Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

N-Heterocyclic Carbene (NHC)-Catalyzed Intramolecular Benzoin Condensation–Oxidation

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1. General information

All the reactions were carried out with an oven dried round bottom flask/Schlenk tube. Reactions were magnetically stirred and monitored by analytical thin layer chromatography (TLC). TLC was performed on Merck silica gel 60 F_{254}; UV lamp was used as visualizing agent, I_2 or $KMnO_4$ as developing agents. Purification of products was carried out by column chromatography by using 60-120/100-200 mesh silica and EtOAc/hexane were used as eluents and concentration under reduced pressure was performed by rotary evaporator at 40-45 ^oC, at appropriate pressure. The yields were given to the isolated products.

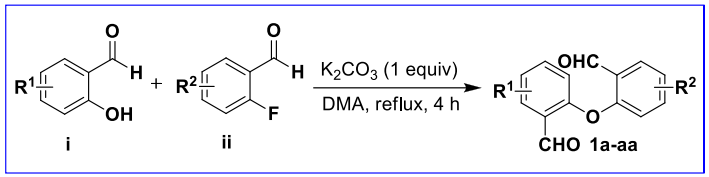
All the solvents, which were used in the reactions were dried and freshly distilled solvents according to their standard procedures, wherever required, and transferred under argon. Dry solvents like DMF, DMSO, CH_3CN, *t*-BuOH, DME and 1,4-dioxane were purchased from Finar Scientifics, India. These were stored over activated 4 Å molecular sieves.

All the reagents, substrates, catalysts, deuterated solvents were purchased from commercial suppliers like as Alfa Aesar, Sigma Aldrich, TCI, S.D Fine chemicals, India. Those were used without further purification.

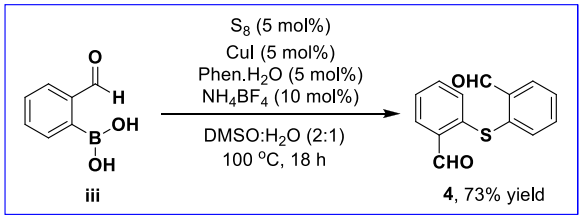
^{1}H-NMR spectra were recorded on 300, 400 and 500 MHz instruments. Chemical shifts are reported in ppm with the reference solvent as the internal standards (TMS = 0; $CDCl_3$ = 7.26; DMSO-d_6 = 2.50). The following abbreviations were used to explain the multiplicity of the spectra (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet). ^{13}C-NMR spectra were recorded on 75, 100, and 125 MHz spectrometers. Peaks which appears at 1.26, 0.86 in ^{1}H-NMR and 29.7 in ^{13}C-NMR corresponds to the residual grease present in the solvent (Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem*. **1997**, *62*, 7512–7515). Mass spectra were analysed by Electrospray Ionization (ESI) method and were obtained on a Shimadzu LCMS-2020 mass spectrometer. High resolution mass spectra were recorded on a Thermo scientific Exactive^{TM} Orbitrap mass spectrometer or Q STAR XL Hybrid MS/M. Melting points (MP) were determined using a Super Fit capillary point apparatus. MPs reported in this work are uncorrected. Infrared spectroscopy (IR-neat) was performed on a BRUKER FT-IR spectrophotometer in chloroform, and IR [KBr] spectra were recorded on a THERMO NICOLET NEXUS 670 FT-IR instrument.

2. Synthesis of starting materials 1a-aa & 4 & 7

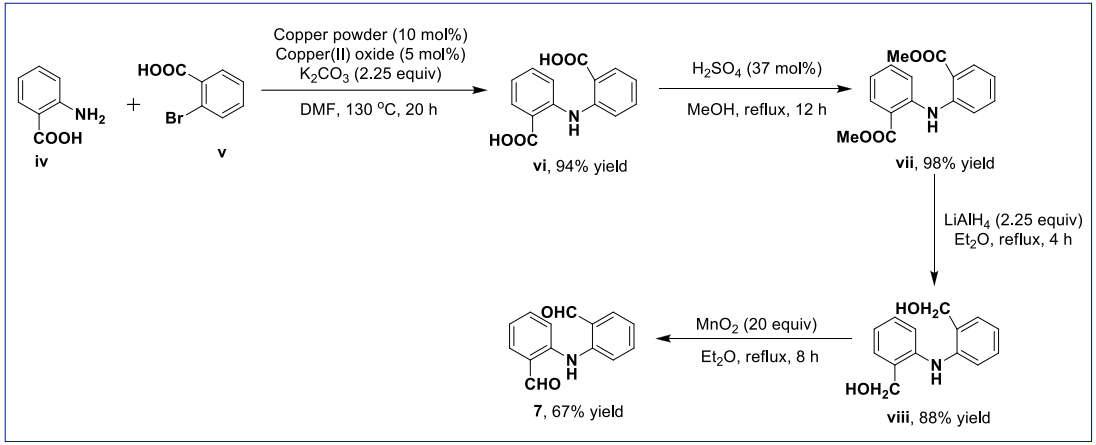
2,2'-Oxydibenzaldehyde 1a was synthesized by using the literature reported method and also adopted for the synthesis of 2,2'-oxydibenzaldehyde derivatives 1b-aa.[1]

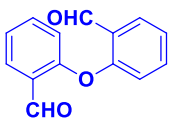


2,2'-Thiodibenzaldehyde 4 was synthesized by using reported method.[2]



2,2'-Azanediyldibenzaldehyde 7 was synthesized by using reported method.[3]

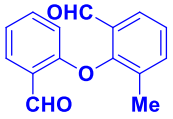




1a, 85%

1b, 63%

1c, 60%



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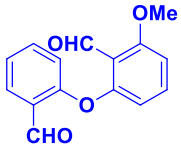

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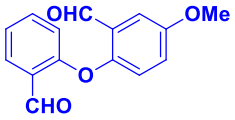

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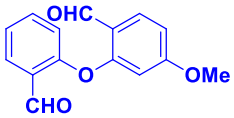

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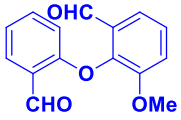

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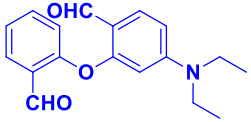

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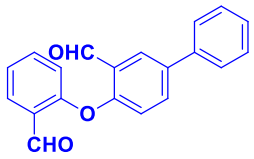

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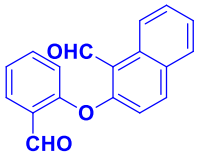

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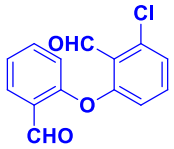

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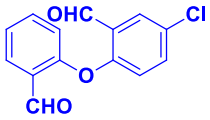

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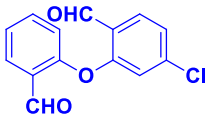

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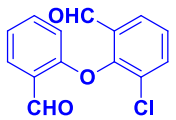

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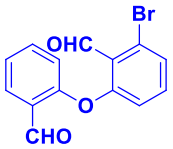

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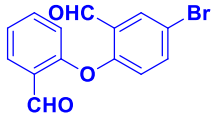
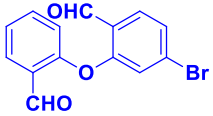


1q, 93%



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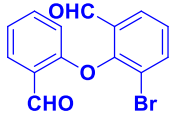

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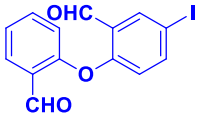

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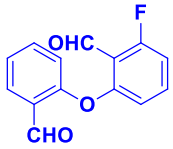
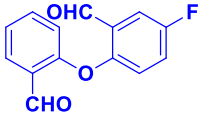
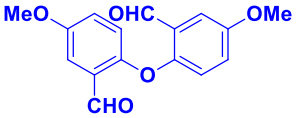


1u, 53%



1v, 55%

1w, 64%



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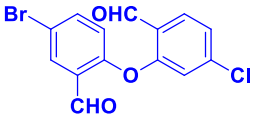
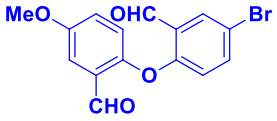


1y, 58%



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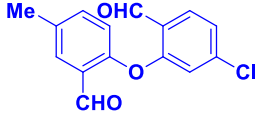
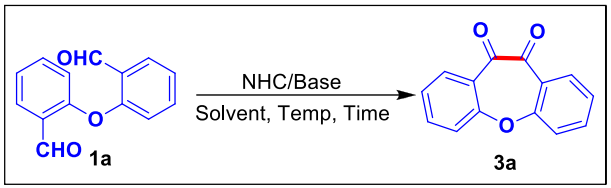


1aa, 68%

3. General procedure for the optimization study

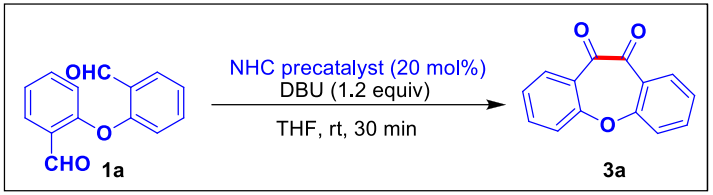


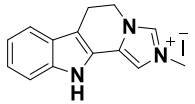
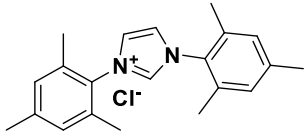
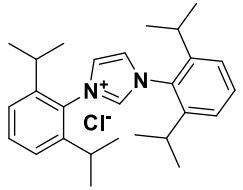
2,2'-Oxydibenzaldehyde **1a** (1 equiv, 0.25 mmol, 56 mg) and NHC precatalyst (0.05 mmol, 20 mol%) were taken in a clean and dried two necked round bottom flask, it was evacuated and back filled with argon gas (2-3 cycles). Then were added dry solvent (2.5 mL) by syringe followed by the drop wise addition of base (1.2 equiv, 0.3 mmol) under positive pressure of argon. Then reaction mixture was stirred at the temperature and time as mentioned in optimization Tables S1-S4. After this time, water (15 mL) was added to the reaction mixture and extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (3 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 5:95) on 60-120 mesh silica gel to afford the dibenzo[*b*,*f*]oxepine-10,11-dione **3a** as a pure product.

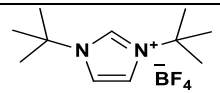
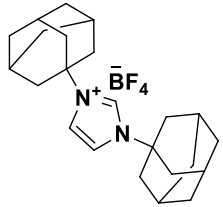
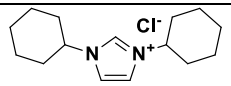
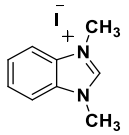
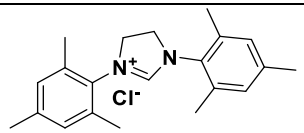
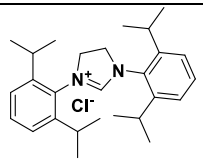
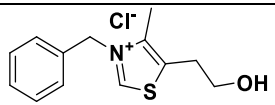
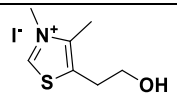
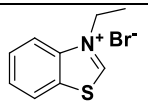
Note: **please see tables S1-S4, for screening of various NHCs, bases, solvents and their ratios/quantities**

4. Optimization survey

Table S1: Screening of various NHC precatalysts



Entry	NHC precatalyst (20 mol%)	Structure of the NHC precatalyst	% Yield of 3a
1	2-methyl-6,11-dihydro-5*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indol-2-ium iodide **A1**		42
2	1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride **A2**		85
3	1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride **A3**		–

4	1,3-Di-*tert*-butylimidazolium tetrafluoroborate **A4**		–
5	1,3-Bis(1-adamantyl)imidazolium tetrafluoroborate **A5**		–
6	1,3-Dicyclohexylimidazolium chloride **A6**		–
7	1,3-Dimethyl-1*H*-benzimidazolium iodide **A7**		–
8	1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride **B1**		48
9	1,3-Bis-(2,6-diisopropylphenyl)imidazolinium chloride **B2**		65
10	**3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride C1**		92
11	5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide **C2**		60
12	3-Ethylbenzothiazolium bromide **C3**		–

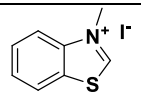
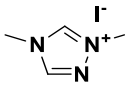
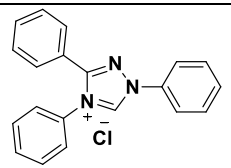
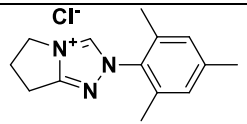
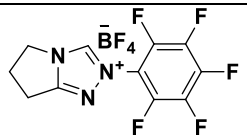
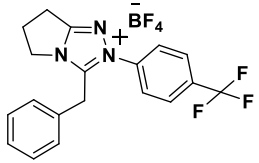
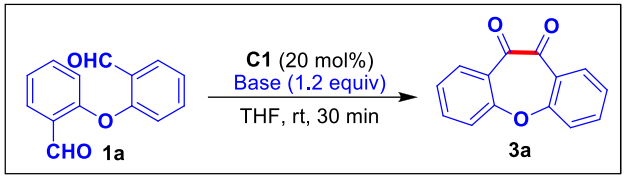
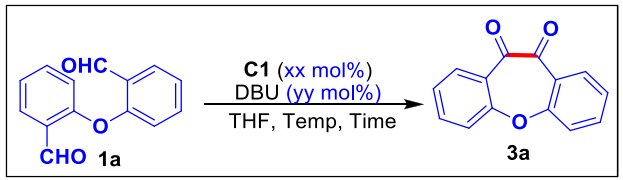
13	3-Methylbenzothiazolium iodide **C4**		–
14	1,4-Dimethyl-1,2,4-triazolium iodide **D1**		58
15	1,3,4-triphenyl-1*H*-1,2,4-triazol-4-ium chloride **D2**		65
16	2-Mesityl-2,5,6,7-tetrahydropyrrolo[2,1-*c*][1,2,4] triazol-4-ium chloride **D3**		52
17	6,7-Dihydro-2-pentafluorophenyl-5*H*-pyrrolo[2,1-*c*]-1,2,4-triazolium tetrafluoroborate **D4**		58
18	(*S*)-Benzyl-2-[4-(trifluoroMethyl)phenyl]-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazolium tetrafluoroborate **D5**		45

Table S2: Screening of various bases



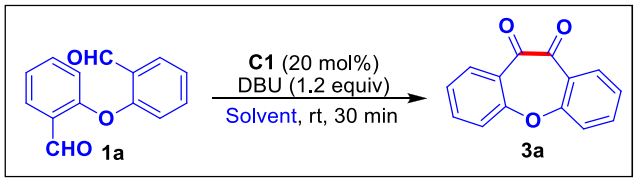
Entry	Base (1.2 equiv)	% Yield of 3a
1	Et_3N	traces
2	1,4-Diazabicyclo[2.2.2]octane (DABCO)	55
3	1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)	55
4	K_2CO_3	45
5	K_3PO_4	–
6	NaH	35
7	Cs_2CO_3	10
8	KOH	traces
9	KO^tBu	34
10	EtOAc	31
11	**1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)**	92

Table S3: Screening of molar equivalents of NHC, DBU and reaction conditions



Entry	NHC precatalyst C1 (xx mol%)	DBU (yy mol%)	Temp. (°C)	Time (min)	% Yield of 3a
1	10	120	RT	30	81
2	15	120	RT	30	84
3	**20**	**120**	**RT**	**30**	**92**
4	20	100	RT	30	85
5	20	50	RT	30	71
6	20	30	RT	30	55
7	20	120	40	30	86
8	20	120	60	30	78
9	20	120	RT	60	78

Table S4: Screening of various solvents



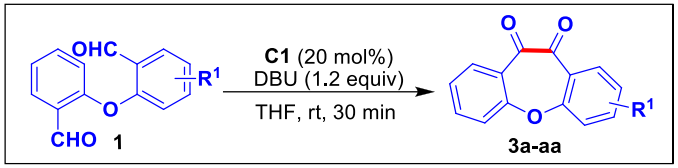
Entry	NHC.C1 (mol%)	DBU (mol%)	Solvent	Temp. (°C)	Time (min)	% Yield of 3a
1	20	120	**THF**	RT	30	92
2	20	120	CH_3CN	RT	30	–
3	20	120	1,4-Dioxane	RT	30	–
4	20	120	Dimethyl sulfoxide (DMSO)	RT	30	85
5	20	120	*N*,*N*-Dimethylformamide (DMF)	RT	30	82
6	20	120	1,2-Dimethoxyethane (DME)	RT	30	61
7	20	120	*t*-BuOH	RT	30	traces
8	20	120	1,2-Dichloroethane (DCE)	RT	30	traces
9	20	120	EtOAc	RT	30	31
10	20	120	Toluene	RT	30	–
11	20	120	$CHCl_3$	RT	30	–
12	20	120	DCM	RT	30	–

Table S5: **Reaction without using NHC precatalyst (or) base**

(Optimized conditions mentioned entry 1, Table S4 were used)

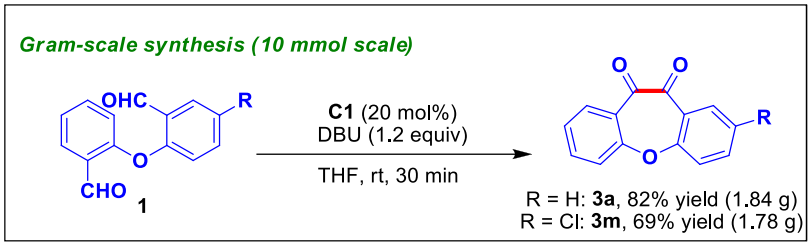
Entry	NHC precatalyst	Base	Solvent	% Yield of 3a
1	3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride **C1**	**No base**	THF	–
2	**No catalyst**	DBU	THF	–

5. General procedure for the synthesis of 3a-aa



General Procedure for the Synthesis of Dibenzo[*b*,*f*]oxepine-10,11-dione Derivatives 3a-aa. The substituted 2,2'-oxydibenzaldehyde **1** (1 equiv, 1 mmol) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL) under a positive pressure of argon. Then the reaction mixture was stirred at the room temperature for 30 minutes. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure on a rotavapor to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane) on silica gel to afford dibenzo[*b*,*f*]oxepine-10,11-dione derivatives **3a-aa** as pure products.

6. Gram-scale syntheses of 3a and 3m



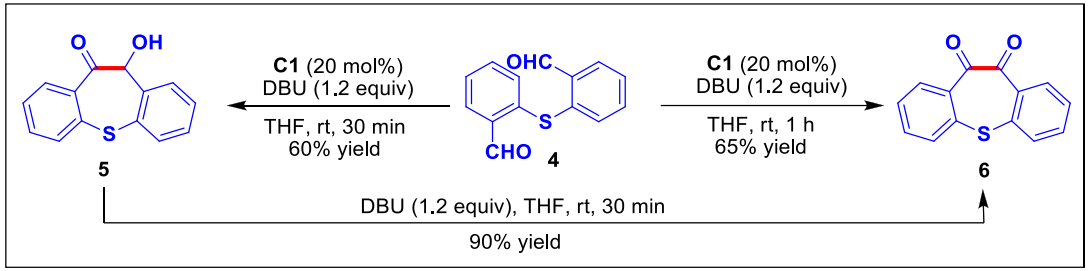
a. Experimental procedure for the gram-scale synthesis of dibenzo[*b,f*]oxepine-10,11-dione 3a:

2,2'-Oxydibenzaldehyde **1a** (1 equiv, 10 mmol, 2.26 g) and NHC precatalyst **C1** (2 mmol, 20 mol%, 540 mg) were taken in a clean and dried two necked round bottom flask, it was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (80 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 12 mmol, 1.7 mL) under positive pressure of argon. Then reaction mixture was stirred at the room temperature for 30 minutes. After this time, water was added to the reaction mixture (150 mL) and extracted with EtOAc (2 x 50 mL). The combined organic extract was washed with brine (30 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 10:90) on 60-120 mesh silica gel to afford the dibenzo[*b,f*]oxepine-10,11-dione **3a** as a yellow solid in 82% yield (1.84 g).

b. Experimental procedure for the gram-scale synthesis of 2-chlorodibenzo[*b,f*]oxepine-10,11-dione 3m:

5-Chloro-2-(2-formylphenoxy)benzaldehyde **1m** (1 equiv, 10 mmol, 2.60 g) and NHC precatalyst **C1** (2 mmol, 20 mol%, 540 mg) were taken in a clean and dried two necked round bottom flask, it was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (80 mL) by syringe followed by the dropwise addition of DBU (1.2 equiv, 12 mmol, 1.7 mL) under positive pressure of argon. Then reaction mixture was stirred at the room temperature for 30 min. After this time, water was added to the reaction mixture (150 mL) and extracted with EtOAc (2 x 50 mL). The combined organic extract was washed with brine (30 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 10:90) on 60-120 mesh silica gel to afford the 2-chlorodibenzo[*b,f*]oxepine-10,11-dione **3m** as a yellow solid in 69% yield (1.78 g).

7. Experimental procedure for the syntheses of 5 and 6



a. Experimental procedure for the synthesis of 11-hydroxydibenzo[*b,f*]thiepin-10(11*H*)-one 5:

2,2'-Thiodibenzaldehyde **4** (1 equiv, 1 mmol, 242 mg) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL) under a positive pressure of argon. Then the reaction mixture was stirred at the room temperature for 30 minutes. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 6:94) on 60-120 mesh silica gel to afford 11-hydroxydibenzo[*b,f*]thiepin-10(11*H*)-one **5** as a yellow solid in a 60% yield.

b. Experimental procedure for the synthesis of dibenzo[*b,f*]thiepine-10,11-dione 6:

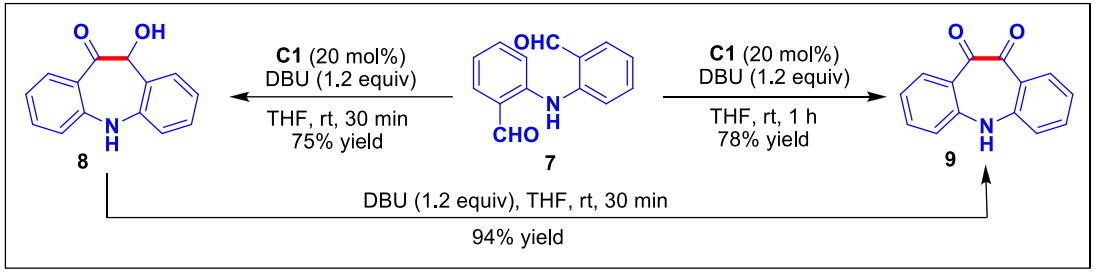
2,2'-Thiodibenzaldehyde **4** (1 equiv, 1 mmol, 242 mg) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL) under a positive pressure of argon. Then the reaction mixture was stirred at the room temperature for 1 h. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified

using column chromatography (EtOAc/Hexane, 5:95) on 60-120 mesh silica gel to afford dibenzo[*b*,*f*]thiepine-10,11-dione **6** as a yellow solid in a 65% yield.

c. Experimental procedure for the synthesis of dibenzo[*b*,*f*]thiepine-10,11-dione 6 from 11-hydroxydibenzo[*b*,*f*]thiepin-10(11*H*)-one 5 in the presence of DBU:

11-Hydroxydibenzo[*b*,*f*]thiepin-10(11*H*)-one **5** (1 equiv, 0.5 mmol, 121 mg) was taken in a 25 mL R.B. flask and add THF (5 mL) solvent followed by the addition of DBU (1.2 equiv, 0.6 mmol, 0.08 mL). Then reaction mixture was stirred at the room temperature for 30 minutes under open air. After this time, water was added to the reaction mixture (30 mL) and extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with brine (5 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 5:95) on 60-120 mesh silica gel to afford dibenzo[*b*,*f*]thiepine-10,11-dione **6** as a yellow solid in a 90% yield.

8. Experimental procedure for the syntheses of 8 and 9



a. Experimental procedure for the synthesis of 11-hydroxy-5*H*-dibenzo[*b*,*f*]azepin-10(11*H*)-one 8:

2,2'-Azanediyldibenzaldehyde **7** (1 equiv, 1 mmol, 225 mg) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL) under a positive pressure of argon. Then the reaction mixture was stirred at the room temperature for 30 minutes. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 5:95) on 60-120 mesh silica gel to afford 11-hydroxy-5*H*-dibenzo[*b*,*f*]azepin-10(11*H*)-one **8** as a yellow solid in a 75% yield.

b. Experimental procedure for the synthesis of 5*H*-dibenzo[*b*,*f*]azepine-10,11-dione 9:

2,2'-Azanediyldibenzaldehyde **7** (1 equiv, 1 mmol, 225 mg) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL) under a positive pressure of argon. Then the reaction mixture was stirred at the room temperature for 1 h. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified

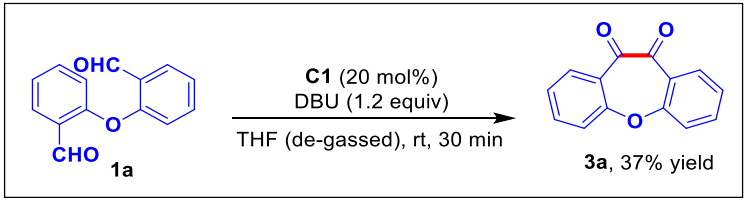
using column chromatography (EtOAc/Hexane, 5:95) on 60-120 mesh silica gel to afford 5*H*-dibenzo[*b*,*f*]azepine-10,11-dione **9** as a yellow solid in a 78% yield.

c. Experimental procedure for the synthesis of 5*H*-dibenzo[*b*,*f*]azepine-10,11-dione 9 from 11-hydroxy-5*H*-dibenzo[*b*,*f*]azepin-10(11*H*)-one 8 in the presence of DBU:

11-Hydroxy-5*H*-dibenzo[*b*,*f*]azepin-10(11*H*)-one **8** (1 equiv, 0.5 mmol, 113 mg) was taken in a 25 mL R.B. flask and add THF (5 mL) solvent followed by the addition of DBU (1.2 equiv, 0.6 mmol, 0.08 mL). Then reaction mixture was stirred at the room temperature for 30 minutes under open air. After this time, water was added to the reaction mixture (30 mL) and extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with brine (5 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 5:95) on silica gel to afford 5*H*-dibenzo[*b*,*f*]azepine-10,11-dione **9** as a yellow solid in a 94% yield.

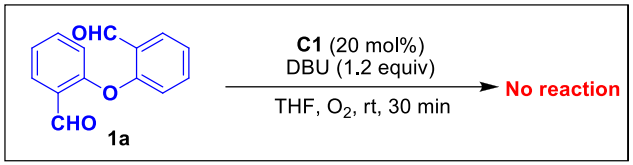
9. Control experiments/Mechanistic studies

a. By using de-gassed solvent (with argon purging):



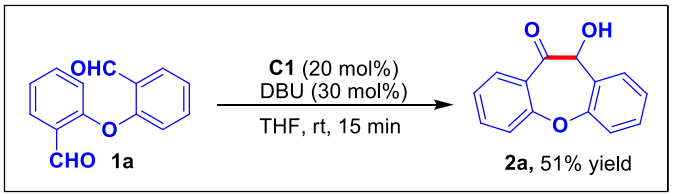
2,2'-Oxydibenzaldehyde **1a** (1 equiv, 1 mmol, 226 mg) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. It was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL, de-gassed) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL) under a positive pressure of argon. Then the reaction mixture was stirred at the room temperature for 30 minutes. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 10:90) on 60-120 mesh silica gel to afford the dibenzo[*b*,*f*]oxepine-10,11-dione **3a** as a yellow solid in a 37% yield.

b. In open air/under oxygen atmosphere:



2,2'-Oxydibenzaldehyde **1a** (1 equiv, 1 mmol, 226 mg) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask. Then were added dry THF (8 mL) by syringe followed by the drop wise addition of DBU (1.2 equiv, 1.2 mmol, 0.17 mL). Then the reaction mixture was stirred at the room temperature for 30 minutes under open air. Then water (40 mL) was added to the reaction mixture and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (10 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 5:95) on silica gel to recover pure unreacted 2,2'-Oxydibenzaldehyde **1a** in a 92% yield.

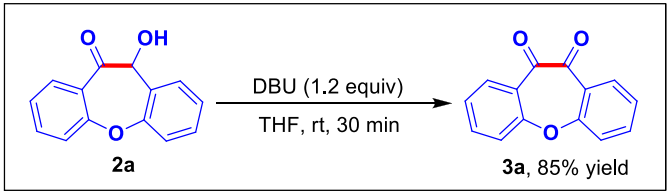
c. Experimental procedure for the synthesis of 11-hydroxydibenzo[*b*,*f*]oxepin-10(11*H*)-one 2a:



2,2'-Oxydibenzaldehyde **1a** (1 equiv, 1 mmol, 0.226 g) and NHC precatalyst **C1** (0.2 mmol, 20 mol%, 54 mg) were taken in a clean and dried two necked round bottom flask, it was evacuated and back filled with argon gas (2-3 cycles). Then were added dry THF (8 mL) by

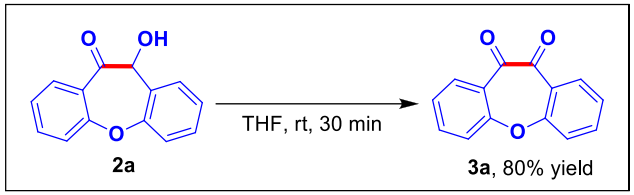
syringe followed by the dropwise addition of DBU (0.3 mmol, 30 mol%, 0.04 mL) under a positive pressure of argon. Then reaction mixture was stirred at room temperature for 15 minutes. After this time, water was added to the reaction mixture (40 mL) and extracted with EtOAc (2 x 15 mL). The combined organic extract was washed with brine (15 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 3:97) on silica gel to afford the 11-hydroxydibenzo[*b*,*f*]oxepin-10(11*H*)-one **2a** as a yellow solid in a 51% yield.

d. Experimental procedure for the synthesis of 2a from 11-hydroxydibenzo[*b*,*f*]oxepin-10(11*H*)-one 3a in the presence of DBU:



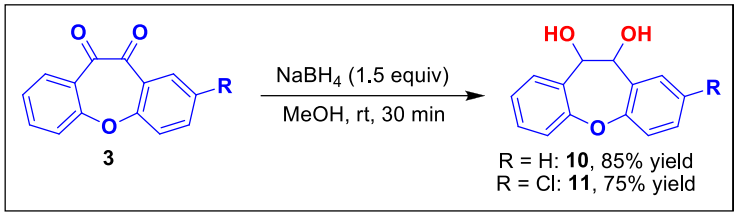
11-Hydroxydibenzo[*b*,*f*]oxepin-10(11*H*)-one **2a** (1 equiv, 0.5 mmol, 113 mg) was taken in a 25 mL R.B. flask and were added THF (5 mL) followed by DBU (1.2 equiv, 0.6 mmol, 0.08 mL). Then reaction mixture was stirred at the room temperature for 30 minutes under open air. After this time, water was added to the reaction mixture (30 mL) and extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with brine (5 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 10:90) on silica gel to afford the dibenzo[*b*,*f*]oxepine-10,11-dione **3a** as a yellow solid in a 85% yield.

e. Experimental procedure for the synthesis of 3a from 11-hydroxydibenzo[*b,f*]oxepin-10(11*H*)-one 2a in the absence of DBU:



11-Hydroxydibenzo[*b,f*]oxepin-10(11*H*)-one **2a** (1 equiv, 0.5 mmol, 113 mg) was taken in a 25 mL R.B. flask and add THF (5 mL) solvent. Then reaction mixture was stirred at the room temperature for 30 minutes under open air. After this time, water was added to the reaction mixture (30 mL) and extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with brine (5 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 10:90) on silica gel to afford the dibenzo[*b,f*]oxepine-10,11-dione **3a** as a yellow solid in a 80% yield.

10. Experimental procedure for the reduction of 3a and 3m by using $NaBH_4$



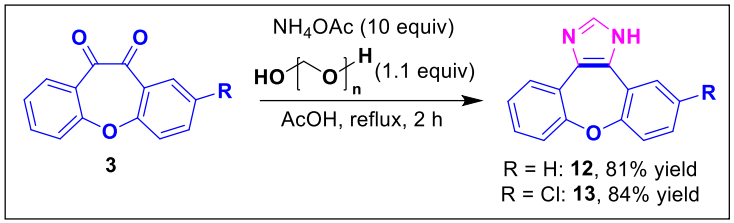
a. Experimental procedure for the reduction of dibenzo[*b,f*]oxepine-10,11-dione 3a by using $NaBH_4$:

Dibenzo[*b,f*]oxepine-10,11-dione **3a** (1 equiv, 1 mmol, 224 mg) was dissolved in MeOH (8 mL) and kept at 0 ^oC, then $NaBH_4$ (1.5 equiv, 1.5 mmol, 57 mg) was added portion-wise at the same temperature and the resulting reaction mixture was stirred at room temperature for 30 min. After this time, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and water was added (30 mL), extracted with EtOAc (2 x 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 40:60) on 60-120 mesh silica gel to afford 10,11-dihydrodibenzo[*b,f*]oxepine-10,11-diol **10** as a white solid in a 85% yield.

b. Experimental procedure for the reduction of 2-chlorodibenzo[*b,f*]oxepine-10,11-dione 3m by using $NaBH_4$:

2-Chlorodibenzo[*b,f*]oxepine-10,11-dione **3m** (1 equiv, 1 mmol, 258 mg) was dissolved in MeOH (8 mL) and kept at 0 ^oC, then $NaBH_4$ (1.5 equiv, 1.5 mmol, 57 mg) was added portion-wise at the same temperature and the resulting reaction mixture was stirred at room temperature for 30 min. After this time, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and water was added (30 mL), extracted with EtOAc (2 x 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 40:60) on 60-120 mesh silica gel to afford 10,11-dihydrodibenzo[*b,f*]oxepine-10,11-diol **11** as a white solid in a 75% yield.

11. Experimental procedure for the synthesis of 12 and 13



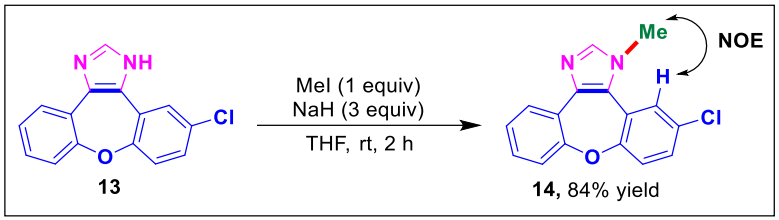
a. Experimental procedure for the synthesis of 1*H*-Dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole 12 from 3a:

Dibenzo[*b*,*f*]oxepine-10,11-dione **3a** (1 equiv, 1 mmol, 224 mg), ammonium acetate (10 equiv, 10 mmol, 770 mg) and paraformaldehyde (1.07 equiv, 1.07 mmol, 32 mg) were taken in a two necked R.B. flask and glacial acetic acid was added (7 mL). Then the reaction mixture was allowed to stir at reflux temperature. After 2 h, the reaction mixture was cooled to room temperature, and water was added (40 mL), extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with aq. Na_2CO_3 (10 mL) and brine (5 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 50:50) on 60-120 mesh silica gel to afford the 1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole **12** as a white solid in a 81% yield.

b. Experimental procedure for the synthesis of 11-Chloro-1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole 13 from 3m:

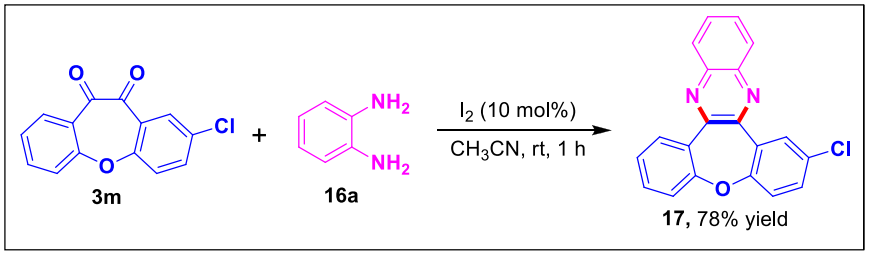
2-Chlorodibenzo[*b*,*f*]oxepine-10,11-dione **3m** (1 equiv, 1 mmol, 258 mg), ammonium acetate (10 equiv, 10 mmol, 770 mg) and paraformaldehyde (1.07 equiv, 1.07 mmol, 32 mg) were taken in a two necked R.B. flask and glacial acetic acid was added (7 mL). Then the reaction mixture was allowed to stirr at reflux temperature. After 2 h, the reaction mixture was cooled to room temperature, and water was added (40 mL), extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with aq. Na_2CO_3 (10 mL) and brine (5 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 50:50) on 60-120 mesh silica gel to afford the 11-chloro-1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole **13** as a white solid in a 84% yield.

12. Experimental procedure for the synthesis of 14 from 13



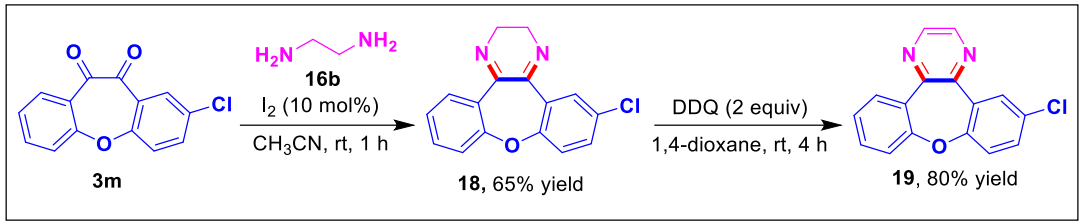
To a solution of 11-chloro-1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole **13** (1 equiv, 1 mmol, 268 mg) in dry THF (10 mL) was added sodium hydride (60% dispersion in mineral oil, 3 equiv, 3 mmol, 120 mg) portion-wise at 0 ^{o}C and the mixture was stirred at the same temperature for 5 min. To this solution was added methyl iodide (1 equiv, 1 mmol, 0.06 mL) at 0 ^{o}C and the reaction mixture was stirred at room temperature for 2 h. After this time, water was added to the reaction mixture (30 mL) and extracted with EtOAc (2 x 10 mL). The combined organic extract was washed with brine (5 mL), the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 40:60) on 60-120 mesh silica gel to afford 11-chloro-1-methyl-1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole **14** as a colorless liquid in a 84% yield.

13. Experimental procedure for the synthesis of 7-chlorodibenzo[2,3:6,7]oxepino[4,5-*b*]quinoxaline 17



To a solution of 2-chlorodibenzo[*b*,*f*]oxepine-10,11-dione **3m** (1 equiv, 0.5 mmol, 129 mg) and *o*-phenylenediamine **16a** (1.2 equiv, 0.6 mmol, 65 mg) in CH_3CN (0.5 mL) was added I_2 (0.05 mmol, 10 mol%, 12 mg). The resultant reaction mixture was stirred at room temperature under open air until all the starting material **3m** was consumed (in 1 h). After this time, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (20 mL) and water was added (30 mL), extracted with EtOAc (2 x 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 5:95) on silica gel to afford 7-chlorodibenzo[2,3:6,7]oxepino[4,5-*b*]quinoxaline **17** as a white solid in a 78% yield.

14. Synthesis of 6-chlorodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine 19



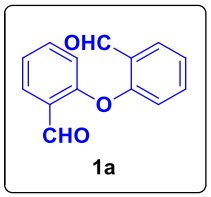
a. Experimental procedure for the synthesis of 6-chloro-2,3-dihydrodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine 18:

To a solution of 2-chlorodibenzo[*b*,*f*]oxepine-10,11-dione **3m** (1 equiv, 1 mmol, 258 mg) and ethylenediamine **16b** (1.2 equiv, 1.2 mmol, 0.08 mL) in CH_3CN (1 mL) was added I_2 (0.1 mmol, 10 mol%, 12 mg). The resultant reaction mixture was stirred at room temperature under open air until all the starting material **3m** was consumed (in 1 h). After this time, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (30 mL). Then water was added (50 mL) and extracted with EtOAc (2 x 20 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 15:85) on silica gel to afford 6-chloro-2,3-dihydrodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine **18** as a white solid in a 65% yield.

b. Experimental procedure for the synthesis of 6-chlorodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine 19:

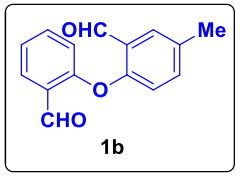
To a solution of 6-chloro-2,3-dihydrodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine **18** (1 equiv, 0.5 mmol, 141 mg) in 1,4-dioxane (8 mL) was added DDQ (2 equiv, 1 mmol, 227mg) at room temperature. The solution turned from yellow to black immediately. After 4 hours solvent was removed under reduced pressure. To the residue 10% aq. NaOH solution (50 mL) was added and the resulting solution was extracted with EtOAc (2 x 10 mL). The combined organic extracts were washed with brine (5 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane, 40:60) on silica gel to afford 6-chlorodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine **19** as a white solid in a 80% yield.

15. Spectroscopic data



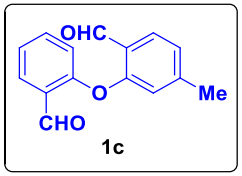
1a

2,2'-Oxydibenzaldehyde (1a):- White solid, 480 mg (2.124 mmol), 85% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 80-82 °C; **IR** ($CHCl_3$) 1222, 1598, 1685, 3078 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.93-6.95 (dd, *J* = 8.3, 0.8 Hz, 2H), 7.27-7.31 (m, 2H), 7.55-7.60 (m, 2H), 7.80-7.97 (dd, *J* = 7.8, 1.8 Hz, 2H), 10.51 (s, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 119.2, 124.7, 127.4, 129.3, 136.1, 159.0, 188.7; **MS** (ESI, *m/z*): $[M+H]^+$ 227; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{11}O_3$ $[M+H]^+$ 227.0703, found 227.0701. The spectroscopic data were in good agreement with the reported data.[1]



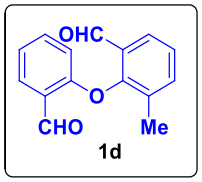
1b

2-(2-Formylphenoxy)-5-methylbenzaldehyde (1b):- Yellow solid, 378 mg (1.575 mmol), 63% yield, R_f = 0.45 (EtOAc/Hex, 10:90); **MP** 94-96 °C; **IR** ($CHCl_3$) 1150, 1214, 1598, 1682, 2855, 3076 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.40 (s, 3H), 6.87-6.89 (d, *J* = 8.4 Hz, 2H), 7.23-7.28 (m, 1H), 7.37-7.42 (m, 1H), 7.52-7.56 (m, 1H), 7.78-7.79 (d, *J* = 2.0 Hz, 1H), 7.96-7.98 (dd, *J* = 7.8, 1.8 Hz, 1H), 10.43 (s, 1H), 10.53 (s, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 20.8, 118.5, 119.8, 124.2, 127.0, 127.3, 129.2, 129.3, 134.8, 136.1, 136.9, 156.6, 159.7, 188.8, 188.9; **MS** (ESI, *m/z*): $[M+H]^+$ 241; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_3$ $[M+H]^+$ 241.0859, found 241.0867.



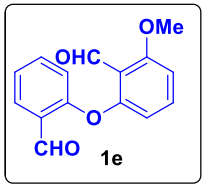
1c

2-(2-Formylphenoxy)-4-methylbenzaldehyde (1c):- Brown solid, 360 mg (1.5 mmol), 60% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 70-72 ^{o}C; **IR** ($CHCl_3$) 1151, 1233, 1599, 1683, 2855, 3076 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.39 (s, 3H), 6.86-6.89 (d, *J* = 8.4 Hz, 2H), 7.22-7.23 (d, *J* = 0.7 Hz, 1H), 7.38-7.40 (m, 1H), 7.51-7.57 (m, 1H), 7.77 (s, 1H), 7.95-7.98 (m, 1H), 10.42 (s, 1H), 10.52 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 22.0, 119.1, 119.6, 124.4, 125.0, 125.7, 127.2, 129.1, 129.2, 136.1, 147.9, 158.9, 159.1, 188.3, 188.7; **MS** (ESI, *m/z*): $[M+H]^+$ 241; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_3$ $[M+H]^+$ 241.0859, found 241.0857.

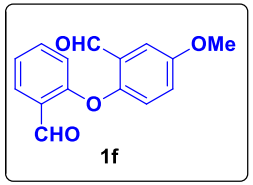


1d

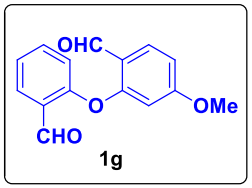
2-(2-Formylphenoxy)-3-methylbenzaldehyde (1d):- Yellow solid, 408 mg (1.700 mmol), 68% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 90-92 ^{o}C; **IR** ($CHCl_3$) 1156, 1222, 1599, 1688, 2869, 3079 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.21 (s, 3H), 6.43-6.45 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.12-7.14 (m, 1H), 7.34-7.44 (m, 2H), 7.57-7.60 (m, 1H), 7.60-7.84 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.95-7.98 (dd, *J* = 7.7, 1.8 Hz, 1H), 10.20 (s, 1H), 10.76 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 16.0, 114.1, 122.8, 124.7, 126.5, 127.5, 129.4, 129.6, 132.7, 136.2, 138.2, 154.2, 160.8, 188.9, 189.0; **MS** (ESI, *m/z*): $[M+H]^+$ 241; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_3$ $[M+H]^+$ 241.0859, found 241.0868.



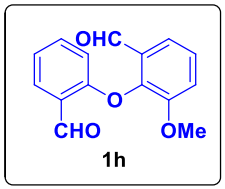
2-(2-Formylphenoxy)-6-methoxybenzaldehyde (1e):- Light red solid, 448 mg (1.750 mmol), 70% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 102-104 °C; **IR** ($CHCl_3$) 1075, 1237, 1596, 1684, 2922, 3078 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.97 (s, 3H), 6.52-6.54 (d, *J* = 8.3 Hz, 1H), 6.81-6.87 (m, 2H), 7.20-7.24 (m, 1H), 7.45-7.53 (m, 2H), 7.94-7.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 10.47 (s, 1H), 10.52 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.4, 107.7, 112.2, 117.0, 118.6, 124.1, 127.1, 128.8, 135.8, 136.0, 158.1, 159.4, 162.7, 188.2, 189.3; **MS** (ESI, *m/z*): $[M+H]^+$ 257; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_4$ $[M+H]^+$ 257.0808, found 257.0825. The spectroscopic data were in good agreement with the reported data. [4]



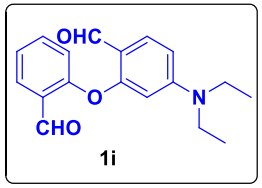
2-(2-Formylphenoxy)-5-methoxybenzaldehyde (1f):- Yellow solid, 627 mg (2.450 mmol), 98% yield, R_f = 0.40 (EtOAc/Hex, 5:95); **MP** 96-98 °C; **IR** ($CHCl_3$) 1152, 1213, 1599, 1684, 2858, 3076 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.87 (s, 3H), 6.79-6.82 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.97-6.99 (d, *J* = 9.0 Hz, 1H), 7.16-7.23 (m, 2H), 7.44-7.45 (d, *J* = 3.2 Hz, 1H), 7.49-7.54 (m, 1H), 7.95-7.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 10.37 (s, 1H), 10.57 (s, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 56.1, 112.5, 121.7, 123.1, 124.4, 125.5, 126.2, 126.5, 132.0, 136.0, 151.5, 156.9, 157.1, 186.2, 186.3; **MS** (ESI, *m/z*): $[M+H]^+$ 257; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_4$ $[M+H]^+$ 257.0808, found 257.0813.



2-(2-Formylphenoxy)-4-methoxybenzaldehyde (1g):- Brown liquid, 416 mg (1.625 mmol), 65% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **IR** ($CHCl_3$) 1156, 1214, 1598, 1681, 2851, 3075 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) 3.80 (s, 3H), 6.36-6.37 (d, *J* = 2.3 Hz, 1H), 6.77-6.81 (dd, *J* = 8.8, 1.7 Hz, 1H), 6.96-6.97 (d, J = 8.3 Hz, 1H), 7.29-7.31 (d, *J* = 7.6 Hz, 1H), 7.55-7.61 (m, 1H), 7.93-7.99 (m, 2H), 10.32 (s, 1H), 10.47 (s, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 56.0, 104.5, 110.5, 119.4, 121.0, 124.8, 127.4, 129.3, 131.2, 136.2, 158.8, 160.8, 166.1, 187.3, 188.7; **MS** (ESI, *m/z*): $[M+H]^+$ 257; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_4$ $[M+H]^+$ 257.0808, found 257.0807.

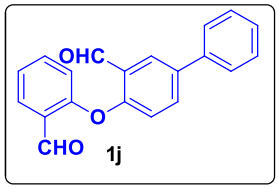


2-(2-Formylphenoxy)-3-methoxybenzaldehyde (1h):- White solid, 531 mg (2.075 mmol), 83% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 93-95 ^oC; **IR** ($CHCl_3$) 1062, 1276, 1590, 1686, 2928, 3086 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.75 (s, 3H), 6.57-6.59 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.13-7.17 (t, *J* = 7.5 Hz, 1H), 7.25-7.28 (m, 1H), 7.35-7.45 (m, 2H), 7.57-7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.94-7.96 (dd, *J* = 7.7, 1.8 Hz, 1H), 10.31 (s, 1H), 10.74 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.3, 114.8, 118.6, 120.0, 122.9, 125.1, 126.7, 128.7, 130.5, 135.7, 145.6, 152.5, 161.2, 188.9, 189.3; **MS** (ESI, *m/z*): $[M+H]^+$ 257; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{13}O_4$ $[M+H]^+$ 257.0808, found 257.0814.



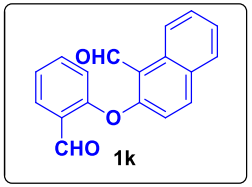
1i

4-(Diethylamino)-2-(2-formylphenoxy)benzaldehyde (1i):- Brown solid, 371 mg (1.249 mmol), 50% yield, R_f = 0.50 (EtOAc/Hex, 10:90); **MP** 92-94 ^{o}C; **IR** ($CHCl_3$) 1000, 1217, 1590, 1689, 2922, 3076 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 1.13-1.16 (t, *J* = 7.1 Hz, 6H), 3.32-3.37 (q, *J* = 7.1 Hz, 4H), 6.02-6.03 (d, *J* = 2.4 Hz, 1H), 6.51-6.54 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.92-6.95 (d, *J* = 8.3 Hz, 1H), 7.20-7.23 (t, *J* = 7.5 Hz, 1H), 7.51-7.55 (m, 1H), 7.83-7.85 (d, *J* = 9.0 Hz, 1H), 7.95-7.98 (dd, *J* = 7.8, 1.8 Hz, 1H), 10.09 (s, 1H), 10.56 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 12.6, 45.0, 101.0, 108.1, 116.1, 118.2, 123.7, 126.7, 128.7, 131.2, 136.0, 153.8, 160.1, 160.8, 186.3, 189.2; **MS** (ESI, *m/z*): $[M+H]^+$ 298; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{20}O_3N$ $[M+H]^+$ 298.1438, found 298.1446.

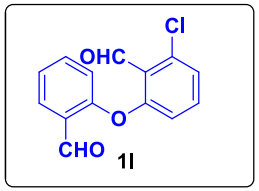


1j

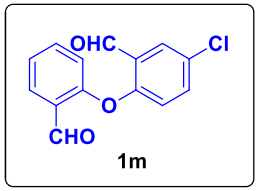
4-(2-Formylphenoxy)biphenyl-3-carbaldehyde (1j):- Brown liquid, 566 mg (1.874 mmol), 75% yield, R_f = 0.50 (EtOAc/Hex, 5:95); **IR** ($CHCl_3$) 1154, 1221, 1599, 1683, 3032, 3063 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.01-7.03 (d, *J*= 8.3 Hz, 2H), 7.28-7.48 (m, 4H), 7.58-7.60 (d, *J* = 7.5 Hz, 3H), 7.78-7.80 (d, *J* = 8.6 Hz, 1H), 7.98-8.00 (d, *J* = 7.6 Hz, 1H), 8.19 (s, 1H), 10.52 (s, 1H), 10.54 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 119.1, 119.2, 119.5, 124.5, 124.6, 126.8, 127.2, 127.3, 127.9, 129.0, 129.1, 129.2, 134.3, 136.0, 137.6, 138.8, 158.1, 158.7, 188.5, 188.6; **MS** (ESI, *m/z*): $[M+H]^+$ 303; **HRMS** (ESI, *m/z*): calcd for $C_{20}H_{15}O_3$ $[M+H]^+$ 303.1016, found 303.1031.



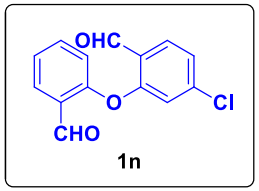
2-(2-Formylphenoxy)-1-naphthaldehyde (1k):- Light red solid, 172 mg (0.623 mmol), 25% yield, R_f = 0.50 (EtOAc/Hex, 10:90); **MP** 148-150 °C; **IR** ($CHCl_3$) 1155, 1225, 1599, 1680, 3077 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.90-6.96 (m, 1H), 7.11-7.13 (d, *J* = 9.0 Hz, 1H), 7.28-7.31 (t, *J* = 7.6 Hz, 1H), 7.54-7.59 (m, 2H), 7.70-7.74 (t, *J* = 7.8 Hz, 1H), 7.85-7.87 (d, *J* = 8.1 Hz, 1H), 8.01-8.09 (m, 2H), 9.32-9.33 (d, *J* = 8.7 Hz, 1H), 10.60 (s, 1H), 10.93 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 118.7, 118.9, 120.8, 124.5, 125.6, 126.6, 127.2, 128.6, 129.4, 130.4, 130.9, 131.4, 136.2, 137.7, 159.3, 160.4, 188.7, 191.1; **MS** (ESI, *m/z*): $[M+H]^+$ 277; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{13}O_3$ $[M+H]^+$ 277.0859, found 277.0869.



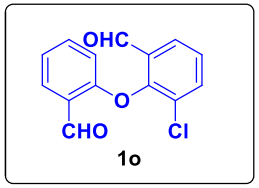
2-Chloro-6-(2-formylphenoxy)benzaldehyde (1l):- White solid, 513 mg (1.973 mmol), 79% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 88-90 °C; **IR** ($CHCl_3$) 769, 1241, 1599, 1693, 3079 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 6.85-6.89 (m, 2H), 7.24-7.30 (m, 2H), 7.43-7.46 (t, *J* = 8.2 Hz, 1H), 7.53-7.56 (m, 1H), 7.94-7.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 10.43 (s, 1H), 10.53 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 118.6, 118.7, 124.6, 125.0, 126.9, 127.1, 129.3, 134.8, 136.0, 137.6, 158.2, 158.8, 188.0, 188.8; **MS** (ESI, *m/z*): $[M+H]^+$ 261; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{35}Cl$ $[M+H]^+$ 261.0313, found 261.0313.



5-Chloro-2-(2-formylphenoxy)benzaldehyde (1m):- White solid, 455 mg (1.75 mmol), 70% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 91-93 °C; **IR** ($CHCl_3$) 760, 1225, 1598, 1686, 3038 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.88-6.90 (d, *J* = 8.8 Hz, 1H), 6.94-6.97 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.30-7.34 (m, 1H), 7.49-7.52 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.58-7.62 (m, 1H), 7.93-7.94 (d, *J* = 2.7 Hz, 1H), 7.97-8.00 (m, 1H), 10.44 (s, 1H), 10.45 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 119.3, 120.5, 125.1, 127.4, 128.2, 128.8, 129.8, 130.4, 135.8, 136.2, 157.5, 158.4, 187.4, 188.4; **MS** (ESI, *m/z*): $[M+H]^+$ 261; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{35}Cl$ $[M+H]^+$ 261.0313, found 261.0302.

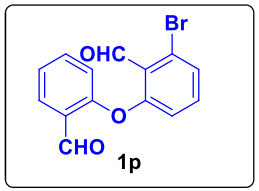


4-Chloro-2-(2-formylphenoxy)benzaldehyde (1n):- white solid, 403 mg (1.550 mmol), 62% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 79-81 °C; **IR** ($CHCl_3$) 755, 1076, 1221, 1588, 1686, 3034 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) 6.87-6.88 (d, *J* = 1.8 Hz, 1H), 7.03-7.05 (d, *J* = 8.2 Hz, 1H), 7.23-7.27 (m, 1H), 7.35-7.40 (t, *J* = 7.6 Hz, 1H), 7.63-7.69 (m, 1H), 7.92-7.93 (d, *J* = 8.4 Hz, 1H), 8.00-8.03 (dd, *J* = 7.7, 1.7 Hz, 1H), 10.42 (s, 1H), 10.47 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 118.6, 121.8, 123.8, 126.1, 126.2, 127.4, 132.1, 134.1, 136.2, 138.8, 156.0, 156.5, 184.9, 185.7; **MS** (ESI, *m/z*): $[M+H]^+$ 261; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{35}Cl$ $[M+H]^+$ 261.0313, found 261.0312.



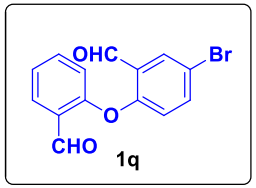
1o

3-Chloro-2-(2-formylphenoxy)benzaldehyde (1o):- White solid, 448 mg (1.723 mmol), 69% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 104-106 ^{o}C; **IR** ($CHCl_3$) 710, 1079, 1225, 1591, 1690, 3034 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.47-6.49 (d, *J* = 8.4 Hz, 1H), 7.15-7.23 (m, 1H), 7.39-7.47 (m, 2H), 7.75-7.79 (m, 1H), 7.91-7.95 (m, 1H), 7.96-8.00 (m, 1H), 10.23 (s, 1H), 10.75 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 114.3, 123.4, 125.0, 127.3, 127.9, 129.2, 129.4, 131.4, 136.0, 137.0, 152.1, 160.1, 187.7, 188.8; **MS** (ESI, *m/z*): $[M+H]^+$ 261; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{35}Cl$ $[M+H]^+$ 261.0313, found 261.0314.

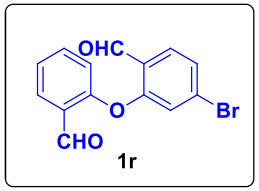


1p

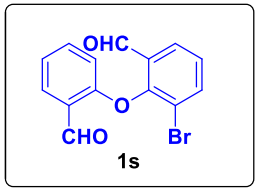
2-Bromo-6-(2-formylphenoxy)benzaldehyde (1p):- Yellow solid, 682 mg (2.251 mmol), 90% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 103-105 ^{o}C; **IR** ($CHCl_3$) 746, 1155, 1214, 1599, 1690, 3020 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.84-6.86 (d, *J* = 8.3 Hz, 1H), 6.93-6.95 (d, *J* = 8.3 Hz, 1H), 7.24-7.28 (t, *J* = 7.5 Hz, 1H), 7.35-7.39 (t, *J* = 8.2 Hz, 1H), 7.50-7.56 (m, 2H), 7.95-7.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 10.42 (s, 1H), 10.45 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 114.0, 120.0, 121.2, 122.0, 126.0, 128.1, 128.9, 129.6, 130.7, 136.2, 164.0, 164.9, 185.7, 185.8; **MS** (ESI, *m/z*): $[M]^+$ 303; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_9O_3{}^{79}BrNa$ $[M+Na]^+$ 326.9627, found 326.9630.



5-Bromo-2-(2-formylphenoxy)benzaldehyde (1q):- Light yellow solid, 704 mg (2.323 mmol), 93% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 88-90 °C; **IR** ($CHCl_3$) 763, 1171, 1226, 1599, 1689, 3079 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.81-6.83 (d, *J* = 8.8 Hz, 1H), 6.95-6.98 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.31-7.35 (t, *J* = 7.6 Hz, 1H), 7.58-7.66 (m, 2H), 7.98-8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.08-8.09 (d, *J* = 2.6 Hz, 1H), 10.43 (s, 1H), 10.44 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 117.7, 119.5, 120.8, 125.2, 127.5, 128.5, 129.9, 131.9, 136.3, 138.7, 158.1, 158.2, 187.3, 188.4; **MS** (ESI, *m/z*): $[M]^+$ 303; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{79}Br$ $[M+H]^+$ 304.9808, found 304.9803.

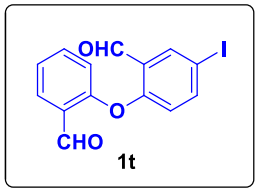


4-Bromo-2-(2-formylphenoxy)benzaldehyde (1r):- White solid, 553 mg (1.825 mmol), 73% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 87-89 °C; **IR** ($CHCl_3$) 758, 1191, 1270, 1603, 1676, 3074 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.01-7.04 (m, 2H), 7.33-7.42 (m, 2H), 7.62-7.66 (m, 1H), 7.83-7.85 (d, *J* = 8.3 Hz, 1H), 7.99-8.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 10.41 (s, 1H), 10.46 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 119.9, 121.7, 125.5, 125.9, 127.6, 127.9, 130.0, 130.4, 130.5, 136.3, 157.7, 159.5, 187.7, 188.3; **MS** (ESI, *m/z*): $[M]^+$ 303; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{79}Br$ $[M+H]^+$ 304.9808, found 304.9813.



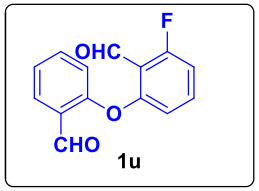
1s

3-Bromo-2-(2-formylphenoxy)benzaldehyde (1s):- Brown solid, 507 mg (1.673 mmol), 67% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 89-91 °C; **IR** ($CHCl_3$) 742, 1269, 1587, 1685, 3090 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.44-6.46 (d, *J* = 8.4 Hz, 1H), 7.17-7.21 (t, *J* = 7.5 Hz, 1H), 7.34-7.38 (m, 1H), 7.42-7.47 (m, 1H), 7.93-8.00 (m, 3H), 10.20 (s, 1H), 10.76 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 114.3, 118.6, 123.4, 125.0, 127.8, 128.7 129.4, 131.5, 135.9, 140.1, 153.2, 160.1, 187.8, 188.8; **MS** (ESI, *m/z*): $[M]^+$ 303; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3{}^{79}Br$ $[M+H]^+$ 304.9808, found 304.9814.



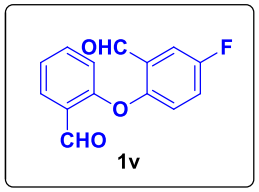
1t

2-(2-Formylphenoxy)-5-iodobenzaldehyde (1t):- White solid, 816 mg (2.325 mmol), 93% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 97-99 °C; **IR** ($CHCl_3$) 594, 1222, 1599, 1682, 3077 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.68-6.70 (d, *J* = 8.7 Hz, 1H), 6.97-6.99 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.32-7.36 (m, 1H), 7.59-7.63 (m, 1H), 7.82-7.85 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.99-8.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.27-8.28 (d, *J* = 2.3 Hz, 1H), 10.41 (s, 1H), 10.44 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 88.8, 121.8, 124.0, 126.1, 127.7, 132.0, 136.2, 140.2, 144.6, 156.5, 156.7, 184.9, 185.7; **MS** (ESI, *m/z*): $[M+H]^+$ 352; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3I$ $[M+H]^+$ 352.9669, found 352.9655.



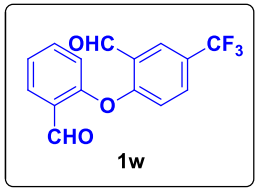
1u

2-Fluoro-6-(2-formylphenoxy)benzaldehyde (1u):- White solid, 323 mg (1.324 mmol), 53% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 78-80 °C; **IR** ($CHCl_3$) 1015, 1211, 1609, 1690, 3090 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.70-6.72 (d, J = 8.4 Hz, 1H), 6.94-7.02 (m, 2H), 7.26-7.32 (t, J = 7.6 Hz, 1H), 7.48-7.53 (m, 1H), 7.56-7.60 (m, 1H), 7.96-7.98 (dd, J = 7.8, 1.7 Hz, 1H), 10.42 (s, 1H), 10.48 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 112.3 (d, J_{C-F} = 21.2 Hz), 114.7 (d, J_{C-F} = 3.6 Hz), 116.5 (d, J_{C-F} = 9.5 Hz), 119.4, 125.0, 127.5, 129.5, 136.1, 136.2 (d, J_{C-F} = 11.0 Hz), 158.3, 158.7 (d, J_{C-F} = 4.4 Hz), 163.9 (d, J_{C-F} = 263.3 Hz), 185.9 (d, J_{C-F} = 4.4 Hz), 188.6; **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -111.2 (s); **MS** (ESI, *m/z*): $[M+H]^+$ 245; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3F$ $[M+H]^+$ 245.0608, found 245.0618. The spectroscopic data were in good agreement with the reported data. [4]



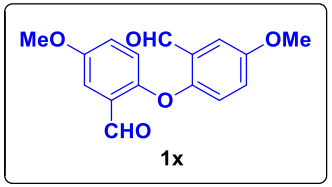
1v

5-Fluoro-2-(2-formylphenoxy)benzaldehyde (1v):- Light red solid, 335 mg (1.373 mmol), 55% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 95-97 °C; **IR** ($CHCl_3$) 1155, 1212, 1397, 1609, 1690, 3090 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 6.87-6.90 (dd, J = 8.3, 0.8 Hz, 1H), 6.97-7.00 (dd, J = 9.0, 4.1 Hz, 1H), 7.27-7.32 (m, 2H), 7.55-7.60 (m, 1H), 7.64-7.67 (dd, J = 8.0, 3.2 Hz, 1H), 7.97-8.00 (dd, J = 7.8, 1.8 Hz, 1H), 10.41 (s, 1H), 10.51 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 115.0 (d, J_{C-F} = 23.4 Hz), 118.5, 121.5 (d, J_{C-F} = 7.3 Hz), 123.1 (d, J_{C-F} = 24.2 Hz), 124.7, 127.1, 128.7 (d, J_{C-F} = 5.8 Hz), 129.7, 136.1, 154.7, 159.3 (d, J_{C-F} = 246.4 Hz), 159.2, 187.5, 188.5; **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -115.7 (s); **MS** (ESI, *m/z*): $[M+H]^+$ 245; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}O_3F$ $[M+H]^+$ 245.0608, found 245.0619.



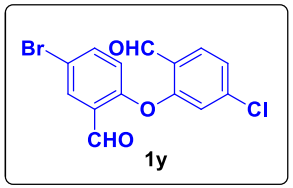
1w

2-(2-Formylphenoxy)-5-(trifluoromethyl)benzaldehyde (1w):- White solid, 470 mg (1.599 mmol), 64% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 83-85 ^{o}C; **IR** ($CHCl_3$) 755, 1076, 1221, 1588, 1686, 3034 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 6.94-6.95 (d, *J* = 8.7 Hz, 1H), 7.08-7.09 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.40-7.43 (t, *J* = 7.6 Hz, 1H), 7.66-7.69 (m, 1H), 7.75-7.77 (dd, *J* = 8.7, 2.0 Hz, 1H), 8.02-804 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.26-8.27 (d, *J* = 2.2 Hz, 1H), 10.37 (s, 1H), 10.59 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 118.1, 120.8, 126.1, 126.5, 126.7, 126.8, 128.0, 130.4, 132.5, 132.6, 136.4, 156.8, 161.8, 187.4, 188.1; **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -62.4 (s); **MS** (ESI, *m/z*): $[M+H]^+$ 295; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{10}O_3F_3$ $[M+H]^+$ 295.0577, found 295.0563.

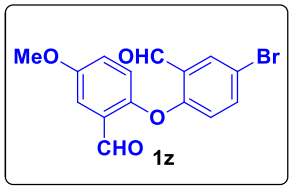


1x

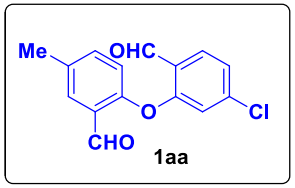
6,6'-Oxybis(3-methoxybenzaldehyde) (1x):- White solid, 429 mg (1.5 mmol), 60% yield, R_f = 0.40 (EtOAc/Hex, 7:93); **MP** 110-112 ^{o}C; **IR** ($CHCl_3$) 1200, 1603, 1683, 2859, 2907, 3073 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) 3.85 (s, 6H), 6.83-6.86 (d, *J* = 9.0 Hz, 2H), 7.10-7.14 (dd, *J* = 9.0, 3.2 Hz, 2H), 7.42-7.43 (d, *J* = 3.1 Hz, 2H), 10.46 (s, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.1, 110.7, 120.5, 123.8, 127.6, 153.8, 156.2, 188.7; **MS** (ESI, *m/z*): $[M+H]^+$ 287; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{15}O_5$ $[M+H]^+$ 287.0914, found 287.0927.



2-(4-Bromo-2-formylphenoxy)-4-chlorobenzaldehyde (1y):- White solid, 489 mg (1.451 mmol), 58% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 120-122 ^{o}C; **IR** ($CHCl_3$) 590, 746, 1218, 1590, 1687, 3021 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) 6.90-6.93 (d, *J* = 9.0 Hz, 2H), 7.27-7.30 (s, 1H), 7.71-7.74 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.92-7.95 (d, *J* = 8.4 Hz, 1H), 8.11-8.12 (d, *J* = 2.4 Hz, 1H), 10.36 (s, 1H), 10.42 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 118.7, 119.0, 121.5, 125.5, 125.6, 128.8, 130.8, 132.5, 138.9, 142.2, 156.8, 159.0, 186.9, 187.2; **MS** (ESI, *m/z*): $[M+H]^+$ 338; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_9O_3{}^{79}Br^{35}Cl$ $[M+H]^+$ 338.9424, found 338.9419.

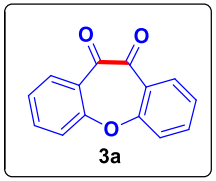


5-Bromo-2-(2-formyl-4-methoxyphenoxy)benzaldehyde (1z):- Light brown solid, 708 mg (2.126 mmol), 85% yield, R_f = 0.5 (EtOAc/Hex, 5:95); **MP** 100-102 ^{o}C; **IR** ($CHCl_3$) 772, 1214, 1588, 1682, 2855, 3079 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.87 (s, 3H), 6.68-6.71 (d, *J* = 8.8 Hz, 1H), 6.97-7.00 (d, *J* = 9.0 Hz, 1H), 7.17-7.20 (dd, *J* = 9.0, 3.2 Hz, 1H), 7.43-7.44 (d, *J* = 3.2 Hz, 1H), 7.57-7.60 (dd, *J* = 8.8, 2.6 Hz, 1H), 8.04-8.05 (d, *J* = 2.5 Hz, 1H), 10.31 (s, 1H), 10.50 (s, 1H), **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.1, 111.4, 116.7, 119.2, 122.2, 123.7, 127.6, 128.5, 131.7, 138.6, 151.4, 157.1, 159.4, 187.5, 188.1; **MS** (ESI, *m/z*): $[M+H]^+$ 334; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{12}O_4{}^{79}Br$ $[M+H]^+$ 334.9913, found 334.9900.



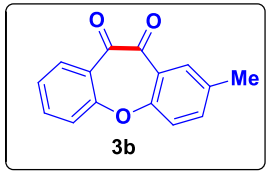
1aa

4-Chloro-2-(2-formyl-4-methylphenoxy)benzaldehyde (1aa):- White solid, 466 mg (1.701 mmol), 68% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 98-100 ^{o}C; **IR** ($CHCl_3$) 750, 1208, 1588, 1682, 2857, 3033 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.41 (s, 3H), 6.81-6.85 (m, 2H), 7.16-7.24 (m, 2H), 7.88-7.93 (dd, *J* = 11.4, 8.2 Hz, 2H), 10.32 (s, 1H), 10.46 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 22.2, 118.7, 120.5, 124.8, 125.4, 125.5, 126.7, 129.9, 130.2, 142.1, 148.3, 157.6, 159.9, 187.7, 188.0; **MS** (ESI, *m/z*): $[M+H]^+$ 275; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{12}O_3{}^{35}Cl$ $[M+H]^+$ 275.0469, found 275.0487.



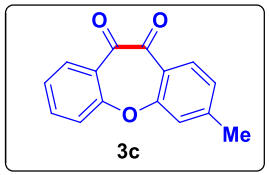
3a

Dibenzo[*b,f*]oxepine-10,11-dione (3a):- Yellow solid, 206 mg (0.920 mmol), 92% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 114-116 ^{o}C; **IR** (KBr) 1283, 1598, 1673, 3073 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 7.33-7.36 (m, 2H), 7.42-7.44 (m, 2H), 7.64-7.67 (m, 2H), 7.98-8.00 (dd, *J* = 7.9, 1.7 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 121.8, 125.7, 126.3, 131.9, 136.1, 157.0, 186.5; **MS** (ESI, *m/z*): $[M+H]^+$ 225; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_9O_3$ $[M+H]^+$ 225.0546, found 225.0561. The spectroscopic data were in good agreement with the reported data. [5,6]



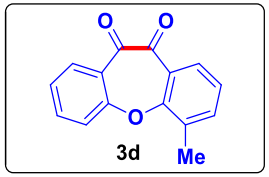
3b

2-Methyldibenzo[*b,f*]oxepine-10,11-dione (3b):- Yellow solid, 202 mg (0.850 mmol), 85% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 115-117 ^{o}C; **IR** ($CHCl_3$) 1219, 1604, 1692, 2853, 2923, 3066 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 2.38 (s, 3H), 7.29-7.32 (t, *J* = 7.8 Hz, 2H), 7.38-7.44 (m, 2H), 7.61-7.64 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.75 (s, 1H), 7.96-7.98 (dd, *J* = 7.7, 1.1 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 20.6, 121.6, 121.7, 125.5, 125.8, 126.1, 131.5, 131.9, 135.6, 136.0, 137.0, 155.0, 157.0, 186.5, 186.6; **MS** (ESI, *m/z*): $[M+H]^+$ 239; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_3$ $[M+H]^+$ 239.0703, found 239.0719.

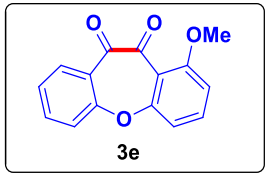


3c

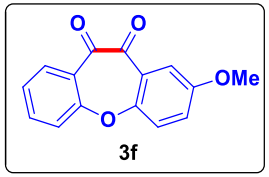
3-Methyldibenzo[*b,f*]oxepine-10,11-dione (3c):- Yellow solid, 193 mg (0.810 mmol), 81% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 99-101 ^{o}C; **IR** ($CHCl_3$) 1214, 1606, 1694, 2853, 2924, 3020 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 2.40 (s, 3H), 7.31-7.34 (dd, *J* = 12.1, 4.6 Hz, 2H), 7.40-7.46 (m, 2H), 7.62-7.66 (m, 1H), 7.76 (s, 1H), 7.98-8.00 (dd, *J* = 7.9, 1.4 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 20.7, 121.6, 121.7, 125.5, 125.8, 126.2, 131.5, 131.9, 135.7, 136.0, 136.7, 155.1, 157.1, 186.6, 186.7; **MS** (ESI, *m/z*): $[M+H]^+$ 239; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_3$ $[M+H]^+$ 239.0703, found 239.0718.



4-Methyldibenzo[*b,f*]oxepine-10,11-dione (3d):- Yellow solid, 207 mg (0.870 mmol), 87% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 111-113 °C; **IR** ($CHCl_3$) 1277, 1611, 1670, 2837, 2939, 3079 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.57 (s, 3H), 7.20-7.25 (m, 2H), 7.32-7.34 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.40-7.42 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.51-7.52 (t, *J* = 8.0 Hz, 1H), 7.73-7.75 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.79-7.81 (dd, *J* = 7.5, 1.4 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 22.0, 118.5, 120.4, 124.7, 125.3, 125.4, 126.5, 129.8, 130.1, 142.0, 148.1, 157.5, 159.8, 187.6, 187.9; **MS** (ESI, *m/z*): $[M+H]^+$ 239; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_3$ $[M+H]^+$ 239.0703, found 239.0718.

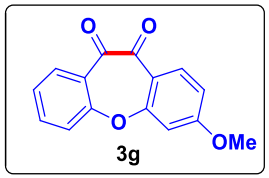


1-Methoxydibenzo[*b,f*]oxepine-10,11-dione (3e):- Yellow solid, 165 mg (0.650 mmol), 65% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 108-110 °C; **IR** ($CHCl_3$) 1216, 1598, 1639, 2896, 2975, 3014 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.94 (s, 3H), 6.86-6.89 (m, 2H), 7.32-7.41 (m, 2H), 7.61-7.65 (m, 1H), 7.91-7.93 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.04-8.06 (d, *J* = 8.4 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 55.9, 111.3, 116.6, 119.1, 122.0, 123.6, 127.5, 128.4, 131.6, 138.4, 151.2, 157.0, 159.2, 187.3, 188.0; **MS** (ESI, *m/z*): $[M+H]^+$ 255; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_4$ $[M+H]^+$ 255.0652, found 255.0660.



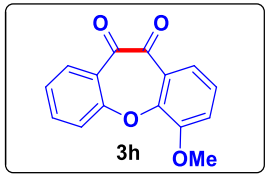
3f

2-Methoxydibenzo[*b,f*]oxepine-10,11-dione (3f):- Yellow solid, 218 mg (0.860 mmol), 86% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 117-119 ^{o}C; **IR** (KBr) 1217, 1602, 1672, 2860, 2926, 3057 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 3.86 (s, 3H), 7.19-7.21 (dd, *J* = 9.0, 3.1 Hz, 1H), 7.31-7.36 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.38-7.41 (dd, *J* = 15.8, 8.4 Hz, 2H), 7.63-7.66 (m, 1H), 7.98-8.00 (d, *J* = 7.9 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.1, 112.5, 121.7, 123.2, 124.4, 125.5, 126.2, 126.5, 131.9, 136.0, 151.5, 156.9, 157.1, 186.2, 186.3; **MS** (ESI, *m/z*): $[M+H]^+$ 255; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_4$ $[M+H]^+$ 255.0652, found 255.0648.

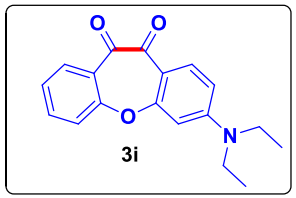


3g

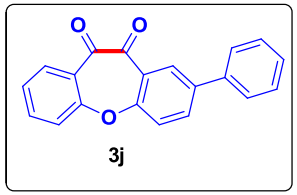
2-Methoxydibenzo[*b,f*]oxepine-10,11-dione (3g):- Yellow solid, 226 mg (0.890 mmol), 89% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 88-90 ^{o}C; **IR** ($CHCl_3$) 1219, 1609, 1697, 2851, 2920, 3081 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.93 (s, 3H), 6.86-6.88 (m, 2H), 7.32-7.41 (m, 2H), 7.61-7.65 (m, 1H), 7.91-7.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.03-8.05 (m, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.1, 105.4, 113.3, 118.8, 121.6, 125.8, 126.9, 131.8, 134.0, 135.6, 156.2, 159.3, 166.2, 184.0, 187.7; **MS** (ESI, *m/z*): $[M+H]^+$ 255; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_4$ $[M+H]^+$ 255.0652, found 255.0667.



4-Methoxydibenzo[*b,f*]oxepine-10,11-dione (3h):- Yellow solid, 211 mg (0.830 mmol), 83% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 124-126 ^{o}C; **IR** ($CHCl_3$) 1220, 1606, 1692, 2852, 2921, 3023 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.99 (s, 3H), 7.18-7.21 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.23-7.27 (m, 1H), 7.31-7.35 (m, 1H), 7.43-7.45 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52-7.54 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.62-7.67 (m, 1H), 8.00-8.02 (dd, *J* = 7.9, 1.7 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 56.7, 117.5, 122.3, 122.4, 125.8, 126.1, 127.1, 129.2, 132.0, 136.1, 147.1, 151.6, 158.2, 185.5, 187.0, **MS** (ESI, *m/z*): $[M+H]^+$ 255; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}O_4$ $[M+H]^+$ 255.0652, found 255.0668.

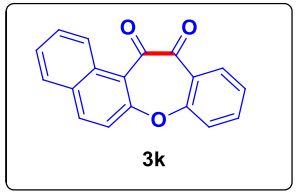


3-(Diethylamino)dibenzo[*b,f*]oxepine-10,11-dione (3i):- Brown liquid, 230 mg (0.780 mmol), 78% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **IR** ($CHCl_3$) 1219, 1599, 1693, 2854, 2970, 3081 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 1.22-1.28 (m, 6H), 3.40-3.52 (m, 4H), 6.43-6.60 (m, 2H), 7.19-7.38 (m, 2H), 7.49-7.62 (m, 1H), 7.71-7.87 (m, 1H), 8.02-8.04 (d, *J* = 9.2 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 12.7, 45.0, 100.8, 109.5, 113.6, 121.4, 125.5, 128.2, 131.4, 134.4, 134.9, 154.0, 156.0, 160.2, 181.8, 189.5; **MS** (ESI, *m/z*): $[M+H]^+$ 296; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{18}O_3N$ $[M+H]^+$ 296.1281, found 296.1291.



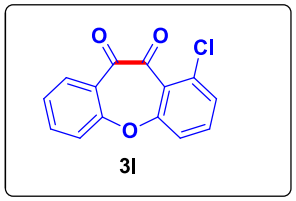
3j

2-Phenyldibenzo[*b*,*f*]oxepine-10,11-dione (3j):- Brown liquid, 240 mg (0.800 mmol), 80% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **IR** ($CHCl_3$) 1222, 1603, 1679, 3073 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 7.33-7.51 (m, 6H), 7.59-7.69 (m, 3H), 7.87-7.89 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.99-8.02 (m, 1H), 8.20-8.21 (d, *J* = 2.4 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 121.7, 121.8, 122.4, 125.7, 126.0, 126.1, 127.1, 128.2, 129.2, 129.9, 131.9, 132.0, 134.6, 136.1, 138.8, 138.9, 156.2, 156.8, 186.5; **MS** (ESI, *m/z*): $[M+H]^+$ 301; **HRMS** (ESI, *m/z*): calcd for $C_{20}H_{13}O_3$ $[M+H]^+$ 301.0859, found 301.0866.



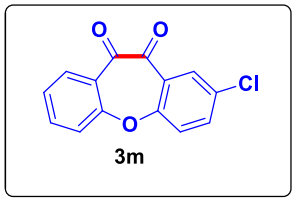
3k

Benzo[*f*]naphtho[2,1-*b*]oxepine-12,13-dione (3k):- Yellow solid, 205 mg (0.750 mmol), 75% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 127-129 ^{o}C; **IR** ($CHCl_3$) 1222, 1600, 1669, 3077 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 7.33-7.36 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.49-7.52 (dd, *J* = 8.3, 4.9 Hz, 2H), 7.54-7.57 (dd, *J* = 11.1, 3.9 Hz, 1H), 7.62-7.72 (m, 2H), 7.87-7.89 (d, *J* = 8.1 Hz, 1H), 8.02-8.04 (d, *J* = 8.9 Hz, 1H), 8.18-8.25 (m, 2H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 120.4, 121.8, 123.0, 124.2, 125.1, 125.3, 126.8, 128.5, 129.3, 131.2, 131.5, 131.6, 135.3, 136.6, 155.7, 158.9, 185.8, 192.4; **MS** (ESI, *m/z*): $[M+H]^+$ 275; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{11}O_3$ $[M+H]^+$ 275.0703, found 275.0711.



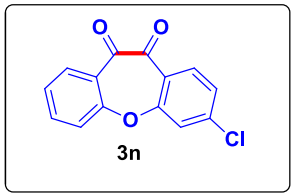
3l

1-Chlorodibenzo[*b,f*]oxepine-10,11-dione (3l):- Yellow solid, 222 mg (0.860 mmol), 86% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 151-153 ^{o}C; **IR** (KBr) 766, 1238, 1591, 1676, 3077 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.30-7.46 (m, 5H), 7.65-7.71 (m, 1H), 8.14-8.17 (dd, *J* = 7.9, 1.6 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 120.2, 121.9, 124.9, 125.9, 128.5, 128.7, 131.8, 133.7, 134.1, 137.1, 157.5, 159.4, 185.1, 189.3; **MS** (ESI, *m/z*): $[M+H]^+$ 259; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{35}Cl$ $[M+H]^+$ 259.0156, found 259.0172.

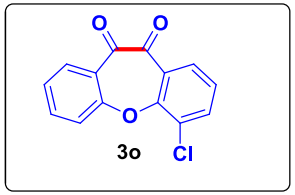


3m

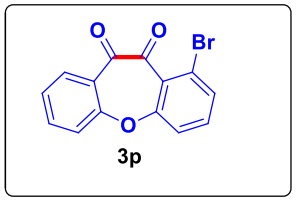
2-Chlorodibenzo[*b,f*]oxepine-10,11-dione (3m):- Light yellow solid, 206 mg (0.800 mmol), 80% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 103-105 ^{o}C; **IR** (KBr) 765, 1242, 1589, 1673, 3071 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.32-7.44 (m, 3H), 7.58-7.61 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.64-7.69 (m, 1H), 7.95-8.01 (m, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 121.7, 121.8, 123.6, 125.7, 131.1, 131.3, 131.9, 132.1, 136.0, 136.2, 155.5, 156.6, 185.0, 185.6; **MS** (ESI, *m/z*): $[M+H]^+$ 259; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{35}Cl$ $[M+H]^+$ 259.0156, found 259.0163. The spectroscopic data were in good agreement with the reported data. [5]



3-Chlorodibenzo[*b,f*]oxepine-10,11-dione (3n):- Light yellow solid, 201 mg (0.780 mmol), 78% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 108-110 ^{o}C; **IR** (KBr) 759, 1224, 1595, 1664, 3071 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.31-7.43 (m, 3H), 7.46-7.47 (d, *J* = 1.9 Hz, 1H), 7.65-7.69 (m, 1H), 7.96-7.99 (m, 2H); **^{13}C{^{1}H}-NMR** (75 MHz, $CDCl_3$) 121.7, 122.1, 124.5, 126.2, 126.3, 126.4, 132.0, 133.2, 136.1, 142.1, 156.4, 157.4, 184.9, 186.2; **MS** (ESI, *m/z*): $[M+H]^+$ 259; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{35}Cl$ $[M+H]^+$ 259.0156, found 259.0162.

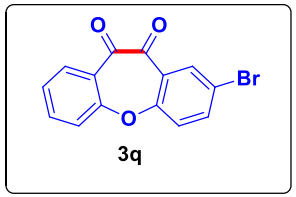


4-Chlorodibenzo[*b,f*]oxepine-10,11-dione (3o):- Light yellow solid, 227 mg (0.880 mmol), 88% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 138-140 ^{o}C; **IR** ($CHCl_3$) 754, 1222, 1593, 1675, 3033 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.28-7.30 (d, *J* = 7.9 Hz, 1H), 7.36-7.40 (m, 1H), 7.60-7.63 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.67-7.73 (m, 2H), 7.81-7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.01-8.04 (dd, *J* = 7.8, 1.7 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 122.6, 126.4, 127.1, 127.3, 129.6, 130.4, 131.8, 132.2, 136.0, 136.4, 153.2, 157.6, 184.8, 185.7; **MS** (ESI, *m/z*): $[M+H]^+$ 259; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{35}Cl$ $[M+H]^+$ 259.0156, found 259.0168.



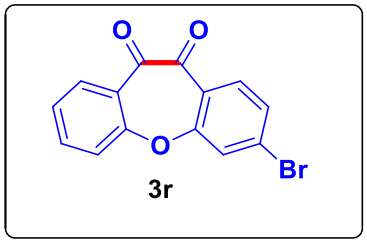
3p

1-Bromodibenzo[*b,f*]oxepine-10,11-dione (3p):- Yellow solid, 268 mg (0.890 mmol), 89% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 137-139 ^{o}C; **IR** ($CHCl_3$) 763, 1224, 1597, 1670, 3074 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.32-7.42 (m, 3H), 7.64-7.75 (m, 2H), 7.97-7.99 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.10-8.11 (d, *J* = 2.5 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 118.6, 121.8, 123.8, 126.1, 126.2, 127.5, 132.1, 134.2, 136.2, 138.9. 156.0, 156.6, 184.9, 185.7; **MS** (ESI, *m/z*): $[M+H]^+$ 302; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{79}Br$ $[M+H]^+$ 302.9651, found 302.9662.

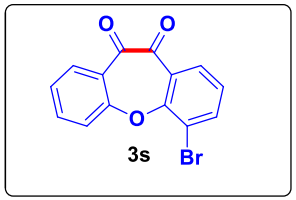


3q

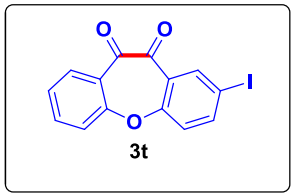
2-Bromodibenzo[b,f]oxepine-10,11-dione (3q):- Yellow solid, 250 mg (0.830 mmol), 83% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 146-148 ^{o}C; **IR** ($CHCl_3$) 752, 1231, 1601, 1696, 3071 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) 7.32-7.43 (m, 3H), 7.63-7.77 (m, 2H), 7.97-8.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.10-8.11 (d, *J* = 2.5 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 118.7, 120.0, 124.9, 125.5, 125.6, 127.7, 130.0, 130.4, 136.3, 142.1, 157.7, 159.7, 187.6, 188.3; **MS** (ESI, *m/z*): $[M+H]^+$ 302; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{79}Br$ $[M+H]^+$ 302.9651, found 302.9657.



3-Bromodibenzo[*b,f*]oxepine-10,11-dione(3r):- Yellow solid, 262 mg (0.870 mmol), 87% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 144-146 ^{o}C; **IR** ($CHCl_3$) 758, 1225, 1603, 1678, 3075 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.31-7.42 (m, 3H), 7.65-7.75 (m, 2H), 7.97-7.99 (d, *J* = 7.8 Hz, 1H), 8.10-8.11 (d, *J* = 2.3 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 118.6, 121.7, 123.8, 126.1, 127.4, 132.0, 134.1, 136.2, 136.4, 138.8, 156.0, 156.5, 184.9, 185.6; **MS** (ESI, *m/z*): $[M+H]^+$ 302; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{79}Br$ $[M+H]^+$ 302.9651, found 302.9648.

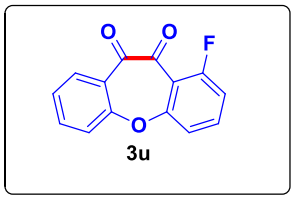


4-Bromodibenzo[*b,f*]oxepine-10,11-dione (3s):- Yellow solid, 271 mg (0.900 mmol), 90% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 124-126 ^{o}C; **IR** ($CHCl_3$) 771, 1225, 1603, 1678, 3033 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.20-7.23 (t, *J* = 7.8 Hz, 1H), 7.36-7.41 (m, 1H), 7.68-7.69 (d, *J* = 3.5 Hz, 2H), 7.85-7.90 (m, 2H), 8.02-8.04 (d, *J* = 7.8 Hz, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) 116.4, 122.7, 126.4, 126.8, 127.1, 129.6, 131.2, 132.2, 136.4, 139.1, 154.0, 157.6, 184.7, 185.8; **MS** (ESI, *m/z*): $[M+H]^+$ 302; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3{}^{79}Br$ $[M+H]^+$ 302.9651, found 302.9658.



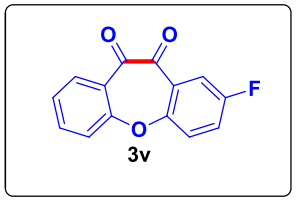
3t

2-Iododibenzo[*b,f*]oxepine-10,11-dione (3t):- Yellow solid, 286 mg (0.820 mmol), 82% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 112-114 ^{o}C; **IR** (KBr) 595, 1221, 1591, 1664, 3068 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.18-7.20 (d, *J* = 8.6 Hz, 1H), 7.34-7.42 (m, 2H), 7.64-7.70 (m, 1H), 7.90-7.98 (m, 2H), 8.27-8.28 (d, *J* = 2.0 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 88.8, 121.8, 124.0, 126.1, 127.7, 132.0, 136.2, 140.2, 144.6, 156.5, 156.7, 184.9, 185.7; **MS** (ESI, *m/z*): $[M+H]^+$ 350; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3I$ $[M+H]^+$ 350.9513, found 350.9534.

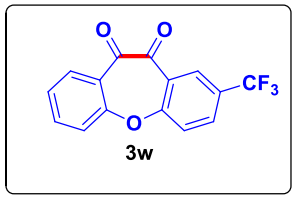


3u

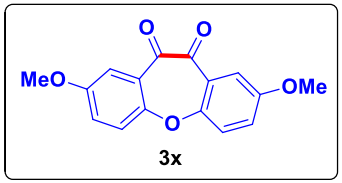
1-Fluorodibenzo[*b,f*]oxepine-10,11-dione (3u):- Yellow solid, 208 mg (0.860 mmol), 86% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 147-149 ^{o}C; **IR** (KBr) 1160, 1238, 1591, 1676, 3077 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.05-7.10 (m, 1H), 7.22-7.24 (m, 1H), 7.31-7.44 (m, 2H), 7.51-7.56 (m, 1H), 7.65-7.70 (m, 1H), 8.12-8.14 (dd, *J* = 7.9, 1.8 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 114.1 (d, J_{C-F} = 21.2 Hz), 117.3 (d, J_{C-F} = 4.4 Hz), 121.9, 122.7, 125.3, 126.0, 132.2, 135.0 (d, J_{C-F} = 11.0 Hz), 136.8, 157.3 (d, J_{C-F} = 2.9 Hz), 158.7, 161.5 (d, J_{C-F} = 263.3 Hz), 184.3, 185.1; **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -116.2 (s); **MS** (ESI, *m/z*): $[M+H]^+$ 243; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3F$ $[M+H]^+$ 243.0452, found 243.0460.



2-Fluorodibenzo[*b,f*]oxepine-10,11-dione (3v):- Yellow solid, 203 mg (0.840 mmol), 84% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 118-120 ^{o}C; **IR** (KBr) 1160, 1215, 1599, 1673, 3071 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.33-7.38 (m, 2H), 7.41-7.45 (m, 2H), 7.65-7.69 (m, 2H), 7.97-8.00 (dd, *J* = 7.9, 1.8 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 117.2 (d, J_{C-F} = 25.0 Hz), 121.7, 123.3, 123.6, 123.9 (d, J_{C-F} = 7.6 Hz), 126.0, 126.6, 132.1, 136.2, 153.5, 157.0, 159.5 (d, J_{C-F} = 247.4 Hz), 185.0, 185.4; **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -111.2 (s); **MS** (ESI, *m/z*): $[M+H]^+$ 243; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_8O_3F$ $[M+H]^+$ 243.0452, found 243.0467.

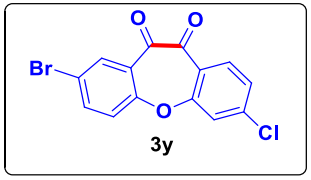


2-(Trifluoromethyl)dibenzo[*b,f*]oxepine-10,11-dione (3w):- Yellow solid, 242 mg (0.830 mmol), 83% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 125-127 ^{o}C; **IR** ($CHCl_3$) 772, 1269, 1602, 1679, 3075 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) 7.38-7.47 (m, 2H), 7.56-7.70 (dd, *J* = 34.6, 7.7 Hz, 2H), 7.88-8.01 (dd, *J* = 28.7, 7.8 Hz, 2H), 8.32 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 121.8, 121.9, 123.1, 125.8, 126.0, 126.4, 129.8, 132.1, 132.6, 136.4, 136.5, 156.1, 158.8, 185.0, 185.7; **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -62.5 (s); **MS** (ESI, *m/z*): $[M+H]^+$ 293; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_8O_3F_3$ $[M+H]^+$ 293.0420, found 293.0430.



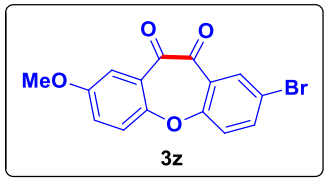
3x

2,8-Dimethoxydibenzo[*b,f*]oxepine-10,11-dione (3x):- Yellow solid, 221 mg (0.780 mmol), 78% yield, R_f = 0.5 (EtOAc/Hex, 8:92); **MP** 116-118 ^{o}C; **IR** ($CHCl_3$) 1270, 1610, 1668, 2938, 3081 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 3.86 (s, 6H), 7.18-7.21 (dd, *J* = 9.0, 3.2 Hz, 2H), 7.32-7.34 (d, *J* = 9.0 Hz, 2H), 7.38-7.39 (d, *J* = 3.2 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.1, 112.4, 123.1, 124.4, 126.4, 151.7, 156.8, 186.0; **MS** (ESI, *m/z*): $[M+H]^+$ 285; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{13}O_5$ $[M+H]^+$ 285.0763, found 285.0754.



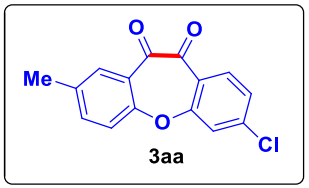
3y

2-Bromo-7-chlorodibenzo[*b,f*]oxepine-10,11-dione (3y):- Yellow solid, 284 mg (0.850 mmol), 85% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 139-141 ^{o}C; **IR** ($CHCl_3$) 590, 746, 1218, 1590, 1687, 3087 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.31-7.36 (m, 2H), 7.45 (s, 1H), 7.74-7.77 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.98-7.99 (d, *J* = 8.5 Hz, 1H), 8.08-8.09 (d, *J* = 2.5 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 119.1, 122.1, 123.7, 124.4, 126.7, 127.6, 133.3, 134.2, 138.9, 142.3, 155.4, 157.0, 184.1, 184.6; **MS** (ESI, *m/z*): $[M+H]^+$ 336; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_7O_3{}^{79}Br^{35}Cl$ $[M+H]^+$ 336.9262, found 336.9277.



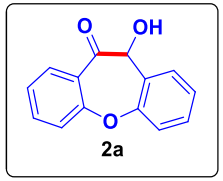
3z

2-Bromo-8-methoxydibenzo[*b,f*]oxepine-10,11-dione (3z):- Yellow solid, 245 mg (0.740 mmol), 74% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 130-132 ^{o}C; **IR** ($CHCl_3$) 758, 1272, 1592, 1677, 2975, 3084 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 3.86 (s, 3H), 7.20-7.22 (dd, *J* = 9.0, 3.2 Hz, 1H), 7.30-7.35 (dd, *J* = 16.9, 8.8 Hz, 2H), 7.37-7.38 (d, *J* = 3.2 Hz, 1H), 7.71-7.73 (dd, *J* = 8.7, 2.5 Hz, 1H), 8.10-8.11 (d, *J* = 2.5 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 56.1, 112.6, 118.3, 123.2, 123.7, 124.5, 126.4, 127.4, 134.1, 138.7, 151.0, 156.2, 157.2, 184.6, 185.5; **MS** (ESI, *m/z*): $[M+H]^+$ 332; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{10}O_4{}^{79}Br$ $[M+H]^+$ 332.9757, found 332.9765.



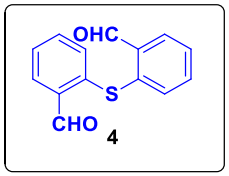
3aa

7-Chloro-2-methyldibenzo[*b,f*]oxepine-10,11-dione (3aa):- Yellow solid, 176 mg (0.650 mmol), 65% yield, R_f = 0.40 (EtOAc/Hex, 10:90); **MP** 112-114 ^{o}C; **IR** ($CHCl_3$) 690, 1269, 1612, 1679, 2924, 3034 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 2.47 (s, 3H), 7.17-7.18 (d, *J* = 8.1 Hz, 1H), 7.23 (s, 1H), 7.30-7.32 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.44-7.45 (d, *J* = 1.8 Hz, 1H), 7.89-7.91 (d, *J* = 8.0 Hz, 1H), 7.94-7.96 (d, *J* = 8.5 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 20.6, 121.6, 121.7, 125.5, 125.8, 126.1, 131.5, 131.9, 135.6, 136.0, 137.0, 155.0, 157.0, 186.5, 186.6; **MS** (ESI, *m/z*): $[M+H]^+$ 273; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{10}O_3{}^{35}Cl$ $[M+H]^+$ 273.0318, found 273.0309.



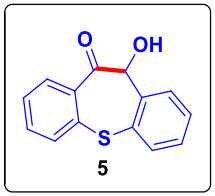
2a

11-Hydroxydibenzo[*b,f*]oxepin-10(11*H*)-one(2a):- Yellow solid, 115 mg (0.510 mmol), 51% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 79-81 ºC; **IR** (KBr) 1181, 1619, 1660, 2932, 3019, 3421 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 4.51-4.52 (d, *J* = 4.8 Hz, 1H), 5.87-5.88 (d, *J* = 4.2 Hz, 1H), 7.23-7.25 (m, 1H), 7.27-7.33 (m, 3H), 7.42-7.44 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.61-7.67 (m, 2H), 8.15-8.17 (dd, *J* = 7.9, 1.8 Hz, 1H); **MS** (ESI, *m/z*): $[M+Na]^+$ 249; The spectroscopic data were in good agreement with the reported data. [6]



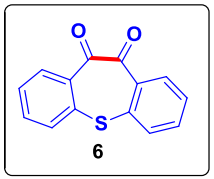
4

2,2'-Thiodibenzaldehyde (4):- White solid, 883 mg (3.649 mmol), 73% yield, R_f = 0.5 (EtOAc/Hex, 7:93); **MP** 92-94 ºC; **IR** (KBr) 1194, 1583, 1689, 3060 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.16-7.19 (dd, *J* = 7.7, 1.2 Hz, 2H), 7.43-7.53 (m, 4H), 7.95-7.98 (dd, *J* = 7.5, 1.7 Hz, 2H), 10.36 (s, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 128.0, 132.0, 132.7, 134.8, 135.1, 138.7, 191.7; **MS** (ESI, *m/z*): $[M+H]^+$ 243; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{11}O_2S$ $[M+H]^+$ 243.0474, found 243.0465; The spectroscopic data were in good agreement with the reported data. [2]



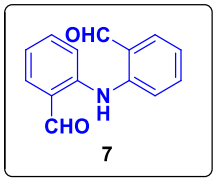
5

11-Hydroxydibenzo[*b,f*]thiepin-10(11*H*)-one (5):- Yellow solid, 146 mg (0.603 mmol), 60% yield, R_f = 0.5 (EtOAc/Hex, 6:94); **MP** 121-123 °C; (**IR-KBr**) 1189, 1585, 1666, 2924, 3061, 3451 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 4.93-4.94 (d, *J* = 5.5 Hz, 1H), 6.21-6.23 (d, *J* = 5.4 Hz, 1H), 7.21-7.25 (m, 1H), 7.34-7.40 (m, 1H), 7.44-7.52 (m, 2H), 7.61-7.72 (m, 3H), 8.34-8.37 (dd, *J* = 8.0, 1.6 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 77.2, 125.6, 127.2, 127.7, 130.1, 130.7, 131.4, 131.5, 132.3, 133.0, 133.5, 140.8, 140.9, 192.9; **MS** (ESI, *m/z*): $[M+H]^+$ 243; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{10}NaO_2S$ $[M+Na]^+$ 265.0299, found 265.0303. The spectroscopic data were in good agreement with the reported data. [7]



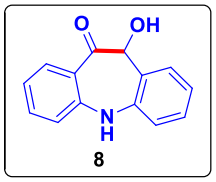
6

Dibenzo[*b,f*]thiepine-10,11-dione (6):- Yellow solid, 156 mg (0.650 mmol), 65% yield, R_f = 0.5 (EtOAc/Hex, 5:95); **MP** 122-124 °C; **IR** (KBr) 1213, 1260, 1663, 1697, 3038 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.42-7.49 (m, 4H), 7.62-7.65 (m, 2H), 7.80-7.83 (m, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 129.5, 131.5, 132.3, 133.2, 134.8, 139.6, 190.8; **MS** (ESI, *m/z*): $[M+H]^+$ 241; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_9O_2S[M+H]^+$ 241.0318, found 241.0326. The spectroscopic data were in good agreement with the reported data. [5]



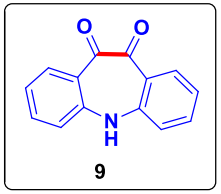
7

2,2'-Azanediyldibenzaldehyde (7):- Yellow solid, 151 mg (0.670 mmol), 67% yield, R_f = 0.5 (EtOAc/Hex, 5:95); **MP** 106-108 ^{o}C; **IR** (KBr) 1187, 1582, 1673, 3070, 3268 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.06-7.11 (m, 2H), 7.44-7.50 (m, 2H), 7.54-7.56 (d, *J* = 8.3 Hz, 2H), 7.70-7.72 (dd, *J* = 7.7, 1.6 Hz, 2H), 10.03 (s, 2H), 11.35 (brs, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 117.8, 121.1, 124.2, 135.0, 136.0, 143.7, 193.0; **MS** (ESI, *m/z*): $[M+H]^+$ 226; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{12}O_2N$ $[M+H]^+$ 226.0863, found 226.0852; The spectroscopic data were in good agreement with the reported data. [3]



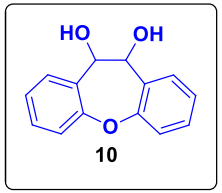
8

11-Hydroxy-5*H*-dibenzo[*b,f*]azepin-10(11*H*)-one (8):- Yellow solid, 168 mg (0.750 mmol), 75% yield, R_f = 0.5 (EtOAc/Hex, 5:95); **MP** 154-156 ^{o}C; **IR** (KBr) 1185, 1613, 1652, 2923, 3015, 3228, 3325 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 4.73-4.74 (d, *J* = 5.4 Hz, 1H), 5.20-5.21 (d, *J* = 5.4 Hz, 1H), 6.71 (brs, 1H), 6.98-7.01 (m, 1H), 7.04-7.09 (m, 2H), 7.22-7.31 (m, 2H), 7.46-7.50 (m, 1H), 7.70-7.71 (d, *J* = 7.6 Hz, 1H), 8.12-8.14 (dd, *J* = 8.0, 1.6 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 75.4, 118.9, 119.5, 120.0, 120.5, 125.0, 125.4, 127.9, 128.1, 130.9, 134.6, 138.2, 147.1, 190.6; **MS** (ESI, *m/z*): $[M+H]^+$ 226; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{11}NNaO_2$ $[M+Na]^+$ 248.0696, found 248.0687.



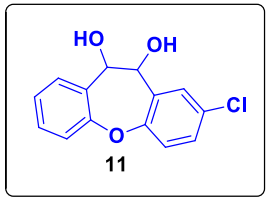
9

5*H*-Dibenzo[*b*,*f*]azepine-10,11-dione (9):- Yellow solid, 174 mg (0.780 mmol), 78% yield, R_f = 0.5 (EtOAc/Hex, 5:95); **MP** 138-140 ^{o}C; **IR** (KBr) 1219, 1627, 1689, 3080, 3268 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 7.71-7.74 (m, 2H), 7.84-7.87 (m, 2H), 8.32-8.34 (d, *J* = 8.8 Hz, 2H), 8.76-8.77 (d, *J* = 8.9 Hz, 2H), 11.56 (brs, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 123.6, 124.0, 129.0, 130.3, 130.7, 149.4, 193.8; **MS** (ESI, *m/z*): $[M+H]^+$ 224; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{13}N_2O_2$ $[M+Na]^+$ 241.0865, found 241.0857; The spectroscopic data were in good agreement with the reported data. [8]



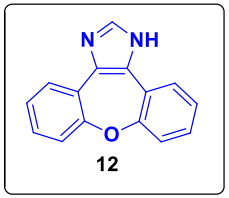
10

10,11-Dihydrodibenzo[*b*,*f*]oxepine-10,11-diol (10):- White solid, 194 mg (0.850 mmol), 85% yield, R_f = 0.4 (EtOAc/Hex, 40:60); **MP** 158-160 ^{o}C; **IR** (KBr) 772, 1220, 1482, 1574, 2921, 3007, 3362 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.84-2.86 (dd, *J* = 3.0, 1.8 Hz, 2H), 5.00-5.05 (m, 2H), 7.17-7.22 (m, 4H), 7.25-7.27 (m, 2H), 7.60-7.62 (dd, *J* = 7.5, 1.6 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 72.8, 121.1, 124.9, 129.6, 130.3, 130.4, 155.3; **MS** (ESI, *m/z*): $[M+NH_4]^+$ 246; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{12}O_3Na$ $[M+Na]^+$ 251.0786, found 251.0790.



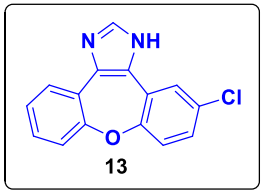
11

2-Chloro-10,11-dihydrodibenzo[b,f]oxepine-10,11-diol (11):- White solid, 196 mg (0.750 mmol), 75% yield, R_f = 0.4 (EtOAc/Hex, 40:60); **MP** 160-162 ^{o}C; **IR** (KBr) 772, 1220, 1476, 1610, 2922, 3009, 3364 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 2.42-2.45 (d, *J* = 8.5 Hz, 1H), 2.60-2.62 (d, *J* = 9.1 Hz, 1H), 5.21-5.23 (d, *J* = 7.9 Hz, 2H), 7.14-7.16 (d, *J* = 8.6 Hz, 1H), 7.18-7.25 (m, 3H), 7.27-7.32 (m, 1H), 7.48-7.53 (m, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 72.7, 73.0, 120.8, 122.2, 125.1, 128.4, 129.0, 129.4, 130.1, 130.3, 132.5, 147.6, 154.4, 155.5; **MS** (ESI, *m/z*): $[M+Na]^+$ 285; **HRMS** (ESI, *m/z*): calcd for $C_{14}H_{11}{}^{35}ClO_3Na$ $[M+Na]^+$ 285.0397, found 285.0398.



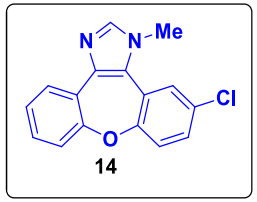
12

1*H*-Dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole (12):- White solid, 189 mg (0.810 mmol), 81% yield, R_f = 0.3 (EtOAc/Hex, 50:50); **MP** 234-236 ^{o}C; **IR** (KBr) 832, 1069, 1187, 1697, 3053, 3117 cm^{-1}; **^{1}H-NMR** (400 MHz, DMSO-d_6) 7.21-7.40 (m, 6H), 7.53-7.55 (d, *J* = 6.0 Hz, 1H), 7.74-7.75 (d, *J* = 6.3 Hz, 1H), 7.95 (s, 1H), 12.90 (brs, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, DMSO-d_6) 121.4, 121.9, 123.6, 125.3, 125.4, 126.1, 127.8, 128.6, 129.2, 135.6, 137.5, 154.2, 154.3; **MS** (ESI, *m/z*): $[M+H]^+$ 235; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{11}N_2O$ $[M+H]^+$ 235.0866, found 235.0873; The spectroscopic data were in good agreement with the reported data. [5]



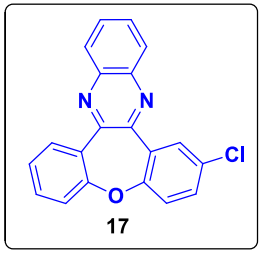
13

11-Chloro-1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole (13):- White solid, 225 mg (0.840 mmol), 84% yield, R_f = 0.3 (EtOAc/Hex, 50:50); **MP** 142-144 ^{o}C; **IR** (KBr) 672, 772, 939, 1692, 3012, 3113 cm^{-1}; **^{1}H-NMR** (400 MHz, DMSO-d$_6$) 7.28-7.43 (m, 5H), 7.53-7.63 (m, 1H), 7.66-7.79 (m, 1H), 7.99 (s, 1H), 13.03 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, DMSO-d$_6$) 122.2, 123.9, 125.4, 126.2, 128.8, 129.2, 130.0, 138.5, 153.2, 154.4; **MS** (ESI, *m/z*): [M+H]$^+$ 269; **HRMS** (ESI, *m/z*): calcd for $C_{15}H_{10}N_2O^{35}Cl$ [M+H]$^+$ 269.0476, found 269.0488; The spectroscopic data were in good agreement with the reported data.[5]



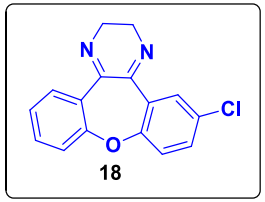
14

11-Chloro-1-methyl-1*H*-dibenzo[2,3:6,7]oxepino[4,5-*d*]imidazole (14):- Colorless liquid, 236 mg (0.840 mmol), 84% yield, R_f = 0.4 (EtOAc/Hex, 40:60); **IR** (KBr) 767, 1213, 1448, 1663, 2924, 3072 cm^{-1}; **^{1}H-NMR** (400 MHz, CDCl$_3$) 3.88 (s, 3H), 7.18-7.25 (m, 3H), 7.35-7.38 (t, *J* = 5.9 Hz, 3H), 7.65 (s, 1H), 7.83 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, CDCl$_3$) 33.6, 122.3, 122.7, 123.0, 125.4, 125.9, 126.6, 127.7, 128.6, 129.3, 129.5, 130.9, 137.2, 140.5, 154.7, 156.3; **MS** (ESI, *m/z*): [M+H]$^+$ 283; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{12}N_2O^{35}Cl$ [M+H]$^+$ 283.0633, found 283.0627.



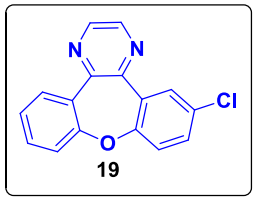
17

7-Chlorodibenzo[2,3:6,7]oxepino[4,5-b]quinoxaline (17):- White solid, 129 mg (0.390 mmol), 78% yield, R_f = 0.45 (EtOAc/Hex, 5:95); **MP** 196-198 ºC; **IR** (KBr) 752, 1174, 1468, 1657, 1678, 3070 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 7.31-7.45 (m, 4H), 7.48-7.53 (m, 1H), 7.79-7.85 (m, 2H), 8.16-8.24 (m, 4H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 121.1, 121.2, 122.6, 126.1, 126.3, 129.5, 130.3, 130.6, 130.8, 131.1, 131.6, 131.8, 132.0, 132.3, 141.7, 142.0, 148.9, 150.0, 159.2, 160.5; **MS** (ESI, *m/z*): $[M+H]^+$ 331; **HRMS** (ESI, *m/z*): calcd for $C_{20}H_{12}N_2O^{35}Cl$ $[M+H]^+$ 331.0633, found 331.0652.



18

6-Chloro-2,3-dihydrodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine (18):- White solid, 183 mg (0.650 mmol), 65% yield, R_f = 0.4 (EtOAc/Hex, 15:85); **MP** 188-190 ºC; **IR** (KBr) 762, 1207, 1447, 1554, 1579, 2895, 3069 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) 3.80 (s, 4H), 7.22-7.27 (m, 3H), 7.33-7.35 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.39-7.44 (m, 1H), 7.80-7.88 (m, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 45.2, 45.4, 121.1, 122.8, 126.0, 129.3, 129.5, 129.9, 130.7, 131.1, 131.9, 132.3, 155.7, 156.4, 156.9, 158.0; **MS** (ESI, *m/z*): $[M+H]^+$ 283; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{12}N_2O^{35}Cl$ $[M+H]^+$ 283.0633, found 283.0648.



19

6-Chlorodibenzo[2,3:6,7]oxepino[4,5-*b*]pyrazine (19):- White solid, 112 mg (0.400 mmol), 80% yield, R_f = 0.5 (EtOAc/Hex, 40:60); **MP** 206-208 ^oC; **IR** (KBr) 767, 1221, 1419, 1532, 1605, 3042 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) 7.29 (s, 1H), 7.30-7.37 (m, 2H), 7.40-7.46 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.48-7.50 (m, 1H), 7.98-8.00 (dd, *J* = 7.7, 1.9 Hz, 2H), 8.68-8.70 (dd, *J* = 9.2, 2.3 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) 121.1, 122.6, 126.1, 129.0, 130.2, 130.4, 130.9, 131.3, 131.4, 131.9, 143.2, 143.7, 148.8, 150.1, 158.6, 160.0; **MS** (ESI, *m/z*): $[M+H]^+$ 281; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{10}N_2O^{35}Cl$ $[M+H]^+$ 281.0476, found 281.0493.

18. References

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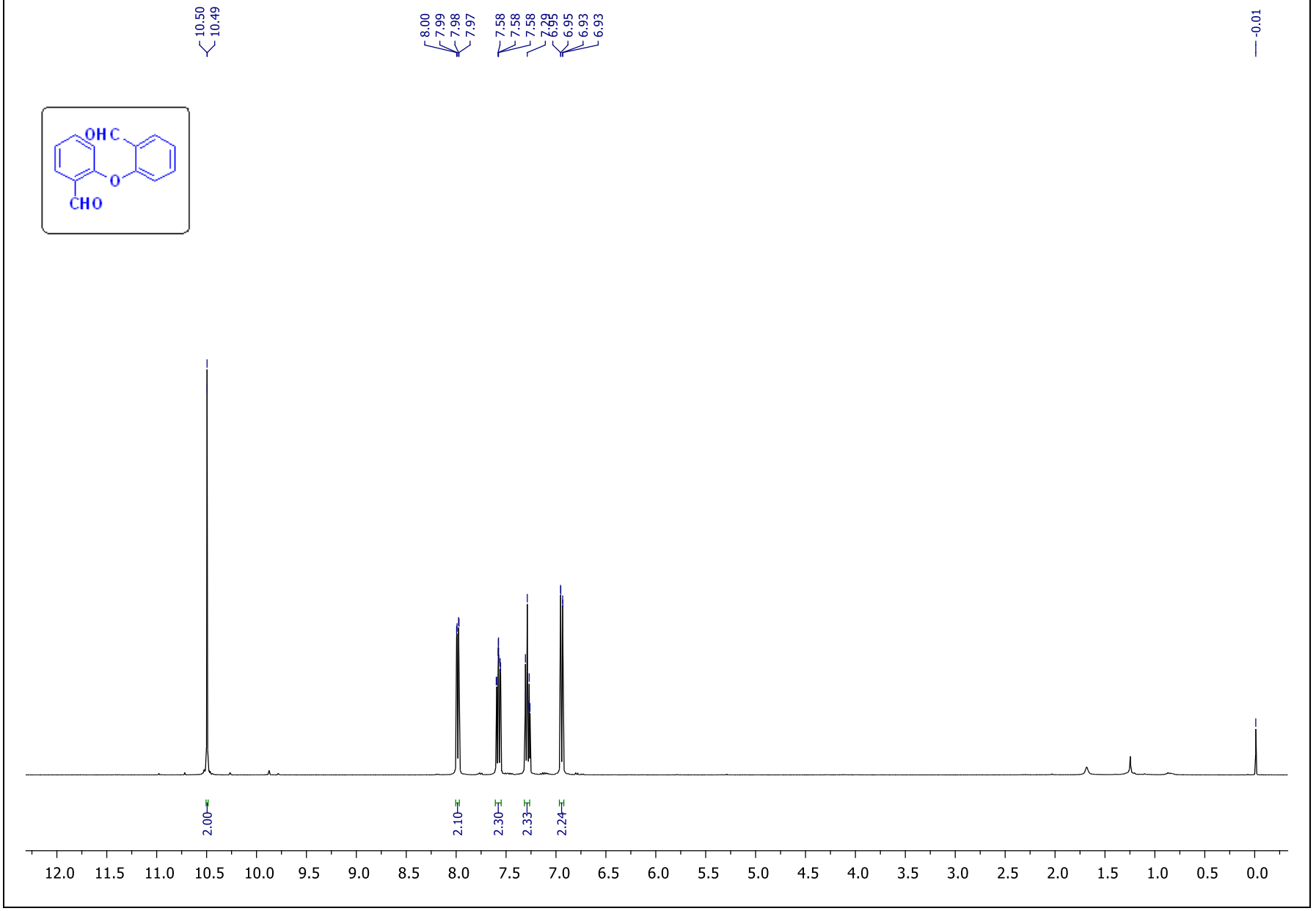
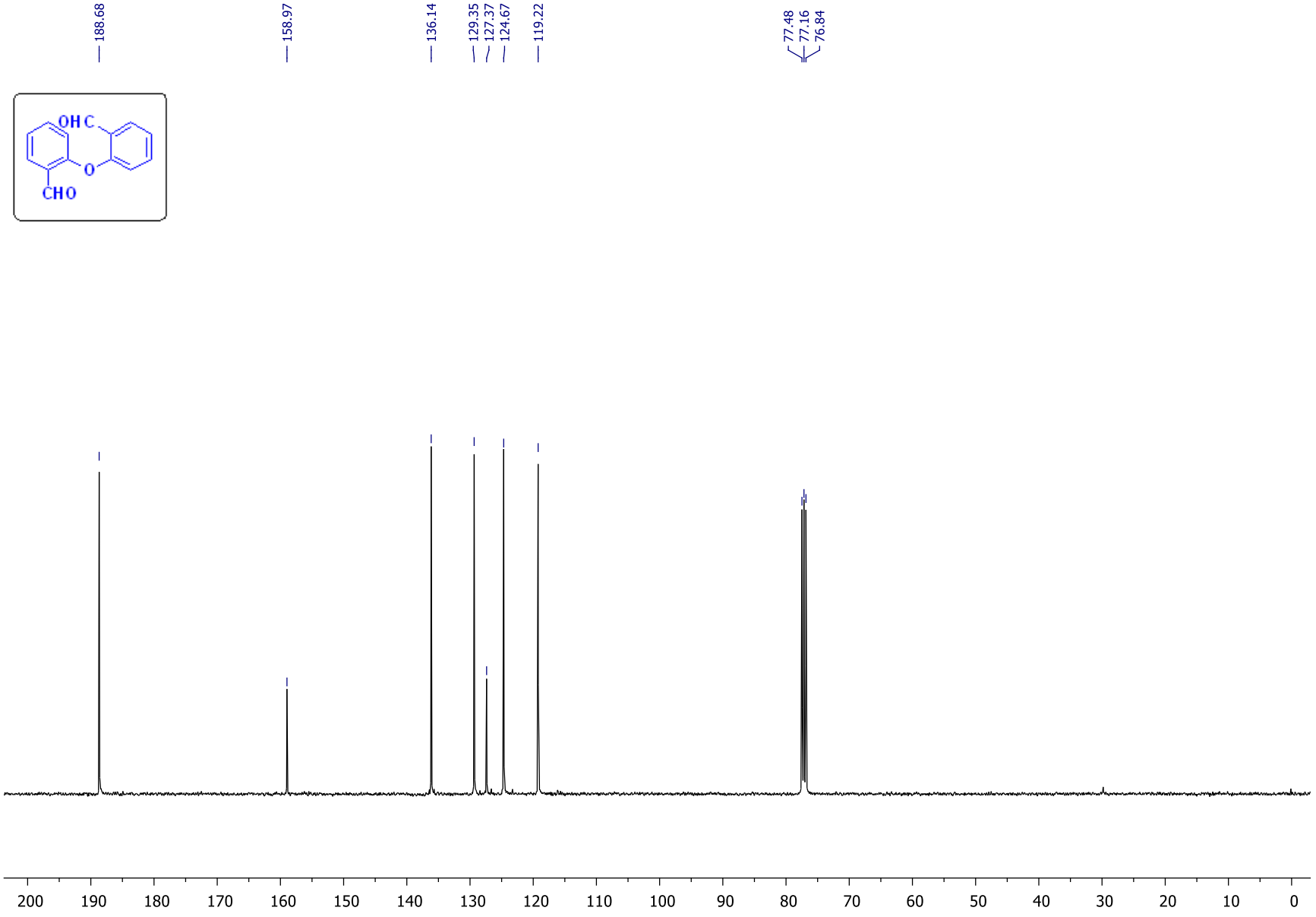
17. Copies of ^{1}H and ^{13}C NMR spectra of the starting materials and products

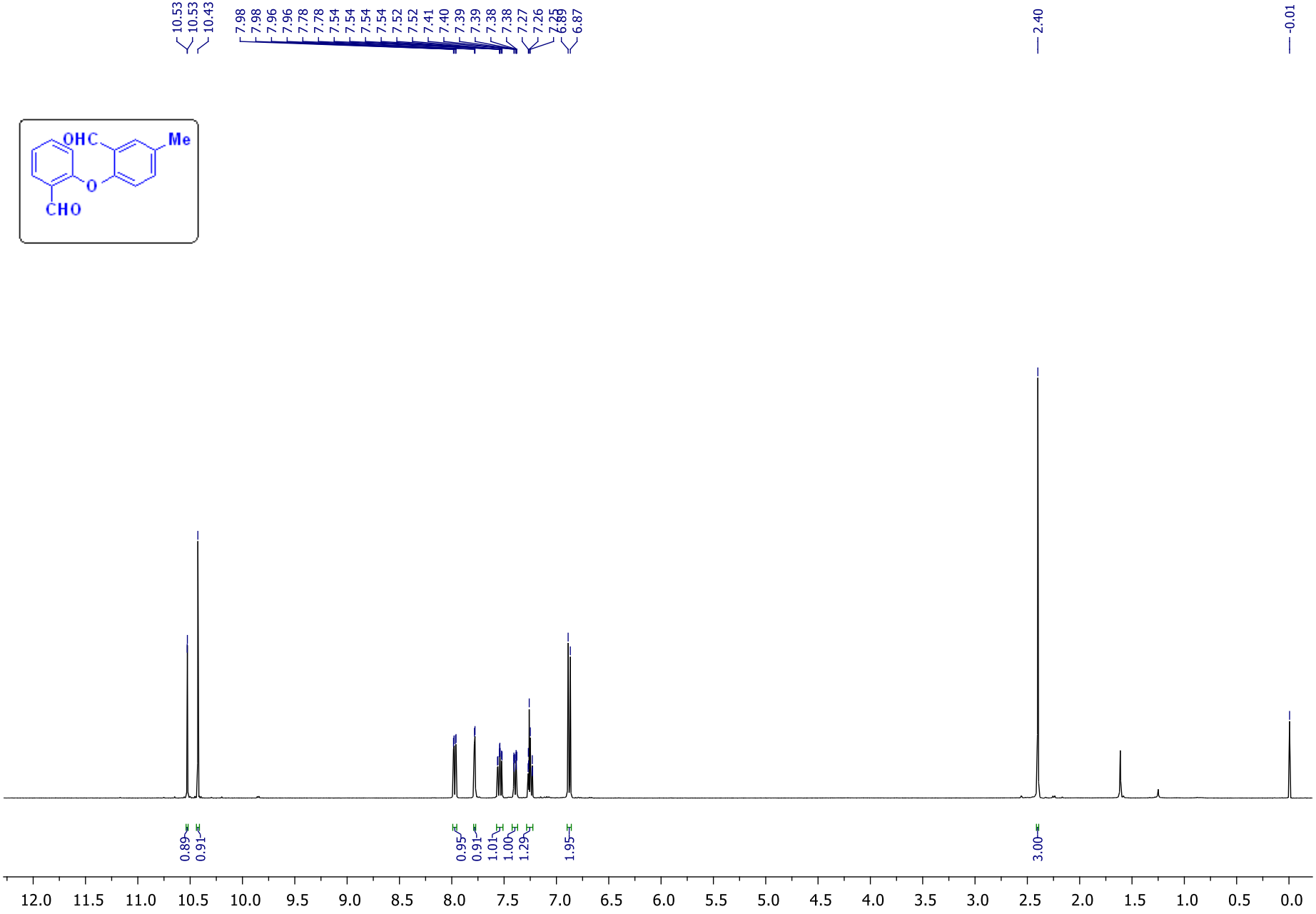
^{1}H-NMR of 1a (400 MHz, $CDCl_3$)



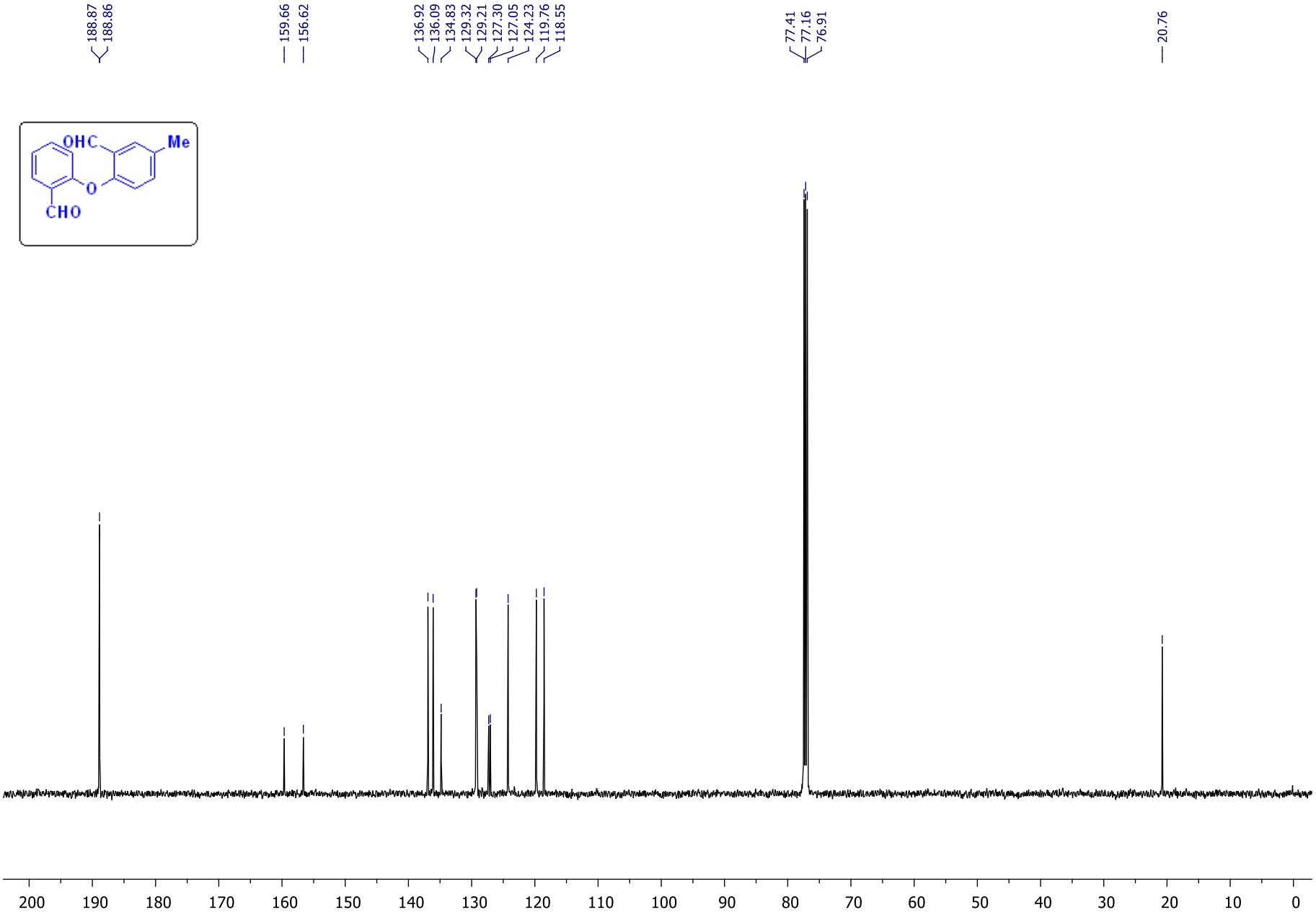
$^{13}C\{^{1}H\}$-NMR of 1a (101 MHz, $CDCl_3$)



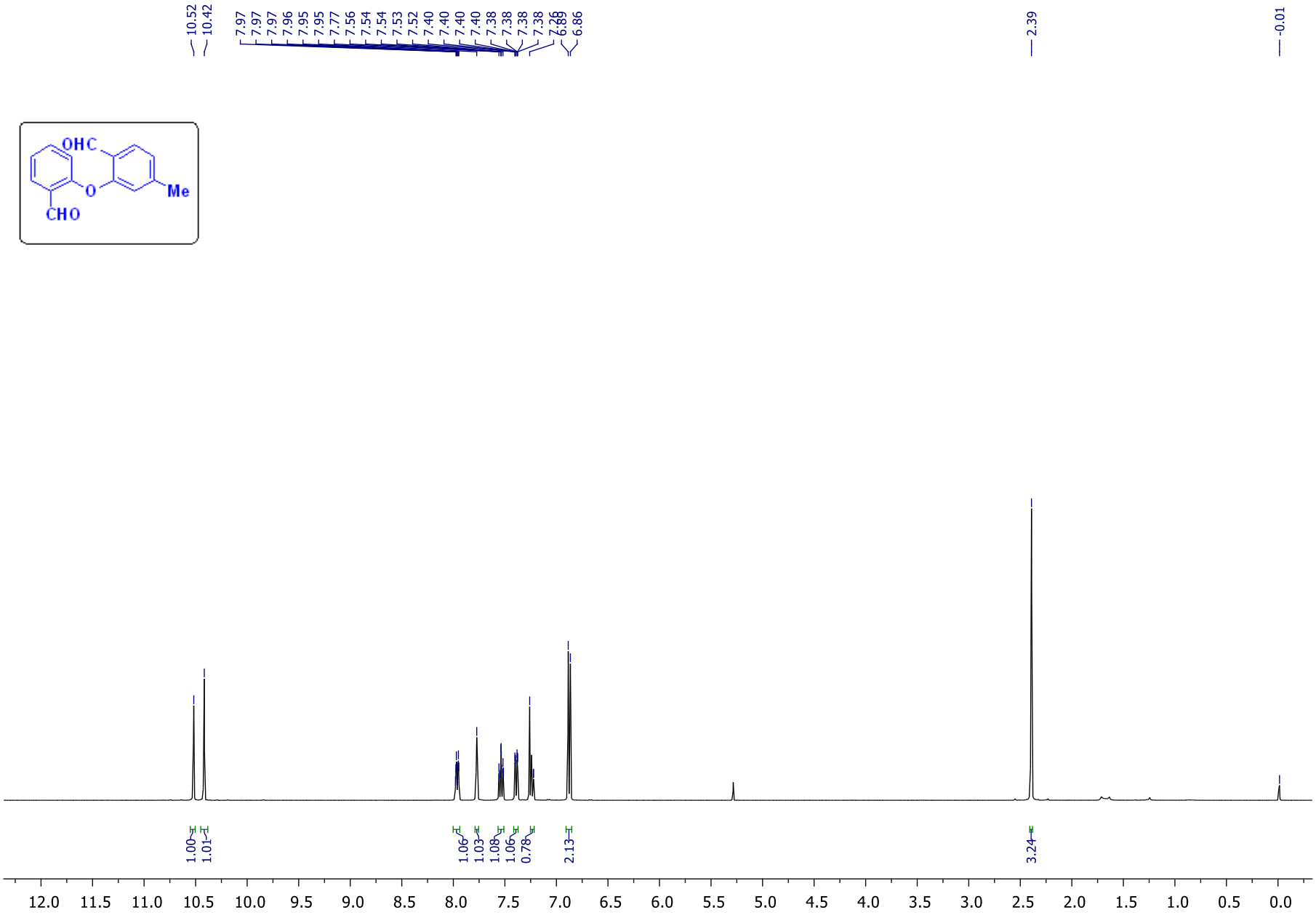
^{1}H-NMR of 1b (400 MHz, $CDCl_3$)



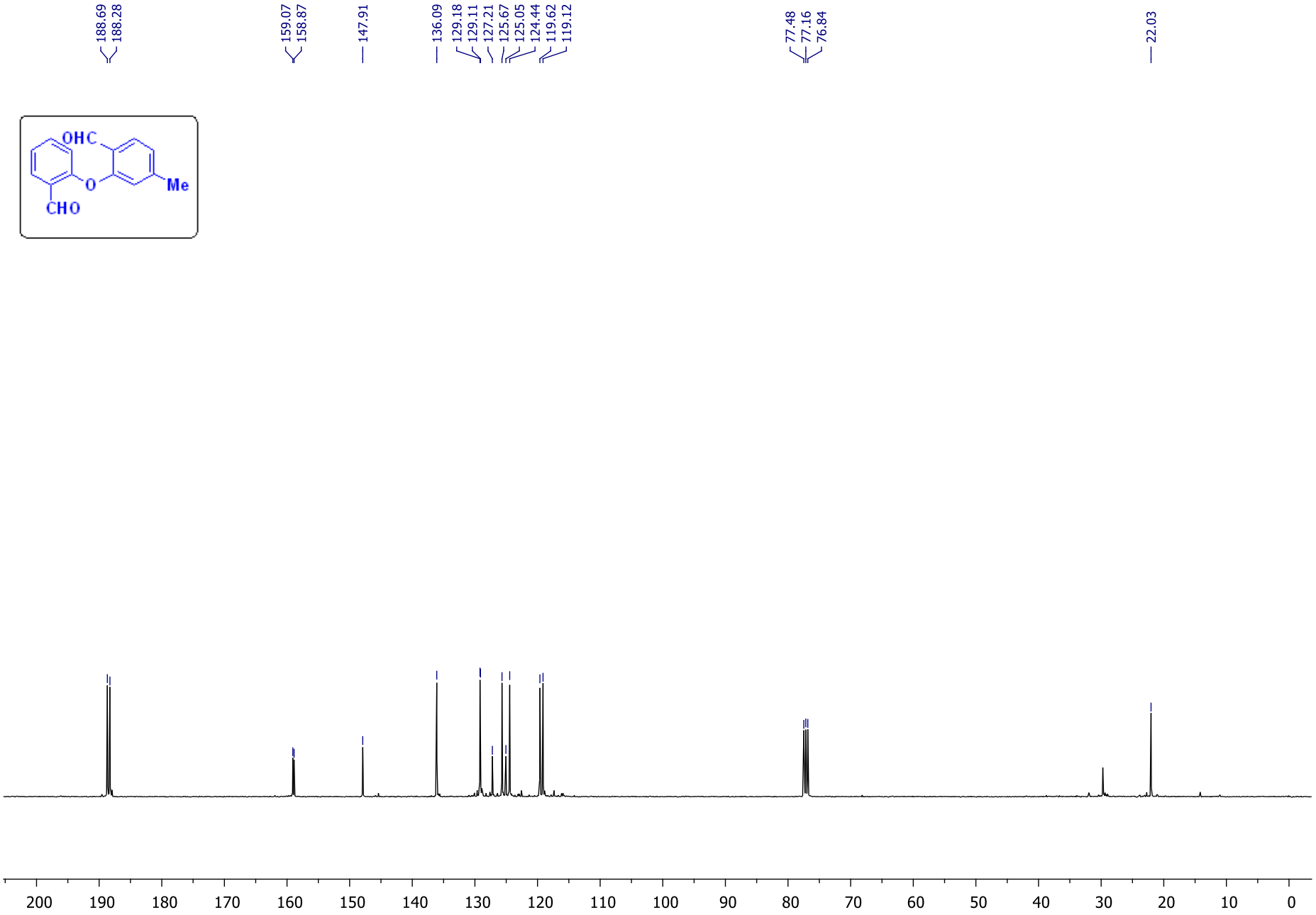
$^{13}C\{^{1}H\}$-NMR of 1b (126 MHz, $CDCl_3$)



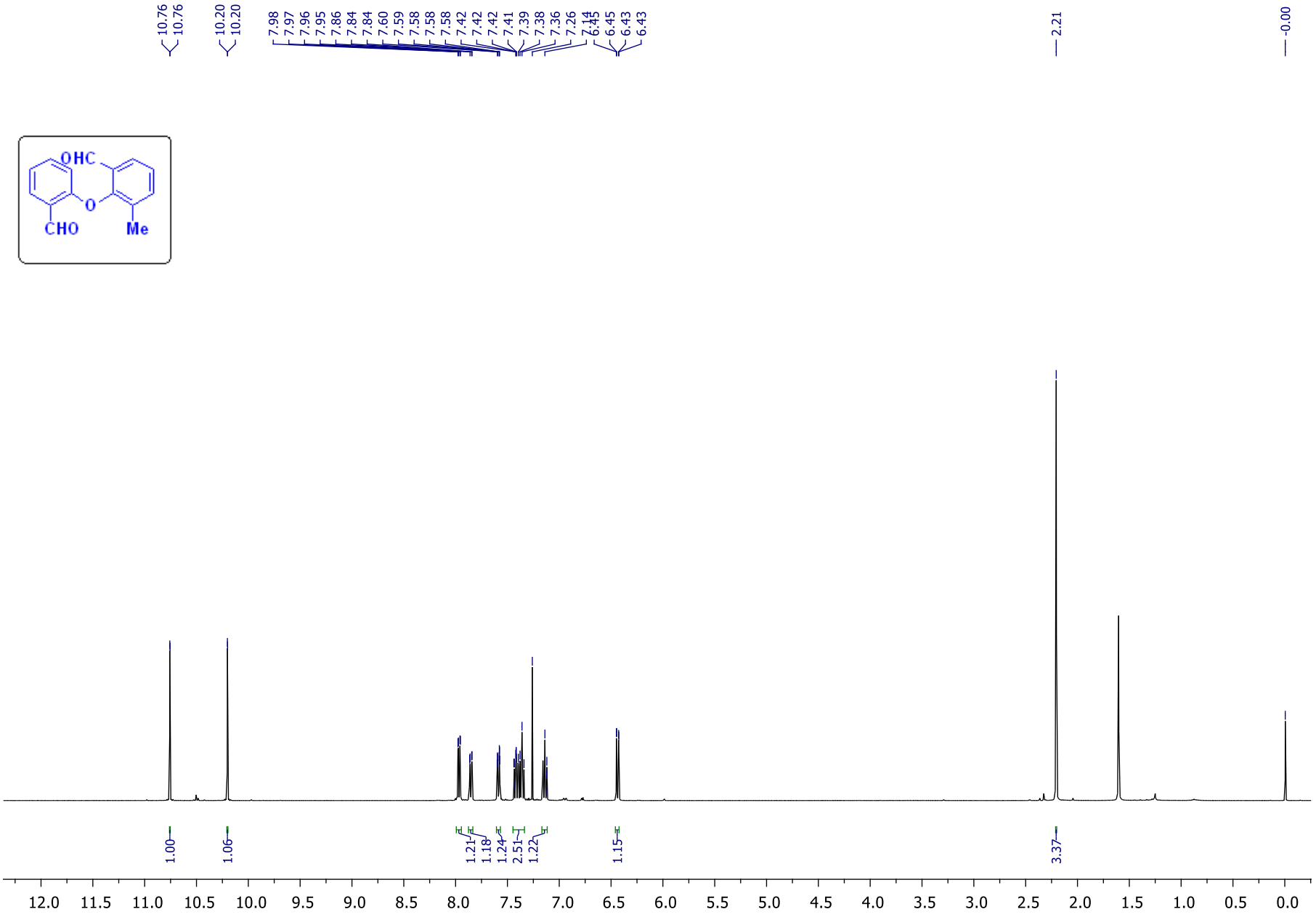
^{1}H-NMR of 1c (400 MHz, $CDCl_3$)



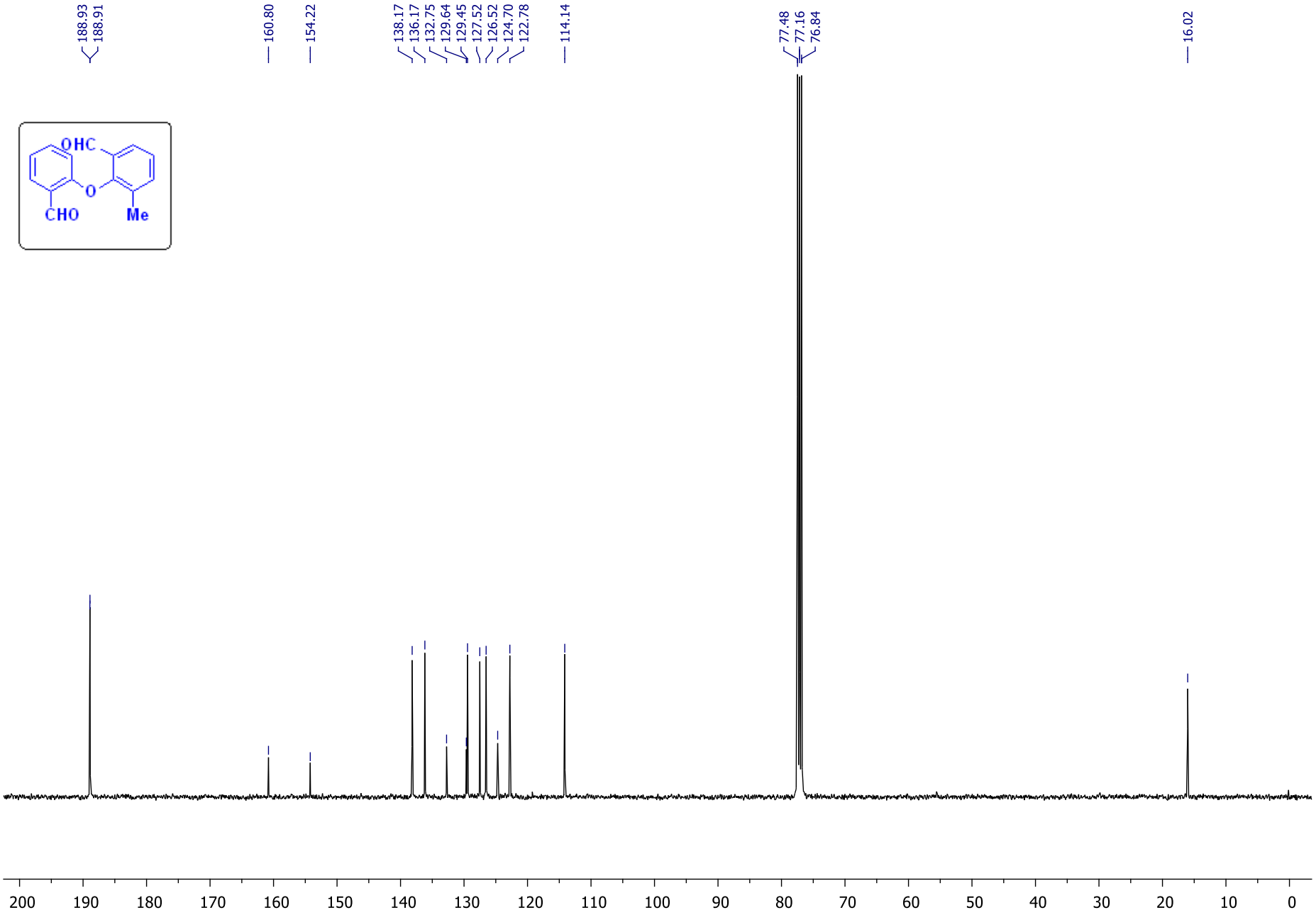
$^{13}C\{^{1}H\}$-NMR of 1c (101 MHz, $CDCl_3$)



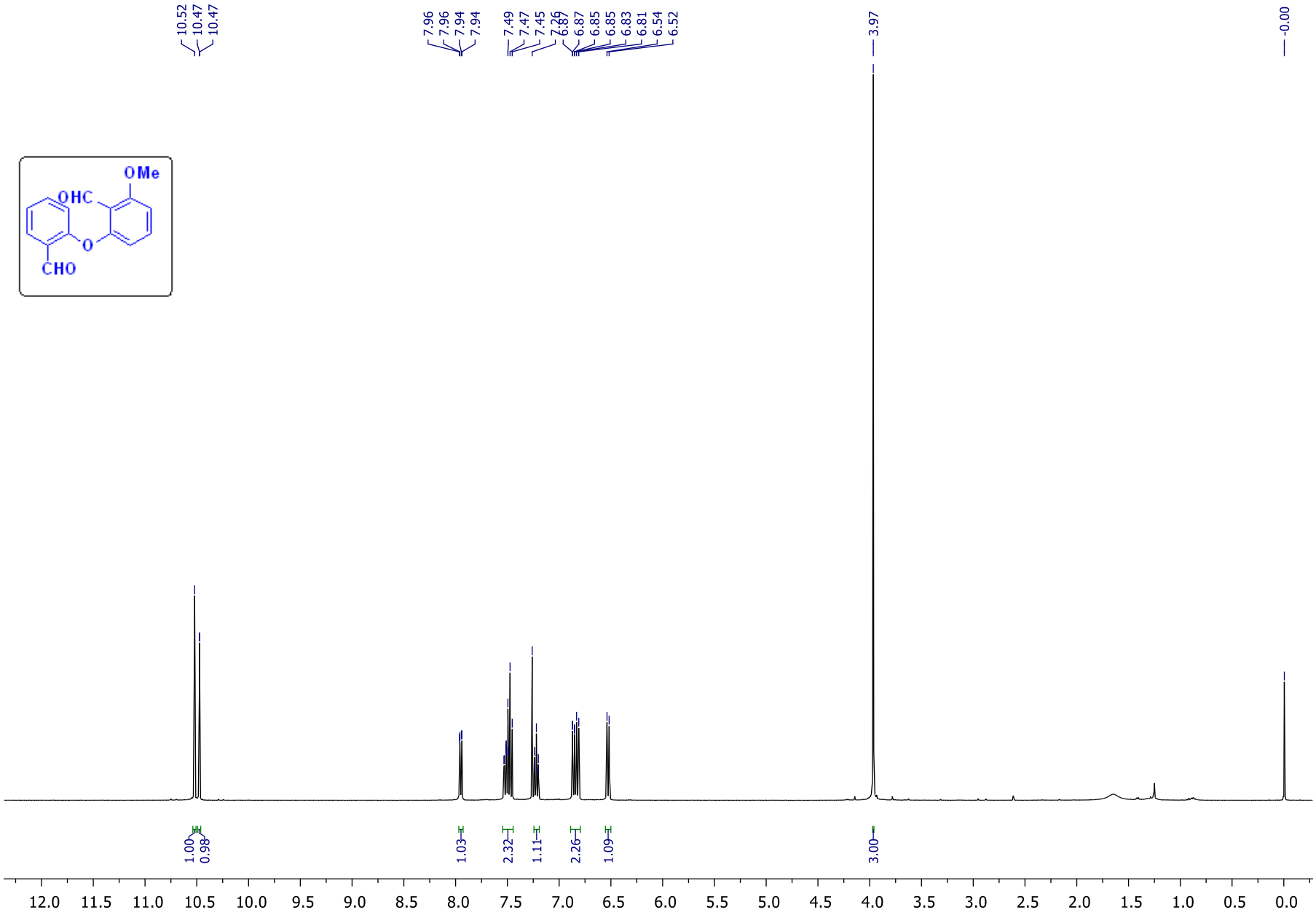
^{1}H-NMR of 1d (400 MHz, $CDCl_3$)



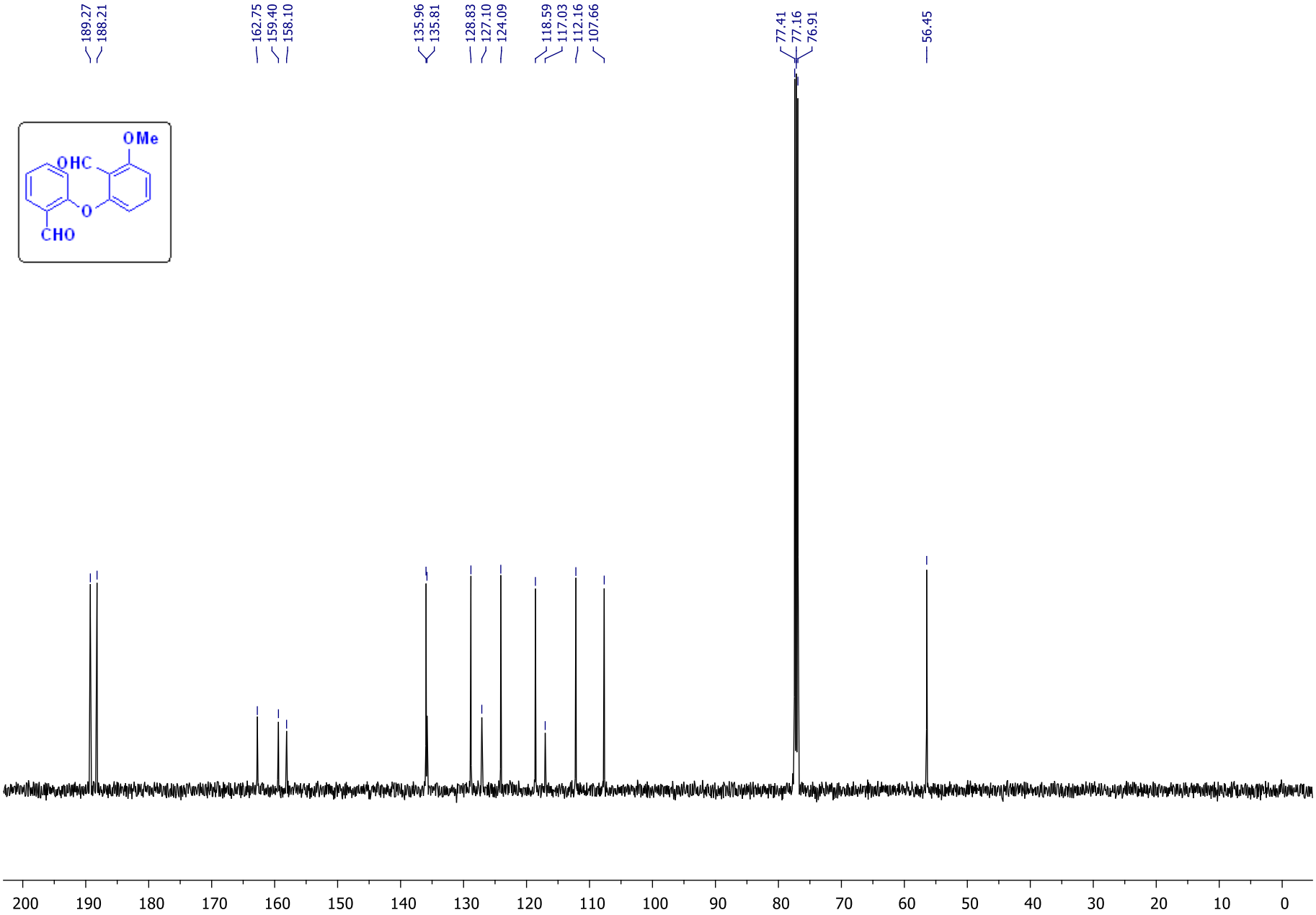
$^{13}C\{^{1}H\}$-NMR of 1d (101 MHz, $CDCl_3$)



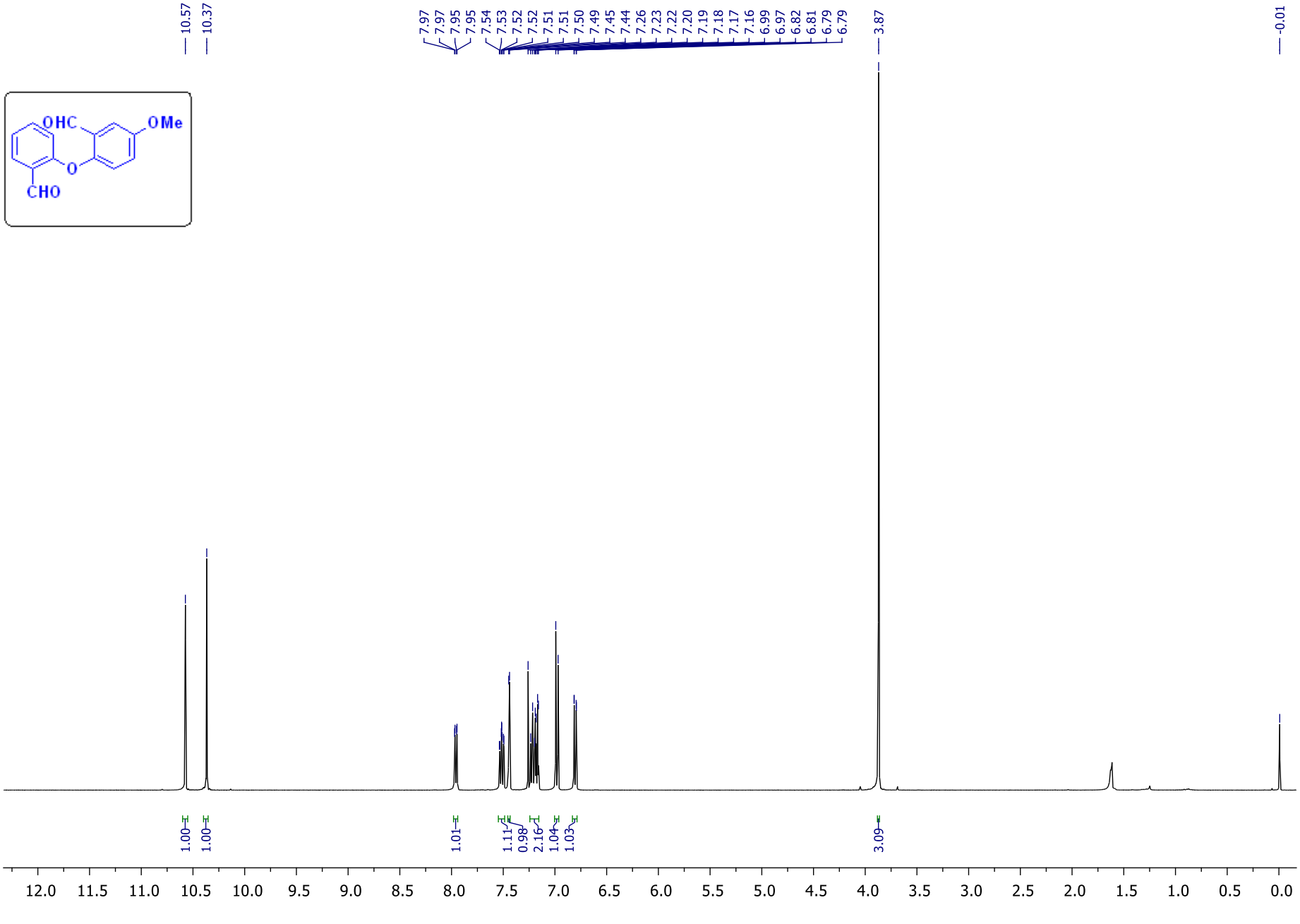
^{1}H-NMR of 1e (400 MHz, $CDCl_3$)



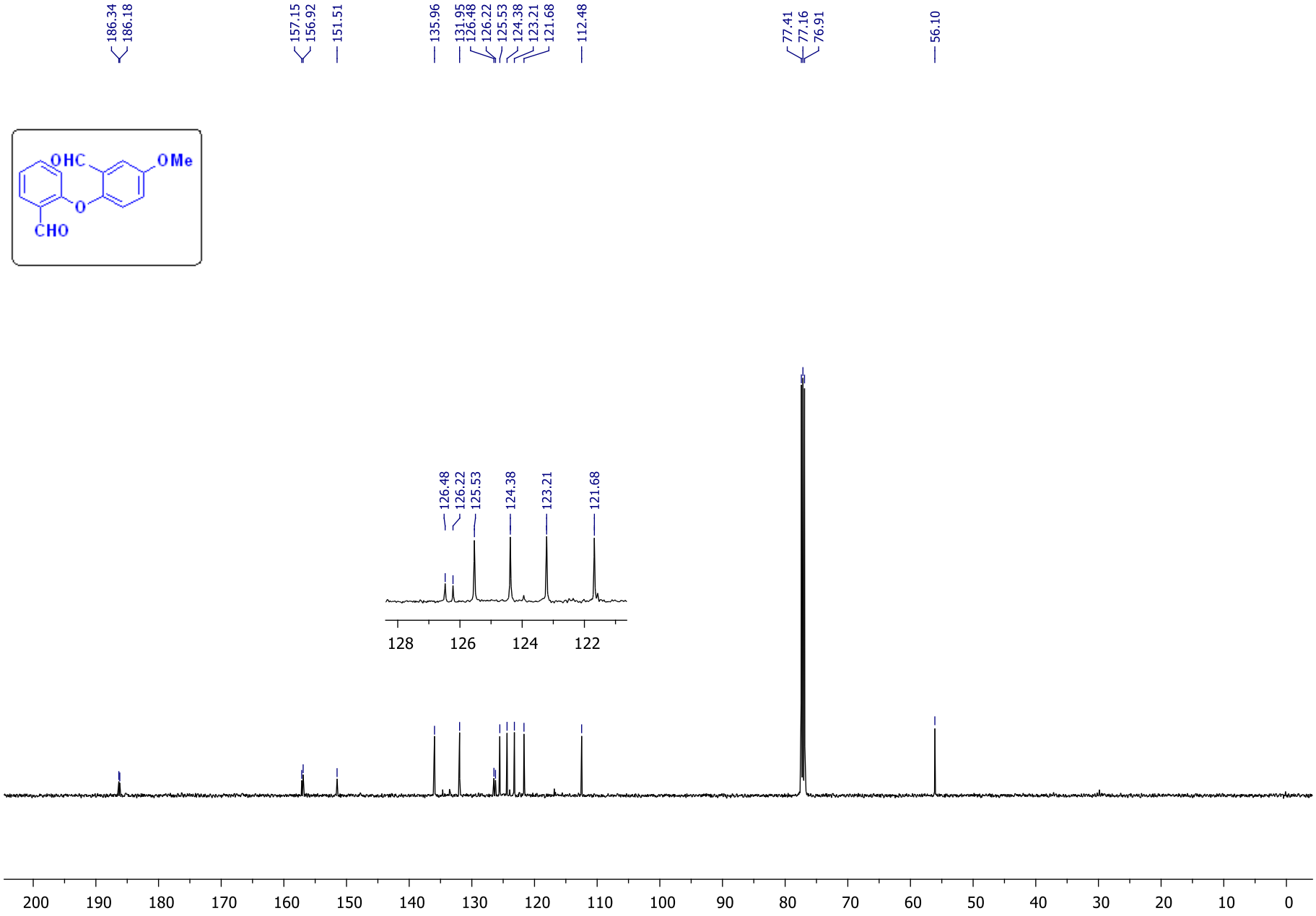
$^{13}C\{^{1}H\}$-NMR of 1e (101 MHz, $CDCl_3$)



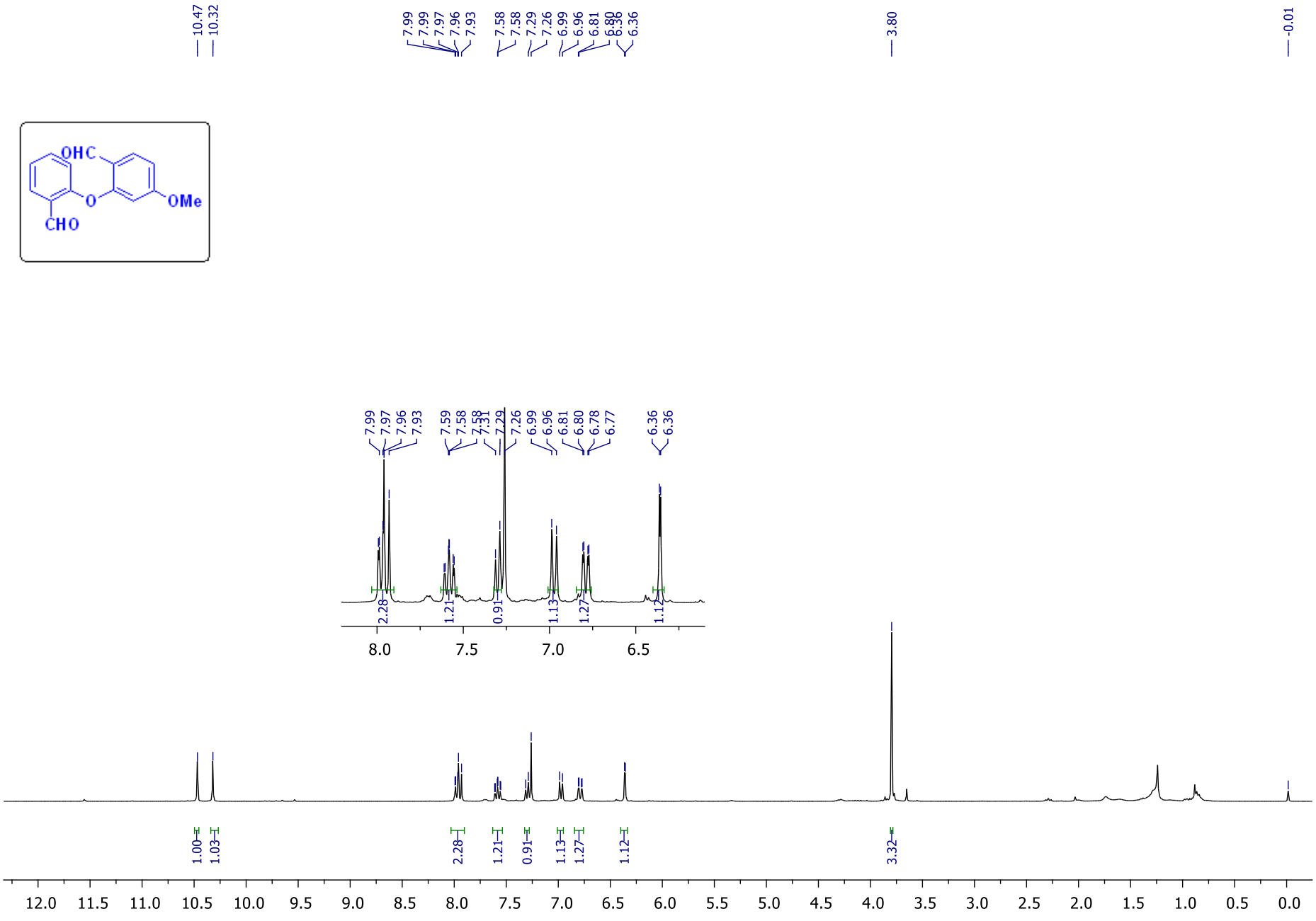
^{1}H-NMR of 1f (400 MHz, $CDCl_3$)



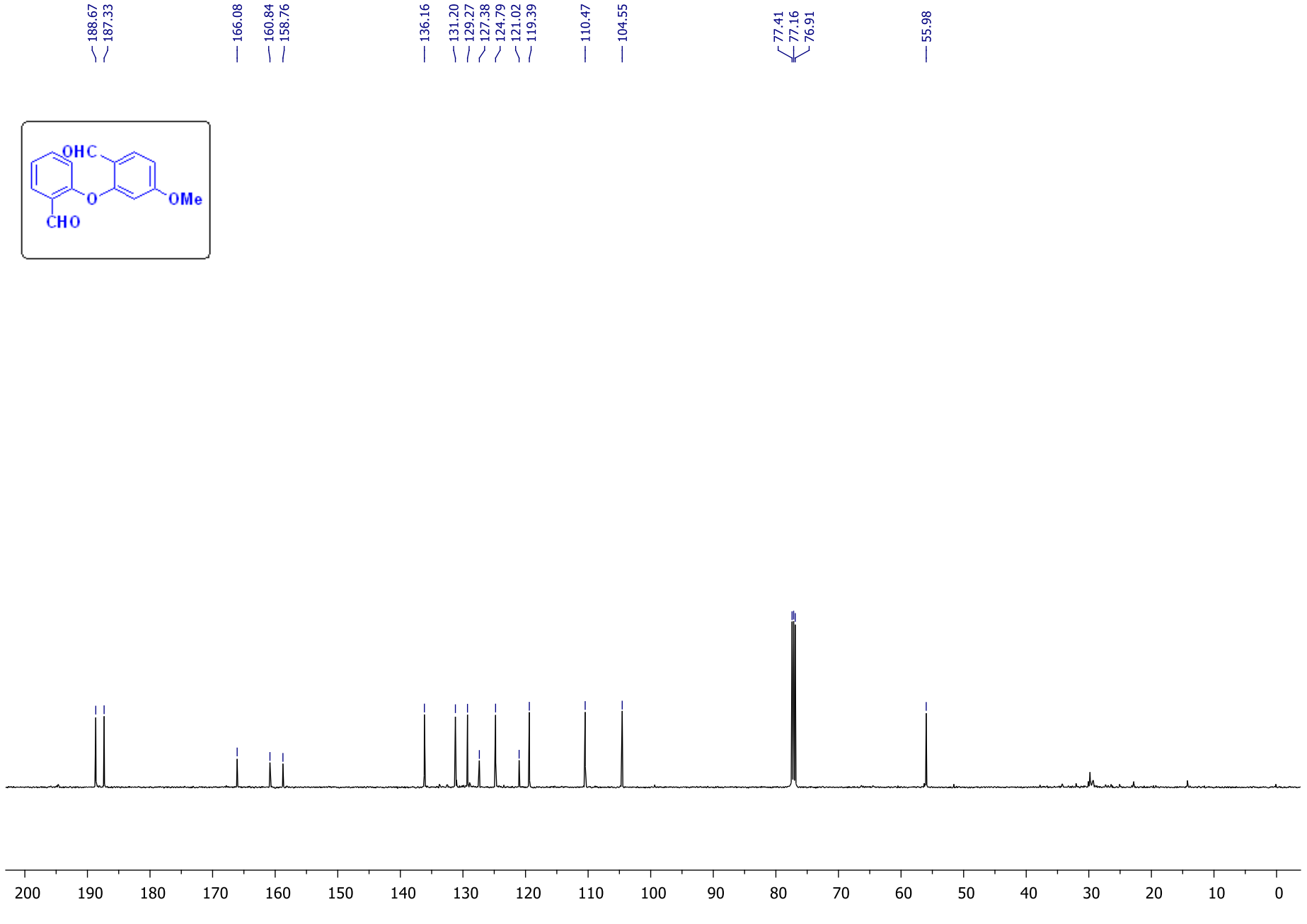
$^{13}C\{^{1}H\}$-NMR of 1f (126 MHz, $CDCl_3$)



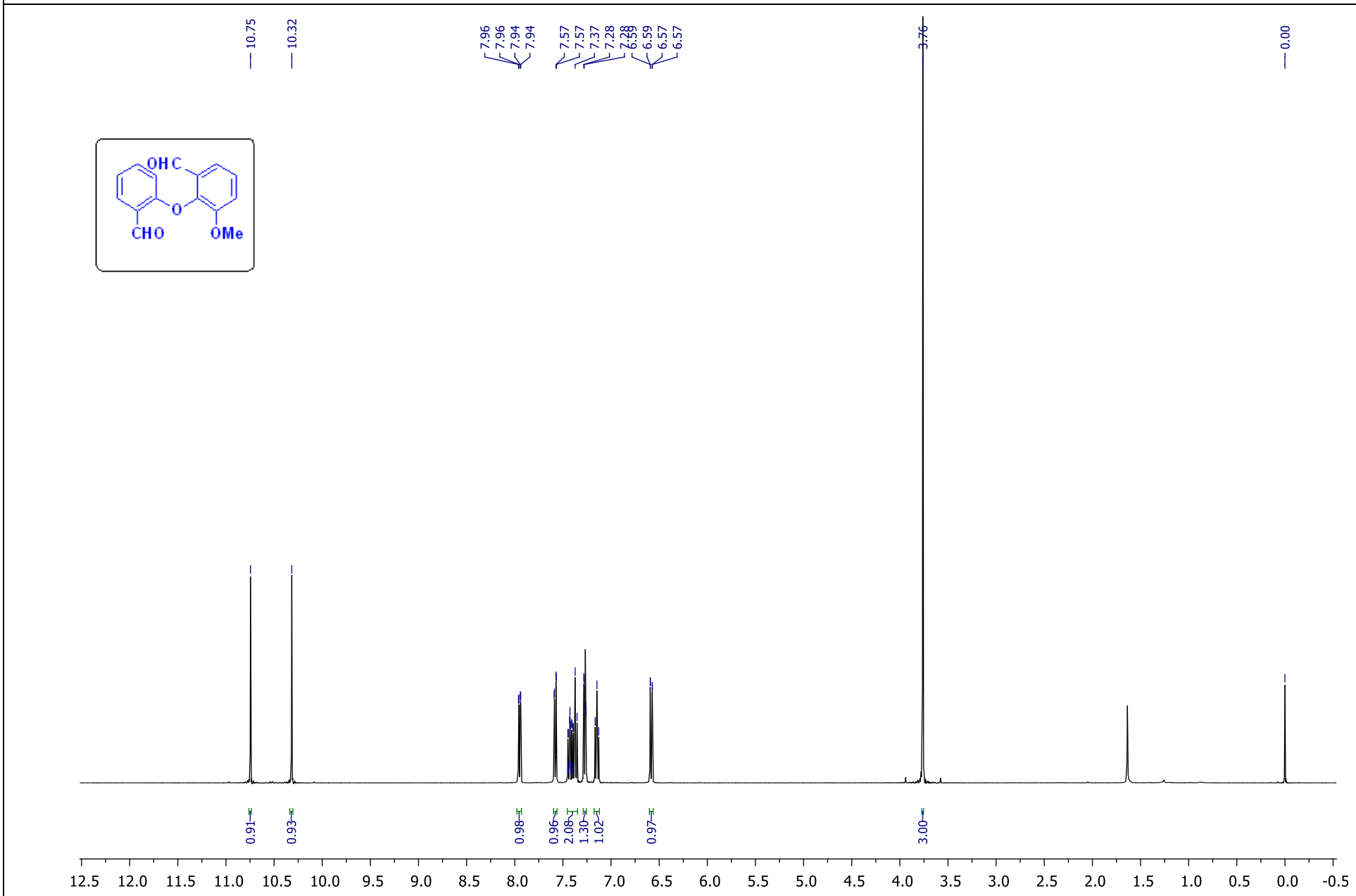
^{1}H-NMR of 1g (300 MHz, $CDCl_3$)



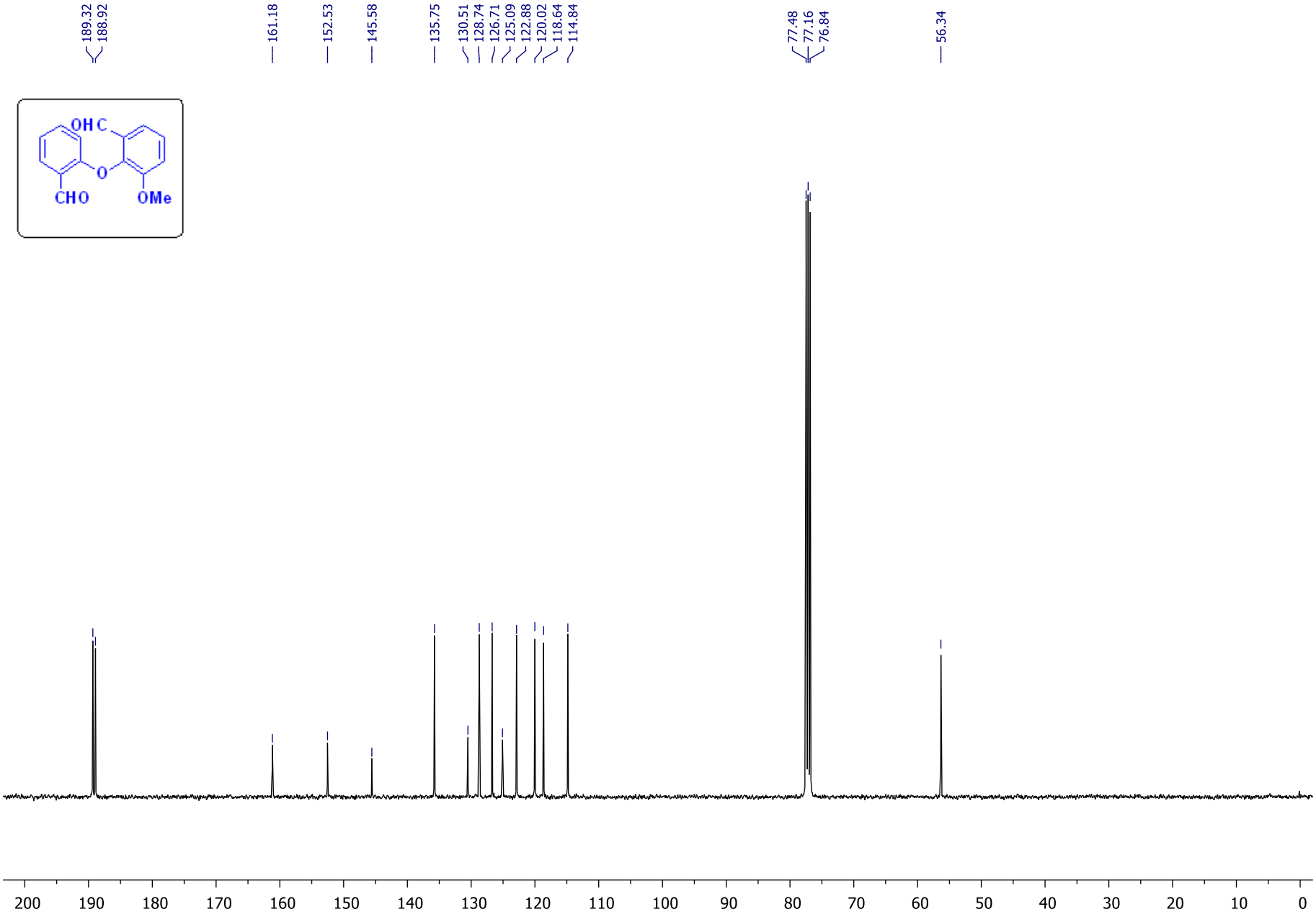
$^{13}C\{^{1}H\}$-NMR of 1g (126 MHz, $CDCl_3$)



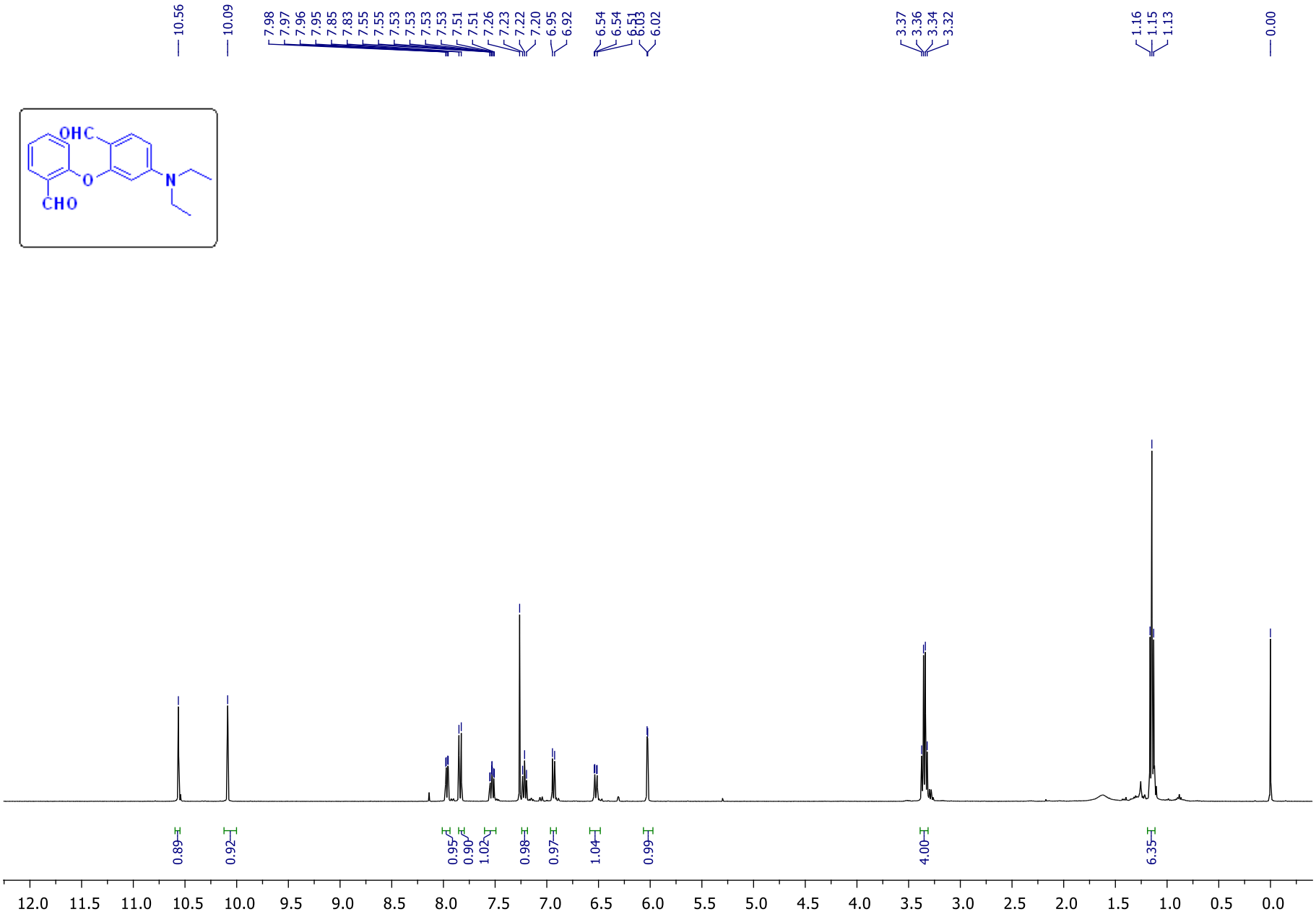
^{1}H-NMR of 1h (400 MHz, $CDCl_3$)



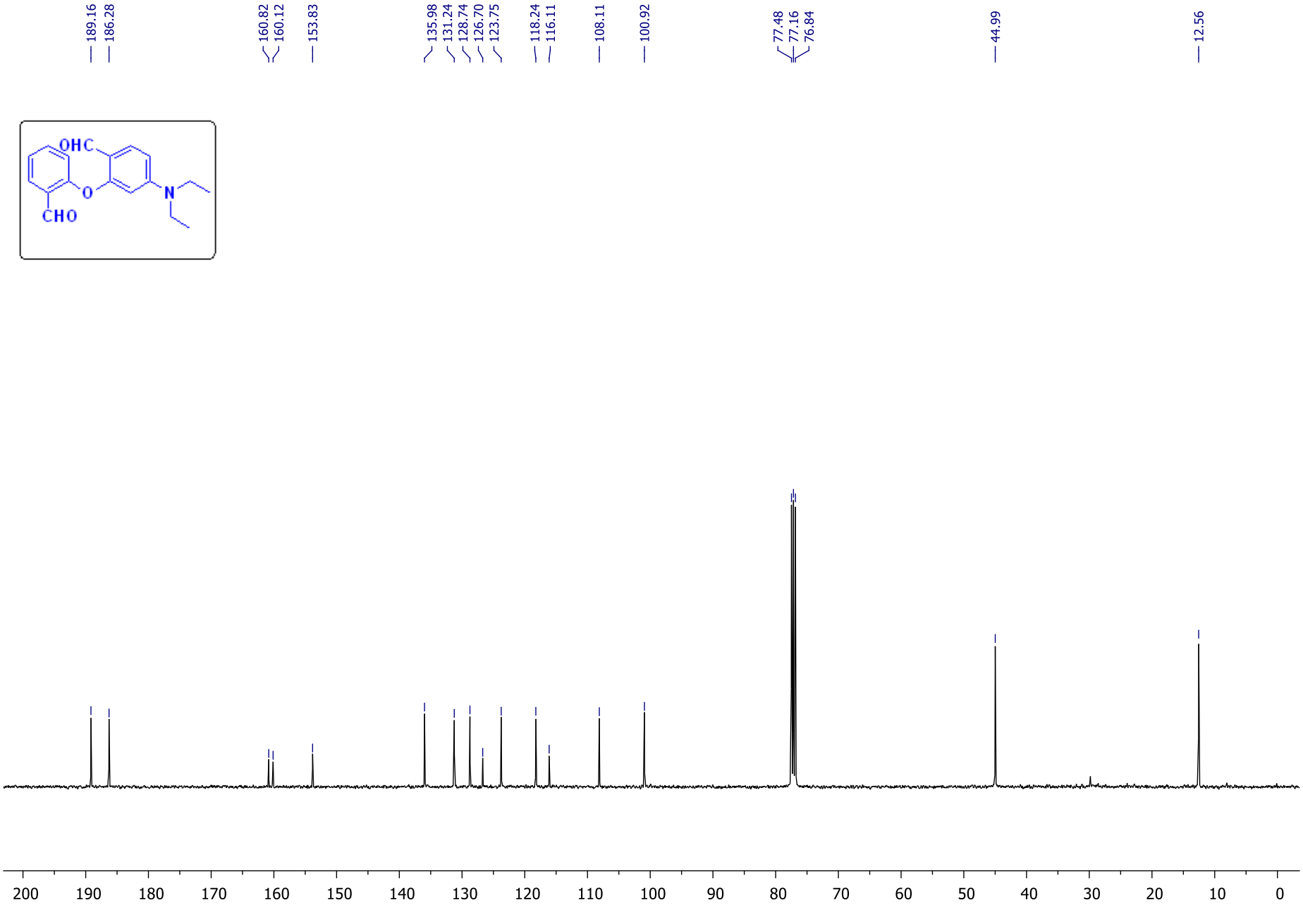
$^{13}C\{^{1}H\}$-NMR of 1h (101 MHz, $CDCl_3$)



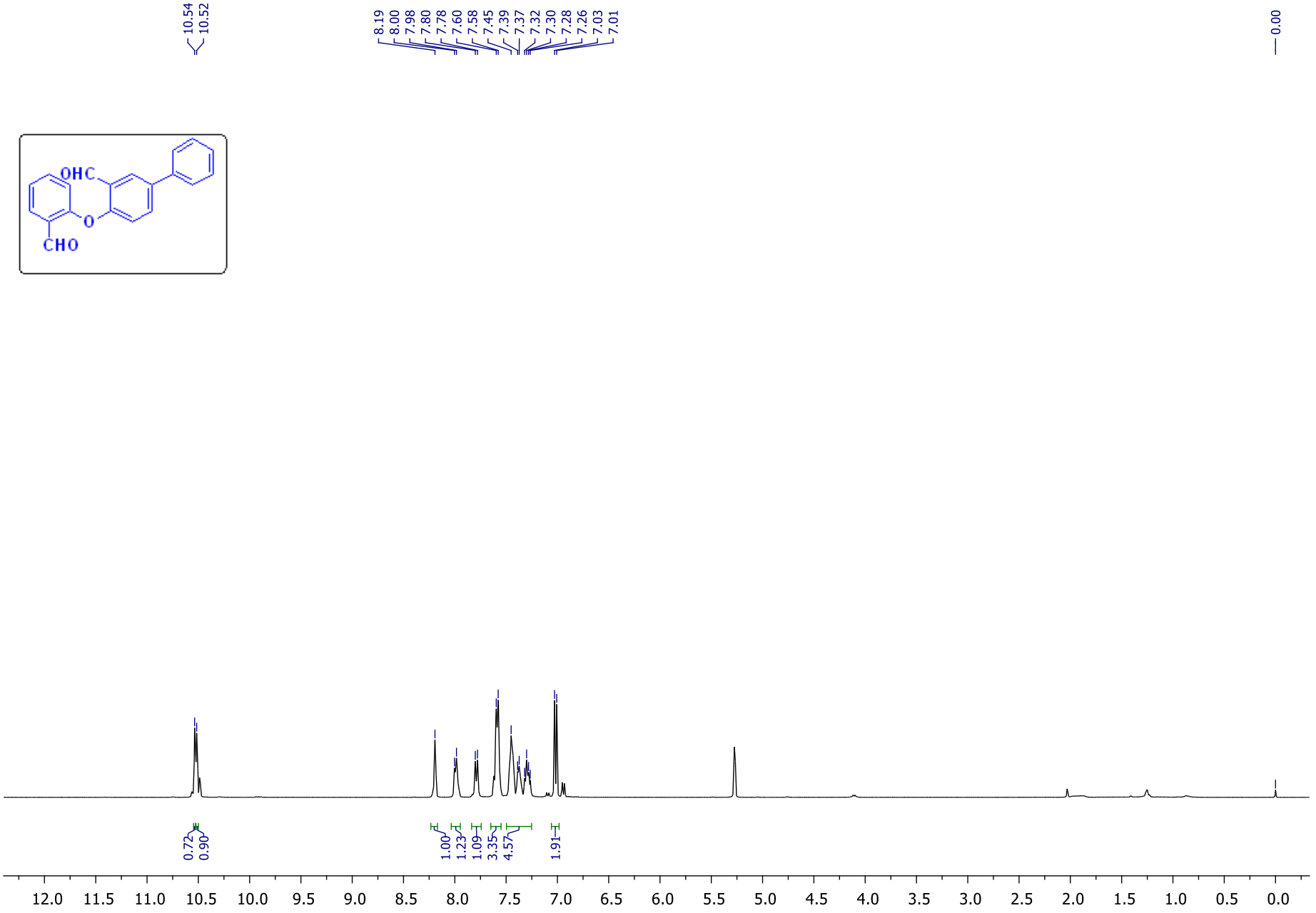
^{1}H-NMR of 1i (400 MHz, $CDCl_3$)



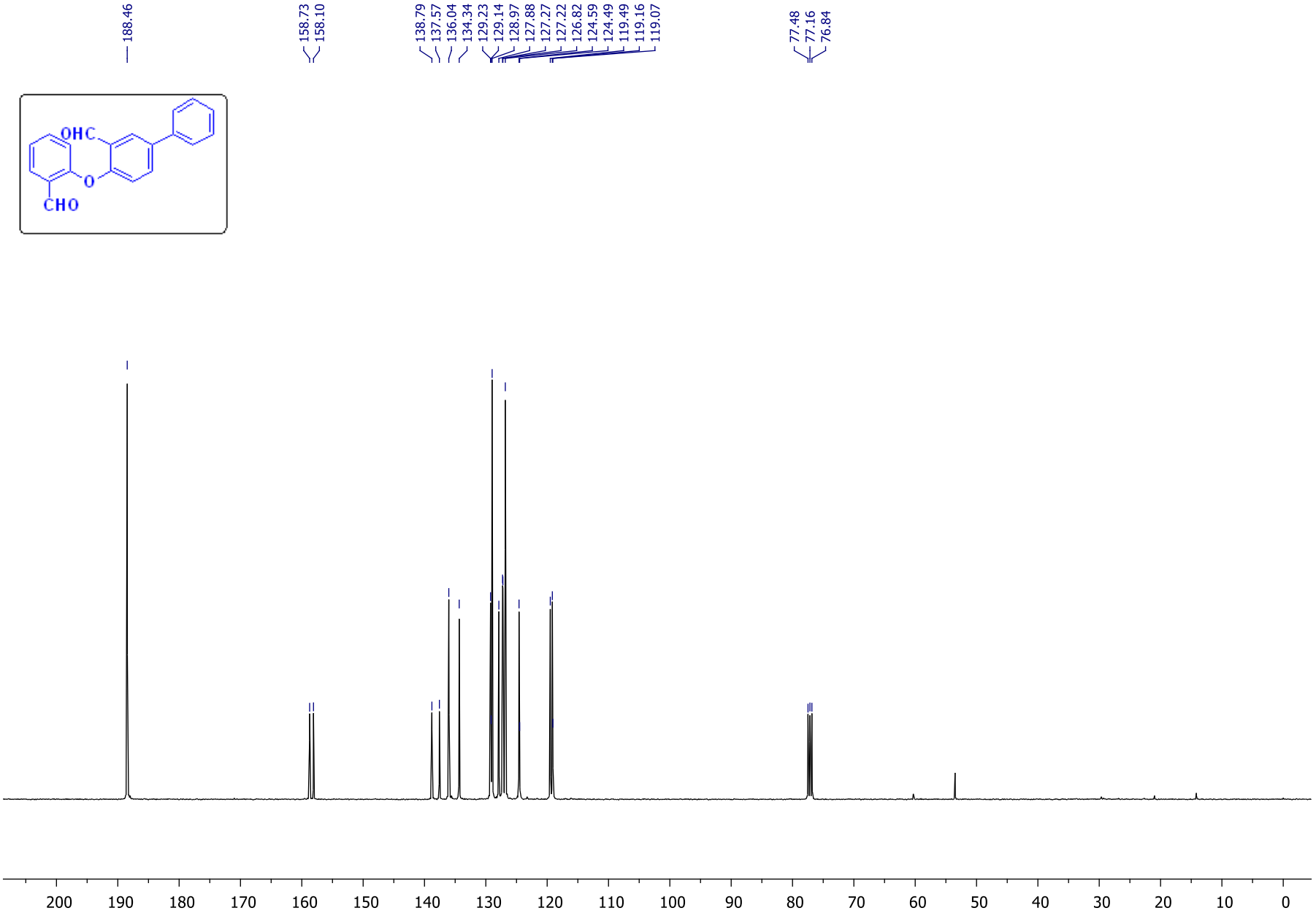
$^{13}C\{^{1}H\}$-NMR of 1i (101 MHz, $CDCl_3$)



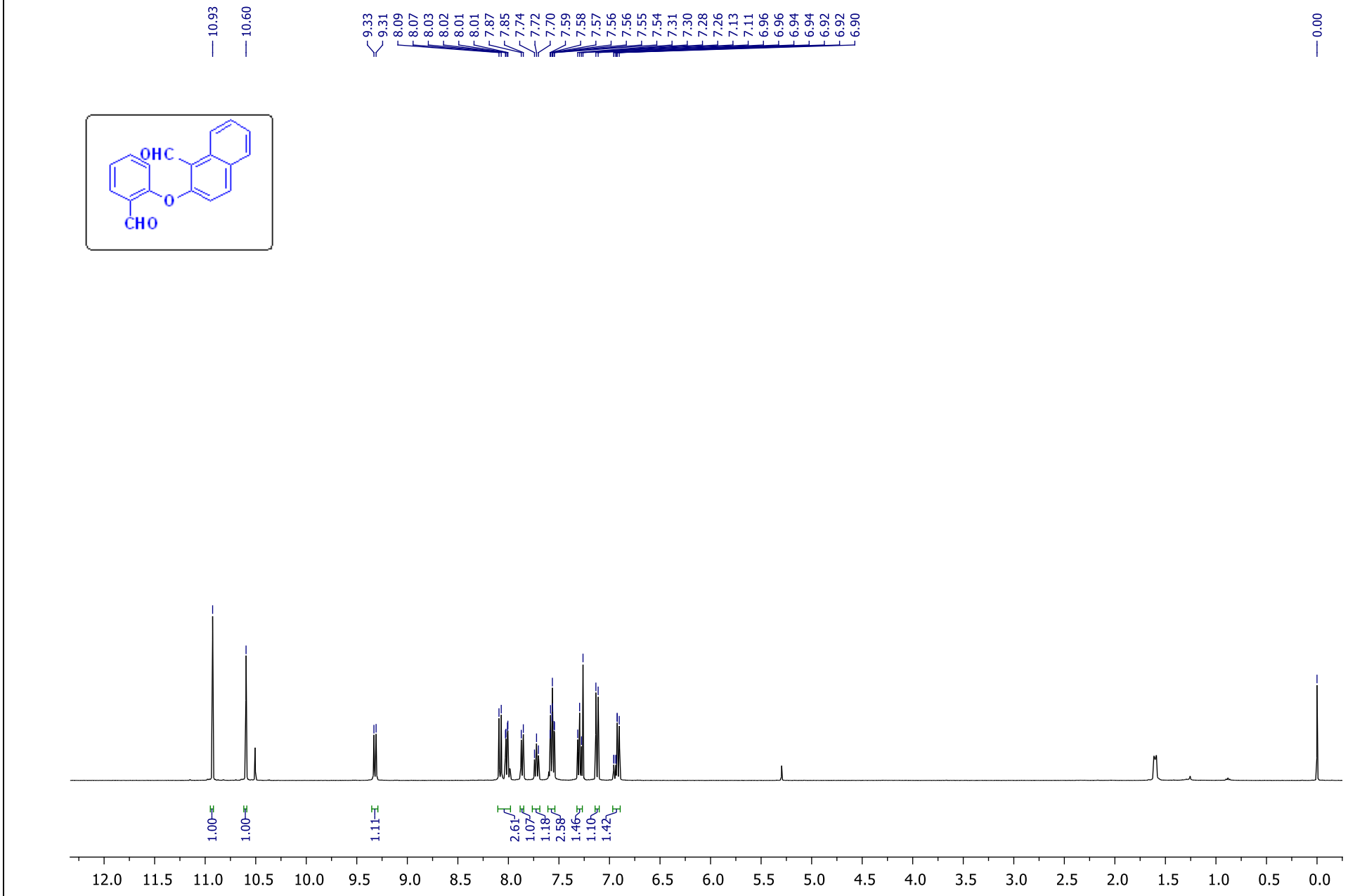
^{1}H-NMR of 1j (400 MHz, $CDCl_3$)



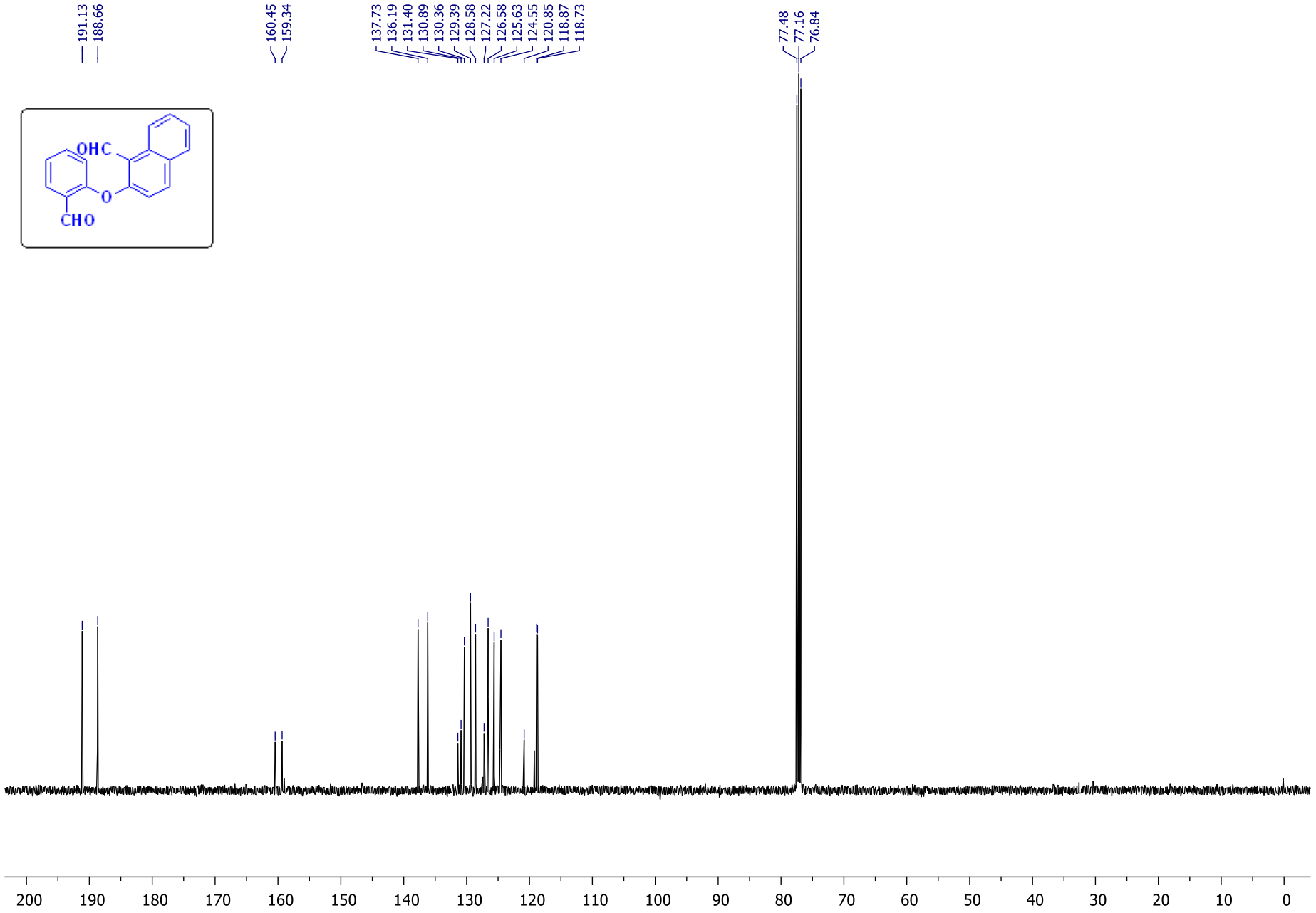
$^{13}C\{^{1}H\}$-NMR of 1j (101 MHz, $CDCl_3$)



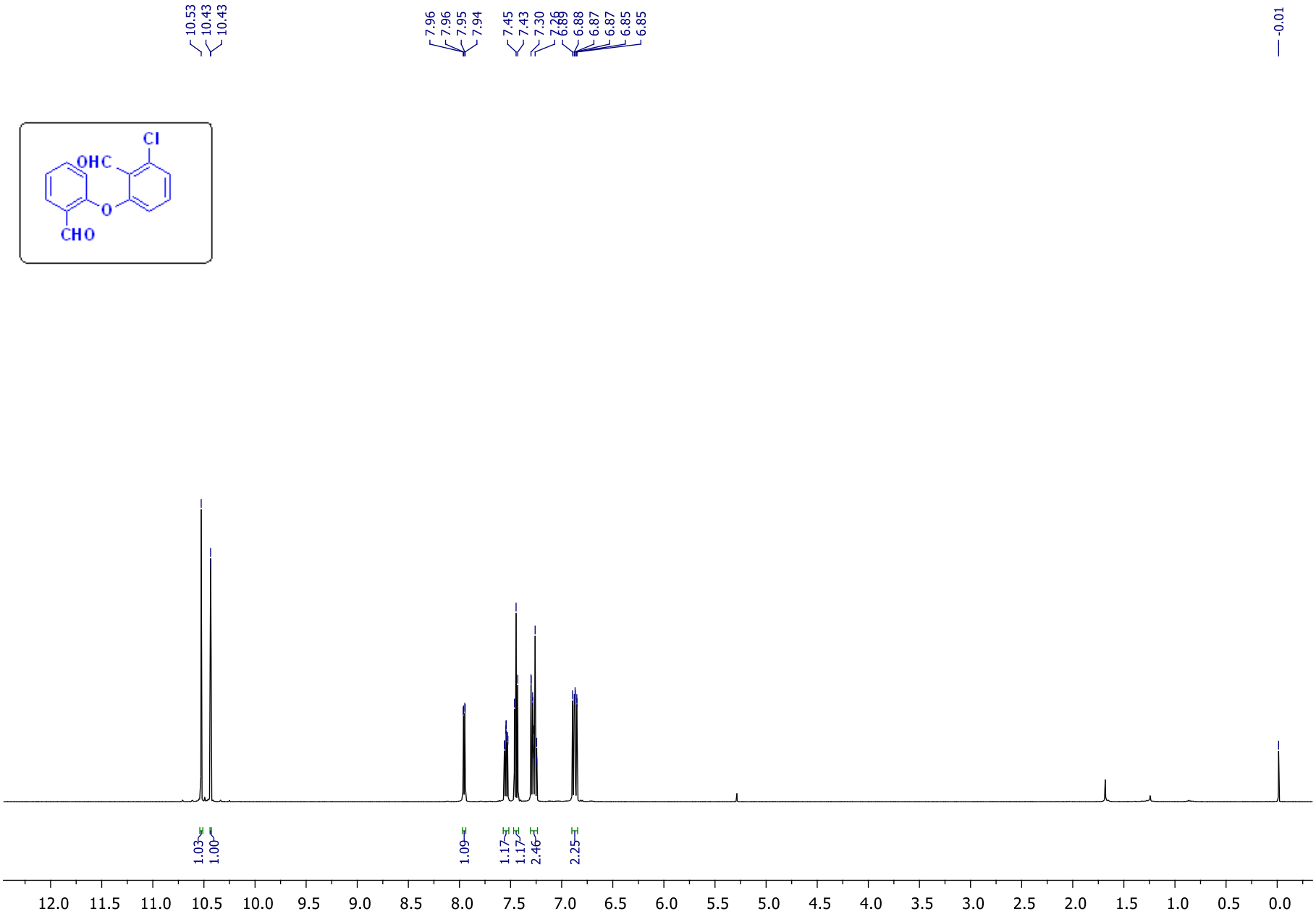
^{1}H-NMR of 1k (400 MHz, $CDCl_3$)



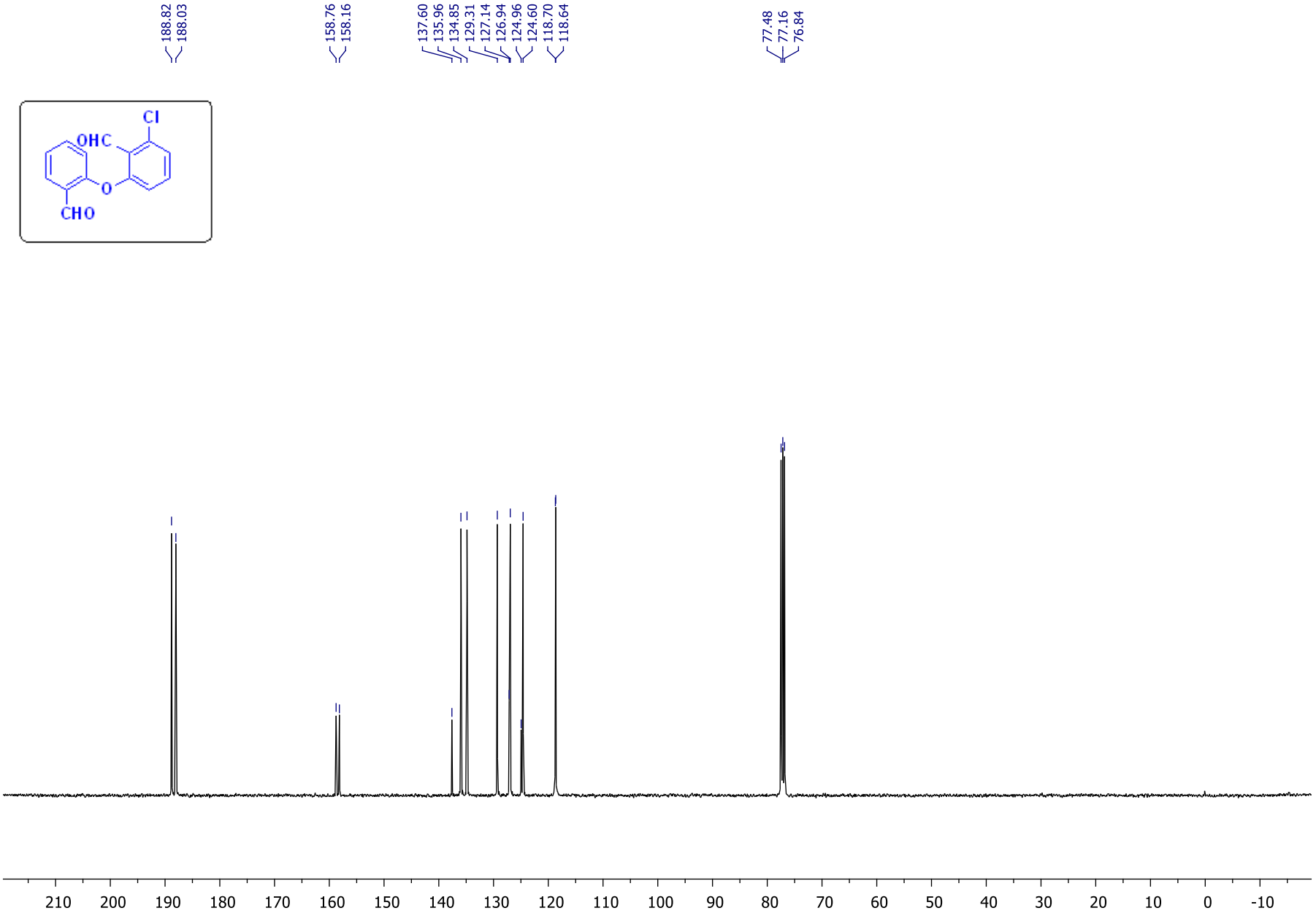
$^{13}C\{^{1}H\}$-NMR of 1k (101 MHz, $CDCl_3$)



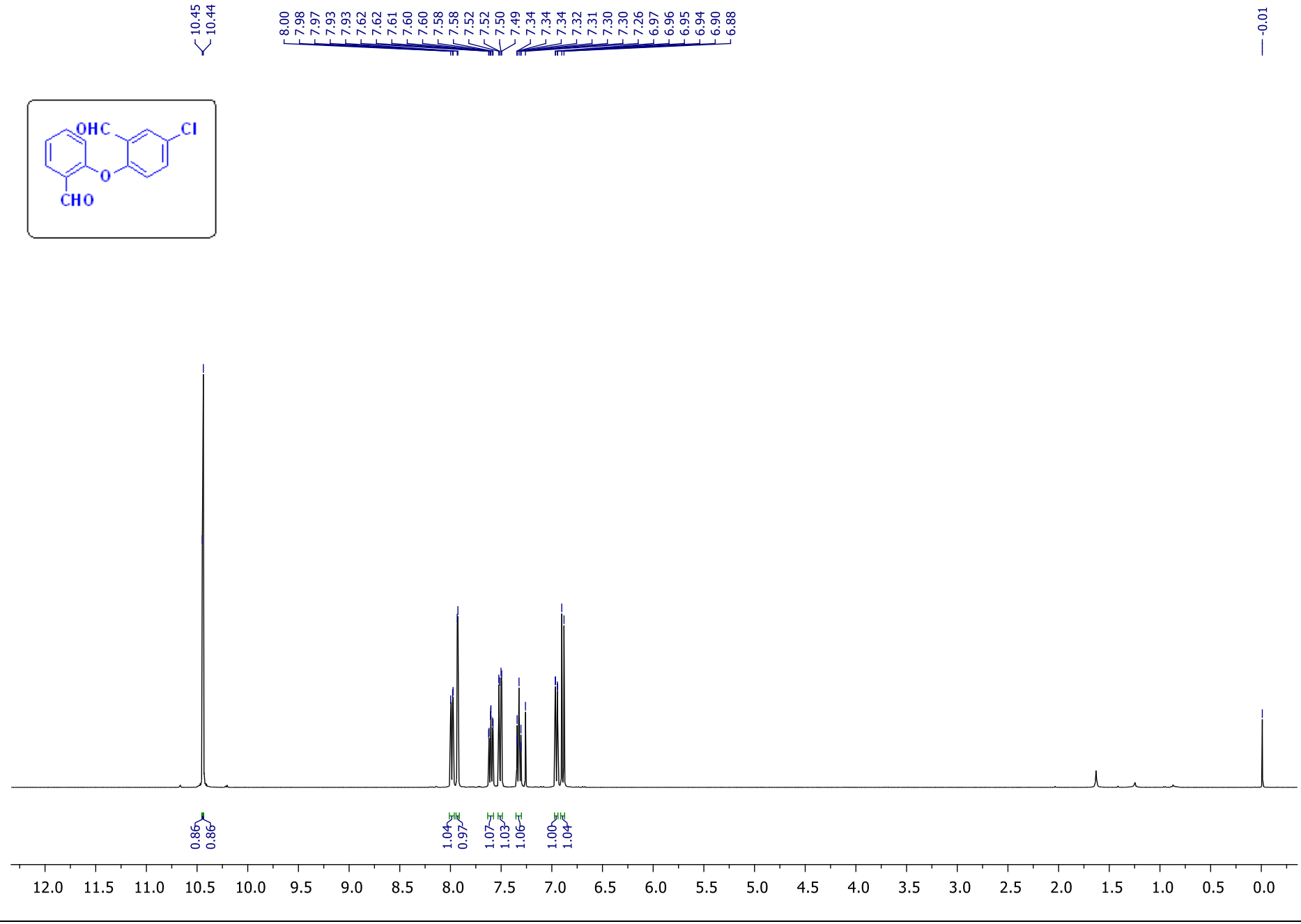
^{1}H-NMR of 1l (500 MHz, $CDCl_3$)



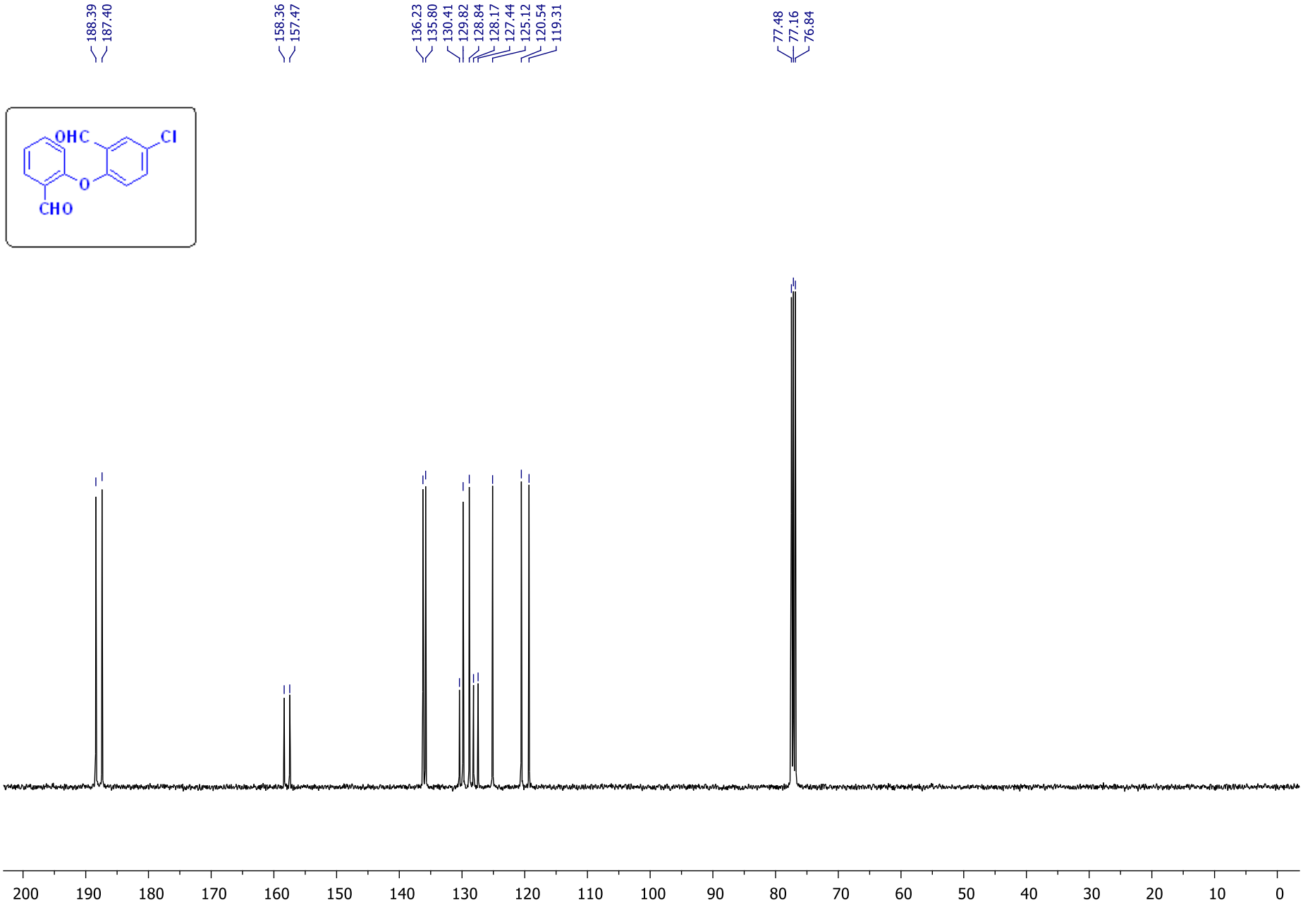
$^{13}C\{^{1}H\}$-NMR of 1l (101 MHz, $CDCl_3$)



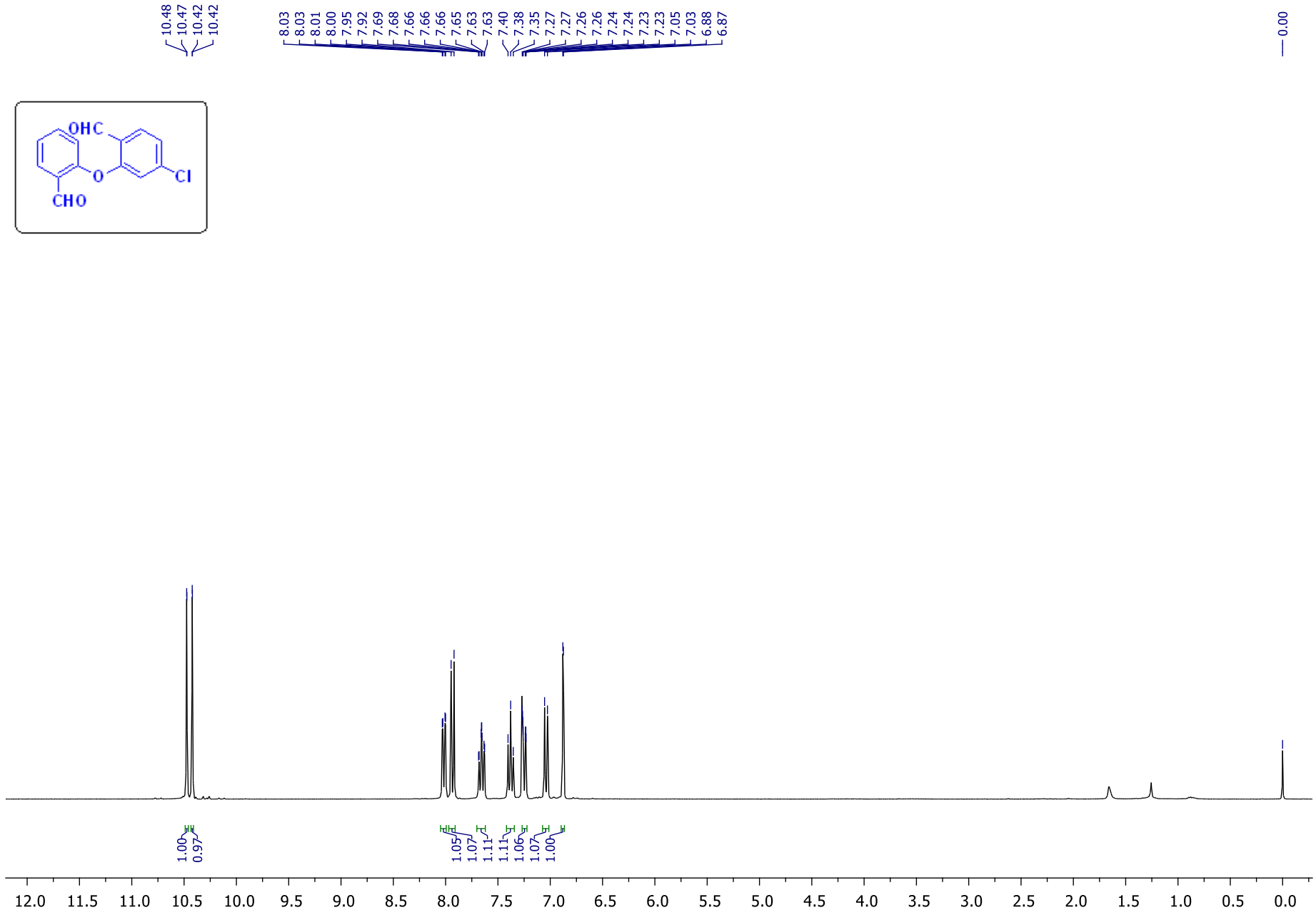
^{1}H-NMR of 1m (400 MHz, $CDCl_3$)



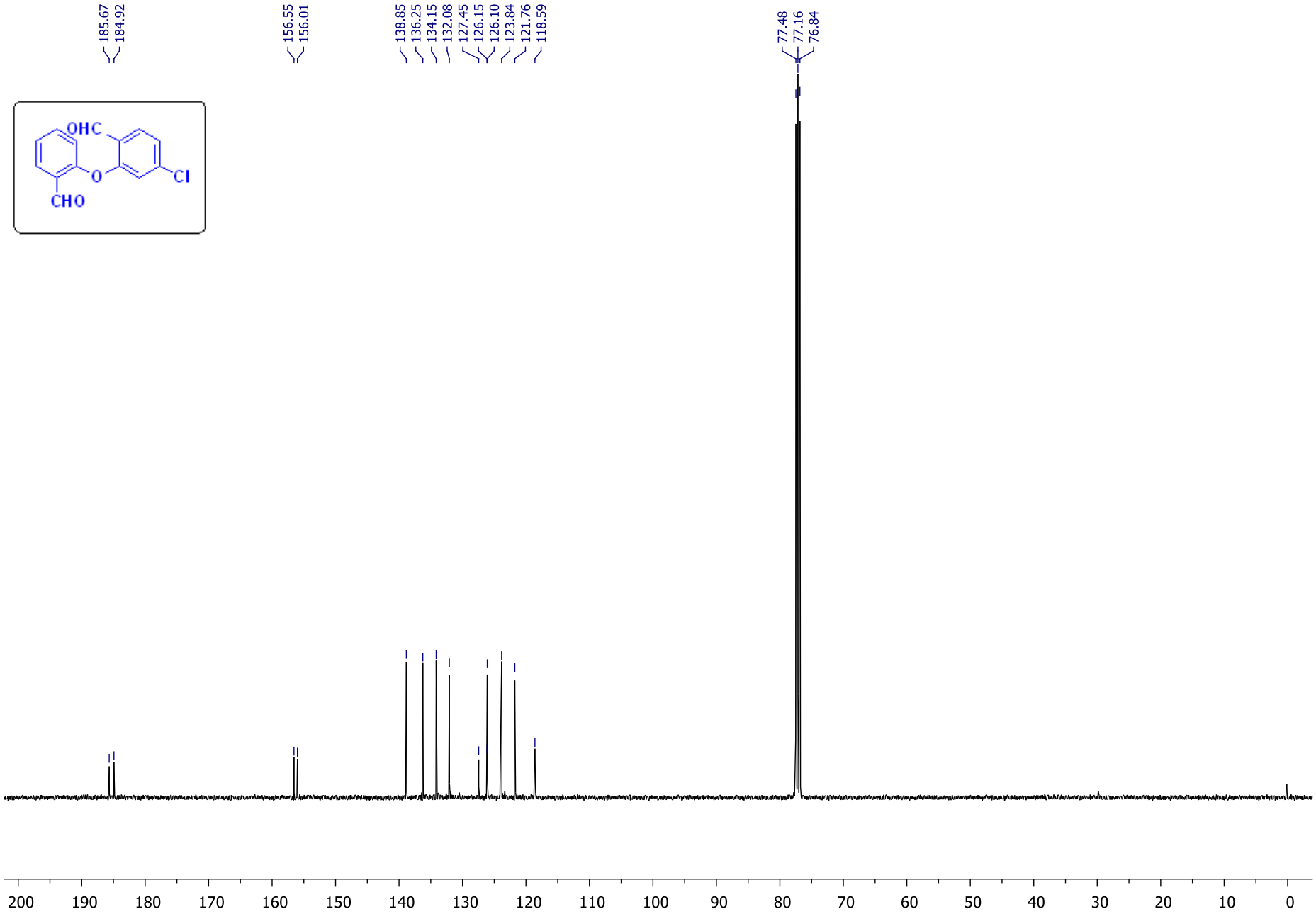
$^{13}C\{^{1}H\}$-NMR of 1m (101 MHz, $CDCl_3$)



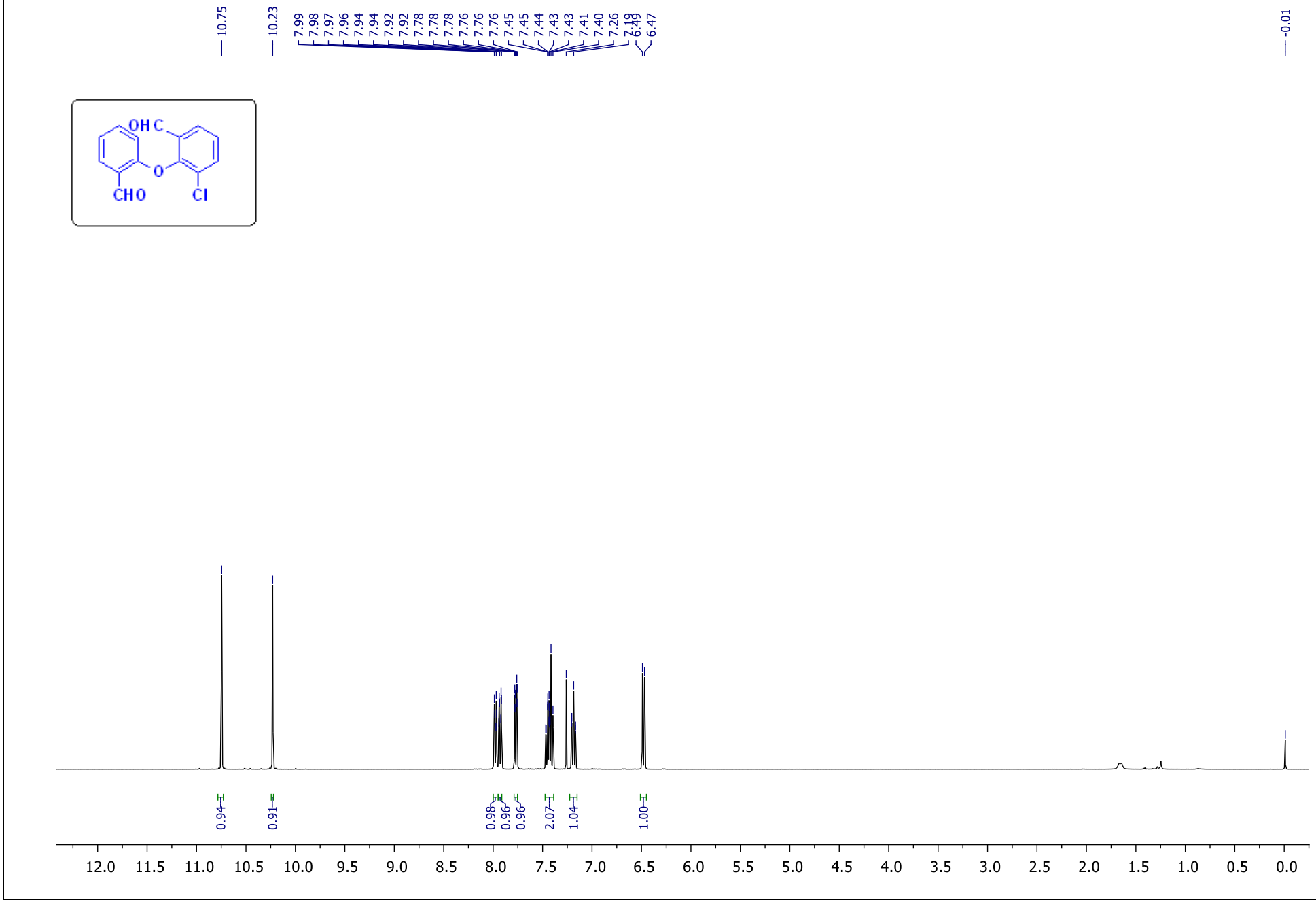
^{1}H-NMR of 1n (300 MHz, $CDCl_3$)



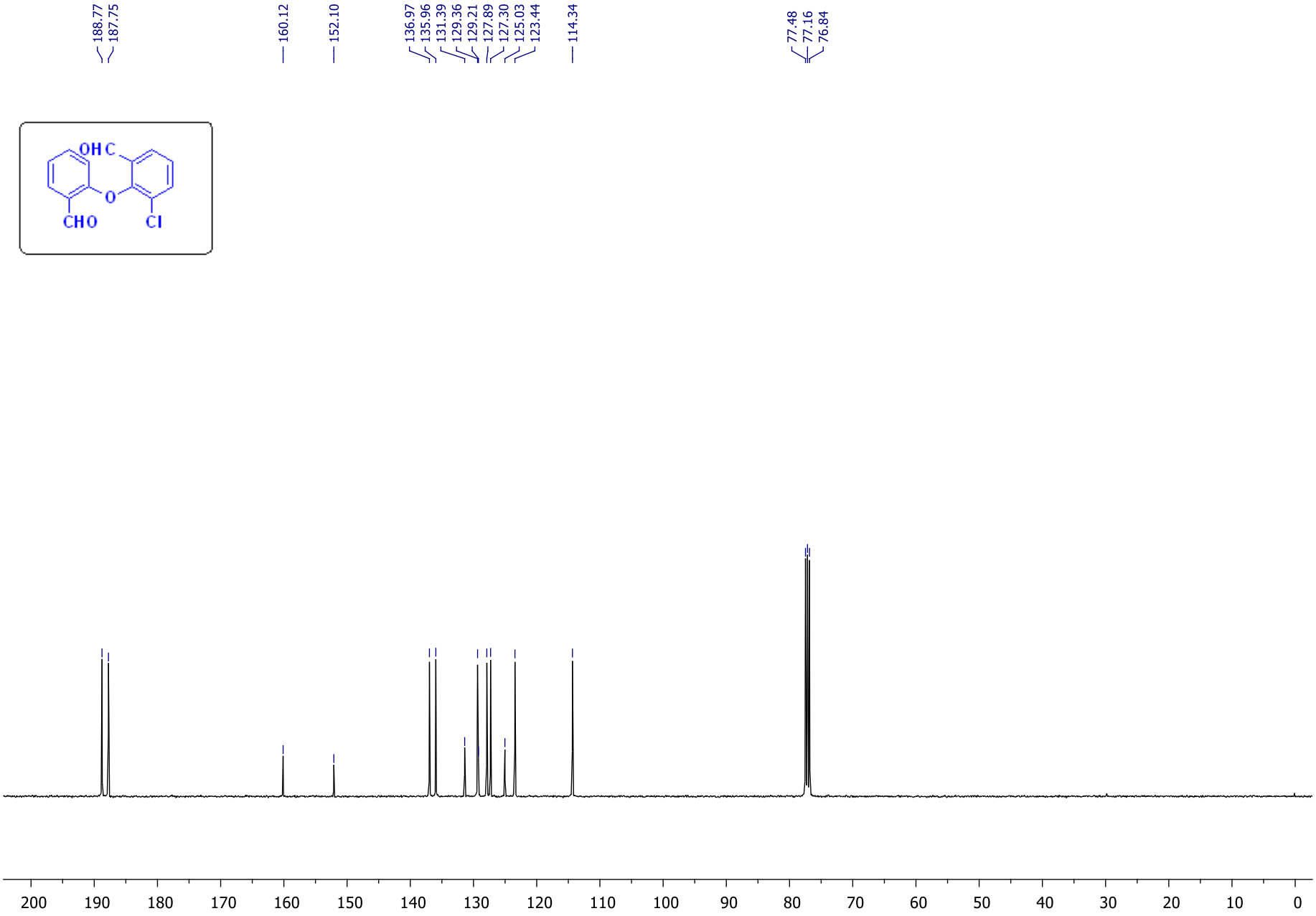
$^{13}C\{^{1}H\}$-NMR of 1n (101 MHz, $CDCl_3$)



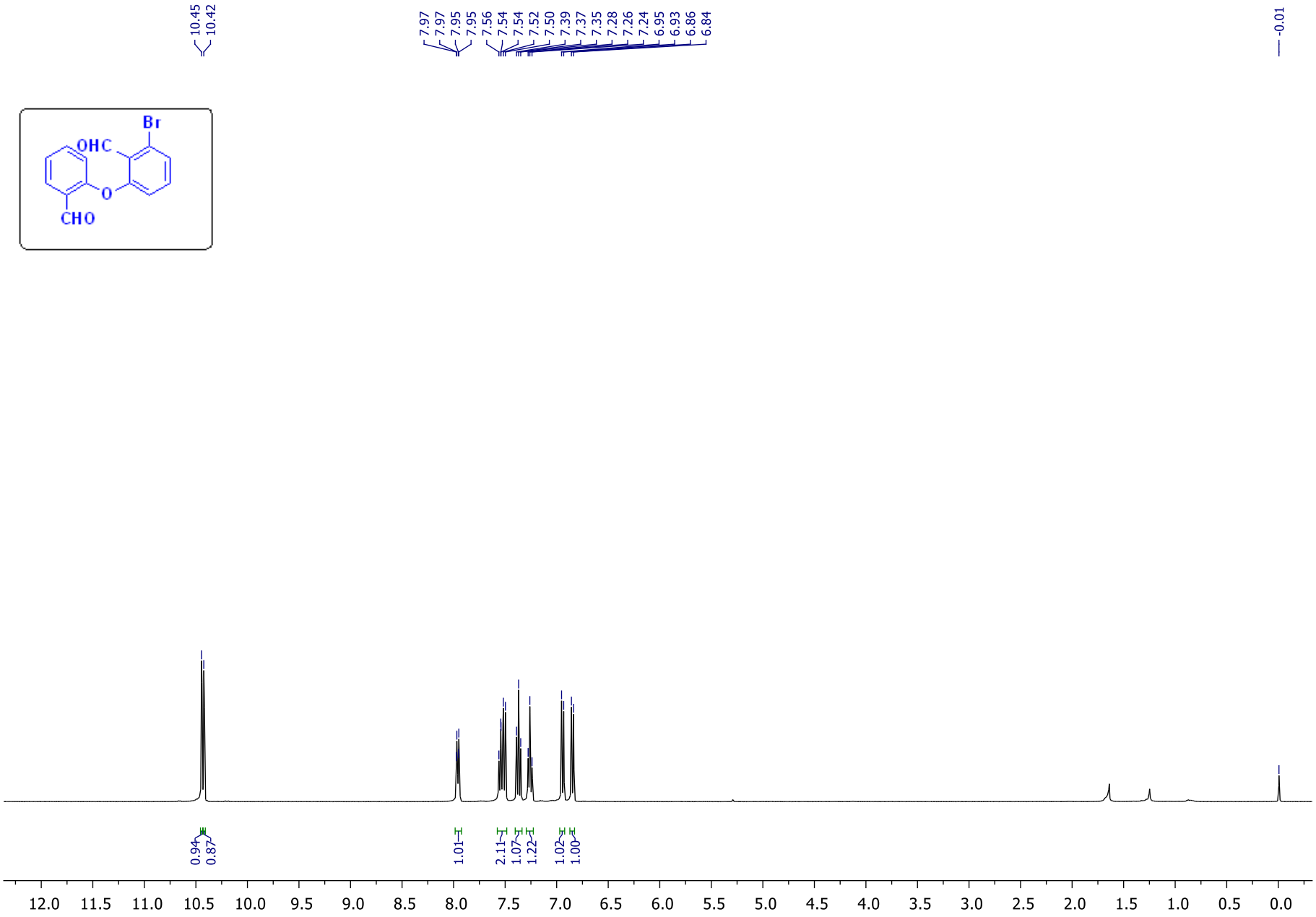
^{1}H-NMR of 1o (400 MHz, $CDCl_3$)



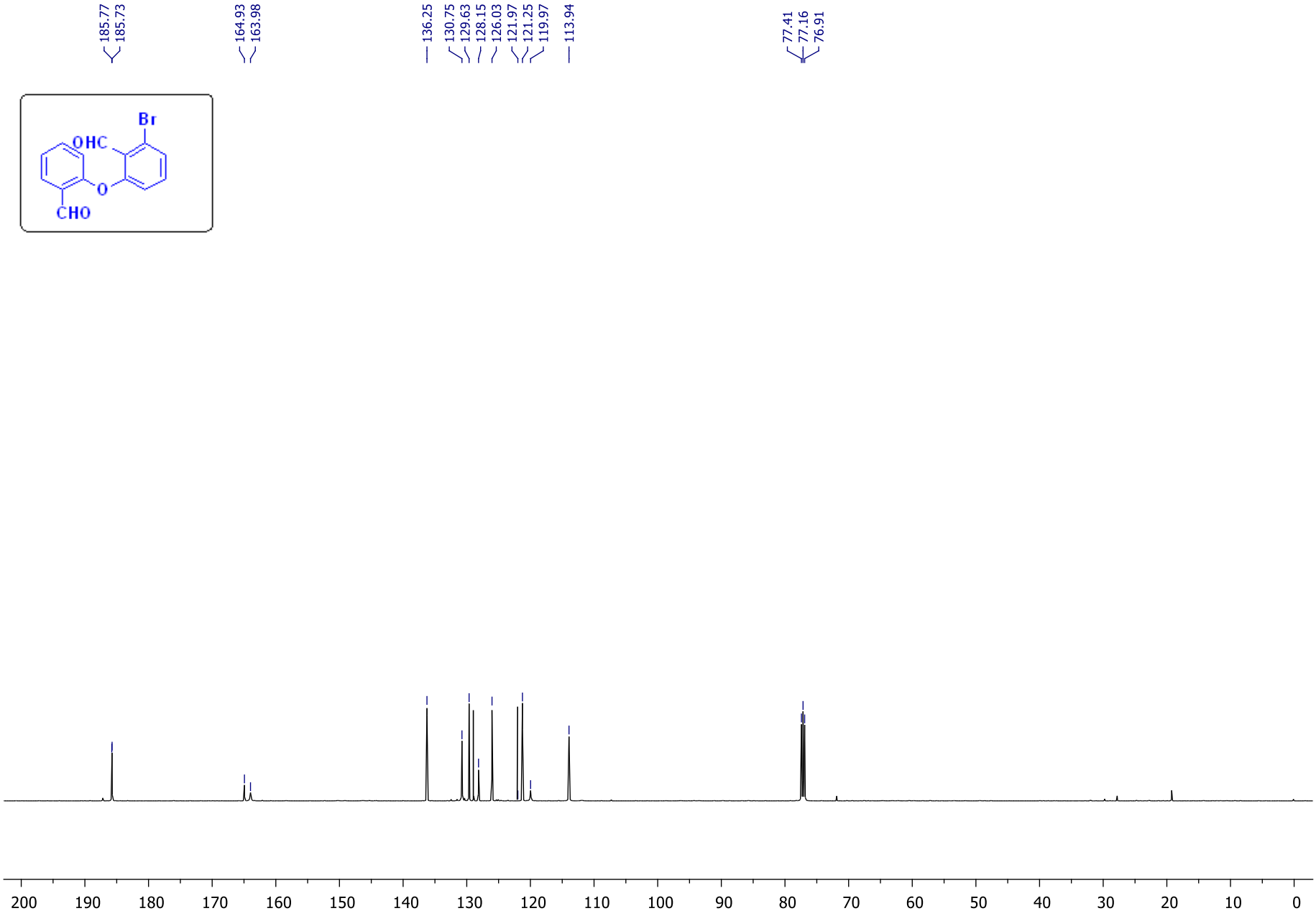
$^{13}C\{^{1}H\}$-NMR of 1o (101 MHz, $CDCl_3$)



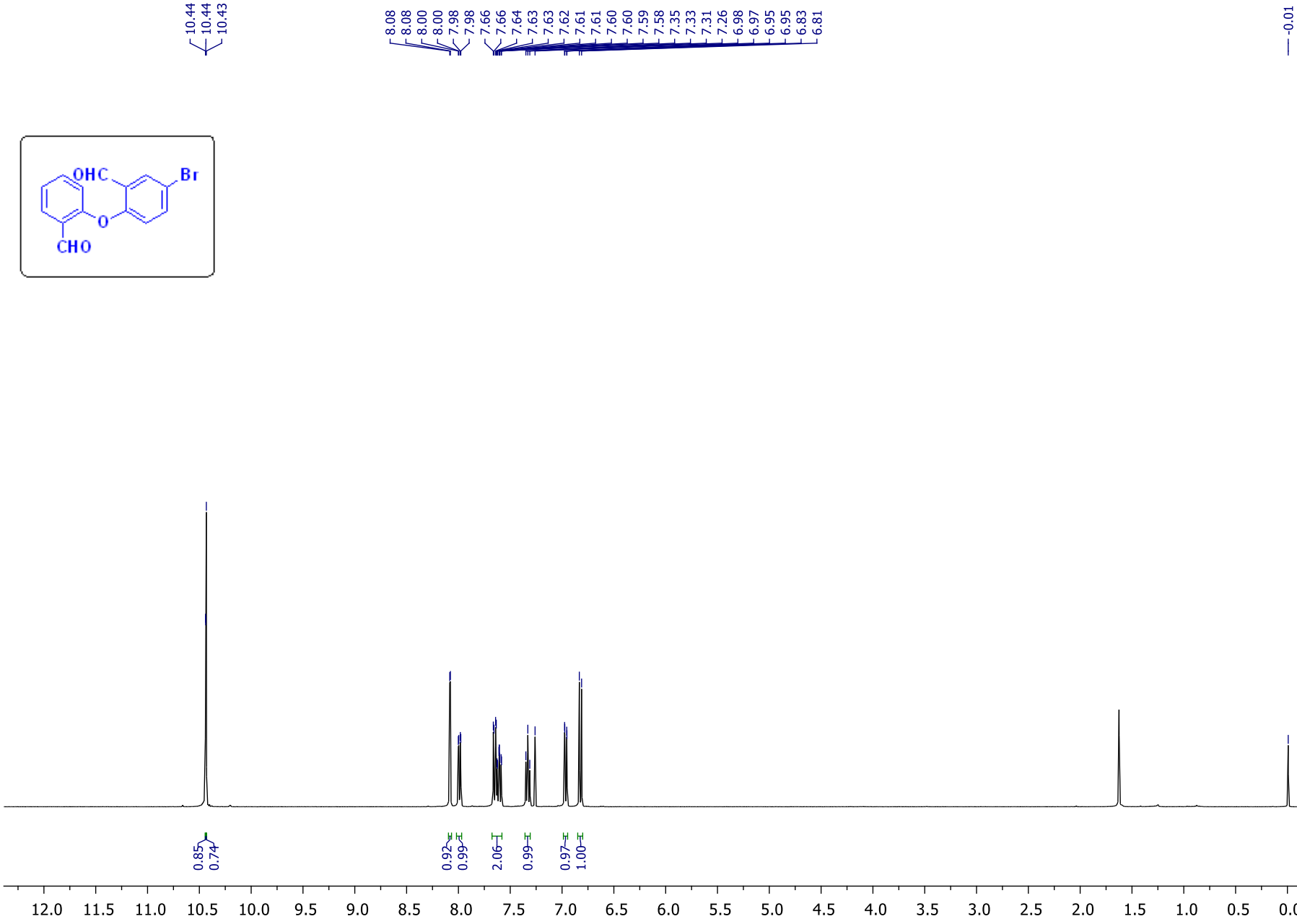
^{1}H-NMR of 1p (400 MHz, $CDCl_3$)



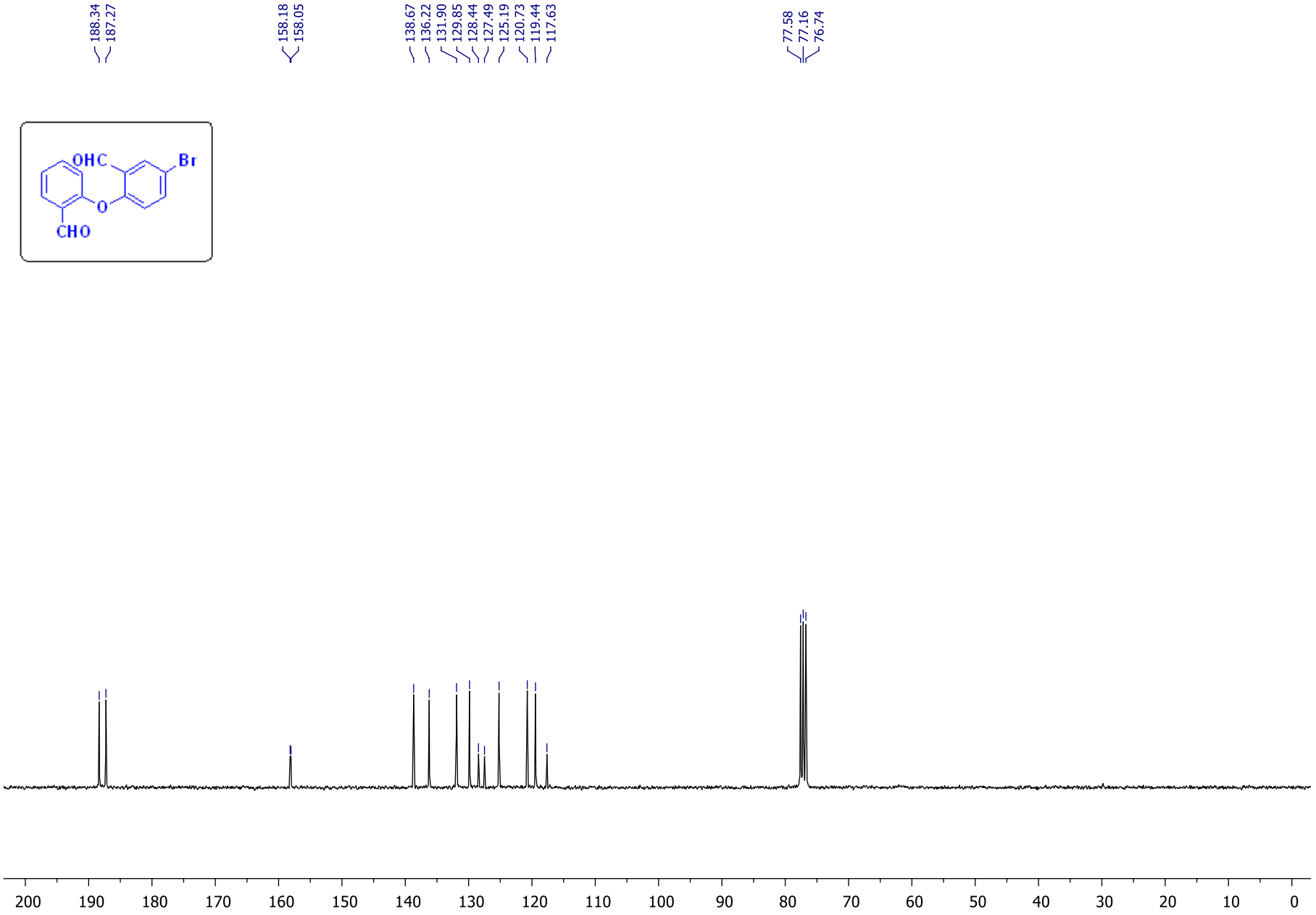
$^{13}C\{^{1}H\}$-NMR of 1p (101 MHz, $CDCl_3$)



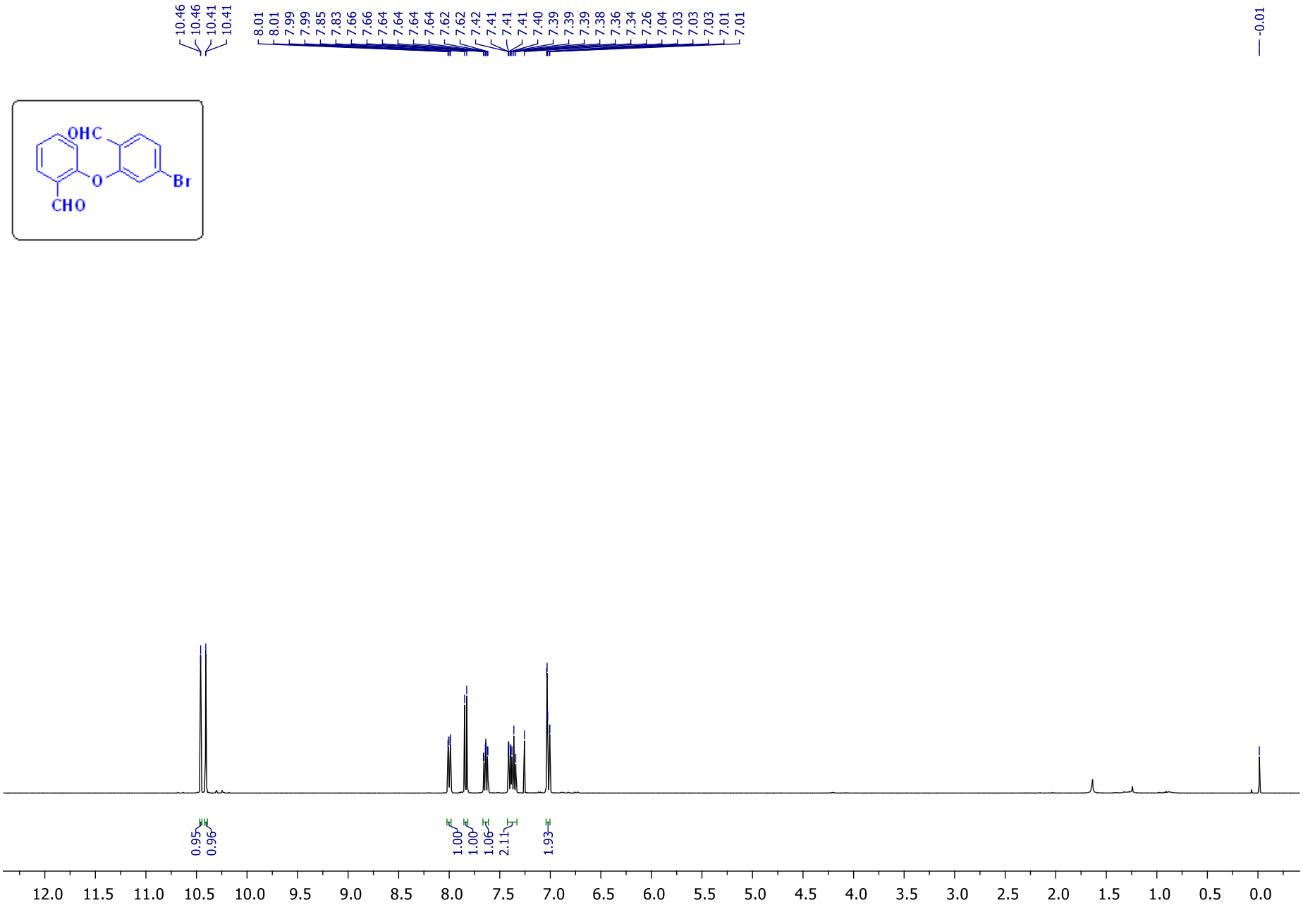
^{1}H-NMR of 1q (400 MHz, $CDCl_3$)



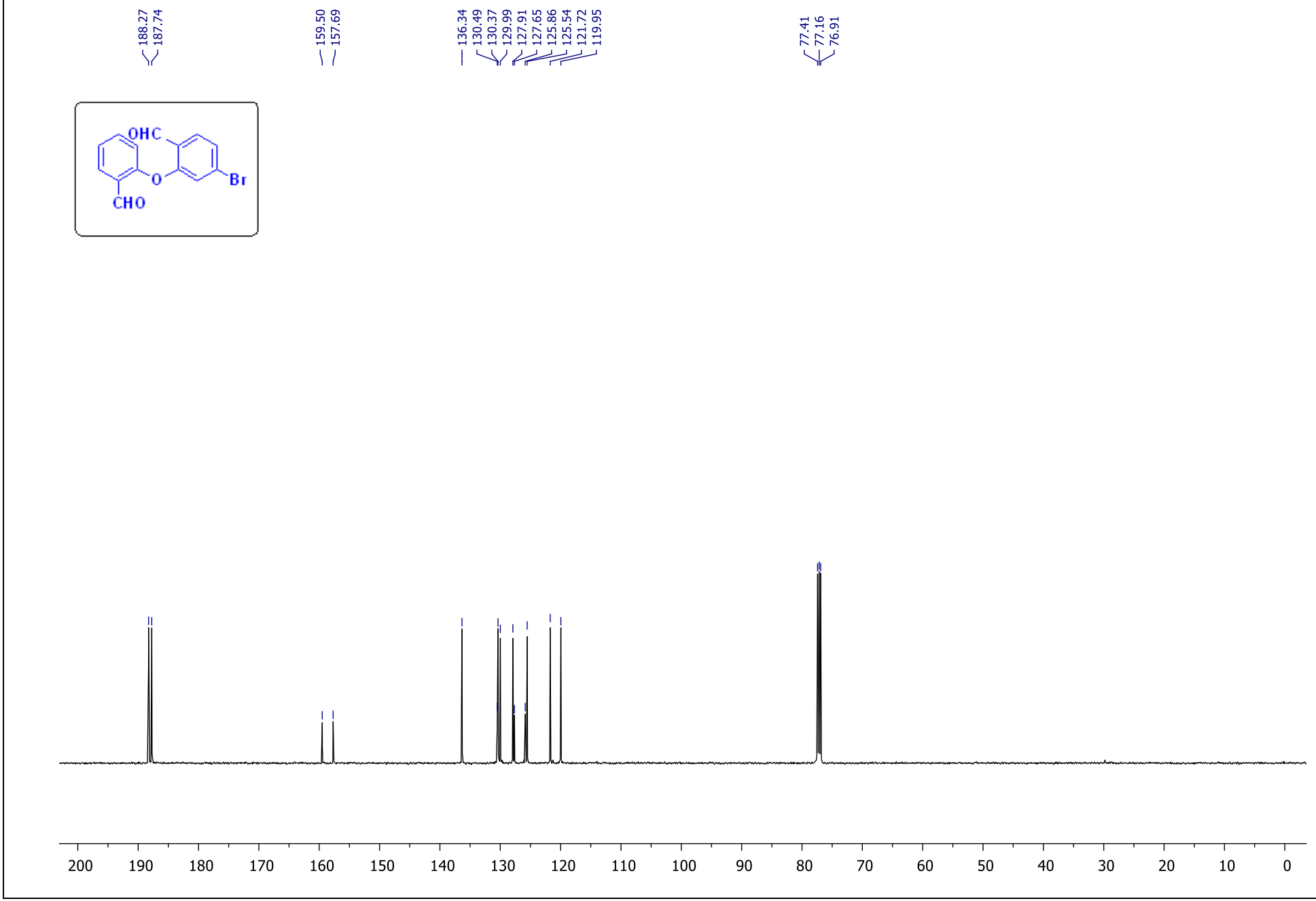
$^{13}C\{^{1}H\}$-NMR of 1q (101 MHz, $CDCl_3$)



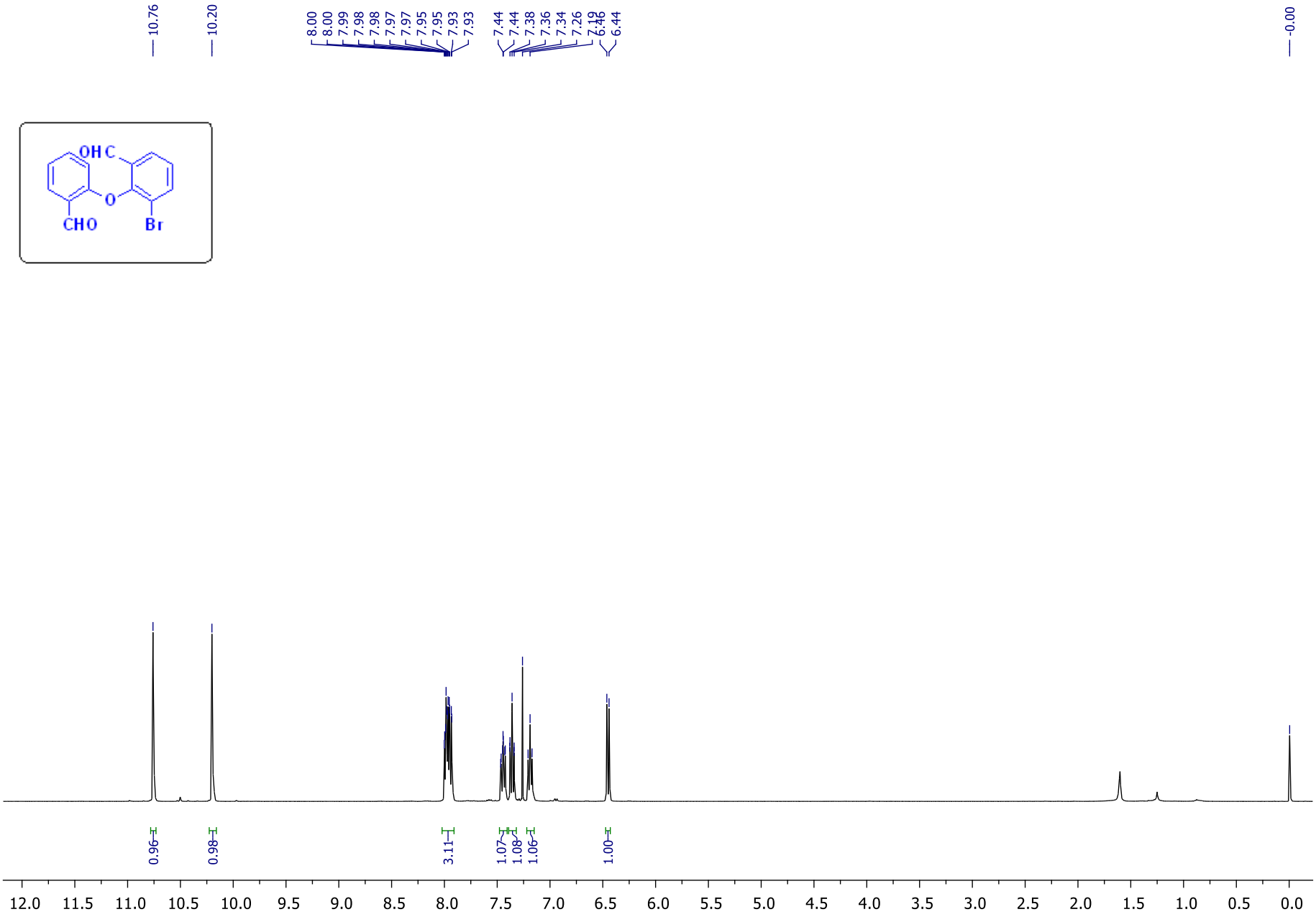
^{1}H-NMR of 1r (400 MHz, $CDCl_3$)



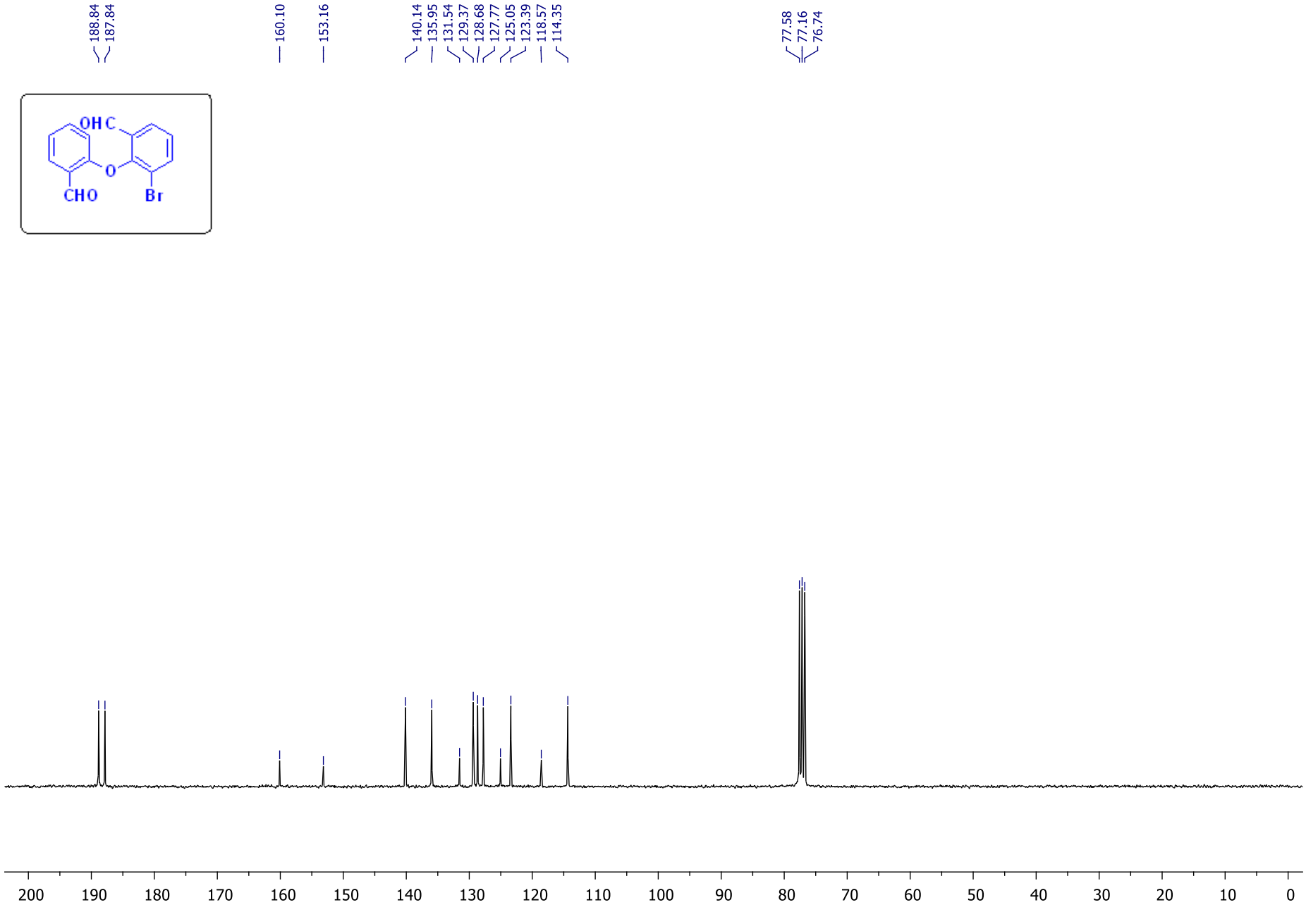
$^{13}C\{^{1}H\}$-NMR of 1r (101 MHz, $CDCl_3$)



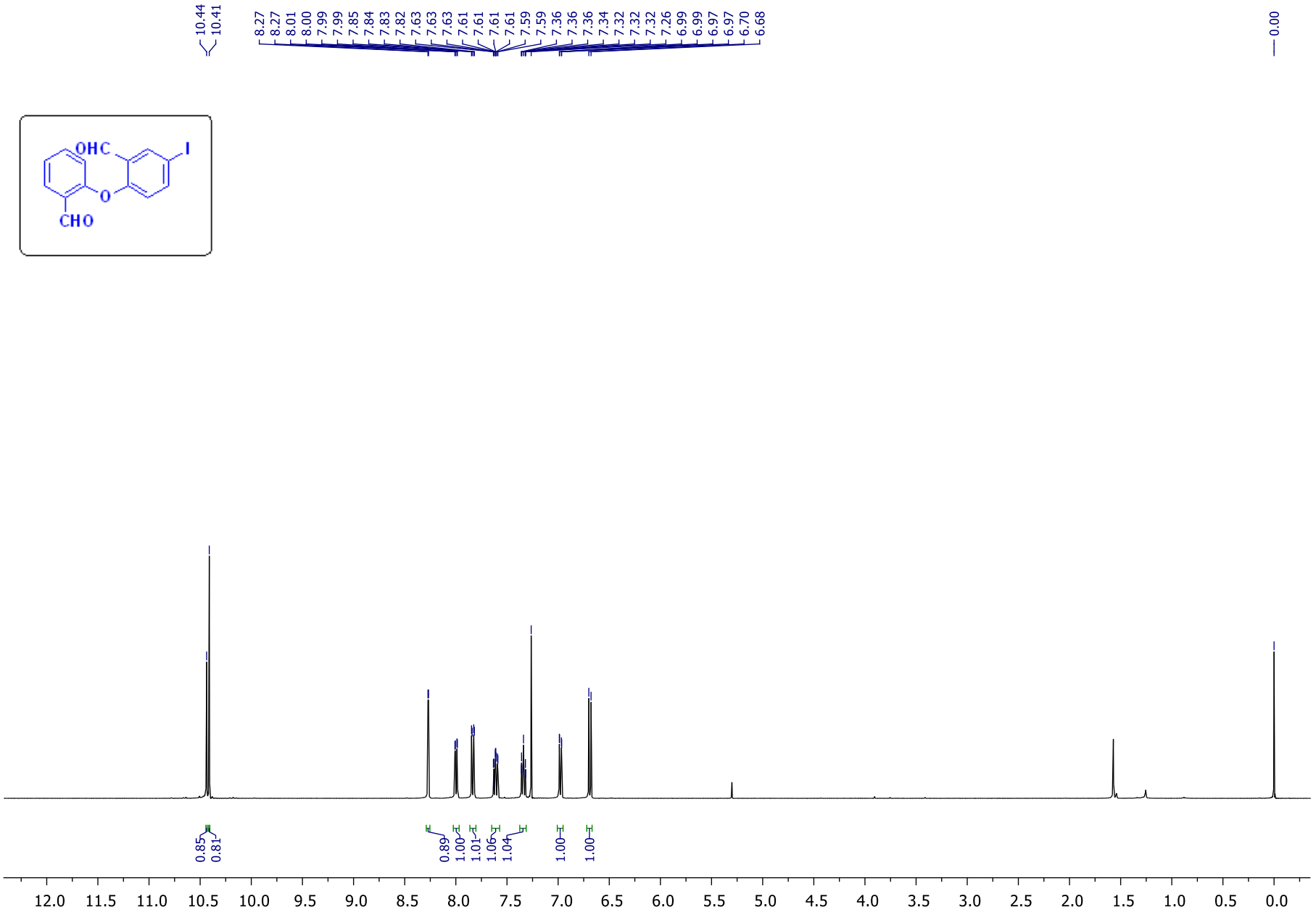
^{1}H-NMR of 1s (400 MHz, $CDCl_3$)



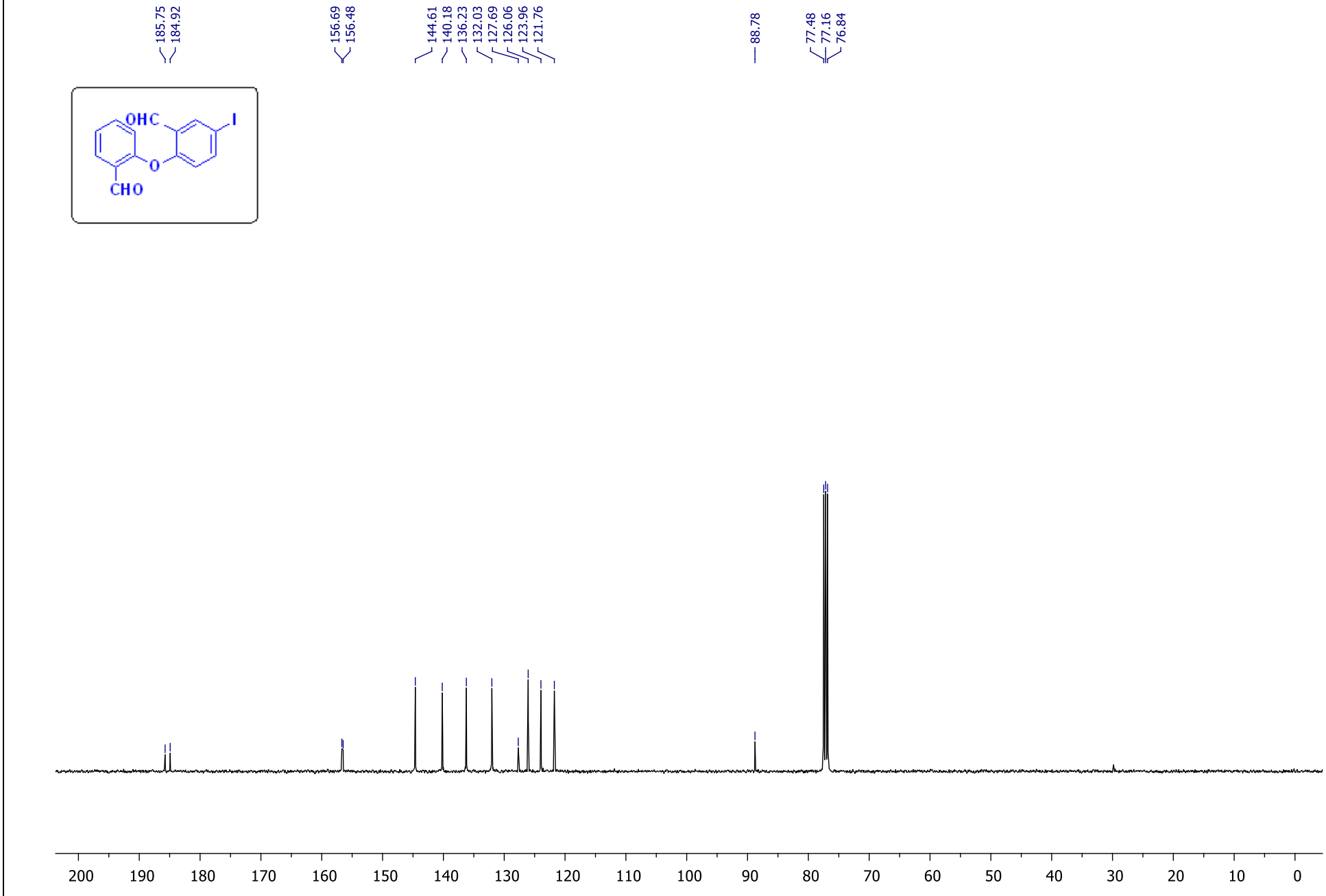
$^{13}C\{^{1}H\}$-NMR of 1s (101 MHz, $CDCl_3$)



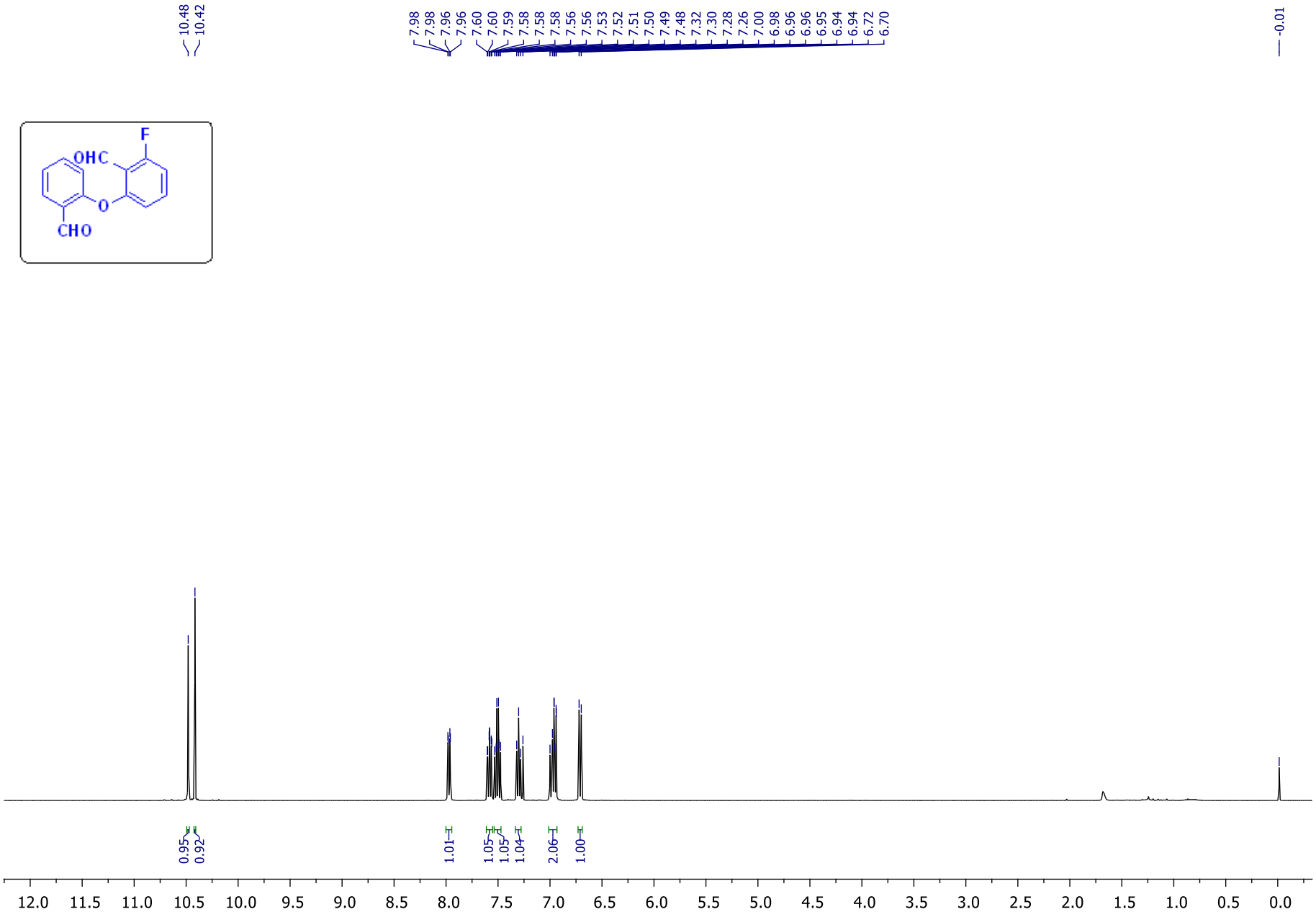
^{1}H-NMR of 1t (400 MHz, $CDCl_3$)



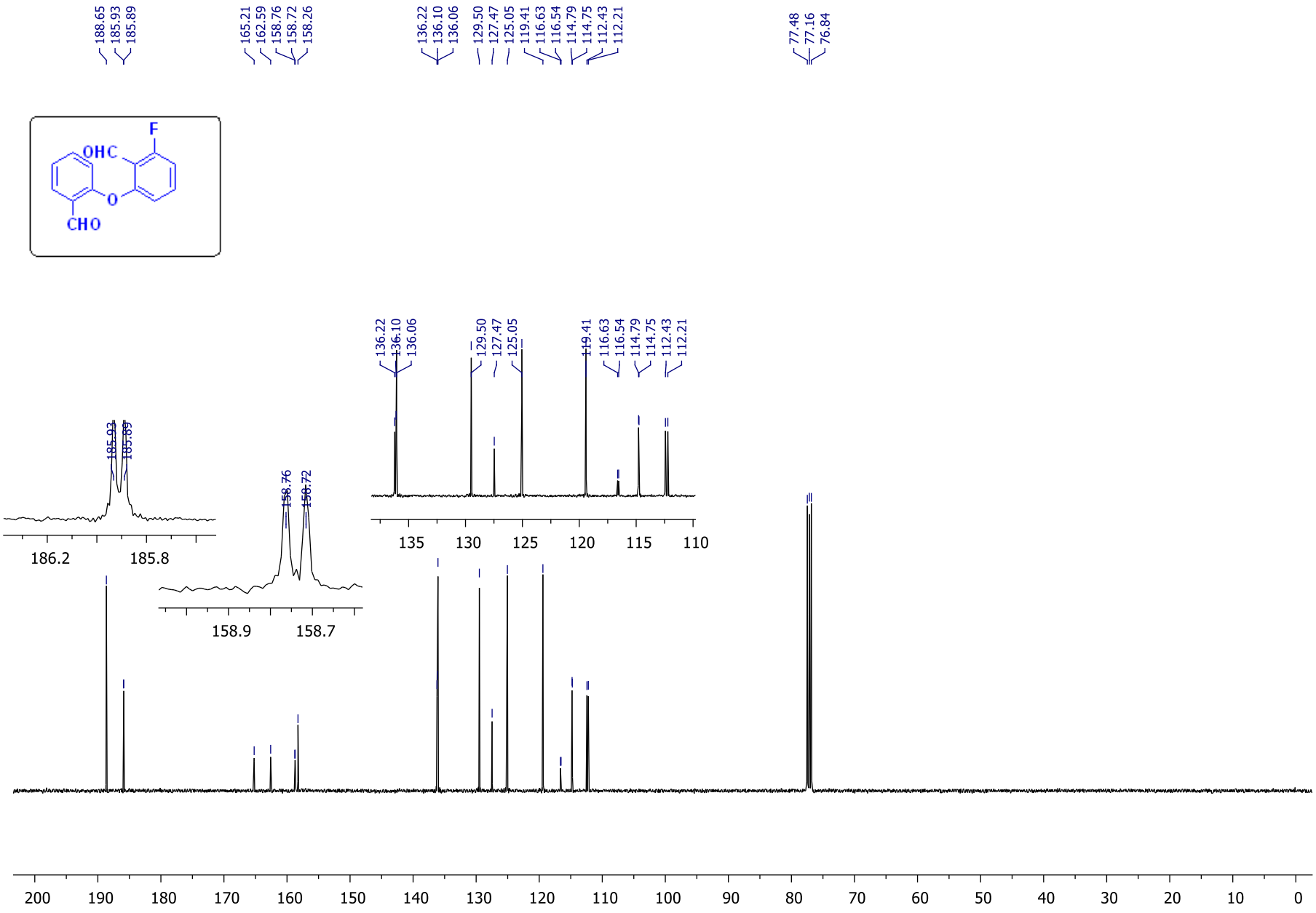
$^{13}C\{^{1}H\}$-NMR of 1t (101 MHz, $CDCl_3$)



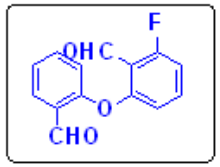
^{1}H-NMR of 1u (400 MHz, $CDCl_3$)



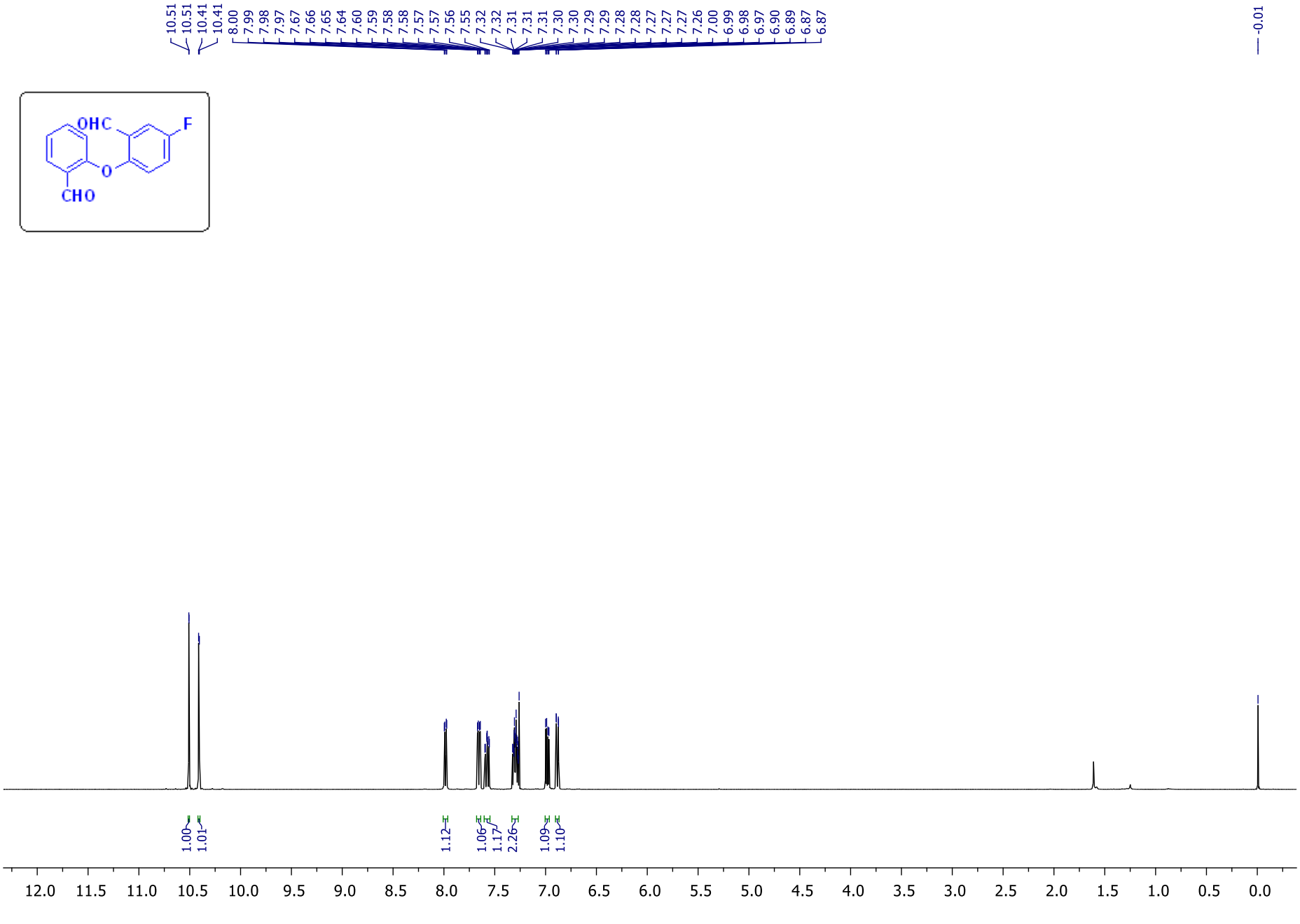
$^{13}C\{^{1}H\}$-NMR of 1u (101 MHz, $CDCl_3$)



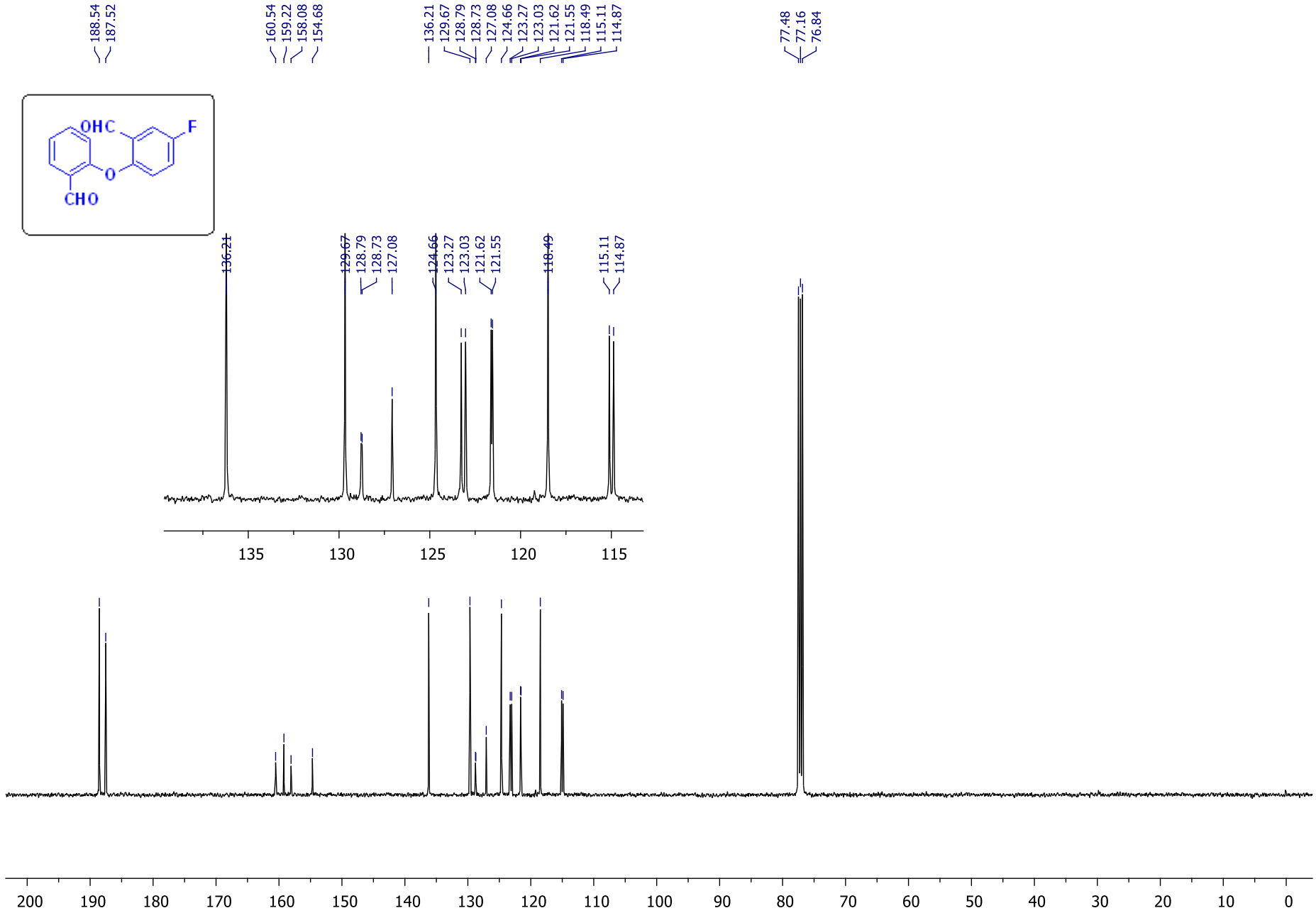
^{19}F-NMR of 1u (377 MHz, $CDCl_3$)



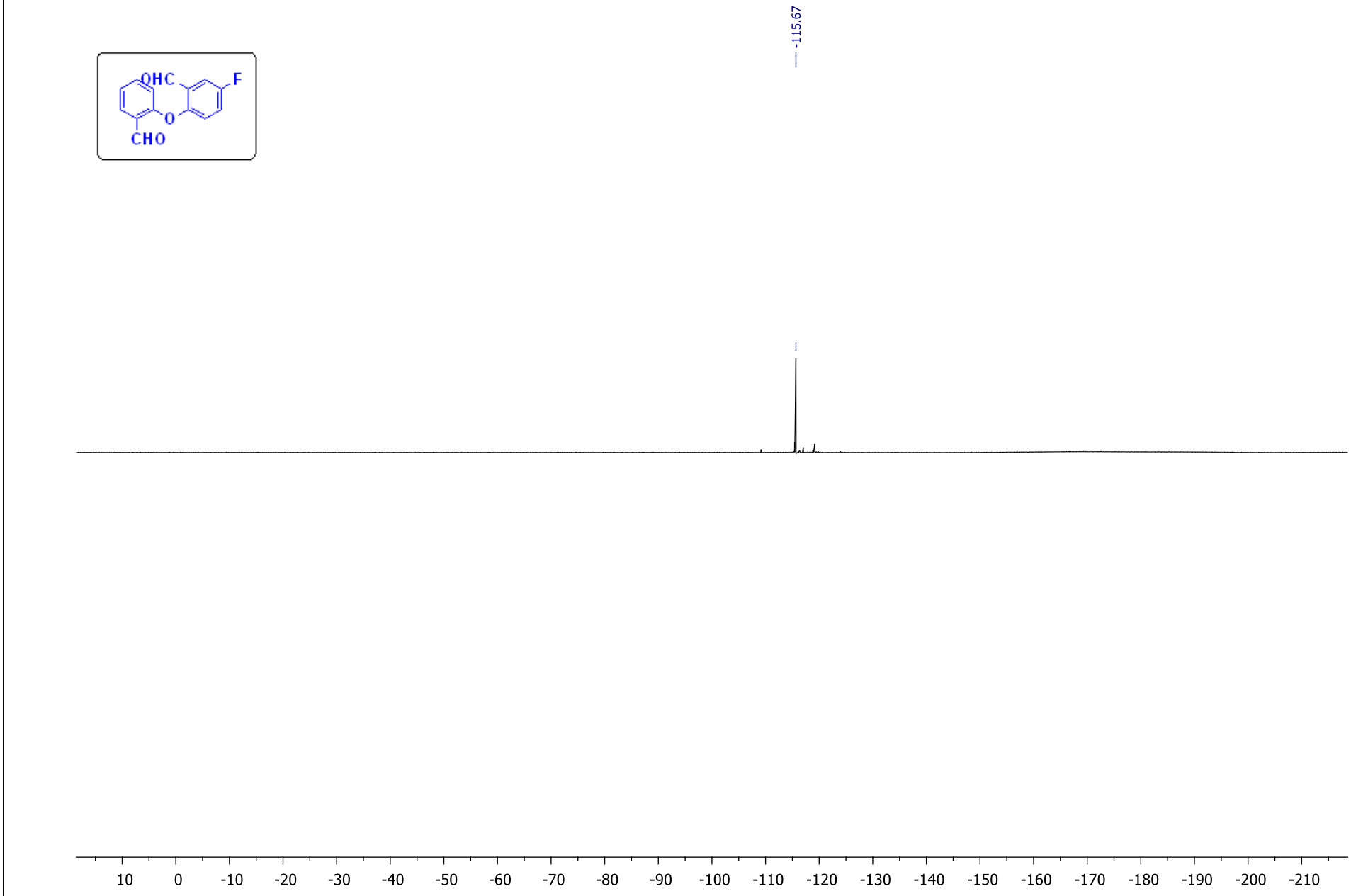
^{1}H-NMR of 1v (400 MHz, $CDCl_3$)



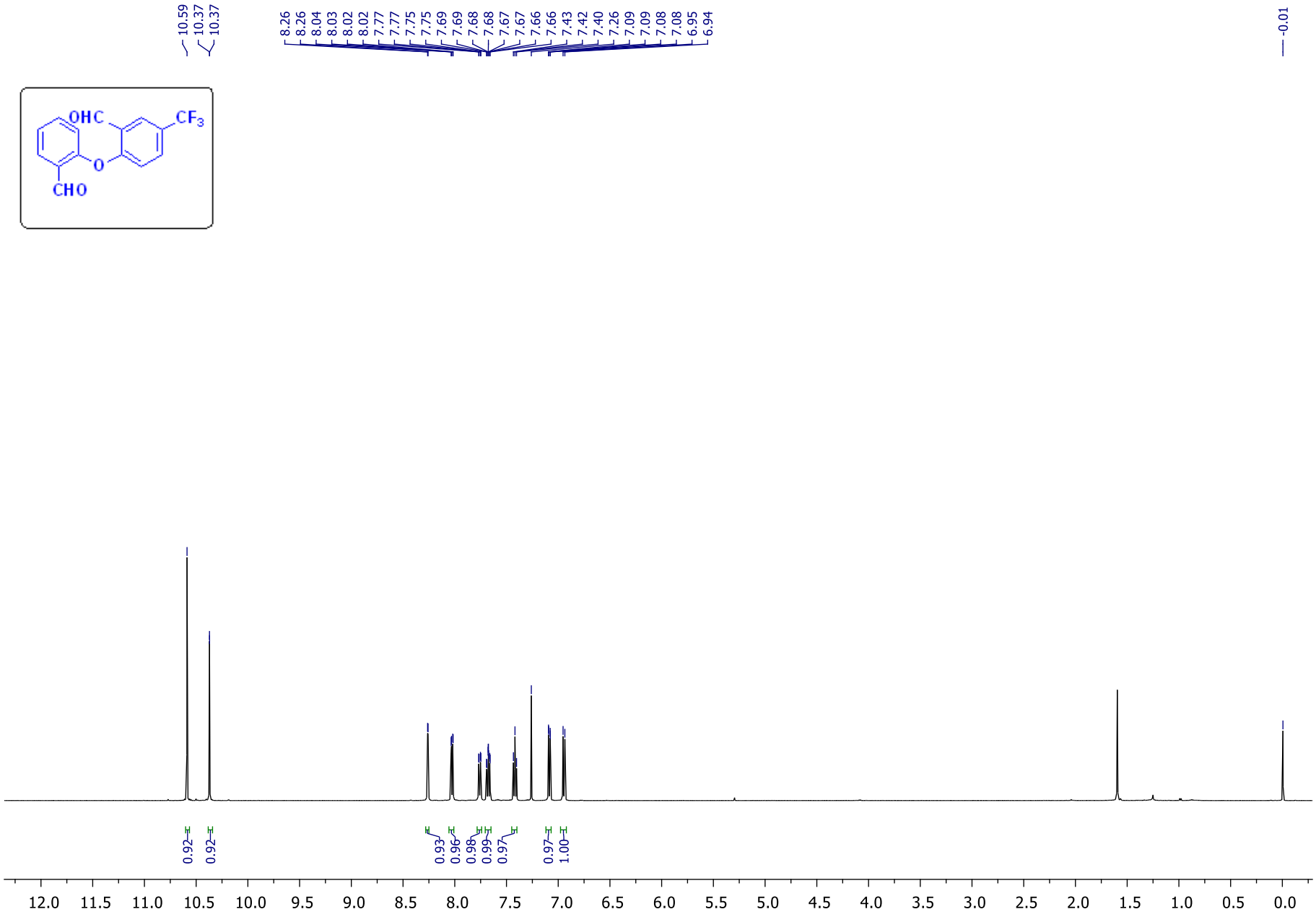
$^{13}C\{^{1}H\}$-NMR of 1v (101 MHz, $CDCl_3$)



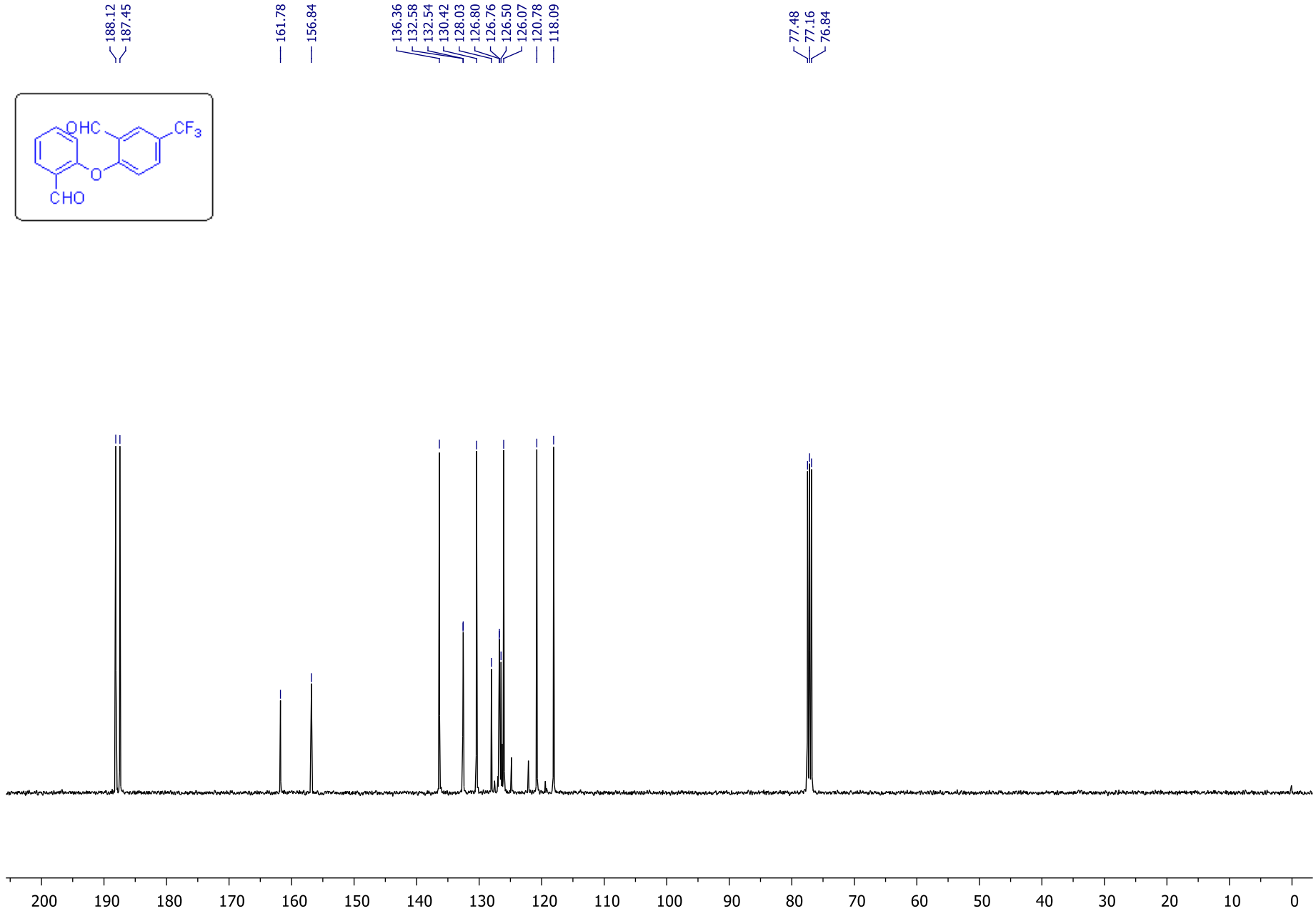
^{19}F-NMR of 1v (377 MHz, $CDCl_3$)



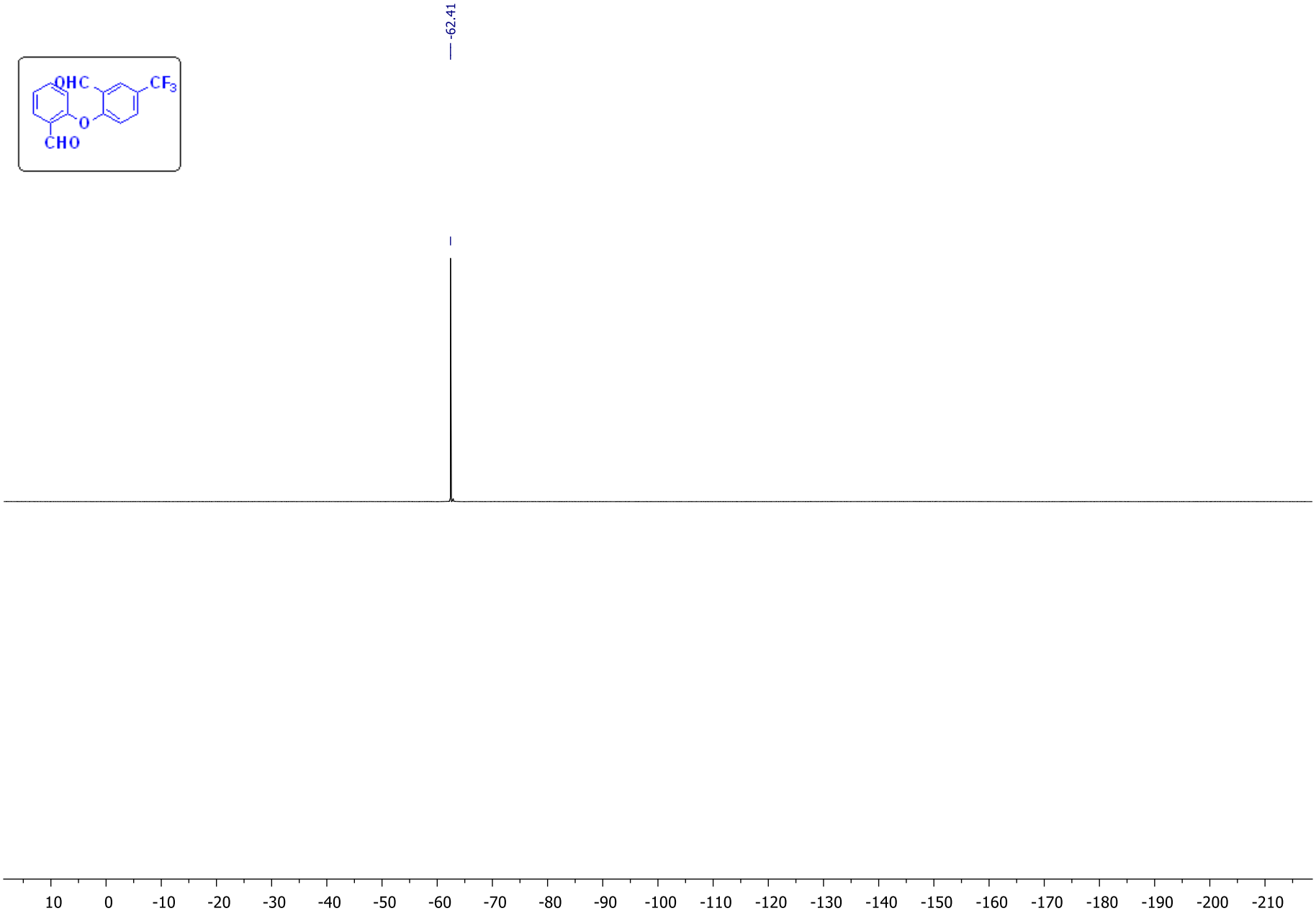
^{1}H-NMR of 1w (500 MHz, $CDCl_3$)



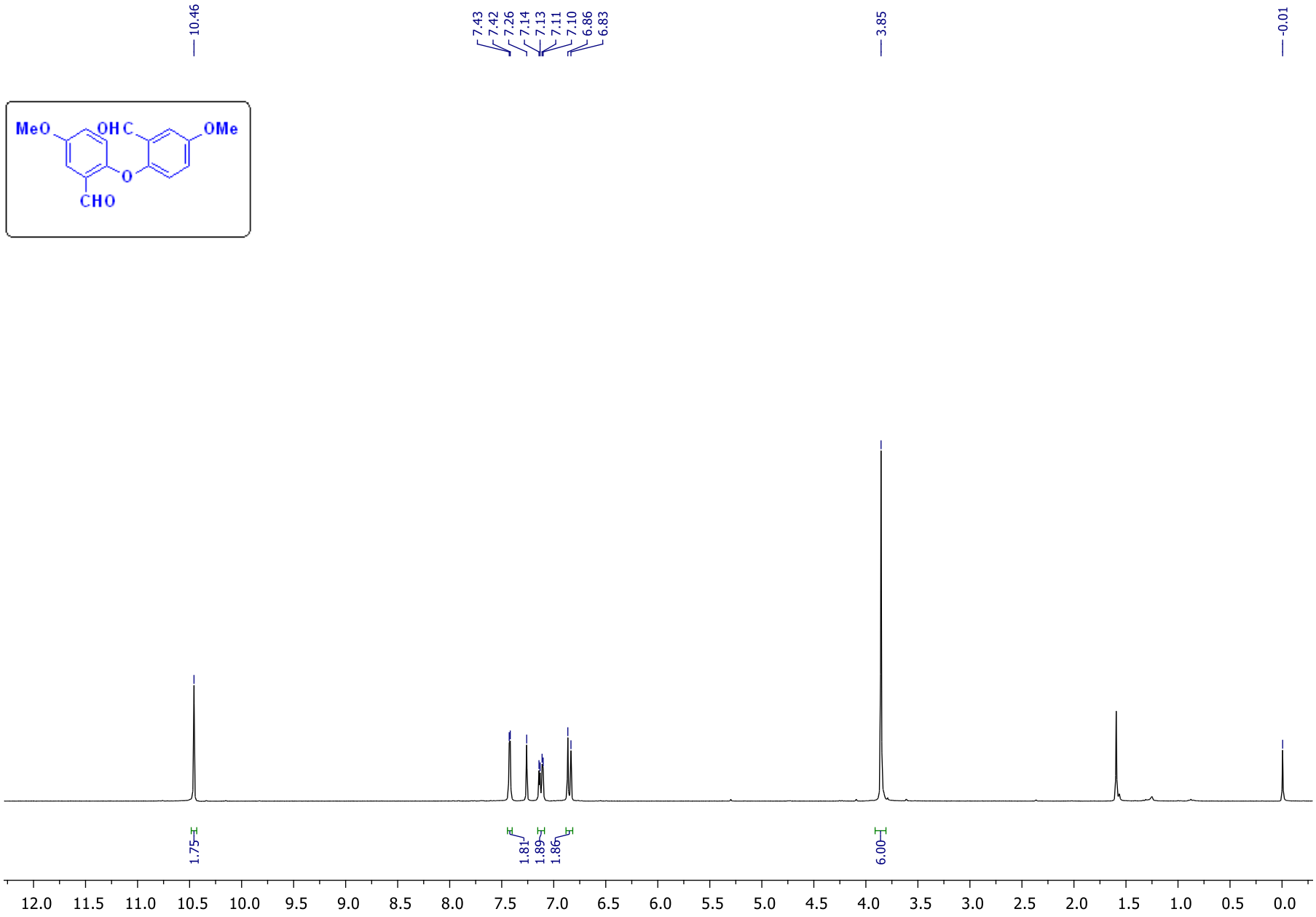
$^{13}C\{^{1}H\}$-NMR of 1w (101 MHz, $CDCl_3$)



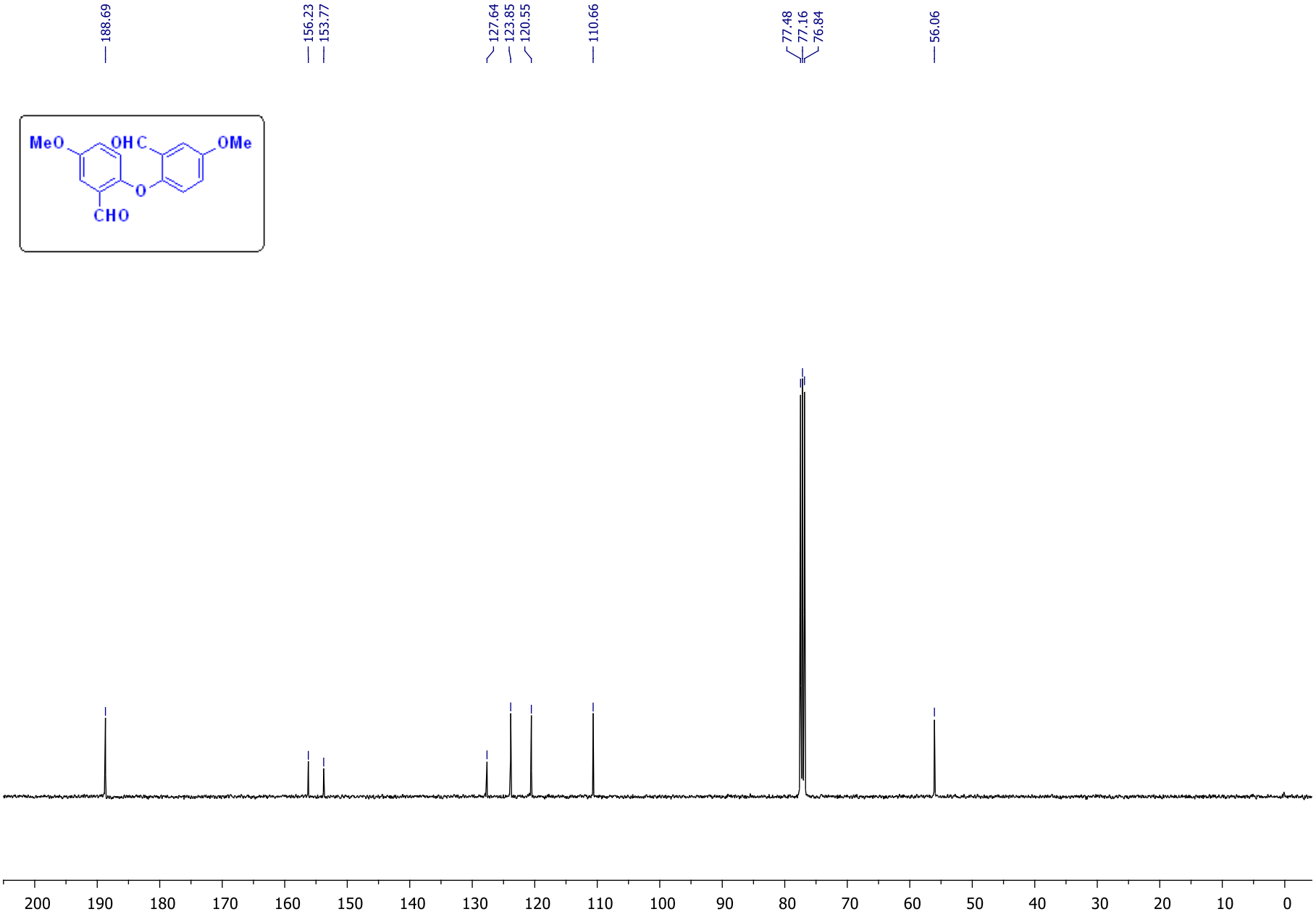
^{19}F-NMR of 1w (377 MHz, $CDCl_3$)



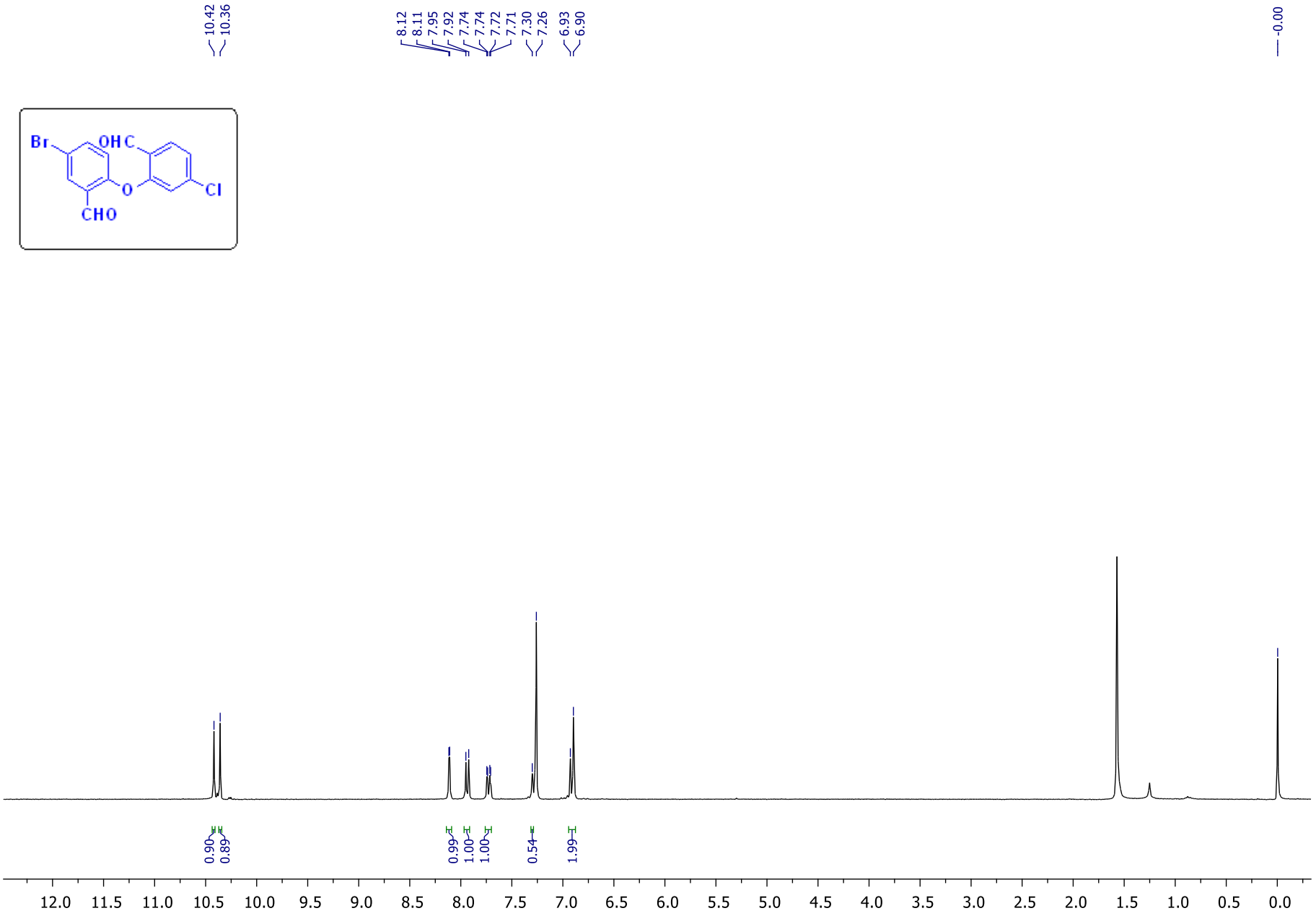
^{1}H-NMR of 1x (300 MHz, $CDCl_3$)



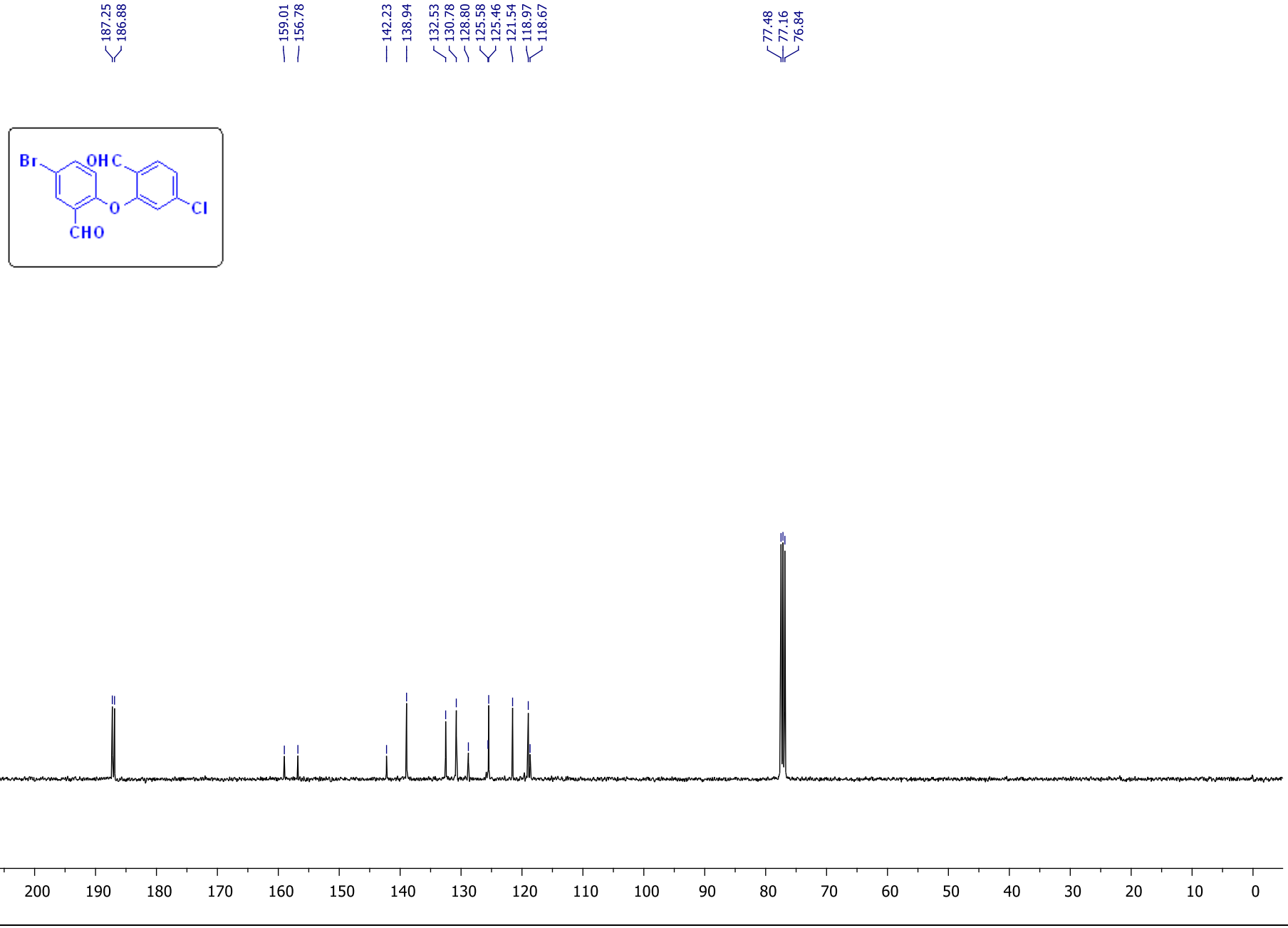
$^{13}C\{^{1}H\}$-NMR of 1x (101 MHz, $CDCl_3$)



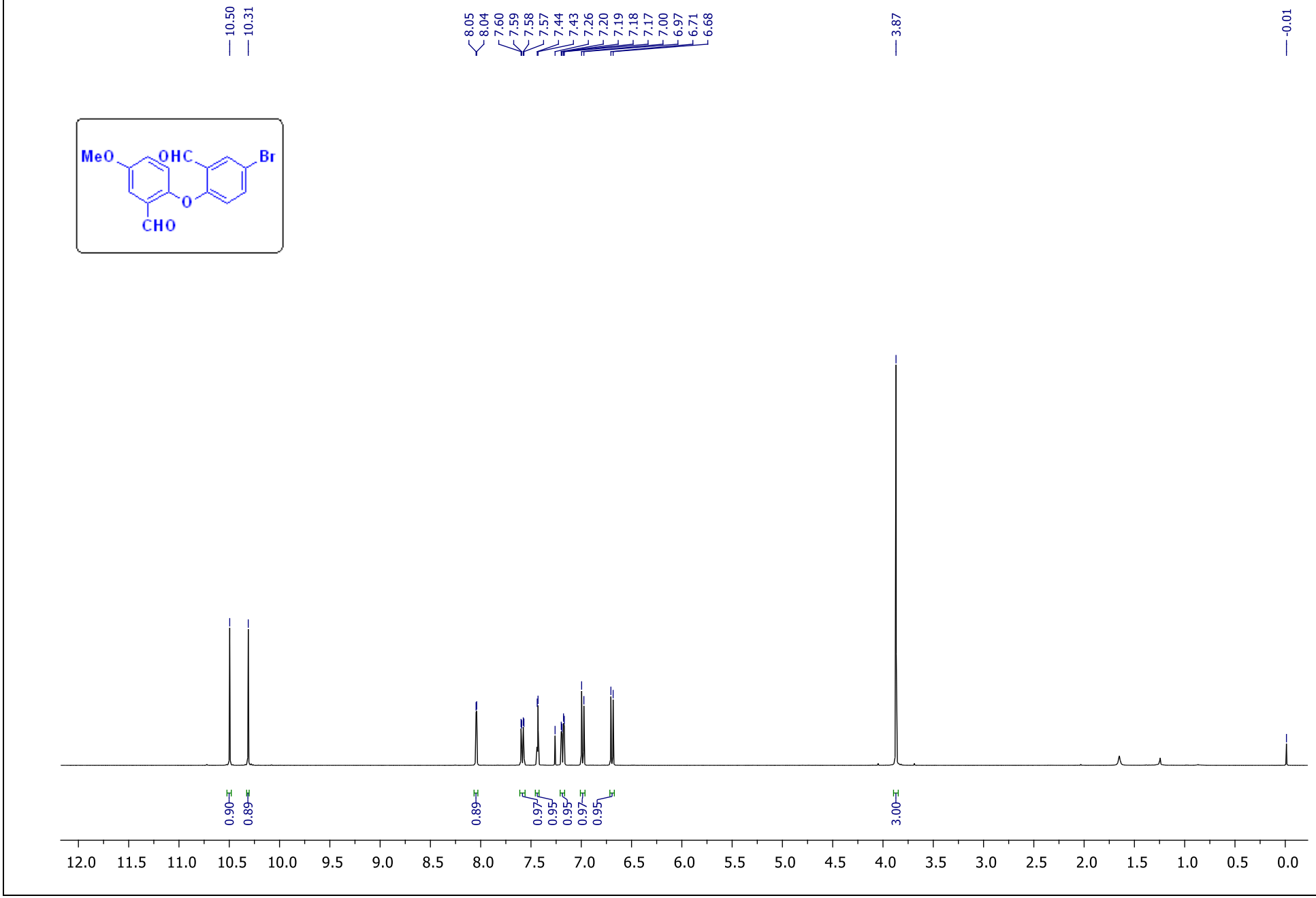
^{1}H-NMR of 1y (300 MHz, $CDCl_3$)



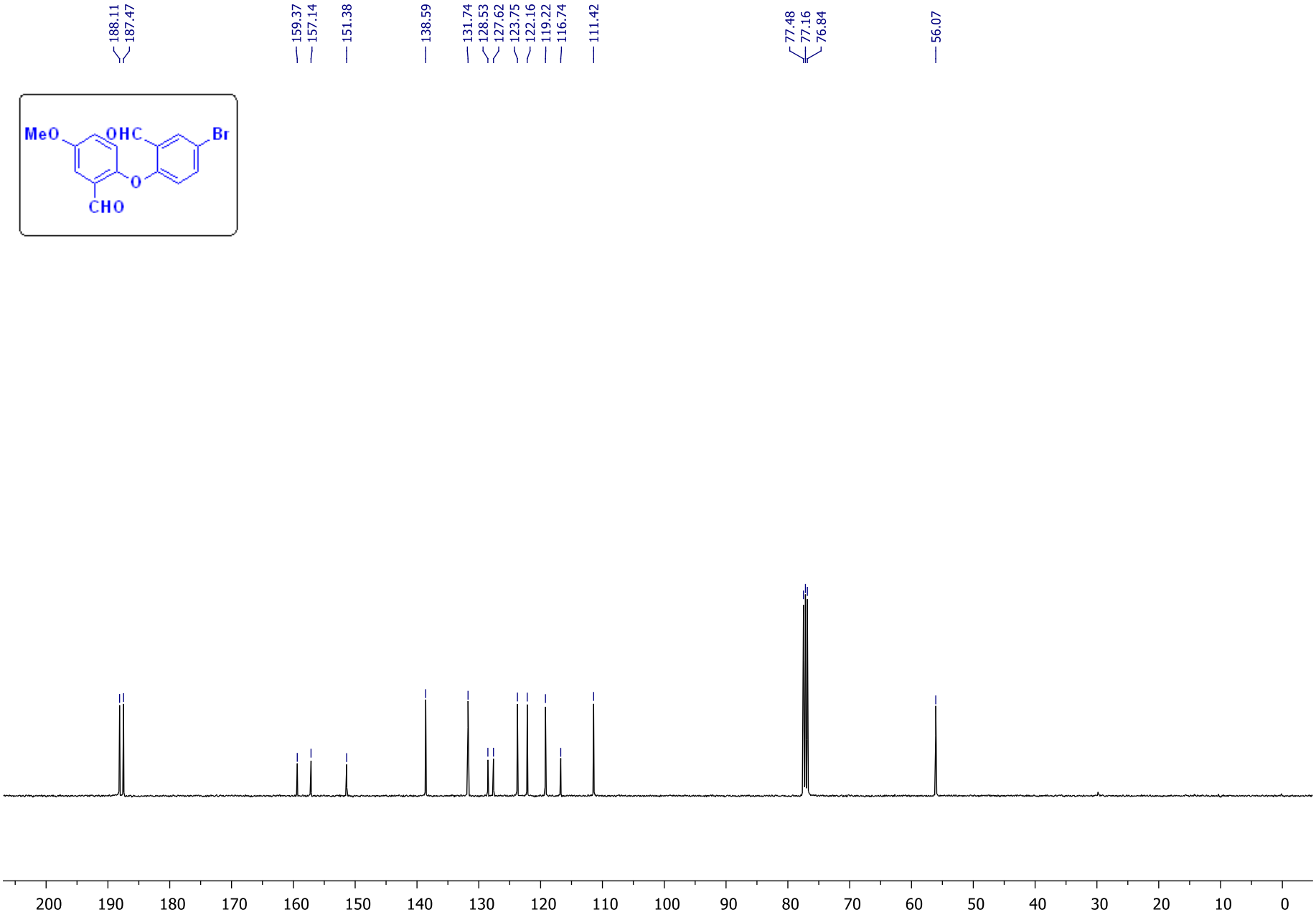
$^{13}C\{^{1}H\}$-NMR of 1y (101 MHz, $CDCl_3$)



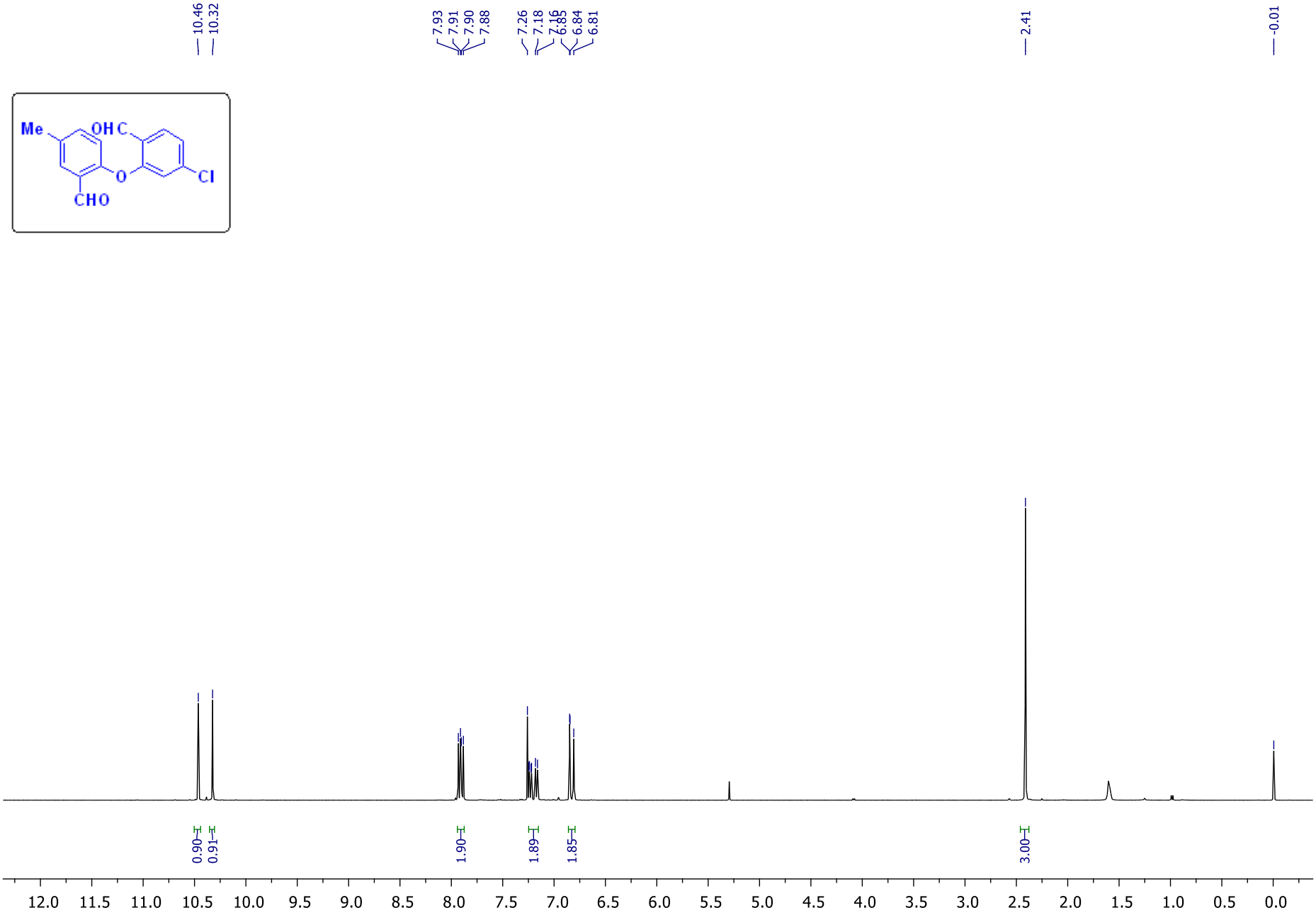
^{1}H-NMR of 1z (400 MHz, $CDCl_3$)



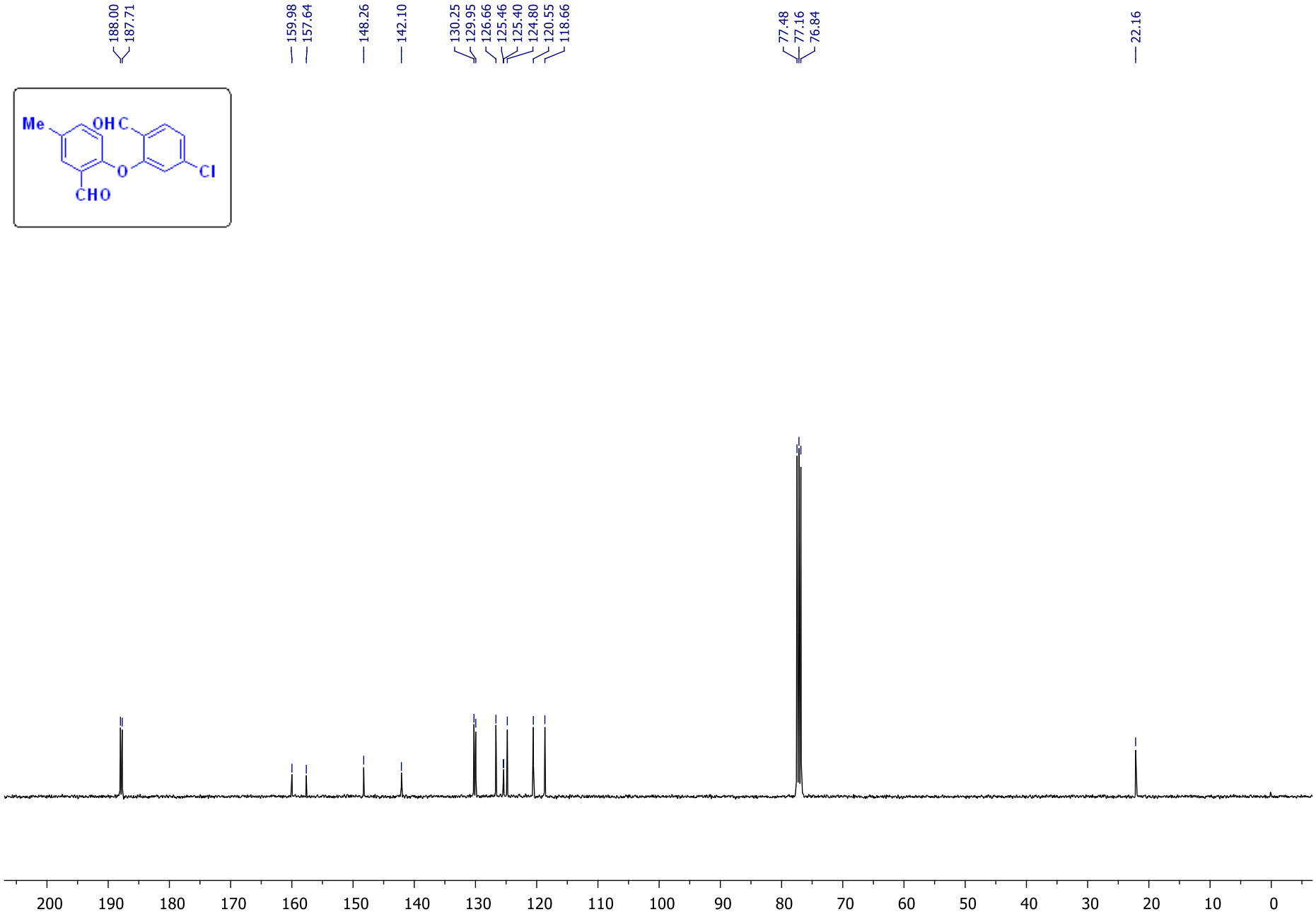
$^{13}C\{^{1}H\}$-NMR of 1z (101 MHz, $CDCl_3$)



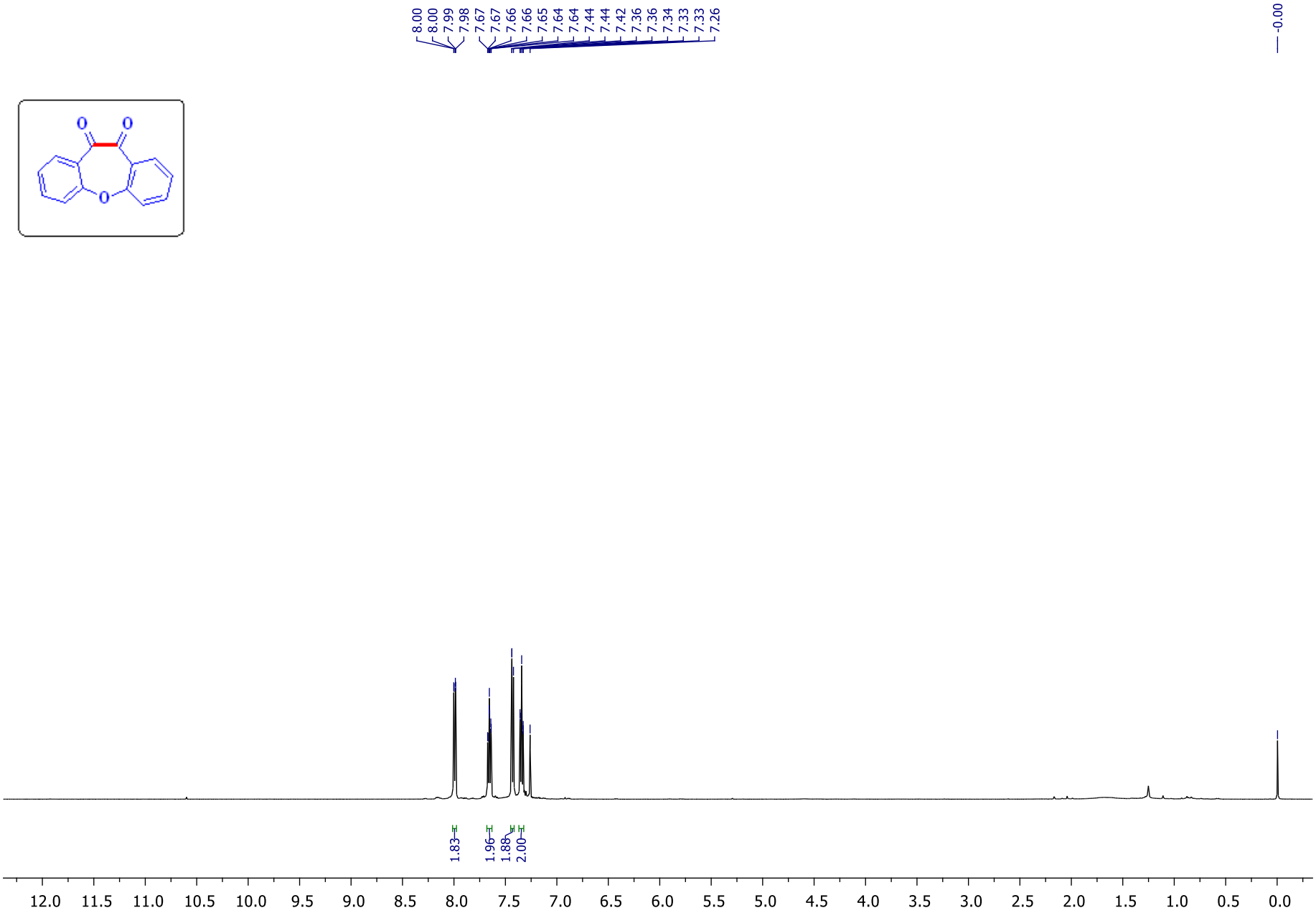
^{1}H-NMR of 1aa (400 MHz, $CDCl_3$)



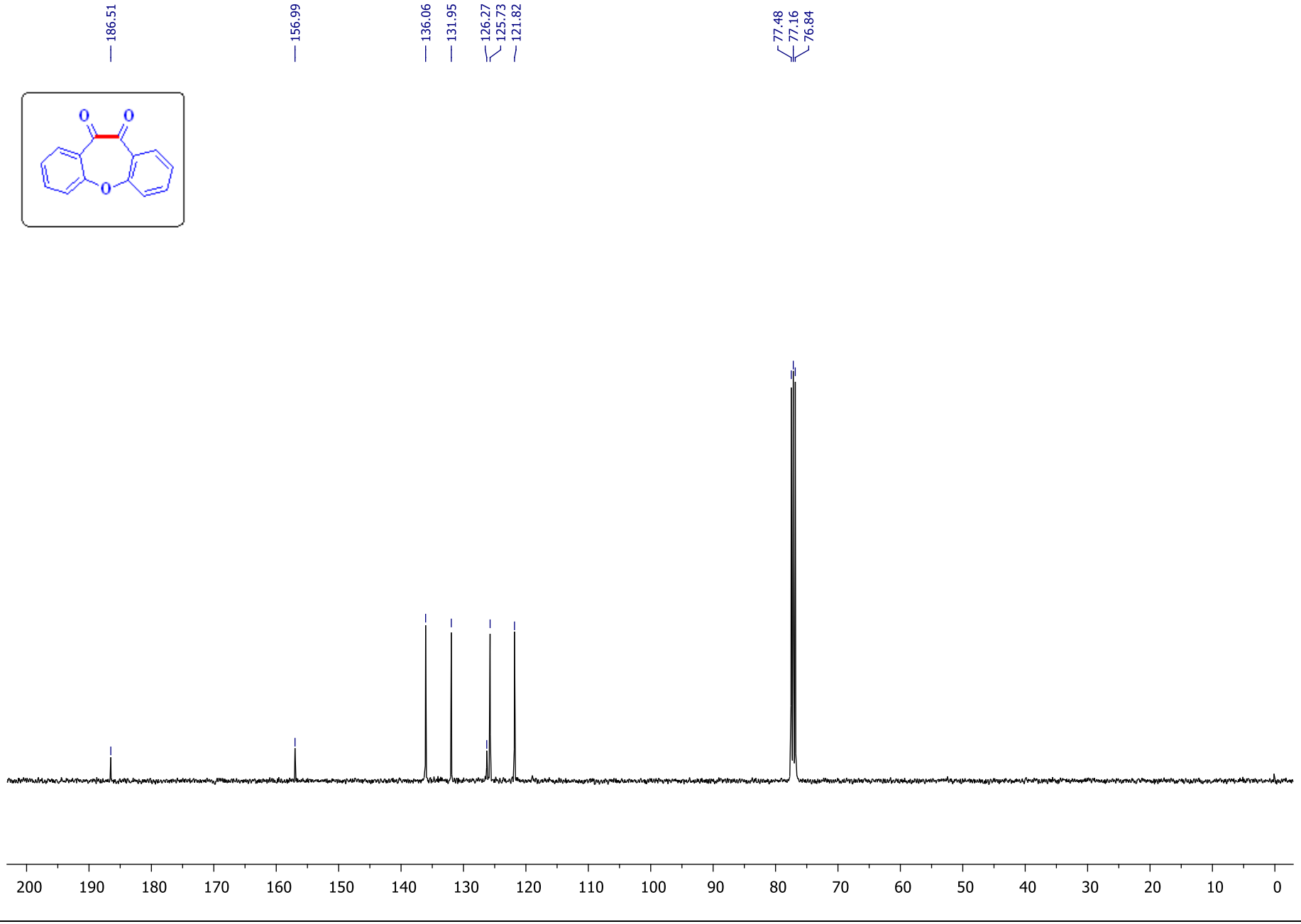
$^{13}C\{^{1}H\}$-NMR of 1aa (101 MHz, $CDCl_3$)



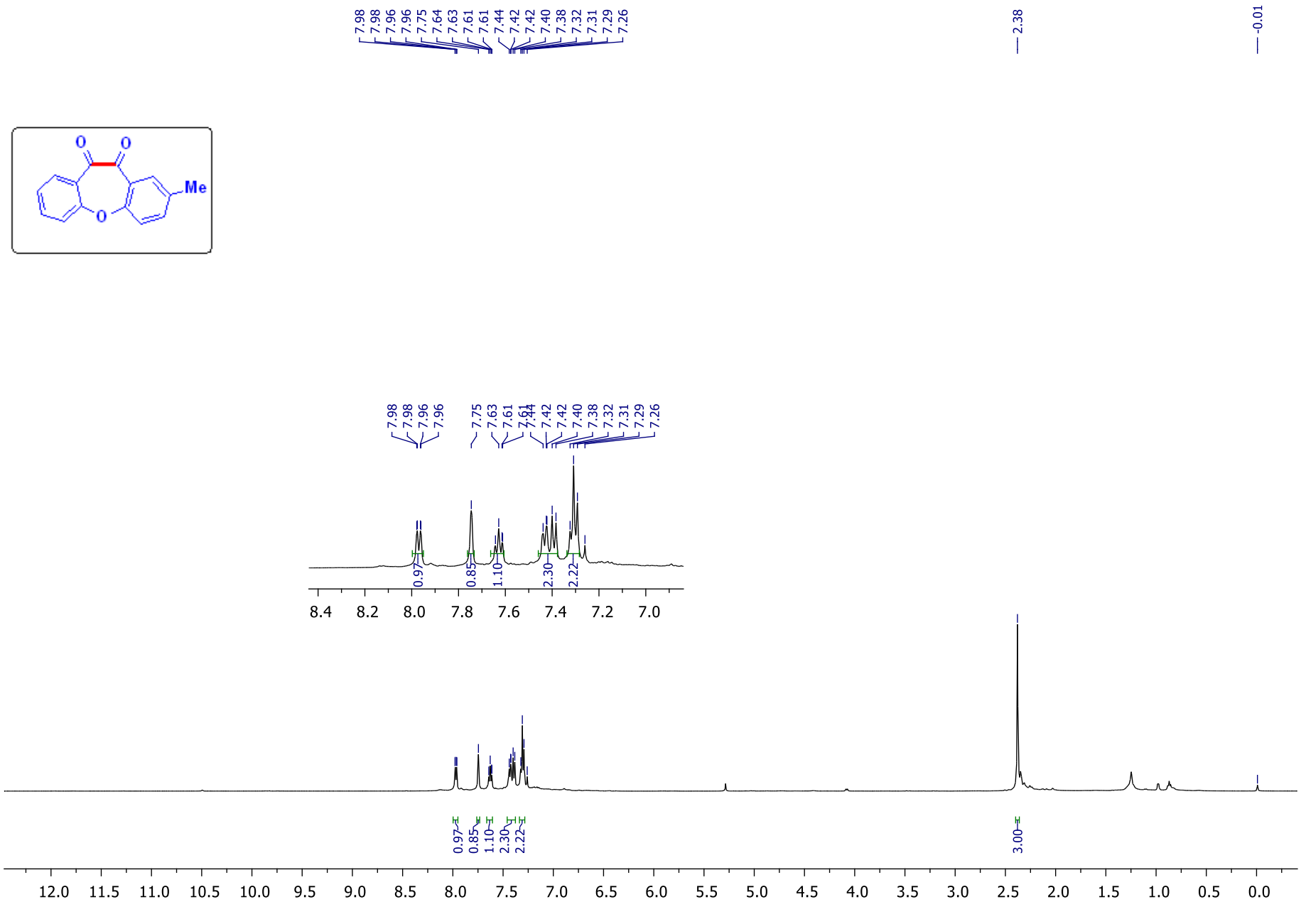
^{1}H-NMR of 3a (500 MHz, $CDCl_3$)



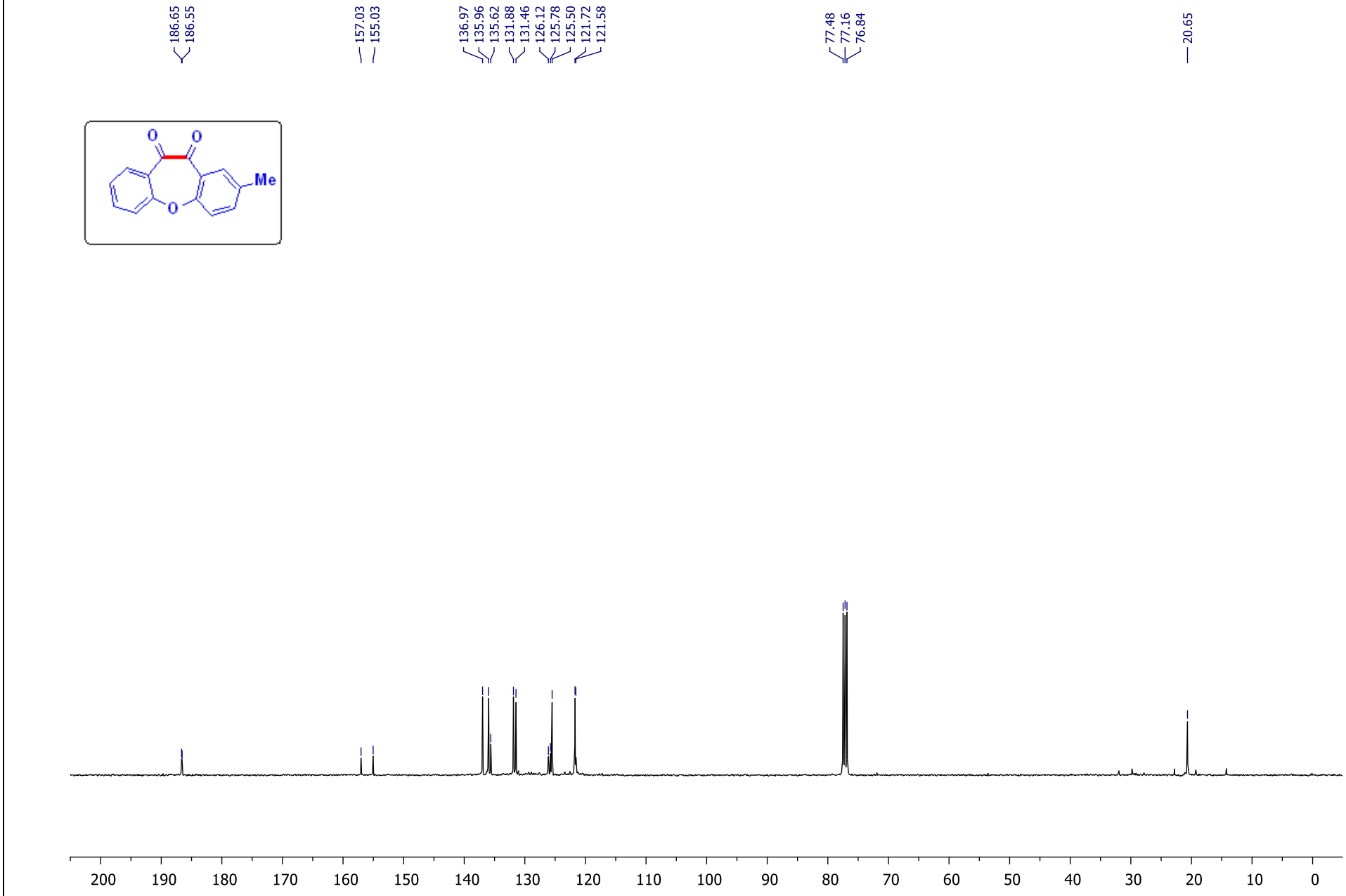
$^{13}C\{^{1}H\}$-NMR of 3a (101 MHz, $CDCl_3$)



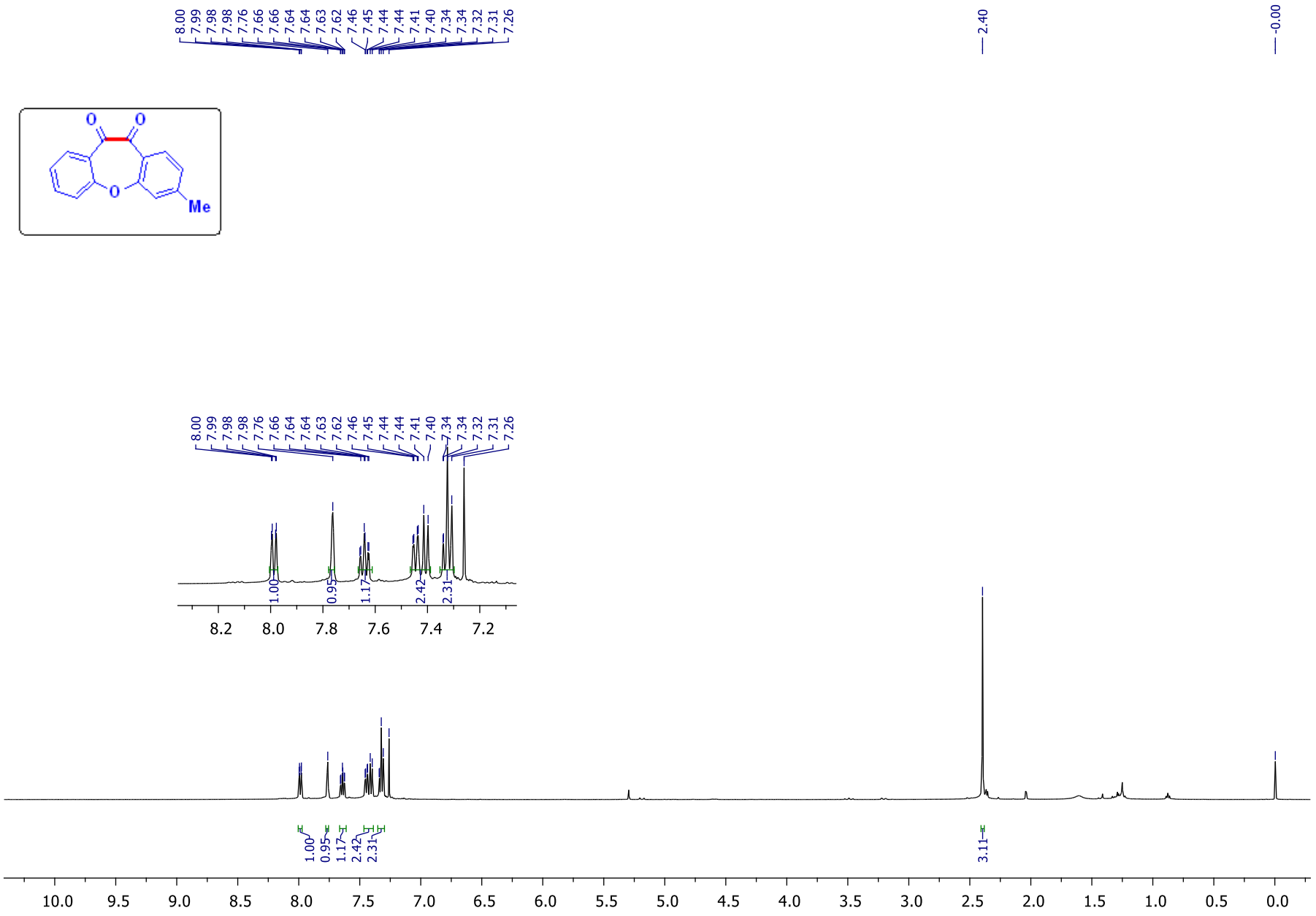
^{1}H-NMR of 3b (500 MHz, $CDCl_3$)



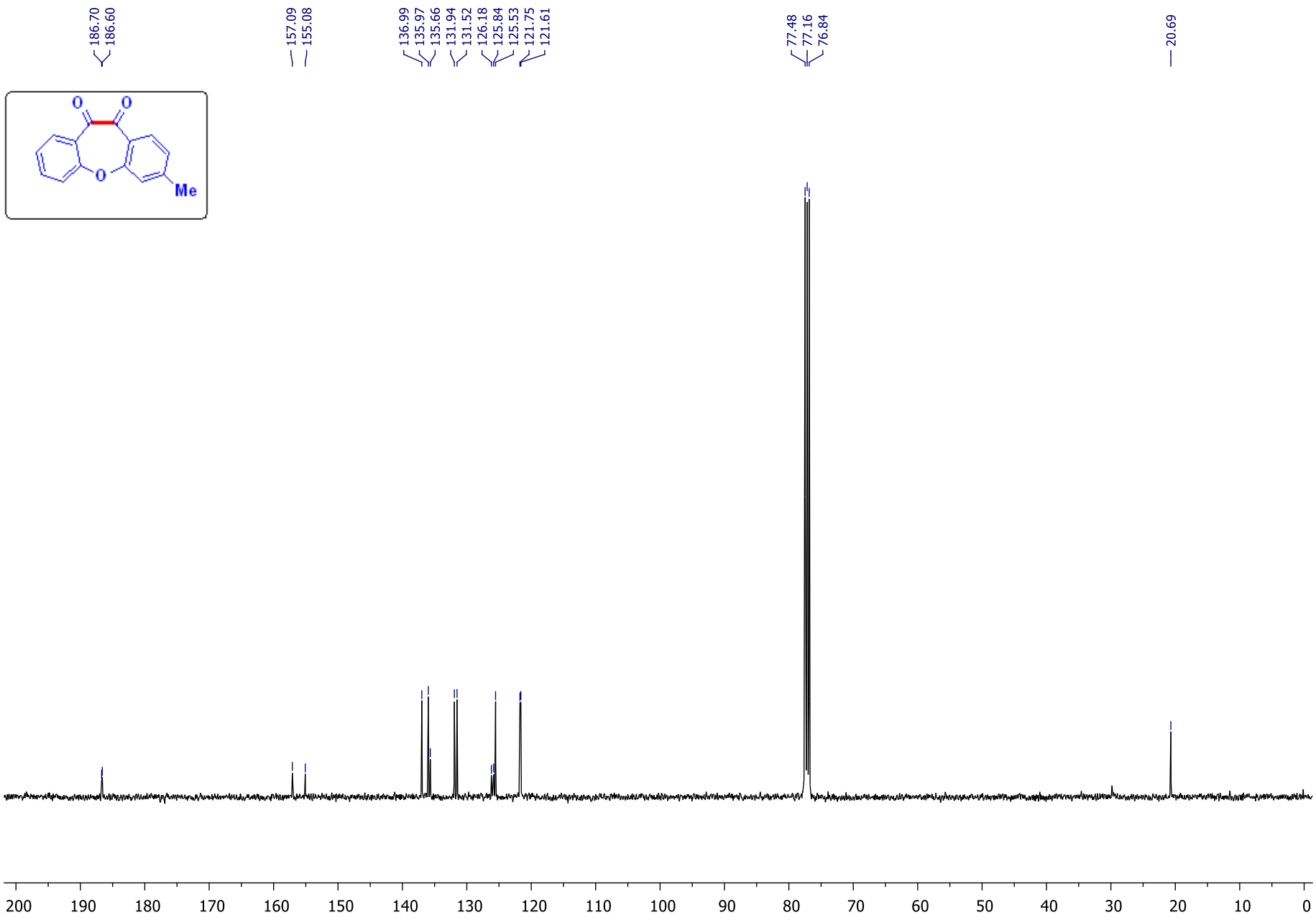
$^{13}C\{^{1}H\}$-NMR of 3b (101 MHz, $CDCl_3$)



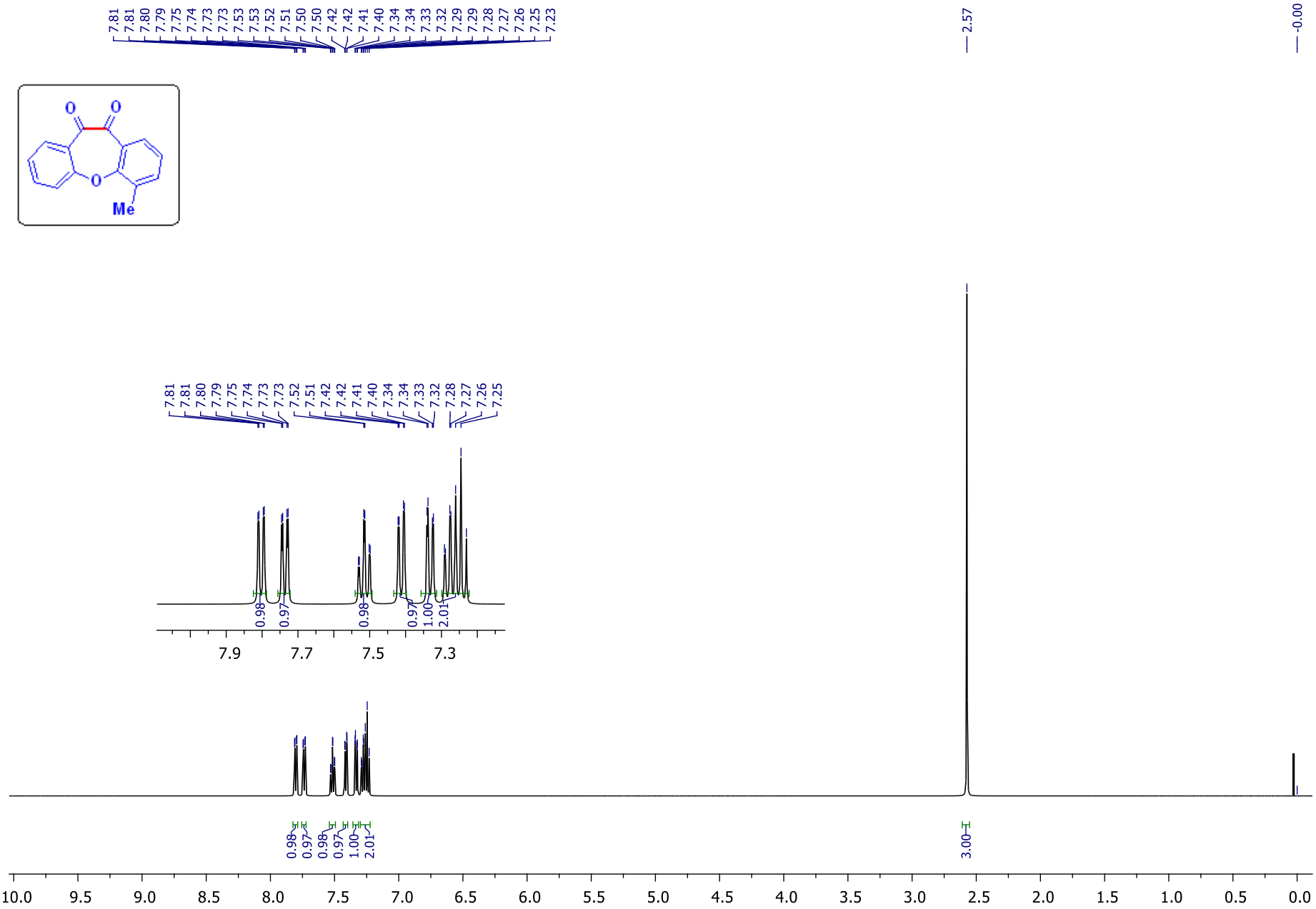
^{1}H-NMR of 3c (500 MHz, $CDCl_3$)



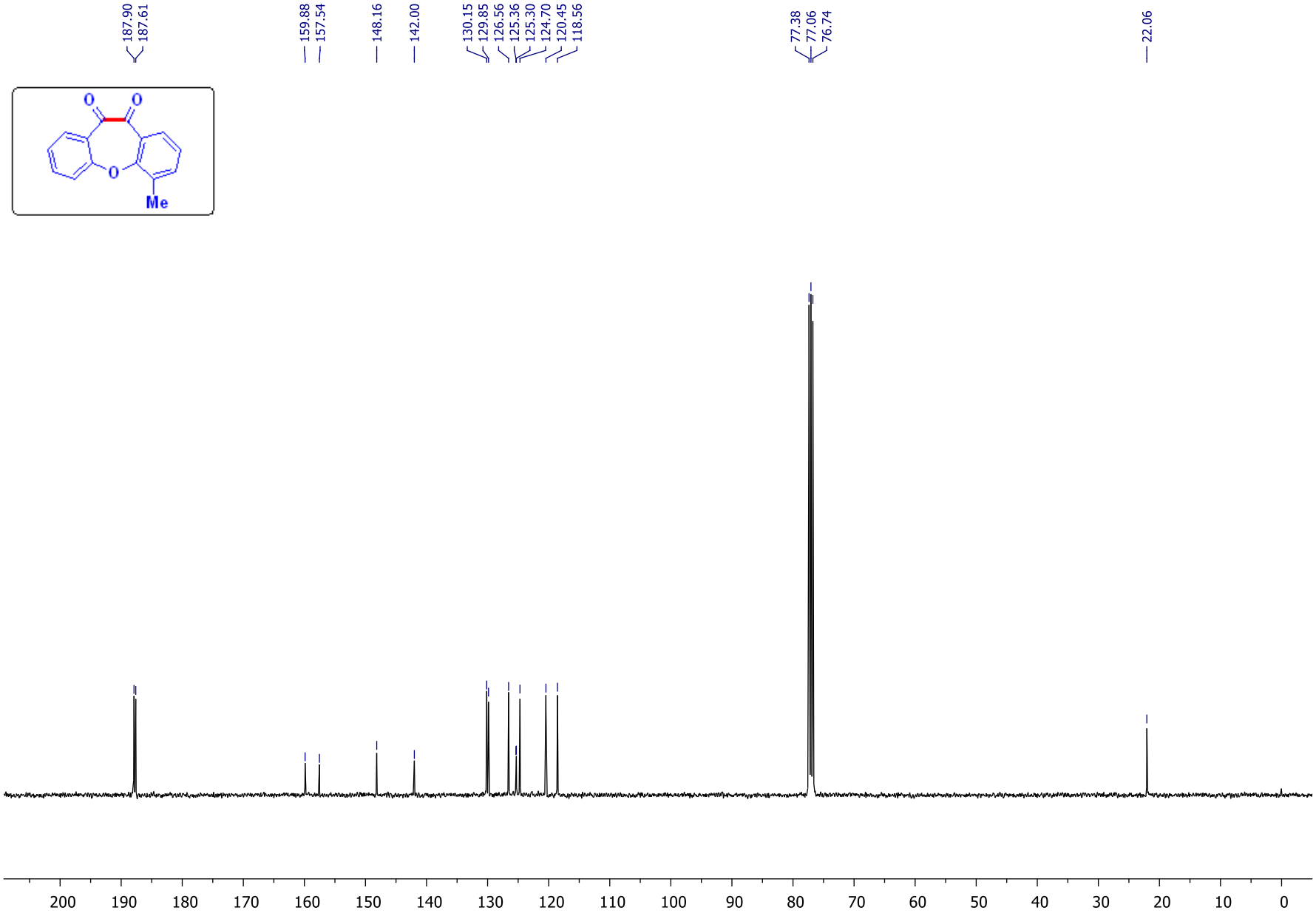
$^{13}C\{^{1}H\}$-NMR of 3c (101 MHz, $CDCl_3$)



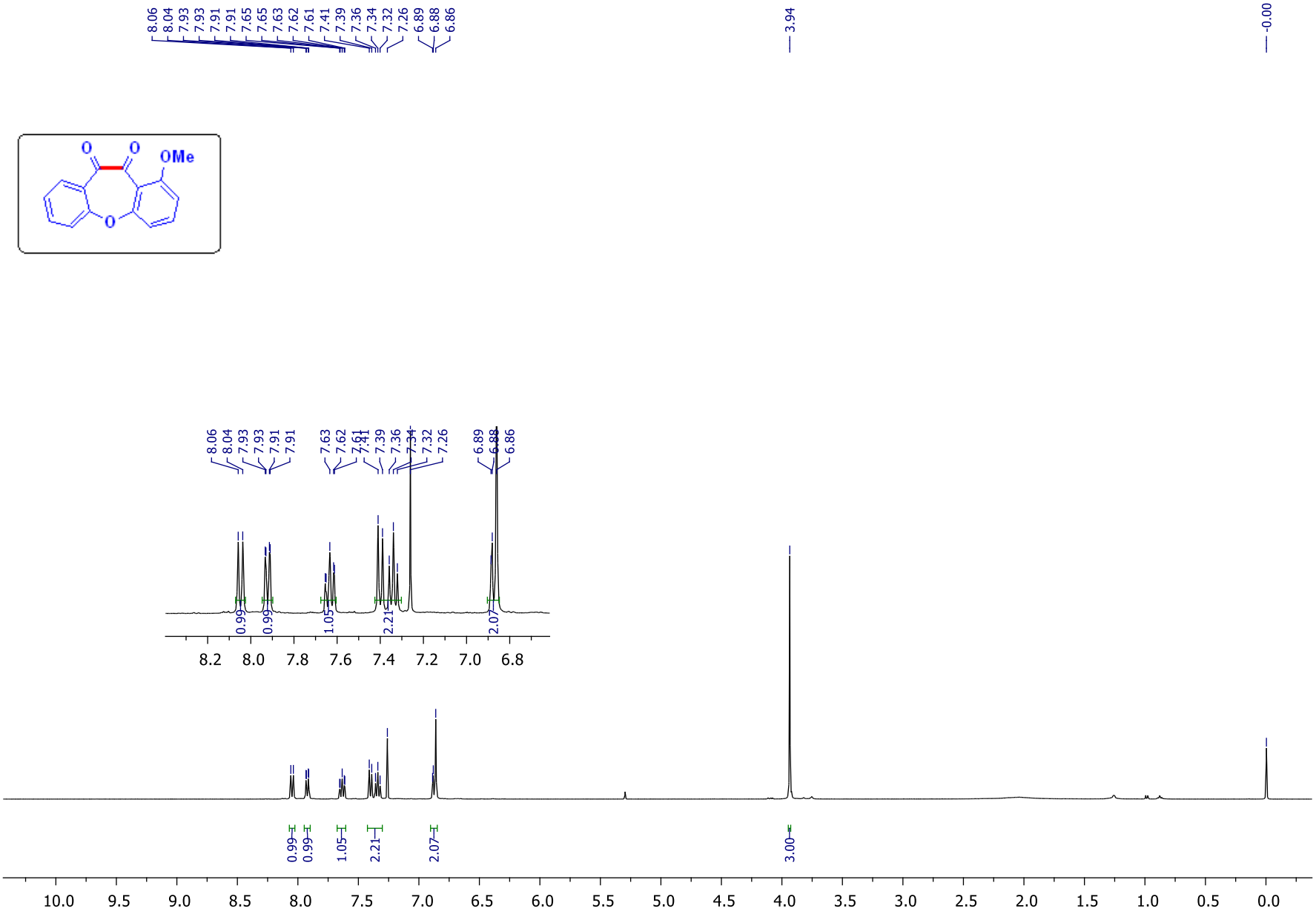
^{1}H-NMR of 3d (500 MHz, $CDCl_3$)



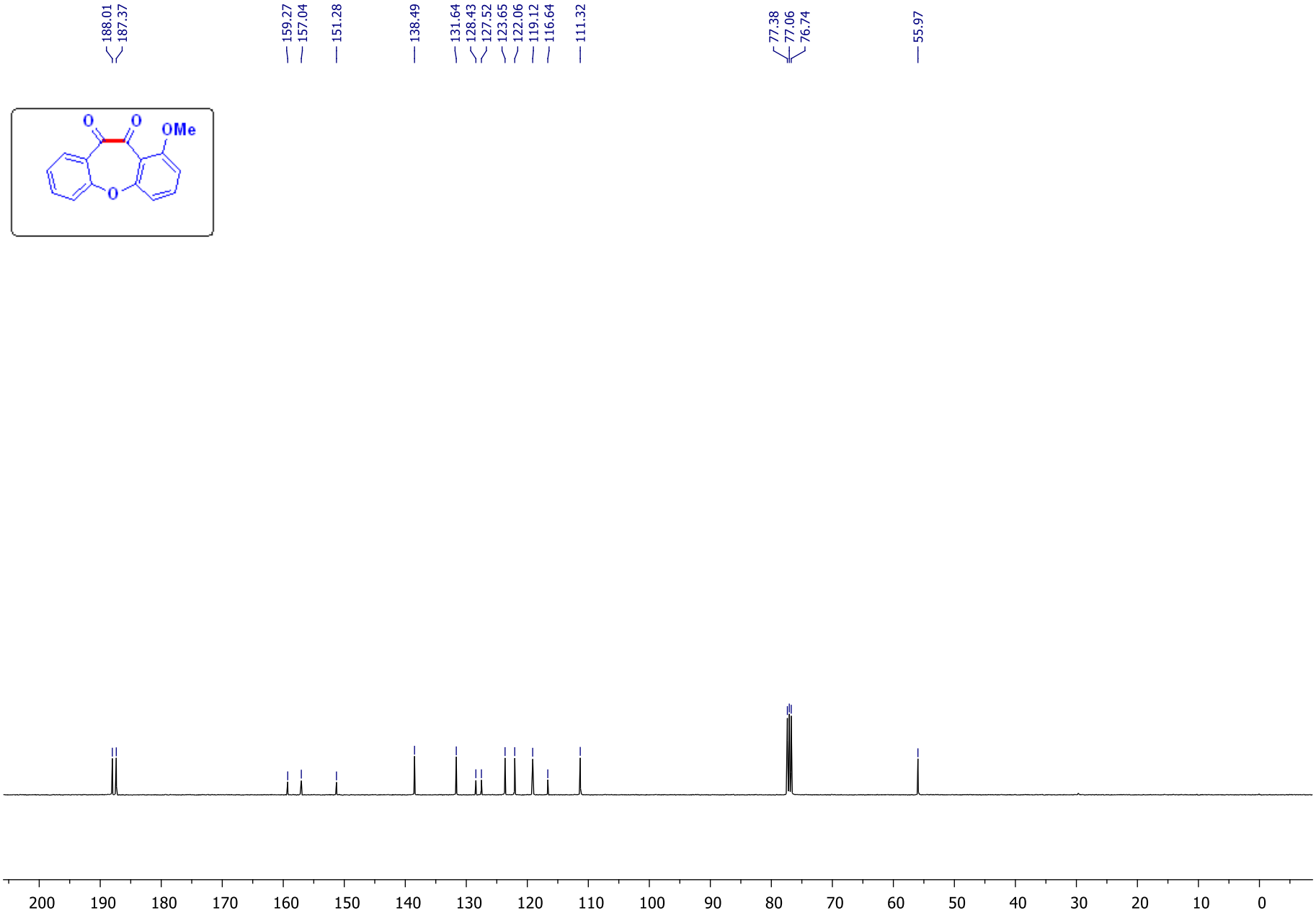
$^{13}C\{^{1}H\}$-NMR of 3d (101 MHz, $CDCl_3$)



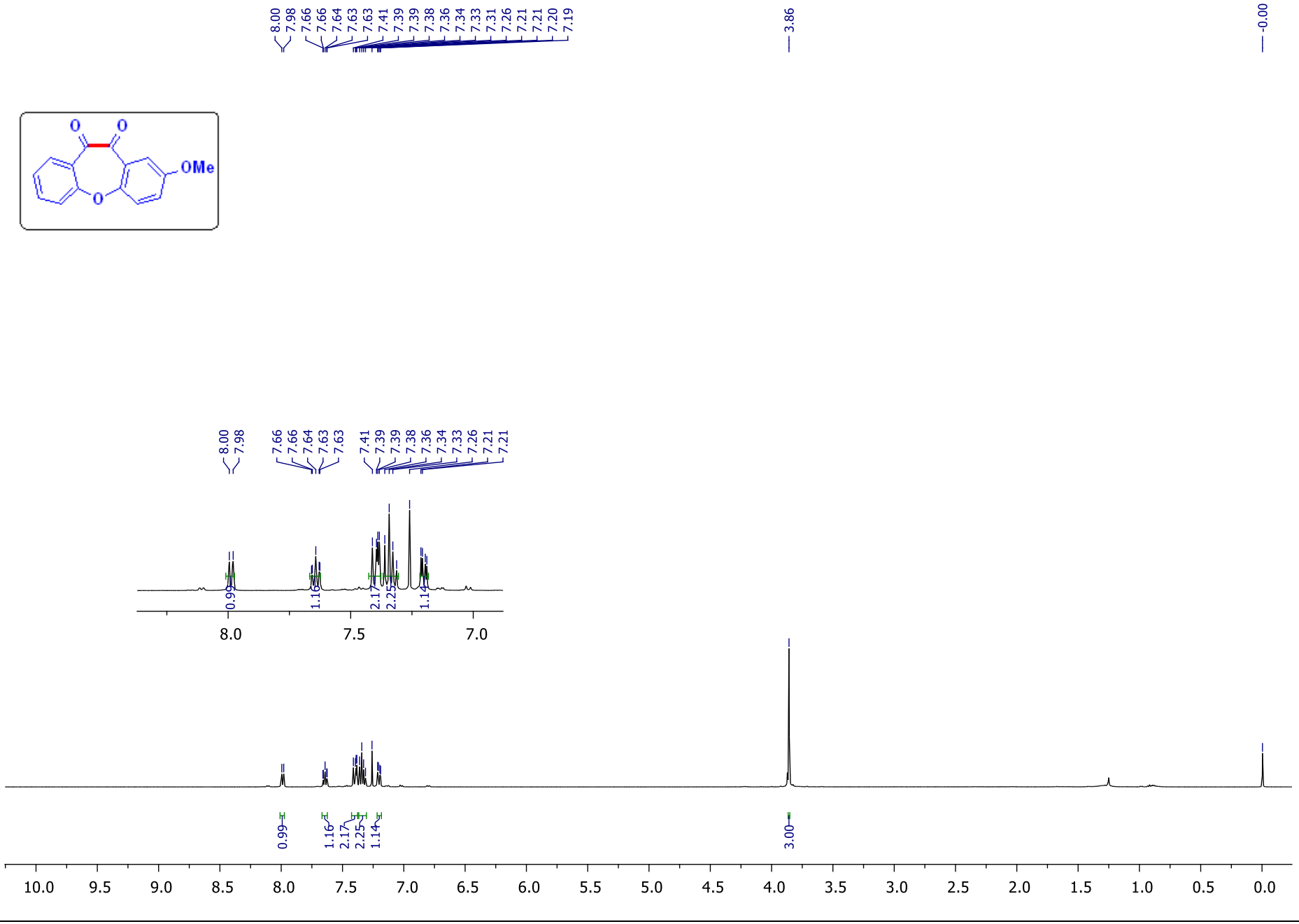
^{1}H-NMR of 3e (400 MHz, $CDCl_3$)



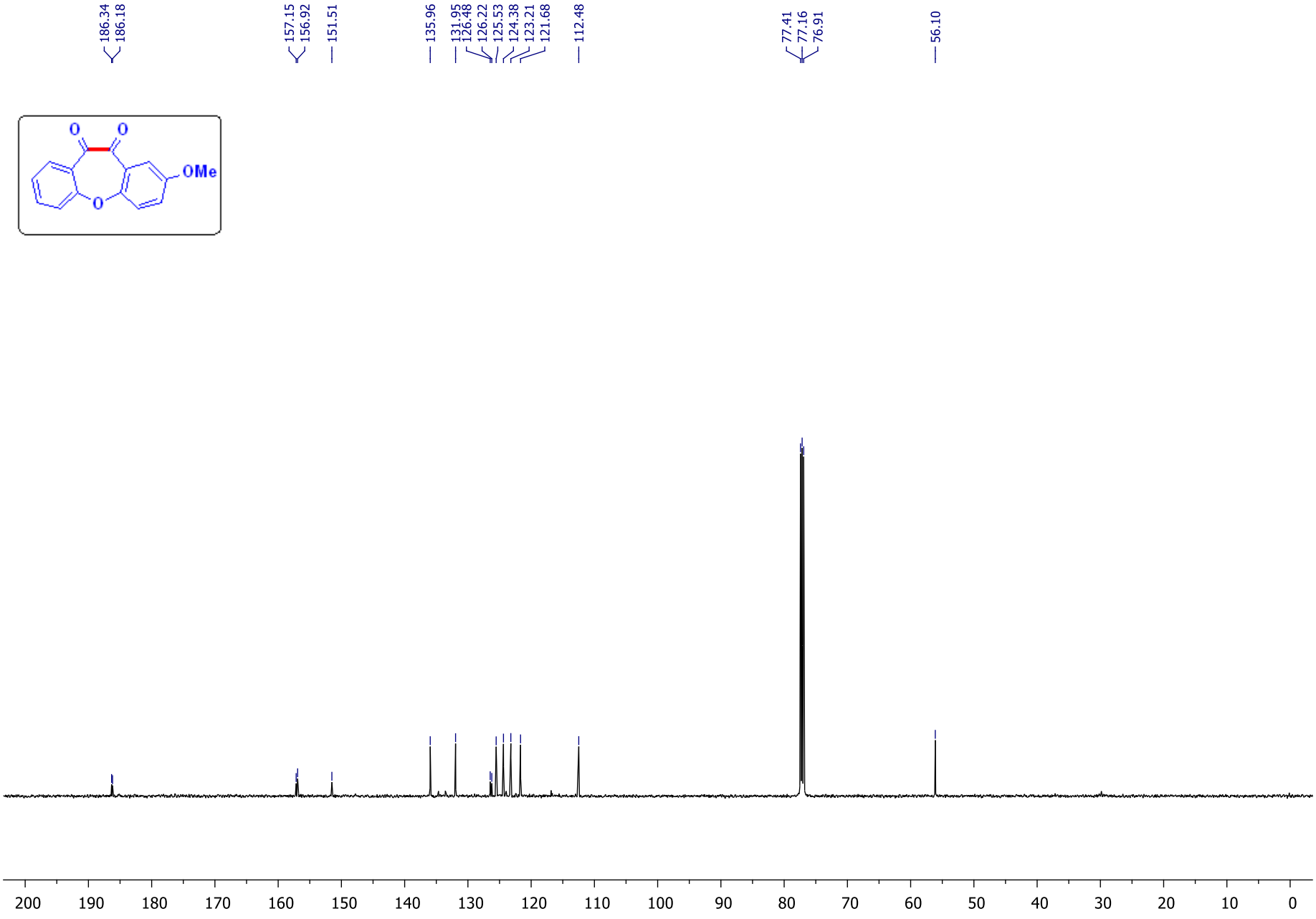
$^{13}C\{^{1}H\}$-NMR of 3e (126 MHz, $CDCl_3$)



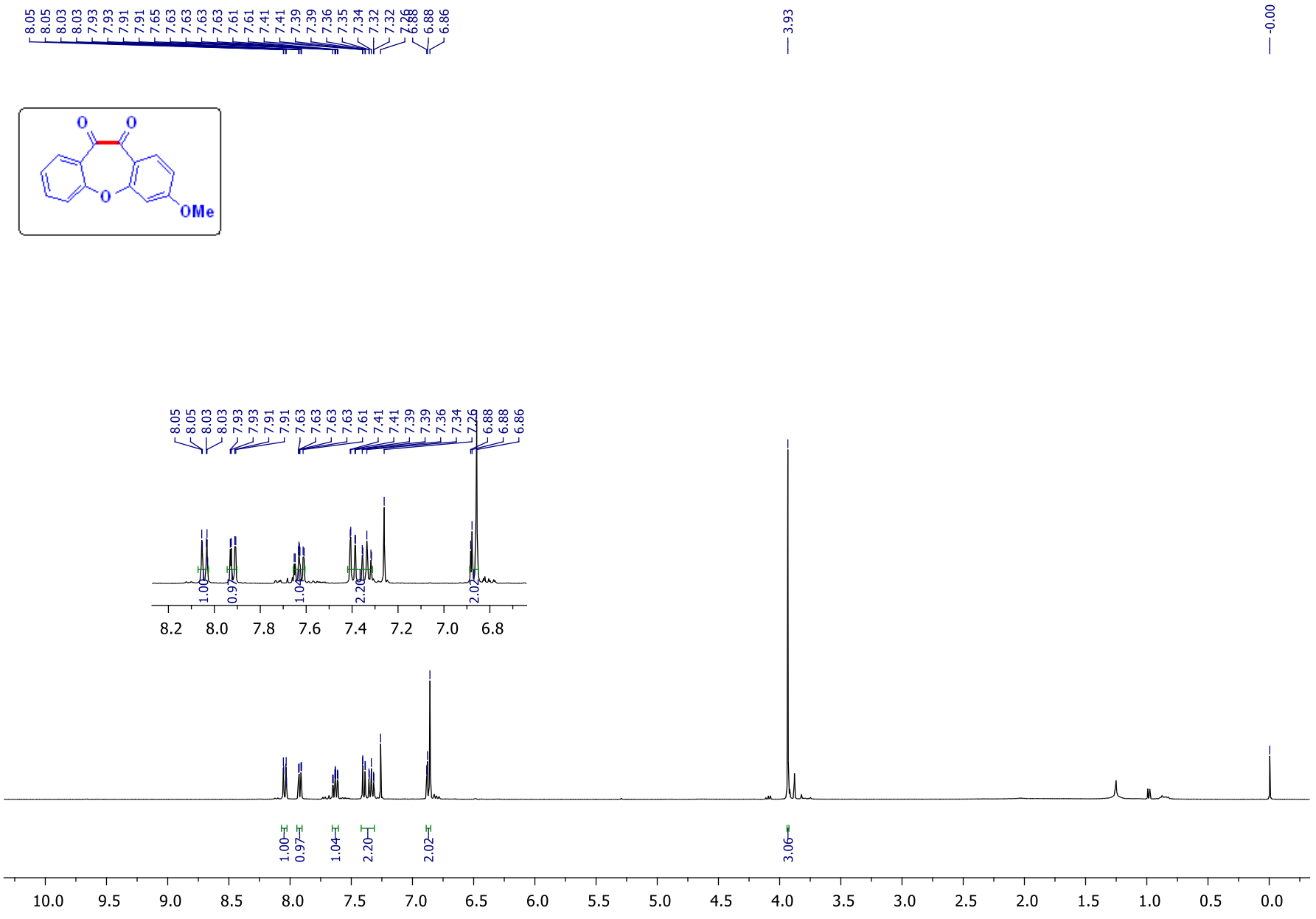
^{1}H-NMR of 3f (500 MHz, $CDCl_3$)



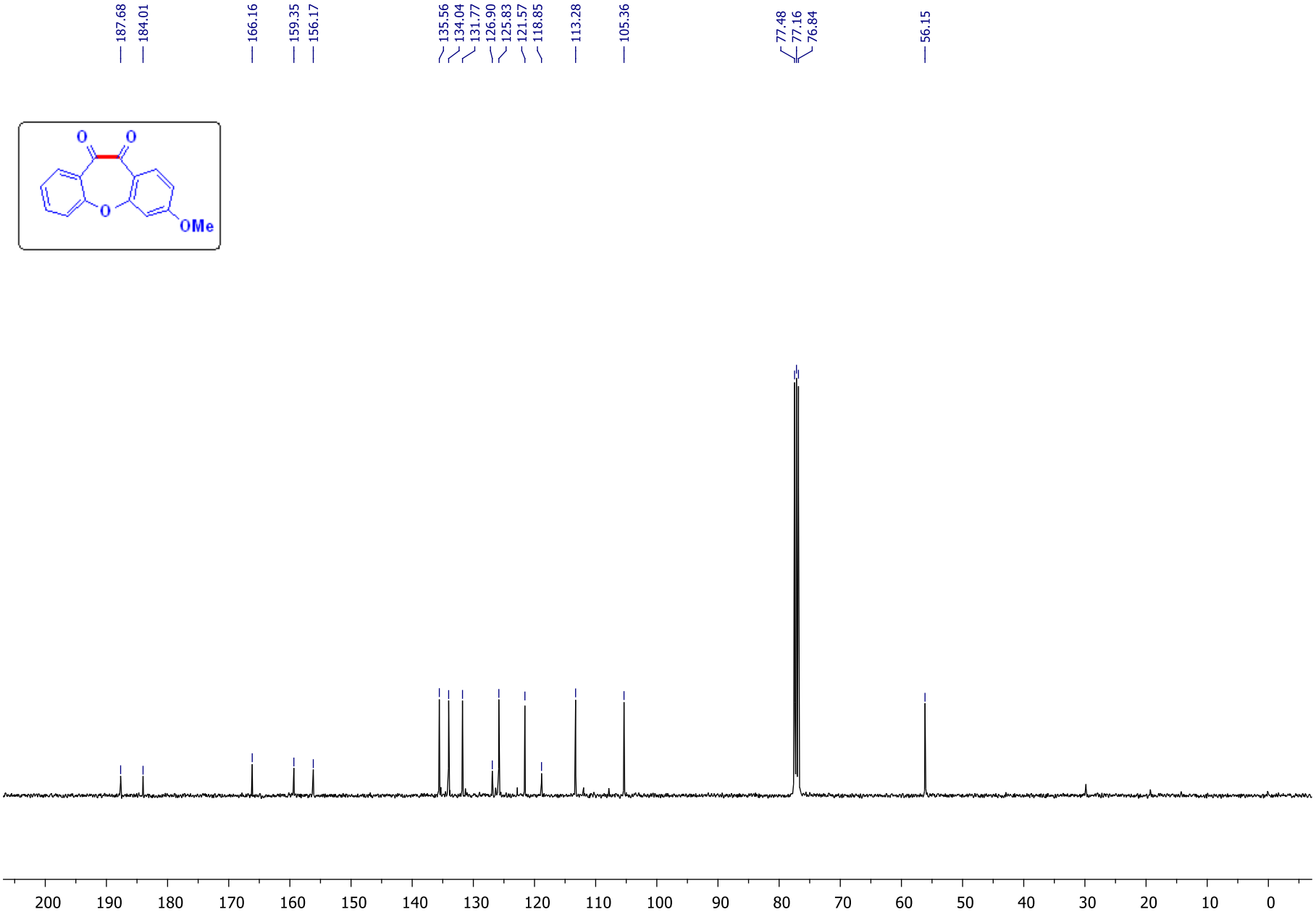
$^{13}C\{^{1}H\}$-NMR of 3f (101 MHz, $CDCl_3$)



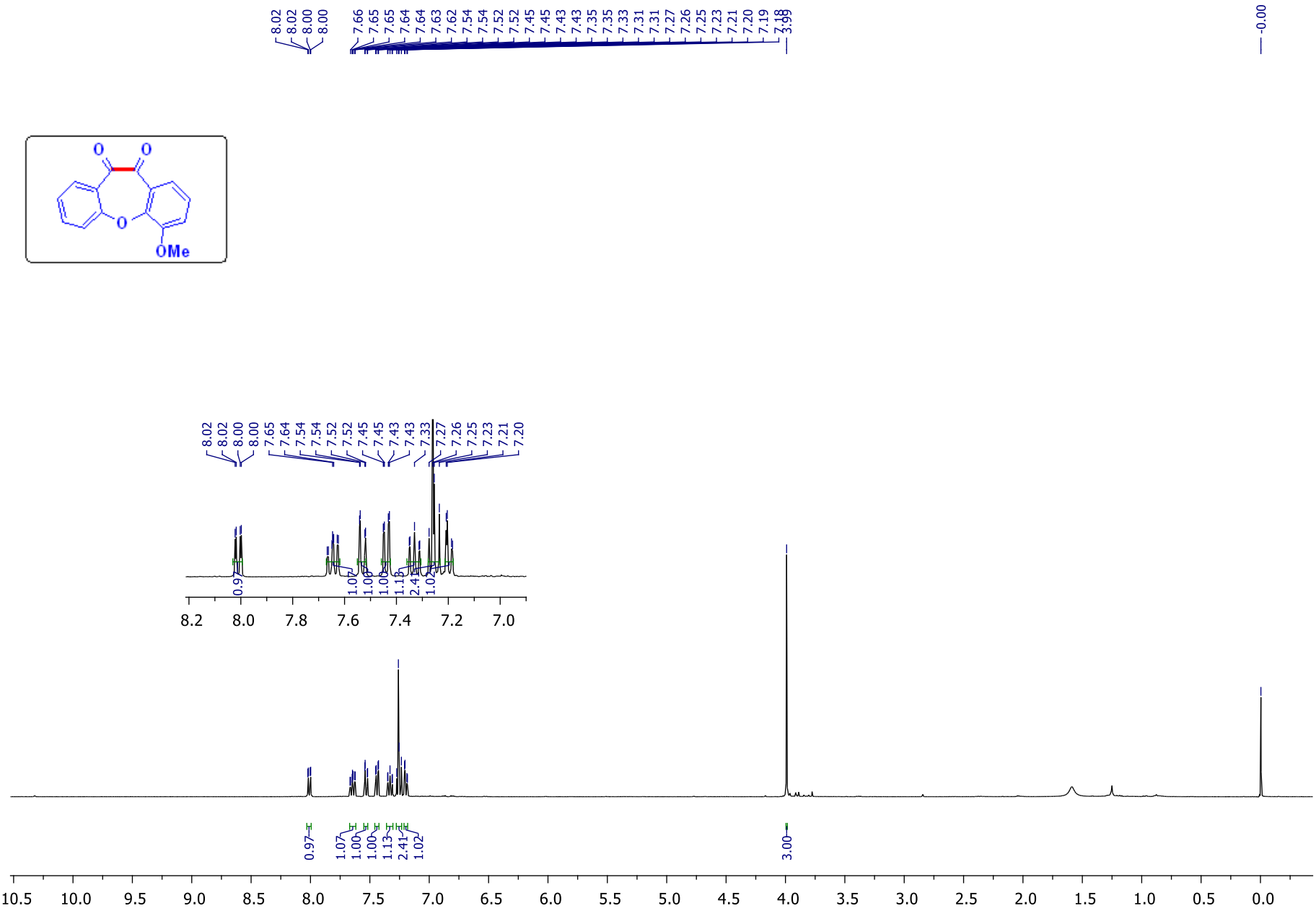
^{1}H-NMR of 3g (400 MHz, $CDCl_3$)



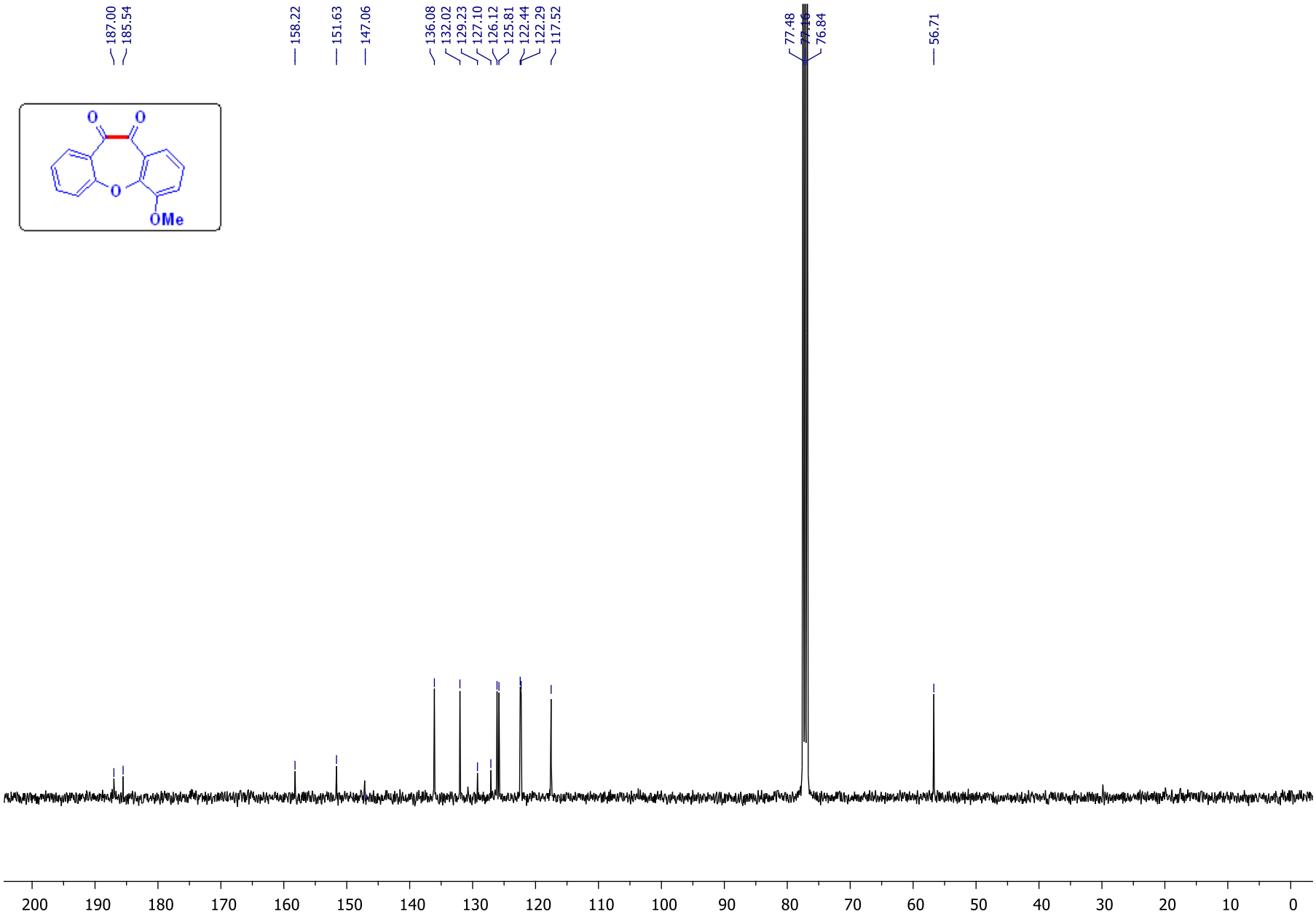
$^{13}C\{^{1}H\}$-NMR of 3g (101 MHz, $CDCl_3$)



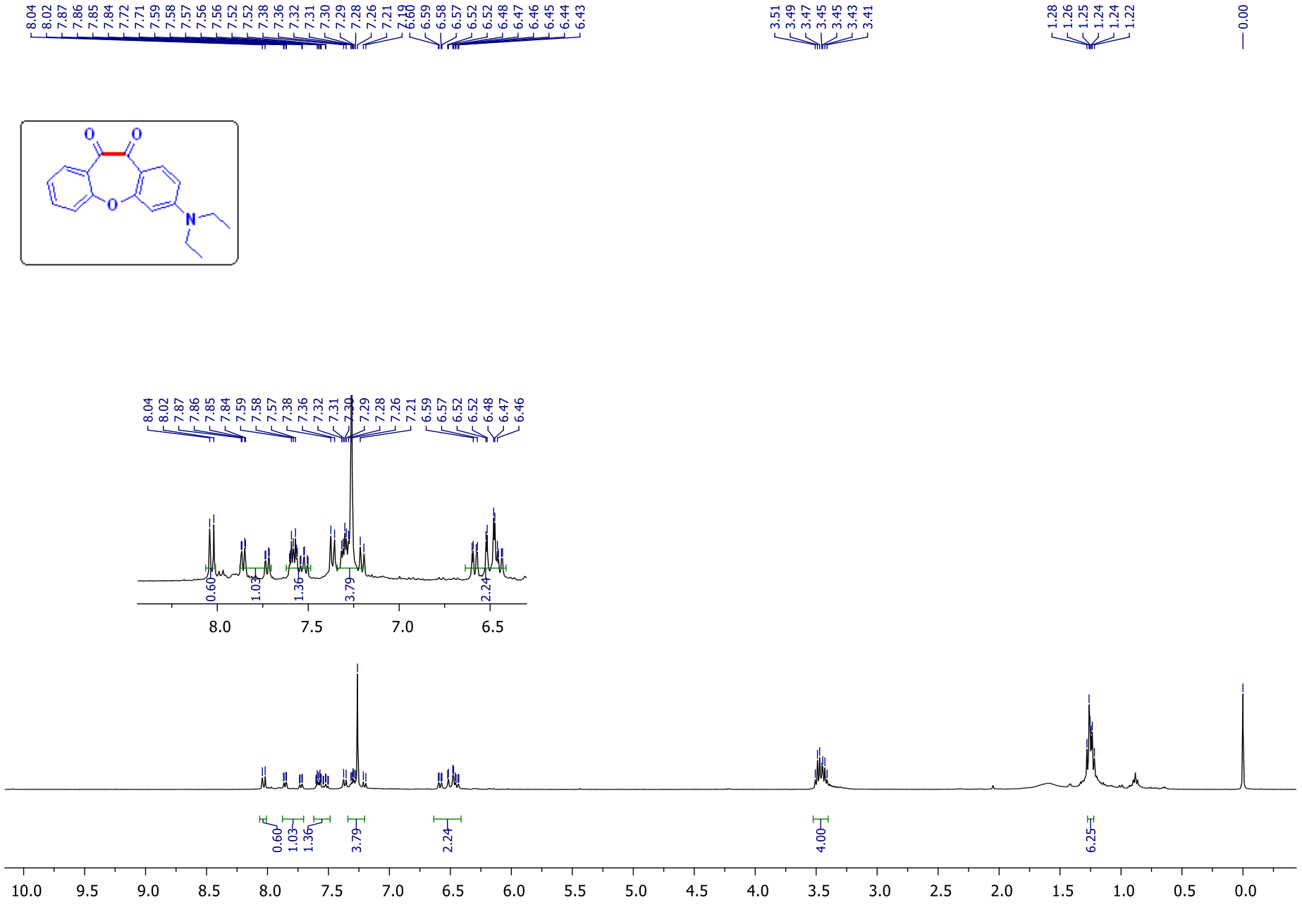
^{1}H-NMR of 3h (400 MHz, $CDCl_3$)



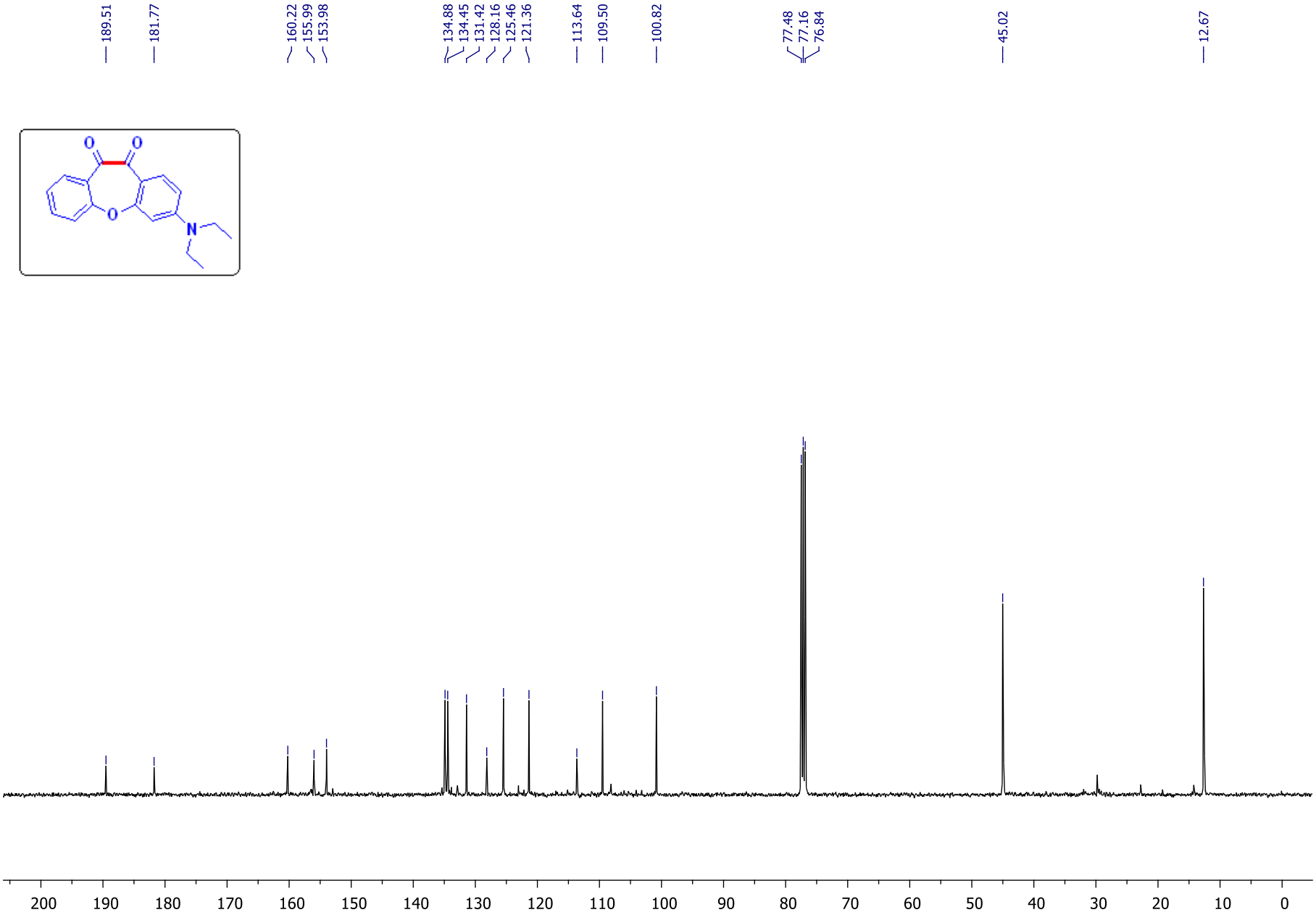
$^{13}C\{^{1}H\}$-NMR of 3h (126 MHz, $CDCl_3$)



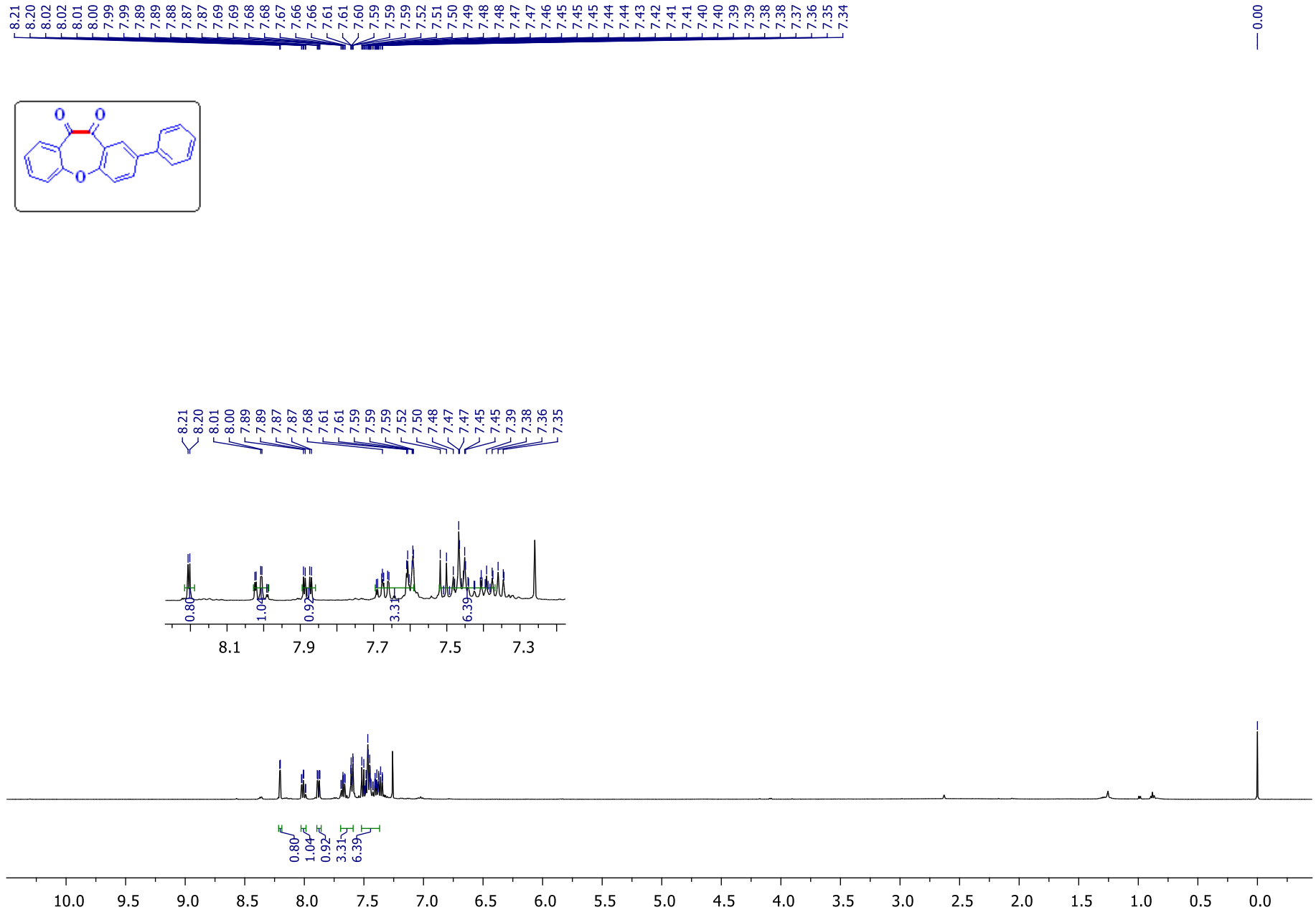
^{1}H-NMR of 3i (400 MHz, $CDCl_3$)



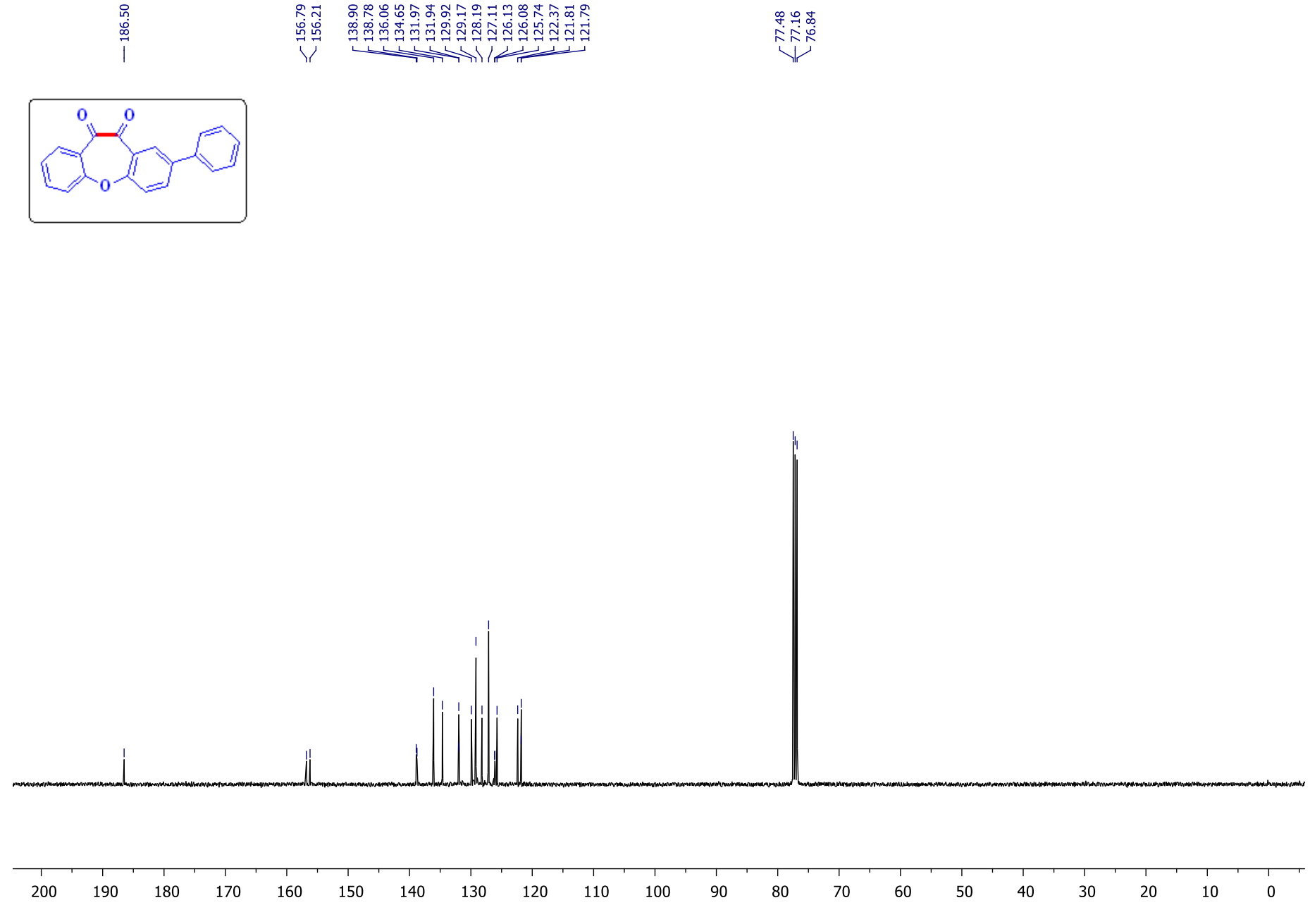
$^{13}C\{^{1}H\}$-NMR of 3i (101 MHz, $CDCl_3$)



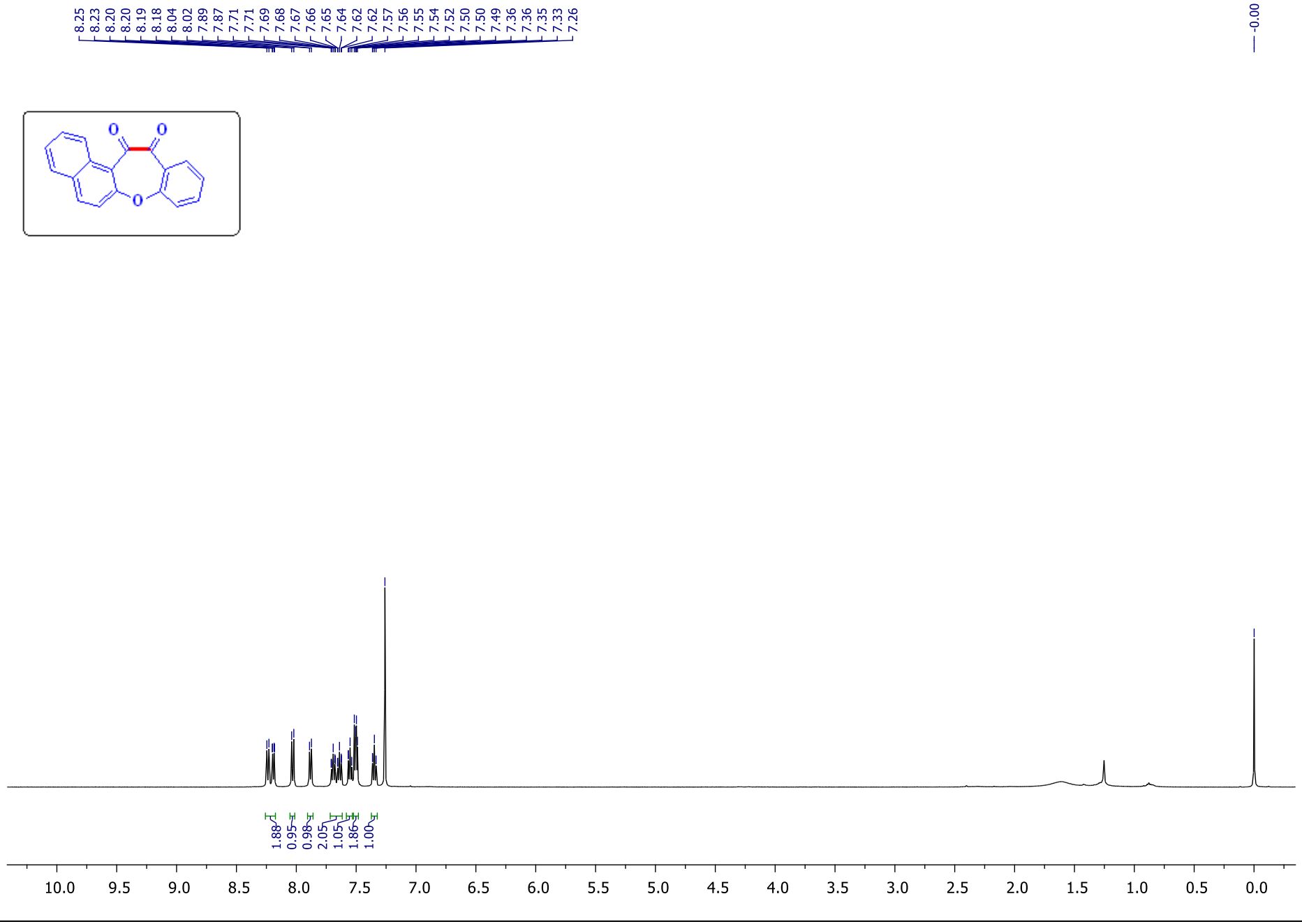
^{1}H-NMR of 3j (500 MHz, $CDCl_3$)



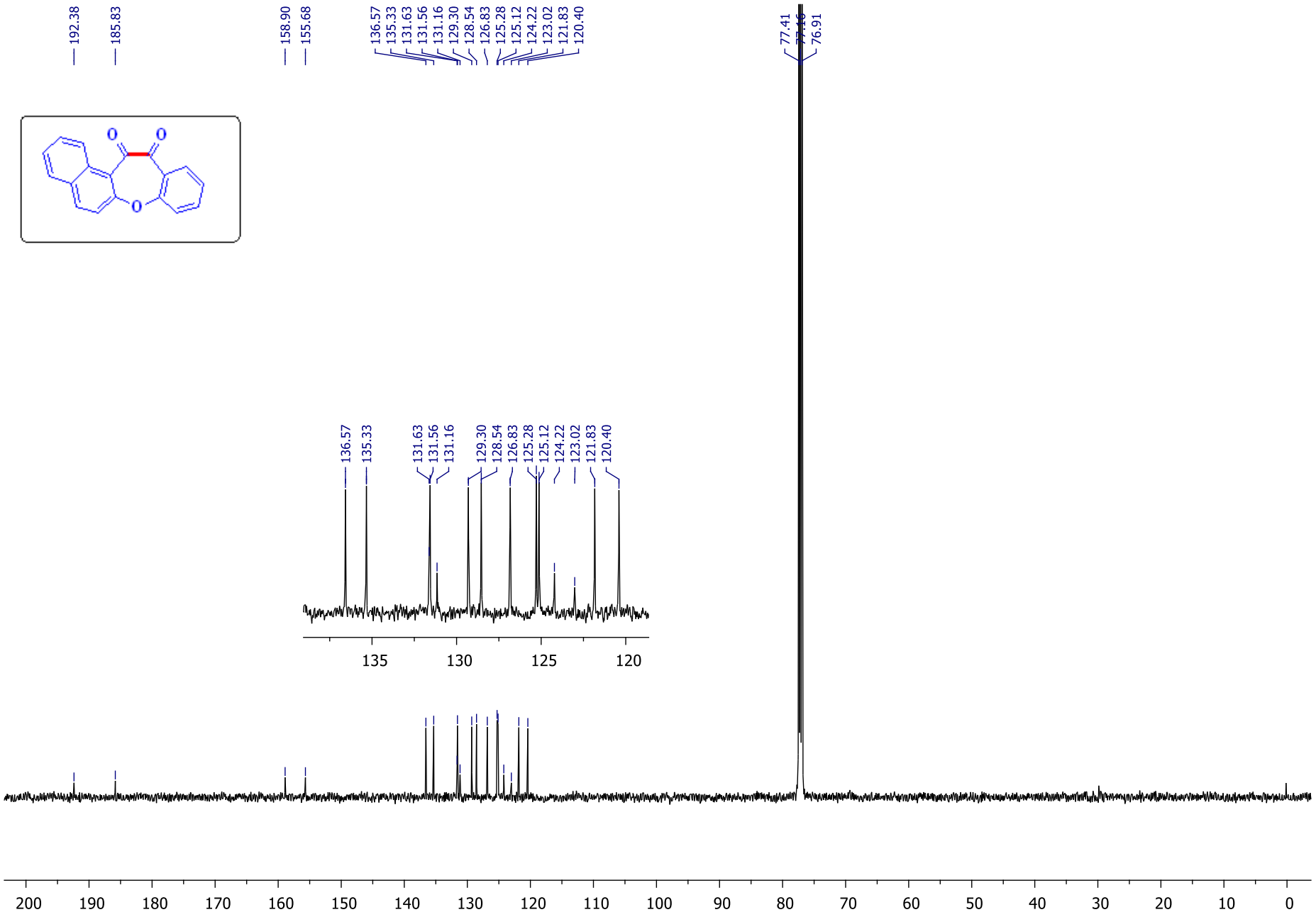
$^{13}C\{^{1}H\}$-NMR of 3j (126 MHz, $CDCl_3$)



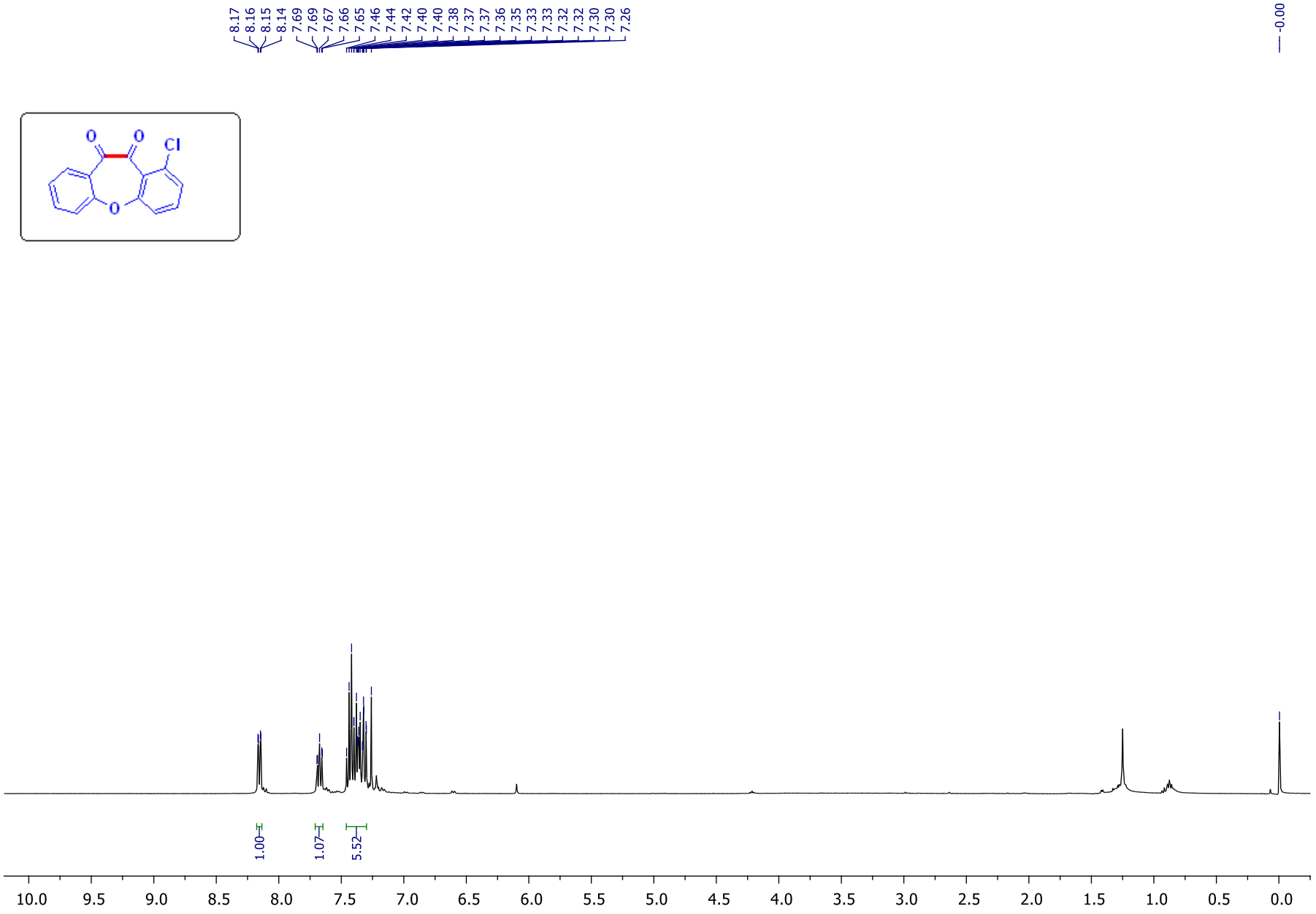
^{1}H-NMR of 3k (500 MHz, $CDCl_3$)



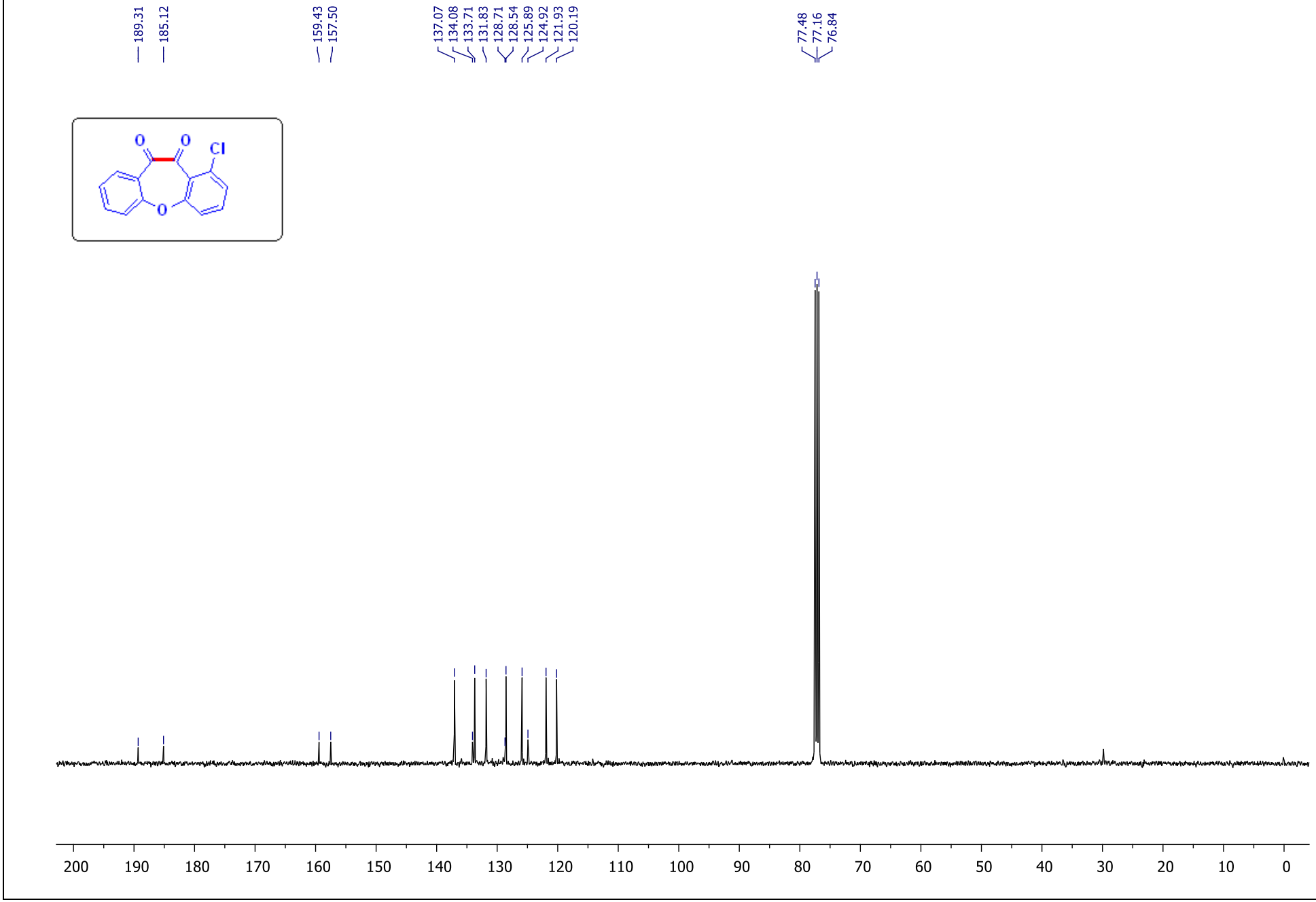
$^{13}C\{^{1}H\}$-NMR of 3k (126 MHz, $CDCl_3$)



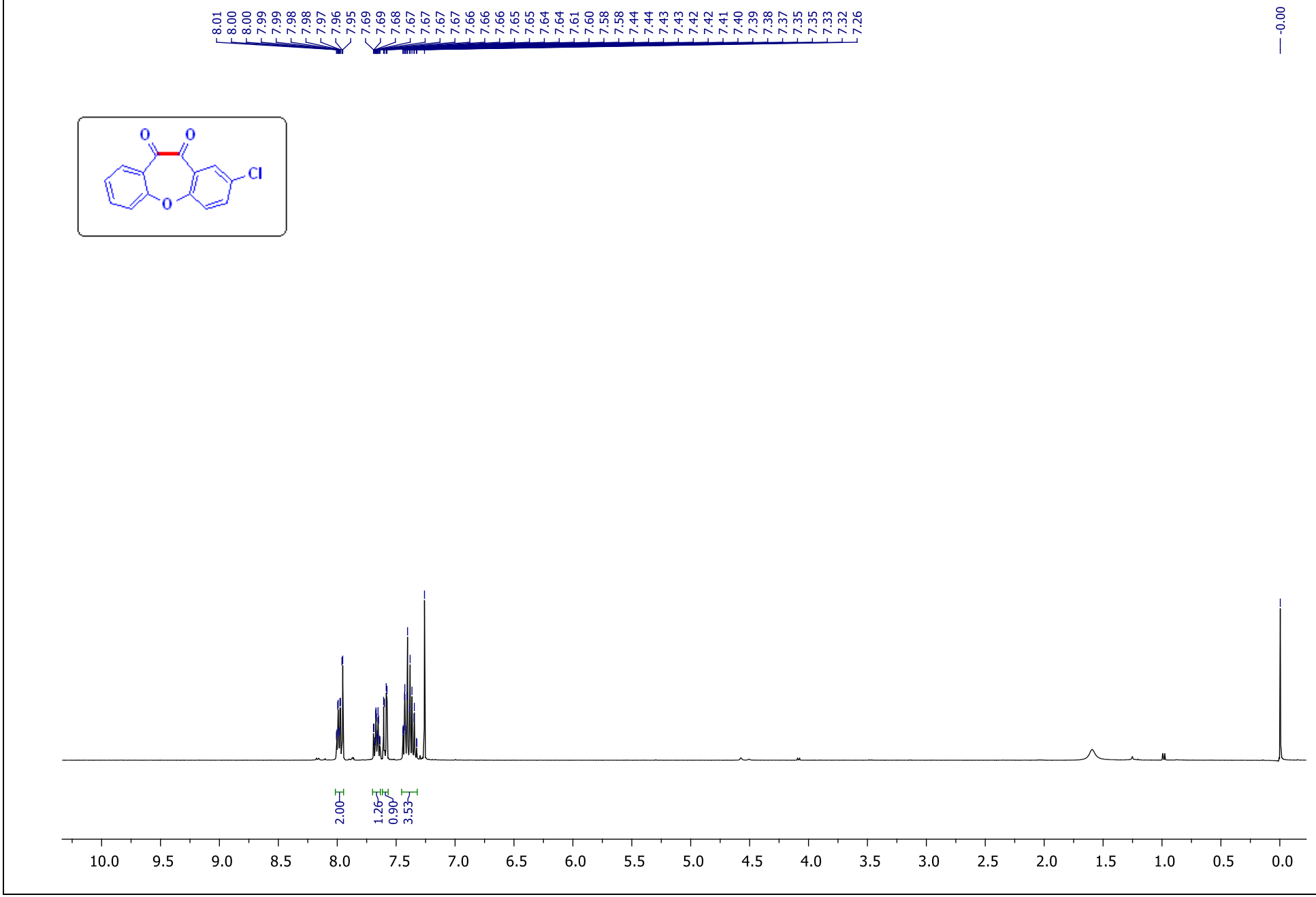
^{1}H-NMR of 3l (400 MHz, $CDCl_3$)



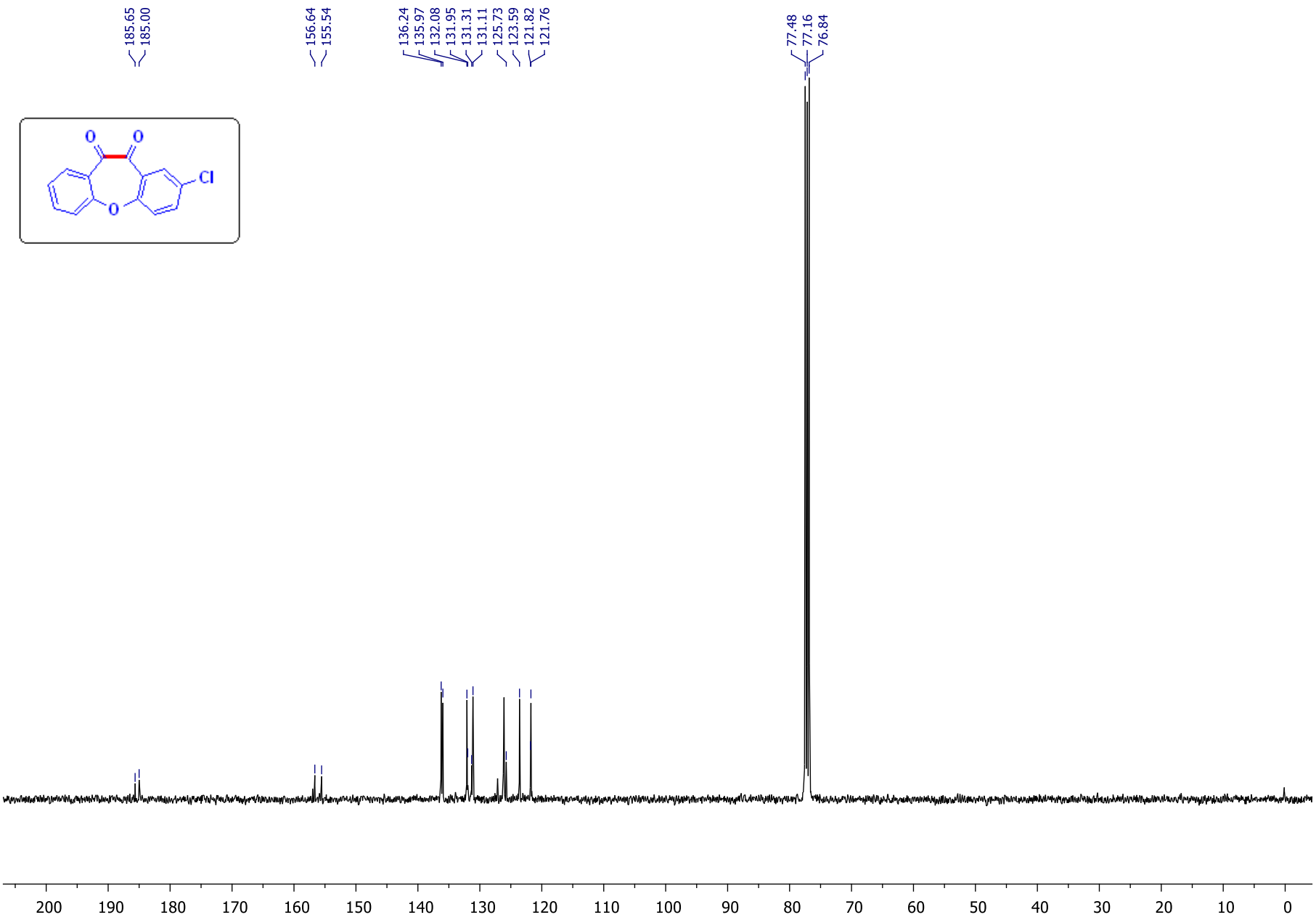
$^{13}C\{^{1}H\}$-NMR of 3l (101 MHz, $CDCl_3$)



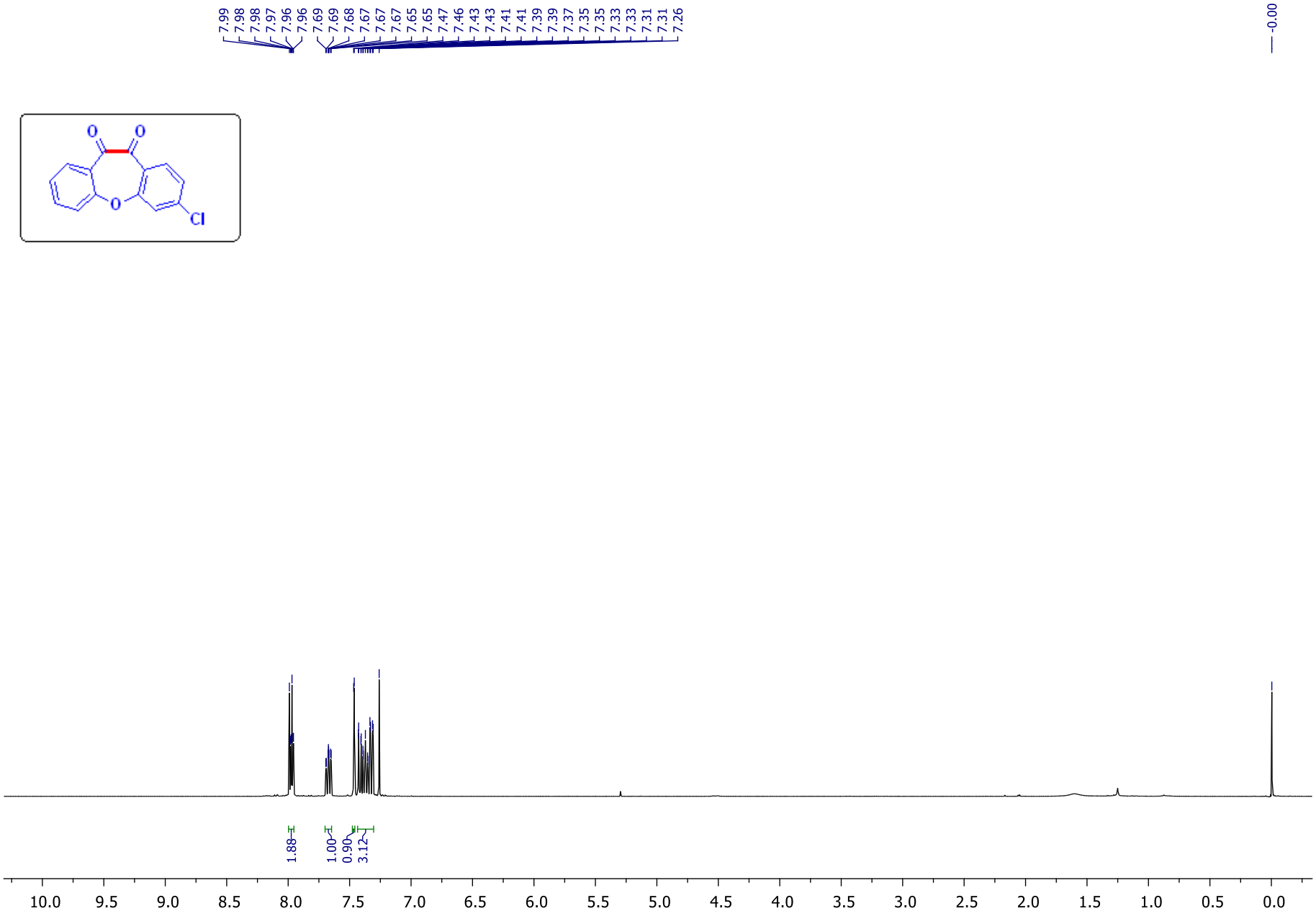
^{1}H-NMR of 3m (400 MHz, $CDCl_3$)



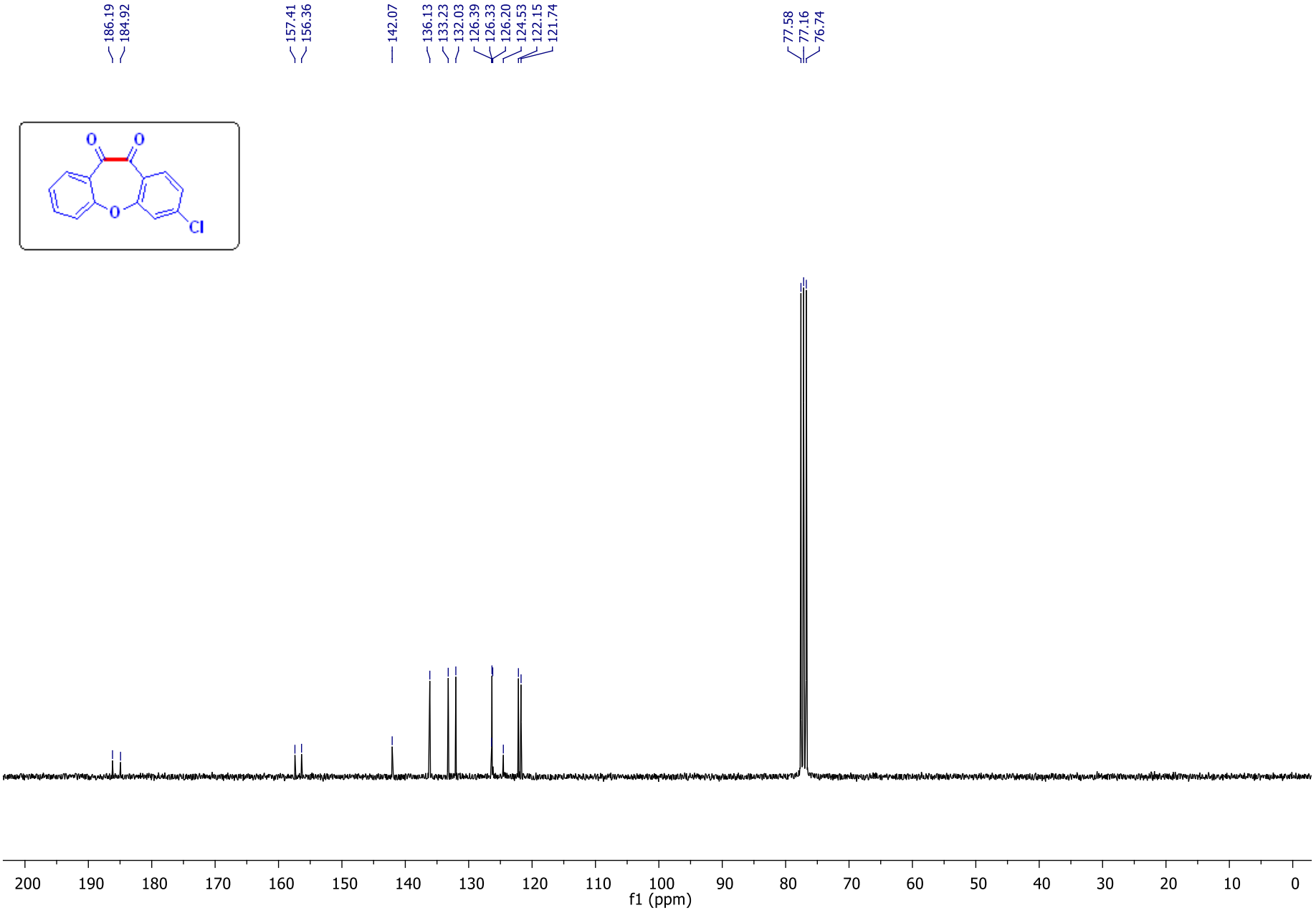
$^{13}C\{^{1}H\}$-NMR of 3m (101 MHz, $CDCl_3$)



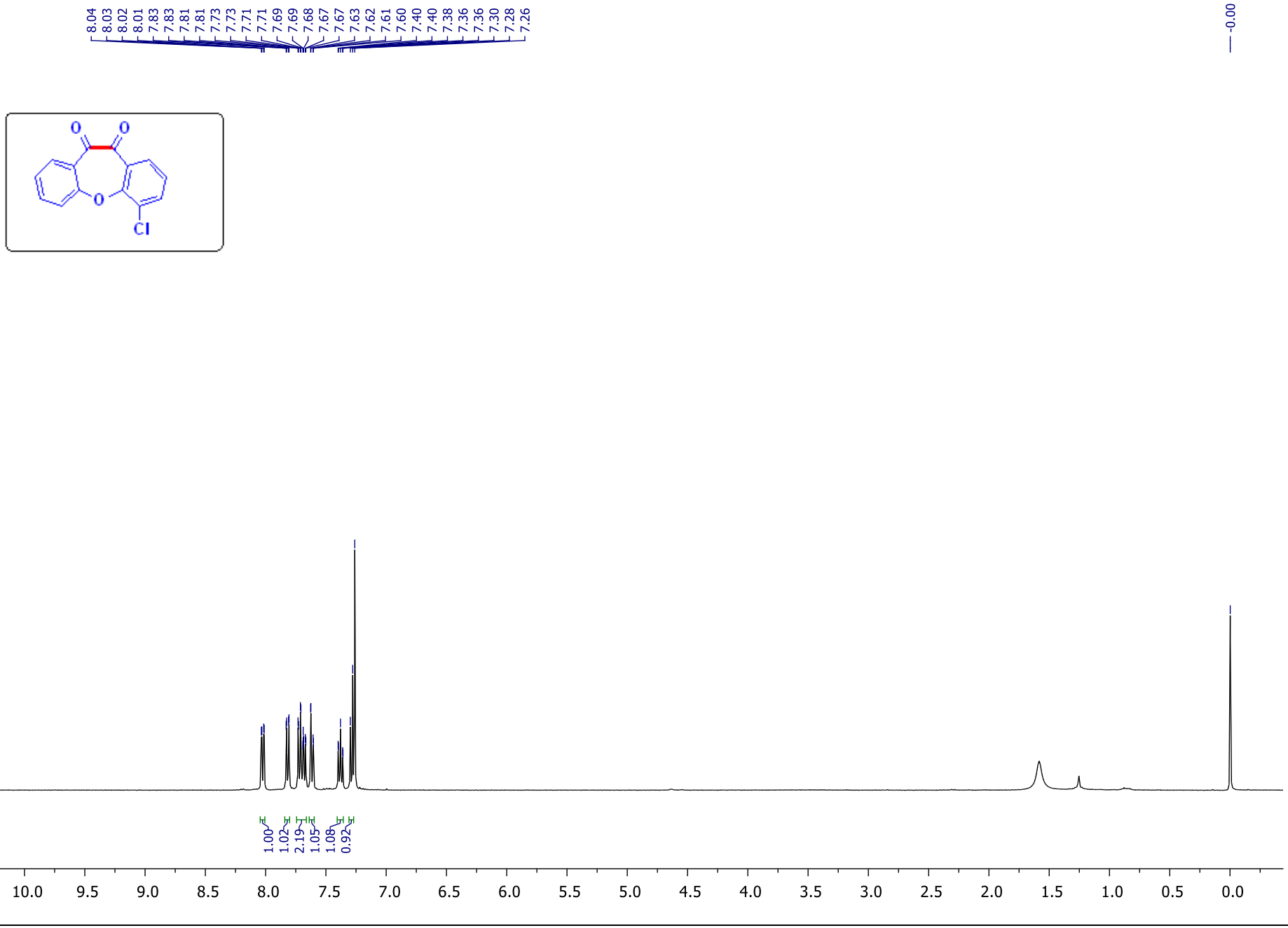
^{1}H-NMR of 3n (400 MHz, $CDCl_3$)



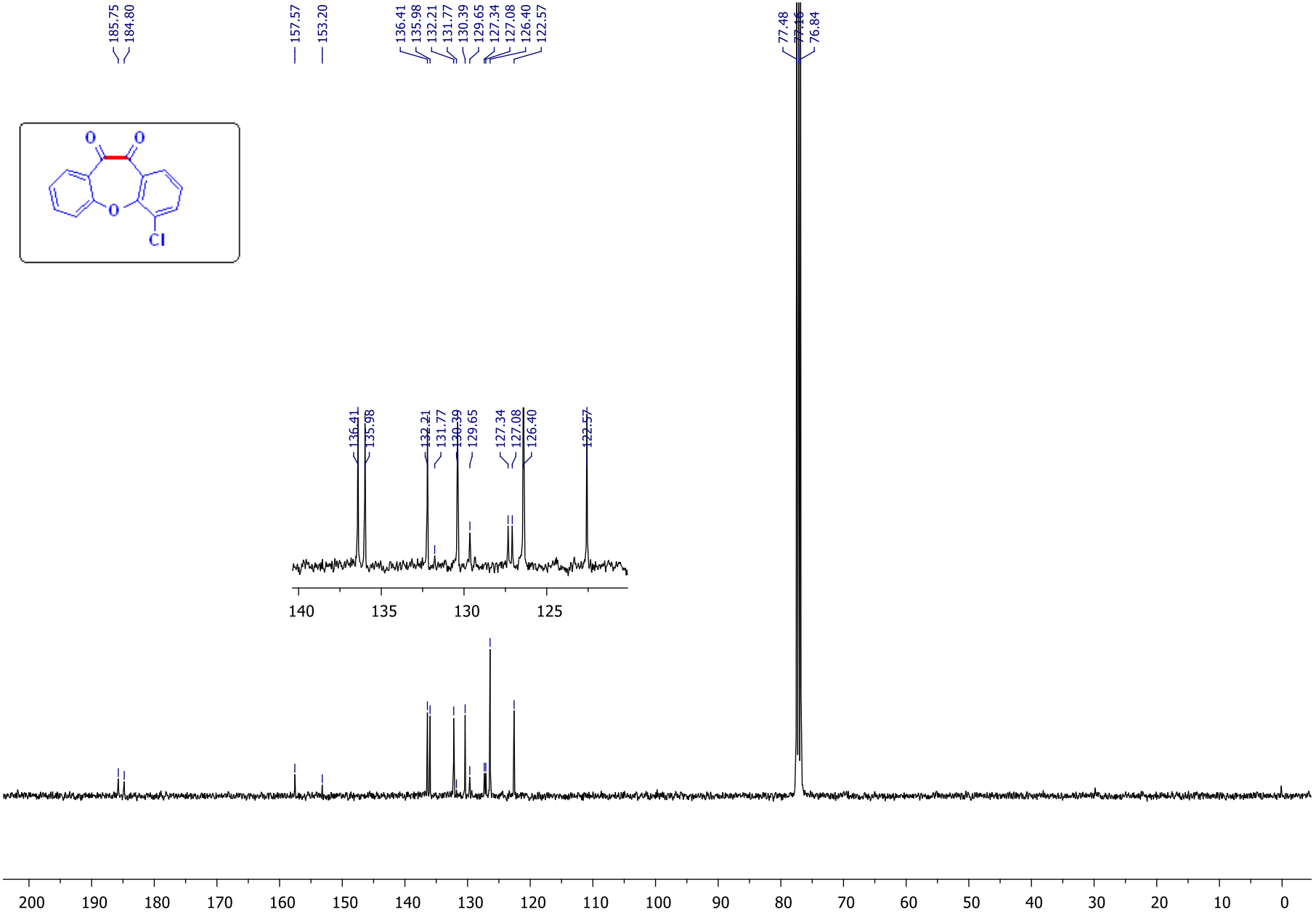
$^{13}C\{^{1}H\}$-NMR of 3n (75 MHz, $CDCl_3$)



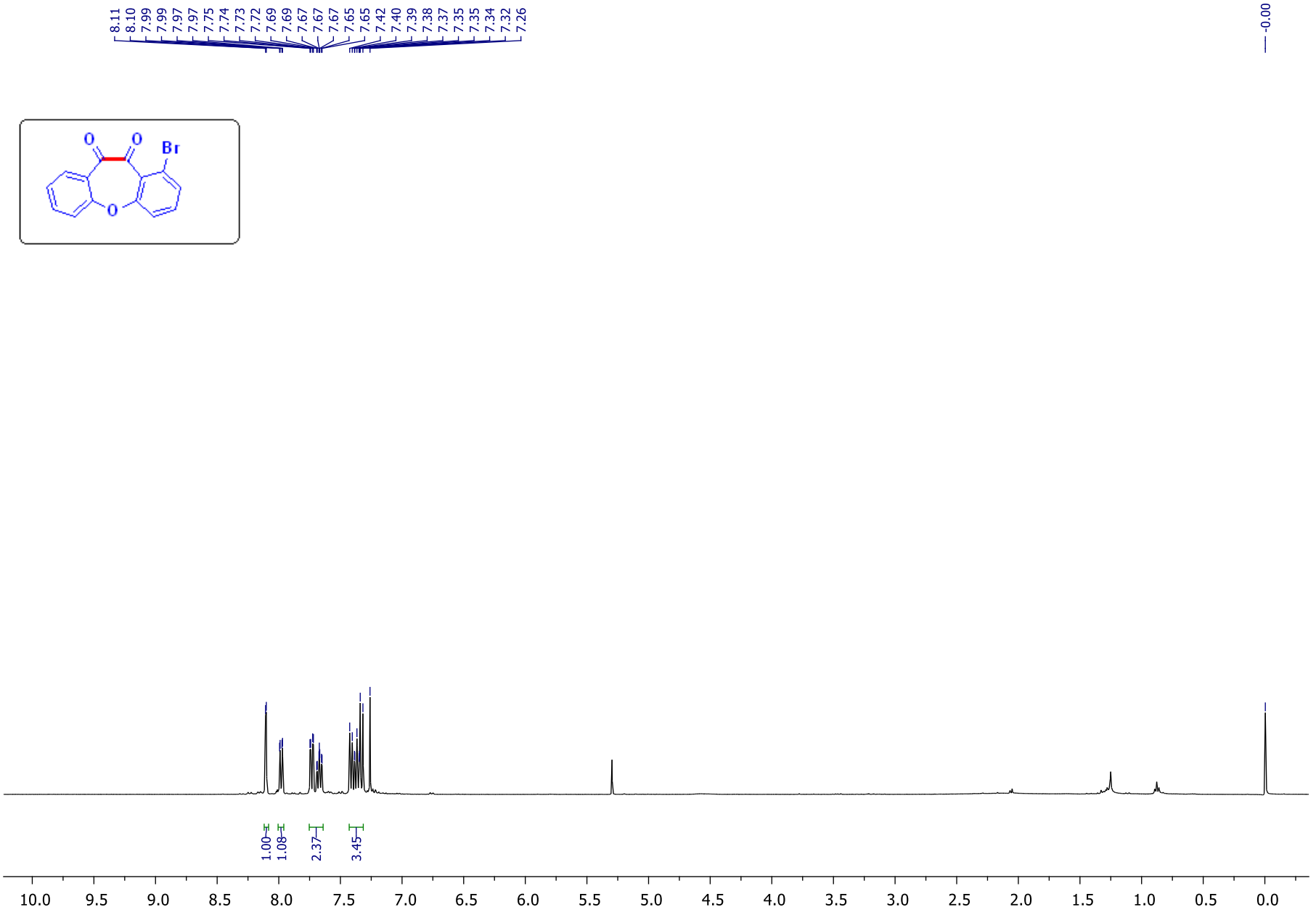
^{1}H-NMR of 3o (400 MHz, $CDCl_3$)



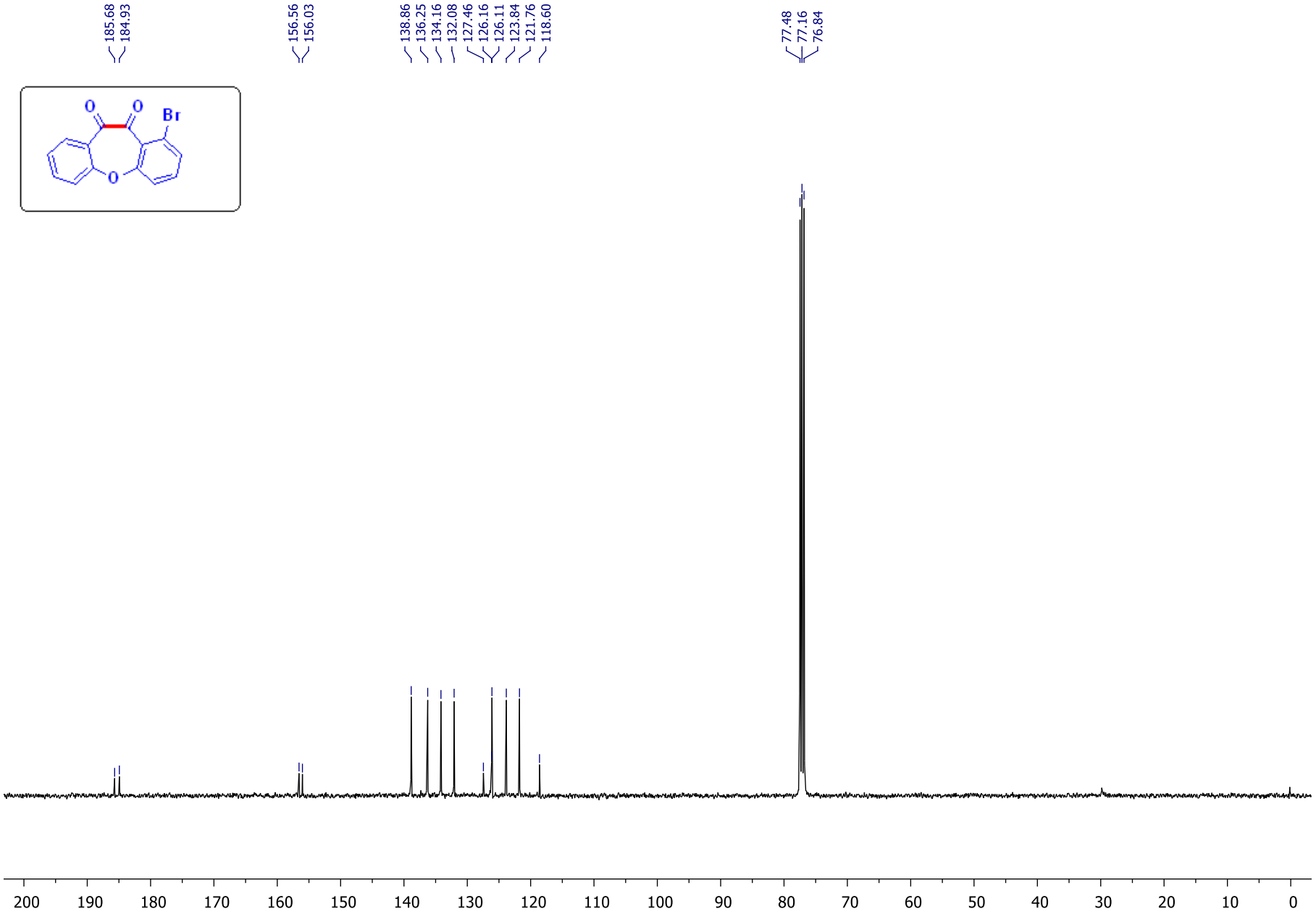
$^{13}C\{^{1}H\}$-NMR of 3o (126 MHz, $CDCl_3$)



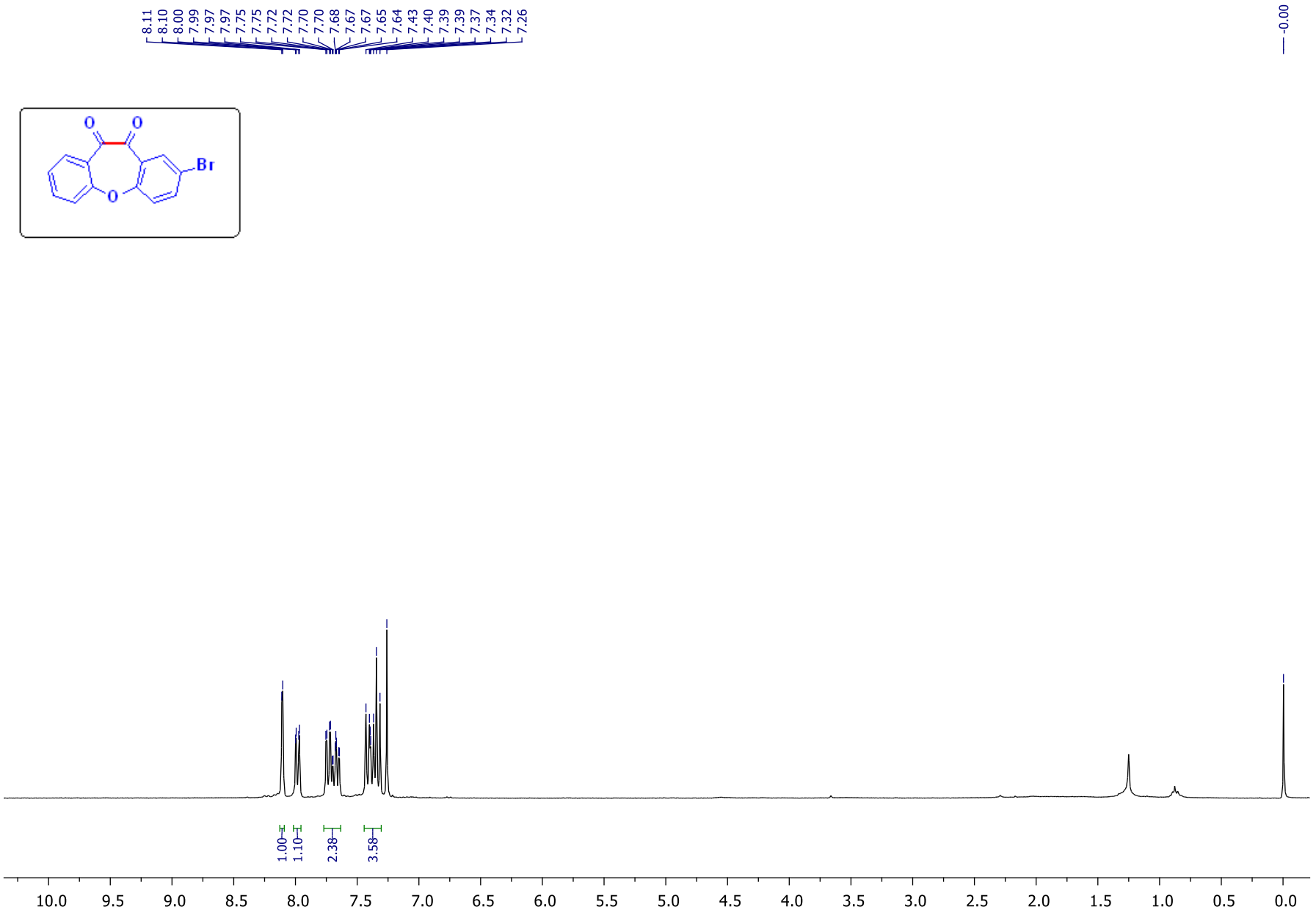
^{1}H-NMR of 3p (400 MHz, $CDCl_3$)



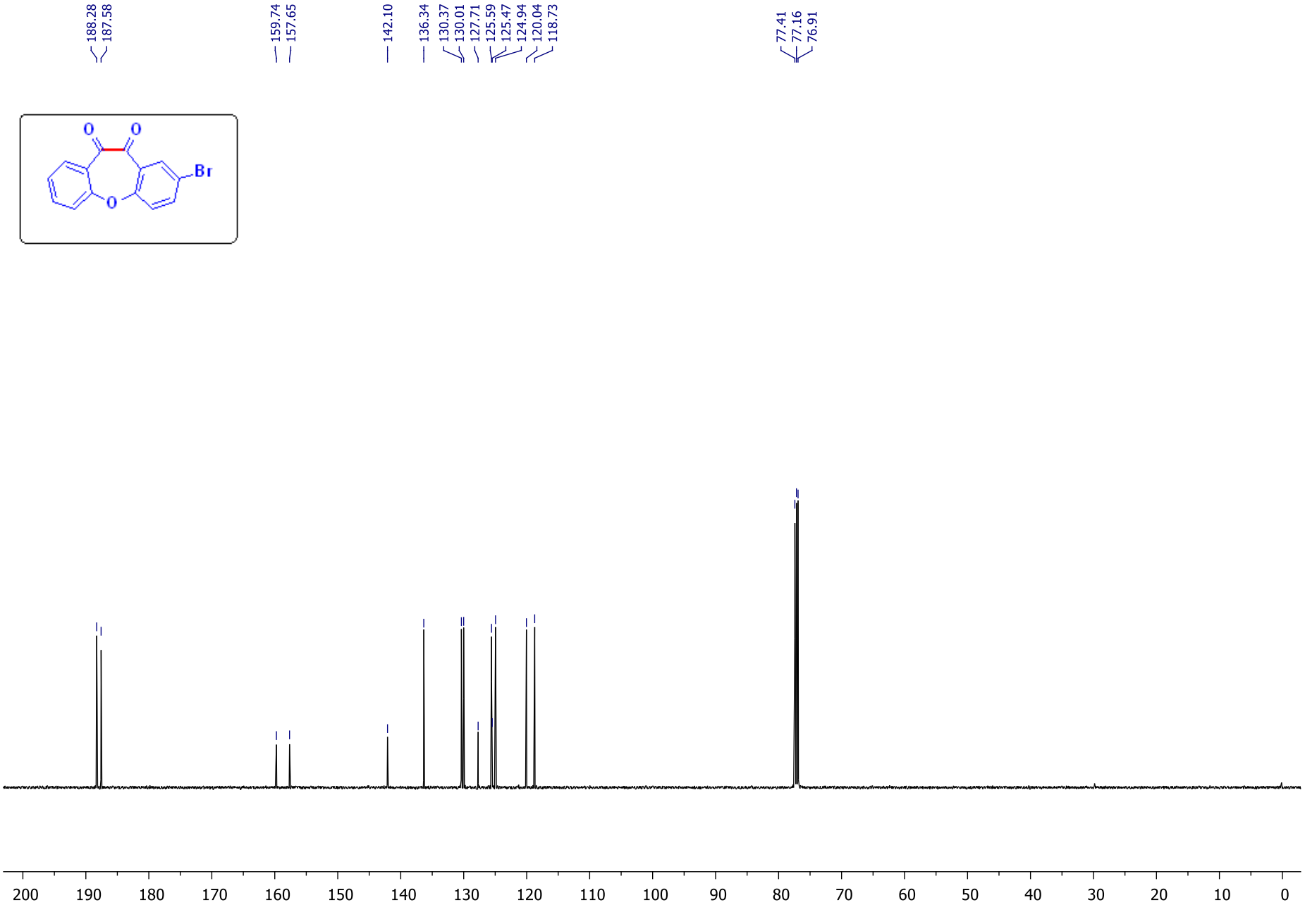
$^{13}C\{^{1}H\}$-NMR of 3p (126 MHz, $CDCl_3$)



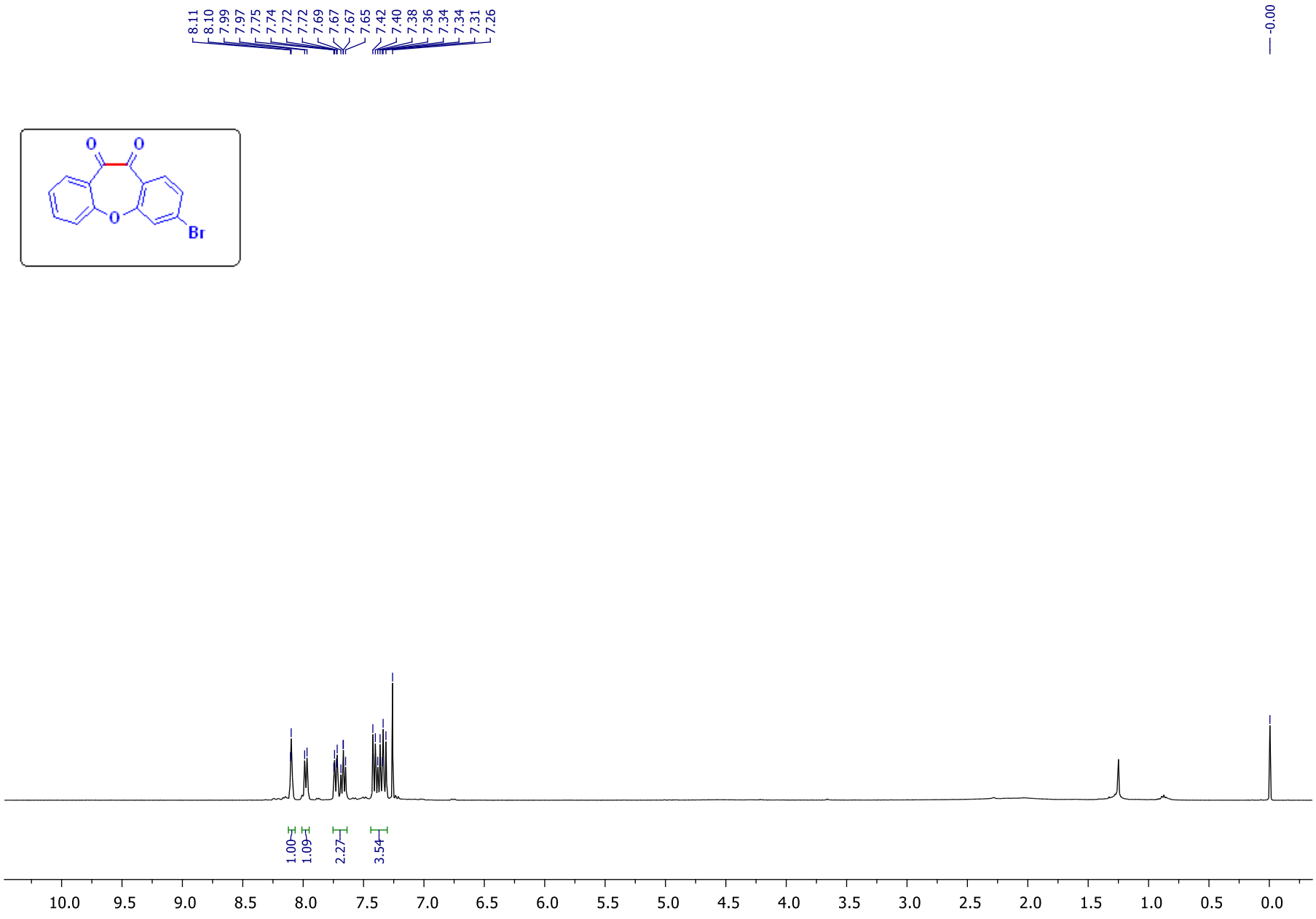
^{1}H-NMR of 3q (300 MHz, $CDCl_3$)



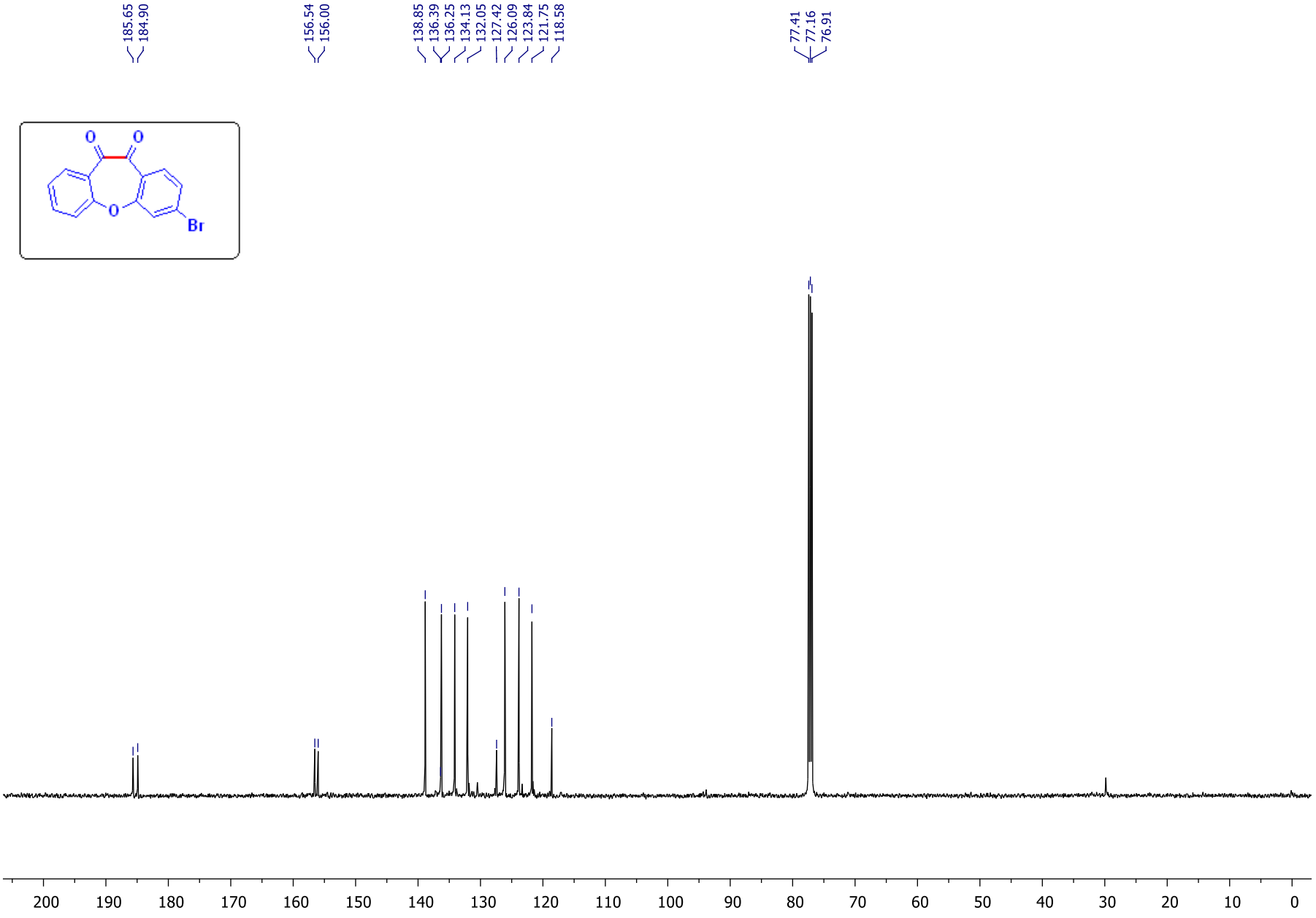
$^{13}C\{^{1}H\}$-NMR of 3q (126 MHz, $CDCl_3$)



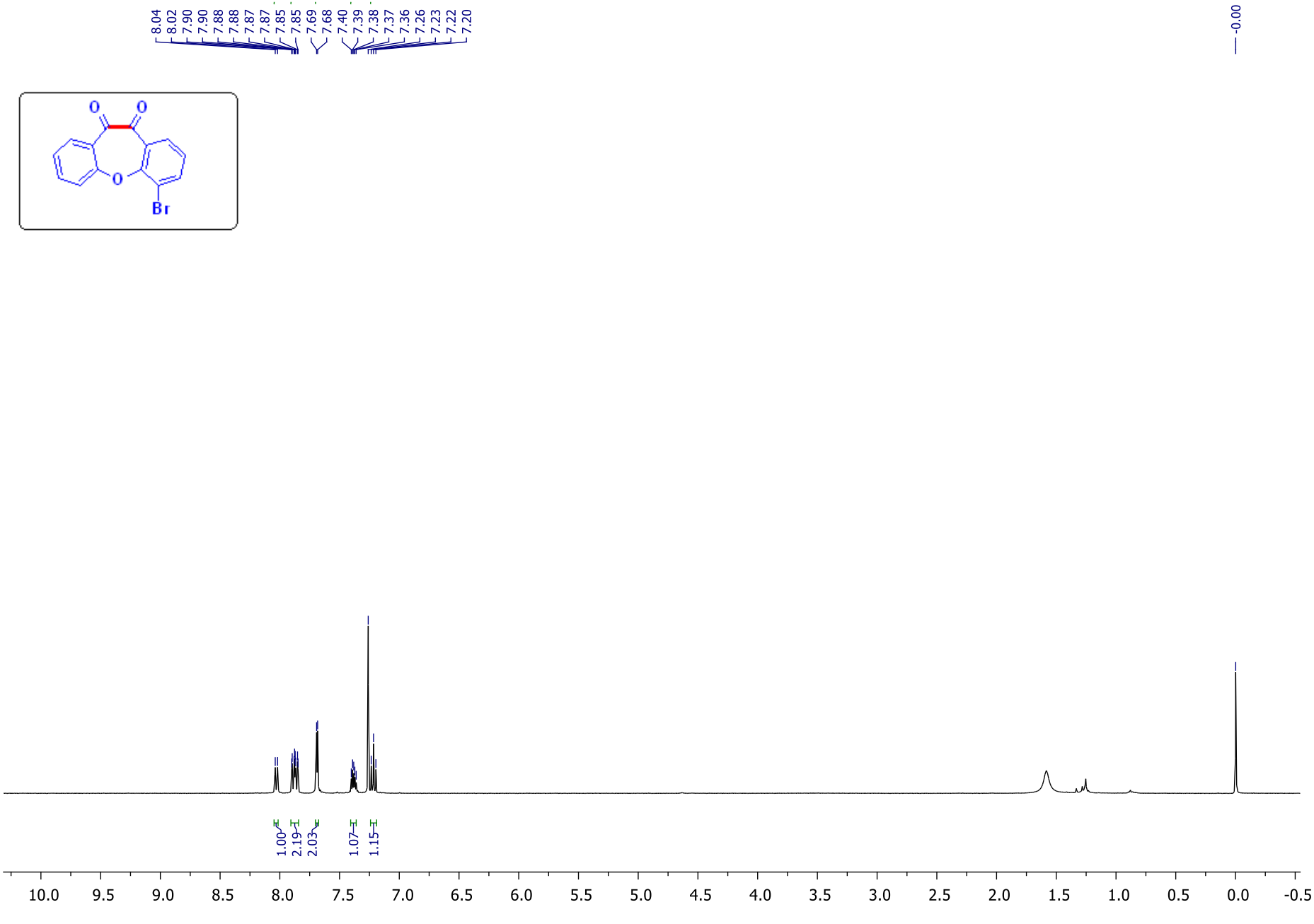
^{1}H-NMR of 3r (400 MHz, $CDCl_3$)



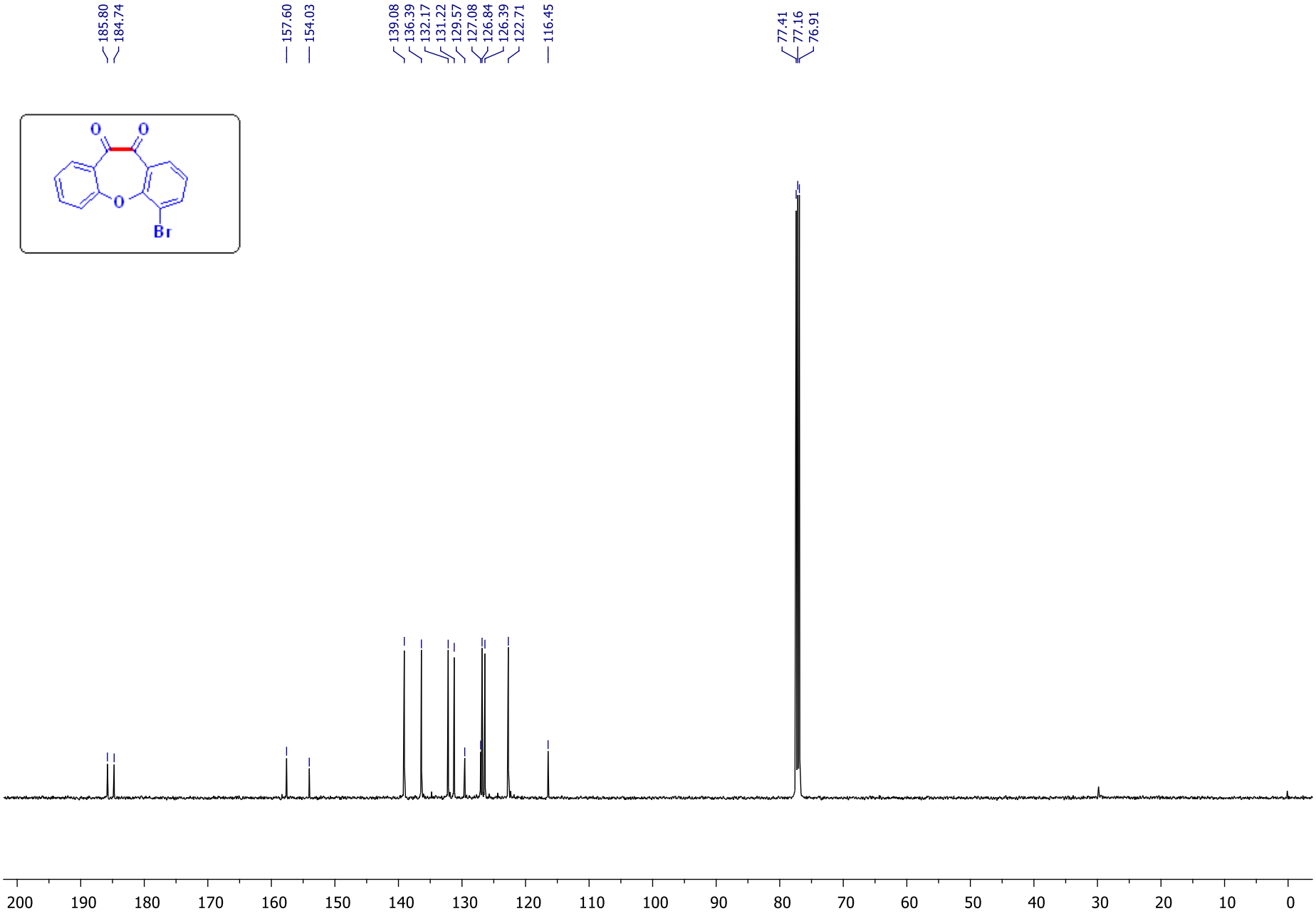
$^{13}C\{^{1}H\}$-NMR of 3r (126 MHz, $CDCl_3$)



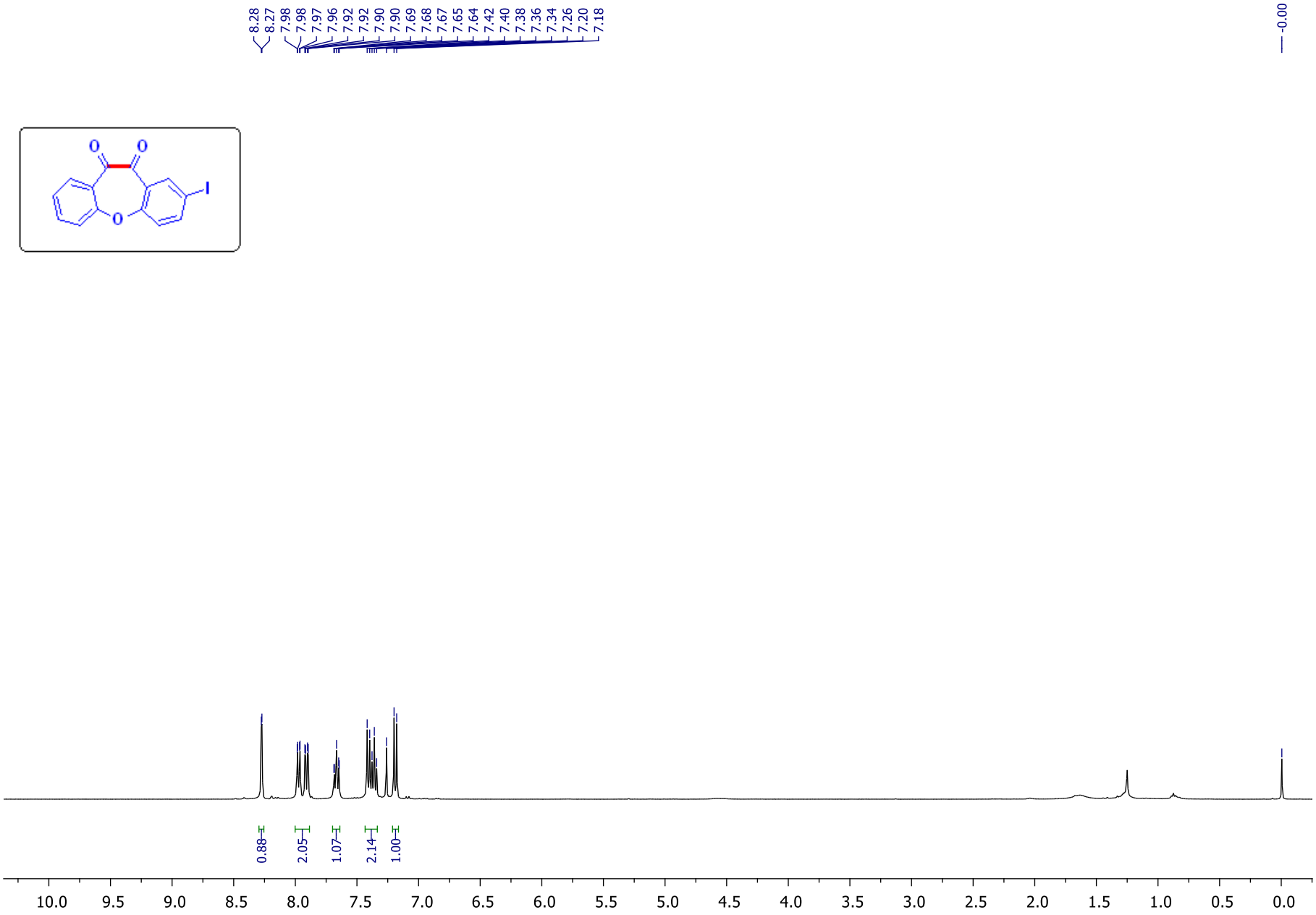
^{1}H-NMR of 3s (400 MHz, $CDCl_3$)



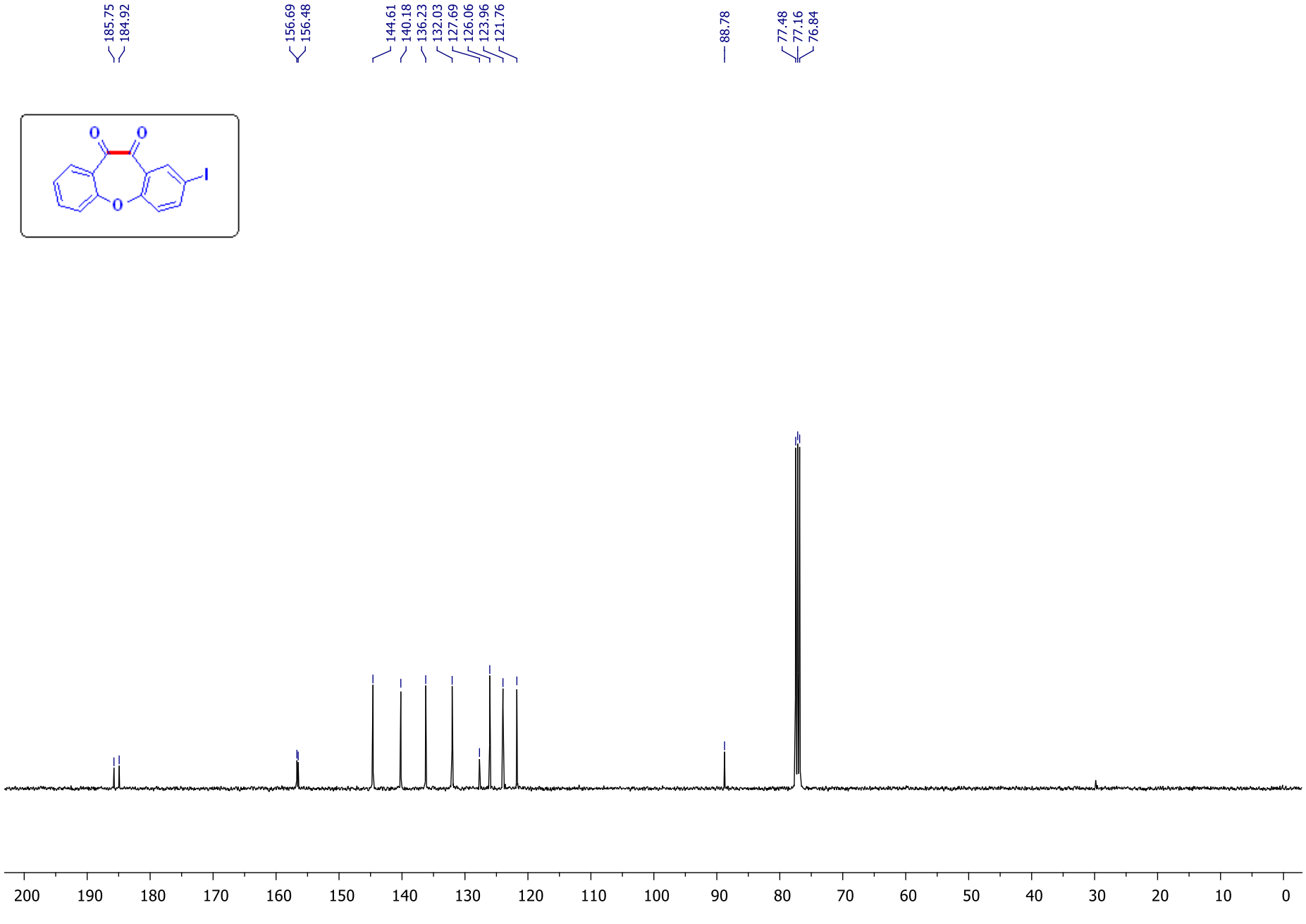
$^{13}C\{^{1}H\}$-NMR of 3s (126 MHz, $CDCl_3$)



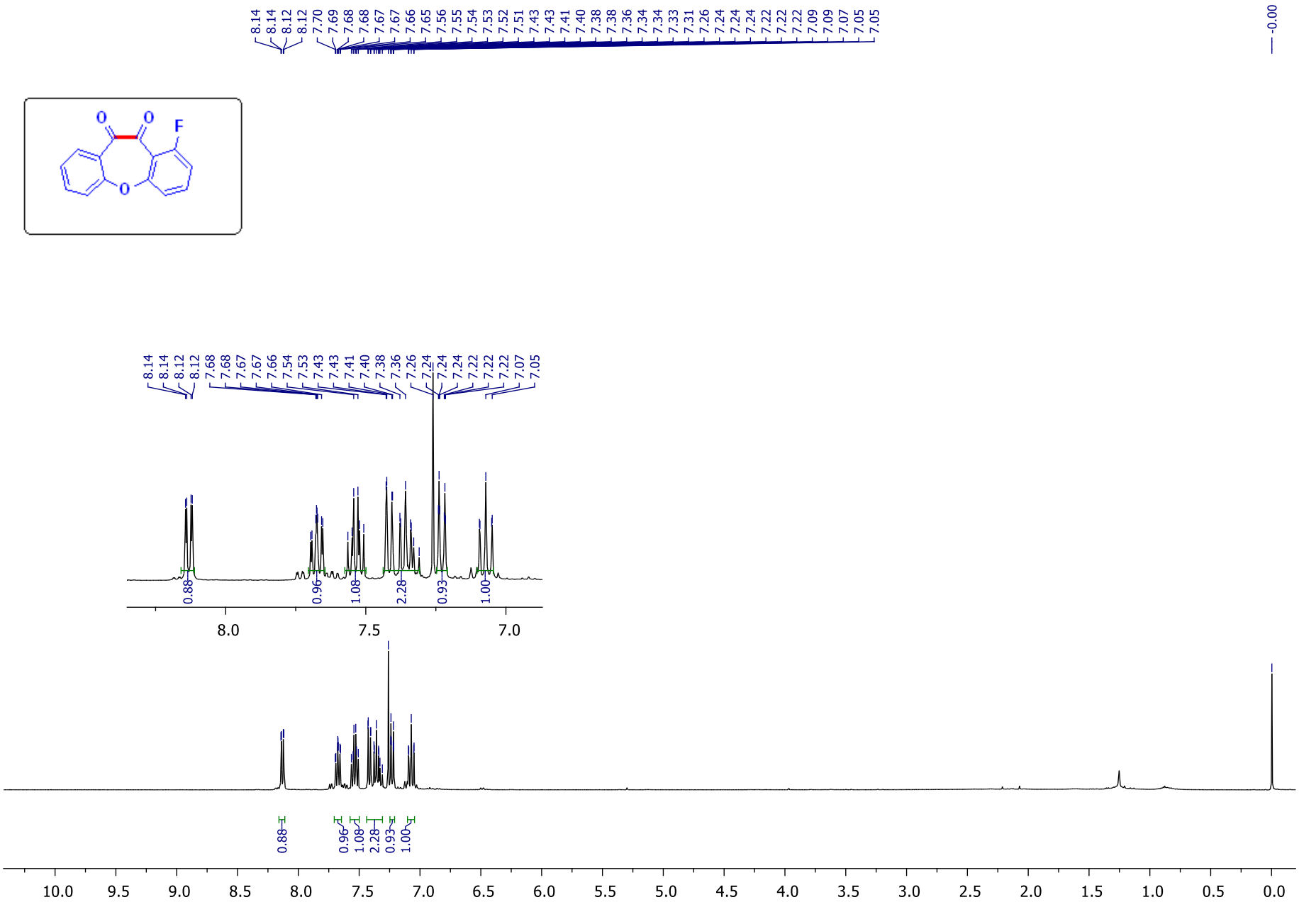
^{1}H-NMR of 3t (400 MHz, $CDCl_3$)



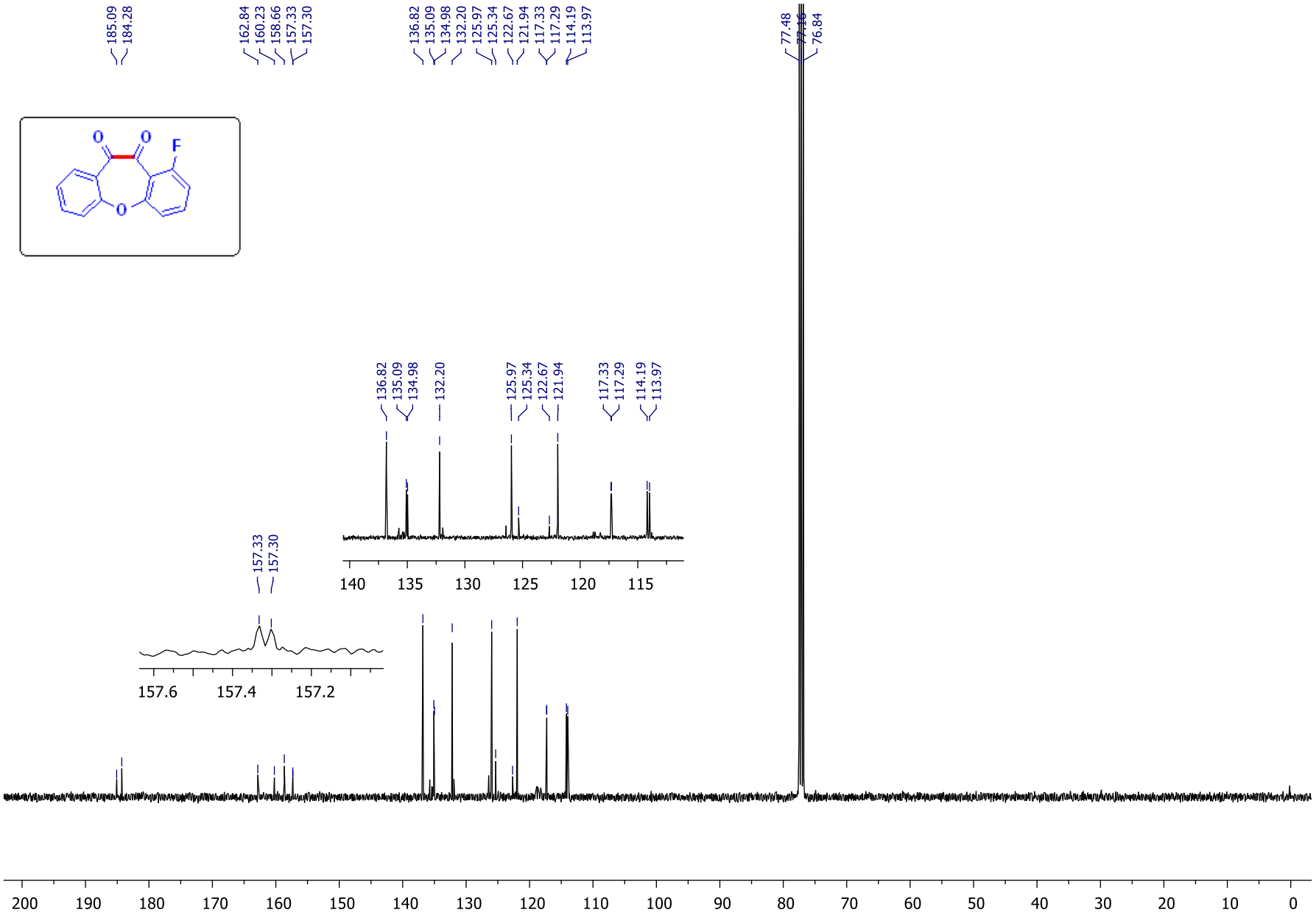
$^{13}C\{^{1}H\}$-NMR of 3t (101 MHz, $CDCl_3$)



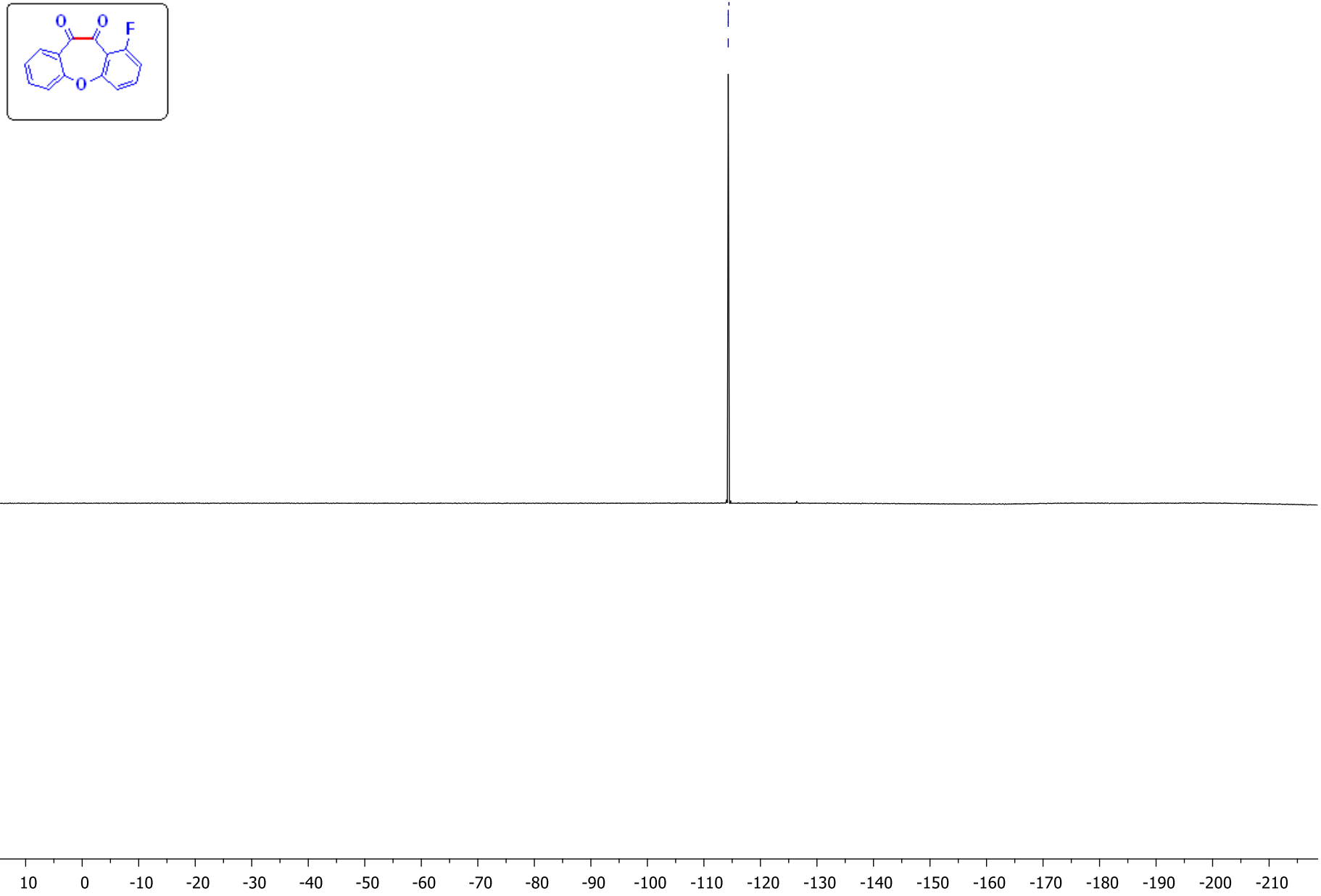
^{1}H-NMR of 3u (400 MHz, $CDCl_3$)



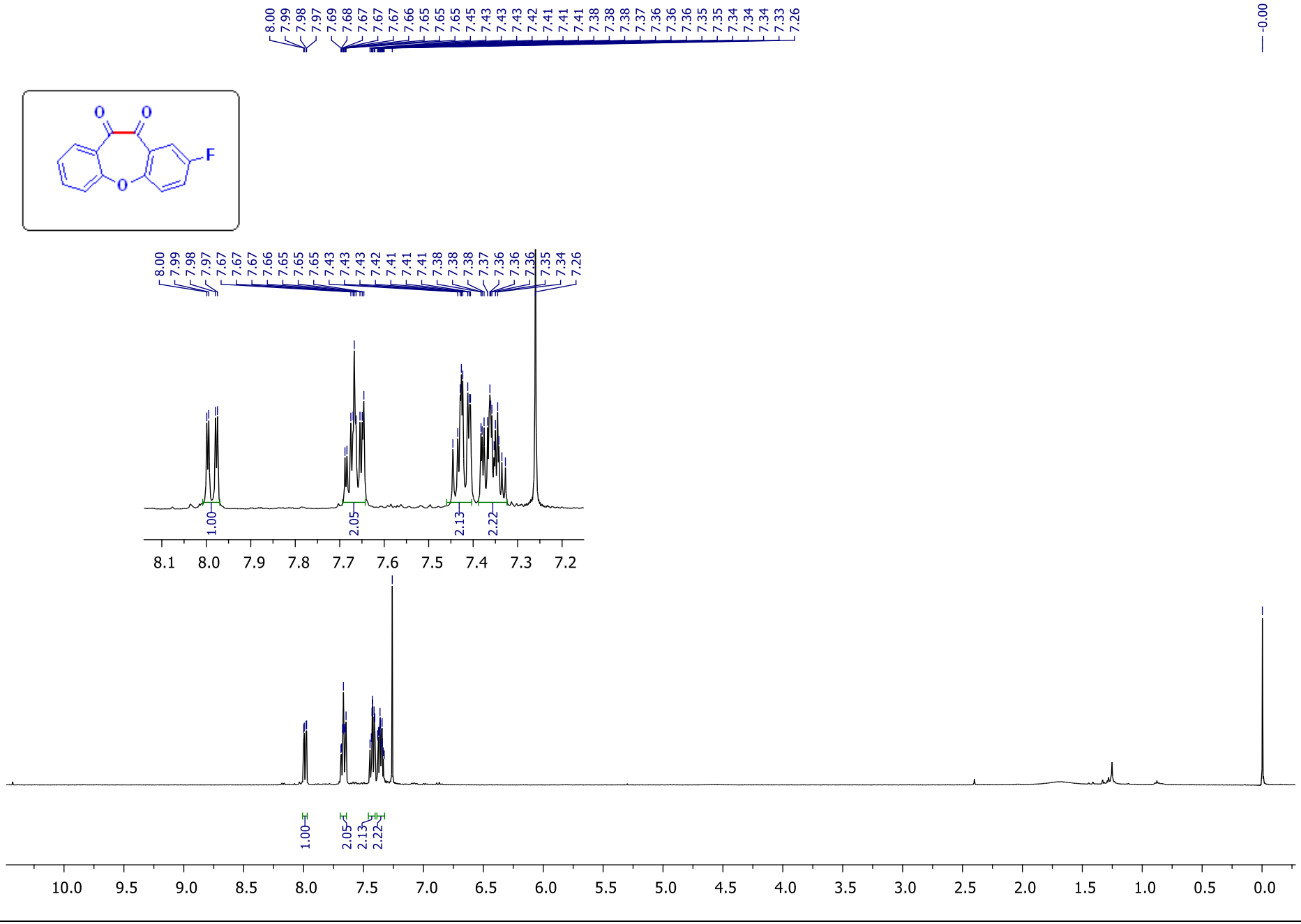
$^{13}C\{^{1}H\}$-NMR of 3u (101 MHz, $CDCl_3$)



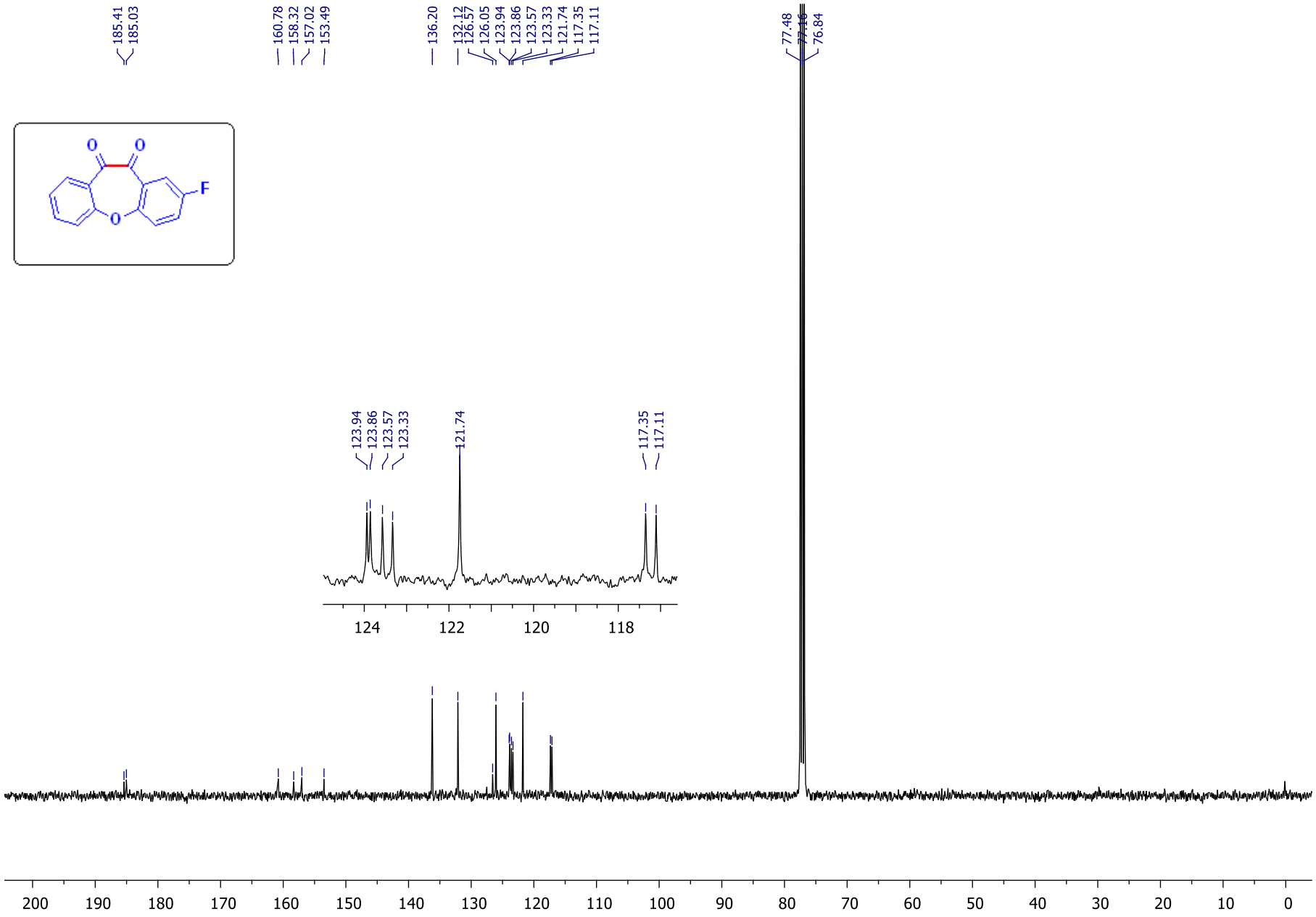
^{19}F-NMR of 3u (377 MHz, $CDCl_3$)



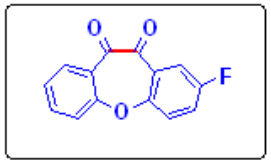
^{1}H-NMR of 3v (400 MHz, $CDCl_3$)



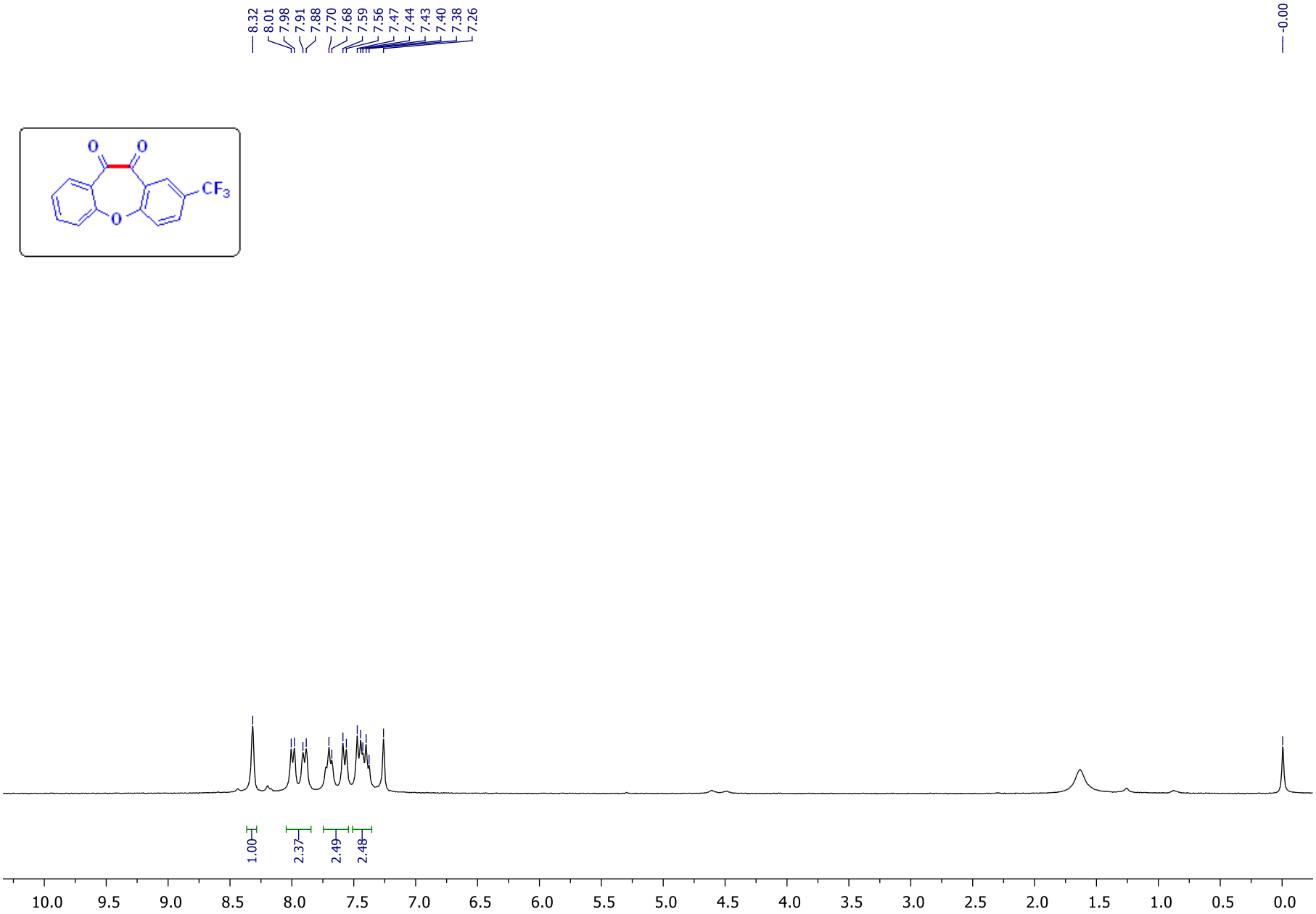
$^{13}C\{^{1}H\}$-NMR of 3v (101 MHz, $CDCl_3$)



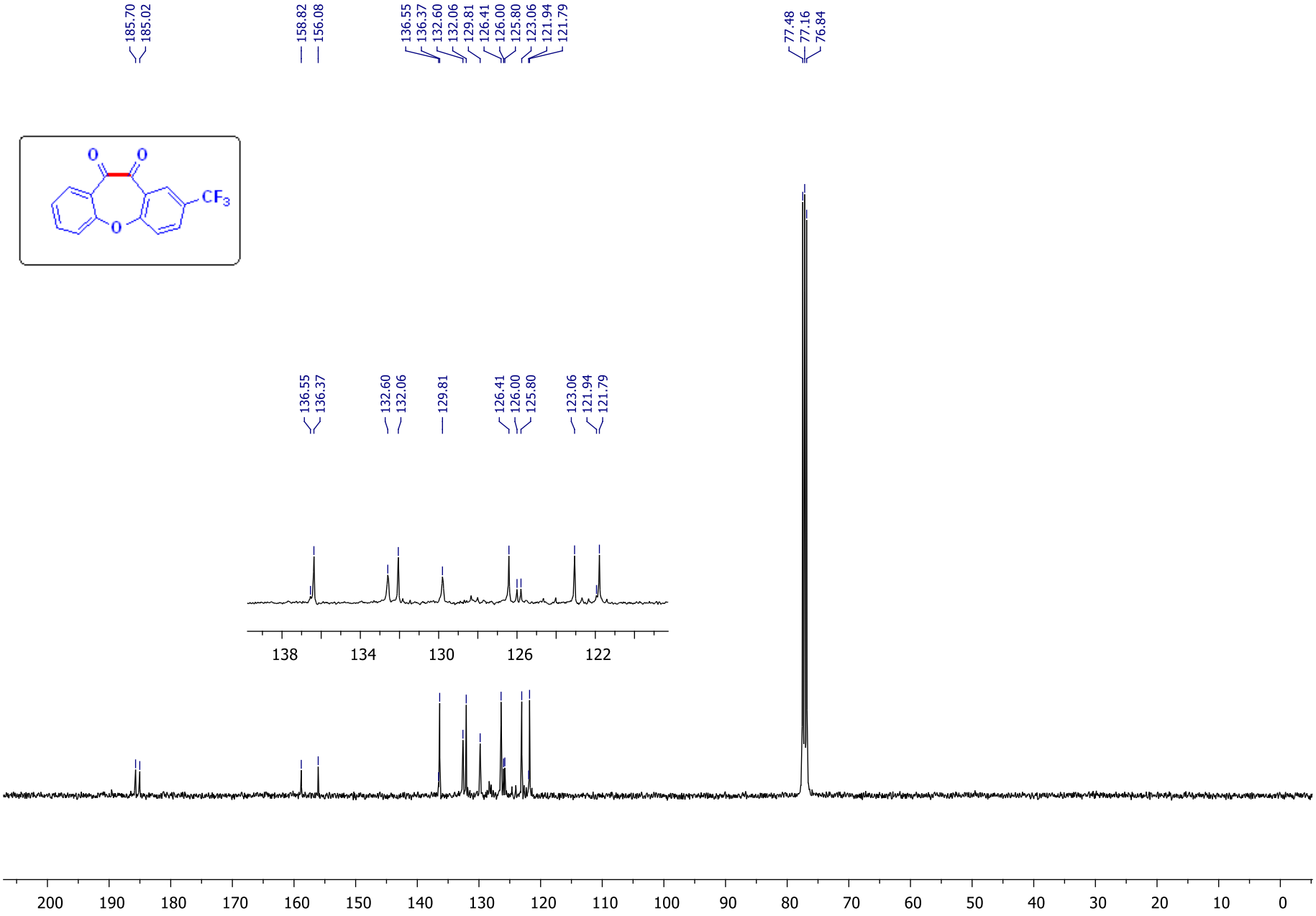
^{19}F-NMR of 3v (377 MHz, $CDCl_3$)



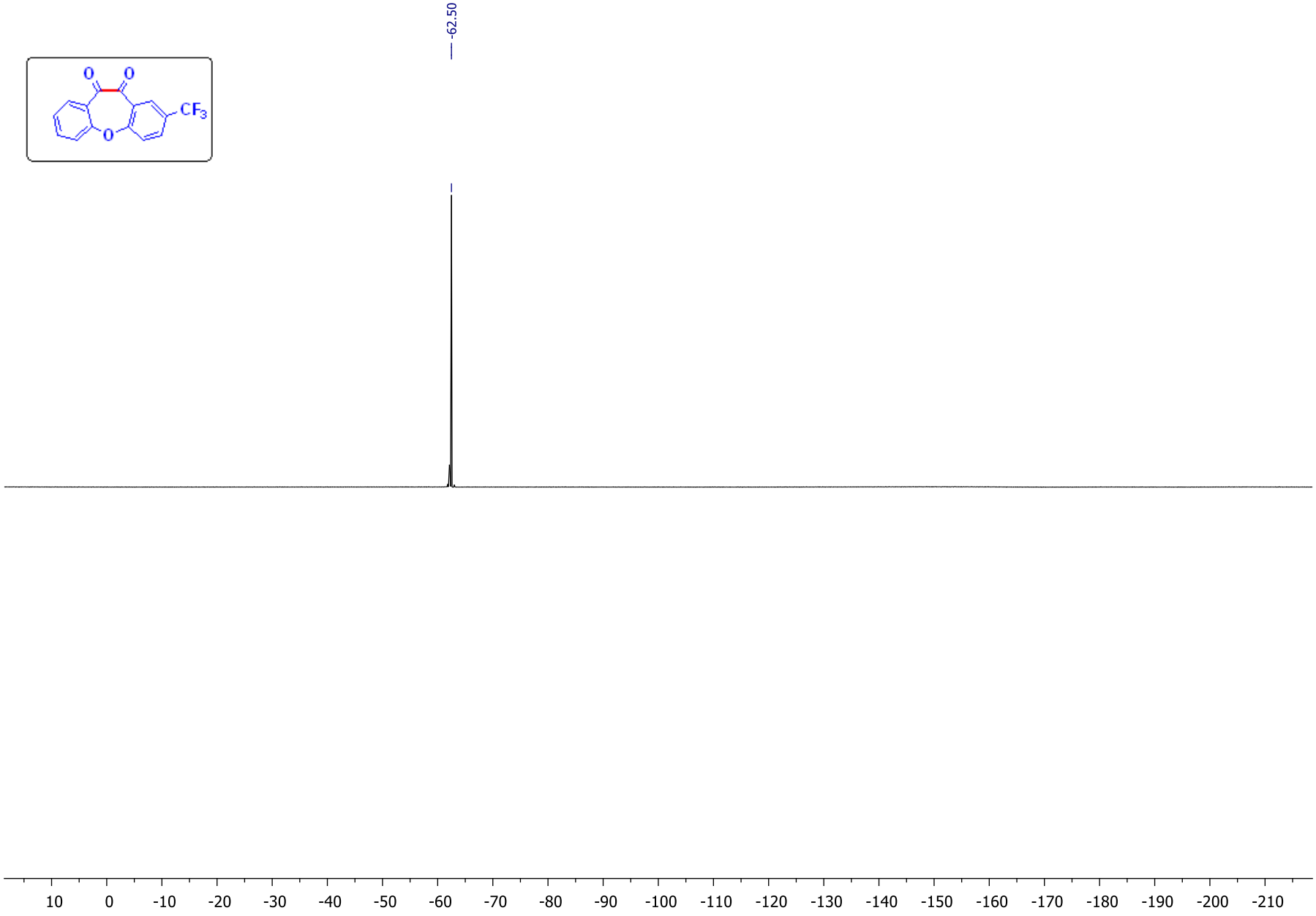
^{1}H-NMR of 3w (300 MHz, $CDCl_3$)



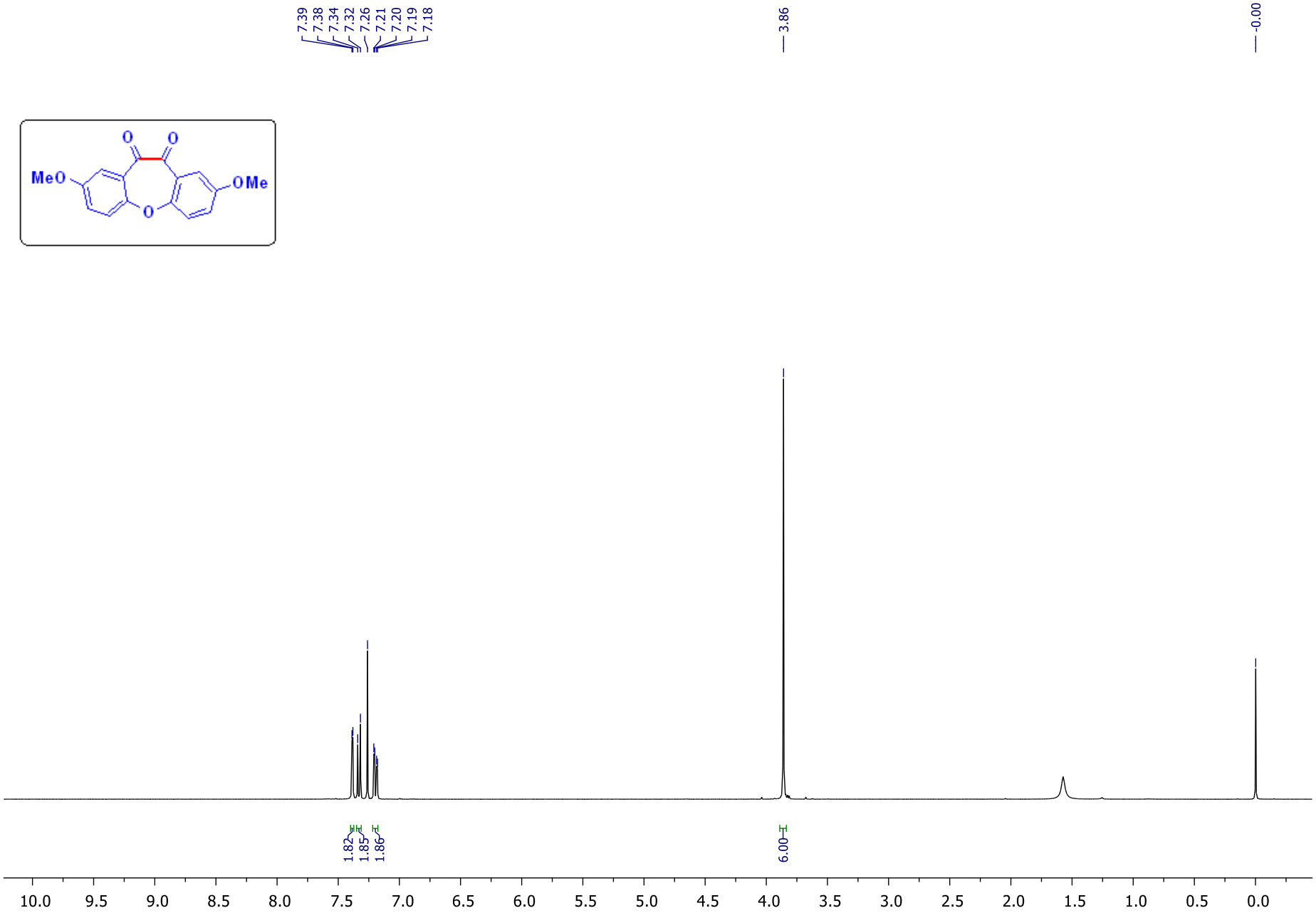
$^{13}C\{^{1}H\}$-NMR of 3w (101 MHz, $CDCl_3$)



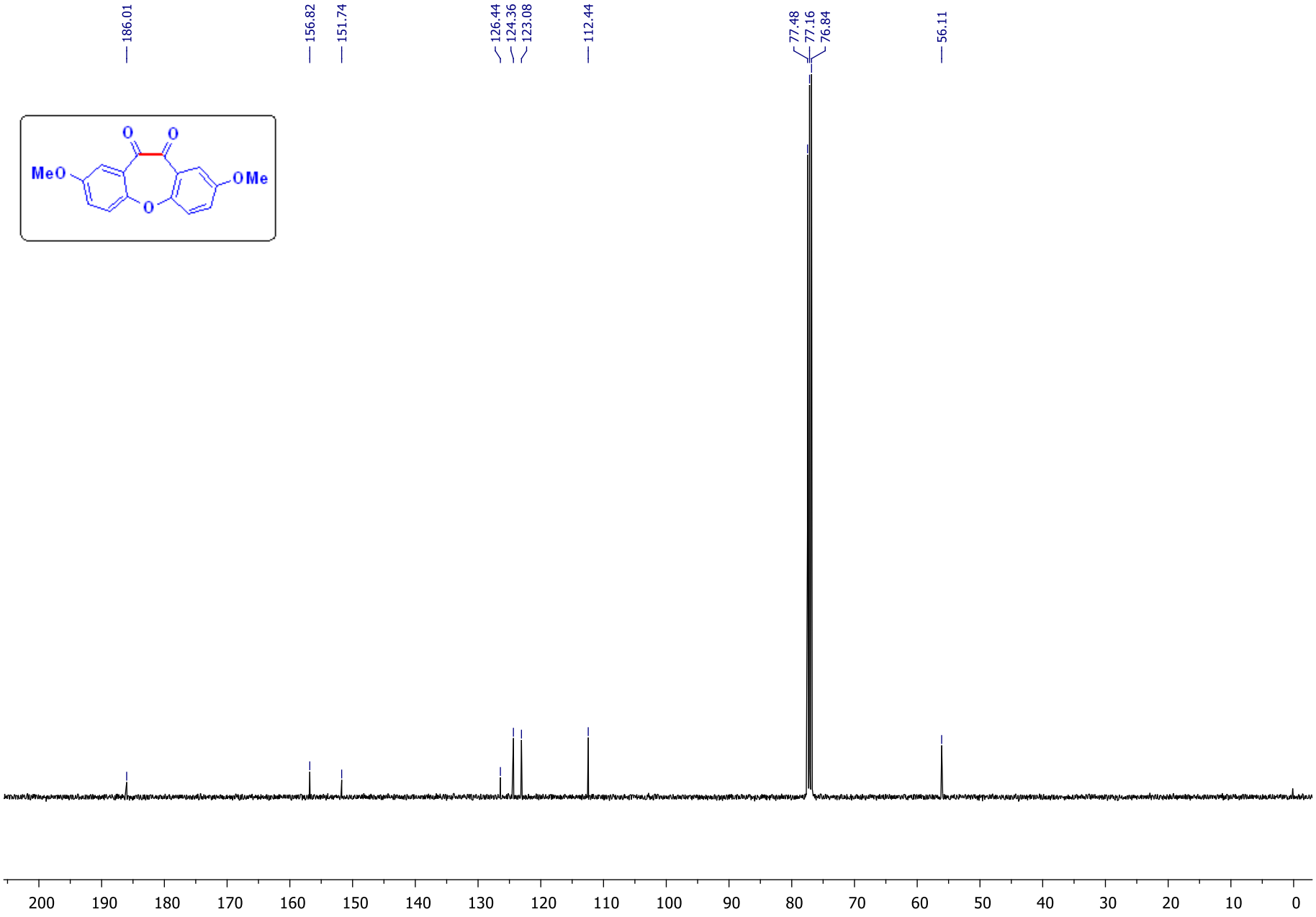
^{19}F-NMR of 3w (377 MHz, $CDCl_3$)



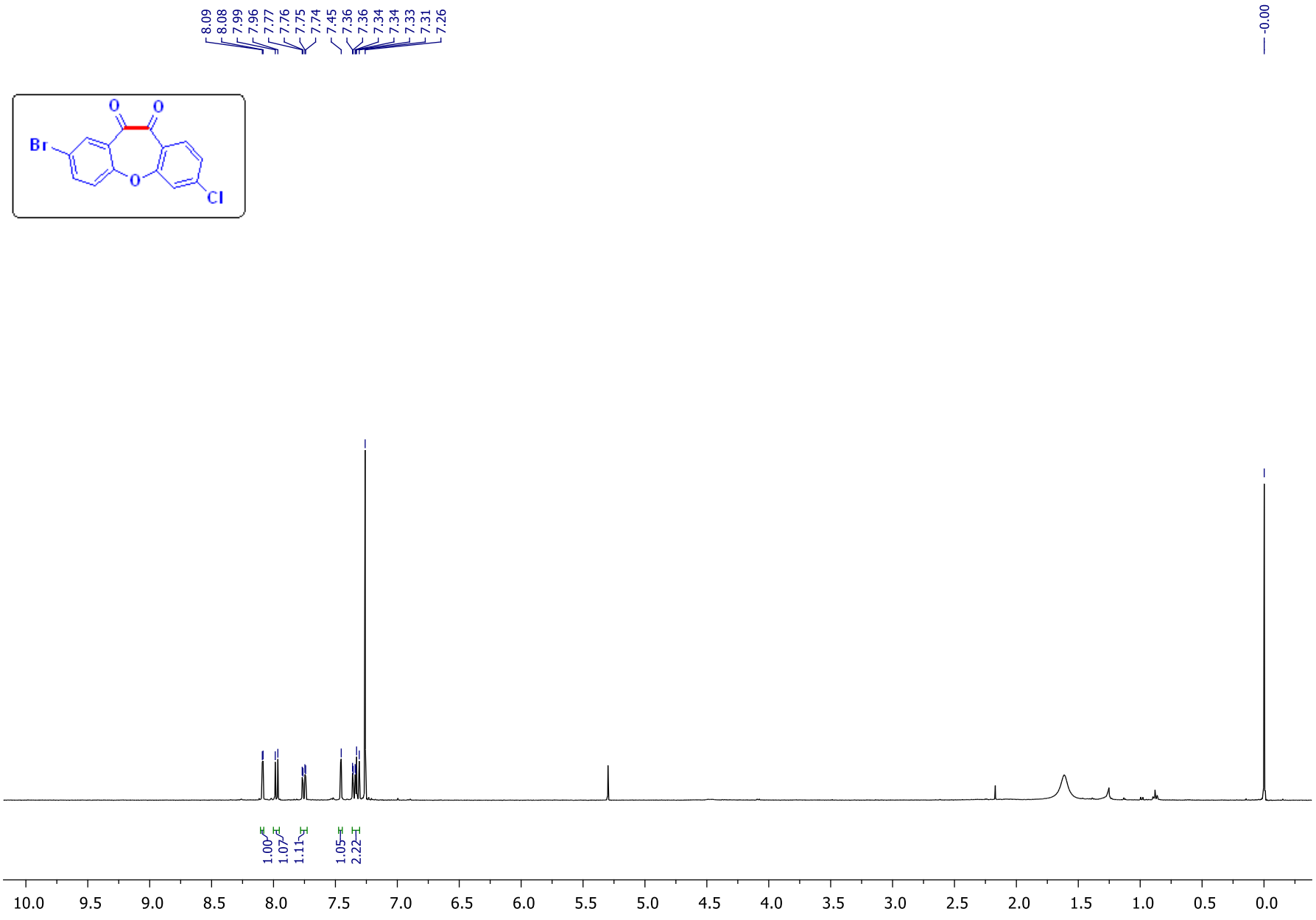
^{1}H-NMR of 3x (400 MHz, $CDCl_3$)



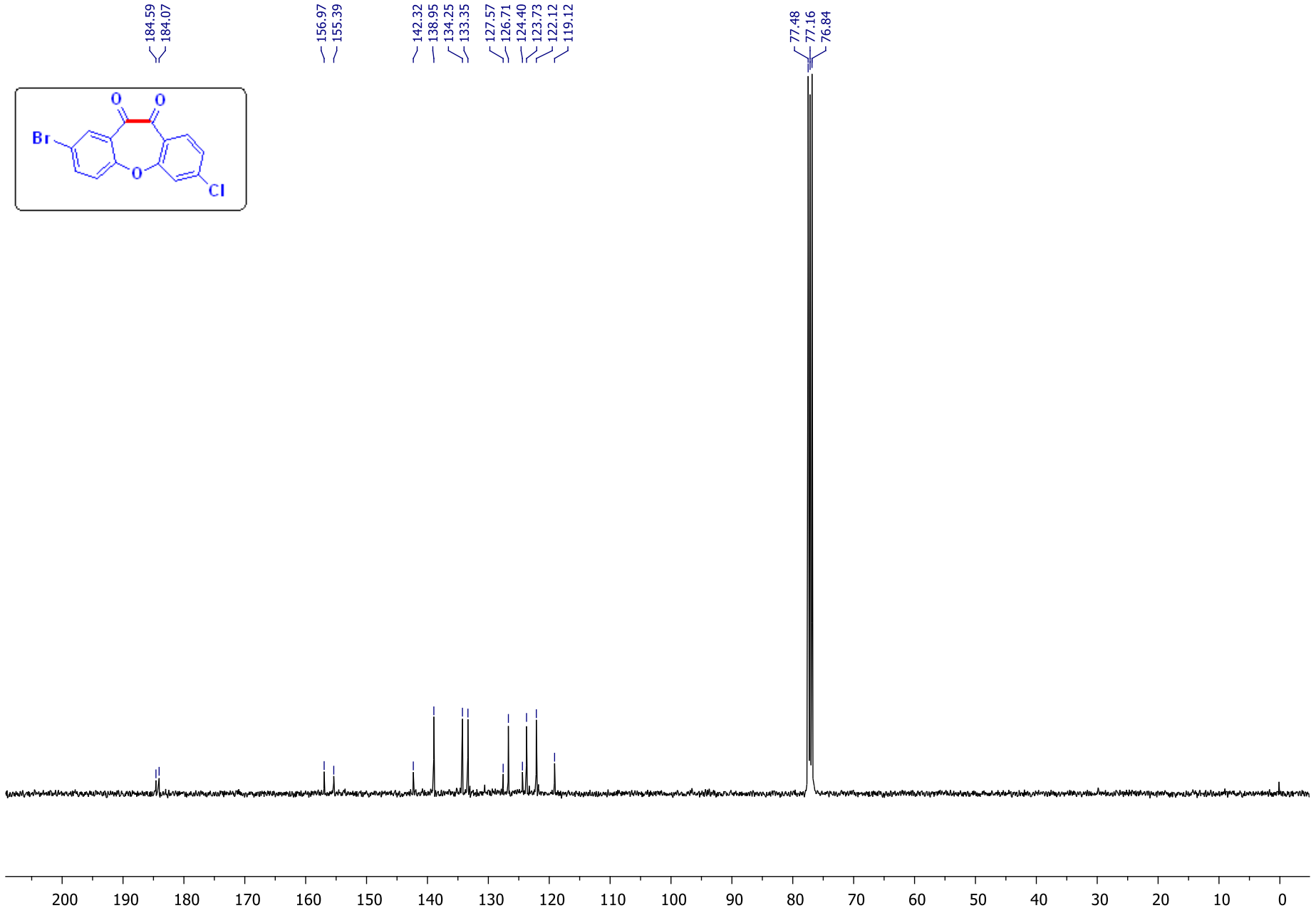
$^{13}C\{^{1}H\}$-NMR of 3x (101 MHz, $CDCl_3$)



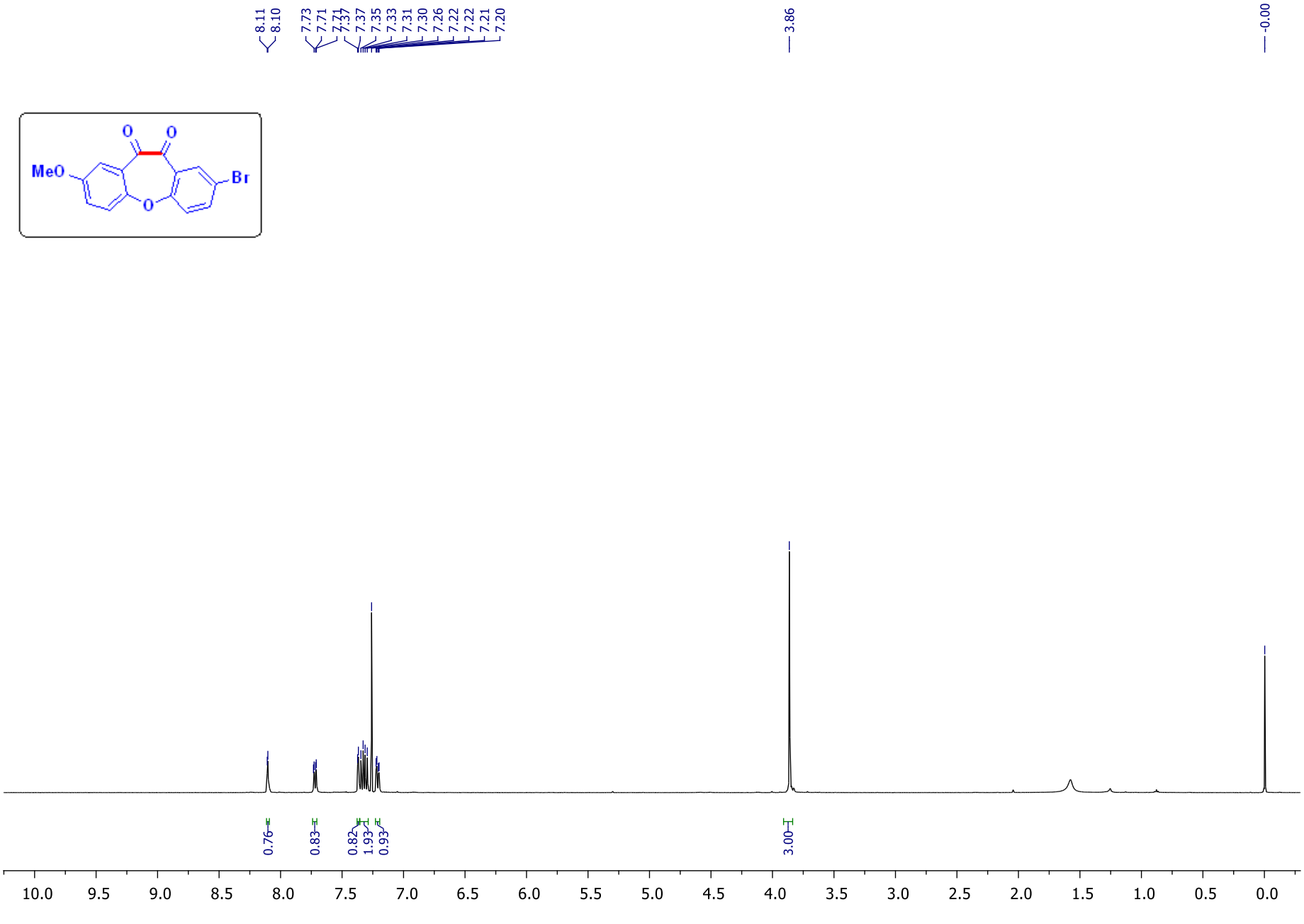
^{1}H-NMR of 3y (400 MHz, $CDCl_3$)



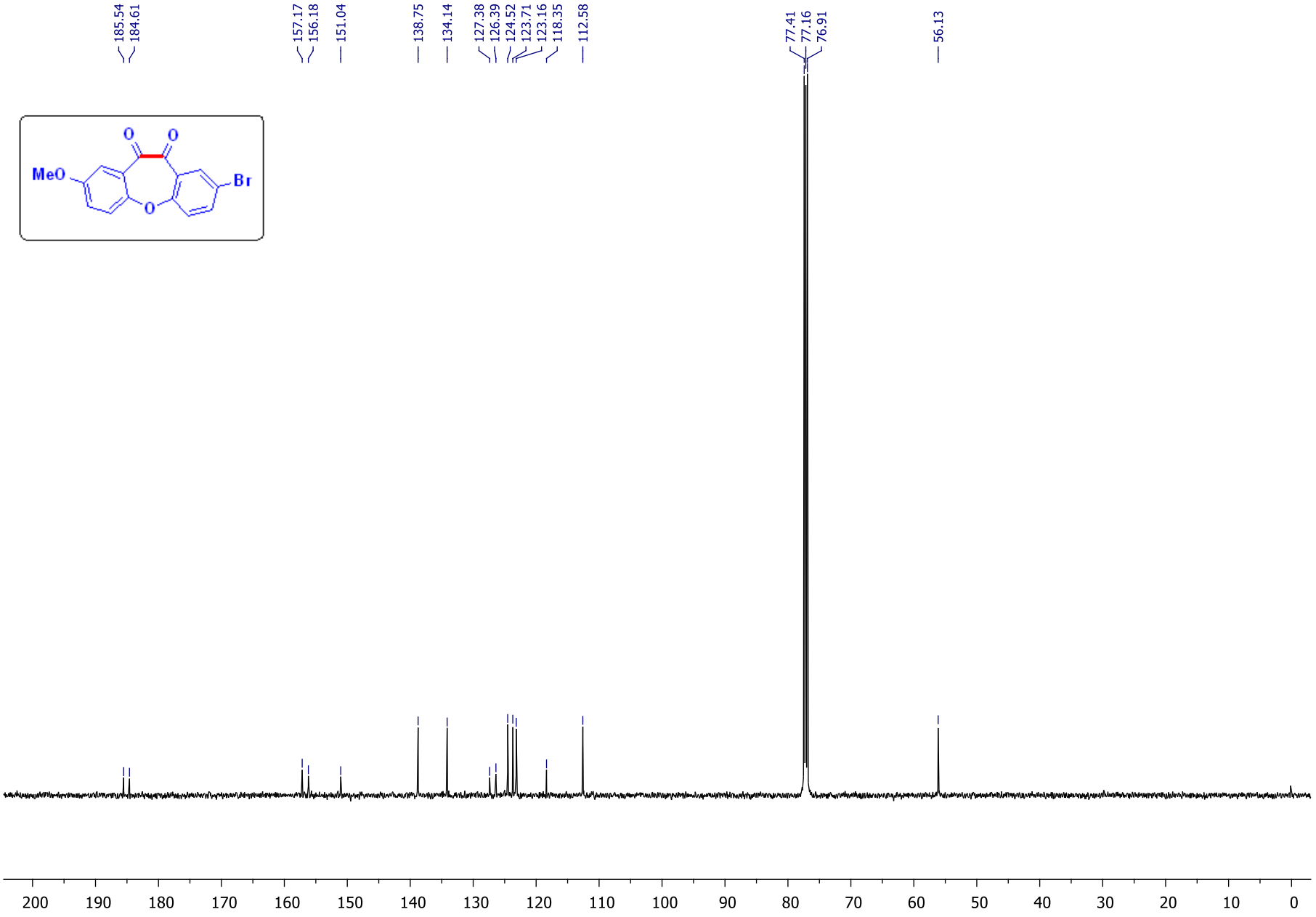
$^{13}C\{^{1}H\}$-NMR of 3y (101 MHz, $CDCl_3$)



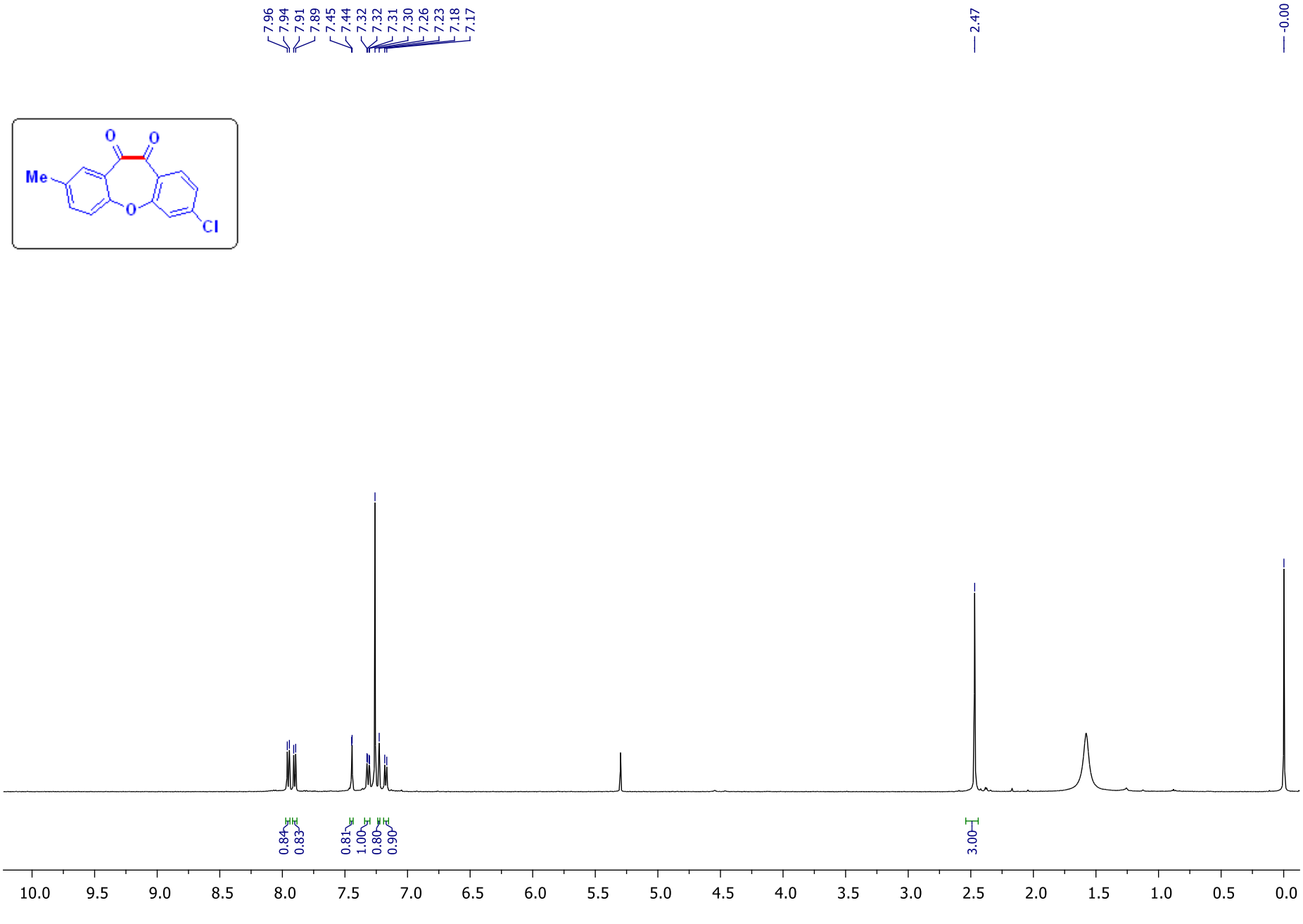
^{1}H-NMR of 3z (500 MHz, $CDCl_3$)



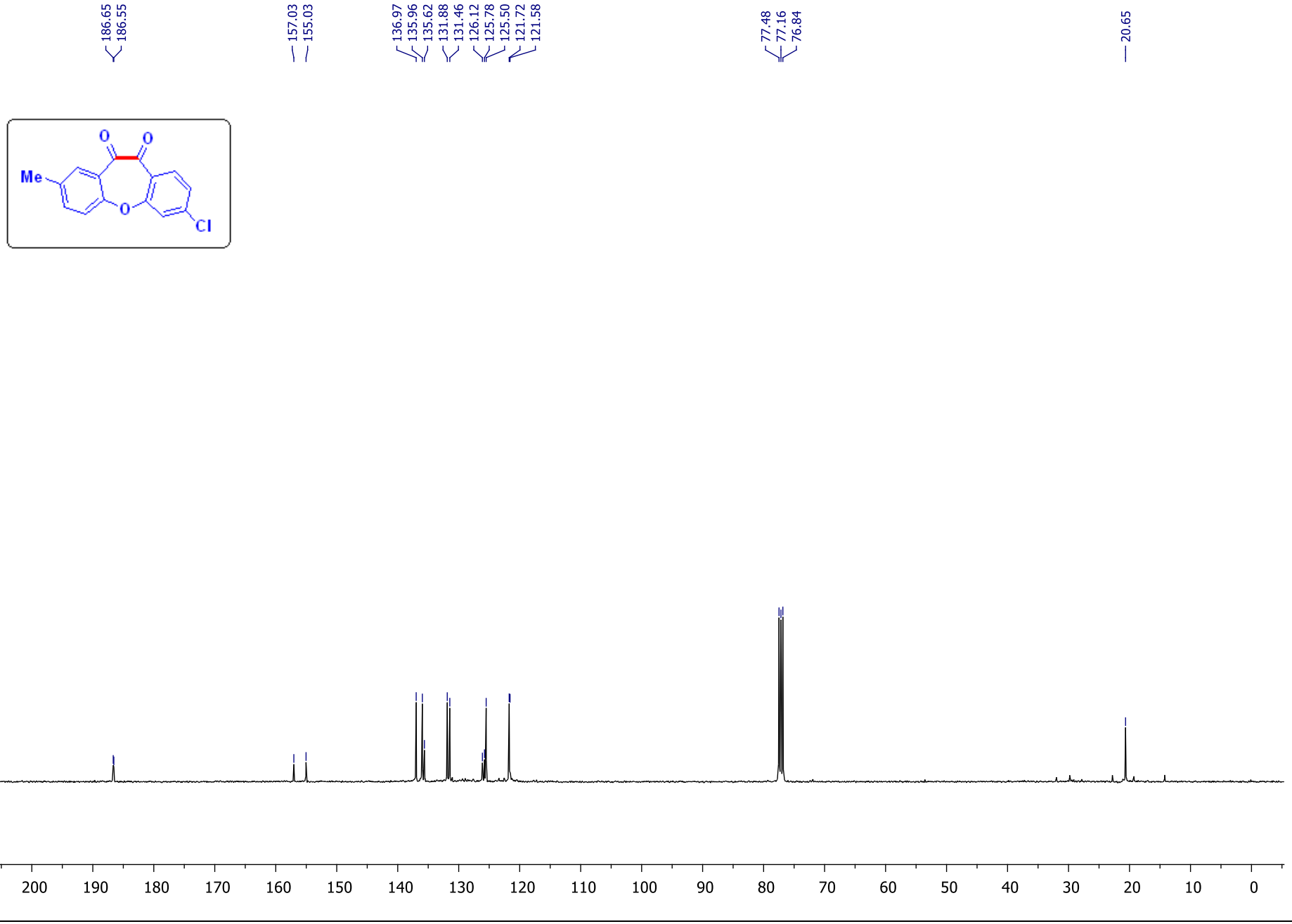
$^{13}C\{^{1}H\}$-NMR of 3z (101 MHz, $CDCl_3$)



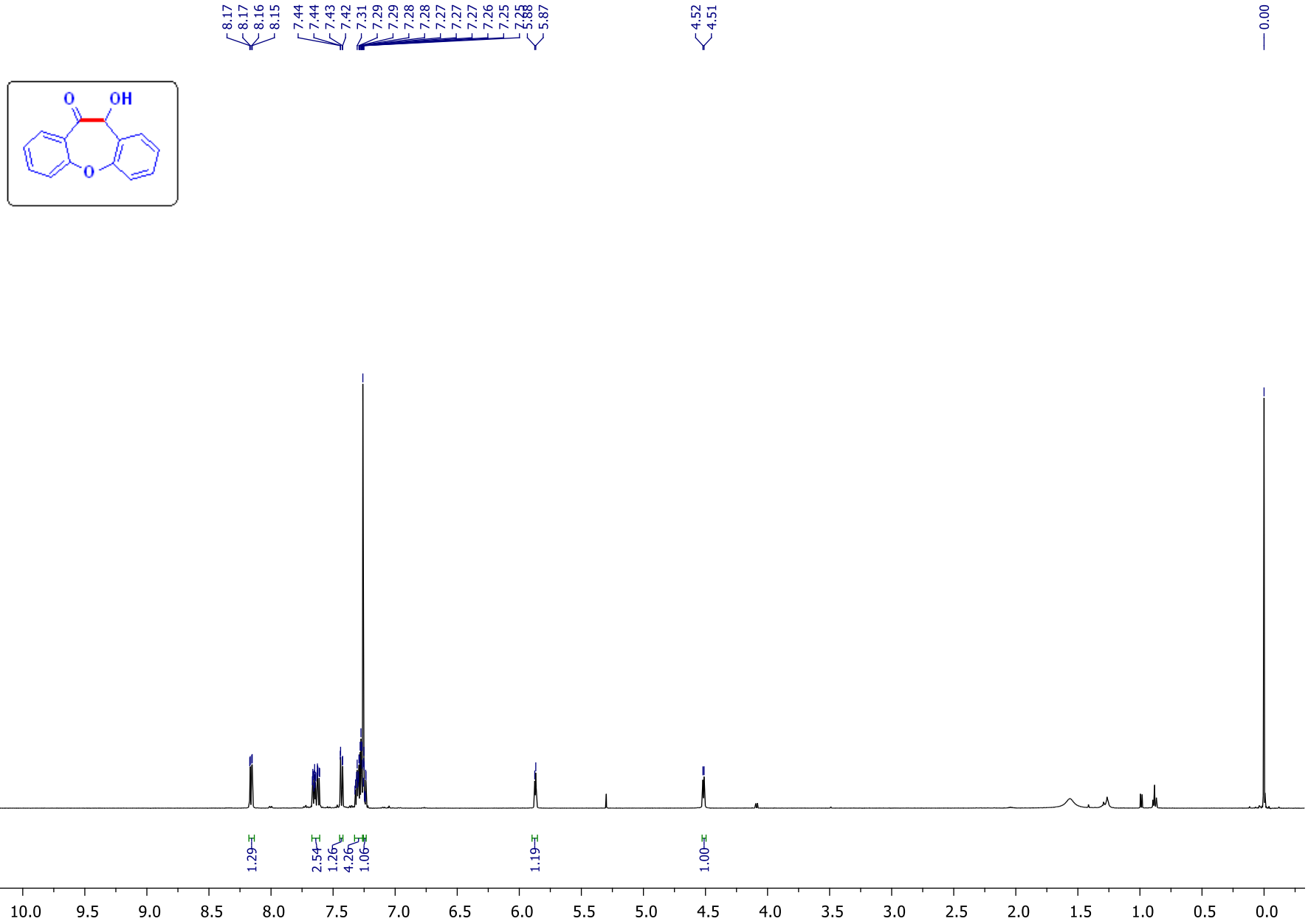
^{1}H-NMR of 3aa (500 MHz, $CDCl_3$)



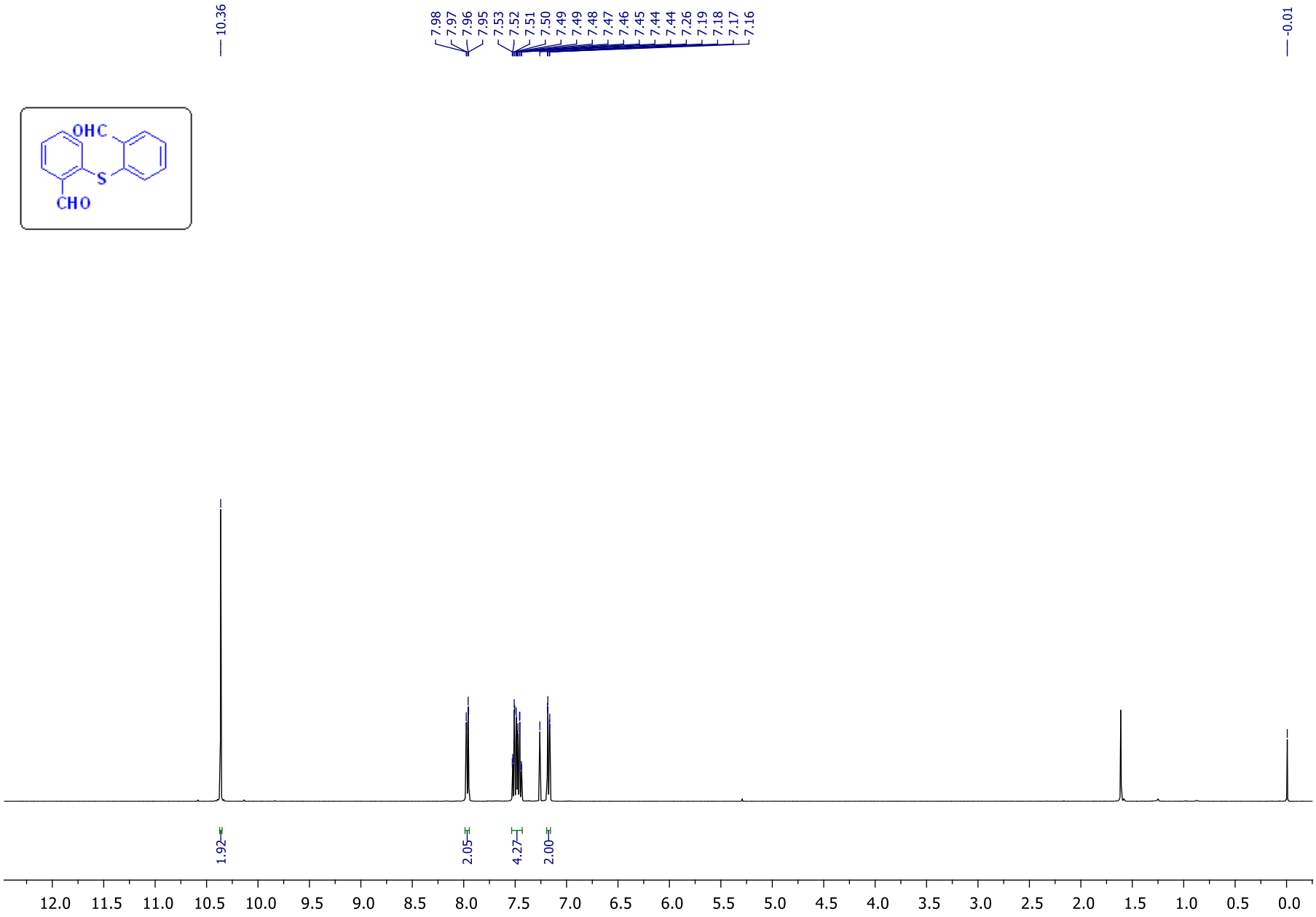
$^{13}C\{^{1}H\}$-NMR of 3aa (101 MHz, $CDCl_3$)



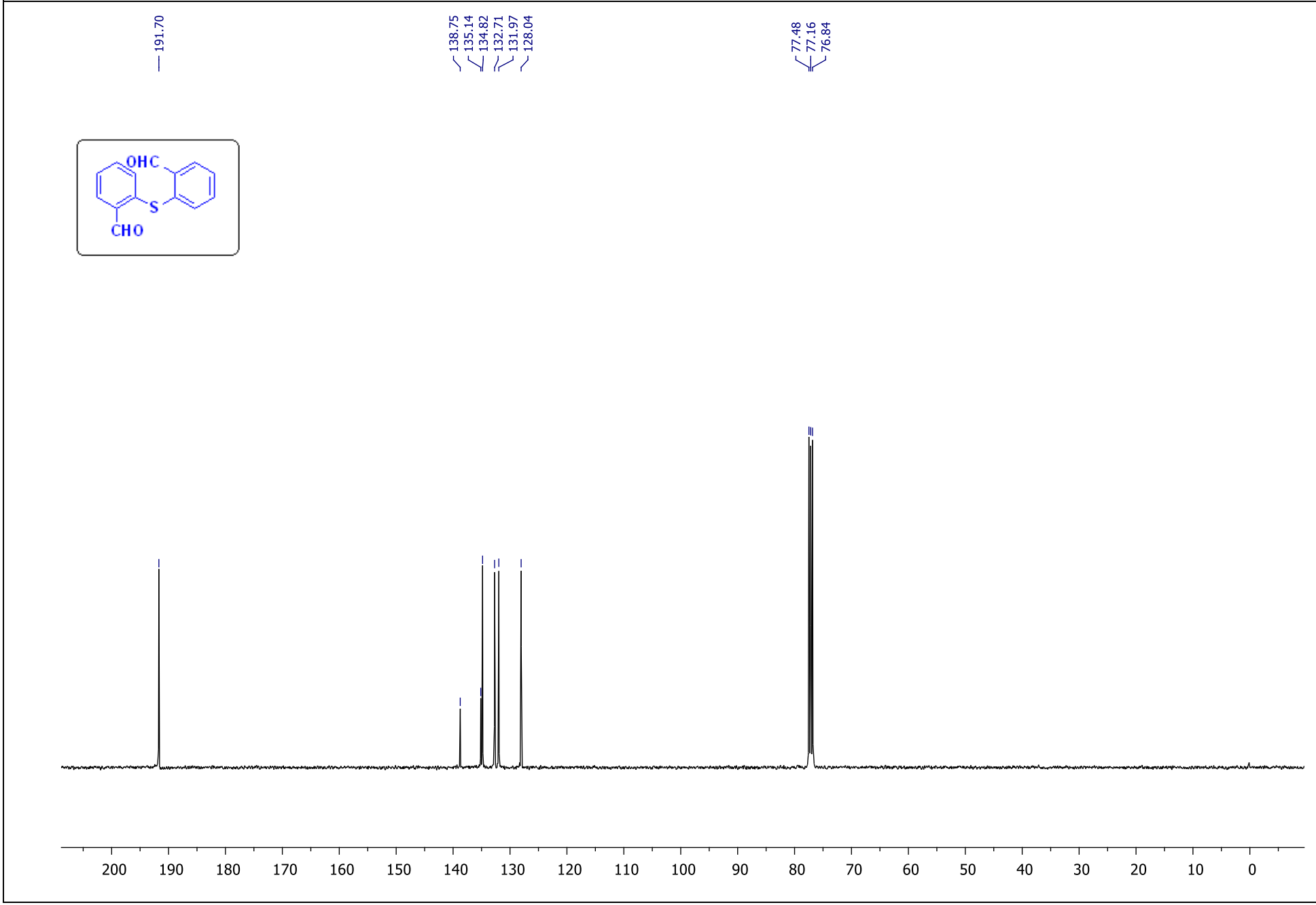
^{1}H-NMR of 2a (500 MHz, $CDCl_3$)



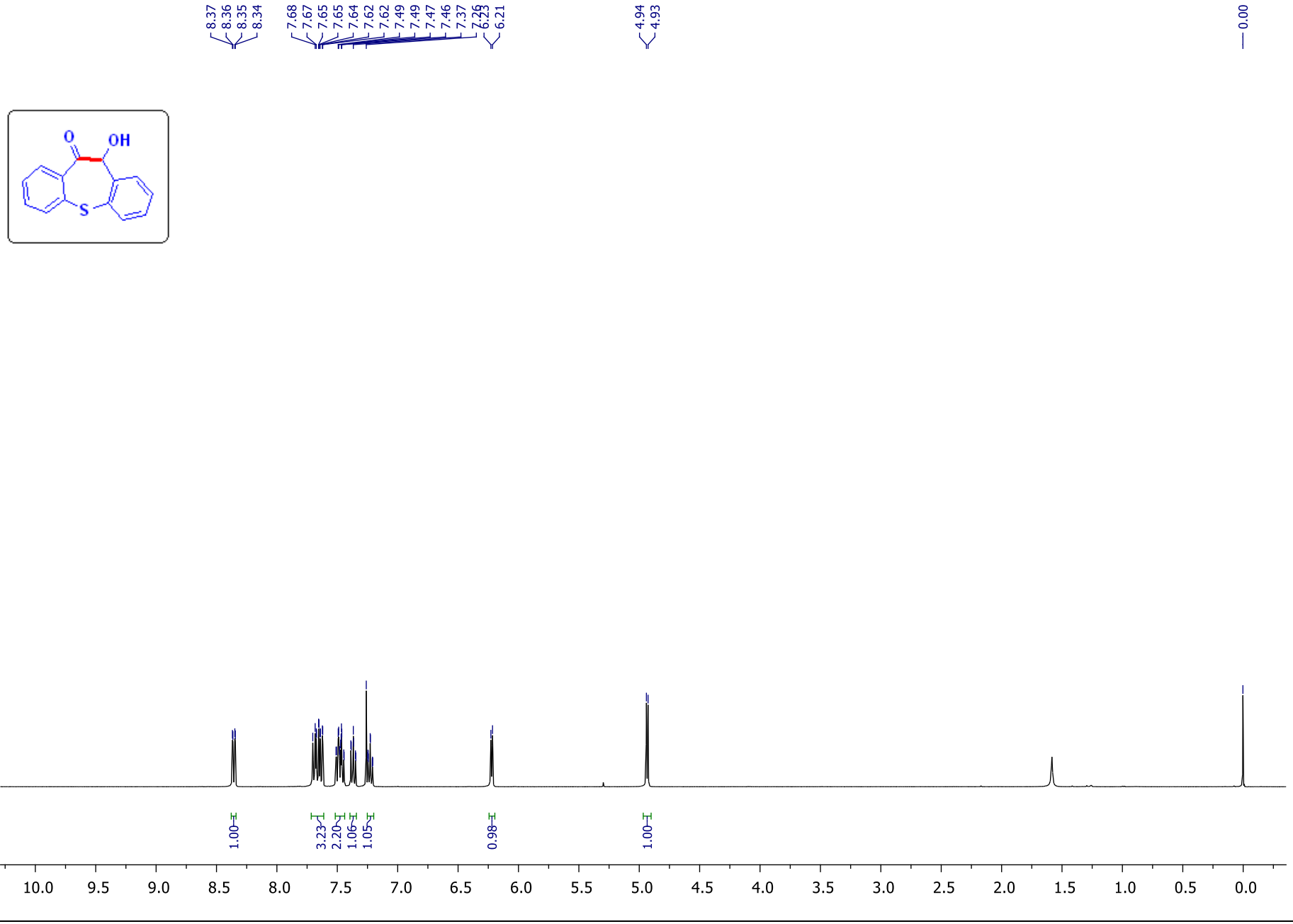
^{1}H-NMR of 4 (400 MHz, $CDCl_3$)



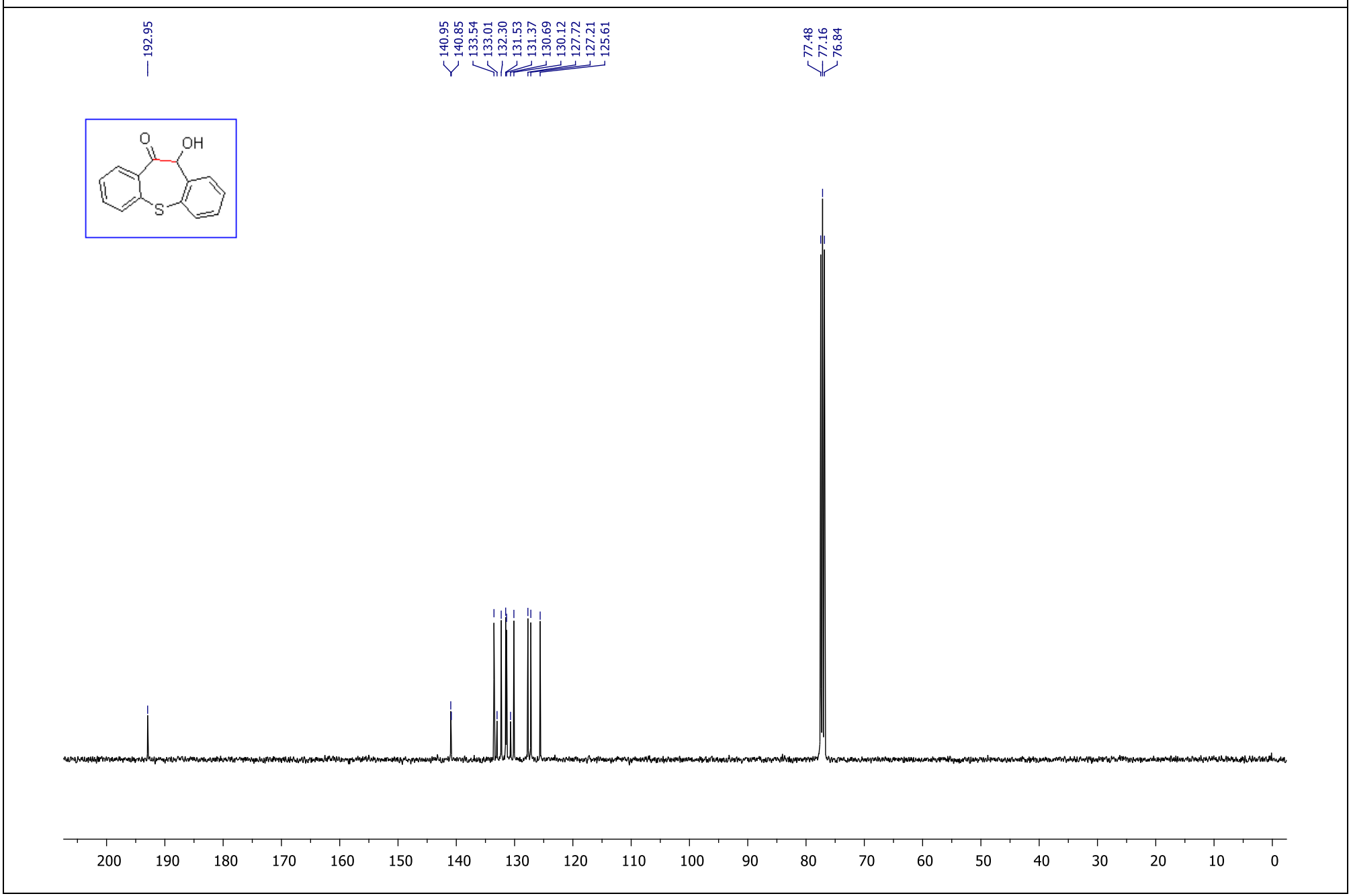
$^{13}C\{^{1}H\}$-NMR of 4 (101 MHz, $CDCl_3$)



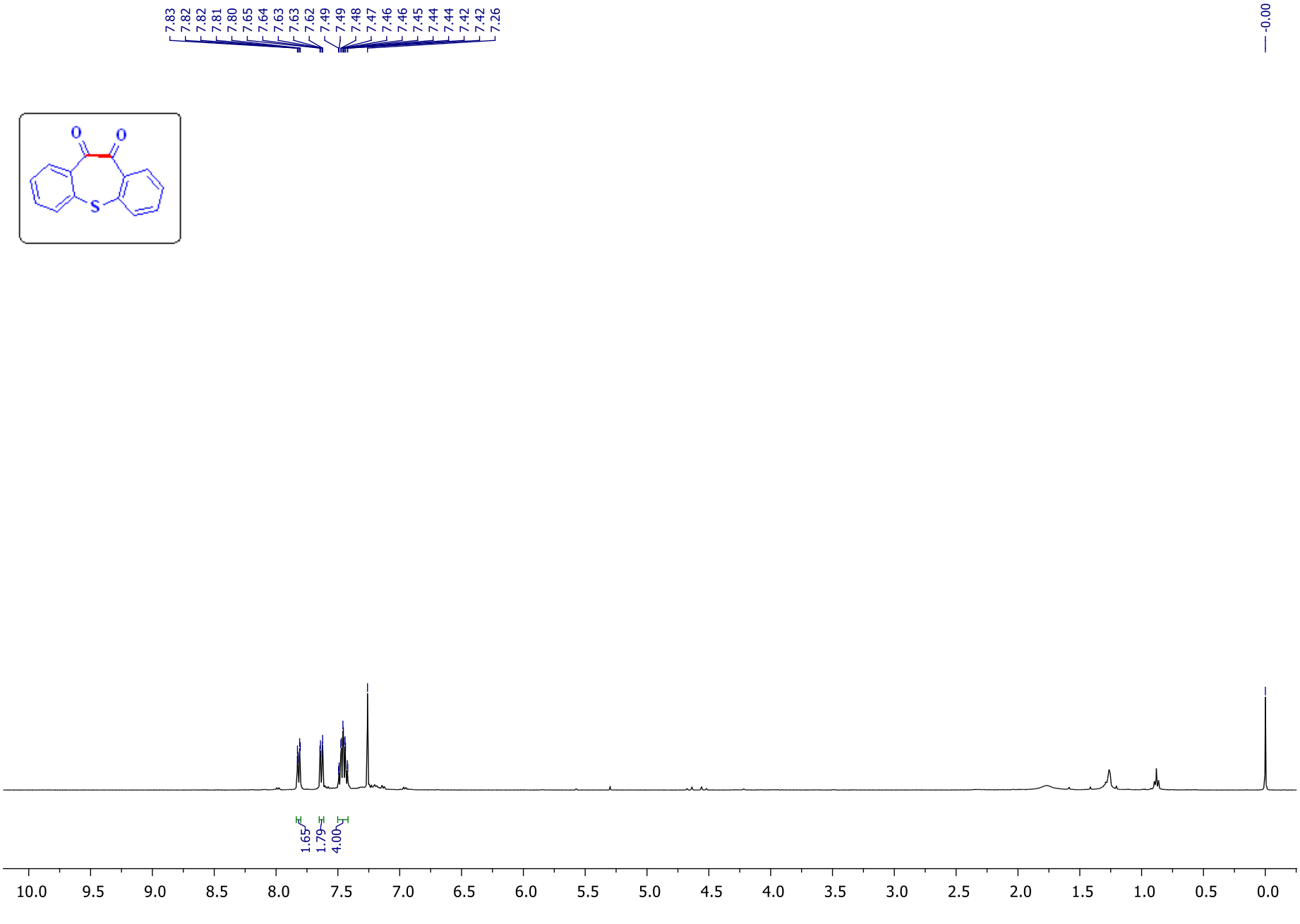
^{1}H-NMR of 5 (400 MHz, $CDCl_3$)



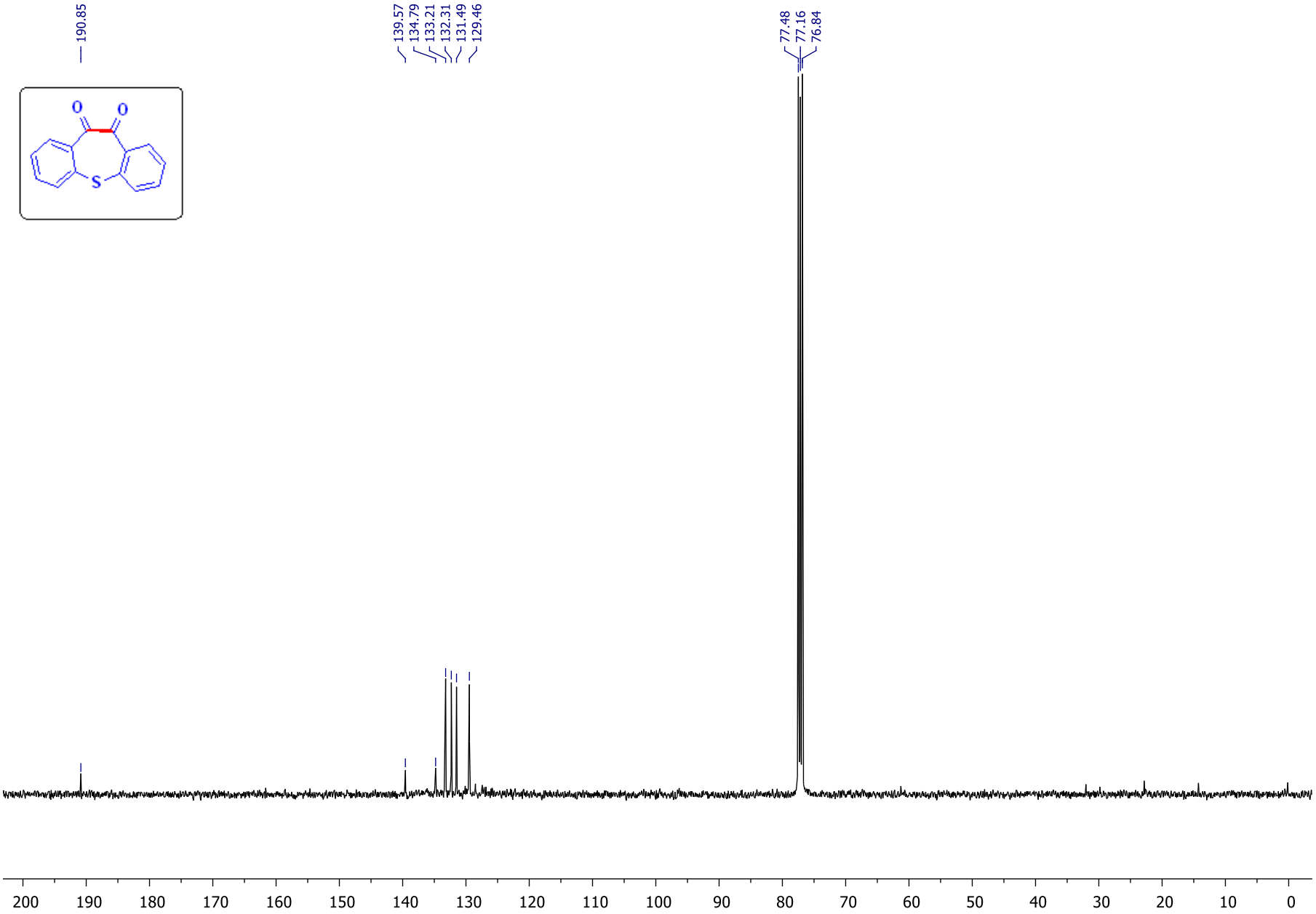
$^{13}C\{^{1}H\}$-NMR of 5 (101 MHz, $CDCl_3$)



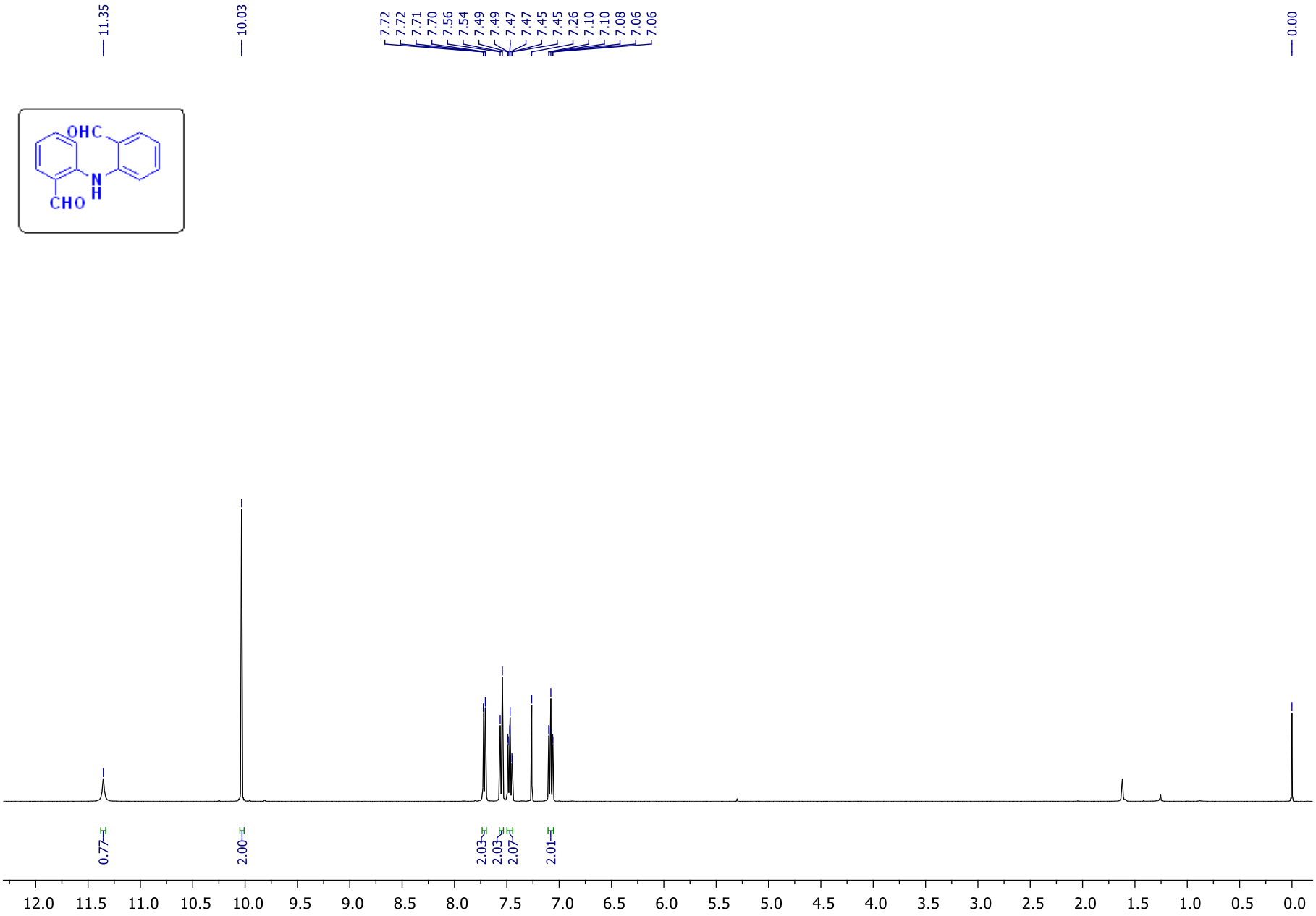
^{1}H-NMR of 6 (400 MHz, $CDCl_3$)



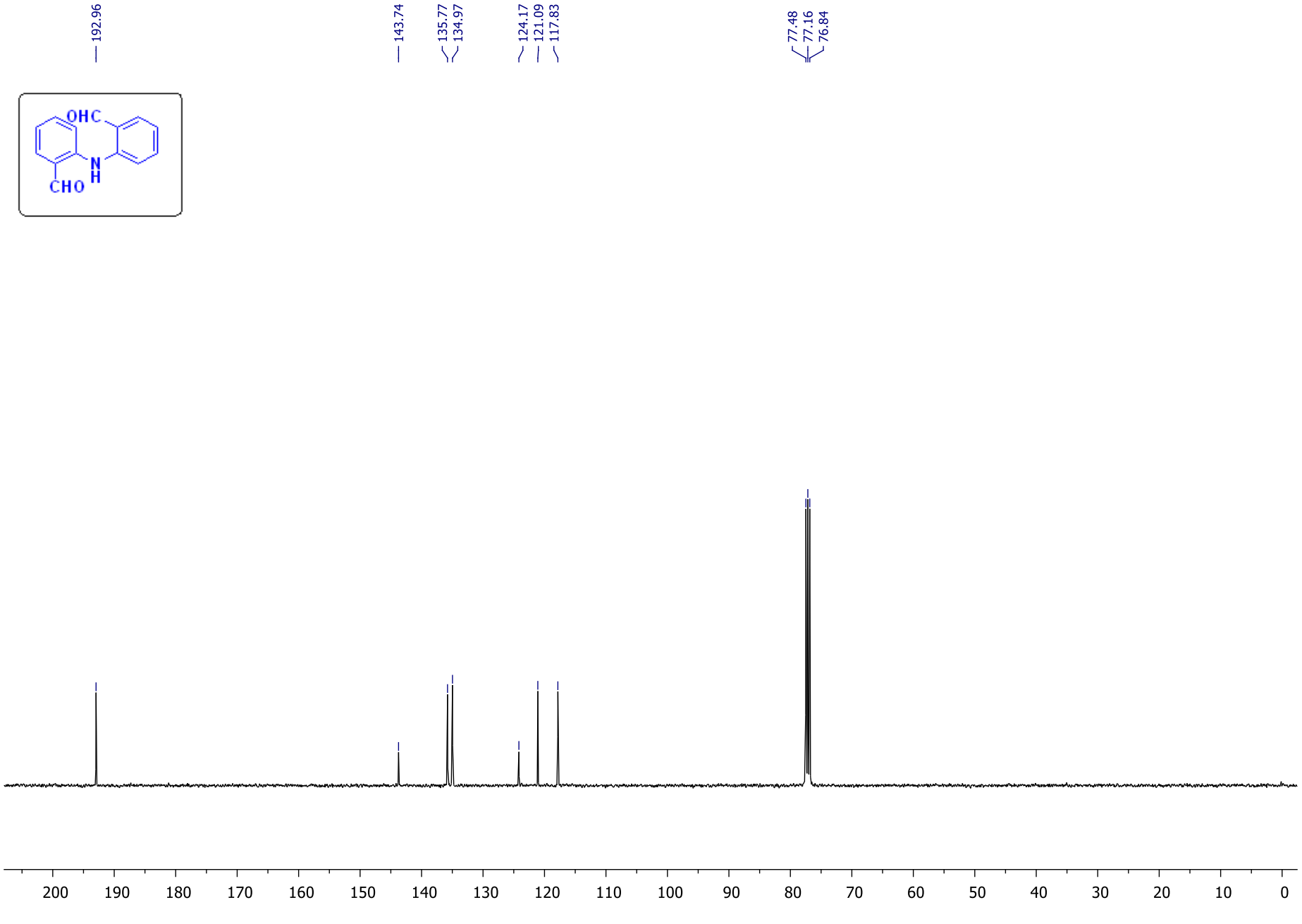
$^{13}C\{^{1}H\}$-NMR of 6 (101 MHz, $CDCl_3$)



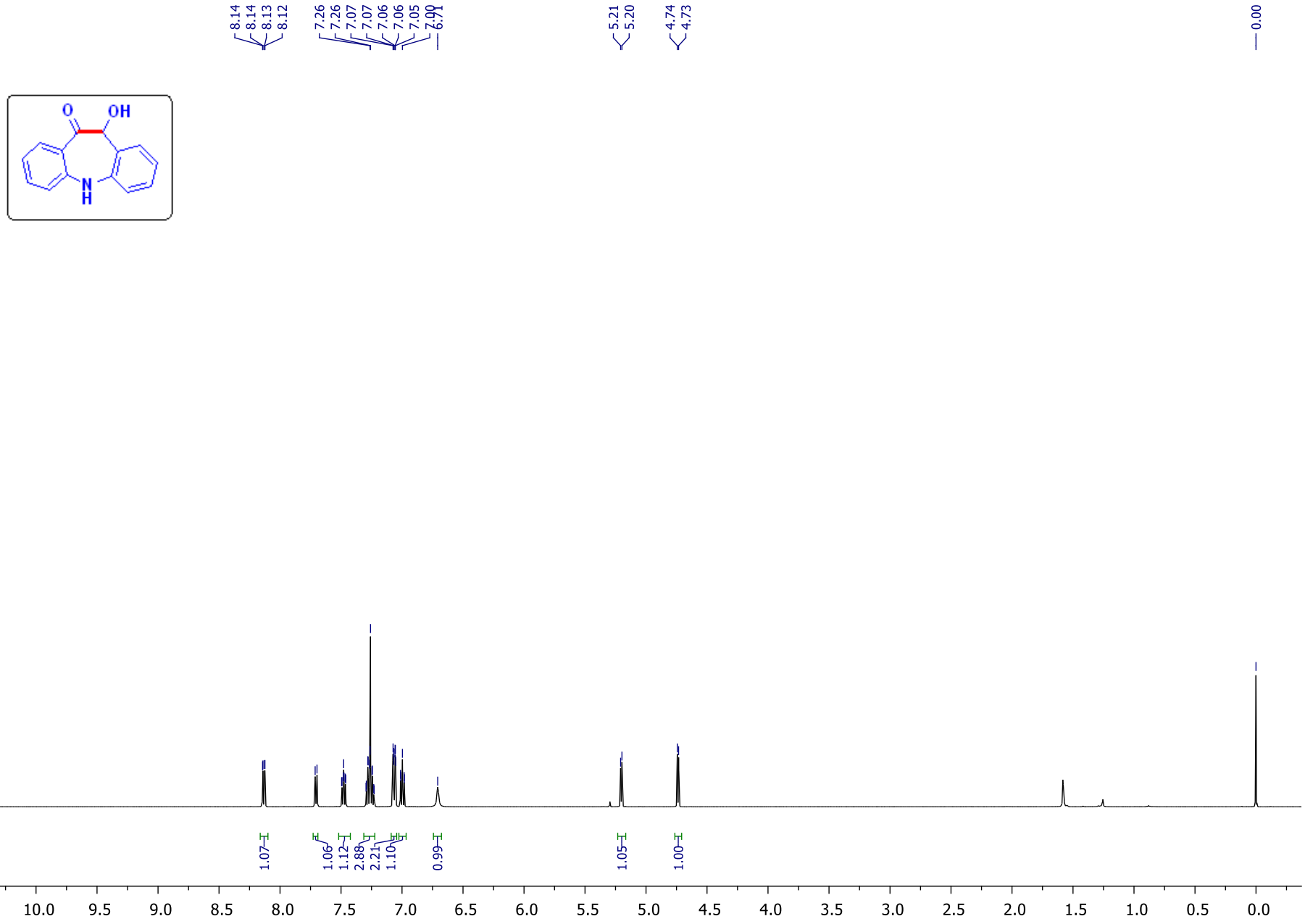
^{1}H-NMR of 7 (400 MHz, $CDCl_3$)



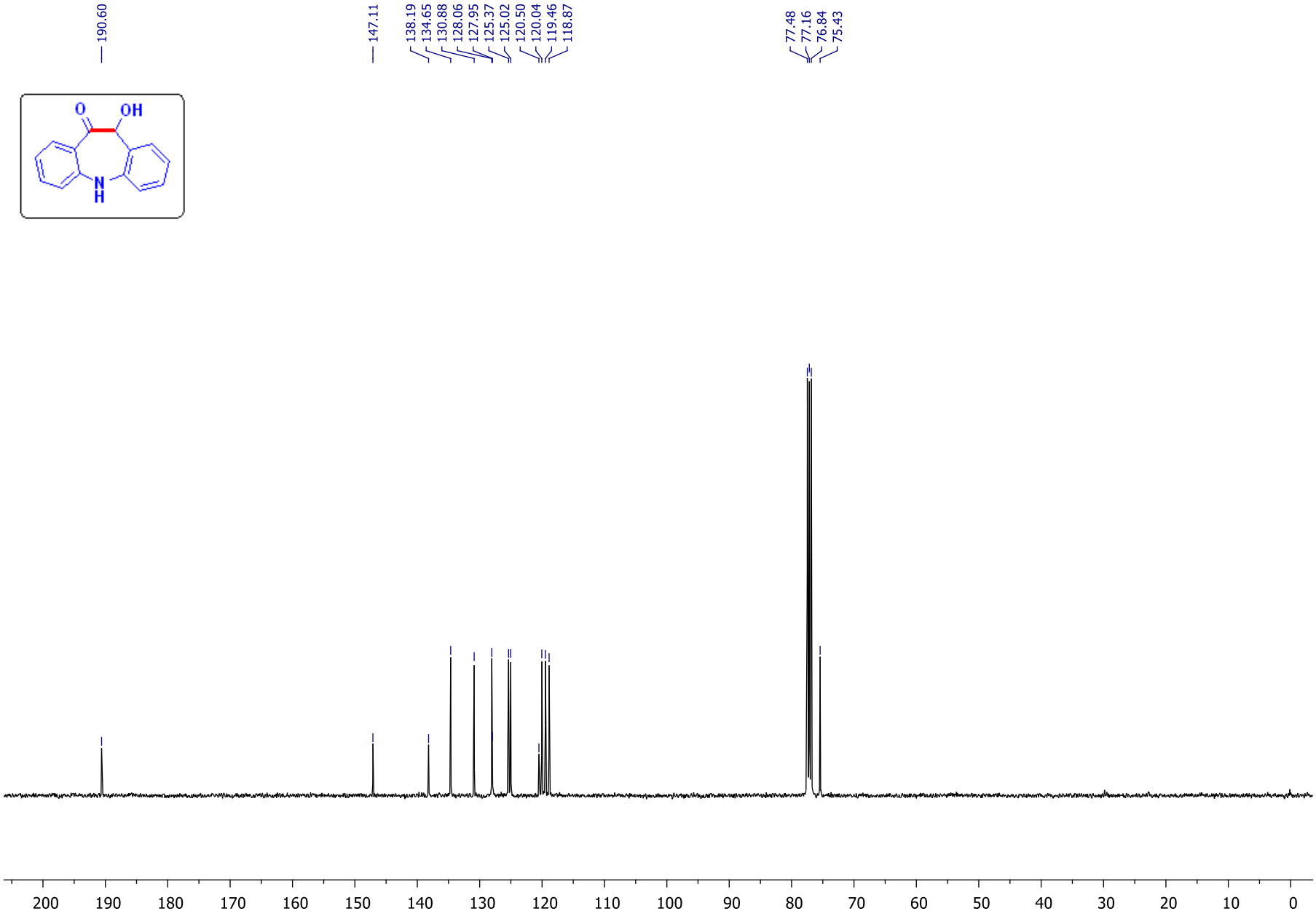
$^{13}C\{^{1}H\}$-NMR of 7 (101 MHz, $CDCl_3$)



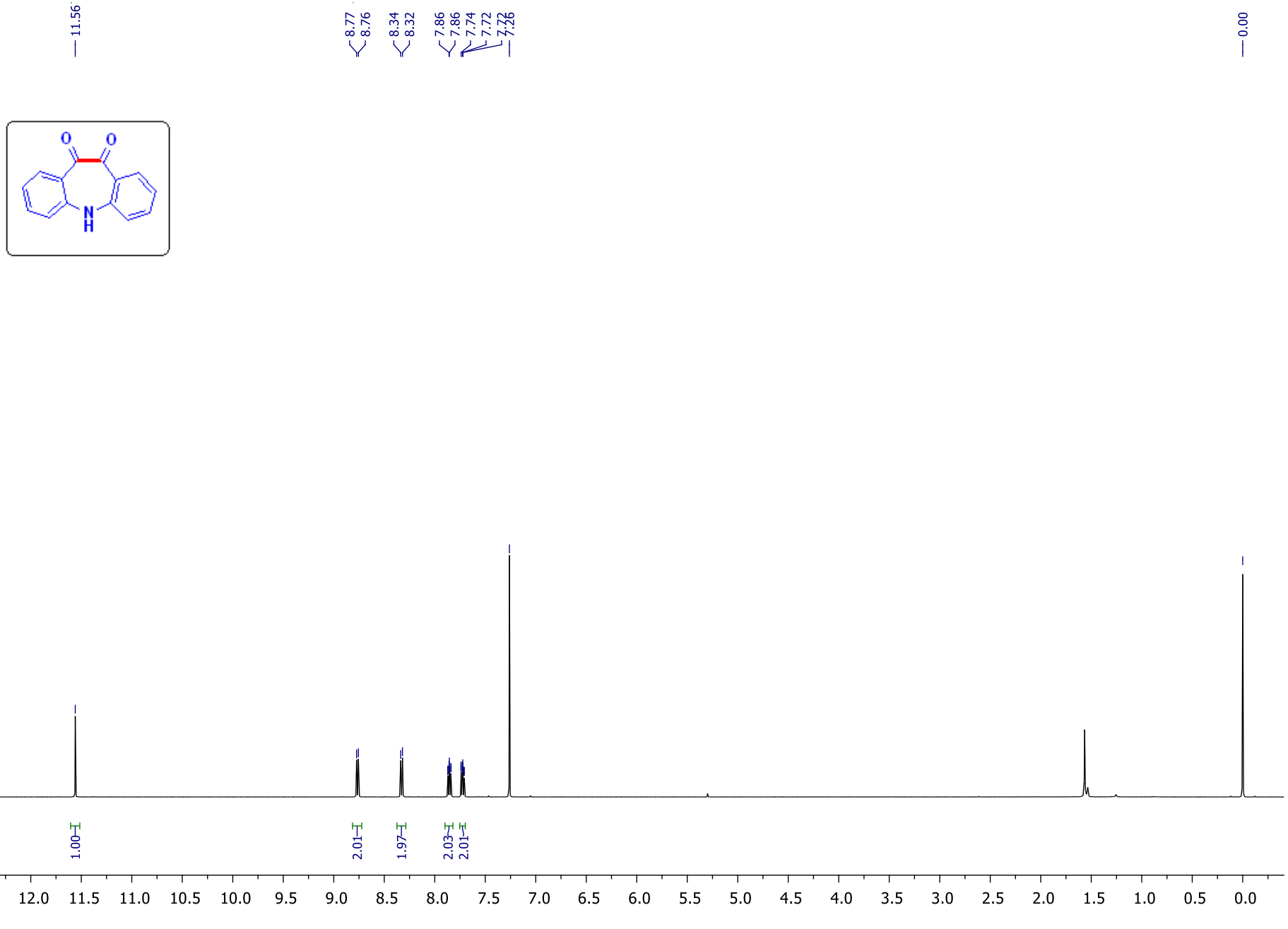
^{1}H-NMR of 8 (500 MHz, $CDCl_3$)



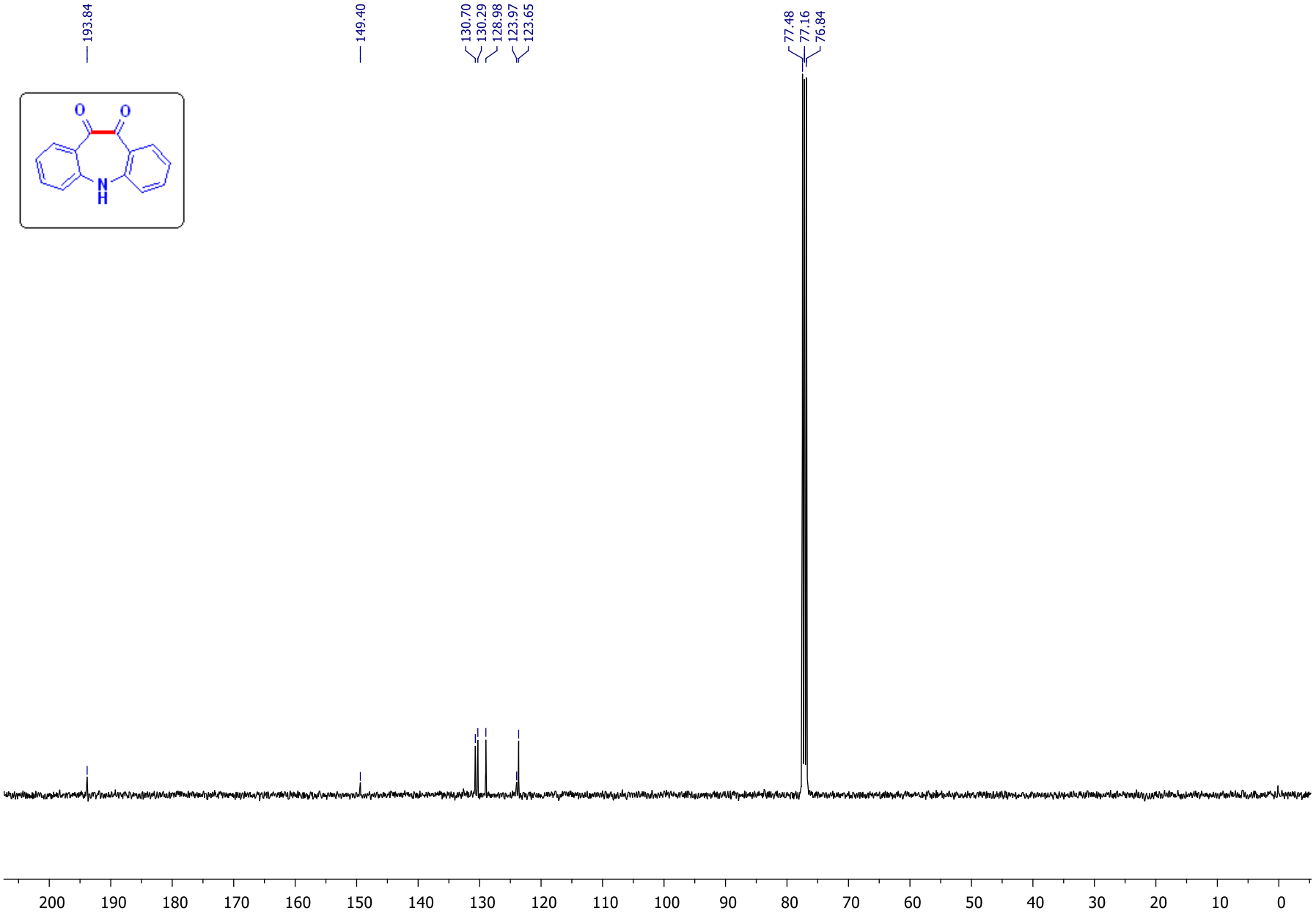
$^{13}C\{^{1}H\}$-NMR of 8 (101 MHz, $CDCl_3$)



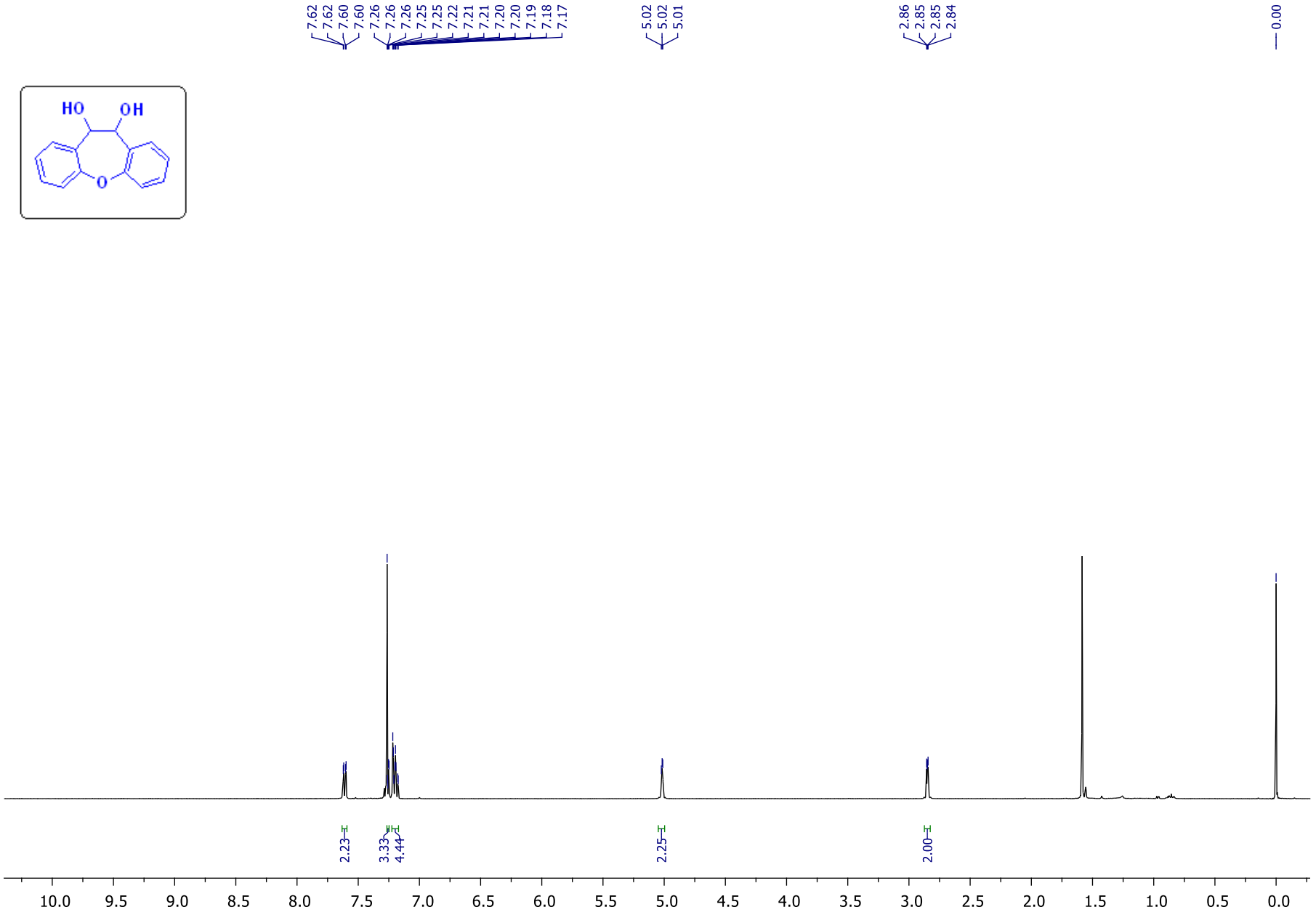
^{1}H-NMR of 9 (500 MHz, $CDCl_3$)



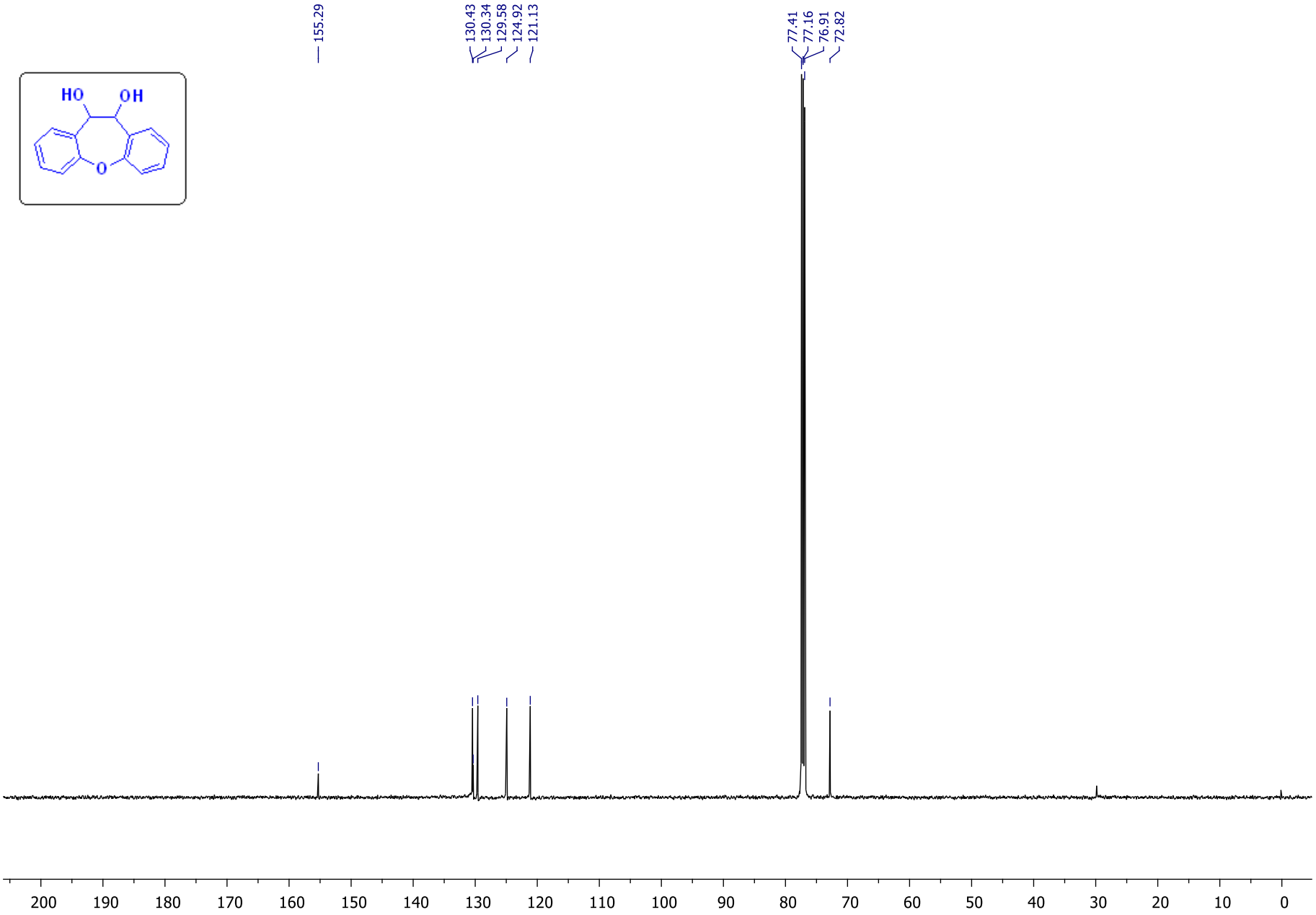
$^{13}C\{^{1}H\}$-NMR of 9 (101 MHz, $CDCl_3$)



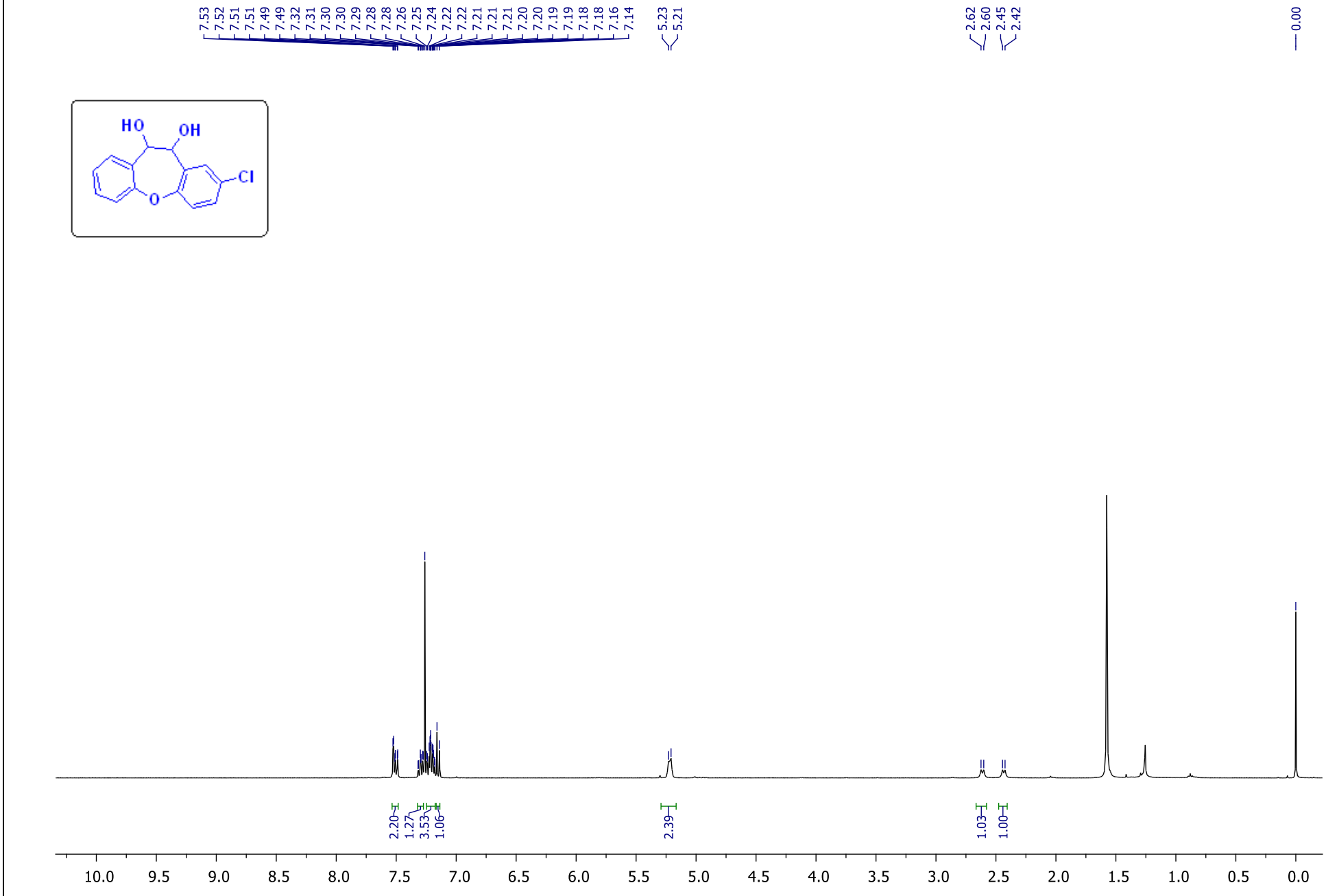
^{1}H-NMR of 10 (400 MHz, $CDCl_3$)



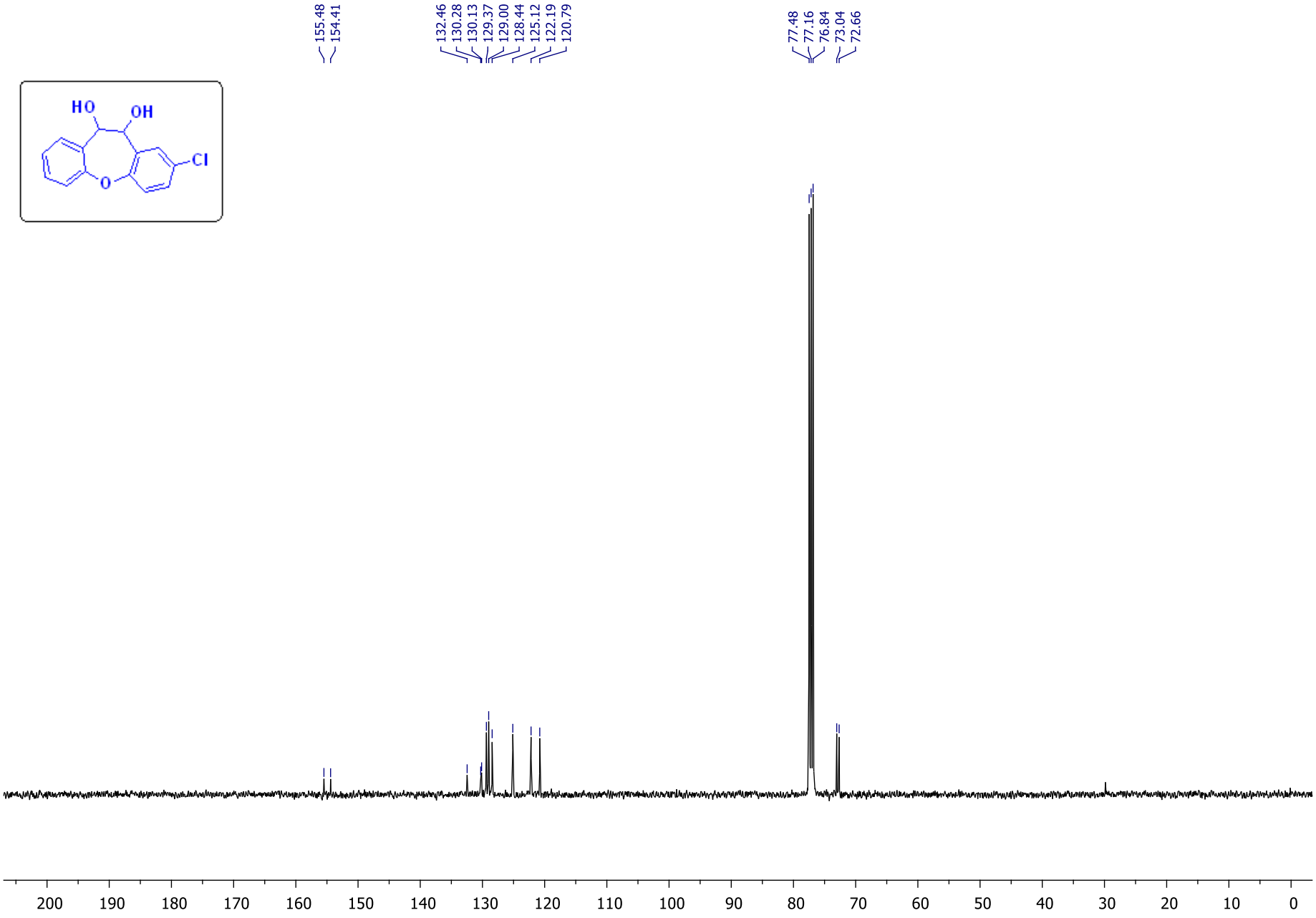
$^{13}C\{^{1}H\}$-NMR of 10 (101 MHz, $CDCl_3$)



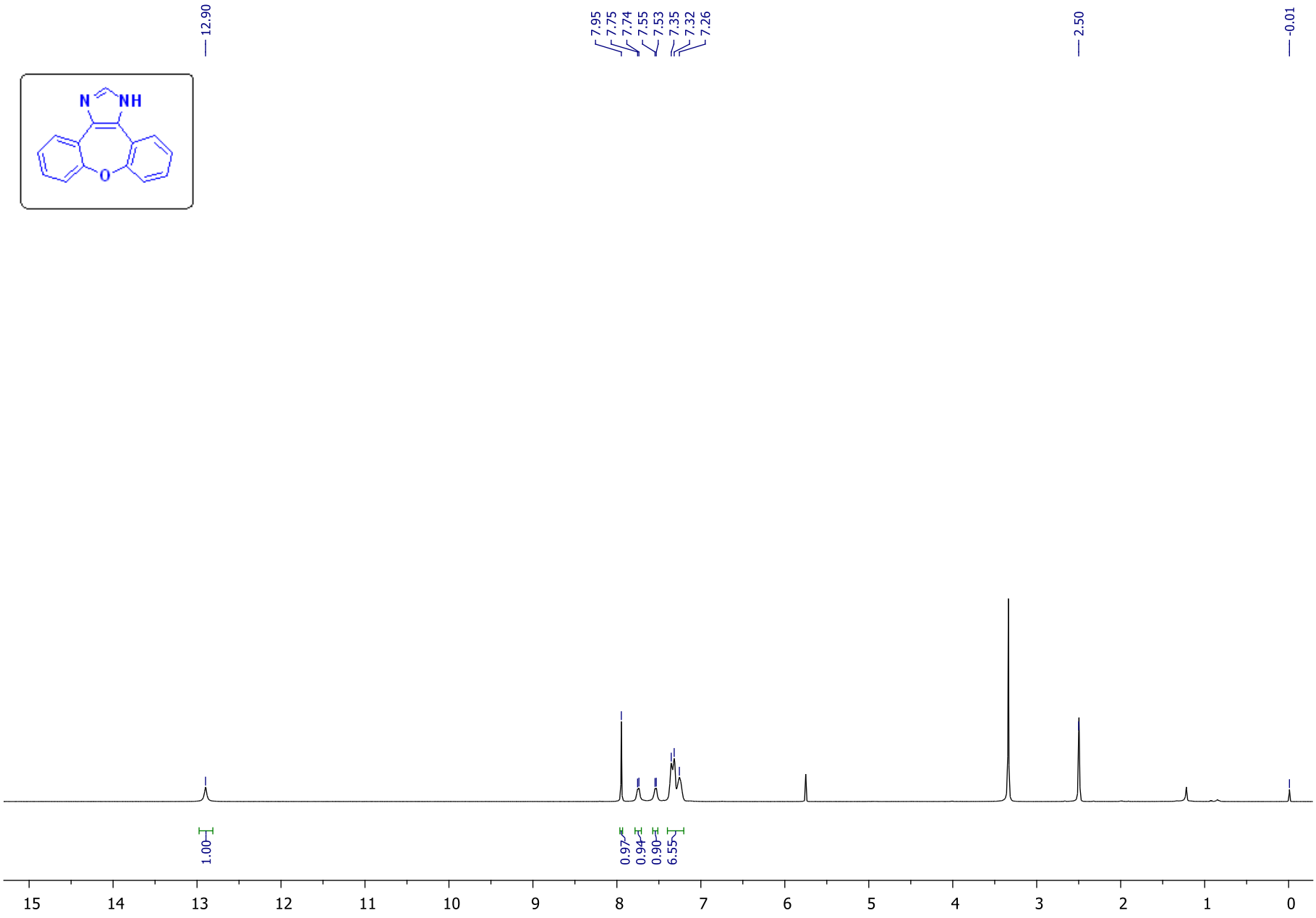
^{1}H-NMR of 11 (400 MHz, $CDCl_3$)



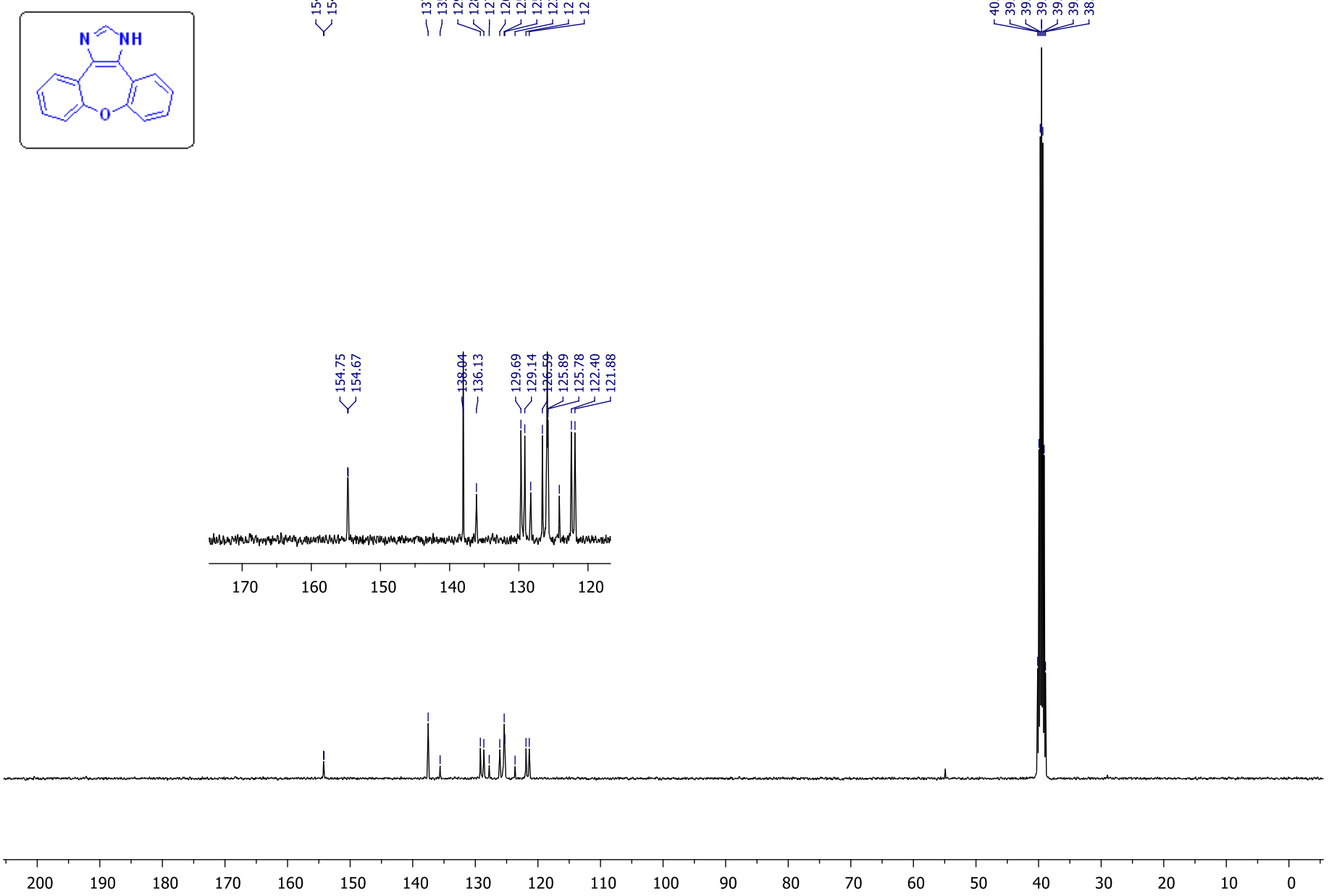
$^{13}C\{^{1}H\}$-NMR of 11 (101 MHz, $CDCl_3$)



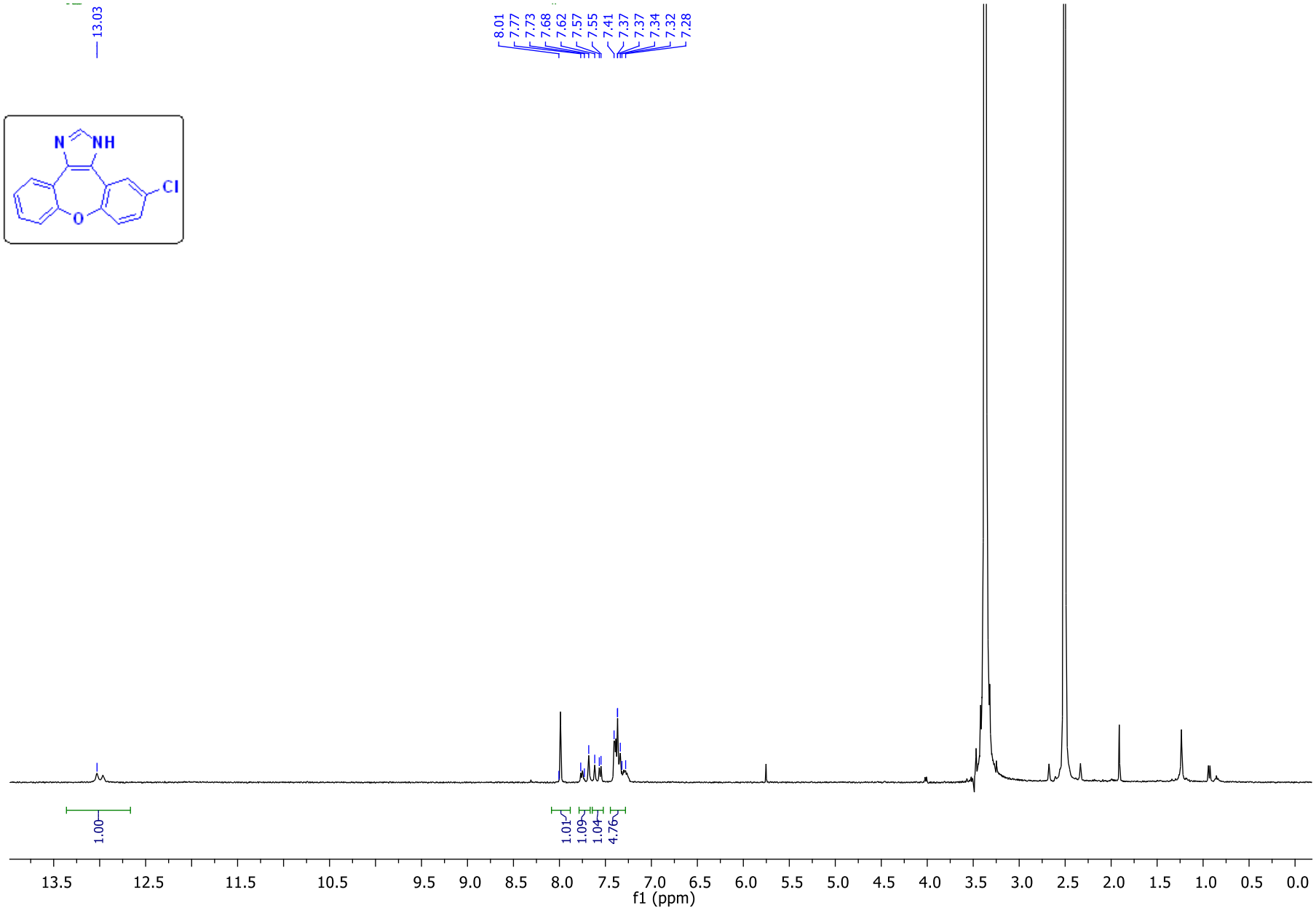
^{1}H-NMR of 12 (400 MHz, DMSO-d_6)



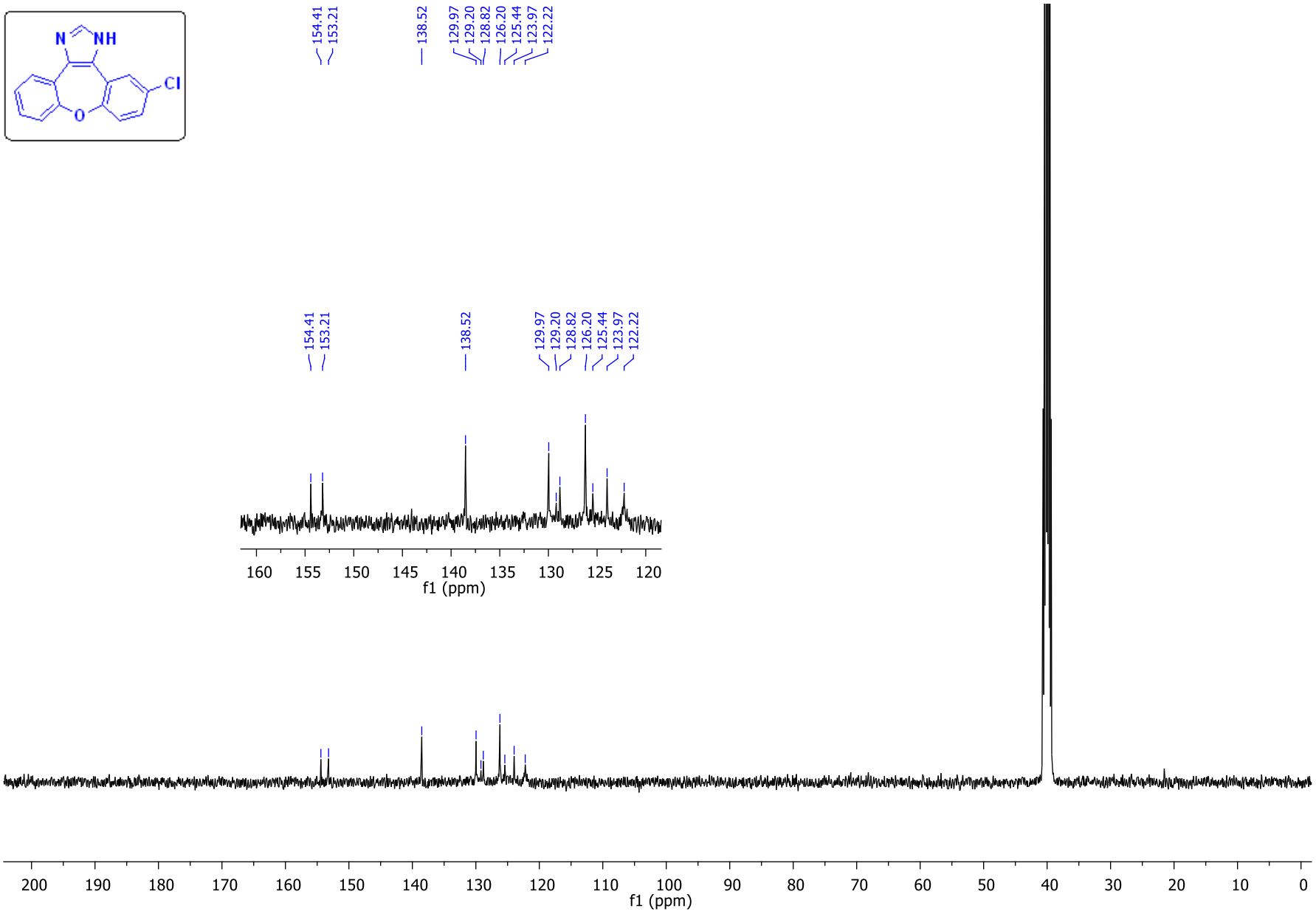
$^{13}C\{^{1}H\}$-NMR of 12 (101 MHz, DMSO-d_6)



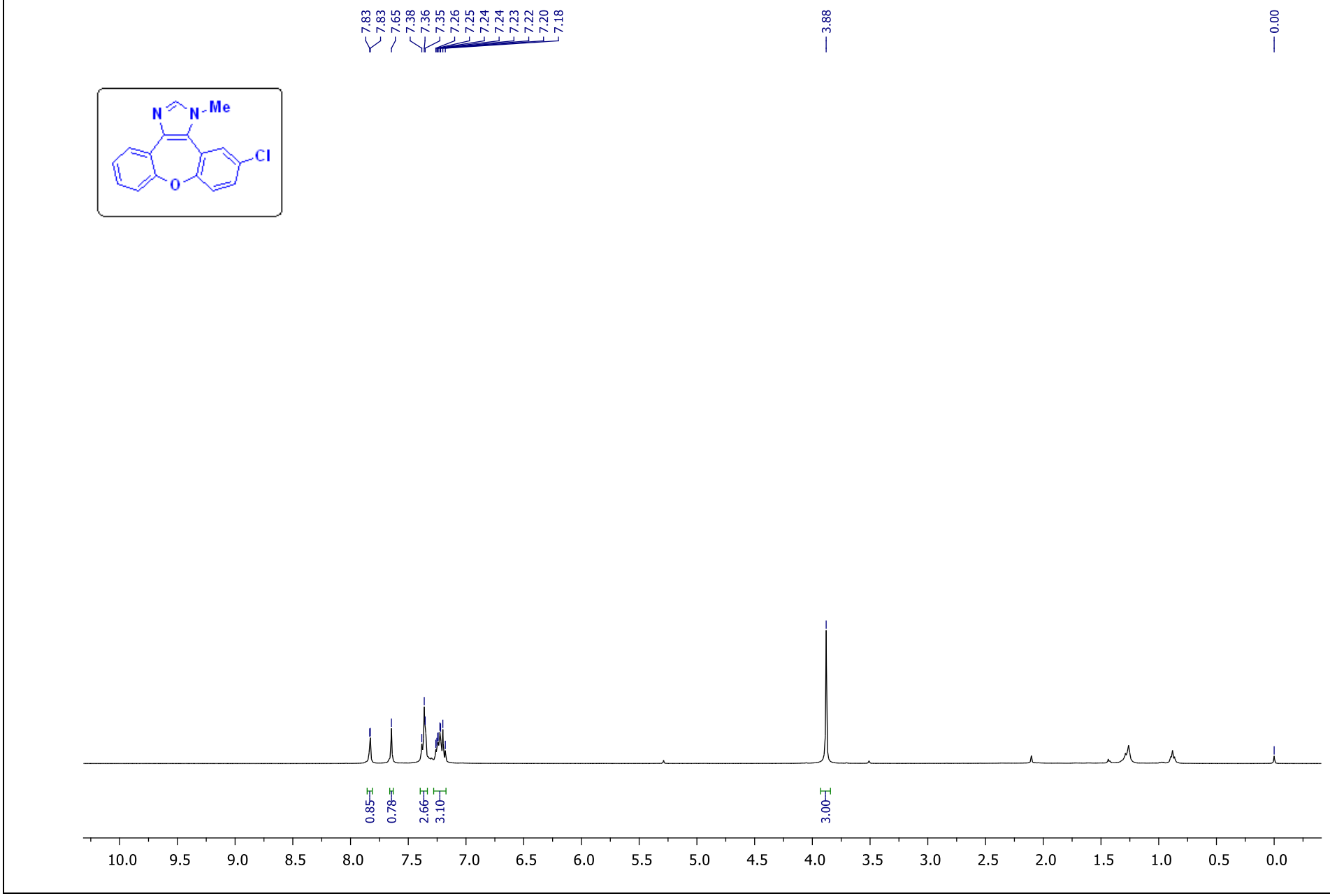
^{1}H-NMR of 13 (400 MHz, DMSO-d_6)



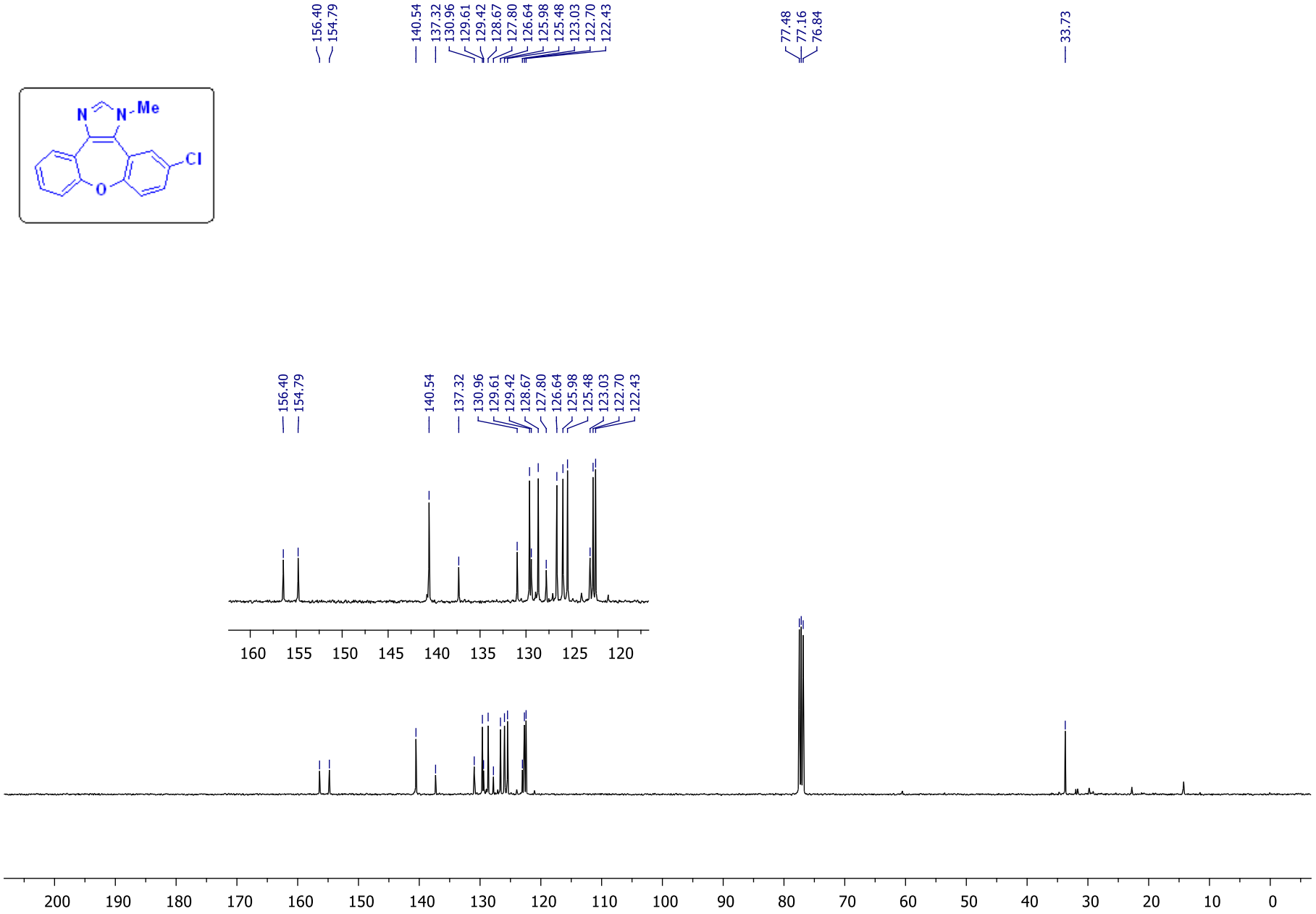
$^{13}C\{^{1}H\}$-NMR of 13 (101 MHz, DMSO-d_6)



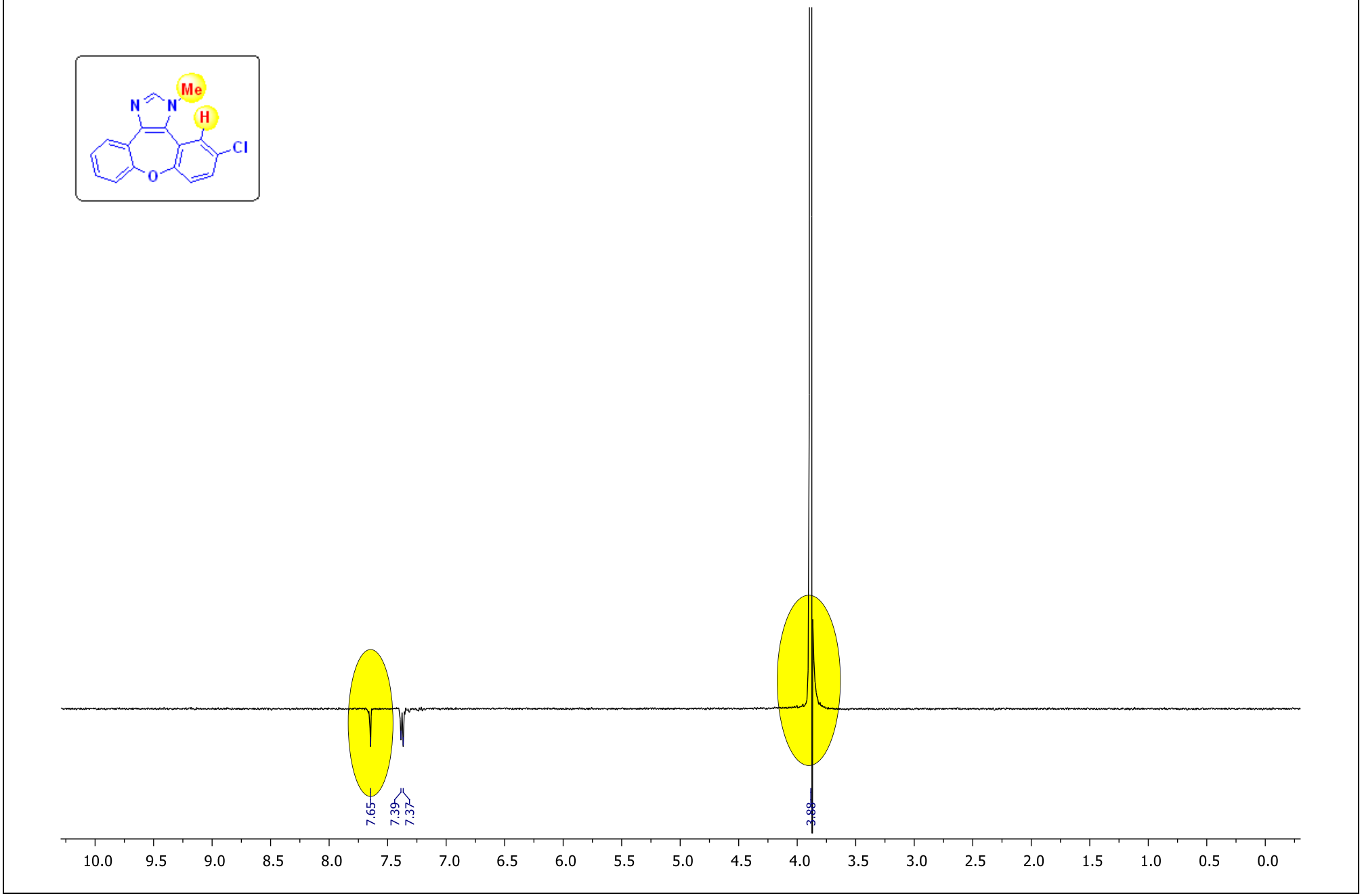
^{1}H-NMR of 14 (400 MHz, $CDCl_3$)



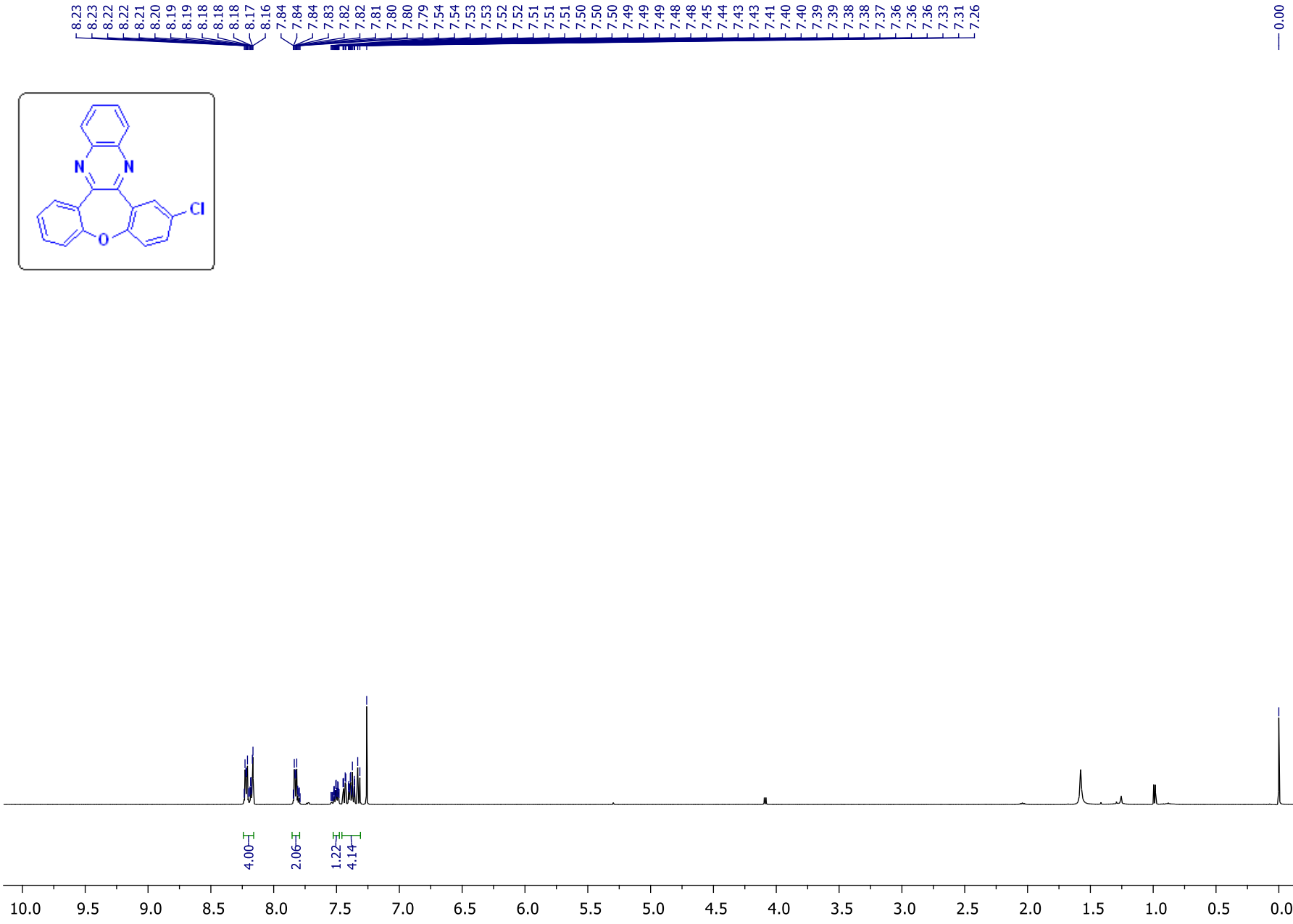
$^{13}C\{^{1}H\}$-NMR of 14 (101 MHz, $CDCl_3$)



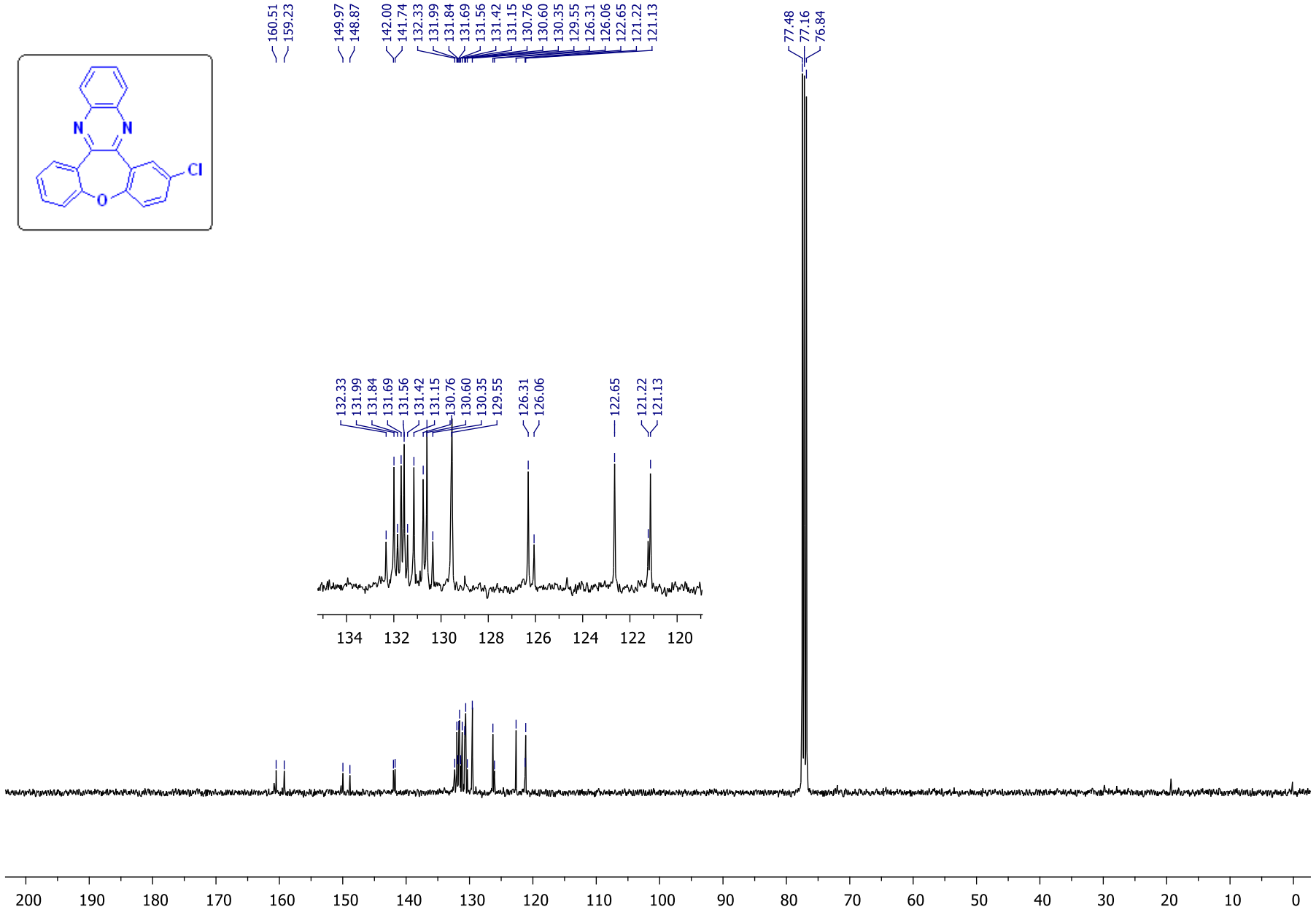
1D NOE spectrum of 14 (400 MHz, $CDCl_3$)



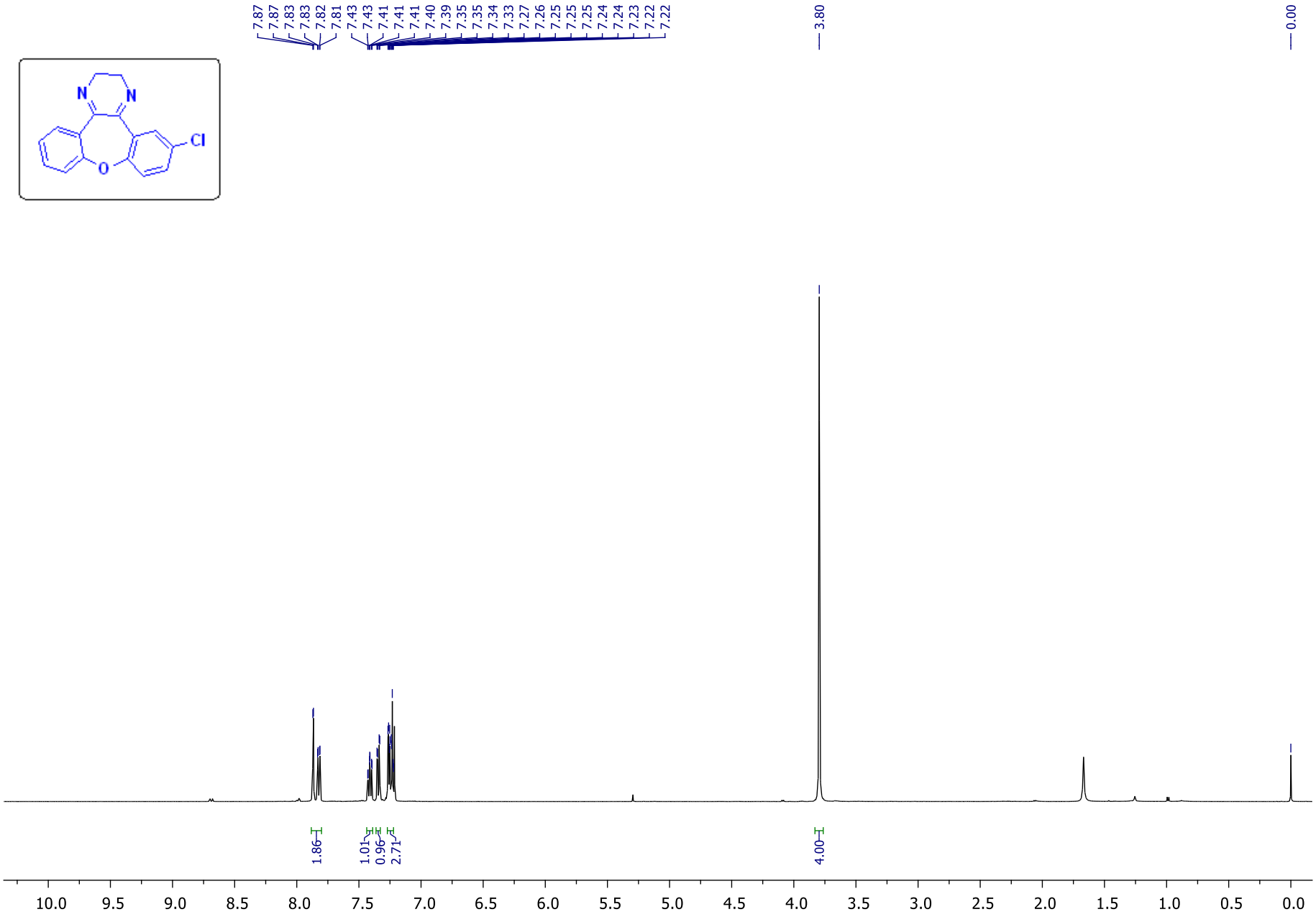
^{1}H-NMR of 17 (500 MHz, $CDCl_3$)



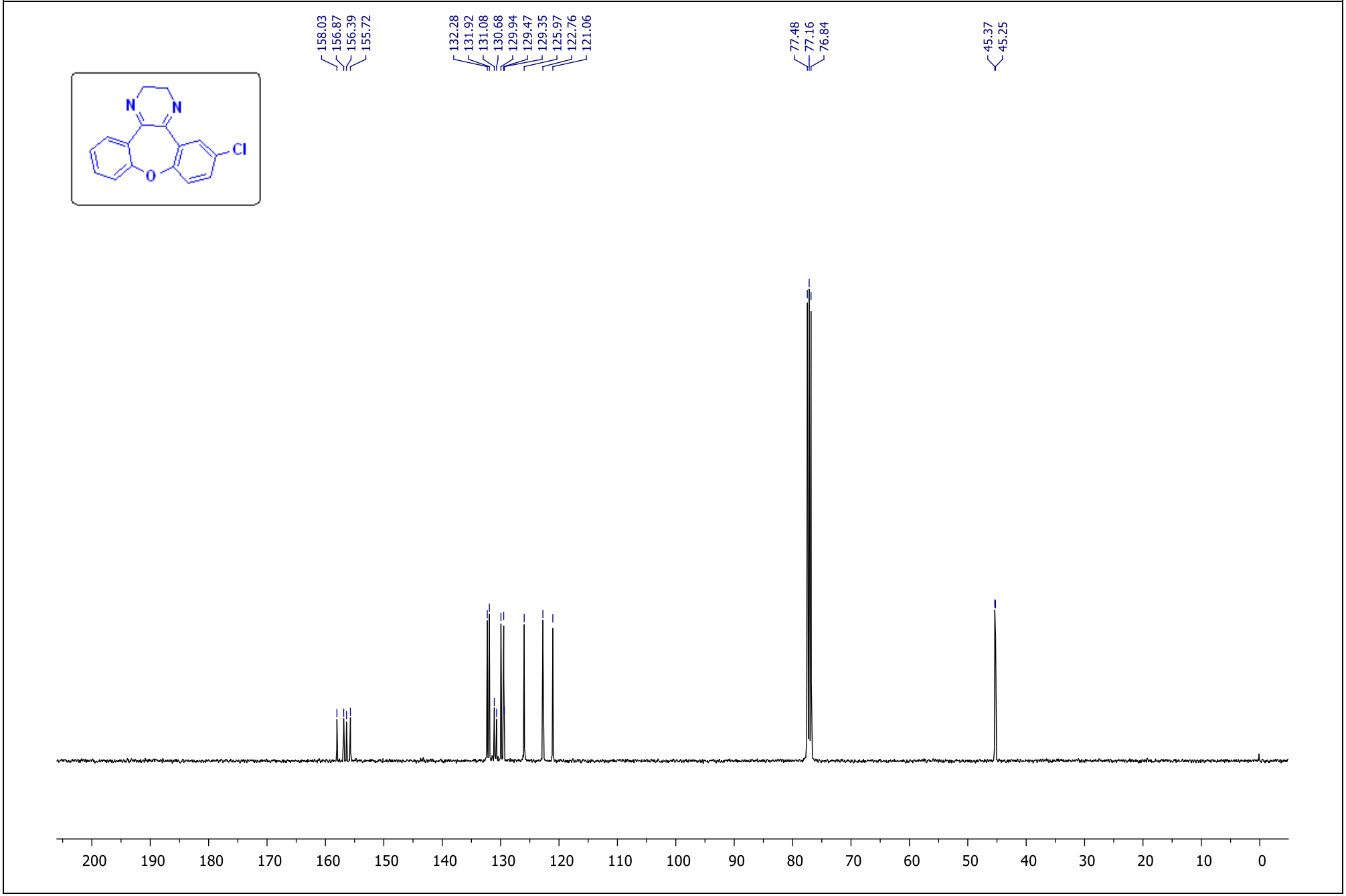
$^{13}C\{^{1}H\}$-NMR of 17 (101 MHz, $CDCl_3$)



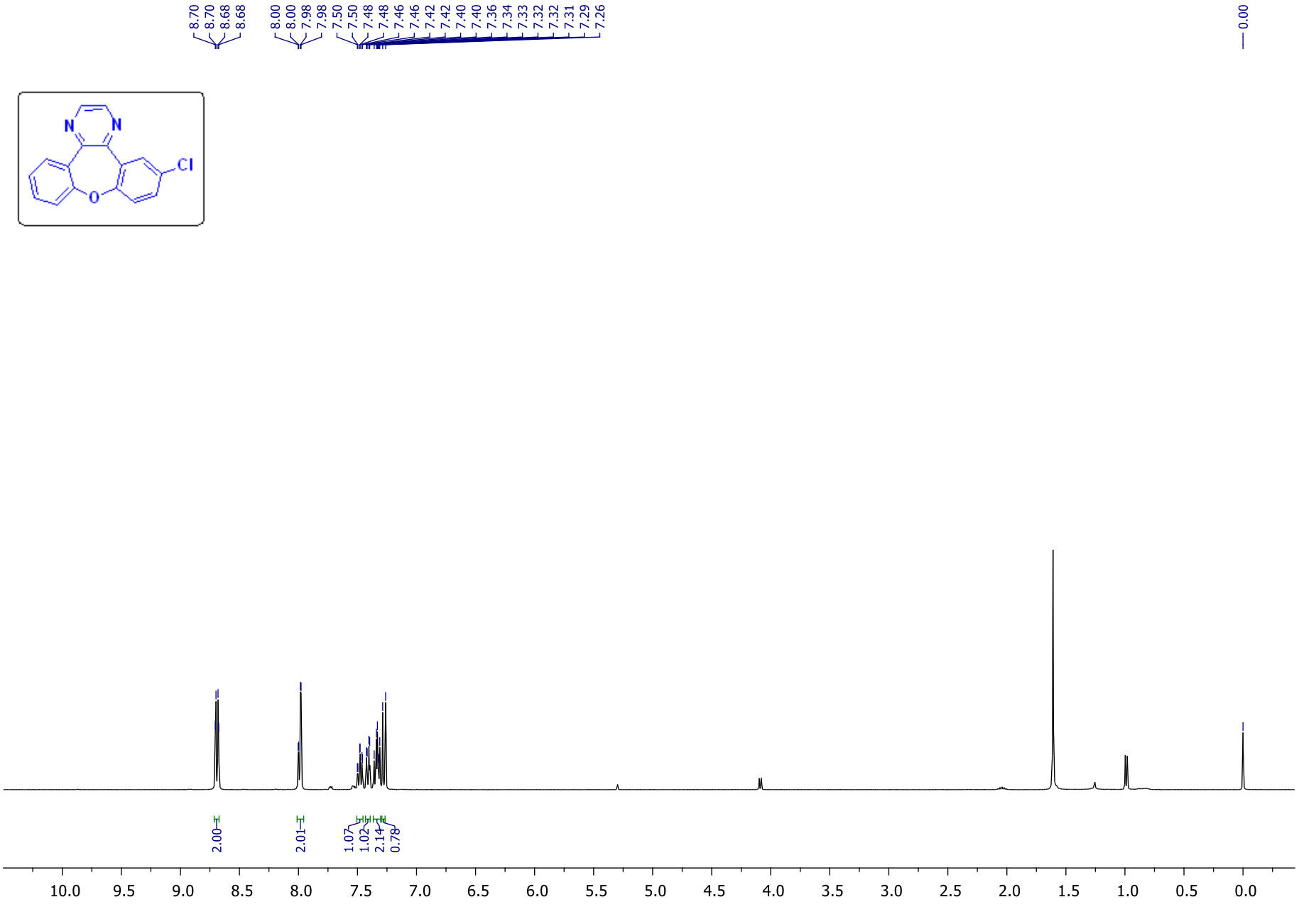
^{1}H-NMR of 18 (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$-NMR of 18 (101 MHz, $CDCl_3$)



^{1}H-NMR of 19 (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$-NMR of 19 (101 MHz, $CDCl_3$)