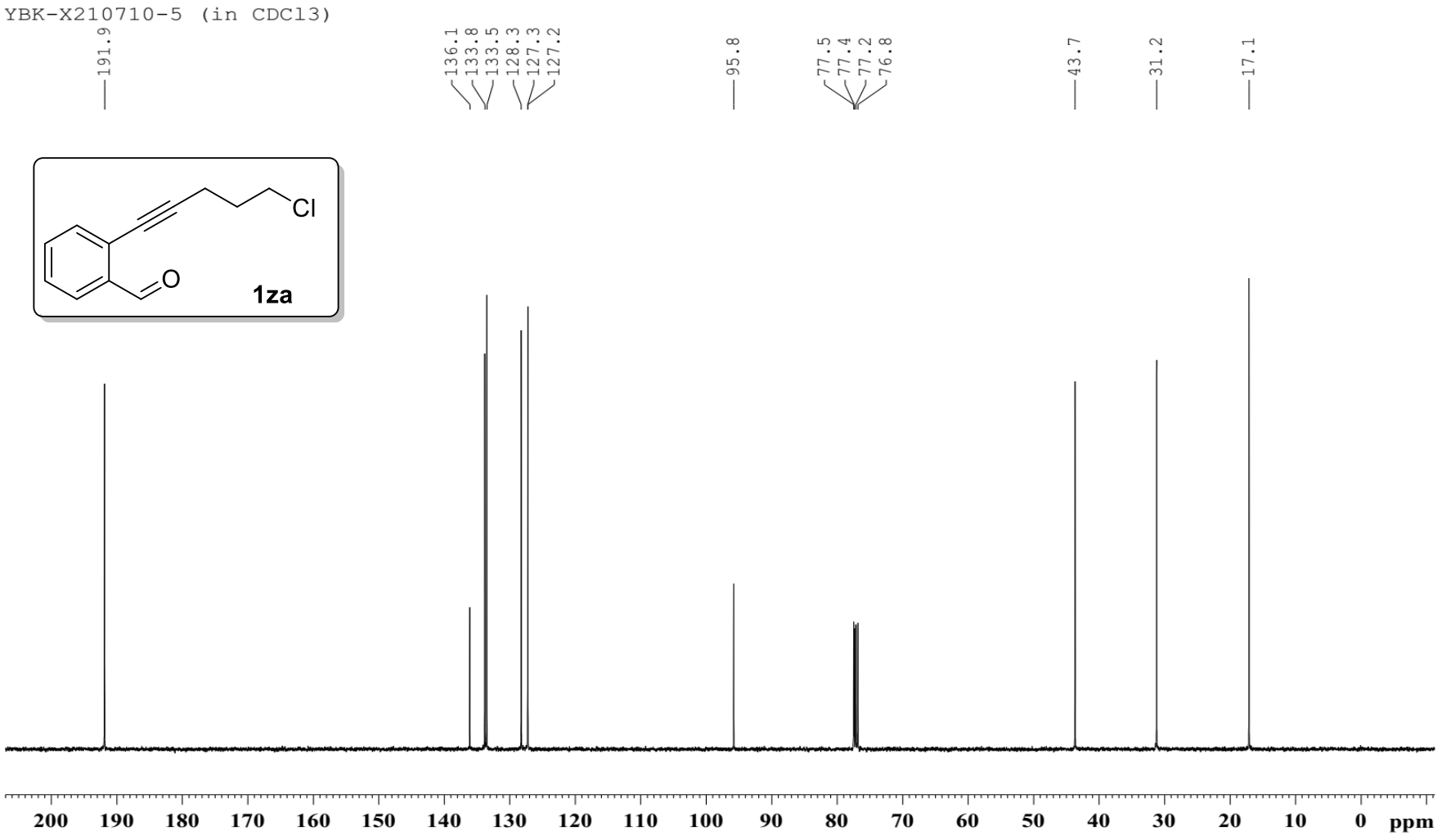
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1z



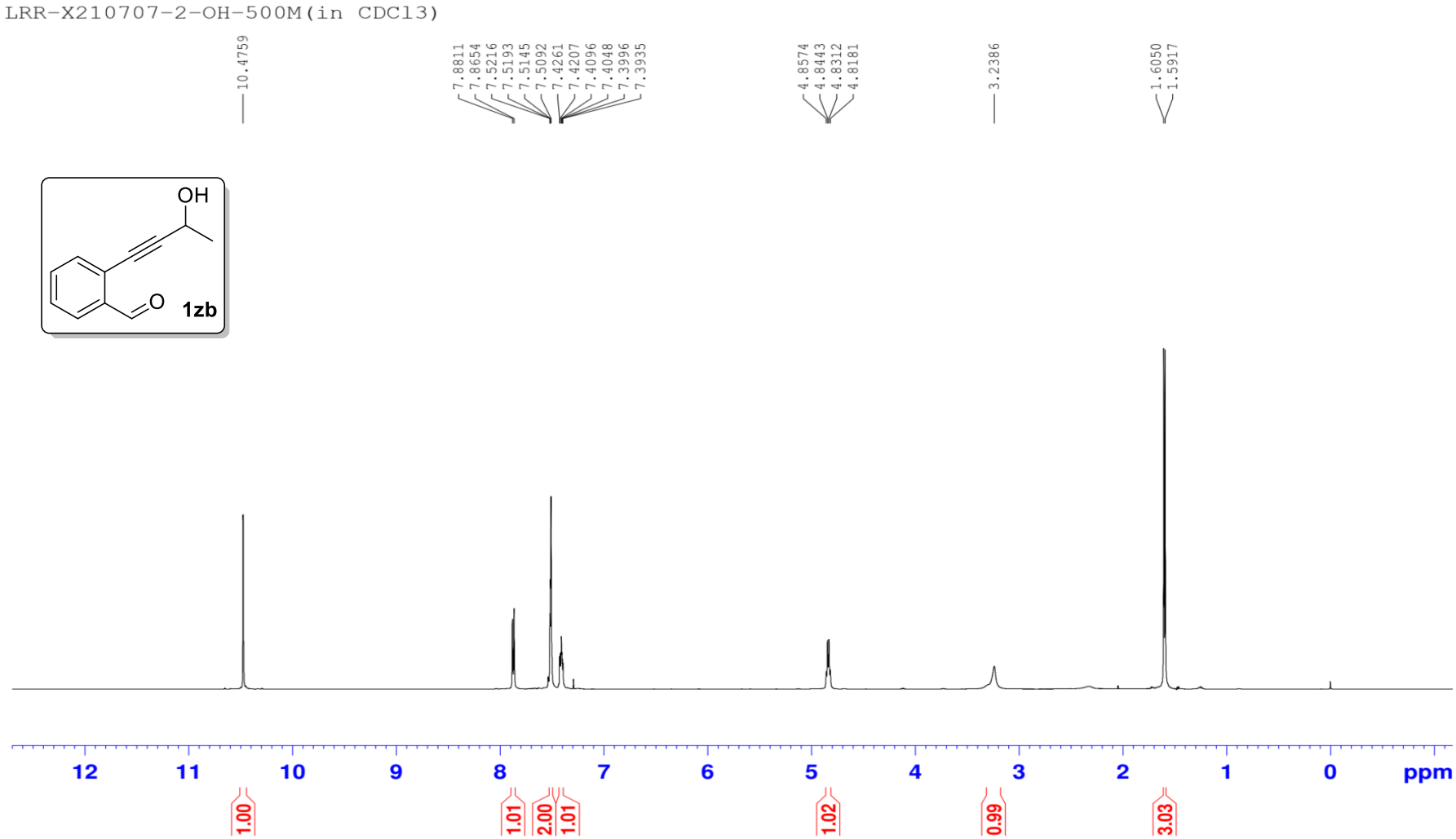
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1za



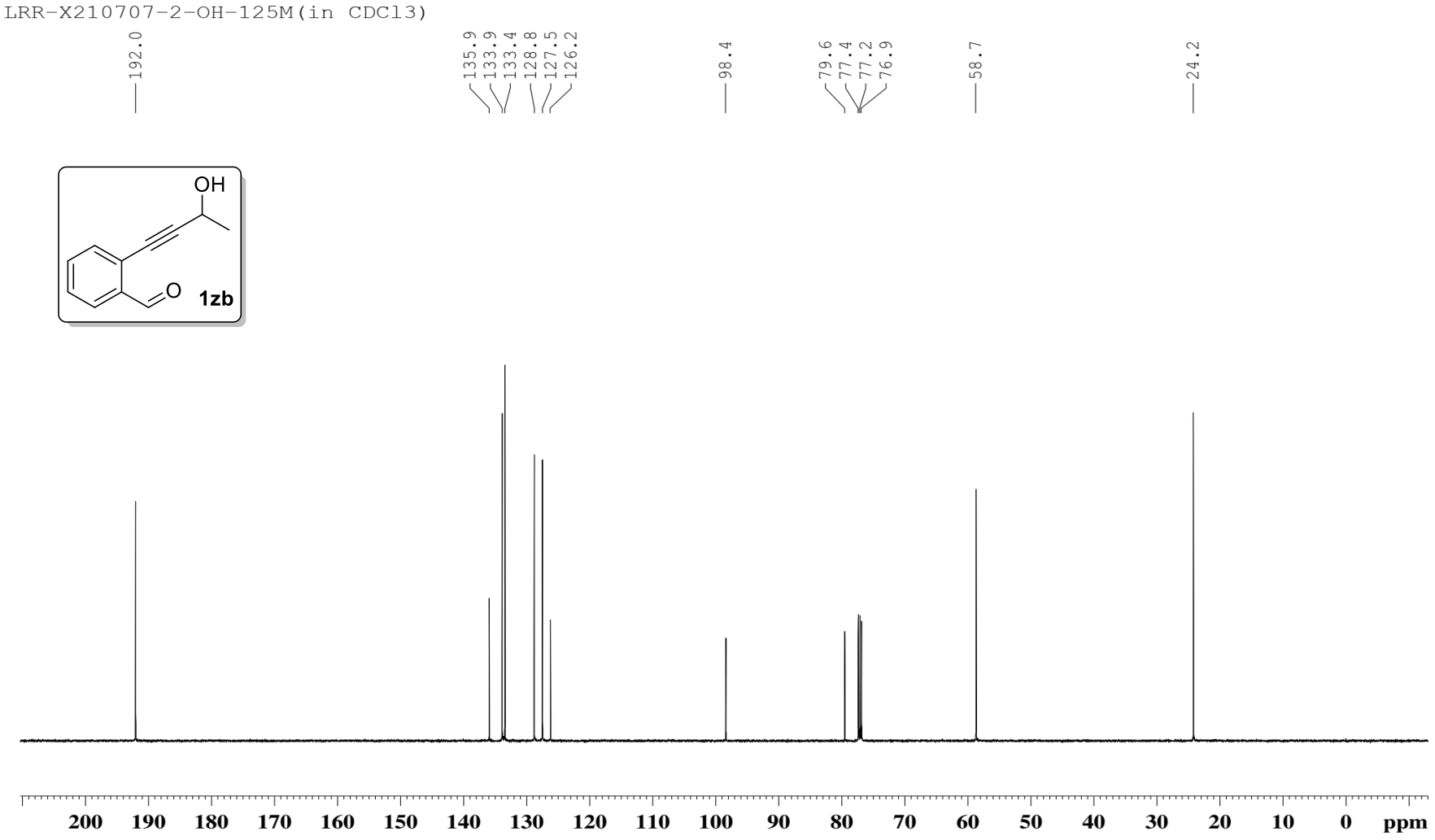
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1za



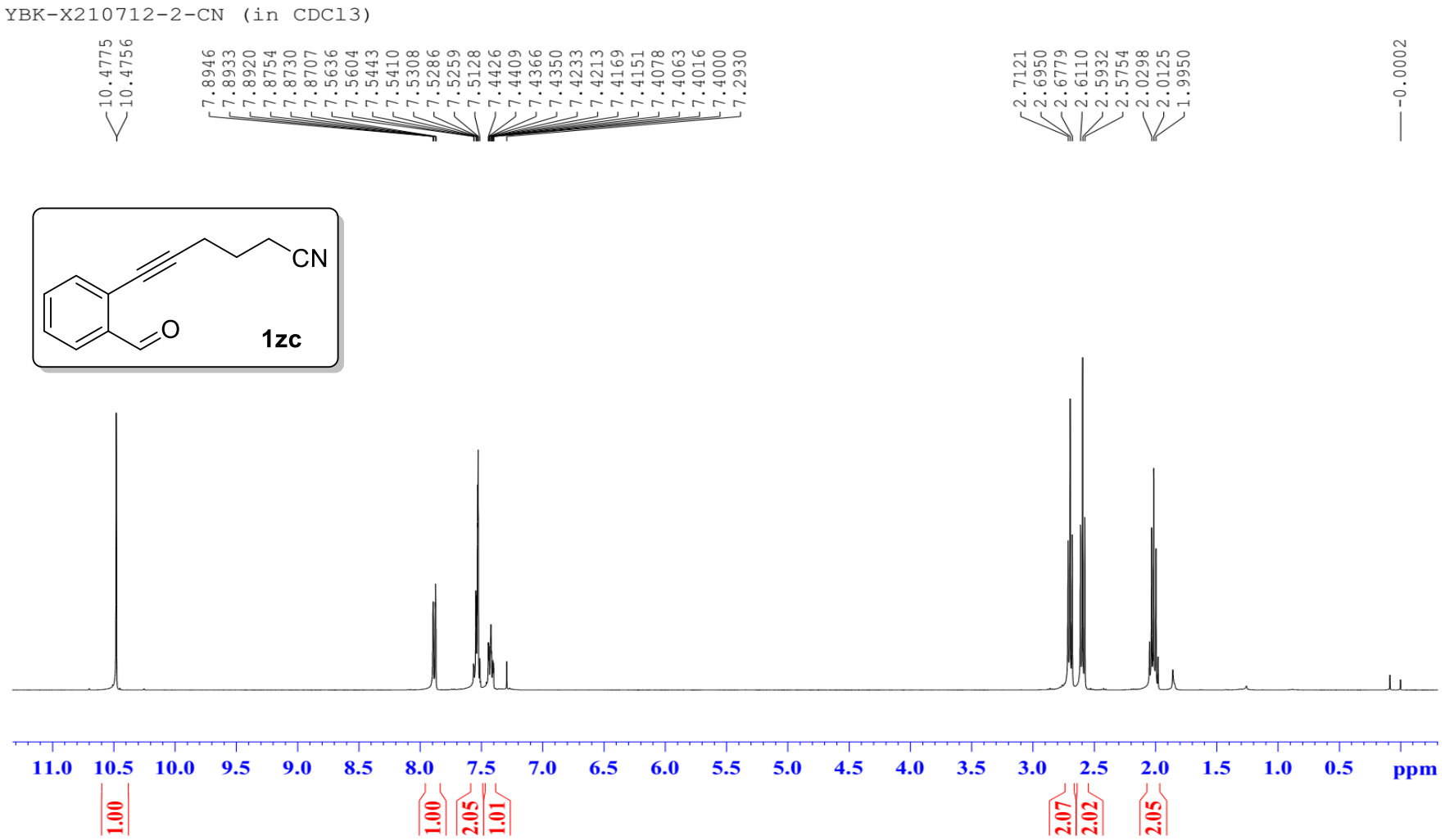
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1zb



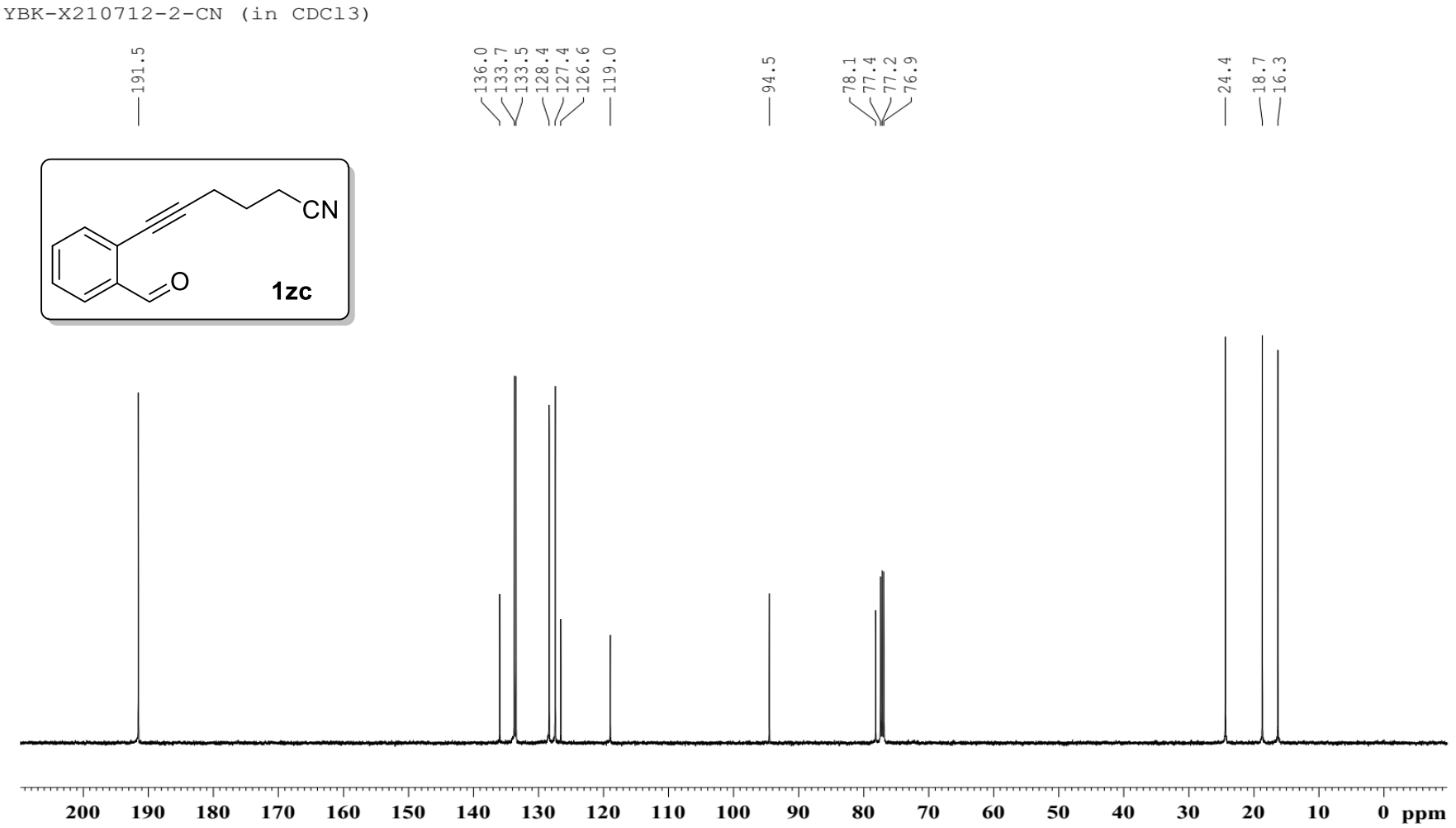
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1zb



^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1zc



^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1zc



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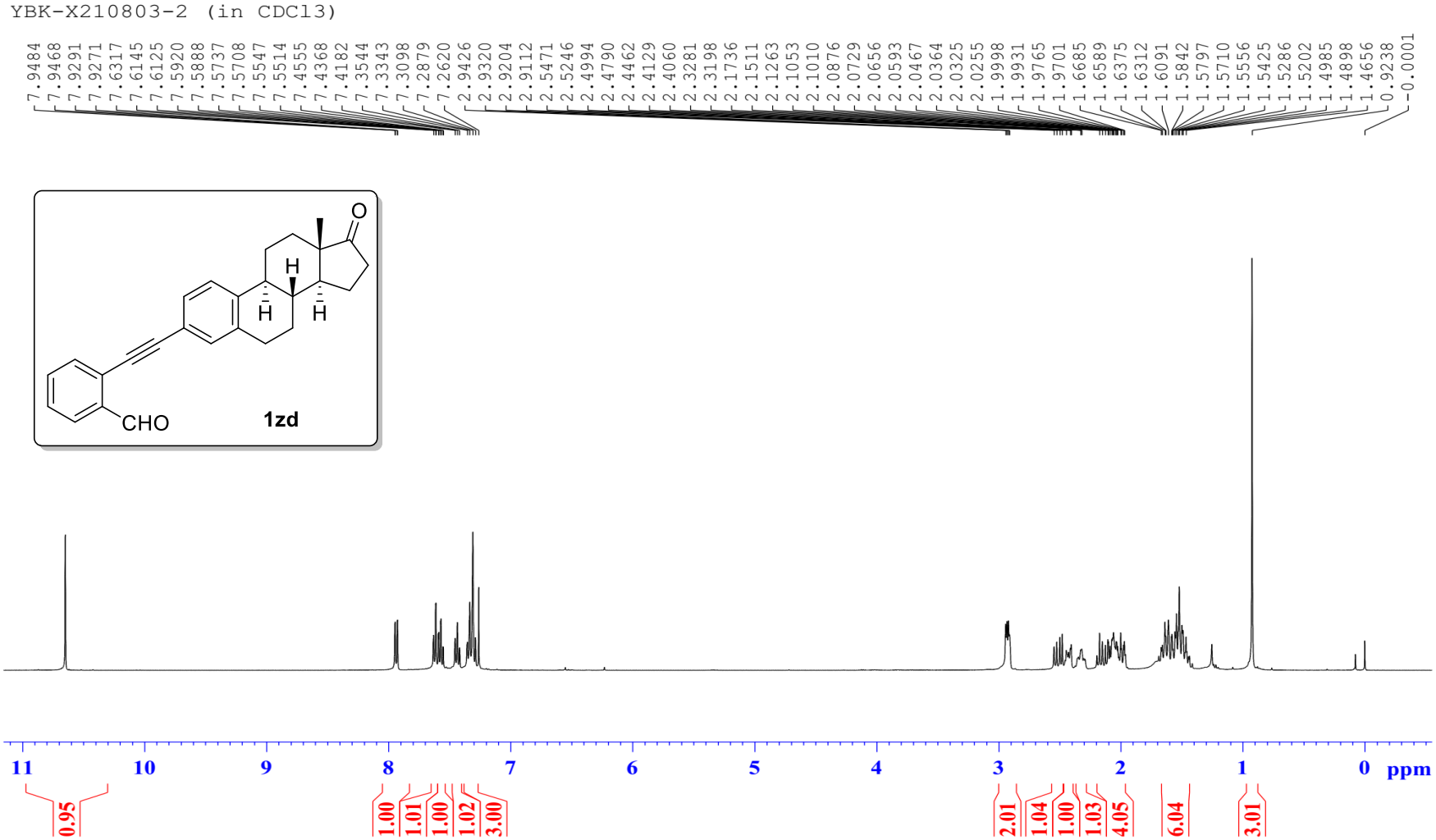
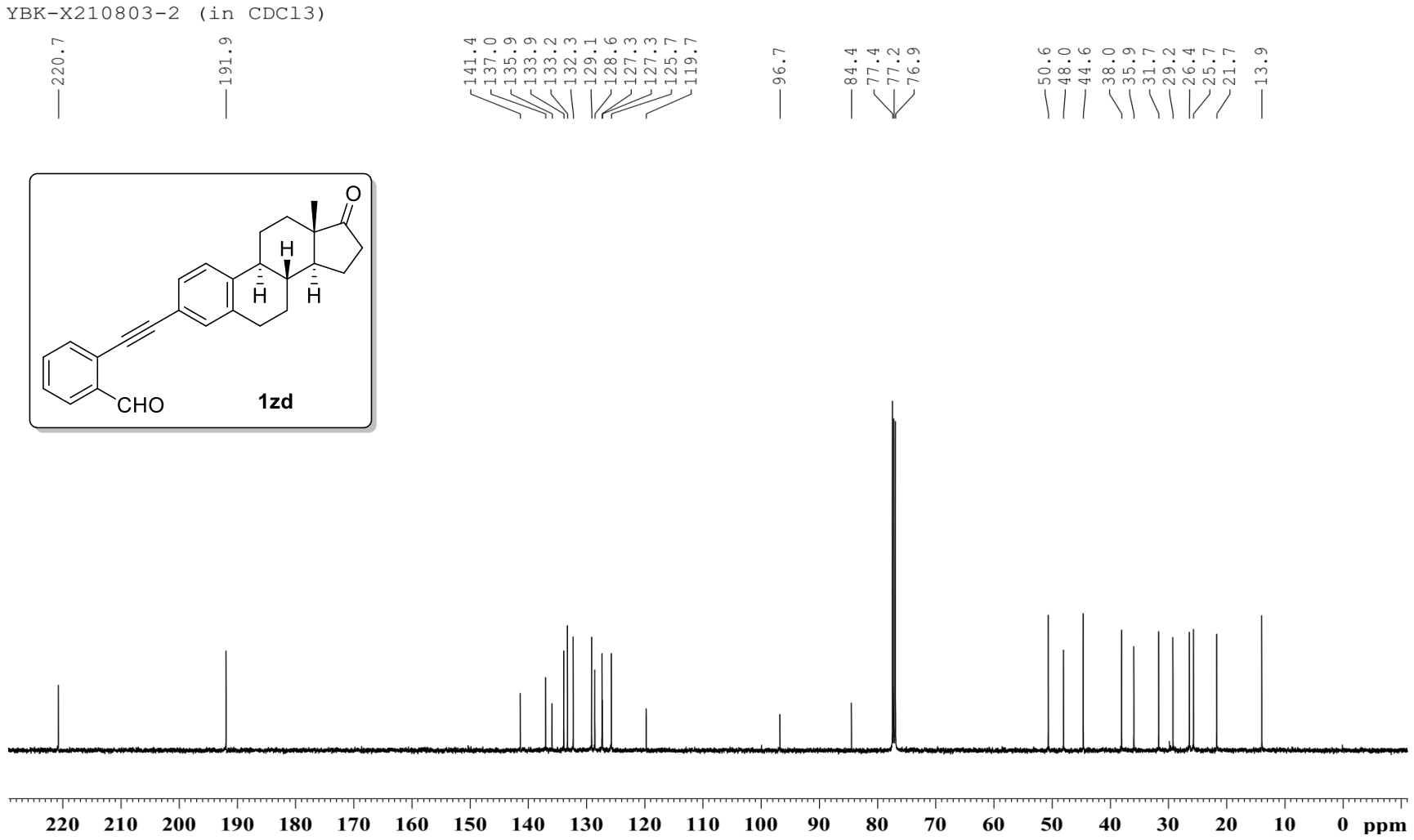
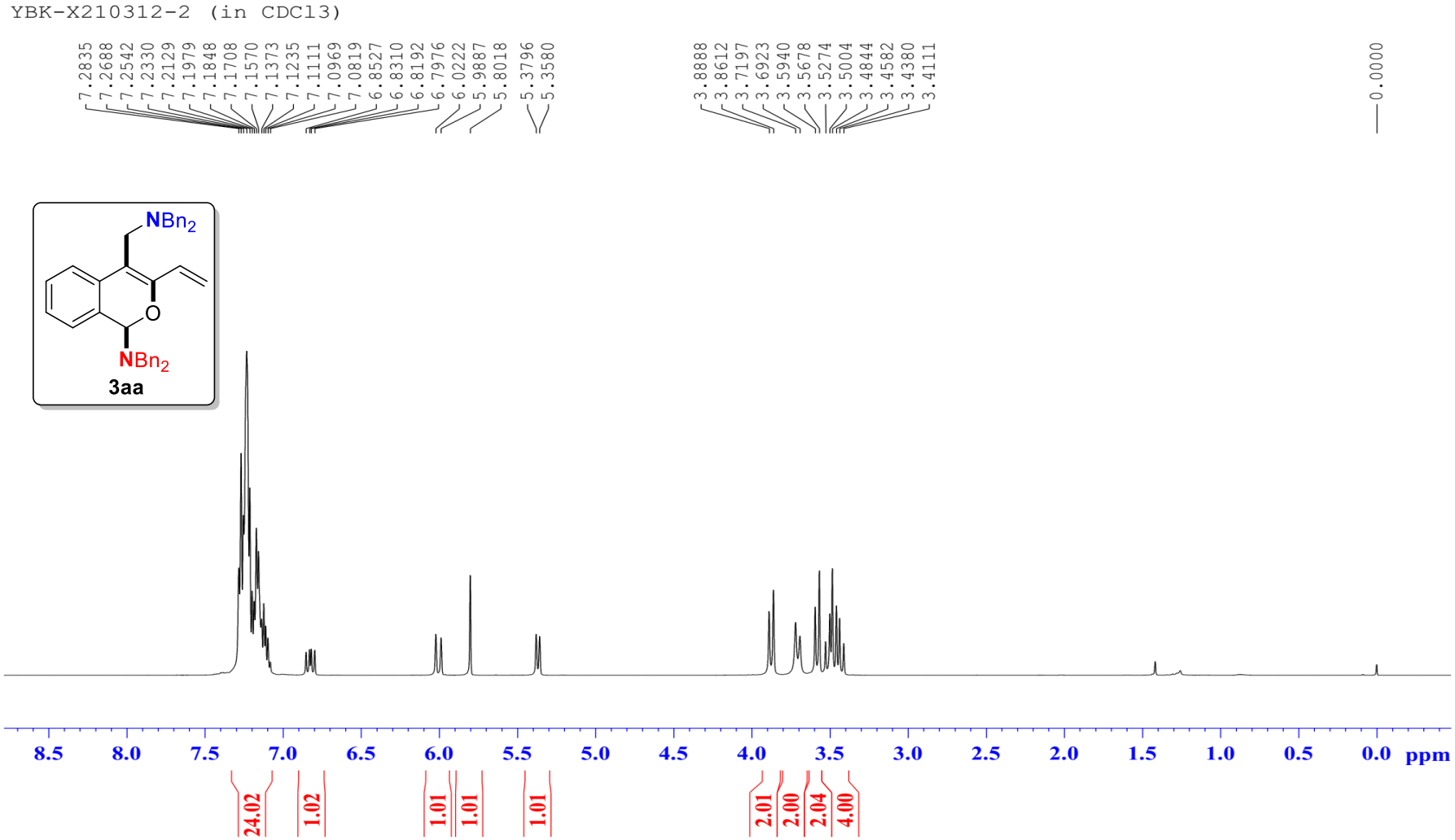


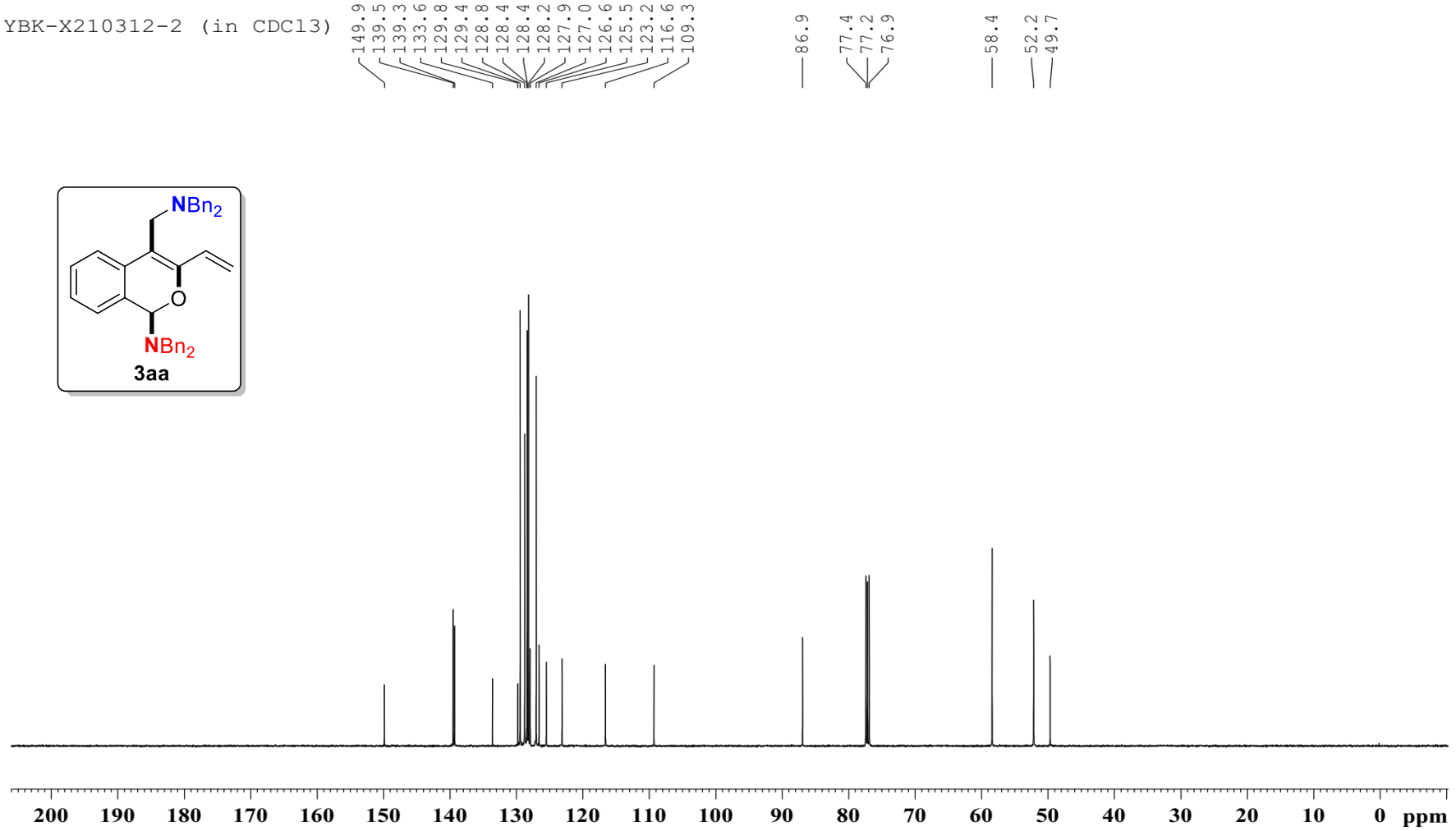
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1zd



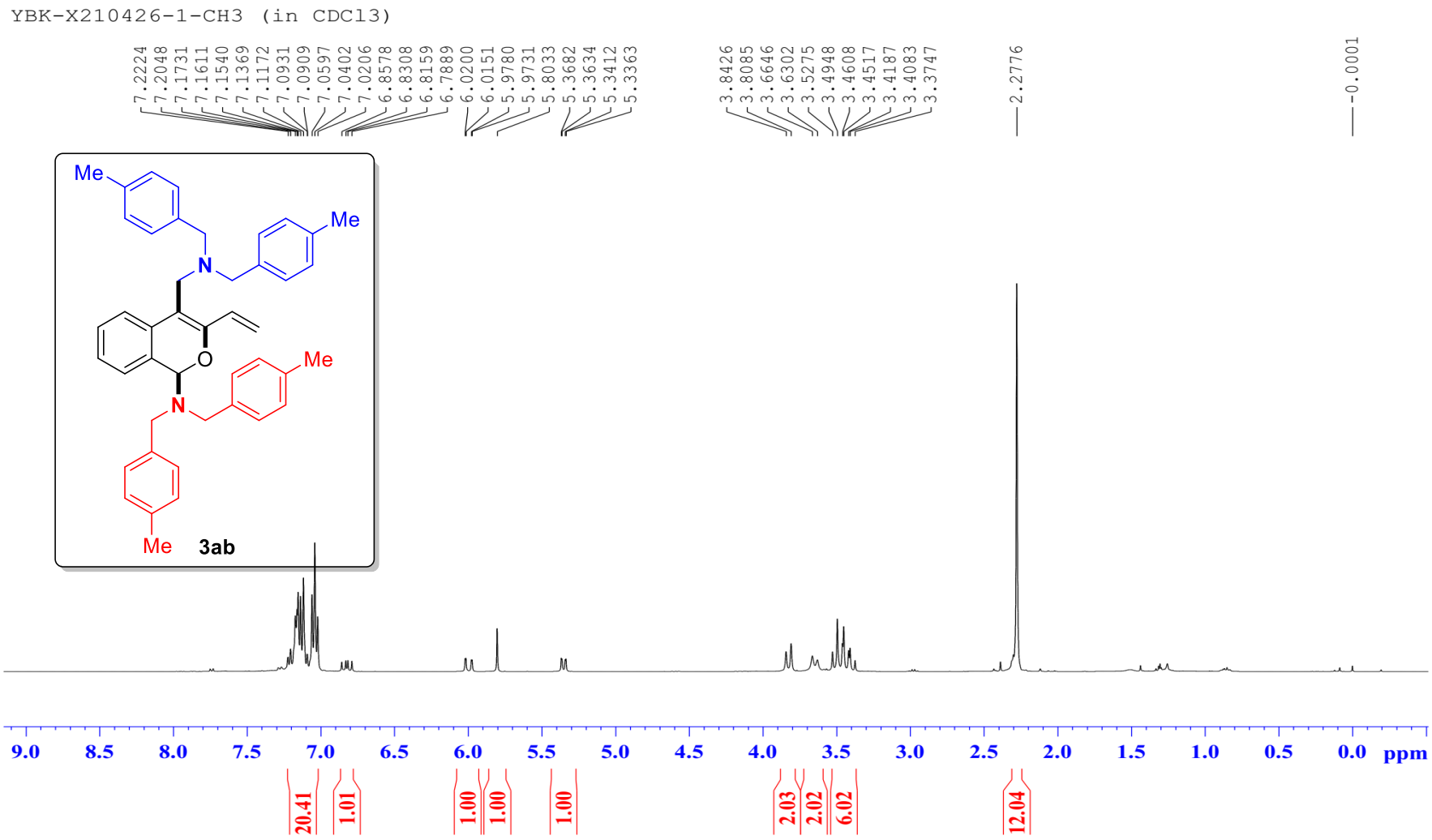
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3aa



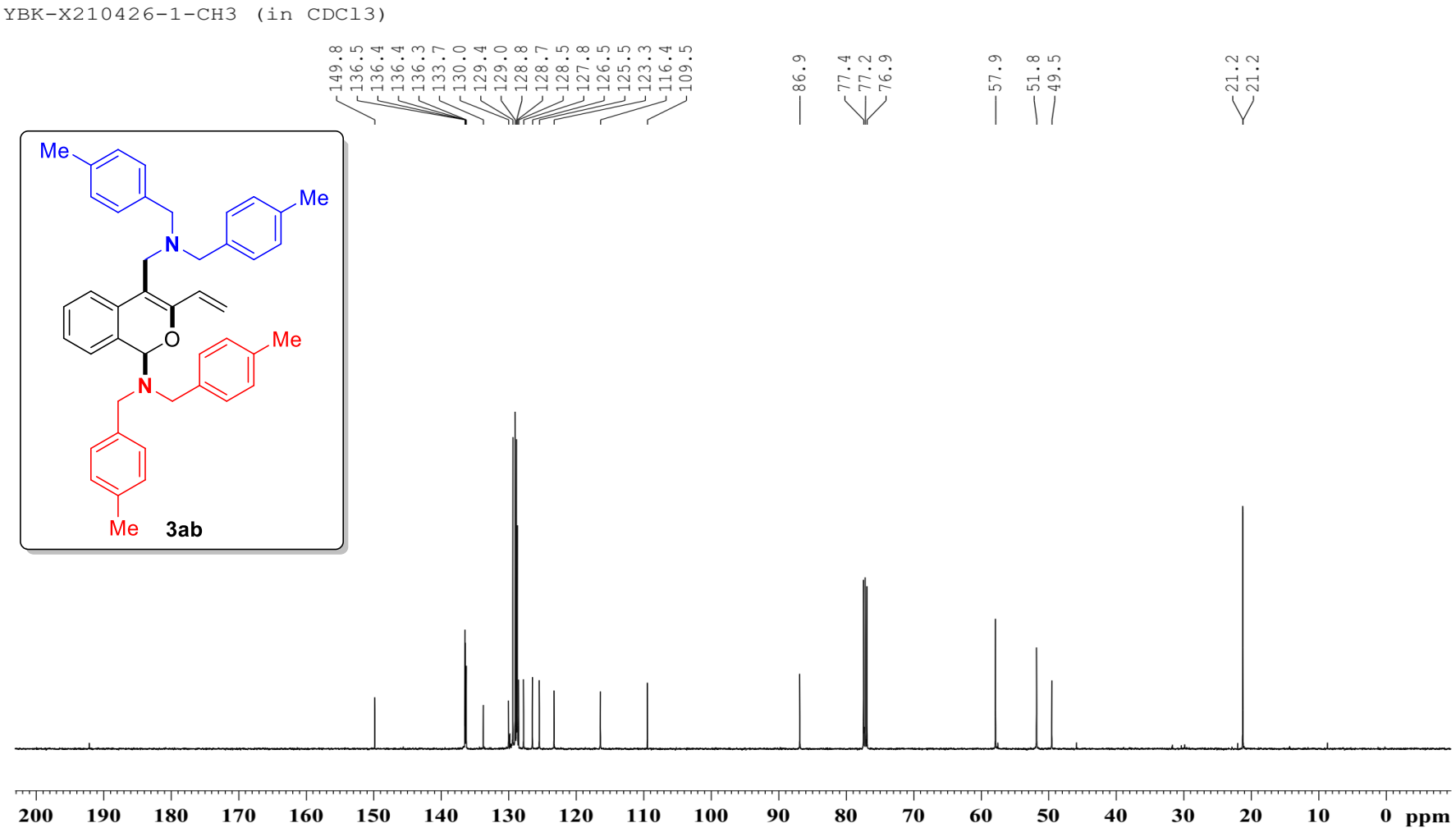
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3aa



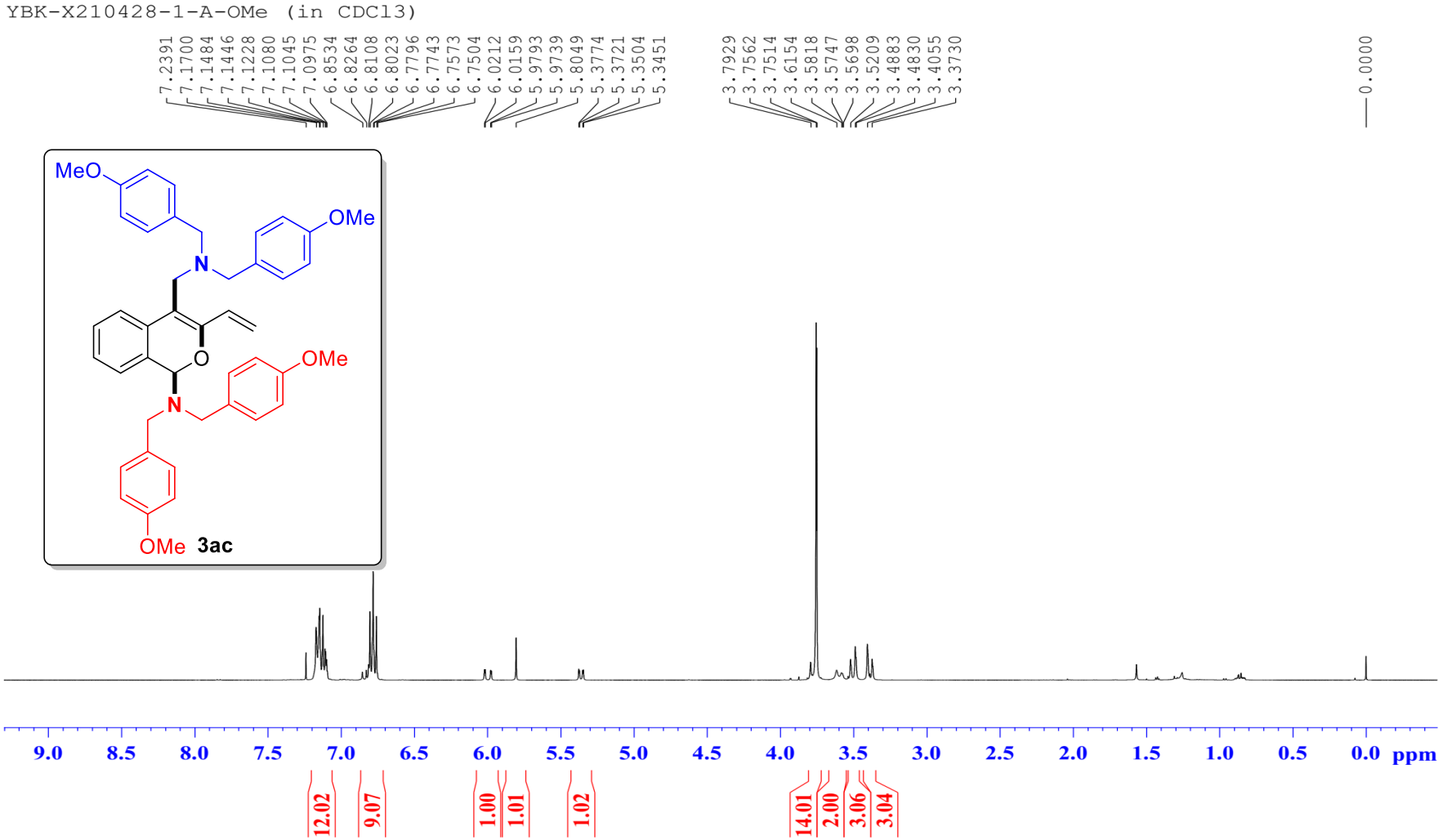
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ab



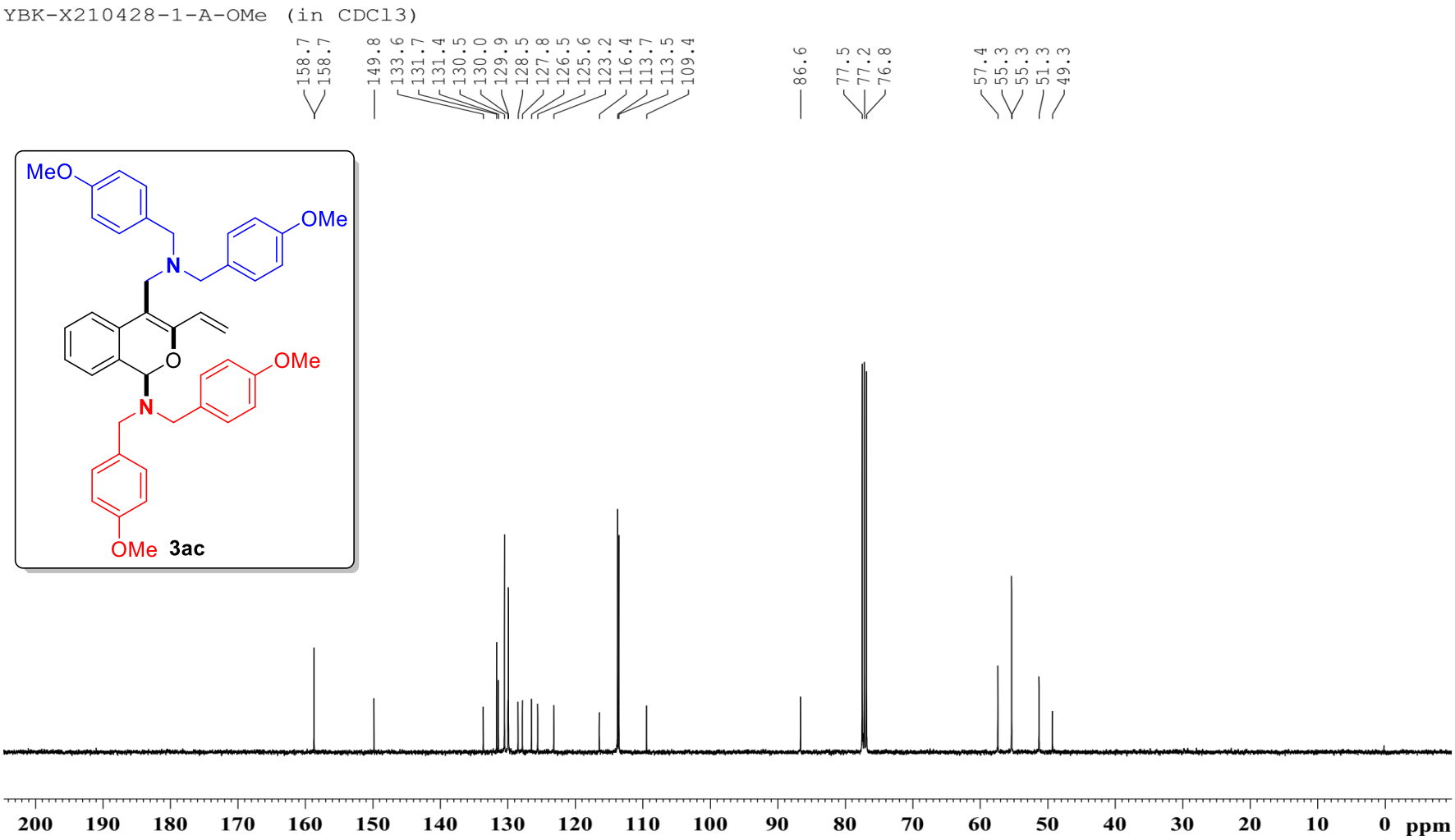
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ab



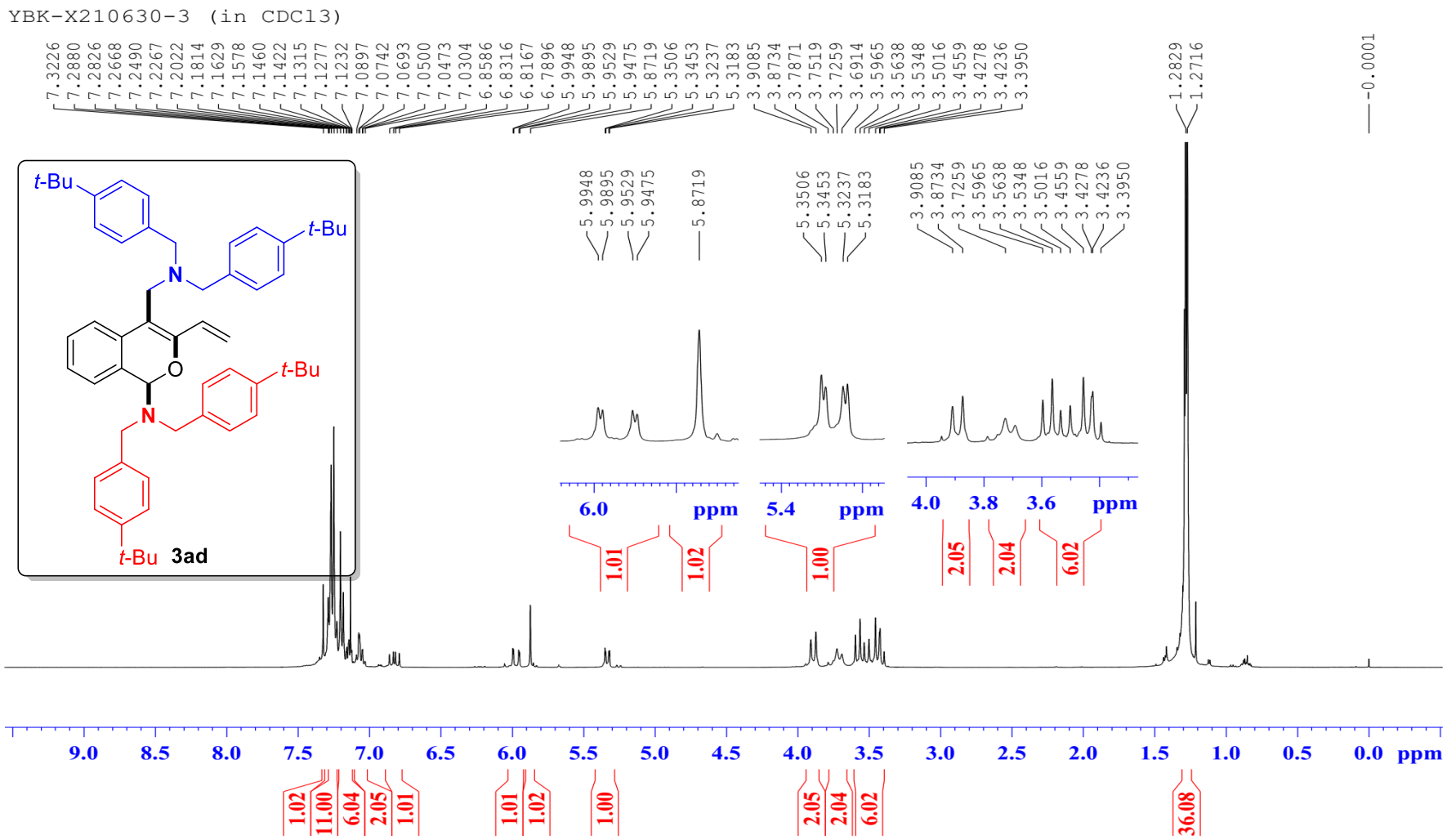
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ac



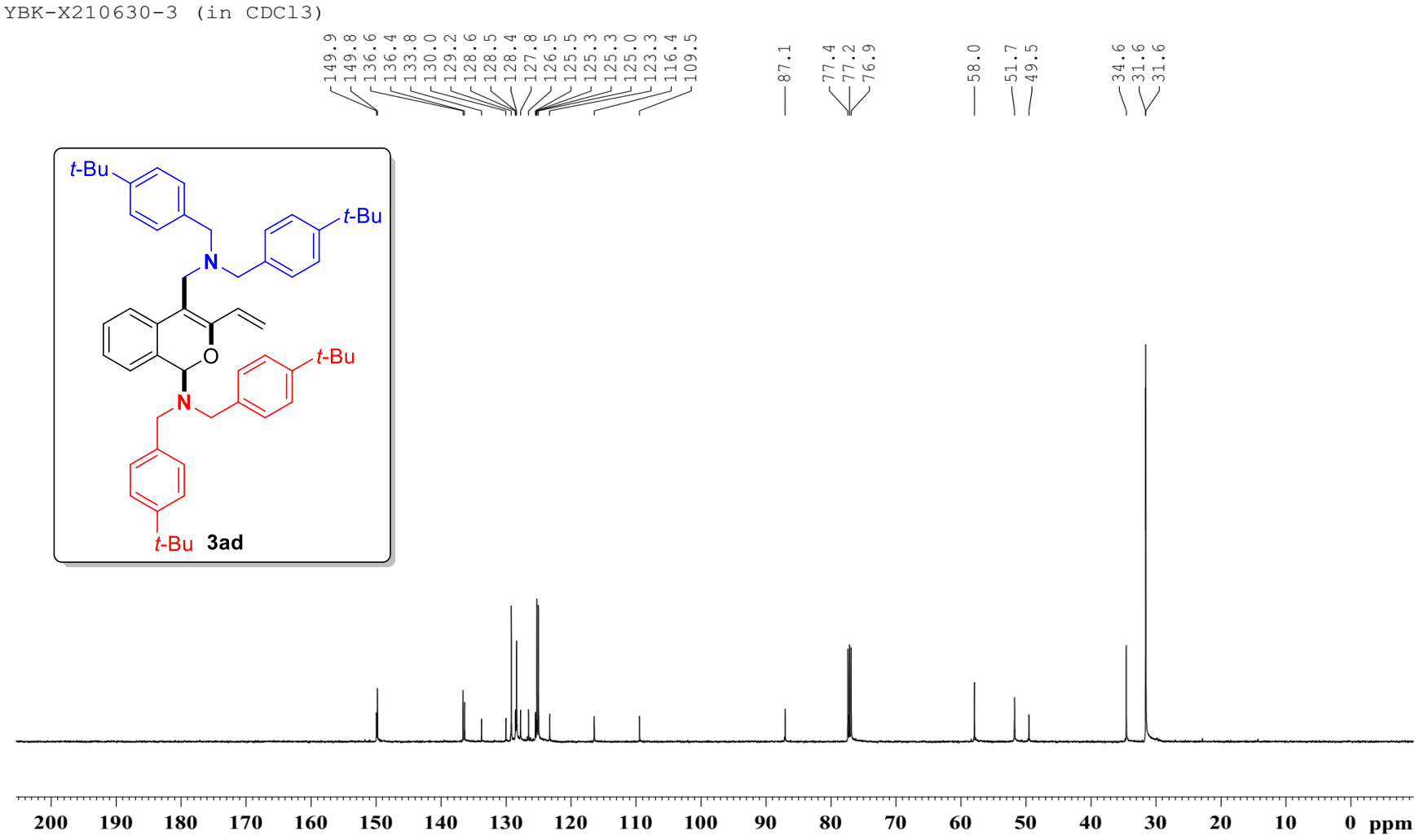
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ac



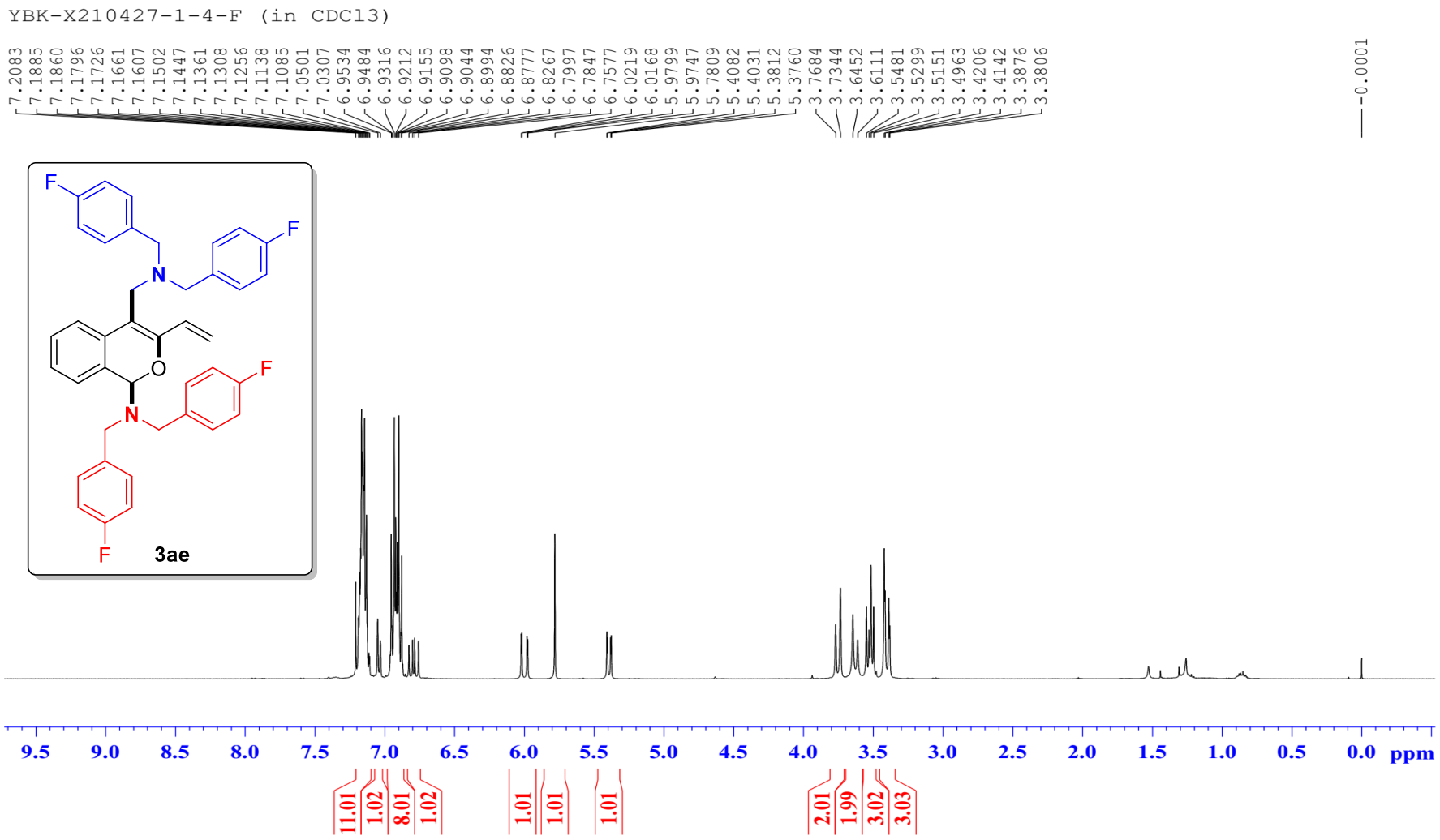
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ad



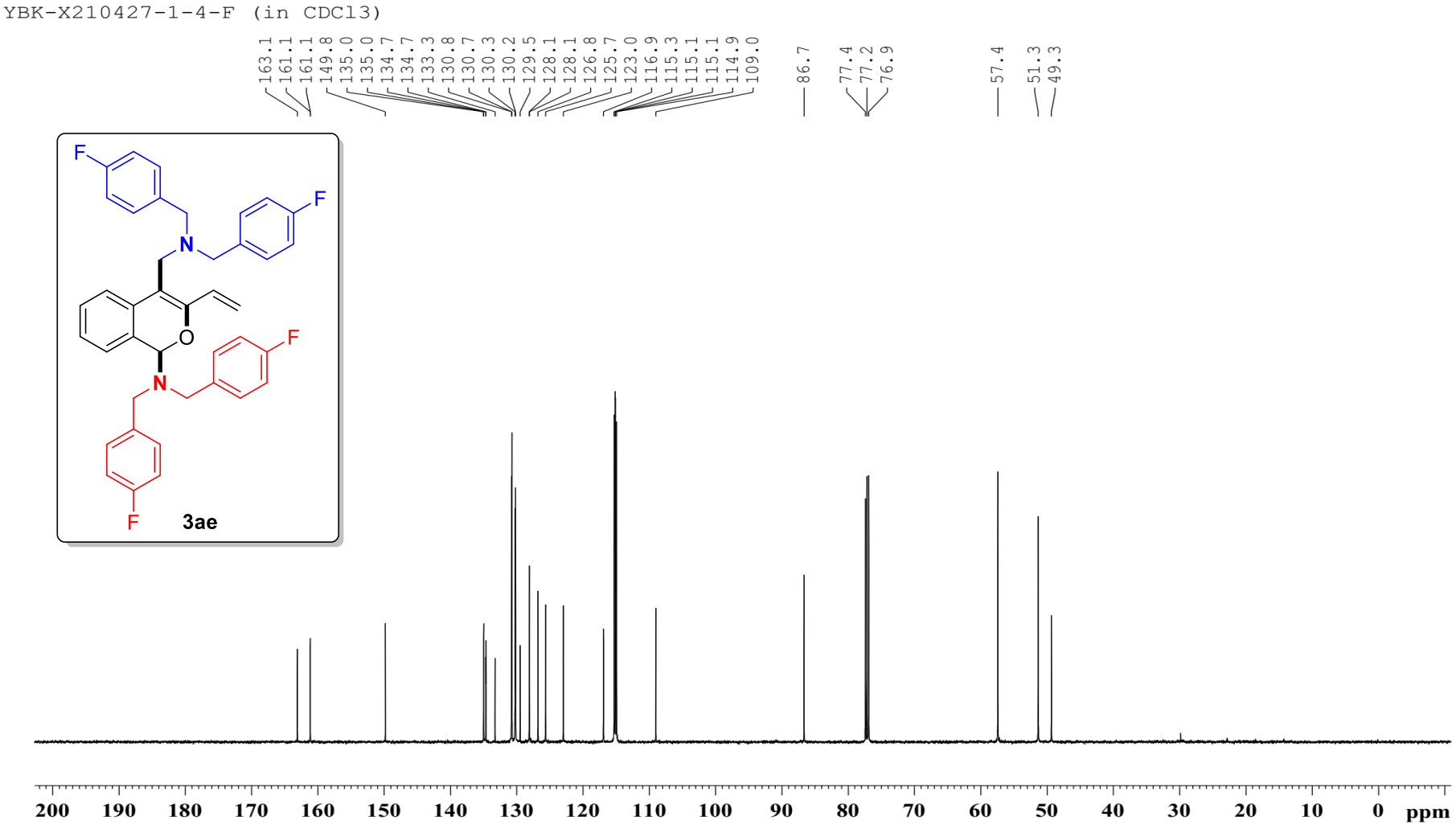
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ad



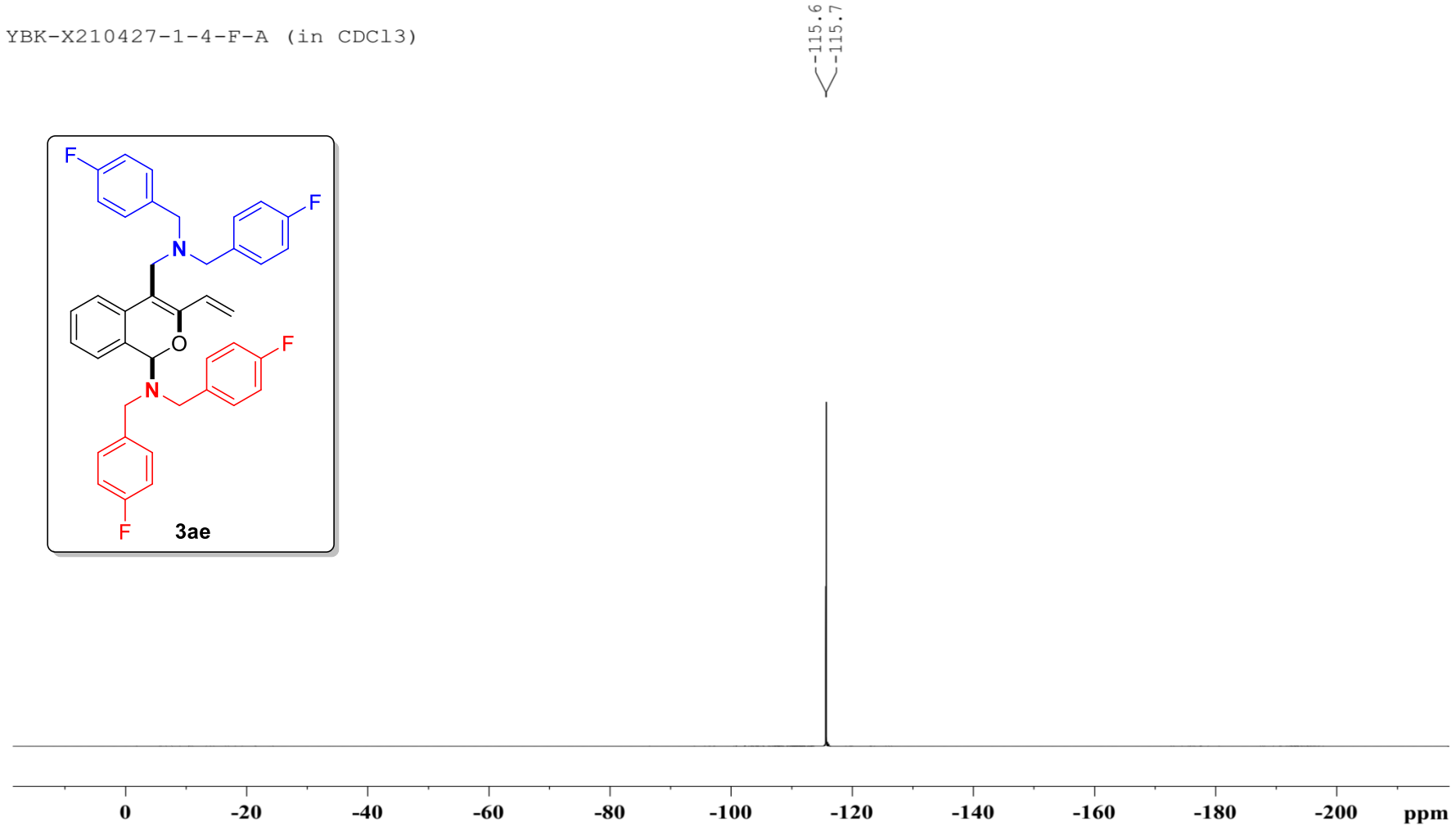
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ae



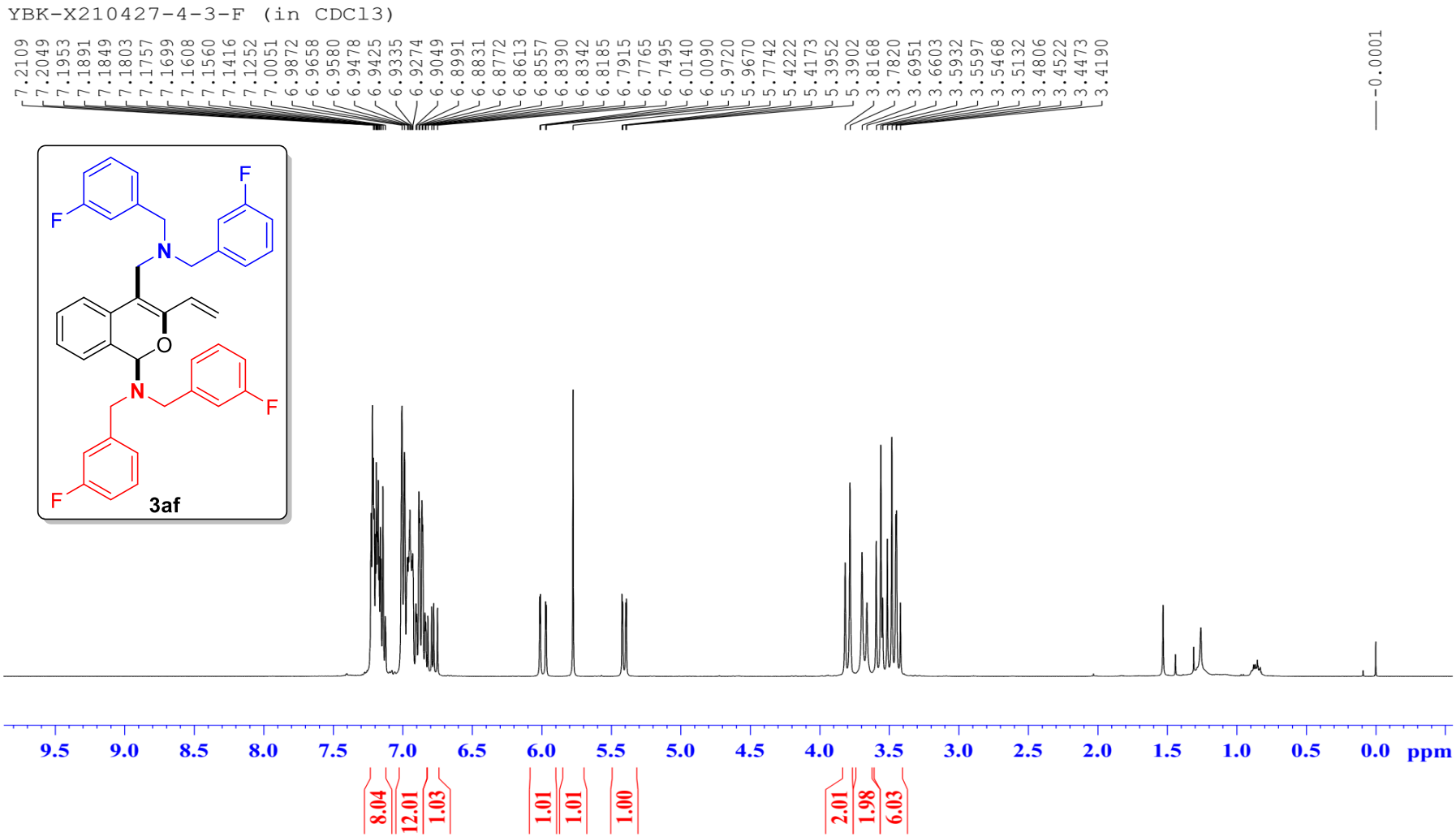
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ae



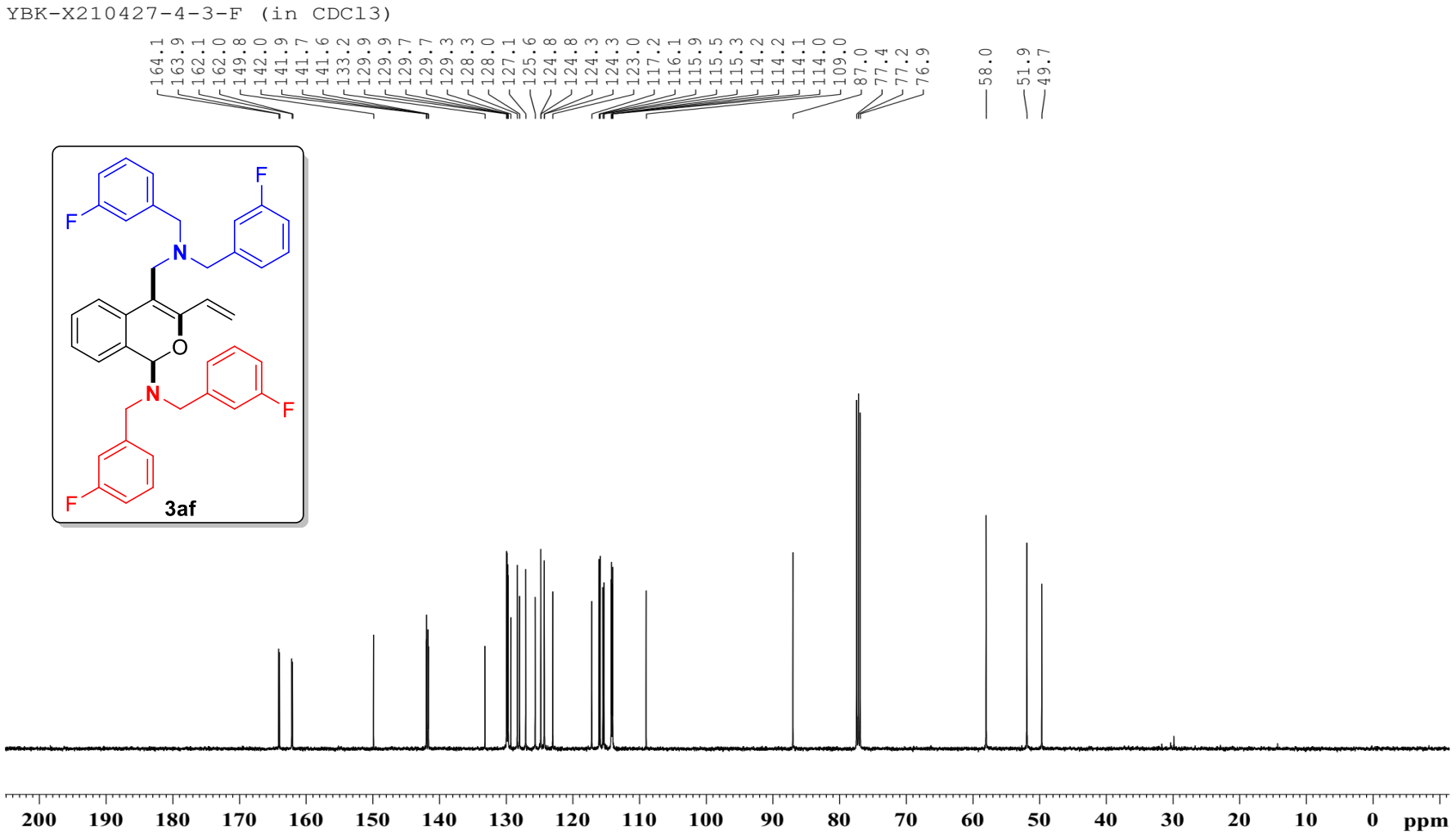
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 3ae



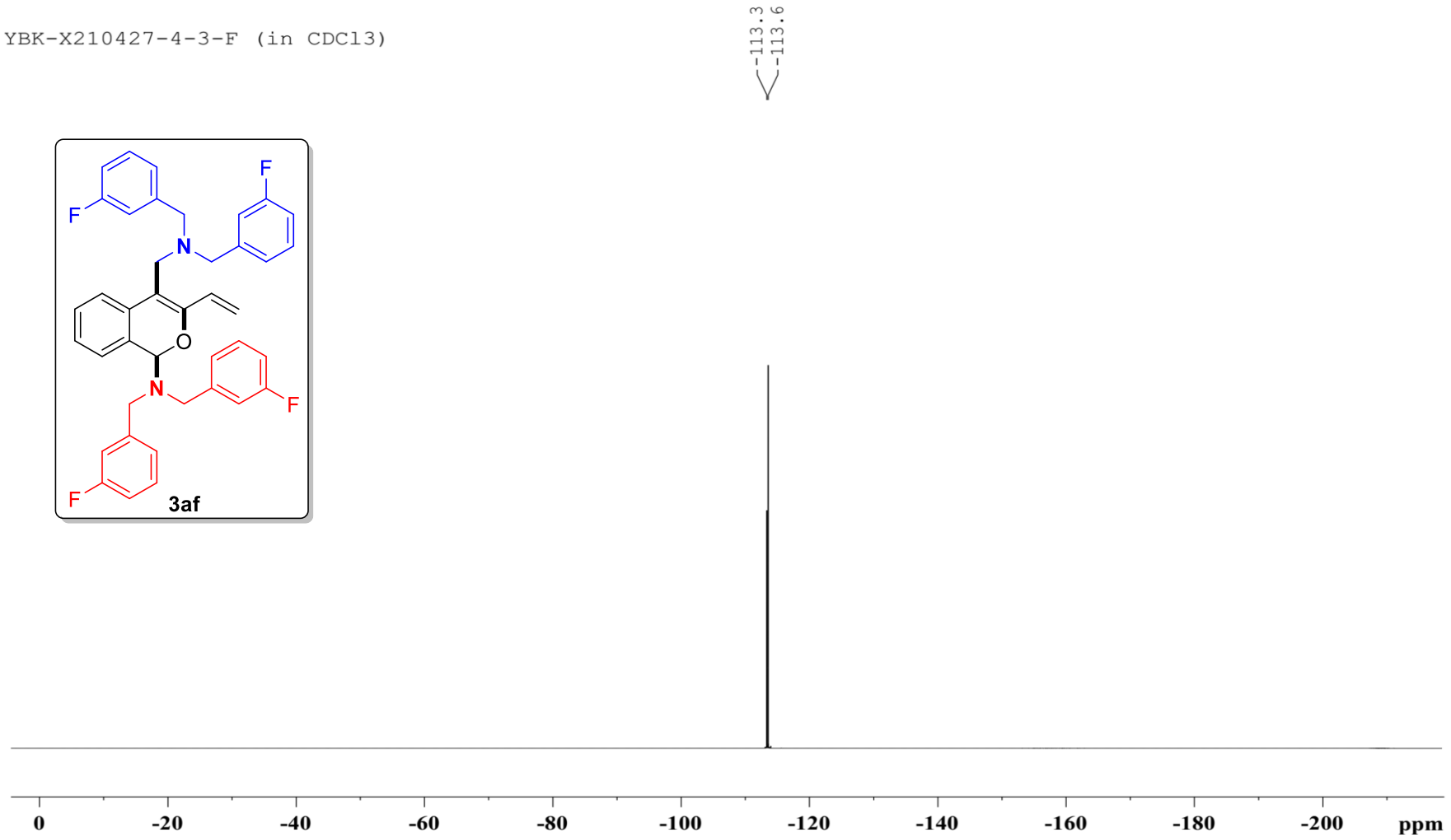
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3af



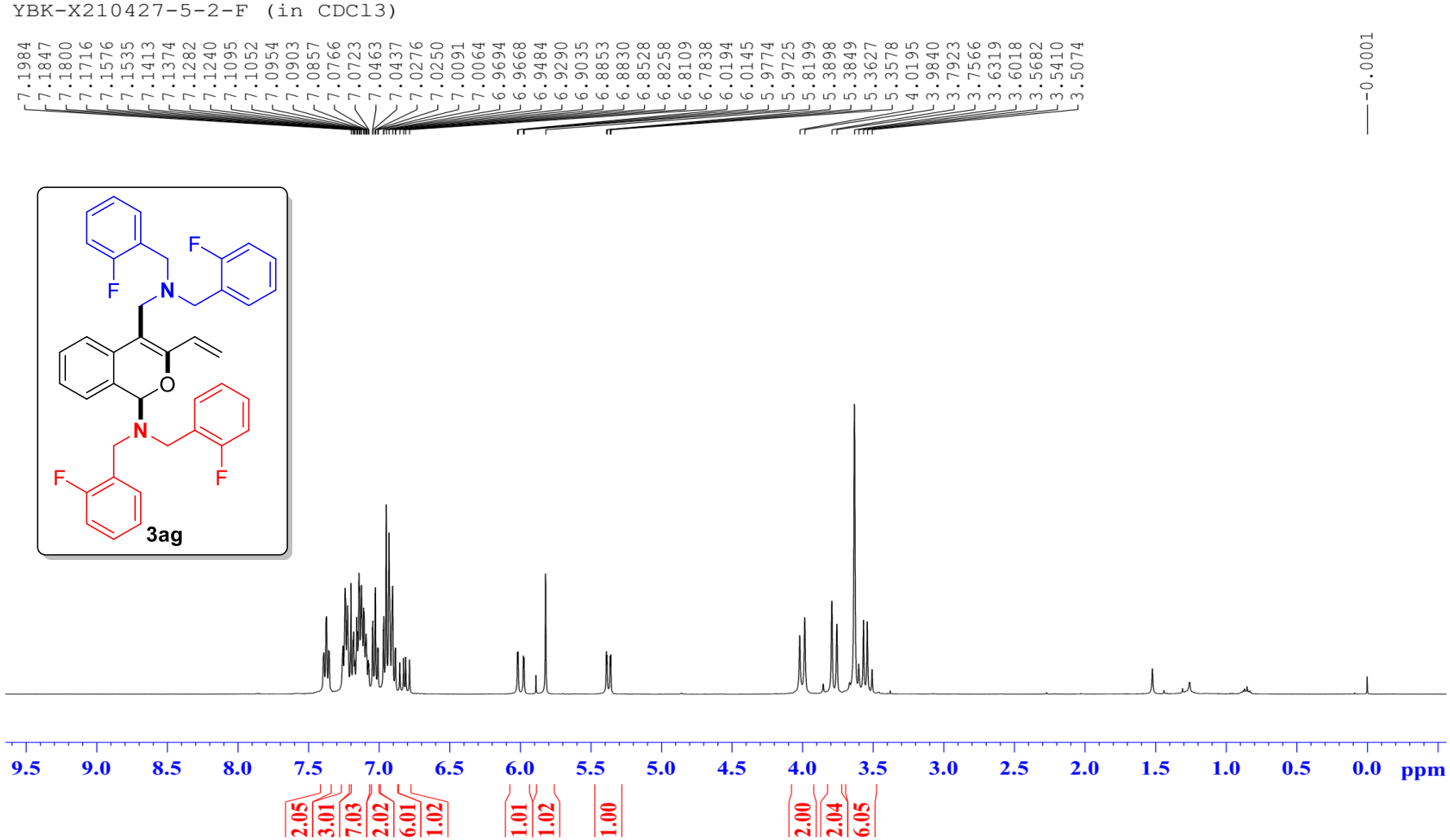
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3af



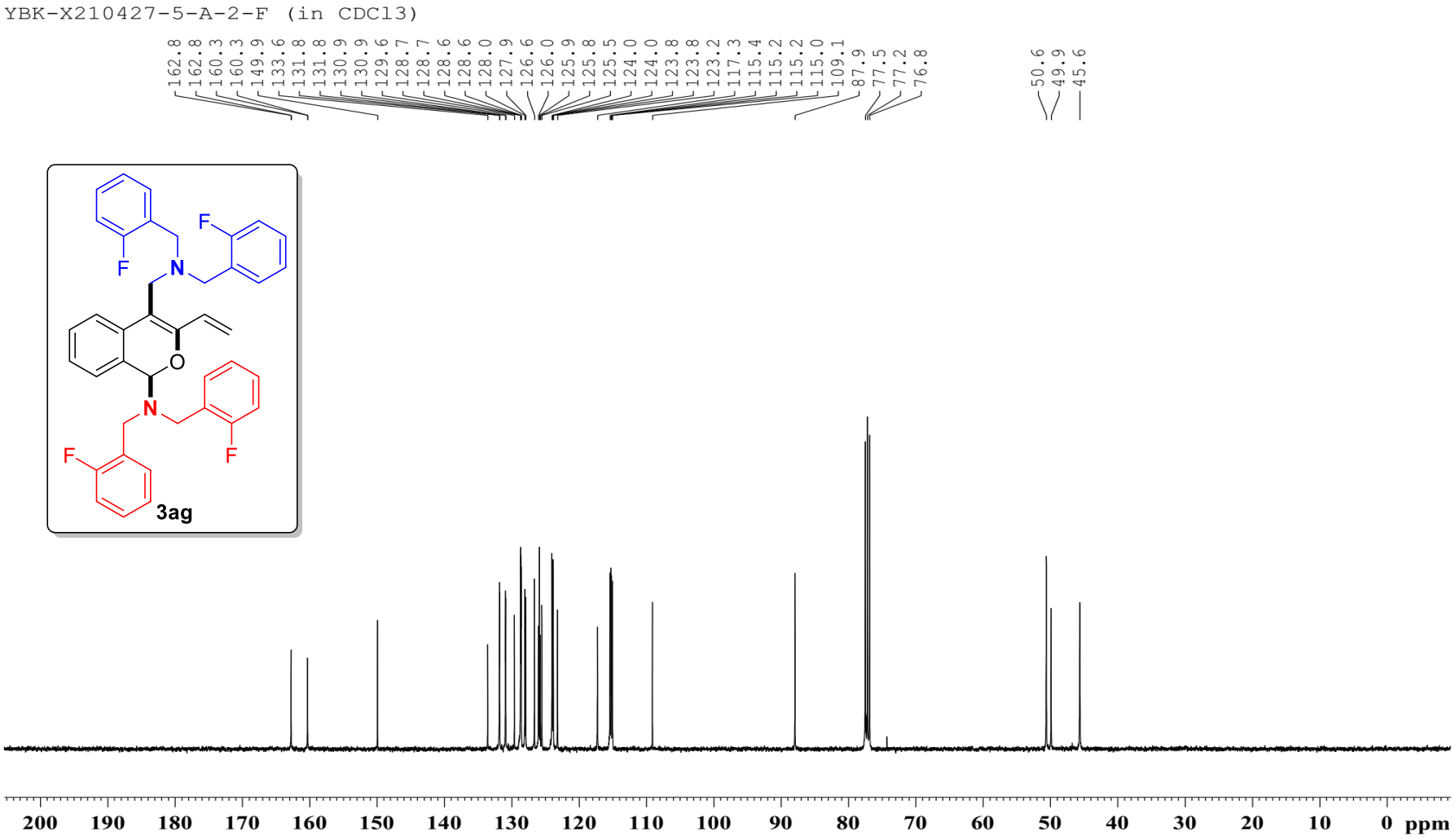
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 3af



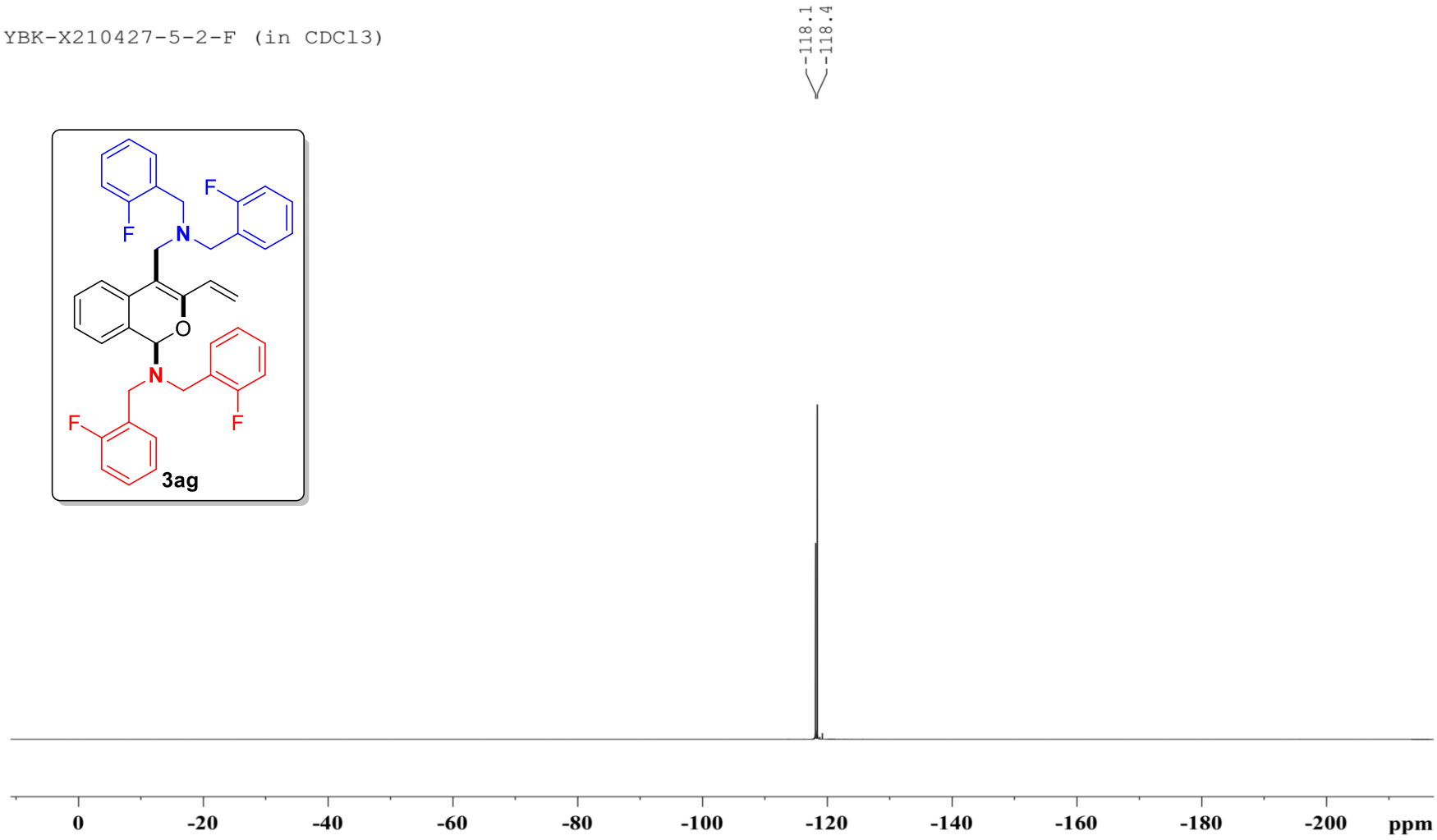
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ag



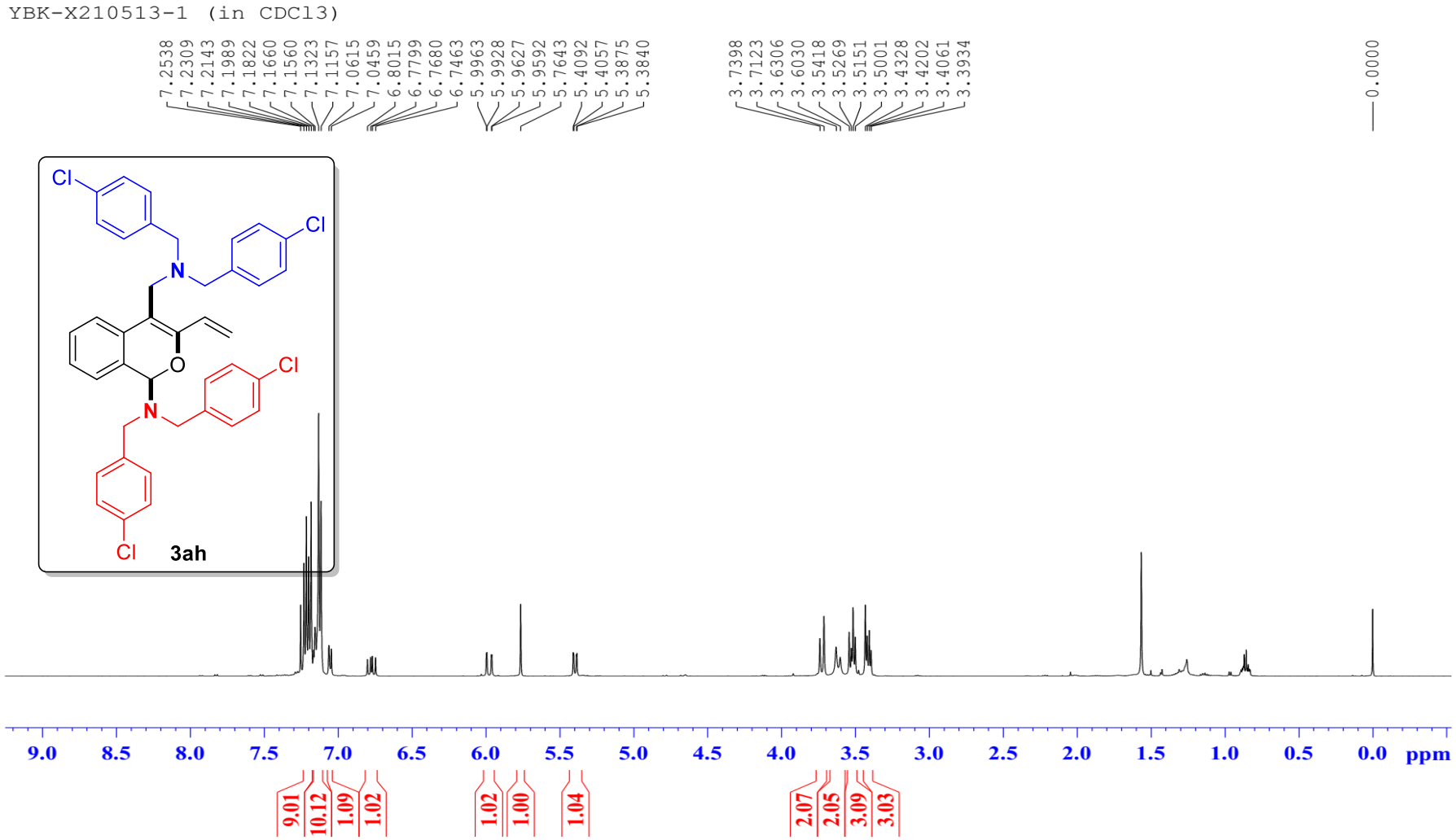
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ag



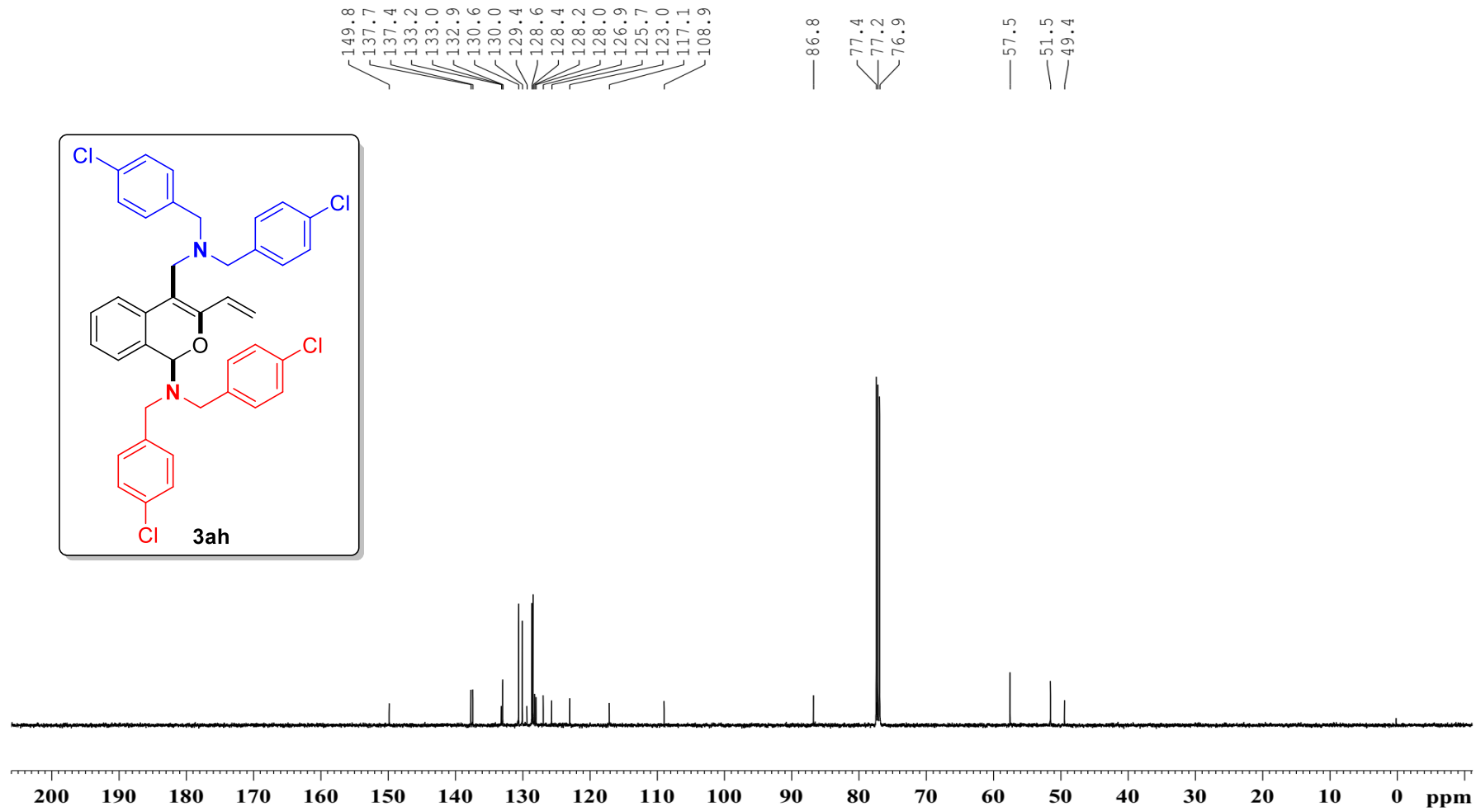
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 3ag



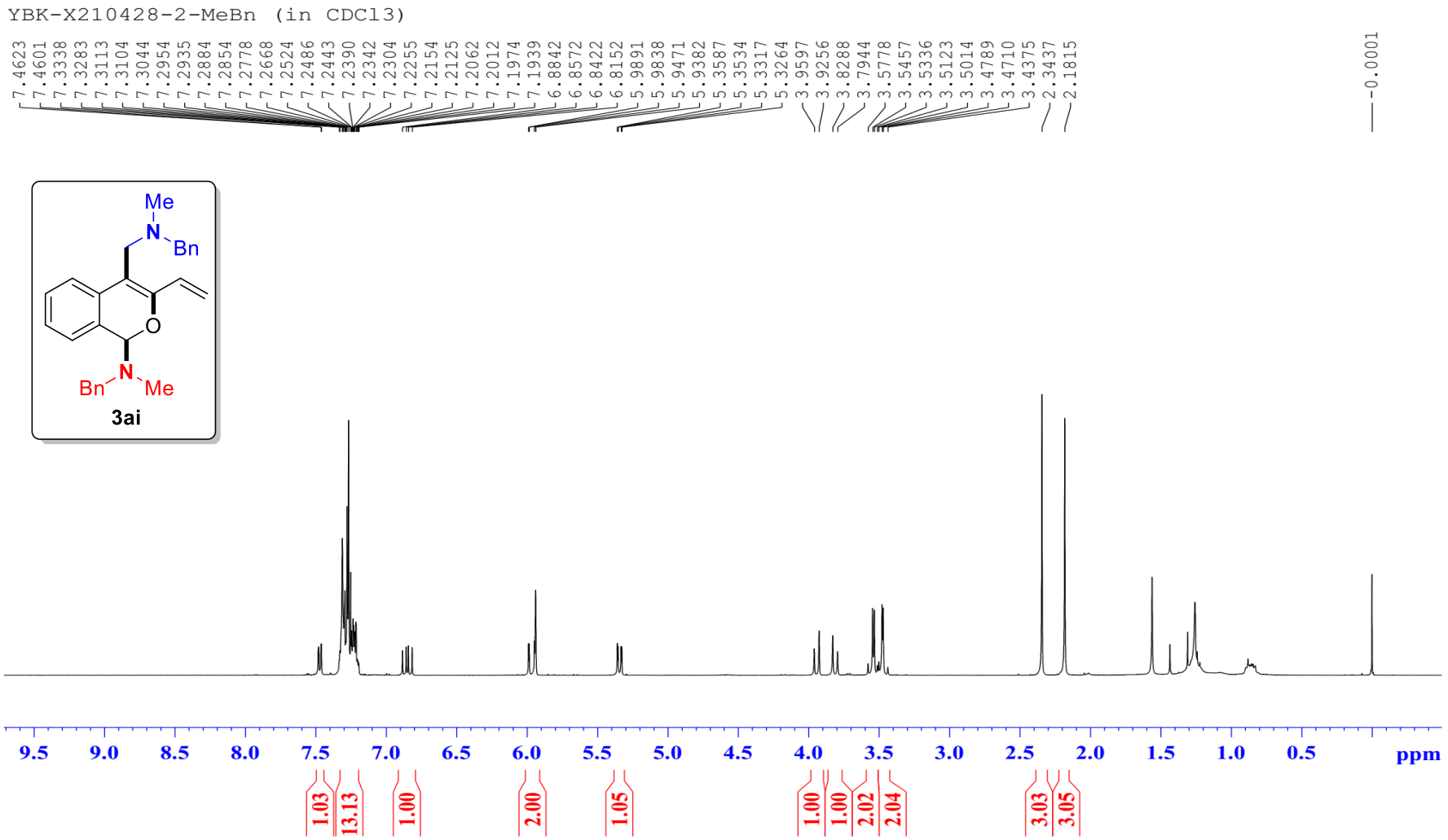
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ah



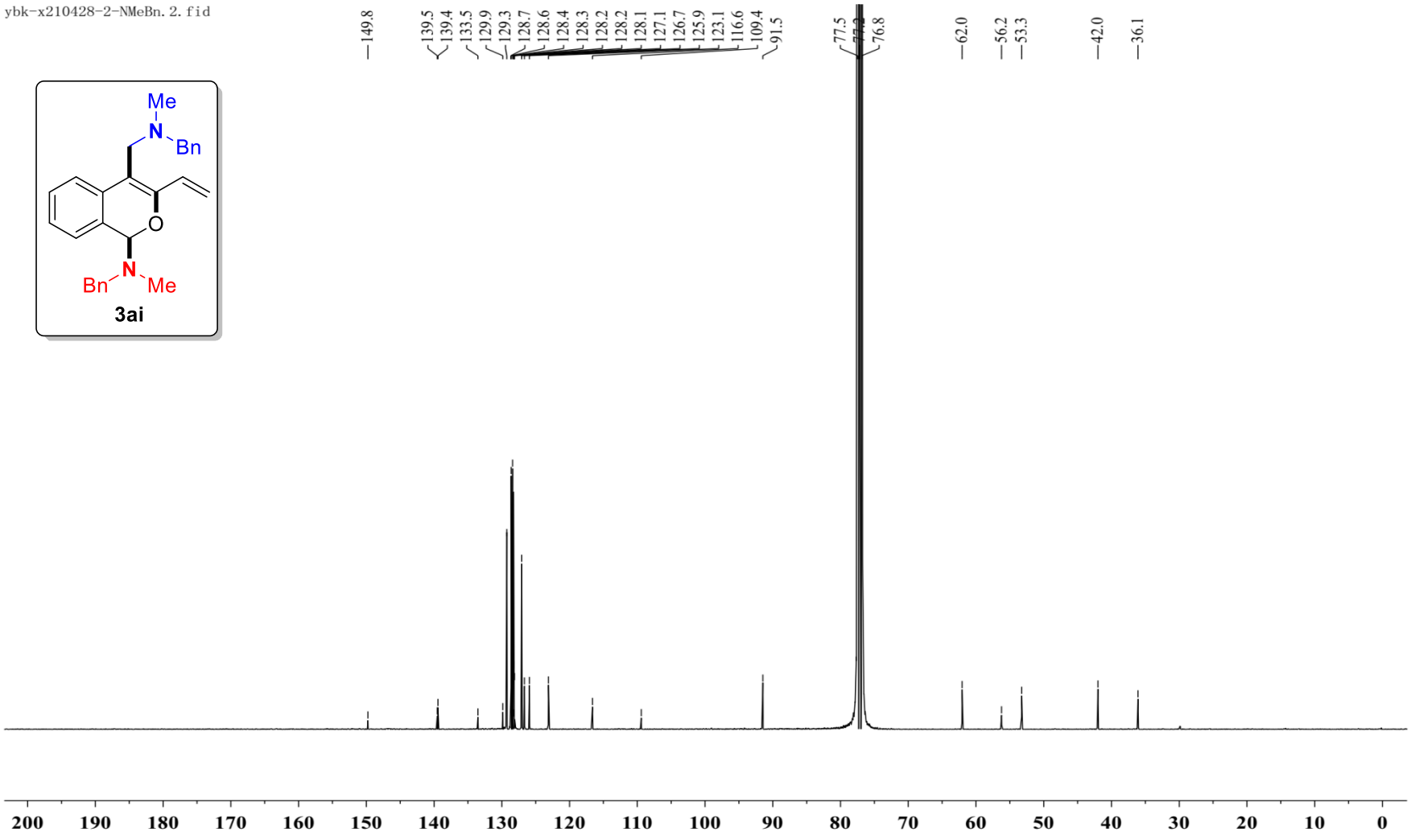
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ah



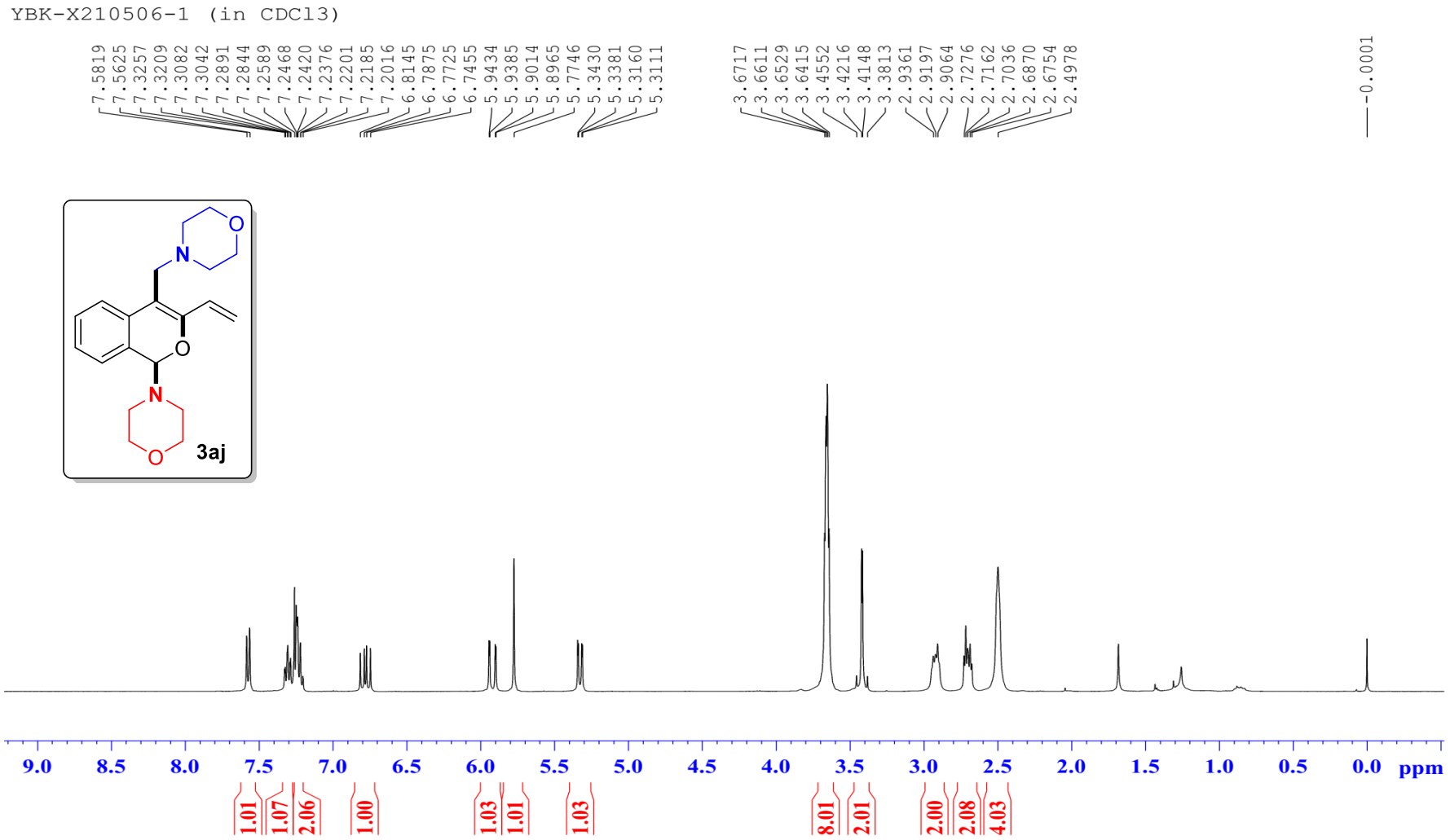
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ai



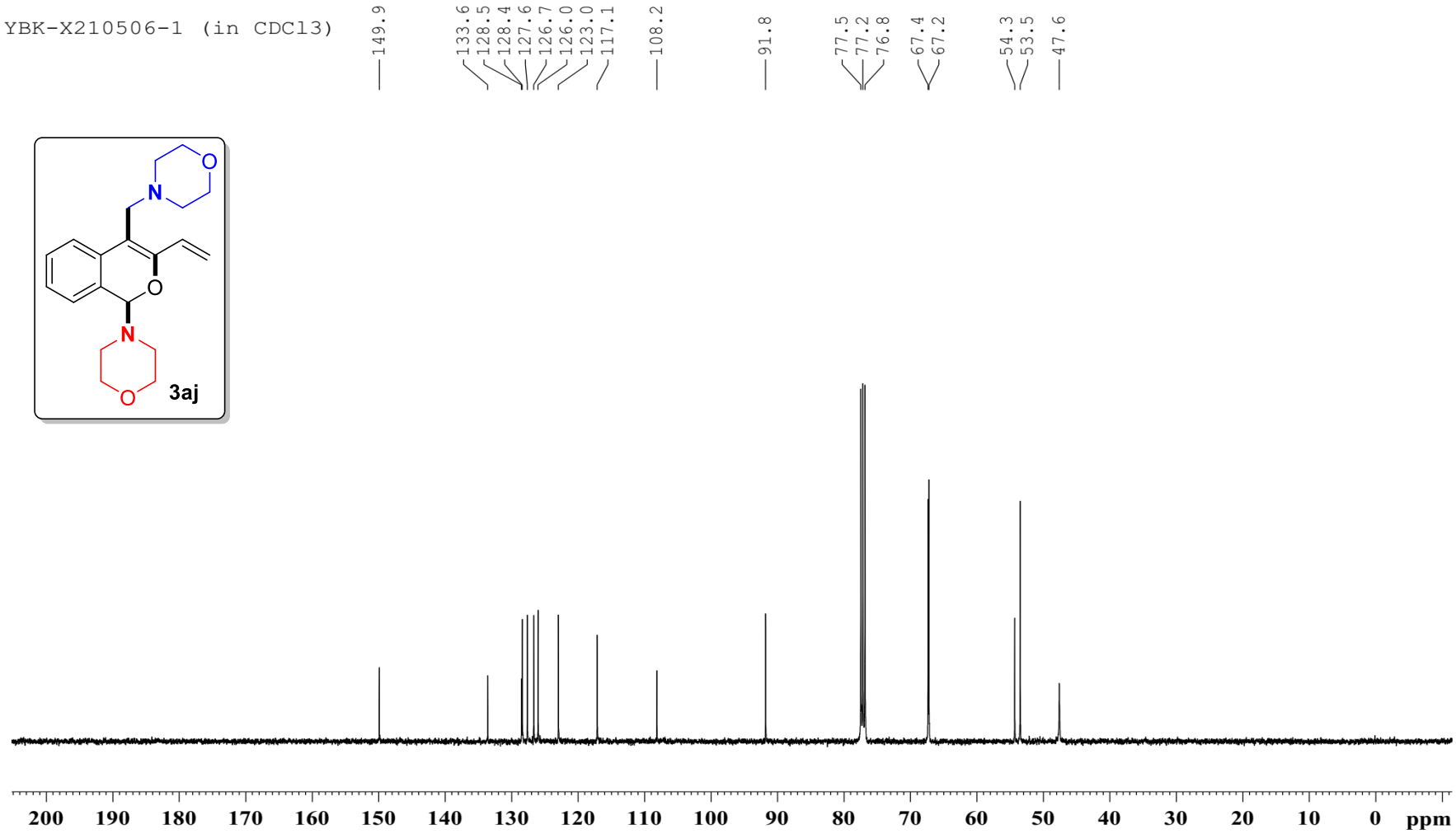
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ai



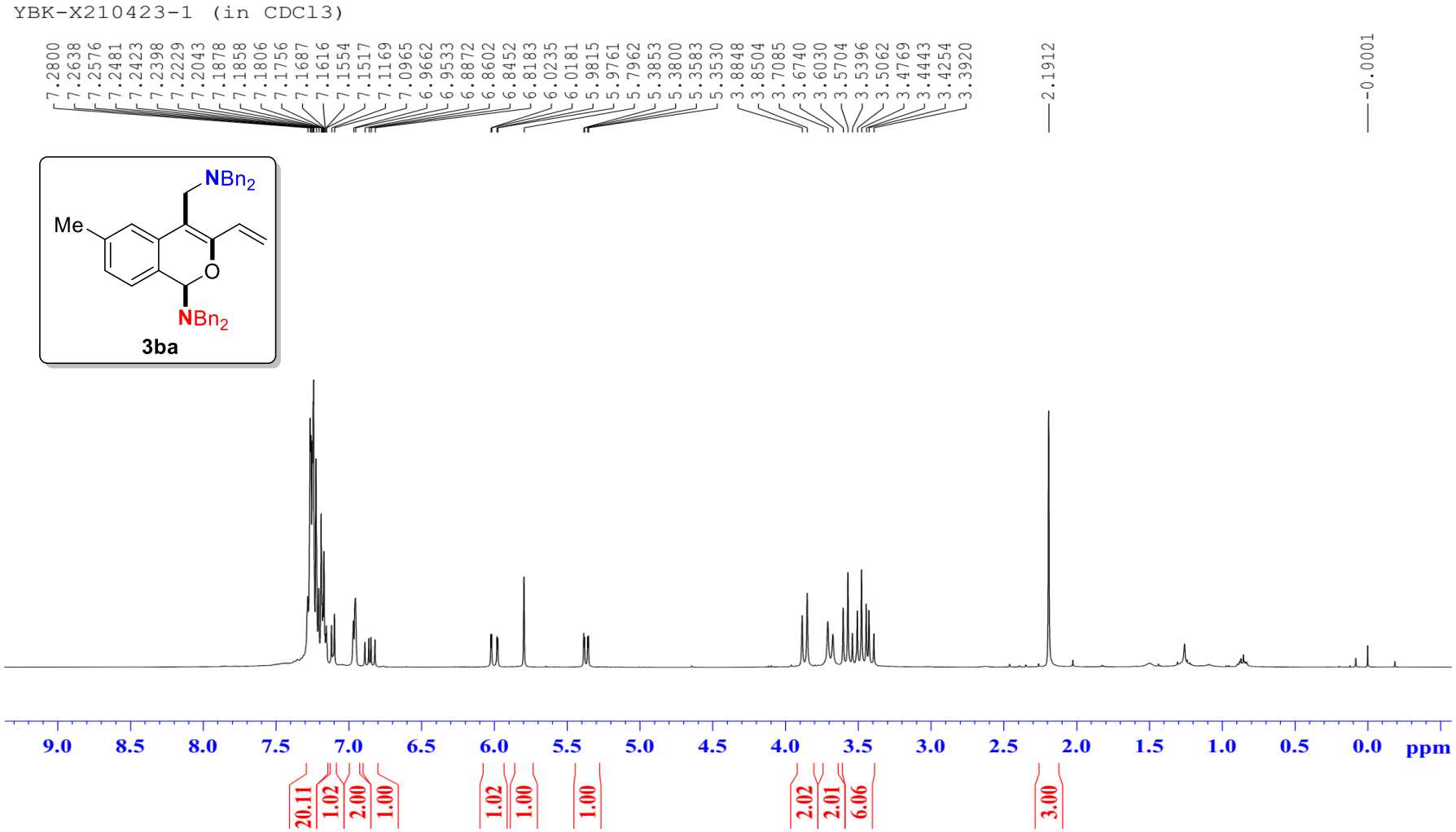
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3aj



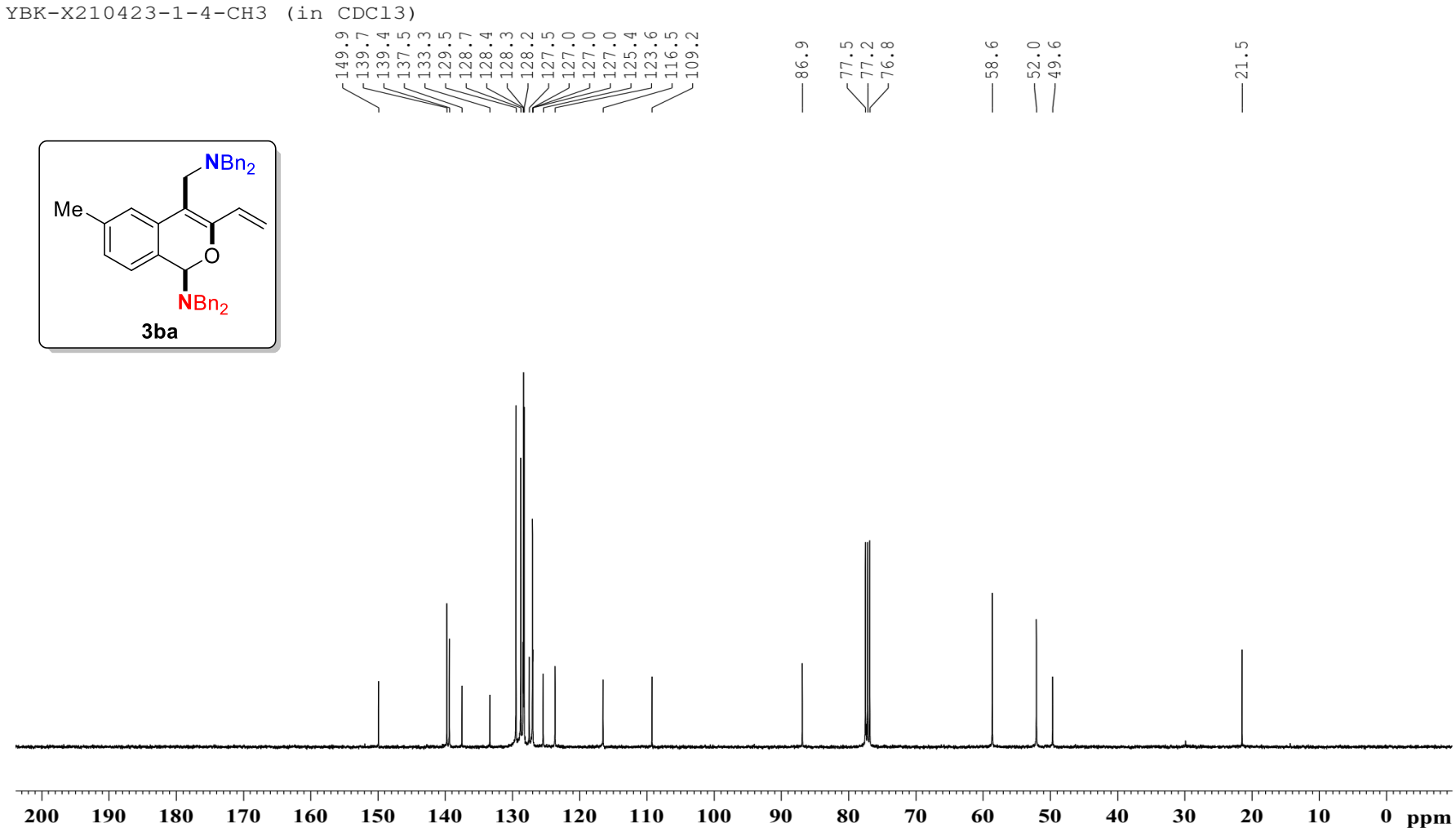
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3aj



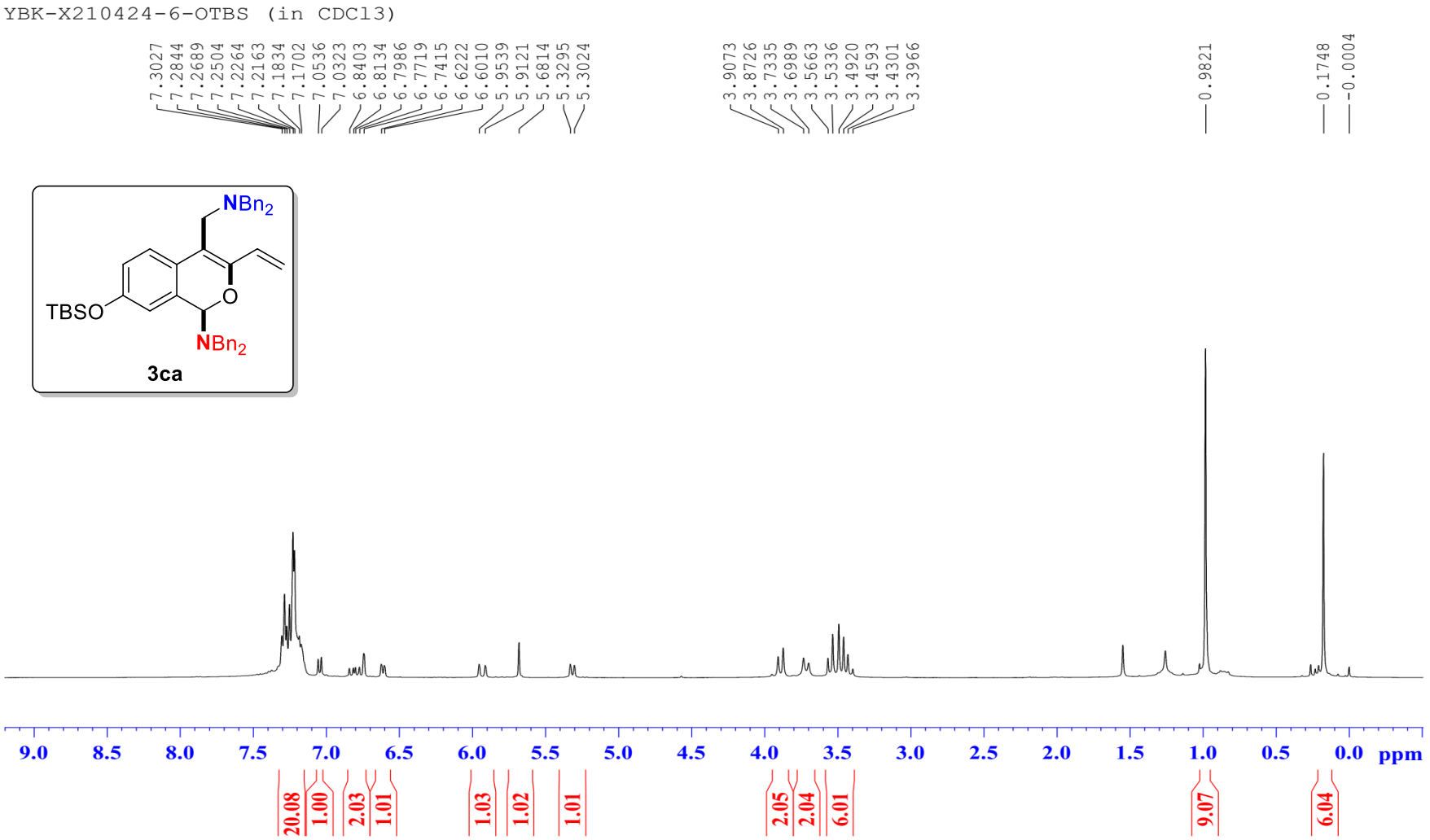
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ba



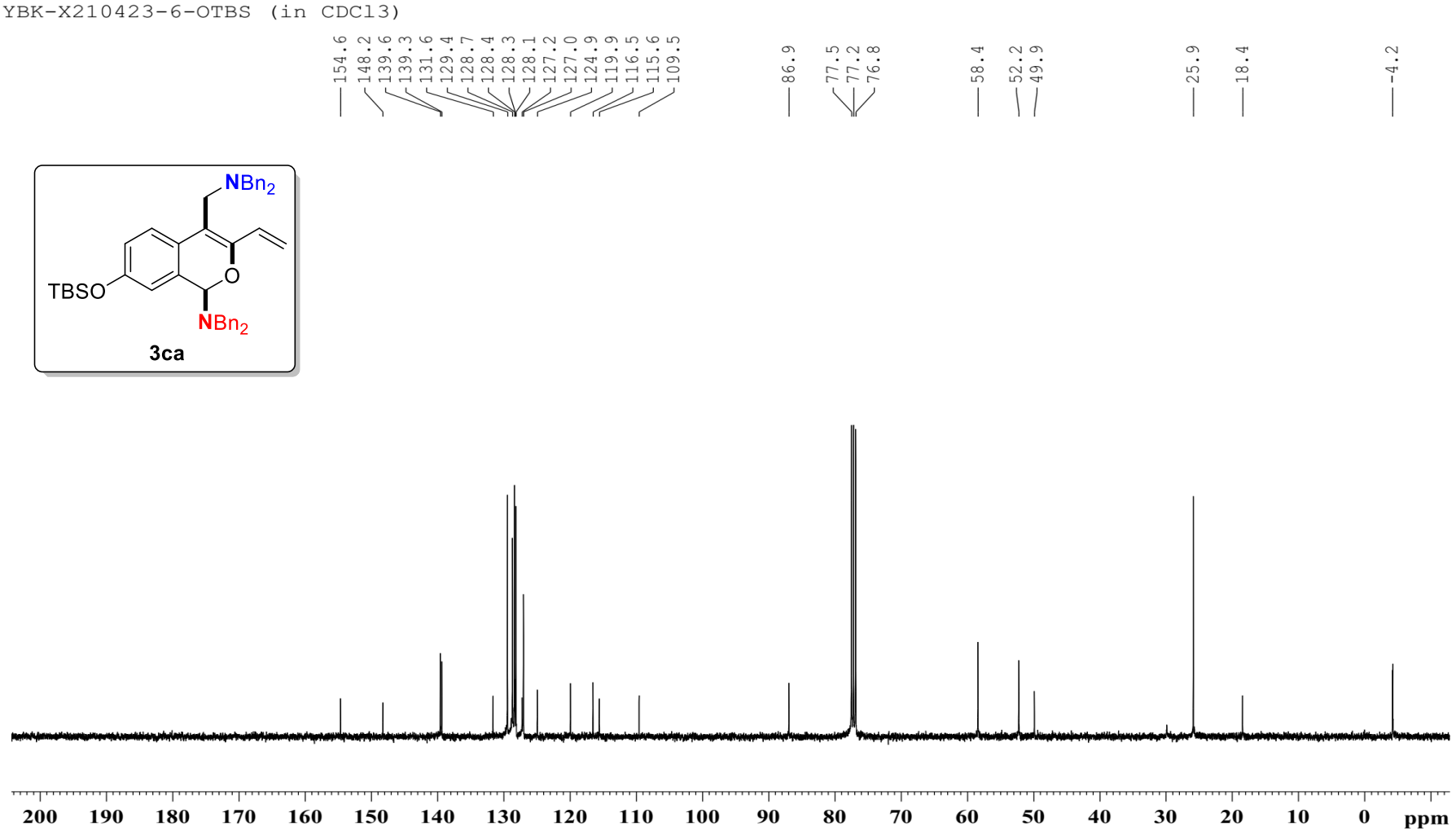
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ba



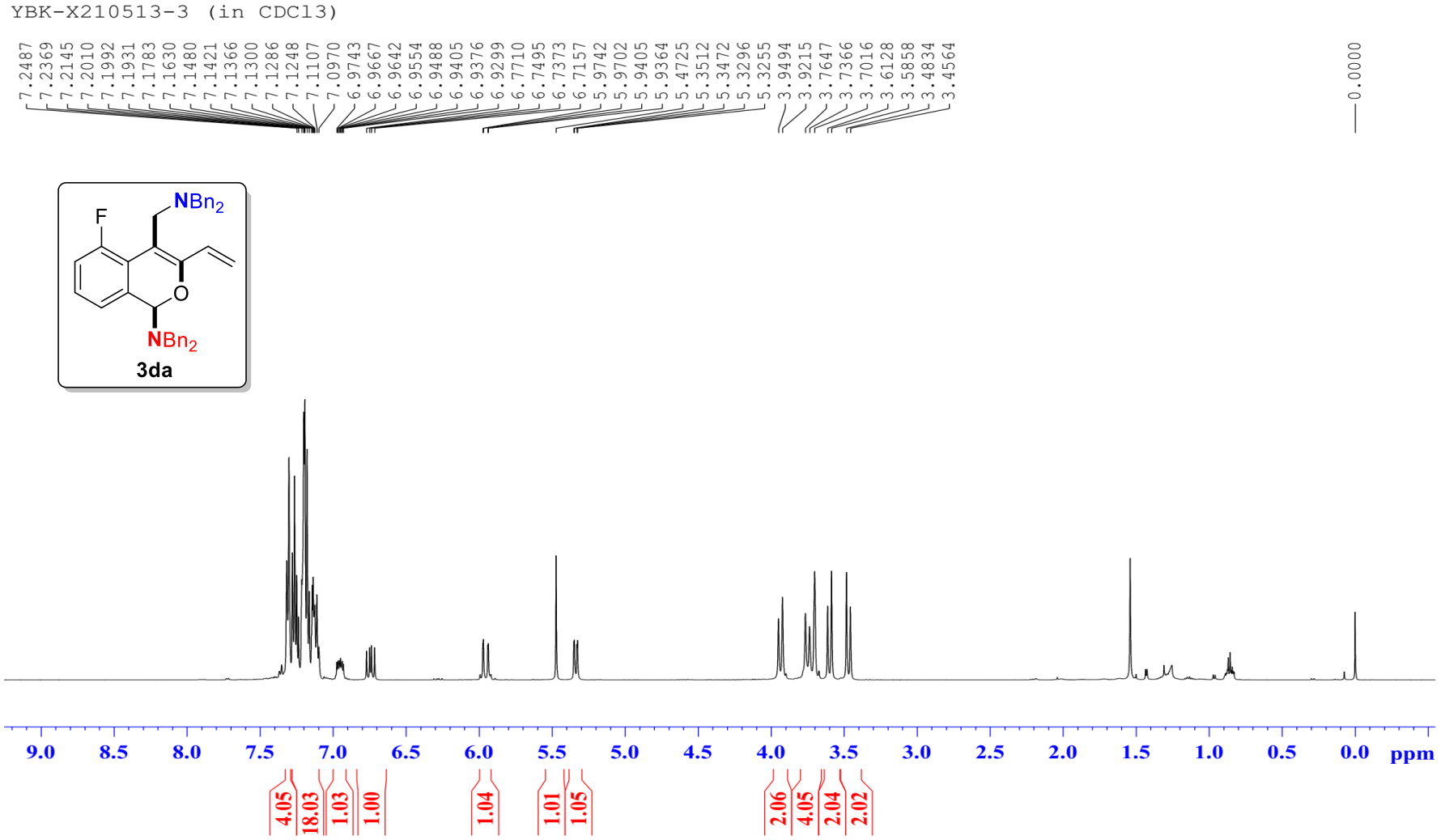
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ca



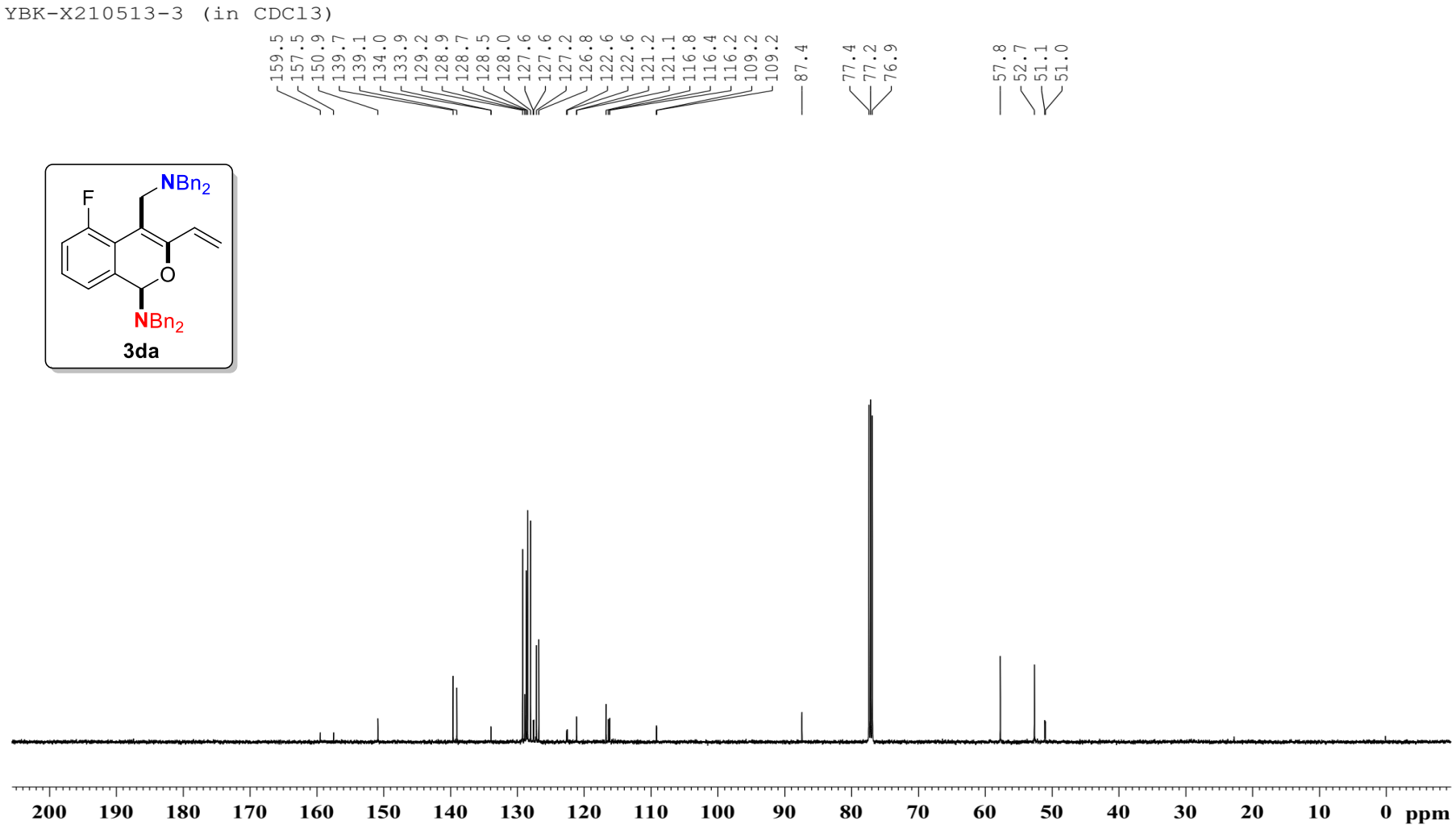
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ca



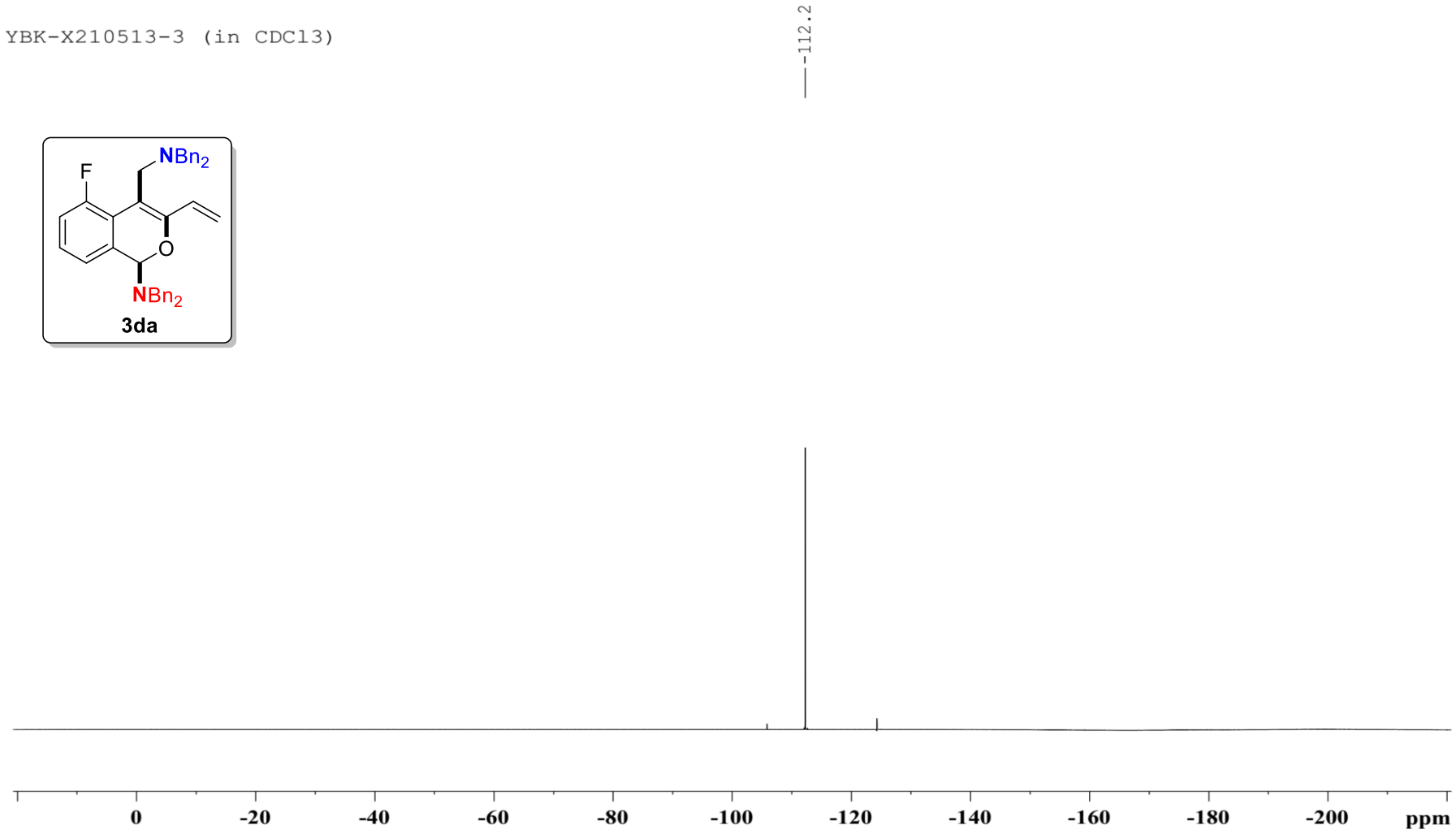
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3da



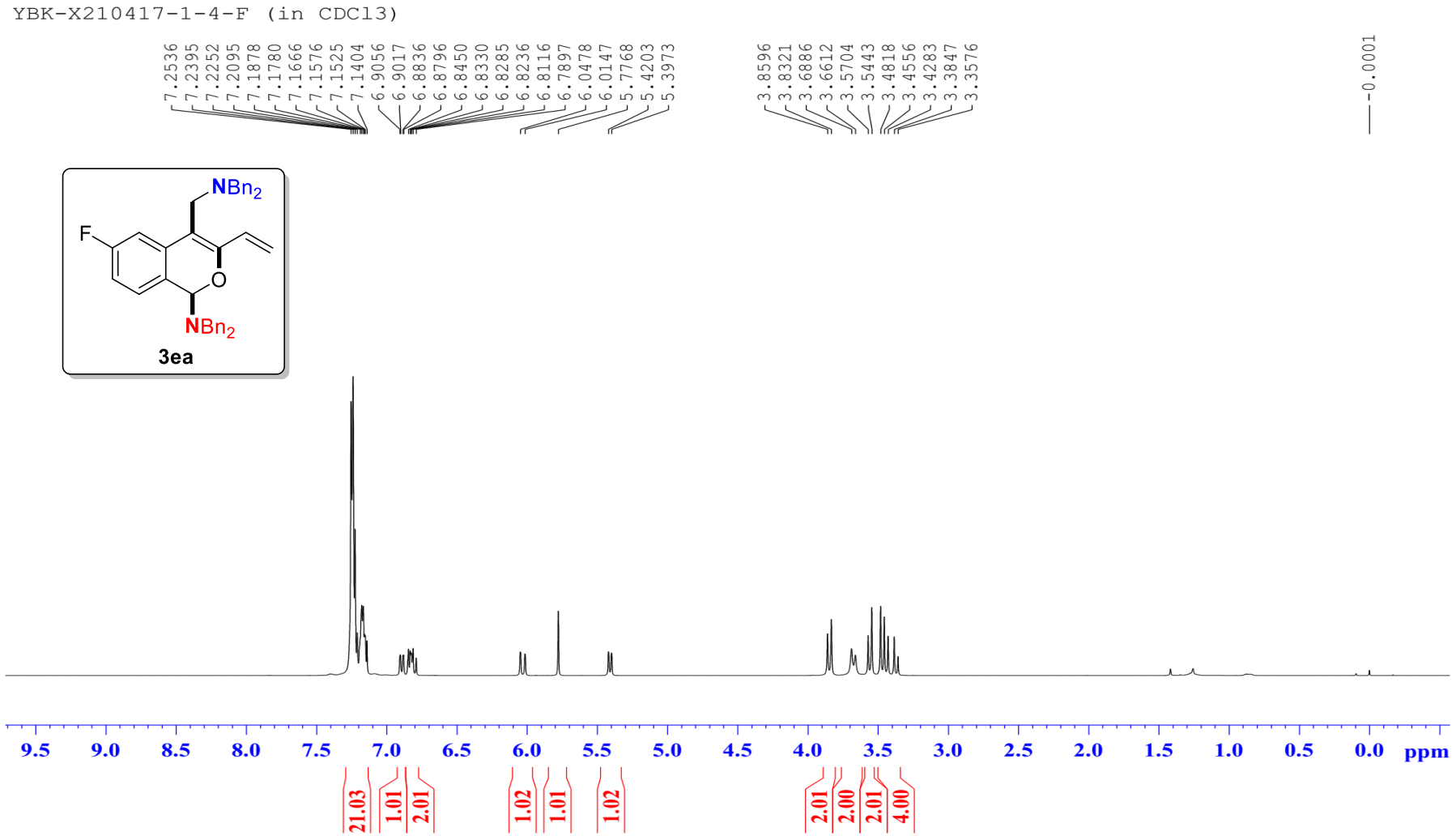
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3da



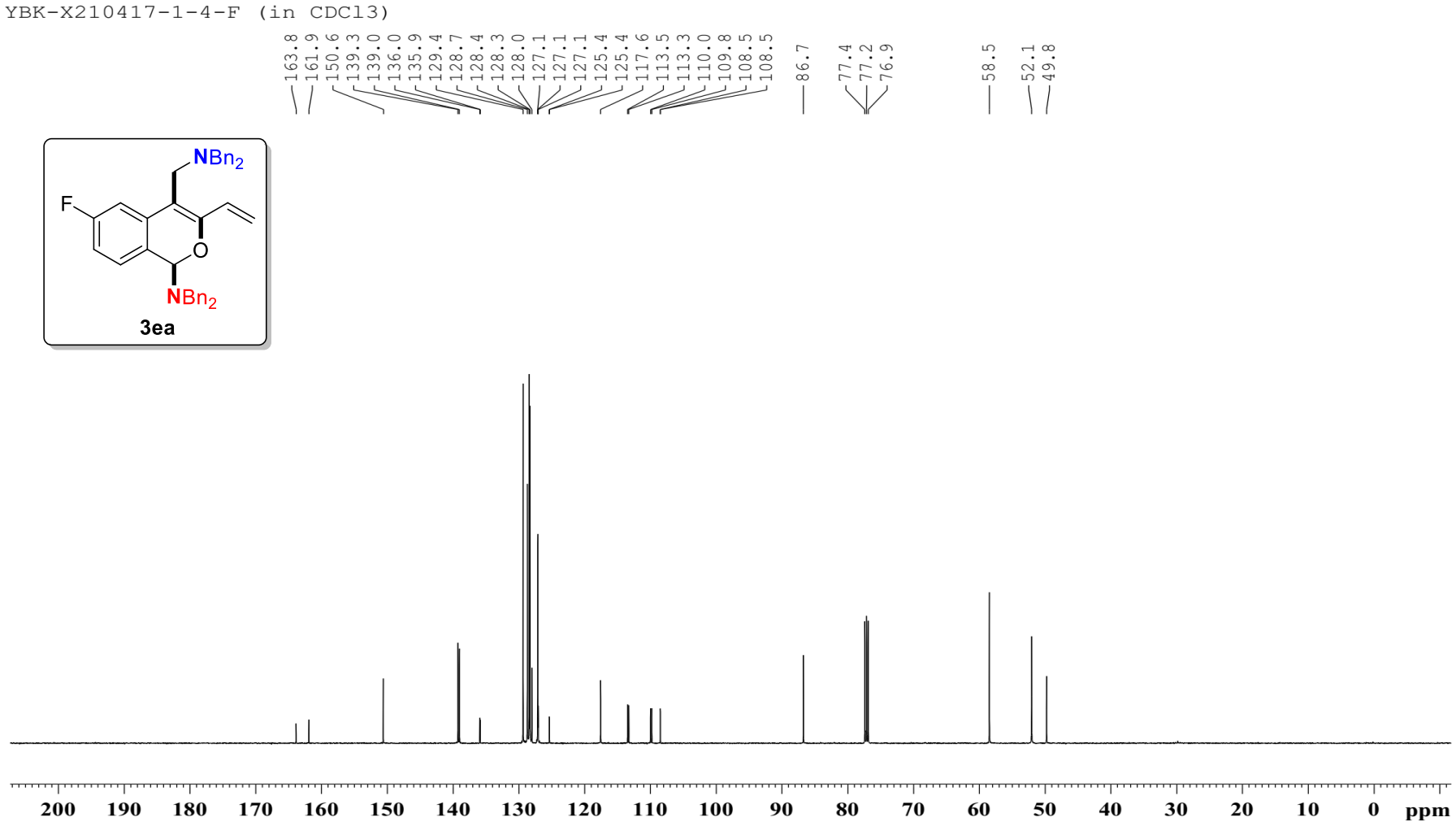
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 3da



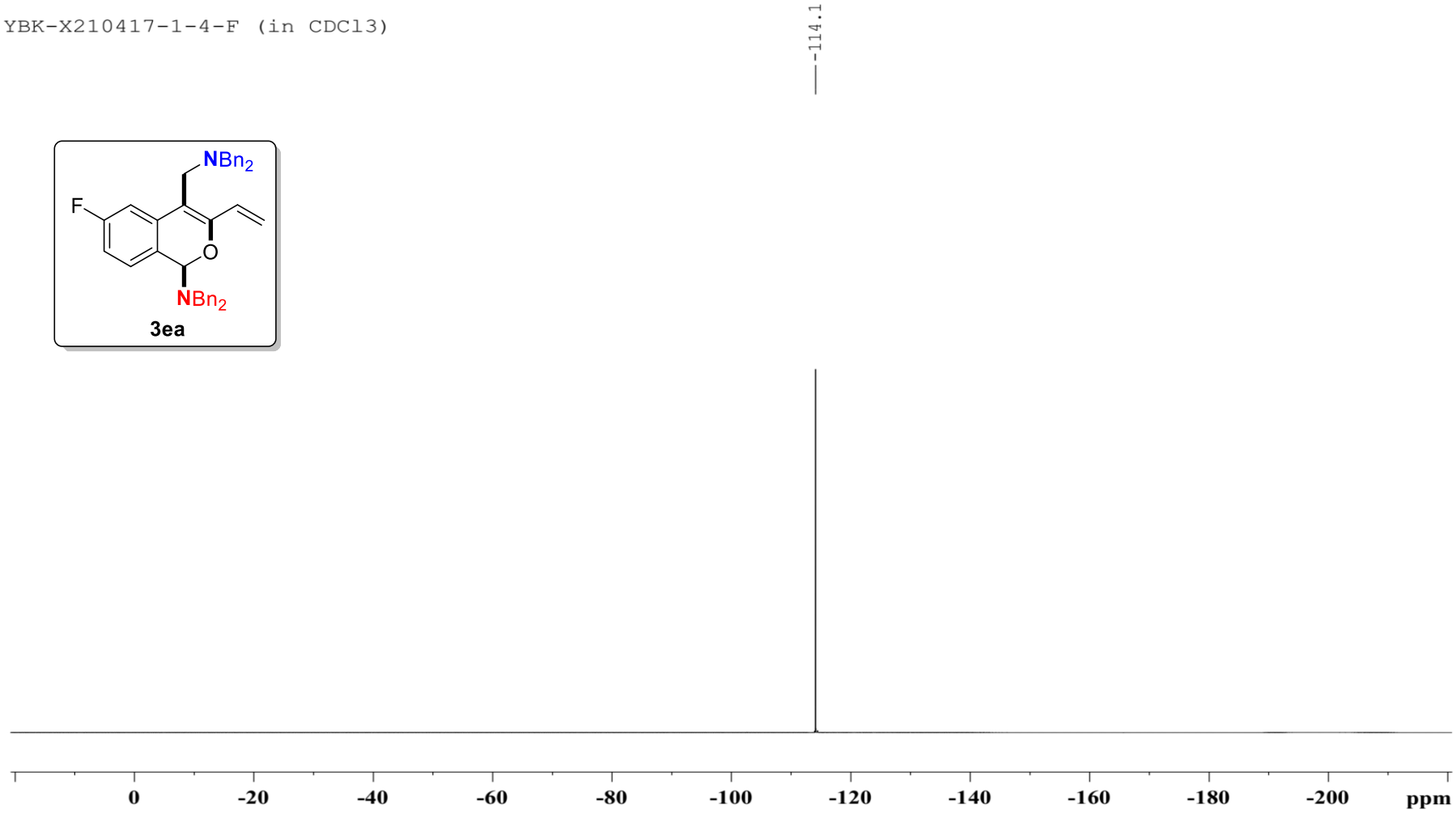
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ea



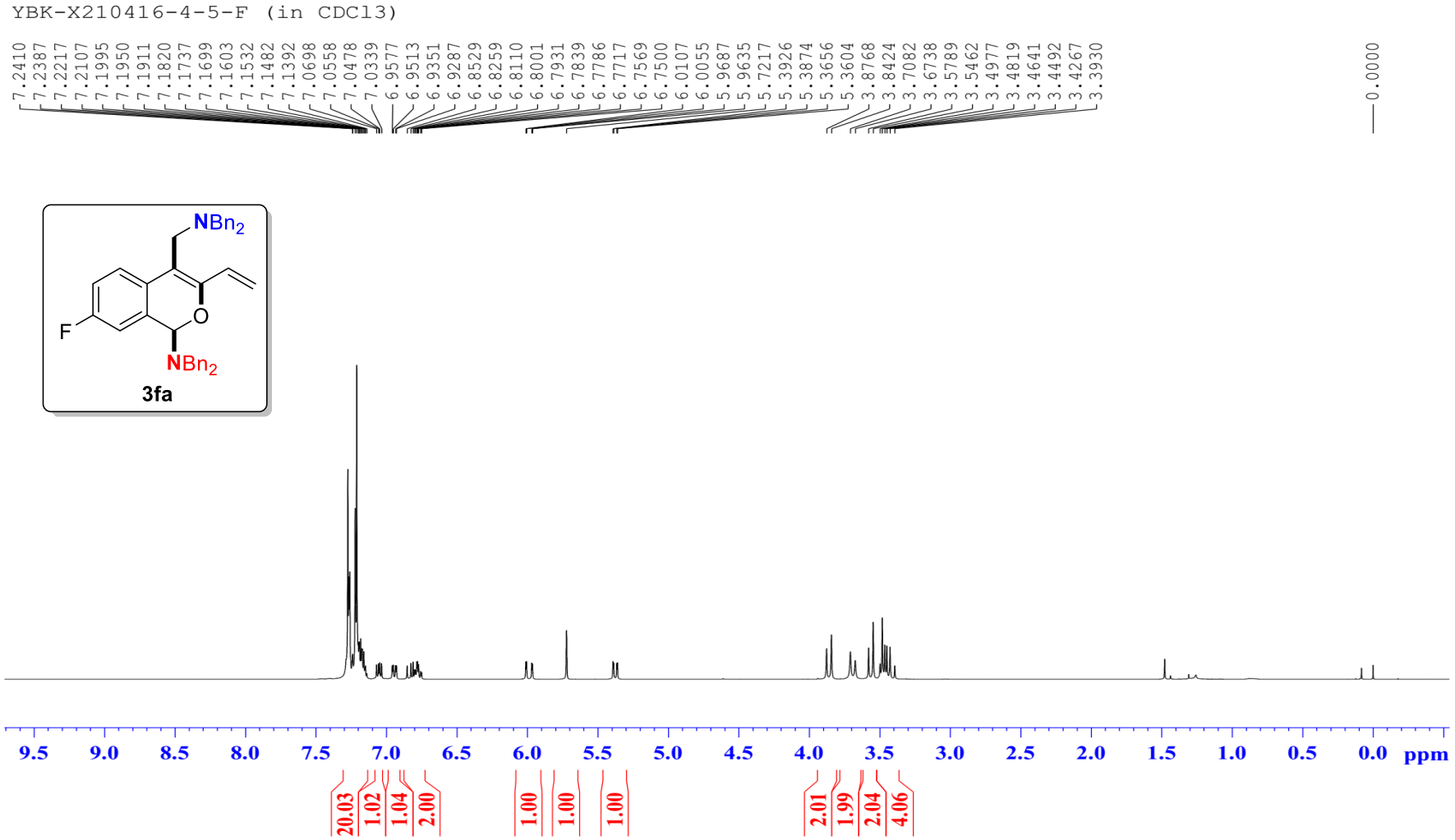
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ea



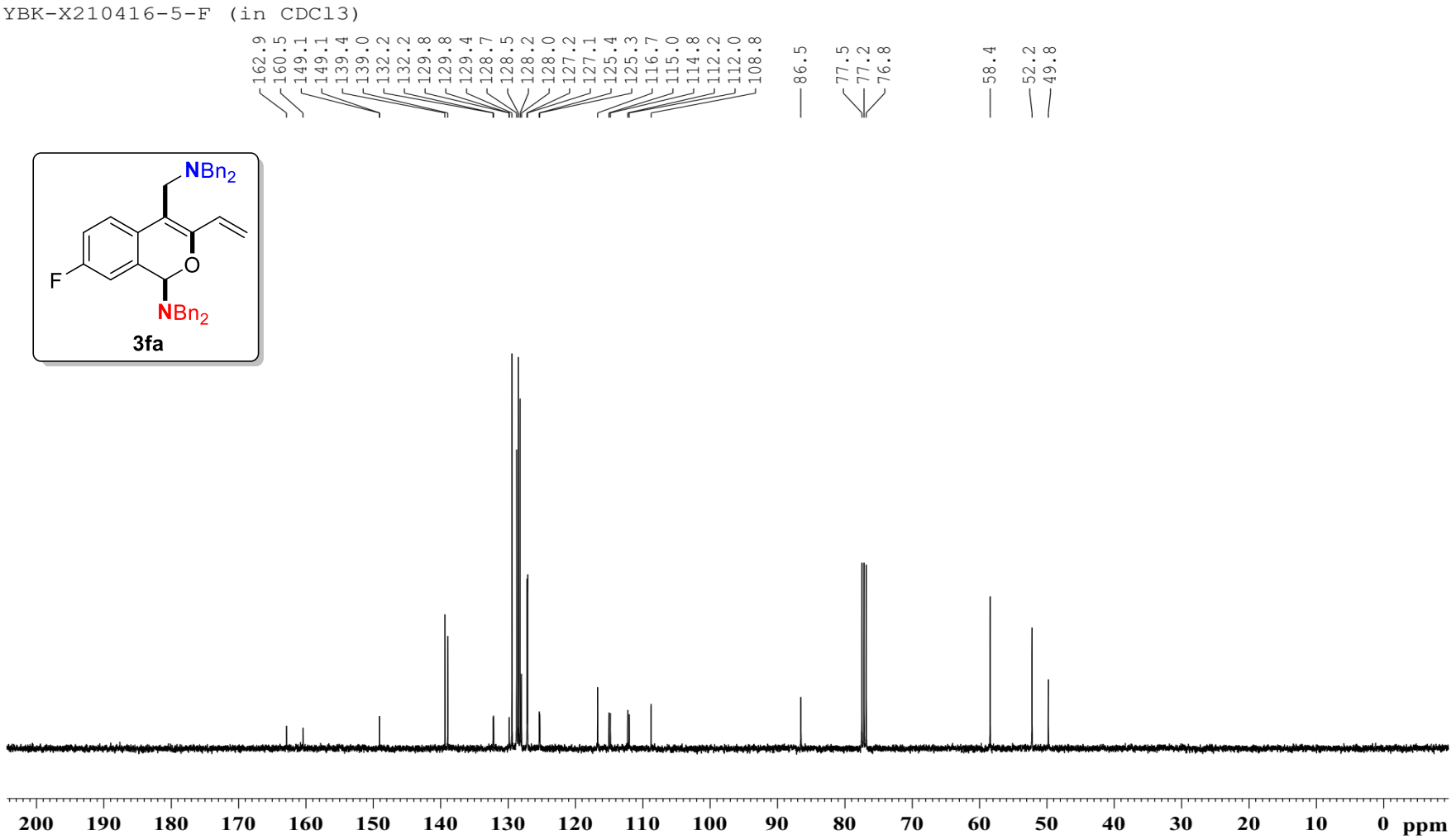
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 3ea



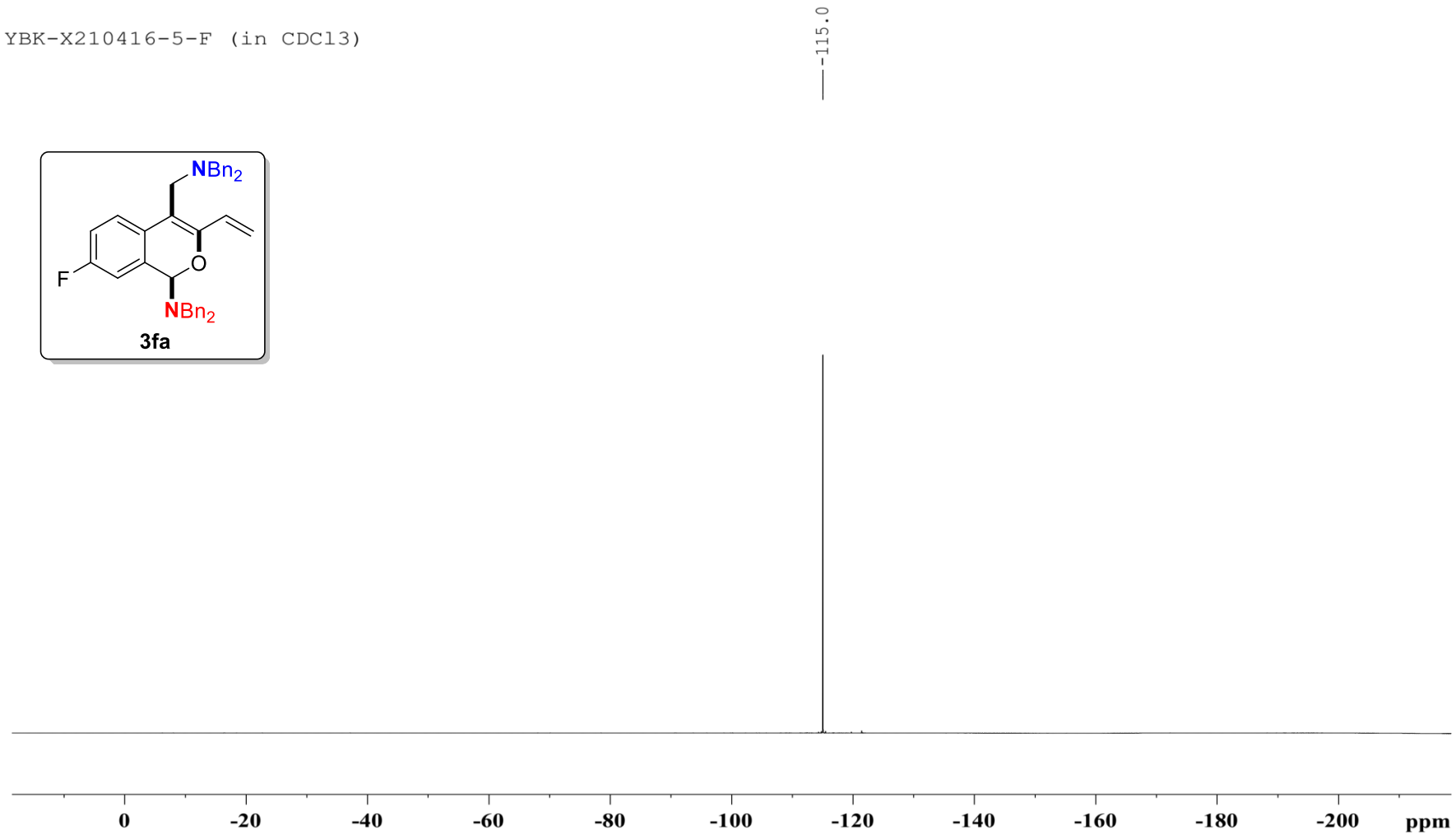
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3fa



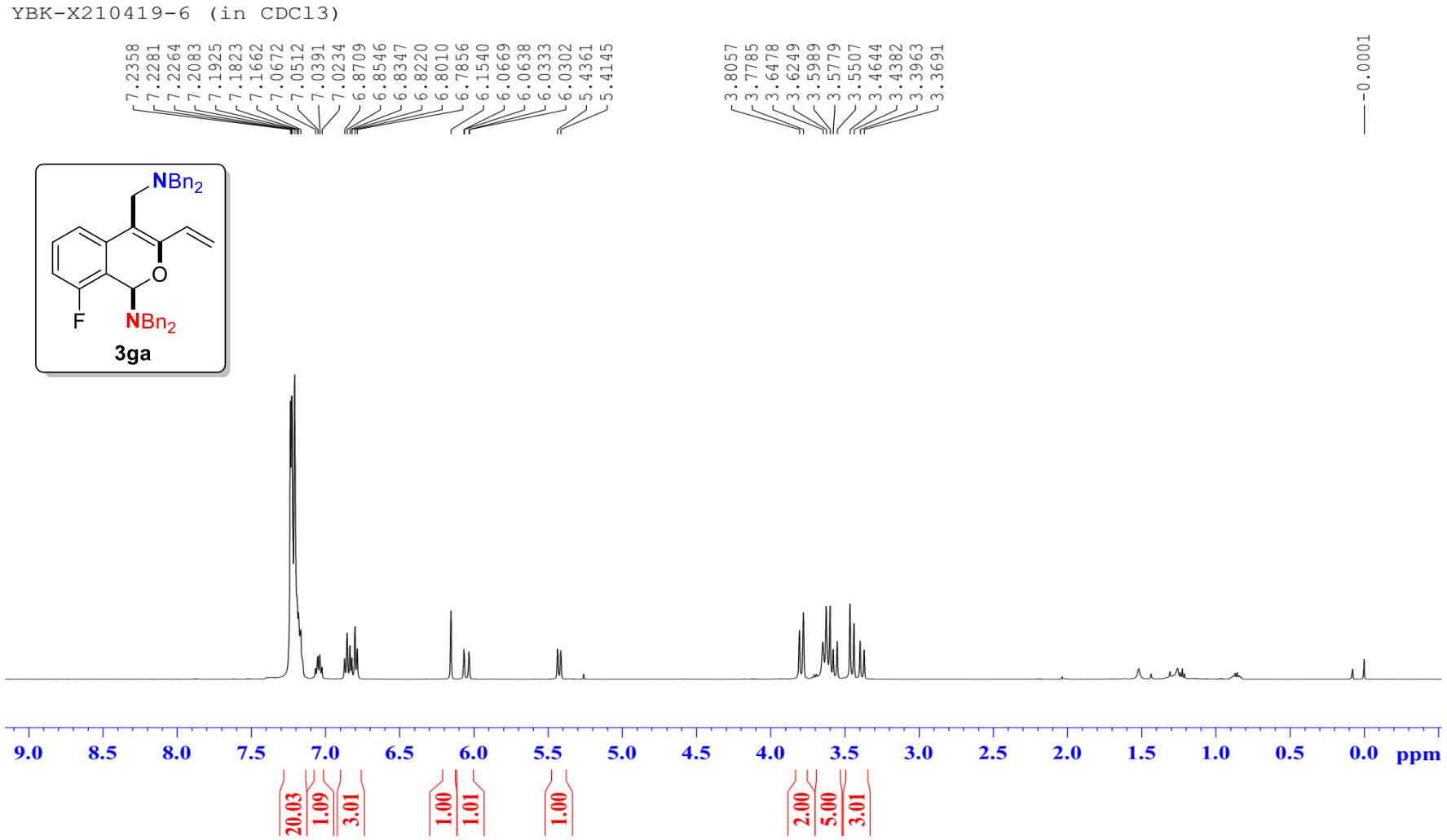
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3fa



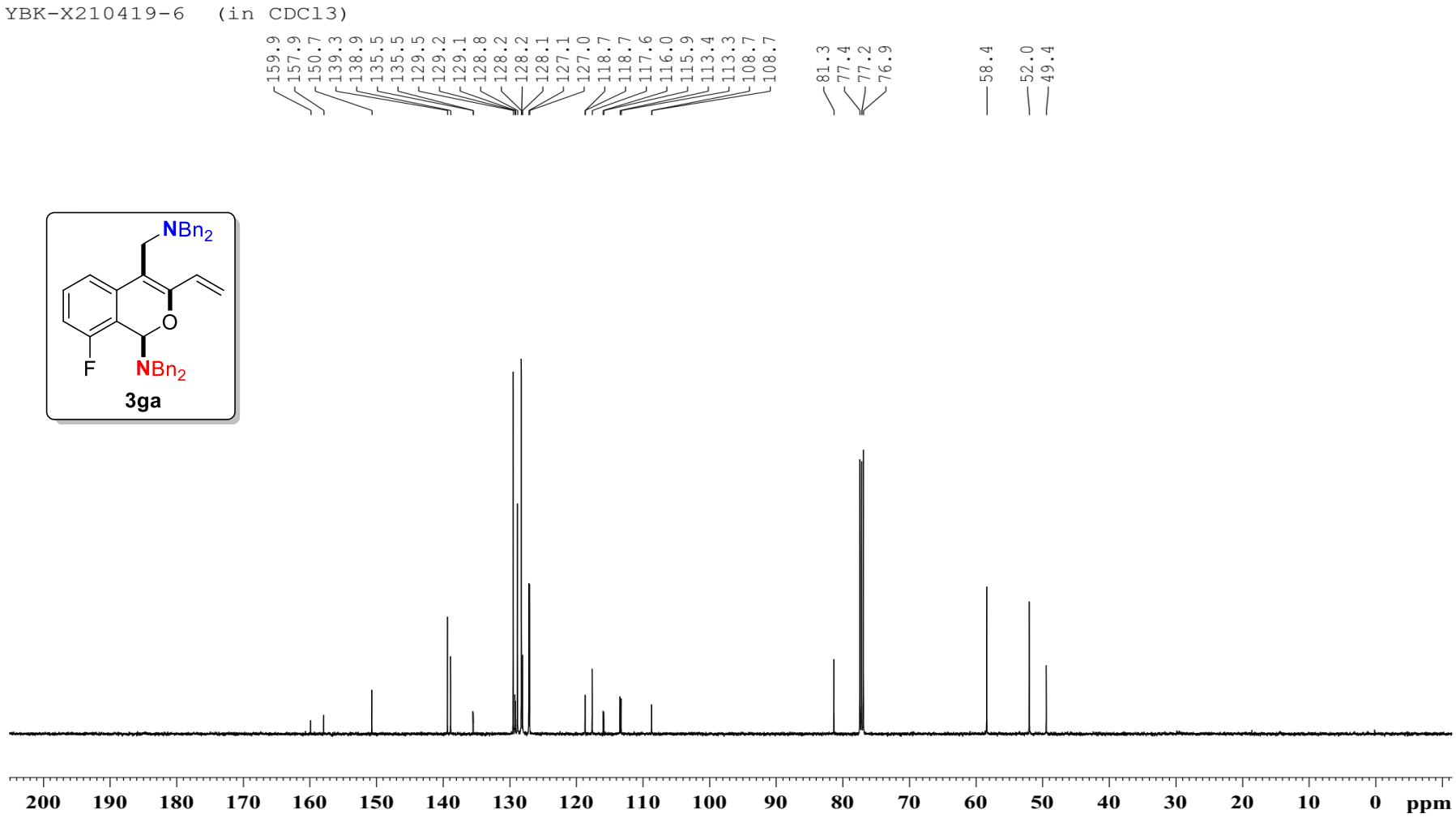
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 3fa



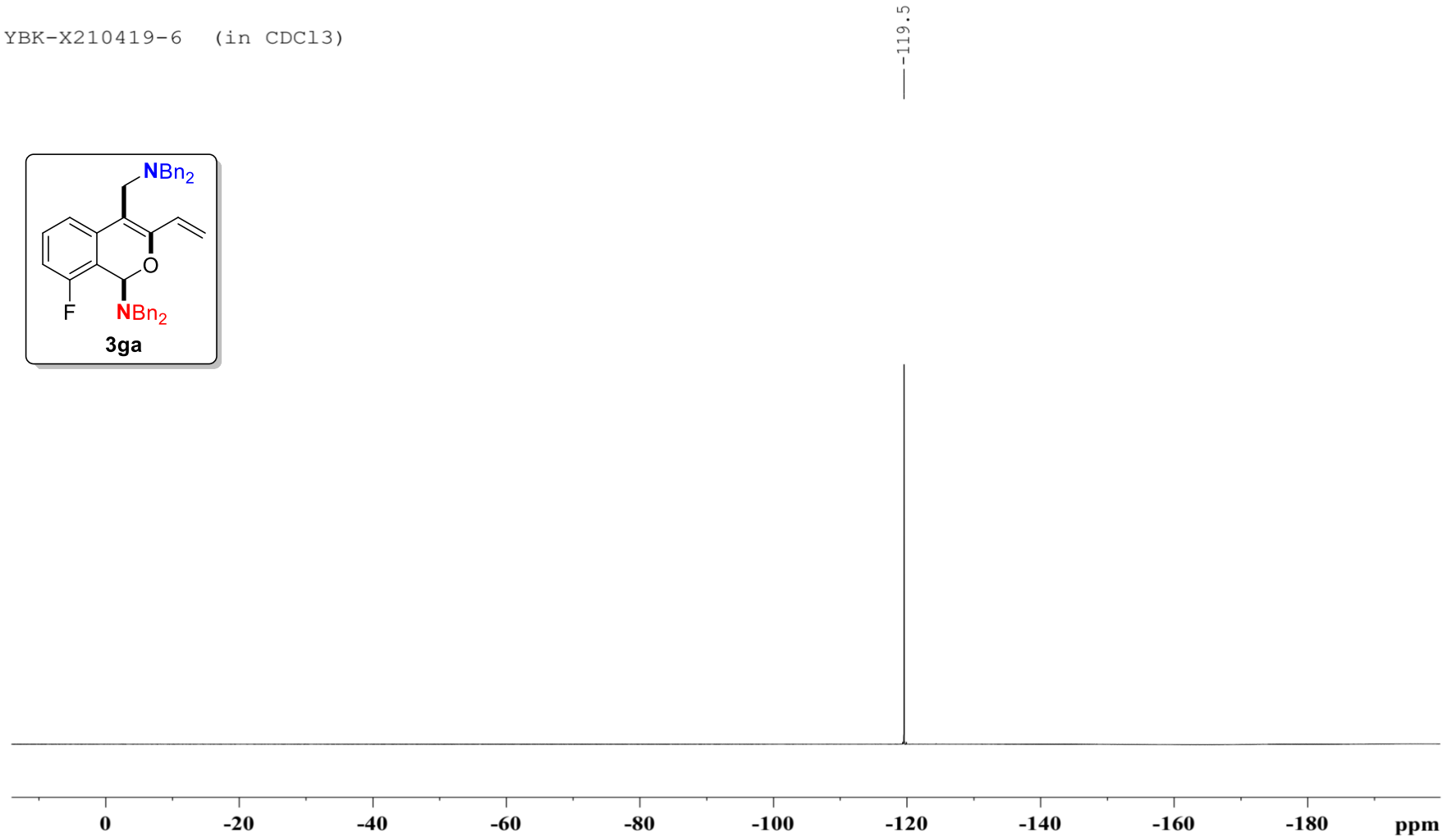
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ga



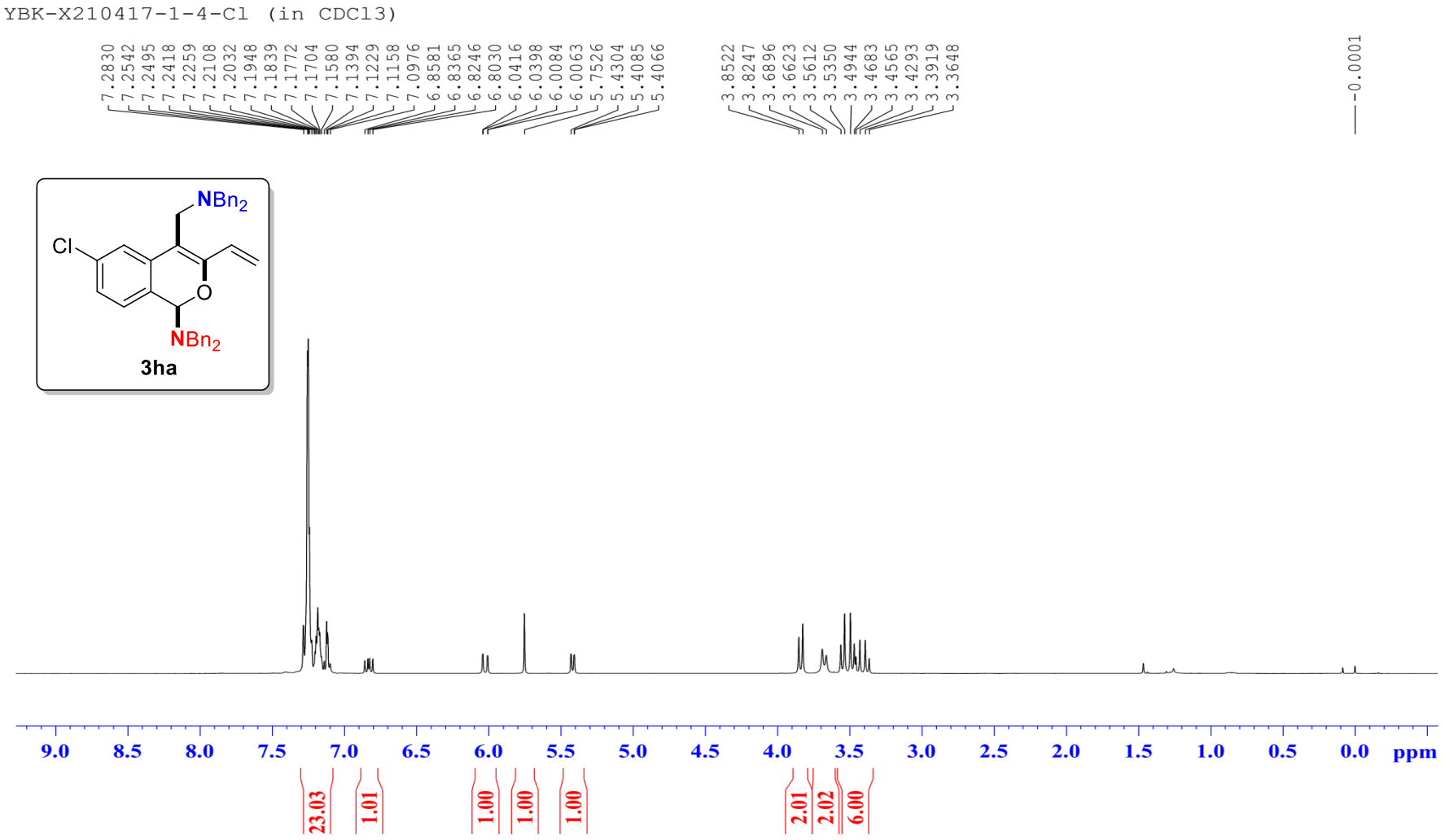
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ga



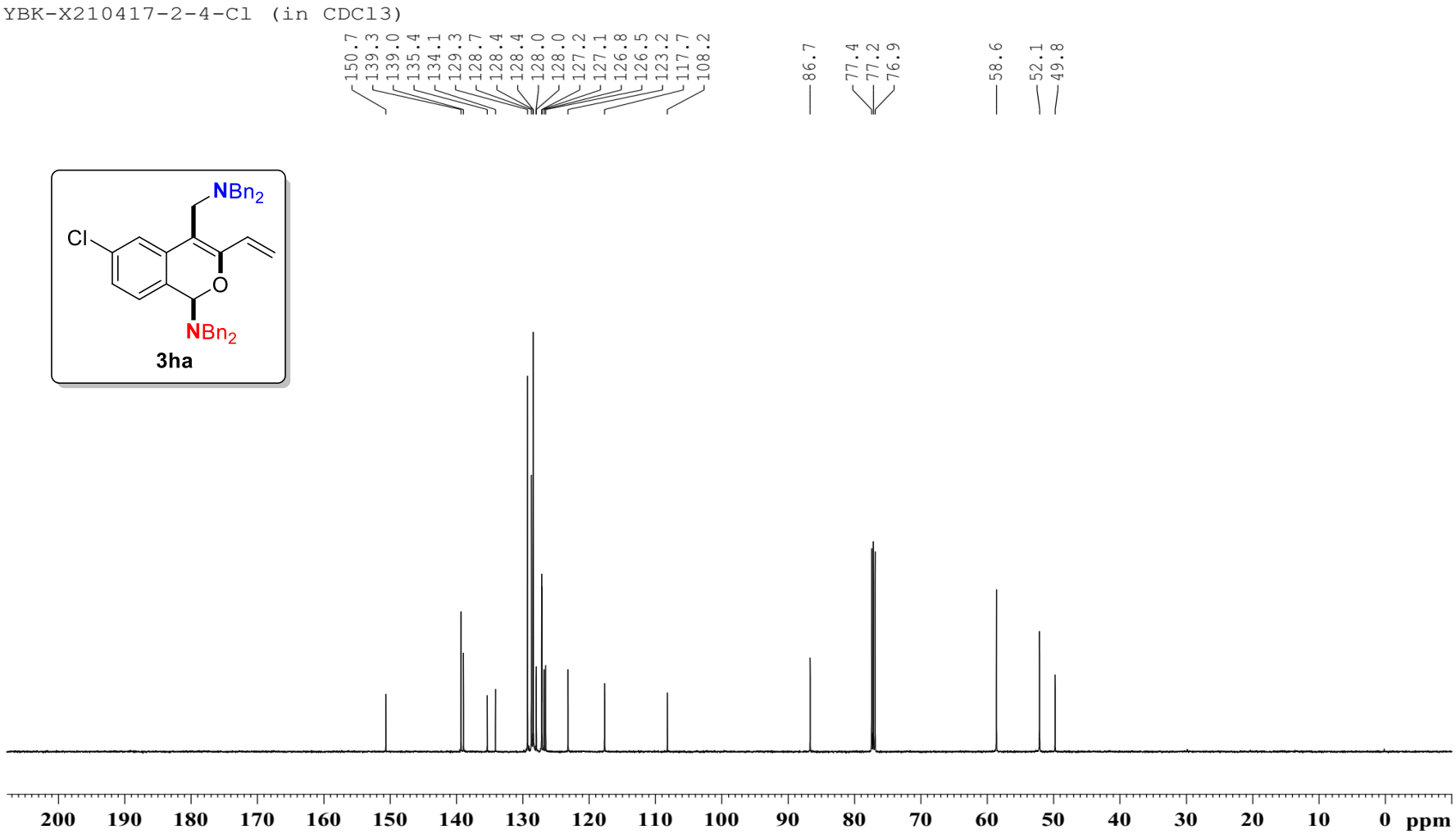
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 3ga



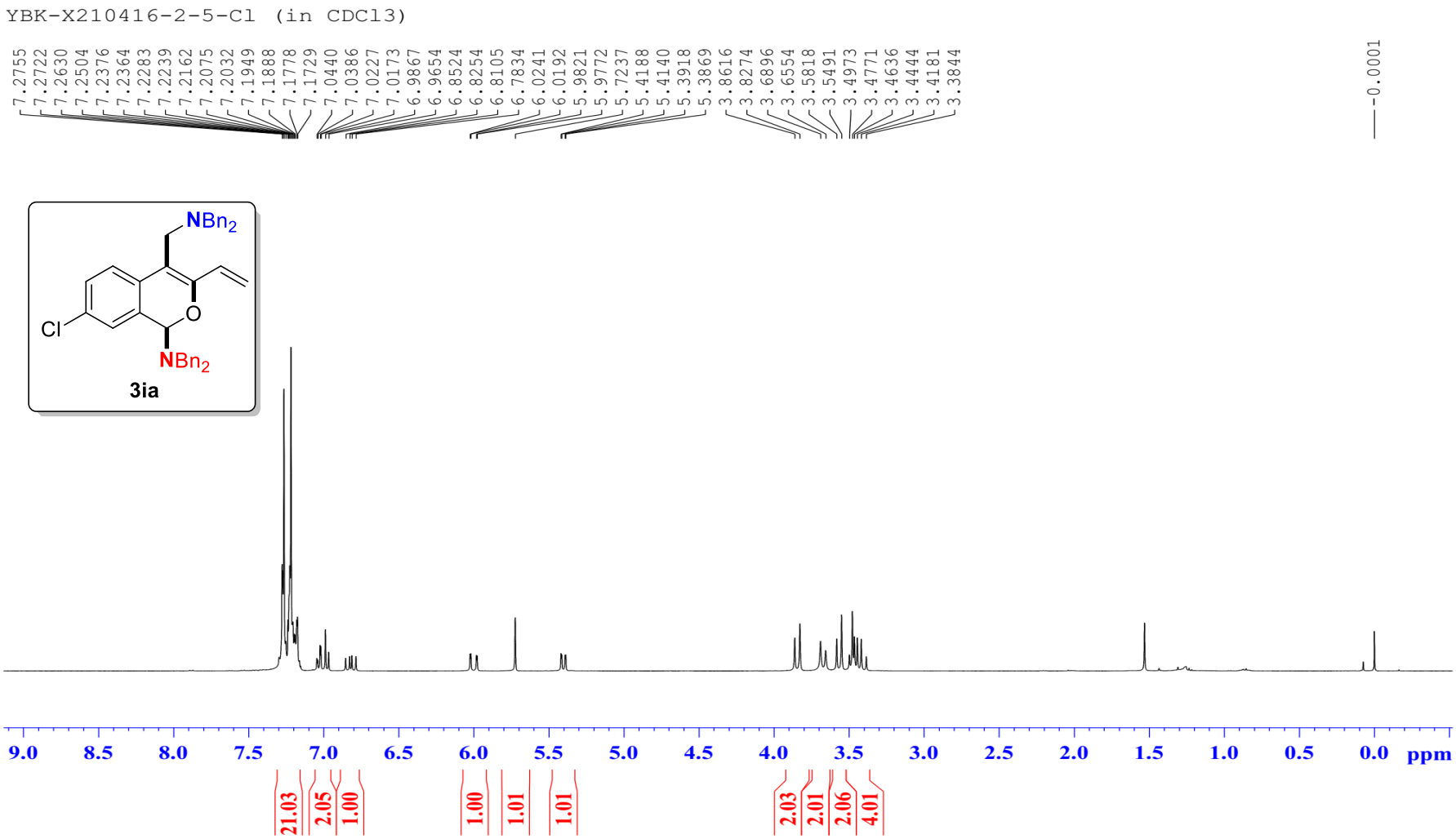
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ha



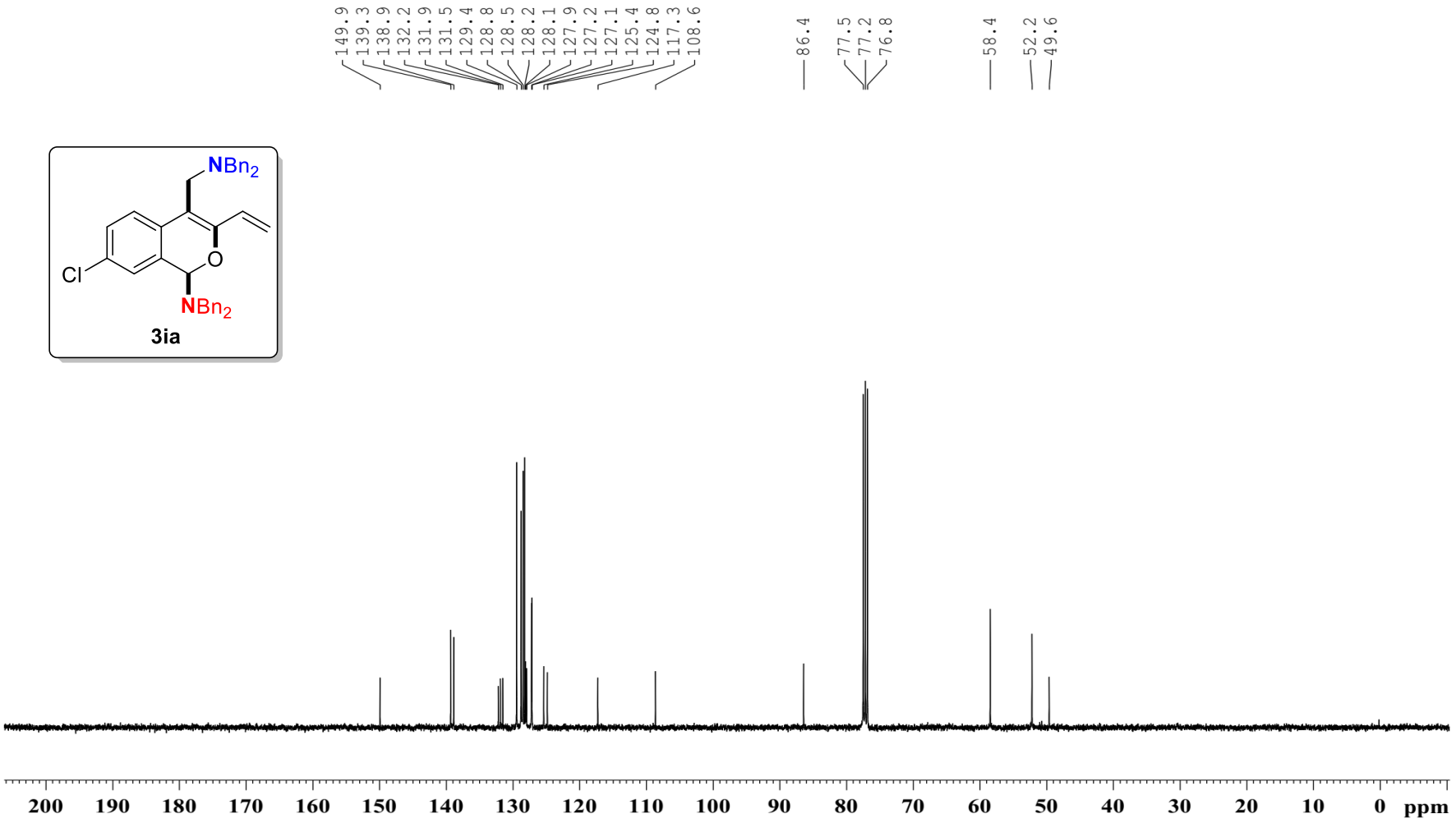
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ha



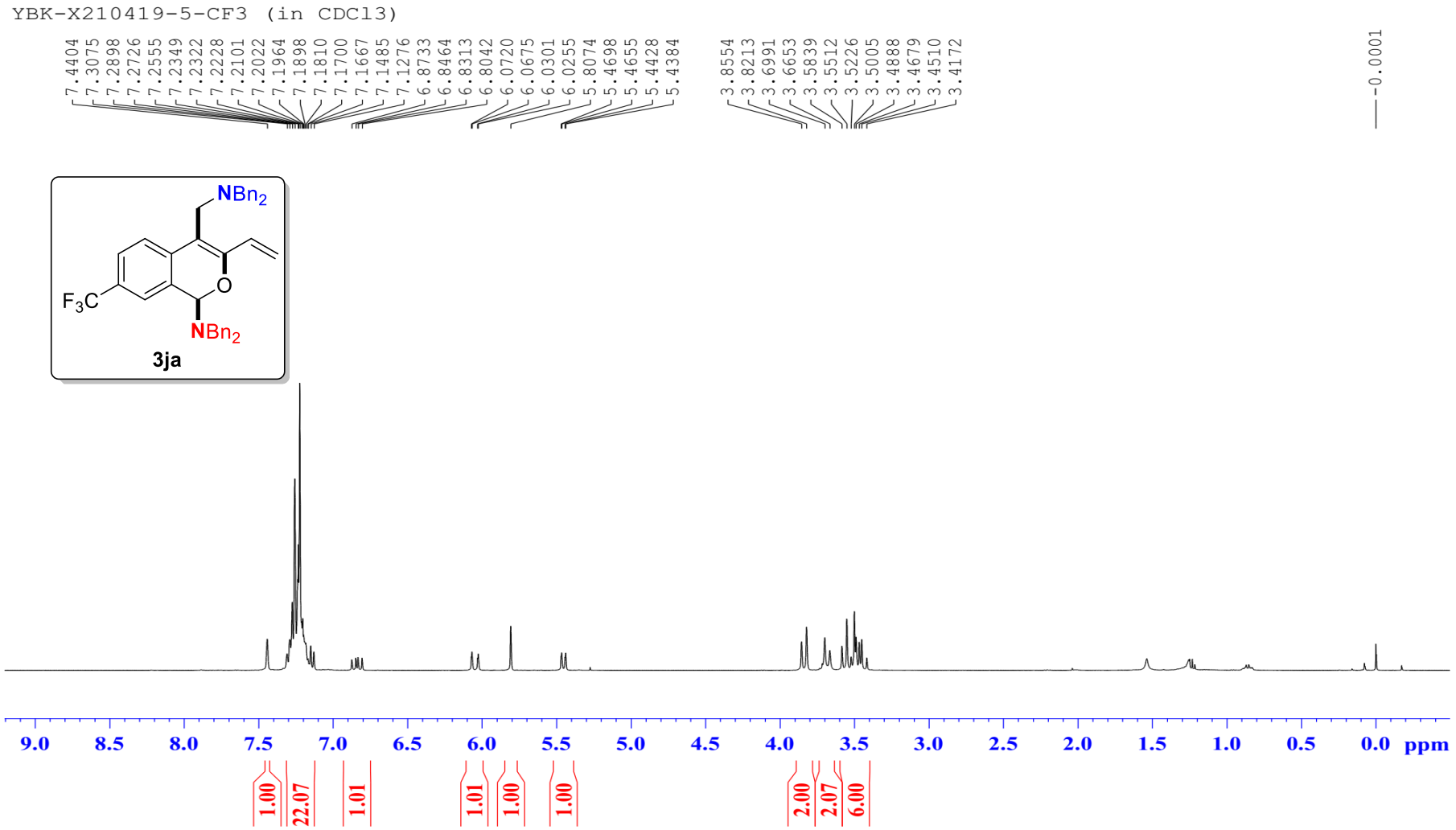
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ia



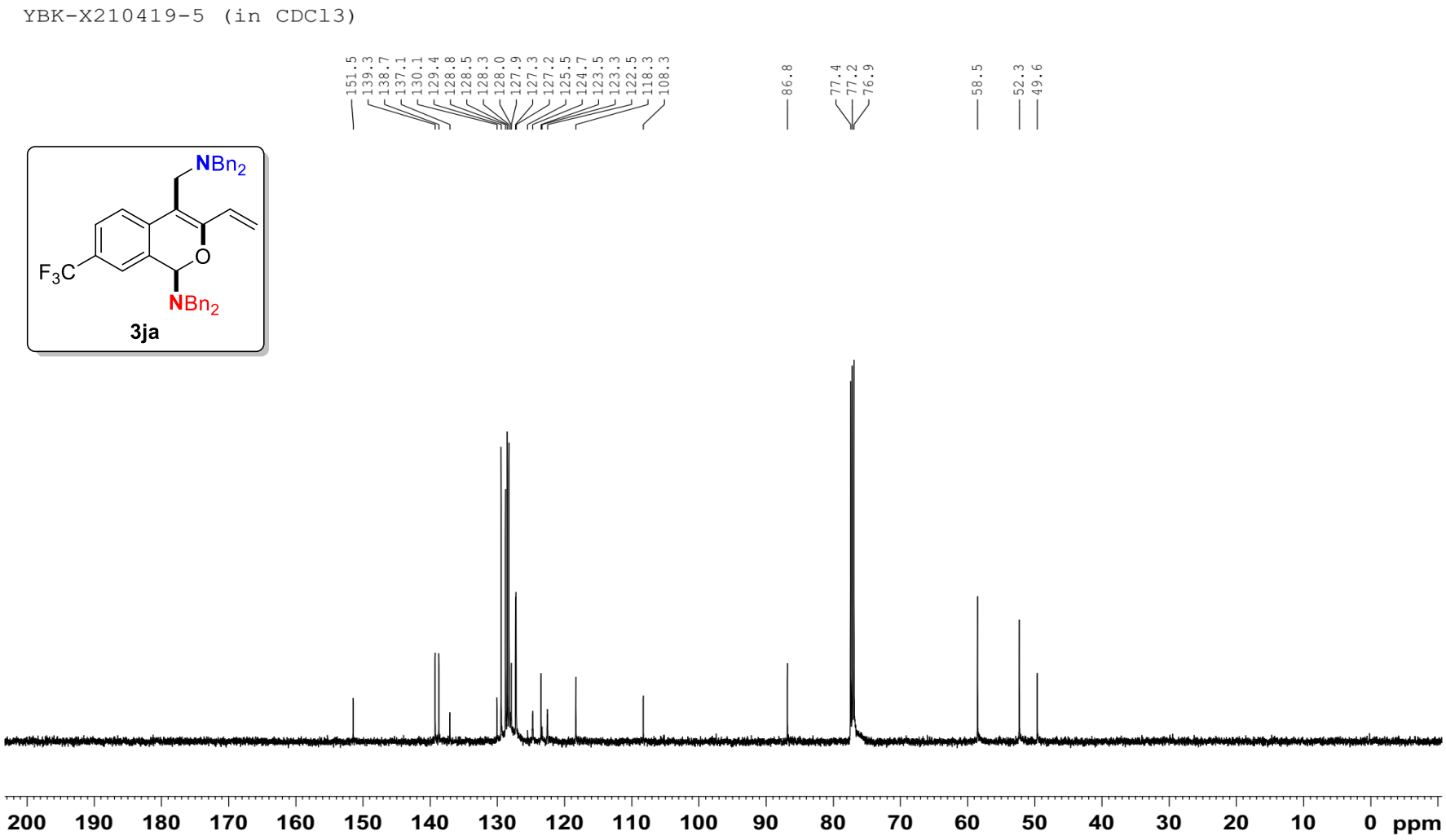
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ia



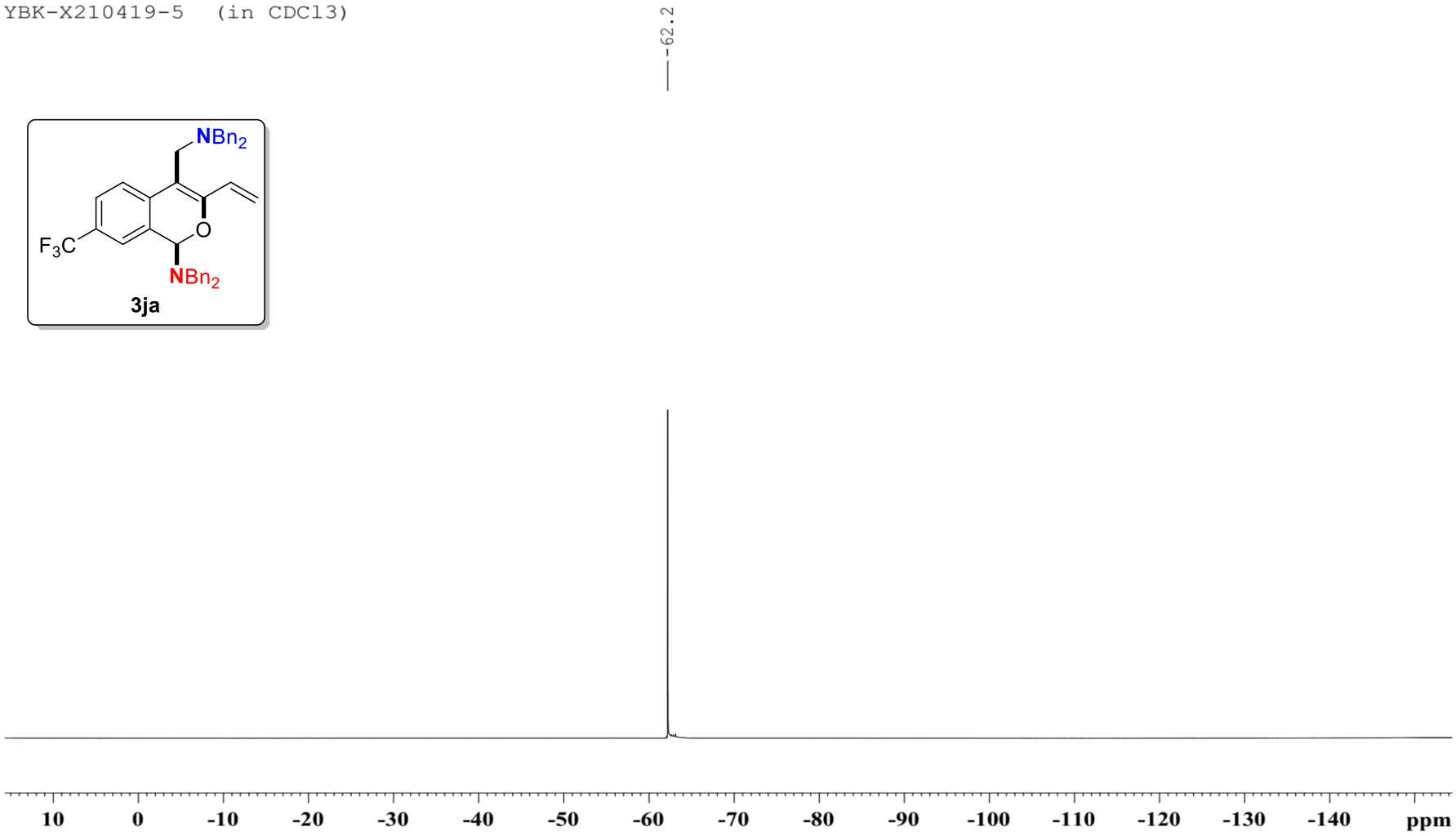
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ja



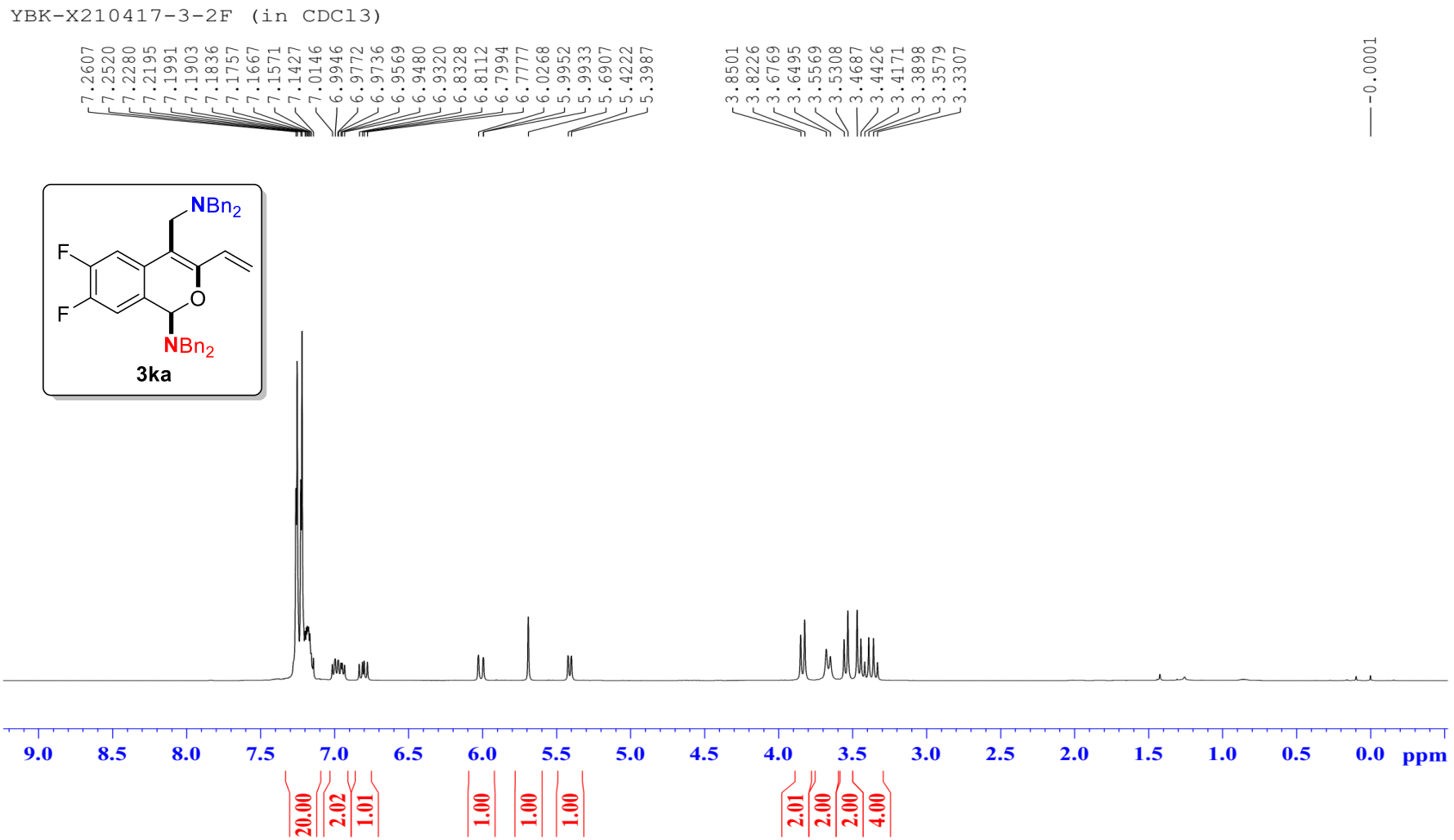
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ja



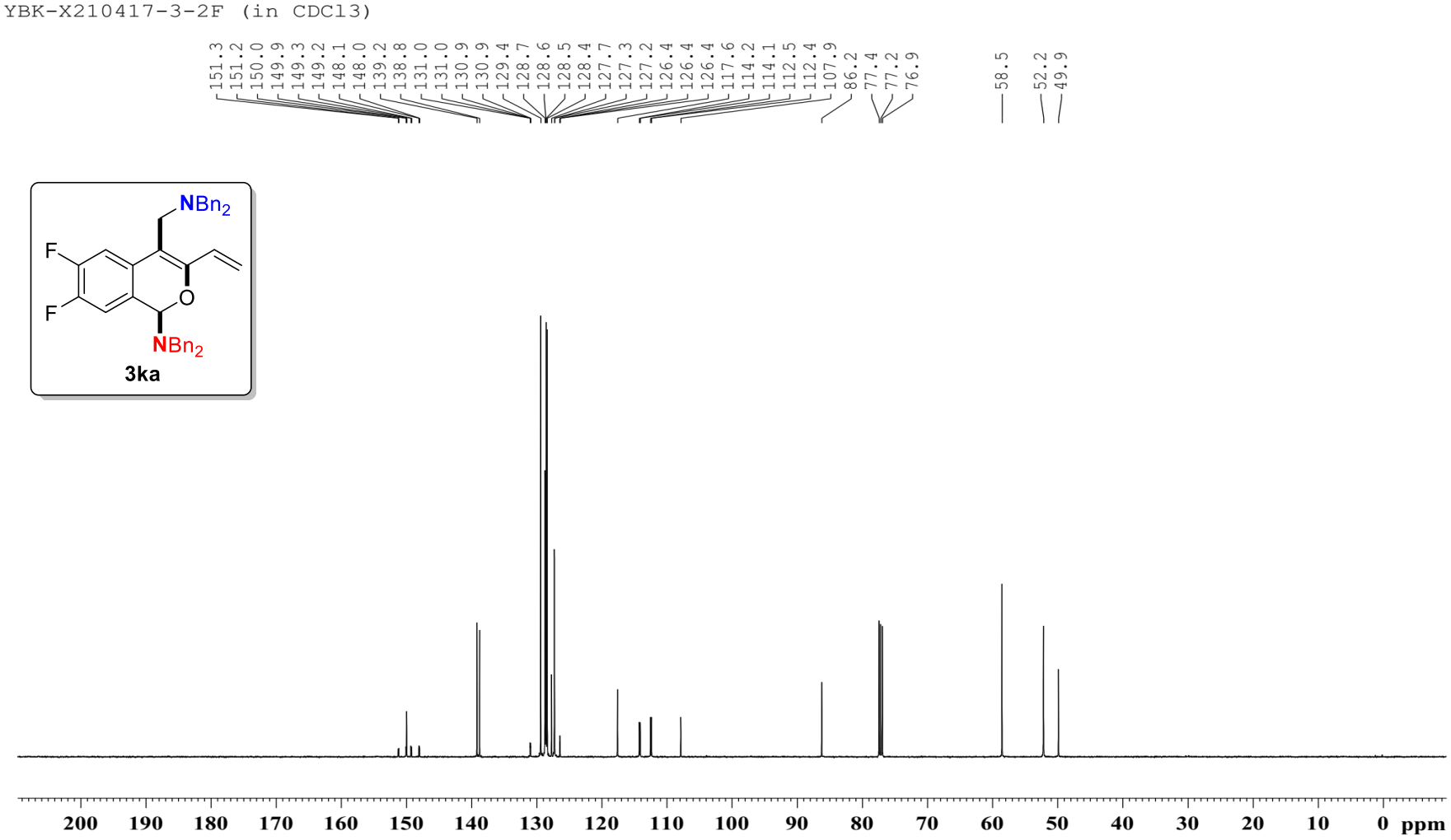
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 3ja



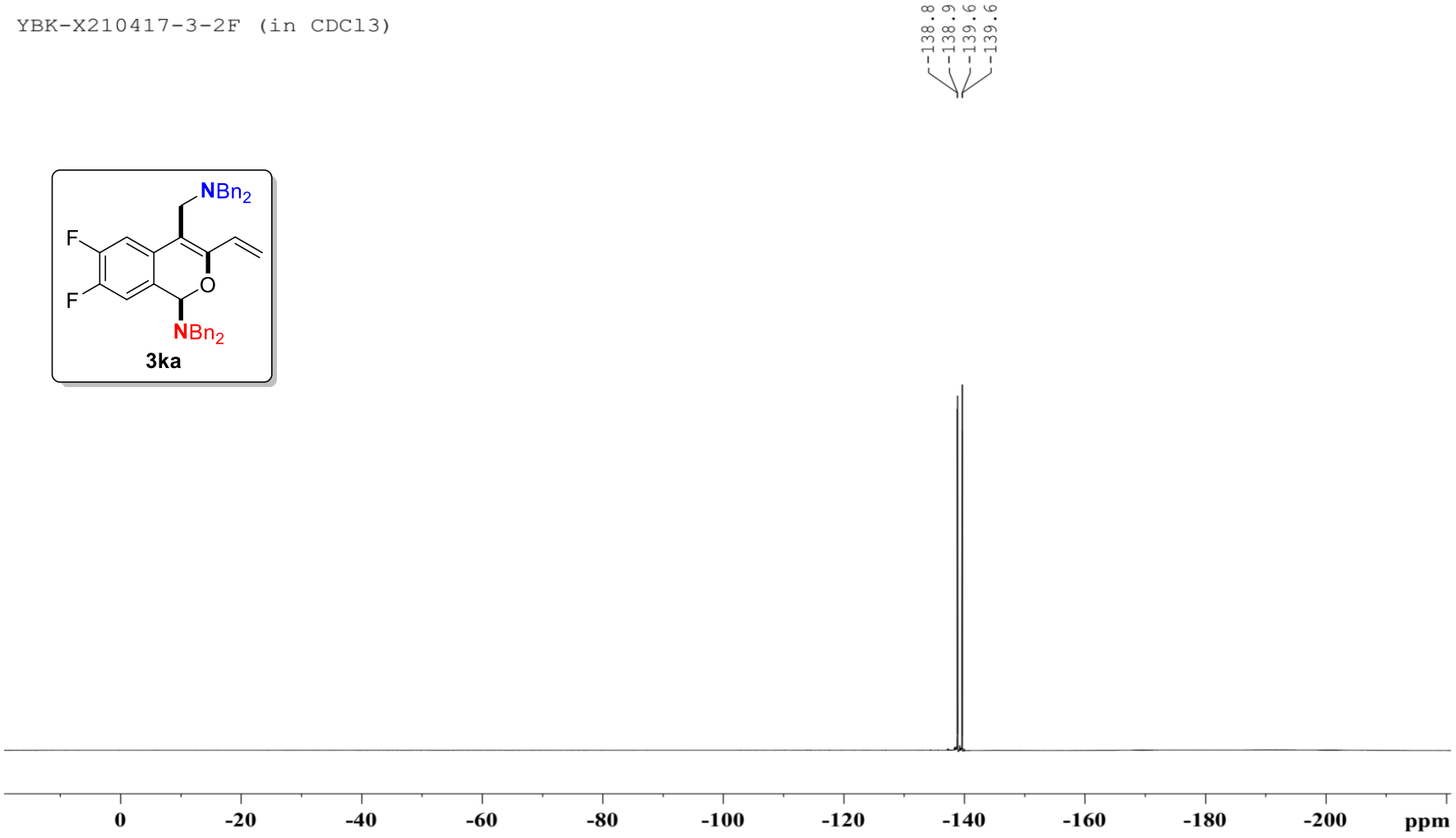
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ka



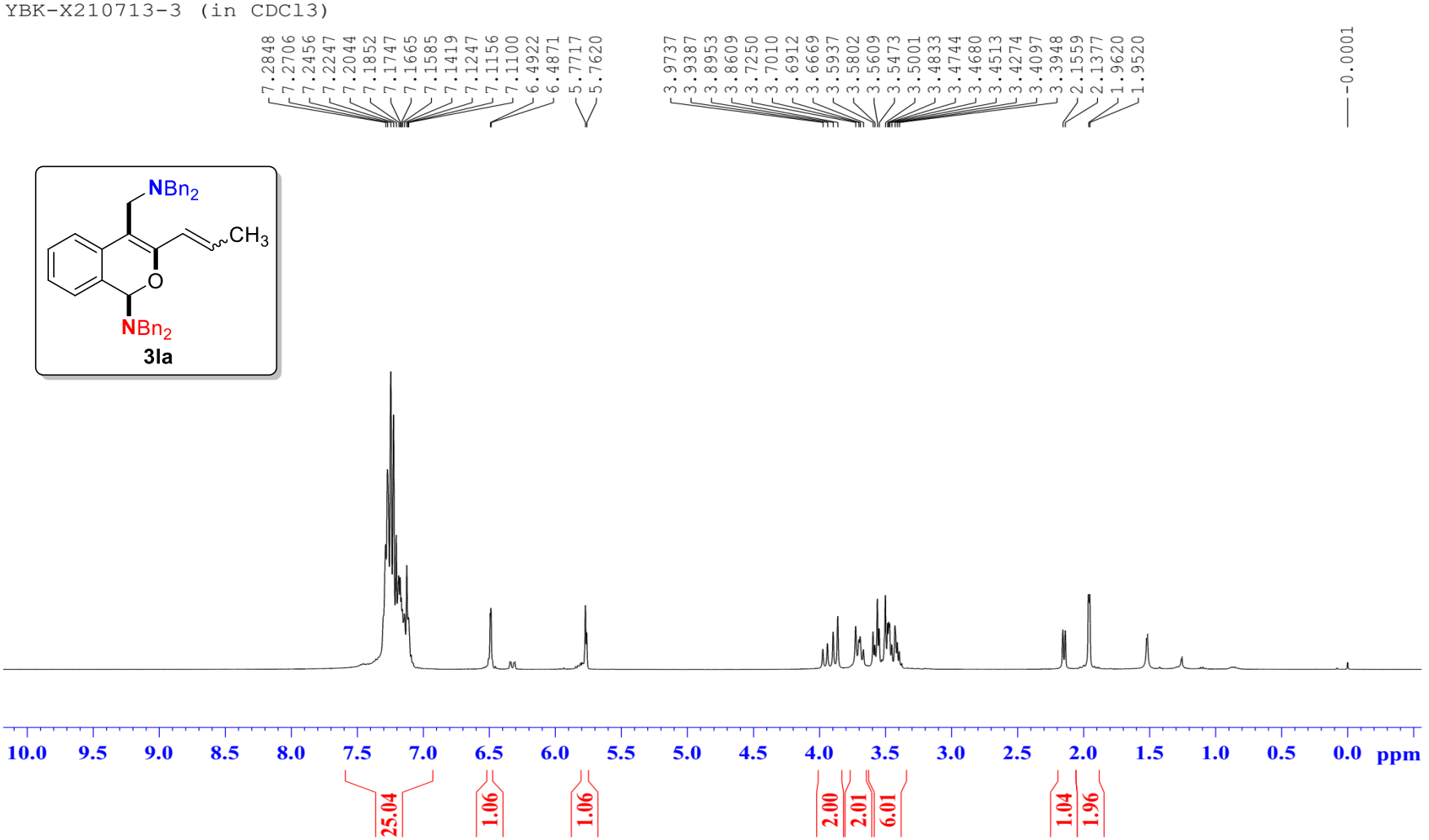
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ka



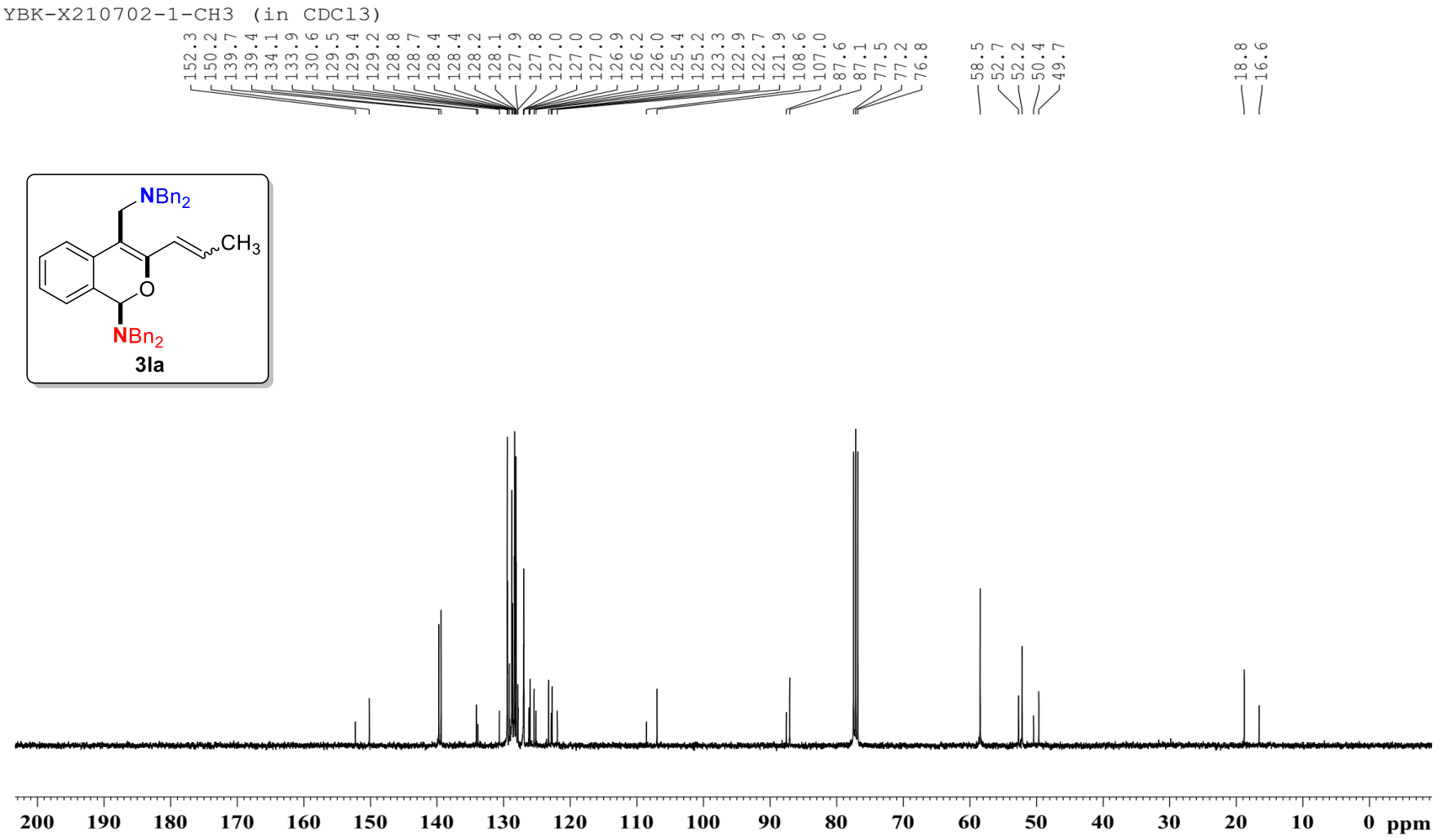
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 3ka



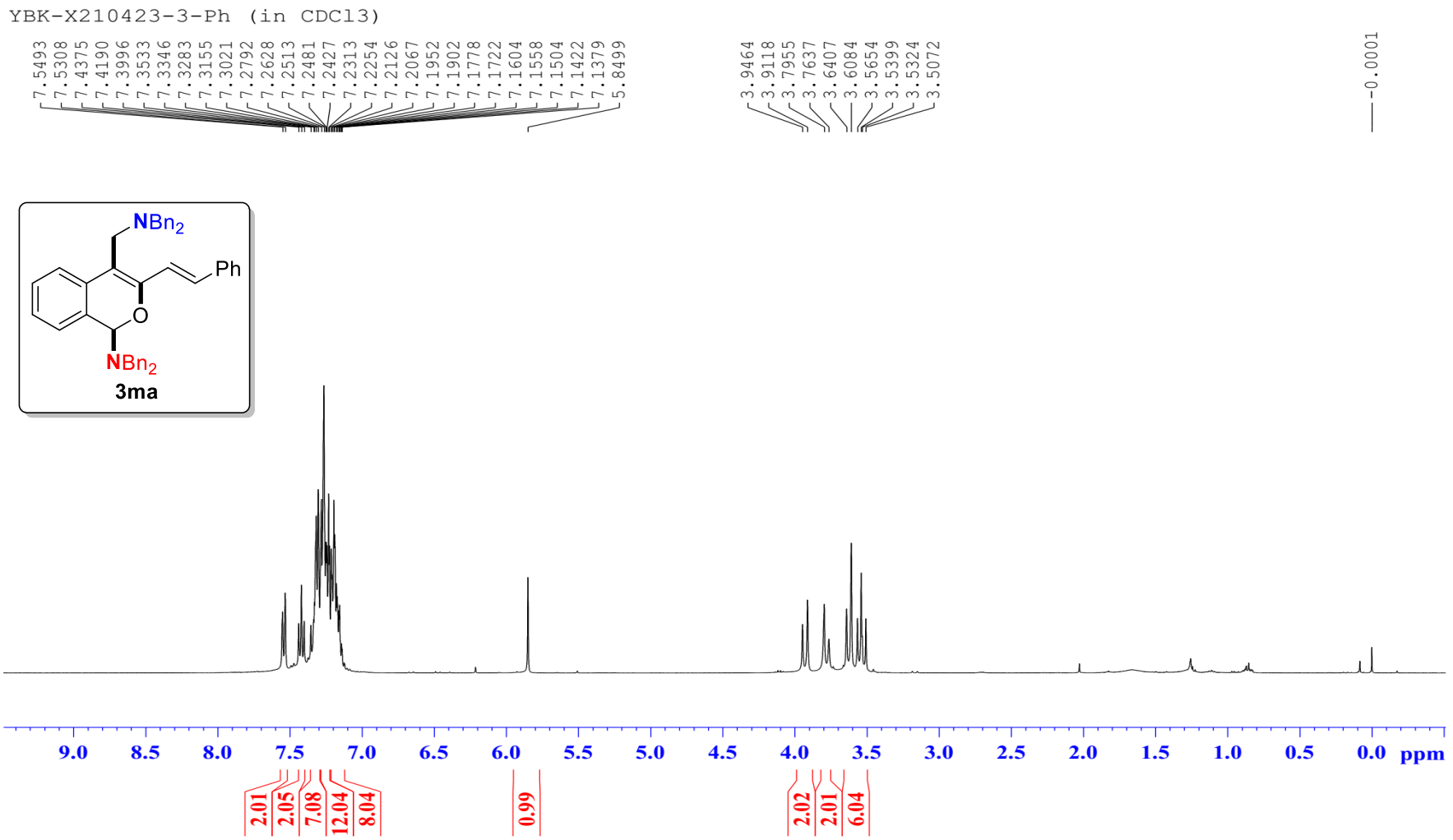
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3la



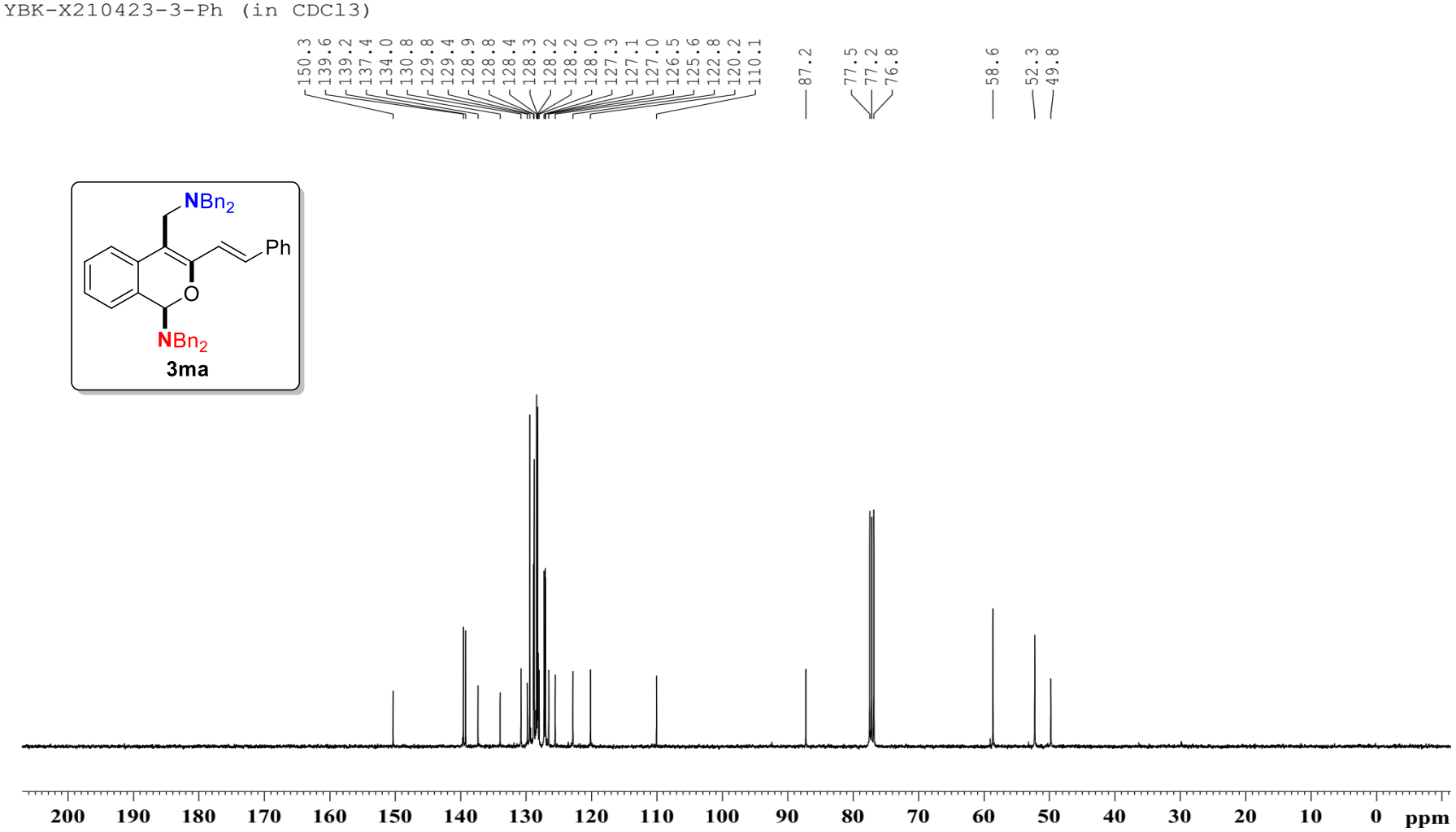
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3la



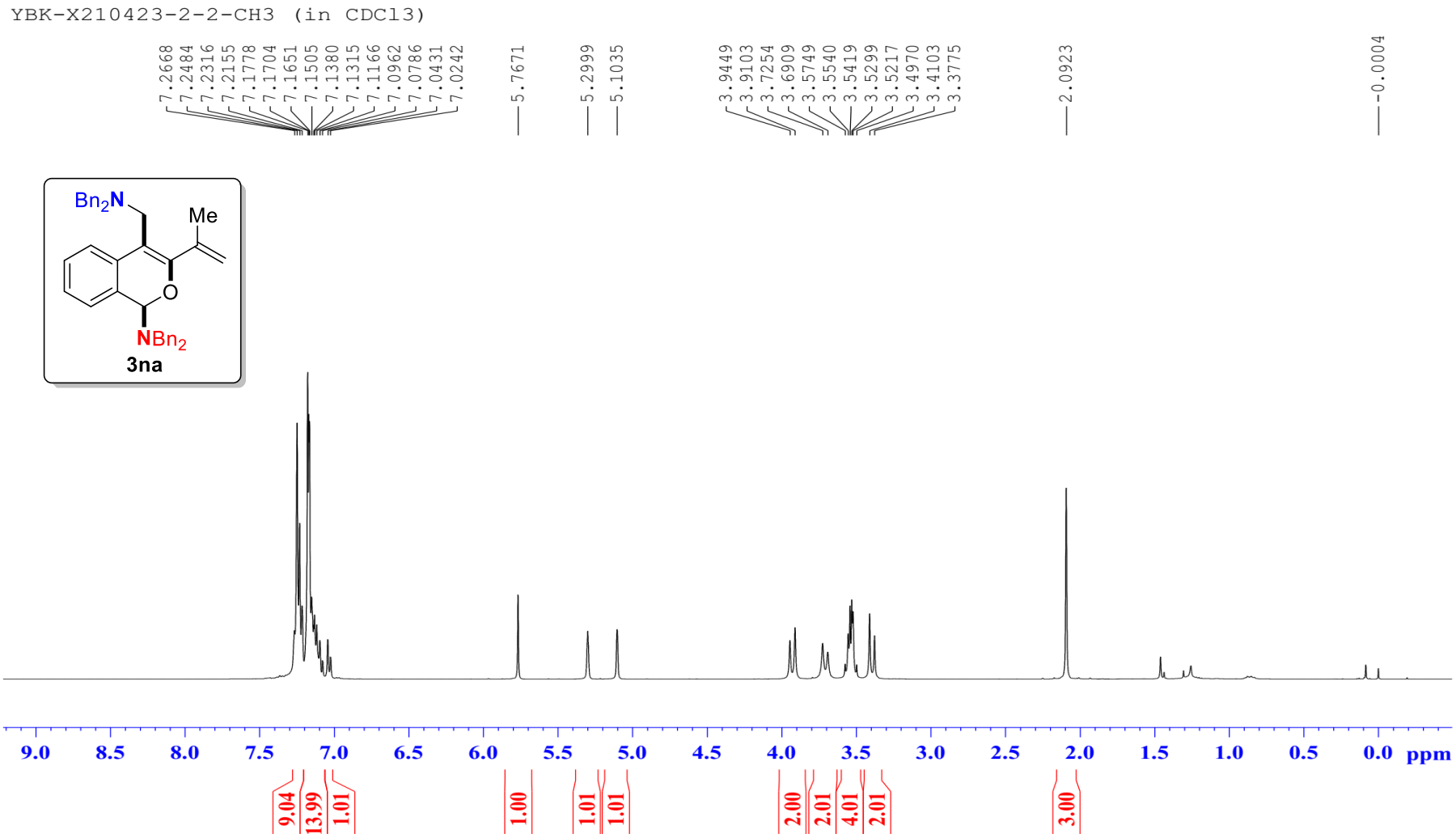
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ma



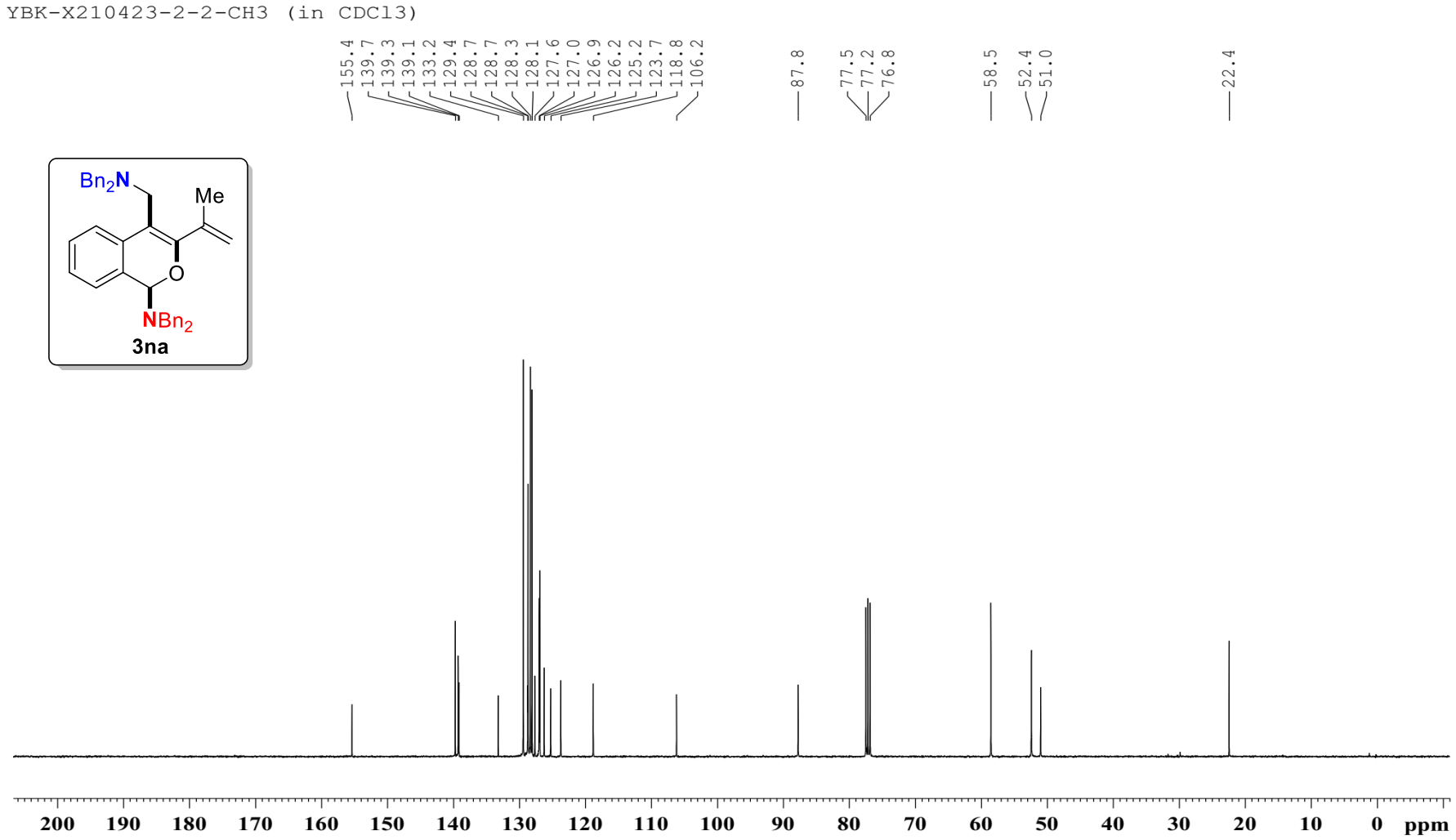
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ma



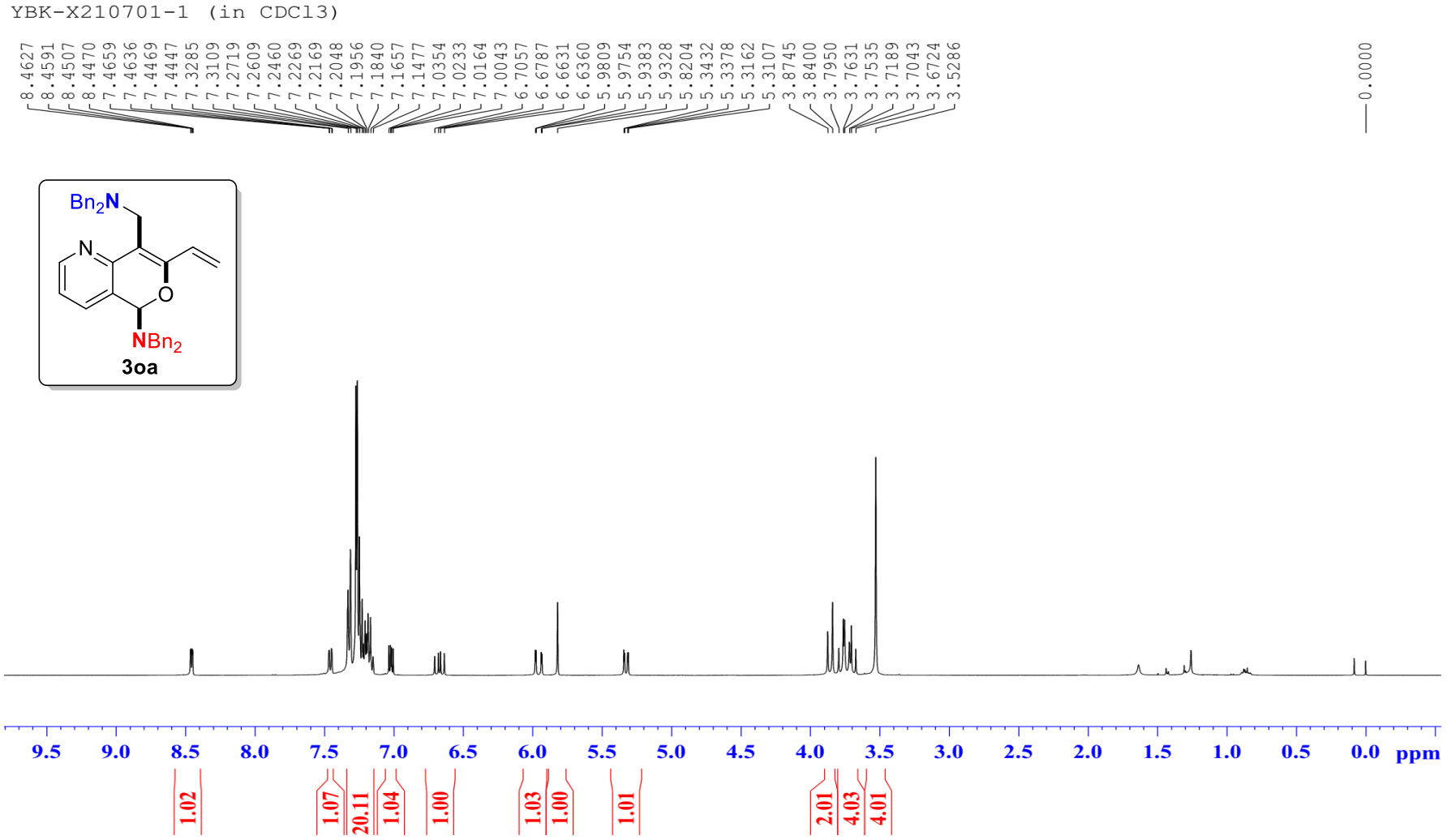
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3na



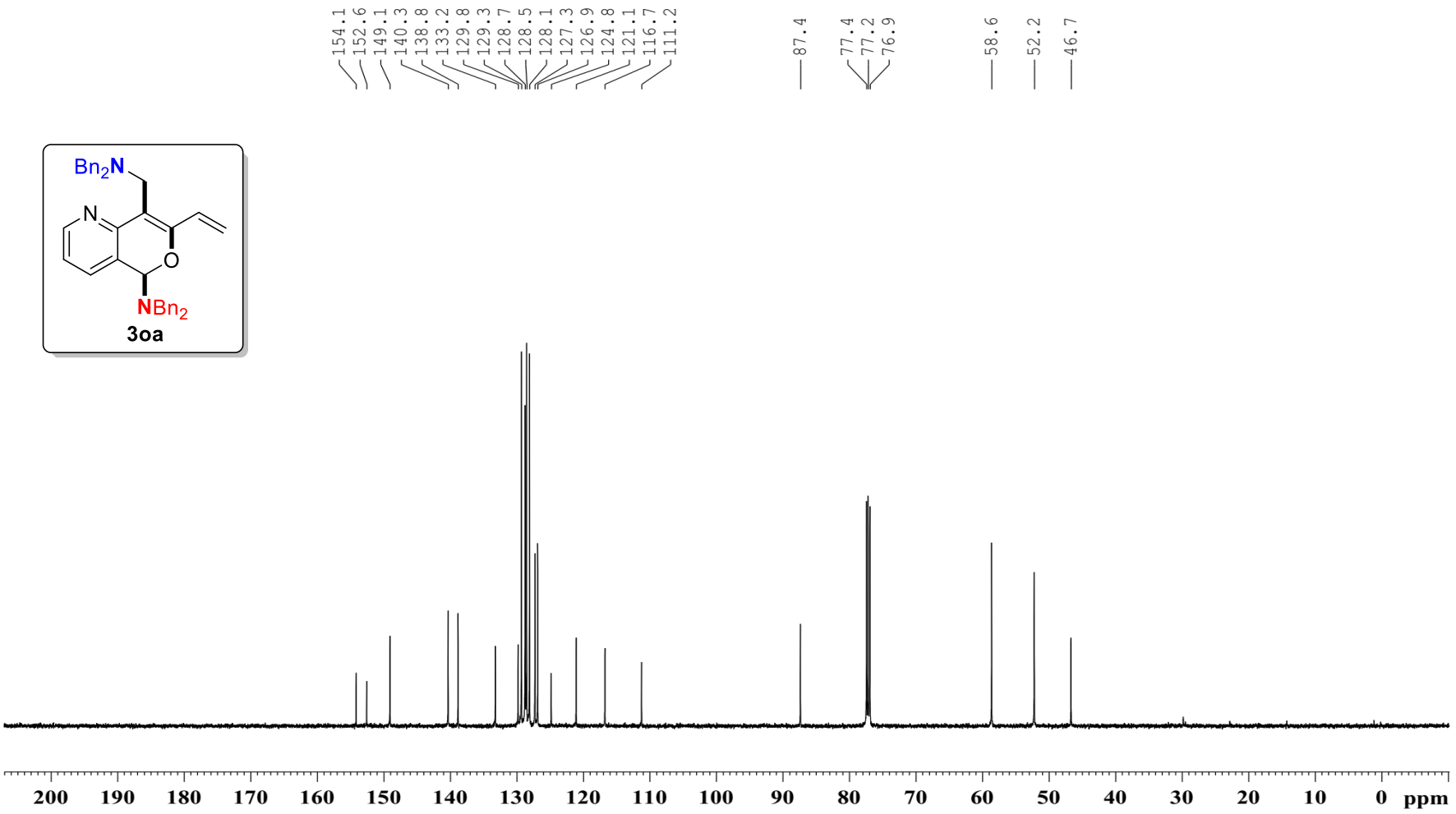
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3na



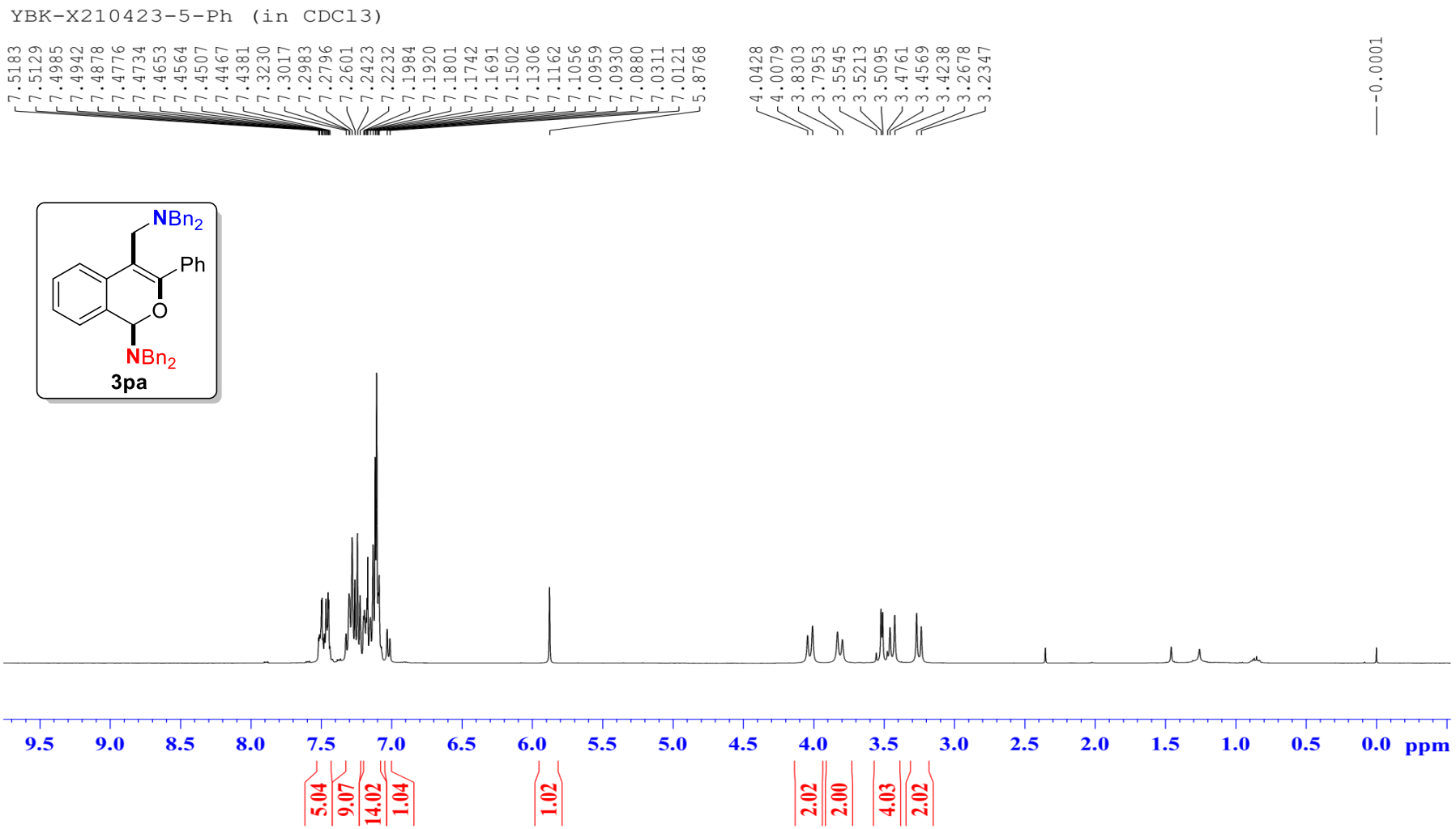
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3oa



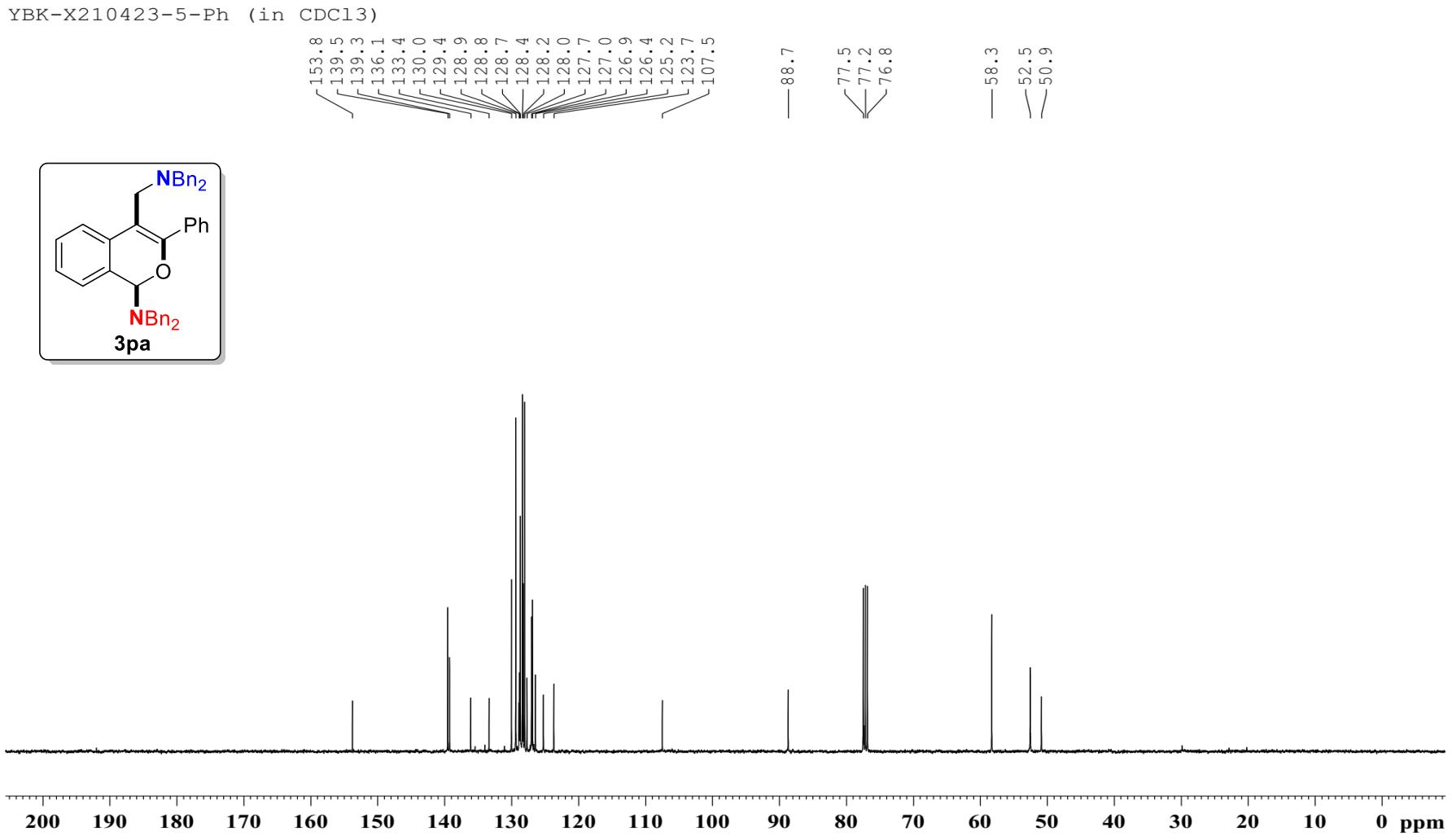
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3oa



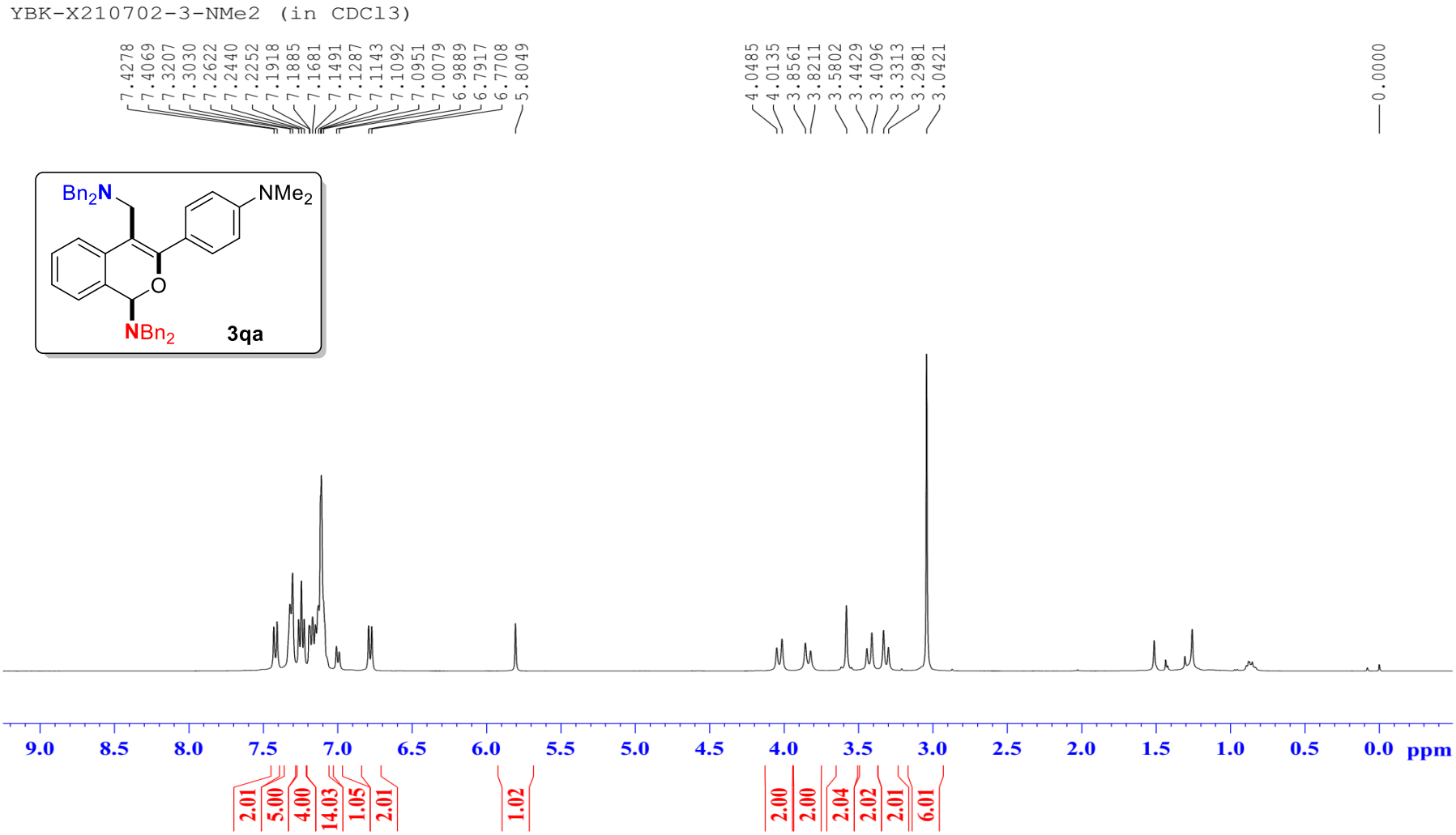
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3pa



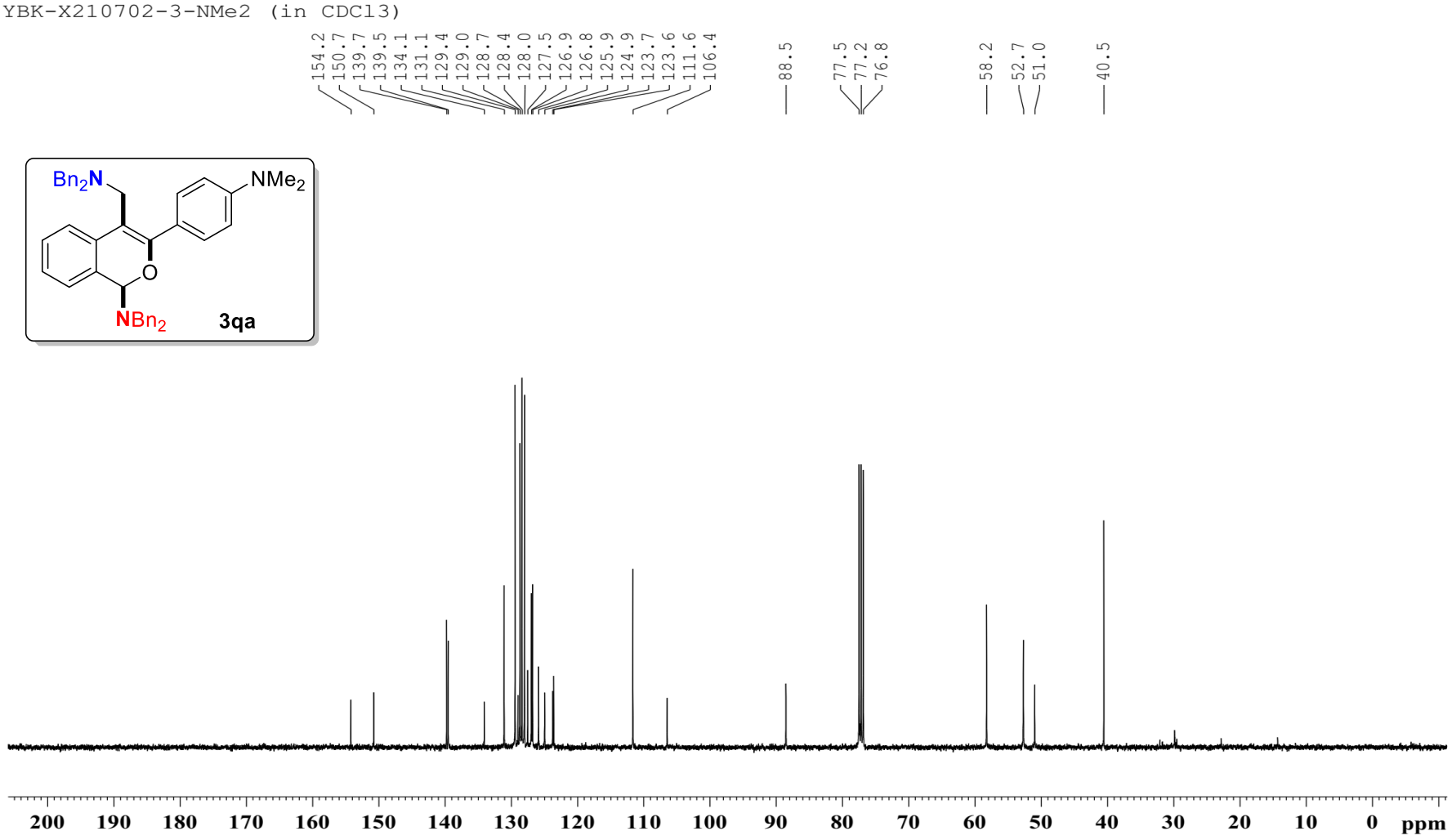
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3pa



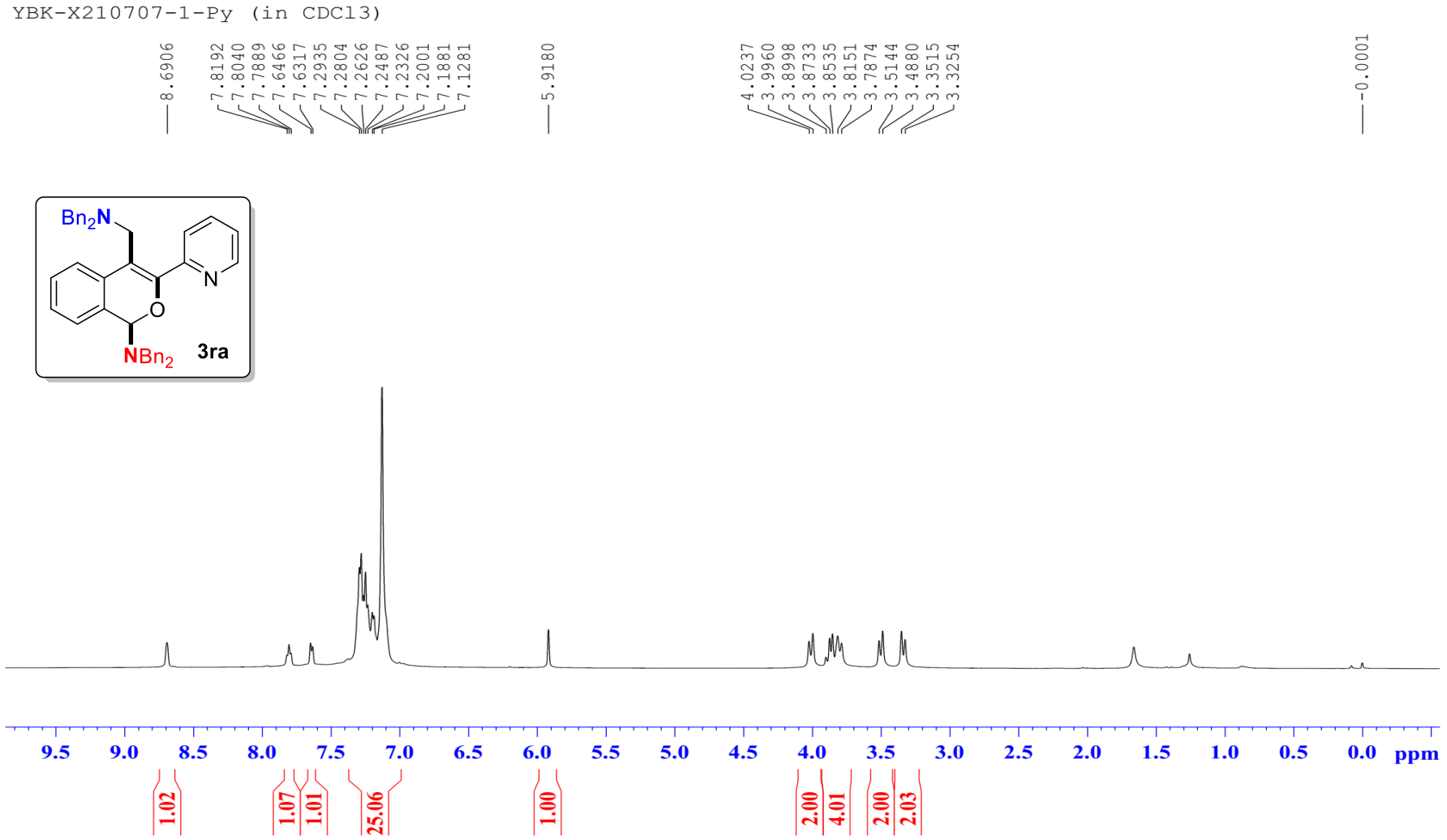
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3qa



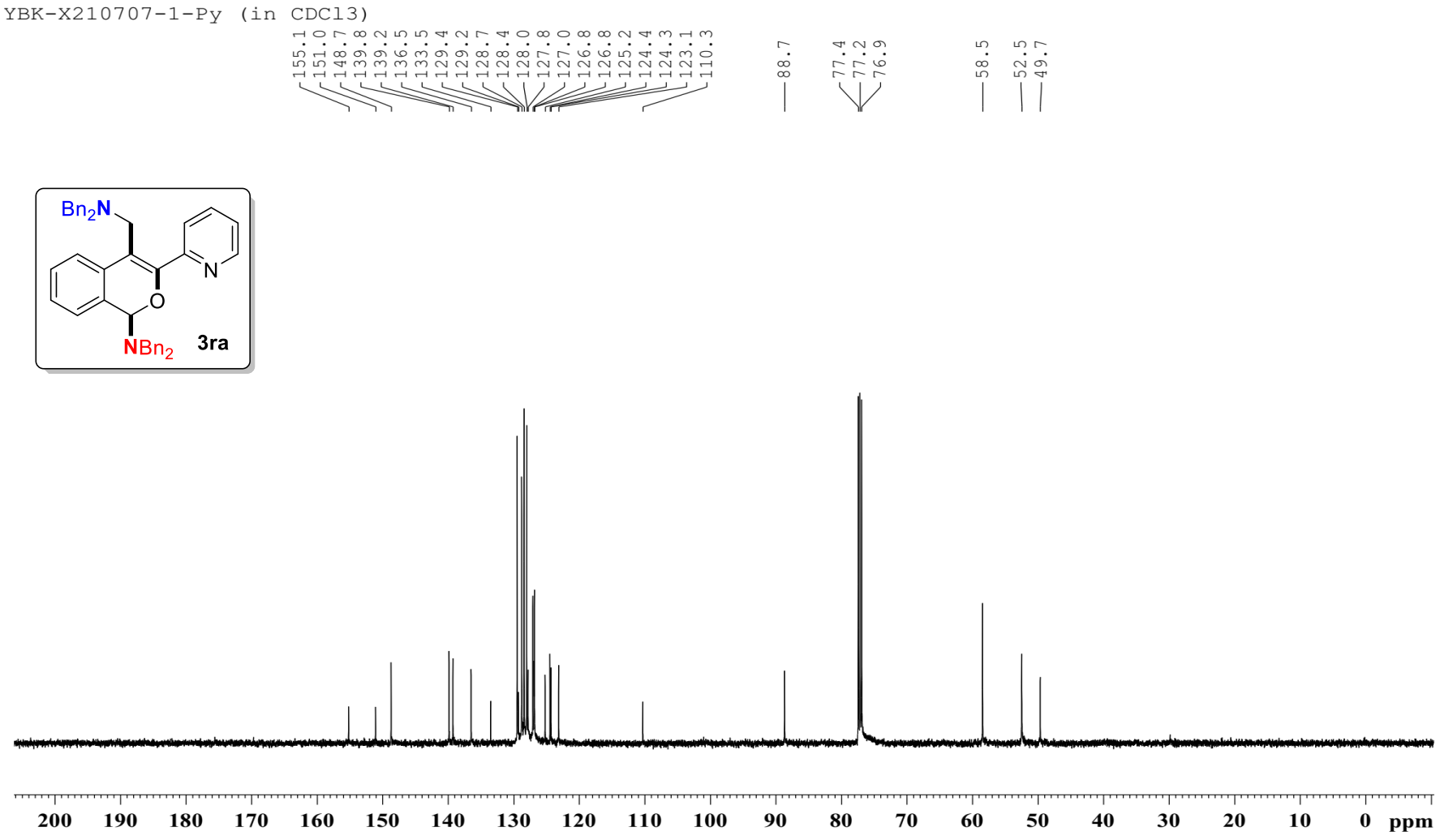
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3qa



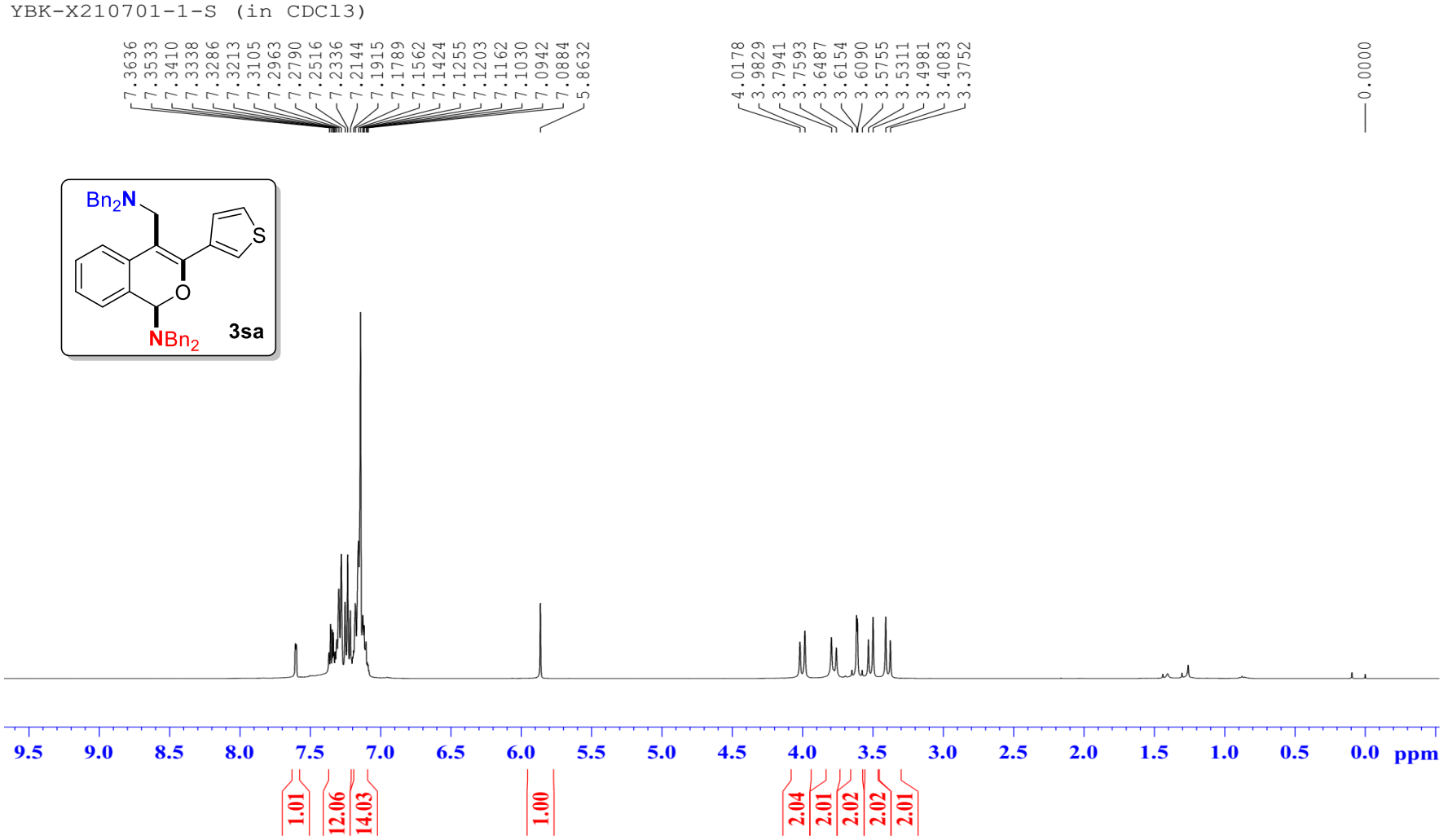
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ra



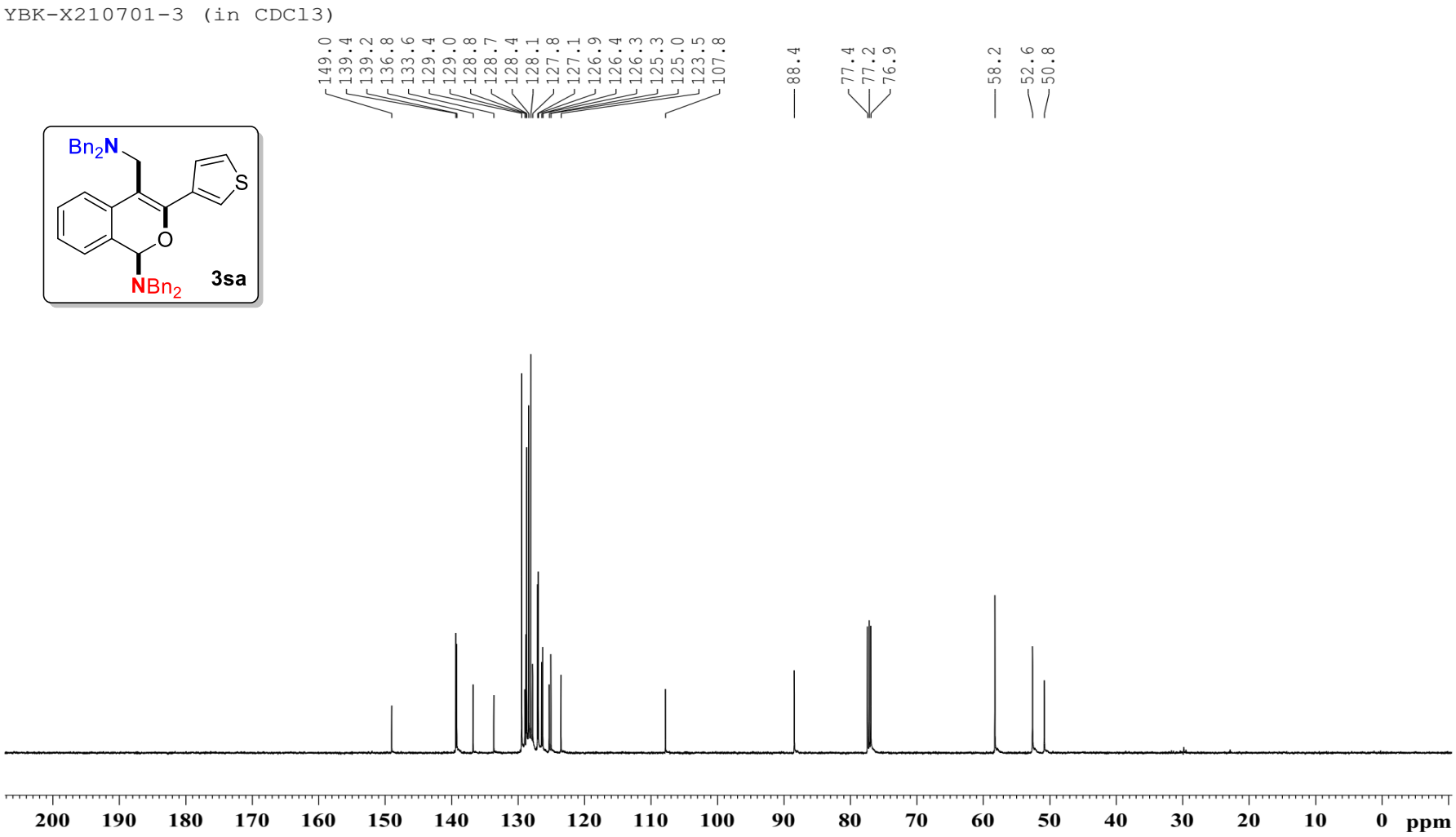
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ra



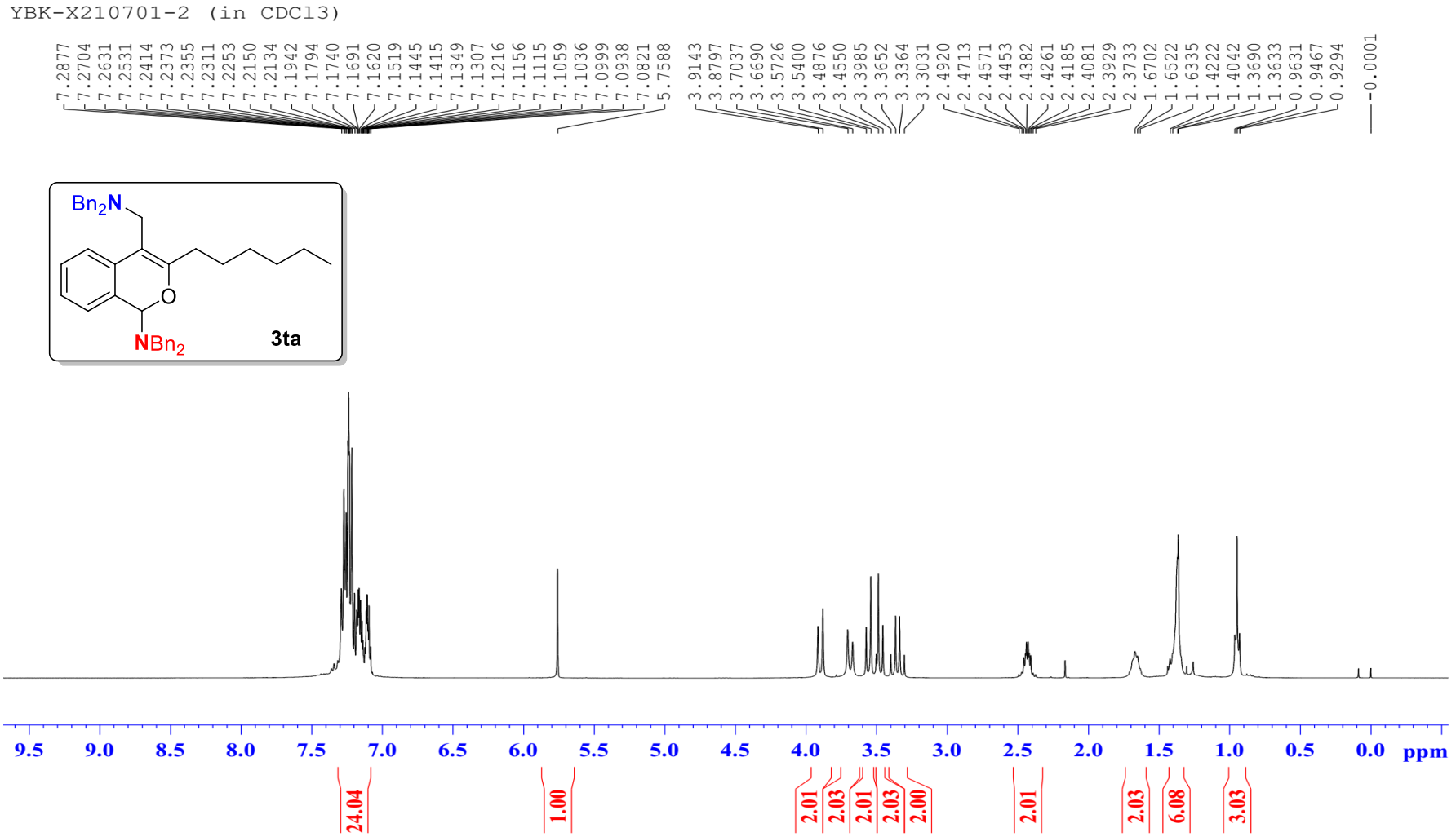
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3sa



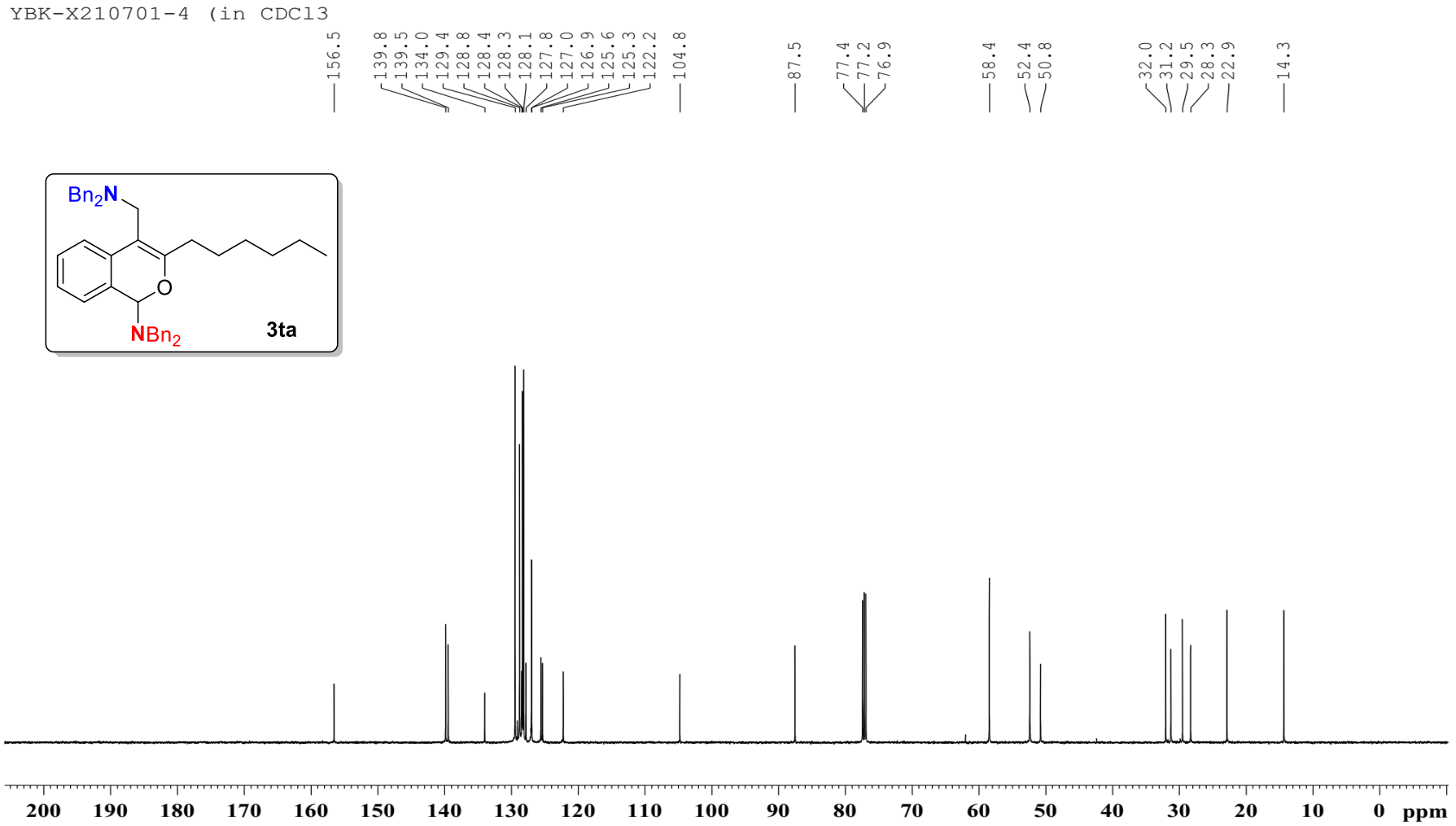
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3sa



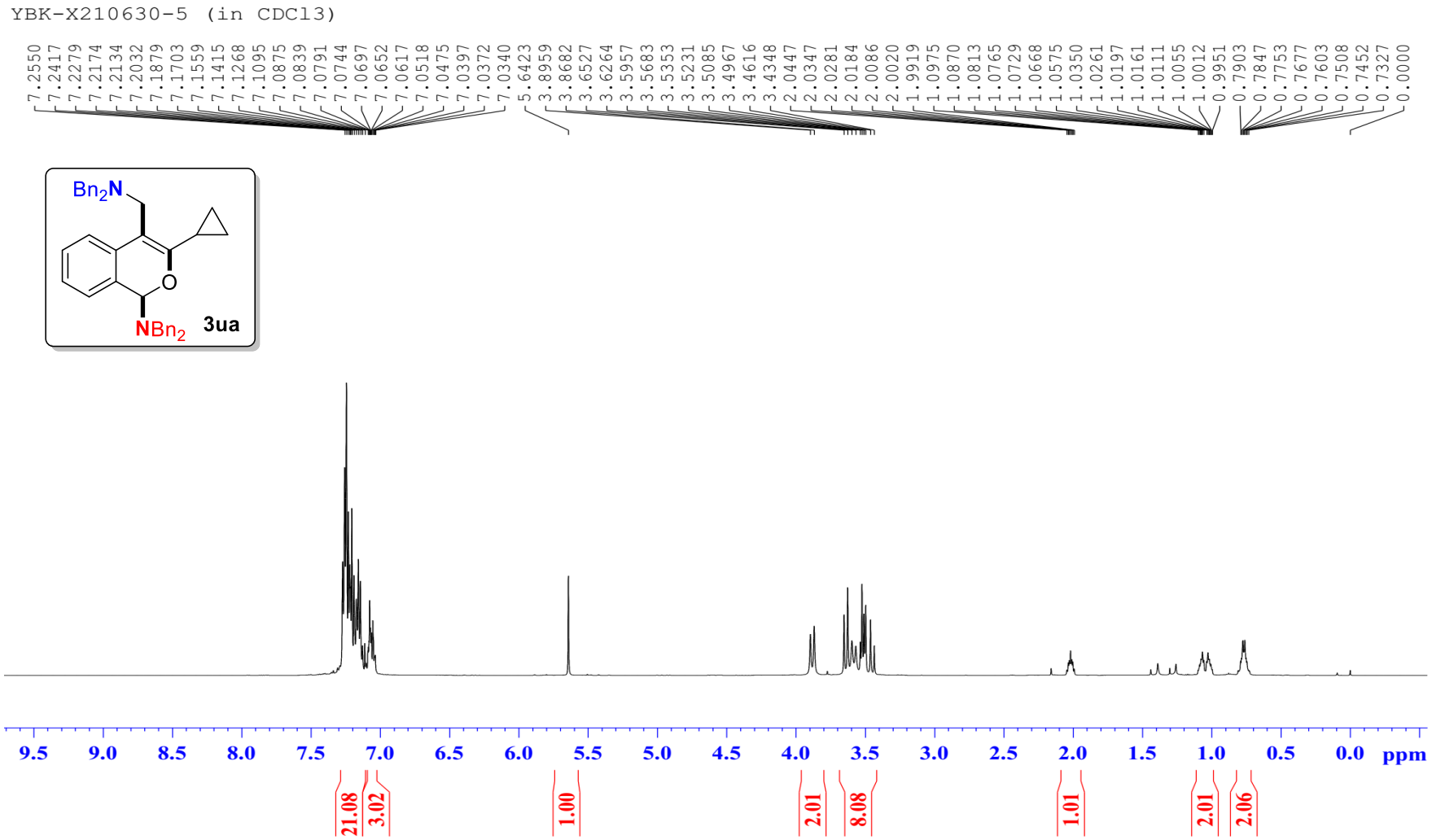
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ta



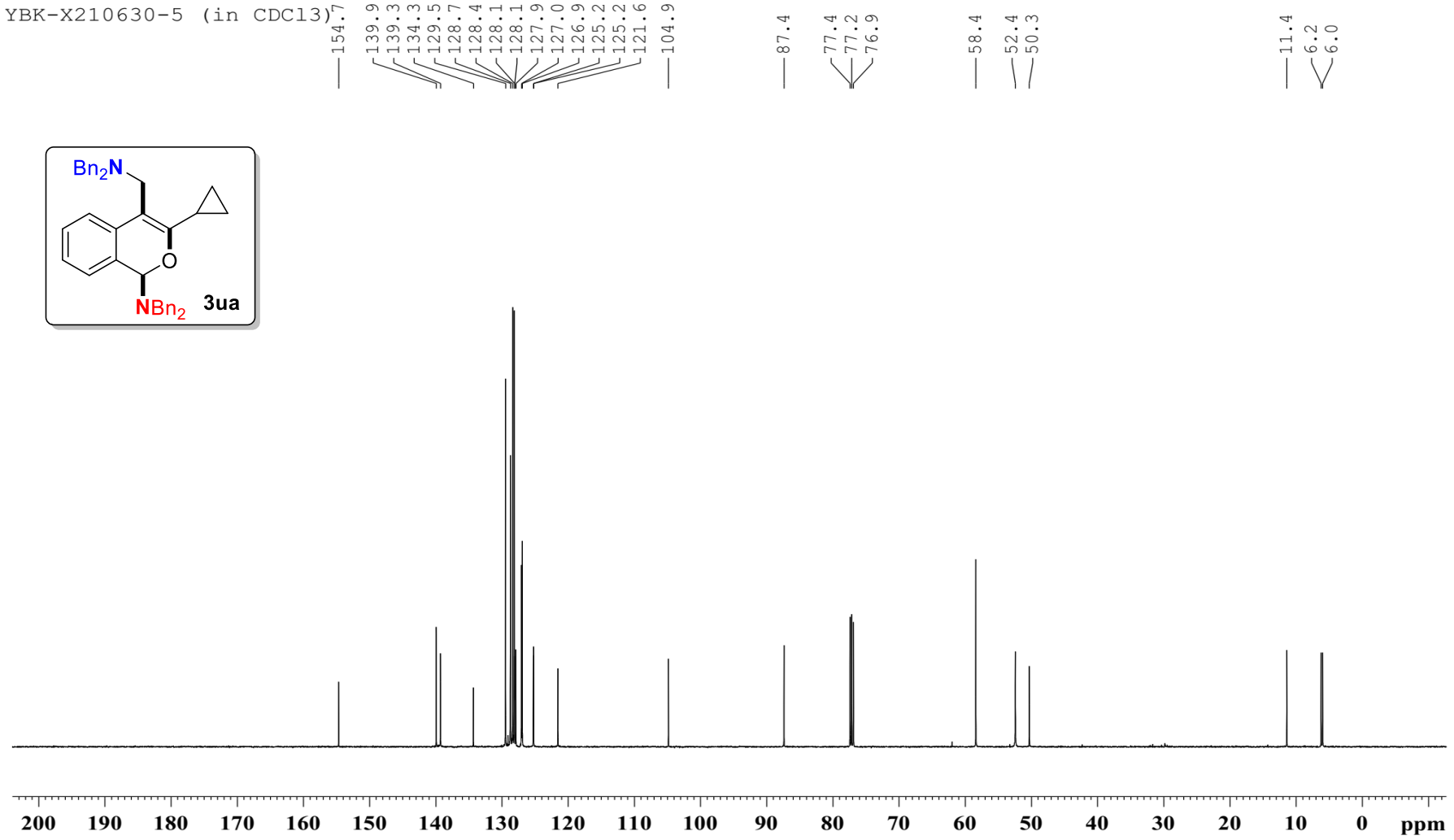
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ta



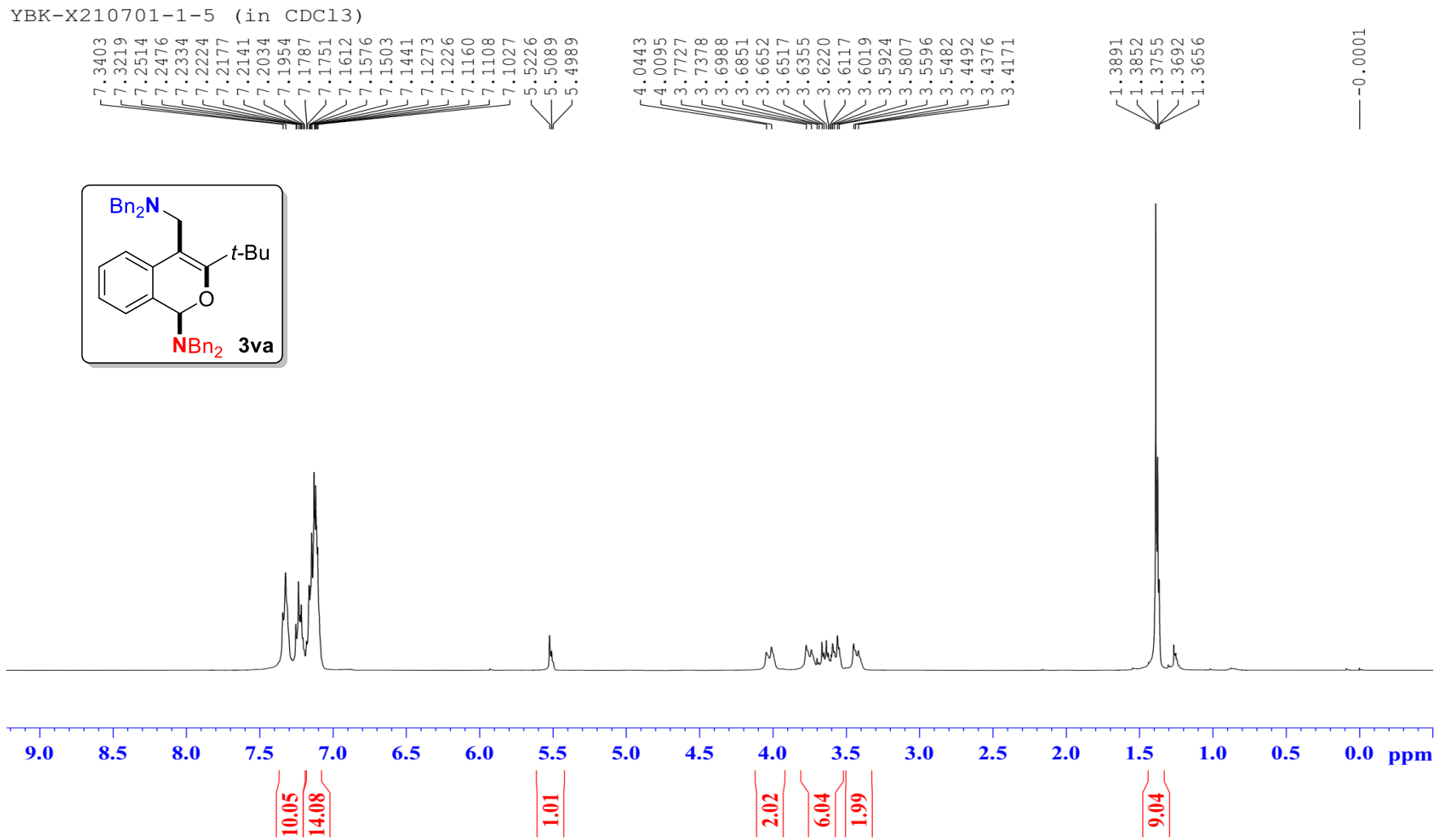
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ua



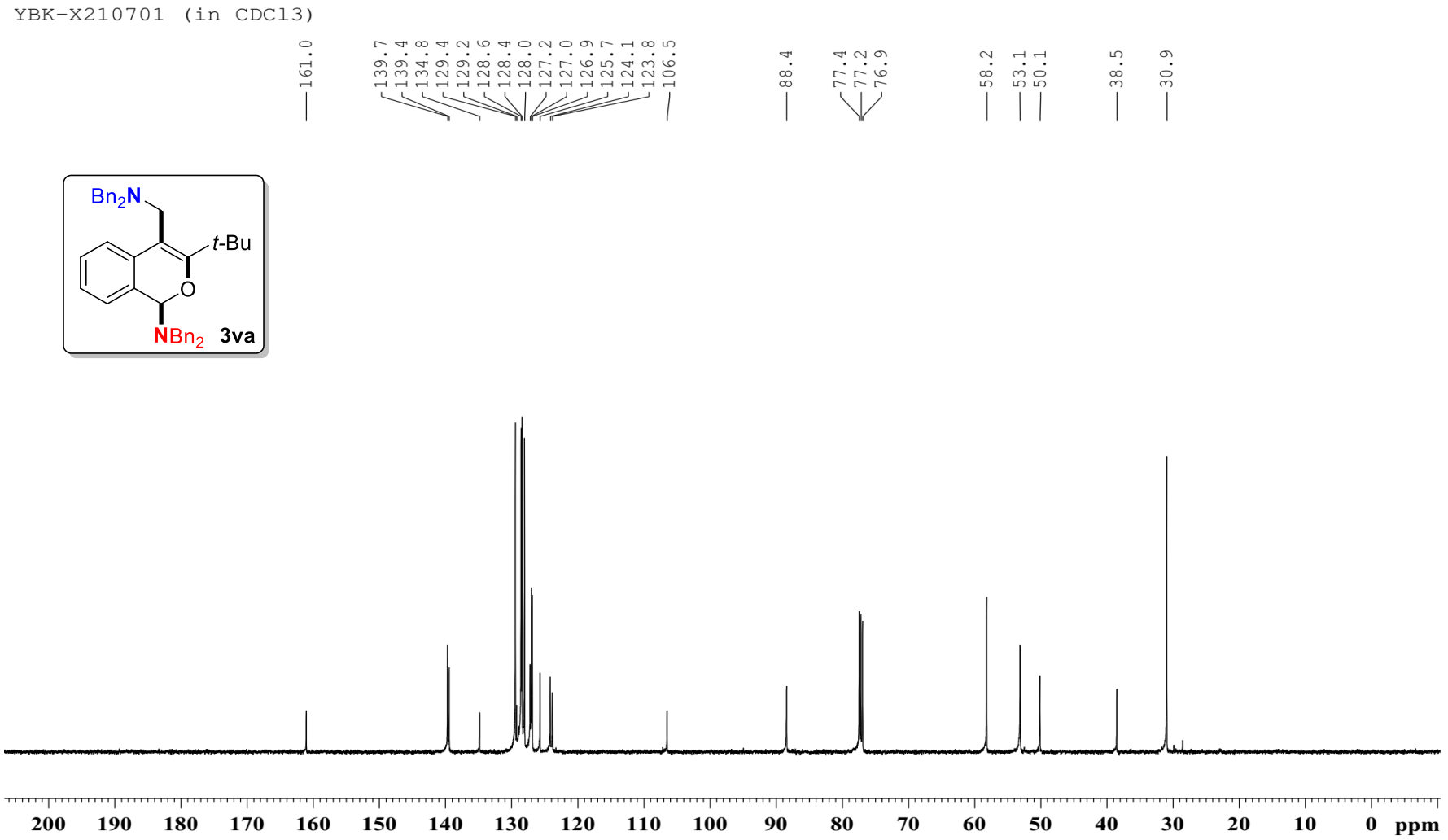
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ua



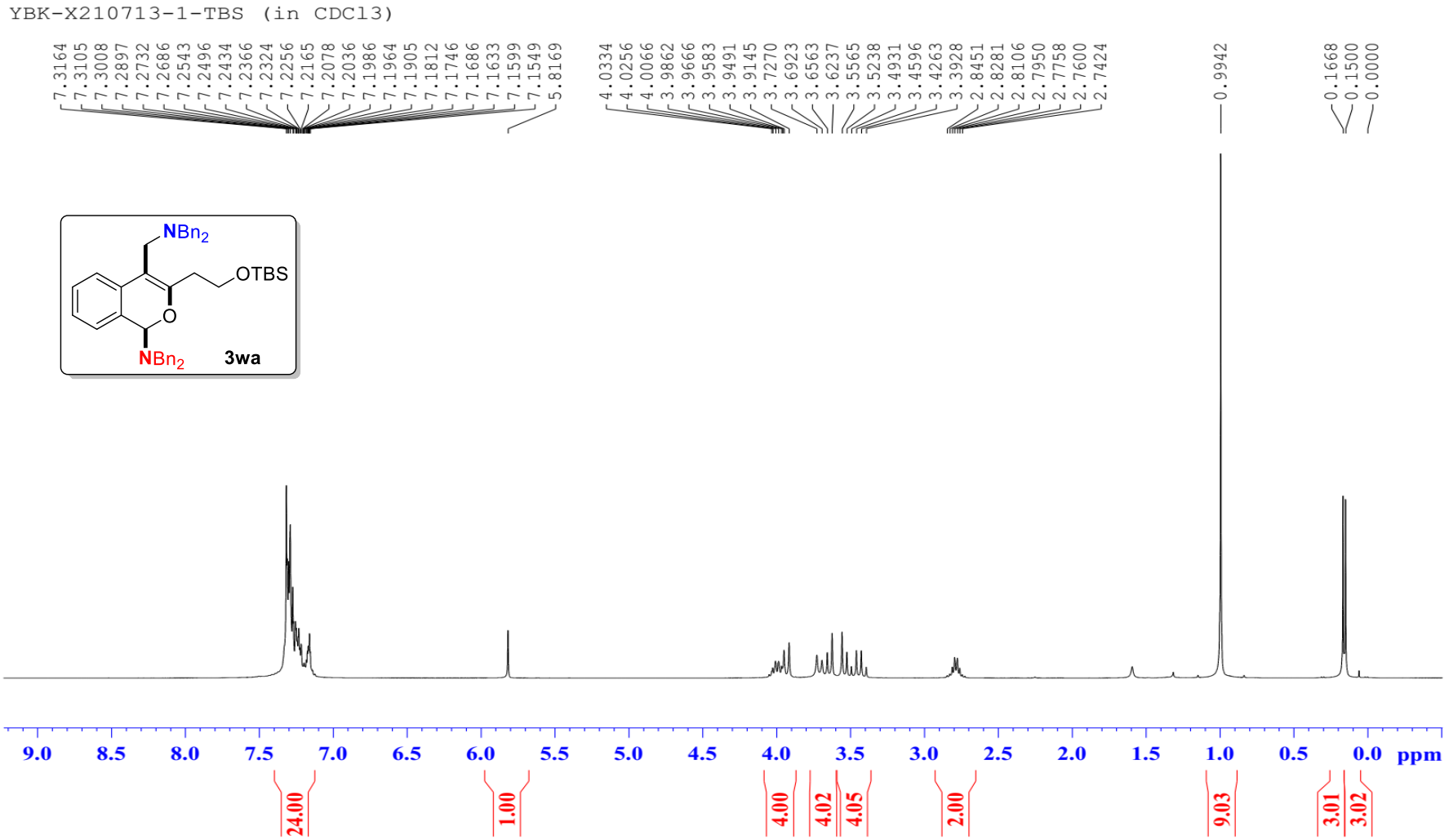
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3va



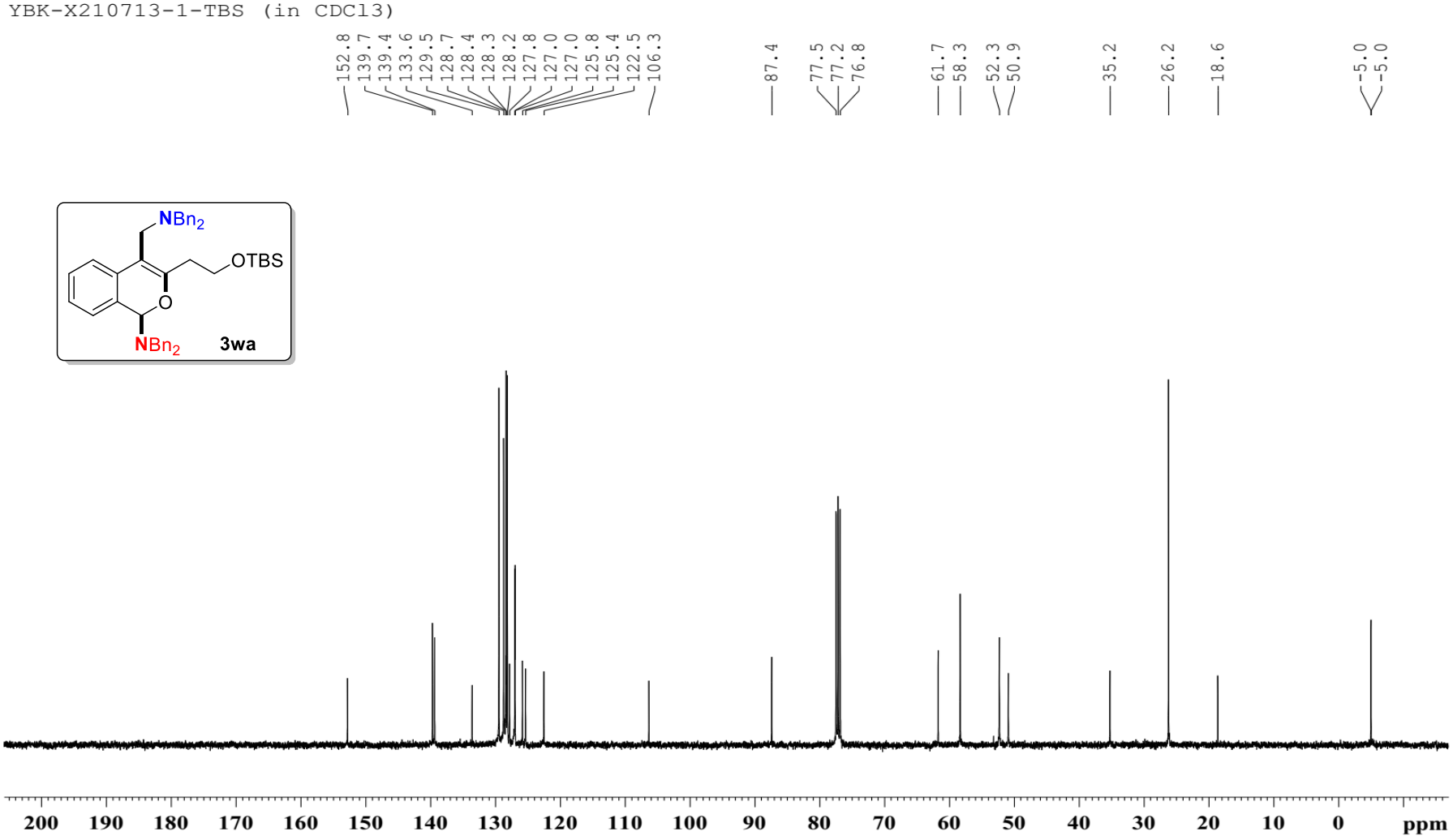
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3va



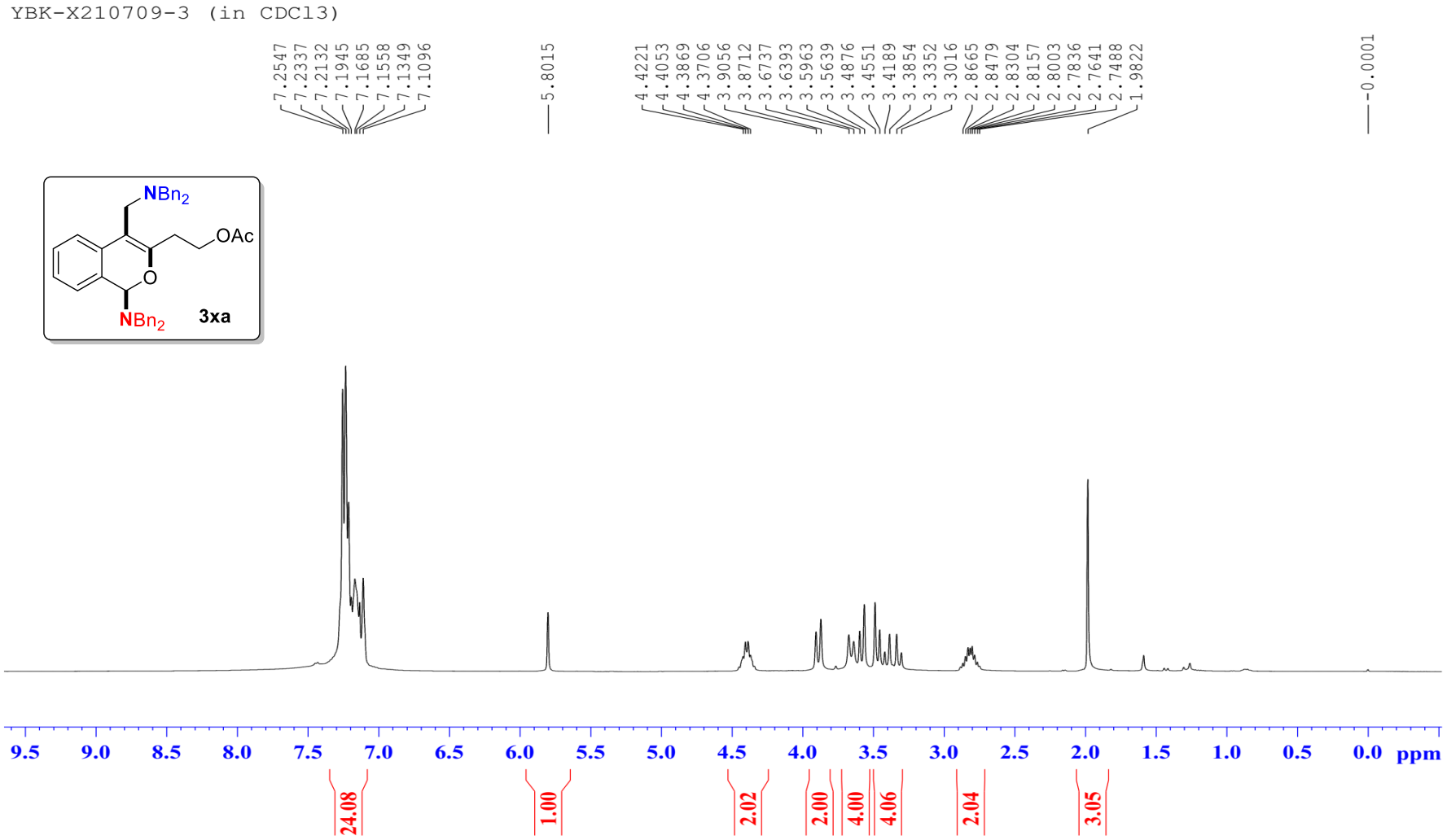
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3wa



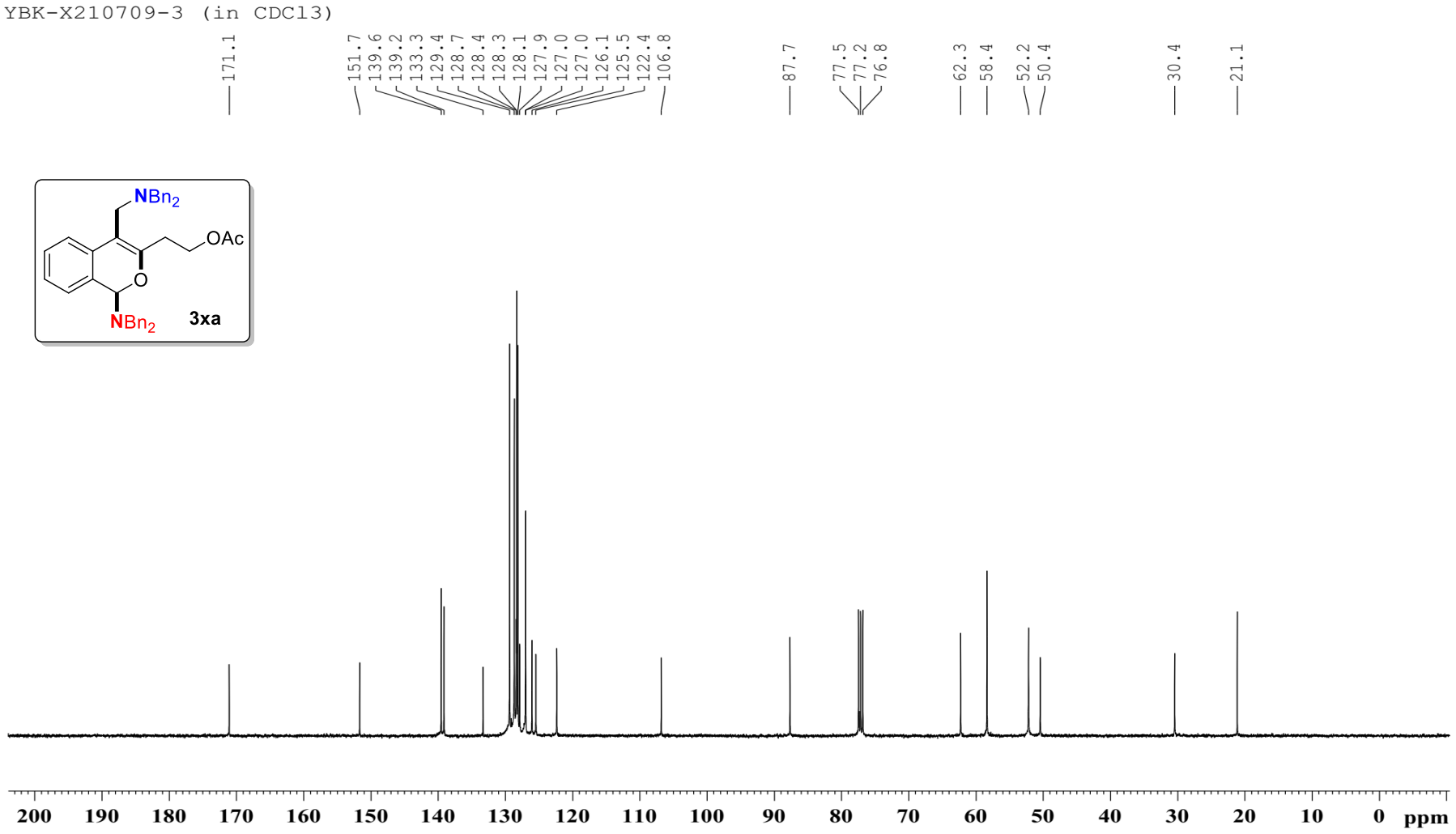
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3wa



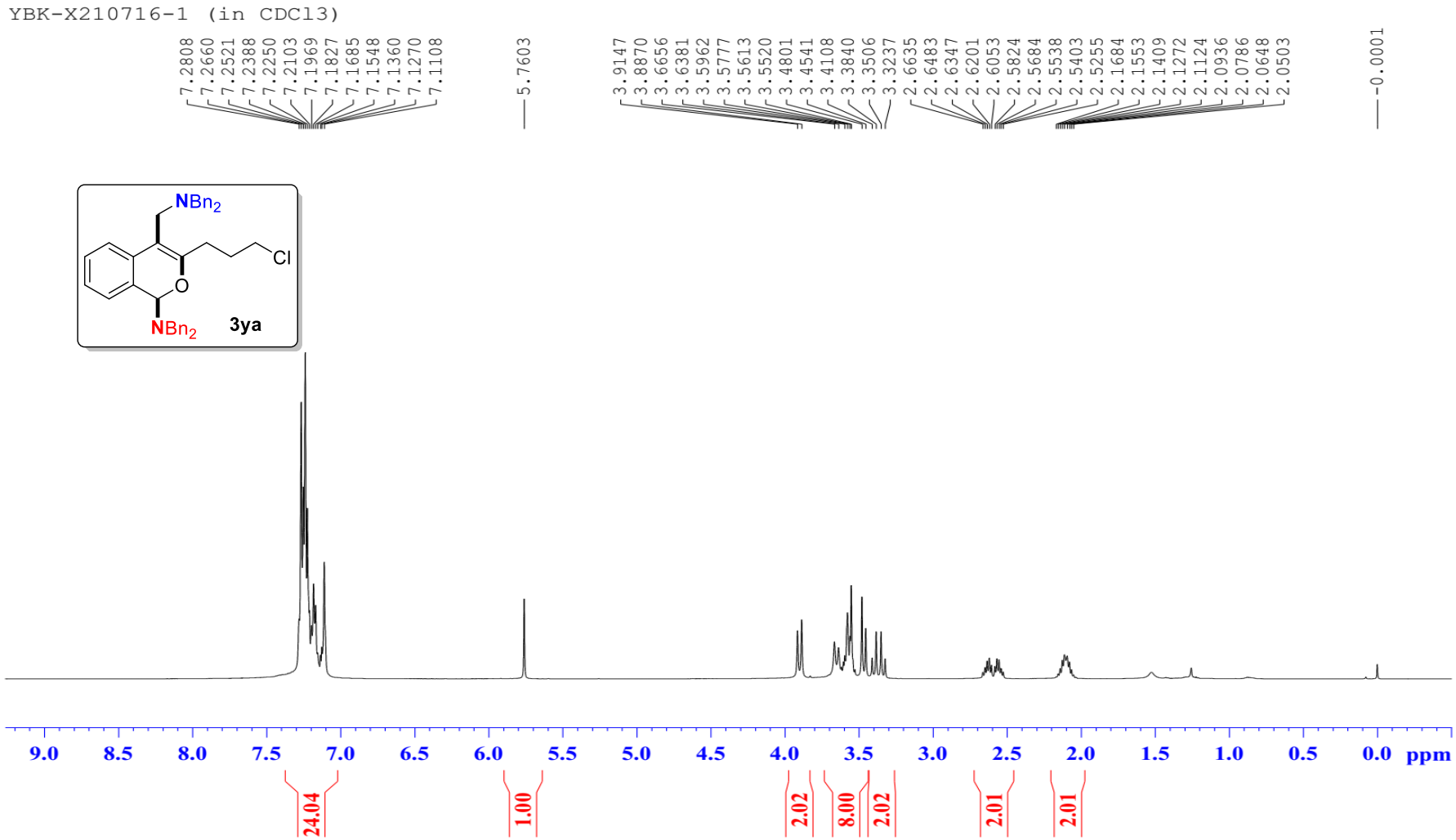
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3xa



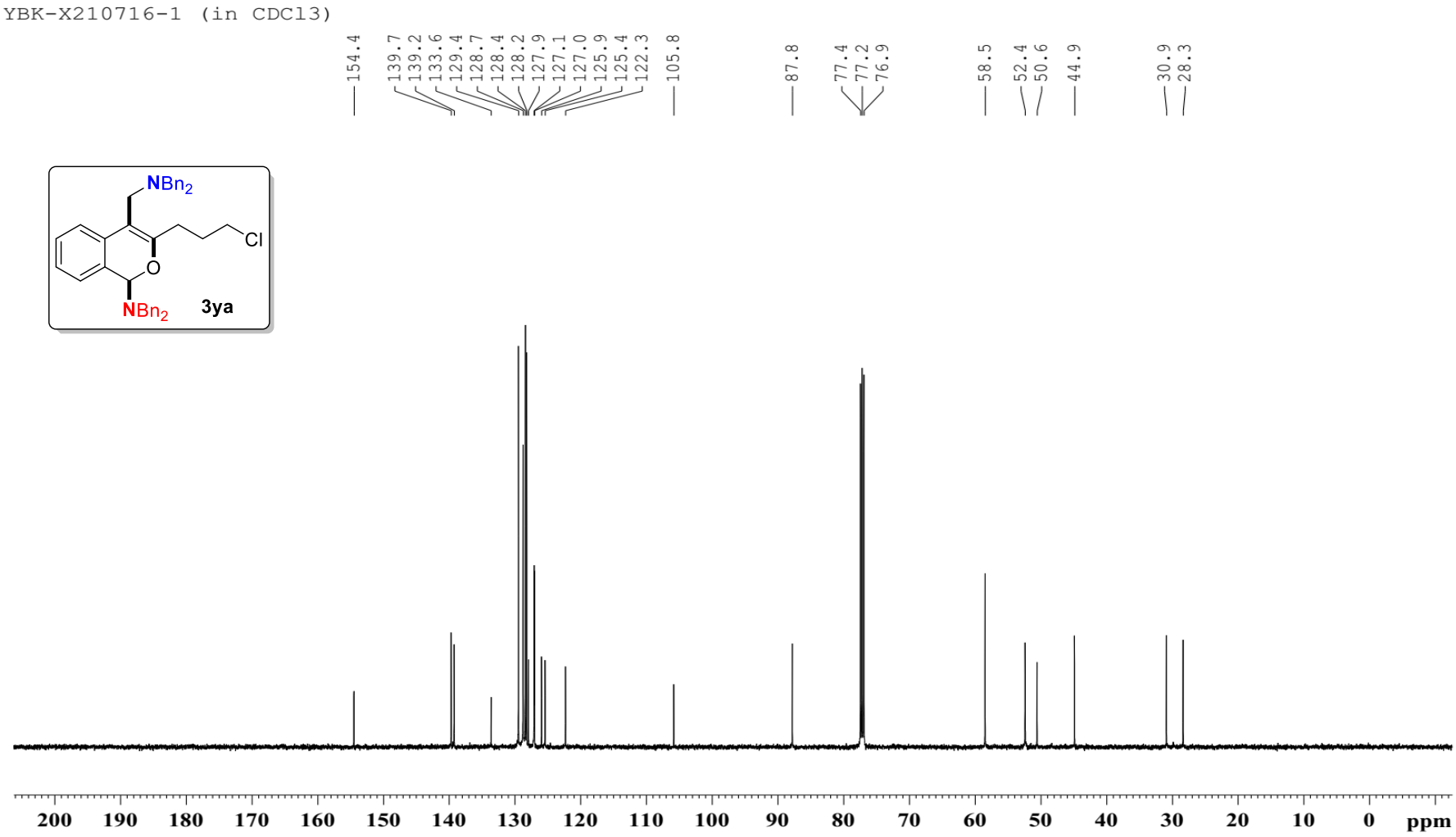
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3xa



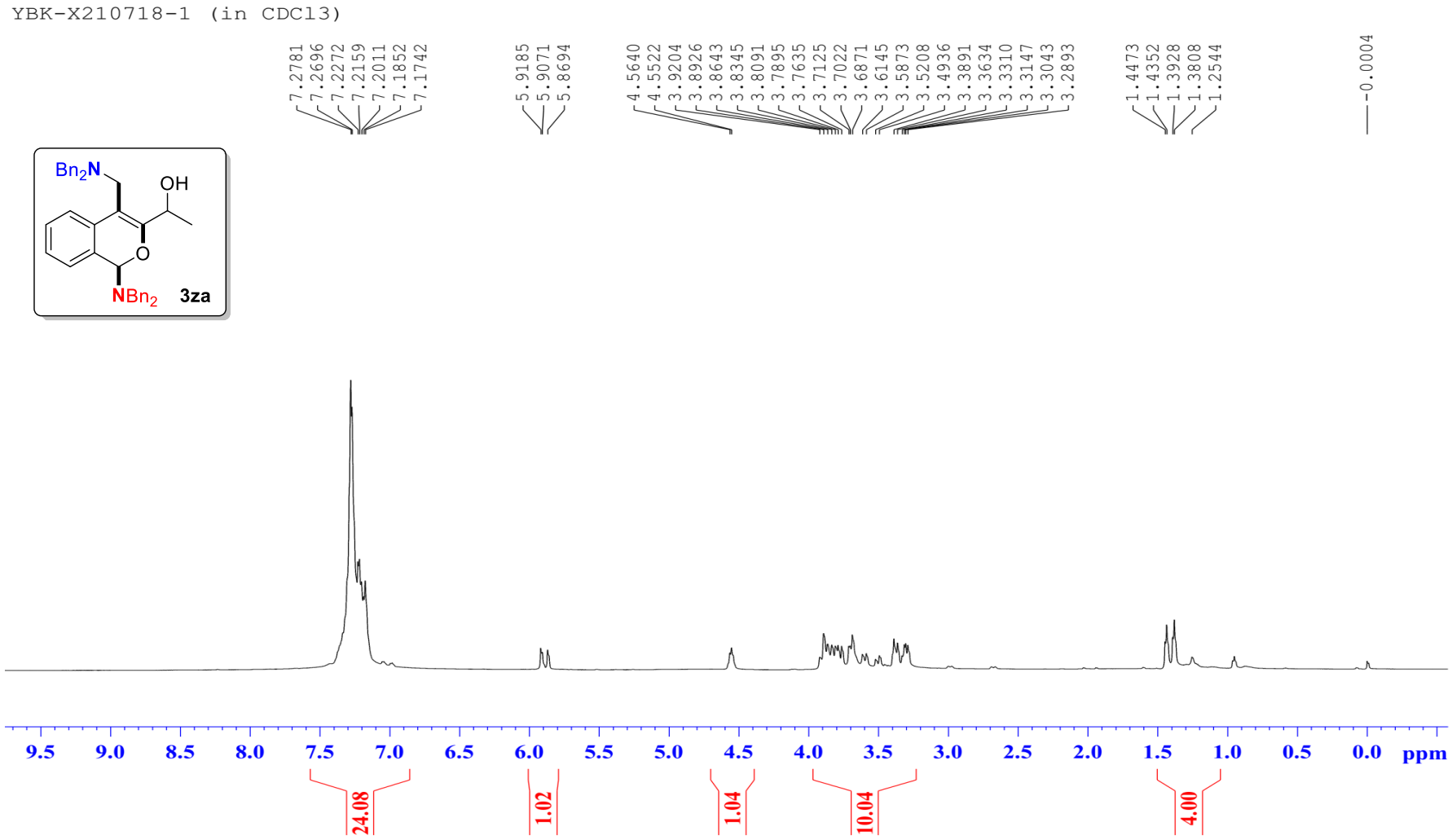
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3ya



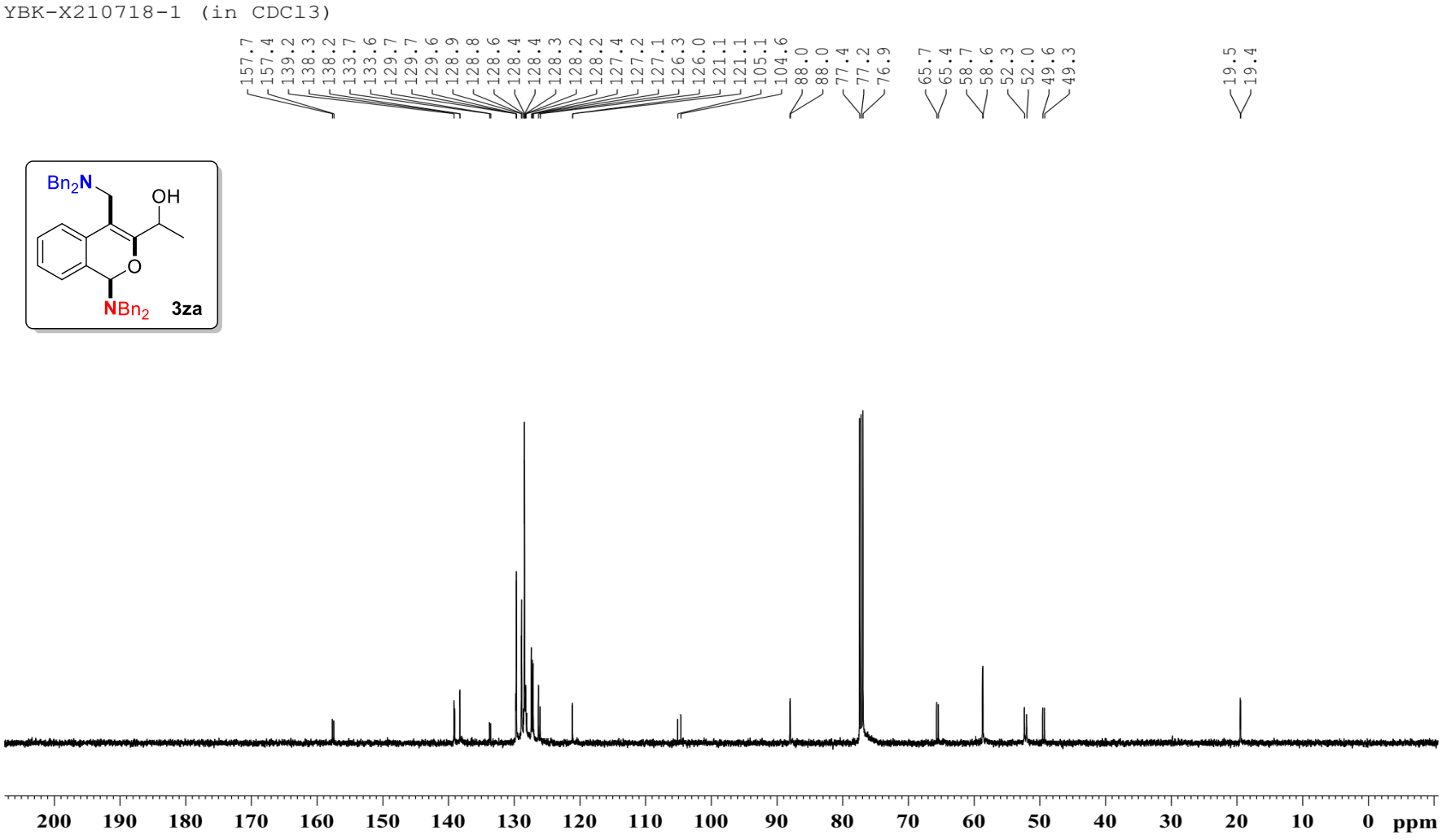
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3ya



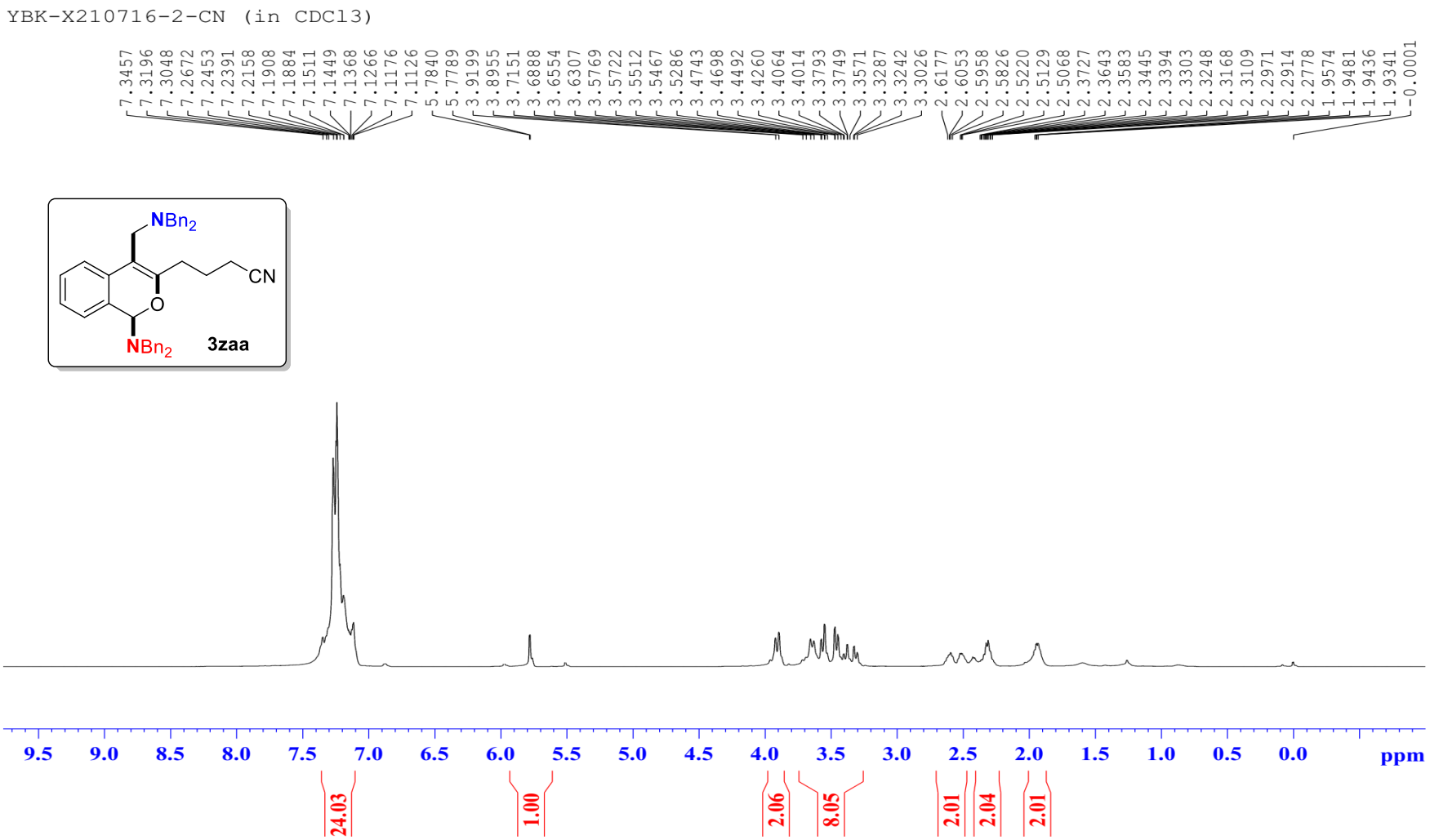
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3za



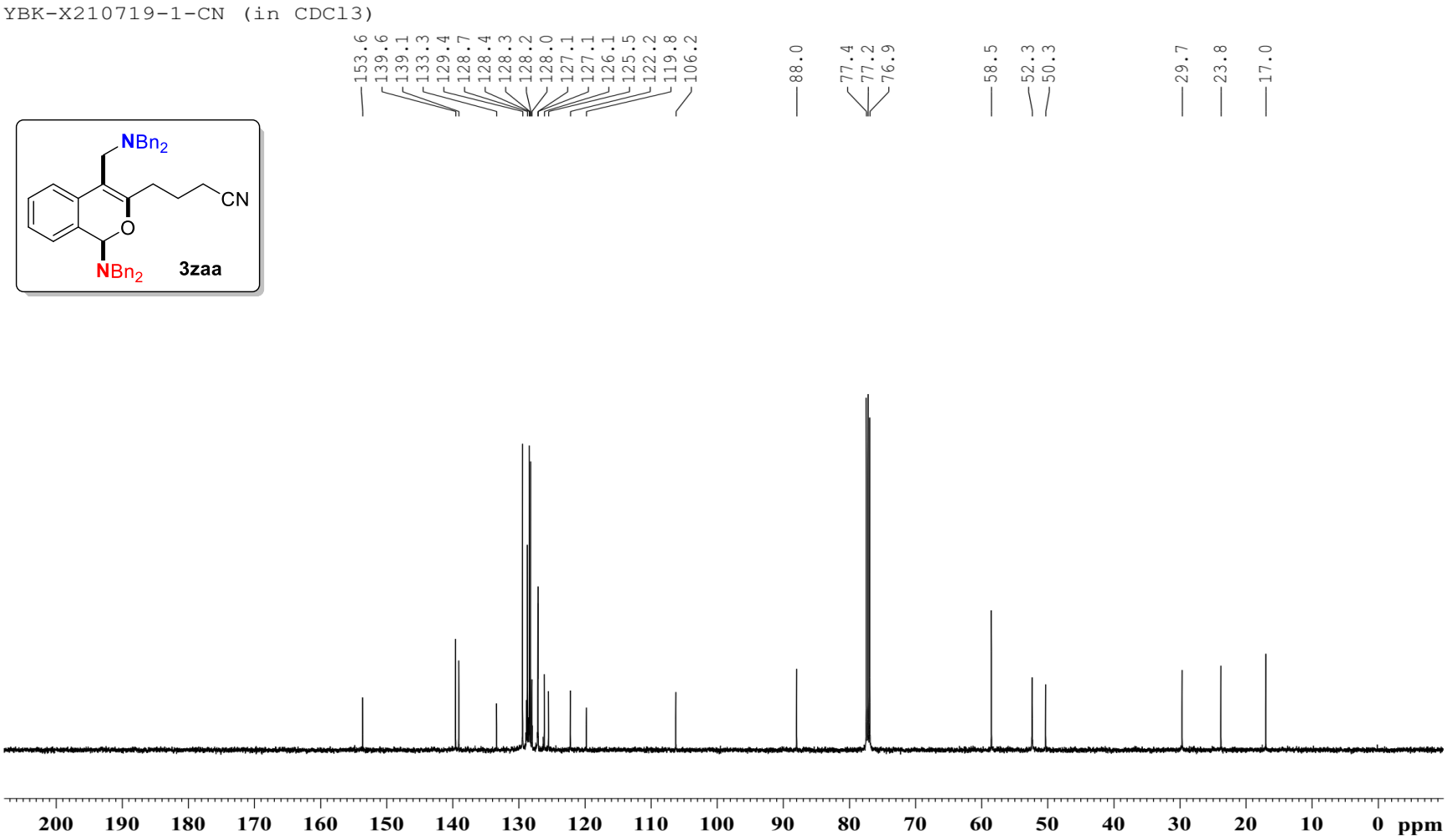
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3za



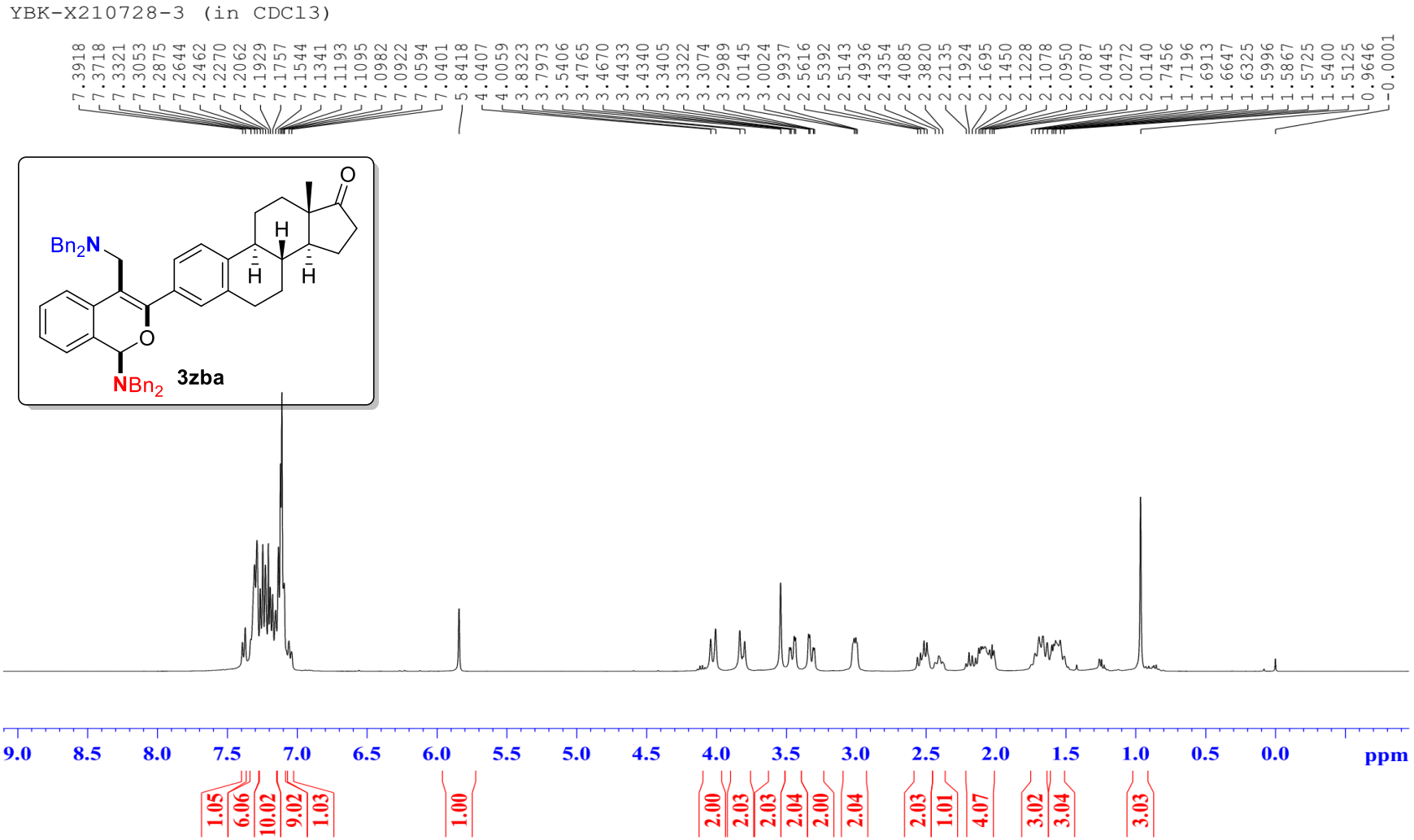
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 3zaa



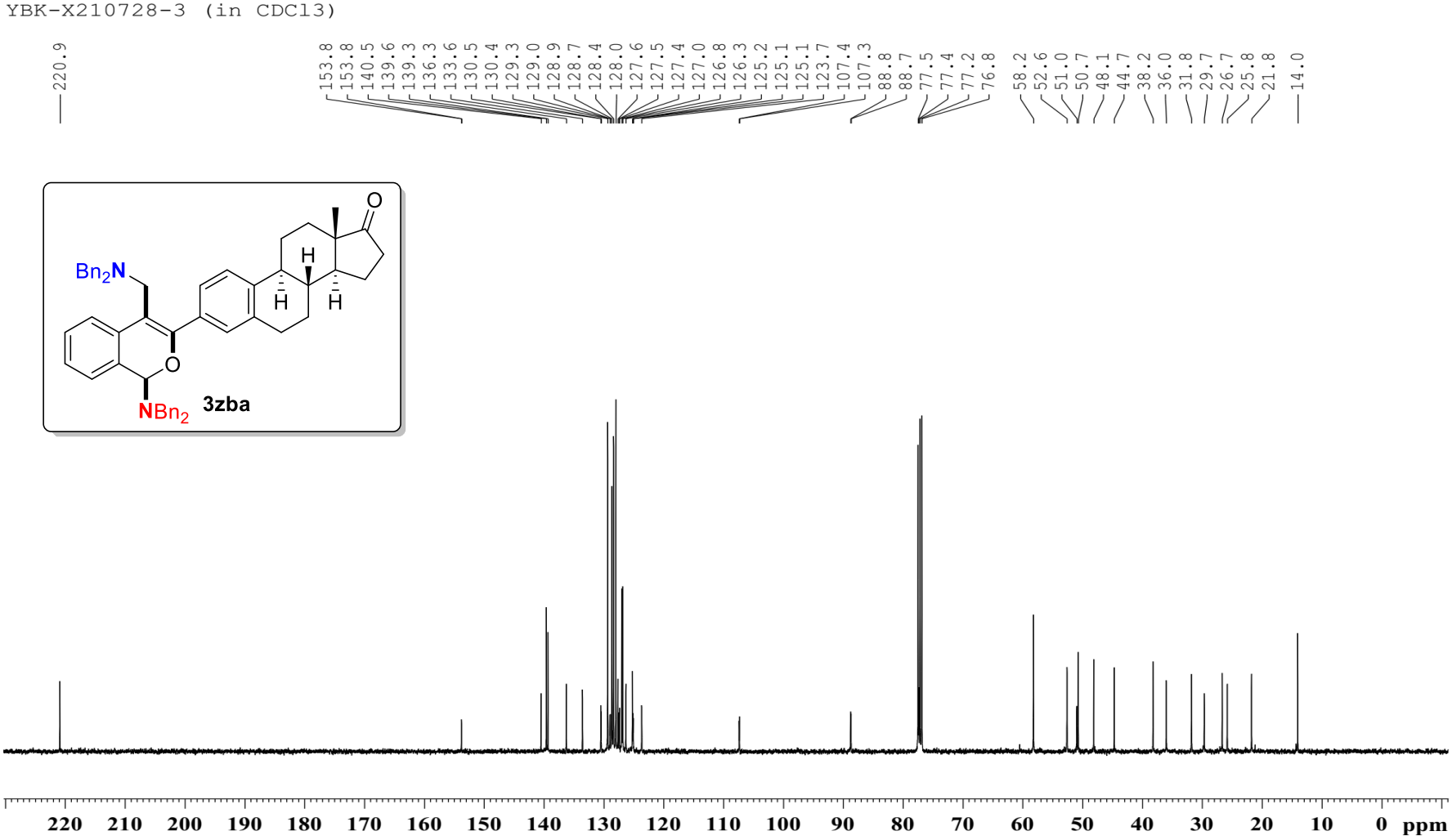
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3zaa



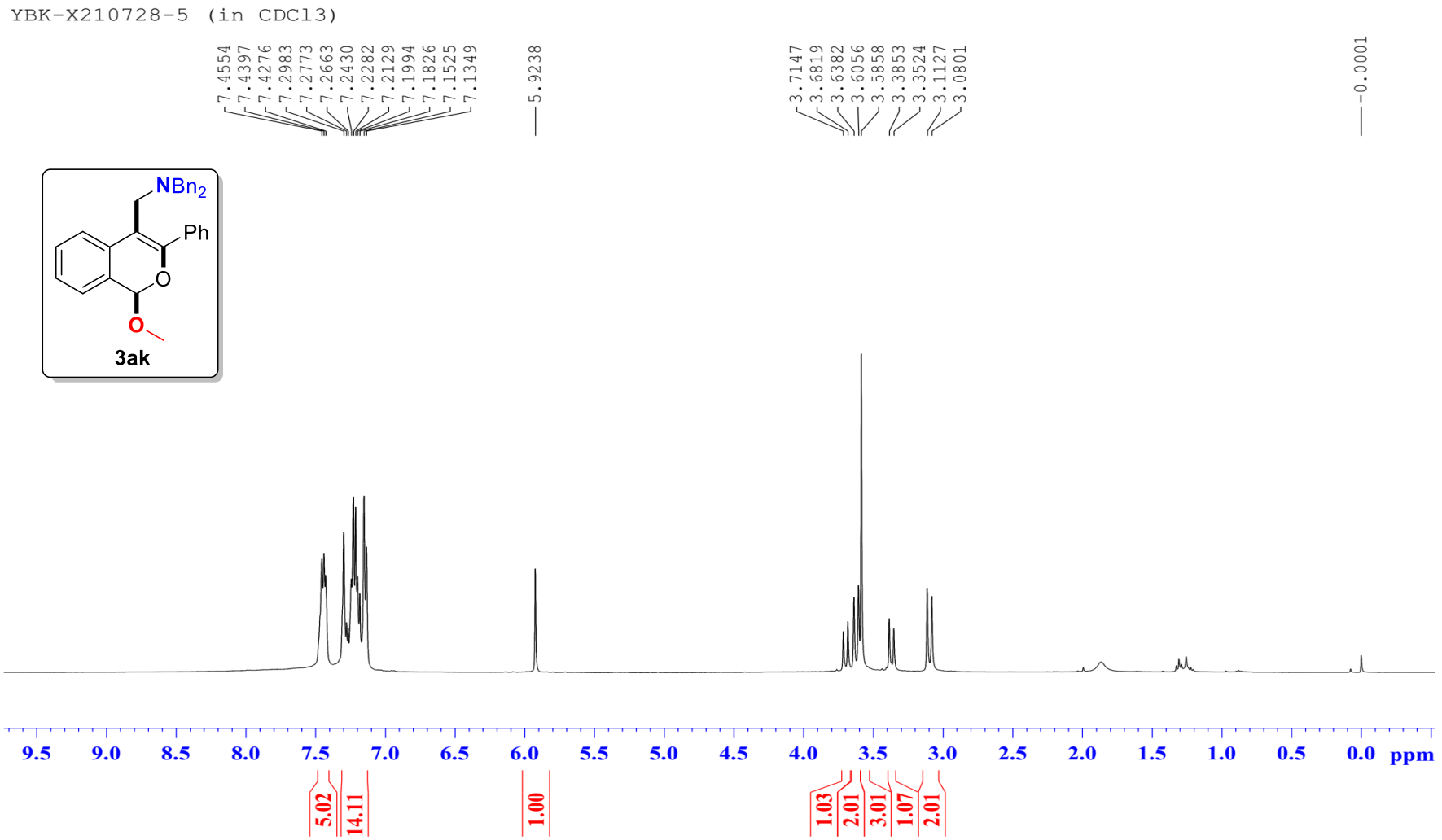
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3zba



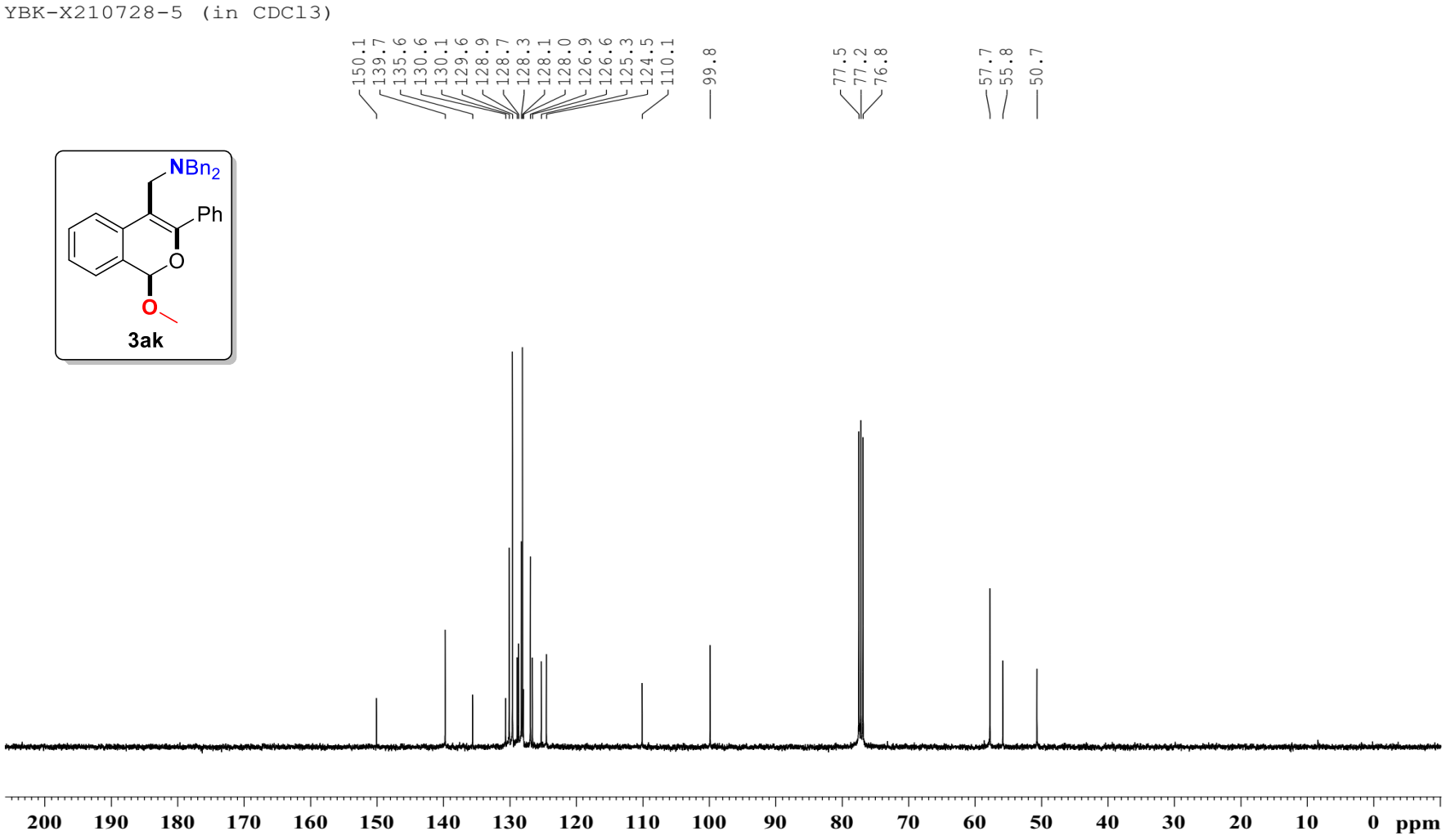
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3zba



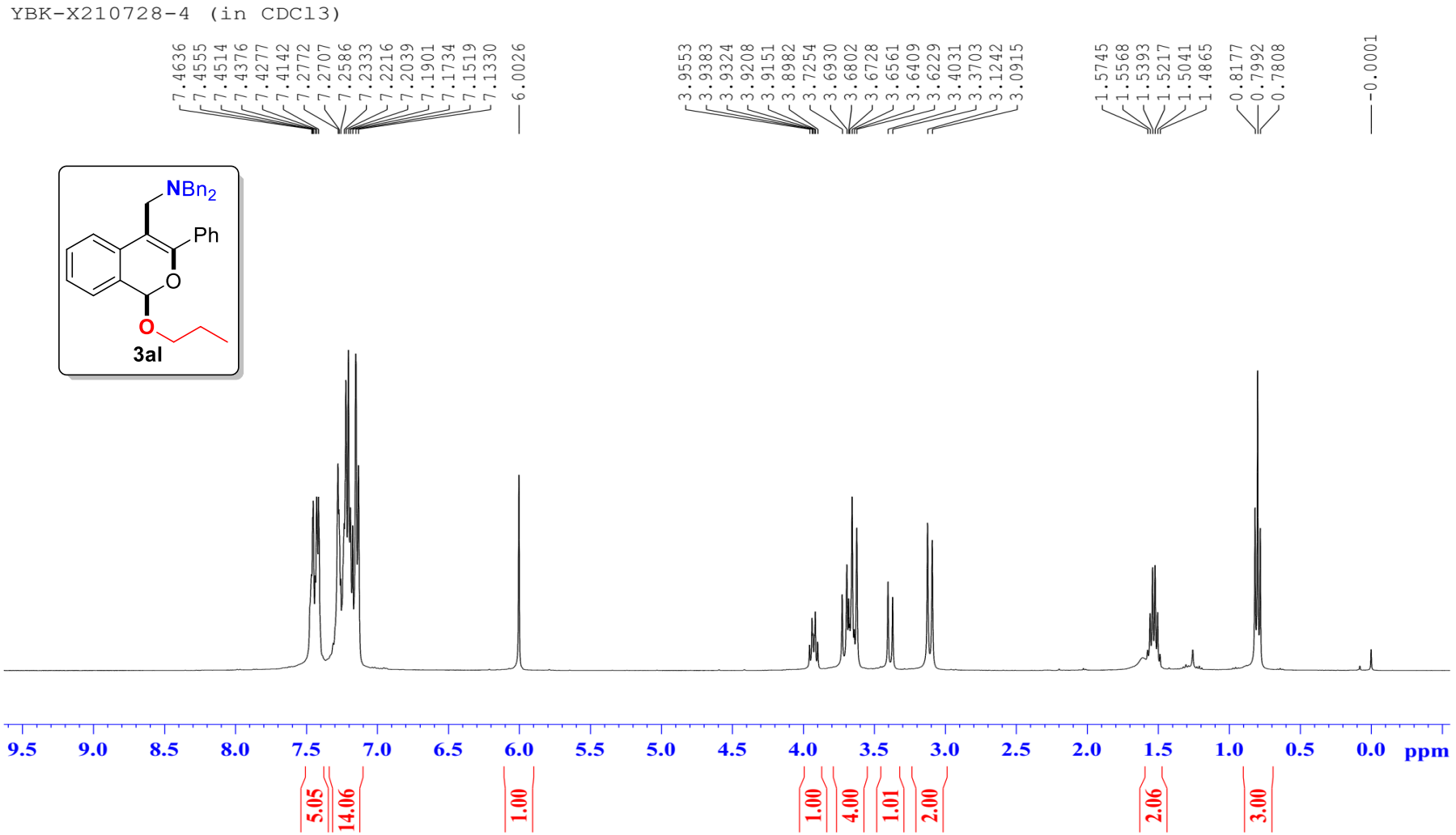
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3ak



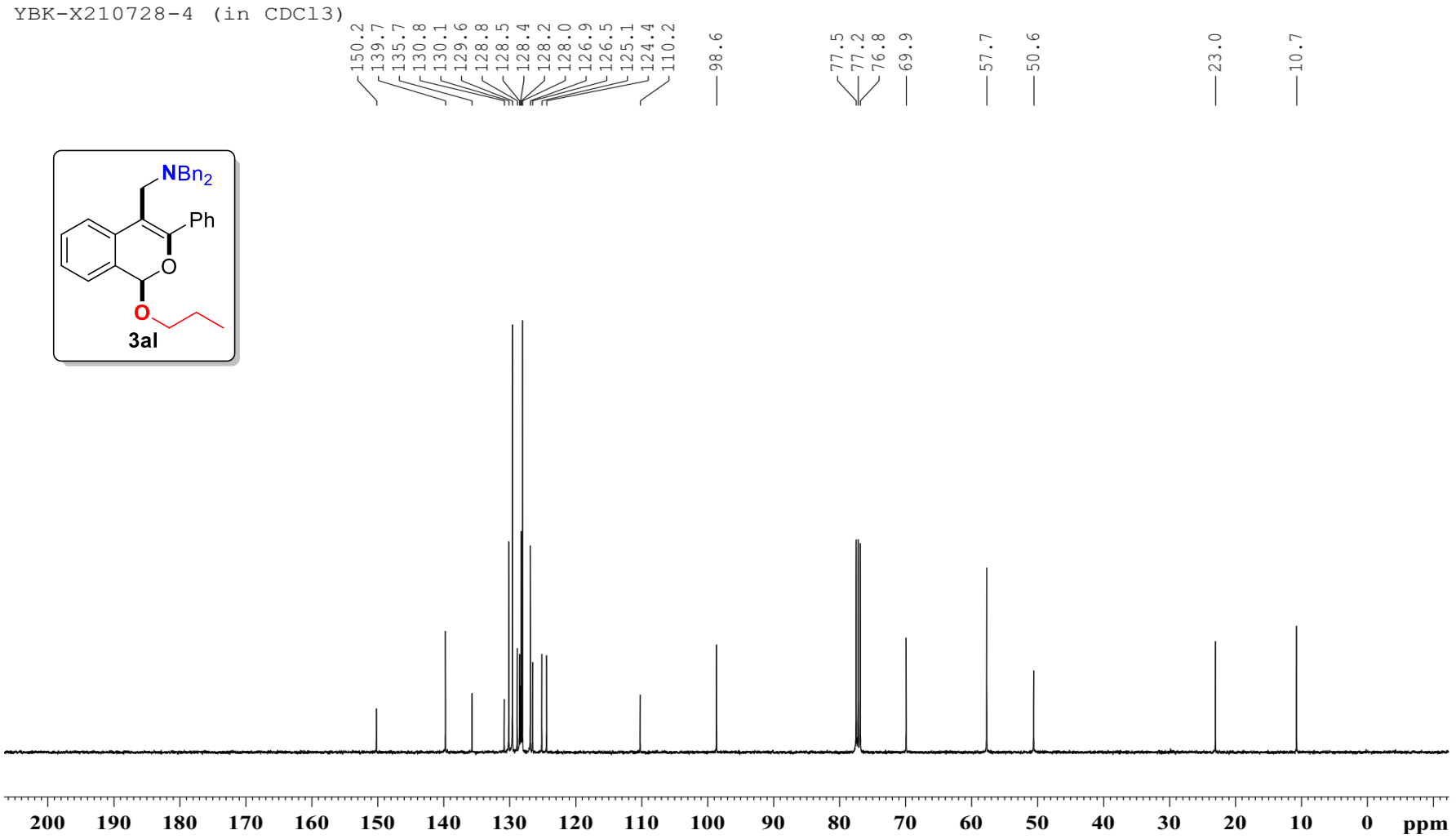
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3ak



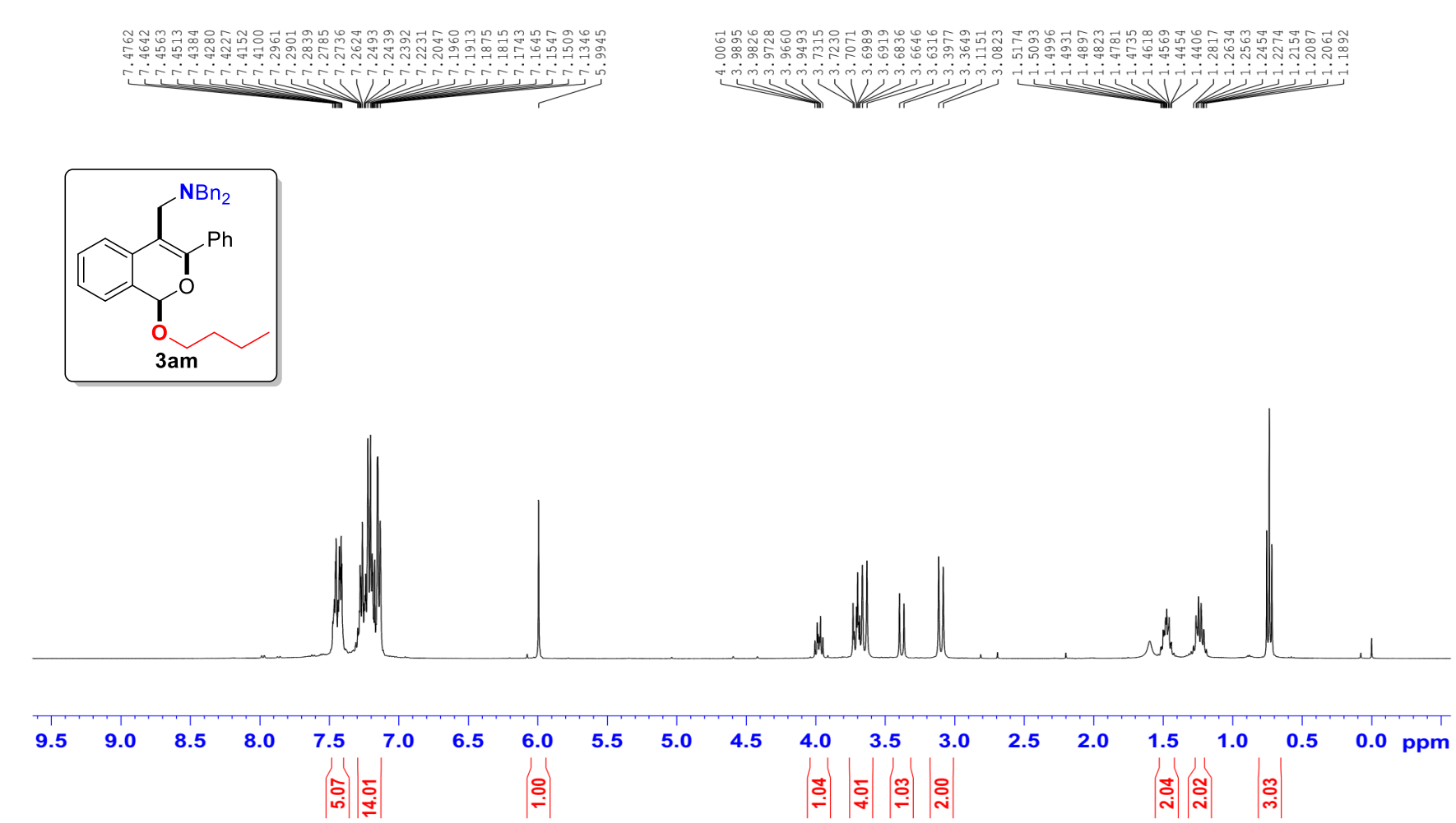
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3al



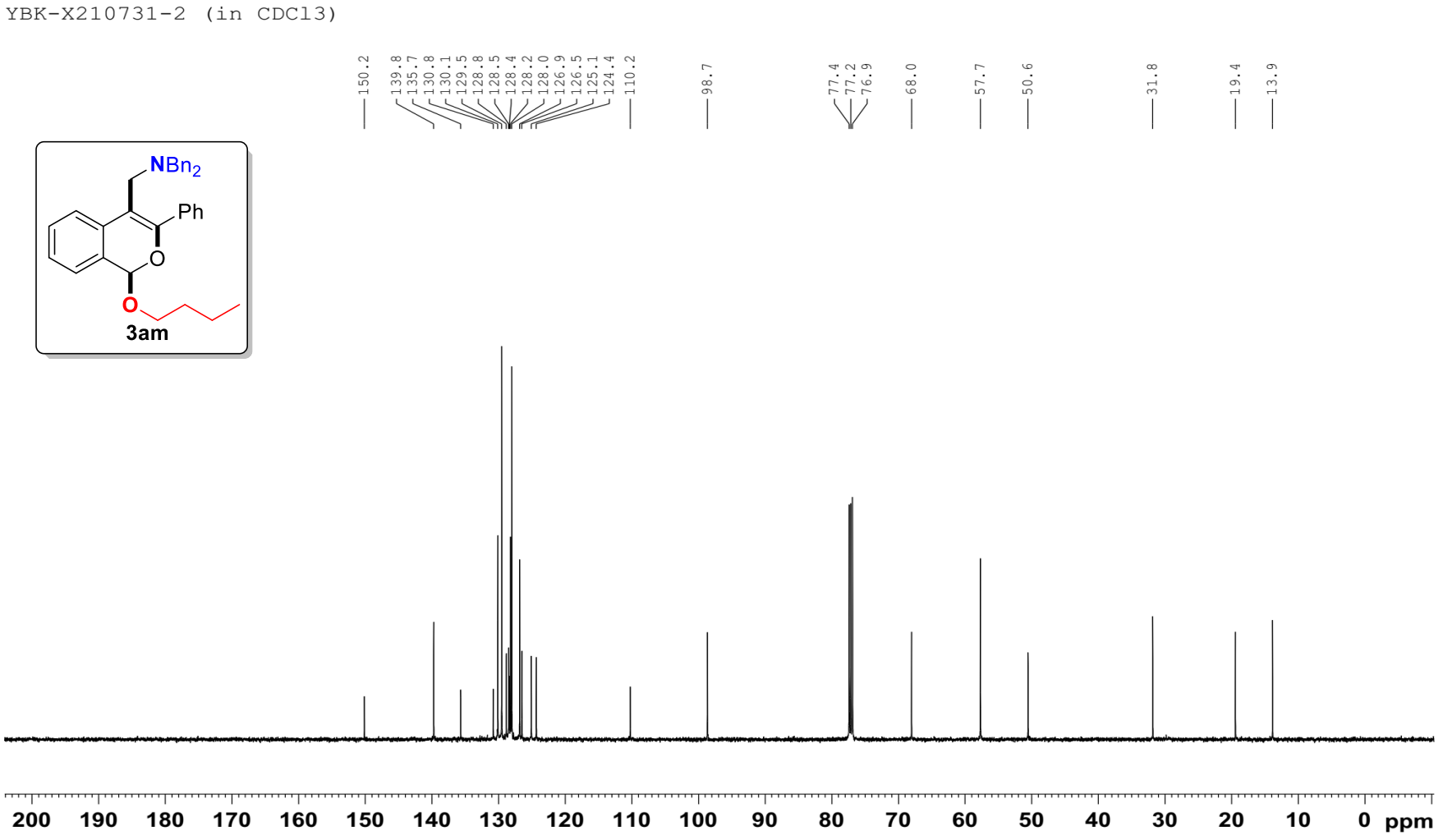
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 3al



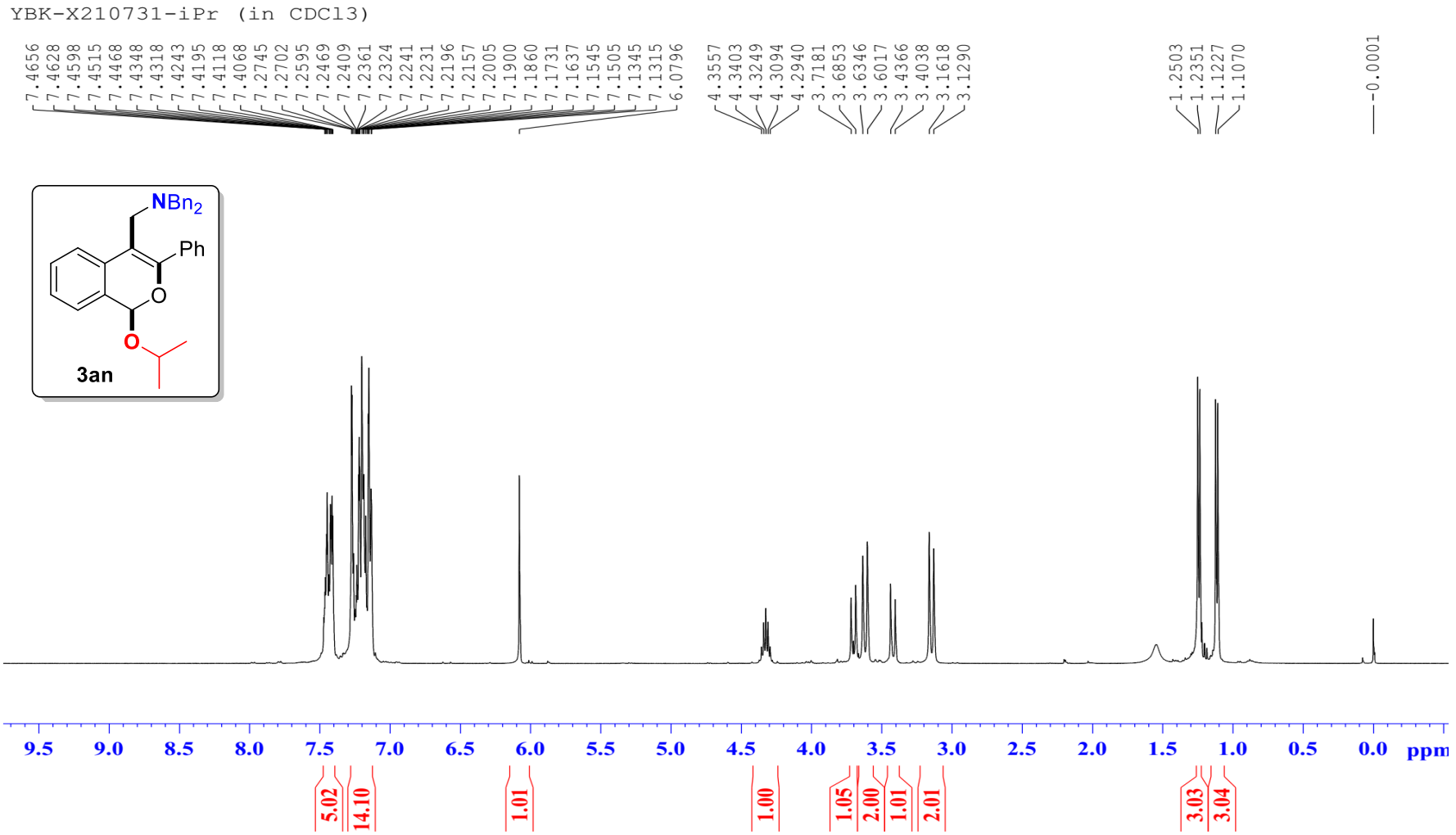
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3am



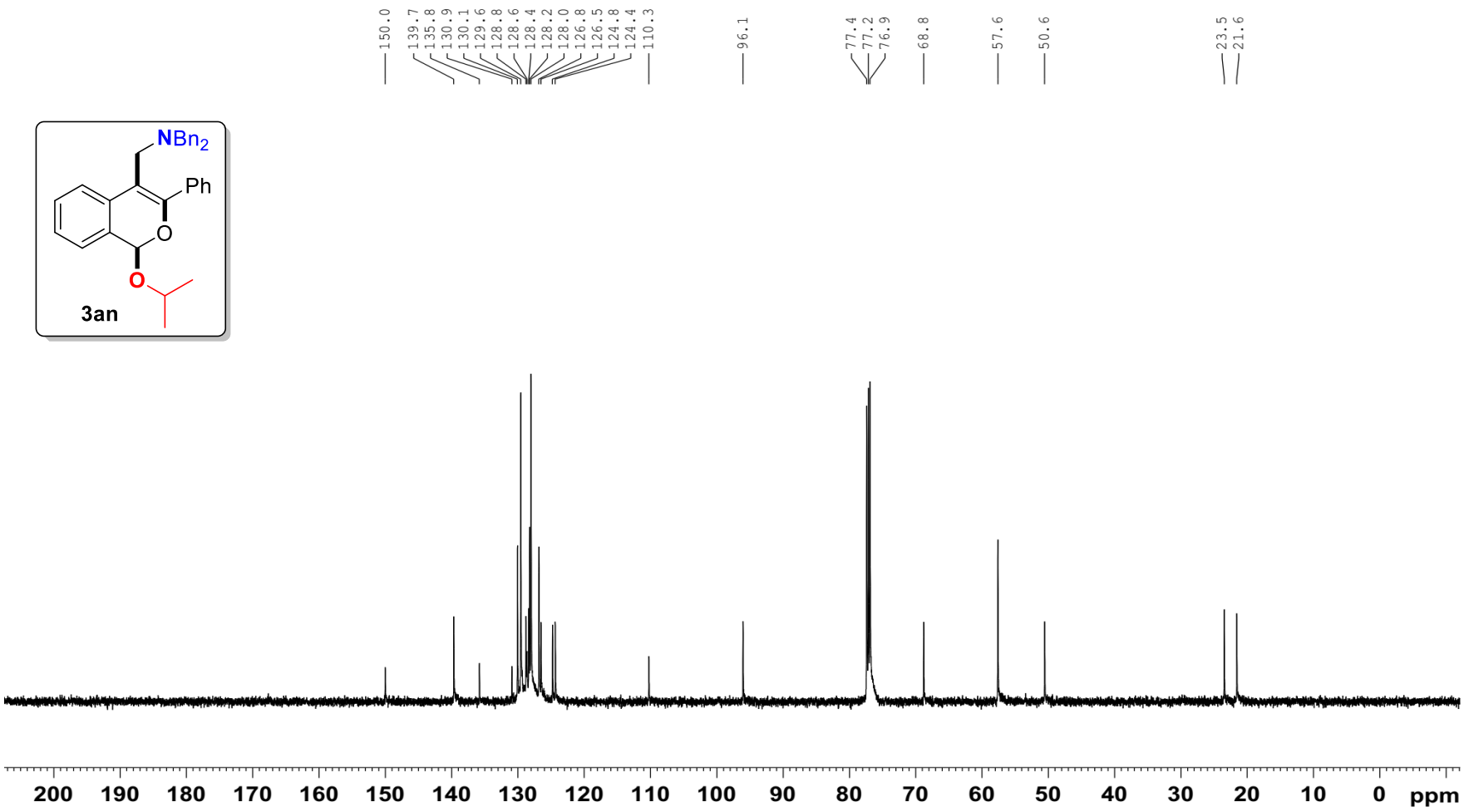
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3am



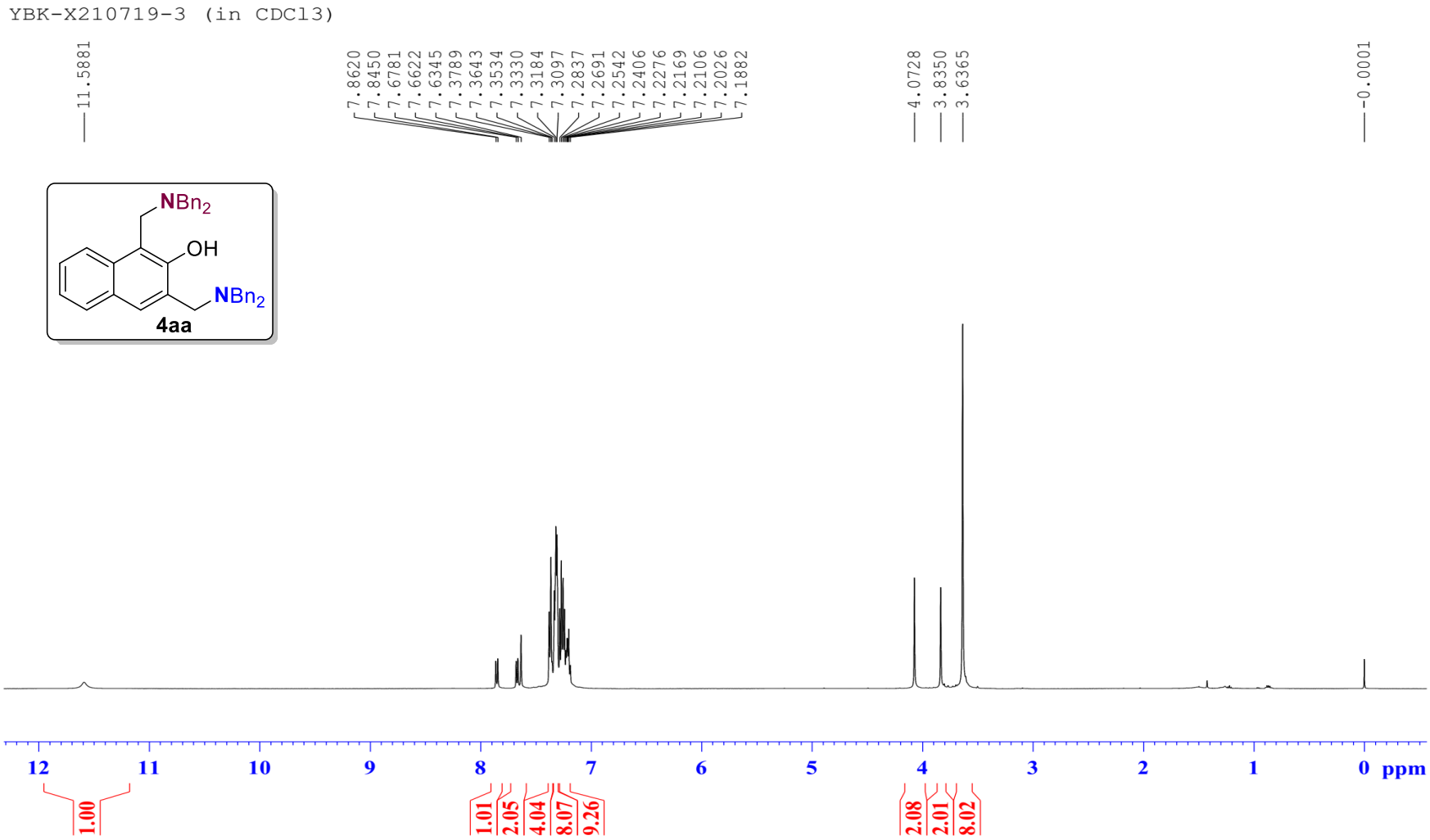
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3an



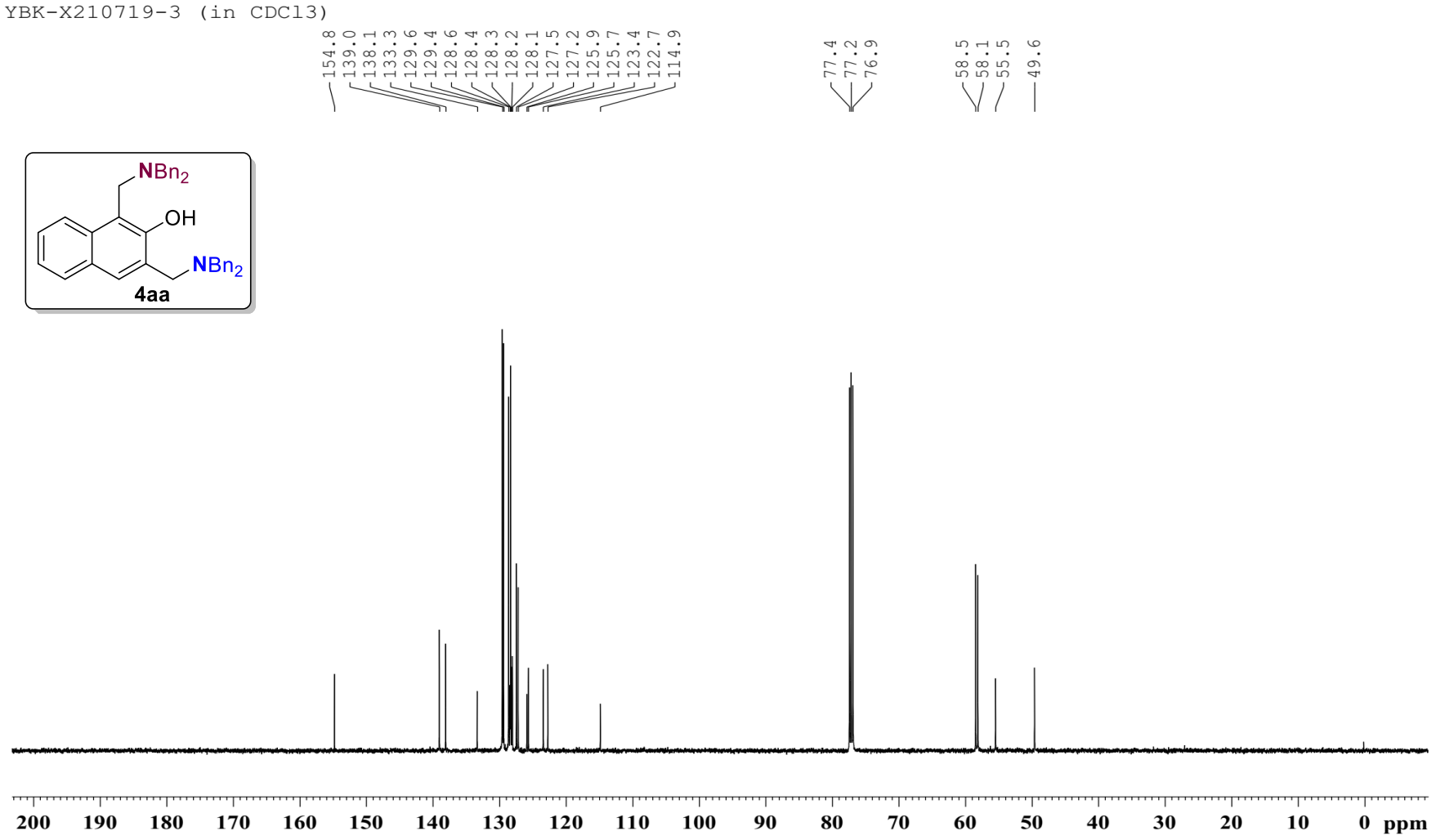
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3an



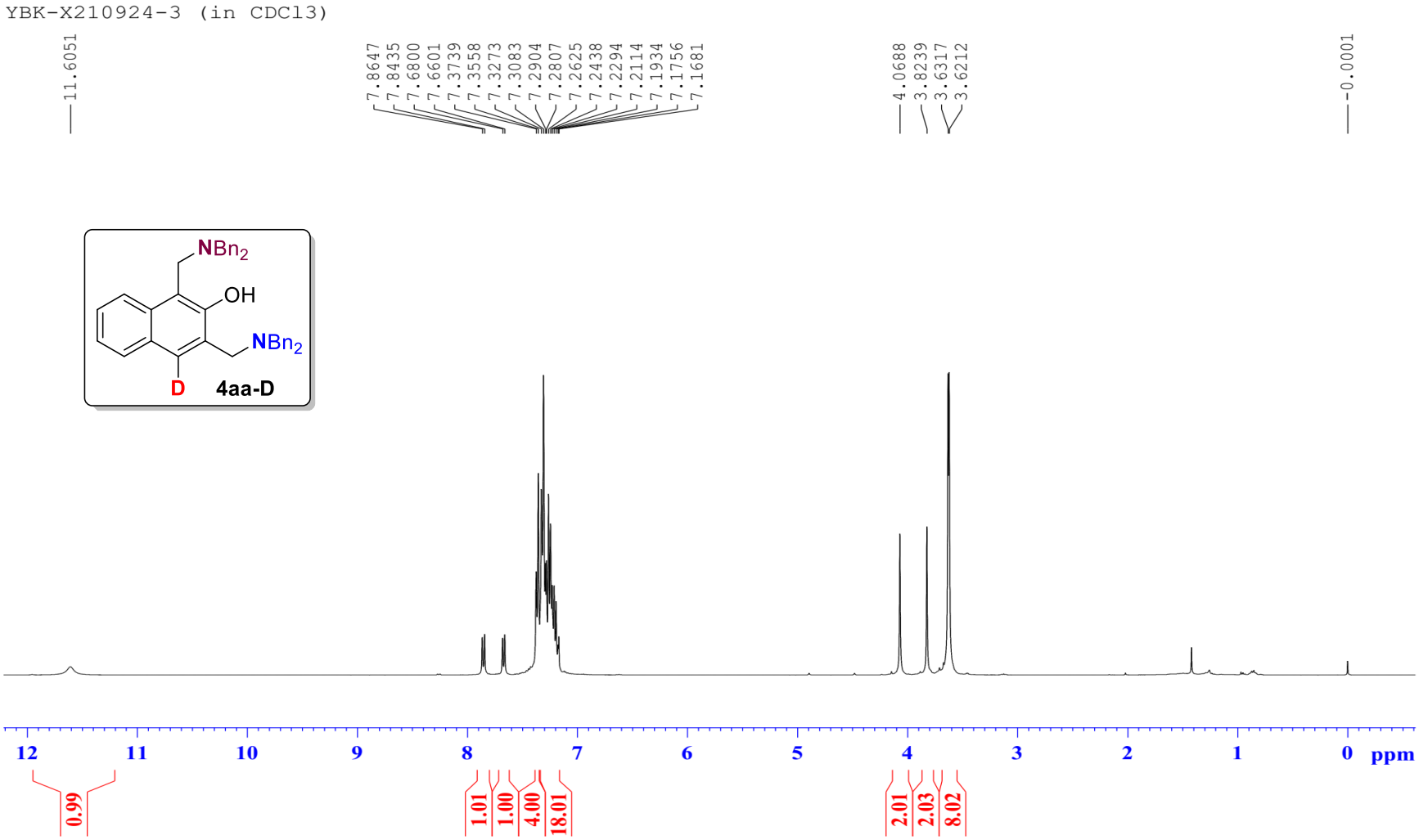
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 4aa



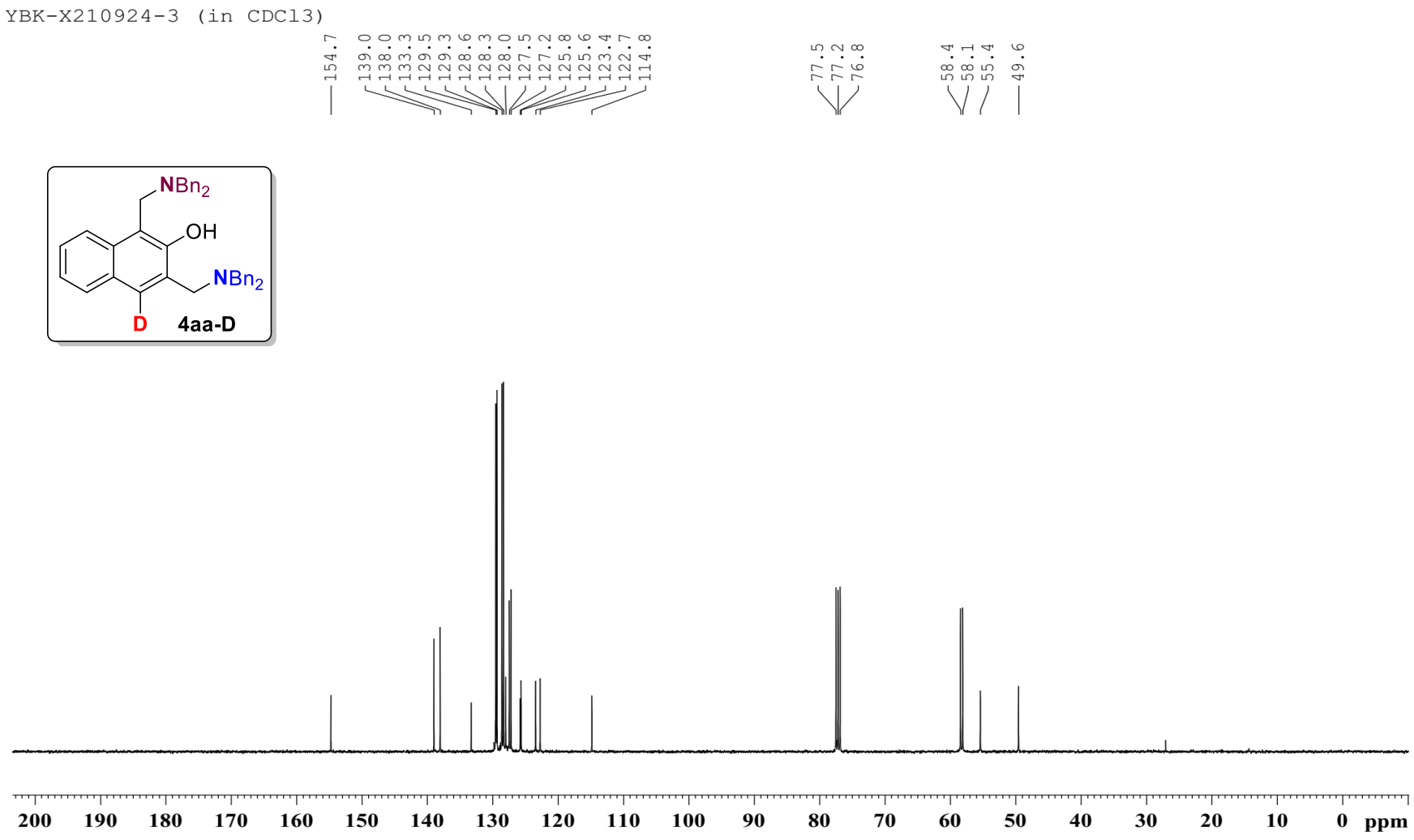
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4aa



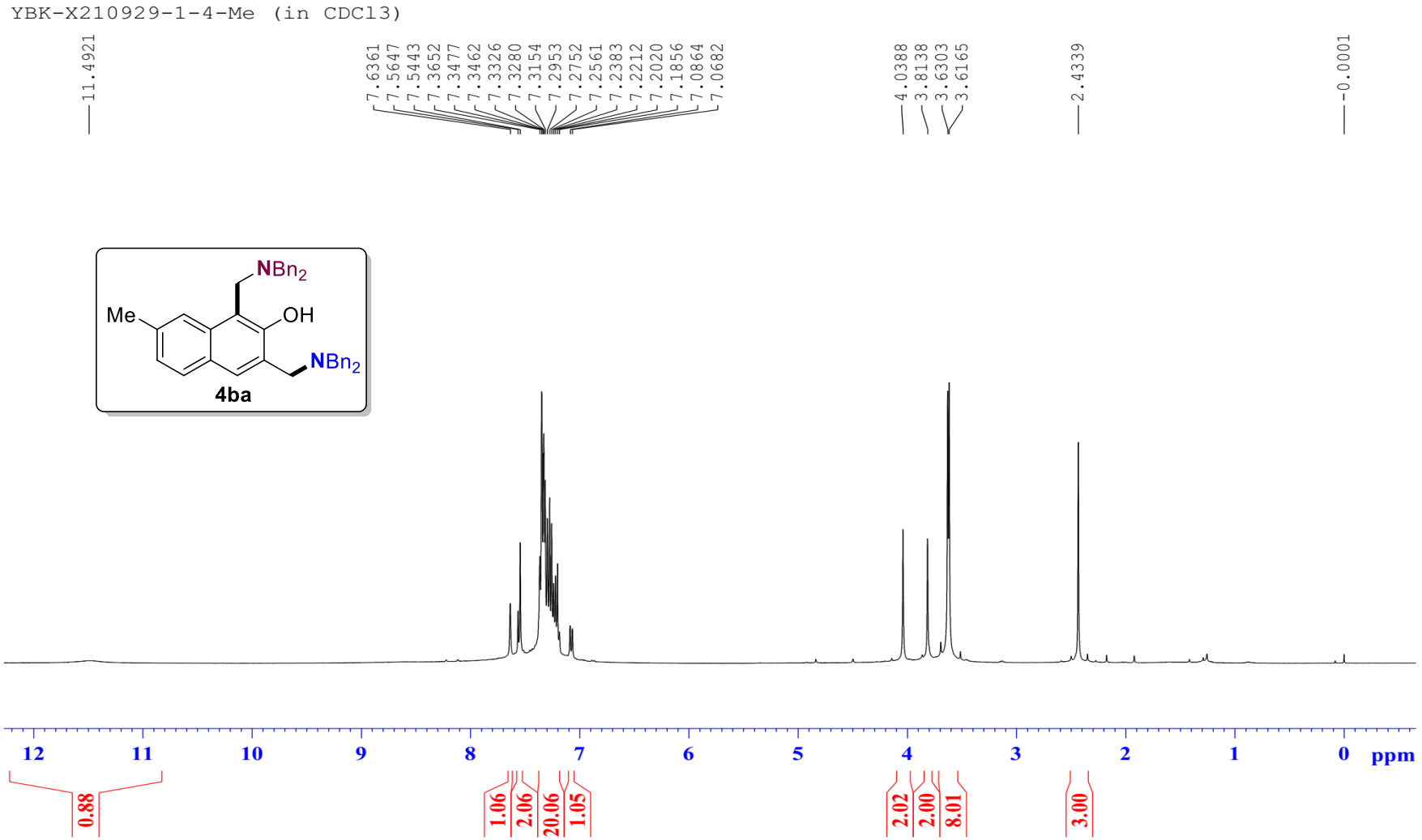
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4aa-D



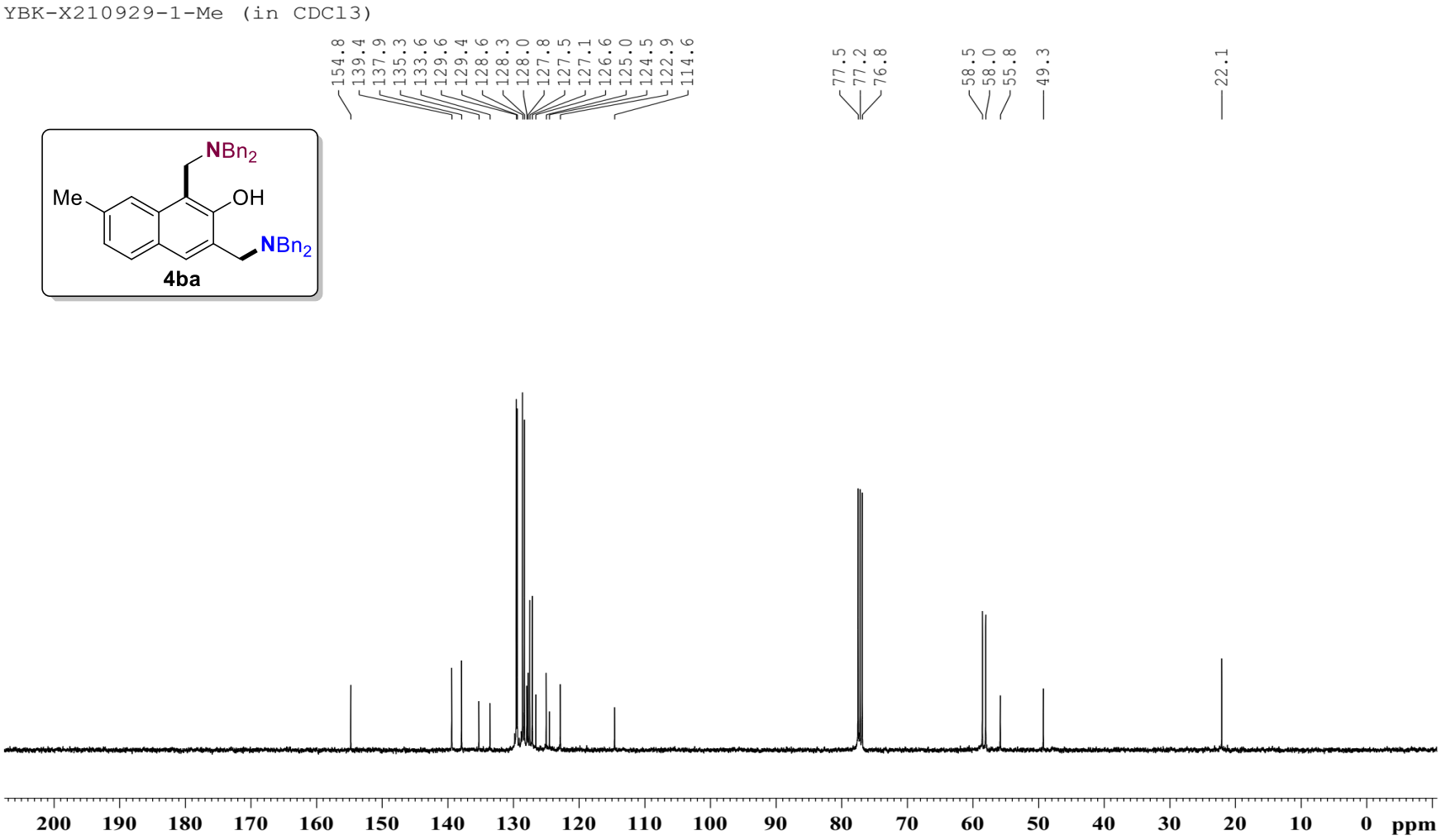
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4aa-D



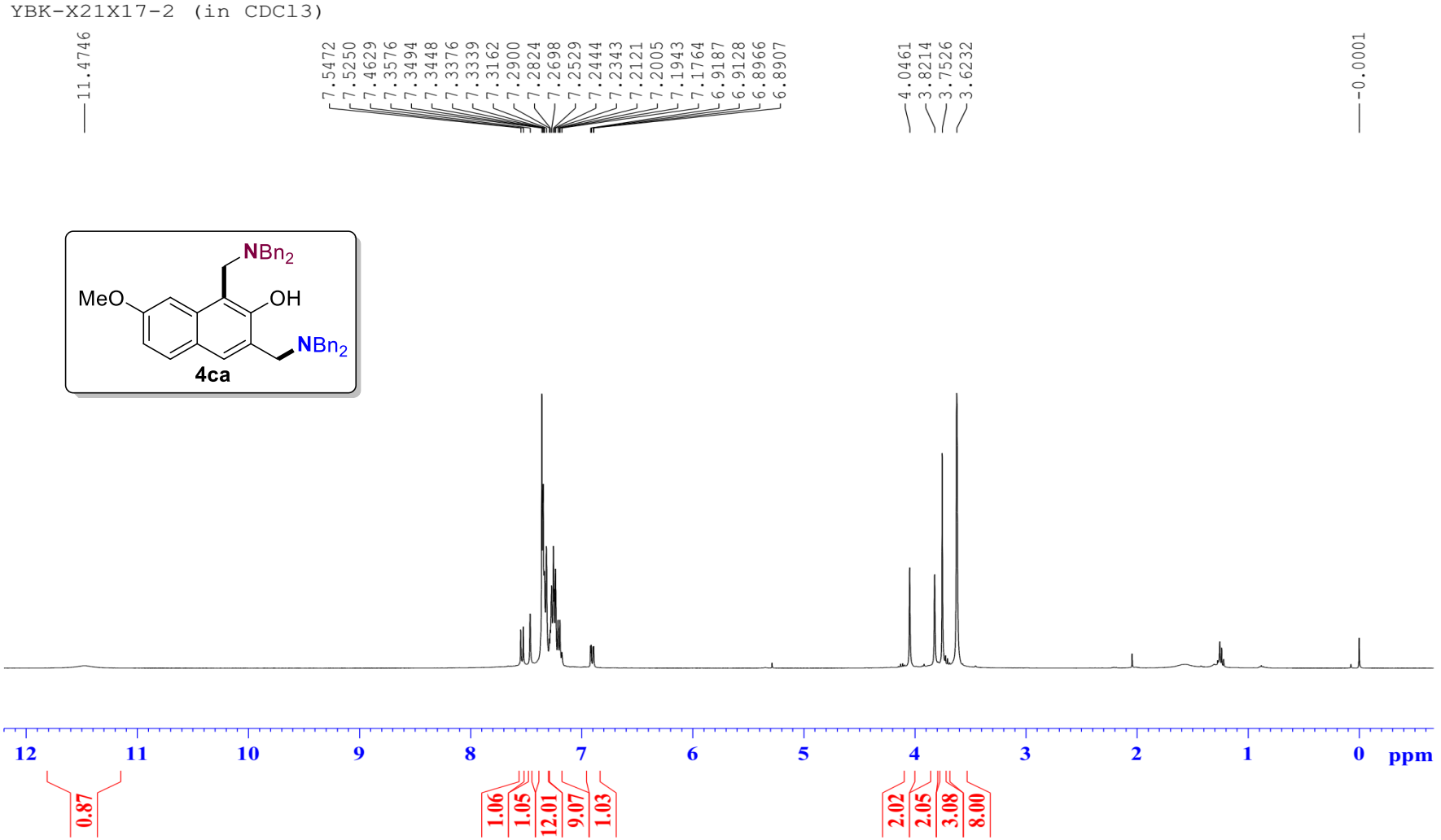
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ba



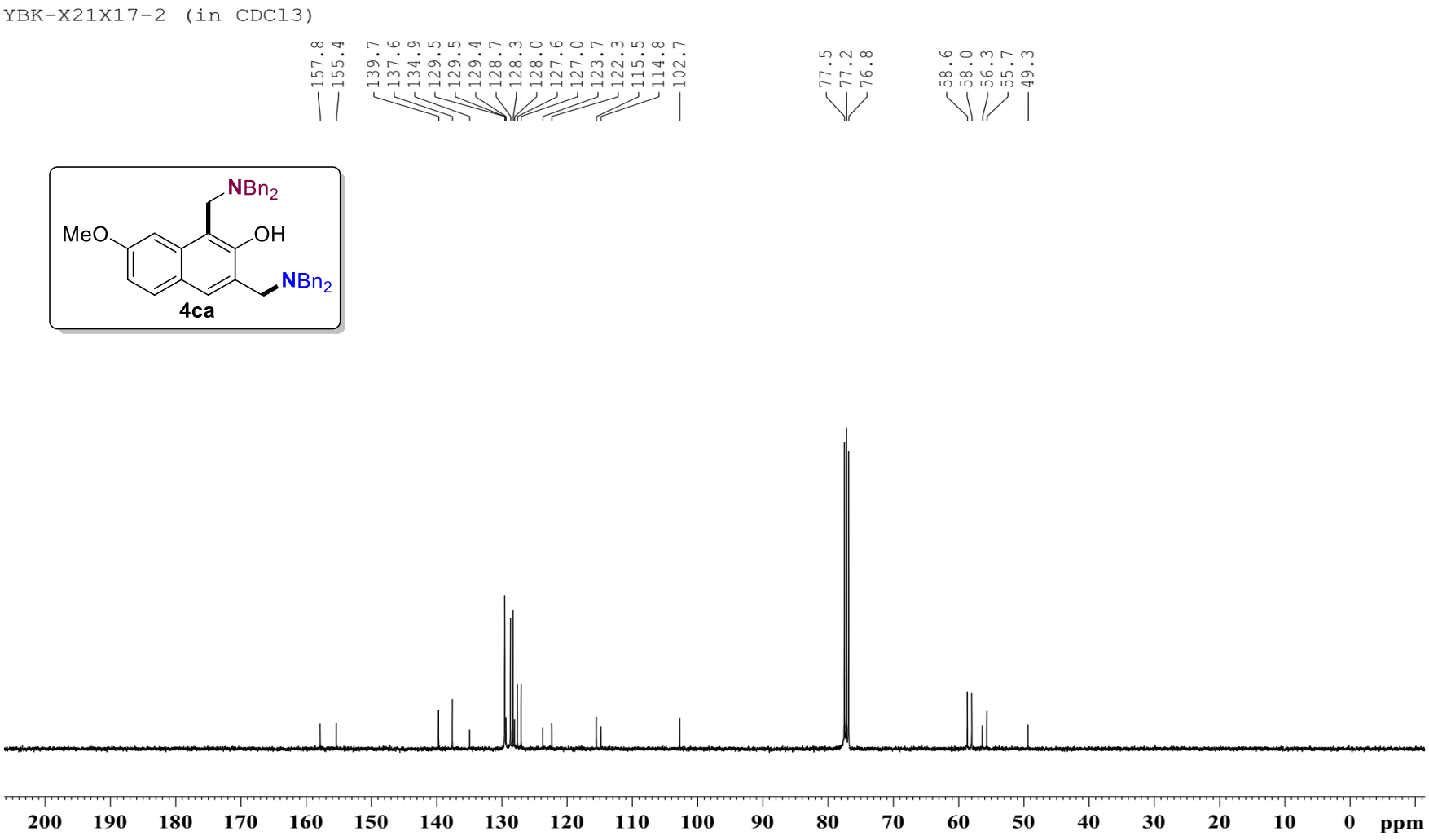
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ba



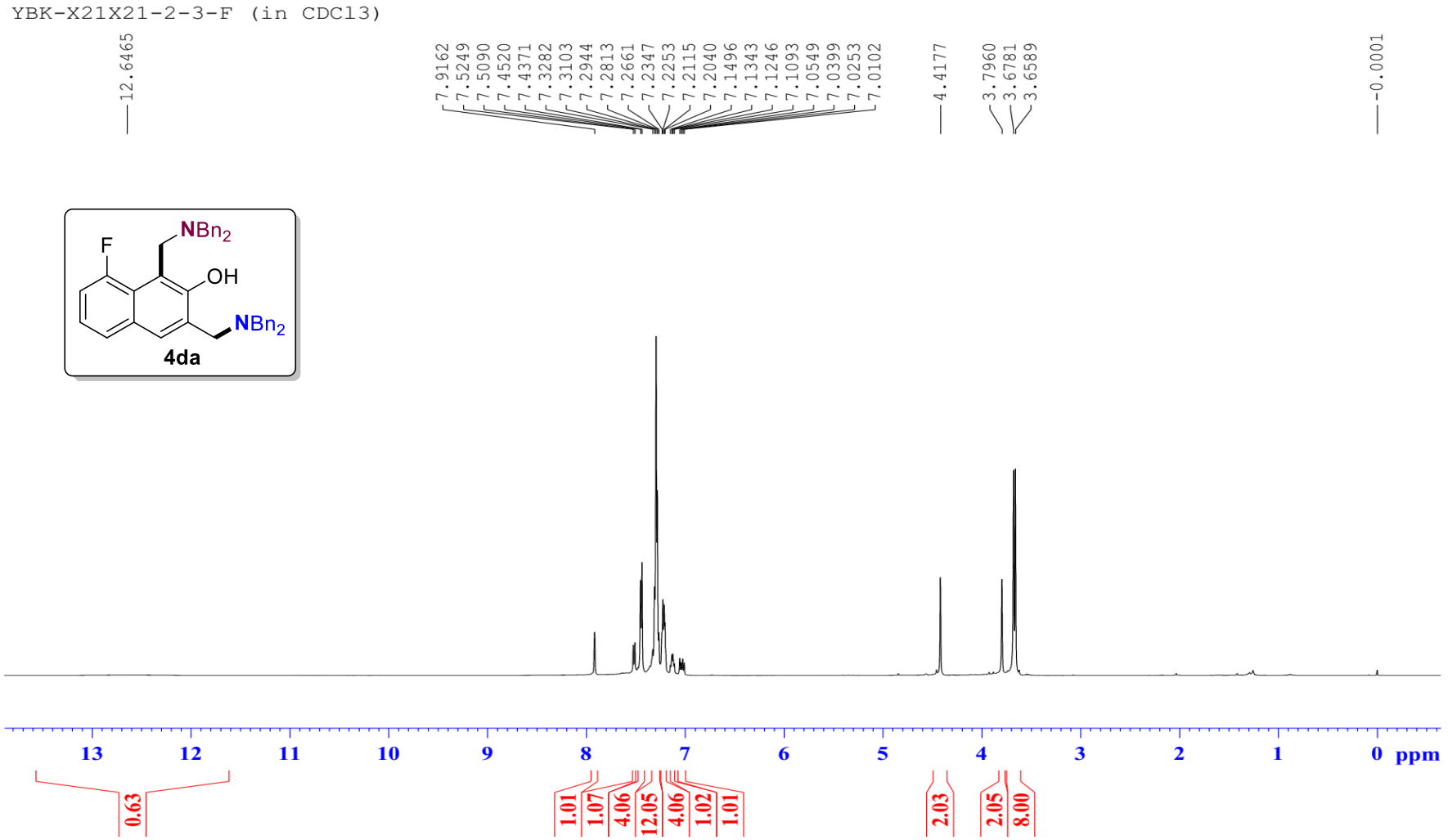
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ca



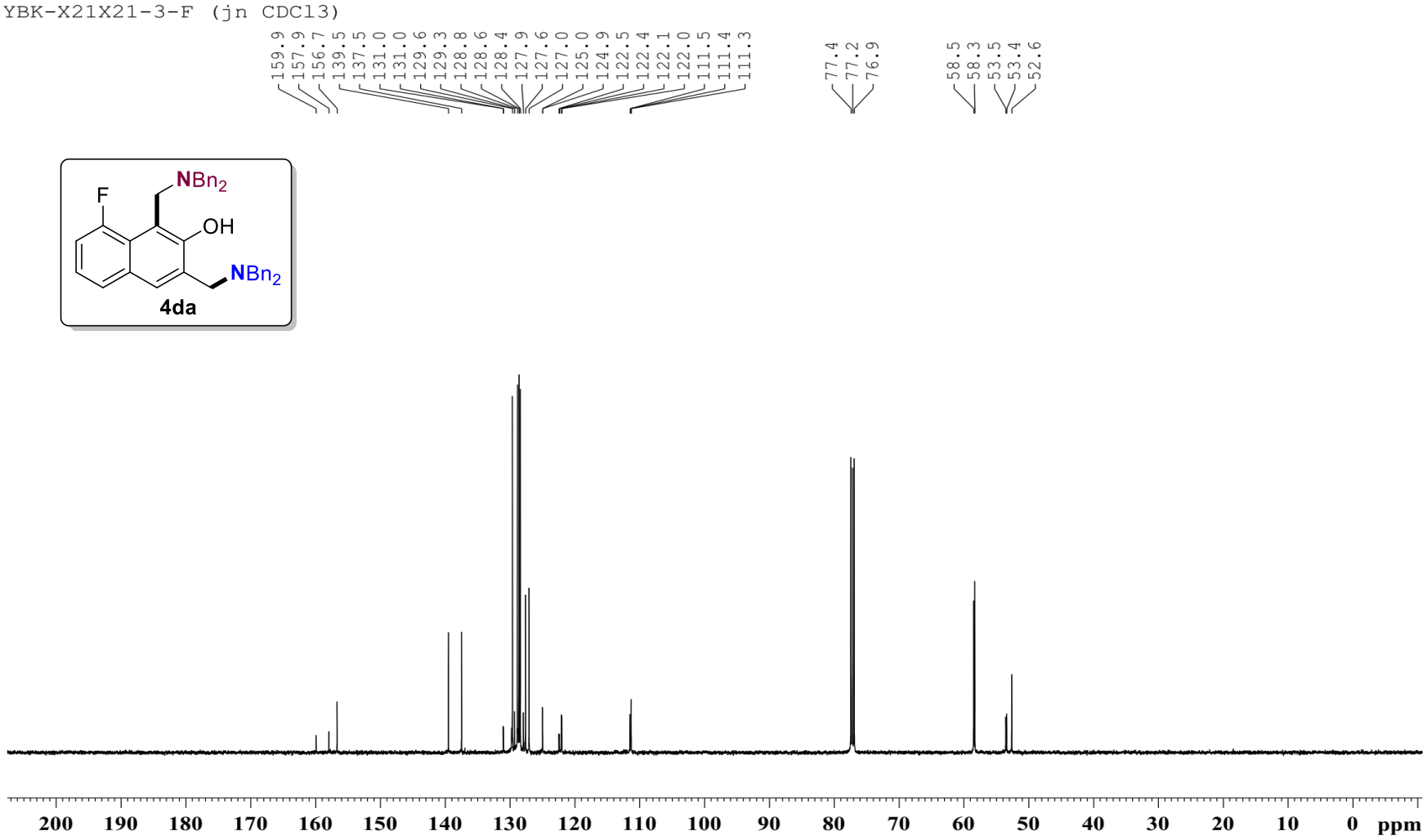
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ca



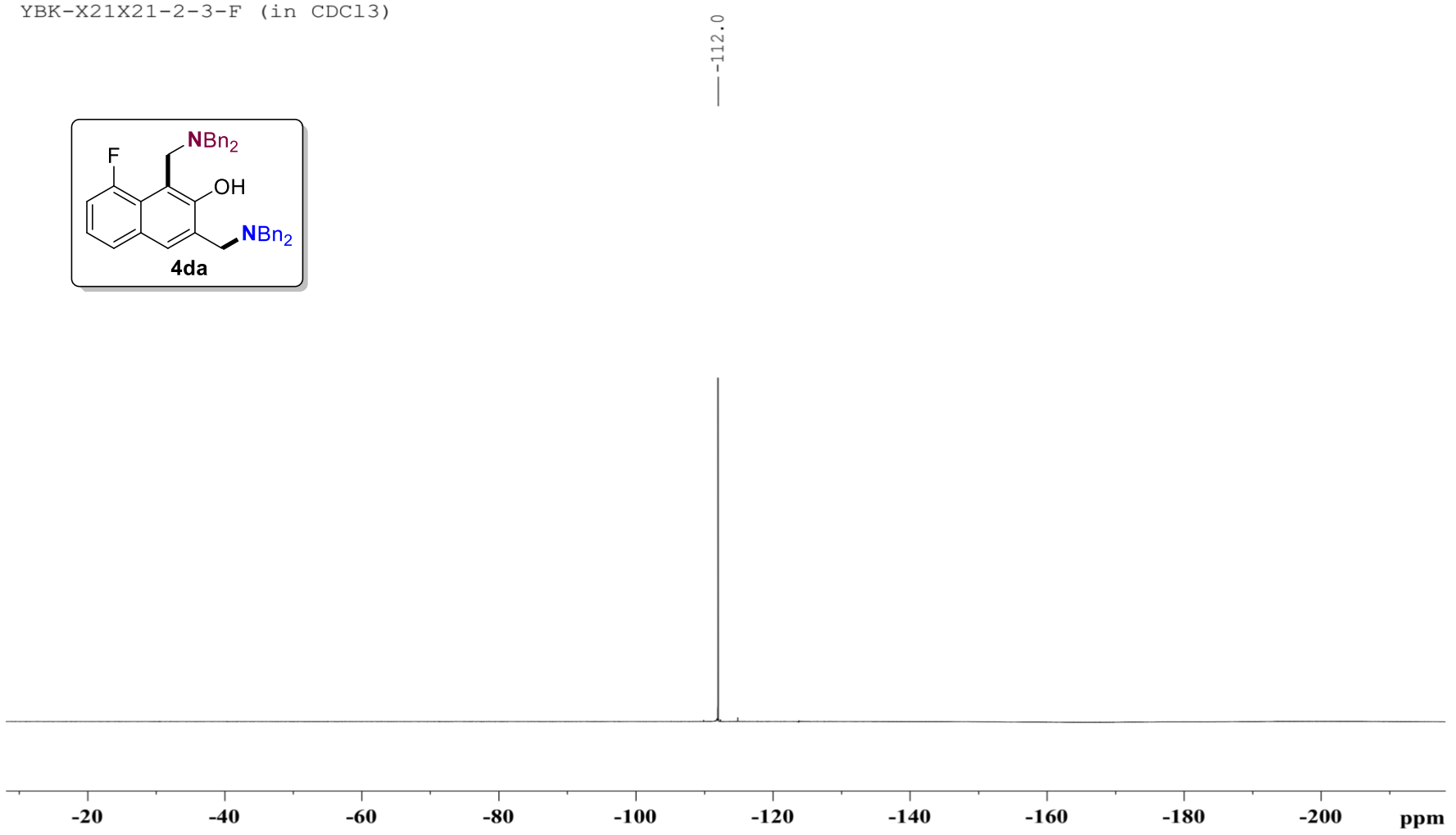
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 4da



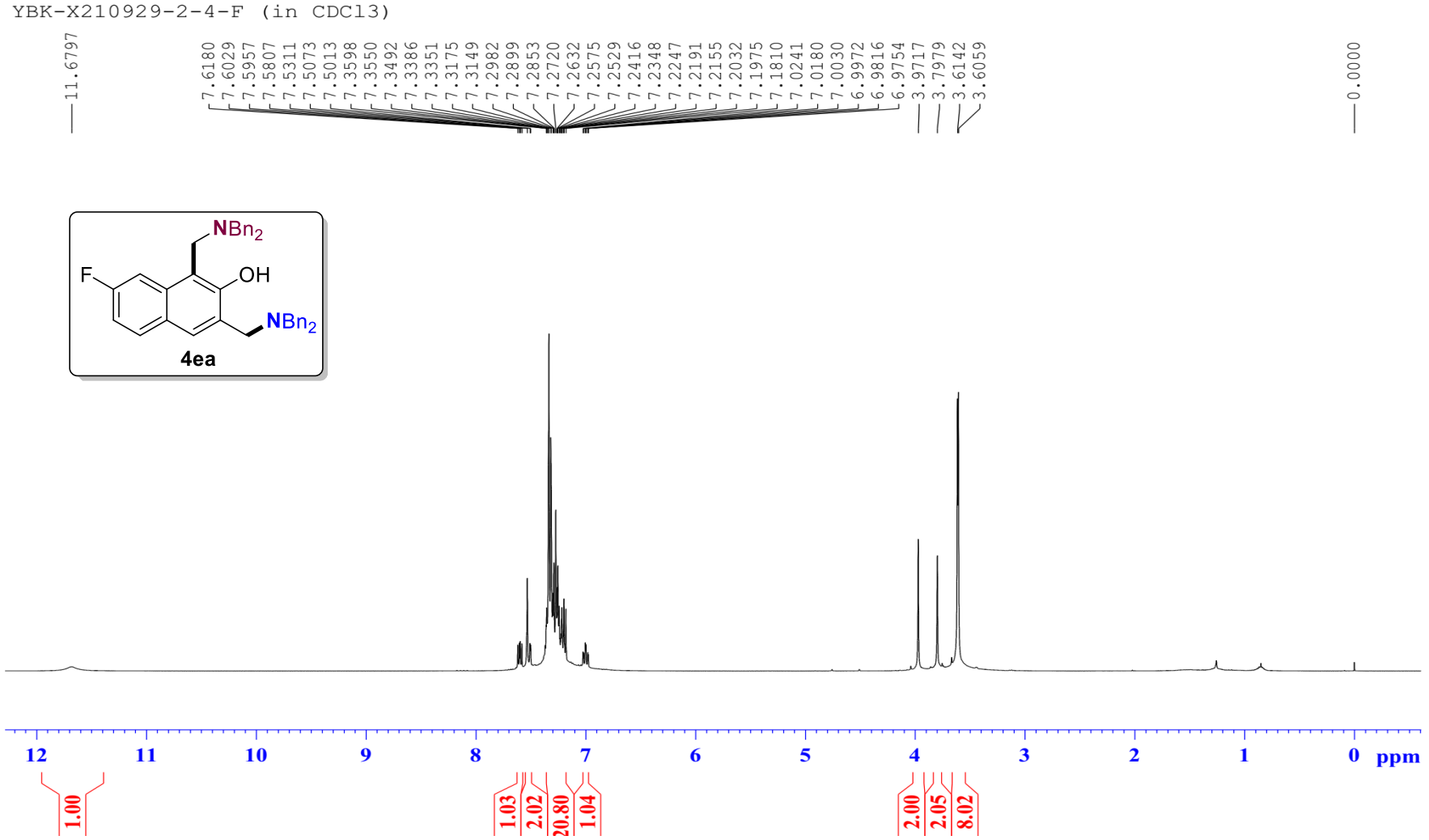
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4da



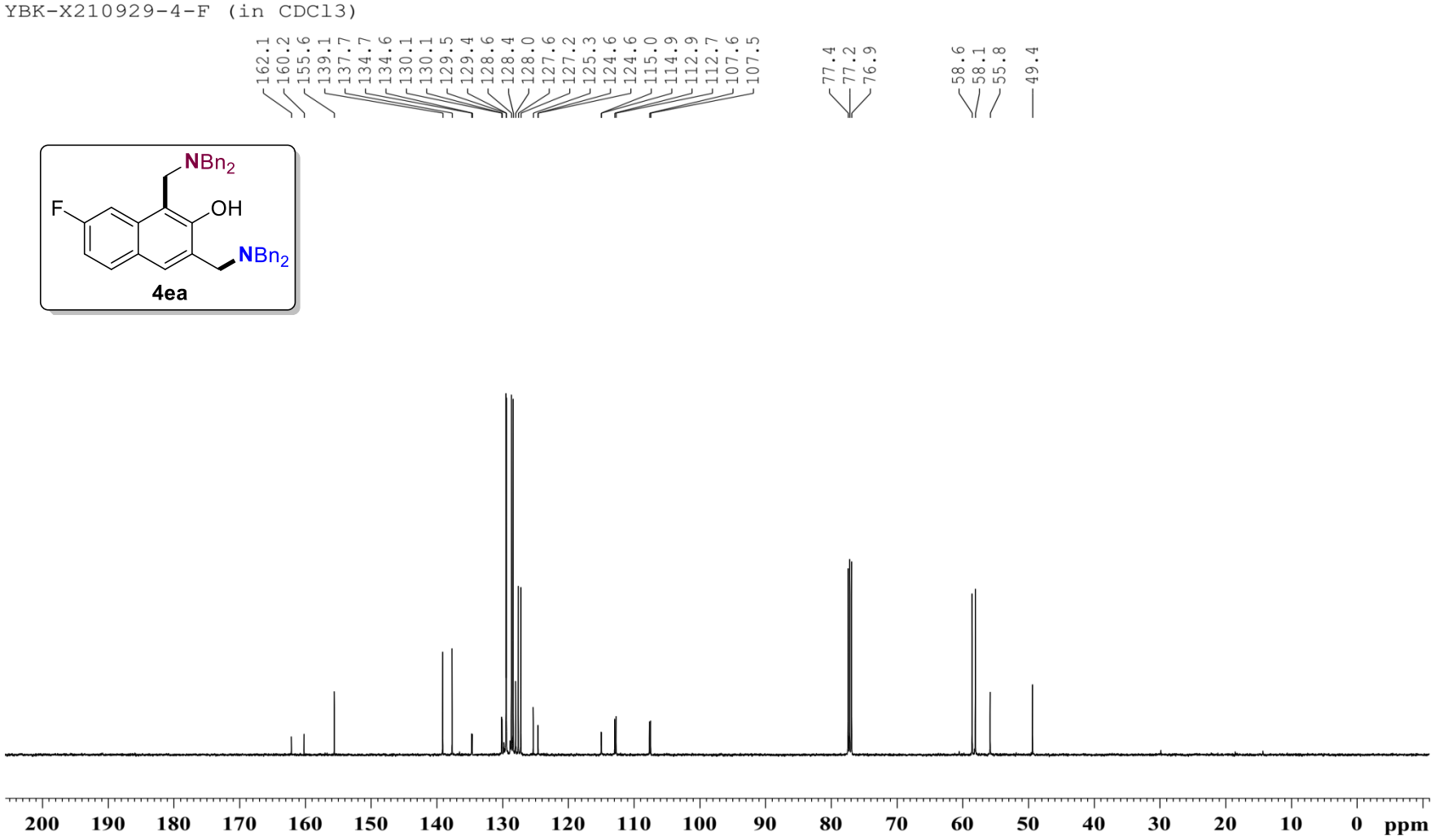
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4da



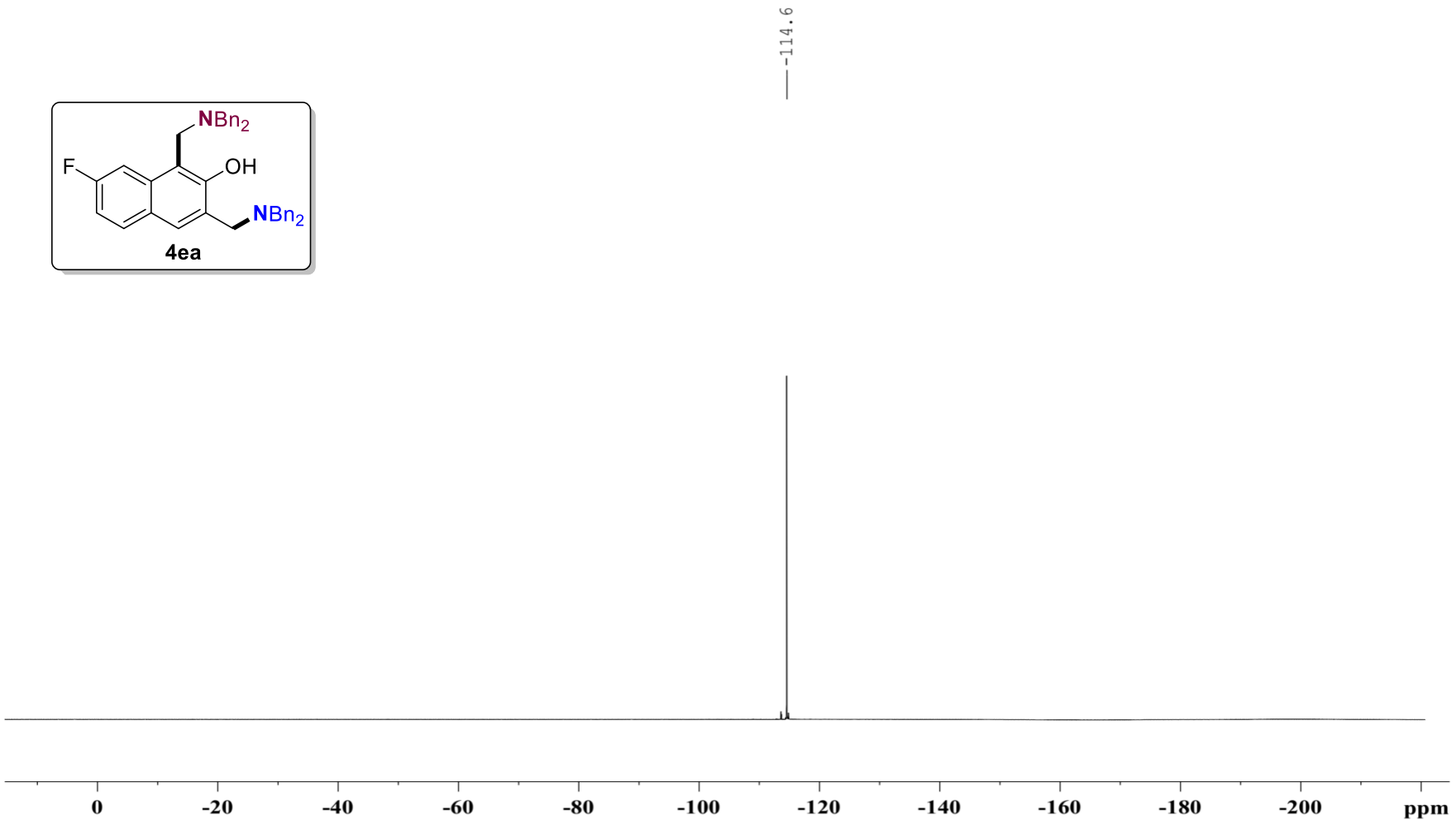
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ea



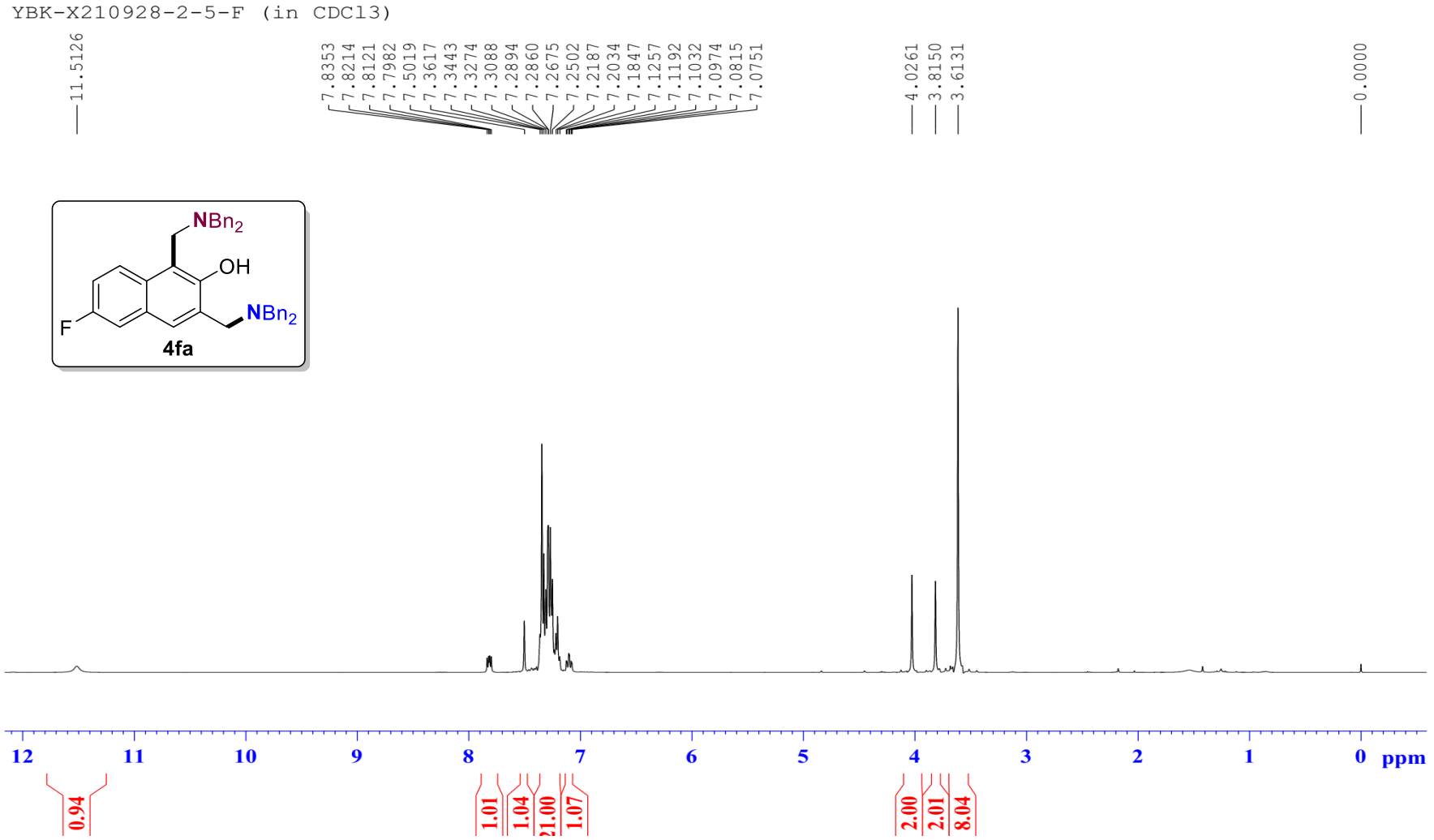
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ea



^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4ea

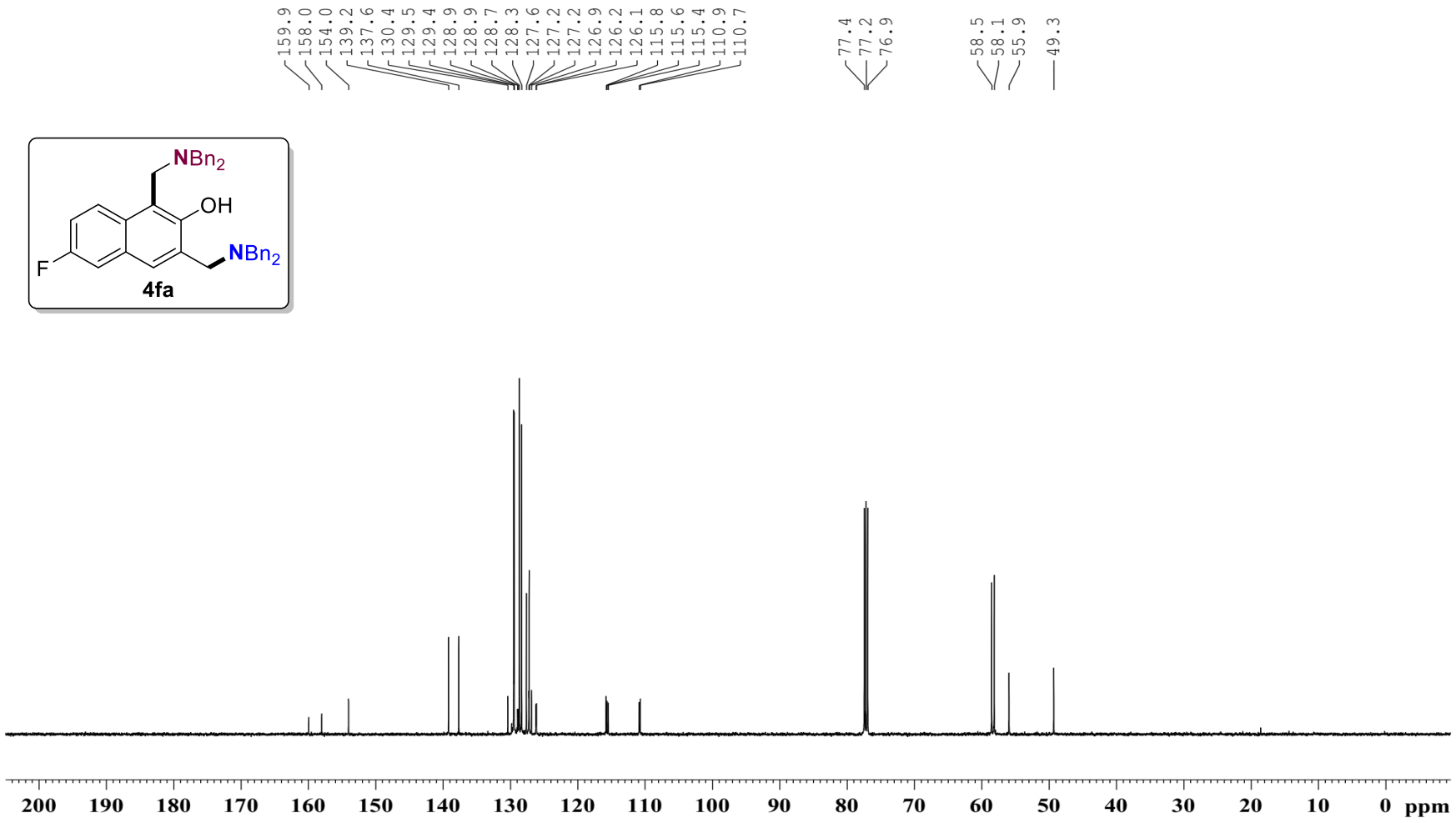


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4fa

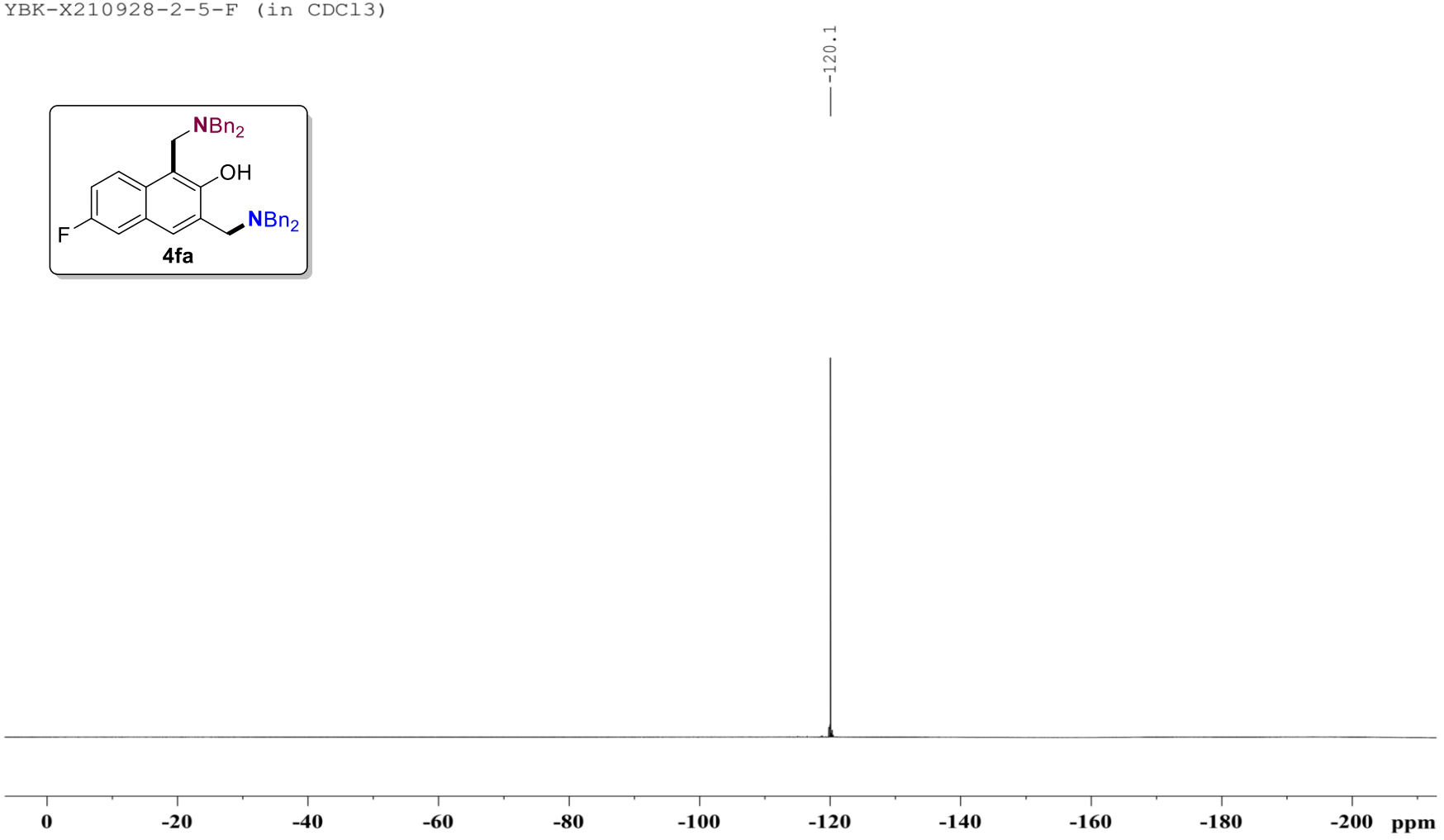


^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4fa

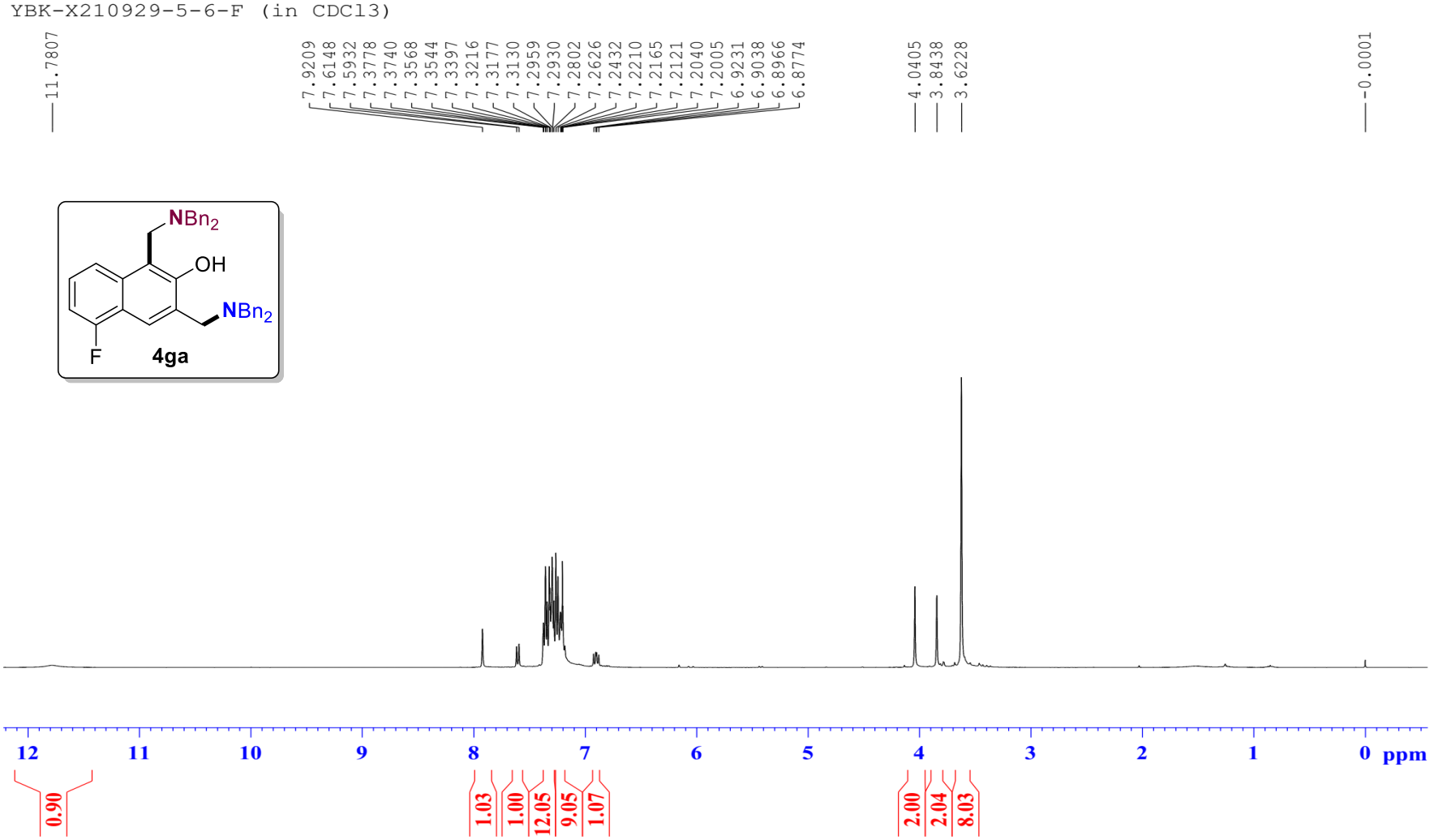
ybk-x210928-2-5-F (in CDCl3)



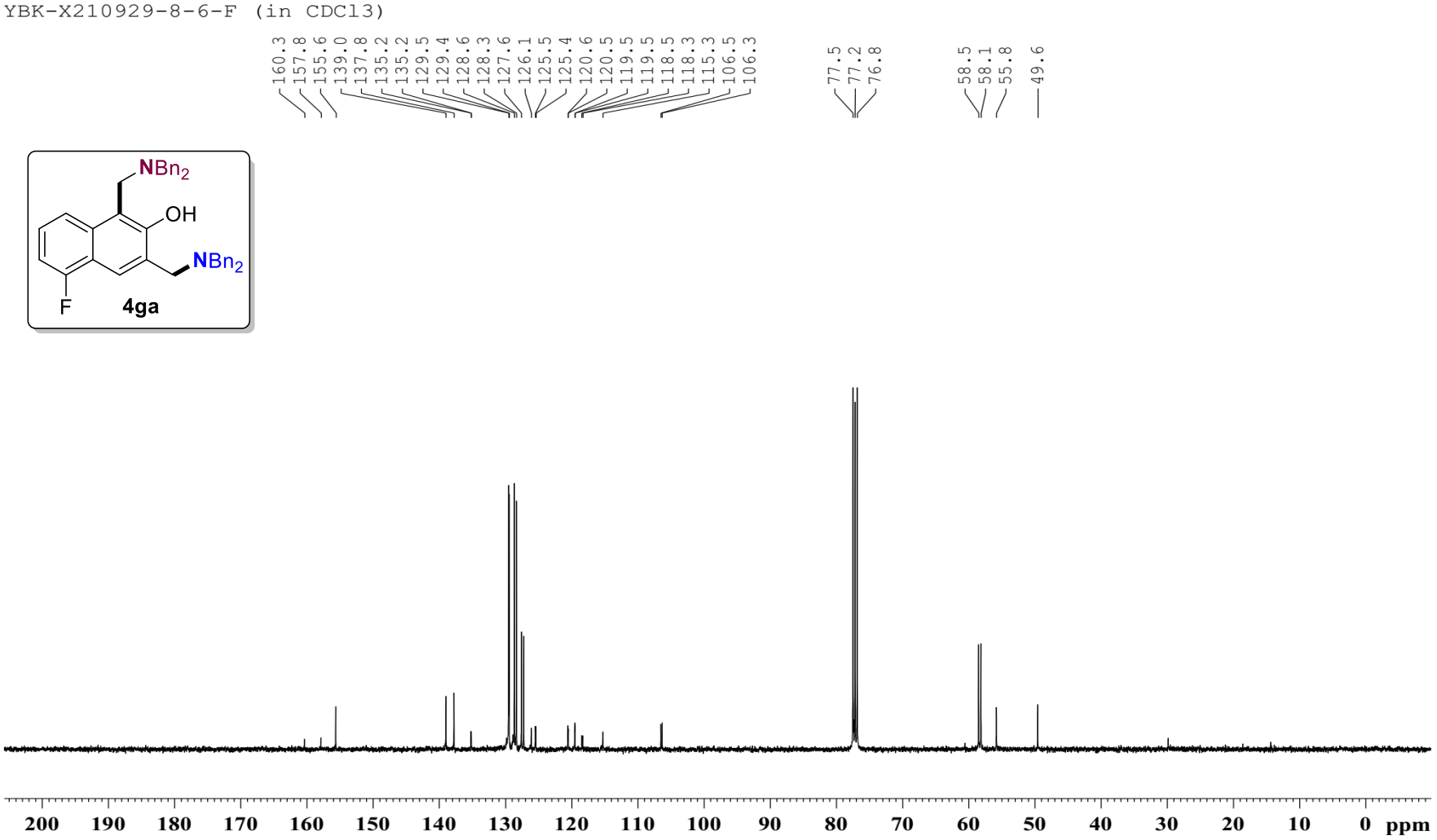
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4fa



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ga

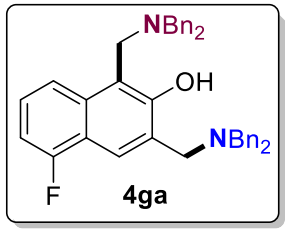


^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ga

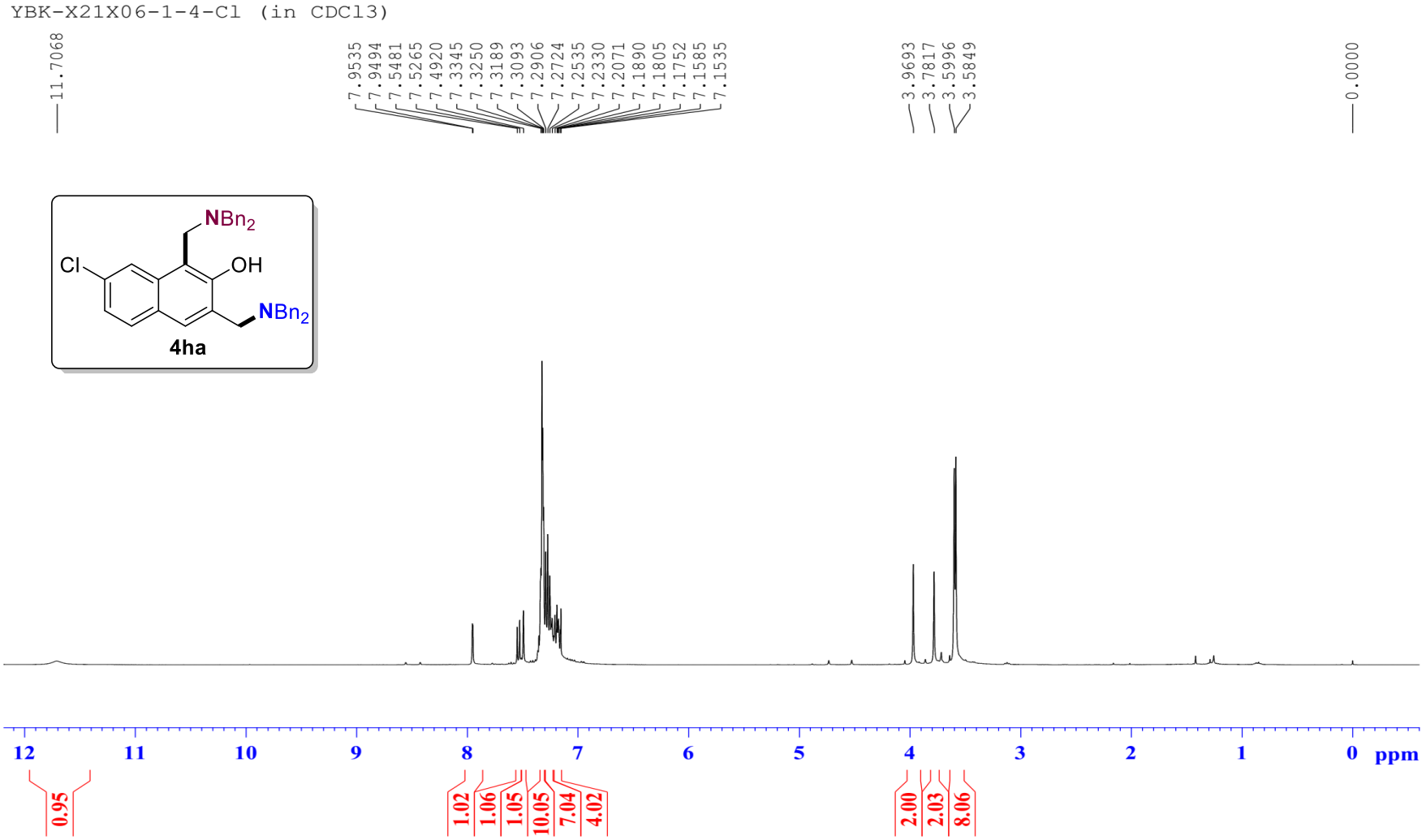


^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4ga

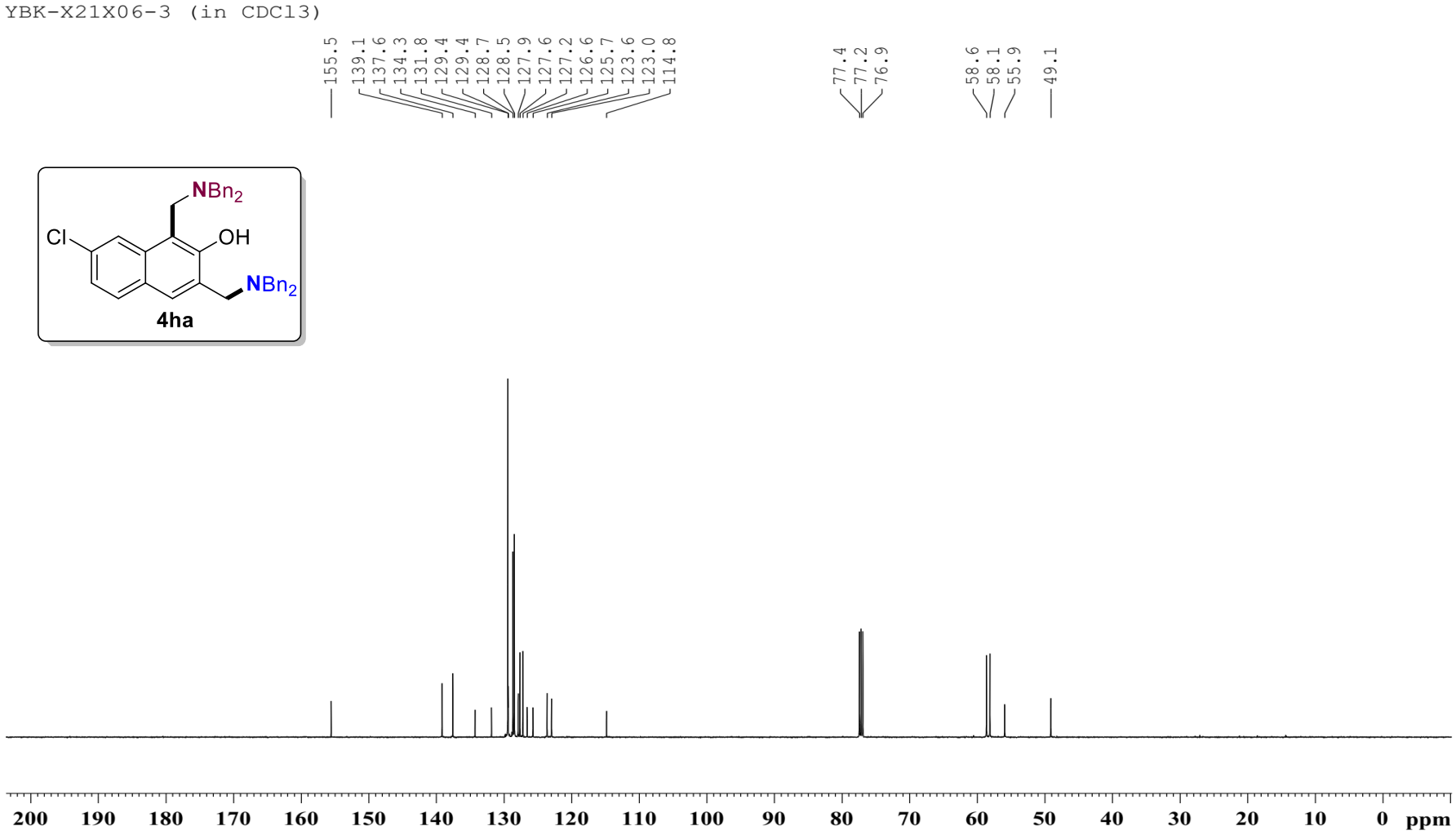
YBK-X210929-5-6-F (in CDCl3)



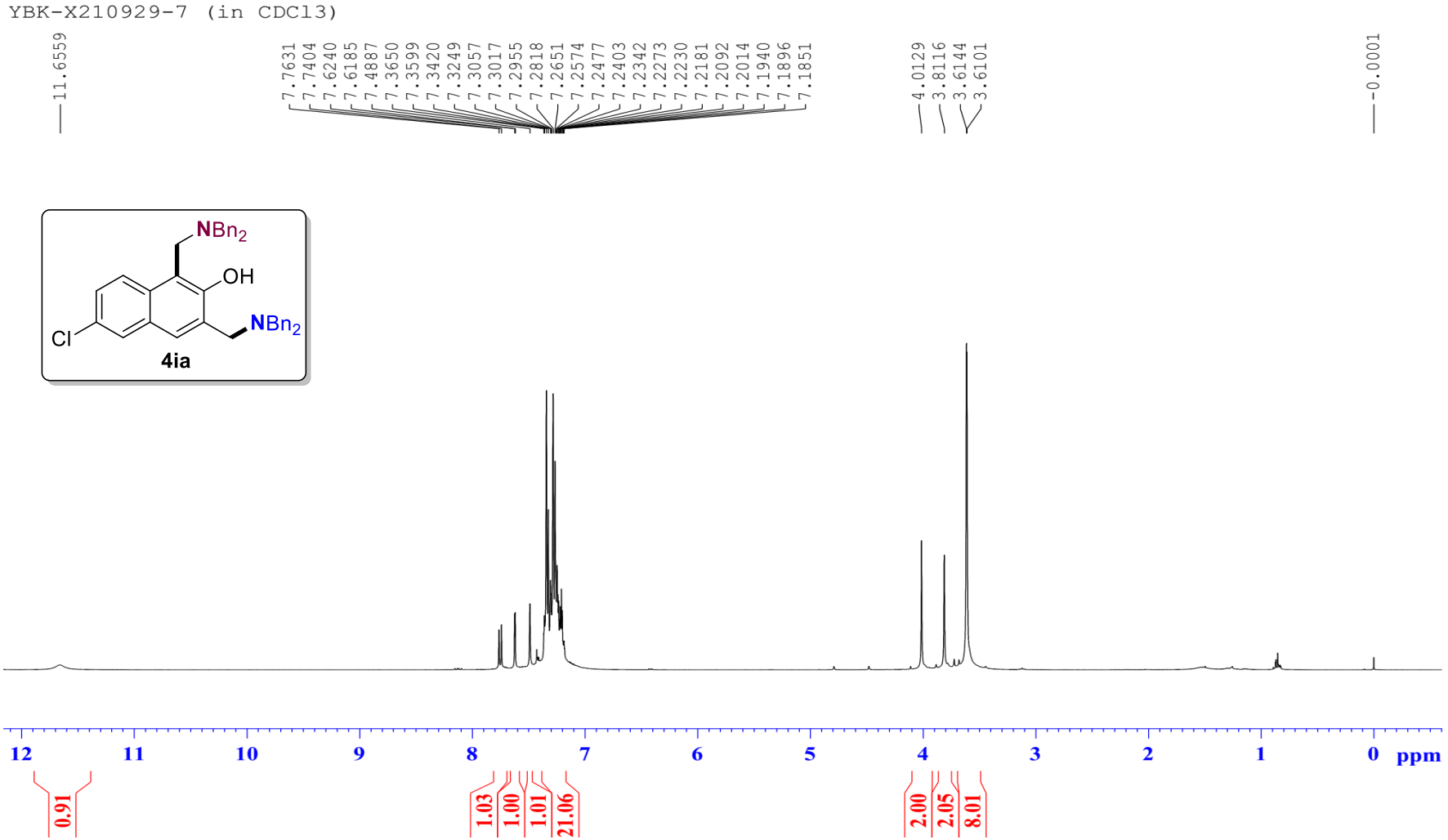
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ha



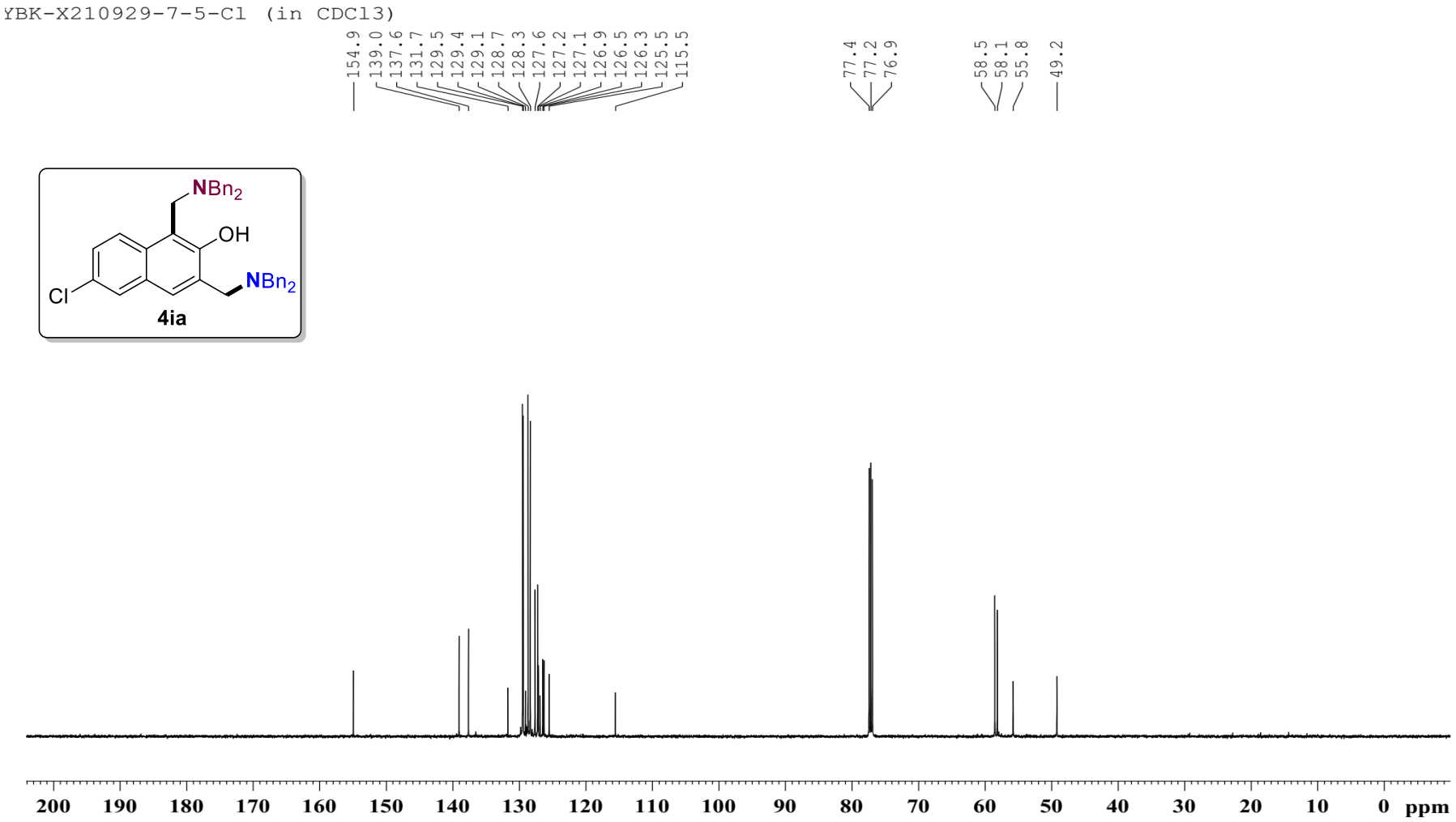
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ha



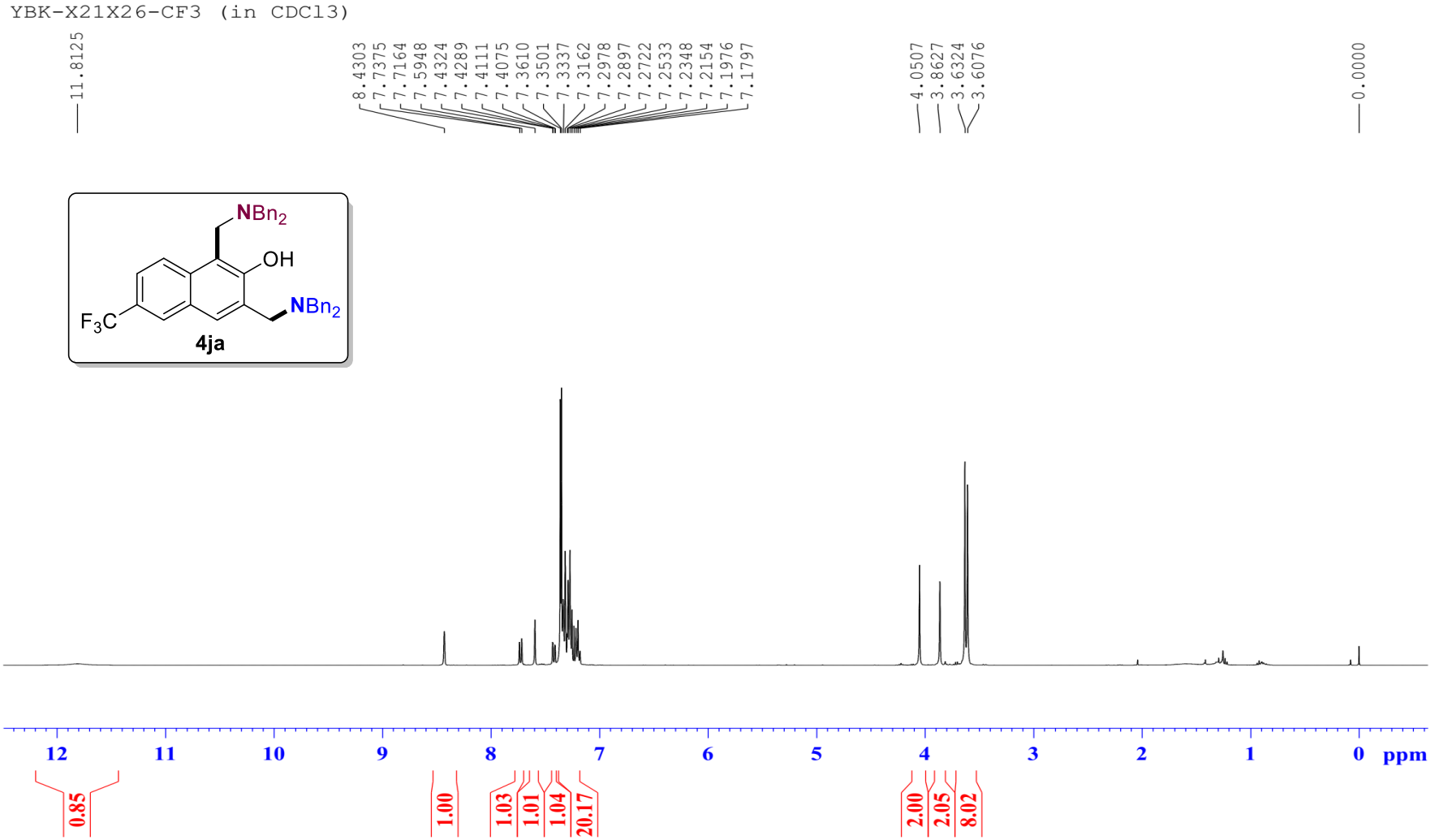
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ia



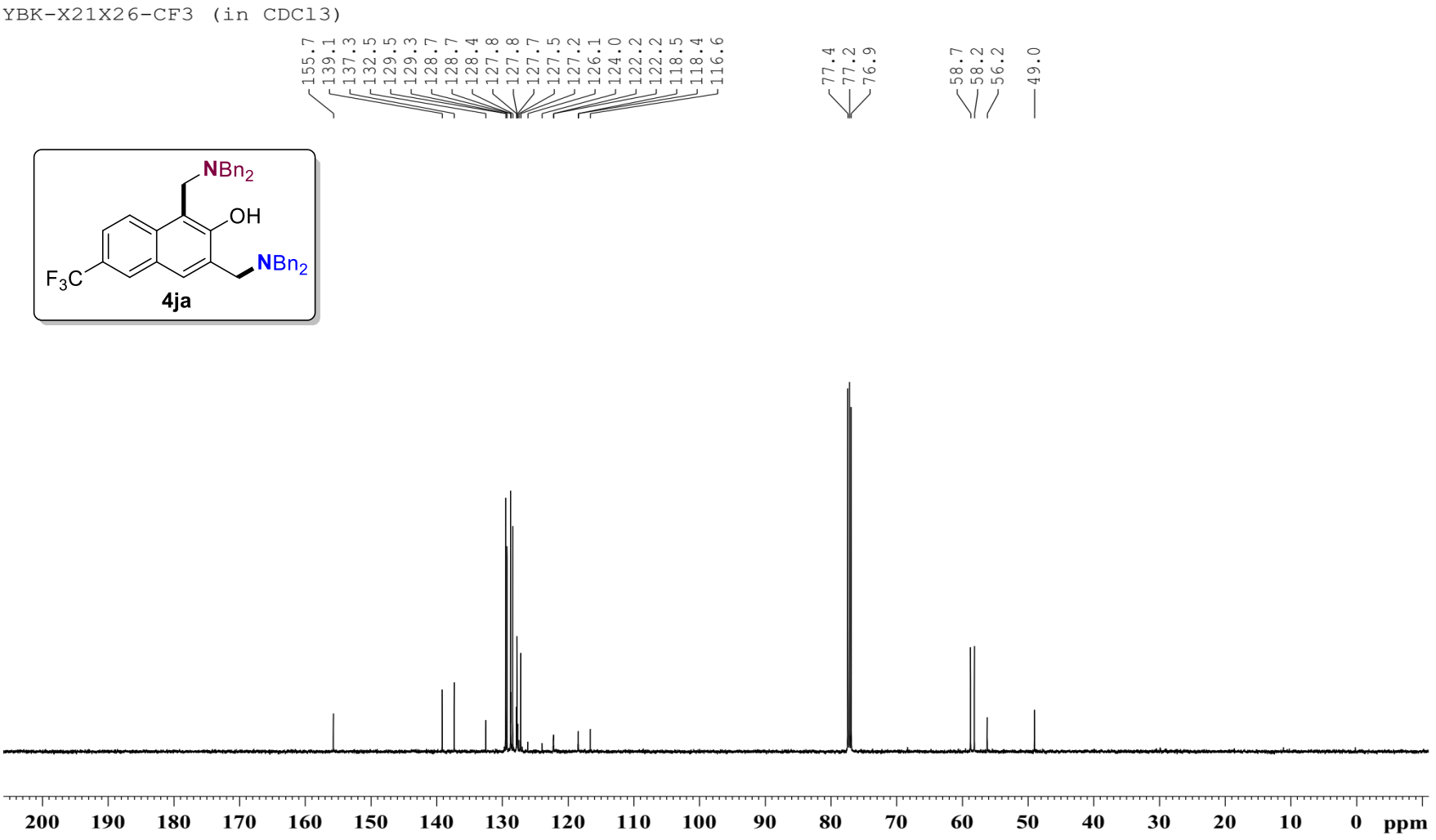
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ia



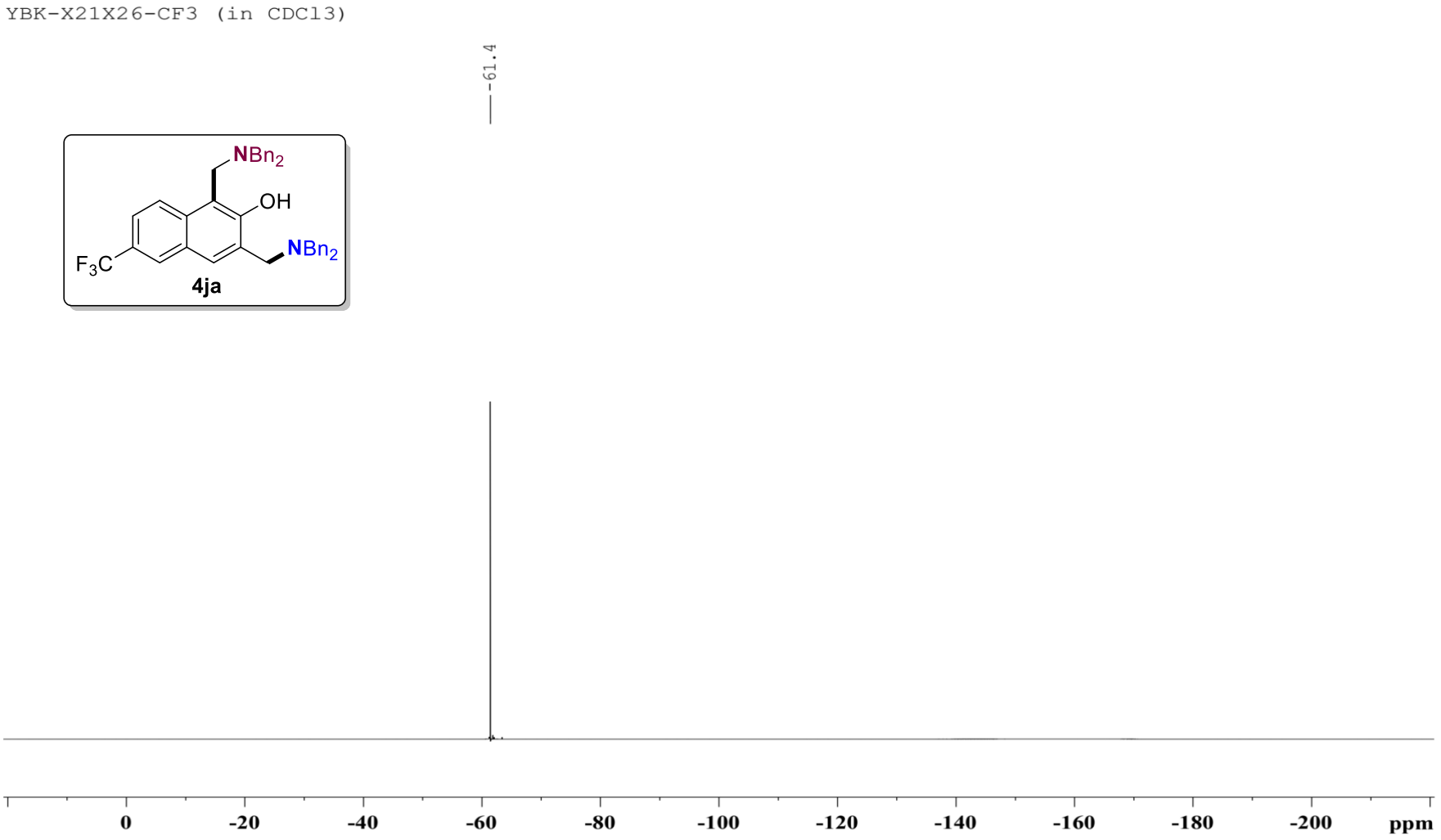
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 4ja



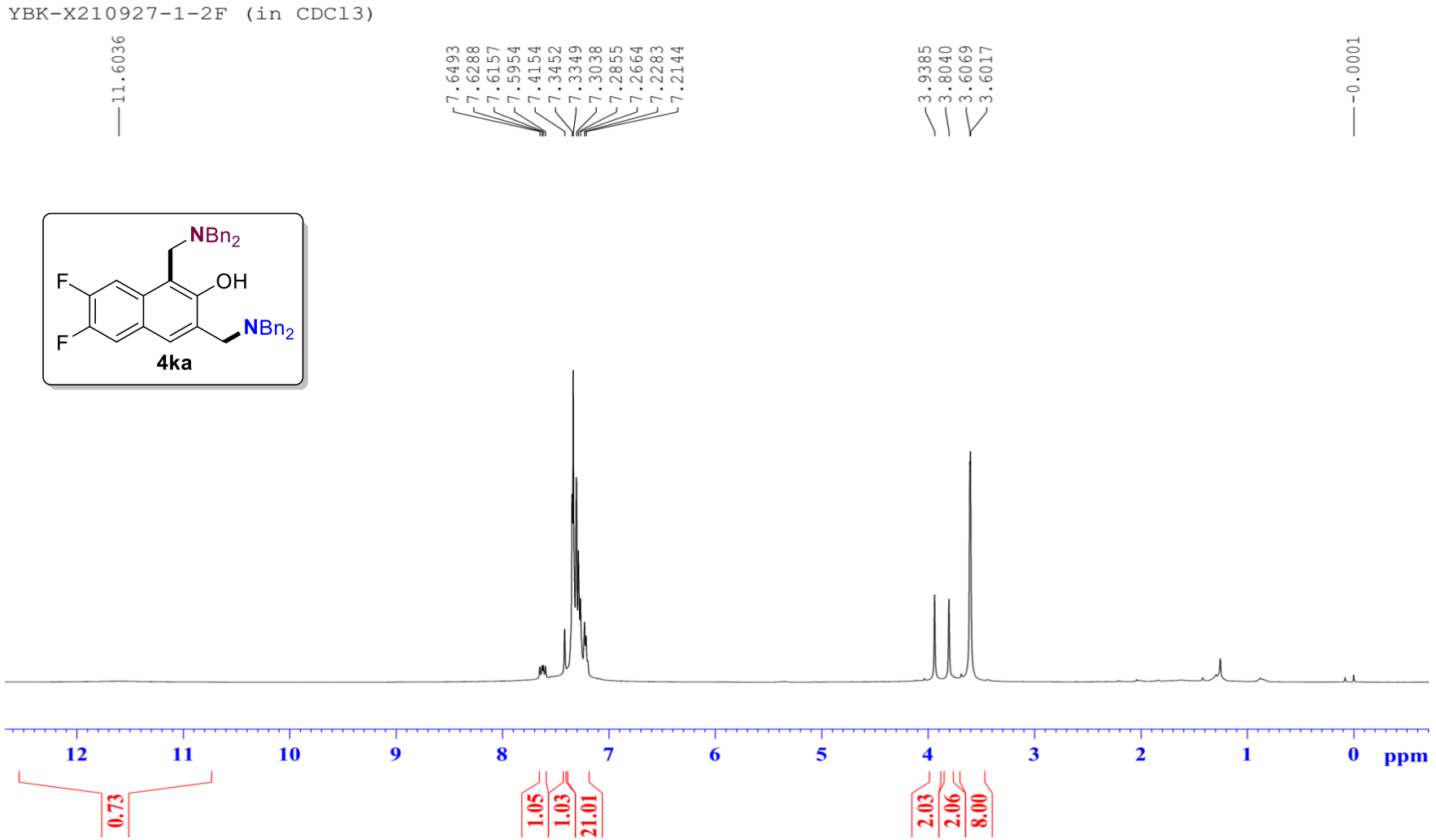
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ja



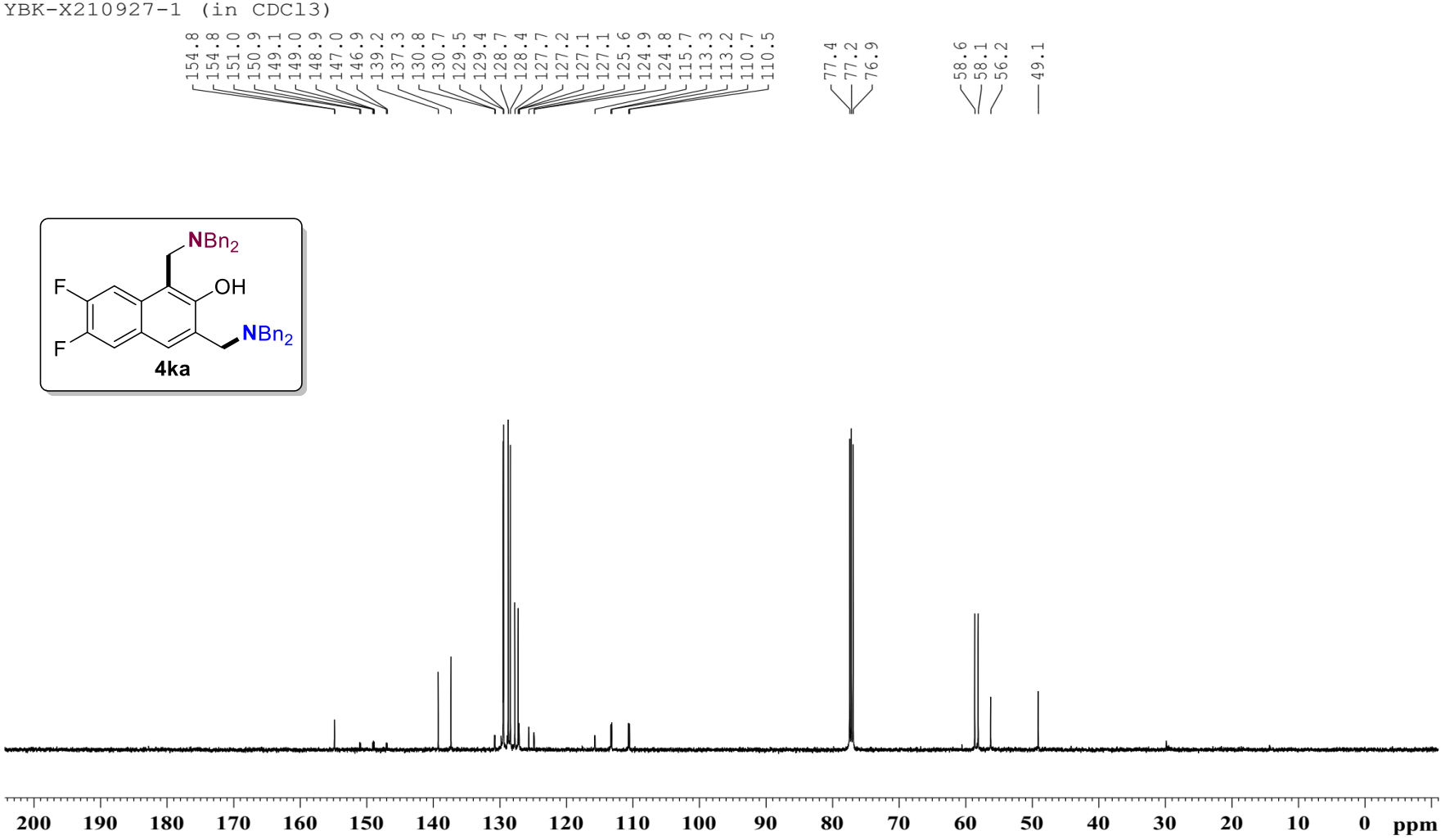
^{19}F NMR (470 MHz, $CDCl_3$) spectra for 4ja



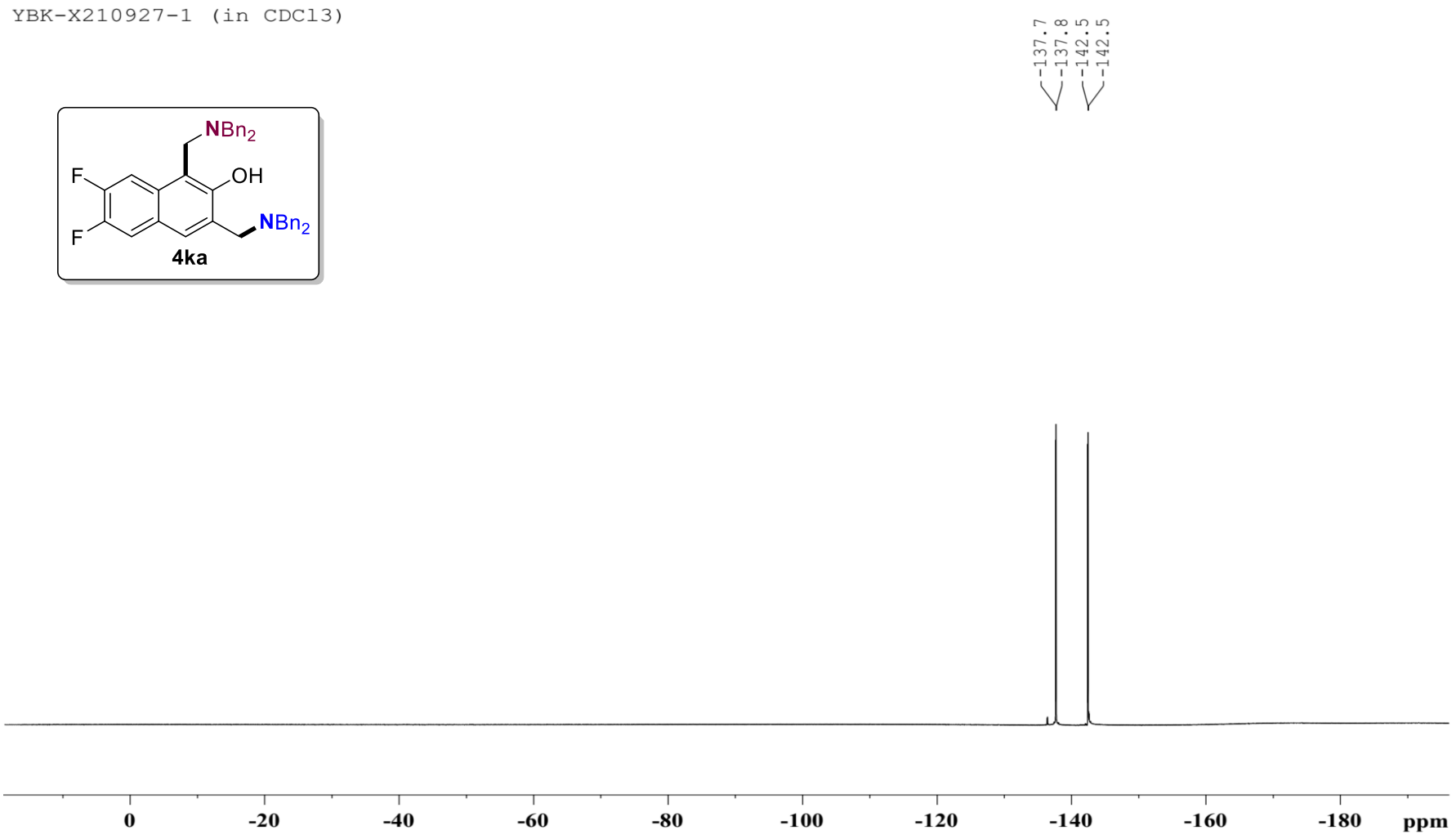
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ka



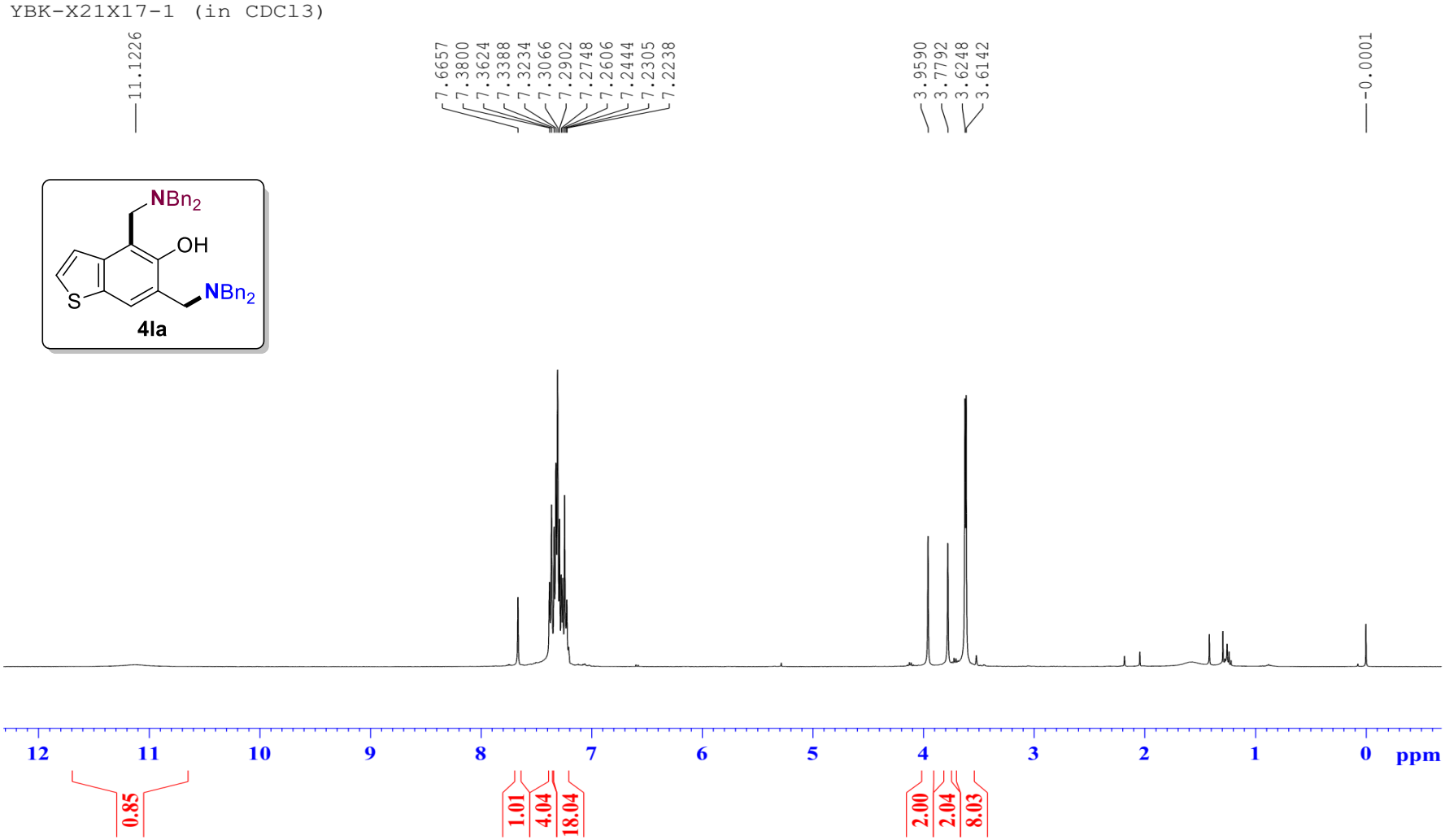
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ka



^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4ka

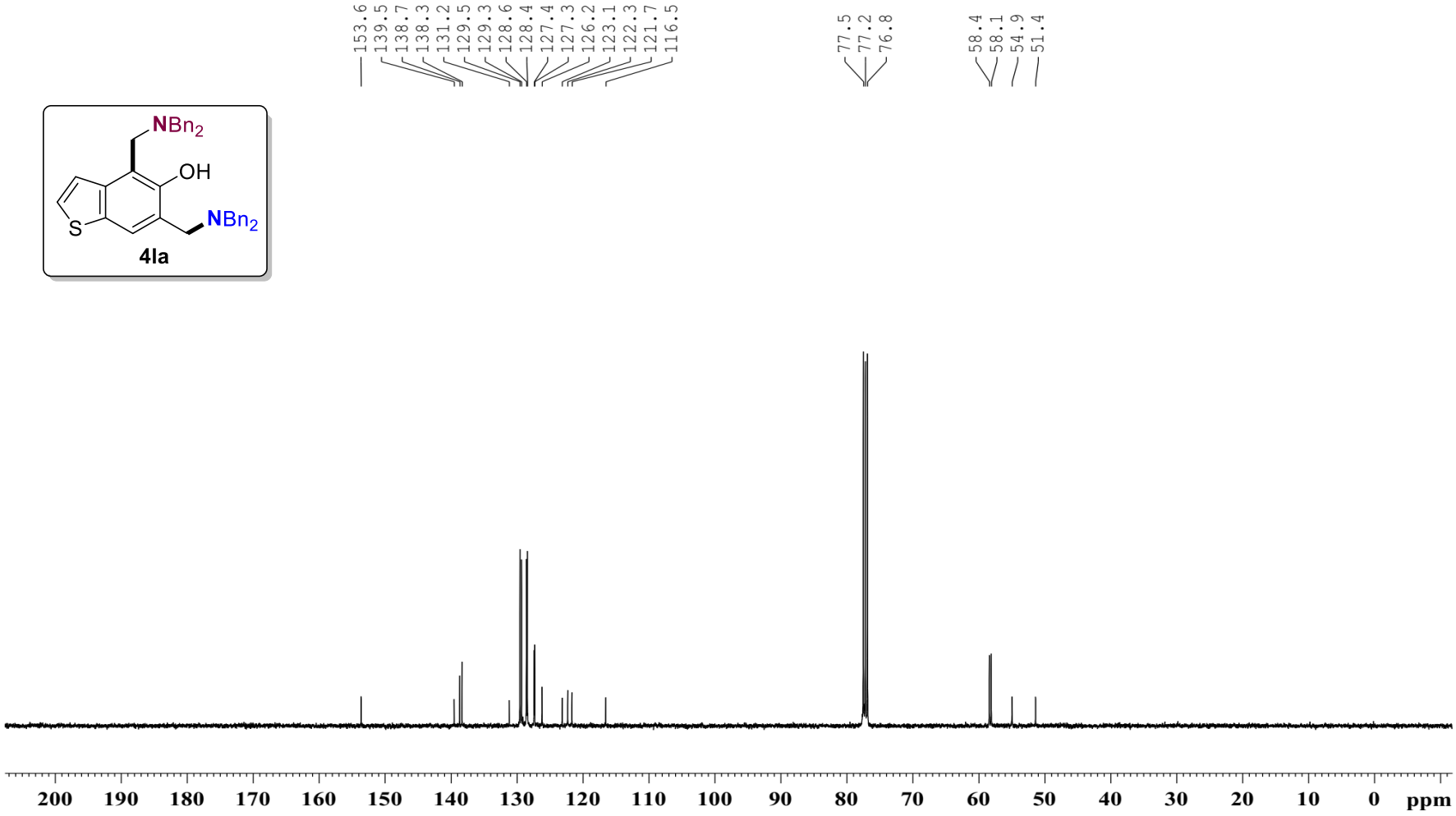


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4la

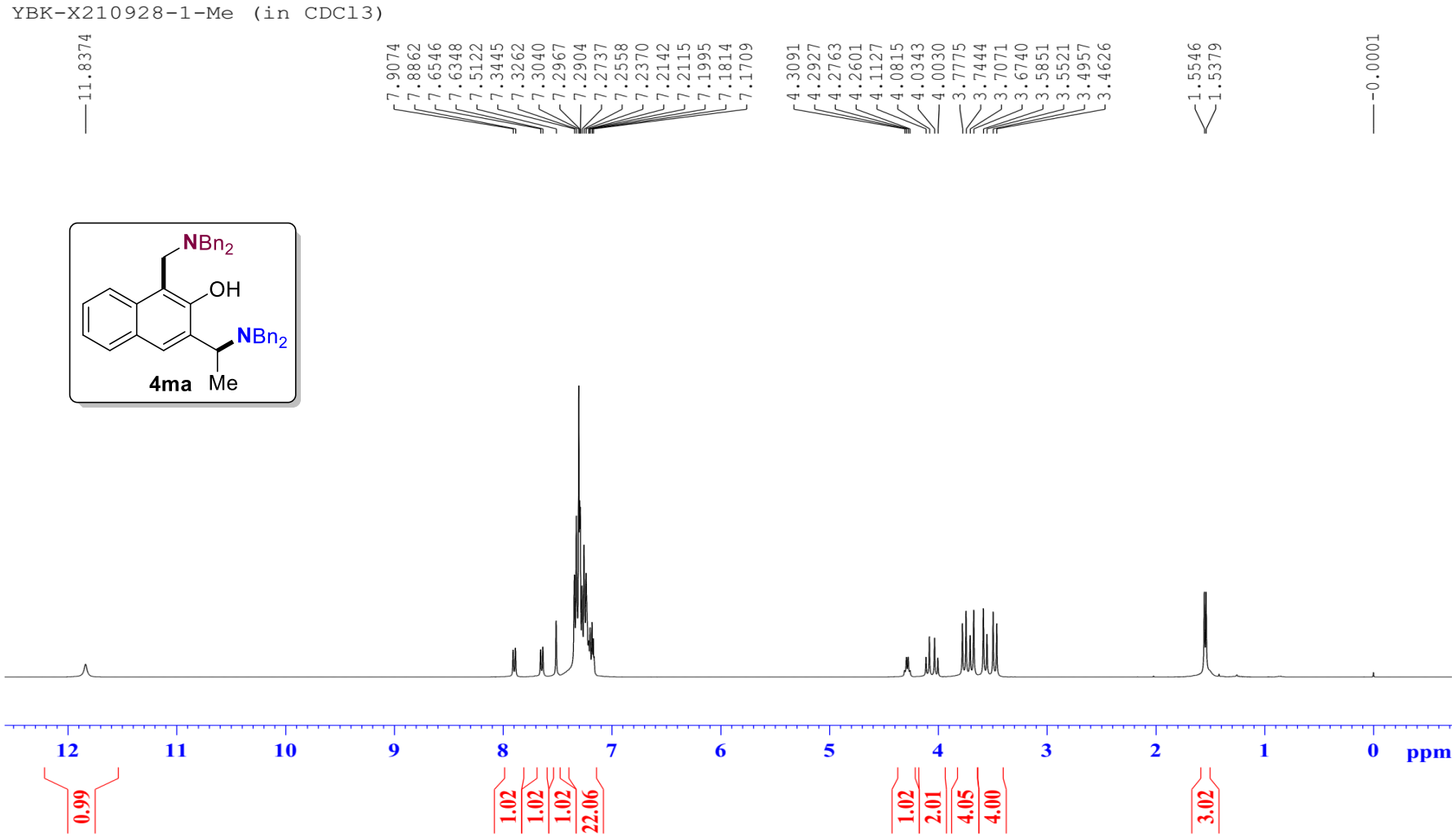


^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4la

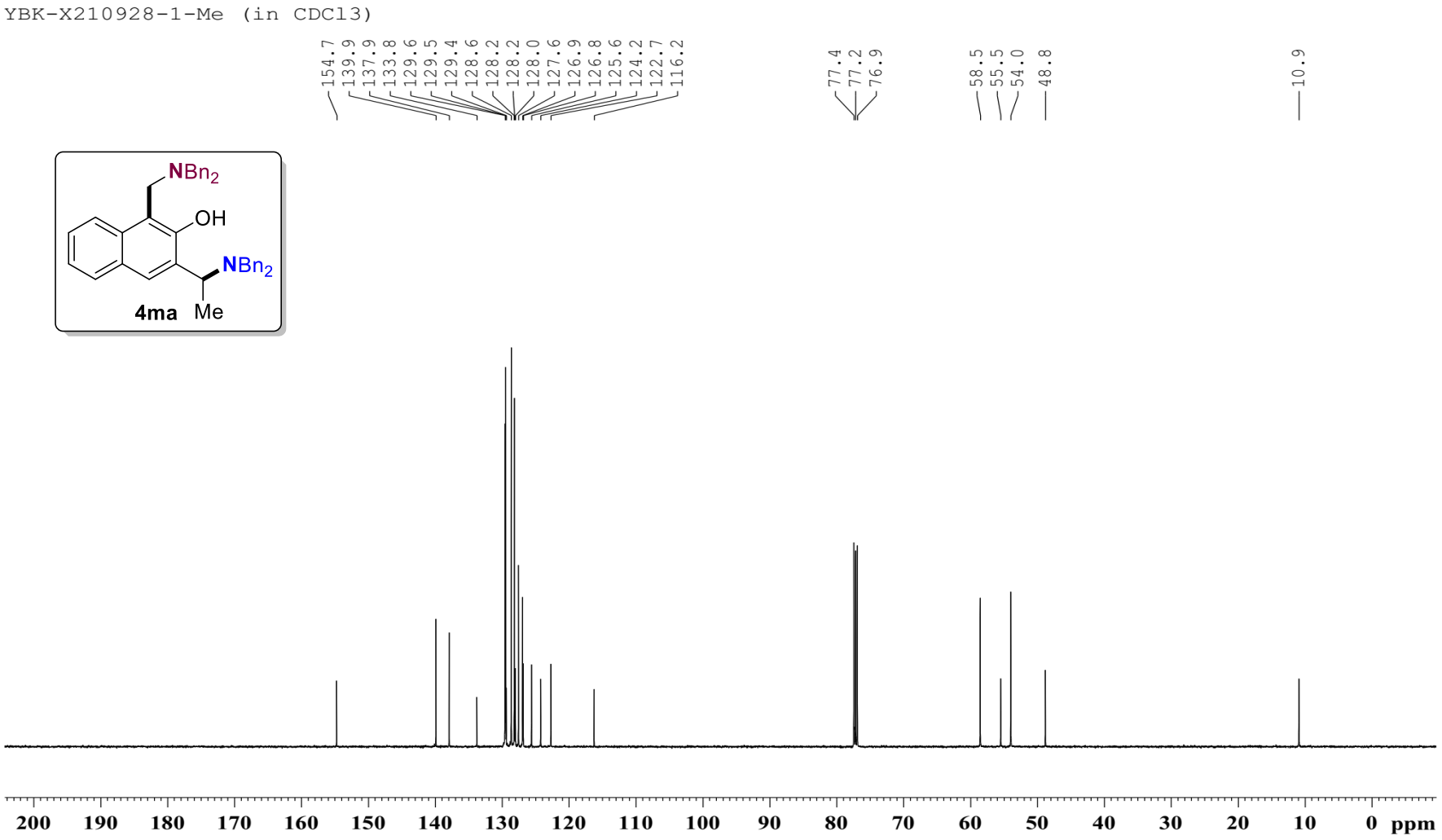
YBK-X21X17-1 (in CDCl3)



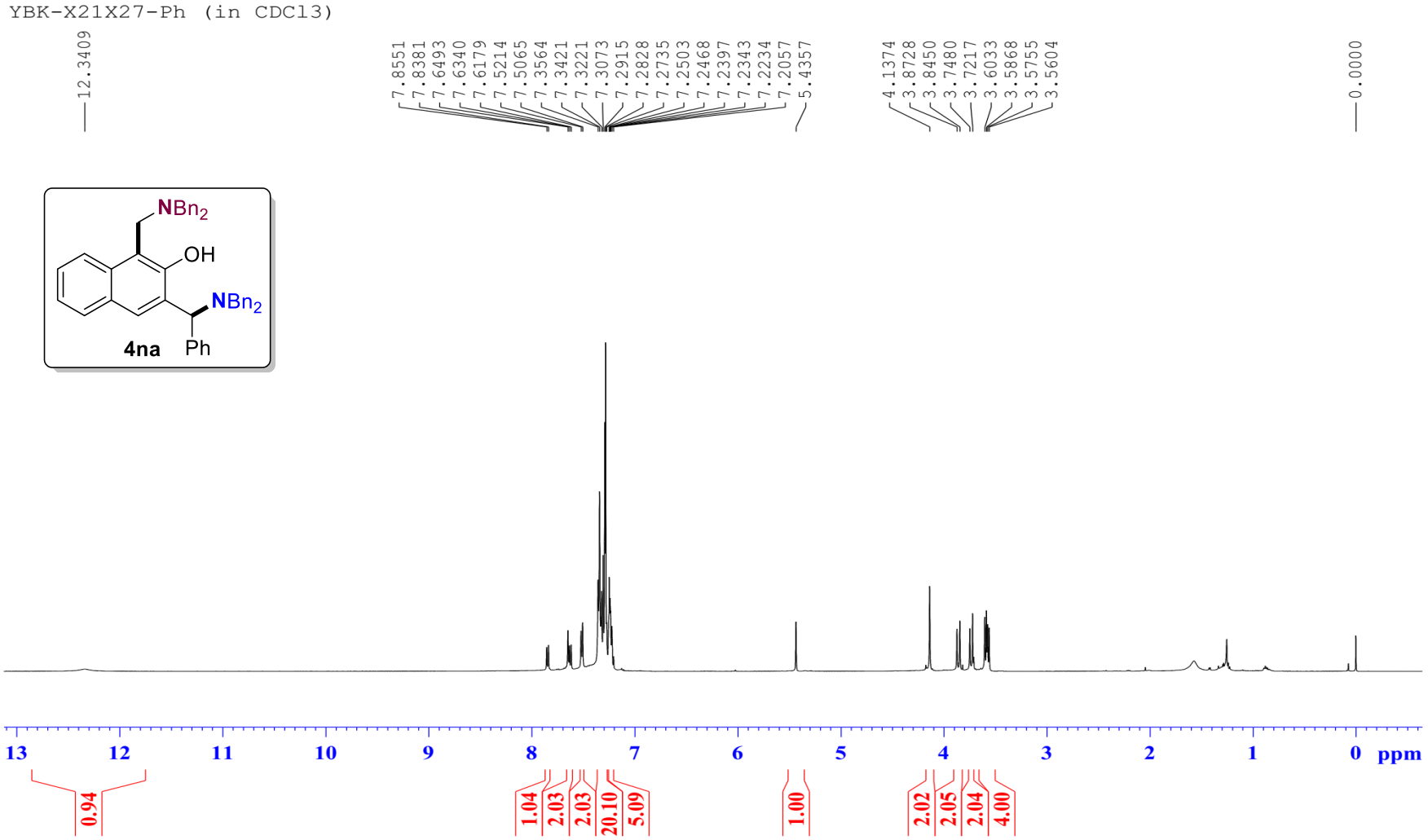
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ma



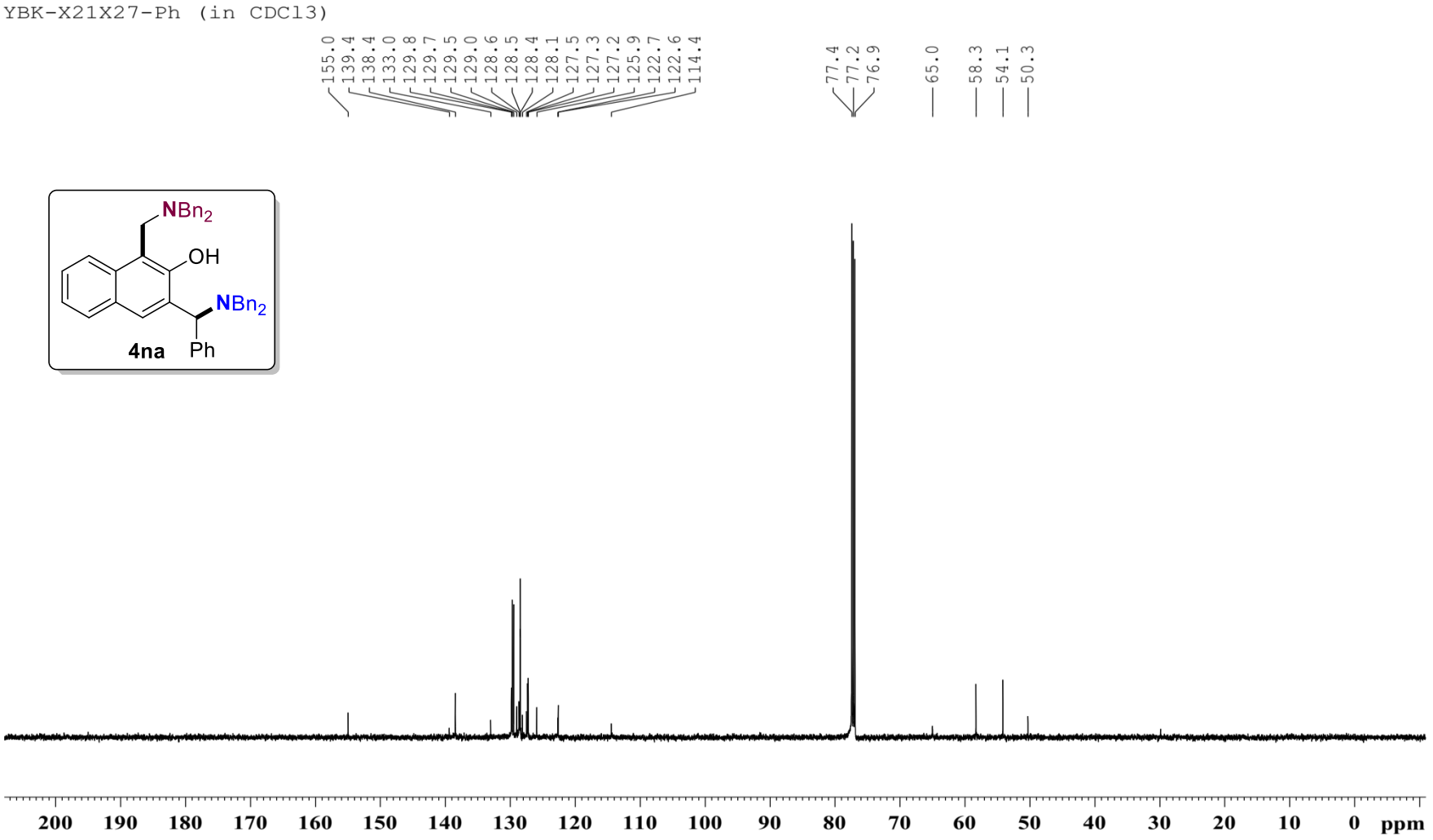
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ma



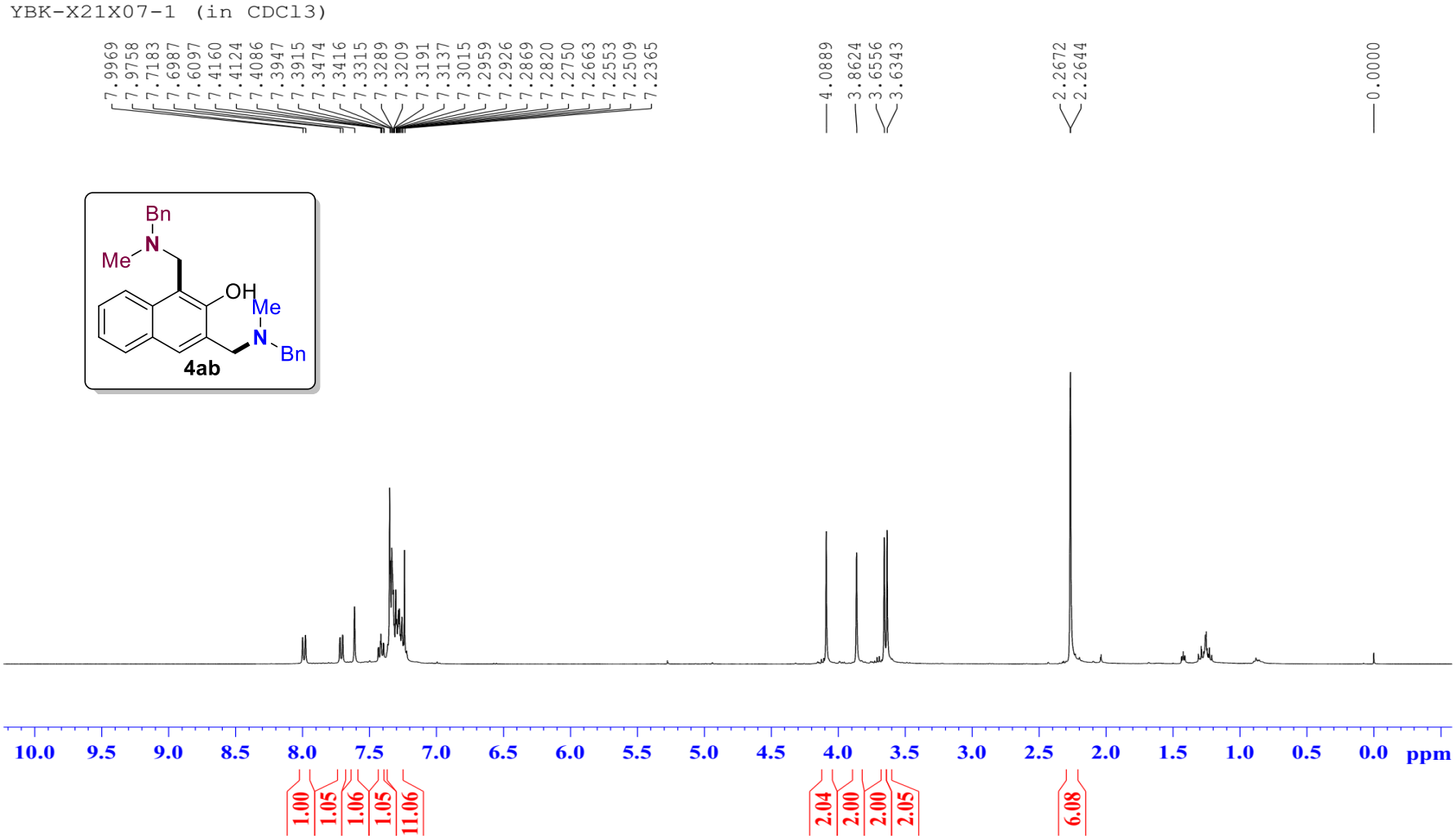
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 4na



^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4na

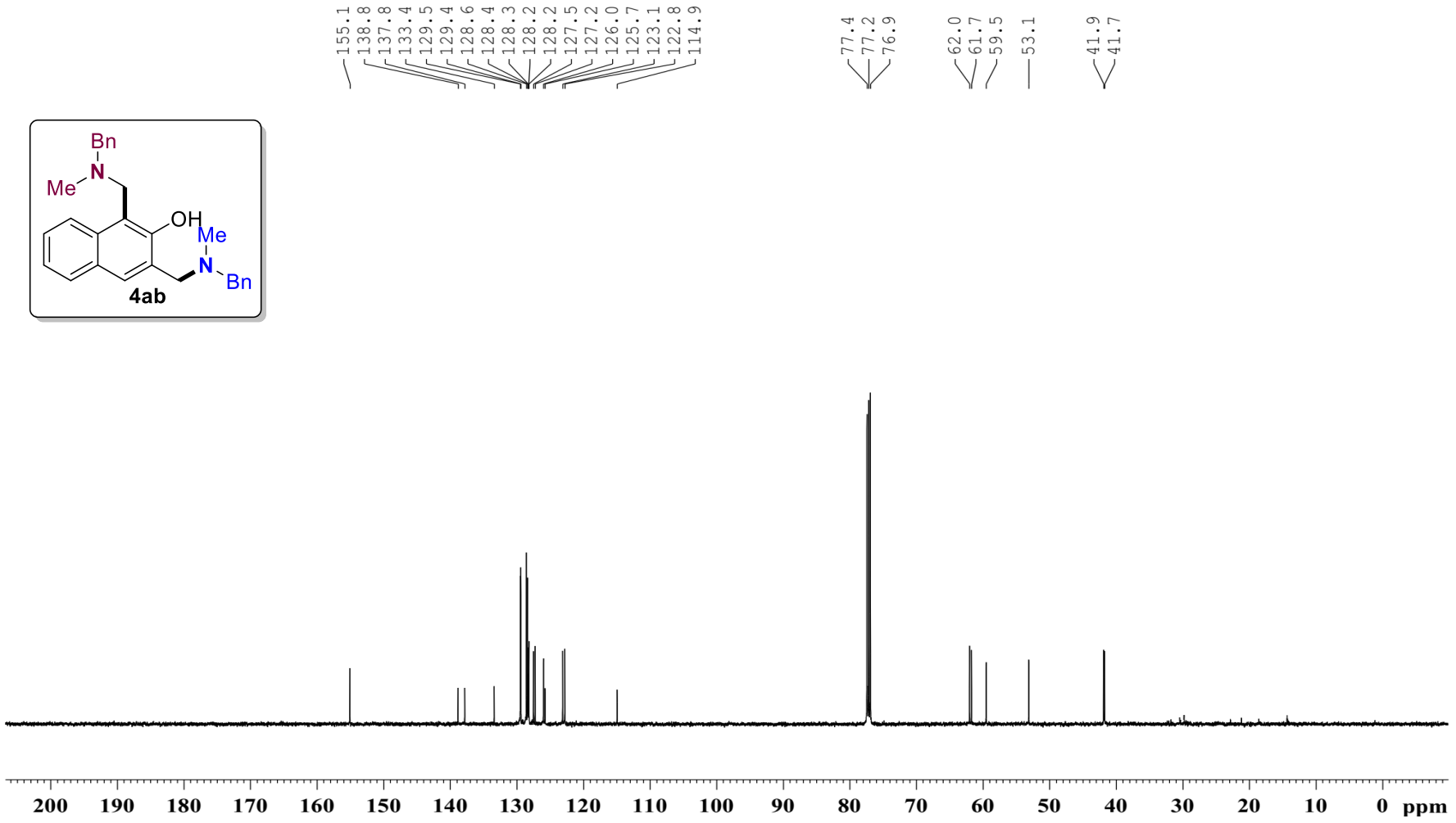


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ab

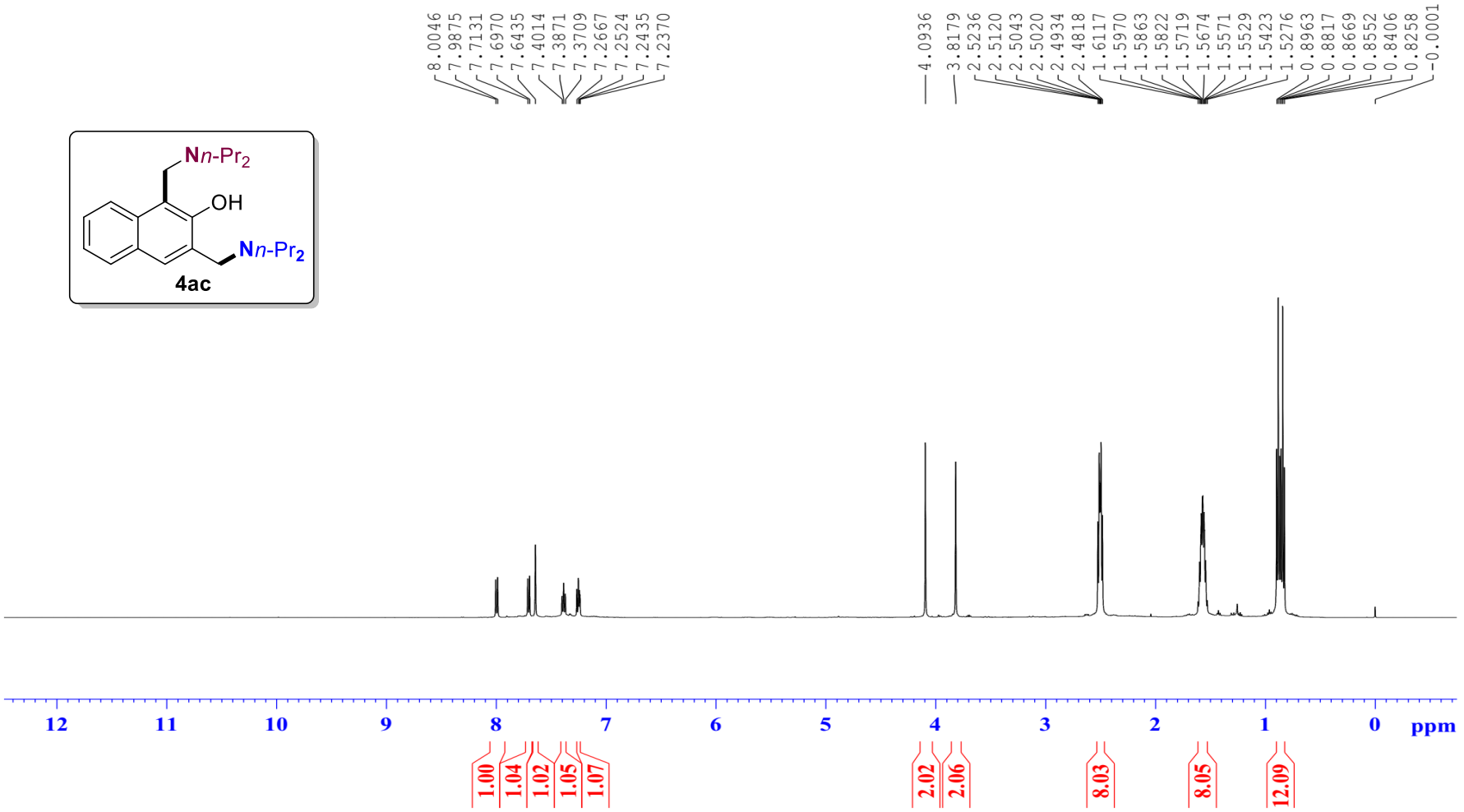


^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ab

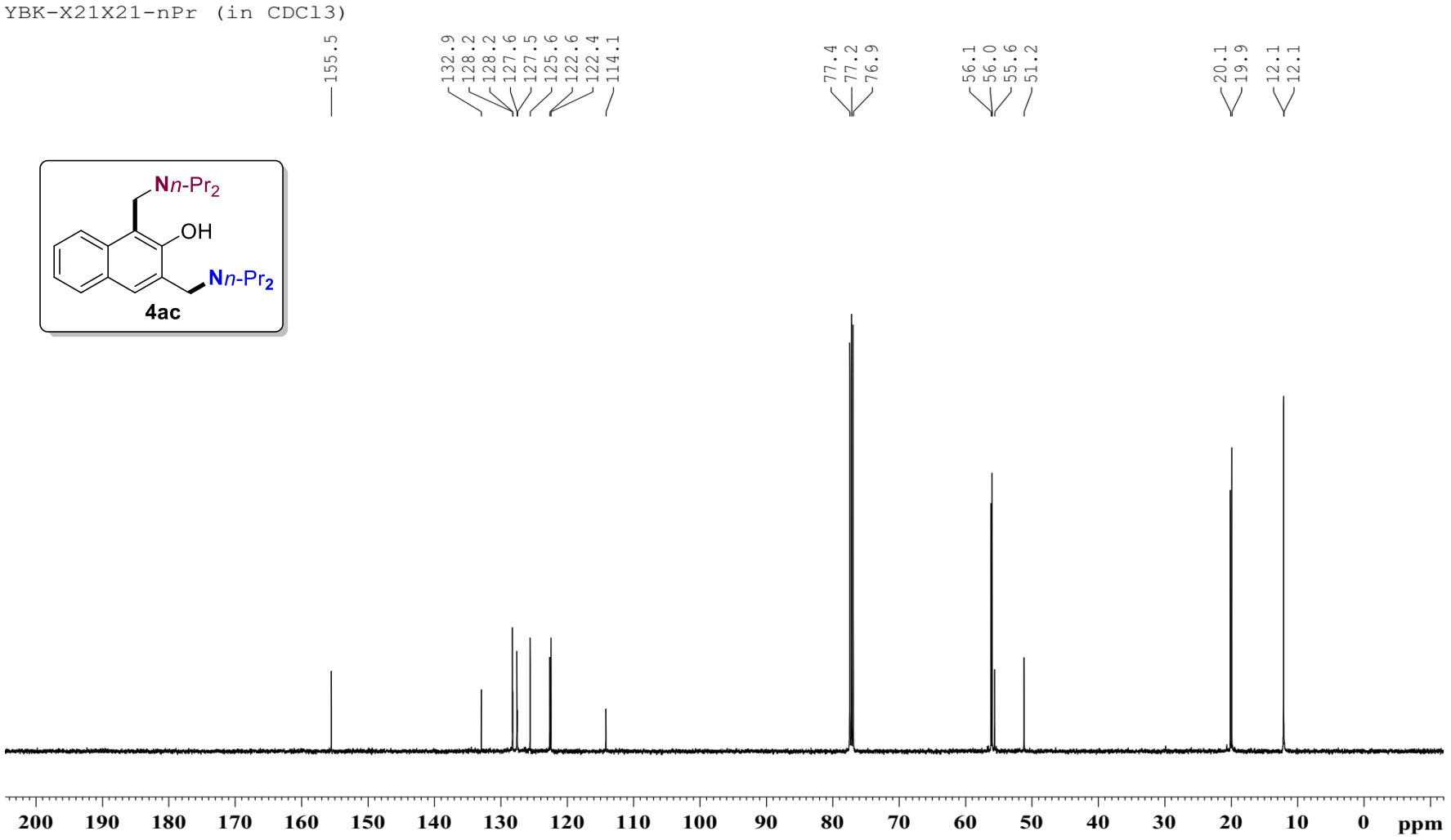
YBK-X21X07-1 (in CDCl3)



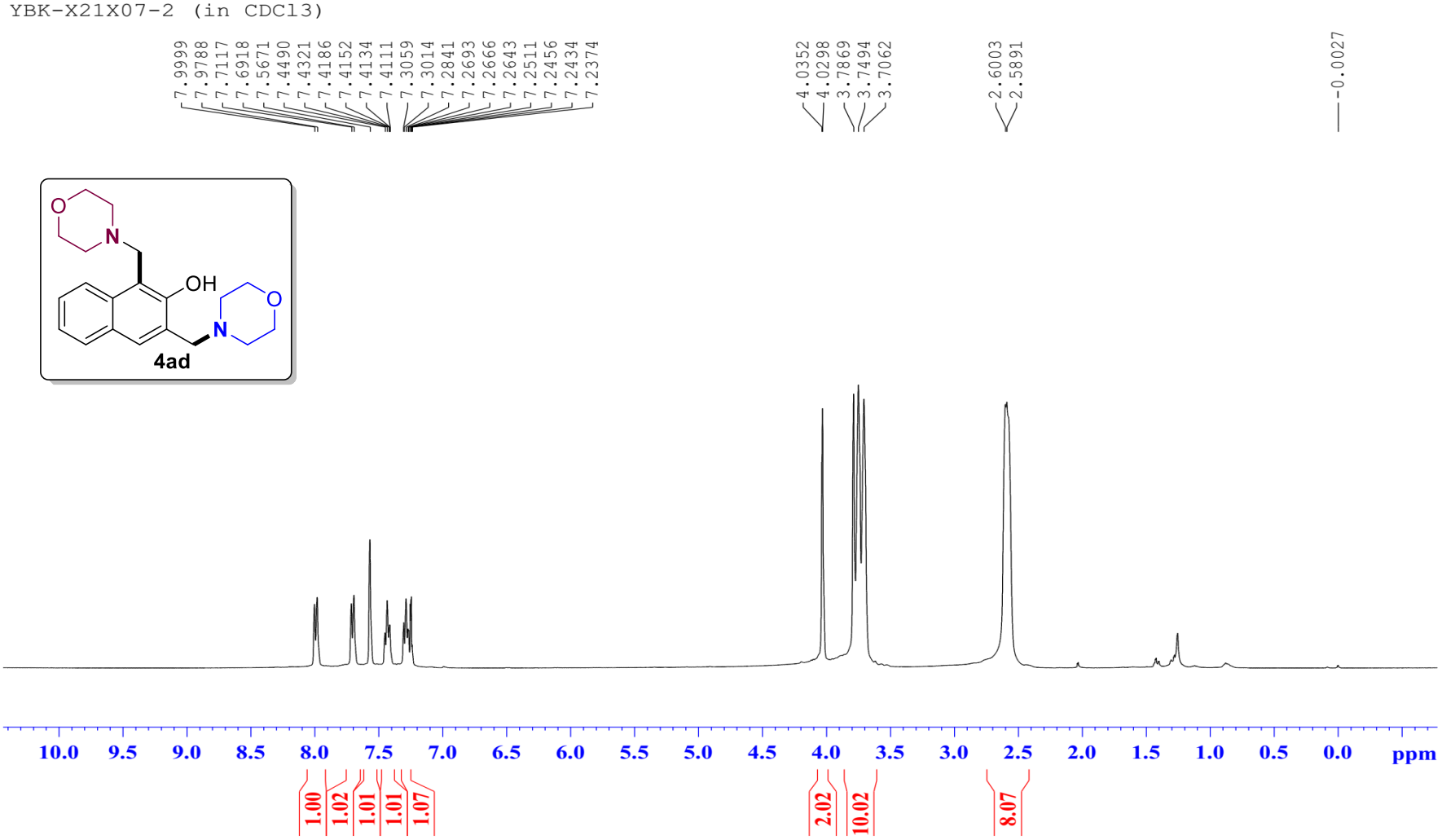
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 4ac



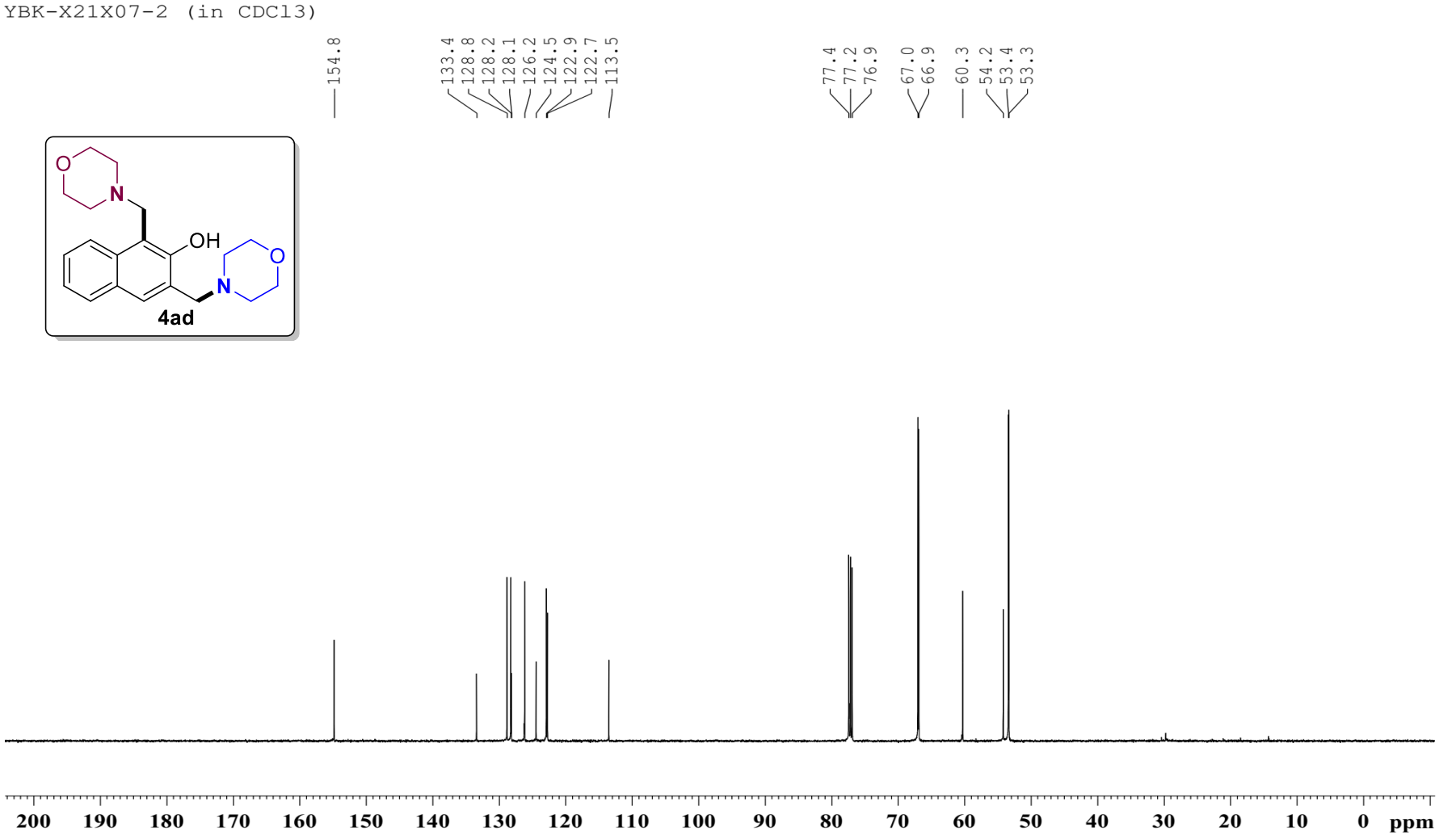
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ac



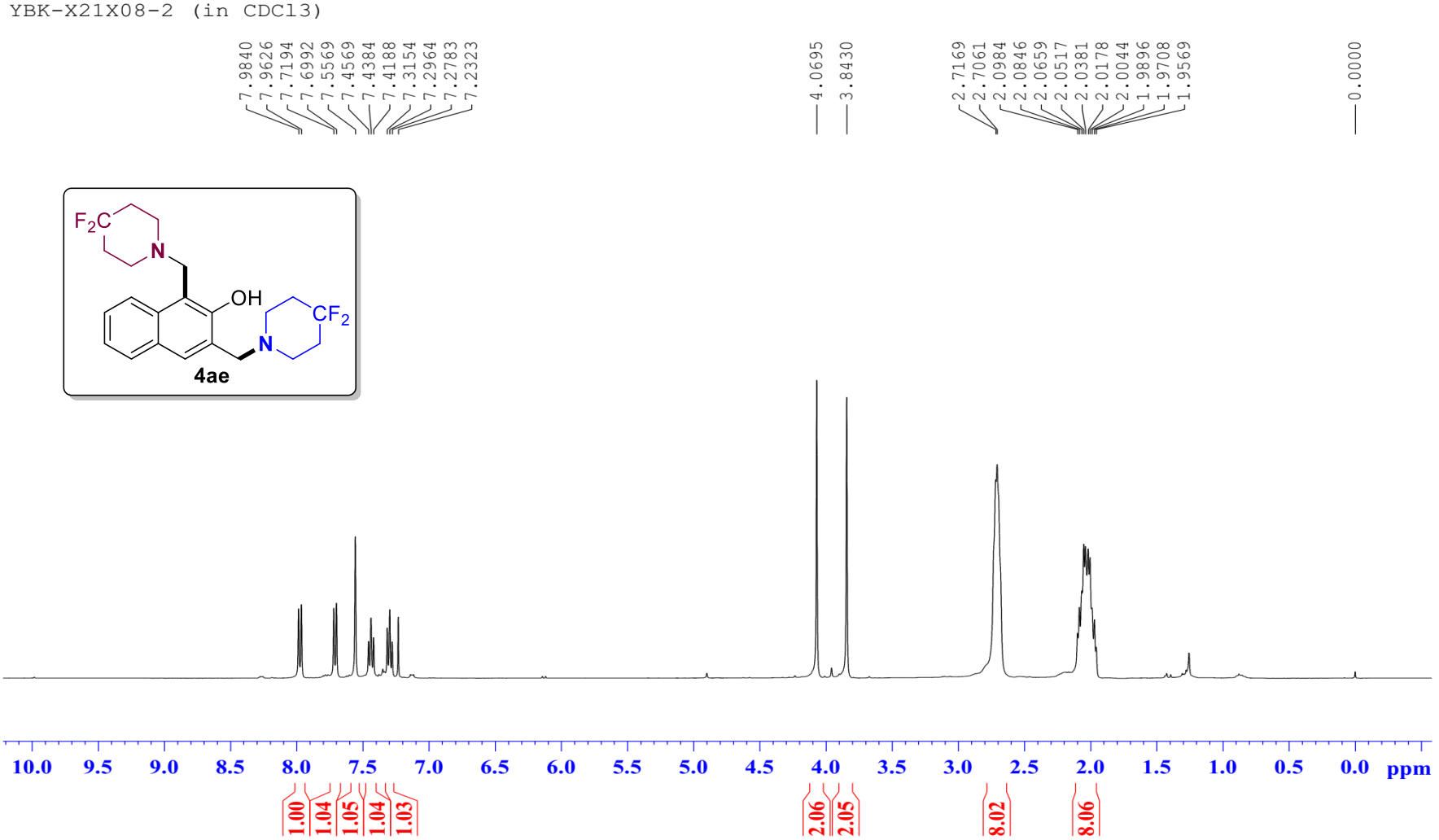
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ad



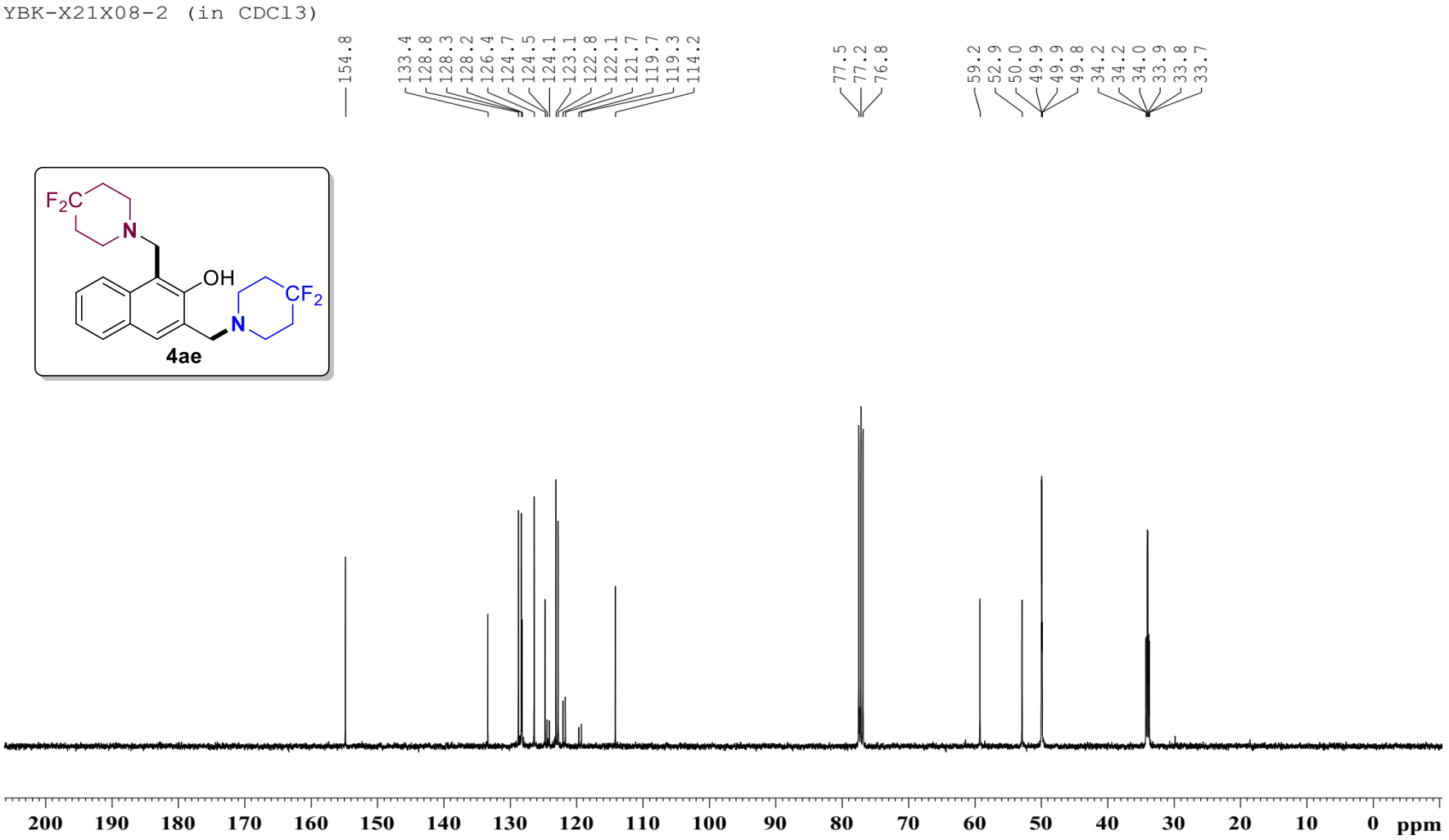
^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ad



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 4ae

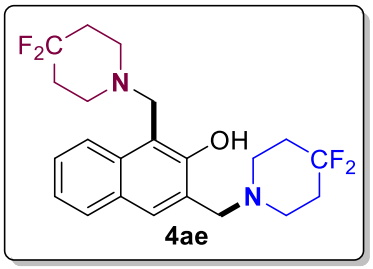


^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ae



^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4ae

YBK-X21X08-2 (in CDCl3)



4ae