Electronic Supplementary Information

Synthesis of tetrahydrocarbazoles through a radical cation [4+2] cycloaddition reaction of 2-vinylindoles

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General Remarks

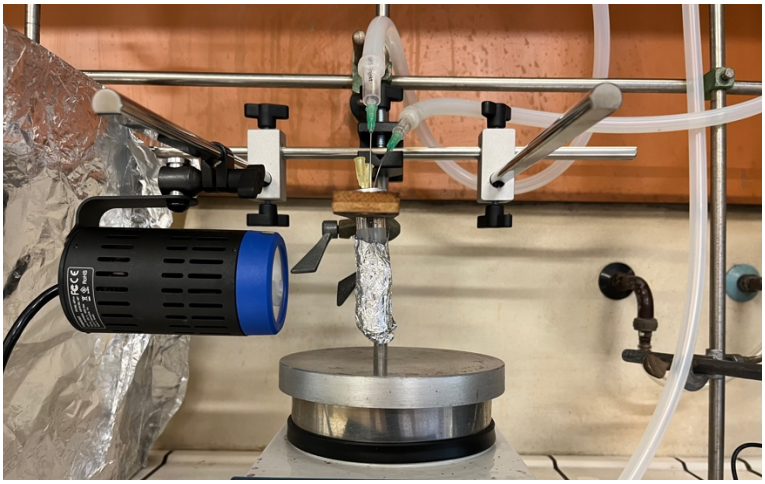
All the reactions, that involve the use of reagents sensitive to oxygen or hydrolysis, were carried out under a nitrogen atmosphere. The glassware was previously dried with a heating gun and set with cycles of vacuum and nitrogen. Syringes, used to transfer reagents and solvents, were previously set under nitrogen atmosphere. All chemicals and solvents are commercially available and were used without further purification. The chromatographic column separations were performed by flash technique, using silica gel (pore size 60., particle size 230–400 mesh, Merck Grade 9385). For thin-layer chromatography (TLC), Silica on TLC Alu foils with fluorescent indicator (254 nm) was employed and the detection was performed by irradiation with UV light (λ = 254 nm and/or 366 nm).

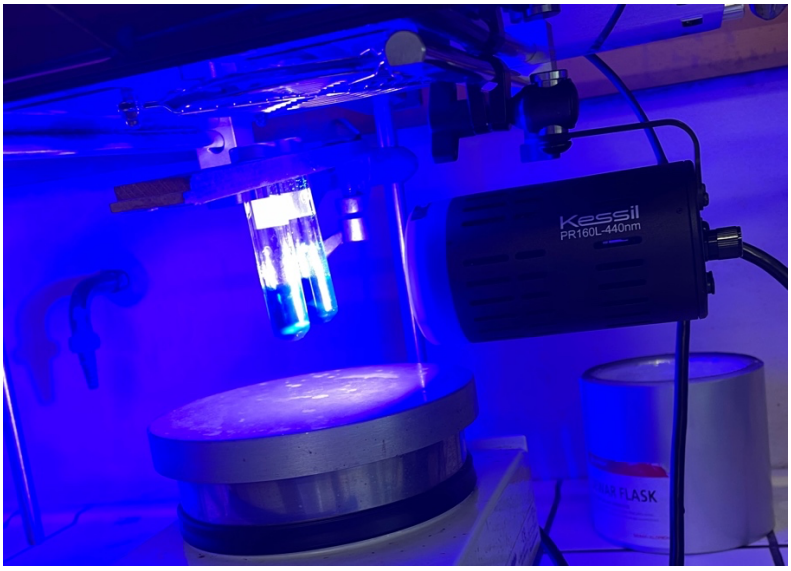
^{1}H NMR analyses were performed with 300 MHz and 400 MHz spectrometer at room temperature.
The coupling constants (J) are expressed in Hertz (Hz), the chemical shifts (δ) in ppm. The multiplicity of the proton spectra were described by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), dt (double triplet), dd (double doublet), m (multiplet), br (broad). ^{13}C NMR analyses were performed with the same instruments at 74.45 MHz and 101 MHz; APT sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. All ^{13}C NMR spectra were recorded with complete proton decoupling.
High resolution mass spectra (HR-MS) were acquared on a Synapt G2-S*i* QTof mass spectrometer (Waters, Milford, MA, USA) equipped with a Zspray ESI-probe (Waters) for electrospray ionization in positive polarity and full scan mode. Data were processed using MassLynx v4.2 software (Waters).
Dienes **2a**, **2c-g** and stryrenes **5a-b,d** were purchased from commercial suppliers and used as received. Cyclopentadiene **2d** was freshly distilled from dicyclopentadiene.
Triarylpyrylium tetrafluoroborates,[1] 2-vinylindoles **1a**,[2] **1b**, **1e**, **1f**, **1n**, **1o**, **1r**,[3] 4-OBn-Styrene[4] **5e** and 2-vinylthiophene[5] **5c** are known compounds and were prepared according to literature procedures. Alkenyl boronates were prepared from the corresponding alkynes following known procedures.[6]

[1] M. Martiny, E. Steckhan, T. Esch, *Chem. Ber.* **1993,** *126*, 1671-1682
[2] V. Ramella, Z. He, C. G. Daniliuc, A. Studer, *Eur. J. Org. Chem.* **2016**, 2268-2273.
[3] V. Pirovano, L. Decataldo, E. Rossi, R. Vicente, *Chem. Commun.* **2013**, *49*, 3594-3596.
[4] J. L. M. Van Nunen, B. F. B. Folmer, R. J. M. Nolte, *J. Am. Chem. Soc.* **1997**, *119*, 283-291.
[5] X. Shi, T. ting Du, Z. Zhang, X. Liu, Y. Yang, N. Xue, X. Jiao, X. Chen, P. Xie, *Bioorg. Chem.* **2022**, *127*, 106015.
[6] a) S. Pereira, M. Srebnik, *Organometallics* **1995**,*14*, 3127-3128; b) C. Yang, Y. Gao, S. Bai, C. Jiang, X. Qi, *J. Am. Chem. Soc.*, **2020**, *142*, 11506.

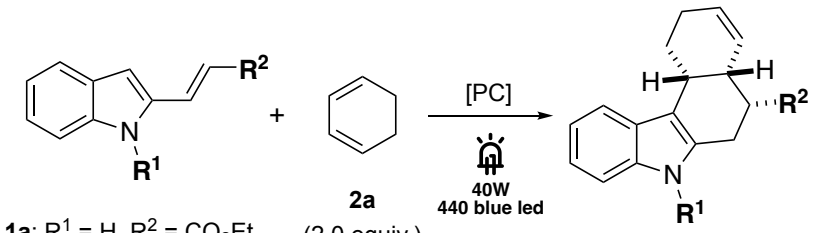
Set-up of photocatalytic reactions

Blue-led irradiation was performed using a Kessil PR160L 440 nm. Catalytic reactions were performed into vials capped with aluminium crimp seals with septa and mounted into a Kessil PR160 RIG with Fan Kit (4 cm from light).





Optimization of reaction conditions for the synthesis of 3a



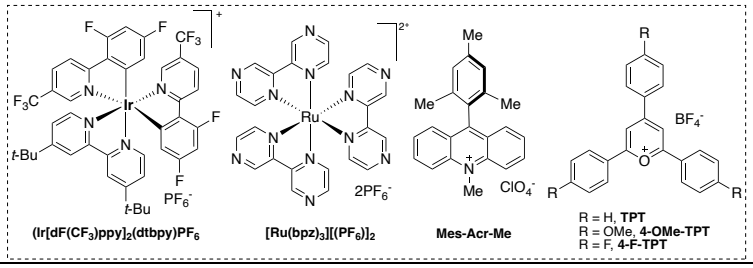
1a: R^1 = H, R^2 = CO_2Et
1b: R^1 = CO_2Et, R^2 = *p*-Tol

(2.0 equiv.)

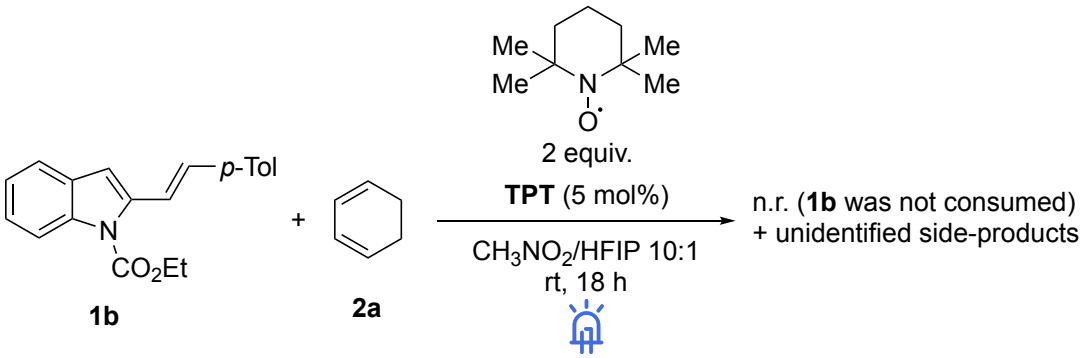
3a, 3b

Entry	1	PC (*n* mol%)	Solvent [M]	Time, h	3(%)[a]
1	**1a**	$Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (2 mol%)	CH_3CN (0.1 M)	1	-[b]
1	**1b**	$(Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (2 mol%)	CH_3CN (0.1 M)	18	-[c]
3	**1a**	$[Ru(bpz)_3][(PF_6)]_2$ (2 mol%)	CH_3CN (0.1 M)	18	-[c]
4	**1b**	$[Ru(bpz)_3][(PF_6)]_2$ (2 mol%)	CH_3CN (0.1 M)	24	-[c]
5	**1a**	Mes-Acr-Me (5 mol%)	CH_3CN (0.1 M)	18	-[c]
6	**1b**	Mes-Acr-Me (5 mol%)	CH_3CN (0.1 M)	18	-[d]
9	**1a**	TPT (5 mol%)	CH_3CN (0.1 M)	18	-[d]
10	**1b**	TPT (5 mol%)	CH_3CN (0.1 M)	18	32
11	**1b**	TPT (5 mol%)	DCE (0.1 M)	18	42
12	**1b**	4-OMe-TPT (5 mol%)	DCE (0.1 M)	18	39
13	**1b**	4-F-TPT (5 mol%)	DCE (0.1 M)	18	26
14	**1b**	TPT (5 mol%)	DCE (0.05 M)	18	38
15	**1b**	TPT (5 mol%)	CH_3NO_2 (0.1 M)	18	48
16	**1b**	TPT (5 mol%)	DCE/HFIP 10:1 (0.1 M)	18	48
17	**1b**	TPT (5 mol%)	DCE/HFIP 1:1 (0.1 M)	18	43
18	**1b**	TPT (5 mol%)	CH_3NO_2/HFIP 10:1 (0.1 M)	18	57
19	**1b**	TPT (5 mol%)	CH_3NO_2/TFE 10:1 (0.1 M)	18	47
20[e]	**1b**	TPT (5 mol%)	CH_3NO_2/HFIP 10:1 (0.1 M)	36	-
21[f]	**1b**	TPT (5 mol%)	CH_3NO_2/HFIP 10:1 (0.1 M)	18	71

Reaction conditions: **1a** or **1b** (0.2 mmol), **2a** (0.4 mmol), catalyst (2-5 mol%) in anhydrous solvent (2 ml) were irradiated with a 40W blue led (λ_{max} = 440 nm) for the stated time under air (entries 1-4) or under N_2 (entries 5-20). [a]Isolated yield (*d.r.* > 20:1). [b] [2+2] cycloaddition product on exocyclic double bond was isolated in 32% yield (*d.r.* = 1.4:1). [c]Unreacted vinylindole was recovered at the end of the reaction. [d]Complex mixture. [e]Reaction was conducted in the dark. [f]4 equivalents of 1,3-CHD were used.



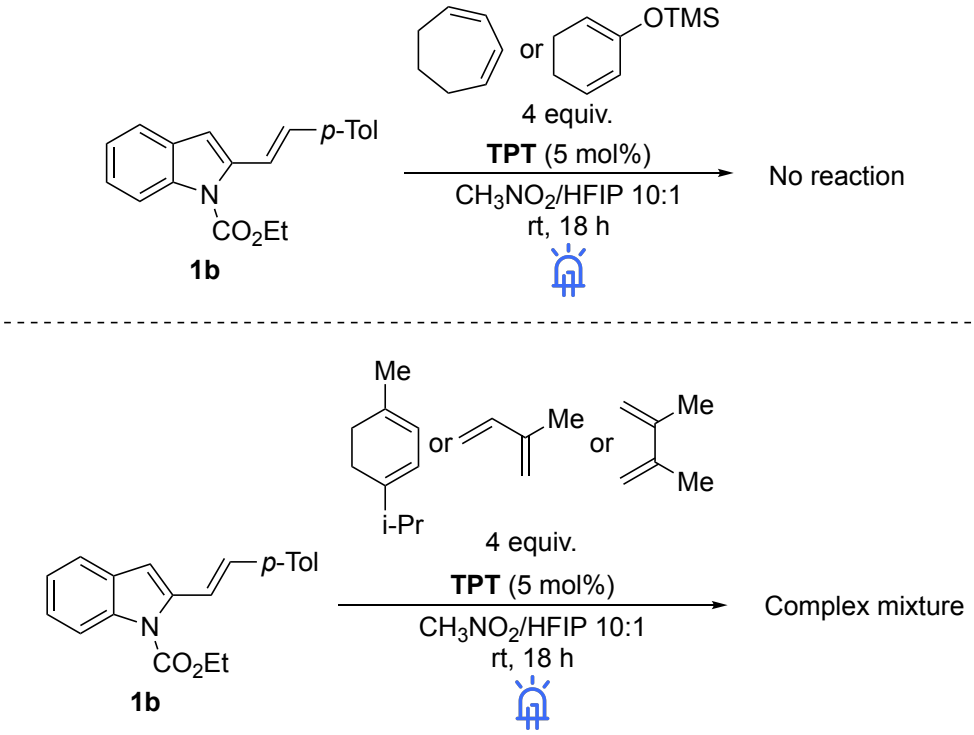
Reaction conducted in the presence of TEMPO



Reaction condition: **1b** (0.2 mmol), **2a** (0.8 mmol, 4 equiv.) and TEMPO (0.4 mmol). **TPT** catalyst (5 mol%), in CH_3NO_2/HFIP 10:1 (2 ml, 0.1 M) at rt for 18 h under 40W blue led irradiation (λmax = 440 nm).

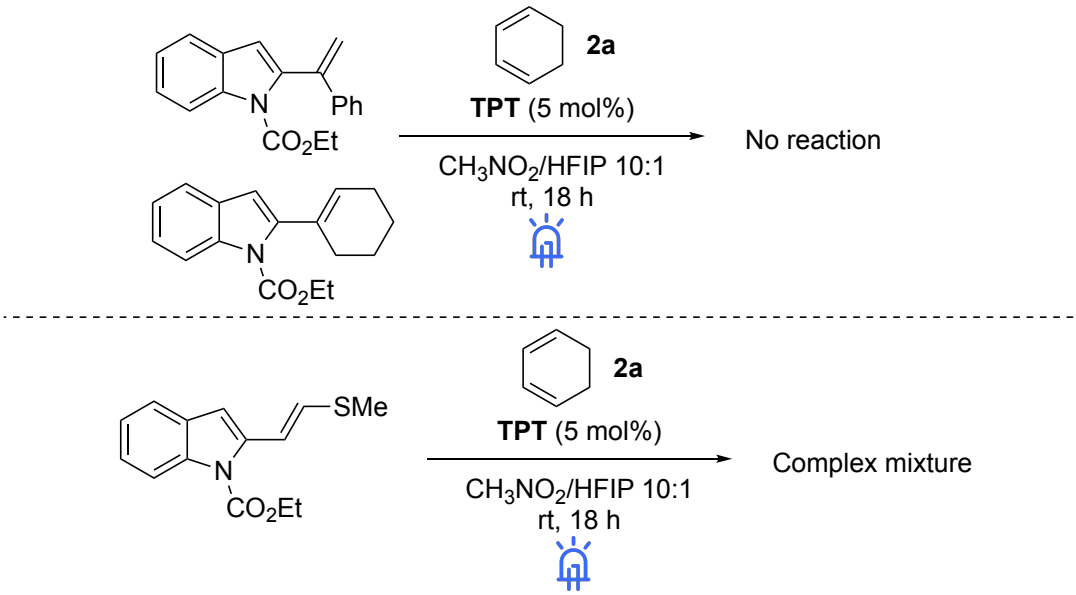
Unsuccessful results

Unsuccessful conjugated alkenes



Reaction condition: **1b** (0.2 mmol), alkene (0.8 mmol, 4 equiv.), **TPT** catalyst (5 mol%), in CH_3NO_2/HFIP 10:1 (2 ml, 0.1 M) at rt for 18 h under 40W blue led irradiation (λmax = 440 nm).

Unsuccessful 2-vinylindoles



Reaction condition: indoles (0.2 mmol), 1,3-CHD (**2a**) (0.8 mmol, 4 equiv.), **TPT** catalyst (5 mol%), in CH_3NO_2/HFIP 10:1 (2 ml, 0.1 M) at rt for 18 h under 40W blue led irradiation (λmax = 440 nm).

Electrochemical measurements

Electrochemical characterization of the compounds **1a** and **1b** was performed by cyclic voltammetry (CV) in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. CV was carried out in a customized three-electrode glass cell, filled with 3 mL solution, containing: Teflon-embedded glassy carbon electrode (0.071 cm^2; Amel), as the working one; AgCl/Ag saturated KCl (Amel), as reference electrode; platinum wire, as counter electrode. To avoid water leakage from the aqueous reference electrode into the working solution, the reference electrode was inserted in a glass double-bridge, ending with a porous frit, filled with the blank solution (CH_3CN + 0.1 M $[(n\text{-}Bu)_4N][PF_6]$).
The working solution contained around 1 mM of the analyte (**1a** or **1b**). Before measurements, solution was deaerated by bubbling N_2 gas for few minutes; nitrogen was fluxed in the cell, just above the solution surface, while recording the current-voltage curves. CV traces were recorded by changing the potential scan rate in a range from 0.02 to 2 V s^{-1}. After each potential cycle, the working electrode was mechanically cleaned using a proper cloth covered by a sludge of alumina (ca. 0.05 μm) suspended in MilliQ water. After that, the electrode was abundantly rinsed with MilliQ water and carefully dried with blotting paper.
After completing the study of a compound, CV traces of ferrocene (Fc) were recorded in the same solution. Half-wave potential ($E_{1/2}$) of the redox couple Fc^+/Fc was then evaluated as average between the forward and the reverse peak potential ($E_{1/2}$ ≈ 0.44 V *vs.* AgCl/Ag, in our conditions) and used to refer all the experimental potentials to the Fc^+/Fc intersolvental redox couple according to the following equation:

$$E_{analyte}\ (vs.\ Fc^+/Fc) = E_{analyte}\ (vs.\ AgCl/Ag) - E_{1/2,Fc+/Fc}\ (vs.\ AgCl/Ag)$$

Potential values referred to the intersolvental redox couple can be directly compared with literature data, even when the potentials of the compounds of interest have been recorded in different organic solvents.

Electrochemical characterization of 1a and 1b compounds by cyclic voltammetry

Cyclic voltammetry curves (Figure S1) showed that both indole substrates undergo chemically irreversible oxidation(s) through single electron transfer process(es) characterized invariably by a faradaic nature and a relatively fast kinetics, as inferred from the small positive shift of the anodic peak potentials by increasing the potential scan rate (Figure S2). The absence of the coupled cathodic peak means that the oxidized product is not stable (at least up to the faster time frame used for the measurements) by converting into an electrochemically inactive compound, as a result of the interaction with the medium and/or of an intra- (or inter-) molecular reaction. The two compounds differ each other's not only in terms of the energetics (thermodynamics) of the electron transfers, with **1b** being more oxidizable than the **1a** analogue, but also in the reaction pathway. While **1a** exhibits a unique oxidation process, resulting in the formation of a radical cation, **1b** shows two subsequent oxidation processes, the second one bringing to the formation of a bication at around 150 mV more positive potential than that generating the radical cation. The relative intensity of the two anodic peaks of **1b** is almost constant by changing the scan rate potentials, thus excluding the second process being related to the oxidation of the initially electrogenerated product (*i.e.*, chemical follow-up reaction).
In conclusion, the differences in the voltammetric patterns point out that the active redox centers in the two substrates are different, thus providing a tentative explanation of why the chemical reaction triggered by the photocatalyst (described in the main text) seems to proceed along two different pathways for **1a** and **1b**, resulting in different products. Further information on how the different substitution of the indole core affects the localization of HOMO level (responsible for the oxidation process) could be obtained by a future investigation by density functional theory calculations.

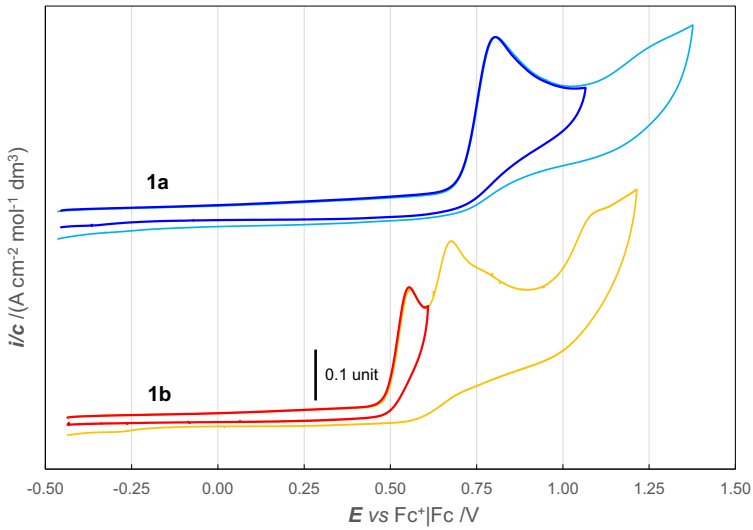


Figure S1. Cyclic voltammetry (CV) traces showing the anodic pattern of compound **1a** (top) and **1b** (bottom). Recorded in CH_3CN + 0.1 M $(n\text{-}Bu)_4N^+PF_6^-$ on glassy carbon electrode, at a scan rate potential of 0.2 V s^{-1}. Current density was normalized for the concentration (c) of each compound.

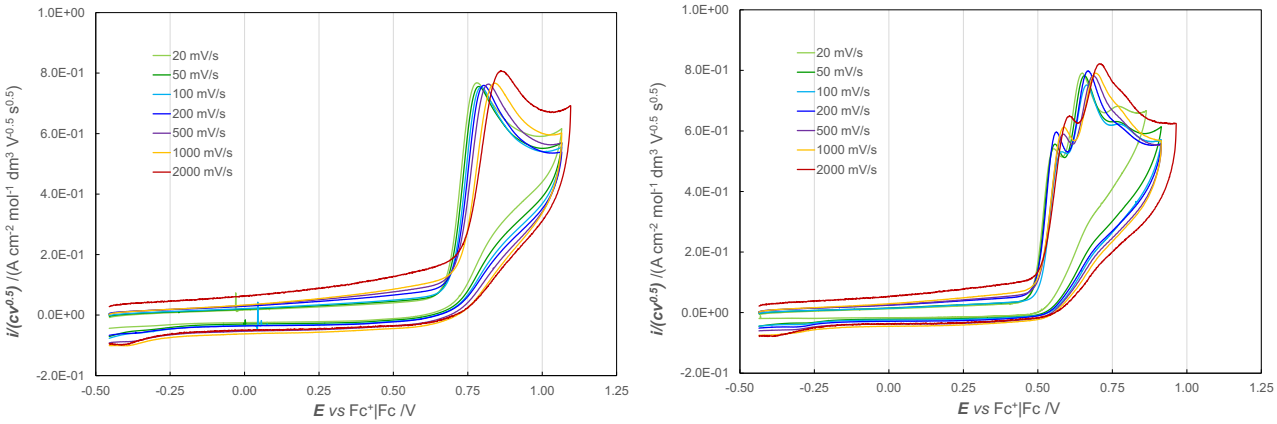
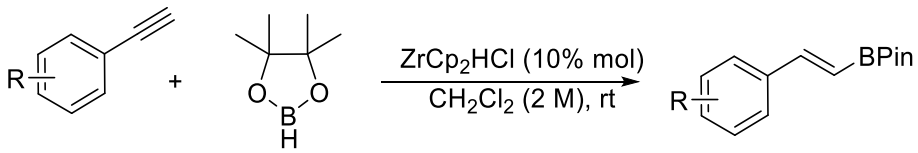


Figure S2. Normalized CV traces of the first oxidation process(es) of the compound **1a** (left) and **1b** (right), recorded with potential scan rates ranging from 0.02 to 2 V s^{-1}. Experimental conditions as in Figure S1.

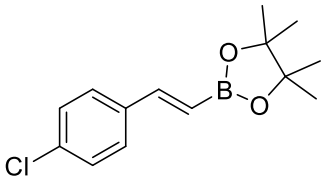
Synthesis of alkenyl boronates



General procedure for the synthesis of alkenyl boronates[5]

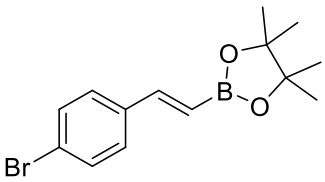
To a N_2-flushed solution of the aryl alkyne (1.0 equiv.), and $ZrCp_2HCl$ (Schwartz's reagent, 10% mol), in anhydrous CH_2Cl_2 (2M), 4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (HBPin, 1.1 equiv.) was added dropwise at 0 °C and the mixture was stirred for 24h at room temperature. Then, the reaction mixture was quenched with H_2O at 0°C and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by flash column chromatography to yield the corresponding (*E*)-2-aryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

(*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



General procedure was followed using 1-chloro-4-ethynylbenzene (1 g, 7.32 mmol), $ZrCp_2HCl$ (189 mg, 0.73 mmol) and HBPin (1.17 ml, 8.05 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 98:2) yielded (*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.3 g, 67%) as a white solid.
^1H NMR (400 MHz, $CDCl_3$): 7.44 – 7.28 (m, 5H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 147.99 (CH), 135.93 (C), 134.58 (C), 128.77 (CH), 128.20 (CH), 83.43 (C), 24.79 (CH_3).
Data are in agreement with those reported in literature.[7]

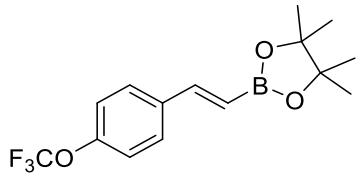
(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



General procedure was followed using 1-bromo-4-ethynylbenzene (500 mg, 2,76 mmol), $ZrCp_2HCl$ (72 mg, 0.28 mmol) and HBPin (439 µl, 3.04 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 95:5) yielded (*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.56 g, 66%) as a colourless oil.
^1H NMR (400 MHz, $CDCl_3$): 7.48 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): 148.07 (CH), 136.42 (C), 131.76 (CH), 128.51 (CH), 122.90 (C), 83.48 (C), 24.81 (CH_3).
Data are in agreement with those reported in literature.[7]

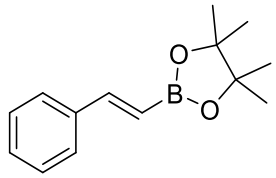
[7] C. Feng, H. Wang, L. Xu, P. Li, *Org. Biomol. Chem.* **2015**, *13*, 7136-7139.

(*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)styryl)-1,3,2-dioxaborolane



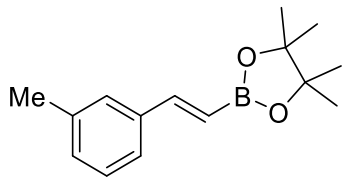
General procedure was followed using 1-trifluoromethoxy-4-ethynylbenzene (600 mg, 3.22 mmol), $ZrCp_2HCl$ (83 mg, 0.32 mmol) and HBPin (514 μl, 3.64 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 95:5) yielded (*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)styryl)-1,3,2-dioxaborolane (0.66 g, 66%) as a colourless oil.
^1H NMR (400 MHz, $CDCl_3$): 7.52 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 18.4 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 6.16 (d, J = 18.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): 149.45 (C), 147.71 (CH), 136.17 (C), 128.33 (CH), 120.94 (CH), 120.44 (q, J_{C-F} = 256.5 Hz, C), 83.49 (C), 24.80 (CH_3).
HRMS (ESI) calculated for $C_{19}H_{18}NO_2$ $[M+H]^+$ requires m/z = 315,1379, found m/z 315.1373.

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane



General procedure was followed using ethynylbenzene (500 mg, 4.95 mmol), $ZrCp_2HCl$ (127 mg, 0.496 mmol) and HBPin (0.79 ml, 5.46 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 95:5) yielded (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (0.94 g, 83%) as a colourless oil.
^1H NMR (400 MHz, $CDCl_3$): 7.52 (m, 2H), 7.43 (d, J = 18.4 Hz, 1H), 7.39 – 7.27 (m, 3H), 6.20 (d, J = 18.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): 149.53 (CH), 137.50 (C), 128.90 (CH), 128.57 (CH), 127.07 (CH), 83.36 (C), 24.82 (CH_3).
Data are in agreement with those reported in literature.[8]

(*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane

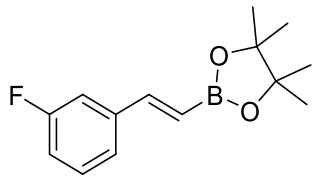


General procedure was followed using 1-ethynyl-3-metilbenzene (500 mg, 4.3 mmol), $ZrCp_2HCl$ (110 mg, 0.43 mmol) and HBPin (0.69 ml, 4.73 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 95:5) yielded (*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (0.84 g, 80%) as a colourless oil.
^1H NMR (400 MHz, $CDCl_3$): 7.40 (d, J = 18.4 Hz, 1H), 7.32 (m, 2H), 7.29 – 7.21 (m, 1H), 7.13 (d, J = 7.4 Hz, 1H), 6.18 (d, J = 18.4 Hz, 1H), 2.37 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): 149.68 (CH), 138.08 (C), 137.49 (C), 129.71 (CH), 128.46 (CH), 127.79 (CH), 124.25 (CH), 83.31 (C), 24.82 (CH_3), 21.39 (CH_3).

[8] J. Zhao, Z. Niu, H. Fu, Y. Li, *Chem. Commun.* **2014**, *50*, 2058-2060.

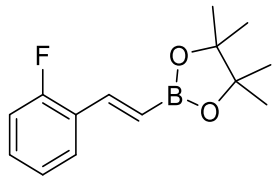
Data are in agreement with those reported in literature.[8]

(*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



General procedure was followed using 1-ethynyl-3-fluorobenzene (500 mg, 4.16 mmol), $ZrCp_2HCl$ (107 mg, 0.416 mmol) and HBPin (0.66 ml, 4.57 mmol). Purification of the crude by flash chromatography (SiO2, hex/ EtOAc 95:5) yielded (*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.66 g, 66%) as a colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): 7.37 (d, J = 18.1 Hz, 1H), 7.31 (m, 1H), 7.26 (d, J = 7.7 Hz, 1H), 7.20 (m, 1H), 7.01 (m, 1H), 6.19 (d, J = 18.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): 163.09 (d, $J_{C\text{-}F}$ = 245.5 Hz, C), 148.06 (d, $J_{C\text{-}F}$ = 2.4 Hz, CH), 139.88 (d, $J_{C\text{-}F}$ = 7.4 Hz, C) 130.02 (d, $J_{C\text{-}F}$ = 8.4 Hz, CH), 122.99 (d, $J_{C\text{-}F}$ = 2.7 Hz, CH), 115.67 (d, $J_{C\text{-}F}$ = 21.4 Hz, CH), 113.29 (d, $J_{C\text{-}F}$ = 21.5 Hz, CH), 83.90 (C), 24.80 (CH_3).
Data are in agreement with those reported in literature.[8]

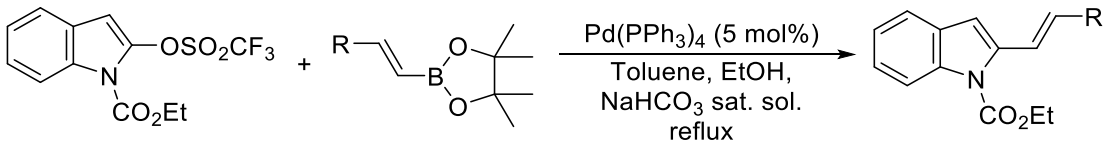
(*E*)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



General procedure (A) was followed using 1-ethynyl-2-fluorobenzene (500 mg, 4.17 mmol), $ZrCp_2HCl$ (107 mg, 0.41 mmol) and HBPin (0.66 ml, 4.58 mmol). Purification of the crude by flash chromatography (SiO2, hex/ EtOAc 98:2) yielded (*E*)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.65 g, 67%) as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (m, 2H), 7.26 (m, 1H), 7.11 (td, J = 7.4, 0.8 Hz, 1H), 7.03 (ddd, J = 10.6, 8.2, 1.2 Hz, 1H), 6.24 (d, J = 18.6 Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 160.68 (d, $J_{C\text{-}F}$ = 251.6 Hz, C), 141.29 (d, $J_{C\text{-}F}$ = 4.1 Hz, CH), 130.15 (d, $J_{C\text{-}F}$ = 8.5 Hz, CH), 127.36 (d, $J_{C\text{-}F}$ = 3.3 Hz, CH), 125.35 (d, $J_{C\text{-}F}$ = 11.7 Hz, C), 124.07 (d, $J_{C\text{-}F}$ = 3.6 Hz, CH), 115.79 (d, $J_{C\text{-}F}$ = 22.0 Hz, CH), 83.43 (C), 24.79 (CH_3).
Data are in agreement with those reported in literature.[8]

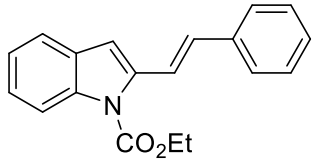
Synthesis of 2-vinylindoles 1c, d, g-m, p, q

General procedure for the synthesis of 2-vinylindoles 1c,d,g-m



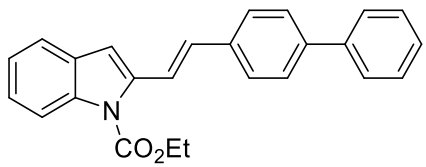
To a N_2-flushed solution of ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (1.0 equiv.) in anhydrous toluene (0.05M), $Pd(PPh_3)_4$ (5 mol%) was added. The reaction mixture was stirred for 30 minutes at room temperature, then a solution of the appropriate alkenyl boronate or boronic acid (1.5 equiv.) in EtOH-sat. Na_2HCO_3 (3:2, 0.05M) was added dropwise at room temperature. The mixture was heated at reflux for 2 hours, cooled at room temperature, quenched with NaCl s.s and extracted with EtOAc (3x). The combined organic layers were dried over Na_2SO_4, filtered and the solvent concentrated under vacuum. The crude was purified by flash column chromatography to yield the corresponding (*E*)-2-vinylindole **1c, d, g-m**.

Ethyl (*E*)-2-styryl-1*H*-indole-1-carboxylate (1c)



General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (300 mg, 0.89 mmol), $Pd(PPh_3)_4$ (51 mg, 0.044 mmol) and (*E*)-2-styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (306 mg, 1.33 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 50:1) yielded **1c** (258 mg, 99%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.14 (m, 1H), 7.80 (dd, *J* = 16.2, 0.8 Hz, 1H), 7.55 (m, 3H), 7.39 (m, 2H), 7.34 – 7.22 (m, 3H), 7.09 (d, *J* = 16.2 Hz, 1H), 6.90 (s, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): 152.12 (C), 139.51 (C), 137.15 (C), 136.78 (C), 130.94 (CH), 129.55 (C), 128.71 (CH), 127.88 (CH), 126.66 (CH), 124.33 (CH), 123.27 (CH), 120.39 (CH), 120.36 (CH), 115.80 (CH), 107.03 (CH), 63.29 (CH_2), 14.41 (CH_3). HRMS (ESI) calculated for $C_{19}H_{17}NO_2Na$ $[M+Na]^+$ requires *m/z* = 314.1157, found *m/z* 314.1160.

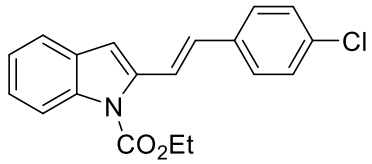
Ethyl (*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1*H*-indole-1-carboxylate (1d)



General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (300 mg, 0.89 mmol), $Pd(PPh_3)_4$ (51 mg, 0.044 mmol) and (*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-boronic acid (306 mg, 1.33 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 50:1) yielded **1d** (260 mg, 97%) as a yellow solid

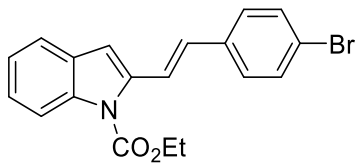
^{1}H NMR (400 MHz, $CDCl_3$): 8.16 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 16.2 Hz, 1H), 7.71 – 7.60 (m, 6H), 7.57 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41– 7.27 (m, 3H), 7.15 (d, *J* = 16.2 Hz, 1H), 6.95 (s, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.57 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.19 (C), 140.64 (C), 140.60 (C), 139.57 (C), 136.84 (C), 136.26 (C), 130.48 (CH), 129.61 (C), 128.85 (CH), 127.40 (CH), 127.14 (CH), 126.95 (CH), 124.40 (CH), 123.33 (CH), 120.44 (CH), 120.39 (CH), 115.86 (CH), 107.10 (CH), 63.35 (CH_2), 14.45 (CH_3). HRMS calculated for $C_{25}H_{21}NO_2Na$ $[M+Na]^+$ requires *m/z* = 390.1470, found *m/z* 390.1472.

Ethyl (*E*)-2-(4-chlorostyryl)-1H-indole-1-carboxylate (1g)



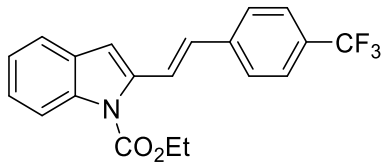
General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (300 mg, 0.89 mmol), $Pd(PPh_3)_4$ (51 mg, 0.044 mmol) and (*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (353 mg, 1.33 mmol). Purification of the crude by flash chromatography (SiO2, hex/ EtOAc 50:1) yielded **1g** (0.25 g, 85%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.10 (m, 1H), 7.77 (dd, *J* = 16.2, 0.9 Hz, 1H), 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.20 (m, 4H), 7.01 (d, *J* = 16.2 Hz, 1H), 6.89 (t, *J* = 0.8 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 152.12 (C), 139.16 (C), 136.70 (C), 135.65 (C), 133.42 (C), 129.51 (CH), 129.45 (CH), 128.86 (CH), 127.79 (CH), 124.48 (CH), 123.33 (CH), 120.92 (CH), 120.46 (CH), 115.82 (CH), 107.27 (CH), 63.36 (CH_2), 14.40 (CH_3). HRMS calculated for $C_{19}H_{16}ClNO_2Na$ $[M+Na]^+$ requires *m/z* = 348.0767, found *m/z* 338.0766.

Ethyl (*E*)-2-(4-bromostyryl)-1*H*-indole-1-carboxylate (1h)



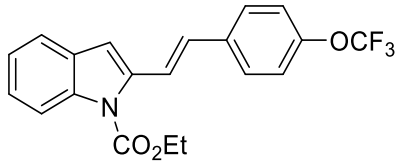
General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (200 mg, 0.62 mmol), $Pd(PPh_3)_4$ (36 mg, 0.03 mmol) and (*E*)-2-styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 0.75 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 50:1) yielded **1h** (150 mg, 66%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 16.2 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.24 (m, 2H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.91 (s, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.54 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.14 (C), 139.18 (C), 136.77 (C), 136.14 (C), 131.84 (CH), 129.58 (CH), 129.49 (C), 128.12 (CH), 124.54 (CH), 123.37 (CH), 121.63 (C), 121.08 (CH), 120.50 (CH), 115.86 (CH), 107.34 (CH), 63.39 (CH_2), 14.42 (CH_3). HRMS calculated for $C_{19}H_{16}BrNO_2Na$ $[M+Na]^+$ requires *m/z* = 392.0262, found *m/z* 392.0266.

Ethyl (*E*)-2-(4-(trifluoromethyl)styryl)-1*H*-indole-1-carboxylate (1i)



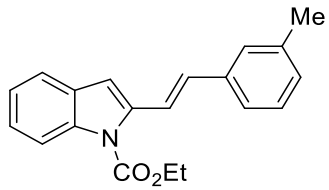
General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (500 mg, 1.48 mmol), $Pd(PPh_3)_4$ (86 mg, 0.074 mmol) and (*E*)-(4-trifluorostyryl)boronic acid (479 mg, 2.22 mol). Purification of the crude by flash chromatography (SiO_2, hex/EtOAc 9:1) yielded **1i** (0.45 g, 86%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.11 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.90 (d, *J* = 16.3 Hz, 1H), 7.61 (s, 4H), 7.57 – 7.52 (m, 1H), 7.37 – 7.22 (m, 2H), 7.08 (d, *J* = 16.2 Hz, 1H), 6.94 (s, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 152.08 (C), 140.59 (C), 138.76 (C), 136.80 (C), 129.38 (q, J_{C-F} = 32.6 Hz, C), 129.35 (C), 129.11 (CH), 126.68 (CH), 125.63 (q, J_{C-F} = 3.78 Hz, CH), 124.73 (CH), 124.17 (q, J_{C-F} = 272 Hz, C) 123.40 (CH), 122.82 (CH), 120.60 (CH), 115.86 (CH), 107.80 (CH), 63.42 (CH_2), 14.38 (CH_3).). HRMS calculated for $C_{20}H_{16}F_3NO_2Na$ $[M+Na]^+$ requires *m/z* = 382.1031, found *m/z* 382.1029.

Ethyl (*E*)-2-(4-(trifluoromethoxy)styryl)-1*H*-indole-1-carboxylate (1j)



General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (300 mg, 0.89 mmol), $Pd(PPh_3)_4$ (51 mg, 0.044 mmol) and (*E*)-2-(4-(trifluoromethoxy)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (419 mg, 1.33 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 50:1) yielded **1j** (297 mg, 89%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 16.2 Hz, 1H), 7.56 (m, 3H), 7.33 (m, 1H), 7.29 (m, 1H), 7.24 (m, 2H), 7.06 (d, *J* = 16.2 Hz, 1H), 6.91 (s, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.14 (C), 148.67 (C), 139.10 (C), 136.77 (C), 135.95 (C), 129.47 (C), 129.22 (CH), 127.86 (CH), 124.56 (CH), 123.37 (CH), 121.39 (CH), 121.21 (CH), 120.52 (CH), 120.51 (q, J_{C-F} = 256.6 Hz, C), 115.86 (CH), 107.37 (CH), 63.39 (CH_2), 14.41 (CH_3). HRMS calculated for $C_{20}H_{16}F_3NO_3Na$ $[M+Na]^+$ requires *m/z* = 398.0980, found *m/z* 398.0985.

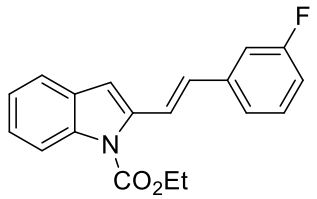
Ethyl (*E*)-2-(3-methylstyryl)-1*H*-indole-1-carboxylate (1k)



General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (275 mg, 0.82 mmol), $Pd(PPh_3)_4$ (47 mg, 0.041 mmol) and (*E*)-2-(3-methylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (298 mg, 1.22 mmol). Purification of the crude by flash chromatography (SiO_2, hex/ EtOAc 50:1) yielded **1k** (245 mg, 98%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.15 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 16.2 Hz, 1H), 7.56 (m, 1H), 7.40 – 7.24 (m, 5H), 7.13 (d, J = 7.4 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 6.91 (s, 1H), 4.58 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.56 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.19 (C), 139.67 (C), 138.28 (C), 137.12 (C), 136.79 (C), 131.15 (CH), 129.62 (C), 128.76 (CH), 128.63 (CH), 127.35 (CH), 124.31 (CH), 123.94 (CH), 123.29 (CH), 120.39 (CH), 120.15 (CH), 115.83 (CH), 106.96 (CH), 63.31 (CH_2), 21.45 (CH_3), 14.42 (CH_3). HRMS calculated for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$ requires m/z = 328.1313, found m/z 328.1311.

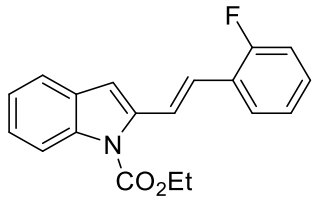
Ethyl (*E*)-2-(3-fluorostyryl)-1*H*-indole-1-carboxylate (1l)



General procedure was followed using 2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (275 mg, 0.815 mmol) and (*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.303 g, 1.22 mmol). Purification by flash chromatography (SiO_2, hexane:EtOAc = 50:1) yielded **1l** (240 mg, 95%) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$): 8.14 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 16.2 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.38-7.22 (m, 5H), 7.07-6.95 (m, 2H), 6.91 (s, 1H), 4.56 (q, J = 7.1 Hz, 2H), 1.54 (t, J = 7.07 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.2 (d, J = 245 Hz, C), 152.1 (C), 139.5 (d, J = 7.7 Hz, C), 139.0 (C), 136.8 (C), 130.1 (d, J = 8.4 Hz, CH), 129.6 (C), 129.5 (CH), 124.6 (CH), 123.4 (CH), 122.6 (CH), 121.7 (CH), 120.5 (CH), 115.9 (CH), 114.7 (d, J = 21 Hz, CH), 112.9 (d, J = 22 Hz, CH), 107.5 (CH), 63.4 (CH_2), 14.4 (CH_3). HRMS calculated for $C_{20}H_{16}FNO_2Na$ $[M+Na]^+$ requires m/z = 332.1063, found m/z 332.1061.

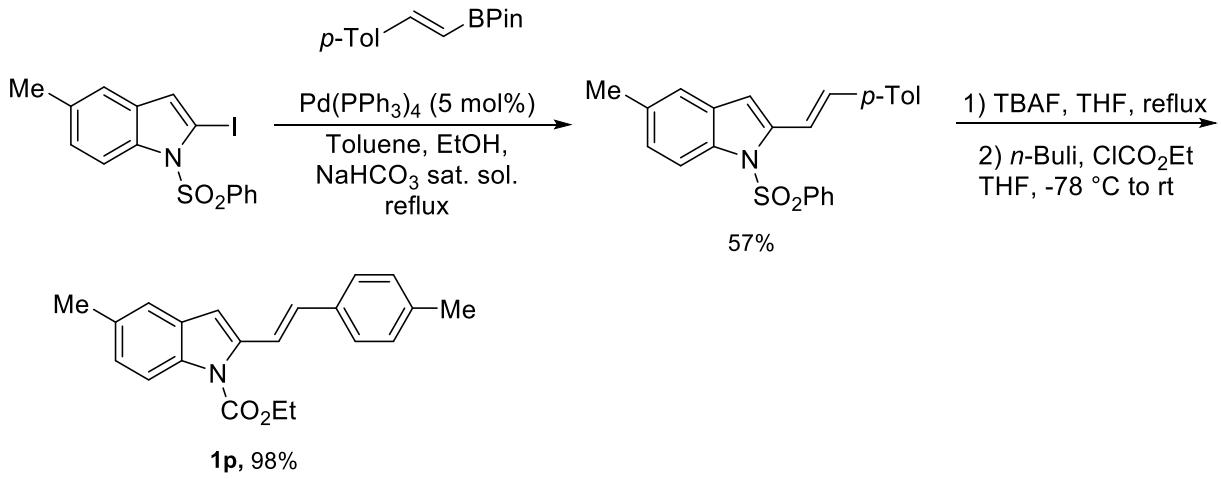
Ethyl (*E*)-2-(2-fluorostyryl)-1*H*-indole-1-carboxylate (1m)



General procedure was followed using ethyl-2-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (275 mg, 0.82 mmol), $Pd(PPh_3)_4$ (47 mg, 0.041 mmol) and (*E*)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (303 mg, 1.22 mmol). Purification of the crude by flash chromatography (SiO2, hex/ EtOAc 50:1) yielded **1m** (252 mg, 98%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): 8.12 (m, 1H), 7.87 (dd, J = 16.4, 0.8 Hz, 1H), 7.62 (td, J = 7.7, 1.8 Hz, 1H), 7.55 (m, 1H), 7.35 – 7.19 (m, 4H), 7.19 – 7.04 (m, 2H), 6.94 (s, 1H), 4.54 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 160.44 (d, $J_{C\text{-}F}$ = 250.2 Hz, C), 152.10 (C), 139.35 (C), 136.80 (C), 129.46 (C), 129.02 (d, $J_{C\text{-}F}$ = 8.4 Hz, CH), 127.35 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH), 125.00 (d, $J_{C\text{-}F}$ = 11.8 Hz, C), 124.50 (CH), 124.23 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH), 123.30 (CH), 123.08 (d, $J_{C\text{-}F}$ = 3.3 Hz, CH) 122.56 (d, $J_{C\text{-}F}$ = 5.7 Hz, CH), 120.51 (CH), 115.82 (d, $J_{C\text{-}F}$ = 22 Hz, CH), 115.80 (CH), 107.47 (CH), 63.36 (CH_2), 14.36 (CH_3). HRMS calculated for $C_{20}H_{16}FNO_2Na$ $[M+Na]^+$ requires m/z = 332.1063, found m/z 332.1060.

Synthesis of (*E*)-5-methyl-2-(4-methylstyryl)-1*H*-indole-1-carboxylate (1p)



1p, 98%

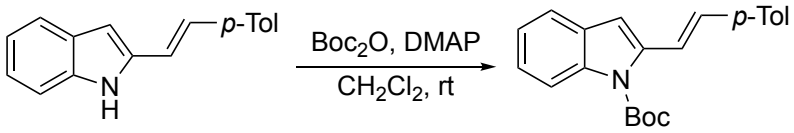
To a N_2-flushed solution of 2-iodo-1-(phenylsulfonyl)-1*H*-indole[9] (0.3 g, 0.75 mmol, 1.0 equiv.) in anhydrous toluene, $Pd(PPh_3)_4$ (43 mg, 5 mol%) was added. The reaction mixture was stirred for 30 minutes at room temperature, then a solution of (*E*)-2-(4-methylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.276 g, 1.13 mmol, 1.5 equiv.) in EtOH-sat. Na_2HCO_3 (3:2) was added dropwise at room temperature. The mixture was heated at reflux for 2 hours, cooled at room temperature and washed with brine. The organic layer was dried over Na_2SO_4, filtered and the solvent concentrated under vacuum. The crude was purified by flash column chromatography (SiO_2, hexane/Toluene 2:1) to yield the corresponding (*E*)-2-vinylindole (166 mg, 57%) as a white solid. This product (200 mg, 0.56 mmol, 1 equiv.) was then dissolved in THF (20 ml), then TBAF (1.12 mL, 1M in THF, 1.12 mmol, 2 equiv.) was added and the reaction mixture was stirred at reflux for 2h. After evaporation of the solvent, the crude was dissolved in water and extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4 and the crude was purified by flash chromatography (SiO_2, hexane/EtOAc 95:5 to 9:1) to obtain the corresponding (*E*)1*H*-vinylindole (125 mg, 97%) as wax.

To a solution of NH-free indole (100 mg, 0.4 mmol,1 equiv.) in anhydrous THF (4 ml), *n*-BuLi (0.27 ml, 1.6 M in hexane, 0.44 mmol,1.1 equiv.) was added dropwise at -78 °C and the reaction was stirred for 30 minutes. Ethylchloroformate (57 µL, 0.60 mmol, 1.2 equiv.) was added dropwise and the reaction was brought to room temperature and stirred for 3 hours. The reaction was quenched with saturated solution of NH_4Cl and the organic layer extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and the crude was purified by flash chromatography (SiO_2, hexane/EtOAc 99:1) to obtain **1p** (107 mg, 99%) as wax.

^{1}H NMR (300 MHz, $CDCl_3$): 7.99 (d, J = 8.5 Hz, 1H), 7.75 (dd, J = 16.2, 0.8 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.31 (m, 1H), 7.18 (d, J = 7.9 Hz, 2H), 7.11 (m, 1H), 7.05 (d, J = 16.2 Hz, 1H), 6.81 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H), 1.52 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.16 (C), 139.74 (C), 137.75 (C), 134.97 (C), 134.45 (C), 132.68 (C), 130.69 (CH), 129.81 (C), 129.41 (CH), 126.57 (CH), 125.59 (CH), 120.21 (CH), 119.44 (CH), 115.44 (CH), 106.51 (CH), 63.13 (CH_2), 21.29 (CH_3), 21.25 (CH_3), 14.41 (CH_3). HRMS calculated for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$ requires *m/z* = 342.1470, found *m/z* 342.1772.

[9]V. Pirovano, E. Brambilla, G. Tseberlidis, Giorgio, *Org. Lett.* **2018**, *20*, 405-408.

Synthesis of *t*-butyl (*E*)-2-(4-methylstyryl)-1*H*-indole-1-carboxylate (1q)



1q, 90%

2-(4-methylstyryl)-1H-indole[3] (180 mg, 0.77 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (4 mL). Boc_2O (505 mg, 2.31 mmol, 3 equiv.) and DMAP (9.4 mg, 10% mol) were added and the reaction was stirred at room temperature overnight. The reaction mixture was washed with brine, the organic layer was dried over Na_2SO_4, and concentrated under vacuum. The crude was purified by flash chromatography (SiO_2, hexane/EtOAc 99:1) to give **1q** (230 mg, 90%).

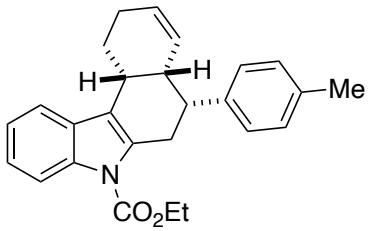
^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 16.2 Hz, 1H), 7.53 (m, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.32 – 7.22 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 16.2 Hz, 1H), 6.85 (s, 1H), 2.38 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 150.65 (C), 139.77 (C), 137.73 (C), 136.89 (C), 134.41 (C), 130.59 (CH), 129.46 (C), 129.41 (CH), 126.57 (CH), 124.01 (CH), 122.95 (CH), 120.22 (CH), 119.74 (CH), 115.71 (CH), 106.45 (CH), 84.02 (C), 28.33 (CH_3), 21.30 (CH_3). HRMS calculated for $C_{22}H_{23}NO_2Na$ $[M+Na]^+$ requires m/z = 356.1626, found m/z 356.1630.

Synthesis of tetrahydrocarbazoles 3b-s, 5a-h and of carbazole 4

General procedure for the synthesis of tetrahydrocarbazoles 3b-s and of carbazole 4

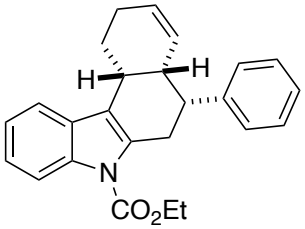
TPT (5 mol%) and 2-vinylindole **1b-q** (0. 2 mmol) were charged into a dry vial equipped with a stirring bar. The vial was capped with an aluminium crimp seal with septum and was evacuated and refilled with N_2 (3x). In the absence of light CH_3NO_2 (1.8 ml), previously degassed with three freeze-pump-thaw cycles, and HFIP (200 μl, final concentration 0.1 M) were added, followed by 1,3-cyclohexadiene (**2a**) or cyclopentadiene (**2b**) (4.0 equiv.) Then, the blue LEDs (440 nm, 40 W) were switched on and the reaction mixture was stirred for 18 h at room temperature (fan cooling). After that time, the solvent was evaporated under vacuum the residue was purified by column chromatography on silica gel to yield the corresponding carbazole **3b-s** and **4**.

Ethyl 5-(*p*-tolyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3b)



General procedure was followed using ethyl (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 3:1) yielded **3b** (55 mg, 71%) as a white gummy solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.22 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.16 (m, 6H), 5.69 (m, 1H), 5.43 (d, *J* = 10.3 Hz, 1H), 4.52 (m, 2H), 3.59 (bs, 1H), 3.29 (m, 2H), 3.22 (m, 1H), 3.02 (bs, 1H), 2.65 (d, *J* = 13.3 Hz, 1H), 2.39 (s, 3H), 1.98 (m, 1H), 1.81 (m, 1H), 1.62 (m, 1H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 151.99 (C), 140.09 (C), 136.73 (C), 136.38 (C), 135.78 (C), 129.77 (CH), 129.41 (C), 129.02 (CH), 127.70 (CH), 124.33 (CH), 123.28 (CH), 122.54 (CH), 118.91(CH), 117.07 (C), 115.62 (CH), 62.80 (CH_2), 42.64 (CH), 41.44 (CH), 33.88 (CH), 26.16 (CH_2), 25.81 (CH_2), 21.43 (CH_2), 21.00 (CH_3), 14.43 (CH_3). HRMS (ESI) calculated for $C_{26}H_{27}NO_2Na$ $[M+Na]^+$ requires *m/z* = 408.1939, found *m/z* 408.1942.

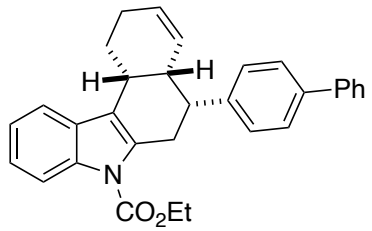
Ethyl 5-phenyl-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3c)



General procedure was followed using ethyl (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1c**) (58 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/ CH_2Cl_2 3:1) yielded **3c** (50 mg, 68%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (m, 1H), 7.65 (m, 1H), 7.45 – 7.33 (m, 4H), 7.32 – 7.19 (m, 3H), 5.67 (m, 1H), 5.40 (d, *J* = 10.2 Hz, 1H), 4.49 (m, 2H), 3.59 (bs, 1H), 3.26 (m, 3H), 3.02 (bs, 1H), 2.61 (m, 1H), 1.96 (m, 1H), 1.79 (m, 1H), 1.65 (m, 1H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.96 (C), 143.12 (C), 136.59 (C), 136.33 (C), 129.85 (CH), 129.33 (C), 128.30 (CH), 127.82 (CH), 126.27 (CH), 124.18 (CH),

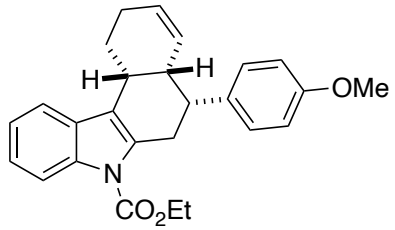
123.29 (CH), 122.53 (CH), 118.89 (CH), 117.04 (C), 115.60 (CH), 62.81 (CH_2), 43.00 (CH), 41.41 (CH), 33.84 (CH), 26.00 (CH_2), 25.76 (CH_2), 21.39 (CH_2), 14.43 (CH_3). HRMS calculated for $C_{25}H_{25}NO_2Na$ $[M+Na]^+$ requires *m/z* = 394.1783, found *m/z* 394.1782.

Ethyl 5-([1,1'-biphenyl]-4-yl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3d)



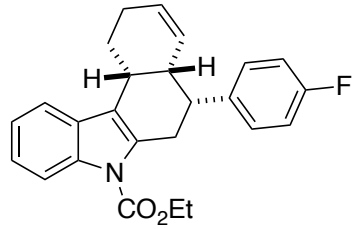
General procedure was followed using ethyl (*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1*H*-indole-1-carboxylate (**1d**) (73 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/Tol 3:1) yielded **3d** (50 mg, 56%) as a white gummy solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (m, 1H), 7.66 (m, 5H), 7.49 (m, 4H), 7.39 (m, 1H), 7.30 (m, 2H), 5.73 (m, 1H), 5.49 (d, *J* = 10.3 Hz, 1H), 4.53 (m, 2H), 3.64 (m, 1H), 3.33 (m, 3H), 3.09 (m, 1H), 2.68 (m, 1H), 2.01 (m, 1H), 1.84 (d, *J* = 17.8 Hz, 1H), 1.68 (m, 1H), 1.54 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.01 (C), 142.30 (C), 140.95 (C), 139.22 (C), 136.59 (C), 136.40 (C), 130.00 (CH), 129.39 (C), 128.78 (CH), 128.27 (CH), 127.24 (CH), 127.17 (CH), 127.04 (CH), 124.24 (CH), 123.36 (CH), 122.60 (CH), 118.95 (CH), 117.13 (C), 115.67 (CH), 62.87 (CH_2), 42.78 (CH), 41.43 (CH), 33.90 (CH), 26.15 (CH_2), 25.82 (CH_2), 21.46 (CH_2), 14.46 (CH_3). HRMS calculated for $C_{31}H_{29}NO_2Na$ $[M+Na]^+$ requires *m/z* = 470.2096, found *m/z* 470.2100.

Ethyl 5-(4-methoxyphenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3e)



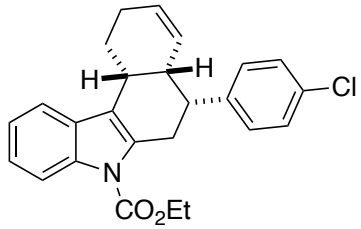
General procedure was followed using ethyl (*E*)-2-(4-methoxystyryl)-1*H*-indole-1-carboxylate (**1e**) (64 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol) for 48 h. Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 3:1) yielded **3e** (33 mg, 42%) as a white gummy solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.22 (d, *J* = 7.7 Hz, 1H), 7.67 (m, 1H), 7.37 – 7.21 (m, 4H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.70 (m, 1H), 5.43 (d, *J* = 10.1 Hz, 1H), 4.52 (m, 2H), 3.86 (s, 3H), 3.59 (bs, 1H), 3.38 – 3.16 (m, 3H), 3.00 (bs, 1H), 2.64 (d, *J* = 13.2 Hz, 1H), 1.98 (m, 1H), 1.82 (m, 1H), 1.66 (m, 1H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 158.07 (C), 152.00 (C), 136.70 (C), 136.37 (C), 135.20 (C), 129.81 (CH), 129.41 (C), 128.72 (CH), 124.34 (CH), 123.29 (CH), 122.55 (CH), 118.92 (CH), 117.08 (C), 115.63 (CH), 113.73 (CH), 62.81 (CH_2), 55.30 (CH_3), 42.21 (CH), 41.46 (CH), 33.82 (CH), 26.36 (CH_2), 25.78 (CH_2), 21.48 (CH_2), 14.44 (CH_3). HRMS calculated for $C_{26}H_{27}NO_3Na$ $[M+Na]^+$ requires *m/z* = 424.1889, found *m/z* 424.1896.

Ethyl 5-(4-fluorophenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3f)



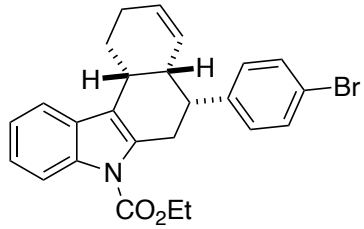
General procedure was followed using ethyl (*E*)-2-(4-fluorostyryl)-1*H*-indole-1-carboxylate (**1f**) (62 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3f** (53 mg, 70%) as a white gummy solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.21 (d, J = 7.7 Hz, 1H), 7.66 (m, 1H), 7.36 (dd, J = 8.6, 5.4 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.08 (t, J = 8.7 Hz, 2H), 5.71 (m, 1H), 5.38 (d, J = 10.3 Hz, 1H), 4.52 (m, 2H), 3.59 (bs, 1H), 3.30 (m, 2H), 3.24 (s, 1H), 3.00 (bs, 1H), 2.62 (d, J = 13.5 Hz, 1H), 1.98 (m, 1H), 1.82 (m, 1H), 1.65 (m, 1H), 1.52 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 161.46 (d, $J_{C\text{-}F}$ = 244 Hz, C), 151.99 (C), 138.78 (d, $J_{C\text{-}F}$ = 3.3 Hz, C), 136.38 (C), 136.33 (C), 130.15 (CH), 129.31 (C), 129.20 (d, $J_{C\text{-}F}$ = 7.8 Hz, CH), 123.91 (CH), 123.38 (CH), 122.60 (CH), 118.93 (CH), 117.09 (C), 115.66 (CH), 115.06 (d, $J_{C\text{-}F}$ = 20.9 Hz, CH), 62.87 (CH_2), 42.35 (CH), 41.40 (CH), 33.79 (CH), 26.31 (CH_2), 25.71 (CH_2), 21.45 (CH_2), 14.44 (CH_3). HRMS (ESI) calculated for $C_{25}H_{24}FNO_2Na$ $[M+Na]^+$ requires m/z = 412.1689, found m/z 412.1693.

Ethyl 5-(4-chlorophenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3g)



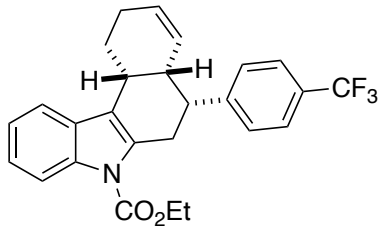
General procedure was followed using ethyl (*E*)-2-(4-chlorostyryl)-1*H*-indole-1-carboxylate (**1g**) (65 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 3:1) yielded **3g** (51 mg, 63%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (m, 1H), 7.64 (m, 1H), 7.38 – 7.26 (m, 5H), 7.23 (m, 1H), 5.69 (m, 1H), 5.34 (d, J = 10.2 Hz, 1H), 4.50 (m, 2H), 3.56 (bs, 1H), 3.34 – 3.22 (m, 2H), 3.17 (m, 1H), 2.97 (bs, 1H), 2.60 (d, J = 13.5 Hz, 1H), 1.95 (m, 1H), 1.80 (m, 1H), 1.66 (m, 1H), 1.50 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.94 (C), 141.61 (C), 136.27 (C), 136.21 (C), 131.99 (C), 130.21 (CH), 129.24 (C), 129.17 (CH), 128.38 (CH), 123.78 (CH), 123.38 (CH), 122.58 (CH), 118.91 (CH), 117.07 (C), 115.63 (CH), 62.87 (CH_2), 42.46 (CH), 41.26 (CH), 33.74 (CH), 26.05 (CH_2), 25.67 (CH_2), 21.41 (CH_2), 14.43 (CH_3). HRMS (ESI) calculated for $C_{25}H_{24}ClNO_2Na$ $[M+Na]^+$ requires m/z = 428.1393, found m/z 428.1398.

Ethyl 5-(4-bromophenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3h)



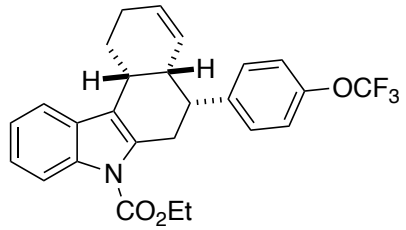
General procedure was followed using ethyl (*E*)-2-(4-bromostyryl)-1*H*-indole-1-carboxylate (**1h**) (74 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/Tol 3:1) yielded **3h** (49 mg, 54%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (m, 1H), 7.64 (m, 1H), 7.52 – 7.45 (m, 2H), 7.31 – 7.19 (m, 4H), 5.69 (m, 1H), 5.32 (m, 1H), 4.50 (m, 2H), 3.56 (bs, 1H), 3.31 – 3.12 (m, 3H), 2.97 (bs, 1H), 2.60 (d, J = 12.6 Hz, 1H), 1.95 (m, 1H), 1.80 (m, 1H), 1.65 (m, 1H), 1.50 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.94 (C), 142.15 (C), 136.27 (C), 136.18 (C), 131.34 (CH), 130.24 (CH), 129.58 (CH), 129.23 (C), 123.76 (CH), 123.39 (CH), 122.59 (CH), 120.06 (C), 118.91 (CH), 117.08 (C), 115.63 (CH), 62.88 (CH_2), 42.52 (CH), 41.22 (CH), 33.74 (CH), 25.98 (CH_2), 25.67 (CH_2), 21.41 (CH_2), 14.43 (CH_3). HRMS (ESI) calculated for $C_{25}H_{24}BrNO_2Na$ $[M+Na]^+$ requires m/z = 472.0888, found m/z 472.0894.

Ethyl 5-(4-(trifluoromethyl)phenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3i)



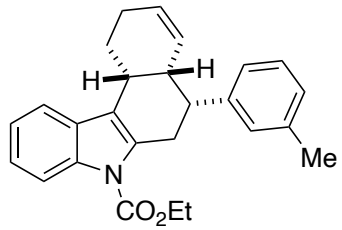
General procedure was followed using ethyl (*E*)-2-(4-(trifluoromethyl)styryl)-1*H*-indole-1-carboxylate (**1i**) (72 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3i** (43 mg, 49%) as a white gummy solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.21 (d, J = 8.0 Hz, 1H), 7.65 (m, 3H), 7.53 (d, J = 8.1 Hz, 2H), 7.34 – 7.23 (m, 2H), 5.73 (m, 1H), 5.34 (m, 1H), 4.53 (m, 2H), 3.62 (bs, 1H), 3.34 (m, 3H), 3.05 (bs, 1H), 2.63 (d, J = 13.0 Hz, 1H), 1.99 (m, 1H), 1.83 (m, 1H), 1.66 (m, 1H), 1.53 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 151.97 (C), 147.35 (C), 136.33 (C), 136.04 (C), 130.49 (CH), 129.22 (C), 128.66 (q, $J_{C\text{-}F}$ = 32.8 Hz, C) , 128.21 (CH), 125.22 (q, $J_{C\text{-}F}$ = 3.77 Hz, CH), 124.81(q, $J_{C\text{-}F}$ = 272 Hz, C) ,123.57 (CH), 123.49 (CH), 122.66 (CH), 118.96 (CH), 117.14 (C), 115.69 (CH), 62.93 (CH_2), 43.02 (CH), 41.27 (CH), 33.81 (CH), 25.93 (CH_2), 25.69 (CH_2), 21.40 (CH_2), 14.44 (CH_3). HRMS (ESI) calculated for $C_{26}H_{24}F_3NO_2Na$ $[M+Na]^+$ requires m/z = 462.1657, found m/z 462.1663

Ethyl 5-(4-(trifluoromethoxy)phenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3j)



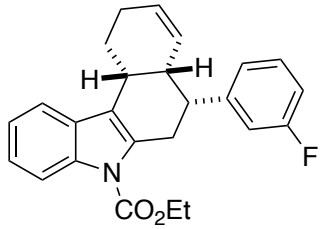
General procedure was followed using ethyl (*E*)-2-(4-(trifluoromethoxy)styryl)-1*H*-indole-1-carboxylate (**1j**) (75 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/Tol 3:1) yielded **3j** (50 mg, 56%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (m, 1H), 7.64 (m, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.30 (m, 1H), 7.25 – 7.19 (m, 3H), 5.70 (m, 1H), 5.35 (d, J = 10.2 Hz, 1H), 4.50 (m, 2H), 3.57 (bs, 1H), 3.36 – 3.18 (m, 3H), 2.99 (bs, 1H), 2.60 (d, J = 13.4 Hz, 1H), 1.95 (m, 1H), 1.81 (m, 1H), 1.65 (m, 1H), 1.50 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.94 (C), 147.62 (C), 141.85 (C), 136.27 (C), 136.15 (C), 130.30 (CH), 129.21 (C), 129.07 (CH), 123.68 (CH), 123.41 (CH), 122.60 (CH), 120.78 (CH), 120.50 (q, $J_{C\text{-}F}$ = 258 Hz, C), 118.91 (CH), 117.06 (C), 115.64 (CH), 62.88 (CH_2), 42.47 (CH), 41.27 (CH), 33.74 (CH), 26.12 (CH_2), 25.68 (CH_2), 21.39 (CH_2), 14.43 (CH_3). HRMS (ESI) calculated for $C_{26}H_{24}F_3NO_3Na$ $[M+Na]^+$ requires m/z = 478.1606, found m/z 478.1606

Ethyl 5-(*m*-tolyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3k)



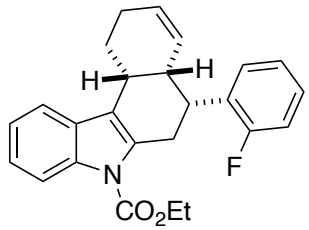
General procedure was followed using ethyl (*E*)-2-(3-methylstyryl)-1*H*-indole-1-carboxylate (**1k**) (61 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3k** (51 mg, 67%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.19 (m, 1H), 7.65 (m, 1H), 7.35 – 7.17 (m, 5H), 7.08 (d, J = 7.3 Hz, 1H), 5.67 (m, 1H), 5.40 (d, J = 10.3 Hz, 1H), 4.50 (m, 2H), 3.58 (bs, 1H), 3.27 (m, 2H), 3.18 (m, 1H), 3.02 (bs, 1H), 2.65 (d, J = 13.1 Hz, 1H), 2.40 (s, 3H), 1.97 (m, 1H), 1.79 (d, J = 16.9 Hz, 1H), 1.66 (m, 1H), 1.50 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.98 (C), 143.08 (C), 137.83 (C), 136.75 (C), 136.30 (C), 129.75 (CH), 129.37 (C), 128.66 (CH), 128.18 (CH), 127.01 (CH), 124.77 (CH), 124.26 (CH), 123.26 (CH), 122.53 (CH), 118.90 (CH), 117.01 (C), 115.60 (CH), 62.81 (CH_2), 42.93 (CH), 41.46 (CH), 33.88 (CH), 25.96 (CH_2), 25.82 (CH_2), 21.60 (CH_3), 21.36 (CH_2), 14.41 (CH_3). HRMS (ESI) calculated for $C_{26}H_{27}NO_2Na$ $[M+Na]^+$ requires m/z = 408.1939, found m/z 408.1938.

Ethyl 5-(3-fluorophenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3l)



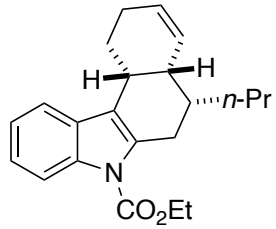
General procedure was followed using ethyl (*E*)-2-(3-fluorostyryl)-1*H*-indole-1-carboxylate (**1l**) (62 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3l** (49 mg, 63%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (m, 1H), 7.64 (m, 1H), 7.40 – 7.20 (m, 3H), 7.17 (d, J = 7.9 Hz, 1H), 7.10 (dt, J = 10.6, 2.2 Hz, 1H), 6.95 (m, 1H), 5.69 (m, 1H), 5.36 (d, J = 10.3 Hz, 1H), 4.50 (m, 2H), 3.57 (bs, 1H), 3.40 – 3.14 (m, 3H), 3.01 (bs, 1H), 2.62 (d, J = 13.5 Hz, 1H), 1.96 (m, 1H), 1.80 (m, 1H), 1.66 (m, 1H), 1.50 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.98 (d, $J^1_{C\text{-}F}$ = 245 Hz, C), 151.95 (C), 145.93 (d, $J^3_{C\text{-}F}$ = 6.9 Hz, C), 136.31 (C), 136.16 (C), 130.23 (CH), 129.67 (d, $J^3_{C\text{-}F}$ = 8.3 Hz, CH), 129.24 (C), 123.82 (CH), 123.47 (d, $J^4_{C\text{-}F}$ = 2.7 Hz, CH), 123.40 (CH), 122.59 (CH), 118.92 (CH), 117.08 (C), 115.64 (CH), 114.78 (d, $J^2_{C\text{-}F}$ = 21.4 Hz, CH), 113.14 (d, $J^2_{C\text{-}F}$ = 21 Hz, CH), 62.89 (CH_2), 42.77 (CH), 41.29 (CH), 33.76 (CH), 26.00 (CH_2), 25.71 (CH_2), 21.37 (CH_2), 14.44 (CH_3). HRMS (ESI) calculated for $C_{25}H_{24}FNO_2Na$ $[M+Na]^+$ requires m/z = 412.1689, found m/z 412.1689.

Ethyl 5-(2-fluorophenyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3m)



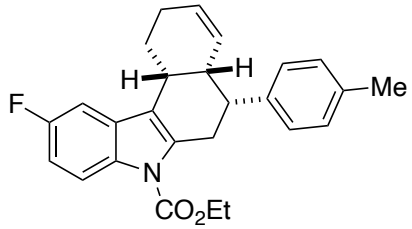
General procedure was followed using ethyl (*E*)-2-(2-fluorostyryl)-1*H*-indole-1-carboxylate (**1m**) (62 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3m** (47 mg, 61%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (m, 1H), 7.65 (m, 1H), 7.41 (td, J=7.6, 1.7 Hz, 1H), 7.32 – 7.20 (m, 3H), 7.17 (td, J=7.5, 1.4 Hz, 1H), 7.08 (m, 1H), 5.69 (m, 1H), 5.38 (d, J=10.5 Hz, 1H), 4.49 (m, 2H), 3.63 (bs, 1H), 3.54 (m, 1H), 3.33 (m, 1H), 3.18 (dd, J=17.0, 4.5 Hz, 1H), 3.02 (bs, 1H), 2.63 (d, J=13.1 Hz, 1H), 1.96 (m, 1H), 1.79 (m, 1H), 1.65 (m, 1H), 1.50 (t, J=7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.10 (d, $J_{C\text{-}F}$ = 250 Hz, C), 151.95(C), 136.33 (C), 136.24 (C), 130.18 (d, $J_{C\text{-}F}$ = 13.67 Hz, C) 129.98 (CH), 129.34 (C), 128.39 (d, $J_{C\text{-}F}$ = 4.5 Hz, CH), 127.80 (d, $J_{C\text{-}F}$ = 8.48 Hz, CH), 124.23 (CH), 123.78 (d, $J_{C\text{-}F}$ = 3.52 Hz, CH), 123.32 (CH), 122.56 (CH), 118.96 (CH), 117.01 (C), 115.59 (CH), 115.39 (d, $J_{C\text{-}F}$ = 22.68 Hz, CH), 62.83 (CH_2), 39.34 (CH), 36.51 (CH), 33.48 (CH), 25.70 (CH_2), 25.36 (CH_2), 21.30 (CH_2), 14.42 (CH_3) . HRMS (ESI) calculated for $C_{25}H_{24}FNO_2Na$ $[M+Na]^+$ requires m/z = 412.1689, found m/z 412.1682.

Ethyl 5-propyl-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3n)



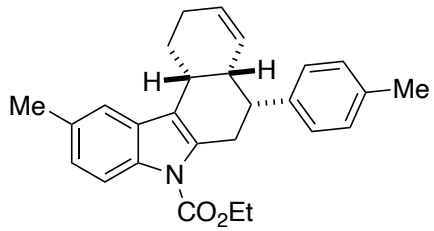
General procedure was followed using ethyl (*E*)-2-(pent-1-en-1-yl)-1*H*-indole-1-carboxylate (**1n**) (51.5 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3n** (37 mg, 55%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (m, 1H), 7.60 (m, 1H), 7.25 – 7.16 (m, 2H), 5.70 (m, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 4.46 (m, 2H), 3.31 (bs, 1H), 3.02 (dd, *J* = 17.6, 4.7 Hz, 1H), 2.68 (bs, 1H), 2.59 (m, 1H), 2.53 (m, 1H), 1.95 (m, 1H), 1.82 (m, 2H), 1.68 (m, 1H), 1.55 (m, 2H), 1.47 (m, 5H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.98 (C), 136.92 (C), 136.19 (C), 129.61 (CH), 129.54 (C), 124.98 (CH), 123.04 (CH), 122.39 (CH), 118.78 (CH), 117.30 (C), 115.53 (CH), 62.66 (CH_2), 38.55 (CH), 37.83 (CH), 35.00 (CH_2), 33.59 (CH), 28.67 (CH_2), 25.85 (CH_2), 21.83 (CH_2), 20.74 (CH_2), 14.40 (CH_3), 14.32 (CH_3). HRMS (ESI) calculated for $C_{22}H_{27}NO_2Na$ $[M+Na]^+$ requires *m/z* = 360.1939, found *m/z* 360.1944.

Ethyl 10-fluoro-5-(*p*-tolyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3o)



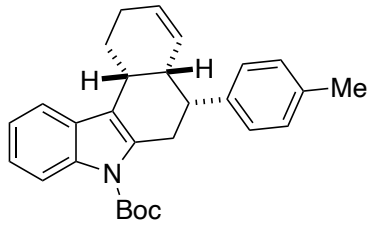
General procedure was followed using ethyl (*E*)-5-fluoro-2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1o**) (41 mg, 0.13 mmol) and 1,3-cyclohexadiene (**2a**) (41.67 mg, 0.52 mmol) for 48 h. Purification of the crude by column chromatography (SiO_2, Hex/Tol 3:1) yielded **3o** (23 mg, 40%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (dd, *J* = 9.1, 4.8 Hz, 1H), 7.29 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.97 (td, *J* = 9.1, 2.6 Hz, 1H), 5.66 (m, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 4.49 (td, *J* = 7.1, 2.6 Hz, 2H), 3.52 (s, 1H), 3.30 – 3.15 (m, 3H), 2.98 (s, 1H), 2.54 (d, *J* = 13.4 Hz, 1H), 2.36 (s, 3H), 1.94 (ddd, *J* = 13.2, 8.2, 4.0 Hz, 1H), 1.80 (d, *J* = 17.7 Hz, 1H), 1.61 (s, 1H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ =159.10 (d, $J_{C\text{-}F}$ = 238.3 Hz, C), 151.71 (C), 139.83 (C), 138.48 (C), 135.85 (C), 132.60 (C) 130.24 (d, $J_{C\text{-}F}$ = 9.4 Hz, C), 129.73 (CH), 129.03 (CH), 127.62 (CH), 124.15 (CH), 116.83 (d, $J_{C\text{-}F}$ = 3.8 Hz, C), 116.37 (d, $J_{C\text{-}F}$ = 9.1 Hz, CH), 110.55 (d, *J* = 24.5 Hz, CH), 104.73 (d, $J_{C\text{-}F}$ = 24.1 Hz, CH), 62.94 (CH_2), 42.47 (CH), 41.33 (CH), 33.70 (CH), 26.21 (CH_2), 25.53 (CH_2), 21.32 (CH_2), 20.98 (CH_3), 14.39 (CH_3). HRMS (ESI) calculated for $C_{26}H_{26}NFO_2Na$ $[M+Na]^+$ requires *m/z* = 426.1845, found *m/z* 426.1852.

Ethyl 10-fluoro-5-(*p*-tolyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3p)



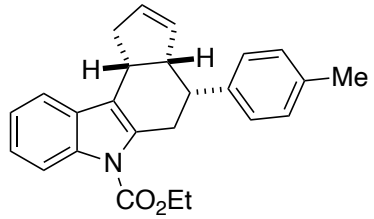
General procedure was followed using ethyl (*E*)-5-methyl-2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1p**) (64 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol) for 48 h. Purification of the crude by column chromatography (SiO_2, Hex/Tol 3:1) yielded **3p** (42 mg, 53%) as a white gummy solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.08 (d, *J* = 8.5 Hz, 1H), 7.45 (s, 1H), 7.30 (m, 2H), 7.20 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 5.70 (m, 1H), 5.43 (d, *J* = 10.3 Hz, 1H), 4.49 (m, 2H), 3.57 (bs, 1H), 3.28 (m, 2H), 3.20 (m, 1H), 3.01 (bs, 1H), 2.65 (d, *J* = 13.0 Hz, 1H), 2.49 (s, 3H), 2.39 (s, 3H), 1.97 (m, 1H), 1.82 (m, 1H), 1.66 (m, 1H), 1.51 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.00 (C), 140.16 (C), 136.79 (C), 135.75 (C), 134.55 (C), 131.90 (C), 129.75 (CH), 129.61 (C), 129.01 (CH), 127.71 (CH), 124.50 (CH), 124.40 (CH), 119.03 (CH), 116.86 (C), 115.26 (CH), 62.69 (CH_2), 42.64 (CH), 41.44 (CH), 33.88 (CH), 26.17 (CH_2), 25.80 (CH_2), 21.51 (CH_3), 21.48 (CH_2), 21.00 (CH_3), 14.44 (CH_3). HRMS (ESI) calculated for $C_{27}H_{29}NO_2Na$ $[M+Na]^+$ requires *m/z* = 422.2096, found *m/z* 422.2100.

***Tert*-butyl 5-(*p*-tolyl)-1,2,4a,5,6,11c-hexahydro-7*H*-benzo[c]carbazole-7-carboxylate (3q)**



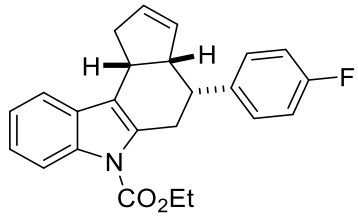
General procedure was followed using *tert*-butyl (*E*)-2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1q**) (67 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 5:1) yielded **3q** (45 mg, 59%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (m, 1H), 7.64 (m, 1H), 7.32 – 7.26 (m, 2H), 7.25 – 7.16 (m, 4H), 5.67 (m, 1H), 5.39 (d, *J* = 10.3 Hz, 1H), 3.57 (bs, 1H), 3.21 (m, 3H), 2.98 (bs, 1H), 2.64 (d, *J* = 13.1 Hz, 1H), 2.37 (s, 3H), 1.95 (m, 1H), 1.79 (m, 1H), 1.69 (s, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): 150.51 (C), 140.20 (C), 136.66 (C), 136.40 (C), 135.72 (C), 129.76 (CH), 129.21 (C), 129.00 (CH), 127.66 (CH), 124.28 (CH), 123.06 (CH), 122.23 (CH), 118.79 (CH), 116.44 (C), 115.50 (CH), 83.36 (C), 42.71 (CH), 41.50 (CH), 33.87 (CH), 28.33 (CH_3), 26.37 (CH_2), 25.84 (CH_2), 21.39 (CH_2), 20.99 (CH_3). HRMS (ESI) calculated for $C_{28}H_{31}NO_2Na$ $[M+Na]^+$ requires *m/z* = 436.2252, found *m/z* 436.2256.

Ethyl 4-(*p*-tolyl)-3a,4,5,10c-tetrahydrocyclopenta[c]carbazole-6(1*H*)-carboxylate (3r)



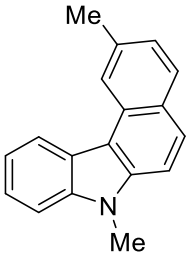
General procedure was followed using ethyl (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and cyclopentadiene (**2b**) (53 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3r** (58 mg, 78%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.16 (m, 1H), 7.47 (m, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.20 (d, J = 7.8 Hz, 2H), 5.70 (m, 1H), 5.65 (m, 1H), 4.47 (m, 2H), 3.80 (t, J = 7.0 Hz, 1H), 3.45 (bs, 1H), 3.37 (m, 1H), 3.22 (m, 2H), 2.89 (m, 1H), 2.57 (m, 1H), 2.38 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 152.00 (C), 141.15 (C), 136.41 (C), 135.77 (C), 135.44 (C), 131.93 (CH), 129.38 (CH), 129.19 (C), 129.14 (CH), 127.53 (CH), 123.48 (CH), 122.59 (CH), 119.59 (C), 118.00 (CH), 115.68 (CH), 62.74 (CH_2), 51.70 (CH), 41.86 (CH), 39.36 (CH_2), 35.53 (CH), 26.39 (CH_2), 21.00 (CH_3), 14.42 (CH_3). HRMS (ESI) calculated for $C_{25}H_{25}NO_2Na$ $[M+Na]^+$ requires *m/z* = 394.1783, found *m/z* 394.1783.

Ethyl 4-(4-fluorophenyl)-3a,4,5,10c-tetrahydrocyclopenta[c]carbazole-6(1*H*)-carboxylate (3s)



General procedure was followed using (*E*)-2-(4-fluorostyryl)-1*H*-indole-1-carboxylate (**1f**) (62 mg, 0.20 mmol) and cyclopentadiene (**2b**) (53 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **3s** (62 mg, 83%) as a white gummy solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (m, 1H), 7.47 (m, 1H), 7.37 (dd, J = 8.5, 5.4 Hz, 2H), 7.27 (m, 2H), 7.07 (t, J = 8.7 Hz, 2H), 5.71 (m, 1H), 5.61 (m, 1H), 4.47 (q, J = 7.1 Hz, 2H), 3.80 (t, J = 7.3 Hz, 1H), 3.40 (m, 2H), 3.19 (m, 2H), 2.90 (m, 1H), 2.56 (d, J = 16.1 Hz, 1H), 1.47 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.42 (d, $J^1_{C\text{-}F}$ = 244.3 Hz, C), 152.00 (C), 139.82 (d, $J^4_{C\text{-}F}$ = 3.1 Hz, C), 136.34 (C), 135.13 (C), 132.33 (CH), 129.10 (C), 129.04 (CH), 128.91 (d, $J^3_{C\text{-}F}$ = 3.9 Hz, CH), 123.57 (CH), 122.64 (CH), 119.57 (C), 118.03 (CH), 115.71 (CH), 115.19 (d, $J^2_{C\text{-}F}$ = 20.9 Hz, CH), 62.81 (CH_2), 51.68 (CH), 41.58 (CH), 39.38 (CH_2), 35.46 (CH), 26.44 (CH_2), 14.43 (CH_3). HRMS (ESI) calculated for $C_{24}H_{22}FNO_2Na$ $[M+Na]^+$ requires *m/z* = 398.1532, found *m/z* 398.1537.

2,7-dimethyl-7*H*-benzo[*c*]carbazole (4)



General procedure was followed using (*E*)-1-methyl-2-(4-methylstyryl)-1*H*-indole (**1r**) (49 mg, 0.20 mmol) and 1,3-cyclohexadiene (**2a**) (64 mg, 0.8 mmol). Purification of the crude by column chromatography (SiO_2, Hex/CH_2Cl_2 4:1) yielded **4** (22mg, 45%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.66 (d, *J* = 8.0 Hz, 1H), 8.63 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.45 (ddd, *J* = 8.1, 5.4, 2.8 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.97 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 139.91 (C), 138.74 (C), 136.72 (C), 130.20 (C), 129.06 (CH), 127.06 (C), 127.03 (CH), 124.86 (CH), 123.94 (CH), 123.56 (C), 122.63 (CH), 122.05 (CH), 119.64 (CH), 114.38 (C), 109.59 (CH), 109.03 (CH), 29.23 (CH_3), 22.40 (CH_3). HRMS (ESI) calculated for $C_{18}H_{15}NNa$ $[M+Na]^+$ requires *m/z* = 268.1102, found *m/z* 268.1109.

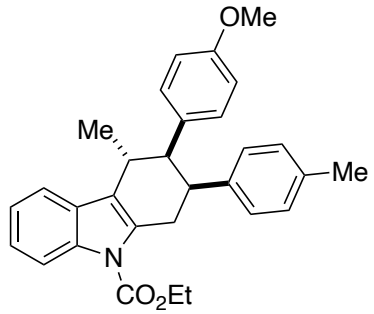
General procedure for the synthesis of tetrahydrocarbazoles 6a-i

TPT (5 mol%) and 2-vinylindole **1b, d, f, k** (0. 2 mmol) were charged into a dry vial equipped with a stirring bar. The vial was capped with an aluminium crimp seal with septum and was evacuated and refilled with N_2 (3x). In the absence of light CH_3NO_2 (1.8 ml), previously degassed with three freeze-pump-thaw cycles, and HFIP (200 µl, final concentration 0.1 M) were added, followed by styrenes **5a-e** (2.0 equiv.) Then, the blue LEDs (440 nm, 40 W) were switched on and the reaction mixture was stirred for 18-24 h at room temperature (fan cooling). After that time, the solvent was evaporated under vacuum the residue was purificated by column chromatography on silica gel to yield the corresponding carbazole **6a-i**.

Ethyl 3-(4-methoxyphenyl)-4-methyl-2-(*p*-tolyl)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6'a/6a)

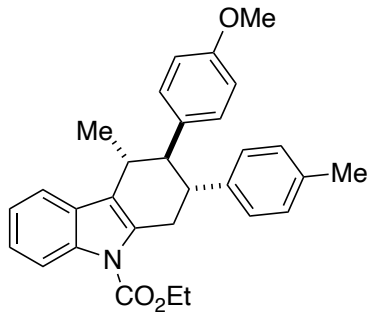
General procedure was followed using (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and *trans*-anethole (**5a**) (59 mg, 0.4 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazole **6'a/6a** (51 mg, 60%, *d.r.* = 2:1). A second chromatographic purification (SiO_2 Hex/Et_3N 98:2) allowed for separation and characterization of both isomers **6'a** and **6a**.

6'a (minor isomer):



^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.29 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.47 (m, 2H), 3.74 (s, 3H), 3.45 (m, 1H), 3.21 (m, 3H), 2.84 (m, 1H), 2.24 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.33 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 157.58 (C), 151.97 (C), 141.25 (C), 136.45 (C), 135.65 (C), 135.14 (C), 134.83 (C), 129.55 (CH), 129.18 (C), 128.74 (CH), 127.86 (CH), 123.47 (CH), 122.58 (CH), 121.33 (C), 119.38 (CH), 115.61 (CH), 113.33 (CH), 62.81(CH_2), 55.06 (CH), 54.95 (CH), 47.16 (CH), 45.81 (CH_3), 36.75 (CH_2), 35.20 (CH_3), 20.98 (CH_3), 19.35 (CH_3). HRMS (ESI) calculated for $C_{30}H_{31}NO_3Na$ $[M+Na]^+$ requires *m/z* = 476.2202, found *m/z* 476.2209.

6a (major isomer):

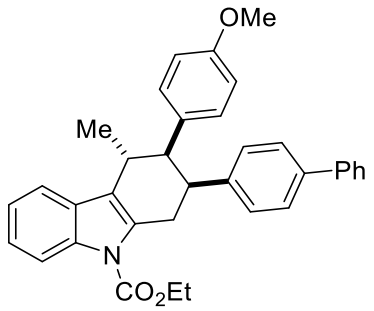


^{1}H NMR (400 MHz, $CDCl_3$): 8.27 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.58 (m, 1H), 7.33 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 6.59 (q, *J* = 8.8 Hz, 4H), 4.49 (m, 2H), 3.74 (s, 3H), 3.58 (m, 1H), 3.39 (m, 2H), 3.04 (m, 2H), 2.35 (s, 3H), 1.61 (d, *J* = 7.0 Hz, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 157.95 (C), 152.09 (C), 139.91 (C), 136.54 (C), 135.68 (C), 135.21 (C), 133.61 (C), 129.87 (CH), 129.10 (C), 128.58 (CH), 128.40 (CH), 123.71 (CH), 122.75 (CH), 121.11 (C), 118.53 (CH), 115.74 (CH), 112.92 (CH), 62.86 (CH_2), 55.10 (CH), 52.07 (CH), 41.13 (CH), 32.71 (CH_3), 29.71 (CH_2), 21.48 (CH_3), 21.05 (CH_3), 14.41 (CH_3). HRMS (ESI) calculated for $C_{30}H_{31}NO_3Na$ $[M+Na]^+$ requires *m/z* = 476.2202, found *m/z* 476.2207.

Ethyl 2-([1,1'-biphenyl]-4-yl)-3-(4-methoxyphenyl)-4-methyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6'b/6b)

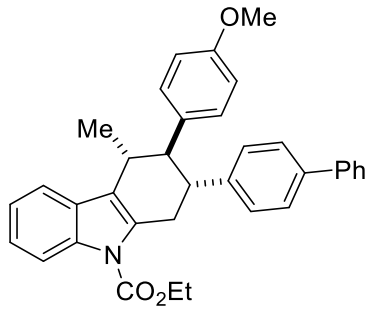
General procedure was followed using (*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1*H*-indole-1-carboxylate (**1d**) (74 mg, 0.20 mmol) and *trans*-anethole (**5a**) (54 mg, 0.4 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazole **6'b/6b** (40 mg, 40%, *d.r.* = 3:1). A second chromatographic purification (SiO_2 Hex/Et_3N 95:5) allowed for separation and characterization of both isomers **6'b** and **6b**.

6'b (minor isomer):



^{1}H NMR (400 MHz, $CDCl_3$): 8.28 (d, *J* = 7.4 Hz, 1H), 7.70 – 7.57 (m, 3H), 7.54 – 7.42 (m, 4H), 7.41 – 7.28 (m, 3H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.61 (s, 4H), 4.66 – 4.40 (m, 2H), 3.74 (s, 3H), 3.67 (m, 1H), 3.51 – 3.38 (m, 2H), 3.18 – 3.03 (m, 2H), 1.64 (d, *J* = 7.0 Hz, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 158.04 (C), 152.10 (C), 142.17 (C), 140.91 (C), 139.00 (C), 136.54 (C), 135.06 (C), 133.44 (C), 129.89 (CH), 129.08 (C), 128.99 (CH), 128.76 (CH), 127.11 (CH), 126.95 (CH), 126.50 (CH), 123.78 (CH), 122.79 (CH), 121.15 (C), 118.58 (CH), 115.78 (CH), 113.00 (CH), 62.91 (CH_2), 55.10 (CH_3), 52.09 (CH), 41.24 (CH), 32.75 (CH), 26.85 (CH_2), 21.51 (CH_3), 14.44 (CH_3). HRMS (ESI) calculated for $C_{35}H_{33}NO_3Na$ $[M+Na]^+$ requires *m/z* = 538.2353, found *m/z* 538.2358.

6b (major isomer):

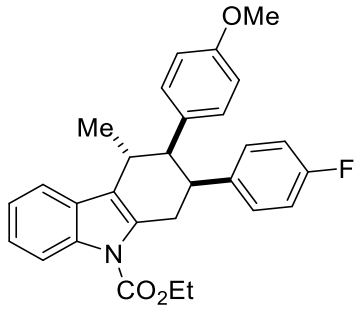


^{1}H NMR (300 MHz, $CDCl_3$): 8.22 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.46 – 7.34 (m, 4H), 7.36 – 7.22 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 4.46 (qd, *J* = 7.1, 1.5 Hz, 2H), 3.71 (s, 3H), 3.48 (t, *J* = 11.1 Hz, 1H), 3.34 – 3.19 (m, 3H), 2.87 (t, *J* = 9.7 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.34 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.64 (C), 151.98 (C), 143.50 (C), 140.89 (C), 138.46 (C), 136.39 (C), 135.37 (C), 134.69 (C), 129.53 (CH), 129.15 (C), 128.64 (CH), 128.42 (CH), 126.95 (CH), 126.84 (CH), 126.66 (CH), 123.52 (CH), 122.62 (CH), 121.36 (C), 119.42 (CH), 115.63 (CH), 113.38 (CH), 62.88 (CH_2), 55.04 (CH_3), 54.89 (CH), 47.29 (CH), 36.68 (CH), 35.05 (CH_2), 19.34 (CH_3), 14.47 (CH_3). HRMS (ESI) calculated for $C_{35}H_{33}NO_3Na$ $[M+Na]^+$ requires *m/z* = 538.2353, found *m/z* 538.2349.

Ethyl -2-(4-fluorophenyl)-3-(4-methoxyphenyl)-4-methyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6'c/6c)

General procedure was followed using (*E*)-2-(4-fluorostyryl)-1*H*-indole-1-carboxylate (**1f**) (62 mg, 0.20 mmol) and *trans*-anethole (**5a**) (54 mg, 0.4 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazole **6'c/6c** (50 mg, 55%, *d.r.* = 3:1). A second chromatographic purification (SiO_2 Hex/Et_3N 95:5) allowed for separation and characterization of both isomers **6'c** and **6c**.

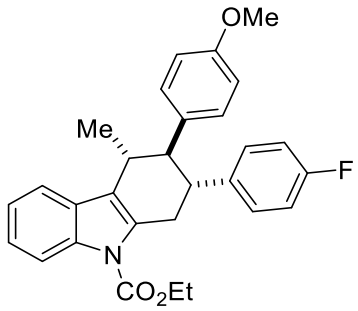
6'c (minor isomer):



^{1}H NMR (400 MHz, $CDCl_3$): 8.25 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 6.6 Hz, 1H), 7.36 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1H), 7.31 (td, *J* = 7.4, 1.3 Hz, 1H), 7.01 – 6.82 (m, 4H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 4.56 – 4.45 (m, 2H), 3.75 (s, 3H), 3.60 (dt, *J* = 10.9, 4.3 Hz, 1H), 3.51 – 3.32 (m, 2H), 3.14 – 2.97 (m, 2H), 1.60 (d, *J* = 7.0 Hz, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 161.48 (d, $J^1_{C\text{-}F}$ = 244.0 Hz, C), 158.08 (C), 152.09 (C),138.65 (d, $J^4_{C\text{-}F}$ = 2.6 Hz, C), 136.47 (C), 134.86 (C), 133.23 (C), 129.89 (d, $J^3_{C\text{-}F}$ = 7.7 Hz, CH), 129.82 (CH), 129.02 (C), 123.82 (CH), 122.81 (CH), 121.10 (C), 118.59 (CH), 115.78 (CH), 114.63 (d, $J^2_{C\text{-}F}$ = 21.0 Hz, CH), 113.05 (CH), 62.94 (CH_2), 55.11 (CH_3), 52.18 (CH), 40.90 (CH), 32.65 (CH), 27.45

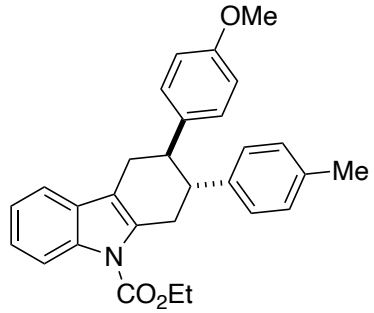
(CH_2), 21.47 (CH_3), 14.42 (CH_3). HRMS (ESI) calculated for $C_{29}H_{28}FNO_3Na$ $[M+Na]^+$ requires *m/z* = 480.1945, found *m/z* 480.1950

6c (major isomer):



^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (m, 1H), 7.56 (m, 1H), 7.38 – 7.18 (m, 2H), 7.11 – 6.94 (m, 4H), 6.85 – 6.77 (m, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.47 (m, 1H), 3.29 – 3.06 (m, 3H), 2.77 (t, *J* = 10.1 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.32 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.00 (d, *J* = 243.4 Hz, C), 157.68 (C), 151.97 (C), 139.99 (d, *J* = 3.2 Hz, C), 136.32 (C), 135.14 (C), 134.52 (C), 129.46 (CH), 129.27 (d, *J* = 7.8 Hz, CH), 129.09 (C), 123.56 (CH), 122.63 (CH), 121.34 (C), 119.43 (CH), 115.62 (CH), 114.82 (d, *J* = 21.1 Hz, CH), 113.41 (CH), 62.90 (CH_2), 55.14 (CH), 55.06 (CH_3), 46.94 (CH), 36.59 (CH), 35.11 (CH_2), 19.31 (CH_3), 14.43 (CH_3). HRMS (ESI) calculated for $C_{29}H_{28}FNO_3Na$ $[M+Na]^+$ requires *m/z* = 480.1945, found *m/z* 480.1948

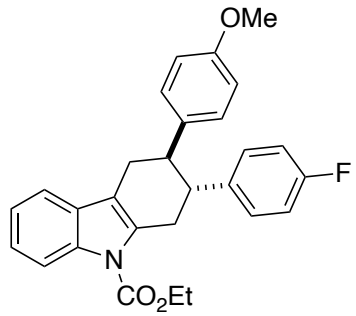
Ethyl 3-(4-methoxyphenyl)-2-(*p*-tolyl)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6d)



General procedure was followed using (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and 4-methoxystyrene (**5b)** (54 mg, 0.4 mmol). Purification of the crude, by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazoles (48 mg, 55%, *d.r.* = 7:1). A second chromatographic purification (SiO_2 Hex/TEA 98:2) allowed for separation and characterization of major isomer **6d**.

^{1}H NMR (400 MHz, $CDCl_3$): 8.27 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.28 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.82 – 6.66 (m, 6H), 4.55 – 4.45 (m, 2H), 3.80 (s, 3H), 3.50 (m, 3H), 3.29 (m, 1H), 3.14 (m, 1H), 2.95 (m, 1H), 2.32 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 158.04 (C), 152.09 (C), 139.13 (C), 136.30 (C), 135.78 (C), 135.13 (C), 134.47 (C), 129.56 (C), 129.48 (CH), 128.50 (CH), 128.46 (CH), 123.85 (CH), 122.84 (CH), 117.86 (CH), 117.05 (C), 115.62 (CH), 113.11 (CH), 62.86 (CH_2), 55.17 (CH), 45.14 (CH_3), 43.39 (CH), 29.73 (CH_2), 25.00 (CH_2), 21.04 (CH_3), 14.42 (CH_3). HRMS (ESI) calculated for $C_{29}H_{29}FNO_3Na$ $[M+Na]^+$ requires *m/z* = 462.2045, found *m/z* 462.2053.

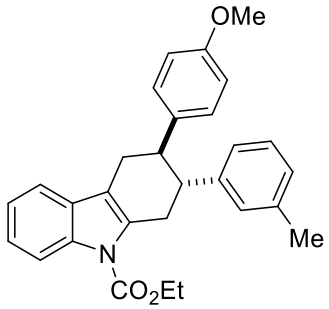
Ethyl 3-(4-methoxyphenyl)-2-(*p*-fluoro)-1,2,3,4-tetrahydro-9H-carbazole-9-carboxylate (6e)



General procedure was followed using (*E*)-2-(4-fluorostyryl)-1*H*-indole-1-carboxylate (**1f**) (62 mg, 0.20 mmol) and 4-methoxystyrene (**5b**) (54 mg, 0.4 mmol). Purification of the crude, by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazole (44 mg, 50%, *d.r.* = 4.4:1). A second chromatographic purification (SiO_2 Hex/TEA 98:2) allowed for separation and characterization of major isomer **6e**.

^{1}H NMR (400 MHz, $CDCl_3$): 8.21 (dd, J = 7.3, 1.2 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.40 – 7.29 (m, 2H), 6.82 (t, J = 8.7 Hz, 2H), 6.77 – 6.65 (m, 6H), 4.57 – 4.47 (m, 2H), 3.79 (s, 3H), 3.59 – 3.50 (m, 2H), 3.41 (m, 1H), 3.24 (m, 1H), 3.09 (m, 1H), 2.86 (m, 1H), 1.47 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 161.55 (d, $J_{C\text{-}F}$ = 244 Hz, C), 158.16 (C), 152.07 (C), 137.81 (C), 136.24 (C), 134.76 (C), 134.13 (C), 129.99 (d, $J_{C\text{-}F}$ = 7.7 Hz, CH) , 129.45 (C), 129.39 (CH), 123.97 (CH), 122.91 (CH), 117.90 (CH), 117.00 (C), 115.66 (CH), 114.48 (d, $J_{C\text{-}F}$ = 20.9 Hz, CH) , 113.22 (C), 62.94 (CH_2), 55.18 (CH_3), 44.86 (CH), 43.33 (CH), 34.42 (CH_3) 29.89 (CH_2), 24.64 (CH_2), 14.42 (CH_3). HRMS (ESI) calculated for $C_{28}H_{26}FNO_3Na$ $[M+Na]^+$ requires *m/z* = 466.1794, found *m/z* 466.1802.

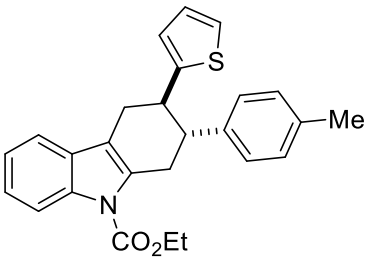
Ethyl 3-(4-methoxyphenyl)-2-(*m*-tolyl)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6f)



General procedure was followed using *E*)-2-(3-methylstyryl)-1*H*-indole-1-carboxylate (**1k**) (61 mg, 0.20 mmol) and 4-methoxystyrene (**5b**) (54 mg, 0.4 mmol). Purification of the crude, by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazole (46 mg, 52%, *d.r.* = 5:1). A second chromatographic purification (SiO_2 Hex/TEA 98:2) allowed for separation and characterization of major isomer **6f**.

^{1}H NMR (400 MHz, $CDCl_3$): 8.27 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 6.8 Hz, 1H), 7.44 – 7.24 (m, 2H), 7.16 – 6.99 (m, 2H), 6.77 – 6.58 (m, 6H), 4.67 – 4.42 (m, 2H), 3.79 (s, 3H), 3.61 – 3.42 (m, 3H), 3.28 (M, 1H), 3.16 (m, 1H), 2.98 (dd, J = 16.4, 6.1 Hz, 1H), 2.24 (s, 3H), 1.50 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 158.08 (C), 152.11 (C), 142.25 (C), 137.14 (C), 136.28 (C), 135.18 (C), 134.29 (C), 129.64 (CH), 129.55 (CH), 127.69 (CH), 127.05 (CH), 125.44 (CH), 123.86 (CH), 122.84 (CH), 117.89 (CH), 116.92 (C), 115.63 (CH), 113.03 (CH), 62.87 (CH_2), 55.20 (CH_3), 45.46 (CH), 43.45 (C), 29.18 (CH_2), 25.35 (CH_2), 21.46 (CH_3), 14.42 (CH_3). HRMS (ESI) calculated for $C_{29}H_{29}NO_3Na$ $[M+Na]^+$ requires *m/z* = 462.2045, found *m/z* 439.2052.

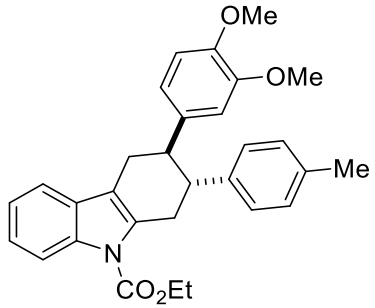
Ethyl 3-(thiophen-2-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6g)



General procedure was followed using (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and 2-vinylthiophene (**5c)** (44 mg, 0.4 mmol). Purification of the crude, by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazoles (40 mg, 48%, *d.r.* = 5:1). Any of the attempted further purification allowed for the separation of major isomer. Therefore, following data refers to the diasteromeric mixture.

^{1}H NMR (400 MHz, $CDCl_3$): 8.26 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.09 – 7.00 (m, 3H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.84 (t, *J* = 4.3 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 4.58 – 4.44 (m, 2H), 3.83 (m, 1H), 3.64 – 3.49 (m, 2H), 3.39 (m, 1H), 3.26 (dd, *J* = 16.3, 5.5 Hz, 1H), 3.03 (dd, *J* = 16.3, 5.4 Hz, 1H), 2.34 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 152.07 (C) 144.92 (C), 139.09 (C), 136.35 (C), 136.10 (C), 135.05 (C), 129.55 (C), 128.65 (CH), 128.18 (CH), 126.02 (CH), 125.13 (CH), 123.96 (CH), 123.23 (CH), 122.88 (CH), 117.87 (CH), 115.97, (C), 115.65 (CH), 62.91 (CH_2), 45.08 (CH), 29.27 (CH_2), 27.14 (CH_2), 40.38 (CH), 21.06 (CH_3), 14.43 (CH_3). Reported picks are referred to the main isomer.

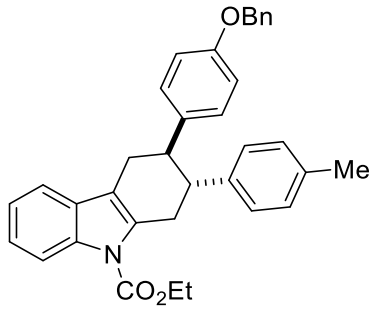
Ethyl 3-(3,4-dimethoxyphenyl)-2-(*p*-tolyl)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6h)



General procedure was followed using (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and 3,4-dimethoxystyrene (**5d)** (131 mg, 0.4 mmol). Purification of the crude, by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazoles (32 mg, 34%, *d.r.* = 7:1). Any of the attempted further purification allowed for the separation of major isomer. Therefore, following data refers to the diasteromeric mixture.

^{1}H NMR (400 MHz, $CDCl_3$): 8.26 (d, *J* = 7.9 Hz, 1H), 7.50 d, *J* = 7.0 Hz, 1H), 7.43 – 7.24 (m, 2H), 7.11 – 6.93 (m, 2H), 6.78 (d, *J* = 7.7 Hz, 2H), 6.75 – 6.63 (m, 1H), 6.52 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.15 (s, 1H), 4.51 (dtt, *J* = 10.3, 7.3, 3.4 Hz, 2H), 3.86 (s, 3H), 3.60 – 3.50 (m, 5H), 3.46 (m, 1H), 3.31 (ddt, *J* = 13.8, 10.1, 3.9 Hz, 1H), 3.12 (m, 1H), 2.96 (m, 1H), 2.31 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). Reported integrals are referred to the main isomer. ^{13}C NMR (101 MHz, $CDCl_3$): 152.08 (C), 147.77 (C), 147.40 (C), 139.29 (C), 136.29 (C), 135.84 (C), 135.06 (C), 134.93 (C), 129.50 (C), 128.61 (CH), 128.50 (CH), 123.88 (CH), 122.87 (CH), 119.98 (CH), 117.85 (CH), 116.92 (C), 115.62 (CH), 112.45 (CH), 110.59 (CH), 62.89 (CH_2), 55.79 (CH_3), 55.37 (CH_3), 45.06 (CH), 43.87 (CH), 34.83 (CH_2), 30.61 (CH_2), 20.96 (CH_3), 14.42 (CH_3). Reported picks are referred to the main isomer.

Ethyl 3-(4-(benzyloxy)phenyl)-2-(*p*-tolyl)-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate (6i)



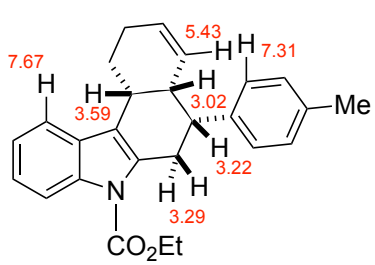
General procedure was followed using (*E*)-2-styryl-1*H*-indole-1-carboxylate (**1b**) (61 mg, 0.20 mmol) and 4-benzyloxystyrene (**5e**) (168 mg, 0.4 mmol). Purification of the crude, by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded a mixture of the corresponding diasteromeric tetrahydrocarbazoles (31 mg, 30%, *d.r.* = 7:1). A second chromatographic purification (SiO_2 Hex/TEA 98:2) allowed for separation and characterization of major isomer **6i.**

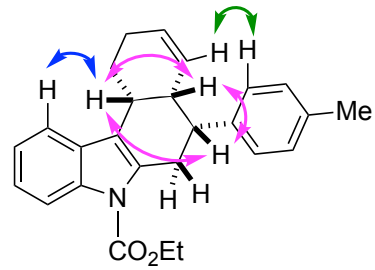
^{1}H NMR (400 MHz, $CDCl_3$): 8.26 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.24 (m, 8H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.87 – 6.65 (m, 6H), 5.04 (s, 2H), 4.51 (qd, *J* = 7.1, 4.0 Hz, 2H), 3.67 – 3.38 (m, 3H), 3.30 (m, 1H), 3.13 (m, 1H), 2.95 (dd, *J* = 16.5, 6.8 Hz, 2H), 2.32 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 157.29 (C), 152.09 (C), 139.10 (C), 137.20 (C), 136.29 (C), 135.79 (C), 135.13 (C), 134.78 (C), 129.55 (C), 129.51 (CH), 128.54 (CH), 128.50 (CH), 128.46 (CH), 127.90 (CH), 127.54 (CH), 123.86 (CH), 122.85 (CH), 117.87 (CH), 117.01 (C), 115.62 (CH), 114.12 (CH), 69.99 (CH_2), 62.87 (CH_2), 45.14 (CH), 43.42 (CH), 29.73 (CH_2), 24.94 (CH_2), 21.04 (CH_3), 14.43 (CH_3). HRMS (ESI) calculated for $C_{35}H_{33}NO_3Na$ $[M+Na]^+$ requires *m/z* = 538.2353, found *m/z* 538.2349.

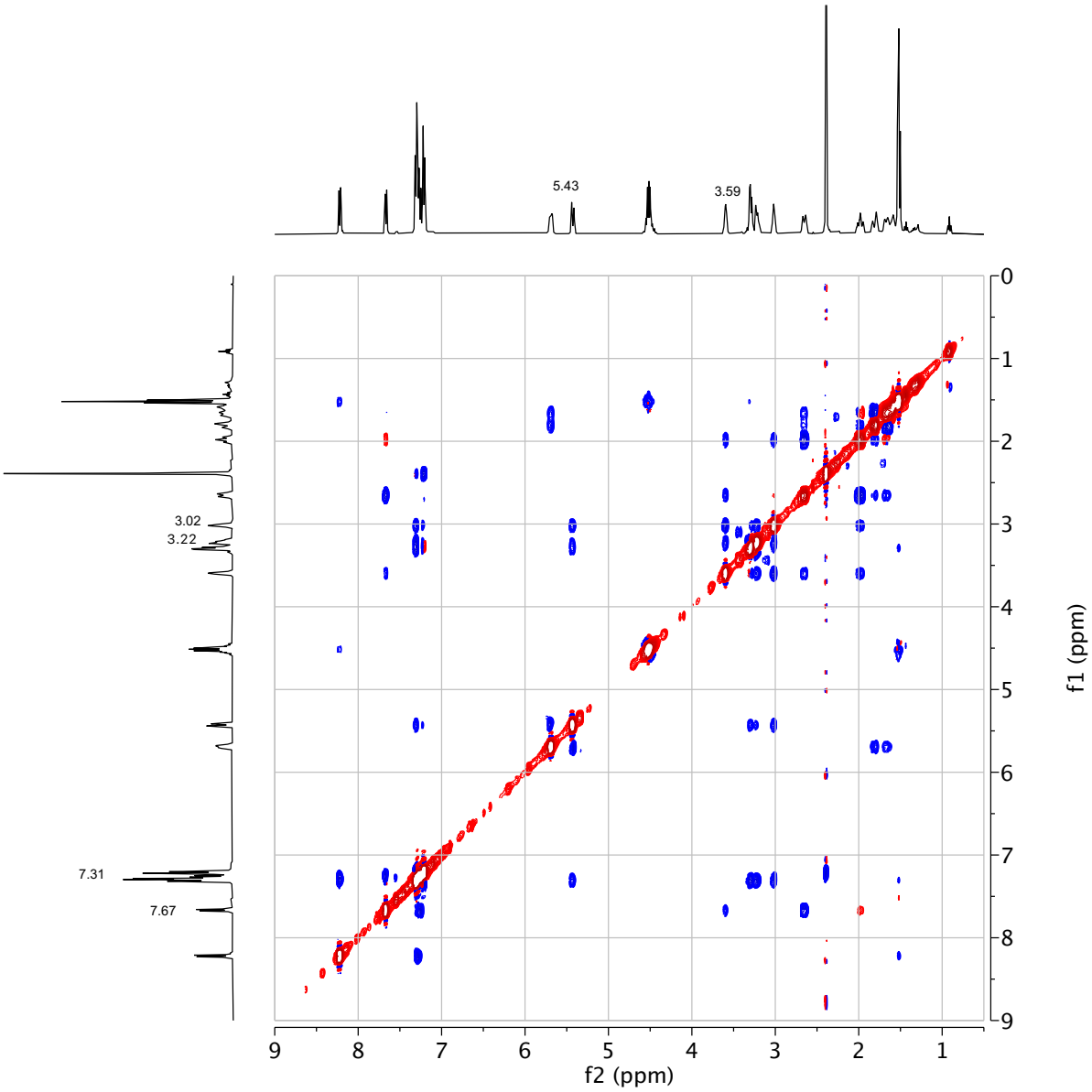
Spectroscopic characterization of products 3b, 4 and 5'a/5a

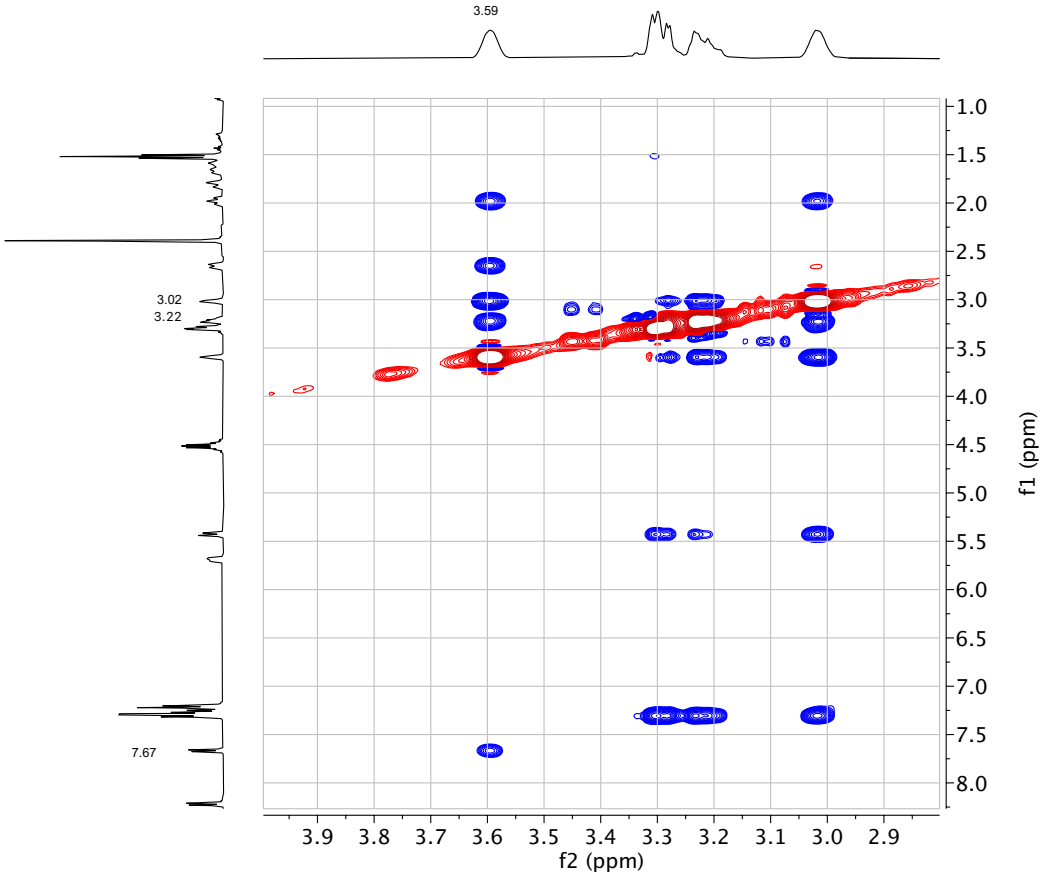
NOESY NMR of products 3b, and 5'a/5a

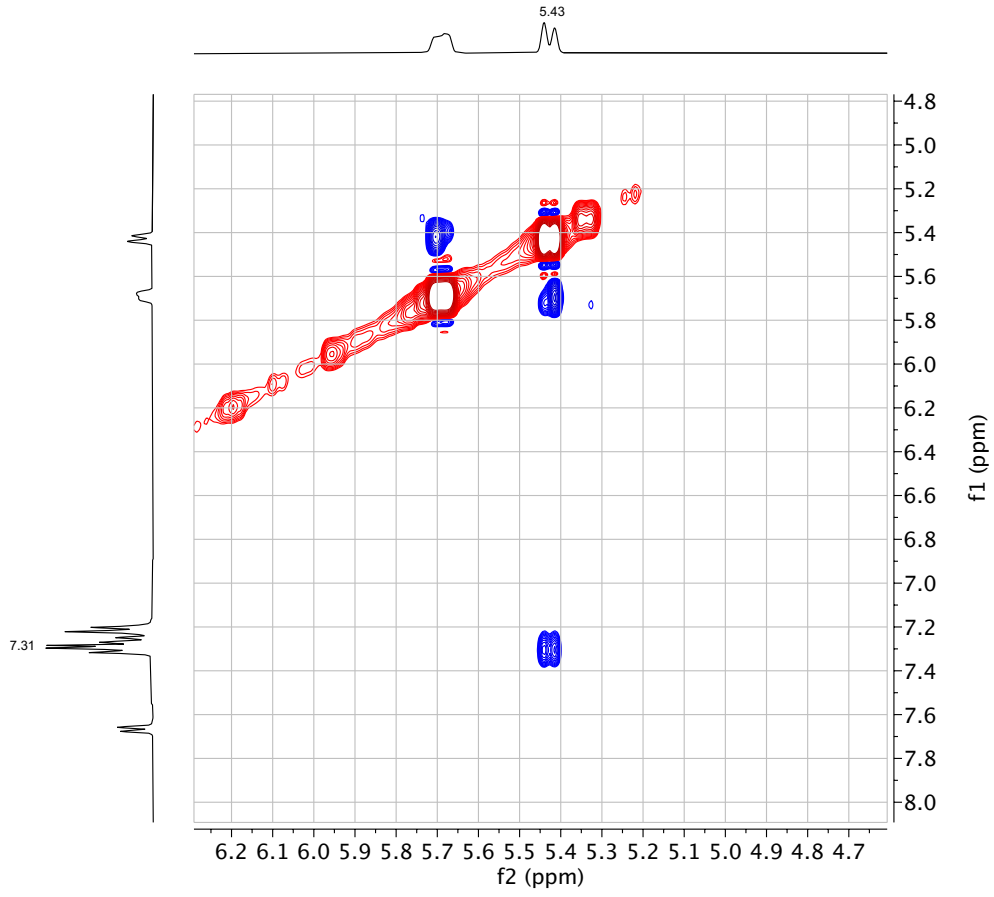
3b, *diagnostic interactions* ($CDCl_3$, 400 MHz)



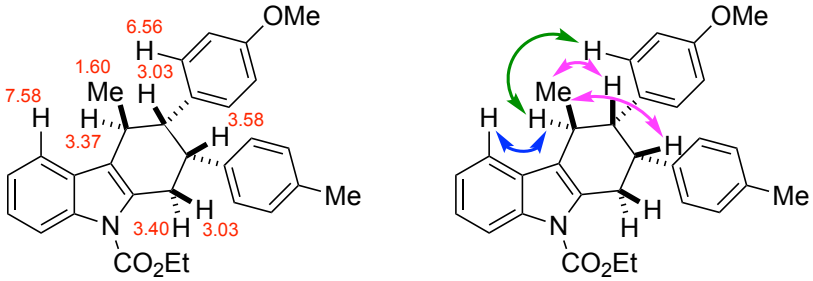


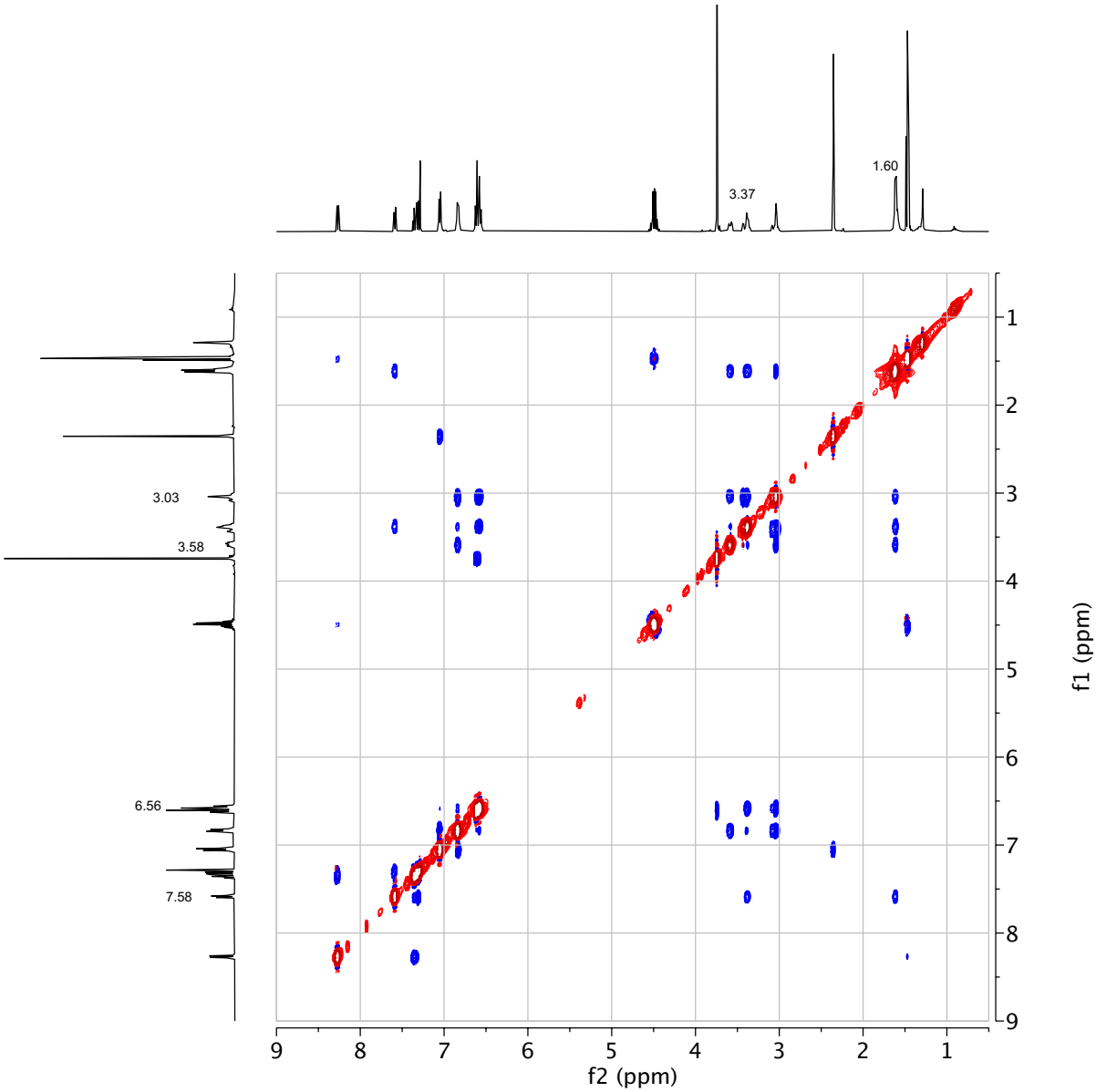


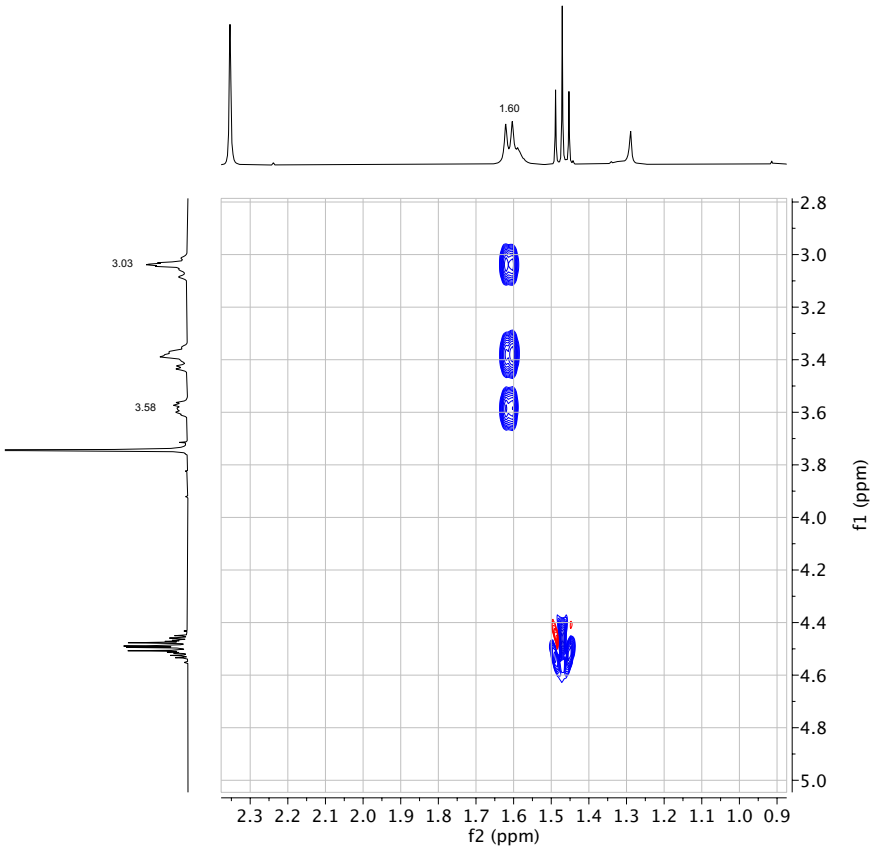

3.59
3.02
3.22
7.67
f2 (ppm)
f1 (ppm)

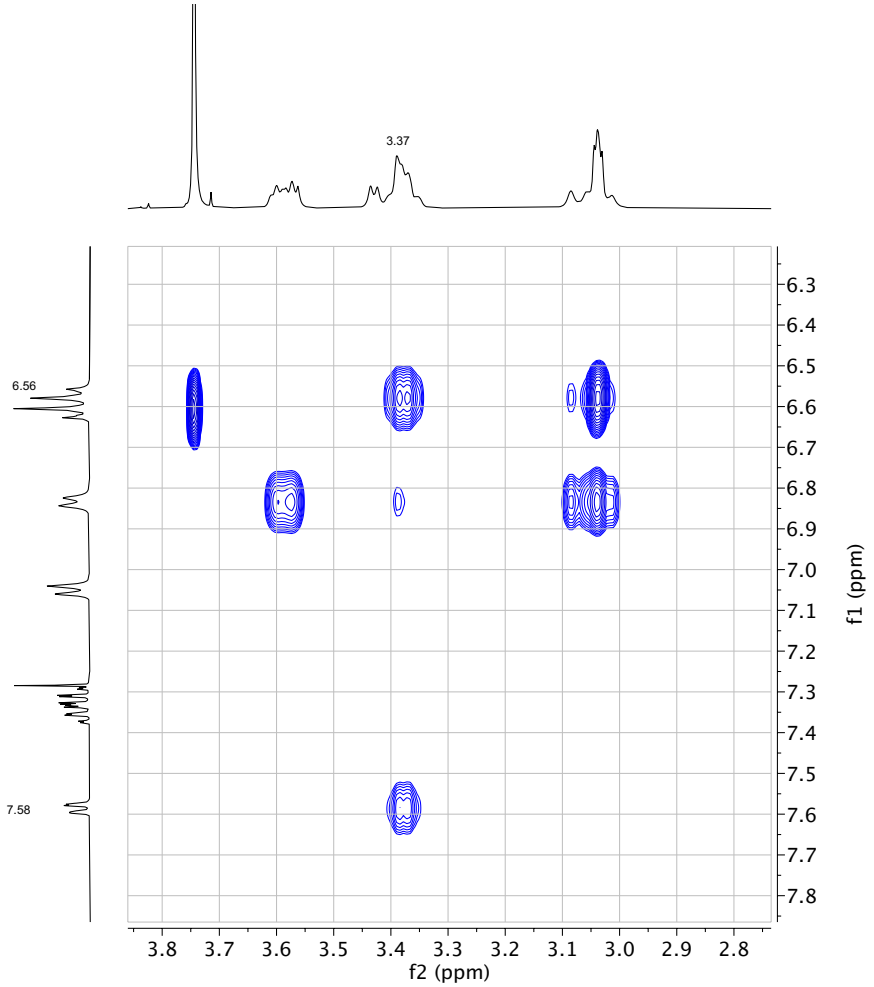

5.43
7.31
f2 (ppm)
f1 (ppm)

5'a (minor isomer), *diagnostic interactions* ((CDCl$_3$, 400 MHz)

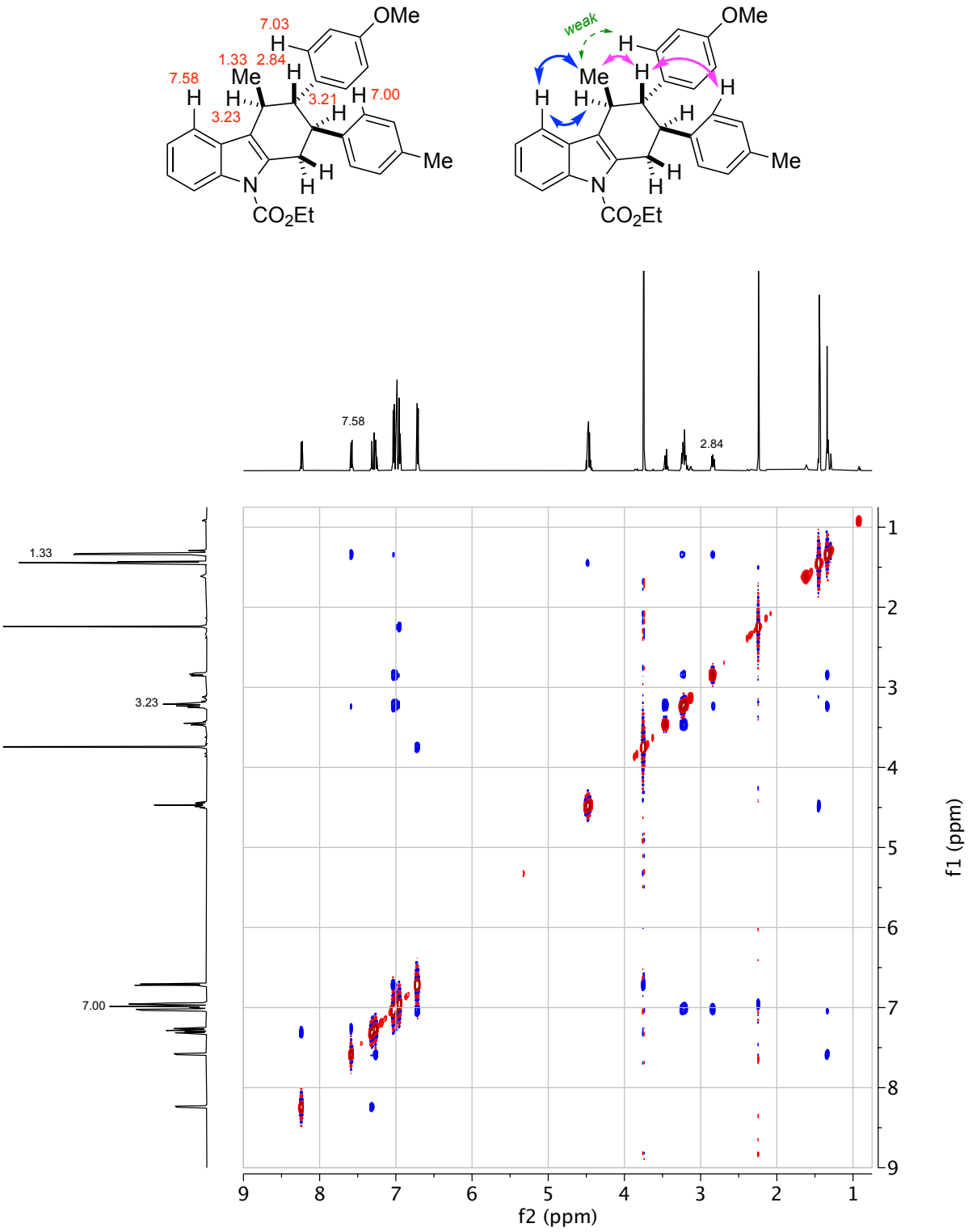


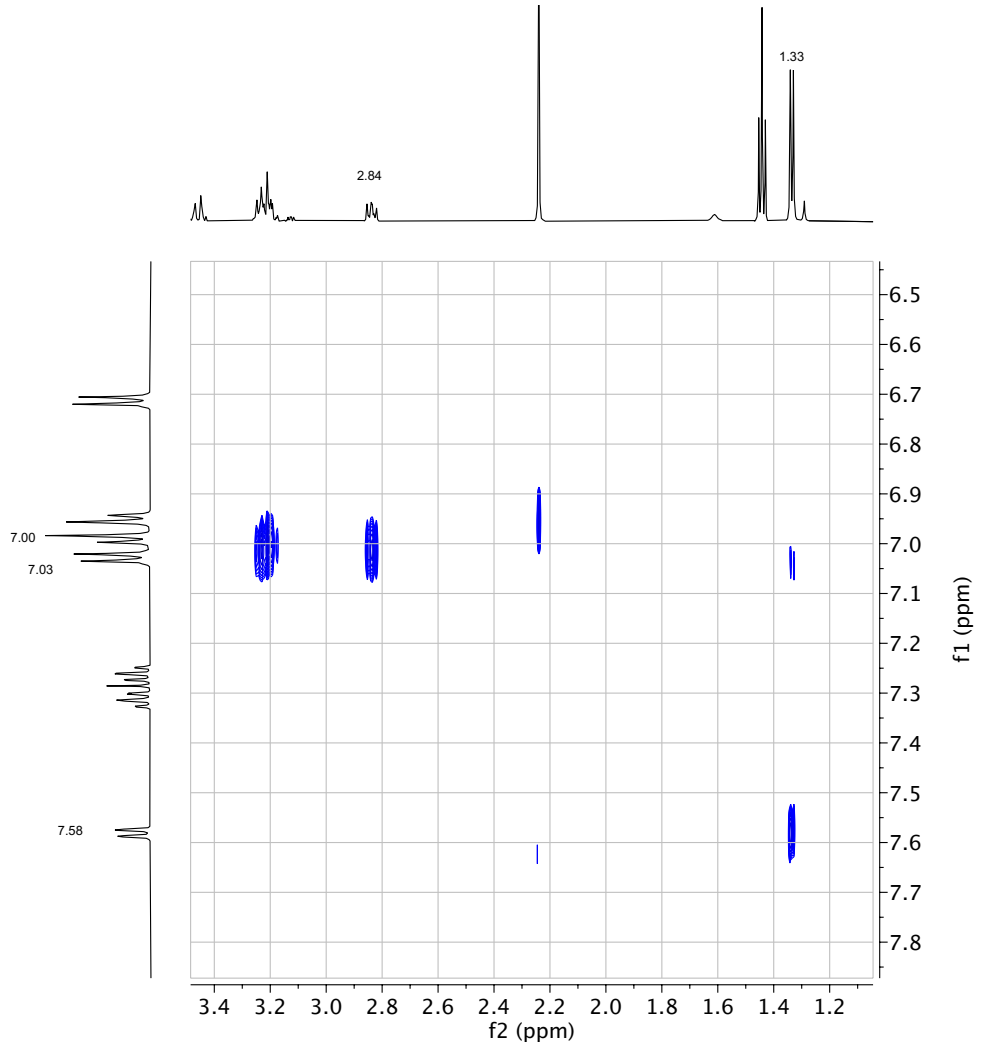



1.60
3.03
3.58
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9
f2 (ppm)


3.37
6.56
7.58
6.3
6.4
6.5
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
f1 (ppm)
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8
f2 (ppm)

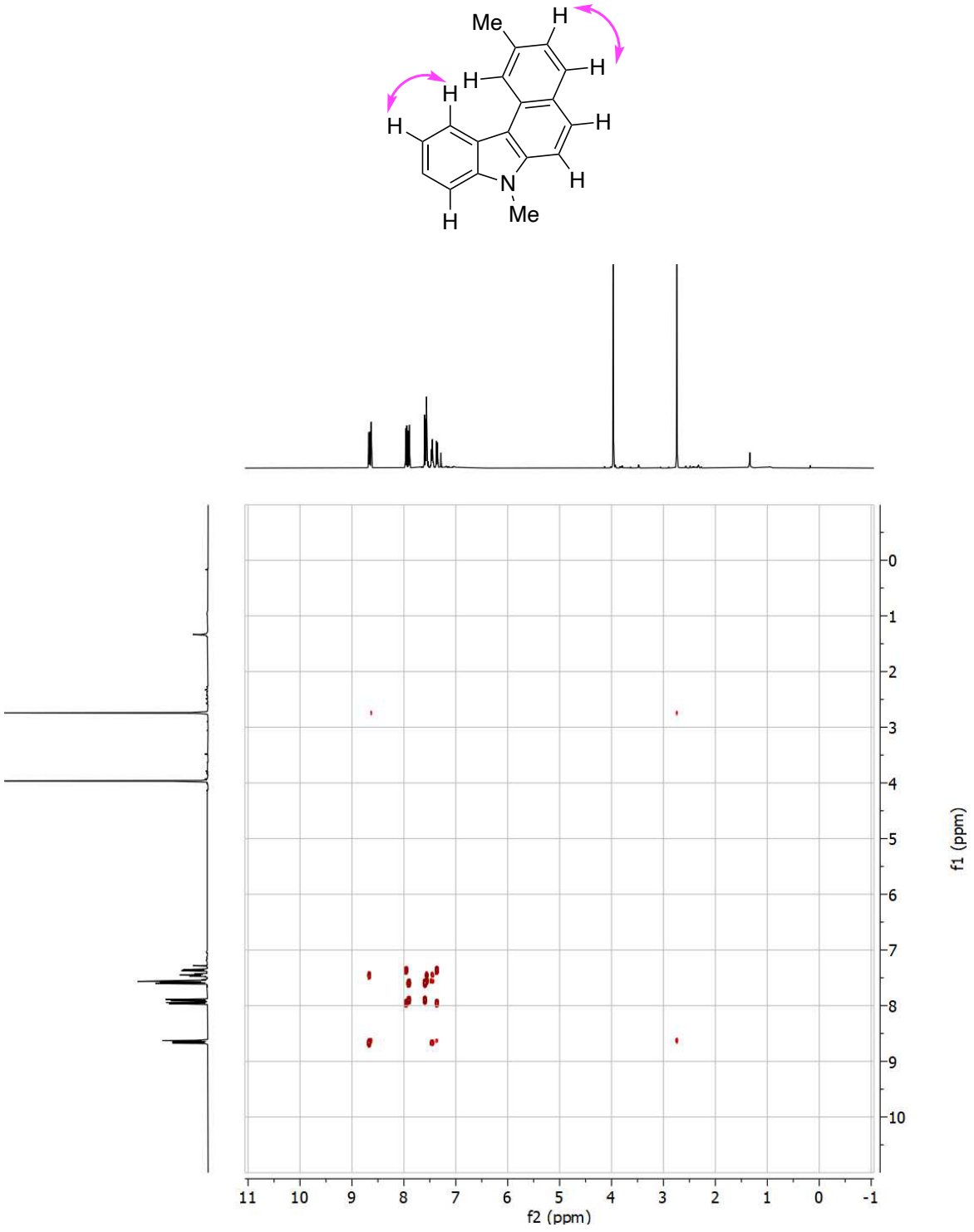
5a (major isomer), *diagnostic interactions* ($CDCl_3$, 600 MHz)

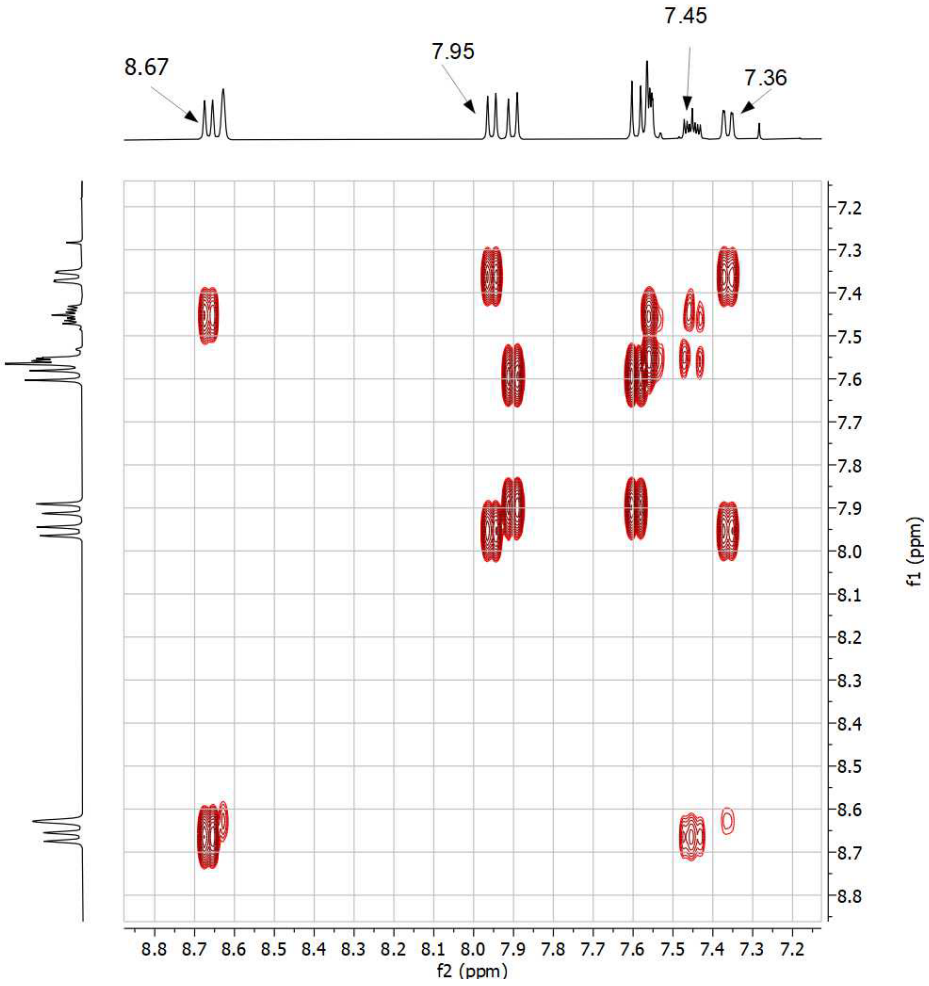



1.33
2.84
7.00
7.03
7.58
6.5
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
f1 (ppm)
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)

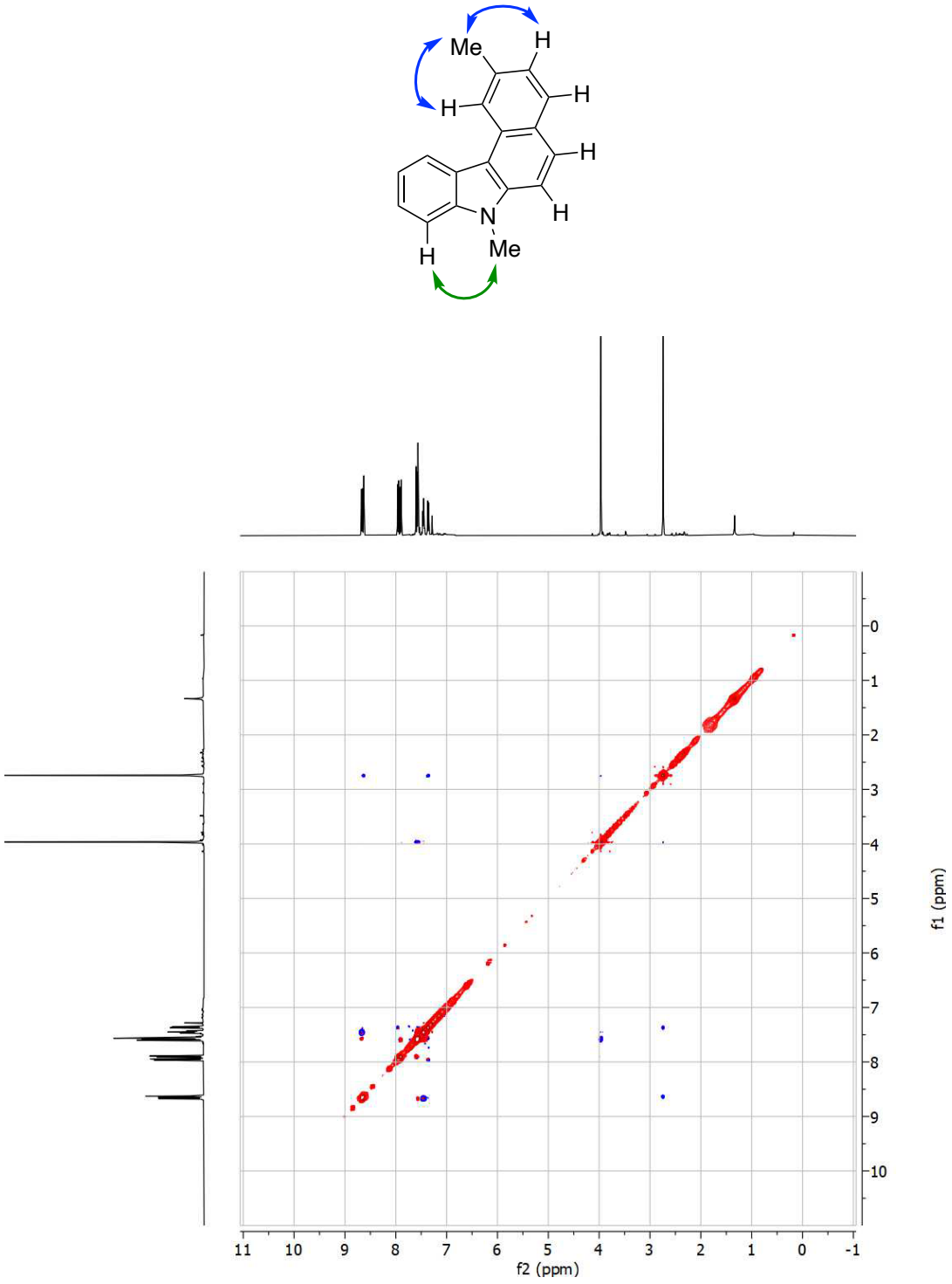
COSY and NOESY NMR of products 4

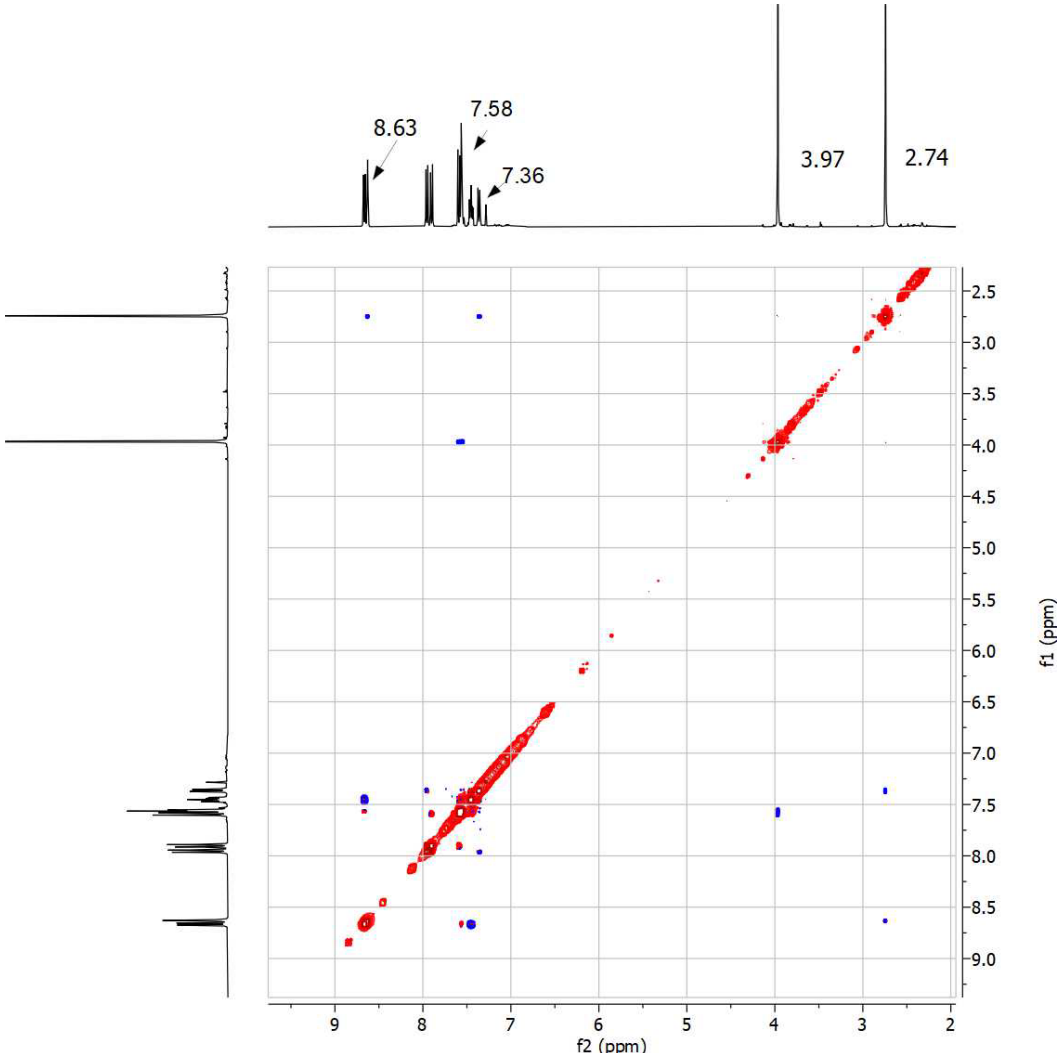
4, COSY *diagnostic interactions* ((CDCl3, 400 MHz)



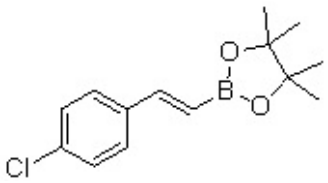

8.67
7.95
7.45
7.36
f1 (ppm)
f2 (ppm)

4, NOESY *diagnostic interactions* ((CDCl3, 400 MHz)

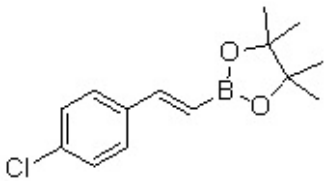



8.63
7.58
7.36
3.97
2.74
f1 (ppm)
f2 (ppm)

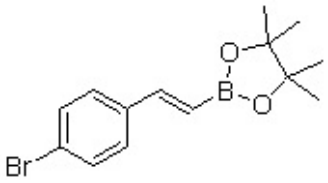
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



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

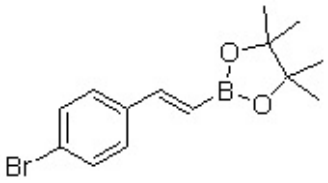


7.49
7.49
7.47
7.37
7.37
7.35
7.32
7.28
6.19
6.15
1.33

1.97
3.30
1.00
12.40

f1 (ppm)

^{13}C NMR (101 MHz, $CDCl_3$)

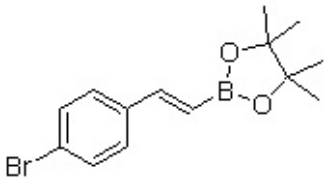


148.07
136.42
131.76
128.52
122.91
83.48
24.82

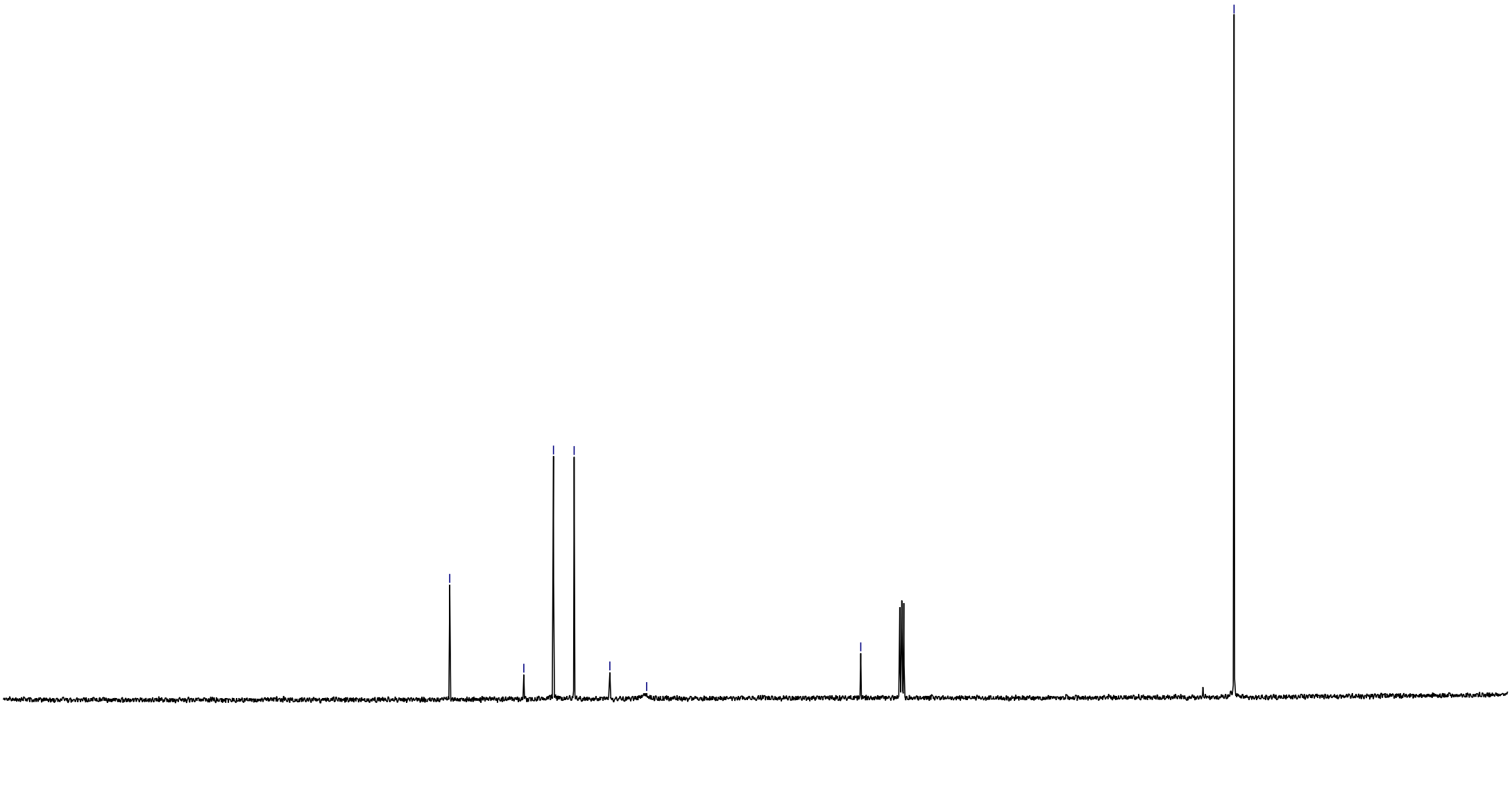
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

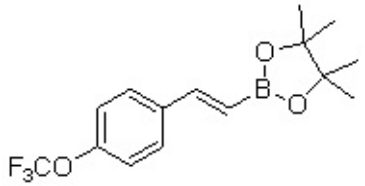
^{13}C NMR (101 MHz, $CDCl_3$)



148.07
136.42
131.76
128.52
122.90
117.12
83.48
24.82



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

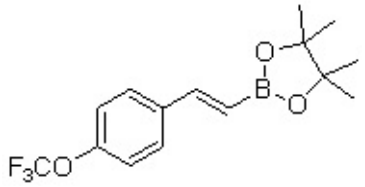


7.53
7.51
7.41
7.36
7.21
7.19
6.18
6.14
1.34

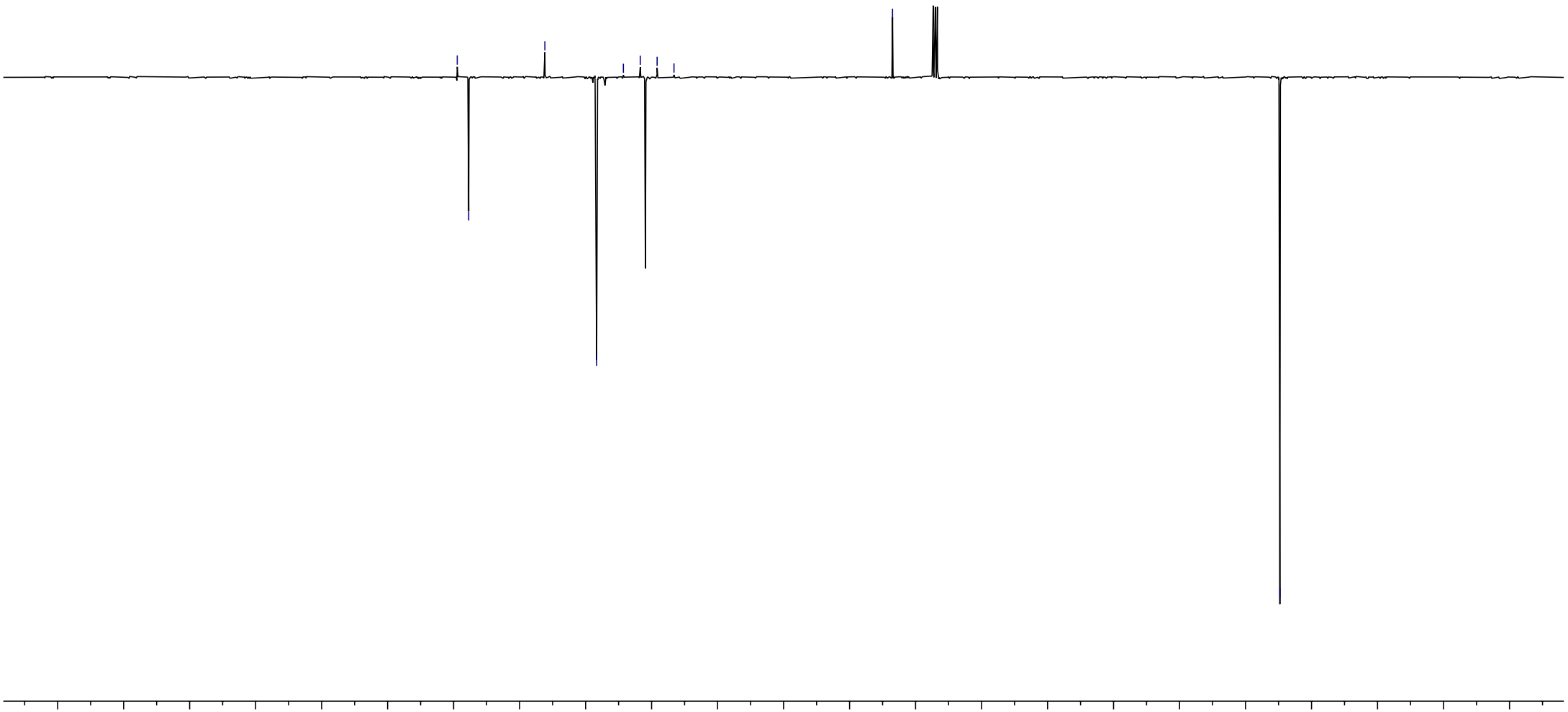
2.12
1.02
1.94
1.00
12.61

f1 (ppm)

^{13}C NMR (101 MHz, $CDCl_3$)



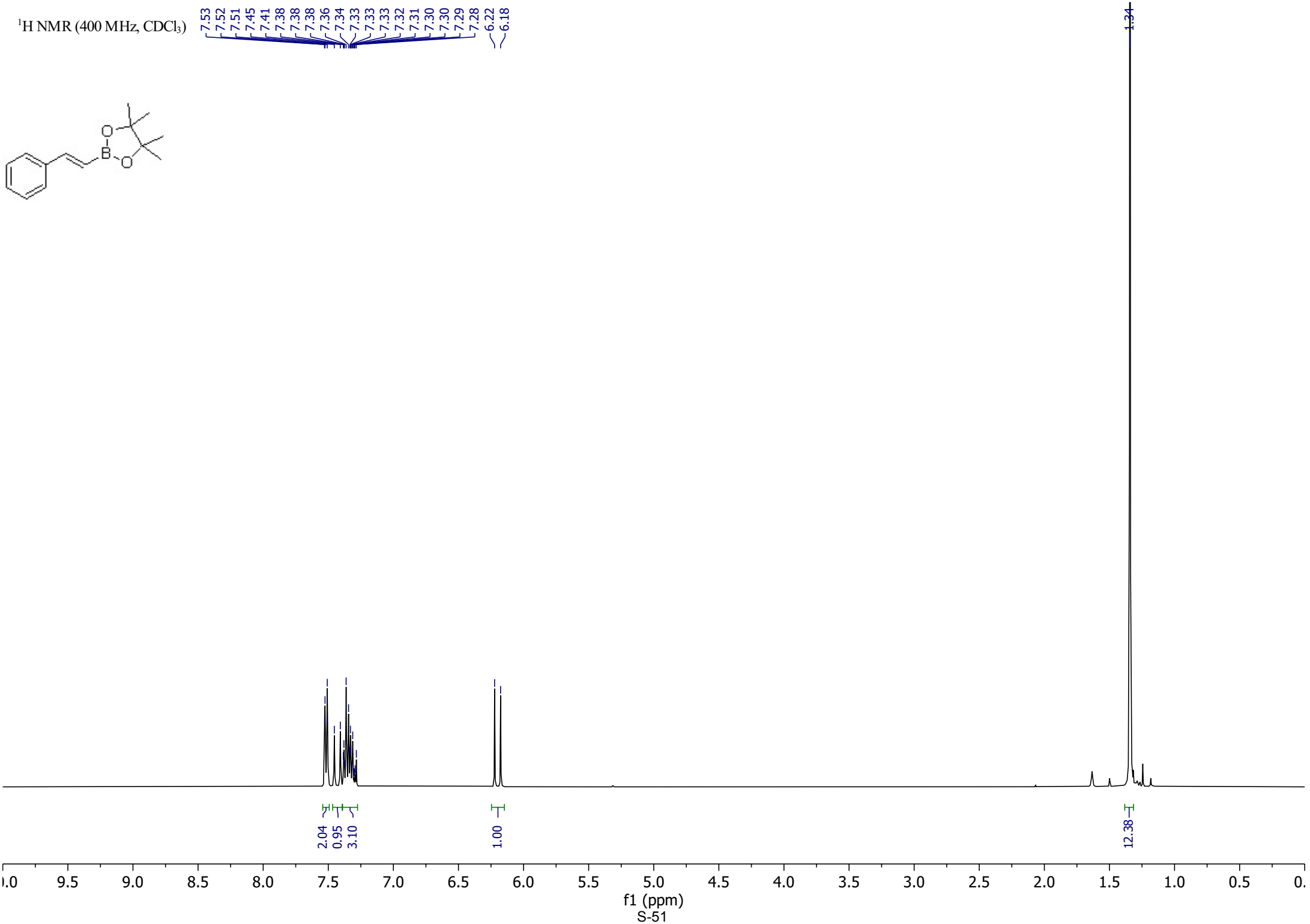
149.45
147.71
136.17
128.33
124.27
121.72
119.16
116.61
83.49
24.80



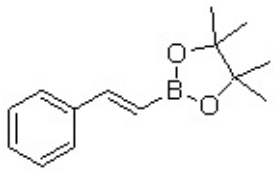
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

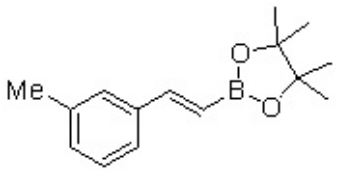
^{1}H NMR (400 MHz, $CDCl_3$)



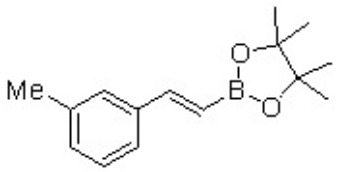
^{13}C NMR (101 MHz, $CDCl_3$)

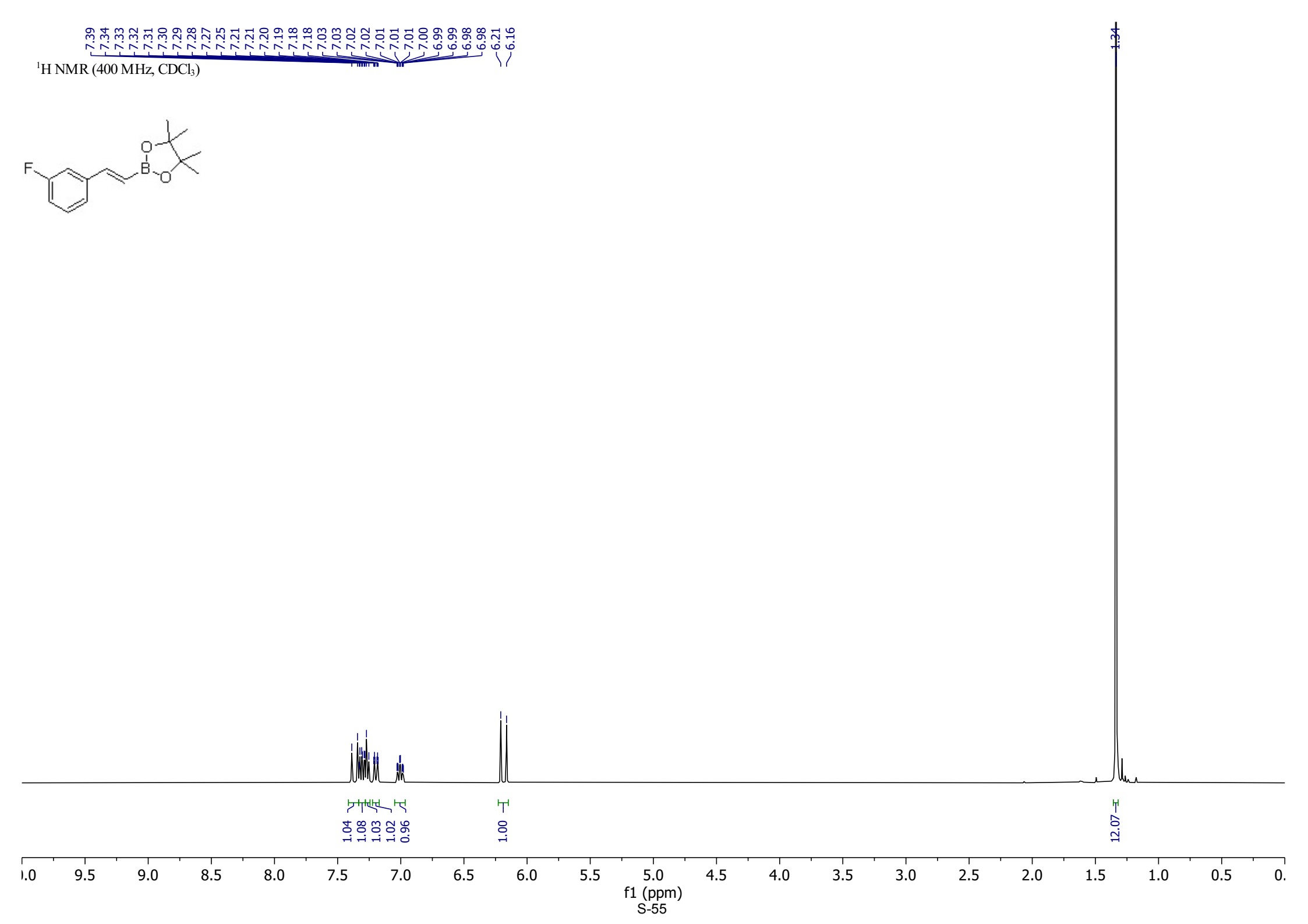


^{1}H NMR (400 MHz, $CDCl_3$)

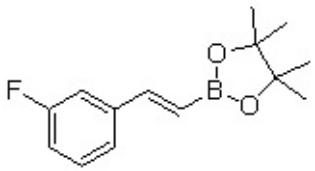


^{13}C NMR (101 MHz, $CDCl_3$)

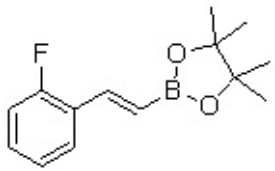



7.39
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.25
7.21
7.21
7.20
7.19
7.18
7.18
7.03
7.03
7.02
7.02
7.01
7.01
7.01
7.00
6.99
6.99
6.98
6.98
6.21
6.16
1.34
^{1}H NMR (400 MHz, $CDCl_3$)
F
O
B
O
1.04
1.08
1.03
1.02
0.96
1.00
12.07
f1 (ppm)

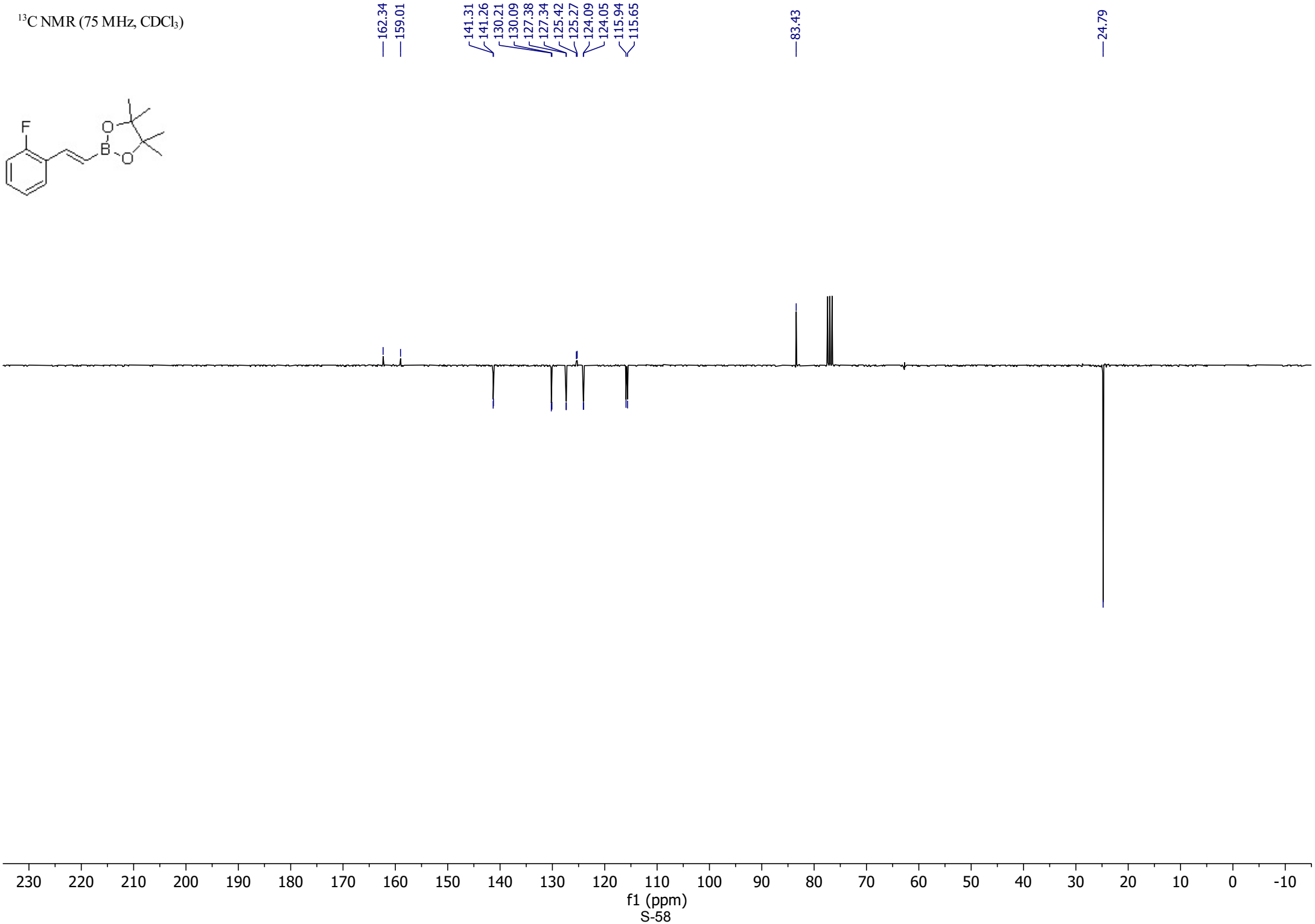
^{13}C NMR (101 MHz, $CDCl_3$)



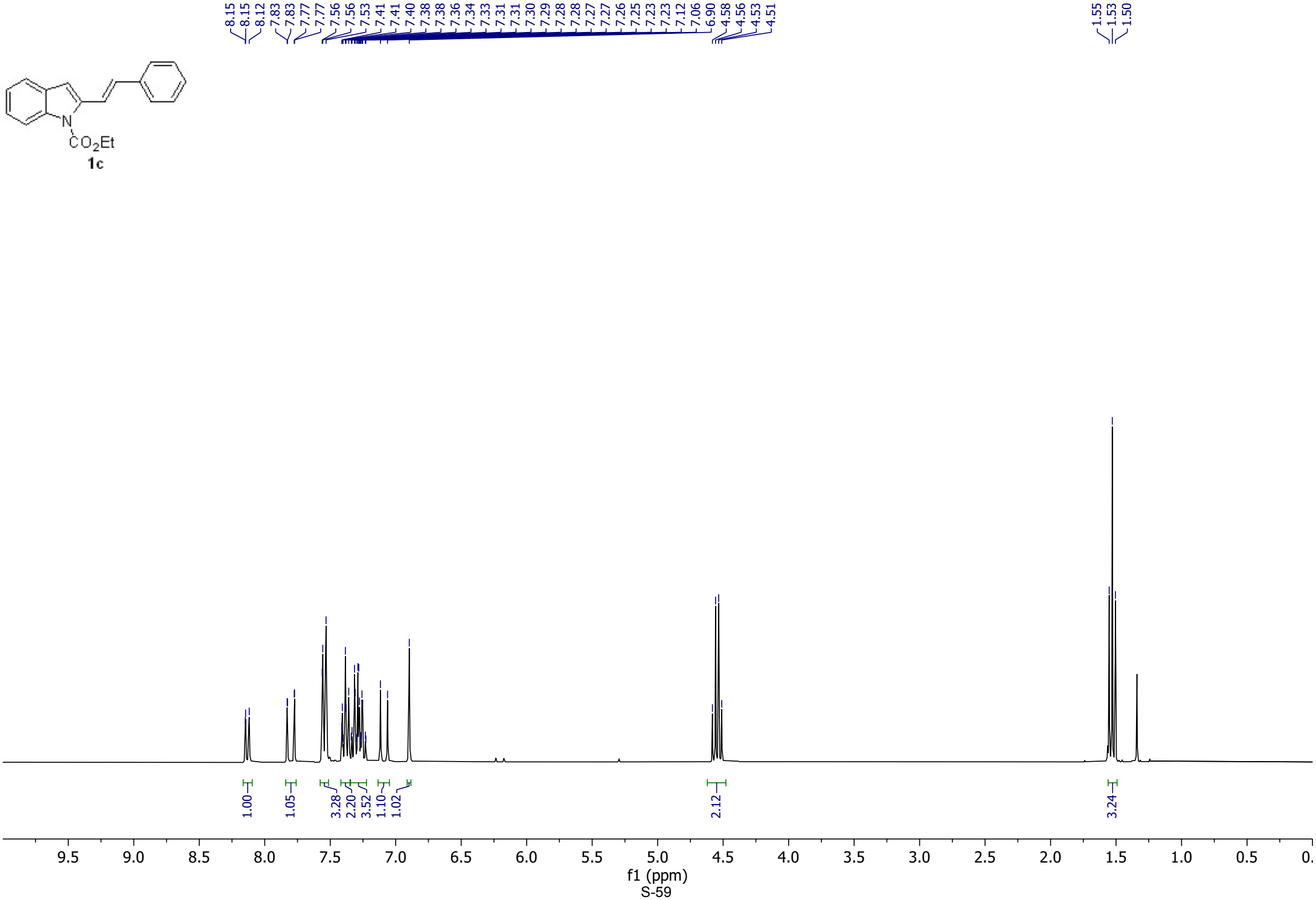
^{1}H NMR (300 MHz, $CDCl_3$)



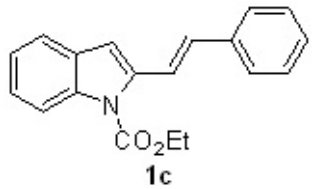
^{13}C NMR (75 MHz, $CDCl_3$)



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

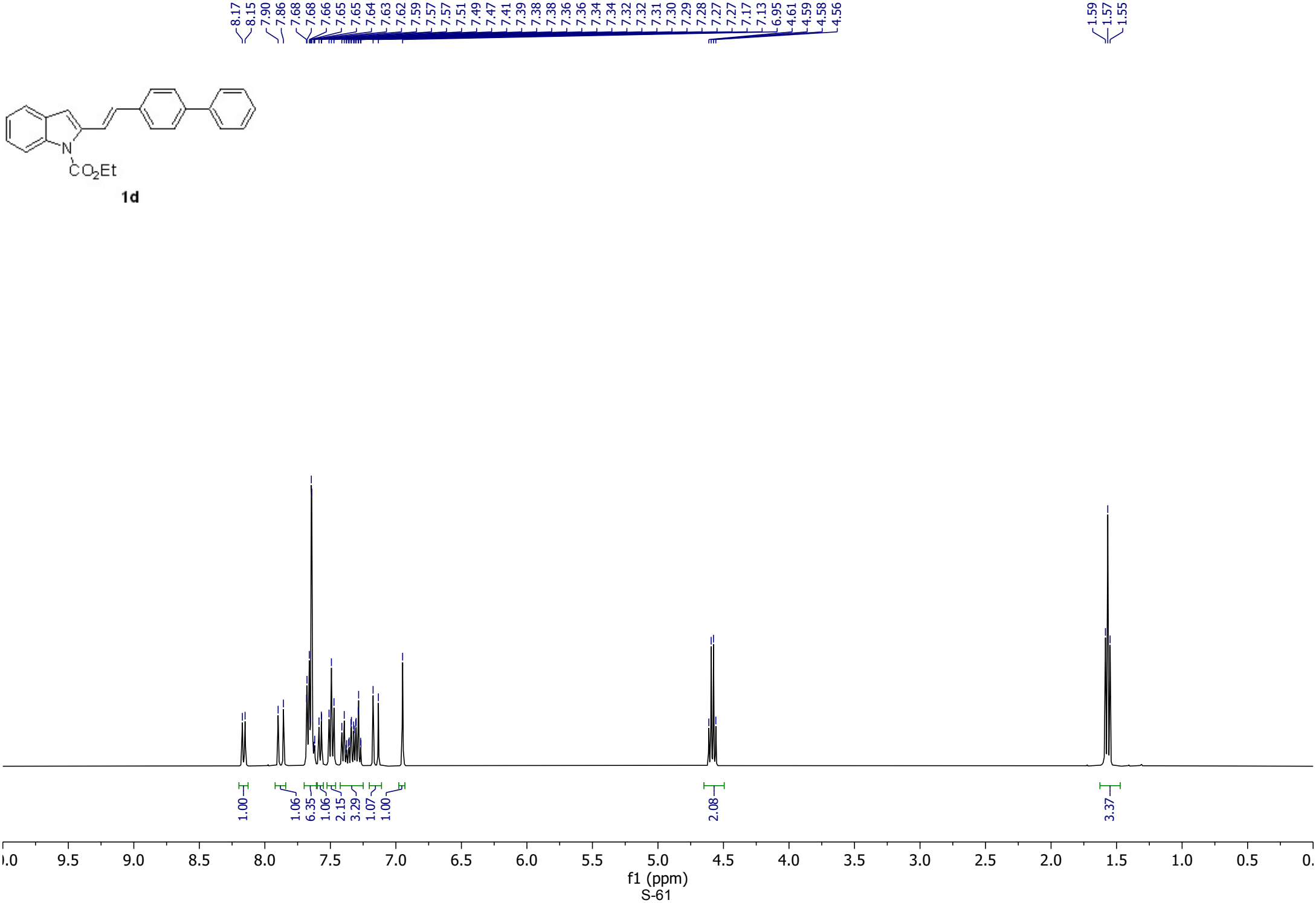


^{13}C NMR (75 MHz, $CDCl_3$)

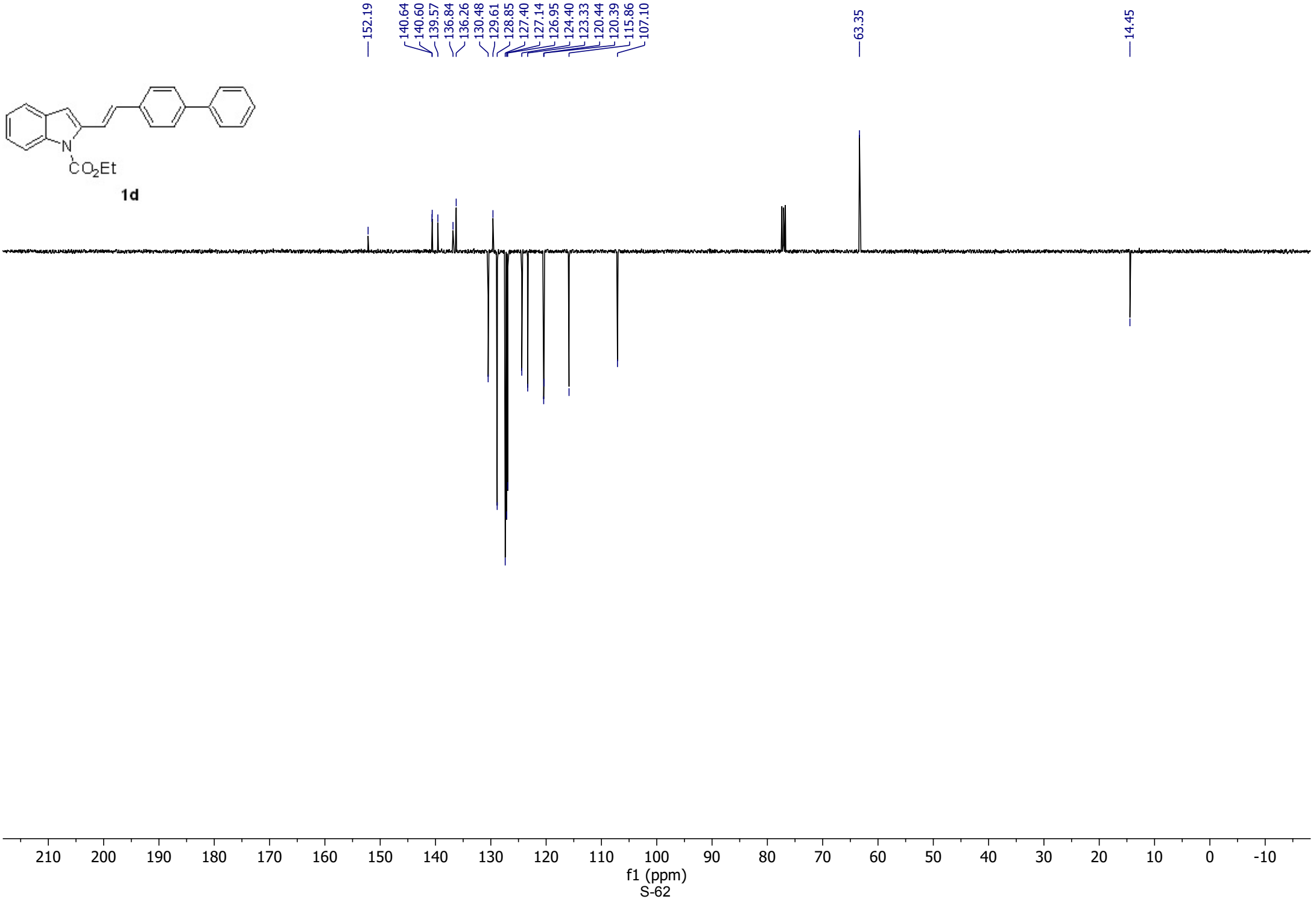


1c

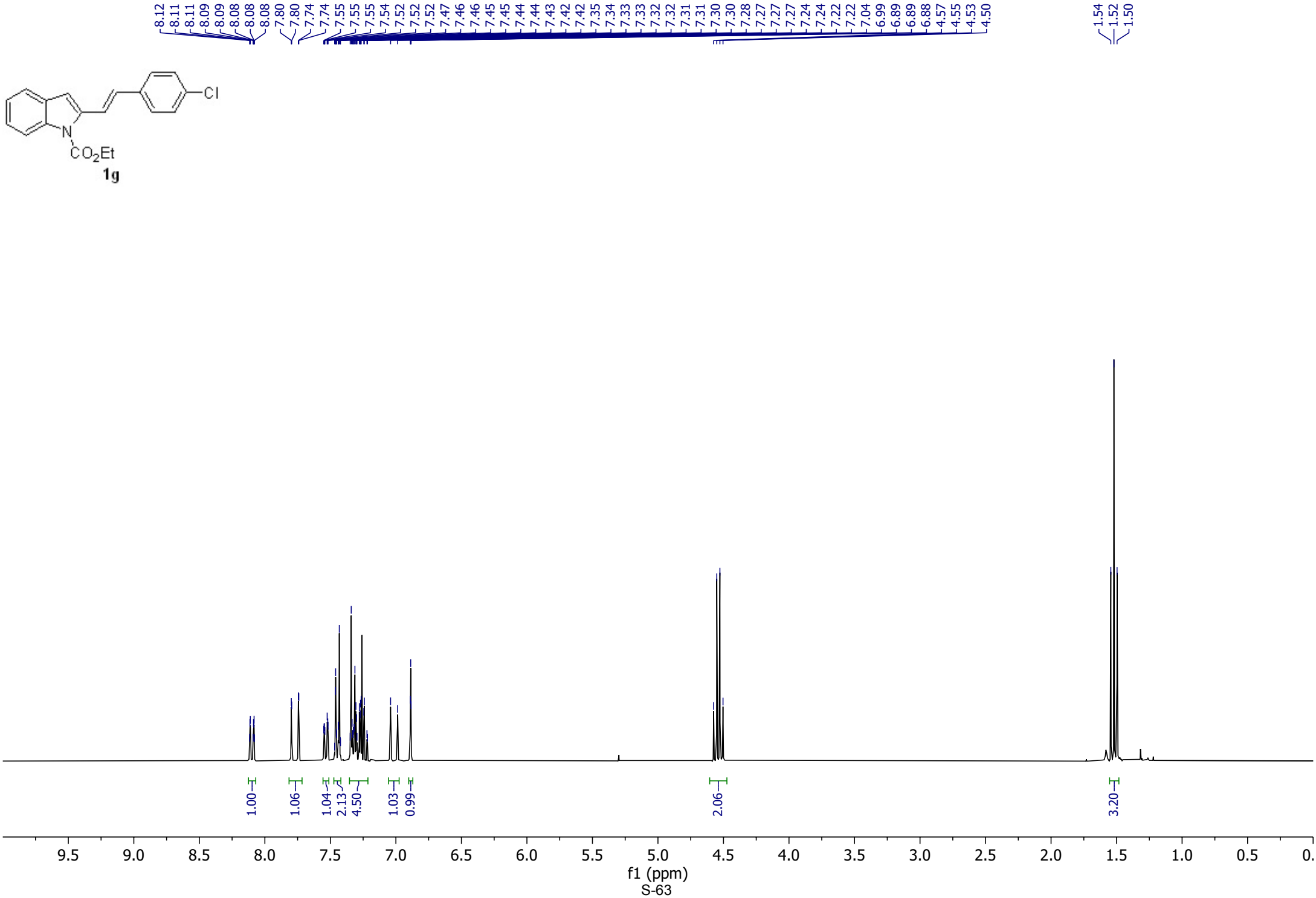
^{1}H NMR (400 MHz, $CDCl_3$)



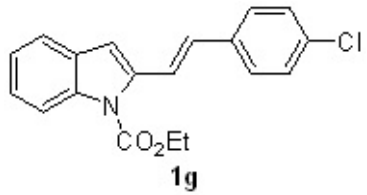
^{13}C NMR (101 MHz, $CDCl_3$)



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

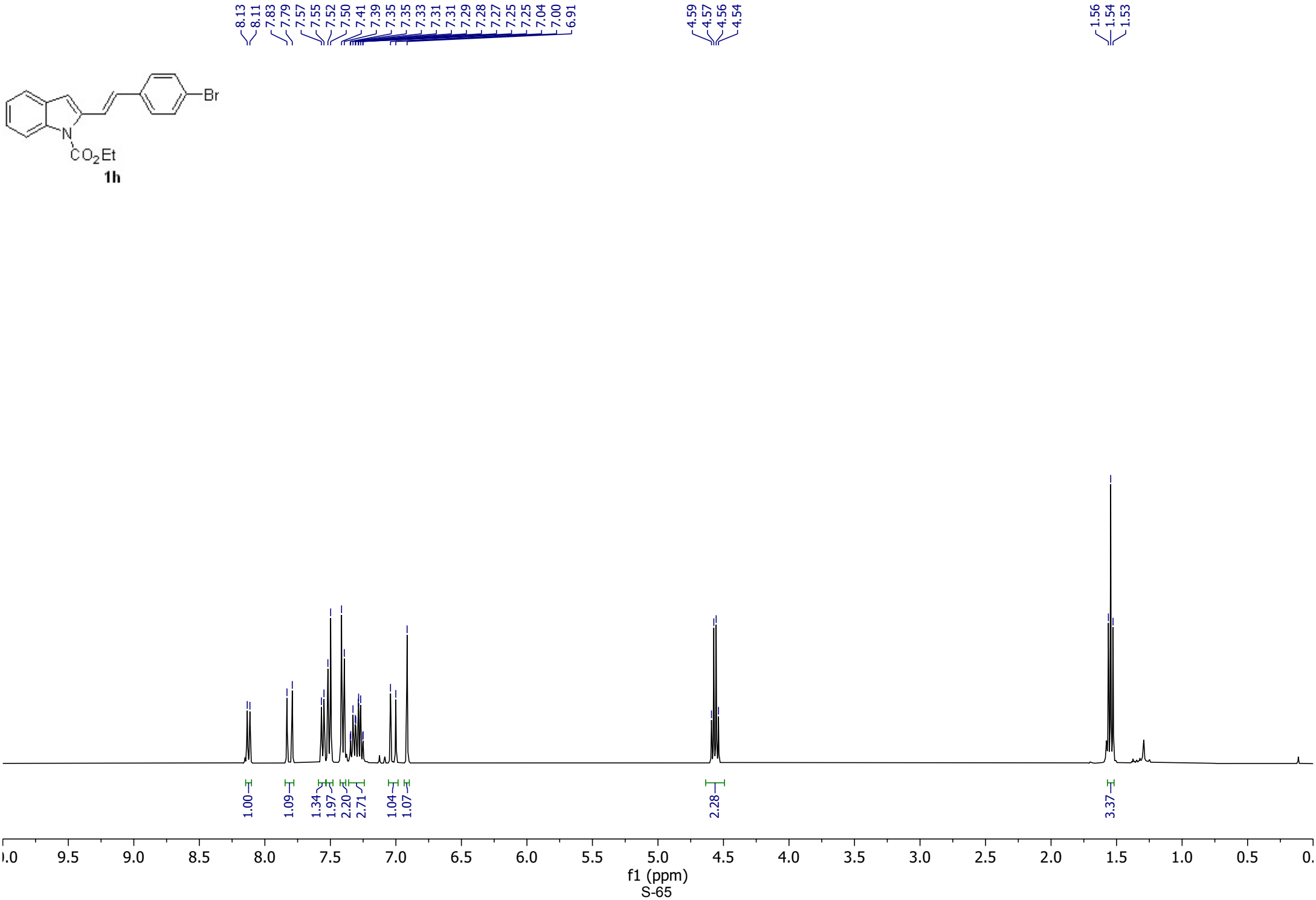


^{13}C NMR (75 MHz, $CDCl_3$)

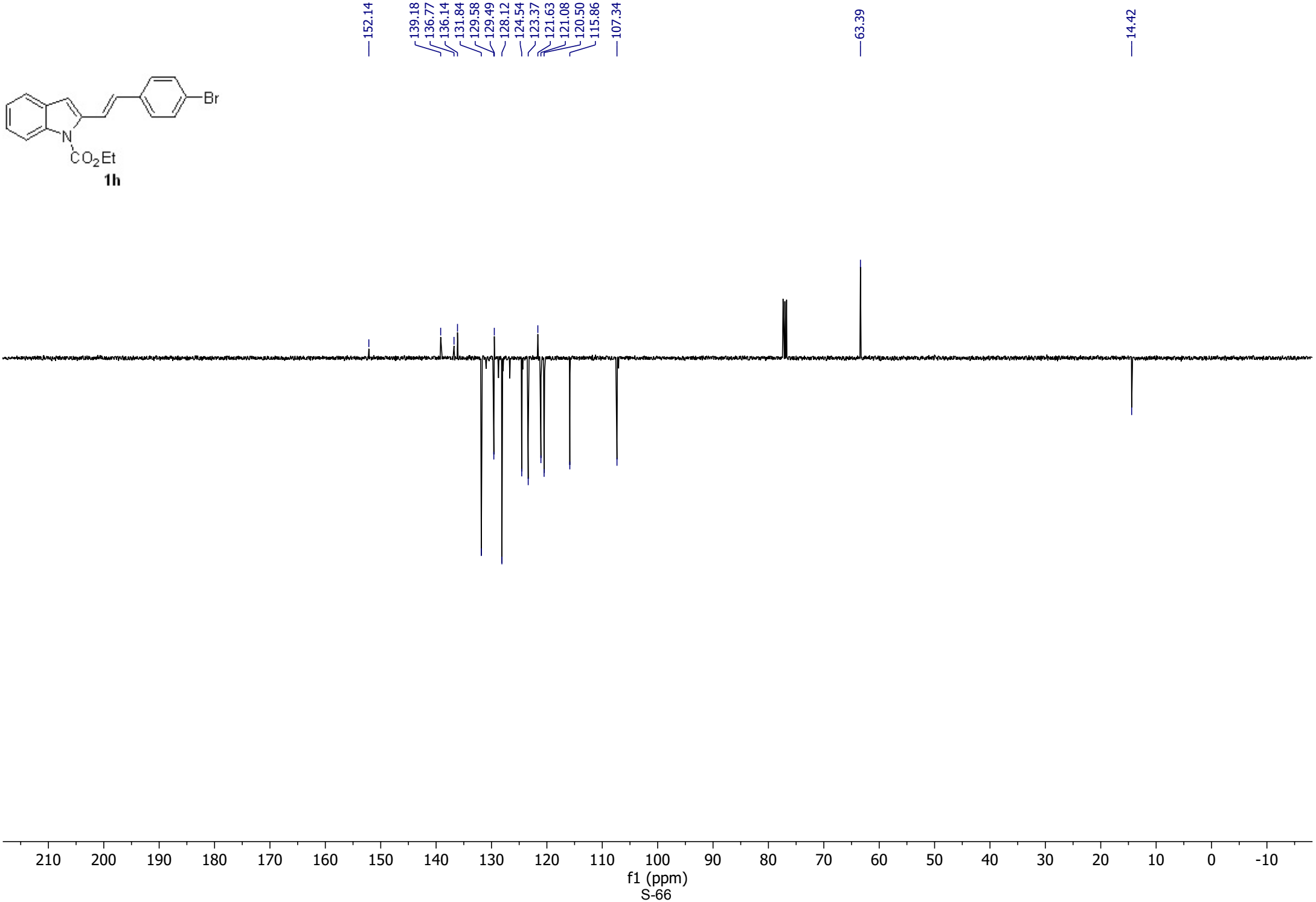


1g

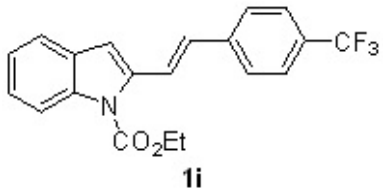
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

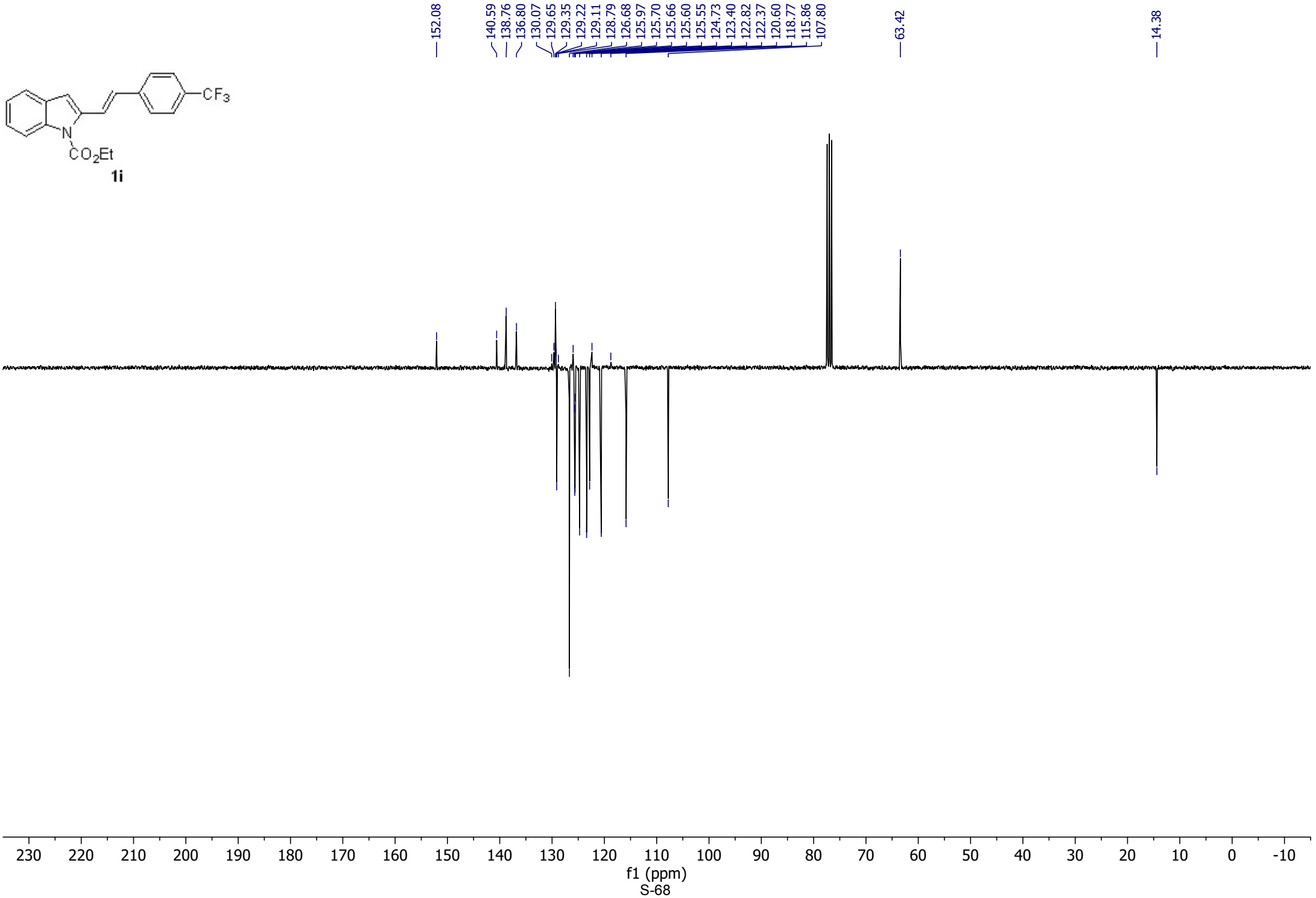


^{1}H NMR (300 MHz, $CDCl_3$)

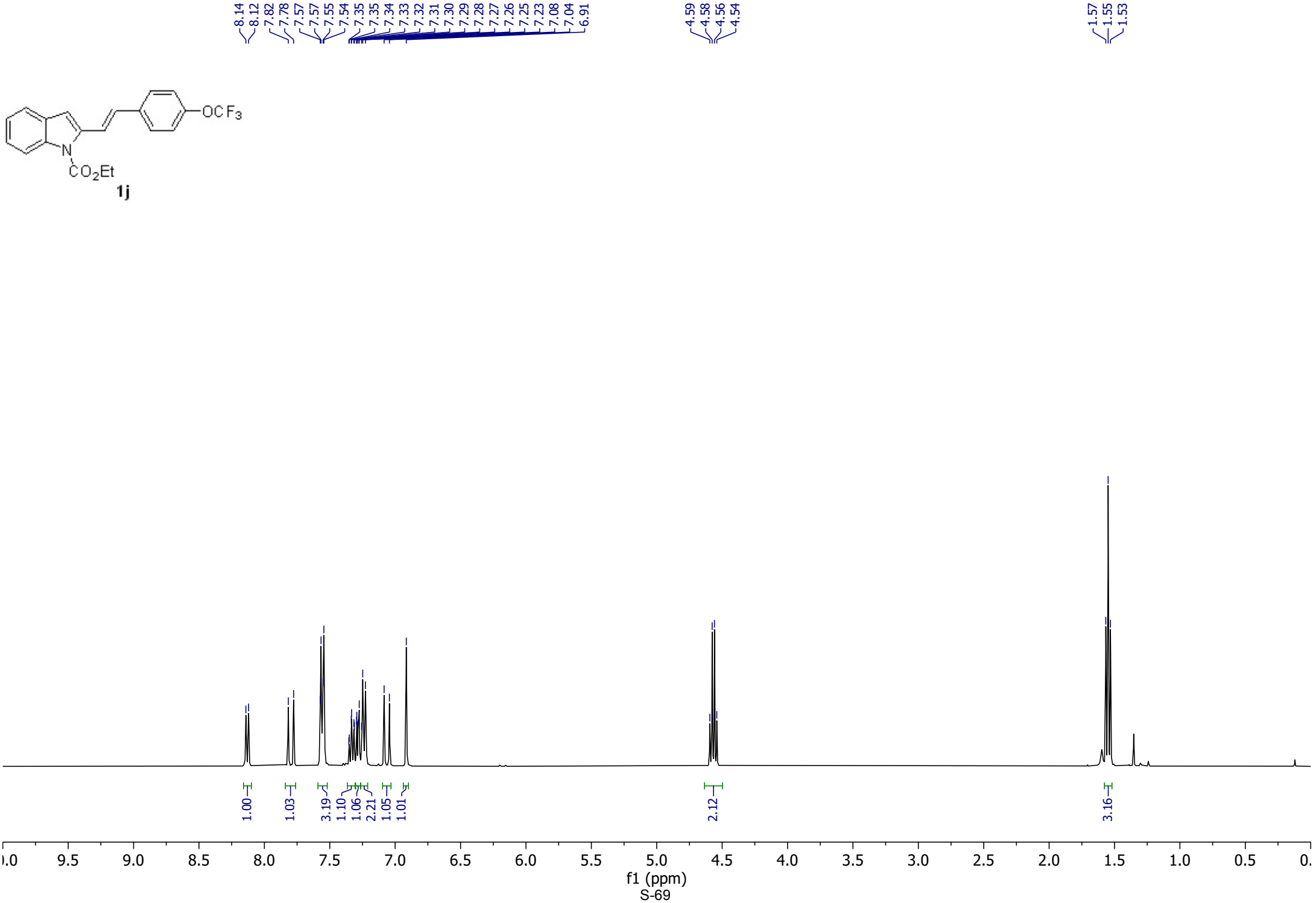


1i

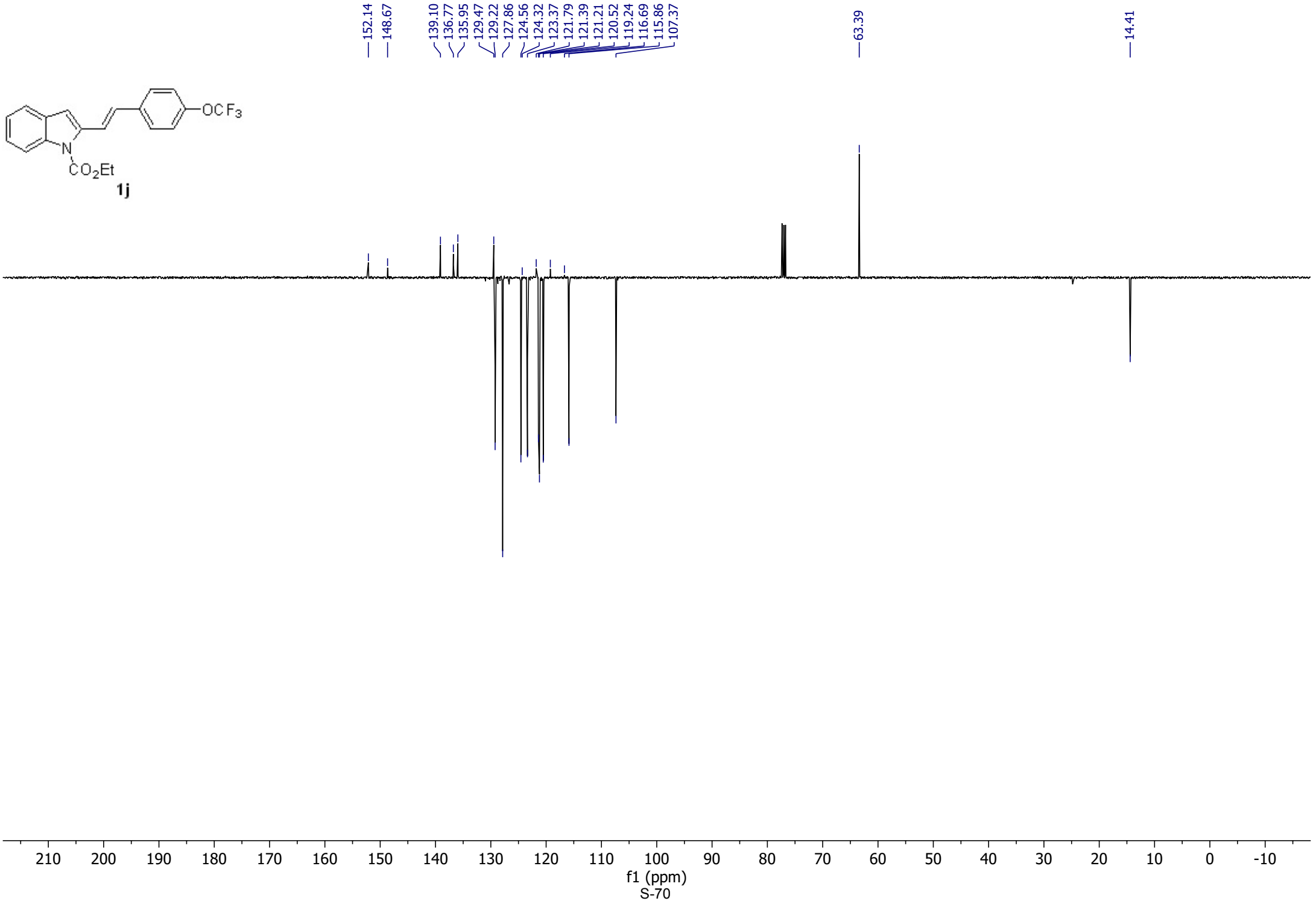
^{13}C NMR (75 MHz, $CDCl_3$)



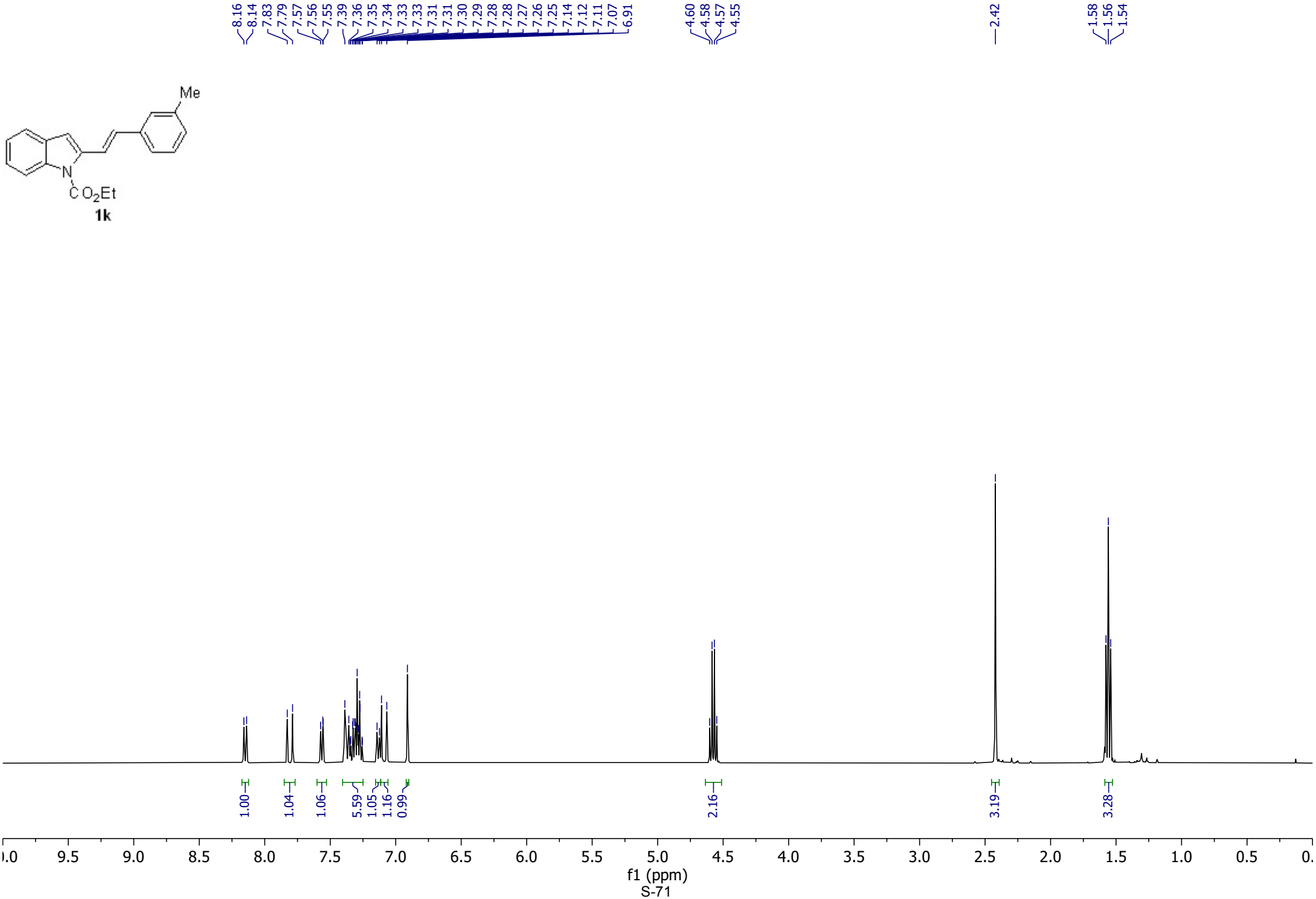
^{1}H NMR (400 MHz, $CDCl_3$)



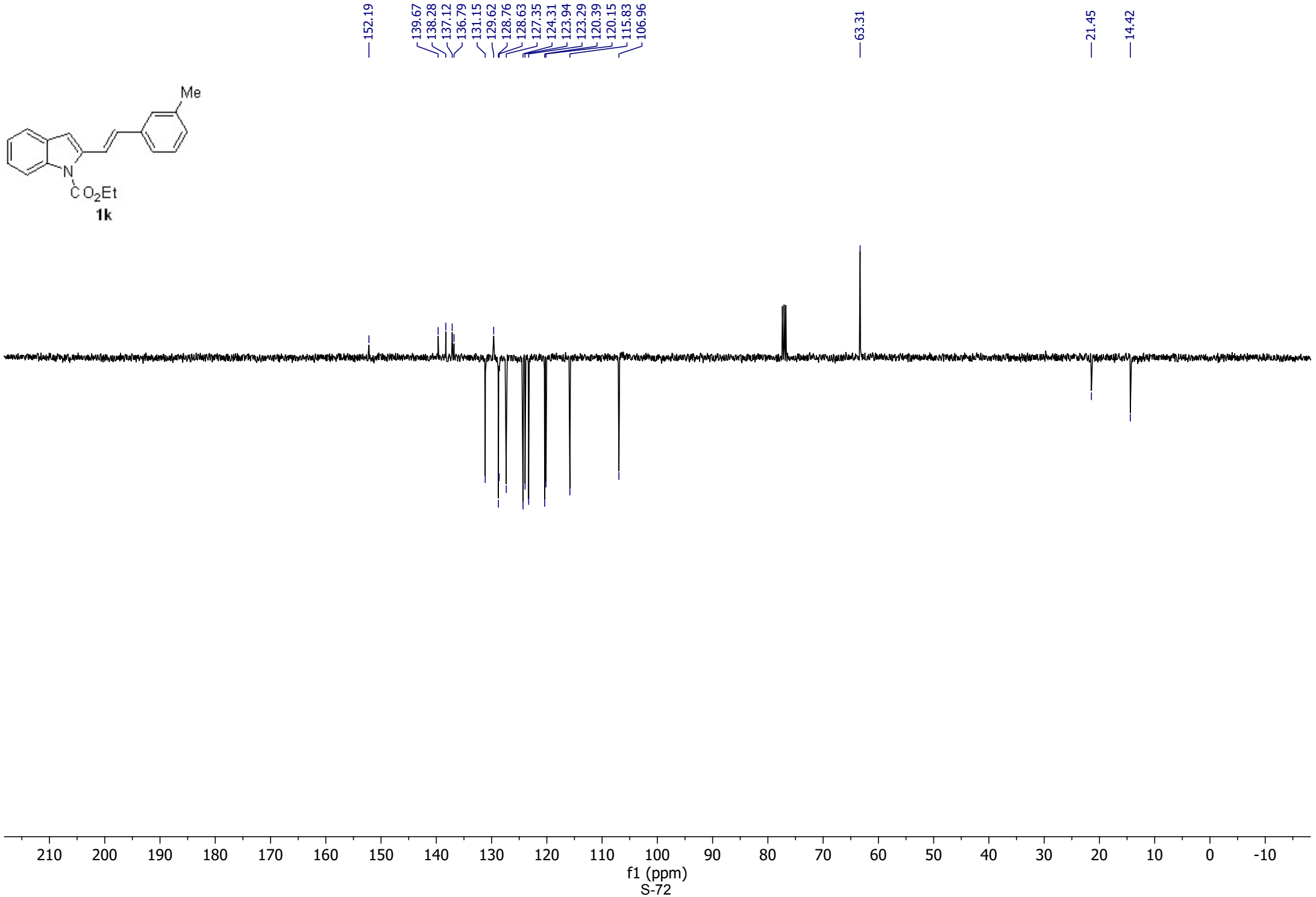
^{13}C NMR (101 MHz, $CDCl_3$)



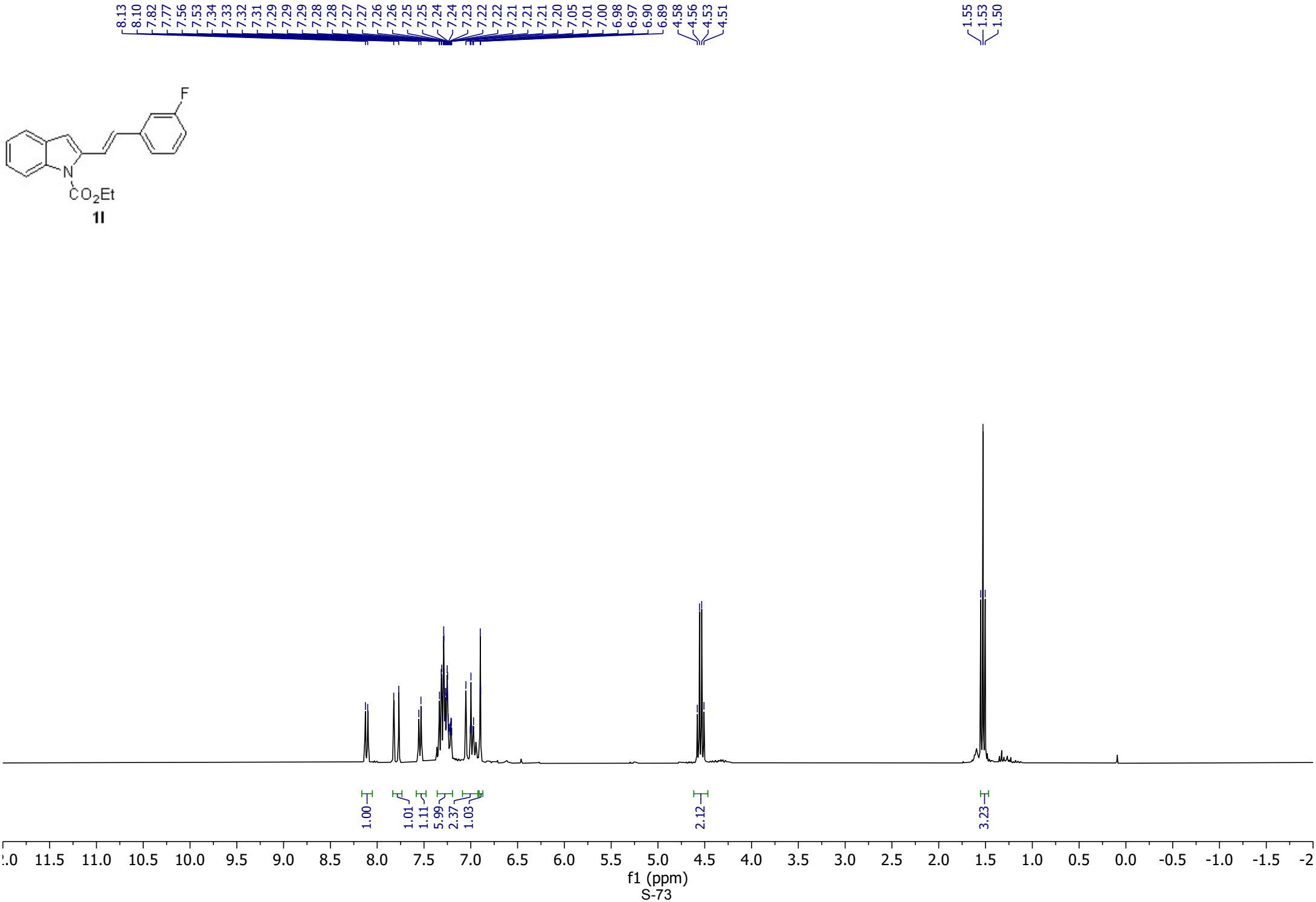
^{1}H NMR (400 MHz, $CDCl_3$)



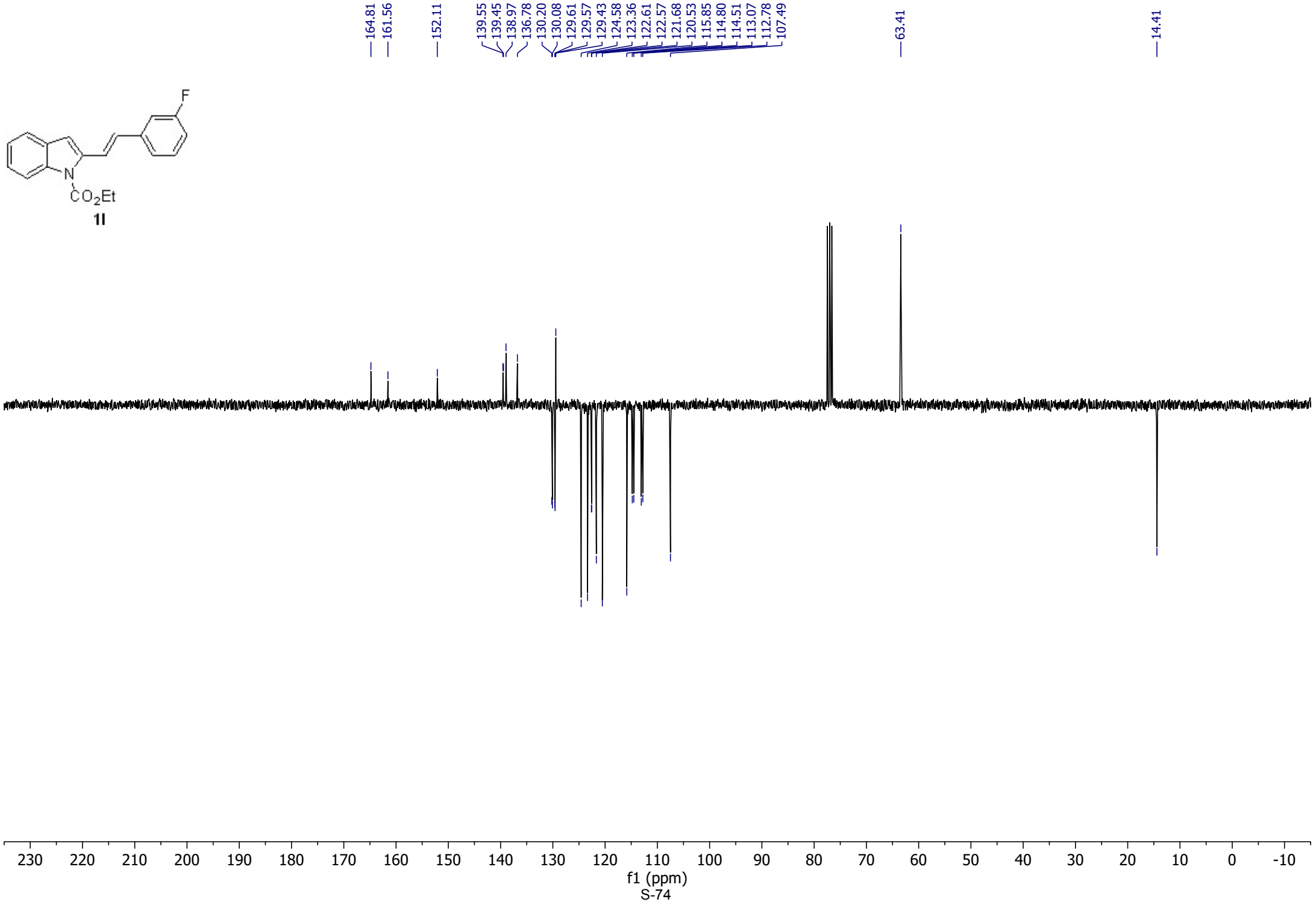
^{13}C NMR (101 MHz, $CDCl_3$)



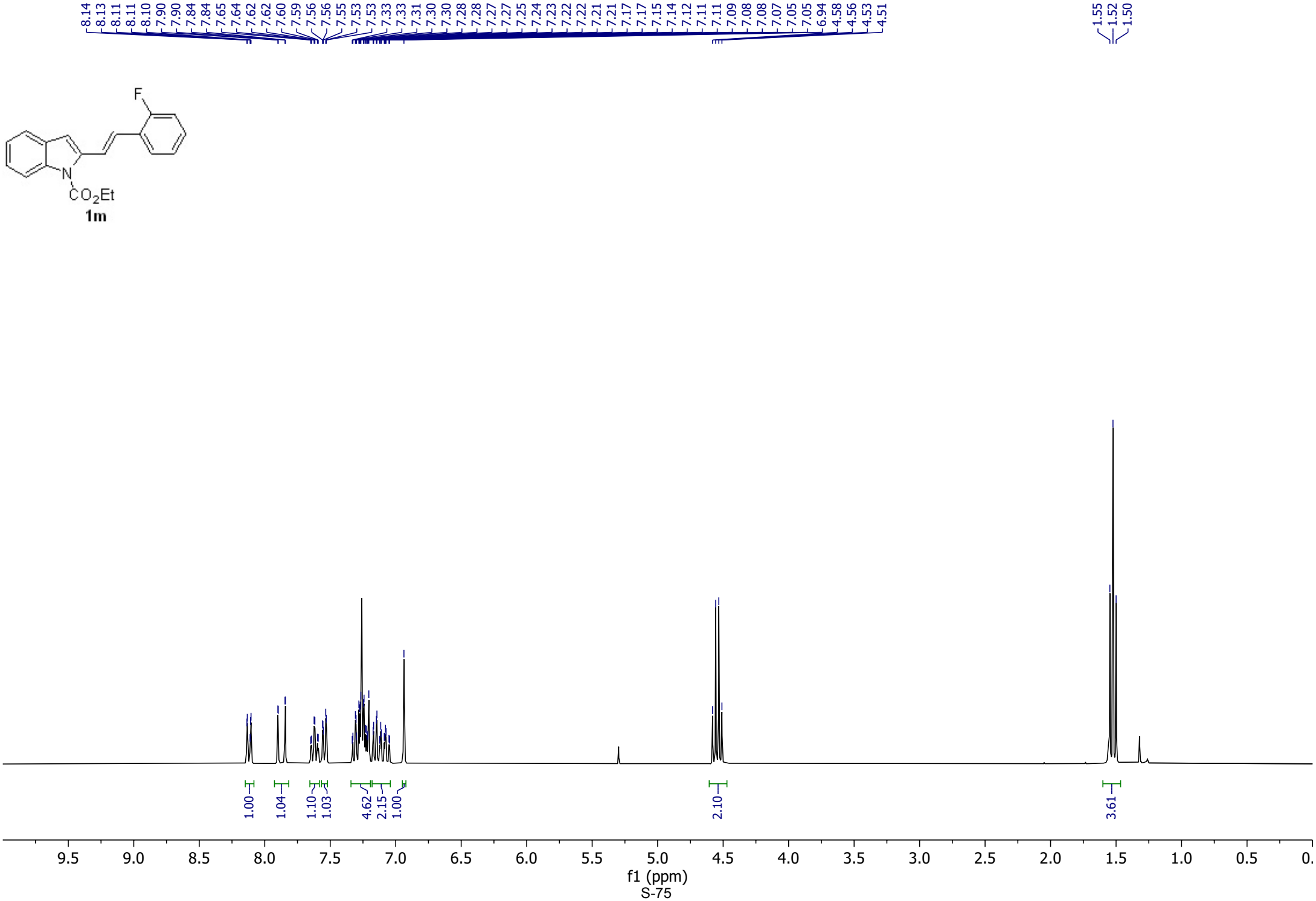
^{1}H NMR (300 MHz, $CDCl_3$)



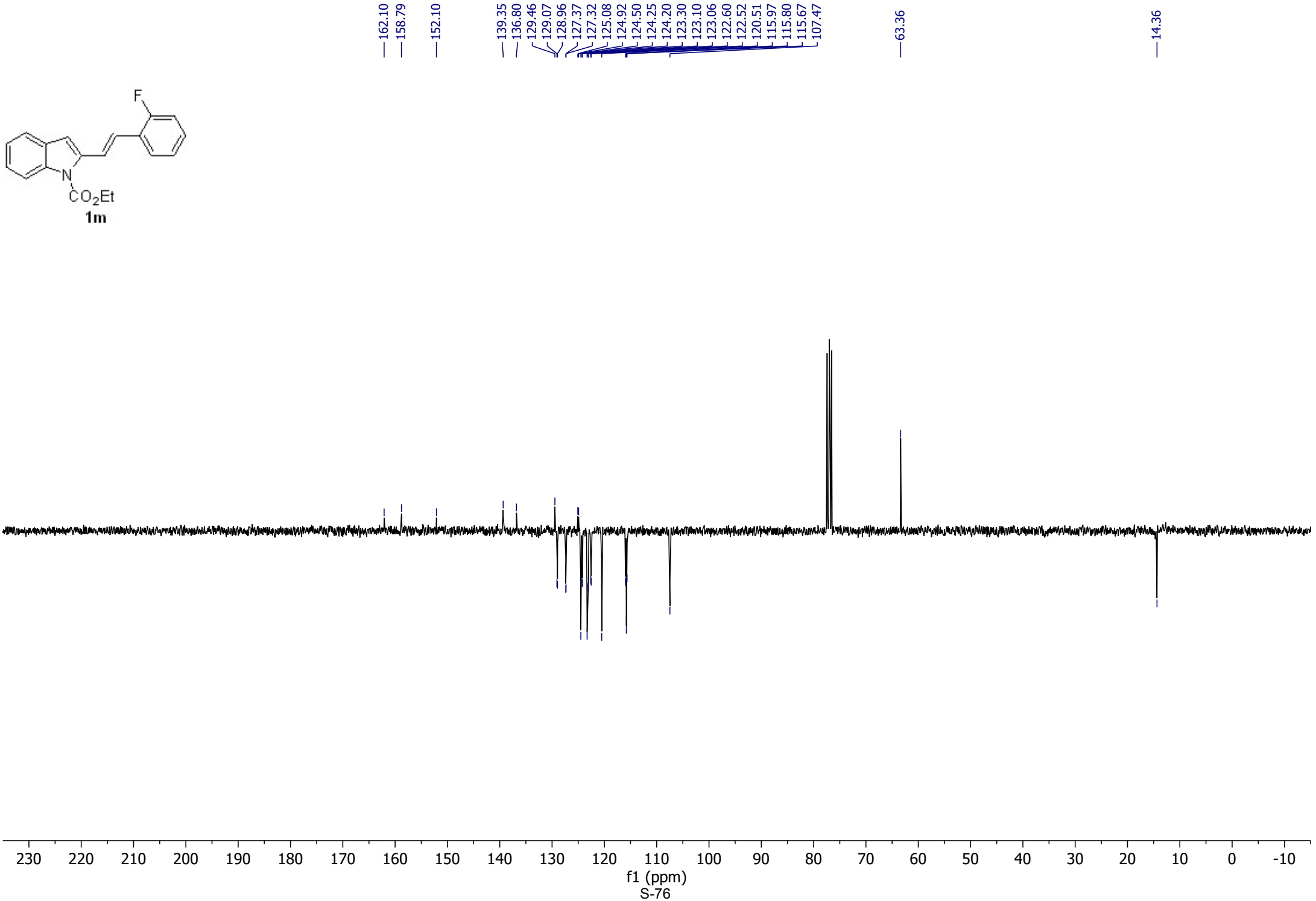
^{13}C NMR (75 MHz, $CDCl_3$)



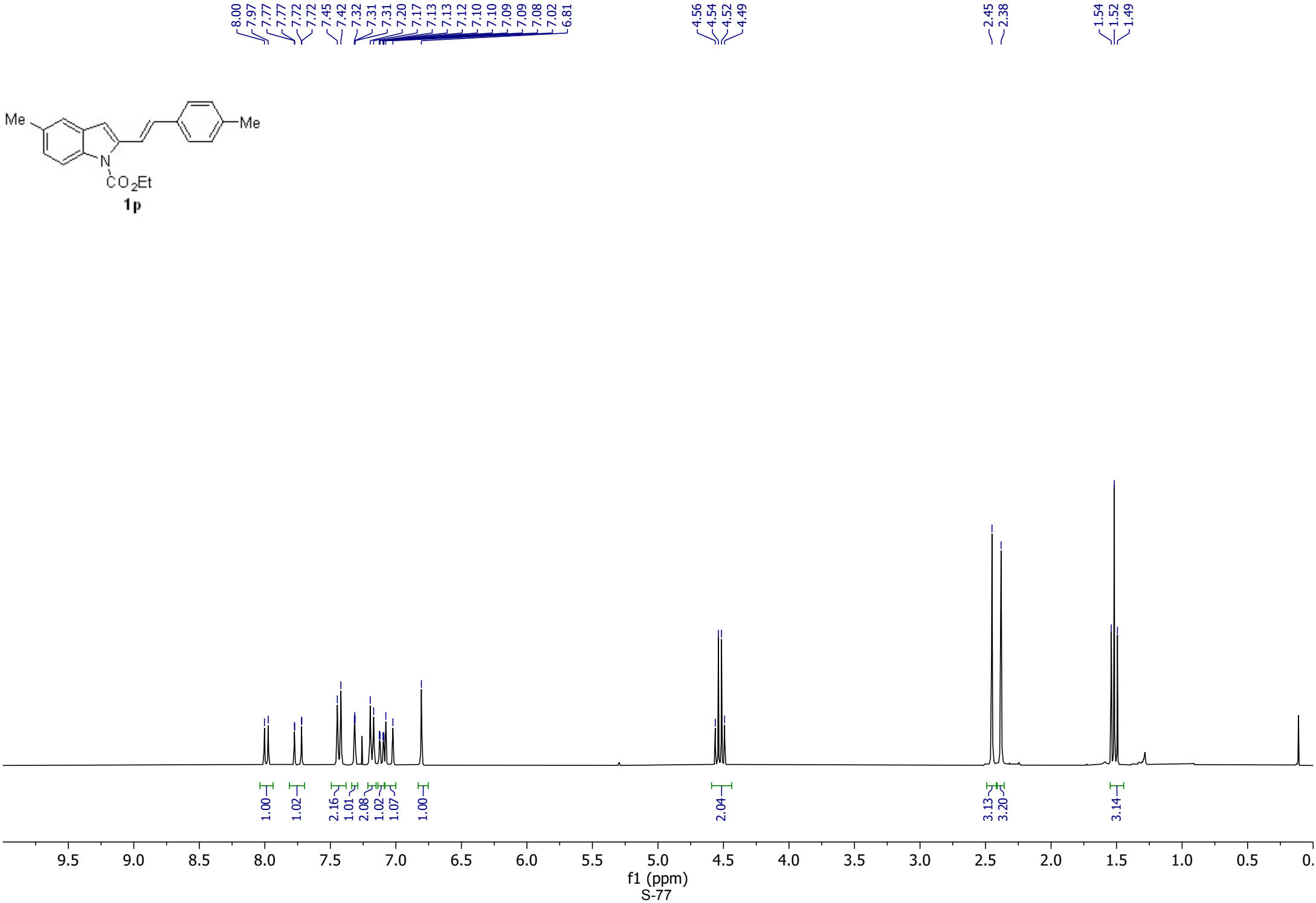
^{1}H NMR (300 MHz, $CDCl_3$)



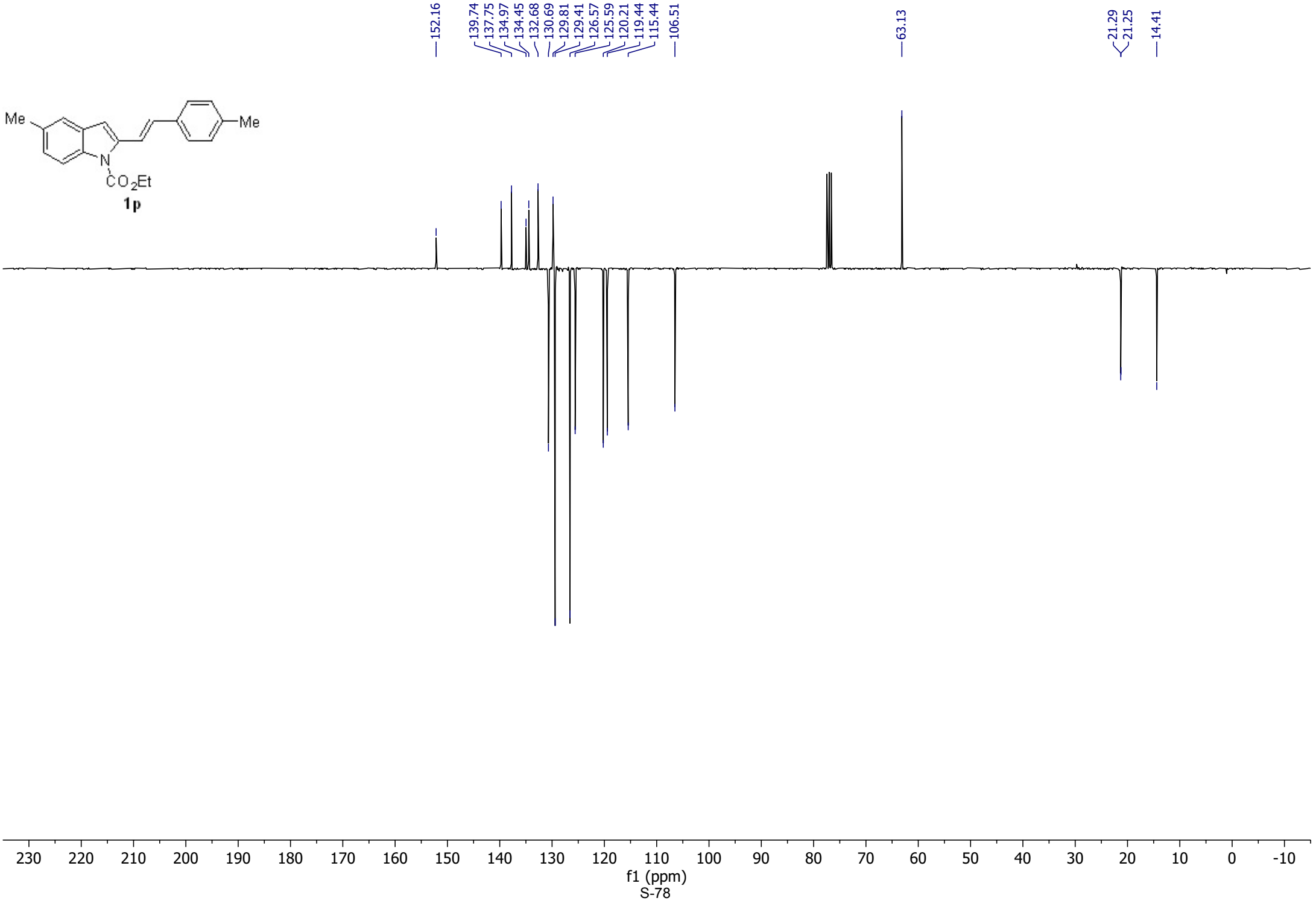
^{13}C NMR (75 MHz, $CDCl_3$)



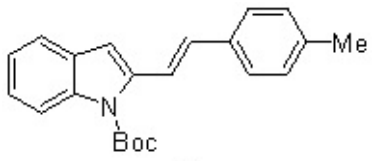
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

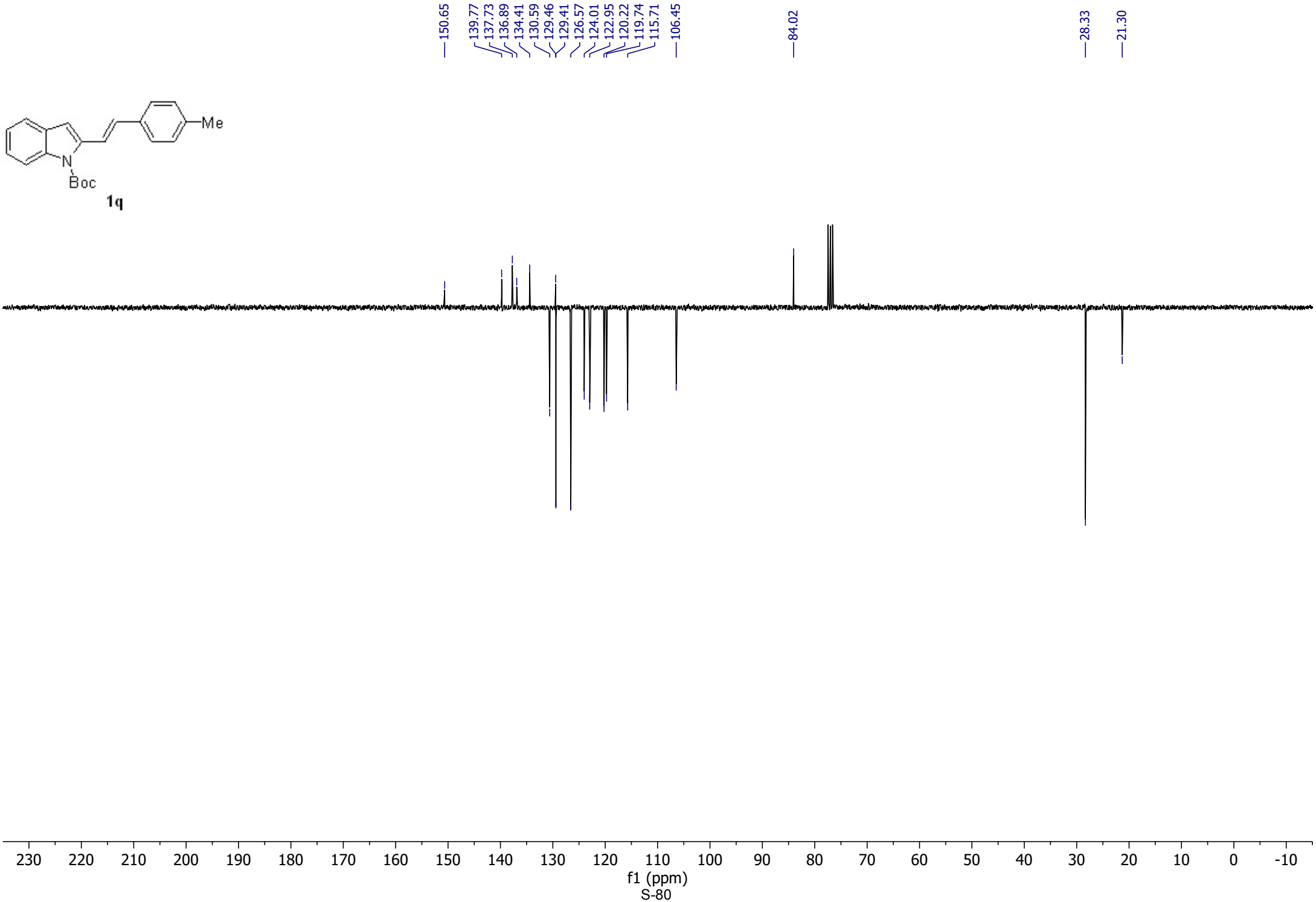


^{1}H NMR (300 MHz, $CDCl_3$)

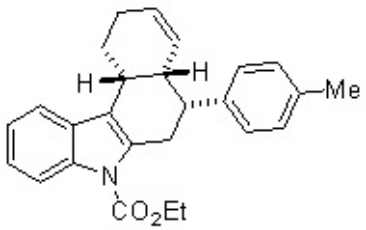


1q

^{13}C NMR (75 MHz, $CDCl_3$)

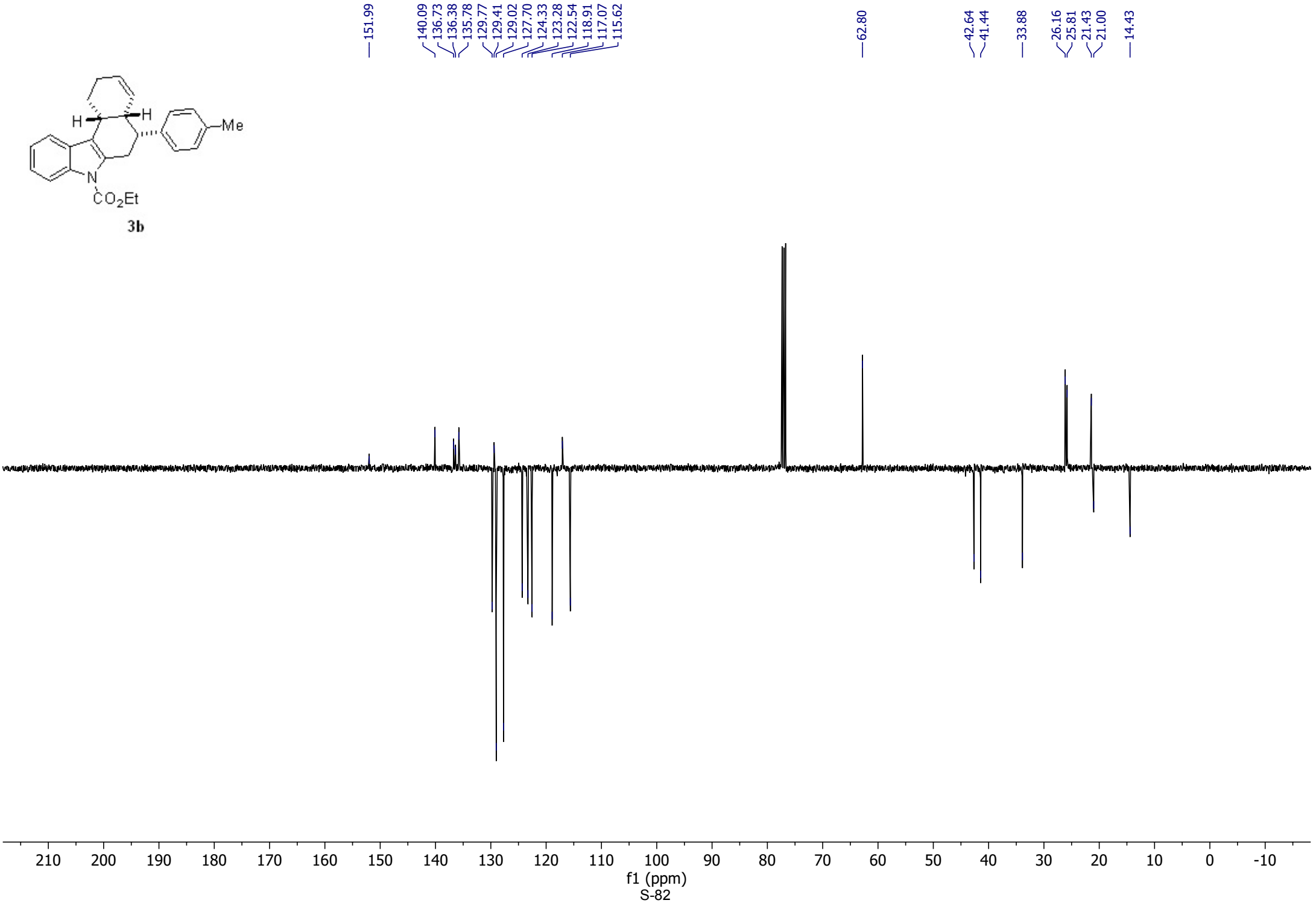


^{1}H NMR (400 MHz, $CDCl_3$)

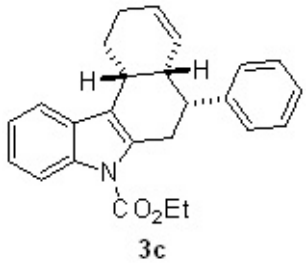


3b

^{13}C NMR (101 MHz, $CDCl_3$)

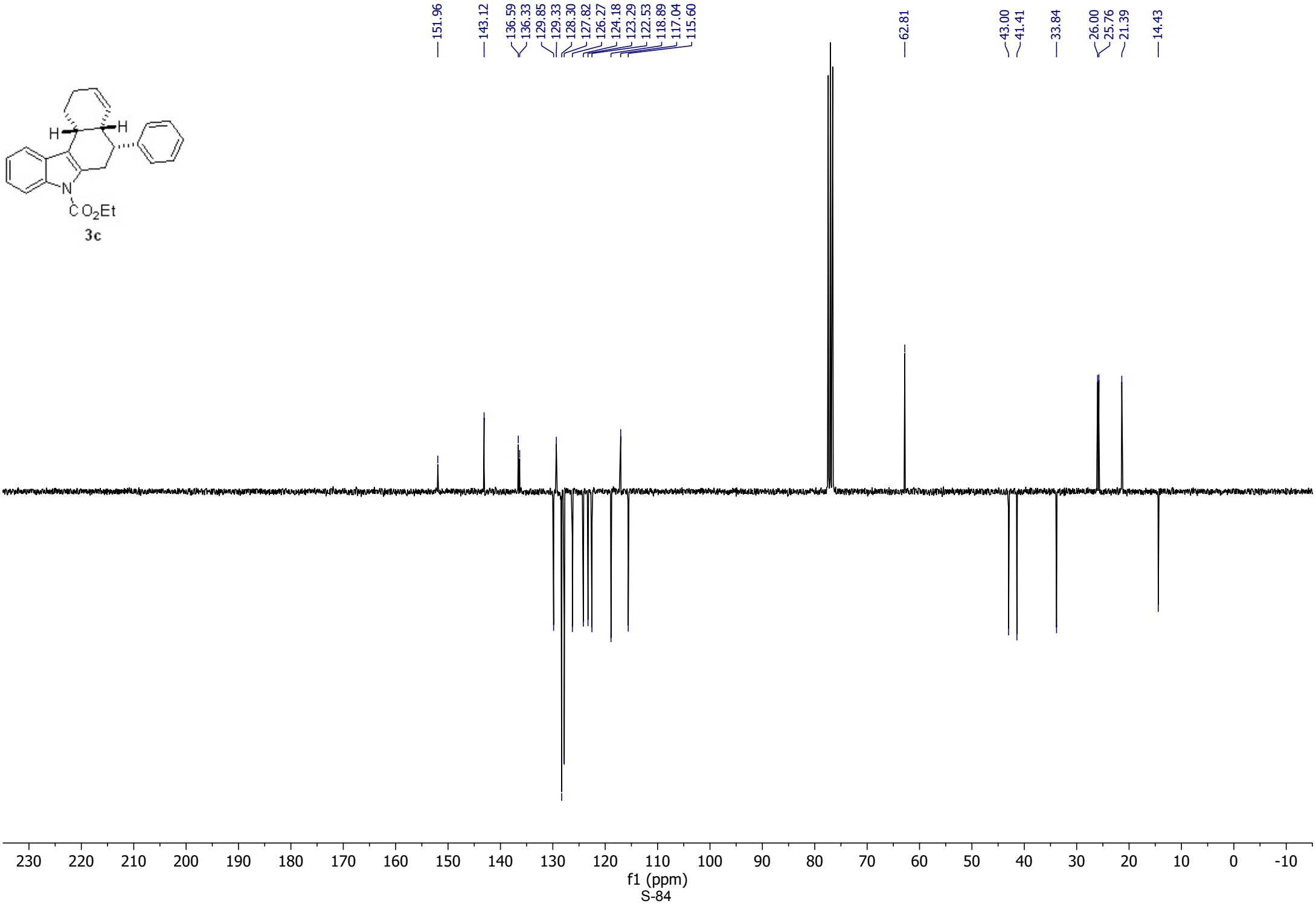


^{1}H NMR (300 MHz, $CDCl_3$)

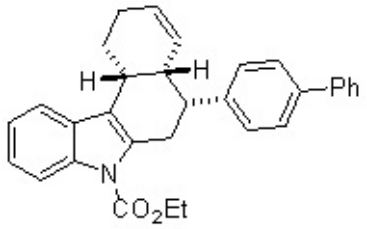


3c

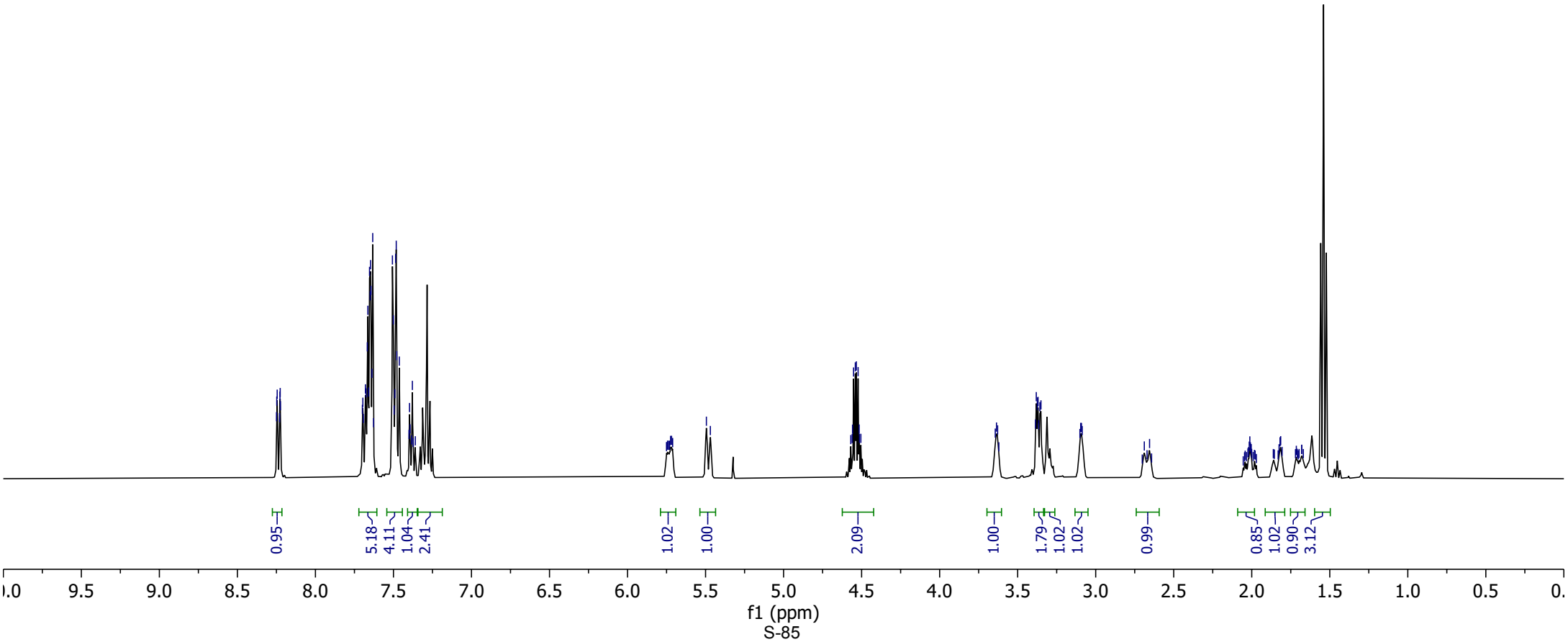
^{13}C NMR (75 MHz, $CDCl_3$).



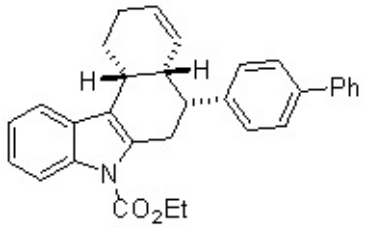
^{1}H NMR (400 MHz, $CDCl_3$)



3d

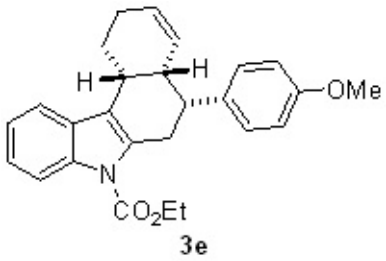


^{13}C NMR (101 MHz, $CDCl_3$)

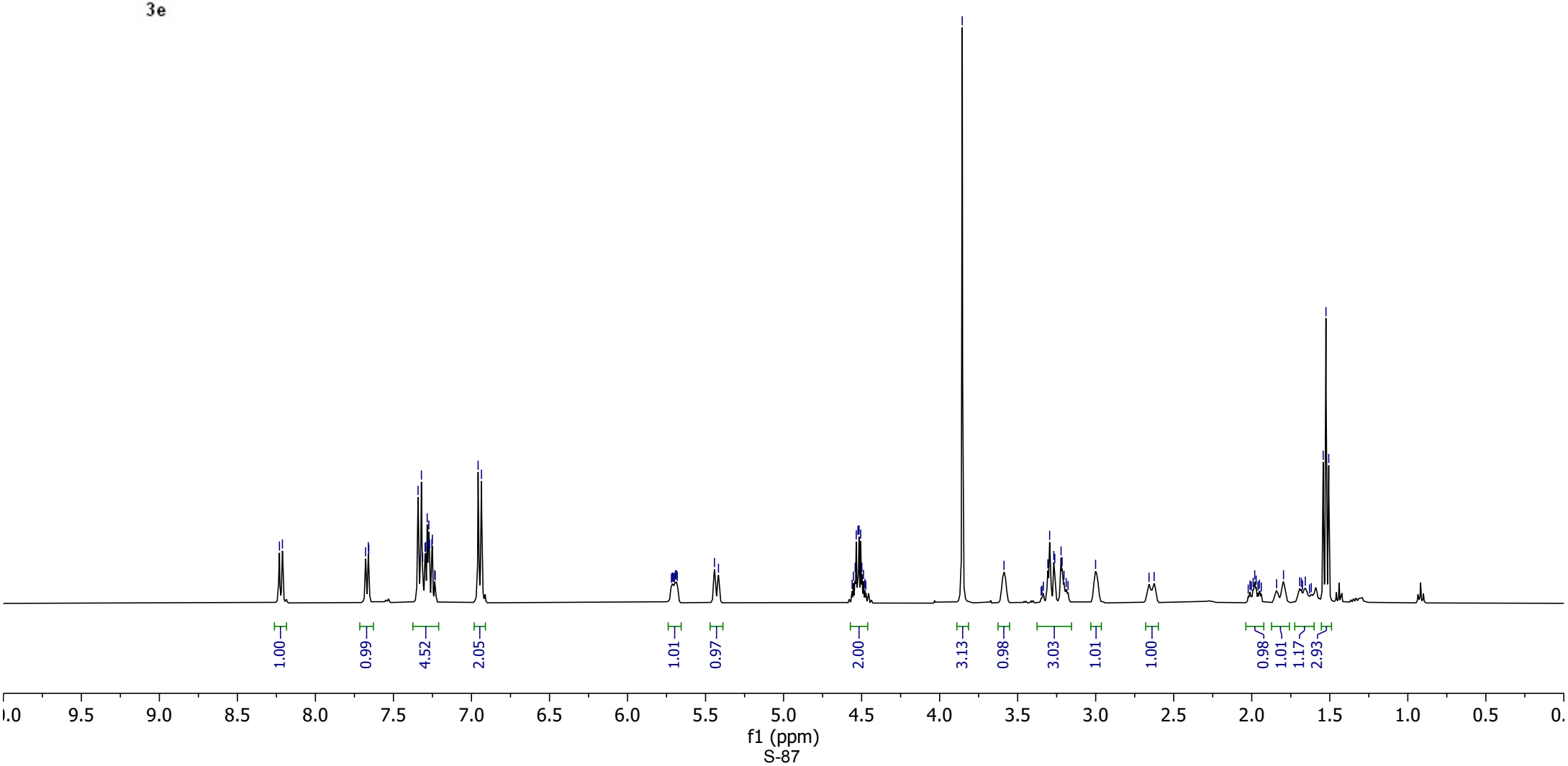


3d

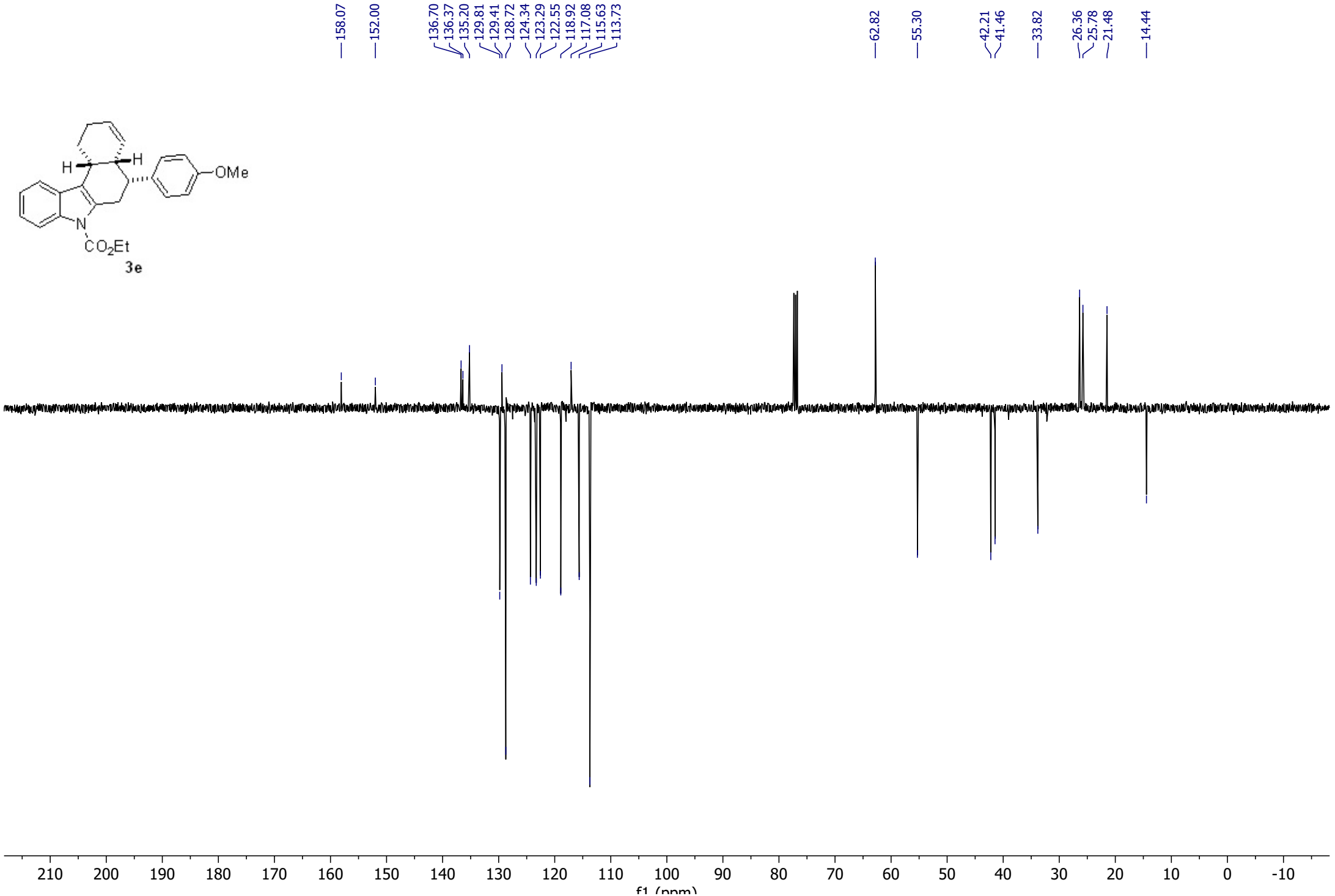
^{1}H NMR (400 MHz, $CDCl_3$)



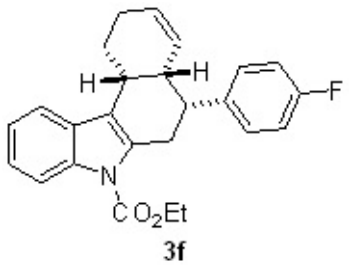
3e



^{13}C NMR (101 MHz, $CDCl_3$)

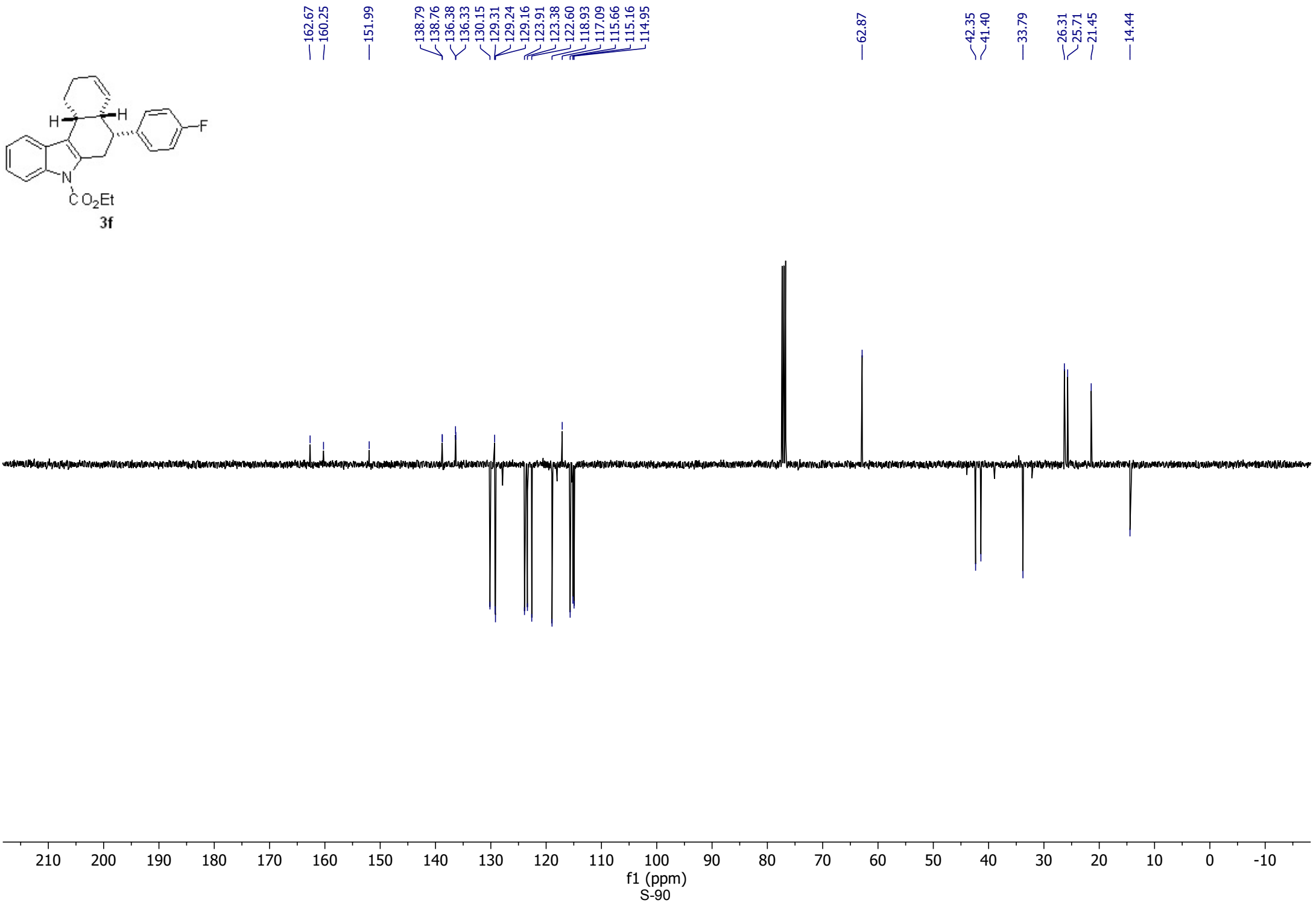


^{1}H NMR (400 MHz, $CDCl_3$)

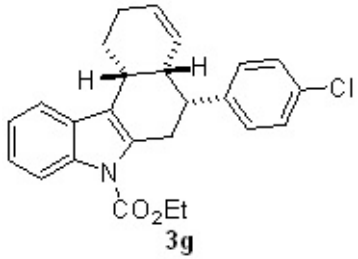


3f

^{13}C NMR (101 MHz, $CDCl_3$)

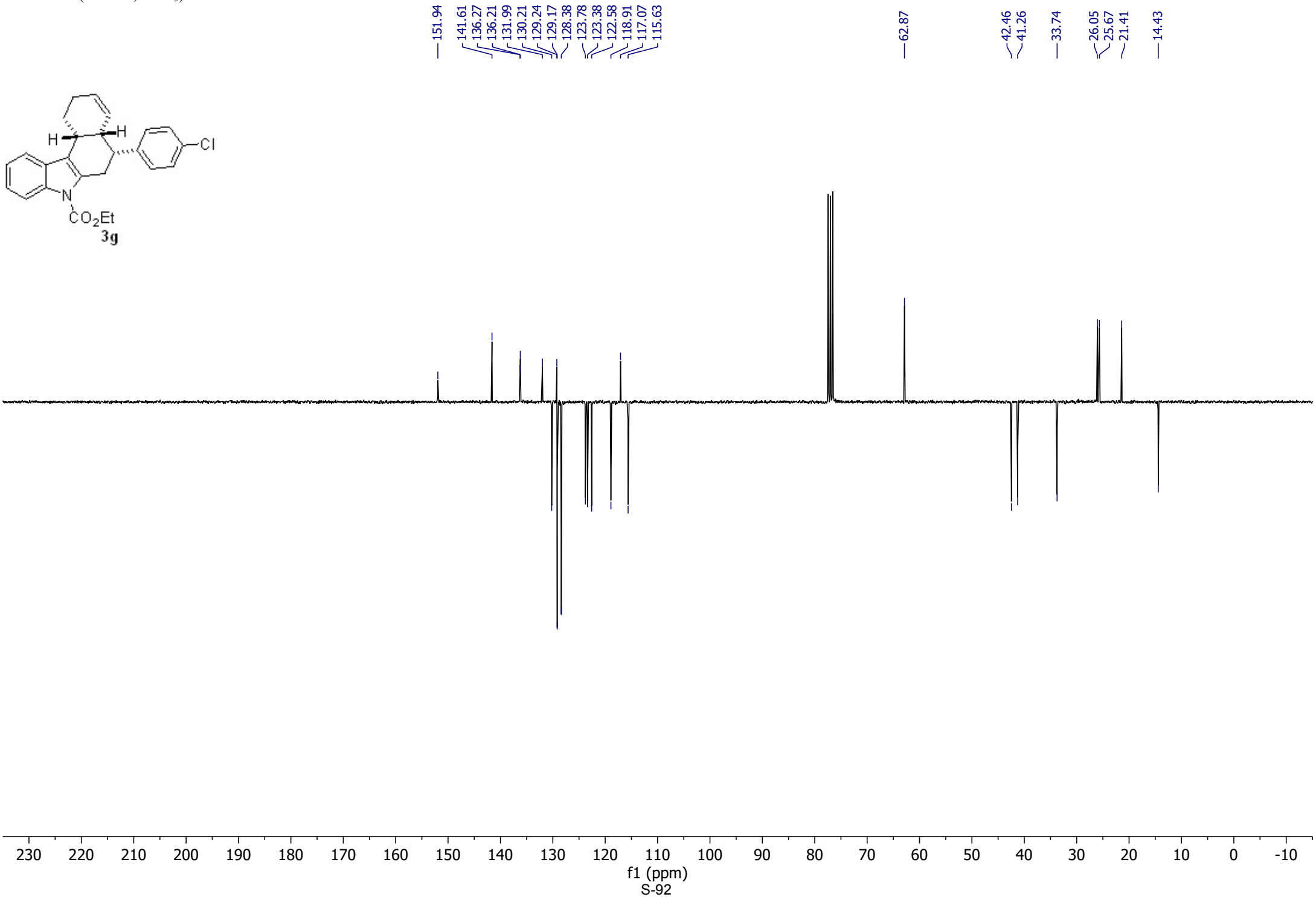


^{1}H NMR (300 MHz, $CDCl_3$)

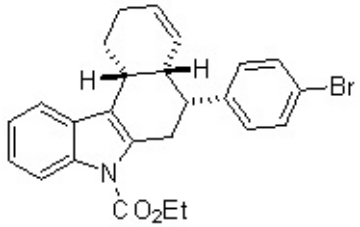


3g

^{13}C NMR (75 MHz, $CDCl_3$)



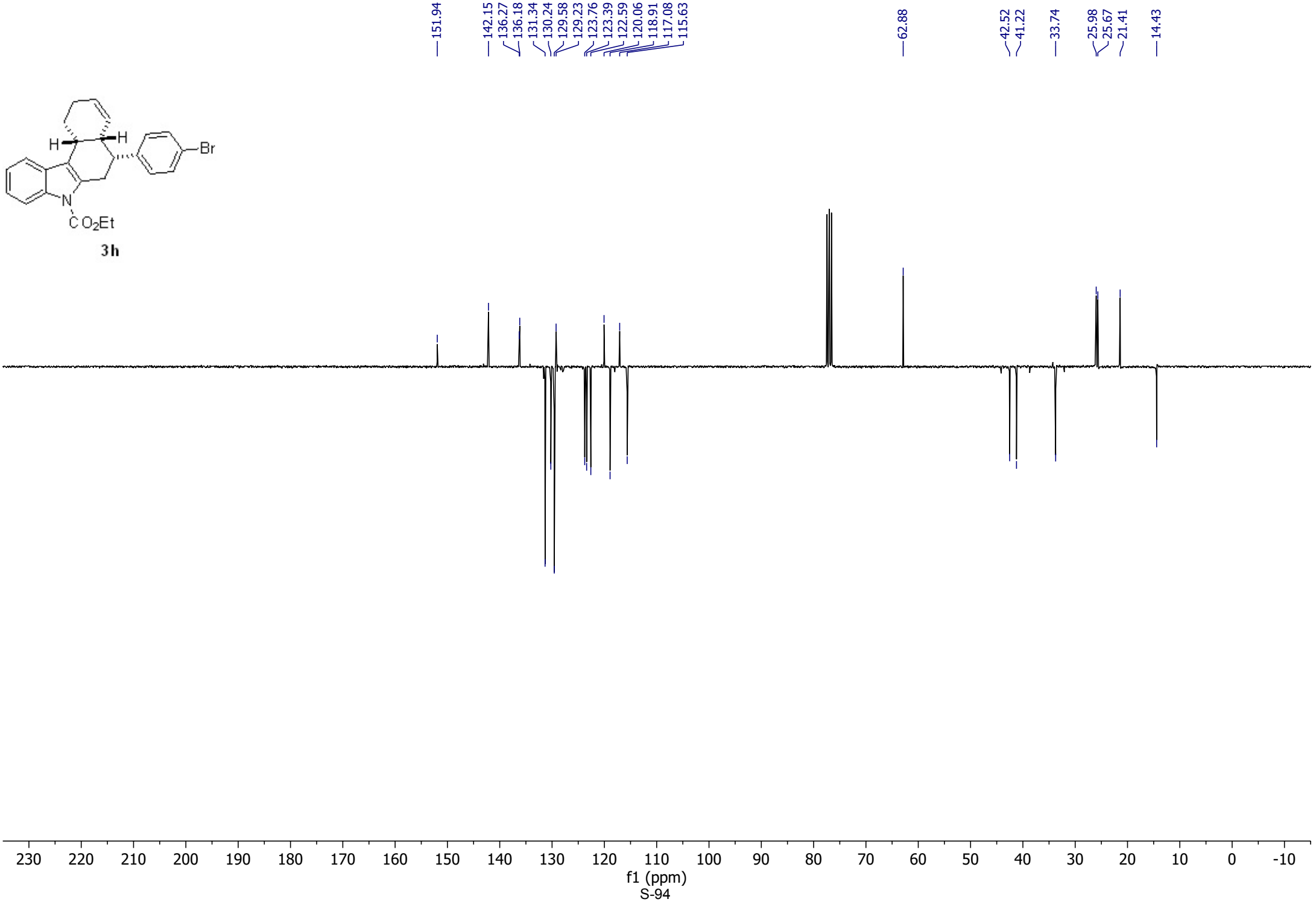
^{1}H NMR (300 MHz, $CDCl_3$)



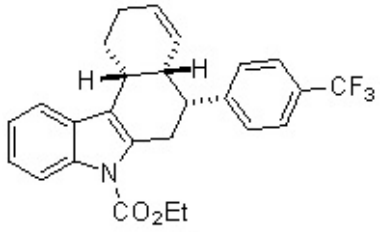
3h

f1 (ppm)

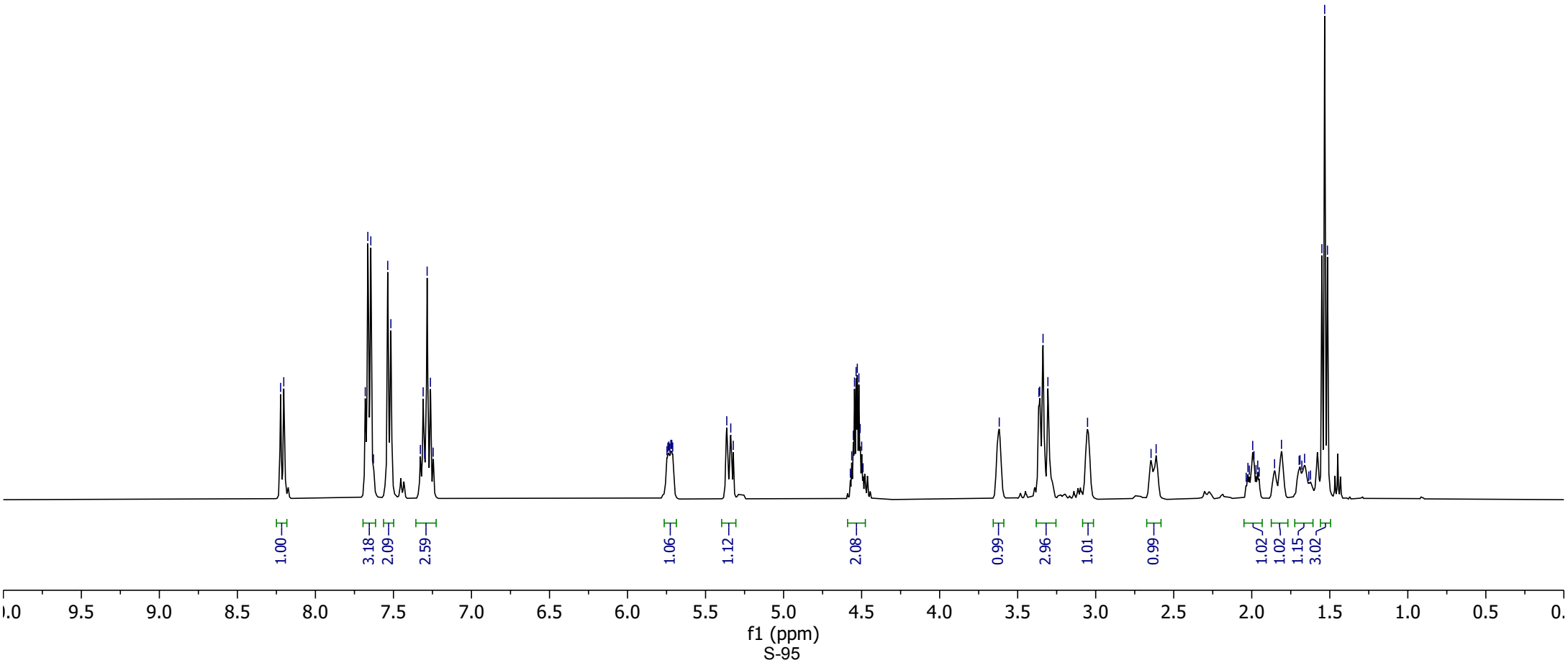
^{13}C NMR (75 MHz, $CDCl_3$)



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

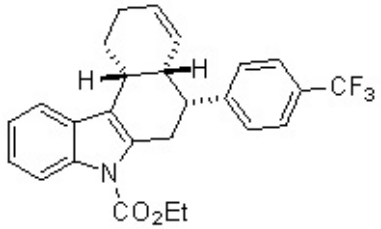


3i

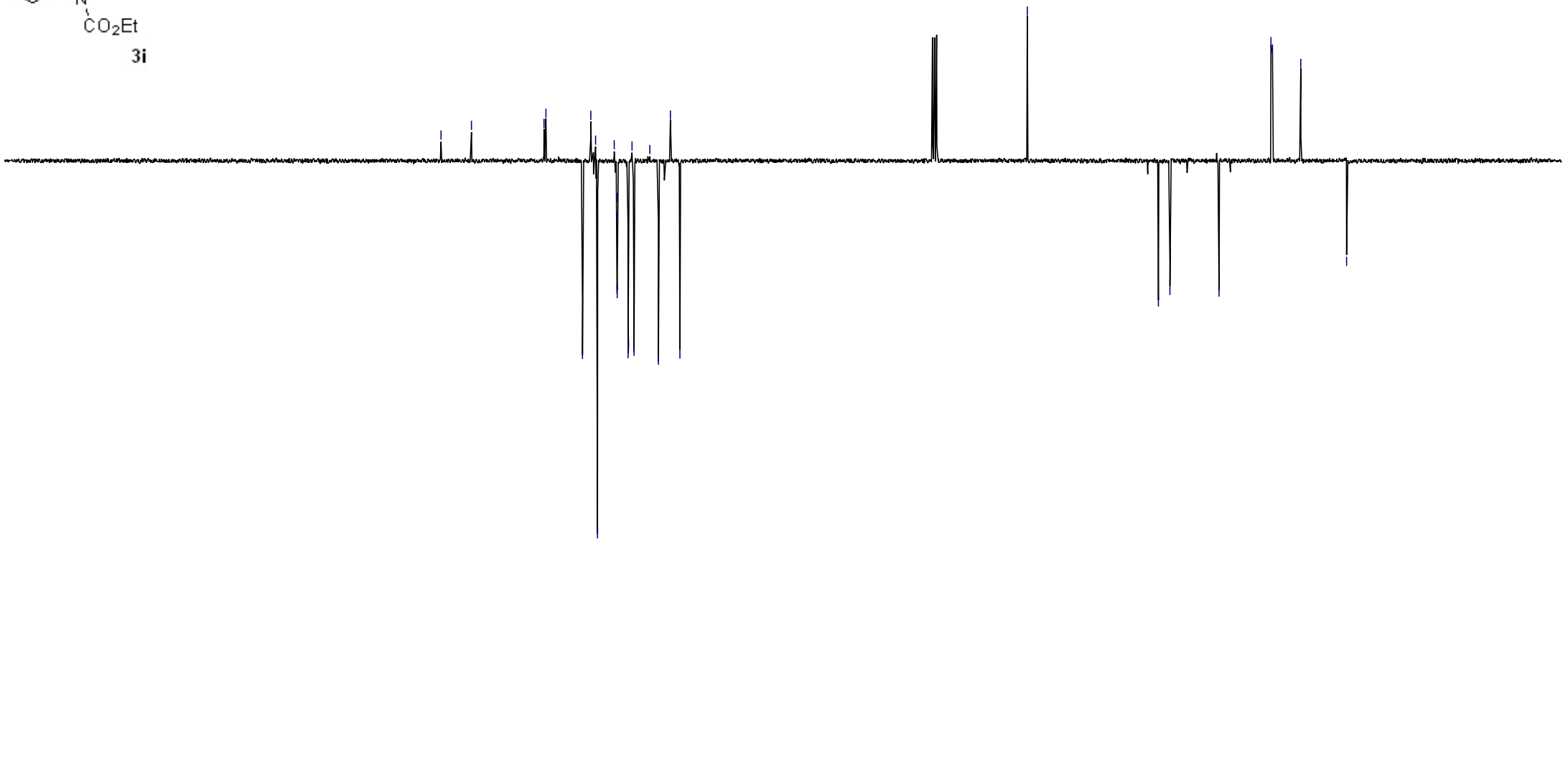


^{13}C NMR (101 MHz, $CDCl_3$)

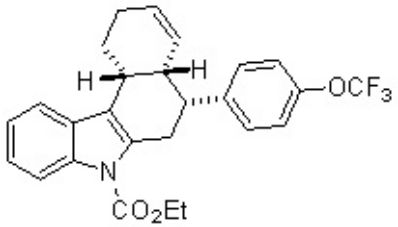
151.97
147.35
136.33
136.04
130.49
129.22
128.50
128.21
125.67
125.29
125.25
125.21
125.18
123.57
123.49
122.97
122.66
120.26
118.96
117.14
115.69
62.93
43.02
41.27
33.81
25.93
25.69
21.40
14.44



3i

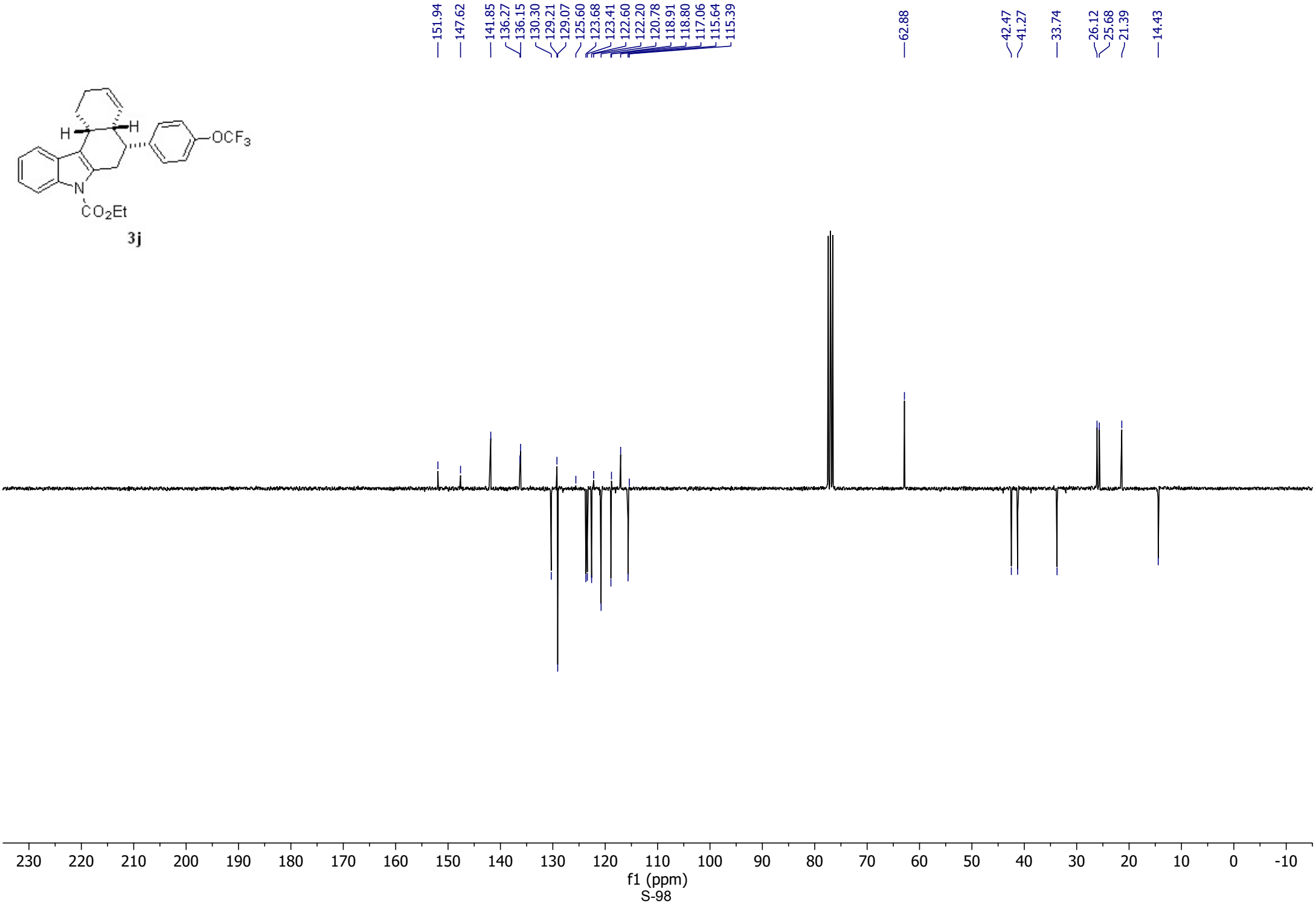


^{1}H NMR (300 MHz, $CDCl_3$)

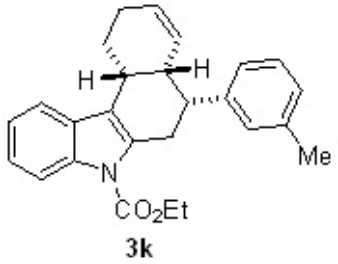


3j

^{13}C NMR (75 MHz, $CDCl_3$)

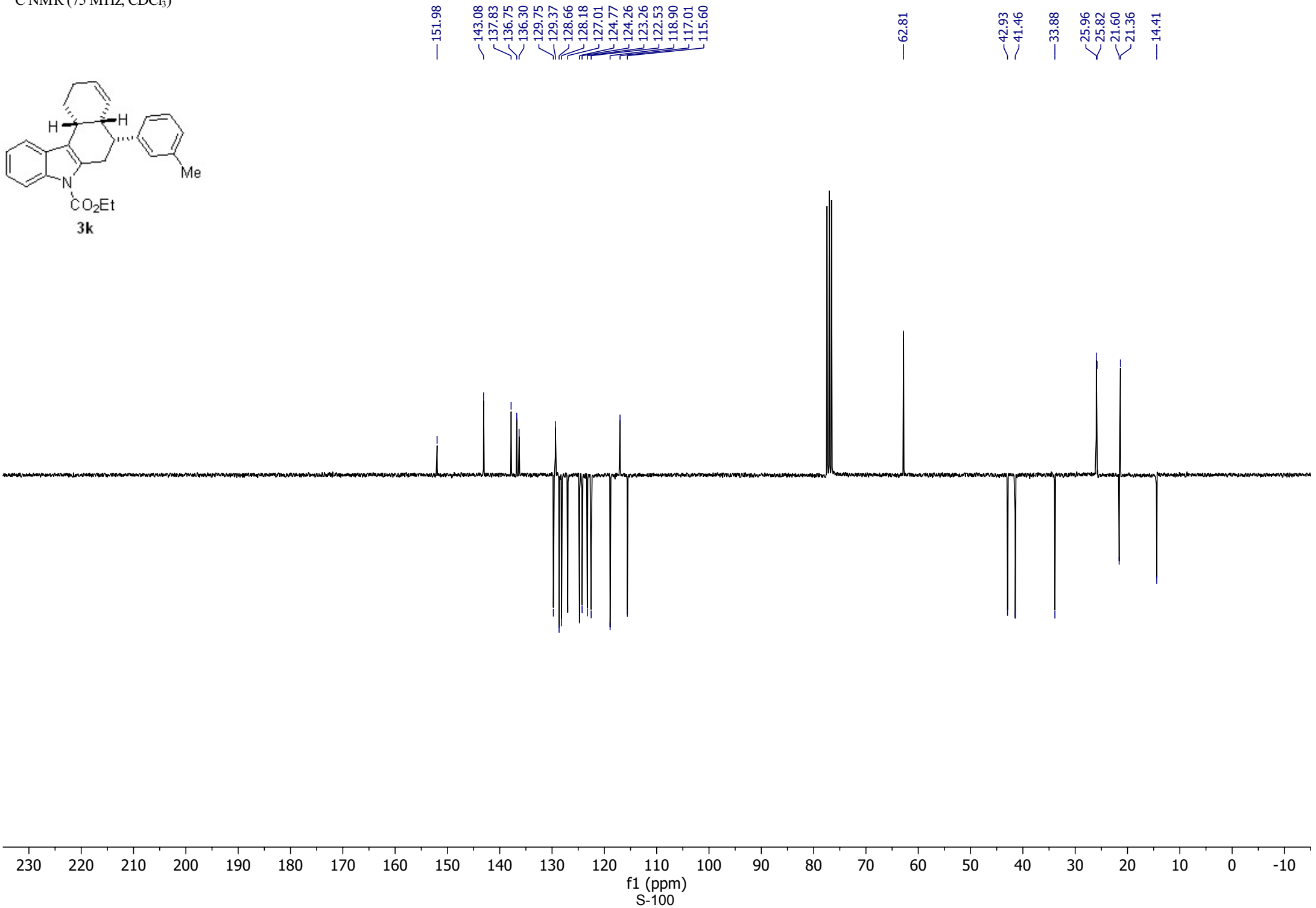


^{1}H NMR (300 MHz, $CDCl_3$)

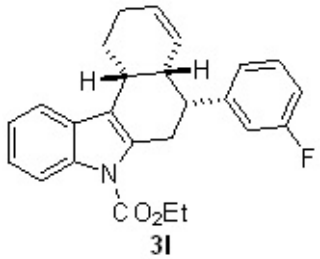


3k

^{13}C NMR (75 MHz, $CDCl_3$)

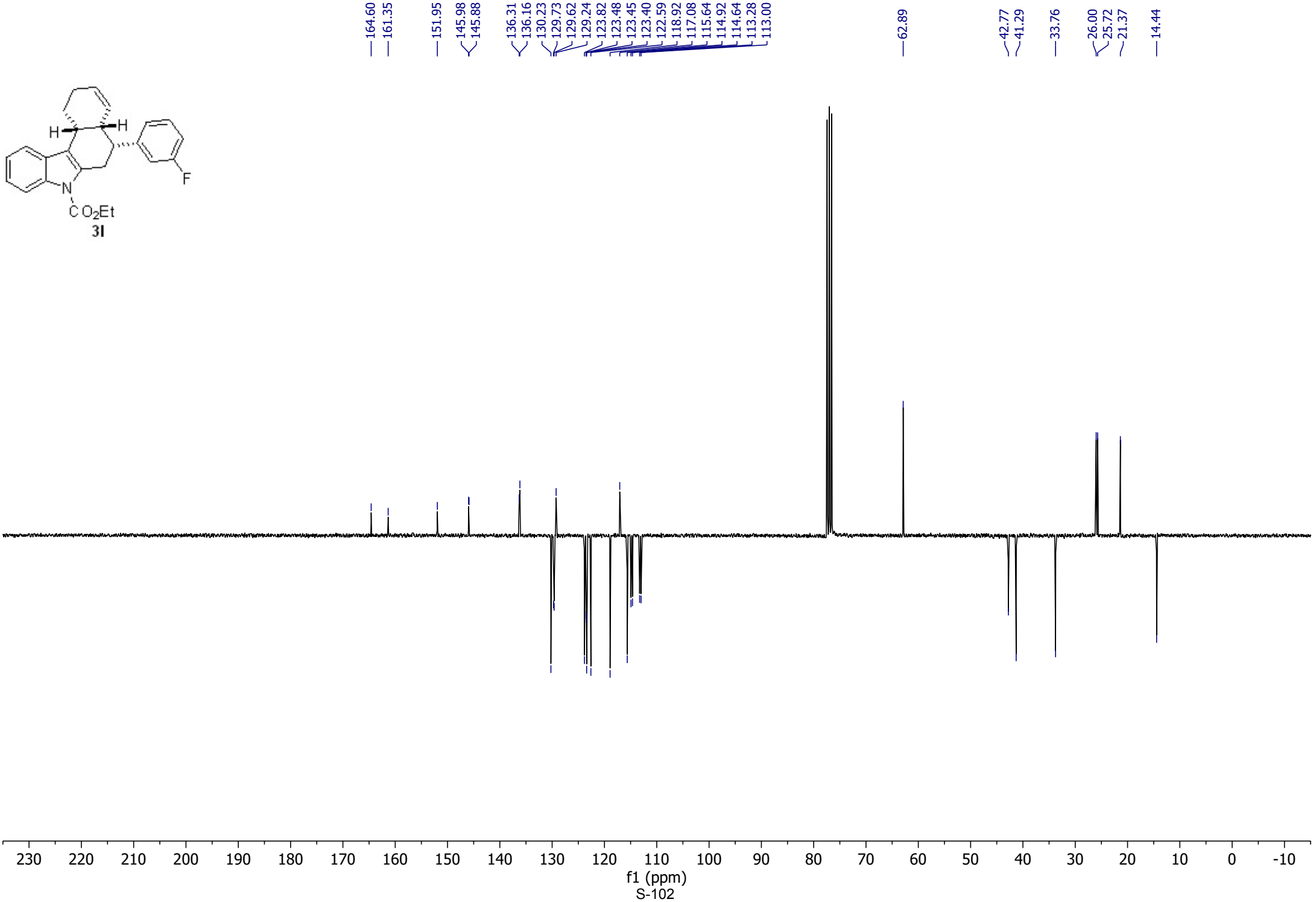


^{1}H NMR (300 MHz, $CDCl_3$)

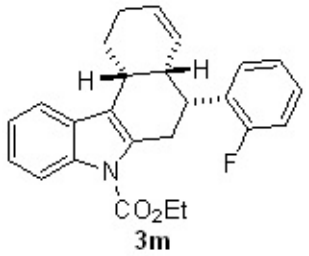


3l

^{13}C NMR (75 MHz, $CDCl_3$)

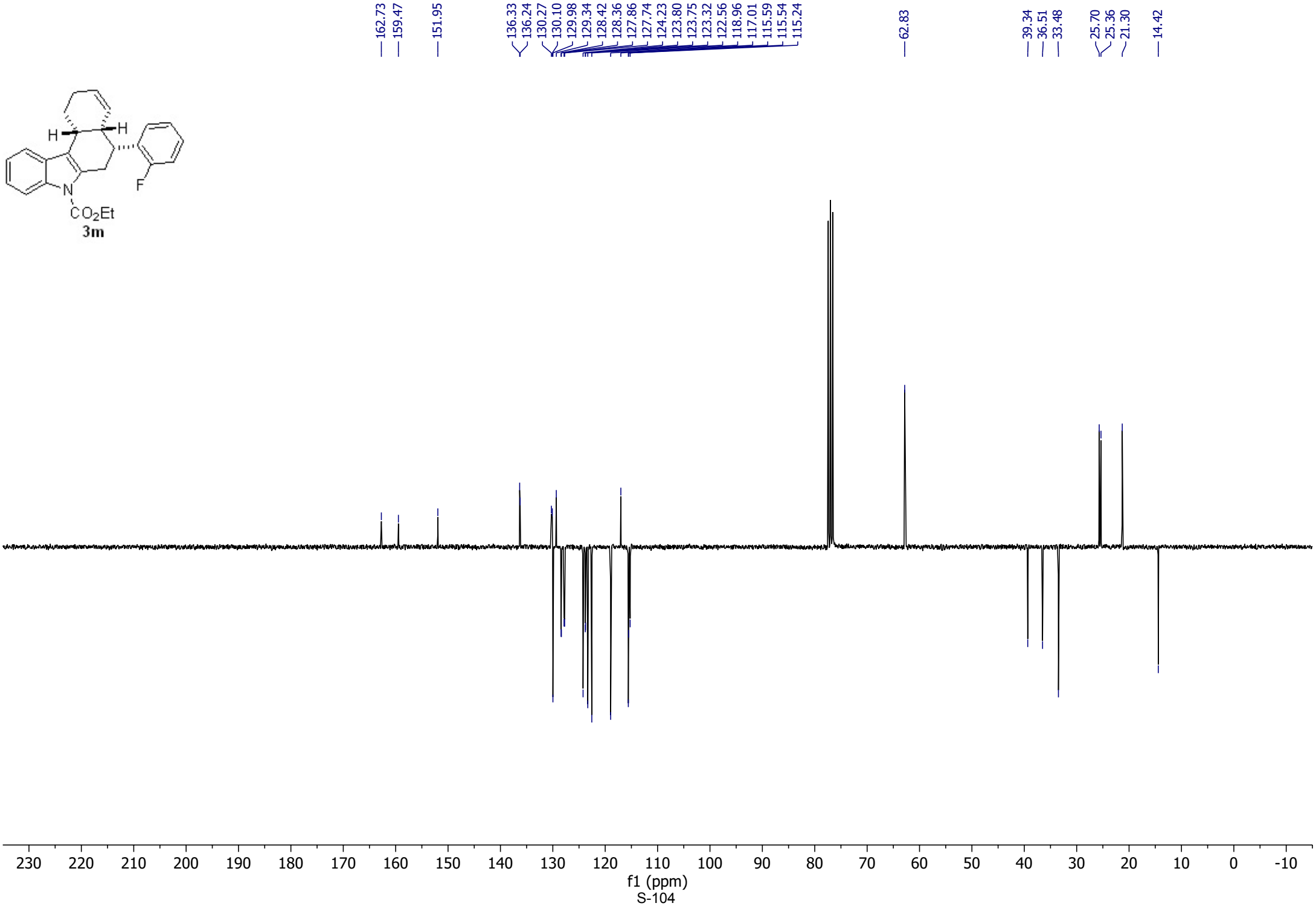


^{1}H NMR (300 MHz, $CDCl_3$)

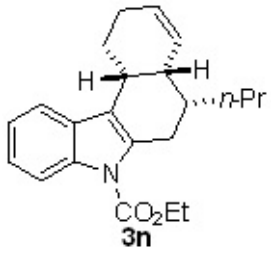


3m

^{13}C NMR (75 MHz, $CDCl_3$)

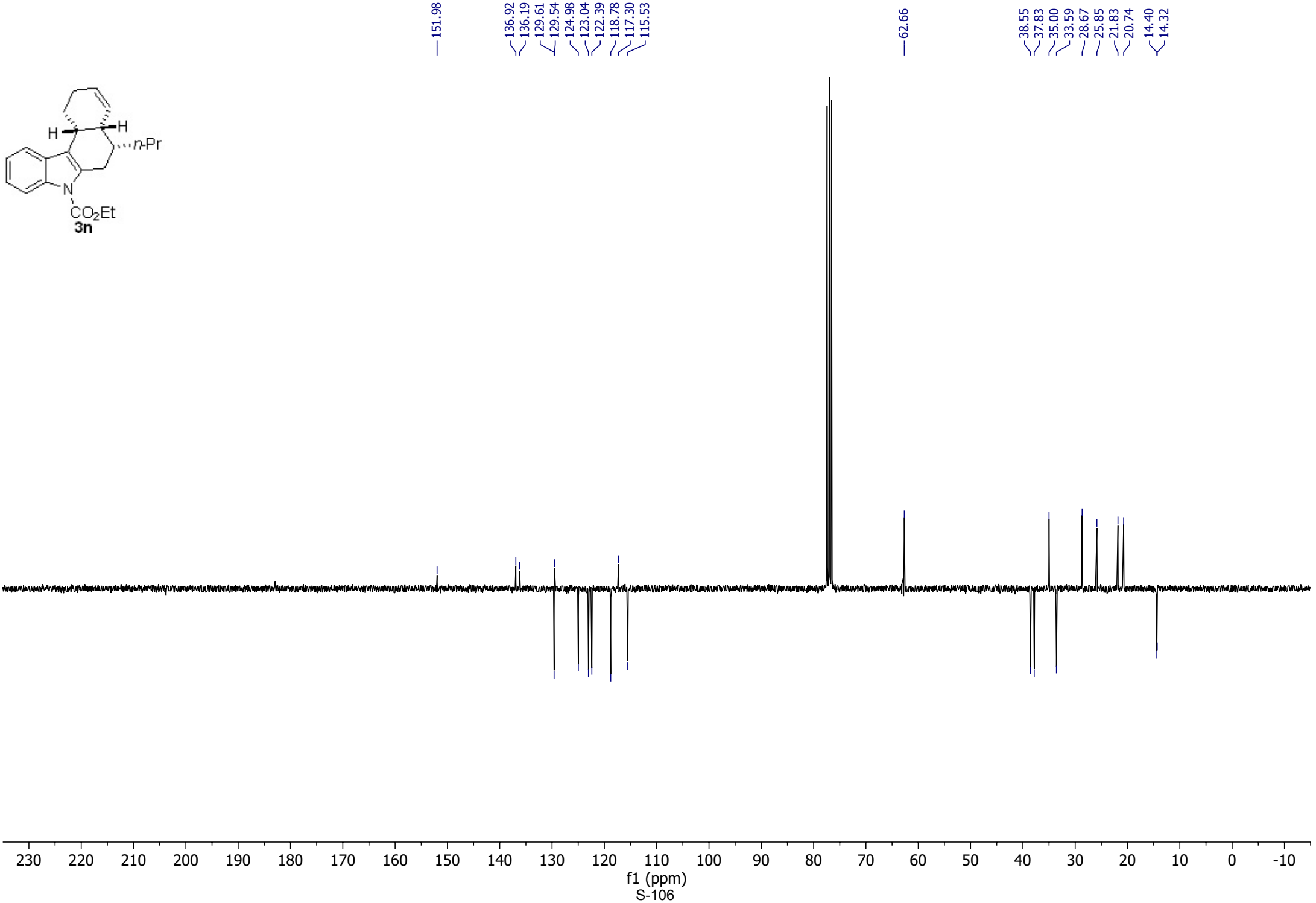


^{1}H NMR (300 MHz, $CDCl_3$)

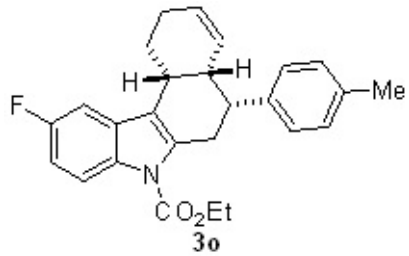


3n

^{13}C NMR (75 MHz, $CDCl_3$)

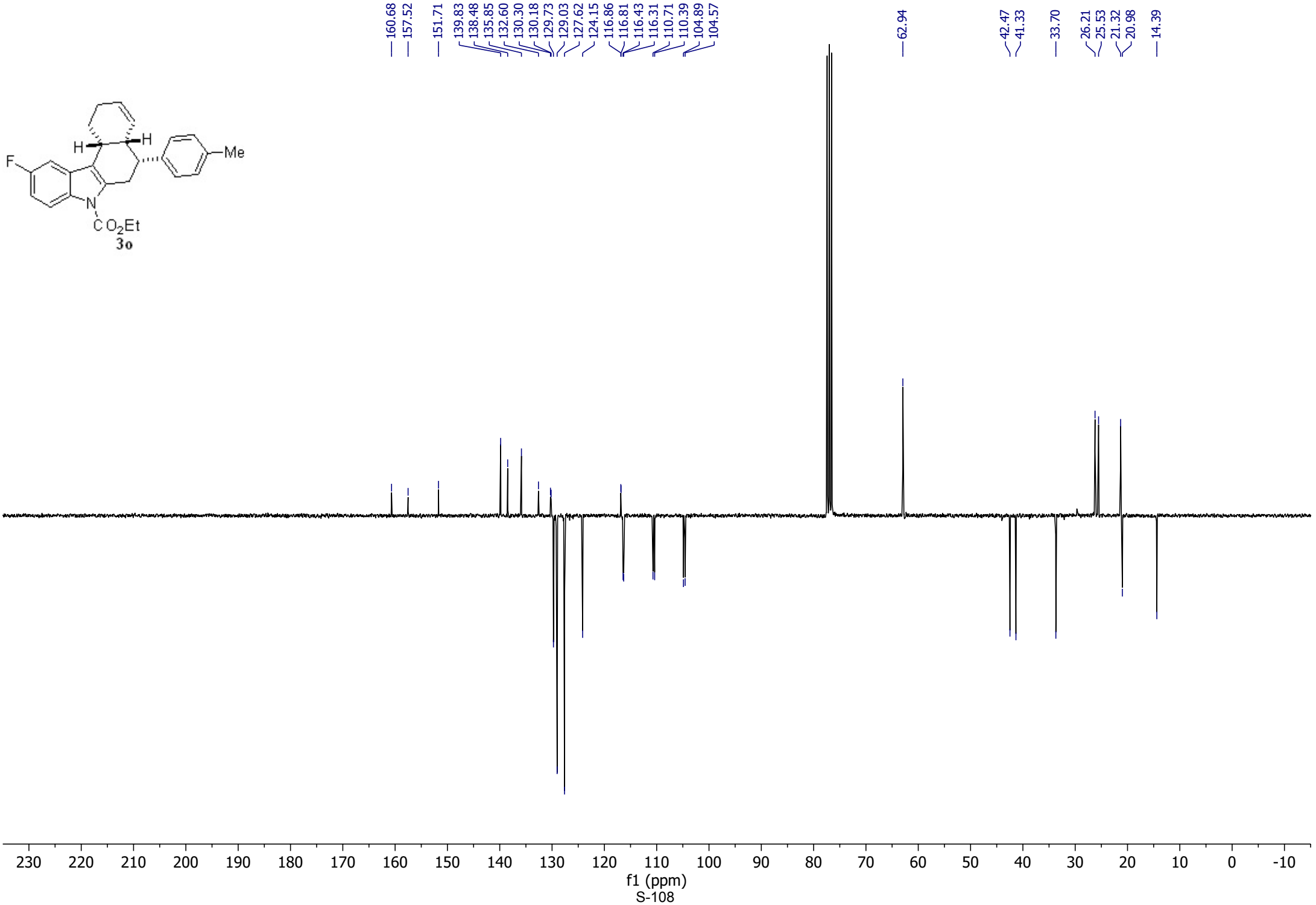


^{1}H NMR (300 MHz, $CDCl_3$)

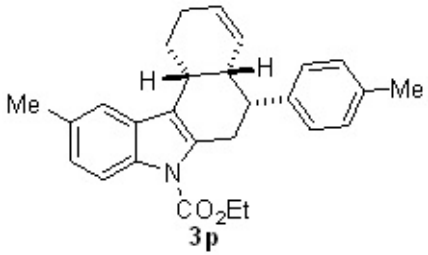


3o

^{13}C NMR (75 MHz, $CDCl_3$)



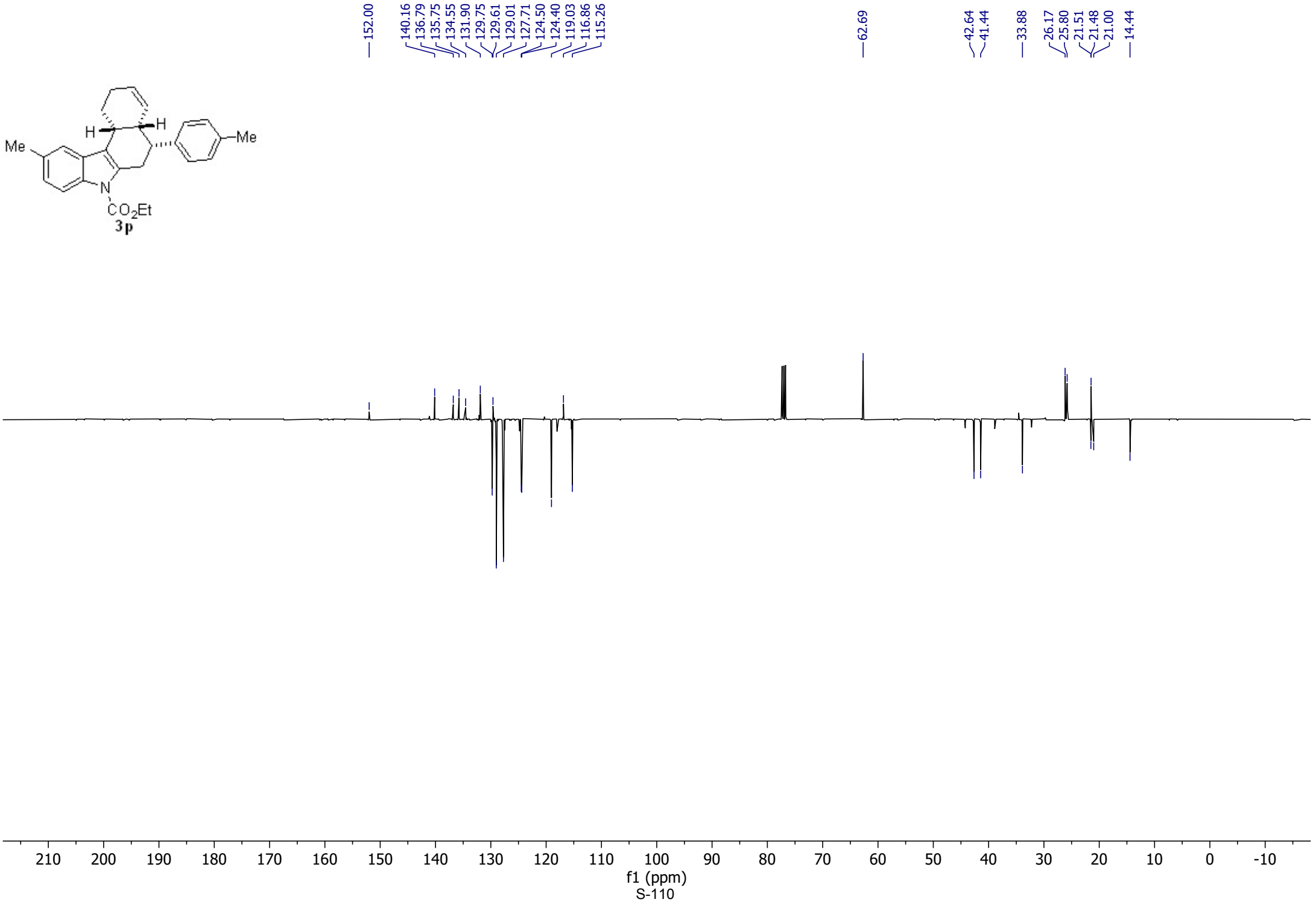
^{1}H NMR (400 MHz, $CDCl_3$)



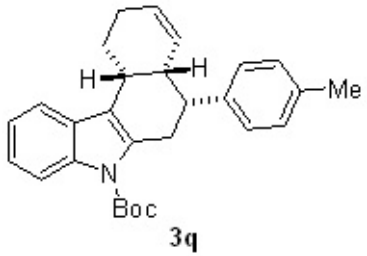
3p

f1 (ppm)

^{13}C NMR (101 MHz, $CDCl_3$)



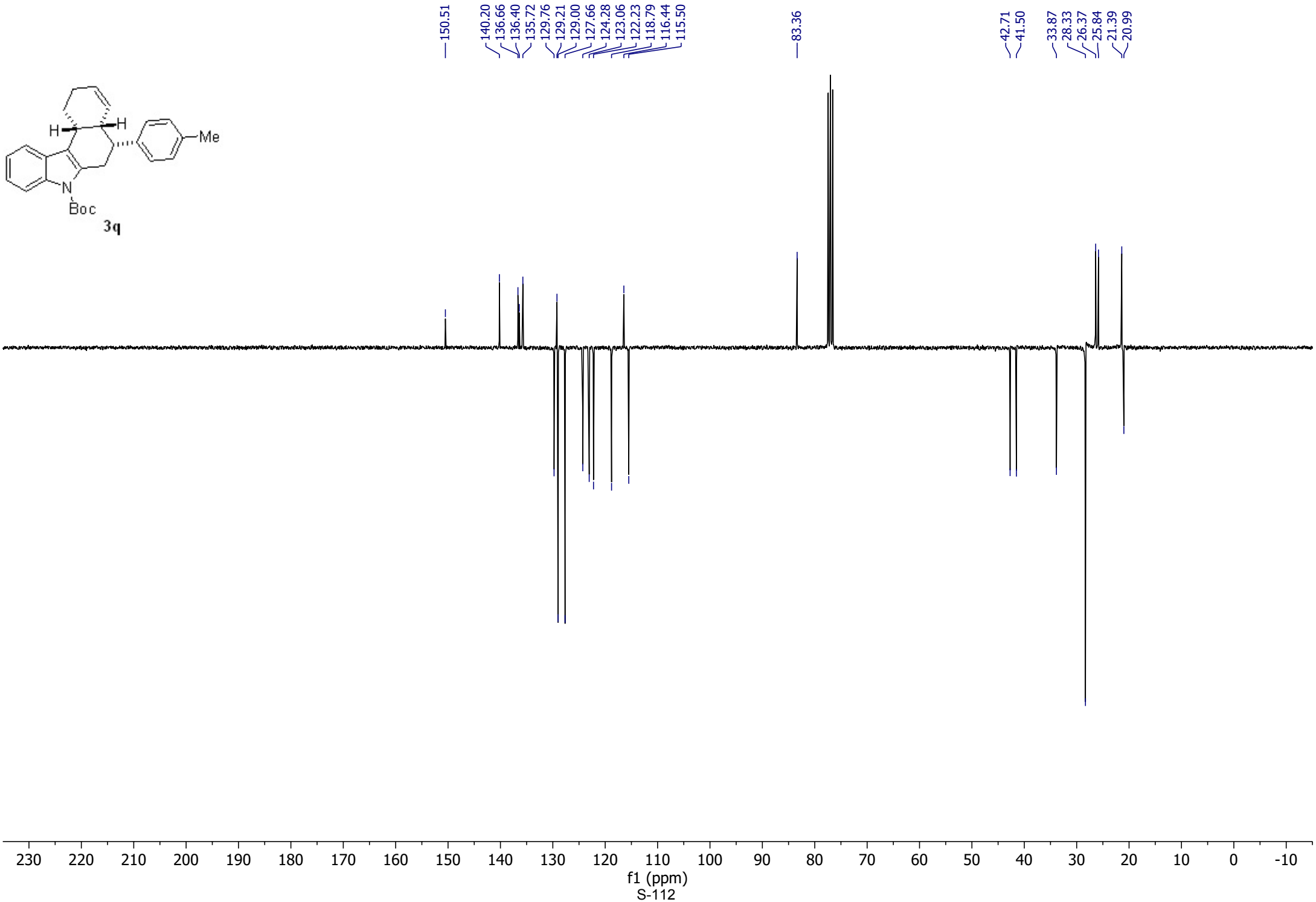
^{1}H NMR (300 MHz, $CDCl_3$)



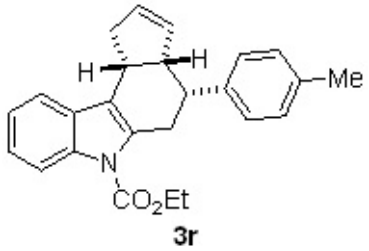
3q

S-111

^{13}C NMR (75 MHz, $CDCl_3$)

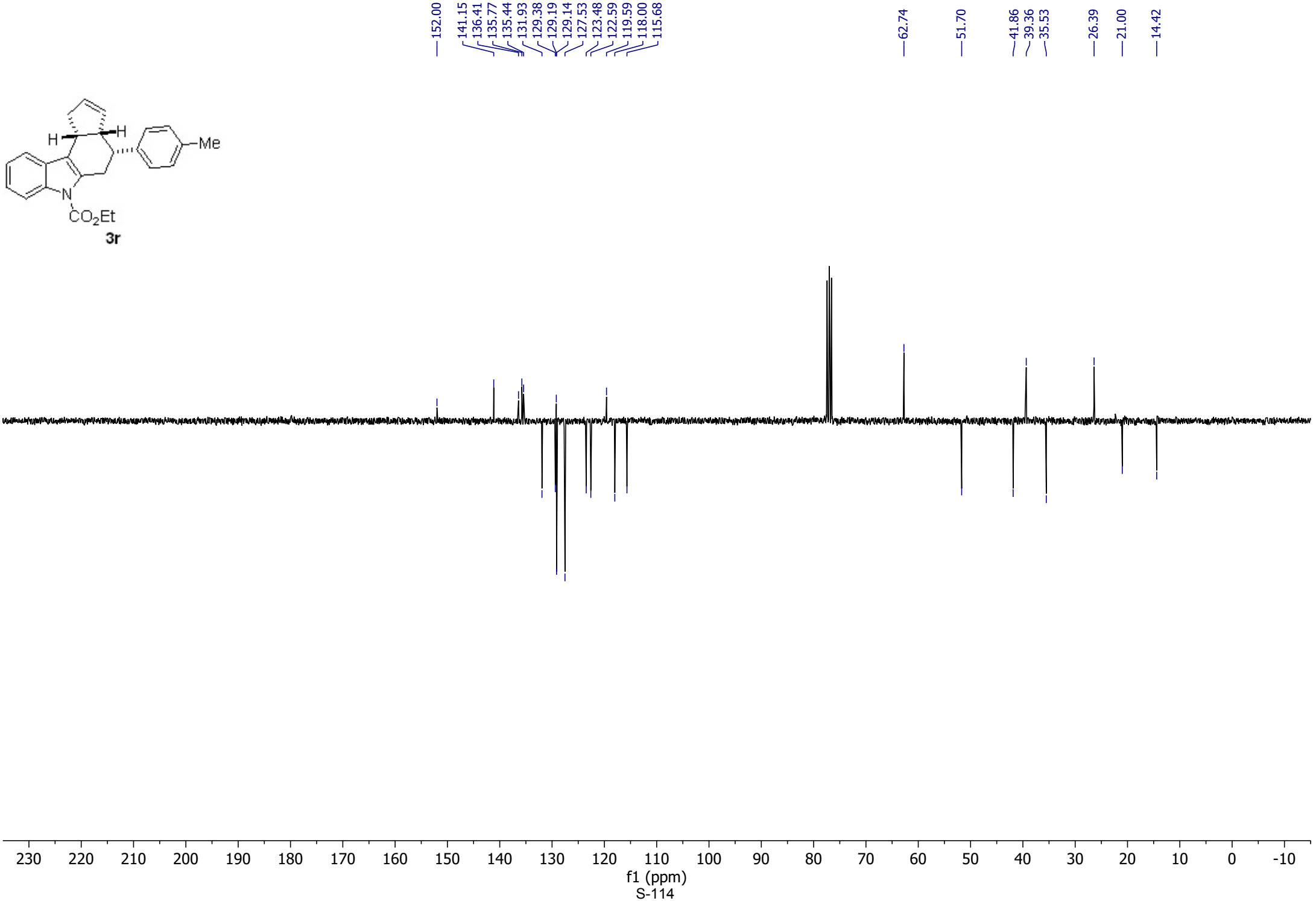


^{1}H NMR (300 MHz, $CDCl_3$)

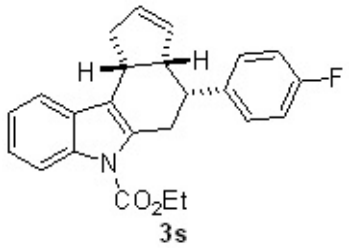


3r

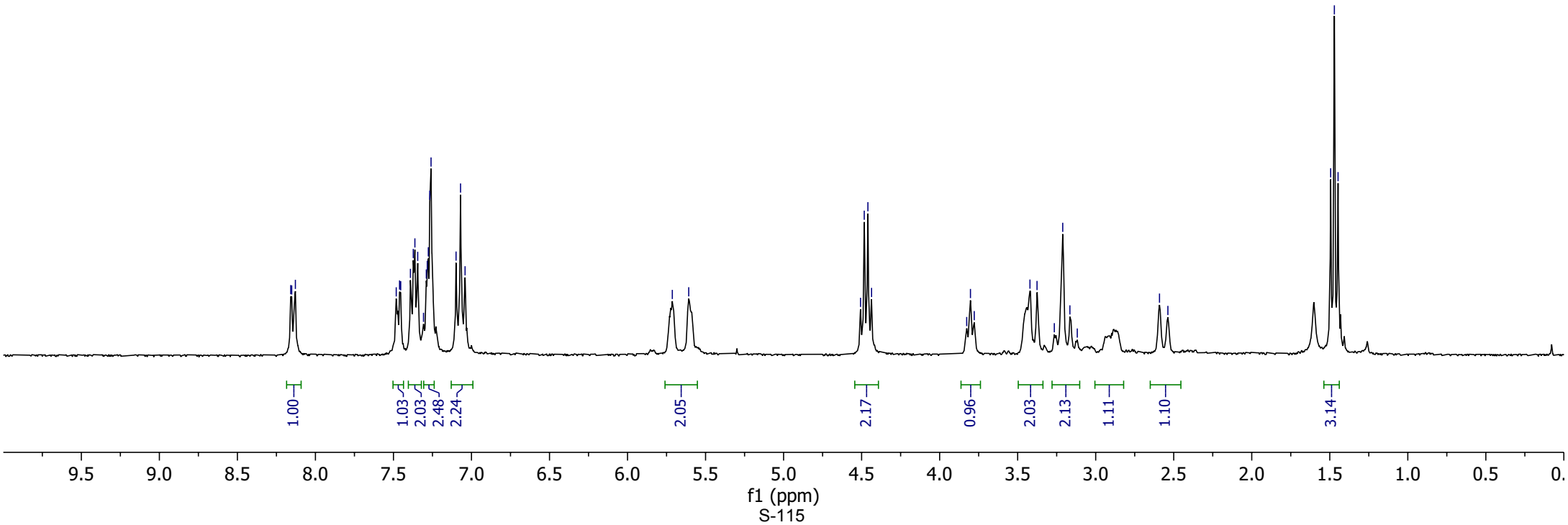
^{13}C NMR (75 MHz, $CDCl_3$)



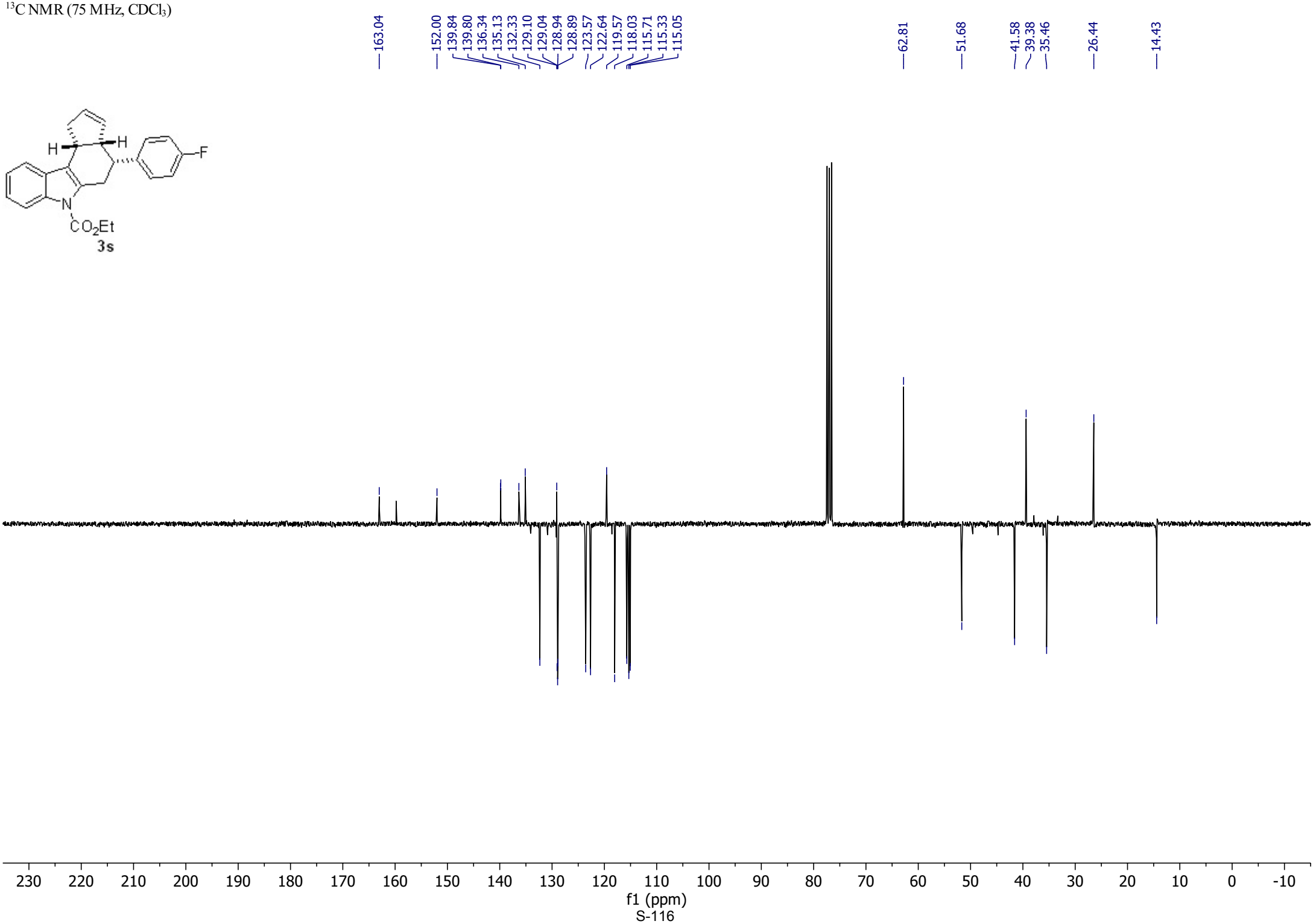
^{1}H NMR (300 MHz, $CDCl_3$)



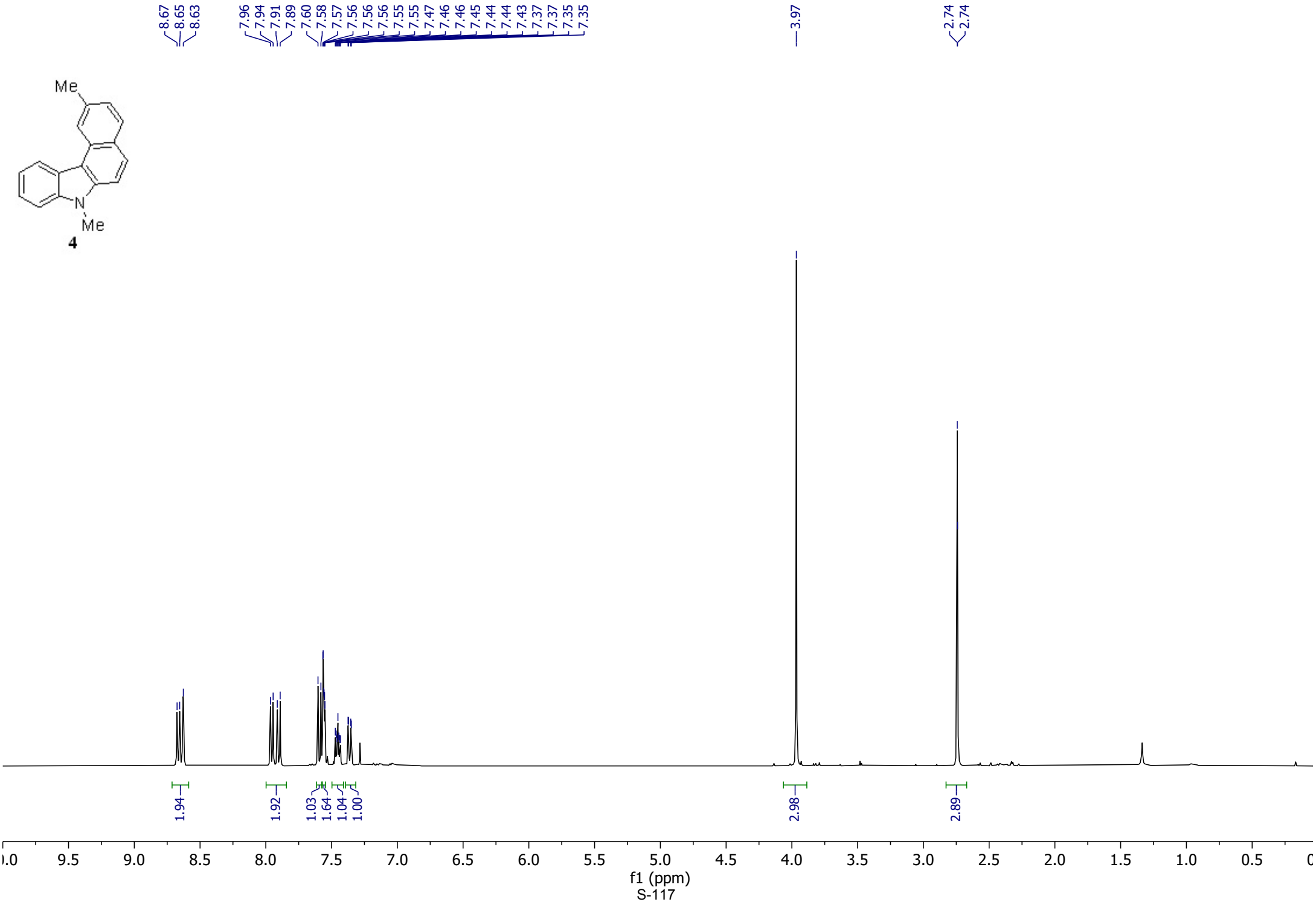
3s



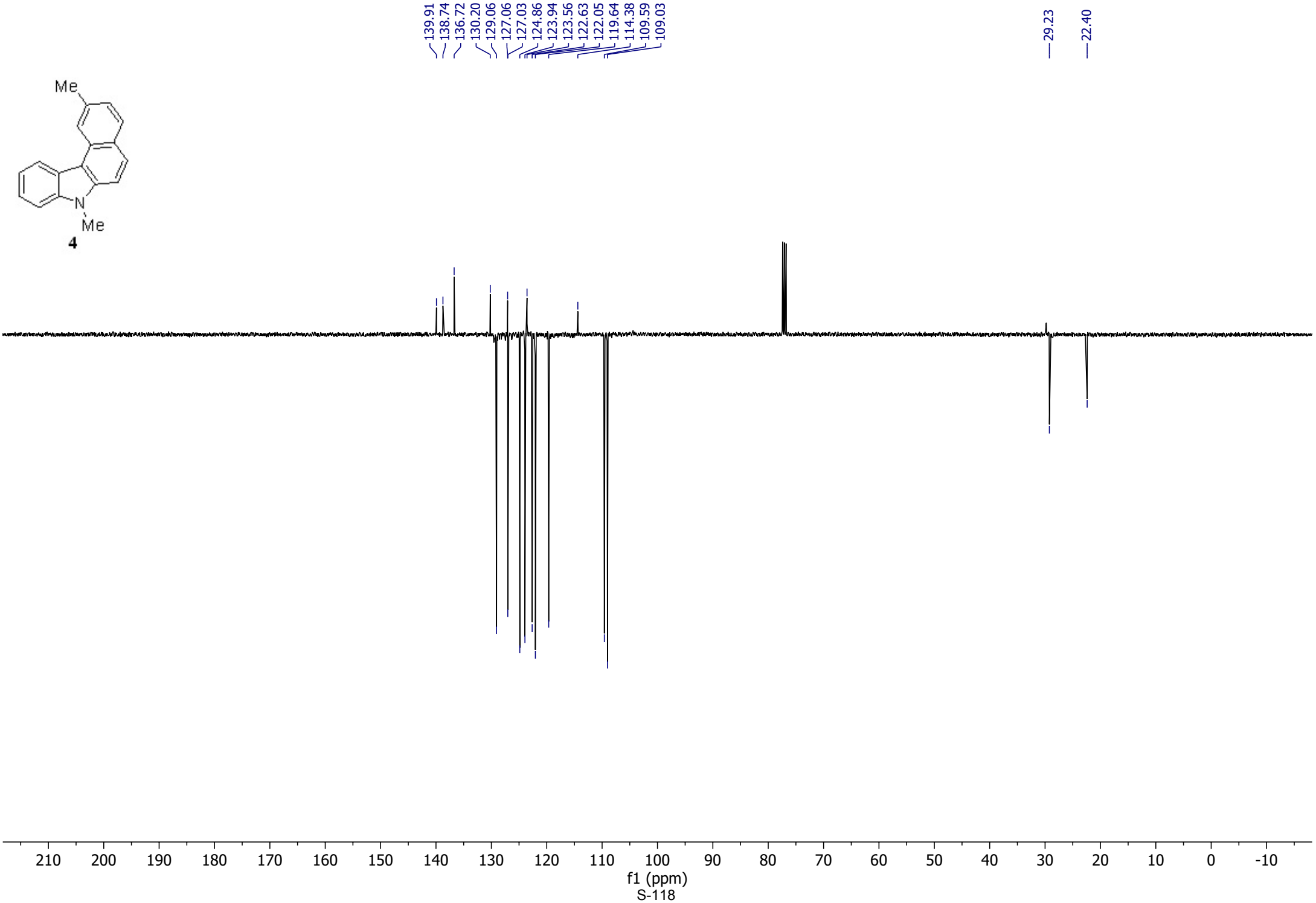
^{13}C NMR (75 MHz, $CDCl_3$)



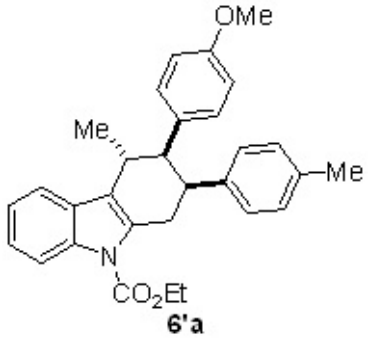
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

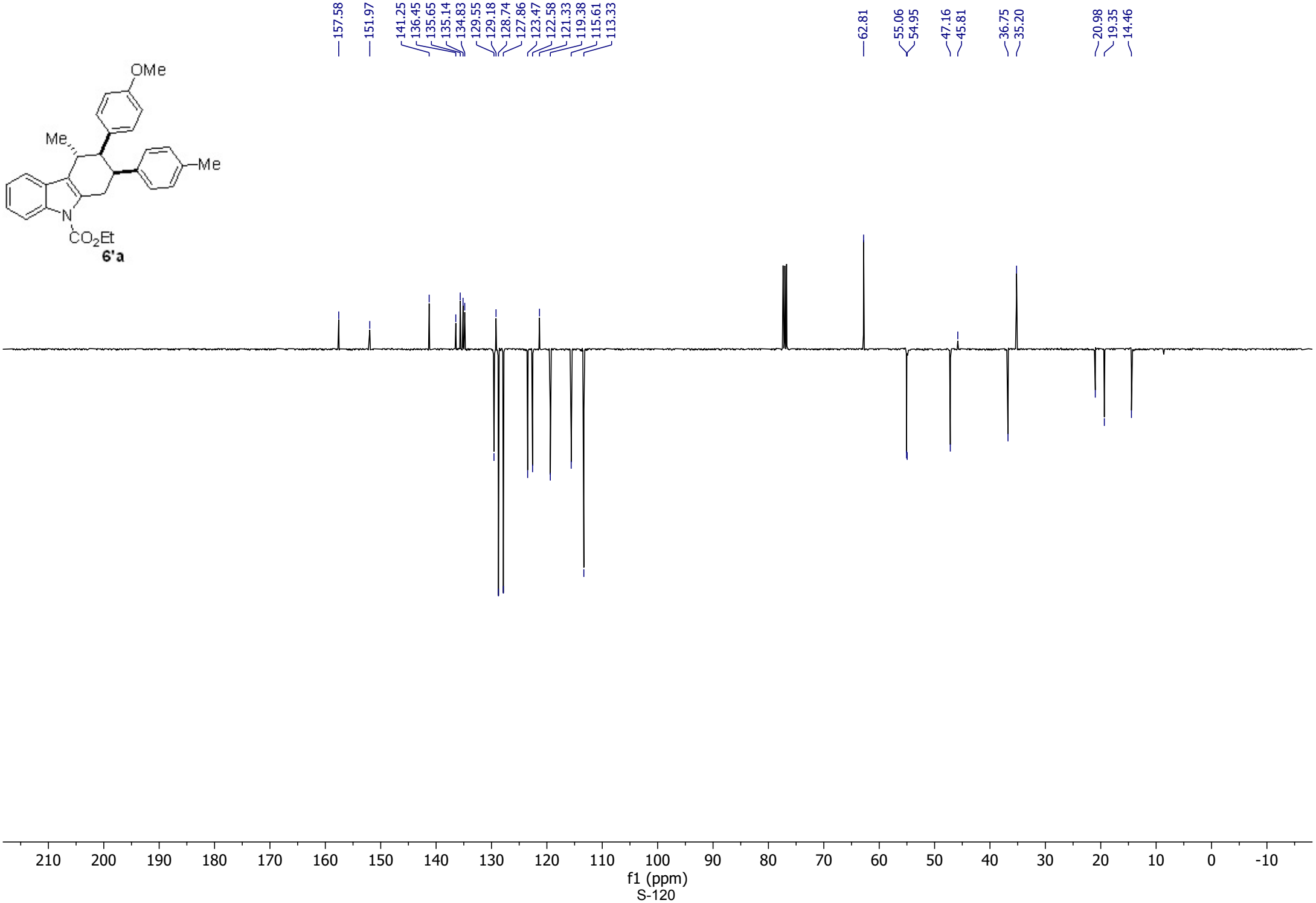


^{1}H NMR (400 MHz, $CDCl_3$)

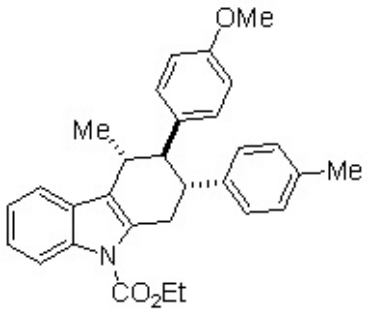


6'a

^{13}C NMR (101 MHz, $CDCl_3$)

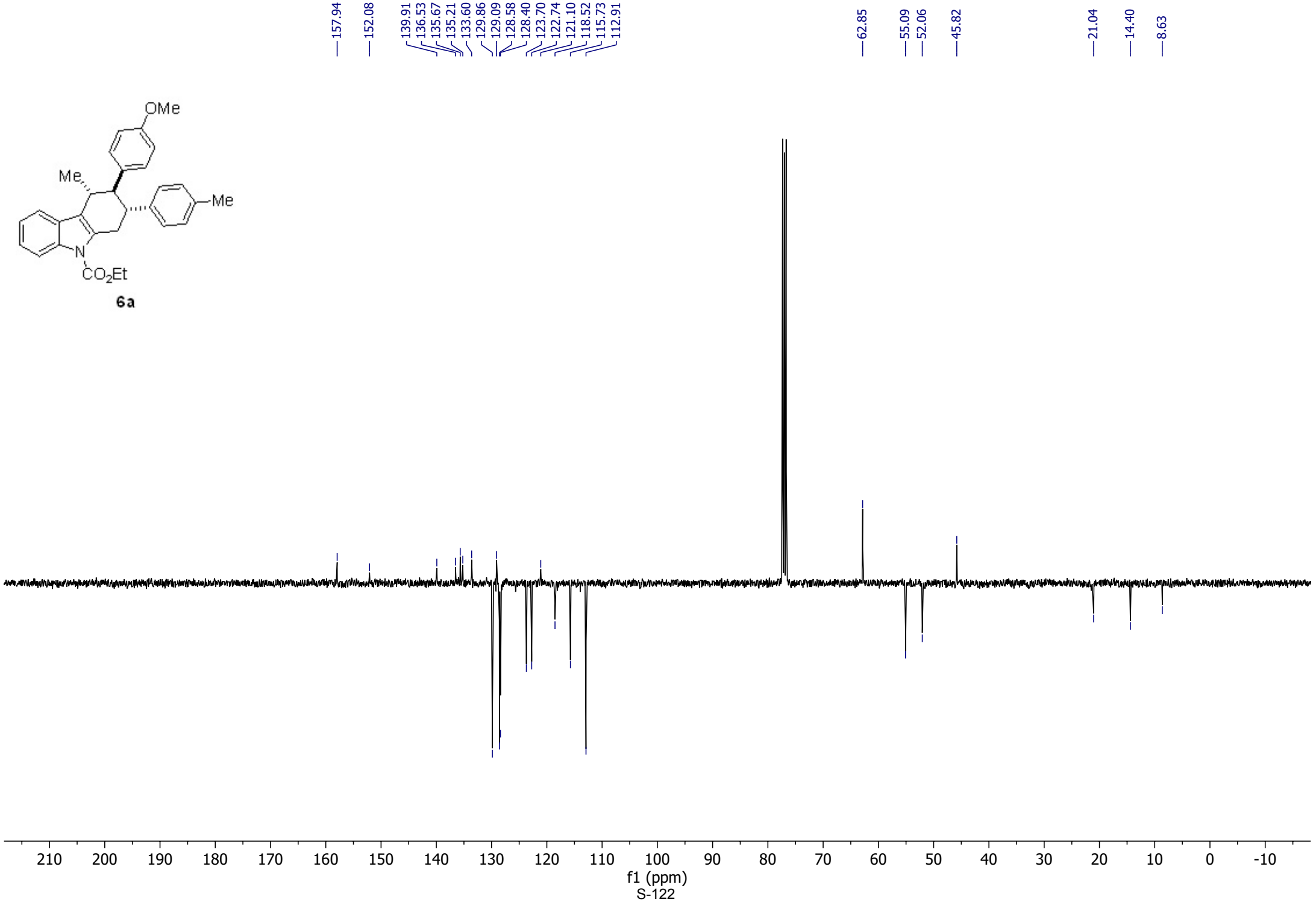


^{1}H NMR (400 MHz, $CDCl_3$)

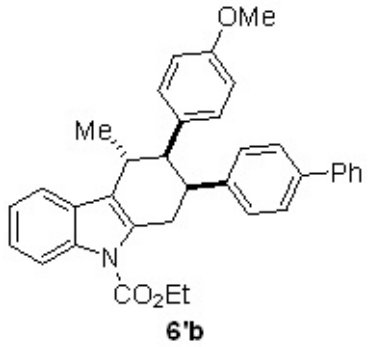


6a

^{13}C NMR (101 MHz, $CDCl_3$)

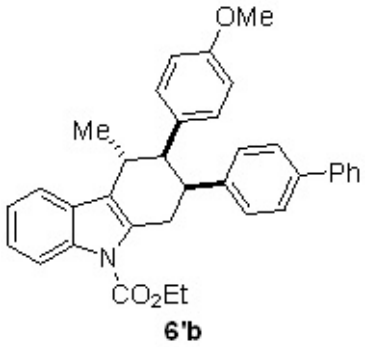


^{1}H NMR (400 MHz, $CDCl_3$)



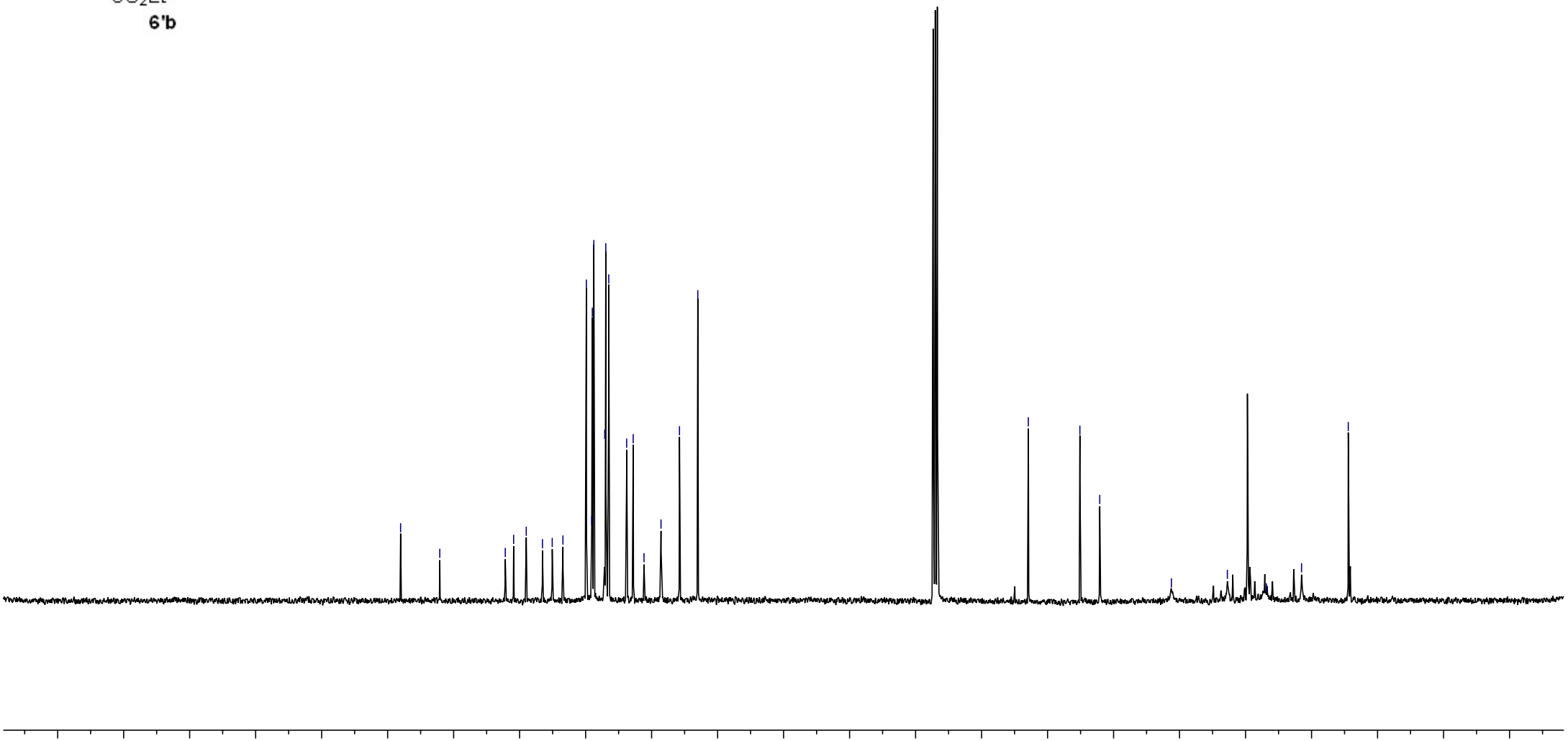
6'b

^{13}C NMR (101 MHz, $CDCl_3$)

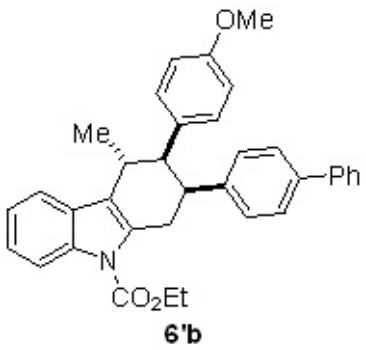


6'b

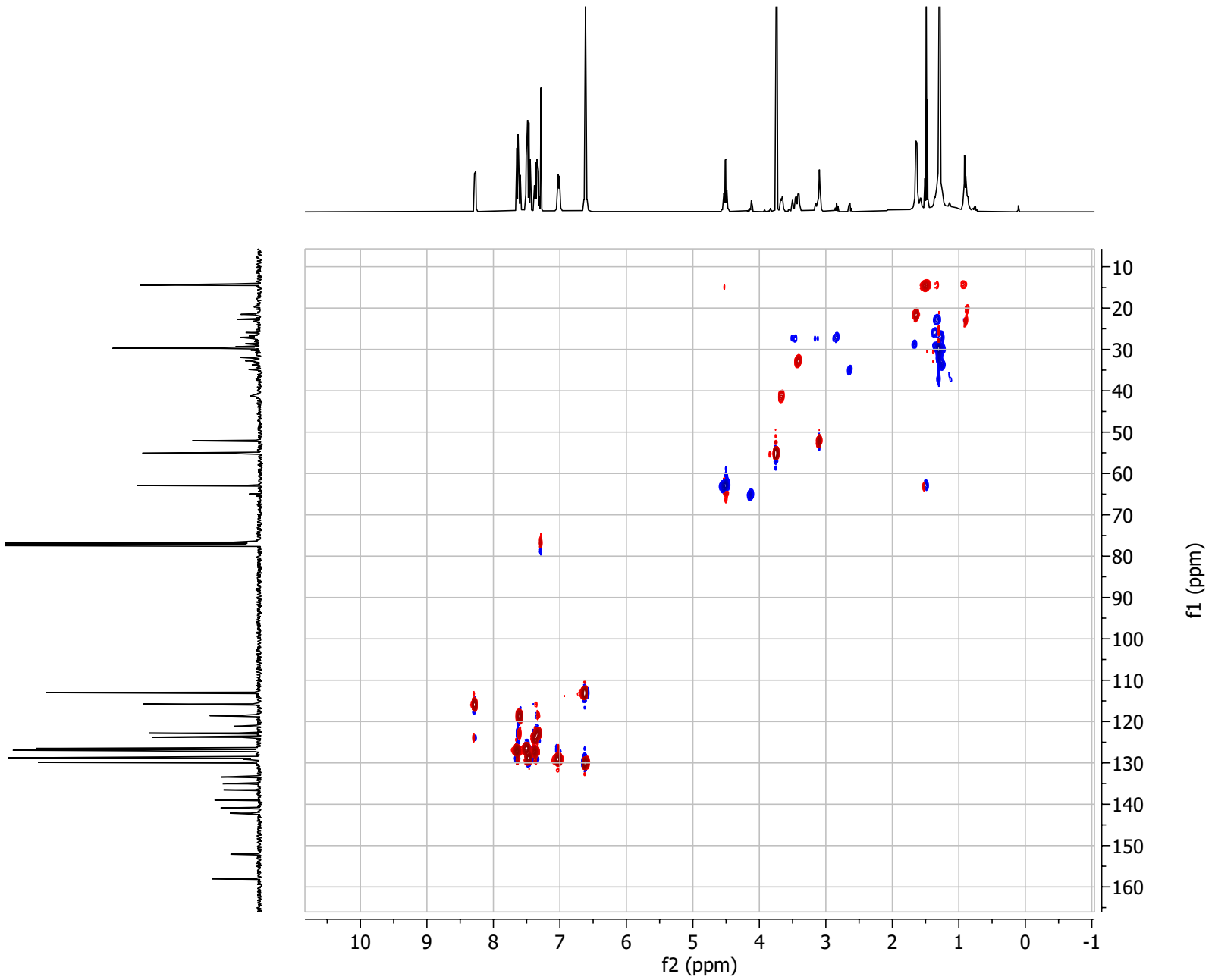
158.04
152.10
142.17
140.91
139.00
136.54
135.06
133.44
129.89
129.08
128.99
128.76
127.11
126.95
126.50
123.78
122.79
121.15
118.58
115.78
113.00
62.91
55.10
52.09
41.24
32.76
26.85
21.52
14.44



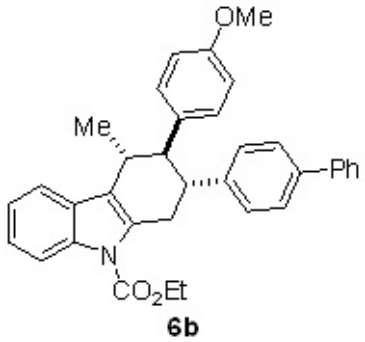
HSQC in $CDCl_3$



6'b

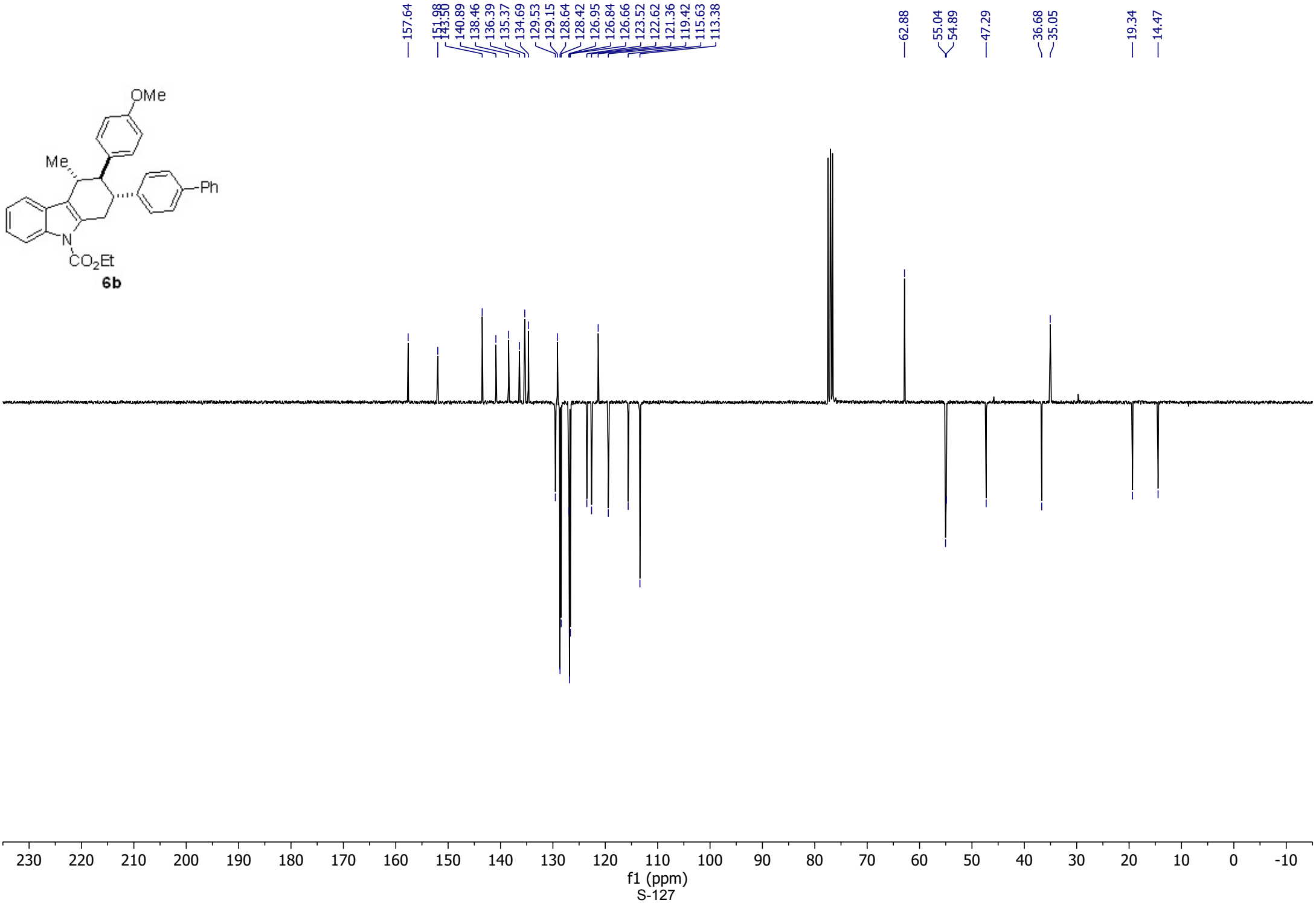


^{1}H NMR (300 MHz, $CDCl_3$)

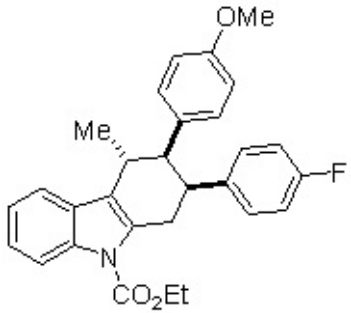


6b

^{13}C NMR (75 MHz, $CDCl_3$)

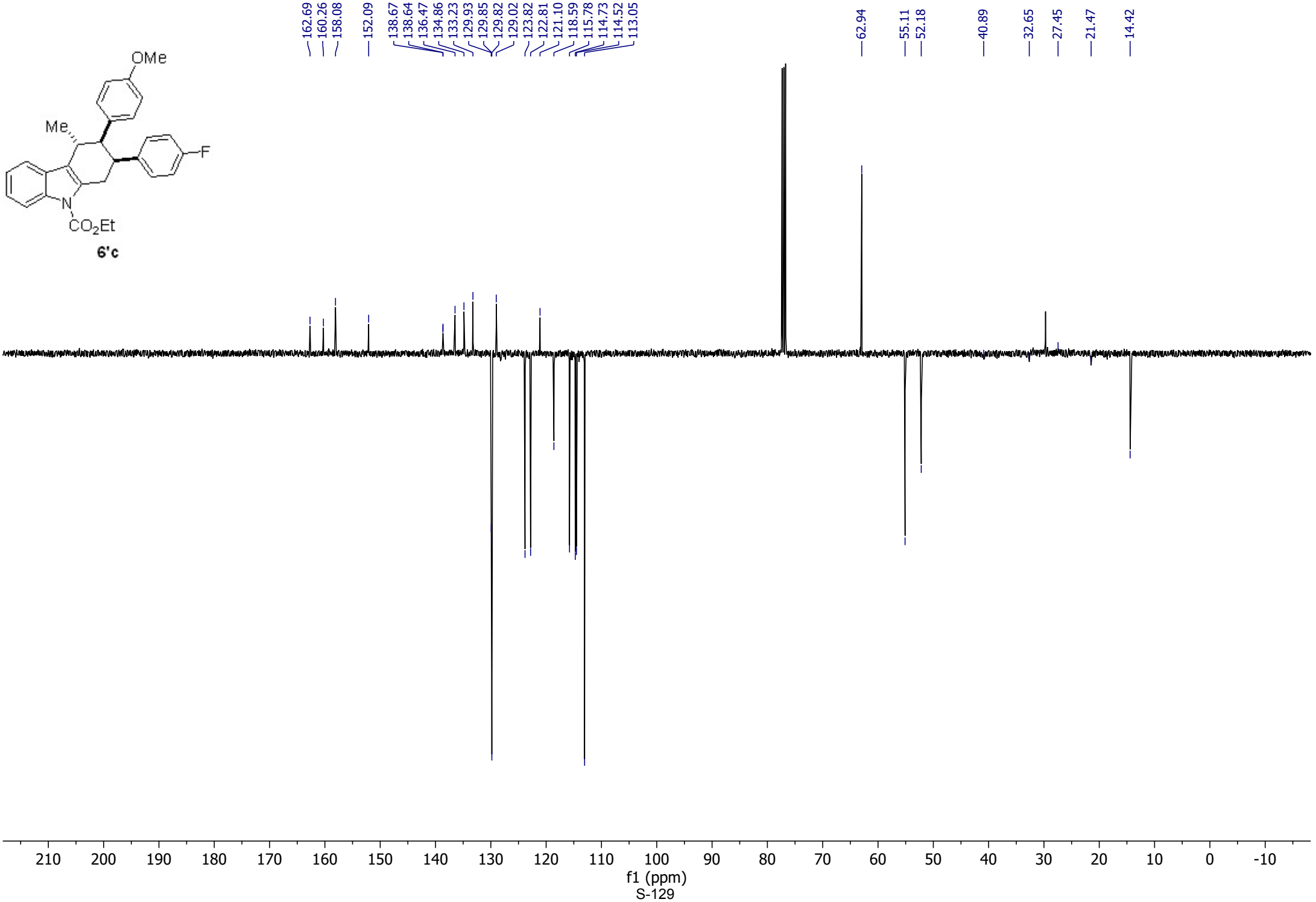


^{1}H NMR (400 MHz, $CDCl_3$)

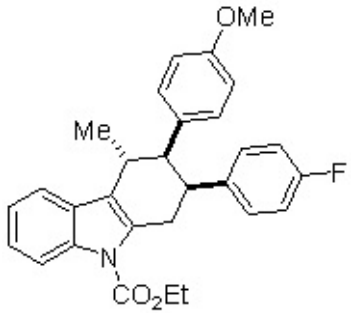


6'c

^{13}C NMR (101 MHz, $CDCl_3$)

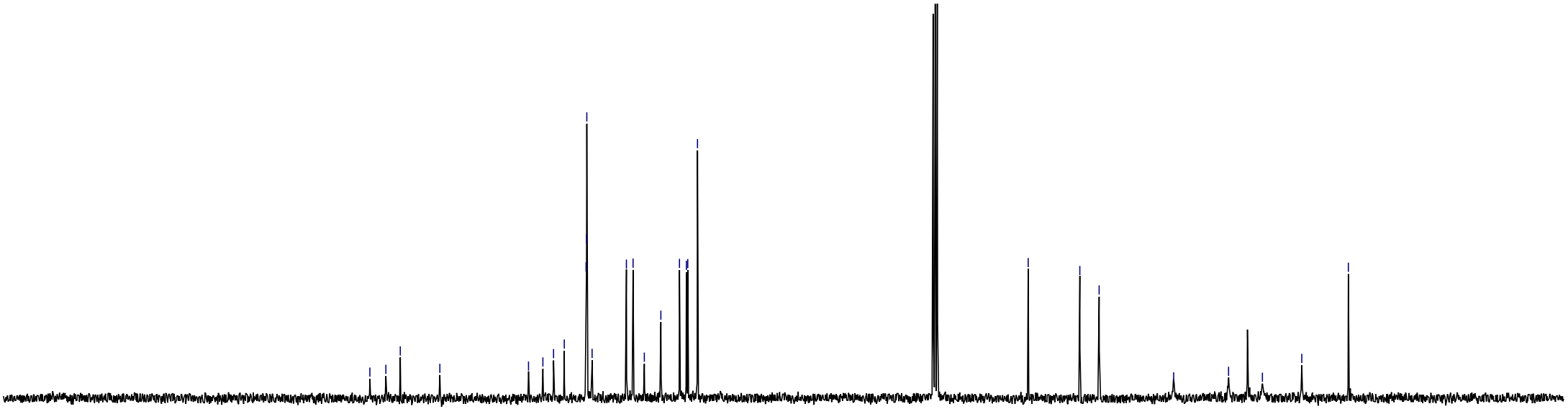


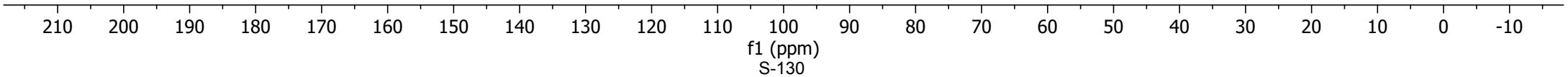
^{13}C NMR (101 MHz, $CDCl_3$)



6'c

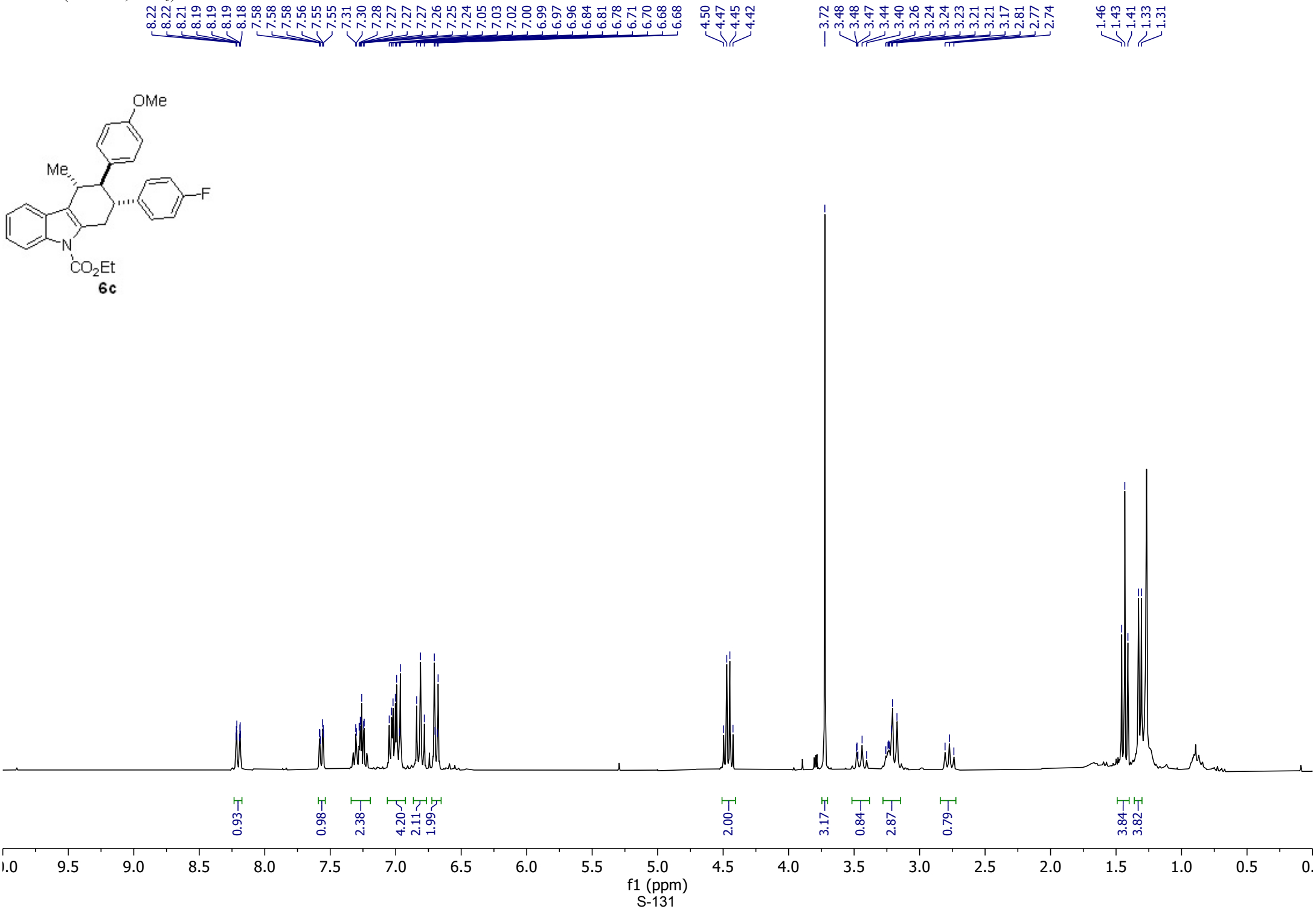
162.69
160.27
158.08
152.09
138.65
136.48
134.86
133.23
129.93
129.86
129.82
129.02
123.82
122.81
121.11
118.60
115.78
114.73
114.52
113.05
62.94
55.11
52.19
40.90
32.58
27.45
21.48
14.42



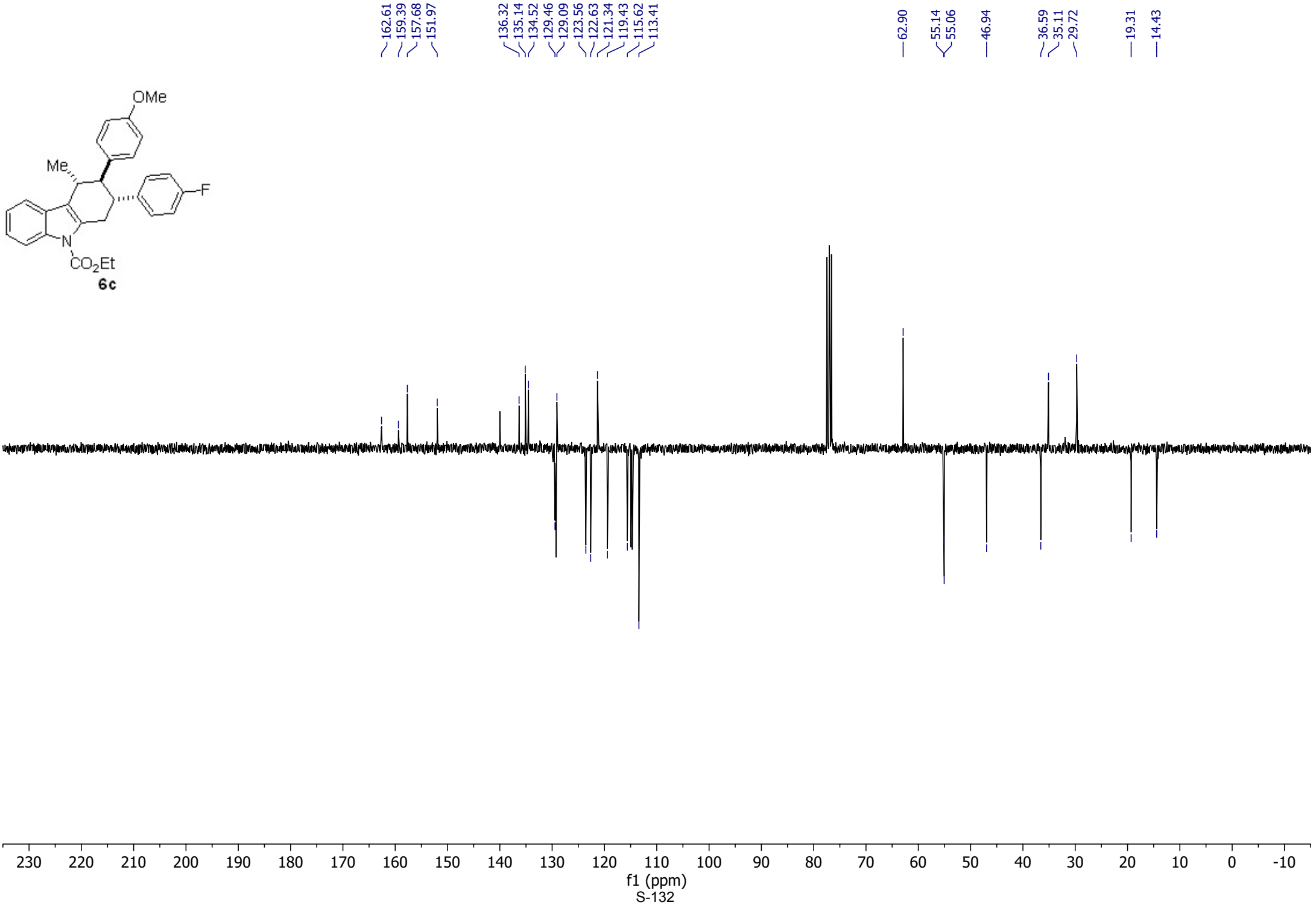


S-130

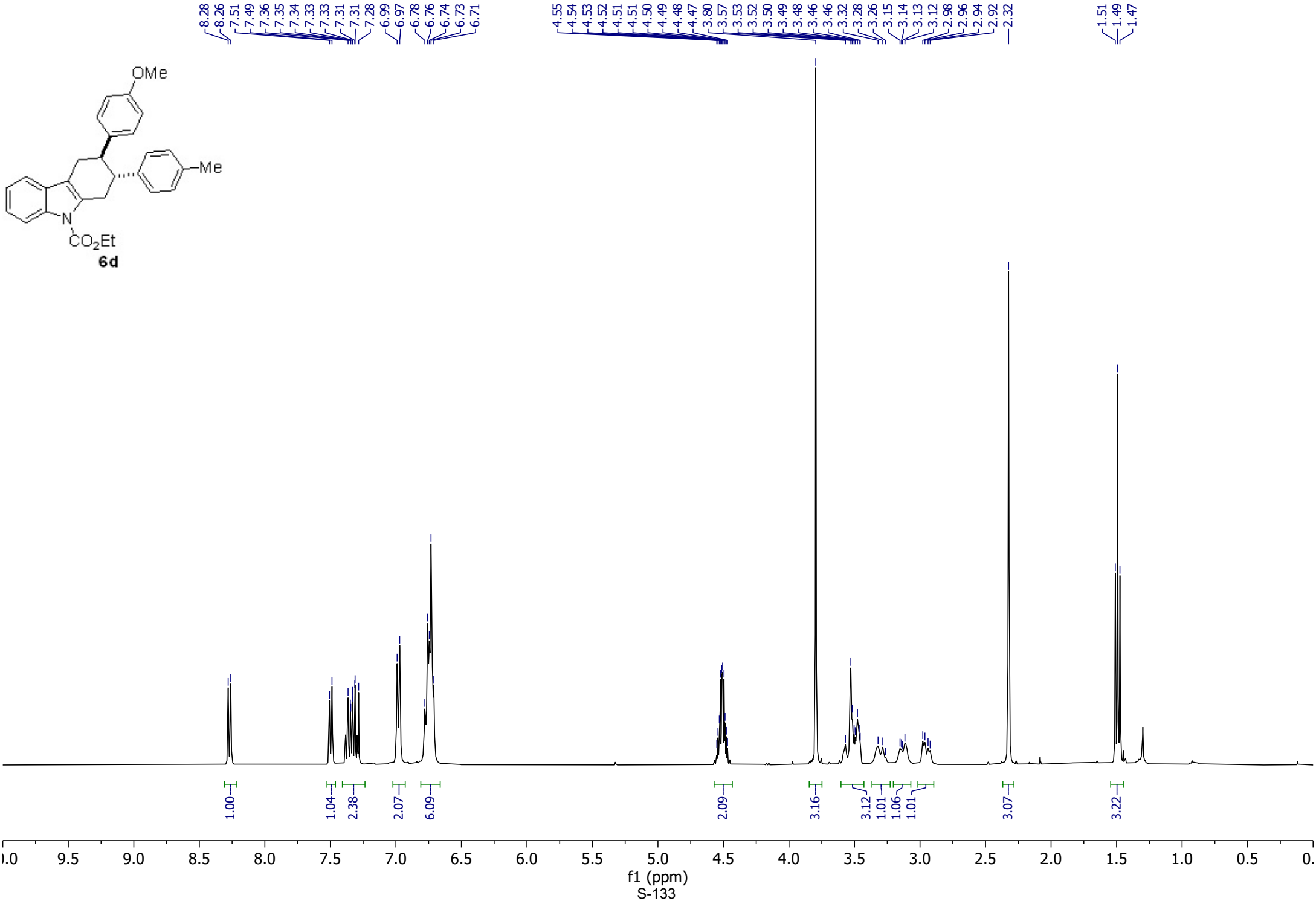
^{1}H NMR (300 MHz, $CDCl_3$)



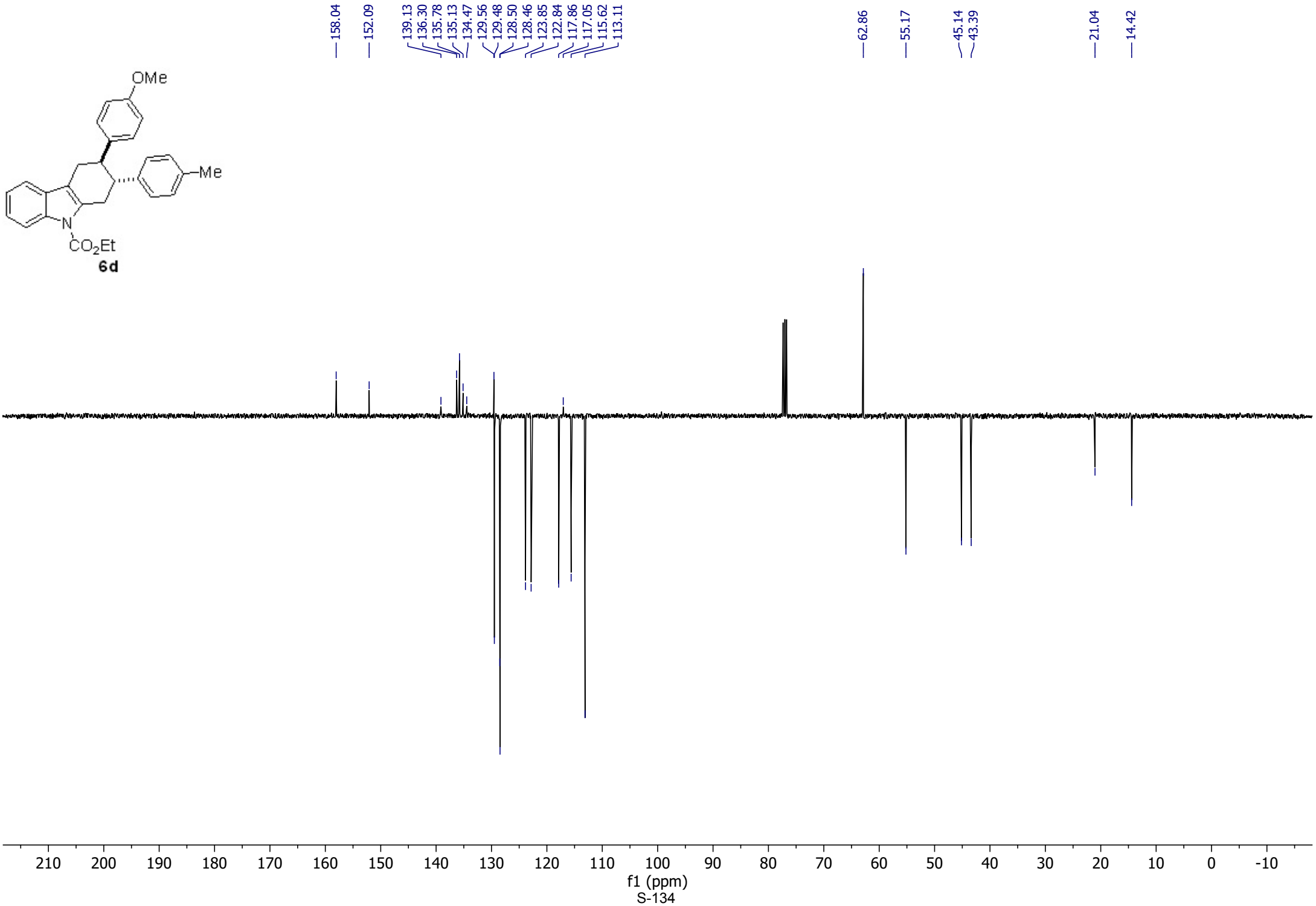
^{13}C NMR (75 MHz, $CDCl_3$):



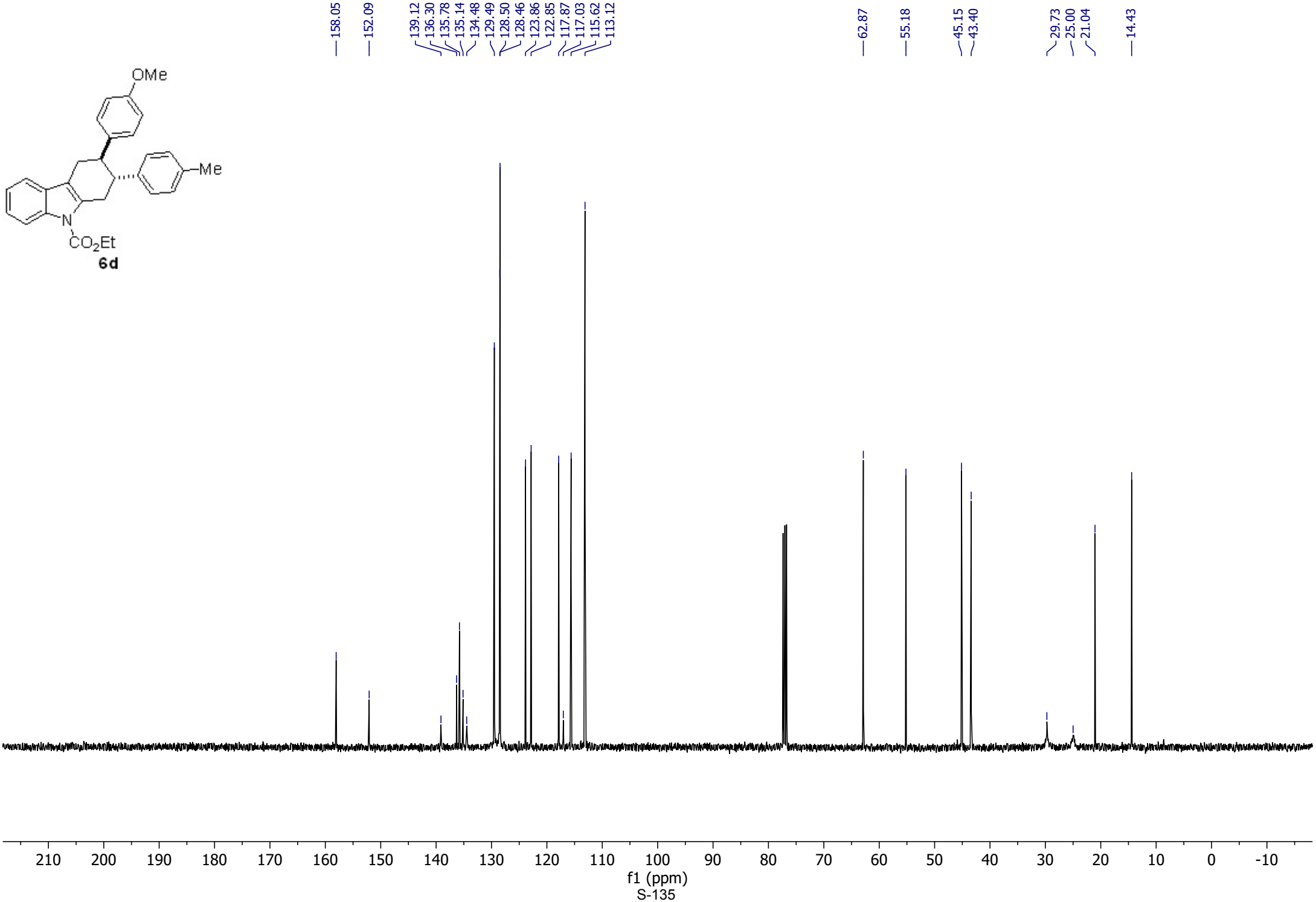
^{1}H NMR (400 MHz, $CDCl_3$)



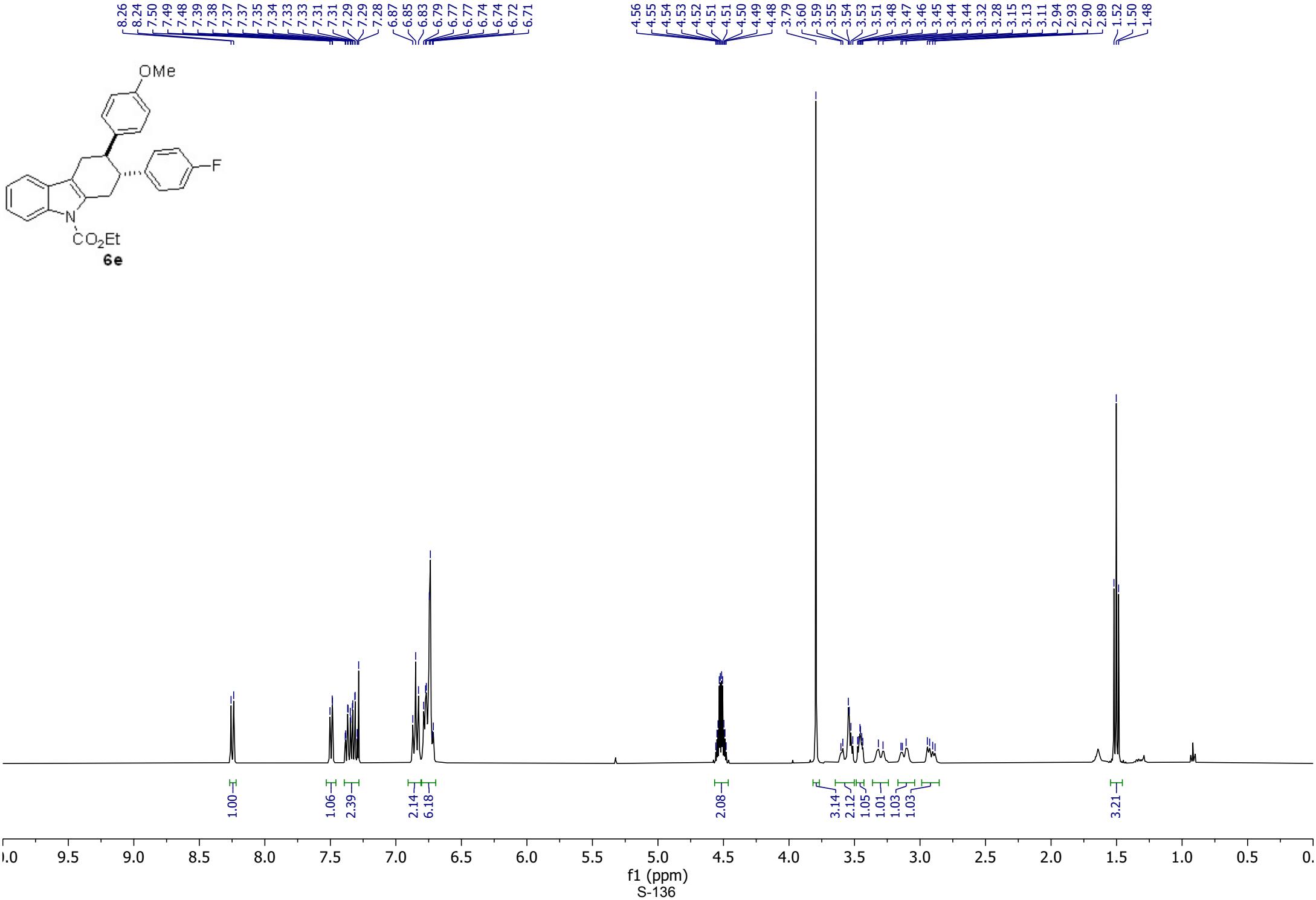
^{13}C NMR (101 MHz, $CDCl_3$)



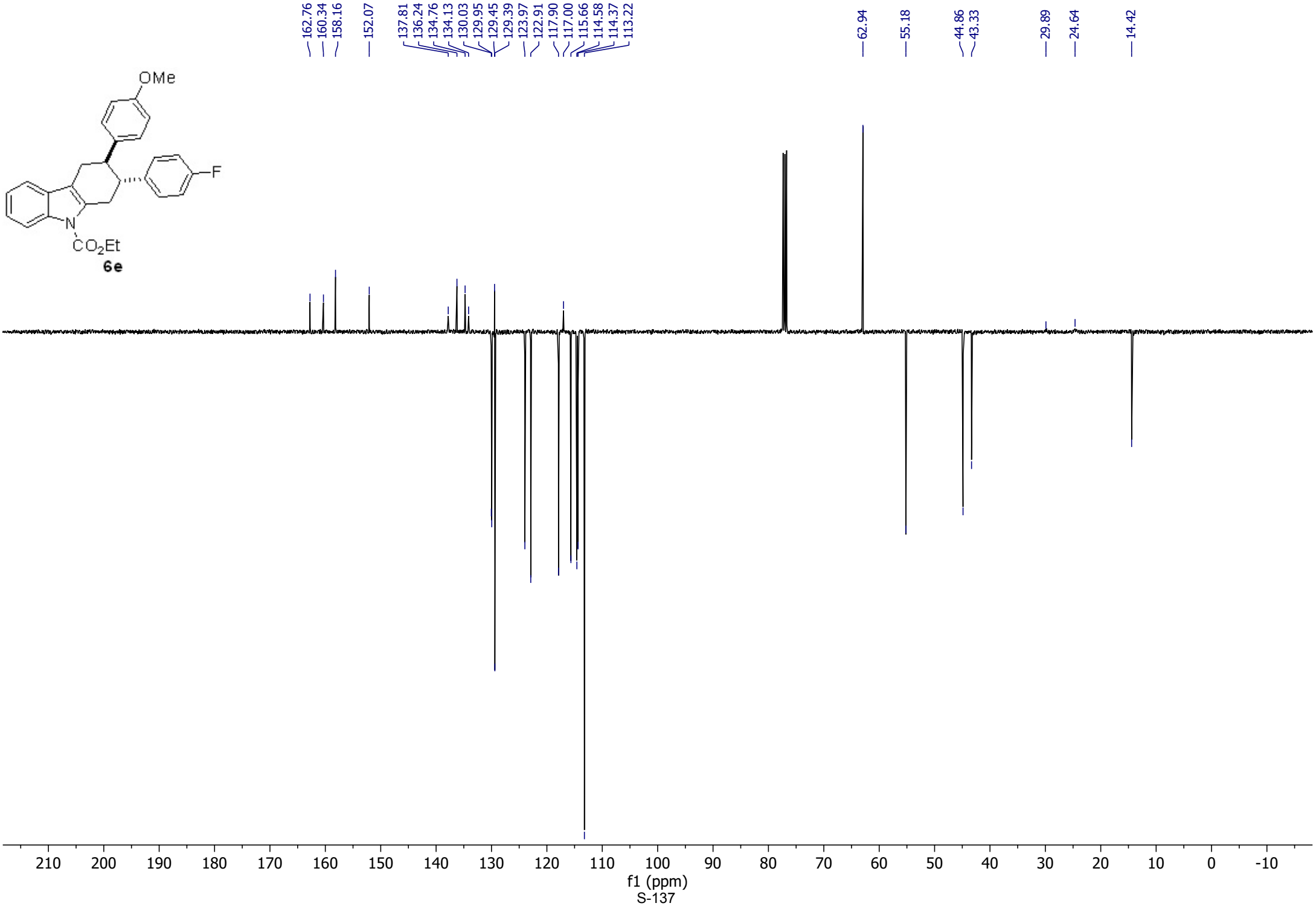
^{13}C NMR (101 MHz, $CDCl_3$)



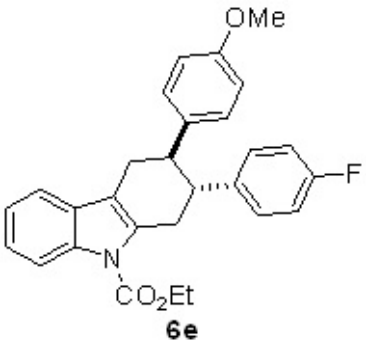
^{1}H NMR (400 MHz, $CDCl_3$)



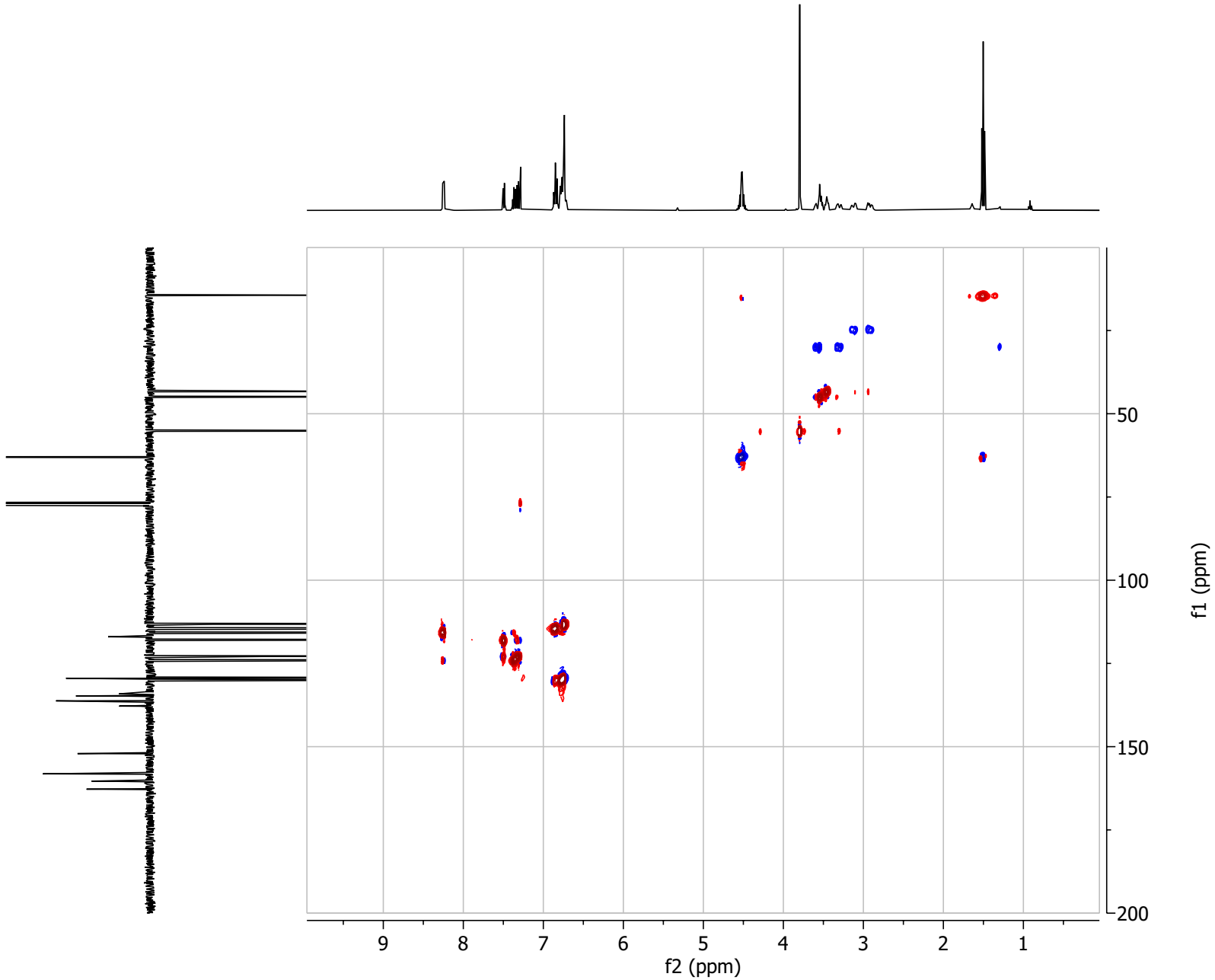
^{13}C NMR (101 MHz, $CDCl_3$)



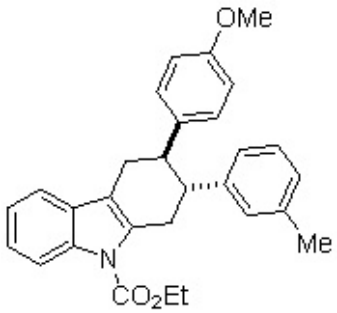
HSQC in $CDCl_3$



6e

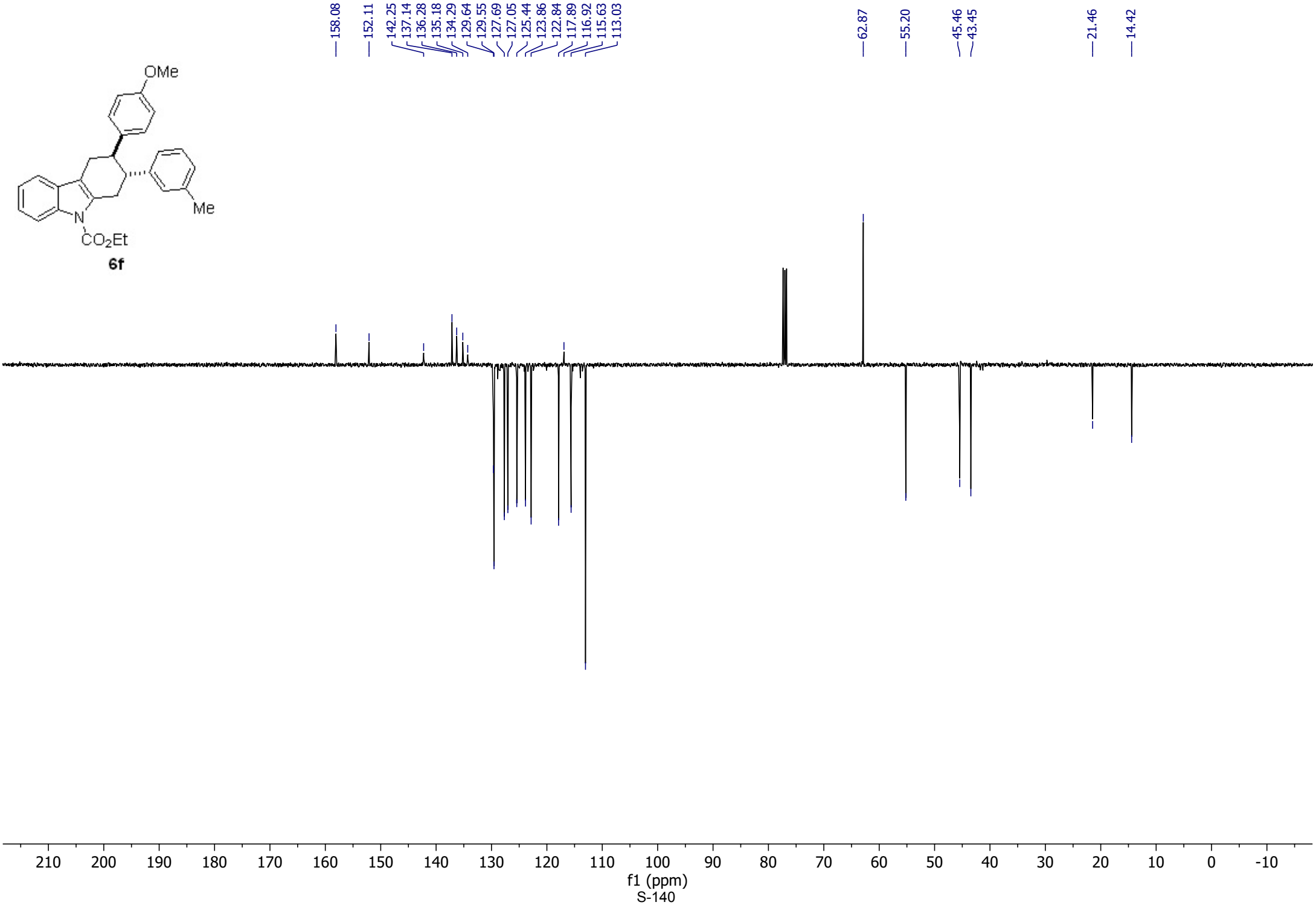


^{1}H NMR (400 MHz, $CDCl_3$)

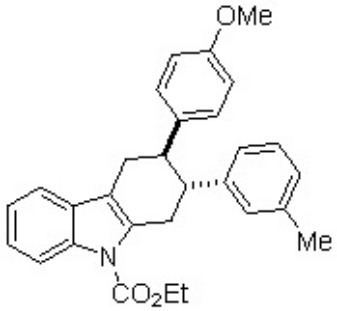


6f

^{13}C NMR (101 MHz, $CDCl_3$)

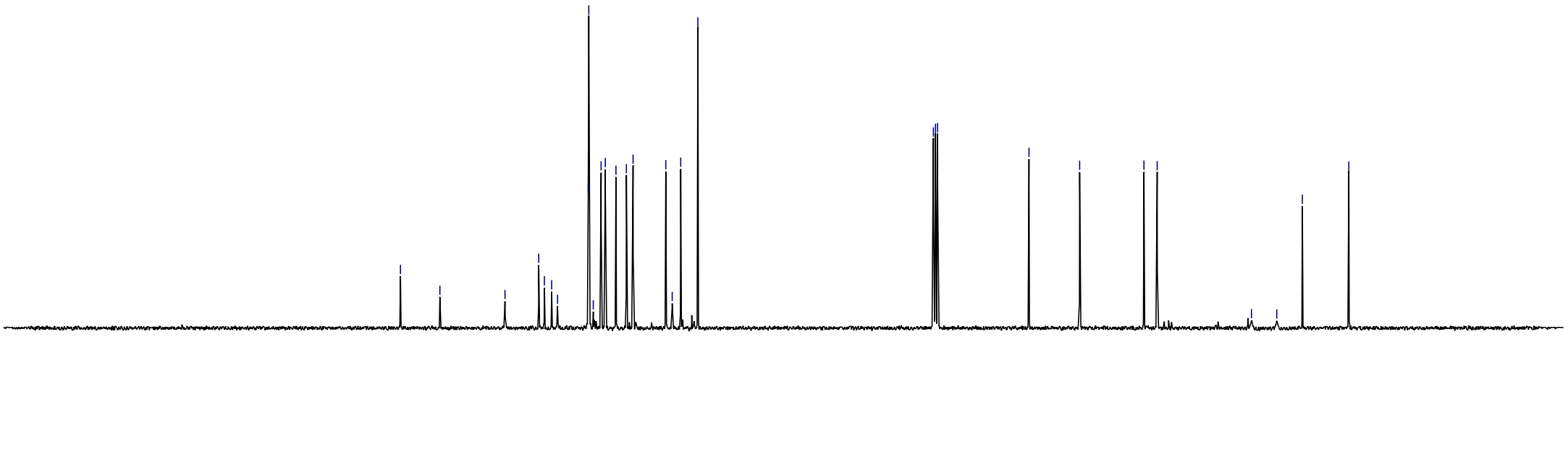


^{13}C NMR (101 MHz, $CDCl_3$)

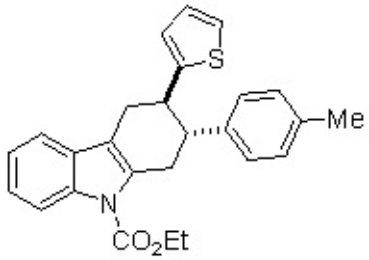


6f

158.08
152.11
142.25
137.14
136.28
135.18
134.29
129.64
129.56
128.87
127.69
127.05
125.44
123.86
122.85
117.89
116.92
115.63
113.03
77.36
77.04
76.73
62.88
55.20
45.47
43.46
29.18
25.35
21.47
14.43

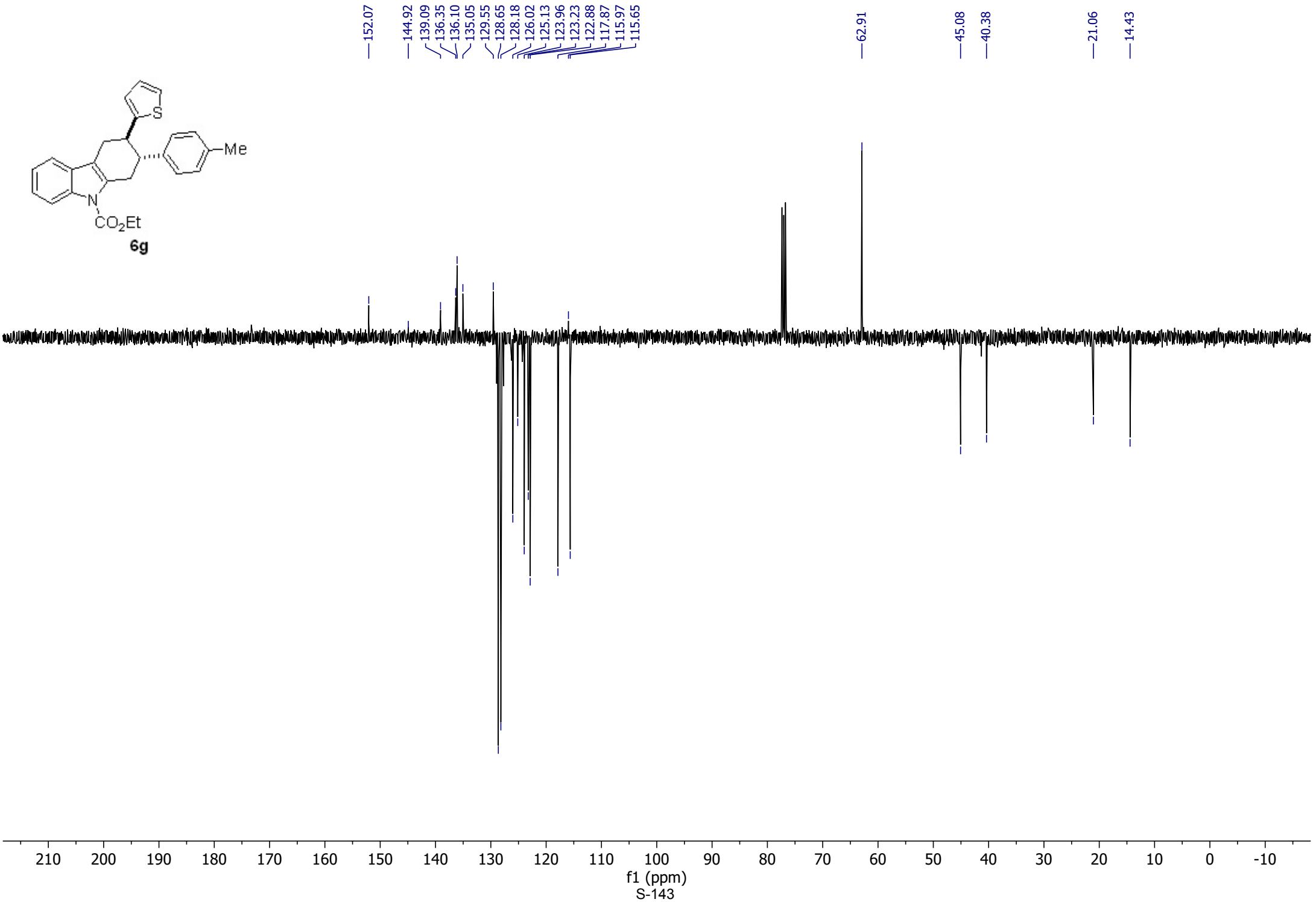


^{1}H NMR (400 MHz, $CDCl_3$)

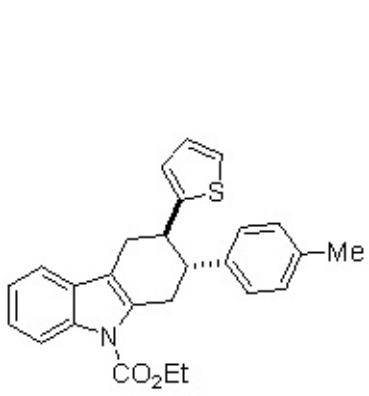


6g

^{13}C NMR (101 MHz, $CDCl_3$)

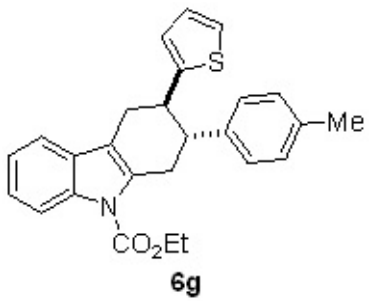


^{13}C NMR (101 MHz, $CDCl_3$)

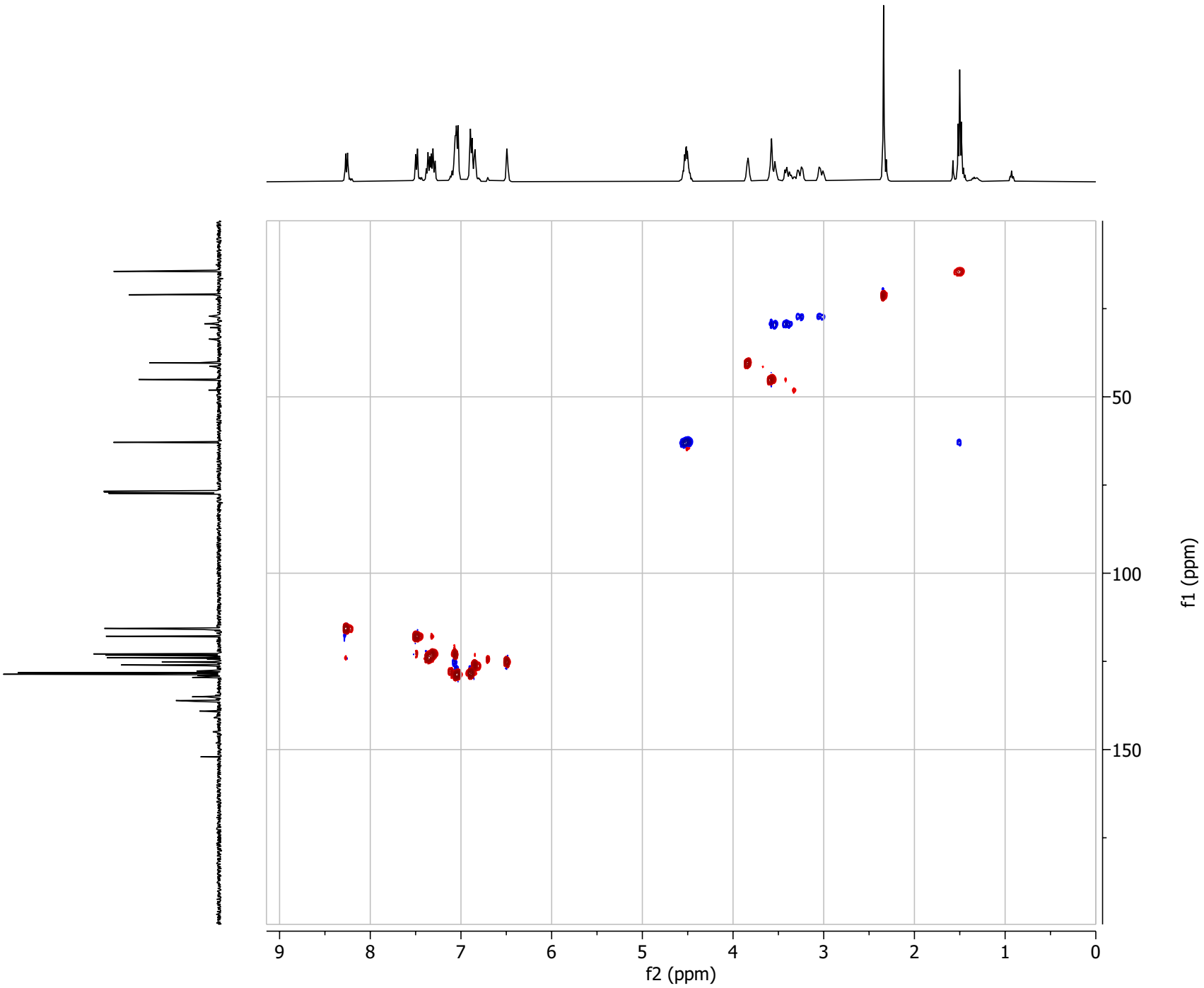


6g

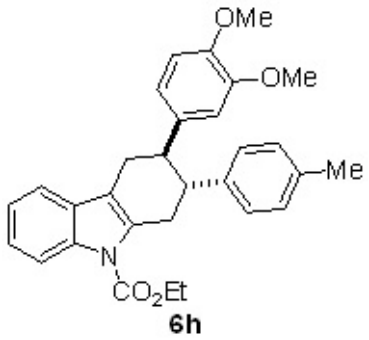
HSQC in $CDCl_3$



6g

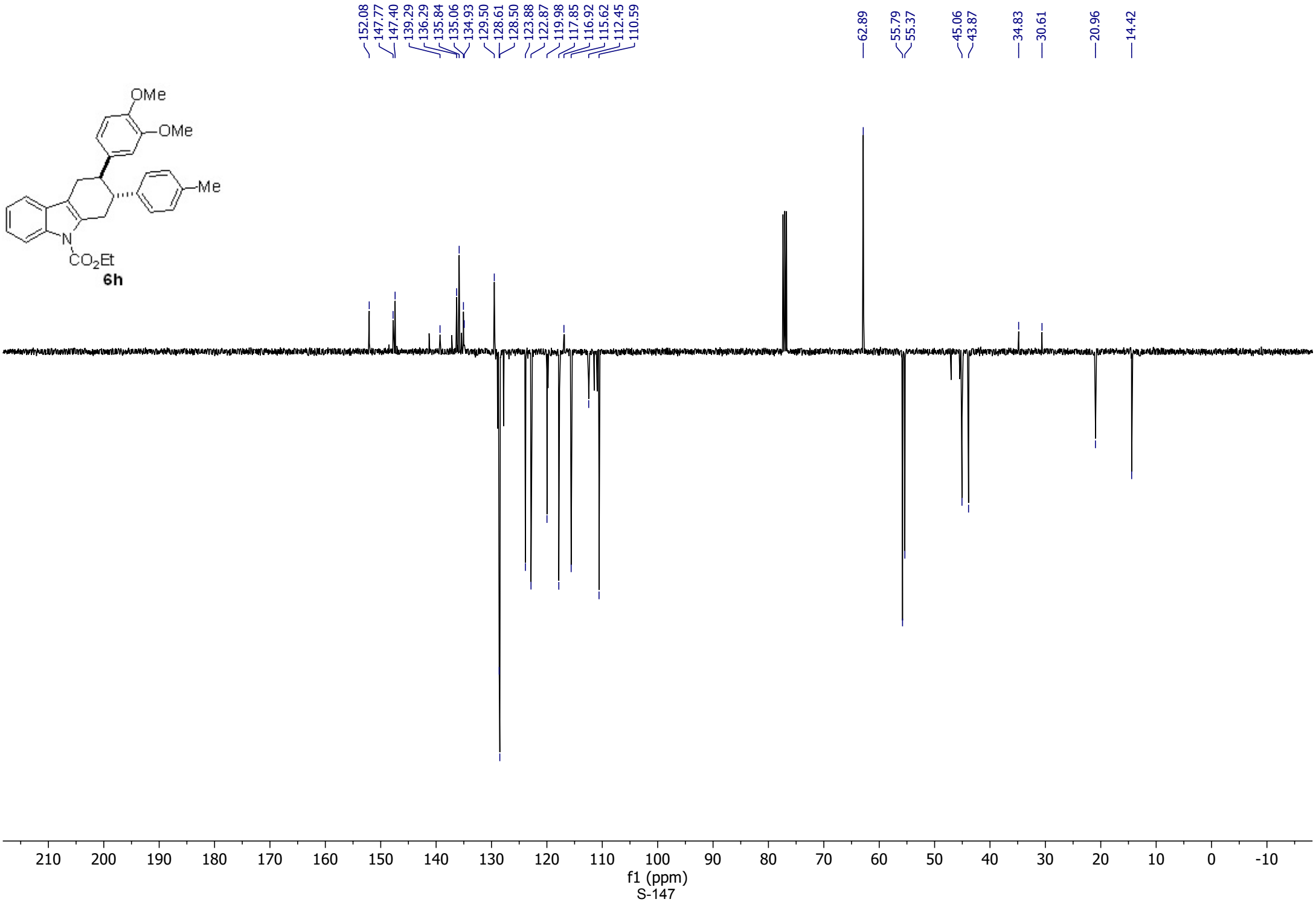


^{1}H NMR (400 MHz, $CDCl_3$)

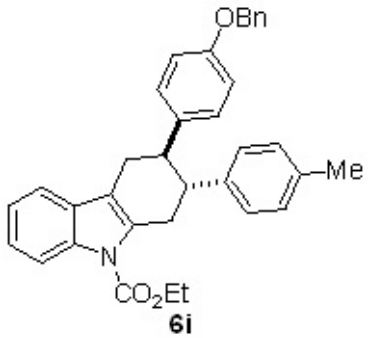


6h

^{13}C NMR (101 MHz, $CDCl_3$)

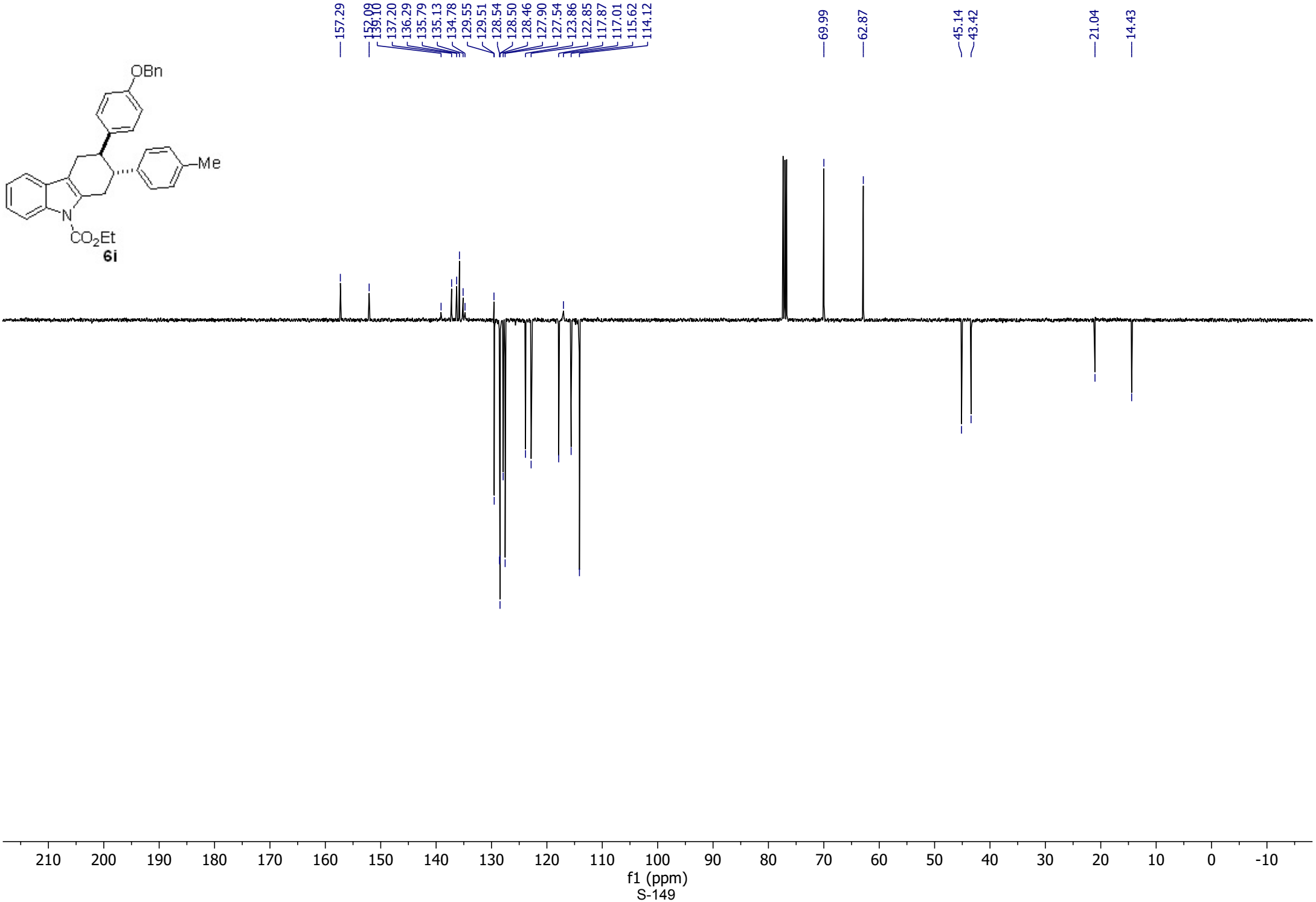


^{1}H NMR (400 MHz, $CDCl_3$)



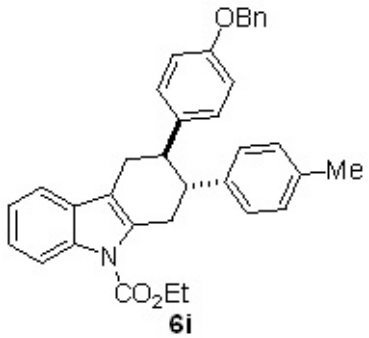
6i

^{13}C NMR (101 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):

157.29, 152.09, 139.10, 137.21, 136.29, 135.79, 135.13, 134.78, 129.55, 129.51, 129.21, 128.54, 128.50, 128.46, 127.90, 127.61, 127.54, 123.86, 122.85, 117.87, 117.01, 115.63, 114.12, 77.36, 77.24, 77.04, 76.72, 69.99, 62.87, 45.14, 43.42, 29.73, 24.94, 21.04, 14.43



6i