Supplementary Information:

Pd^{II}-Catalyzed methoxylation of $C(sp^3)$–H bonds adjacent to benzoxazoles and benzothiazoles

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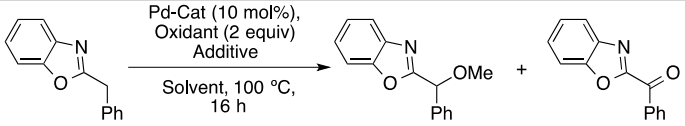
Table S1: Optimization of the Reaction Conditions for the Dehydrogenative Methoxylation

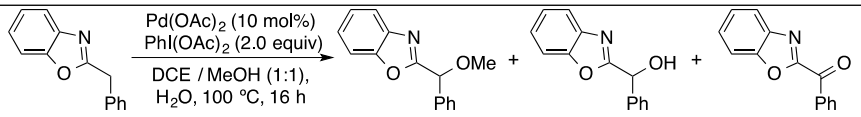


1a **2a** **3**

No	Catalyst	Oxidant	Additive (eq)	Solvent	2 (%)	3 (%)
1	$Pd(OAc)_2$	BQ	–	–	0	21
2	$Pd(OAc)_2$	$K_2S_2O_8$	–	–	14	<5
3	$Pd(OAc)_2$	Oxone	–	–	0	<5
4	$Pd(OAc)_2$	Ag_2CO_3	–	–	0	0
6	$Pd(OAc)_2$	$PhI(OAc)_2$	–	–	70	10
7	$Pd(OAc)_2$	$PhI(OAc)_2$	K_2CO_3 (2)	–	25	9
8	$Pd(OAc)_2$	$PhI(OAc)_2$	K_3PO_4 (2)	–	48	10
9	$Pd(OAc)_2$	$PhI(OAc)_2$	KO^{t}Bu (2)	–	38	9
10	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$ (2)	–	33	18
11	$Pd(OAc)_2$	$PhI(OAc)_2$	NaOAc (2)	–	30	18
12	$Pd(OAc)_2$	$PhI(OAc)_2$	NaOEt (2)	–	50	9
13	$Pd(OAc)_2$	$PhI(OAc)_2$	DBU (2)	–	30	21
14	$Pd(OAc)_2$	$PhI(OAc)_2$	DABCO (2)	–	0	<5
15	$Pd(OAc)_2$	$PhI(OAc)_2$	Pyridine (3)	–	8	0
16	$Pd(OAc)_2$	$PhI(OAc)_2$	Et_3N (3)	–	8	0
17	$Pd(OAc)_2$	$PhI(OAc)_2$	Et_2NH (3)	–	11	<5
18	$Pd(OAc)_2$	$PhI(OAc)_2$	AcOH (3)	–	12	30
19	$Pd(OAc)_2$	$PhI(OAc)_2$	TFA (3)	–	7	12
20[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	Toluene	12	0
21[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	THF	9	<5
22[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	Dioxane	10	<5
23[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	Ether	0	40
24[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	MeCN	16	10
25[a]	**$Pd(OAc)_2$**	**$PhI(OAc)_2$**	**–**	**DCE**	**82**	**0**
26[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DMF	21	25
27[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DMSO	0	15
28[a]	$PdCl_2$	$PhI(OAc)_2$	–	DCE	35	12
29[a]	$Pd(TFA)_2$	$PhI(OAc)_2$	–	DCE	9	12
30[a]	$Pd(dba)_2$	$PhI(OAc)_2$	–	DCE	48	9
31[a]	$Pd_2(dba)_3$	$PhI(OAc)_2$	–	DCE	46	10
32[a]	$PdCl_2$	$PhI(OAc)_2$	acac (0.2)	DCE	0	0
33[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	acac (0.2)	DCE	0	0
34[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	glycine (0.2)	DCE	0	0
35[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	P(o-Tol)$_3$ (0.2)	DCE	75	0
36[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	*rac*-BINAP (0.2)	DCE	74	0
37[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	Ac-Gly-OH (0.2)	DCE	80	0
38[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	O_2-balloon	DCE	64	21
39[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	N_2-balloon	DCE	41	<5
40[a]	$Pd(OAc)_2$	$PhI(OAc)_2$	4 Å MS	DCE	61	8
41[a,b]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	64	trace
42[a,c]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	73	trace
43[a,d]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	64	8
44[a,e]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	21	15
45[a]	$Pd(OAc)_2$	–	–	DCE	<5	0
46[a]	–	$PhI(OAc)_2$	–	DCE	0	0
47[f]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	61	0
48[a,g]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	66	0
49[a,h]	$Pd(OAc)_2$	$PhI(OAc)_2$	–	DCE	52	0

Reaction conditions: **1a** (0.2 mmol), Pd-Cat. (10 mol%), Oxidant (0.4 mmol), additive, MeOH (2 mL), 100 ˚C, 16 h; Isolated yields. [a] (1.0 mL MeOH + 1.0 mL solvent) was used in entries 20–49. [b] 24 h. [c] 90 ºC. [d] 60 ºC. [e] 25 ºC. [f] 0.25 mL MeOH + 1.75 mL DCE. [g] 5 mol% $Pd(OAc)_2$. [h] 1.5 equiv $PhI(OAc)_2$

Table S2: Effects of varying amounts of water in the reaction outcome:



1a 2a 2a' 3

Sr. No.	Amount of H_2O (µL)	2a (%)	2a' (%)	3 (%)
1	50	78	N.D.	trace
2	100	70	N.D.	trace
3	500	61	8	12
4	1000	45	12	23
5[a]	1000	–	28	37

Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (0.4 mmol), DCE (1 mL), MeOH (1 mL), H_2O, 100 ˚C, 16 h; Isolated yields. [a] In the absence of MeOH.

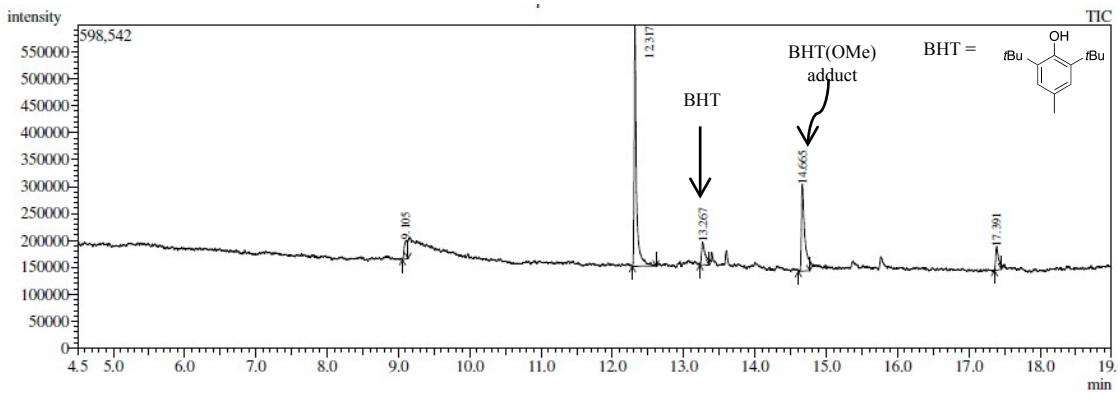
Mechanistic studies

Experiment with TEMPO:

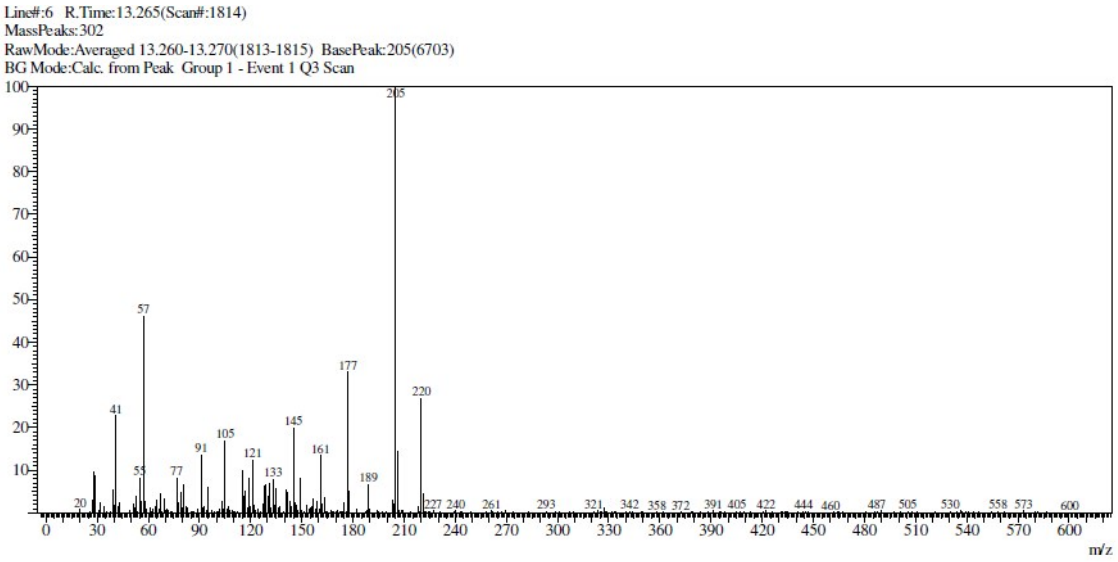
A 20 mL Schlenk tube was charged with 2-benzylbenzo[*d*]oxazole **1a** (31 mg, 0.15 mmol, 1 equiv), palladium(II) acetate (3 mg, 0.015 mmol, 10 mol%), iodobenzene diacetate (97 mg, 0.3 mmol, 2 equiv) and TEMPO (35 mg, 0.225 mmol, 1.5 equiv). To it, anhydrous dichloroethane (0.75 mL) and methanol (0.75 mL) were added. The tube was attached with a coil-condenser equipped with a glass stopper and chilled water circulator and the reaction mixture was stirred at 100 ºC for 16 h. After cooling, the solvent was evaporated and the residue was then directly subjected to flash column chromatography on silica-gel to recover the starting material **1a** (26 mg, 84%).

Experiment with BHT:

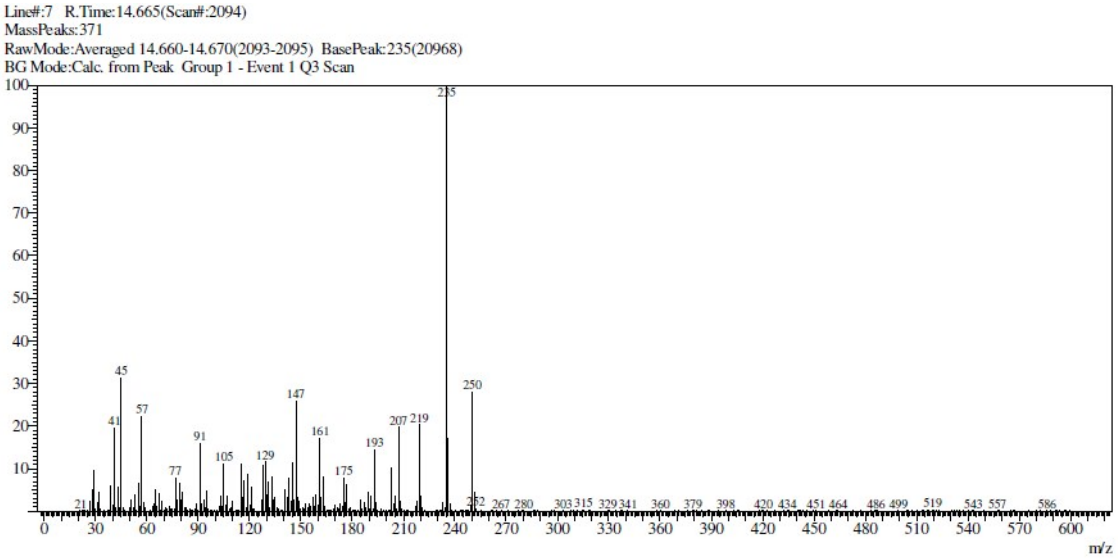
A 20 mL Schlenk tube was charged with 2-benzylbenzo[*d*]oxazole **1a** (31 mg, 0.15 mmol, 1 equiv), palladium(II) acetate (3 mg, 0.015 mmol, 10 mol%), iodobenzene diacetate (97 mg, 0.3 mmol, 2 equiv) and BHT (50 mg, 0.225 mmol, 1.5 equiv). To it, anhydrous dichloroethane (0.75 mL) and methanol (0.75 mL) were added. The tube was attached with a coil-condenser equipped with a glass stopper and chilled water circulator and the reaction mixture was stirred at 100 ºC for 16 h. After cooling, an aliquot (0.2 mL) from the reaction mixture was withdrawn and diluted with EtOAc (2 mL) and washed with water (1 mL). The organic layer was dried over Na_2SO_4, and subsequently submitted to GC-MS, which shows the formation of the BHT(OMe) adduct (m/z = 250). The rest of the solvent from the crude reaction mixture was evaporated and the residue was then directly subjected to flash column chromatography on silica-gel to recover the starting material **1a** (24 mg, 76%).



GCMS spectrum of BHT (m/z = 230, R_t = 13.267 min):

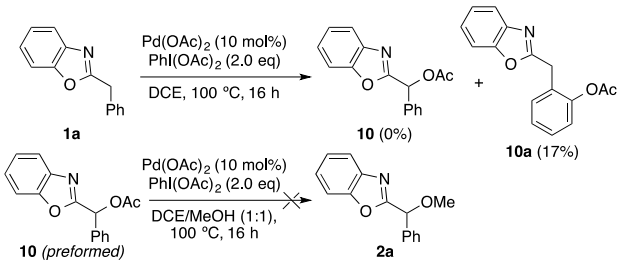


GCMS spectrum of BHT(OMe) adduct (m/z = 250, R_t = 14.665 min):



Evidence against the Formation of an Acetoxyalkane Intermediate:

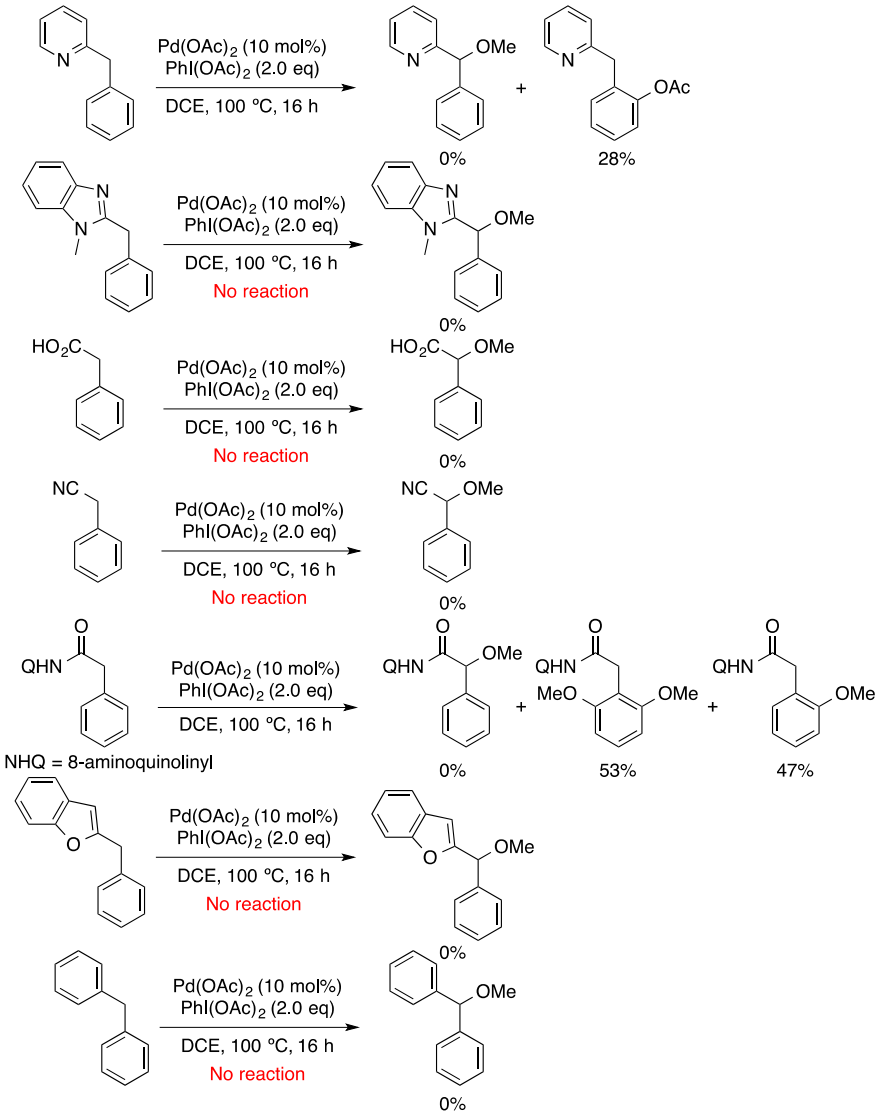
A reaction pathway consisting of acetoxylation of **1a** and the subsequent methoxylation of the resulting compound **10** was excluded based on the following experimental results:



A 20 mL Schlenk tube was charged with 2-benzylbenzo[*d*]oxazole **1a** (31 mg, 0.15 mmol, 1 equiv), palladium(II) acetate (3 mg, 0.015 mmol, 10 mol%), iodobenzene diacetate (97 mg, 0.3 mmol, 2 equiv). To it, anhydrous dichloroethane (0.75 mL) was added. The tube was attached with a coil-condenser equipped with a glass stopper and chilled water circulator and the reaction mixture was stirred at 100 ºC for 16 h. After cooling, the solvent was evaporated and the residue was then directly subjected to flash column chromatography on silica-gel to recover the starting material **1a** (18 mg, 57%) accompanied by a small extent of the phenyl ring acetoxylation product **10a** (7 mg, 17%).

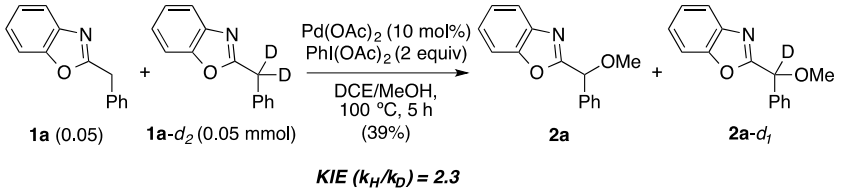
A 20 mL Schlenk tube was charged with preformed **10** (27 mg, 0.1 mmol, 1 equiv), palladium(II) acetate (2.3 mg, 0.01 mmol, 10 mol%), iodobenzene diacetate (64 mg, 0.2 mmol, 2 equiv). To it, anhydrous dichloroethane (0.5 mL) and methanol (0.5 mL) were added. The tube was attached with a coil-condenser equipped with a glass stopper and chilled water circulator and the reaction mixture was stirred at 100 ºC for 16 h. The reaction however led to a mixture of unreacted starting material **10** and several unwanted by-products. The desired compound **2a** was not formed even in traces.

Attempted methoxylation of various benzylic substrates containing coordinating and non-coordinating functions e.g., 2-pyridyl, 1-methylbenzimidazolyl, carboxylic acid, nitrile, 8-aminoquinolinocarbonyl, 2-benzofuranyl and phenyl under the optimized reaction condition:

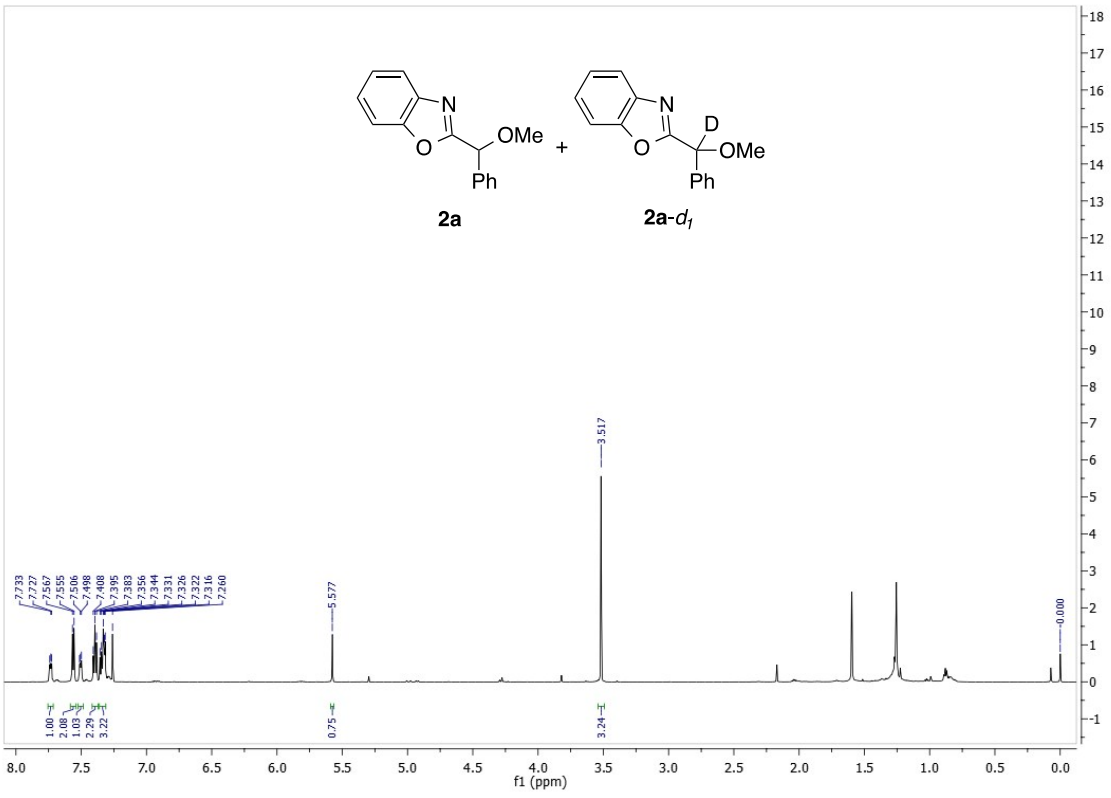


Intermolecular Kinetic Isotope Effect Study:

For estimating the intermolecular kinetic isotope effect (KIE), a 1:1 mixture of **1a** and the doubly deuterated substrate **1a-*d*$_2$** was subjected to the standard reaction condition for 5 h and the product mixture was purified by column chromatography over silica gel. The H/D ratio of the product mixture as found by ^{1}H NMR analysis indicated an intermolecular KIE of k_H/k_D = 2.3. This result implies that the cleavage of the C(sp^3)–H bond is possibly involved in the rate-limiting step.

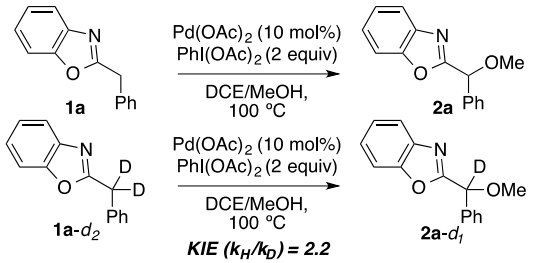


^{1}H NMR analysis for the determination of the intermolecular Kinetic Isotope Effect:



Determination of KIE by independent parallel experiment

Two independent reactions with **1a** and **1a**-d_2 under the optimal reaction conditions were conducted: A 20 mL Schlenk tube was charged with **1a** (42 mg, 0.2 mmol, 1.00 equiv) or **1a**-d_2 (44 mg, 0.2 mmol, 1.00 equiv), palladium(II) acetate (4.5 mg, 0.02 mmol, 10 mol%) and iodobenzene diacetate (129 mg, 0.4 mmol, 2.00 equiv). To it, anhydrous dichloroethane (1 mL) and methanol (1 mL) were added sequentially. The tube was attached with a coil-condenser equipped with a glass stopper and chilled water circulator. The reaction mixture was stirred at 100 ºC for the required time as indicated in the following table. An aliquot of 0.1 mL was withdrawn periodically and passed through a small bed of silica-gel and the product formation was monitored by GC analysis (Figure S1). Comparison of the two individual reactions indicated a kinetic isotope effect of 2.2.



Time (min)	30	60	90	120
1a (%)	2.1	5.4	8.3	10.7
1a-d_2 (%)	0.8	1.8	2.8	4.9

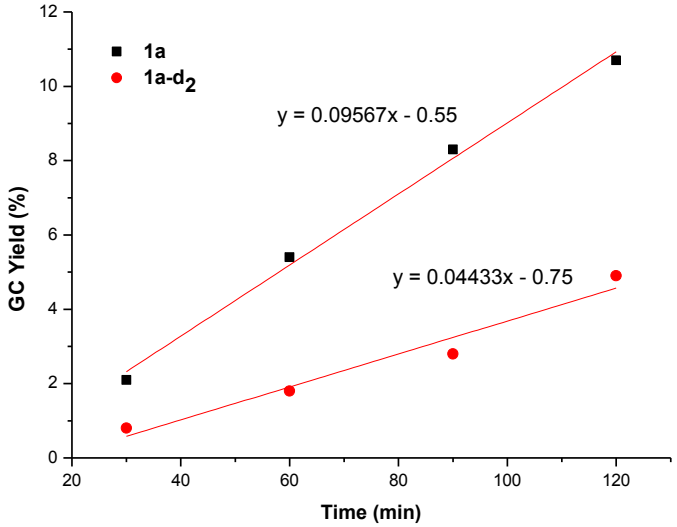


Figure S1: Independent parallel experiments with **1a** and **1a**-d_2 as monitored by GC analysis

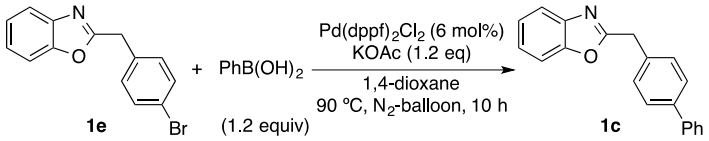
Preparative Methods and Characterization of All Substrates And Products

General Methods. NMR spectra were recorded on Jeol Resonance ECZ 600R spectrometer (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, 564 MHz for ^{19}F) and Bruker AvanceII 500 spectrometer (500 MHz for ^{1}H NMR, 121 MHz for ^{13}C NMR). Chemical shifts were reported in ppm on the δ scale relative to Me_4Si (δ = 0.00 for ^{1}H-NMR) and $CDCl_3$ (δ = 77.160 for ^{13}C-NMR). Multiplicities are indicated as: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on Perkin Elmer Spectrum GX FT-IR system. HRMS (SI) spectra were recorded on a Micromass Q-Tof microTM instrument. GCMS spectral data were acquired on a Shimadzu GC-2010 Plus coupled with GCMS-TQ8040 instrument. All low temperature reactions were performed in a Siskin Profichill RFC-90 immersion cooler instrument. For thin-layer chromatography (TLC) analysis throughout this work, Macherey-Nagel pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used. Solvents e.g. DMF, DMSO, Toluene, THF, Dioxan and DCM were dried by standard drying techniques.[1] All other solvents and commercially available compounds were used without further purification.

Preparation of Substrates:

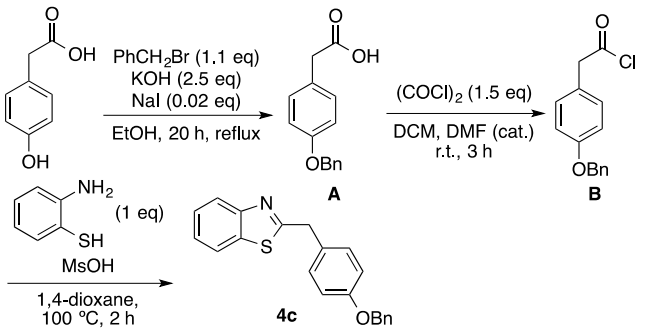
Substrates **1a, 1b, 1d–1o,** and **4a, 4b, 4f–4h, 4j–4p** were prepared by reported methods.[2] Substrates **1c**, **4c–4e** and **4i** were prepared as follows:

Preparation of Compound 1c:



A mixture of **1e** (158.5 mg, 0.55 mmol), benzeneboronic acid (80 mg, 0.66 mmol, 1.2 equiv), $Pd(dppf)_2Cl_2$ (25 mg, 0.031 mmol) and potassium acetate (230 mg, 1.66 mmol) was dissolved in anhydrous 1,4-dioxane (10 mL) and heated at 90 ºC under nitrogen atmosphere for 10 h. After cooling to room temperature, the mixture was poured into water (20 mL) and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography using hexane/diethyl ether (9:1) as the eluent to afford pure product **1c** (133 mg, yield: 85%) as a yellow solid. R_f = 0.6 (Hexane:Et_2O = 4:1). mp = 91 ºC. IR (KBr): ν = 3144, 1612, 1402, 1141, 749 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69–7.70 (m, 1H), 7.56–7.57 (m, 4H), 7.40–7.48 (m, 5H), 7.28–7.34 (m, 3H), 4.31 (s, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.27, 151.20, 141.49, 140.81, 140.46, 133.90, 129.56 (2C), 128.89 (2C), 127.72 (2C), 127.45, 127.20 (2C), 124.87, 124.35, 119.98, 110.61, 35.04 ppm. HRMS (ESI): *m/z* calcd. for $C_{20}H_{16}NO$ $[M + H]^+$, 286.1232; found, 286.1252.

Preparation of Compound 4c:

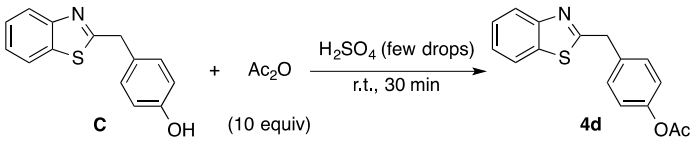


4-Hydroxyphenylacetic acid (1.52 g, 10 mmol, 1 equiv), benzyl bromide (1.88 g, 11 mmol, 1.1 equiv), KOH (1.4 g, 25 mmol, 2.5 equiv), and NaI (29.98 mg, 0.2 mmol, 0.02 equiv) were dissolved in absolute EtOH (78.4 mL) and refluxed for 20 h. The solution was allowed to stand at r.t. and then treated with 3 N aq HCl (45 mL). The precipitate was filtered, washed with H_2O (30 mL), and dried under vacuum to give the compound **4c** as a colorless powder. Yield = 1.5 g, 60%. R_f = 0.50 (hexane-EtOAc, 1:1).

To a solution of **A** (606 mg, 2.5 mmol, 1 equiv) in dry CH_2Cl_2 (9.6 mL) at 0 °C under N_2 was added dropwise oxalyl chloride (3.75 mmol, 1.5 equiv) followed by a catalytic amount of dry DMF (3 drops). The reaction mixture was stirred at room temperature until the reaction was complete (typically 3 h). The volatiles were evaporated under reduced pressure and the resulting crude acid chloride was used directly for the next step without further purification.

To the resulting residue (**B**), anhydrous dioxane (5 mL), 2-amino thiophenol (313 mg, 2.5 mmol, 1 equiv) and CH_3SO_3H (0.5 mL) were added successively. The resultant mixture was stirred at 100 ºC for 2 h (TLC). After completion of the reaction, dioxane was removed and the residue was diluted with EtOAc (10 mL), followed by saturated aq. $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×5 mL). The combined EtOAc extracts were washed with H_2O (3×5 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product which was purified by column chromatography to furnish the compound **4c** (497 mg, 60%). R_f = 0.5 (Hexane:EtOAc = 4:1). mp 99 ºC. IR (KBr): ν = 3133, 1639, 1402, 1246, 754 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.42 – 7.45 (m, 3H), 7.38 (t, J = 7.2 Hz, 2H), 7.28 – 7.34 (m, 4H), 6.96 (d, J = 7.8, 2H), 5.05 (s, 2H), 4.37 (s, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.03, 158.26, 153.45, 137.05, 135.80, 130.42 (2C), 129.73, 128.73 (2C), 128.13, 127.62 (2C), 126.07, 124.89, 122.88, 121.65, 115.32 (2C), 70.18, 39.93 ppm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{17}NOSNa$ $[M + Na]^+$, 354.0929; found, 354.0951.

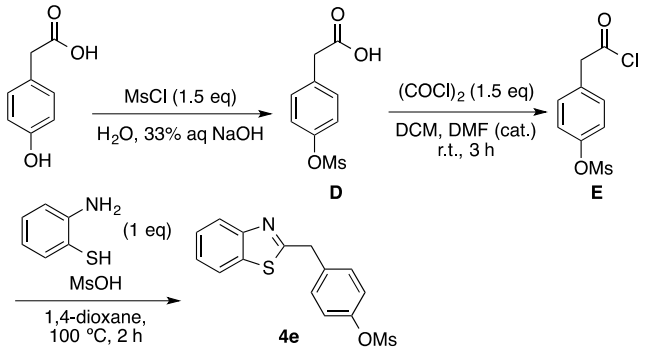
Preparation of Compound 4d:



A solution of **C** (1.93 g, 8 mmol) and concentrated sulfuric acid (3 drops) in acetic anhydride (8.17 g, 7.6 mL, 10 equiv) at room temperature were stirred for 30 minute. The reaction mixture was poured in water (14.2 mL) and extracted with DCM (3 × 15 mL). The combined organic extracts were successively washed with a saturated aqueous solution of Na_2CO_3 (2 × 15 mL), brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to obtain a yellow oil which was purified by column chromatography to afford **4d** as a dark yellow solid (2.04 g, 90% yield). R_f = 0.5 (Hexane:EtOAc = 4:1). mp = 45 ºC. IR (KBr): ν = 3122, 1639,

1402, 1197, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.32–7.38 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 2H), 2.28 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.67, 169.49, 153.36, 149.99, 135.74, 134.81, 130.25 (2C), 126.13, 125.01, 122.90, 122.05 (2C), 121.66, 40.00, 21.23 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{13}NO_2SNa$ $[M + Na]^+$, 306.0565; found, 306.0647.

Preparation of Compound 4e:

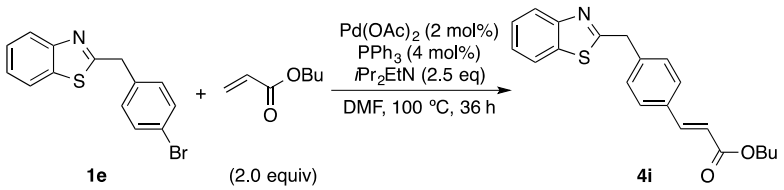


A 25 mL R.B. flask was charged with 0.6 mL of water and 1.2 mL of 33% aq. sodium hydroxide solution. The solution was cooled to 0–5°C and 4-hydroxyphenylacetic acid (1.22 g, 8 mmol) was slowly added with stirring. The temperature was increased up to 30°C. The solution was then cooled to 0°C to 15°C. To the cooled solution, 0.83 mL of methanesulfonyl chloride was slowly added. Here, the pH of the reaction solution was maintained between 11–11.5 by the addition of dilute NaOH (prepared from 3.7 ml of water and 1.5 ml of sodium hydroxide). After the complete addition of methanesulfonyl chloride, it was stirred as long at pH 11–11.5 as the pH value remained constant without addition of sodium hydroxide solution. Then a further 0.25 mL of methanesulfonyl chloride was slowly added to this under cooling and the pH value was kept constant at 11–11.5 by the addition of dilute NaOH solution as described above. After completing the addition of the methanesulfonyl chloride, it was stirred so long at pH 11–11.5 until the pH value remained constant without addition of sodium hydroxide solution. To the resulting reaction mixture, a solution of 2.7 mL of water and 0.75 ml of glacial acetic acid was slowly added to precipitate the product. It was filtered and thoroughly washed with water. The crude product **D** obtained after drying at 50 ºC under vacuum was used directly in the next step. Yield = 1.47 g, 80%.

To a solution of **D** (576 mg, 2.5 mmol, 1 equiv) in dry CH_2Cl_2 (9.6 mL) at 0 °C under N_2 was added dropwise oxalyl chloride (3.75 mmol, 1.5 equiv) and a catalytic amount of dry DMF (3 drops). The reaction mixture was stirred at room temperature until the reaction was complete (typically 3 h). The volatiles were evaporated under reduced pressure and the resulting crude acid chloride was used directly for the next step without further purification.

To the resulting residue (**E**), anhydrous dioxane (5 mL), 2-aminothiophenol (313 mg, 2.5 mmol, 1 equiv) and CH_3SO_3H (0.5 mL) were added successively. The resultant mixture was stirred at 100 ºC for 2 h (TLC). The resultant mixture was stirred at 100 ºC for 2 h (TLC). After completion of the reaction, dioxane was removed and the residue was diluted with EtOAc (10 mL), followed by saturated aq. $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×5 mL). The combined EtOAc extracts were washed with H_2O (3×5 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product which was purified by column chromatography to furnish the compound **4e**. Yield = 559 mg, 70%. R_f = 0.5 (Hexane:EtOAc = 4:1). mp = 80 ºC. IR (KBr): ν = 3144, 1639, 1409, 1152, 870 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.0 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.26–7.27 (m, 2H), 4.45 (s, 2H), 3.13 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.88, 153.34, 148.50, 136.68, 135.66, 130.84 (2C), 126.26, 125.18, 122.98, 122.51 (2C), 121.70, 39.88, 37.48 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{14}NO_3S_2[M + H]^+$, 320.0415; found, 320.0438.

Preparation of Compound 4i:

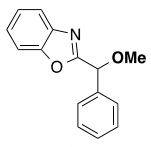


A 50 mL R.B. flask was charged with a mixture of **1e** (456 mg, 1.5 mmol), $Pd(OAc)_2$ (7 mg, 2 mol%) and PPh_3 (16 mg, 0.06 mmol) in DMF (3 mL) under nitrogen atmosphere. To it, butyl acrylate (385 mg, 2 equiv) and *N,N*-diisopropyl ethyl amine (481 mg, 2.5 equiv) were added and the whole mixture was heated at 100 °C for 36 h. After cooling to room temperature, it was acidified with 1N HCl and extracted with ethyl acetate. The organic layer was washed with 1N HCl and then water, combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography to give **4i** as a brown solid. Yield = 422 mg, 80%. R_f = 0.5 (Hexane:Et_2O = 4:1). mp = 68 ºC. IR (KBr): ν = 3144, 1628, 1402, 1163, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 16.2 Hz, 1H), 7.44 – 7.51 (m, 3H), 7.33 – 7.39 (m, 3H), 6.43 (d, *J* = 16.2 Hz, 1H), 4.45 (s, 2H), 4.20 (t, J = 7.2 Hz, 2H), 1.66 – 1.71 (m, 2H), 1.41 – 1.45 (m, 2H), 0.96 (t, J = 7.8 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.24, 167.21, 153.38, 144.10, 139.50, 135.75, 133.76, 129.81 (2C), 128.68 (2C), 126.22, 125.12, 122.99, 121.70, 118.54, 64.61, 40.49, 30.90, 19.34, 13.89 ppm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{21}NO_2SNa$ $[M + Na]^+$, 374.1191; found, 374.1159.

General Procedure A. Dehydrogenative methoxylation of 2-alkyl-2-benzoxazoles (1) or 2-alkyl-2-benzthiazoles (4) with methanol:

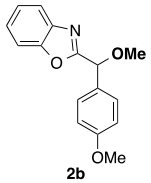
A 20 mL Schlenk tube was charged with 2-alkyl-2-benzoxazoles (**1**) or 2-alkyl-2-benzthiazoles (**4**) (0.2 mmol, 1.00 equiv), palladium(II) acetate (4.5 mg, 0.02 mmol, 10 mol%) and iodobenzene diacetate (129 mg, 0.4 mmol, 2.00 equiv). To it, anhydrous dichloroethane (1 mL) and methanol (1 mL) were added sequentially. The tube was attached with a coil-condenser equipped with a glass stopper and chilled water circulator. The reaction mixture was stirred at 100 ºC for the required time (TLC). After completion, the solvent was evaporated from the reaction mixture and the residue was then directly subjected to flash column chromatography on silica-gel to provide the corresponding methoxy-functionalized benzoxazole/benzothiazole-derivatives (**2** or **5**).

Characterization of methoxy-functionalized benzoxazoles (2a–2n).



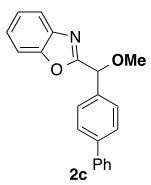
2a

2-(methoxy(phenyl)methyl)benzo[d]oxazole (**2a**) was prepared according to the general procedure A using 2-benzylbenzo[*d*]oxazole **1a** (42 mg, 0.2 mmol) as the starting material. Thick yellow liquid (39 mg, 82%). R_f = 0.3 (Hexane:EtOAc = 9:1). IR (neat): ν = 2928, 1589, 1490, 1258, 754 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.72–7.74 (m, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.47–7.49 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.28 –7.33 (m, 3H), 5.57 (s, 1H), 3.50 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.48, 150.98, 140.82, 136.88, 128.92, 128.84 (2C), 127.28 (2C), 125.38, 124.55, 120.46, 111.00, 79.51, 57.78 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{14}NO_2$ $[M + H]^+$, 240.1025; found, 240.1032.



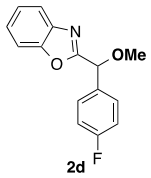
2b

2-(methoxy(4-methoxyphenyl)methyl)benzo[d]oxazole (**2b**) was prepared according to the general procedure A using 2-(4-methoxybenzyl)benzo[*d*]oxazole **1b** (48 mg, 0.2 mmol) as the starting material. Colorless liquid (39 mg, 73%). R_f = 0.3 (Hexane:Et_2O = 4:1). IR (neat): ν = 3133, 1645, 1402, 1103, 605 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.72–7.74 (m, 1H), 7.48–7.51 (m, 3H), 7.31–7.33 (m, 2H), 6.91–6.93 (m, 2H), 5.52 (s, 1H), 3.80 (s, 3H), 3.49 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.80, 160.13, 150.98, 140.89, 128.98, 128.81 (2C), 125.36, 124.57, 120.48, 114.29 (2C), 111.03, 79.16, 57.62, 55.43 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{15}NO_3Na$ $[M + Na]^+$, 292.0950; found, 292.0947.



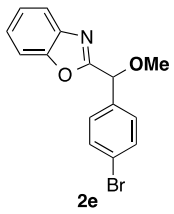
2c

2-([1,1'-biphenyl]-4-yl(methoxy)methyl)benzo[d]oxazole (**2c**) was prepared according to the general procedure A using 2-([1,1'-biphenyl]-4-ylmethyl)benzo[*d*]oxazole **1c** (57 mg, 0.2 mmol) as the starting material. Yellow solid (47 mg, 75%). mp = 79 ºC. R_f = 0.3 (Hexane:Et_2O = 9:1. IR (KBr): ν = 3128, 1639, 1402, 1091, 743 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.74–7.76 (m, 1H), 7.61–7.64 (m, 4H), 7.56–7.57 (m, 2H), 7.51–7.53 (m, 1H), 7.42 (t, J = 7.2, 2H), 7.32–7.35 (m, 3H), 5.62 (s, 1H), 3.55 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.50, 151.05, 141.94, 140.88, 140.69, 135.87, 128.93 (2C), 127.79 (2C), 127.67(2C), 127.64, 127.28 (2C), 125.48, 124.64, 120.53, 111.08, 79.33, 57.89 ppm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{17}NO_2Na$ $[M + Na]^+$, 338.1157; found, 338.1164.



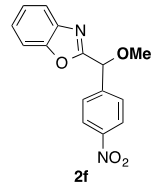
2d

2-((4-fluorophenyl)(methoxy)methyl)benzo[d]oxazole (**2d**) was prepared according to the general procedure A using 2-(4-fluorobenzyl)benzo[*d*]oxazole **1d** (45 mg, 0.2 mmol) as the starting material. Thick yellow liquid (40 mg, 78%). R_f = 0.5 (Hexane:Et_2O = 8.5:1.5). IR (neat): ν = 2928, 1230, 1097, 826, 749 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73–7.74 (m, 1H), 7.50–7.55 (m, 3H), 7.33–7.34 (m,, 2H), 7.08 (t, J = 9.0, 2H), 5.56 (s, 1H), 3.51 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.28, 163.08 (d, J_{C-F} = 247.5 Hz), 151.01, 140.81, 132.78, 129.16 (d, J_{C-F} = 8.5 Hz, 2C), 125.57, 124.70, 120.56, 115.88 (d, J_{C-F} = 21.6 Hz, 2C), 111.06, 78.84, 57.83 ppm. ^{19}F NMR (564 MHz, $CDCl_3$) δ –112.76 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}FNO_2$ $[M + H]^+$, 258.0930; found, 258.0934.



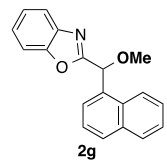
2e

2-((4-bromophenyl)(methoxy)methyl)benzo[d]oxazole (**2e**) was prepared according to the general procedure A using 2-(4-bromobenzyl)benzo[*d*]oxazole **1e** (58 mg, 0.2 mmol) as the starting material. Brown solid (55 mg, 87%). R_f = 0.3 (Hexane:Et_2O = 8.5:1.5). mp = 62 ºC. IR (KBr): ν = 3128, 1639, 1402, 1092, 743 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73–7.74 (m, 1H), 7.50–7.53 (m, 3H), 7.43–7.45 (m, 2H), 7.33–7.34 (m, 2H), 5.54 (s, 1H), 3.51 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.94, 151.00, 140.75, 135.97, 132.05 (2C), 128.94 (2C), 125.62, 124.72, 123.06, 120.56, 111.06, 78.83, 57.90 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}BrNO_2$ $[M + H]^+$, 318.0130; found, 318.0117.



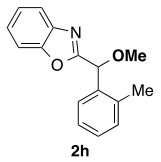
2f

2-(methoxy(4-nitrophenyl)methyl)benzo[d]oxazole (**2f**) was prepared according to the general procedure A using 2-(4-nitrobenzyl)benzo[*d*]oxazole **1f** (51 mg, 0.2 mmol) as the starting material. Light yellow solid (40 mg, 70%). R_f = 0.4 (Hexane:Et_2O = 4:1). mp = 108 ºC. IR (KBr): ν = 3144, 1634, 1402, 1091, 611 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.25–8.26 (m, 2H), 7.75 (d, J = 8.4 Hz, 3H), 7.51–7.53 (m, 1H), 7.35–7.37 (m, 2H), 5.69 (s, 1H), 3.57 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.09, 151.07, 148.24, 143.98, 140.65, 128.00 (2C), 125.96, 124.95, 124.09 (2C), 120.69, 111.15, 78.42, 58.24 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}N_2O_4$ $[M + H]^+$, 285.0875; found, 285.0876.



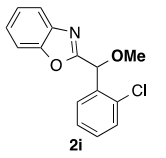
2g

2-(methoxy(naphthalen-1-yl)methyl)benzo[d]oxazole (**2g**) was prepared according to the general procedure A using 2-(naphthalen-1-ylmethyl)benzo[*d*]oxazole **1g** (52 mg, 0.2 mmol) as the starting material. Light yellow solid (32 mg, 55%). R_f = 0.4 (Hexane:Et_2O = 8.5:1.5). mp = 54 ºC. IR (KBr): ν = 3128, 1634, 1402, 1108, 627 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 9.0 Hz, 1H), 7.84 – 7.87 (m, 3H), 7.73 – 7.74 (m, 1H), 7.43 – 7.55 (m, 4H), 7.27 – 7.30 (m, 2H), 6.24 (s, 1H), 3.59 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.42, 150.94, 140.91, 134.00, 132.36, 130.88, 129.70, 128.94, 126.79, 125.99, 125.94, 125.51, 125.37, 124.55, 123.60, 120.51, 111.03, 77.64, 57.98 ppm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_2$ $[M + H]^+$, 290.1181; found, 290.1179.



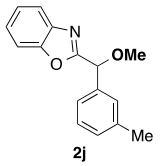
2h

2-(methoxy(o-tolyl)methyl)benzo[d]oxazole (**2h**) was prepared according to the general procedure A using 2-(2-methylbenzyl)benzo[*d*]oxazole **1h** (45 mg, 0.2 mmol) as the starting material. Brown liquid (33 mg, 65%). R_f = 0.5 (Hexane:Et_2O = 8.5:15). IR (neat): ν = 3105, 1645, 1402, 1086, 737 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73 –7.74 (m, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.48 – 7.50 (m, 1H), 7.23 – 7.32 (m, 4H), 7.17 – 7.20 (m, 1H), 5.77 (s, 1H), 3.52 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.25, 150.99, 140.88, 136.30, 135.13, 130.85, 128.79, 127.35, 126.57, 125.38, 124.57, 120.50, 111.06, 76.74, 57.85, 19.42 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{15}NO_2Na$ $[M + Na]^+$, 276.1000; found, 276.1009.



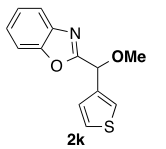
2i

2-((2-chlorophenyl)(methoxy)methyl)benzo[d]oxazole (**2i**) was prepared according to the general procedure A using 2-(2-chlorobenzyl)benzo[*d*]oxazole **1i** (49 mg, 0.2 mmol) as the starting material. Thick colourless liquid (40 mg, 73%). R_f = 0.6 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1628, 1462, 1097, 749 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.78 (m, 2H), 7.50 – 7.51 (m, 1H), 7.28 – 7.40 (m, 5H), 6.03 (s, 1H), 3.55 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.46, 150.93, 140.88, 134.71, 133.44, 130.04, 129.70, 128.84, 127.47, 125.51, 124.60, 120.66, 111.01, 75.62, 58.10 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}ClNO_2$ $[M + H]^+$, 274.0635; found, 274.0626.



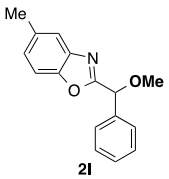
2j

2-(methoxy(m-tolyl)methyl)benzo[d]oxazole (**2j**) was prepared according to the general procedure A using 2-(3-methylbenzyl)benzo[*d*]oxazole **1j** (45 mg, 0.2 mmol) as the starting material. Brown liquid (41 mg, 81%). R_f = 0.4 (Hexane:Et_2O = 8.5:1.5. IR (neat): ν = 3133, 1634, 1402, 1246, 832 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.74 (m, 1H), 7.49 – 7.51 (m, 1H), 7.34 –7.37 (m, 2H), 7.27 – 7.33 (m, 3H), 7.14 – 7.15 (m, 1H), 5.54 (s, 1H), 3.51 (s, 3H), 2.35 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.62, 150.99, 140.88, 138.64, 136.81, 129.73, 128.75, 127.87, 125.34, 124.54, 124.39, 120.46, 111.03, 79.57, 57.79, 21.53 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{16}NO_2$ $[M + H]^+$, 254.1181; found, 254.1185.



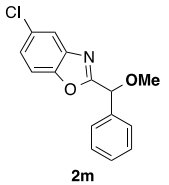
2k

2-(methoxy(thiophen-3-yl)methyl)benzo[d]oxazole (**2k**) was prepared according to the general procedure A using 2-(thiophen-3-ylmethyl)benzo[*d*]oxazole **1k** (43 mg, 0.2 mmol) as the starting material. Light yellow liquid (23 mg, 47%). R_f = 0.3 (Hexane:Et_2O = 8.5:1.5). IR (neat): ν = 2928, 1645, 1451, 1097, 749 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.75 (m, 1H), 7.53 – 7.54 (m, 1H), 7.47 (s, 1H), 7.34 – 7.35 (m, 3H), 7.25 (d, J = 4.8 Hz, 1H), 5.68 (s, 1H), 3.50 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.10, 151.01, 140.84, 137.77, 126.74, 126.46, 125.55, 124.67, 124.13, 120.55, 111.10, 75.63, 57.73 ppm. HRMS (ESI): *m/z* calcd. for $C_{13}H_{12}NO_2S$ $[M + H]^+$, 246.0589; found, 246.0594.



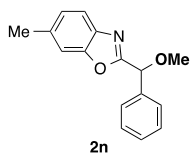
2l

2-(methoxy(phenyl)methyl)-5-methylbenzo[d]oxazole (**2l**) was prepared according to the general procedure A using 2-benzyl-5-methylbenzo[*d*]oxazole **1l** (45 mg, 0.2 mmol) as the starting material. Brown liquid (37 mg, 73%). R_f = 0.3 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1573, 1456, 1091, 732 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 2H), 7.51 (s, 1H), 7.33–7.39 (m, 4H), 7.12 (d, J = 8.4 Hz, 1H), 5.55 (s, 1H), 3.50 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.56, 149.25, 141.02, 136.98, 134.43, 128.89, 128.84 (2C), 127.30 (2C), 126.50, 120.32, 110.37, 79.54, 57.77, 21.53 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{16}NO_2$ $[M + H]^+$, 254.1181; found, 254.1171.



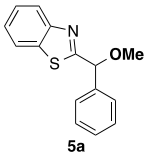
2m

5-chloro-2-(methoxy(phenyl)methyl)benzo[d]oxazole (**2m**) was prepared according to the general procedure A using 2-benzyl-5-chlorobenzo[*d*]oxazole **1m** (49 mg, 0.2 mmol) as starting material. colourless liquid (36 mg, 66%). R_f = 0.4 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1573, 1456, 1252, 1097, 705 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.39 – 7.42 (m, 3H), 7.36 – 7.37 (m, 1H), 7.29 – 7.30 (m, 1H), 5.55 (s, 1H), 3.51 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.98, 149.59, 142.01, 136.58, 130.15, 129.15, 128.98 (2C), 127.35 (2C), 125.81, 120.51, 111.80, 79.45, 57.87 ppm. HRMS (ESI): *m/z* calcd. For $C_{15}H_{12}ClNO_2Na$ $[M + Na]^+$, 296.0454; found, 296.0520.



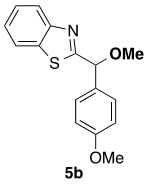
2n

2-(methoxy(phenyl)methyl)-6-methylbenzo[d]oxazole (**2n**) was prepared according to the general procedure A using 2-benzyl-6-methylbenzo[*d*]oxazole **1n** (45 mg, 0.2 mmol) as the starting material. Yellow liquid (36 mg, 71%). R_f = 0.4 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1744, 1451, 1224, 1091, 809 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.32 –7.34 (m, 1H), 7.30 (s, 1H), 7.13 (d, J = 8.4 Hz, 1H), 5.55 (s, 1H), 3.50 (s, 3H), 2.45 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.96, 151.34, 138.67, 137.05, 135.89, 128.89, 128.85 (2C), 127.31 (2C), 125.81, 119.80, 111.18, 79.55, 57.79, 21.86 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{15}NO_2Na$ $[M + Na]^+$, 276.1000; found, 276.1112.



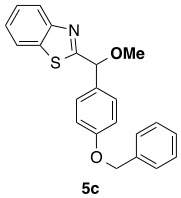
5a

2-(methoxy(phenyl)methyl)benzo[d]thiazole (**5a**) was prepared according to the general procedure A using 2-benzylbenzo[*d*]thiazole **4a** (45 mg, 0.2 mmol) as starting material. Thick yellow liquid (43 mg, 84%). R_f = 0.5 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1744, 1366, 1224, 1025, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.35–7.38 (m, 3H), 7.30–7.34 (m, 1H), 5.67 (s, 1H), 3.53 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.73, 153.17, 139.11, 135.27, 128.85 (2C), 128.64, 127.09 (2C), 126.07, 125.21, 123.36, 121.91, 83.68, 57.80 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}NOSNa$ $[M + Na]^+$, 278.0616; found, 278.0588.



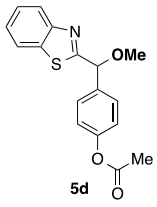
5b

2-(methoxy(4-methoxyphenyl)methyl)benzo[d]thiazole (**5b**) was prepared according to the general procedure A using 2-(4-methoxybenzyl)benzo[*d*]thiazole **4b** (51 mg, 0.2 mmol) as the starting material. Colorless solid (38 mg, 67%). R_f = 0.3 (Hexane:Et_2O = 4:1). mp = 46 ºC. IR (KBr): ν = 3139, 1634, 1402, 1080, 837 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.42–7.45 (m, 3H), 7.35 (t, J = 7.8 Hz, 1H), 6.89–6.91 (m, 2H), 5.62 (s, 1H), 3.79 (s, 3H), 3.50 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.05, 159.89, 153.23, 135.24, 131.25, 128.51 (2C), 126.04, 125.16, 123.34, 121.90, 114.26 (2C), 83.30, 57.61, 55.42 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{16}NO_2S$ $[M + H]^+$, 286.0902; found, 286.0902.



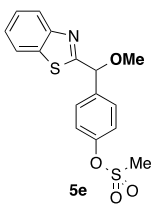
5c

2-((4-(benzyloxy)phenyl)(methoxy)methyl)benzo[d]thiazole (**5c**) was prepared according to the general procedure A using 2-(4-(benzyloxy)benzyl)benzo[*d*]thiazole **4c** (66 mg, 0.2 mmol) as the starting material. Colourless liquid (54 mg, 75%). R_f = 0.4 (Hexane:Et_2O = 4:1). IR (neat): ν = 2928, 1606, 1451, 1235, 732 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.39 – 7.43 (m, 5H), 7.30 –7.37 (m, 4H), 6.97 (d, J = 8.4 Hz, 2H), 5.61 (s, 1H), 5.03 (s, 2H), 3.49 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.03, 159.12, 153.22, 136.95, 135.23, 131.52, 128.73 (2C), 128.54 (2C), 128.14, 127.60 (2C), 126.05, 125.17, 123.34, 121.91, 115.17 (2C), 83.29, 70.17, 57.64 ppm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{20}NO_2S$ $[M + H]^+$, 362.1215; found, 362.1222.



5d

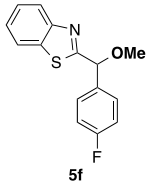
4-(benzo[d]thiazol-2-yl(methoxy)methyl)phenyl acetate (**5d**) was prepared according to the general procedure A using 4-(benzo[*d*]thiazol-2-ylmethyl)phenyl acetate **4d** (57 mg, 0.2 mmol) as the starting material. Yellow solid (40 mg, 64%). R_f = 0.5 (Hexane:EtOAc = 4:1). mp = 82 ºC. IR (KBr): ν = 3099, 1756, 1634, 1402, 1192, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.53–7.54 (m, 2H), 7.45 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.09–7.11 (m, 2H), 5.67 (s, 1H), 3.53 (s, 3H), 2.28 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.43, 169.43, 153.15, 150.81, 136.64 (2C), 135.23, 128.19 (2C), 126.14, 125.30, 123.37, 121.97 (2C), 83.09, 57.89, 21.28 ppm. HRMS (ESI): *m/z* calcd. for $C_{17}H_{16}NO_3S$ $[M + H]^+$, 314.0851; found, 314.0845.



5e

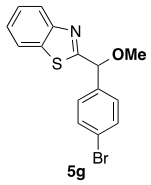
4-(benzo[d]thiazol-2-yl(methoxy)methyl)phenyl methanesulfonate (**5e**) was prepared according to the general procedure A using 4-(benzo[*d*]thiazol-2-ylmethyl)phenyl methanesulfonate **4e** (64 mg, 0.2 mmol) as the starting material. Colorless solid (59 mg, 85%). R_f = 0.3 (Hexane:EtOAc = 4:1). mp = 150 ºC. IR (KBr): ν = 2950, 1639, 1462, 1163, 959 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.58–7.60 (m, 2H), 7.47 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.29–7.30 (m, 2H), 5.68 (s, 1H), 3.55 (s, 3H), 3.12 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.02, 153.15, 149.24, 138.53, 135.18, 128.71

(2C), 126.24, 125.43, 123.39, 122.39 (2C), 121.99, 82.85, 58.03, 37.53 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{16}NO_4S_2$ $[M + H]^+$, 350.0521; found, 350.0511.



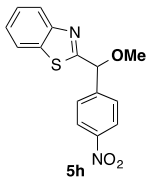
5f

*2-((4-fluorophenyl)(methoxy)methyl)benzo[d]thiazole (**5f**)* was prepared according to the general procedure A using 2-(4-fluorobenzyl)benzo[*d*]thiazole **4f** (49 mg, 0.2 mmol) as the starting material. Light yellow liquid (40 mg, 74%). R_f = 0.5 (Hexane:Et_2O = 8.5:1.5). IR (neat): ν = 2928, 1600, 1506, 1224, 1091, 766 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.44 – 7.50 (m, 3H), 7.37 (t, J = 7.8 Hz, 1H), 7.04 – 7.07 (m, 2H), 5.65 (s, 1H), 3.52 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.50, 162.87 (d, $J_{C\text{-}F}$ = 247.34 Hz), 153.15, 135.19, 134.96 (d, $J_{C\text{-}F}$ = 2.72 Hz), 128.88 (d, $J_{C\text{-}F}$ = 8.46 Hz, 2C), 126.17, 125.33, 123.37, 121.96, 115.80 (d, $J_{C\text{-}F}$ = 21.74 Hz, 2C), 82.98, 57.81 ppm. ^{19}F NMR (564 MHz, $CDCl_3$) □ –113.29 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}FNOS$ $[M + H]^+$, 274.0702; found, 274.0707.



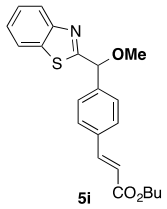
5g

2-((4-bromophenyl)(methoxy)methyl)benzo[d]thiazole (**5g**) was prepared according to the general procedure A using 2-(4-bromobenzyl)benzo[*d*]thiazole **4g** (61 mg, 0.2 mmol) as the starting material. Colorless liquid (46 mg, 69%). R_f = 0.5 (Hexane: Et_2O = 9:1). IR (neat): ν = 2928, 1645, 1468, 1163, 1048, 826 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.44–7.51 (m, 3H), 7.36–7.41 (m, 3H), 5.62 (s, 1H), 3.52 (s, 3H) ppm.^{13}C NMR (151 MHz, $CDCl_3$) δ 173.09, 153.15, 138.18, 135.20, 132.00 (2C), 128.74 (2C), 126.19, 125.38, 123.40, 122.70, 121.97, 83.00, 57.88 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}NOSBr$ $[M + H]^+$, 333.9901; found, 333.9900.



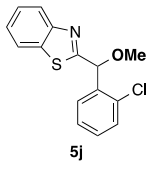
5h

2-(methoxy(4-nitrophenyl)methyl)benzo[d]thiazole (**5h**) was prepared according to the general procedure A using 2-(4-nitrobenzyl)benzo[*d*]thiazole **4h** (54 mg, 0.2 mmol) as the starting material. Thick yellow liquid (45 mg, 75%). R_f = 0.3 (Hexane:Et_2O = 8.5:1.5). IR (neat): ν = 2928, 1517, 1346, 1091, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.24 (m, 2H), 8.00 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 9.0 Hz, 2H), 7.47 – 7.49 (m, 1H), 7.38 –7.41 (m, 1H), 5.77 (s, 1H), 3.58 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.08, 153.11, 148.00, 146.16, 135.20, 127.76 (2C), 126.39, 125.65, 124.05 (2C), 123.49, 122.05, 82.64, 58.24 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}N_2O_3S$ $[M + H]^+$, 301.0647; found, 301.0653.



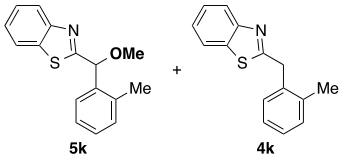
5i

Butyl-3-(4-(benzo[d]thiazol-2-yl(methoxy)methyl)phenyl)acrylate (**5i**) was prepared according to the general procedure A using butyl-3-(4-(benzo[*d*]thiazol-2-ylmethyl)phenyl)acrylate **4i** (70 mg, 0.2 mmol) as the starting material. Colourless liquid (42 mg, 55%). R_f = 0.5 (Hexane:Et_2O = 3:2). IR (neat): ν = 2956, 1711, 1456, 1313, 1169, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 16.2 Hz, 1H), 7.52 –7.55 (m, 4H), 7.44 (t, J = 7.8 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 5.68 (s, 1H), 4.20 (t, J = 6.6 Hz, 2H), 3.53 (s, 3H), 1.65 – 1.70 (m, 2H), 1.40 – 1.44 (m, 2H), 0.95 (t, J = 7.8 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.08, 167.05, 153.12, 143.94, 141.15, 135.18, 134.75, 128.47 (2C), 127.49 (2C), 126.11, 125.29, 123.34, 121.91, 118.85, 83.20, 64.55, 57.86, 30.84, 19.28, 13.84 ppm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{24}NO_3S$ $[M + H]^+$, 382.1477; found, 382.1496.

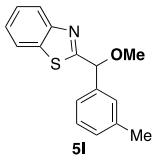


5j

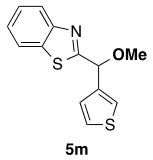
*2-((2-chlorophenyl)(methoxy)methyl)benzo[d]thiazole (**5j**)* was prepared according to the general procedure A using 2-(2-chlorobenzyl)benzo[*d*]thiazole **4j** (52 mg, 0.2 mmol) as the starting material. Colourless liquid (41 mg, 81%). R_f = 0.5 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1672, 1440, 1091, 760 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.60 – 7.61 (m, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.40 – 7.41 (m, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.27 – 7.33 (m, 2H), 6.14 (s, 1H), 3.55 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.77, 153.30, 136.89, 135.29, 133.88, 129.89, 129.86, 128.62, 127.46, 126.13, 125.33, 123.64, 121.83, 79.60, 57.99 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}ClNOS$ $[M + H]^+$, 290.0406; found, 290.0407.



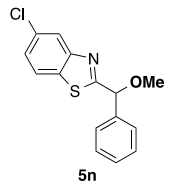
2-(methoxy(o-tolyl)methyl)benzo[d]thiazole (**5k**) was prepared according to the general procedure A using 2-(2-methylbenzyl)benzo[*d*]thiazole **4k** (48 mg, 0.2 mmol) as the starting material. **5k** was obtained as an inseparable mixture with **4k** after passing the crude reaction mixture through a small bed of silica gel. Thick colourless liquid (51 mg, 59% **5k** + 41% **4k** based on ^{1}H NMR analysis). R_f = 0.5 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1606, 1451, 1313, 1086, 737 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.42 –7.43 (m, 2H), 7.30 –7.35 (m, 3H), 7.16 –7.25 (m, 6H), 5.85 (s, 1H), 4.43 (s, 2H), 3.52 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.21, 171.80, 153.42, 153.16, 137.42, 137.13, 136.53, 135.78, 135.66, 135.45, 130.91, 130.84, 130.30, 128.56, 127.96, 126.78, 126.57, 126.48, 126.06, 126.02, 125.21, 124.86, 123.43, 122.83, 121.86, 121.64, 80.86, 57.73, 38.66, 19.81, 19.67 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{16}NOS$ [M + H]$^+$, 270.0953; found, 270.0962.



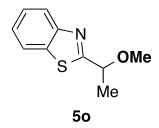
2-(methoxy(m-tolyl)methyl)benzo[d]thiazole (**5l**) was prepared according to the general procedure A using 2-(3-methylbenzyl)benzo[*d*]thiazole **4l** (48 mg, 0.2 mmol) as the starting material. Thick yellow liquid (44 mg, 81%). R_f = 0.6 (Hexane:Et_2O = 8.5:1.5). IR (neat): ν = 2928, 1512, 1451, 1091, 760 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.31 – 7.35 (m, 3H), 7.24 – 7.25 (m, 1H), 7.11 (d, J = 7.2 Hz, 1H), 5.63 (s, 1H), 3.51 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.81, 153.16, 138.97, 138.55, 135.23, 129.41, 128.72, 127.69, 126.00, 125.13, 124.17, 123.31, 121.86, 83.71, 57.73, 21.55 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{14}NOS$ [M – H]$^+$, 268.0796; found, 268.0795.



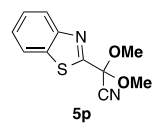
2-(methoxy(thiophen-3-yl)methyl)benzo[d]thiazole (**5m**) was prepared according to the general procedure A using 2-(thiophen-3-ylmethyl)benzo[*d*]thiazole **4m** (46 mg, 0.2 mmol) as the starting material. Thick brown liquid (26 mg, 50%). R_f = 0.4 (Hexane:Et_2O = 8.5:1.5). IR (neat): ν = 2928, 1717, 1435, 1169, 1091, 760 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.8, 1H), 7.42 (s, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.31 (s, 1H), 7.15 (d, J = 4.8 Hz , 1H), 5.77 (s, 1H), 3.53 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.18, 153.13, 140.15, 135.28, 126.66, 126.18, 126.14, 125.34, 123.41, 123.40, 121.98, 80.03, 57.83 ppm. HRMS (ESI): *m/z* calcd. for $C_{13}H_{11}NOS_2Na$ [M + Na]$^+$, 284.0180; found, 284.0303.



5-chloro-2-(methoxy(phenyl)methyl)benzo[d]thiazole (**5n**) was prepared according to the general procedure A using 2-benzyl-5-chlorobenzo[*d*]thiazole **4n** (52 mg, 0.2 mmol) as the starting material. Golden yellow solid (39 mg, 67%). R_f = 0.5 (Hexane:Et_2O = 9:1). mp = 86 ºC. IR (KBr): ν = 2928, 1612, 1435, 1070, 798 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.38 (t, 7.2 Hz, 2H), 7.31 – 7.33 (m, 2H), 5.64 (s, 1H), 3.52 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 175.84, 154.09, 138.77, 133.51, 132.08, 128.91 (2C), 128.78, 127.10 (2C), 125.70, 123.19, 122.61, 83.54, 57.80 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{12}ClNOSNa$ [M + Na]$^+$, 312.0226; found, 312.0224.



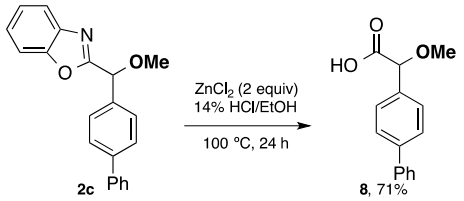
2-(1-methoxyethyl)benzo[d]thiazole (**5o**) was prepared according to the general procedure A using 2-ethylbenzo[*d*]thiazole **4o** (65 mg, 0.4 mmol) as the starting material. Thick yellow liquid (22 mg, 28%). R_f = 0.5 (Hexane:Et_2O = 9:1). IR (neat): ν = 2928, 1650, 1451, 1263, 1091, 754 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 4.75 – 4.78 (m, 1H), 3.46 (s, 3H), 1.64 (d, J = 6.6 Hz, 3H) ppm. ^{13}C NMR δ 175.86, 153.20, 135.07, 126.08, 125.19, 123.11, 122.04, 78.05, 57.70, 22.41 ppm. HRMS (ESI): *m/z* calcd. for $C_{10}H_{12}NOS$ [M + H]$^+$, 194.0640; found, 194.0637.



2-(benzo[d]thiazol-2-yl)-2,2-dimethoxyacetonitrile (**5p**) was prepared according to the general procedure A using 2-(benzo[*d*]thiazol-2-yl)acetonitrile **4p** (35 mg, 0.2 mmol) as the starting material. Colourless liquid (42 mg, 90%). R_f = 0.5 (Hexane:Et_2O = 4:1). IR (neat): ν = 2950, 1639, 1445, 1246, 799 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 3.57 (s, 6H) ppm. ^{13}C NMR (151

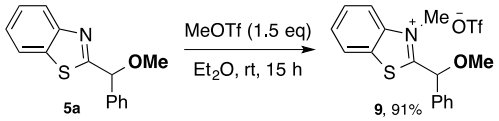
MHz, $CDCl_3$) δ 164.17, 152.71, 135.50, 126.88, 126.70, 124.64, 122.03, 113.88, 96.88, 52.72 (2C) ppm. HRMS (ESI): *m/z* calcd. for $C_{11}H_{11}N_2O_2S$ $[M + H]^+$, 235.0541; found, 235.0555.

Representative procedure for the removal of benzoxazole protection from 2c:



A 25 mL R.B. flask was charged with **2c** (57 mg, 0.18 mmol, 1.0 equiv), $ZnCl_2$ (49 mg, 0.36 mmol, 2.0 equiv), 14% HCl (1.5 mL) and EtOH (1.5 mL). The reaction mixture was stirred at 100 ºC using a coil-condenser for 24 h. After completion, the resulting mixture was diluted with DCM (5 mL) and extracted with saturated aqueous $NaHCO_3$ solution (3 x 15 mL). The combined aqueous layer was acidified with concentrated HCl and then extracted with DCM (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuum to give the crude carboxylic acid **8**, which was further purified by column chromatography over silica-gel. Brown solid (31 mg, 71%). mp = 120 ºC. R_f = 0.5 (DCM:MeOH = 9.5:0.5). IR (KBr): ν = 3128, 1639, 1402, 1114, 622 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 7.64 (t, J = 8.4 Hz, 4H), 7.45 – 7.49 (m, 4H), 7.35 – 7.38 (m, 1H), 4.73 (s, 1H), 3.57 (s, 3H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.03, 139.86, 139.76, 137.10, 131.03, 128.95 (3C), 127.97, 127.48, 126.67 (2C), 126.48, 66.37, 56.38 ppm.
ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{14}O_3Na$ $[M + Na]^+$, 265.0841; found, 265.0824.

Synthesis of N-methylated azolium triflate 9 from 5a:



Compound **9** was prepared using a reported protocol described by Mayr *et al.*[3] Under nitrogen atmosphere, a 25 mL rb was charged with **5a** (153 mg, 0.6 mmol, 1 eq.) in anhydrous Et_2O (5 mL). To it, was added MeOTf (148 mg, 0.9 mmol, 1.5 eq.) *via* syringe and the reaction mixture was allowed to stir for 16 h at room temperature. The solvent was then decanted and the residue was washed with cooled Et_2O (3 x 5 mL) and hexane (3 x 5 mL) and dried under vacuum to afford a colorless powder (229 mg, 91%). The characterization data are in agreement with that of the reported compound.[3] ^1H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 9.0, 1H), 7.79 – 7.83 (m, 1H), 7.72 – 7.74 (m, 1H), 7.52 (m, 2H), 7.47(s, 3H), 6.39 (s, 1H), 4.15 (s, 3H), 3.54 (s, 3H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.03, 139.86, 139.76, 137.10, 131.03, 128.95 (3C), 127.97, 127.48, 126.67 (2C), 126.48, 66.37, 56.38 ppm. HRMS (ESI): *m/z* calcd. for $[C_{16}H_{16}NOS]^+$ is 270.0947; found, 270.1260.

References:

1. L. F. Armarego and D. D. Perrin, In *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Oxford: USA, 2000.

2. (a) G. Z. Li, J. Jiang, F. Zhang, F. Xiao, G.-J. Denga, *Org. Biomol. Chem.*, 2017, **15**, 10024; (b) Y. Huang, D. Yan, X. Wang, P. Zhou, W. Wu and H. Jiang, *Chem. Commun.*, 2018, **54**, 1742; (c) S. Florio, P. Lorusso, R. Luisi, C. Granito, L. Ronzini and L. Troisi, *Eur. J. Org. Chem.*, 2004, 2118; (d) Z.-L. Li, L.-K. Jin and C. Cai, *Org. Chem. Frontiers*, 2017, **4**, 2039; (e) M. S. Mayo, X. Yu, X. Zhou, X. Feng, Y. Yamamoto and M. Bao, *Org. Lett.*, 2014, **16**, 764; (f) R. S. Reshma, V. U. Jeankumar, N. Kapoor, S. Saxena, K. A. Bobesh, A. R. Vachaspathy, P. E. Kolattukudy and D. Sriram, *Bioorg. Med. Chem.*, 2017, **25**, 2761; (g) T. B. Nguyen and P.

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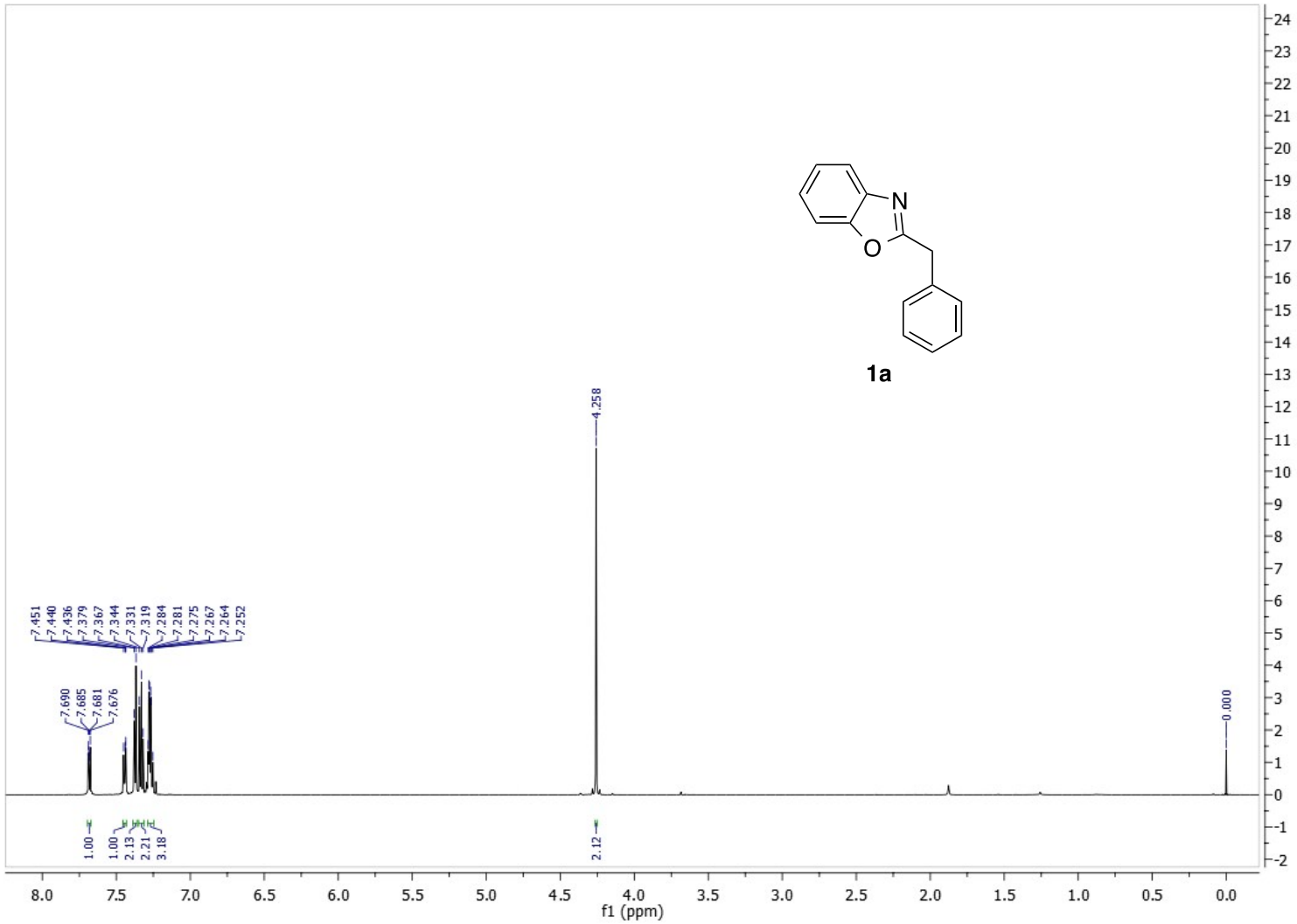
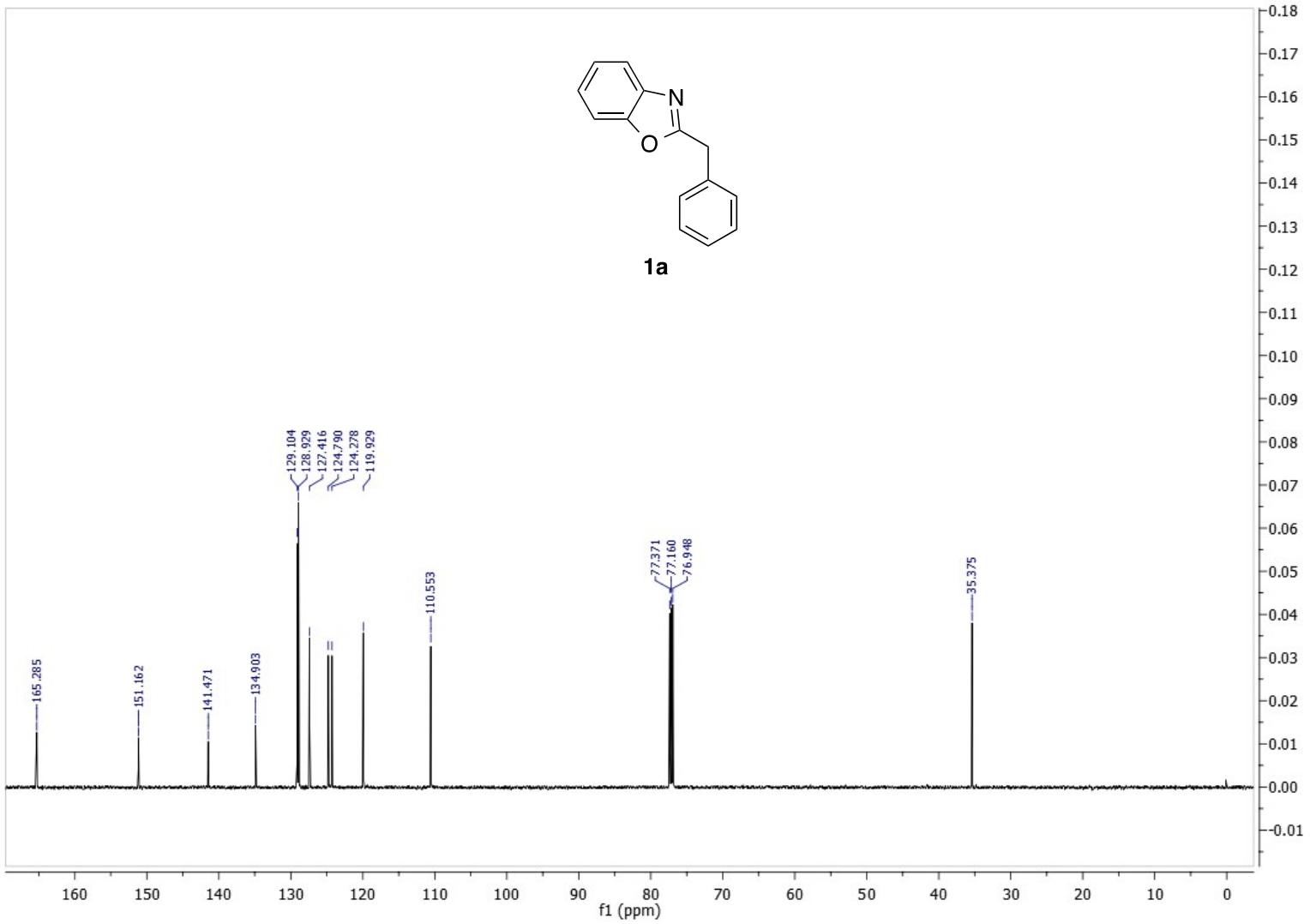
3. B. Maji and H. Mayr, *Angew. Chem., Int. Ed.*, 2012, **51**, 10408.

NMR spectra of all substrates

^{1}H NMR (600 MHz, $CDCl_3$):



^{13}C NMR (151 MHz, $CDCl_3$):



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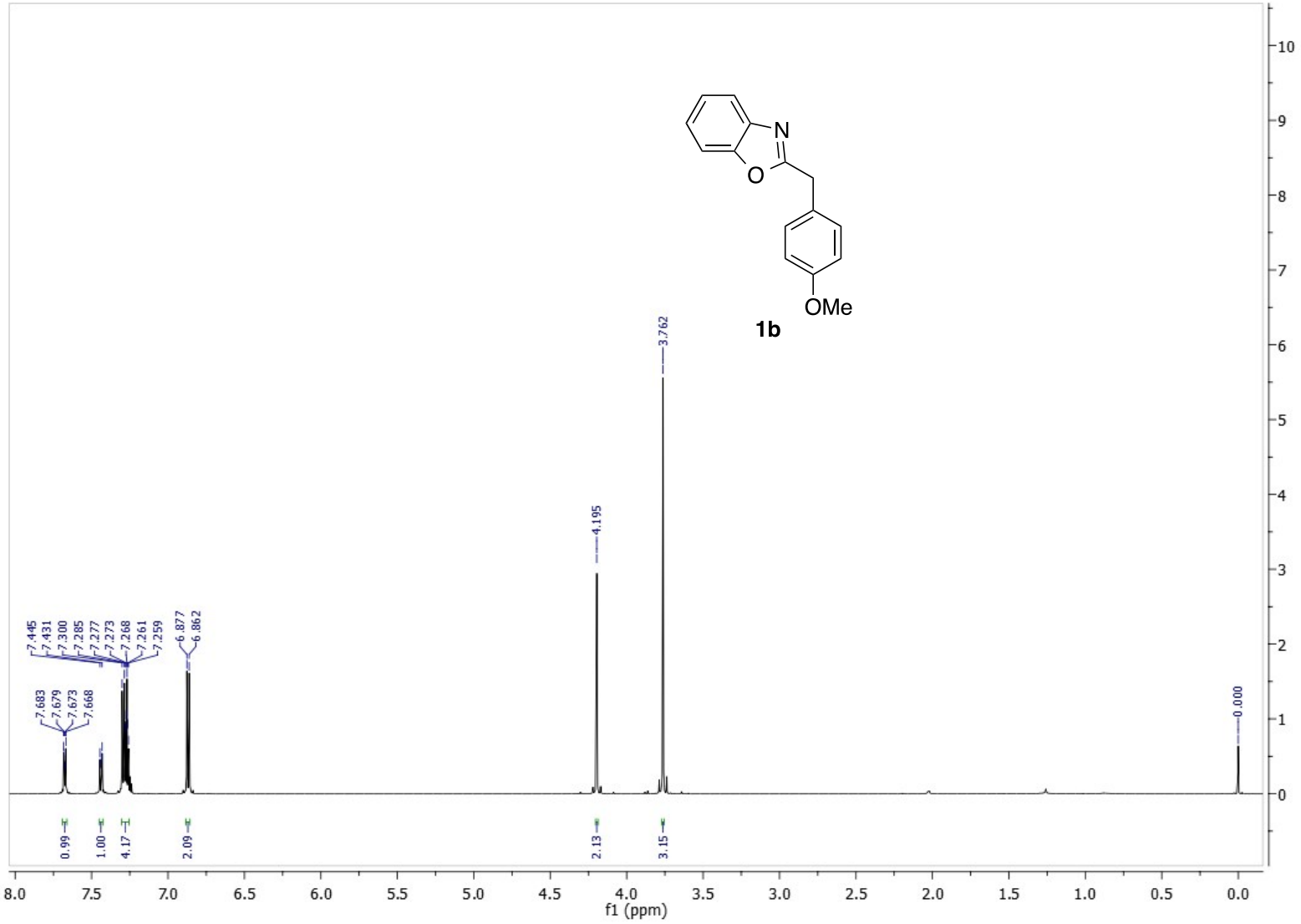

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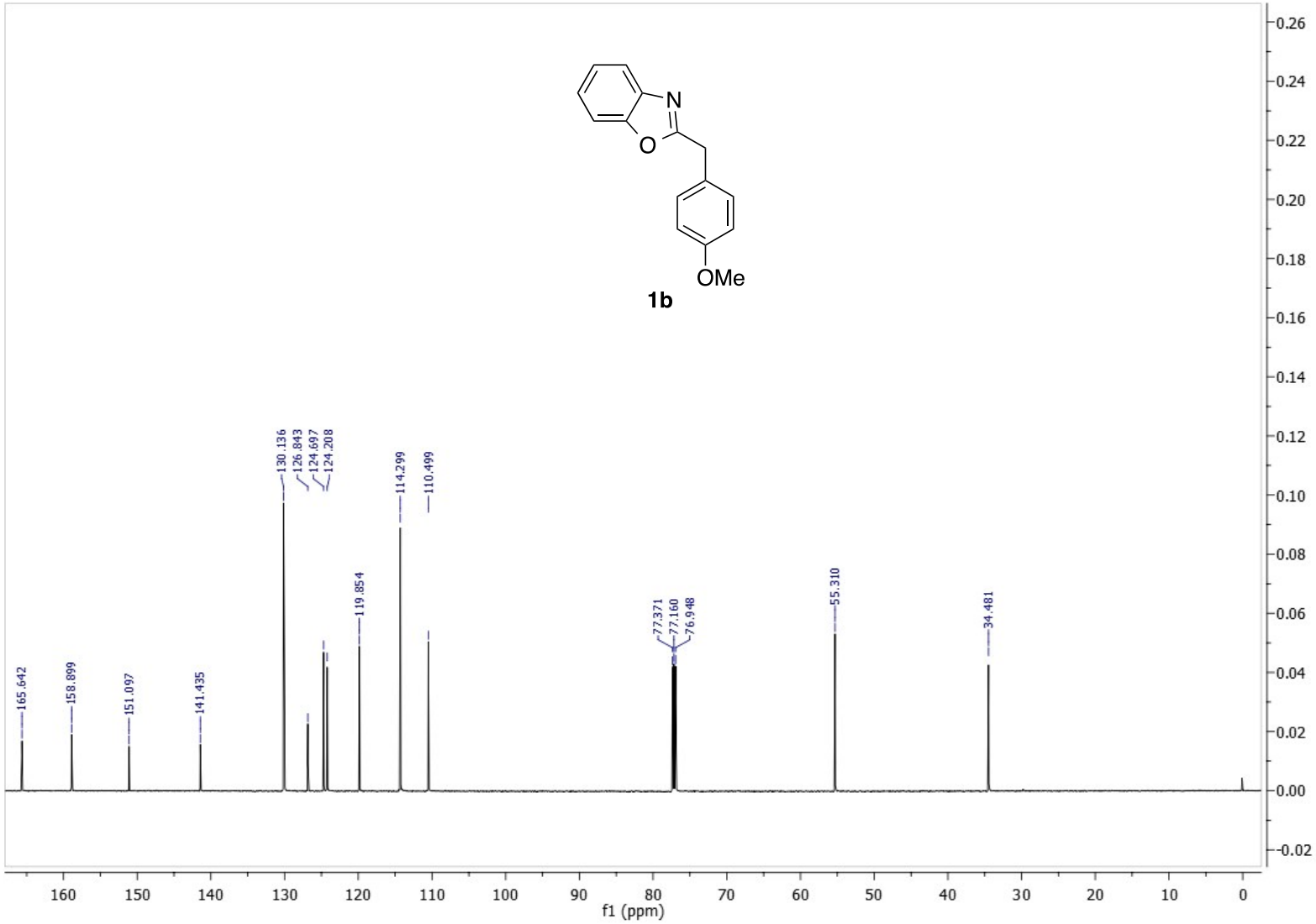

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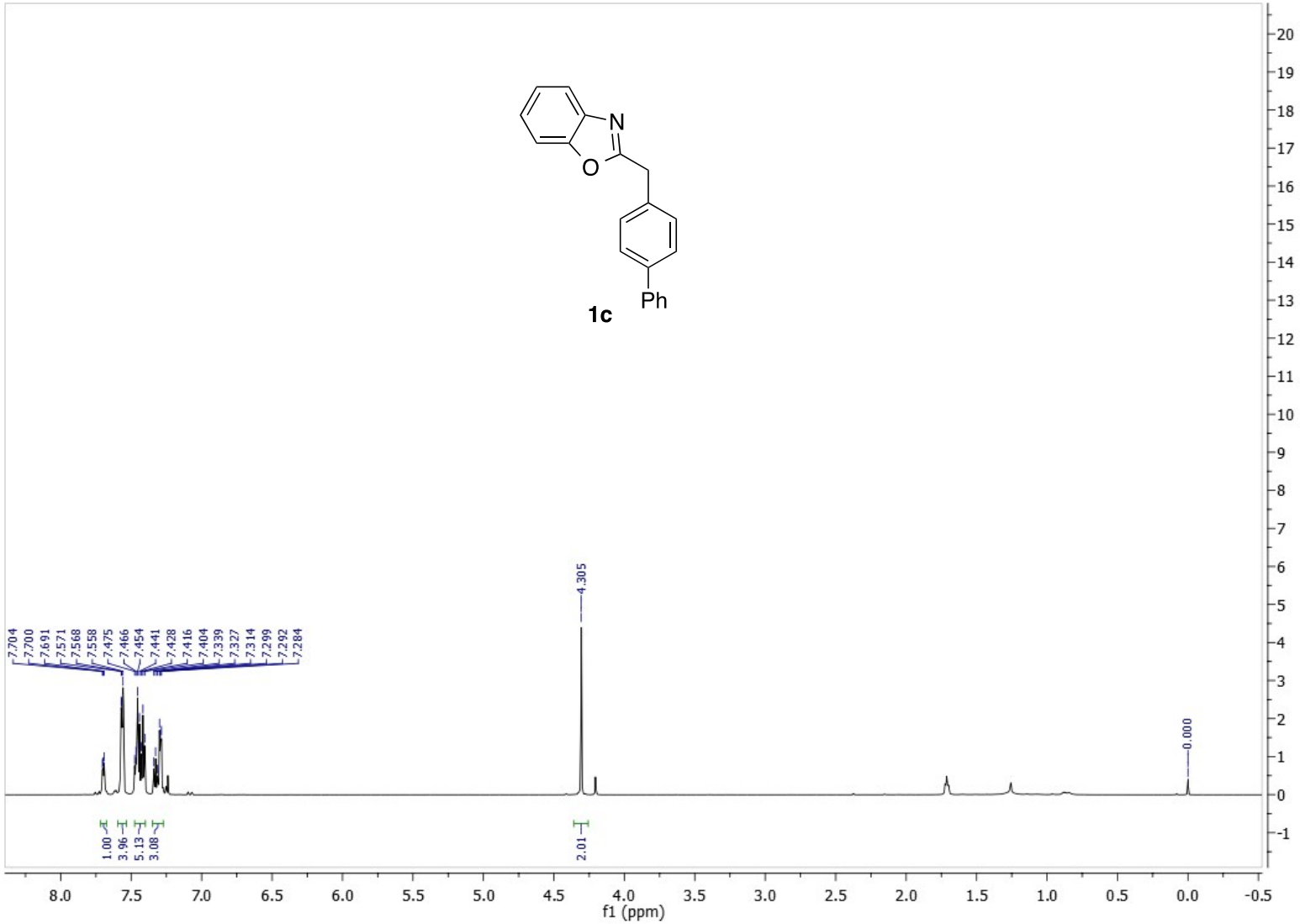

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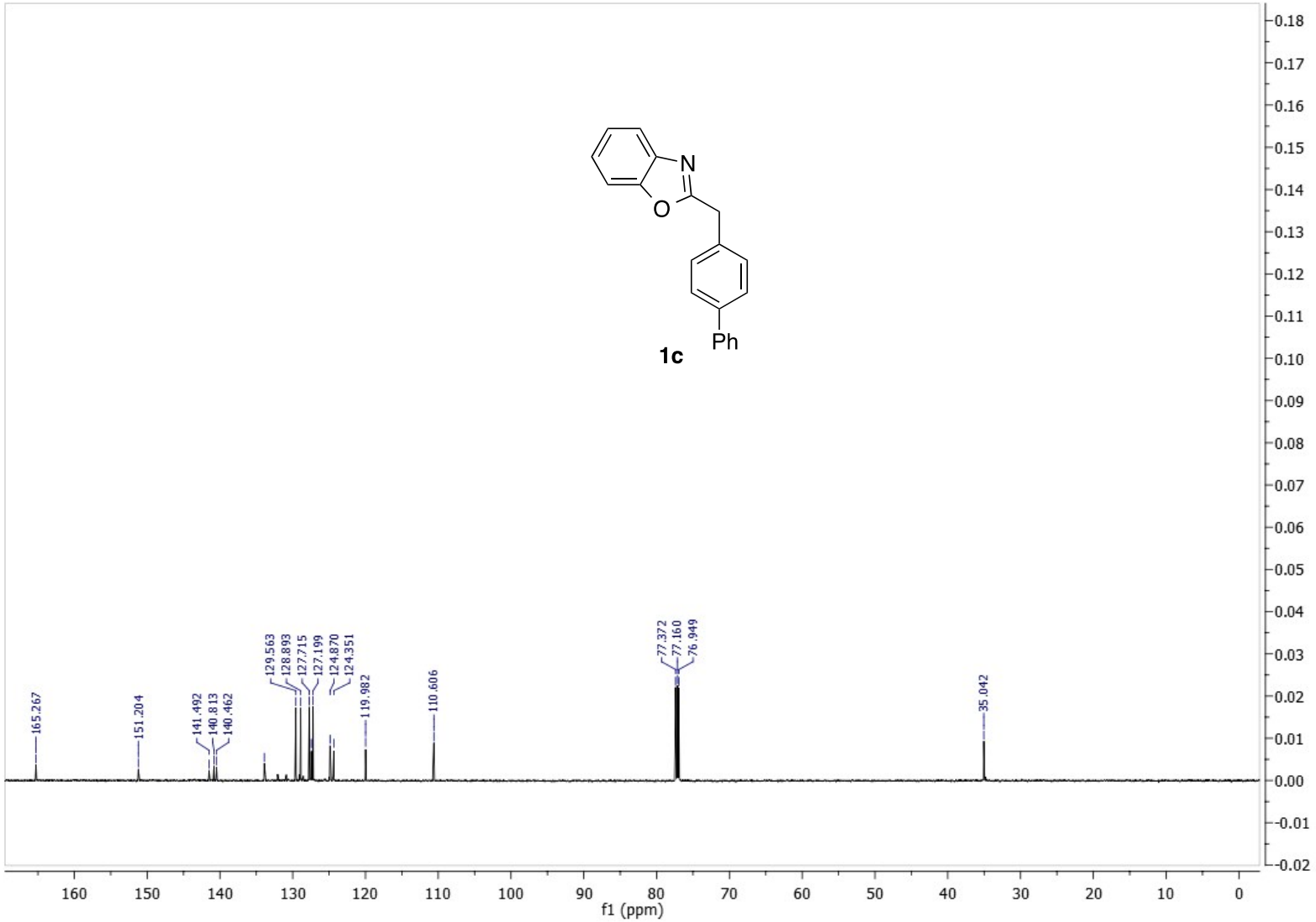

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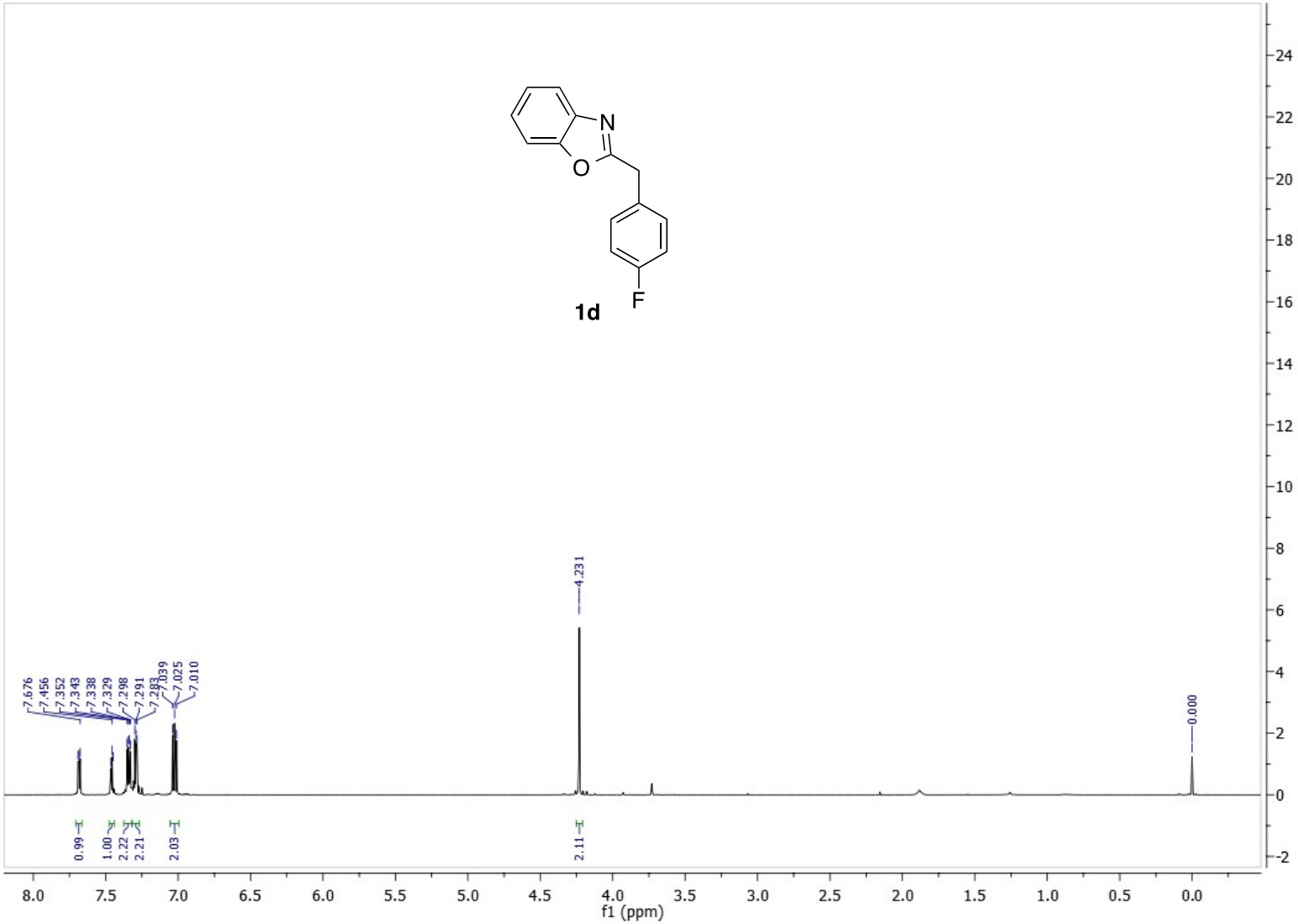

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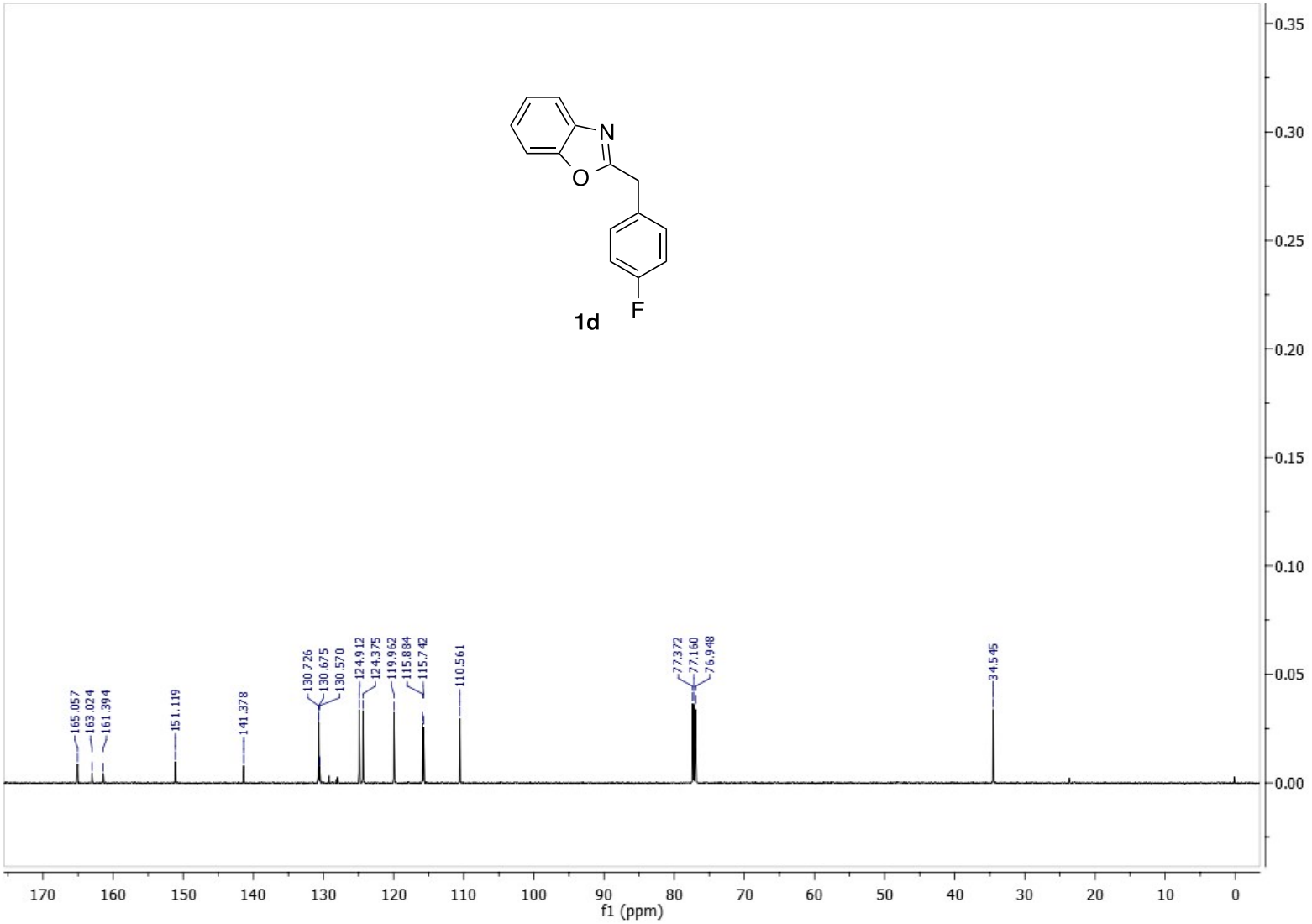

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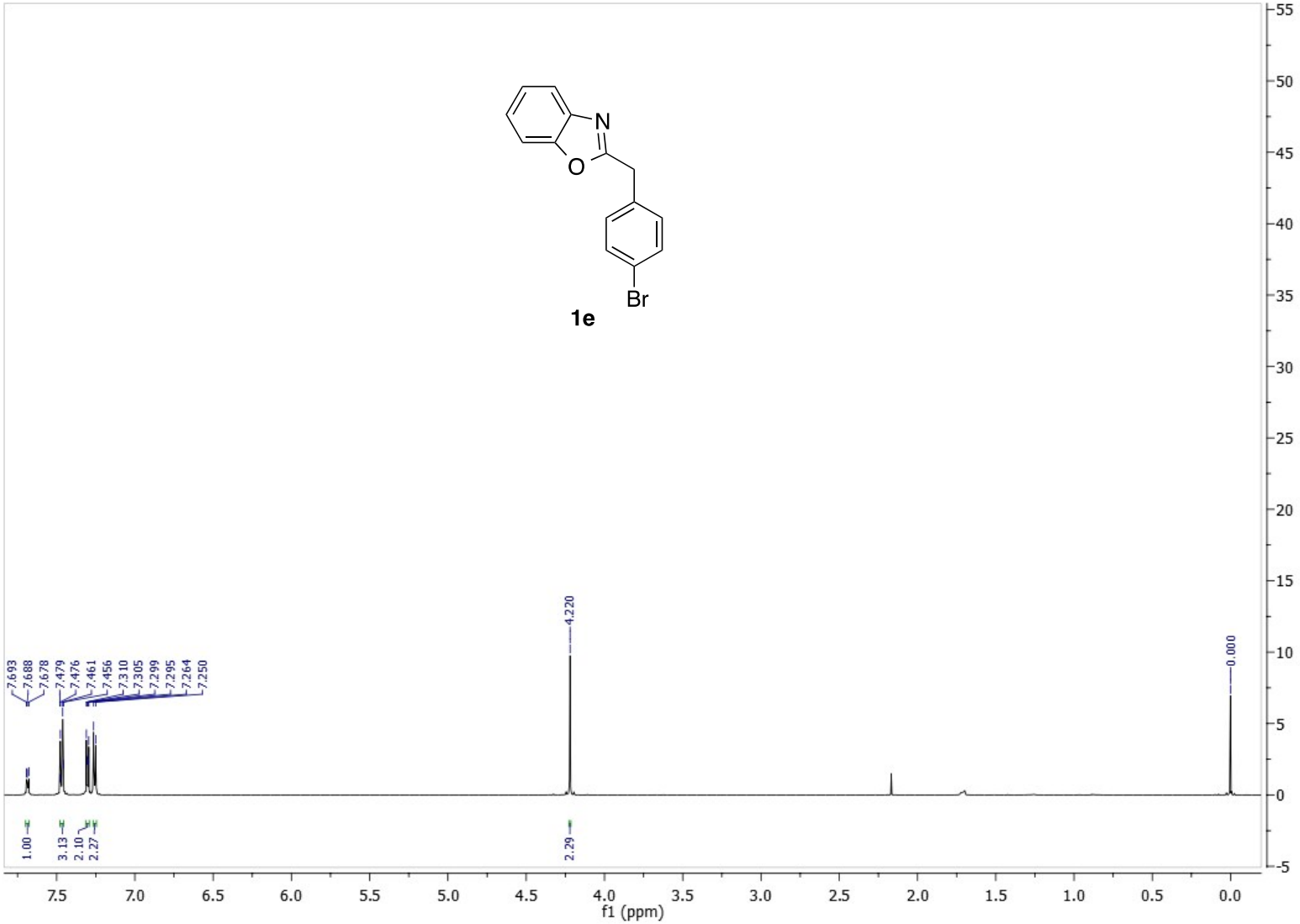

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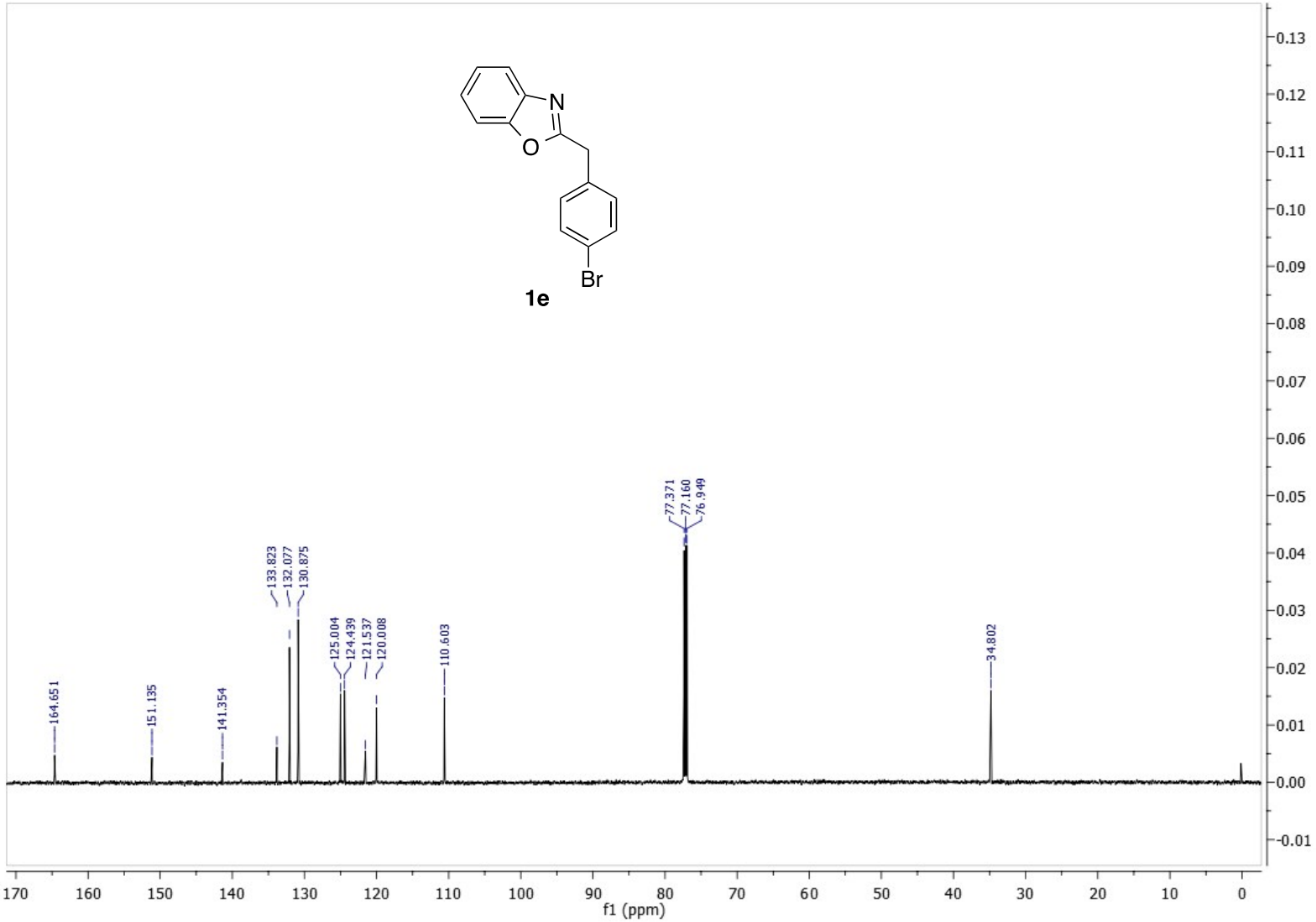

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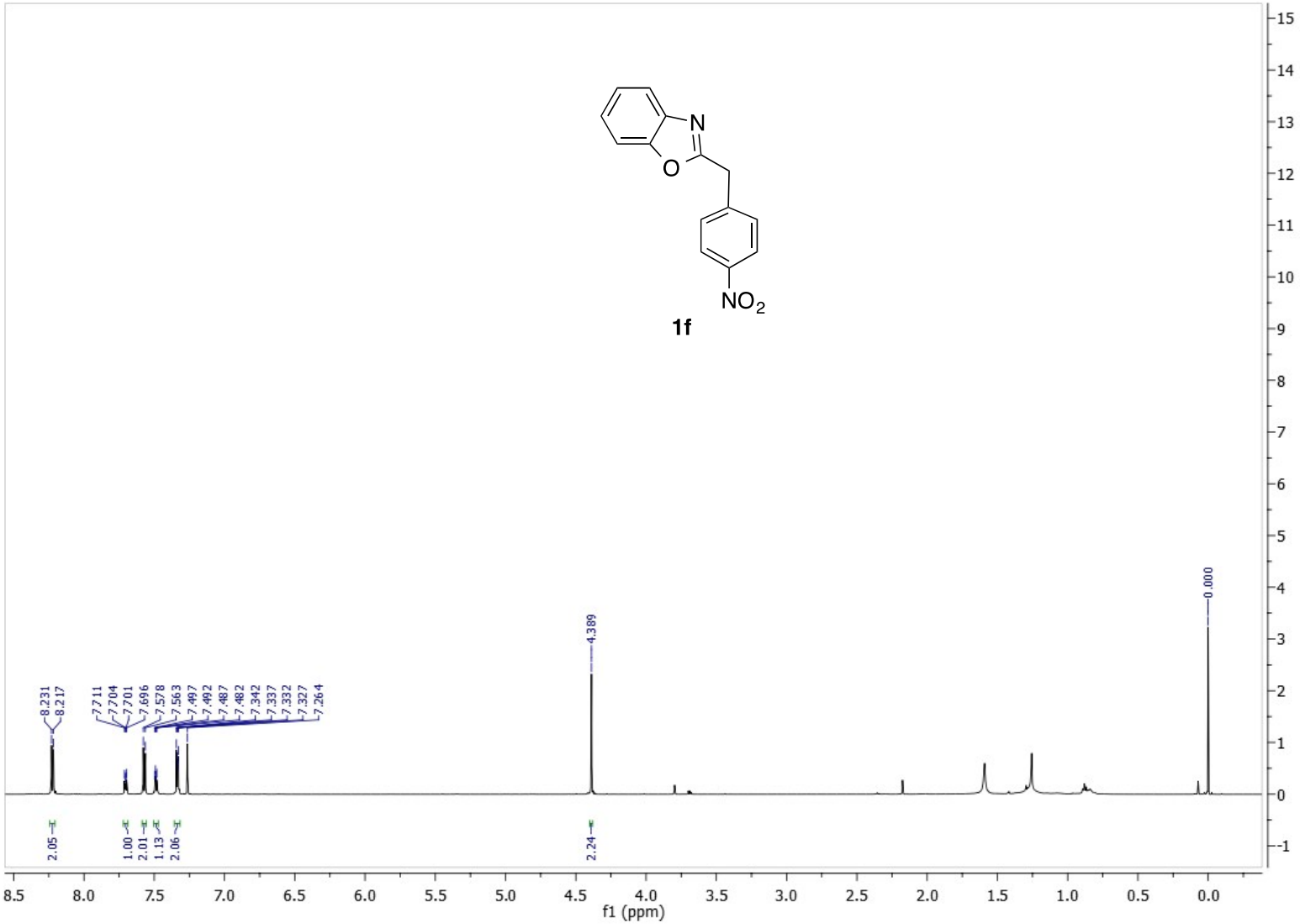

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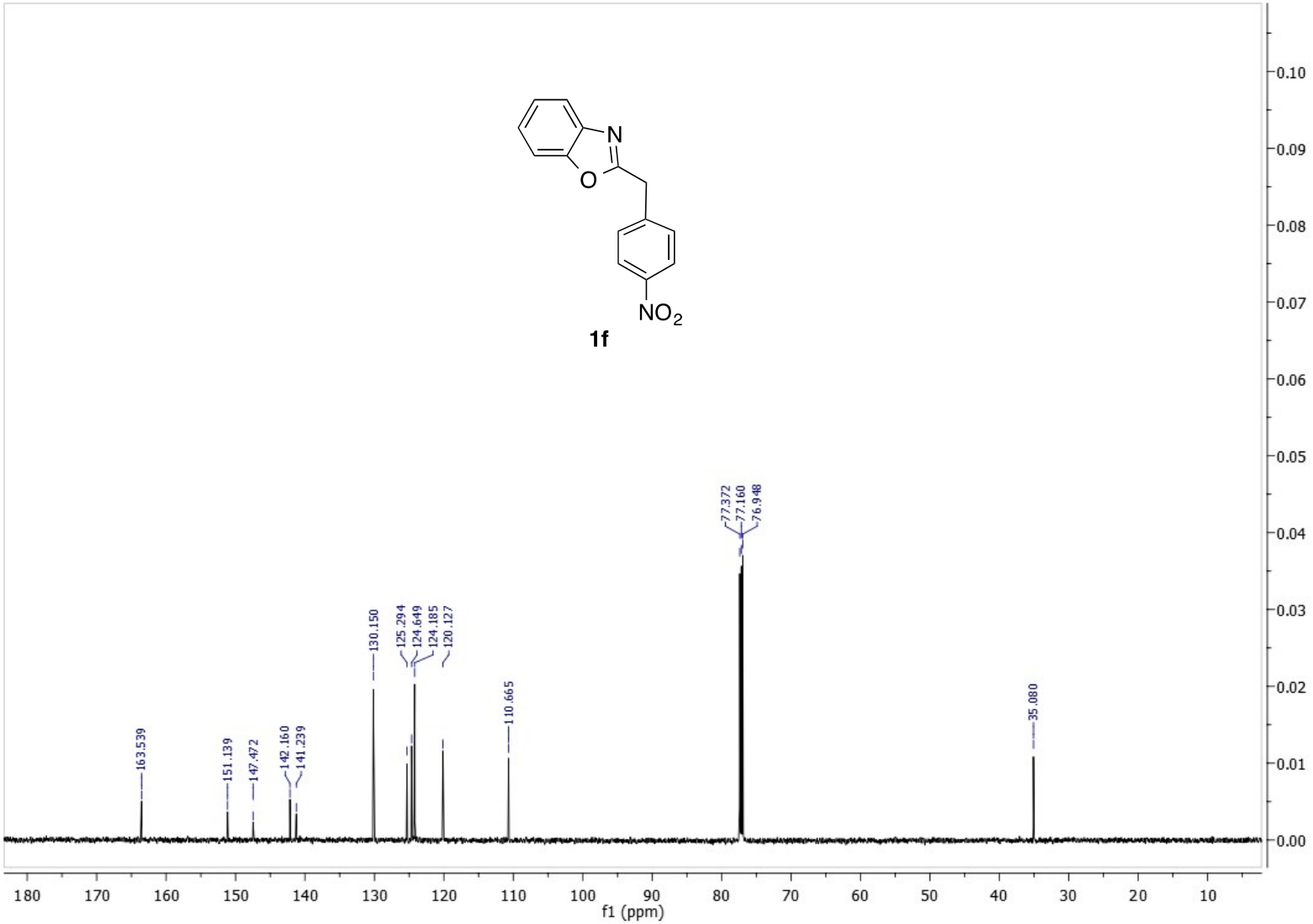

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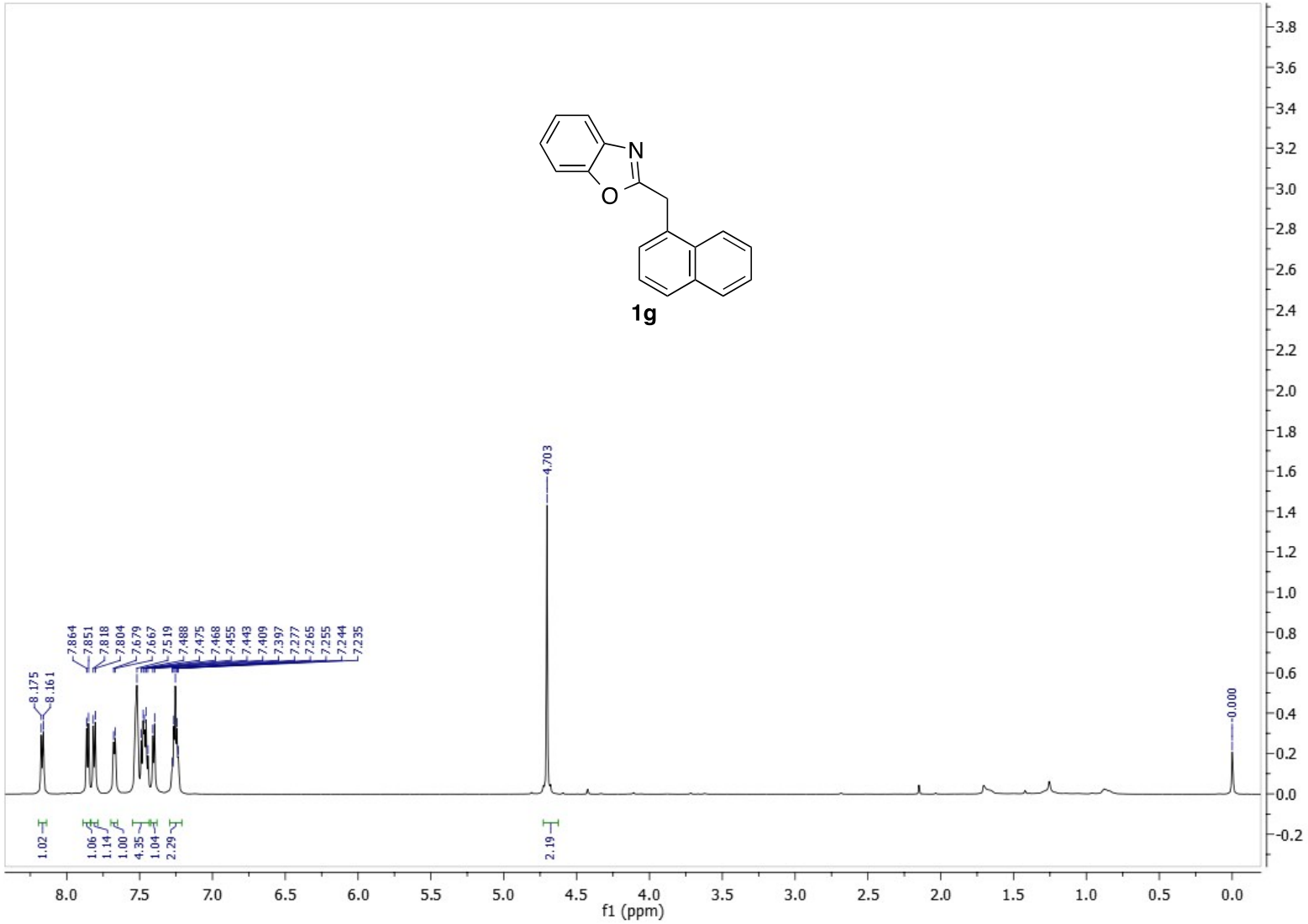

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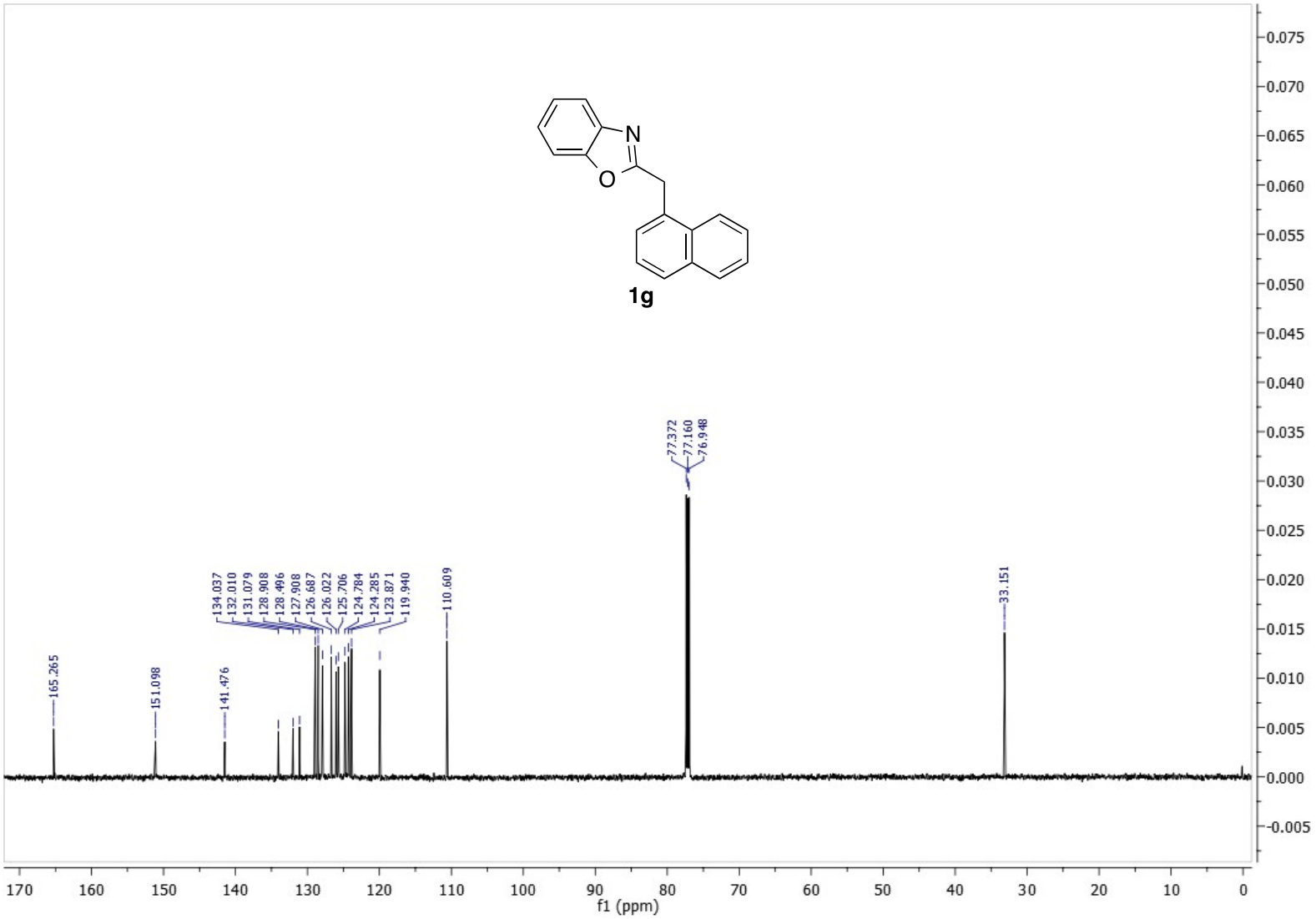

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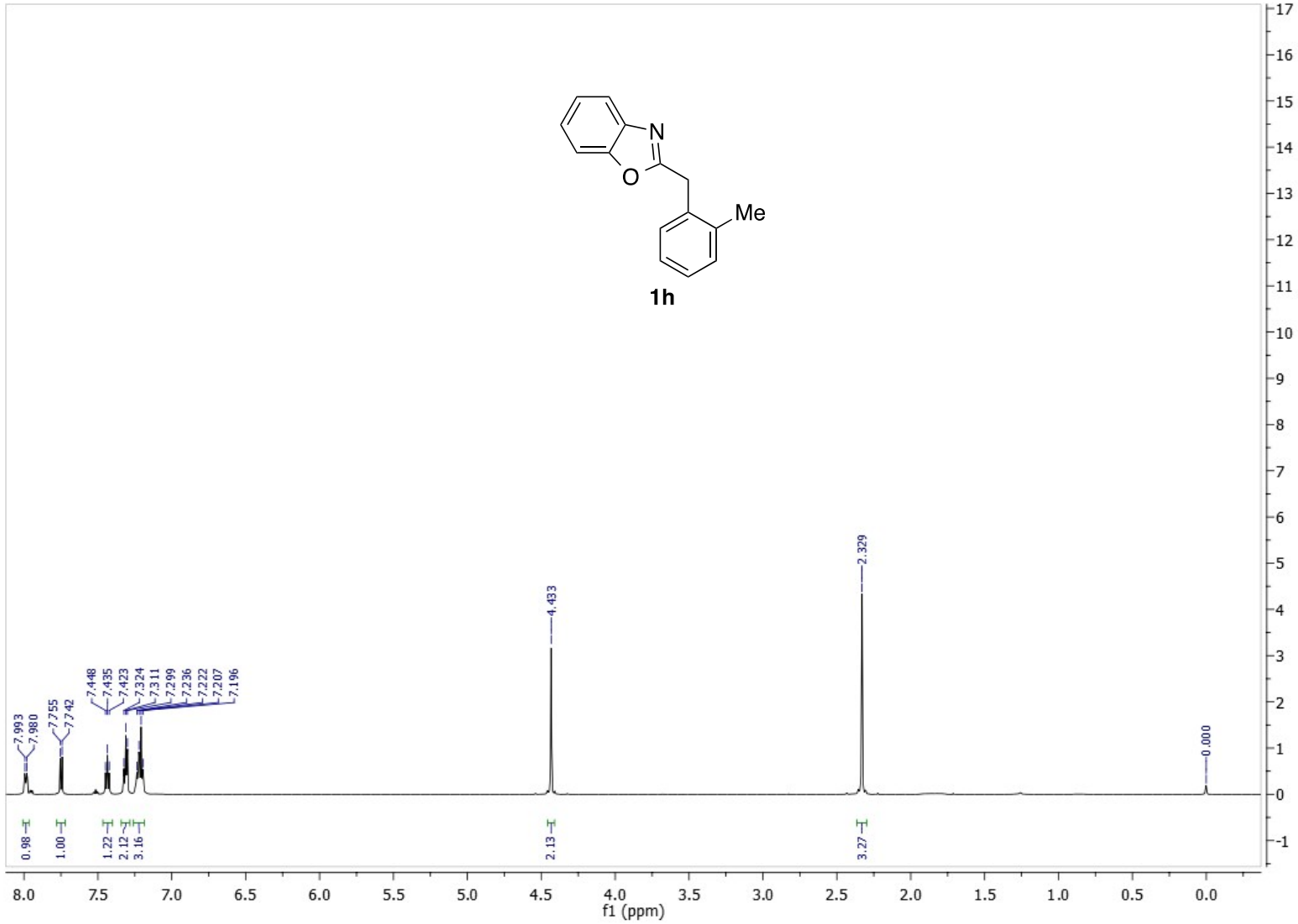

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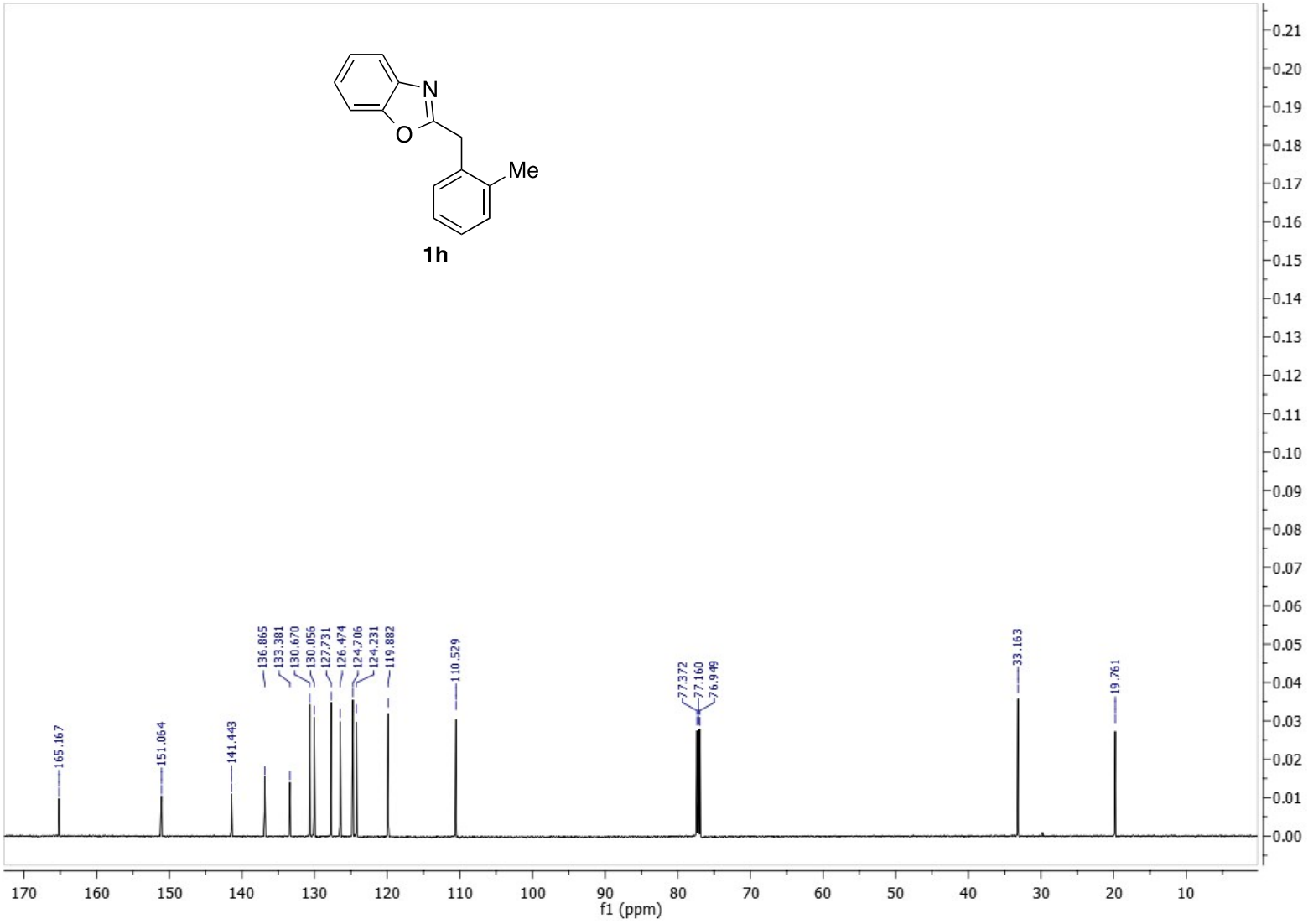

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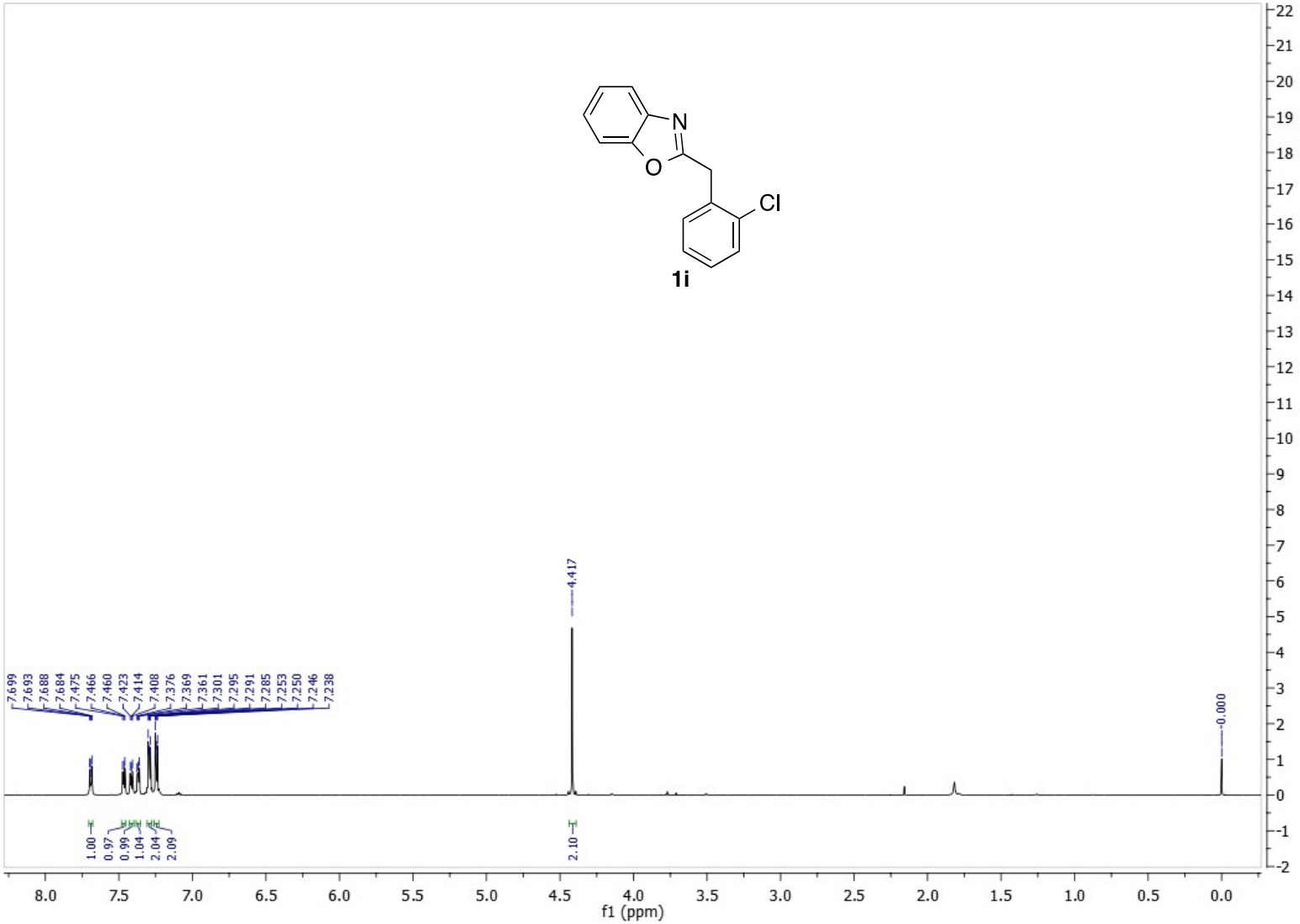

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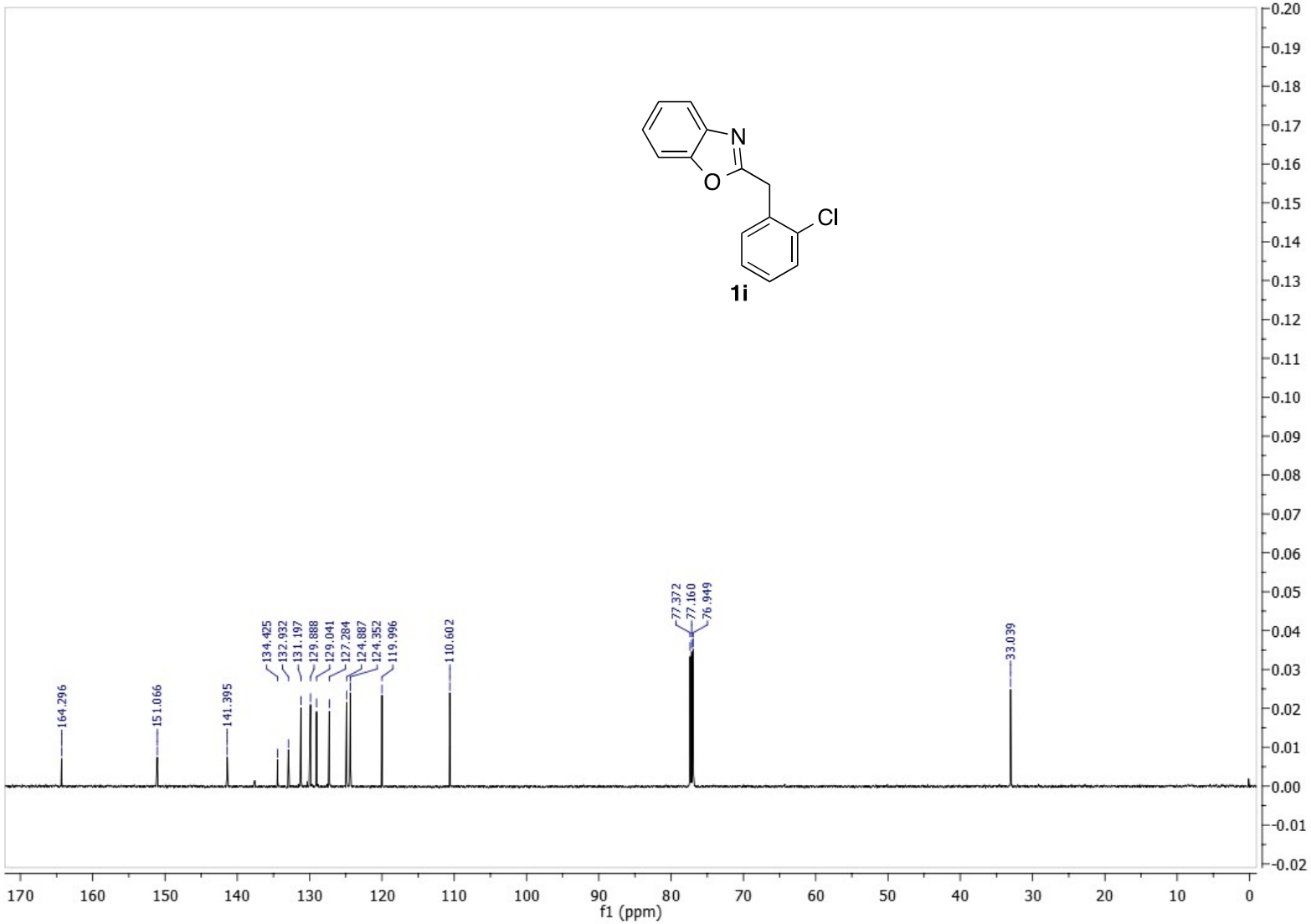

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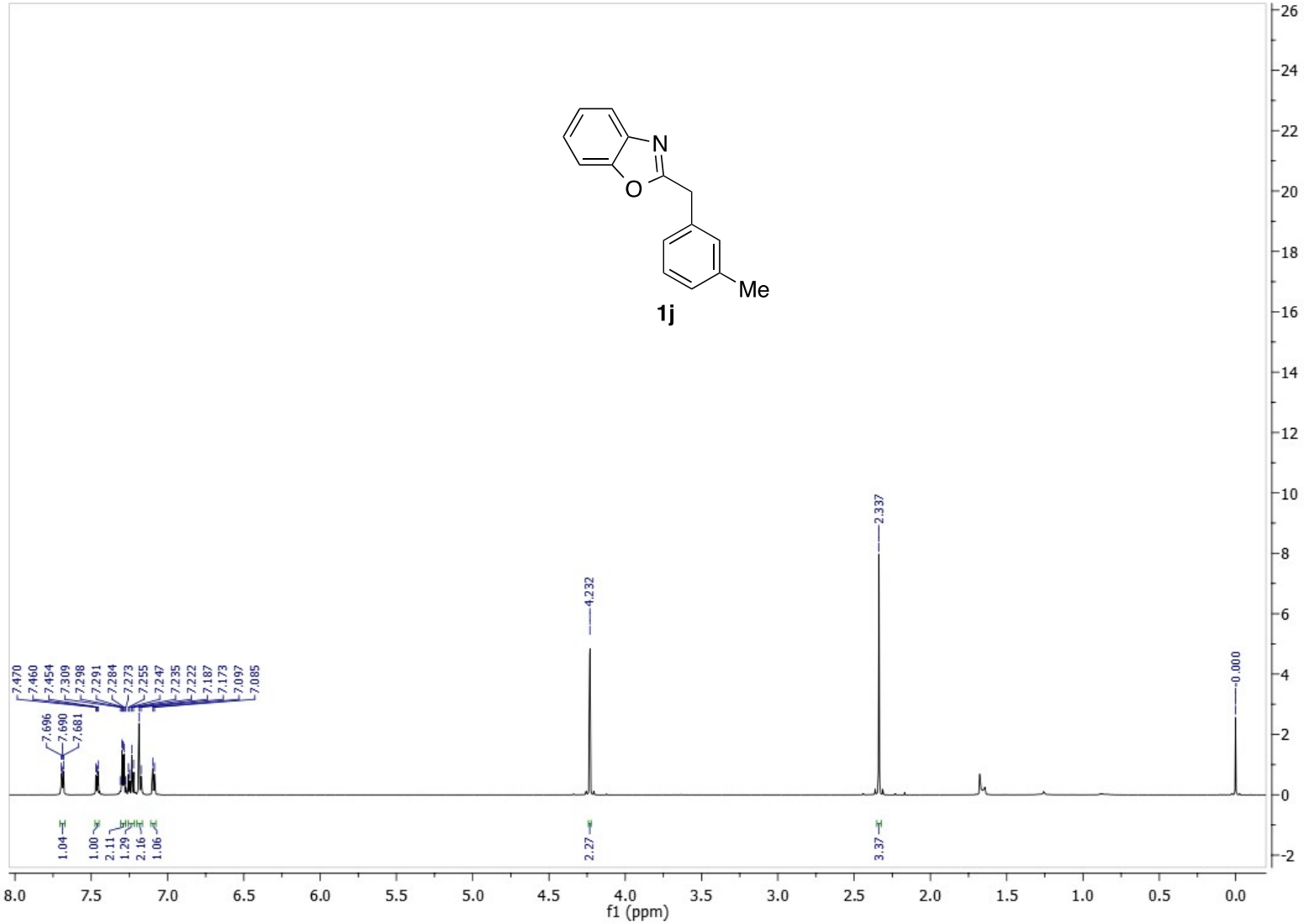

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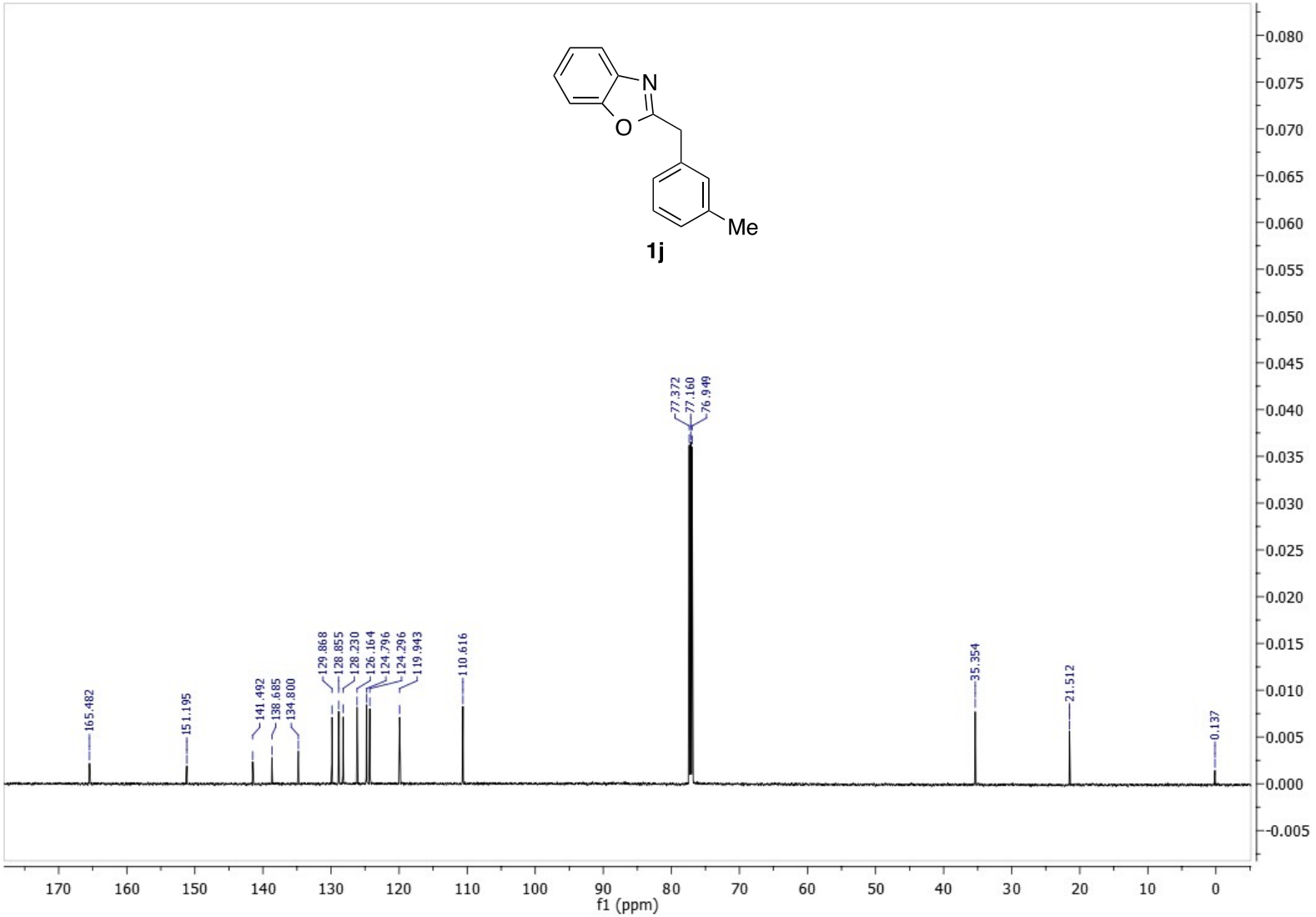

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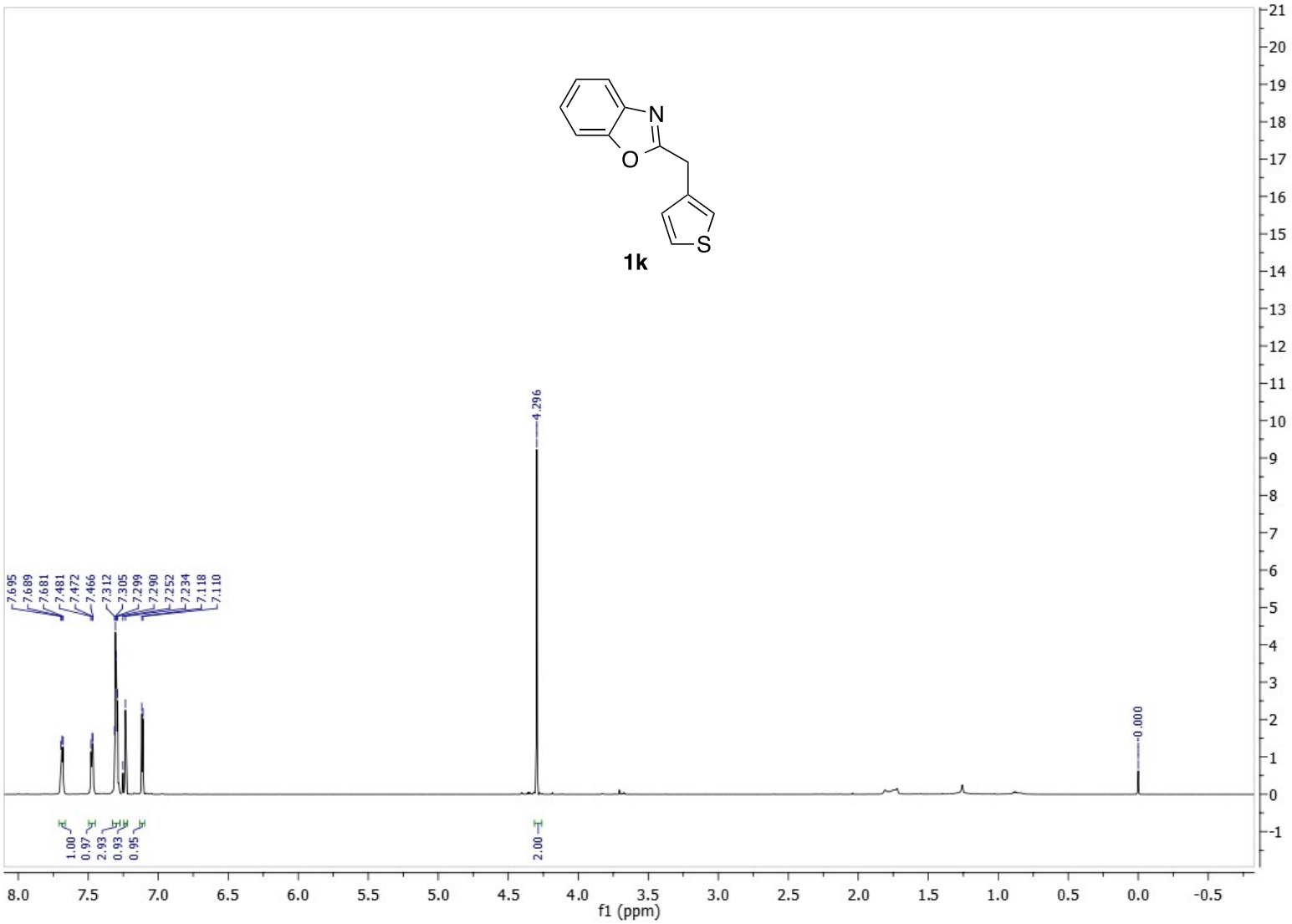

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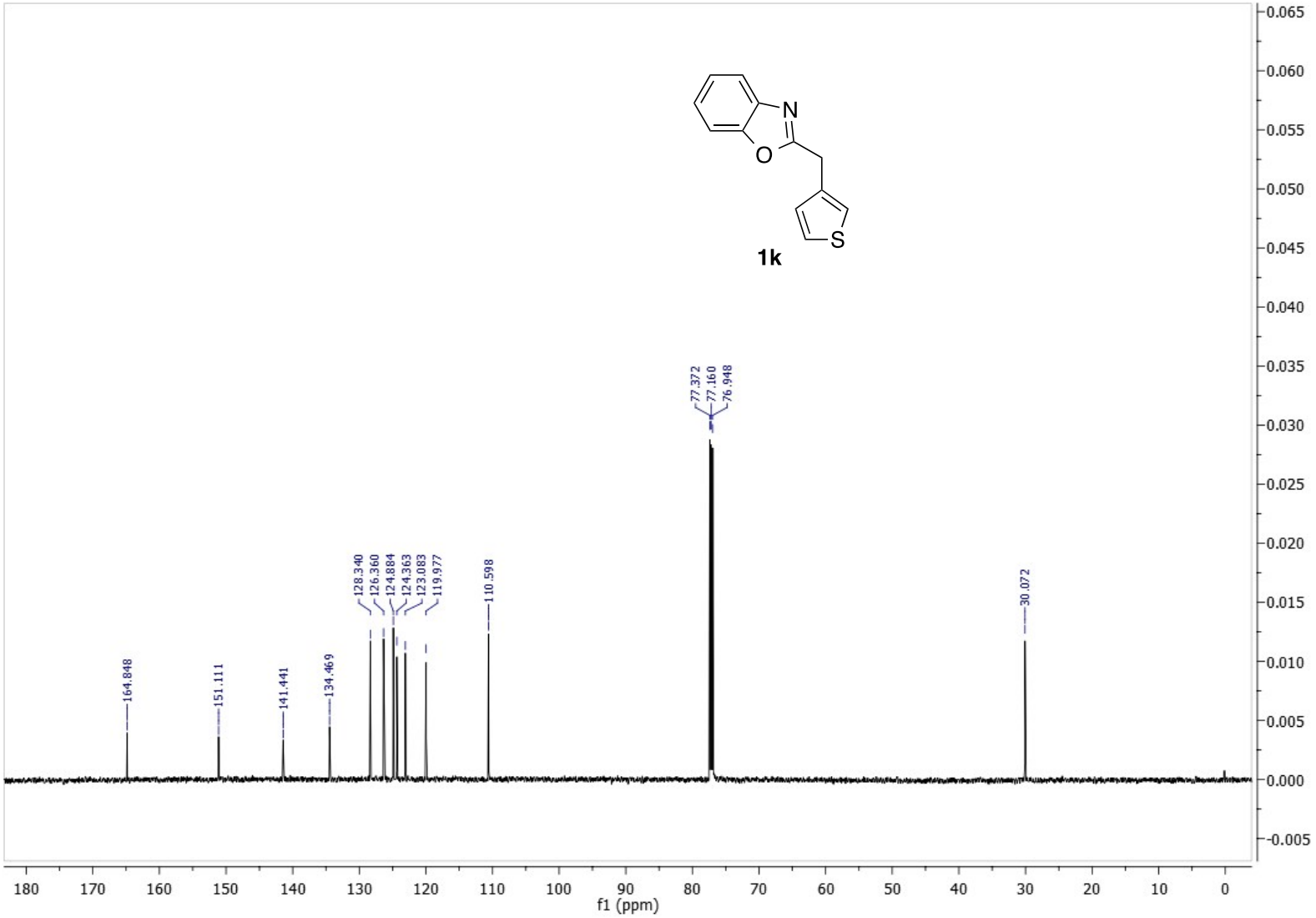

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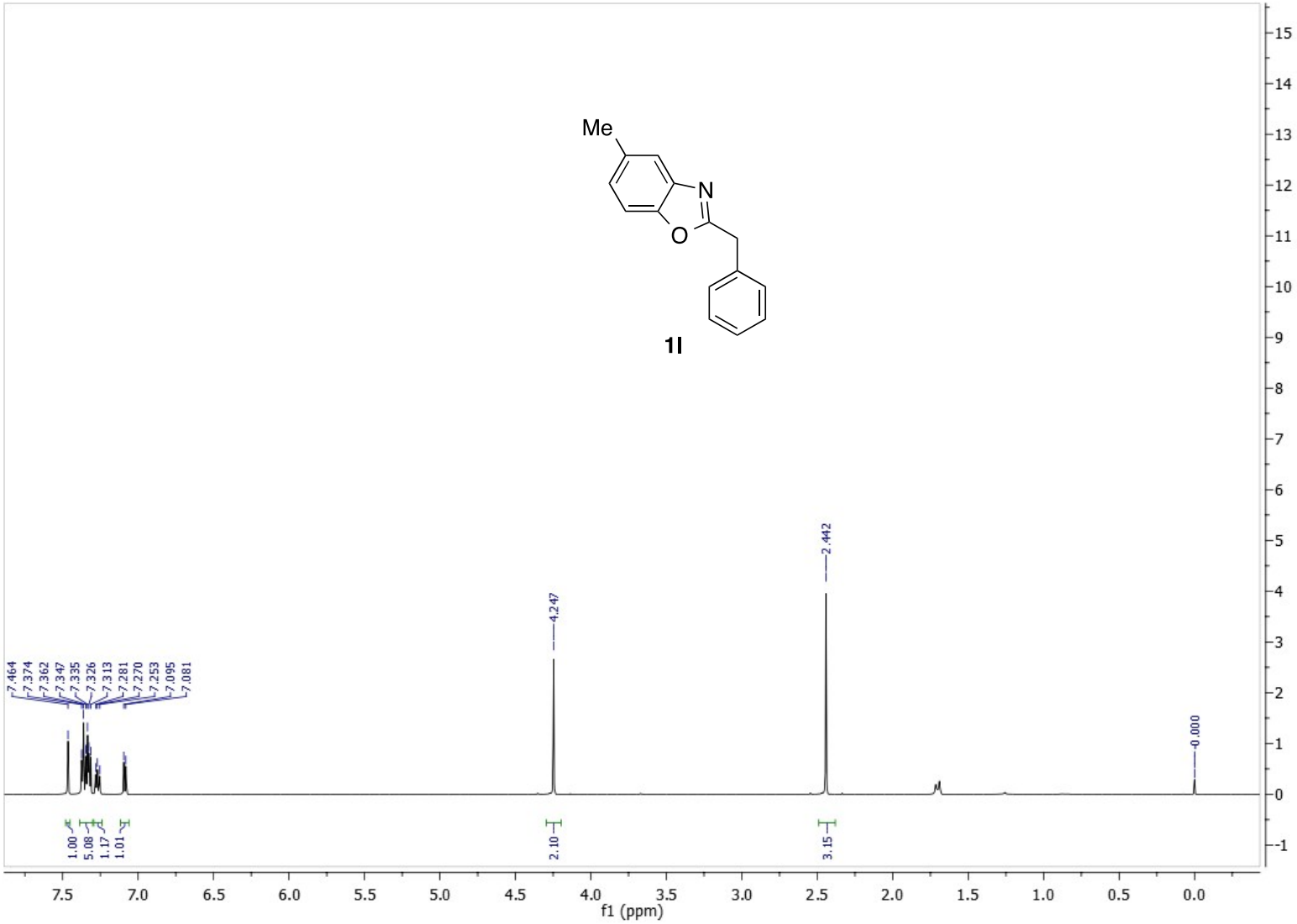

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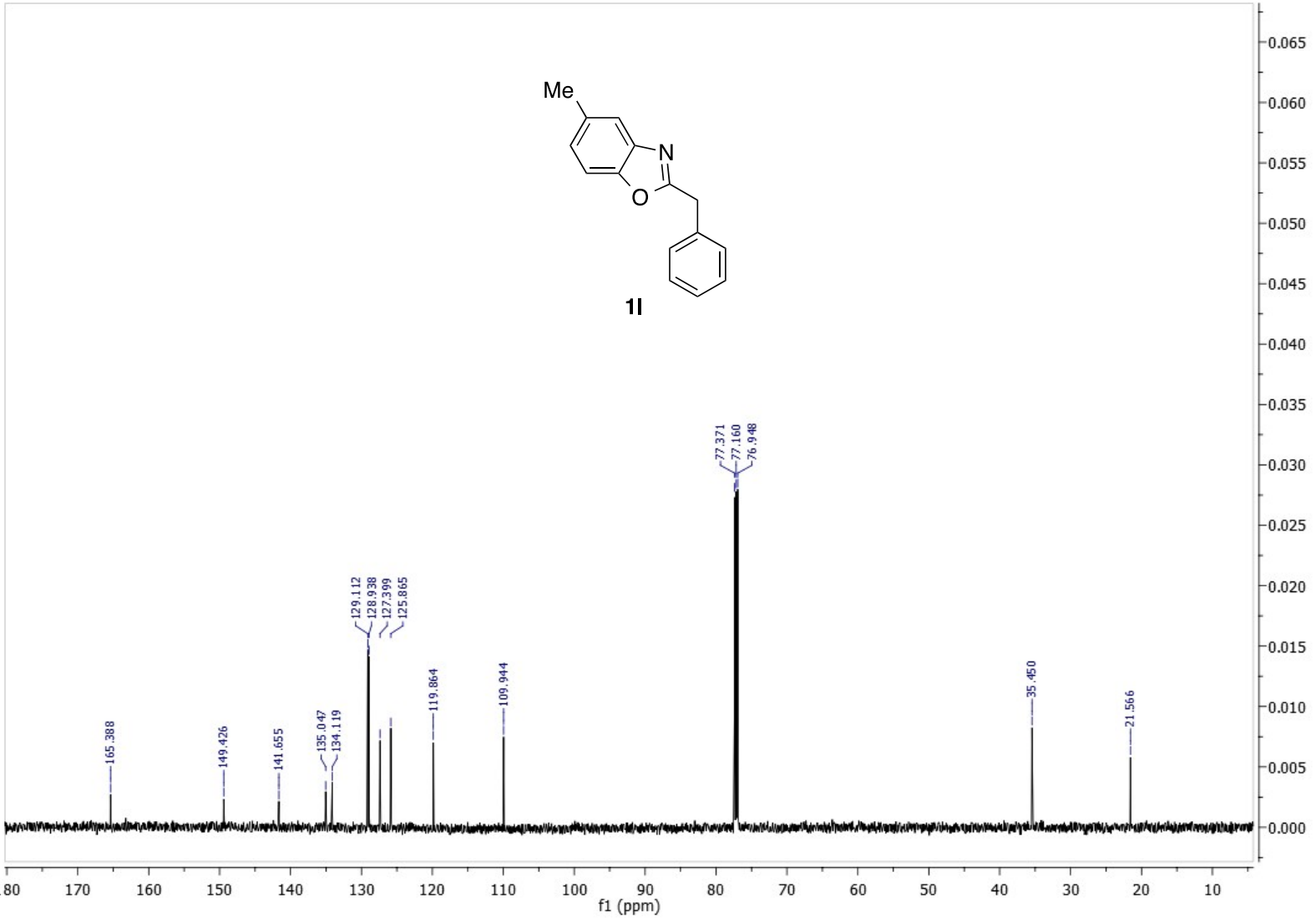

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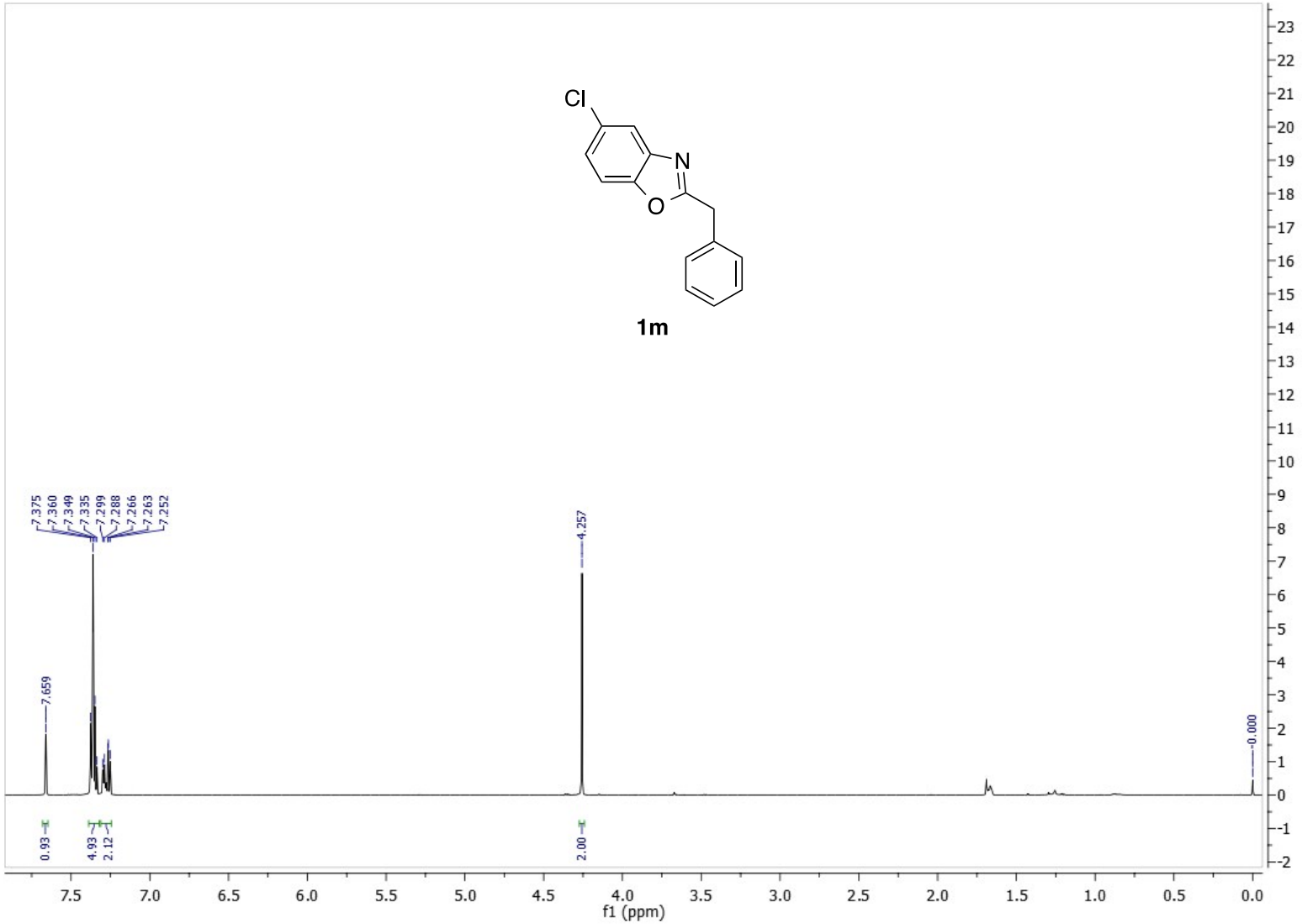

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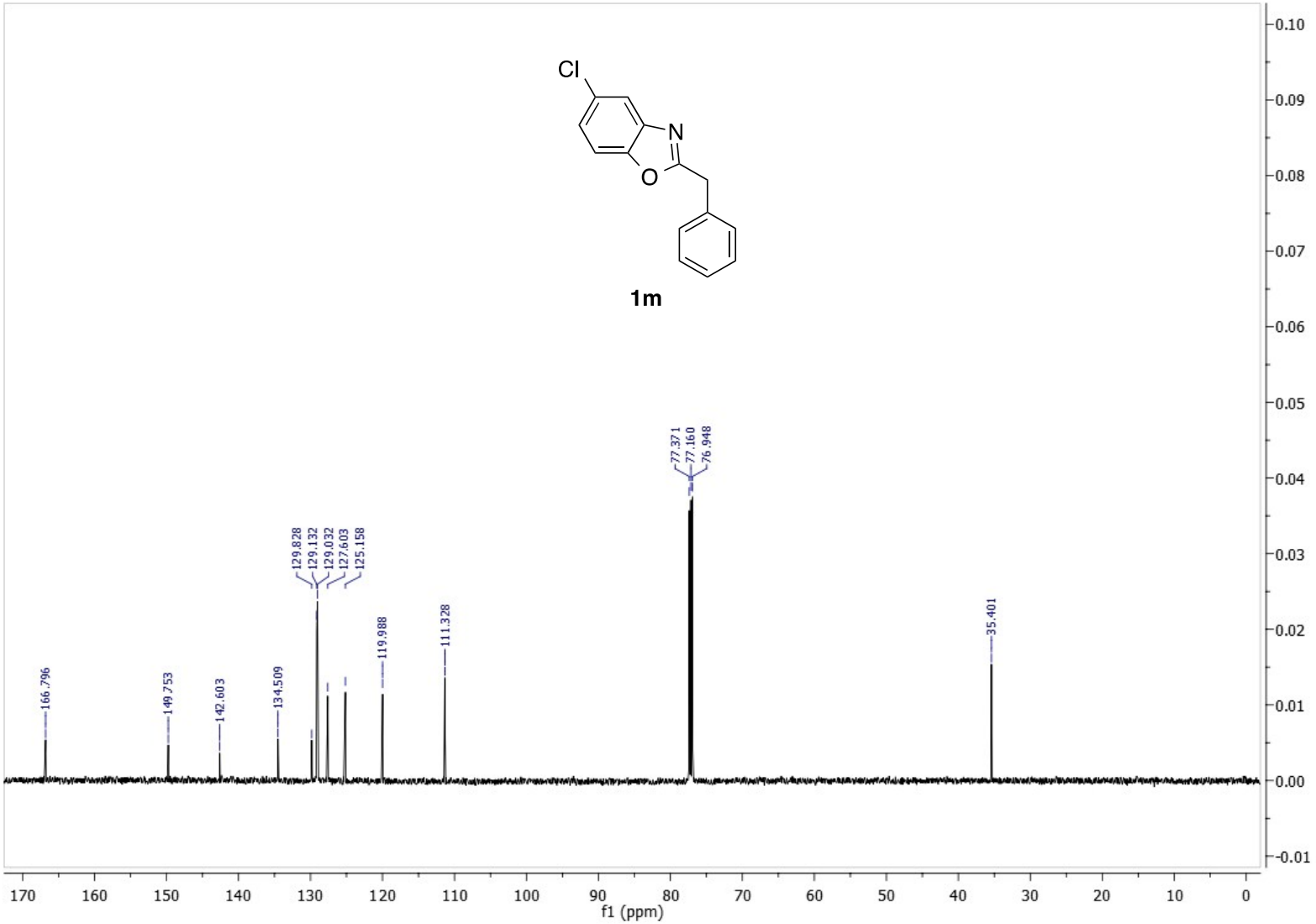

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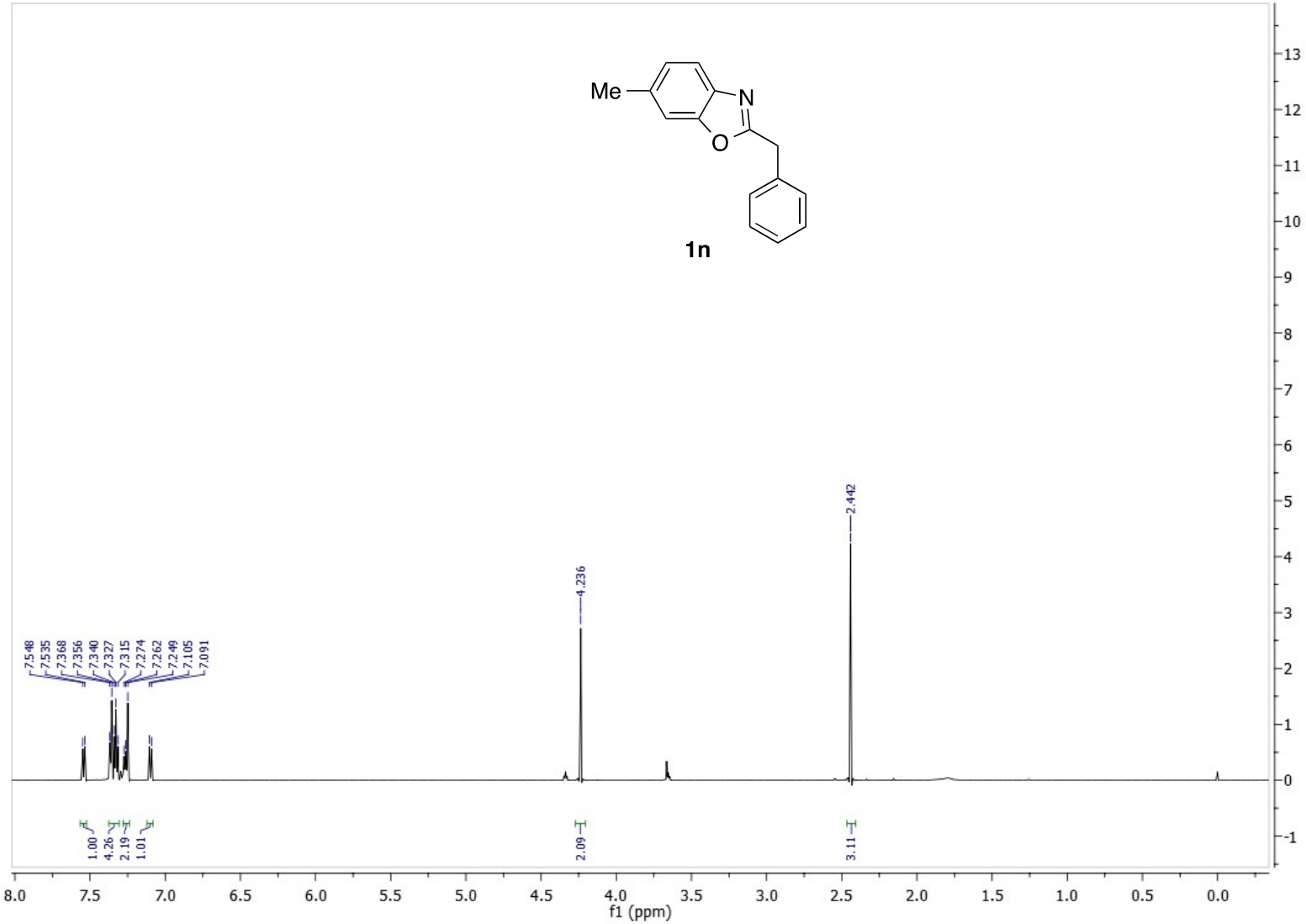
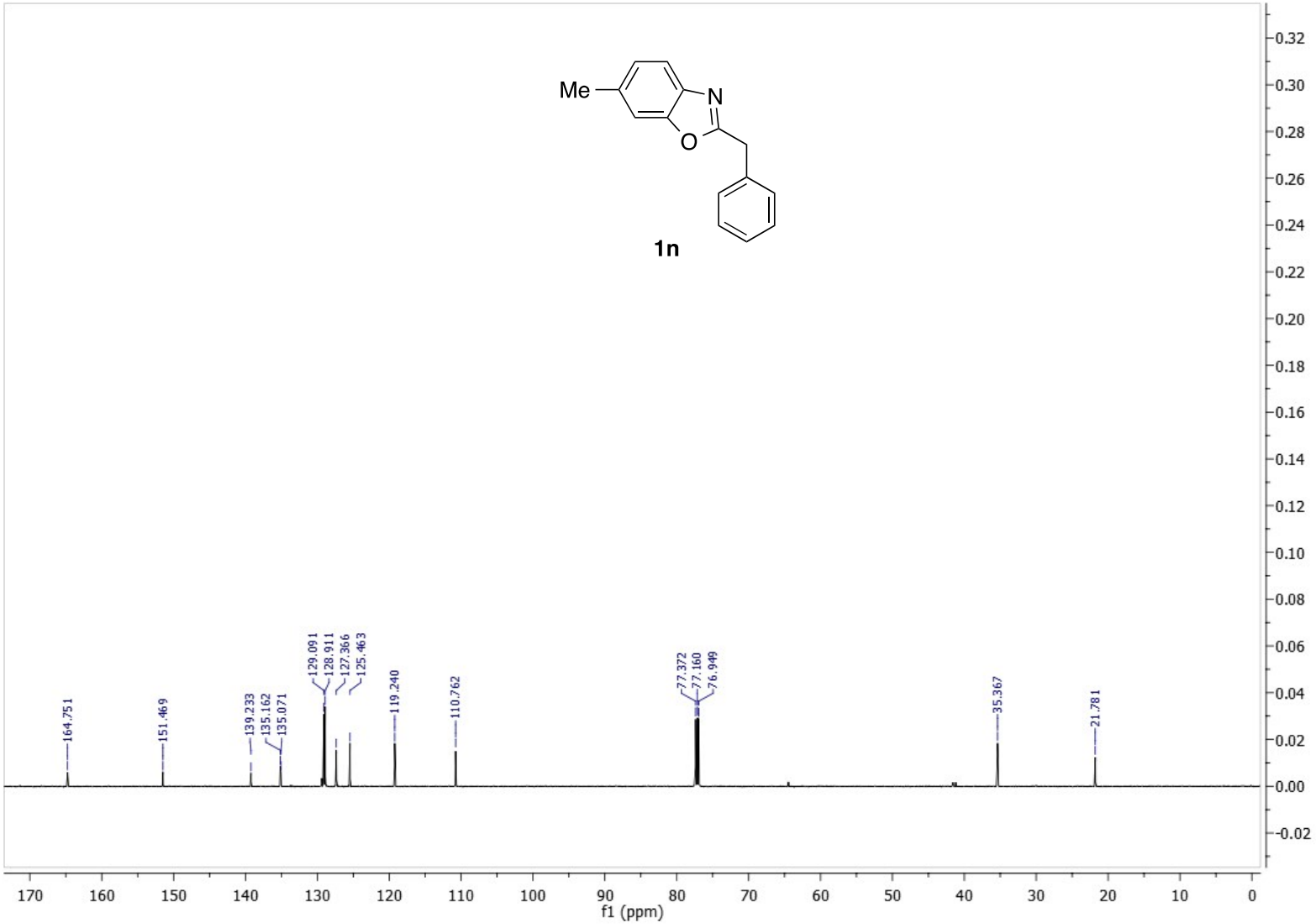
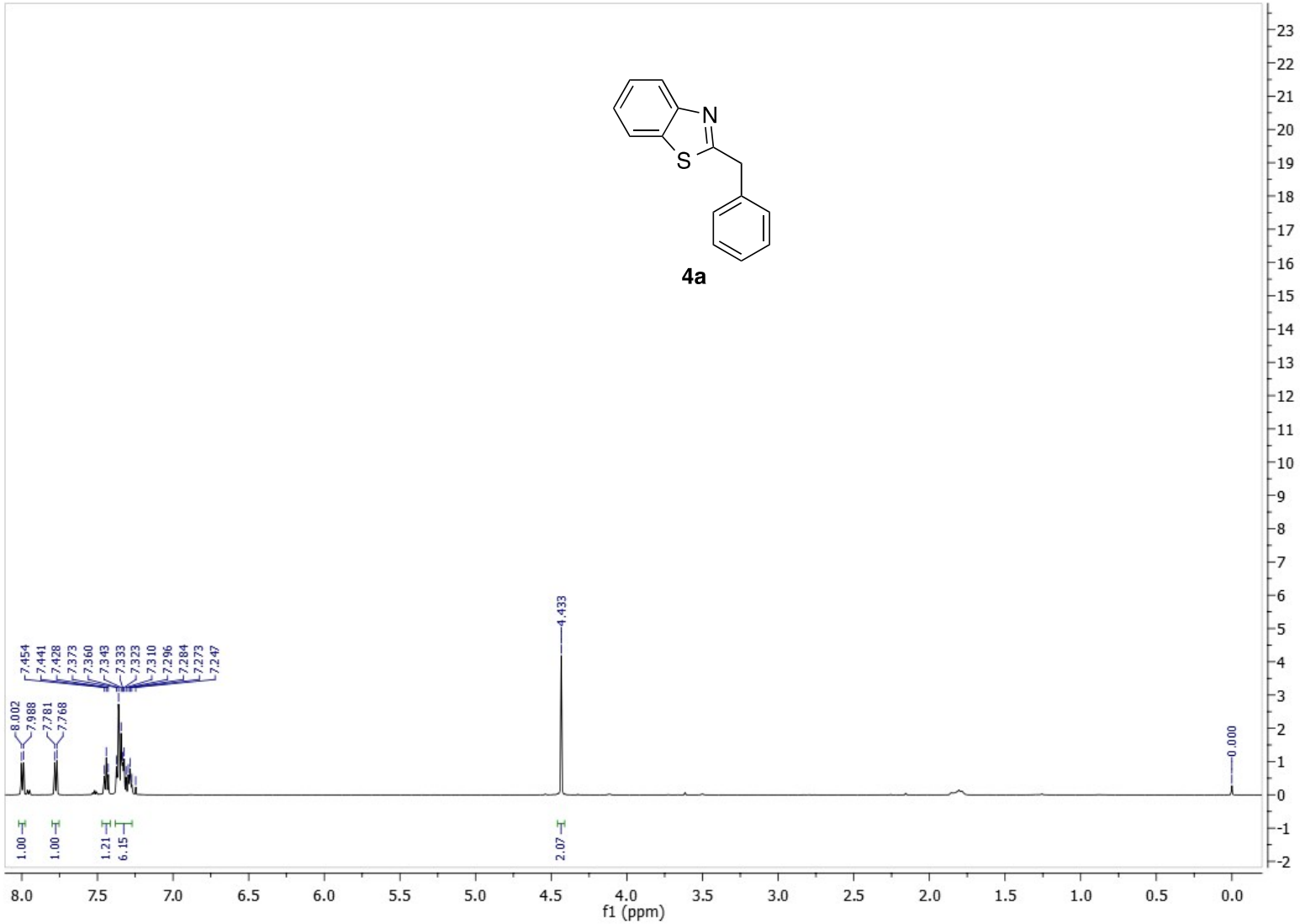


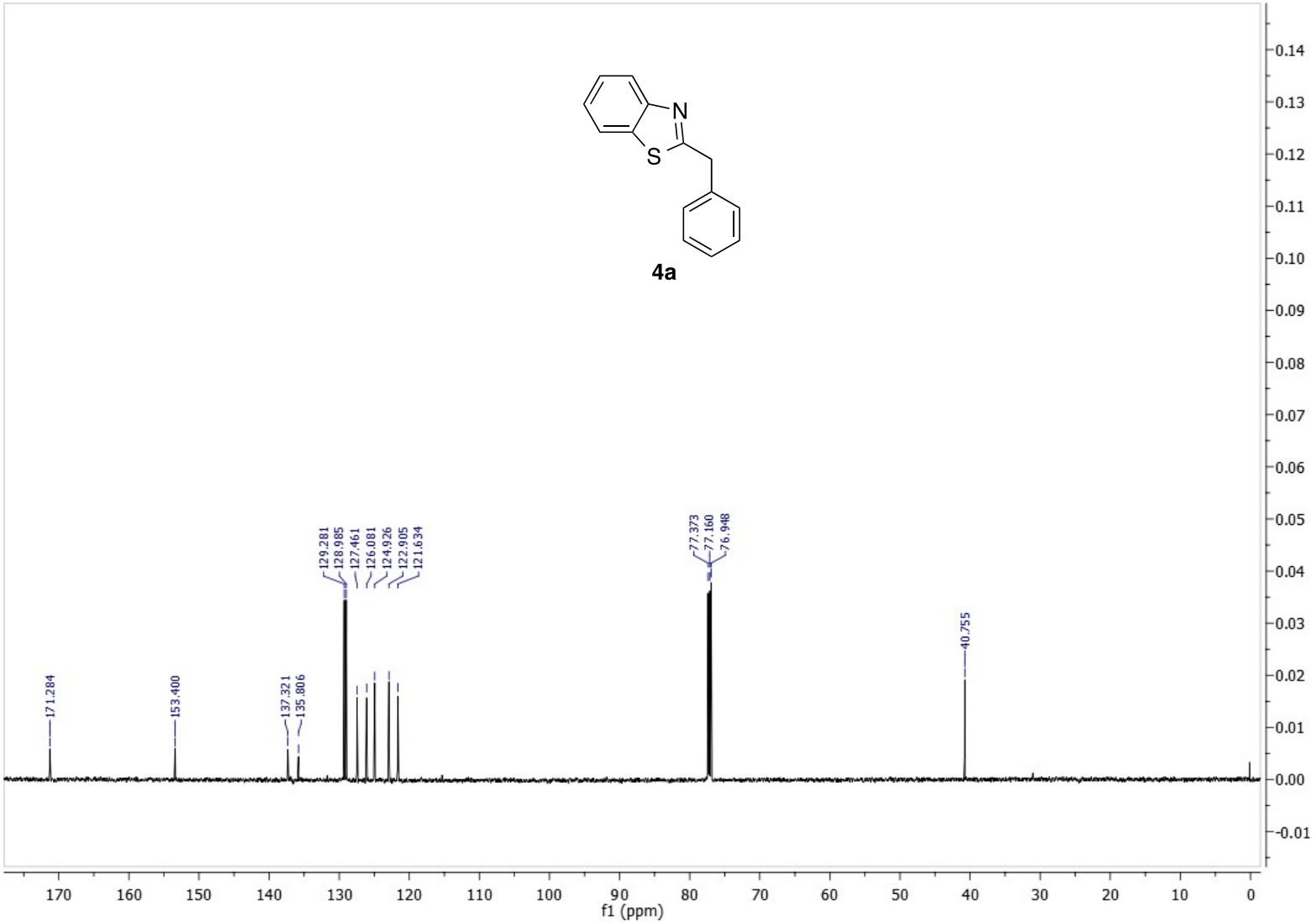
^{13}C NMR (151 MHz, $CDCl_3$):



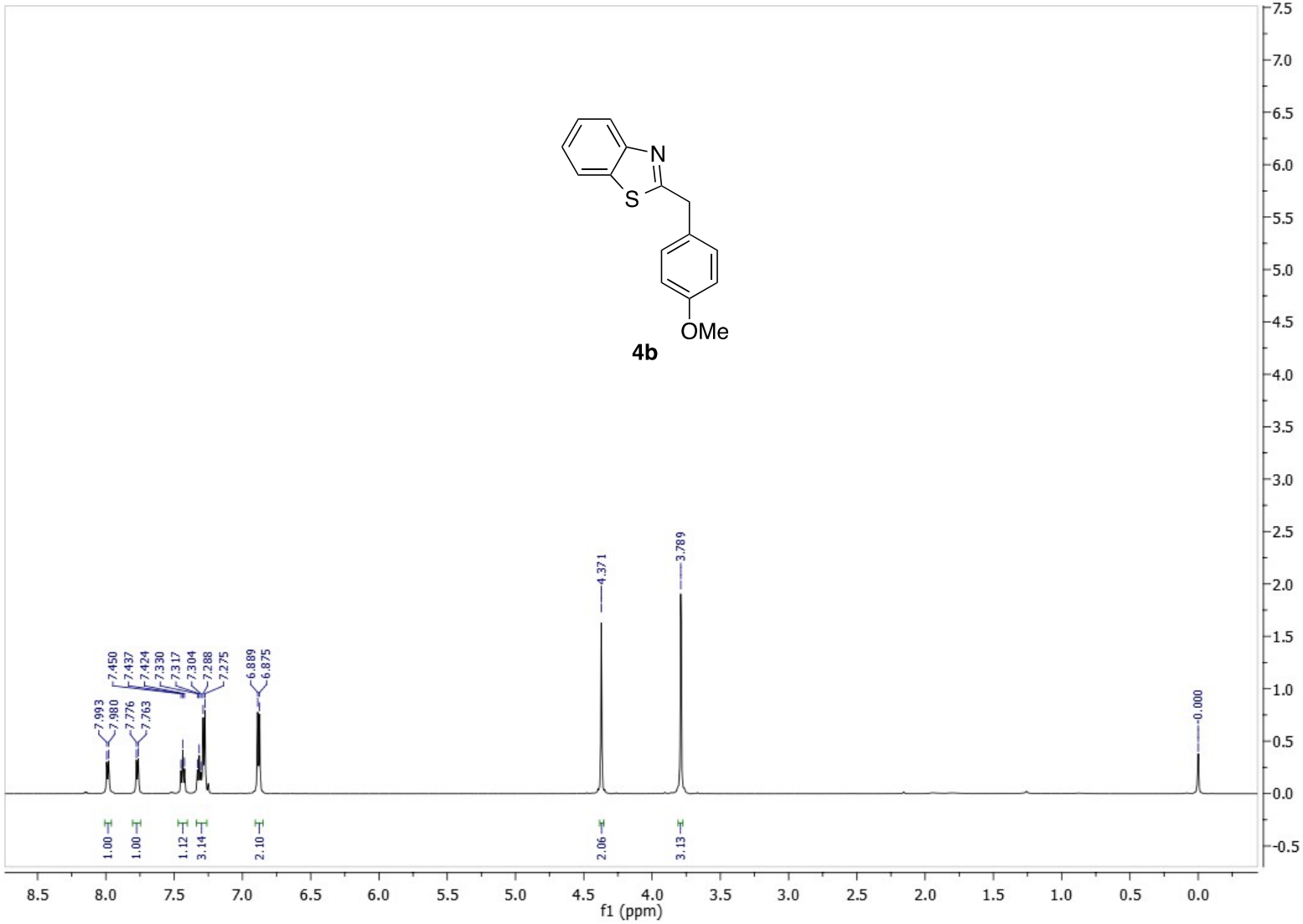
^{1}H NMR (600 MHz, $CDCl_3$):



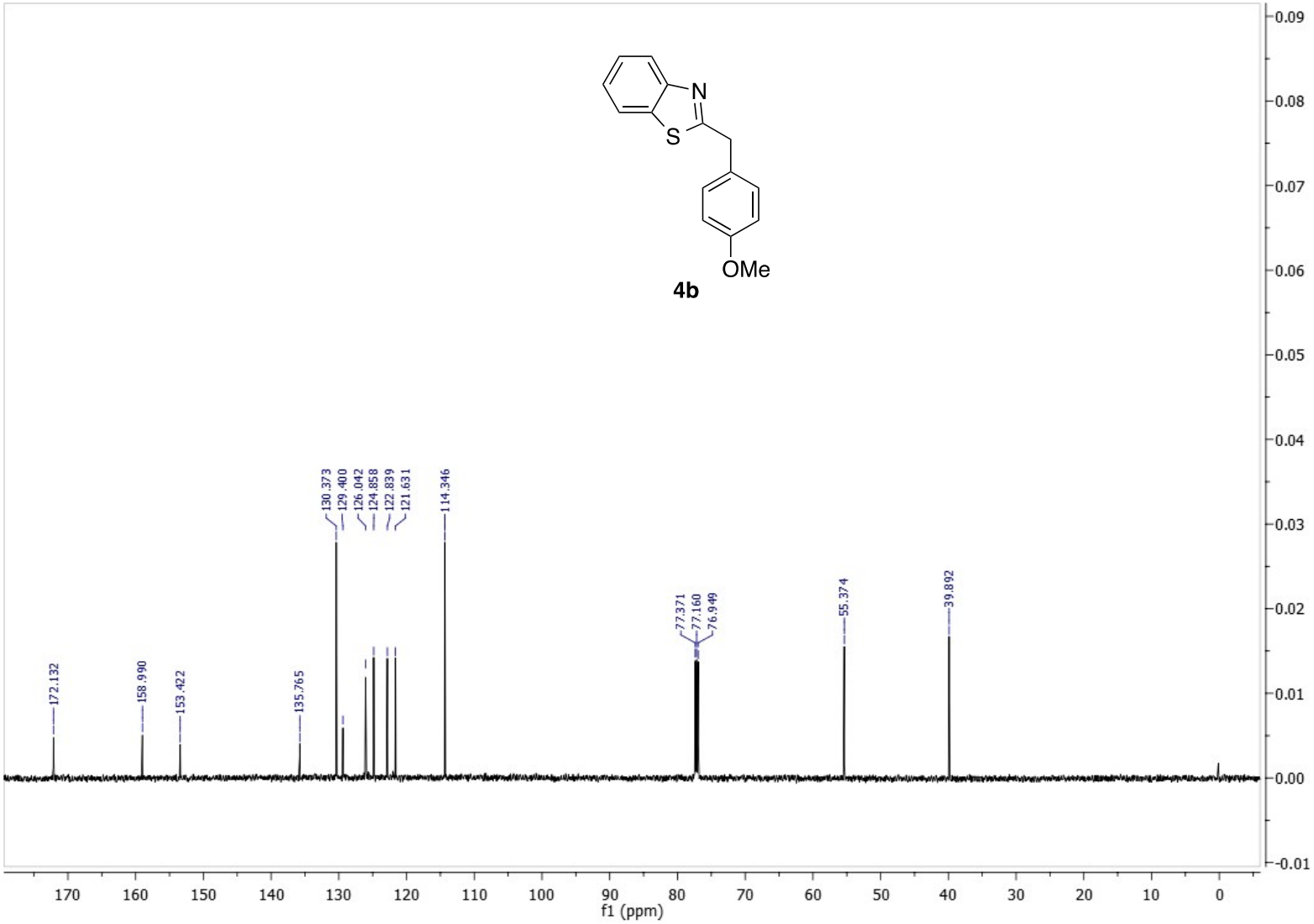
^{13}C NMR (151 MHz, $CDCl_3$):



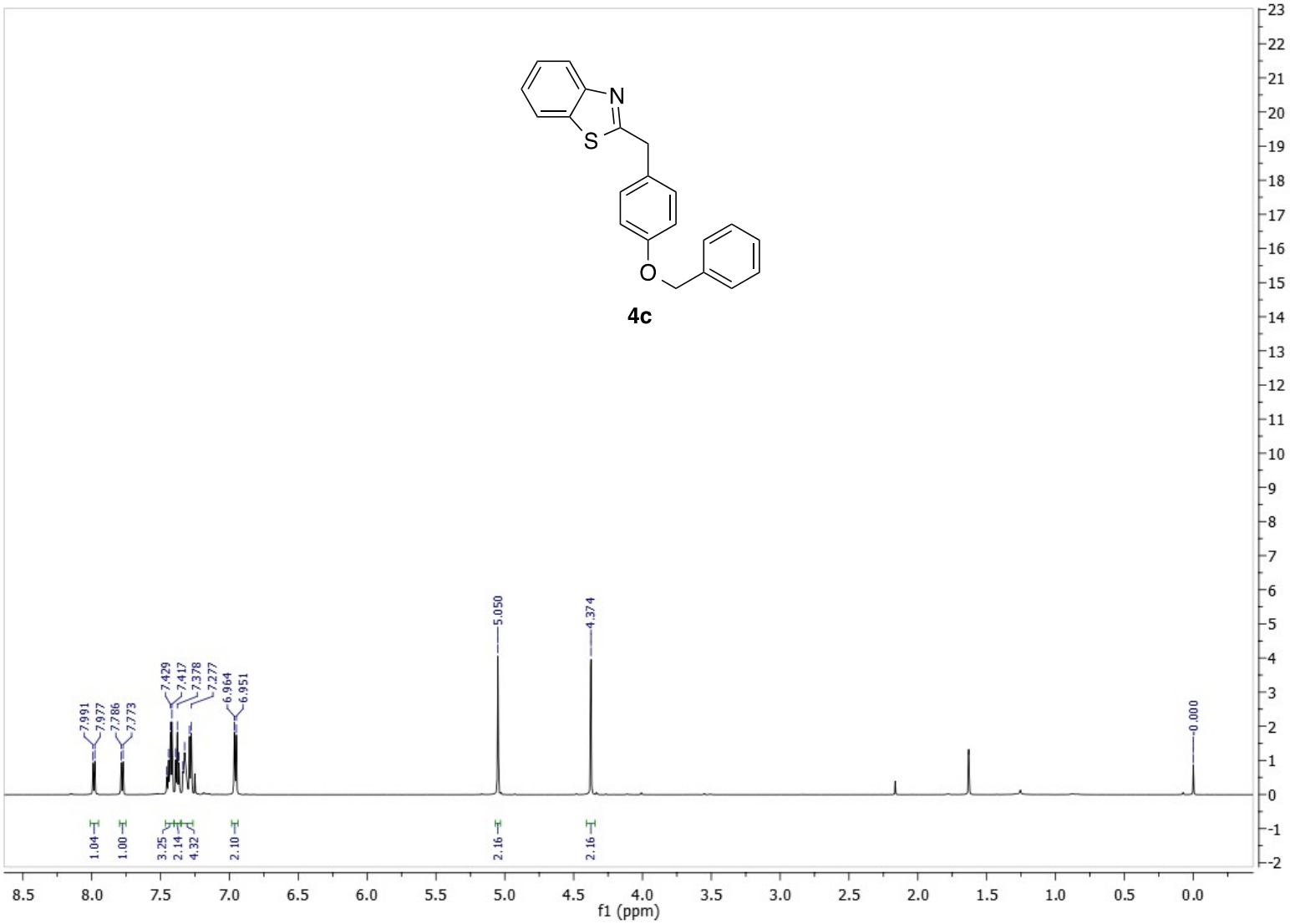
^{1}H NMR (600 MHz, $CDCl_3$):



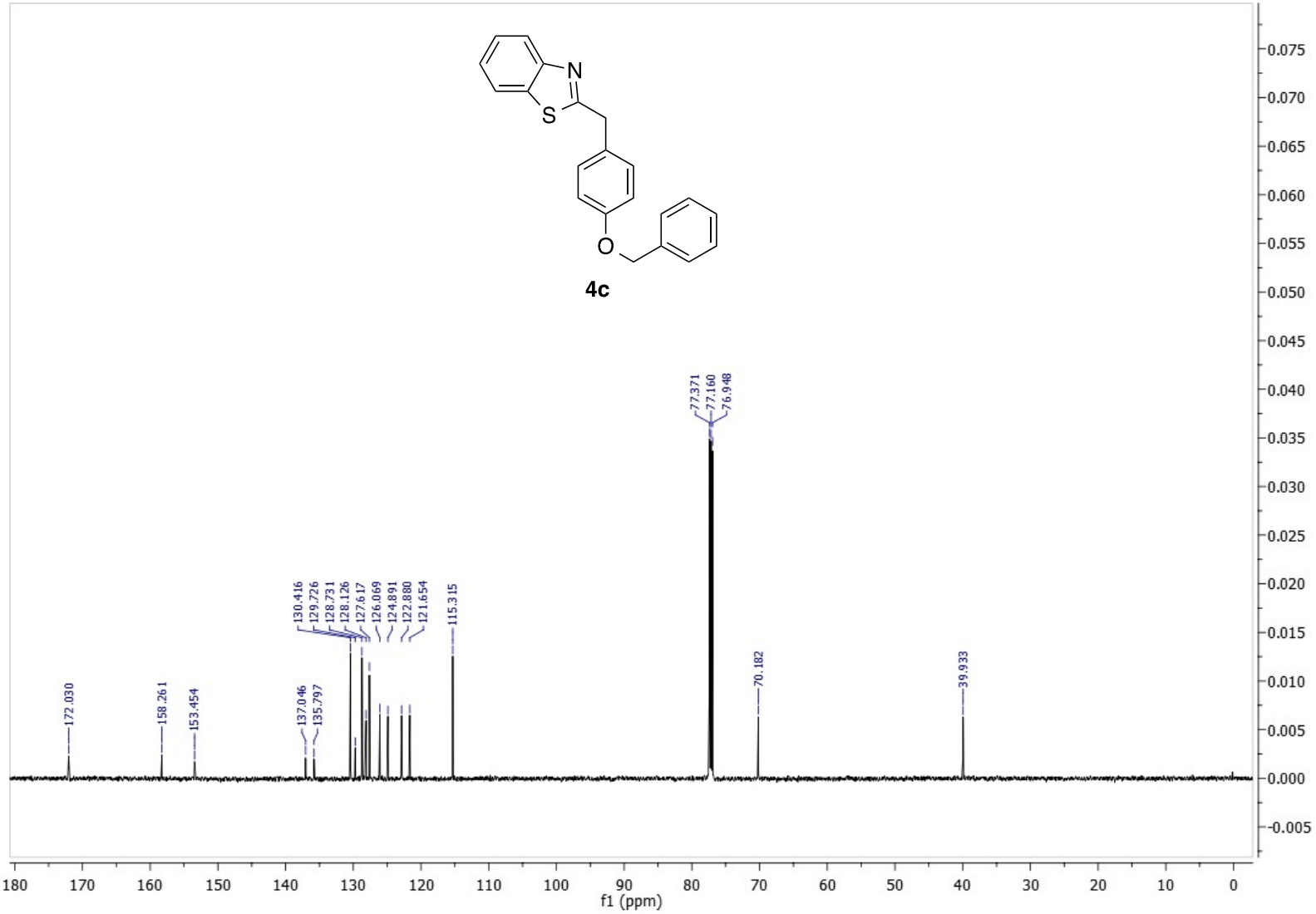
^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):



^{13}C NMR (151 MHz, $CDCl_3$):



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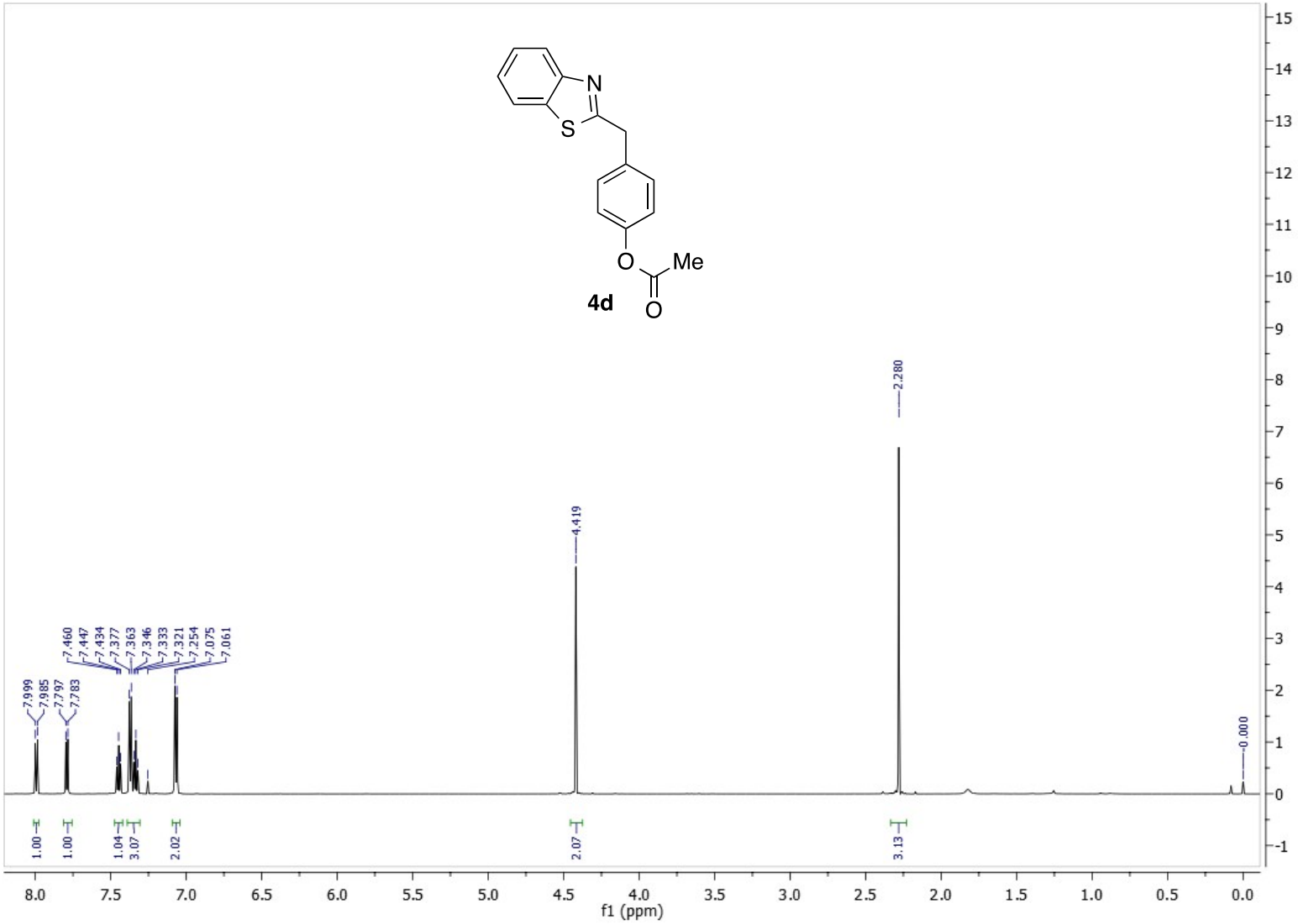
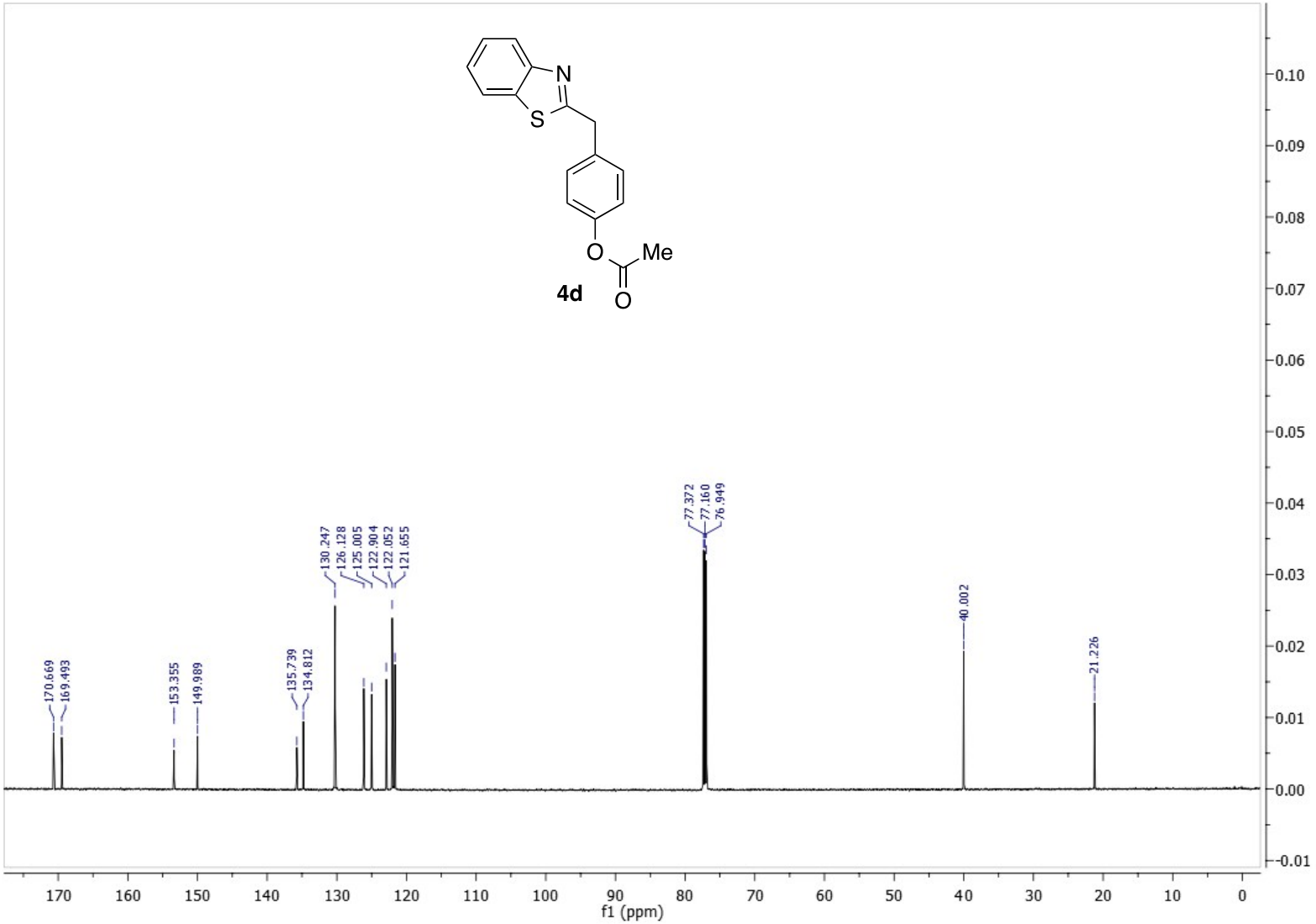
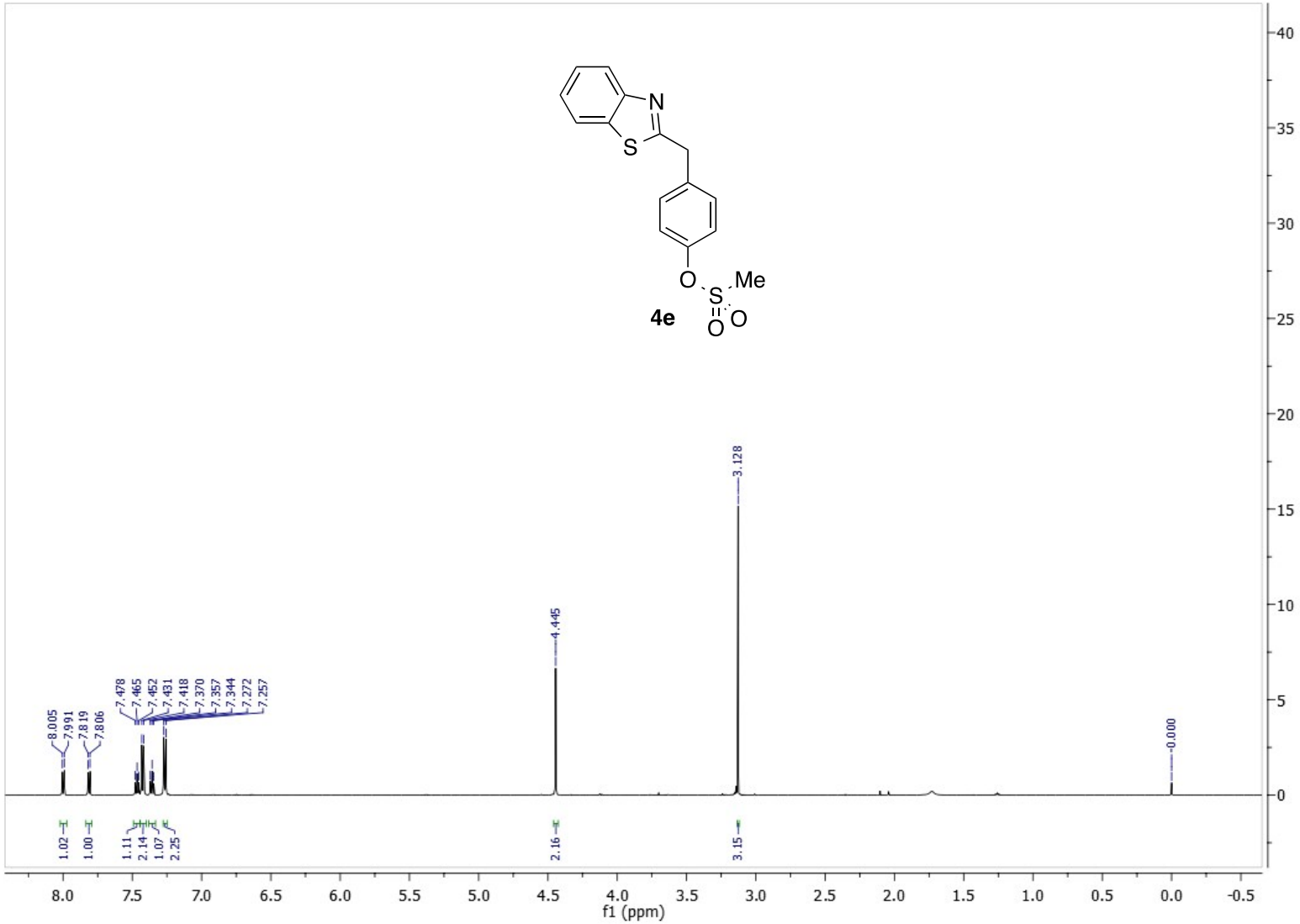


^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):



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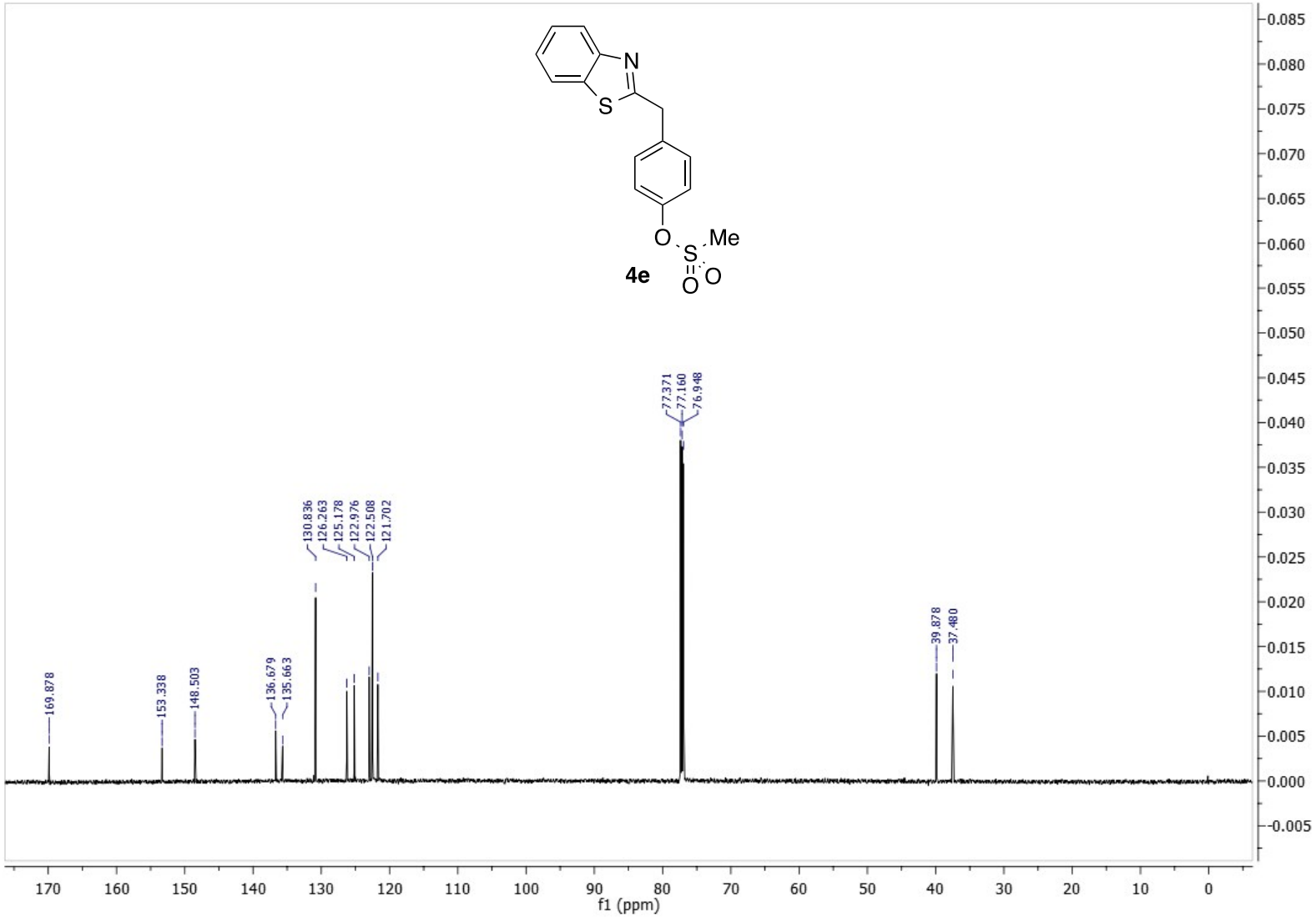

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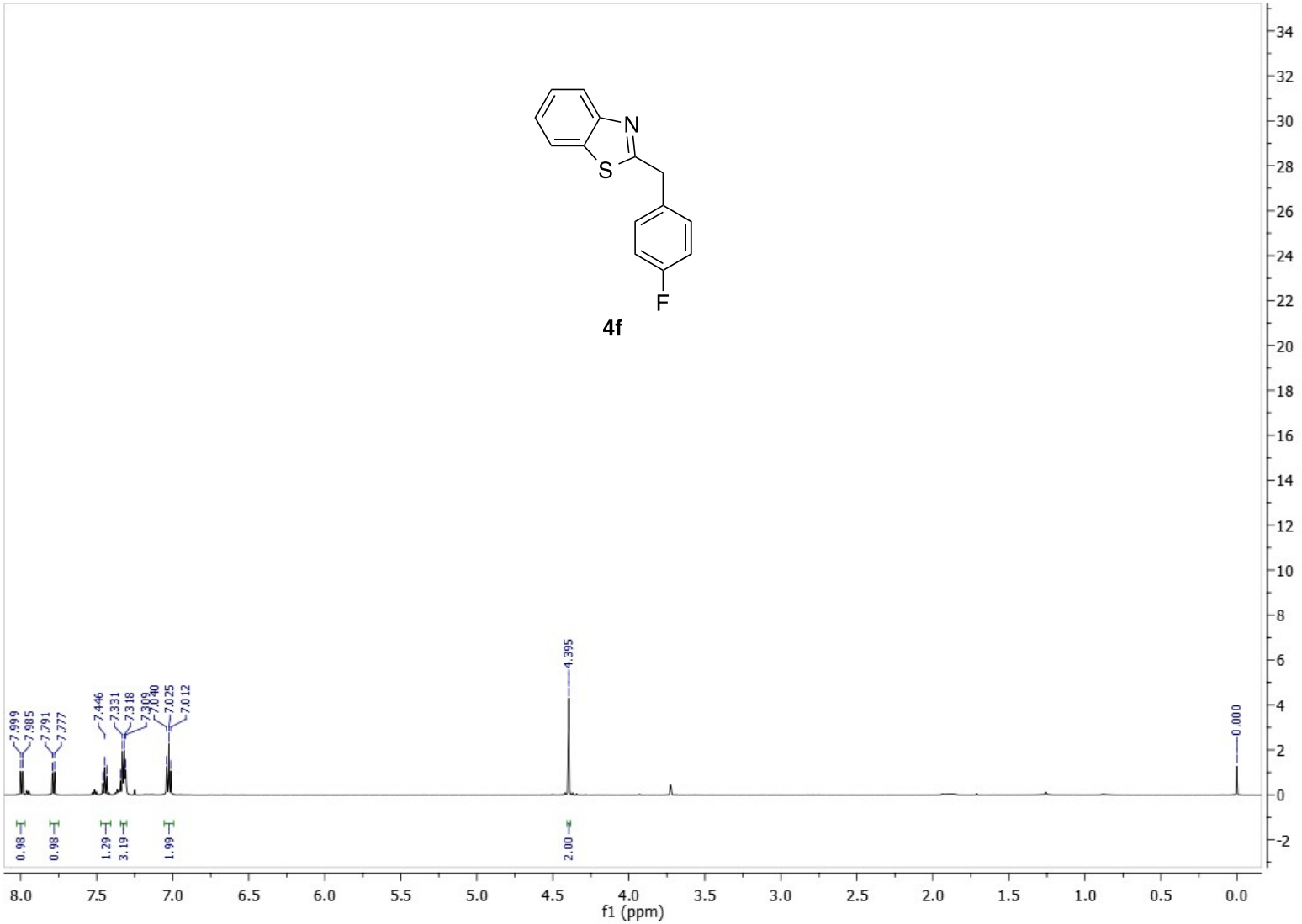

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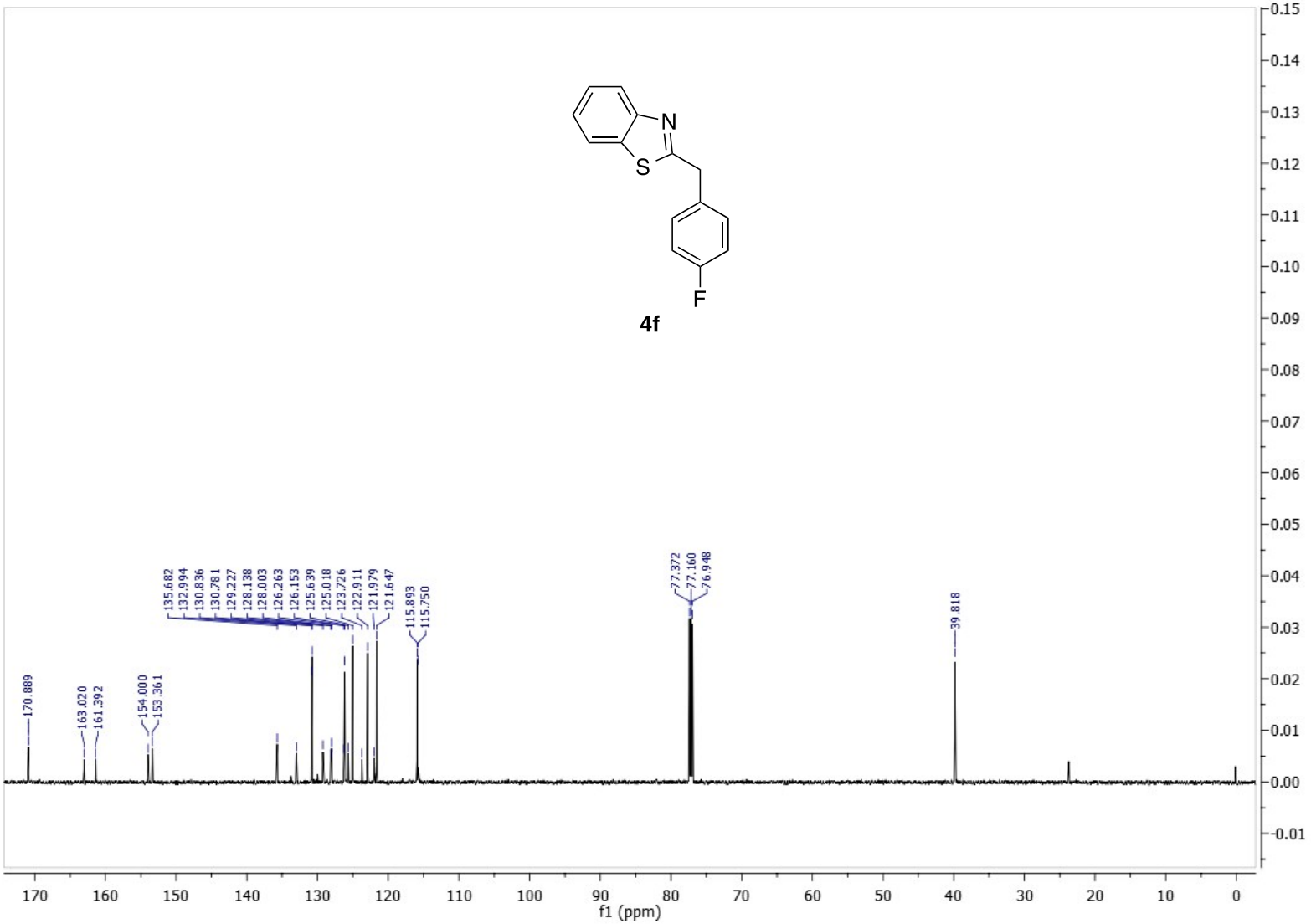

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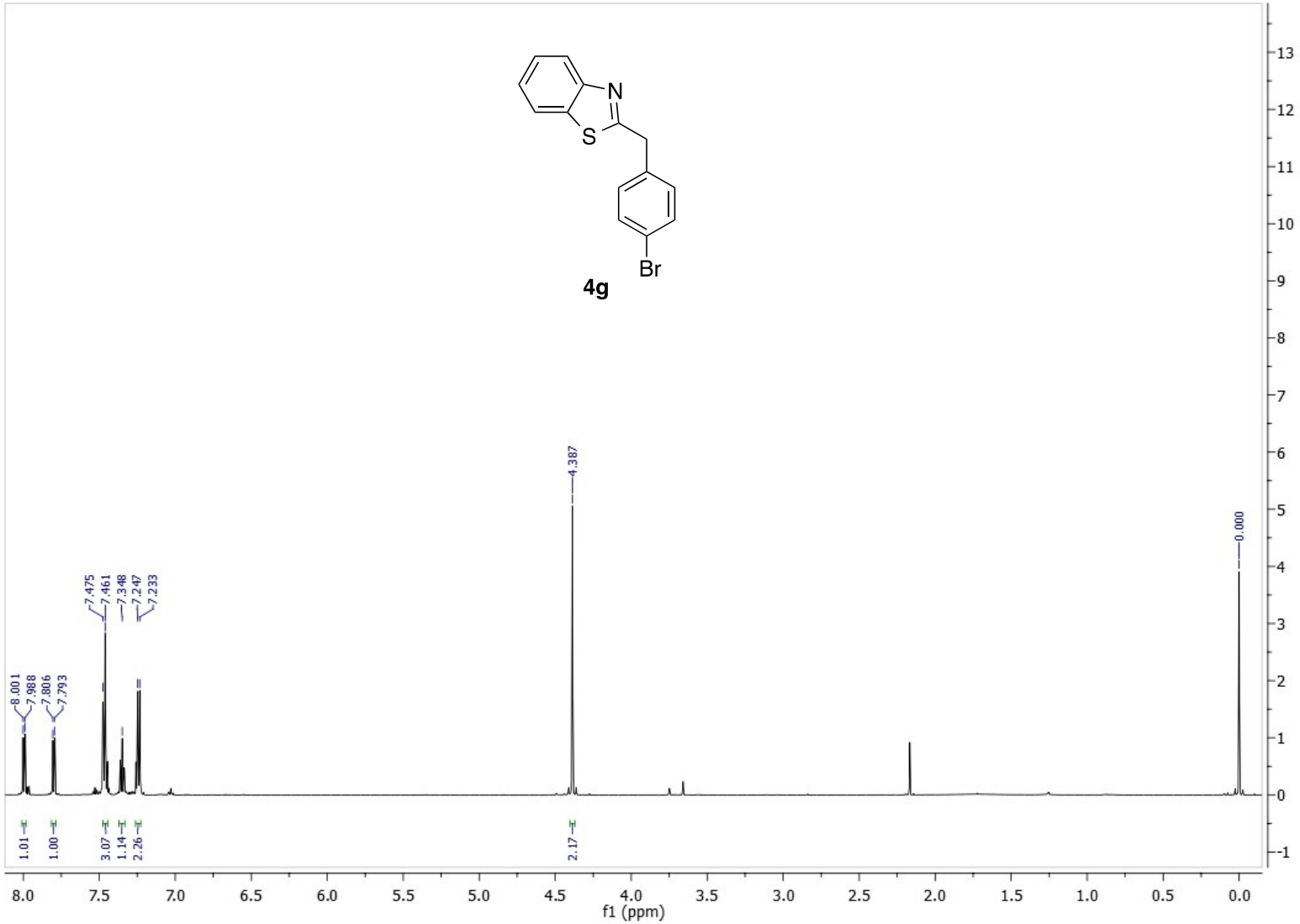
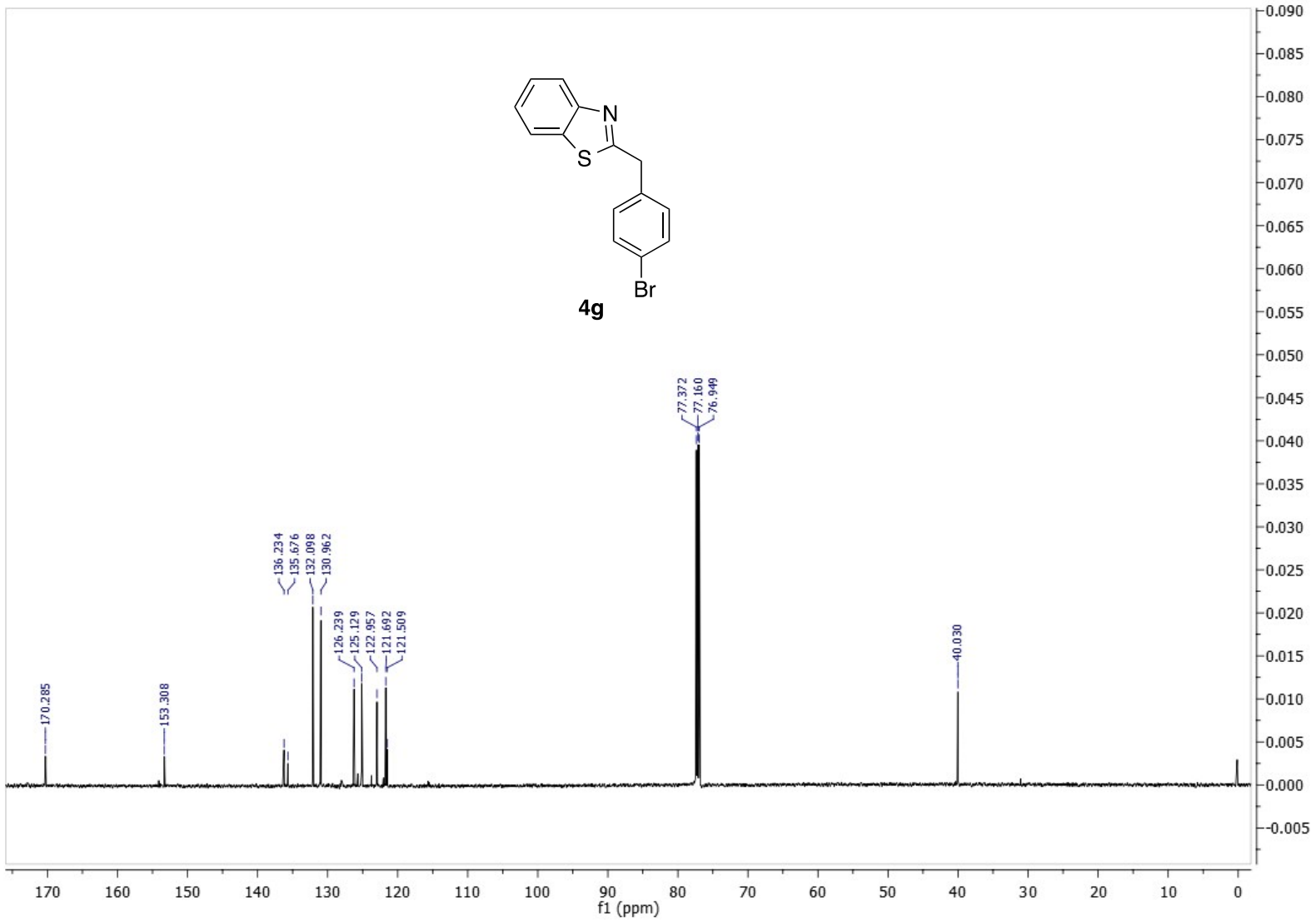


^{13}C NMR (151 MHz, $CDCl_3$):



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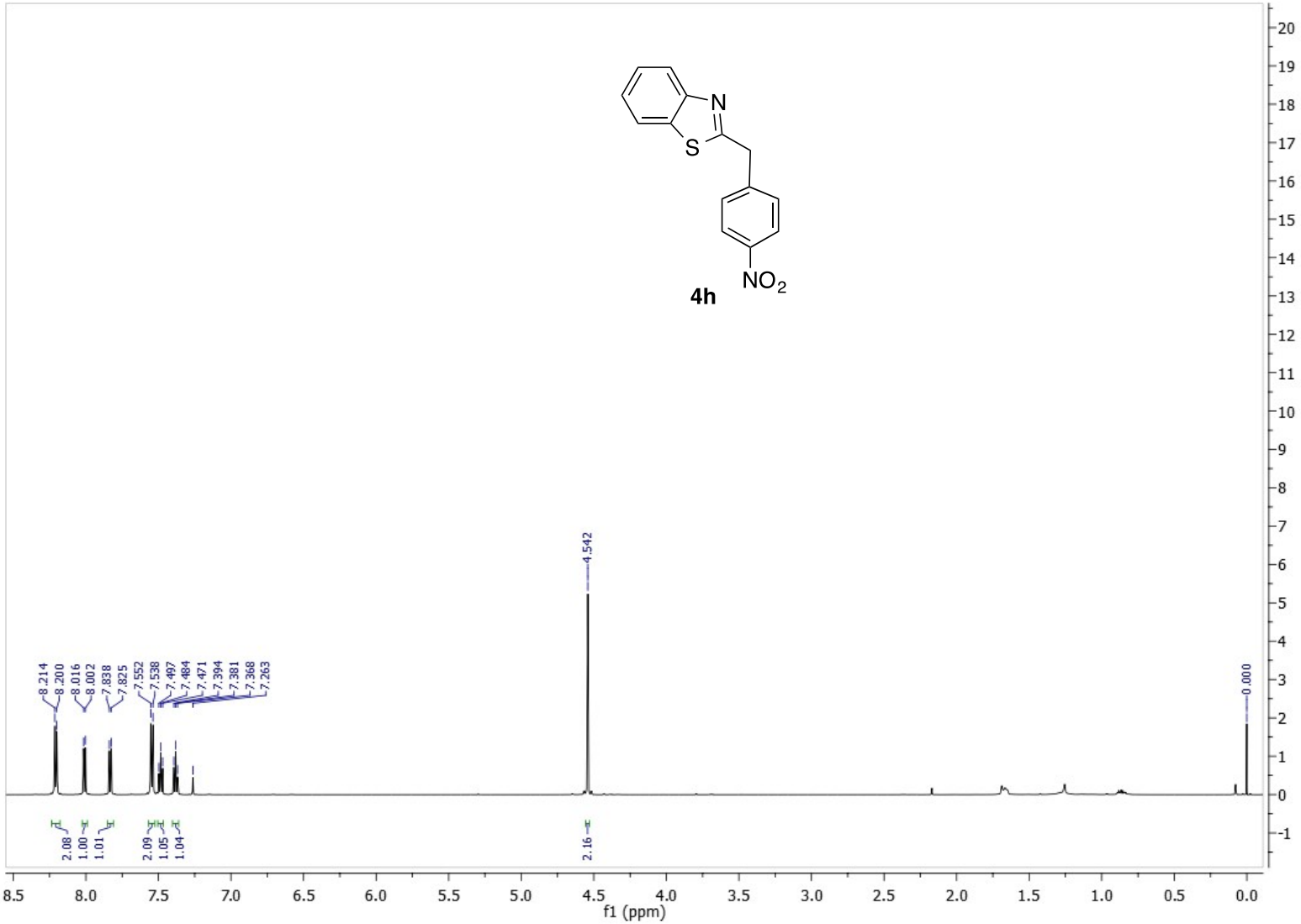
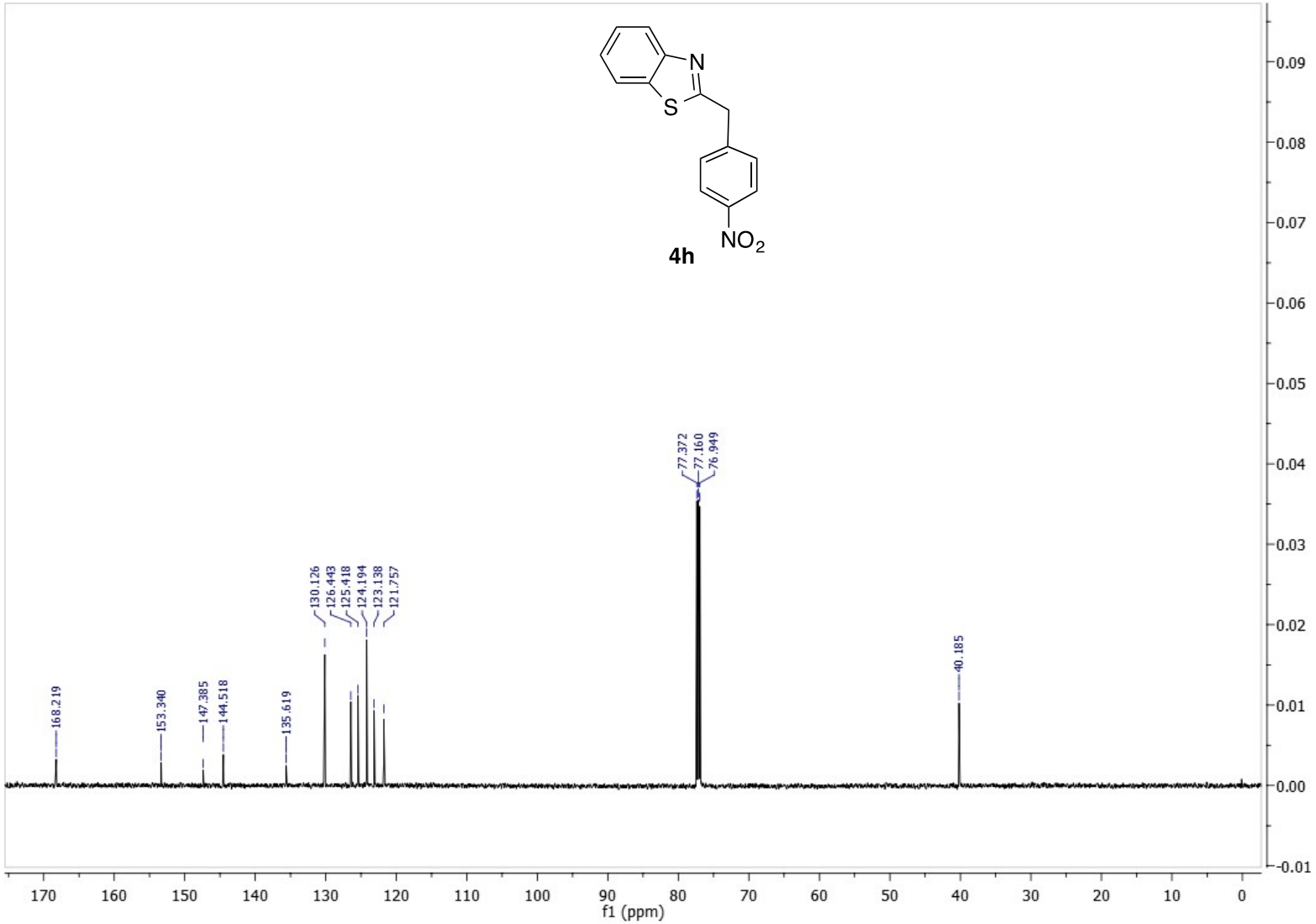
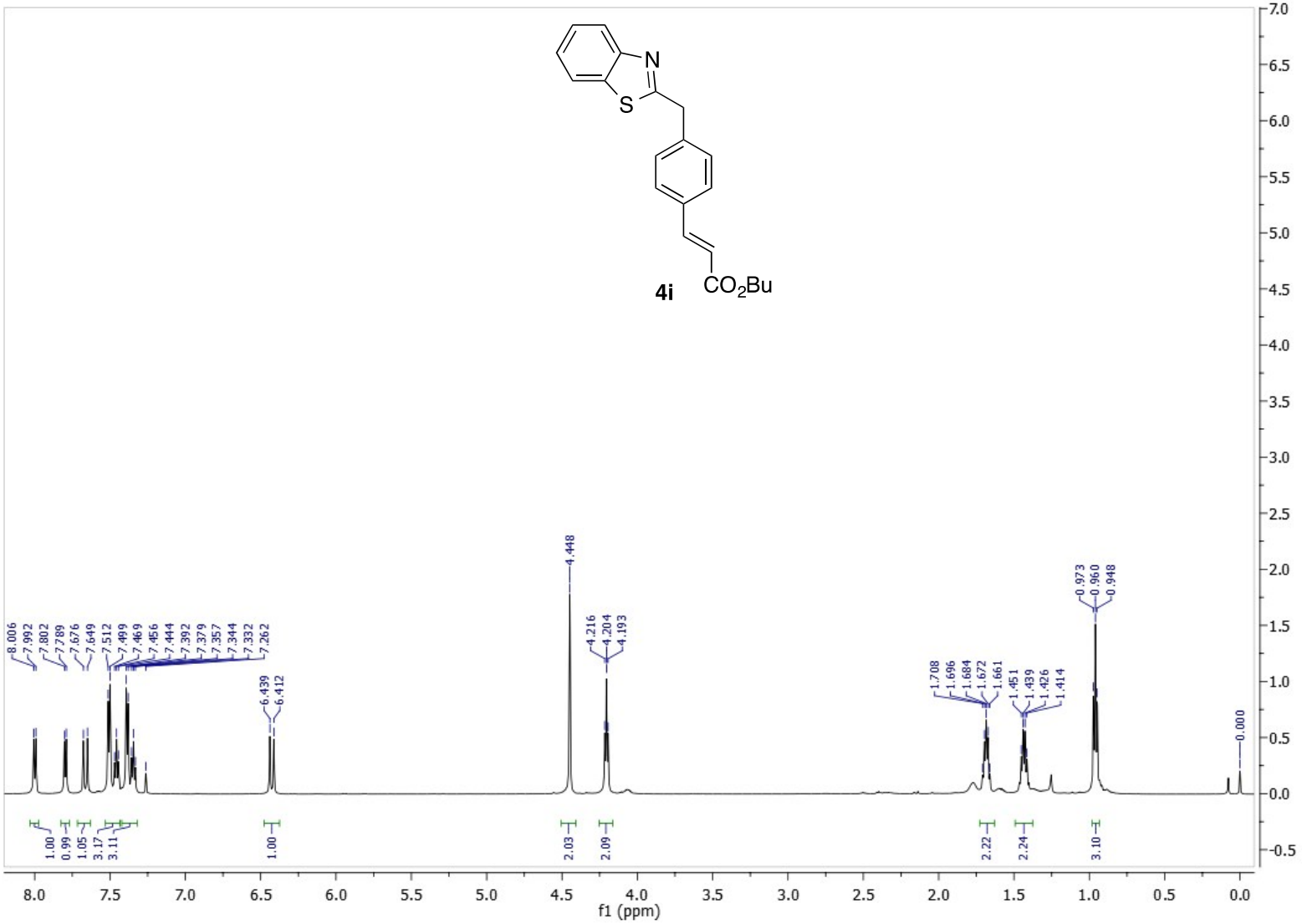


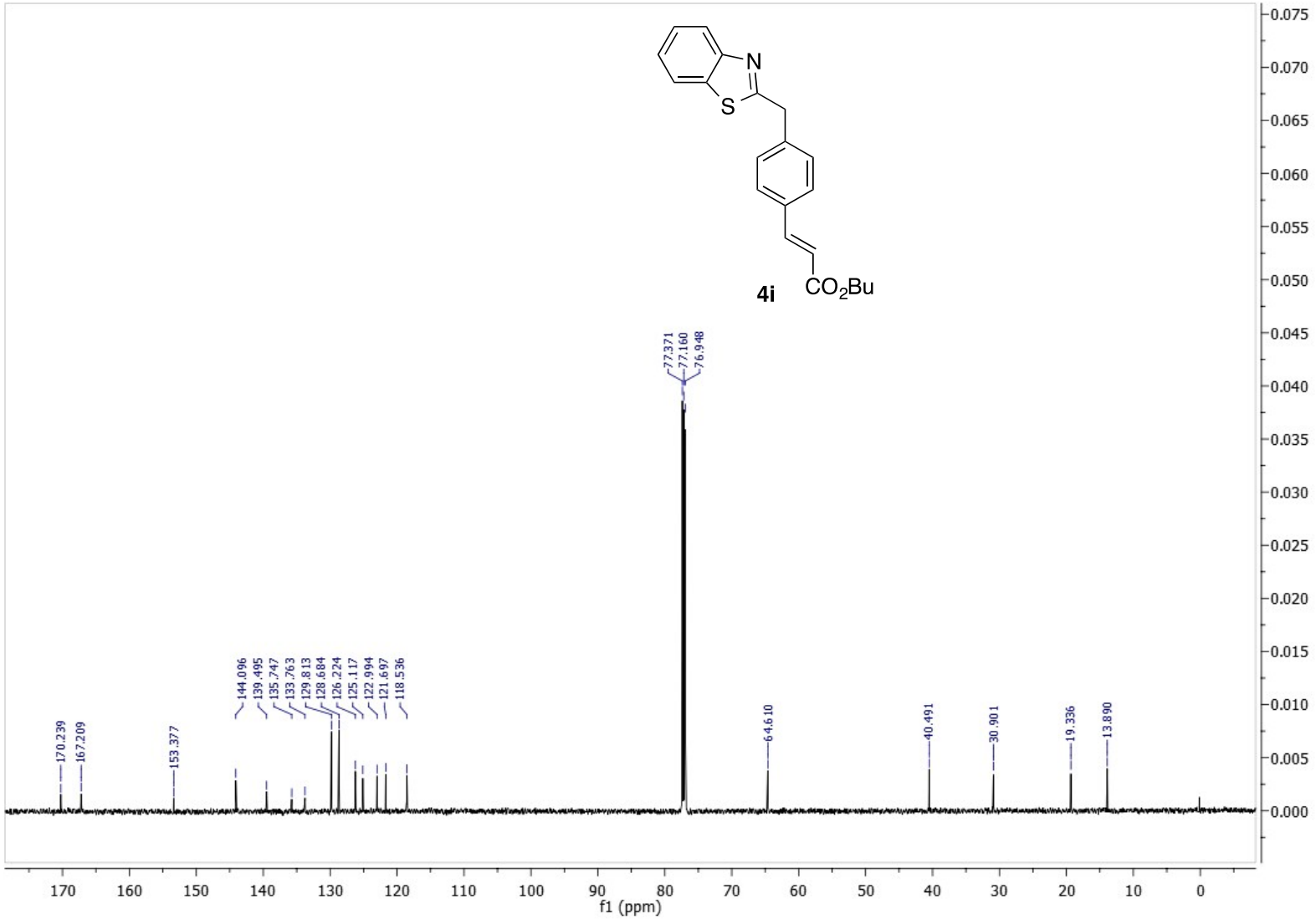
^{13}C NMR (151 MHz, $CDCl_3$):



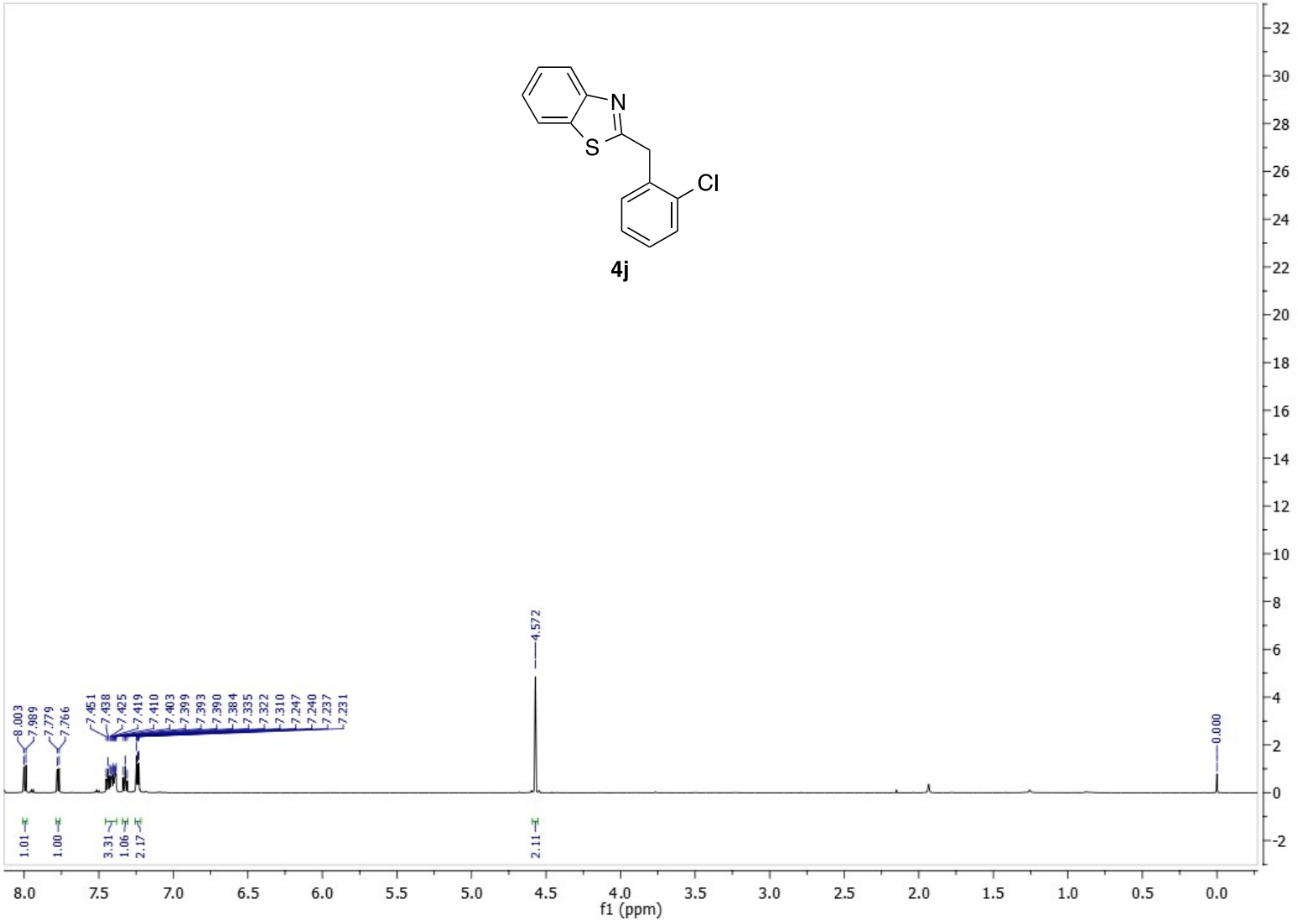
^{1}H NMR (600 MHz, $CDCl_3$):



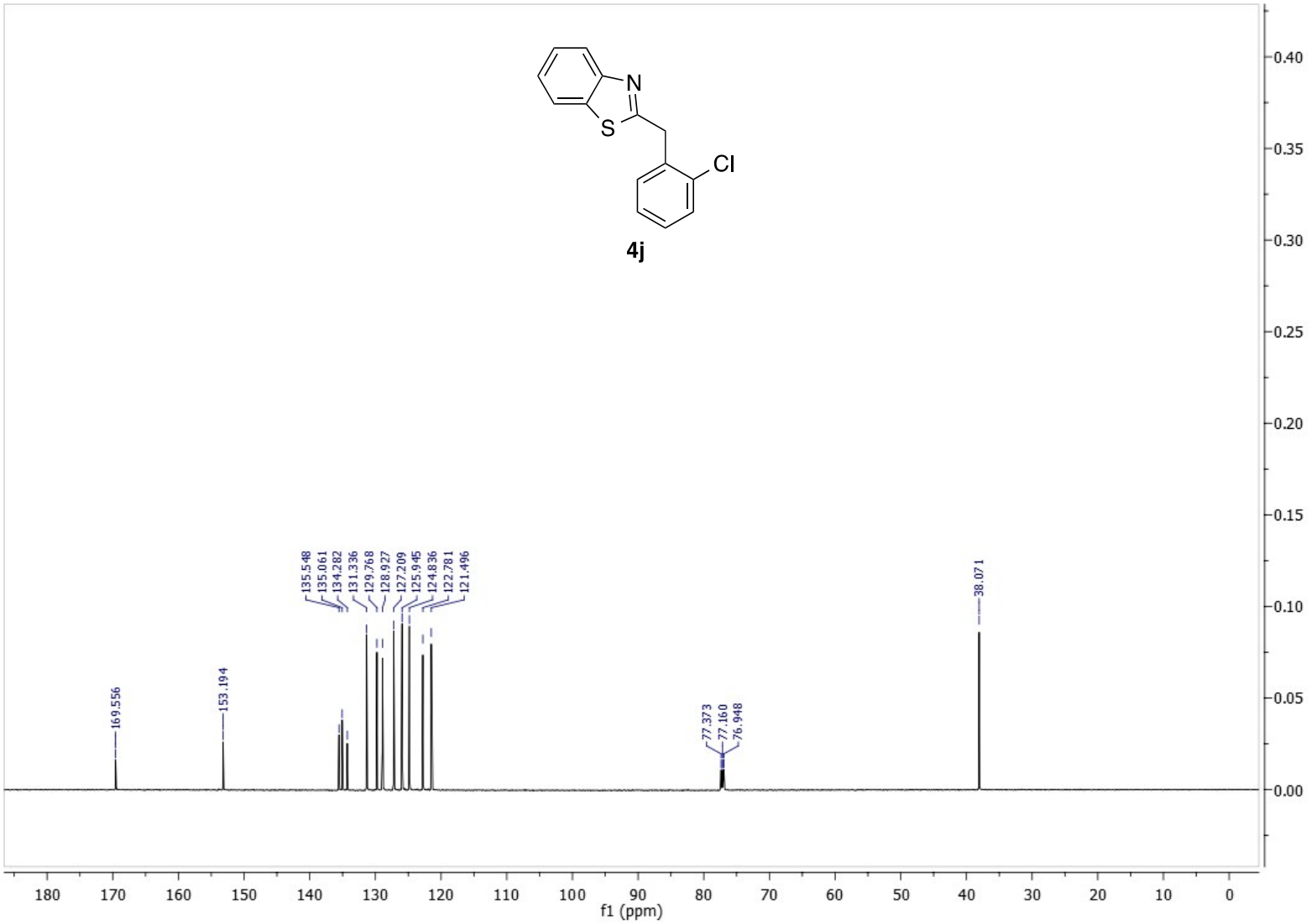
^{13}C NMR (151 MHz, $CDCl_3$):



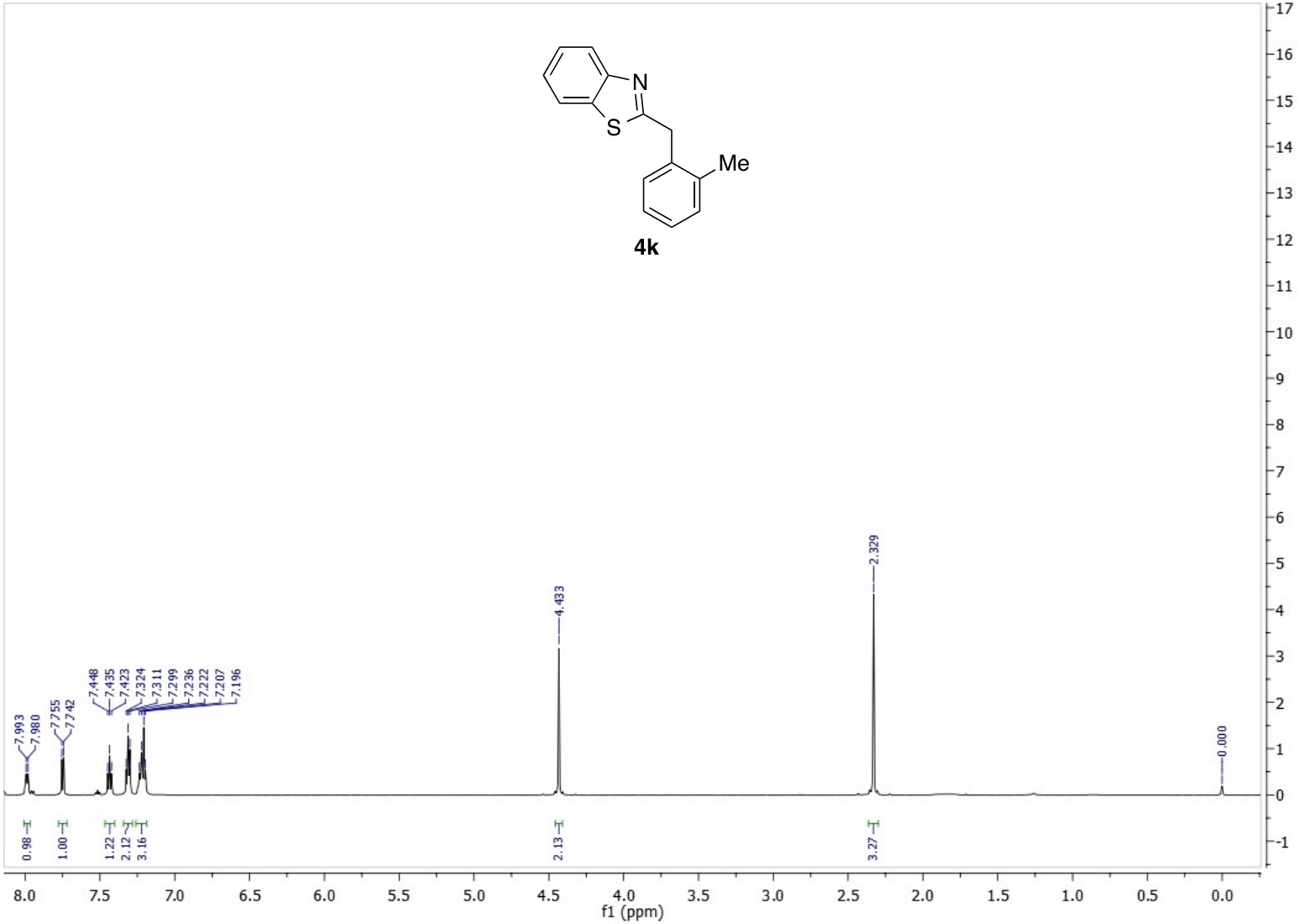
^{1}H NMR (600 MHz, $CDCl_3$):



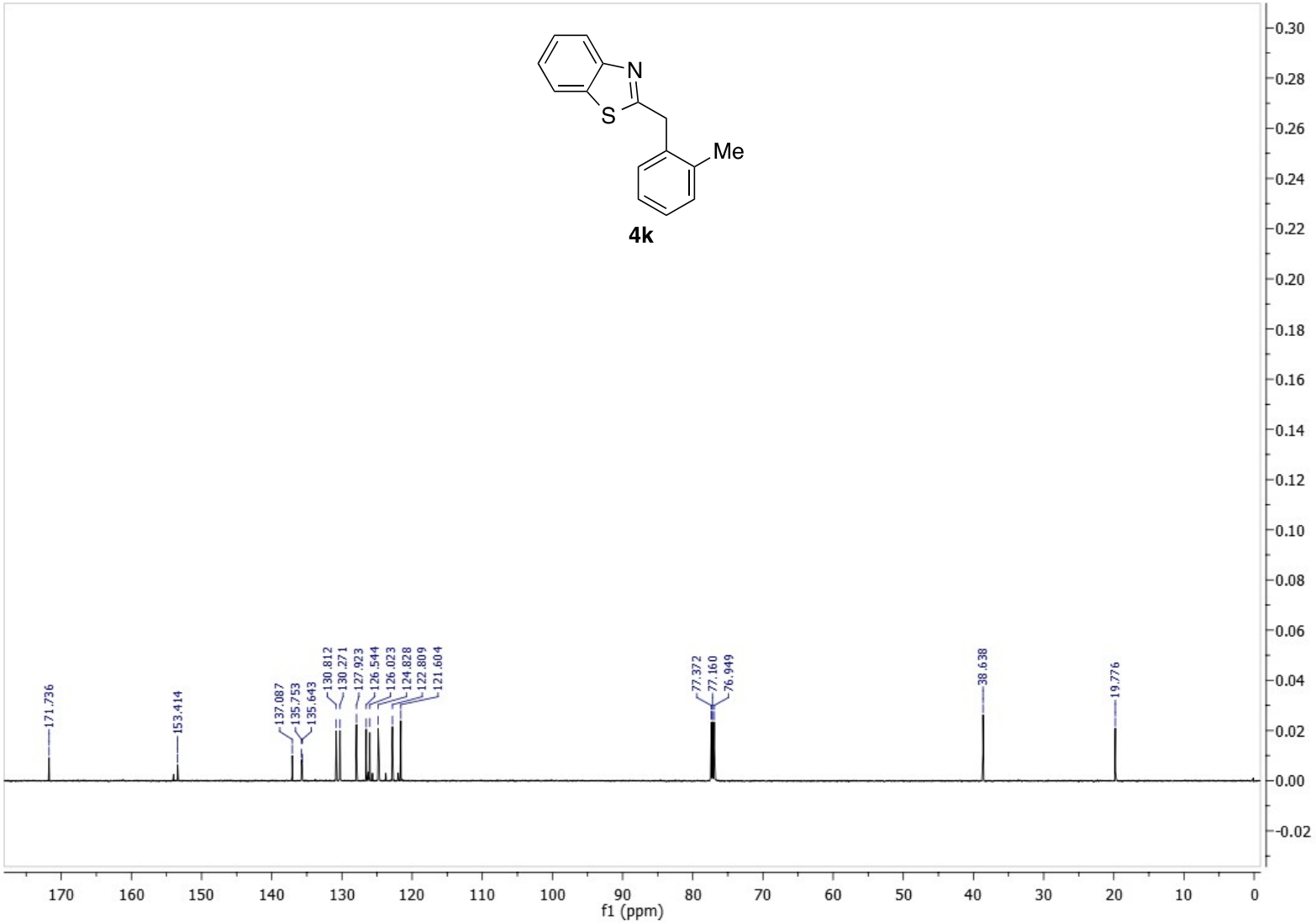
^{13}C NMR (151 MHz, $CDCl_3$):



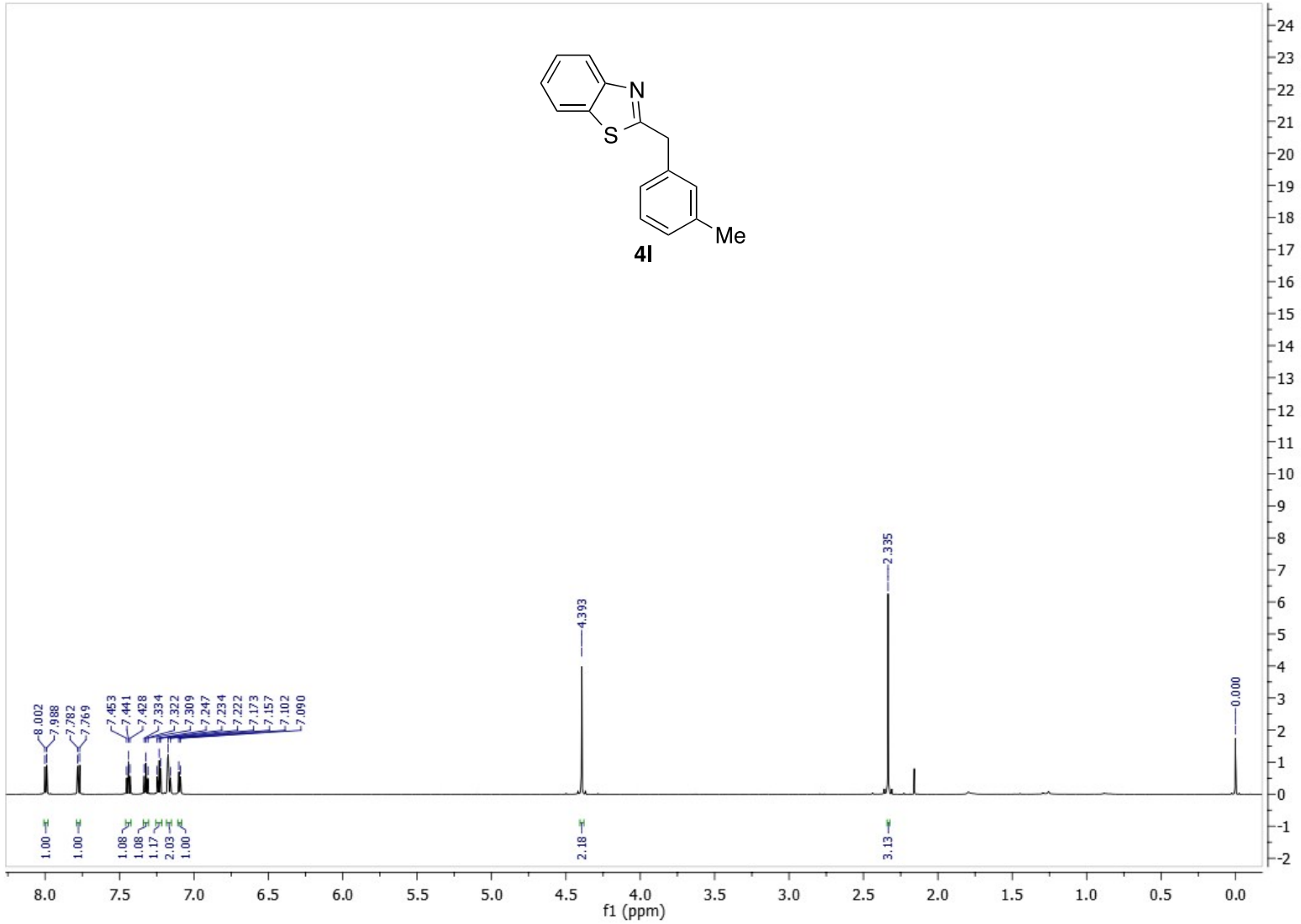
^{1}H NMR (600 MHz, $CDCl_3$):



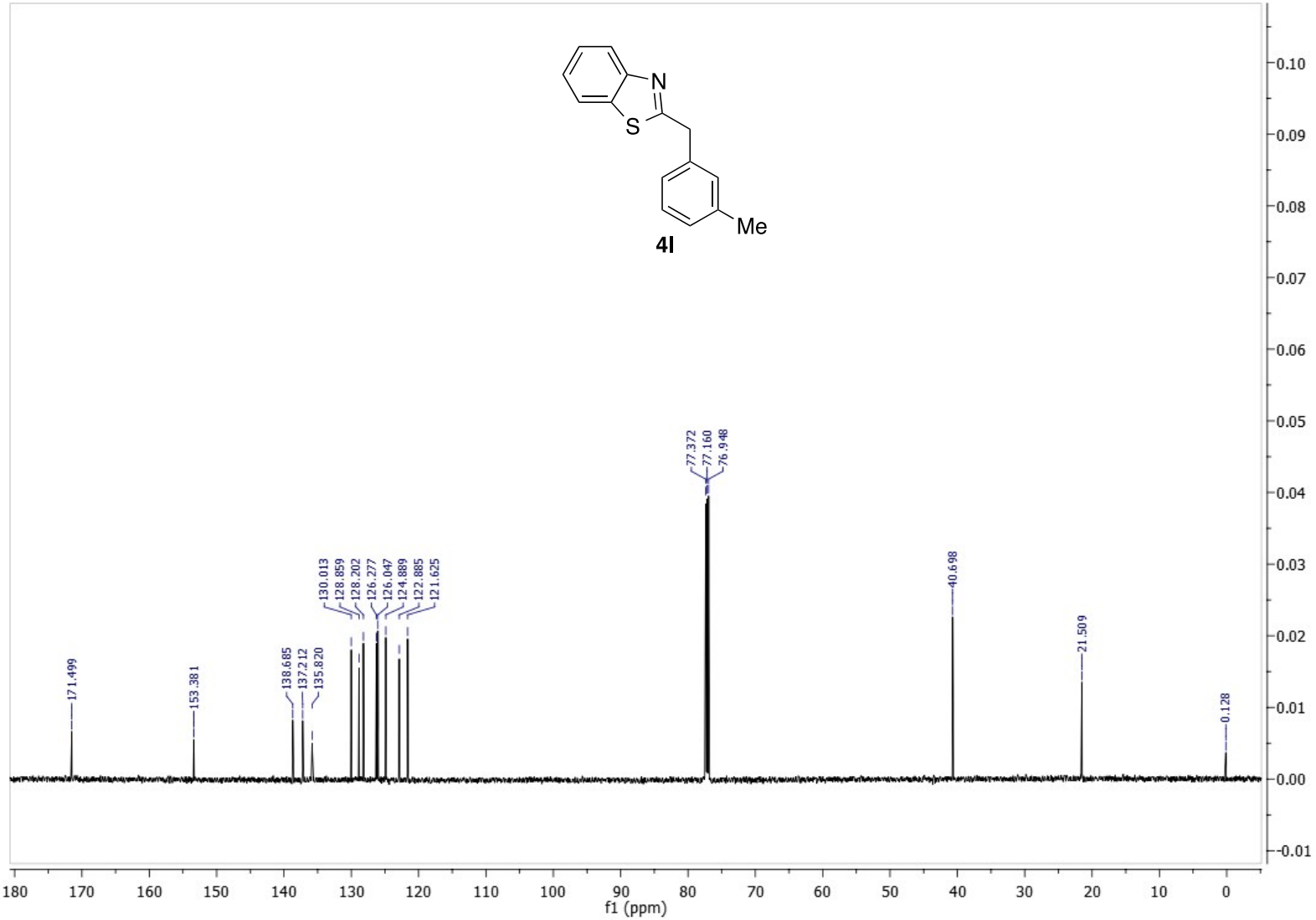
^{13}C NMR (151 MHz, $CDCl_3$):



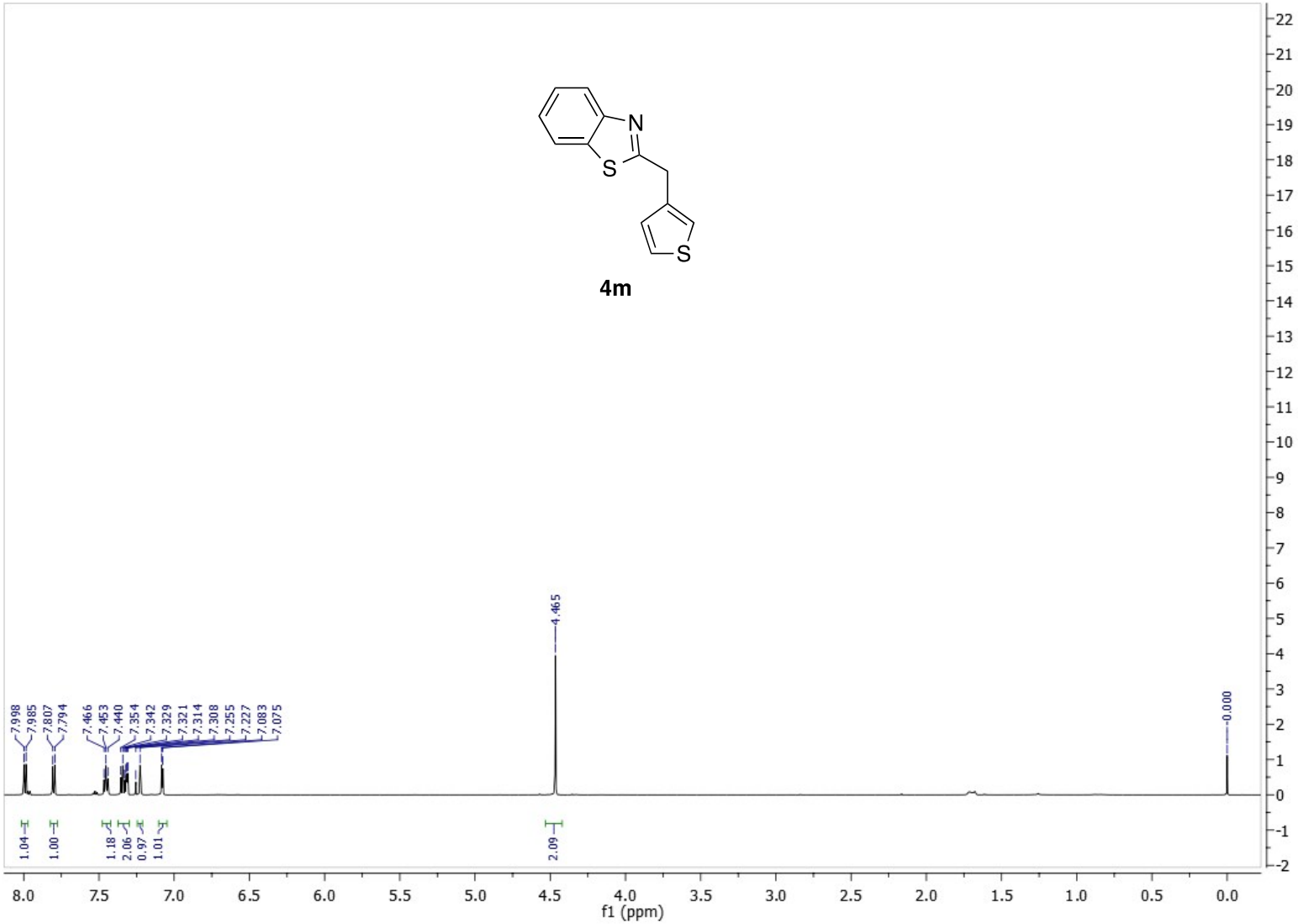
^{1}H NMR (600 MHz, $CDCl_3$):



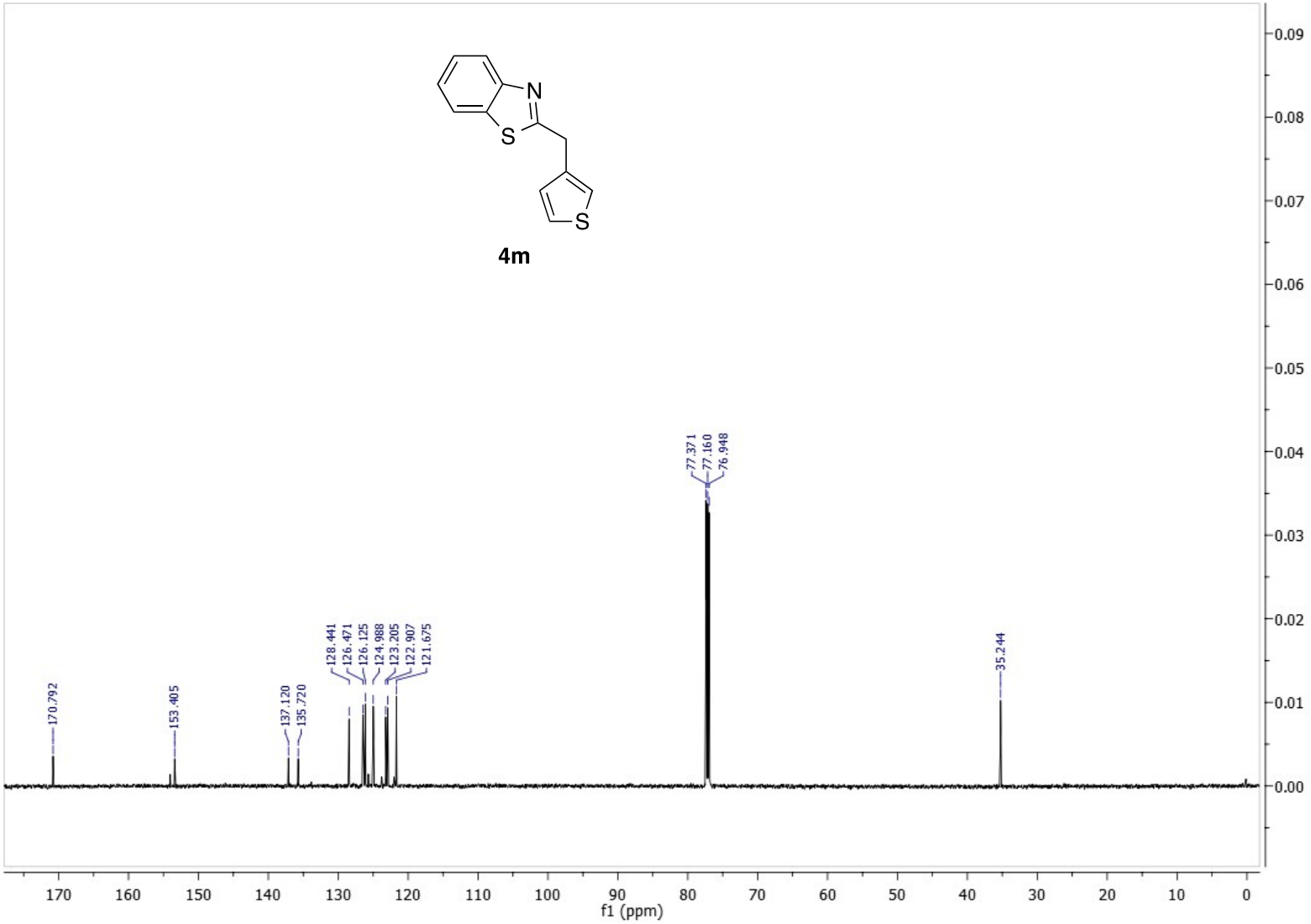
^{13}C NMR (151 MHz, $CDCl_3$):



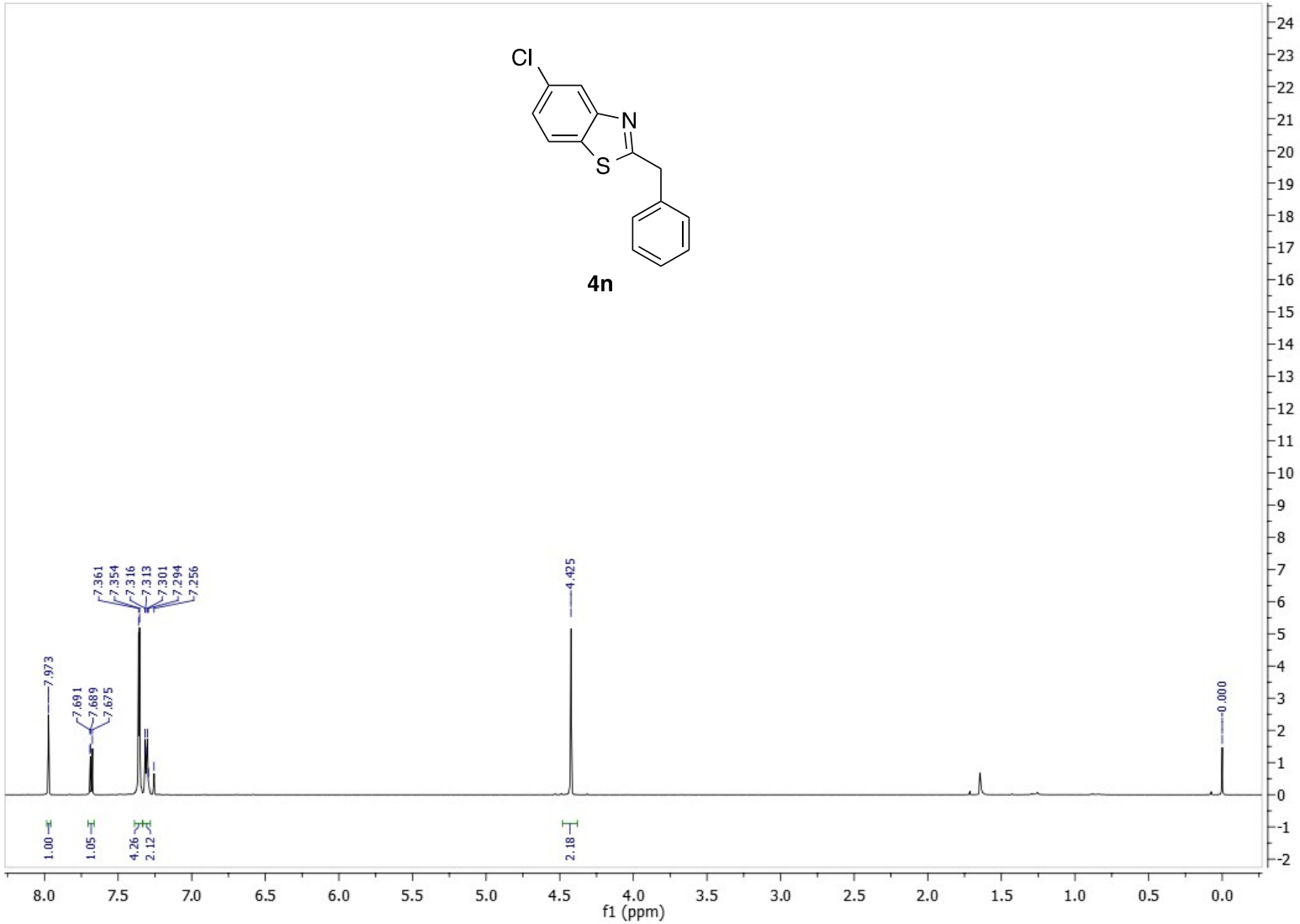
^{1}H NMR (600 MHz, $CDCl_3$):



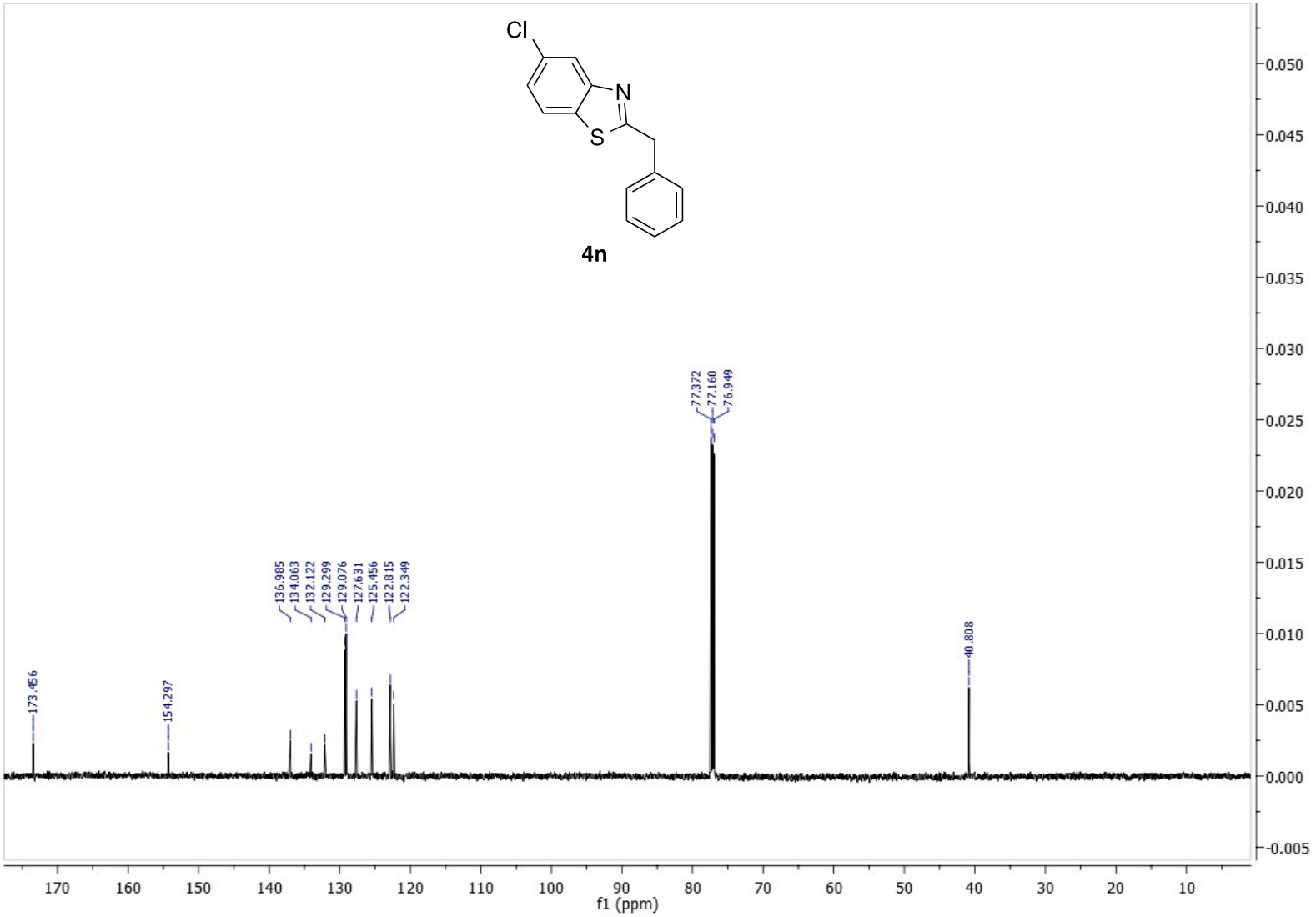
^{13}C NMR (151 MHz, $CDCl_3$):



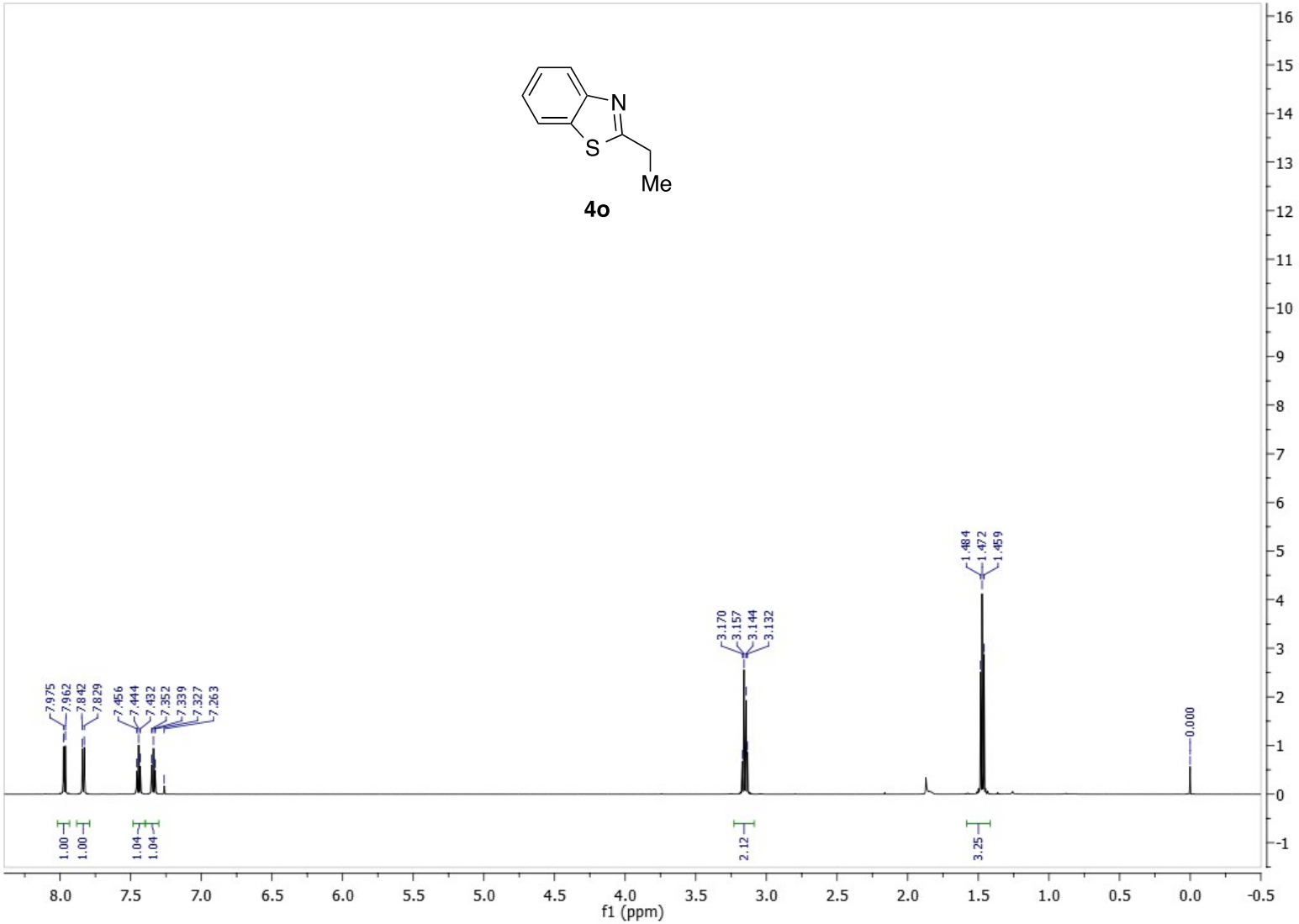
^{1}H NMR (600 MHz, $CDCl_3$):



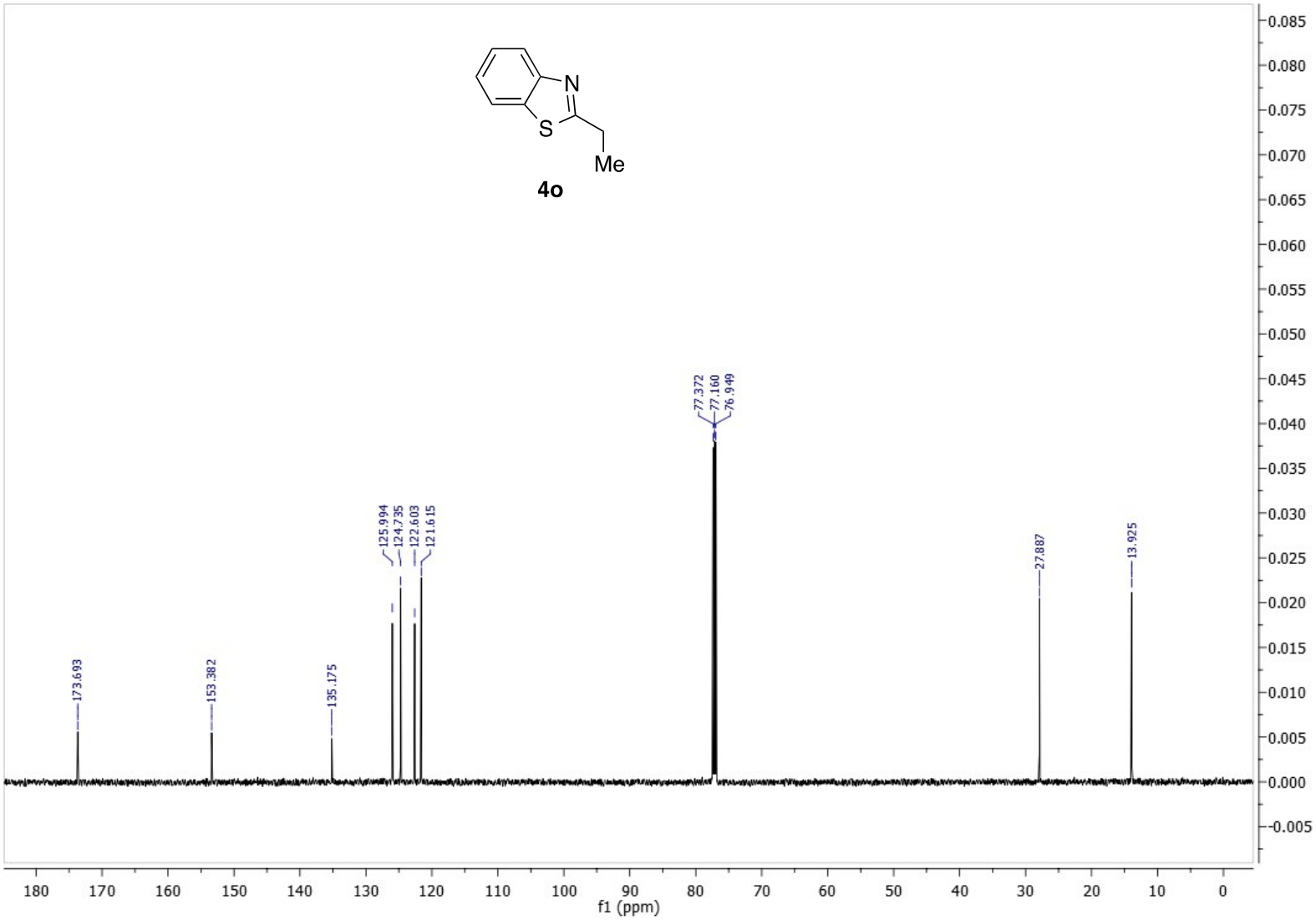
^{13}C NMR (151 MHz, $CDCl_3$):



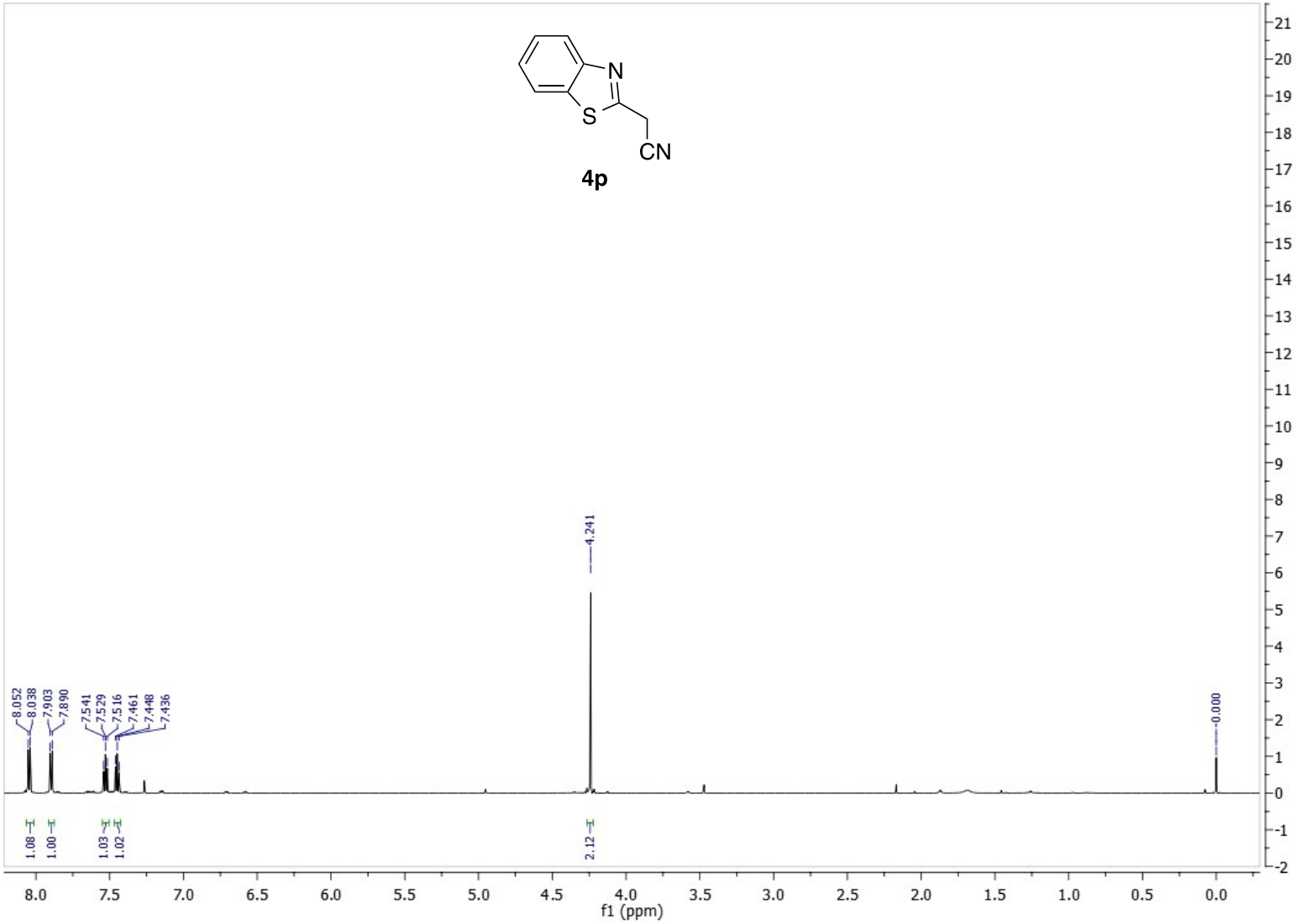
^{1}H NMR (600 MHz, $CDCl_3$):



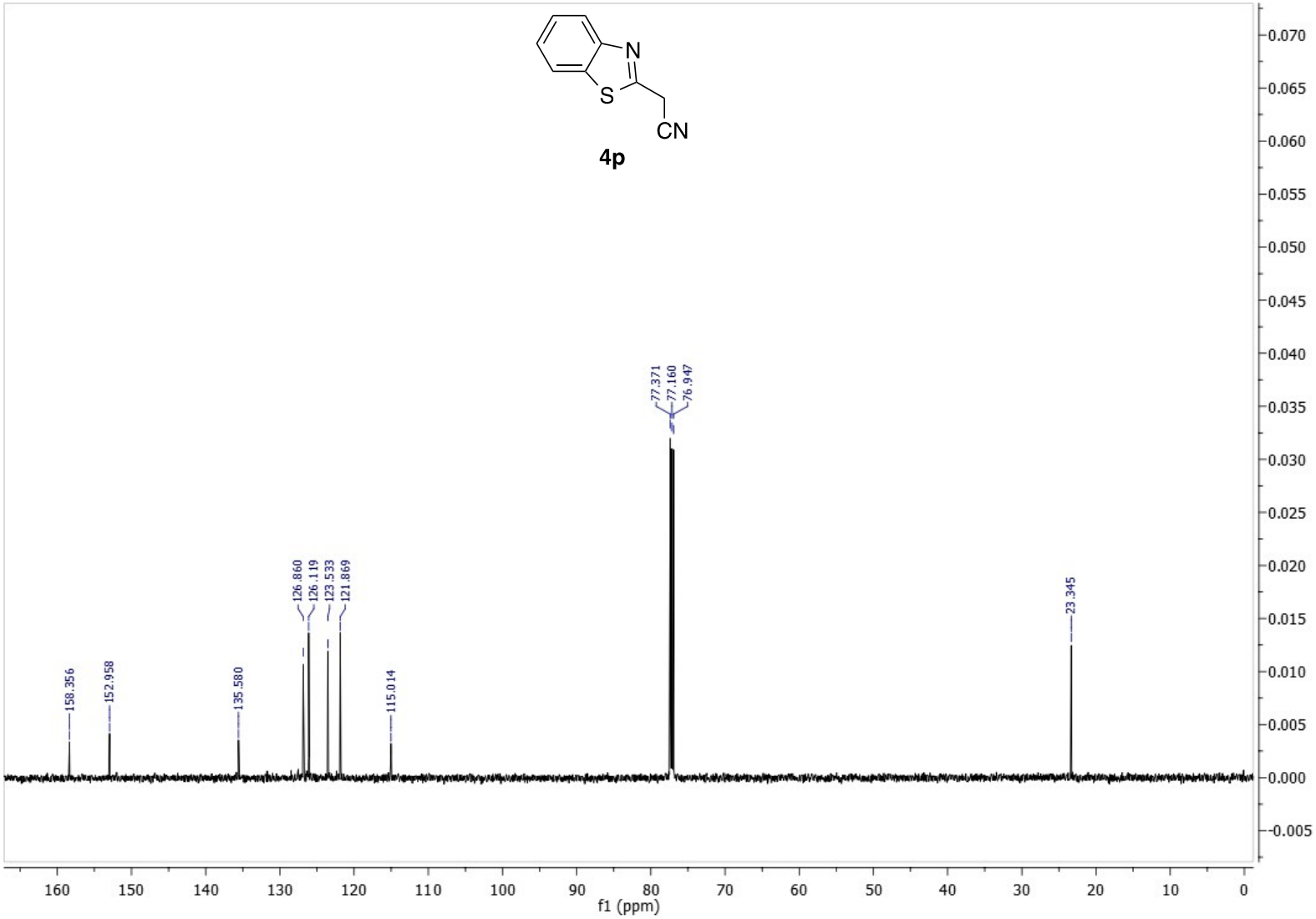
^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):

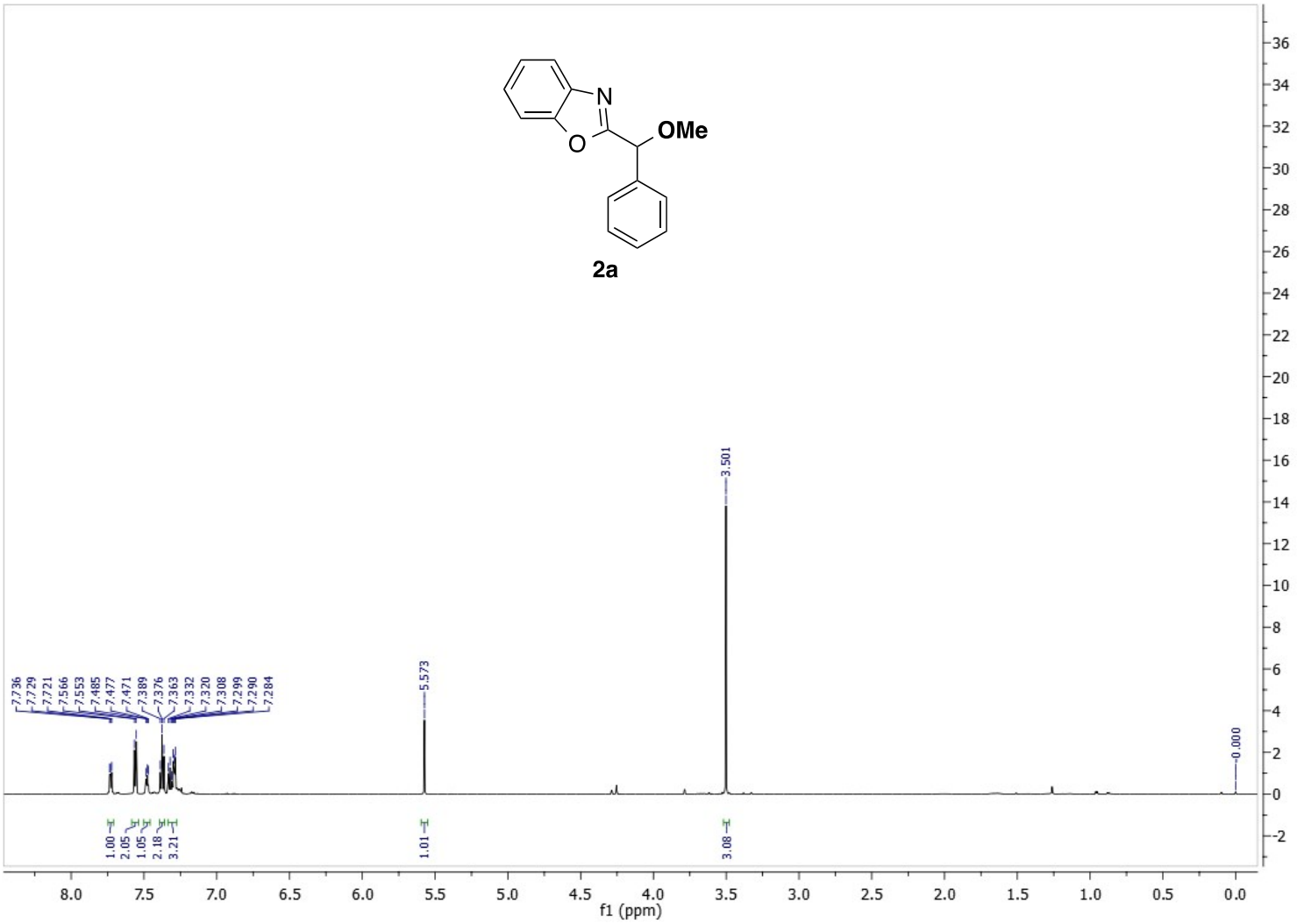


^{13}C NMR (151 MHz, $CDCl_3$):



NMR spectra of all products

^{1}H NMR (600 MHz, $CDCl_3$):



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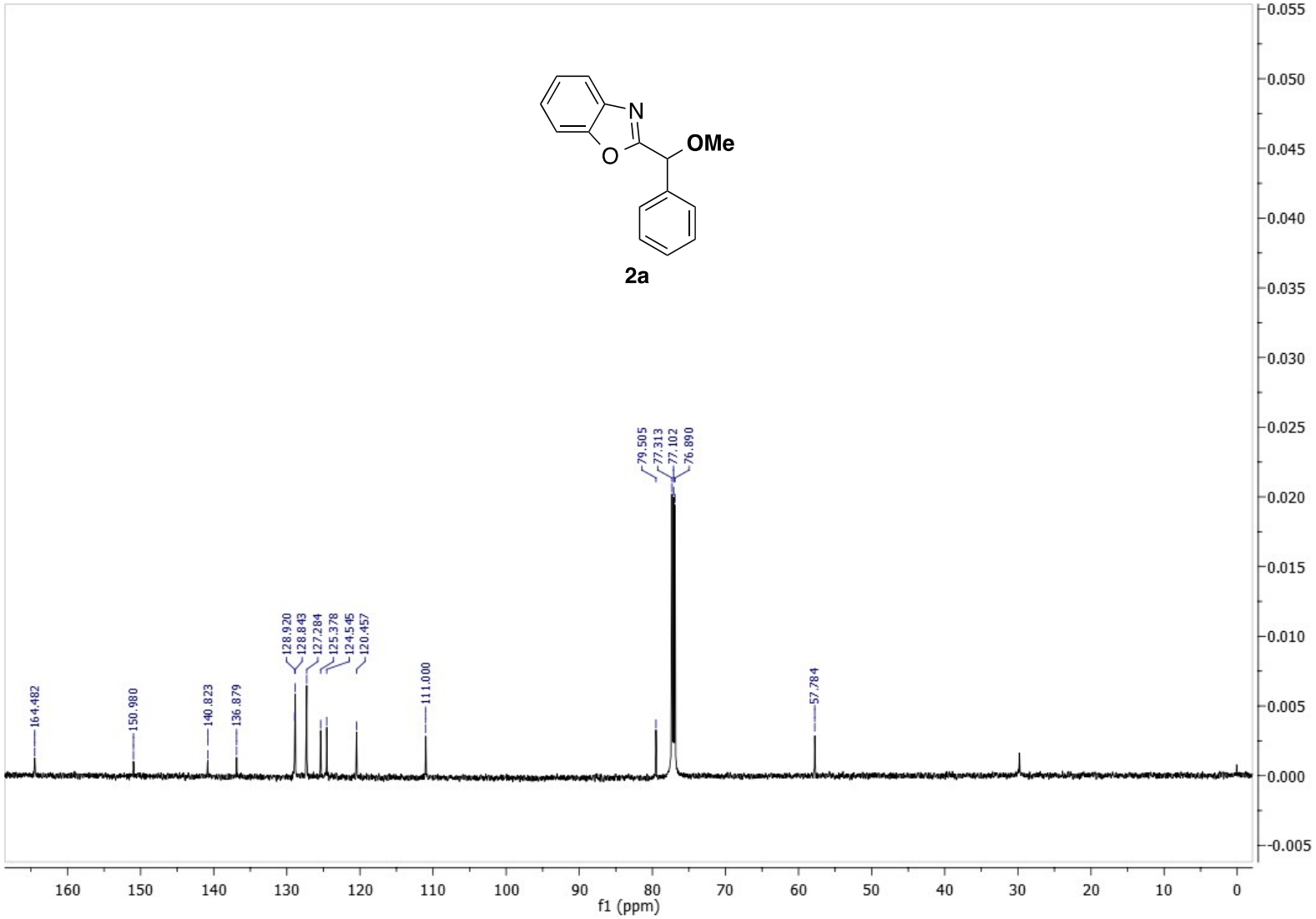
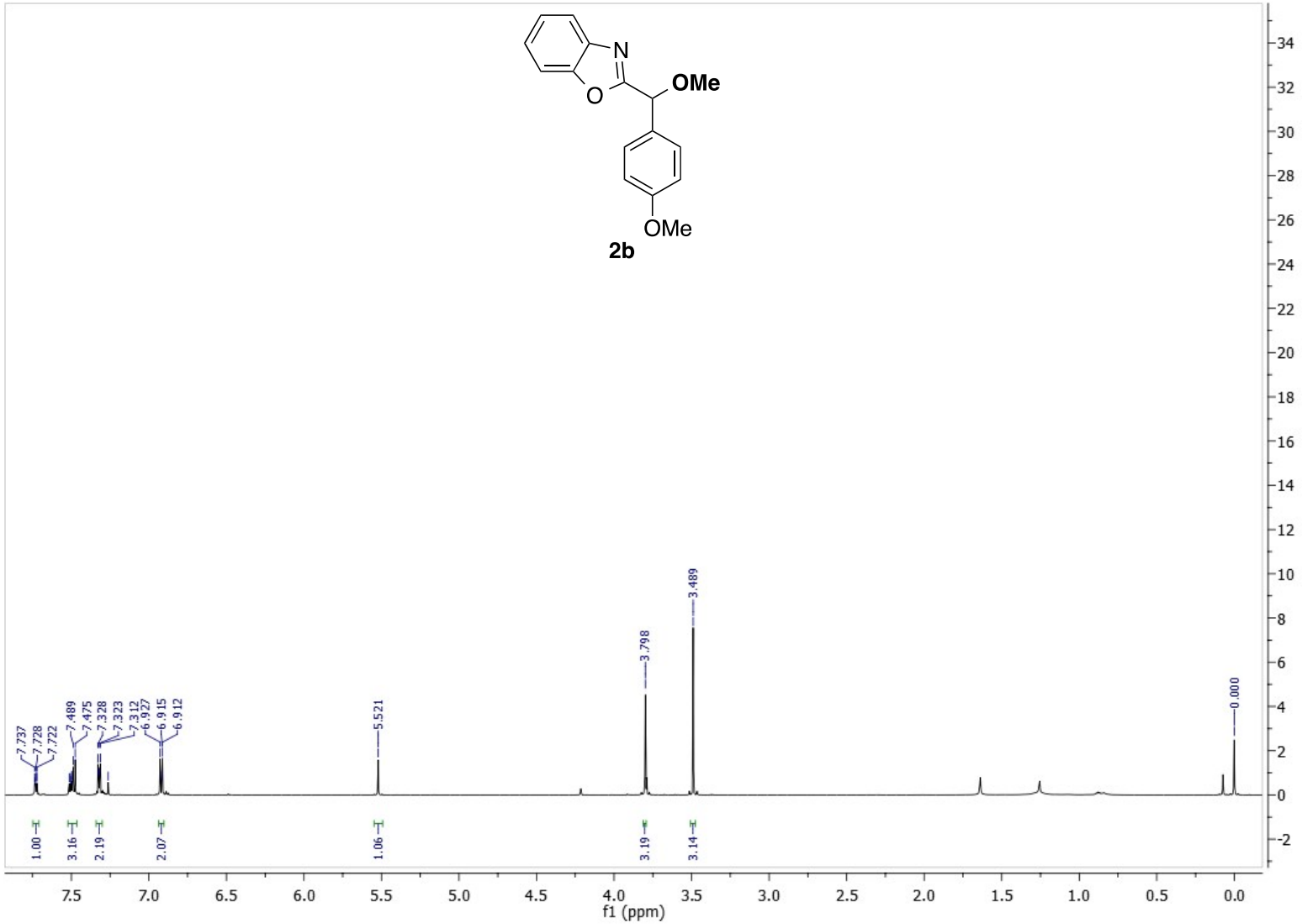
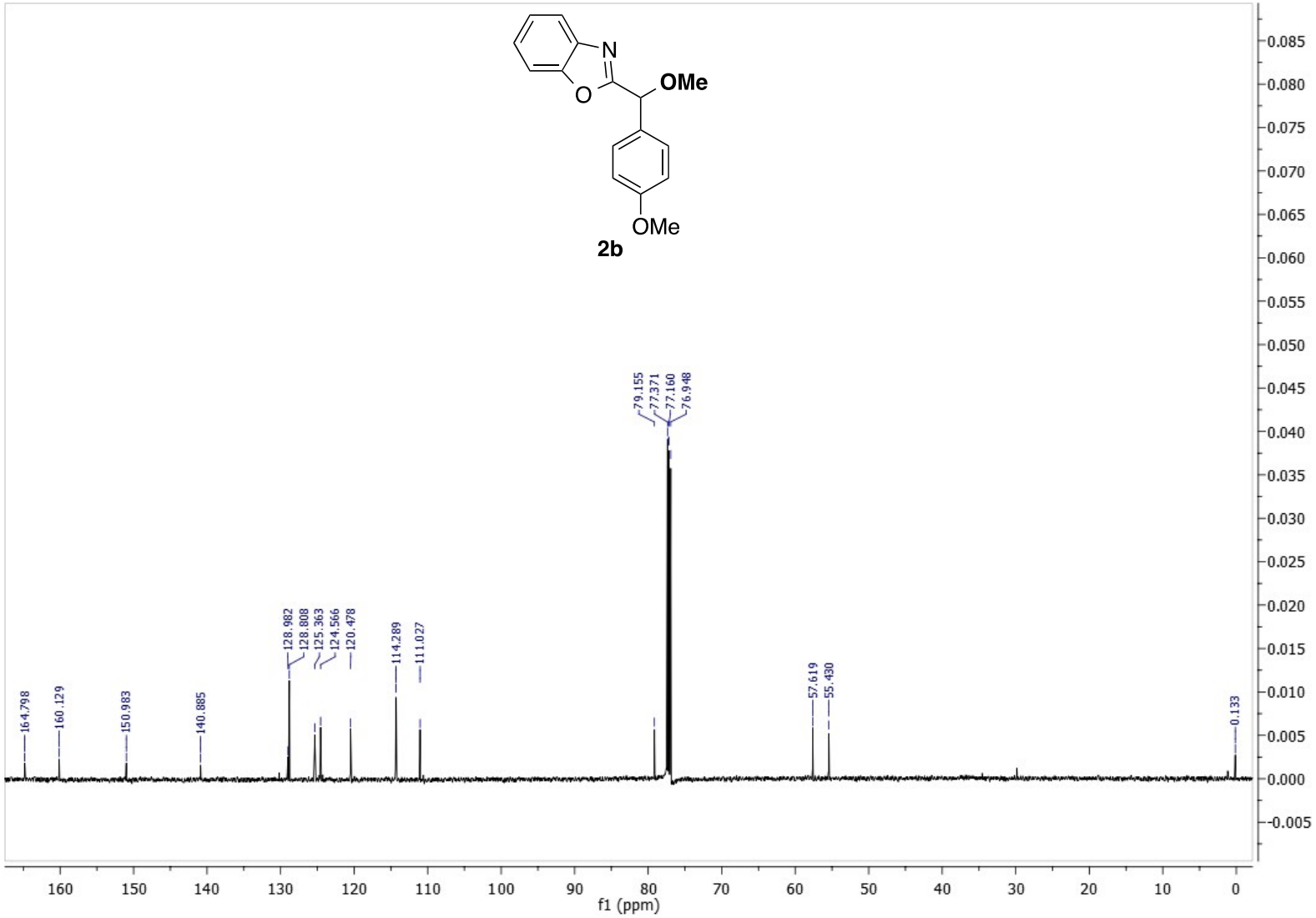


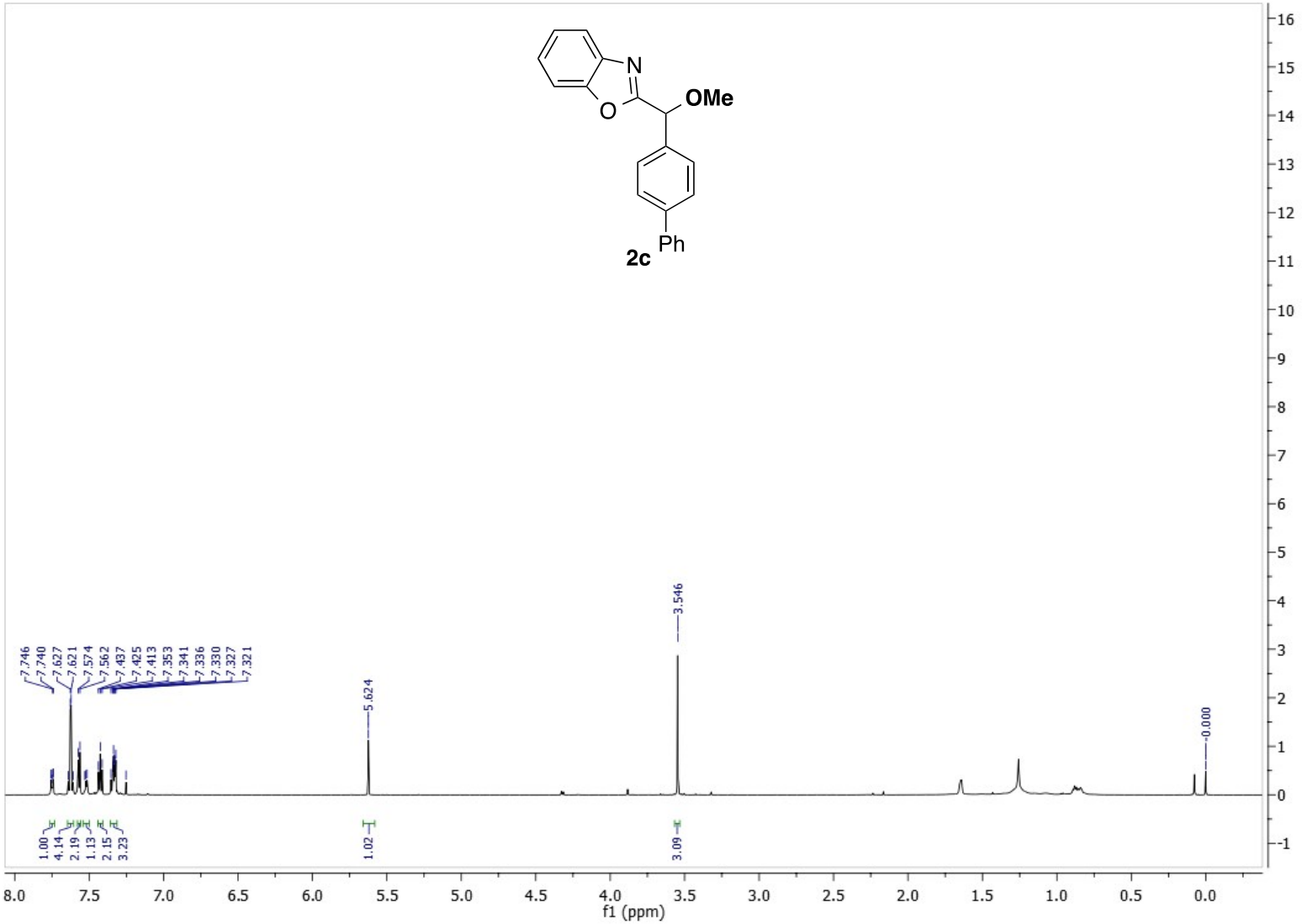
^{1}H NMR (600 MHz, $CDCl_3$):



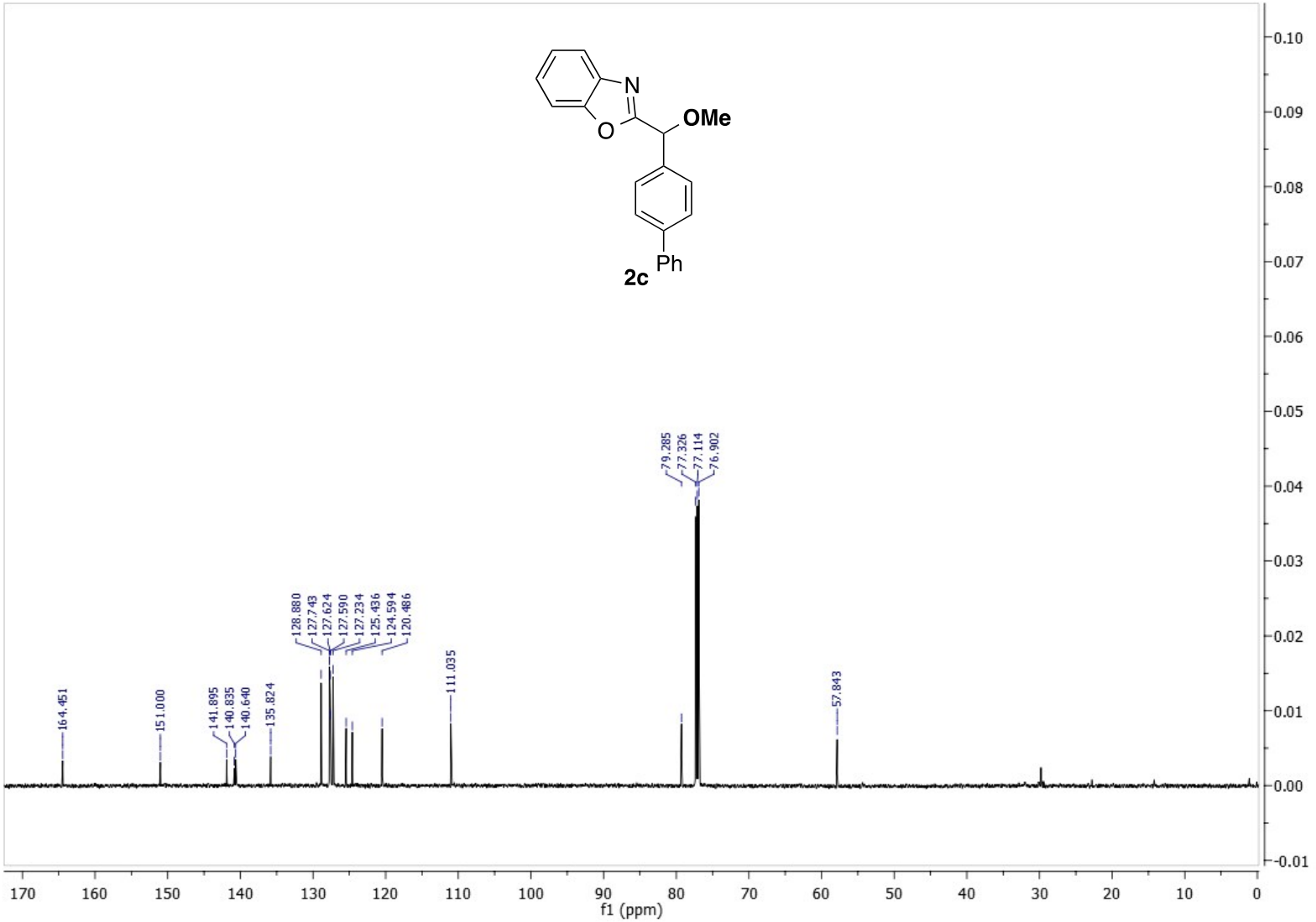
^{13}C NMR (151 MHz, $CDCl_3$):



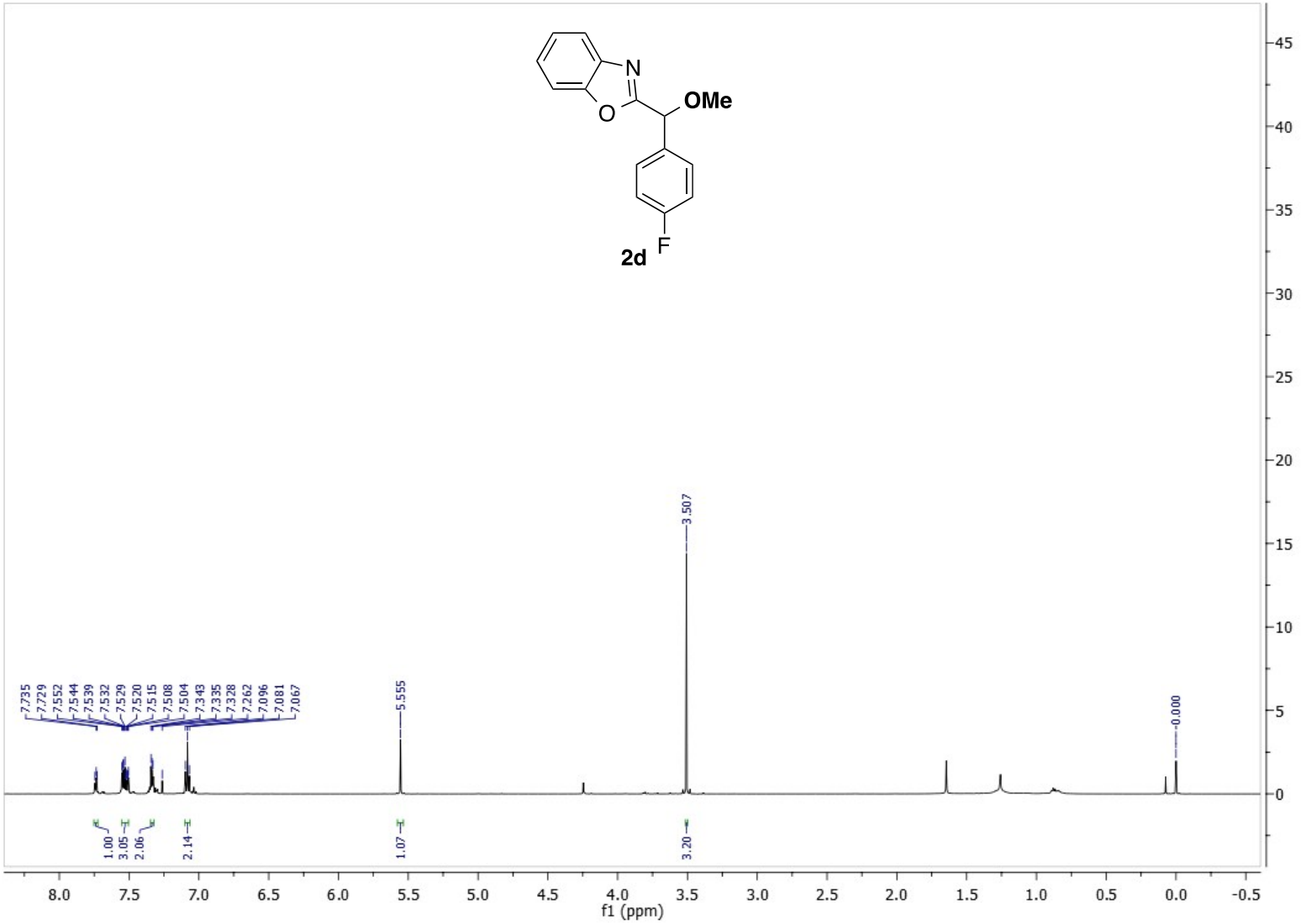
^{1}H NMR (600 MHz, $CDCl_3$):



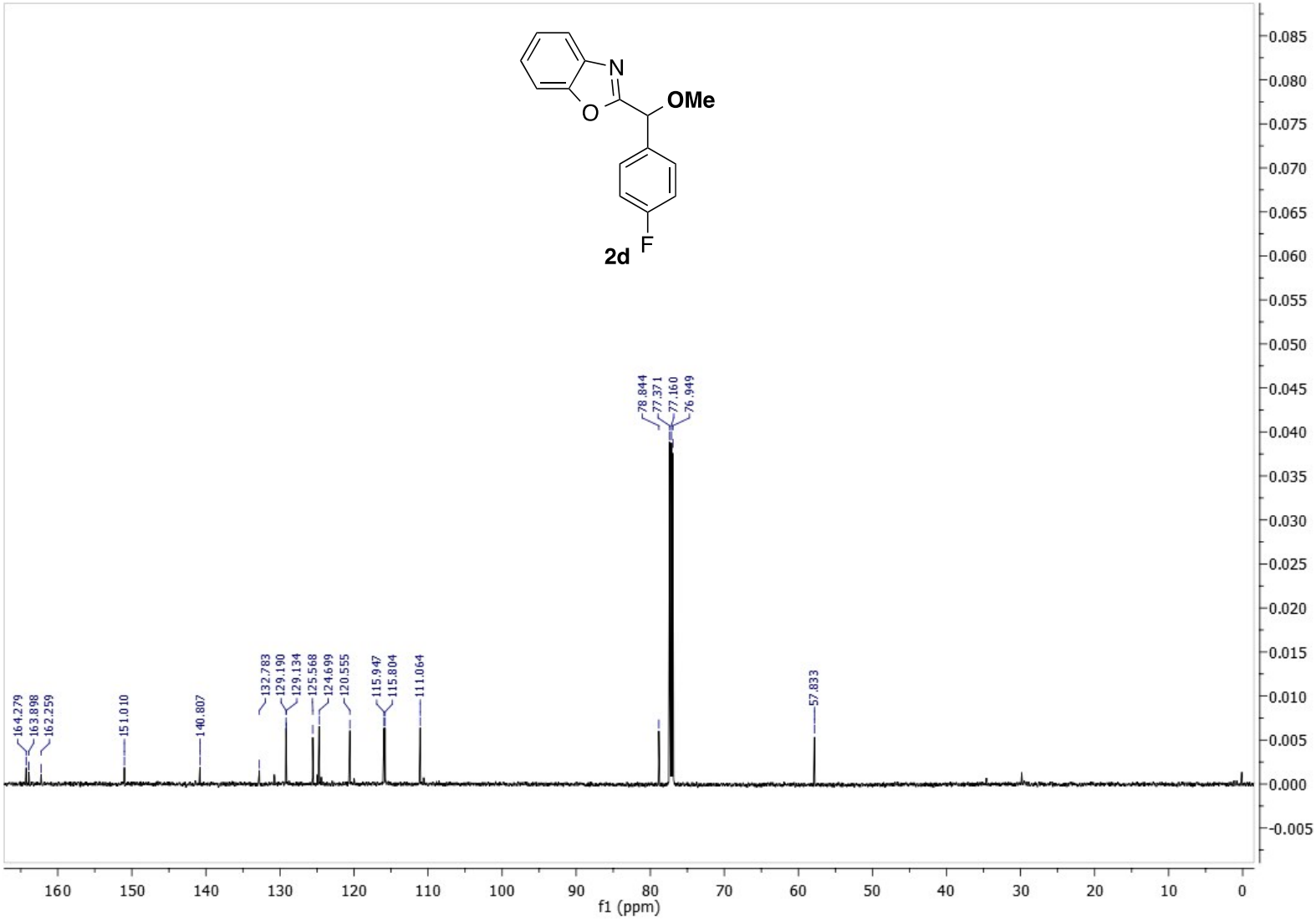
^{13}C NMR (151 MHz, $CDCl_3$):



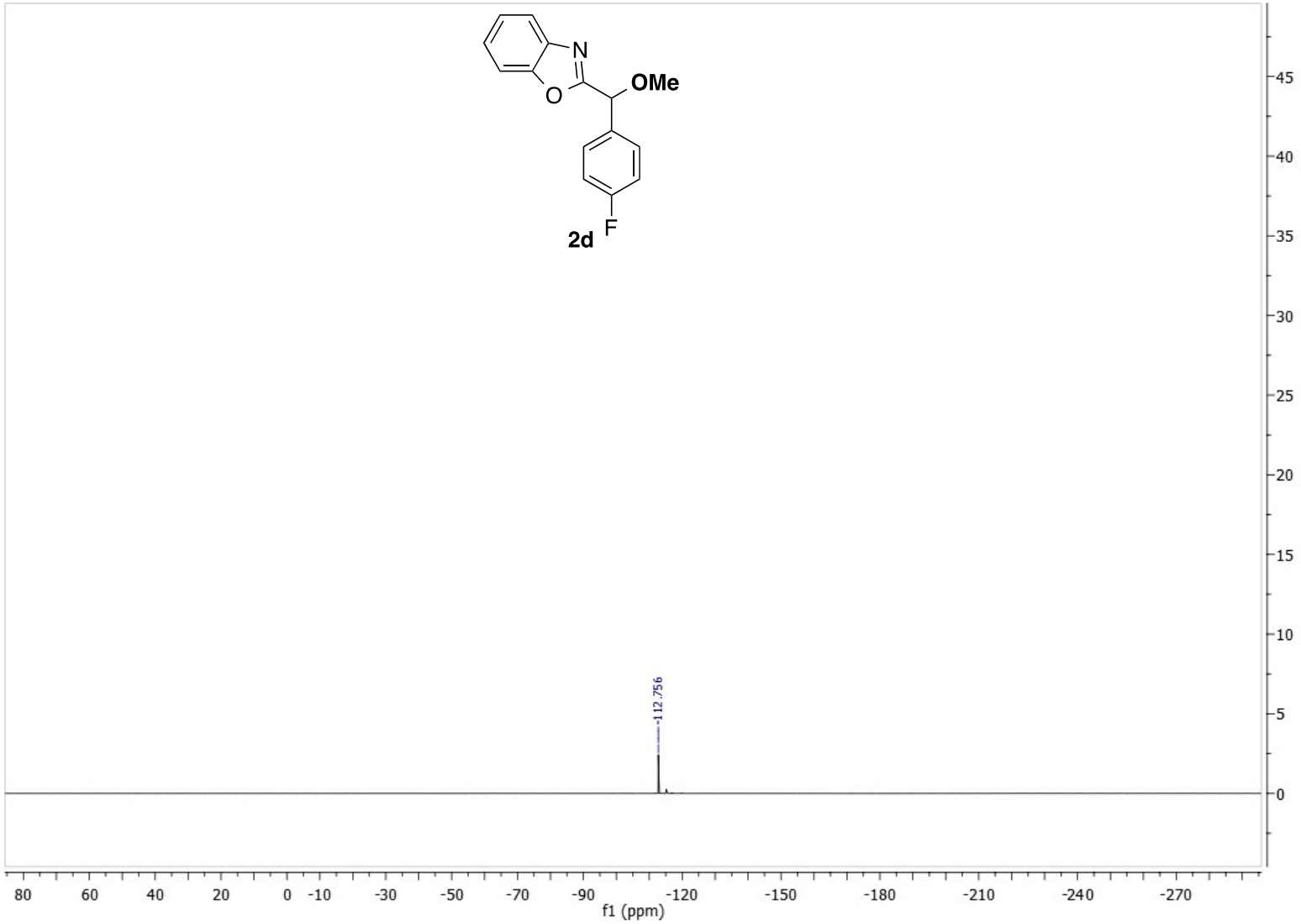
^{1}H NMR (600 MHz, $CDCl_3$):



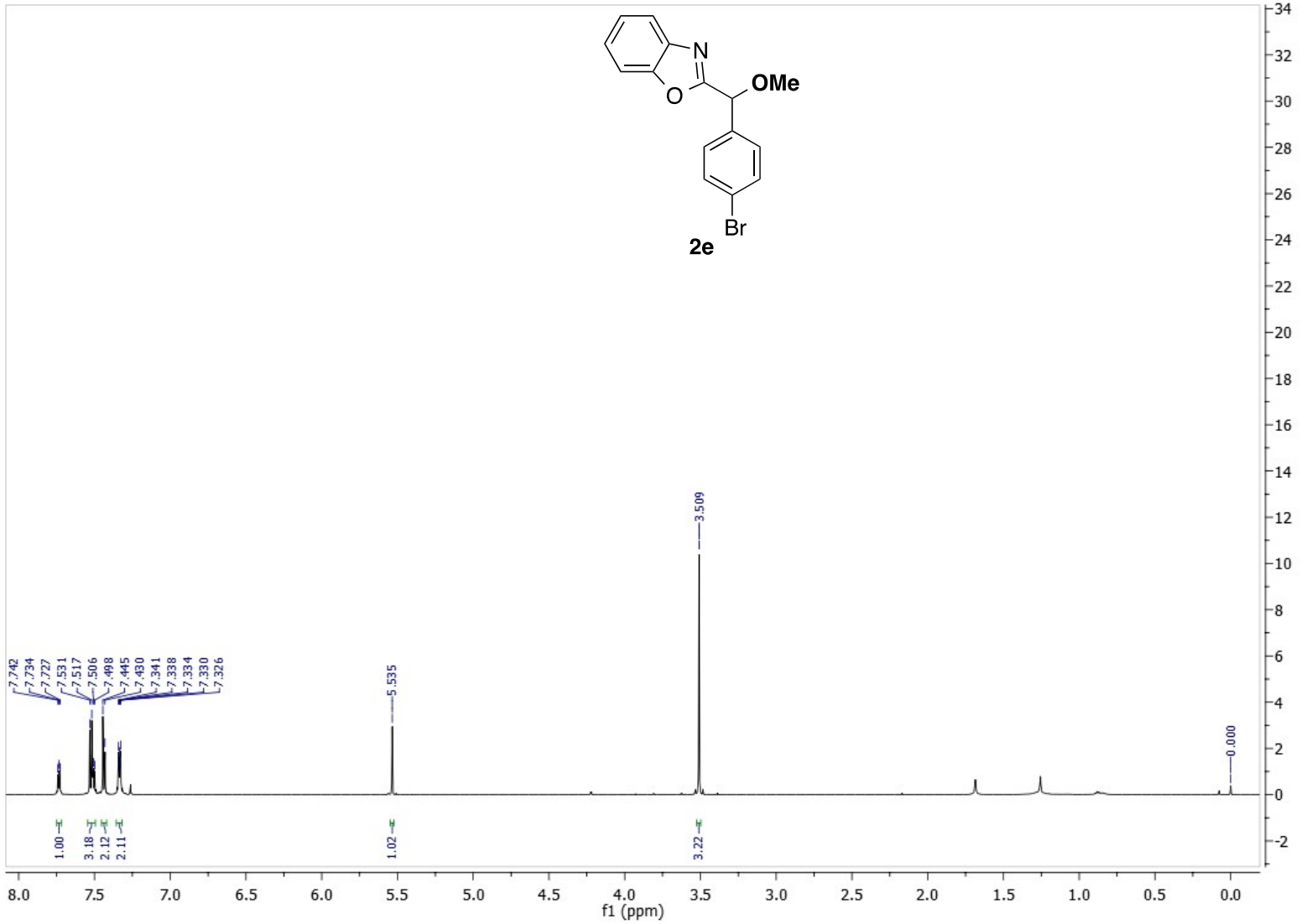
^{13}C NMR (151 MHz, $CDCl_3$):



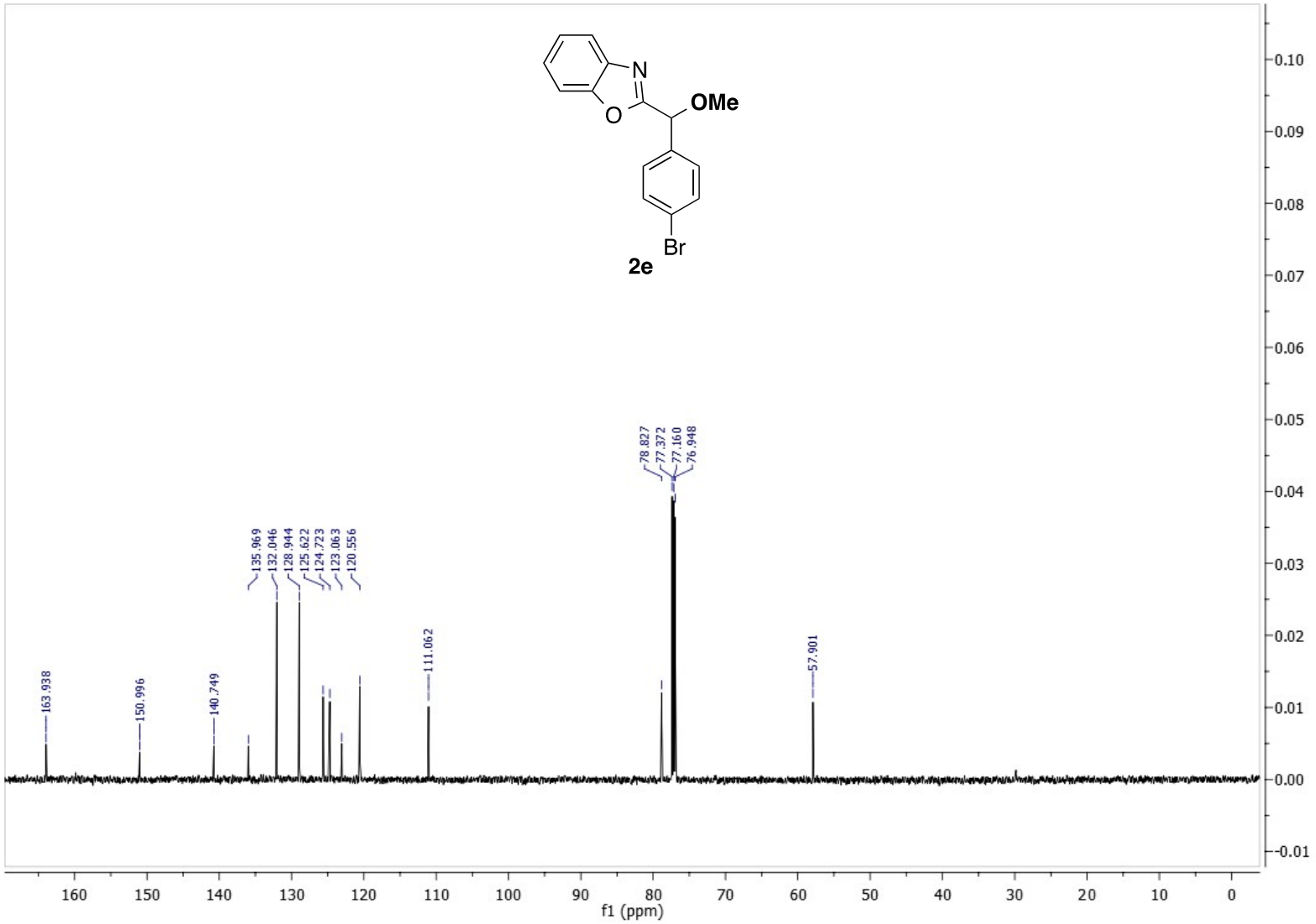
^{19}F NMR (564 MHz, $CDCl_3$):



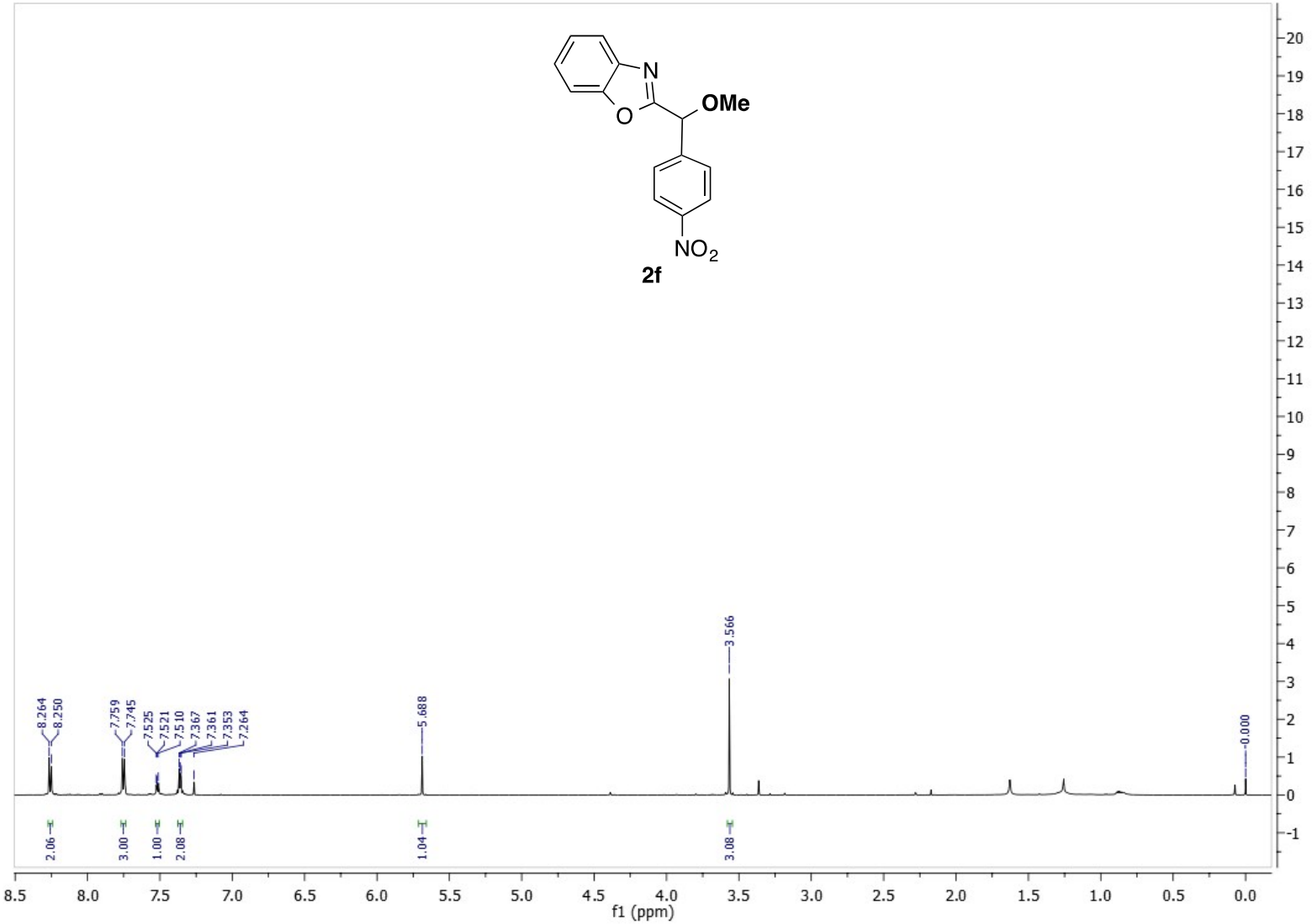
^{1}H NMR (600 MHz, $CDCl_3$):



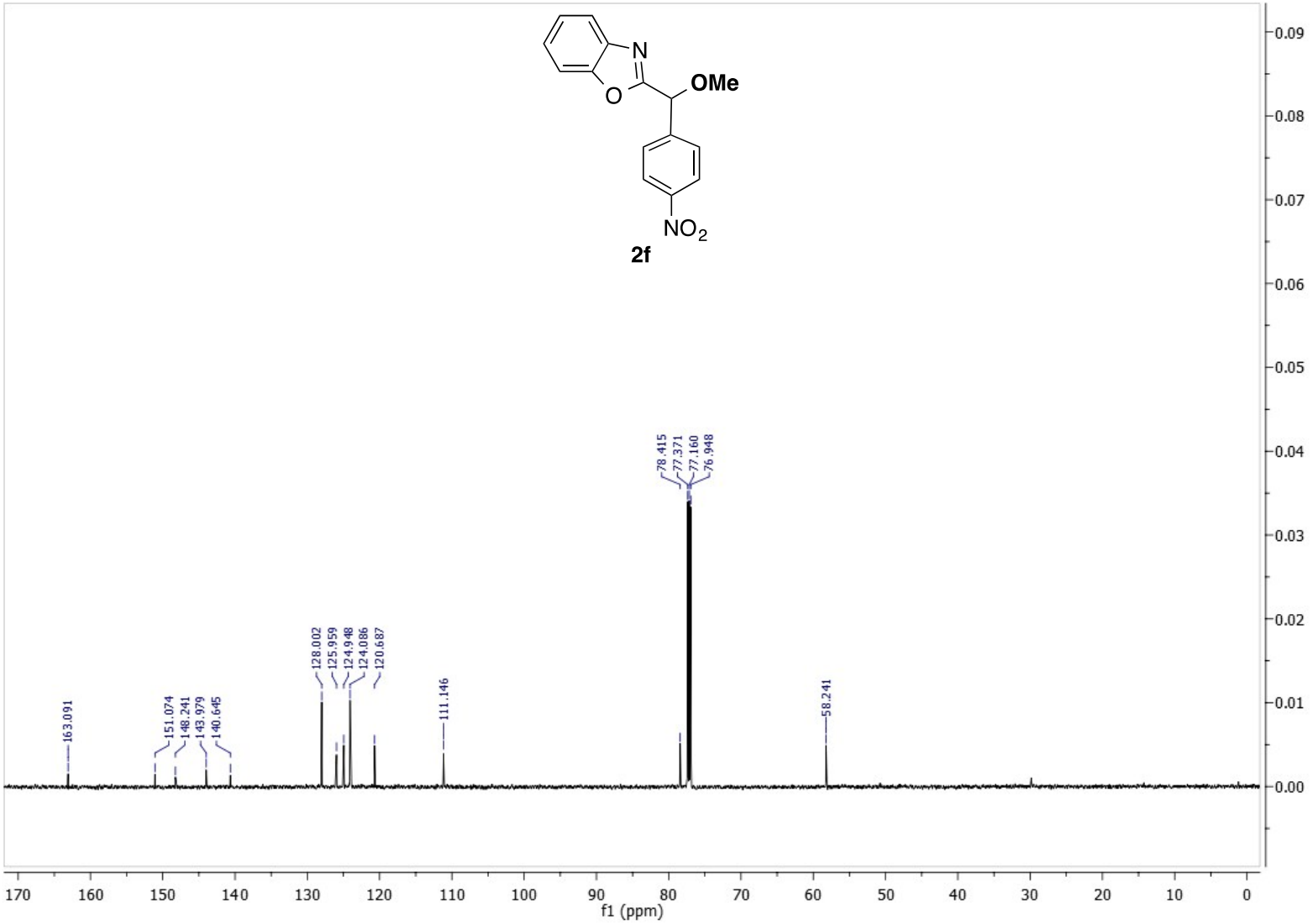
^{13}C NMR (151 MHz, $CDCl_3$):



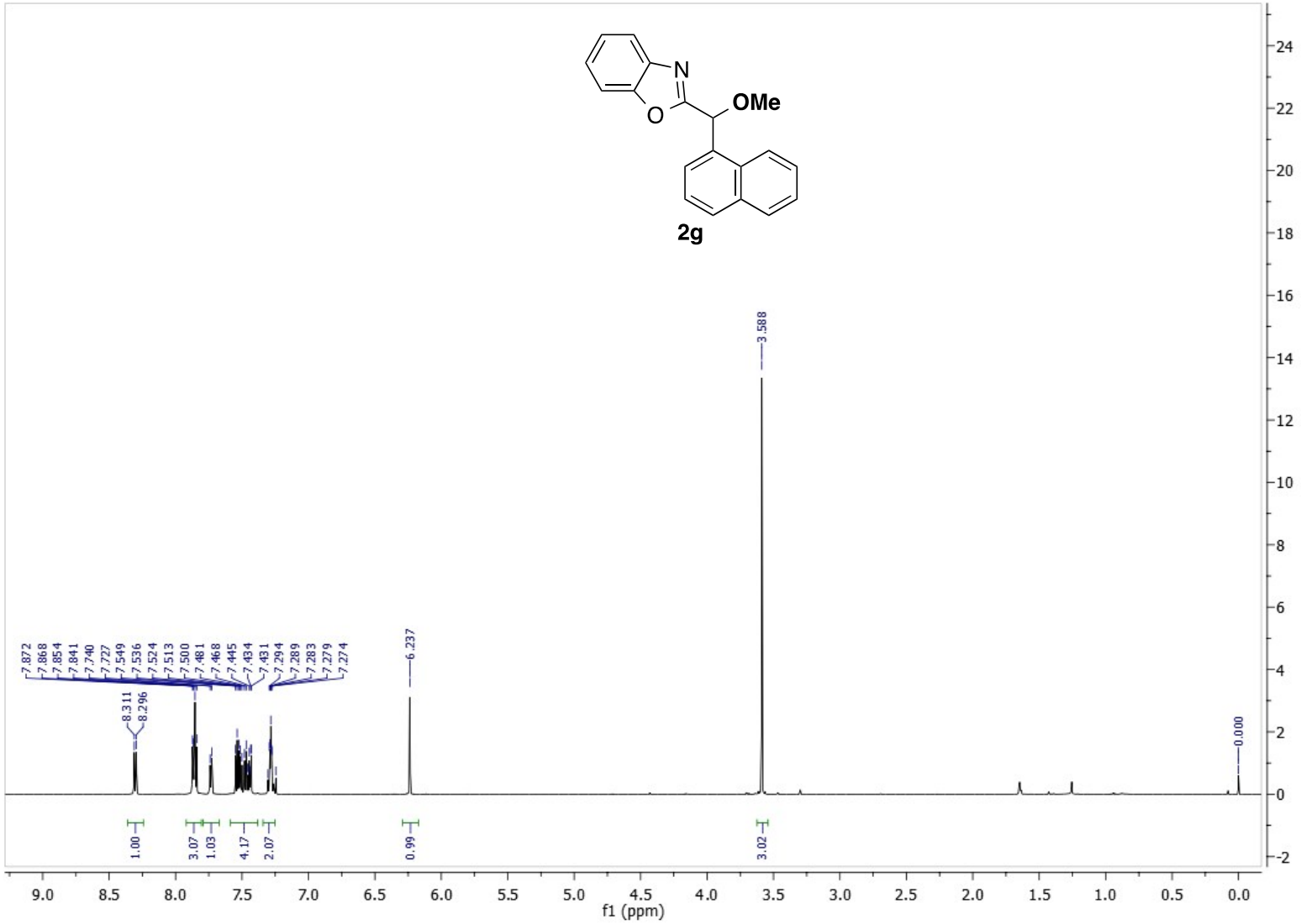
^{1}H NMR (600 MHz, $CDCl_3$):



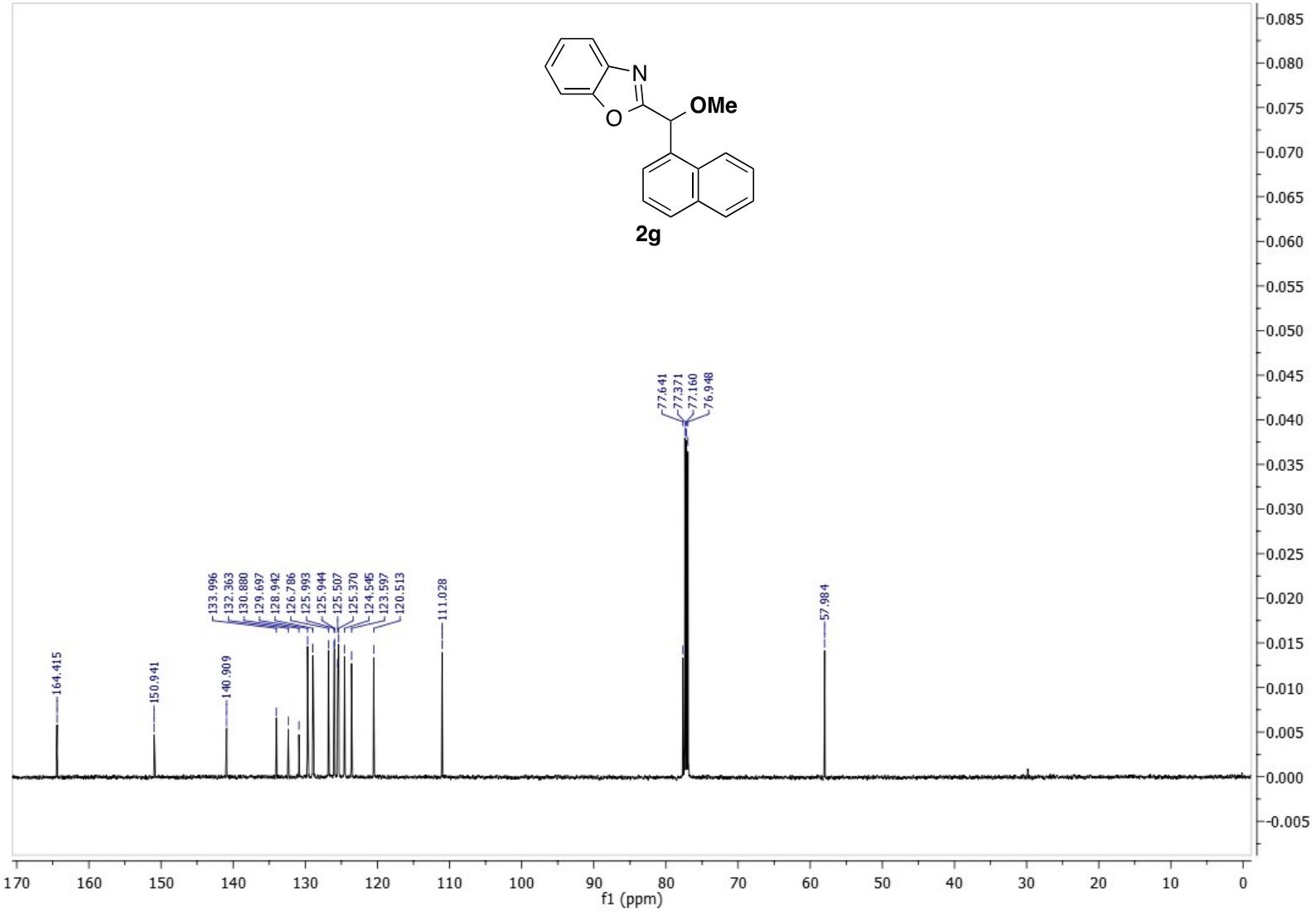
^{13}C NMR (151 MHz, $CDCl_3$):



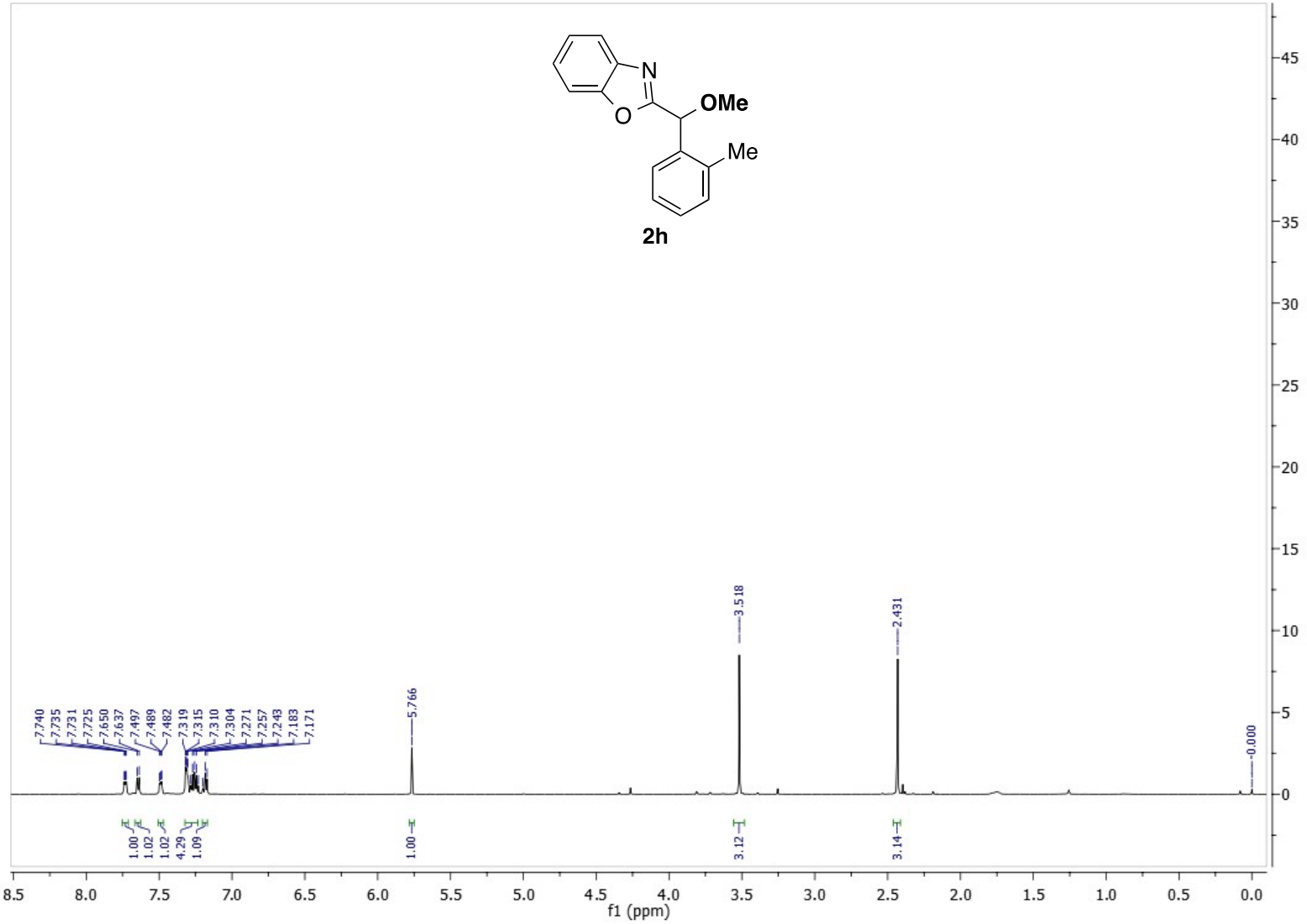
^{1}H NMR (600 MHz, $CDCl_3$):



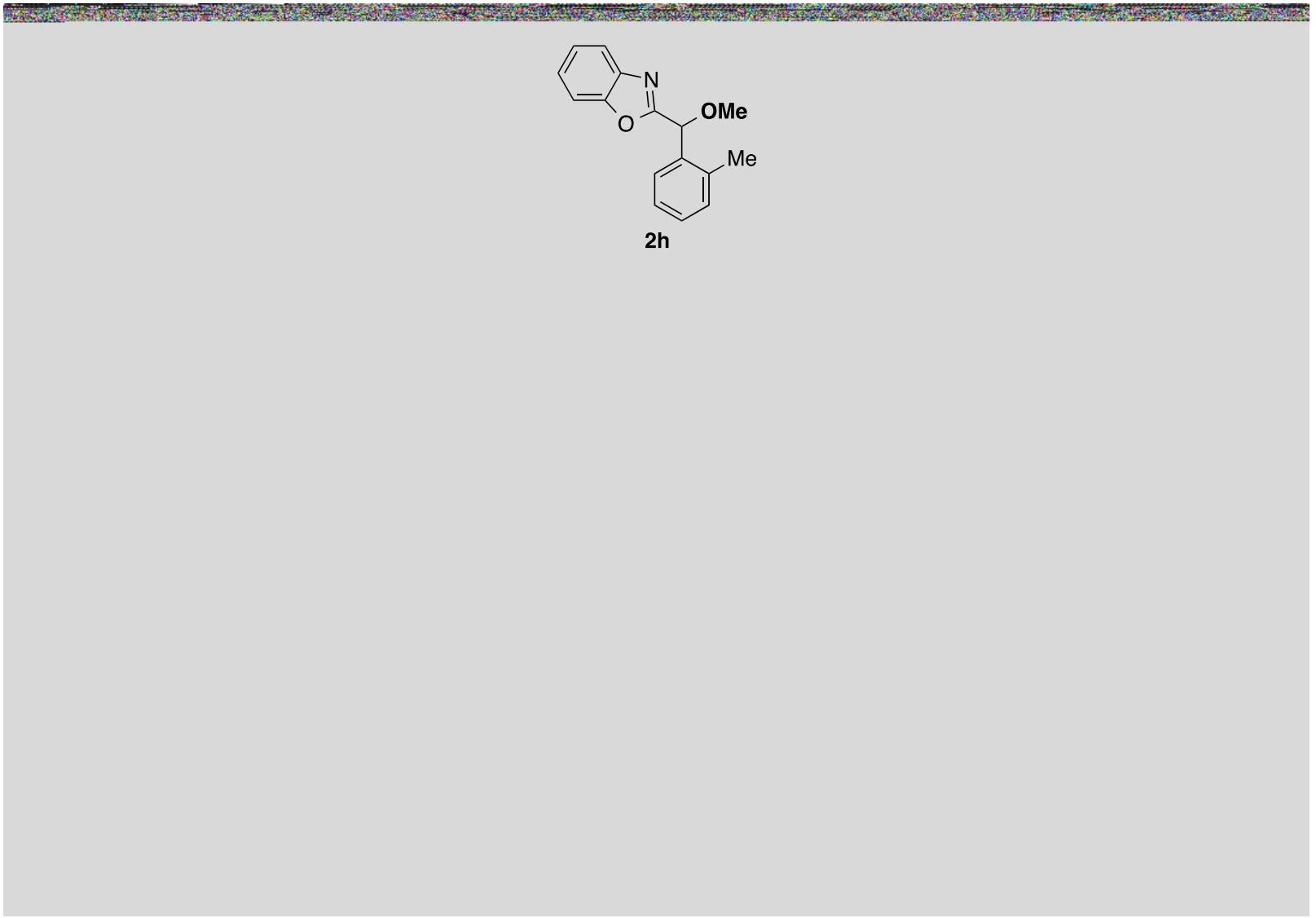
^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):

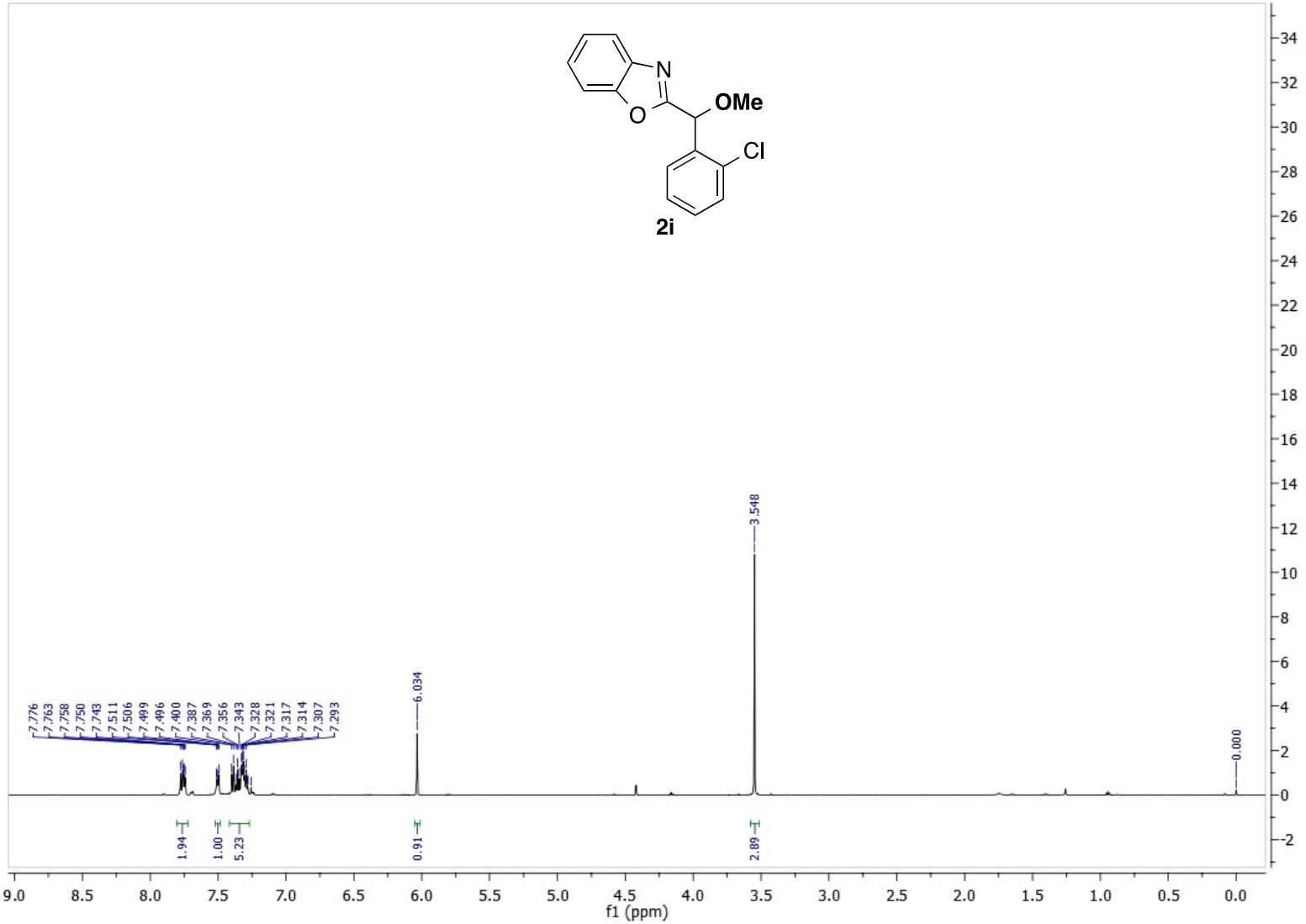


^{13}C NMR (151 MHz, $CDCl_3$):

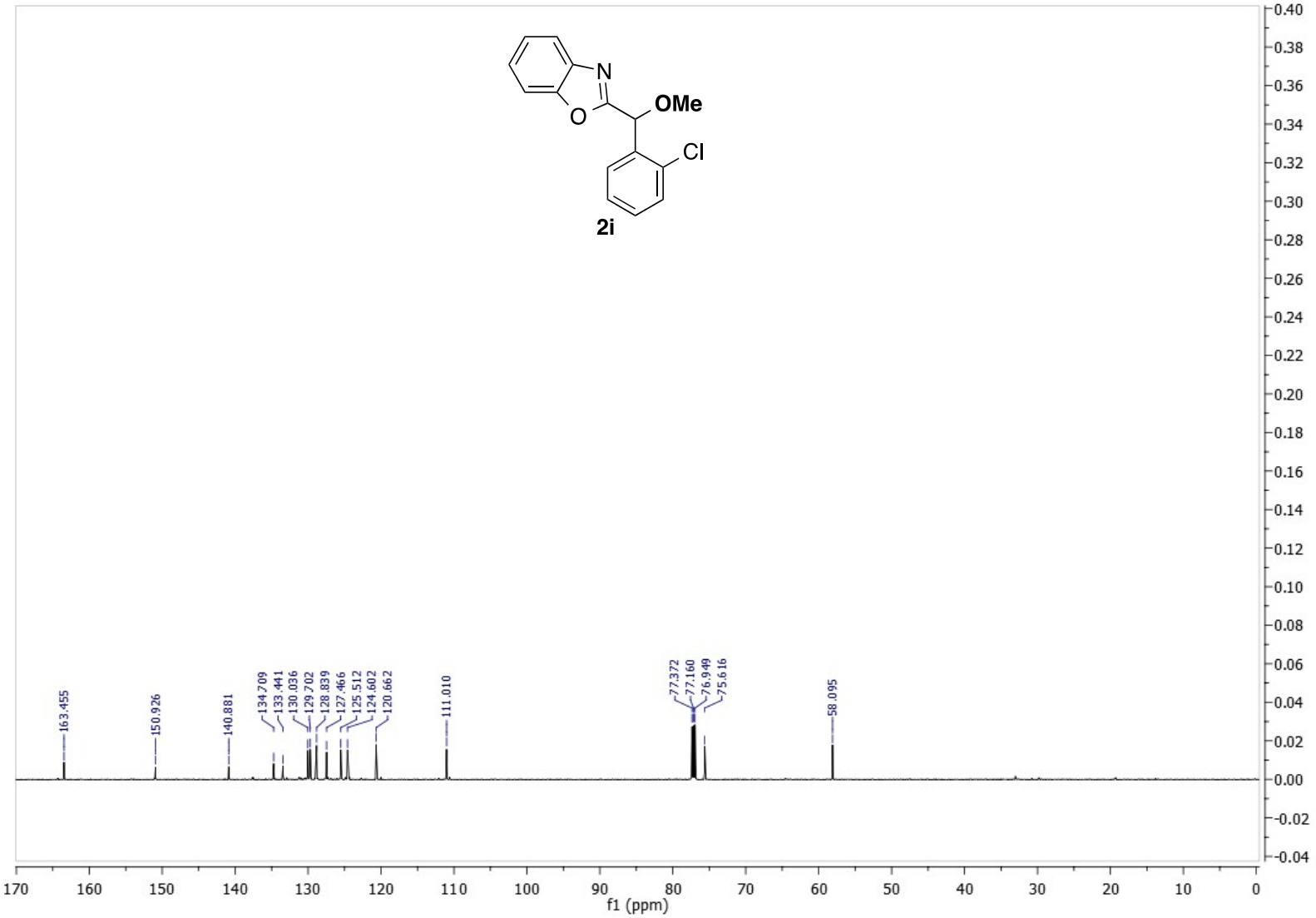


2h

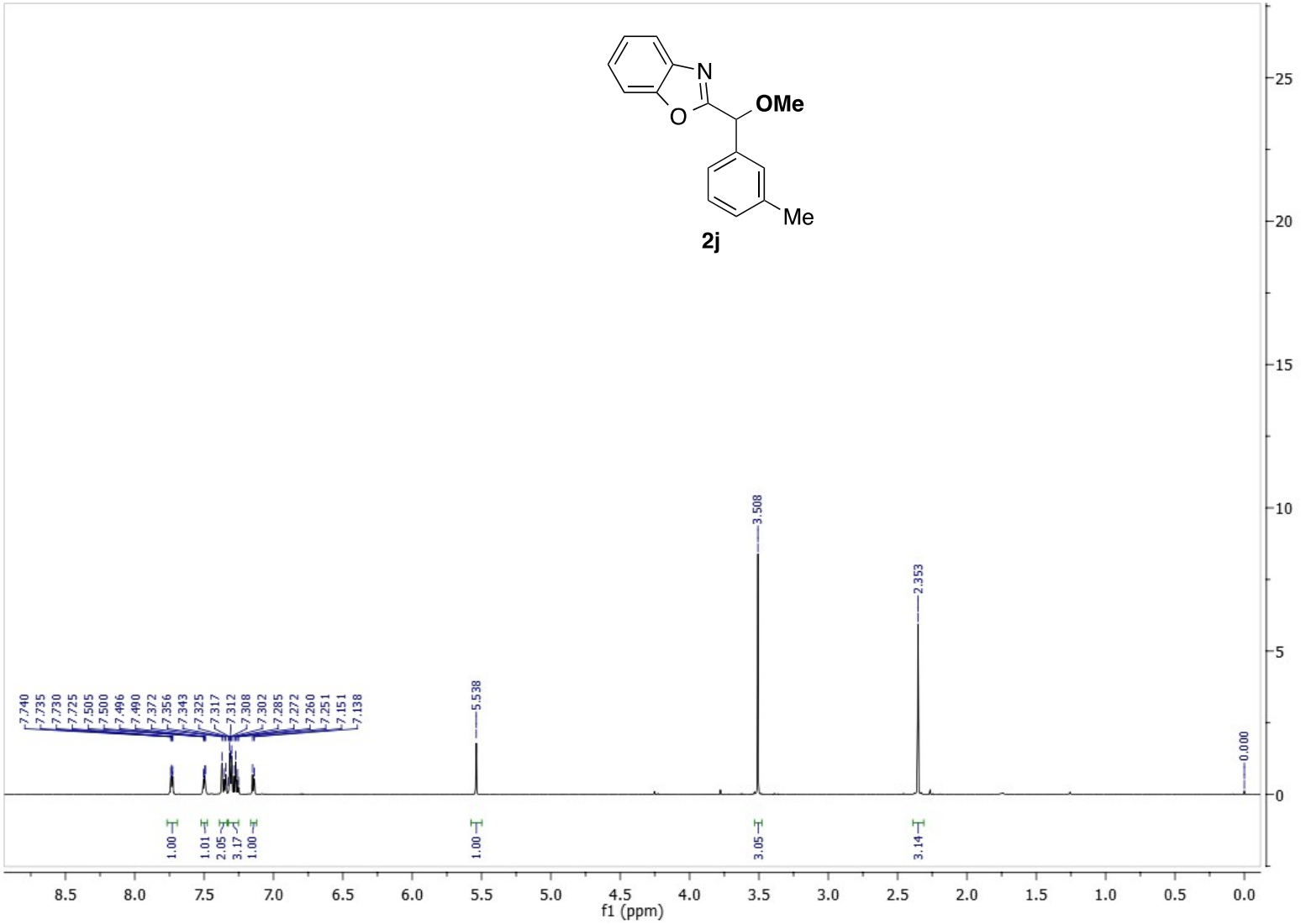
^{1}H NMR (600 MHz, $CDCl_3$):



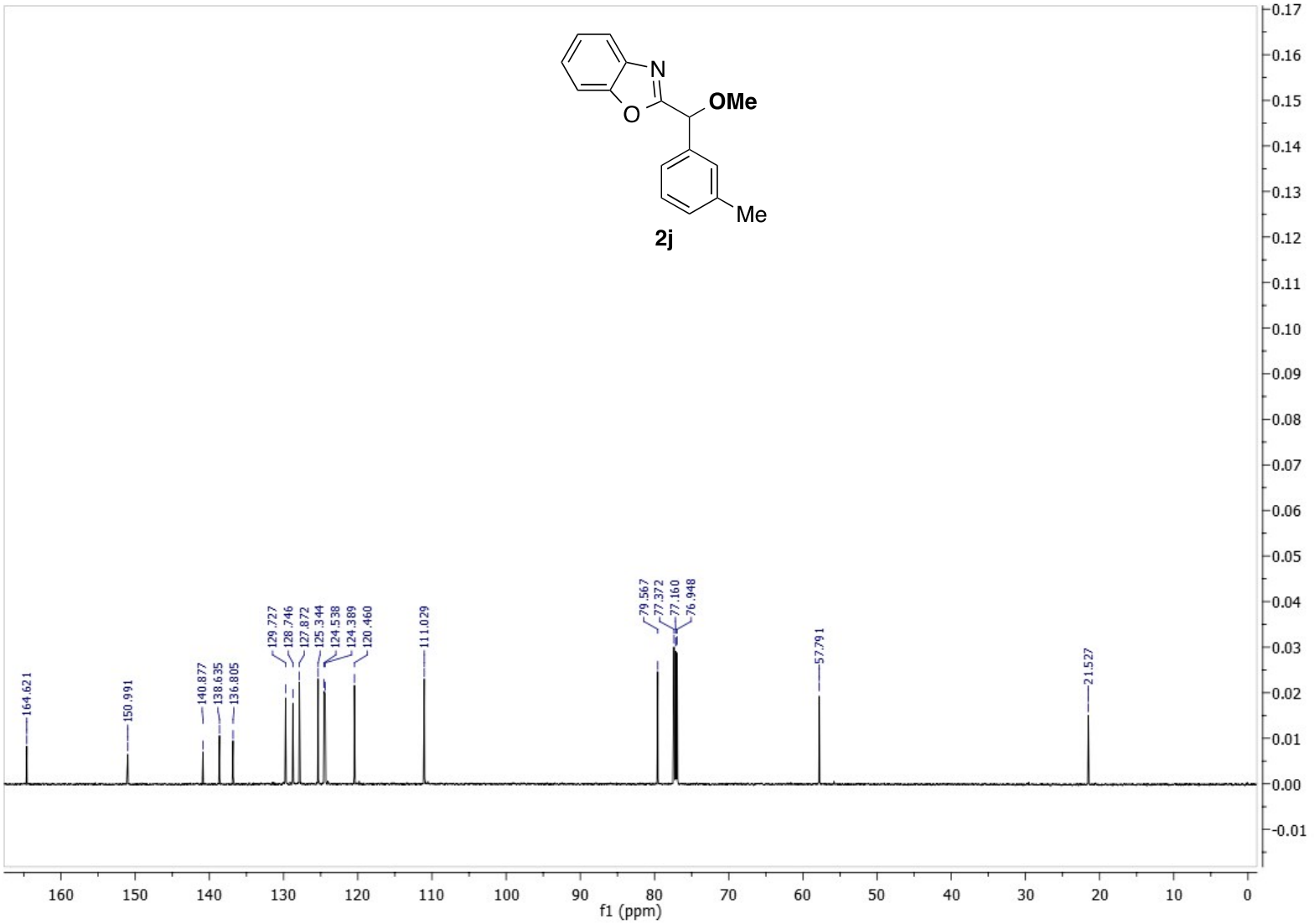
^{13}C NMR (151 MHz, $CDCl_3$):



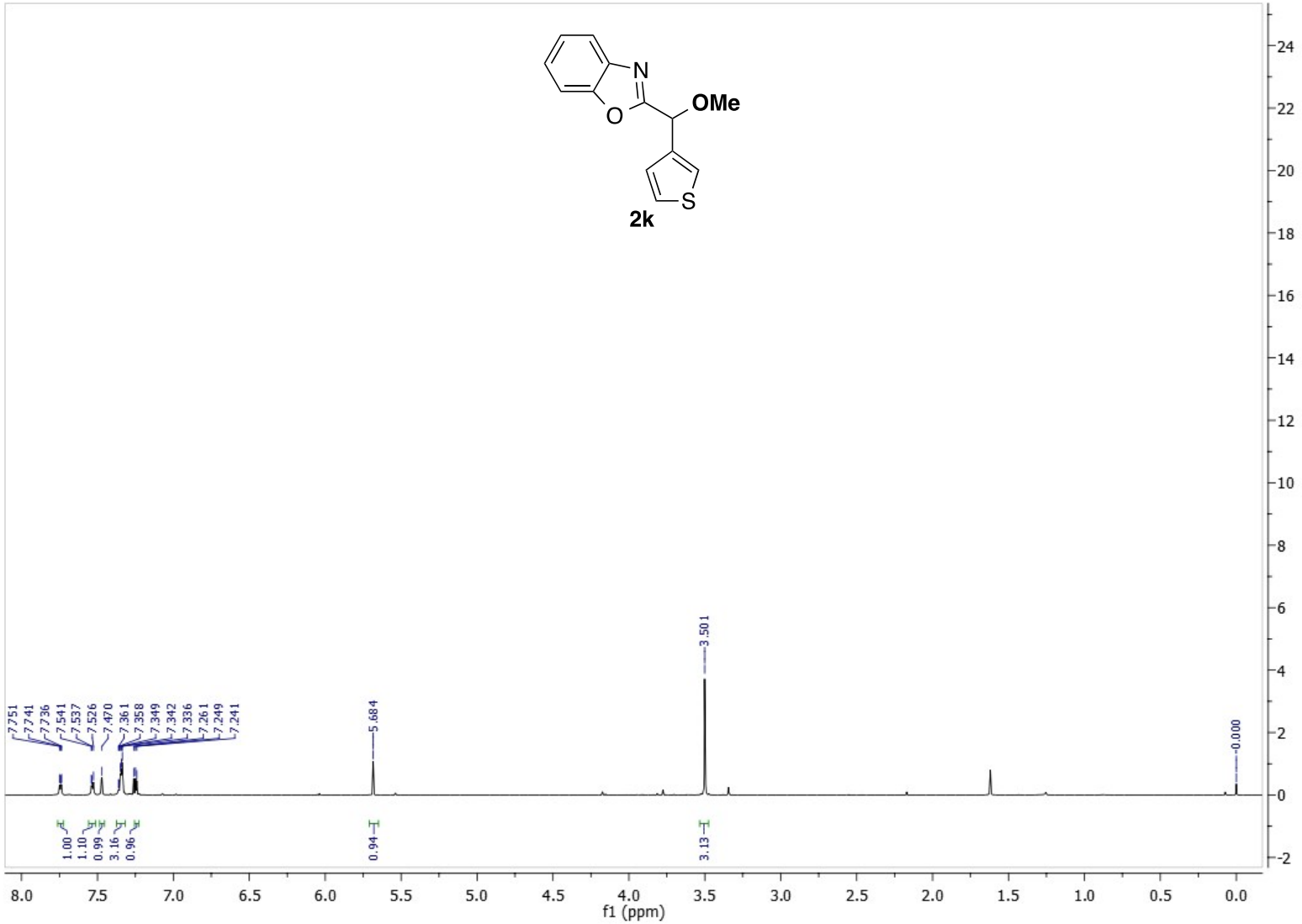
^{1}H NMR (600 MHz, $CDCl_3$):



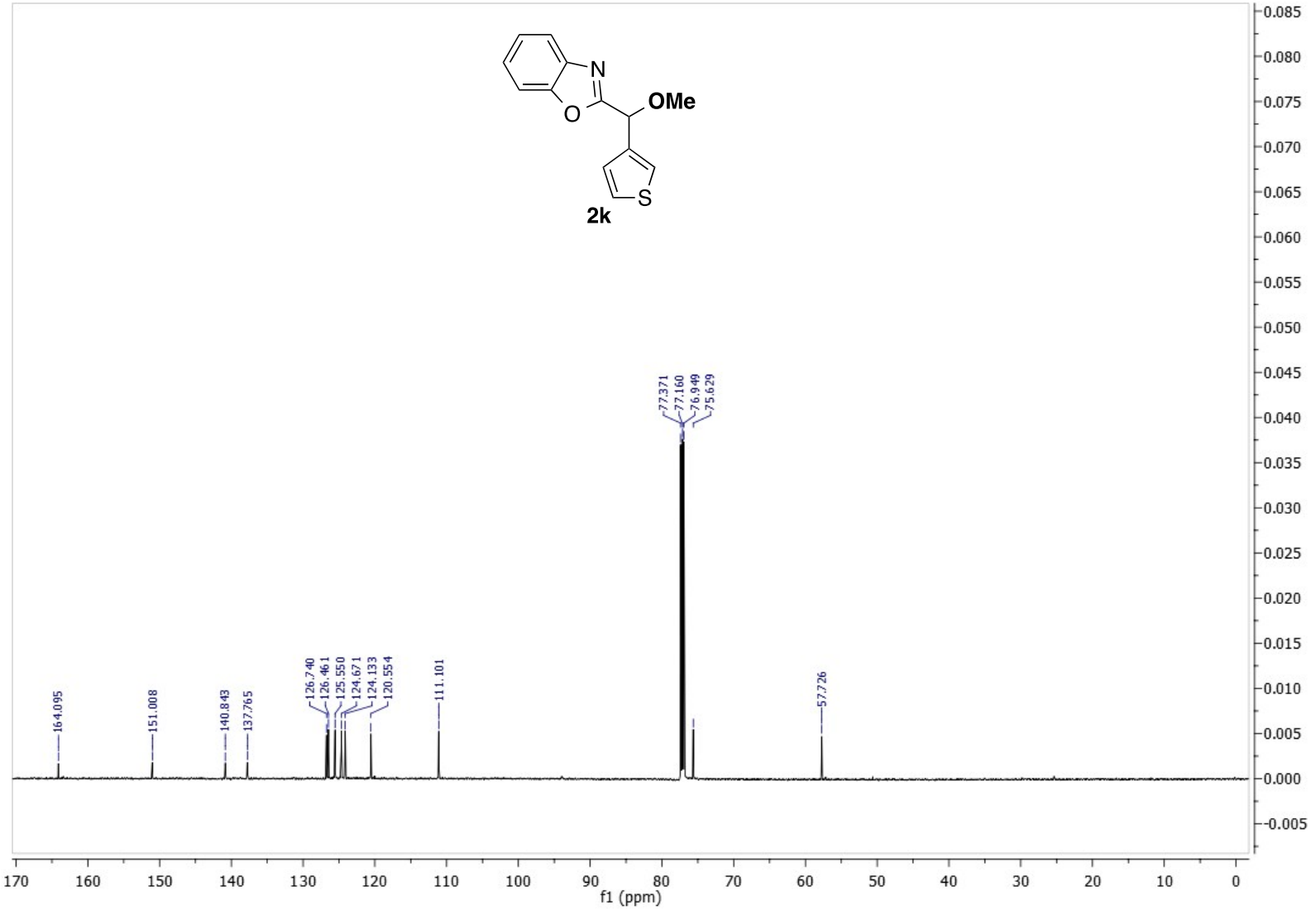
^{13}C NMR (151 MHz, $CDCl_3$):



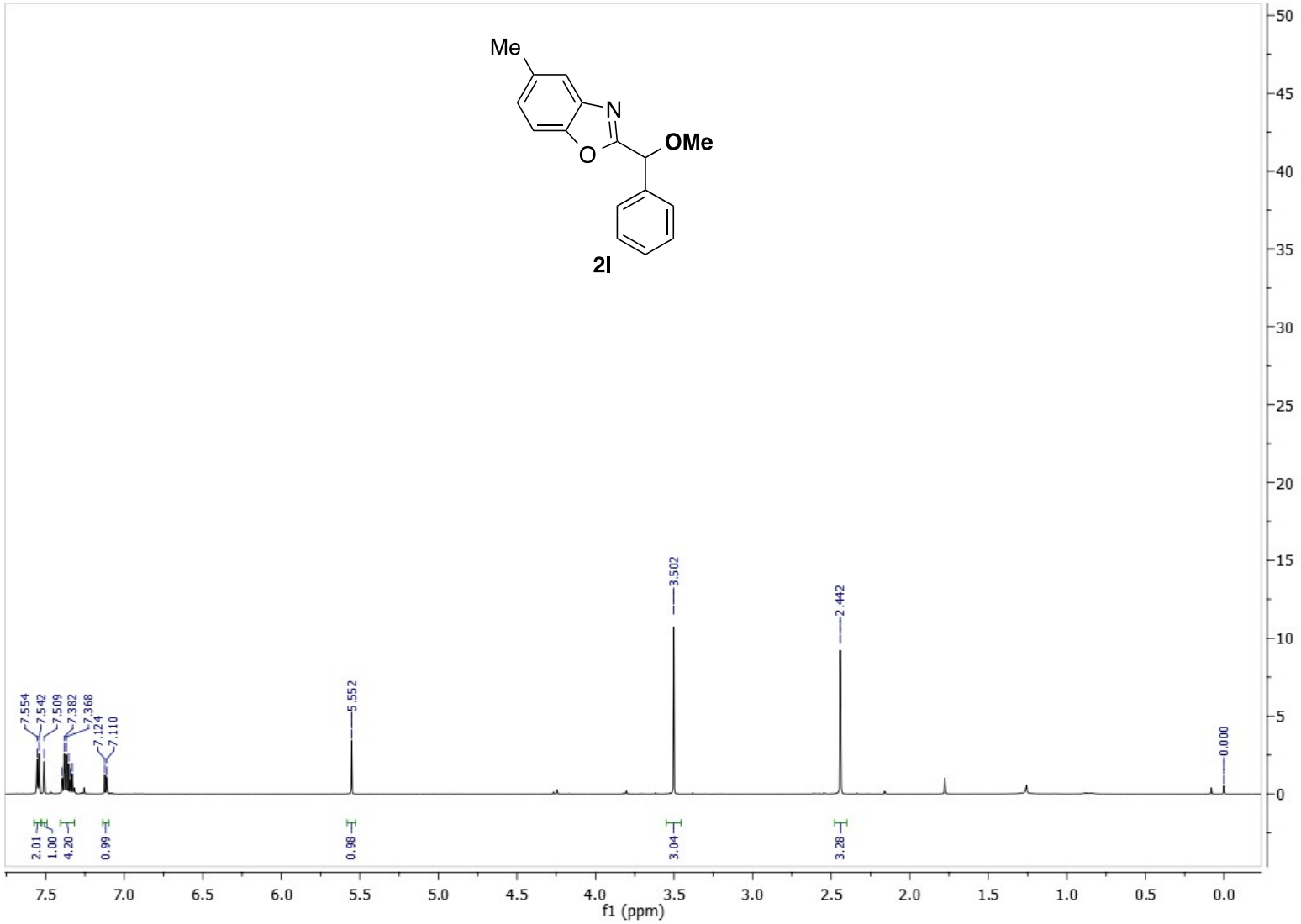
^{1}H NMR (600 MHz, $CDCl_3$):



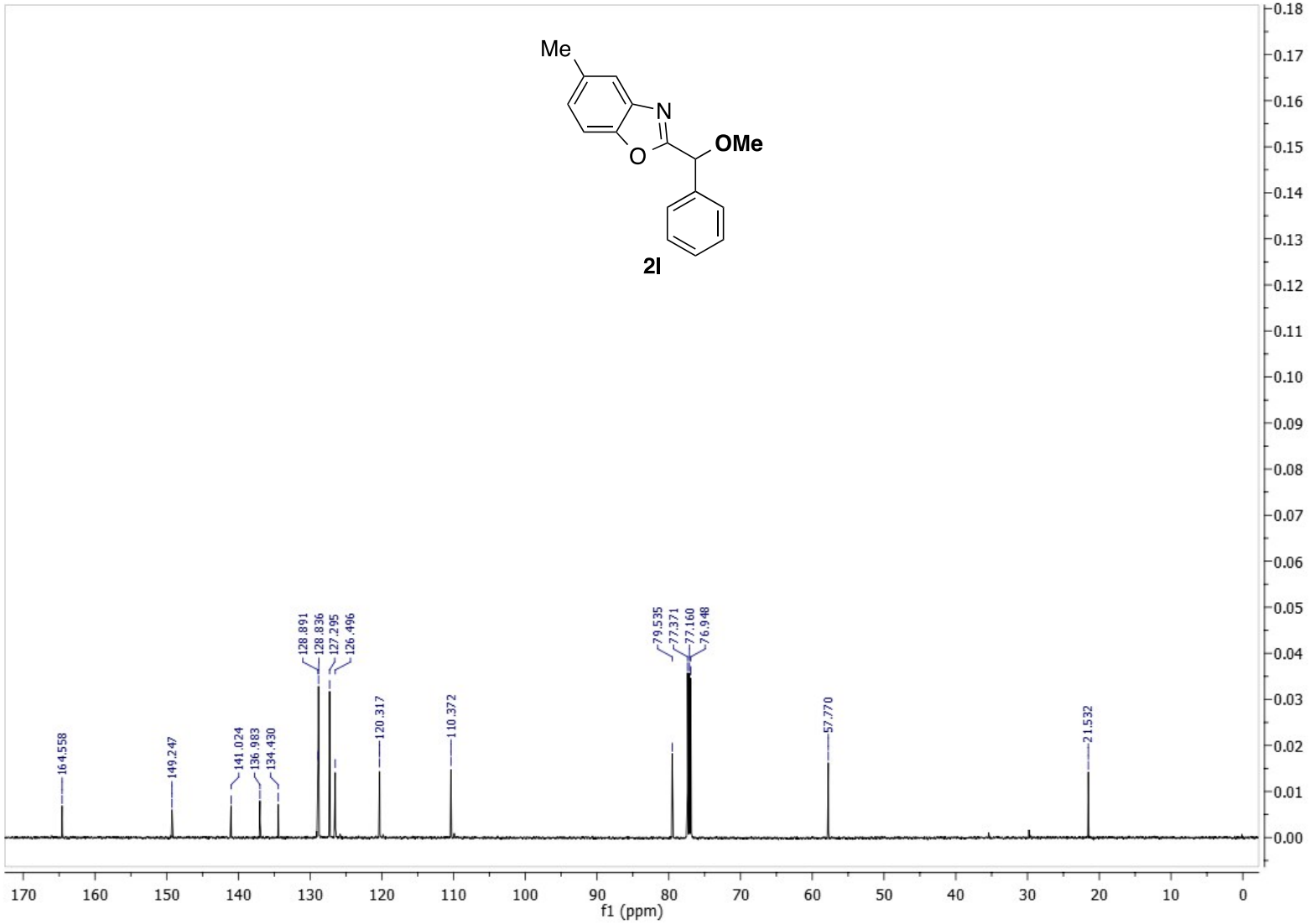
^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):



^{13}C NMR (151 MHz, $CDCl_3$):



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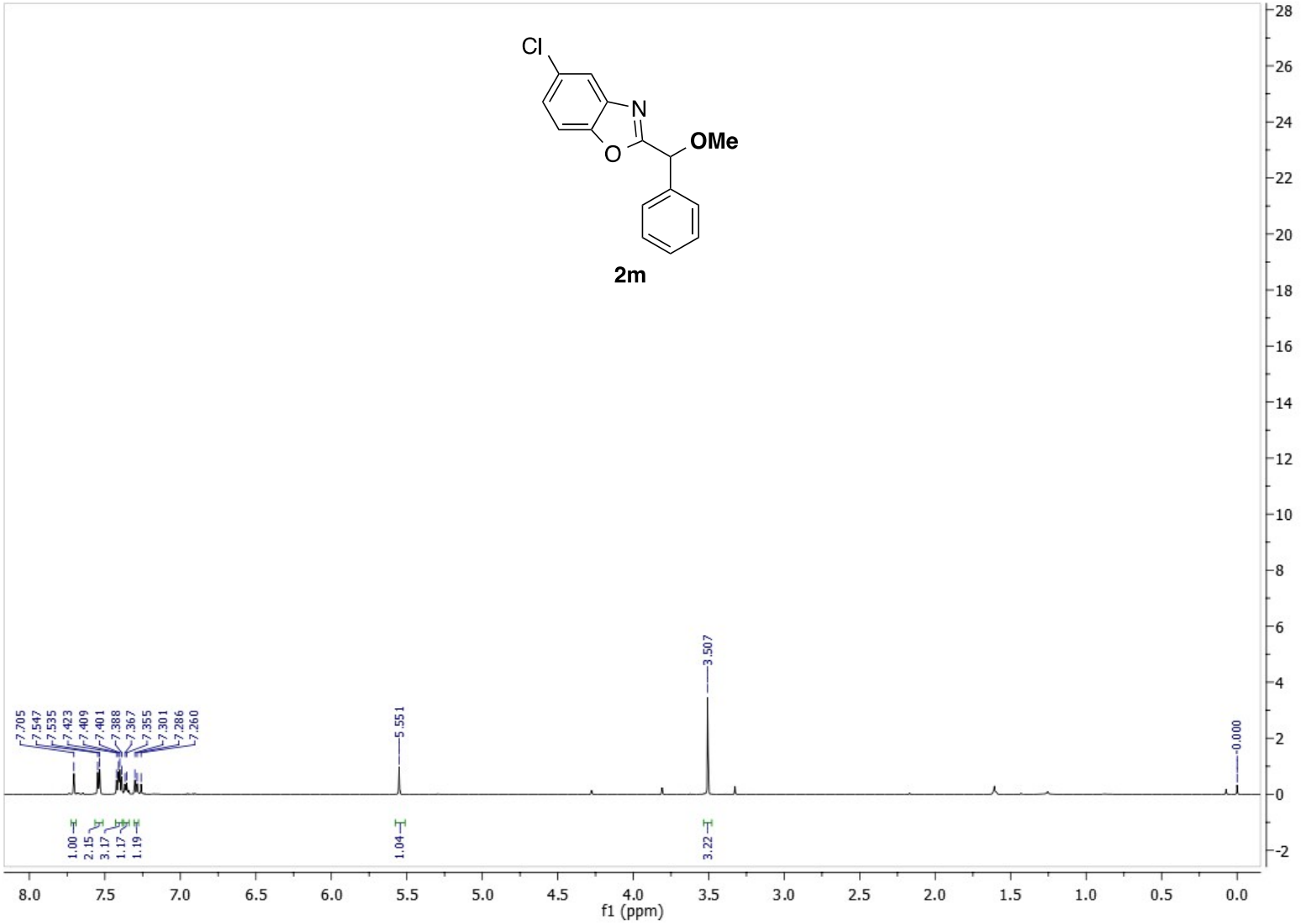
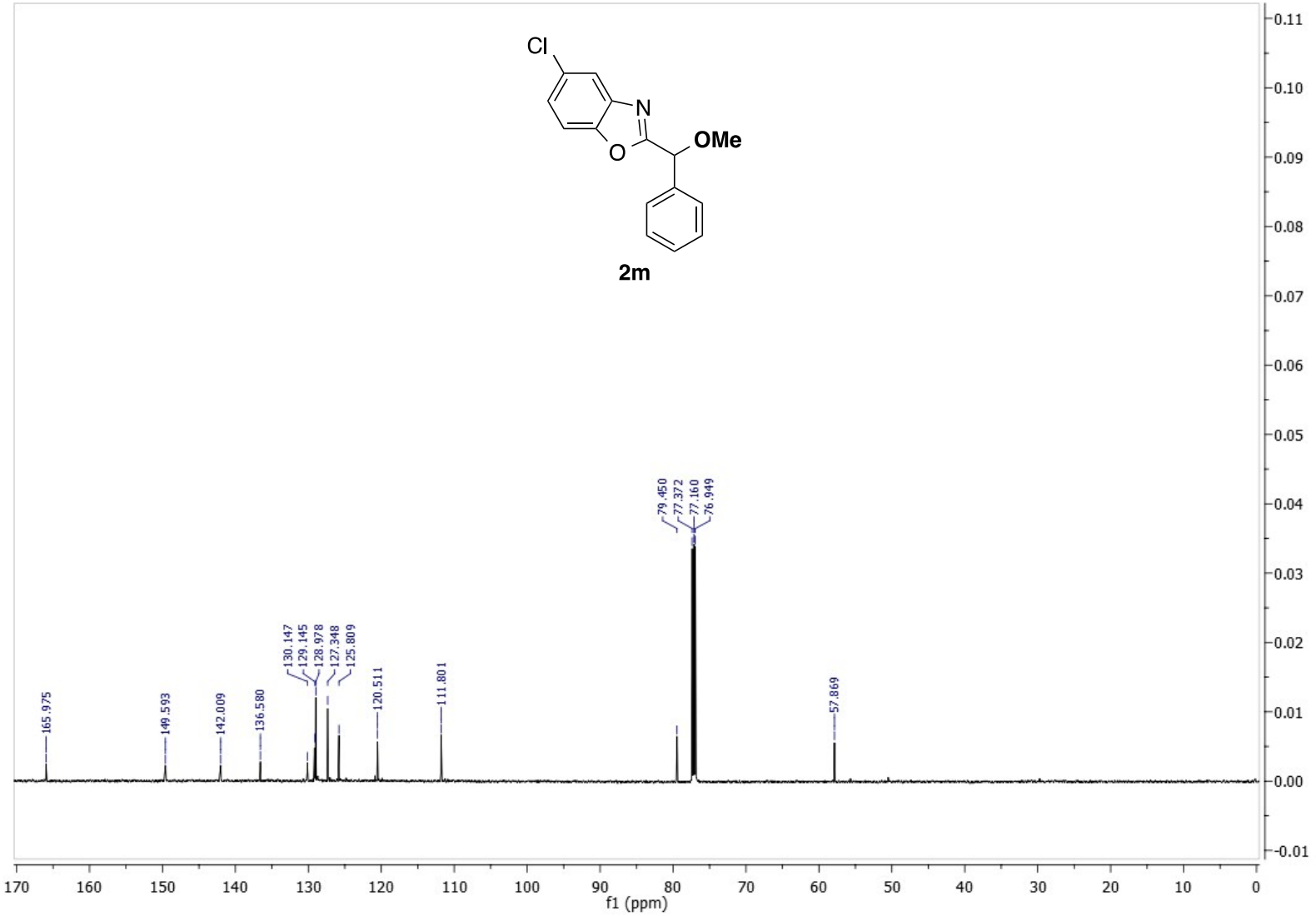


^{13}C NMR (151 MHz, $CDCl_3$):



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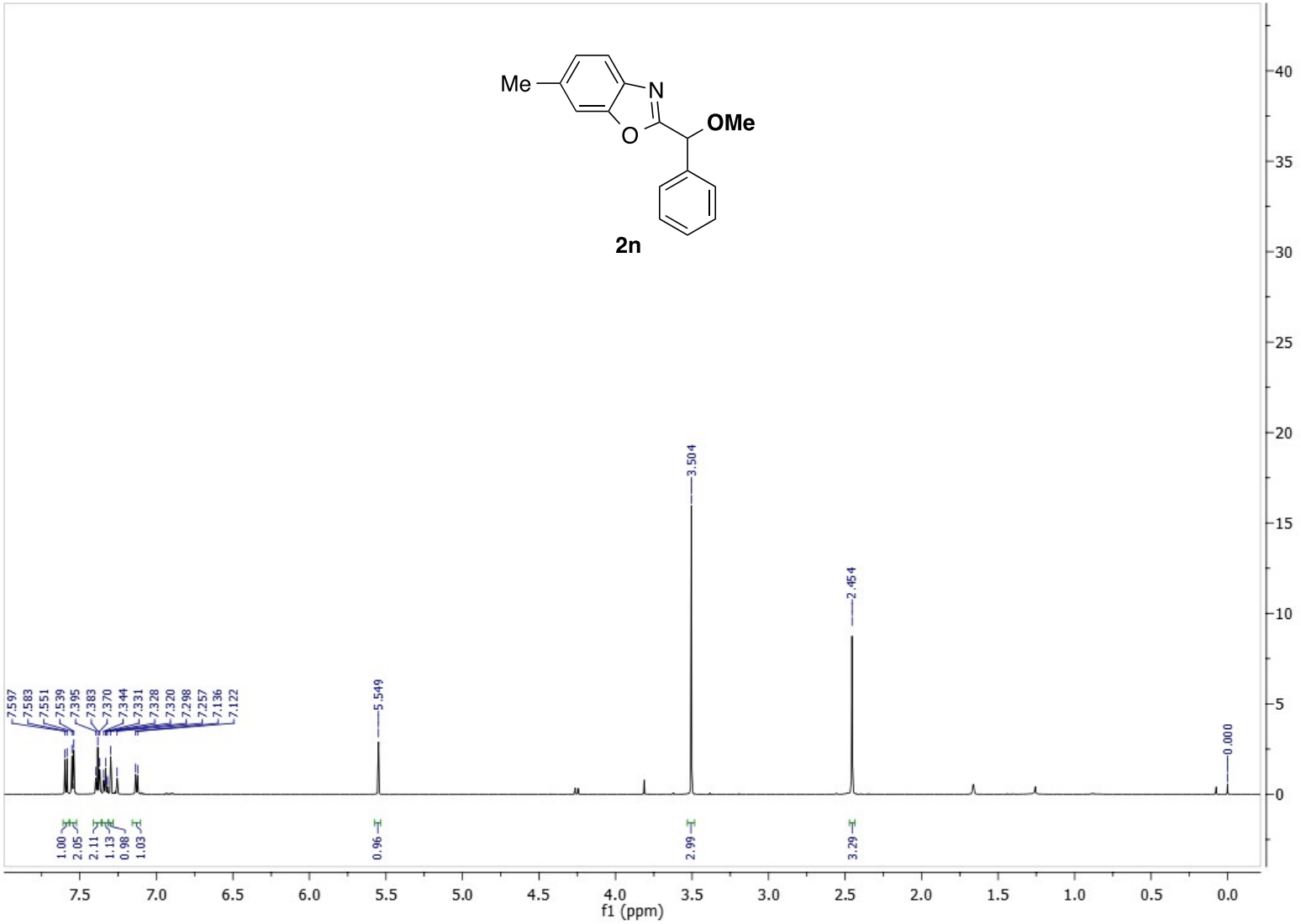

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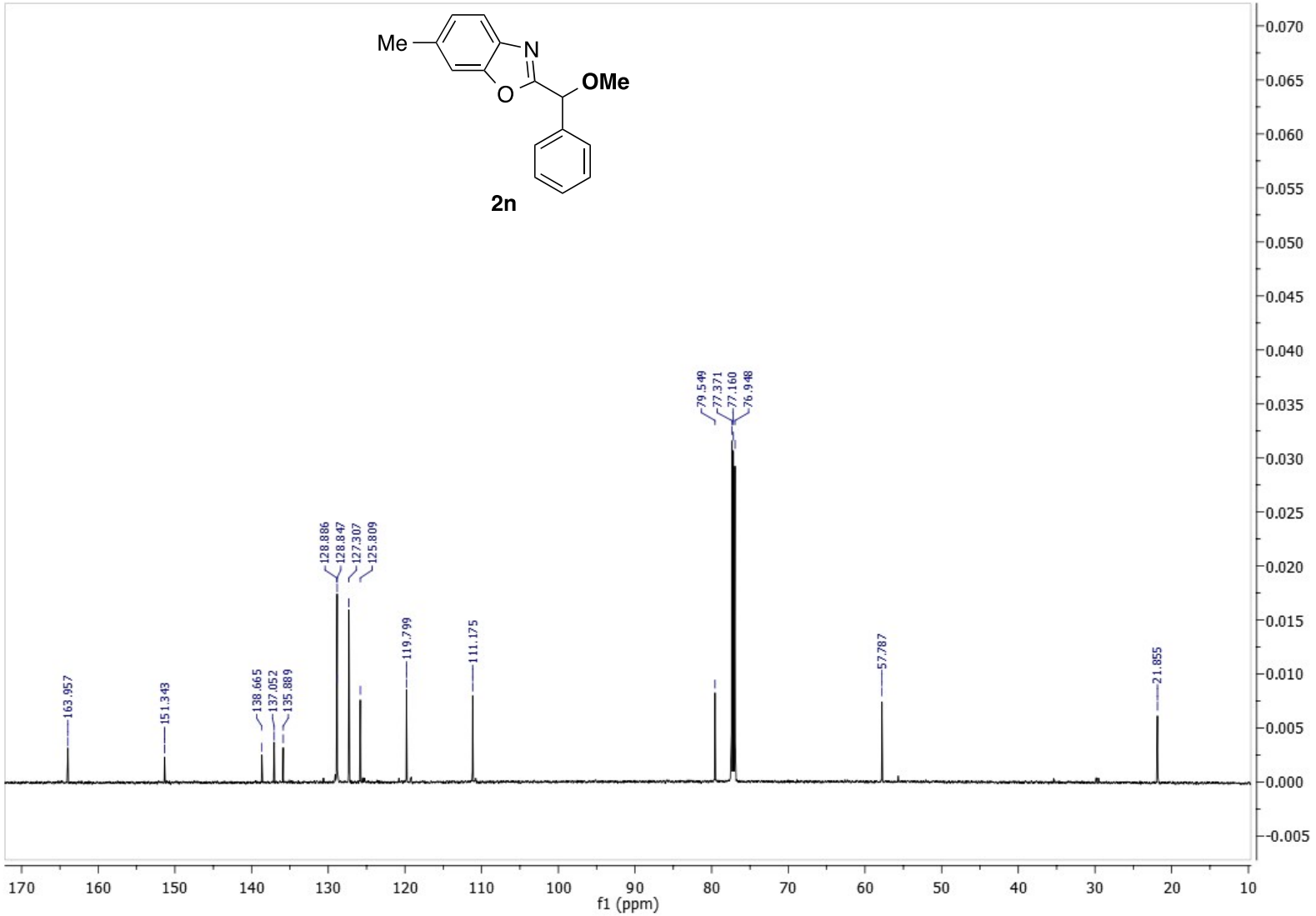

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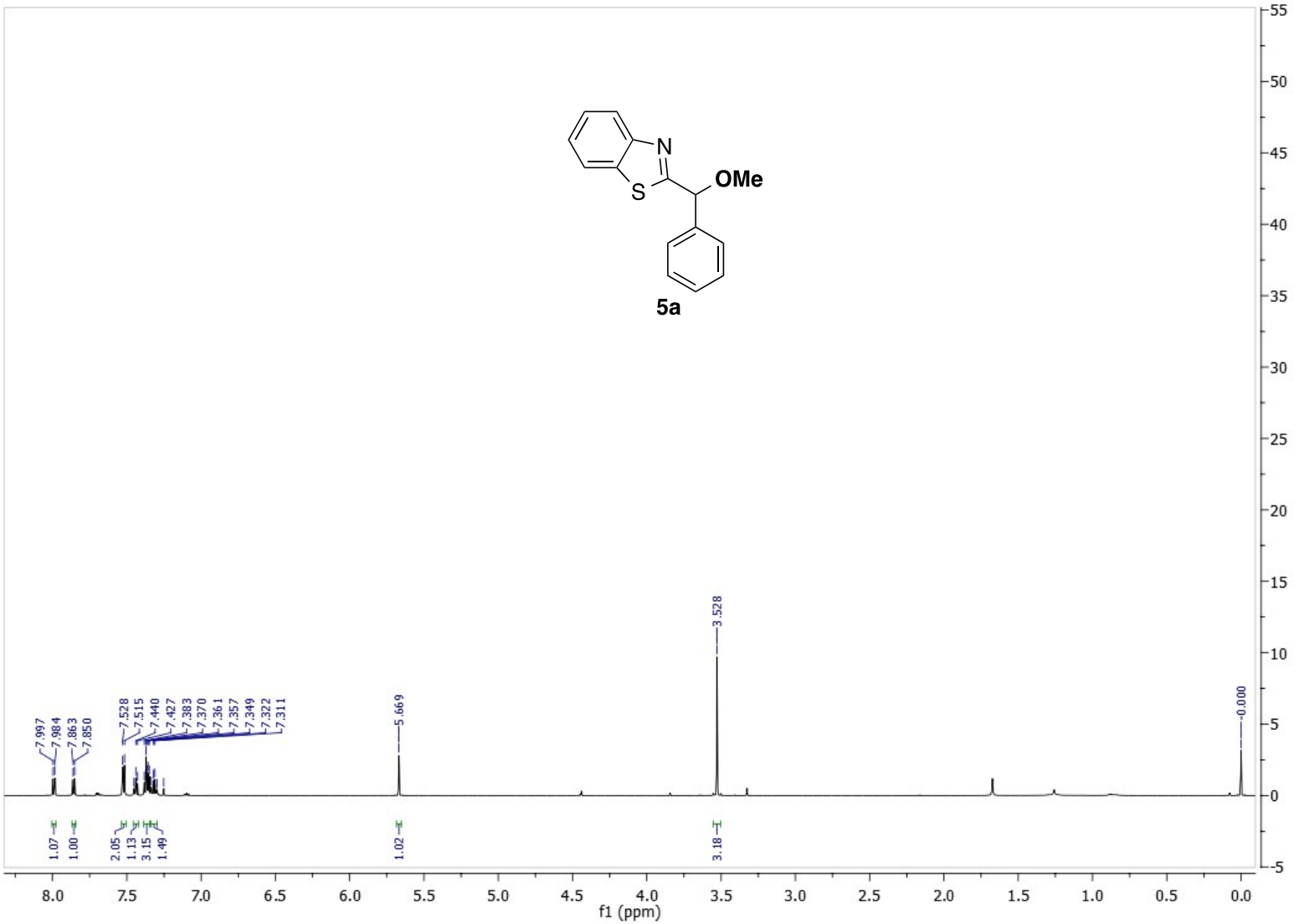

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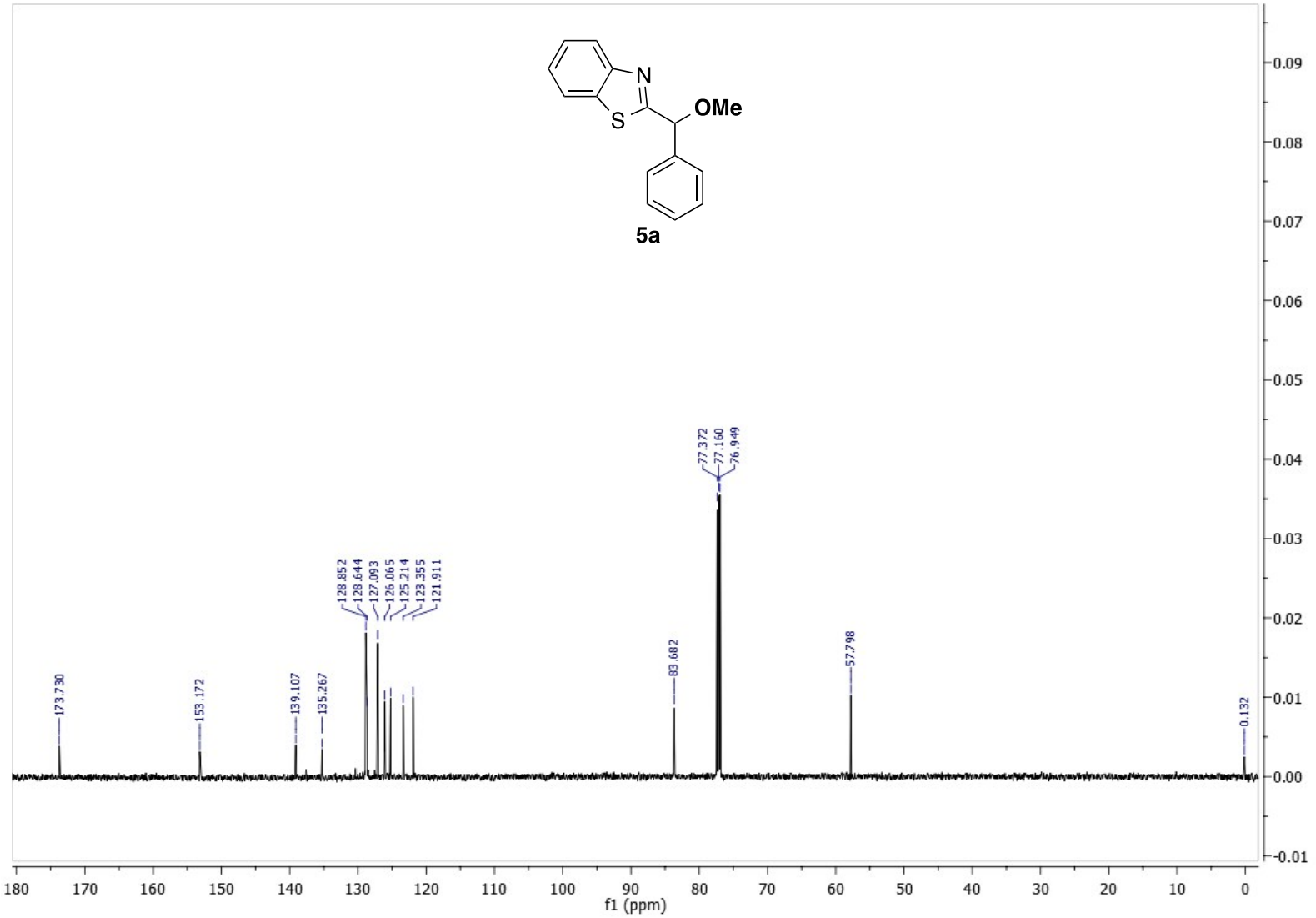

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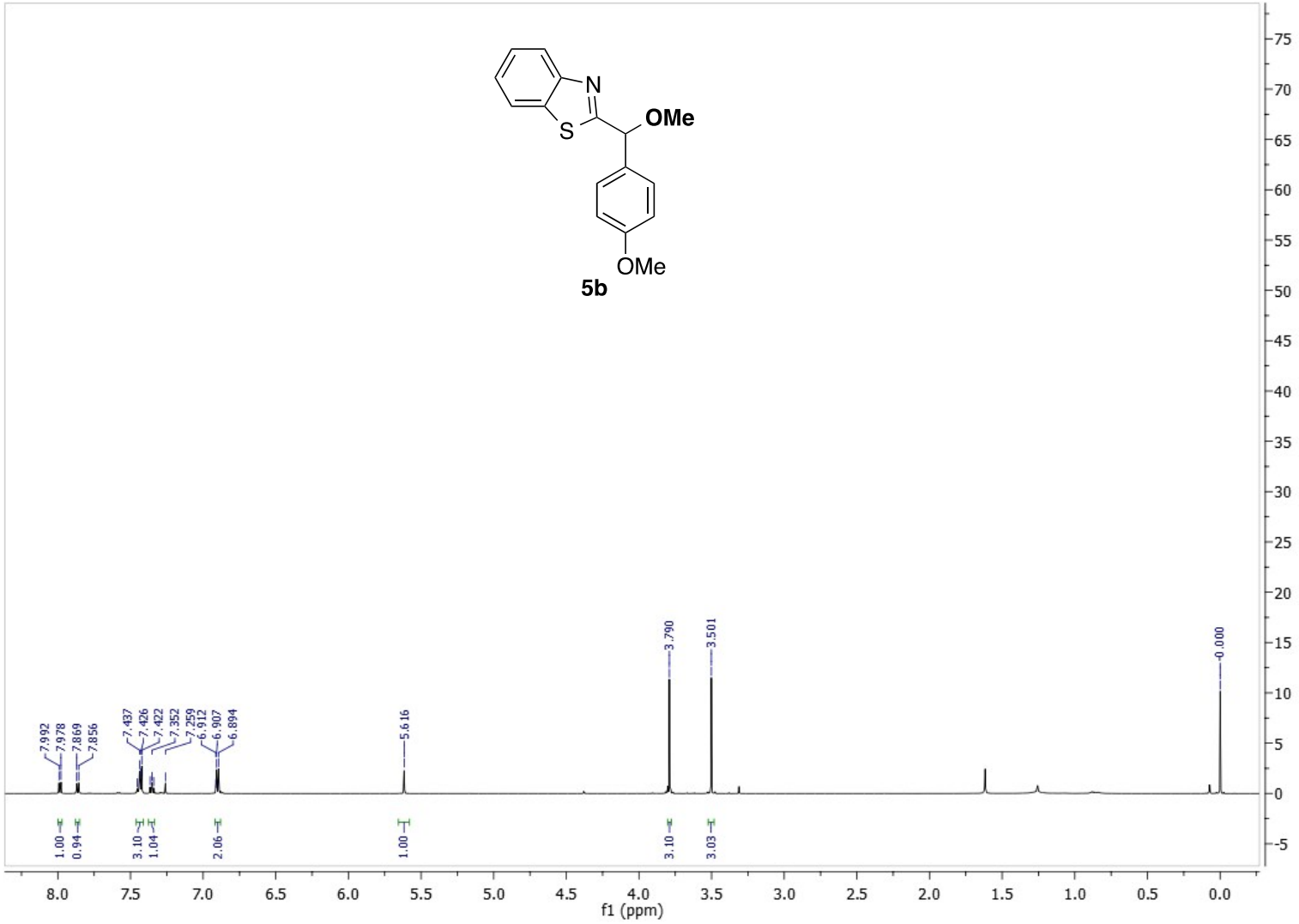

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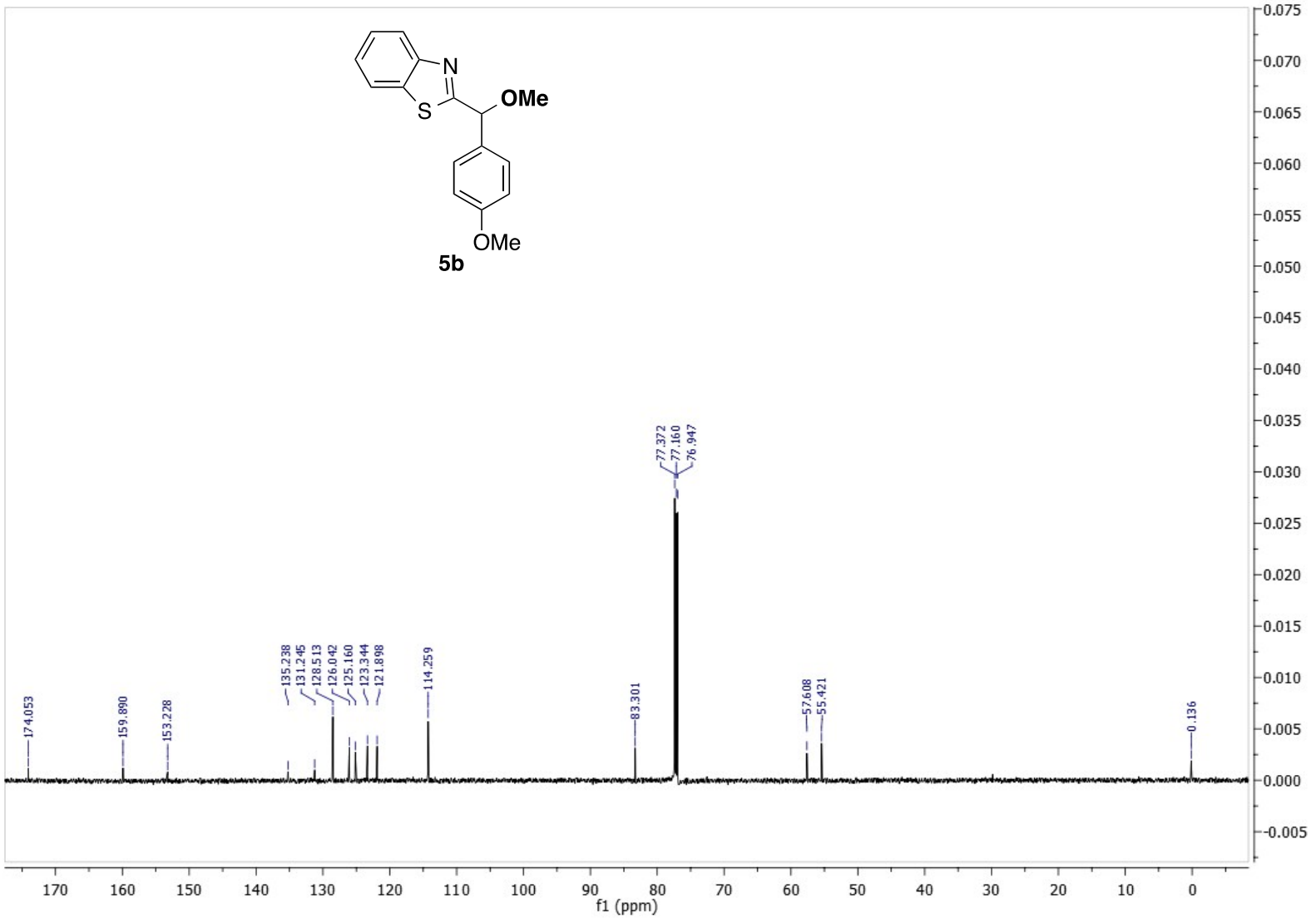

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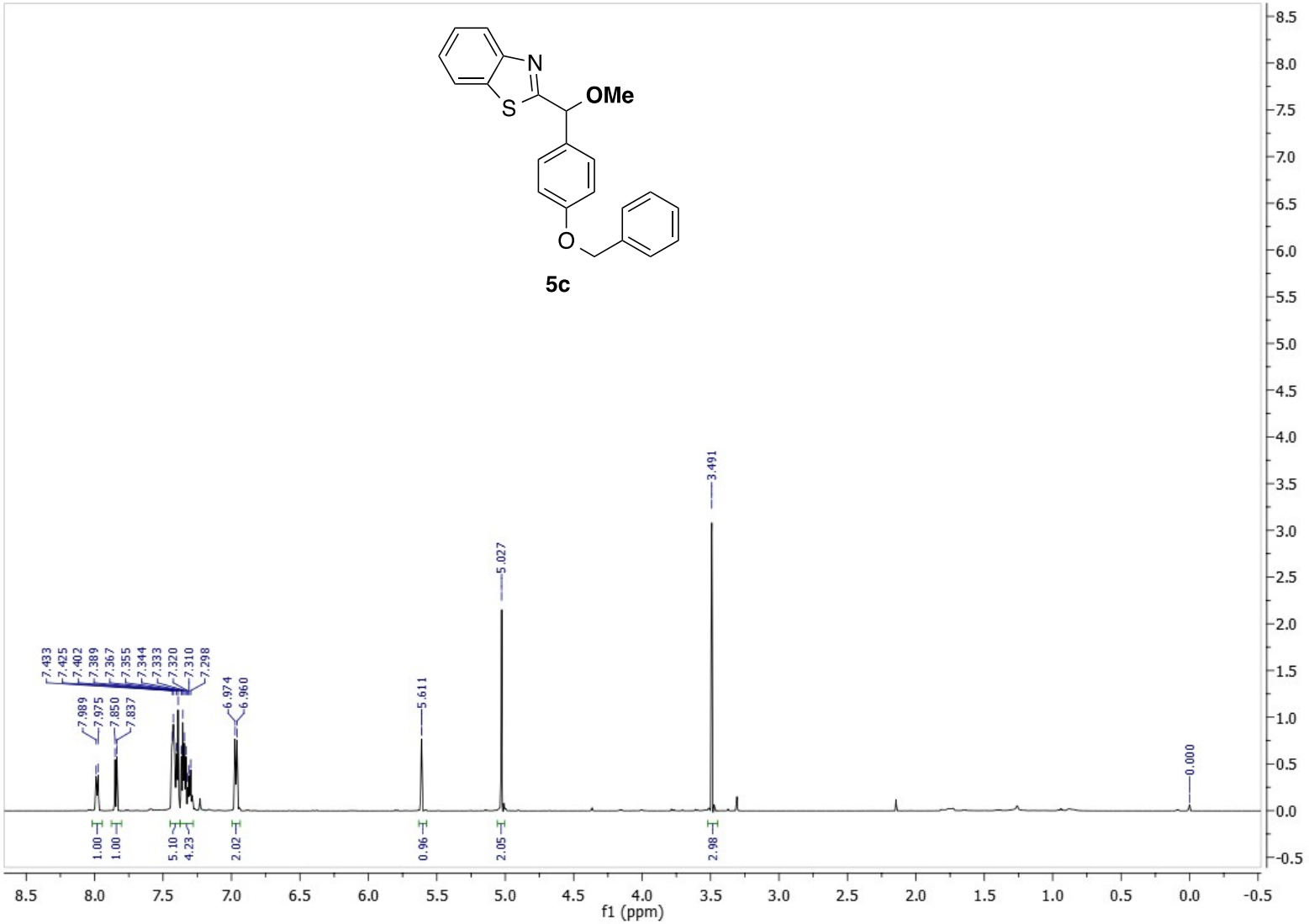
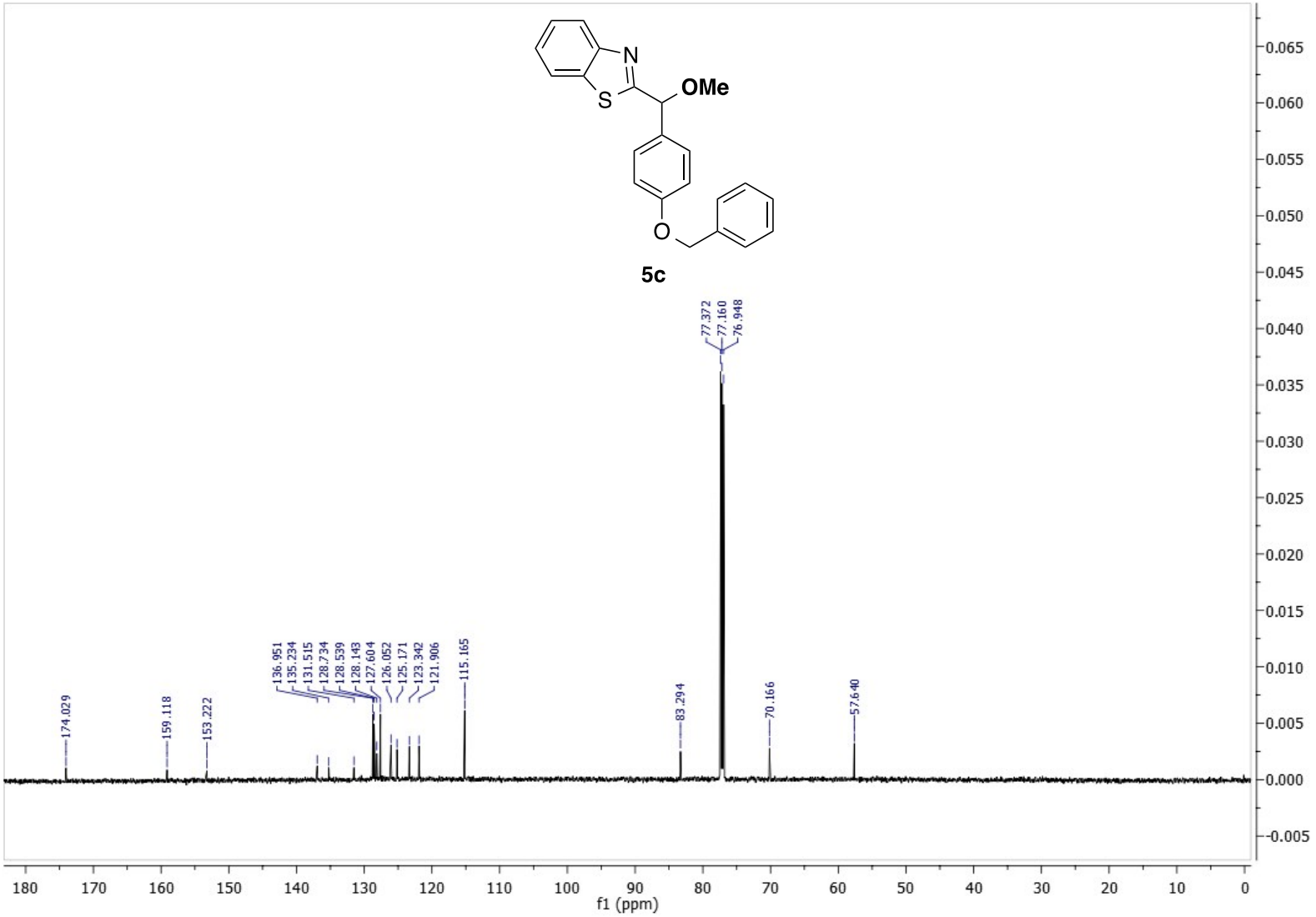
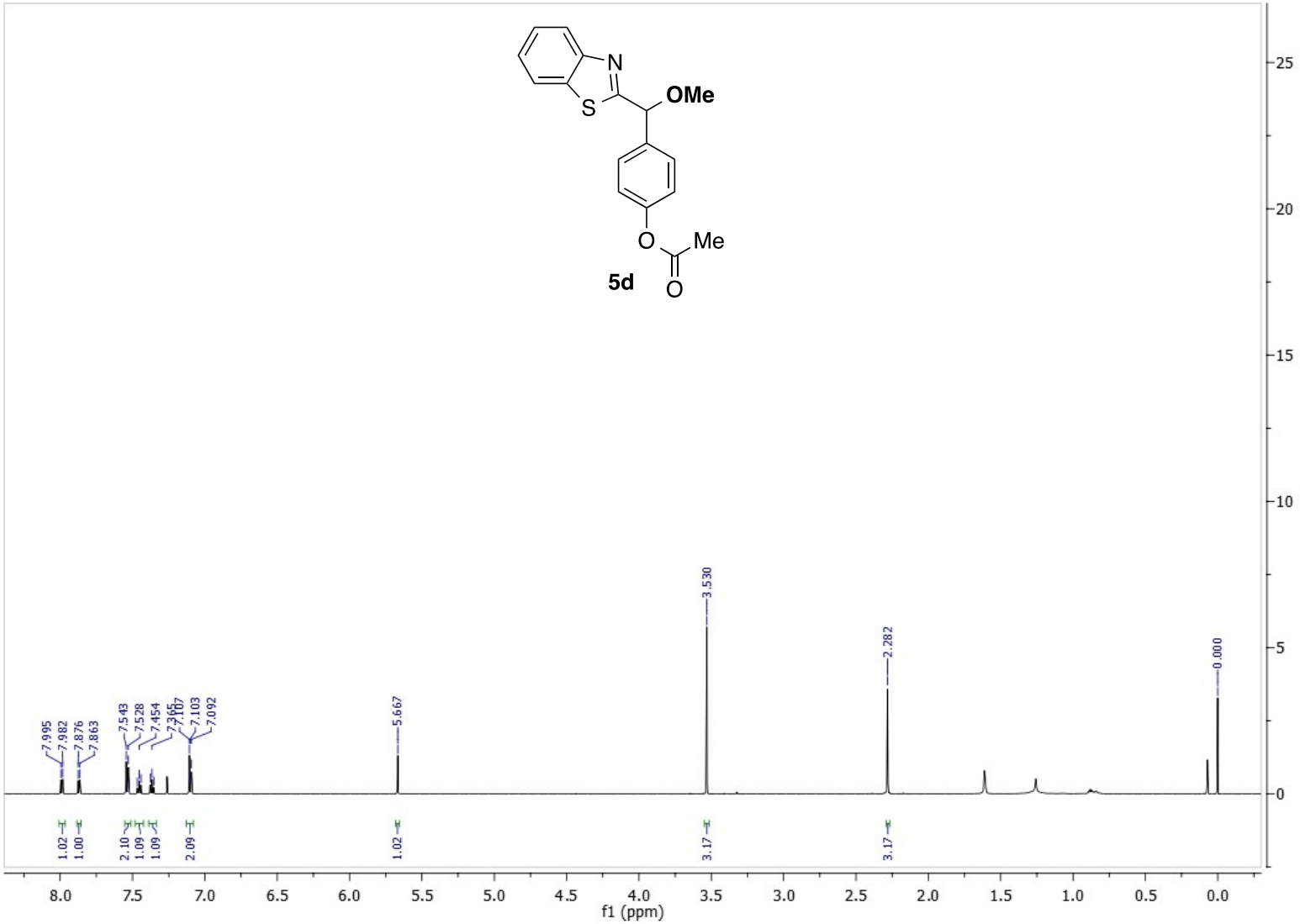


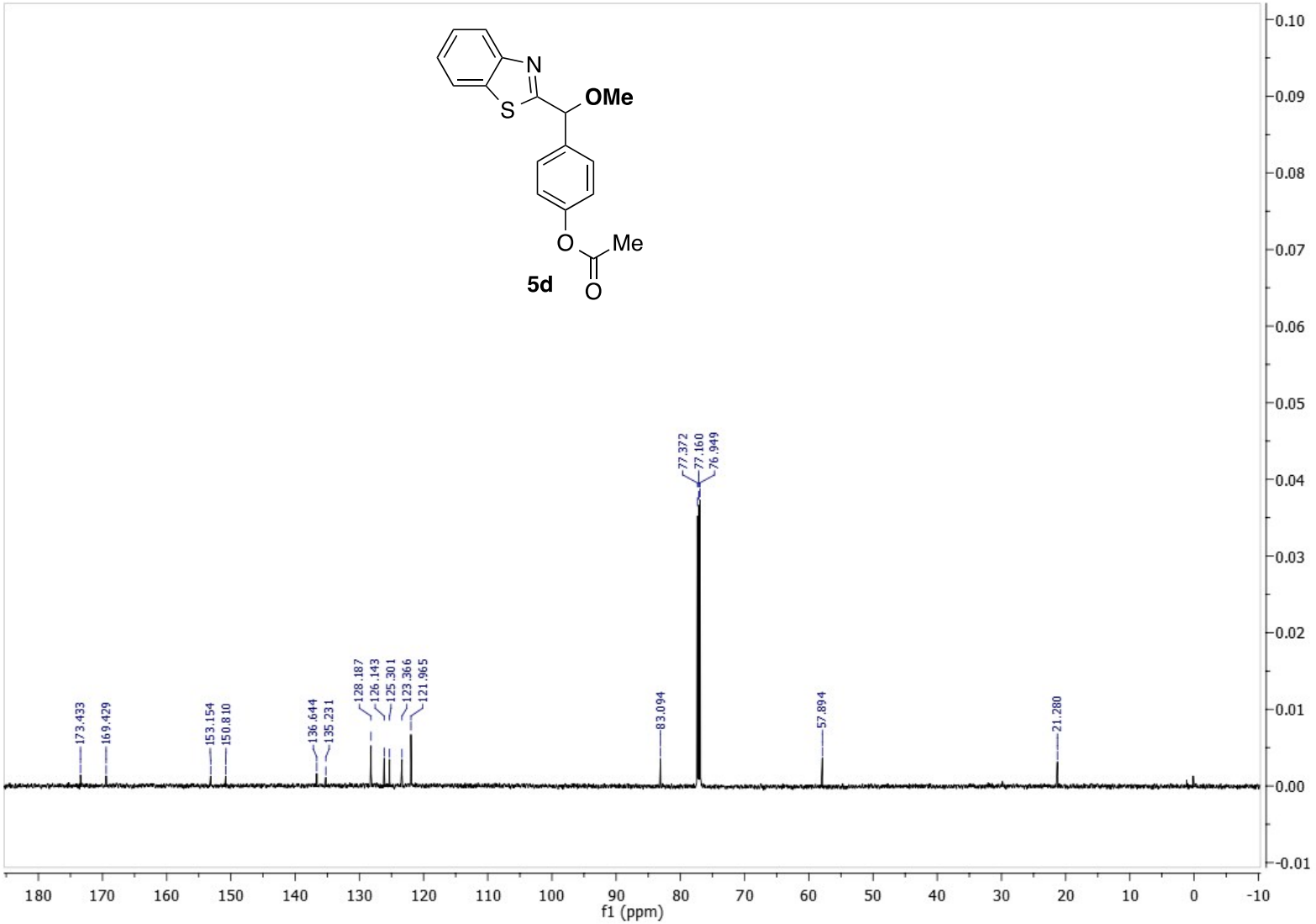
^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):



^{13}C NMR (151 MHz, $CDCl_3$):



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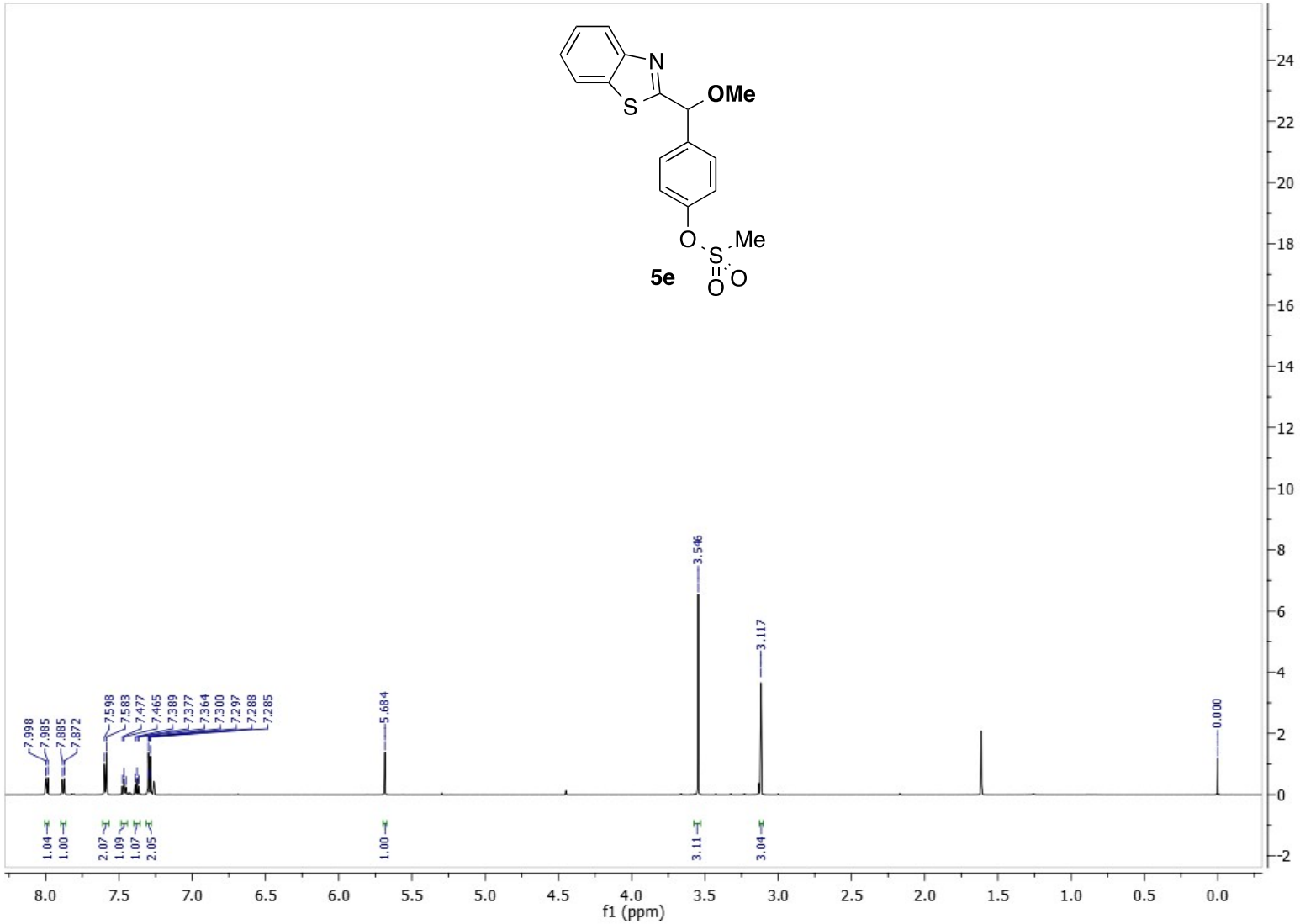

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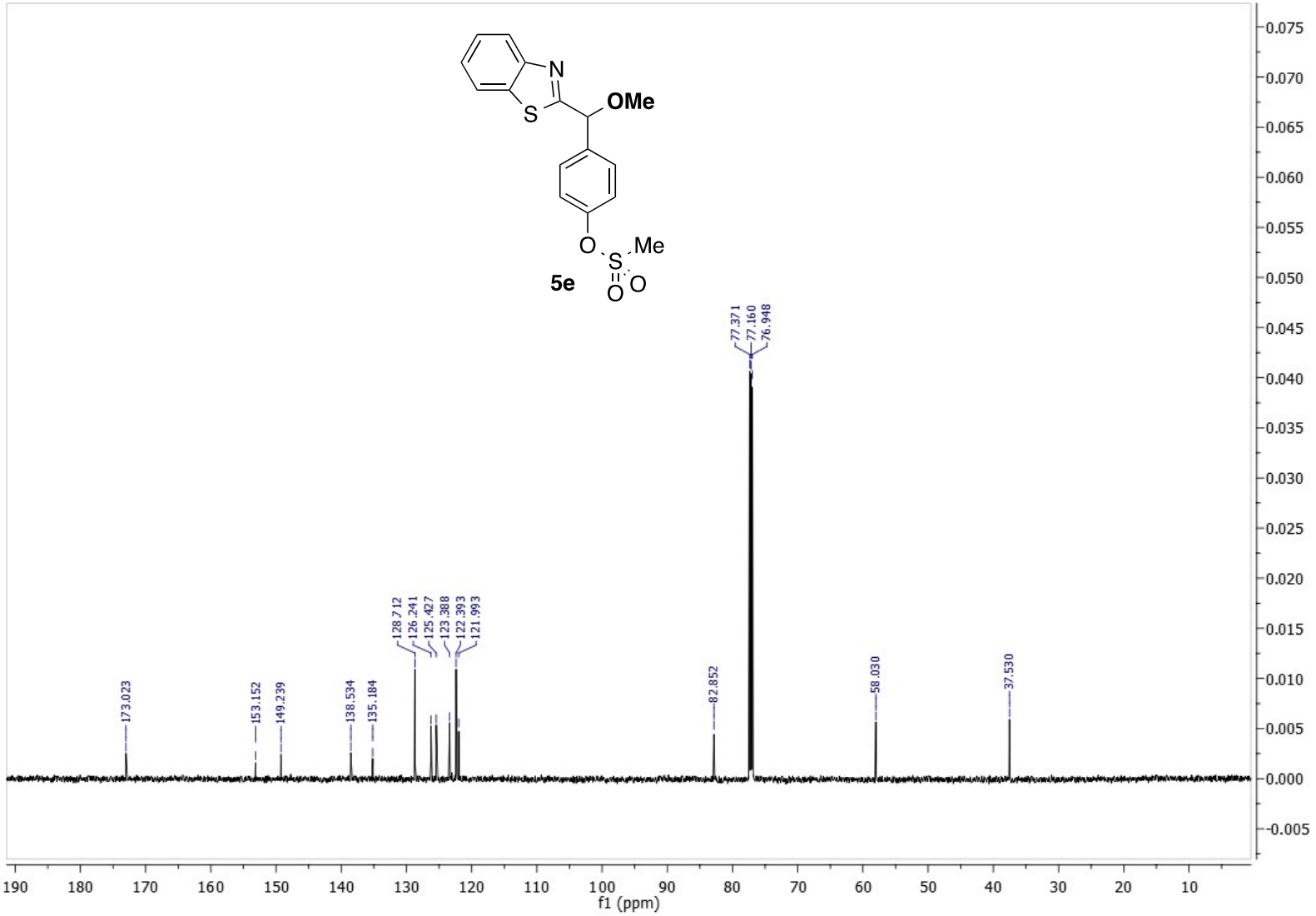

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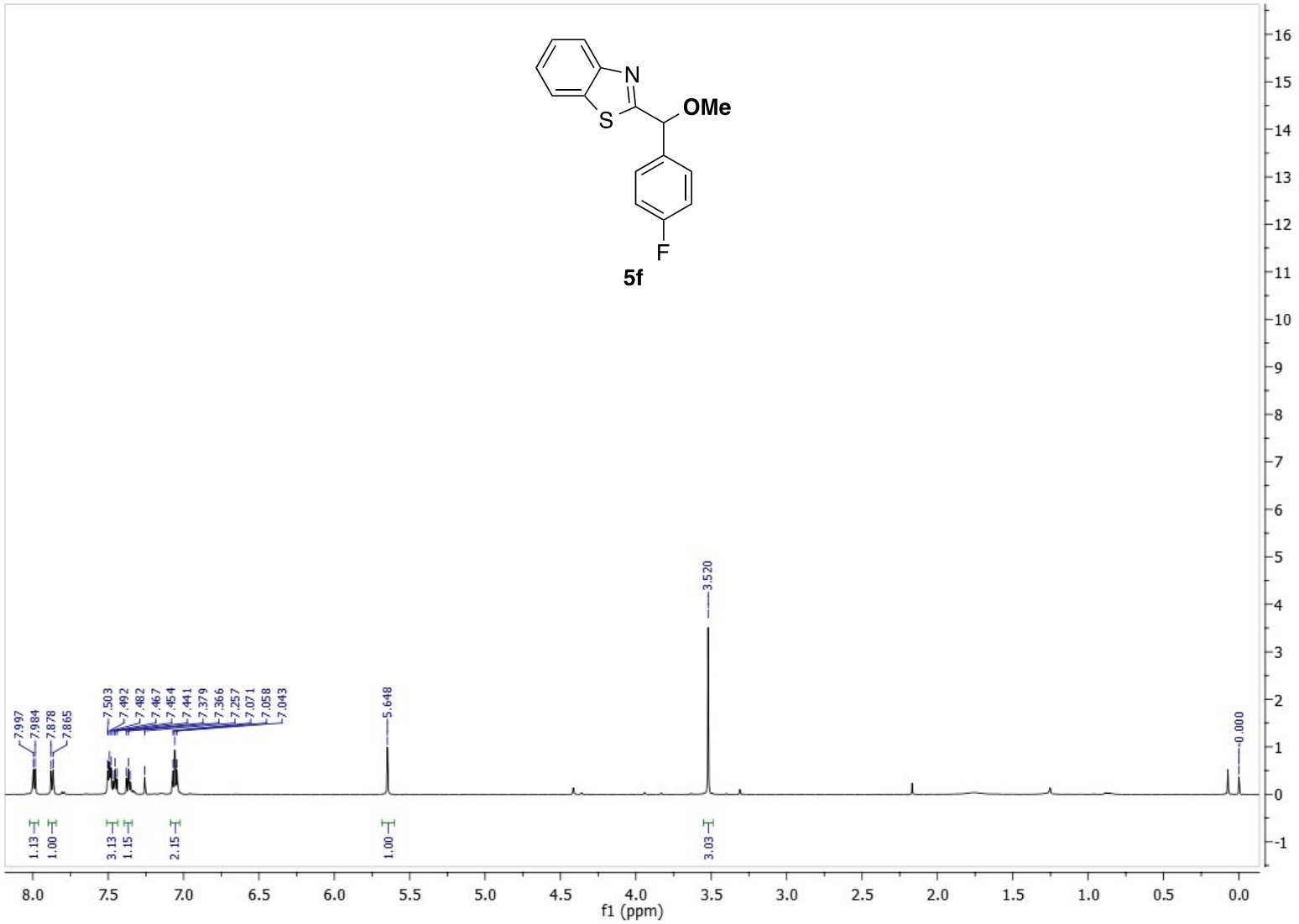
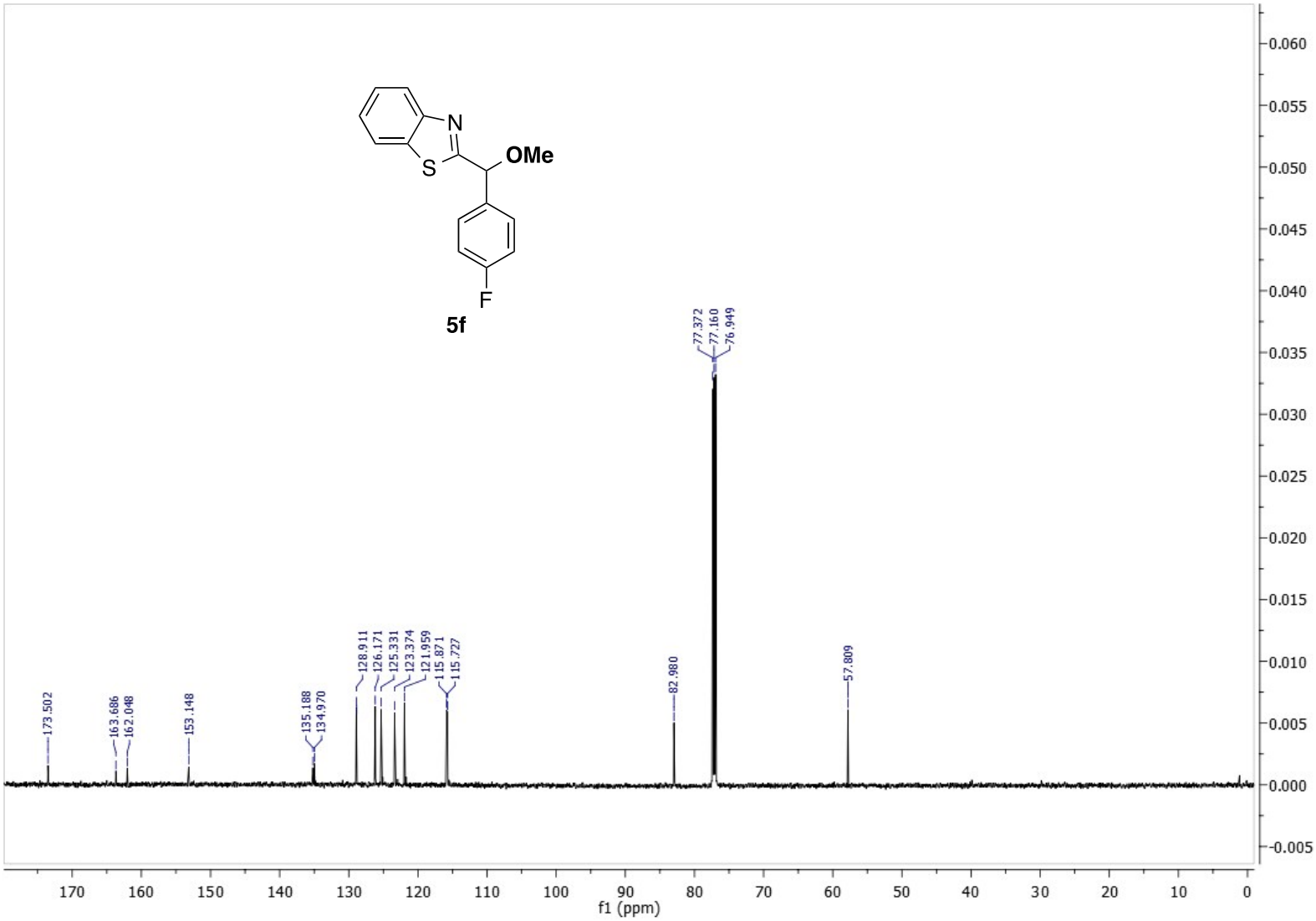
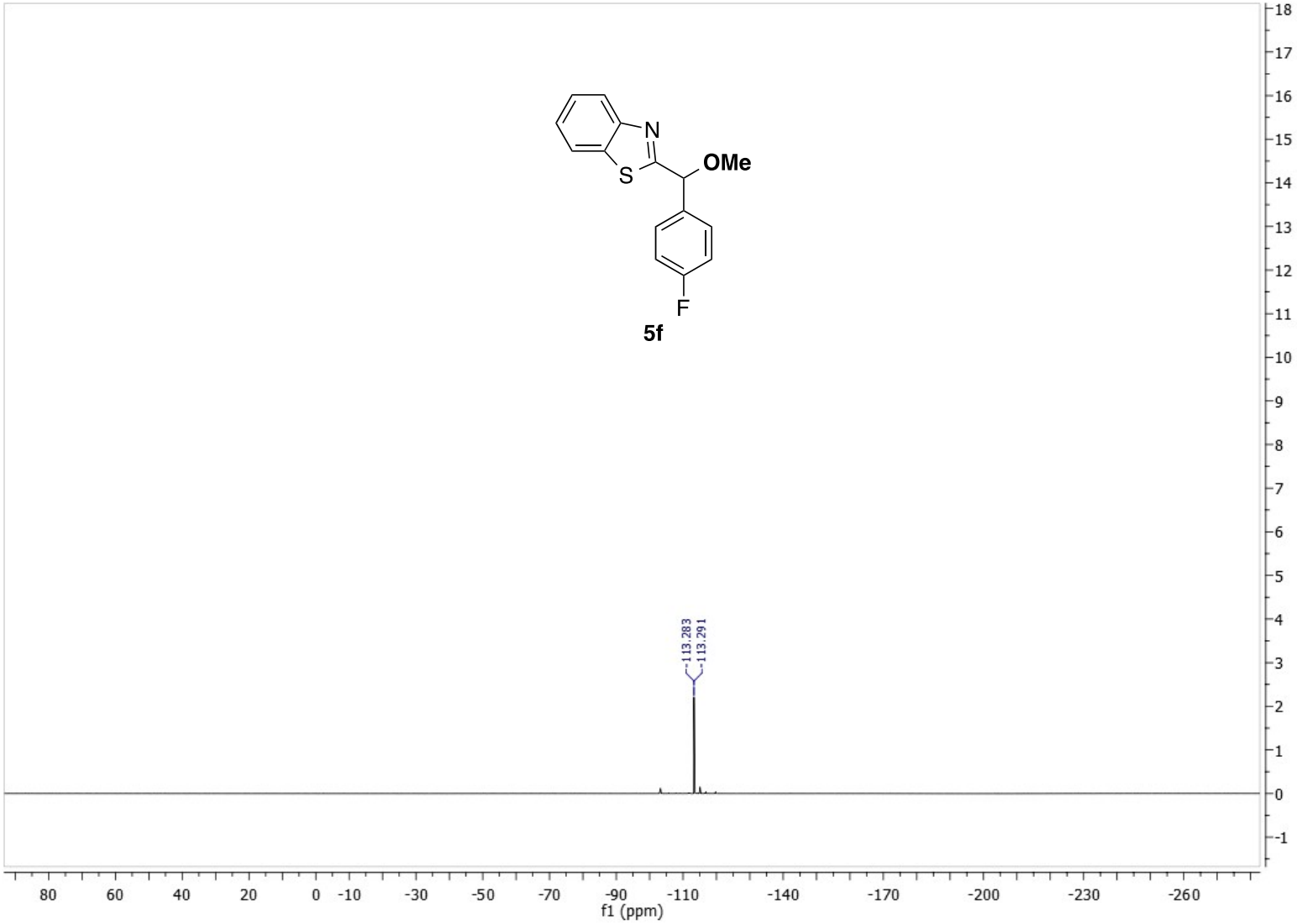


^{13}C NMR (151 MHz, $CDCl_3$):



^{19}F NMR (564 MHz, $CDCl_3$):



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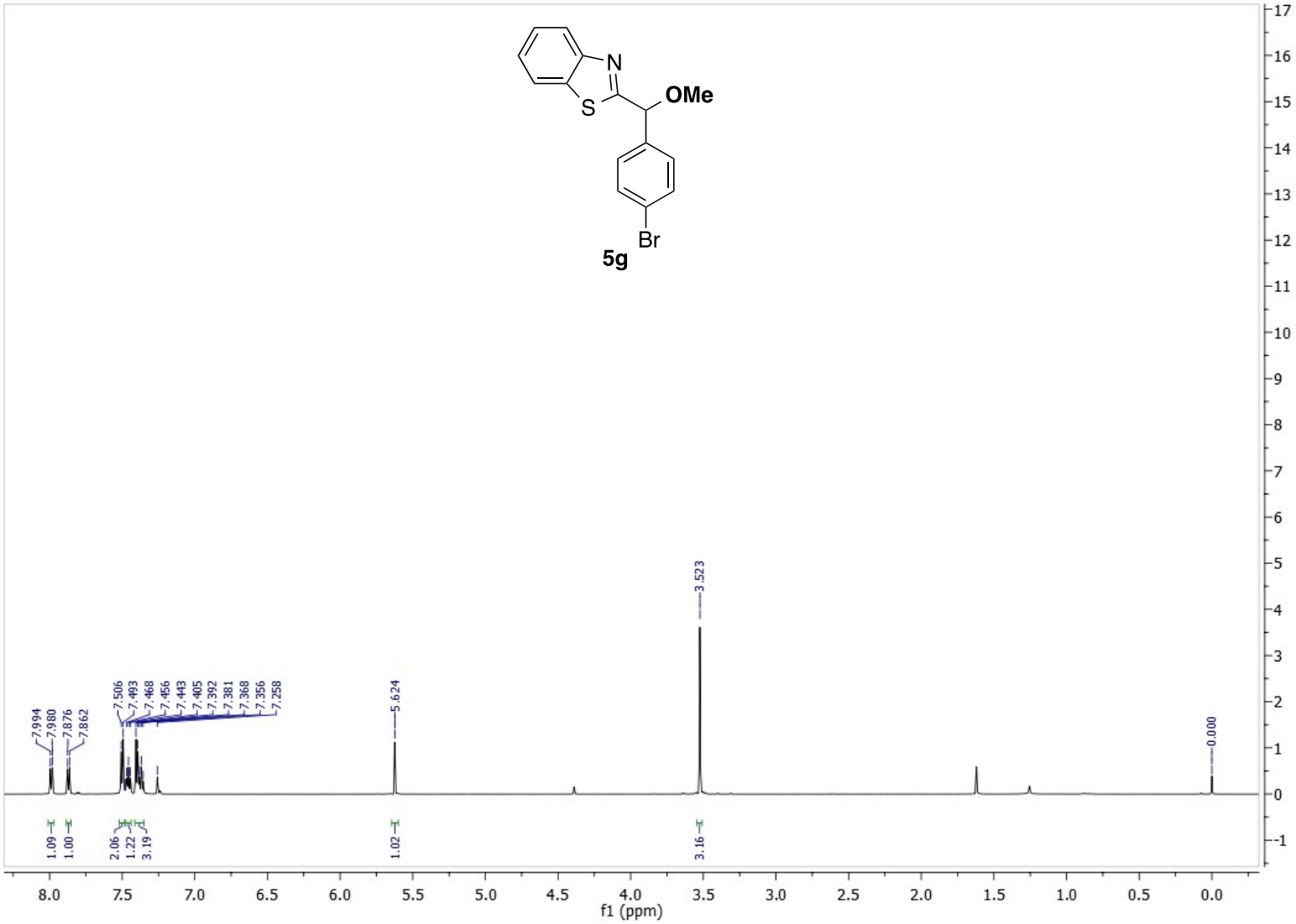
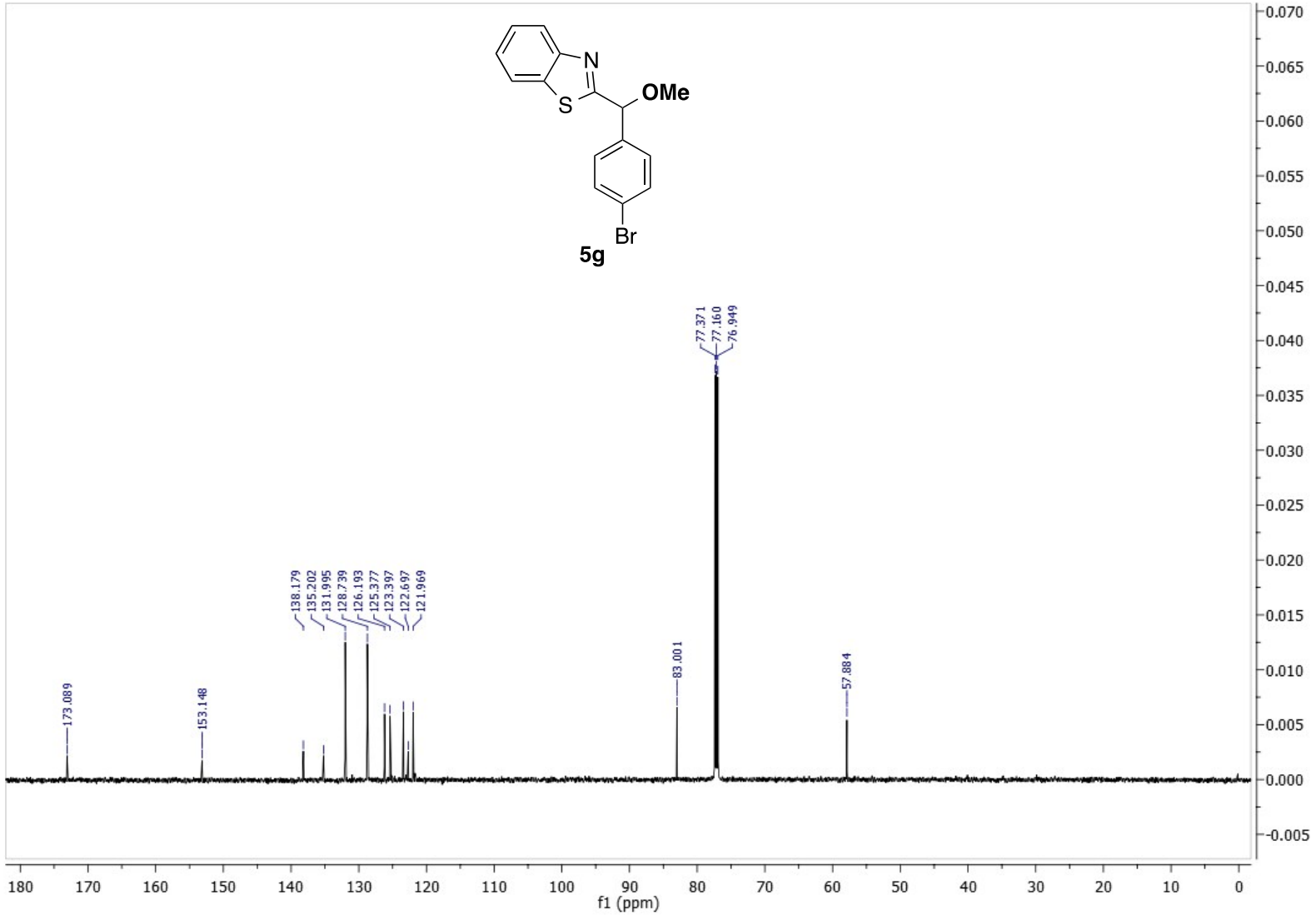
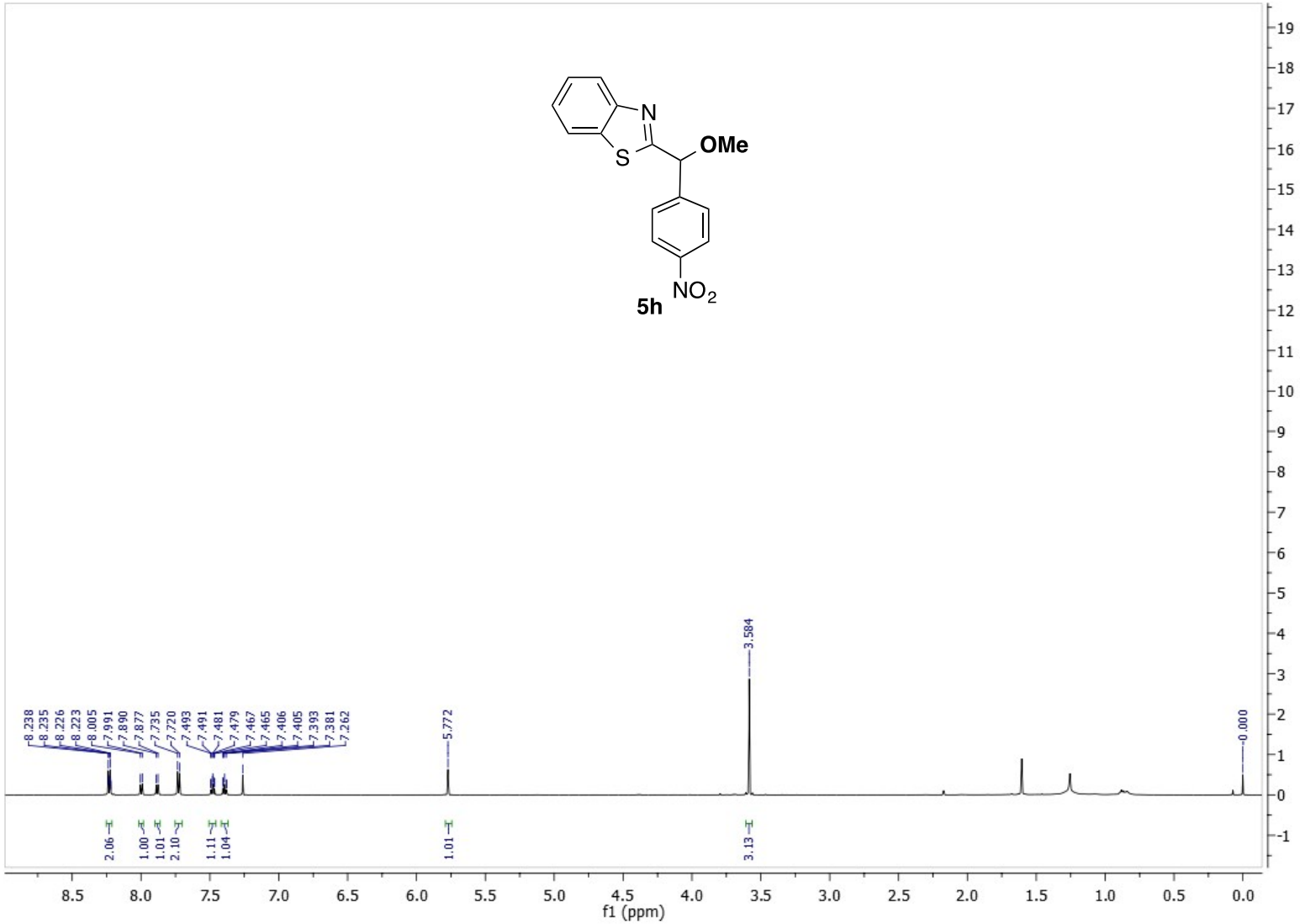


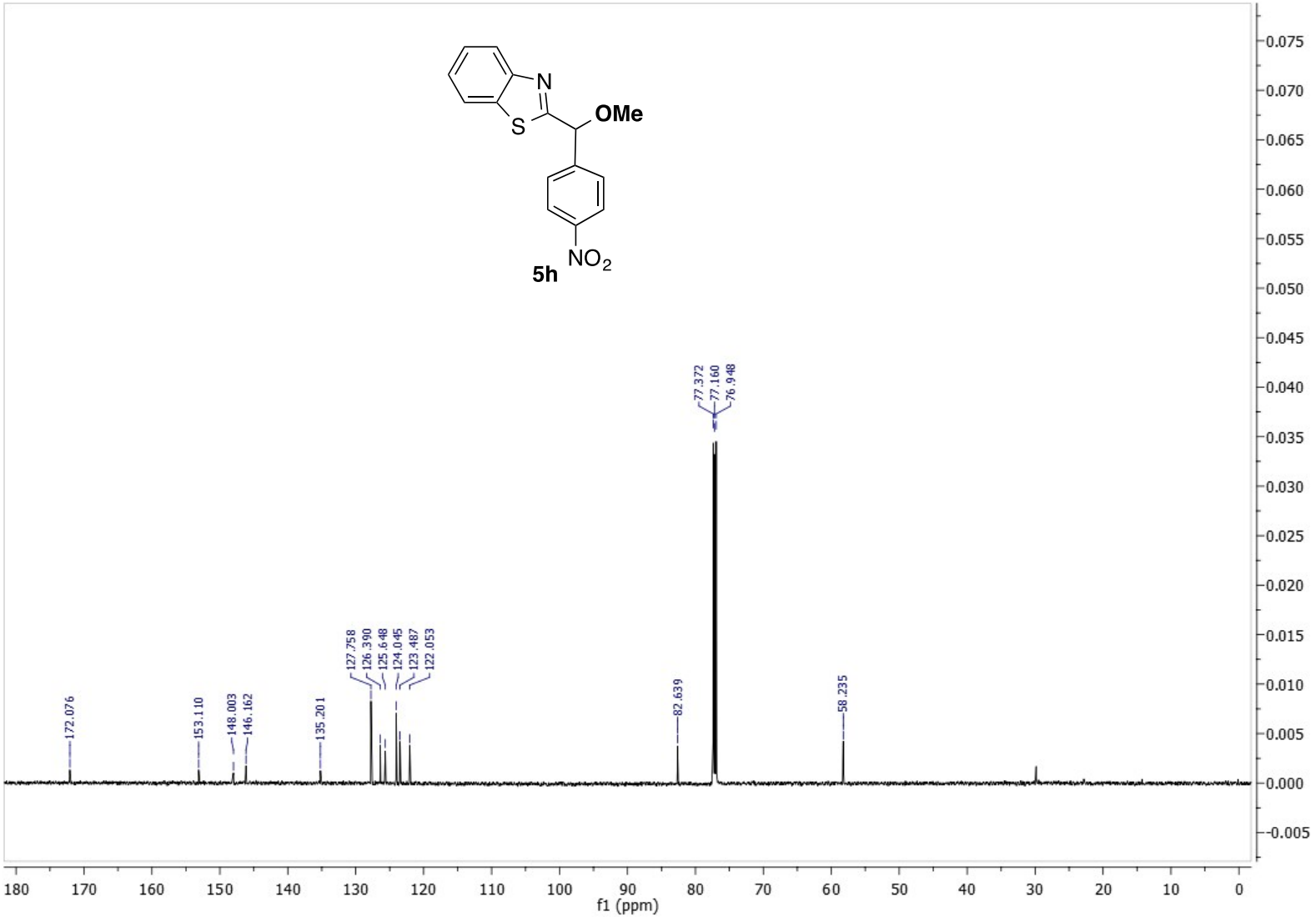
^{13}C NMR (151 MHz, $CDCl_3$):



^{1}H NMR (600 MHz, $CDCl_3$):



^{13}C NMR (151 MHz, $CDCl_3$):



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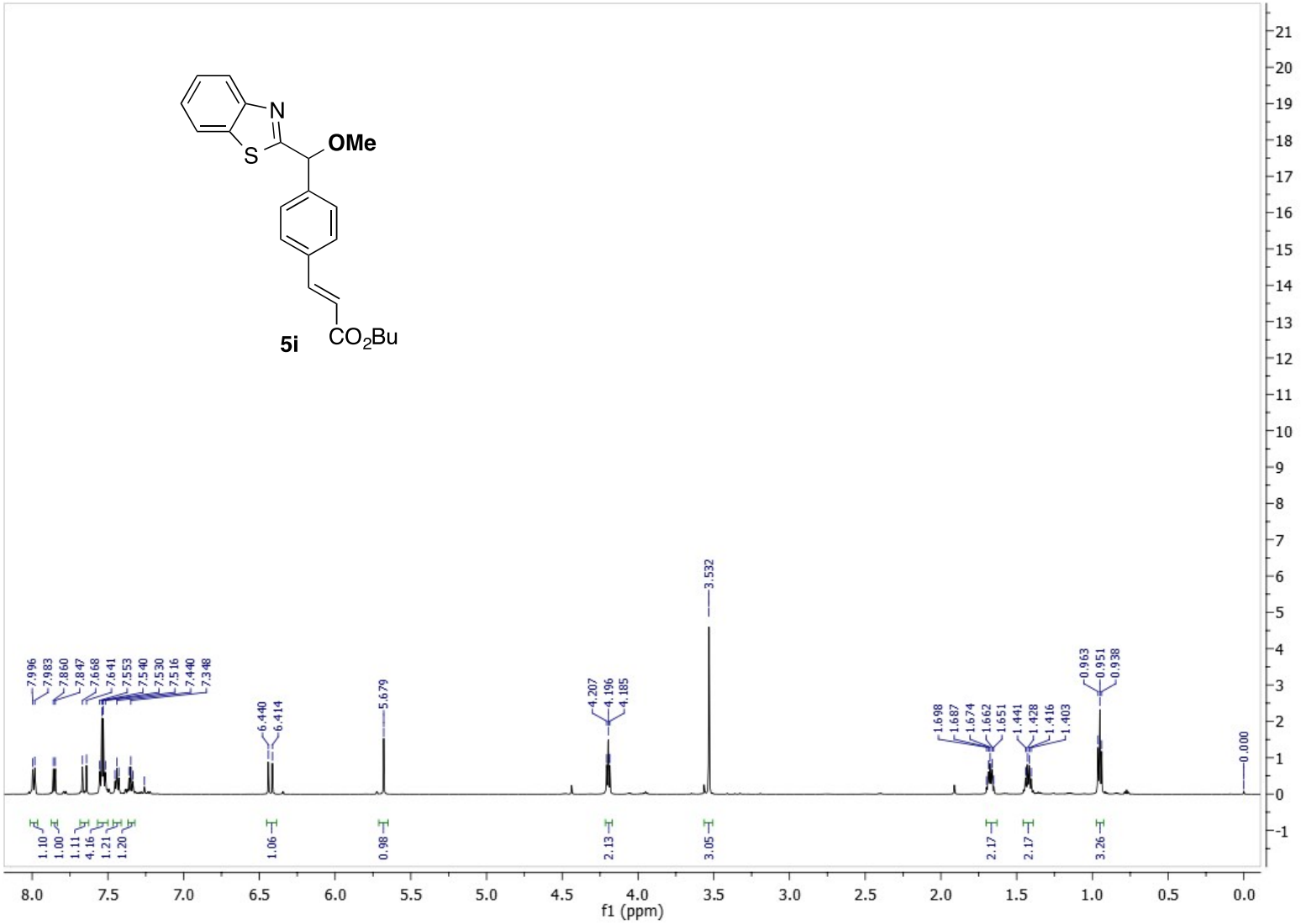

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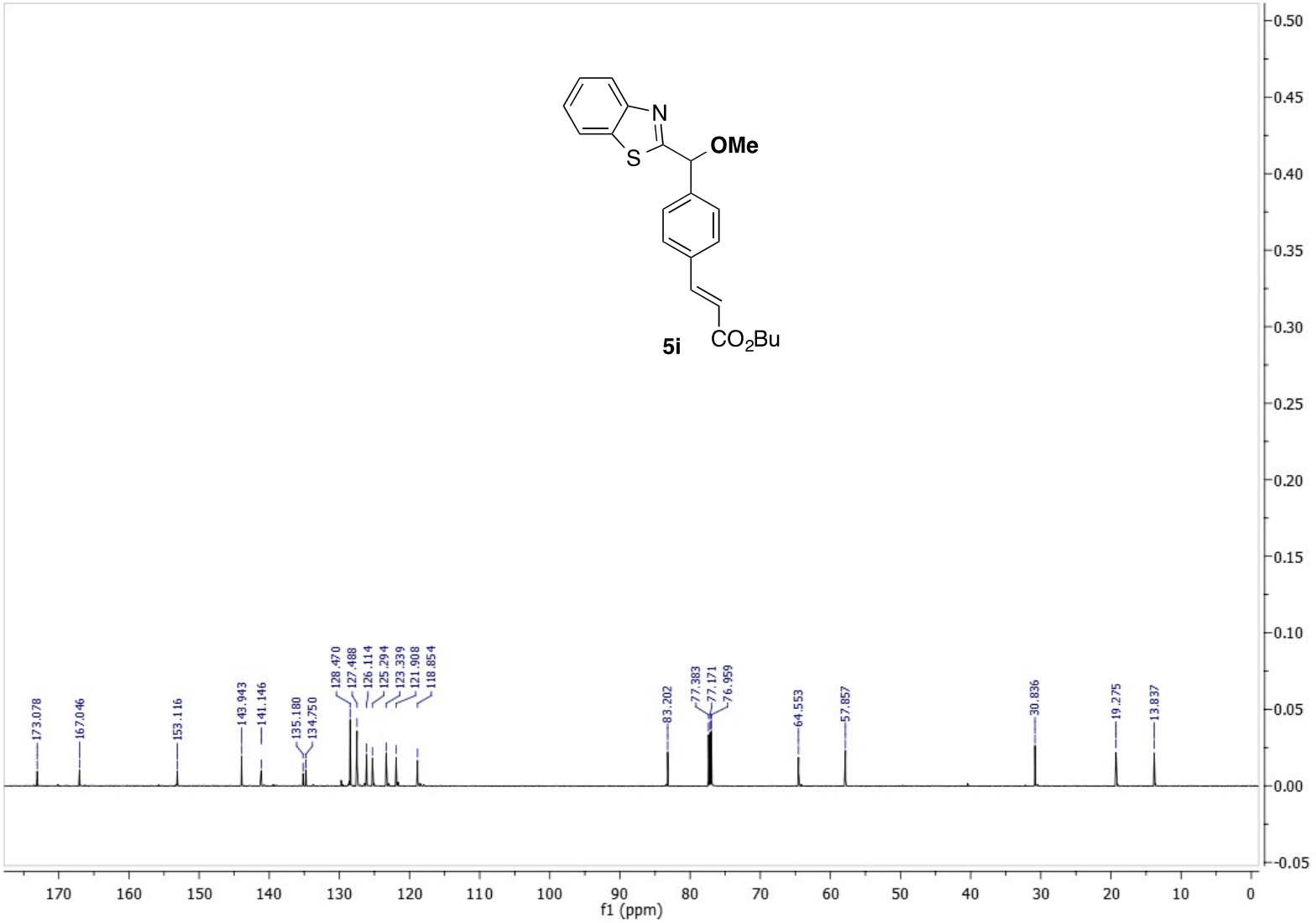

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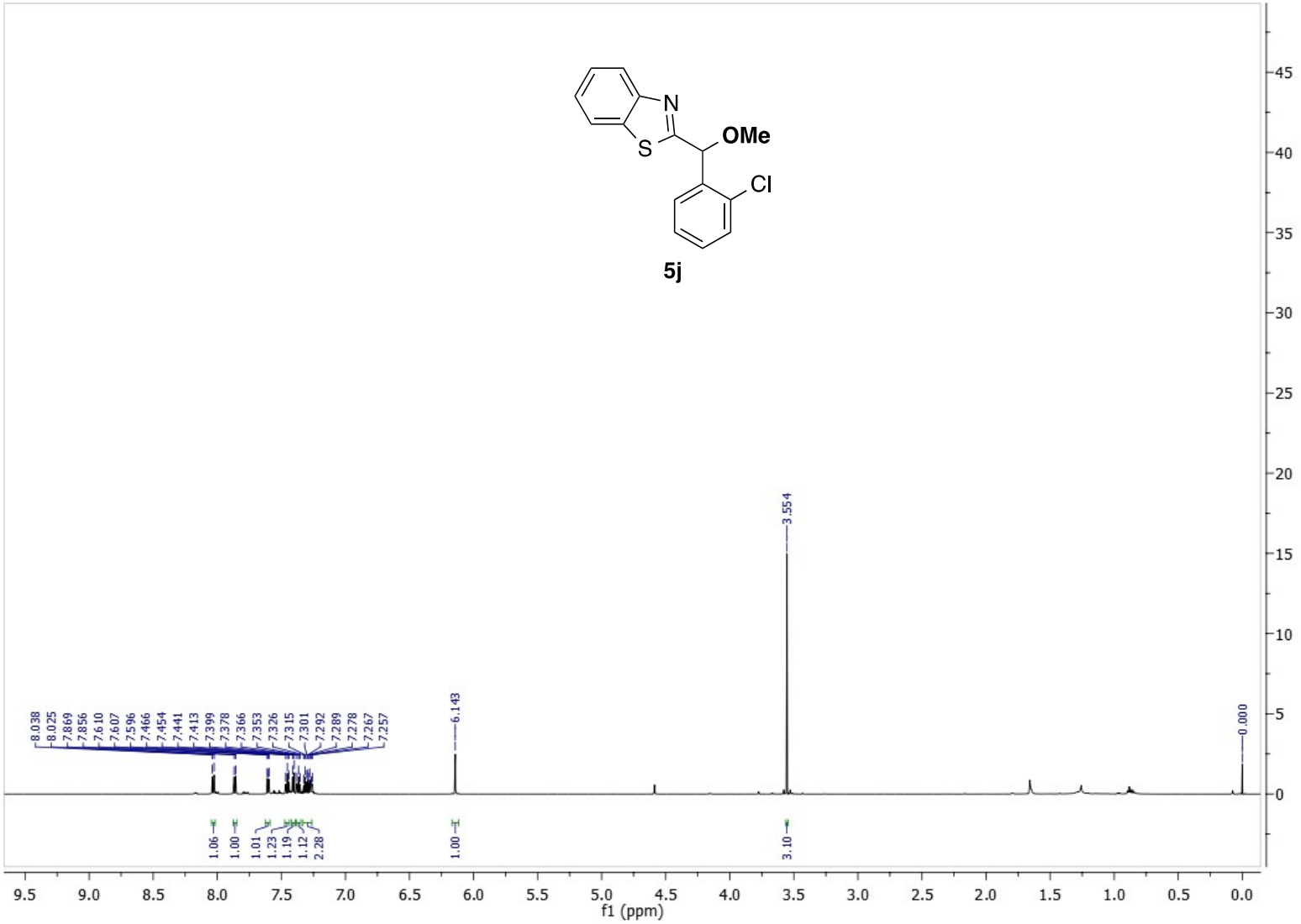
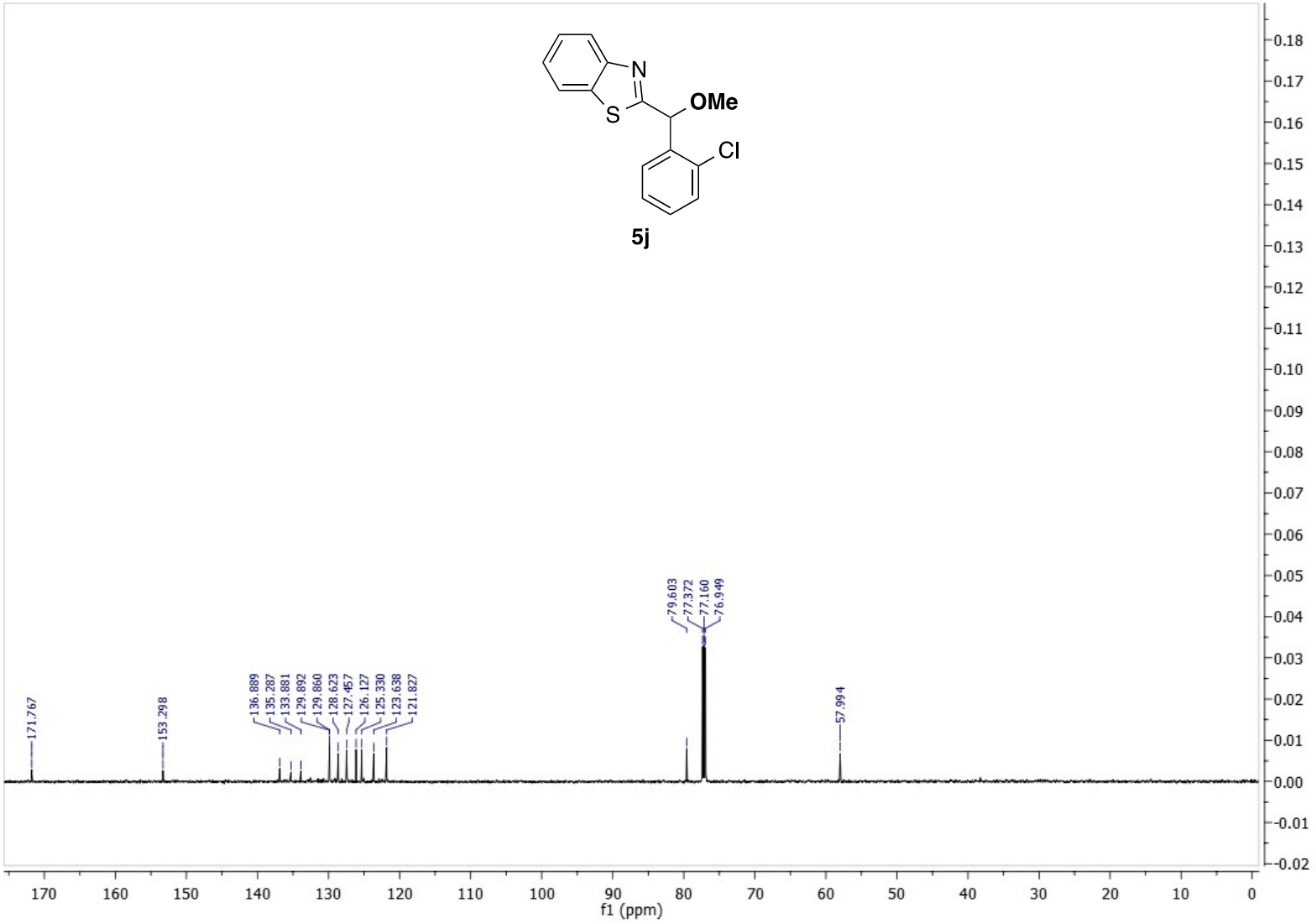


^{13}C NMR (151 MHz, $CDCl_3$):



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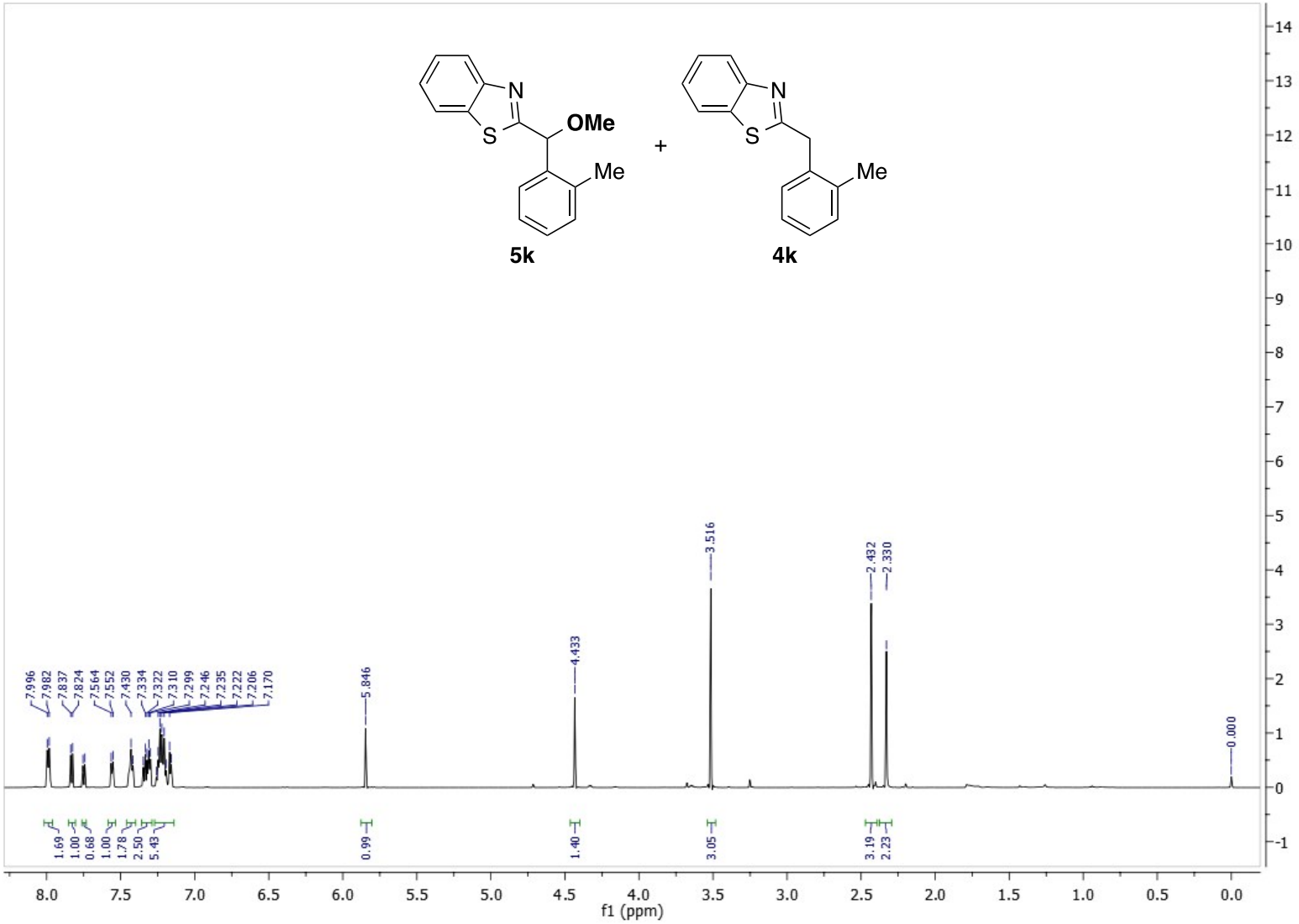
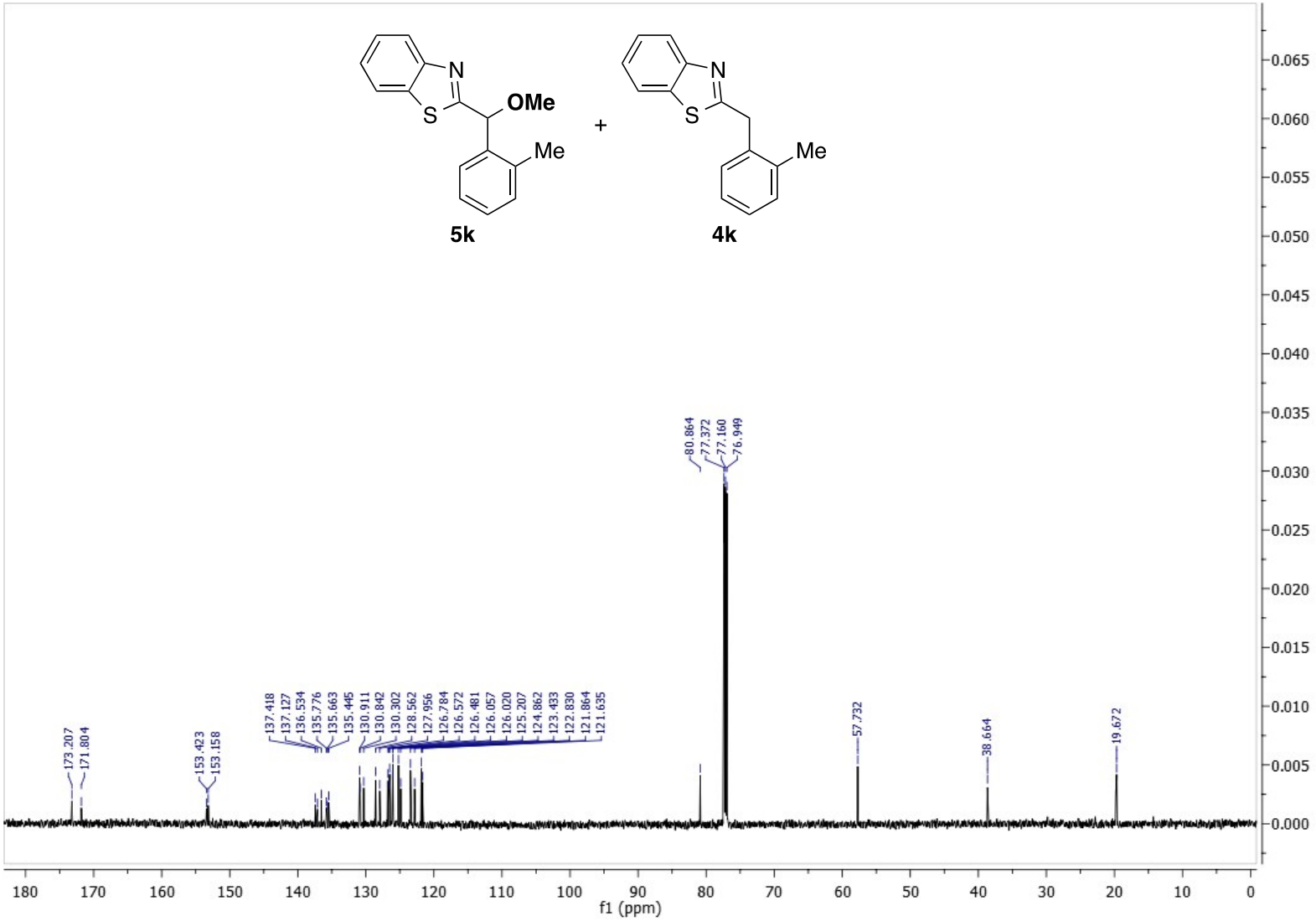


^{13}C NMR (151 MHz, $CDCl_3$):



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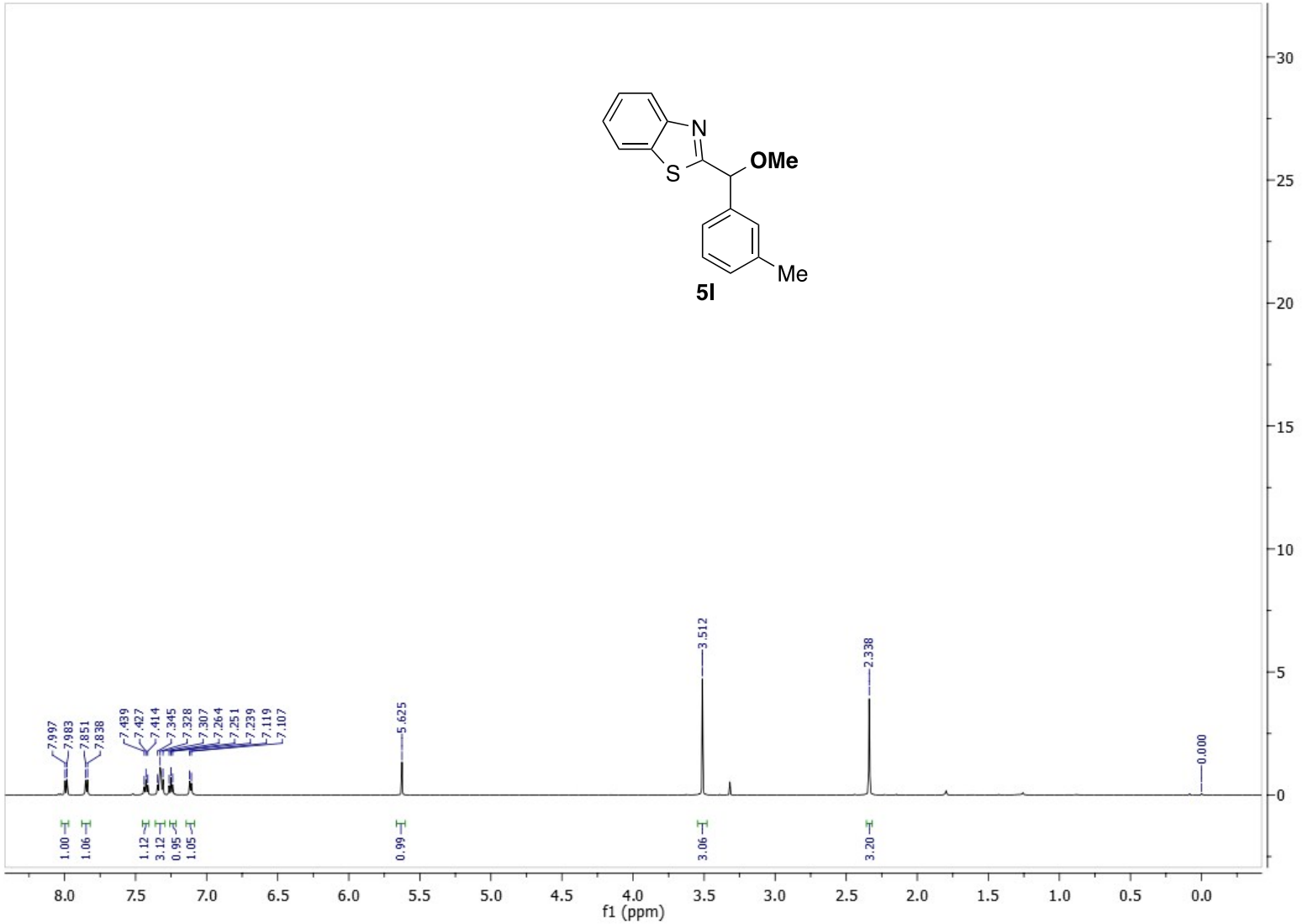
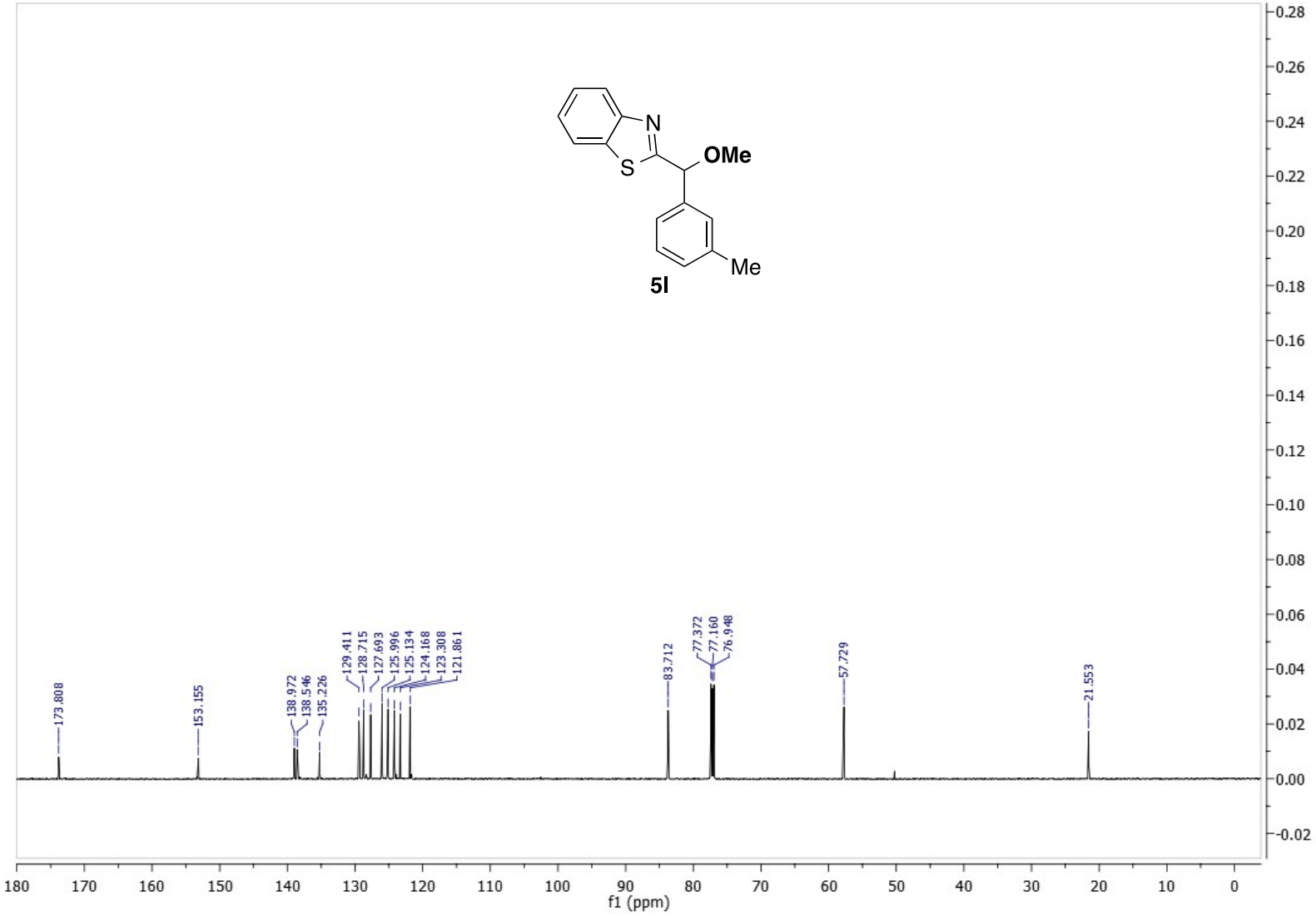


^{13}C NMR (151 MHz, $CDCl_3$):



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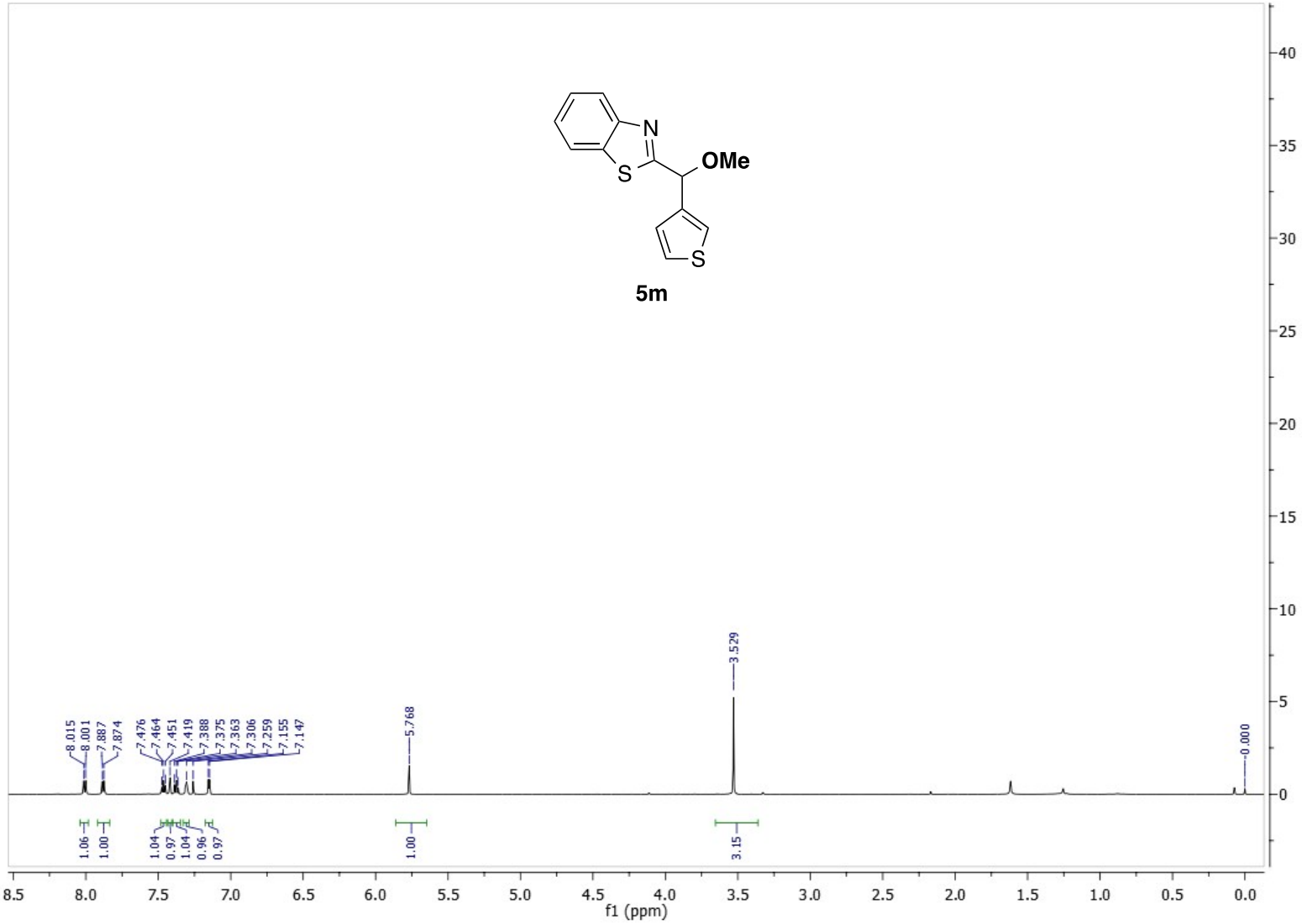

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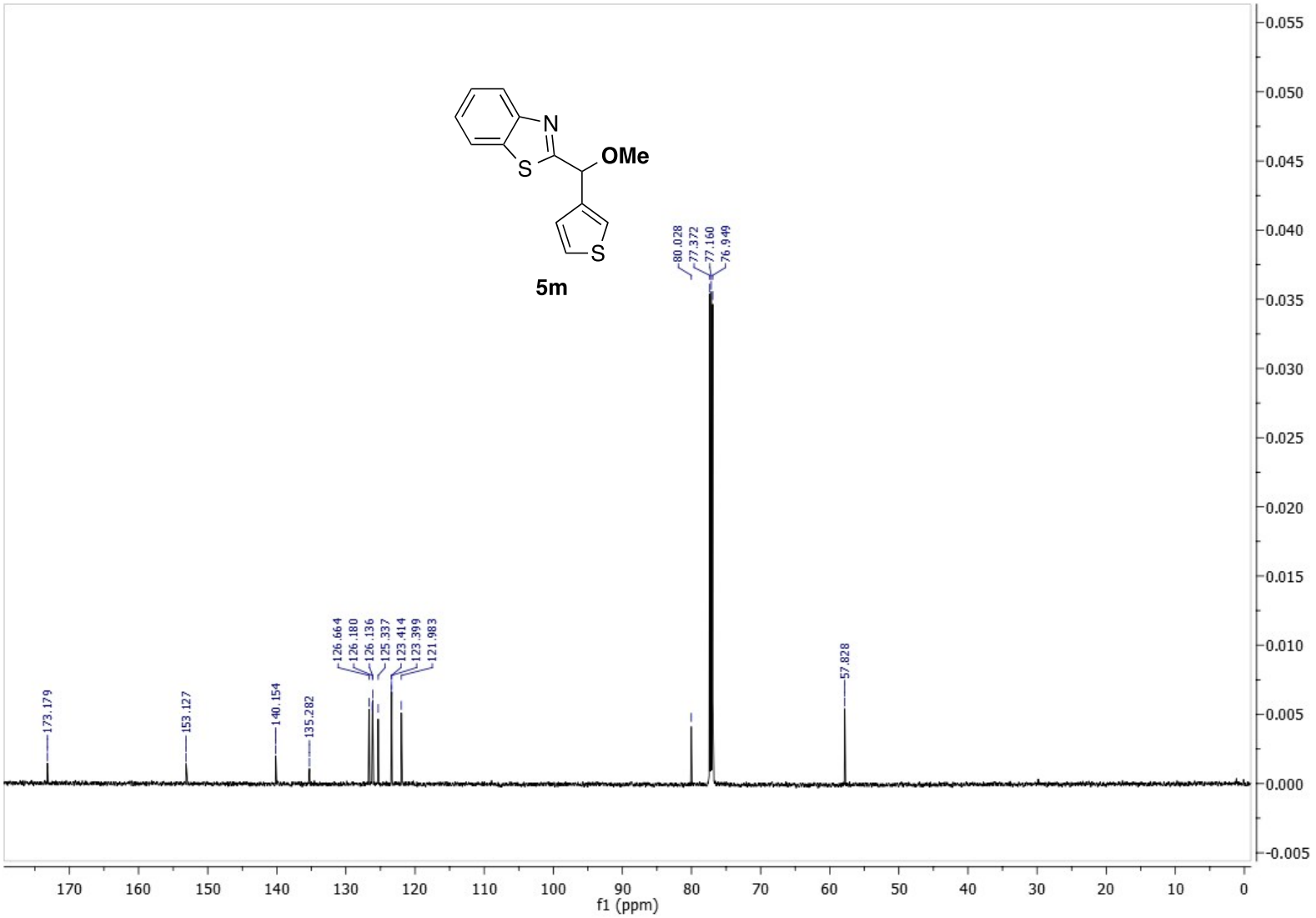

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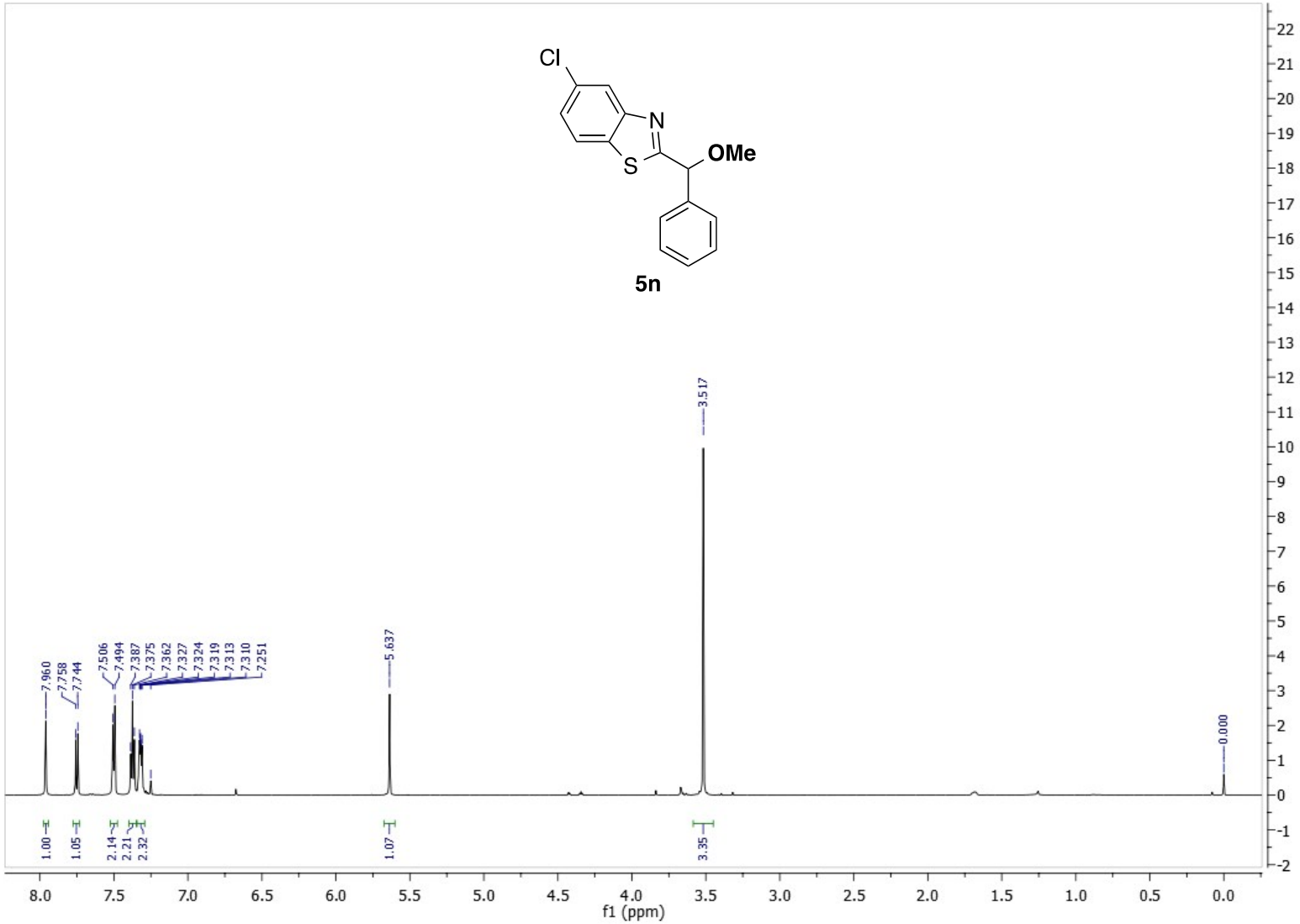

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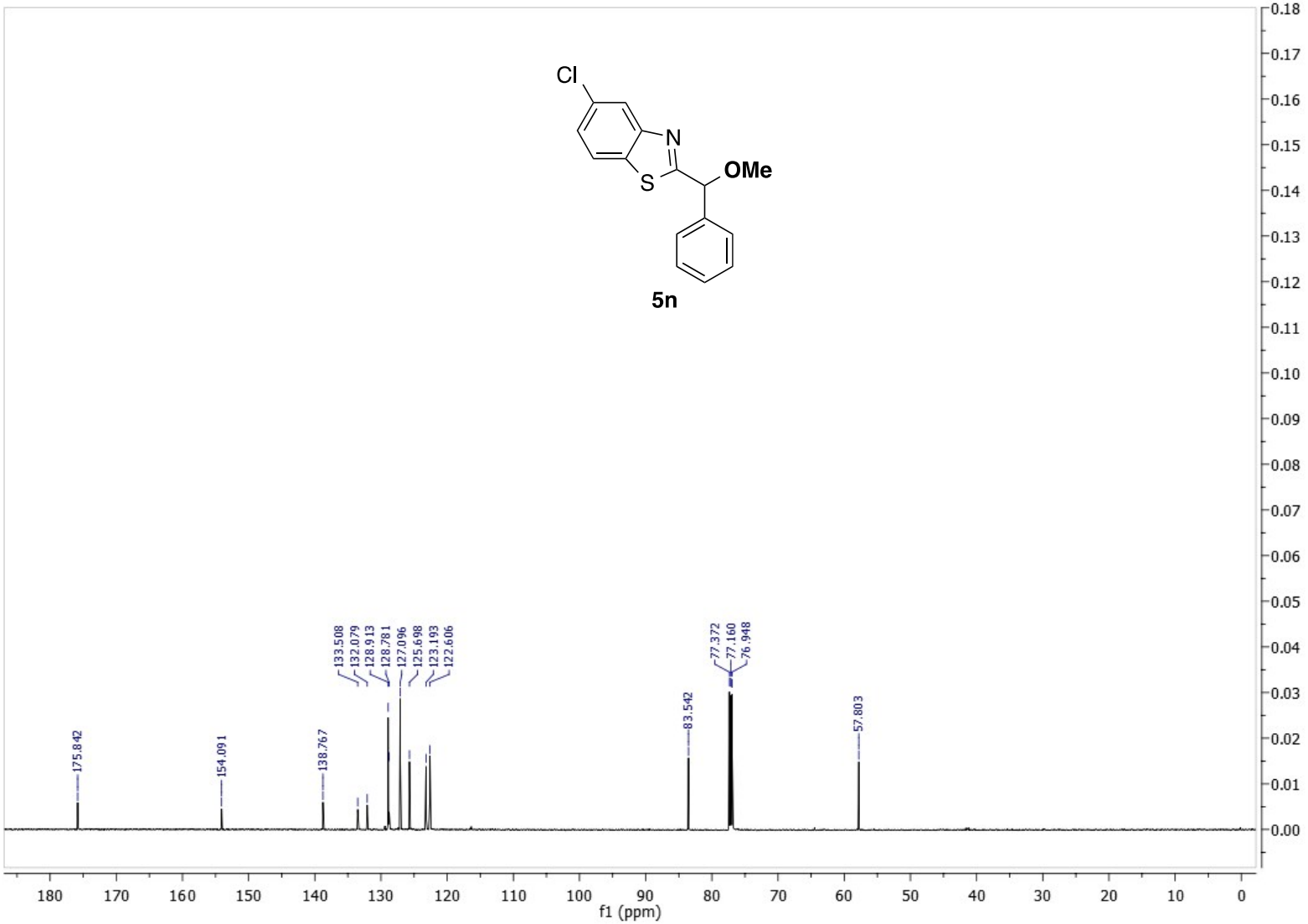

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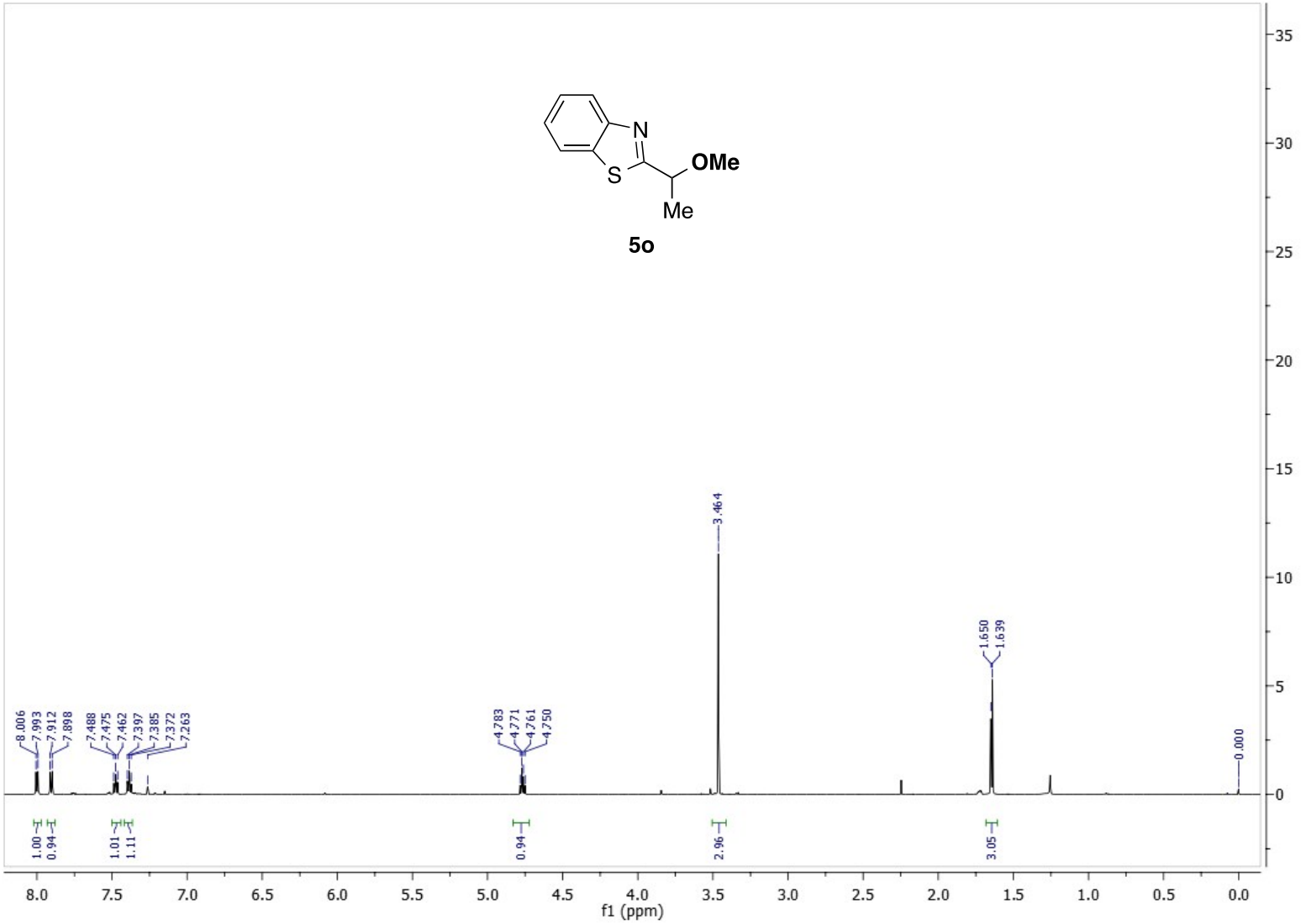
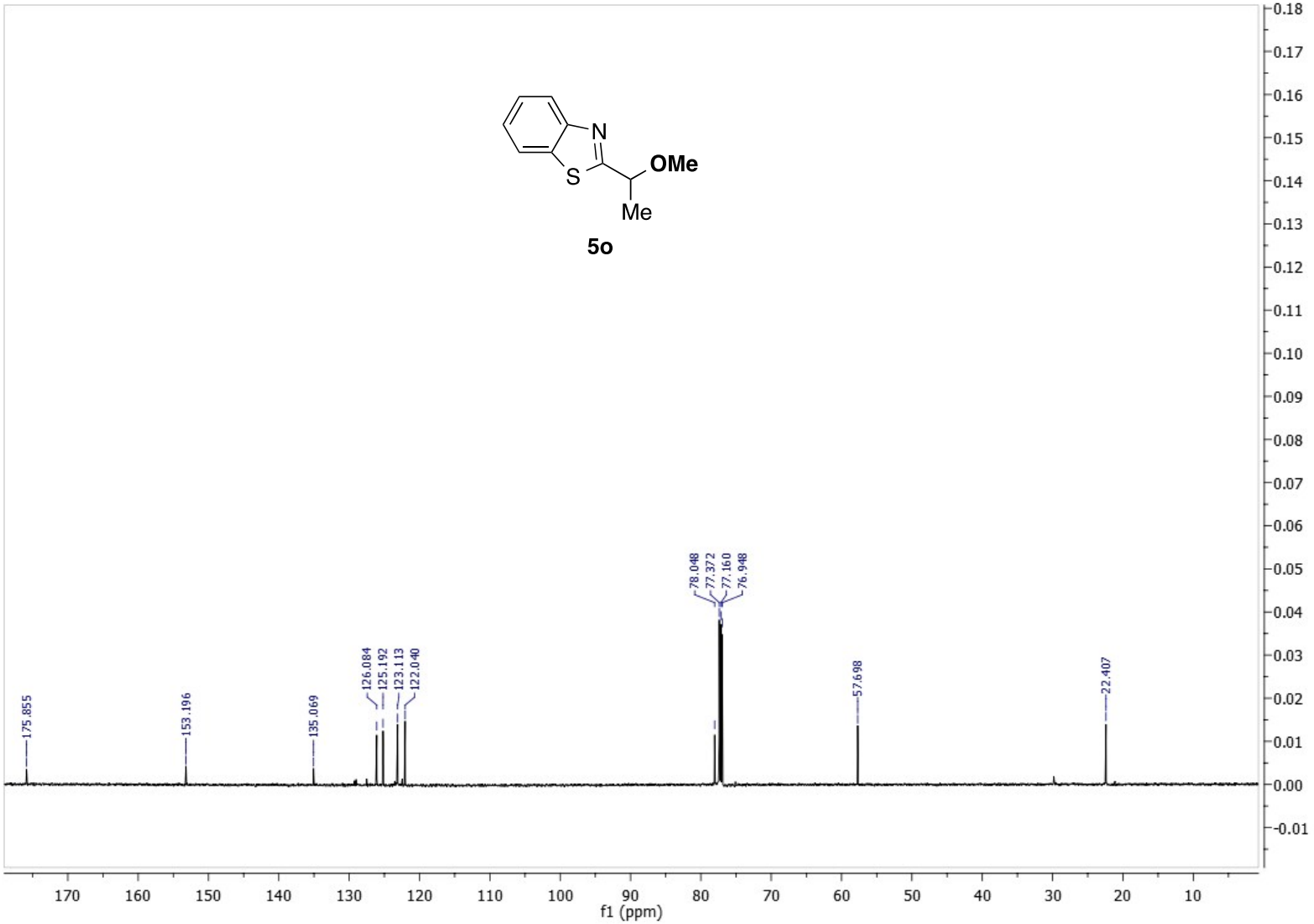


^{13}C NMR (151 MHz, $CDCl_3$):



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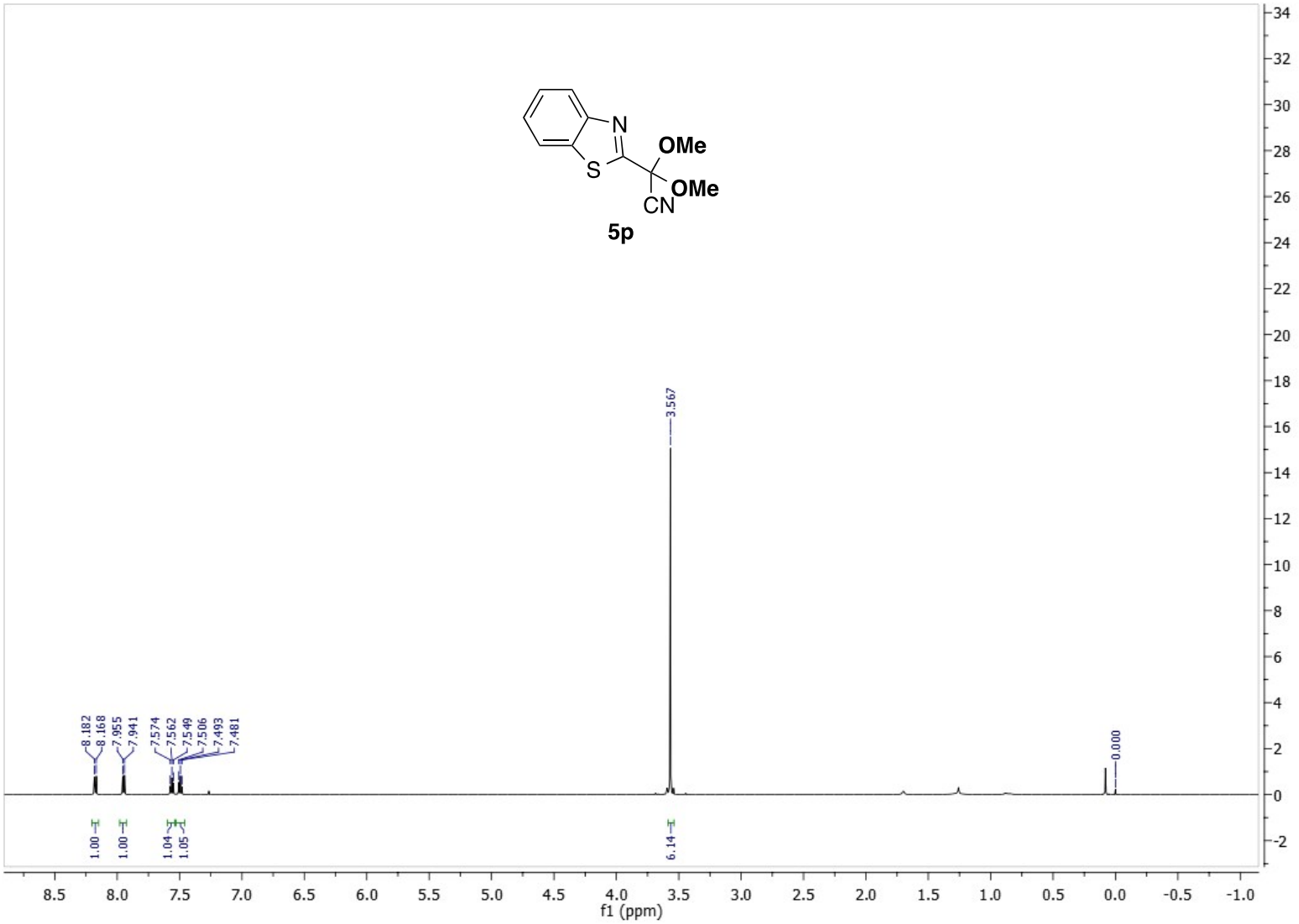

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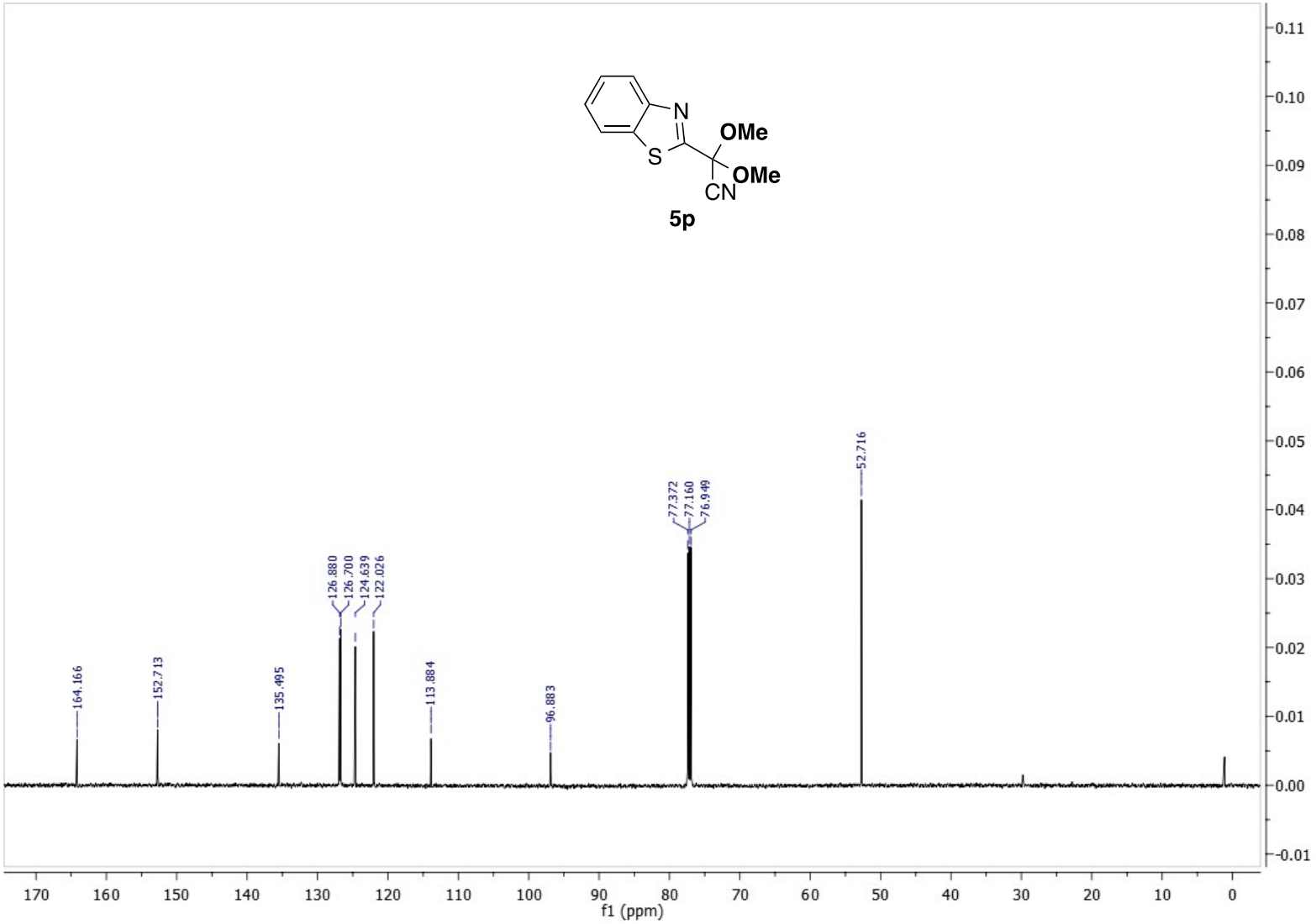

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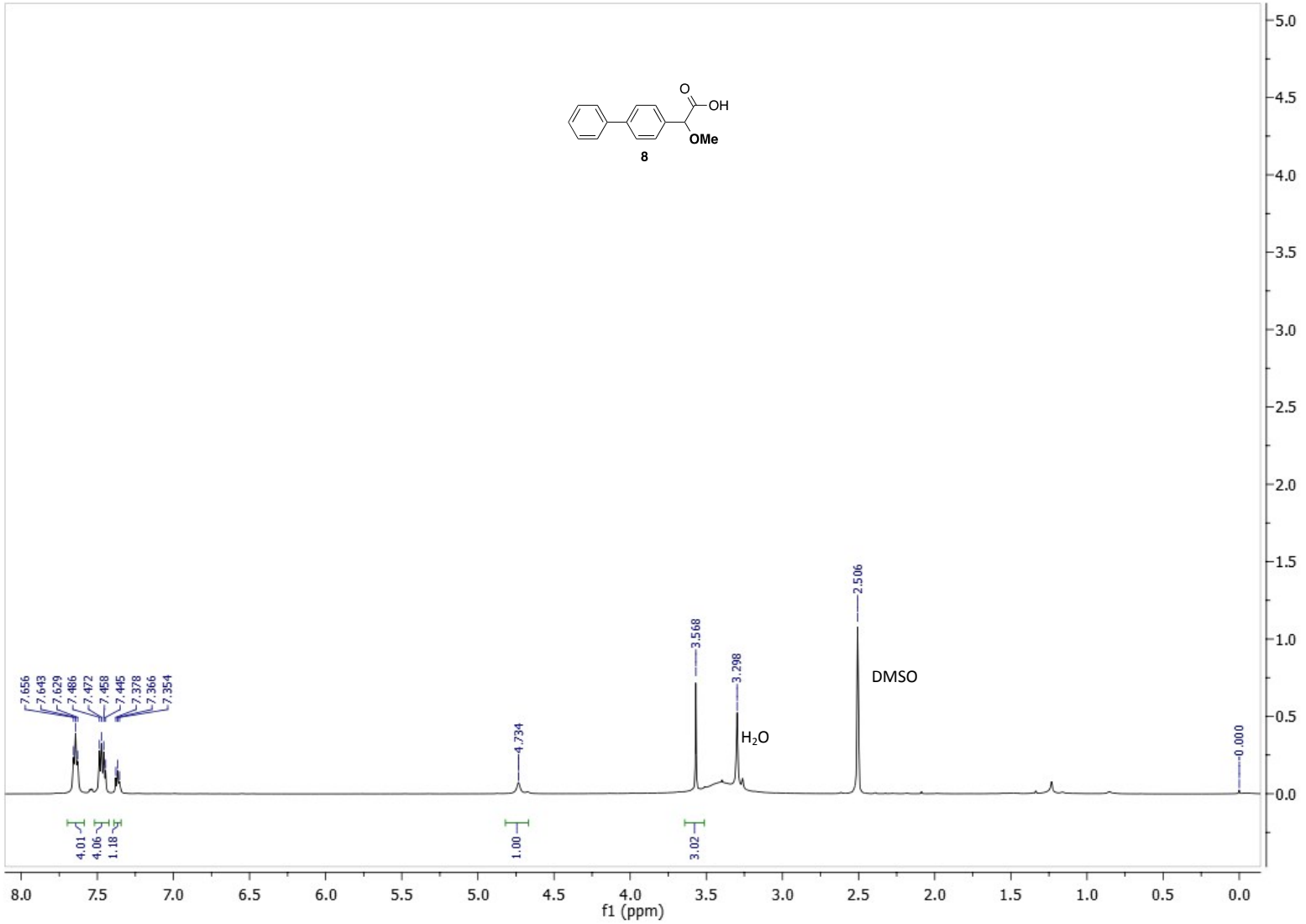
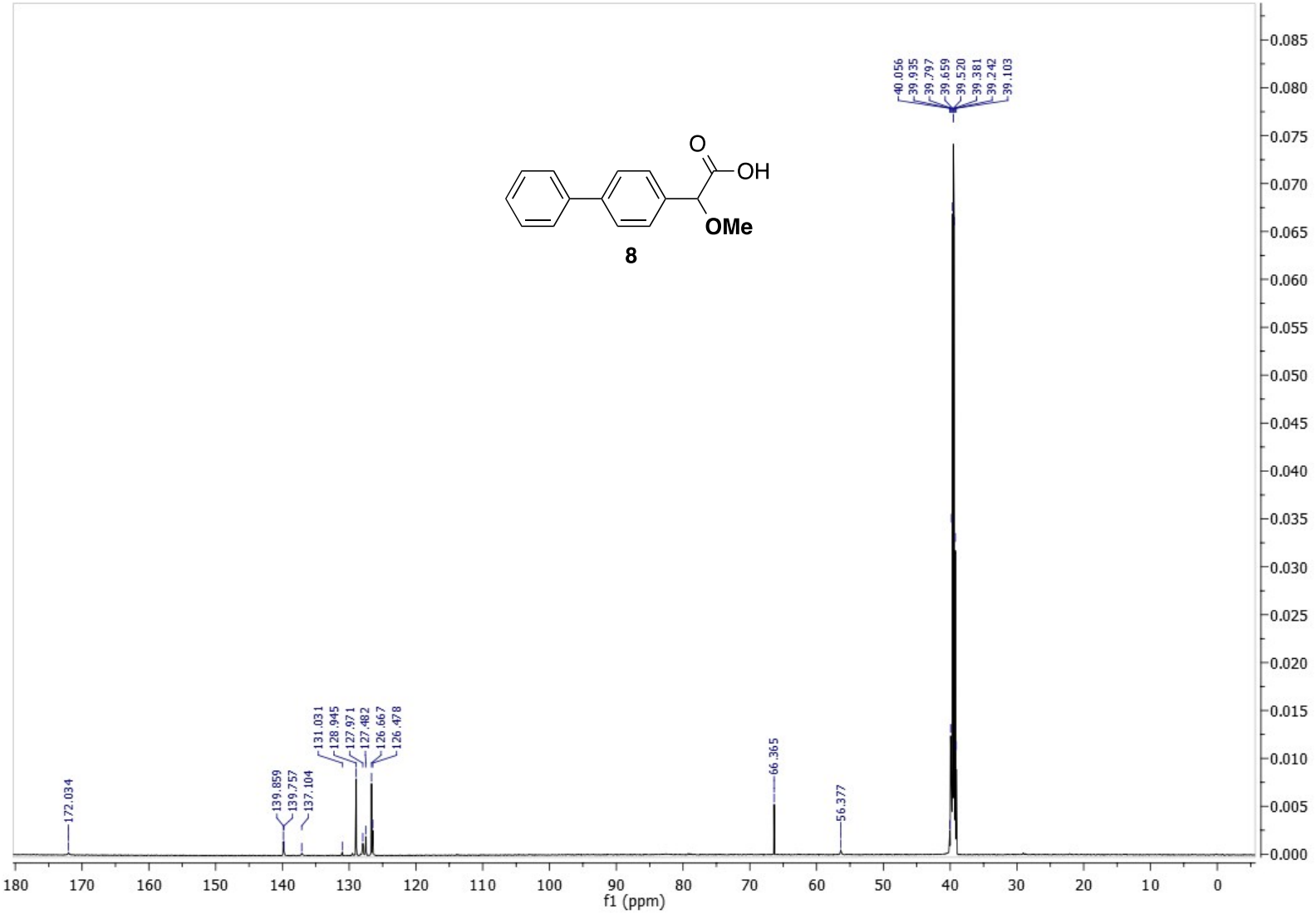


^{13}C NMR (151 MHz, DMSO-d_6):



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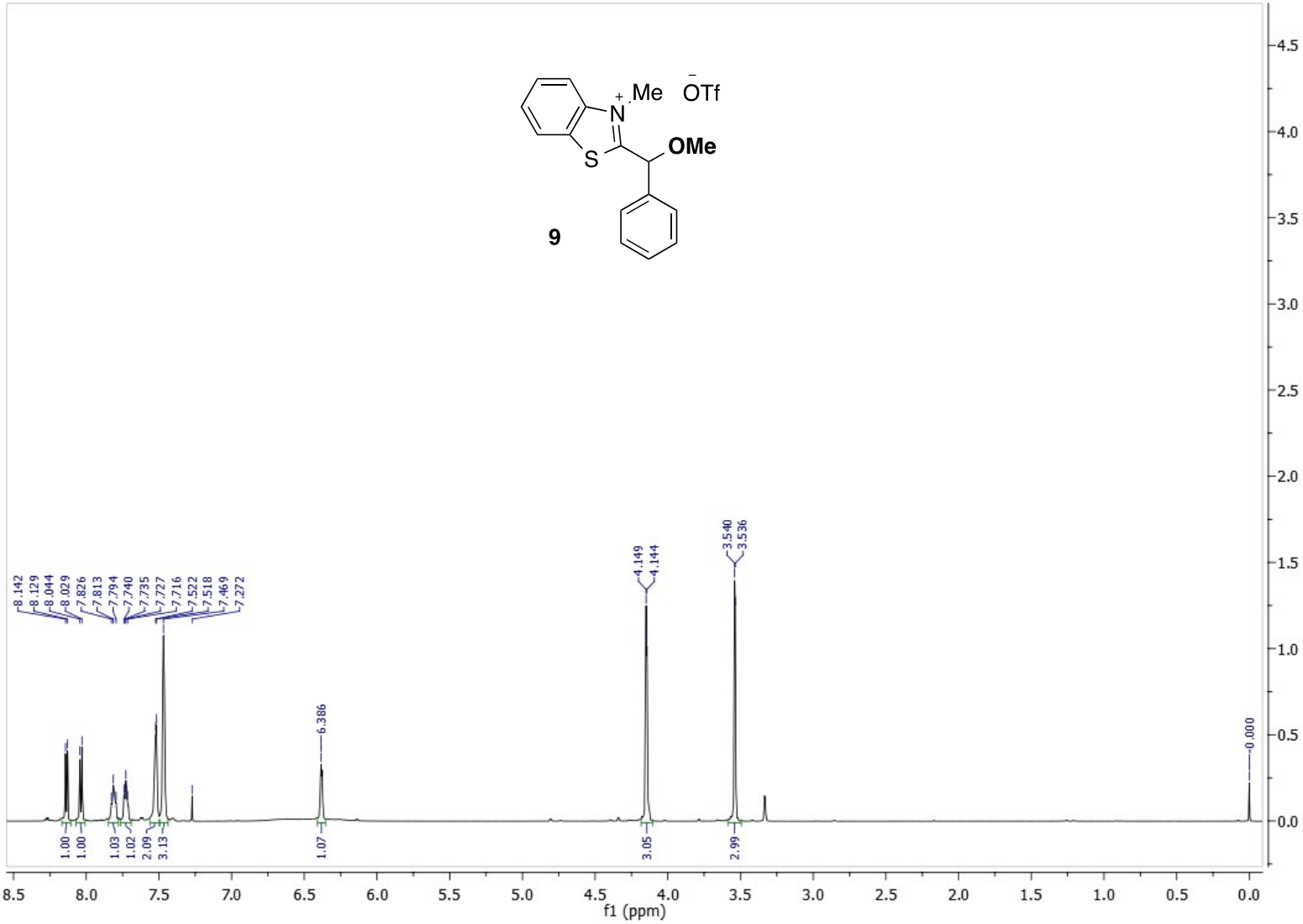

^{13}C NMR (151 MHz, $CDCl_3$):