A Formal [4+1] Annulation incorporating Styrylogous Aldol Condensation to Access Functionalized 2-Styryl-benzofurans

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1. General Information

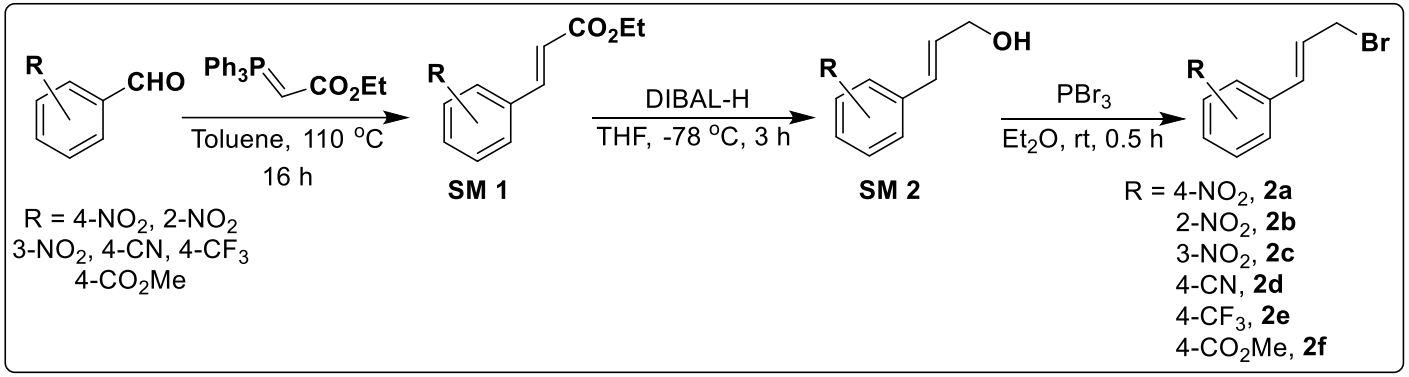
All the reactions were carried out in an oven-dried round bottom flask/screw cap-vial. Reactions were magnetically stirred and monitored by analytical thin layer chromatography (TLC). TLC was performed on Merck silica gel 60 F_{254}; UV lamp was used as a visualizing agent; I_2 or $KMnO_4$ were used as developing agents. Purification of products was carried out by column chromatography using 60-120/100-200/230-400 mesh silica, and EtOAc/hexane was used as eluents, and concentration under reduced pressure was performed by rotary evaporator at 40-45 ^oC. The yields were given for the isolated products.

All the reaction solvents such as THF, DMC, DCE, DMF, DMSO, CH_3CN, toluene, *t*-BuOH, DME and 1,4-dioxane were purchased from commercial sources. All the reagents, substrates, bases, and deuterated solvents were purchased from commercial suppliers such as Alfa Aesar, Sigma Aldrich, TCI, S.D Fine chemicals, India. These were used without further purification.

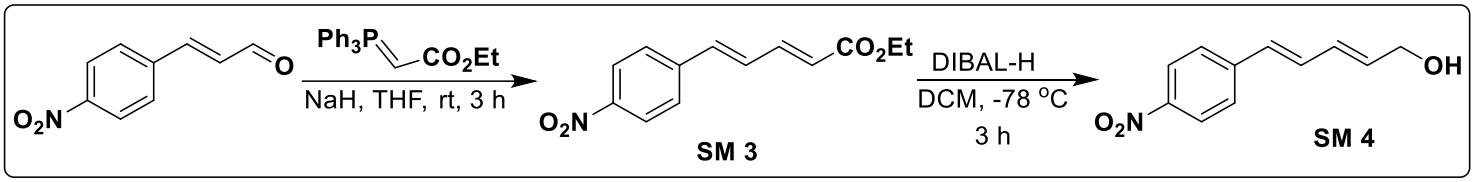
^{1}H-NMR spectra were recorded on 300, 400 and 500 MHz instruments. Chemical shifts are reported in ppm with the reference solvent as the internal standard (TMS = 0; $CDCl_3$ = 7.26; DMSO-d_6 = 2.50). The following abbreviations were used to explain the multiplicity of the spectra: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are represented in *Hz*. **^{13}C{^{1}H}-NMR** spectra were recorded on 75, 101, 126 and 151 MHz spectrometers. **^{19}F-NMR** spectra were recorded on a 376 MHz spectrometer. Peaks at 1.26, 0.86 in **^{1}H-NMR** and 29.7 in **^{13}C{^{1}H}-NMR** correspond 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 analyzed by the Electrospray Ionization (ESI) method and were obtained on a Shimadzu LCMS-2020 mass spectrometer. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific Exactive^{TM} Orbitrap mass spectrometer or Q-STAR XL Hybrid MS/MS. Melting points (MP) were determined using a Superfit (India) capillary point apparatus. MPs reported in this work are uncorrected. Infrared spectroscopy was performed on a BRUKER FT-IR spectrophotometer in chloroform and KBr spectra were recorded on a Bruker OPUS FT-IR instrument.

2. Synthesis of starting materials

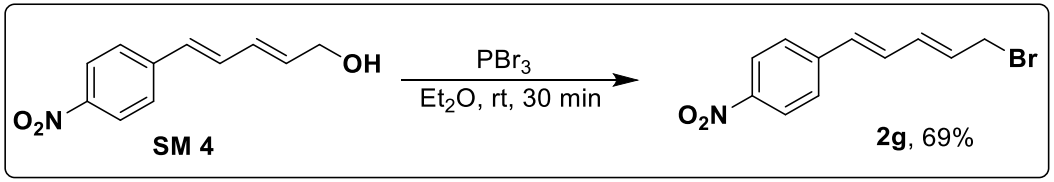
2.1 Substituted cinnamyl bromide derivatives (2a-2f) were synthesized according to literature reports:[1]



2.2 (2*E*,4*E*)-5-Phenylpenta-2,4-dien-1-ol (SM 4) was synthesized according to literature reports:[2]

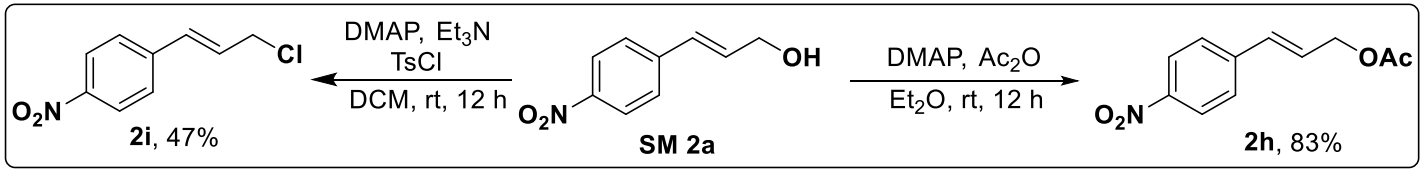


2.3 Synthesis of 1-((1*E*,3*E*)-5-bromopenta-1,3-dien-1-yl)-4-nitrobenzene (2g):

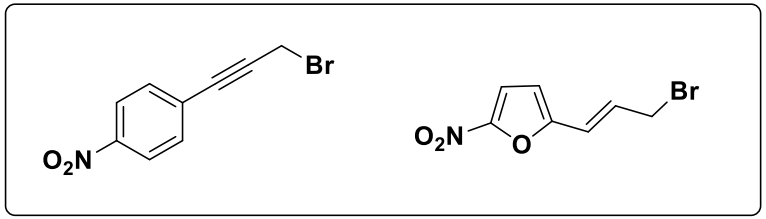


An oven-dried 50 mL RB flask was charged with a solution of (2*E*,4*E*)-5-(4-nitrophenyl)penta-2,4-dien-1-ol **SM 4** (1 equiv, 2 mmol, 410 mg) in diethyl ether (15 mL) at 0 ^{o}C under a N_2 atmosphere. Then, PBr_3 (0.4 equiv, 0.8 mmol, 0.08 mL) was added slowly, and the resulting reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with 10 mL of a saturated aqueous solution of $NaHCO_3$ and extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed with a saturated aqueous solution of sodium thiosulfate (15 mL) and brine (10 mL) and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/Hex, 10:90) on silica gel to afford **2g** of product as a yellow solid in 69% yield.

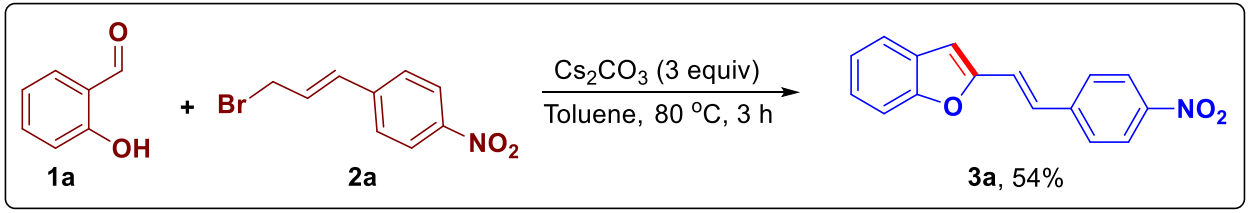
2.4 (*E*)-3-(4-Nitrophenyl)allyl acetate (2h) and (*E*)-1-(3-chloroprop-1-en-1-yl)-4-nitrobenzene (2i) were synthesized according to literature reports:[3]



Starting materials with unproductive reactions:

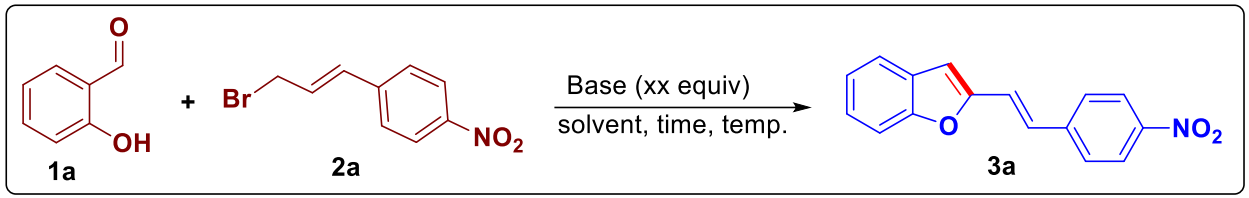


3. Experimental procedure for the synthesis of (*E*)-2-(4-nitrostyryl)benzofuran 3a



Salicylaldehyde **1a** (1 equiv, 0.5 mmol, 61 mg) and (*E*)-1-(3-bromoprop-1-en-1-yl)-4-nitrobenzene **2a** (1.3 equiv, 0.65 mmol, 157 mg) were taken in a 15 mL clean and dry screw caped-vial then were added toluene (4 mL) followed by Cs_2CO_3 (3 equiv, 1.5 mmol, 489 mg). The reaction mixture was stirred at 80 ^oC (temperature of the metal block). After completion of the reaction (monitored by TLC), the reaction mixture was diluted with water (10 mL) and extracted using EtOAc (2 x 100 mL). The combined organic layer was washed with brine (5 mL) and the separated organic layer was dried with anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/hexane, 5:95) on silica gel to obtain (*E*)-2-(4-nitrostyryl)benzofuran **3a** as a yellow solid in 54% yield.

4. General procedure for the optimization study of the sequential *O*-allylation and intramolecular styrylogous aldol condensation

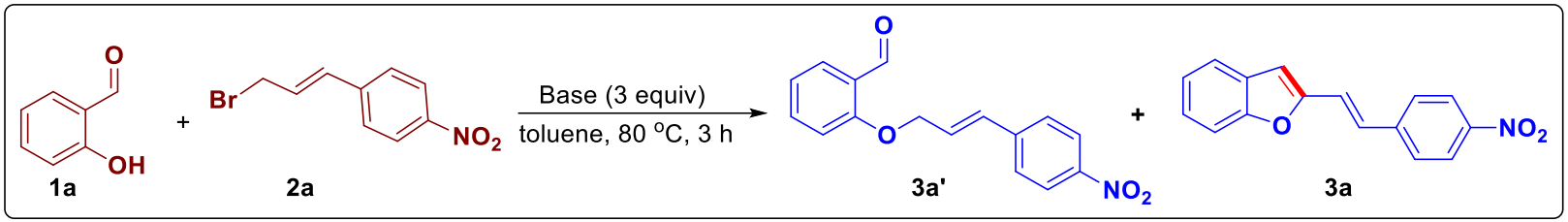


Salicylaldehyde **1a** (1 equiv, 0.5 mmol, 61 mg), and (*E*)-1-(3-bromoprop-1-en-1-yl)-4-nitrobenzene **2a** (1.3 equiv, 0.65 mmol, 129 mg) were taken in a 15 mL clean and dry screw caped-vial with solvent (4 mL); base (3 equiv, 1.5 mmol) was added to the reaction mixture and then stirred at the temperature (temperature of the heated metal block) and time as mentioned in the optimization Tables T1-T3. After this time, the reaction mixture was cooled to room temperature, diluted with water (20 mL), and extracted with ethyl acetate (2 x 20 mL). The combined organic layer was washed with brine (5 mL) and the separated organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/Hexane, 5:95) on 100-200 mesh silica gel to afford the (*E*)-2-(4-nitrostyryl)benzofuran **3a** as a pure product.

Note: **please see tables S1-S3, for screening of various bases, solvents, leaving groups and reaction conditions**

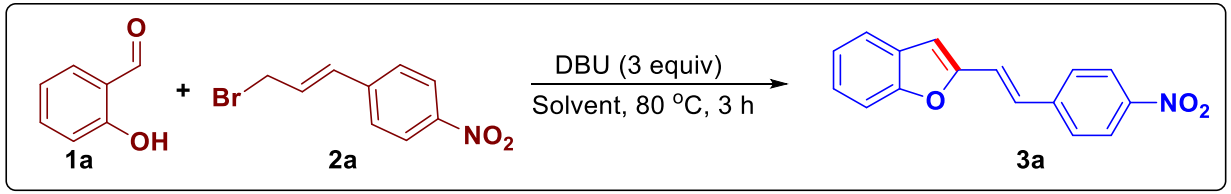
5. Optimization survey

Table S1: Screening of various bases



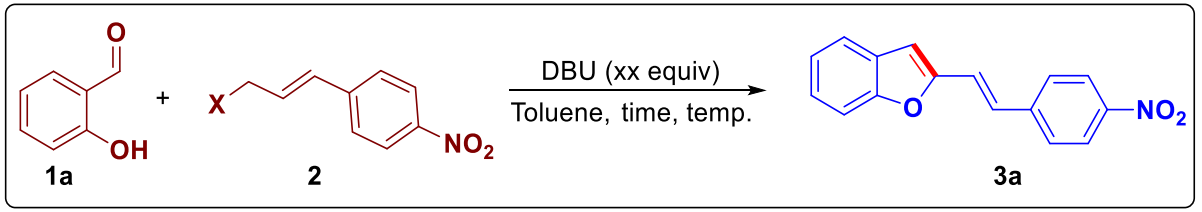
Entry	Base	% Yield of 3a'	% Yield of 3a
1	Cs_2CO_3	–	54
2	K_2CO_3	38	–
3	KO^tBu	–	62
4	K_3PO_4	44	–
5	**1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)**	–	**71**
6	Et_3N	58	trace
7	NaH	38	30
8	KOH		30
9	No Base	–	–

Table S2: Screening of various solvents



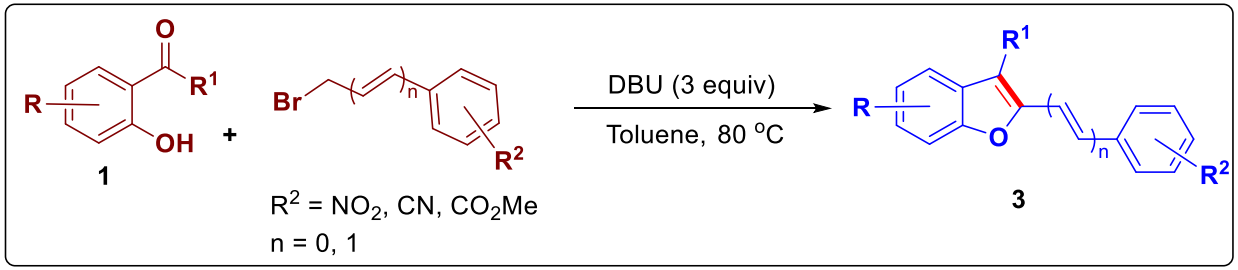
Entry	Solvent	Temp (°C)	% Yield of 3a
1	**Toluene**	**80**	**71**
2	DMF	80	60
3	CH_3CN	80	58
4	Dimethyl sulfoxide (DMSO)	80	52
5	*t*-BuOH	80	trace
6	1,2-Dichloroethane (DCE)	80	trace
7	THF	80	43
8	NMP	80	64

Table S3: Screening of leaving group X in 2, molar equivalents of DBU and reaction conditions



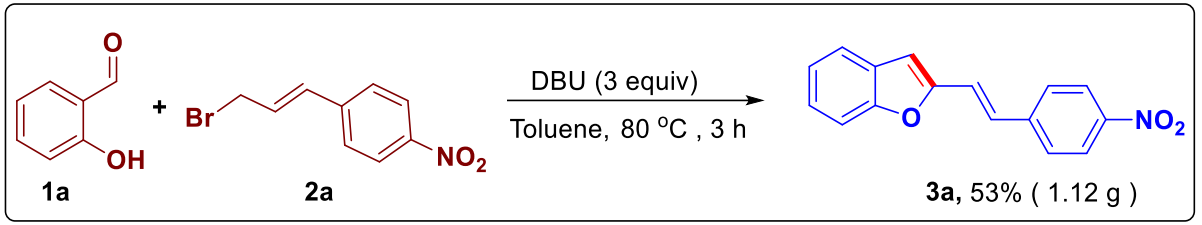
Entry	DBU (xx equiv)	X in 2	Temp (°C)	Time (h)	% Yield of 3a
1	2	Br	80	3	42
2	**3**	**Br**	**80**	**3**	**71**
3	4	Br	80	3	67
4	3	Br	40	3	-
5	3	Br	60	3	30
6	3	Br	120	3	52
7	3	Br	80	1	22
8	3	Br	80	2	47
9	3	Br	80	12	66
10	3	OAc	80	3	63
11	3	Cl	80	3	54
12	-	Br	80	3	-

6. General procedure for the synthesis of substituted benzofuran derivatives 3a-3af



Substituted *ortho*-hydroxy aryl aldehyde/ketone **1** (1 equiv, 0.5 mmol) and the substituted cinnamyl bromide **2** (1.2 equiv, 0.6 mmol) were taken in a 15 mL clean and dry screw caped-vial in toluene (4 mL); DBU (3 equiv, 1.5 mmol, 0.22 mL) was added to the reaction mixture. The reaction mixture was then stirred at 80 ^{o}C (temperature of the metal block). After consumption of the starting material, the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with brine (5 mL) and the organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/Hexane) on 100-200 mesh silica gel to afford the desired compounds **3a-3af** as pure products.

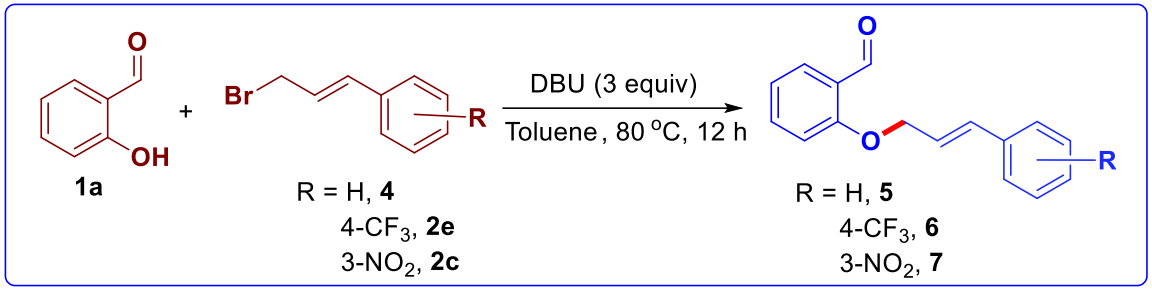
7. Gram-scale synthesis of 3a



1a 2a **3a**, 53% (1.12 g)

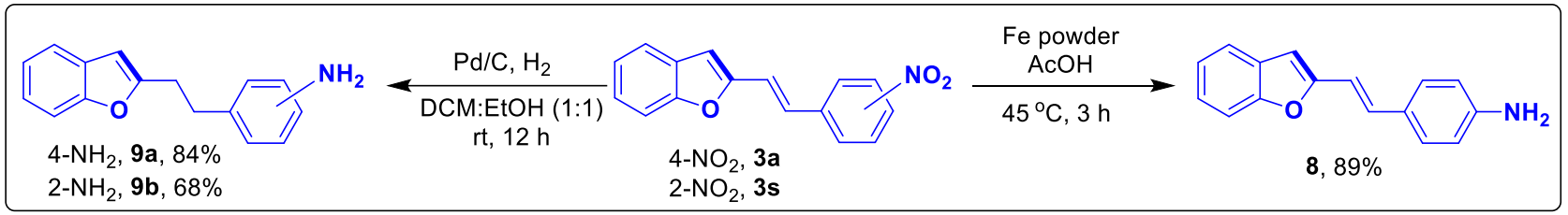
Salicylaldehyde **1a** (1 equiv, 8 mmol, 0.98 mL), and (*E*)-1-(3-bromoprop-1-en-1-yl)-4-nitrobenzene **2a** (1.2 equiv, 9.6 mmol, 2.3 g) were taken in a clean and dried round bottom flask in toluene (70 mL); DBU (3 equiv, 24 mmol, 3.65 mL) was added to the reaction mixture. Then the reaction mixture was stirred at 80 ^{o}C (oil bath) for 3 h. After this time, the reaction mixture was cooled to room temperature, diluted with water (120 mL), and extracted with ethyl acetate (2 × 50 mL). The combined organic layer was washed with brine (30 mL) and the organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/Hexane, 10:90) on 100-200 mesh silica gel to afford **3a** as a yellow solid in 53% yield (1.12 g).

8. Control experiments



Salicylaldehyde **1a** (1 equiv, 0.5 mmol, 0.5 mL), and substituted cinnamyl bromide **4/2e/2c** (1.2 equiv, 0.6 mmol) were taken in a 15 mL clean and dry screw caped-vial in toluene (4 mL); DBU (3 equiv, 1.5 mmol, 0.22 mL) was added to the reaction mixture. The reaction mixture was stirred at 80 ^{o}C (temperature of the heated metal block) 12 h. After this time, the reaction mixture was cooled to room temperature, diluted with water (30 mL), and extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with brine (10 mL) and the organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/Hexane, 5:95) on 100-200 mesh silica gel to afford the corresponding *O*-cinnamyl derivatives **5**, **6** and **7** in 87%, 34% and 60% yields, respectively.

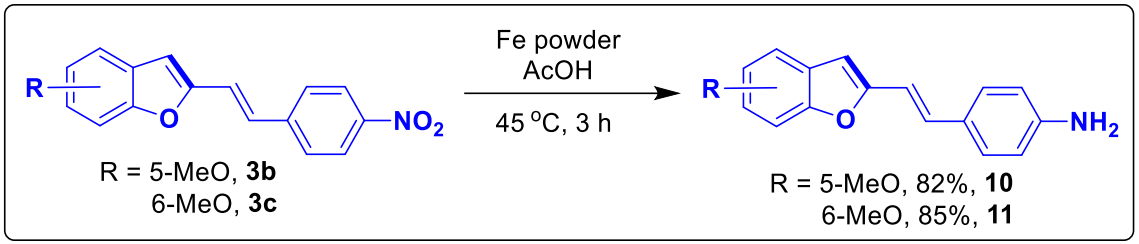
9. Post-synthetic transformations of benzofuran 3a and 3s



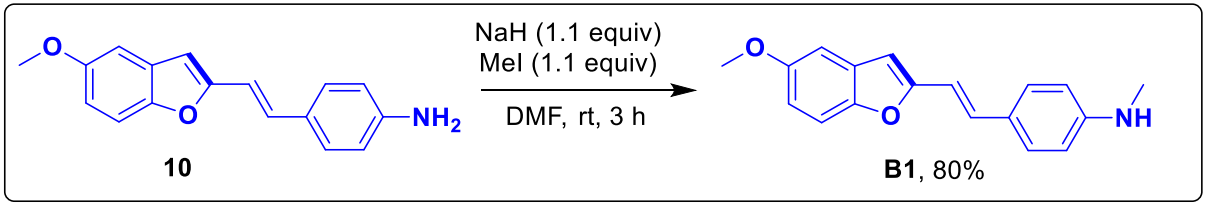
To a solution of (*E*)-2-(4-nitrostyryl)benzofuran **3a** (1 equiv, 0.5 mmol, 133 mg) in AcOH (2 mL) was added Fe powder (5 equiv, 2.5 mmol, 138 mg) and the mixture was heated at 45 °C for 3 h. Then the reaction mixture was cooled to room temperature and poured into ice water, followed by neutralization with saturated $NaHCO_3$ solution. The precipitated solid was separated by filtration through a Celite® bed, which was repeatedly washed with EtOAc (2 x 10 mL). The obtained filtrate was concentrated under reduced pressure to afford a crude reaction mixture. The crude extract was further diluted with water (20 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with brine (10 mL) and the organic phase was dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to give a crude residue. The crude was purified by column chromatography (EtOAc/Hexane, 20:80) on 100-200 mesh silica gel to afford **8** as a brown solid in 89% yield.

In an RB flask, a stirred solution of **3a/3s** (1 equiv, 0.38 mmol, 100 mg) in EtOH: DCM (3 mL each) was taken. To this stirred solution, 10% (wt/v) Pd/C (70 mg) was added at room temperature, and the flask was purged with N_2. The reaction mixture was evacuated (1-3 sec) by applying a vacuum and filled with H2; then the reaction mixture was stirred under an H_2 (balloon) atmosphere for 12 h. The mixture was then filtered through a plug of Celite® pad, washed with EtOH (2 x 10 mL), and the filtrate was concentrated. The crude product was purified by column chromatography (EtOAc/hexane) to afford products **9a** and **9b** in 84% and 68% yield, respectively.

10. Synthesis of biologically active aminostyryl-benzofurans B1 and B2

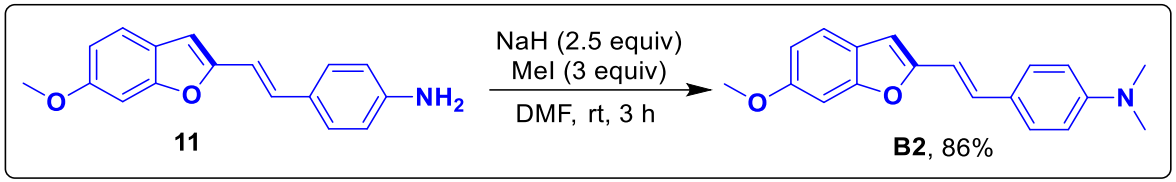


To a solution of (*E*)-5-methoxy-2-(4-nitrostyryl)benzofuran **3b**/(*E*)-6-methoxy-2-(4-nitrostyryl)benzofuran **3c** (1 equiv, 0.5 mmol) in AcOH (2 mL) was added Fe powder (5 equiv, 2.5 mmol, 138 mg) and the mixture was heated at 45 °C for 3 h. The reaction mixture was then cooled to rt and poured into ice water, followed by neutralization with saturated $NaHCO_3$ solution. The precipitated solid was separated by filtration through a Celite® bed, which was repeatedly washed with EtOAc (2 x 10 mL). The obtained filtrate was concentrated under reduced pressure to afford a crude reaction mixture. The crude extract was diluted with water (20 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with brine (10 mL) and the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain **10** or **11**. They were taken to the next step without further purification.



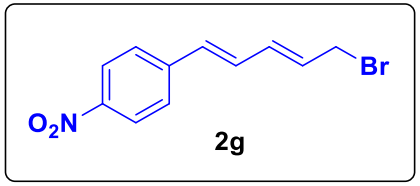
To a solution of substituted benzofuran **10** (1 equiv, 0.25 mmol, 72 mg) in DMF (5 mL) at 0 °C under N_2 atmosphere, NaH (1.1 equiv, 0.28 mmol, 11 mg) was added slowly, and the resulting reaction mixture was stirred at 0 °C for 30 min. After this time, iodomethane (1.1 equiv, 0.28 mmol, 0.017 mL) was added to the reaction mixture slowly, and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was

then quenched with cold water (10 mL) and extracted with EtOAc (2 x 10 mL). The combined organic phase was washed with brine (5 mL) and dried over anhydrous Na_2SO_4, and the filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane) on 100-200 mesh silica gel to afford the desired compound **B1** in 80% yield.

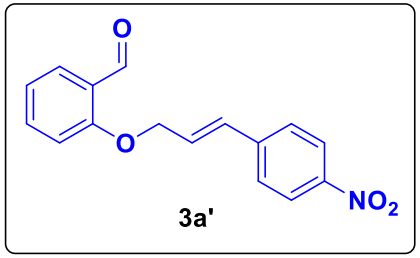


To a solution of substituted benzofuran **11** (1 equiv, 0.25 mmol, 72 mg) in DMF (5 mL) at 0 ^oC under N_2 atmosphere, NaH (2.5 equiv, 0.265 mmol, 25 mg) was added slowly, and the resulting reaction mixture was stirred at 0 ^oC for 30 min. After this time, iodomethane (3 equiv, 0.75 mmol, 0.05 mL) was slowly added to the reaction mixture, and the resulting mixture was stirred at room temperature for 3 h. Then, the reaction mixture was quenched with cold water (20 mL) and extracted with EtOAc (2 x 20 mL). The combined organic phase was washed with brine (10 mL) and dried over anhydrous Na_2SO_4, and the filtrate was concentrated under reduced pressure to obtain a crude residue. The crude was purified using column chromatography (EtOAc/Hexane) on 100-200 mesh silica gel to afford the desired compound **B2** in 86% yield.

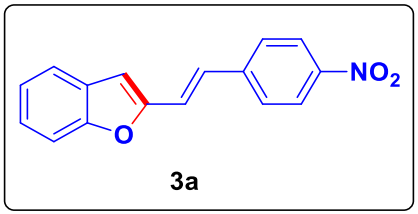
11. Spectral data



1-((1*E*,3*E*)-5-Bromopenta-1,3-dien-1-yl)-4-nitrobenzene (2g):- Yellow solid, 368 mg (1.38 mmol), 69% yield; R_f = 0.5 (EtOAc/Hex, 5:95); **MP** 116-118 ^oC; **IR** ($CHCl_3$) 3031, 2928, 1589, 1507, 1332 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.49 (m, 2H), 6.90 (dd, *J* = 15.6, 10.6 Hz, 1H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.51 – 6.44 (m, 1H), 6.19 – 6.08 (m, 1H), 4.09 (d, *J* = 7.9 Hz, 2H); **^{13}C{^{1}H}-NMR** (151 MHz, $CDCl_3$) δ = 147.1, 143.3, 134.2, 132.3, 131.9, 127.1, 124.2, 32.5; **HRMS** (ESI, *m/z*): calcd for $C_{11}H_9O_2N^{79}Br$ $[M-H]^+$ 265.9817, found 265.9843.

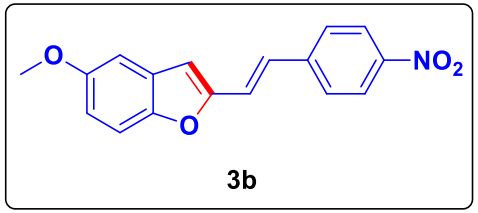


(*E*)-2-((3-(4-Nitrophenyl)allyl)oxy)benzaldehyde (3a'):- White solid, 82 mg (0.29 mmol), 58% yield, R_f = 0.3 (EtOAc/Hex, 10:90); **MP** 113-115 ^oC; **IR** ($CHCl_3$) 3024, 1685, 1596, 1515, 1341 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 10.57 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.87 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.57 (dd, *J* = 11.4, 5.2 Hz, 3H), 7.13 – 6.99 (m, 2H), 6.86 (d, *J* = 16.1 Hz, 1H), 6.64 – 6.58 (m, 1H), 4.88 (dd, *J* = 5.1, 1.5 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 189.7, 160.7, 147.4, 142.7, 136.1, 130.8, 129.0, 128.6, 127.3, 125.3, 124.2, 121.4, 112.9, 68.5; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{14}O_4N$ $[M+H]^+$ 284.0923, found 284.0901. The spectroscopic data were in good agreement with the reported data.[4]



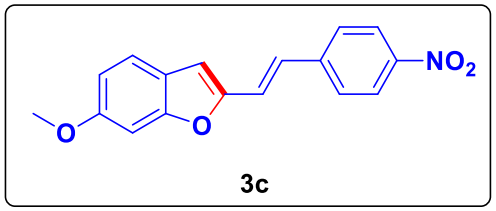
3a

(*E*)-2-(4-Nitrostyryl)benzofuran (3a):- Yellow solid, 94 mg (0.355 mmol), 71% yield, R_f = 0.6 (EtOAc/Hex, 5:95); **MP** 167-169 ^oC; **IR** ($CHCl_3$) 3061, 1591, 1511, 1337, 948 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 16.1 Hz, 1H), 6.82 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.3, 154.0, 147.1, 128.9, 127.6, 127.2, 125.7, 124.4, 123.4, 121.4, 120.7, 111.2, 107.9; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{12}O_3N$ $[M+H]^+$ 266.0817., found 266.0823.



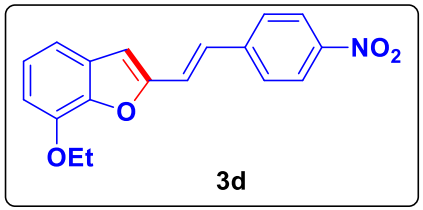
3b

(*E*)-5-Methoxy-2-(4-nitrostyryl)benzofuran (3b):- Yellow solid, 105 mg (0.355 mmol), 71% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 195-197 ^oC; **IR** ($CHCl_3$) 3077, 2921, 1593, 1510, 1337, 948 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.21 (d, *J* = 10.3 Hz, 1H), 7.06 (d, *J* = 16.1 Hz, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.69 (s, 1H), 3.79 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 156.3, 154.8, 150.4, 147.1, 143.2, 129.5, 127.4, 127.1, 124.4, 120.7, 114.7, 111.7, 108.1, 103.5, 56.1; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{14}O_4N$ $[M+H]^+$ 296.0923, found 296.0939.



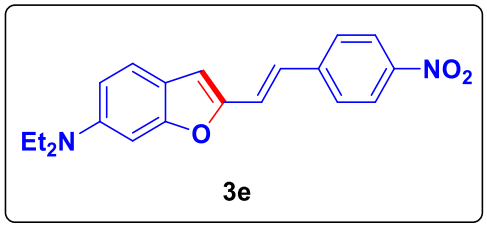
3c

(*E*)-6-Methoxy-2-(4-nitrostyryl)benzofuran (3c):- Red solid, 112 mg (0.38 mmol), 76% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 162-164 °C; **IR** ($CHCl_3$) 3076, 2923, 1618, 1589, 1511, 1336, 957 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 6.2 Hz, 1H), 7.15 (d, *J* = 16.1 Hz, 1H), 7.07 (s, 1H), 6.93 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.79 (s, 1H), 3.93 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 159.2, 156.5, 153.4, 146.8, 143.5, 126.9, 126.1, 124.3, 122.3, 121.6, 120.7, 112.5, 108.1, 95.8, 55.9; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{14}O_4N$ $[M+H]^+$ 296.0923, found 296.0935.



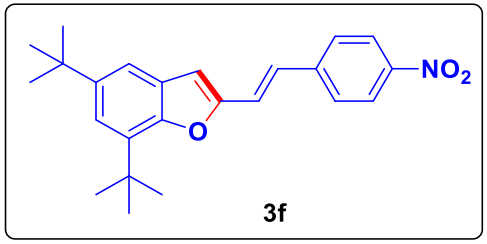
3d

(*E*)-7-Ethoxy-2-(4-nitrostyryl)benzofuran (3d):- Yellow solid, 100 mg (0.425 mmol), 65% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 118-120 °C; **IR** ($CHCl_3$) 3076, 2981, 1590, 1511, 1332, 949 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 16.2 Hz, 1H), 7.19 – 7.11 (m, 3H), 6.85 (dd, *J* = 6.2, 2.6 Hz, 1H), 6.81 (s, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 1.56 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 154.1, 147.1, 144.7, 144.6, 143.2, 130.6, 127.8, 127.1, 124.3, 124.0, 120.5, 113.6, 109.0, 108.0, 64.8, 15.1; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{16}O_4N$ $[M+H]^+$ 310.10738, found 310.10744.



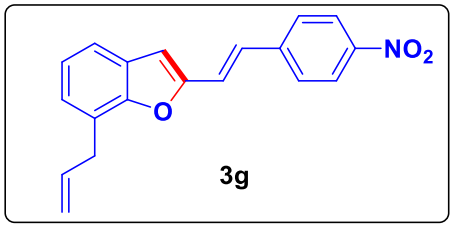
3e

(*E*)-*N*,*N*-Diethyl-2-(4-nitrostyryl)benzofuran-6-amine (3e):- Light black solid, 109 mg (0.325 mmol), 65% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 146-148 ^oC; **IR** ($CHCl_3$) 3062, 2967, 2922, 1617, 1583, 1335, 949 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.11 (q, *J* = 16.0 Hz, 2H), 6.76 – 6.65 (m, 3H), 3.43 (q, *J* = 7.0 Hz, 4H), 1.22 (t, *J* = 7.0 Hz, 6H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 158.1, 151.8, 147.6, 146.5, 144.0, 126.6, 124.4, 124.2, 121.7, 120.9, 118.2, 110.0, 108.8, 93.4, 45.1, 12.7; **HRMS** (ESI, *m/z*): calcd for $C_{20}H_{21}O_3N_2$ $[M+H]^+$ 337.1552, found 337.1541.

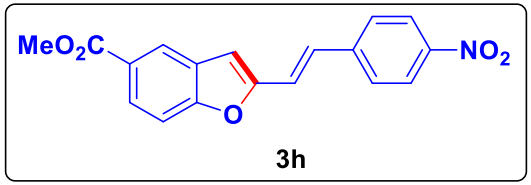


3f

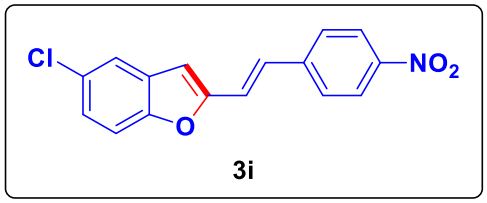
(*E*)-5,7-Di-*tert*-butyl-2-(4-nitrostyryl)benzofuran (3f):- Yellow solid, 70 mg (0.185 mmol), 37% yield, R_f = 0.7 (EtOAc/Hex, 5:95); **MP** 87-89 ^oC; **IR** ($CHCl_3$) 3069, 2958, 1593, 1517, 1340, 956 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.17 (d, *J* = 16.1 Hz, 1H), 6.78 (s, 1H), 1.57 (s, 9H), 1.38 (s, 9H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 153.3, 151.8, 147.0, 146.2, 143.5, 133.9, 129.1, 127.1, 126.6, 124.3, 121.2, 120.7, 115.4, 108.3, 35.0, 34.7, 32.0, 30.2; **HRMS** (ESI, *m/z*): calcd for $C_{24}H_{28}O_3N$ $[M+H]^+$ 378.2069, found 378.2059.



(*E*)-7-Allyl-2-(4-nitrostyryl)benzofuran (3g):- Yellow solid, 90 mg (0.295 mmol), 59% yield, R_f = 0.4 (EtOAc/Hex, 5:95); **MP** 147-149 ^oC; **IR** ($CHCl_3$) 3079, 2923, 1592, 1514, 1337, 954 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.43 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.33 (d, *J* = 16.1 Hz, 1H), 7.21 – 7.13 (m, 3H), 6.82 (s, 1H), 6.18 – 6.08 (m, 1H), 5.24 – 5.14 (m, 2H), 3.74 (d, *J* = 6.7 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 153.8, 147.1, 143.3, 135.9, 128.7, 127.4, 127.1, 125.8, 124.4, 123.8, 123.6, 120.8, 119.4, 116.5, 108.2, 34.0; **HRMS** (ESI, *m/z*): calcd for $C_{19}H_{14}O_3N$ $[M-H]^+$ 304.0968, found 304.0979.

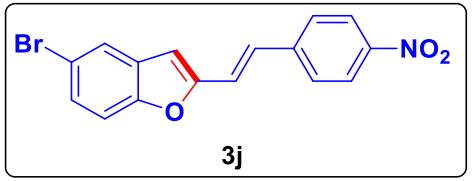


Methyl (*E*)-2-(4-nitrostyryl)benzofuran-5-carboxylate (3h):- Yellow solid, 76 mg (0.235 mmol), 47% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 156-158 ^oC; **IR** ($CHCl_3$) 3081, 2986, 1717, 1514, 1333 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 1.5 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 16.2 Hz, 1H), 7.16 (d, *J* = 16.1 Hz, 1H), 6.87 (s, 1H), 3.95 (s, 3H); **^{13}C{^{1}H}-NMR** (151 MHz, $CDCl_3$) δ = 167.2, 157.8, 155.4, 147.4, 142.9, 129.0, 128.6, 128.3, 128.0, 127.6, 127.3, 125.8, 124.4, 123.8, 120.2, 111.1, 107.8, 52.3; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{13}O_5N$ $[M]^+$ 323.0788, found 323.0791.



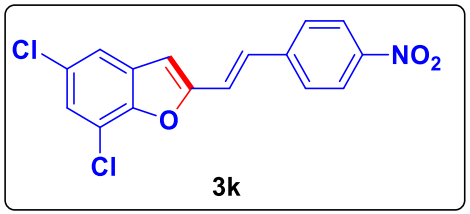
3i

(*E*)-5-Chloro-2-(4-nitrostyryl)benzofuran (3i):- Yellow solid, 85 mg (0.265 mmol), 57% yield, R_f = 0.7 (EtOAc/Hex, 10:90); **MP** 215-217 ^oC; **IR** ($CHCl_3$) 3083, 1604, 1519, 1343, 958 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.43 – 7.28 (m, 3H), 7.13 (d, *J* = 16.1 Hz, 1H), 6.76 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.4, 153.7, 147.3, 142.9, 130.3, 128.9, 128.6, 127.3, 125.8, 124.4, 120.9, 120.2, 112.2, 107.1; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{11}O_3N^{35}Cl$ $[M+H]^+$ 300.0427, found 300.0412.



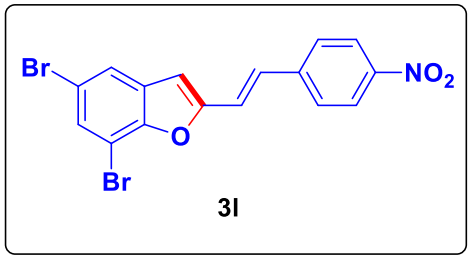
3j

(*E*)-5-Bromo-2-(4-nitrostyryl)benzofuran (3j):- Yellow solid, 110 mg (0.32 mmol), 64% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 207-209 ^oC; **IR** ($CHCl_3$) 3081, 1588, 1507, 1333, 948 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.28 – 8.21 (m, 2H), 7.72 – 7.62 (m, 3H), 7.43 – 7.34 (m, 3H), 7.13 (d, *J* = 16.1 Hz, 1H), 6.75 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.3, 154.0, 147.3, 142.8, 130.9, 128.6, 128.5, 127.3, 124.4, 124.0, 120.2, 116.4, 112.7, 106.9; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{11}O_3N^{79}Br$ $[M+H]^+$ 343.9922, found 343.9883.



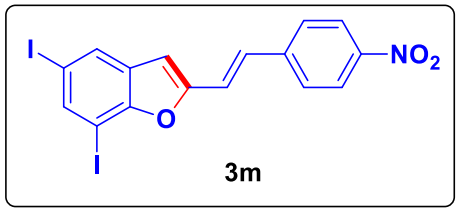
3k

(*E*)-5,7-Dichloro-2-(4-nitrostyryl)benzofuran (3k):- Yellow solid, 100 mg (0.3 mmol), 60% yield, R_f = 0.7 (EtOAc/Hex, 10:90); **MP** 211-213 ^oC; **IR** ($CHCl_3$) 3081, 1593, 1512, 1337, 947 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.28 – 8.21 (m, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.44 (dd, *J* = 9.0, 7.1 Hz, 2H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.13 (d, *J* = 16.2 Hz, 1H), 6.78 (s, 1H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 156.1, 149.7, 147.5, 142.5, 131.2, 129.7, 129.2, 127.5, 125.6, 124.4, 119.6, 119.5, 117.3, 107.2; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_9O_3N^{35}Cl_2$ $[M]^+$ 332.9954, found 332.9955.

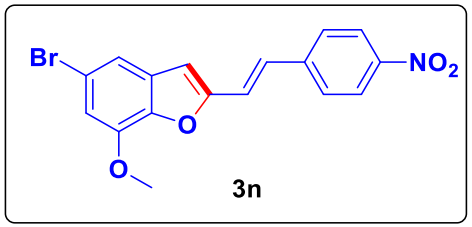


3l

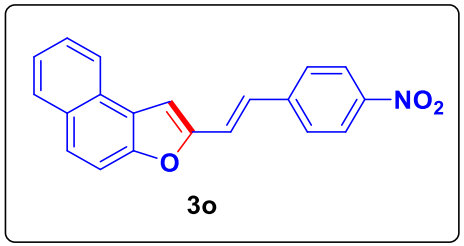
(*E*)-5,7-Dibromo-2-(4-nitrostyryl)benzofuran (3l):- Yellow solid, 120 mg (0.285 mmol), 57% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 149-151 ^oC; **IR** ($CHCl_3$) 3078, 1594, 1513, 1338, 941 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.62 (dd, *J* = 12.6, 1.7 Hz, 2H), 7.49 – 7.41 (m, 1H), 7.13 (d, *J* = 16.2 Hz, 1H), 6.81 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.9, 151.4, 147.5, 142.5, 134.8, 131.5, 130.7, 129.7, 128.1, 127.5, 124.4, 123.1, 119.5, 116.5, 107.1, 104.7; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_9O_3N^{79}Br_2$ $[M]^+$ 420.8944, found 420.8942.



(*E*)-5,7-Diiodo-2-(4-nitrostyryl)benzofuran (3m):- Yellow solid, 137 mg (0.265 mmol), 53% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 162-164 ^oC; **IR** ($CHCl_3$) 3069, 1591, 1511, 1336, 953 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 1.4 Hz, 1H), 7.84 (d, *J* = 1.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 16.1 Hz, 1H), 7.12 (d, *J* = 16.1 Hz, 1H), 6.83 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.2, 155.1, 147.5, 142.6, 141.4, 131.1, 130.1, 129.7, 127.5, 124.4, 119.6, 107.0, 87.0, 76.0; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_9O_3NI_2$ $[M]^+$ 516.8666, found 516.8862.

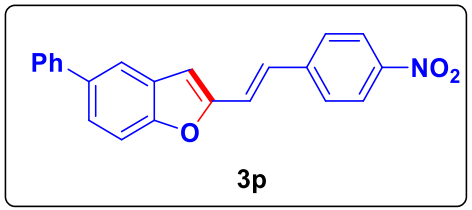


(*E*)-5-Bromo-7-methoxy-2-(4-nitrostyryl)benzofuran (3n):- Yellow solid, 108 mg (0.29 mmol), 58% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 110-112 ^oC; **IR** ($CHCl_3$) 3081, 2923, 1592, 1514, 1339, 957 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 16.2 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 7.12 (d, *J* = 16.2 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 6.74 (s, 1H), 4.04 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.1, 147.3, 145.6, 143.5, 142.9, 131.7, 128.7, 127.3, 124.4, 120.0, 116.4, 116.3, 111.2, 107.1, 56.5; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{13}{}^{79}BrO_4N$ $[M+H]^+$ 374.0028, found 374.0038.



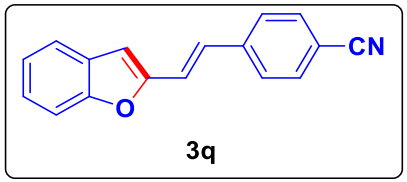
3o

(*E*)-2-(4-Nitrostyryl)naphtho[2,1-*b*]furan (3o):- Yellow solid, 123 mg (0.39 mmol), 78% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 220-222 °C; **IR** ($CHCl_3$) 3060, 2922, 1592, 1514, 1339, 954 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 3H), 7.63 – 7.59 (m, 1H), 7.53 – 7.50 (m, 1H), 7.36 (d, *J* = 16.1 Hz, 1H), 7.31 (s, 1H), 7.23 (d, *J* = 16.1 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 153.6, 153.2, 147.0, 143.4, 130.6, 130.5, 129.1, 127.0, 126.9, 126.84, 126.75, 125.1, 124.4, 123.6, 120.7, 112.2, 106.9; **HRMS** (ESI, *m/z*): calcd for $C_{20}H_{14}O_3N$ $[M+H]^+$ 316.0895, found 316.0924.



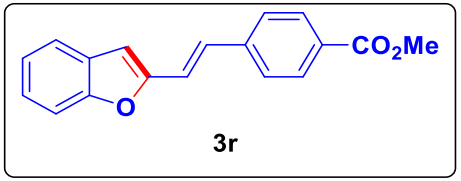
3p

(*E*)-2-(4-Nitrostyryl)-5-phenylbenzofuran (3p):- Yellow solid, 124 mg (0.365 mmol), 73% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 166-168 °C; **IR** ($CHCl_3$) 3057, 2922, 1593, 1514, 1340, 959 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.7 Hz, 2H), 7.76 (s, 1H), 7.64 (dd, *J* = 16.1, 8.0 Hz, 4H), 7.57 – 7.54 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 11.7, 4.3 Hz, 2H), 7.17 (d, *J* = 16.1 Hz, 1H), 6.86 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.0, 154. 7, 147.2, 144.0, 143.2, 141.5, 140.1, 127.1, 129.5, 128.9, 127.8, 127.5, 127.2, 125.5, 124.4, 120.6, 119.9, 111.3, 108.1; **HRMS** (ESI, *m/z*): calcd for $C_{22}H_{16}O_3N$ $[M+H]^+$ 342.1130, found 342.1107.



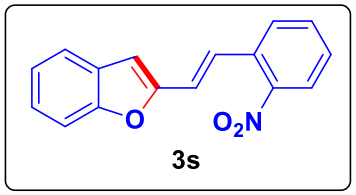
3q

(*E*)-4-(2-(Benzofuran-2-yl)vinyl)benzonitrile (3q):- White solid, 43 mg (0.175 mmol), 35% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 165-167 ^oC; **IR** ($CHCl_3$) 3039, 2219, 1594, 1449, 945 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.48 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.26 – 7.21 (m, 2H), 7.09 (d, *J* = 16.1 Hz, 1H), 6.77 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.2, 154.1, 141.2, 132.7, 128.9, 128.0, 127.1, 125.5, 123.3, 121.3, 119.8, 119.1, 111.2, 111.1, 107.5; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{12}ON$ $[M+H]^+$ 246.0919, found 246.0909. The spectroscopic data were in good agreement with the reported data.[5]



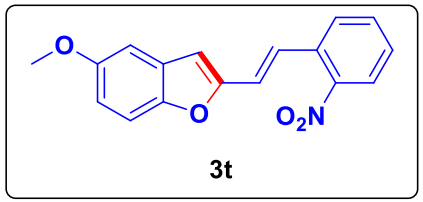
3r

Methyl (*E*)-4-(2-(benzofuran-2-yl)vinyl)benzoate (3r):- White solid, 26 mg (0.095 mmol), 19% yield, R_f = 0.3 (EtOAc/Hex, 5:95); **MP** 176-178 ^oC; **IR** ($CHCl_3$) 3024, 2987, 1716, 1423, 963 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 15.4, 7.9 Hz, 3H), 7.50 – 7.47 (m, 1H), 7.36 – 7.28 (m, 2H), 7.24 – 7.20 (m, 1H), 7.11 (d, *J* = 16.1 Hz, 1H), 6.75 (s, 1H), 3.93 (s, 3H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 166.9, 155.2, 154.6, 141.2, 130.2, 129.5, 129.1, 126.6, 125.2, 123.2, 121.2, 118.9, 111.1, 106.7, 52.3; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{15}O_3$ $[M+H]^+$ 279.1021, found 279.1001.



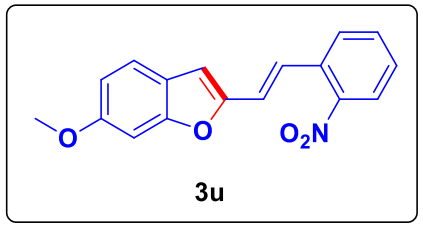
3s

(*E*)-2-(2-Nitrostyryl)benzofuran (3s):- Yellow solid, 90 mg (0.34 mmol), 68% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 103-105 ^oC; **IR** ($CHCl_3$) 3067, 1587, 1511, 1339, 943 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.80-7.74 (m, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.34 – 7.30 (m, 1H), 7.25 – 7.21 (m, 1H), 7.02 (d, *J* = 15.9 Hz, 1H), 6.79 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.3, 154.2, 148.3, 133.2, 132.3, 128.9, 128.5, 127.9, 125.5, 125.0, 124.7, 123.2, 121.4, 121.3, 111.4, 107.3; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{12}O_3N$ $[M+H]^+$ 266.0817, found 266.0798.



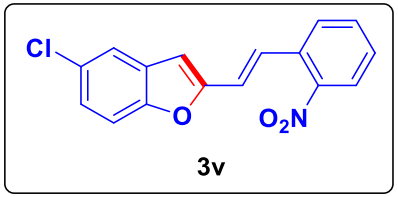
3t

(*E*)-5-Methoxy-2-(2-nitrostyryl)benzofuran (3t):- Yellow solid, 90 mg (0.305 mmol), 61% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 104-106 ^oC; **IR** ($CHCl_3$) 3084, 2923, 1604, 1518, 1472, 952 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 16.3, 8.3 Hz, 2H), 7.03 – 6.89 (m, 3H), 6.73 (s, 1H), 3.85 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 156.2, 155.0, 150.3, 148.3, 133.2, 132.3, 129.4, 128.4, 127.9, 125.0, 124.5, 121.5, 114.4, 111.9, 107.4, 103.5, 56.0; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{14}O_4N$ $[M+H]^+$ 296.0923, found 296.0924.



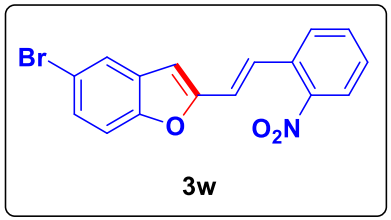
3u

(*E*)-6-Methoxy-2-(2-nitrostyryl)benzofuran (3u):- Yellow Liquid, 96 mg (0.325 mmol), 65% yield, R_f = 0.7 (EtOAc/Hex, 10:90); **IR** ($CHCl_3$) 3075, 2925, 1694, 1605, 1520, 1265, 958 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 7.95 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 15.9 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.43 – 7.37 (m, 2H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.71 (s, 1H), 3.88 (s, 3H); **^{13}C{^{1}H}-NMR** (151 MHz, $CDCl_3$) δ = 159.1, 156.5, 153.6, 148.2, 133.1, 132.4, 128.2, 127.7, 125.0, 123.1, 122.2, 121.47, 121.45, 112.5, 107.5, 95.8, 55.9; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{14}O_4N$ $[M+H]^+$ 296.0923, found 296.0928.



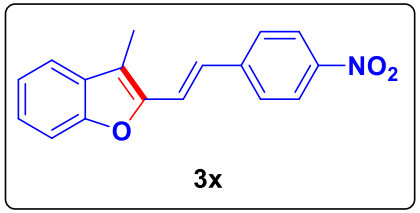
3v

(*E*)-5-Chloro-2-(2-nitrostyryl)benzofuran (3v):- Yellow solid, 111 mg (0.37 mmol), 74% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 123-125 ºC; **IR** ($CHCl_3$) 3078, 1521, 1453, 1345, 955 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.1 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.43 (dd, *J* = 16.5, 8.3 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 6.72 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.6, 153.6, 148.3, 133.3, 132.0, 130.2, 128.8, 128.0, 125.8, 125.6, 125.1, 120.9, 120.8, 112.4, 106.5; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{11}O_3N^{35}Cl$ $[M+H]^+$ 300.0427, found 300.0405.



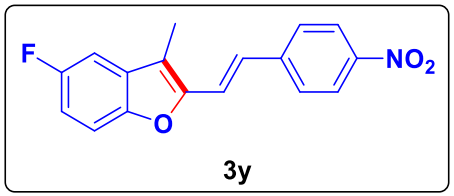
3w

(*E*)-5-Bromo-2-(2-nitrostyryl)benzofuran (3w):- Yellow solid, 117 mg (0.34 mmol), 68% yield, R_f = 0.7 (EtOAc/Hex, 10:90); **MP** 140-142 ^oC; **IR** ($CHCl_3$) 3077, 1604, 1517, 1440, 1342, 950 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 15.1, 12.0 Hz, 2H), 7.63 (dd, *J* = 17.8, 10.3 Hz, 2H), 7.48 – 7.34 (m, 3H), 6.97 (d, *J* = 15.9 Hz, 1H), 6.71 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.4, 154.0, 148.3, 133.3, 132.0, 130.9, 128.8, 128.3, 128.0, 125.9, 125.1, 123.8, 120.9, 116.3, 112.8, 106.4; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{11}O_3N^{79}Br$ $[M+H]^+$ 343.9922, found 343.9889.



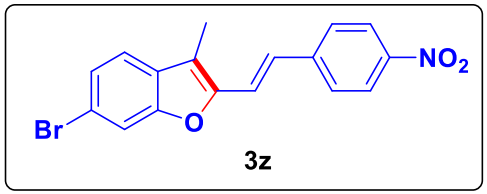
3x

(*E*)-3-Methyl-2-(4-nitrostyryl)benzofuran (3x):- Yellow solid, 60 mg (0.215 mmol), 43% yield, R_f = 0.6 (EtOAc/Hex, 5:95); **MP** 175-177 ^oC; **IR** ($CHCl_3$) 3077, 2920, 1596, 1517, 1344, 948 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.27 (dd, *J* = 5.5, 4.5 Hz, 2H), 7.21 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 154.6, 149.8, 146.9, 143.7, 130.4, 127.0, 126.1, 125.9, 124.4, 122.9, 119.8, 118.7, 116.9, 111.0, 8.5; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{14}O_3N$ $[M+H]^+$ 20974, found 280.1001.



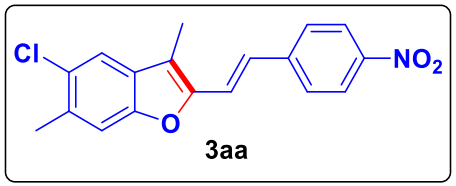
3y

(*E*)-5-Fluoro-3-methyl-2-(4-nitrostyryl)benzofuran (3y):- Yellow solid, 92 mg (0.31 mmol), 62% yield, R_f = 0.7 (EtOAc/Hex, 10:90); **MP** 203-205 °C; **IR** ($CHCl_3$) 3087, 2920, 1591, 1336, 1181, 957 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.27 – 8.21 (m, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.37 (dd, *J* = 8.9, 4.0 Hz, 1H), 7.30 (d, *J* = 16.0 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.07 – 7.02 (m, 1H), 2.35 (s, 3H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 159.38 (d, *J* = 239.4 Hz), 151.5, 150.8, 147.1, 143.4, 131.2 (d, *J* = 10 Hz), 127.1, 126.9, 124.4, 118.4, 116.8, 113.4 (d, *J* = 26.5 Hz), 111.7 (d, *J* = 9.4 Hz), 105.4 (d, *J* = 25.2 Hz), 8.5; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -120.6; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{12}O_3NF$ $[M]^+$ 297.0801, found 297.0760.



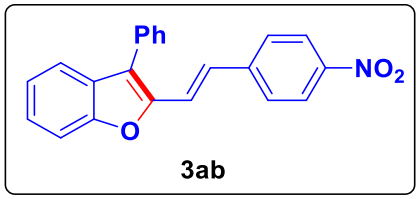
3z

(*E*)-6-Bromo-3-methyl-2-(4-nitrostyryl)benzofuran (3z):- Yellow solid, 120 mg (0.335 mmol), 67% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 192-194 °C; **IR** ($CHCl_3$) 3079, 2921, 1588, 1512, 1337, 950 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.62 – 7.61 (m, 1H), 7.37 (d, *J* = 1.3 Hz, 2H), 7.29 (d, *J* = 16.1 Hz, 1H), 7.17 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 154.8, 150.5, 147.1, 143.4, 129.5, 127.1, 126.8, 126.3, 124.4, 120.7, 119.2, 118.2, 116.5, 114.5, 8.4; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{12}O_3N^{79}Br$ $[M]^+$ 357.0001, found 357.0019.



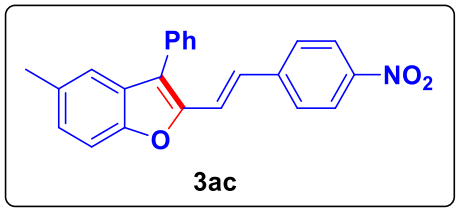
3aa

(*E*)-5-Chloro-3,6-dimethyl-2-(4-nitrostyryl)benzofuran (3aa):- Yellow solid, 65 mg (0.2 mmol), 40% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 189-191 °C; **IR** (KBr) 2921, 1591, 1425, 1103, 876 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.47 (s, 1H), 7.31 (s, 1H), 7.26 (d, *J* = 16 Hz, 1H), 7.16 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 153.3, 150.5, 147.0, 143.5, 133.9, 129.6, 129.2, 127.0, 126.4, 124.4, 119.6, 118.4, 116.2, 112.8, 21.2, 8.5; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{15}N^{35}ClO_3$ $[M+H]^+$ 328.0740, found 328.0754.



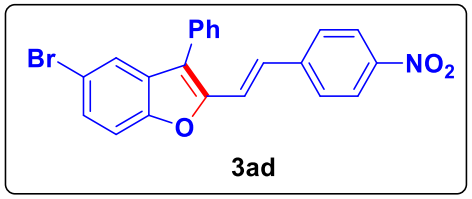
3ab

(*E*)-2-(4-Nitrostyryl)-3-phenylbenzofuran (3ab):- Yellow solid, 95 mg (0.28 mmol), 56% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 186-188 °C; **IR** ($CHCl_3$) 3061, 1590, 1514, 1338, 967 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.67 – 7.61 (m, 2H), 7.61 – 7.53 (m, 5H), 7.50 – 7.46 (m, 1H), 7.39 (dd, *J* = 12.7, 5.6 Hz, 2H), 7.31 – 7.23 (m, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 154.6, 149.7, 146.9, 144.3, 131.8, 129.5, 129.1, 128.7, 128.1, 128.0, 127.1, 126.1, 124.2, 123.4, 122.5, 120.5, 119.3, 111.2; **HRMS** (ESI, *m/z*): calcd for $C_{22}H_{16}O_3N$ $[M+H]^+$ 342.1130, found 342.1118.



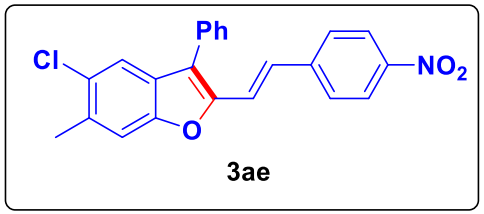
3ac

(*E*)-5-Methyl-2-(4-nitrostyryl)-3-phenylbenzofuran (3ac):- Yellow solid, 75 mg (0.21 mmol), 42% yield, R_f = 0.5 (EtOAc/Hex, 10:90); **MP** 180-182 °C; **IR** ($CHCl_3$) 3082, 2923, 1590, 1336, 946 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.7 Hz, 2H), 7.58 (dd, *J* = 10.2, 6.5 Hz, 6H), 7.49 – 7.40 (m, 4H), 7.23 – 7.18 (m, 2H), 2.45 (s, 3H); **^{13}C{^{1}H}-NMR** (151 MHz, $CDCl_3$) δ = 153.1, 149.9, 146.8, 143.4, 133.0, 131.9, 129.5, 129.1, 128.8, 128.0, 127.7, 127.5, 127.1, 124.2, 122.3, 120.2, 119.4, 110.7, 21.4; **HRMS** (ESI, *m/z*): calcd for $C_{23}H_{18}O_3N$ $[M+H]^+$ 356.1287, found 356.1238.



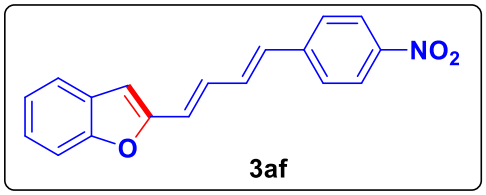
3ad

(*E*)-5-Bromo-2-(4-nitrostyryl)-3-phenylbenzofuran (3ad):- Yellow solid, 170 mg (0.405 mmol), 81% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 178-180 °C; **IR** ($CHCl_3$) 3049, 2921, 1589, 1512, 1338, 948 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.63 – 7.54 (m, 6H), 7.54 – 7.50 (m, 1H), 7.50 – 7.45 (m, 2H), 7.42 (t, *J* = 6.3 Hz, 1H), 7.22 (d, *J* = 16.1 Hz, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 153.5, 151.0, 147.2, 143.1, 131.2, 130.9, 129.5, 129.4, 129.0, 128.5, 127.4, 124.4, 123.2, 121.8, 118.9, 116.6, 112.8; **HRMS** (ESI, *m/z*): calcd for $C_{22}H_{14}O_3N^{79}Br$ $[M]^+$ 419.0157, found 419.0132.



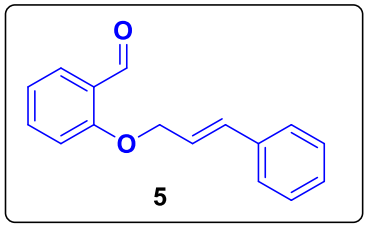
3ae

(*E*)-5-Chloro-6-methyl-2-(4-nitrostyryl)-3-phenylbenzofuran (3ae):- Yellow solid, 113 mg (0.29 mmol), 58% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 131-133 ºC; **IR** ($CHCl_3$) 3058, 2921, 1588, 1515, 1339, 966 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.8 Hz, 2H), 7.60 (dd, *J* = 5.5, 3.2 Hz, 3H), 7.58 – 7.52 (m, 4H), 7.51 – 7.45 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 16.0 Hz, 1H), 2.52 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 153.4, 150.4, 147.1, 143.3, 134.4, 131.5, 129.9, 129.5, 129.4, 128.4, 128.3, 128.1, 127.2, 124.4, 121.9, 120.3, 119.2, 113.0, 21.2; **HRMS** (ESI, *m/z*): calcd for $C_{23}H_{16}O_3N^{35}Cl$ $[M]^+$ 389.0819, found 389.0793.



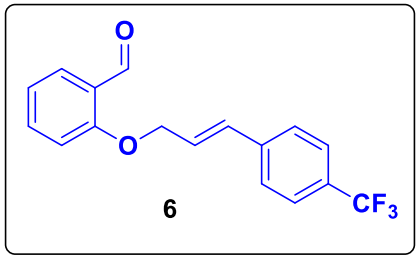
3af

2-((1*E*,3*E*)-4-(4-Nitrophenyl)buta-1,3-dien-1-yl)benzofuran (3af):- Yellow solid, 52 mg (0.18 mmol), 36% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 209-211 ºC; **IR** ($CHCl_3$) 3059, 1586, 1514, 1338, 962 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.8 Hz, 2H), 7.55 (dd, *J* = 12.9, 8.2 Hz, 3H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.32-7.28 (m, 1H), 7.24 – 7.20 (m, 1H), 7.15 (dd, *J* = 14.6, 11.0 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.78 (d, *J* = 14.8 Hz, 1H), 6.72 – 6.67 (m, 2H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 155.3, 154.5, 146.9, 143.7, 133.0, 131.7, 129.9, 129.1, 127.3, 127.0, 125.4, 124.3, 123.2, 123.0, 121.2, 111.1, 106.8; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{13}O_3N$ $[M]^+$ 291.0895, found 291.0898.



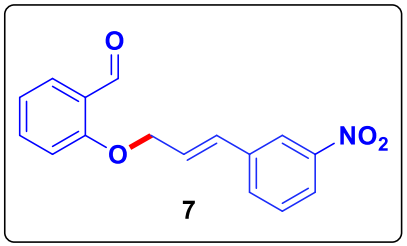
5

2-(Cinnamyloxy)benzaldehyde (5):- White solid, 207 mg (0.87 mmol), 87% yield, R_f = 0.6 (EtOAc/Hex, 5:95); **MP** 60-62 °C; **IR** ($CHCl_3$) 3027, 2862, 1684, 1597, 1456 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 10.58 (d, *J* = 0.7 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64 – 7.46 (m, 5H), 7.09 – 7.02 (m, 2H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.53 (dt, *J* = 16.0, 5.4 Hz, 1H), 4.86 (dd, *J* = 5.4, 1.5 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 189.8, 160.9, 139.7, 136.1, 131.8, 130.2, 129.9, 128.9, 126.9, 126.3, 125.8 (q, *J* = 3.6 Hz), 125.3, 121.3, 112.9, 68.8; **Mass** (ESI, *m/z*): 261 [M+Na]. The spectroscopic data were in good agreement with the reported data.[4]



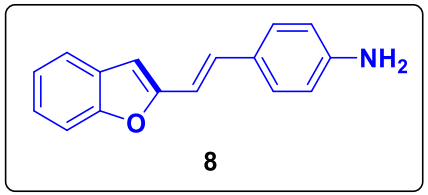
6

(*E*)-2-((3-(4-(Trifluoromethyl)phenyl)allyl)oxy)benzaldehyde (6):- Off-white solid, 52 mg (0.17 mmol), 34% yield, R_f = 0.6 (EtOAc/Hex, 10:90); **MP** 103-105 °C; **IR** ($CHCl_3$) 2924, 2884, 1684, 1597, 1324, 963 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 10.58 (d, *J* = 0.7 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64 – 7.46 (m, 5H), 7.09 – 7.02 (m, 2H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.53 (dt, *J* = 16.0, 5.4 Hz, 1H), 4.86 (dd, *J* = 5.4, 1.5 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 189.8, 160.9, 139.7, 136.1, 131.8, 130.2, 129.9, 128.9, 126.9, 126.3, 125.8 (q, *J* = 3.6 Hz), 125.3, 121.3, 112.9, 68.8; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -62.6; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{12}O_2F_3$ $[M-H]^+$ 305.0789, found 305.0804.



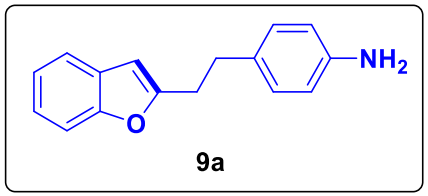
7

(*E*)-2-((3-(3-Nitrophenyl)allyl)oxy)benzaldehyde (7):- White solid, 85 mg (0.30 mmol), 60% yield, R_f = 0.7 (EtOAc/Hex, 10:90); **MP** 140-142 ^oC; **IR** ($CHCl_3$) 2924, 2856, 1683, 1527, 1348, 946 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 10.57 (s, 1H), 8.26 (d, *J* = 1.8 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.86 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.06 (dd, *J* = 13.1, 8.0 Hz, 2H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.62 – 6.53 (m, 1H), 4.87 (dd, *J* = 5.2, 1.4 Hz, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 189.7, 160.8, 148.8, 138.1, 136.1, 132.6, 130.8, 129.8, 128.9, 127.0, 125.3, 122.8, 121.33, 121.25, 112.9, 68.5; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{13}O_4NNa$ $[M+Na]^+$ 306.0742, found 306.0727.



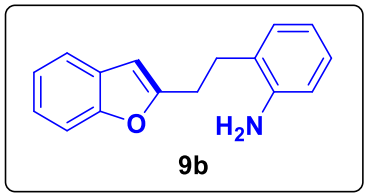
8

(*E*)-4-(2-(Benzofuran-2-yl)vinyl)aniline (8):- Brown solid8 105 mg (0.445 mmol), 89% yield, R_f = 0.3 (EtOAc/Hex, 20:80); **MP** 133-135 ^oC; **IR** ($CHCl_3$) 3375, 3029, 2922, 1606, 1254 cm^{-1}; **^{1}H-NMR** (400 MHz, DMSO-d_6) δ = 7.58 – 7.49 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.13 (d, *J* = 16.2 Hz, 1H), 6.90 (d, *J* = 16.2 Hz, 1H), 6.76 (s, 1H), 6.58 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 2H); **^{13}C{^{1}H}-NMR** (75 MHz, DMSO-d6) δ 155.9, 153.9, 149.4, 130.9, 129.1, 128.1, 124.0, 123.7, 122.9, 120.5, 113.9, 110.8, 110.5, 103.0; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{14}ON$ $[M+H]^+$ 236.1075, found 236.1059.



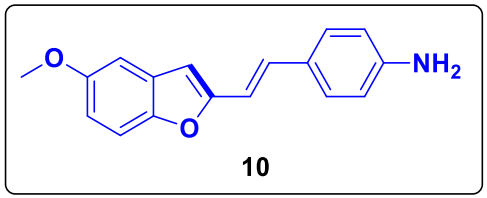
9a

4-(2-(Benzofuran-2-yl)ethyl)aniline (9a):- Brown solid, 76 mg (0.319 mmol), 84% yield, R_f = 0.4 (EtOAc/Hex, 20:80); **MP** 107-109 ^oC; **IR** ($CHCl_3$) 3443, 3360, 2921, 1617, 1514 cm^{-1}; **^{1}H-NMR** (400 MHz, DMSO-d_6) δ = 7.50 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.26 – 7.12 (m, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.56 – 6.45 (m, 3H), 5.08 (br, 2H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.84 (t, *J* = 7.7 Hz, 2H); **^{13}C{^{1}H}-NMR** (126 MHz, DMSO-d_6) δ 158.8, 153.9, 146.2, 128.7, 128.5, 128.0, 123.2, 122.5, 120.3, 114.2, 110.6, 102.3, 32.4, 30.0; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{16}ON$ $[M+H]^+$ 238.1232, found 238.1222.



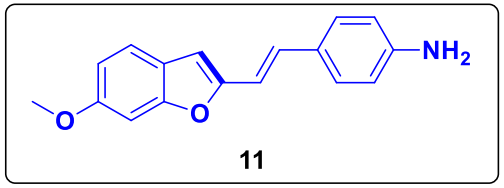
9b

2-(2-(Benzofuran-2-yl)ethyl)aniline (9b):- Off-white solid, 61 mg (0.26 mmol), 68% yield, R_f = 0.4 (EtOAc/Hex, 20:80); **MP** 107-109 ^oC; **IR** ($CHCl_3$) 3440, 3366, 2918, 1612, 1515 cm^{-1}; **^{1}H-NMR** (500 MHz, DMSO-d_6) δ = 7.56 – 7.47 (m, 2H), 7.23 – 7.16 (m, 2H), 6.96 – 6.87 (m, 2H), 6.66 – 6.59 (m, 2H), 6.48 – 6.45 (m, 1H), 4.93 (bs, 2H), 3.05 – 3.00 (m, 2H), 2.90 – 2.85 (m, 2H); **^{13}C{^{1}H}-NMR** (126 MHz, DMSO d_6) δ = 159.0, 153.9, 146.1, 128.8, 128.6, 126.8, 123.8, 123.2, 122.5, 120.3, 116.2, 114.7, 110.6, 102.2, 28.5, 26.9; **HRMS** (ESI, *m/z*): calcd for $C_{16}H_{16}ON$ $[M+H]^+$ 238.1226, found 238.1235.



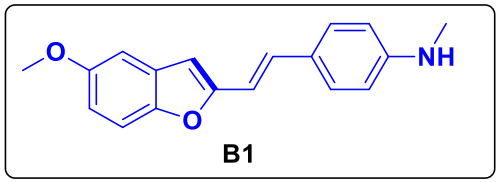
10

(*E*)-4-(2-(5-Methoxybenzofuran-2-yl)vinyl)aniline (10):- Light brown solid, 109 mg (0.41 mmol), 82% yield, R_f = 0.4 (EtOAc/Hex, 20:80); **MP** 198-200 ^oC; **IR** ($CHCl_3$) 3348, 2924, 1594, 1508, 1464, 961 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 7.34 (t, *J* = 8.2 Hz, 3H), 7.20 (d, *J* = 16.1 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.79 (d, *J* = 16.1 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 3.84 (s, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 156.8, 156.1, 149.9, 146.8, 130.5, 130.1, 128.2, 127.4, 115.3, 113.1, 112.7, 111.2, 111.2, 103.9, 103.3, 56.1; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{16}O_2N$ $[M+H]^+$ 266.1181, found 266.1194. The spectroscopic data were in good agreement with the reported data. [6]



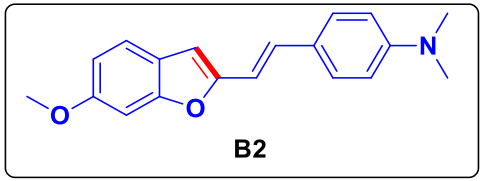
11

(*E*)-4-(2-(6-Methoxybenzofuran-2-yl)vinyl)aniline (11):- Brown solid, 113 mg (0.425 mmol), 85% yield, R_f = 0.5 (EtOAc/Hex, 20:80); **MP** 105-107 ^oC; **IR** ($CHCl_3$) 3376, 3008, 2925, 1613, 1488, 957 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.35 (dd, *J* = 10.8, 8.5 Hz, 3H), 7.15 (d, *J* = 16.1 Hz, 1H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.70 – 6.66 (m, 2H), 6.51 (s, 1H), 3.86 (s, 3H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 158.1, 155.9, 155.3, 146.6, 129.2, 128.0, 127.6, 122.9, 120.7, 115.3, 113.2, 111.6, 103.7, 95.9, 55.9; **HRMS** (ESI, *m/z*): calcd for $C_{17}H_{16}O_2N$ $[M+H]^+$ 266.1181, found 266.1179. The spectroscopic data were in good agreement with the reported data.[6]



B1

(*E*)-4-(2-(5-Methoxybenzofuran-2-yl)vinyl)-*N*-methylaniline (B1):- Brown solid, 114 mg (0.41 mmol), 82% yield, R_f = 0.4 (EtOAc/Hex, 10:90); **MP** 188-190 ^oC; **IR** ($CHCl_3$) 3401, 2923, 1599, 1517, 1467, 962 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 16.1 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.77 (d, *J* = 16.1 Hz, 1H), 6.60 (d, *J* = 8.6 Hz, 2H), 6.51 (s, 1H), 3.84 (s, 3H), 2.88 (s, 3H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 157.0, 156.0, 149.9, 149.6, 130.8, 130.2, 128.2, 126.0, 112.6, 112.4, 111.2, 103.6, 103.2, 56.1, 30.7; **HRMS** (ESI, *m/z*): calcd for $C_{18}H_{18}O_2N$ $[M+H]^+$ 280.1338, found 280.1327. The spectroscopic data were in good agreement with the reported data. [6]

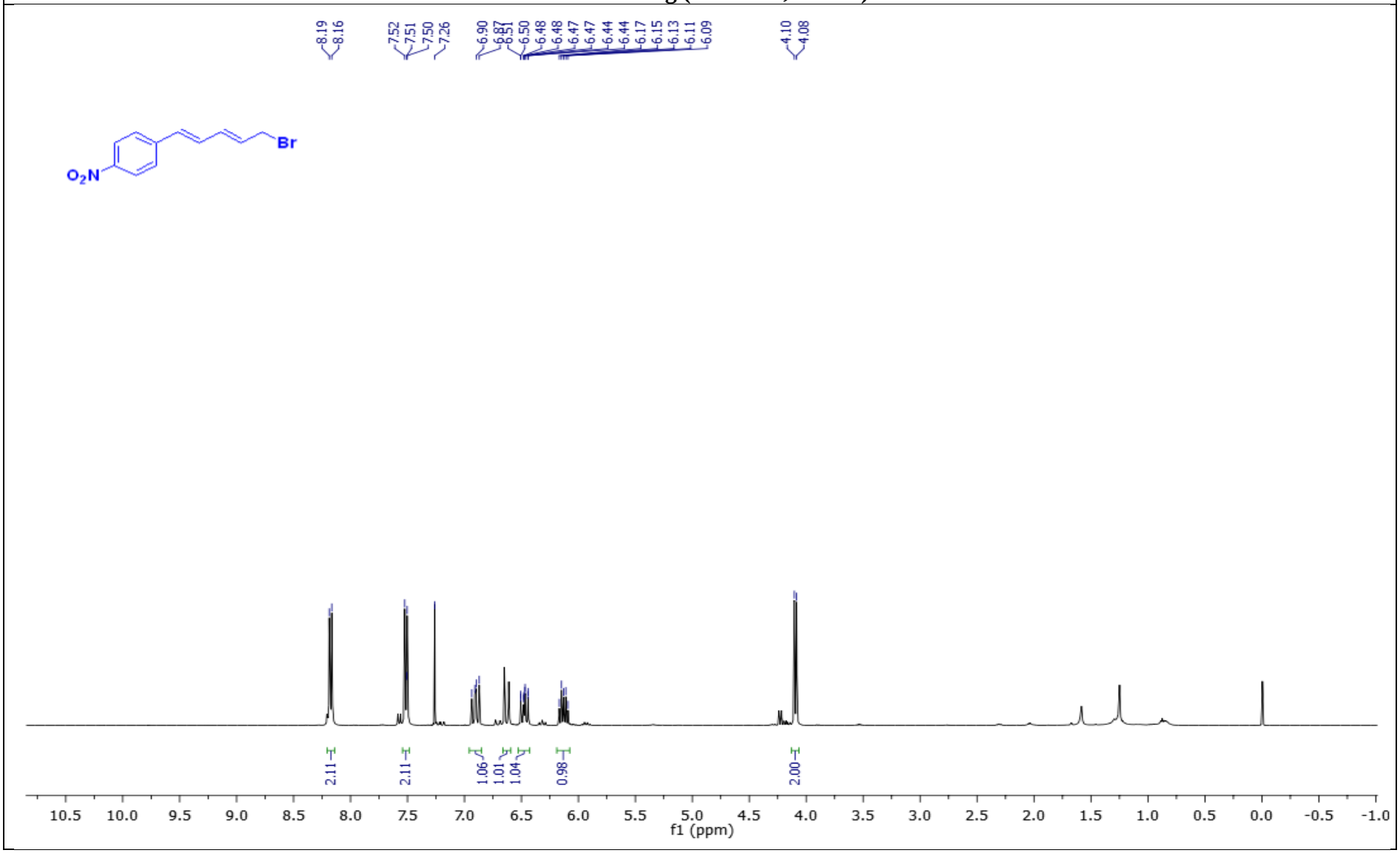


B2

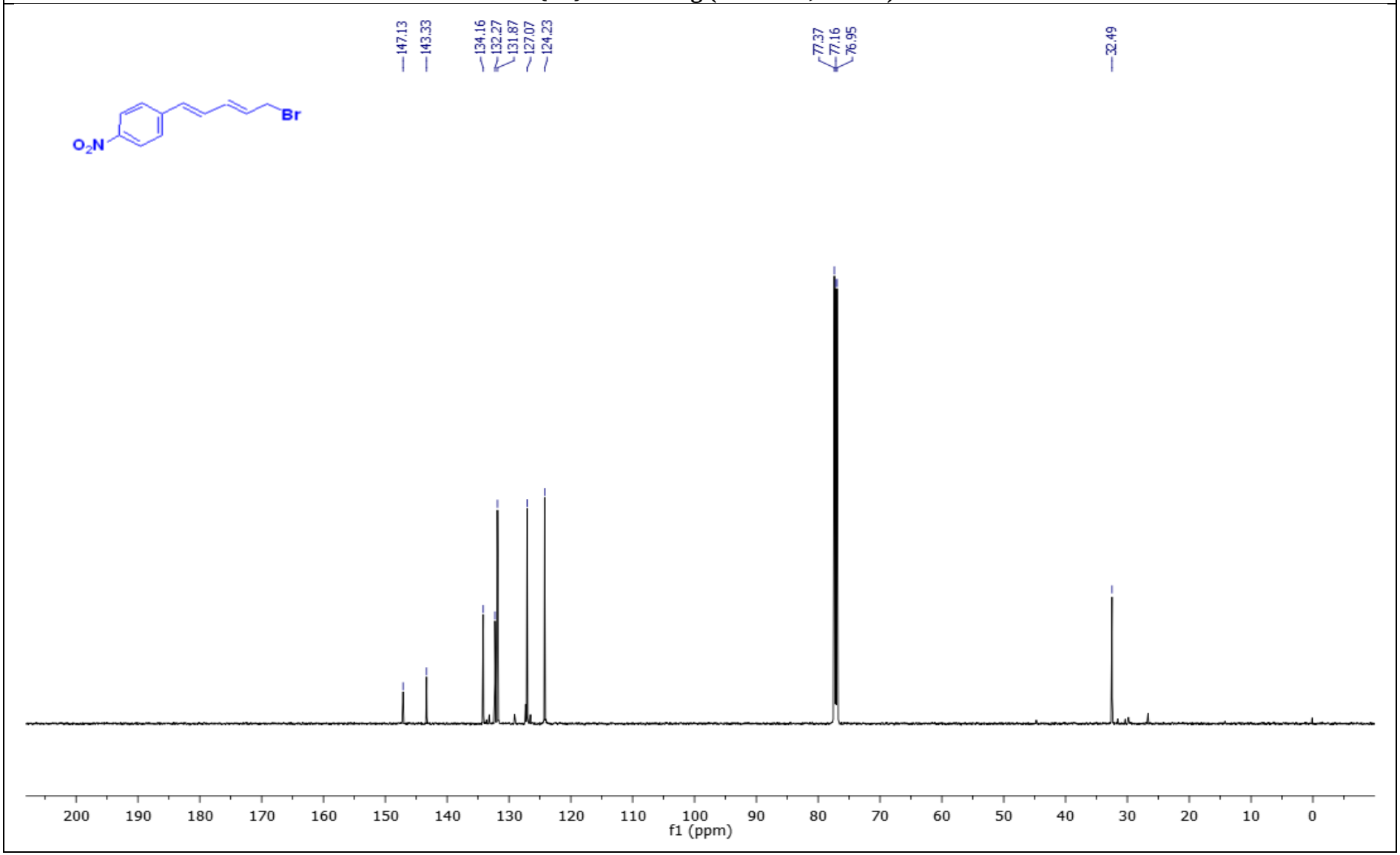
(*E*)-4-(2-(6-Methoxybenzofuran-2-yl)vinyl)-*N*,*N*-dimethylaniline (B2):- Off white solid, 126 mg (0.43 mmol), 86% yield, R_f = 0.3 (EtOAc/Hex, 10:90); **MP** 163-165 ^oC; **IR** ($CHCl_3$) 3049, 2922, 1606, 1487, 1356, 959 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 16.1 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.85 – 6.69 (m, 4H), 6.49 (s, 1H), 3.86 (s, 3H), 3.00 (s, 6H); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ = 157.1, 156.1, 149.9, 130.6, 130.5, 130.2, 128.1, 112.5, 112.4, 111.2, 103.6, 103.2, 56.1, 40.6; **HRMS** (ESI, *m/z*): calcd for $C_{19}H_{20}O_2N$ $[M+H]^+$ 294.1494, found 294.1506. The spectroscopic data were in good agreement with the reported data. [6]

12. Copies of spectra (^{1}H-NMR and ^{13}C{^{1}H}-NMR)

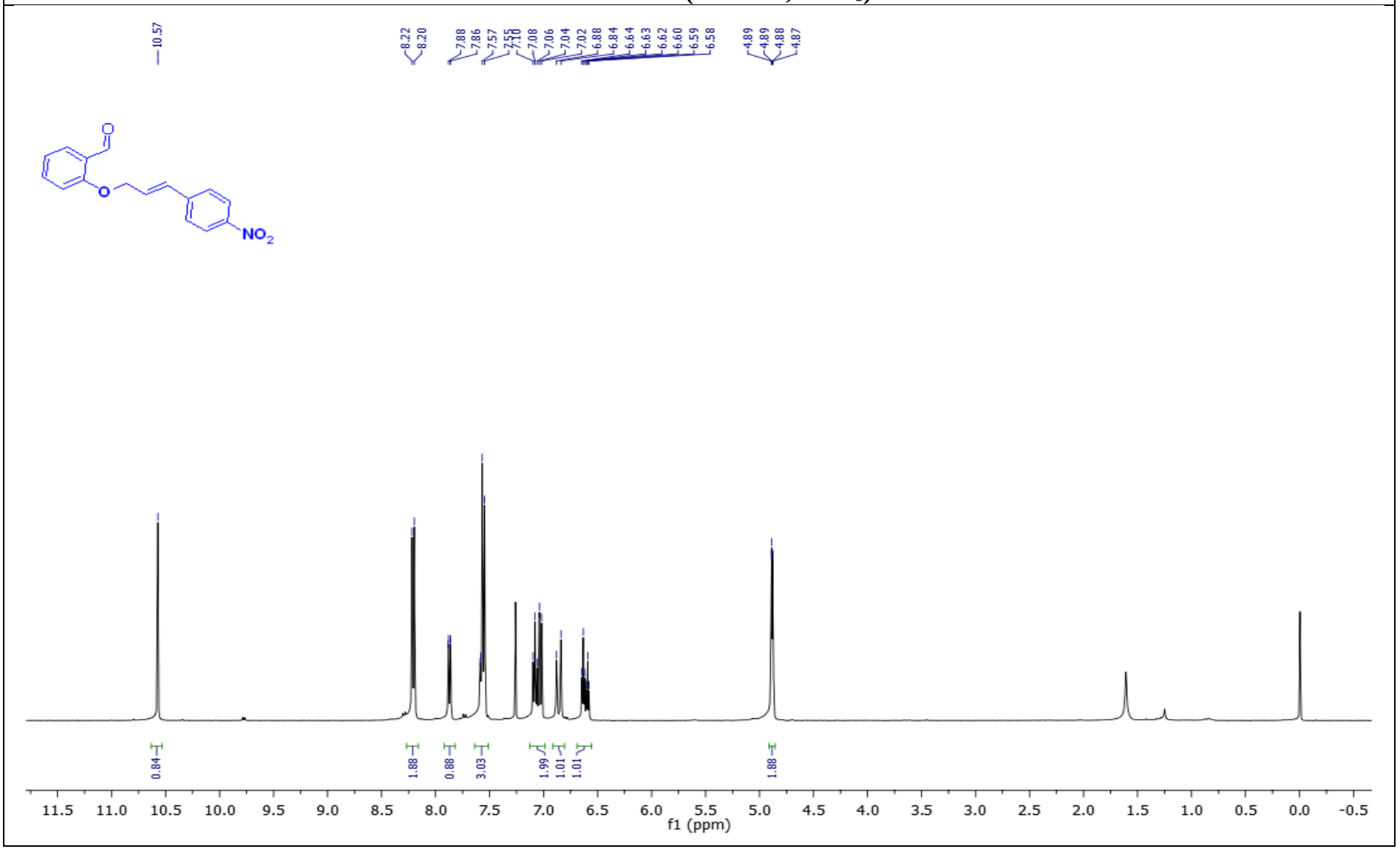
^{1}H-NMR of 2g (400 MHz, $CDCl_3$)



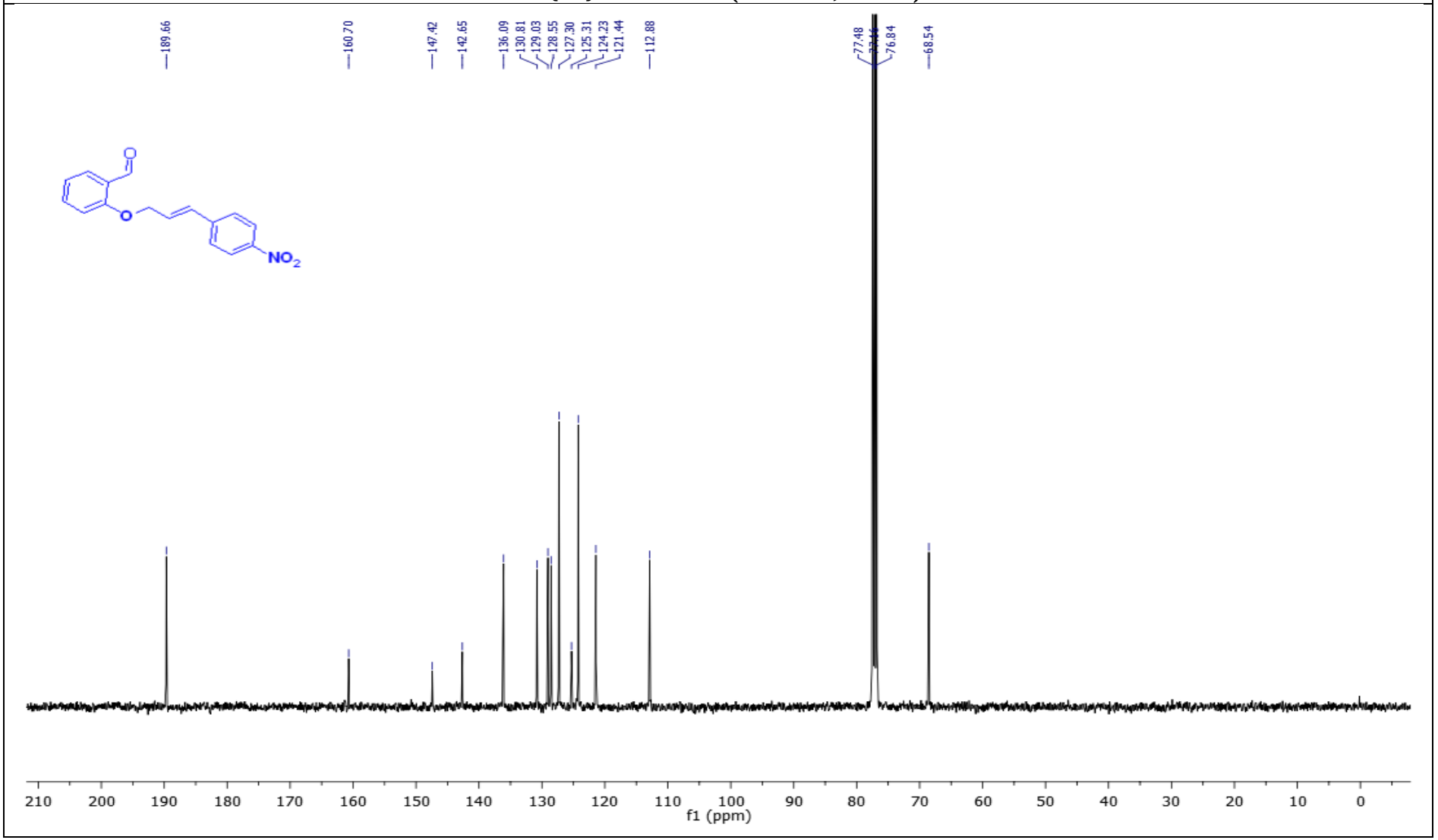
$^{13}C\{^{1}H\}$-NMR of 2g (151 MHz, $CDCl_3$)



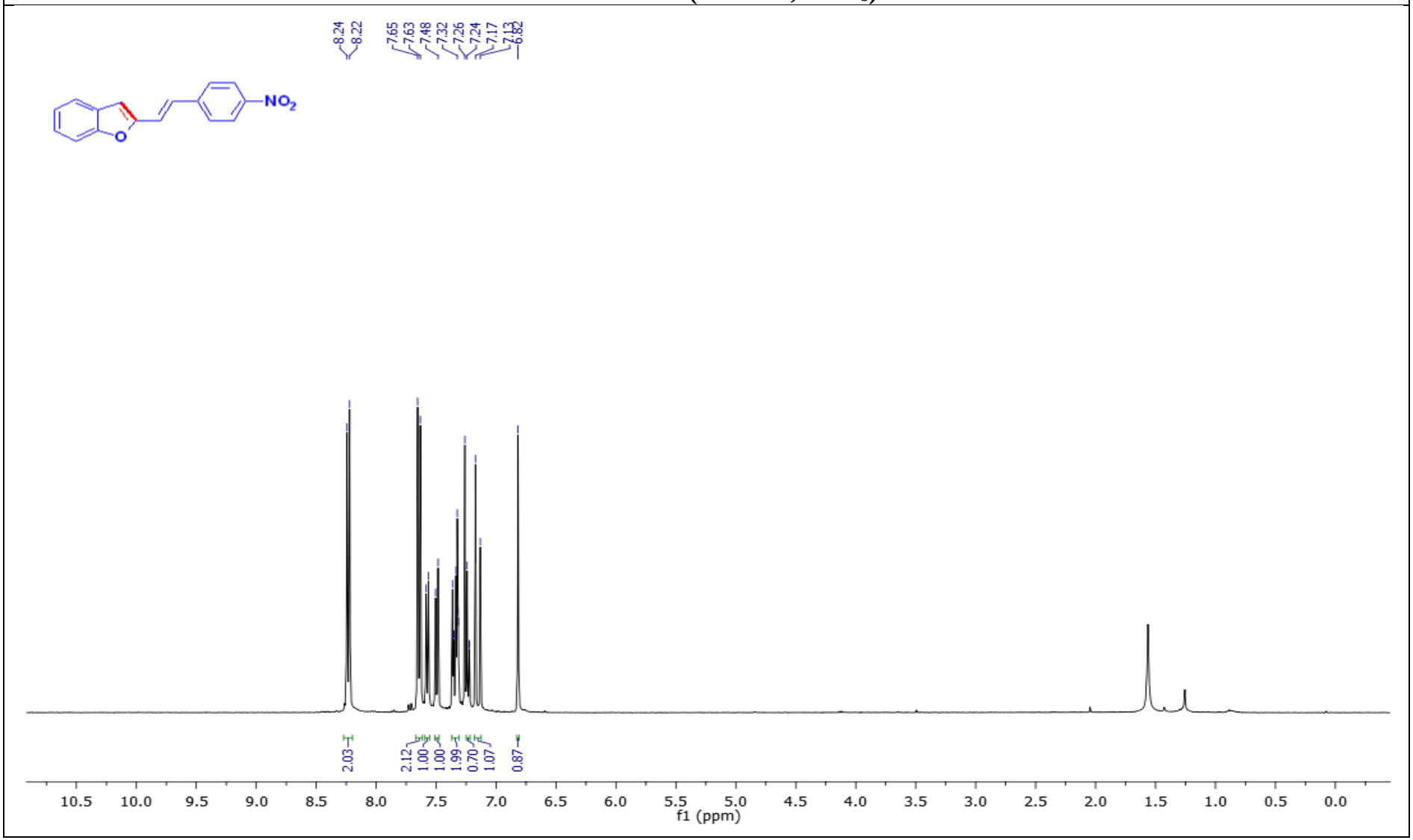
^{1}H-NMR of 3a' (400 MHz, $CDCl_3$)



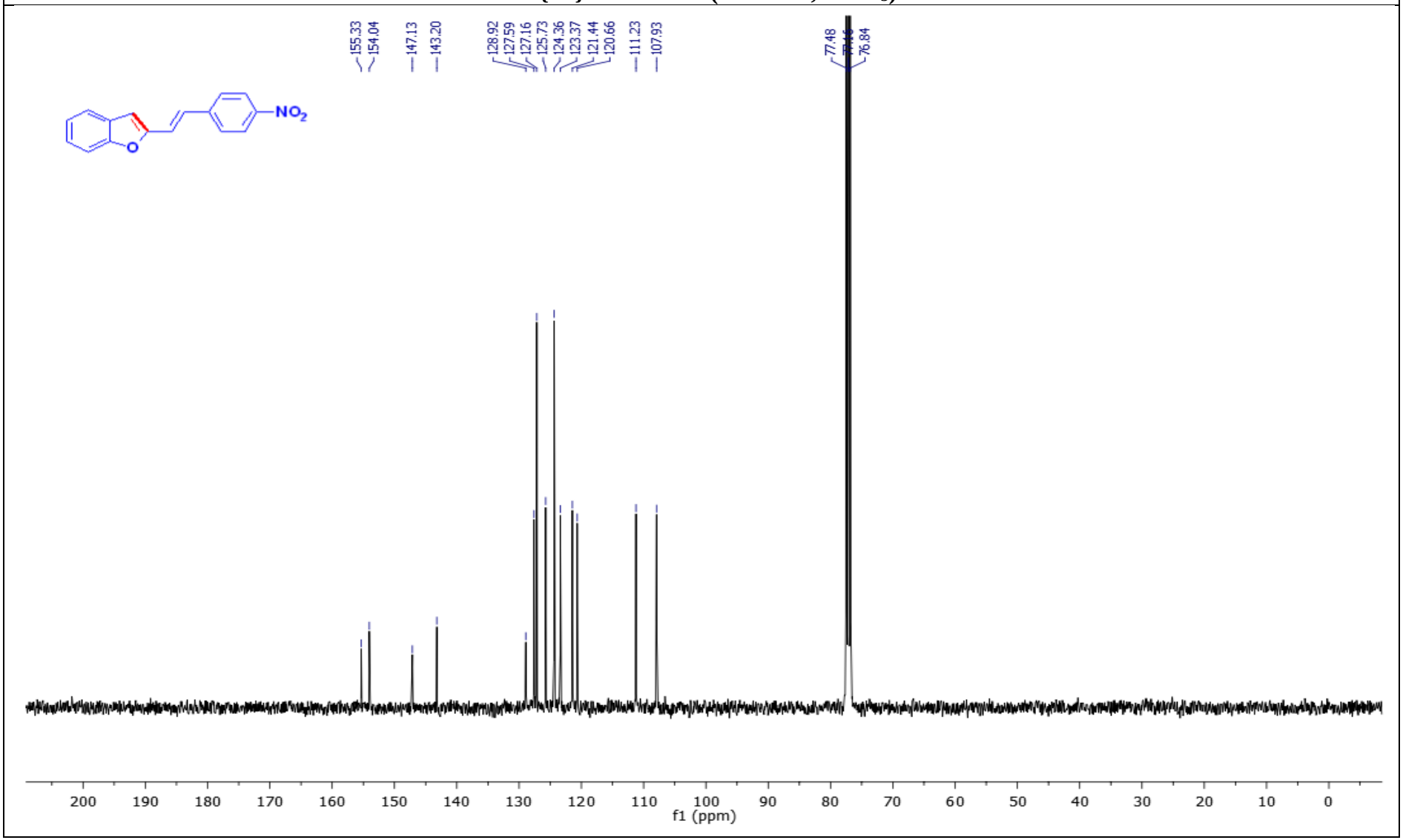
$^{13}C\{^{1}H\}$-NMR of 3a' (101 MHz, $CDCl_3$)



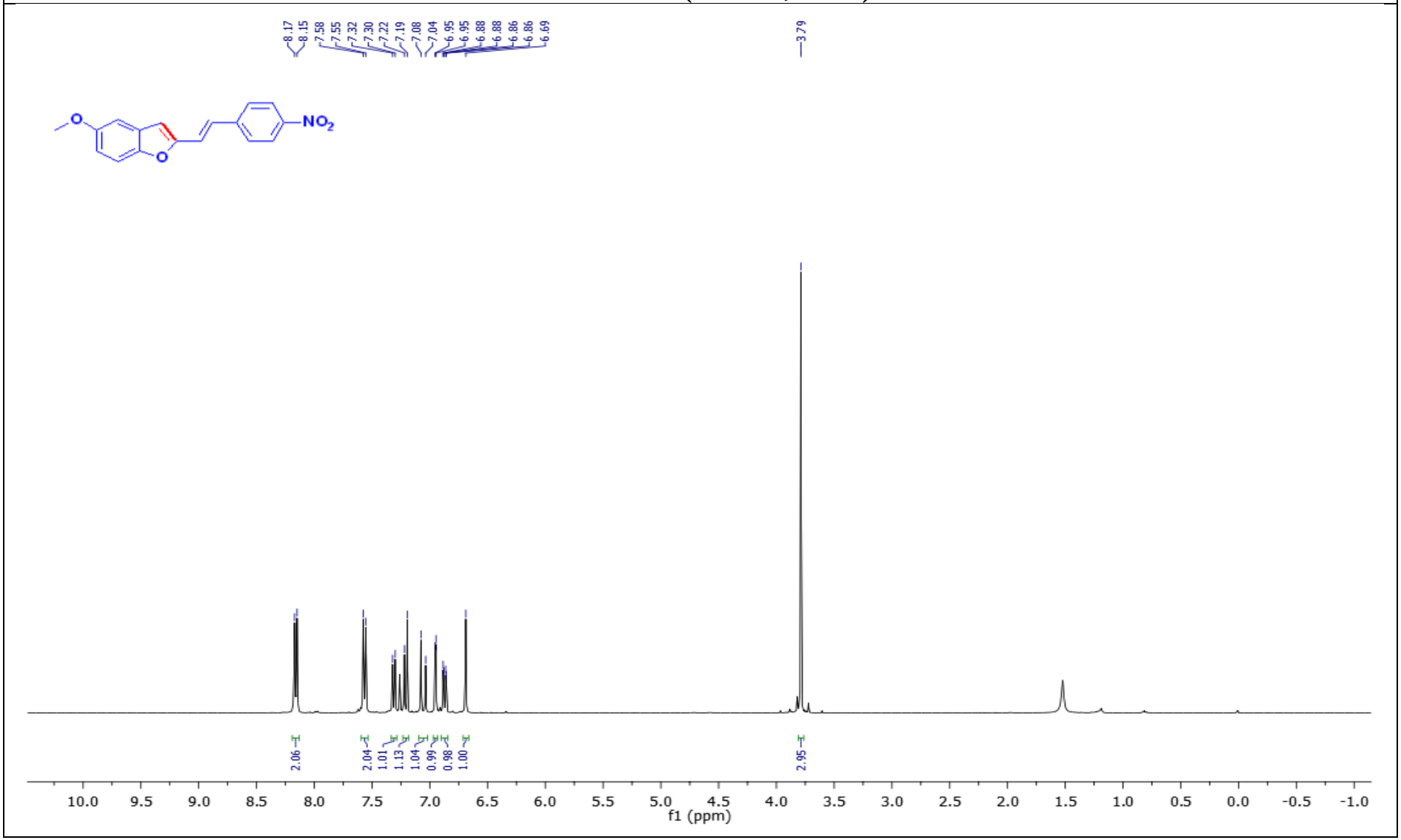
^{1}H-NMR of 3a (500 MHz, $CDCl_3$)



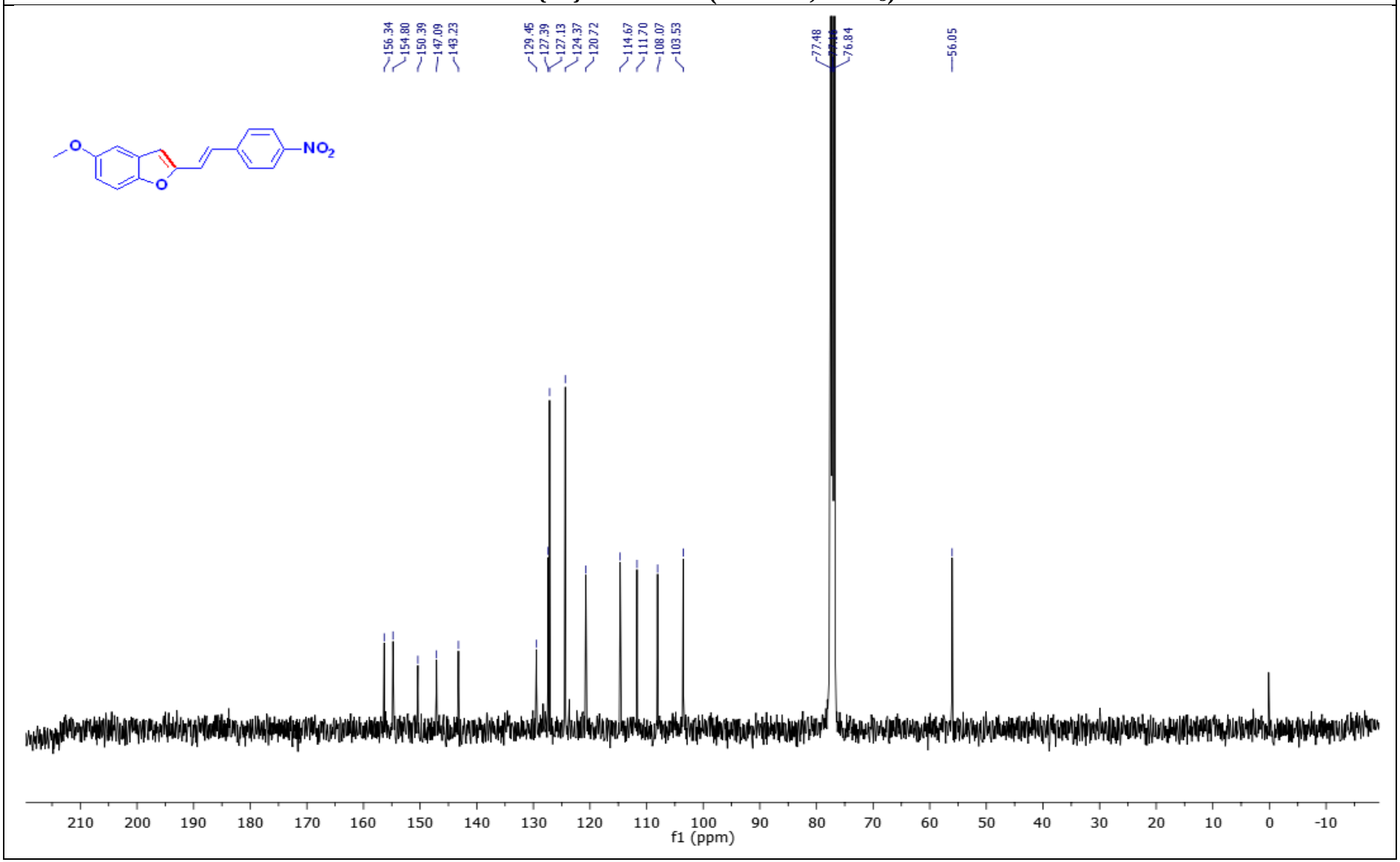
$^{13}C\{^{1}H\}$-NMR of 3a (101 MHz, $CDCl_3$)



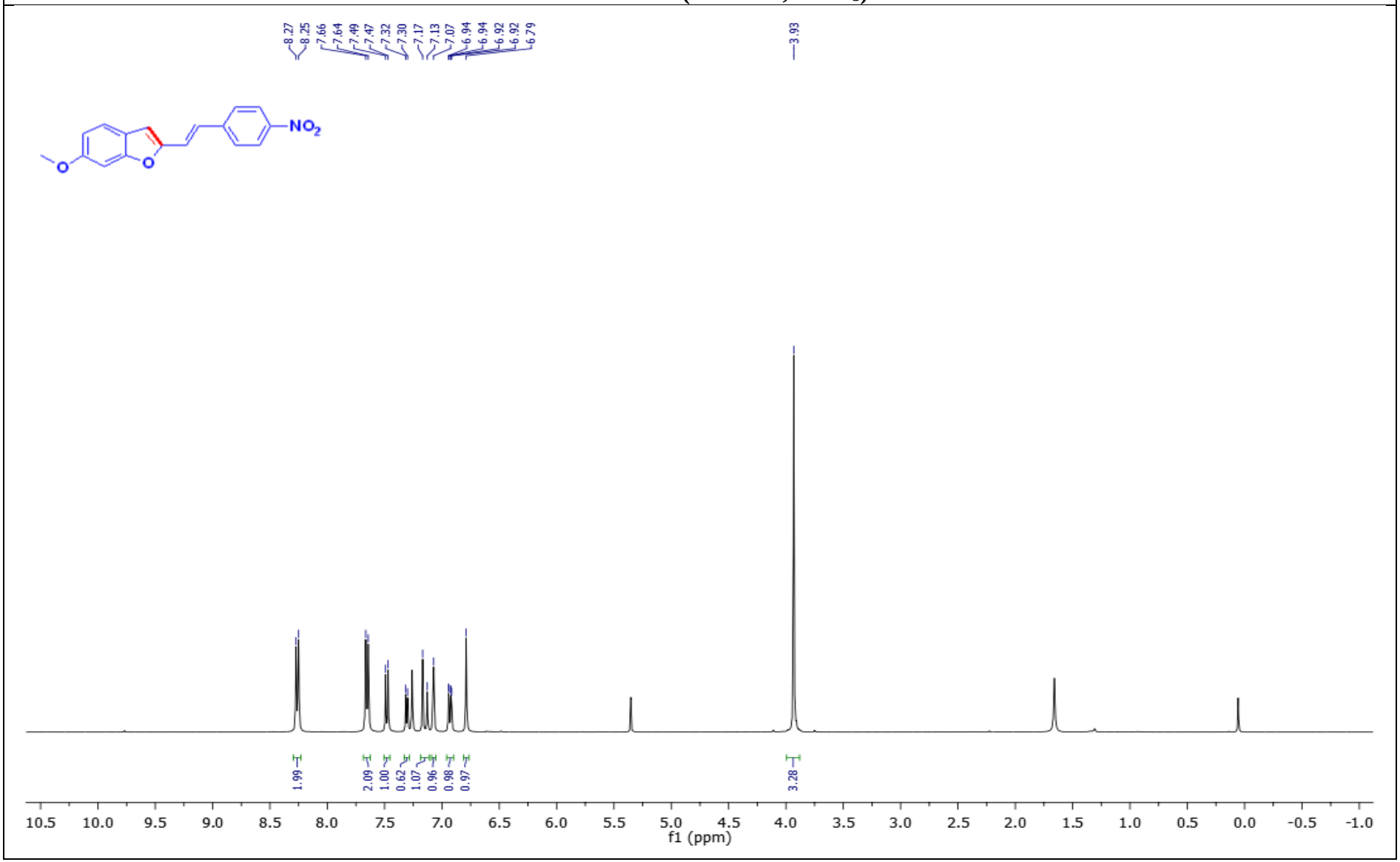
^{1}H-NMR of 3b (400 MHz, $CDCl_3$)



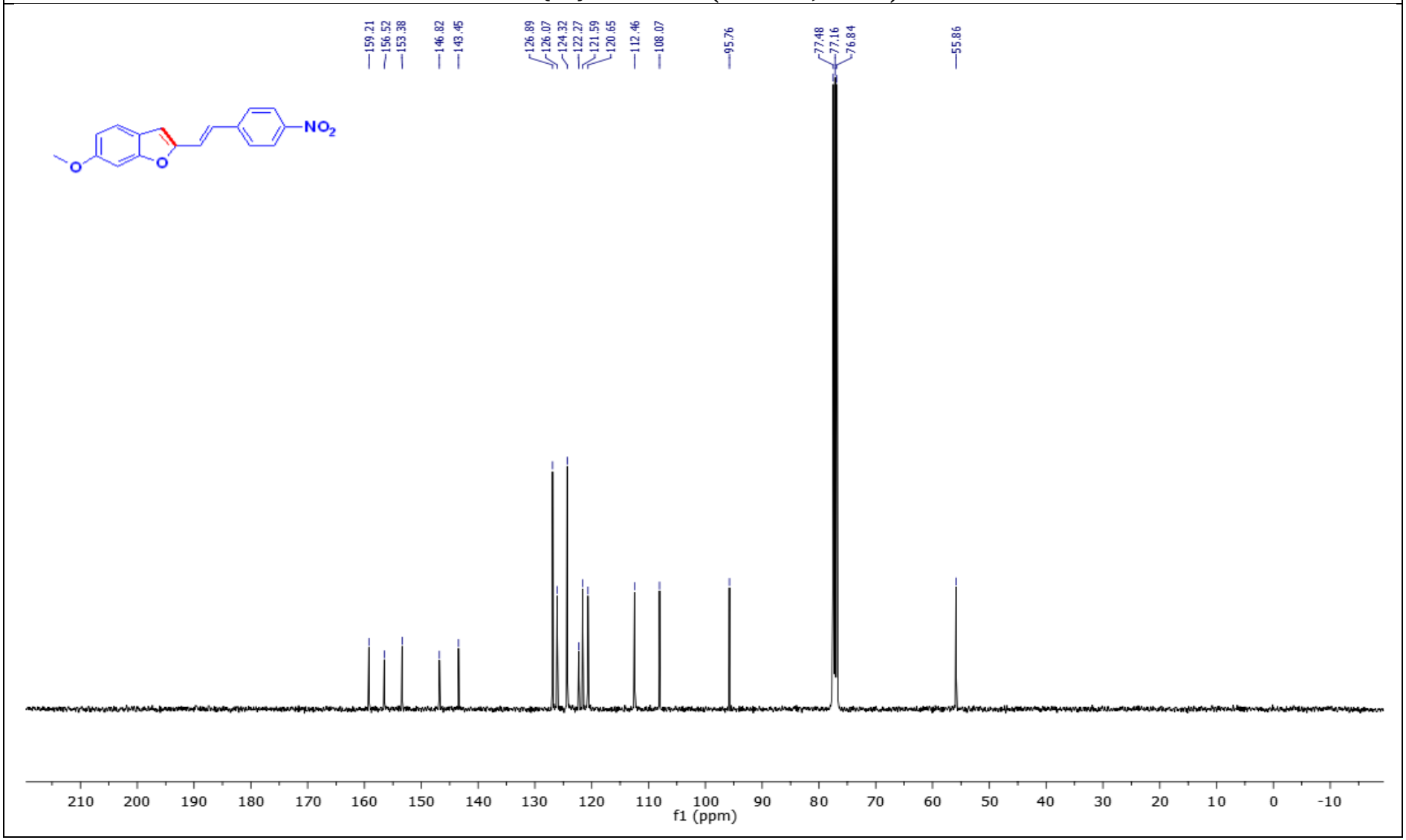
$^{13}C\{^{1}H\}$-NMR of 3b (101 MHz, $CDCl_3$)



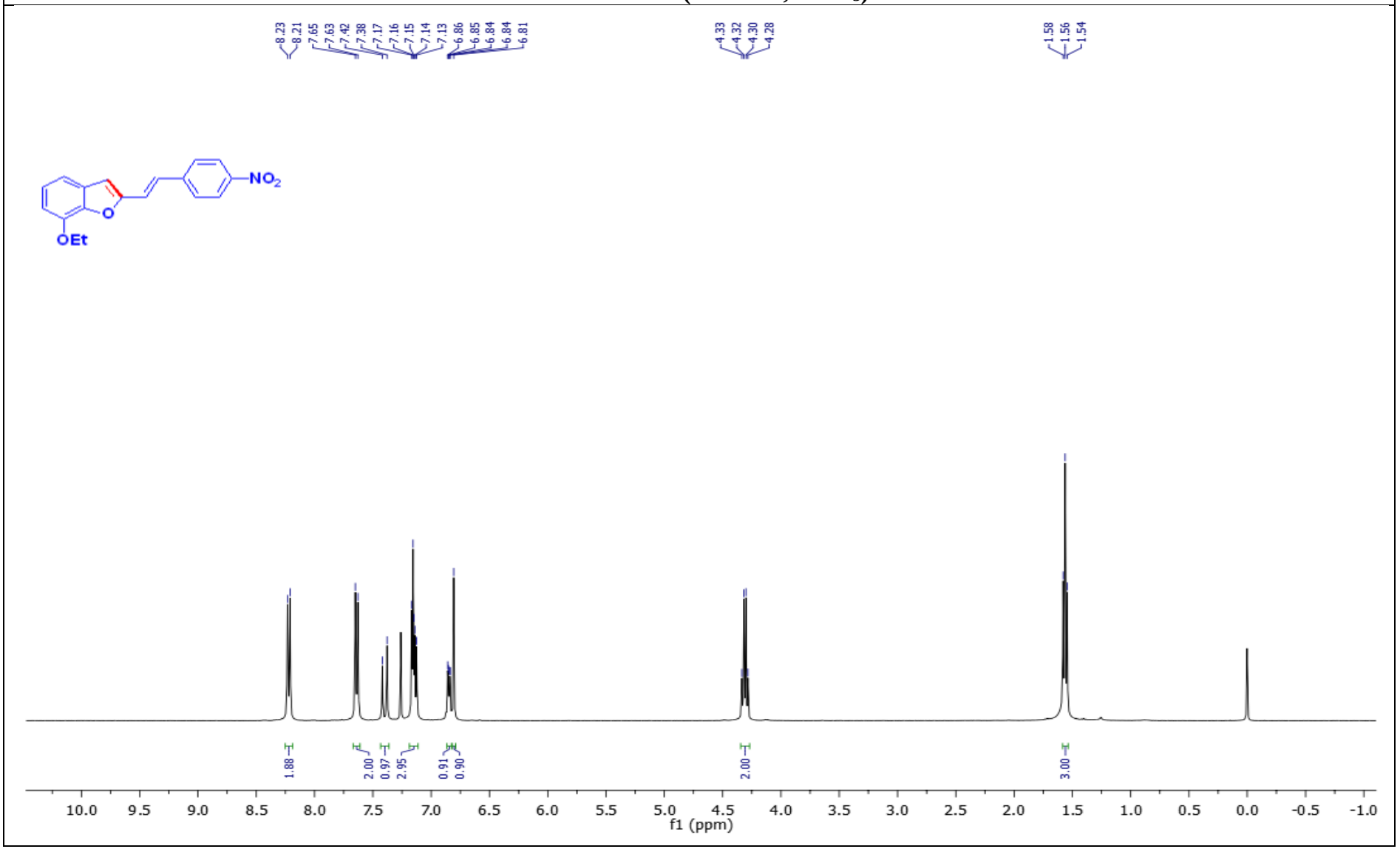
^{1}H-NMR of 3c (400 MHz, $CDCl_3$)



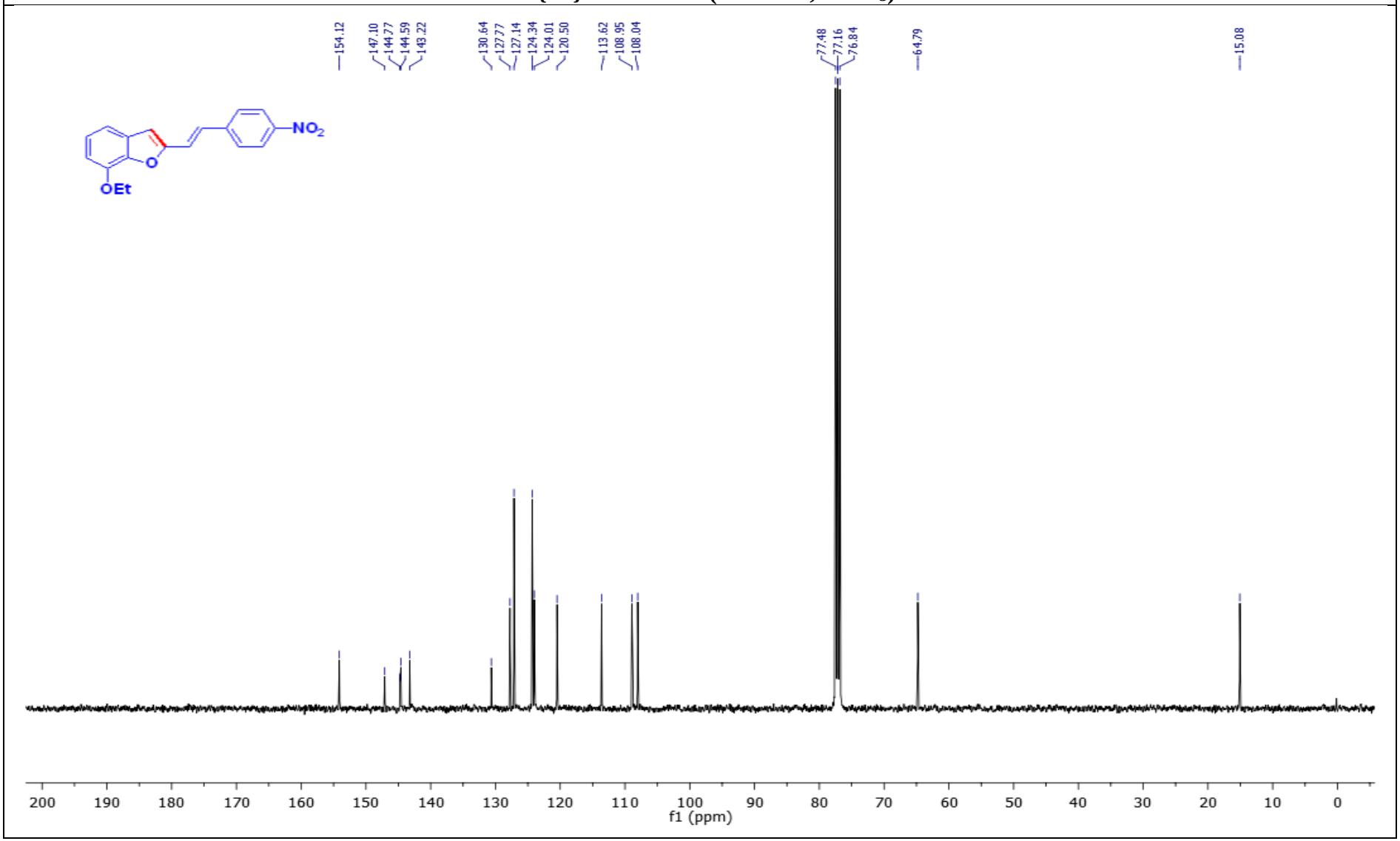
$^{13}C\{^{1}H\}$-NMR of 3c (101 MHz, $CDCl_3$)



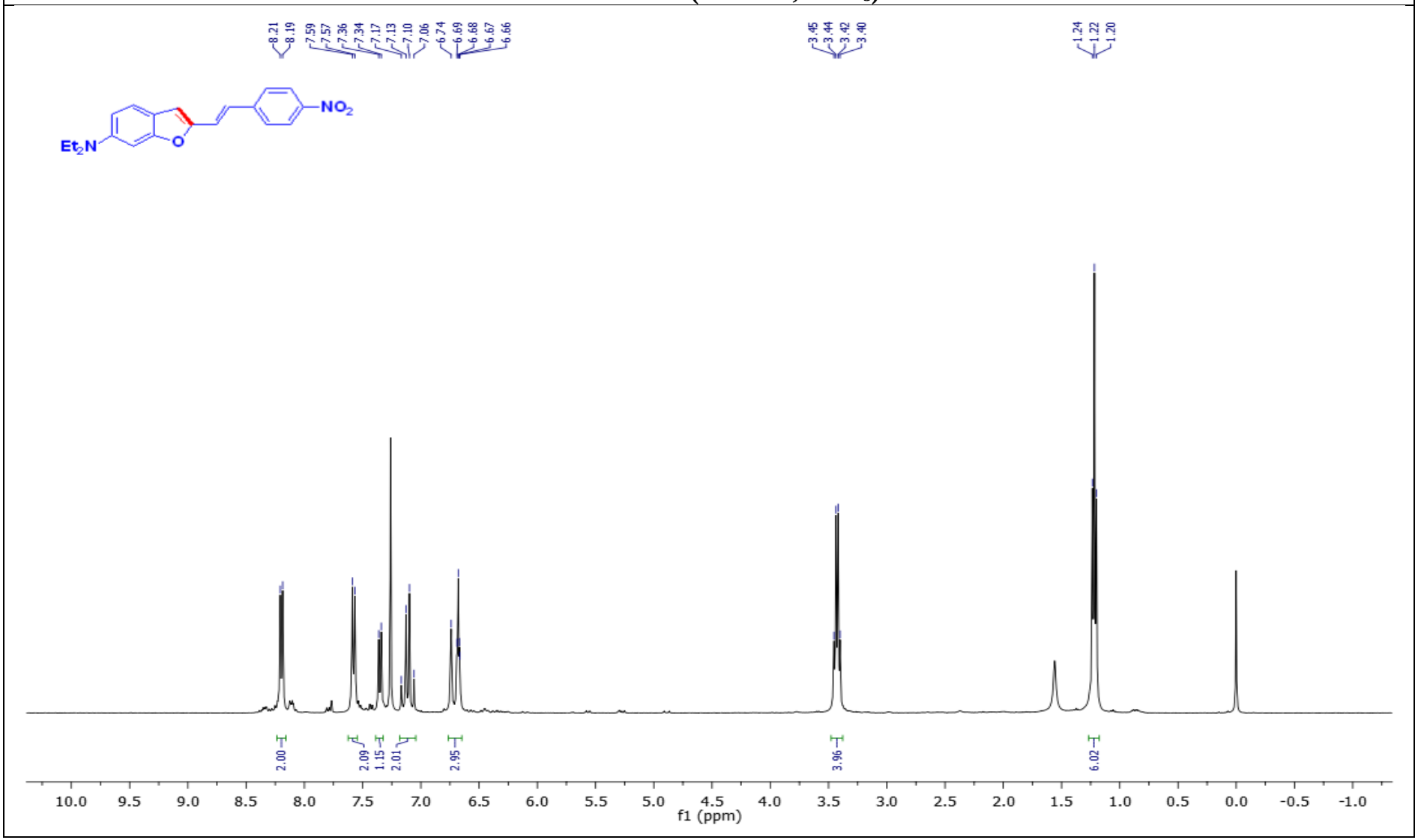
^{1}H-NMR of 3d (400 MHz, $CDCl_3$)



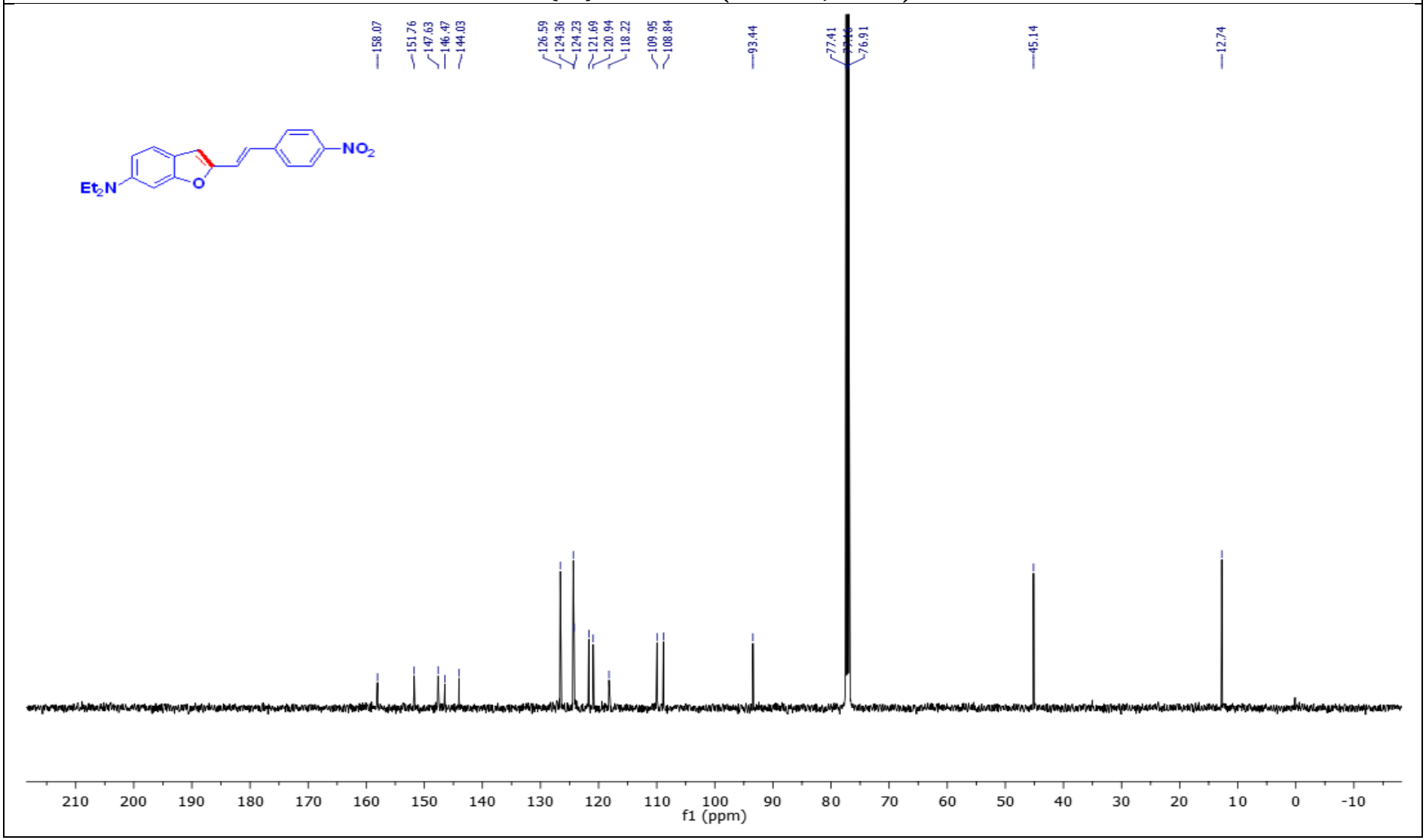
$^{13}C\{^{1}H\}$-NMR of 3d (101 MHz, $CDCl_3$)



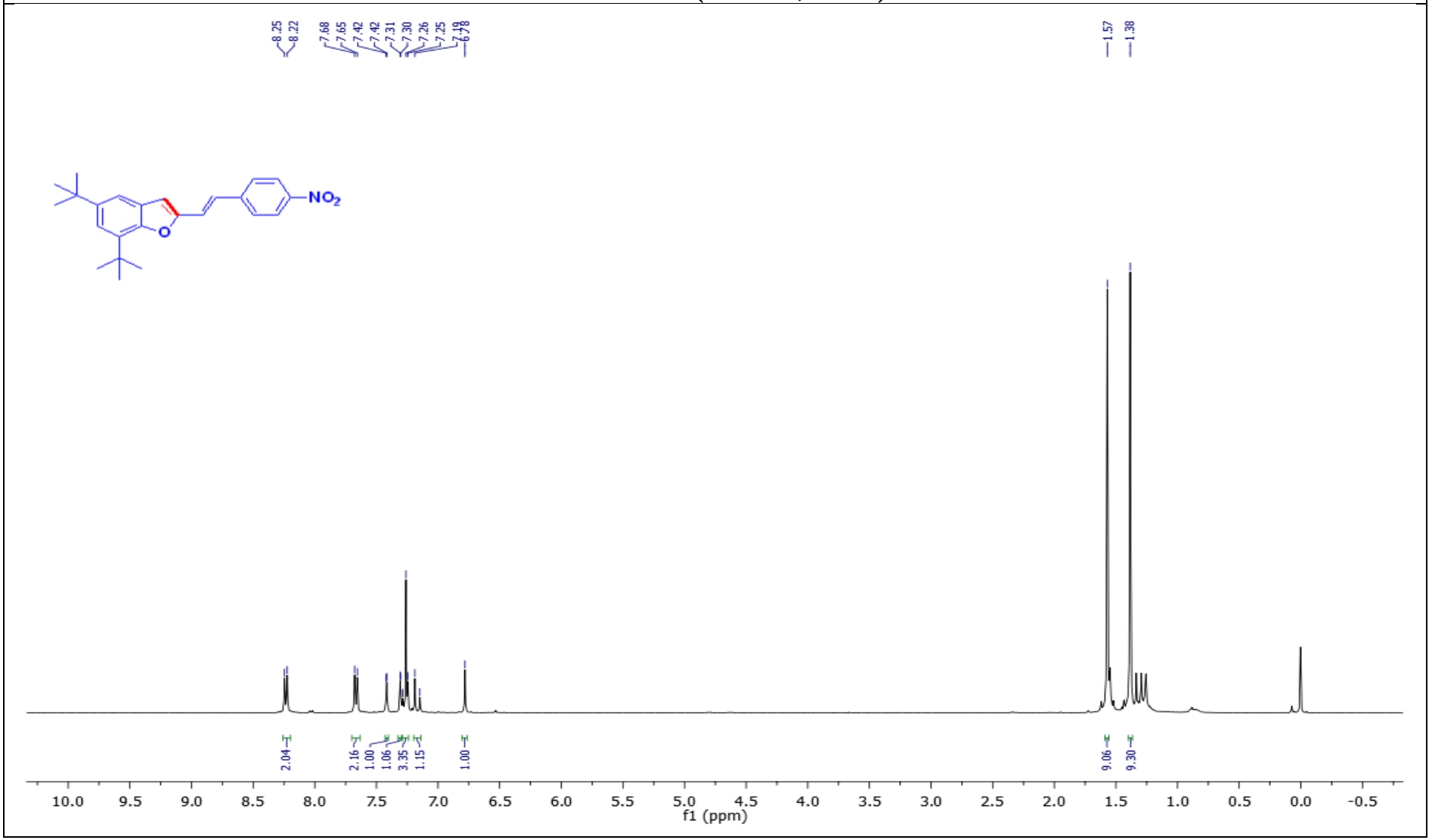
^{1}H-NMR of 3e (400 MHz, $CDCl_3$)



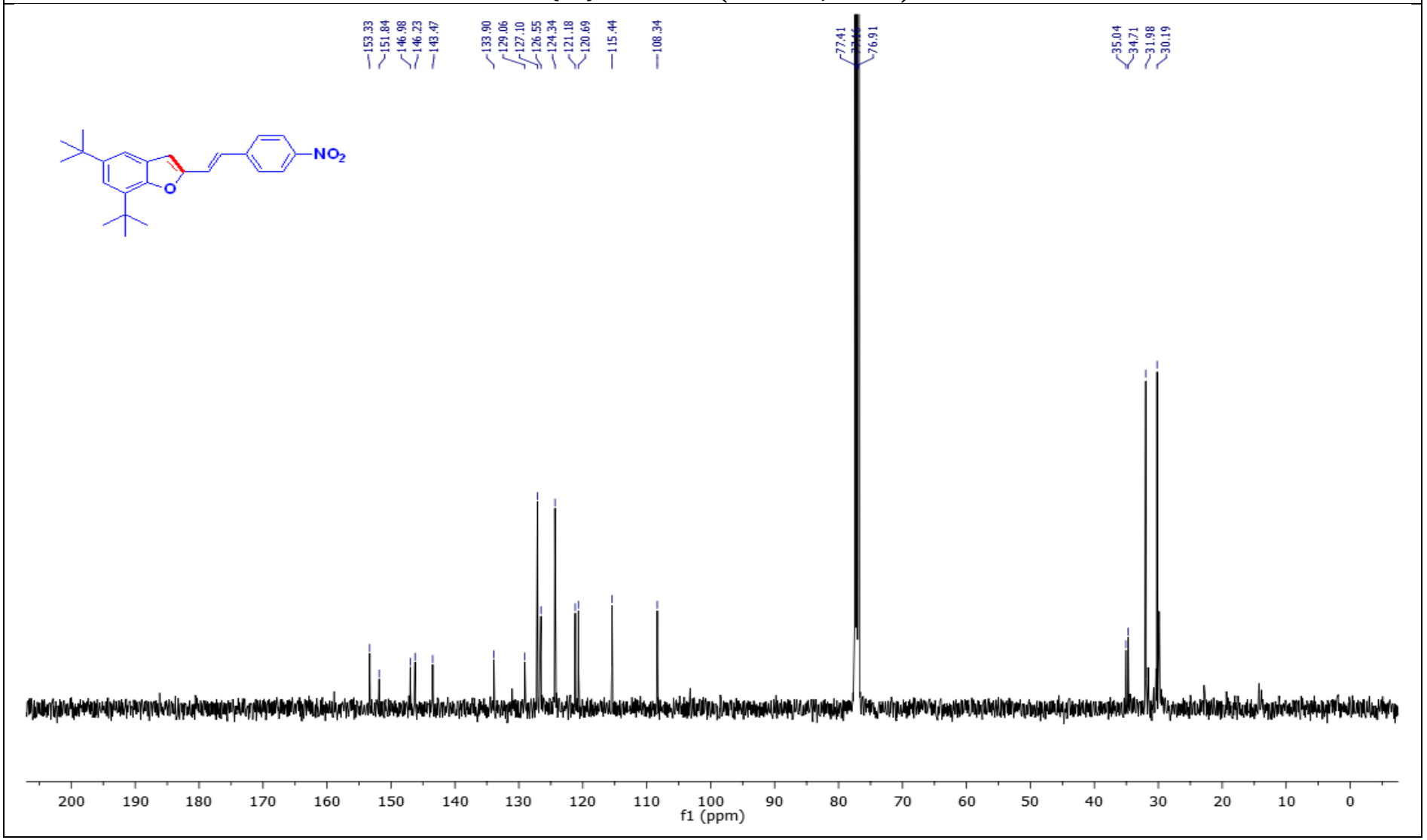
$^{13}C\{^{1}H\}$-NMR of 3e (126 MHz, $CDCl_3$)



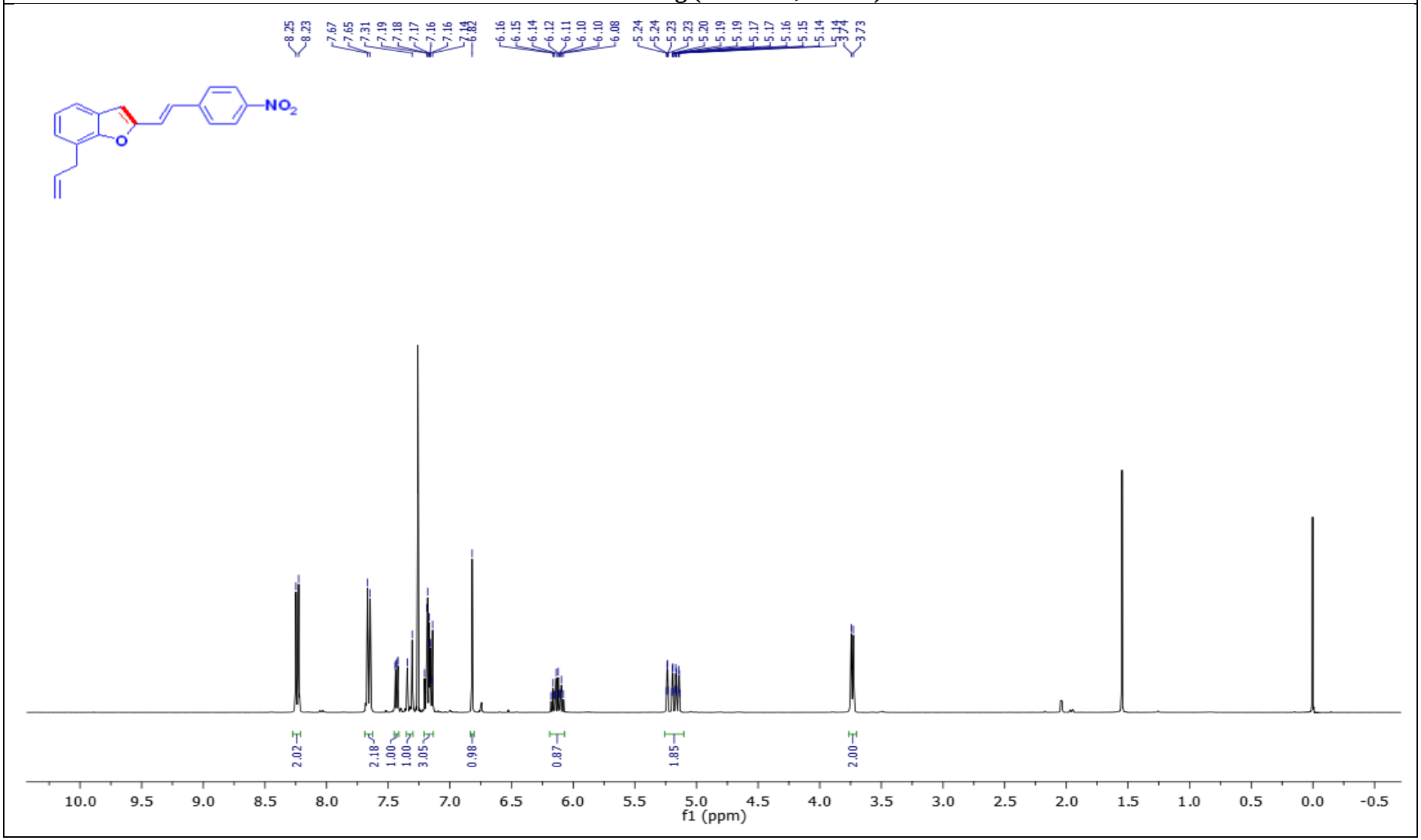
^{1}H-NMR of 3f (400 MHz, $CDCl_3$)



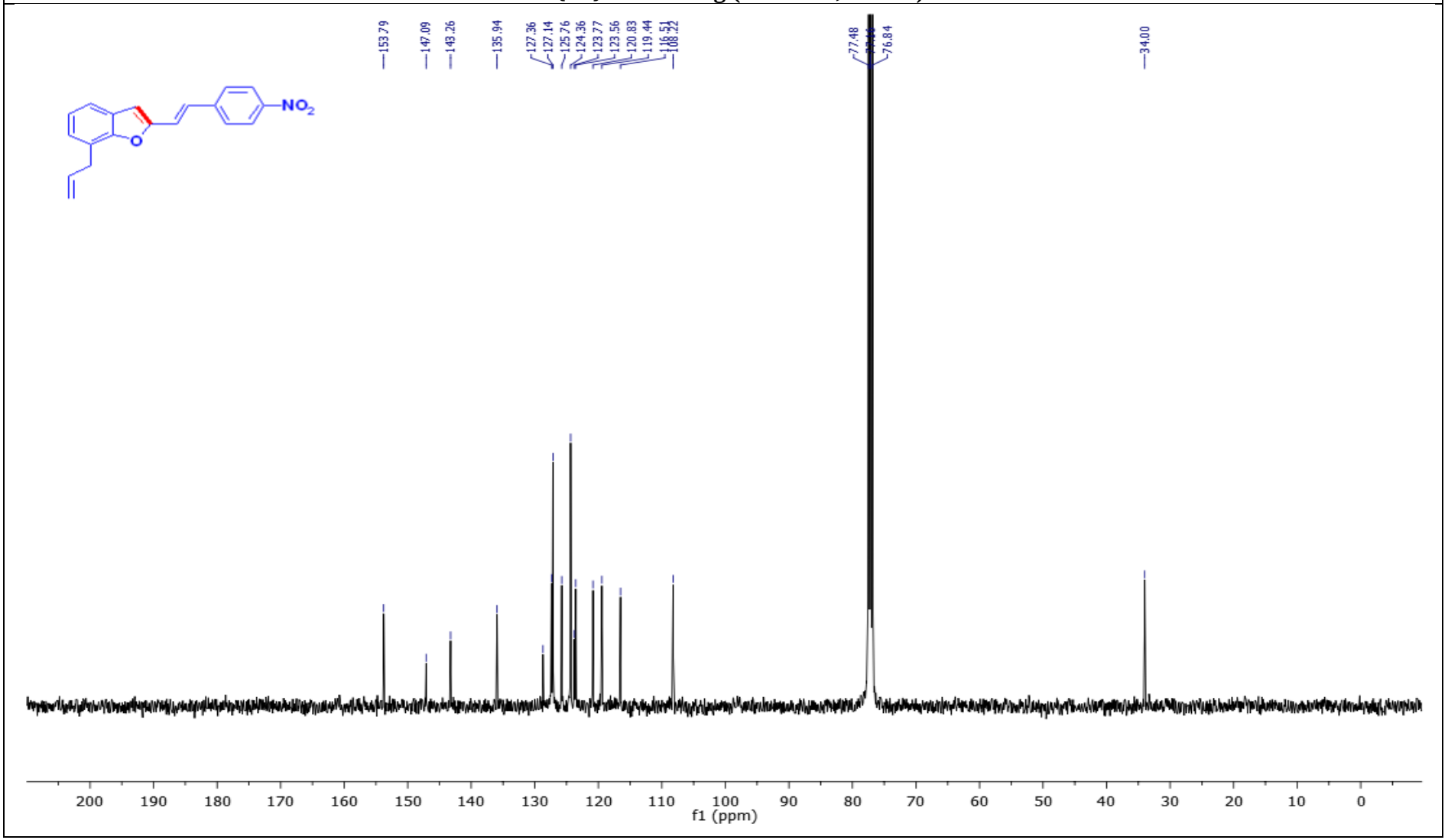
$^{13}C\{^{1}H\}$-NMR of 3f (126 MHz, $CDCl_3$)



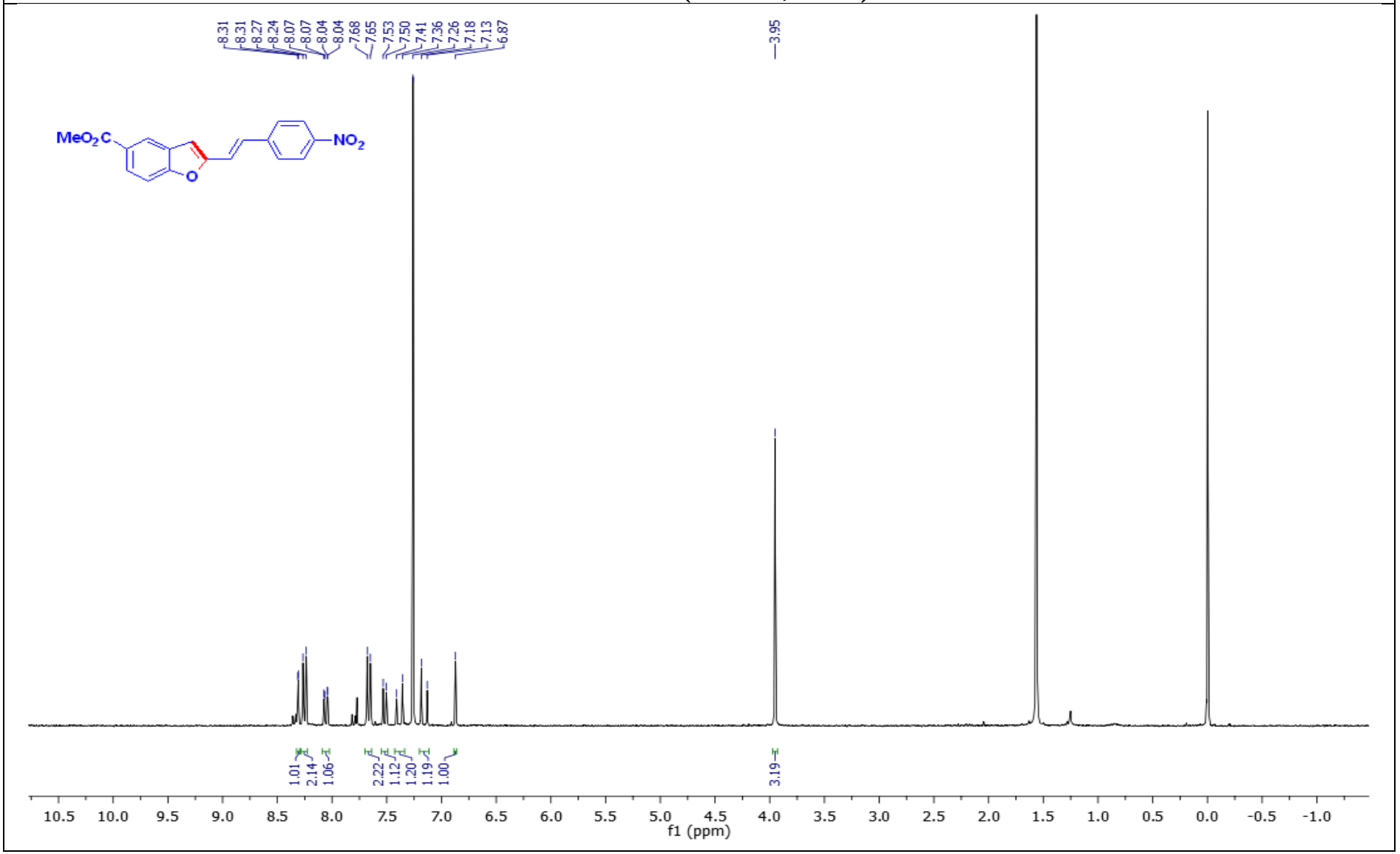
^{1}H-NMR of 3g (400 MHz, $CDCl_3$)



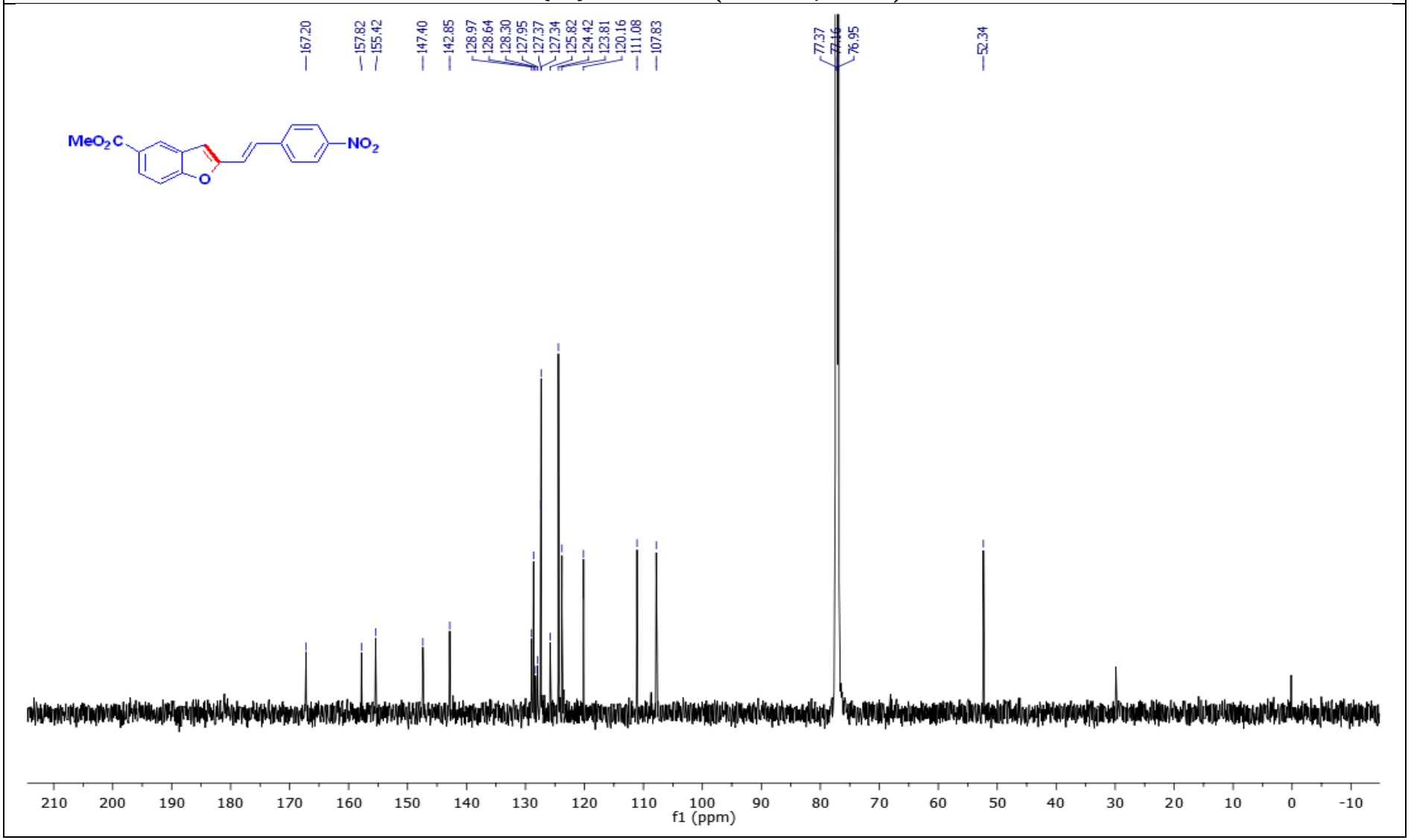
$^{13}C\{^{1}H\}$-NMR of 3g (101 MHz, $CDCl_3$)



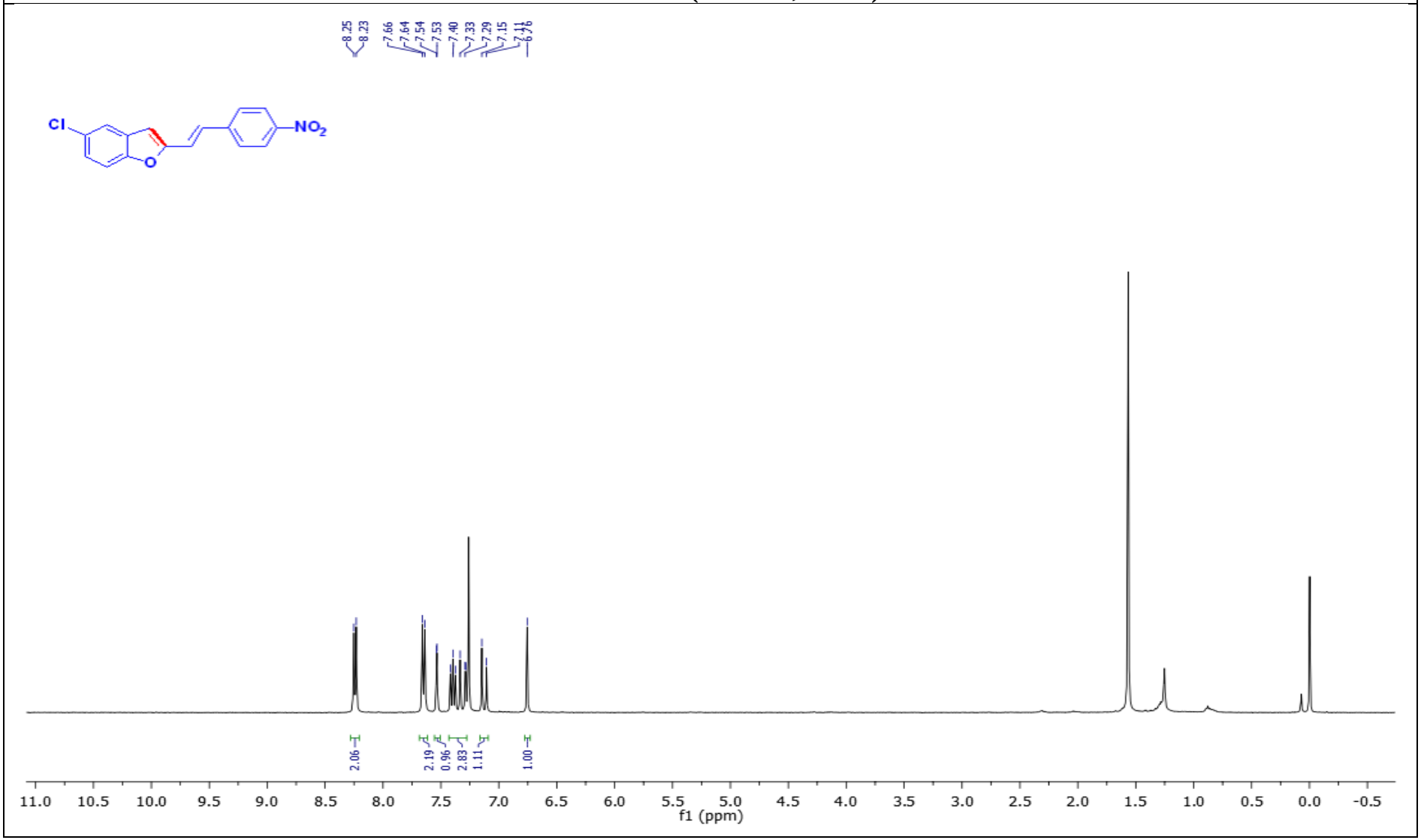
^{1}H-NMR of 3h (300 MHz, $CDCl_3$)



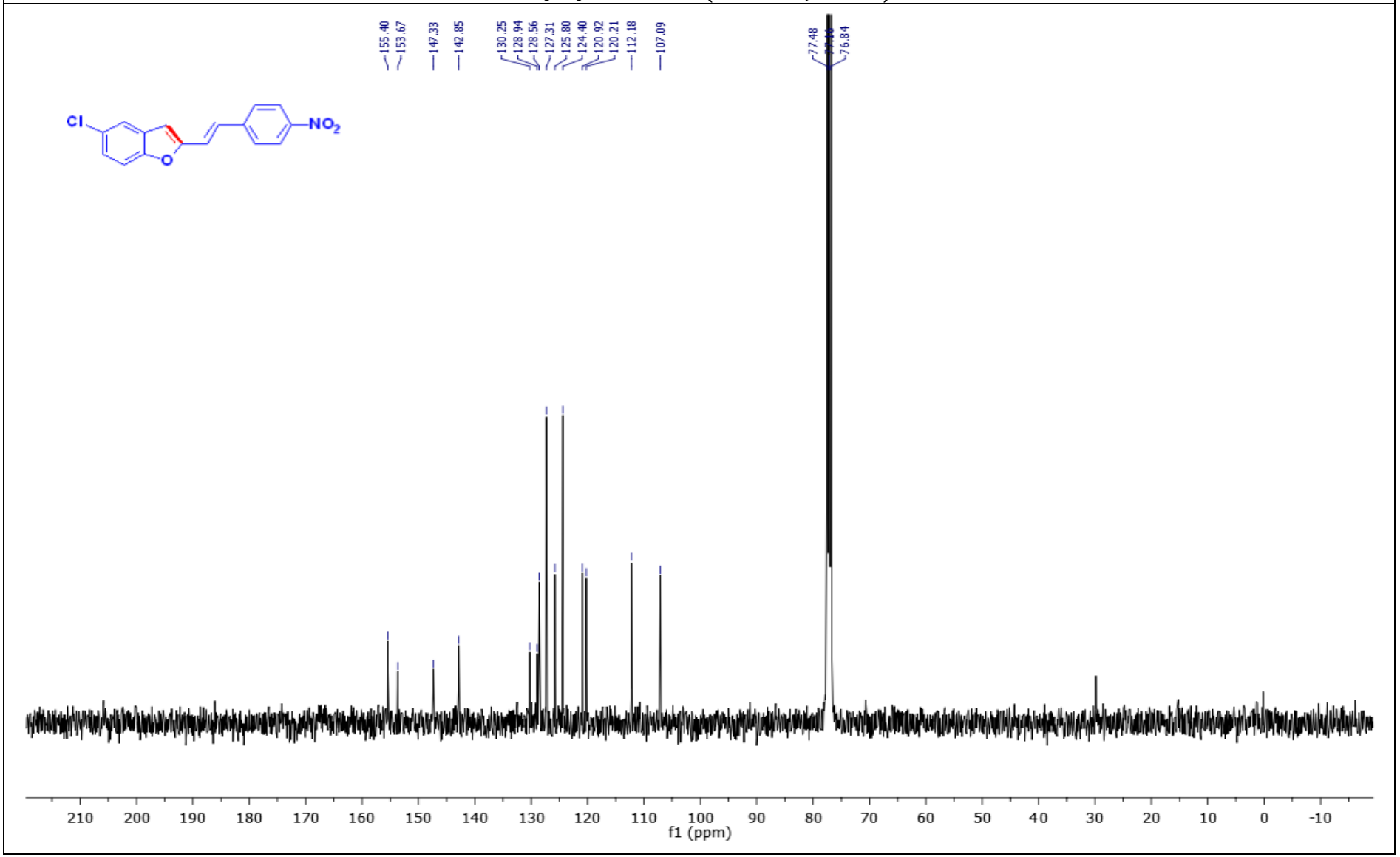
$^{13}C\{^{1}H\}$-NMR of 3h (151 MHz, $CDCl_3$)



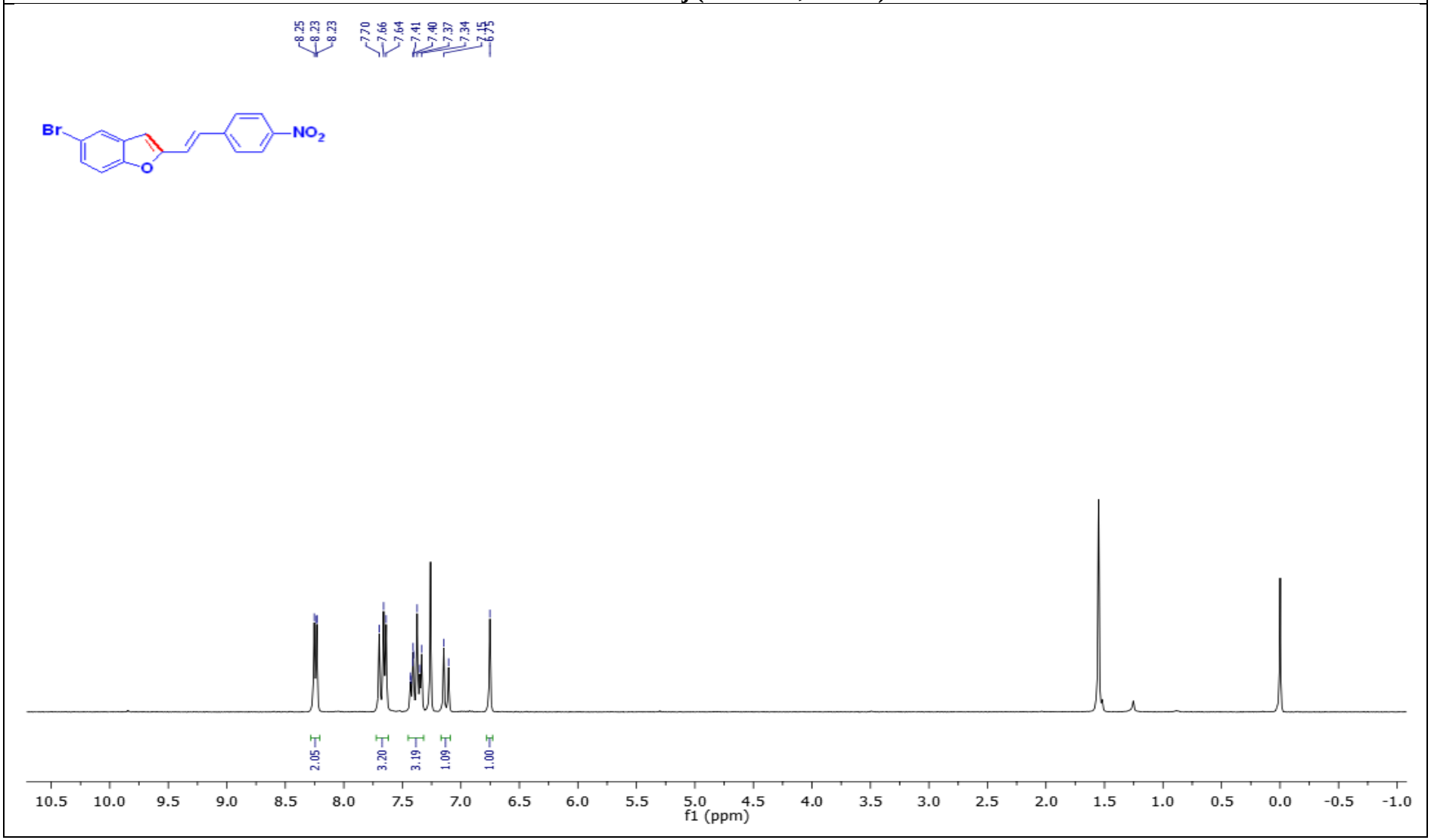
^{1}H-NMR of 3i (400 MHz, $CDCl_3$)



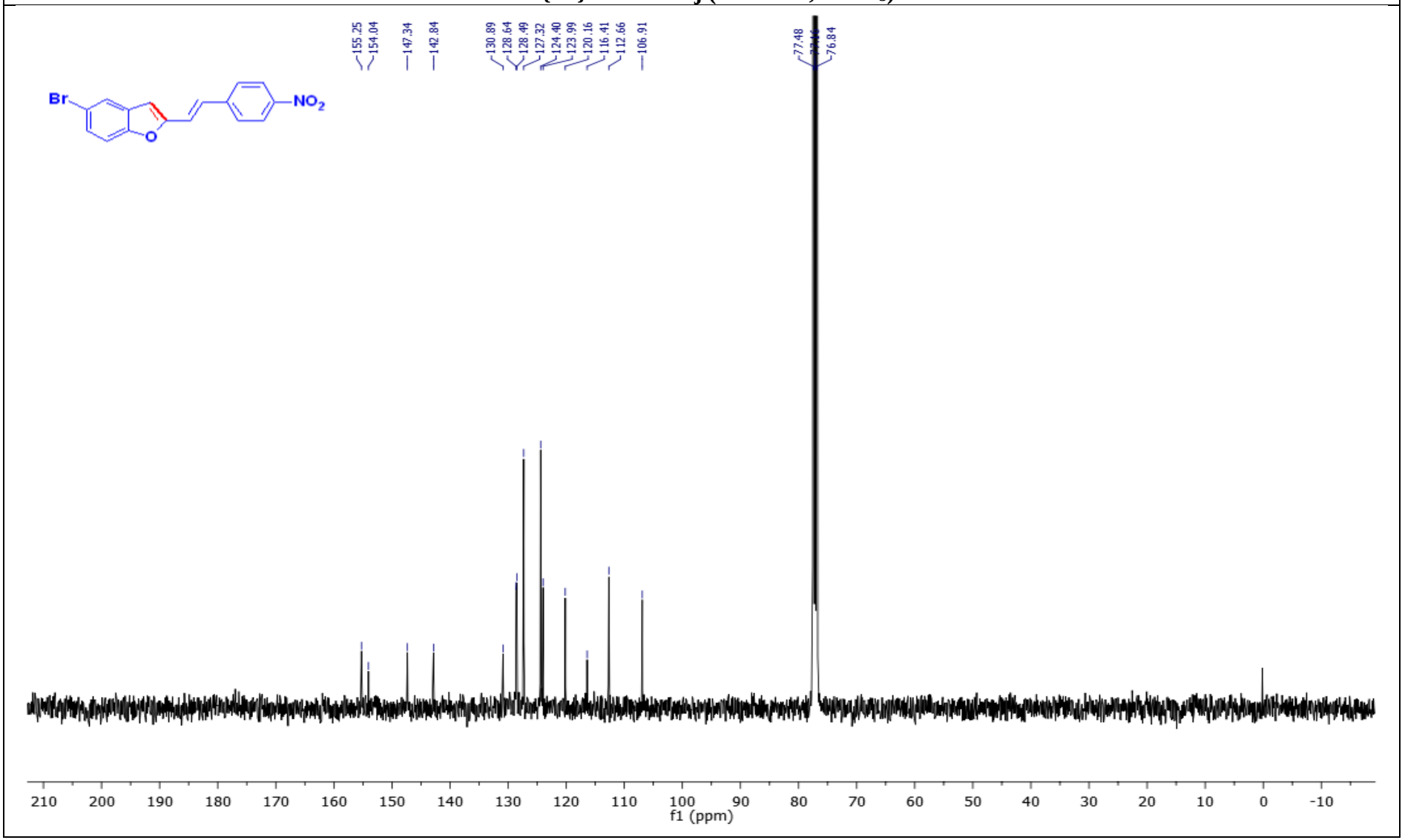
$^{13}C\{^{1}H\}$-NMR of 3i (101 MHz, $CDCl_3$)



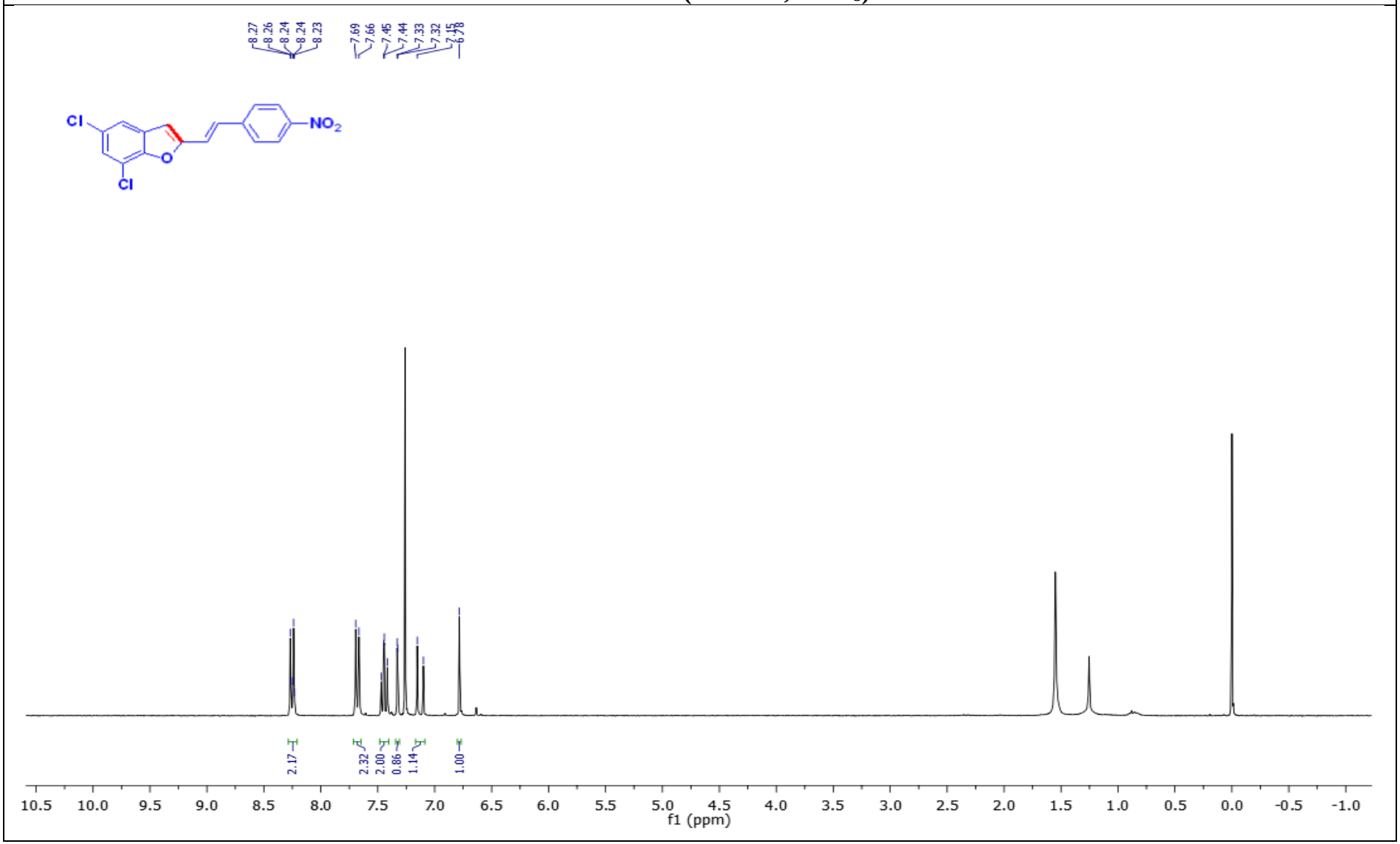
^{1}H-NMR of 3j (400 MHz, $CDCl_3$)



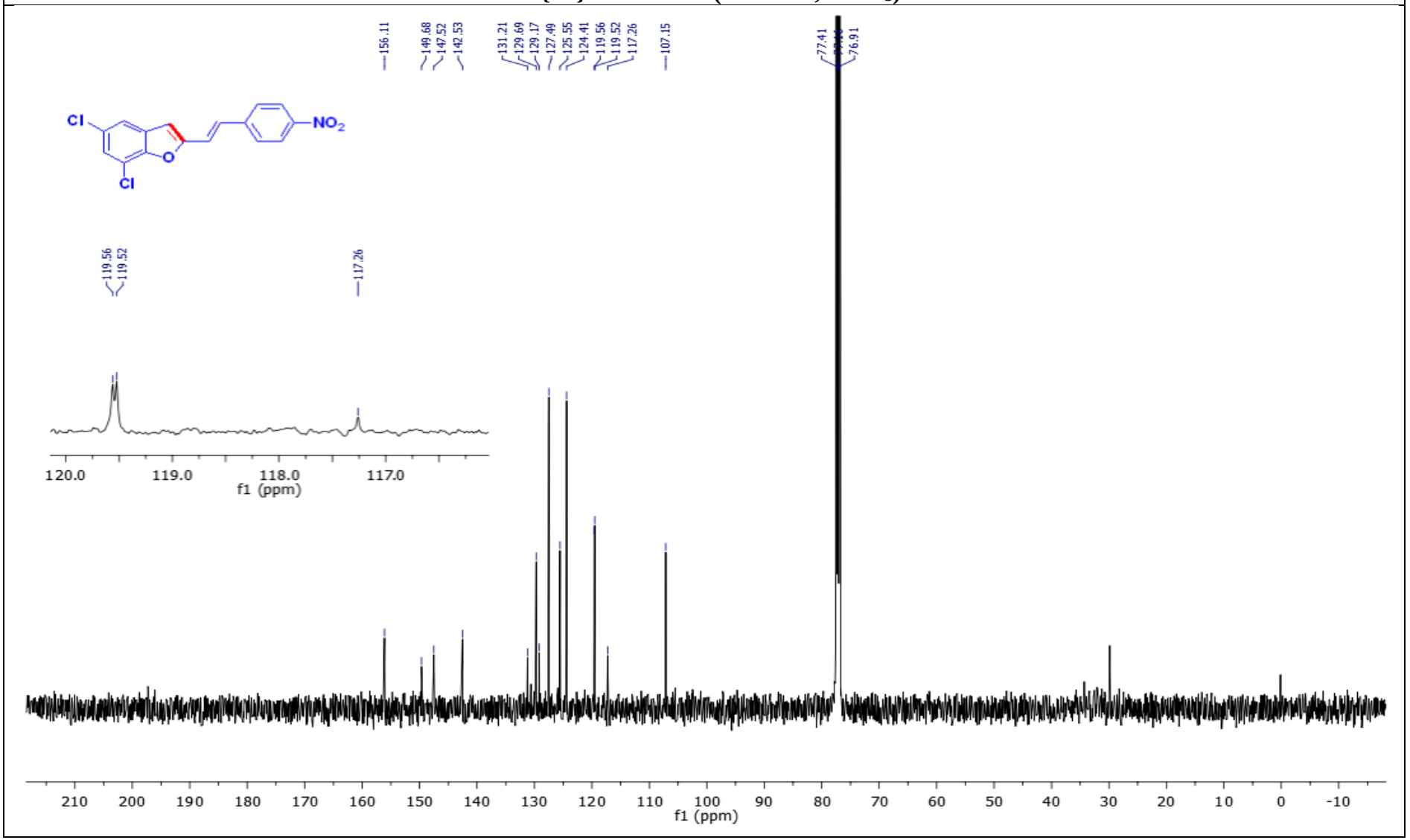
$^{13}C\{^{1}H\}$-NMR of 3j (101 MHz, $CDCl_3$)



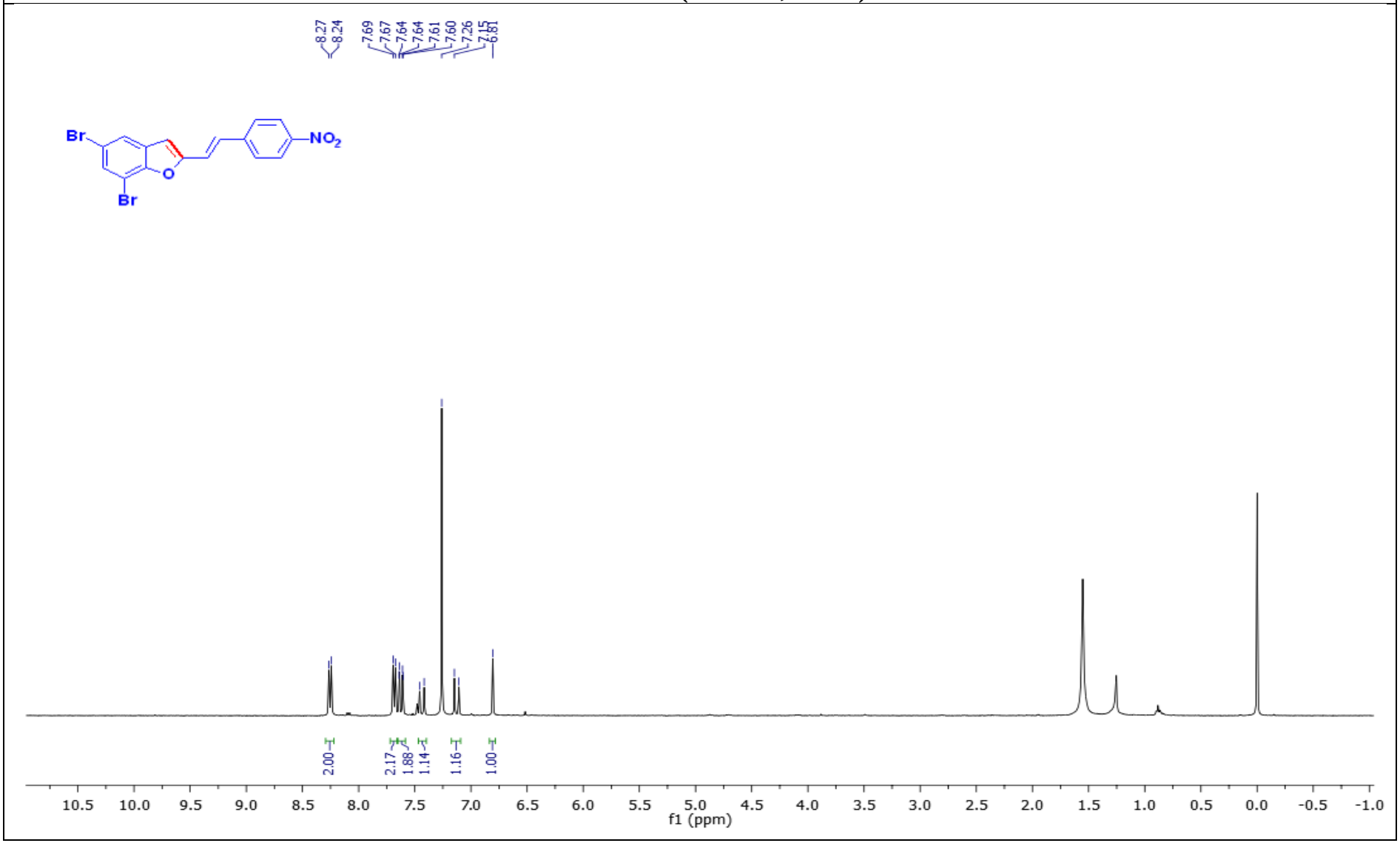
^{1}H-NMR of 3k (300 MHz, $CDCl_3$)



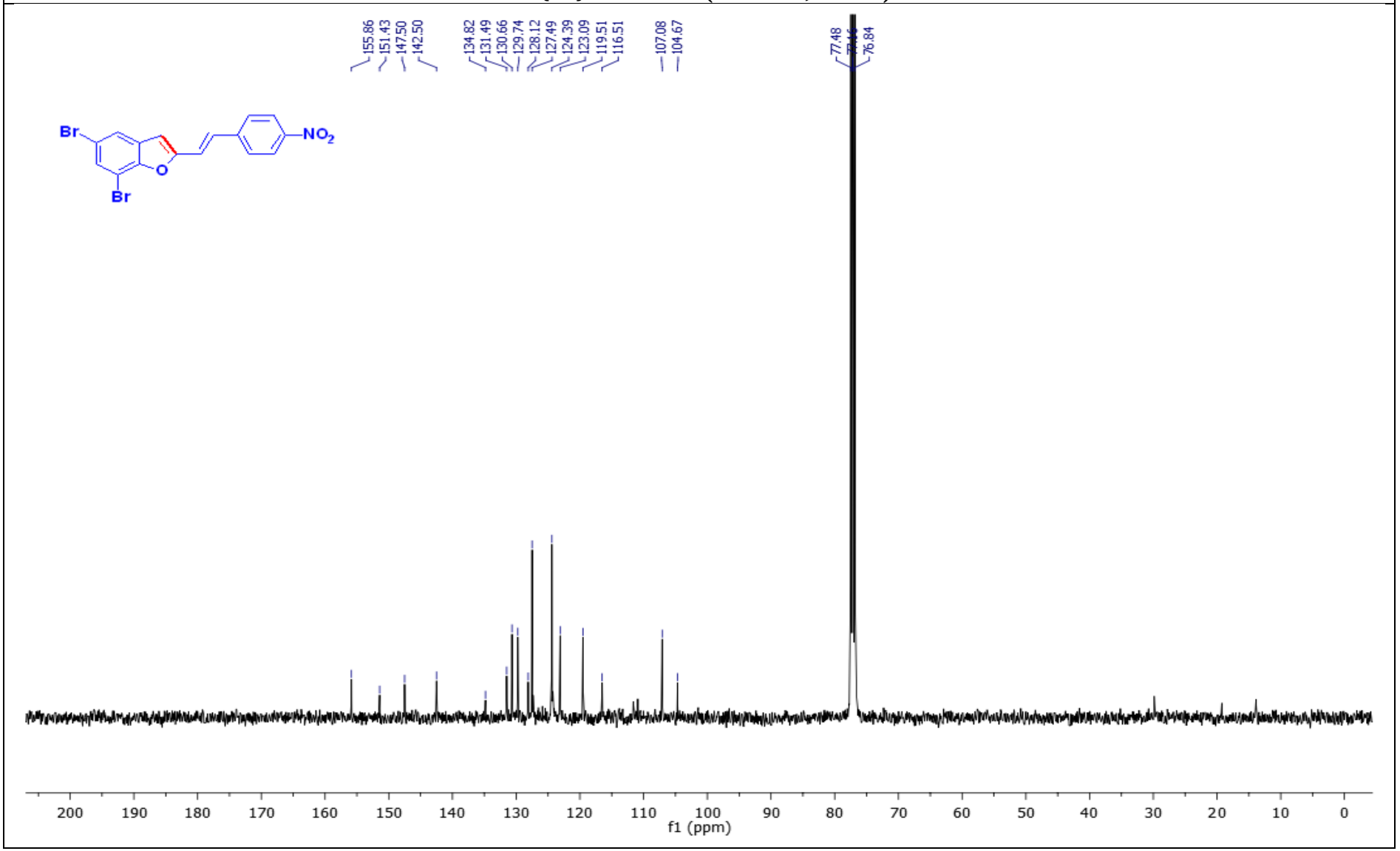
$^{13}C\{^{1}H\}$-NMR of 3k (126 MHz, $CDCl_3$)



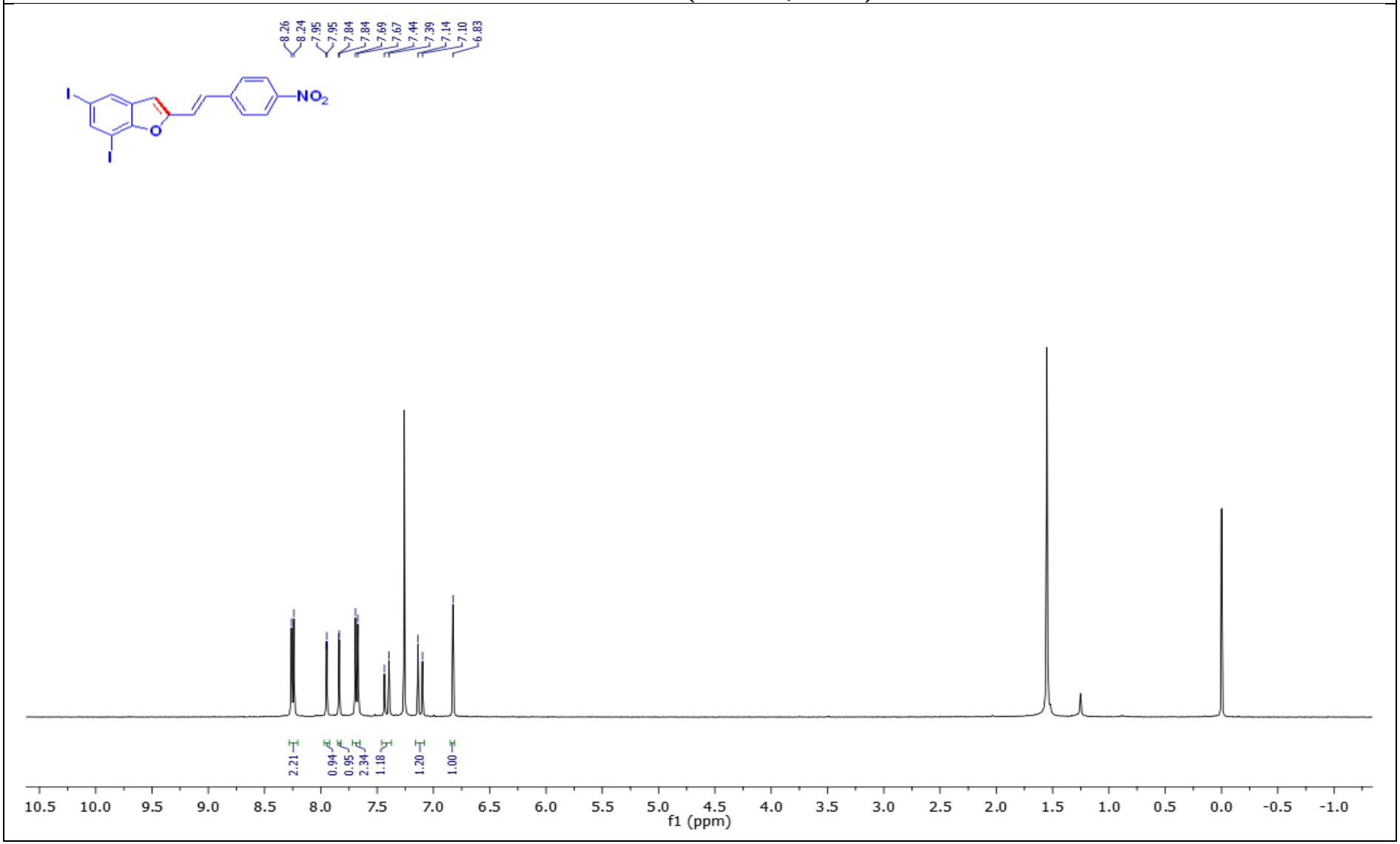
^{1}H-NMR of 3l (400 MHz, $CDCl_3$)



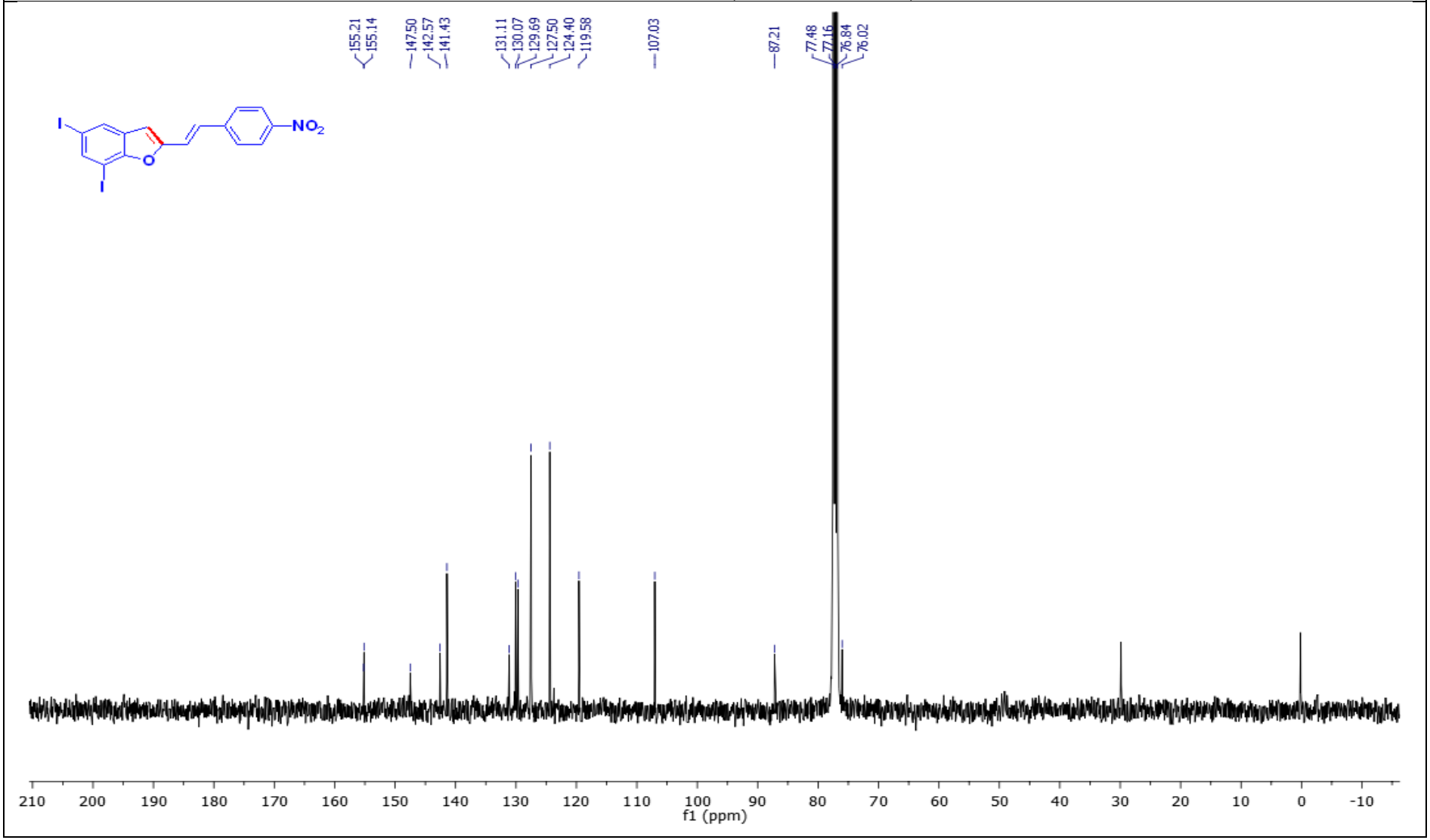
$^{13}C\{^{1}H\}$-NMR of 3l (101 MHz, $CDCl_3$)



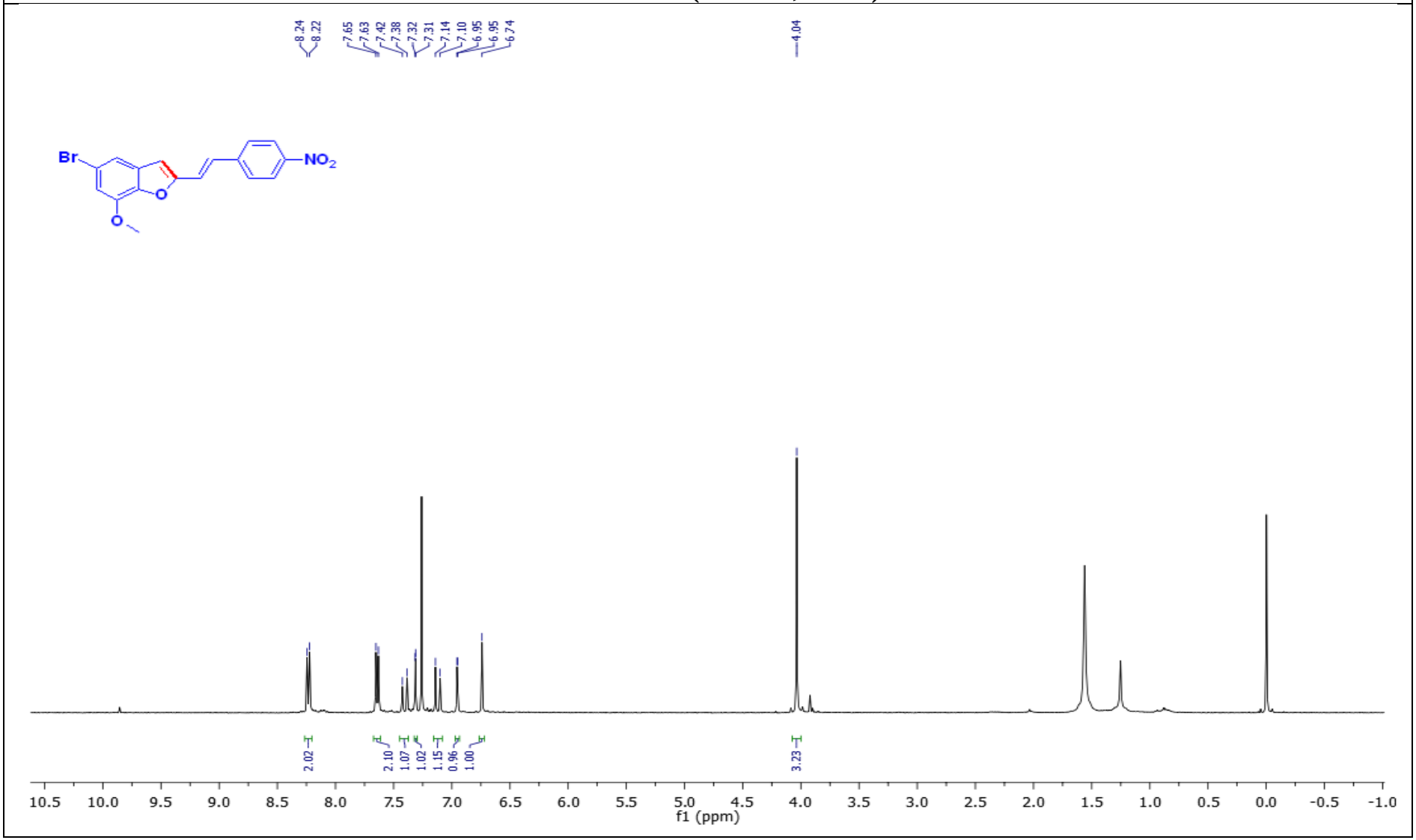
^{1}H-NMR of 3m (400 MHz, $CDCl_3$)



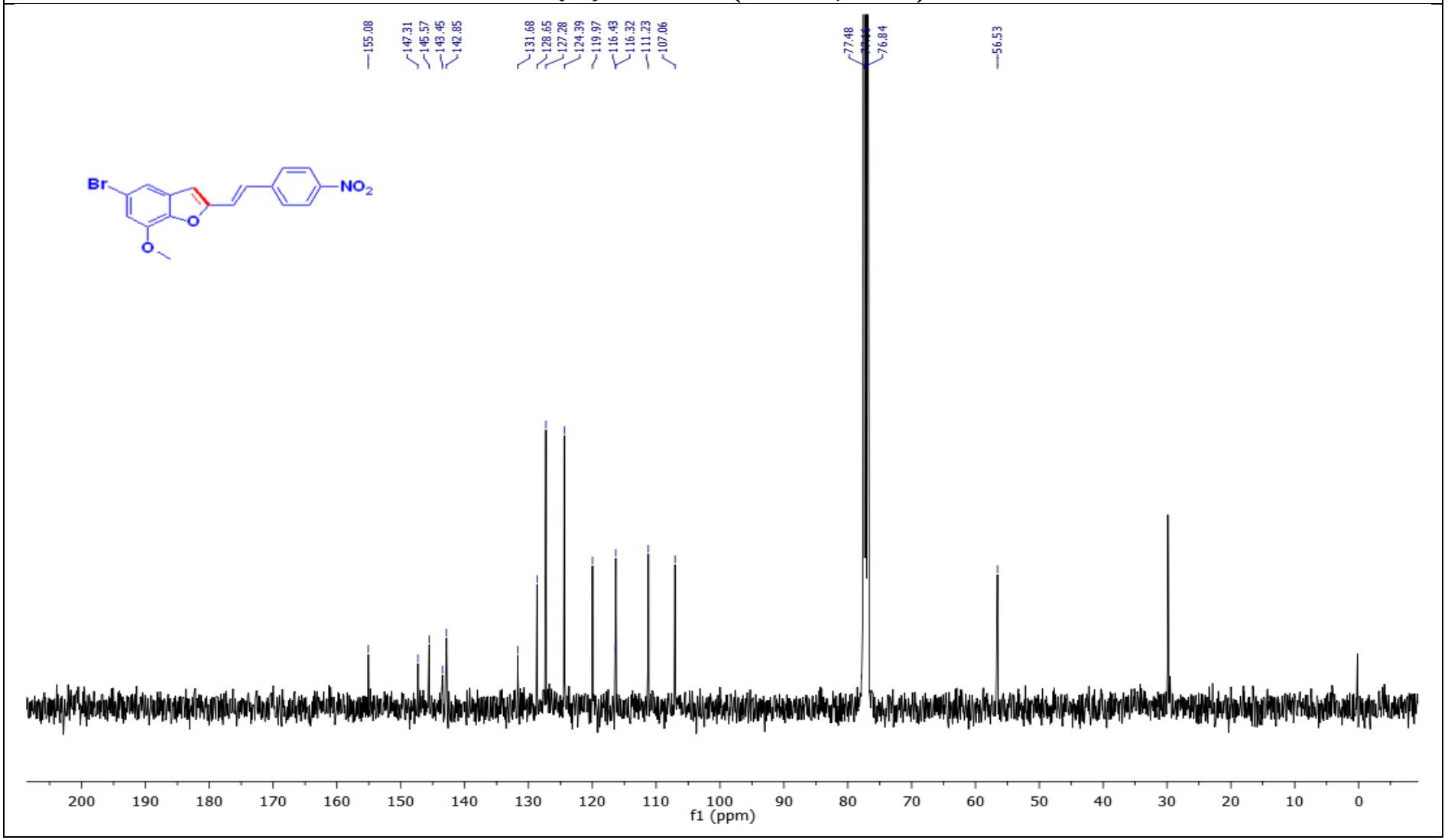
$^{13}C\{^{1}H\}$-NMR of 3m (101 MHz, $CDCl_3$)



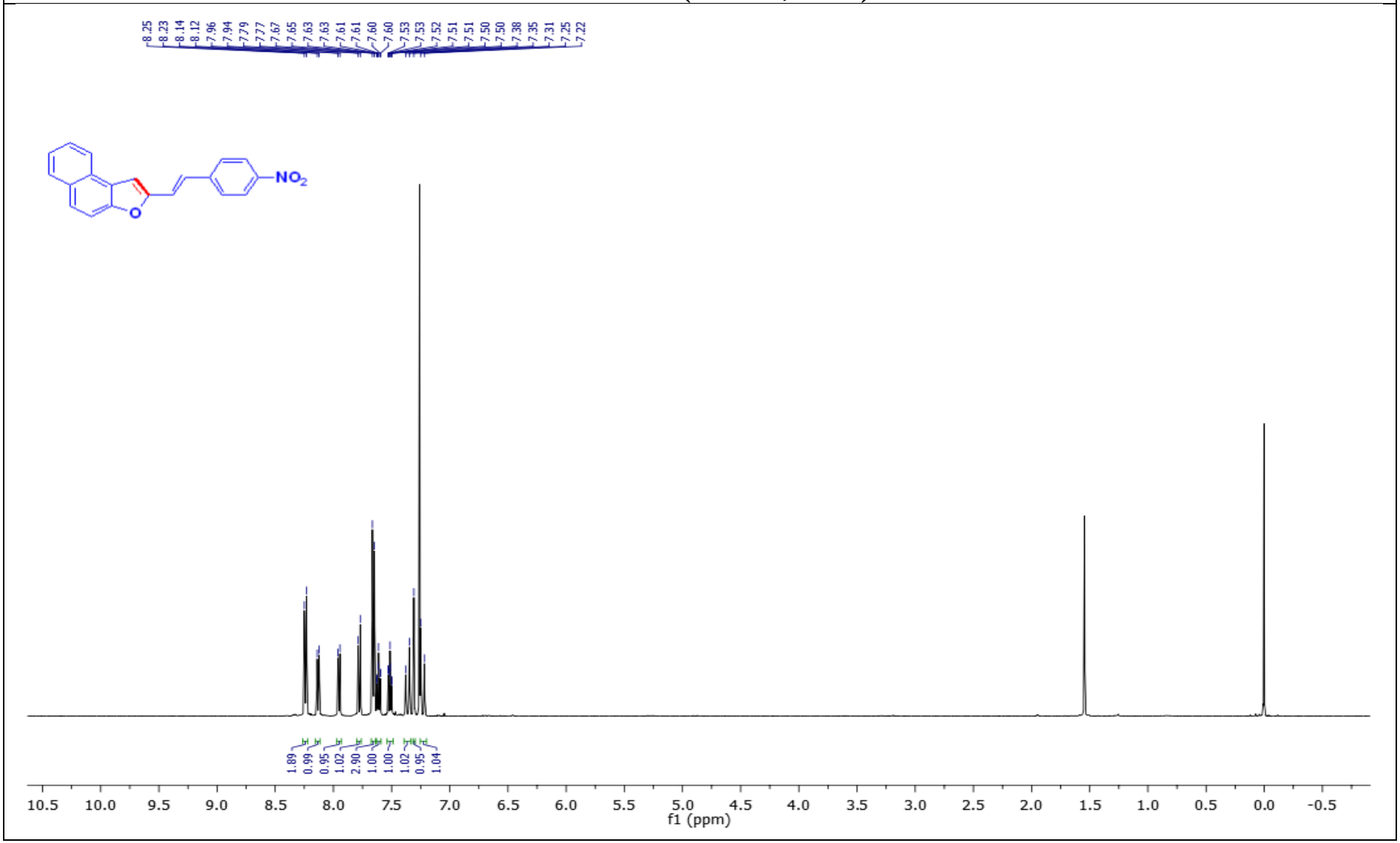
^{1}H-NMR of 3n (400 MHz, $CDCl_3$)



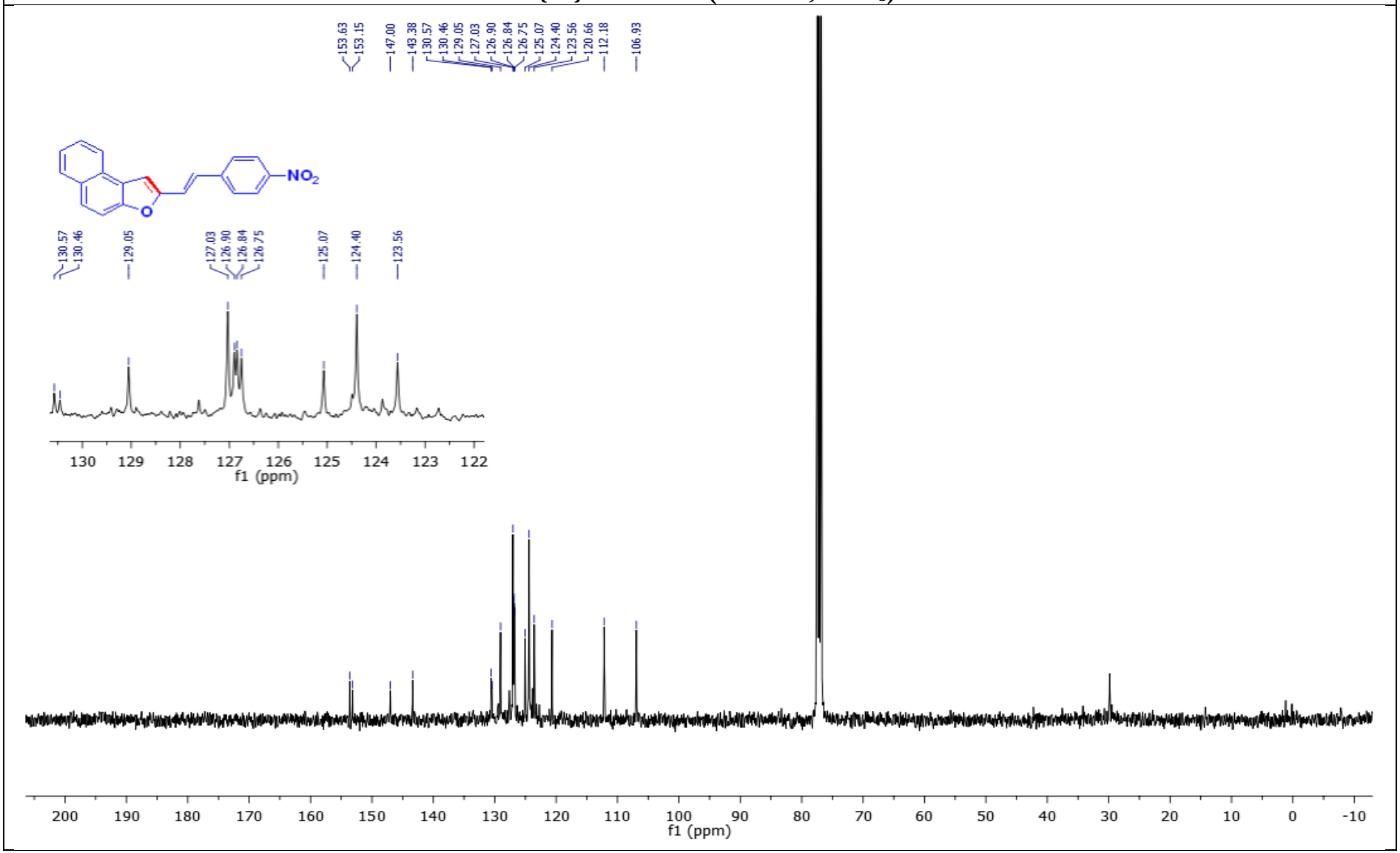
$^{13}C\{^{1}H\}$-NMR of 3n (101 MHz, $CDCl_3$)



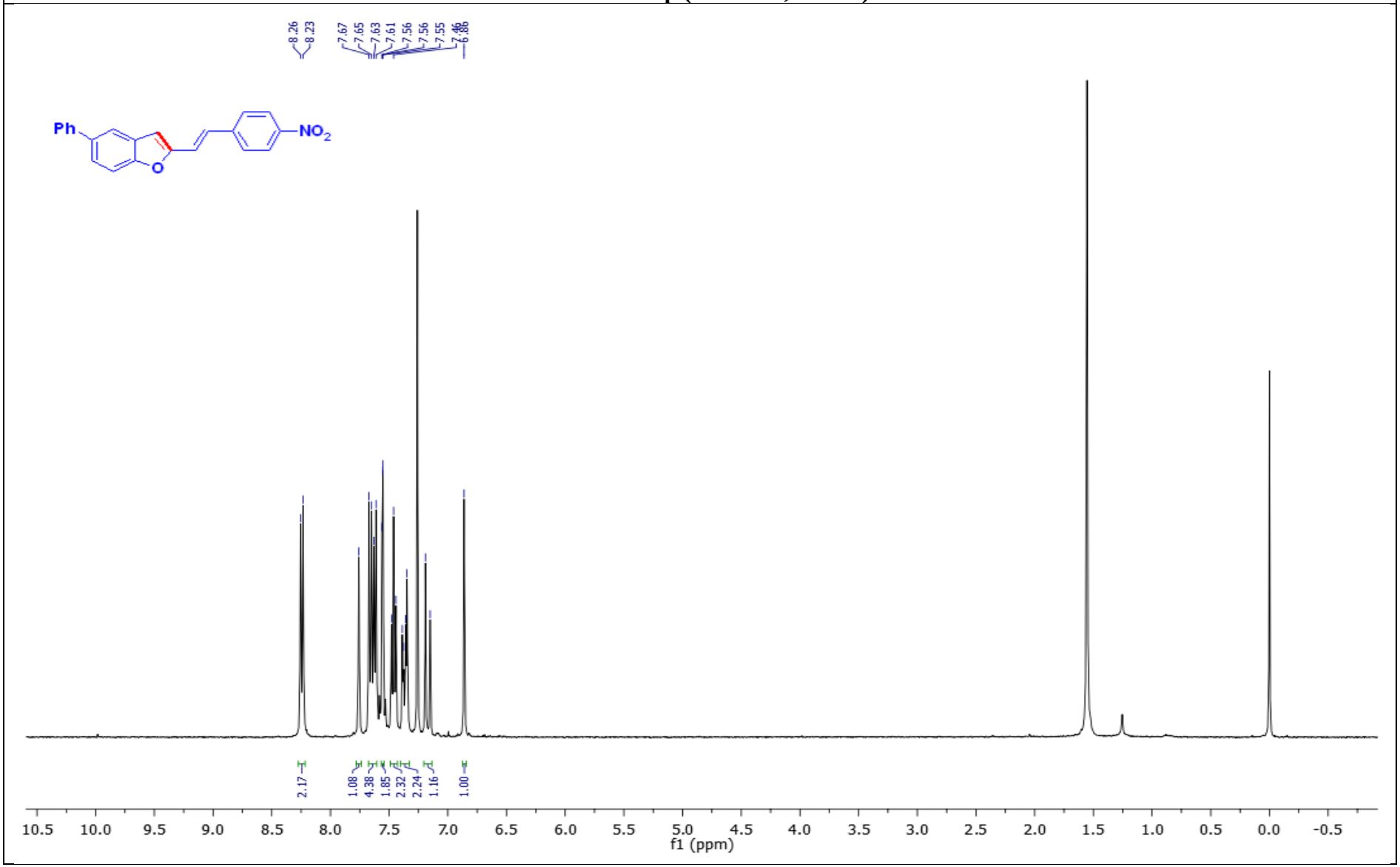
^{1}H-NMR of 3o (500 MHz, $CDCl_3$)



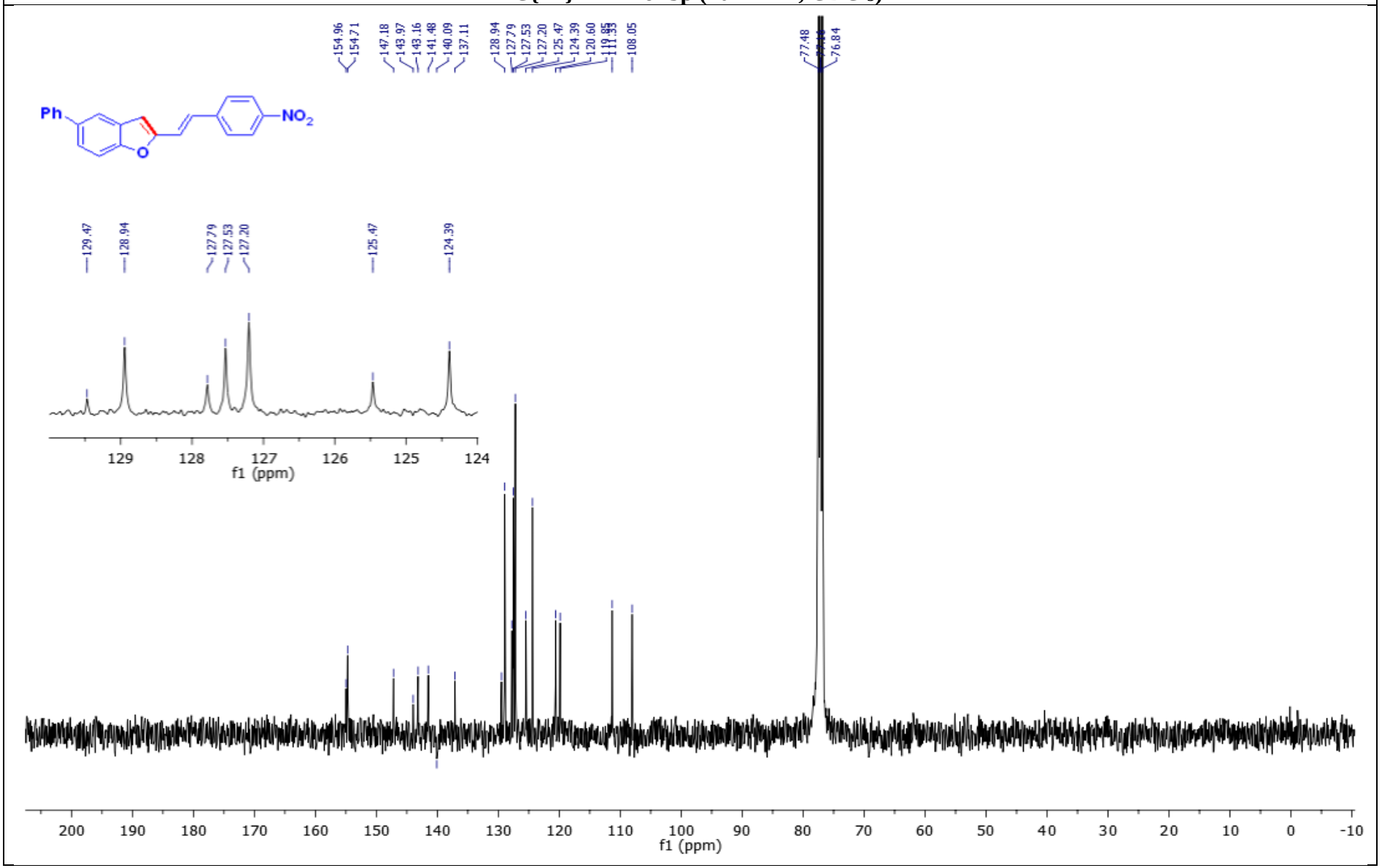
$^{13}C\{^{1}H\}$-NMR of 3o (101 MHz, $CDCl_3$)



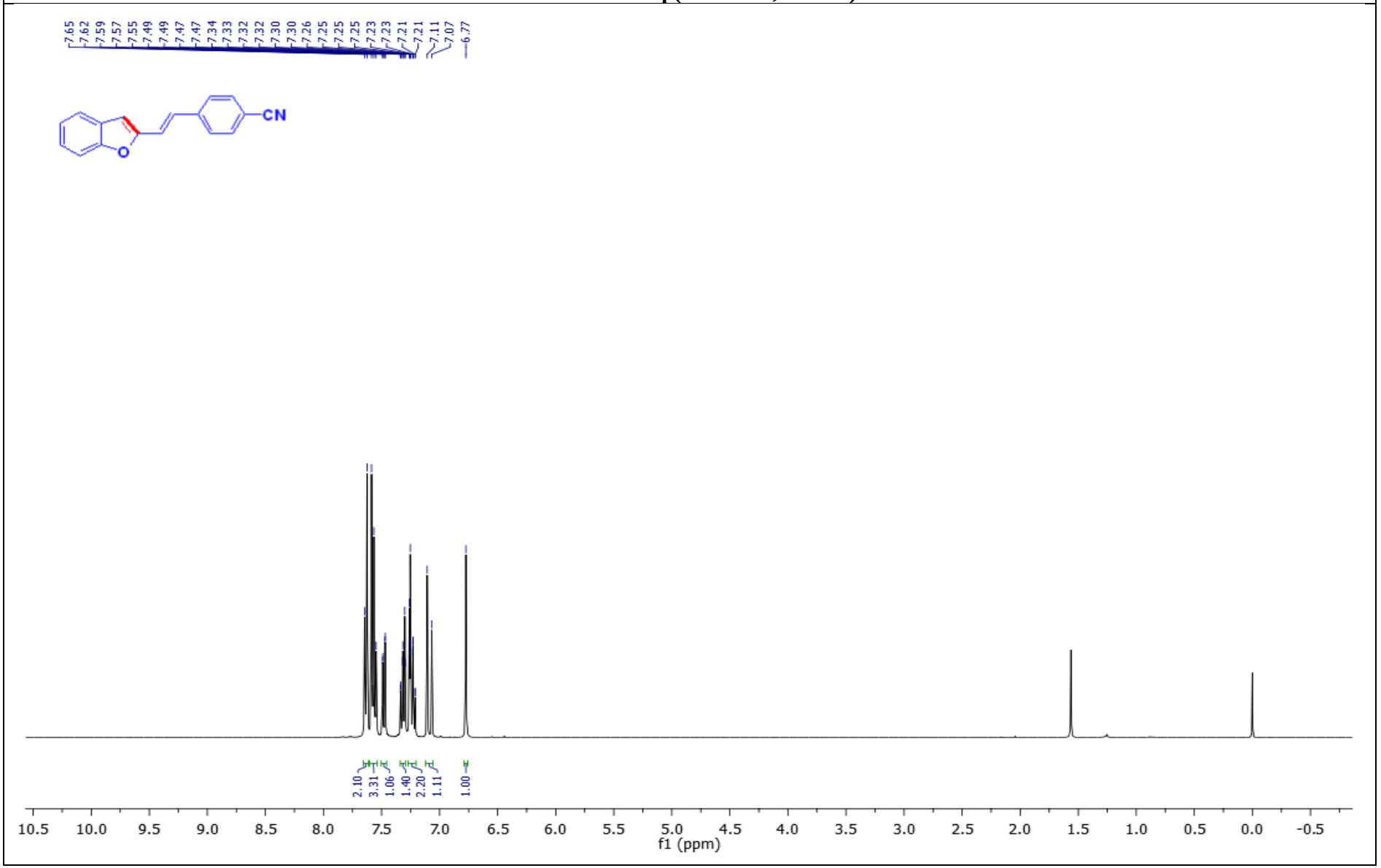
^{1}H-NMR of 3p (400 MHz, $CDCl_3$)



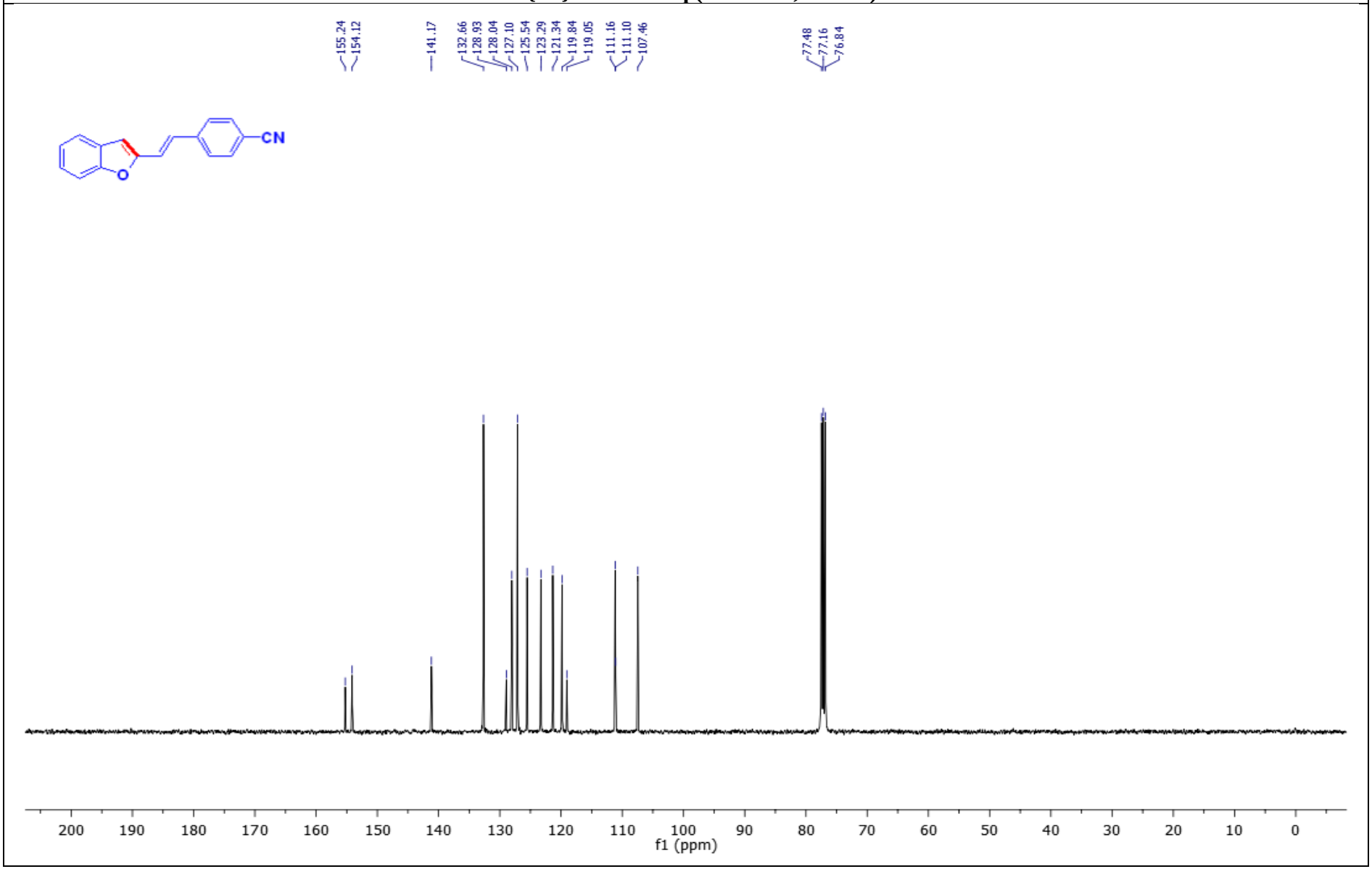
$^{13}C\{^{1}H\}$-NMR of 3p (101 MHz, $CDCl_3$)



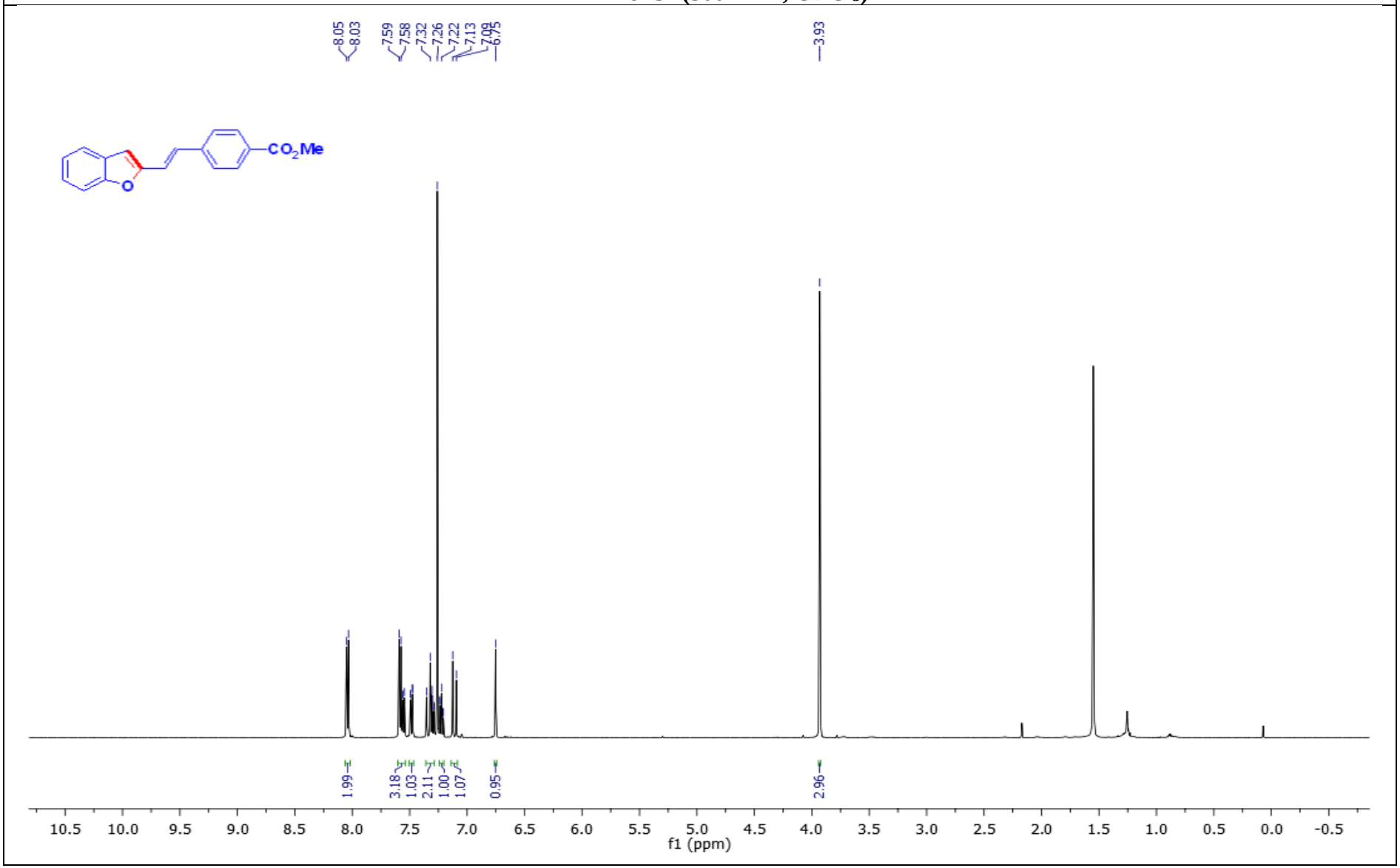
^{1}H-NMR of 3q (400 MHz, $CDCl_3$)



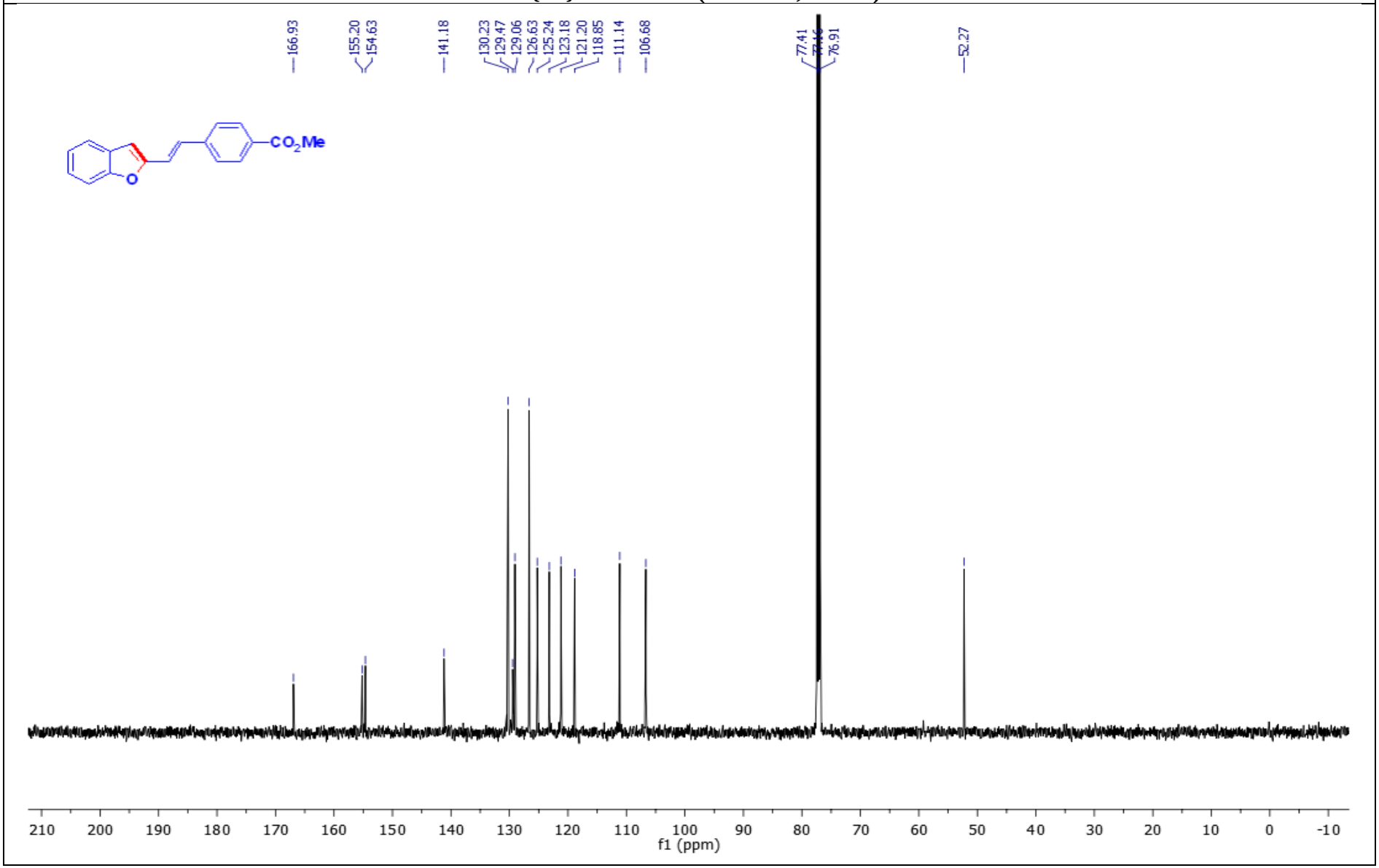
$^{13}C\{^{1}H\}$-NMR of 3q (101 MHz, $CDCl_3$)



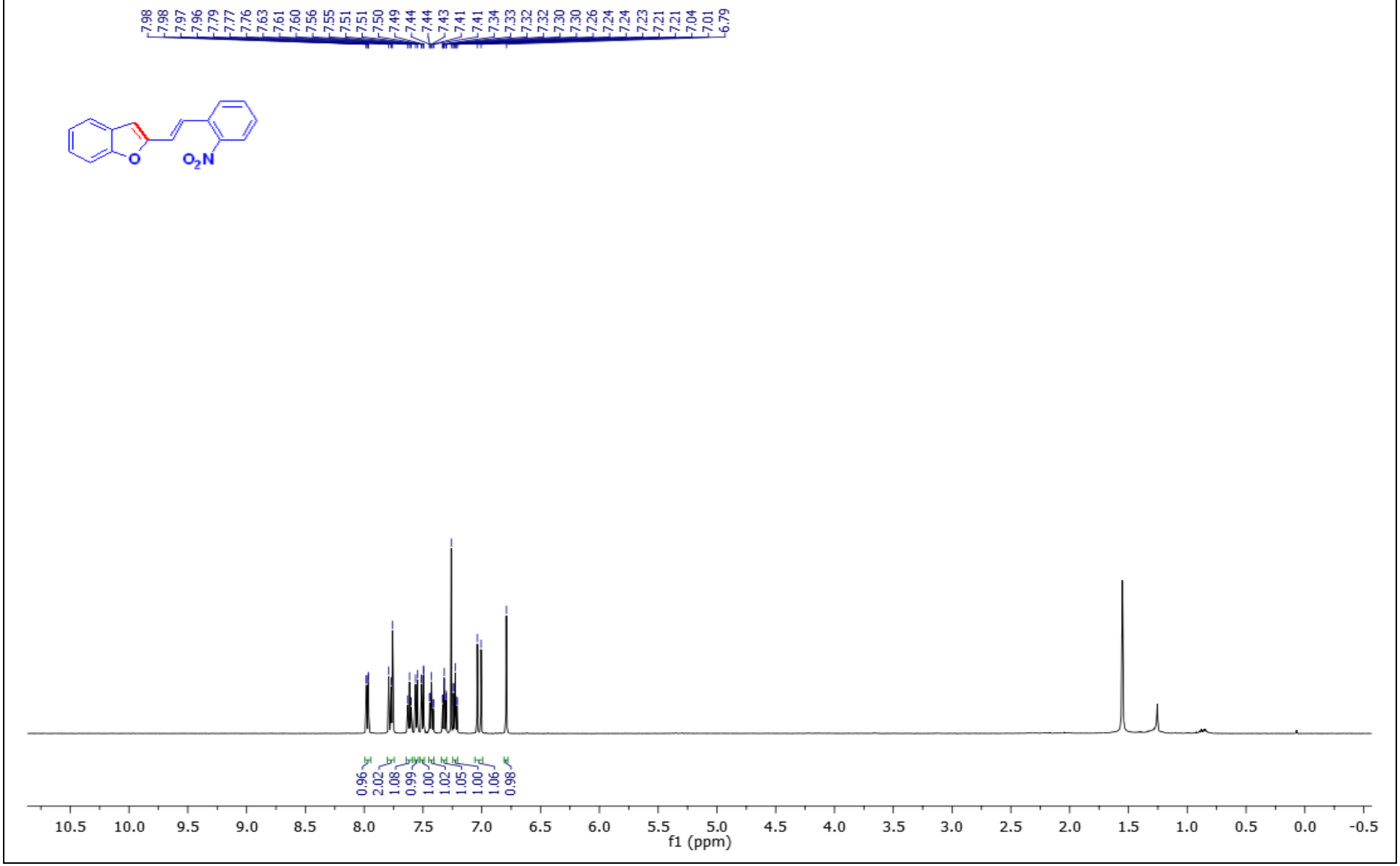
^{1}H-NMR of 3r (500 MHz, $CDCl_3$)



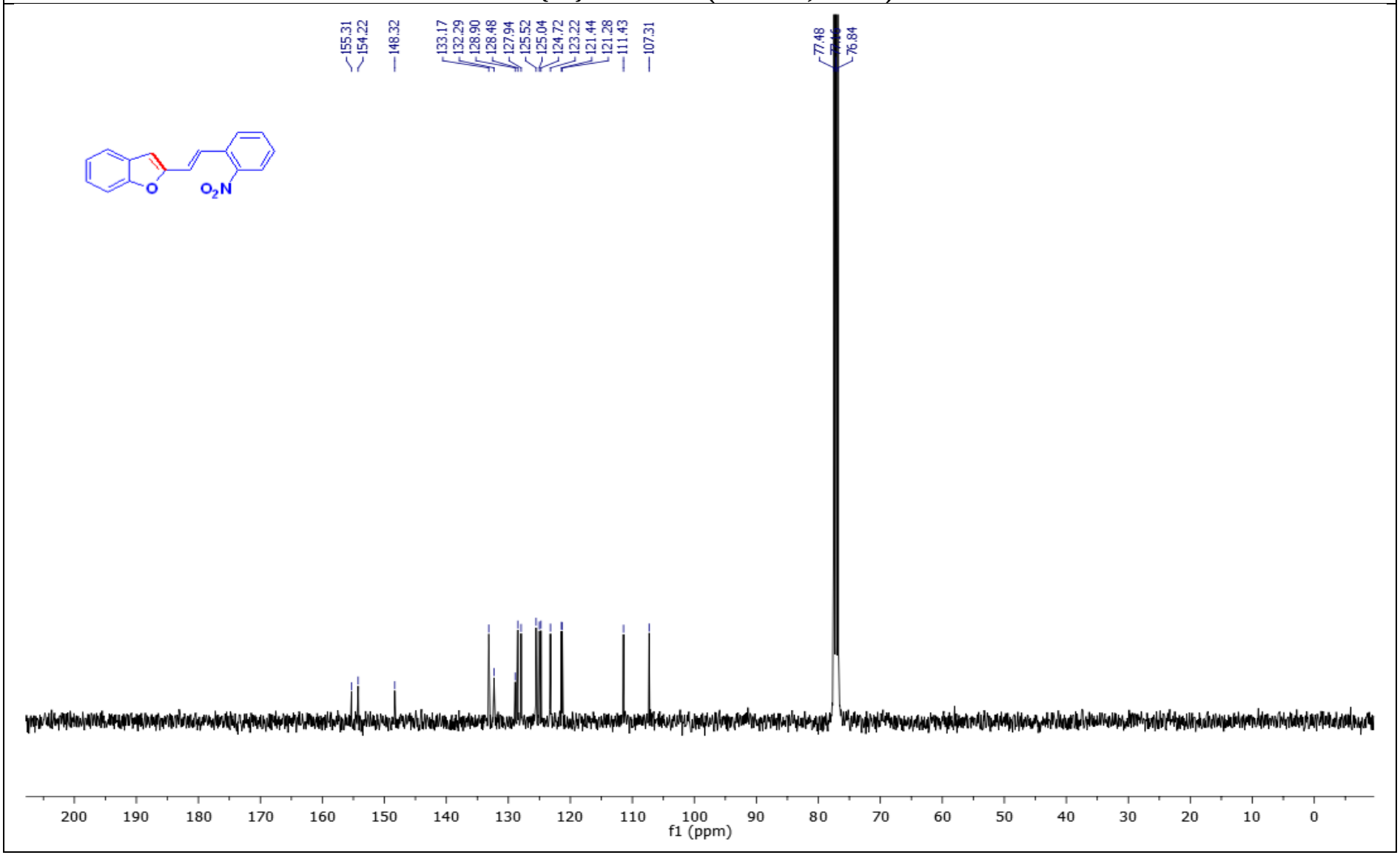
$^{13}C\{^{1}H\}$-NMR of 3r (126 MHz, $CDCl_3$)



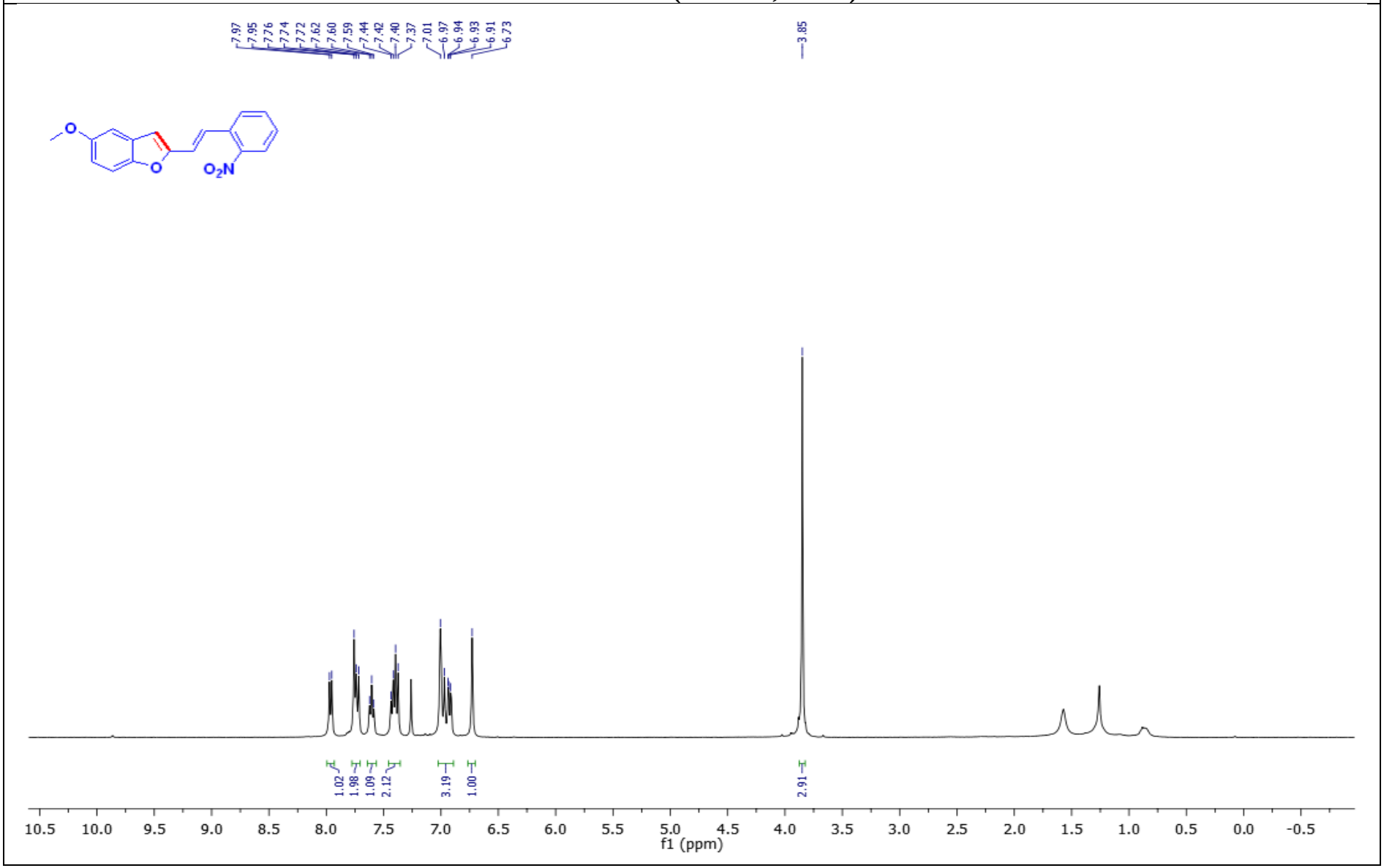
^{1}H-NMR of 3s (500 MHz, $CDCl_3$)



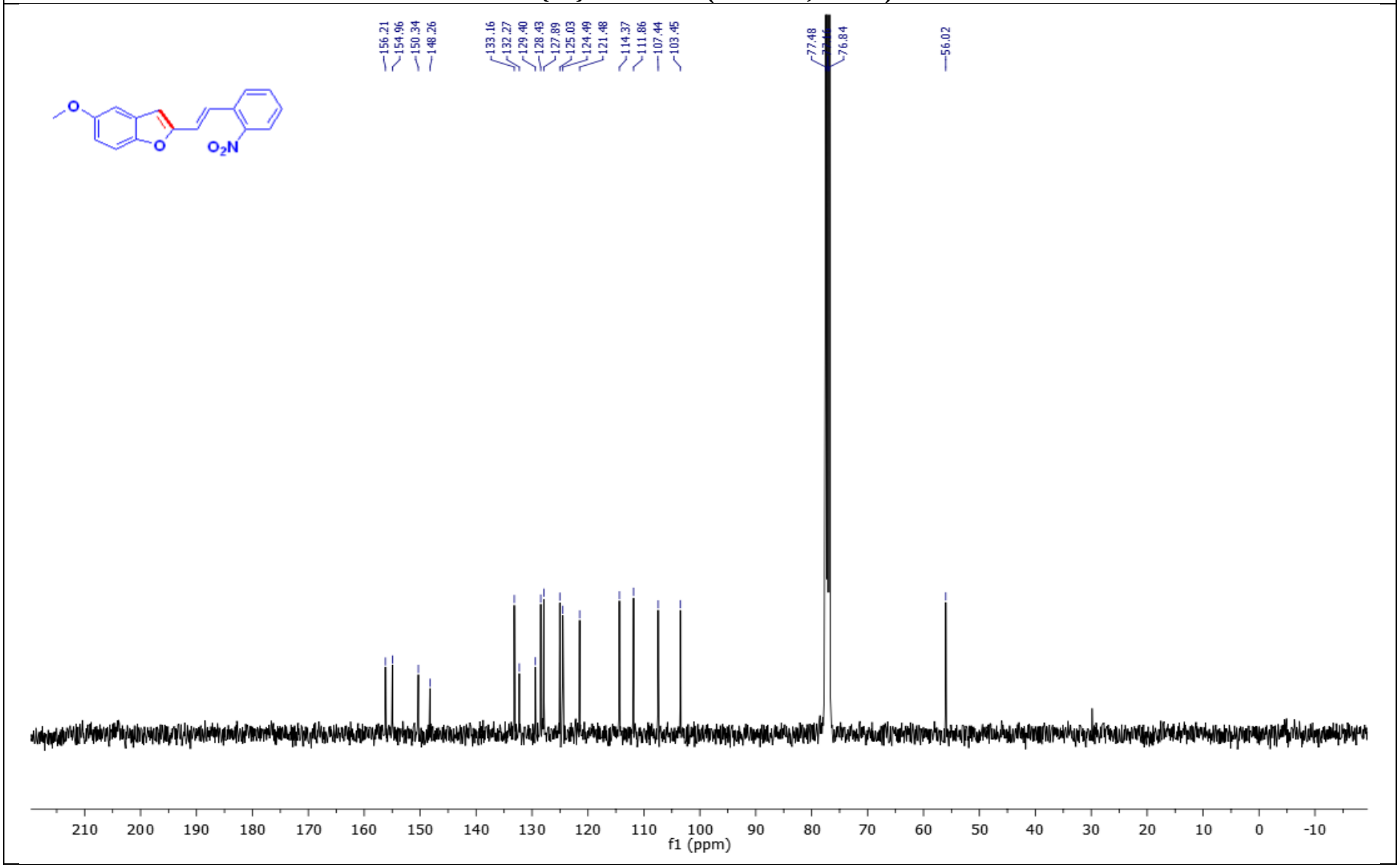
$^{13}C\{^{1}H\}$-NMR of 3s (101 MHz, $CDCl_3$)



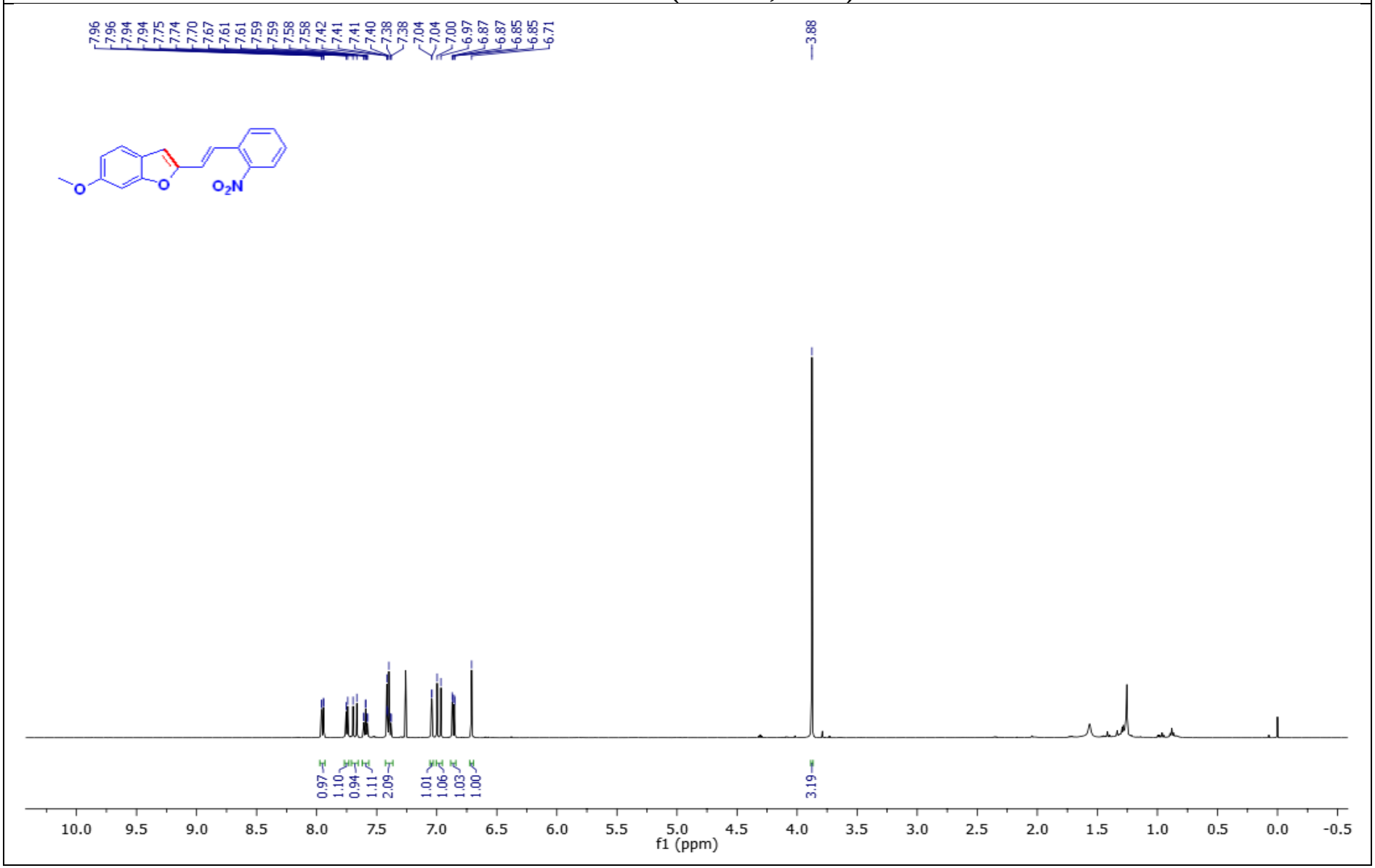
^{1}H-NMR of 3t (400 MHz, $CDCl_3$)



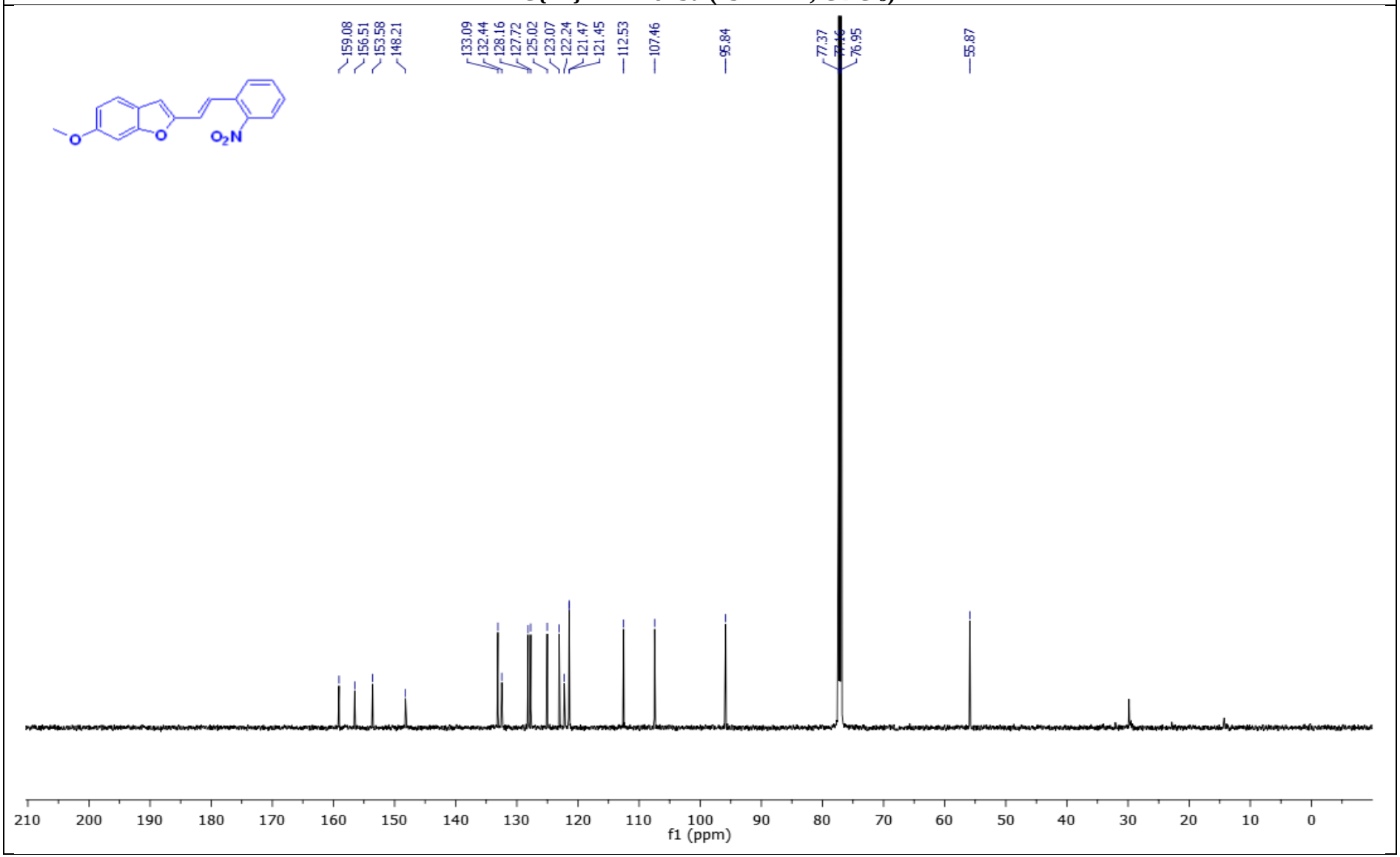
$^{13}C\{^{1}H\}$-NMR of 3t (101 MHz, $CDCl_3$)



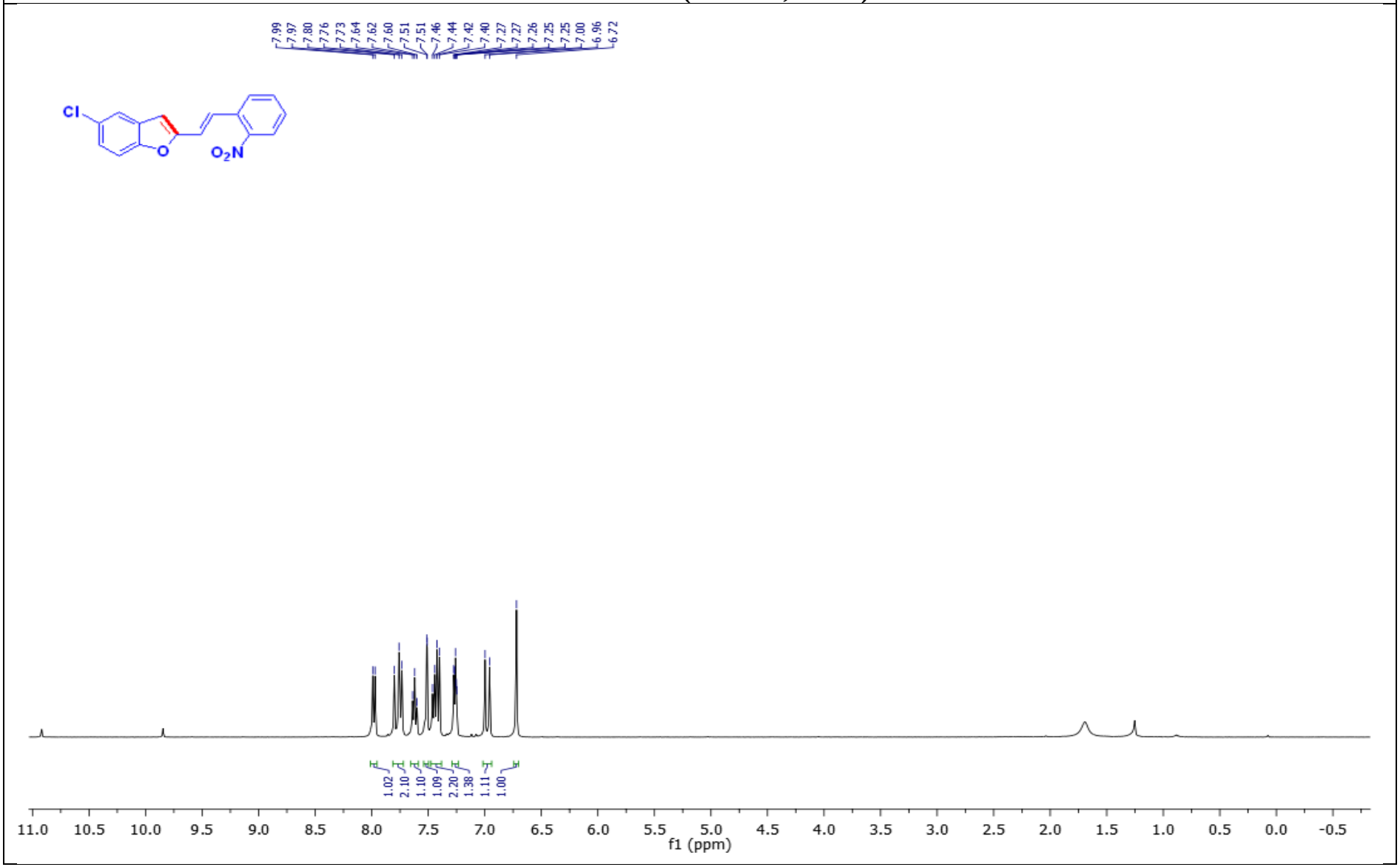
^{1}H-NMR of 3u (500 MHz, $CDCl_3$)



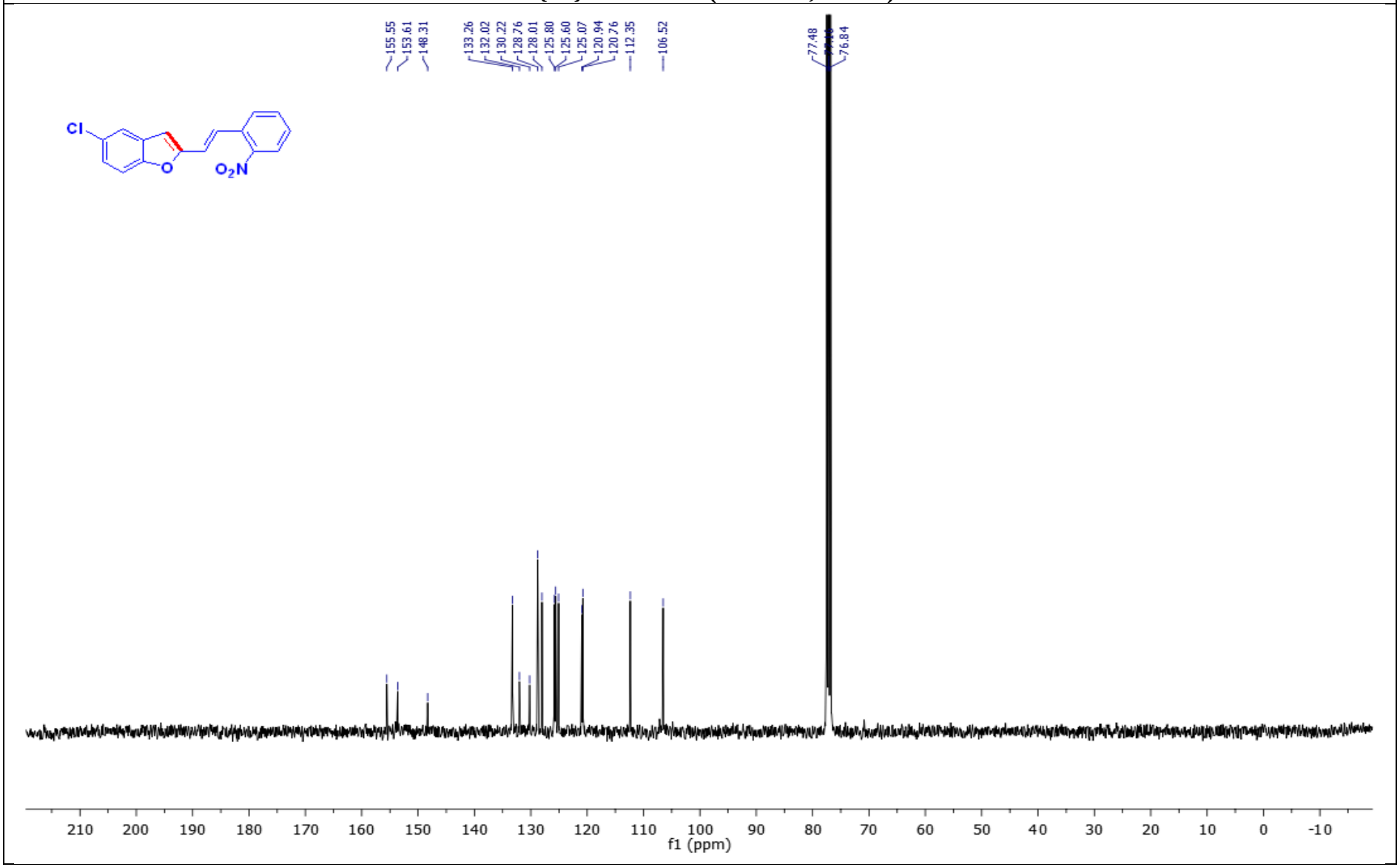
$^{13}C\{^{1}H\}$-NMR of 3u (151 MHz, $CDCl_3$)



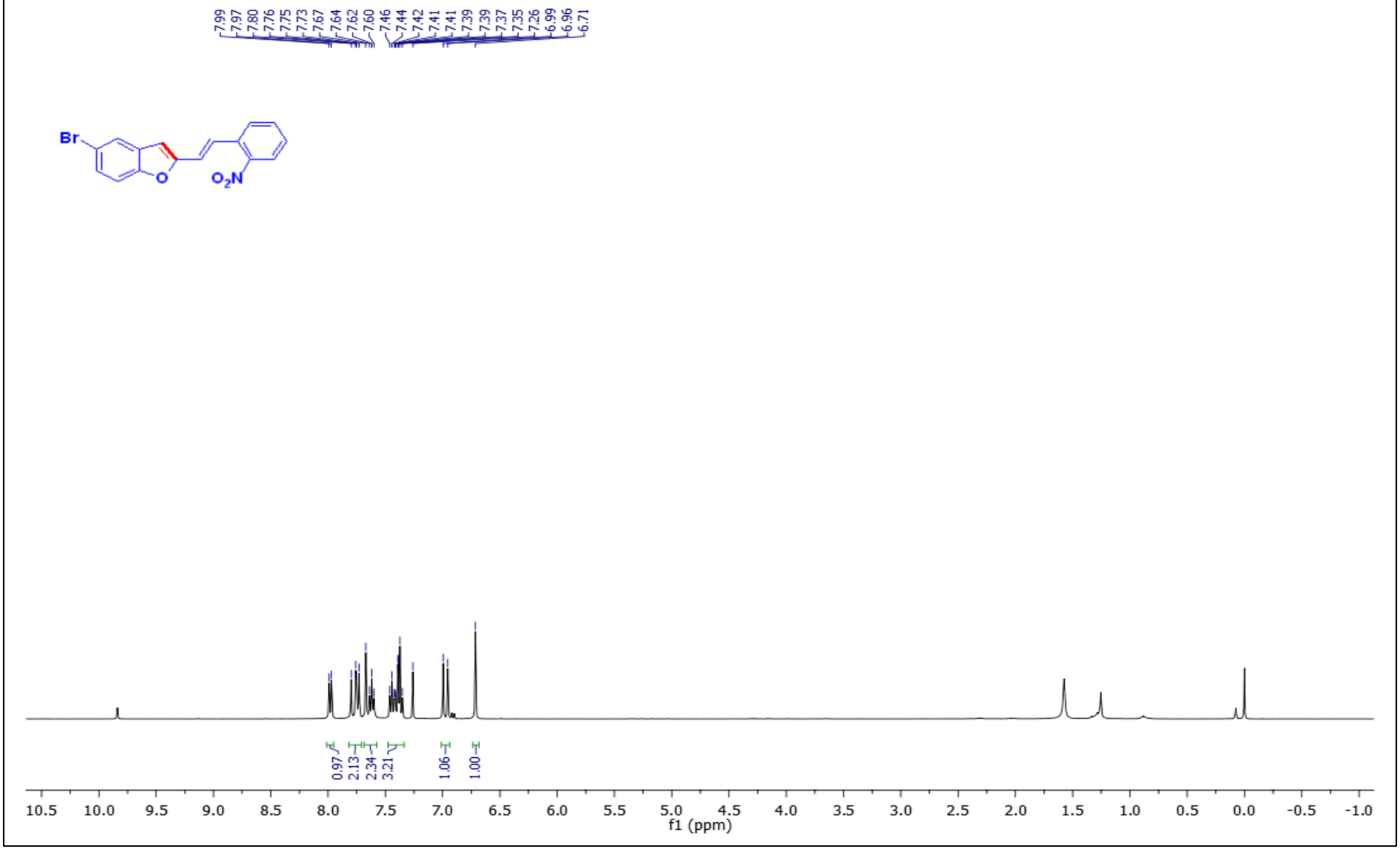
^{1}H-NMR of 3v (400 MHz, $CDCl_3$)



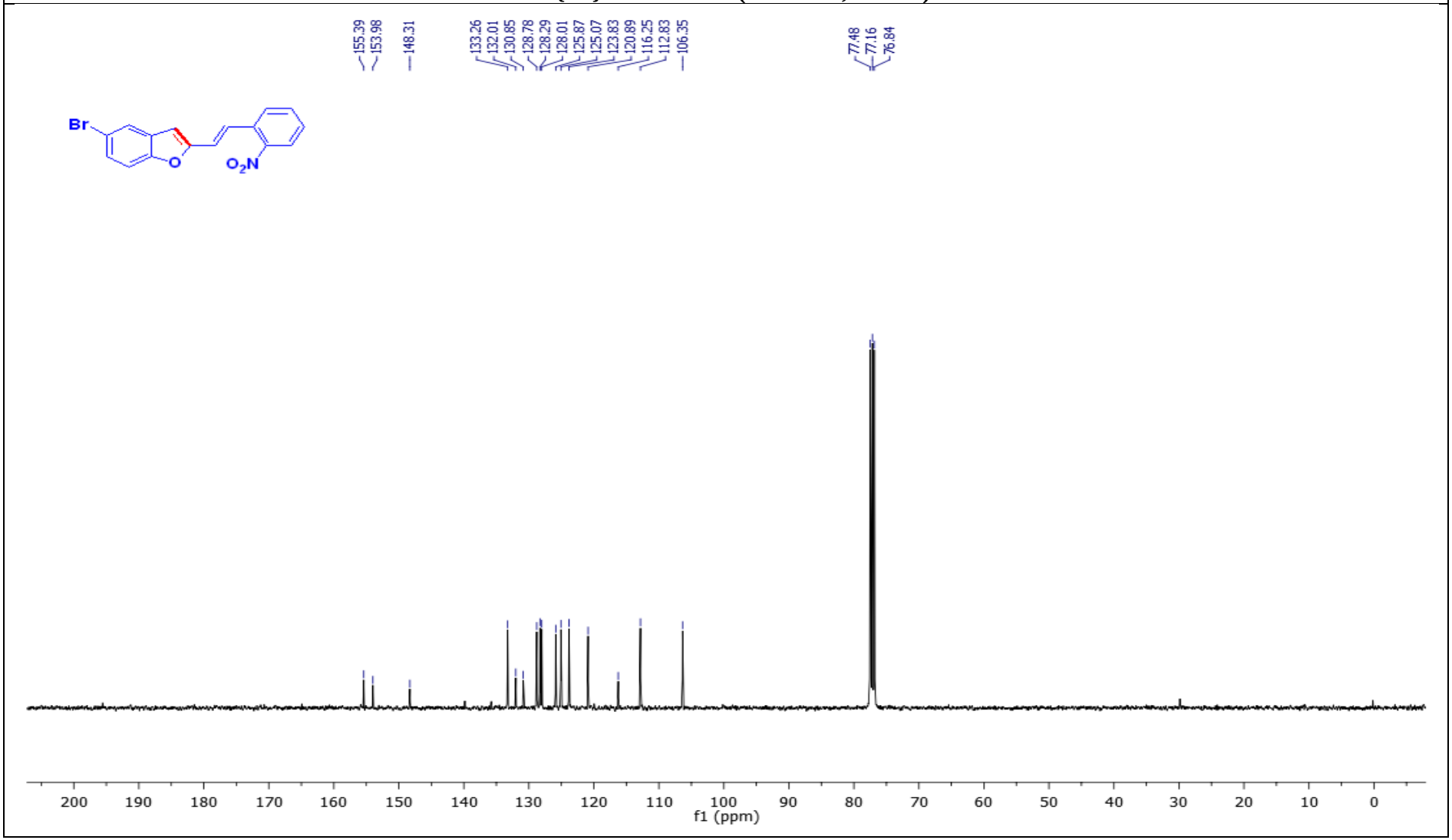
$^{13}C\{^{1}H\}$-NMR of 3v (101 MHz, $CDCl_3$)



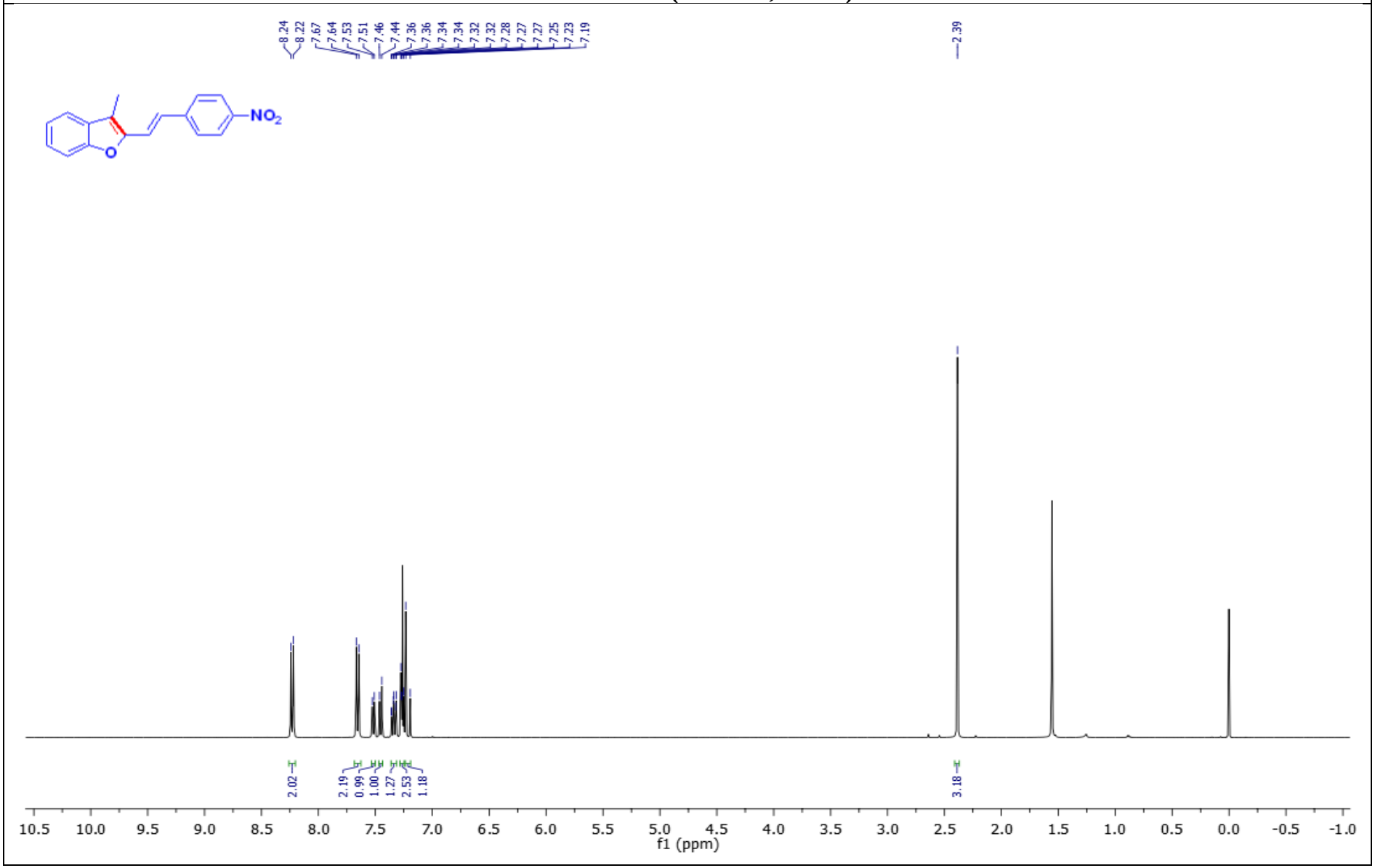
^{1}H-NMR of 3w (400 MHz, $CDCl_3$)



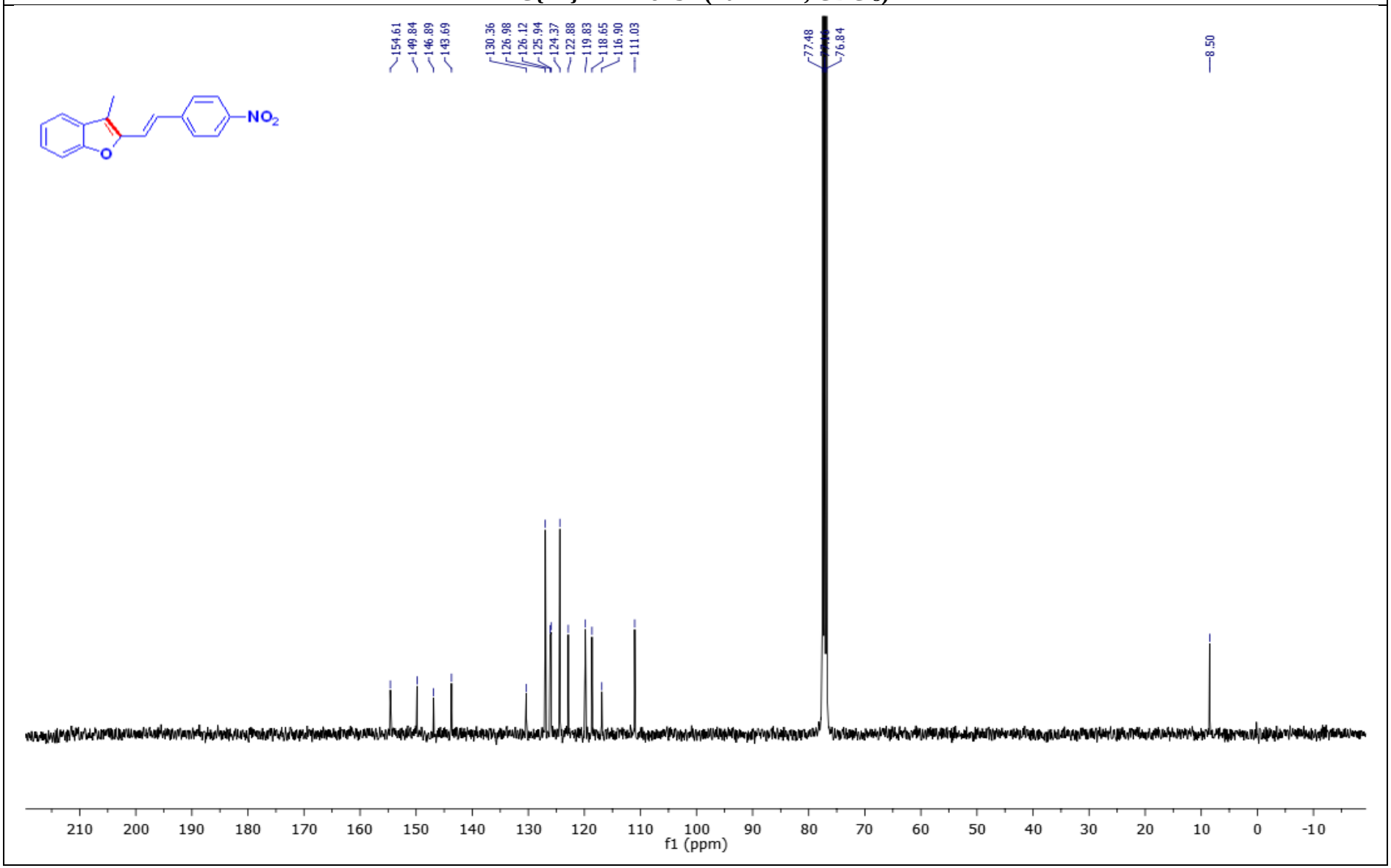
$^{13}C\{^{1}H\}$-NMR of 3w (101 MHz, $CDCl_3$)



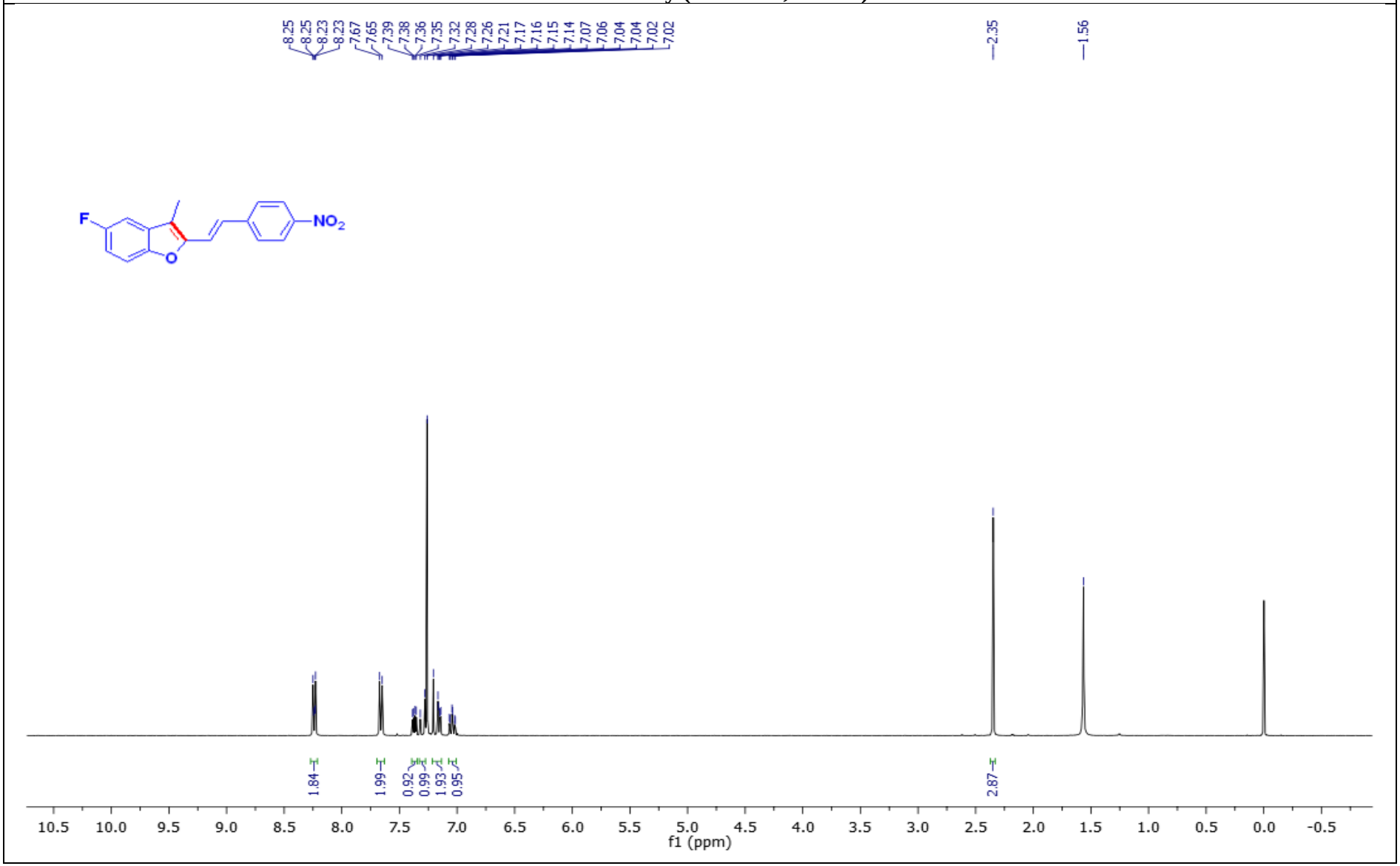
^{1}H-NMR of 3x (400 MHz, $CDCl_3$)



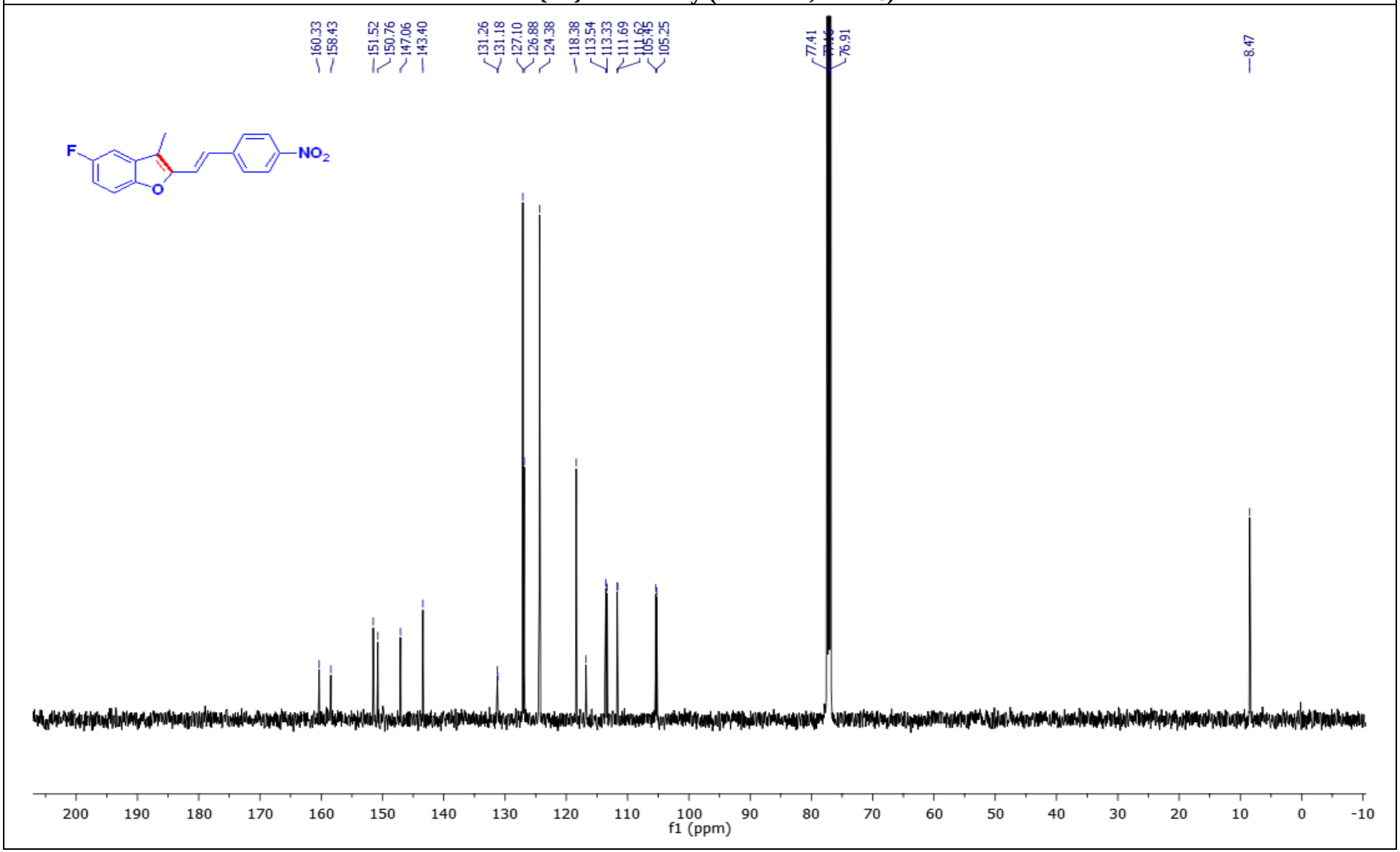
$^{13}C\{^{1}H\}$-NMR of 3x (101 MHz, $CDCl_3$)



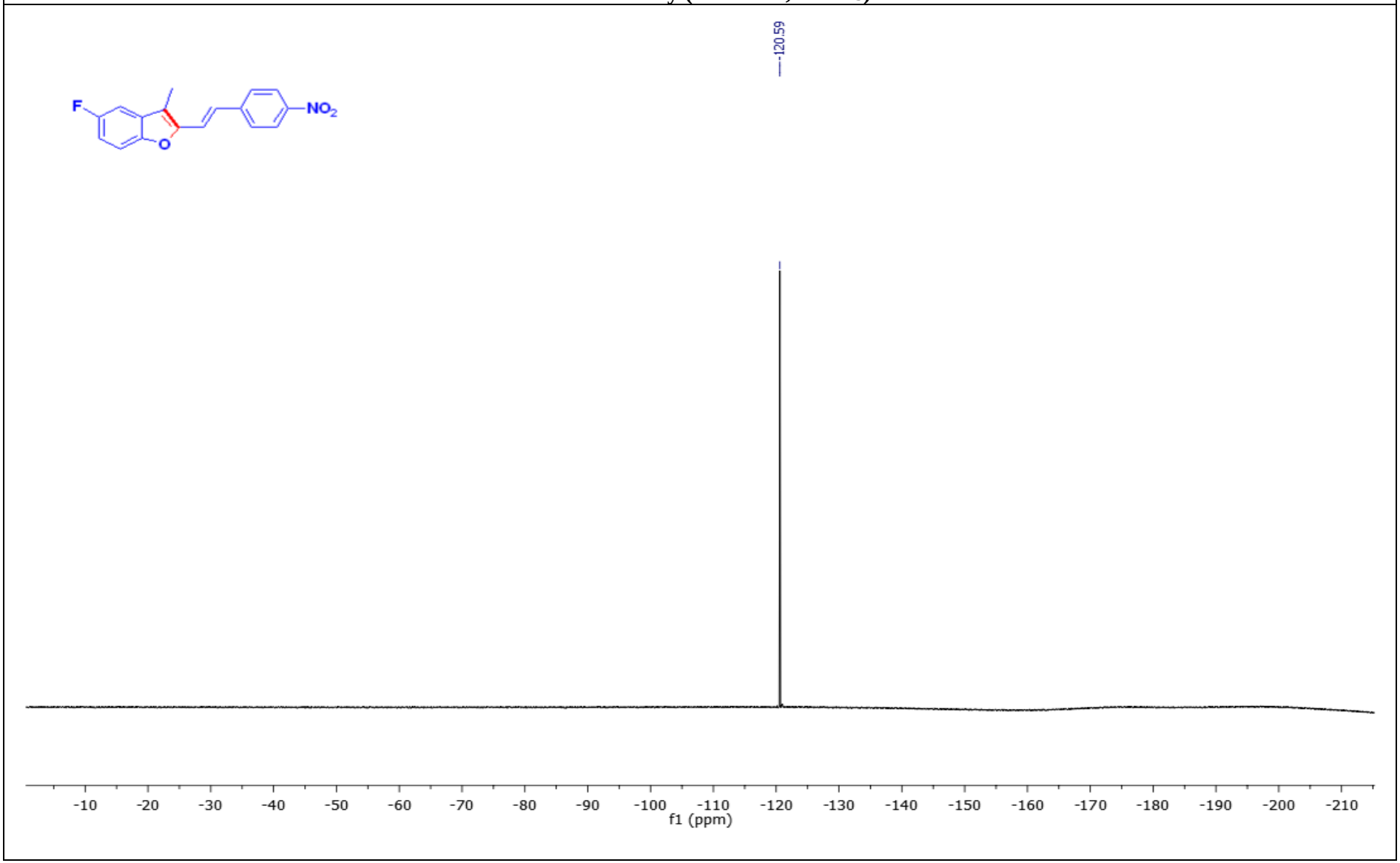
^{1}H-NMR of 3y (400 MHz, $CDCl_3$)



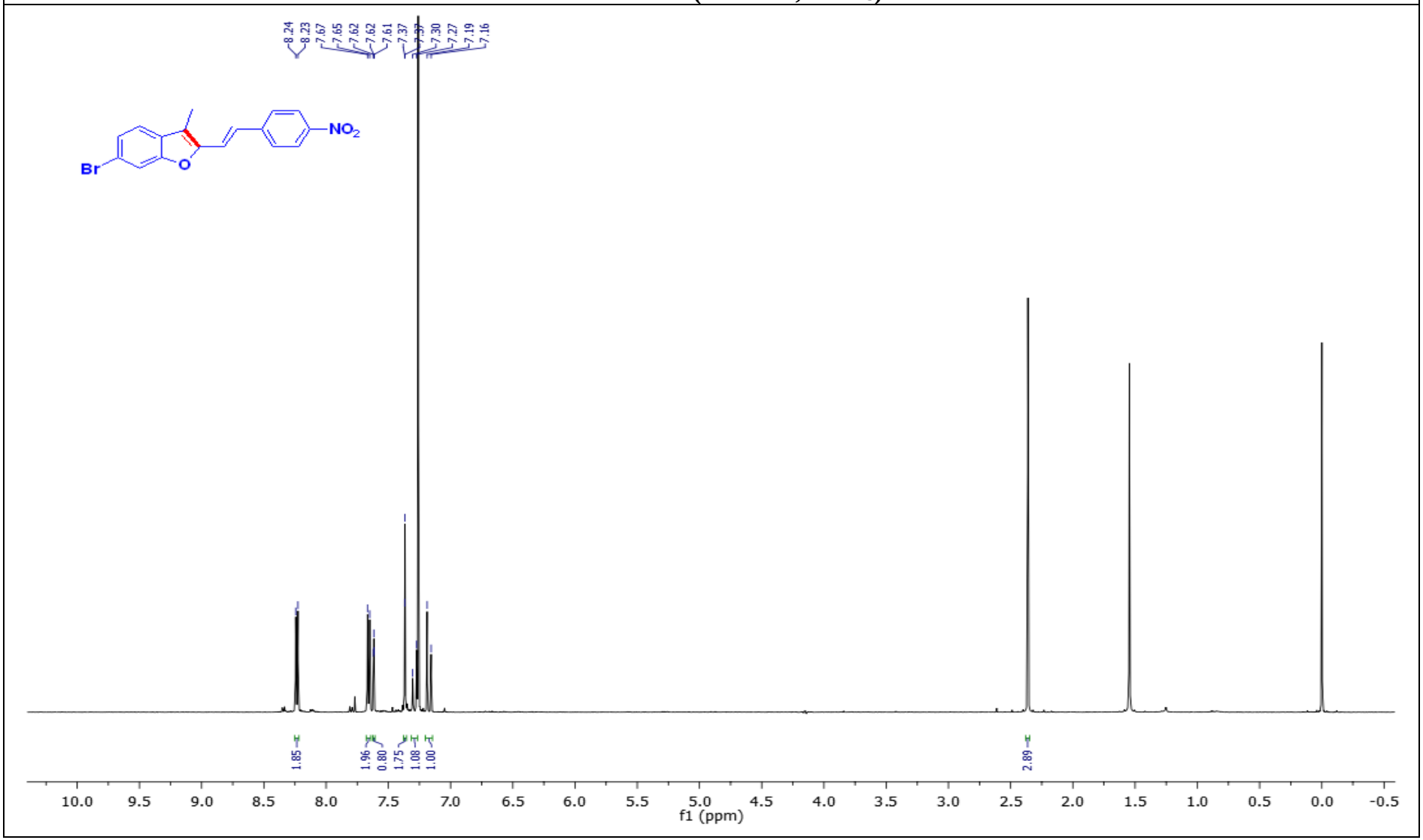
$^{13}C\{^{1}H\}$-NMR of 3y (126 MHz, $CDCl_3$)



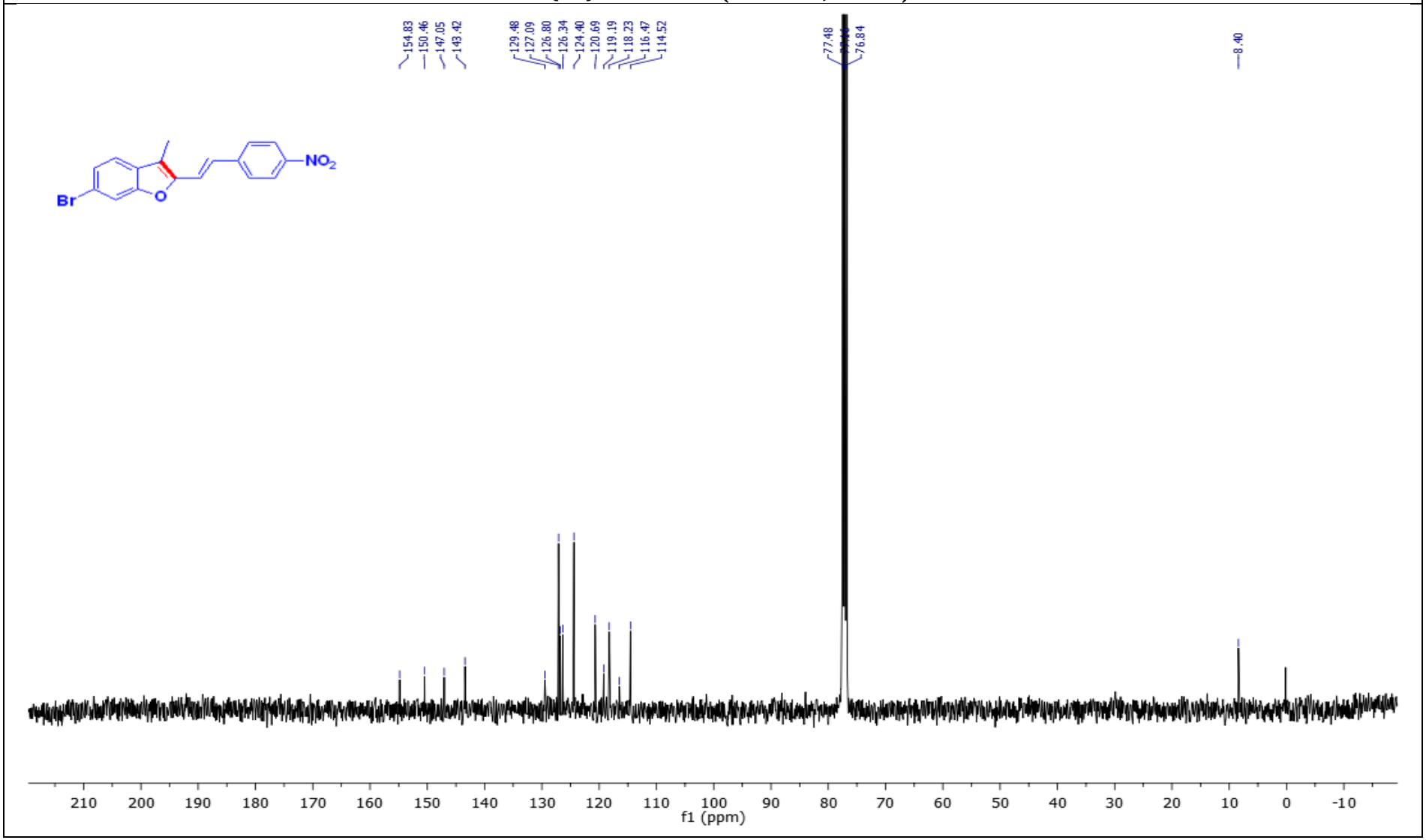
^{19}F-NMR of 3y (376 MHz, $CDCl_3$)



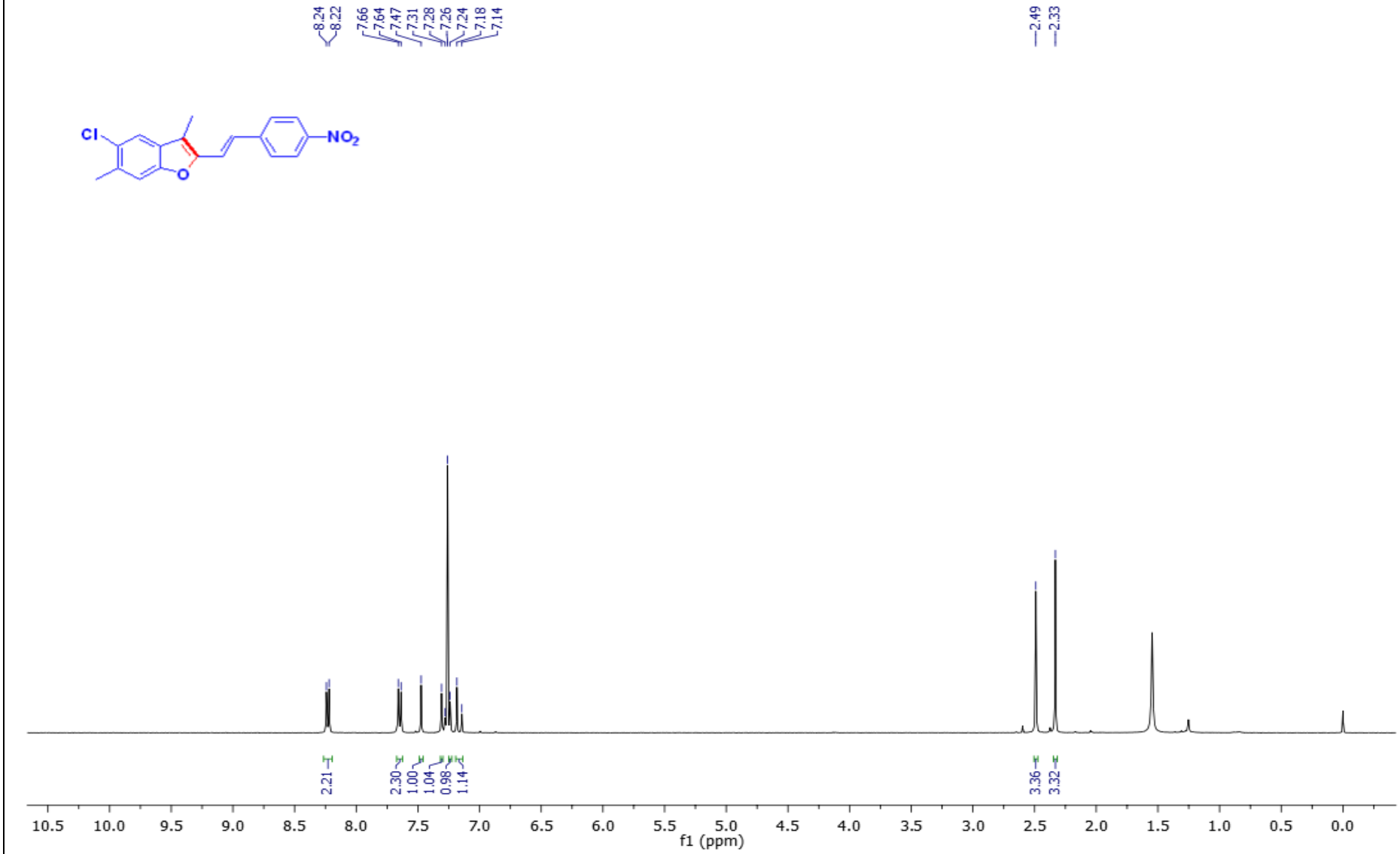
^{1}H-NMR of 3z (500 MHz, $CDCl_3$)



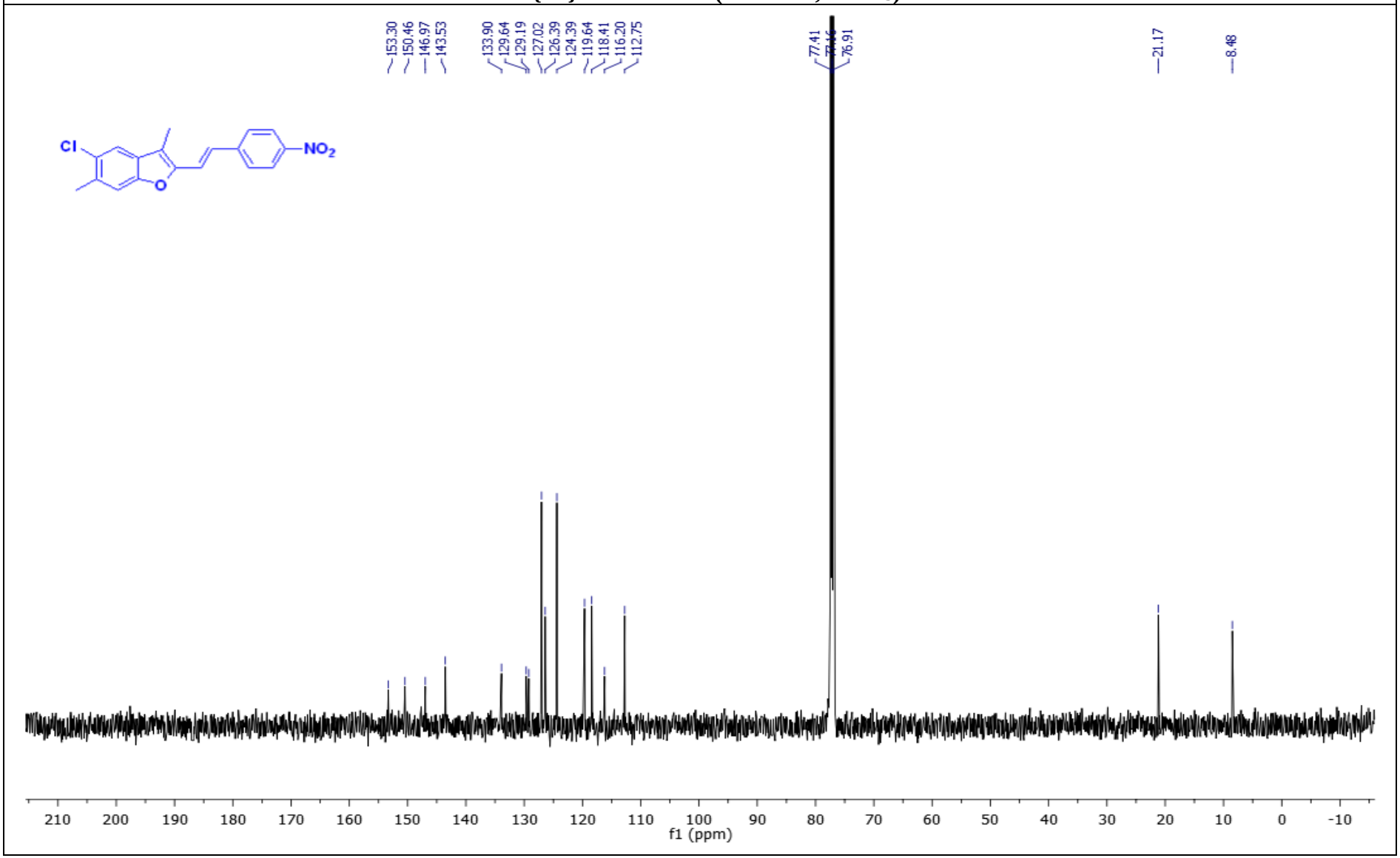
$^{13}C\{^{1}H\}$-NMR of 3z (101 MHz, $CDCl_3$)



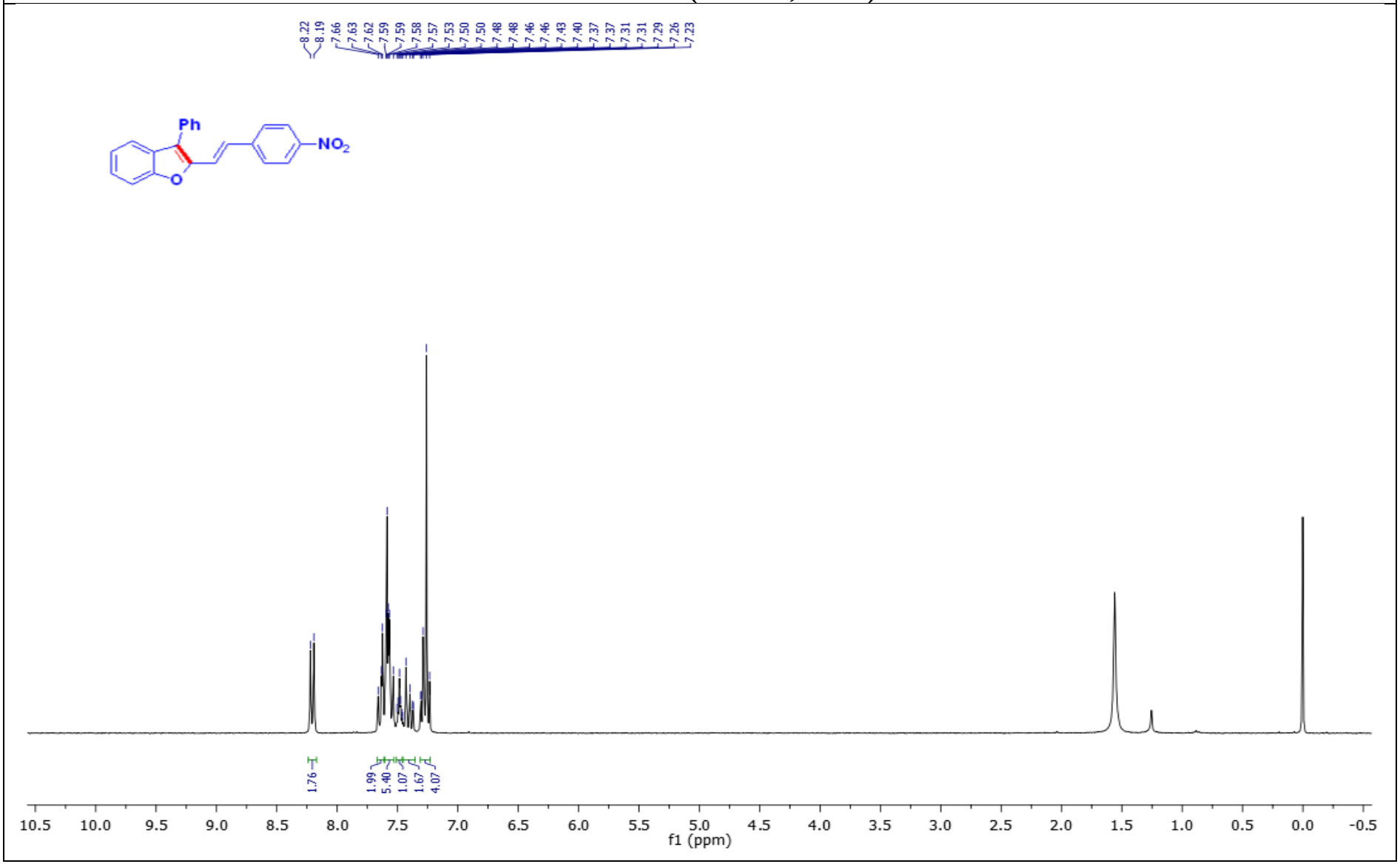
^{1}H-NMR of 3aa (400 MHz, $CDCl_3$)



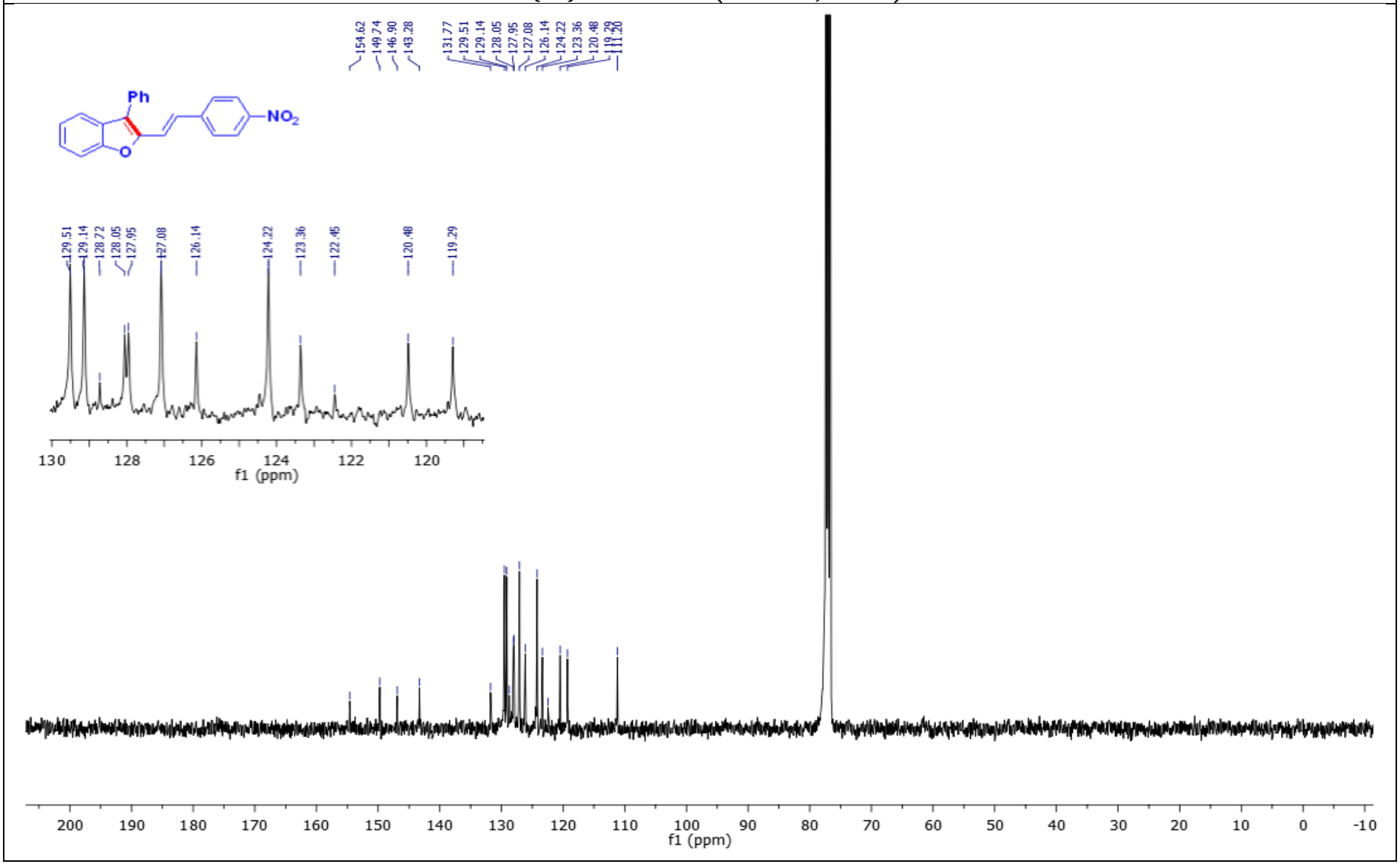
$^{13}C\{^{1}H\}$-NMR of 3aa (126 MHz, $CDCl_3$)



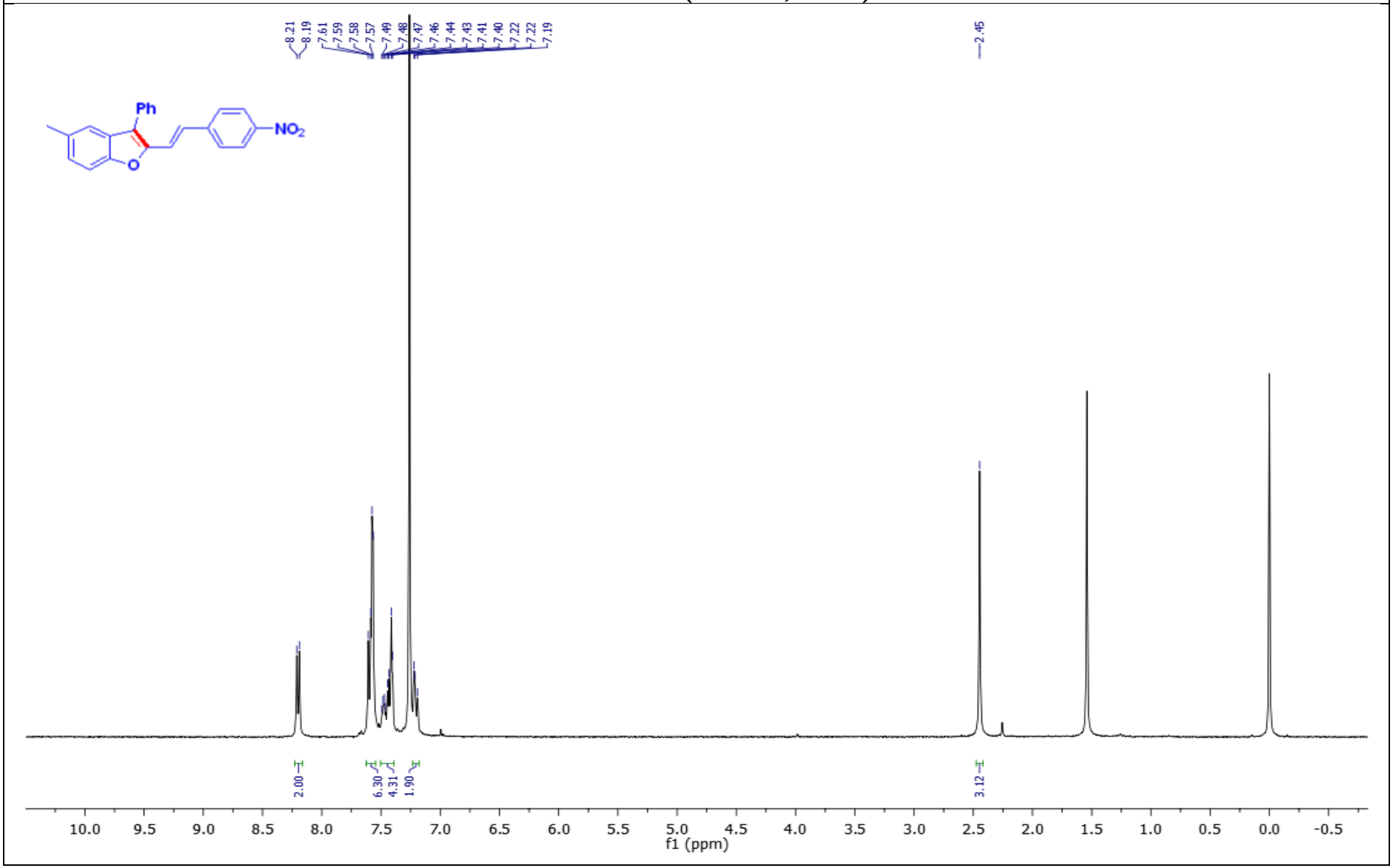
^{1}H-NMR of 3ab (300 MHz, $CDCl_3$)



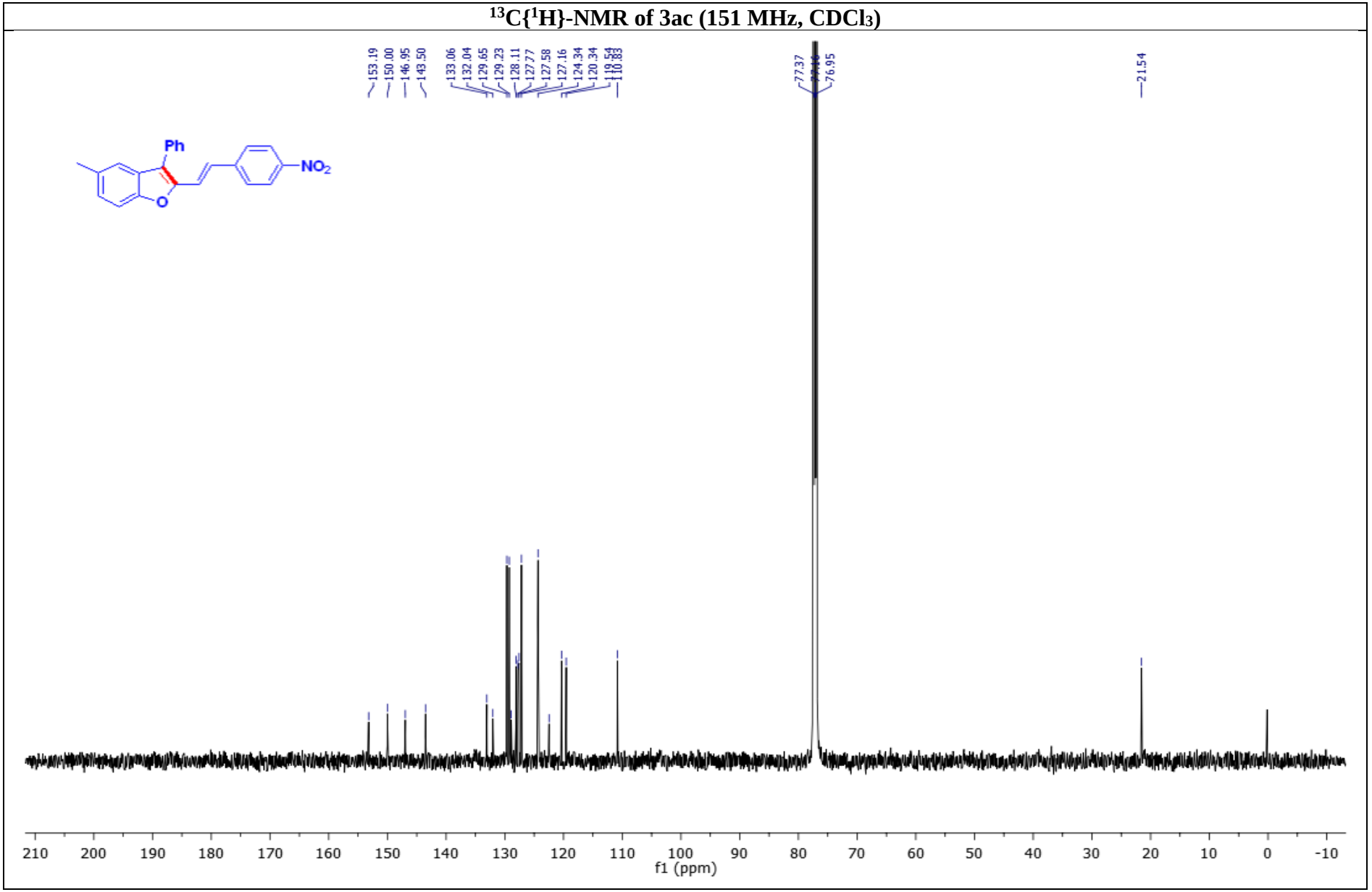
$^{13}C\{^{1}H\}$-NMR of 3ab (101 MHz, $CDCl_3$)



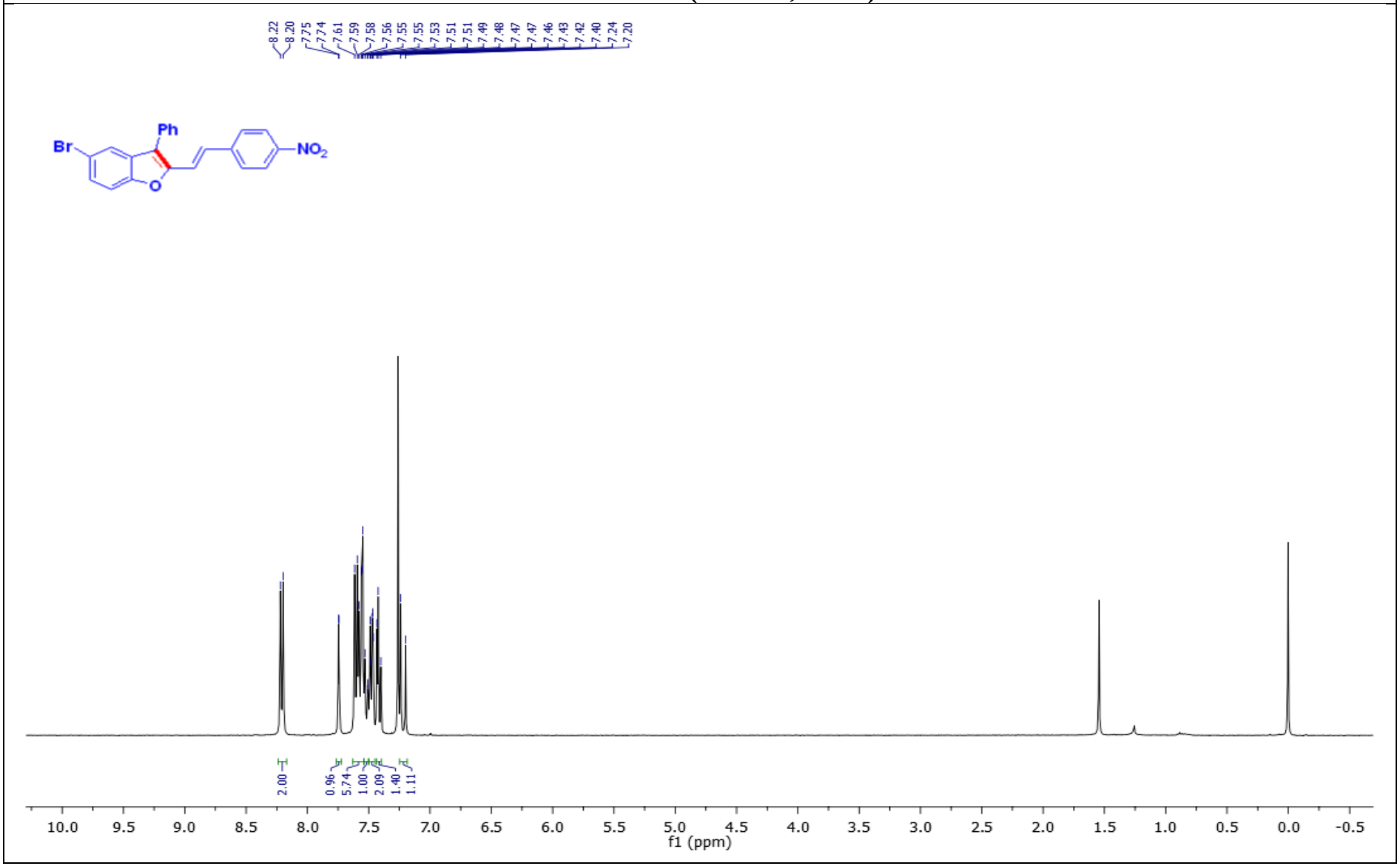
^{1}H-NMR of 3ac (400 MHz, $CDCl_3$)



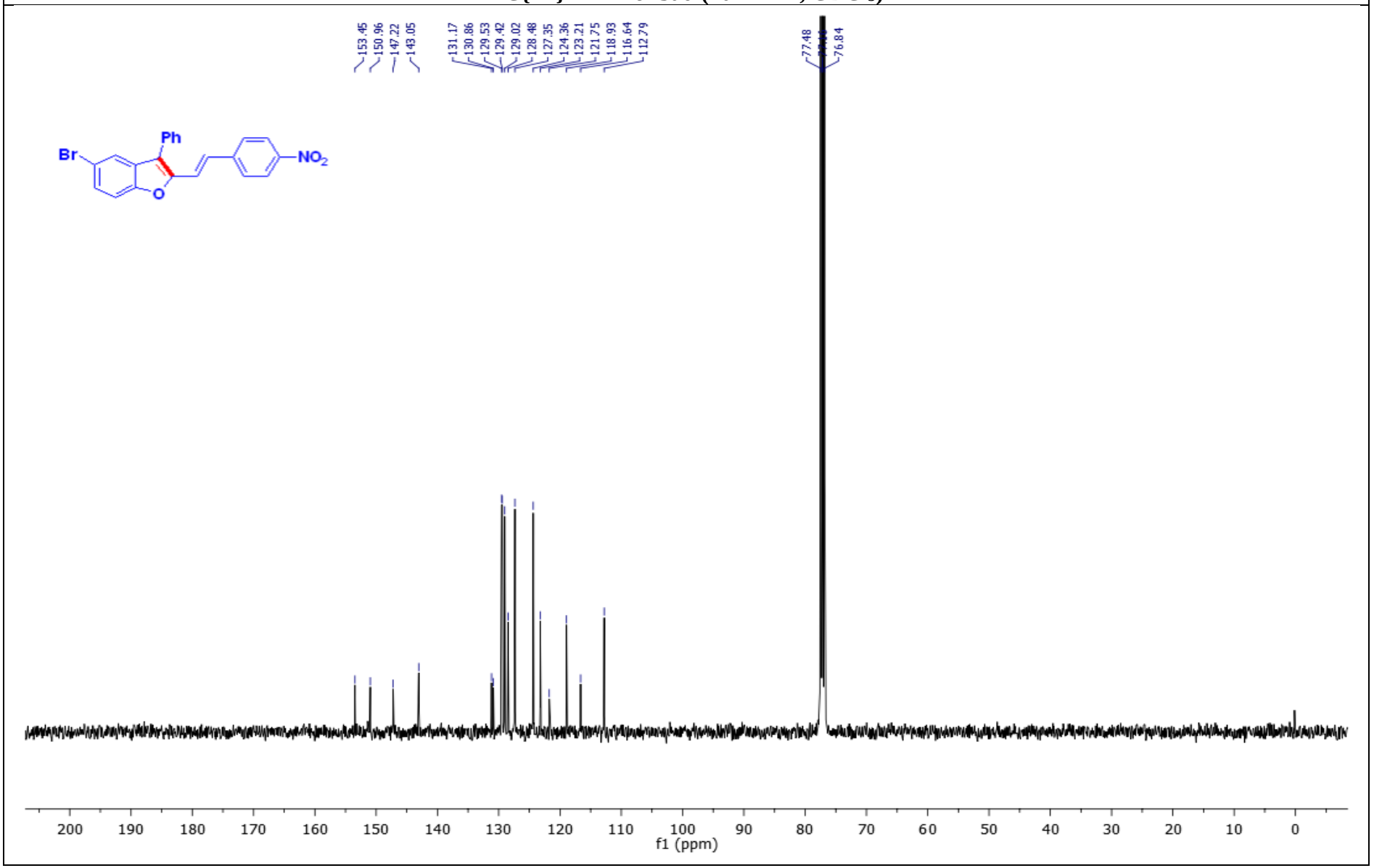
$^{13}C\{^{1}H\}$-NMR of 3ac (151 MHz, $CDCl_3$)



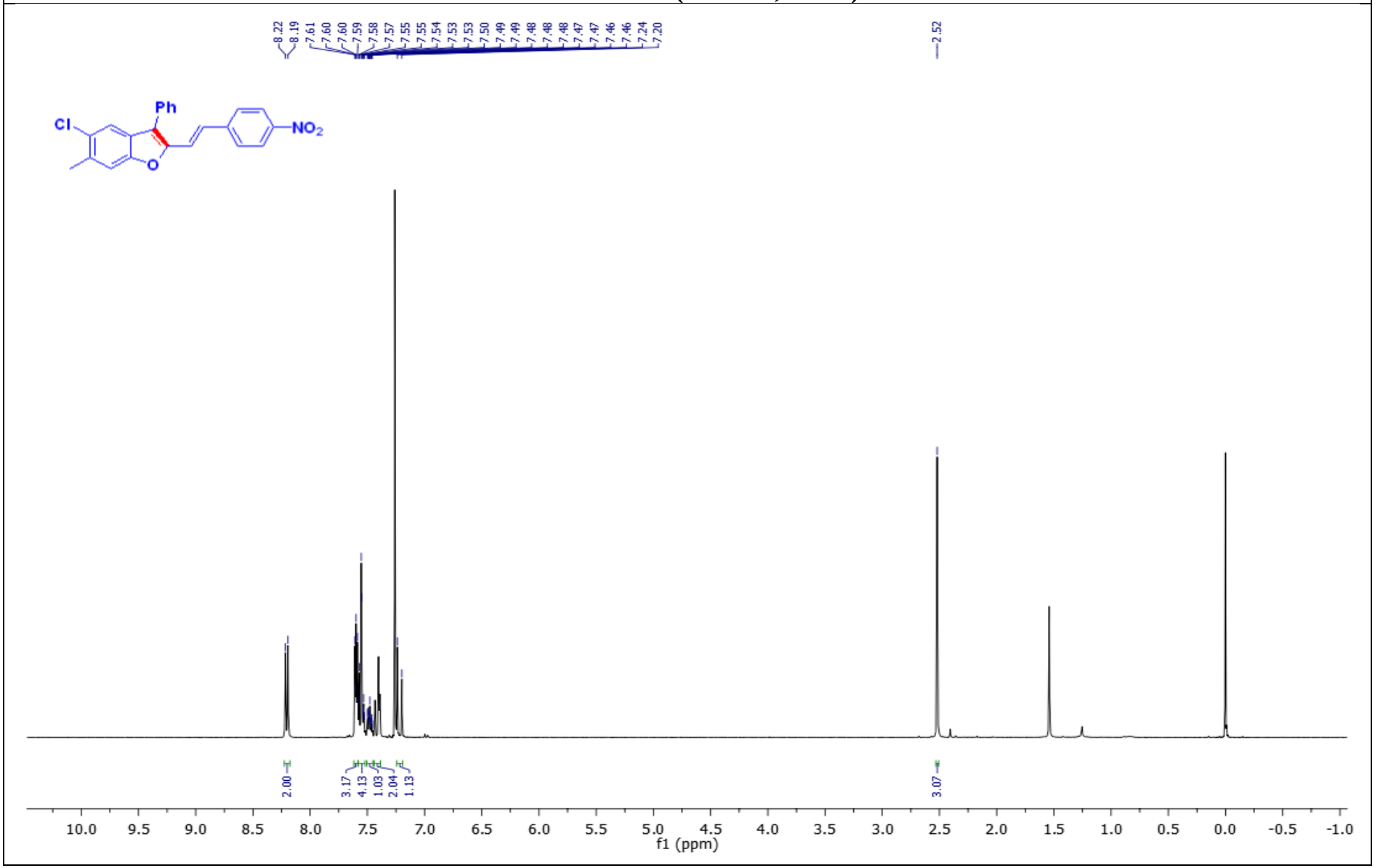
^{1}H-NMR of 3ad (400 MHz, $CDCl_3$)



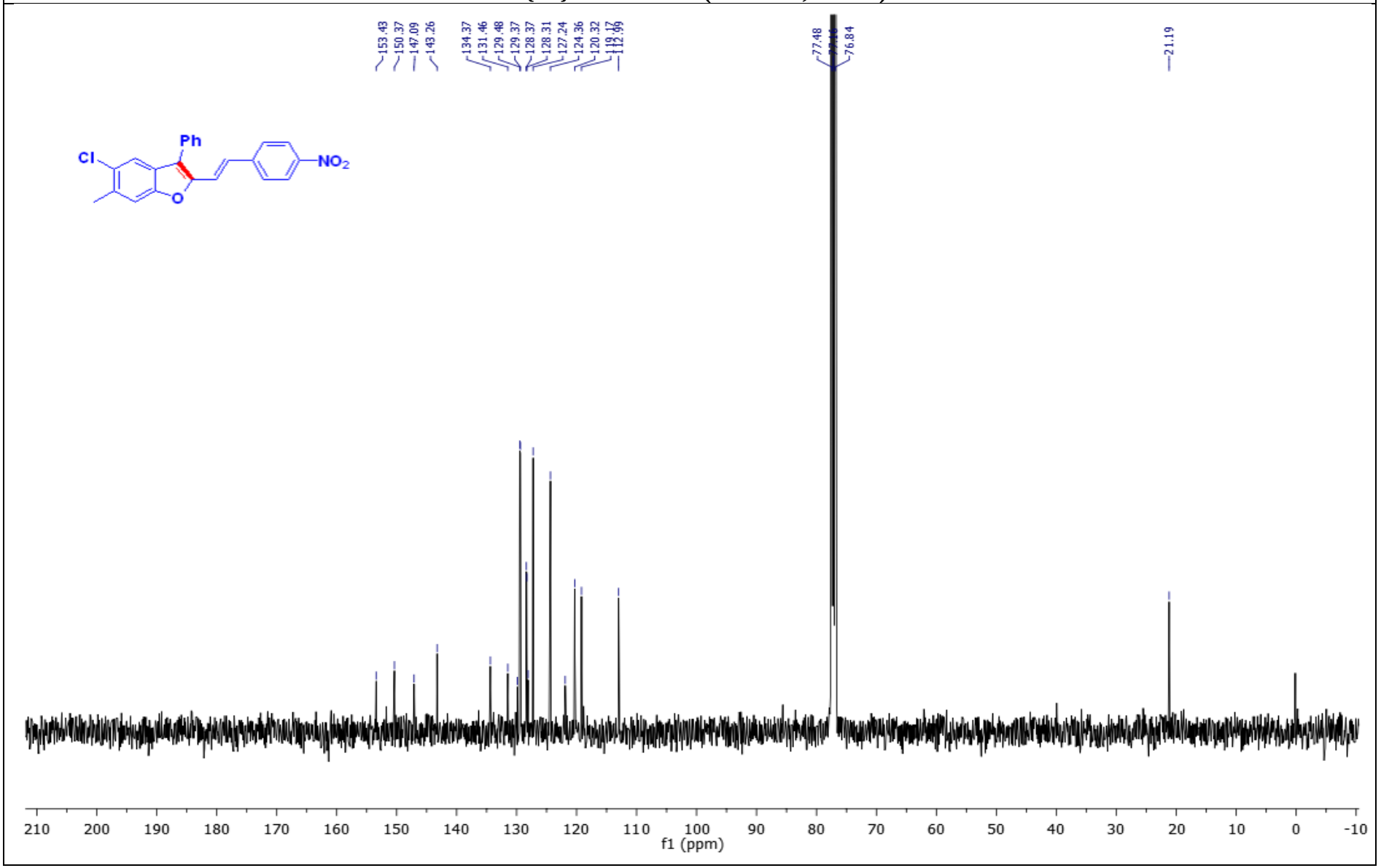
$^{13}C\{^{1}H\}$-NMR of 3ad (101 MHz, $CDCl_3$)



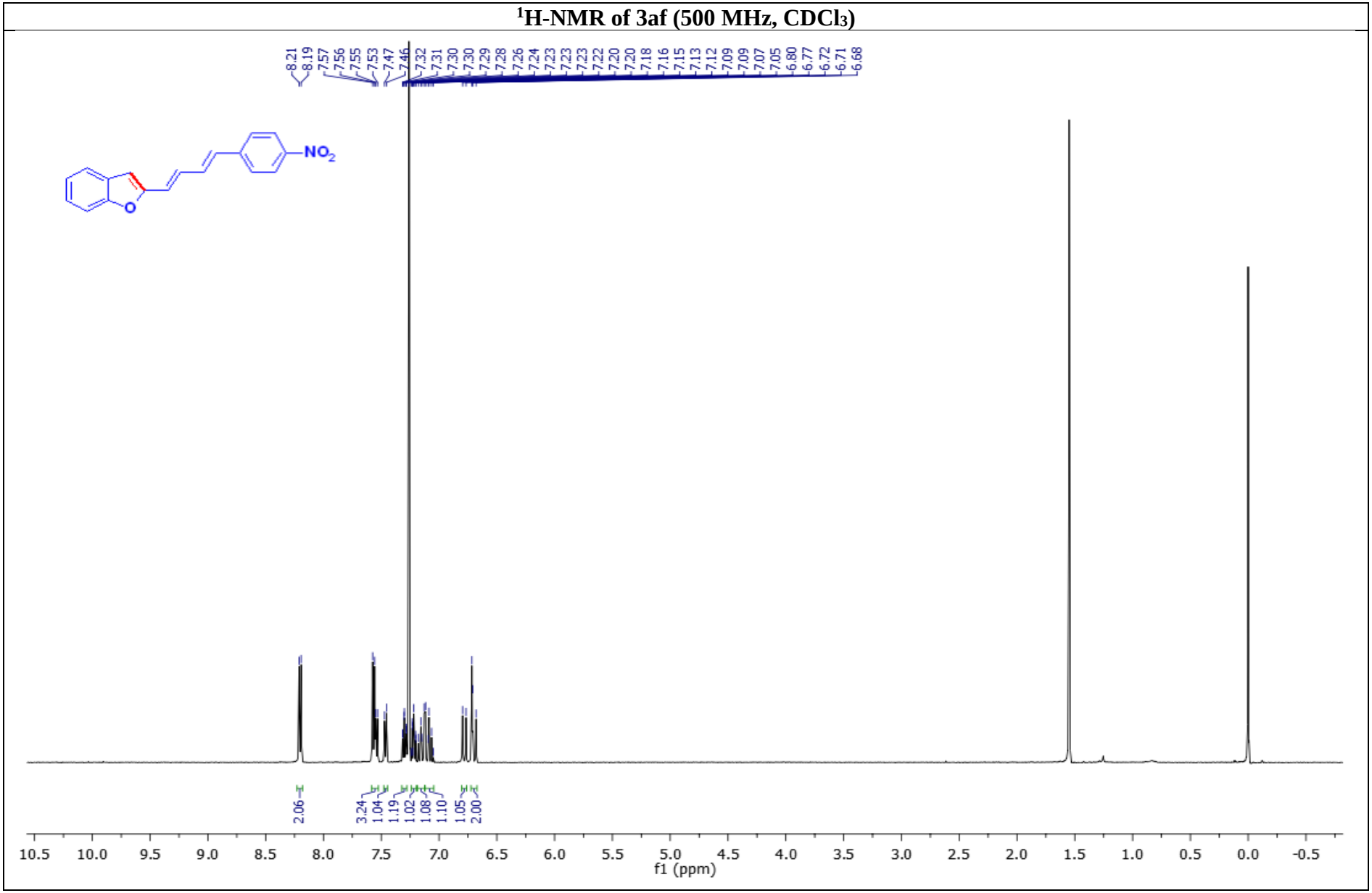
^{1}H-NMR of 3ae (400 MHz, $CDCl_3$)



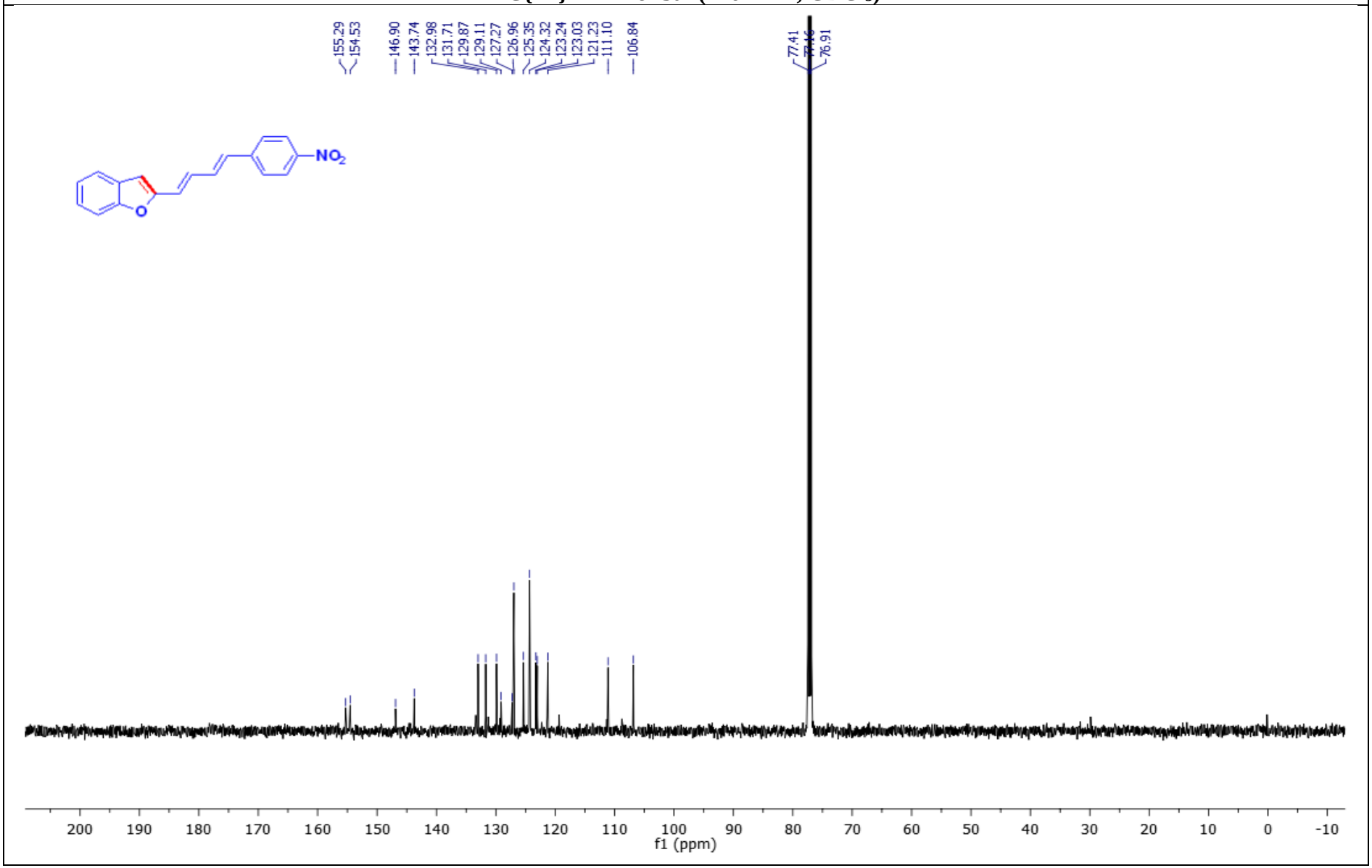
$^{13}C\{^{1}H\}$-NMR of 3ae (101 MHz, $CDCl_3$)



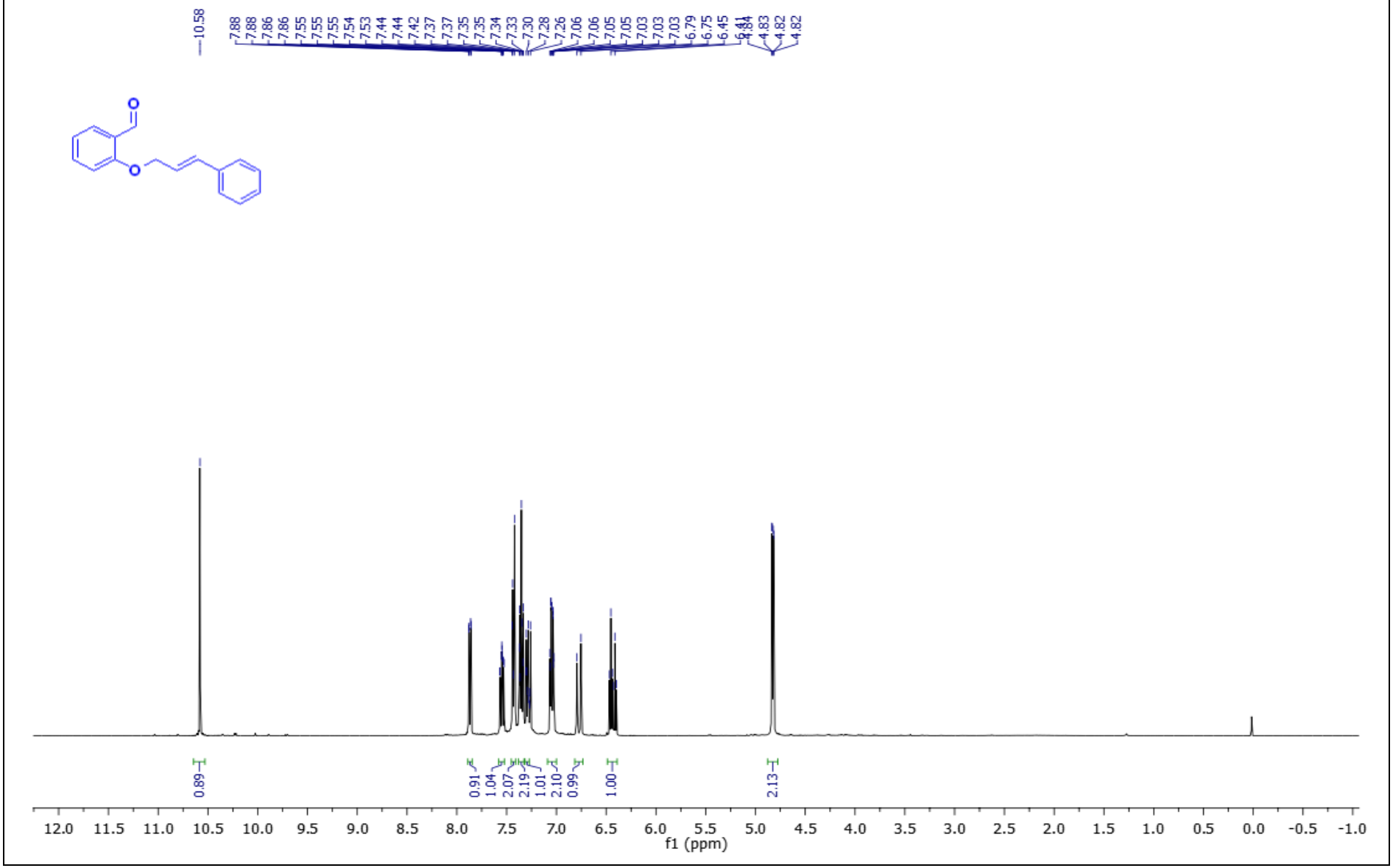
^{1}H-NMR of 3af (500 MHz, $CDCl_3$)



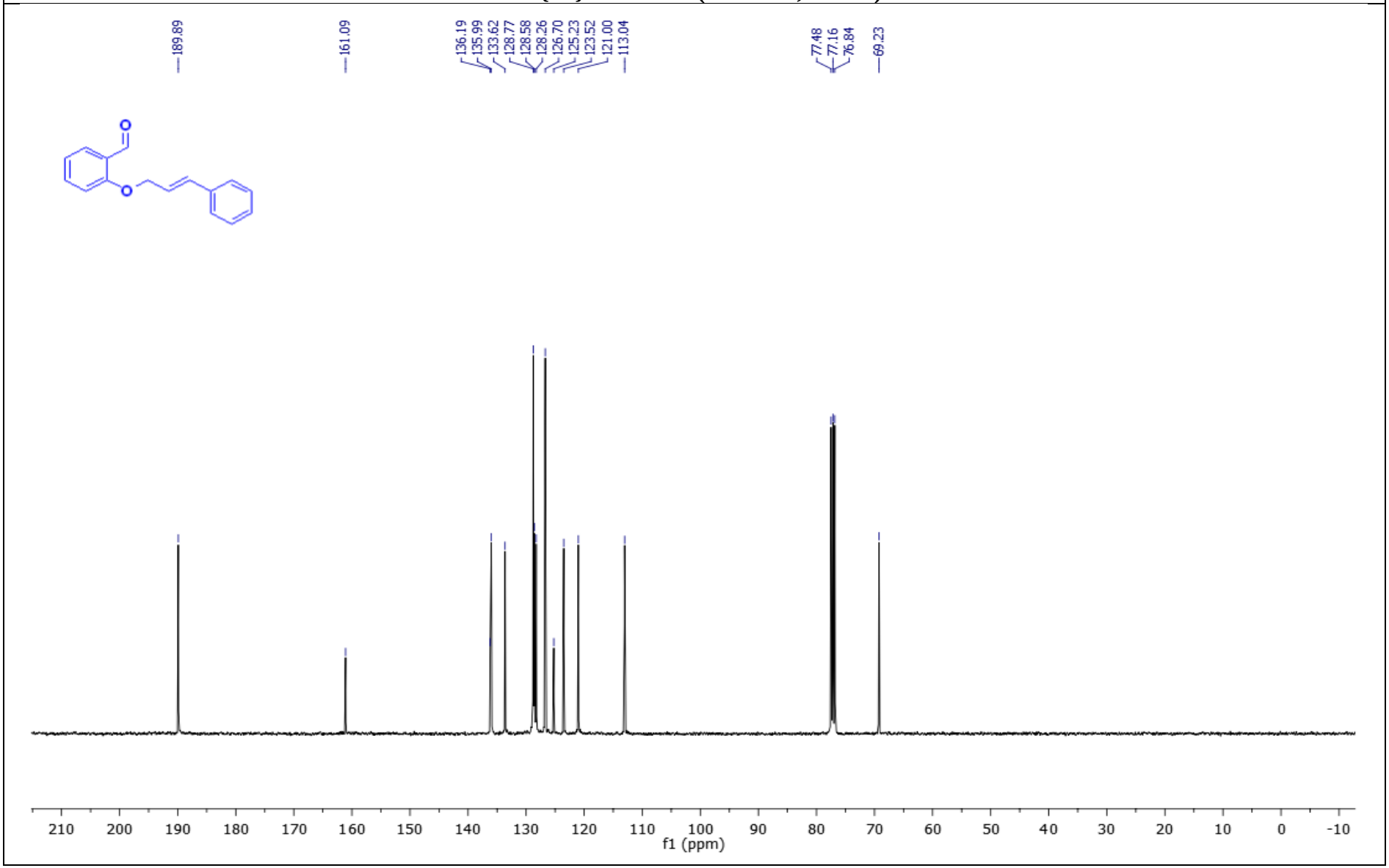
$^{13}C\{^{1}H\}$-NMR of 3af (126 MHz, $CDCl_3$)



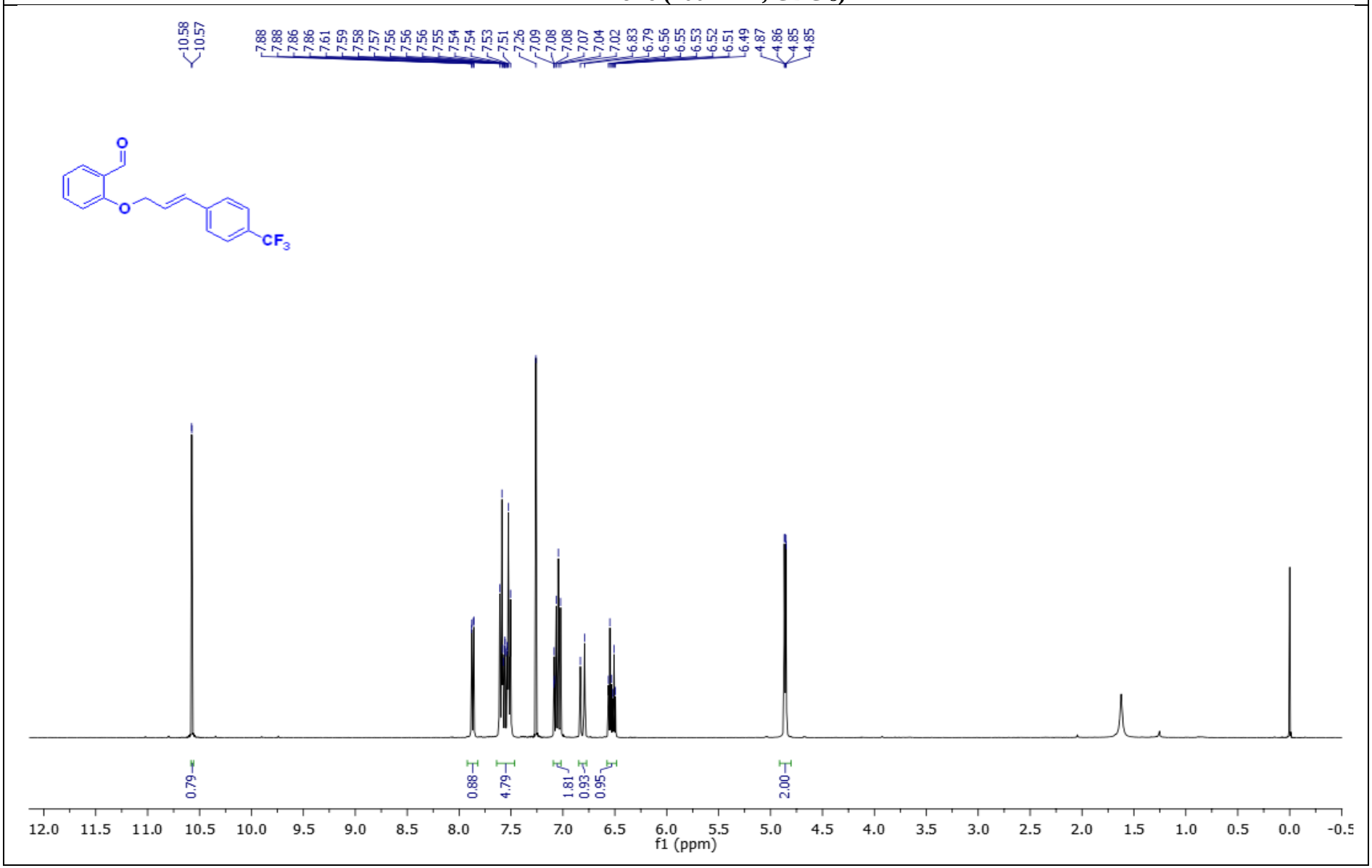
^{1}H-NMR of 5 (400 MHz, $CDCl_3$)



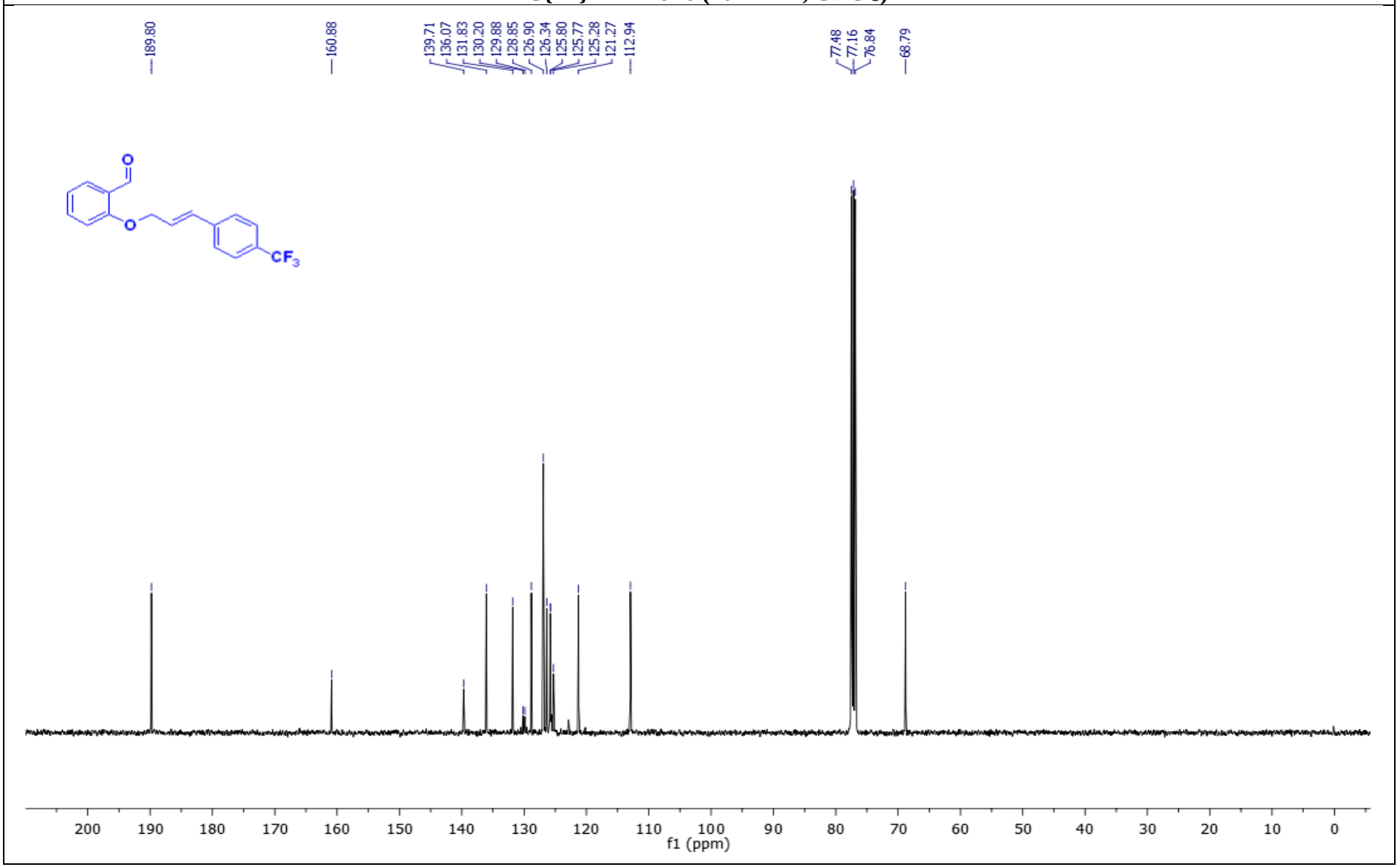
$^{13}C\{^{1}H\}$-NMR of 5 (101 MHz, $CDCl_3$)



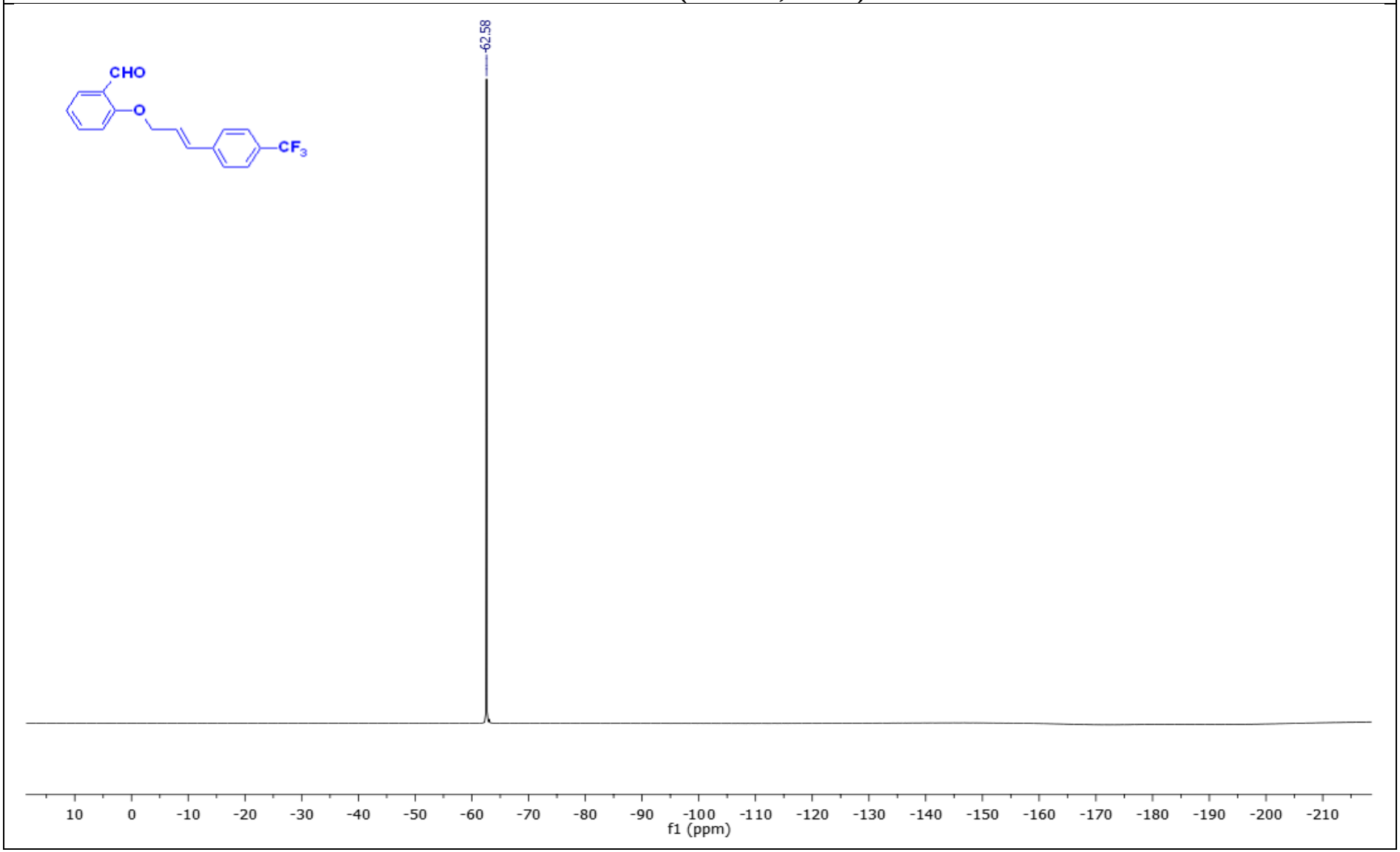
^{1}H-NMR of 6 (400 MHz, $CDCl_3$)



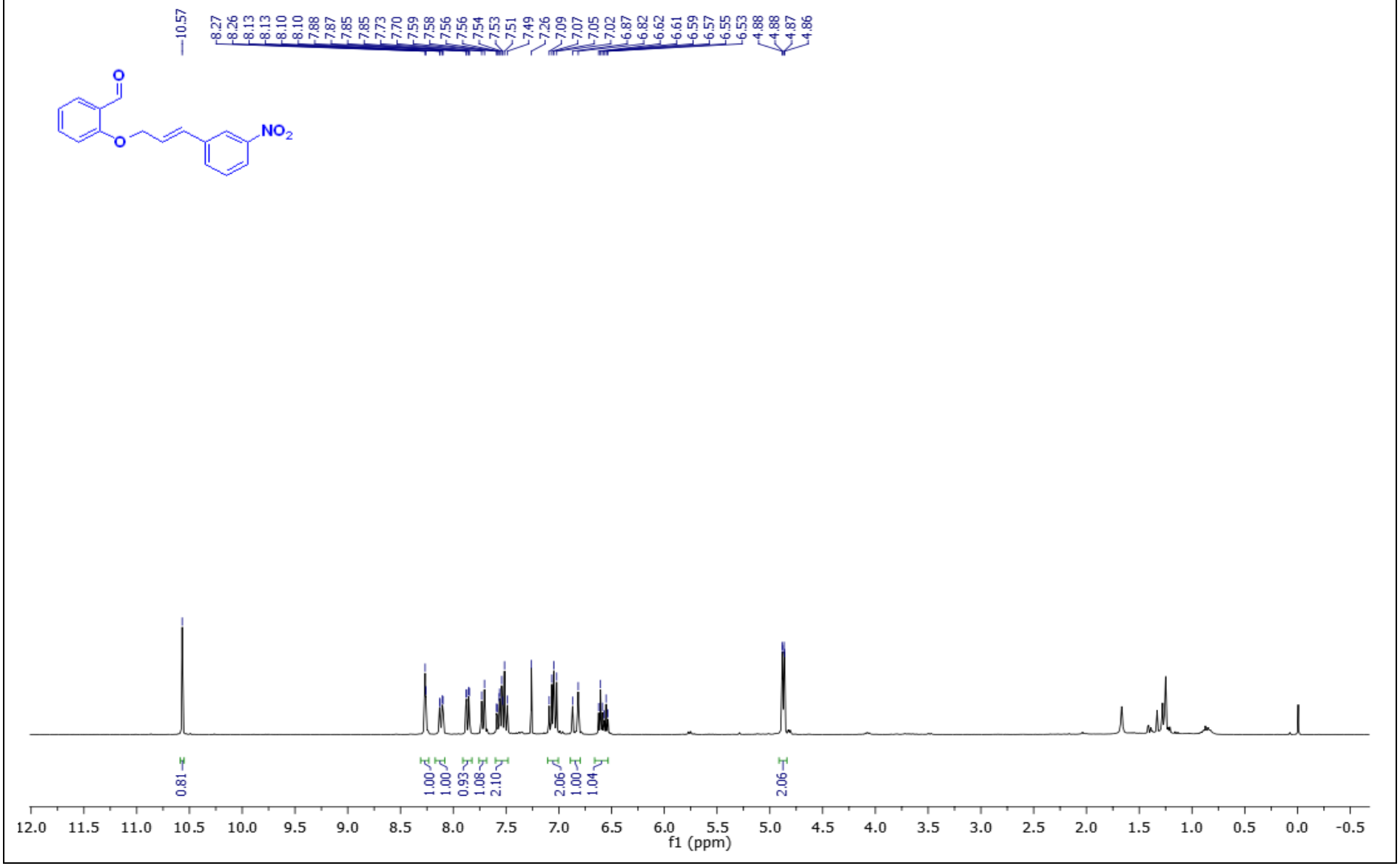
$^{13}C\{^{1}H\}$-NMR of 6 (101 MHz, $CDCl_3$)



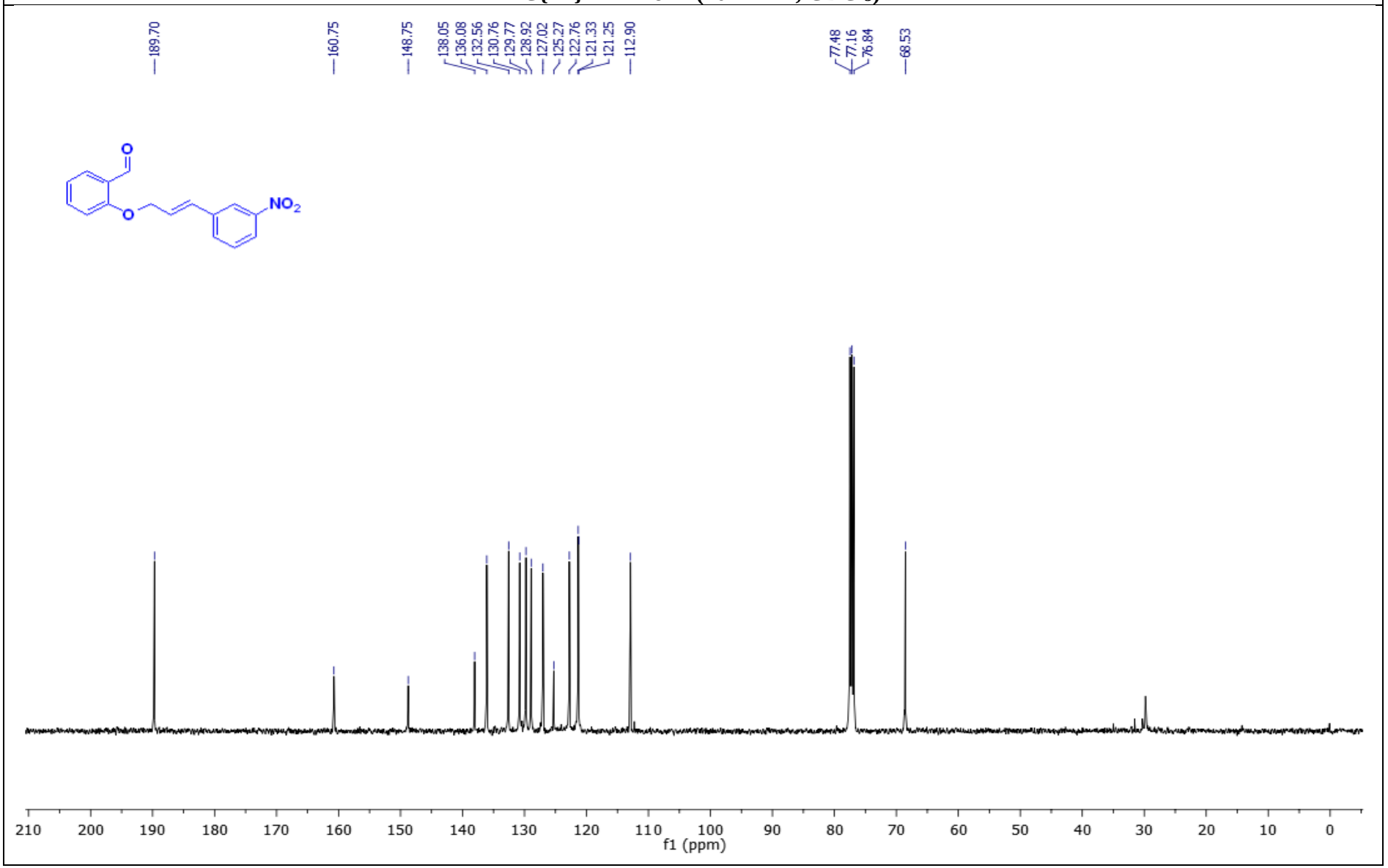
^{19}F-NMR of 6 (376 MHz, $CDCl_3$)



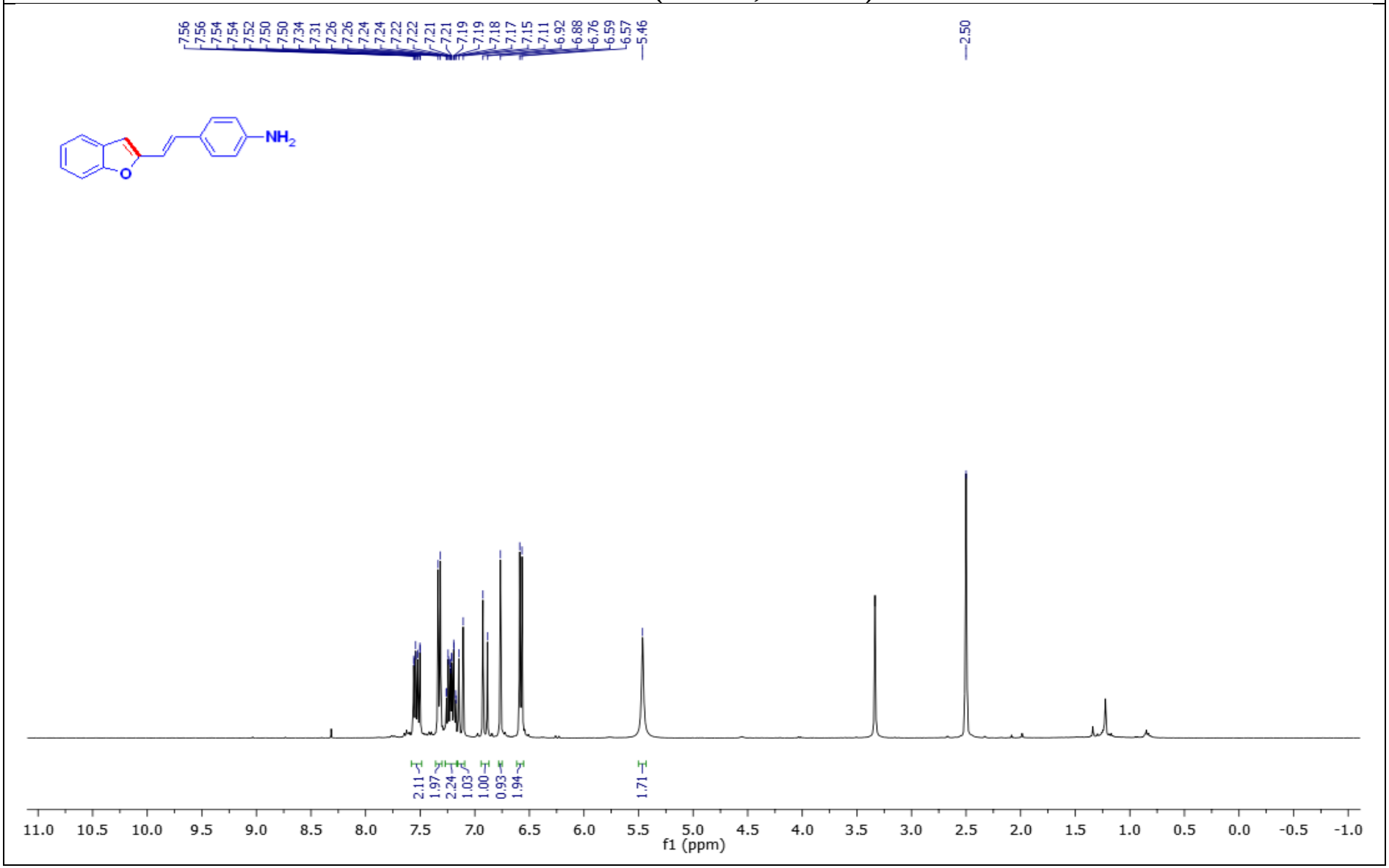
^{1}H-NMR of 7 (300 MHz, $CDCl_3$)



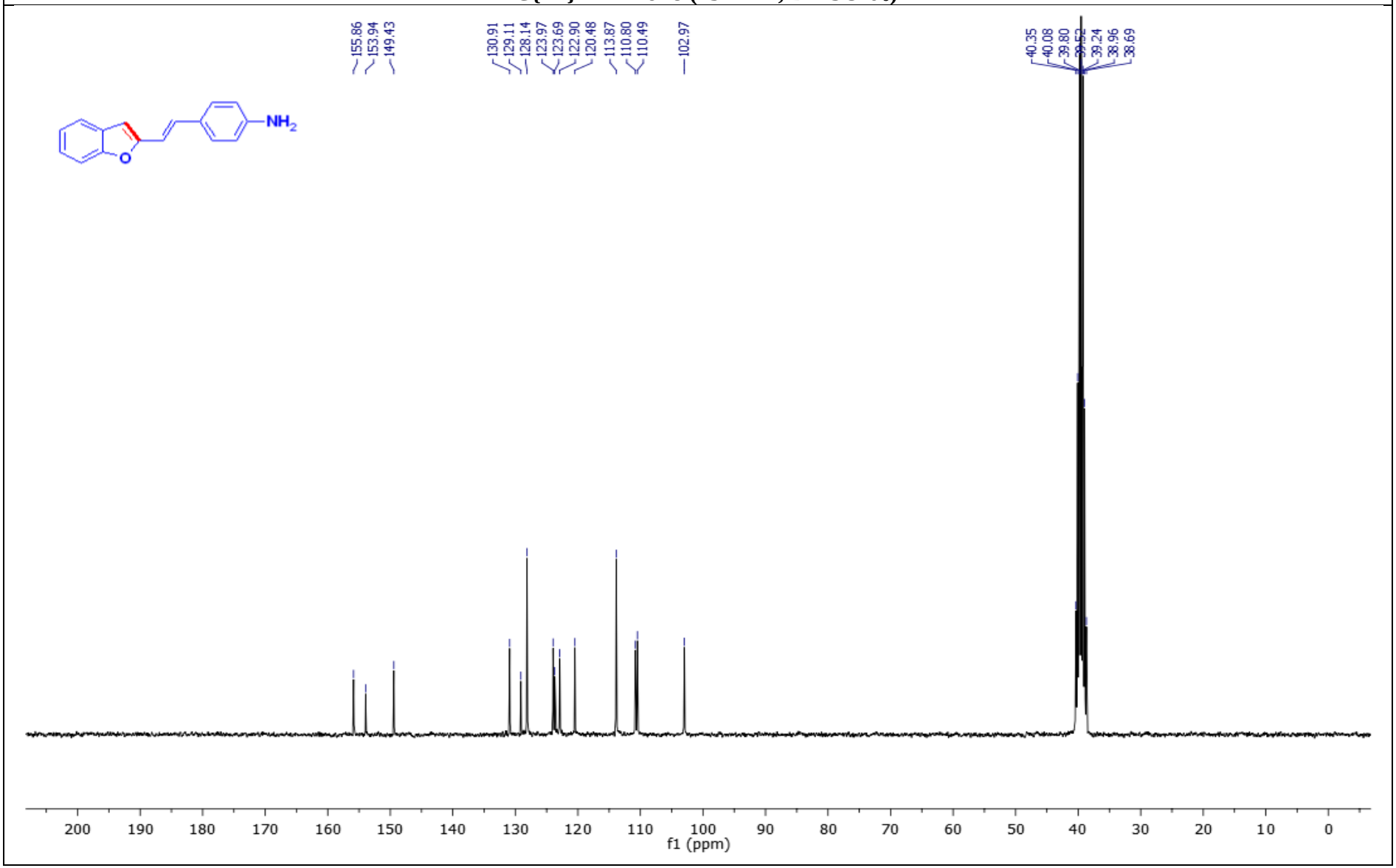
$^{13}C\{^{1}H\}$-NMR of 7 (101 MHz, $CDCl_3$)



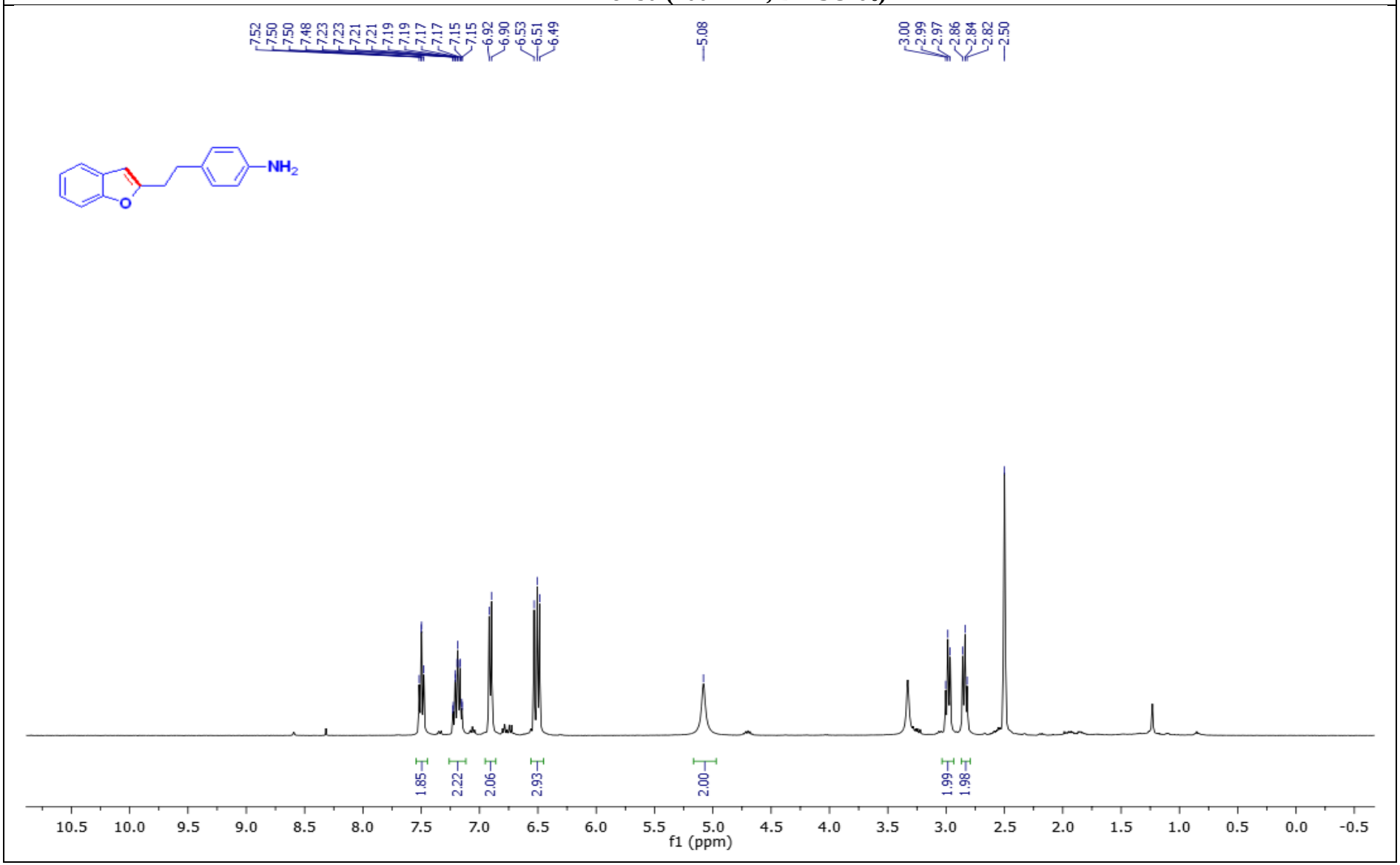
^{1}H-NMR of 8 (400 MHz, DMSO-d$_6$)



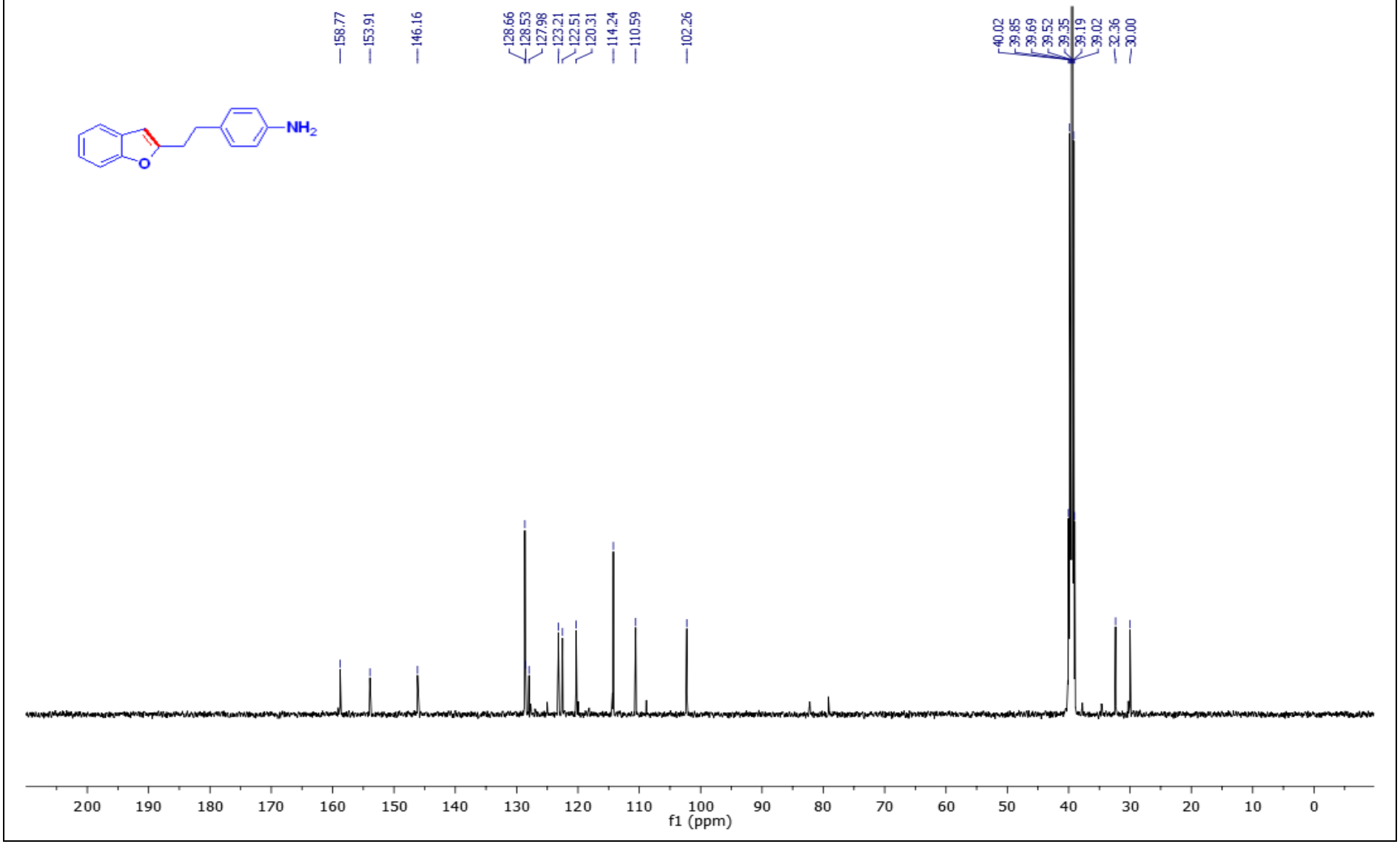
$^{13}C\{^{1}H\}$-NMR of 8 (75 MHz, DMSO-d_6)



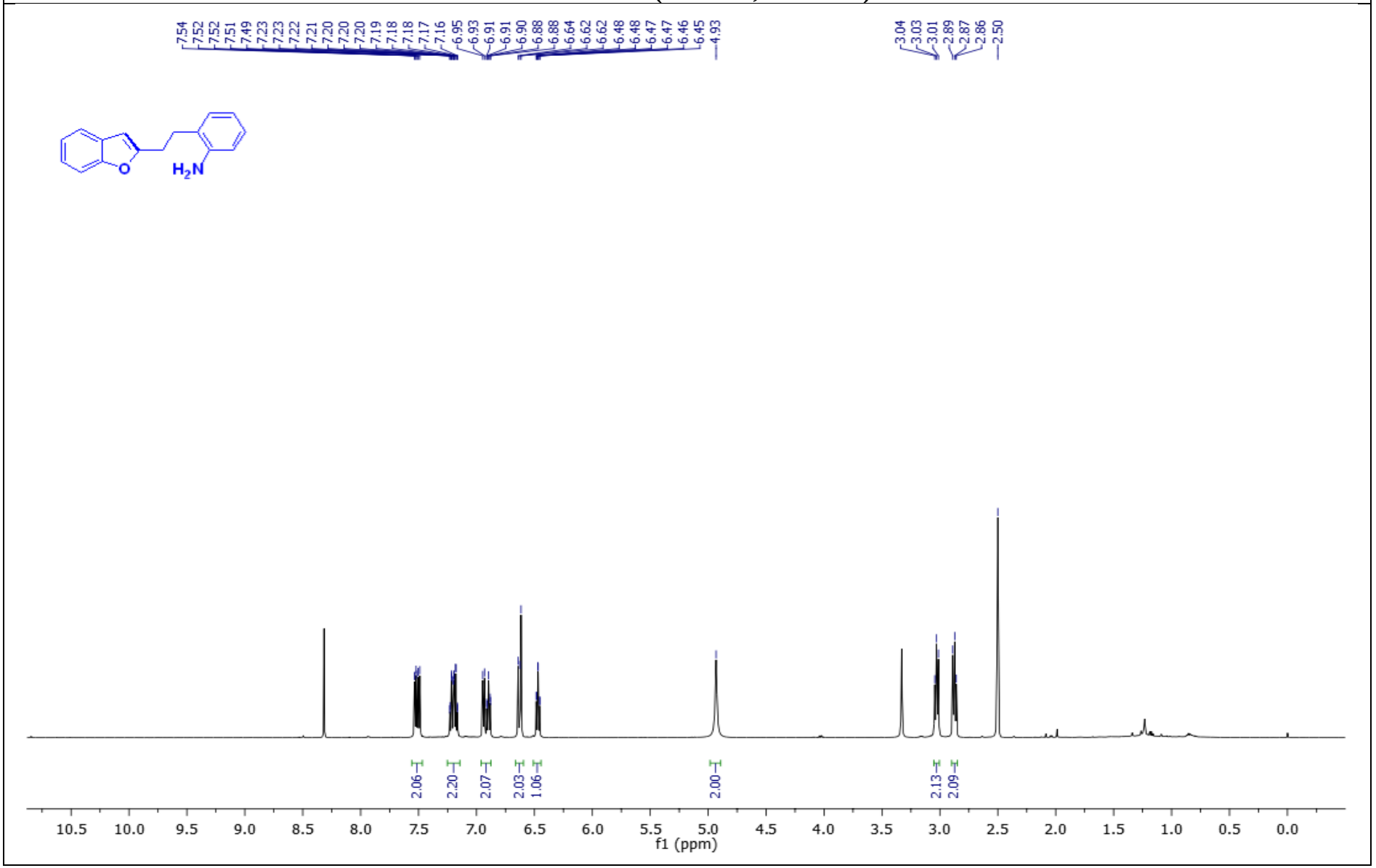
^{1}H-NMR of 9a (400 MHz, DMSO-d$_6$)



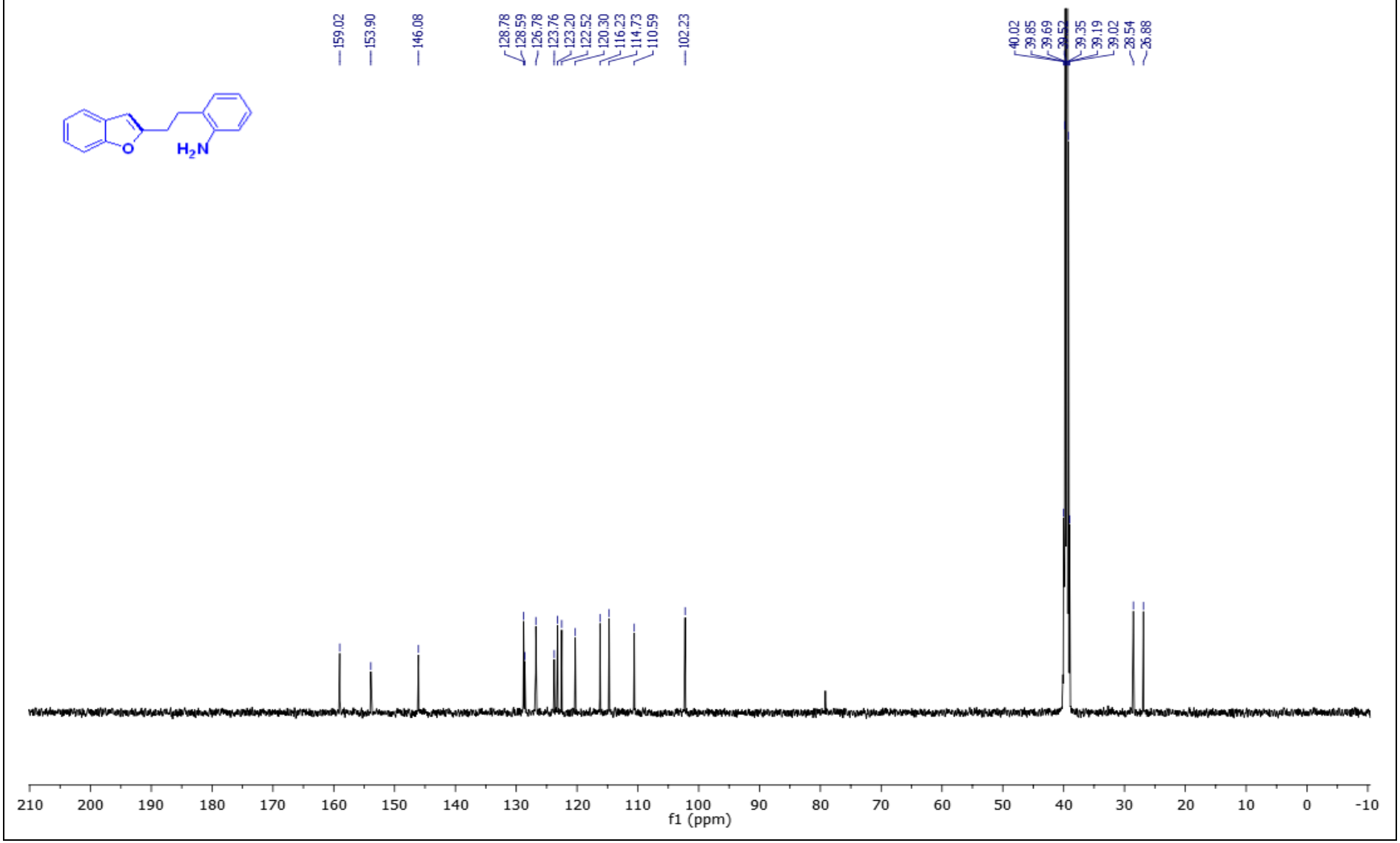
$^{13}C\{^{1}H\}$-NMR of 9a (126 MHz, DMSO-d_6)



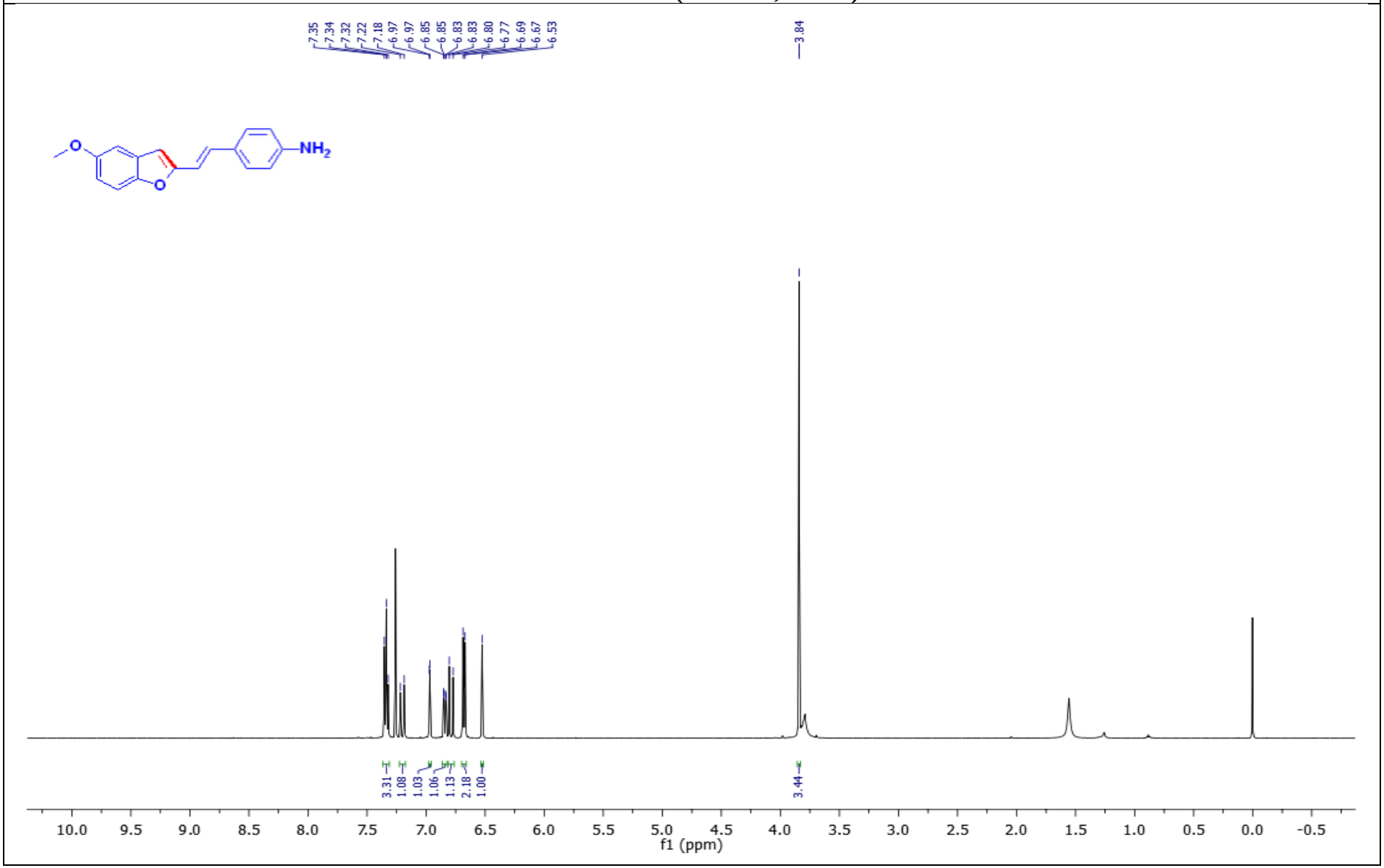
^{1}H-NMR of 9b (500 MHz, DMSO-d$_6$)



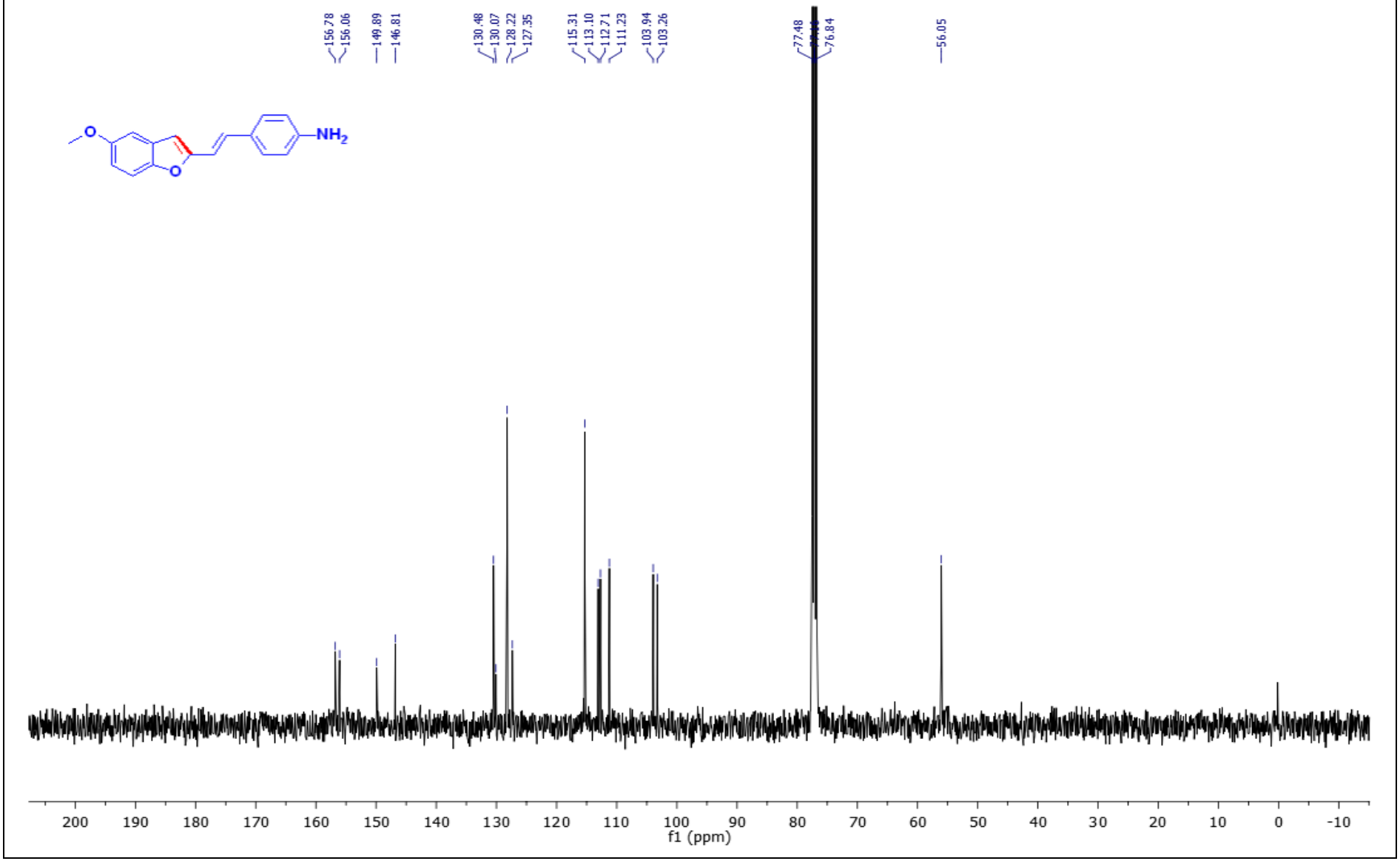
$^{13}C\{^{1}H\}$-NMR of 9b (126 MHz, DMSO-d_6)



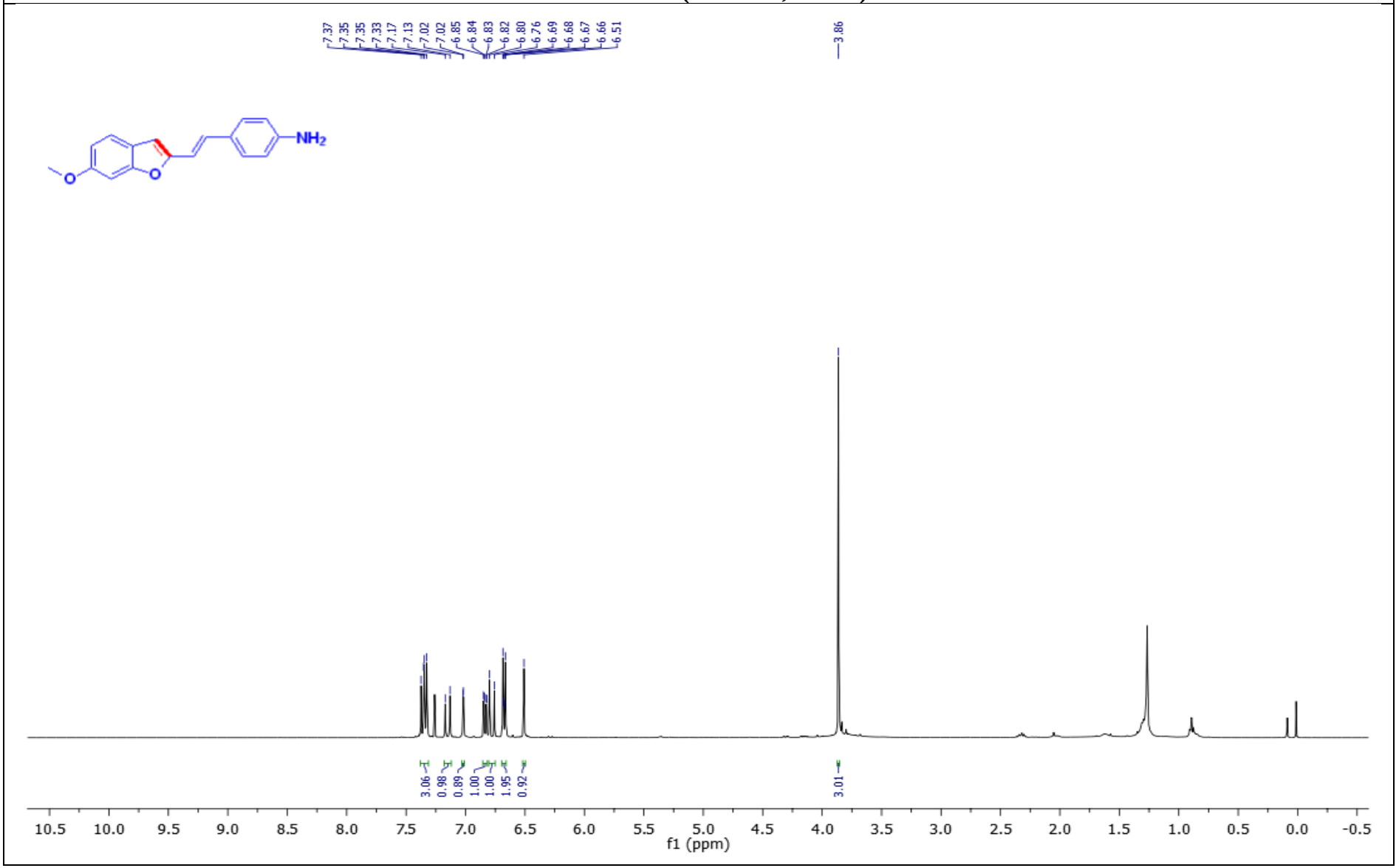
^{1}H-NMR of 10 (500 MHz, $CDCl_3$)



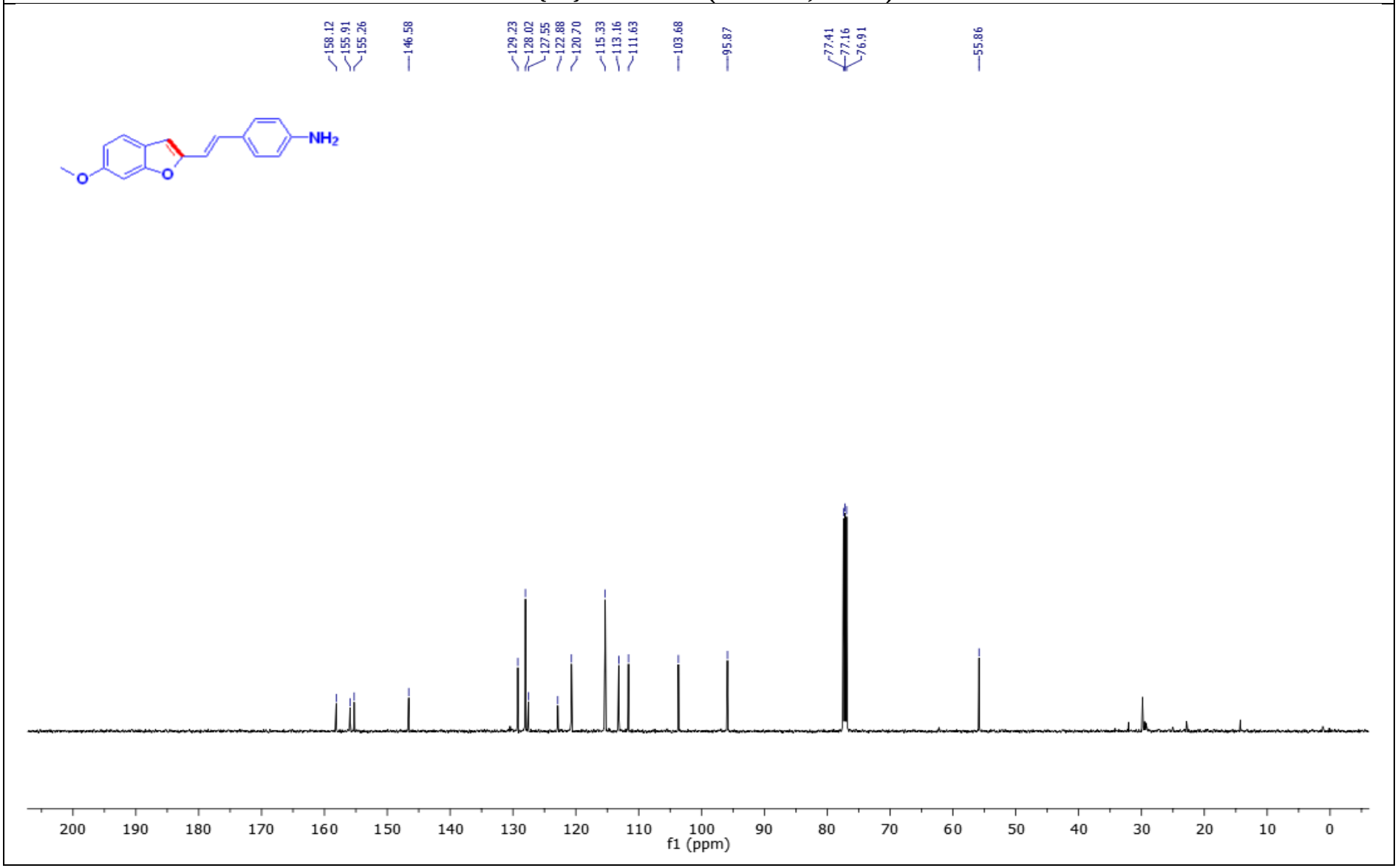
$^{13}C\{^{1}H\}$-NMR of 10 (101 MHz, $CDCl_3$)



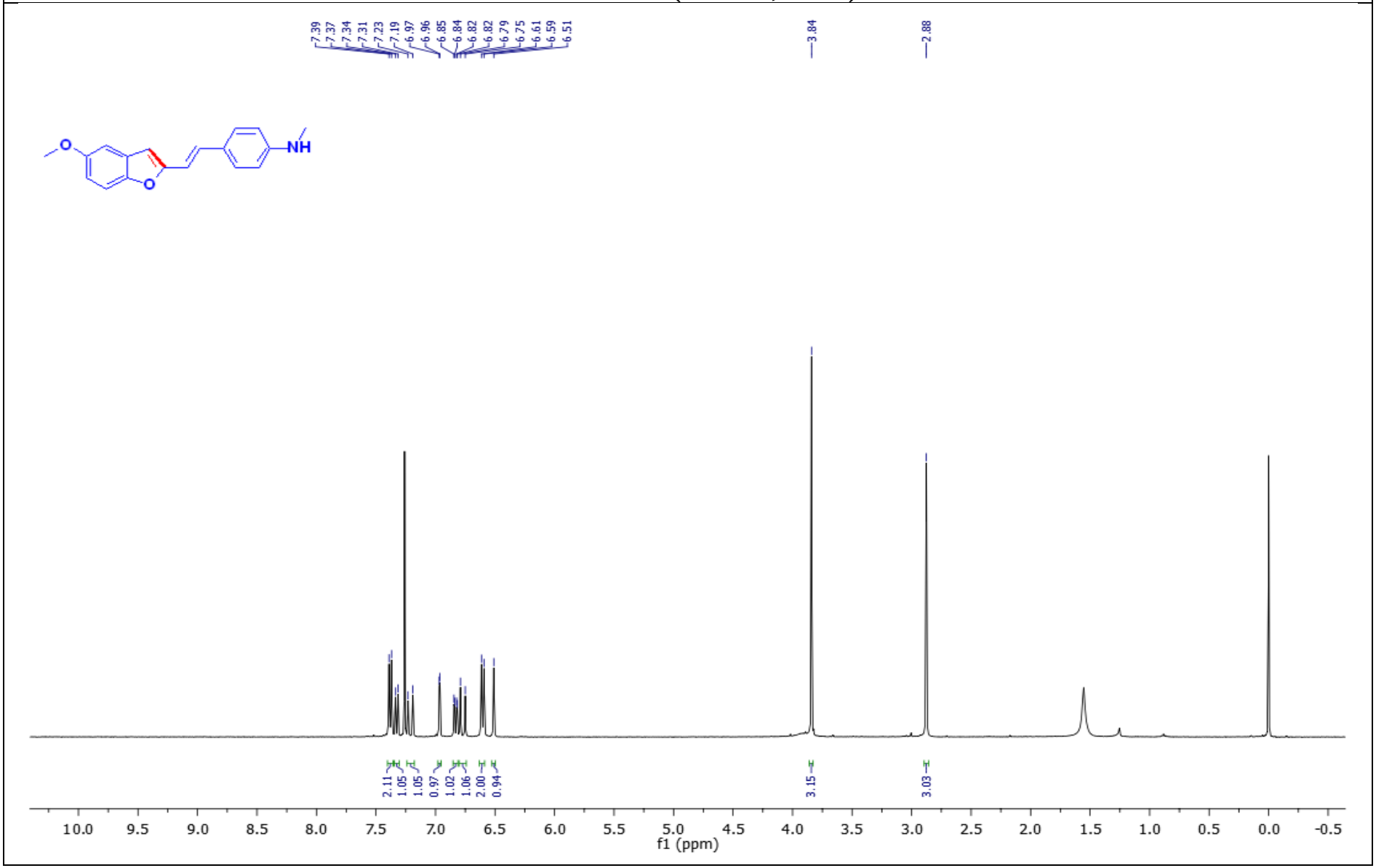
^{1}H-NMR of 11 (400 MHz, $CDCl_3$)



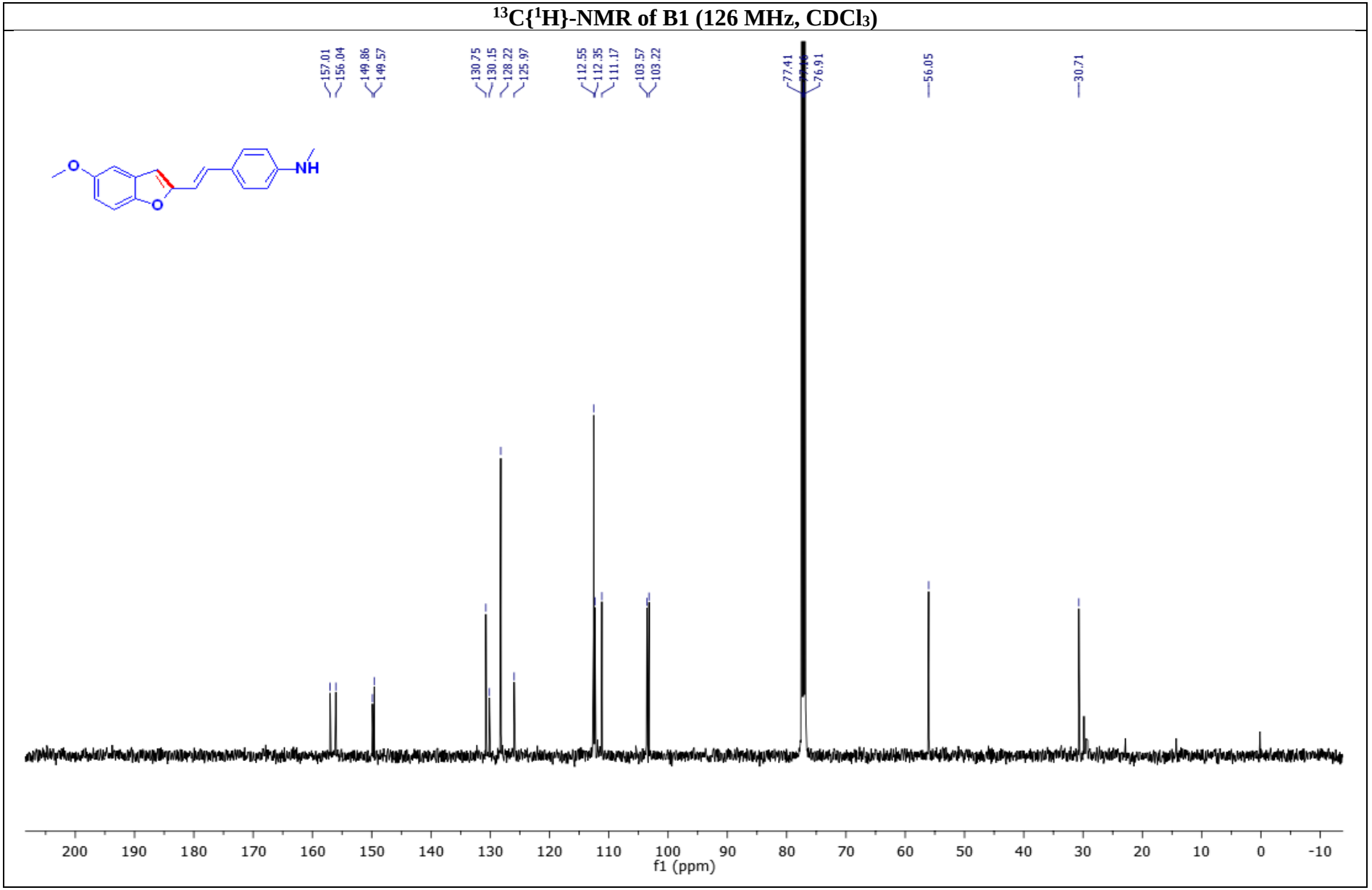
$^{13}C\{^{1}H\}$-NMR of 11 (126 MHz, $CDCl_3$)



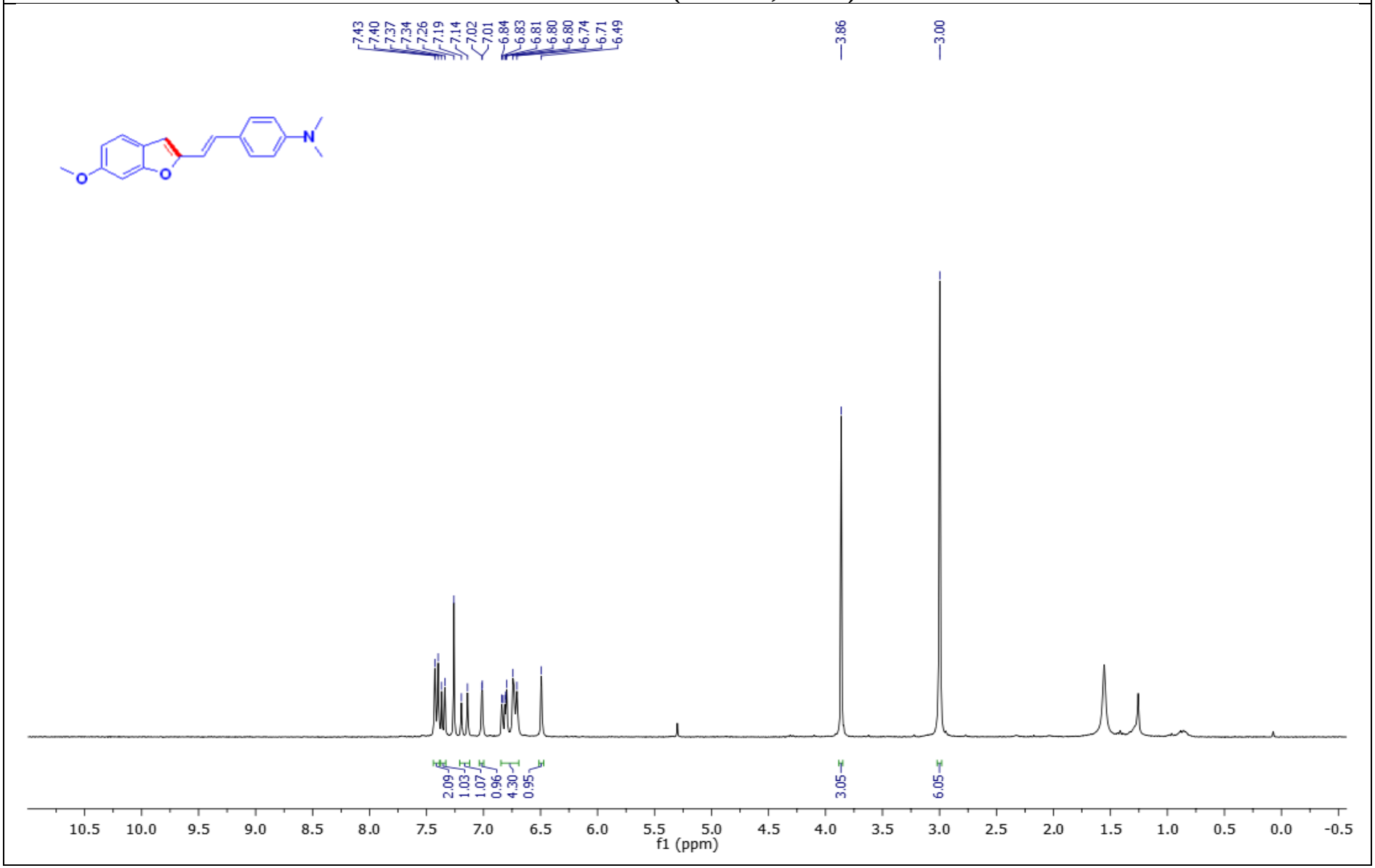
^{1}H-NMR of B1 (400 MHz, $CDCl_3$)



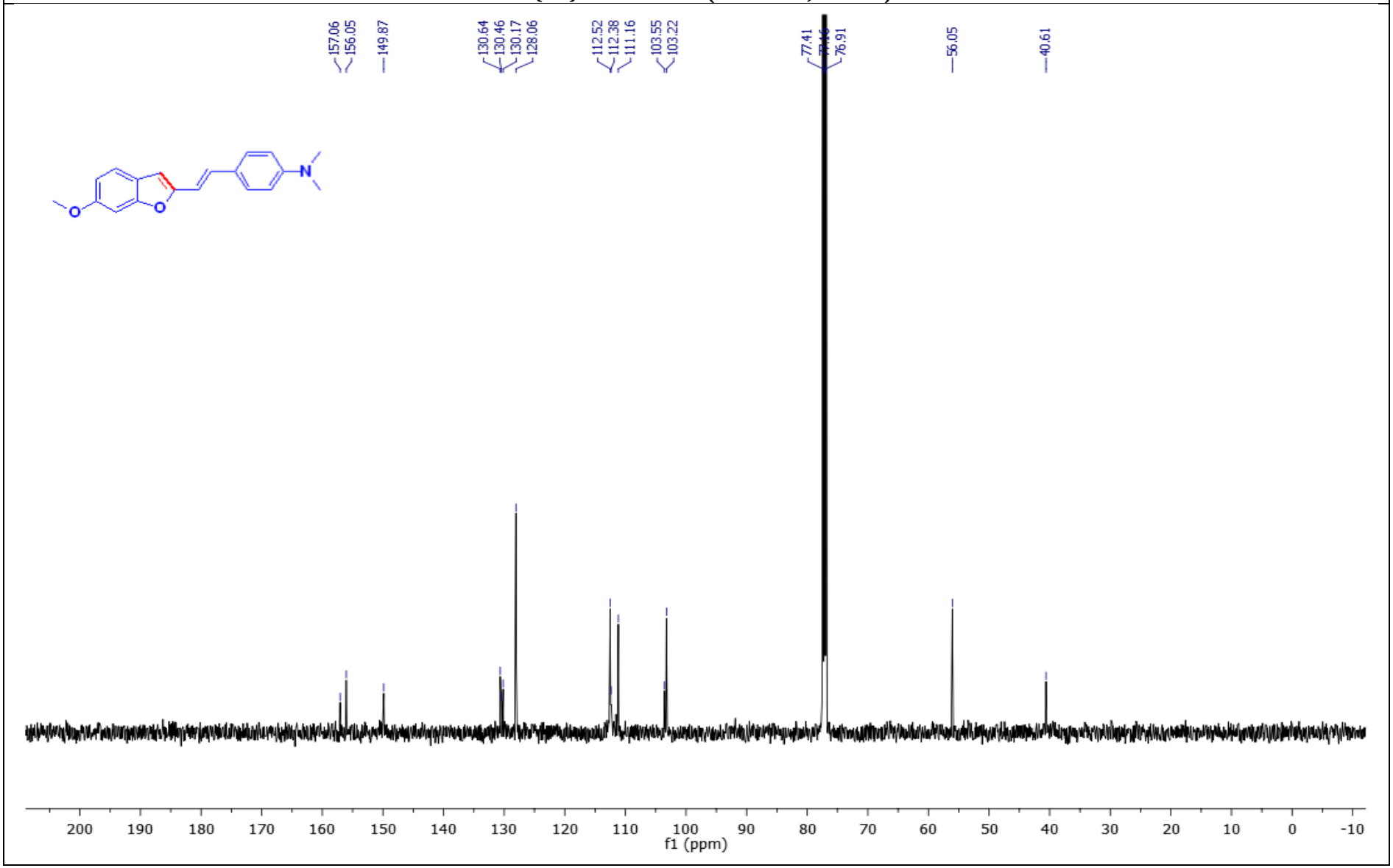
$^{13}C\{^{1}H\}$-NMR of B1 (126 MHz, $CDCl_3$)



^{1}H-NMR of B2 (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$-NMR of B2 (126 MHz, $CDCl_3$)



13. Crystallographic data for compound 3aa

Method of Crystallization: The crystal of compound **3aa** was obtained using the slow evaporation method in chloroform at room temperature.

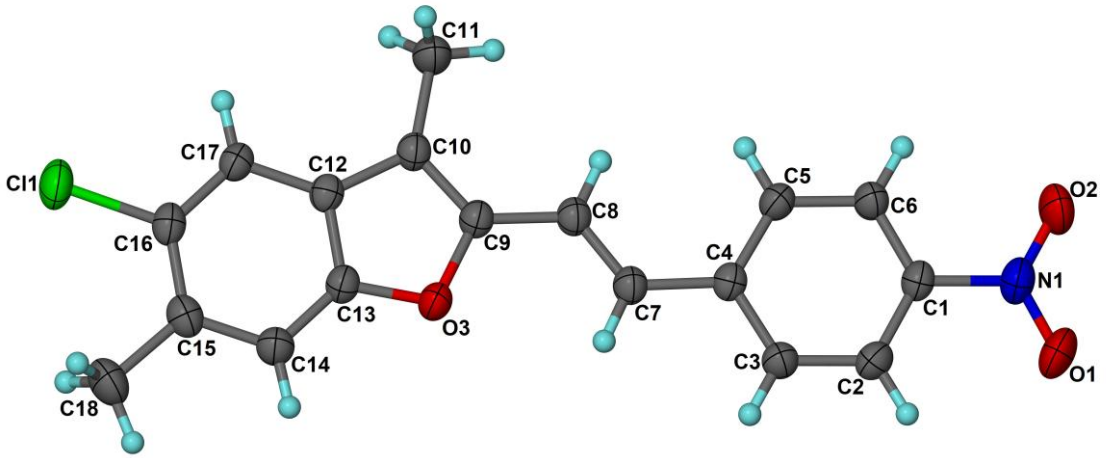


Figure caption: ORTEP diagram of compound **3aa** with the atom numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for compound 3aa: $C_{18}H_{14}ClNO_3$, M = 327.75, Monoclinic, Space group P21/n (No.14), a = 7.3216(10)Å, b = 17.174(2)Å, c = 2 .5583(16)Å, α = 90°, β = 100.459(4)°, γ = 90°, V = 1552.8(4)Å3, Z = 4, Dc = 1.402 g/cm3, F000 = 680, Bruker D8 VENTURE PHOTON C14 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, 2θmax = 55º, μ = 0.260 mm-1, 15183 reflections collected, 3553 unique (Rint = 0.0437), 210 parameters, R1 = 0.0513, wR2 = 0.1249, R indices based on 2302 reflections with I > 2σ(I) (refinement on F2), Final GooF = 1.061, largest difference hole and peak = -0.281 and 0.229 e.Å-3. **CCDC deposition number 2445252** contains the supplementary crystallographic data for this paper, which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/.

Crystal data collection for compound 3aa:

X-ray data for the compound were collected at room temperature on a Bruker D8 VENTURE instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON C14 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[6] The structure was solved using the intrinsic phasing method[7] and further refined with the SHELXL[7-9] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. **CCDC deposition number 2445252** contains the supplementary crystallographic data for this paper, which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/.

14. References

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