

Supporting Information

Electrochemical Nozaki–Hiyama–Kishi Coupling: Scope, Applications, and Mechanism

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Table of Contents

General Experimental.....	5
Optimization Details	6
Preparation of Alkenyl Bromides	8
Compound S6.....	8
Compound S17.....	12
Compound S18.....	12
Preparation of NHPI Redox-Active Esters (General Procedure B)	15
Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Racemic, General Procedure C)	16
Graphical Guide for Electrochemical Nozaki–Hiyama–Kishi Coupling (Racemic).....	17
Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Asymmetric, General Procedure D) .	20
Graphical Guide for Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Asymmetric)....	22
Electrochemical Decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling (General Procedure E)	
.....	24
Graphical Guide for Electrochemical Decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling	25
Troubleshooting: Frequently Asked Questions	27
Experimental Procedures and Characterization Data	30
Compound 3	30
Compound 4	30
Compound 5	31
Compound 6	31
Compound 7	32
Compound 8	33
Compound 9	33
Compound 10	34
Compound 11	34
Compound 12	35
Compound 13	35
Compound 14	36
Compound 15	37
Compound 16	37
Compound 17	38
Compound 18	38
Compound 19	39
Compound 20	39
Compound 21	40
Compound 22	41
Compound 23	41
Compound 24	42
Compound 25	42
Compound 26	43
Compound 27	44
Compound 28	44

Compound 29	45
Compound 30	45
Compound 31	46
Compound 32	46
Compound 33	47
Compound 34	47
Compound 35	48
Compound 36	49
Compound 37	49
Compound 38	50
Compound 46	51
Compound 47a	51
Compound 47b	52
Compound 49	53
Compound 50a	54
Compound 50b	54
Compound 51	55
Compound 52	56
Compound 54	57
Compound 55a	58
Compound 55b	58
Compound 57	60
Compound S28	62
Compound 60	63
Compound 61	63
Compound 62	64
Compound 63	65
Compound 64	65
Compound 65	66
Compound 66	66
Compound 67	67
Compound 68	67
Compound 69	68
Compound 70	69
Compound 71	69
Compound 72	70
Compound 73	71
Compound 74	71
Compound 75	72
Compound 76	73
Compound 77	73
Compound 78	74
Compound 79	74
Compound 80	75

Compound 84	76
Reaction Progress Kinetic Analysis	77
Procedure for electrochemical NHK reaction	77
Analysis	78
Results	78
Procedure for classical NHK reaction	79
Results	81
Procedure for electrochemical decarboxylative NHK reaction	83
Procedure for classical decarboxylative NHK reaction	84
Results	85
General Details for UV-vis Spectroscopy and Electroanalytical Studies	88
Cyclic Voltammetry	91
UV-vis Studies	100
UV-vis Spectroelectrochemical Studies	102
References	106
NMR Spectra	111

General Experimental

Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), *N,N*-dimethylformamide (DMF), and acetonitrile (CH_3CN) were obtained by passing the previously degassed solvents through an activated alumina column. $\text{NiCl}_2\cdot\text{glyme}$ (98%) was purchased from Sigma-Aldrich. CrCl_2 was purchased from Strem and stored in the glovebox. Cp_2ZrCl_2 was purchased from Sigma-Aldrich. Cp_2ZrHCl was purchased from Strem and stored in the glovebox. Tetrabutylammonium bromide (TBAB) was purchased from Combi-Blocks. NiBr_2 was purchased from Sigma-Aldrich. CrCl_3 and TMSCl was purchased from Oakwood Chemical. Proton Sponge was purchased from Alfa Aesar. All the other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous material. TLC was performed on 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, and cerium ammonium molybdate (CAM) or KMnO_4 and heat as developing agents. NMR spectra were recorded on Bruker DRX-600, DRX-500, and AMX-400 instruments and are calibrated using residual undeuterated solvent (CHCl_3 at 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR; C_6H_6 at 7.16 ppm ^1H NMR, 128.06 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). High-resolution mass spectra (HRMS) were recorded on Waters LC with G2-XS TOF mass spectrometer by electrospray ionization time-of-flight reflectron experiments. GCMS (EI) were recorded on Agilent 7820A GC systems and 5975 Series MSD. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected.

Optimization Details

Evaluation of electrolytes

Reaction scheme for the evaluation of electrolytes:

c1ccccc1CC=O (0.2 mmol) + CC(=C)Br (0.4 mmol)

 Reagents: NiBr_2 (2 mol%), CrCl_2 (20 mol%), Cp_2ZrCl_2 (1.0 equiv), DMF, **electrolytes (0.1 M)**

 Conditions: $\text{Al}(+)/\text{Ni foam}(-)$, $E_{\text{cell}} = 2 \text{ V}$, 5.9 F/mol

 Product: c1ccccc1CC(O)C(=C)C

entry	electrolytes	yield (%)
1	TBAPF ₆	37
2	TBABF ₄	41
3	TBAB	42
4	TBAClO ₄	40
5	LiClO ₄	41
6	LiCl	16
7	LiBr	38

Evaluation of ligands for Ni

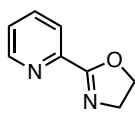
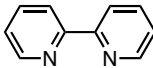
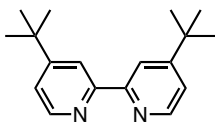
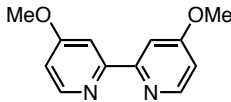
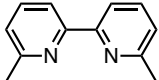
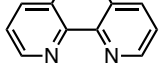
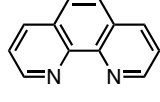
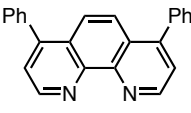
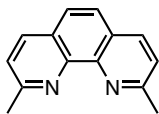
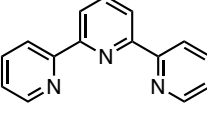
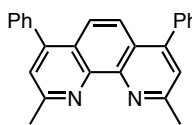
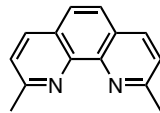
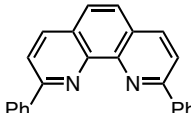
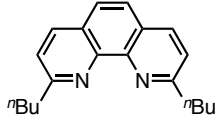
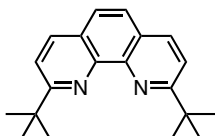
Reaction scheme for the evaluation of ligands for Ni:

c1ccccc1CC=O (0.2 mmol) + CC(=C)Br (0.4 mmol)

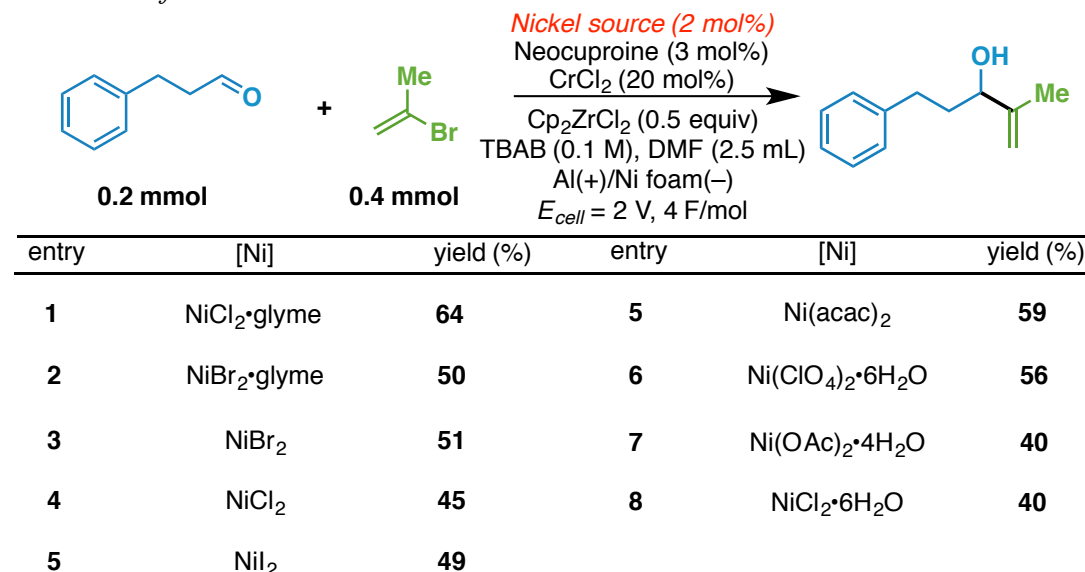
 Reagents: $\text{NiCl}_2 \cdot \text{glyme}$ (2 mol%), **Ligand (3 mol%)**, CrCl_2 (20 mol%)

 Conditions: Cp_2ZrCl_2 (0.5 equiv), TBAB (0.1 M), DMF (2.5 mL), $\text{Al}(+)/\text{Ni foam}(-)$, $E_{\text{cell}} = 2 \text{ V}$, 4 F/mol

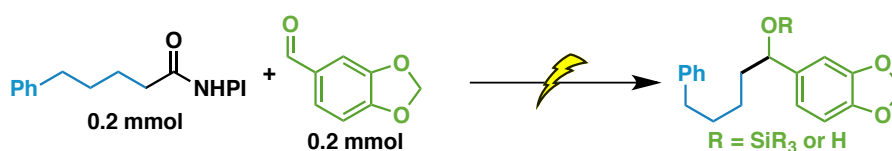
 Product: c1ccccc1CC(O)C(=C)C

 29%	 40%	 25%	 33%
 42%	 37%	 37% + 37% SM	 35%
 64%	 47%	 60%	$\text{Ni}(\text{dppp})\text{Cl}_2$ 58%
 25% + 41% SM	 58%	 64%	 49%
	 70%	 27% + 45% SM	

Evaluation of nickel sources

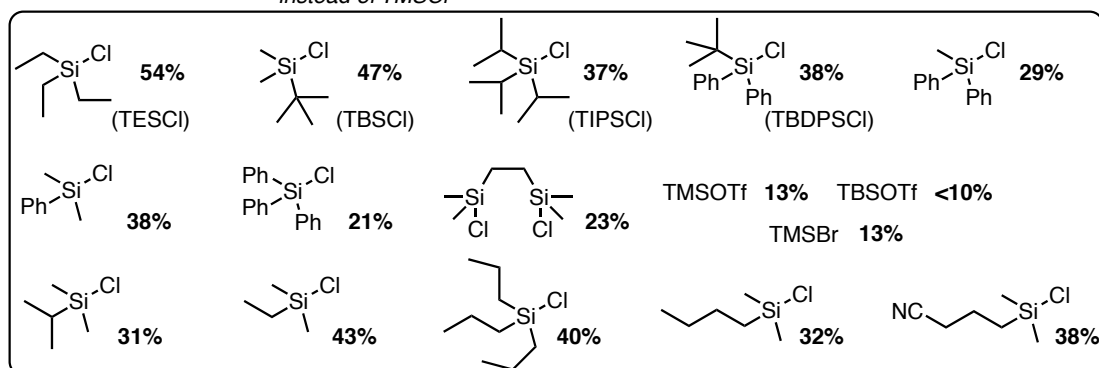


Electrochemical decarboxylative NHK coupling



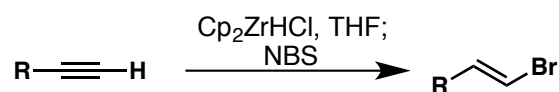
0.2 mmol RAE, 0.2 mmol aldehyde,
CrCl₃ (20 mol%), TMSCl (2.0 eq.),
TBAClO₄ (0.1 M), DMF (2.5 mL),
Al(+)/Ni foam(-), 2.5 mA, 12 h **36% yield**

evaluation of different chlorosilanes instead of TMSCl



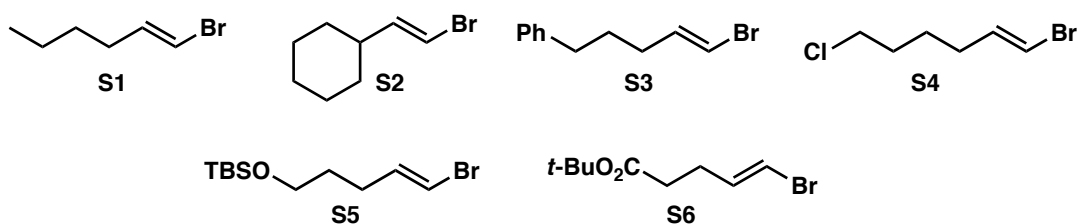
Preparation of Alkenyl Bromides

General Procedure A1

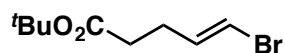


Schwartz's reagent (1.1 equiv) was added to a flame-dried round-bottom flask containing a magnetic stir bar in the glovebox. *Note: Schwartz's reagent was stored in a glovebox to ensure the quality of the reagent.* The round-bottom flask was removed from the glovebox, placed under Ar atmosphere, and wrapped in aluminum foil to keep it from light. THF (0.5 M) was added via syringe, and the alkyne (1 equiv) was added dropwise to the stirring mixture. The reaction mixture was stirred for one hour, and *N*-bromosuccinimide was added in one portion (1.1 equiv). The reaction mixture was stirred for 30 min, then quenched with saturated aq. NaHCO₃ solution. The solution was extracted with ether, and the organic layer was dried with Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography over silica gel.

The following alkenyl bromides were prepared following **General Procedure A1**. The NMR spectra of **S1**,¹ **S2**,² **S3**,² **S4**,³ and **S5**⁴ matched those reported in literature. The characterization data for **S6** is reported below.



Compound S6



Prepared from *tert*-butyl pent-4-ynoate⁵ following **General Procedure A1** with 64 % yield.

Physical State: yellowish oil.

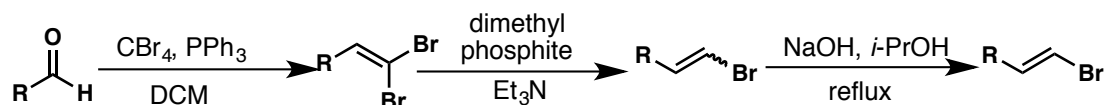
$R_f = 0.6$ (hexanes/EtOAc 9:1, KMnO₄).

¹H NMR (500 MHz, CDCl₃): δ 6.20 – 6.11 (m, 1H), 6.11 – 6.04 (m, 1H), 2.33 – 2.27 (m, 4H), 1.43 (s, 9H).

¹³C NMR (126 MHz, CDCl₃): δ 171.8, 136.2, 105.7, 80.7, 34.5, 28.6, 28.2.

The desired mass for HRMS was not observed.

General Procedure A2

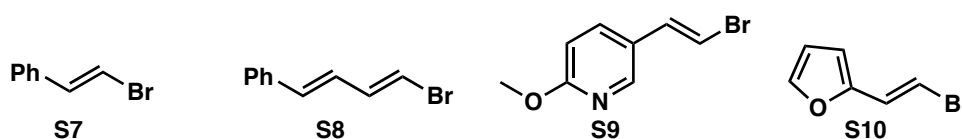


A flame-dried round-bottom flask equipped with a magnetic stir bar was charged with tetrabromomethane (2 equiv) and triphenylphosphine (4 equiv). DCM (0.5 M) was added, and the reaction was cooled to 0 °C. The aldehyde (1 equiv) was dissolved in DCM (0.5 M) and added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred until TLC showed aldehyde was fully consumed. Pentane was added, and triphenylphosphine oxide (TPPO) precipitated out. Filtration and evaporation of the solvent afforded the crude dibromide, which was directly used for the next step.

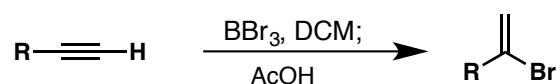
The dibromoalkene (1 equiv) and dimethyl phosphite (3 equiv) were added to a round-bottom flask with a magnetic stir bar and sealed under Ar. The solution was cooled to 0 °C, and triethylamine (3 equiv) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with water and extracted with Et₂O. The organic layer was washed with brine, dried with Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica) to afford the alkenyl bromide.

The crude alkenyl bromide (1.0 equiv) was dissolved in *i*PrOH (0.5 M), NaOH (1.0 equiv) was added, and the mixture was heated to reflux for 1.5 hours. The reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with ether, washed with 1 M HCl, and dried over Na₂SO₄. After filtration and concentration, the crude product was purified by flash chromatography (silica).

The following alkenyl bromides were prepared following **General Procedure A2**. The NMR spectra of **S7**,⁶ **S8**,⁶ **S9**,⁷ and **S10**⁶ matched those reported in literature.

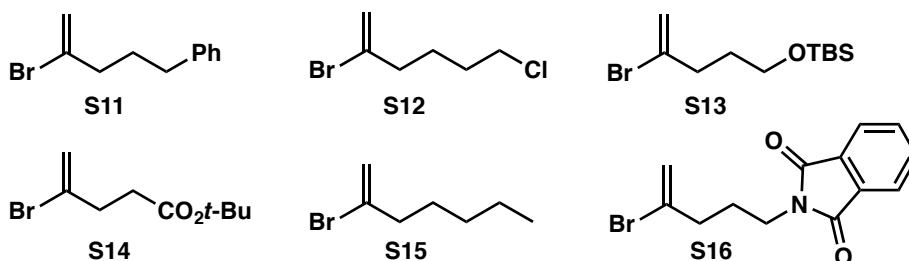


General Procedure A3



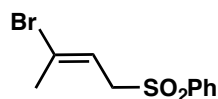
A solution of boron tribromide (0.5 equiv) in DCM (1 M) was cooled to $-78\text{ }^{\circ}\text{C}$ in an oven-dried round-bottom flask under Ar atmosphere. To this was added alkyne (1.0 equiv) dropwise. The reaction mixture was stirred for 1 hour at $-78\text{ }^{\circ}\text{C}$, allowed to warm to room temperature, and stirred for an additional 2 hours. Subsequently, acetic acid (30 equiv) was carefully added, and this solution was stirred for another hour at room temperature. The reaction mixture was quenched with saturated aq. NaHCO_3 solution and extracted with DCM. The combined organic layers were washed with brine, dried with Na_2SO_4 , filtered, and concentrated in vacuo. The crude mixture was purified by column chromatography.

The following alkenyl bromides were prepared following **General Procedure A3**. The NMR spectra of **S11**,⁸ **S12**,⁹ **S13**,¹⁰ **S14**,¹¹ **S15**,¹² and **S16**¹³ matched those reported in literature.



Other Alkenyl Bromides

Compound S17



(*E*)-3-bromobut-2-en-1-ol¹⁴ (1.0 equiv), triethylamine (1.5 equiv), and DMAP (0.1 equiv) were dissolved in DCM (0.1 M). MsCl (1.2 equiv) was added dropwise to the solution at 0 °C. The reaction mixture was stirred for 1 hour and quenched with saturated NaHCO₃ (aq.) solution. The organic layer was separated, washed with 1 M HCl and brine, dried, and concentrated. The crude mixture was dissolved in DMF (0.2 M), and sodium benzenesulfonic acid (2.0 equiv) was added. The reaction mixture was stirred for 30 min. The solution was poured into water and extracted with ether. The organic layer was washed with brine, then dried with Na₂SO₄, filtered, and concentrated. The crude product was purified by silica gel chromatography.

Physical State: colorless sticky oil.

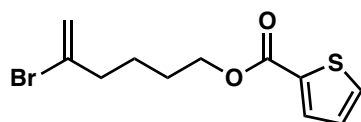
*R*_f = 0.43 (hexanes/EtOAc 2:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 7.92 – 7.86 (m, 2H), 7.72 – 7.65 (m, 1H), 7.59 (dd, *J* = 8.4, 7.2 Hz, 2H), 5.87 (tq, *J* = 8.4, 1.5 Hz, 1H), 3.75 (d, *J* = 8.3 Hz, 2H), 1.93 – 1.90 (m, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 138.2, 134.2, 129.7, 129.5, 128.7, 118.4, 56.8, 23.4.

HRMS: Calc'd for C₁₀H₁₂BrO₂S, [M+H]⁺ 274.9736; found 274.9683.

Compound S18



5-bromohex-5-en-1-ol¹⁵ (1.0 equiv), 2-thiophenecarboxylic acid (1.5 equiv), and DMAP (0.1 equiv) were dissolved in DCM (0.1 M). EDCI (1.5 equiv) was added slowly to the solution, and the reaction mixture was stirred overnight. After TLC showed alcohol was fully consumed, the reaction mixture was quenched with saturated

NaHCO₃ (aq.) solution and extracted with DCM. The organic layer was washed with brine, then dried with Na₂SO₄, filtered, and concentrated. The crude product was purified by silica gel chromatography.

Physical State: yellow oil.

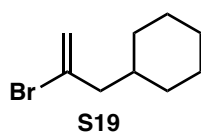
R_f = 0.5 (hexanes/EtOAc 9:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 7.80 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.60 (q, *J* = 1.3 Hz, 1H), 5.42 (d, *J* = 1.7 Hz, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.50 (td, *J* = 7.1, 1.2 Hz, 2H), 1.81 – 1.69 (m, 4H).

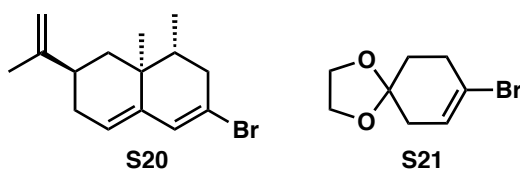
¹³C NMR (126 MHz, CDCl₃): δ 162.3, 134.1, 134.0, 133.4, 132.4, 127.8, 117.1, 64.8, 40.9, 27.5, 24.4.

HRMS: Calc'd for C₁₁H₁₄BrO₂S, [M+H]⁺ 288.9892; found 288.9848.

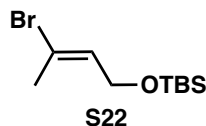
Alkenyl bromide **S19** was prepared according to a procedure reported by Breit and coworkers.¹²



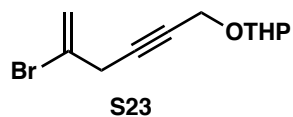
Alkenyl bromides **S20** and **S21** were prepared according to a procedure reported by Reisman and coworkers.¹⁶



Alkenyl bromide **S22** was prepared according to a procedure reported by Pattenden and coworkers.¹⁷



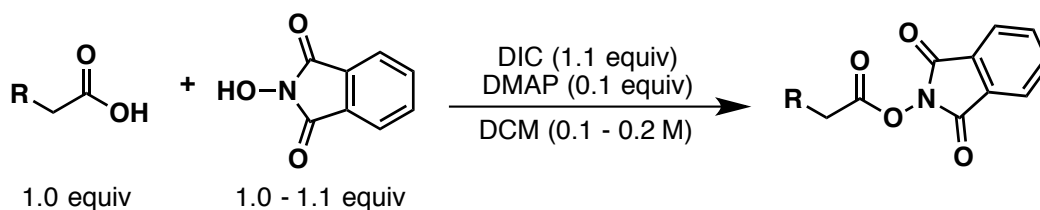
Alkenyl bromide **S23** was prepared according to a procedure reported by Chakraborty and coworkers.¹⁸



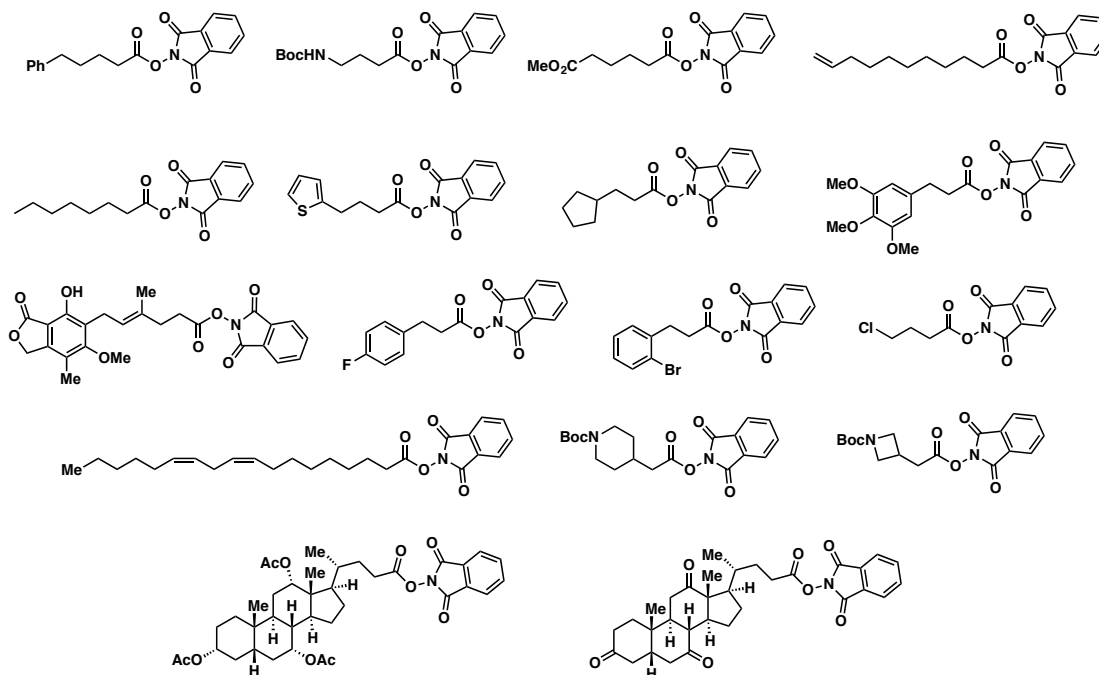
2-Bromopropene was purchased from a commercial source (Combi-Blocks).

1-Bromoethene was purchased from a commercial source (Acros) as 1.0 M solution in THF.

Preparation of NHPI Redox-Active Esters (General Procedure B)



NHPI esters were prepared according to a previously reported procedure.¹⁹ A round-bottom flask or culture tube was charged with carboxylic acid (1.0 equiv), *N*-hydroxyphthalimide (1.0 – 1.1 equiv), and DMAP (0.1 equiv). DCM was added (0.1 – 0.2 M), and the mixture was stirred vigorously. [Note: Carboxylic acid was added via syringe (*if liquid*)]. DIC (1.1 equiv) was then added dropwise via syringe, and the reaction mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 and 12 hours. The mixture was filtered (through a thin pad of Celite, SiO₂, or frit funnel) and rinsed with additional DCM and Et₂O. Solvents were removed under reduced pressure, and purification of the crude mixture by column chromatography afforded the desired NHPI redox-active ester. If necessary, the NHPI redox-active ester could be further recrystallized from DCM/MeOH.

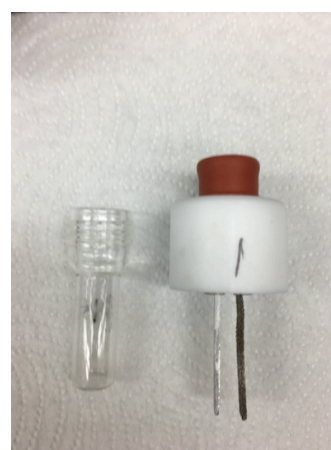
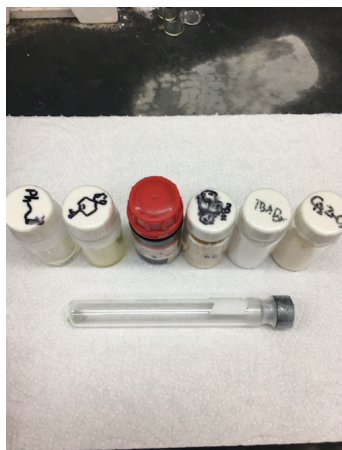
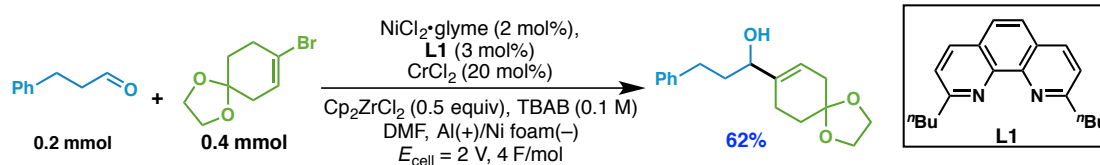


Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Racemic, General Procedure C)

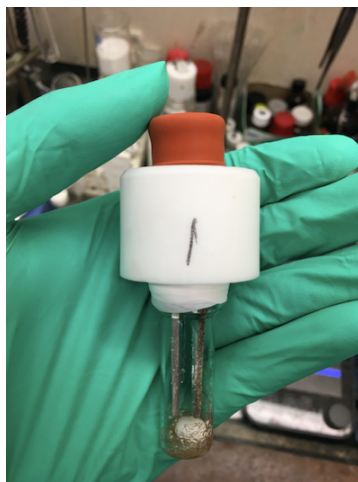
Preparation of CrCl₂ solution in DMF (0.08 M): A screw-capped culture tube was charged with CrCl₂ (30 mg, 0.24 mmol) in the glovebox. The tube was removed from the glovebox and placed under an argon balloon, whereupon degassed DMF (3 mL) was added via a syringe. The resulting mixture was sonicated until a homogeneous green solution was obtained.

Procedure for the electrochemical Nozaki–Hiyama–Kishi reaction: An ElectroSyn vial (5 mL) with a magnetic stir bar was charged with NiCl₂·glyme (0.9 mg, 0.004 mmol, 2 mol%), 2,9-dibutyl-1,10-phenanthroline (1.8 mg, 0.006 mmol, 3 mol%), aldehyde (0.2 mmol, 1.0 equiv), alkenyl bromide (0.4 mmol, 2.0 equiv), Cp₂ZrCl₂ (29 mg, 0.1 mmol, 0.5 equiv), and TBAB (0.1 M, 80 mg). The ElectroSyn vial cap equipped with anode (aluminum) and cathode (nickel foam) was inserted into the mixture. The vial was then evacuated, and backfilled with an argon balloon for three cycles. *[Note: volatile aldehyde and alkenyl bromide should be added after this step.]* CrCl₂ solution in DMF (0.5 mL, 0.04 mmol, 20 mol%) and additional DMF (2.0 mL) were added to the vial via syringe. The ElectroSyn was set up as follows: *New exp. > Constant voltage > 2 V > No ref. electrode > Total charge > 0.2 mmol, 4 F/mol > No alternating polarity > Start.* After the reaction stopped, the ElectroSyn vial cap was removed and electrodes were rinsed with EtOAc. Water was added, and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography or preparative thin-layer chromatography to furnish the desired product.

Graphical Guide for Electrochemical Nozaki–Hiyama–Kishi Coupling (Racemic)



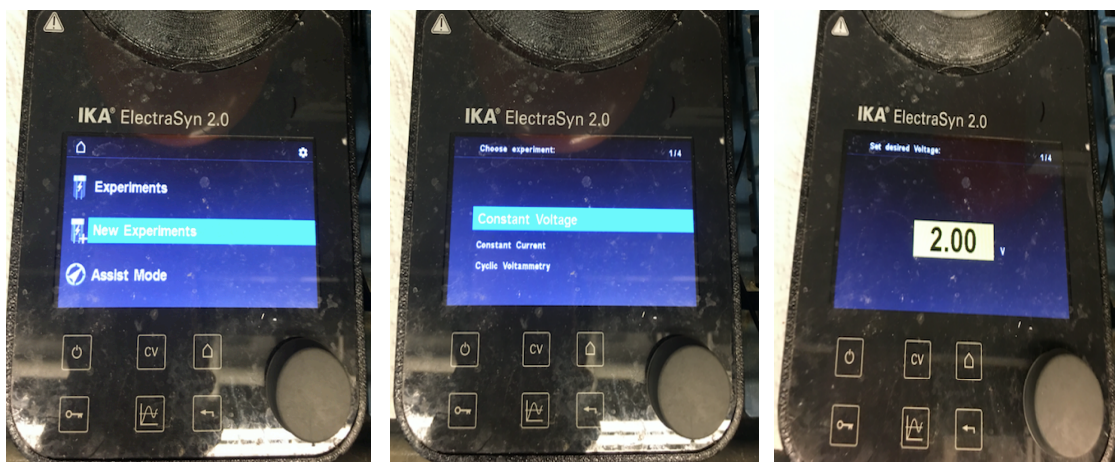
Left: all reagents for this reaction. **Center:** electrodes and parts needed. **Right:** connect the electrodes to the ElectroSyn cap.



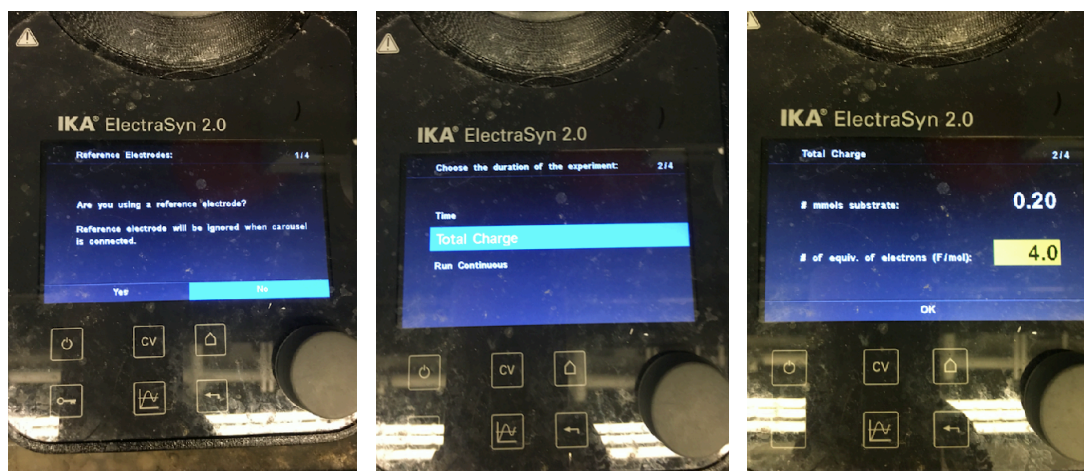
Left: weigh all reagents into an ElectroSyn vial wrapped with Teflon tape. **Center:** fasten the ElectroSyn cap to the vial. **Right:** connect the reaction vial to a vacuum line through a needle.



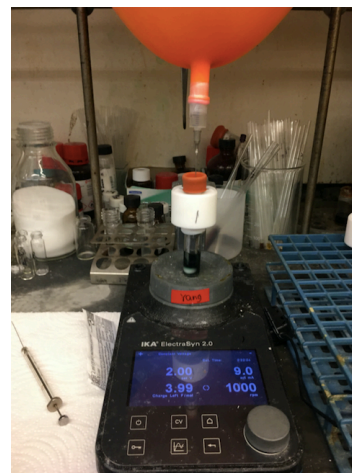
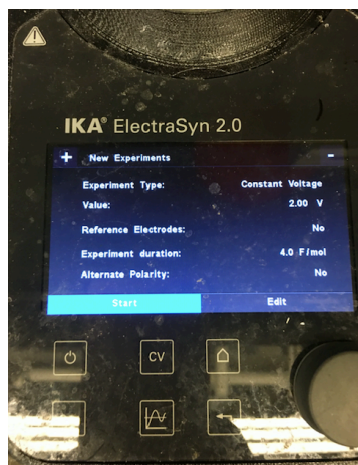
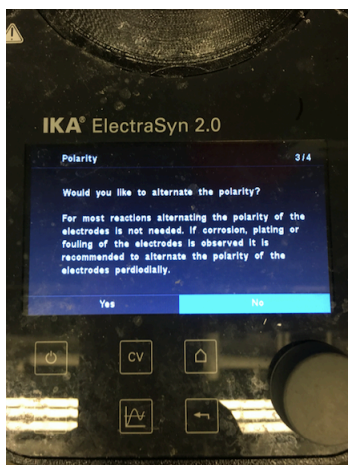
Left: evacuate and backfill the reaction vial with an argon balloon for three cycles. **Center:** add degassed DMF (1.5 mL) to the vial and stir for 2 minutes. **Right:** add degassed DMF (7 mL) to the culture tube containing CrCl_2 (35 mg, 0.28 mmol).



Left: select "New Experiments". **Center:** select "Constant Voltage". **Right:** set the voltage to "2.00 V".



Left: no need to use reference electrode. **Center:** select "Total Charge". **Right:** select 0.2 mmol of substrate and 4.0 F/mol.



Left: no need to alternate the polarity. **Center:** start the reaction when ready. **Right:** add 1.0 mL CrCl_2 solution in DMF to the vial and start the reaction.



Left: after completion of reaction, transfer the reaction mixture and rinse the electrodes into a separatory funnel with EtOAc and water. **Center:** wash the organic layer with brine. **Right:** obtain crude product.

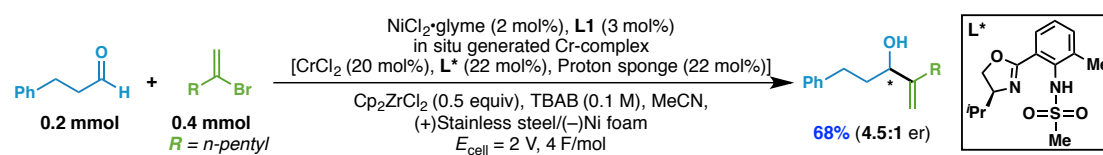
Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Asymmetric, General Procedure D)

Preparation of CrCl₂-Ligand complex solution in CH₃CN (0.08 M): A screw-capped culture tube with a magnetic stir bar was charged with CrCl₂ (30 mg, 0.24 mmol, 1.0 equiv), Proton Sponge (57 mg, 0.26 mmol, 1.1 equiv), and (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide (78 mg, 0.26 mmol, 1.1 equiv) in the glovebox. The tube was removed from the glovebox and placed under an argon balloon, whereupon degassed CH₃CN (3 mL) was added via a syringe. The resulting mixture was stirred at room temperature for one hour until a homogeneous solution was obtained.

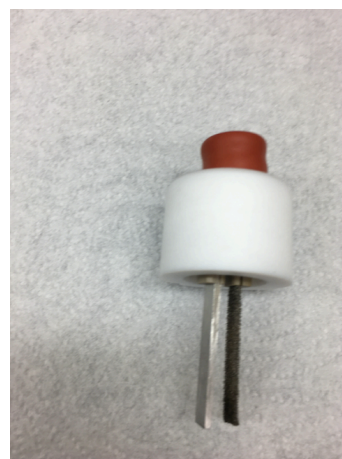
Procedure for the electrochemical Nozaki–Hiyama–Kishi reaction: An ElectroSyn vial (5 mL) with a magnetic stir bar was charged with NiCl₂·glyme (0.9 mg, 0.004 mmol, 2 mol%), 2,9-dibutyl-1,10-phenanthroline (1.8 mg, 0.006 mmol, 3 mol%), aldehyde (0.2 mmol, 1.0 equiv), alkenyl bromide (0.4 mmol, 2.0 equiv), Cp₂ZrCl₂ (29 mg, 0.1 mmol, 0.5 equiv), and TBAB (0.1 M, 80 mg). The ElectroSyn vial cap equipped with anode (stainless steel) and cathode (nickel foam) was inserted into the mixture. The vial was then evacuated and backfilled with an argon balloon for three cycles. [*Note: volatile aldehyde and alkenyl bromide should be added after this step.*] CrCl₂-Ligand complex solution in CH₃CN (0.5 mL, 0.04 mmol, 20 mol%) and additional CH₃CN (2.0 mL) were added to the vial via syringe. The ElectroSyn was set up as follows: *New exp. > Constant voltage > 2 V > No ref. electrode > Total charge > 0.2 mmol, 4 F/mol > No alternating polarity > Start.* After the reaction stopped, the ElectroSyn vial cap was removed and electrodes were rinsed with EtOAc. Water was added and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography or preparative thin-layer chromatography to furnish the desired product.

Enantiomeric ratio was determined by Mosher ester analysis using the following procedure: The product from above step (50 μmol , 1.0 equiv) and (*R*)-Mosher acid (35 mg, 150 μmol , 3.0 equiv) were dissolved in 1 mL DCM (0.05 M) and stirred at room temperature until dissolved. Dicyclohexylcarbodiimide (DCC) (31 mg, 150 μmol , 3.0 equiv) and DMAP (18 mg, 150 μmol , 3.0 equiv) were then added, and the reaction progress was monitored by TLC until starting material was completely consumed. The reaction mixture was diluted with Et_2O , partitioned with water, extracted with Et_2O , and the combined extracts dried over anhydrous Na_2SO_4 . The organic extracts were filtered, the solvent was evaporated in vacuo, and the residue was dissolved in CDCl_3 to determine er.

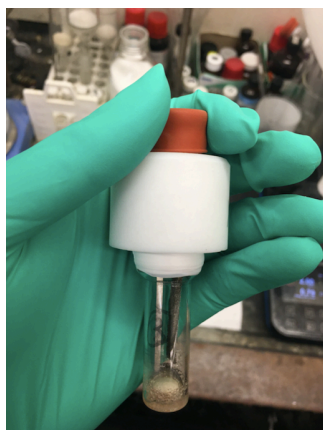
Graphical Guide for Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Asymmetric)



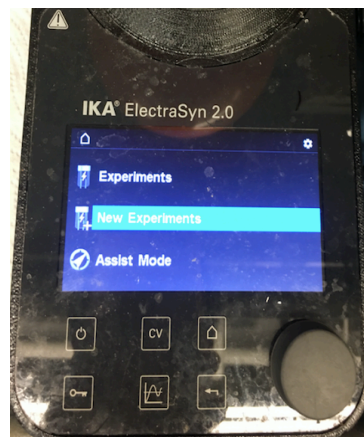
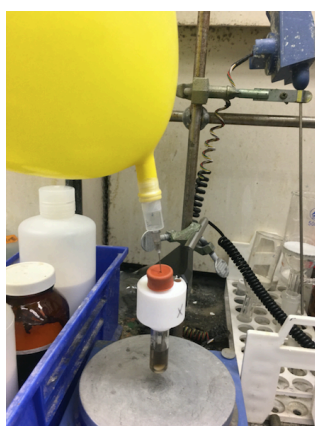
Left: all reagents for Cr-complex formation reaction. **Center:** weigh all the reagents in a culture tube, and then evacuate and backfill with argon three times. **Right:** add degassed CH₃CN to the culture tube and stir vigorously for 1 hour.



Left: all reagents for this reaction. **Center:** all the electrodes and parts for this reaction. **Right:** connect the electrodes to the ElectraSyn cap.



Left: weigh all the materials into the vial and fasten the cap to the vial. **Center:** evacuate and backfill with argon three times. **Right:** add degassed CH_3CN to the culture tube and stir for 2 minutes.



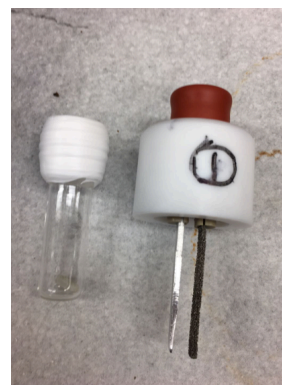
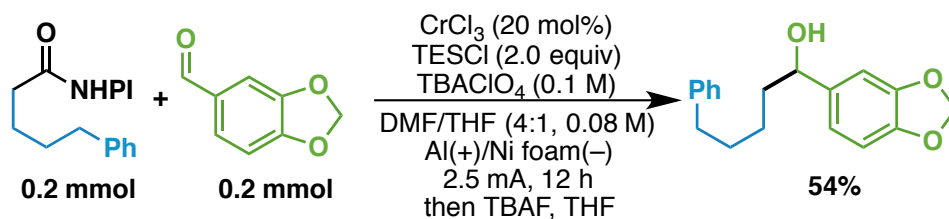
Left: homogeneous solution after one hour. **Center:** add 1 mL solution to the ElectraSyn vial. **Right:** set up the same parameters with General Procedure D.

Electrochemical Decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling (General Procedure E)

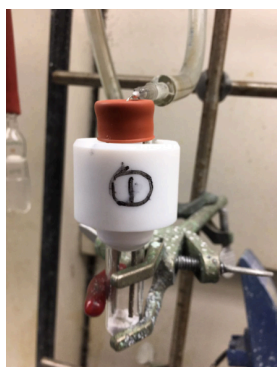
Procedure for the electrochemical decarboxylative Nozaki–Hiyama–Kishi (NHK)

Coupling: An ElectroSyn vial (5 mL) with a magnetic stir bar was charged with aldehyde (0.2 mmol, 1.0 equiv), redox-active ester (0.2 mmol, 1.0 equiv), CrCl_3 (6.4 mg, 0.04 mmol, 0.2 equiv), and TBAClO_4 (0.1 M, 85 mg). The ElectroSyn vial cap equipped with anode (aluminum) and cathode (nickel foam) was inserted into the mixture. The vial was then evacuated and backfilled with an argon balloon for three cycles. [Note: volatile aldehyde should be added after this step.] Then DMF (2.0 mL), THF (0.5 mL), and TESC1 (67 μL , 0.4 mmol, 2.0 equiv) were added to the vial via syringe. The ElectroSyn was set up as follows: *New exp. > Constant current > 2.5 mA > No ref. electrode > Time > 12 h > No alternating polarity > Start*. After the reaction was completed, the ElectroSyn vial cap was removed, and the electrodes were rinsed with EtOAc. Water was added, and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The crude material was then dissolved in THF (2 mL), and TBAF (1.0 M in THF, 0.3 mL) was added. After 2 h, the reaction was quenched with sat. NH_4Cl (aq.) and extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The crude mixture was then purified by flash column chromatography or preparative thin-layer chromatography to furnish the desired product.

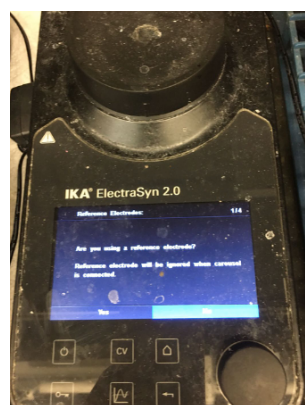
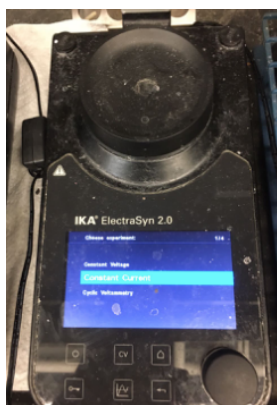
Graphical Guide for Electrochemical Decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling



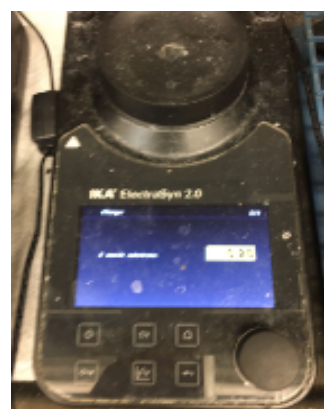
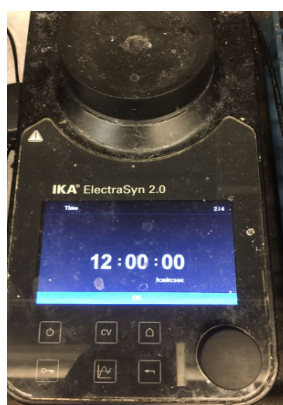
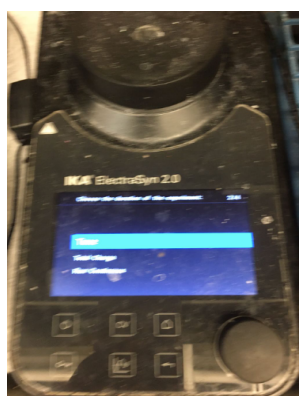
Left: all the electrodes and parts for this reaction. **Center:** all reagents for this reaction. **Right:** connect the electrodes to the ElectroSyn cap.



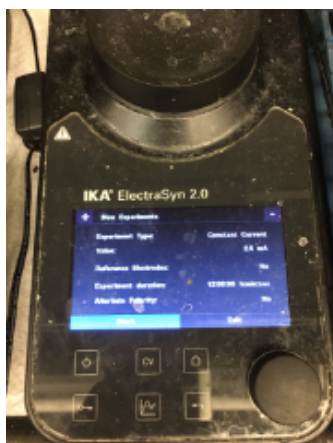
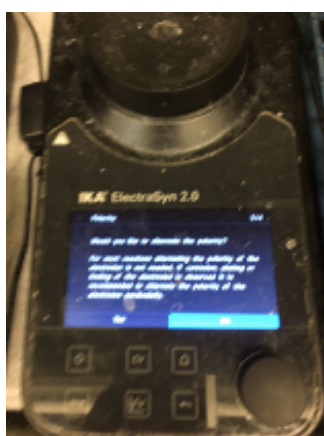
Left: weigh all the materials into the vial and fasten the cap to the vial; then evacuate and backfill with argon three times. **Center:** add 2.0 mL DMF and 0.5 mL THF. **Right:** add 67 μ L TESCl via micro syringe.



Left: select "constant current". **Center:** select "2.5 mA". **Right:** no need to use a reference electrode.



Left: select "Time". **Center:** select "12:00:00". **Right:** select "0.2 mmol".



Left: no need to alternate the polarity. **Center:** start the reaction when ready. **Right:** reaction completed.

Troubleshooting: Frequently Asked Questions

Electrochemical NHK coupling of alkenyl bromide and aldehyde

Question 1:

Are there any precautions that need to be taken for running this reaction?

Answer:

We used all the reagents without any special handling, but the CrCl_2 was weighed into a culture tube in the glovebox and taken out for use. The reaction is not particularly air-sensitive as it proceeds without freeze-pump-thaw. However, evacuation-argon backfill cycle and degassed solvent are still required to ensure the yield.

Question 2:

What can I do if I cannot reproduce the yield?

Answer:

Based on our experiences, certain aldehyde substrates will gradually be oxidized to acid, even when stored in the refrigerator under argon. Therefore, purification of aldehyde via flash column chromatography before use is recommended. Also, certain alkenyl bromides (such as (*E*)-2-(2-bromoethenyl)furan) are extremely unstable and should be used immediately after preparation. If the substrates are unlikely to be the cause of irreproducibility, make sure the reaction is degassed and the cap is screwed on tightly. Wrapping enough Teflon tape around the rim of the vial is an easy and effective way to improve sealing.

Question 3:

How do I clean the electrodes after the reaction?

Answer:

First, wash the electrodes with 1 N HCl, distilled water, and acetone. Then dry them in an oven. Once dried, scrape the aluminum electrodes with a razor blade to make the surface smooth and shiny.

Question 4:

What is the byproduct of this reaction?

Answer:

The major side reactions are homocoupling and proto-dehalogenation of the alkenyl halides. Sometimes, reduction of aldehyde to corresponding alcohol may also be observed.

Question 5:

How can I monitor the reaction and determine the yield?

Answer:

We have evaluated the reaction time on the standard substrate, which indicates 4 F/mol is enough for full conversion on 0.2 mmol scale. We ran the reaction without monitoring after 4 F/mol passed. Then, the reaction mixture was transferred into a separation funnel with EtOAc. The organic layer was washed with brine twice, dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. The yield was determined by crude ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

Question 6:

Is stirring crucial for this reaction?

Answer:

Stirring is crucial, and low yields will be obtained without stirring. Our preferred stirring rate is from 500 to 1000 rpm.

Question 7:

Does a longer reaction time cause a decrease in yield?

Answer:

We left the reaction running for 6 F/mol during optimization, and no significant decrease of yield was observed. In addition, we tested the stability of the model product under this reaction condition, and it was fully recovered from the reaction mixture.

Question 8:

Where can I get the electrode materials?

Answer:

Everything required for setting up this reaction can be obtained from IKA. (<https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/>).

Question 9:

How long does these reactions typically proceed?

Answer:

Reaction time varies based on different substrates, and typically ranges from 4–8 hours.

Electrochemical decarboxylative NHK coupling

Question 1:

Do I need a glovebox to run the reaction?

Answer:

We do not need a glovebox for electrochemical decarboxylative NHK coupling because we use CrCl_3 instead of CrCl_2 .

Question 2:

Are there any indicative color changes during the reaction?

Answer:

Yes, the color of the reaction mixture first turned to green, indicating the formation of a Cr(II) species, and ultimately became black or brown.

Question 3:

Why do you use TESCl? Have you tried other chlorosilanes?

Answer:

For extensive screening of chlorosilane, see the optimization part of SI.

Question 4:

Do I need to run this reaction under inert atmosphere?

Answer:

An inert atmosphere is required (N_2 or Ar) to ensure the full consumption of starting materials.

Question 5:

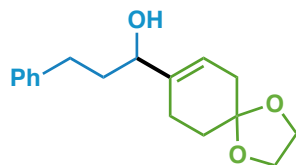
Since CrCl_3 is not soluble in DMF, did any soluble Cr source improve the yields?

Answer:

We tried several soluble Cr sources, such as $\text{CrCl}_3 \cdot 3\text{THF}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{CrCl}_3 \cdot \text{dtbpy}$, and did not obtain higher yields.

Experimental Procedures and Characterization Data

Compound 3



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 34.1 mg (62%) of the title compound **3**.

Physical State: colorless oil.

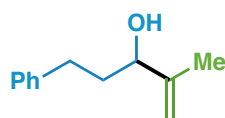
R_f = 0.46 (hexanes/EtOAc 2:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.28 (dd, J = 7.6, 0.9 Hz, 2H), 7.22 – 7.16 (m, 3H), 5.59 (ddd, J = 3.7, 2.6, 1.1 Hz, 1H), 4.06 (t, J = 6.6 Hz, 1H), 4.00 – 3.96 (m, 4H), 2.73 (ddd, J = 13.8, 9.0, 6.7 Hz, 1H), 2.62 (ddd, J = 13.8, 8.8, 7.1 Hz, 1H), 2.35 – 2.16 (m, 4H), 1.92 – 1.84 (m, 2H), 1.76 (ddd, J = 7.1, 6.2, 1.0 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 142.2, 139.8, 128.6, 128.5, 125.9, 120.4, 108.2, 75.2, 64.5, 36.7, 35.7, 32.2, 31.1, 23.0.

HRMS: Calc'd for $\text{C}_{17}\text{H}_{21}\text{O}_2$, $[\text{M}-\text{OH}]^+$ 257.1536; found 257.1548.

Compound 4



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 23.3 mg (66%) of the title compound **4**.

Physical State: colorless oil.

R_f = 0.50 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

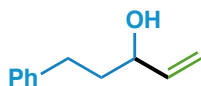
^1H NMR (500 MHz, CDCl_3): δ 7.30 (td, J = 7.4, 1.4 Hz, 2H), 7.25 – 7.17 (m, 3H), 4.99 (dt, J = 1.9, 0.9 Hz, 1H), 4.89 (t, J = 1.7 Hz, 1H), 4.10 (t, J = 6.5 Hz, 1H), 2.70 (dddd, J = 44.1, 13.9, 9.3, 6.7 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.77 – 1.73 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3): δ 147.5, 142.1, 128.6, 128.5, 125.9, 111.4, 75.4, 36.7,

32.0, 17.7.

Spectroscopic data are in accordance with that reported in the literature.²⁰

Compound 5



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 20.4 mg (63%) of the title compound **5**.

Physical State: colorless oil.

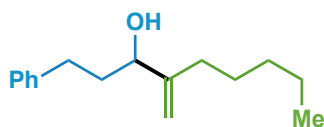
R_f = 0.38 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 5.91 (ddd, J = 17.3, 10.4, 6.2 Hz, 1H), 5.25 (dt, J = 17.2, 1.4 Hz, 1H), 5.15 (dt, J = 10.5, 1.3 Hz, 1H), 4.14 (dtt, J = 7.3, 6.0, 1.3 Hz, 1H), 2.81 – 2.66 (m, 2H), 1.93 – 1.81 (m, 2H).

¹³C NMR (126 MHz, CDCl₃): δ 142.0, 141.1, 128.6, 128.5, 126.0, 115.1, 72.6, 38.7, 31.8.

Spectroscopic data are in accordance with that reported in the literature.²¹

Compound 6



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 25.1 mg (54%) of the title compound **6**.

Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 31.5 mg (68%) of the title compound **40** and er was determined to be 4.5:1 by Mosher ester analysis.

Physical State: colorless oil.

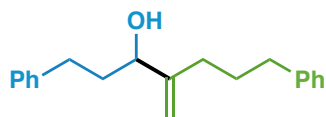
R_f = 0.60 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.05 (p, *J* = 1.1 Hz, 1H), 4.89 (q, *J* = 1.5 Hz, 1H), 4.11 (t, *J* = 6.8 Hz, 1H), 2.76 (ddd, *J* = 13.8, 10.0, 5.7 Hz, 1H), 2.66 (ddd, *J* = 13.8, 9.9, 6.5 Hz, 1H), 2.13 – 2.03 (m, 1H), 2.02 – 1.95 (m, 1H), 1.95 – 1.82 (m, 2H), 1.53 (d, *J* = 3.2 Hz, 1H), 1.51 – 1.43 (m, 2H), 1.32 (qt, *J* = 6.9, 3.6 Hz, 4H), 0.90 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 152.2, 142.2, 128.6, 128.5, 125.9, 109.6, 74.9, 37.3, 32.1, 31.9, 31.6, 27.8, 22.7, 14.2.

HRMS: Calc'd for C₁₆H₂₃, [M-OH]⁺ 215.1794; found 215.1793.

Compound 7



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 37.0 mg (66%) of the title compound **7**.

Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 34.2 mg (61%) of the title compound **42** and er was determined to be 4.0:1 by Mosher ester analysis.

Physical State: colorless oil.

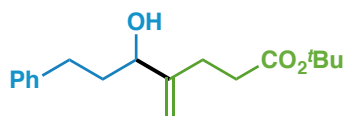
R_f = 0.50 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.31 – 7.27 (m, 4H), 7.19 (ddt, *J* = 8.7, 5.7, 1.7 Hz, 6H), 5.08 (p, *J* = 1.0 Hz, 1H), 4.91 (q, *J* = 1.5 Hz, 1H), 4.10 (dt, *J* = 7.8, 3.7 Hz, 1H), 2.75 (ddd, *J* = 13.7, 9.9, 5.7 Hz, 1H), 2.65 (qt, *J* = 9.3, 4.6 Hz, 3H), 2.15 (dtd, *J* = 14.8, 8.3, 7.5, 1.2 Hz, 1H), 2.08 – 2.02 (m, 1H), 1.94 – 1.78 (m, 4H), 1.50 (d, *J* = 3.6 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 151.7, 142.4, 142.1, 128.59, 128.55, 128.52, 128.47, 125.97, 125.92, 109.9, 74.9, 37.2, 35.9, 32.1, 31.1, 29.9.

HRMS: Calc'd for C₂₀H₂₃, [M-OH]⁺ 263.1794; found 263.1793.

Compound 8



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 31.4 mg (54%) of the title compound **8**.

Physical State: colorless oil.

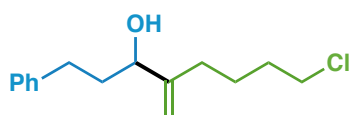
R_f = 0.50 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.31 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 5.09 – 5.06 (m, 1H), 4.87 (d, J = 1.4 Hz, 1H), 4.12 (td, J = 6.6, 2.8 Hz, 1H), 2.74 (dt, J = 13.8, 7.9 Hz, 1H), 2.64 (dt, J = 13.8, 8.0 Hz, 1H), 2.48 – 2.38 (m, 3H), 2.32 – 2.22 (m, 1H), 2.00 (d, J = 3.6 Hz, 1H), 1.89 (td, J = 8.1, 6.6 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3): δ 172.9, 150.5, 142.1, 128.6, 128.5, 126.0, 110.7, 80.7, 75.1, 37.2, 34.1, 32.1, 28.3, 26.1.

HRMS: Calc'd for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{Na}$, $[\text{M}+\text{Na}]^+$ 313.1774; found 313.1784.

Compound 9



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 36.0 mg (71%) of the title compound **9**.

Physical State: colorless oil.

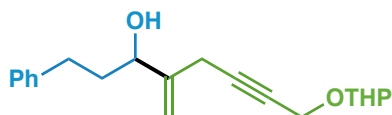
R_f = 0.43 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.32 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 5.08 (p, J = 1.0 Hz, 1H), 4.90 (q, J = 1.5 Hz, 1H), 4.11 (dd, J = 7.8, 5.0 Hz, 1H), 3.55 (t, J = 6.6 Hz, 2H), 2.76 (ddd, J = 13.7, 9.7, 5.9 Hz, 1H), 2.65 (ddd, J = 13.8, 9.6, 6.6 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.08 – 1.98 (m, 1H), 1.94 – 1.78 (m, 4H), 1.67 – 1.60 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 151.3, 142.0, 128.6, 128.5, 126.0, 110.2, 74.9, 45.0, 37.2, 32.5, 32.1, 30.7, 25.3.

HRMS: Calc'd for C₁₅H₂₀Cl, [M-OH]⁺ 235.1248; found 215.1288.

Compound 10



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 25.2 mg (40%) of the title compound **10**.

Physical State: yellowish oil.

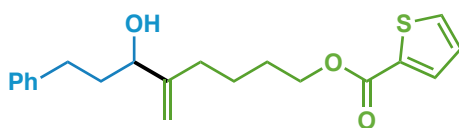
R_f = 0.27 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 7.28 (td, *J* = 7.3, 1.5 Hz, 2H), 7.23 – 7.16 (m, 3H), 5.26 (q, *J* = 1.6 Hz, 1H), 5.15 (q, *J* = 1.2 Hz, 1H), 4.82 (t, *J* = 3.5 Hz, 1H), 4.35 – 4.16 (m, 3H), 3.84 (ddd, *J* = 11.5, 9.0, 3.0 Hz, 1H), 3.53 (dtd, *J* = 11.2, 4.4, 1.6 Hz, 1H), 3.15 – 2.97 (m, 2H), 2.80 – 2.62 (m, 2H), 1.96 – 1.50 (m, 9H).

¹³C NMR (126 MHz, CDCl₃): δ 146.2, 141.9, 128.6, 128.5, 126.0, 112.6, 96.9, 83.3, 78.9, 74.2, 62.2, 54.7, 36.8, 32.0, 30.4, 25.5, 21.9, 19.2.

HRMS: Calc'd for C₂₀H₂₇O₃, [M+H]⁺ 315.1955; found 315.1953.

Compound 11



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 22.7 mg (33%) of the title compound **11**.

Physical State: yellowish oil.

R_f = 0.30 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

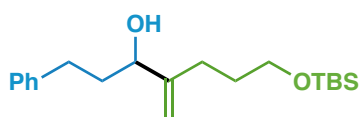
¹H NMR (600 MHz, CDCl₃): δ 7.79 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.54 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 – 7.17 (m, 3H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.08 (s, 1H), 4.90 (d, *J* = 1.6 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 2H), 4.11 (dt, *J* = 8.3, 4.4 Hz, 1H), 2.76 (ddd, *J* = 13.8, 9.9, 5.7 Hz, 1H), 2.65 (ddd, *J* = 13.8, 9.8, 6.5 Hz, 1H), 2.17

(dt, $J = 15.7, 7.9$ Hz, 1H), 2.07 (dt, $J = 15.5, 7.6$ Hz, 1H), 1.94 – 1.84 (m, 2H), 1.79 (tt, $J = 8.7, 6.7$ Hz, 2H), 1.62 (p, $J = 7.4, 7.0$ Hz, 2H), 1.54 (d, $J = 4.0$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 162.5, 151.4, 142.1, 134.1, 133.5, 132.4, 128.6, 128.5, 127.9, 126.0, 110.1, 65.1, 37.3, 32.2, 31.0, 28.7, 24.5.

HRMS: Calc'd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{S}$, $[\text{M}-\text{OH}]^+$ 327.1413; found 327.1418.

Compound 12



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 40.8 mg (61%) of the title compound **12**.

Following **General Procedure D** on 0.2 mmol scale using (*R*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 34.8 mg (52%) of the title compound **41** and er was determined to be 4.2:1 by Mosher ester analysis.

Physical State: colorless oil.

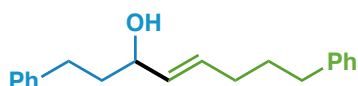
$R_f = 0.34$ (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.30 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 5.08 – 5.03 (m, 1H), 4.89 (q, $J = 1.5$ Hz, 1H), 4.14 – 4.08 (m, 1H), 3.65 (t, $J = 6.2$ Hz, 2H), 2.74 (ddd, $J = 13.7, 9.6, 6.1$ Hz, 1H), 2.64 (ddd, $J = 13.8, 9.6, 6.7$ Hz, 1H), 2.21 – 2.14 (m, 1H), 2.10 – 2.02 (m, 1H), 1.93 – 1.82 (m, 2H), 1.76 – 1.67 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3): δ 151.6, 142.2, 128.6, 128.5, 125.9, 110.2, 75.1, 63.0, 37.3, 32.2, 31.4, 27.9, 26.1, 18.5, –5.1.

HRMS: Calc'd for $\text{C}_{20}\text{H}_{35}\text{O}_2\text{Si}$, $[\text{M}+\text{H}]^+$ 335.2401; found 335.2395.

Compound 13



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 22.0 mg (39%) of the title compound **13**.

Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (3:1 hexanes/EtOAc) afforded 45.0 mg (80%) of the title compound **45** and er was determined to be 1.4:1 by Mosher ester analysis.

Physical State: colorless oil.

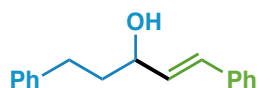
R_f = 0.35 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.32 – 7.25 (m, 4H), 7.23 – 7.15 (m, 6H), 5.68 (dtd, J = 15.4, 6.7, 1.0 Hz, 1H), 5.52 (ddt, J = 15.4, 7.0, 1.4 Hz, 1H), 4.08 (q, J = 6.7 Hz, 1H), 2.77 – 2.59 (m, 4H), 2.14 – 2.05 (m, 2H), 1.94 – 1.76 (m, 2H), 1.73 (tt, J = 7.6, 6.7 Hz, 2H), 1.43 (s, 1H).

^{13}C NMR (126 MHz, CDCl_3): δ 142.4, 142.1, 133.4, 132.1, 128.6, 128.5, 128.4, 125.94, 125.88, 72.5, 39.0, 35.5, 31.94, 31.87, 31.0.

HRMS: Calc'd for $\text{C}_{20}\text{H}_{23}$, $[\text{M}-\text{OH}]^+$ 263.1794; found 263.1796.

Compound 14



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 26.2 mg (55%) of the title compound **14**.

Physical State: colorless oil.

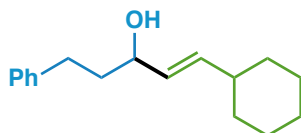
R_f = 0.40 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.41 – 7.36 (m, 2H), 7.35 – 7.27 (m, 4H), 7.27 – 7.17 (m, 4H), 6.62 – 6.56 (m, 1H), 6.25 (dd, J = 15.9, 6.8 Hz, 1H), 4.31 (d, J = 6.7 Hz, 1H), 2.77 (dddd, J = 23.2, 13.9, 9.3, 6.5 Hz, 2H), 2.04 – 1.90 (m, 2H), 1.62 (d, J = 3.6 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 141.9, 136.8, 132.3, 130.8, 128.8, 128.62, 128.57, 127.9, 126.6, 126.0, 72.5, 38.9, 31.9.

Spectroscopic data are in accordance with that reported in the literature.²²

Compound 15



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 13.2 mg (27%) of the title compound **15**.

Physical State: colorless oil.

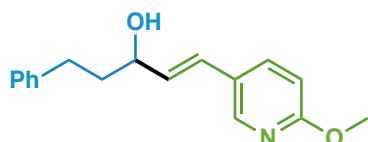
R_f = 0.48 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 5.60 (ddd, J = 15.6, 6.6, 0.9 Hz, 1H), 5.45 (ddd, J = 15.5, 7.1, 1.3 Hz, 1H), 4.06 (q, J = 6.7 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.00 – 1.62 (m, 8H), 1.33 – 1.03 (m, 6H).

^{13}C NMR (126 MHz, CDCl_3): δ 142.2, 138.5, 130.3, 128.6, 128.5, 125.9, 72.7, 40.4, 39.0, 33.1, 33.0, 32.0, 26.3, 26.1.

Spectroscopic data are in accordance with that reported in the literature.²²

Compound 16



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 33.4 mg (62%) of the title compound **16**.

Physical State: colorless oil.

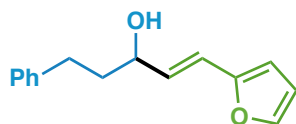
R_f = 0.18 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 8.09 (d, J = 2.5 Hz, 1H), 7.64 (dd, J = 8.6, 2.5 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.23 – 7.18 (m, 3H), 6.71 (dt, J = 8.7, 0.6 Hz, 1H), 6.50 (dd, J = 15.9, 1.1 Hz, 1H), 6.13 (dd, J = 15.9, 6.7 Hz, 1H), 4.29 (tdd, J = 6.9, 5.6, 1.2 Hz, 1H), 3.94 (s, 3H), 2.83 – 2.70 (m, 2H), 2.02 – 1.89 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 163.8, 145.8, 141.8, 135.7, 131.7, 128.59, 128.56, 126.8, 126.04, 125.96, 111.1, 72.4, 53.7, 38.9, 31.9.

HRMS: Calc'd for $\text{C}_{17}\text{H}_{20}\text{NO}_2$, $[\text{M}+\text{H}]^+$ 270.1489; found 270.1488.

Compound 17



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 20.0 mg (44%) of the title compound **17**.

Physical State: yellowish oil.

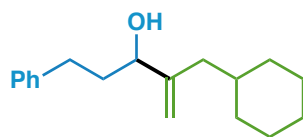
R_f = 0.34 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.36 (d, J = 1.8 Hz, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.24 – 7.18 (m, 3H), 6.45 – 6.37 (m, 2H), 6.26 – 6.18 (m, 2H), 4.28 (q, J = 6.5, 5.9 Hz, 1H), 2.81 – 2.70 (m, 2H), 2.00 – 1.89 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 152.5, 142.2, 141.9, 130.9, 128.60, 128.55, 126.0, 118.9, 111.5, 108.3, 72.0, 38.9, 31.8.

Spectroscopic data are in accordance with that reported in the literature.²²

Compound 18



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (5:1 hexanes/EtOAc) afforded 20.0 mg (39%) of the title compound **18**.

Physical State: colorless oil.

R_f = 0.66 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

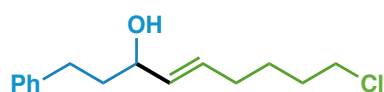
^1H NMR (500 MHz, CDCl_3): δ 7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.10 (d, J = 1.4 Hz, 1H), 4.86 (d, J = 1.5 Hz, 1H), 4.07 (t, J = 6.3 Hz, 1H), 2.76 (ddd, J = 13.9, 10.1,

5.5 Hz, 1H), 2.66 (ddd, $J = 13.8, 10.0, 6.4$ Hz, 1H), 2.01 – 1.87 (m, 3H), 1.82 (dddd, $J = 13.6, 10.0, 7.8, 5.5$ Hz, 1H), 1.76 – 1.62 (m, 5H), 1.51 – 1.39 (m, 2H), 1.29 – 1.11 (m, 3H), 0.92 – 0.81 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 150.2, 142.3, 128.6, 128.5, 125.9, 110.7, 74.5, 40.4, 37.3, 36.1, 33.8, 33.4, 32.1, 26.7, 26.5, 26.4.

HRMS: Calc'd for $\text{C}_{18}\text{H}_{25}$, $[\text{M}-\text{OH}]^+$ 241.1951; found 241.1951.

Compound 19



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 25.3 mg (50%) of the title compound **19**.

Physical State: colorless oil.

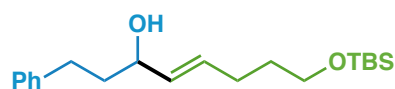
$R_f = 0.35$ (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.30 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 5.65 (dtd, $J = 15.4, 6.7, 1.0$ Hz, 1H), 5.55 – 5.50 (m, 1H), 4.08 (q, $J = 6.7$ Hz, 1H), 3.54 (t, $J = 6.6$ Hz, 2H), 2.74 – 2.63 (m, 2H), 2.11 – 2.05 (m, 2H), 1.91 – 1.76 (m, 4H), 1.58 (s, 1H), 1.57 – 1.51 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 142.1, 133.6, 131.6, 128.6, 128.5, 126.0, 72.5, 45.0, 39.0, 32.2, 31.9, 31.5, 26.5.

HRMS: Calc'd for $\text{C}_{15}\text{H}_{20}\text{Cl}$, $[\text{M}-\text{OH}]^+$ 235.1248; found 215.1259.

Compound 20



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 24.0 mg (36%) of the title compound **20**.

Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1

hexanes/EtOAc) afforded 54.0 mg (81%) of the title compound **43** and er was determined to be 1.2:1 by Mosher ester analysis.

Physical State: colorless oil.

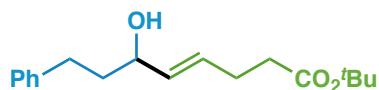
R_f = 0.50 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.67 (dtd, J = 15.4, 6.8, 1.0 Hz, 1H), 5.52 (ddt, J = 15.4, 7.1, 1.4 Hz, 1H), 4.08 (q, J = 6.7 Hz, 1H), 3.62 (t, J = 6.4 Hz, 2H), 2.74 – 2.64 (m, 2H), 2.14 – 2.07 (m, 2H), 1.92 – 1.76 (m, 2H), 1.64 – 1.57 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (151 MHz, CDCl_3): δ 142.1, 133.2, 132.1, 128.6, 128.5, 125.9, 72.5, 62.6, 38.9, 32.4, 31.9, 28.6, 26.1, 18.5, –5.1.

Spectroscopic data are in accordance with that reported in the literature.²³

Compound 21



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 30.2 mg (52%) of the title compound **21**.

Physical State: colorless oil.

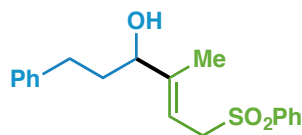
R_f = 0.55 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.30 – 7.26 (m, 2H), 7.18 (dd, J = 8.9, 7.3 Hz, 3H), 5.70 – 5.63 (m, 1H), 5.55 (ddt, J = 15.5, 7.0, 1.2 Hz, 1H), 4.07 (q, J = 6.6 Hz, 1H), 2.68 (qdd, J = 13.9, 9.3, 6.4 Hz, 2H), 2.37 – 2.27 (m, 4H), 1.91 – 1.75 (m, 2H), 1.60 – 1.53 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3): δ 172.5, 142.1, 133.9, 130.4, 128.6, 128.5, 125.9, 80.5, 72.3, 38.8, 35.2, 31.8, 28.3, 27.7.

The desired mass for HRMS was not observed.

Compound 22



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 40.3 mg (61%) of the title compound **22**.

Physical State: colorless oil.

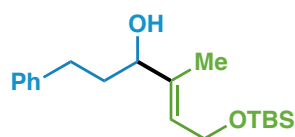
R_f = 0.23 (hexanes/EtOAc 2:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.90 – 7.86 (m, 2H), 7.65 – 7.60 (m, 1H), 7.55 – 7.50 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.49 (tt, J = 7.9, 1.3 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.91 – 3.82 (m, 2H), 2.66 (ddd, J = 13.9, 9.3, 6.2 Hz, 1H), 2.55 (ddd, J = 13.8, 9.2, 7.0 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.65 (d, J = 3.6 Hz, 1H), 1.39 (d, J = 1.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3): δ 148.1, 141.7, 138.9, 133.9, 129.3, 128.6, 128.5, 126.1, 111.7, 76.2, 55.8, 36.6, 31.9, 12.2.

HRMS: Calc'd for $\text{C}_{19}\text{H}_{21}\text{O}_2\text{S}$, $[\text{M}-\text{OH}]^+$ 313.1257; found 313.1251.

Compound 23



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 32.0 mg (50%) of the title compound **23**.

Physical State: colorless oil.

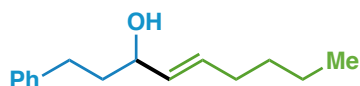
R_f = 0.33 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 5.56 (tt, J = 6.0, 1.2 Hz, 1H), 4.29 – 4.18 (m, 2H), 4.11 – 3.99 (m, 1H), 2.71 (ddd, J = 13.7, 9.5, 6.2 Hz, 1H), 2.61 (ddd, J = 13.8, 9.4, 6.7 Hz, 1H), 1.91 – 1.81 (m, 2H), 1.63 (q, J = 1.0 Hz, 3H), 1.50 (d, J = 3.3 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H).

¹³C NMR (151 MHz, CDCl₃): δ 142.1, 138.3, 128.6, 128.5, 126.6, 126.0, 76.8, 60.1, 36.5, 32.2, 26.1, 18.6, 11.9, −4.95, −4.97.

HRMS: Calc'd for C₁₉H₃₃O₂Si, [M+H]⁺ 321.2244; found 321.2243.

Compound 24



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 18.0 mg (41%) of the title compound **24**.

Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 30.0 mg (69%) of the title compound **44** and er was determined to be 1.3:1 by Mosher ester analysis.

Physical State: colorless oil.

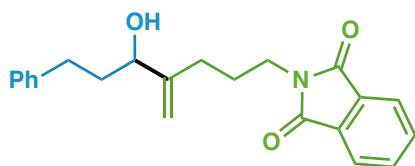
R_f = 0.50 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 5.66 (dtd, *J* = 15.4, 6.7, 0.9 Hz, 1H), 5.50 (ddt, *J* = 15.4, 7.1, 1.4 Hz, 1H), 4.08 (q, *J* = 6.7 Hz, 1H), 2.69 (qdd, *J* = 13.8, 9.5, 6.4 Hz, 2H), 2.08 – 2.01 (m, 2H), 1.93 – 1.76 (m, 2H), 1.48 – 1.42 (m, 1H), 1.40 – 1.28 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 142.2, 132.9, 132.8, 128.6, 128.5, 125.9, 72.6, 39.0, 32.02, 31.95, 31.5, 22.3, 14.1.

Spectroscopic data are in accordance with that reported in the literature.²⁴

Compound 25



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 40.5 mg (58%) of the title compound **25**.

Physical State: colorless oil.

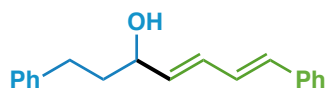
R_f = 0.17 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.84 (dd, J = 5.4, 3.0 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 5.11 – 5.08 (m, 1H), 4.92 (q, J = 1.5 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.72 (td, J = 7.0, 2.4 Hz, 2H), 2.74 (ddd, J = 13.8, 8.9, 6.8 Hz, 1H), 2.63 (ddd, J = 13.8, 9.0, 7.1 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.11 – 2.03 (m, 1H), 1.94 – 1.84 (m, 4H), 1.82 (d, J = 3.6 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 168.6, 150.3, 142.1, 134.1, 132.2, 128.6, 125.9, 123.4, 110.6, 75.0, 37.7, 37.1, 28.3, 26.6.

HRMS: Calc'd for $\text{C}_{22}\text{H}_{24}\text{NO}_3$, $[\text{M}+\text{H}]^+$ 350.1751; found 350.1747.

Compound 26



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 11.2 mg (21%) of the title compound **26**.

Physical State: colorless oil.

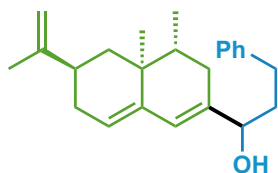
R_f = 0.24 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.41 – 7.39 (m, 2H), 7.34 – 7.28 (m, 4H), 7.25 – 7.18 (m, 4H), 6.78 (ddd, J = 15.7, 10.5, 0.8 Hz, 1H), 6.56 (d, J = 15.6 Hz, 1H), 6.40 (ddt, J = 15.2, 10.5, 1.0 Hz, 1H), 5.86 (dd, J = 15.2, 6.8 Hz, 1H), 4.24 (q, J = 6.6 Hz, 1H), 2.74 (dddd, J = 23.2, 13.9, 9.4, 6.4 Hz, 2H), 1.99 – 1.85 (m, 2H), 1.57 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 141.9, 137.3, 136.4, 133.0, 131.2, 128.8, 128.61, 128.56, 128.3, 127.8, 126.5, 126.0, 72.2, 38.9, 31.9.

Spectroscopic data are in accordance with that reported in the literature.²⁵

Compound 27



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 35.7 mg (53%) of the title compound **27**.

Physical State: colorless oil.

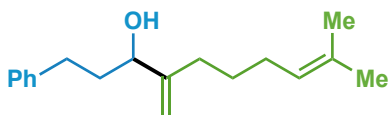
R_f = 0.48 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 5.98 (s, 0.37H), 5.94 (d, J = 2.3 Hz, 0.63H), 5.49 (dd, J = 5.1, 3.0 Hz, 1H), 4.75 (dp, J = 4.9, 1.5 Hz, 2H), 4.08 (dt, J = 13.7, 6.9 Hz, 1H), 2.75 – 2.57 (m, 2H), 2.48 – 2.41 (m, 1H), 2.29 – 2.17 (m, 1H), 2.01 – 1.82 (m, 5H), 1.78 – 1.72 (m, 4H), 1.52 (dq, J = 11.2, 6.7, 4.6 Hz, 2H), 1.18 (td, J = 12.7, 2.1 Hz, 1H), 0.94 – 0.88 (m, 6H).

^{13}C NMR (151 MHz, CDCl_3): δ 150.4, 150.3, 142.2, 142.1, 141.9, 141.8, 138.6, 128.59, 128.56, 128.52, 128.51, 125.97, 125.95, 125.93, 124.1, 123.9, 123.5, 108.84, 108.81, 75.6, 75.0, 40.3, 40.2, 39.2, 39.0, 37.44, 37.40, 37.1, 36.6, 36.42, 36.36, 32.4, 32.0, 31.6, 31.37, 31.35, 29.9, 20.8, 17.58, 17.56, 14.97, 14.96.

HRMS: Calc'd for $\text{C}_{24}\text{H}_{31}$, $[\text{M}-\text{OH}]^+$ 319.2420; found 319.2417.

Compound 28



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (9:1 hexanes/EtOAc) afforded 26.3 mg (51%) of the title compound **28**.

Physical State: colorless oil.

R_f = 0.32 (hexanes/EtOAc 9:1, *p*-anisaldehyde).

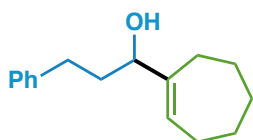
^1H NMR (500 MHz, CDCl_3): δ 7.29 (t, J = 7.5 Hz, 2H), 7.23 – 7.17 (m, 3H), 5.12 (tdd,

$J = 5.8, 2.9, 1.5$ Hz, 1H), 5.05 (t, $J = 1.1$ Hz, 1H), 4.88 (q, $J = 1.5$ Hz, 1H), 4.10 (dd, $J = 7.8, 5.0$ Hz, 1H), 2.81 – 2.72 (m, 1H), 2.65 (ddd, $J = 13.8, 9.8, 6.5$ Hz, 1H), 2.09 (dq, $J = 14.7, 7.3, 6.7$ Hz, 1H), 2.04 – 1.97 (m, 3H), 1.94 – 1.81 (m, 2H), 1.69 (d, $J = 1.5$ Hz, 3H), 1.60 (s, 3H), 1.51 (p, $J = 7.7$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3): δ 152.1, 142.2, 131.9, 128.6, 128.5, 126.0, 124.5, 109.7, 75.0, 37.3, 32.2, 31.2, 28.4, 28.0, 25.9, 17.9.

HRMS: Calc'd for $\text{C}_{18}\text{H}_{27}\text{O}$, $[\text{M}+\text{H}]^+$ 259.2056; found 259.2064.

Compound 29



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (9:1 hexanes/EtOAc) afforded 25.6 mg (56%) of the title compound **29**.

Physical State: yellowish oil.

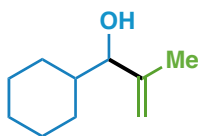
$R_f = 0.48$ (hexanes/EtOAc 6:1, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.28 (t, $J = 7.6$ Hz, 2H), 7.22 – 7.17 (m, 3H), 5.80 (t, $J = 6.4$ Hz, 1H), 4.01 (t, $J = 6.6$ Hz, 1H), 2.70 (ddd, $J = 13.8, 9.1, 6.9$ Hz, 1H), 2.64 – 2.57 (m, 1H), 2.14 (qd, $J = 10.0, 8.5, 3.7$ Hz, 4H), 1.86 – 1.72 (m, 4H), 1.55 – 1.45 (m, 5H).

^{13}C NMR (126 MHz, CDCl_3): δ 146.3, 142.3, 128.6, 128.5, 128.4, 125.9, 77.5, 36.7, 32.8, 32.4, 28.3, 27.9, 27.4, 27.2.

HRMS: Calc'd for $\text{C}_{16}\text{H}_{21}$, $[\text{M}-\text{OH}]^+$ 213.1638; found 213.1642.

Compound 30



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1

hexanes/EtOAc) afforded 18.2 mg (59%) of the title compound **30**.

Physical State: colorless oil.

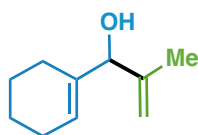
R_f = 0.55 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 4.91 – 4.84 (m, 2H), 3.74 (d, J = 7.5 Hz, 1H), 1.93 (dq, J = 13.9, 3.5, 1.7 Hz, 1H), 1.81 – 1.61 (m, 6H), 1.56 – 1.38 (m, 3H), 1.28 – 1.10 (m, 4H), 1.02 – 0.91 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 146.6, 112.5, 81.1, 40.7, 29.8, 28.5, 26.6, 26.4, 26.2, 17.6.

Spectroscopic data are in accordance with that reported in the literature.²⁶

Compound 31



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 17.0 mg (56%) of the title compound **31**.

Physical State: colorless oil.

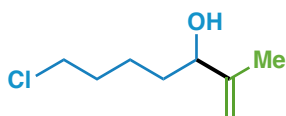
R_f = 0.50 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 5.76 (ddt, J = 5.0, 3.7, 1.8 Hz, 1H), 5.04 (dt, J = 2.1, 1.0 Hz, 1H), 4.91 (q, J = 1.4 Hz, 1H), 4.38 (s, 1H), 2.05 (dtd, J = 6.9, 3.6, 1.7 Hz, 2H), 1.96 – 1.89 (m, 1H), 1.85 – 1.77 (m, 1H), 1.64 – 1.52 (m, 8H).

^{13}C NMR (126 MHz, CDCl_3): δ 145.7, 137.7, 124.2, 110.8, 79.8, 25.2, 23.8, 22.8, 22.7, 18.7.

Spectroscopic data are in accordance with that reported in the literature.²⁷

Compound 32



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 22.4 mg (69%) of the title compound **32**.

Physical State: colorless oil.

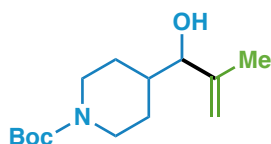
R_f = 0.48 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 4.95 (dt, J = 1.9, 1.0 Hz, 1H), 4.85 (p, J = 1.6 Hz, 1H), 4.07 (t, J = 6.2 Hz, 1H), 3.54 (t, J = 6.7 Hz, 2H), 1.81 (tt, J = 7.3, 6.5 Hz, 2H), 1.72 (t, J = 1.2 Hz, 3H), 1.61 – 1.50 (m, 5H).

^{13}C NMR (126 MHz, CDCl_3): δ 147.5, 111.4, 75.9, 45.1, 34.2, 32.6, 23.1, 17.6.

The desired mass for HRMS was not observed.

Compound 33



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 38.3 mg (75%) of the title compound **33**.

Physical State: colorless oil.

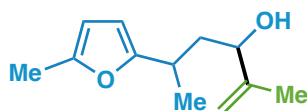
R_f = 0.21 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 4.91 – 4.83 (m, 2H), 4.10 (s, 2H), 3.74 (dd, J = 8.0, 2.6 Hz, 1H), 2.64 (s, 2H), 1.88 (dq, J = 13.2, 2.8 Hz, 1H), 1.76 (s, 1H), 1.70 (q, J = 1.5 Hz, 3H), 1.55 (dt, J = 11.5, 7.6, 3.7 Hz, 1H), 1.43 (d, J = 1.9 Hz, 10H), 1.15 (pd, J = 13.0, 4.3 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 155.0, 145.9, 113.1, 80.3, 79.4, 43.9, 39.1, 28.7, 28.6, 28.0, 17.3.

HRMS: Calc'd for $\text{C}_9\text{H}_{18}\text{NO}$, $[\text{M-Boc}+2\text{H}]^+$ 156.1383; found 156.1383.

Compound 34



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 25.6 mg (66%) of the title compound **34**.

Physical State: yellowish oil.

R_f = 0.48 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 5.90 – 5.81 (m, 2H), 4.94 (ddp, J = 2.9, 1.9, 0.9 Hz, 1H), 4.83 (dp, J = 13.7, 1.6 Hz, 1H), 4.12 (dd, J = 8.3, 5.1 Hz, 0.55H), 4.02 (dd, J = 8.9, 4.2 Hz, 0.48H), 3.04 – 2.85 (m, 1H), 2.25 (t, J = 1.3 Hz, 3H), 1.97 – 1.83 (m, 1H), 1.73 (dt, J = 10.2, 1.2 Hz, 3H), 1.71 – 1.62 (m, 1H), 1.56 (s, 1H), 1.26 (dd, J = 7.0, 5.9 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 158.5, 158.2, 150.44, 150.40, 147.9, 147.6, 111.4, 110.8, 105.79, 105.76, 104.7, 104.4, 74.1, 74.0, 41.7, 41.4, 30.2, 20.4, 19.3, 17.9, 17.6, 13.69, 13.67.

HRMS: Calc'd for $\text{C}_{12}\text{H}_{19}\text{O}_2$, $[\text{M}+\text{H}]^+$ 195.1380; found 195.1367.

Compound 35



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 24.7 mg (63%) of the title compound **35**.

Physical State: colorless oil.

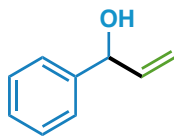
R_f = 0.58 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 5.10 (ddt, J = 8.8, 7.1, 1.5 Hz, 1H), 4.94 (ddt, J = 8.0, 1.9, 0.9 Hz, 1H), 4.82 (dp, J = 5.0, 1.6 Hz, 1H), 4.16 (ddd, J = 10.7, 7.9, 4.8 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.72 (dt, J = 5.9, 1.2 Hz, 3H), 1.68 (t, J = 1.4 Hz, 3H), 1.60 (s, 3H), 1.57 – 1.47 (m, 2H), 1.43 – 1.25 (m, 2H), 1.23 – 1.13 (m, 1H), 0.93 (dd, J = 6.6, 5.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3): δ 148.6, 147.9, 131.39, 131.36, 124.9, 111.5, 110.5, 74.6, 73.9, 42.9, 42.4, 37.8, 37.1, 29.5, 29.2, 25.9, 25.6, 25.5, 20.2, 19.4, 17.9, 17.8, 17.2.

HRMS: Calc'd for $\text{C}_{13}\text{H}_{25}\text{O}$, $[\text{M}+\text{H}]^+$ 197.1900; found 197.1900.

Compound 36



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 16.1 mg (59%) of the title compound **36**.

Physical State: colorless oil.

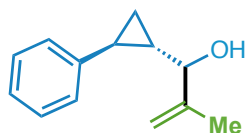
R_f = 0.38 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 6.06 (ddd, J = 17.2, 10.3, 6.0 Hz, 1H), 5.39 – 5.33 (m, 1H), 5.25 – 5.17 (m, 2H), 2.00 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 142.7, 140.4, 128.7, 127.9, 126.5, 115.3, 75.5.

Spectroscopic data are in accordance with that reported in the literature.²⁹

Compound 37



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 20.3 mg (66%) of the title compound **37**.

Less polar isomer:

Physical State: colorless oil.

$[\alpha]_D^{20}$ = +1.2 (c 0.5, CHCl_3).

R_f = 0.40 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.29 – 7.24 (m, 2H), 7.18 – 7.13 (m, 1H), 7.11 – 7.07 (m, 2H), 5.01 (dt, J = 1.8, 0.9 Hz, 1H), 4.86 (p, J = 1.6 Hz, 1H), 3.64 (d, J = 7.8 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.85 (t, J = 1.2 Hz, 3H), 1.64 (s, 1H), 1.38 – 1.32 (m, 1H), 1.03 – 0.97 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 147.1, 142.6, 128.5, 126.0, 125.8, 111.1, 79.2, 28.4, 21.5, 18.5, 13.7.

HRMS: Calc'd for C₁₃H₁₅, [M-OH]⁺ 171.1168; found 171.1164.

More polar isomer:

Physical State: colorless oil.

$[\alpha]_D^{20} = -0.6$ (c 0.6, CHCl₃).

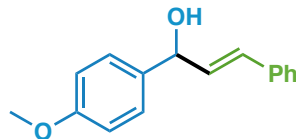
$R_f = 0.33$ (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.28 – 7.23 (m, 2H), 7.18 – 7.14 (m, 1H), 7.08 – 7.03 (m, 2H), 5.02 (dt, $J = 1.9, 1.0$ Hz, 1H), 4.85 (q, $J = 1.7$ Hz, 1H), 3.61 (d, $J = 8.0$ Hz, 1H), 1.88 (dt, $J = 8.8, 5.0$ Hz, 1H), 1.82 (t, $J = 1.2$ Hz, 3H), 1.65 (s, 1H), 1.34 (tdd, $J = 8.2, 5.6, 4.5$ Hz, 1H), 1.09 (dt, $J = 8.8, 5.3$ Hz, 1H), 1.03 (dt, $J = 8.4, 5.2$ Hz, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 147.2, 142.3, 128.5, 126.0, 125.8, 110.9, 79.1, 28.2, 21.5, 18.8, 13.8.

HRMS: Calc'd for C₁₃H₁₅, [M-OH]⁺ 171.1168; found 171.1167.

Compound 38



Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 34.0 mg (71%) of the title compound **38**.

Physical State: colorless oil.

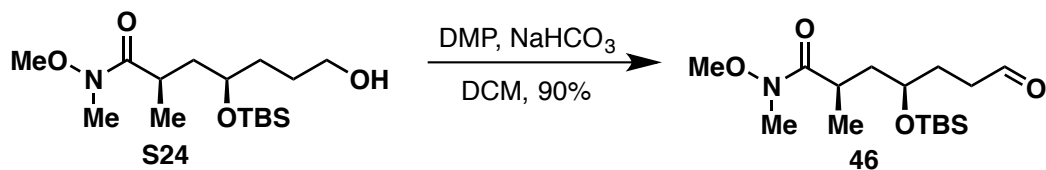
$R_f = 0.48$ (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.42 – 7.37 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 (dd, $J = 8.4, 6.9$ Hz, 2H), 7.27 – 7.21 (m, 1H), 6.94 – 6.88 (m, 2H), 6.68 (dd, $J = 15.9, 1.3$ Hz, 1H), 6.39 (dd, $J = 15.8, 6.3$ Hz, 1H), 5.37 – 5.33 (m, 1H), 3.81 (s, 3H), 2.10 (s, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 159.4, 136.7, 135.1, 131.8, 130.3, 128.7, 127.8, 126.7, 114.1, 74.8, 55.4.

Spectroscopic data are in accordance with that reported in the literature.²⁸

Compound 46



To a stirred solution of alcohol **S24** [generously provided by Eisai] (667 mg, 2.0 mmol, 1.0 equiv) and NaHCO₃ (840 mg, 10.0 mmol, 5 equiv) in DCM (20 mL) was added Dess–Martin periodinane (1.27 g, 3.0 mmol, 1.5 equiv) at 0 °C. After 3 hours, the reaction mixture was quenched with saturated NaHCO₃ (10 mL) and aqueous Na₂SO₃ (40 mL). After extraction with DCM, the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and filtered. The solvent was evaporated under vacuum, and the residue was purified by flash column chromatography with hexanes/EtOAc (4:1) to give aldehyde **46** (610 mg, 1.84 mmol, 92%).

Physical State: colorless oil.

R_f = 0.67 (hexanes/EtOAc 3:2, *p*-anisaldehyde).

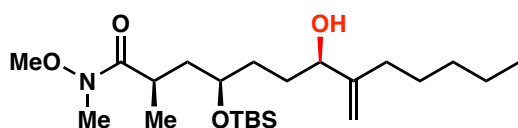
$[\alpha]_D^{20}$ = +12.0 (c 1.0, CHCl₃).

¹H NMR (600 MHz, CDCl₃): δ 9.77 (t, *J* = 1.6 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.69 (s, 3H), 3.16 (s, 3H), 2.95 (s, 1H), 2.51 (dddd, *J* = 8.1, 6.4, 3.3, 1.5 Hz, 2H), 1.91 – 1.79 (m, 2H), 1.72 – 1.65 (m, 1H), 1.44 (dt, *J* = 13.8, 6.3 Hz, 1H), 1.12 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.02 (d, *J* = 1.2 Hz, 6H).

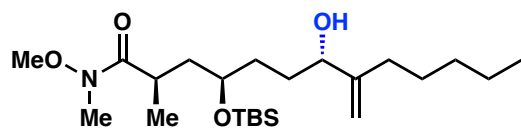
¹³C NMR (151 MHz, CDCl₃): δ 202.6, 177.7, 69.8, 61.5, 40.5, 39.4, 32.4, 32.2, 28.9, 26.0, 18.2, 18.1, –4.2, –4.5.

HRMS: Calc'd for C₁₆H₃₄NO₄Si, [M+H]⁺ 332.2252; found 332.2256.

Compound 47a



Compound 47b



Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:2 hexanes/EtOAc) afforded 57.5 mg (67%) of **47a** and **47b** as a mixture of inseparable diastereoisomers (**47a/47b** = 4.4:1).

Following **General Procedure D** on 0.2 mmol scale using (*R*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:2 hexanes/EtOAc) afforded 60.0 mg (71%) of **47a** and **47b** as a mixture of inseparable diastereoisomers (**47a/47b** = 1:4.5).

Physical State: colorless oil.

R_f = 0.67 (hexanes/EtOAc 3:2, *p*-anisaldehyde).

47a: $^1\text{H NMR}$ (500 MHz, C_6D_6): δ 5.15 (dq, J = 1.9, 0.9 Hz, 0.19H), 5.13 (dq, J = 1.9, 1.0 Hz, 0.84H), 4.88 (p, J = 1.6 Hz, 1H), 4.04 (dd, J = 7.4, 4.2 Hz, 1H), 3.90 (ddd, J = 10.1, 8.0, 5.6 Hz, 1H), 3.20 (s, 3H), 3.11 (s, 1H), 2.92 (d, J = 2.2 Hz, 3H), 2.30 (tt, J = 8.6, 5.3 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.00 (dt, J = 15.5, 7.8 Hz, 1H), 1.85 – 1.62 (m, 5H), 1.58 (dddd, J = 13.7, 6.8, 5.2, 3.4 Hz, 1H), 1.52 – 1.45 (m, 2H), 1.36 – 1.23 (m, 5H), 1.18 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 2.0 Hz, 9H), 0.93 – 0.86 (m, 3H), 0.16 – 0.09 (m, 6H).

$^{13}\text{C NMR}$ (126 MHz, C_6D_6): δ 177.8, 153.0, 108.9, 75.3, 71.4, 60.9, 41.0, 33.6, 32.6, 32.4, 32.2, 32.0, 31.0, 28.2, 26.3, 23.0, 18.8, 18.4, 14.3, –3.9, –4.3.

HRMS: Calc'd for $\text{C}_{23}\text{H}_{48}\text{NO}_4$, $[\text{M}+\text{H}]^+$ 430.3347; found 430.3343.

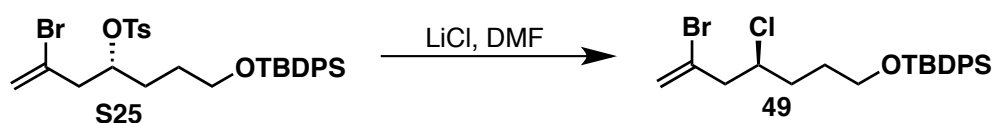
47b: $^1\text{H NMR}$ (600 MHz, C_6D_6): δ 5.15 (s, 0.79H), 5.14 (s, 0.19H), 4.88 (q, J = 1.7 Hz, 1H), 4.05 (td, J = 9.4, 8.2, 4.3 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.20 (d, J = 2.4 Hz, 3H), 3.12 (s, 1H), 2.92 (d, J = 2.8 Hz, 3H), 2.30 (ddd, J = 13.7, 8.8, 5.1 Hz, 1H), 2.18

–2.09 (m, 1H), 2.00 (dt, $J = 15.5, 7.8$ Hz, 1H), 1.90 – 1.62 (m, 4H), 1.58 (ddd, $J = 13.5, 6.8, 4.9$ Hz, 1H), 1.49 (p, $J = 7.8$ Hz, 2H), 1.34 – 1.24 (m, 4H), 1.17 (d, $J = 7.0$ Hz, 3H), 1.01 (d, $J = 2.6$ Hz, 9H), 0.93 – 0.87 (m, 3H), 0.16 – 0.11 (m, 6H).

^{13}C NMR (151 MHz, C_6D_6): δ 177.8, 152.9, 108.9, 75.1, 71.5, 60.9, 41.1, 33.7, 32.5, 32.4, 32.2, 32.0, 31.4, 28.2, 26.3, 23.0, 18.9, 18.4, 14.3, –3.9, –4.3.

HRMS: Calc'd for $\text{C}_{23}\text{H}_{48}\text{NO}_4$, $[\text{M}+\text{H}]^+$ 430.3347; found 430.3348.

Compound 49



A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with alkenyl bromide **S25** [generously provided by Eisai] (3.0 g, 5.0 mmol, 1.0 equiv) and LiCl (636 mg, 15.0 mmol, 3 equiv). Anhydrous DMF (10 mL) was added, and the resulting solution was stirred at 90 °C in a preheated oil bath for 1 h. After cooling to room temperature, the mixture was poured into water and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 , and filtered. The solvent was evaporated under vacuum, and the residue was purified by flash column chromatography with hexanes/EtOAc (20:1) to give **49** (1.58 g, 3.4 mmol, 68%).

Physical State: colorless oil.

$[\alpha]_{\text{D}}^{20} = -4.0$ (c 1.0, CHCl_3).

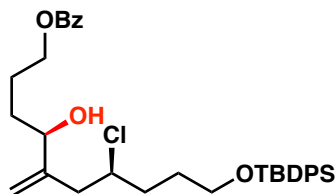
$R_f = 0.50$ (hexanes/EtOAc 20:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.70 – 7.65 (m, 4H), 7.46 – 7.37 (m, 6H), 5.71 (dt, $J = 1.9, 1.1$ Hz, 1H), 5.55 (d, $J = 1.8$ Hz, 1H), 4.23 (tdd, $J = 8.1, 5.8, 3.8$ Hz, 1H), 3.77 – 3.66 (m, 2H), 2.86 – 2.74 (m, 2H), 2.04 – 1.92 (m, 1H), 1.87 – 1.67 (m, 3H), 1.06 (s, 9H).

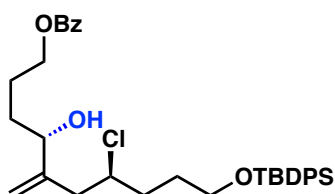
^{13}C NMR (126 MHz, CDCl_3): δ 135.7, 134.0, 129.8, 129.7, 127.8, 120.1, 63.2, 60.0, 50.3, 34.1, 29.4, 27.0, 19.4.

HRMS: Calc'd for $\text{C}_{23}\text{H}_{31}\text{BrClOSi}$, $[\text{M}+\text{H}]^+$ 465.1011; found 465.1016.

Compound 50a



Compound 50b



Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl₂-complex (0.4 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (150 mg), aluminum as sacrificial anode instead of stainless steel, 6 F/mol. Purification by PTLC (5:1 hexanes/EtOAc) afforded 63.7 mg (55%) of **50a** and **50b** as a mixture of inseparable diastereoisomers (**50a/50b** = 6.1:1).

Following **General Procedure D** on 0.2 mmol scale using (*R*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl₂-complex (0.4 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (150 mg), aluminum as sacrificial anode instead of stainless steel, 6 F/mol. Purification by PTLC (5:1 hexanes/EtOAc) afforded 60.0 mg (52%) of **50a** and **50b** as a mixture of inseparable diastereoisomers (**50a/50b** = 1:4.5).

Physical State: colorless oil.

R_f = 0.30 (hexanes/EtOAc 6:1, UV, *p*-anisaldehyde).

50a: ¹H NMR (600 MHz, CDCl₃): δ 8.06 – 8.02 (m, 2H), 7.69 – 7.65 (m, 4H), 7.57 – 7.53 (m, 1H), 7.45 – 7.37 (m, 8H), 5.22 (d, *J* = 1.1 Hz, 1H), 5.01 (d, *J* = 1.4 Hz, 1H),

4.40 – 4.33 (m, 2H), 4.17 (dddd, $J = 14.1, 8.7, 5.3, 3.3$ Hz, 2H), 3.75 – 3.66 (m, 2H), 2.63 – 2.56 (m, 1H), 2.46 (dd, $J = 15.2, 5.3$ Hz, 0.88H), 2.42 (ddd, $J = 15.4, 8.9, 1.0$ Hz, 0.14H), 2.00 (dddd, $J = 13.5, 9.6, 5.5, 3.5$ Hz, 1H), 1.91 (dtd, $J = 13.8, 6.3, 3.1$ Hz, 1H), 1.86 – 1.66 (m, 8H), 1.06 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3): δ 166.8, 147.5, 135.68, 135.67, 134.0, 133.9, 133.0, 130.4, 129.8, 129.7, 128.5, 127.8, 113.7, 74.7, 64.9, 63.3, 61.8, 41.0, 34.8, 31.9, 29.5, 27.0, 25.1, 19.4.

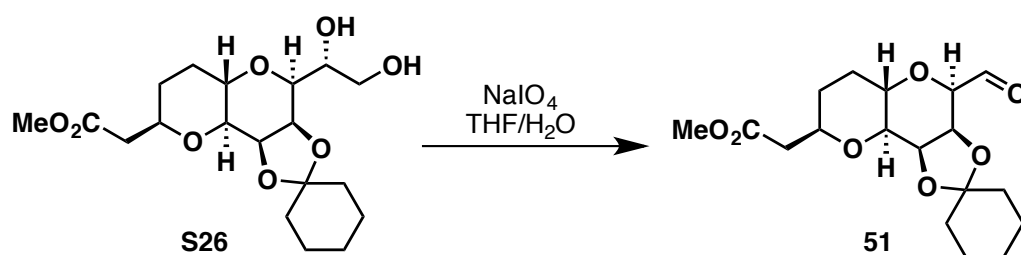
HRMS: Calc'd for $\text{C}_{34}\text{H}_{44}\text{ClO}_4\text{Si}$, $[\text{M}+\text{H}]^+$ 579.2692; found 579.2687.

50b: ^1H NMR (600 MHz, CDCl_3): δ 8.04 (dt, $J = 8.4, 1.4$ Hz, 2H), 7.66 (dt, $J = 6.7, 1.5$ Hz, 4H), 7.56 – 7.53 (m, 1H), 7.45 – 7.37 (m, 8H), 5.21 (dd, $J = 3.7, 1.0$ Hz, 1H), 5.01 (d, $J = 1.3$ Hz, 1H), 4.40 – 4.33 (m, 2H), 4.23 – 4.13 (m, 2H), 3.73 – 3.66 (m, 2H), 2.59 (td, $J = 15.0, 6.9$ Hz, 1H), 2.46 (dd, $J = 15.2, 5.4$ Hz, 0.18H), 2.41 (ddd, $J = 15.3, 9.0, 1.1$ Hz, 0.82H), 1.98 (dddd, $J = 13.6, 9.8, 5.3, 3.6$ Hz, 1H), 1.93 – 1.86 (m, 1H), 1.86 – 1.62 (m, 8H), 1.05 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3): δ 166.8, 147.6, 135.7, 134.0, 133.0, 130.5, 129.8, 129.7, 128.5, 127.8, 113.8, 75.0, 64.9, 63.4, 62.1, 41.2, 35.1, 31.7, 29.5, 27.0, 25.2, 19.4.

HRMS: Calc'd for $\text{C}_{34}\text{H}_{44}\text{ClO}_4\text{Si}$, $[\text{M}+\text{H}]^+$ 579.2692; found 579.2090.

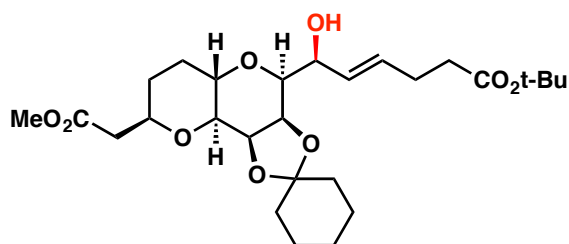
Compound 51



To a stirred solution of diol **S26** [generously provided by Eisai] (773 mg, 2.0 mmol, 1.0 equiv) in $\text{THF}/\text{H}_2\text{O}$ (10 mL/10 mL) was added NaIO_4 (642 mg, 3.0 mmol, 1.5 equiv) at 0 °C. The resulting mixture was then stirred at room temperature until TLC showed the diol was completely consumed. The solution was filtered through a pad of Celite and washed with EtOAc. The combined organic solution was washed with aq. Na_2SO_3

solution, dried over Na₂SO₄, and filtered. The solvent was evaporated under vacuum and the residue was used directly in the next step without further purification.

Compound 52



Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (1:1 hexanes/EtOAc) afforded 79.0 mg (78%) of the title compound **52** as a mixture of inseparable diastereoisomers (dr > 20:1).

Following **General Procedure D** on 0.2 mmol scale using (*R*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (1:1 hexanes/EtOAc) afforded 60.0 mg (73%) of the title compound **52** as a mixture of inseparable diastereoisomers (dr = 14:1).

Physical State: colorless oil.

R_f = 0.42 (hexanes/EtOAc 1:1, *p*-anisaldehyde).

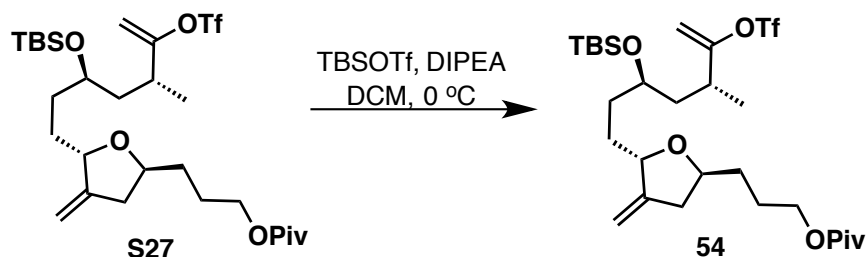
¹H NMR (600 MHz, CDCl₃): δ 5.80 (dtd, *J* = 15.5, 6.4, 1.4 Hz, 1H), 5.57 (dtd, *J* = 15.4, 5.9, 1.4 Hz, 1H), 5.48 (dd, *J* = 15.3, 7.1 Hz, 0.05H), 4.56 – 4.48 (m, 2H), 4.31 – 4.21 (m, 1H), 3.89 (td, *J* = 10.7, 4.7 Hz, 1H), 3.81 (dtd, *J* = 11.2, 6.5, 2.1 Hz, 1H), 3.65 (s, 3H), 3.54 (dd, *J* = 5.4, 1.6 Hz, 1H), 3.45 (dd, *J* = 10.2, 3.0 Hz, 1H), 2.93 (s, 1H), 2.69 (dd, *J* = 16.1, 7.0 Hz, 1H), 2.41 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.36 – 2.26 (m, 4H), 2.15 – 2.07 (m, 1H), 1.86 – 1.38 (m, 25H).

¹³C NMR (151 MHz, CDCl₃): δ 172.4, 171.6, 131.0, 130.5, 111.3, 80.4, 76.4, 75.3, 74.2, 73.0, 71.8, 71.4, 66.4, 51.8, 40.4, 35.6, 35.1, 33.4, 30.7, 30.1, 28.2, 27.9, 25.2,

24.2, 23.8.

HRMS: Calc'd for C₂₇H₄₂NaO₉, [M+Na]⁺ 533.2721; found 533.2719.

Compound 54



To a solution of alcohol **S27** [generously provided by Eisai] (250 mg, 0.5 mmol, 1.0 equiv) in DCM (5 mL) was added successively DIPEA (260 μ L, 1.5 mmol, 3.0 equiv) and TBSOTf (140 μ L, 0.6 mmol, 1.2 equiv) at 0 °C. After 30 min, the reaction mixture was quenched with aq. NaHCO₃ solution. The organic layer was separated, and the aqueous layer was extracted with DCM three times. The combined organic layers were washed with brine, dried over Na₂SO₄, and filtered. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography with hexanes/EtOAc (10:1) to give **54** (295 mg, 0.48 mmol, 96%).

Physical State: colorless oil.

$[\alpha]_D^{20} = -30.4$ (c 1.0, CHCl₃).

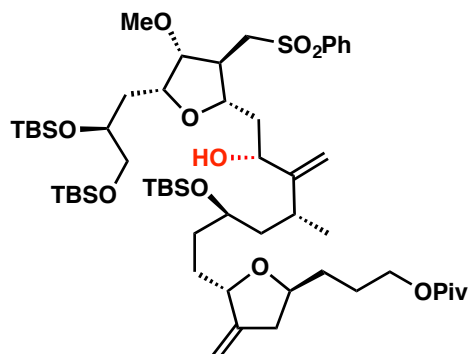
$R_f = 0.77$ (hexanes/EtOAc 3:1, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 5.07 (d, $J = 3.9$ Hz, 1H), 4.96 (q, $J = 2.2$ Hz, 1H), 4.89 (d, $J = 3.9$ Hz, 1H), 4.82 (q, $J = 2.2$ Hz, 1H), 4.35 – 4.30 (m, 1H), 4.05 (td, $J = 6.3, 3.4$ Hz, 2H), 3.99 (q, $J = 6.4$ Hz, 1H), 3.78 – 3.72 (m, 1H), 2.65 (ddq, $J = 15.4, 6.2, 2.0$ Hz, 1H), 2.55 (p, $J = 6.9$ Hz, 1H), 2.27 – 2.19 (m, 1H), 1.77 – 1.39 (m, 11H), 1.17 (s, 9H), 1.14 (d, $J = 6.9$ Hz, 3H), 0.87 (s, 9H), 0.03 (d, $J = 7.9$ Hz, 6H).

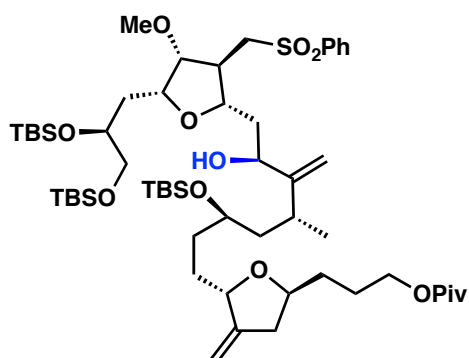
¹³C NMR (126 MHz, CDCl₃): δ 178.6, 160.6, 151.7, 118.5 (q, $J_{C-F} = 319.6$ Hz), 105.0, 102.3, 79.8, 76.9, 69.9, 64.3, 40.9, 39.0, 38.8, 35.6, 33.2, 31.7, 30.4, 27.3, 26.0, 25.4, 18.9, 18.2, -3.9, -4.5.

HRMS: Calc'd for C₂₈H₅₀F₃O₇SSi, [M+H]⁺ 615.2999; found 615.3002.

Compound 55a



Compound 55b



Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl₂-complex (0.4 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:1 hexanes/EtOAc) afforded 65.0 mg (31%) of the title compound **55a**.

55a: Physical State: colorless oil.

$[\alpha]_D^{20} = -23.5$ (c 1.0, CHCl₃).

$R_f = 0.57$ (hexanes/EtOAc 3:1, UV, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.93 (dt, *J* = 7.2, 1.3 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 5.12 (s, 1H), 4.96 (q, *J* = 2.1 Hz, 1H), 4.86 (s, 1H), 4.83 (q, *J* = 2.1 Hz, 1H), 4.34 – 4.29 (m, 1H), 4.12 – 3.98 (m, 4H), 3.92 (td, *J* = 6.5, 3.4 Hz, 1H),

3.80 – 3.65 (m, 4H), 3.56 (dd, $J = 10.3, 5.4$ Hz, 1H), 3.47 (dd, $J = 10.3, 5.4$ Hz, 1H), 3.38 (s, 3H), 3.16 – 3.05 (m, 2H), 2.66 (ddt, $J = 17.1, 6.0, 1.9$ Hz, 1H), 2.56 (dt, $J = 9.8, 5.1$ Hz, 1H), 2.23 (ddd, $J = 15.3, 6.0, 2.5$ Hz, 1H), 2.11 (q, $J = 6.9$ Hz, 1H), 2.04 – 1.96 (m, 1H), 1.88 – 1.59 (m, 10H), 1.45 (dddd, $J = 27.4, 13.4, 6.4, 2.5$ Hz, 4H), 1.18 (d, $J = 1.0$ Hz, 9H), 1.04 (d, $J = 6.8$ Hz, 3H), 0.91 – 0.85 (m, 30H), 0.10 – 0.01 (m, 20H).

^{13}C NMR (151 MHz, CDCl_3): δ 178.7, 157.5, 151.8, 139.7, 134.1, 129.6, 128.0, 108.1, 105.0, 85.8, 83.5, 80.2, 79.0, 76.8, 73.4, 71.3, 71.1, 67.9, 64.4, 58.2, 57.6, 45.2, 44.6, 41.6, 38.94, 38.86, 33.5, 33.0, 32.9, 31.7, 31.0, 27.3, 26.12, 26.06, 25.4, 21.3, 18.5, 18.30, 18.27, -4.0, -4.05, -4.09, -4.6, -5.2.

HRMS: Calc'd for $\text{C}_{56}\text{H}_{102}\text{NaO}_{11}\text{SSi}_3$, $[\text{M}+\text{Na}]^+$ 1089.6343; found 1089.6338.

Following **General Procedure D** on 0.2 mmol scale using (*R*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: $\text{NiCl}_2 \cdot \text{glyme}$ (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl_2 -complex (0.4 equiv), Cp_2ZrCl_2 (1.0 equiv), 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:1 hexanes/EtOAc) afforded 67.0 mg (32%) of the title compound **55b**.

55b: Physical State: colorless oil.

$[\alpha]_{\text{D}}^{20} = -32.5$ (c 1.0, CHCl_3).

$R_f = 0.52$ (hexanes/EtOAc 3:1, UV, *p*-anisaldehyde).

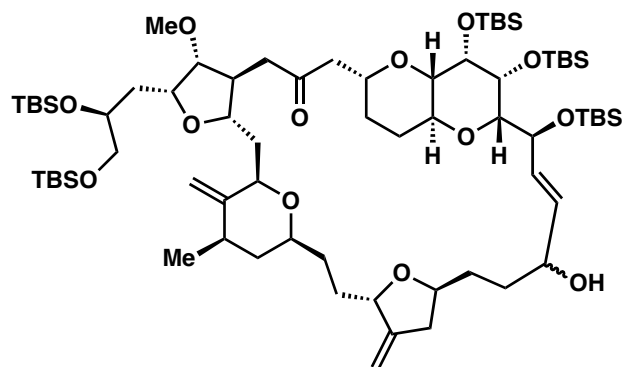
^1H NMR (500 MHz, CDCl_3): δ 7.95 – 7.89 (m, 2H), 7.70 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 5.00 (s, 1H), 4.96 (d, $J = 2.1$ Hz, 1H), 4.85 – 4.81 (m, 2H), 4.32 (d, $J = 5.8$ Hz, 1H), 4.25 – 4.17 (m, 1H), 4.11 – 3.97 (m, 3H), 3.89 – 3.74 (m, 4H), 3.64 (q, $J = 5.8$ Hz, 1H), 3.57 (dd, $J = 10.3, 5.6$ Hz, 1H), 3.48 (dd, $J = 10.3, 5.1$ Hz, 1H), 3.41 (s, 3H), 3.15 (dd, $J = 14.2, 4.0$ Hz, 1H), 3.05 (dd, $J = 14.1, 10.1$ Hz, 1H), 2.67 (ddq, $J = 15.5, 6.3, 2.0$ Hz, 1H), 2.53 (dt, $J = 10.0, 4.9$ Hz, 1H), 2.34 – 2.19 (m, 2H), 2.02 – 1.93 (m, 1H), 1.85 – 1.44 (m, 14H), 1.18 (s, 9H), 1.01 (d, $J = 6.9$ Hz, 3H), 0.91 – 0.83 (m, 27H), 0.10 – 0.01 (m, 18H).

^{13}C NMR (126 MHz, CDCl_3): δ 178.7, 158.0, 151.7, 139.8, 134.0, 129.6, 128.0, 109.2, 105.0, 85.8, 81.4, 80.0, 78.7, 76.9, 71.83, 71.80, 71.5, 68.0, 64.4, 58.1, 57.6, 44.4, 44.3, 41.5, 38.93, 38.86, 33.5, 32.4, 31.7, 31.4, 30.9, 27.3, 26.2, 26.13, 26.09, 25.4, 23.1, 18.5,

18.33, 18.31, -4.0, -4.2, -4.3, -4.6, -5.2.

HRMS: Calc'd for C₅₆H₁₀₂NaO₁₁SSi₃, [M+Na]⁺ 1089.6343; found 1089.6348.

Compound 57



Following **General Procedure D** on 0.2 mmol scale using (*S*)-*N*-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (400 mg), CH₃CN (10 mL, c = 20 mM), 6 F/mol. Purification by PTLC (4:1 hexanes/EtOAc) afforded 67.4 mg (31%) compound **57a** and 67.0 mg (31%) compound **57b**.

Less polar isomer, **57a**:

Physical State: white foam.

[α]_D²⁰ = -37.1 (c 1.0, CHCl₃).

*R*_f = 0.48 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 5.83 (dd, *J* = 15.6, 9.2 Hz, 1H), 5.63 (dd, *J* = 15.6, 8.5 Hz, 1H), 5.02 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.96 (q, *J* = 2.2 Hz, 1H), 4.90 (s, 1H), 4.83 – 4.76 (m, 2H), 4.26 (d, *J* = 6.7 Hz, 1H), 4.09 – 4.03 (m, 2H), 3.98 (p, *J* = 6.2 Hz, 1H), 3.93 – 3.76 (m, 6H), 3.73 (ddd, *J* = 8.1, 5.1, 3.2 Hz, 1H), 3.57 (dt, *J* = 10.2, 4.7 Hz, 2H), 3.53 – 3.46 (m, 2H), 3.44 – 3.41 (m, 1H), 3.28 (s, 3H), 2.91 – 2.78 (m, 2H), 2.66 (ddq, *J* = 15.6, 6.3, 1.8 Hz, 1H), 2.60 – 2.47 (m, 3H), 2.43 – 2.34 (m, 1H), 2.33 – 2.21 (m, 2H), 2.08 – 1.91 (m, 3H), 1.79 (dddd, *J* = 27.6, 13.9, 5.7, 3.4 Hz, 4H), 1.71 – 1.60 (m,

2H), 1.58 – 1.48 (m, 6H), 1.45 – 1.36 (m, 2H), 1.33 – 1.22 (m, 2H), 1.08 (d, $J = 6.5$ Hz, 3H), 0.97 (s, 9H), 0.92 (s, 9H), 0.88 (d, $J = 3.8$ Hz, 18H), 0.84 (s, 9H), 0.14 – 0.09 (m, 12H), 0.06 (d, $J = 4.6$ Hz, 6H), 0.05 – 0.01 (m, 12H).

^{13}C NMR (126 MHz, CDCl_3): δ 207.8, 151.7, 151.1, 134.9, 133.7, 105.04, 104.96, 87.6, 81.7, 80.8, 79.5, 79.0, 77.6, 77.4, 77.1, 75.6, 73.9, 73.6, 73.2, 72.5, 71.6, 70.8, 68.0, 63.7, 57.1, 49.2, 47.2, 44.3, 42.6, 38.9, 36.5, 35.8, 33.72, 33.70, 32.4, 31.4, 31.3, 30.5, 28.8, 27.0, 26.5, 26.4, 26.2, 26.1, 19.5, 18.9, 18.6, 18.3, 18.2, -2.0, -3.0, -3.7, -3.9, -4.1, -4.4, -4.5, -4.6, -5.16, -5.18.

HRMS: Calc'd for $\text{C}_{70}\text{H}_{132}\text{NaO}_{13}\text{Si}_5$, $[\text{M}+\text{Na}]^+$ 1343.8406; found 1343.8406.

More polar isomer, 57b:

Physical State: white foam.

$[\alpha]_{\text{D}}^{20} = -33.0$ (c 1.0, CHCl_3).

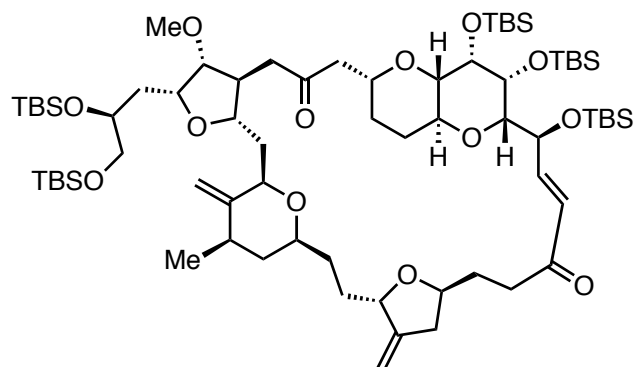
$R_f = 0.40$ (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 6.07 (ddd, $J = 15.8, 7.5, 1.6$ Hz, 1H), 5.76 (dd, $J = 15.7, 4.7$ Hz, 1H), 4.96 (dq, $J = 4.2, 1.9$ Hz, 2H), 4.91 (s, 1H), 4.79 (t, $J = 2.3$ Hz, 2H), 4.31 – 4.21 (m, 2H), 4.12 – 4.00 (m, 2H), 3.94 – 3.75 (m, 7H), 3.72 (q, $J = 5.6$ Hz, 1H), 3.65 – 3.52 (m, 3H), 3.49 (dd, $J = 10.3, 5.2$ Hz, 1H), 3.42 (dd, $J = 3.8, 1.2$ Hz, 1H), 3.27 (s, 3H), 2.91 (dd, $J = 9.6, 2.4$ Hz, 1H), 2.81 (dd, $J = 15.8, 6.2$ Hz, 1H), 2.68 – 2.48 (m, 4H), 2.40 – 2.23 (m, 3H), 2.02 (t, $J = 5.9$ Hz, 2H), 1.95 (ddd, $J = 13.8, 6.3, 5.2$ Hz, 1H), 1.90 – 1.85 (m, 1H), 1.85 – 1.79 (m, 1H), 1.76 (dt, $J = 13.9, 6.9$ Hz, 2H), 1.72 – 1.62 (m, 4H), 1.55 (ddd, $J = 19.8, 6.8, 3.7$ Hz, 4H), 1.46 – 1.35 (m, 2H), 1.32 – 1.23 (m, 2H), 1.08 (d, $J = 6.5$ Hz, 3H), 0.96 (s, 9H), 0.93 (s, 9H), 0.88 (d, $J = 3.7$ Hz, 18H), 0.86 (s, 9H), 0.14 – 0.08 (m, 12H), 0.06 (d, $J = 4.4$ Hz, 6H), 0.06 – -0.02 (m, 12H).

^{13}C NMR (126 MHz, CDCl_3): δ 207.8, 151.8, 151.0, 134.4, 130.2, 105.0, 87.4, 81.8, 80.9, 79.5, 79.0, 77.6, 77.03, 76.99, 75.7, 73.6, 73.0, 71.8, 71.6, 71.5, 70.9, 68.0, 64.1, 57.1, 49.0, 47.6, 44.3, 42.4, 38.6, 36.5, 35.8, 33.7, 33.0, 32.6, 31.2, 30.6, 30.3, 28.8, 26.9, 26.5, 26.4, 26.2, 26.1, 19.3, 18.9, 18.6, 18.31, 18.28, 18.2, -2.7, -3.5, -3.7, -3.9, -4.2, -4.3, -4.5, -4.6, -5.16, -5.18.

HRMS: Calc'd for $\text{C}_{70}\text{H}_{132}\text{NaO}_{13}\text{Si}_5$, $[\text{M}+\text{Na}]^+$ 1343.8406; found 1343.8403.

Compound S28



Two culture tubes were separately charged with **57a** (60 mg, 0.046 mmol, 1.0 equiv) and **57b** (60 mg, 0.046 mmol, 1.0 equiv). Then DCM (1 mL), NaHCO₃ (12 mg, 0.14 mmol, 3.0 equiv), and DMP (24 mg, 0.055 mmol, 1.2 equiv) were successively added to each reaction mixture. After 4 h, the reaction mixtures were separately quenched with aq. Na₂SO₃ and aq. NaHCO₃. For each reaction mixture, the organic layer was separated, the aqueous layer was extracted with DCM, and the combined organic layers were concentrated *in vacuo*. The crude residues were purified by flash column chromatography with hexanes/EtOAc (4:1) to give **S28** (47 mg, 78% yield from **57a** and 49 mg, 81% yield from **57b**).

Physical State: colorless oil.

$[\alpha]_D^{20} = -44.5$ (c 1.0, CHCl₃).

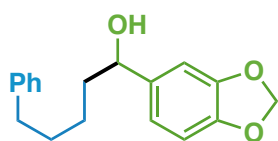
$R_f = 0.57$ (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.26 (dd, $J = 16.4, 5.9$ Hz, 1H), 6.34 (dd, $J = 16.4, 1.3$ Hz, 1H), 5.02 – 4.98 (m, 2H), 4.88 (s, 1H), 4.83 (q, $J = 2.2$ Hz, 1H), 4.78 (d, $J = 1.9$ Hz, 1H), 4.26 – 4.20 (m, 1H), 4.09 – 4.01 (m, 3H), 3.92 – 3.76 (m, 5H), 3.72 – 3.67 (m, 1H), 3.55 (td, $J = 9.6, 8.9, 5.9$ Hz, 2H), 3.49 (dd, $J = 10.3, 5.1$ Hz, 1H), 3.44 – 3.38 (m, 2H), 3.30 (s, 3H), 2.94 (dd, $J = 9.6, 2.3$ Hz, 1H), 2.85 (dd, $J = 15.8, 7.1$ Hz, 1H), 2.76 – 2.61 (m, 4H), 2.54 – 2.42 (m, 3H), 2.27 (tdd, $J = 16.6, 7.5, 4.1$ Hz, 2H), 2.04 (ddd, $J = 14.4, 8.0, 2.2$ Hz, 1H), 1.93 (dddd, $J = 16.7, 11.2, 7.8, 5.8$ Hz, 2H), 1.85 – 1.64 (m, 7H), 1.59 – 1.53 (m, 2H), 1.47 – 1.38 (m, 1H), 1.32 (td, $J = 9.7, 8.4, 4.0$ Hz, 2H), 1.07 (d, $J = 6.5$ Hz, 3H), 0.97 (s, 9H), 0.93 (s, 9H), 0.87 (d, $J = 6.0$ Hz, 27H), 0.19 (s, 3H), 0.14 (s, 3H), 0.12 (s, 6H), 0.06 (d, $J = 8.2$ Hz, 6H), 0.04 – 0.02 (m, 9H), -0.05 (s, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 207.8, 200.2, 151.2, 151.1, 146.5, 131.3, 105.5, 104.9, 87.6, 83.8, 80.7, 79.3, 78.8, 77.6, 77.5, 76.7, 75.6, 73.8, 72.7, 71.6, 71.0, 70.6, 68.0, 66.0, 57.1, 48.9, 47.7, 43.7, 42.5, 38.8, 35.9, 35.8, 33.6, 32.2, 32.1, 31.0, 29.5, 28.6, 26.9, 26.4, 26.2, 26.14, 26.09, 19.3, 19.0, 18.5, 18.3, 18.2, 18.1, -3.1, -3.3, -4.0, -4.1, -4.2, -4.4, -4.61, -4.63, -5.17, -5.19.

Spectroscopic data are in accordance with that reported in the literature.³⁰

Compound 60



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 30.0 mg (53%) of the title compound **60**.

Physical State: colorless oil.

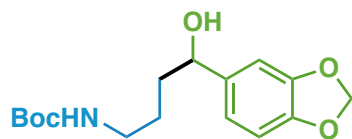
R_f = 0.24 (hexanes/EtOAc 5:1, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.29 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 6.85 (t, *J* = 1.1 Hz, 1H), 6.76 (d, *J* = 1.1 Hz, 2H), 5.94 (s, 2H), 4.56 (dd, *J* = 7.4, 6.0 Hz, 1H), 2.60 (dd, *J* = 8.9, 6.7 Hz, 2H), 1.89 (s, 1H), 1.84 – 1.77 (m, 1H), 1.72 – 1.61 (m, 3H), 1.45 (ddtd, *J* = 15.5, 10.4, 7.3, 5.3 Hz, 1H), 1.31 (dtt, *J* = 11.0, 8.1, 5.6 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 147.9, 147.0, 142.7, 139.1, 128.5, 128.4, 125.8, 119.4, 108.1, 106.5, 101.1, 74.5, 39.0, 36.0, 31.5, 25.7.

Spectroscopic data are in accordance with that reported in the literature.³¹

Compound 61



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 31.6 mg (51%) of the title compound **61**.

Physical State: yellowish oil.

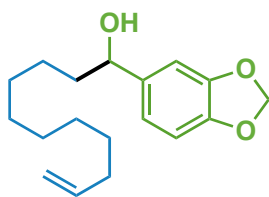
R_f = 0.24 (hexanes/EtOAc 2:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 6.84 (d, J = 1.5 Hz, 1H), 6.78 – 6.72 (m, 2H), 5.93 (s, 2H), 4.65 – 4.56 (m, 2H), 3.19 – 3.08 (m, 2H), 1.80 – 1.72 (m, 1H), 1.66 (ddt, J = 13.5, 9.5, 5.7 Hz, 1H), 1.55 (ddd, J = 17.3, 13.9, 7.4 Hz, 1H), 1.48 (d, J = 13.8 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3): δ 156.2, 147.9, 147.0, 138.9, 119.3, 108.2, 106.4, 101.1, 79.3, 74.1, 40.4, 36.1, 28.5, 26.6.

HRMS: Calc'd for $\text{C}_{16}\text{H}_{23}\text{NO}_5\text{Na}$, $[\text{M}+\text{Na}]^+$ 332.1468; found 332.1474.

Compound 62



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 36.6 mg (63%) of the title compound **62**.

Physical State: colorless oil.

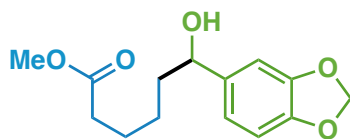
R_f = 0.52 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 6.86 (d, J = 1.4 Hz, 1H), 6.80 – 6.74 (m, 2H), 5.94 (s, 2H), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (dq, J = 17.1, 1.8 Hz, 1H), 4.92 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 4.56 (dd, J = 7.4, 6.1 Hz, 1H), 2.06 – 2.00 (m, 2H), 1.82 (s, 1H), 1.80 – 1.73 (m, 1H), 1.64 (ddt, J = 13.1, 9.8, 5.5 Hz, 1H), 1.40 – 1.33 (m, 3H), 1.32 – 1.20 (m, 10H).

^{13}C NMR (151 MHz, CDCl_3): δ 147.9, 147.0, 139.4, 139.2, 119.5, 114.3, 108.2, 106.5, 101.1, 74.7, 39.2, 33.9, 29.6, 29.5, 29.2, 29.0, 26.0.

HRMS: Calc'd for $\text{C}_{18}\text{H}_{25}\text{O}_2$, $[\text{M}-\text{OH}]^+$ 273.1849; found 273.1850.

Compound 63



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 19.7 mg (37%) of the title compound **63**.

Physical State: colorless oil.

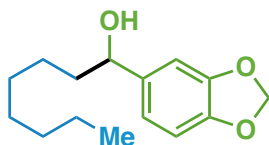
R_f = 0.40 (hexanes/EtOAc 2:1, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 6.84 (dt, J = 1.2, 0.6 Hz, 1H), 6.76 (t, J = 1.0 Hz, 2H), 5.94 (s, 2H), 4.57 (dd, J = 7.4, 5.9 Hz, 1H), 3.65 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 1.82 – 1.74 (m, 1H), 1.69 – 1.60 (m, 3H), 1.46 – 1.37 (m, 1H), 1.32 – 1.24 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3): δ 174.3, 147.9, 147.1, 138.9, 119.4, 108.2, 106.5, 101.1, 74.3, 51.6, 38.7, 34.1, 25.5, 24.9.

HRMS: Calc'd for $\text{C}_{14}\text{H}_{17}\text{O}_4$, $[\text{M}-\text{OH}]^+$ 249.1121; found 249.1116.

Compound 64



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 27.5 mg (55%) of the title compound **64**.

Physical State: colorless oil.

R_f = 0.50 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 6.86 (d, J = 1.5 Hz, 1H), 6.80 – 6.74 (m, 2H), 5.95 (s, 2H), 4.57 (dd, J = 7.4, 6.1 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.68 – 1.62 (m, 1H), 1.41 – 1.33 (m, 1H), 1.33 – 1.20 (m, 9H), 0.87 (t, J = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 147.9, 147.0, 139.2, 119.5, 108.2, 106.5, 101.1, 74.7, 39.2, 32.0, 29.6, 29.4, 26.0, 22.8, 14.2.

HRMS: Calc'd for $\text{C}_{15}\text{H}_{21}\text{O}_2$, $[\text{M}-\text{OH}]^+$ 233.1536; found 233.1532.

Chemical structure of 1-(3-(2-methylthiophen-2-yl)propyl)-2,3-dihydro-1,4-benzodioxole. The structure consists of a 2-methylthiophene ring connected via a propyl chain to a 1,4-benzodioxole ring system.

Physical State: colorless oil.

¹H NMR (500 MHz, CDCl₃): δ 7.10 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.87 – 6.83 (m, 1H), 6.76 (dt, *J* = 3.6, 1.3 Hz, 3H), 5.95 (s, 2H), 4.60 (dd, *J* = 7.3, 5.6 Hz, 1H), 2.84 (td, *J* = 7.4, 0.9 Hz, 2H), 1.89 – 1.62 (m, 5H).

HRMS: Calc'd for C₁₅H₁₅O₂S, [M-OH]⁺ 259.0787; found 259.0782.

The chemical structure shows a cyclopentyl ring connected via a methylene group to a chiral carbon atom. This chiral carbon is also bonded to a hydroxyl group (OH) and a 5-(benzo[d][1,3]dioxol-5-yl) group. The stereochemistry at the chiral center is indicated by a wedge bond to the hydroxyl group and a dashed bond to the cyclopentylmethyl group.

Physical State: colorless oil.

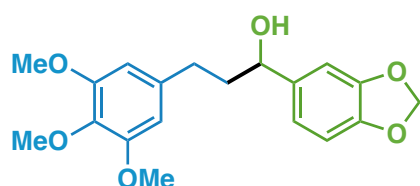
¹H NMR (500 MHz, CDCl₃): δ 6.86 (dt, *J* = 1.3, 0.5 Hz, 1H), 6.81 – 6.73 (m, 2H), 5.94 (s, 2H), 4.58 – 4.52 (m, 1H), 1.86 (s, 1H), 1.82 – 1.64 (m, 5H), 1.62 – 1.53 (m, 2H), 1.53 – 1.46 (m, 2H), 1.43 – 1.36 (m, 1H), 1.27 – 1.18 (m, 1H), 1.10 – 1.00 (m,

2H).

¹³C NMR (126 MHz, CDCl₃): δ 147.9, 147.0, 139.2, 119.5, 108.2, 106.5, 101.1, 74.9, 40.2, 38.4, 32.82, 32.78, 32.4, 25.3.

HRMS: Calc'd for C₁₅H₁₉O₂, [M-OH]⁺ 231.1380; found 231.1379.

Compound 67



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 27.0 mg (39%) of the title compound **67**.

Physical State: colorless oil.

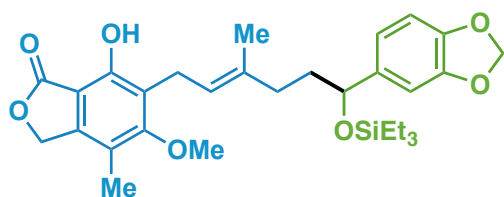
R_f = 0.28 (hexanes/EtOAc 2:1, *p*-anisaldehyde).

¹H NMR (500 MHz, CDCl₃): δ 6.88 (d, *J* = 1.6 Hz, 1H), 6.82 – 6.74 (m, 2H), 6.39 (s, 2H), 5.95 (s, 2H), 4.61 (dd, *J* = 7.7, 5.5 Hz, 1H), 3.83 (s, 6H), 3.82 (s, 3H), 2.70 – 2.63 (m, 1H), 2.58 (ddd, *J* = 13.8, 9.7, 6.3 Hz, 1H), 2.10 (dddd, *J* = 13.5, 9.7, 7.7, 5.8 Hz, 1H), 1.97 (dddd, *J* = 13.6, 10.0, 6.3, 5.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃): δ 153.3, 148.0, 147.2, 138.7, 137.6, 136.2, 119.5, 108.2, 106.5, 105.4, 101.2, 73.9, 61.0, 56.2, 40.5, 32.6.

HRMS: Calc'd for C₁₉H₂₁O₅, [M-OH]⁺ 329.1384; found 329.1383.

Compound 68



Following **General Procedure E** (without desilylation) on 0.2 mmol scale. Purification

by PTLC (2:1 hexanes/EtOAc) afforded 30.3 mg (28%) of the title compound **68**.

Physical State: colorless oil.

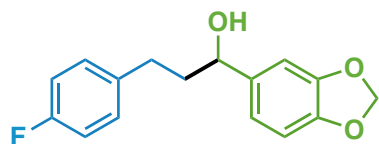
R_f = 0.36 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.67 (s, 1H), 6.78 (d, J = 1.6 Hz, 1H), 6.71 – 6.64 (m, 2H), 5.94 – 5.89 (m, 2H), 5.21 – 5.14 (m, 3H), 4.47 (dd, J = 7.2, 5.5 Hz, 1H), 3.76 (s, 3H), 3.38 (d, J = 7.0 Hz, 2H), 2.14 (s, 3H), 2.03 – 1.97 (m, 1H), 1.90 (ddd, J = 14.5, 10.2, 5.4 Hz, 1H), 1.79 – 1.73 (m, 4H), 1.64 (ddt, J = 13.4, 10.7, 5.4 Hz, 1H), 0.84 (t, J = 7.9 Hz, 9H), 0.47 (qd, J = 7.9, 4.3 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3): δ 173.1, 163.8, 153.8, 147.5, 146.5, 144.0, 140.0, 135.7, 122.6, 121.9, 119.2, 116.8, 107.8, 106.6, 106.5, 100.9, 74.6, 70.2, 61.1, 39.2, 35.8, 22.7, 16.5, 11.7, 6.9, 4.9.

HRMS: Calc'd for $\text{C}_{24}\text{H}_{25}\text{O}_6$, $[\text{M}-\text{OH}]^+$ 409.1646; found 409.1648.

Compound 69



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 22.5 mg (41%) of the title compound **69**.

Physical State: yellowish oil.

R_f = 0.28 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.16 – 7.10 (m, 2H), 6.99 – 6.93 (m, 2H), 6.88 – 6.85 (m, 1H), 6.77 (d, J = 1.1 Hz, 2H), 5.95 (s, 2H), 4.58 (dd, J = 7.7, 5.6 Hz, 1H), 2.69 (ddd, J = 15.1, 9.8, 5.7 Hz, 1H), 2.63 – 2.57 (m, 1H), 2.07 (dddd, J = 13.5, 9.5, 7.7, 5.8 Hz, 1H), 1.94 (dddd, J = 13.6, 9.8, 6.4, 5.5 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 161.4 (d, J = 243.3 Hz), 148.0, 147.2, 138.7, 137.4 (d, J = 3.3 Hz), 129.9 (d, J = 7.7 Hz), 119.5, 115.2 (d, J = 21.1 Hz), 108.3, 106.5, 101.2, 73.8, 40.7, 31.4.

^{19}F NMR (376 MHz, CDCl_3): δ -120.36.

HRMS: Calc'd for C₁₆H₁₄FO₂, [M-OH]⁺ 257.0972; found 257.0969.

Compound 70



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 47.1 mg (61%) of the title compound **70**.

Physical State: colorless oil.

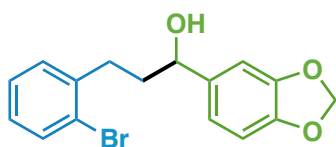
R_f = 0.46 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 6.86 (d, J = 1.5 Hz, 1H), 6.80 – 6.74 (m, 2H), 5.94 (s, 2H), 5.42 – 5.29 (m, 4H), 4.56 (dd, J = 7.4, 6.1 Hz, 1H), 2.77 (t, J = 6.9 Hz, 2H), 2.09 – 1.99 (m, 4H), 1.83 – 1.72 (m, 2H), 1.64 (ddt, J = 13.3, 10.1, 5.6 Hz, 1H), 1.41 – 1.20 (m, 16H), 0.89 (t, J = 6.9 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 147.9, 147.0, 139.2, 130.3, 130.2, 128.12, 128.06, 119.5, 108.1, 106.5, 101.1, 74.7, 39.2, 31.7, 29.8, 29.62, 29.58, 29.5, 29.4, 27.34, 27.33, 26.0, 25.8, 22.7, 14.2.

HRMS: Calc'd for C₂₅H₃₉O₃, [M+H]⁺ 387.2889; found 387.2894.

Compound 71



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 24.0 mg (36%) of the title compound **71**.

Physical State: colorless oil.

R_f = 0.32 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

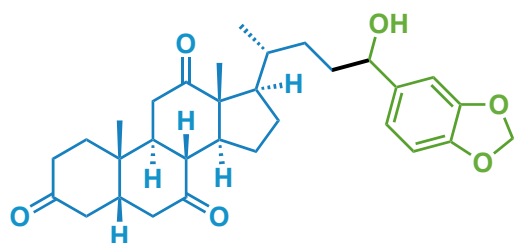
¹H NMR (600 MHz, CDCl₃): δ 7.54 – 7.49 (m, 1H), 7.24 – 7.19 (m, 2H), 7.05 (dt, J =

7.8, 4.5 Hz, 1H), 6.90 (d, $J = 1.7$ Hz, 1H), 6.82 (dd, $J = 7.9, 1.7$ Hz, 1H), 6.78 (d, $J = 7.9$ Hz, 1H), 5.95 (d, $J = 0.6$ Hz, 2H), 4.64 (dd, $J = 7.8, 5.4$ Hz, 1H), 2.87 (ddd, $J = 13.7, 10.3, 5.3$ Hz, 1H), 2.74 (ddd, $J = 13.7, 10.1, 6.2$ Hz, 1H), 2.12 – 1.96 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 148.0, 147.2, 141.2, 138.6, 133.0, 130.5, 127.8, 127.6, 124.6, 119.5, 108.3, 106.6, 101.2, 73.9, 39.0, 32.7.

Spectroscopic data are in accordance with that reported in the literature.³²

Compound 72



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (1:2 hexanes/EtOAc) afforded 50.0 mg (49%) of the title compound **72**.

Physical State: white foam.

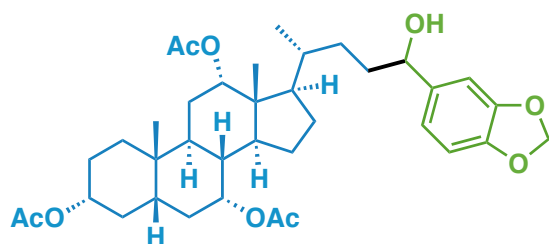
$R_f = 0.18$ (hexanes/EtOAc 1:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 6.86 – 6.82 (m, 1H), 6.76 (d, $J = 2.0$ Hz, 2H), 5.94 (d, $J = 3.3$ Hz, 2H), 4.53 (dd, $J = 7.6, 5.5$ Hz, 0.45H), 4.50 (t, $J = 6.7$ Hz, 0.60H), 2.93 – 2.79 (m, 3H), 2.35 – 2.16 (m, 6H), 2.14 – 2.07 (m, 2H), 2.05 – 1.52 (m, 10H), 1.38 (s, 3H), 1.29 – 1.19 (m, 4H), 1.04 (d, $J = 3.9$ Hz, 3H), 0.82 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 212.18, 212.16, 209.3, 208.9, 147.91, 147.86, 147.0, 146.9, 139.2, 139.0, 119.6, 119.4, 108.2, 108.1, 106.51, 106.47, 101.11, 101.09, 75.2, 74.8, 57.0, 51.89, 51.87, 49.1, 47.0, 45.8, 45.7, 45.6, 45.1, 42.9, 38.7, 36.6, 36.12, 36.06, 35.9, 35.4, 31.6, 31.4, 27.8, 25.3, 22.0, 19.13, 19.09, 12.0.

HRMS: Calc'd for $\text{C}_{31}\text{H}_{39}\text{O}_5$, $[\text{M}-\text{OH}]^+$ 491.2792; found 491.2807.

Compound 73



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 79.5 mg (62%) of the title compound **73**.

Physical State: white foam.

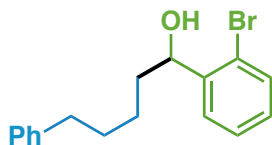
R_f = 0.53 (hexanes/EtOAc 1:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 6.83 (s, 1H), 6.74 (s, 2H), 5.93 (d, J = 2.7 Hz, 2H), 5.05 (d, J = 3.4 Hz, 1H), 4.87 (q, J = 3.2 Hz, 1H), 4.59 – 4.45 (m, 2H), 2.10 (d, J = 5.2 Hz, 3H), 2.06 (d, J = 5.6 Hz, 3H), 2.04 – 1.88 (m, 7H), 1.86 – 1.54 (m, 10H), 1.52 – 1.42 (m, 3H), 1.39 – 1.01 (m, 8H), 0.89 (s, 3H), 0.78 (d, J = 6.6 Hz, 3H), 0.69 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.52, 170.51, 147.86, 147.84, 147.0, 146.9, 139.2, 139.0, 119.5, 119.3, 108.1, 106.5, 106.4, 101.08, 101.07, 75.6, 75.2, 74.9, 74.2, 70.8, 47.59, 47.55, 45.1, 43.5, 43.4, 41.0, 37.8, 35.42, 35.36, 34.9, 34.83, 34.78, 34.7, 34.4, 31.9, 31.3, 28.98, 28.97, 27.3, 27.2, 27.0, 25.7, 22.9, 22.7, 21.7, 21.59, 21.57, 21.56, 18.00, 17.97, 12.4, 12.3.

HRMS: Calc'd for $\text{C}_{37}\text{H}_{51}\text{O}_8$, $[\text{M}-\text{OH}]^+$ 623.3578; found 623.3589.

Compound 74



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 19.8 mg (31%) of the title compound **74**.

Physical State: colorless oil.

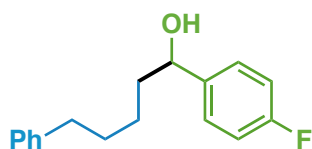
R_f = 0.52 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

¹H NMR (600 MHz, CDCl₃): δ 7.55 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.34 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.18 (ddt, *J* = 7.5, 3.4, 1.9 Hz, 3H), 7.13 (td, *J* = 7.6, 1.7 Hz, 1H), 5.08 (dd, *J* = 8.4, 4.1 Hz, 1H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.82 (d, *J* = 3.9 Hz, 1H), 1.70 (dddd, *J* = 24.5, 10.9, 8.6, 6.3 Hz, 3H), 1.62 – 1.54 (m, 1H), 1.52 – 1.45 (m, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 144.0, 142.7, 132.8, 128.9, 128.6, 128.4, 127.9, 127.4, 125.8, 122.1, 73.0, 37.6, 36.0, 31.4, 25.6.

The desired mass for HRMS was not observed.

Compound 75



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 20.2 mg (39%) of the title compound **75**.

Physical State: yellow oil.

R_f = 0.46 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

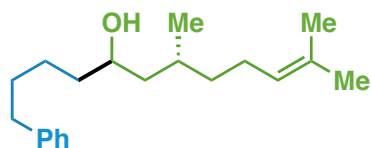
¹H NMR (500 MHz, CDCl₃): δ 7.33 – 7.23 (m, 4H), 7.21 – 7.12 (m, 3H), 7.06 – 6.99 (m, 2H), 4.65 (dd, *J* = 7.5, 5.8 Hz, 1H), 2.60 (dd, *J* = 8.6, 6.9 Hz, 2H), 1.86 – 1.78 (m, 1H), 1.74 – 1.62 (m, 3H), 1.51 – 1.42 (m, 1H), 1.36 – 1.28 (m, 1H).

¹³C NMR (126 MHz, CDCl₃): δ 162.3 (d, *J* = 245.4 Hz), 142.6, 140.7, 128.5, 128.4, 127.6 (d, *J* = 8.1 Hz), 125.8, 115.4 (d, *J* = 21.2 Hz), 74.1, 39.2, 36.0, 31.5, 25.6.

¹⁹F NMR (376 MHz, CDCl₃): δ –117.83.

Spectroscopic data are in accordance with that reported in the literature.³³

Compound 76



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 29.0 mg (51%) of the title compound **76**.

Physical State: colorless oil.

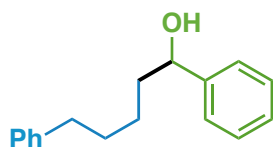
R_f = 0.42 (hexanes/EtOAc 6:1, *p*-anisaldehyde).

^1H NMR (500 MHz, CDCl_3): δ 7.31 – 7.24 (m, 2H), 7.18 (dt, J = 7.0, 3.0 Hz, 3H), 5.11 (td, J = 7.0, 3.5 Hz, 1H), 3.74 – 3.64 (m, 1H), 2.63 (t, J = 7.7 Hz, 2H), 1.98 (ddt, J = 22.8, 15.1, 7.2 Hz, 2H), 1.70 – 1.57 (m, 8H), 1.53 – 1.09 (m, 10H), 0.91 (dd, J = 8.3, 6.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3): δ 142.8, 131.41, 131.36, 128.5, 128.4, 125.8, 124.9, 70.0, 69.7, 45.4, 45.1, 38.4, 38.1, 37.7, 36.8, 36.10, 36.09, 31.7, 29.4, 29.1, 25.9, 25.6, 25.53, 25.51, 25.4, 20.5, 19.3, 17.8.

HRMS: Calc'd for $\text{C}_{20}\text{H}_{31}$, $[\text{M}-\text{OH}]^+$ 271.2420; found 271.2423.

Compound 77



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 26.5 mg (55%) of the title compound **77**.

Physical State: colorless oil.

R_f = 0.44 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

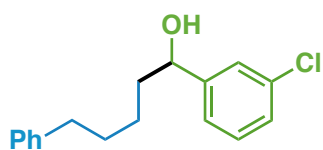
^1H NMR (500 MHz, CDCl_3): δ 7.39 – 7.31 (m, 4H), 7.32 – 7.24 (m, 3H), 7.22 – 7.13 (m, 3H), 4.67 (dd, J = 7.6, 5.7 Hz, 1H), 2.64 – 2.55 (m, 2H), 1.85 (dddd, J = 13.0, 10.4, 7.6, 5.2 Hz, 1H), 1.75 (ddt, J = 13.5, 10.3, 5.6 Hz, 1H), 1.69 – 1.62 (m, 2H), 1.55 – 1.47

(m, 1H), 1.41 – 1.32 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3): δ 145.0, 142.7, 128.6, 128.5, 128.4, 127.7, 126.0, 125.8, 74.7, 39.1, 36.0, 31.5, 25.7.

Spectroscopic data are in accordance with that reported in the literature.³³

Compound 78



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 25.8 mg (47%) of the title compound **78**.

Physical State: colorless oil.

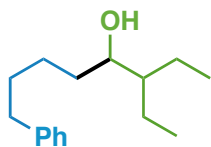
R_f = 0.48 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.34 (t, J = 1.8 Hz, 1H), 7.30 – 7.22 (m, 4H), 7.22 – 7.13 (m, 4H), 4.64 (dd, J = 7.7, 5.5 Hz, 1H), 2.60 (t, J = 7.7 Hz, 2H), 1.79 (ddd, J = 10.4, 7.8, 5.2 Hz, 1H), 1.74 – 1.62 (m, 3H), 1.52 – 1.44 (m, 1H), 1.40 – 1.32 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 147.1, 142.6, 134.5, 129.9, 128.5, 128.4, 127.7, 126.2, 125.8, 124.2, 74.1, 39.1, 35.9, 31.4, 25.5.

The desired mass for HRMS was not observed.

Compound 79



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 21.0 mg (45%) of the title compound **79**.

Physical State: colorless oil.

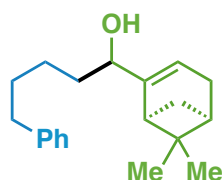
R_f = 0.44 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.30 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 3.61 (dt, J = 8.3, 4.1 Hz, 1H), 2.69 – 2.58 (m, 2H), 1.68 – 1.61 (m, 2H), 1.56 – 1.26 (m, 9H), 1.20 – 1.16 (m, 1H), 0.90 (td, J = 7.5, 1.3 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3): δ 142.8, 128.6, 128.4, 125.8, 73.3, 47.0, 36.1, 34.1, 31.7, 26.2, 22.2, 21.3, 12.1, 12.0.

The desired mass for HRMS was not observed.

Compound 80



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 23.8 mg (42%) of the title compound **80**.

Physical State: colorless oil.

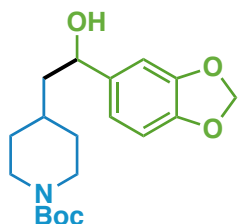
R_f = 0.46 (hexanes/EtOAc 4:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 5.41 (dtq, J = 4.4, 2.8, 1.3 Hz, 1H), 3.98 (q, J = 6.8 Hz, 1H), 2.61 (td, J = 7.7, 6.8, 1.9 Hz, 2H), 2.44 – 2.38 (m, 1H), 2.34 – 2.18 (m, 3H), 2.10 (ddq, J = 6.1, 3.1, 1.5 Hz, 1H), 1.64 (p, J = 7.6 Hz, 2H), 1.53 – 1.33 (m, 5H), 1.33 – 1.25 (m, 3H), 1.11 (dd, J = 31.0, 8.6 Hz, 1H), 0.81 (d, J = 25.1 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 150.8, 150.2, 142.8, 128.5, 128.4, 125.8, 118.3, 117.7, 75.1, 75.0, 42.2, 41.9, 41.2, 41.1, 37.90, 37.87, 36.1, 36.0, 34.7, 34.4, 32.01, 31.95, 31.6, 31.5, 31.3, 31.2, 26.4, 26.3, 25.7, 25.5, 21.5.

HRMS: Calc'd for $\text{C}_{20}\text{H}_{27}$, $[\text{M}-\text{OH}]^+$ 267.2107; found 267.2112.

Compound 84



Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 16.0 mg (23%) of the title compound **84**.

Physical State: colorless oil.

R_f = 0.36 (hexanes/EtOAc 2:1, *p*-anisaldehyde).

^1H NMR (600 MHz, CDCl_3): δ 6.86 (d, J = 1.4 Hz, 1H), 6.77 (d, J = 1.7 Hz, 2H), 5.95 (s, 2H), 4.70 (dd, J = 8.5, 5.1 Hz, 1H), 4.06 (s, 2H), 2.67 (s, 2H), 1.77 – 1.65 (m, 4H), 1.57 – 1.48 (m, 2H), 1.45 (s, 9H), 1.13 (ddd, J = 23.6, 12.0, 4.1 Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 155.0, 148.1, 147.2, 139.1, 119.4, 108.3, 106.4, 101.2, 79.4, 71.9, 45.9, 32.8, 28.6.

HRMS: Calc'd for $\text{C}_{14}\text{H}_{20}\text{NO}_3$, $[\text{M}-\text{Boc}+2\text{H}]^+$ 250.1438; found 250.1438.

Reaction Progress Kinetic Analysis

Procedure for electrochemical NHK reaction

Preparation of nickel catalyst stock solution in DMF (0.008 M, solution A): A screw-capped culture tube equipped with a magnetic stir bar was charged with $\text{NiCl}_2\cdot\text{glyme}$ (9 mg, 0.04 mmol) and 2,9-dibutyl-1,10-phenanthroline (18 mg, 0.06 mmol). The atmosphere was exchanged by 3 cycles of vacuum/Ar. Degassed DMF (5 mL) was added via a syringe, and the mixture was stirred for 5 min to give a homogeneous pink solution.

Preparation of CrCl_2 stock solution in DMF (0.04 M, solution B): A screw-capped culture tube was charged with CrCl_2 (30 mg, 0.24 mmol) in the glovebox. The tube was removed from the glovebox and placed under an argon balloon, whereupon degassed DMF (6 mL) was added via a syringe. The resulting mixture was sonicated until a homogeneous green solution was obtained.

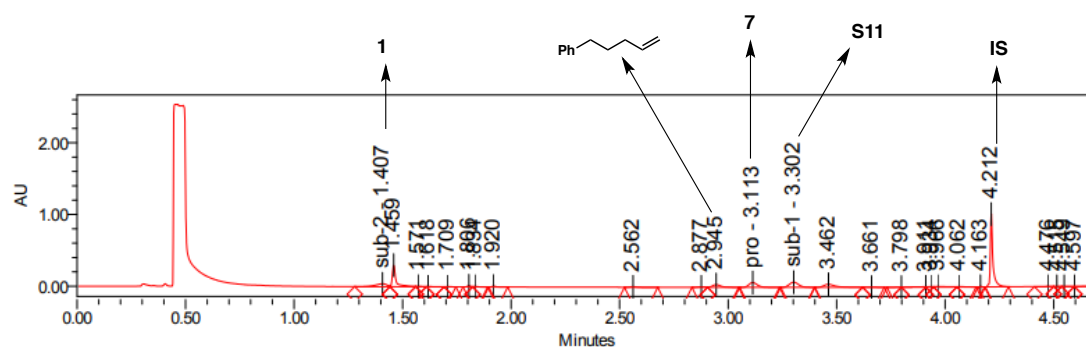
To a 5 mL ElectraSyn vial equipped with a magnetic stir bar was added 3-phenylpropionaldehyde (sub-2, 26.8 mg, 0.2 mmol), (4-bromopent-4-en-1-yl)benzene (sub-1, 90.0 mg, 0.4 mmol), Cp_2ZrCl_2 (29.0 mg, 0.1 mmol), TBAB (80.6 mg, 0.25 mmol), and 4,4'-di-*tert*-butylbiphenyl (26.6 mg, 0.1 mmol). The vial cap equipped with aluminum anode and nickel foam cathode was tightened and the atmosphere was exchanged by cycling vacuum then argon (via a balloon). Degassed DMF (1.0 mL), solution A (0.5 mL), and solution B (1.0 mL) were added to the vial sequentially. The mixture was subjected to 10 mA constant current condition at a stir speed of 1000 rpm for 100 minutes which signified time = 0. Aliquots ($\sim 20\ \mu\text{L}$) were removed from the reaction at the indicated times and directly injected into 0.4 mL CH_3CN in a filter vial without any further quench and subjected to analysis.

Analysis

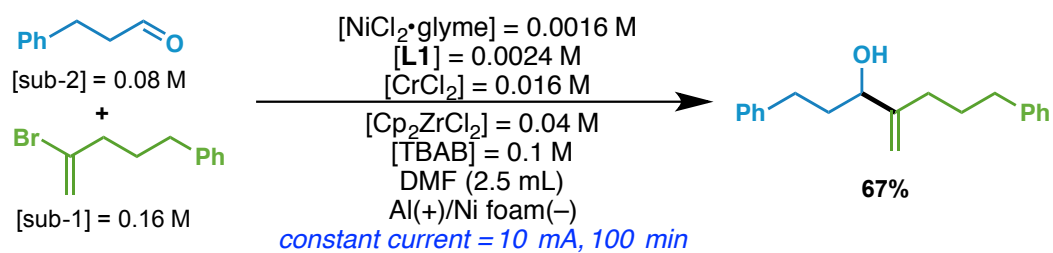
The reaction mixtures were analyzed on a Waters I-Class LC equipped with a Waters BEH C18 column (1.7 μm , 2.1 $\times$ 105 mm). The analyses was performed under gradient conditions at 55 $^{\circ}\text{C}$ using a gradient based on (A) 0.1% NH_4OH in water and (B) CH_3CN (15–99% B over 3.5 minutes, held at 99% B for 0.2 minutes).

Retention times for relevant species: (4-bromopent-4-en-1-yl)benzene (**S11**) 3.239 minutes (detection wavelength 285 nm), 3-phenylpropionaldehyde (**1**) 1.382 minutes (detection wavelength 285 nm), product (**7**) 3.032 minutes (detection wavelength 285 nm), pent-4-en-1-ylbenzene 3.077 minutes (detection wavelength 285 nm), 4,4'-di-*tert*-butylbiphenyl 4.219 minutes (detection wavelength 222 nm). Analyte concentrations were calculated against 4,4'-di-*tert*-butylbiphenyl as internal standard, and all analytes were calibrated separately using a series of ten calibration solutions of different concentrations, with the highest concentration of the series being 10 mM.

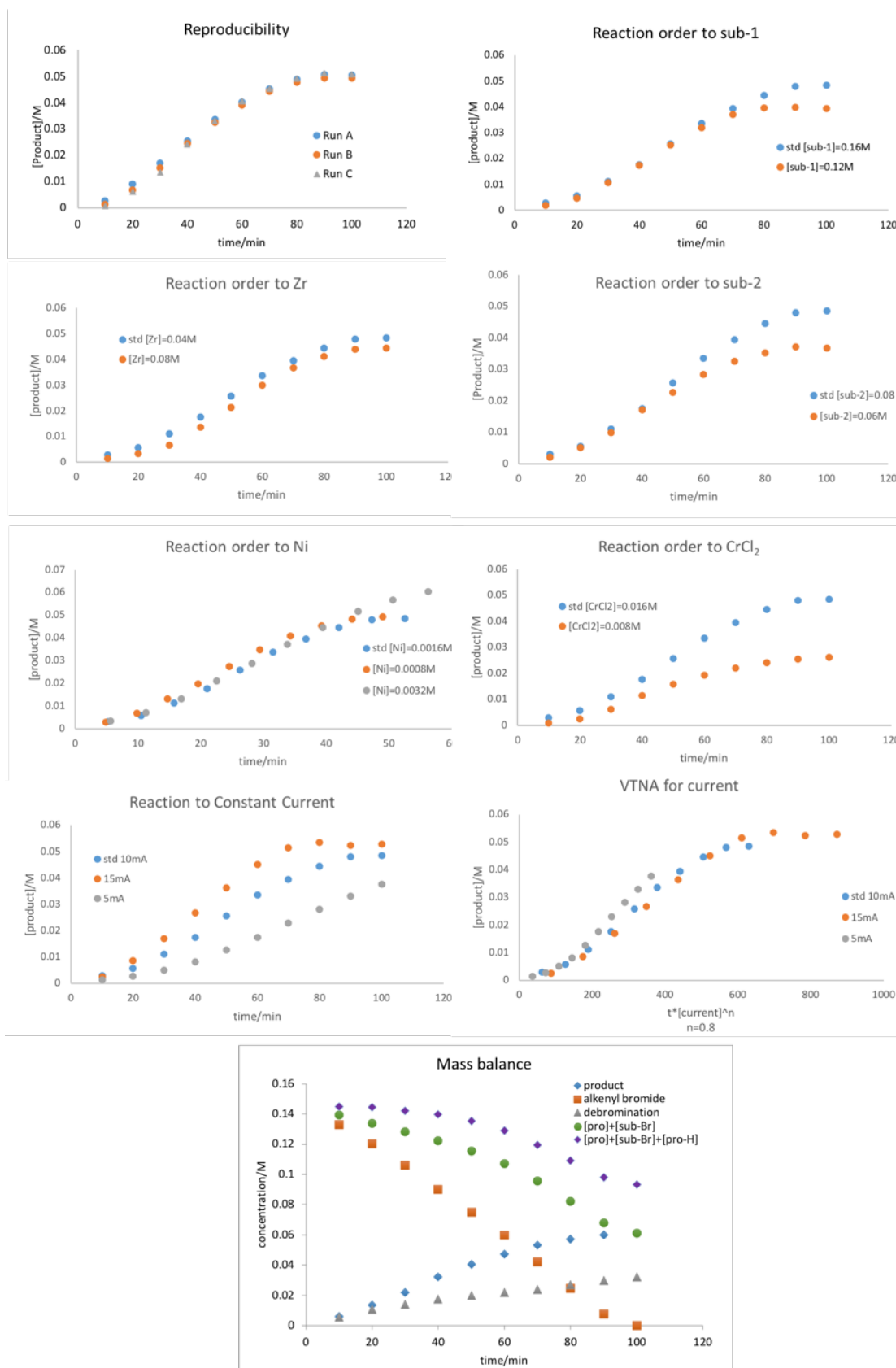
HPLC trace



Results



	[sub-1] (M)	[sub-2] (M)	[Ni] (M)	[L1] (M)	[Cr] (M)	[Zr] (M)	Current (mA)
Std	0.16	0.08	0.0016	0.0024	0.016	0.04	10
Sub-2	0.16	0.06	0.0016	0.0024	0.016	0.04	10
Sub-1	0.12	0.08	0.0016	0.0024	0.016	0.04	10
Ni-a	0.16	0.08	0.0008	0.0012	0.016	0.04	10
Ni-b	0.16	0.08	0.0032	0.0084	0.016	0.04	10
Cr	0.16	0.08	0.0016	0.0024	0.008	0.04	10
Zr	0.16	0.08	0.0016	0.0024	0.016	0.08	10
Current-a	0.16	0.08	0.0016	0.0024	0.016	0.04	15
Current-b	0.16	0.08	0.0016	0.0024	0.016	0.04	5



Procedure for classical NHK reaction

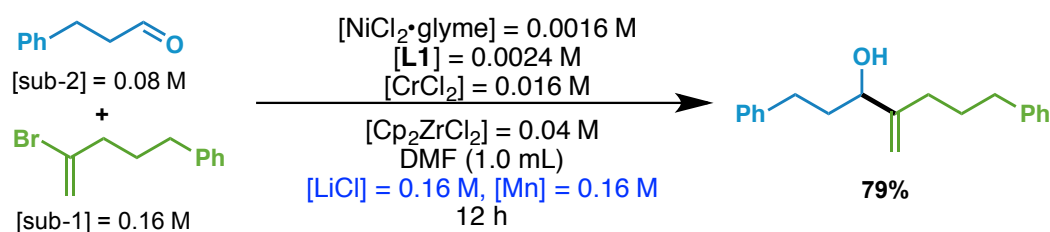
Preparation of nickel catalyst stock solution in DMF: In a glovebox, $\text{NiCl}_2\cdot\text{glyme}$ (17.6 mg, 0.08 mmol) and 2,9-dibutyl-1,10-phenanthroline (35 mg, 0.12 mmol) were added into a 3 mL volumetric flask with DMF to form a Ni catalyst stock solution A.

Preparation of LiCl , CrCl_2 , and Cp_2ZrCl_2 stock solution in DMF: In glovebox, LiCl (43.4 mg, 1 mmol), CrCl_2 (24.6 mg, 0.2 mmol), and Cp_2ZrCl_2 (146.2 mg, 0.5 mmol) were added into a 5 mL volumetric flask with DMF as solvent to form a stock solution B.

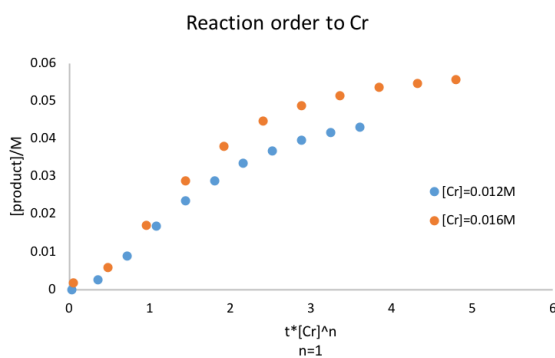
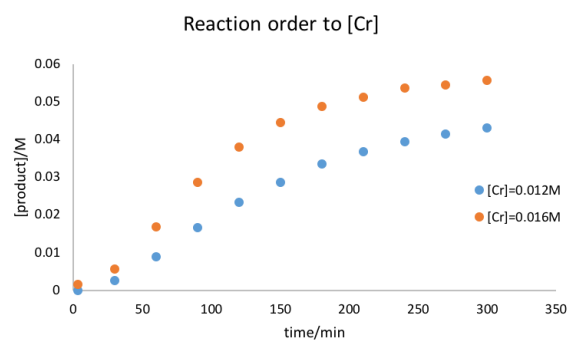
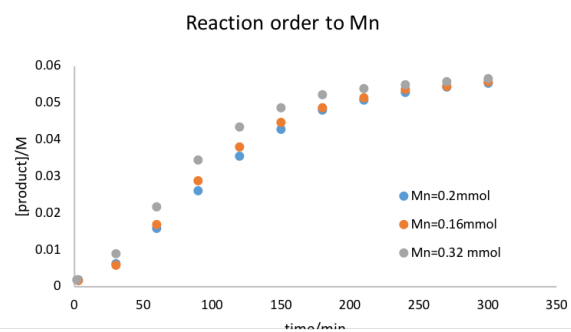
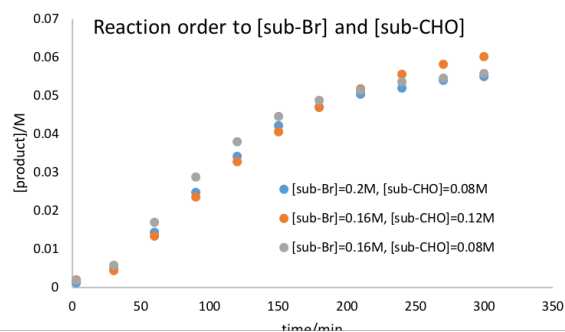
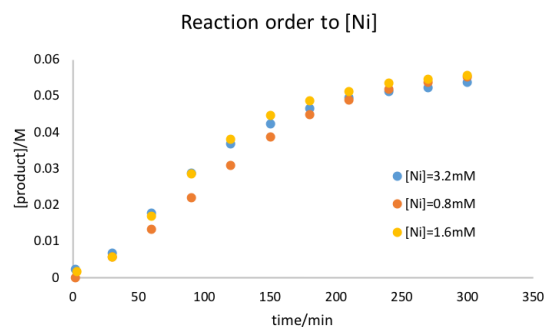
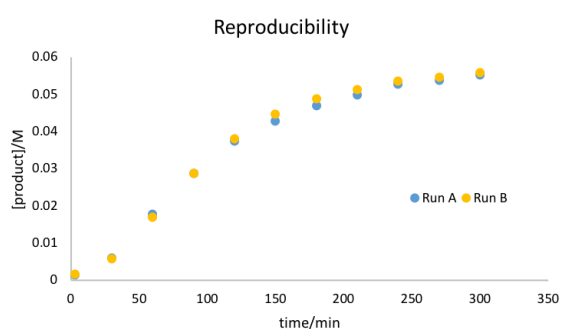
Preparation of sub-1 and sub-2 stock solution in DMF: To a 1 mL volumetric flask were added (4-bromopent-4-en-1-yl)benzene (sub-1, 119.5 mg, 0.53 mmol), 3-phenylpropionaldehyde (sub-2, 35.7 mg, 0.266 mmol), and DMF as solvent to form stock solution C.

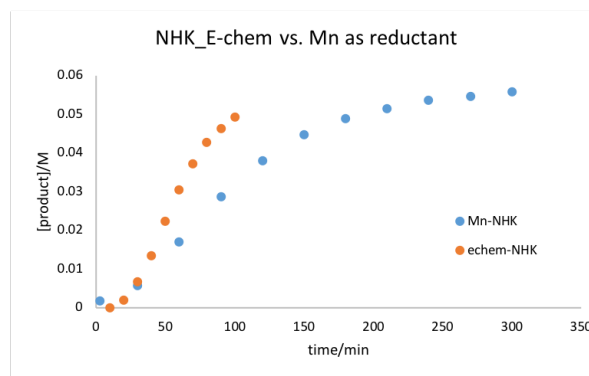
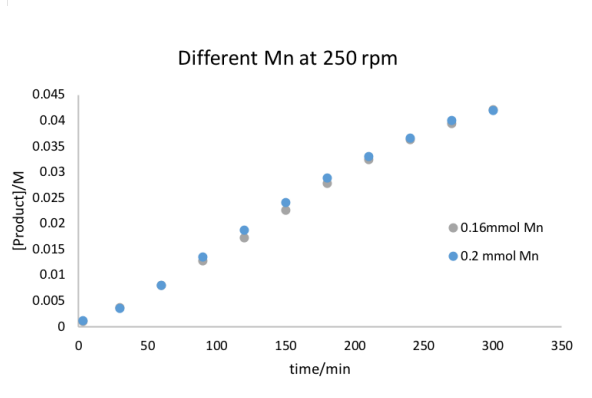
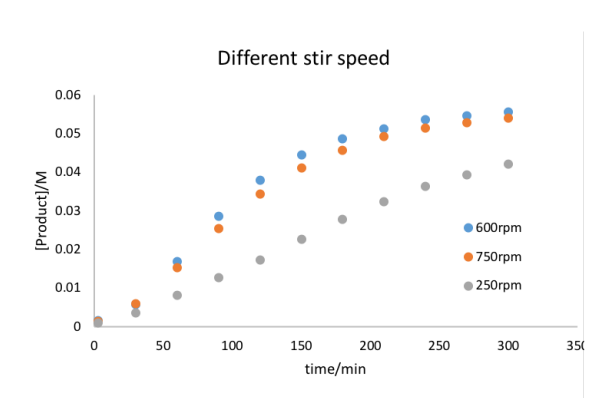
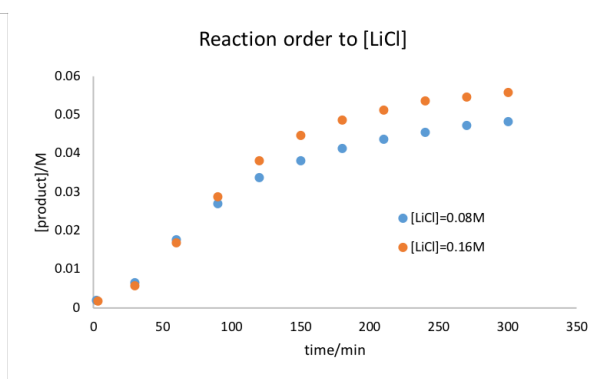
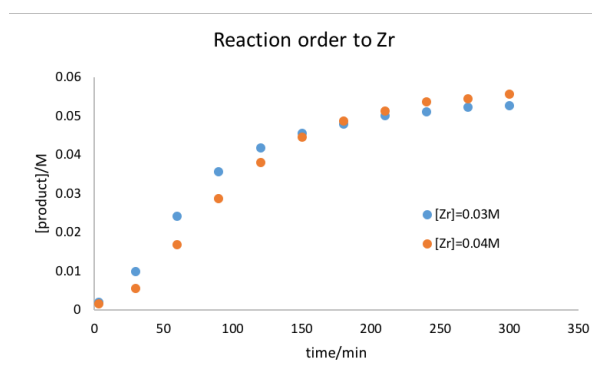
In the glovebox, to a 1 dram glass vial equipped with a magnetic stir bar, Mn (0.16 mmol, 8.8 mg) was added, then stock solution C (sub-1 and sub-2, 0.3 mL) and stock solution B (LiCl , CrCl_2 , and Cp_2ZrCl_2 , 0.4 mL) were added into the reaction vial. 4,4'-Di-*tert*-butylbiphenyl was added as internal standard. The reaction was started by adding stock solution A (Ni catalyst and Ligand). The aliquots were taken every 30 min and quenched with CH_3CN (0.1% TFA, 0.4 mL), then added to the filter vial (PTFE, 0.2 μm) and analyzed by RP-LC.

Results



	[sub-1] (M)	[sub-2] (M)	[Ni] (mM)	[L1] (mM)	[Cr] (M)	[Zr] (M)	Mn (M)	[LiCl] (M)
Std	0.16	0.08	1.6	2.4	0.016	0.04	0.16	0.16
Sub-2	0.16	0.12	1.6	2.4	0.016	0.04	0.16	0.16
Sub-1	0.2	0.08	1.6	2.4	0.016	0.04	0.16	0.16
Ni-a	0.16	0.08	3.2	4.8	0.016	0.04	0.16	0.16
Ni-b	0.16	0.08	0.8	1.2	0.016	0.04	0.16	0.16
Cr	0.16	0.08	1.6	2.4	0.012	0.04	0.16	0.16
Zr	0.16	0.08	1.6	2.4	0.016	0.03	0.16	0.16
Mn	0.16	0.08	1.6	2.4	0.016	0.04	0.08	0.16
LiCl	0.16	0.08	1.6	2.4	0.016	0.04	0.16	0.08





Procedure for electrochemical decarboxylative NHK reaction

To a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added aldehyde (30 mg, 0.2 mmol), redox-active ester (32.3 mg, 0.2 mmol), CrCl_3 (6.4 mg, 0.04 mmol, 0.2 equiv), TBAClO_4 (85 mg, 0.25 mmol, 0.1 M), and 4,4'-di-*tert*-butylbiphenyl (26.6 mg, 0.1 mmol). The vial cap equipped with aluminum anode and nickel foam cathode was tightened and the atmosphere was exchanged by cycling vacuum then argon (via a balloon). Then DMF (2.0 mL), THF (0.5 mL), and TESC1 (67 μL , 0.4 mmol, 2.0 equiv) were added to the vial sequentially. The mixture was subjected to 2.5 mA constant current condition at a stir speed of 1000 rpm for 300 minutes which signified time = 0. Aliquots (~ 20 μL) were removed from the reaction at the indicated times and directly injected into 0.4 mL CH_3CN in a filter vial without any further quench and subjected to analysis.

Procedure for classical decarboxylative NHK reaction

Preparation of RAE, aldehyde, and 4,4'-di-*tert*-butylbiphenyl (internal standard)

stock solution in DMF/THF: To a 3 mL volumetric flask were added RAE (258.4 mg, 0.8 mmol), aldehyde (120 mg, 0.8 mmol), 4,4'-di-*tert*-butylbiphenyl (106.4 mg, 0.4 mmol), and DMF/THF (4:1) to form stock solution A.

Preparation of TESC1 stock solution in DMF/THF: To a volumetric flask were added TESC1 (241.1 mg, 1.6 mmol) and DMF/THF (4:1) to form stock solution B.

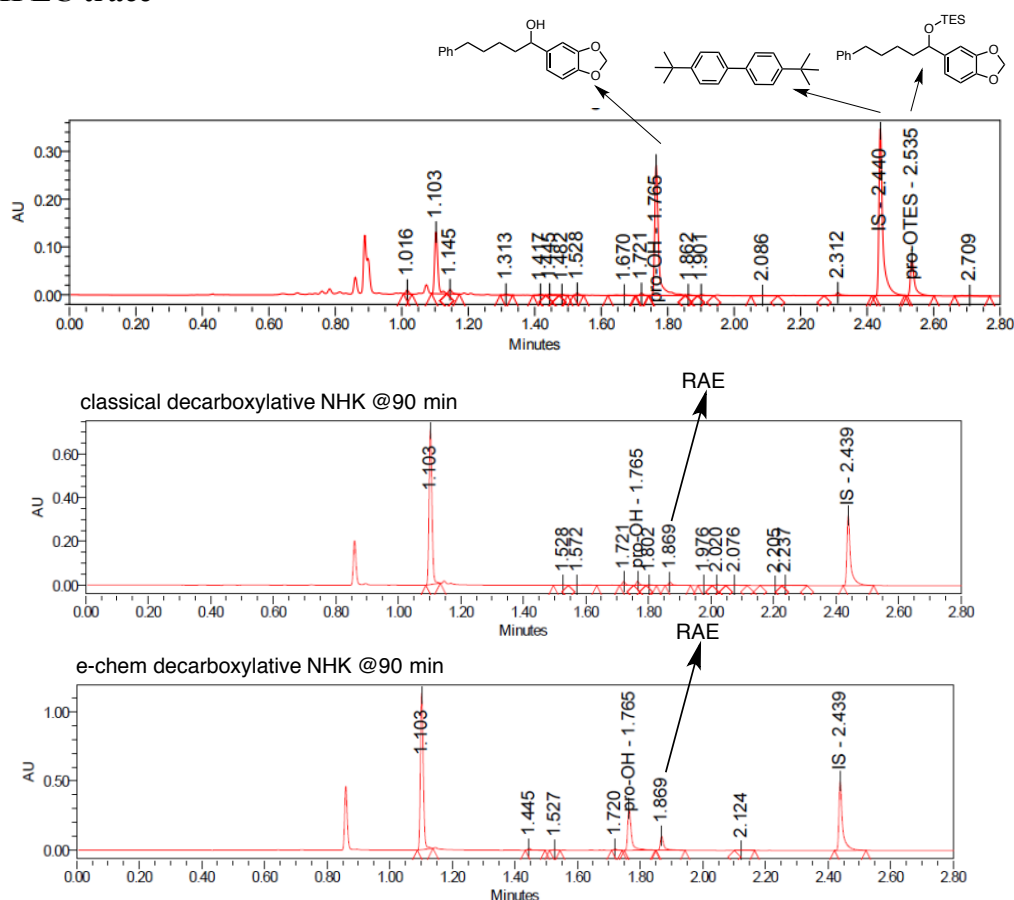
In the glovebox, to a 1 dram glass vial equipped with a magnetic stir bar, Mn (0.16 mmol, 8.8 mg) was added, then stock solution A (RAE, aldehyde, and internal standard, 0.3 mL) and CrCl_3 (2.53 mg, 0.016mmol) were added into a reaction vial. The reaction was started by adding TESC1 (stock solution B, 0.4 mL). The aliquots were taken every 30 min and quenched with CH_3CN (0.1% TFA, 0.4 mL), then added to the filter vial (PTFE, 0.2 μm) and analyzed by RP-LC.

Analysis

The reaction mixtures were analyzed on a Waters I-Class LC with a Waters UPLC BEH C18 column (1.7 μm , 2.1 $\times$ 105 mm) using a 0.1% aqueous formic acid/ CH_3CN gradient (0.6 mL/min, 15–99% CH_3CN over 2.1 minutes, followed by an isocratic hold at 99% CH_3CN) at 55 $^\circ\text{C}$.

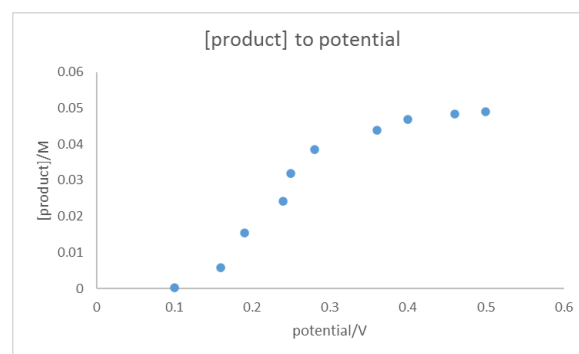
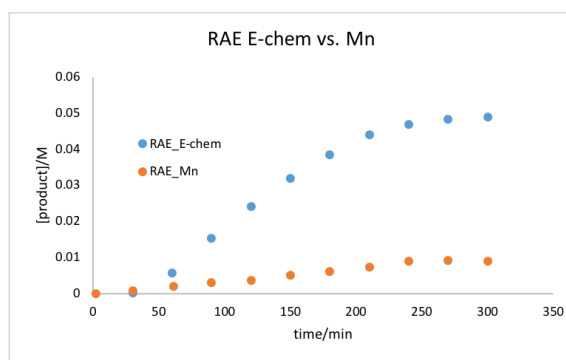
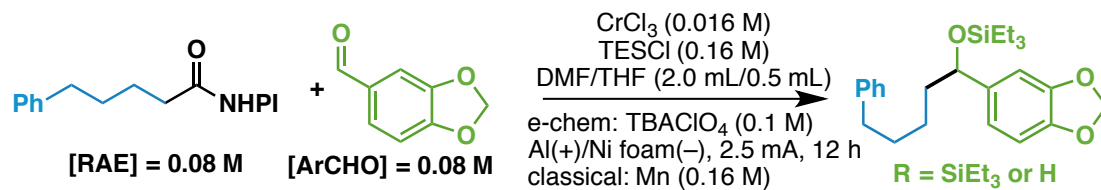
Retention times for relevant species: compound **60** 1.765 minutes (detection wavelength 286 nm), compound **85** 2.535 minutes (detection wavelength 286 nm), 4,4'-di-*tert*-butylbiphenyl 2.440 minutes (detection wavelength 286 nm). Analyte concentrations were calculated against 4,4'-di-*tert*-butylbiphenyl as internal standard, and all analytes were calibrated separately using a series of ten calibration solutions of different concentrations with the highest concentration of the series being 10 mM.

HPLC trace



Compare LC traces at 90 min for both reactions, the trace of e-chem looks much cleaner and with less by product, while trace with Mn, the peak of RAE almost decompose.

Results

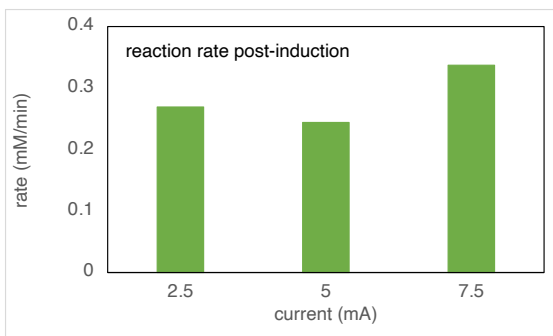
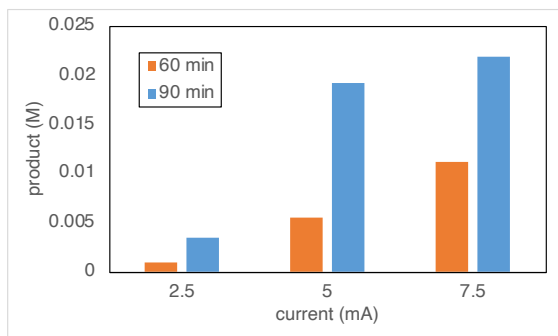


	[RAE] (M)	[ArCHO] (M)	[CrCl ₃] (M)	[TESCl] (M)	Current (mA)	Mn (M)
E-Chem	0.08	0.08	0.016	0.16	2.5	
Mn_RAE	0.08	0.08	0.016	0.16		0.16

Effect of current:

Reaction exhibits an induction period that is proportional to current.

Rate is not influenced by current post-induction period.



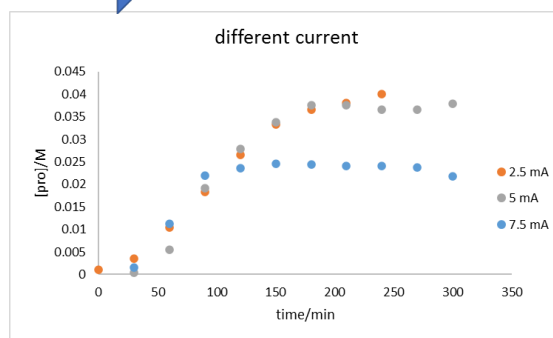
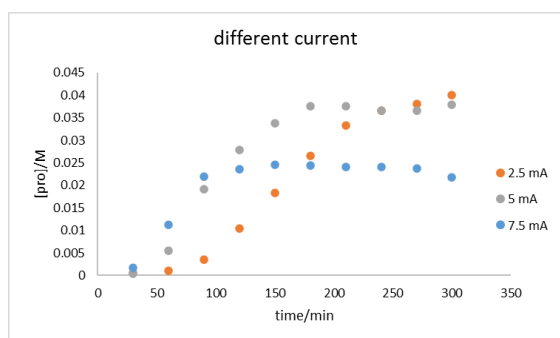
Kinetic with current:

Induction period, CrCl_3 do not soluble at the first 30 min;

Reaction with RAE show 0th order in current;

Current at 7.5 mA decompose the RAE substrate.

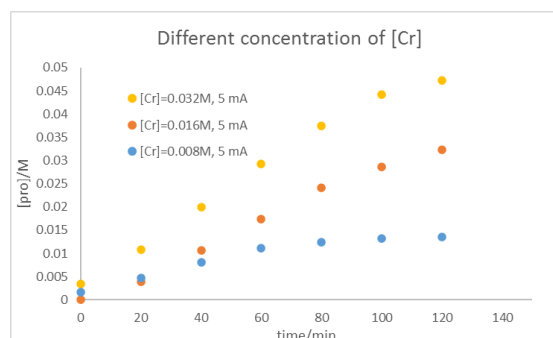
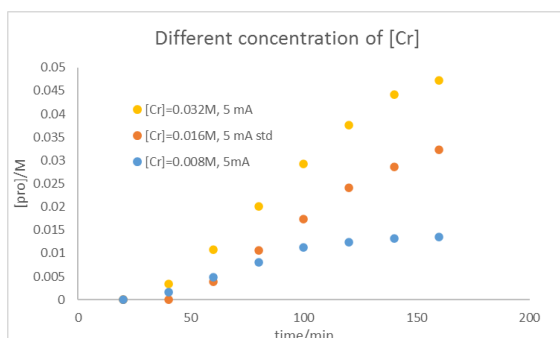
*Time shift of 2.5 mA
for induction period*



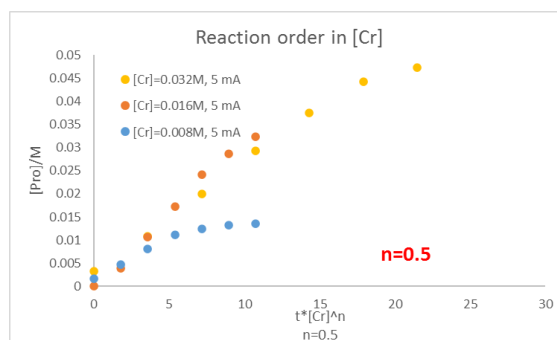
Kinetic with [Cr]:

Reaction show 0.5th order in [Cr];

Reaction with 0.008M of [Cr], reaction stop at 100 min, suggest the catalyst decompose.



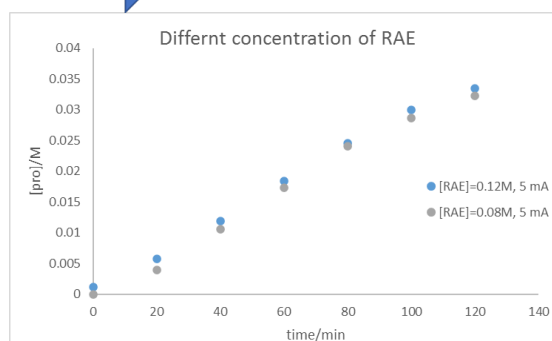
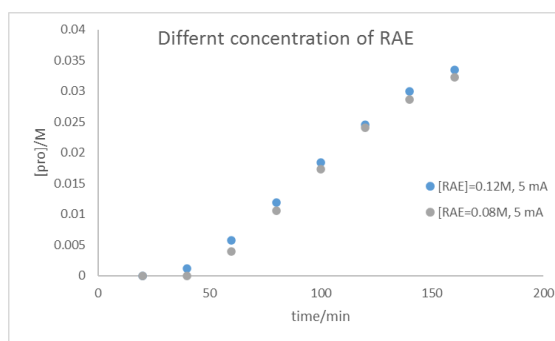
Remove the induction period



Kinetic with [RAE]:

Reaction show 0th order in [RAE]

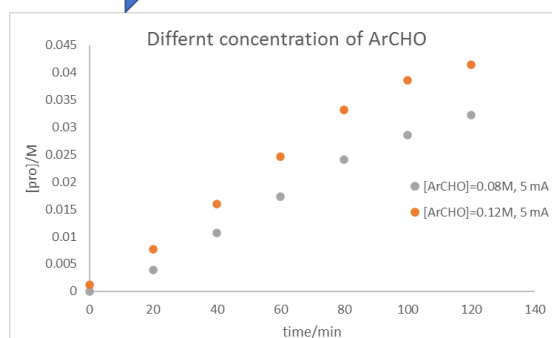
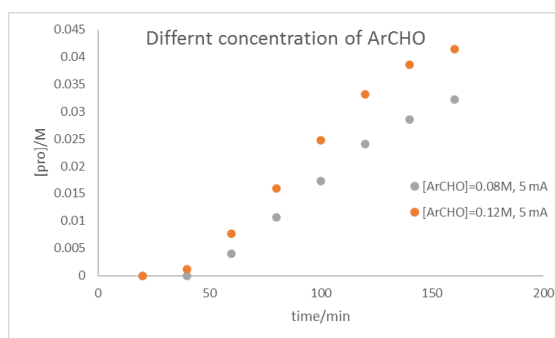
*Time shift of
induction period*



Kinetic with [ArCHO]:

Reaction show positive order in [ArCHO]

*Time shift of
induction period*



General Details for UV-vis Spectroscopy and Electroanalytical Studies

UV-vis Spectroscopy

UV–visible (UV-vis) spectra were collected with either a Cary 50 Bio UV-vis or Cary 500 UV-vis near-IR (NIR) spectrophotometer. Samples were prepared inside a nitrogen-filled glovebox using air-tight quartz cuvettes.

Electrochemistry

Electrochemical experiments were performed using a standard three-electrode cell with a glassy carbon (GC) working electrode (3 mm diameter) or Ni wire [10931 Nickel wire, 0.25 mm diameter, Puratronic, 99.994% (metals basis)] working electrode, a 0.01 M $\text{Ag}^{+/0}$ (AgNO_3) in CH_3CN non-aqueous reference electrode, and a 3.175 mm diameter aluminum (Al) rod (K&S Precision Metals) counter electrode. Voltammograms were collected in a nitrogen-filled glovebox in DMF with TBAPF_6 (0.1–0.2 M) (TBA = tetrabutylammonium) supporting electrolyte. A Gamry Reference 600 potentiostat was used for all room temperature voltammetry. All voltammograms were electronically compensated using positive-feedback iR -compensation at 90% of the R_u , which was measured by potentiostatic electrochemical impedance spectroscopy. Ferrocene (Fc) or cobaltocenium hexafluorophosphate (Co) served as the internal potential standard, and all potentials were referenced relative to $\text{Fc}^{+/0}$.

UV-vis Spectroelectrochemistry

In situ spectroelectrochemical measurements were performed in a nitrogen-filled glovebox with a quartz spectroelectrochemical cell with a 0.17 mm path length from Pine Research Instrumentation (AKSTCKIT3), a custom working electrode prepared from Ni mesh (Alfa Aesar, 44128 Nickel gauze, 100 mesh woven from 0.1 mm diameter wire) and Ni wire [10931 Nickel wire, 0.25 mm diameter, Puratronic, 99.994% (metals basis)], and an Al wire counter electrode [(Alfa Aesar, aluminum wire, 1.0 mm diameter, annealed, Puratronic, 99.9995% (metals basis))]. Measurements were recorded using either an Analytical Instrument Systems, Inc. DT2000 deuterium-tungsten light source

coupled to Stellarnet Black Comet UV-vis and DWARF-Star NIR spectrometers or a Hamamatsu L1179 deuterium light source coupled to an Ocean Optics USB4000-UV-Vis-ES spectrometer. The cell was placed in an Ocean Optics CUV-UV cuvette holder connected to the spectrometer by 600 μm core optical fibers.

Assembly of the UV-vis Spectroelectrochemical Cell

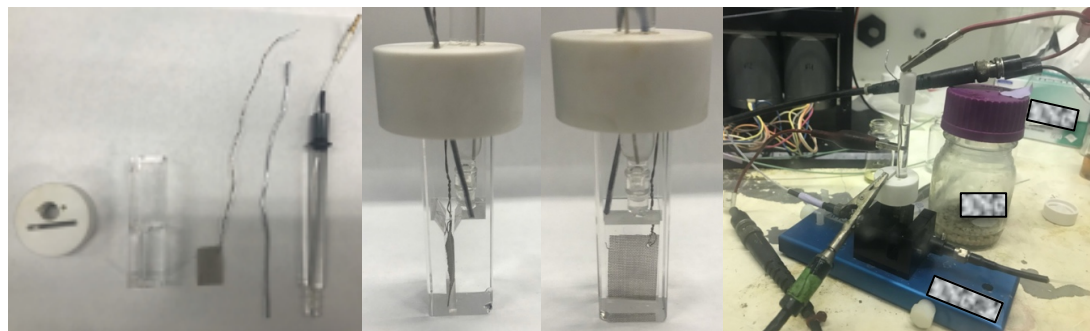


Figure S1: (Left) Individual components of spectroelectrochemical cell from left to right: PTFE cap, spectroelectrochemical cuvette, custom Ni-mesh working electrode, aluminum wire counter electrode, reference electrode. (Middle) Assembled spectroelectrochemical cell side profile. (Middle) Assembled spectroelectrochemical cell front on profile. (Right) Assembled spectroelectrochemical cell placed inside cuvette holder connected to both optics and potentiostat cables inside a glovebox.

Cyclic Voltammetry

Identification of CV Waves

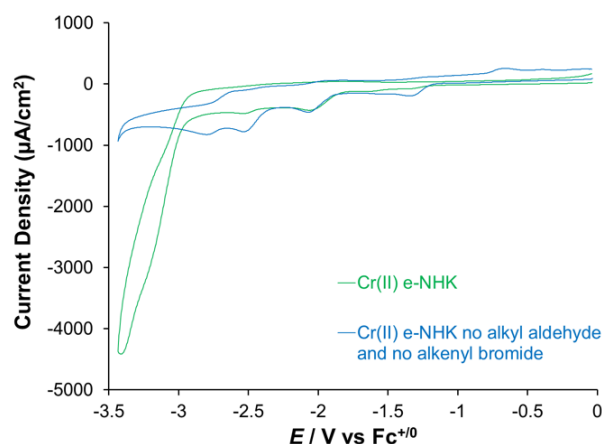


Figure S2: Full Cr(II) e-NHK: [S11] = 104 mM, [1] = 52 mM, [CrCl₂] = 2 mM, [Cp₂ZrCl₂] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L4] = 0.3 mM. **Cr(II) e-NHK no aldehyde or alkenyl bromide:** [CrCl₂] = 2 mM, [Cp₂ZrCl₂] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L4] = 0.3 mM. All CV experiments were run in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc^{+/0}.

After multiple attempts to observe a catalytic current for the analytical cyclic voltammetry of the Cr(II) e-NHK, we could not correlate any changes in current to the catalytic wave of the e-NHK, which had an expected onset potential of -1.6 V vs a nonaqueous AgNO₃ reference electrode. However, upon cathodic scan near the potential limit of the solvent window, we observed a substantial current (Figure S2 green) near -3.2 V vs Fc^{+/0} for **Cr(II) e-NHK no aldehyde or alkenyl bromide**. Recent electrochemical benchmarking studies by Nicewicz and coworkers suggest strongly reducing potentials are needed for direct reduction of alkyl aldehyde functional groups.³⁴ Therefore, we suspect the substantial current detected near -3.2 V vs Fc^{+/0} for **Cr(II) e-NHK no aldehyde or alkenyl bromide** is likely the direct reduction of **1** at the working electrode.

Since we demonstrated that Cr(III) salts were productive catalysts for the e-NHK, we opted to try this source of Cr for our analytical voltammetry studies and were

gratified to observe a cathodic current (-2.0 V vs $\text{Fc}^{+/0}$) that corresponded to the catalytic wave of the e-NHK (see Figures S6 and S3 below).

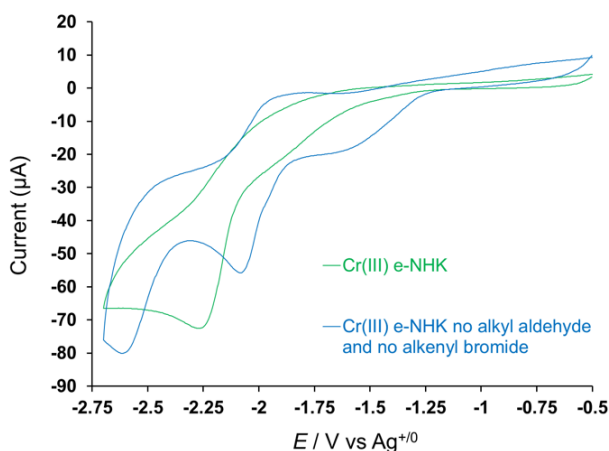


Figure S3: Cr(III) e-NHK: $[\text{S11}] = 104$ mM, $[\mathbf{1}] = 52$ mM, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2$ mM, $[\text{Cp}_2\text{ZrCl}_2] = 2$ mM, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2$ mM, $[\mathbf{L4}] = 0.3$ mM. **Cr(III) e-NHK no aldehyde or alkenyl bromide:** $[\text{CrCl}_3 \cdot 3\text{THF}] = 2$ mM, $[\text{Cp}_2\text{ZrCl}_2] = 2$ mM, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2$ mM, $[\mathbf{L4}] = 0.3$ mM. All CV experiments were run in DMF with $[\text{TBAPF}_6] = 0.1$ M and acquired with a scan rate of 100 mV/s, Ni-wire working electrode, and Al counter electrode. All potentials are referenced against a 0.01 M $\text{Ag}^{+/0}$ (AgNO_3) non-aqueous (CH_3CN) reference electrode.

During our optimization studies, we observed that utilizing a Ni-foam working electrode improved the bulk electrolysis yield; however, higher quality analytical CV data were obtained when a GC working electrode was used instead of a Ni-wire. We note that the general features of the CV (see Figure S6) data are comparable whether collected with a GC working electrode or a Ni-wire working electrode.

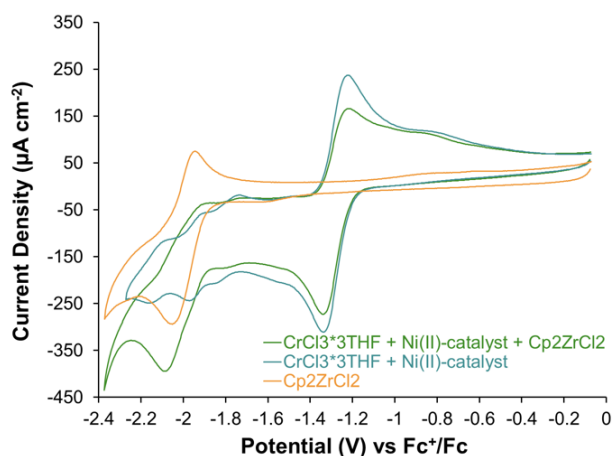


Figure S4: $\text{CrCl}_3 \cdot 3\text{THF}$ + Ni(II) catalyst: $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. $\text{CrCl}_3 \cdot 3\text{THF}$ + Ni(II) catalyst + Cp_2ZrCl_2 : $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$. Cp_2ZrCl_2 : $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$. All CV experiments were run in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$ and acquired with a scan rate of 100 mV/s , GC working electrode, and Al counter electrode. All potentials referenced to $\text{Fc}^{+/0}$.

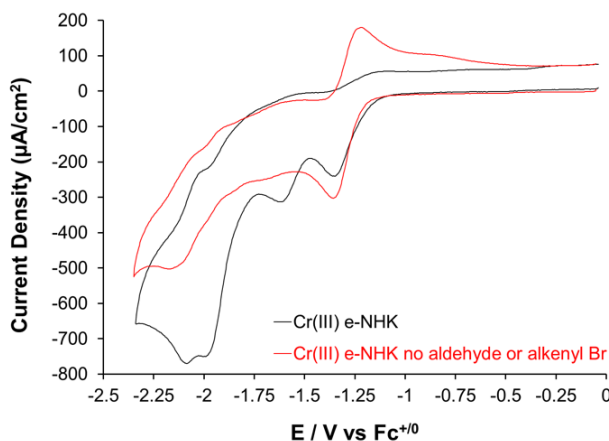


Figure S5: Cr(III) e-NHK : $[\text{S11}] = 104 \text{ mM}$, $[\text{1}] = 52 \text{ mM}$, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. **$\text{Cr(III) e-NHK no aldehyde or alkenyl bromide}$** : $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. All CV experiments were run in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$ and acquired with a scan rate of 100 mV/s , GC working electrode, and Al counter electrode. All potentials referenced to $\text{Fc}^{+/0}$.

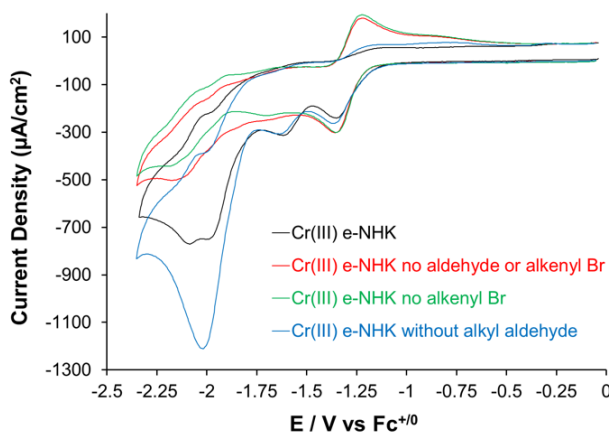


Figure S6: Cr(III) e-NHK : $[\text{S11}] = 104 \text{ mM}$, $[\text{1}] = 52 \text{ mM}$, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. **$\text{Cr(III) e-NHK no aldehyde or alkenyl bromide}$** : $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. **$\text{Cr(III) e-NHK without alkenyl bromide}$** : $[\text{S11}] = 104 \text{ mM}$, $[\text{1}] = 0 \text{ mM}$, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. **$\text{Cr(III) e-NHK without alkyl aldehyde}$** : $[\text{S11}] = 104 \text{ mM}$, $[\text{1}] = 52 \text{ mM}$, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$. All CV experiments were run in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$

and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to $\text{Fc}^{+/0}$.

During the course of our e-NHK kinetics experiments for the bulk electrolysis, we believe a significant amount of alkenyl bromide dehalogenation occurs concomitantly with productive e-NHK catalysis. We suggest the catalytic current in the absence of alkyl aldehyde corresponds to this electrocatalytic dehalogenation process. Nédélec and coworkers have previously reported electrocatalytic low-valent Ni homocoupling of alkenyl bromides under similar electrolysis conditions.³⁵

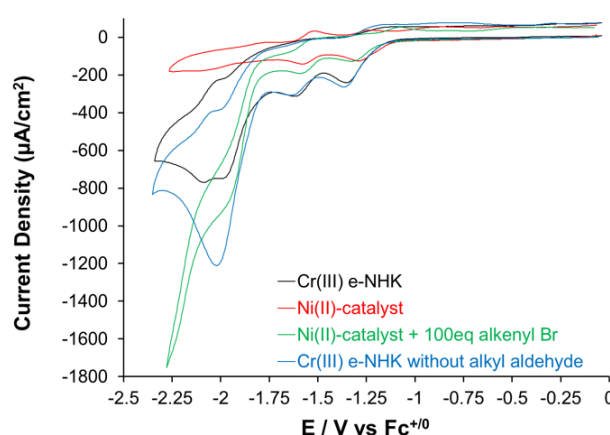


Figure S7: Cr(III) e-NHK: [S11] = 104 mM, [1] = 52 mM, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, [L4] = 0.3 mM. **Ni(II) catalyst:** $[\text{NiCl}_2 \cdot \text{DME}] = 0.5 \text{ mM}$, [L4] = 0.75 mM. **Cr(III) e-NHK without alkyl aldehyde:** [S11] = 104 mM, [1] = 0 mM, $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, [L4] = 0.3 mM. **Ni(II)-catalyst + 100 equiv alkenyl bromide:** [S11] = 50 mM, $[\text{NiCl}_2 \cdot \text{DME}] = 0.5 \text{ mM}$, [L4] = 0.75 mM. All CV experiments were run in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$ and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to $\text{Fc}^{+/0}$.

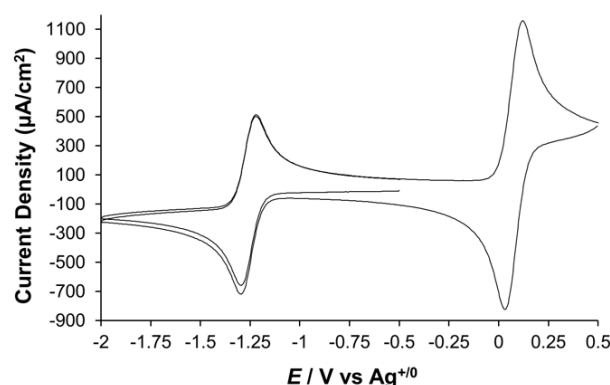


Figure S8: A mixture of ferrocene with cobaltocenium hexafluorophosphate (Co) in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials are referenced against a 0.01 M Ag^{+/0} (AgNO₃) non-aqueous (CH₃CN) reference electrode.

When acquiring voltammetry with the Ni-based working electrodes, we observe an OCP of -0.6 V vs Fc^{+/0}. Therefore, we relied upon Cp₂CoPF₆ as an external electrochemical reference when conducting voltammetry with the Ni-mesh in the spectroelectrochemical experiments. We then referenced the Cp₂CoPF₆ formal potential to ferrocene as shown above.

Catalytic Current Dependence on Substrate/Catalyst Concentration

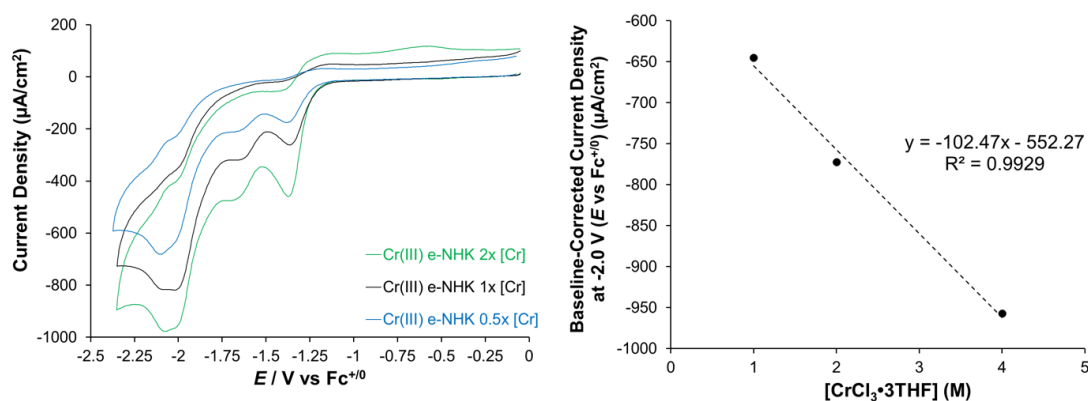


Figure S9: (Left) Cyclic voltammograms of e-NHK with varied [CrCl₃·3THF]: **4 mM, 2 mM, 1 mM**. All experiments have [S11] = 80 mM, [1] = 46 mM, [Cp₂ZrCl₂] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L4] = 0.3 mM. All CV experiments were run in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc^{+/0}. **(Right)** [CrCl₃·3THF] vs current at -2.0 V (E vs. Fc^{+/0}).

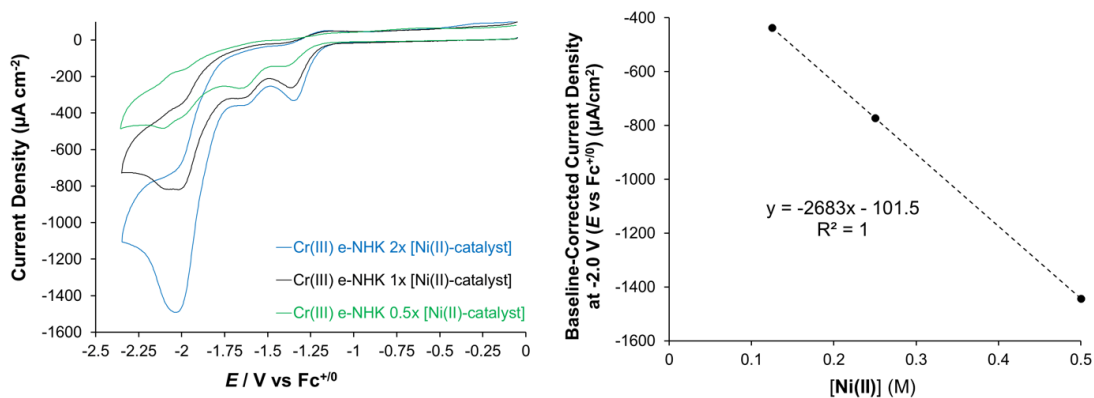


Figure S10: (Left) CVs of e-NHK with varied [Ni(II)]: **0.5 mM, 0.25 mM, 0.125 mM**. All experiments have [S11] = 80 mM, [1] = 46 mM, $[Cp_2ZrCl_2] = 2$ mM, $[CrCl_3 \cdot 3THF] = 2$ mM, and Ni/L4 as 1:1.5. All CV experiments were run in DMF with $[TBAPF_6] = 0.1$ M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to $Fc^{+/0}$. **(Right)** [Ni(II)] vs current at -2.0 V (E vs. $Fc^{+/0}$).

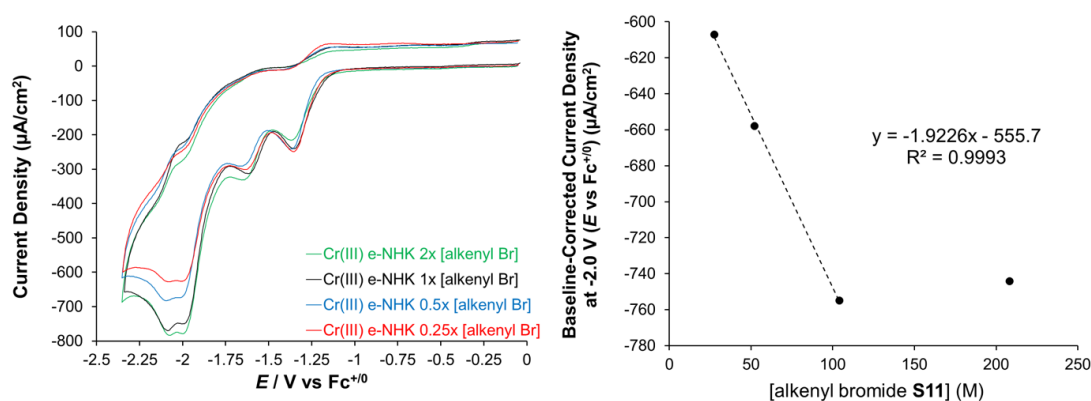


Figure S11: (Left) Cyclic voltammograms of e-NHK with varied [S11]: **208 mM, 104 mM, 52 mM, 27 mM**. All experiments have [1] = 53 mM, $[Cp_2ZrCl_2] = 2$ mM, $[CrCl_3 \cdot 3THF] = 2$ mM, $[NiCl_2 \cdot DME] = 0.2$ mM, and [L4] = 0.3 mM. All CV experiments were run in DMF with $[TBAPF_6] = 0.1$ M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to $Fc^{+/0}$. **(Right)** [S11] vs current at -2.0 V (E vs. $Fc^{+/0}$).

Scan Rate Dependence

All scan rate dependency studies were conducted in DMF with $[TBAPF_6] = 0.1$ M. The voltammetry was acquired with a freshly polished GC working electrode and Al counter electrode. All potentials referenced to $Fc^{+/0}$.

A linear correlation between baseline-corrected current density and square root of the scan rate was observed for all CV mixtures illustrated below.

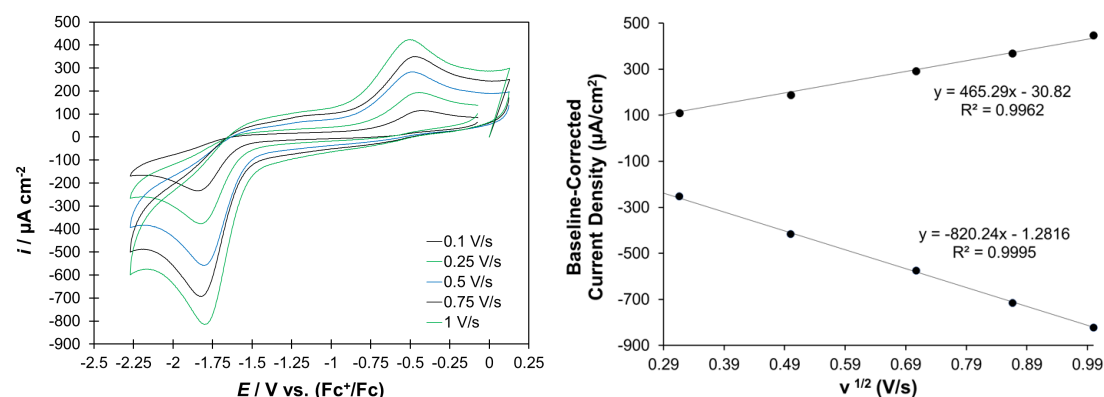


Figure S12: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$ with corresponding Randles-Sevcik plot.

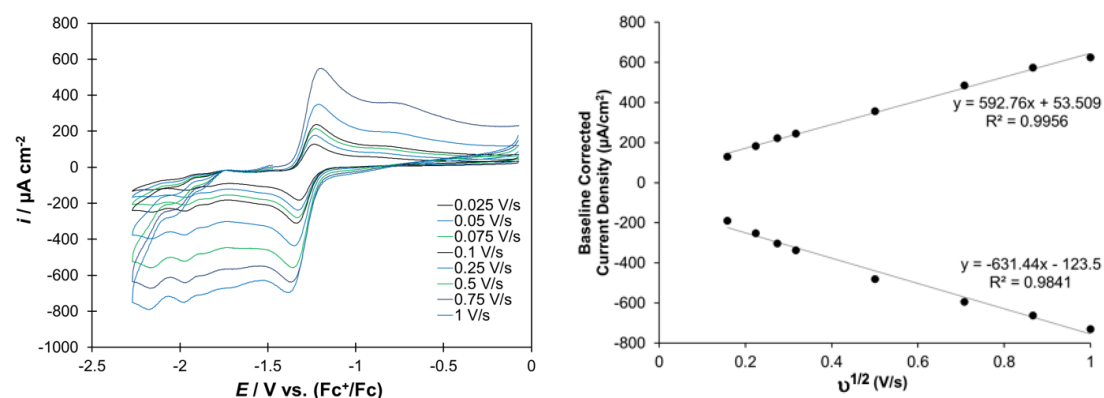


Figure S13: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, and $[\text{L4}] = 0.3 \text{ mM}$ with corresponding Randles-Sevcik plot for wave near $-1.4 \text{ V vs Fc}^{+/0}$.

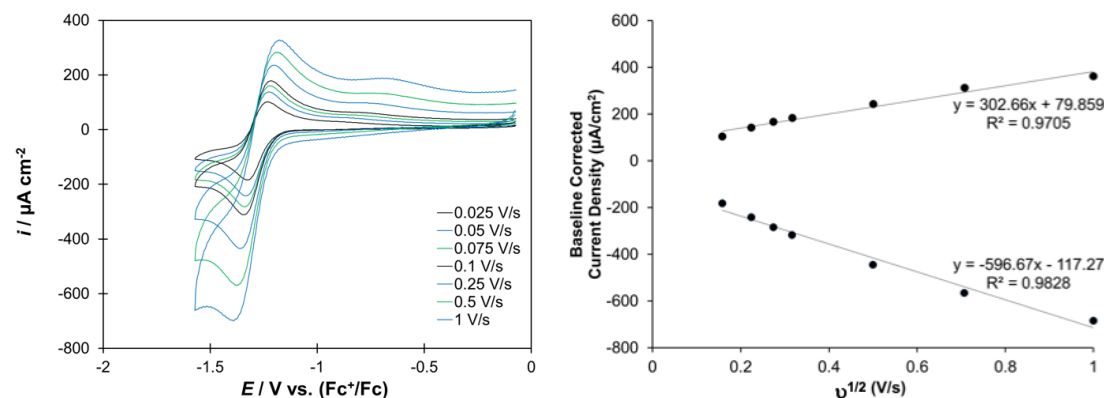


Figure S14: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, and $[\text{L4}] = 0.3 \text{ mM}$ with truncated potential window along with corresponding Randles-Sevcik plot.

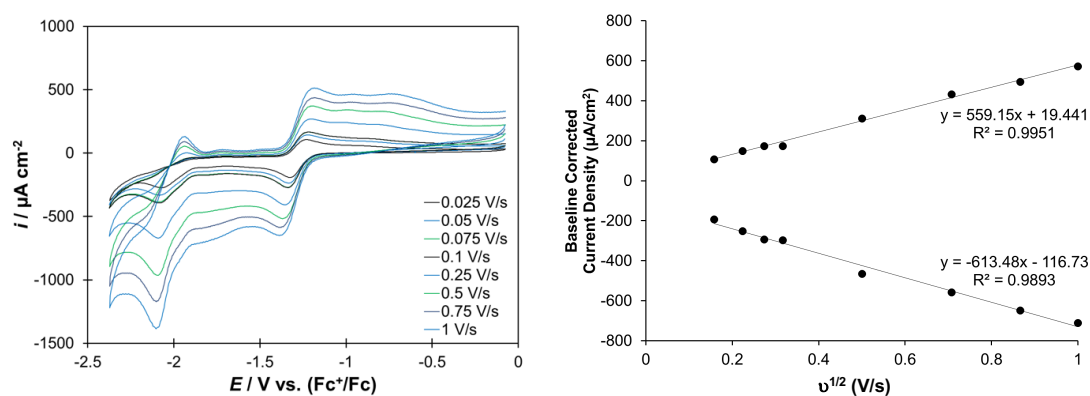


Figure S15: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$, and $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$ with corresponding Randles-Sevcik plot for wave near $-1.4 \text{ V vs Fc}^{+/0}$.

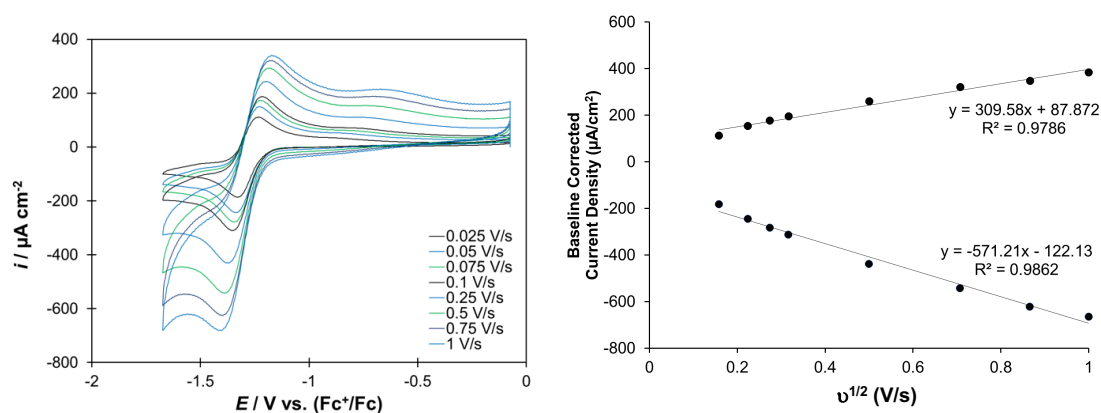


Figure S16: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$, and $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$ with truncated potential window along with corresponding Randles-Sevcik plot.

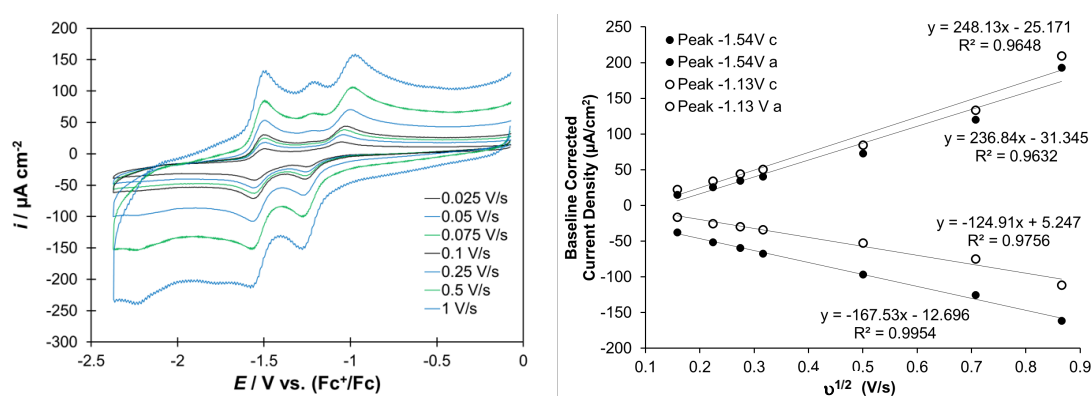


Figure S17: Scan rate dependence for $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$ and $[\text{L4}] = 0.3 \text{ mM}$ with corresponding Randles-Sevcik plot.

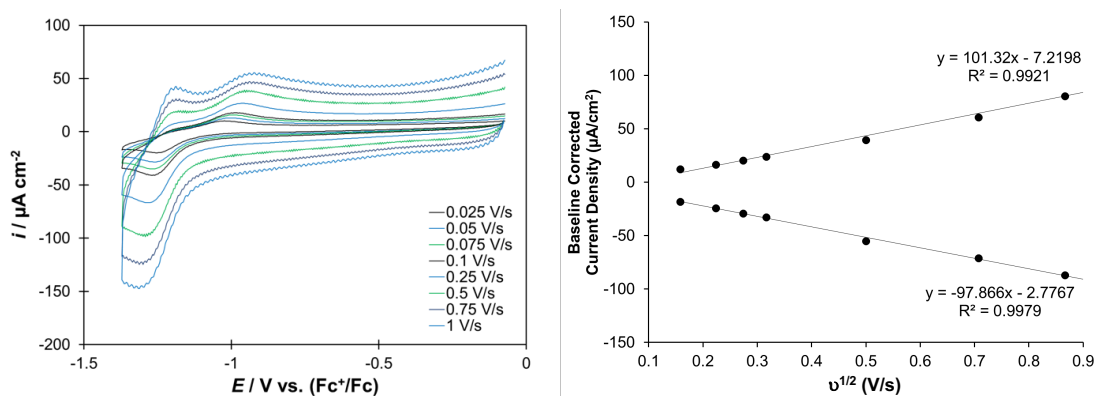


Figure S18: Scan rate dependence for $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$ and $[\text{L4}] = 0.3 \text{ mM}$ with truncated potential window along with corresponding Randles-Sevcik plot.

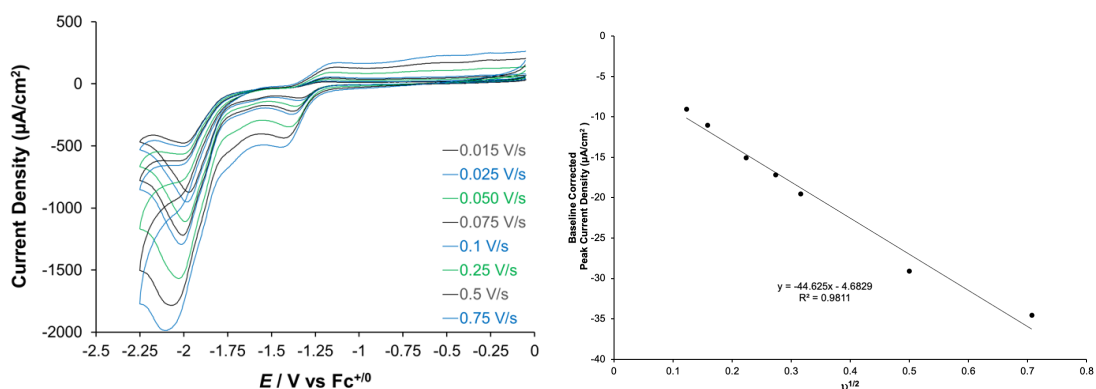


Figure S19: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{1}] = 70 \text{ mM}$, and $[\text{S11}] = 140 \text{ mM}$ with corresponding Randles-Sevcik plot for wave near $-2.0 \text{ V vs Fc}^{+/0}$.

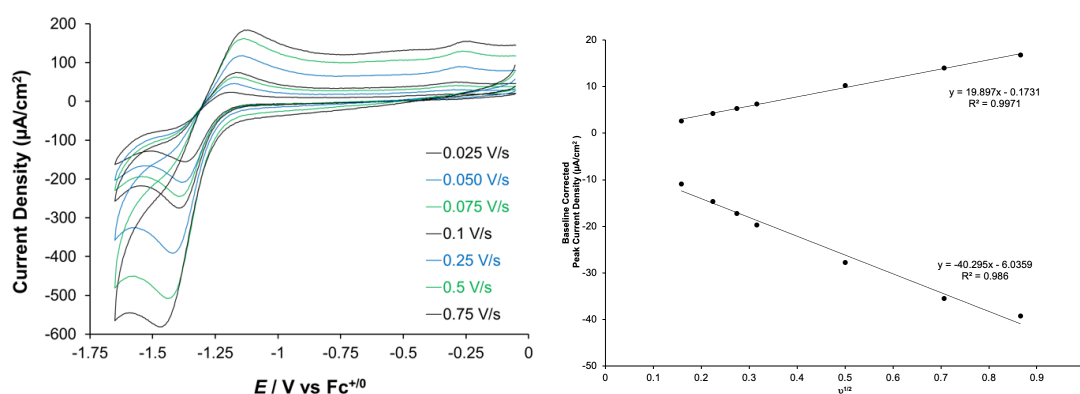


Figure S20: Scan rate dependence for $[\text{CrCl}_3 \cdot 3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, $[\text{L4}] = 0.3 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$, $[\text{1}] = 70 \text{ mM}$, and $[\text{S11}] = 140 \text{ mM}$ with truncated potential window along with corresponding Randles-Sevcik plot.

UV-vis Studies

All UV-vis studies were acquired in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$.

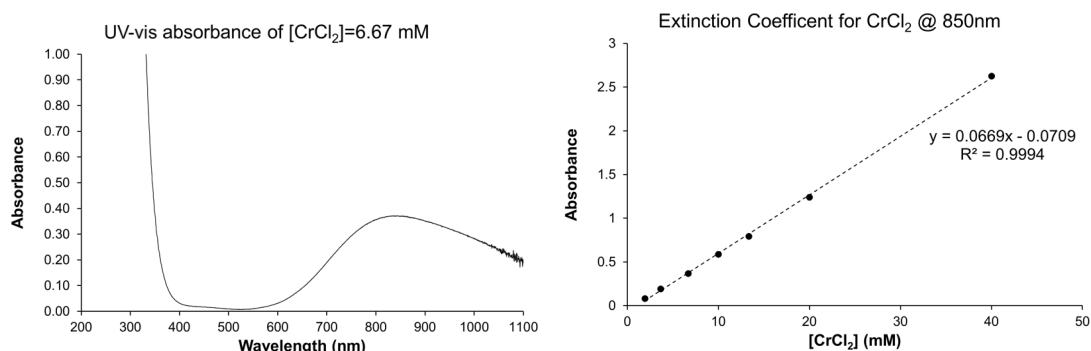


Figure S21: (Left) UV-vis absorbance of $[\text{CrCl}_2] = 6.67 \text{ mM}$. (Right) Plot of $[\text{CrCl}_2]$ versus absorbance at 850 nm.

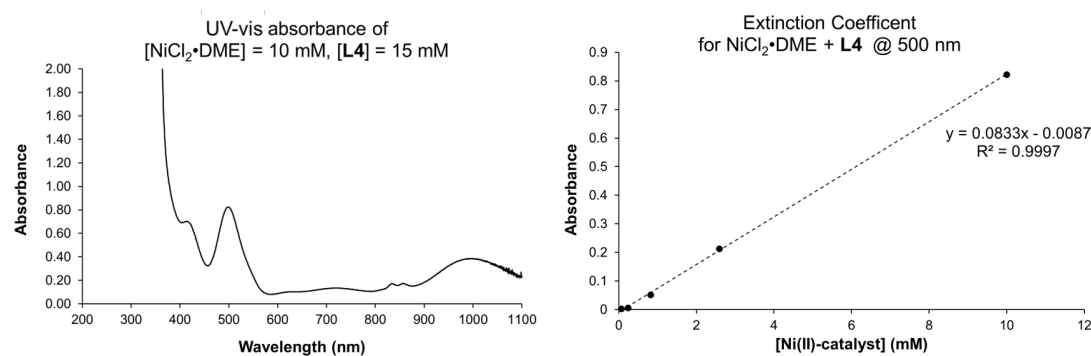


Figure S22: (Left) UV-vis absorbance of $[\text{NiCl}_2 \cdot \text{DME}] = 10 \text{ mM}$ and $[\text{L4}] = 15 \text{ mM}$. (Right) Plot of $[\text{Ni(II)}]$ versus absorbance at 500 nm.

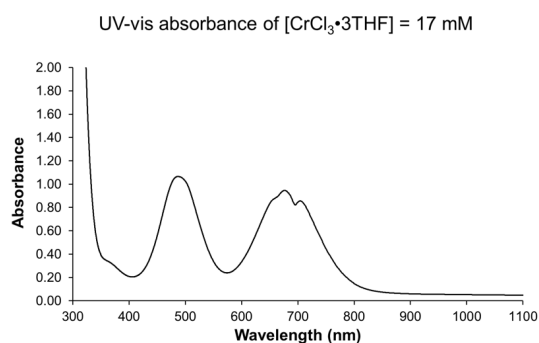


Figure S23: UV-vis absorbance of $[\text{CrCl}_3 \cdot 3\text{THF}] = 17 \text{ mM}$.

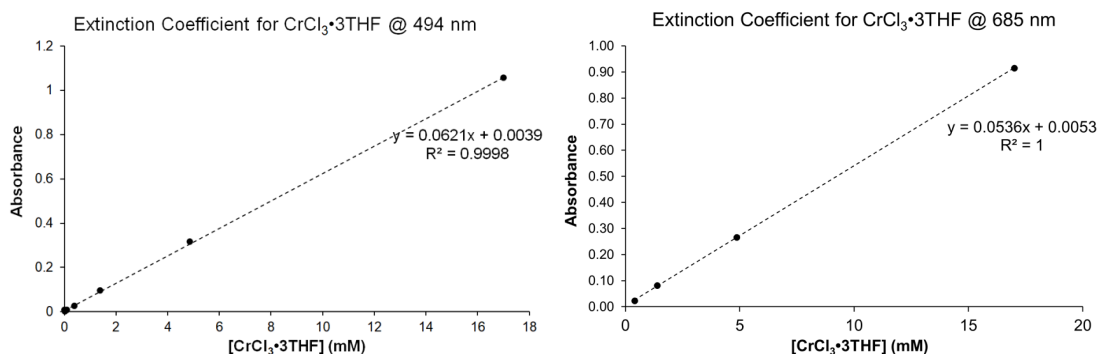


Figure S24: (Left) Plot of $[\text{CrCl}_3 \cdot 3\text{THF}]$ versus absorbance at 494 nm. (Right) Plot of $[\text{CrCl}_3 \cdot 3\text{THF}]$ versus absorbance at 685 nm.

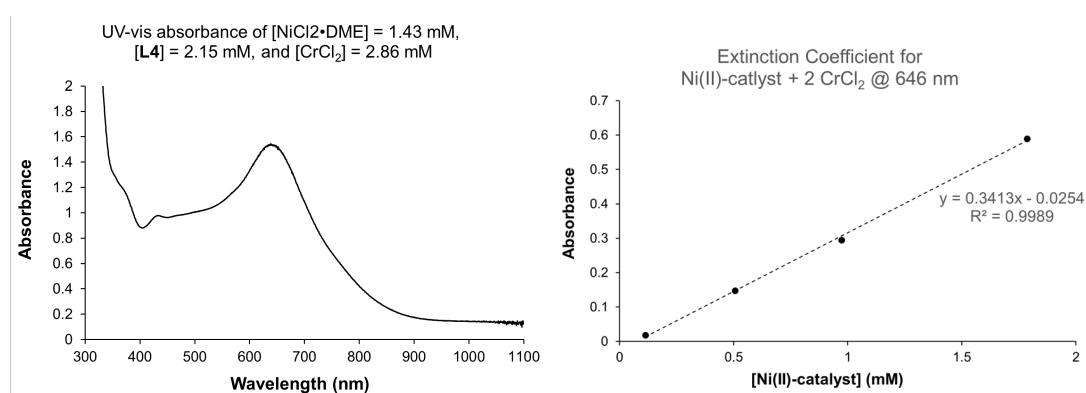


Figure S25: (Left) UV-vis absorbance of $[\text{CrCl}_2] = 2.86 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 1.43 \text{ mM}$ and $[\text{L4}] = 2.15 \text{ mM}$. (Right) Plot of $[\text{Ni(II)}]$ versus absorbance at 646 nm.

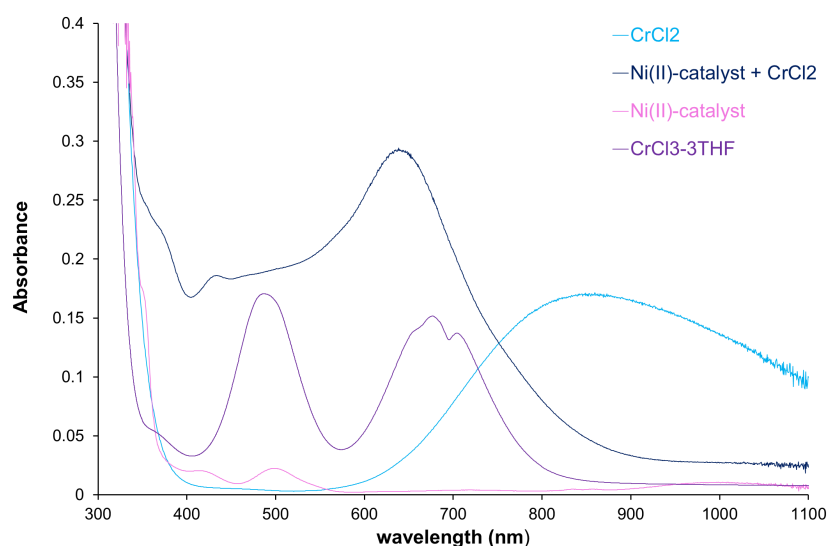


Figure S26: A UV-vis spectrum of relevant e-NHK components that has been normalized for the concentration of the reaction component as well as the path length for the spectroelectrochemical cell (0.17 cm). CrCl_2 : $[\text{CrCl}_2] = 16 \text{ mM}$, $\text{CrCl}_3 \cdot 3\text{THF}$:

$[\text{CrCl}_3 \cdot 3\text{THF}] = 16 \text{ mM}$, Ni(II)-catalyst : $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, and $[\text{L4}] = 0.3 \text{ mM}$.
 $\text{Ni(II)-catalyst} + \text{CrCl}_2$: $[\text{CrCl}_2] = 0.4 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0.2 \text{ mM}$, and $[\text{L4}] = 0.3 \text{ mM}$. All UV-vis data were acquired in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$.

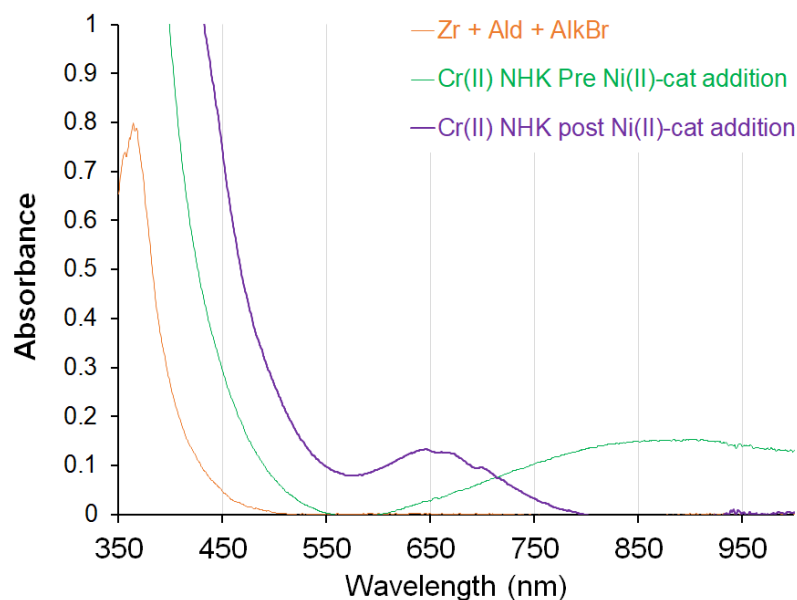


Figure S27: UV-vis of relevant e-NHK mixtures acquire with spectroelectrochemical setup. Zr + Ald + AlkBr: $[\text{Cp}_2\text{ZrCl}_2] = 40 \text{ mM}$, $[\text{1}] = 80 \text{ mM}$, $[\text{S11}] = 160 \text{ mM}$. Cr(II) NHK Pre Ni(II)-cat addition: $[\text{S11}] = 160 \text{ mM}$, $[\text{1}] = 80 \text{ mM}$, $[\text{CrCl}_2] = 16 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 40 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 0 \text{ mM}$, $[\text{L4}] = 0 \text{ mM}$. Cr(II) NHK post Ni(II)-cat addition: $[\text{S11}] = 160 \text{ mM}$, $[\text{1}] = 80 \text{ mM}$, $[\text{CrCl}_2] = 16 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 40 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 1.6 \text{ mM}$, $[\text{L4}] = 2.4 \text{ mM}$. All UV-vis experiments were run in DMF with $[\text{TBAPF}_6] = 0.1 \text{ M}$.

UV-vis Spectroelectrochemical Studies

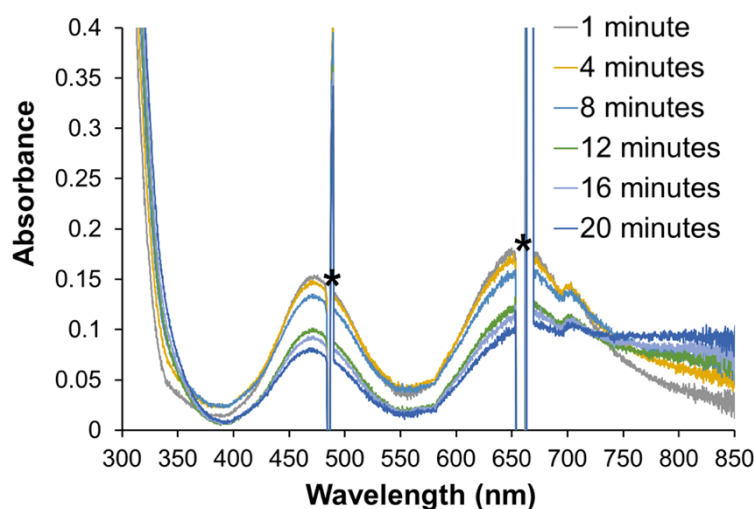


Figure S28: Absorbance versus time for the bulk electrolysis of $\text{CrCl}_3 \cdot 3\text{THF}$ to Cr(II) at $-1.6 \text{ V vs Ag}^{+/0}$: $[\text{CrCl}_3 \cdot 3\text{THF}] = 0.016 \text{ M}$, $[\text{TBAPF}_6] = 0.1 \text{ M}$, DMF, a Ni-mesh working electrode, and aluminum wire counter electrode. Potentials are referenced against a $0.01 \text{ M Ag}^{+/0}$ non-aqueous reference electrode. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

A constant potential of $-1.6 \text{ V vs Ag}^{+/0}$ was applied to a solution of $\text{CrCl}_3 \cdot 3\text{THF}$ to demonstrate the bulk electroreduction of Cr(III) to Cr(II) for the UV-vis spectroelectrochemical setup. At open circuit potential, the $\text{CrCl}_3 \cdot 3\text{THF}$ solution exhibits ligand field transitions typical for pseudo-octahedral Cr(III) (${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ ($\lambda_{\text{max}} = 677 \text{ nm}$) ${}^4\text{T}_{1g}$ ($\lambda_{\text{max}} = 487 \text{ nm}$) in O_h symmetry). Upon commencing the bulk electroreduction of Cr(III) at $-1.6 \text{ V vs Ag}^{+/0}$, these Cr(III) ligand field transitions gradually disappear, and new absorbances associated with high-spin, pseudo-octahedral Cr(II) (${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ ($\lambda_{\text{max}} = 843 \text{ nm}$) in O_h symmetry) concomitantly appear. These temporal spectroelectrochemical results confirm the successful one-electron bulk electroreduction of Cr(III) to Cr(II) by application of a potential of $-1.6 \text{ V vs Ag}^{+/0}$.

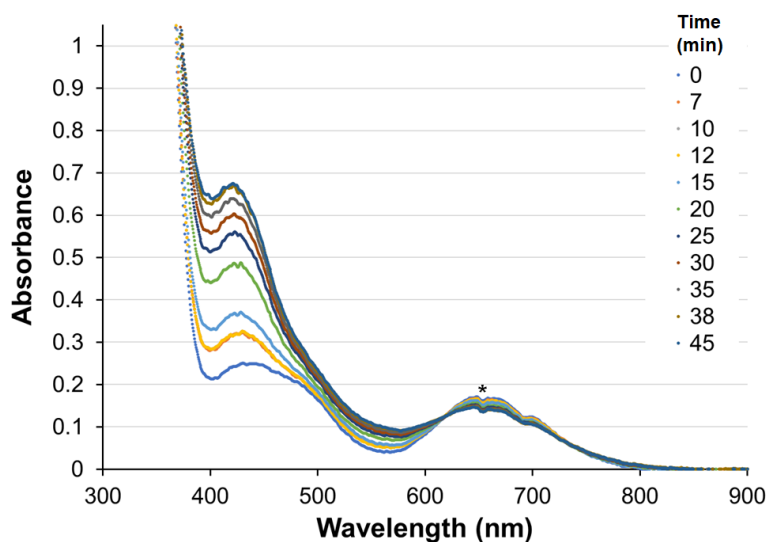


Figure S29: Temporal monitoring of the bulk electrolysis for the Cr(III) -based e-NHK: $[\text{S11}] = 160 \text{ mM}$, $[\text{1}] = 80 \text{ mM}$, $[\text{CrCl}_3 \cdot 3\text{THF}] = 16 \text{ mM}$, $[\text{Cp}_2\text{ZrCl}_2] = 40 \text{ mM}$, $[\text{NiCl}_2 \cdot \text{DME}] = 1.6 \text{ mM}$, $[\text{L4}] = 2.4 \text{ mM}$, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm . All potentials referenced with $\text{Co}^{+/0}$ and then referenced to $\text{Fc}^{+/0}$. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of $-1.5 \text{ V vs Fc}^{+/0}$ was applied for 15 minutes and then a potential $-2.0 \text{ V vs Fc}^{+/0}$ was applied for 30 minutes. * Indicates

portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

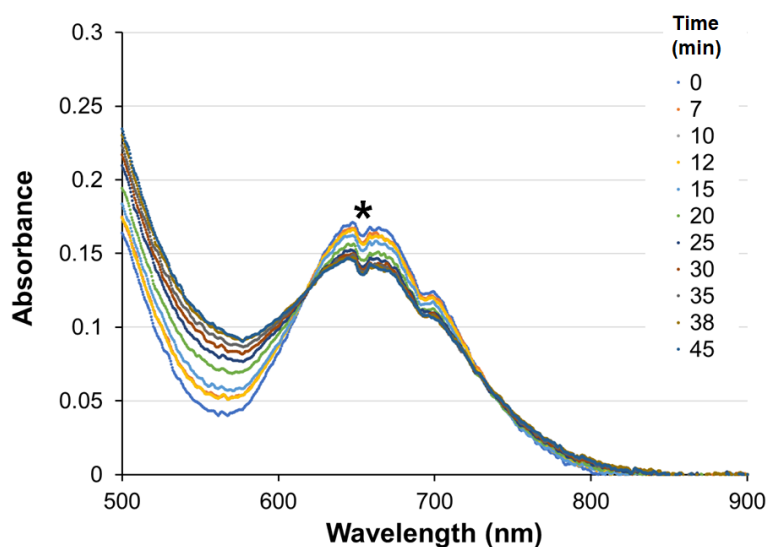


Figure S30: Temporal monitoring of the bulk electrolysis for the Cr(III)-based e-NHK: [S11] = 160 mM, [1] = 80 mM, [CrCl₃·3THF] = 16 mM, [Cp₂ZrCl₂] = 40 mM, [NiCl₂·DME] = 1.6 mM, [L4] = 2.4 mM, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm. All potentials referenced with Co⁺⁰ and then referenced to Fc⁺⁰. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of -1.5 V vs Fc⁺⁰ was applied for 15 minutes and then a potential -2.0 V vs Fc⁺⁰ was applied for 30 minutes. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

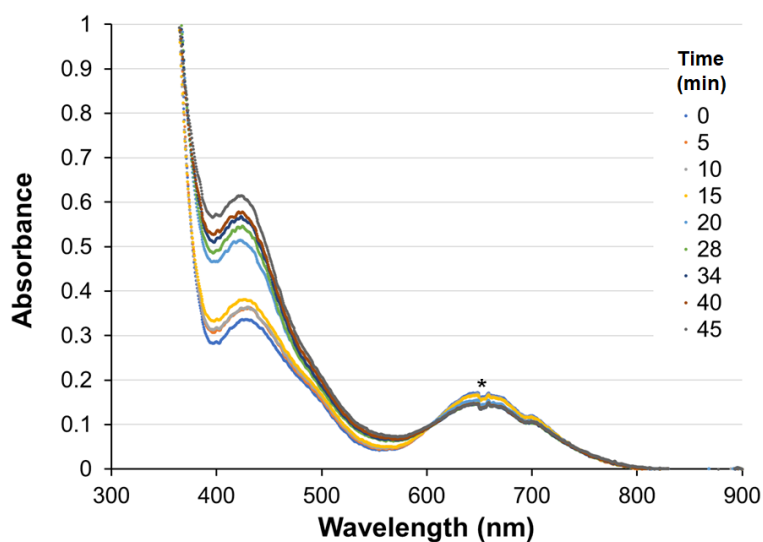


Figure S31: Temporal monitoring of the bulk electrolysis for the Cr(II)-based e-NHK: [S11] = 160 mM, [1] = 80 mM, [CrCl₂] = 16 mM, [Cp₂ZrCl₂] = 40 mM, [NiCl₂·DME]

= 1.6 mM, [L4] = 2.4 mM, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm. All potentials referenced to $\text{Co}^{+/0}$. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of $-1.5\text{ V vs Fc}^{+/0}$ was applied for 15 minutes and then a potential $-2.0\text{ V vs Fc}^{+/0}$ was applied for 30 minutes. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

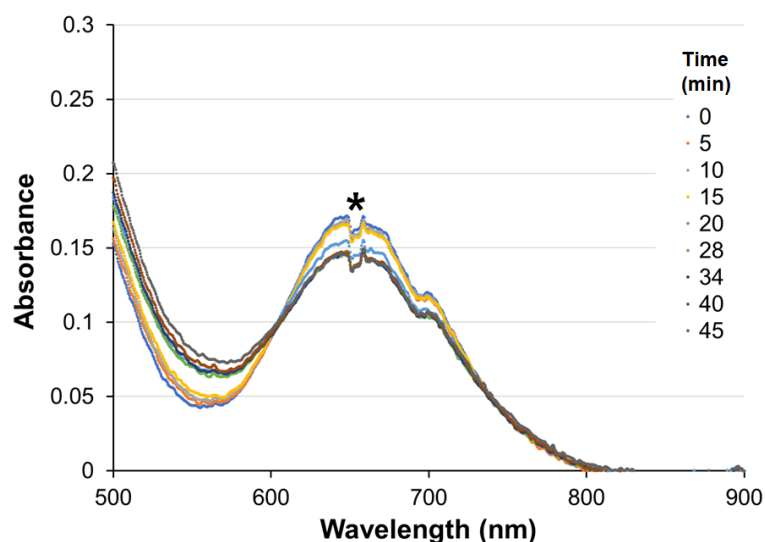


Figure S32: Temporal monitoring of the bulk electrolysis for the Cr(II)-based e-NHK: [S11] = 160 mM, [1] = 80 mM, $[\text{CrCl}_2]$ = 16 mM, $[\text{Cp}_2\text{ZrCl}_2]$ = 40 mM, $[\text{NiCl}_2 \cdot \text{DME}]$ = 1.6 mM, [L4] = 2.4 mM, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm. All potentials referenced to $\text{Co}^{+/0}$. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of $-1.5\text{ V vs Fc}^{+/0}$ was applied for 15 minutes and then a potential $-2.0\text{ V vs Fc}^{+/0}$ was applied for 30 minutes. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

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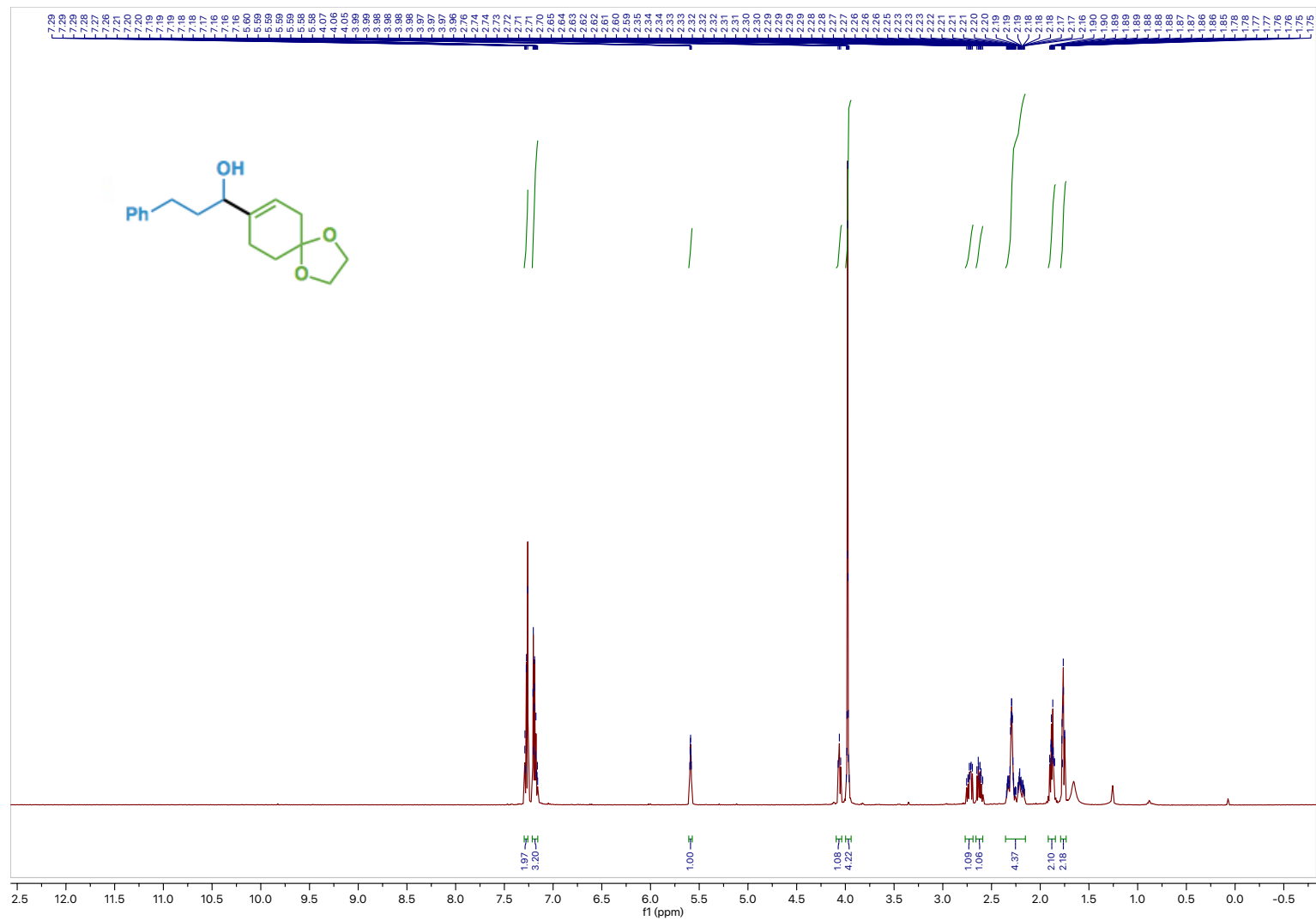
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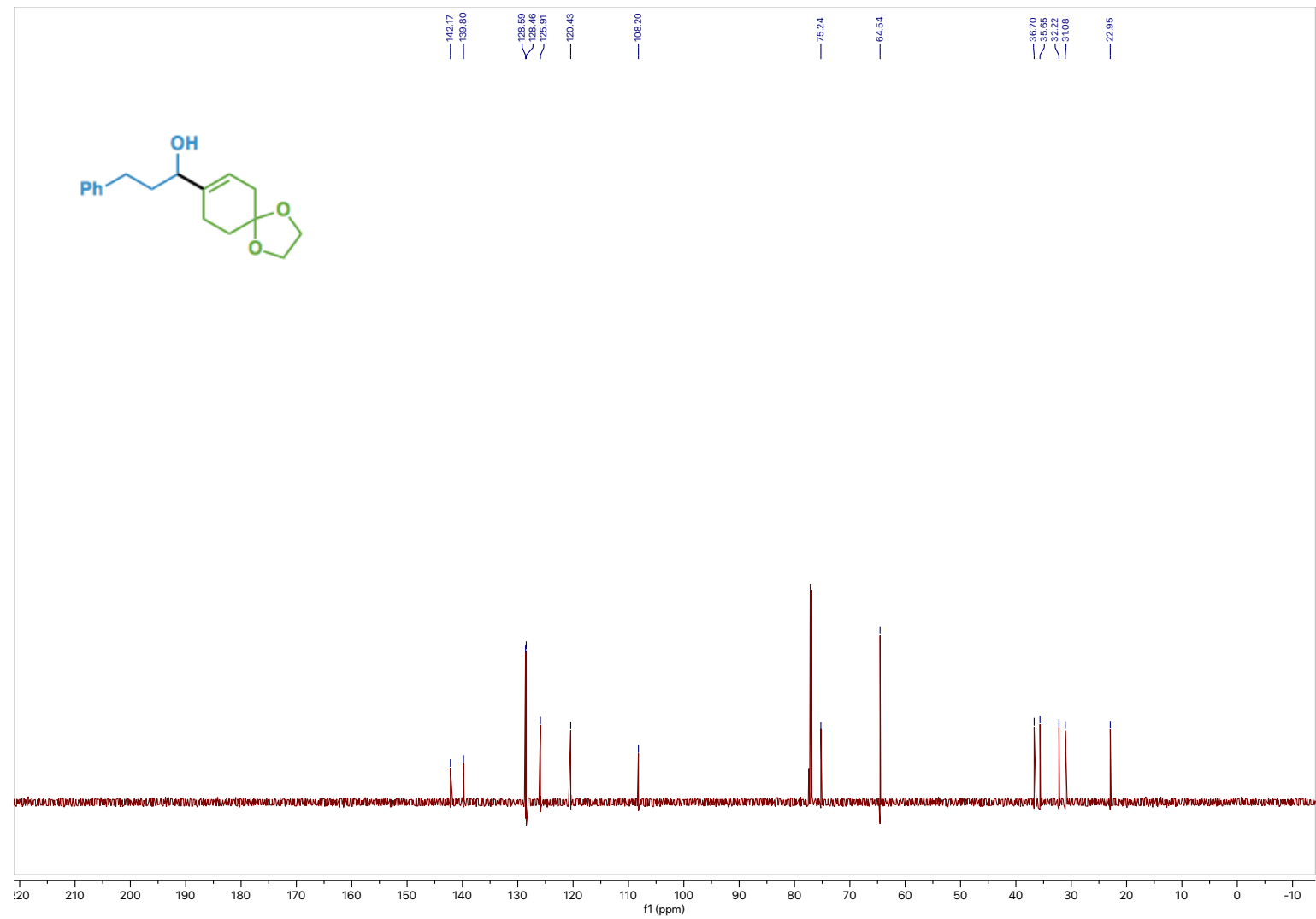
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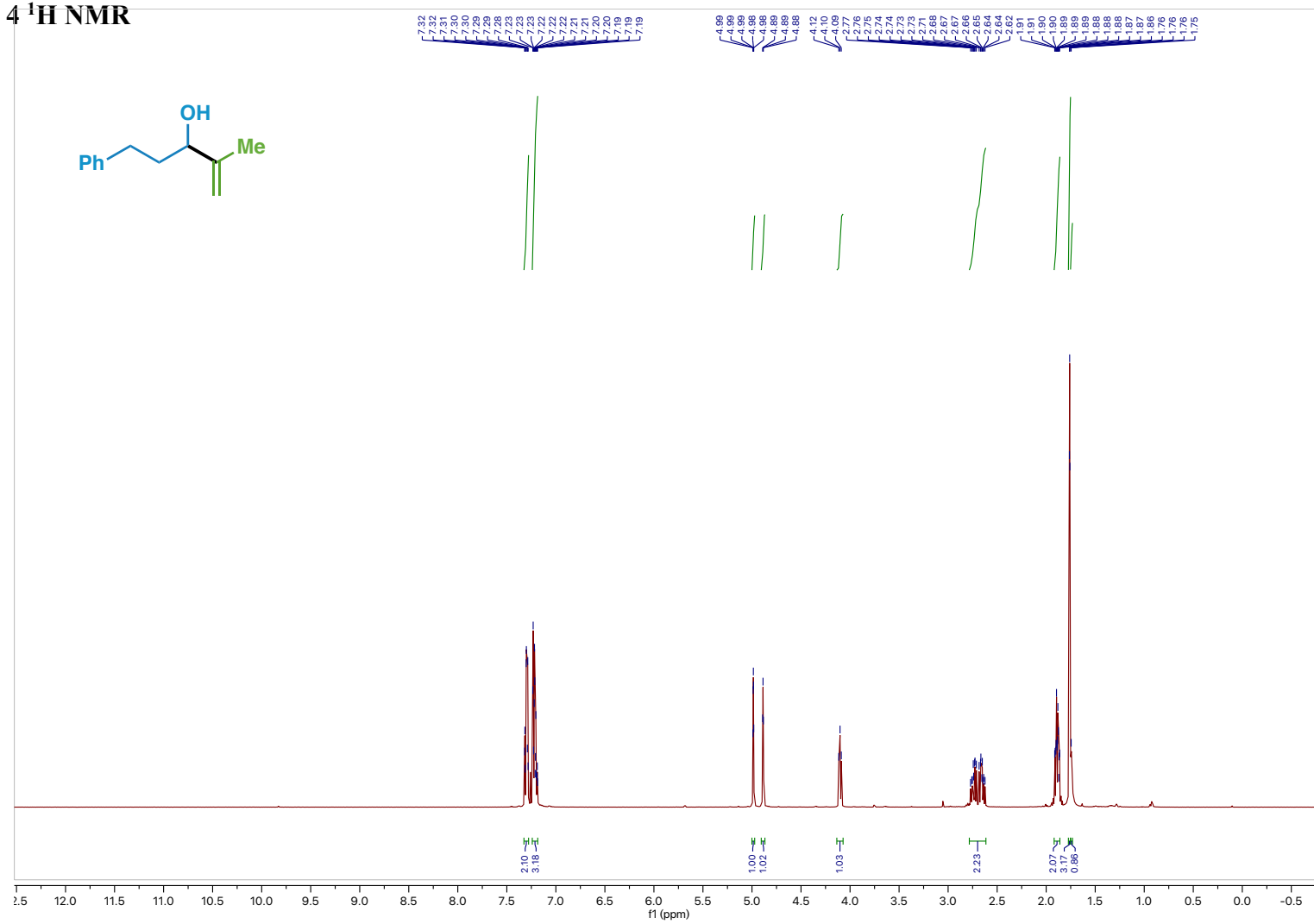
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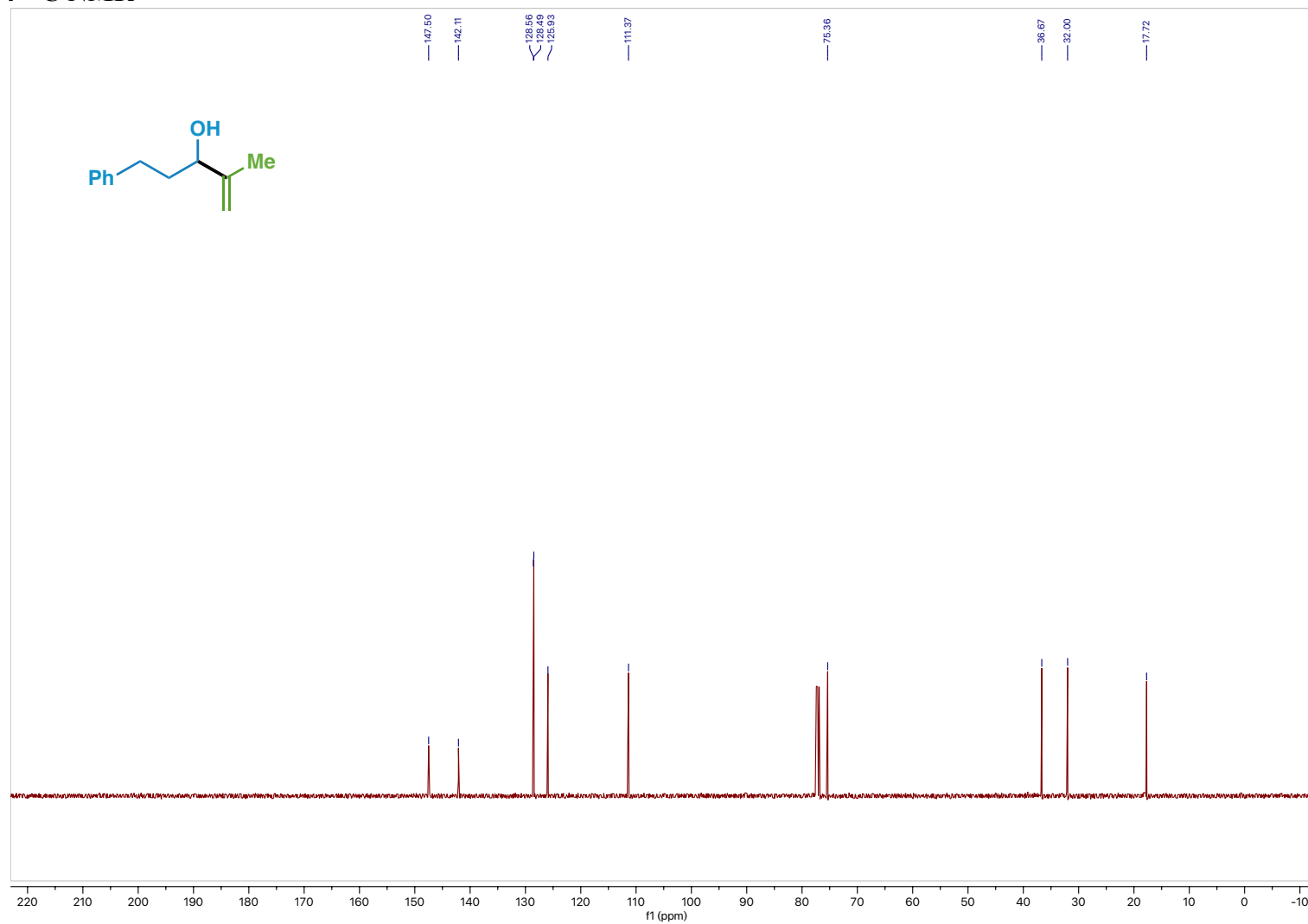
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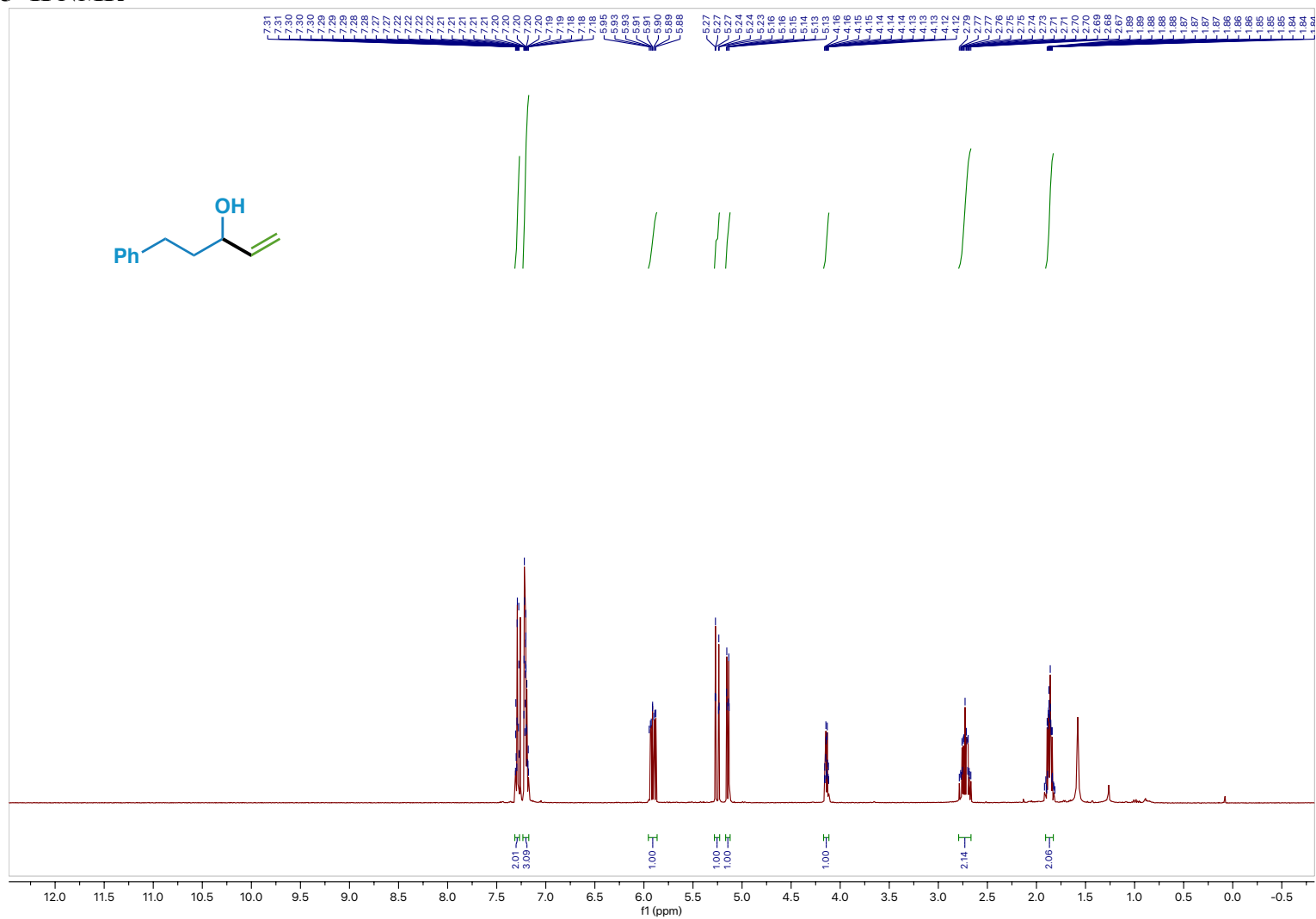
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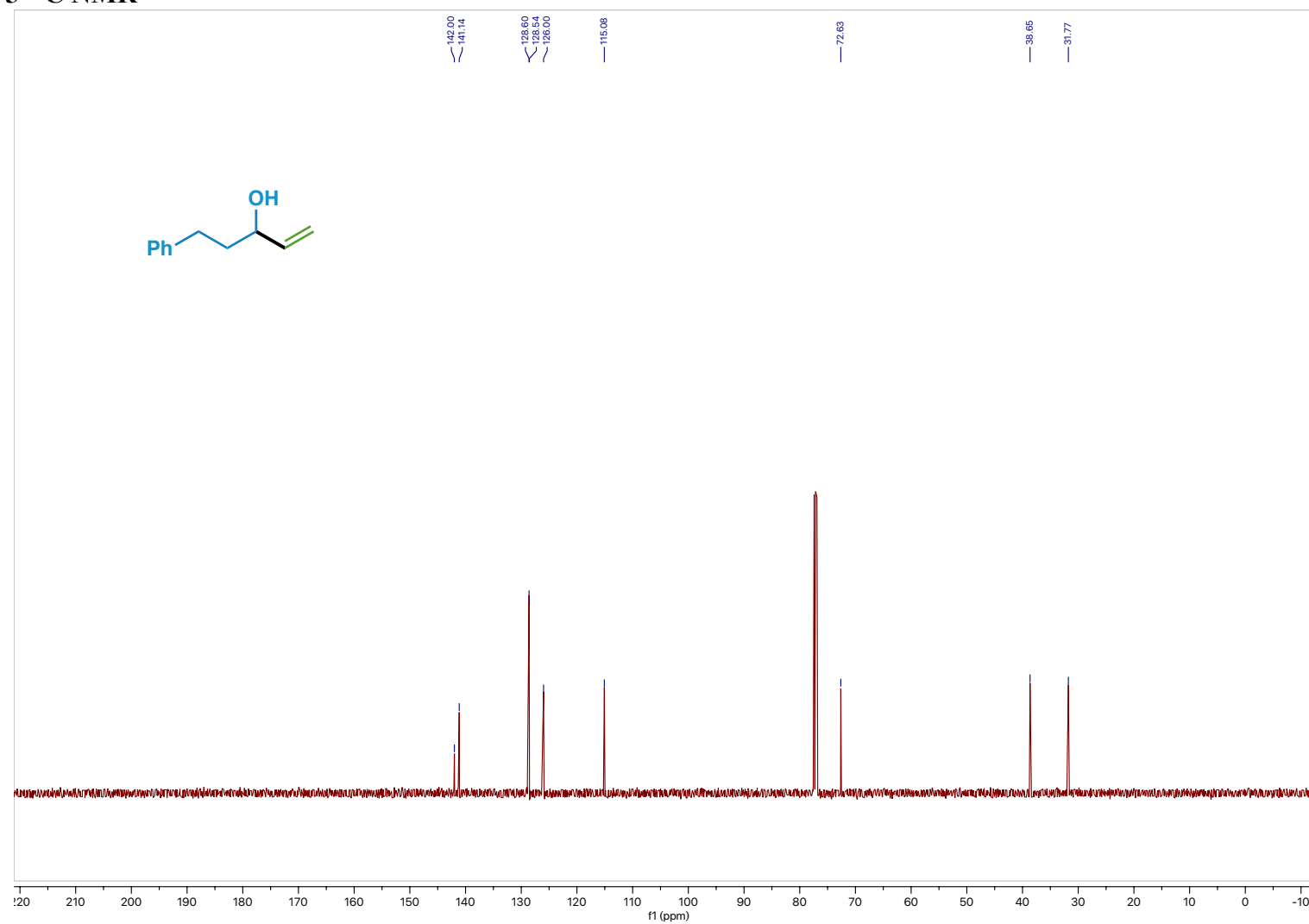
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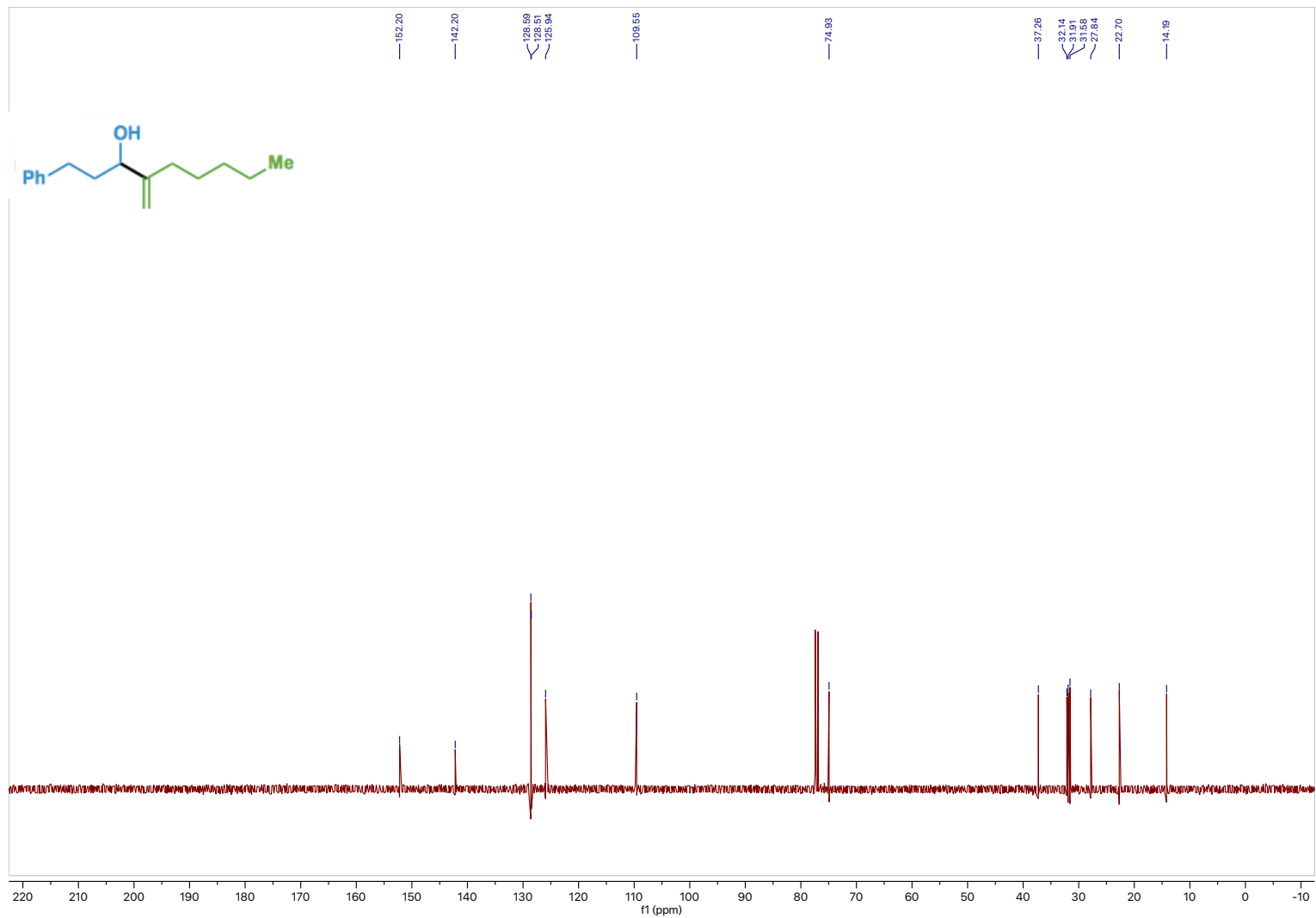
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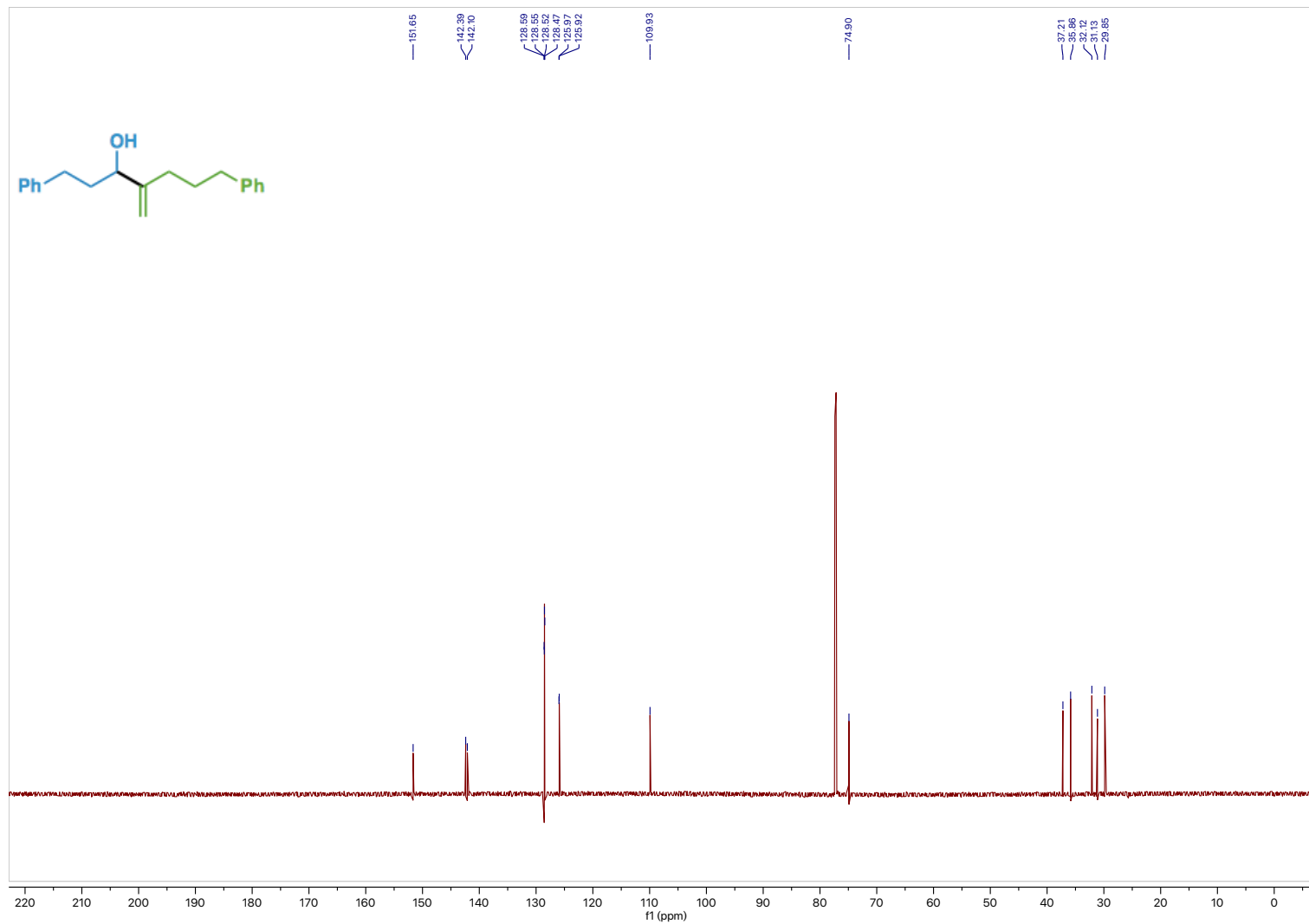
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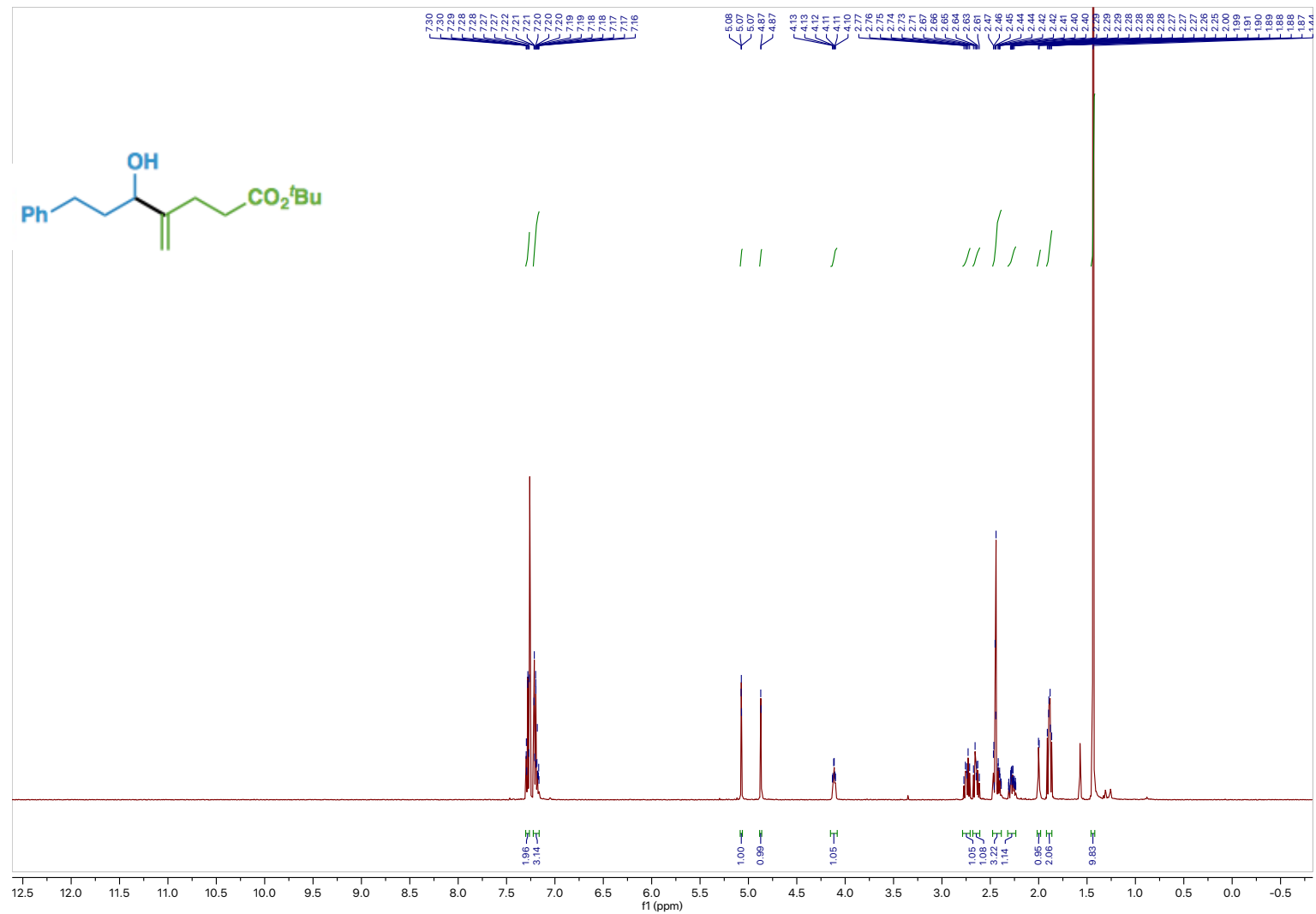
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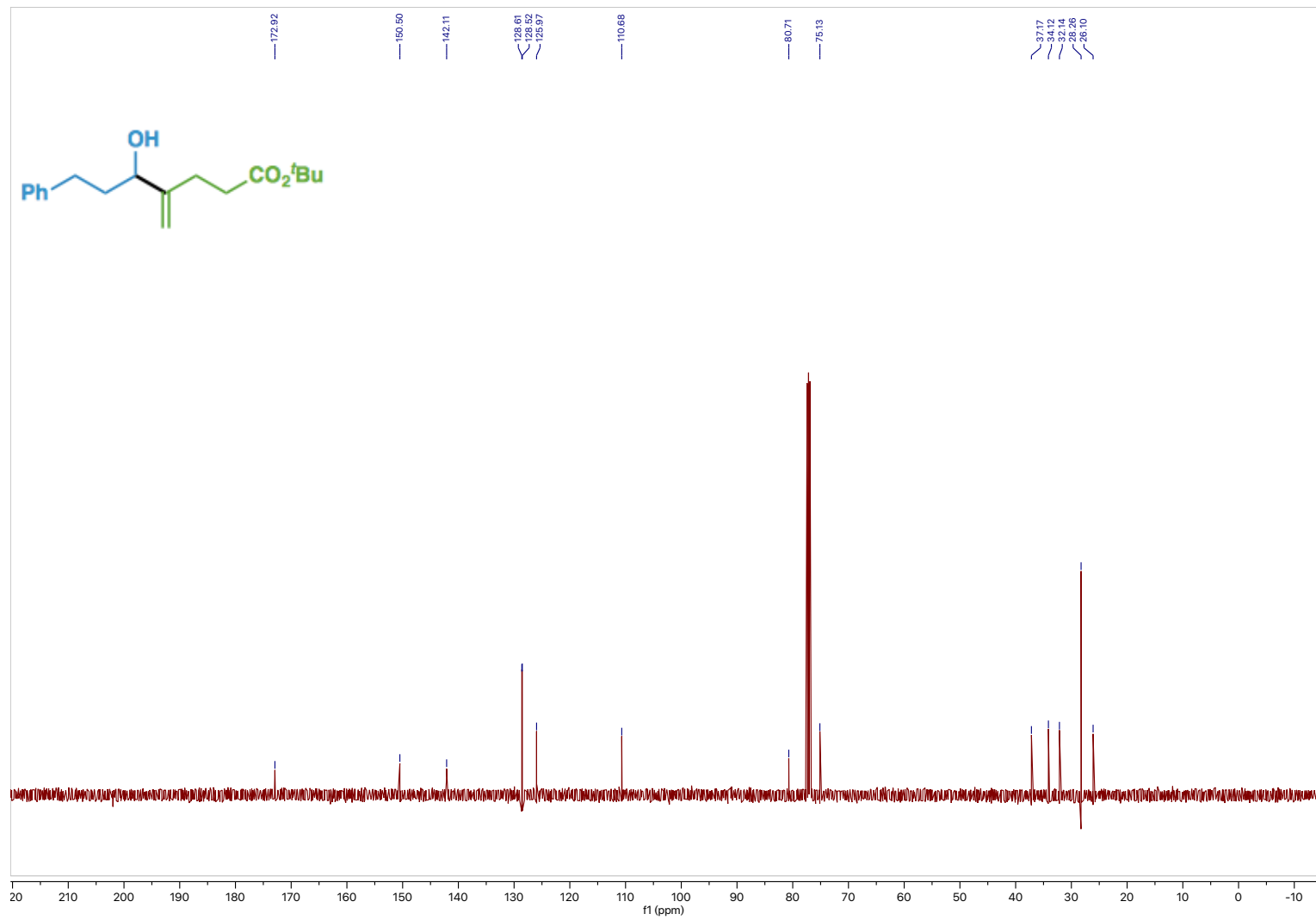
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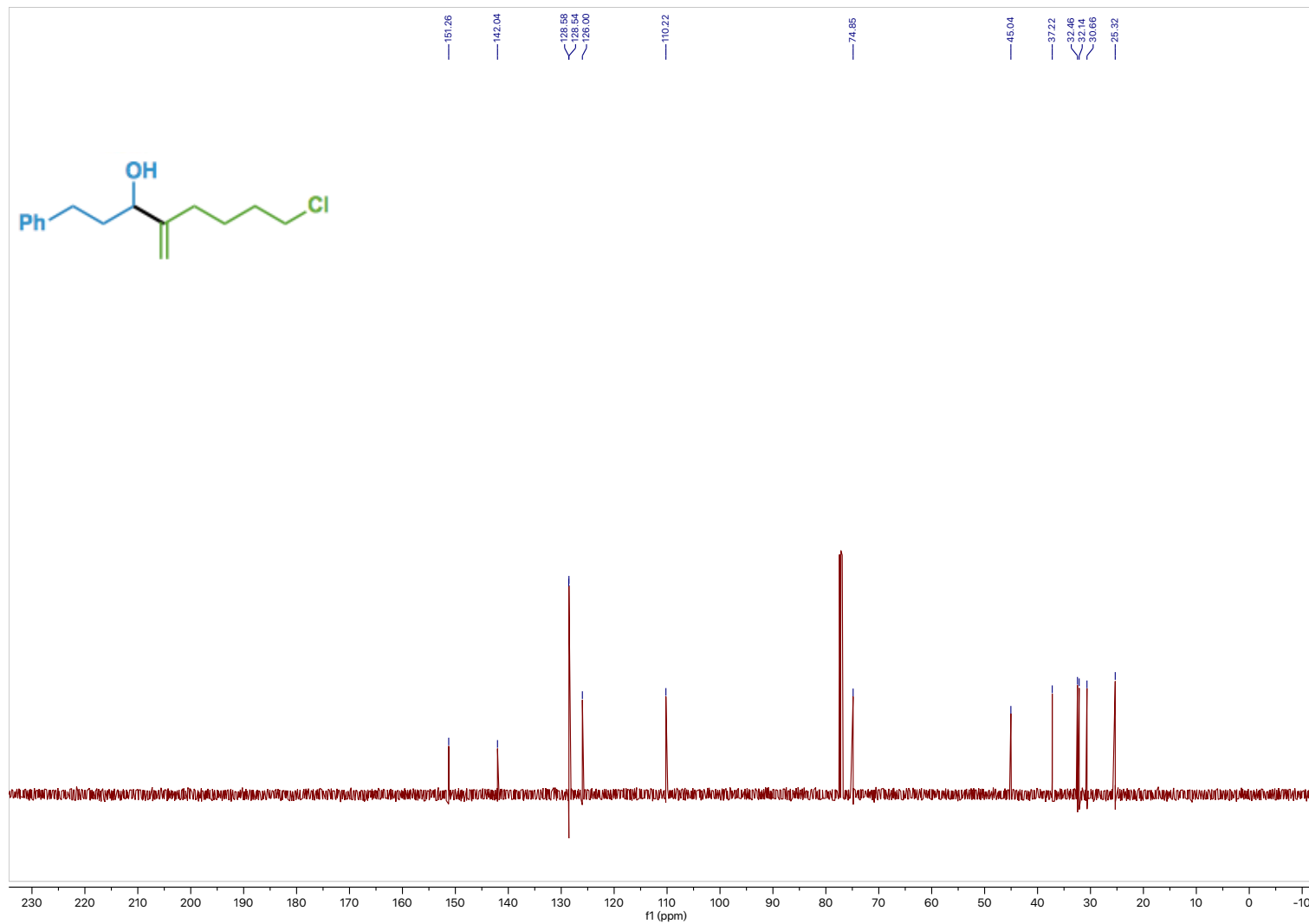
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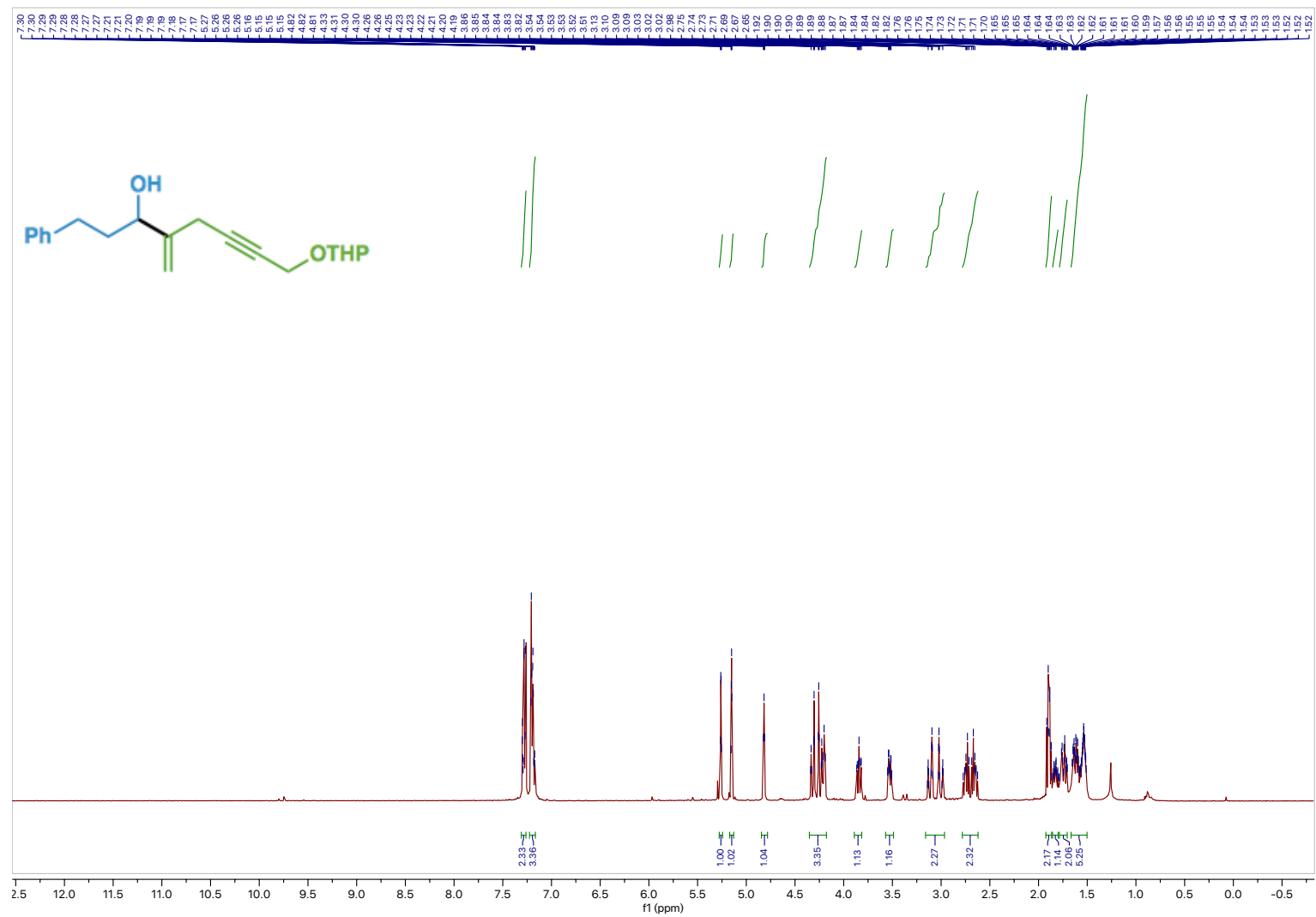
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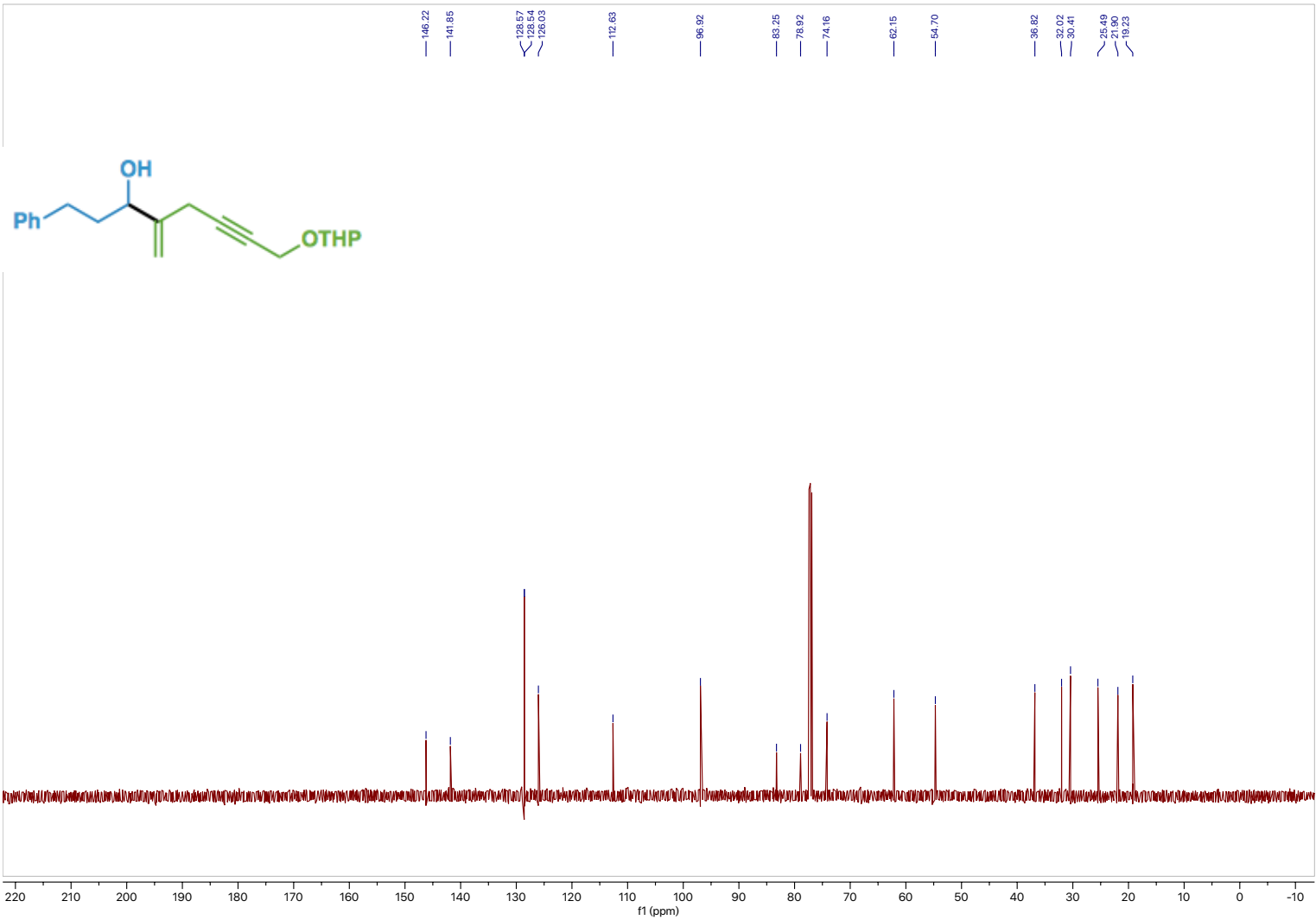
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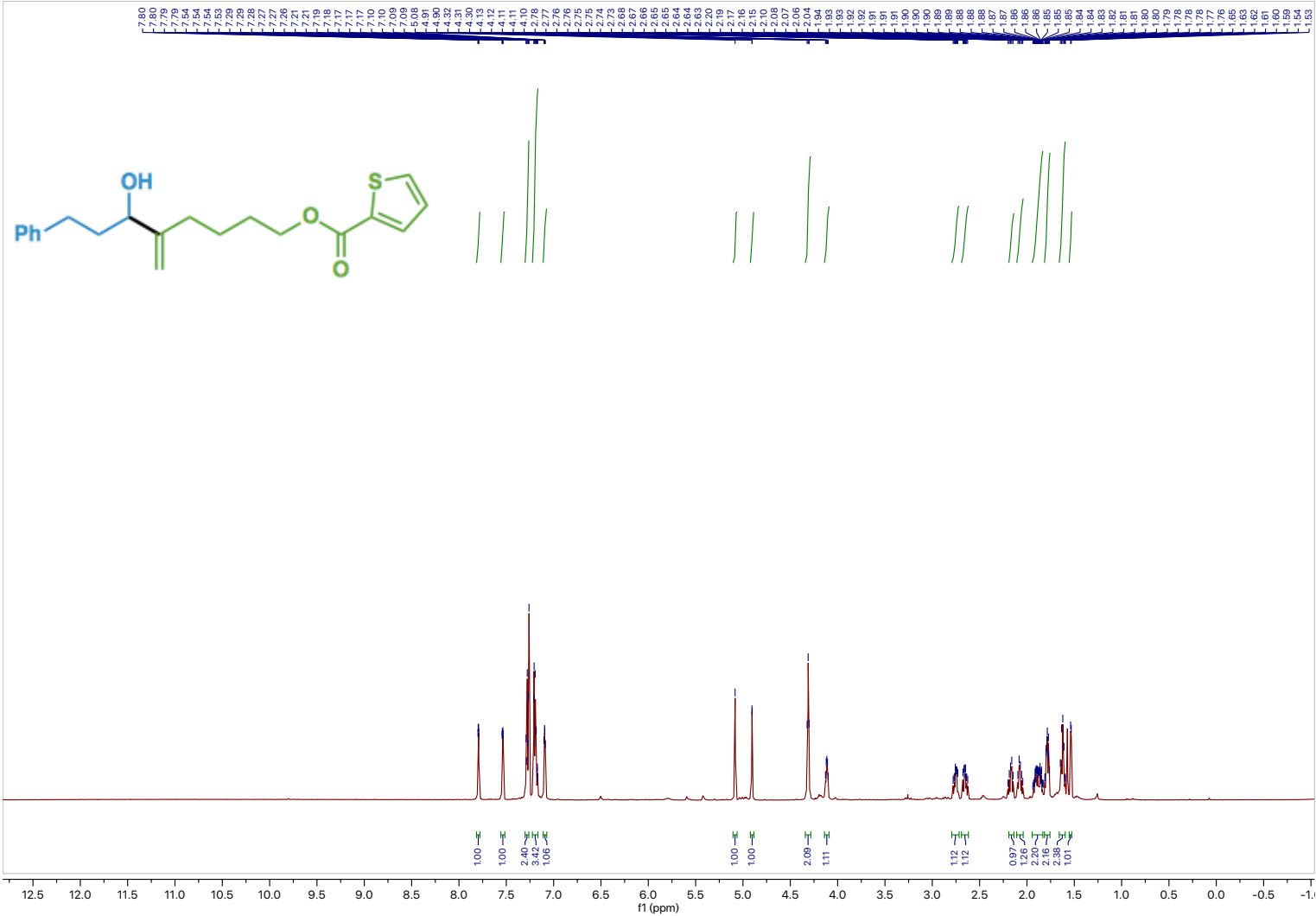
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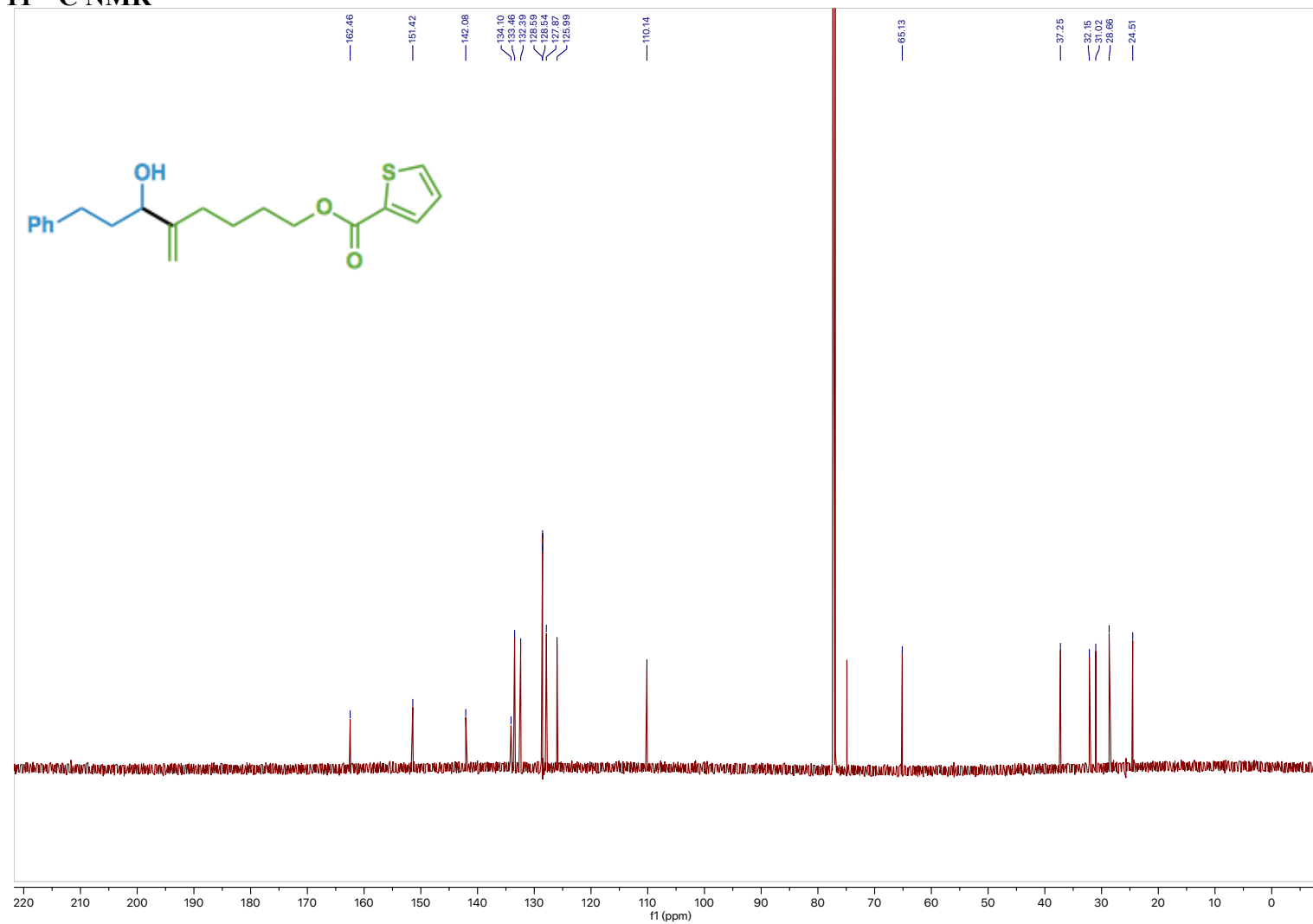
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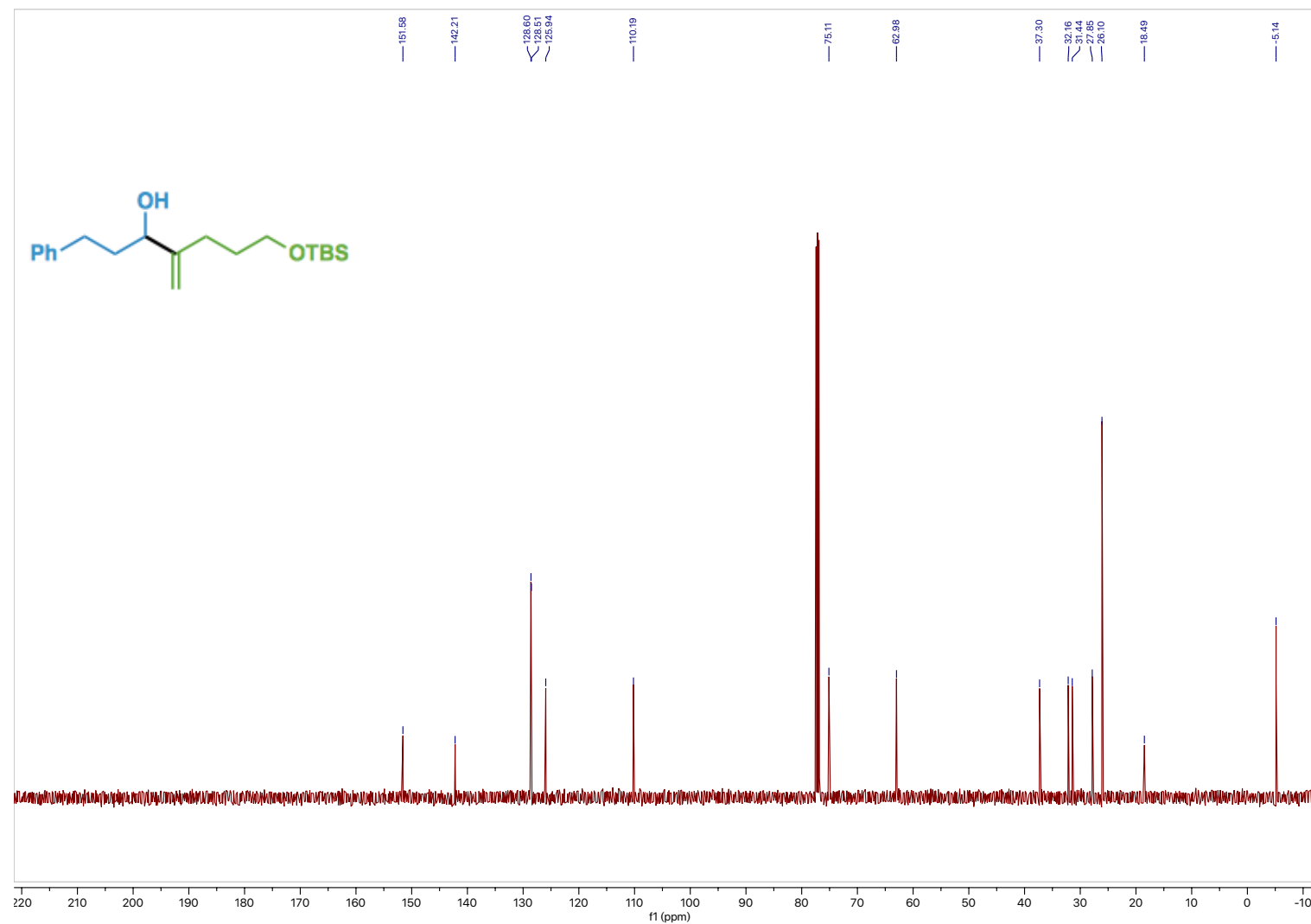
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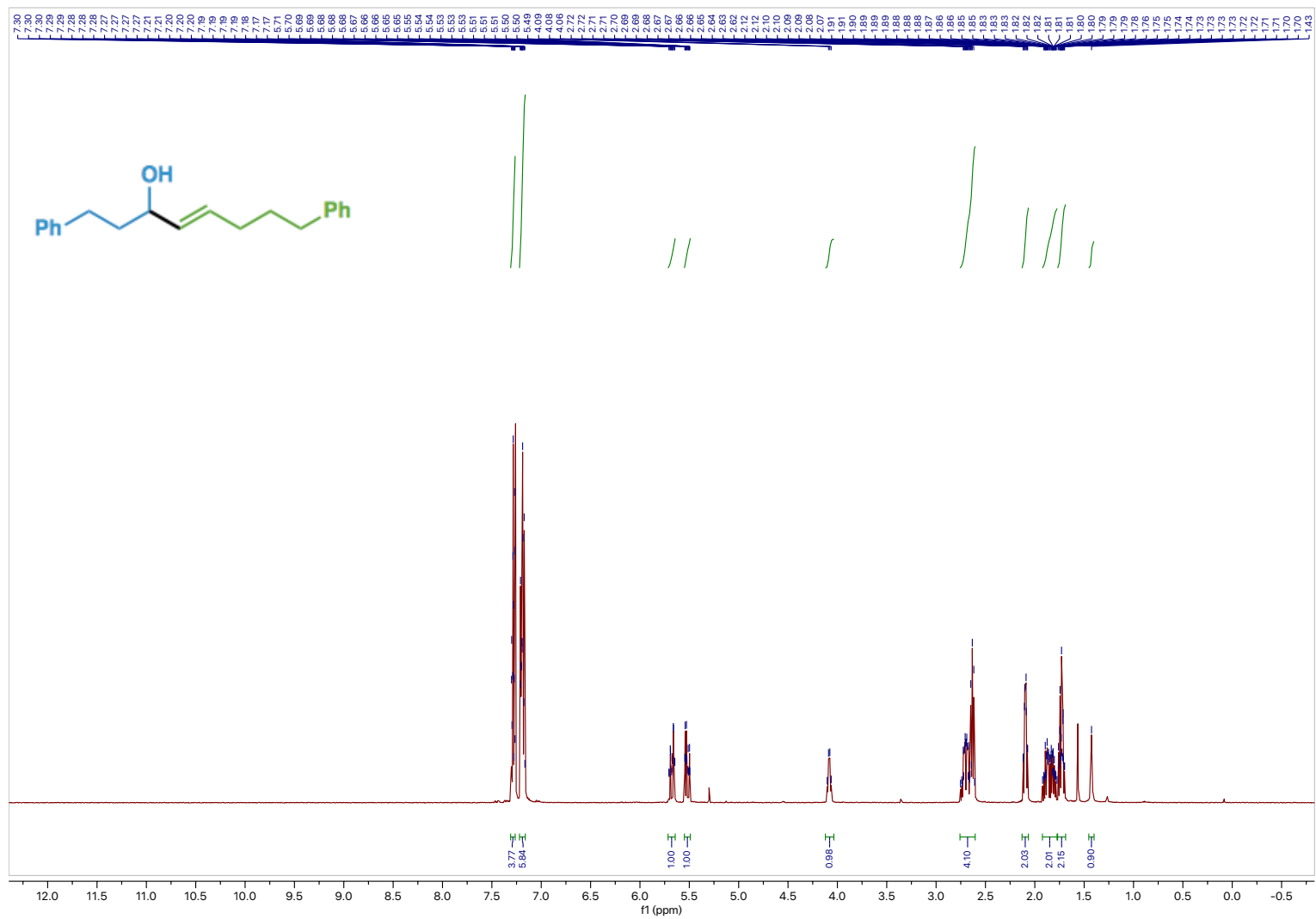
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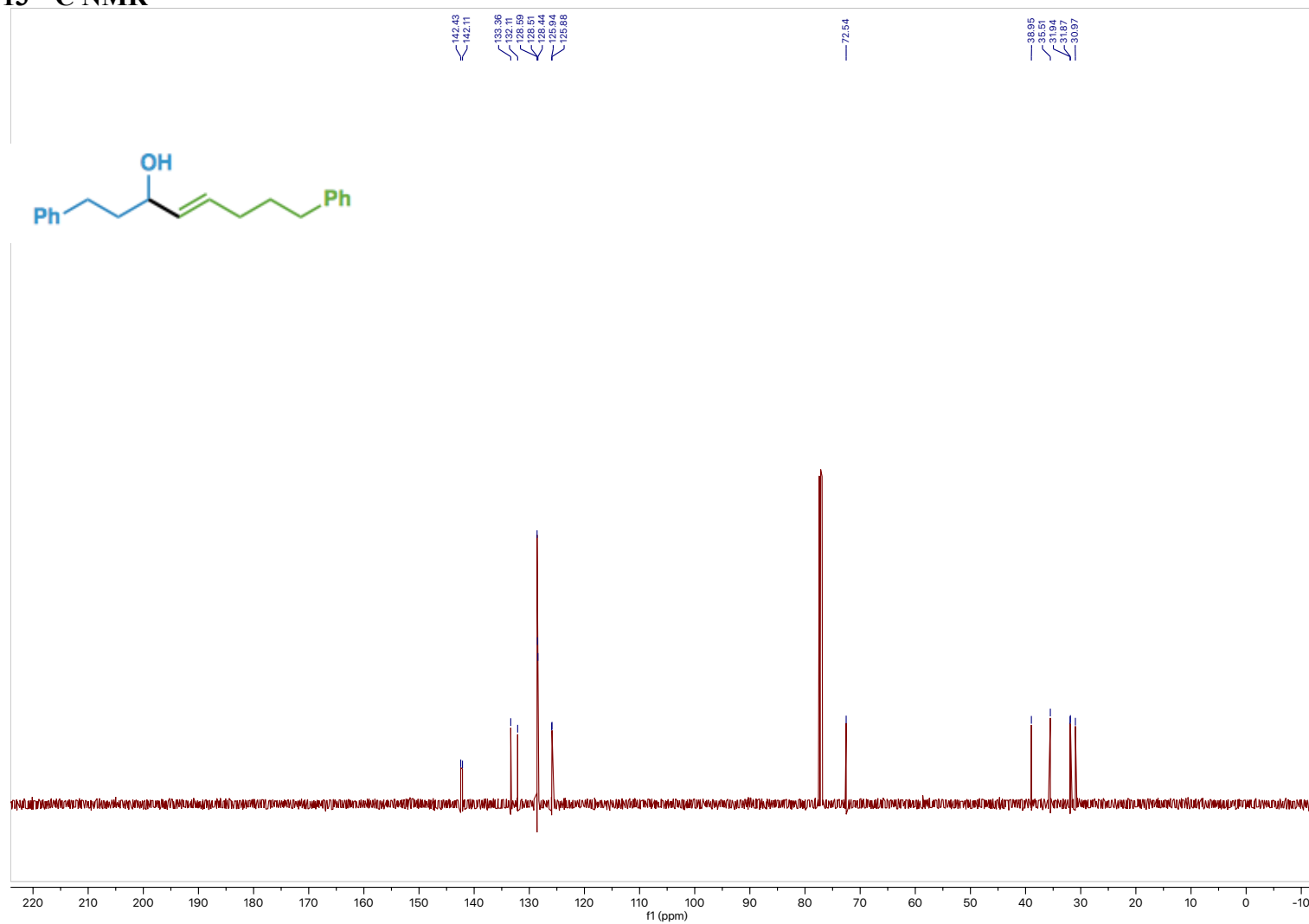
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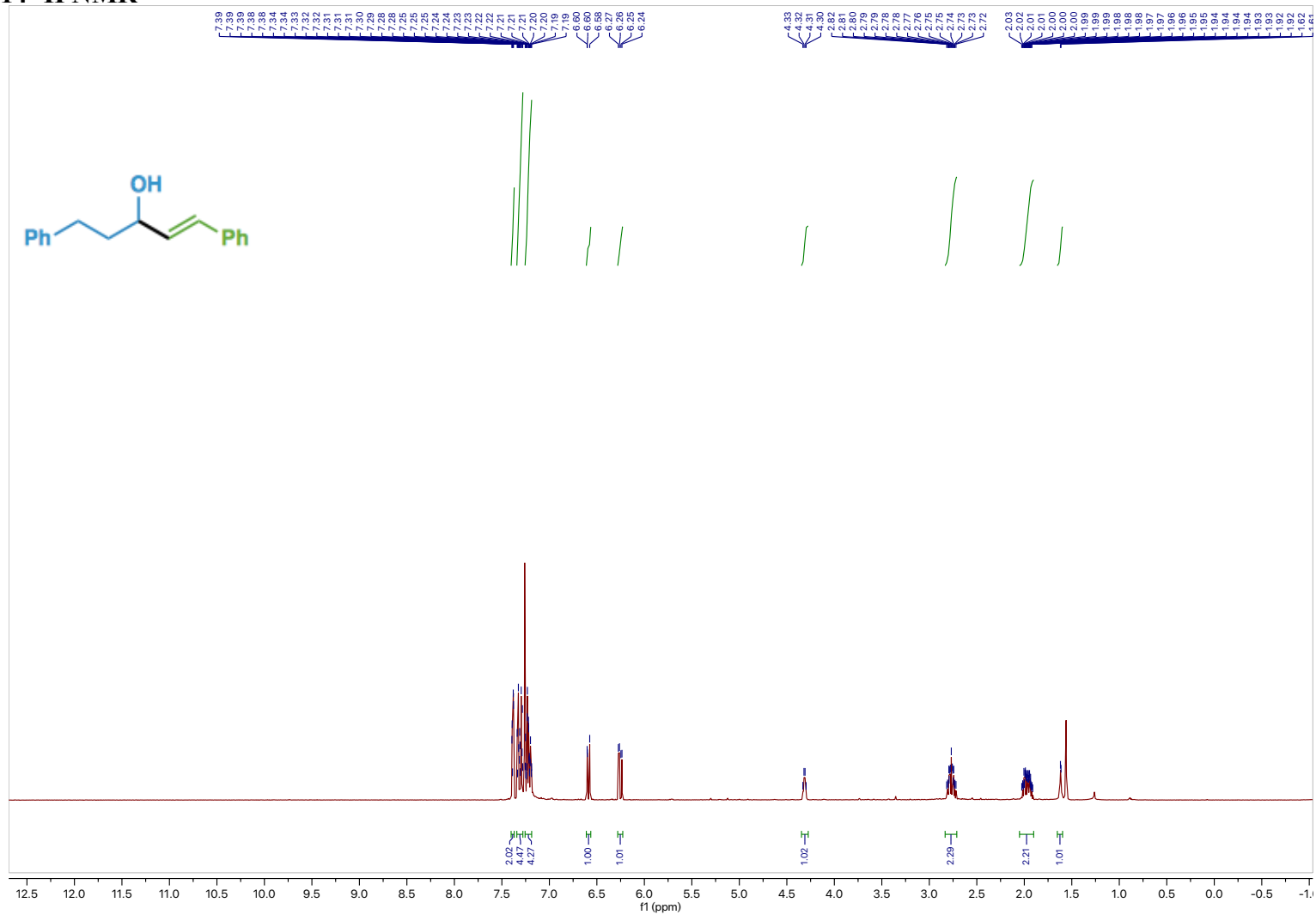
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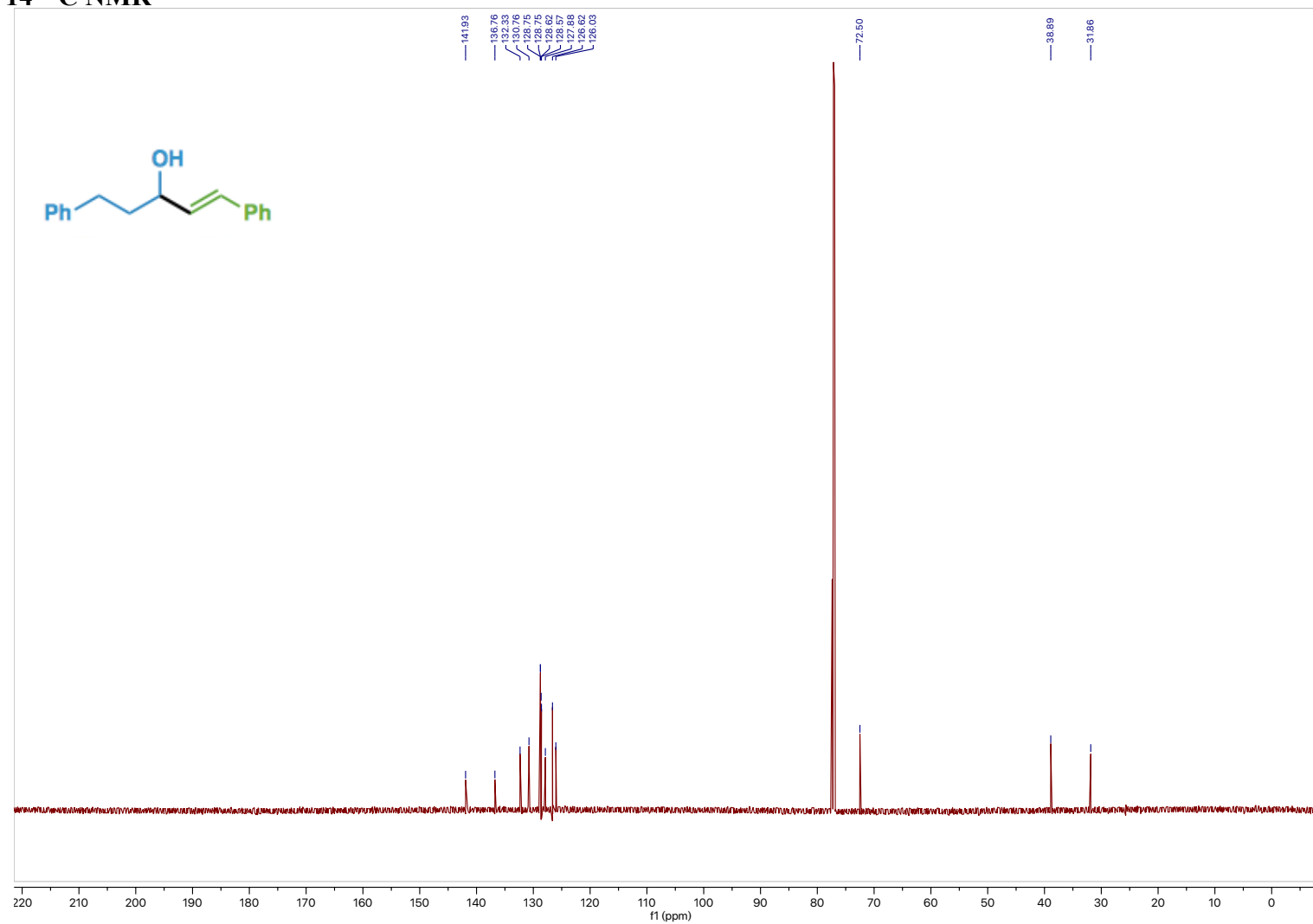
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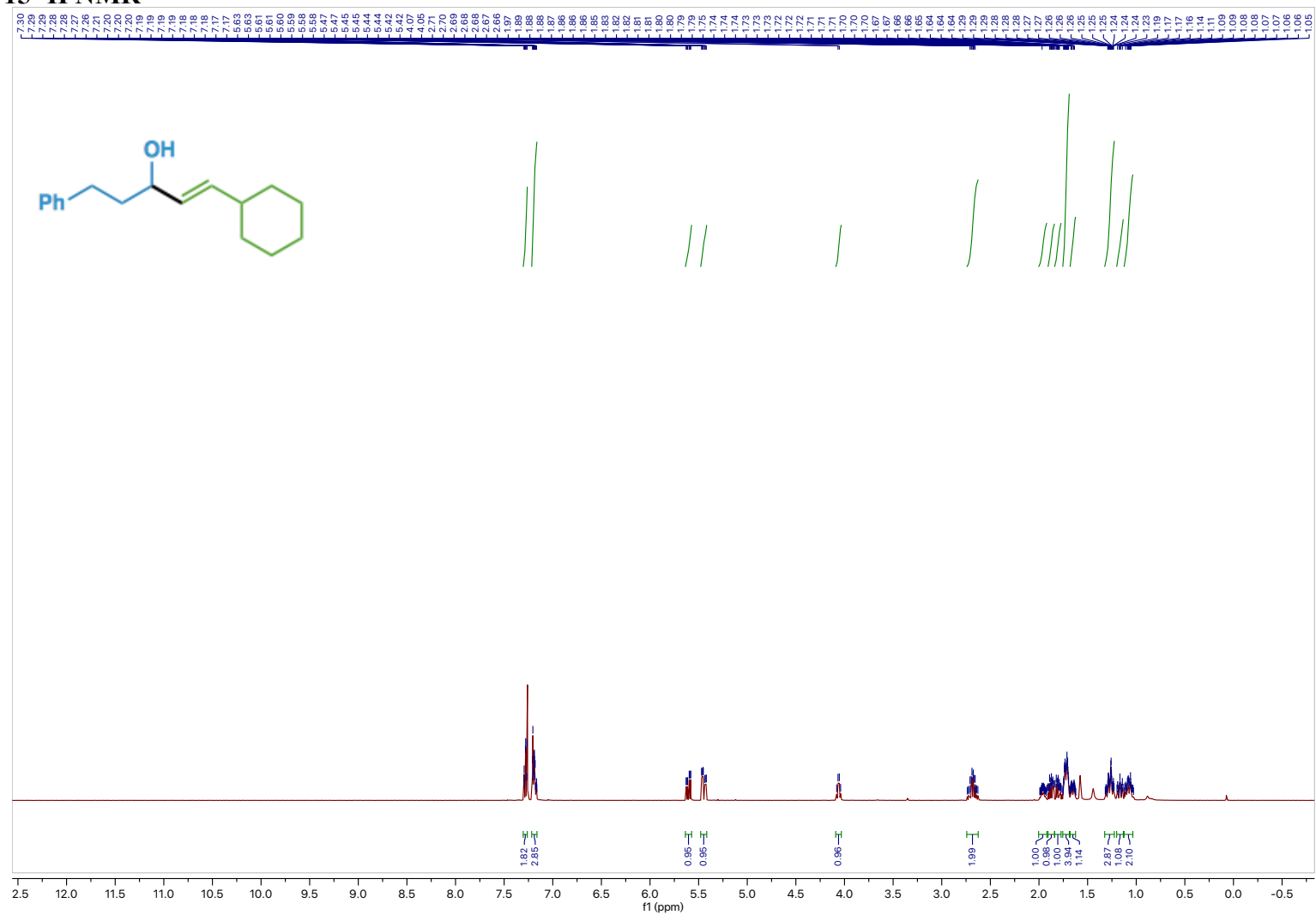
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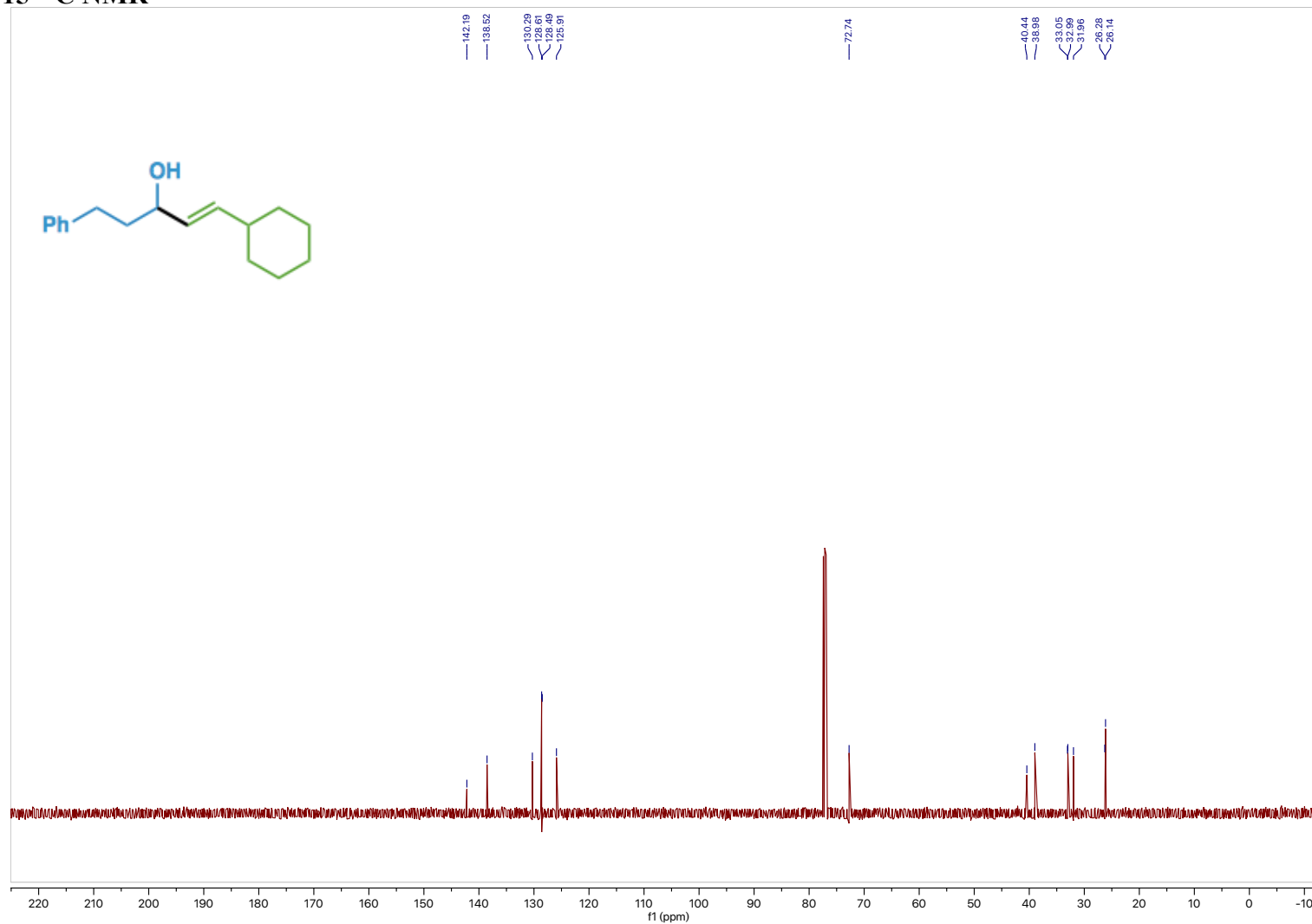
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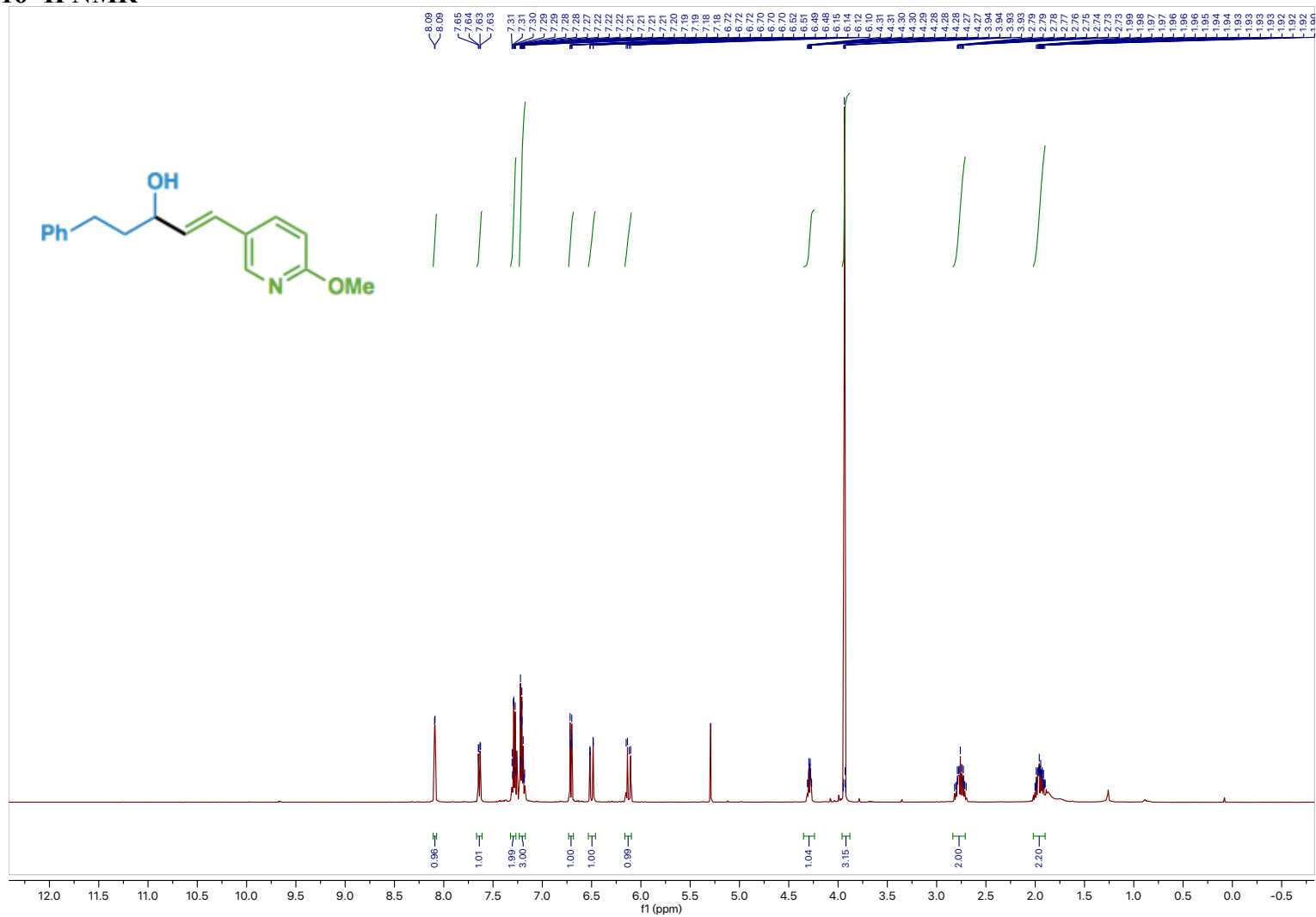
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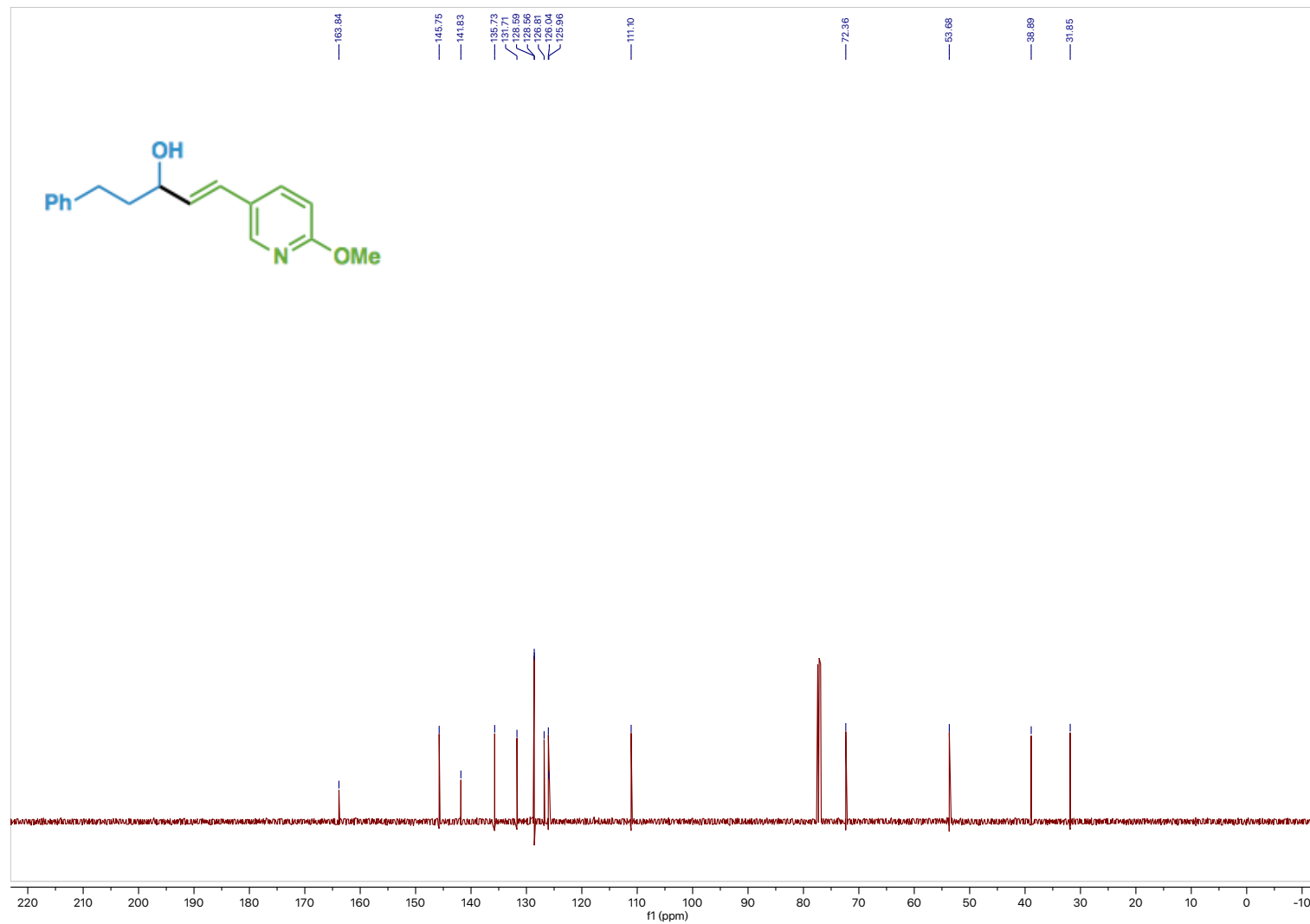
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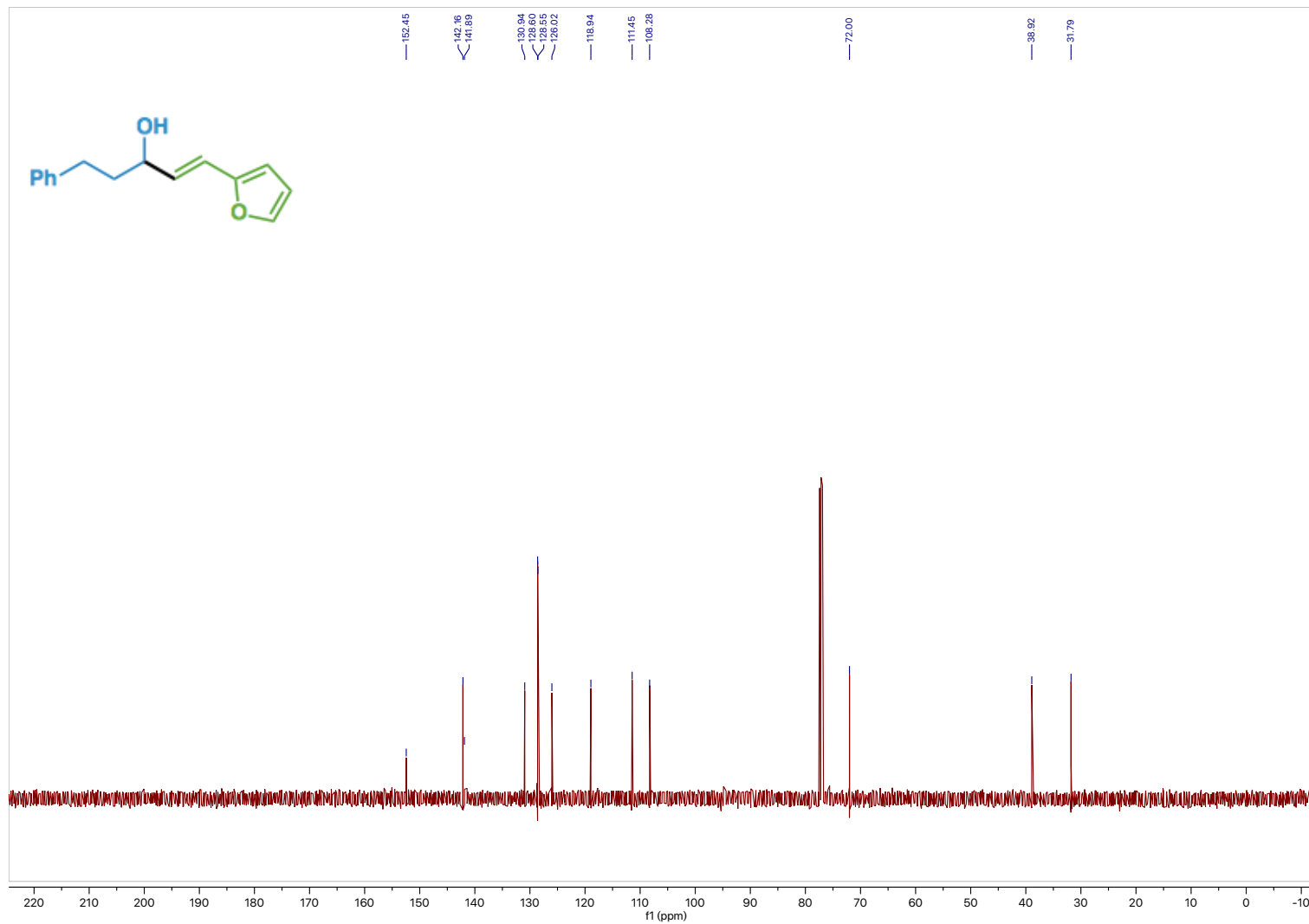
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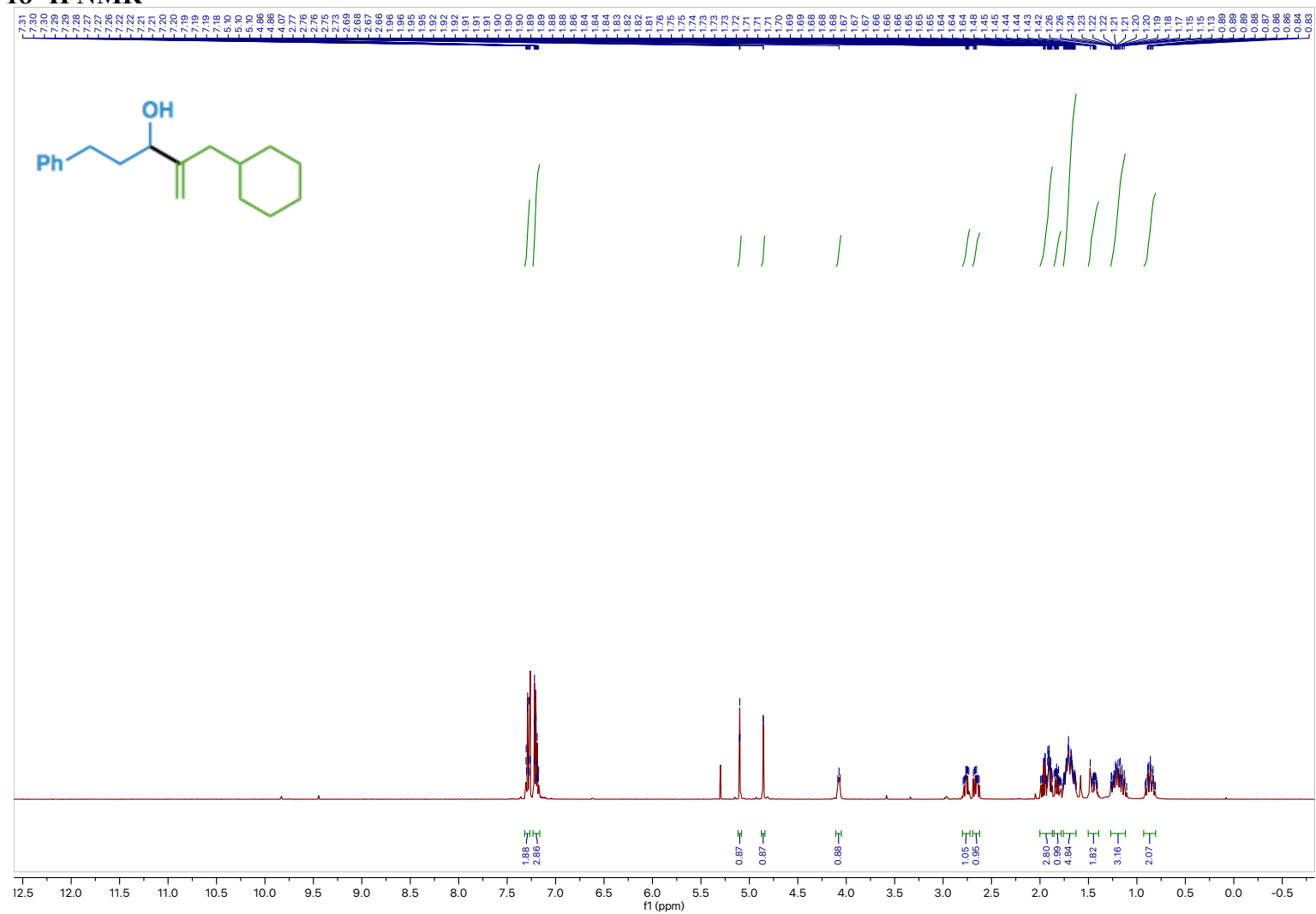
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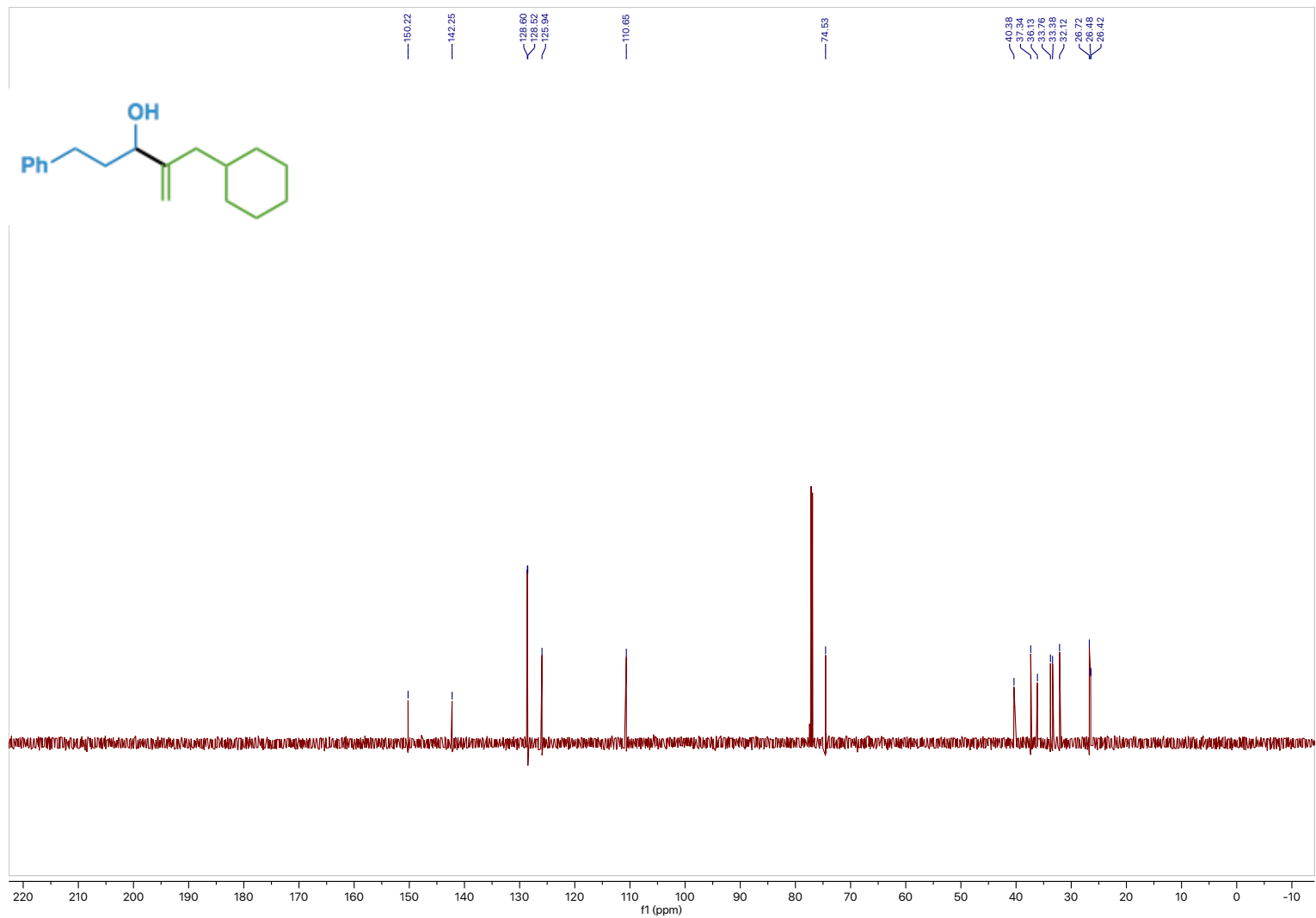
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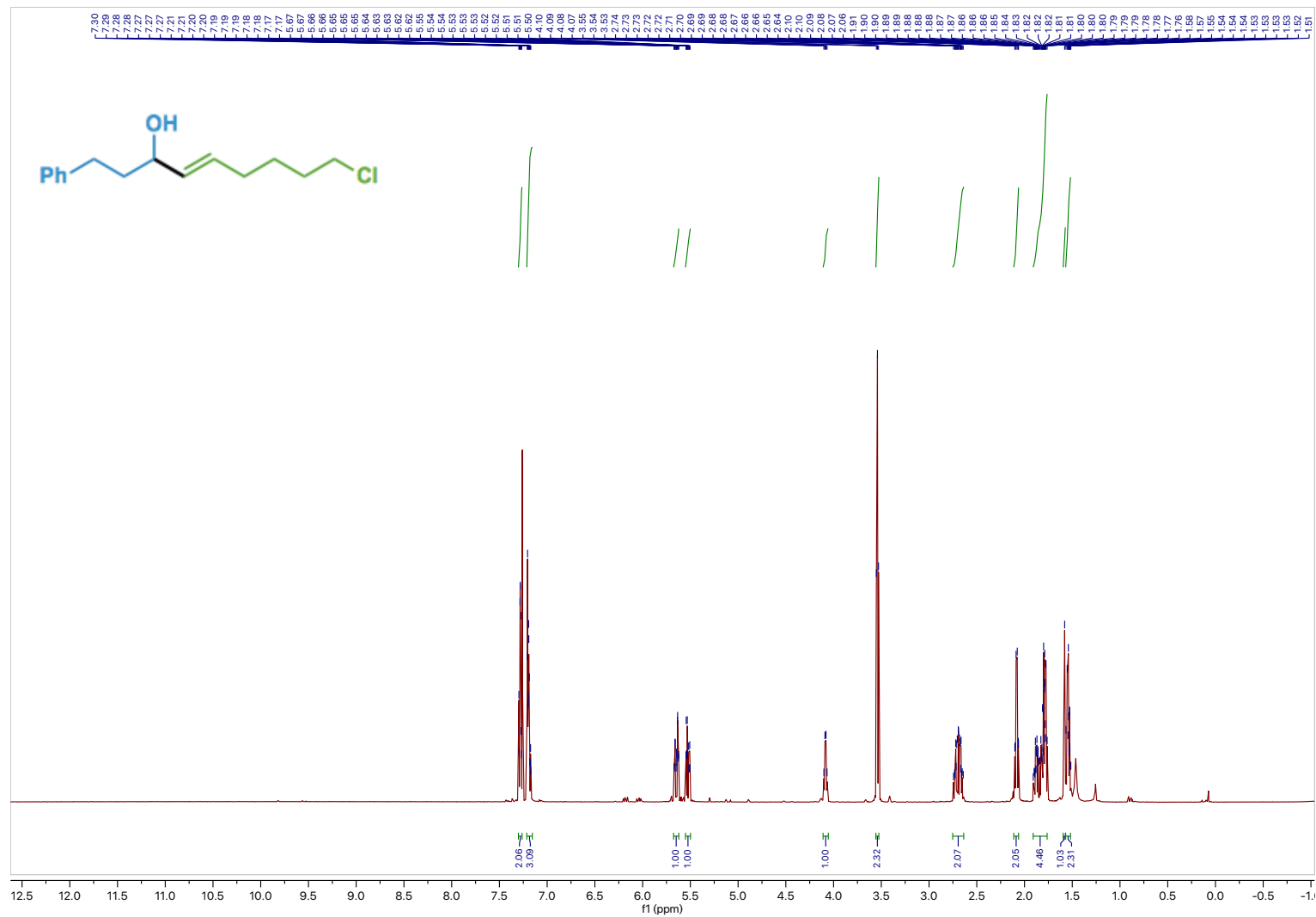
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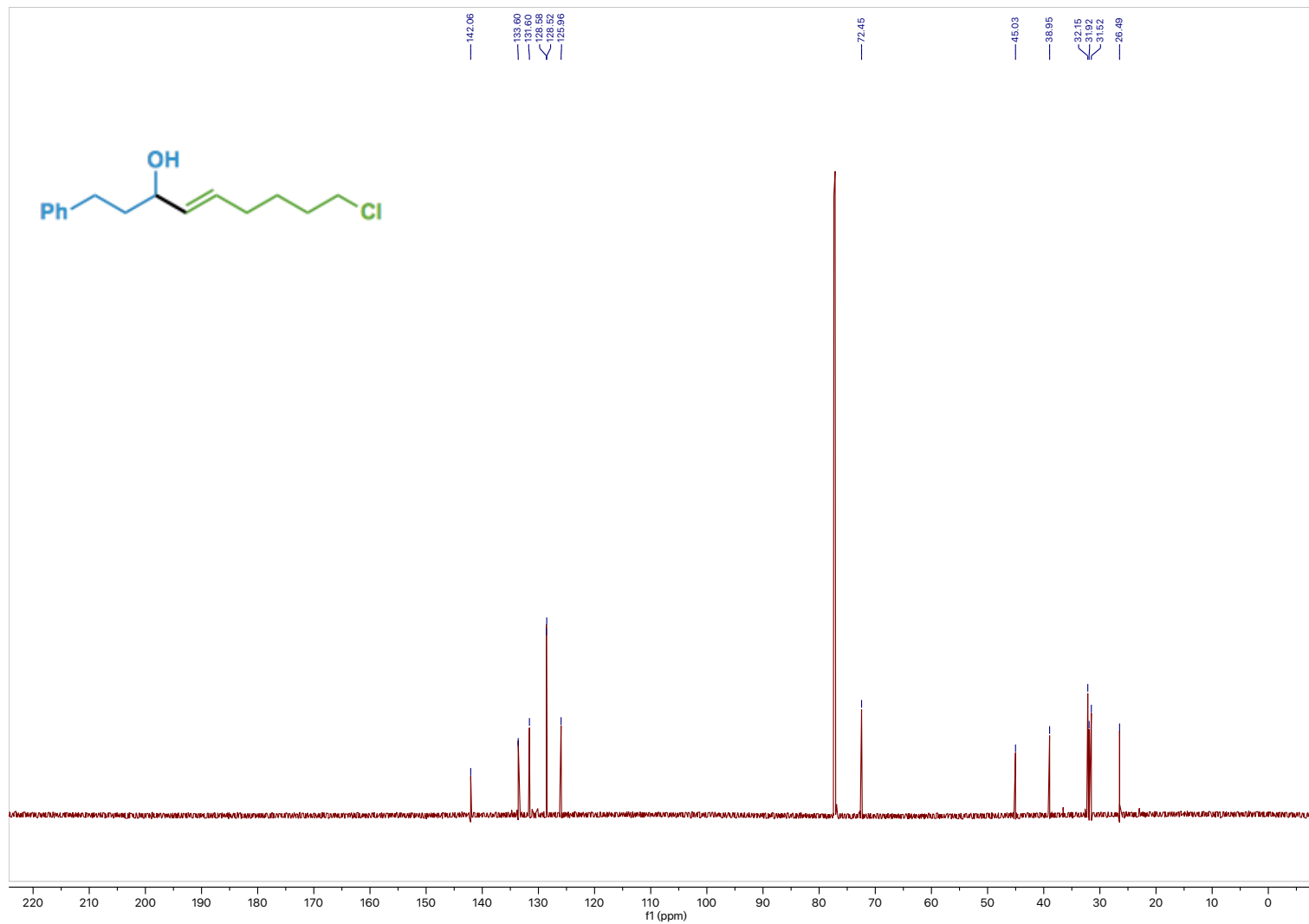
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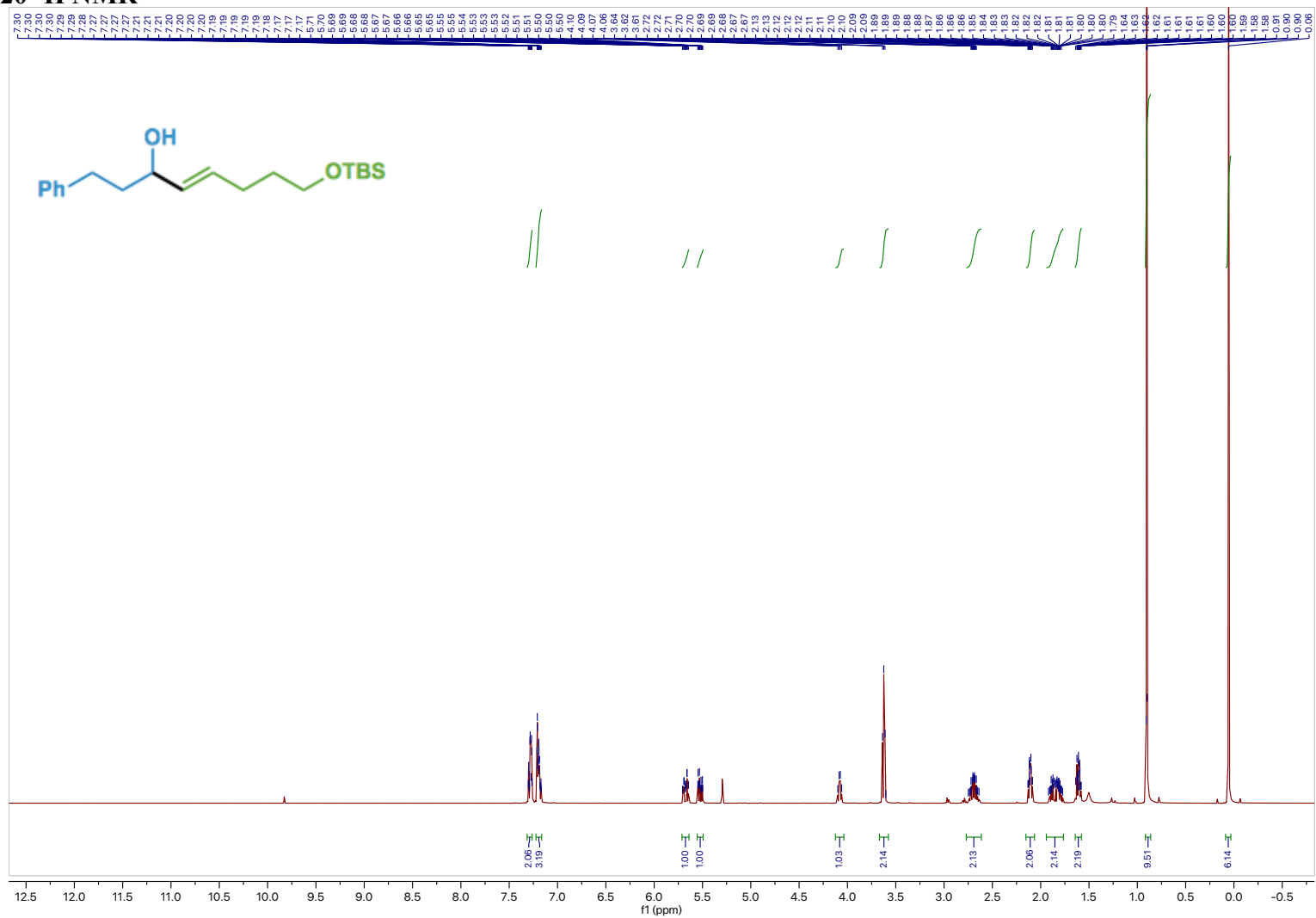
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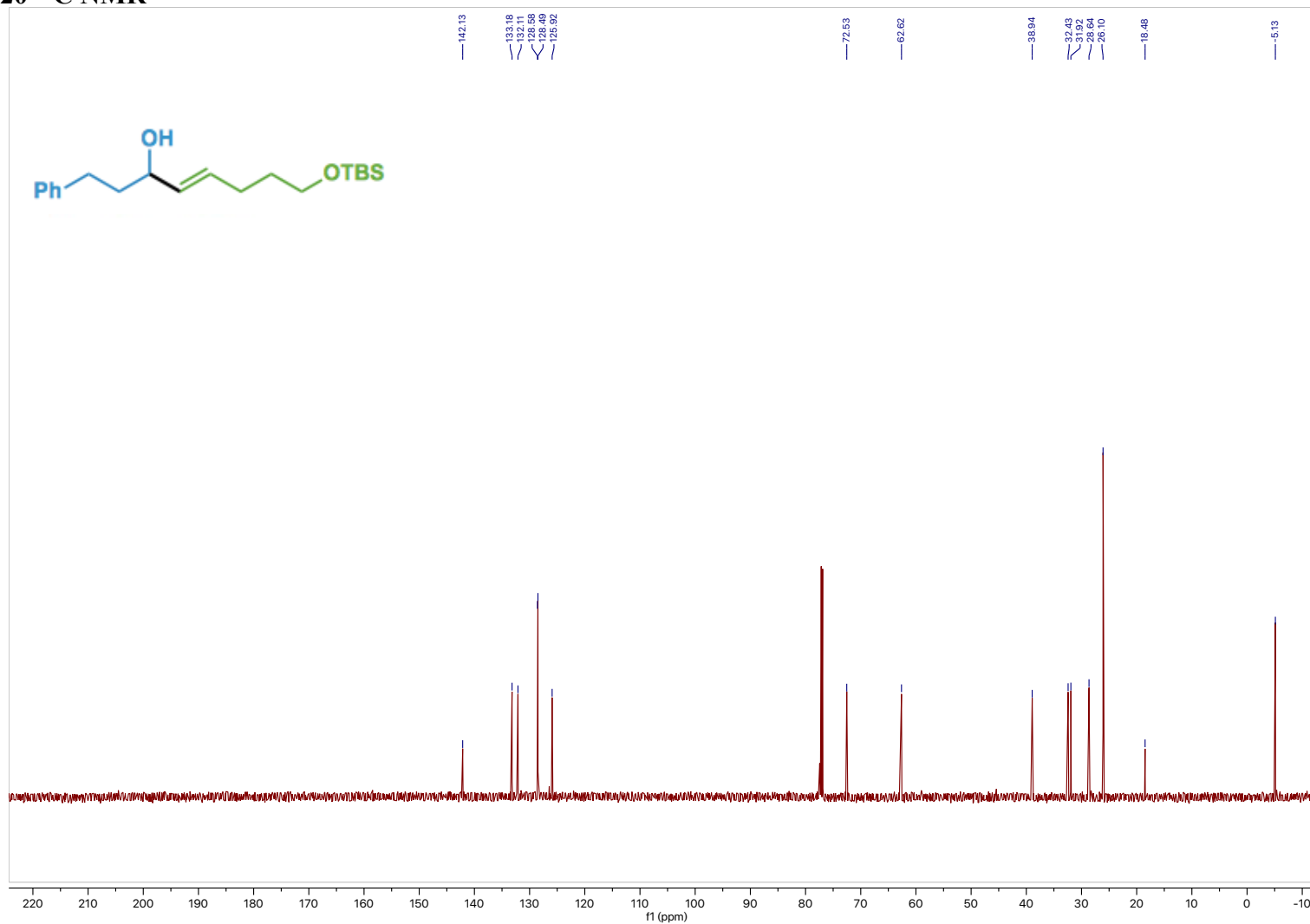
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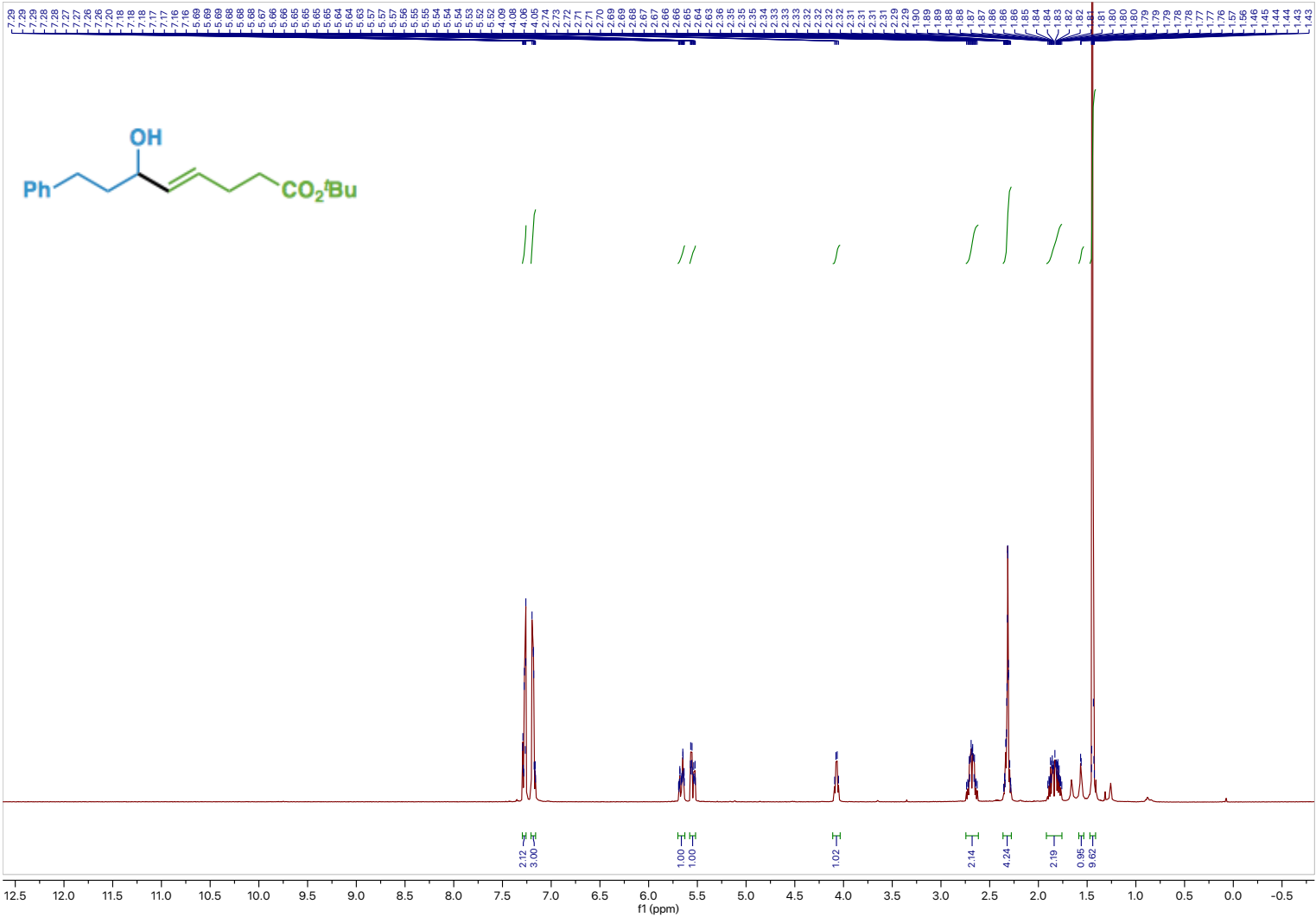
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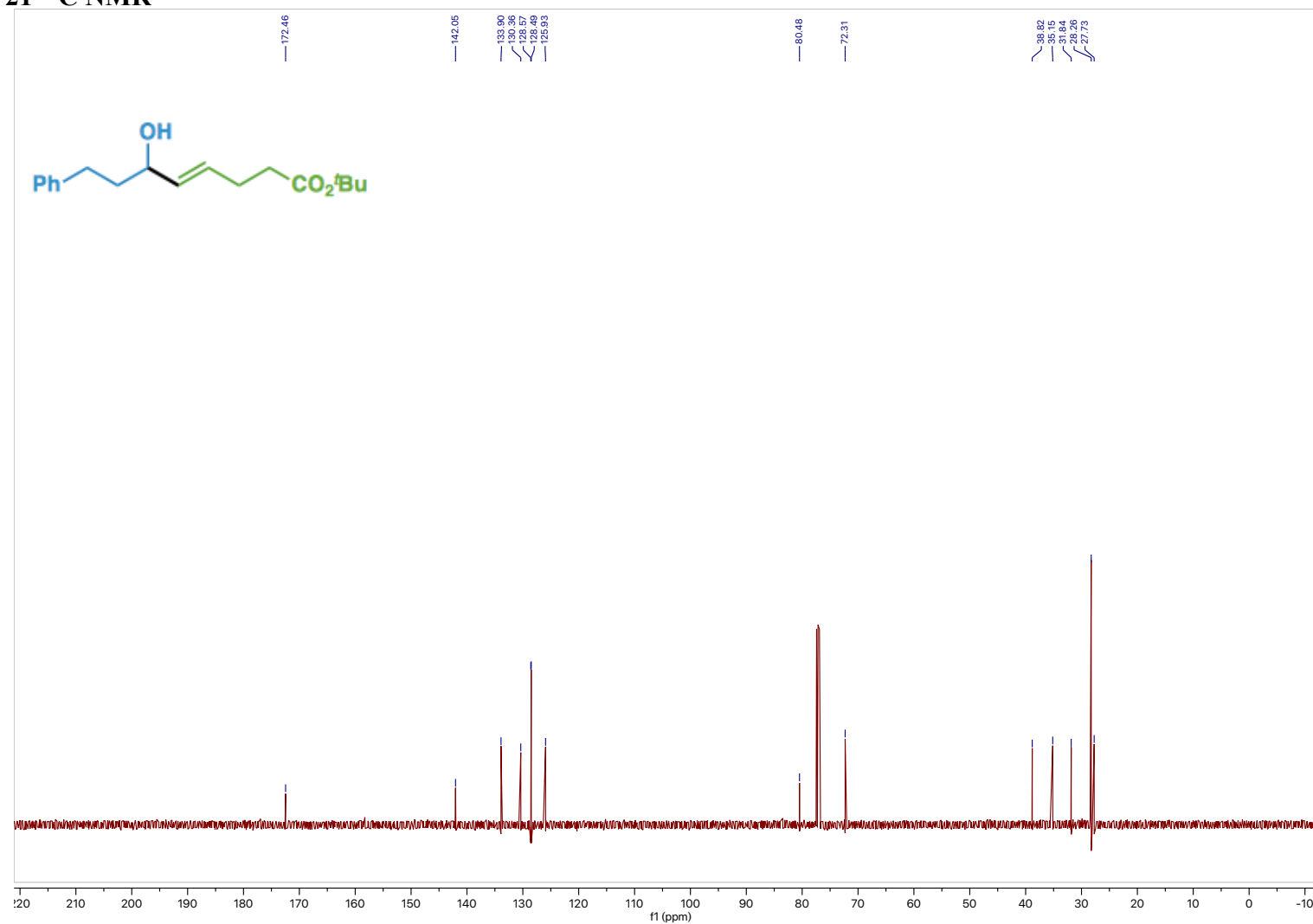
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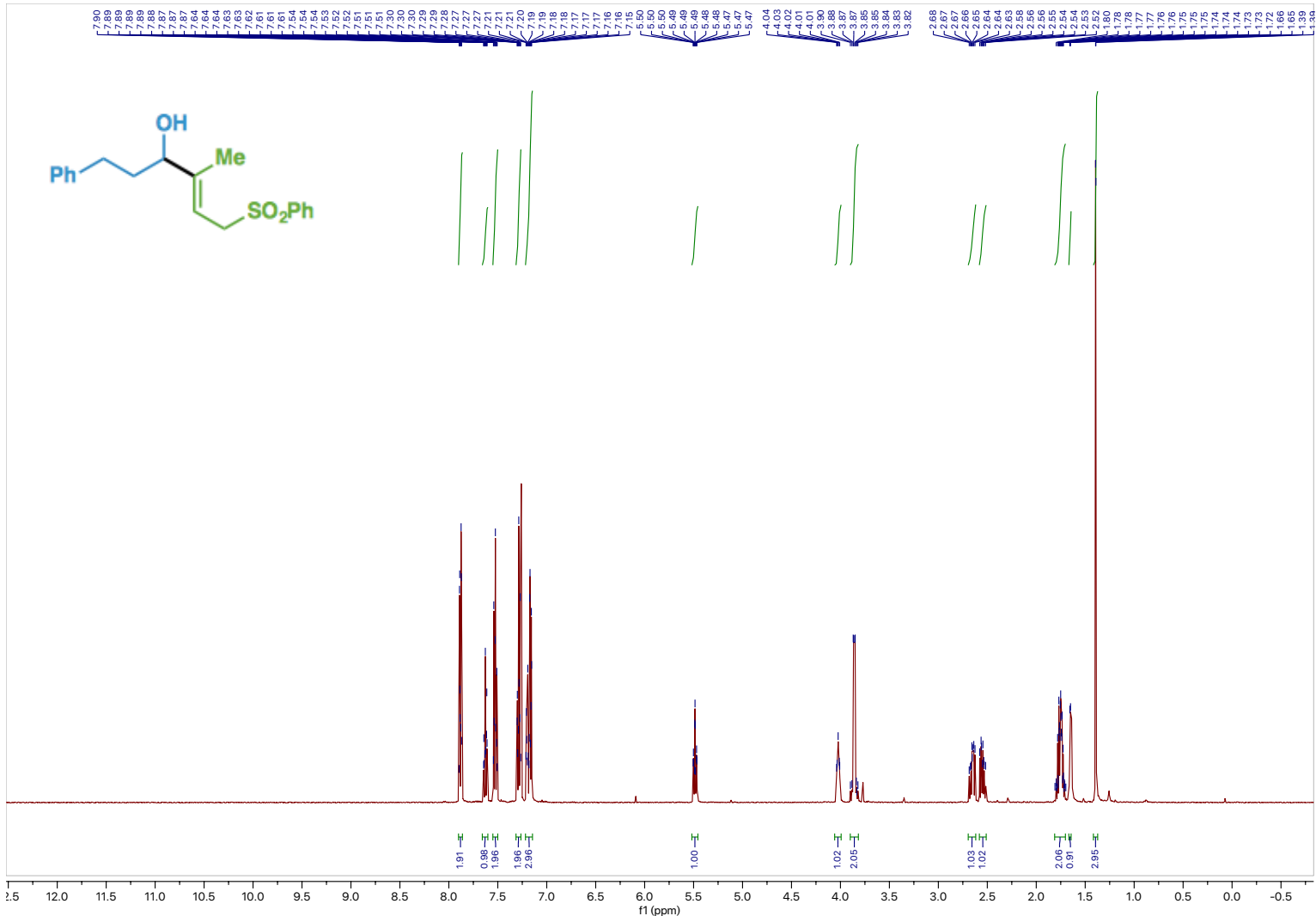
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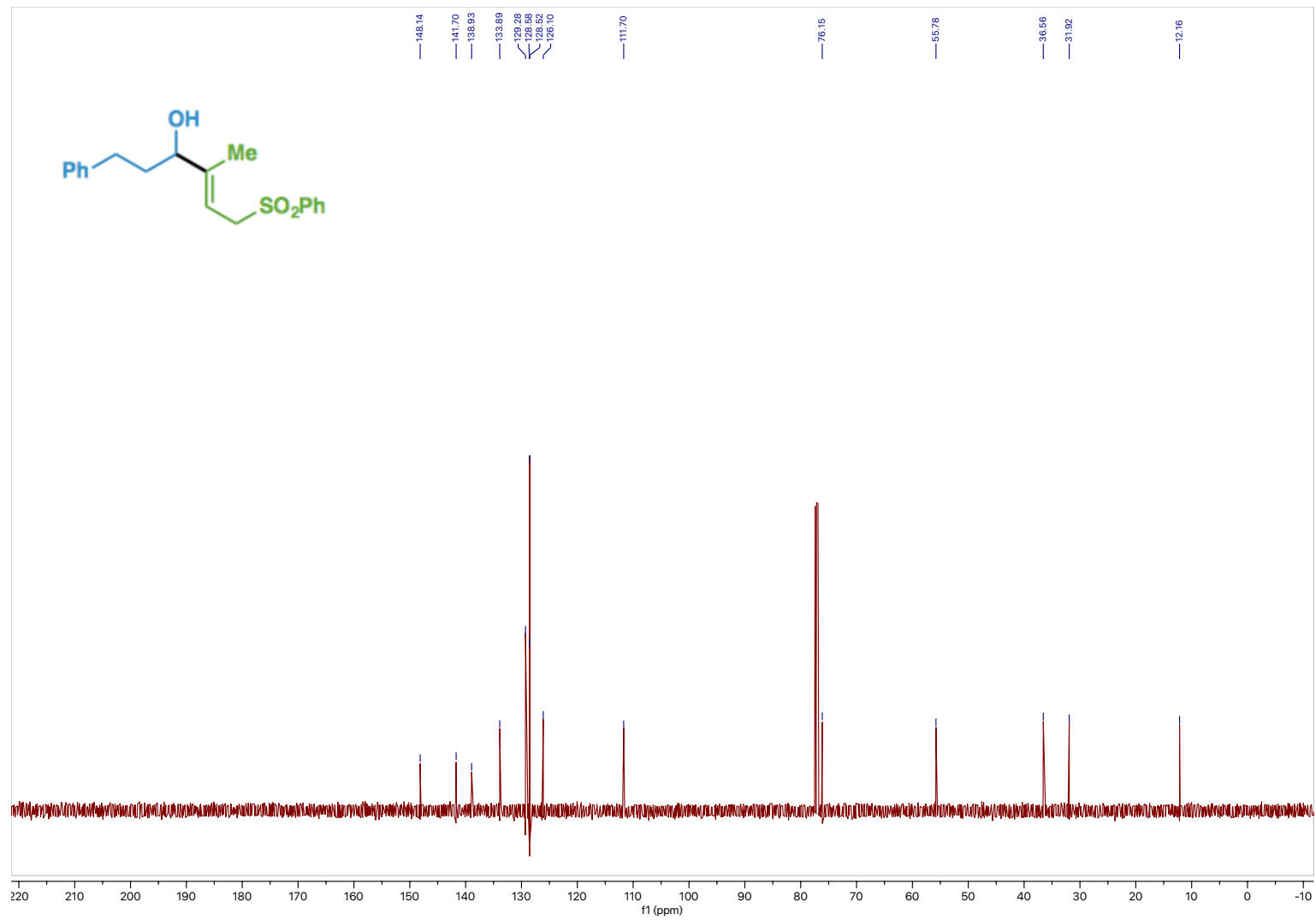
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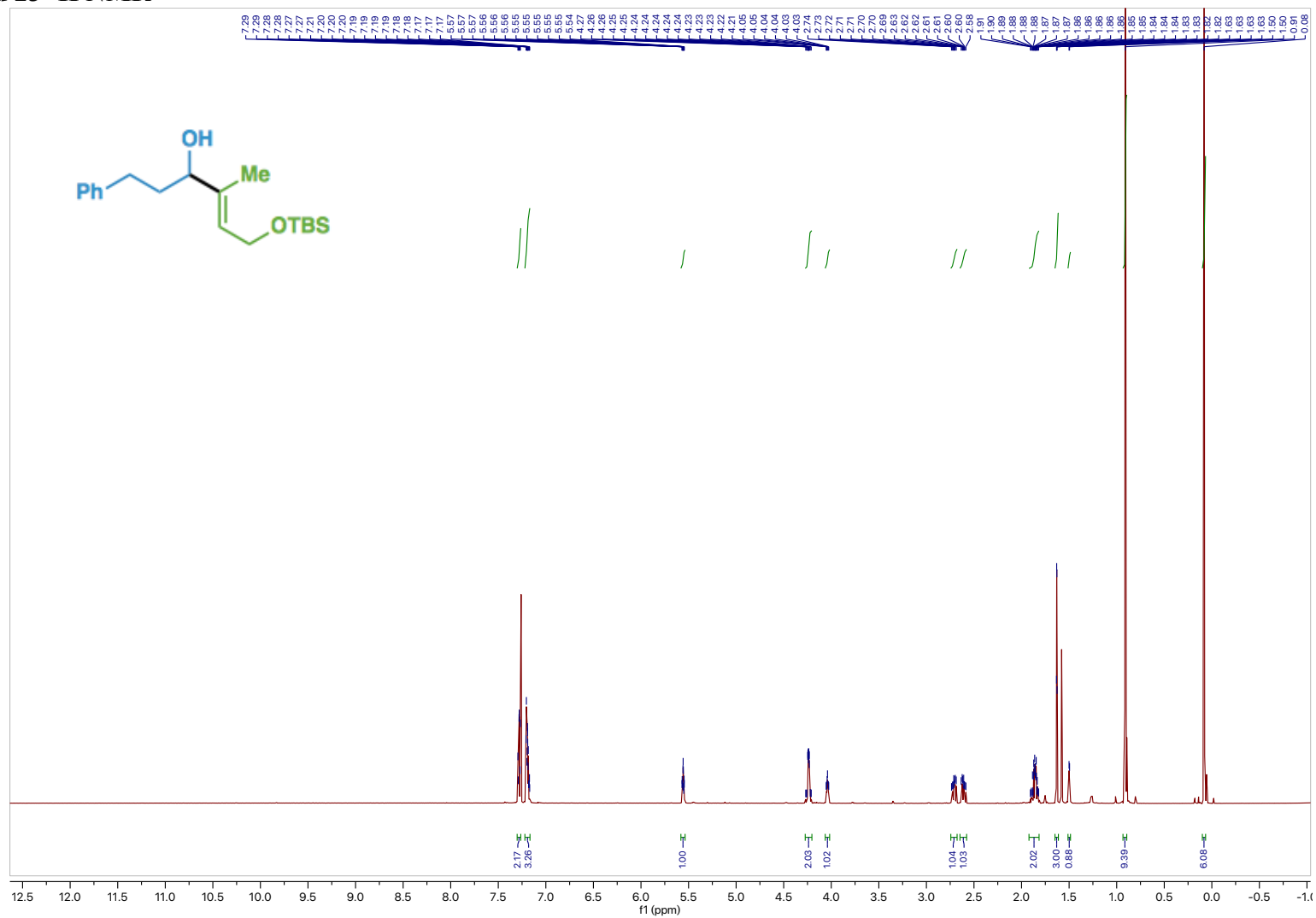
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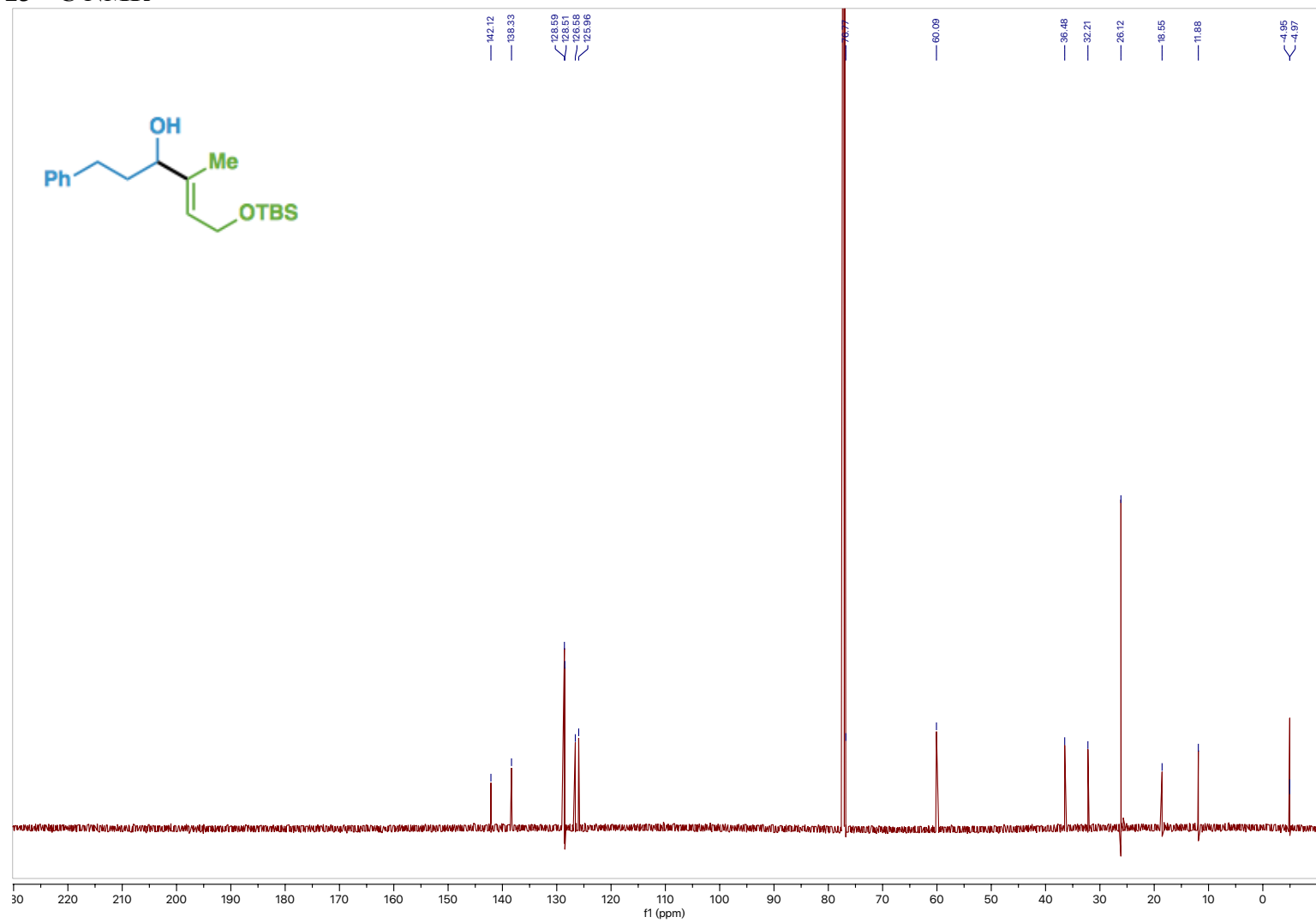
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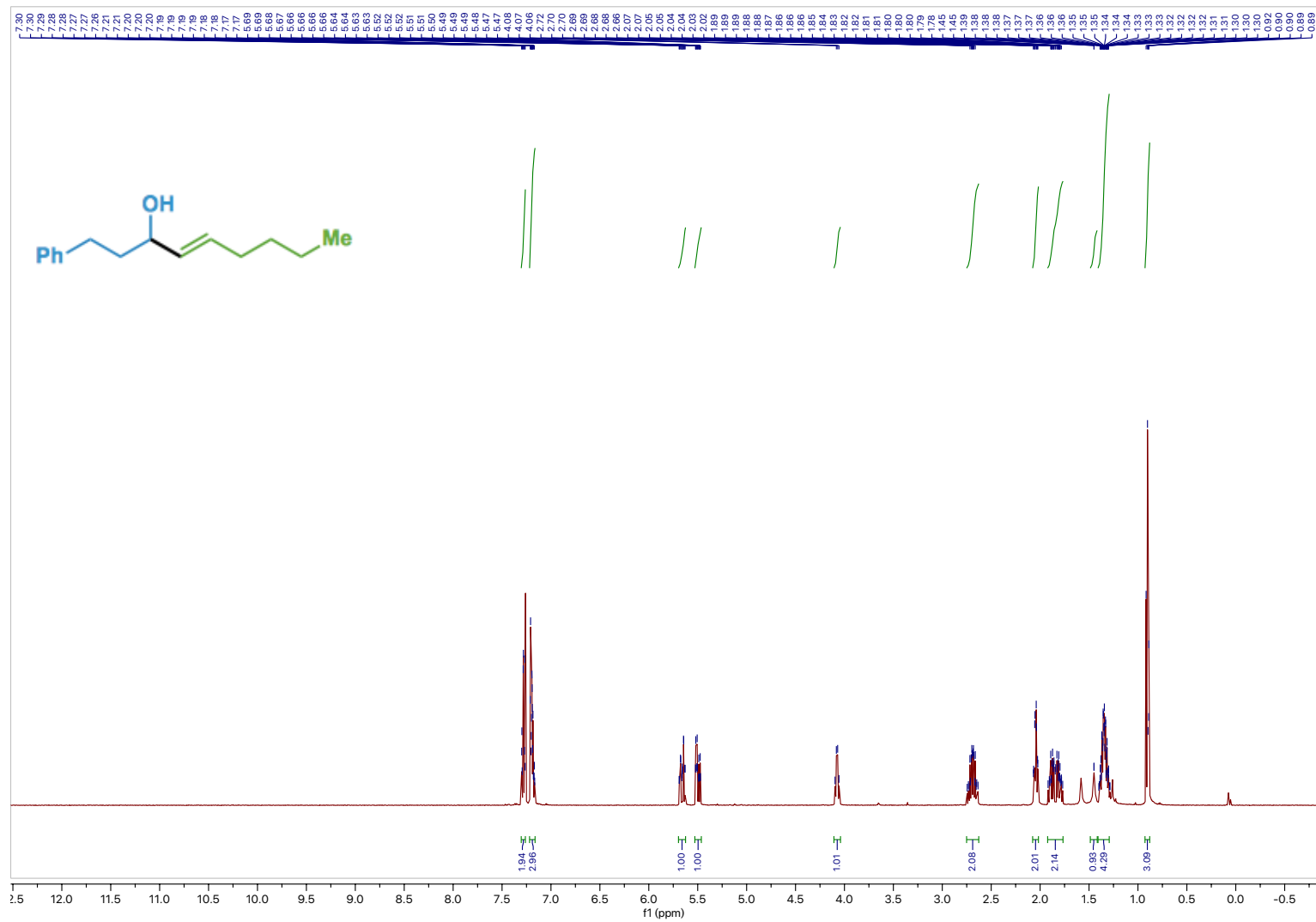
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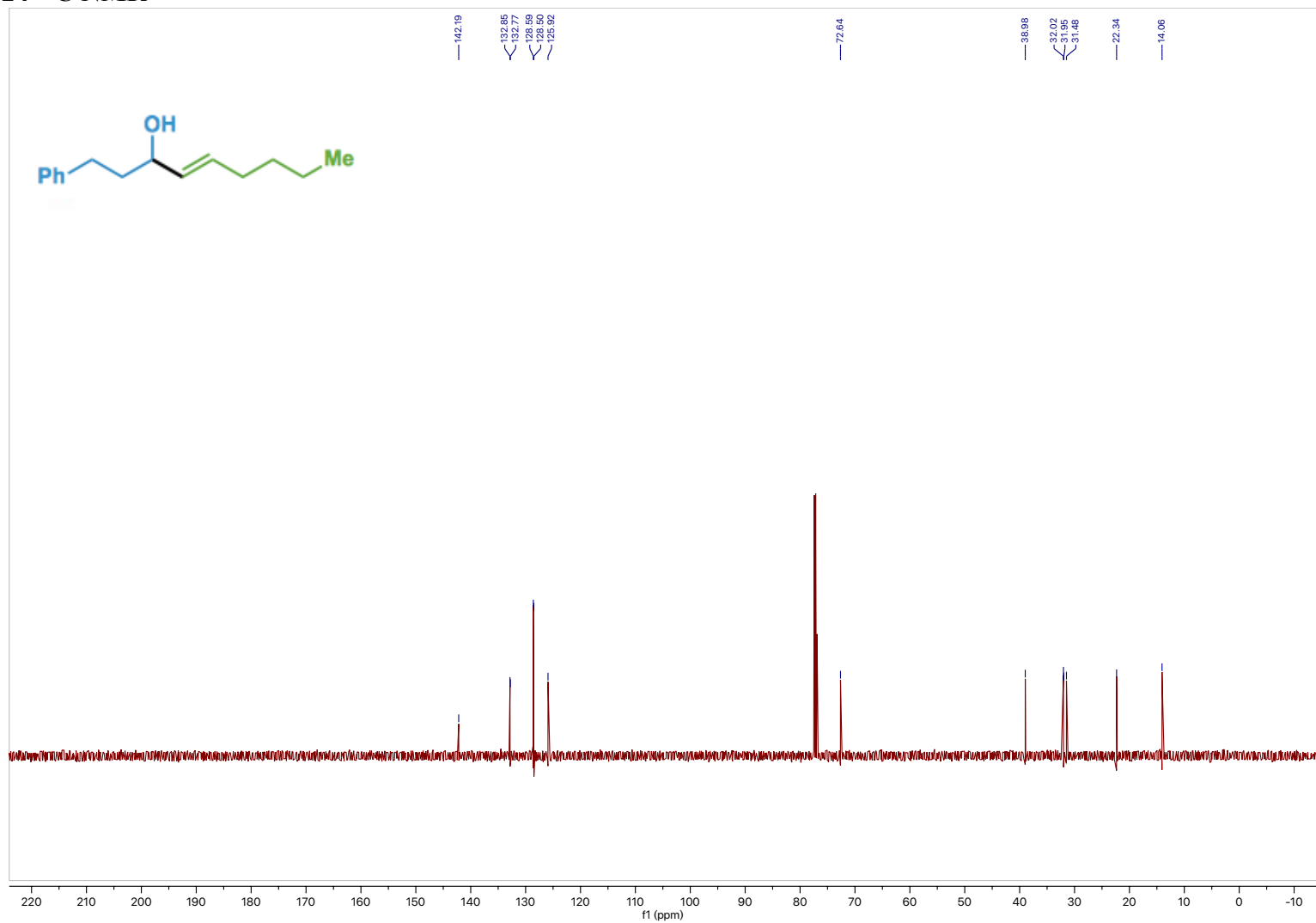
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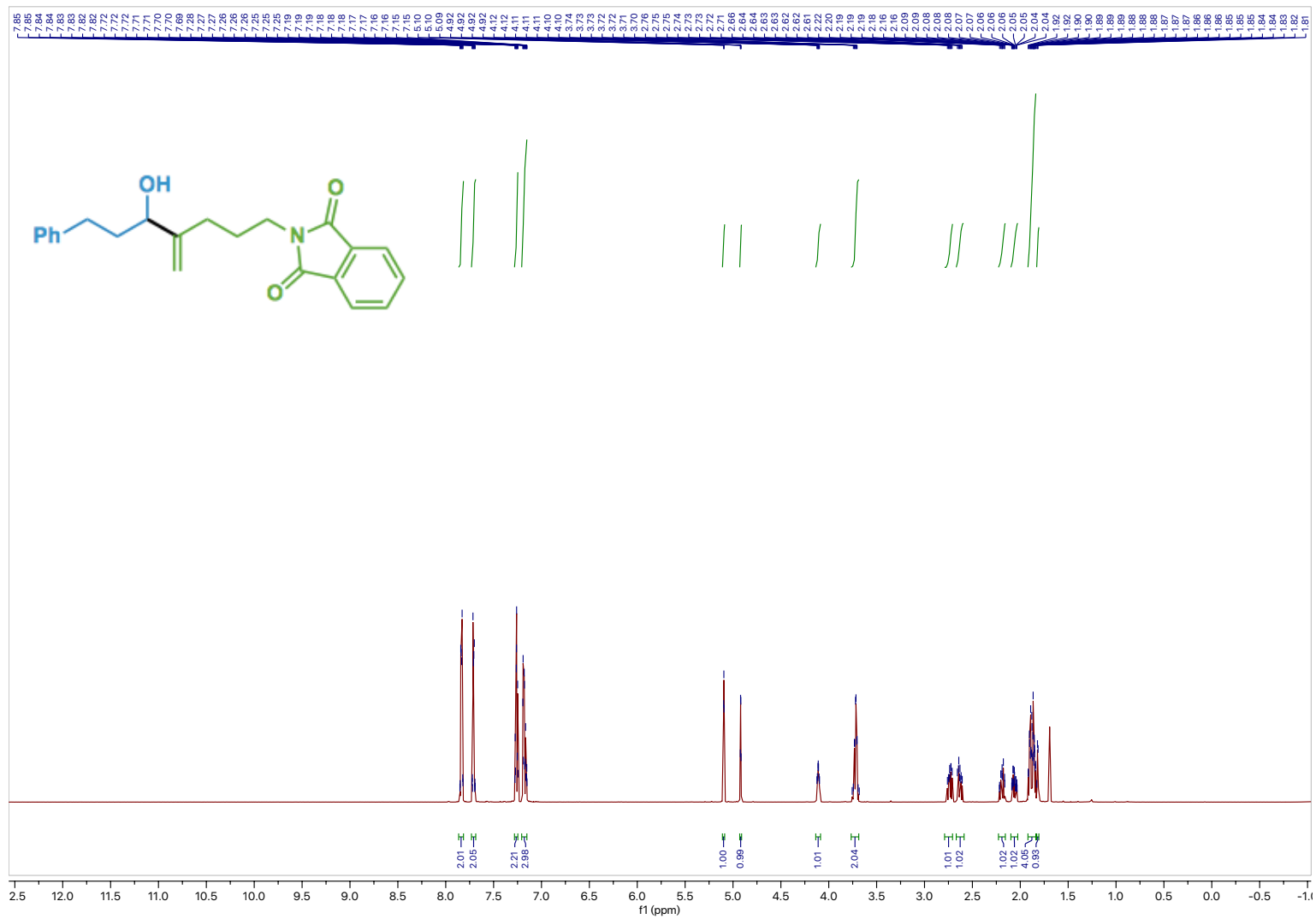
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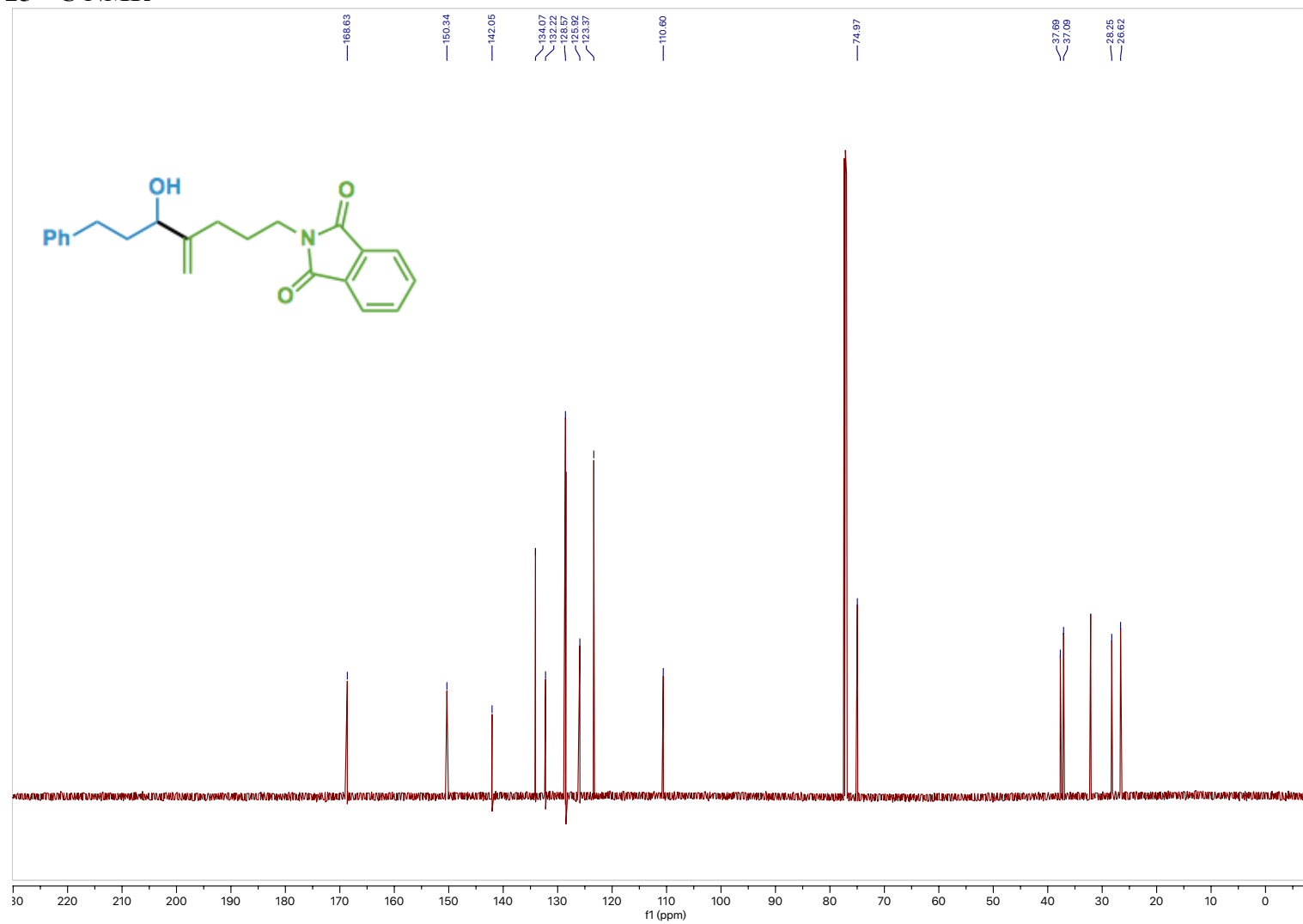
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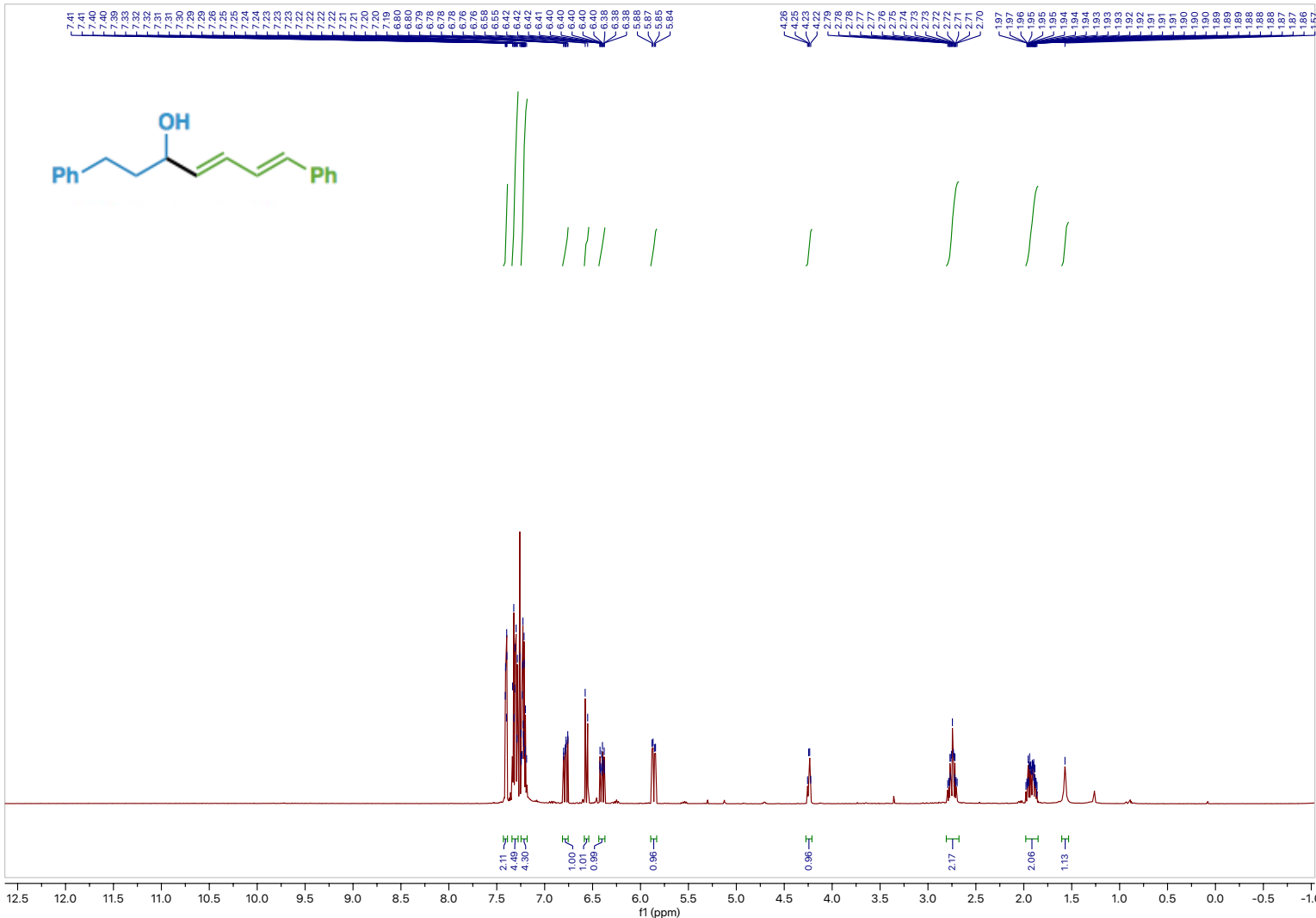
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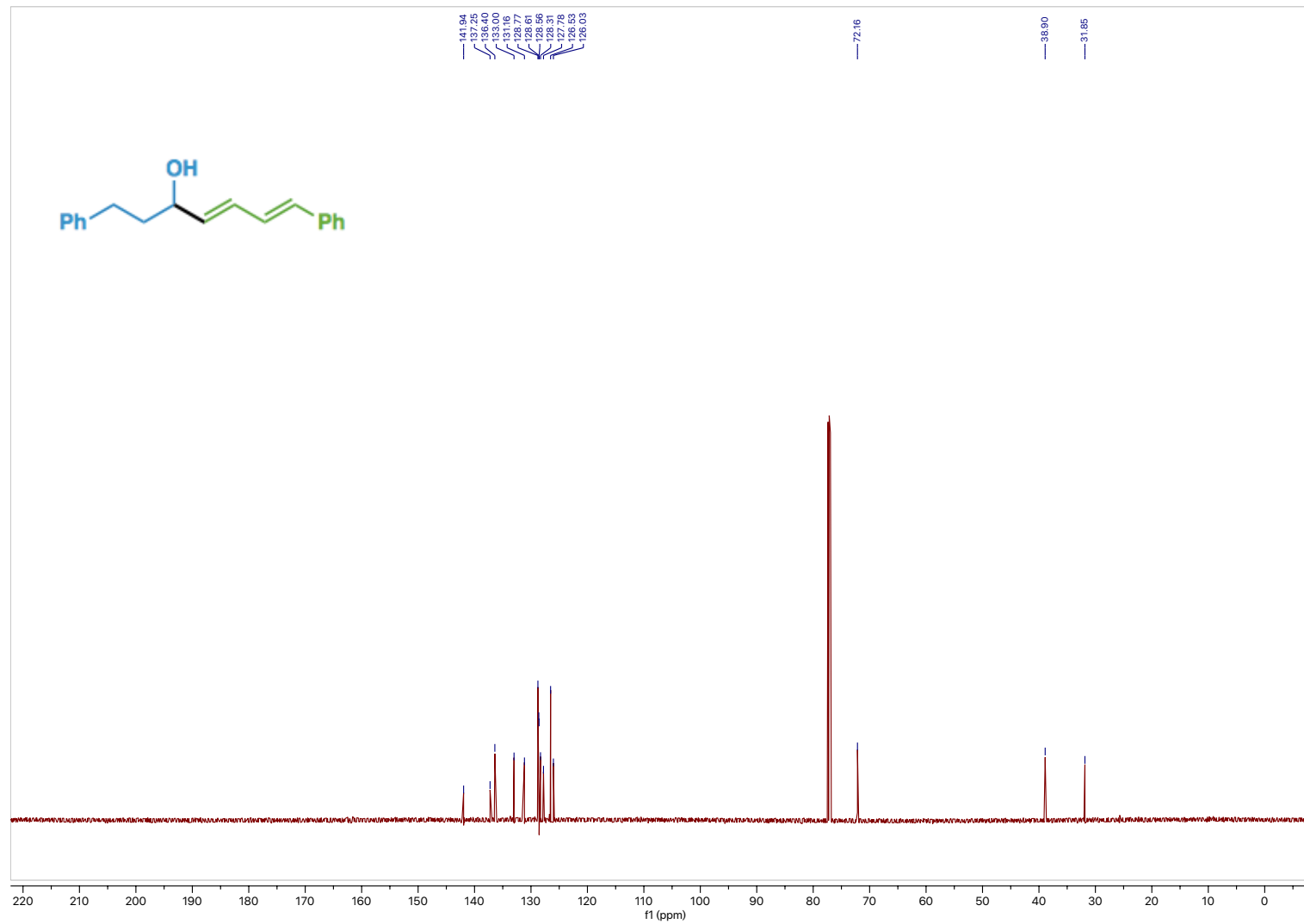
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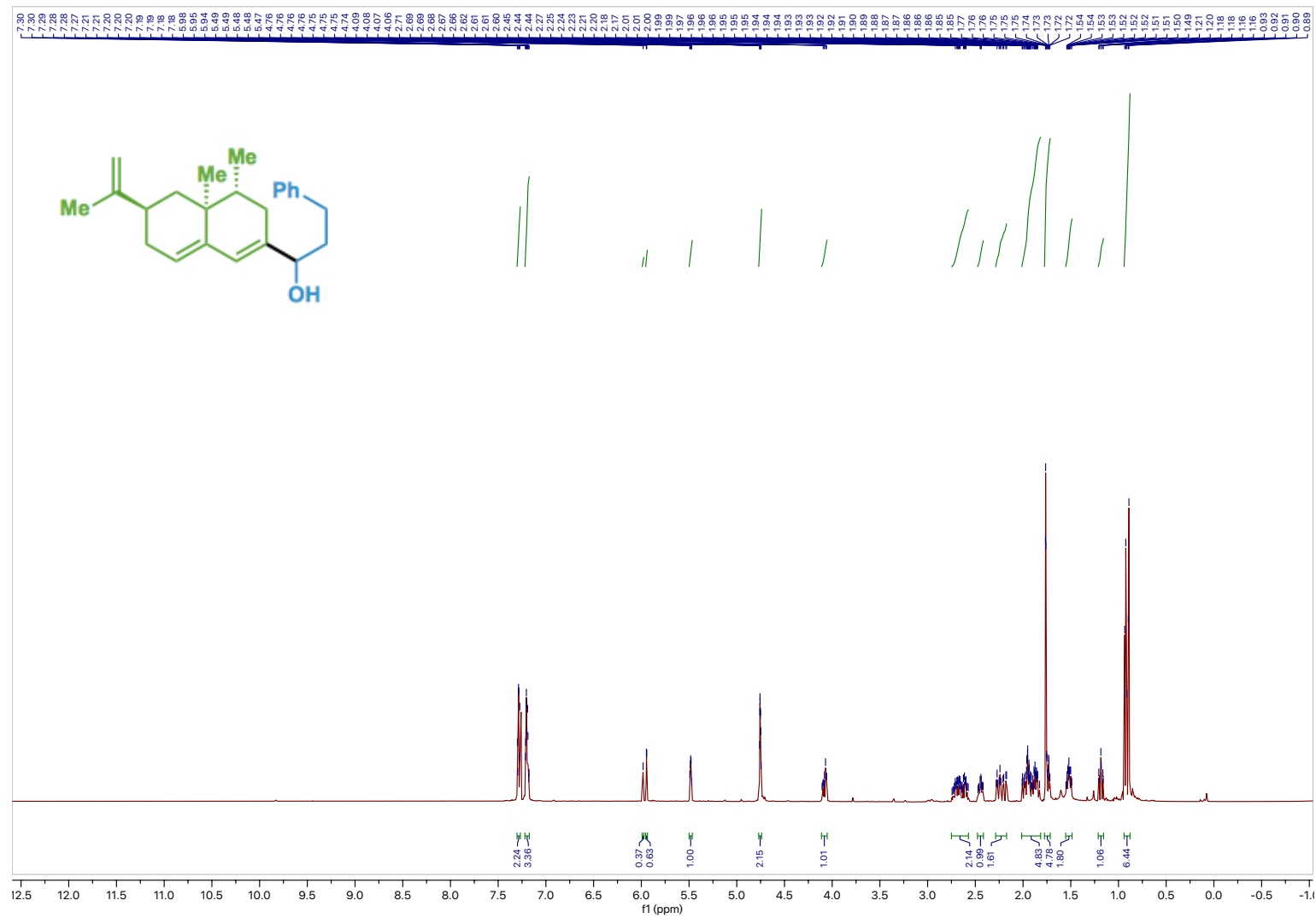
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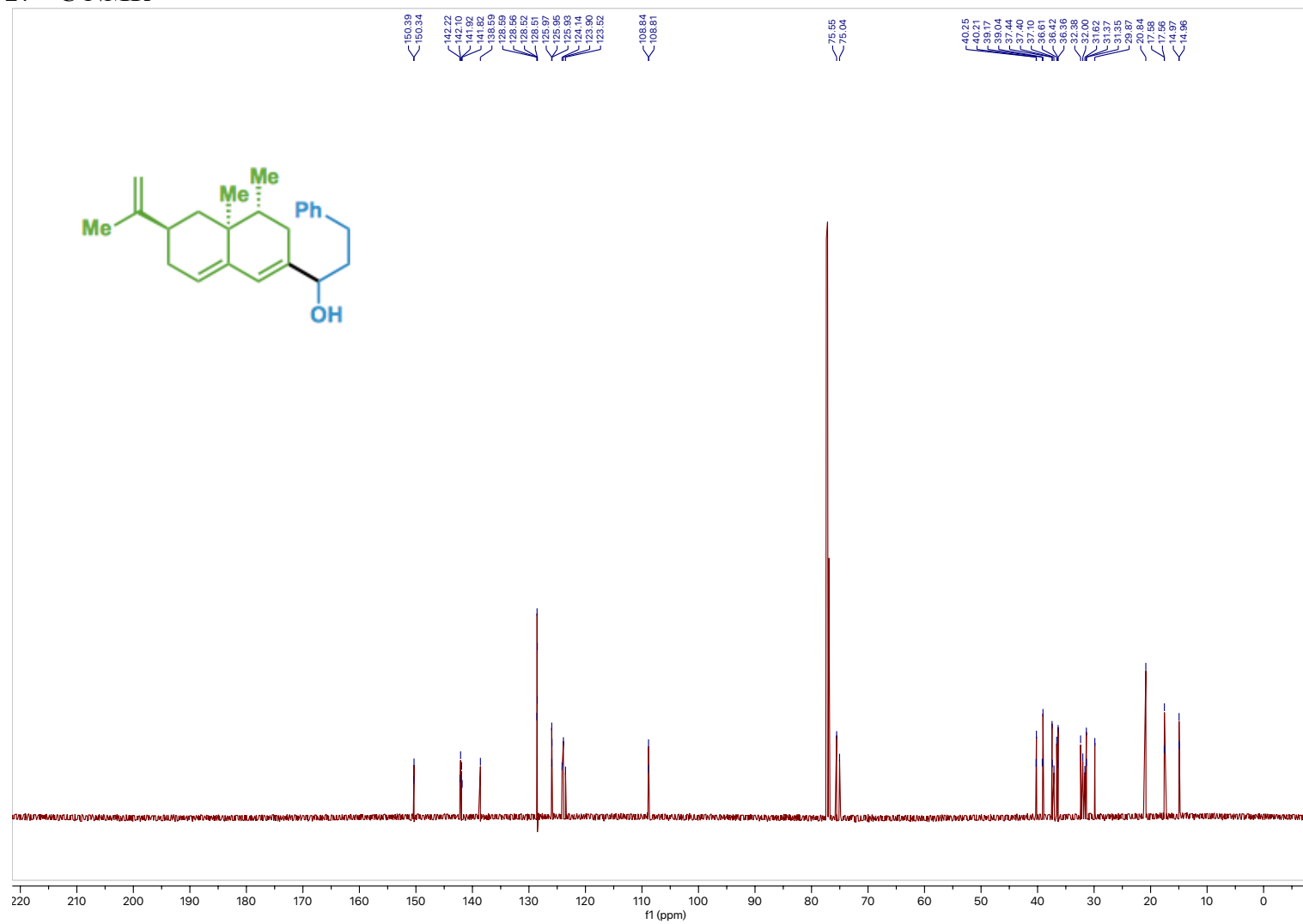
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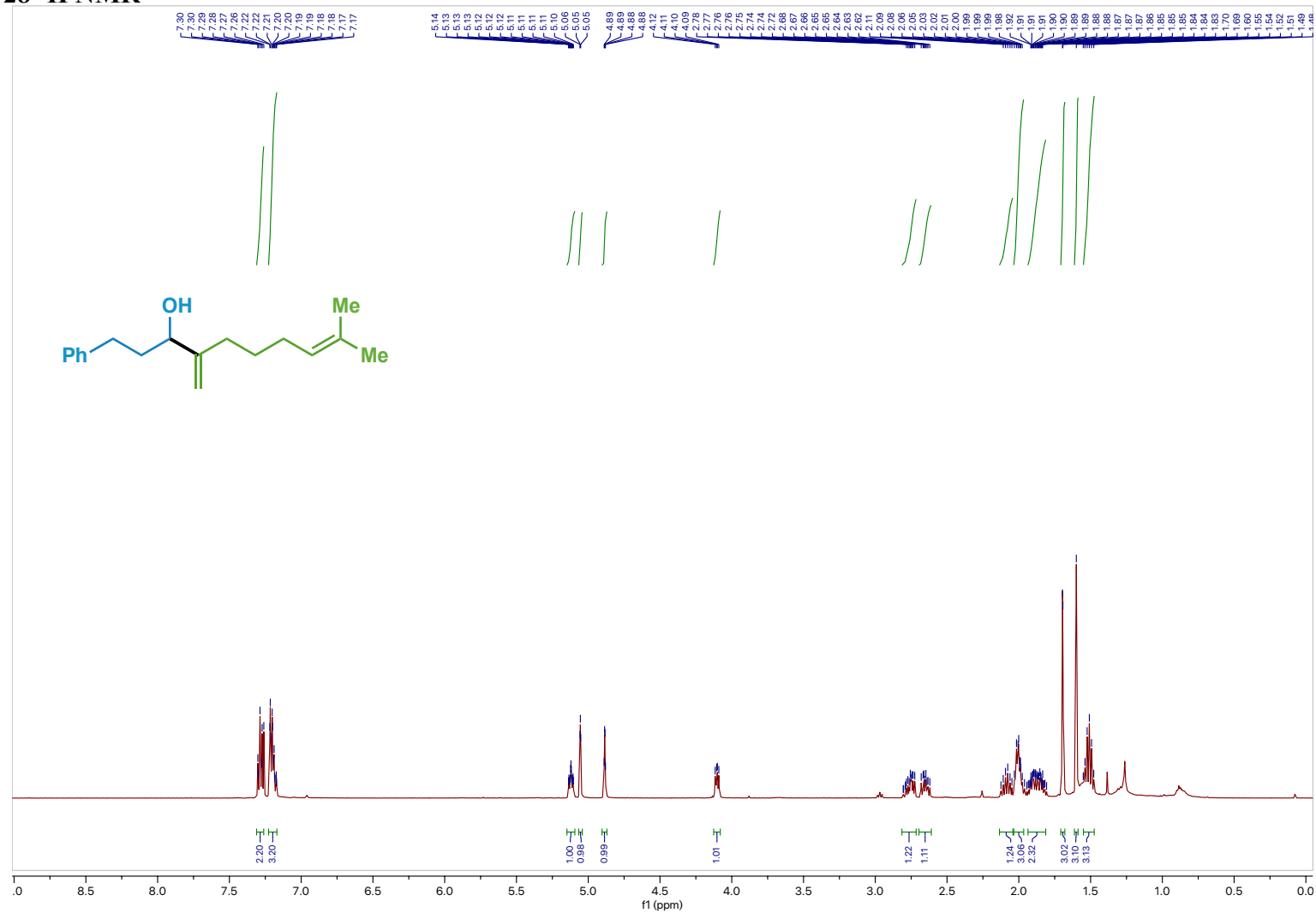
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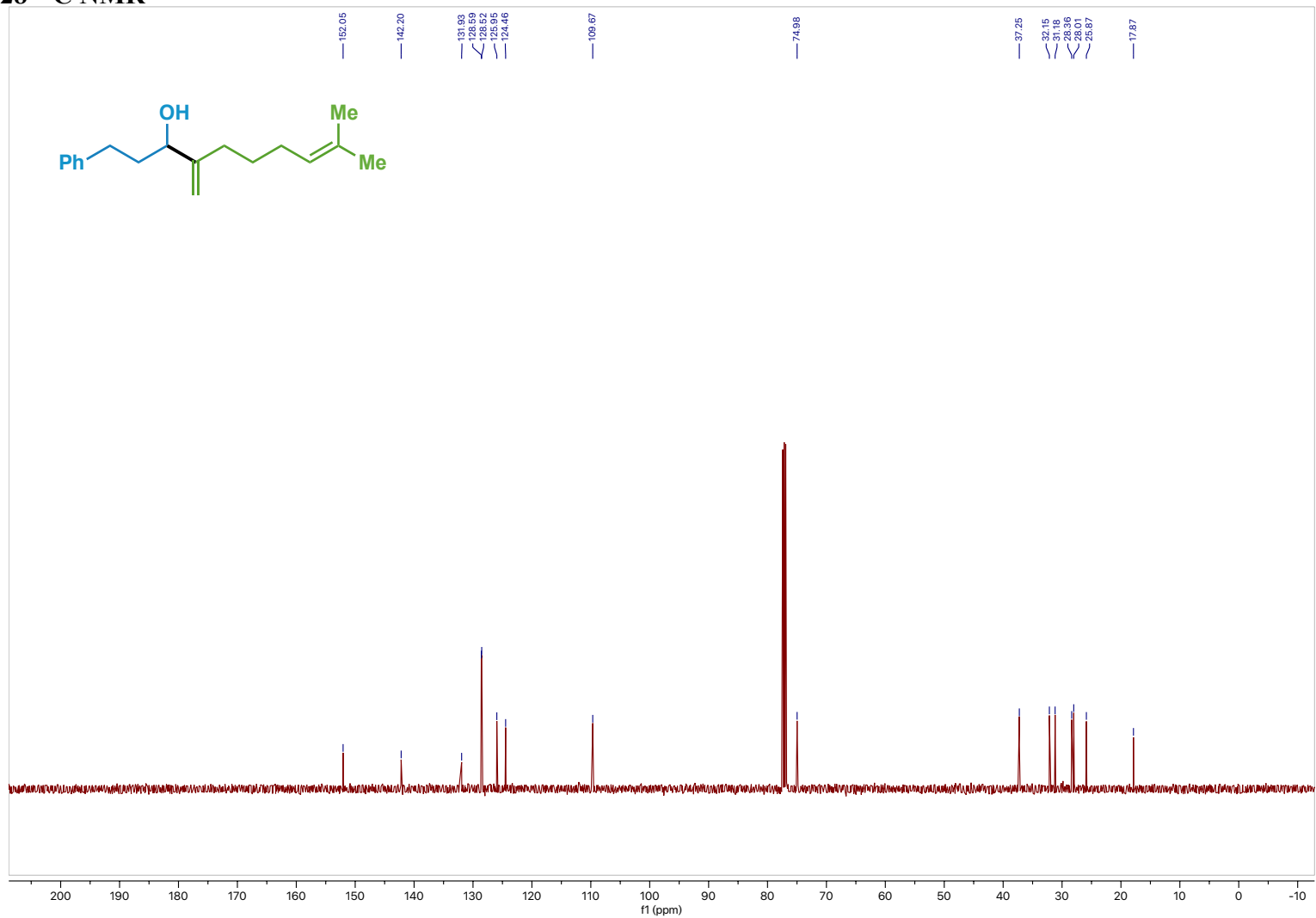
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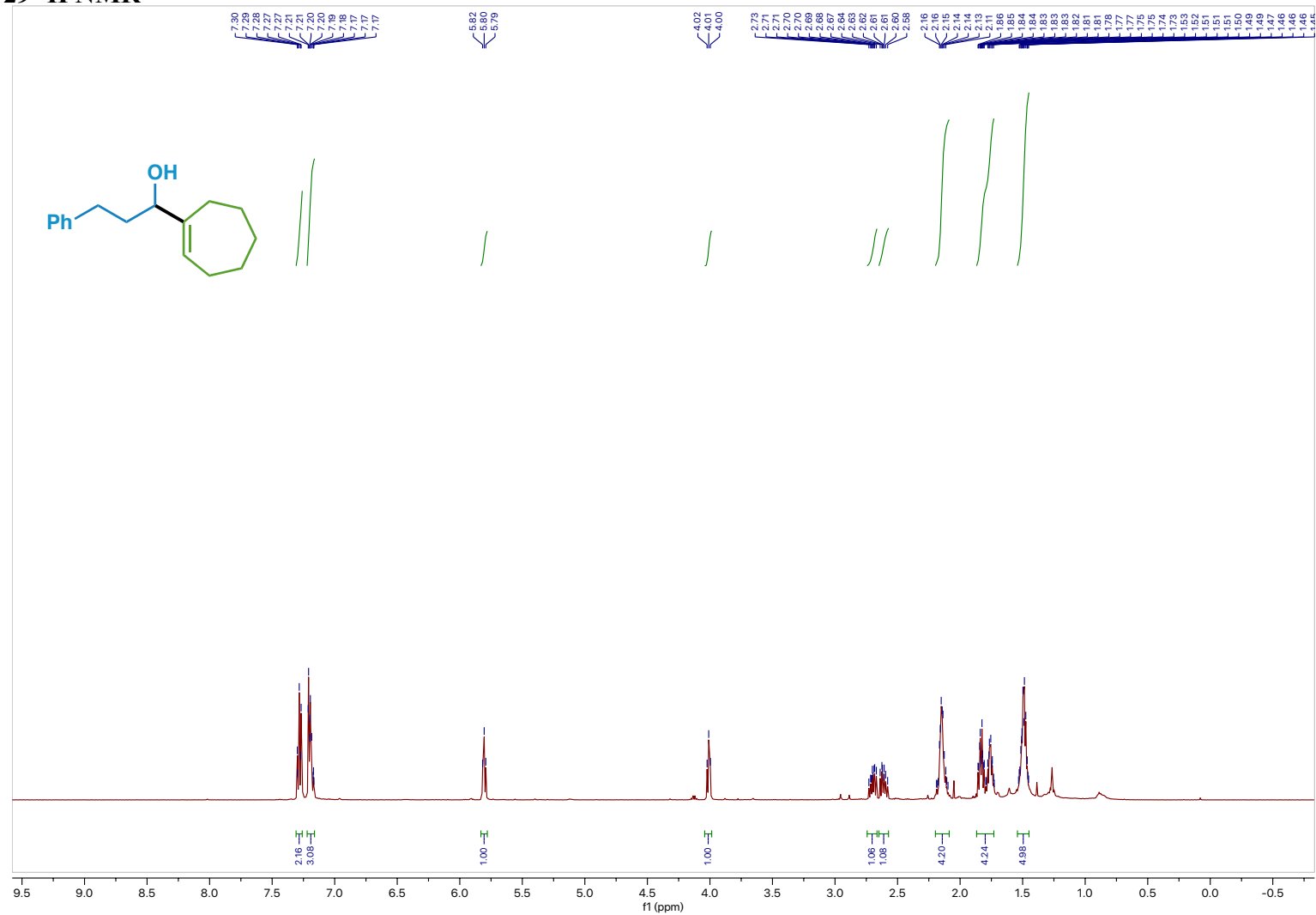
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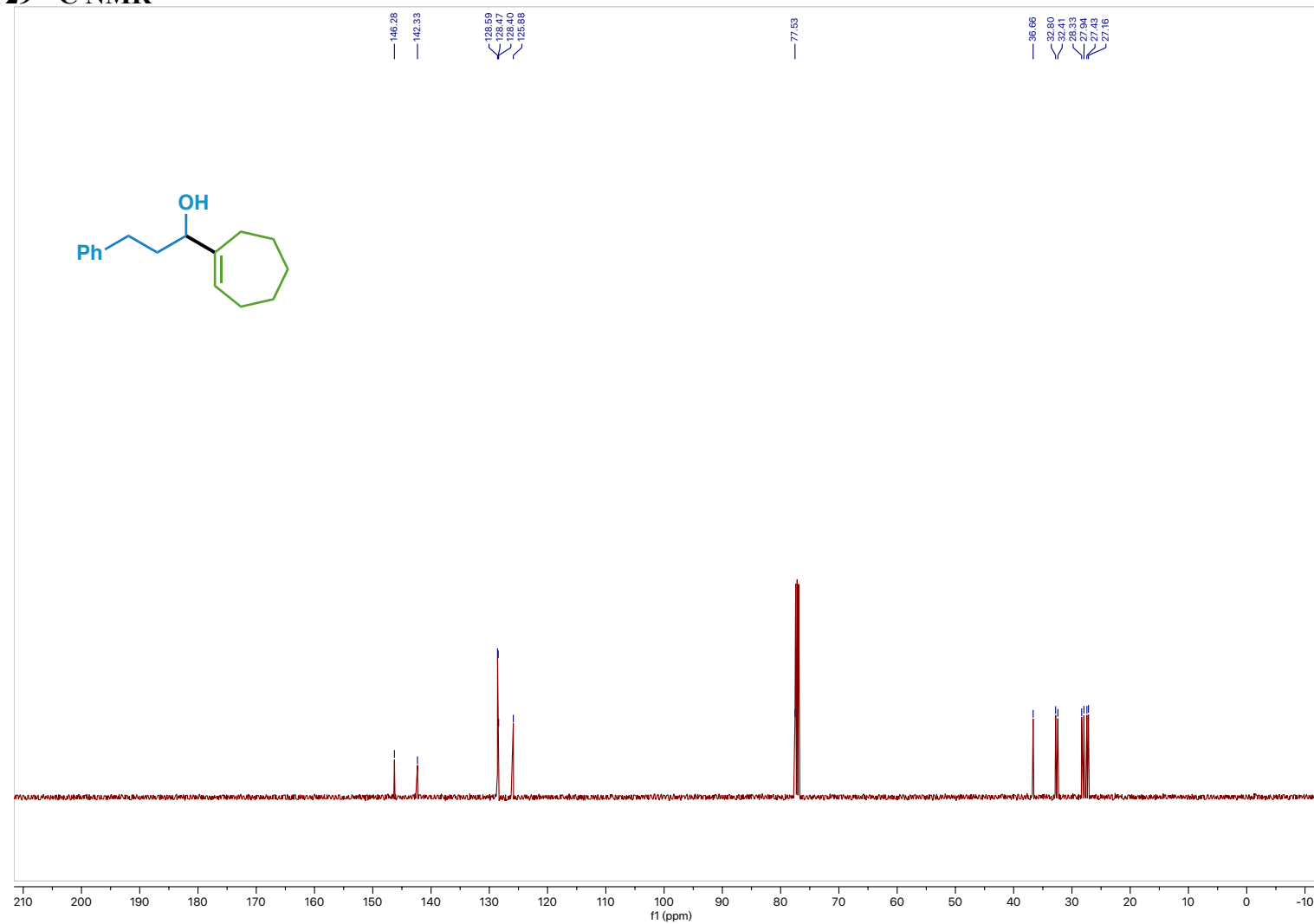
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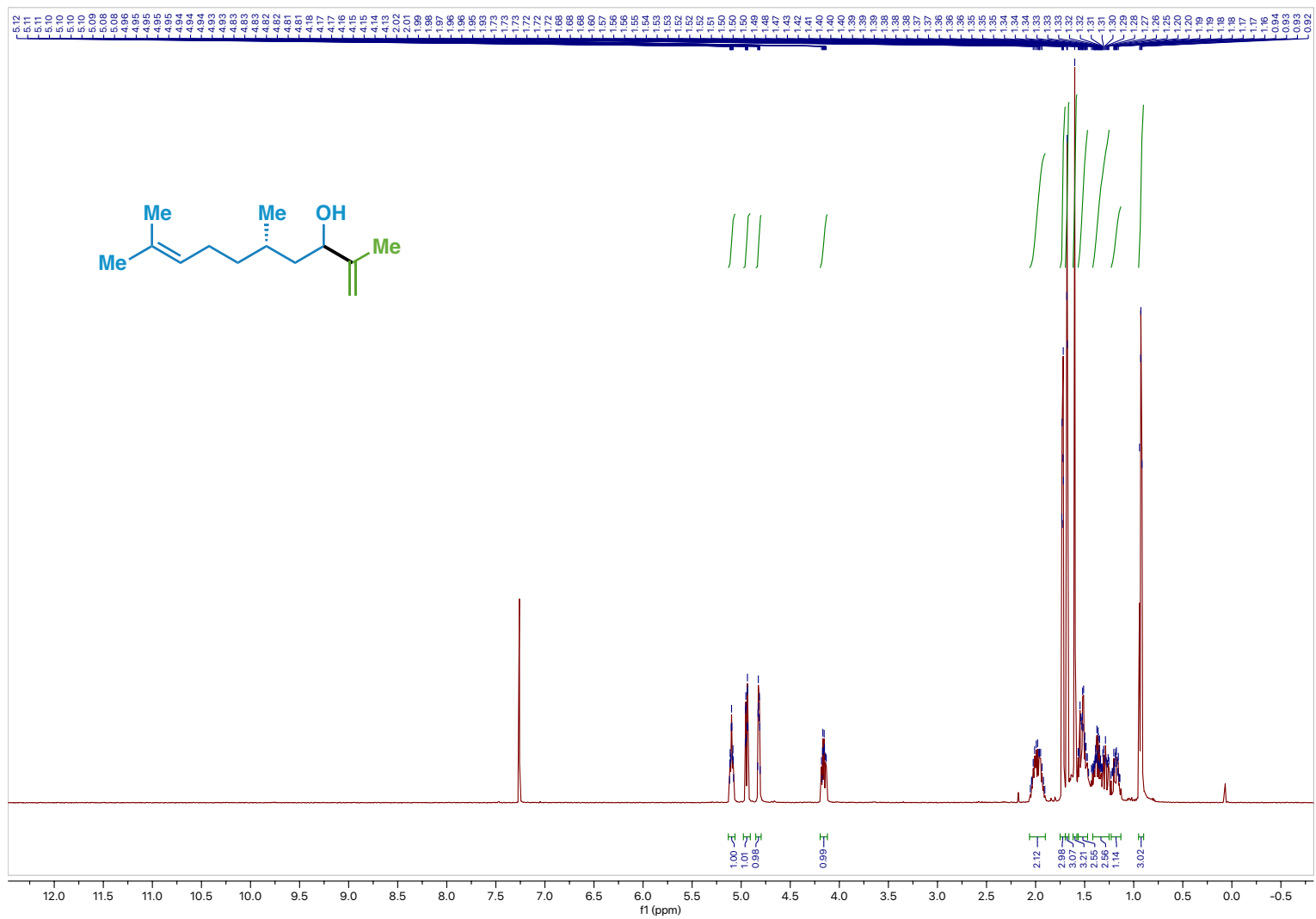
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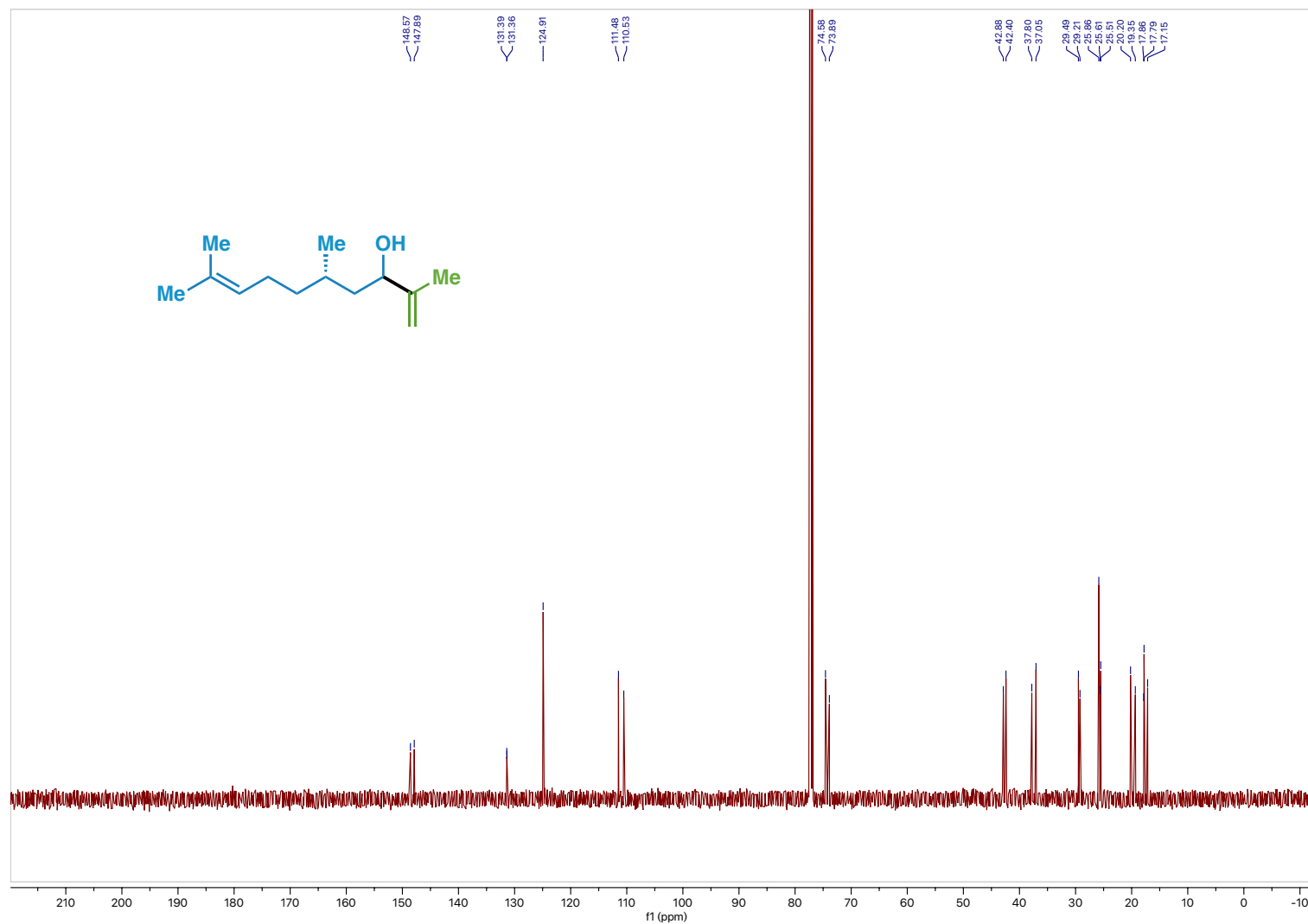
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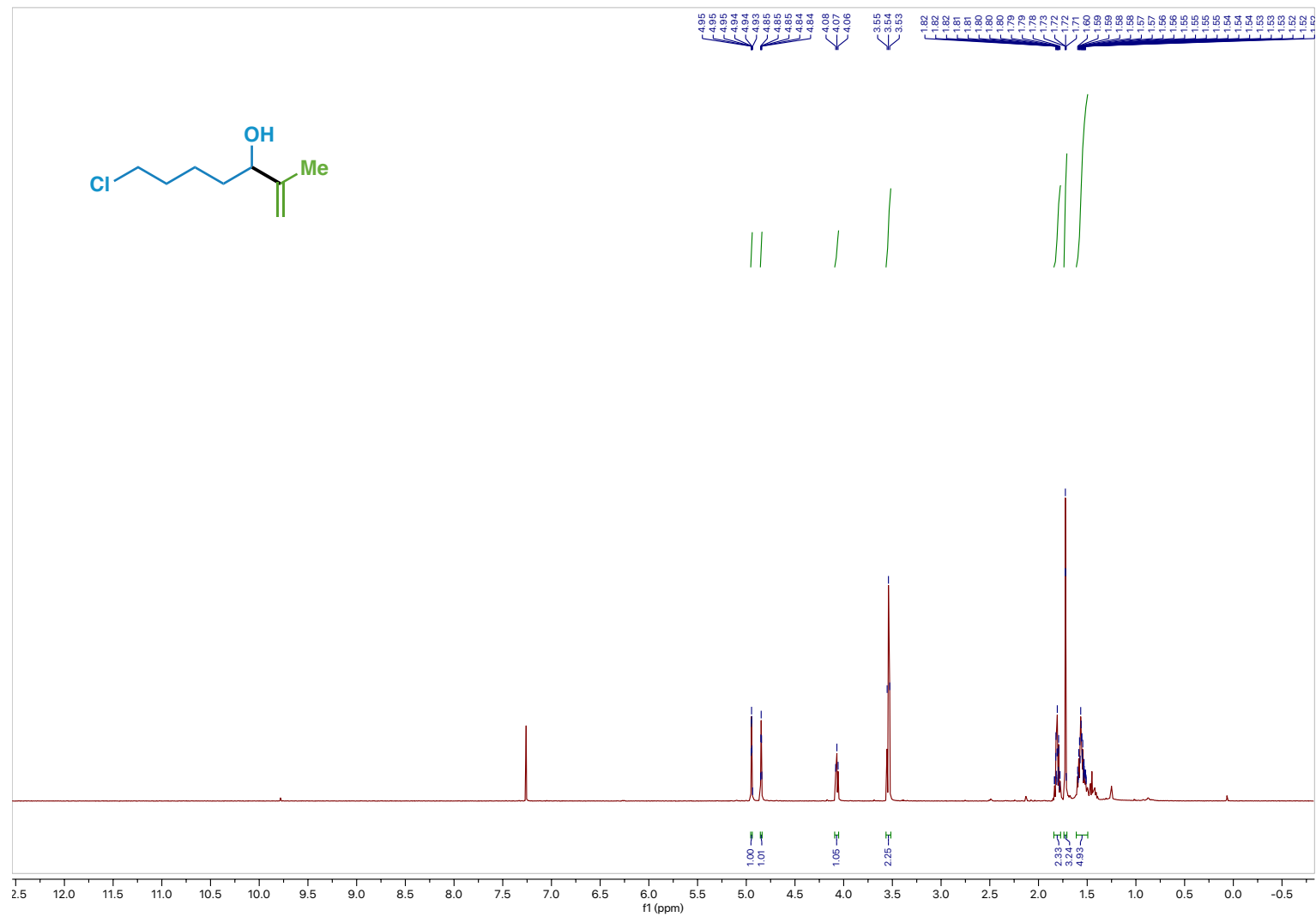
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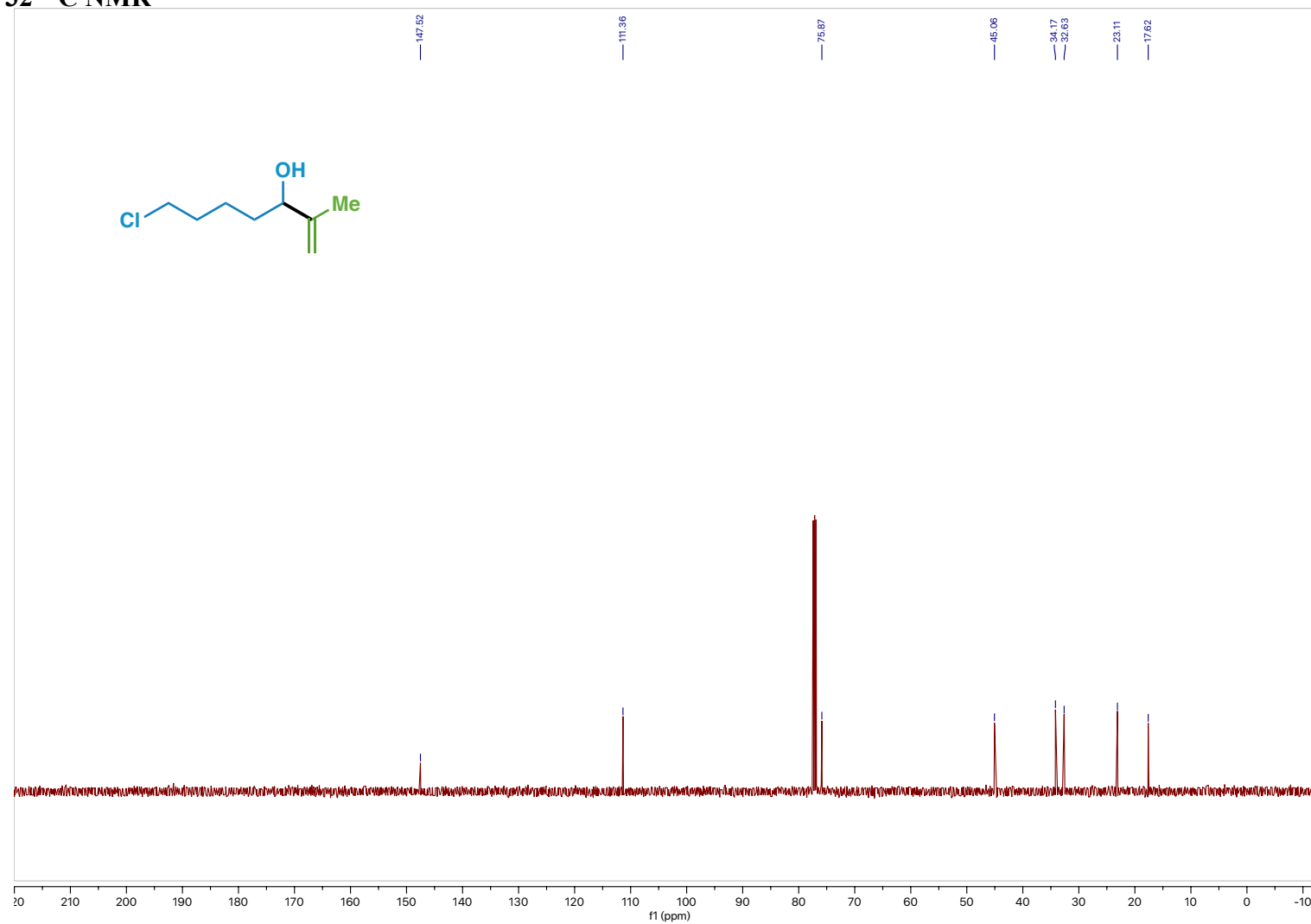
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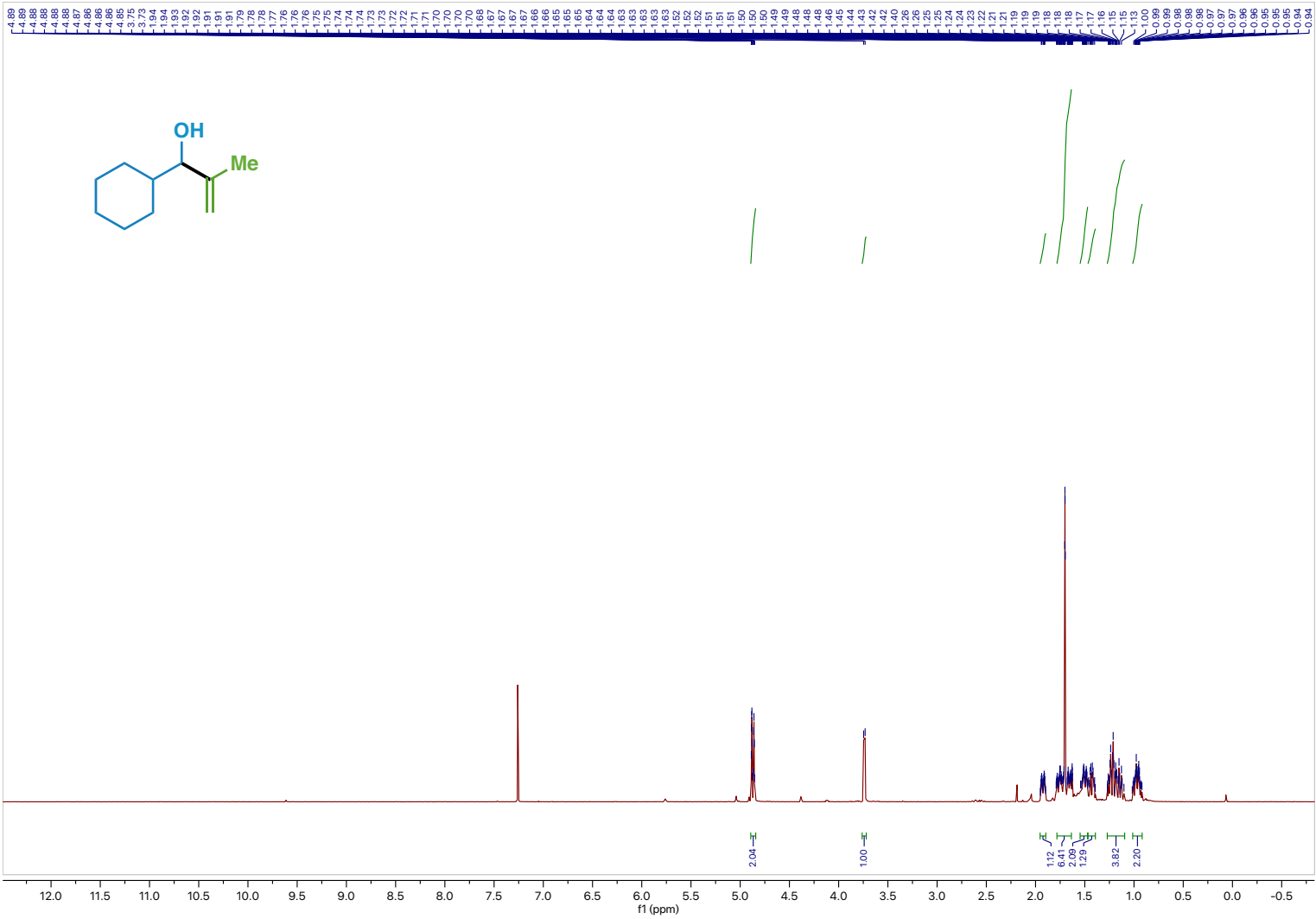
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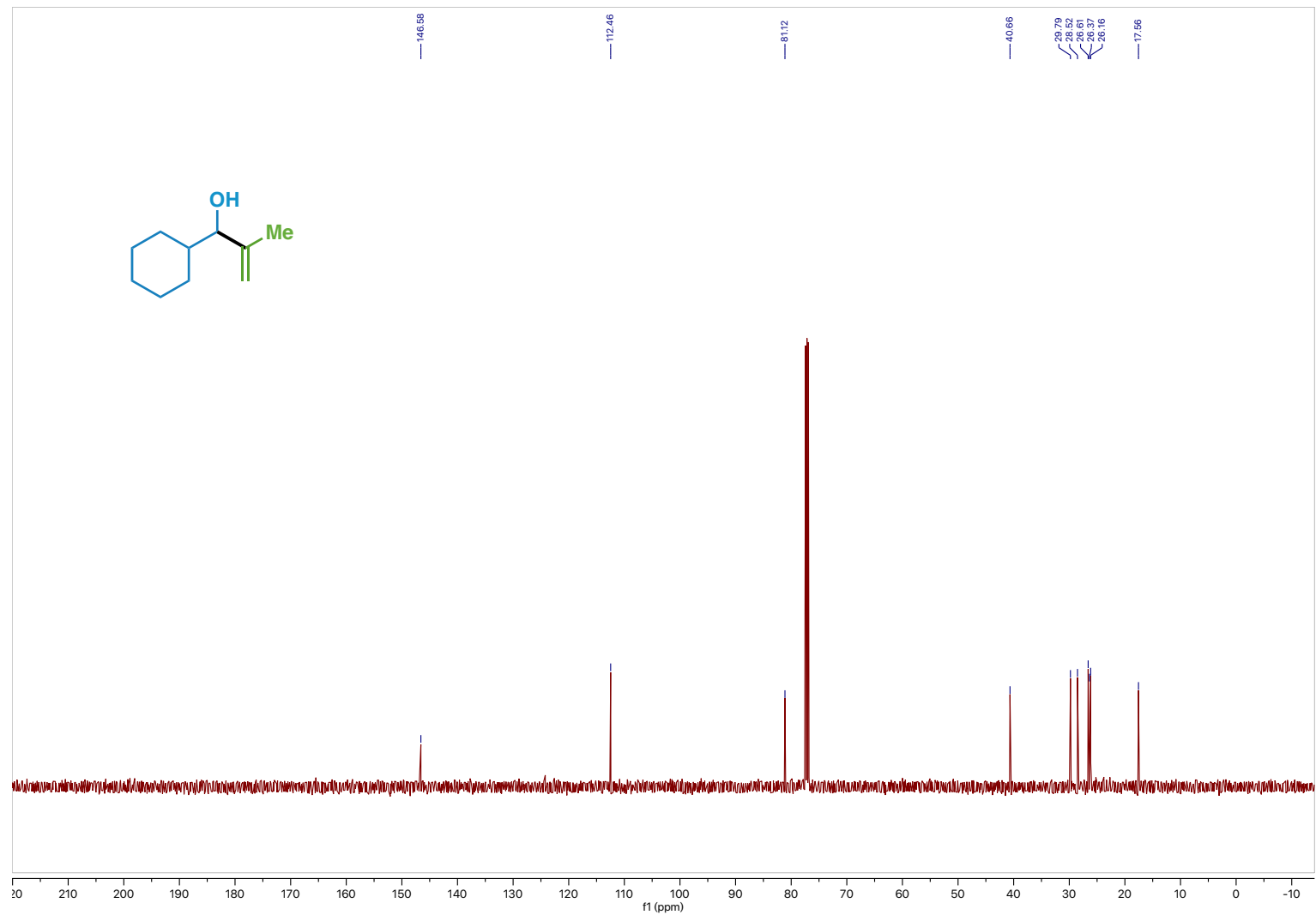
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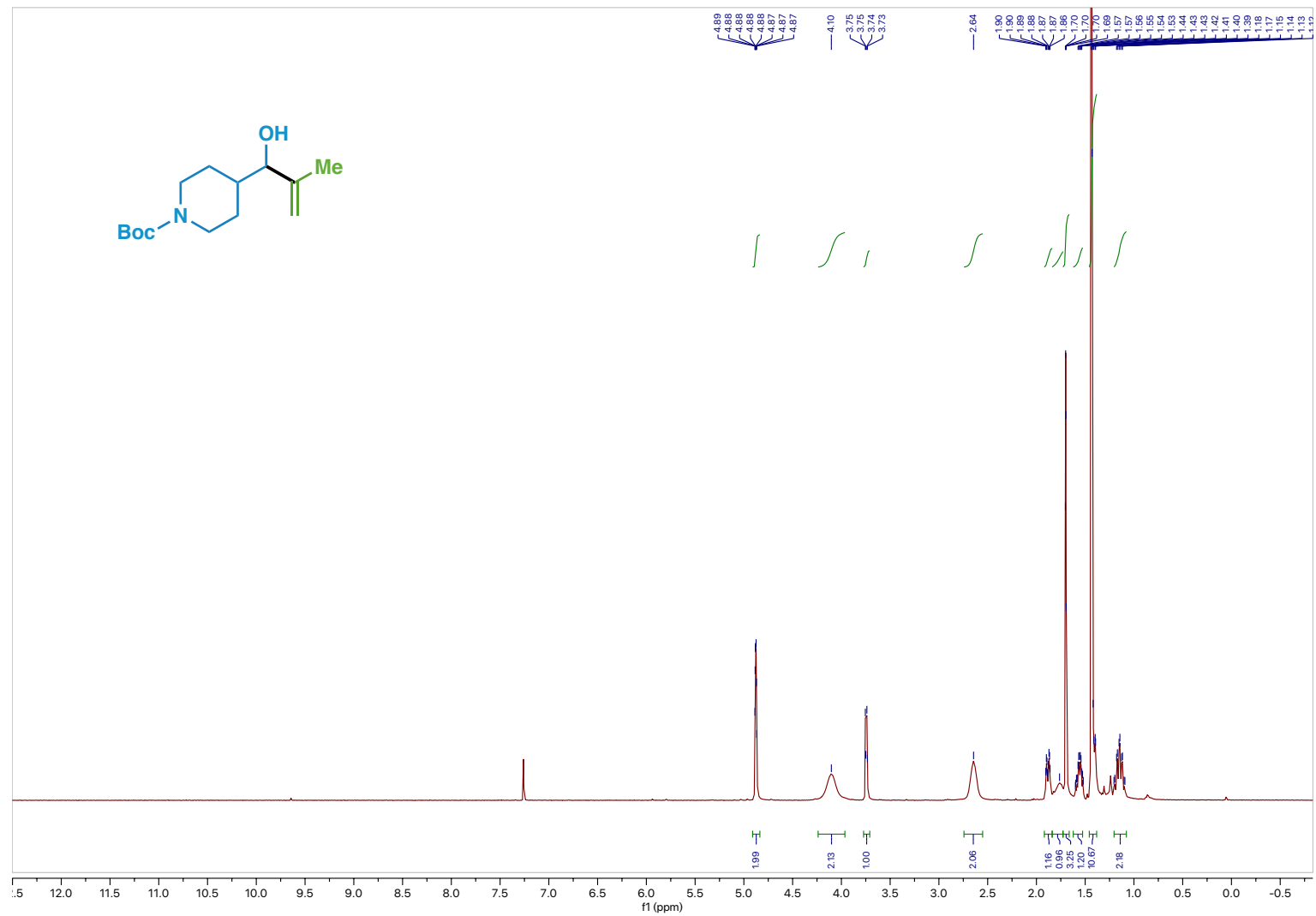
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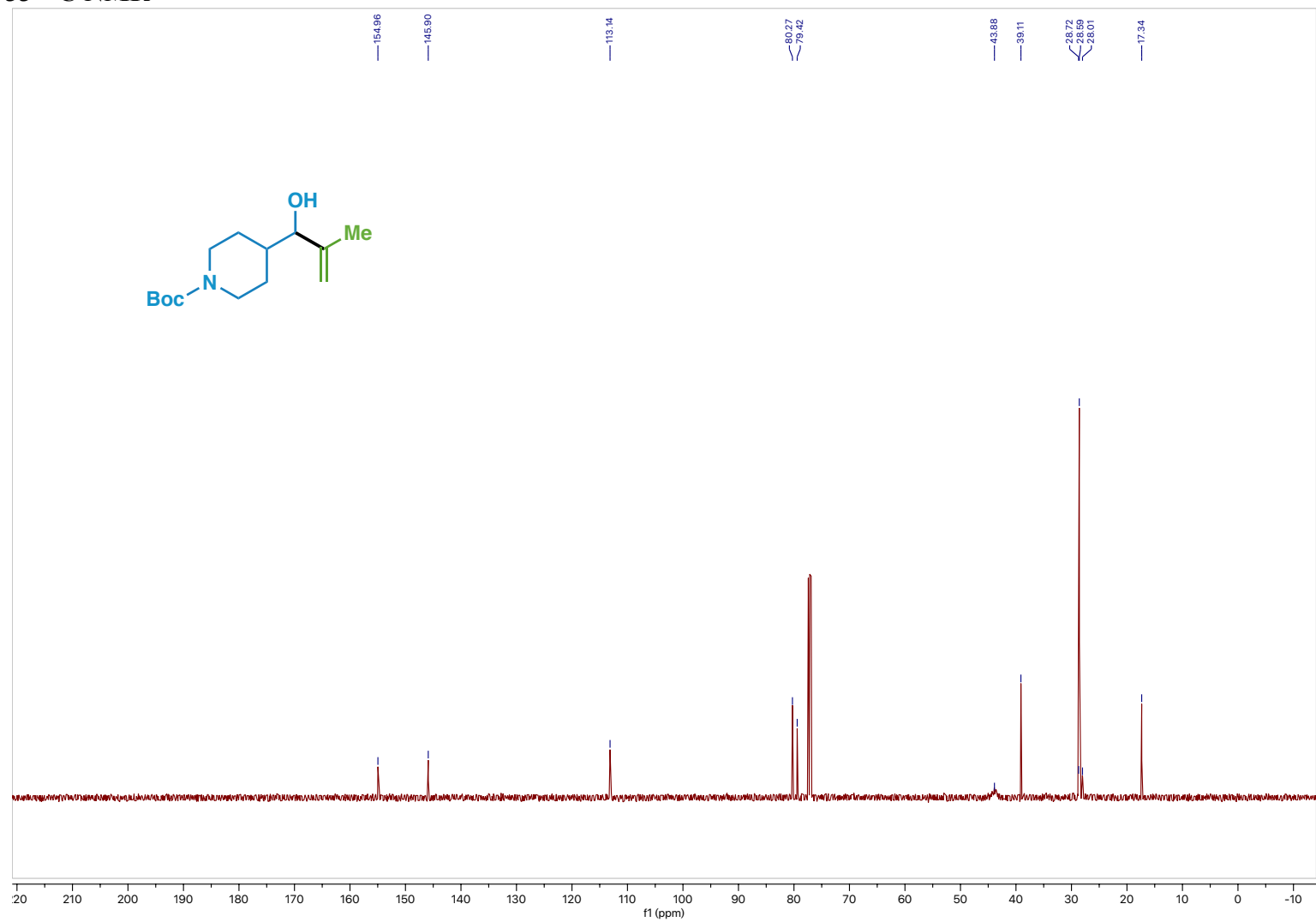
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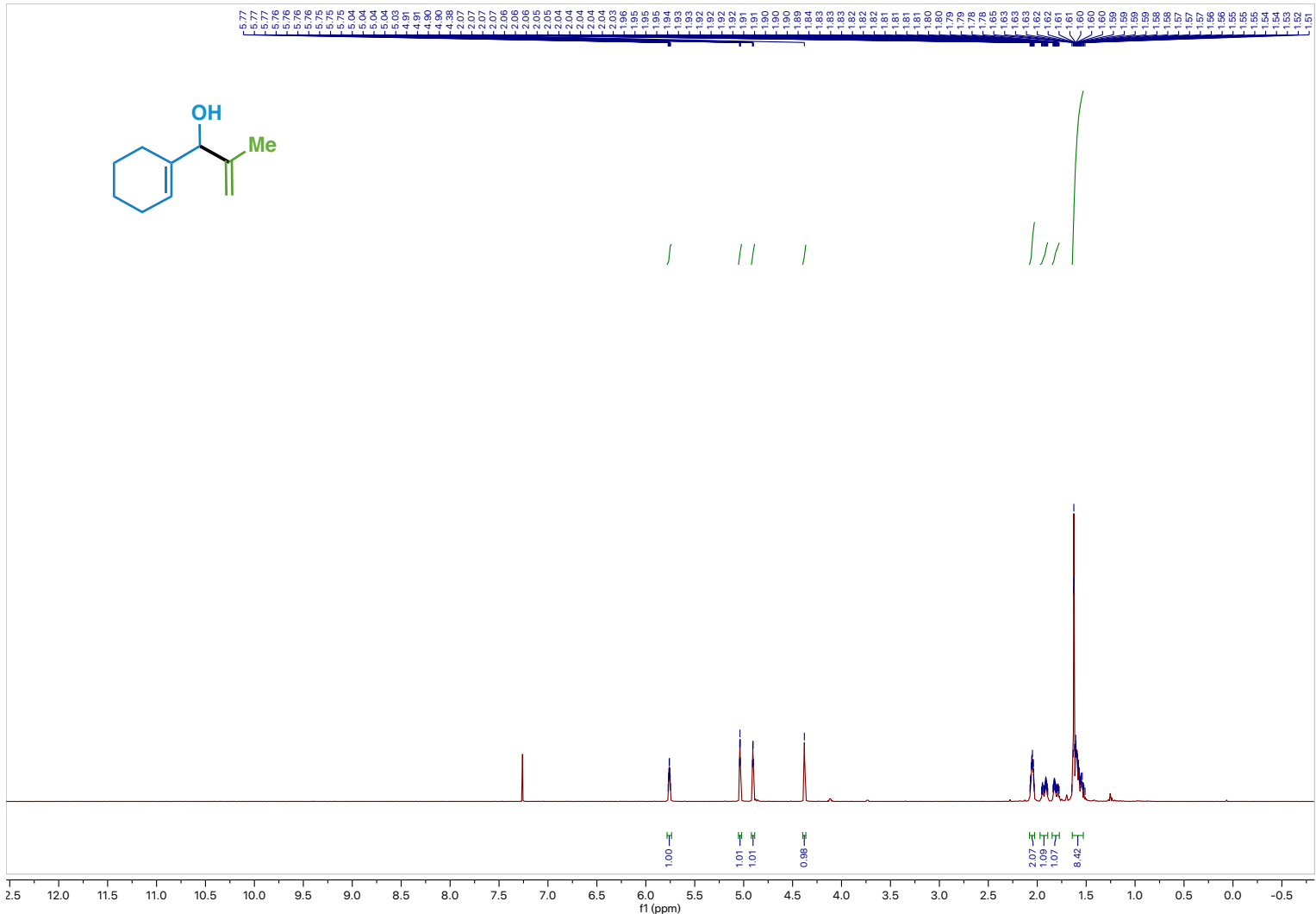
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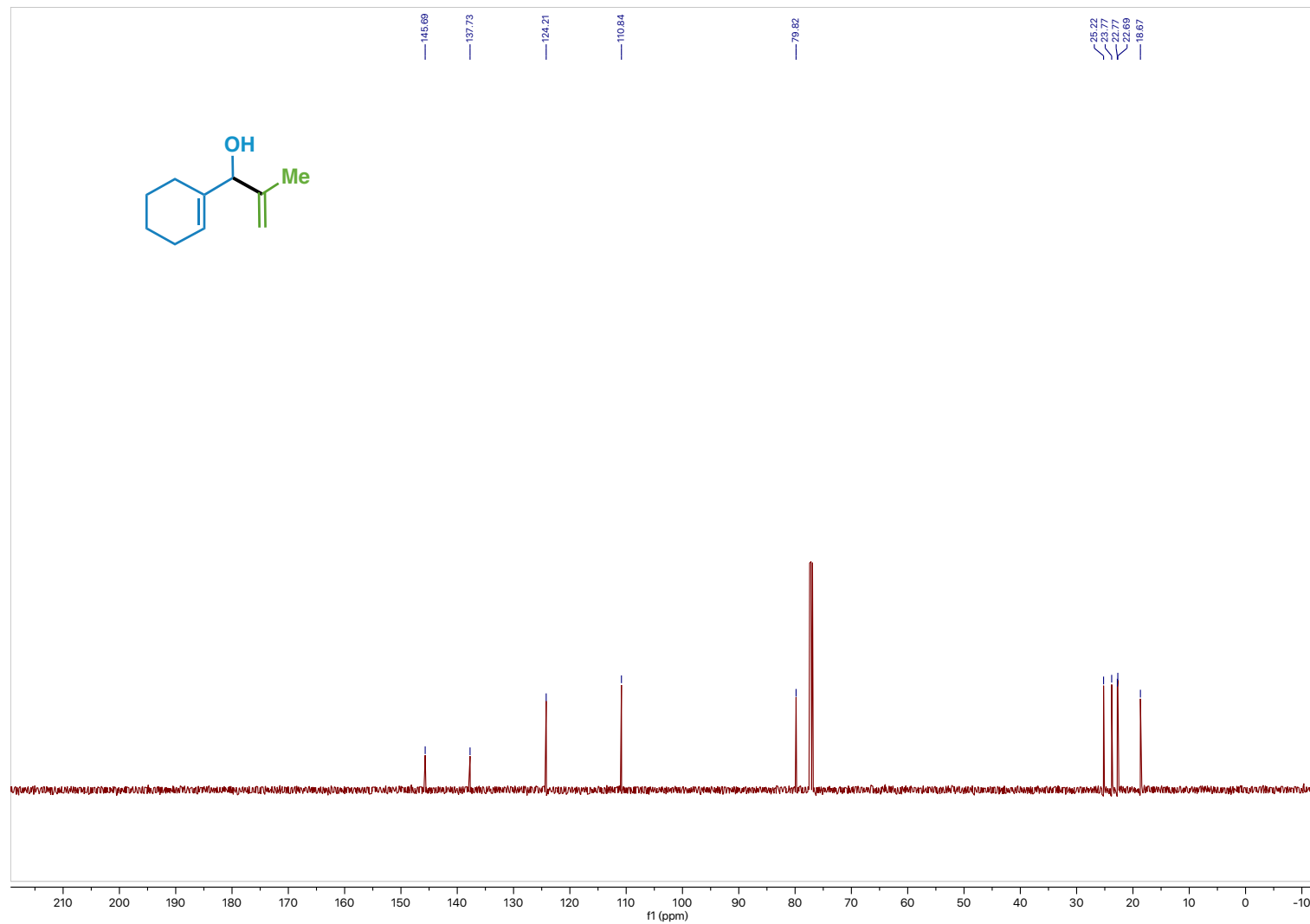
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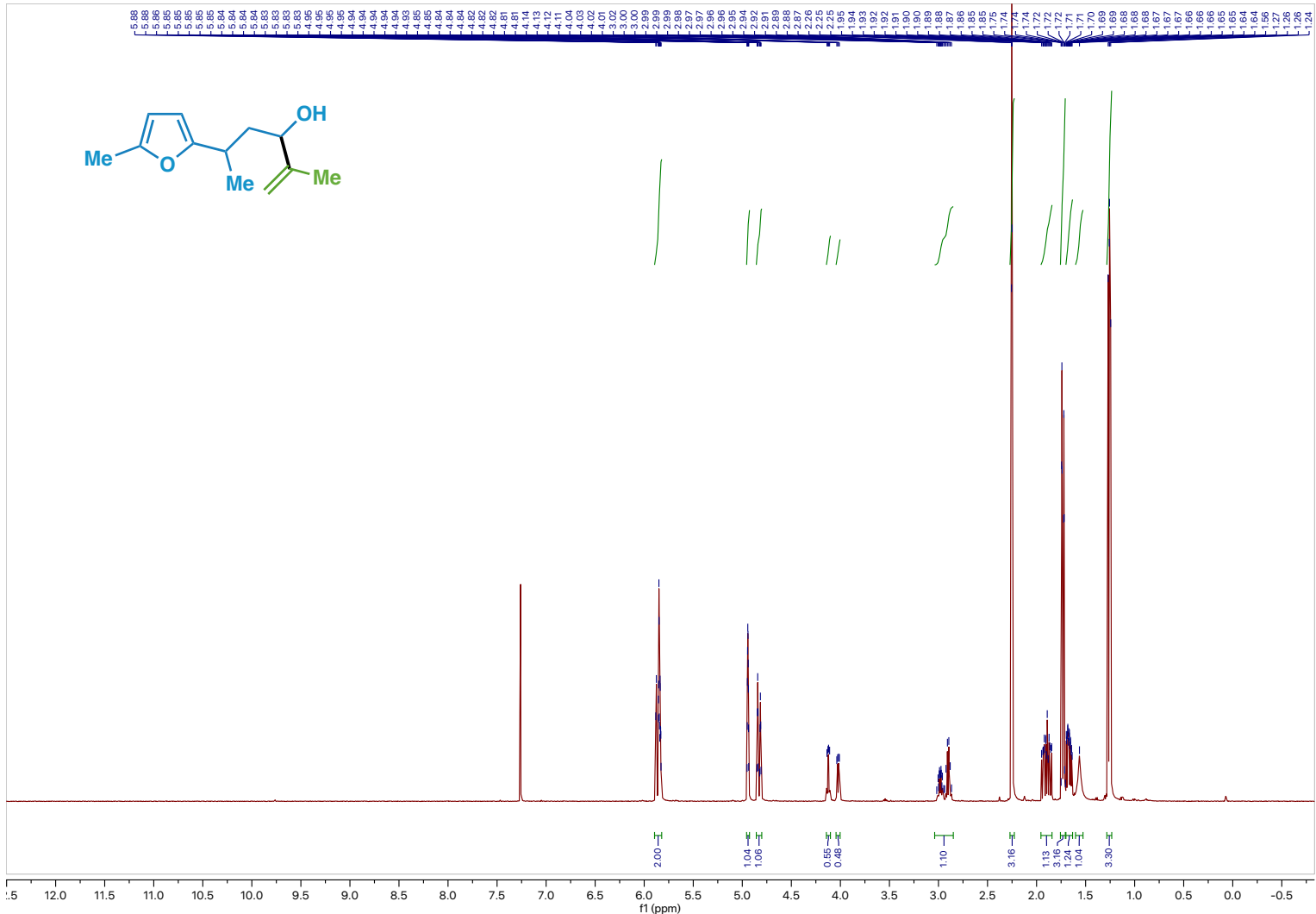
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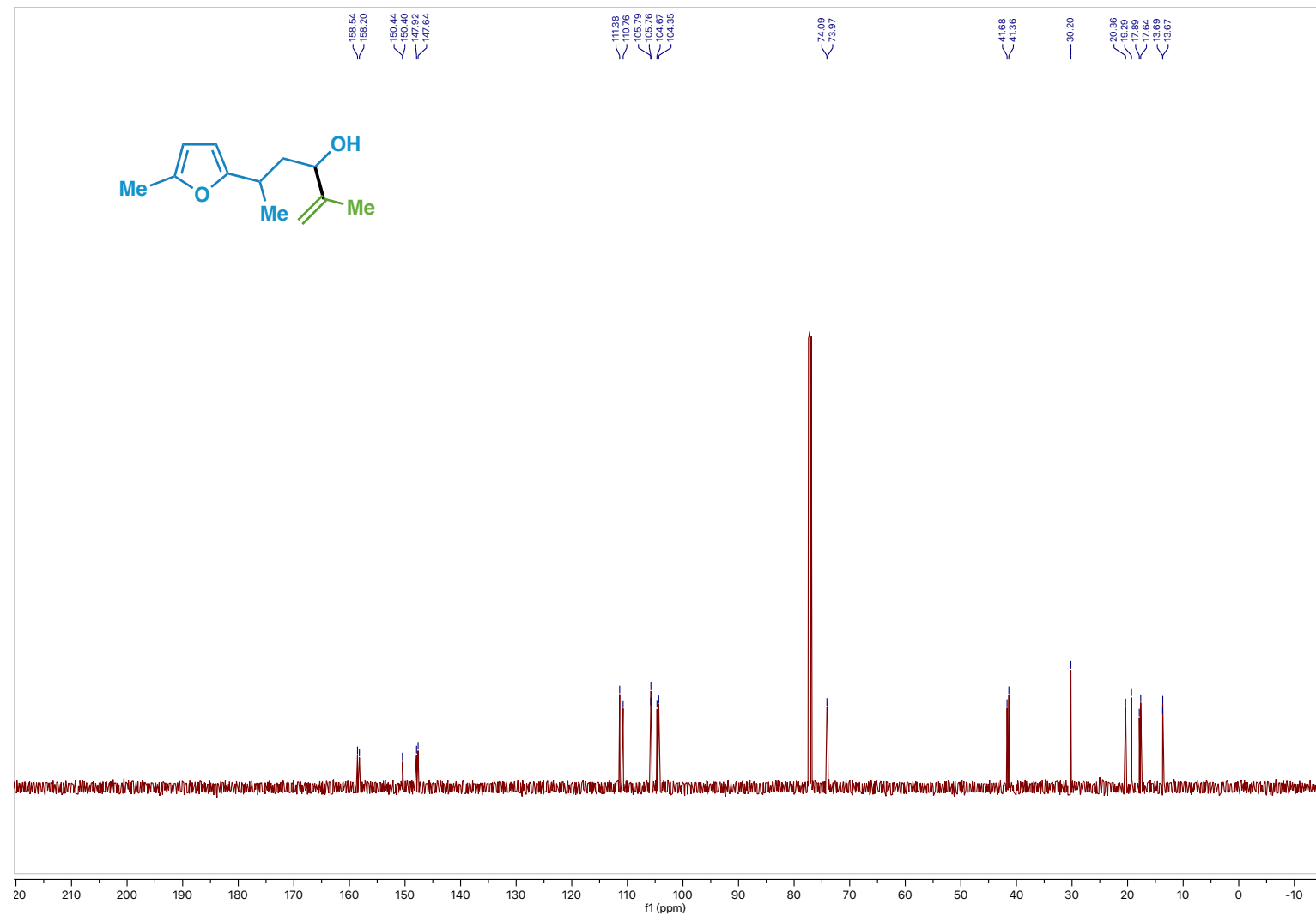
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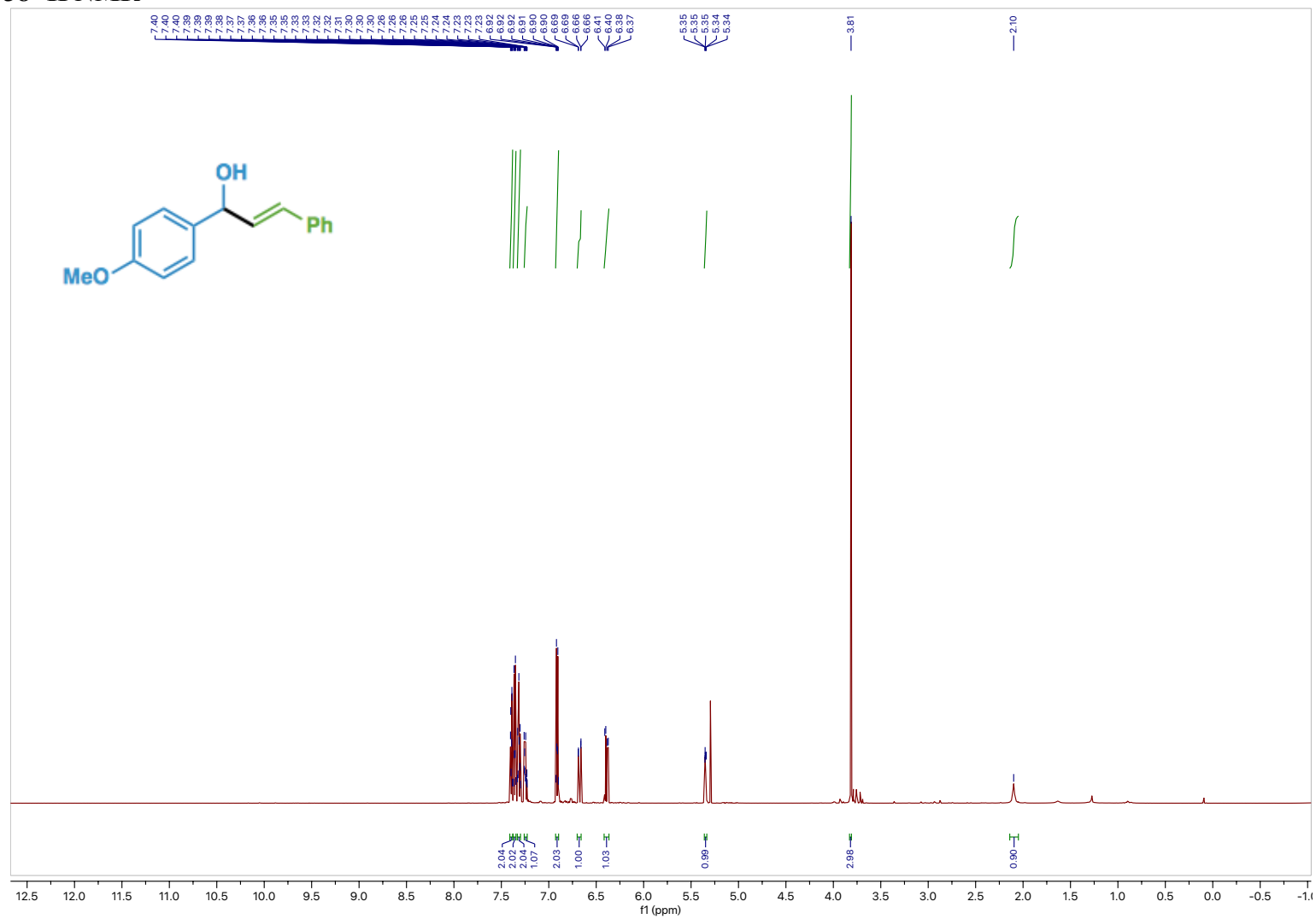
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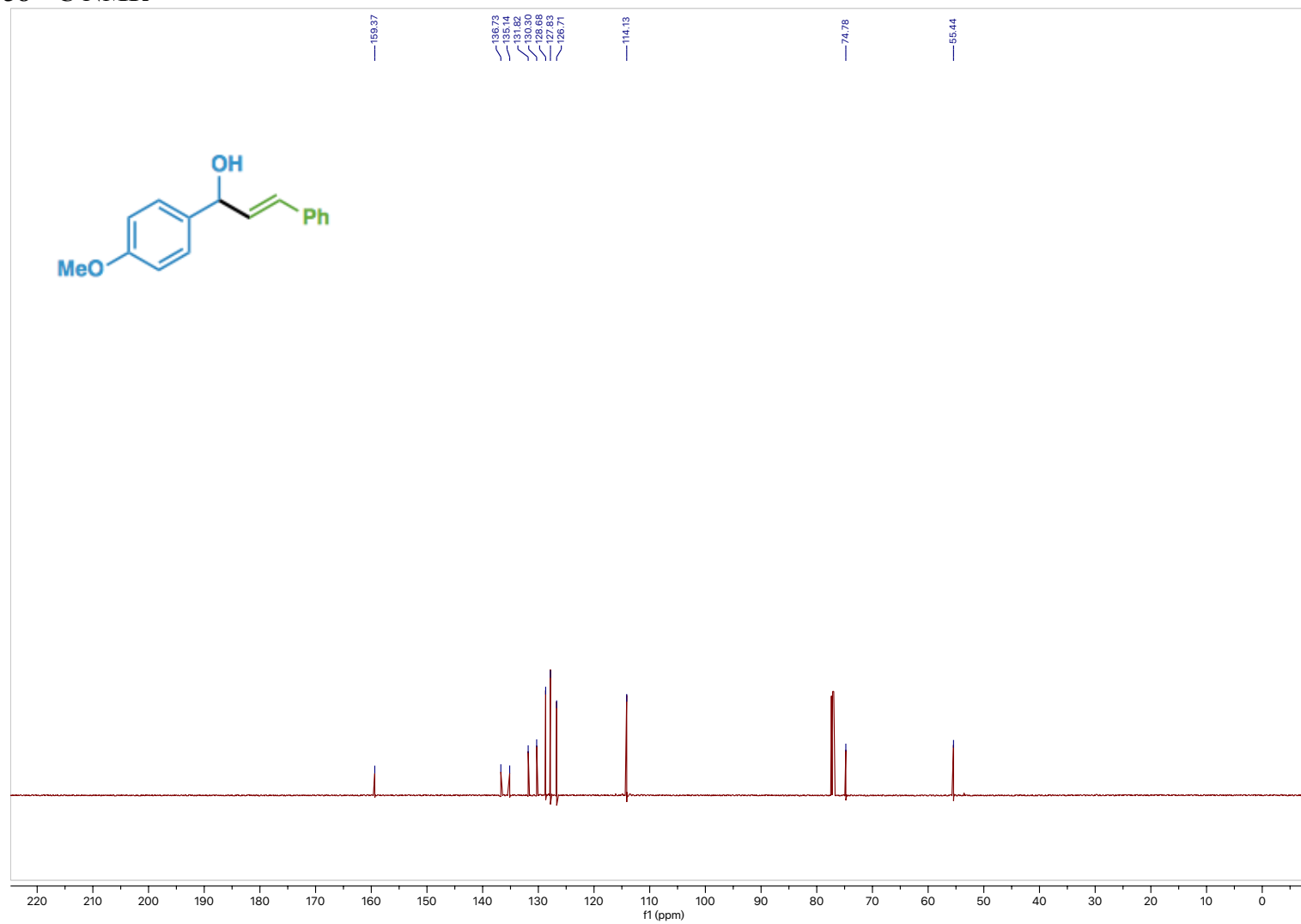
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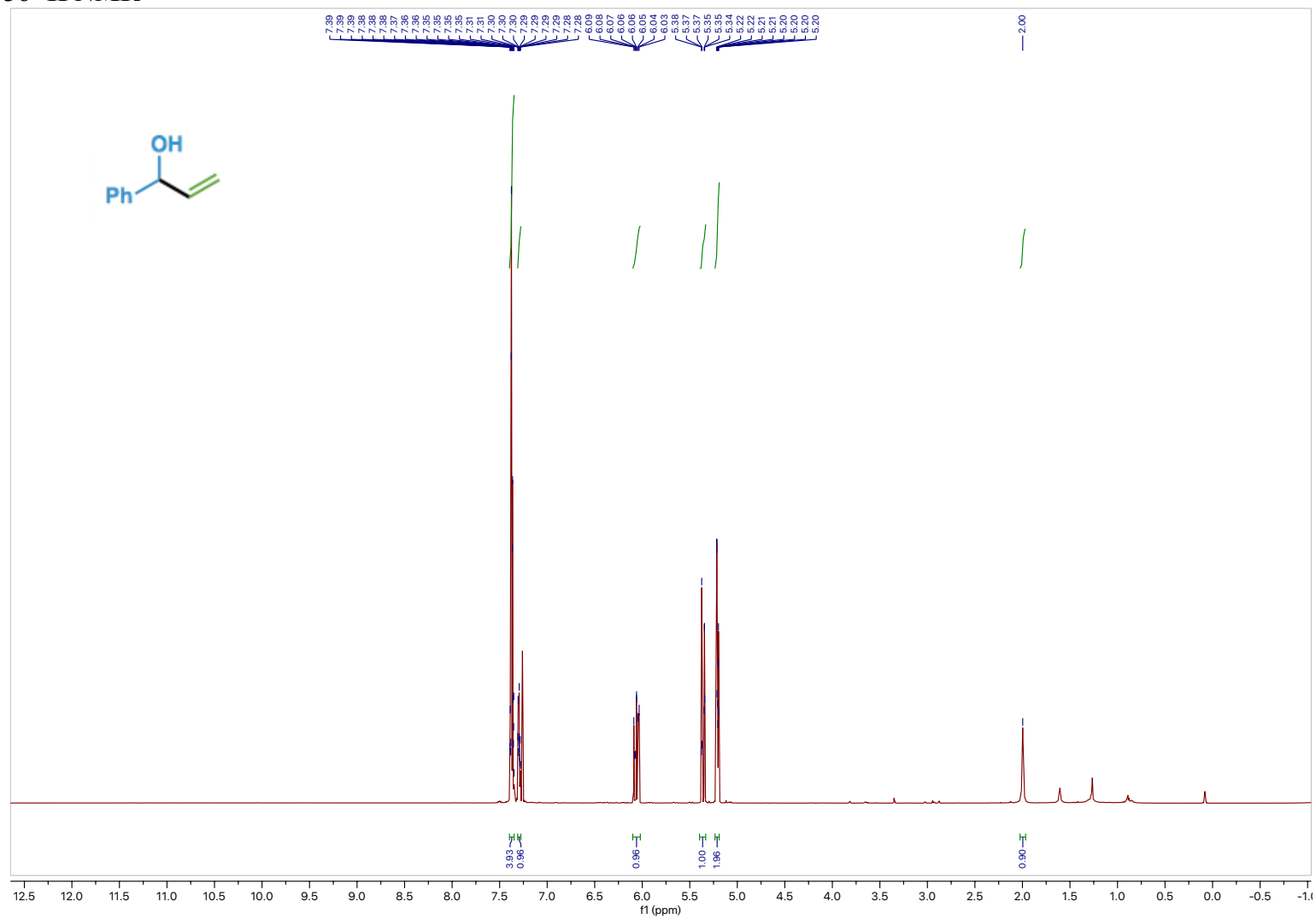
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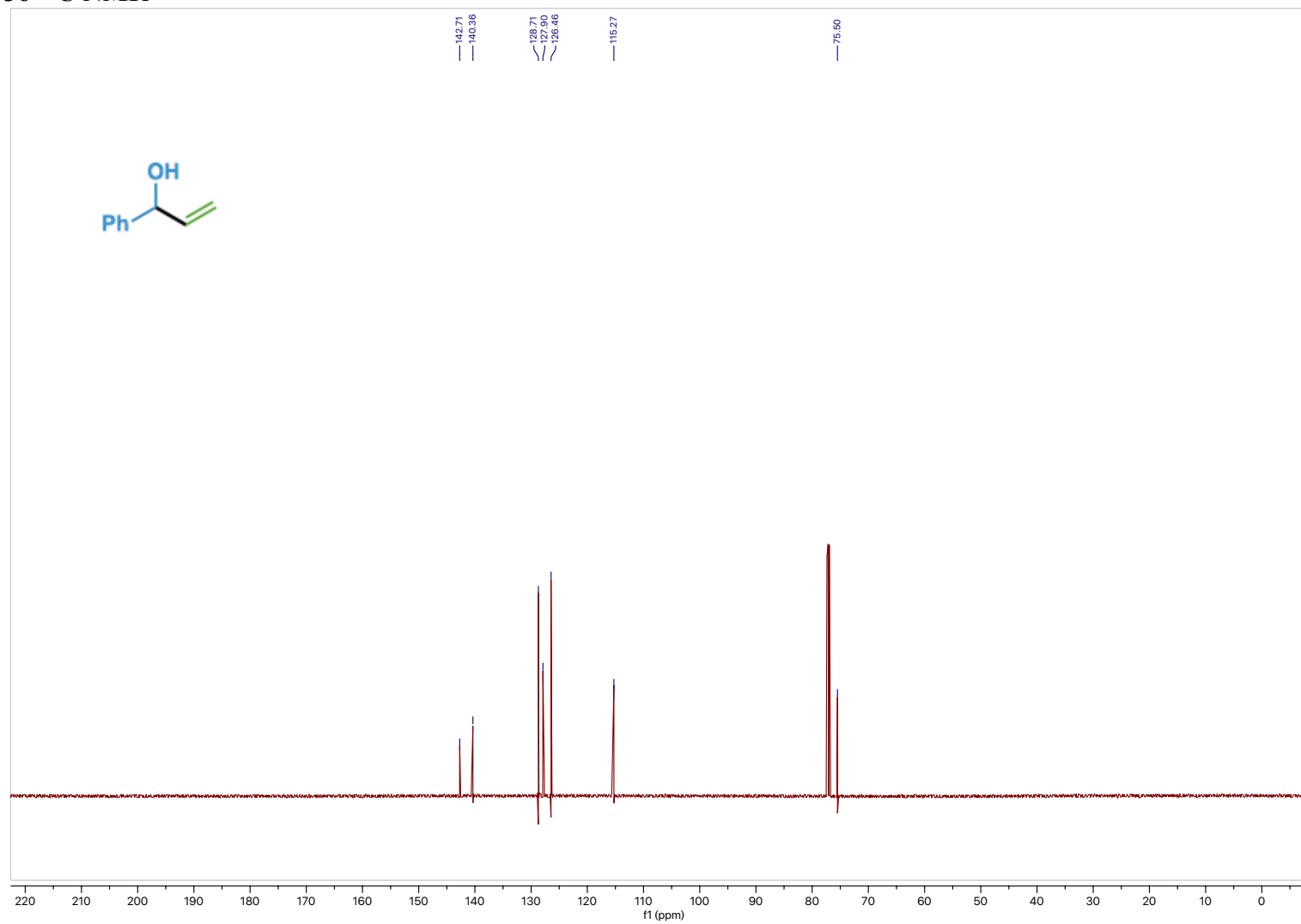
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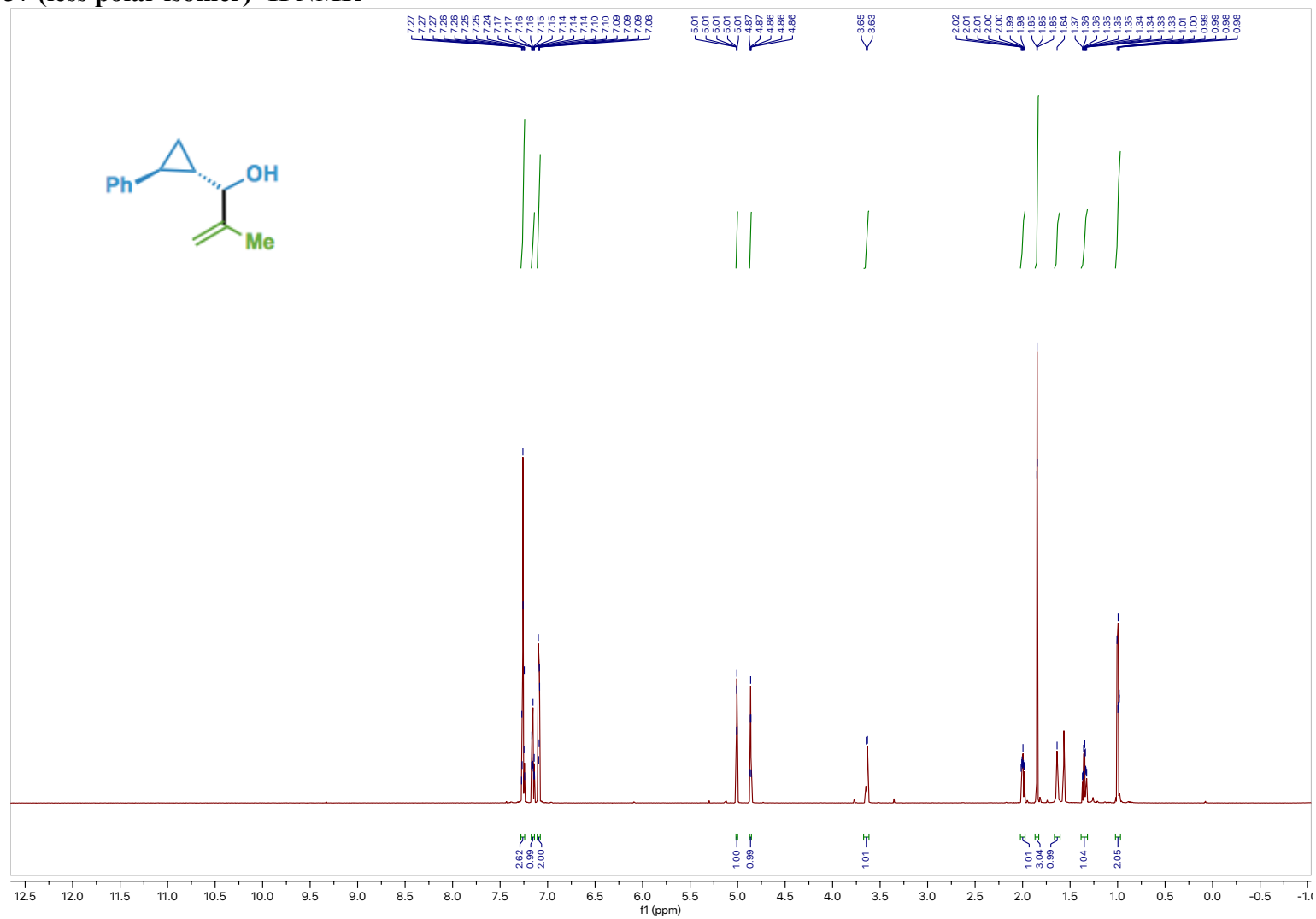
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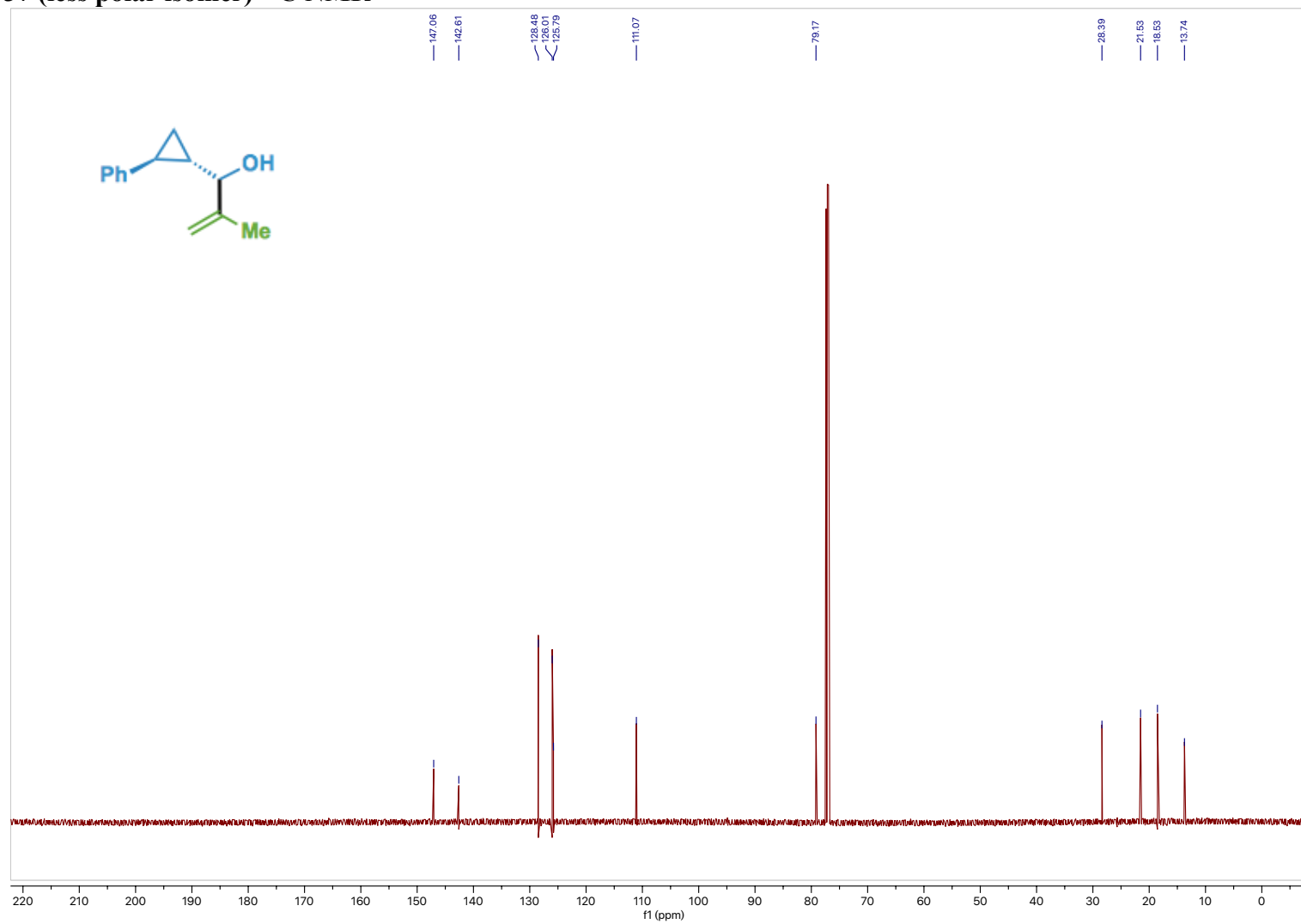
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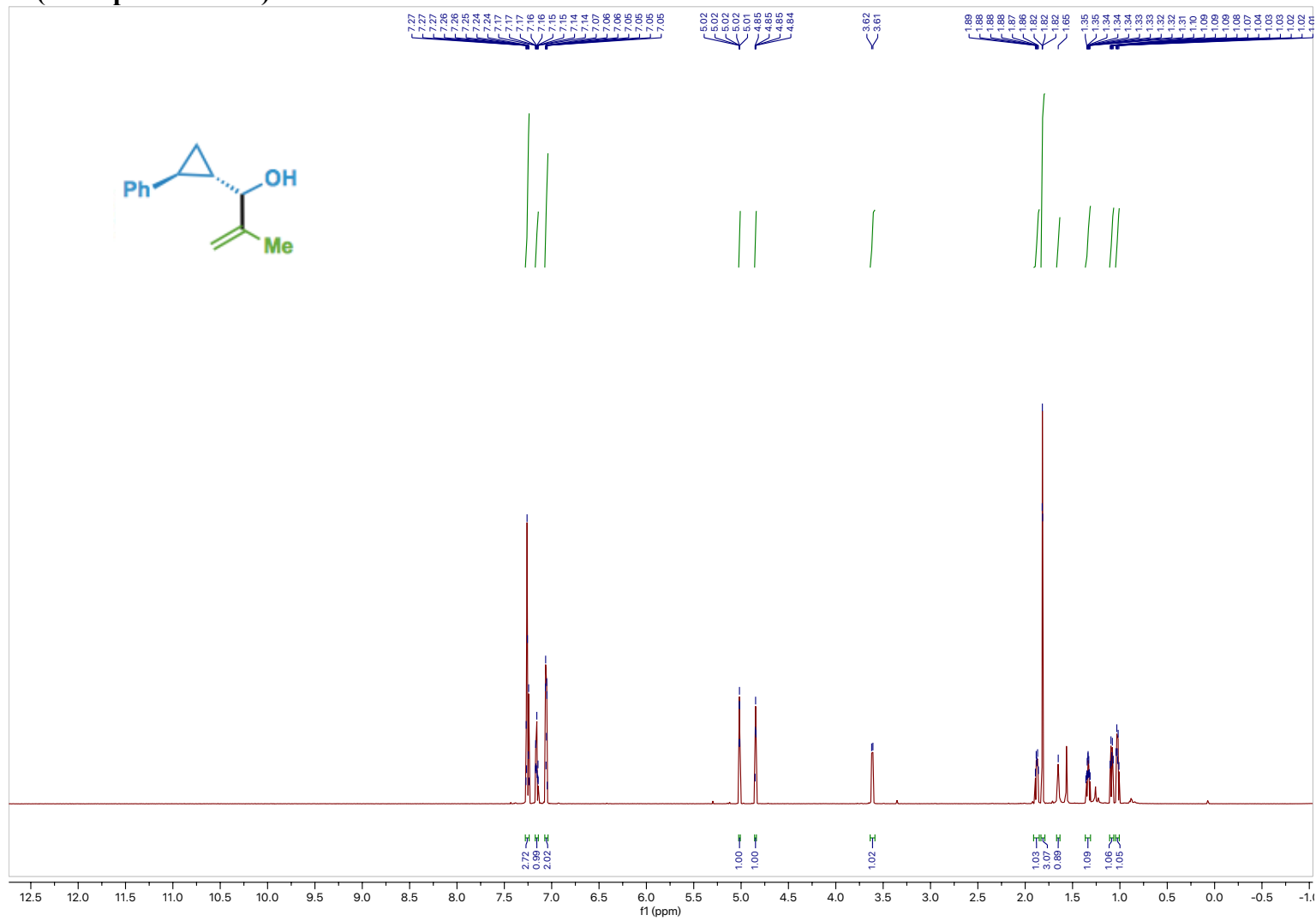
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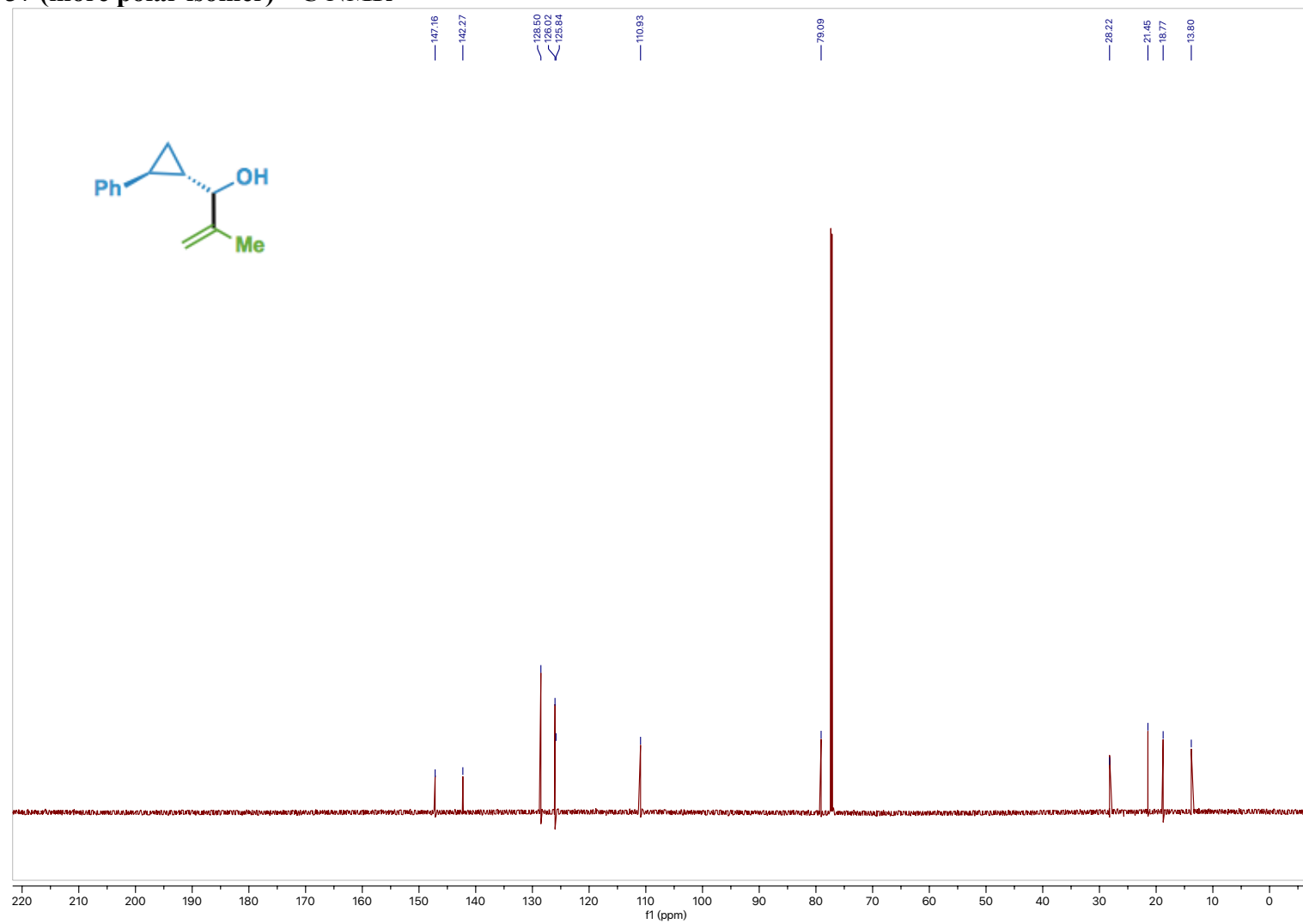
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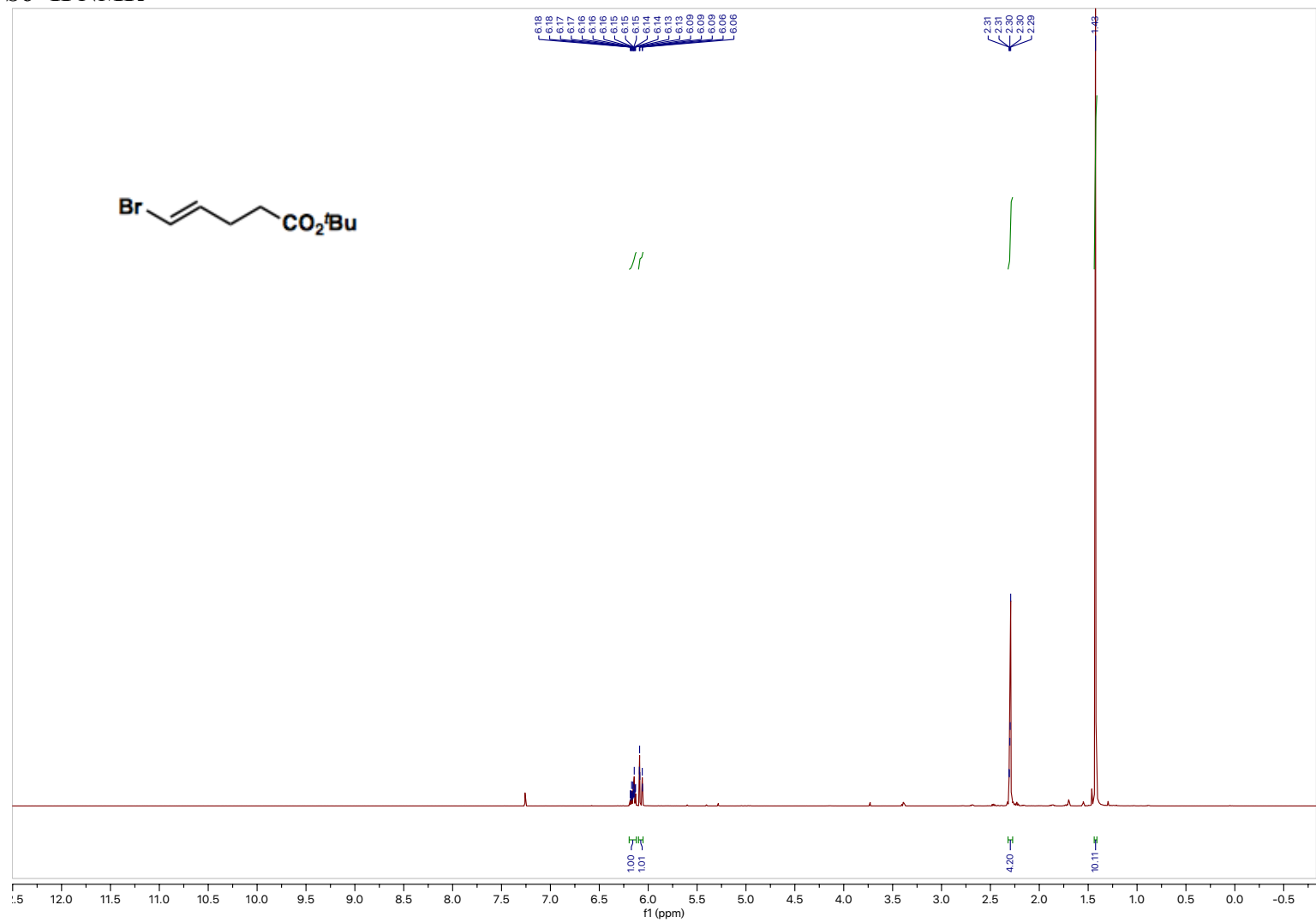
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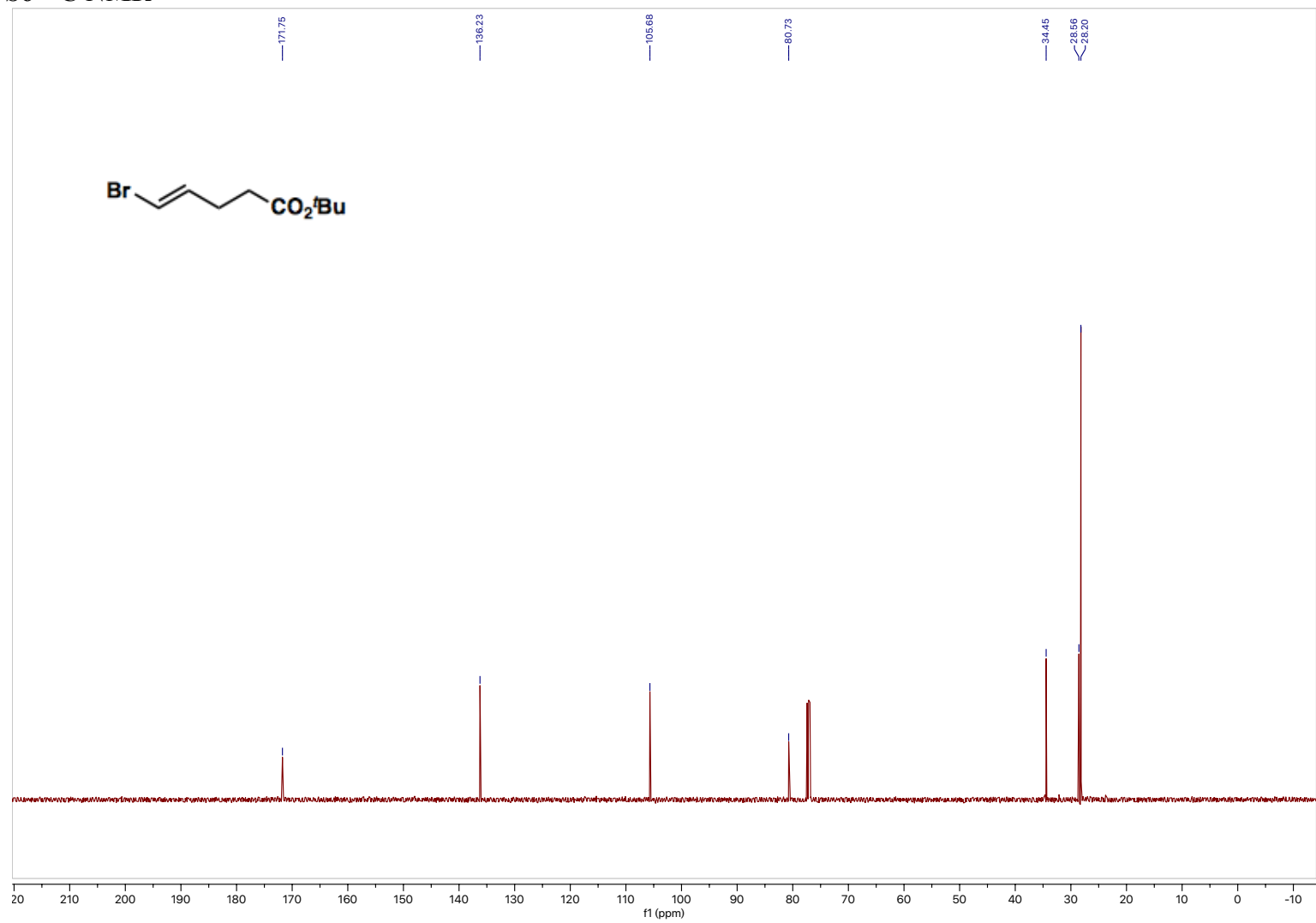
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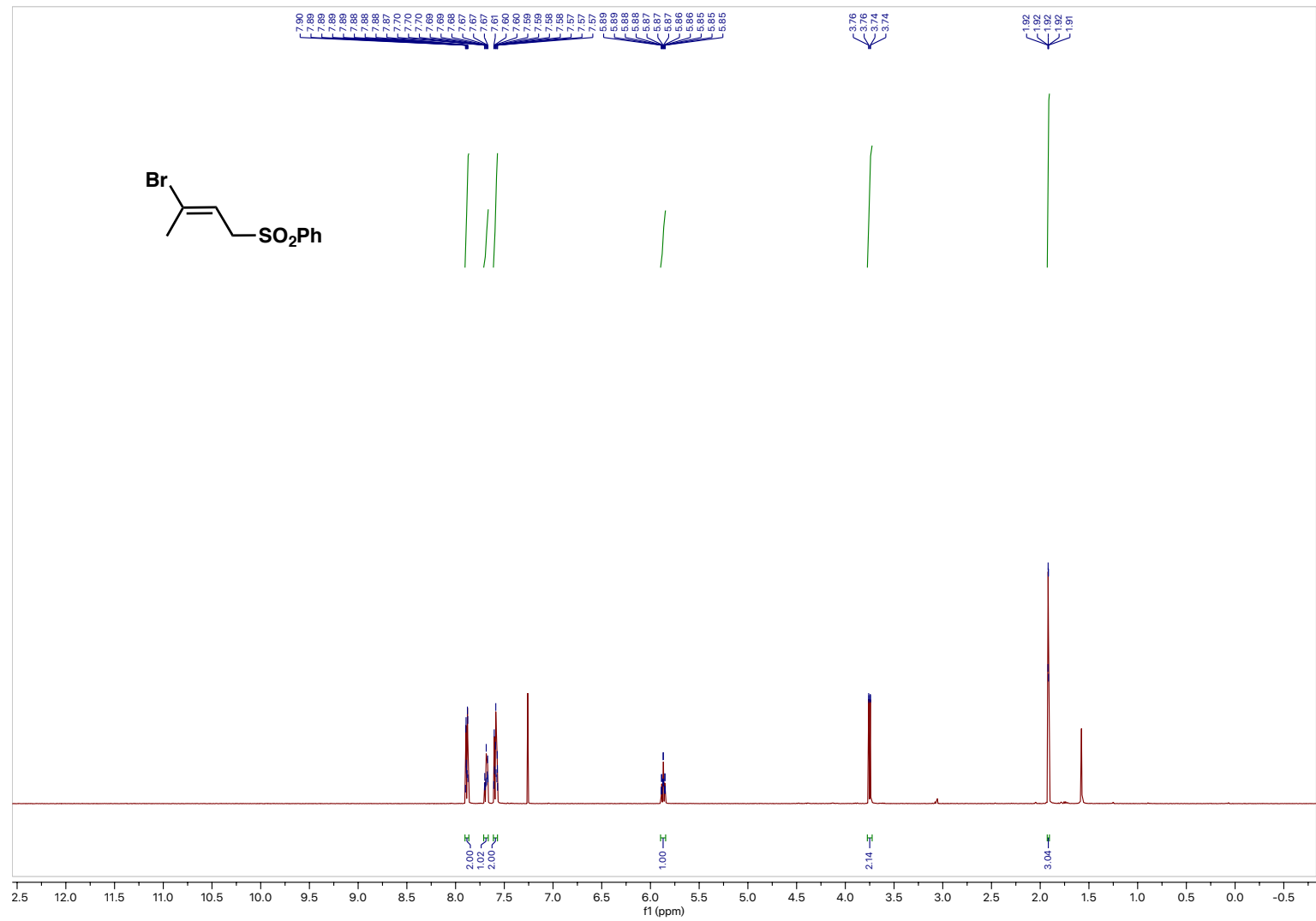
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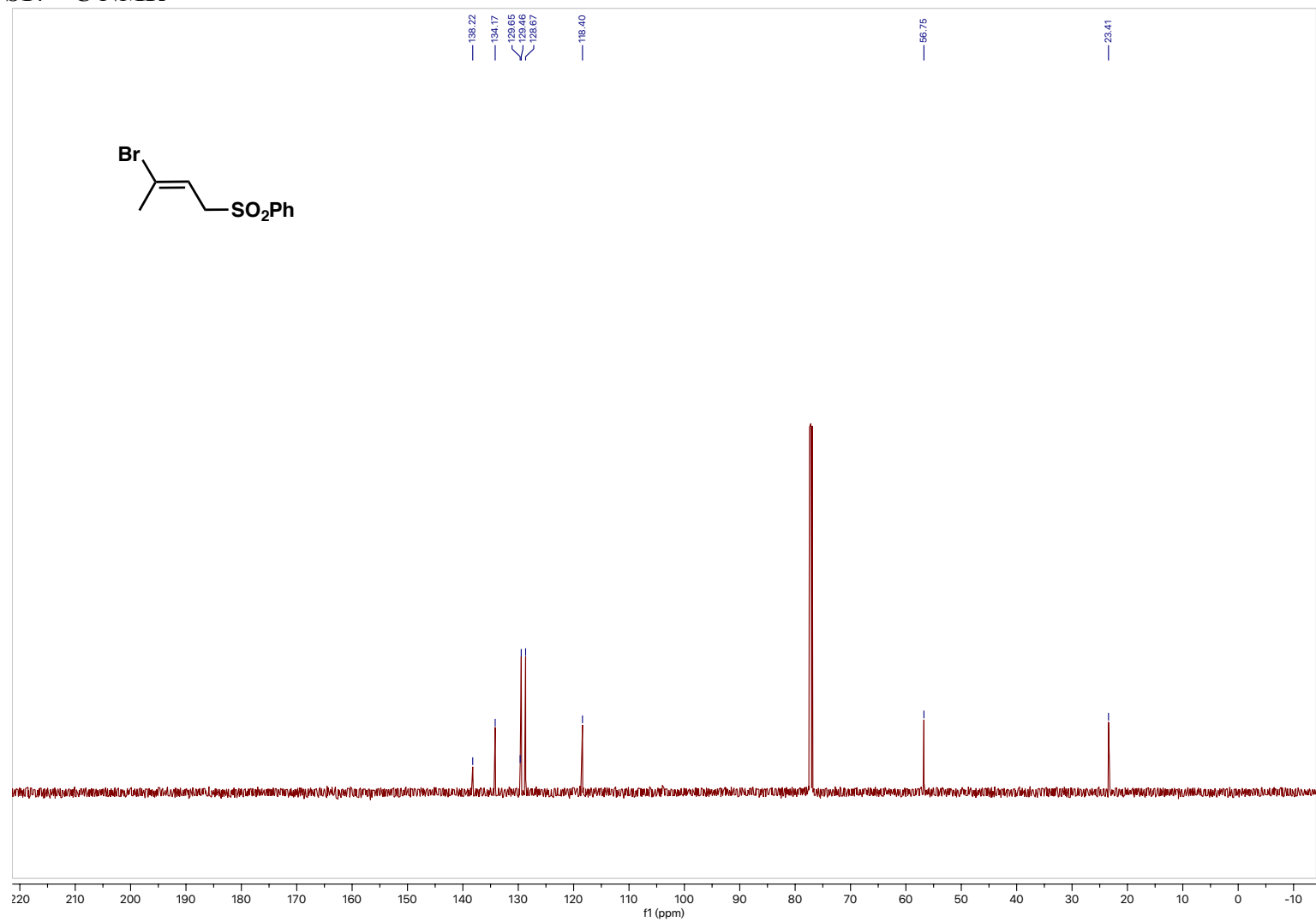
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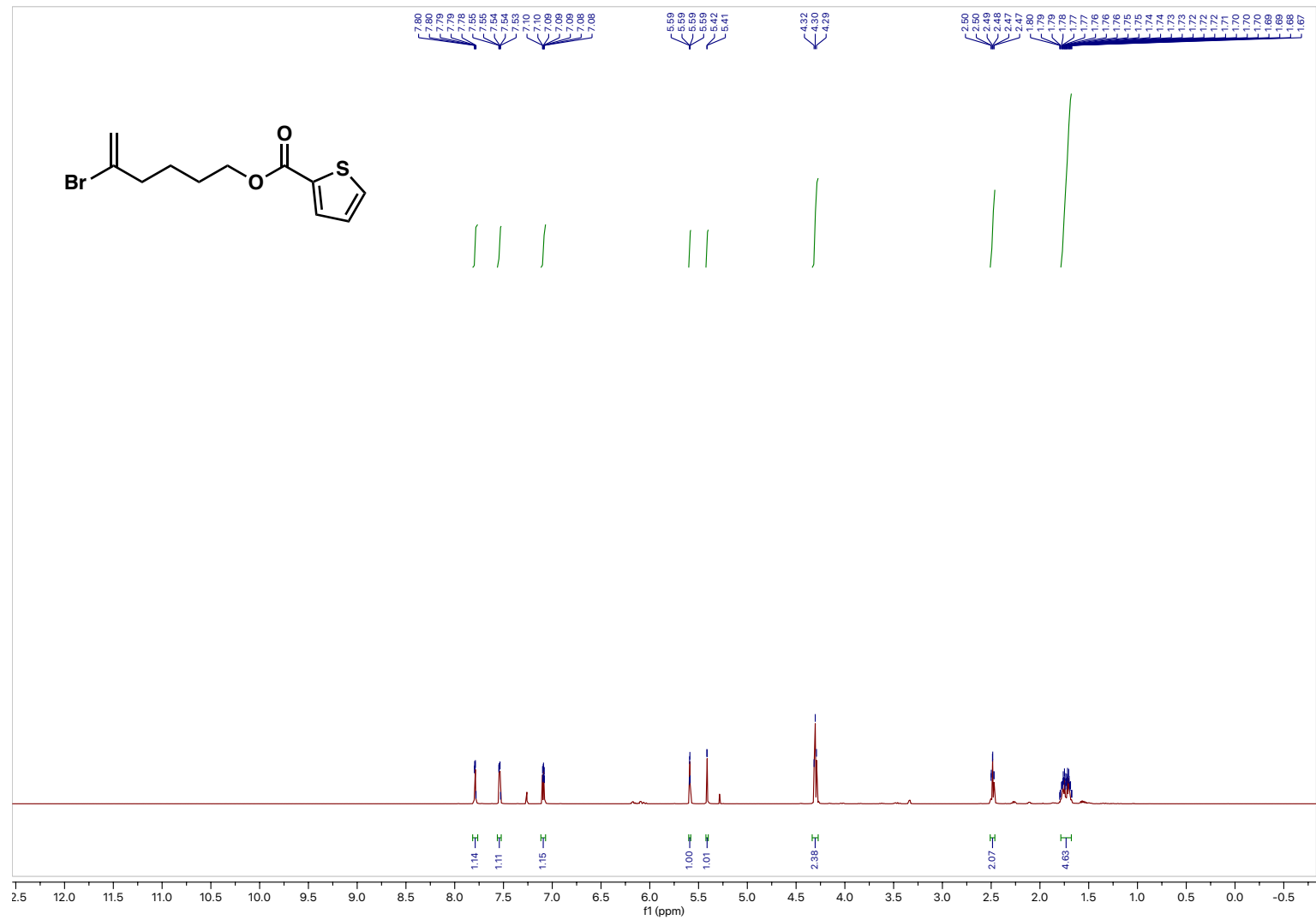
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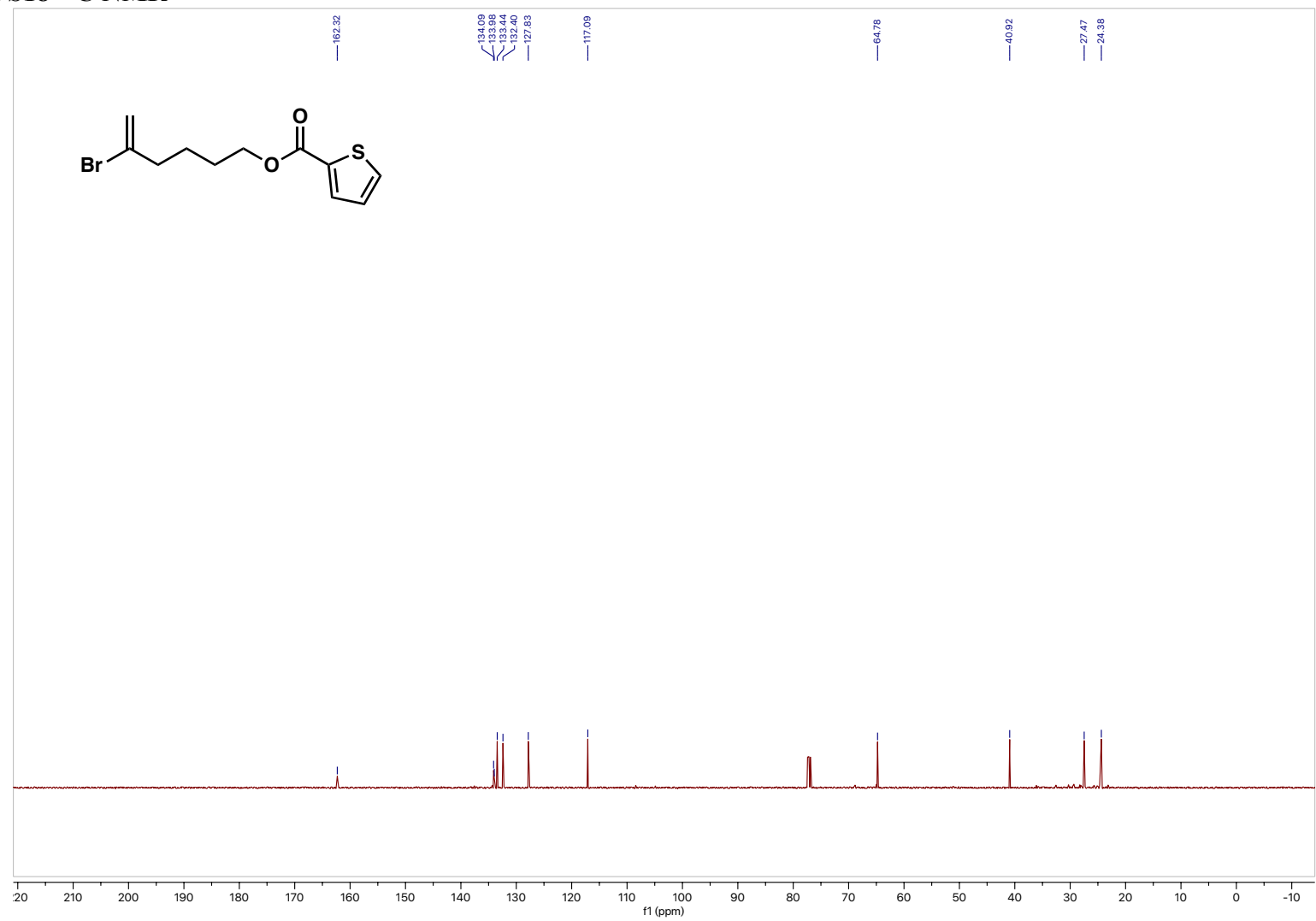
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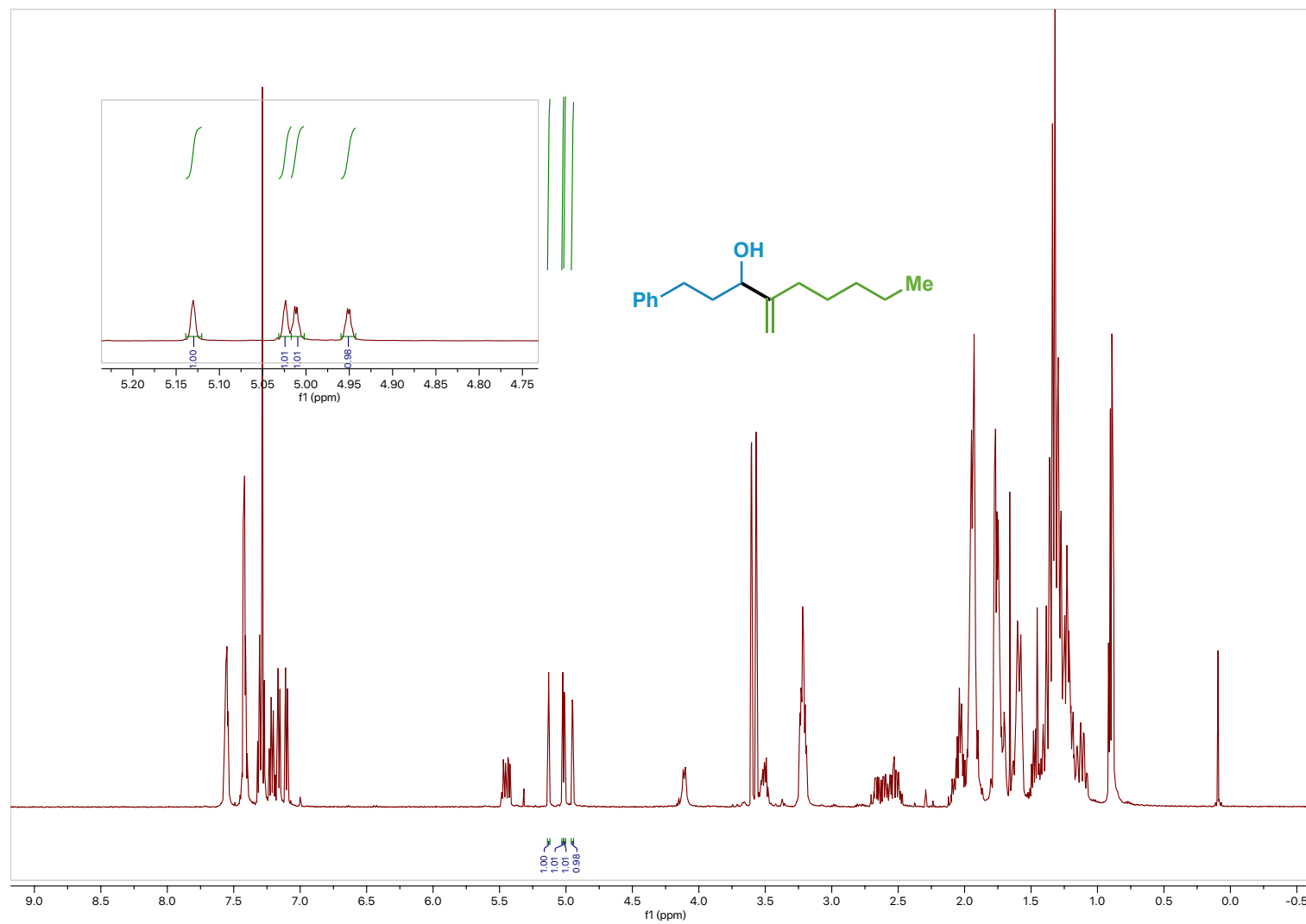
Compound S18 ¹H NMR



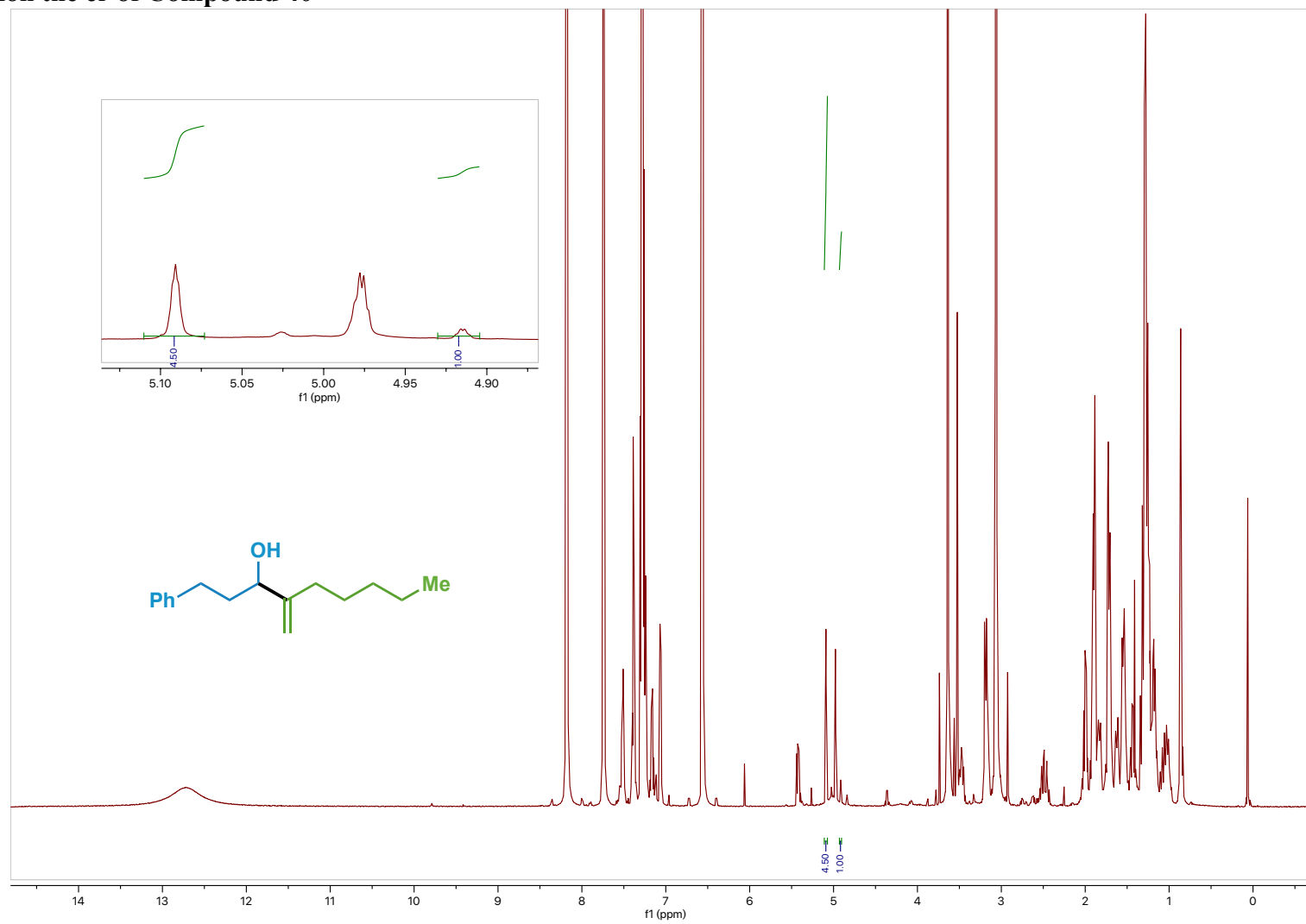
Compound S18 ¹³C NMR



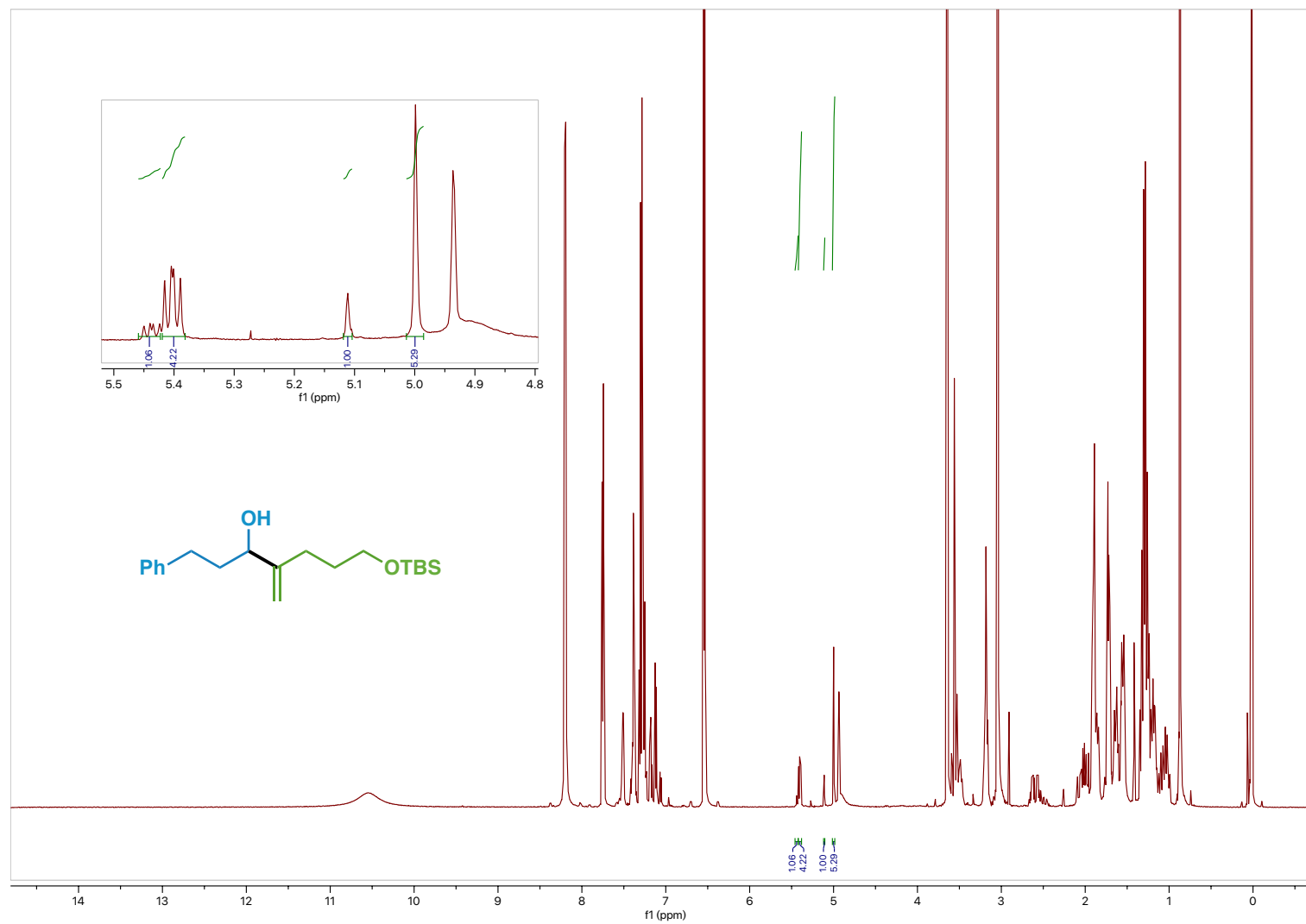
Determination the er of Compound 40 (from racemic 40)



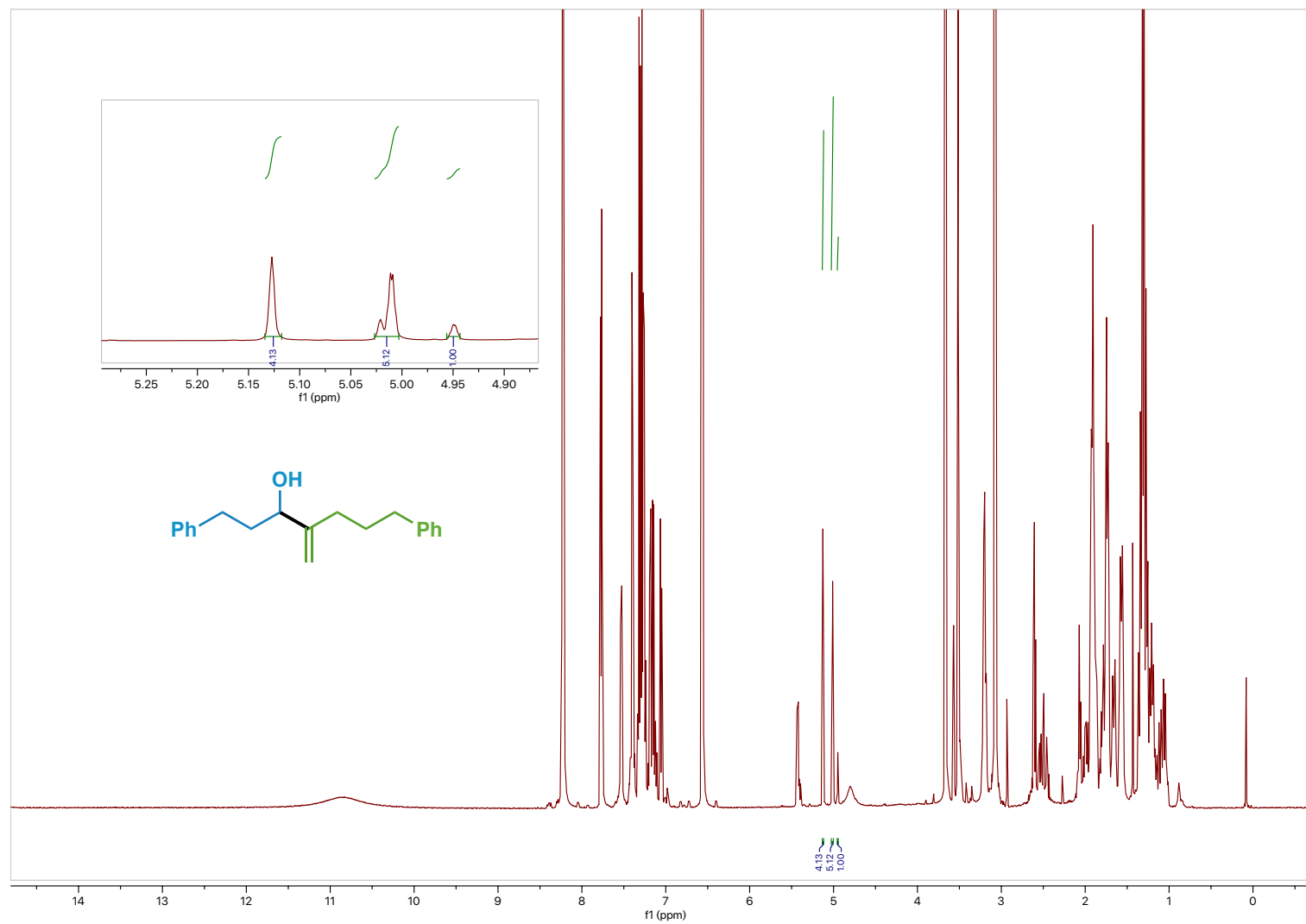
Determination the er of Compound 40



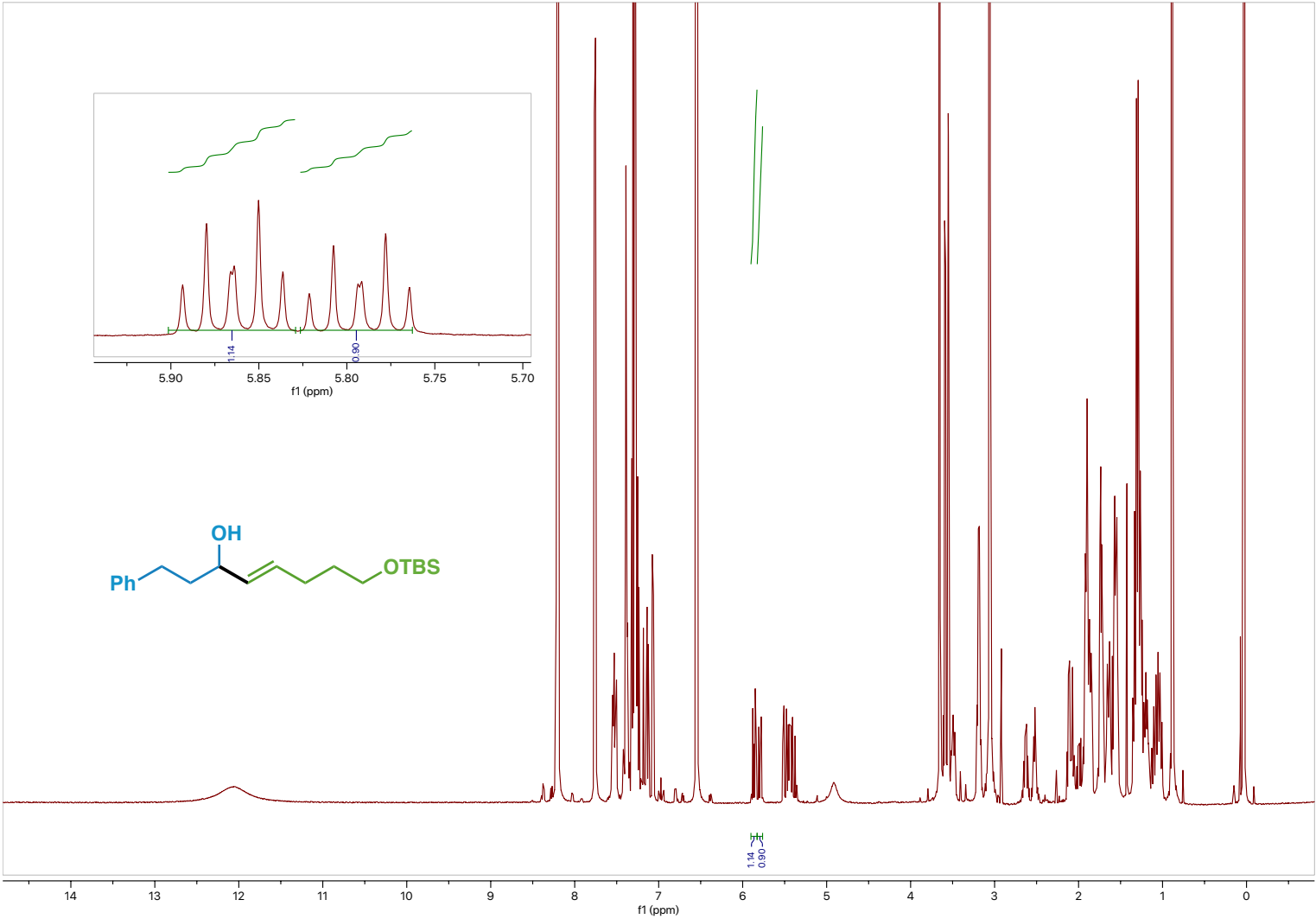
Determination the er of Compound 41



Determination the er of Compound 42

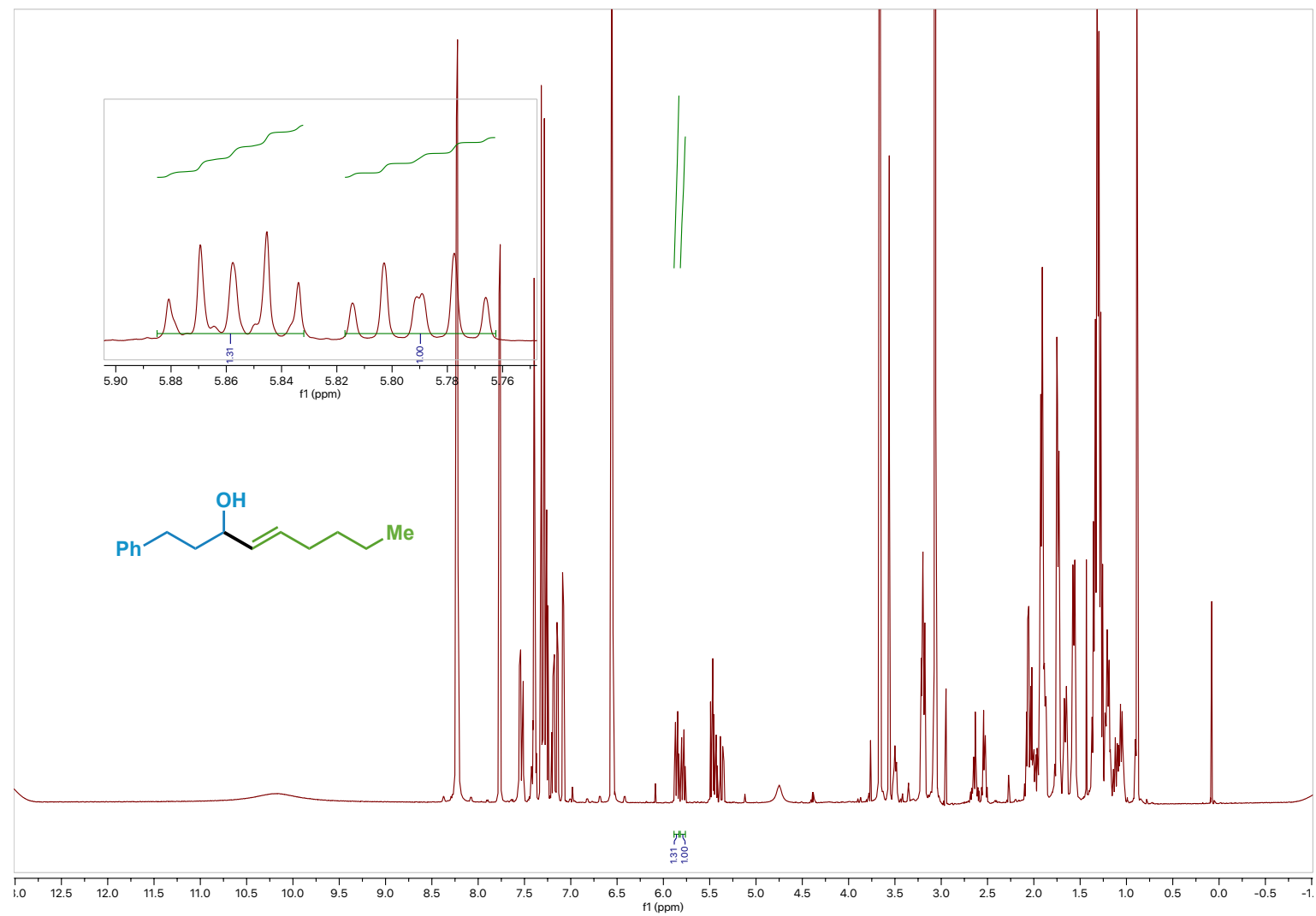


Determination the er of Compound 43

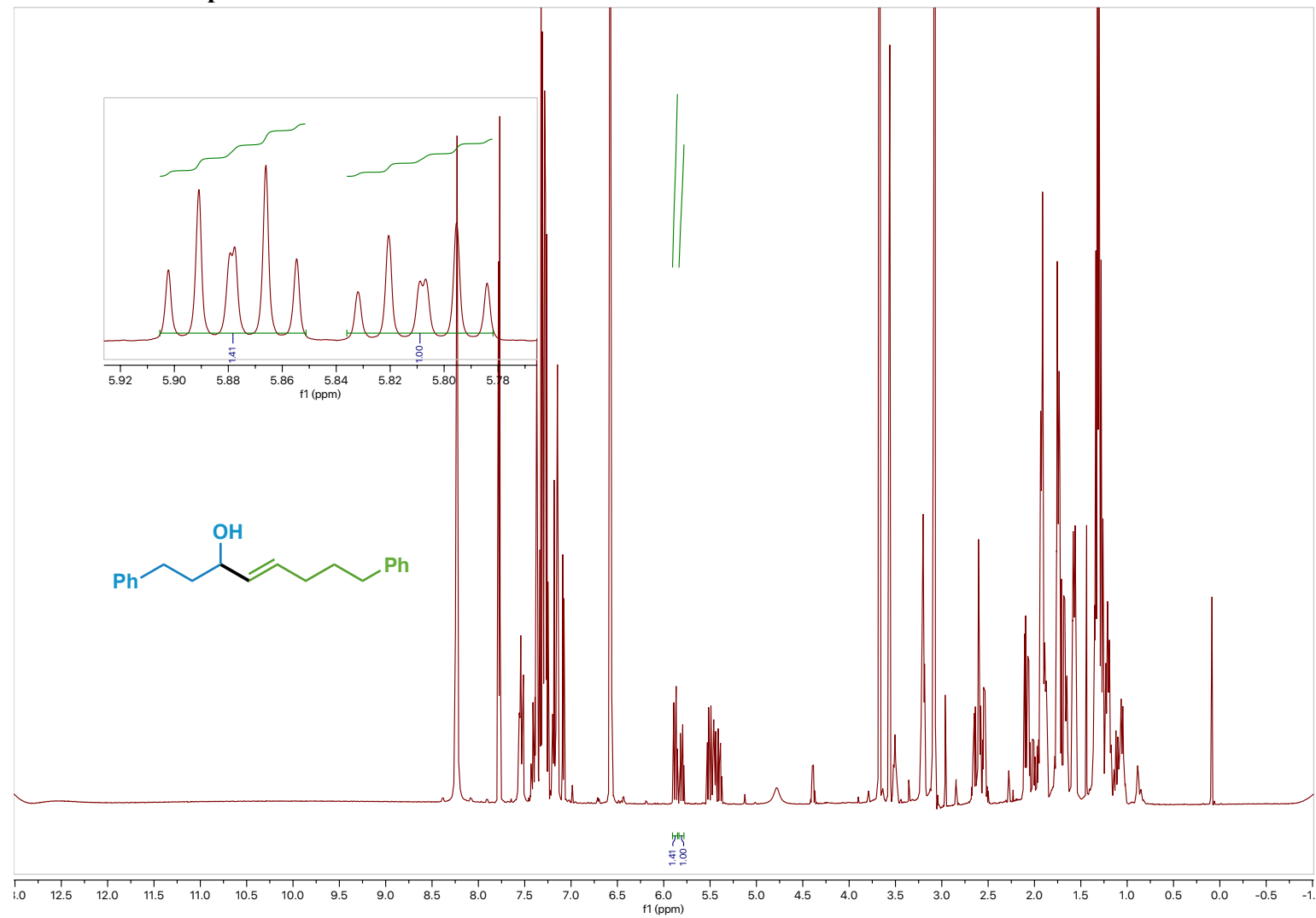


S195

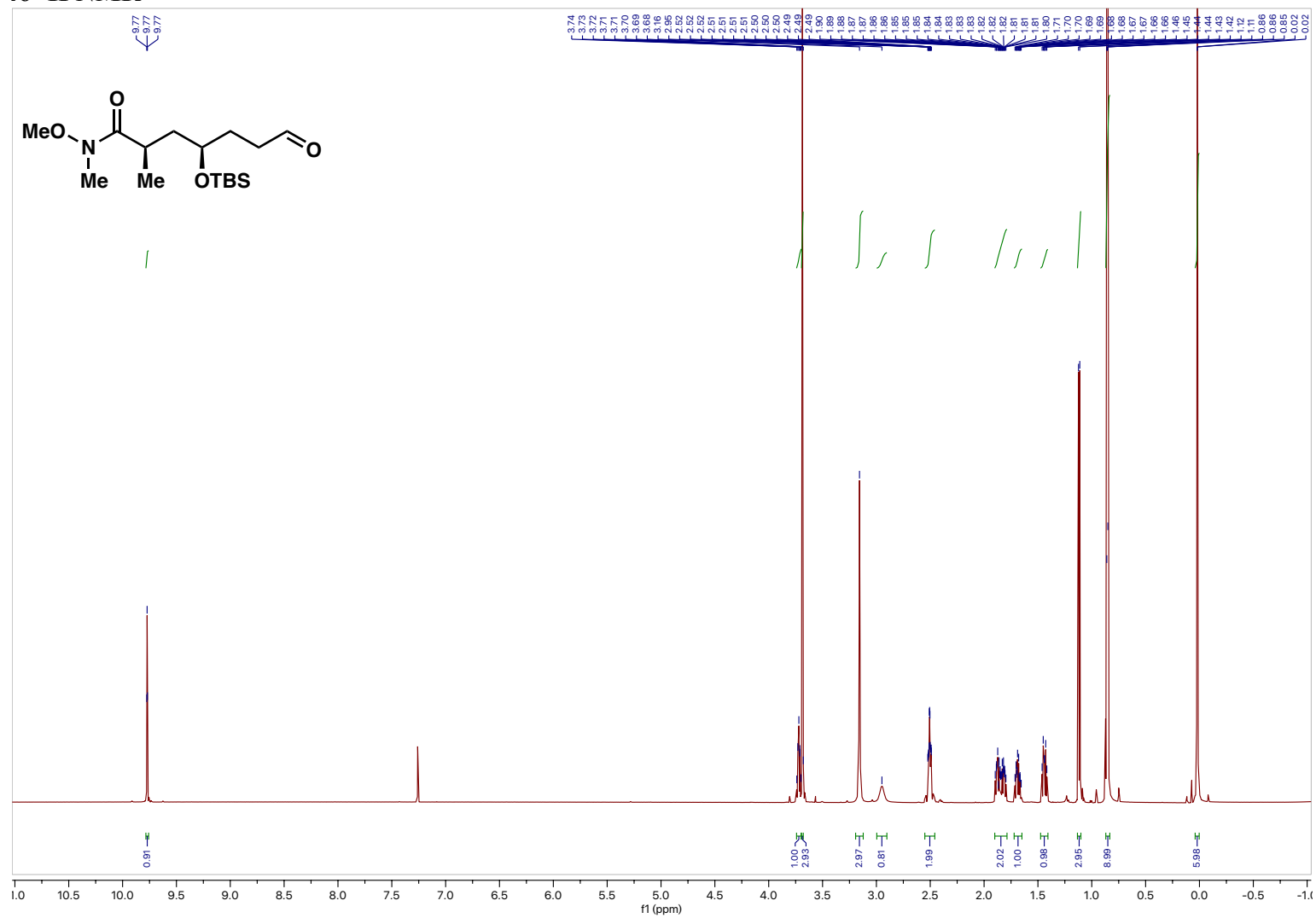
Determination the er of Compound 44



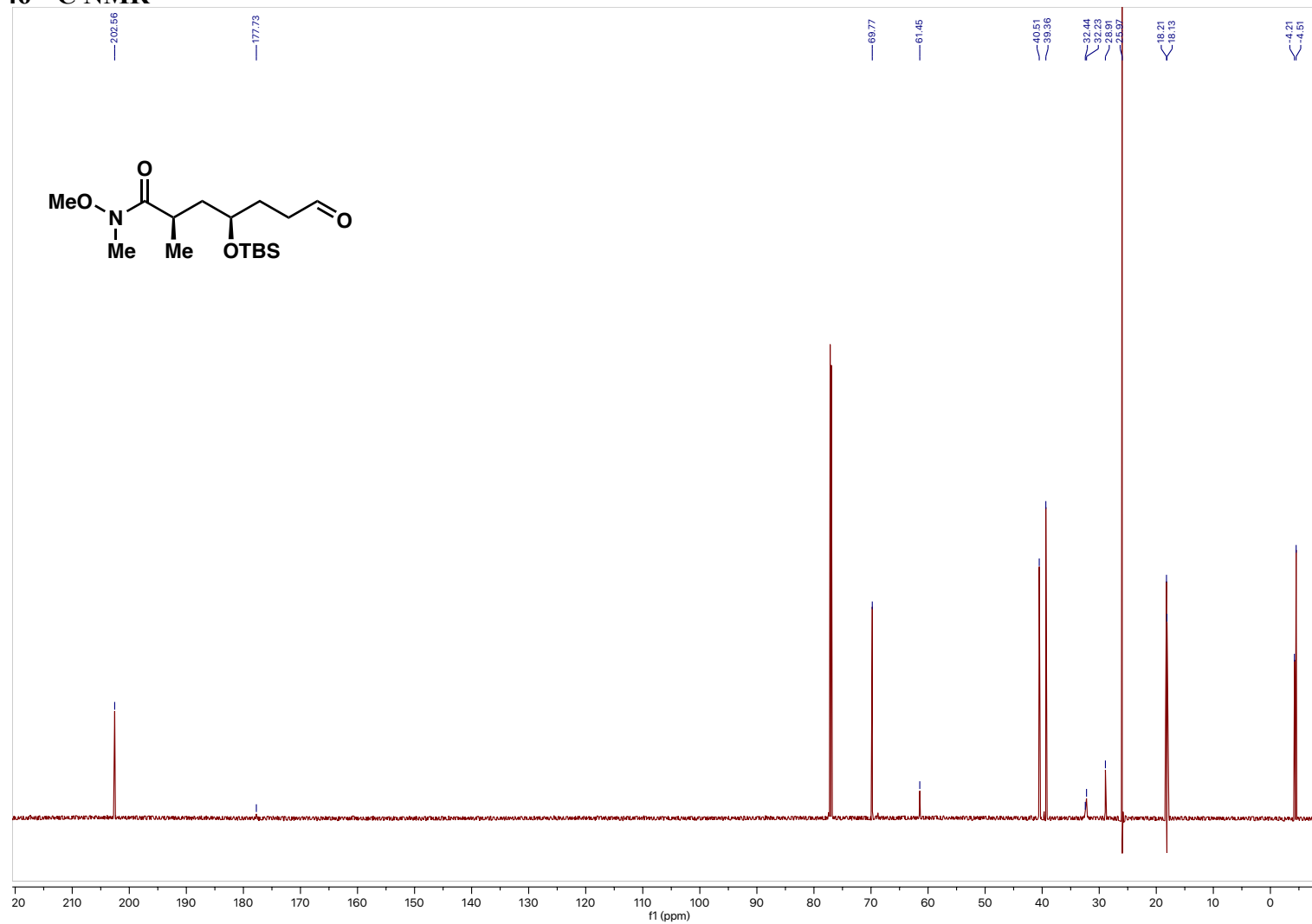
Determination the er of Compound 45



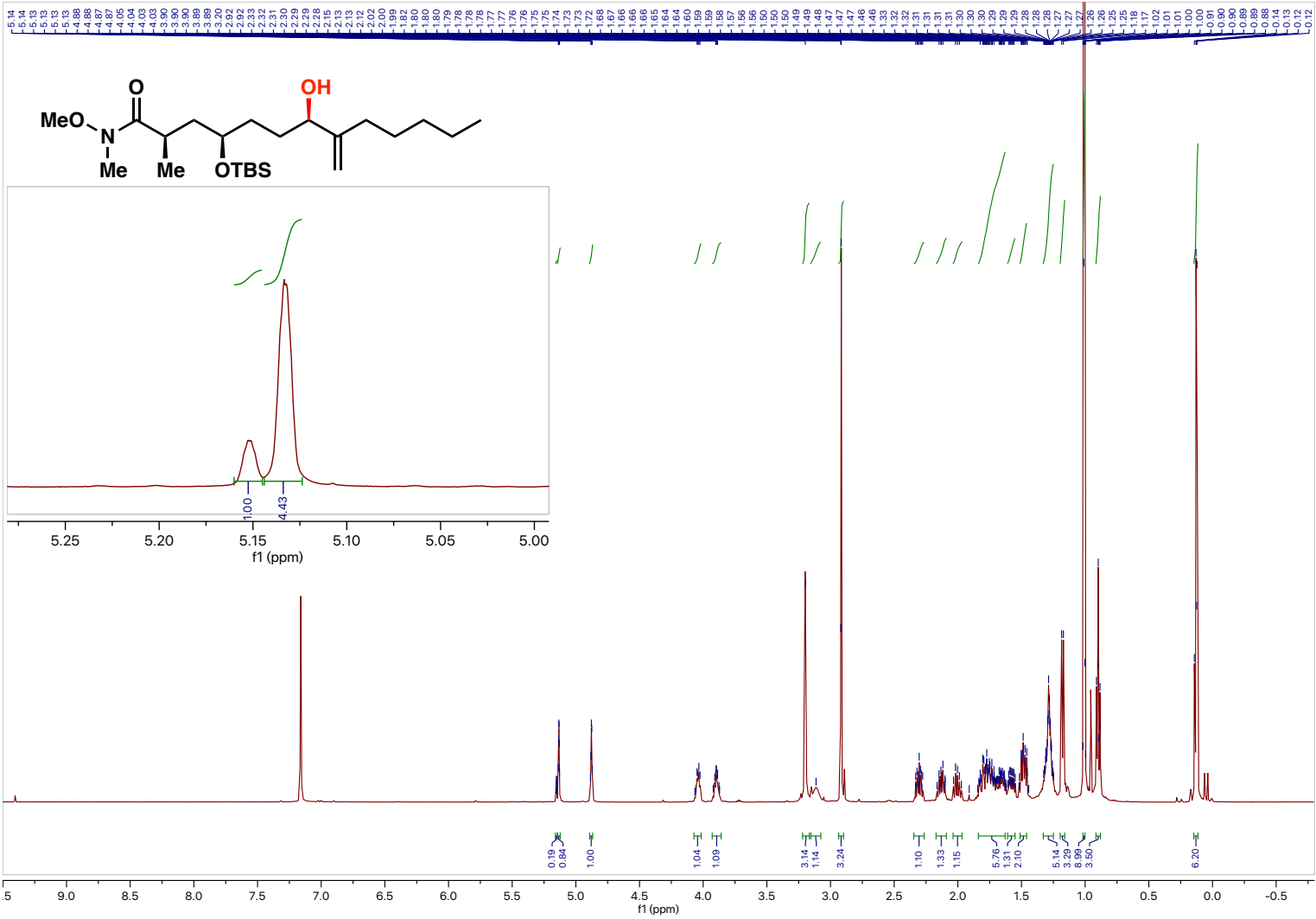
Compound 46 ¹H NMR



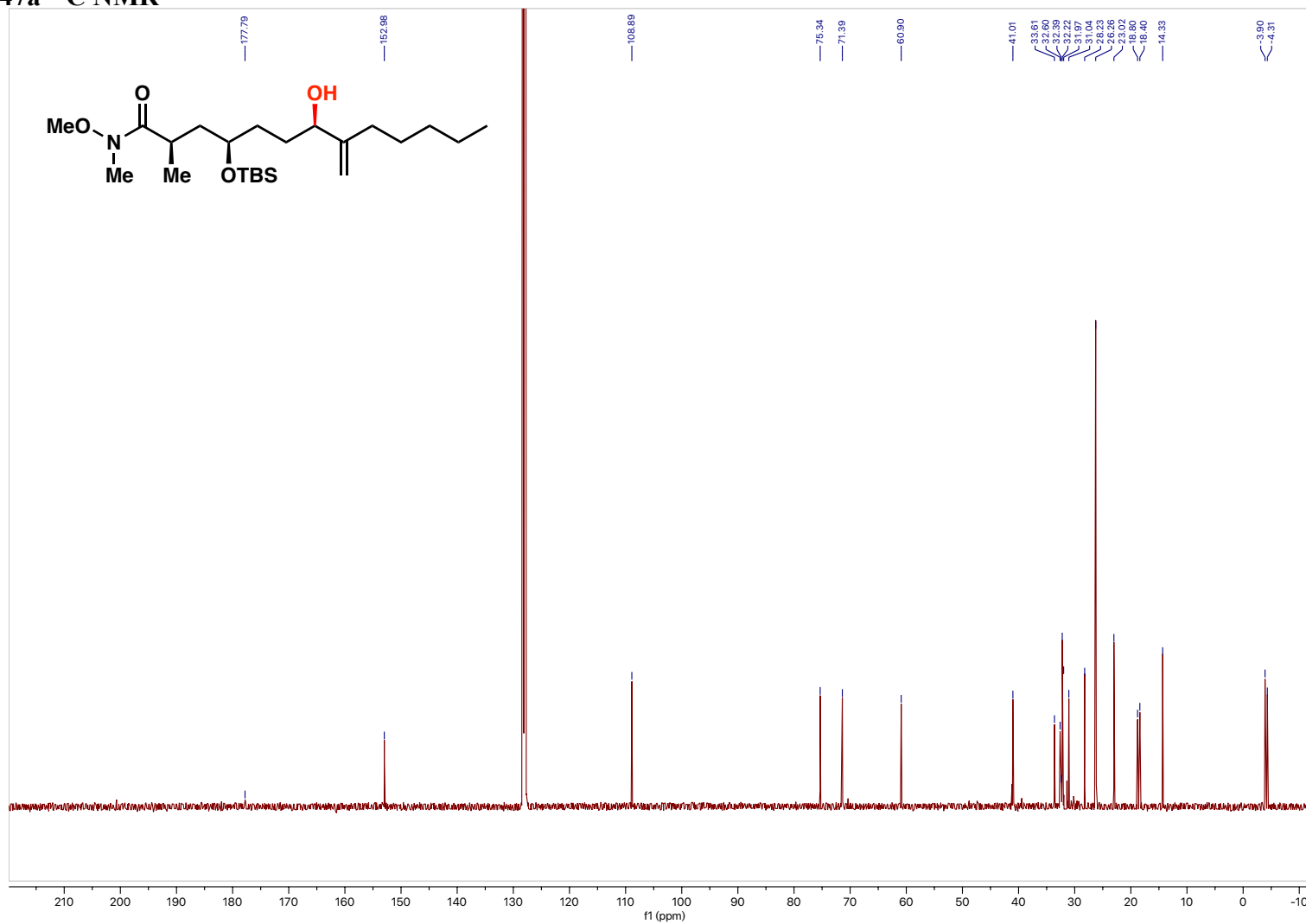
Compound 46 ^{13}C NMR



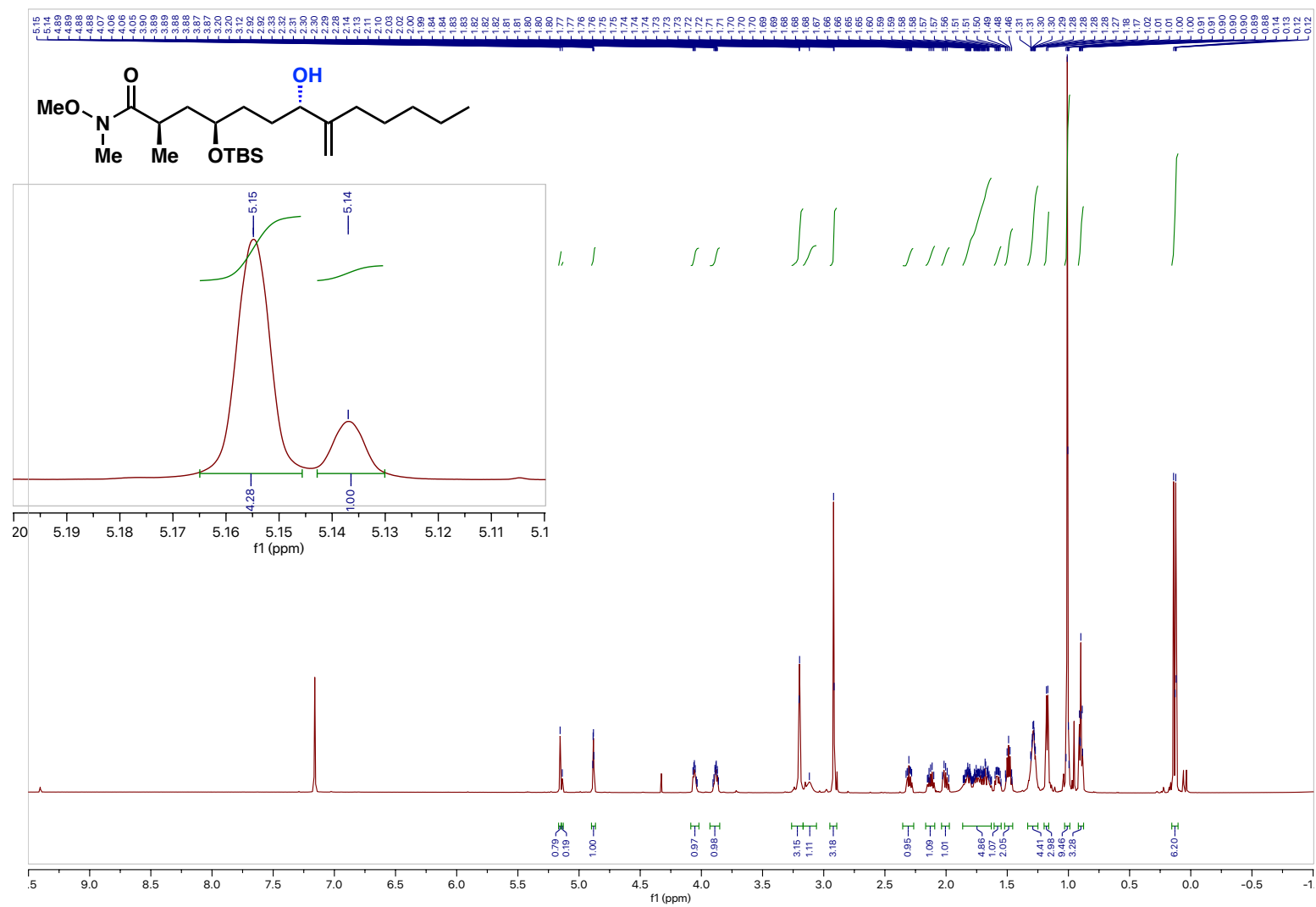
Compound 47a ¹H NMR



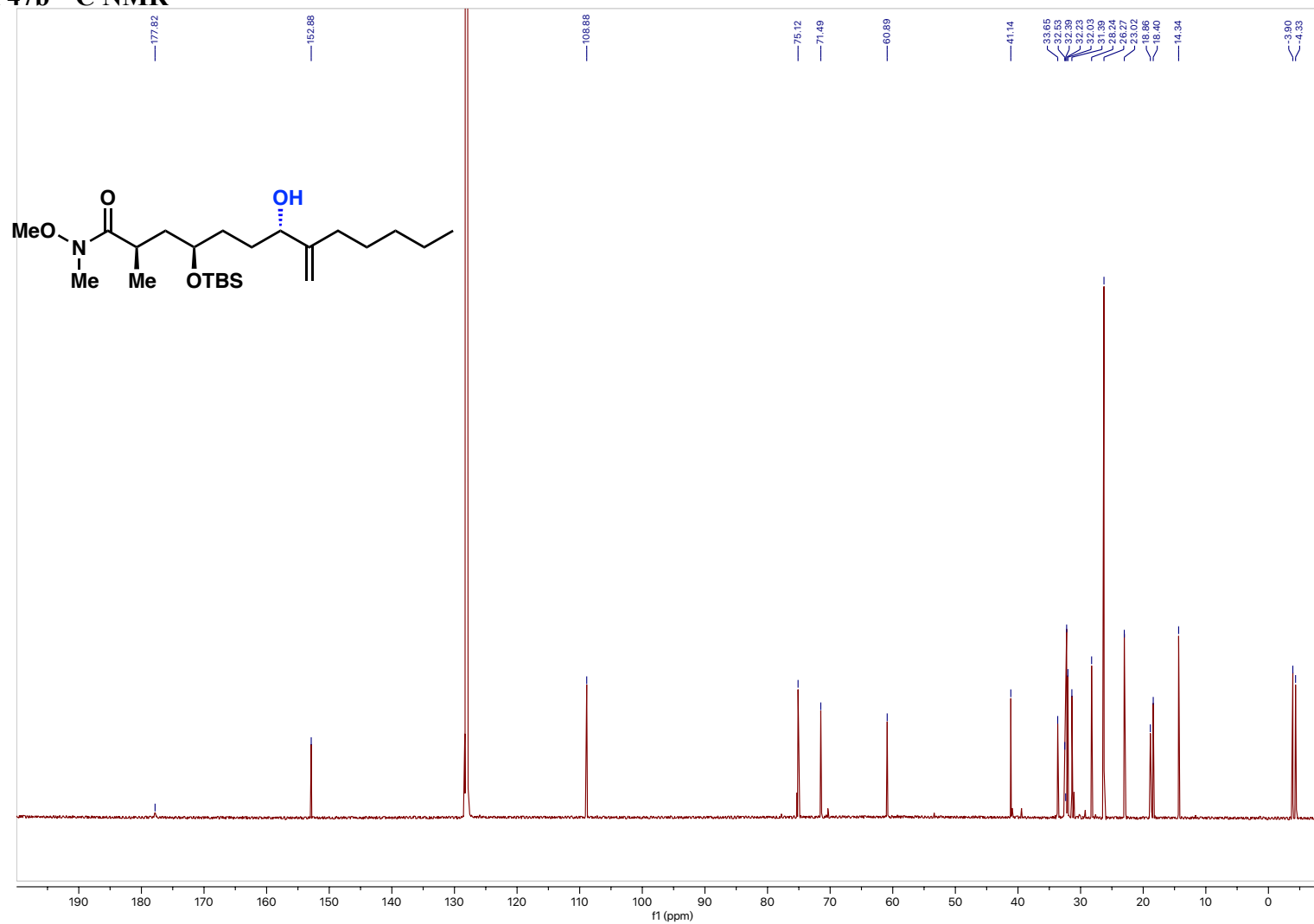
Compound 47a ¹³C NMR



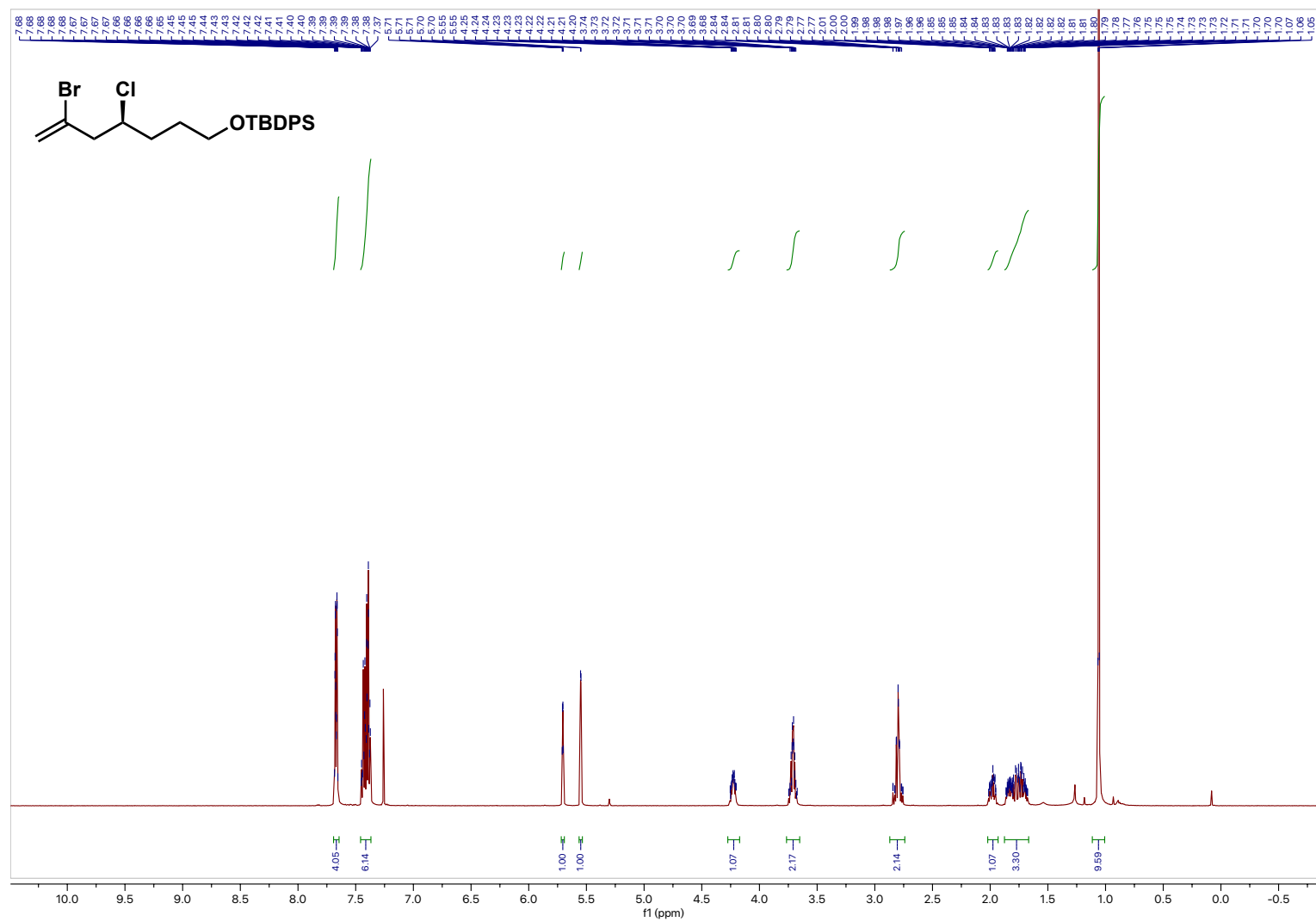
Compound 47b ¹H NMR



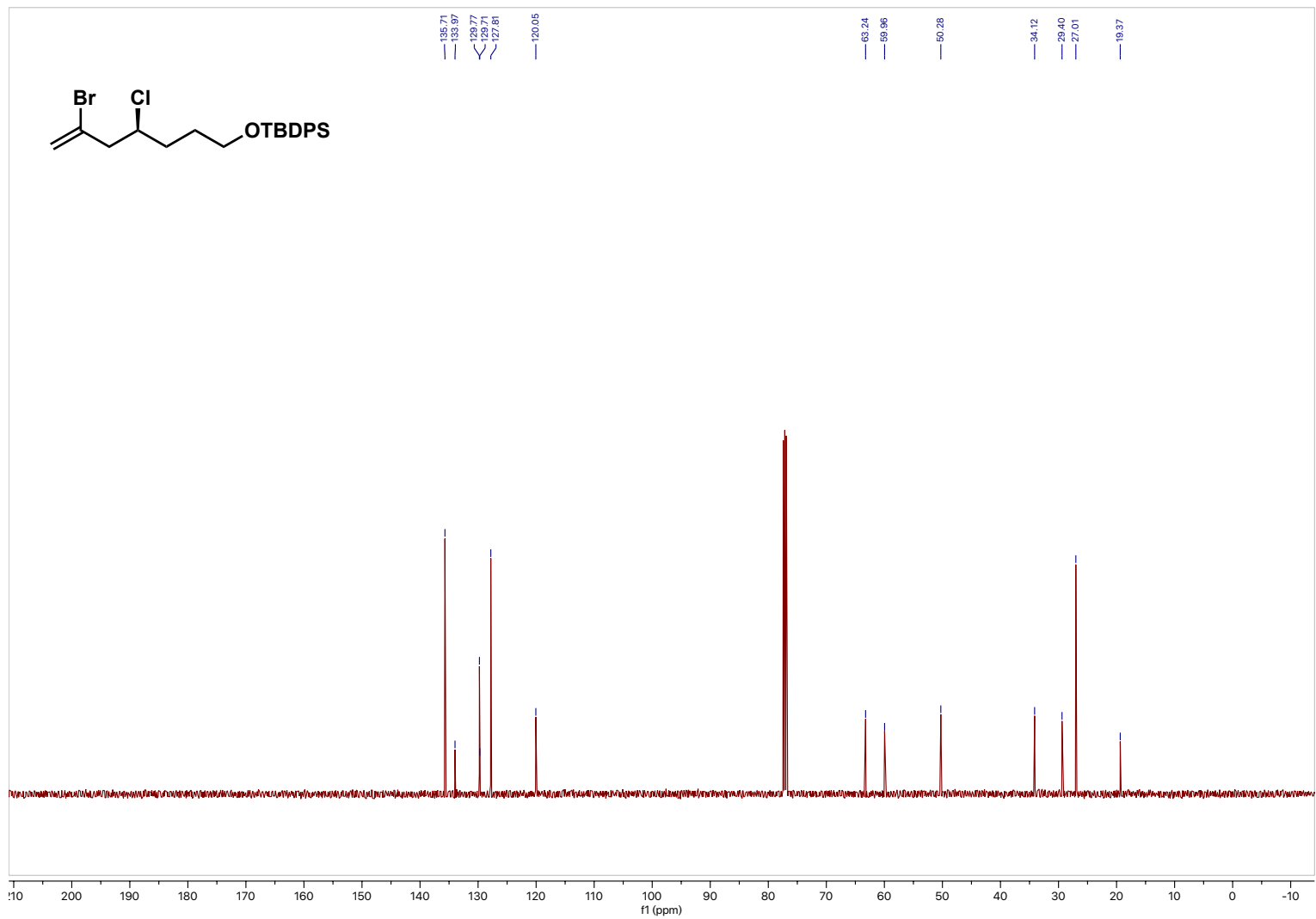
Compound 47b ¹³C NMR



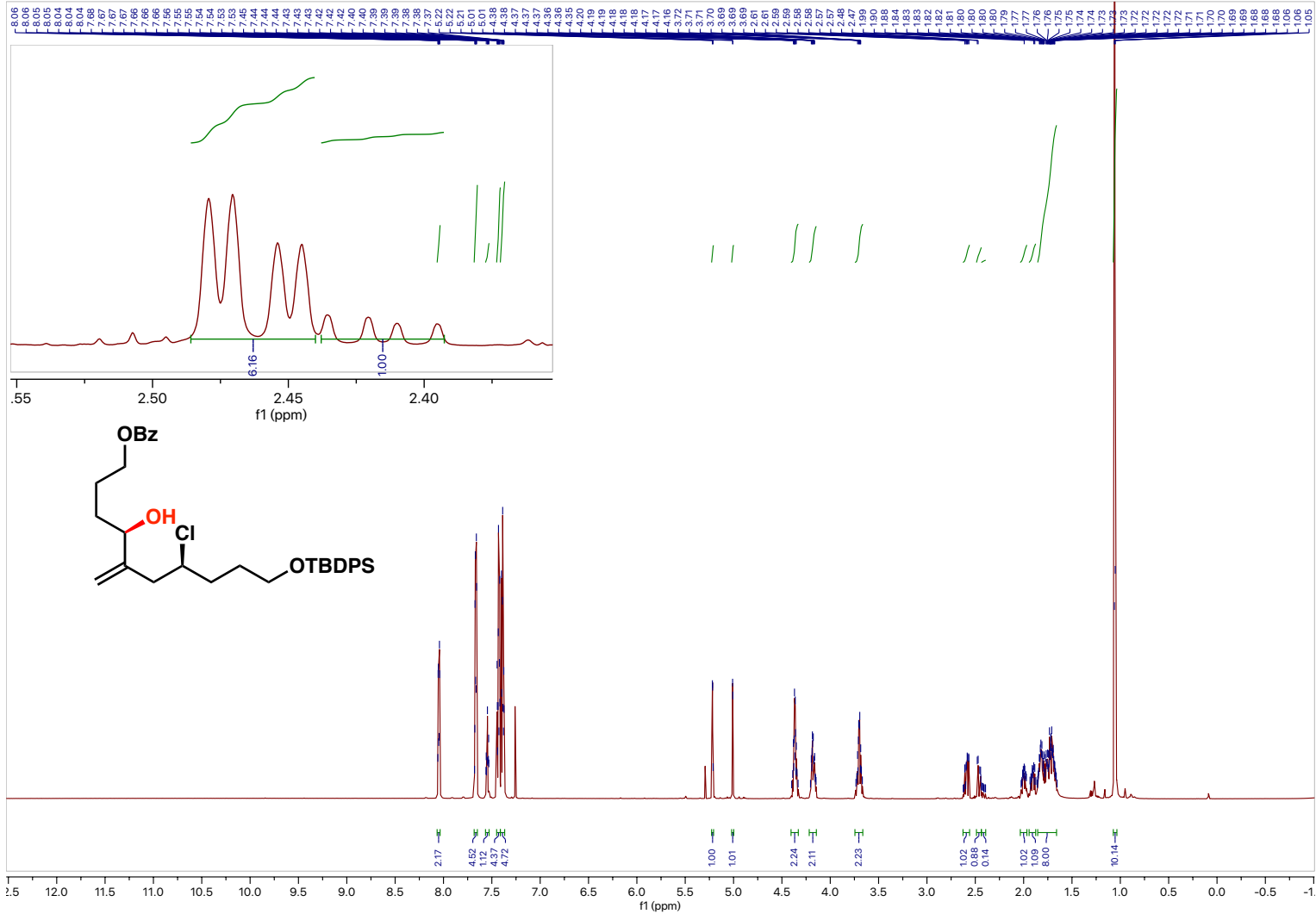
Compound 49 ¹H NMR



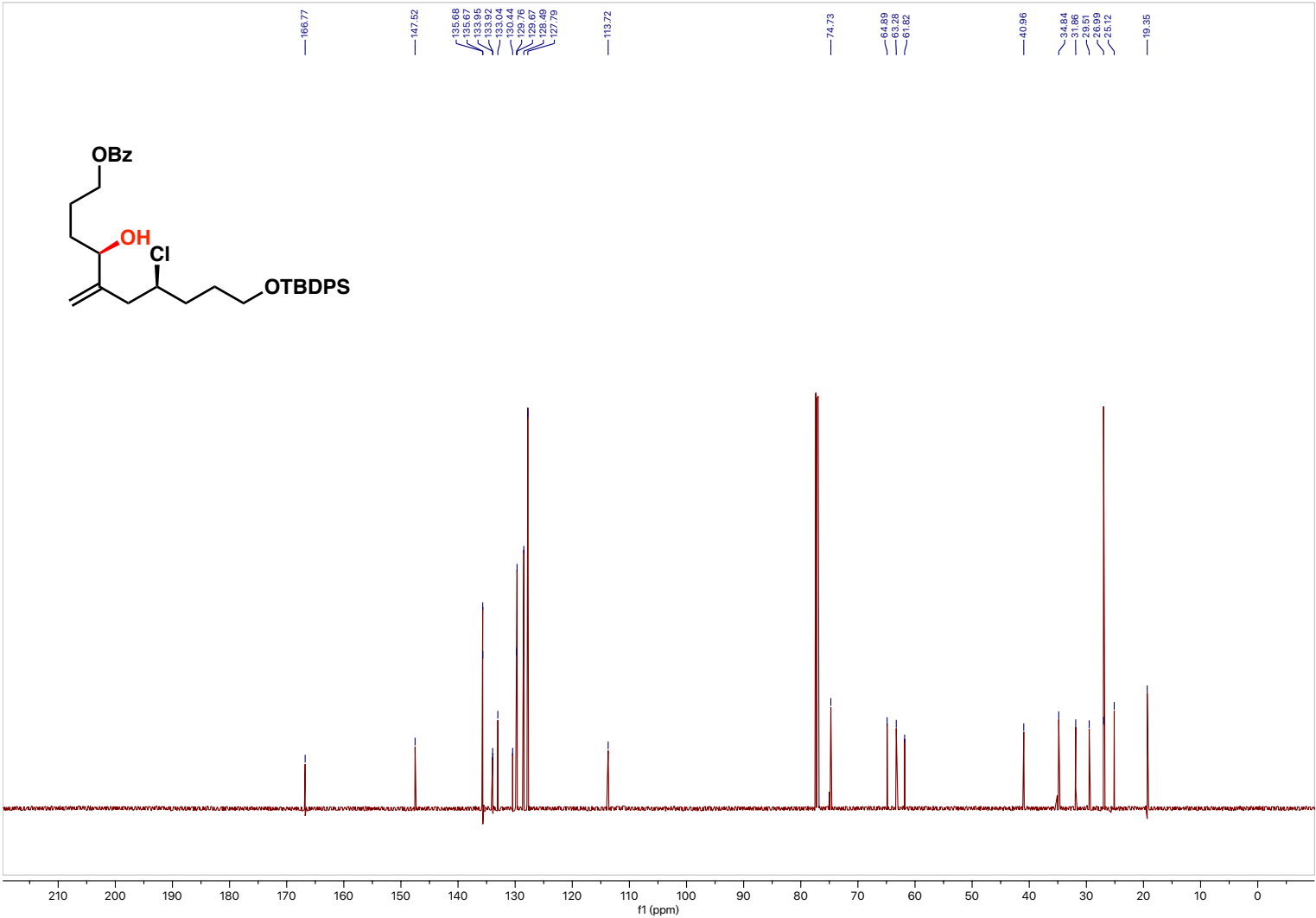
Compound 49 ¹³C NMR



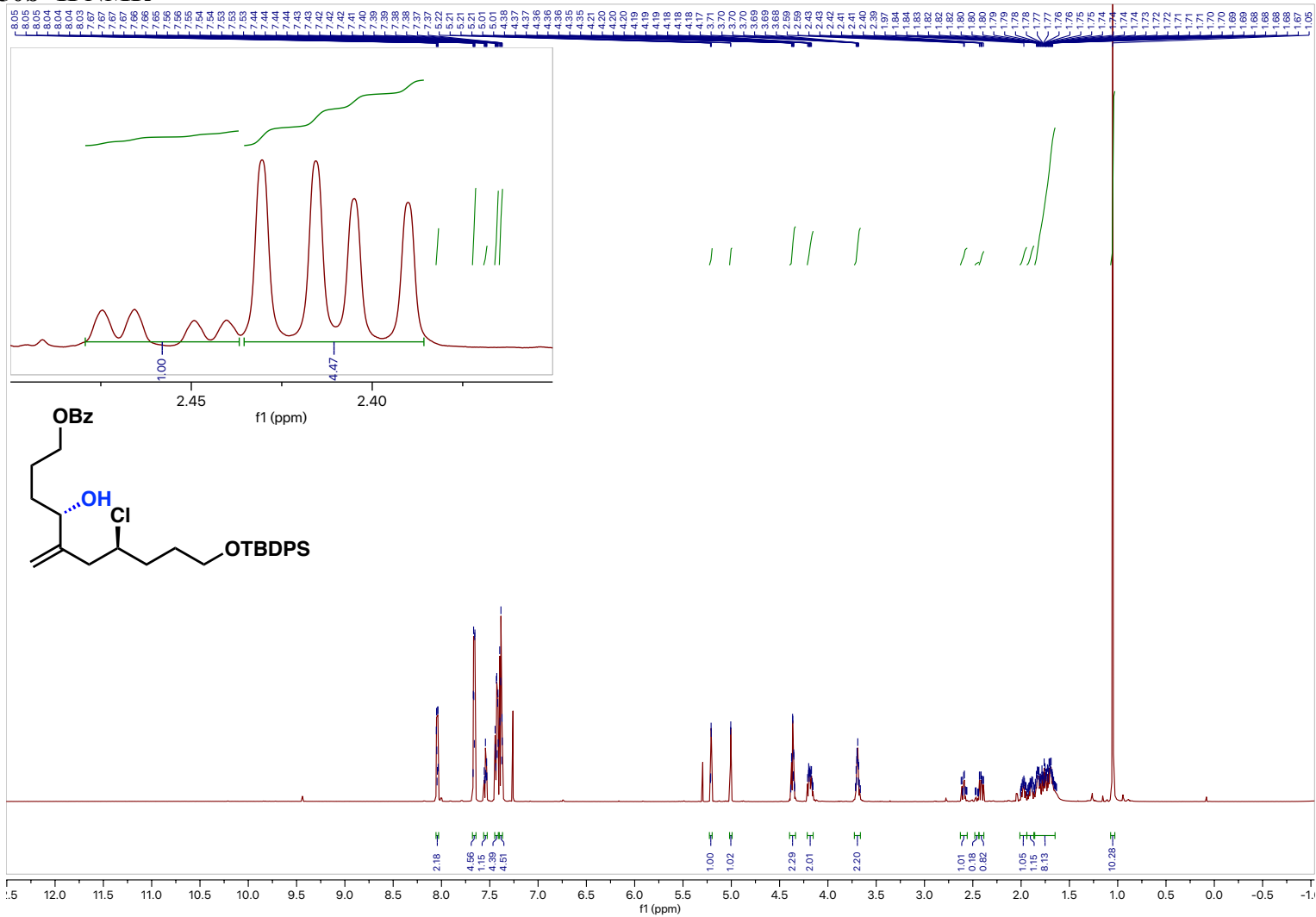
Compound 50a ¹H NMR



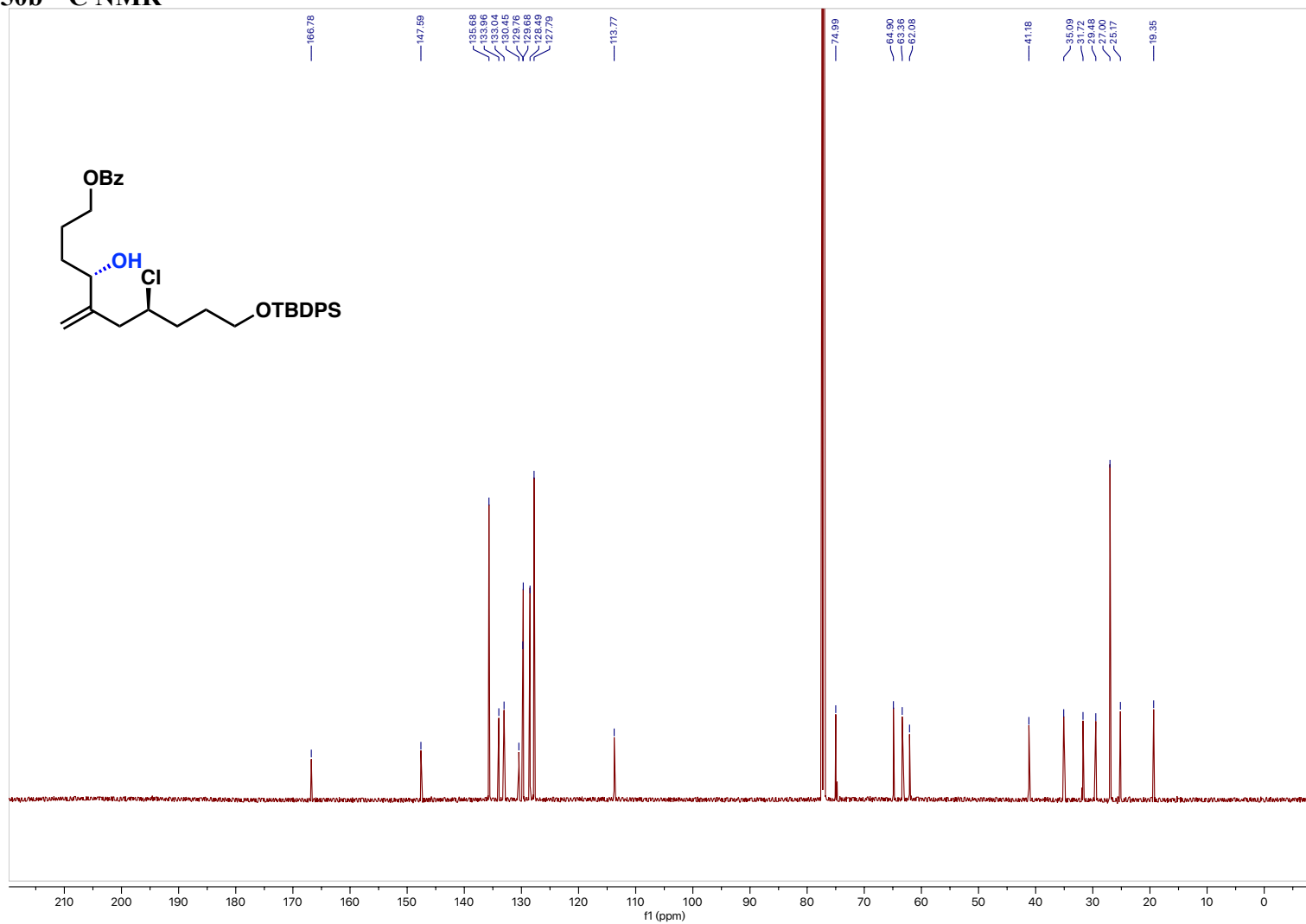
Compound 50a ¹³C NMR



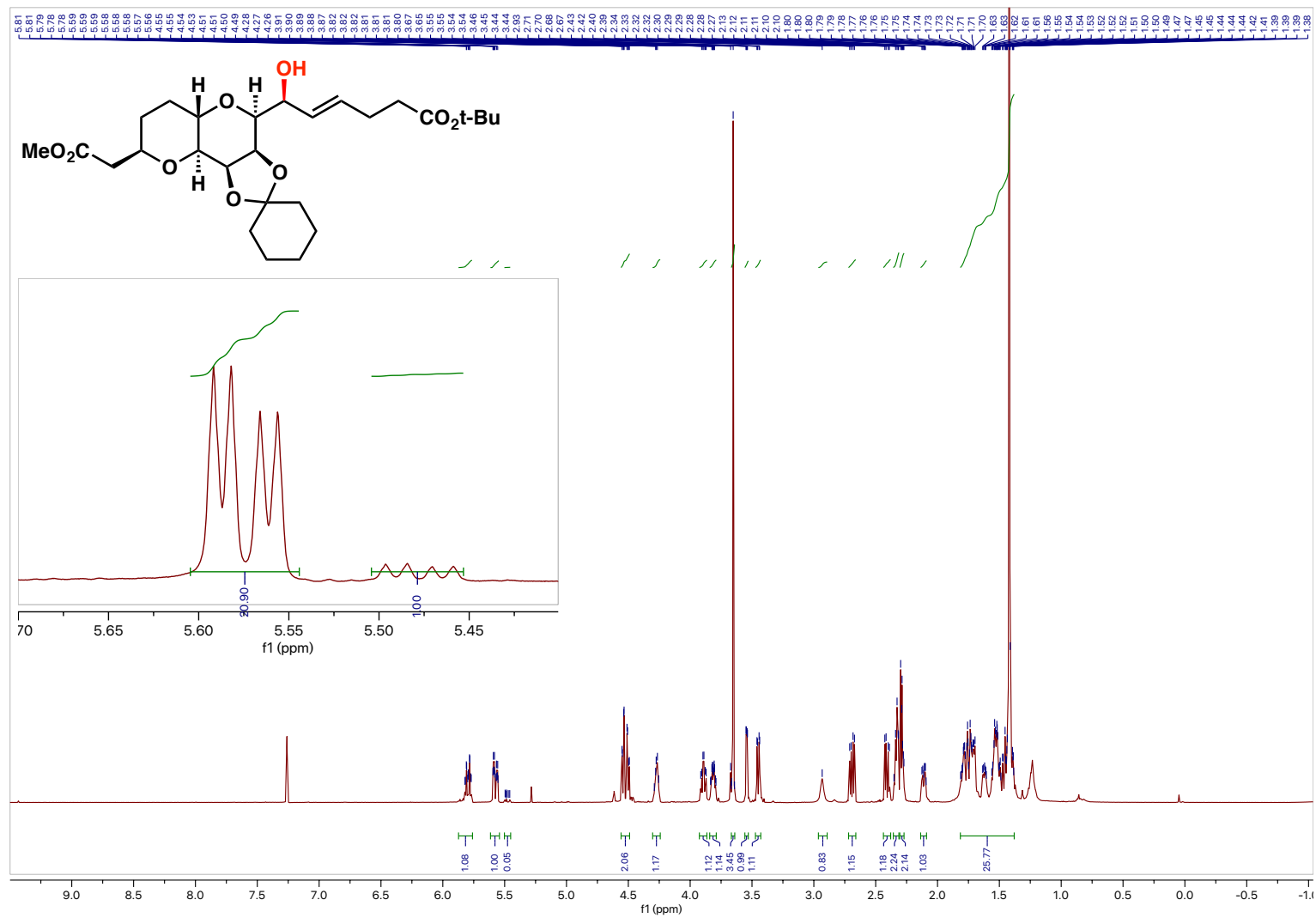
Compound 50b ¹H NMR



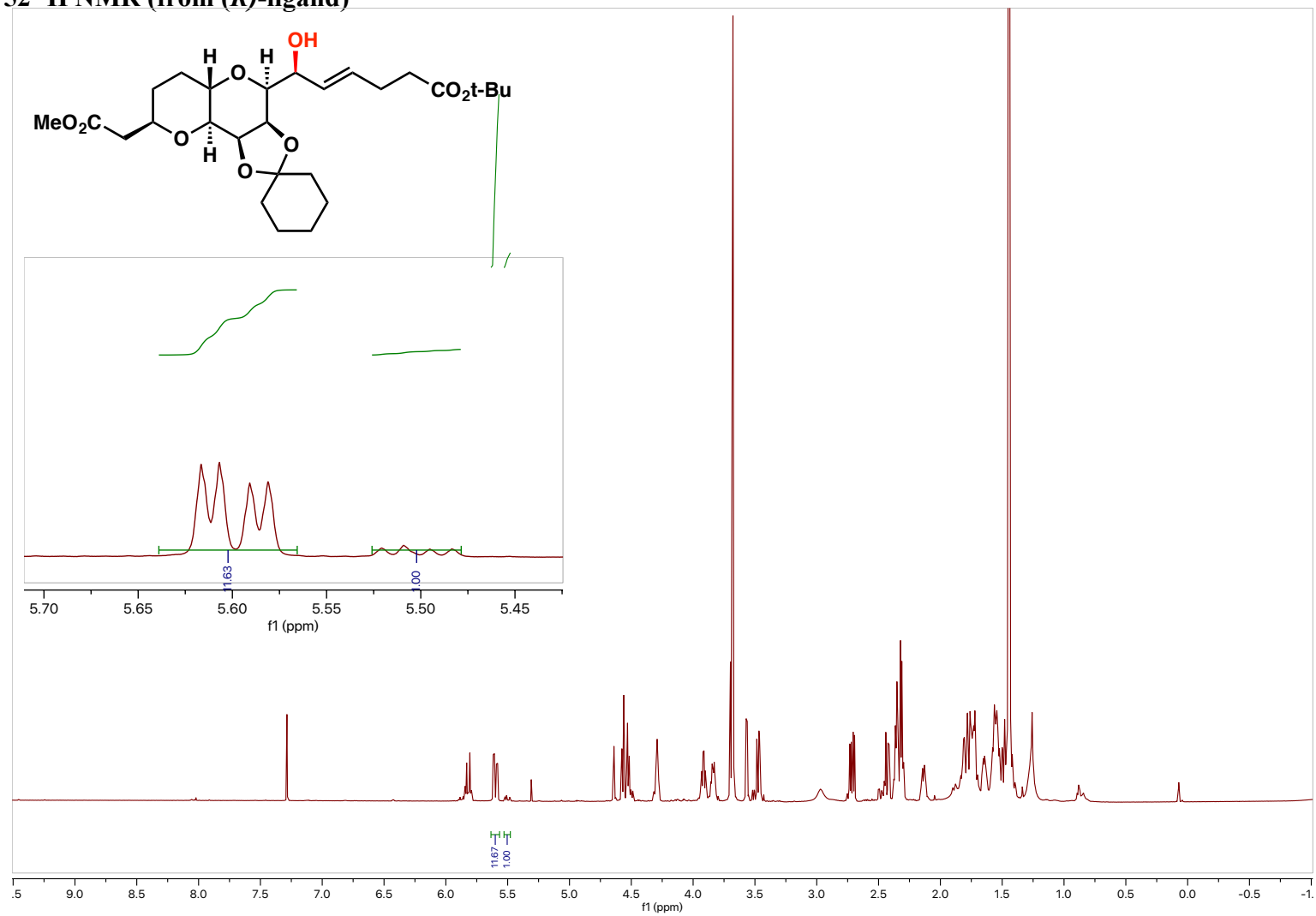
Compound 50b ¹³C NMR



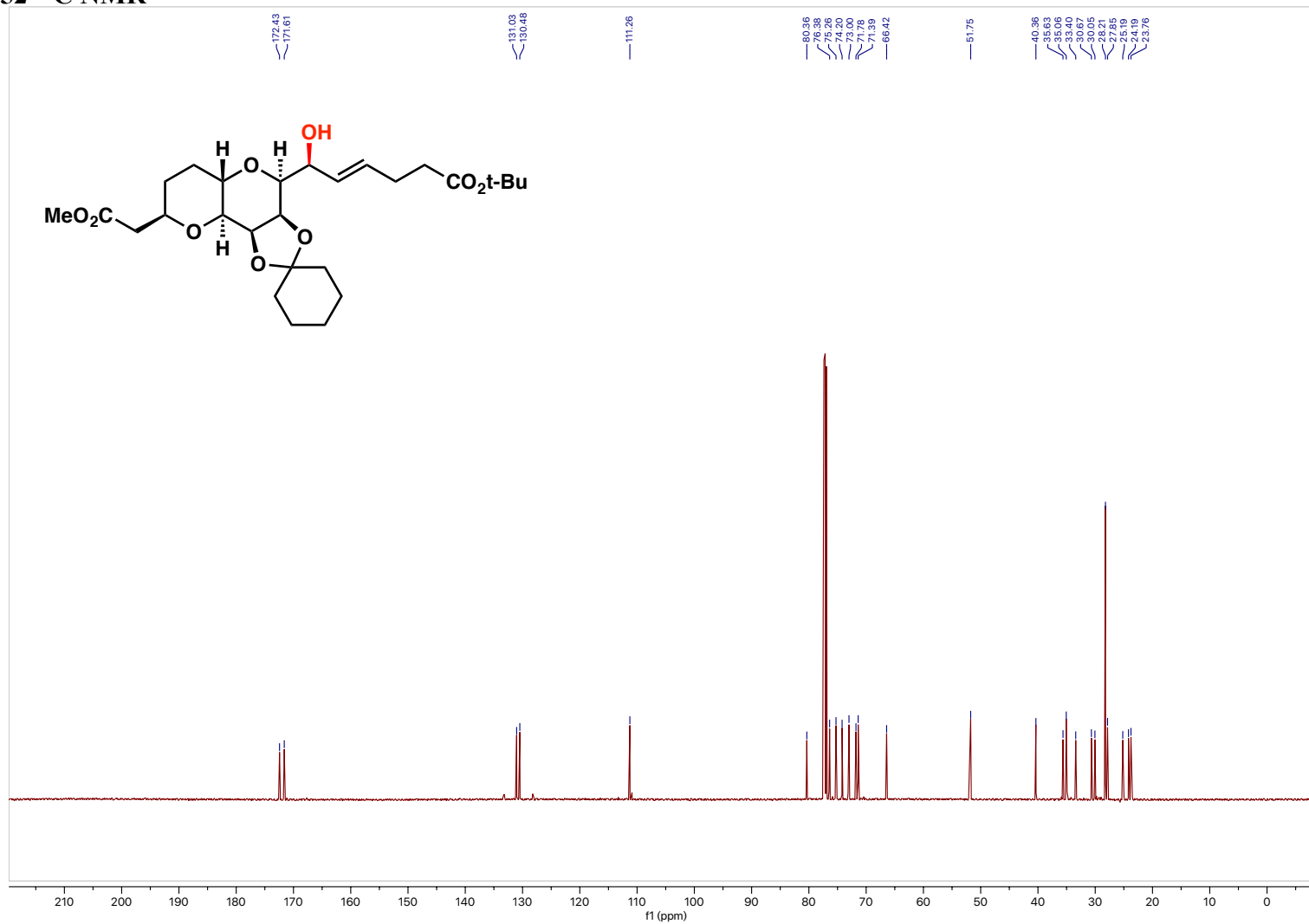
Compound 52 ¹H NMR (from (*S*)-ligand)



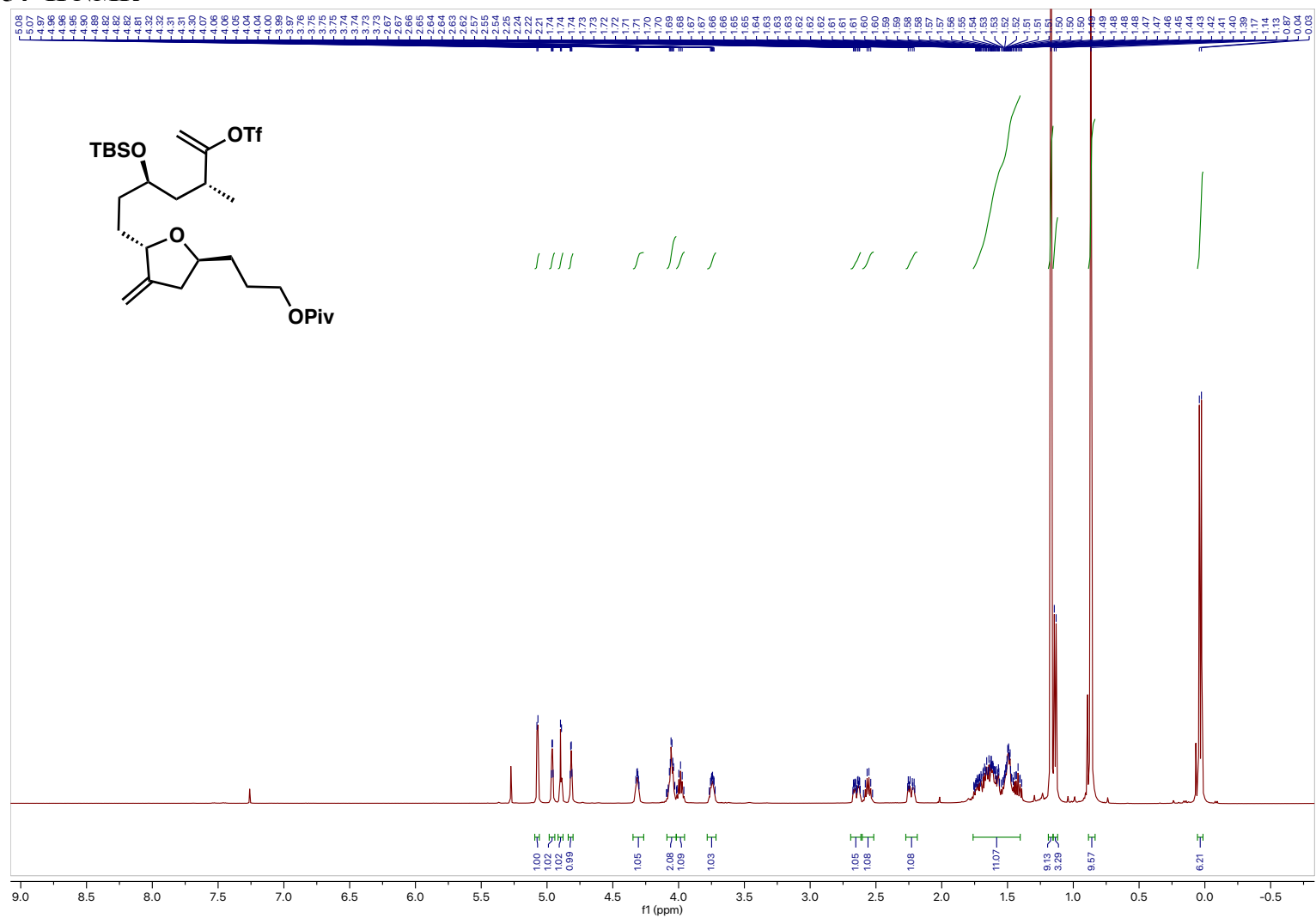
Compound 52 ^1H NMR (from (*R*)-ligand)



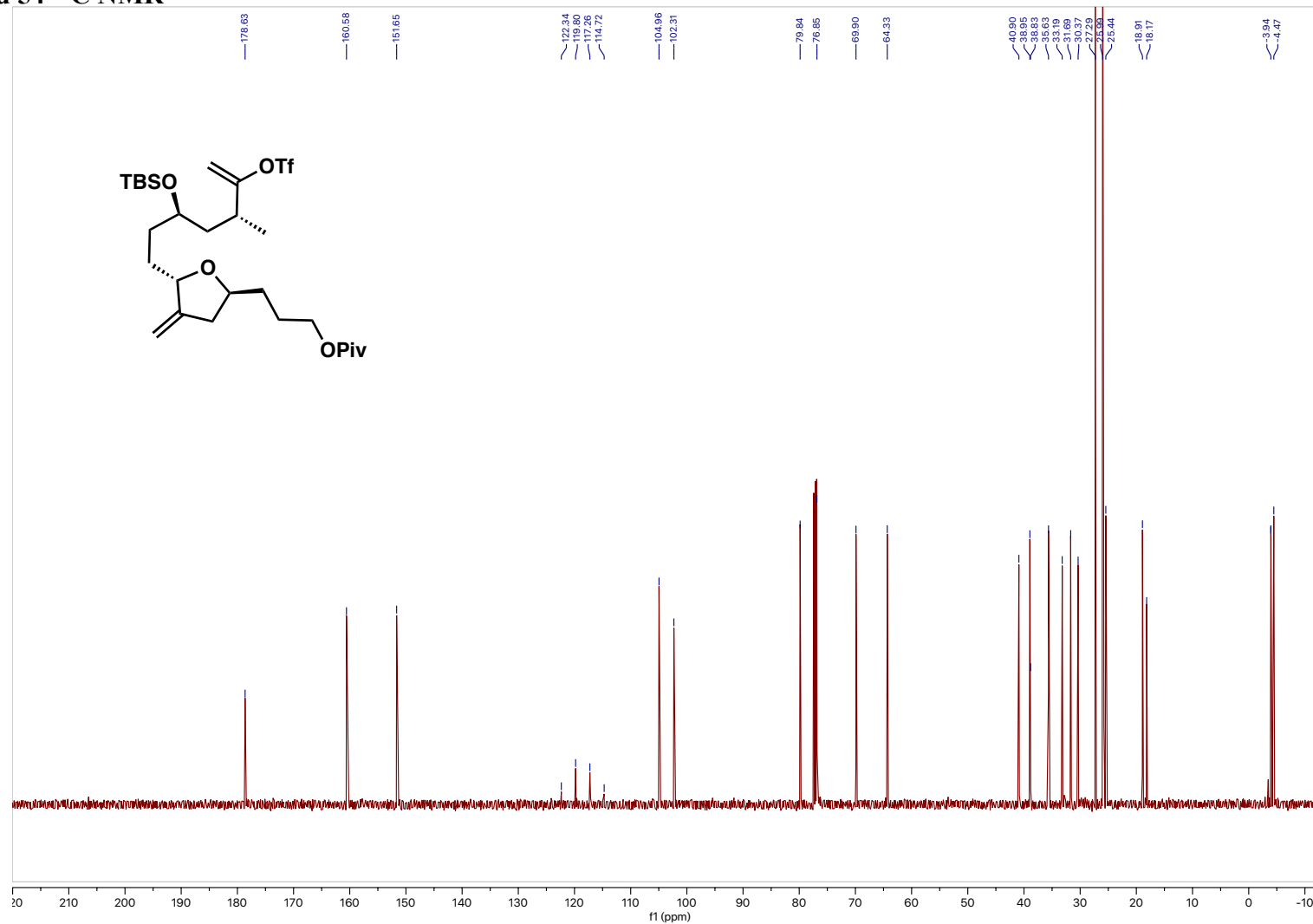
Compound 52 ¹³C NMR



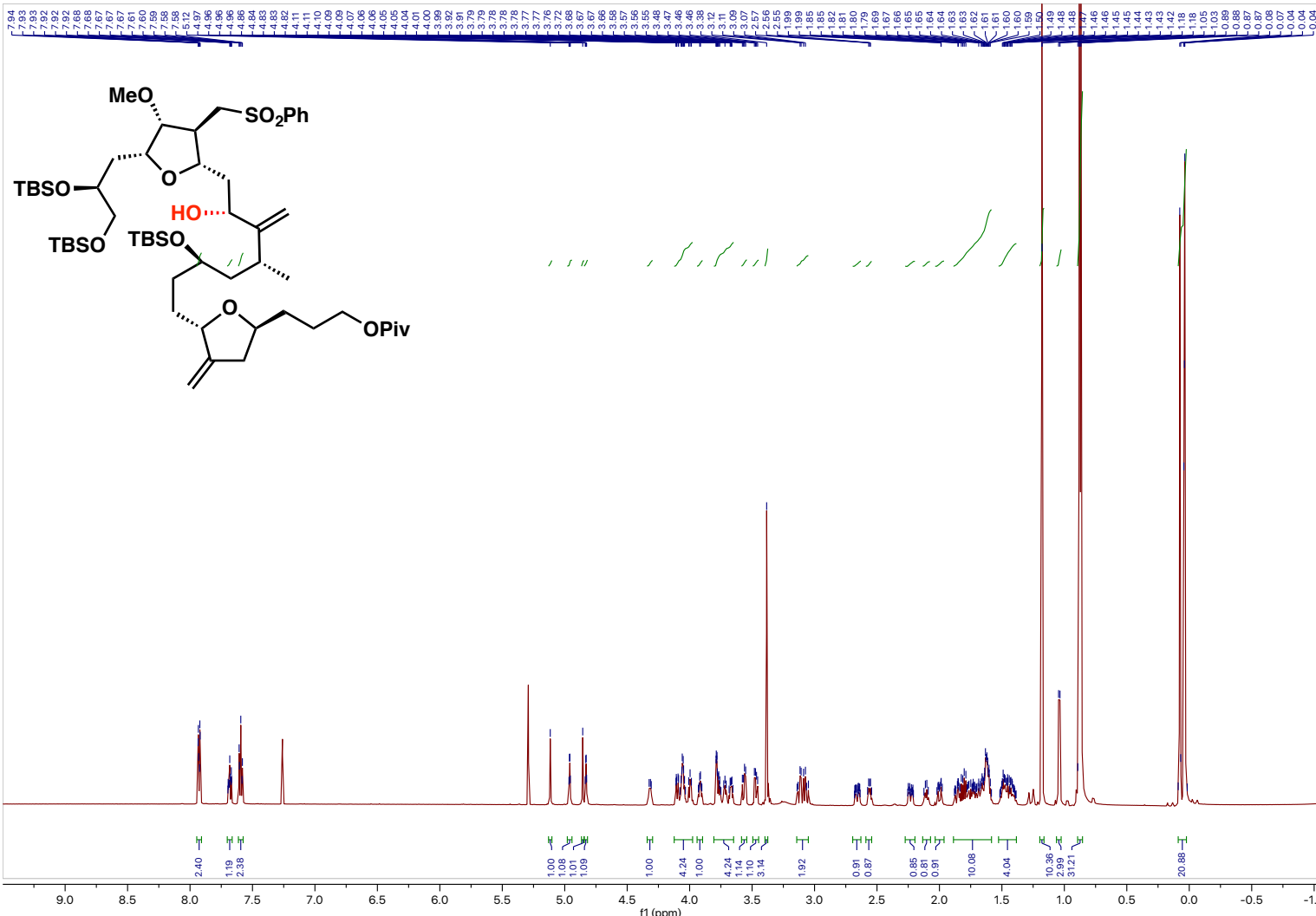
Compound 54 ¹H NMR



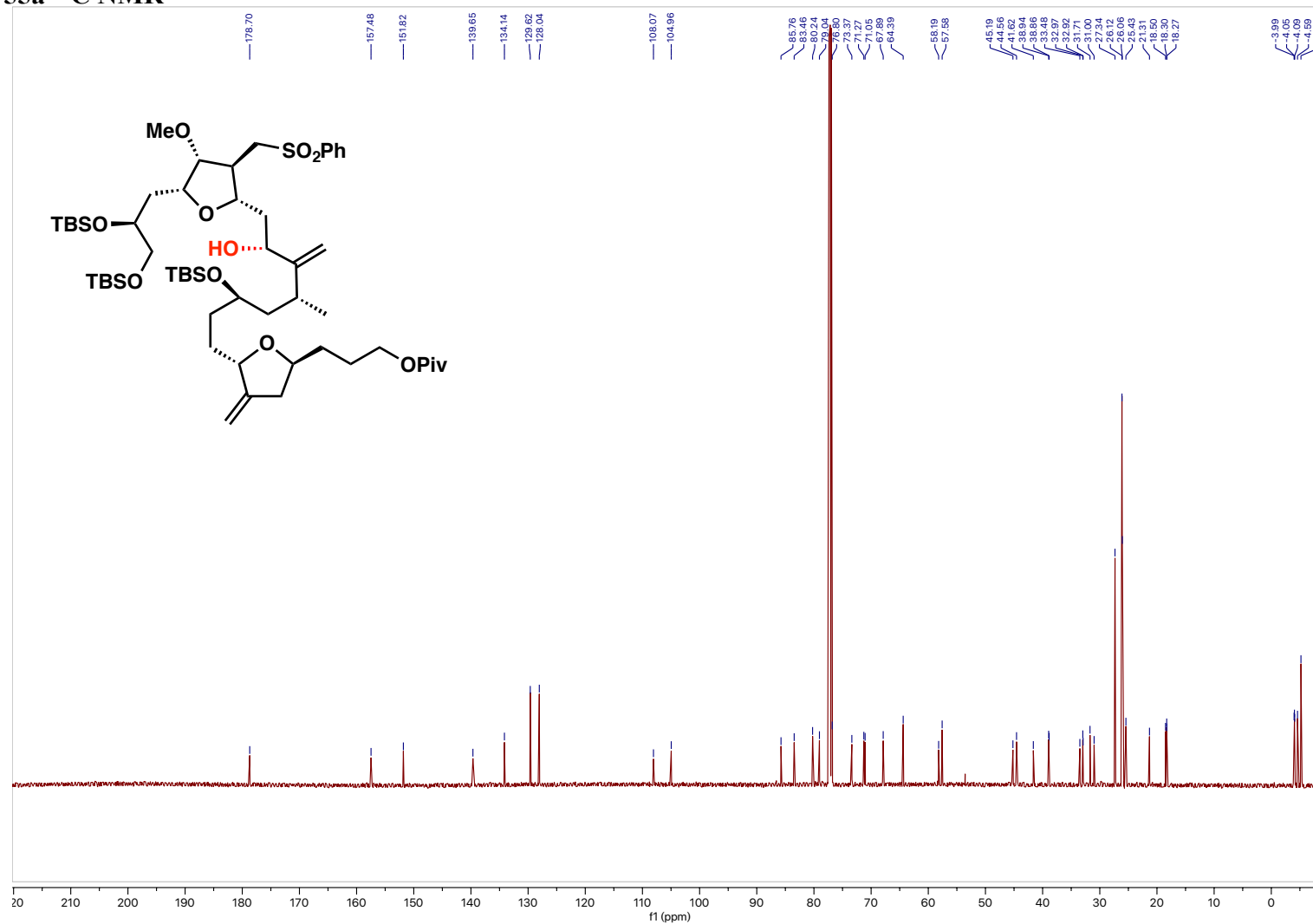
Compound 54 ¹³C NMR



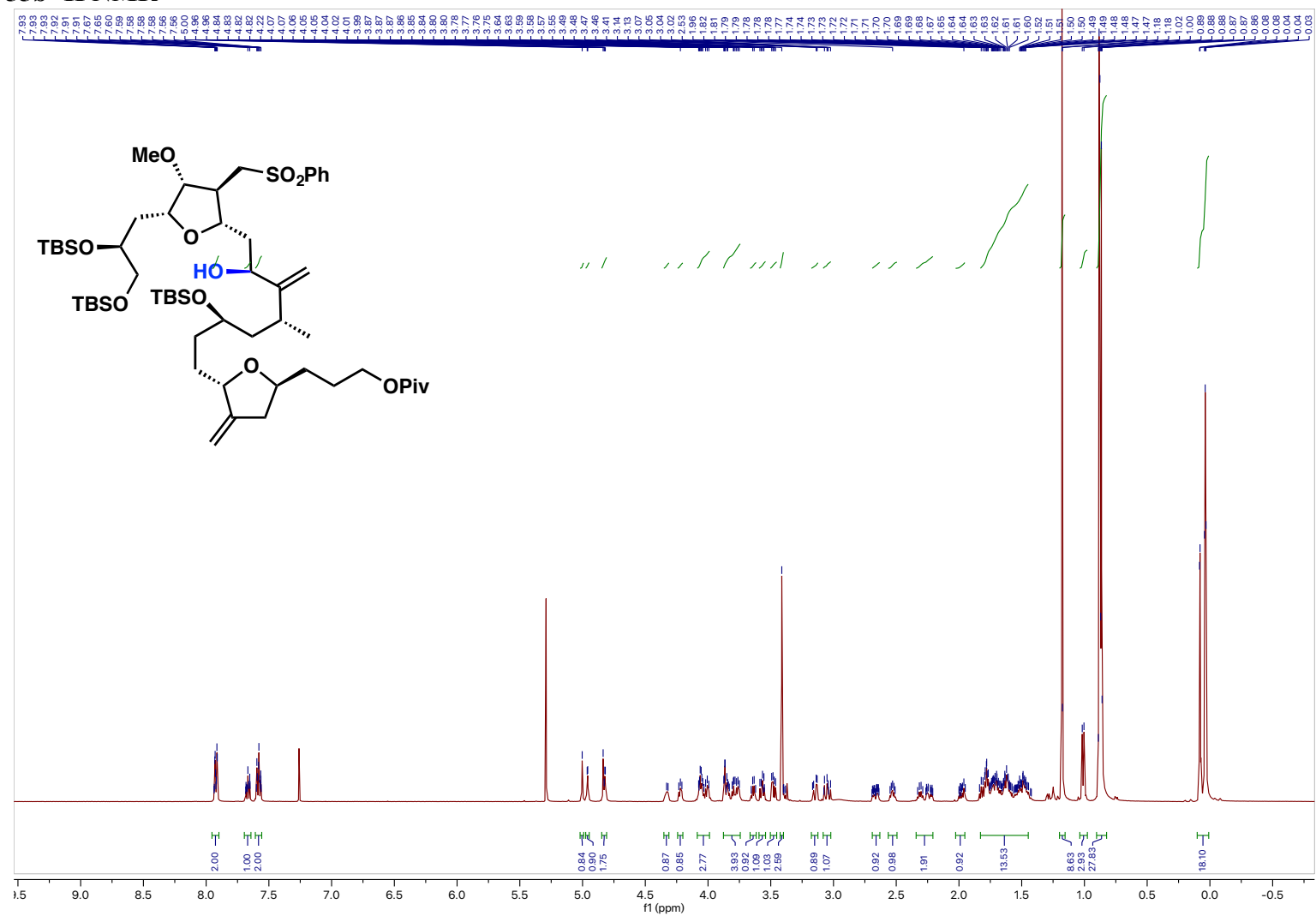
Compound 55a ¹H NMR



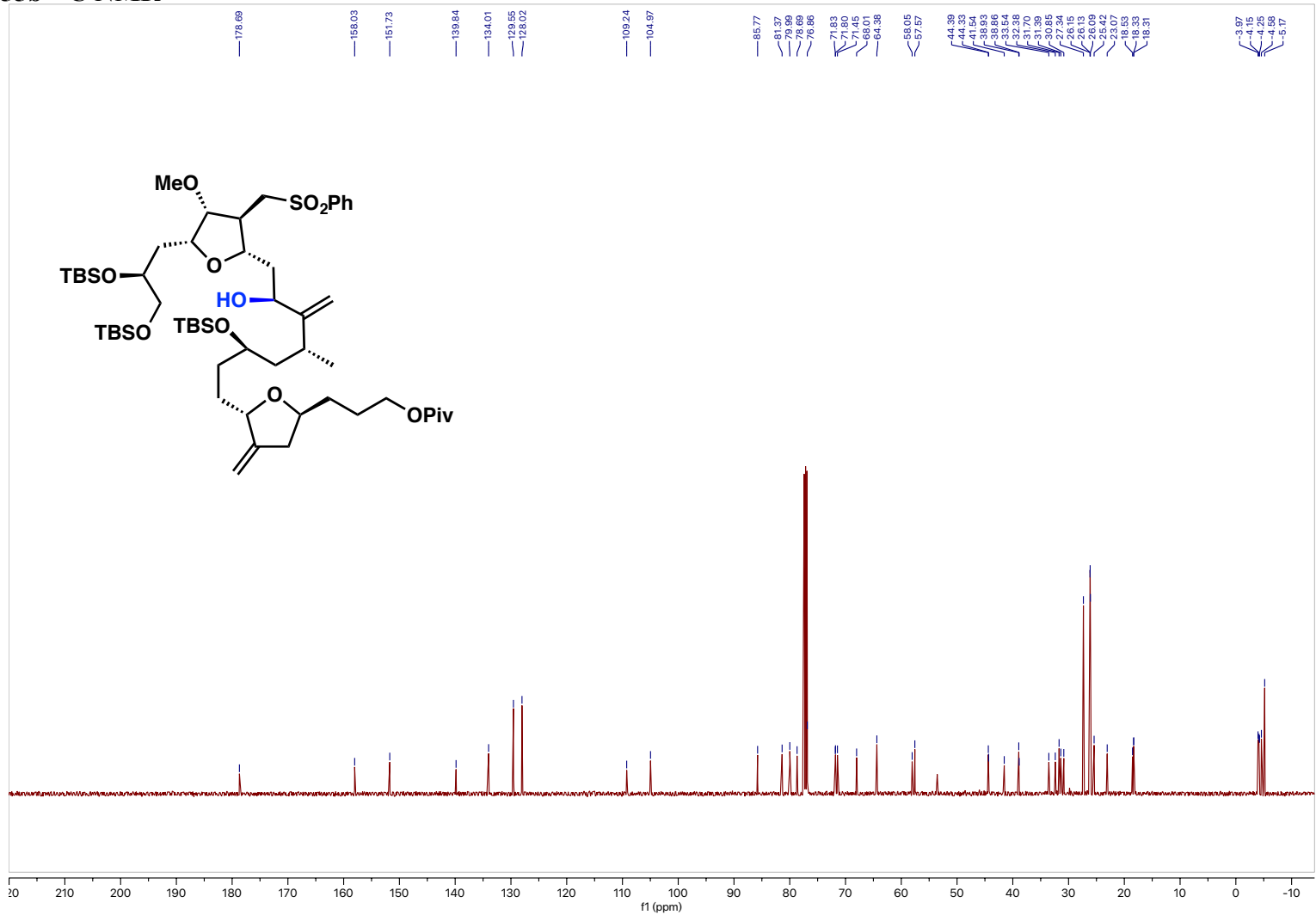
Compound 55a ¹³C NMR



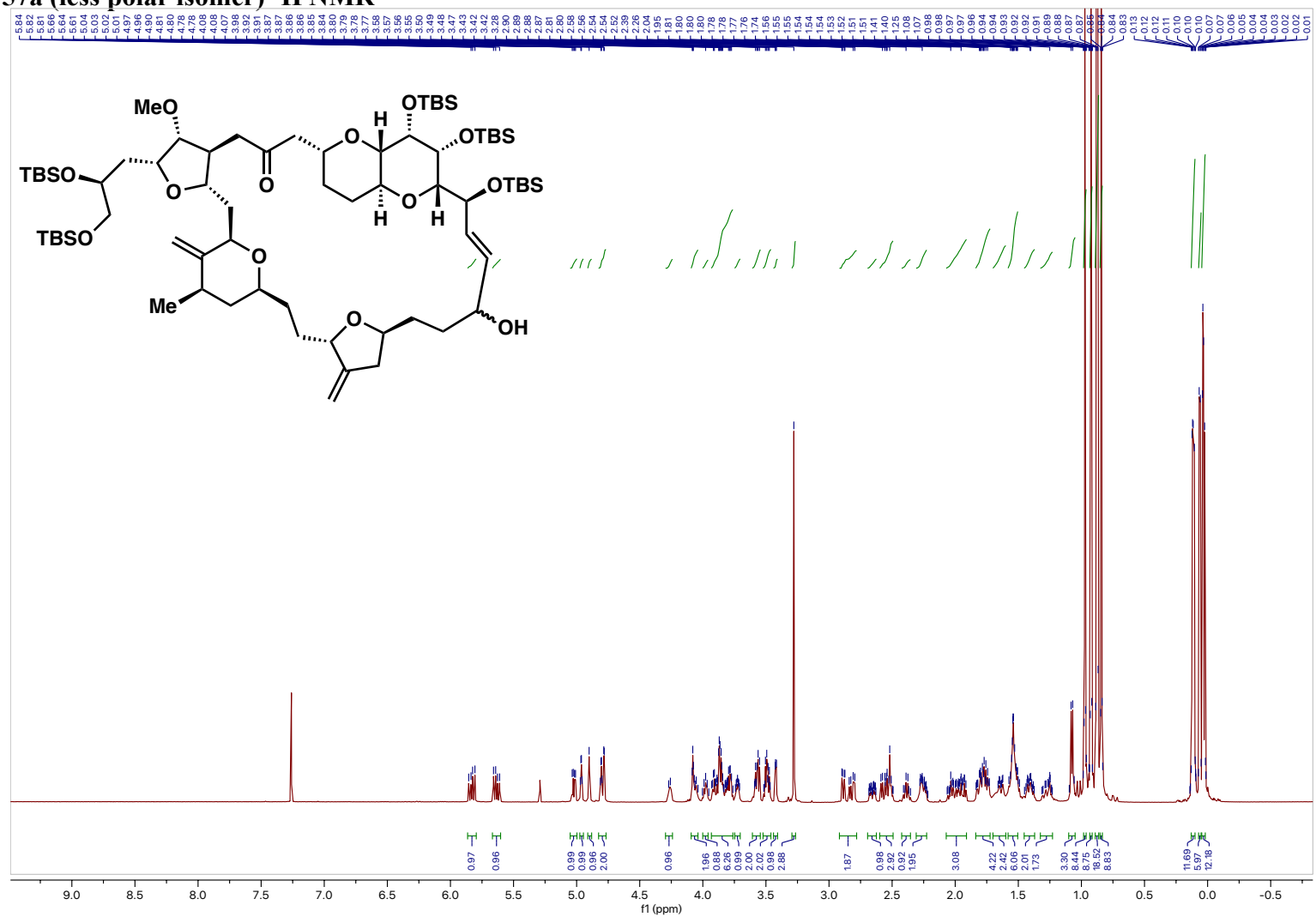
Compound 55b ¹H NMR



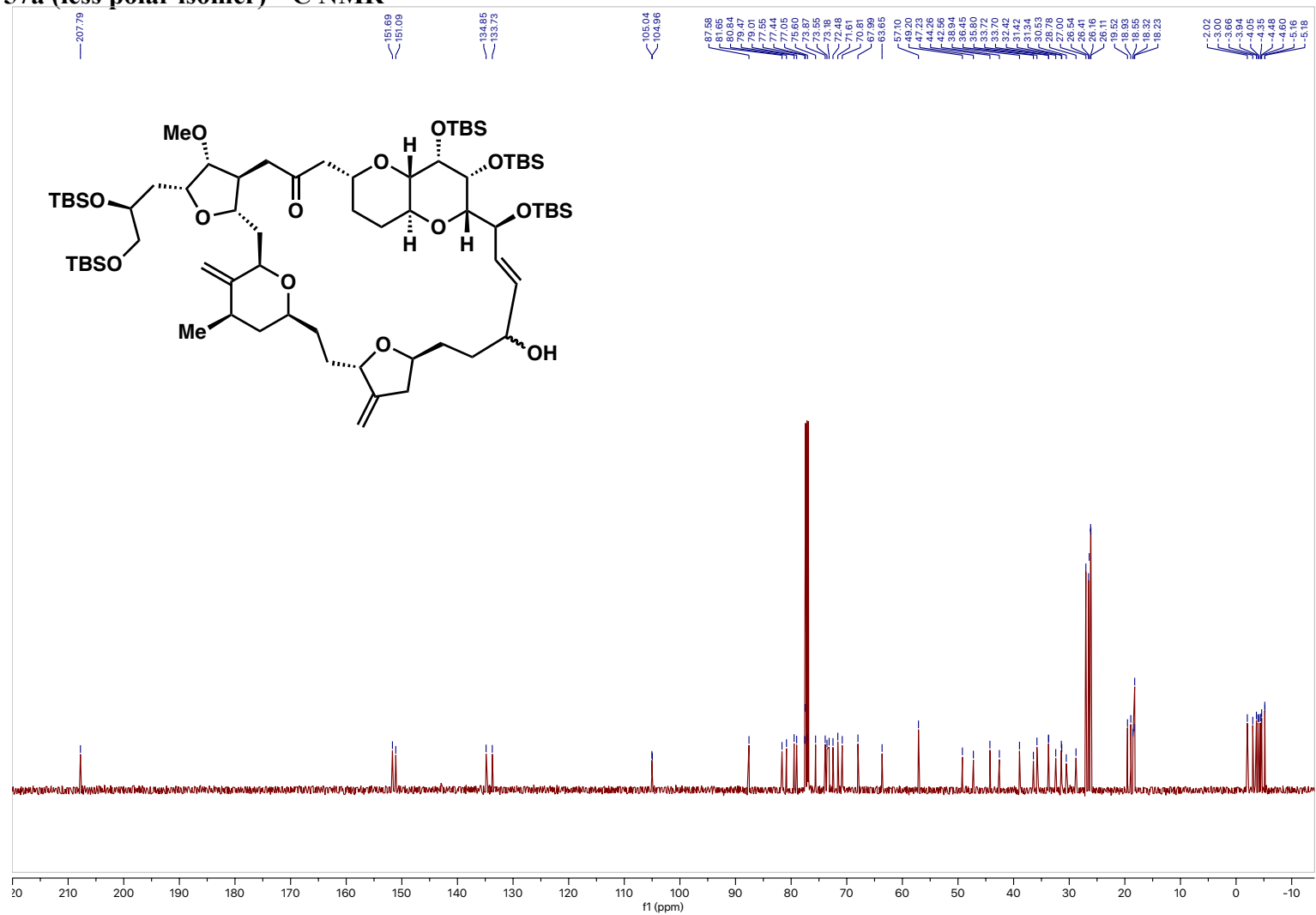
Compound 55b ¹³C NMR



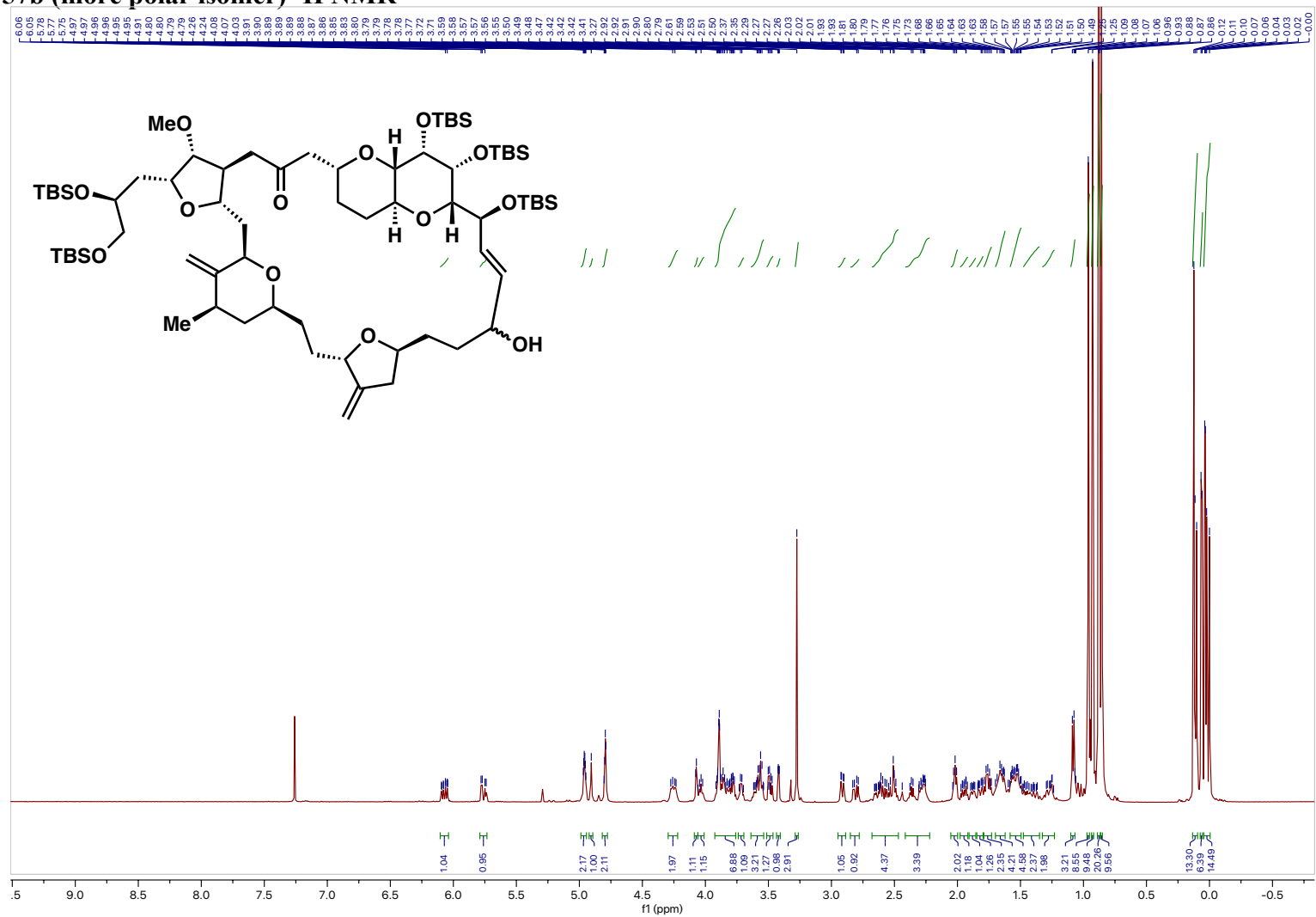
Compound 57a (less polar isomer) ¹H NMR



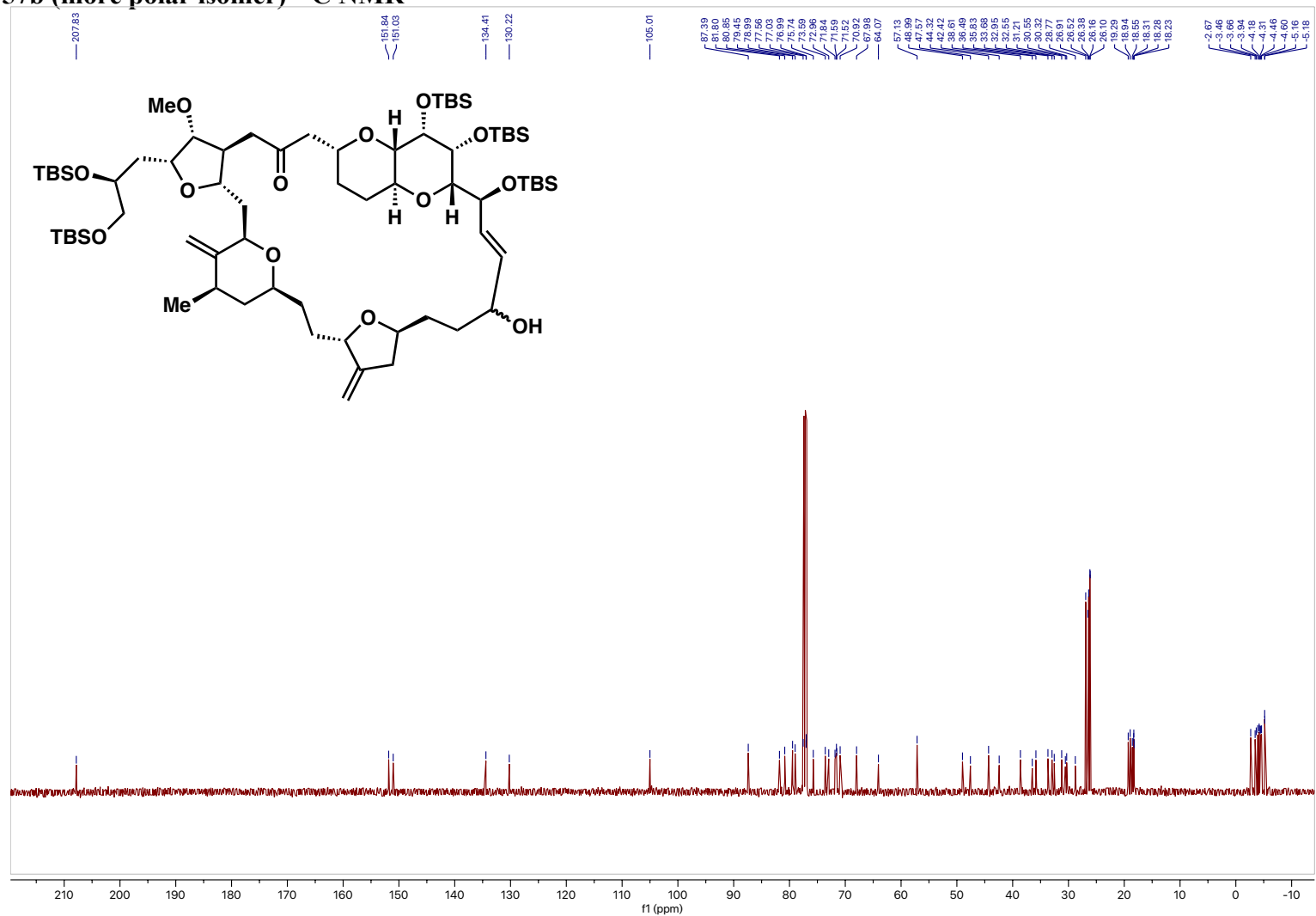
Compound 57a (less polar isomer) ^{13}C NMR



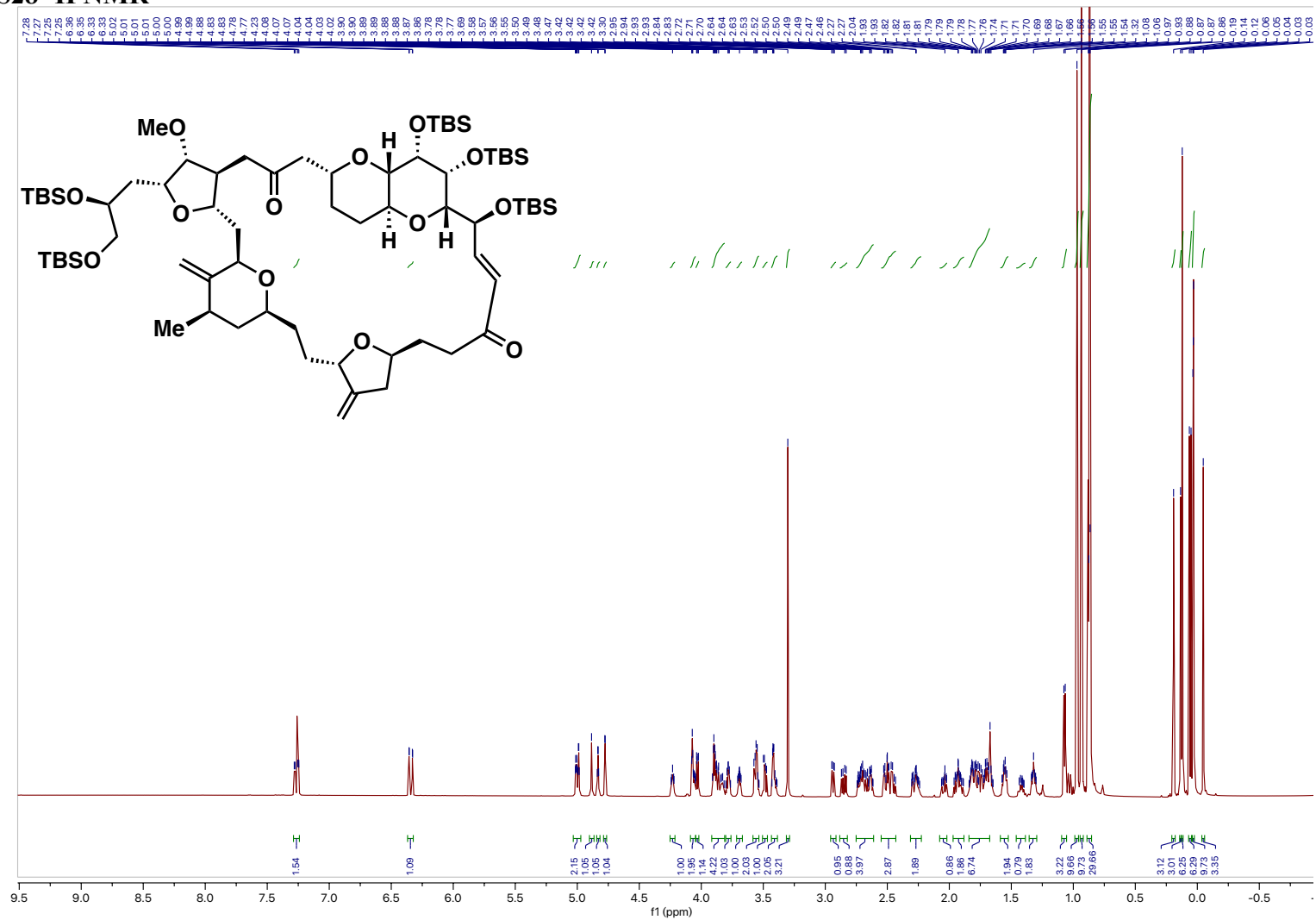
Compound 57b (more polar isomer) ¹H NMR



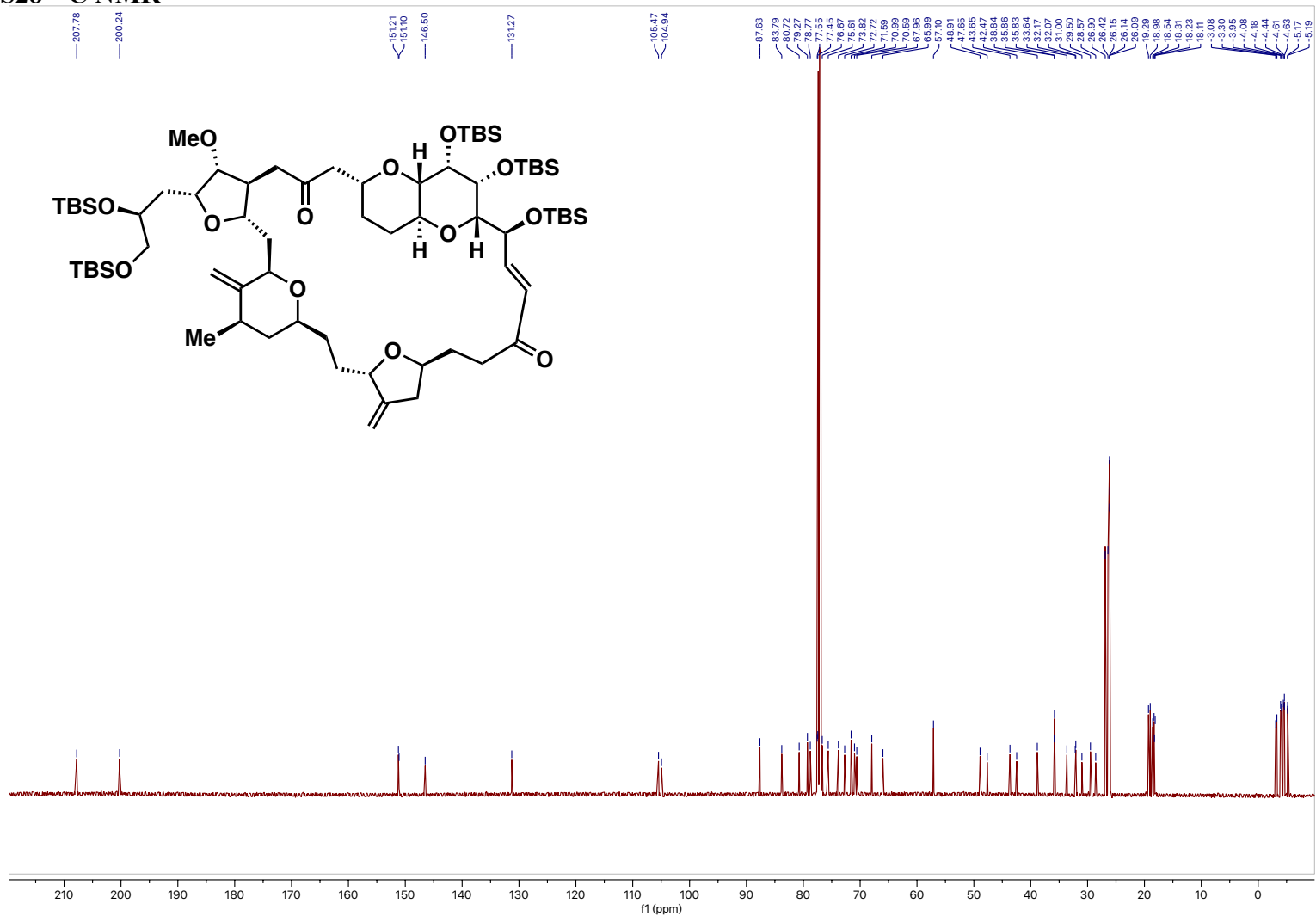
Compound 57b (more polar isomer) ^{13}C NMR



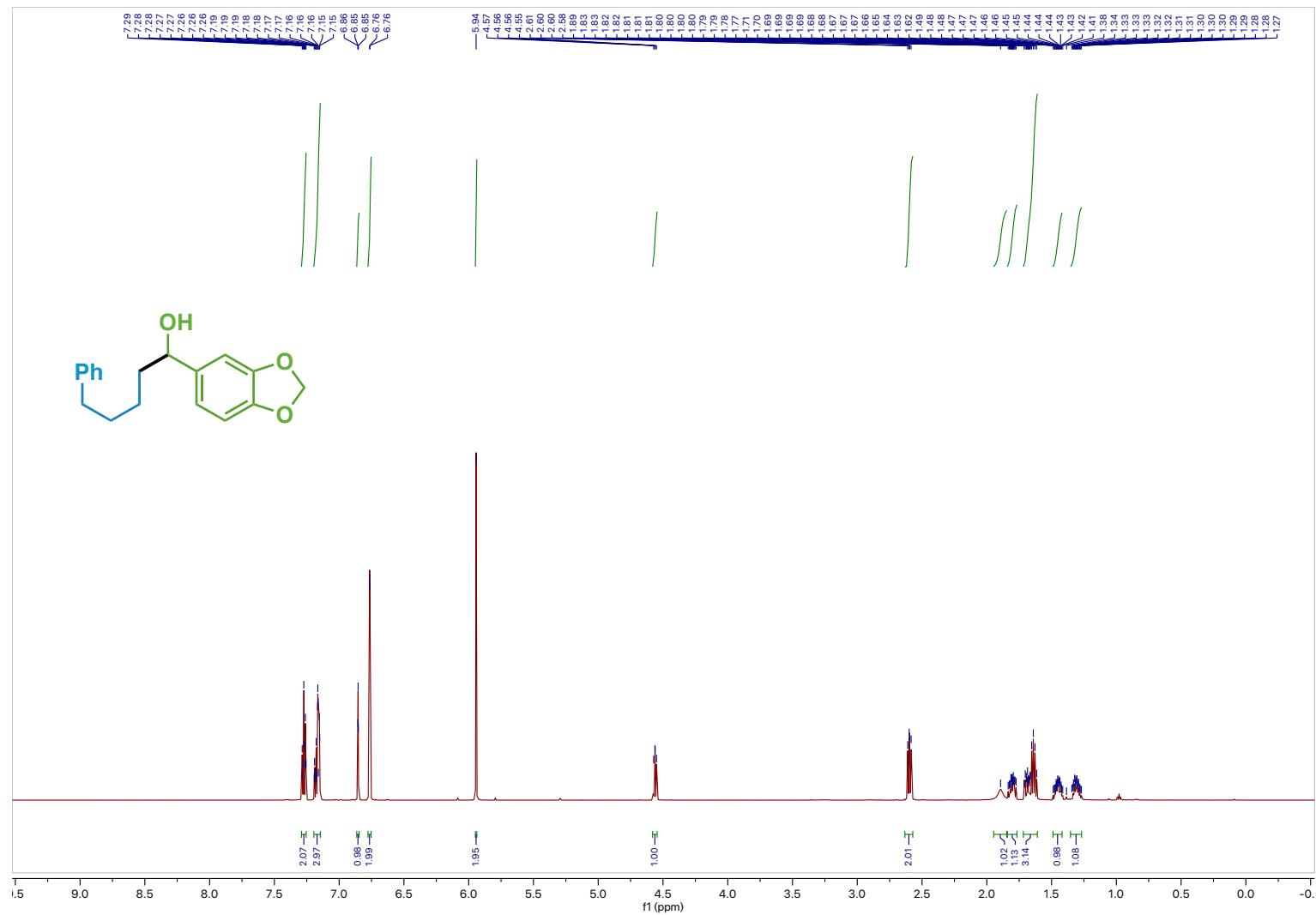
Compound S28 ¹H NMR



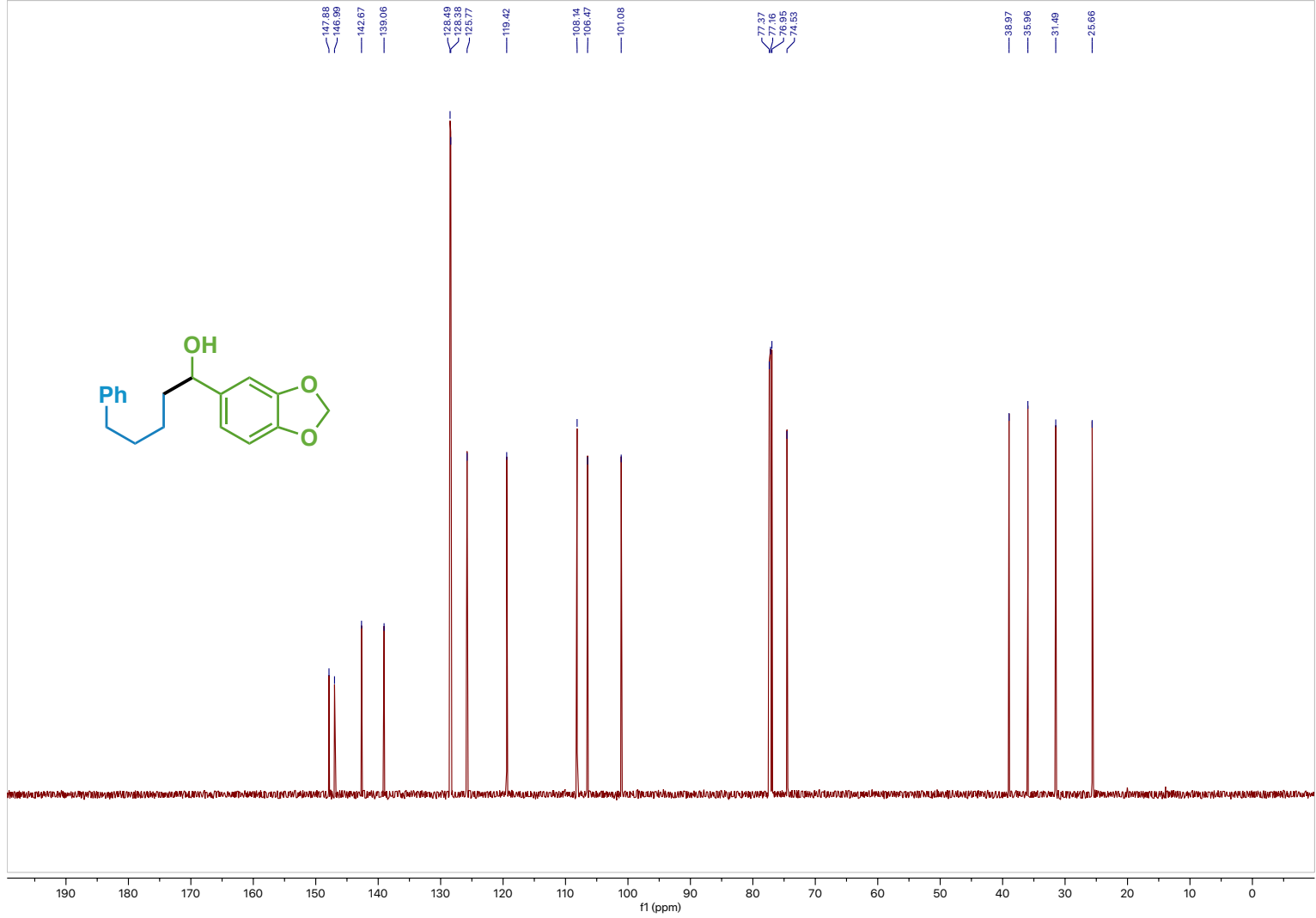
Compound S28 ¹³C NMR



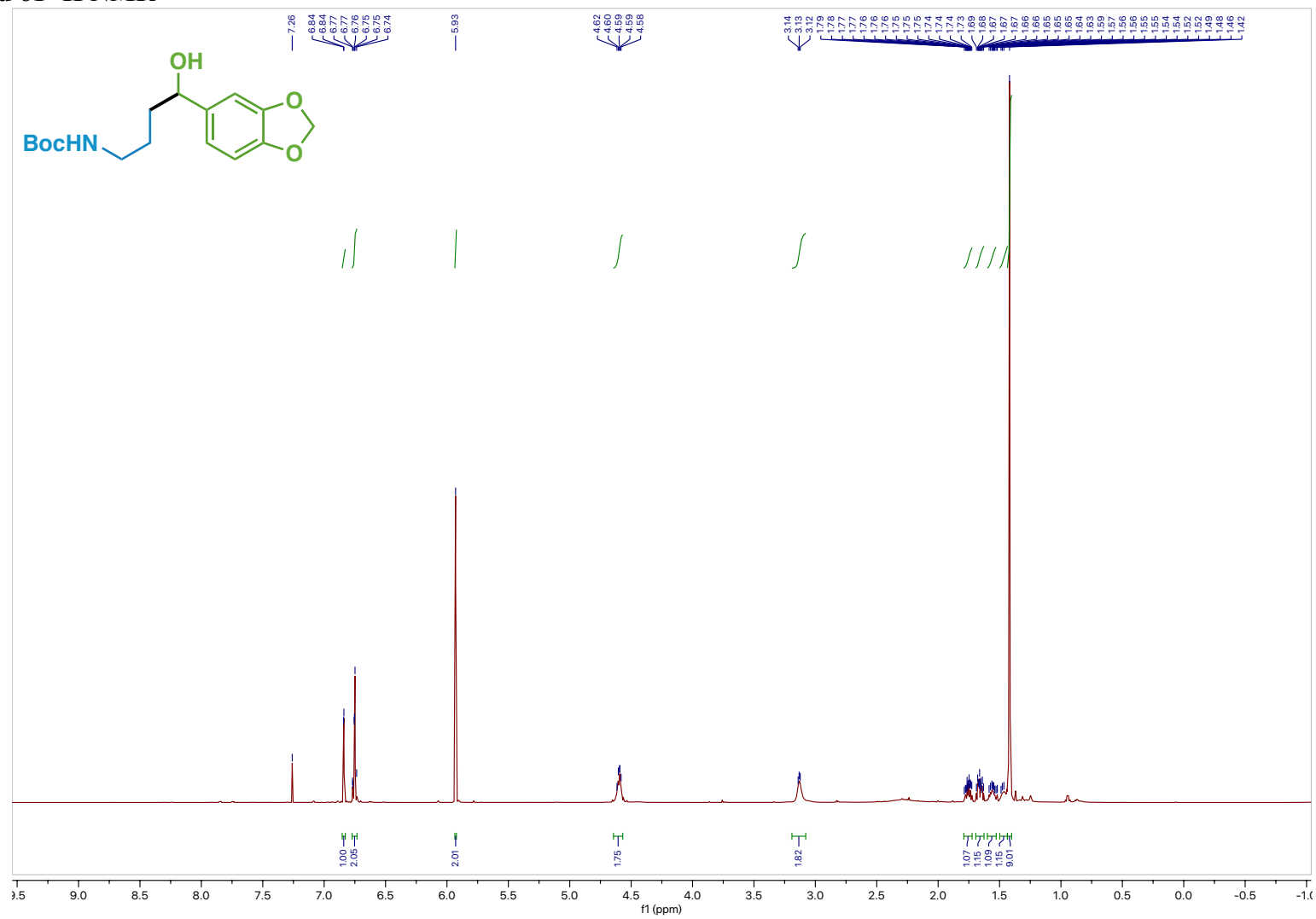
Compound 60 ¹H NMR



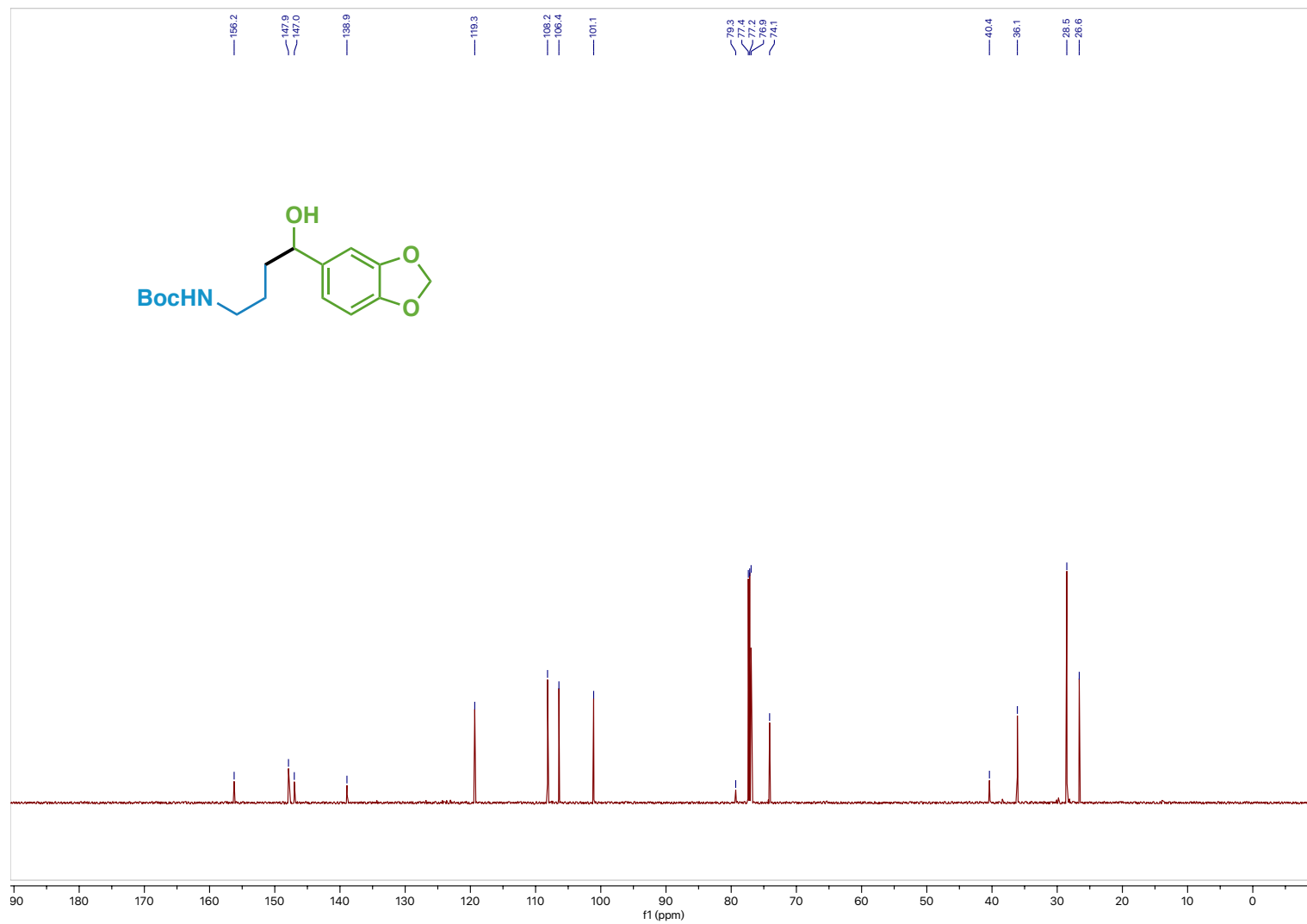
Compound 60 ¹³C NMR



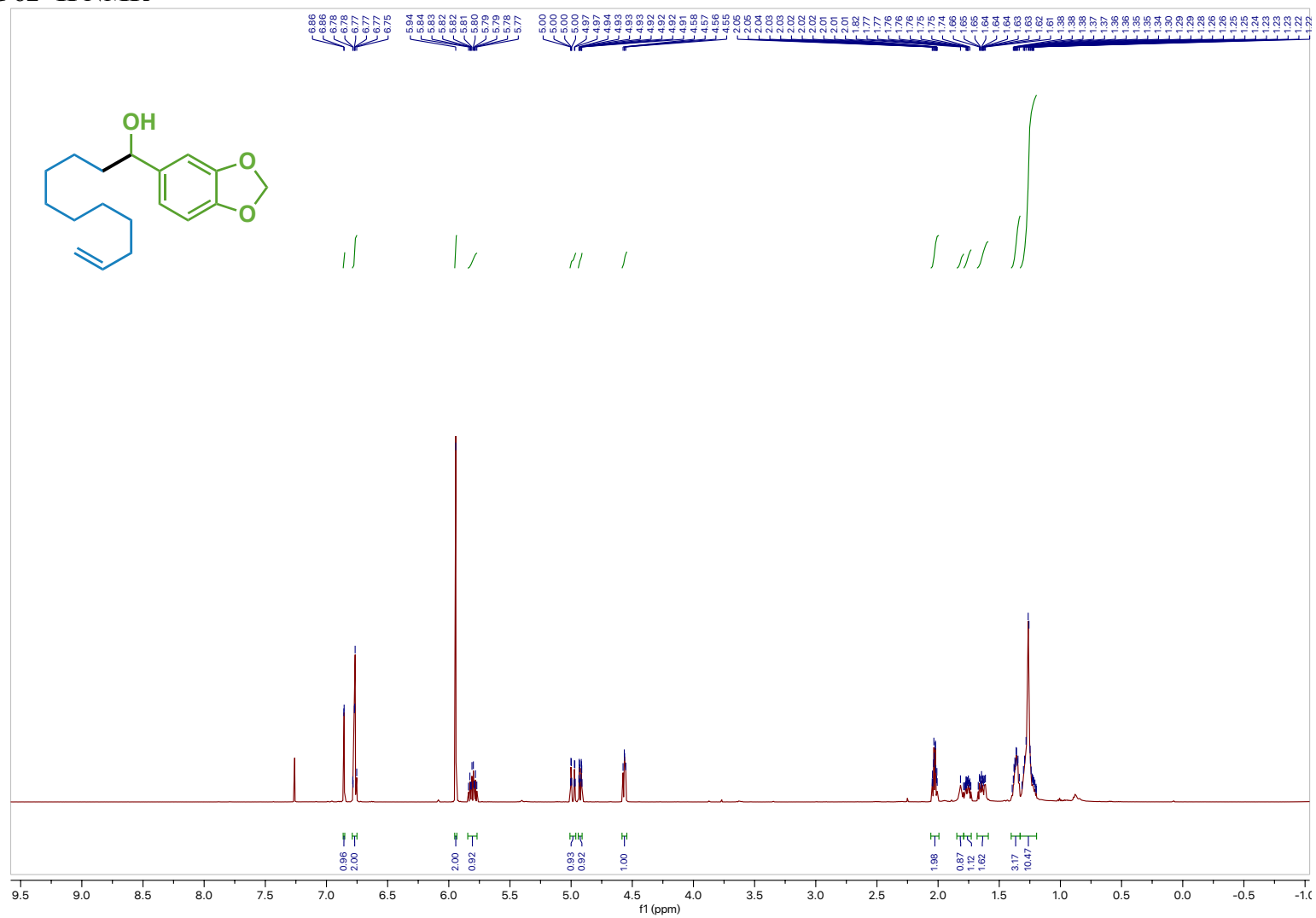
Compound 61 ¹H NMR



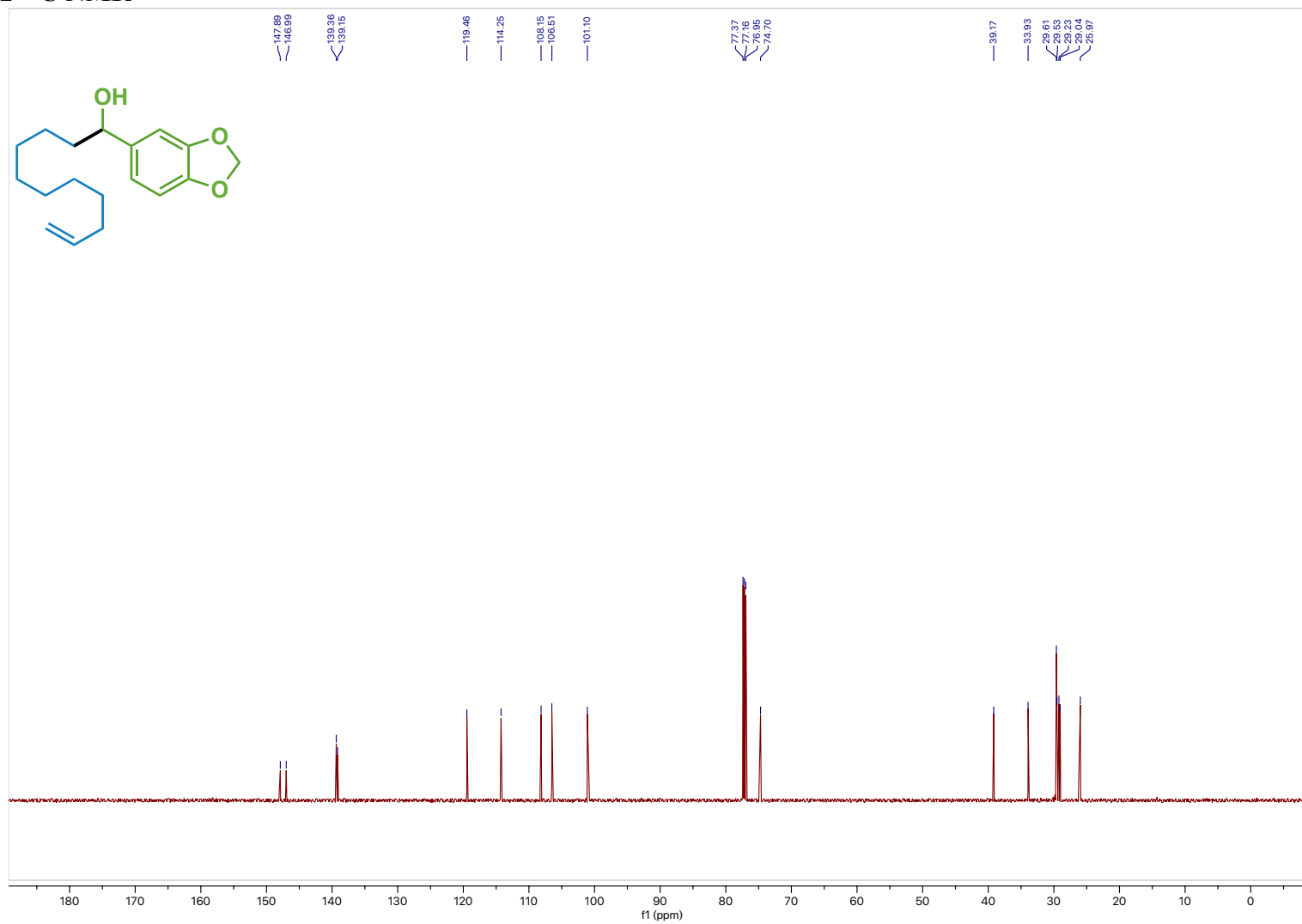
Compound 61 ¹³C NMR



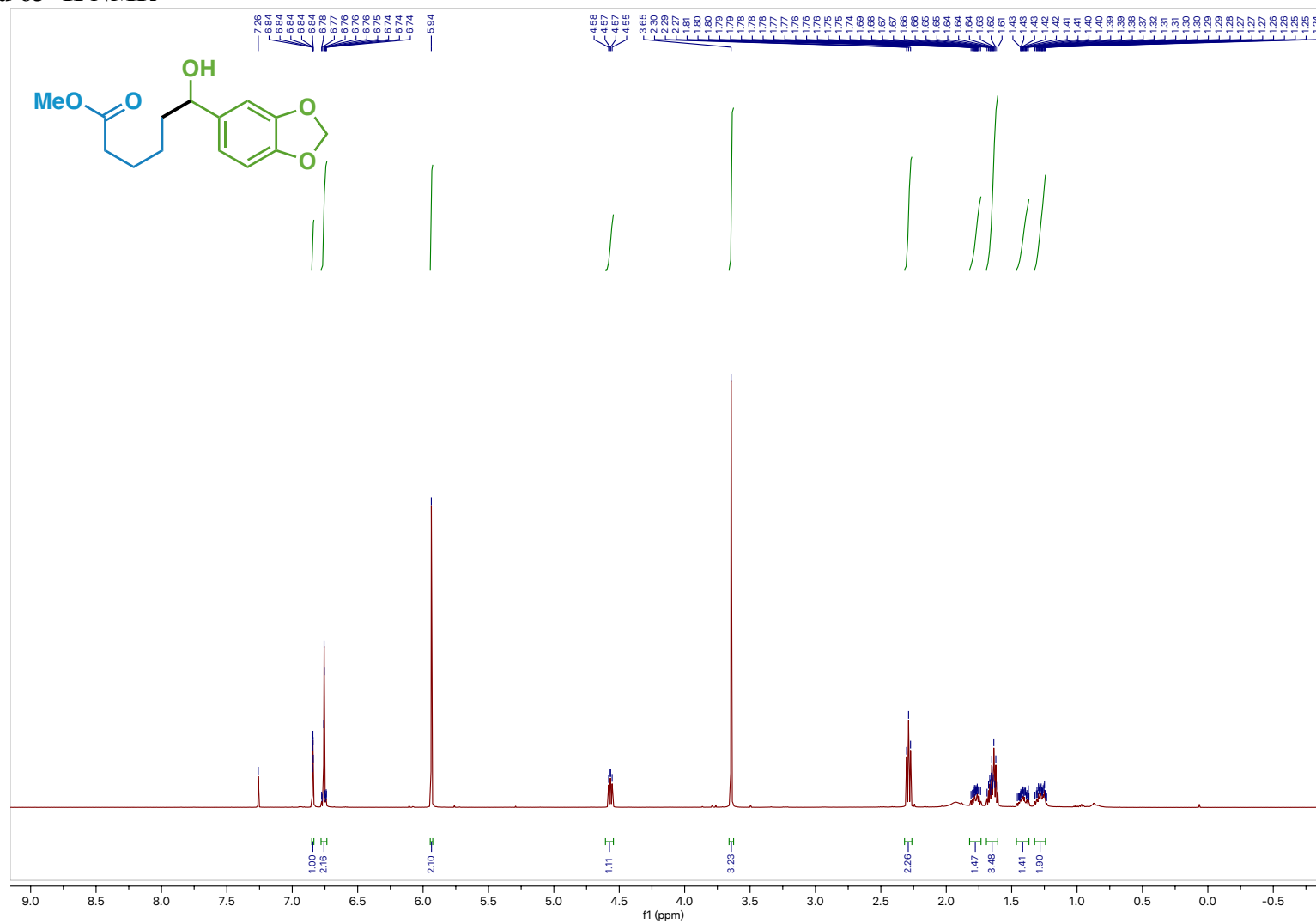
Compound 62 ¹H NMR



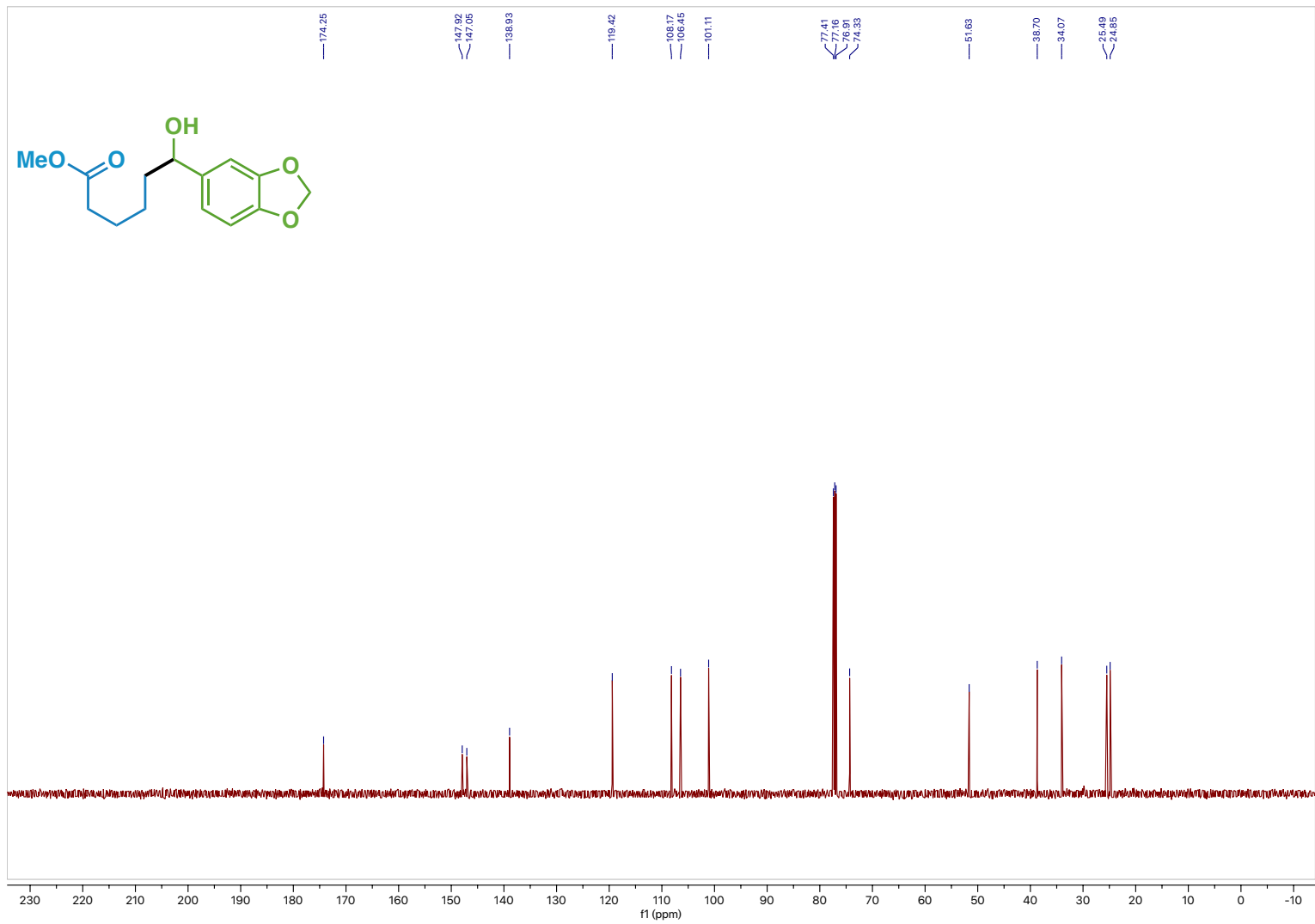
Compound 62 ¹³C NMR



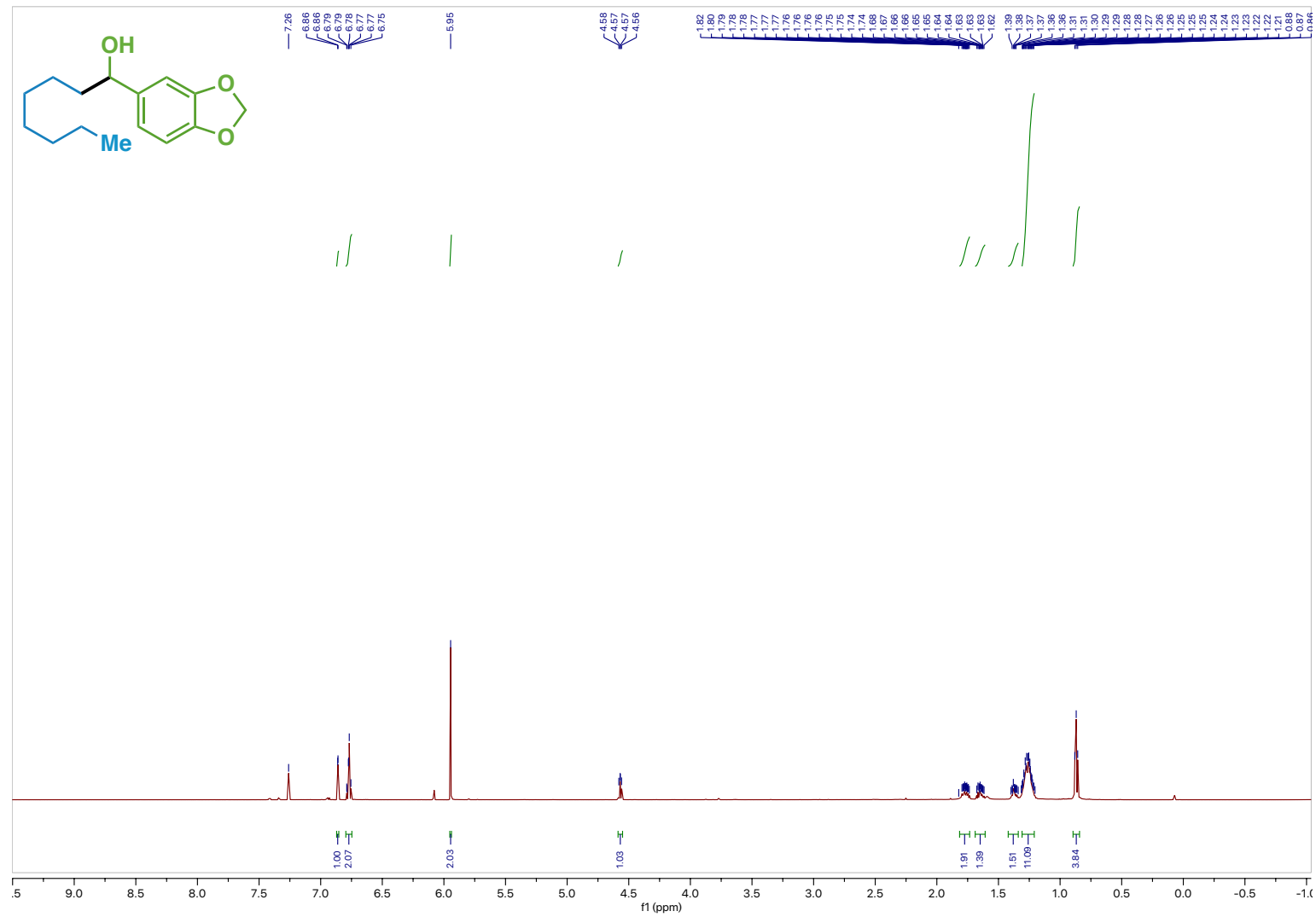
Compound 63 ¹H NMR



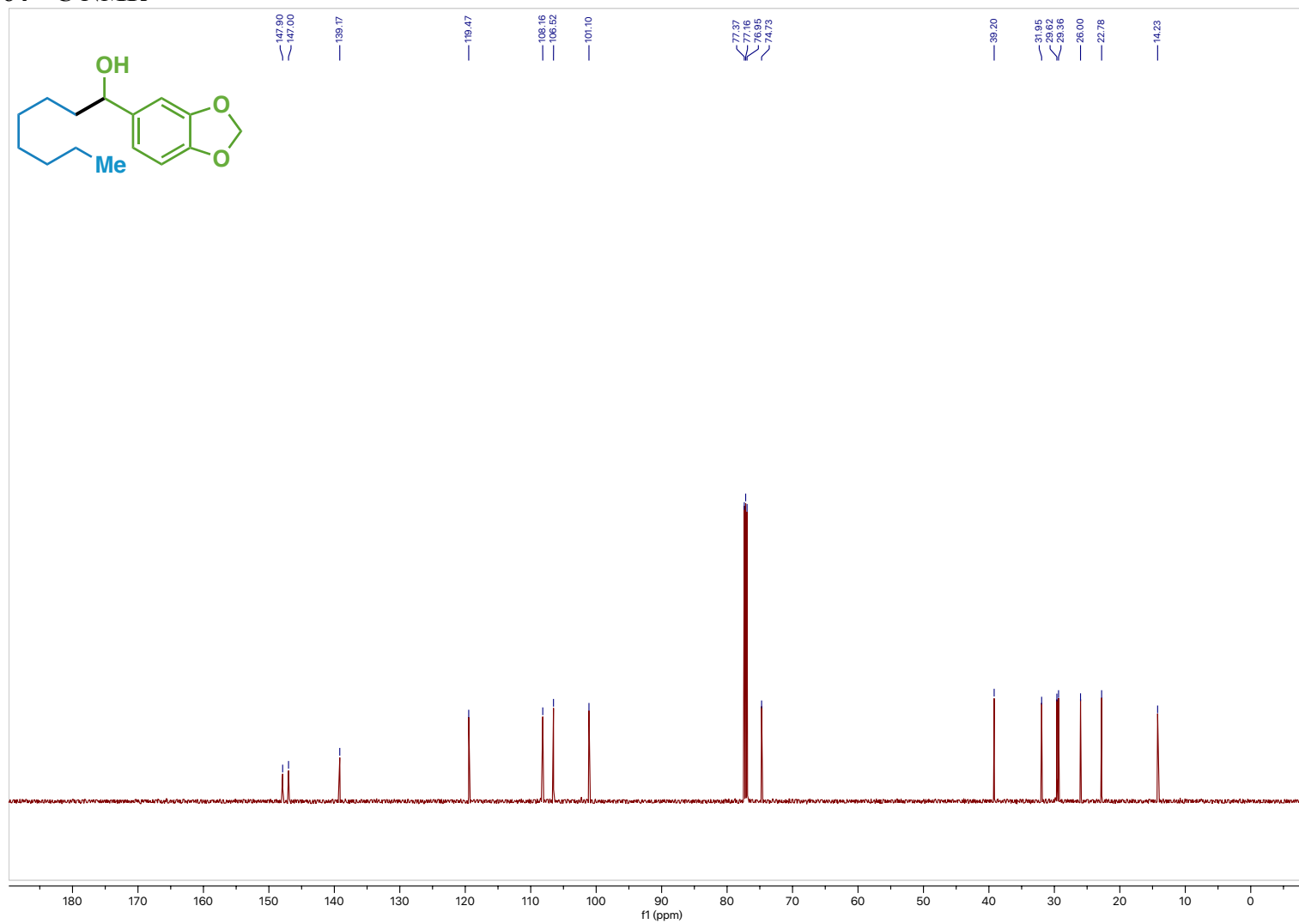
Compound 63 ¹³C NMR



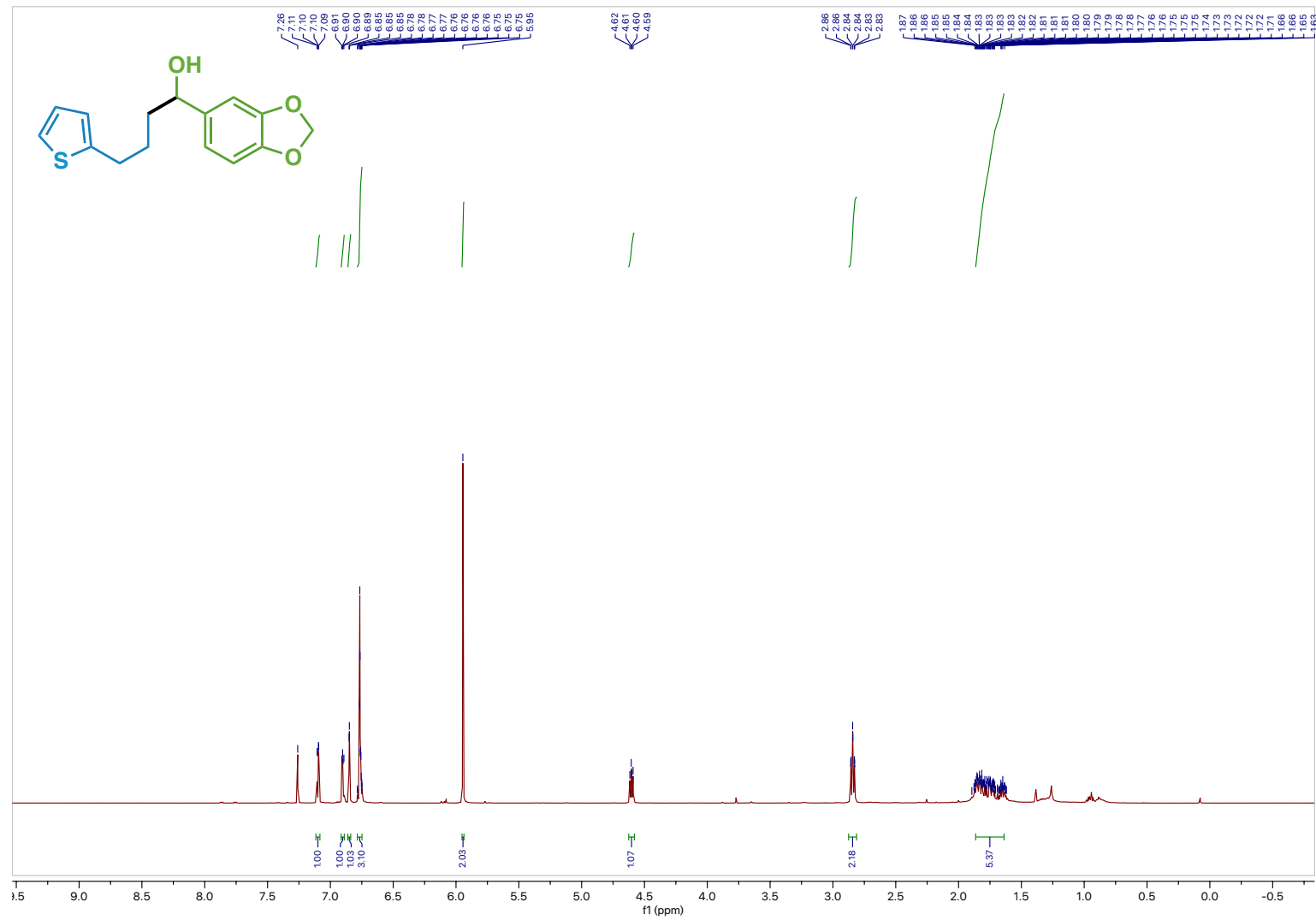
Compound 64 ¹H NMR



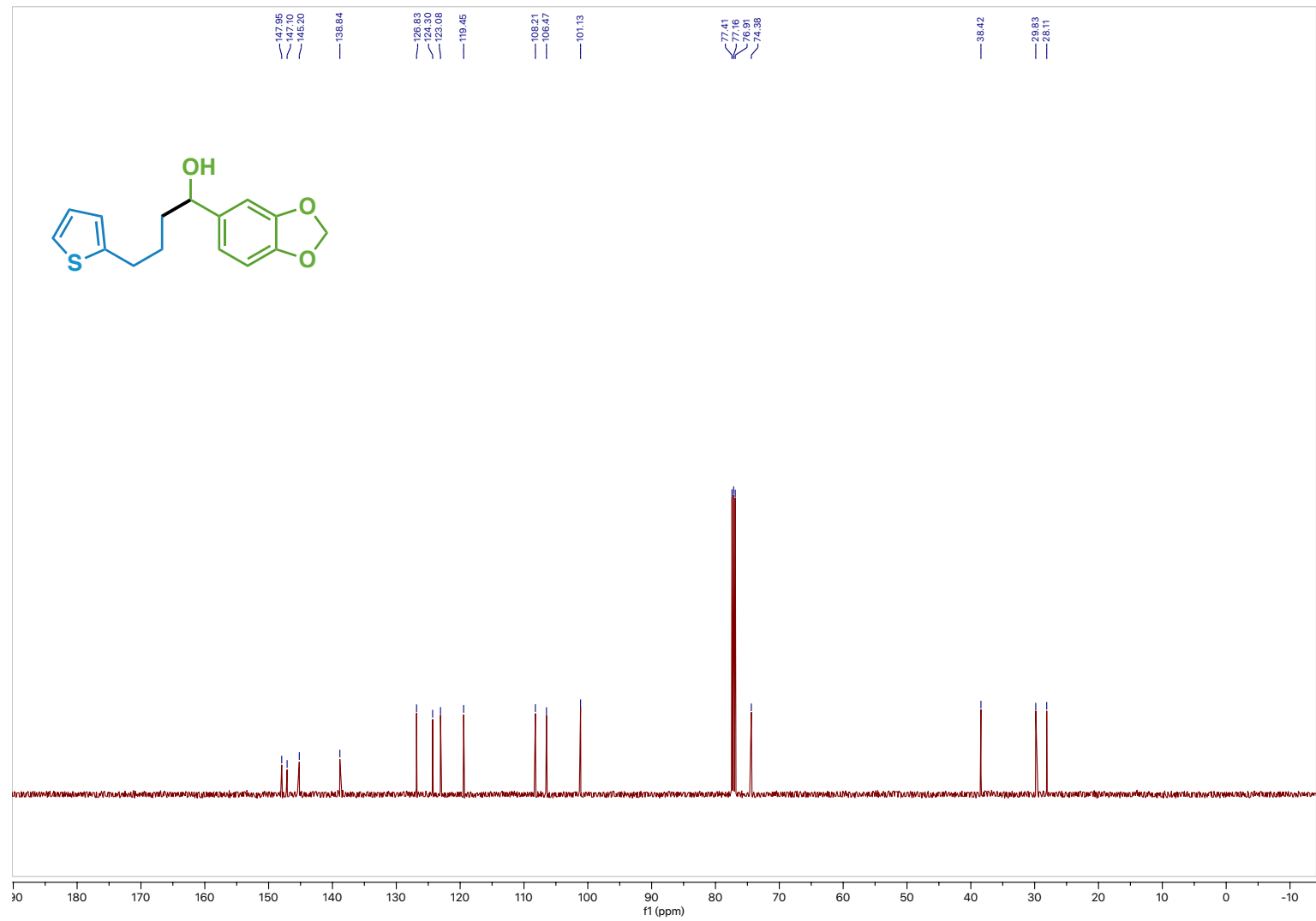
Compound 64 ¹³C NMR



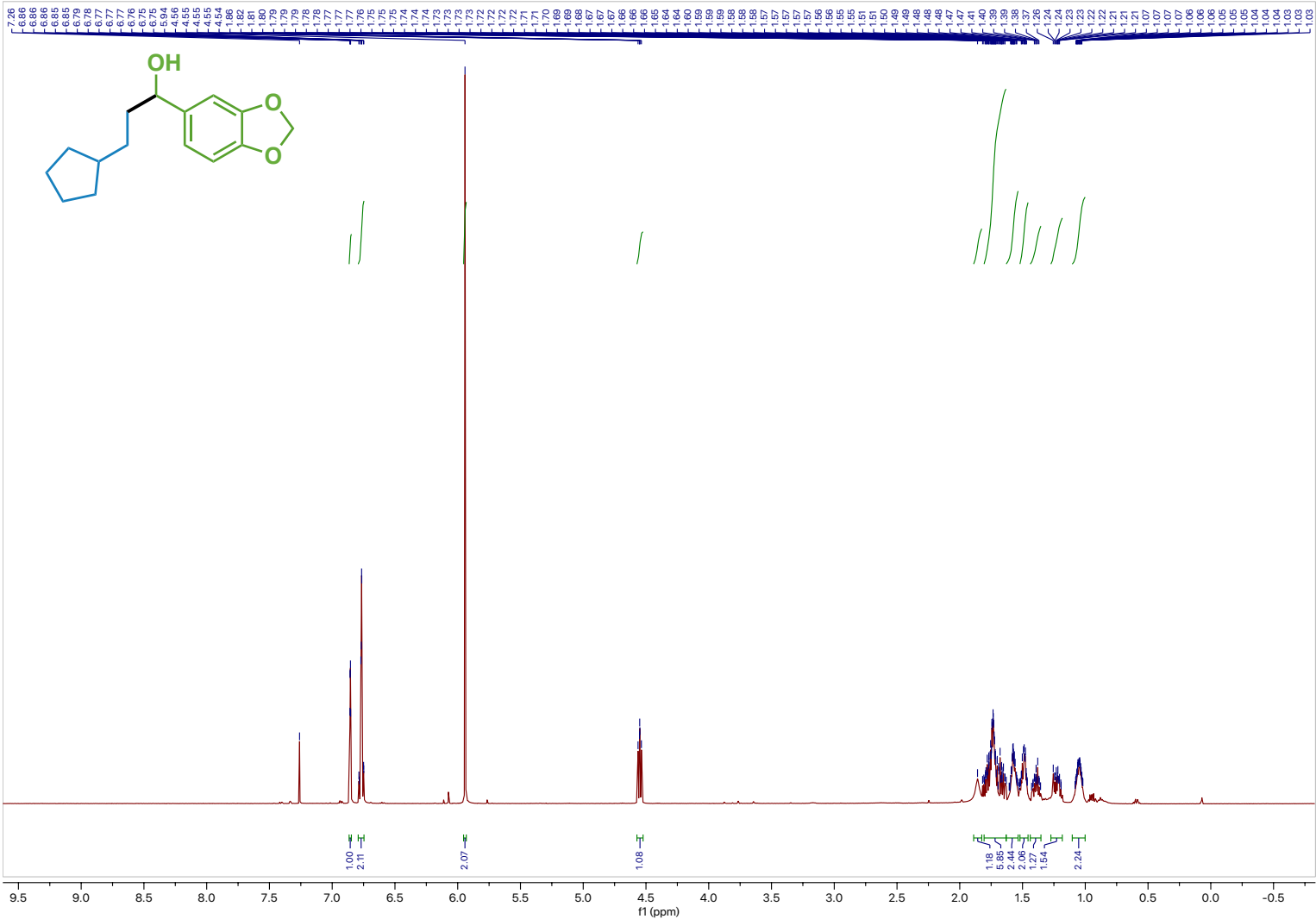
Compound 65 ¹H NMR



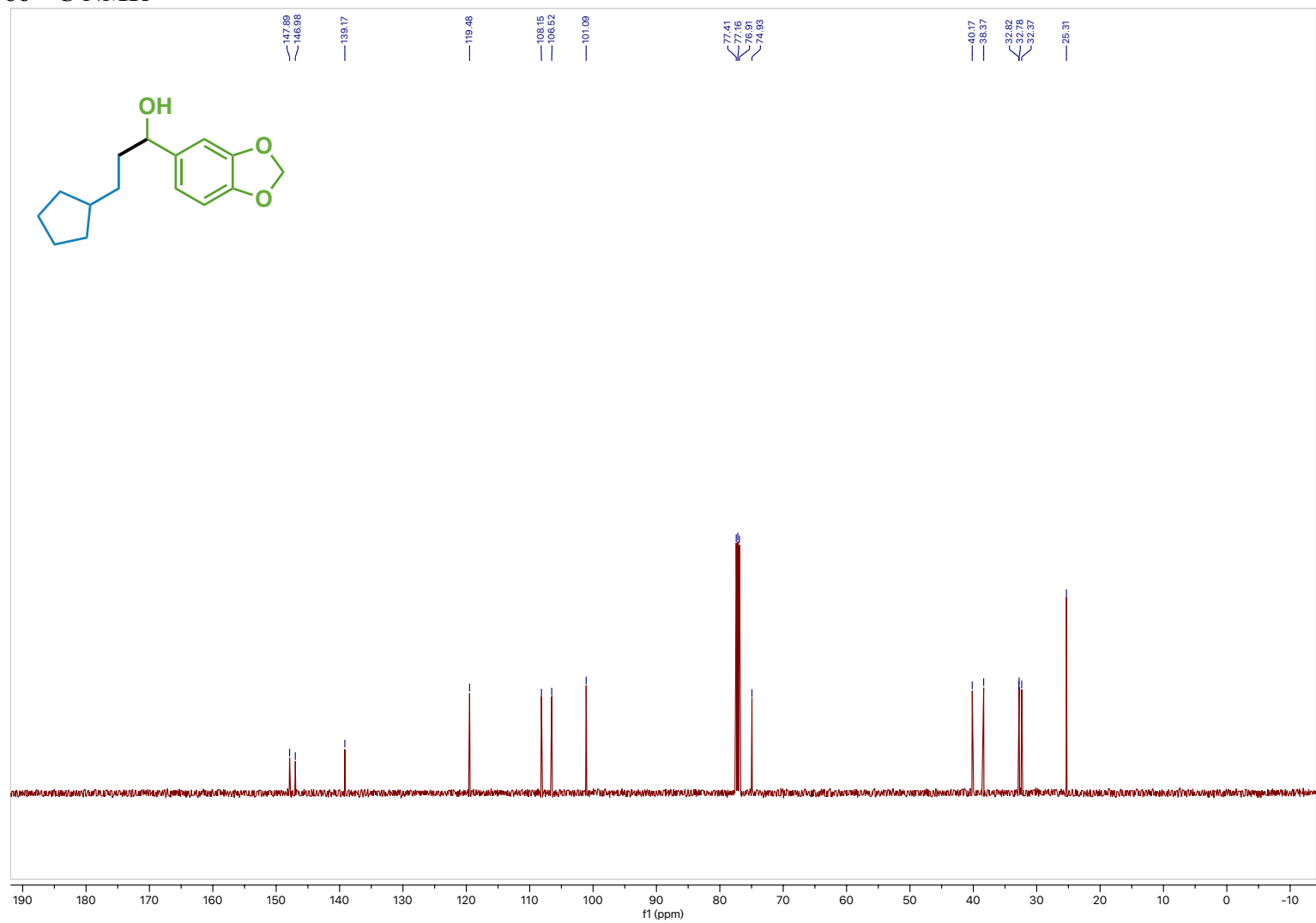
Compound 65 ¹³C NMR



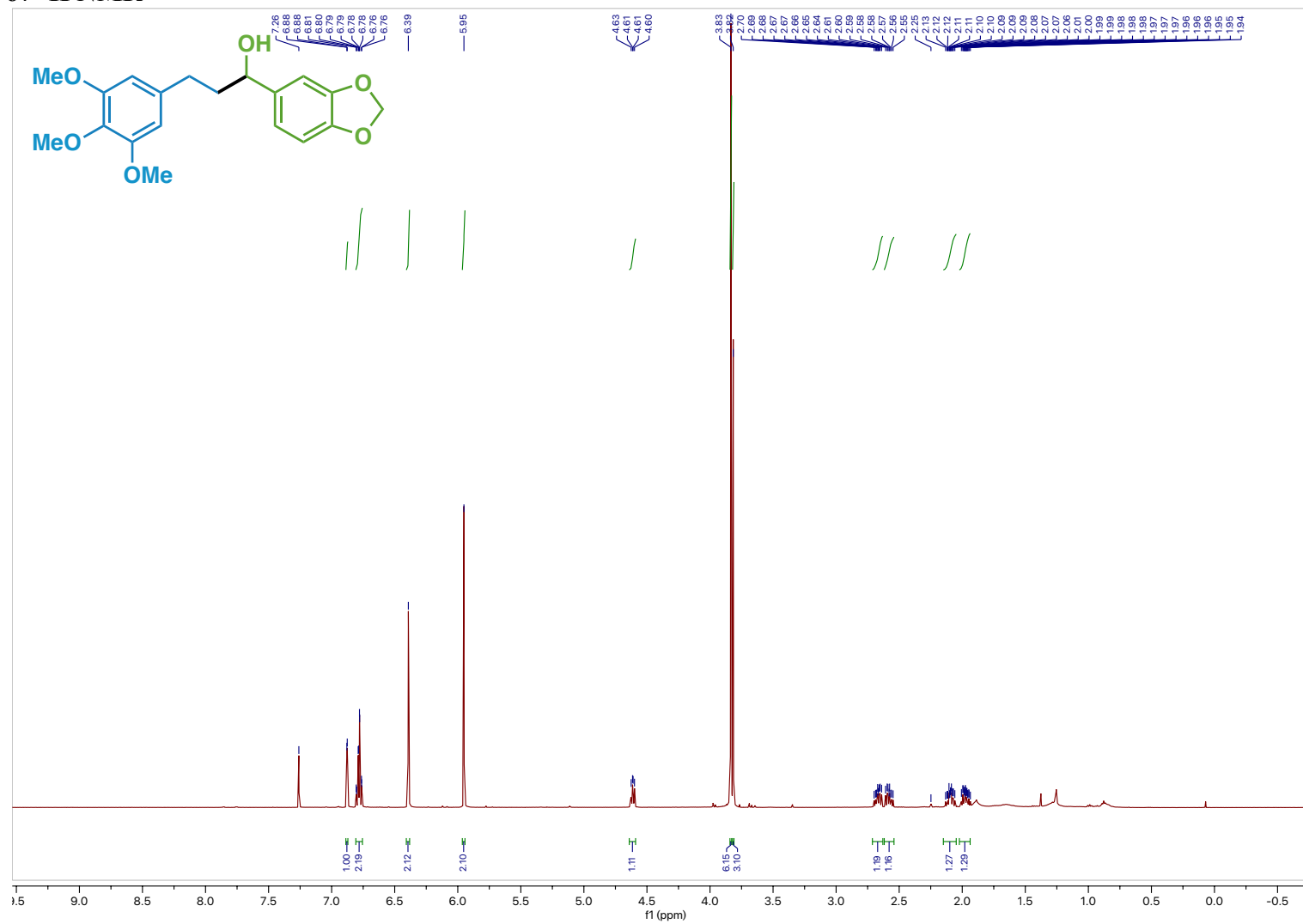
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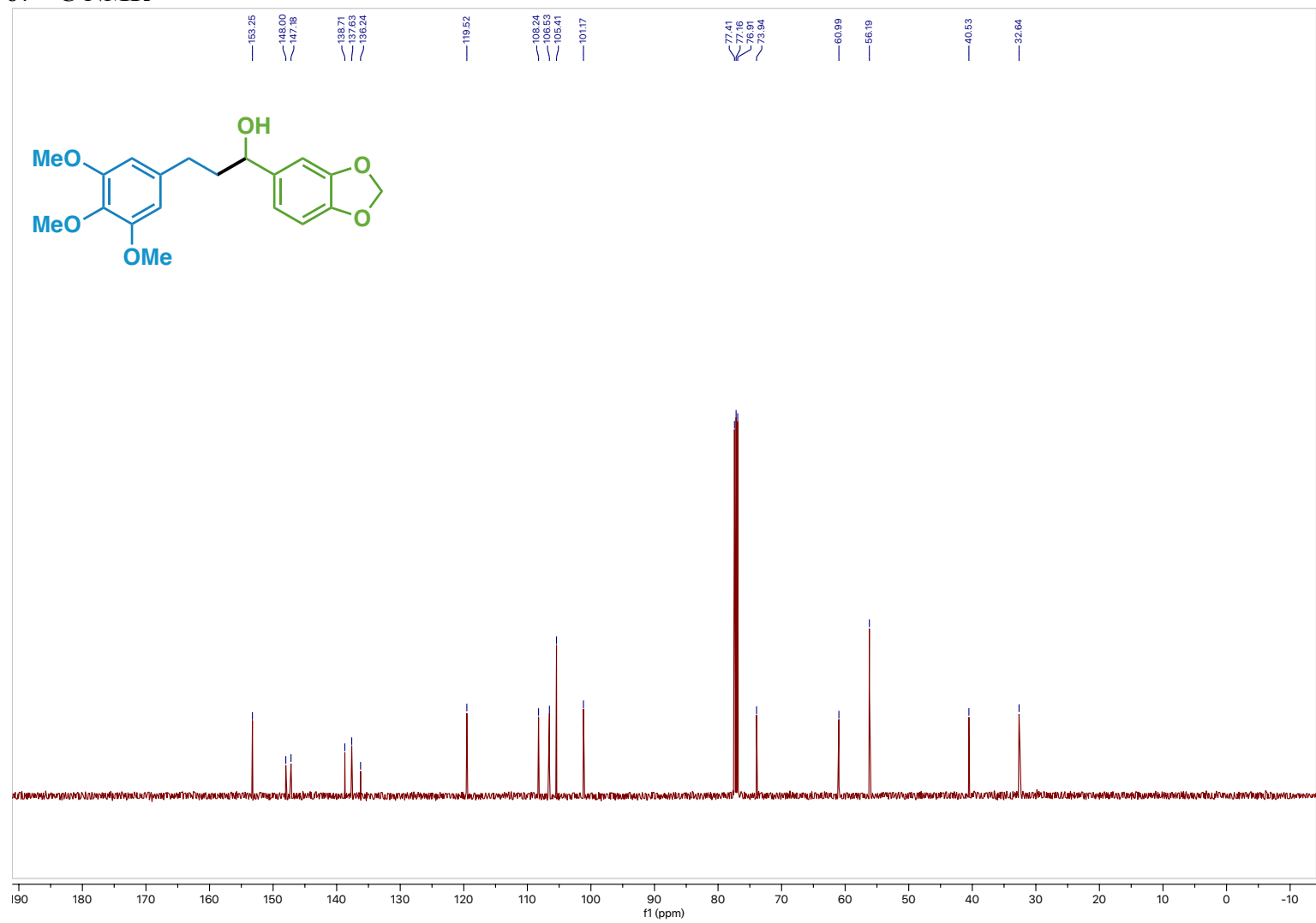
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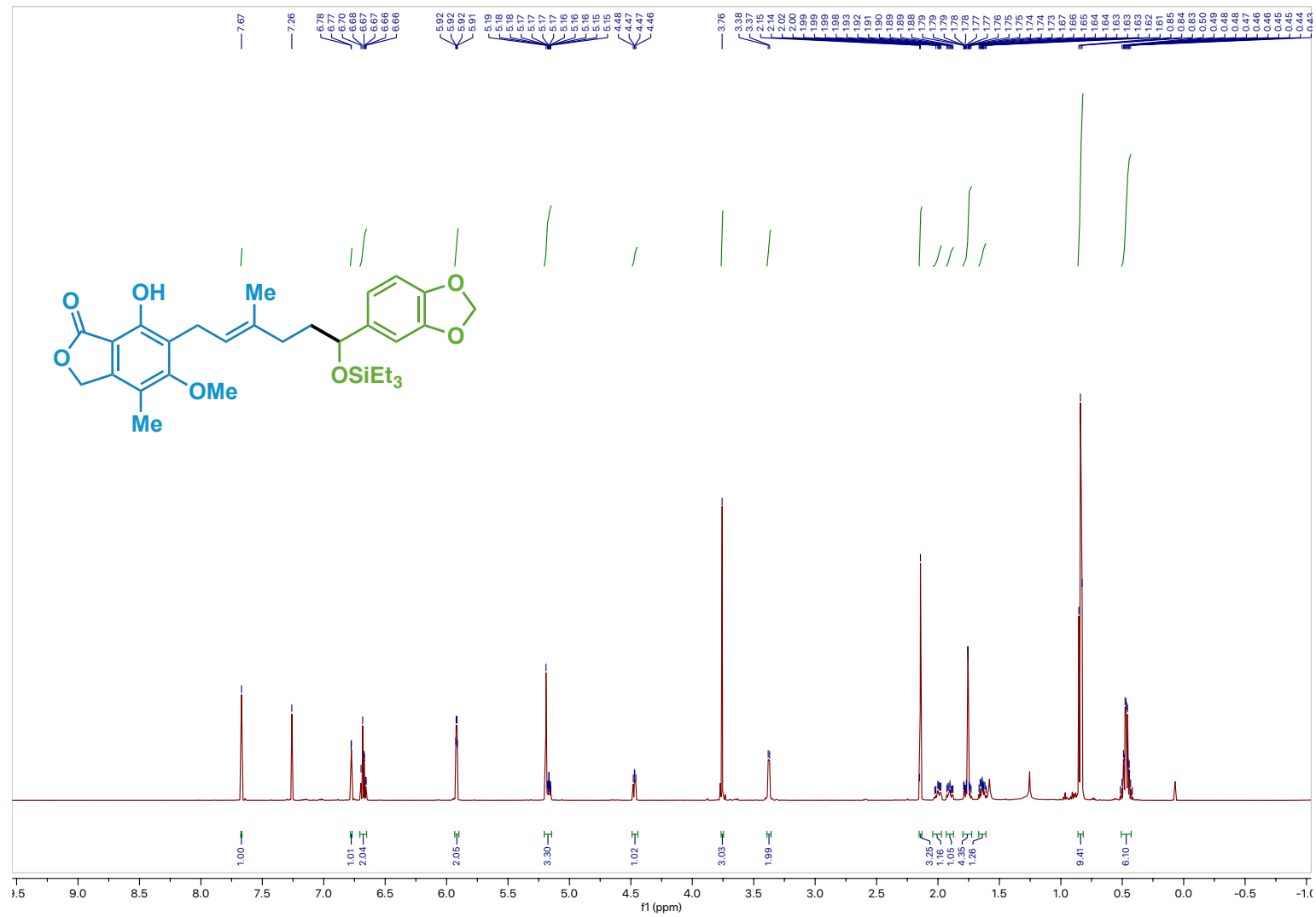
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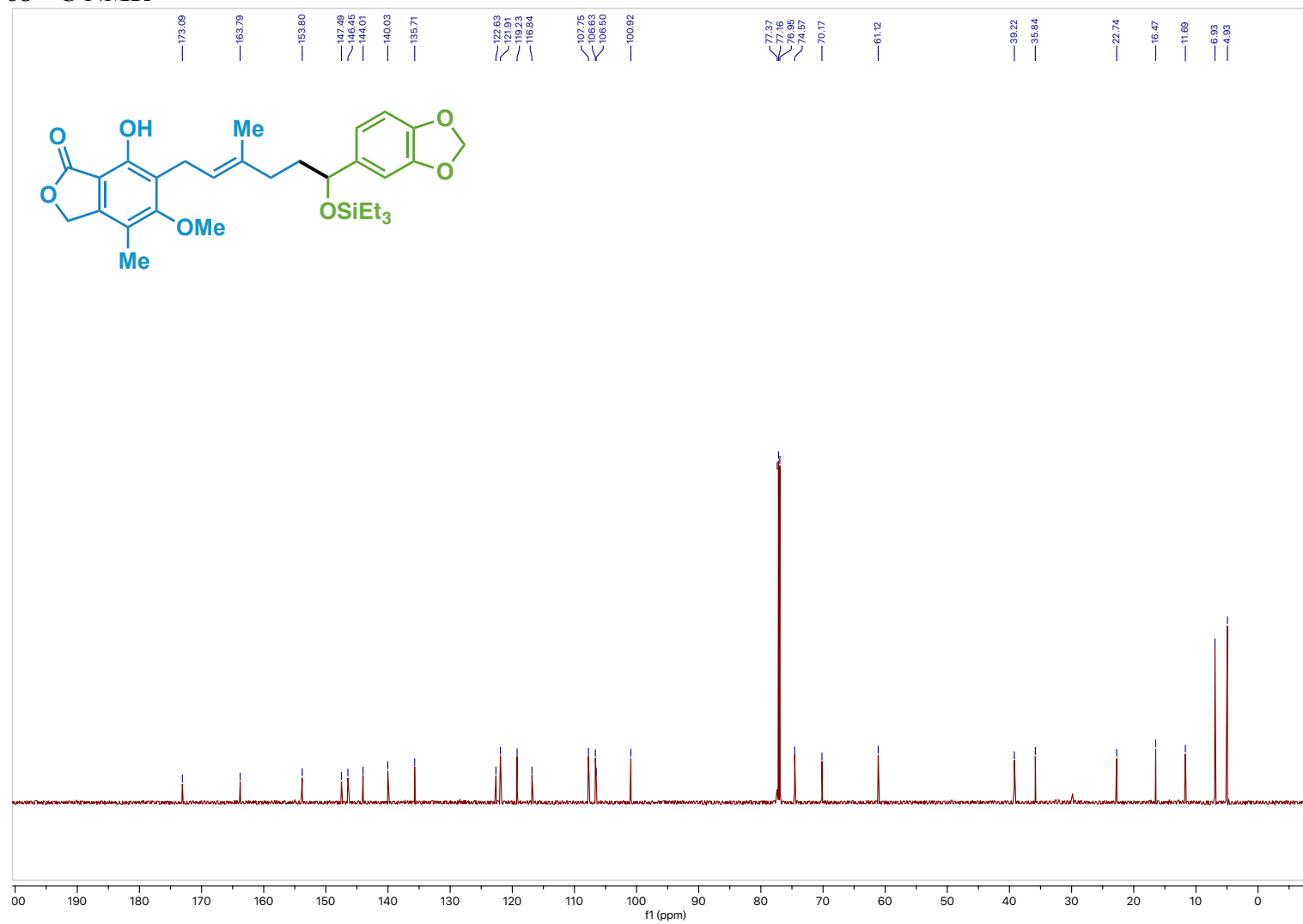
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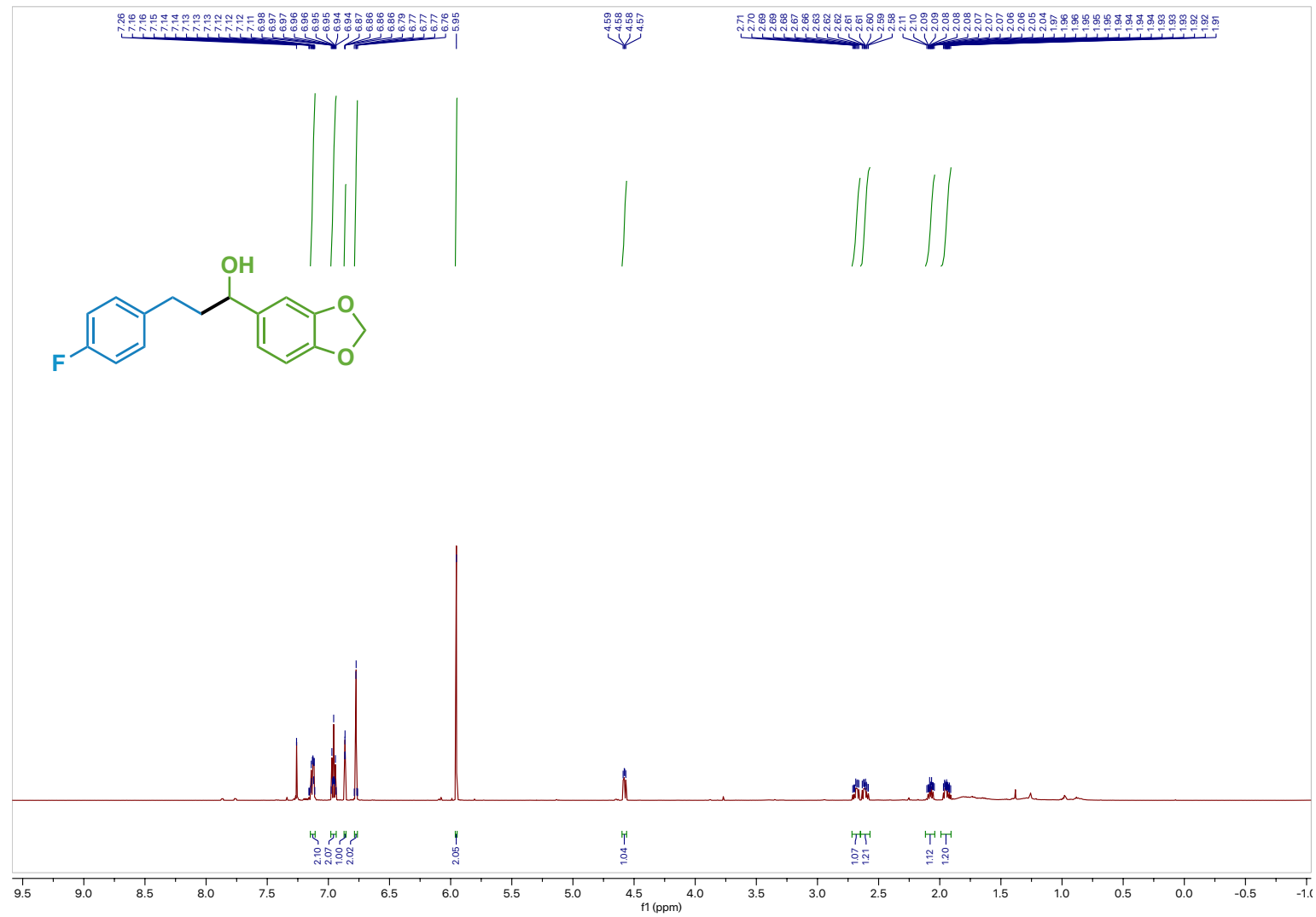
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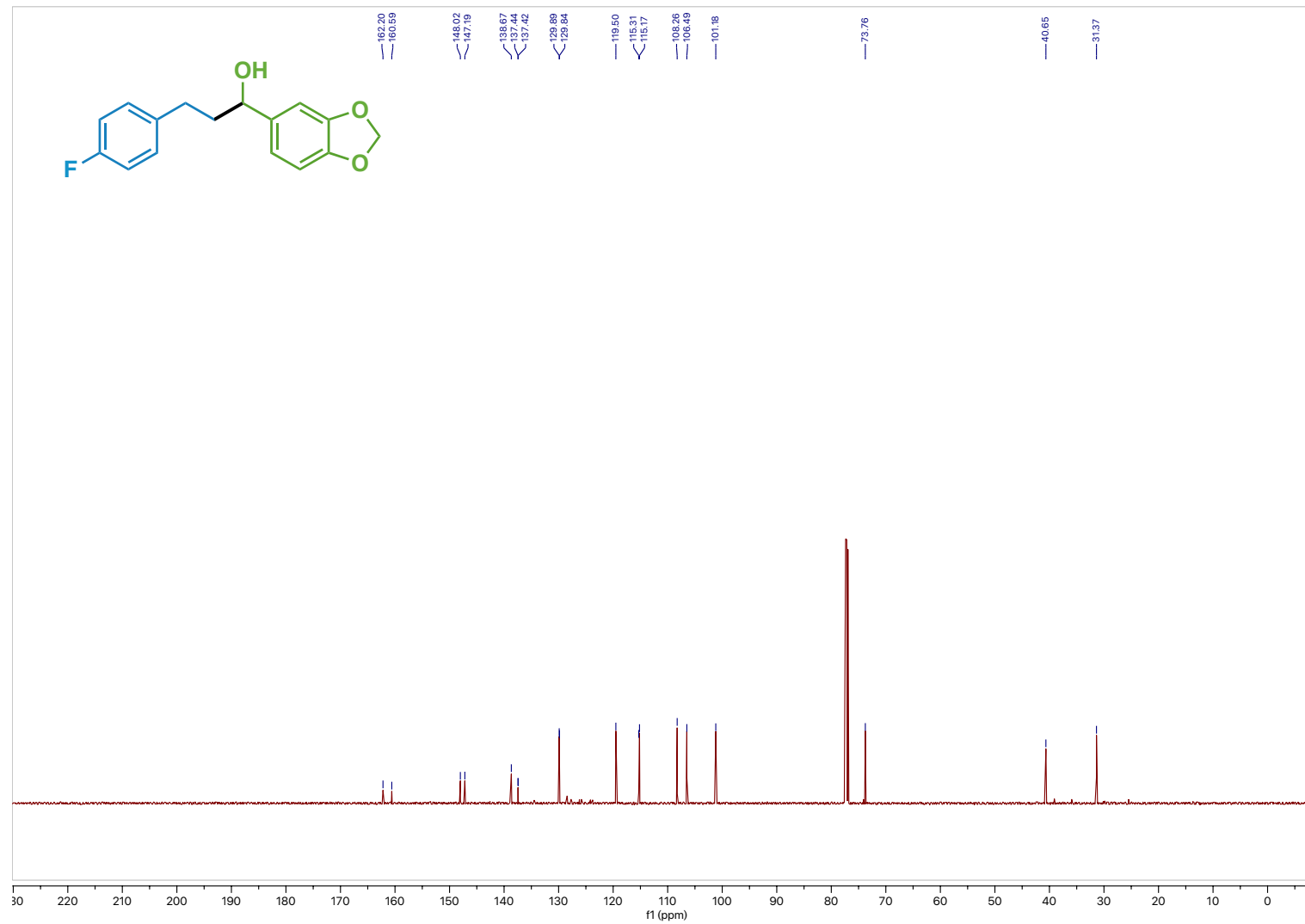
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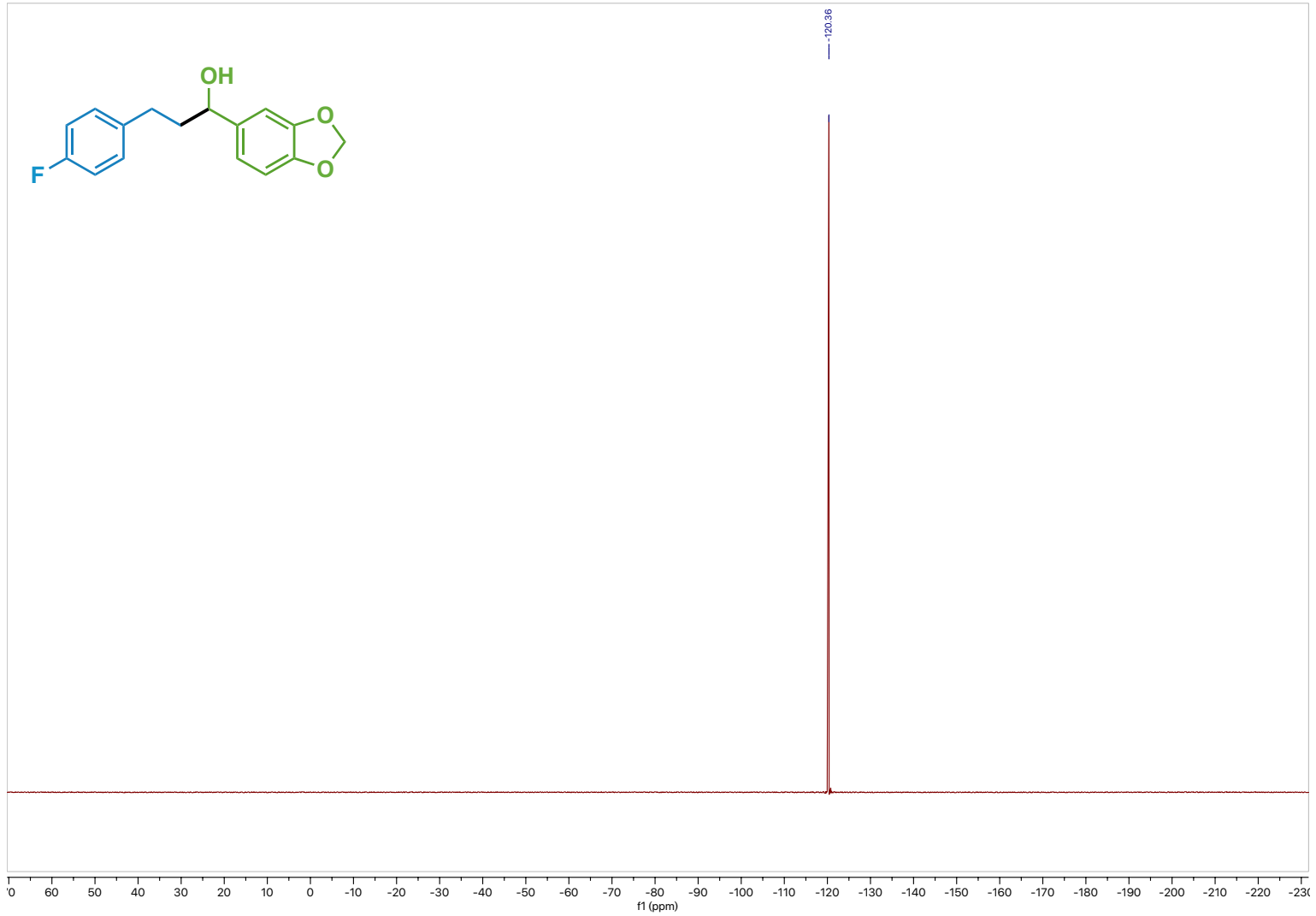
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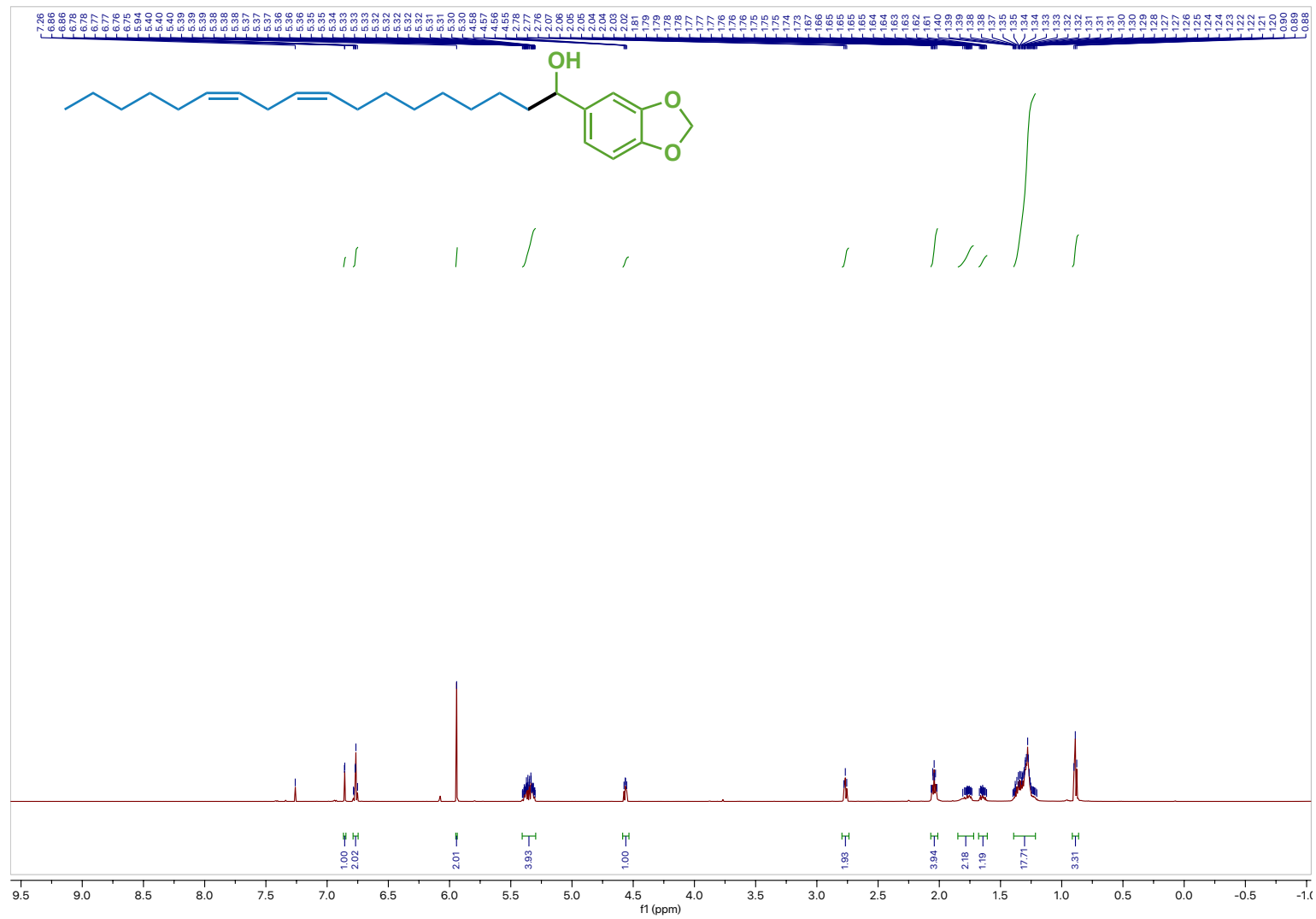
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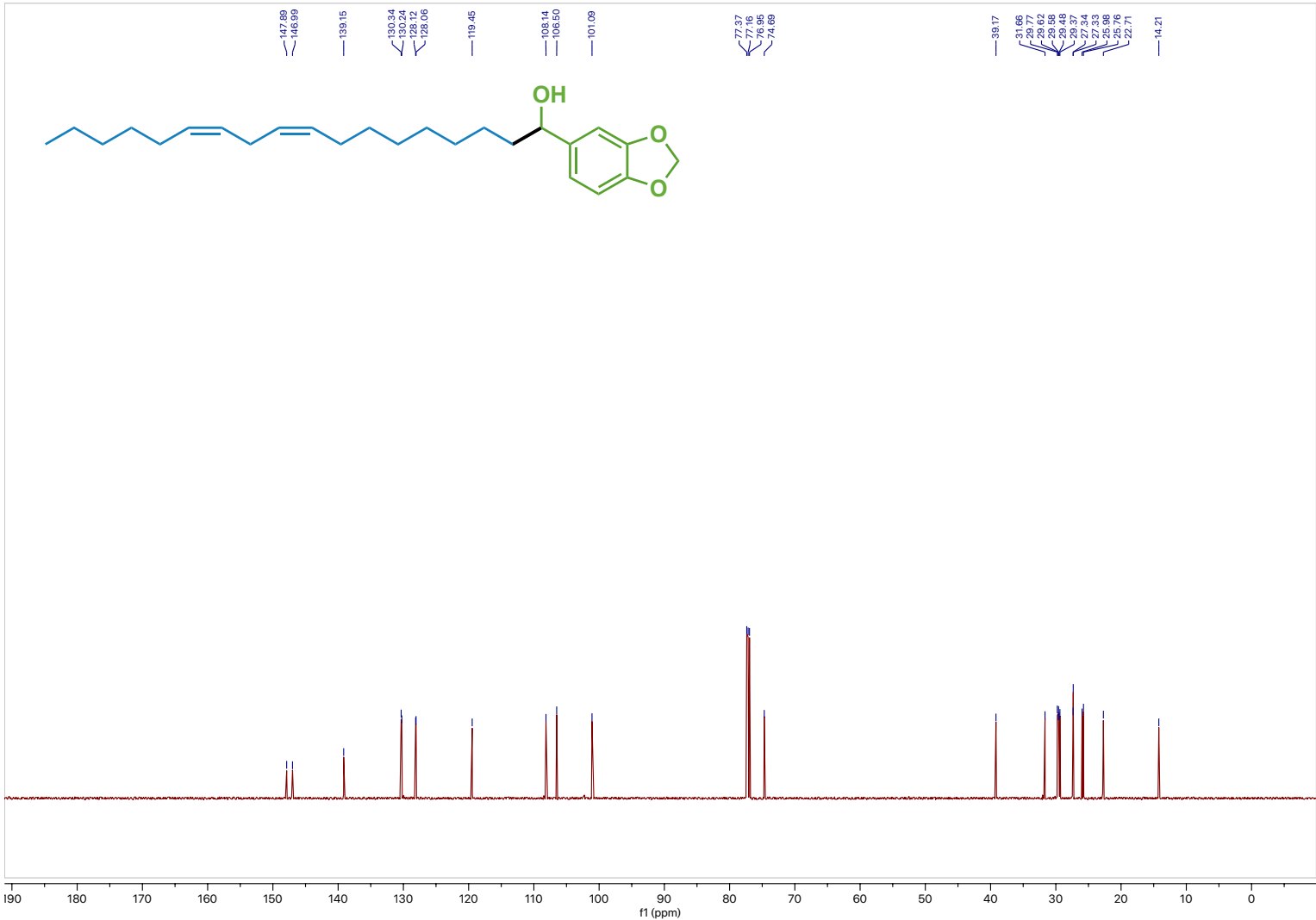
Compound 69 ¹⁹F NMR



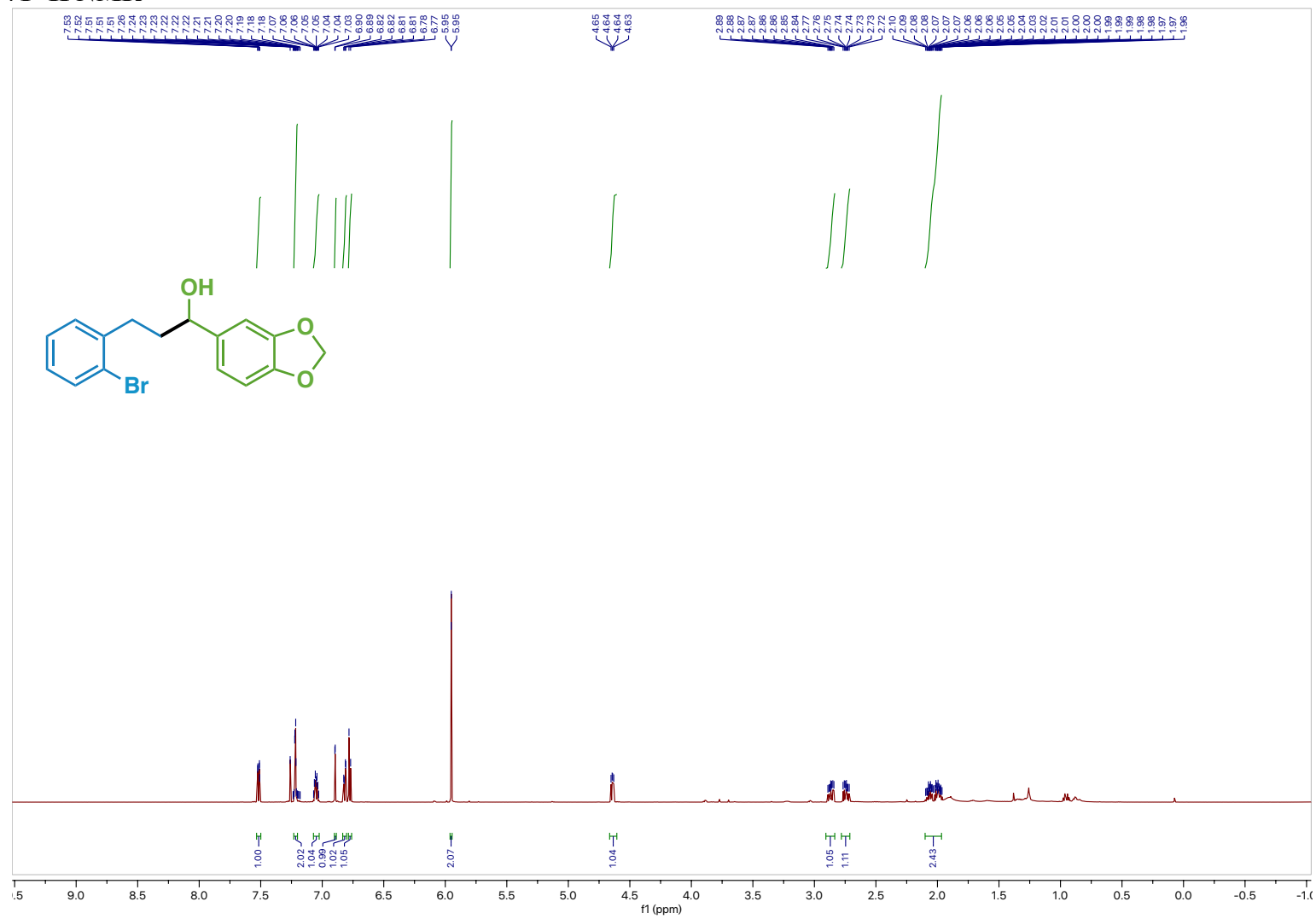
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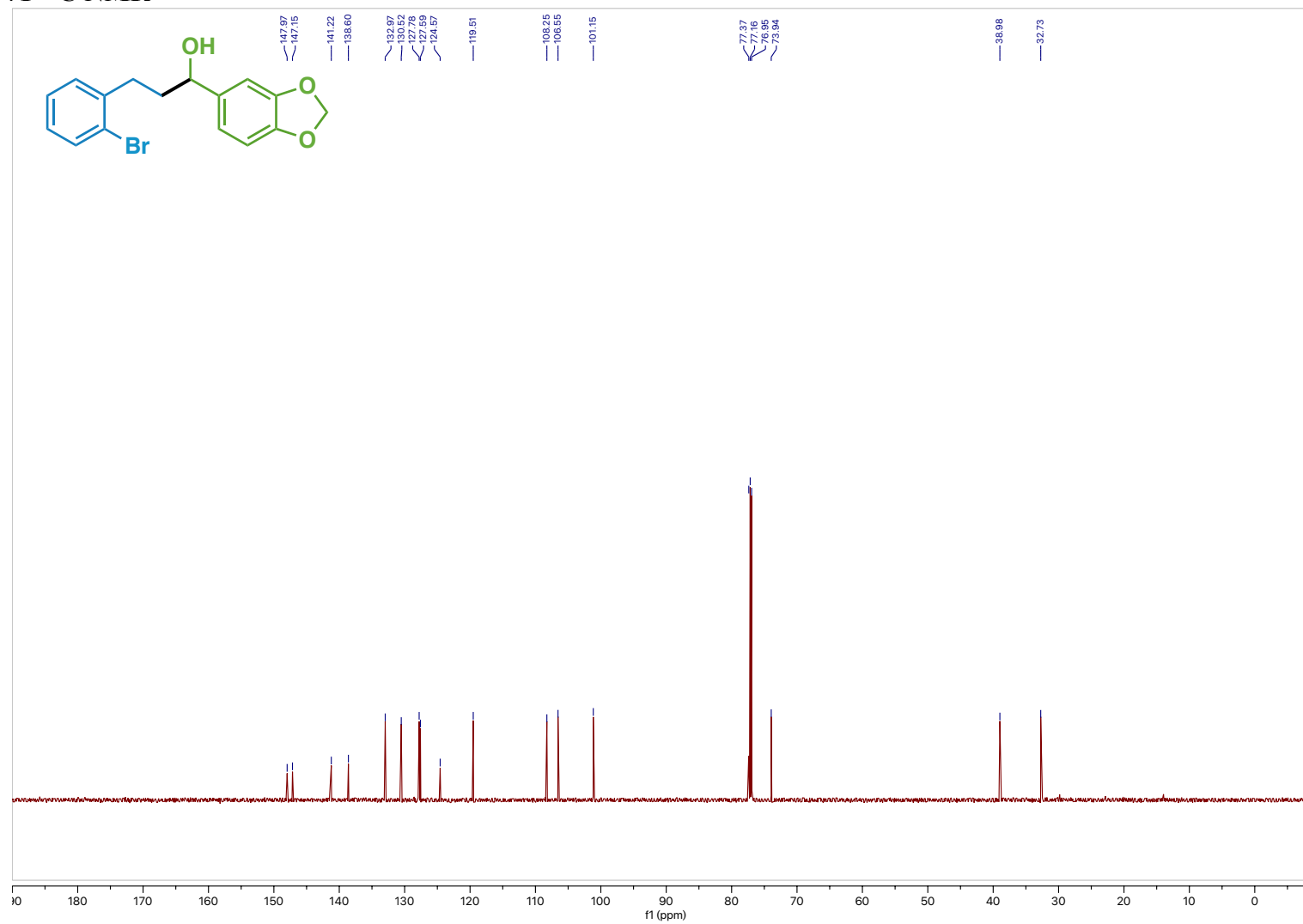
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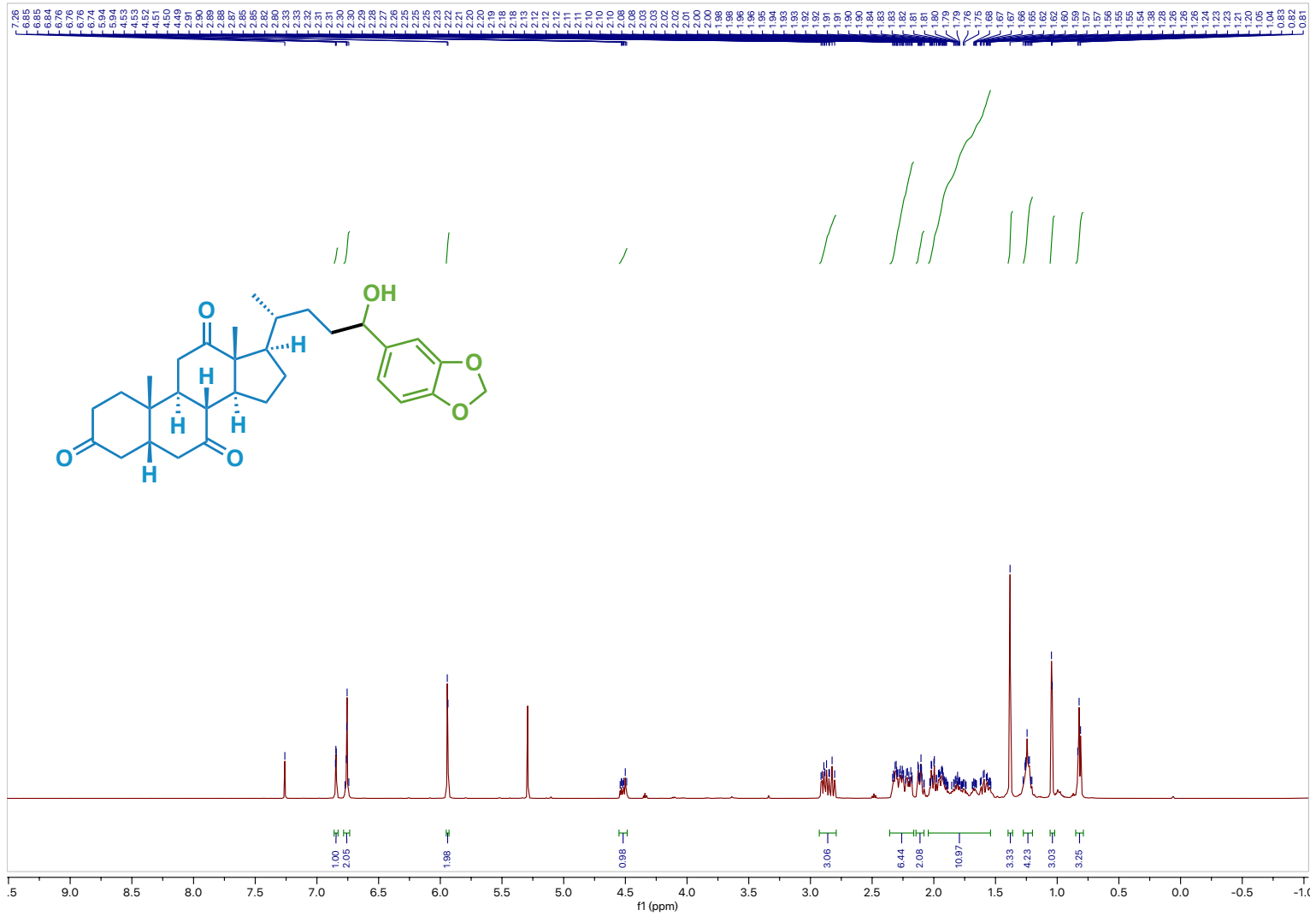
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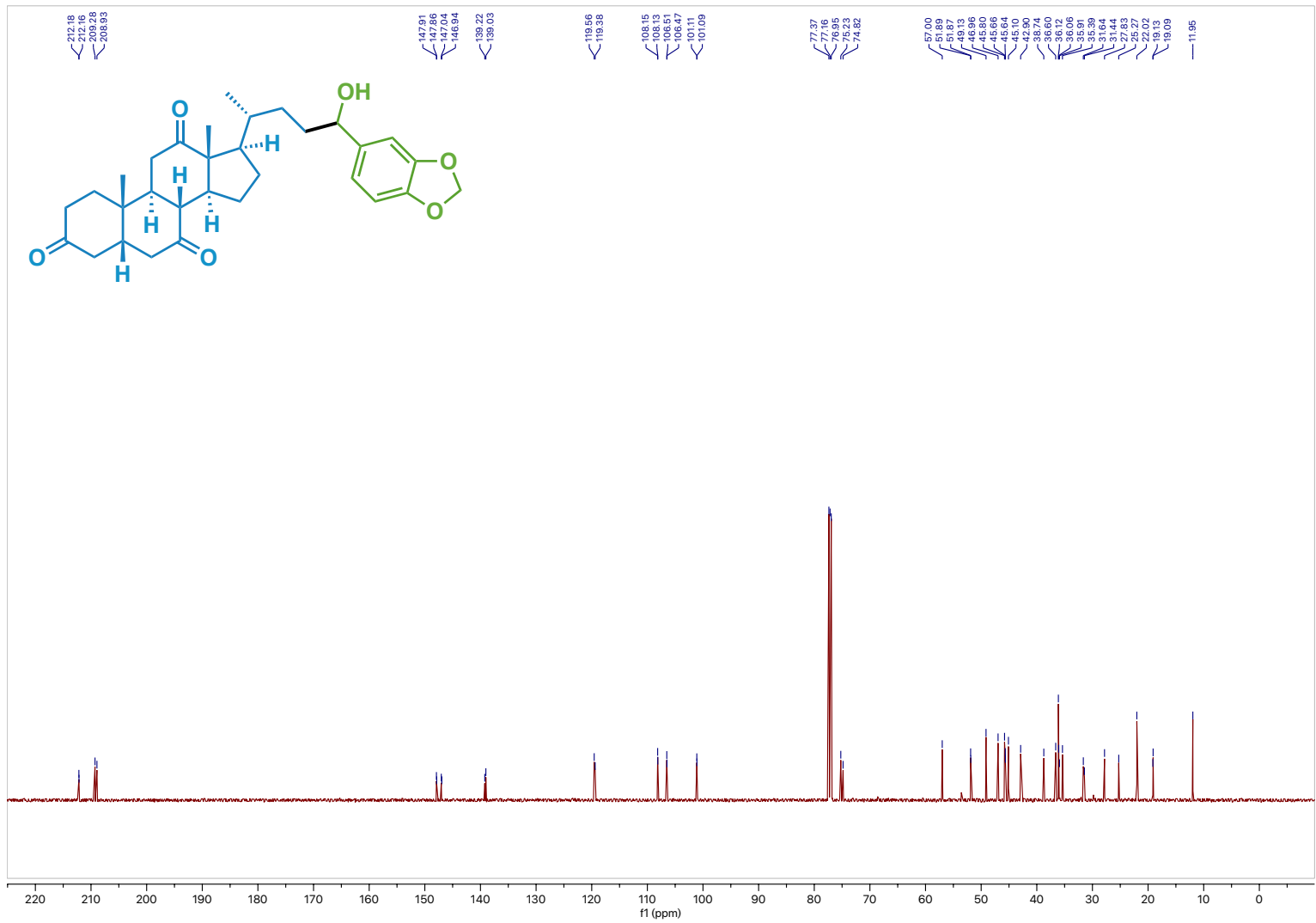
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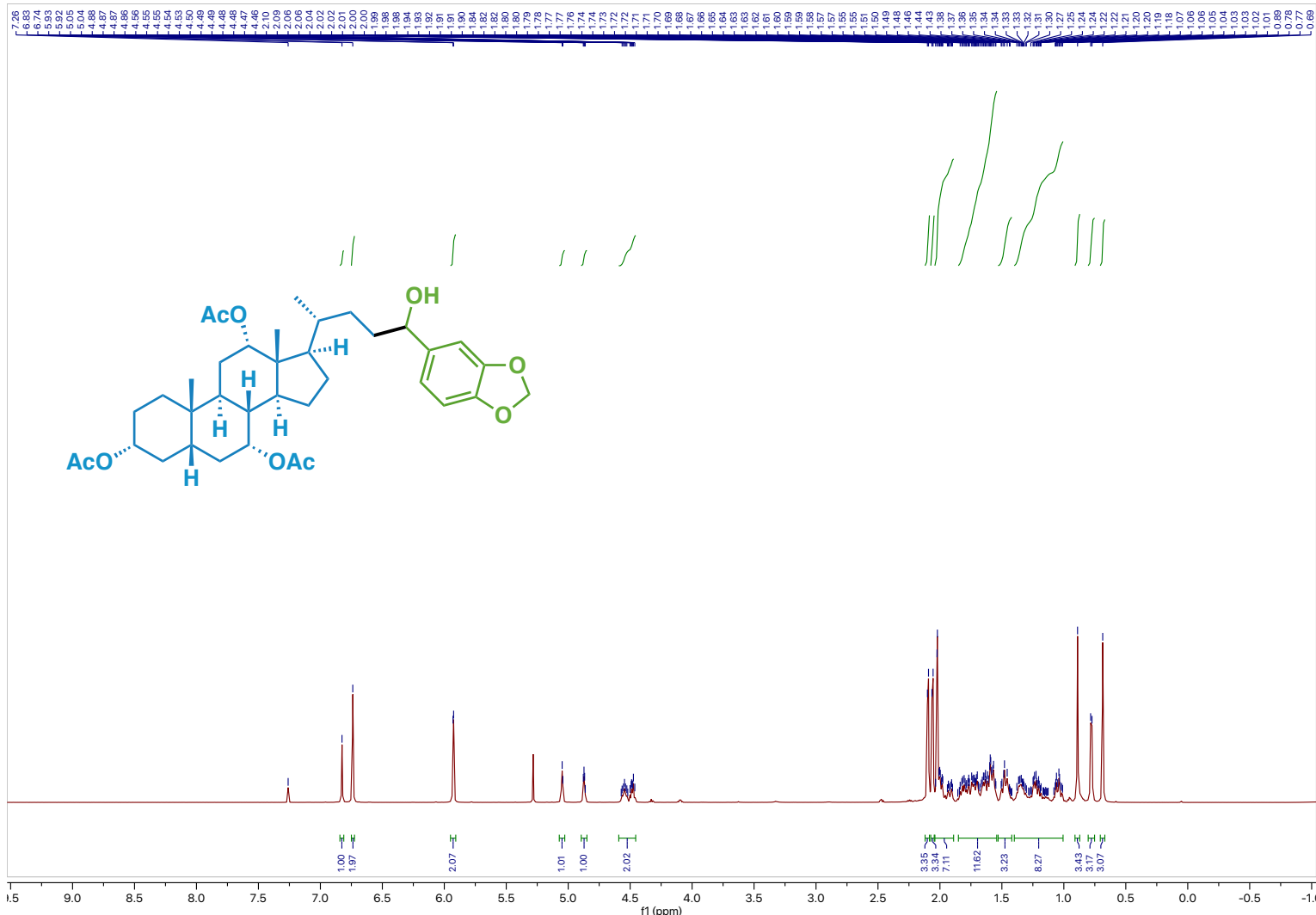
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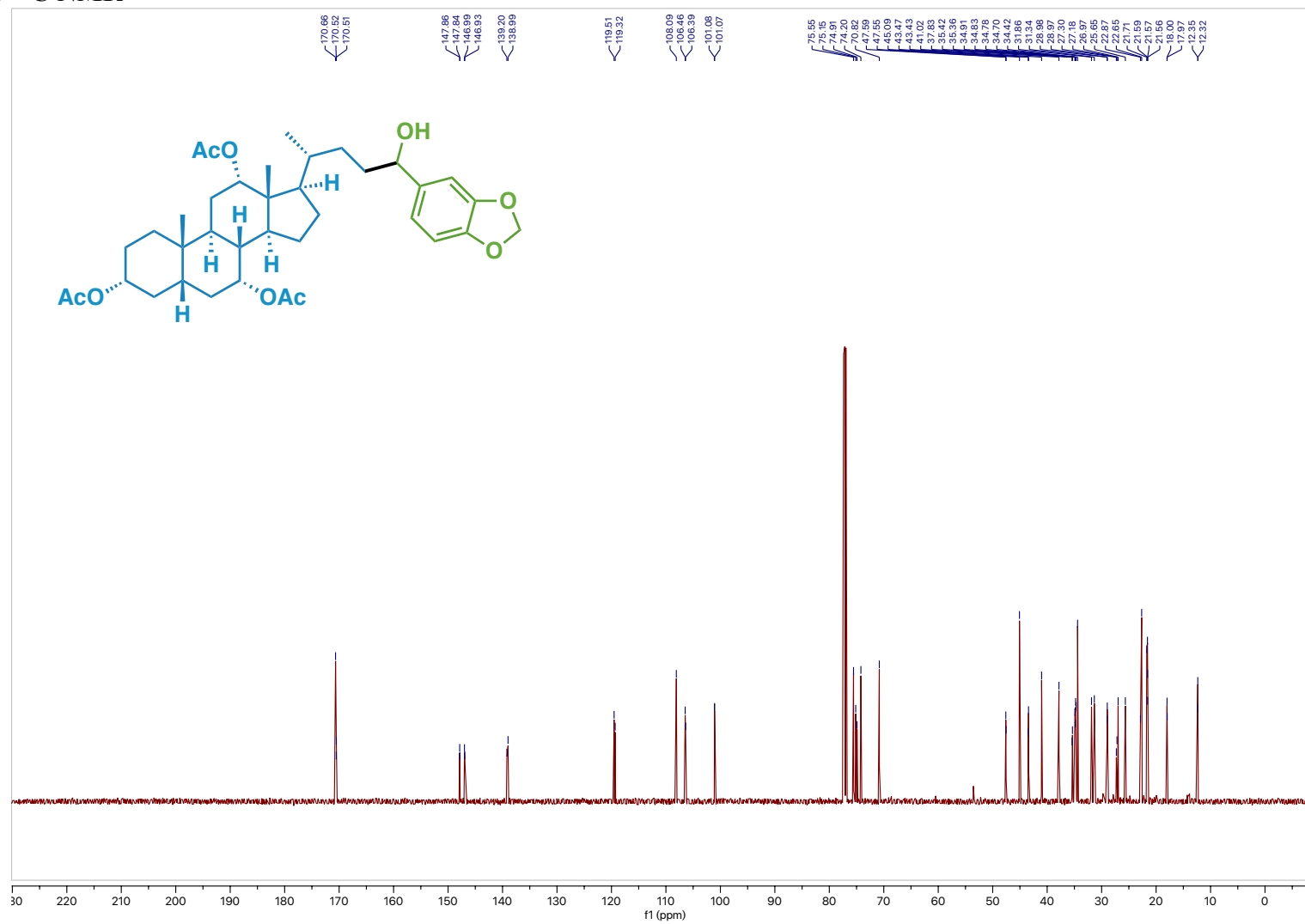
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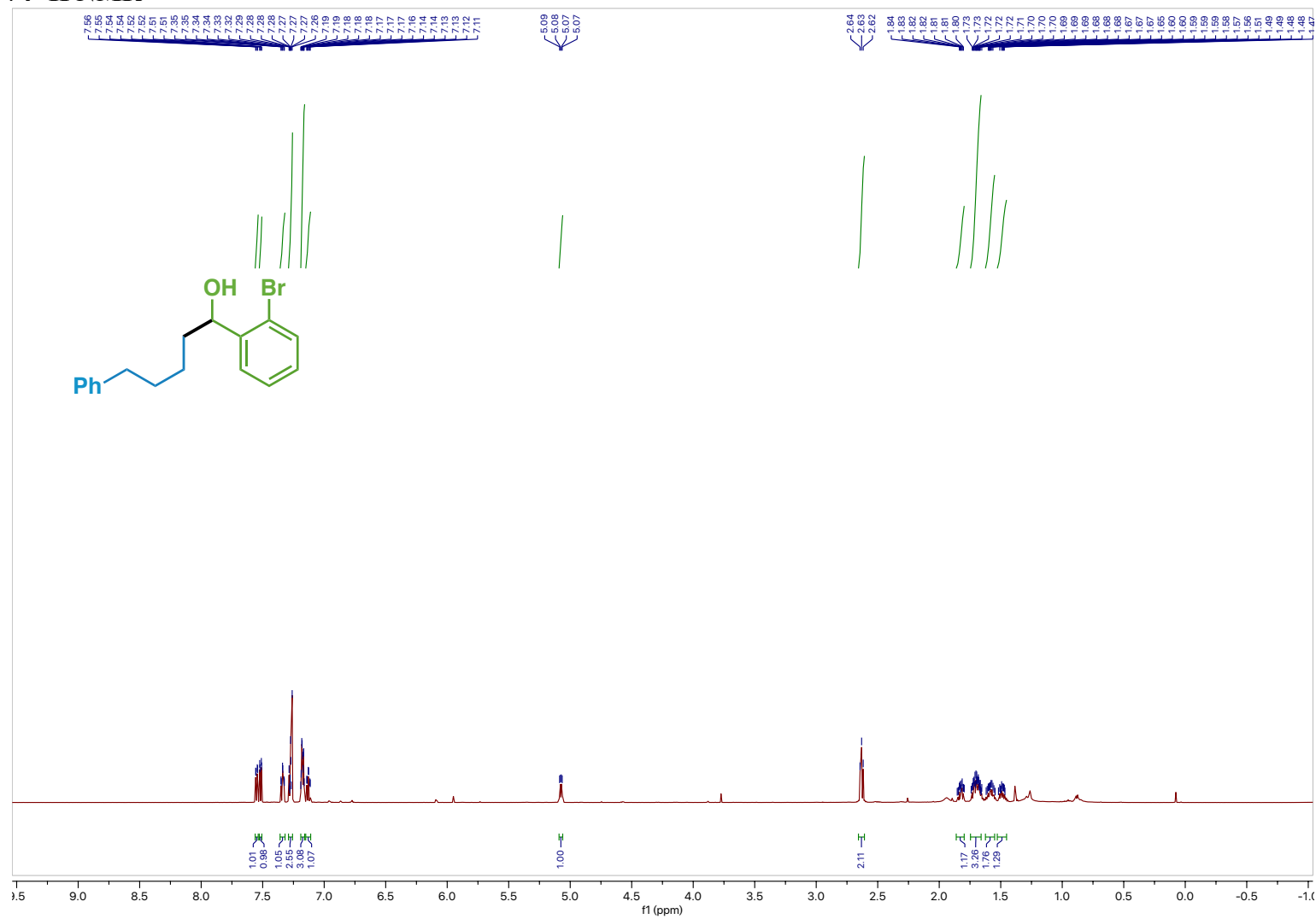
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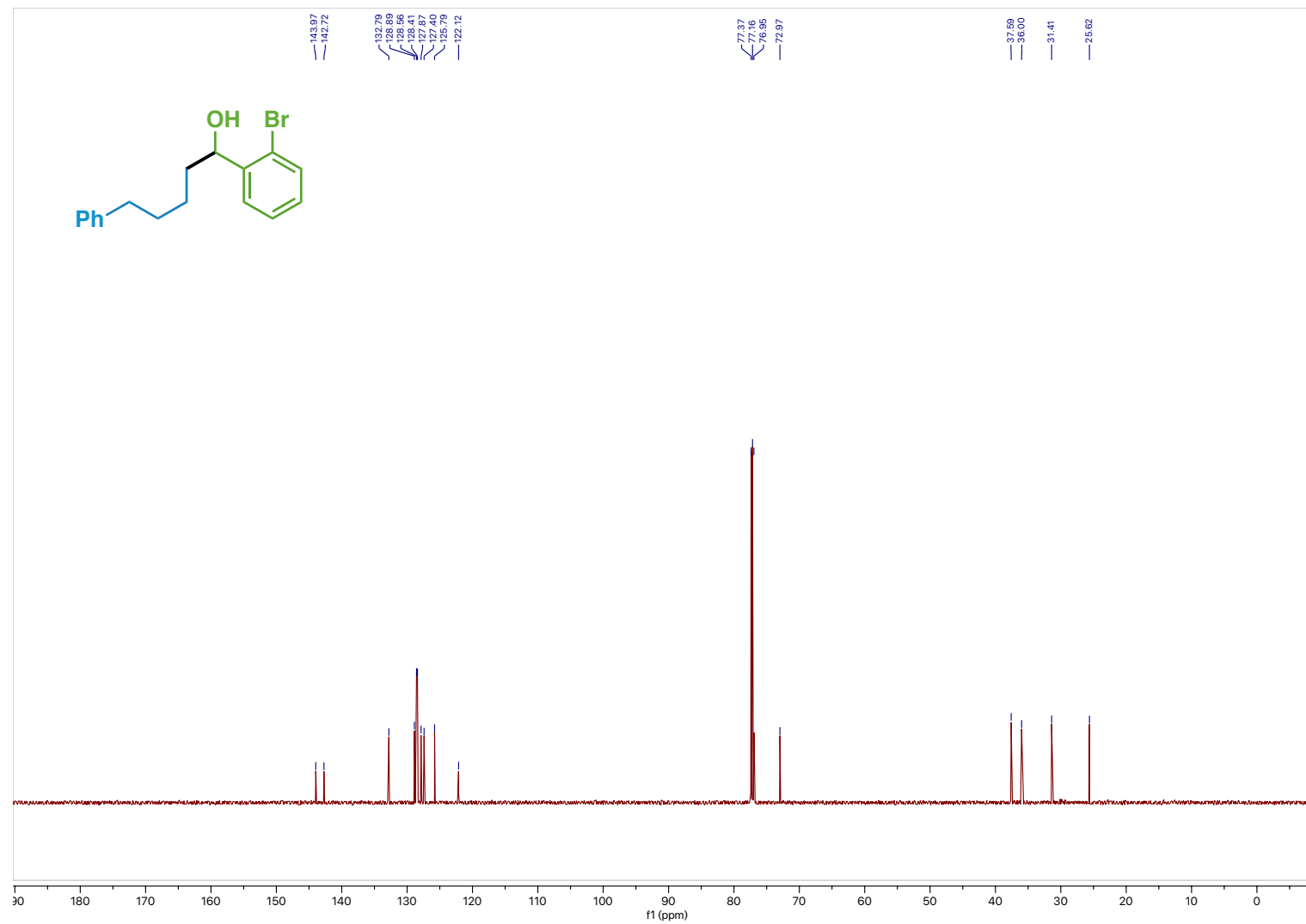
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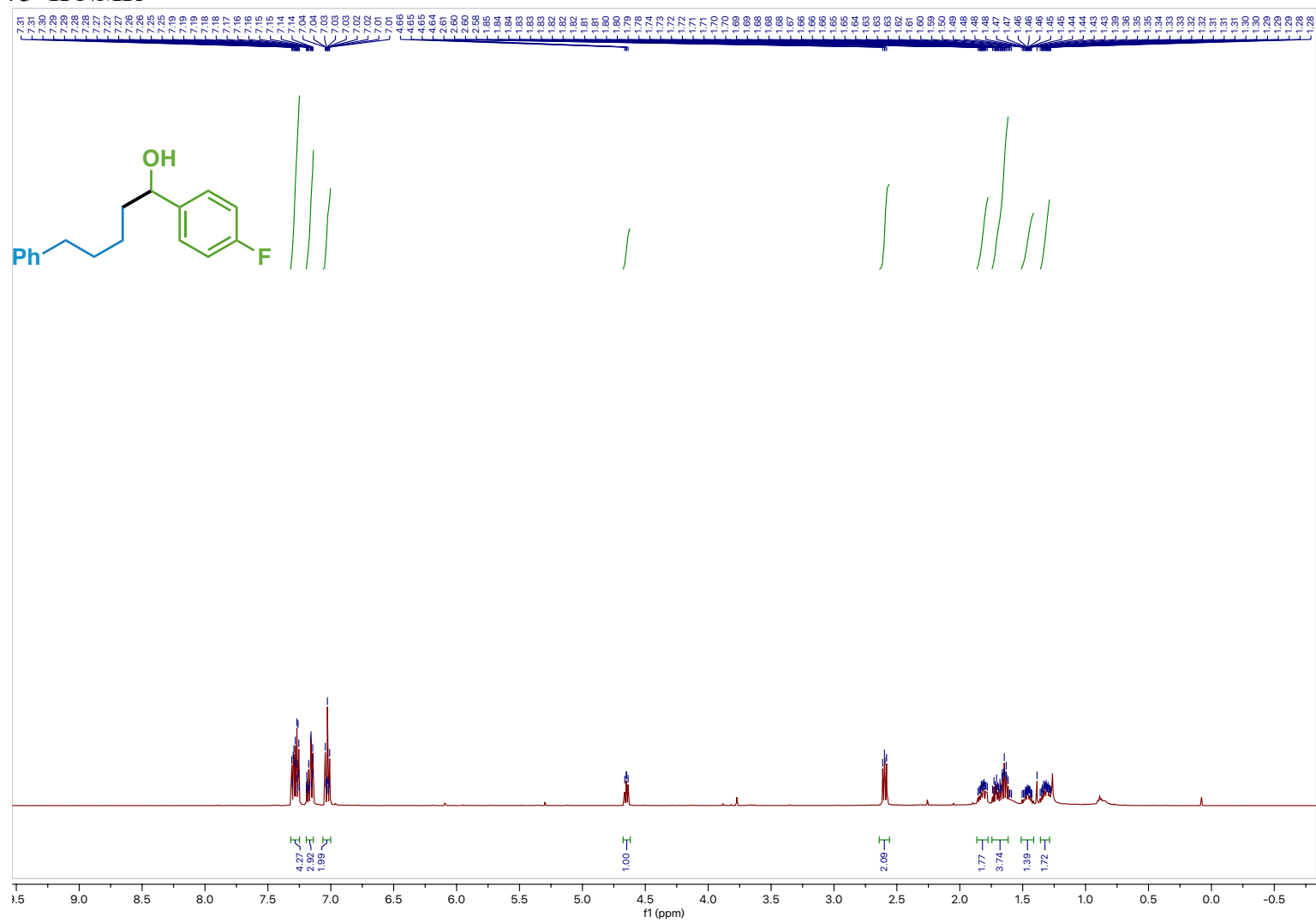
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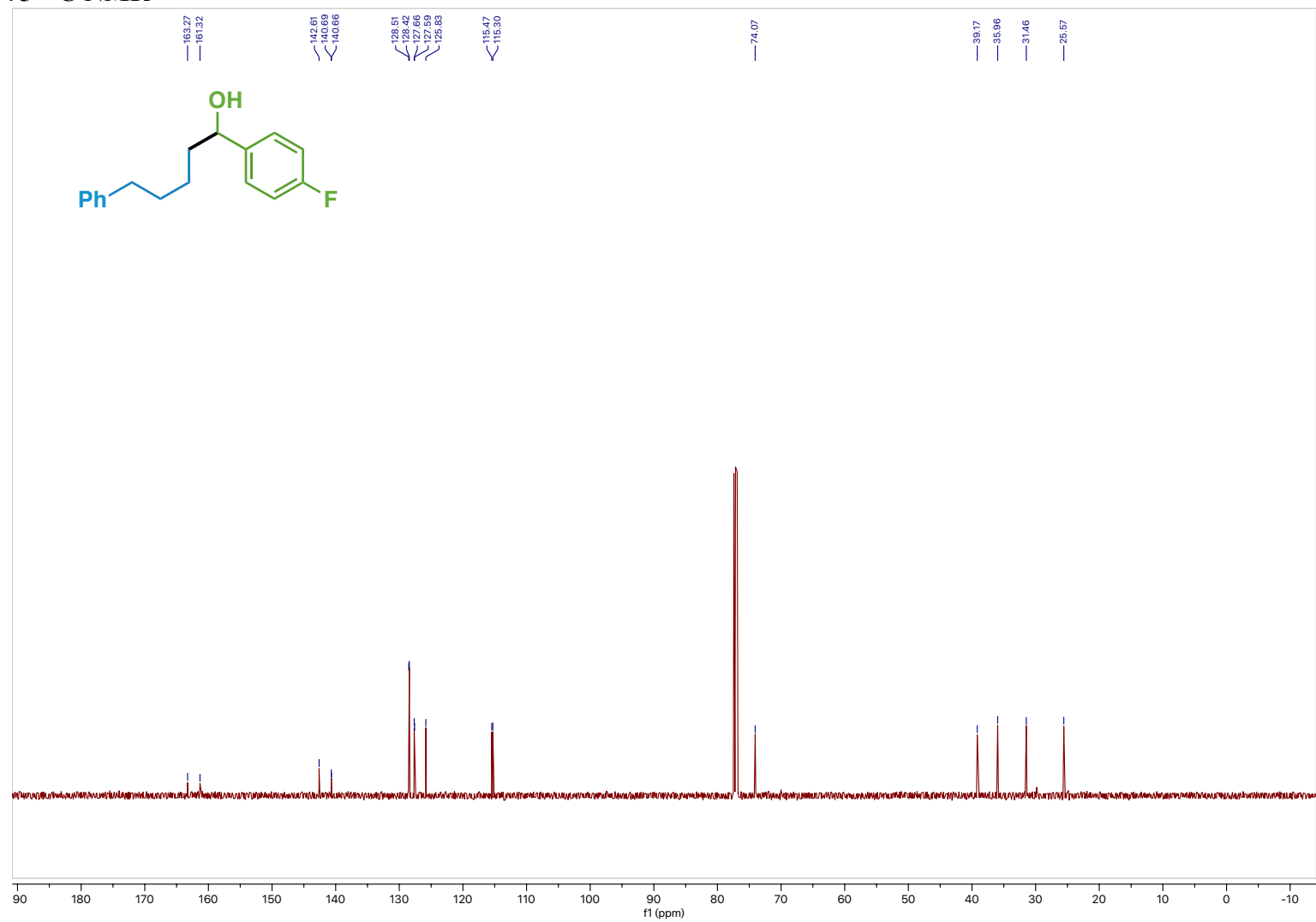
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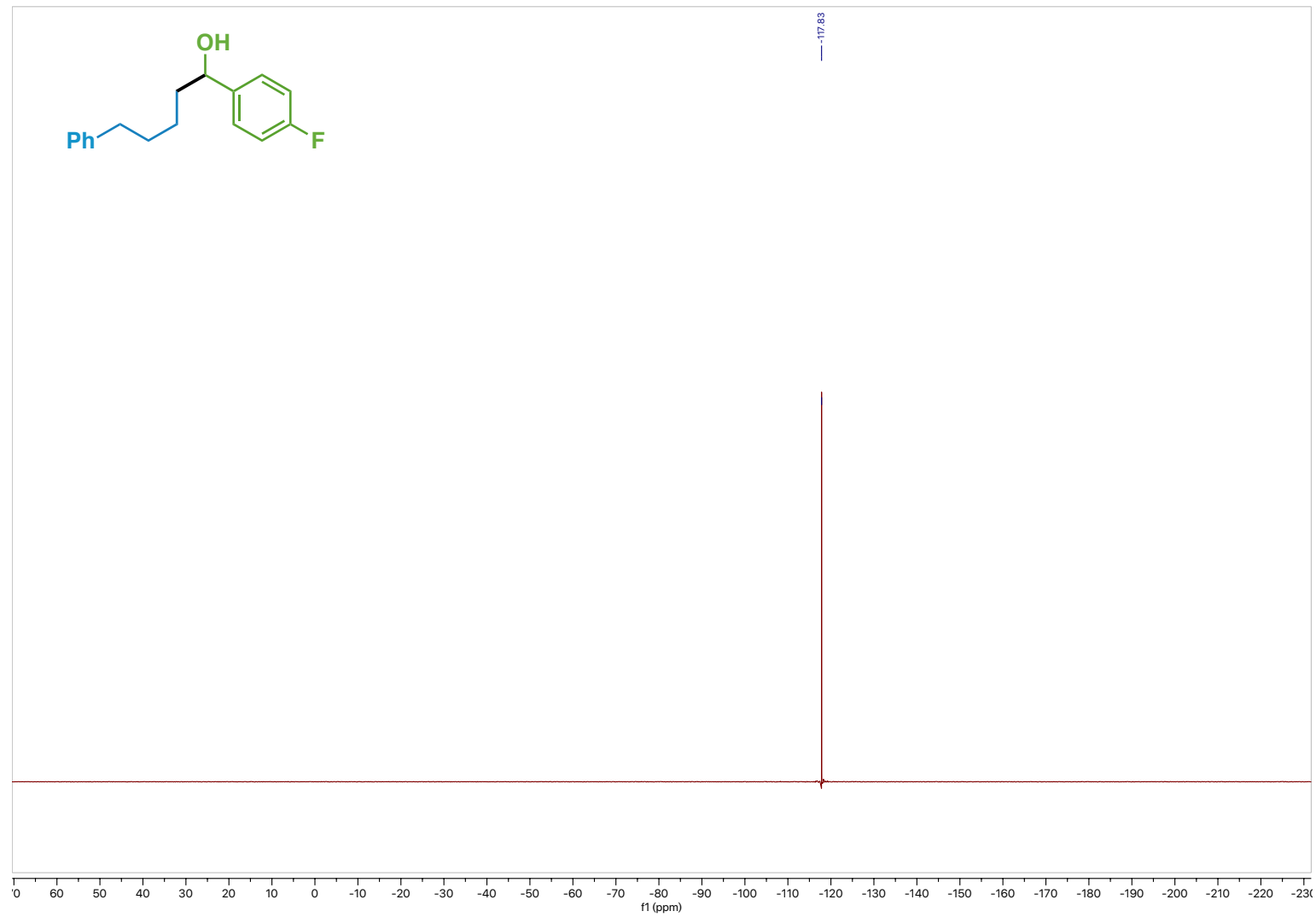
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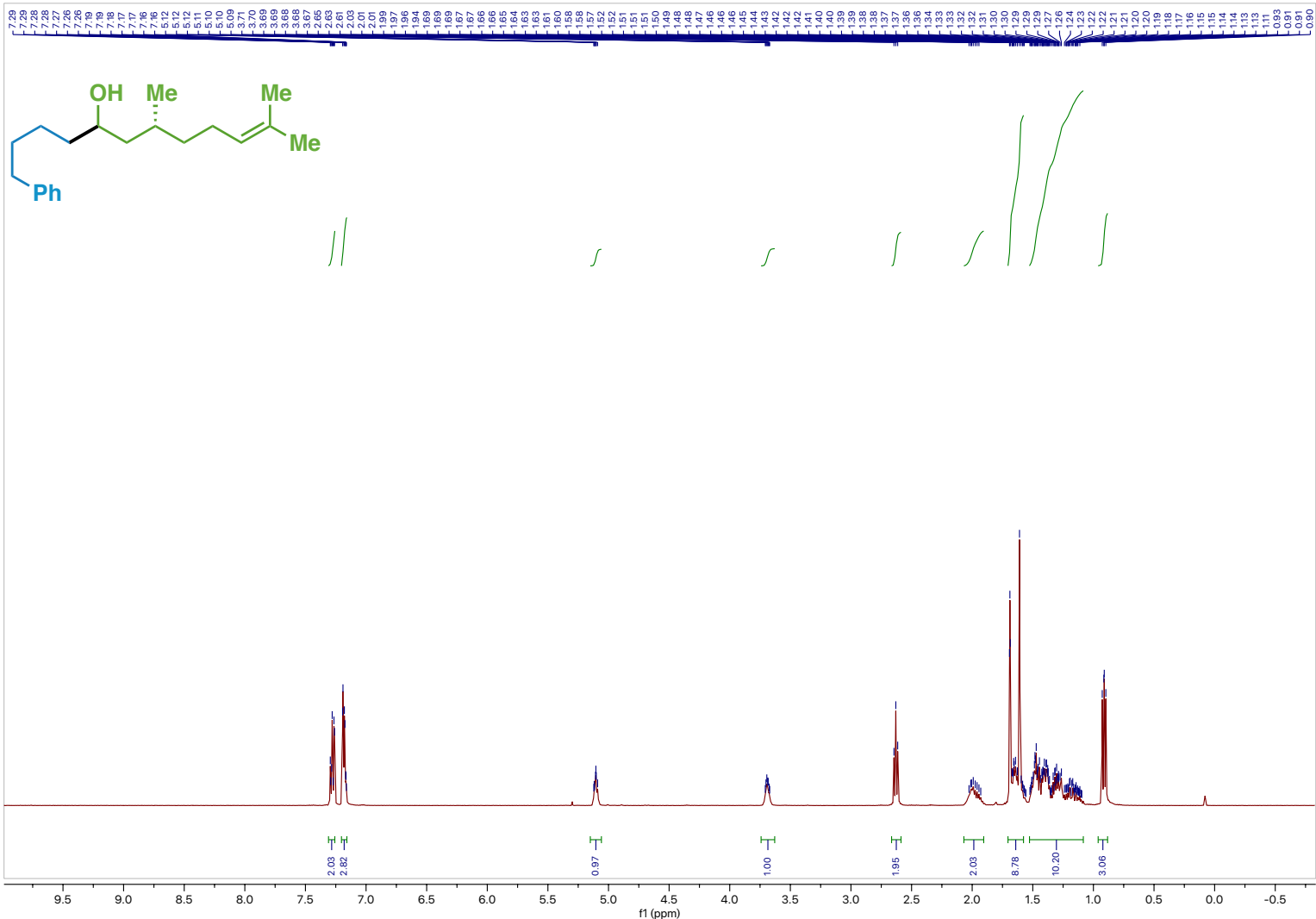
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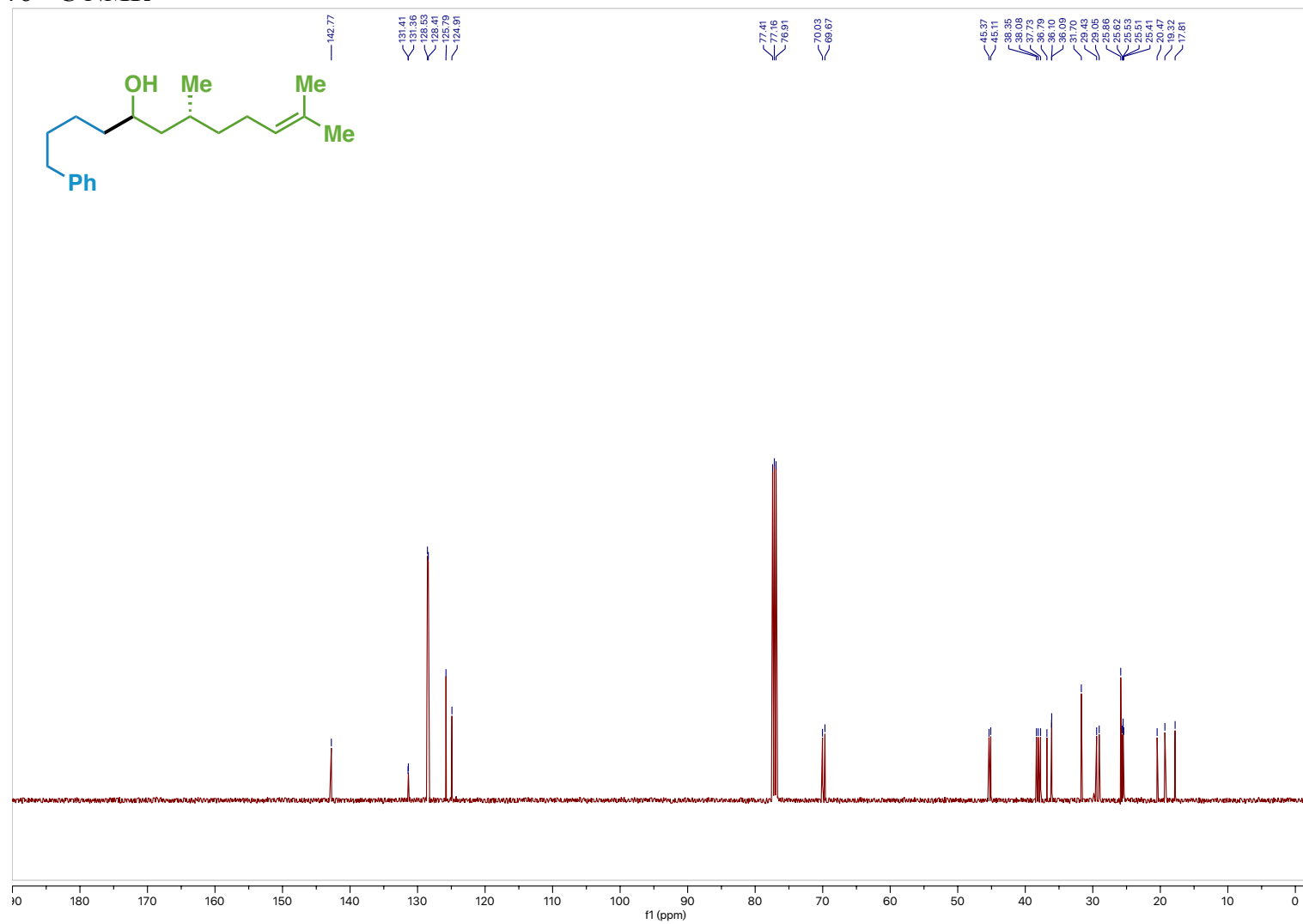
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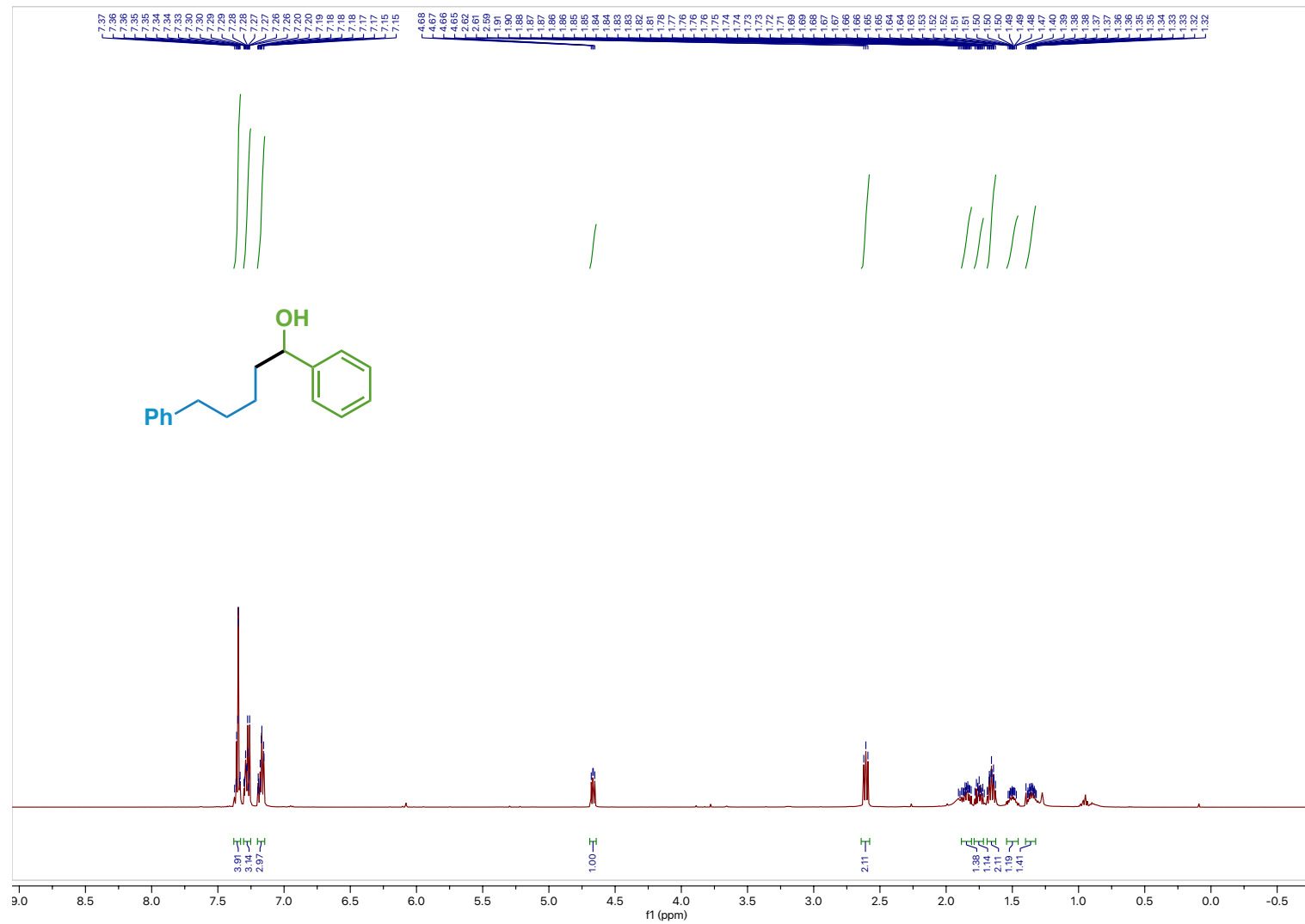
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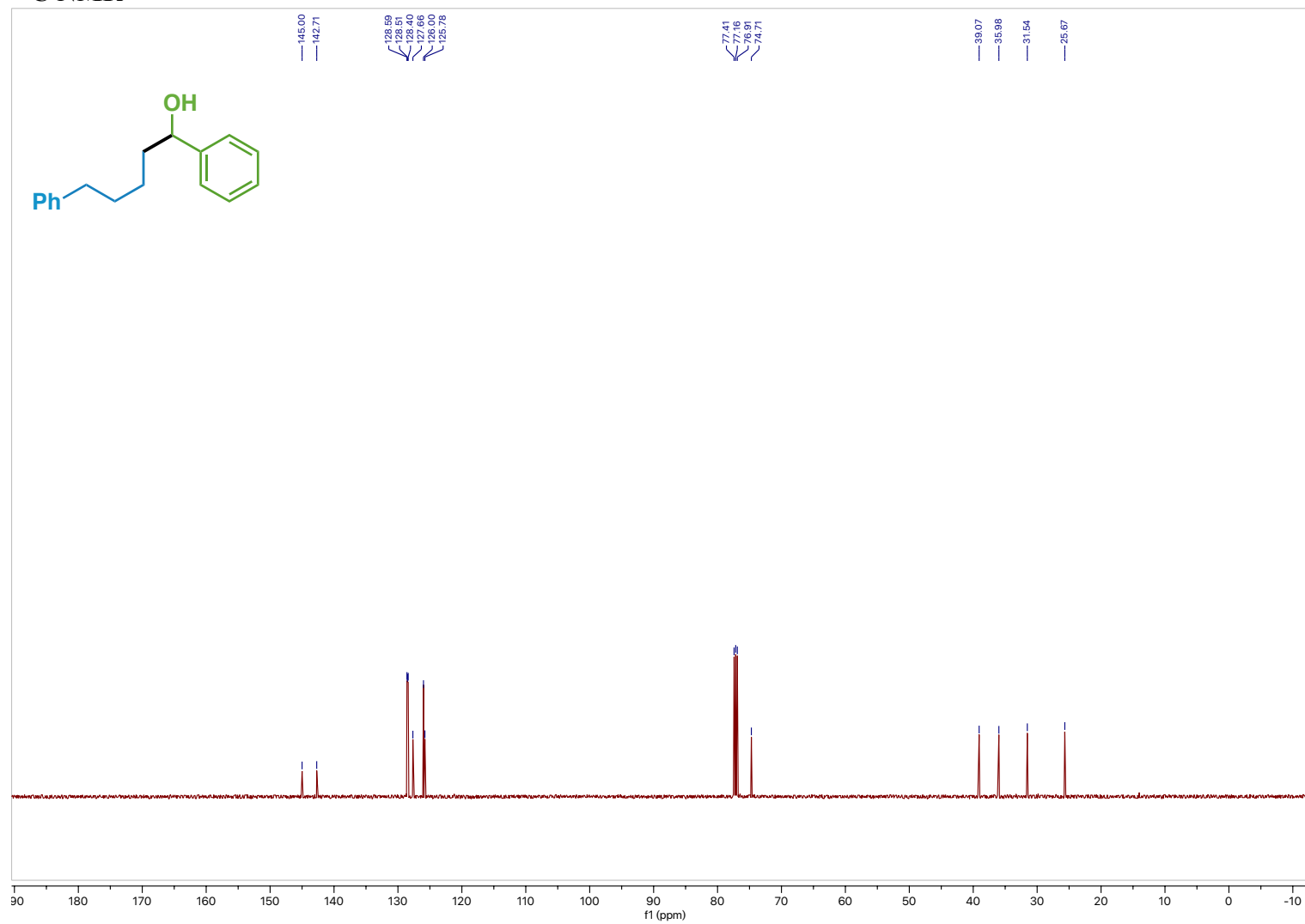
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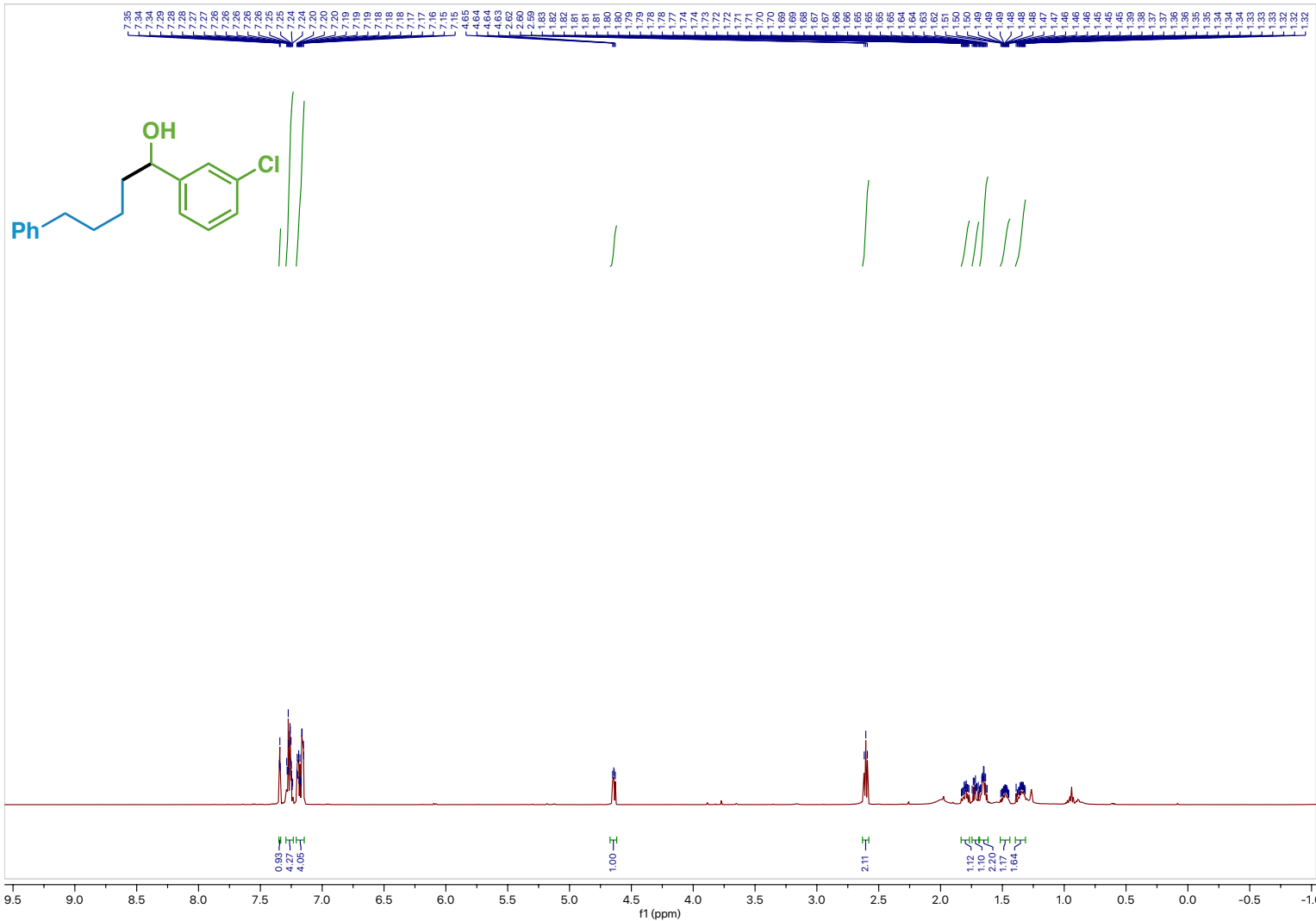
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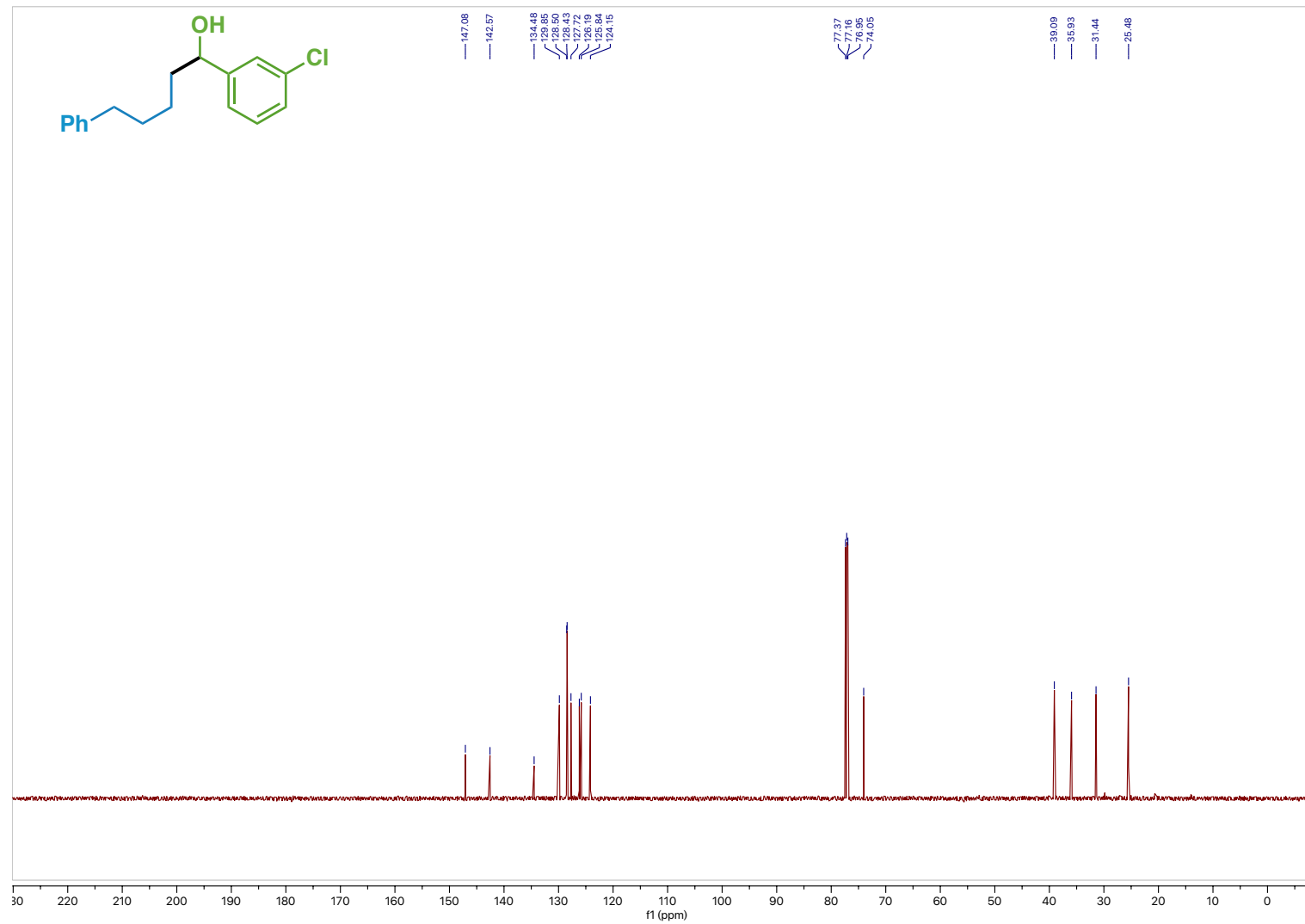
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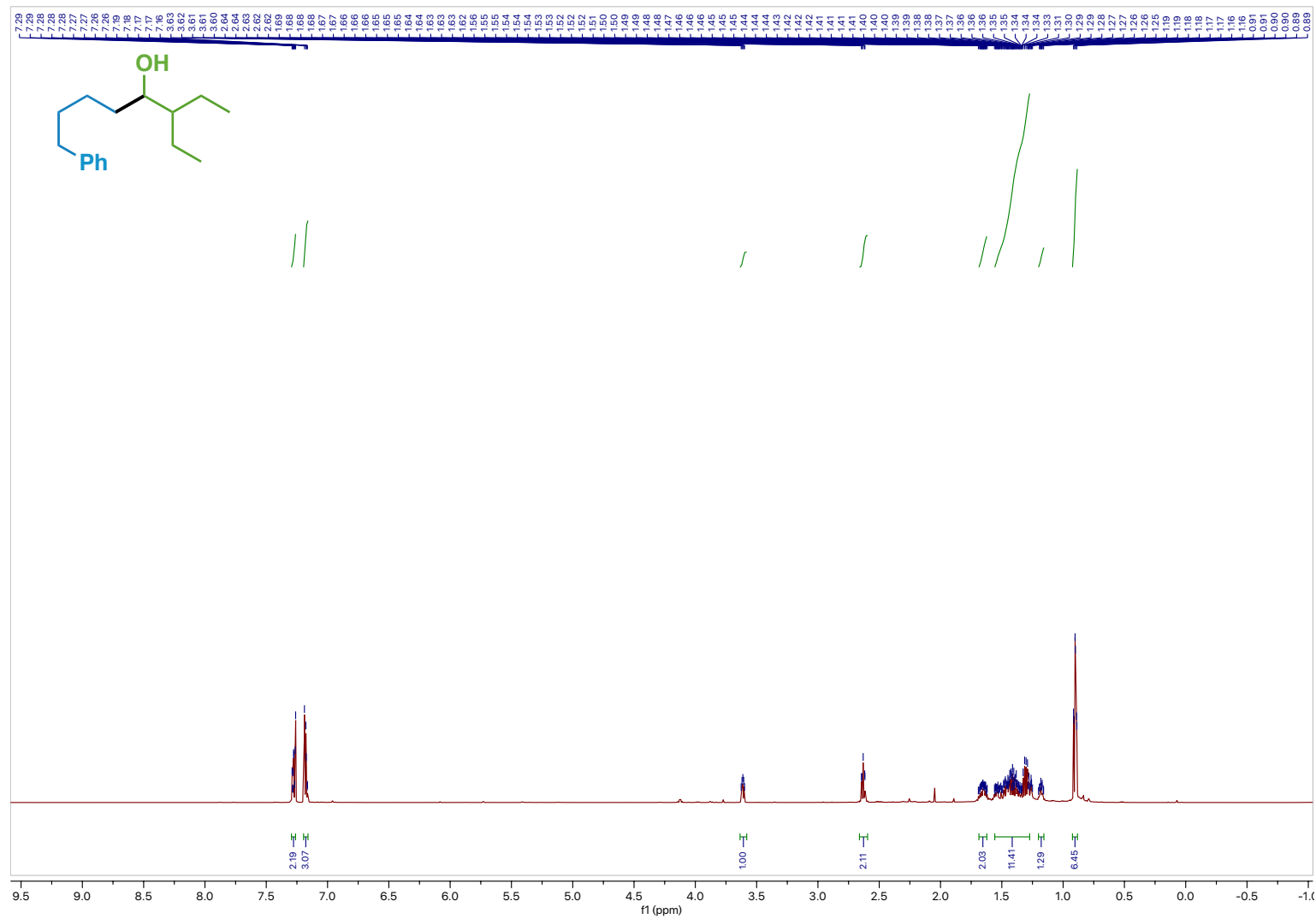
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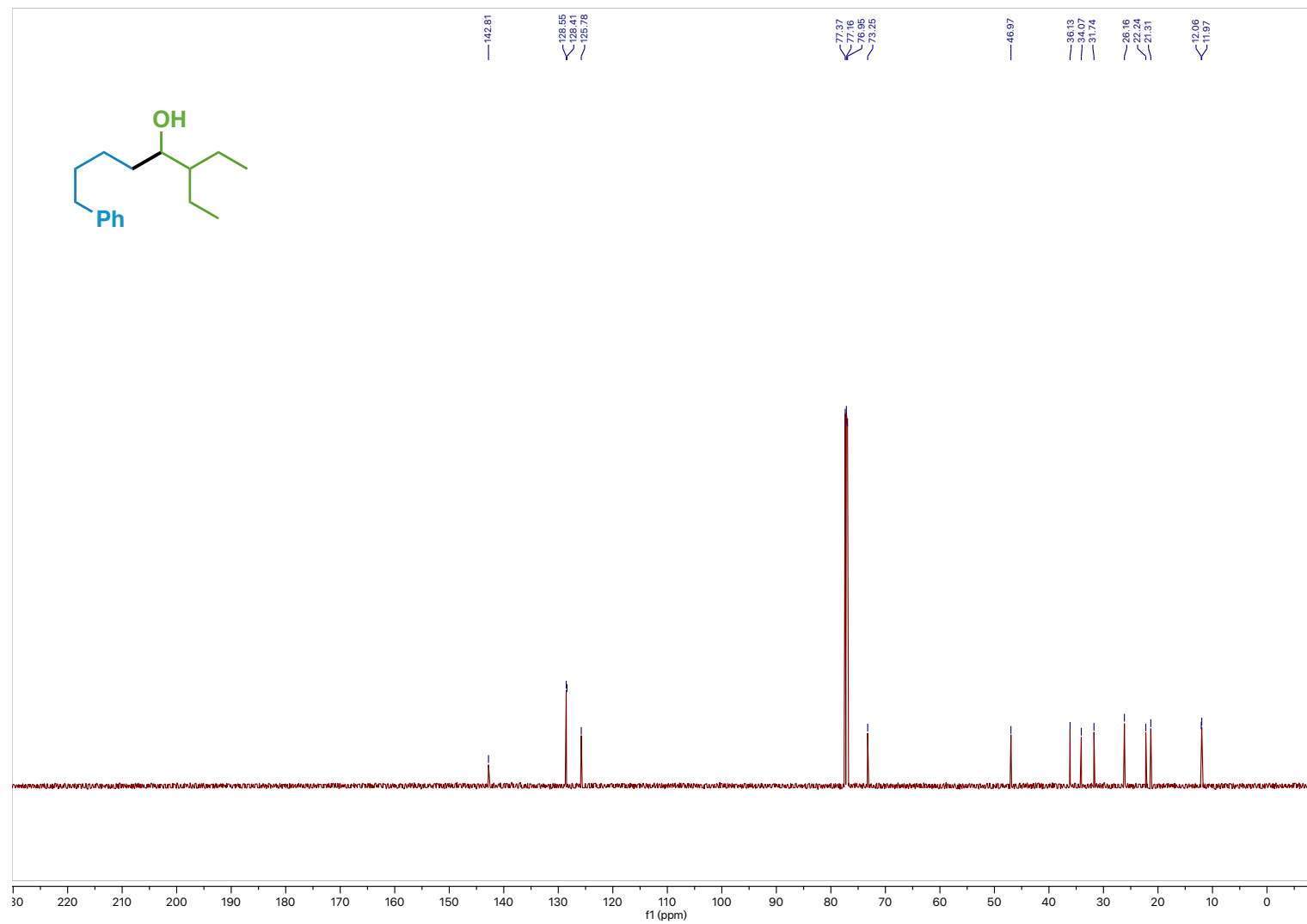
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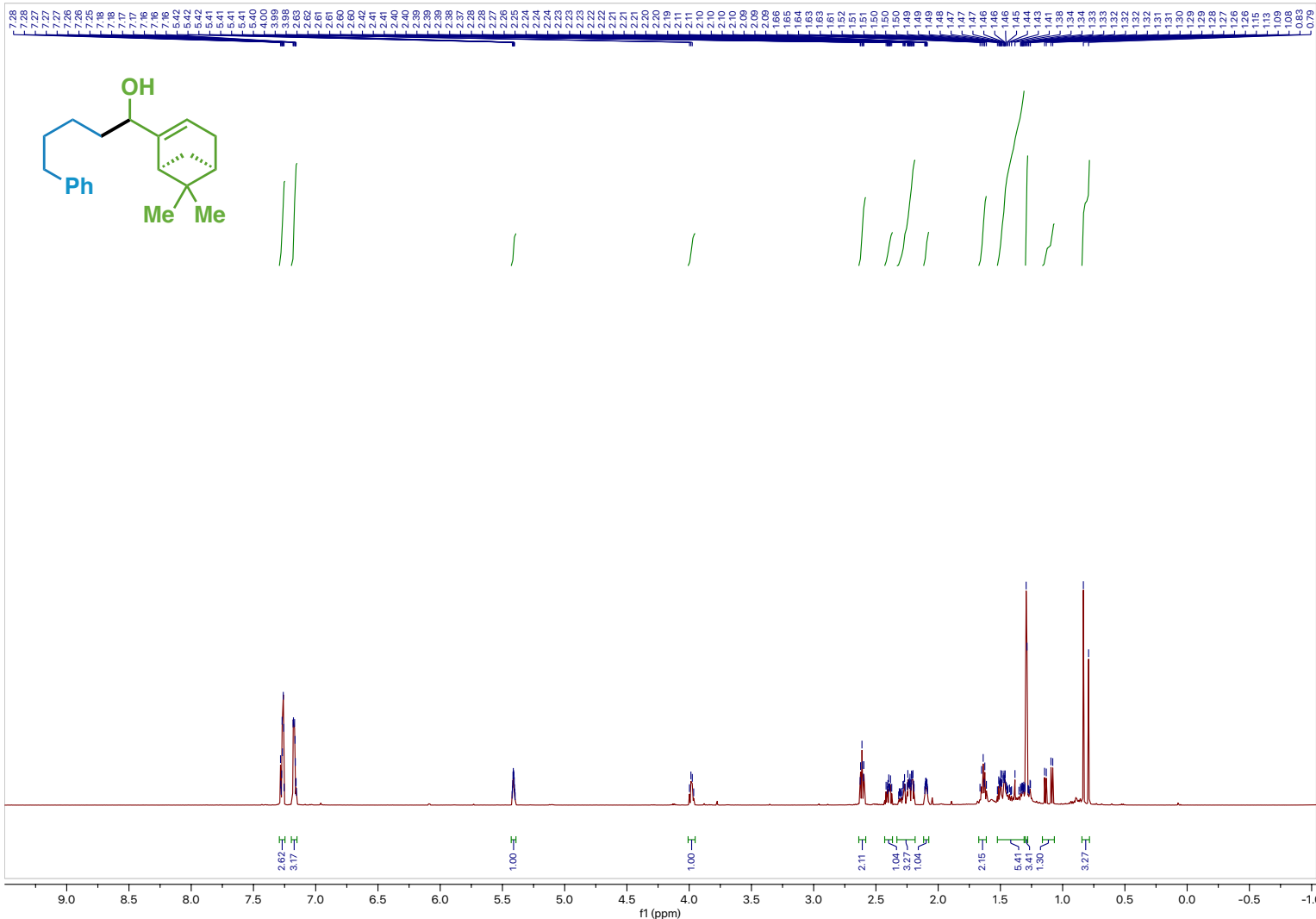
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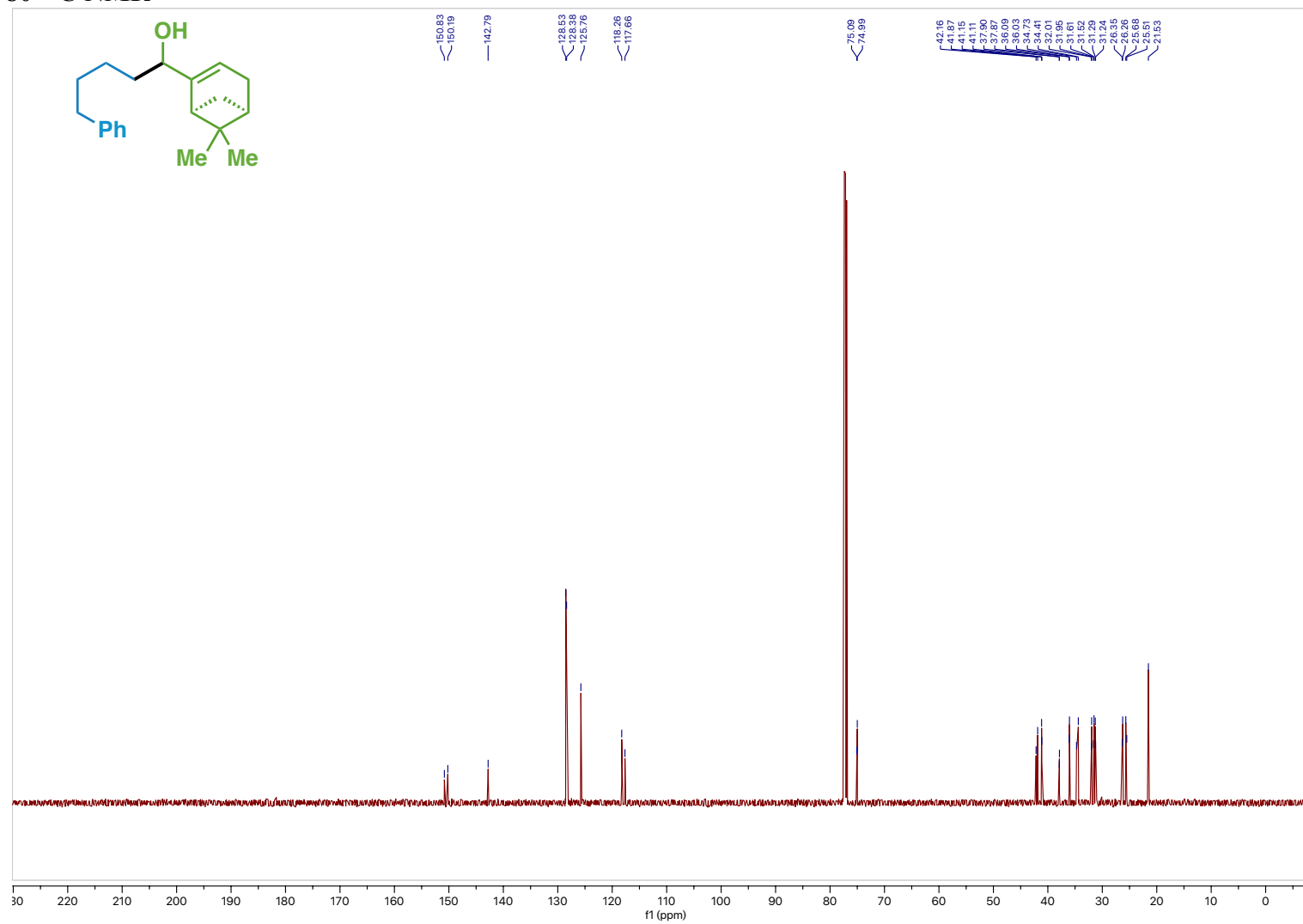
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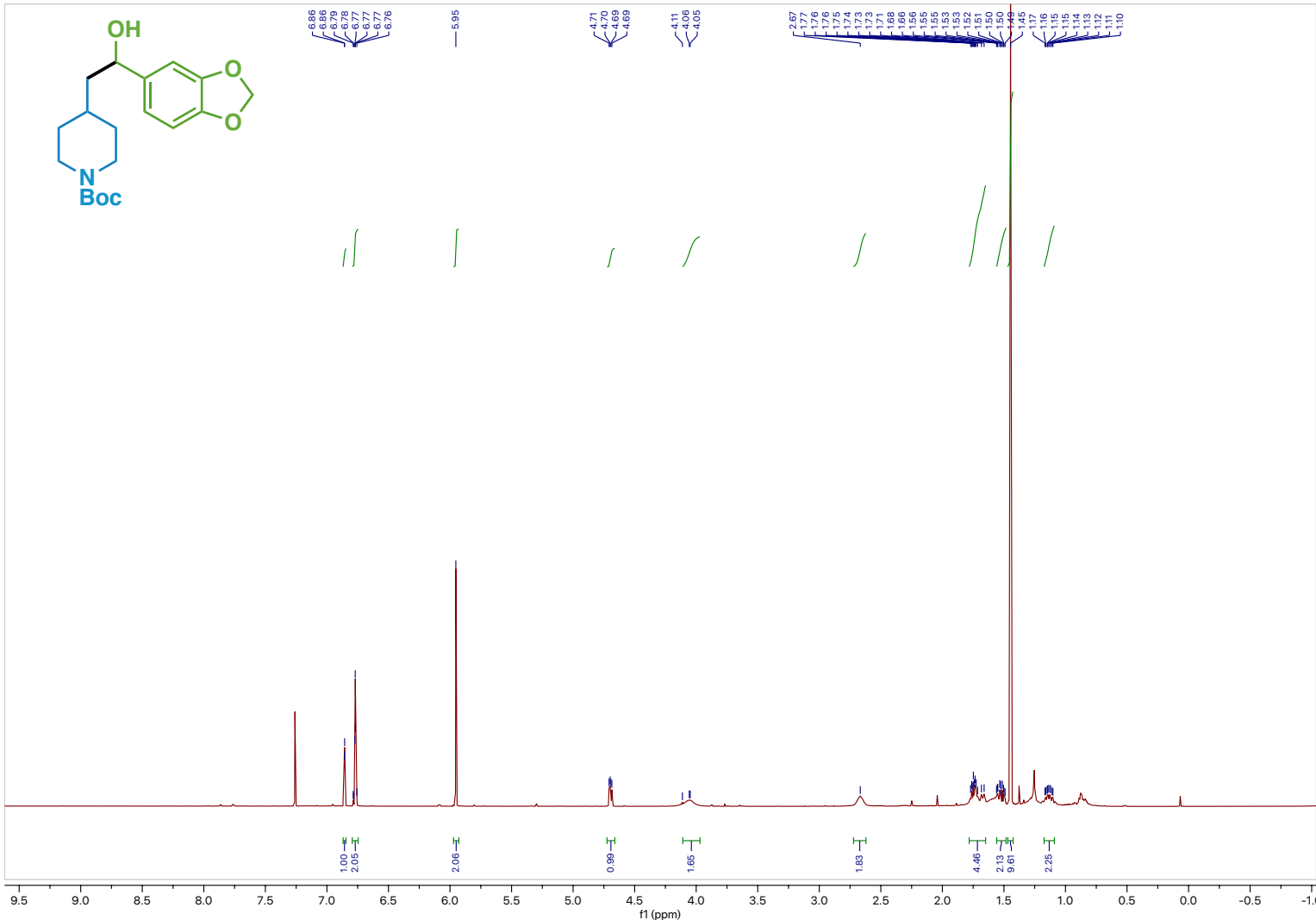
Compound 80 ¹H NMR



Compound 80 ¹³C NMR



Compound 84 ¹H NMR



Compound 84 ¹³C NMR

