Cobalt-Electrocatalytic Hydrogen Atom Transfer for Functionalization of Unsaturated C–C Bonds

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GENERAL METHODS

Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. Isolated yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. Acetonitrile (MeCN), dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF) were obtained by passing the previously degassed solvents through an activated alumina column. For determination of ^{1}H NMR yields, cyclohexanecarboxaldehyde, nitromethane, 1,4-bis(trifluoromethyl)benzene or 1,3,5-trimethoxybenzene were used as internal standards (automatic baseline correction was applied). Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60 F_{254}), using short-wave UV light (254 nm) for visualization, and *p*-anisaldehyde or potassium permanganate as developing agents. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm) or basic Al_2O_3. NMR spectra were recorded on Bruker DRX-600, DRX-500, and AMX-400 instruments, and chemical shifts for ^{1}H and ^{13}C NMR are reported relative to the solvent peaks (7.26 ppm for ^{1}H NMR in $CDCl_3$, 77.16 ppm for ^{13}C NMR in $CDCl_3$). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. High–resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer using ESI ion source, a Waters LC-TOF (I-Class and G2-XS) mass spectrometer using ESI or APCI ion sources, and a Thermo Fisher Scientific LTQ Orbitrap XL mass spectrometer using ESI ion source. GC-MS (EI) was recorded on Agilent 7820A GC systems and 5975 Series MSD using *n*-decane as an internal standard. Optical rotation data was recorded on an Anton Paar 100 Modular Circular Polarimeter.

SOURCE OF REAGENTS

$CoBr_2$(glyme) (95% or 98%) was purchased from Strem [CAS 18346-57-1, cat# 27-0350]. (*R*,*R*)-(−)-*N*,*N*′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) was purchased from Sigma-Aldrich [176763-62-5, cat# 474592] or combi-blocks [cat# QC-5129]. (*S*,*S*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane diaminocobalt(II) was purchased from Sigma-Aldrich [188264-84-8, cat# 474606] or combi-blocks [cat# QN-4551]. 6,6`-dimethyl-bipyridine was purchased from combi-blocks [4411-80-7, cat# QB-2287]. 4,4'dimethoxy-bipyridine was purchased from combi-blocks [17217-57-1, cat# OR-4171]. Commercial chemicals were obtained from suppliers and used as received unless otherwise specified.

ELECTRODE MATERIALS/DIMENSIONS

The tin, nickel-foam, zinc, and magnesium electrodes used in this work were bought from IKA (for 0.2−0.5 mmol scale). Other electrodes used or tested in this work were obtained from IKA (https://www.ika.com/en). For experiments using an ElectraSyn vial, the dimensions of the electrodes were approximately W7 × D1.5 × H55 mm (with the submerged exterior surface of the electrode approximately W7 × D1.5 × H20 mm), unless otherwise stated. For experiments on larger scales, dimensions of electrodes have been specified in the relevant experimental section. Continuous flow system reactor and its components were purchased from Hangzhou Saiao Electrochemical

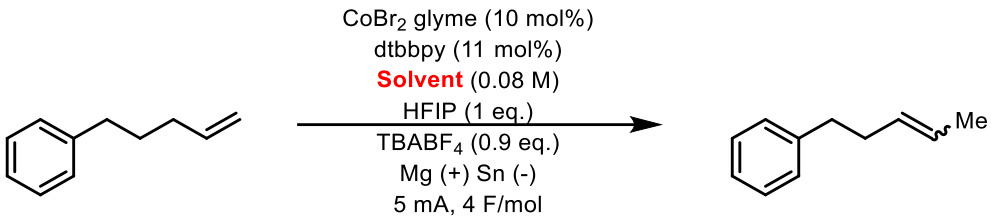
Technology Co. Ltd, China. Zinc, stainless steel, graphite plate as electrode were purchased from McMaster Carr, Magnesium plate as sacrificial anode was purchased from Amazon Inc.

Optimization of Reactions Parameters

Mono-substituted Alkene Isomerization

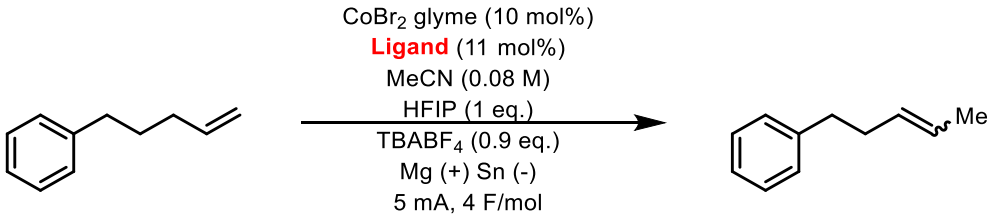
All optimization reactions were carried out on 0.2 mmol scale. The crude reaction mixture was analyzed by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Evaluation of solvent (Table 1)



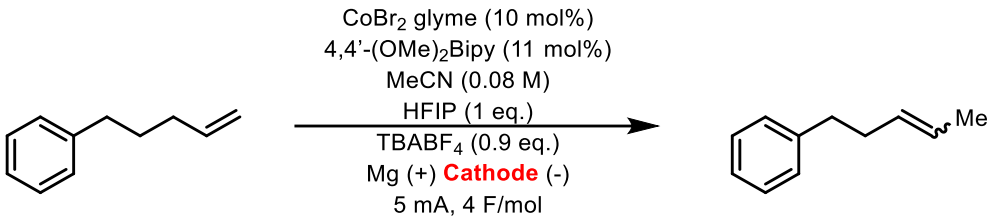
Solvent	Product	SM
MeCN	59%*	19%
Acetone	19%*	50%
THF	41%*	14%
Dioxane	19%*	9%
EtOAc	20%*	30%

Evaluation of ligand (Table 2)



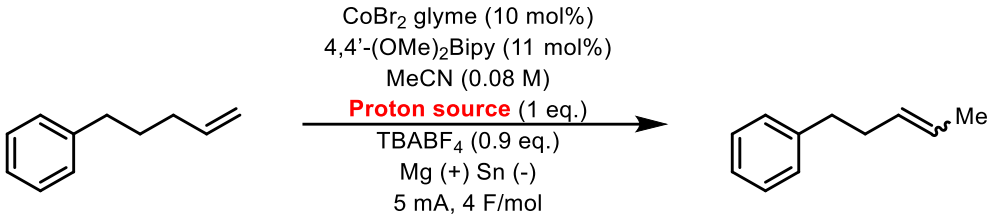
Ligand	Product	SM
4,4'-(*t*Bu)$_2$Bipy	59%*	19%
4,4'-(CF$_3$)$_2$Bipy	20%*	17%
4,4'-(CH$_3$)$_2$Bipy	56%*	20%
6,6'-(CH$_3$)$_2$Bipy	29%*	10%
4,4'-(OCH$_3$)$_2$Bipy	67%*	20%

Evaluation of cathode (Table 3)



Cathode	Product	SM
Tin	67%*	20%
GCE	11%*	10%
Ni	48%*	22%
Ni-foam	19%*	45%
Stainless steel	32%*	19%

Evaluation of proton source (Table 4)



Proton source	Product	SM
HFIP	67%*	20%
BuSH	N.D.*	75%
*i*PrOH	Traces*	30%
MeOH	19%*	8%
Et_3N HCl	36%	5%
Et_3N HBF_4[a]	51%	22%
Et_3N HBF_4[a,b]	61%	17%
Et_3N HBF_4[a,b,c]	82%	traces

[a] No supporting electrolyte used

[b] 3 eq. of Proton source used

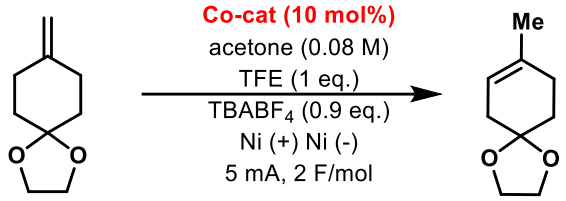
[c] 2.5 mA applied

* Irreproducible results

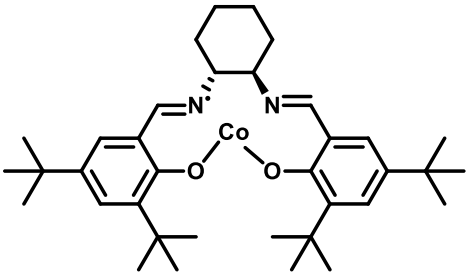
TERMINAL DI-SUBSTITUTED ALKENE ISOMERIZATION

All optimization reactions were carried out on 0.2 mmol scale. The crude reaction mixture was analyzed by ^{1}H-NMR using cyclohexyane-aldehyde as internal standard.

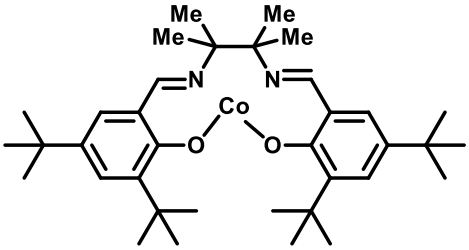
Evaluation of Co-cat (Table 5)



Co-cat	Product	SM
$Co(acac)_2$	ND	82%
Co(salen)-1	6%	75%
Salcomine	ND	74%
$Co(OAc)_2$	ND	90%
$Co(dpm)_2$	ND	87%

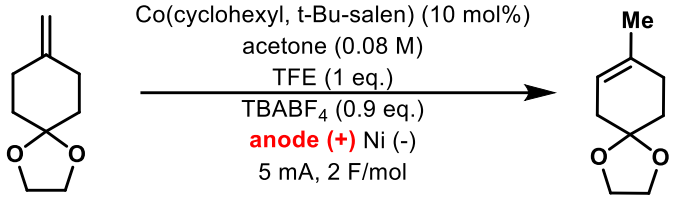


Co(salen)-1



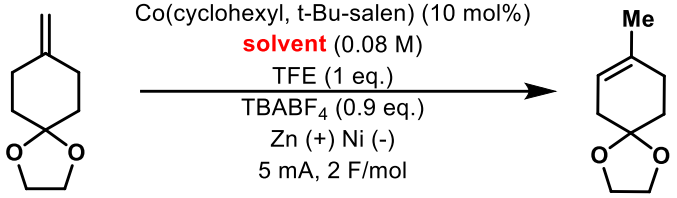
Co(salen)-2

Evaluation of anode (Table 6)



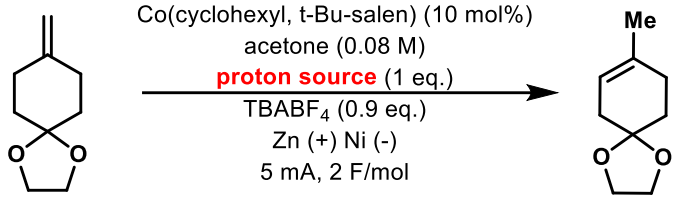
Anode	Product	SM
Ni	6%	75%
Zn	48%	40%
Mg	25%	53%
RVC	ND	88%
Al	10%	65%

Evaluation of solvent (Table 7)



Solvent	Product	SM
acetone	48%	40%
THF	35%	43%
DMF	ND	53%
DCM	ND	82%
MeCN	10%	75%

Evaluation of H^+ source (Table 8)

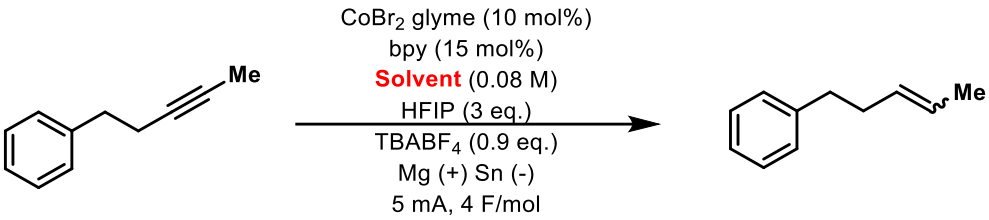


Proton source	Product	SM
TFE	48%	40%
HFIP	84%	> 1%
AcOH	33%	49%
TsOH	ND	74%
Et_3NHBF_3	60%	23%

Z-SELECTIVE ALKYNE SEMI-REDUCTION

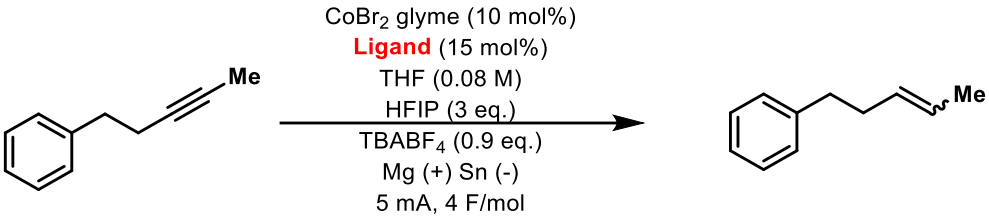
All optimization reactions were carried out on 0.2 mmol scale. The crude reaction mixture was analyzed by ^{1}H-NMR using cyclohexyane-aldehyde or 1,3,5-trimethoxybenzene as internal standard.

Evaluation of solvent (Table 9)



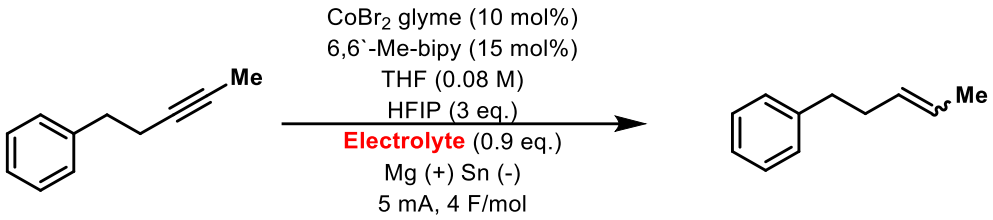
Solvent	Product	Z/E ratio
MeCN	6%	-
Acetone	8%	-
THF	15%	6/1
DMF	ND	-
EtOAc	ND	-

Evaluation of Ligand (Table 10)



Solvent	Product	Z/E ratio
bpy	15%	6/1
tyrp	ND	-
6,6-Me-bpy	30%	15/1
4,4-tBu-bpy	10%	10/1
di-Me-pyrox	traces	-

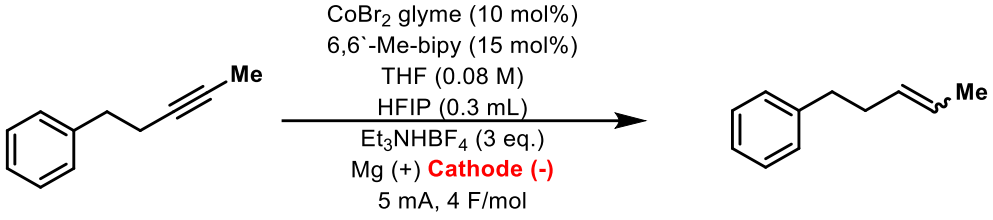
Evaluation of Electrolyte (Table 11)



Electrolyte	Product	SM	Over-reduction
$TBABF_4$ [a,b]	29%	63%	<5%
TBAI[b]	0%	89%	0%
$TBAPF_6$ [a,b]	25%	70%	<5%
$Et_3N\ HBF_4$ [a,b,c]	36%	38%	<5%
$Et_3N\ HBF_4$ [c,d,e]	65%	<5%	16%
$Et_3N\ HBF_4$ [e,f]	39%	<5%	45%
$Et_3N\ HBF_4$ [e,g]	65%	<5%	18%
$Et_3N\ HBF_4$ [e,g,h]	63%	19%	9%

[a] Result not reproducible [b] Experiment had to be interrupted due to high voltage after 2-4 F/mol (U = 30 V) [c] No HFIP initially used [d] When the voltage exceeded 25 V, 100 µL of HFIP was added and the voltage dropped immediately by 10 – 20 V. [e] 3.0 eq. of $Et_3N\ HBF_4$ used. [f] $TBABF_4$ (1.3 eq.) was additionally used. [g] 300 µL HFIP used. [h] 6.5 F/mol applied.

Evaluation of Cathode (Table 12)

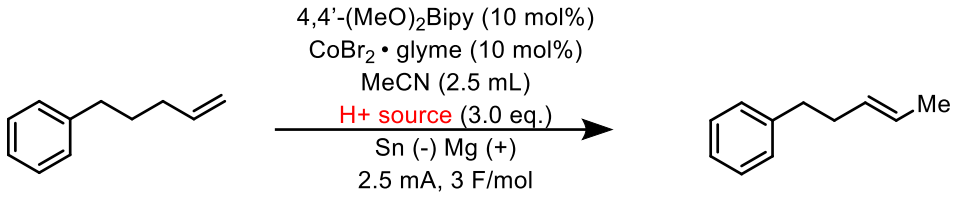


Cathode	Product	SM	Over-reduction
Tin	65%	0%	18%
Zn	70%	10%	15%
Ni-foam	58%	0%	15%
RVC	62%	10%	22%
SS	66%	0%	14%
Mg	65%	0%	33%
C	0%	0%	89%
Cu	0%	0%	83%
C[1]	50%	0%	39%
C[1,2]	85%	0%	6%

[1] 3.7 F/mol [2] 200 µL HFIP instead of 300 µL

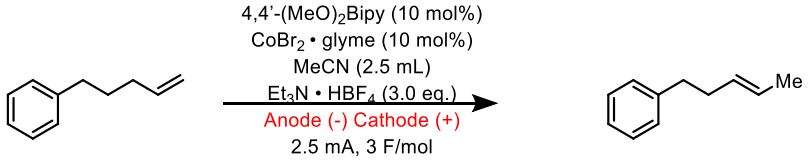
E/Z selectivity screening

Proton source:



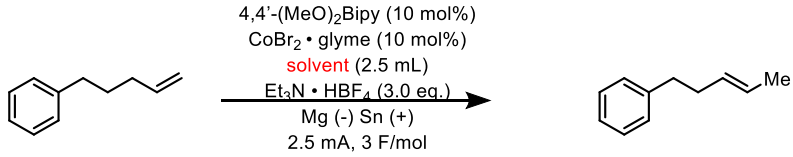
Acid	E/Z
DIPEA • HBF_4	77:23
Pempidine • HBF_4	76:24
Protonsponge • HBF_4	78:22
Et_3N • TFA	77:23
Et_3N • TfOH	76:24
Et_3N • *p*TSA	No reaction

Electrode material:



Anode	Cathode	E/Z
Mg	Au	79:21
Mg	Cu	74:26
Sn	Sn	No conversion
Mg	Bronzelead	80:20
Ni_f	Sn	No conversion
Cu	Sn	No conversion
Ni_p	Sn	No conversion

Solvent:

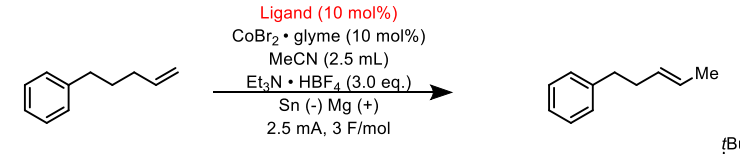


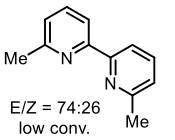
Solvent	E/Z
THF	no isomerization
DMF	no isomerization
DMA	no isomerization
DMSO	no isomerization
MeOH	no isomerization
*iso*propanol	no isomerization
dioxane	no isomerization

Solvent	E/Z
MeCN	79/21
MeCN:toluene	80/20
MeC:DMF	low conversion
MeCN:DMSO	no isomerization
MeCN:THF	no isomerization
MeCN;MeOH	no isomerization
t-BuCN	no isomerization

Solvent	E/Z
t-BuCN:MeCN	no isomerization
iPrCN	no isomerization
malononitrile	no isomerization
phenylnitrile	no isomerization
benzylnitrile	no isomerization
EtOAc	no isomerization

Ligands:





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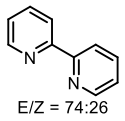

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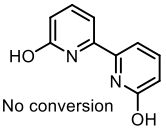

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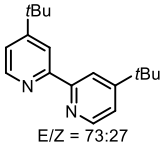

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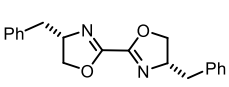

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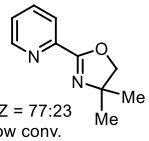

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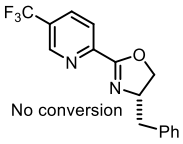

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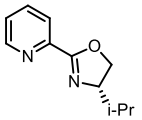

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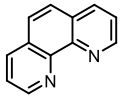

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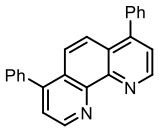

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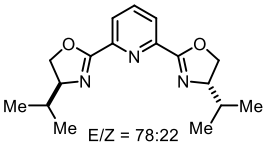
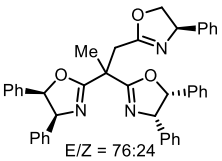
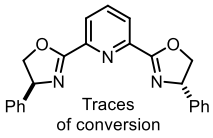


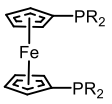
E/Z = 78:22



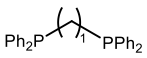
E/Z = 76:24



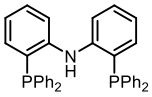
Traces
of conversion



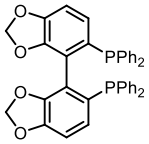
R = Ph E/Z = 49:51
R = *t*bu E/Z = 48:52



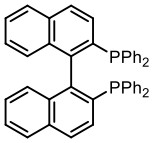
n = 1 no conversion
n = 2 E/Z = 52:48 - low conversion
n = 4 no conversion



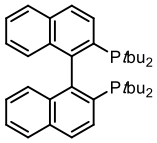
traces product



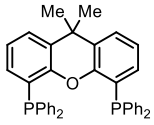
E/Z = 75:25



No conversion



No conversion



E/Z = 51:49

P(*t*bu)2Me (20 mol%)

E/Z = 38:62

PPh3 (20 mol%)

E/Z = 42:48

P(OPh3) (20 mol%)

No conversion

AsPh3 (20 mol%)

No conversion

P(adamantyl)2 (20 mol%)

No conversion

PMes3 (20 mol%)

Traces
of conversion

P(*o*-Tol)3 (20 mol%)

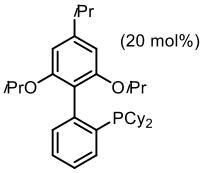
No conversion

P(2,4,6-(MeO)3C6H2)3 (20 mol%)

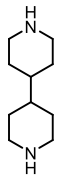
No conversion

PCy3 • HBF4 + DIPEA (20 mol%)

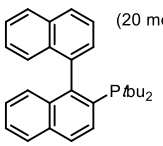
No conversion



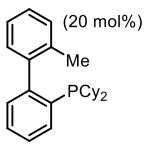
No conversion



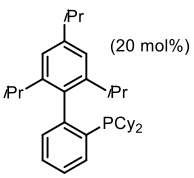
E/Z = 68:32



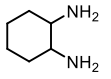
No conversion



No conversion

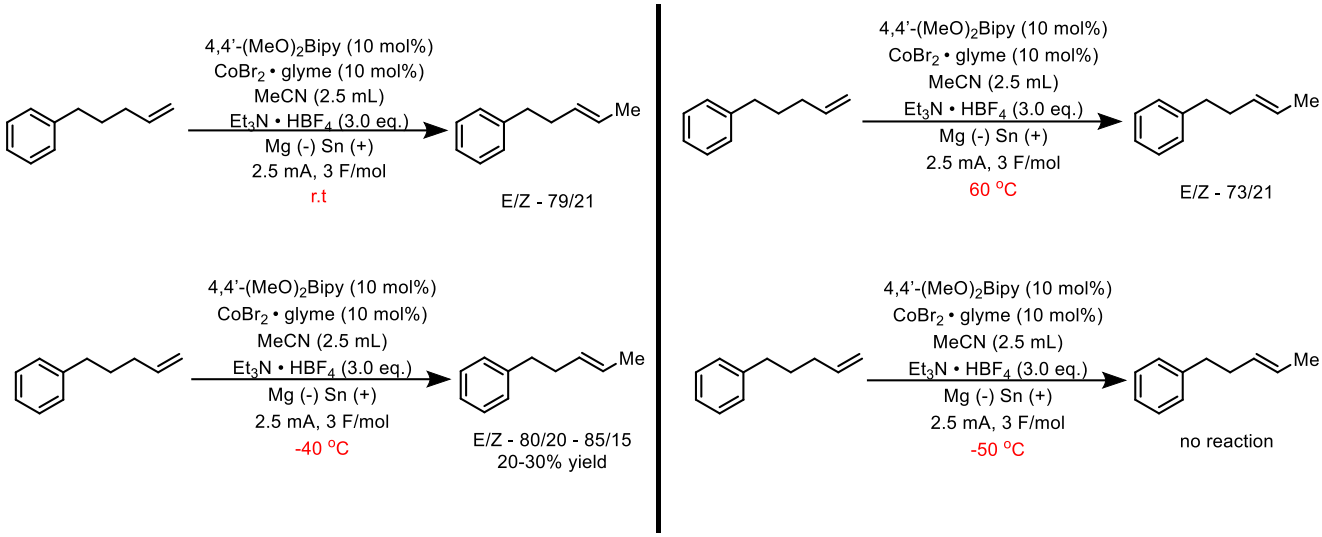


No conversion



low conversion

Temperature:



STARTING MATERIALS SYNTHESIS

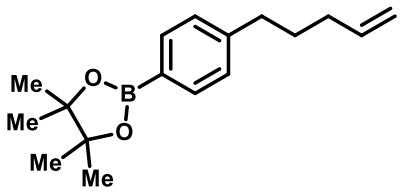
Alkene substrates: Substrates leading to the following products are commercially available: **13, 14, 45, 46, 62, 74** and **Co(salen)-1**. The substrates leading to the following products were synthesized according to literature procedures: **3**[1], **4**[2], **5**[3], **6**[4], **7**[5], **8**[6], **9**[7], **10**[8], **11**[9], **12**[10], **15**[11], **16**[12], **17**[13], **19**[14], **21**[14], **24**[15], **26-31**[15], **32**[16], **34**[17], **35**[18], **49**[19], **57**[20], **59**[21], **65**[15], **68**[22], **70**[15], **72**[23] and **Co(salen)-2**[24].

Synthesis of Et_3NHBF_4

Et_3N (1.0 eq.) in Et_2O (*ca.* 0.2 M), add HBF_4*OEt_2 (1.0 eq.) dropwise (slowly, the Ether might start to boil suddenly) and stirred for 15 minutes. The reaction mixture was carefully concentrated to dryness to afford the desired salt.

Note: The salt is hydroscopic and if necessary azeotrope drying using toluene was used (can be repeated 3 times).

Compound 1



To the solution of 1-bromo-4-(pent-4-en-1-yl)benzene (5.0 mmol, 1.0 equiv.) in DMF (20 mL) was added B_2Pin_2 (1.1 equiv.) and KOAc (3.0 equiv.). The suspension was degassed with an argon balloon for 10 min. $PdCl_2$(dppf) (0.1 equiv.) was added and the reaction was heated to 90 °C and stirred overnight. After cooling to room temperature, water was added to quench the reaction. The mixture was extracted with Et_2O, and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered and volatiles were removed. The crude was purified by column chromatography (Hexanes/EtOAc = 20/1) to afforded 1.25 g (92%) of the product.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 5.84 (ddt, *J* = 17.0, 9.7, 6.6 Hz, 1H), 5.08 – 4.97 (m, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.10 (q, *J* = 7.3 Hz, 2H), 1.74 (p, *J* = 7.8 Hz, 2H), 1.36 (s, 12H).

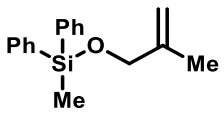
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 138.6, 134.98, 128.1, 114.9, 83.7, 35.6, 33.4, 30.6, 25.0.

Physical State: pale yellow oil.

GC/MS (EI): 117 (98%), 130 (87%), 144 (100%), 173 (80%), 217 (78%), 230 (67%), 272 (13%).

TLC: R_f = 0.38 (20:1 Hexanes: EtOAc).

Compound S1



A solution of methyl allyl alcohol (1.0 mmol, 1.0 eq.) in DCM (10 mL, 0.1 M) was cooled to 0 °C and Et_3N (4.0 mmol, 4.0 eq.) was slowly added. After 5 min, diphenylmethyl-silane-chloride (1.5 mmol, 1.5 eq.) was added dropwise and the resulting mixture was stirred at rt for 5 hr. Saturated aqueous solution of $NaHCO_3$ (10 mL) was added and layers were separated. Aqueous layer was extracted with DCM (3 x 10 mL) and combined organic layers were washed

with brine (5 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The product was purified by column to give 227 mg (85 %) of colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H), 7.45 – 7.36 (m, 6H), 5.08 (td, *J* = 1.7, 0.8 Hz, 1H), 4.86 (dq, *J* = 2.7, 1.4 Hz, 1H), 4.16 – 4.12 (m, 2H), 1.73 (dq, *J* = 1.5, 0.7 Hz, 3H), 0.68 (s, 3H).

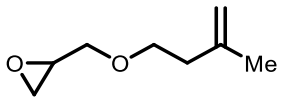
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 134.4, 134.0, 129.8, 129.6, 127.9, 127.7, 109.8, 67.0, 19.1, -0.6.

Physical State: colorless oil.

GC/MS (EI): 91 (100%), 129 (64%), 144 (37%), 268 (0.1%).

TLC: R_f = 0.38 (Hexanes).

Compound S2



The preparation of compound **S2** was carried out according to the literature procedure.[25]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.73 (s, 1H), 3.73 (dd, *J* = 11.6, 3.1 Hz, 1H), 3.61 (ddt, *J* = 33.5, 9.4, 6.9 Hz, 2H), 3.39 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.14 (ddd, *J* = 5.9, 4.1, 2.8 Hz, 1H), 2.79 (t, *J* = 4.6 Hz, 1H), 2.60 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.31 (t, *J* = 6.9 Hz, 2H), 1.75 (s, 3H).

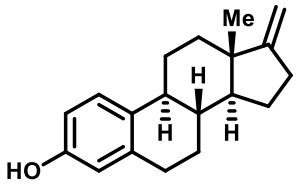
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 111.7, 71.6, 70.0, 50.9, 44.4, 37.8, 22.8.

Physical State: colorless oil.

GC/MS (EI): 57 (68%), 68 (100%), 142 (0.3%).

TLC: R_f = 0.58 (4:1 Hexanes: EtOAc).

Compound S3



The preparation compound **S3** was carried out according to the literature procedure.[26]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 4.86 (s, 1H), 4.69 (s, 2H), 2.84 (qdd, *J* = 14.6, 8.8, 5.2 Hz, 2H), 2.55 (ddd, *J* = 17.3, 10.0, 2.2 Hz, 1H), 2.32 (dddd, *J* = 34.8, 17.3, 8.1, 2.9 Hz, 2H), 2.21 (td, *J* = 11.0, 4.3 Hz, 1H), 2.01 – 1.91 (m, 2H), 1.82 (dddd, *J* = 11.3, 8.6, 6.5, 1.8 Hz, 1H), 1.75 (s, 1H), 1.54 (qd, *J* = 13.0, 3.7 Hz, 1H), 1.49 – 1.35 (m, 4H), 1.25 (ddd, *J* = 12.3, 10.5, 6.2 Hz, 1H), 0.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 153.4, 138.5, 133.0, 126.7, 115.4, 112.8, 101.0, 53.6, 44.5, 44.1, 38.9, 35.8, 29.8, 29.6, 27.7, 26.7, 24.0, 18.7.

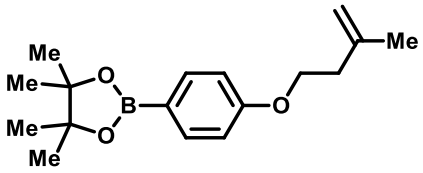
Physical State: white solid.

HRMS (ESI-TOF): calc'd for $C_{19}H_{25}O$ $[M+H]^+$: 269.1905; found 269.1913.

TLC: R_f = 0.51 (4:1 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = +58.1 (*c* = 1.0, $CHCl_3$).

Compound S4



A flame dried flask was charged with triphenylphosphine (1.2 equiv.), THF (10 mL), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (2.0 mmol, 1.0 equiv.), and 2-methyl-1-buten-4-ol (1.1 equiv.). The reaction mixture was cooled to 0 °C with an ice bath. To the cooled reaction mixture was dropwise added diisopropyl azodicaboxylate (DIAD) (1.2 equiv.). The reaction mixture was allowed to warm to rt and stirred overnight. Volatiles were removed under reduced pressure and the crude product was purified by column chromatography (Hexanes/EtOAc = 4/1) to yield 390 mg (68%) of corresponding aryl alkyl ether.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.84 (s, 1H), 4.80 (s, 1H), 4.10 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.80 (s, 3H), 1.33 (s, 12H).

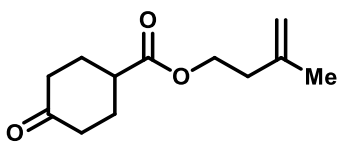
^{13}C NMR (151 MHz, $CDCl_3$): δ 161.6, 142.3, 136.6, 114.1, 112.2, 83.7, 66.4, 37.3, 25.0, 23.0.

Physical State: pale yellow oil.

HRMS (ESI-TOF): calc'd for $C_{17}H_{26}BO_4$ $[M+OH]^-$: 304.1966; found 304.1965.

TLC: R_f = 0.43 (4:1 Hexanes: EtOAc).

Compound S5



To a mixture of 4-oxocyclohexanecarboxylic acid (2.0 mmol, 1.0 equiv.) and 2-methyl-1-buten-4-ol (1.2 equiv.) in CH_2Cl_2 (10 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (1.5 equiv.) and 4-(dimethylamino)pyridine (DMAP) (0.1 equiv.) and the reaction was stirred overnight at room temperature. The

reaction was quenched with brine and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and volatiles were removed. The crude was purified by column chromatography (Hexanes/EtOAc = 4/1) to yield 360 mg (86%) of corresponding ester.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.73 (s, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 2.74 (tt, *J* = 9.7, 4.0 Hz, 1H), 2.47 (dt, *J* = 14.9, 5.4 Hz, 2H), 2.39 – 2.30 (m, 4H), 2.18 (dq, *J* = 15.1, 5.4 Hz, 2H), 2.01 (dtd, *J* = 14.5, 10.1, 4.9 Hz, 2H), 1.75 (s, 3H).

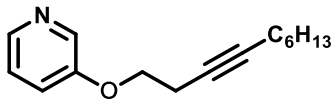
^{13}C NMR (151 MHz, $CDCl_3$) δ 210.2, 174.2, 141.6, 112.6, 62.8, 40.8, 39.8, 36.9, 28.6, 22.5.

Physical State: colorless oil.

GC/MS (EI): 55 (30%), 68 (100%), 97 (25%), 125 (13%), 210 (0.3%).

TLC: R_f = 0.48 (4:1 Hexanes: EtOAc).

Compound S6



A flame dried flask was charged with triphenylphosphine (1.2 equiv.), THF (10 mL), 3-hydroxypyridine (2.0 mmol, 1.0 equiv.), and 3-decyn-1-ol (1.1 equiv.). The reaction mixture was cooled to 0 °C with an ice bath. To the cooled reaction mixture was dropwise added diisopropyl azodicaboxylate (DIAD) (1.2 equiv.). The reaction mixture was allowed to warm to rt and stirred for 3 days. Volatiles were removed under reduced pressure and the crude product was purified by column chromatography (Hexanes/ EtOAc = 3/1) to yield 315 mg (68%) of corresponding aryl alkyl ether.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.22 (s, 1H), 7.21 (s, 1H), 4.09 (t, *J* = 7.1 Hz, 2H), 2.69 – 2.56 (m, 2H), 2.21 – 2.04 (m, 2H), 1.51 – 1.43 (m, 2H), 1.40 – 1.32 (m, 2H), 1.33 – 1.20 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H).

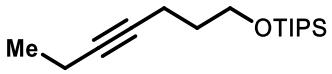
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 142.4, 138.2, 124.0, 121.5, 82.6, 75.5, 67.2, 31.5, 29.0, 28.6, 22.7, 20.0, 18.8, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55 (82%), 67 (100%), 78 (98%), 95 (88%), 174 (74%), 230 (88%), 231 (12%).

TLC: R_f = 0.55 (3:1 Hexanes: EtOAc).

Compound S7



A solution of (hept-4-yn-1-yloxy)triisopropylsilane (537 mg, 2.0 mmol) in THF (2 mL) in flame dried flask was cooled to −78 °C, *n*-BuLi (1.5 eq., 2.5 M hexane solution, 1.2 mL, 3.0 mmol) was added, and the mixture was stirred at the same temperature for 15 min. Ethyl iodide (2.0 eq., 623 mg, 322 µL, 4.0 mmol) was added, and the mixture was warmed to room temperature. After 1.5 h of stirring, the reaction was quenched by addition of a sat. NH_4Cl solution, and the aqueous solution was extracted with CH_2Cl_2 (3 x 10 mL) and dried over Na_2SO_4. After filtration, evaporation of the solvent gave a residue, which was chromatographed on silica gel (Hexanes) to afford the product in 39% yield (210.8 mg, 0.78 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (t, *J* = 6.2 Hz, 2H), 2.25 (tt, *J* = 7.1, 2.4 Hz, 2H), 2.15 (qt, *J* = 7.5, 2.4 Hz, 2H), 1.75 – 1.66 (m, 2H), 1.13 (s, 24H).

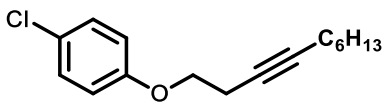
^{13}C NMR (126 MHz, $CDCl_3$): δ 81.9, 79.3, 62.2, 32.5, 18.2, 15.3, 14.5, 12.6, 12.2.

Physical State: Colorless liquid.

GC/MS (EI): 185 (100%), 227 (93%), 143 (48%), 268 (0.04%).

$\boldsymbol{R_f}$ = 0.29 (Hexanes).

Compound S8



A flame dried flask was charged with triphenylphosphine (1.2 equiv.), THF (10 mL), 4-chloro-phenol (2.0 mmol, 1.0 equiv.), and 3-decyn-1-ol (1.1 equiv.). The reaction mixture was cooled to 0 °C with an ice bath. To the cooled reaction mixture was dropwise added diisopropyl azodicaboxylate (DIAD) (1.2 equiv.). The reaction mixture was allowed to warm to rt and stirred overnight. Volatiles were removed under reduced pressure and the crude product was purified by column chromatography (Hexanes/Et_2O = 40/1) to yield 307 mg (58%) of corresponding aryl alkyl ether.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 4.02 (td, *J* = 7.1, 1.1 Hz, 2H), 2.63 (ddd, *J* = 7.2, 4.8, 2.4 Hz, 2H), 2.15 (tq, *J* = 7.1, 1.8 Hz, 2H), 1.48 (p, *J* = 7.2 Hz, 2H), 1.43 – 1.33 (m, 2H), 1.34 – 1.20 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 2H).

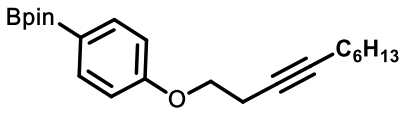
^{13}C NMR (151 MHz, $CDCl_3$): δ 157.4, 129.4, 125.9, 116.1, 82.4, 75.7, 67.2, 31.5, 29.0, 28.7, 22.7, 20.0, 18.9, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55 (46%), 67 (61%), 81 (100%), 95 (86%), 128 (46%), 264 (21%).

TLC: R_f = 0.78 (40:1 Hexanes: Et_2O).

Compound S9



A flame dried flask was charged with triphenylphosphine (1.2 equiv.), THF (10 mL), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (2.0 mmol, 1.0 equiv.), and 3-decyn-1-ol (1.1 equiv.). The reaction mixture was cooled to 0 °C with an ice bath. To the cooled reaction mixture was dropwise added diisopropyl azodicaboxylate (DIAD) (1.2 equiv.). The reaction mixture was allowed to warm to rt and stirred overnight. Volatiles were removed under reduced pressure and the crude product was purified by column chromatography (Hexanes/ EtOAc = 20/1) to yield 455 mg (64%) of corresponding aryl alkyl ether.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 4.07 (t, *J* = 7.3 Hz, 2H), 2.83 – 2.66 (m, 2H), 2.15 (d, *J* = 14.3 Hz, 2H), 1.48 (p, *J* = 7.2 Hz, 2H), 1.44 – 1.20 (m, 18H), 0.89 (t, *J* = 6.9 Hz, 3H).

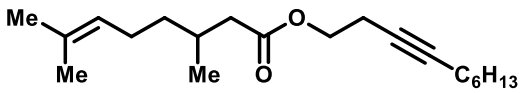
^{13}C NMR (151 MHz, $CDCl_3$): δ 161.3, 136.7, 136.6, 114.1, 83.7, 82.3, 75.8, 66.6, 31.5, 29.0, 28.7, 25.0, 22.7, 19.9, 18.9, 14.2.

Physical State: colorless oil.

GC/MS (EI): 207 (100%), 95 (86%), 356 (22%).

TLC: R_f = 0.45 (20:1 Hexanes: EtOAc).

Compound S10



To a mixture of racemic citronellic acid (2.0 mmol, 1.0 equiv.) and 3-decyn-1-ol (1.2 equiv.) in CH_2Cl_2 (10 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (1.5 equiv.) and 4-(dimethylamino)pyridine (DMAP) (0.1 equiv.) and the reaction was stirred overnight at room temperature. The reaction was quenched with brine and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and volatiles were removed. The crude was purified by column chromatography (Hexanes/EtOAc = 40/1) to yield 582 mg (95%) of corresponding ester.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.12 – 5.03 (m, 1H), 4.13 (t, *J* = 7.0 Hz, 2H), 2.52 – 2.42 (m, 2H), 2.32 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.21 – 2.07 (m, 3H), 2.05 – 1.81 (m, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.46 (p, *J* = 7.2 Hz, 2H), 1.40 – 1.32 (m, 2H), 1.34 – 1.20 (m, 4H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H).

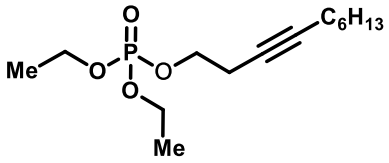
^{13}C NMR (151 MHz, $CDCl_3$): δ 173.2, 131.6, 124.4, 82.2, 75.7, 62.8, 41.8, 36.9, 31.5, 30.2, 29.0, 28.6, 25.8, 25.5, 22.7, 19.7, 19.4, 18.8, 17.8, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55 (50%), 69 (100%), 81 (162%), 95 (56%), 109 (44%), 301 (0.3%).

TLC: R_f = 0.51 (40:1 Hexanes: EtOAc).

Compound S11



A flame-dried flask is successively charged with dec-3-yn-1-ol (309 mg, 352 µL, 2.0 mmol), Et_3N (303 mg, 3.0 mmol), DMAP (61 mg, 0.5 mmol), and CH_2Cl_2 (10 mL). The reaction mixture is cooled to 0°C and diethyl chlorophosphate (1.5 eq., 518 mg, 437 µL, 3.0 mmol) is added dropwise to the solution. The resulting suspension is allowed to warm to room temperature and stirred for further 6 h at this temperature. After completion (TLC monitoring), the reaction is carefully quenched with saturated aqueous NH_4Cl solution, and the aqueous phase is extracted with CH_2Cl_2 (3 ×50 mL). The combined organic phases are washed with water and dried over anhydrous Na_2SO_4, filtered and volatiles were evaporated under reduced pressure. The crude was purified by column chromatography (Hex/EtOAc, 100: 0 - 1:1) to yield 91% (528.4 mg, 1.82 mmol) of the desired compound as an orange liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.20 – 3.99 (m, 6H), 2.62 – 2.48 (m, 2H), 2.21 – 2.08 (m, 2H), 1.53 – 1.40 (m, 2H), 1.40 – 1.15 (m, 12H), 0.93 – 0.84 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 82.6, 74.9, 65.9 (d, *J* = 5.8 Hz), 63.9 (d, *J* = 5.8 Hz), 31.5, 28.9, 28.6, 22.6, 21.1 (d, *J* = 7.5 Hz), 18.8, 16.3 (d, *J* = 6.7), 14.2.

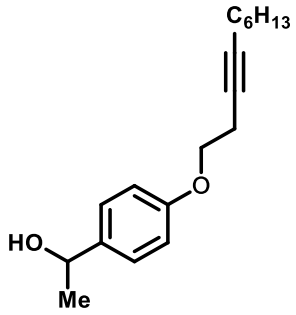
^{31}P NMR (162 MHz, $CDCl_3$): δ -1.25 (p, *J* = 8.1 Hz).

Physical State: Orange liquid.

HRMS (ESI): calcd for $C_{14}H_{28}O_4P_1$ $[M+H]^+$ 291.1725, found 291.1732.

R_f = 0.34 (Hex/EtOAc, 1:1).

Compound S12



A flame dried flask was charged with triphenylphosphine (315 mg, 2.4 mmol, 1.2 equiv.), 4-hydroxyacetophenone (300 mg, 2.2 mmol, 1.1 eq.), THF (8 mL), and dec-3-yn-1-ol (309 mg, 352 µL, 2.0 mmol). The reaction mixture was cooled to 0 °C with an ice bath. To the cooled reaction mixture was dropwise added diisopropyl azodicaboxylate (DIAD) (485 mg, 471 µL, 2.4 mmol, 1.2 equiv.). The reaction mixture was allowed to warm to rt and stirred for 24 h. Volatiles were removed under reduced pressure to leave a yellowish oil. The mixture was suspended in Et_2O to crash out solid triphenylphospine oxide, which was then removed by filtration through a plug of celite. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Hex/EtOAc, 100:0 - 60:40) to yield 54% (over two steps, 310.5 mg, 1.14 mmol) as a colorless liquid. The resulting ketone was dissolved in MeOH (3 mL) and CH_2Cl_2 (3 mL) and $NaBH_4$ (43 mg, 1.14 mmol 1.0 eq.) was slowly added and the mixture was stirred for 4 h. Volatiles were removed under reduced pressure and the residue was dissolved in a mixture of Hexanes and EtOAc (50:50) which was filtered through a pad of silica. After evaporation of the solvent the desired alcohol was obtained in >95% yield (312.8 mg, 1.14 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.85 (q, *J* = 6.4 Hz, 1H), 4.04 (t, *J* = 7.3 Hz, 2H), 2.63 (tt, *J* = 7.2, 2.3 Hz, 2H), 2.15 (tt, *J* = 7.2, 2.3 Hz, 2H), 1.77 (brs, 1H), 1.53 – 1.43 (m, 5H), 1.43 – 1.34 (m, 2H), 1.33 – 1.25 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H).

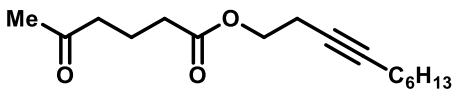
^{13}C NMR (151 MHz, $CDCl_3$): δ 158.1, 138.4, 126.8, 114.7, 82.3, 75.8, 70.1, 66.9, 31.5, 28.7, 25.2, 22.7, 19.9, 18.9, 14.2.

Physical State: Colorless liquid.

HRMS (ESI): calcd for $C_{18}H_{27}O_2$ $[M\text{-}OH]^+$ 257.1905, found 257.1909.

R_f = 0.69 (Hex/EtOAc, 1:1).

Compound S13



To a mixture of 5-oxo-hexanoic acid (260 mg, 2.0 mmol) and pent-3-yne-1-ol (168 mg, 2.0 mmol, 1.0 eq.) in CH_2Cl_2 (8 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (466 mg, 3.0 mmol, 1.5 eq.) and 4-(dimethylamino)pyridine (DMAP) (20 mol%, 49 mg) and the reaction was stirred for 4 h at room temperature. The reaction was quenched with aqueous HCl (1 M, 5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases where dried over Na_2SO_4, filtered and volatiles were removed. The crude was dissolved in a mixture if Hexanes and EtOAc (60:40) and filtered over a pad of silica. The desired compound was isolated in 89% yield (1.78 mmol, 349 mg) as a yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.12 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.51 – 2.40 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 1H), 2.14 (s, 3H), 1.96 – 1.82 (m, 2H), 1.82 – 1.69 (m, 3H).

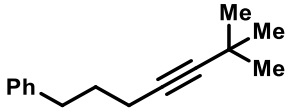
^{13}C NMR (100 MHz, $CDCl_3$): δ 208.2, 173.1, 77.4, 74.8, 62.9, 42.5, 33.2, 30.1, 19.3, 18.9, 3.6.

Physical State: Yellowish liquid.

GC/MS (EI): 113 (100%), 66 (90%), 85 (70%), 131 (21%), 131 (21%), 196.1 (0.02%).

R_f = 0.38 (Hex/EtOAc, 7:3).

Compound S14



A solution of *tert* butyl acetylene (1.0 mmol) in THF (2 mL) in flame dried flask was cooled to −78 °C, *n*-BuLi (1.5 eq., 2.5 M hexane solution, 0.6 mL, 1.5 mmol) was added, and the mixture was stirred at the same temperature for 15 min. Bromo-propyl benzene (2.0 eq., 2.0 mmol) was added, and the mixture was warmed to room temperature. After 1.5 h of stirring, the reaction was quenched by addition of a sat. NH_4Cl solution, and the aqueous solution was extracted with CH_2Cl_2 (3 x 10 mL) and dried over Na_2SO_4. After filtration, evaporation of the solvent gave a residue, which was chromatographed on silica gel (Hexanes) to afford the product in 57% yield (0.57 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 2.77 – 2.72 (m, 2H), 2.19 (t, *J* = 7.0 Hz, 2H), 1.83 (p, *J* = 7.1 Hz, 2H), 1.26 (d, *J* = 1.0 Hz, 9H).

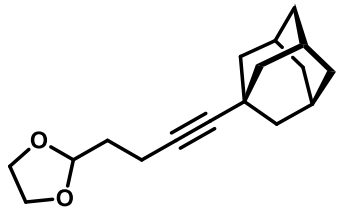
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.0, 128.6, 128.3, 125.8, 89.7, 78.0, 34.8, 31.4, 30.9, 27.4, 18.2.

GC/MS (EI): 125 (100%), 73 (87%), 135 (25%), 260 (4%).

Physical State: Colorless oil.

R_f = 0.5 (Hex/EtOAc, 40:1).

Compound S15



A solution of 1-ethynyladamantane (321 mg, 2.0 mmol) in THF (2 mL) in flame dried flask was cooled to −78 °C, *n*-BuLi (1.5 eq., 2.5 M hexane solution, 1.2 mL, 3.0 mmol) was added, and the mixture was stirred at the same temperature for 15 min. 2-(2-bromoethyl)-1,3-dioxolane (2.0 eq., 724 mg, 470 µL, 4.0 mmol) was added, and the mixture was warmed to room temperature. After 36 h of stirring, the reaction was quenched by addition of a sat. NH_4Cl solution, and the aqueous solution was extracted with CH_2Cl_2 (3 x 10 mL) and dried over Na_2SO_4. After filtration, evaporation of the solvent gave a residue, which was purified by column chromatography (Hex/EtOAc, 100:0 - 80:20) in 67% yield (348.6 mg, 1.34 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.97 (td, *J* = 4.9, 1.0 Hz, 1H), 4.03 – 3.90 (m, 2H), 3.91 – 3.79 (m, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.92 (d, *J* = 13.1 Hz, 3H), 1.86 – 1.78 (m, 8H), 1.66 (d, *J* = 6.4 Hz, 6H).

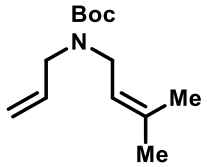
^{13}C NMR (126 MHz, $CDCl_3$): δ 103.6, 95.4, 89.4, 65.0, 43.4, 36.6, 33.8, 29.6, 28.2, 13.9.

Physical State: Colorless liquid.

GC/MS (EI): 125 (100%), 73 (87%), 135 (25%), 260 (4%).

R_f = 0.53 (Hex/EtOAc, 9:1).

Compound S16



To the solution of *N*-*tert*-butoxycarbonylprop-2-en-1-amine (2.0 mmol, 1.0 equiv.) in DMF (10 mL) was added NaH (60% dispersion in mineral oil) (1.5 equiv.) and the mixture was stirred for 30 min. at room temperature. Prenyl bromide (2.0 equiv.) was added dropwise over 1 min. The reaction was stirred overnight and quenched with brine, extracted with Et_2O, washed with water and brine. The organic phase was dried over Na_2SO_4, filtered and volatiles

were removed. The crude was purified by column chromatography (Hexanes/EtOAc = 20/1) to yield 403 mg (90%) of corresponding product.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.85 – 5.67 (m, 1H), 5.26 – 4.98 (m, 3H), 3.79 (brs, 4H), 1.71 (s, 3H), 1.63 (d, *J* = 2.4 Hz, 3H), 1.45 (s, 9H).

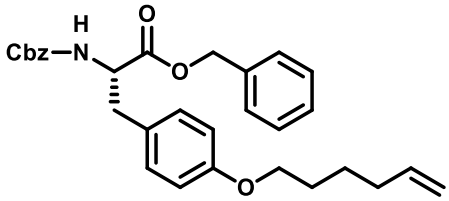
^{13}C NMR (151 MHz, $CDCl_3$): δ 155.6, 134.5, 121.5, 120.8, 79.5, 48.5, 43.8, 28.6, 25.8, 17.9.

Physical State: colorless oil.

GC/MS (EI): 57 (100%), 69 (40%), 154 (23%), 169 (22%), 225 (0.3%).

TLC: R_f = 0.55 (4:1 Hexanes: EtOAc).

Compound S17



A flame dried flask was charged with triphenylphosphine (1.2 equiv.), THF (10 mL), benzyl *N*-carbobenzyloxy-*L*-tyrosine (2.0 mmol, 1.0 equiv.), and 5-hexen-1-ol (1.1 equiv.). The reaction mixture was cooled to 0 °C with an ice bath. To the cooled reaction mixture was dropwise added diisopropyl azodicaboxylate (DIAD) (1.2 equiv.). The reaction mixture was allowed to warm to rt and stirred overnight. Volatiles were removed under reduced pressure and the crude product was purified by column chromatography (Hexanes/EtOAc = 4/1) to yield 810 mg (83%) of corresponding aryl alkyl ether.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (s, 10H), 6.90 (dd, *J* = 8.6, 2.8 Hz, 2H), 6.73 (dd, *J* = 8.7, 2.7 Hz, 2H), 5.90 – 5.78 (m, 1H), 5.32 – 4.89 (m, 7H), 4.74 – 4.62 (m, 1H), 3.91 (td, *J* = 6.5, 1.8 Hz, 2H), 3.05 (d, *J* = 5.7 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.83 – 1.74 (m, 2H), 1.64 – 1.54 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.6, 158.4, 155.7, 138.7, 136.4, 135.3, 130.4, 128.7, 128.7, 128.6, 128.3, 128.2, 127.4, 114.9, 114.7, 67.8, 67.3, 67.1, 55.1, 37.4, 33.6, 28.8, 25.5.

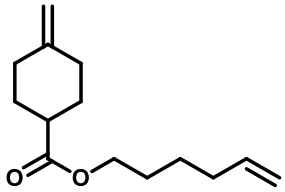
Physical State: white solid.

HRMS (ESI-TOF): calc'd for $C_{30}H_{34}NO_5$ $[M+H]^+$:488.2437; found 488.2430.

TLC: R_f = 0.62 (4:1 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = +4.6 (*c* = 1.0, $CHCl_3$).

Compound 50



To a mixture of 4-oxocyclohexanecarboxylic acid (2.0 mmol, 1.0 equiv.) and 5-hexen-1-ol (1.2 equiv.) in CH_2Cl_2 (10 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (1.5 equiv.) and 4-(dimethylamino)pyridine (DMAP) (0.1 equiv.) and the reaction was stirred overnight at room temperature. The reaction was quenched with brine and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and volatiles were removed. The crude was used in next step without further purification.

To a round bottom flask containing a magnetic stir bar was added the methyl triphenylphosphonium bromide (2.0 equiv.), KO^{t}Bu (2.0 equiv.), and toluene (20 mL). The mixture was stirred at 90 °C for 30 min. and then cooled to rt. The ketone obtained in last step was dissolved in 5 mL toluene and added to the mixture. The reaction was stirred at room temperature overnight. To the mixture was added 100 mL hexanes and stirred for 10 min. The precipitate was filtered off through a layer of silica. After removal of volatiles, the crude was purified by column chromatography (Hexanes/EtOAc = 20/1) to yield 240 mg (54%) of corresponding product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.71 (dtd, *J* = 4.8, 2.4, 1.2 Hz, 1H), 5.09 – 4.94 (m, 2H), 4.78 – 4.71 (m, 2H), 3.85 (s, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 2.23 – 2.10 (m, 4H), 1.99 (dddt, *J* = 17.7, 11.5, 4.0, 2.0 Hz, 1H), 1.90 – 1.82 (m, 1H), 1.76 (t, *J* = 1.0 Hz, 3H), 1.73 – 1.64 (m, 2H), 1.50 (dtd, *J* = 12.8, 11.1, 6.0 Hz, 1H).

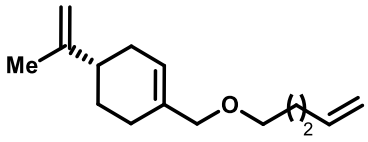
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 138.4, 134.9, 124.1, 114.6, 108.6, 75.2, 69.2, 41.1, 30.5, 30.4, 29.0, 27.5, 26.4, 20.8.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 67 (42%), 79 (33%), 94 (83%), 122 (28%), 194 (5%), 222 (0.1%).

TLC: R_f = 0.72 (20:1 Hexanes: EtOAc).

Compound 53



To the solution of (-)-perillyl alcohol (2.0 mmol, 1.0 equiv.) in DMF (10 mL) was added NaH (60% dispersion in mineral oil) (1.5 equiv.) and the mixture was stirred for 30 min. at room temperature. 5-Bromo-1-pentene (2.0 equiv.) was added dropwise over 1 min. The reaction was stirred overnight and quenched with brine, extracted with Et_2O, washed with water and brine. The organic phase was dried over Na_2SO_4, filtered and volatiles were removed. The crude was purified by column chromatography (Hexanes/EtOAc = 20/1) to yield 388 mg (88%) of corresponding ether.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.71 (dtd, *J* = 4.8, 2.4, 1.2 Hz, 1H), 5.09 – 4.94 (m, 2H), 4.78 – 4.71 (m, 2H), 3.85 (s, 2H), 3.40 (s, 2H), 2.23 – 2.10 (m, 6H), 1.99 (m, 1H), 1.90 – 1.82 (m, 1H), 1.76 (t, *J* = 1.1 Hz, 3H), 1.73 – 1.64 (m, 2H), 1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.94, 138.42, 134.94, 124.07, 114.64, 108.59, 75.18, 69.24, 41.15, 30.50, 30.40, 28.99, 27.50, 26.41, 20.79.

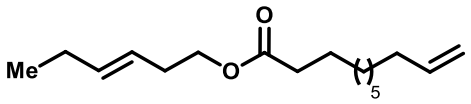
Physical State: colorless oil.

GC/MS (EI): 55 (50%), 69 (90%), 79 (80%), 93 (100%), 119 (50%), 177 (20%), 220 (15%).

TLC: R_f = 0.51 (20:1 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = -64.2 (*c* = 1.0, $CHCl_3$).

Compound 55



To a mixture of 10-undecenoic acid (2.0 mmol, 1.0 equiv.) and (*E*)-3-hexen-1-ol (1.2 equiv.) in CH_2Cl_2 (10 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (1.5 equiv.) and 4-(dimethylamino)pyridine (DMAP) (0.1 equiv.) and the reaction was stirred overnight at room temperature. The reaction was quenched with brine and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and volatiles were removed. The crude was purified by column chromatography (Hexanes/EtOAc = 20/1) to yield 480 mg (90%) of corresponding ester.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.57 (dt, *J* = 15.0, 6.4 Hz, 1H), 5.42 – 5.34 (m, 1H), 5.01 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.95 (dd, *J* = 10.4, 2.1 Hz, 1H), 4.09 (t, *J* = 6.9 Hz, 2H), 2.32 (dt, *J* = 17.2, 7.2 Hz, 4H), 2.08 – 2.05 (m, 4H), 1.63 (p, *J* = 7.8, 7.4 Hz, 2H), 1.39 (p, *J* = 6.9 Hz, 2H), 1.31 (p, *J* = 5.8, 4.8 Hz, 8H), 0.99 (t, *J* = 7.4 Hz, 3H).

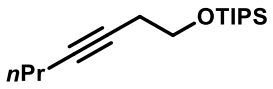
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 139.2, 135.0, 124.1, 114.1, 63.9, 34.4, 33.8, 32.0, 29.3, 29.2, 29.1, 29.1, 28.9, 25.6, 25.0, 13.7.

Physical State: colorless oil.

GC/MS (EI): 55 (44%), 67 (53%), 82 (100%), 266 (0.3%).

TLC: R_f = 0.50 (20:1 Hexanes: EtOAc).

Compound 63



To a flame dried 500 ml round bottom flask equipped with a magnetic stir bar, sodium hydride (3.75 g, 93.8 mmol, 1.05 equiv, 60% wt. dispersion in mineral oil) were placed under argon. THF (300 ml, 0.3 M) was added to the flask and the suspension was cooled with ice bath. To this cold suspension, alcohol (10.0 g, 89.3 mmol, 1.0 equiv) was added dropwise and stirring was continued. Subsequently, TIPSCl (17.2 g, 89.3 mmol, 1.0 equiv.) was added dropwise into the solution at 0°C. After complete addition of TIPSCl, the solution was allowed to warm to room temperature and stirring was continued for 2 h. The reaction mixture was quenched with sat. NH_4Cl and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography (10:1 Hexane: EtOAc) to afford the desired product as a colorless liquid (91%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (t, *J* = 7.4 Hz, 2H), 2.42 (tt, *J* = 7.5, 2.5 Hz, 2H), 2.14 (tt, *J* = 7.1, 2.5 Hz, 2H), 1.52 (hept, *J* = 7.3, 6.6 Hz, 3H), 1.17 – 1.05 (m, 22H), 0.98 (t, *J* = 7.4 Hz, 3H).

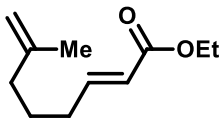
^{13}C NMR (151 MHz, $CDCl_3$) δ 81.3, 62.7, 23.3, 22.4, 20.8, 18.0, 17.9, 17.7, 13.5, 12.3, 12.0.

Physical State: colorless oil.

GC/MS (EI): 75 (77%), 103 (82%), 155 (52%), 183 (68%), 228 (100%), 268 (0.1%).

TLC: R_f = 0.5 (Hexanes).

Compound 66



Title compound was prepared following the reported method.[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.82 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.70 (d, *J* = 19.4 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.19 (qd, *J* = 7.0, 1.6 Hz, 2H), 2.03 (t, *J* = 7.6 Hz, 2H), 1.71 (s, 3H), 1.65 – 1.56 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

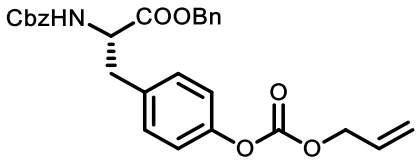
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 149.1, 145.2, 121.6, 110.5, 60.3, 37.2, 31.8, 26.0, 22.4, 14.4.

Physical State: colorless oil.

GC/MS (EI): 53 (64%), 67 (81%), 81 (100%), 93 (89%), 114 (44%), 182 (1%).

TLC: R_f = 0.31 (20:1 Hexanes: EtOAc).

Compound 76



To a solution of the phenol compound (405 mg, 0.1 mmol, 1 eq.) in THF (0.1 M) was added anhydrous Et_3N (202 uL, 0.3 mmol, 2 eq.) followed by allyl chloroformate (130 uL, 0.13 mmol, 1.3 eq.). The mixture was heated at reflux overnight. After cooling to room temperature, the reaction mixture was filtered, concentrated, redissolved in DCM, washed with water and then dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (3:2 EtOAc/hexanes) gave the title product in 78% yield (381.4 mg, 0.78 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.25 (m, 10H), 7.08 – 6.99 (m, 4H), 6.03 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.46 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.36 (dq, *J* = 10.4, 1.2 Hz, 1H), 5.30 (dd, *J* = 10.1, 2.6 Hz, 1H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.17 – 5.08 (m, 3H), 4.78 – 4.68 (m, 3H), 3.13 (qd, *J* = 14.0, 5.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 153.4, 150.2, 136.2, 135.0, 133.4, 131.1, 130.4, 128.7, 128.7, 128.7, 128.6, 128.6, 128.6, 128.2, 128.1, 127.0, 121.1, 119.6, 69.2, 67.4, 67.0, 54.7, 37.5.

Physical State: white solid.

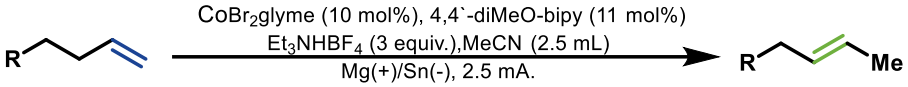
HRMMS (ESI): calcd for $C_{28}H_{28}NO_7$ $[M+H]^+$ 490.1866, found 490.1870

TLC: R_f = 0.45 (3:2 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = +4.1 (*c* = 1.0, $CHCl_3$).

EXPERIMENTAL PROCEDURE FOR ALKENE ISOMERIZATION

GENERAL PROCEDURE A. TERMINAL MONO-SUBSTITUTED ALKENE



Unless otherwise specified, the reaction was carried out on 0.2 mmol scale. A 5 mL Electrasyn-vial equipped with a magnetic stirring bar and wrapped with one layer of Teflon tape on the screw thread was charged with 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol).

In a separate long tube (8 mL) the starting material was charged (0.2 mmol) and the tube was evacuated and backfilled with argon. Dry and degassed MeCN (2.5 mL) was added to the tube. The sealed tube was quickly shaken, and a balloon filled with argon was bubbled through the solution for 1 minute.

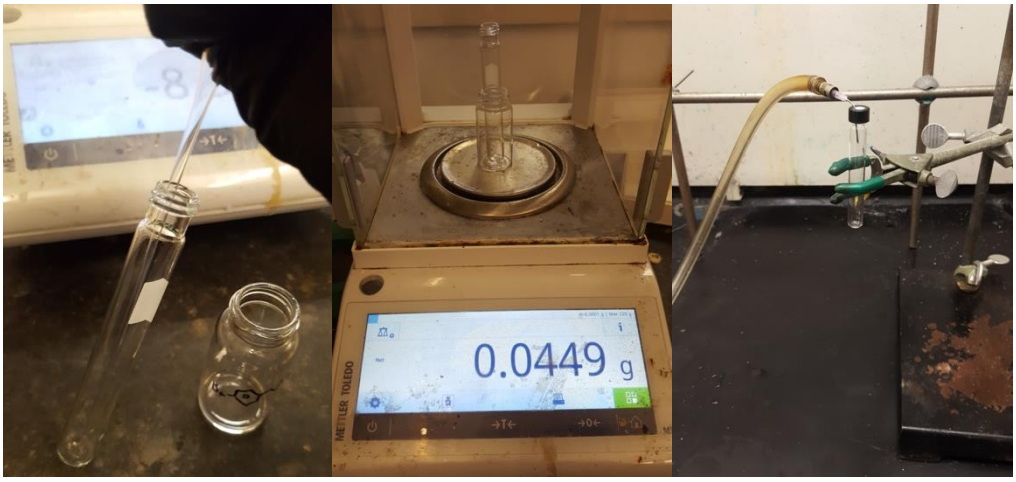
The aforementioned Electrasyn-vial was then quickly charged with $CoBr_2$*glyme (6.2 mg, 20 µmol) and Et_3N*HBF_4 (114 mg) (*N.B.* both substances are hygroscopic, especially the triethylamine salt. Weighing in a vial is recommended.). The Vial was sealed with the cap carrying a magnesium or zinc anode and a tin cathode and evacuated for 1-2 minutes (It is important to ensure that the cap is properly sealed at this stage) and backfilled with argon. The MeCN solution of starting material was added with a 3-mL syringe, which was previously purged with argon. The vial was electrolyzed for 3 or 4 F/mol with 1.3 or 2.5 mA applied. (The cell has typically a very low voltage at the beginning with magnesium anode (<0.1 V), however, with zinc anode the overall potential is around 2 V).

Thereafter, the crude reaction mixture was filtered through a short plug of silica and the solvent was evaporated under reduced pressure.

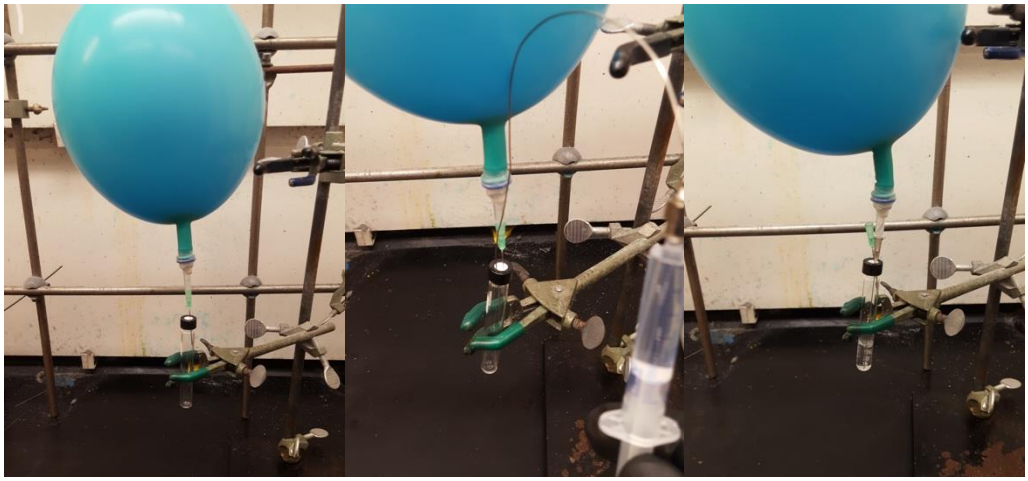
If the reaction gives you high voltage at the beginning of the reaction, there is likely a connectivity issue. Opening the vial at this stage makes the result not really reliable but bubbling argon through the solution for a few minutes after the vessel is sealed again can help.

Graphical Guide

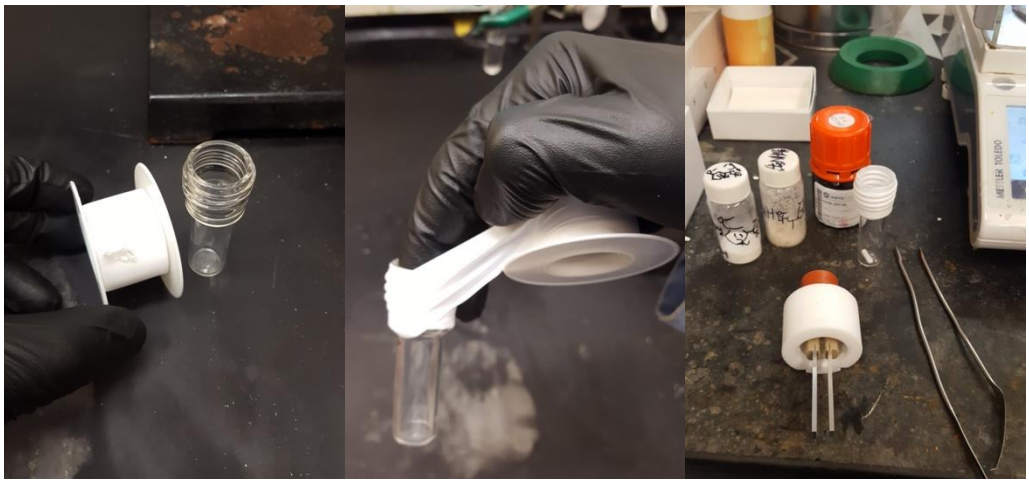
Photos were taken from the Isomerization of compound 11.



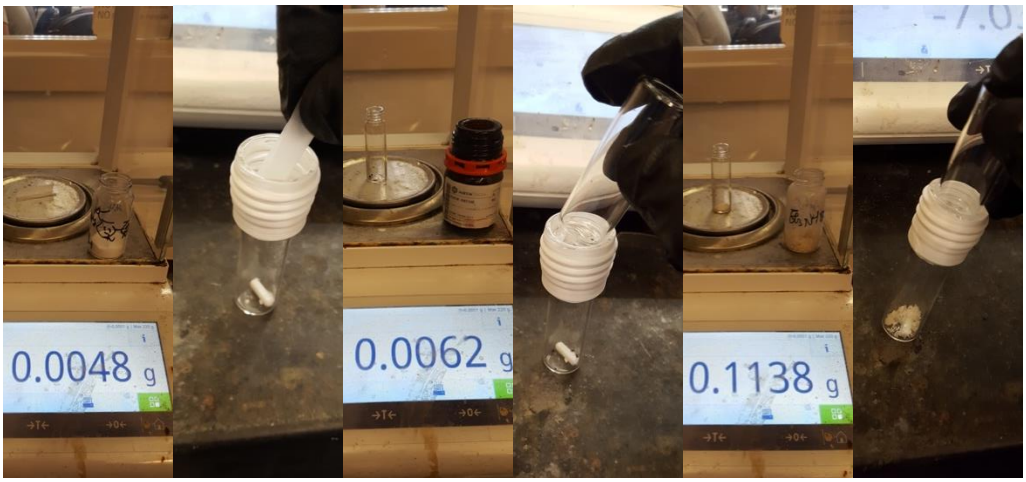
Left/Center: Starting material (44.9 mg) is weight in a reaction tube. **Right:** The tube is evacuated.



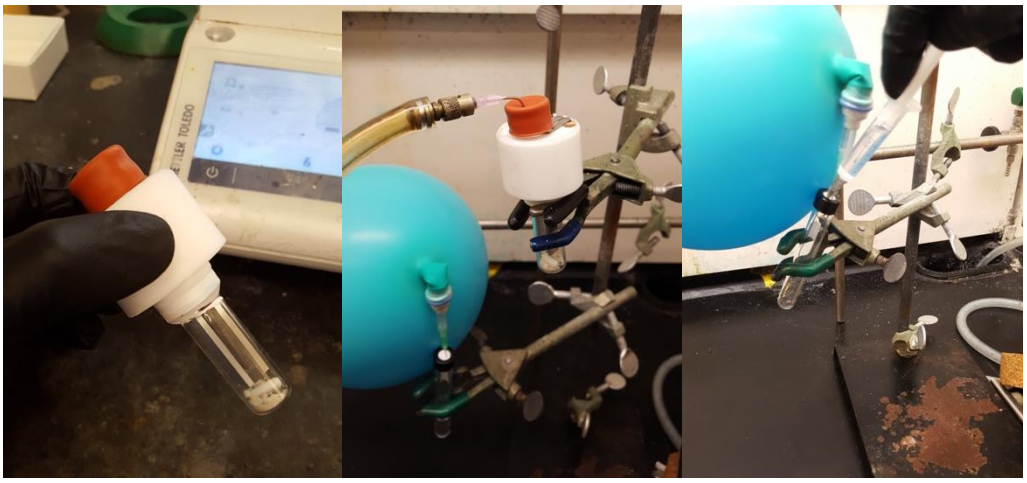
Left: The tube is backfilled with argon. **Center:** MeCN (2.5 mL). **Right:** Argon is bubbled through the solution for 1 min.



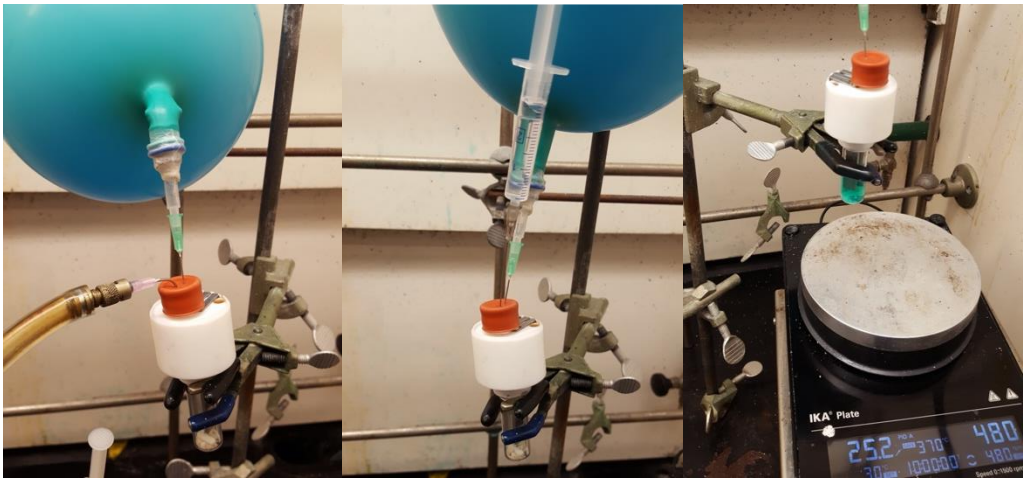
Left/Center: An Electrasyn vial (5 mL) is wrapped with Teflon-tape. **Right:** The ligand (4,4'-Dimethoxy-2,2'-Bipyridine), the proton-source (Et_3NHBF_4), the Cobalt source ($CoBr_2$•Glyme), the vial and an Electrasyn cap equipped with a tin (right), a magnesium electrode (left) and a septum.



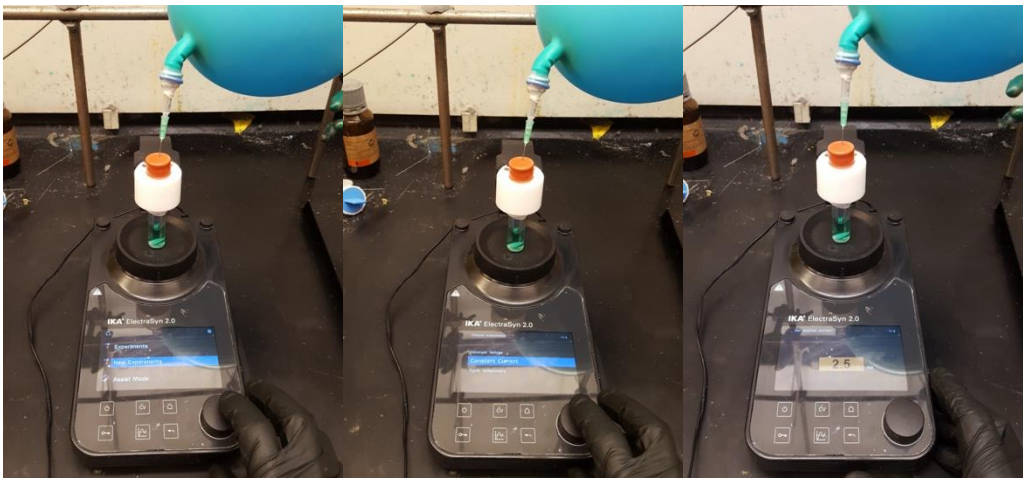
Left: 4,4'-Dimethyoxy-2,2'-bipyridine (4.8 mg). **Center:** $CoBr_2$•Glyme (6.2 mg). **Right:** Et_3NHBF_4 (113.8 mg). *N.B.*: The cobalt and the triethylamine salt are hygroscopic and we recommend weighting them in a glass vial.



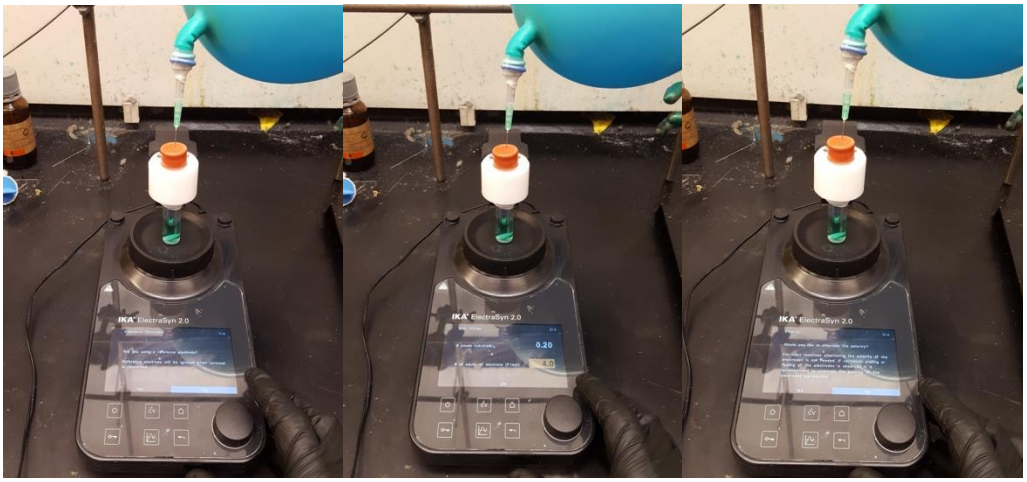
Left: The vial is tightly closed with the cap. **Center:** The vial is evacuated. **Right:** The MeCN solution of the starting material is pulled into a syringe.



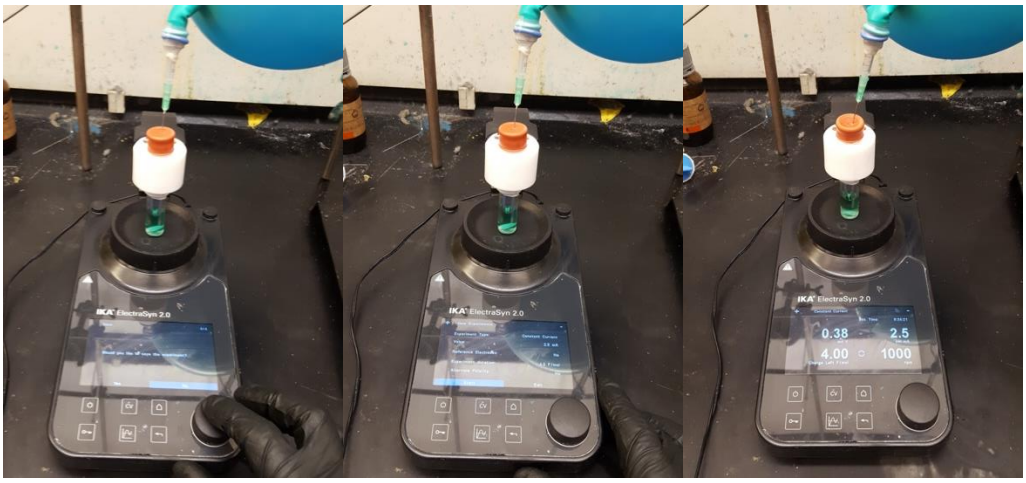
Left: The Electrasyn vial is backfilled with argon. **Center:** Addition of the starting material solution. **Right:** The vial is stirred until the solution is clear (10-30 seconds).



Left: The electrochemical cell was plugged into ElectraSyn 2.0. Select ‘New Experiments’. **Center:** Select ‘Constant Current’. **Right:** Set the current to 2.5 mA.



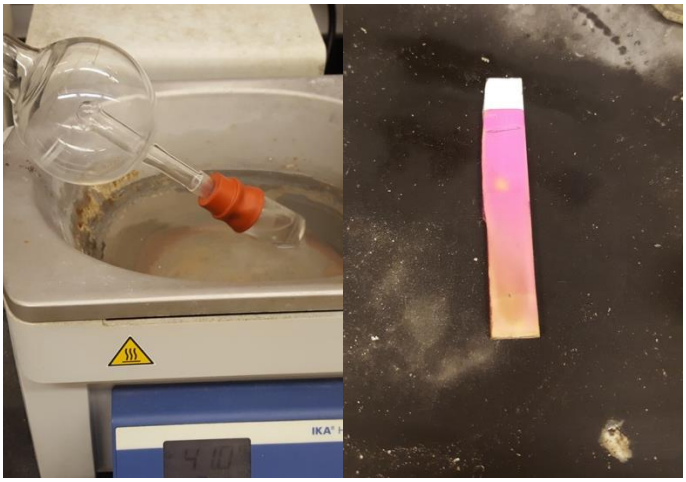
Left: No need to use a reference electrode. **Center:** Select ‘Total Charge’. Set 0.2 mmol substrate and 4.0 F/mol. **Right:** No alternate polarity.



Left: Saving the experimental parameters is optional. **Center:** ElectraSyn is ready. **Right:** Run the experiment and stir at 1000 rpm.

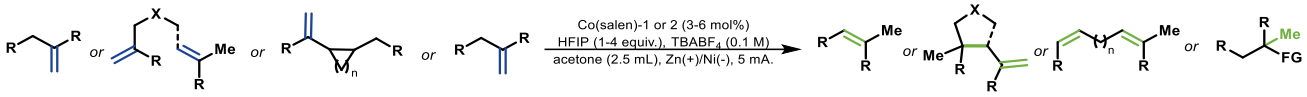
Left: The reaction turns red and retains that color until the end of the reaction. **Center:** A silica plug is prepared. **Right:** At the end of the reaction the electrodes are rinsed with hexanes. For more polar compounds Et_2O or EtOAc is used.

The crude is charged and filtered through the silica plug with hexanes as the solvent. For more polar compounds Et_2O or EtOAc is used.



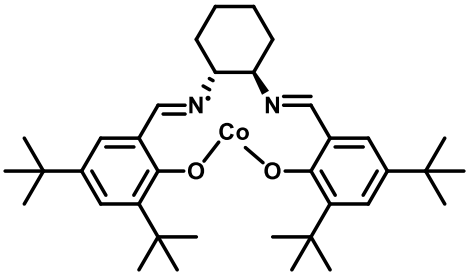
Left: Volatiles are evaporated under reduced pressure. **Center:** The TLC shows just a single spot (R_f = 0.65 in pure hexanes).

GENERAL PROCEDURE B. TERMINAL DI-SUBSTITUTED ALKENE, CYCLOISOMERIZATION, STRAINED-RINGS ISOMERIZATION, HYDROFUNCTIONALIZATION

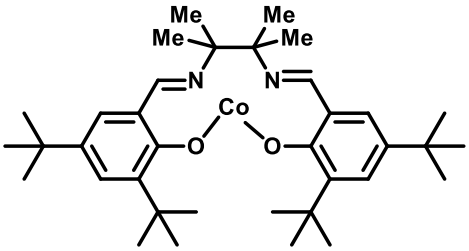


Unless otherwise specified, the reaction was carried out on 0.2 mmol scale. A 5ml Electra-Syn vial was equipped with a stir bar and charged with the corresponding alkene or diene (0.2 mmol). Acetone (2.5 mL), Co(salen)-1 or Co(salen)-2 (3-6 mol%) and HFIP (0.2-0.8 mmol) were added to the vial followed by the addition of solid $TBABF_4$ (60 mg, 0.1 M). The Electra-Syn vial cap equipped with anode (Zinc) and cathode (Nickel) was inserted into the reaction mixture. After pre-stirring for 5 minutes under argon, the reaction mixture was electrolyzed under a constant current of 5mA for 0.5-3 F/mol.

Structures of Co(salen)-1 and Co(salen)-2



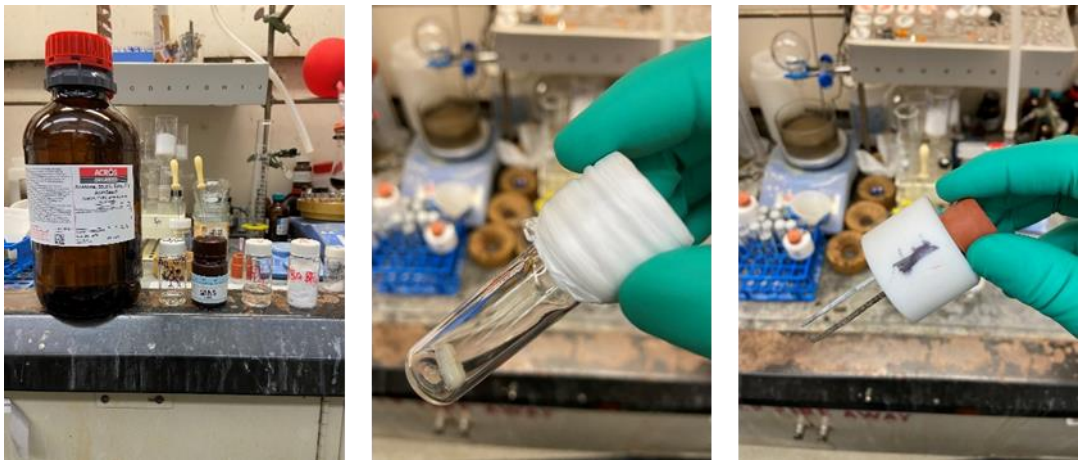
Co(salen)-1



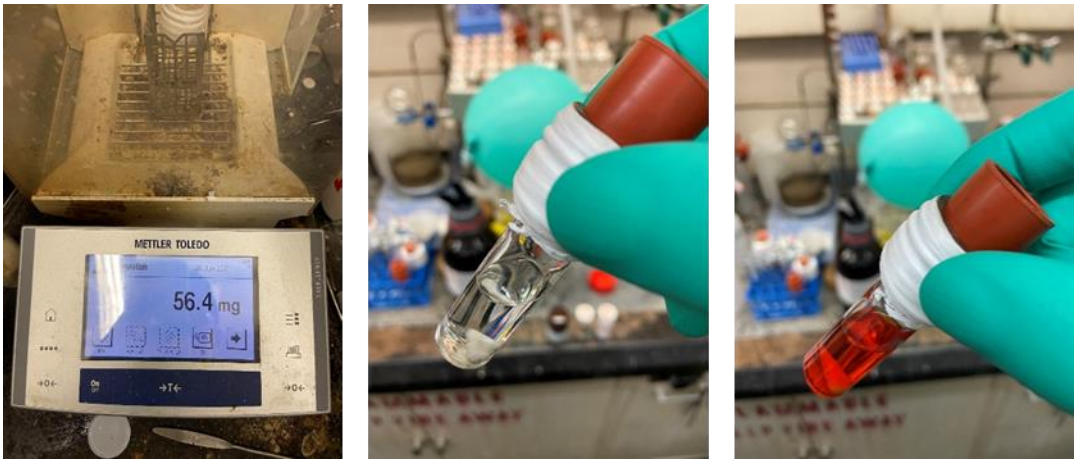
Co(salen)-2

Graphical Guide

Photos were taken from the cycloisomerization of compound **26**.

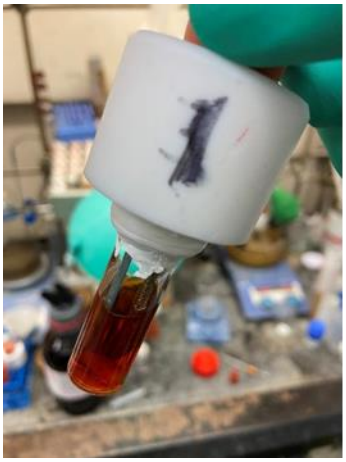


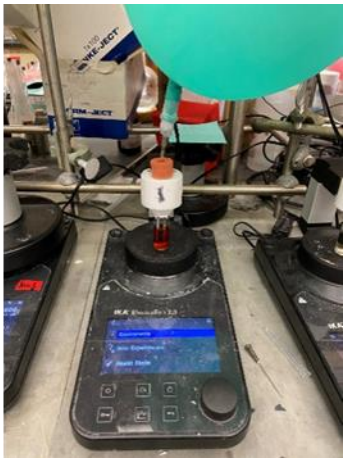
Left: All reagents for this reaction. **Center:** ElectraSyn 2.0 vial (5 mL, wrapped with Teflon tape) with a stir bar. **Right:** ElectraSyn 2.0 cap equipped with Zinc (left side) and Nickel foam electrodes (right side).



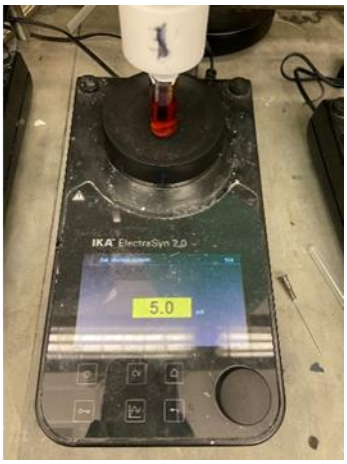
Left: Starting material of **26 (**56.5 mg). **Center:** Acetone (2.5 mL). **Right:** Cobalt catalyst (4.8 mg).


Left: HFIP (21 μL). **Center:** $TBABF_4$ (60 mg). **Right:** All reagents were added.



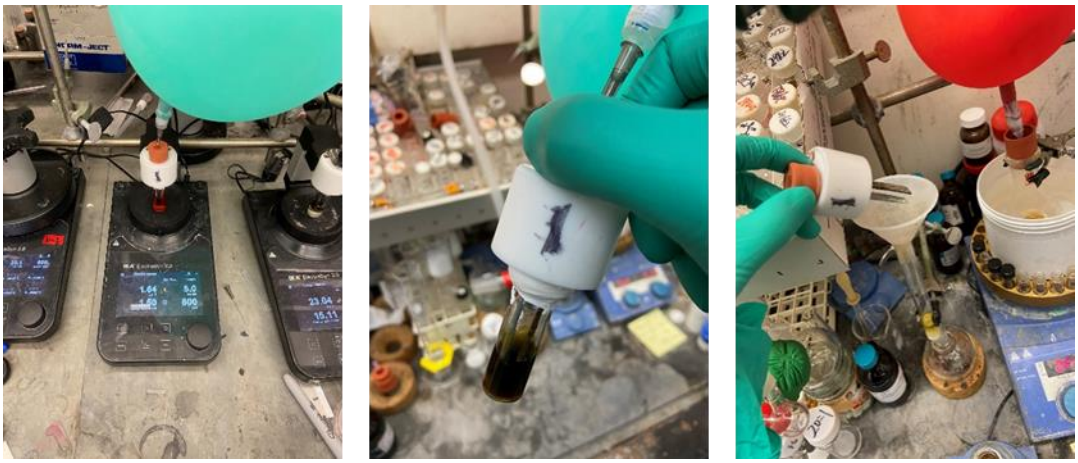
Left: The cap was tightly screwed into the vial. **Center:** Purging with Argon for 5 min. **Right:** The electrochemical cell was plugged into ElectraSyn 2.0.



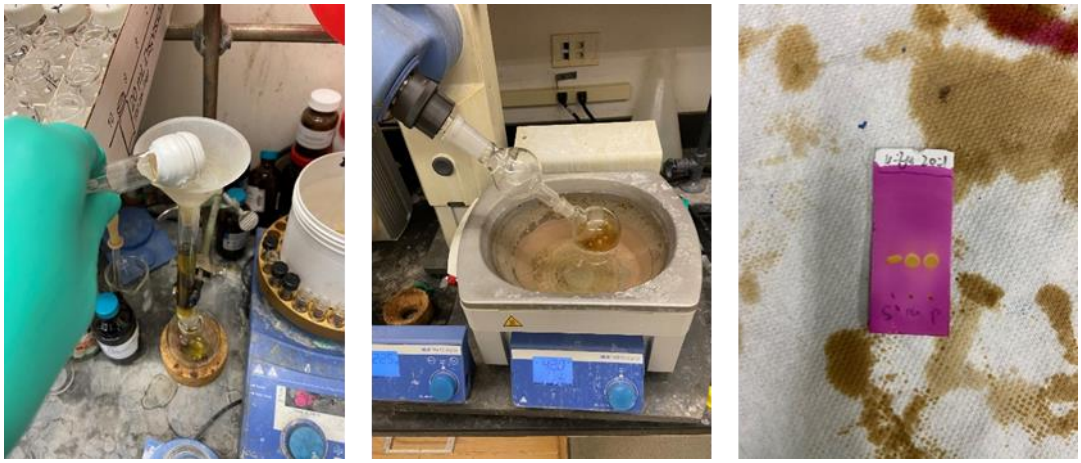
Left: Select ‘New Experiments’. **Center:** Select ‘Constant Current’. **Right:** Set the current to 5 mA.

Left: No need to use a reference electrode. **Center:** Select 'Total Charge'. **Right:** Set 0.2 mmol substrate and 1.5 F/mol.

Left: No alternate polarity. **Center:** Saving the experimental parameters is optional. **Right:** ElectraSyn is ready.

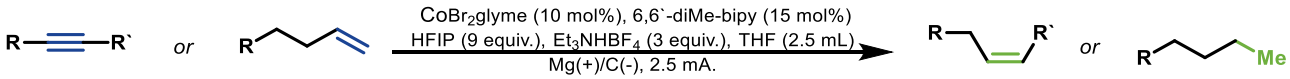


Left: Start the reaction with a stirring speed of 600 rpm. **Center:** Reaction completed. **Right:** Electrodes were rinsed with Et_2O and filtered through a thin layer of silica.



Left: Reaction mixture was diluted with Et_2O and filtered through a thin layer of silica. **Center:** Removal of solvent. **Right:** Crude TLC (20:1 Hexanes: EA).

GENERAL PROCEDURE C. TERMINAL ALKENE AND INTERNAL ALKYNE REDUCTION



A 5 mL Electrasyn-vial equipped with a magnetic stirring bar and wrapped with one layer of Teflon tape on the screw thread was charged with 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol).

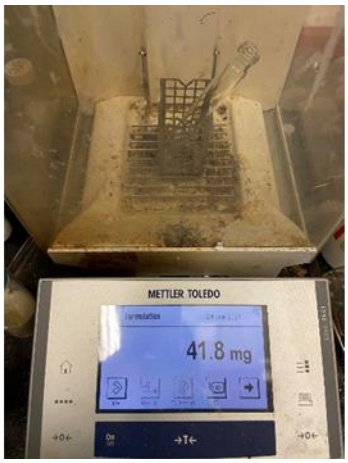
In a separate long tube (8 mL) the starting material was charged (0.2 mmol) and the tube was evacuated and backfilled with argon. Dry and degassed THF (2.2 mL) and HFIP (300 µL) were added to the tube. The sealed tube was quickly shaken, and a balloon filled with argon was bubbled through the solution for 30 seconds.

The aforementioned Electrasyn-vial was then quickly charged with $CoBr_2$*glyme (6.2 mg, 20 µmol), and Et_3N*HBF_4 (114 mg). The Vial was sealed with the cap carrying a magnesium anode and a graphite cathode and evacuated for 1-2 minutes and backfilled with argon. The THF solution of starting material was added with a 3-mL syringe, which was previously purged with argon. The vial was electrolyzed for 10 F/mol with 5 mA applied.

Graphical Guide

Photos were taken from the reduction of compound **49**.


Left: All reagents for this reaction. **Right:** ElectraSyn 2.0 vial (5 mL, wrapped with Teflon tape) with a stir bar.

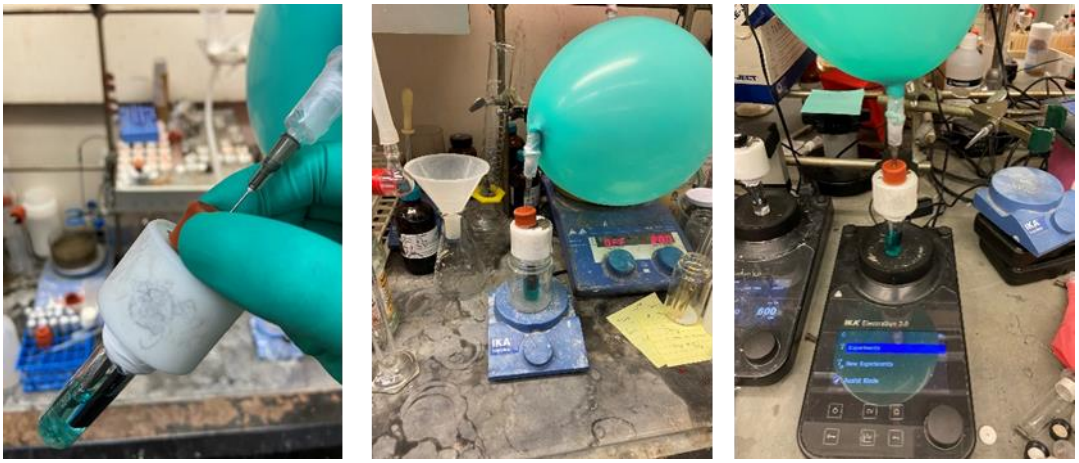



Left: ElectraSyn 2.0 cap equipped with Mg (left side) and graphite electrodes (right side). **Center:** Starting material of **49 (**41.8 mg) in 8 mL tube. **Right:** The tube was connected to a vacuum line through a needle and evacuated.

Left: Backfilled with argon. **Center:** THF (2.2 mL) and HFIP (0.3 mL). **Right:** Purging with Argon for 5 min.

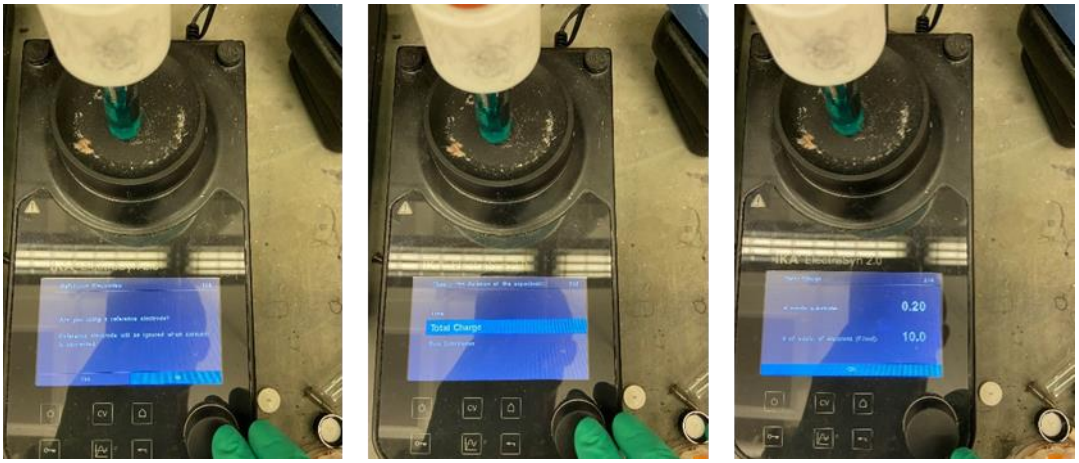
Left: $CoBr_2$.glyme (6.2 mg). **Center:** 6,6-Me_2-bpy (5.5 mg). **Right:** Et_3NHBF_4 (114 mg).

Left: The cap was tightly screwed into the vial. **Center:** The reaction vessel was connected to a vacuum line through a needle and evacuated. **Right:** Backfilled with argon.

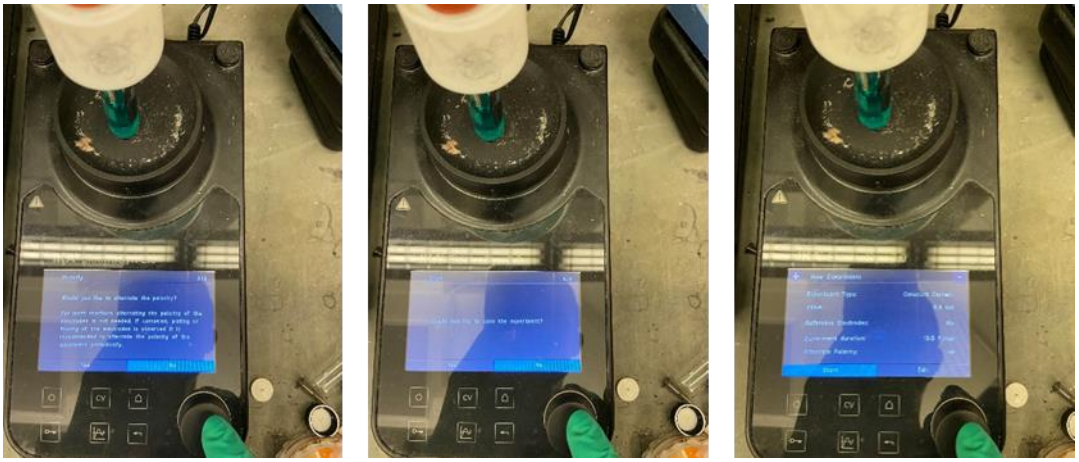


Left: Addition of starting material solution via syringe. **Center:** The reaction mixture was stirred for 1 min. **Right:** The electrochemical cell was plugged into ElectraSyn 2.0.

Left: Select ‘New Experiments’. **Center:** Select ‘Constant Current’. **Right:** Set the current to 5 mA.



Left: No need to use a reference electrode. **Center:** Select ‘Total Charge’. **Right:** Set 0.2 mmol substrate and 10 F/mol.

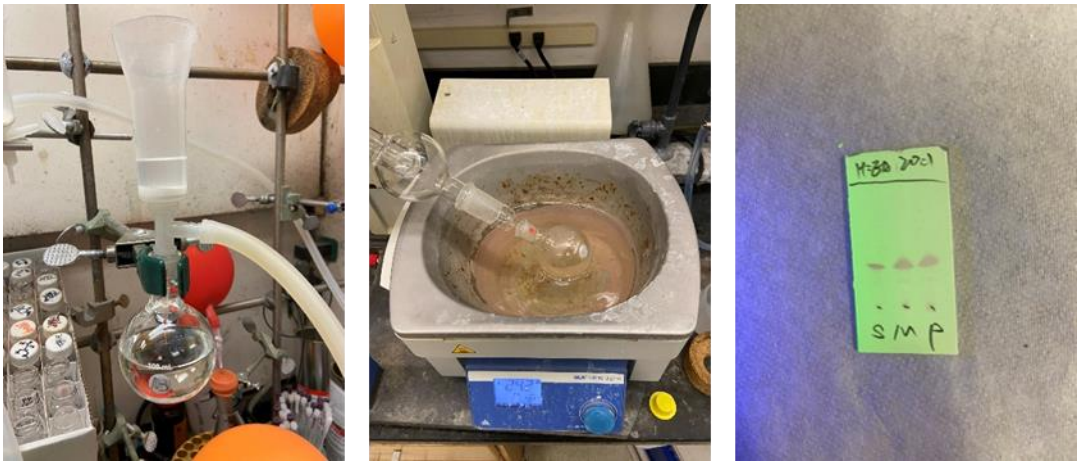


Left: No alternate polarity. **Center:** Saving the experimental parameters is optional. **Right:** ElectraSyn is ready.


Left: Start the reaction with a stirring speed of 600 rpm. **Center:** Reaction completed. **Right:** Electrodes were rinsed with Et_2O and transferred into a separatory funnel.

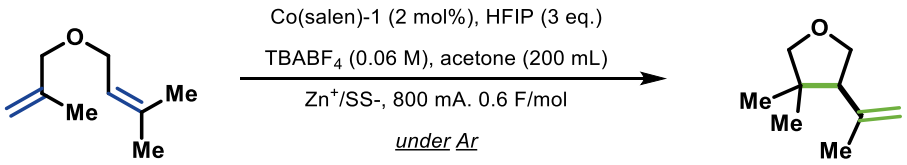


Left: Reaction mixture was transferred into a separatory funnel with Et_2O. **Center:** Washed with water. **Right:** Dried over Na_2SO_4.



Left: Filter off Na_2SO_4. **Center:** Removal of solvent. **Right:** Crude TLC (20:1 Hexanes: EA).

GENERAL PROCEDURE D. 100 GRAM SCALE CYCLOISOMERIZATION REACTION IN RECYCLE FLOW



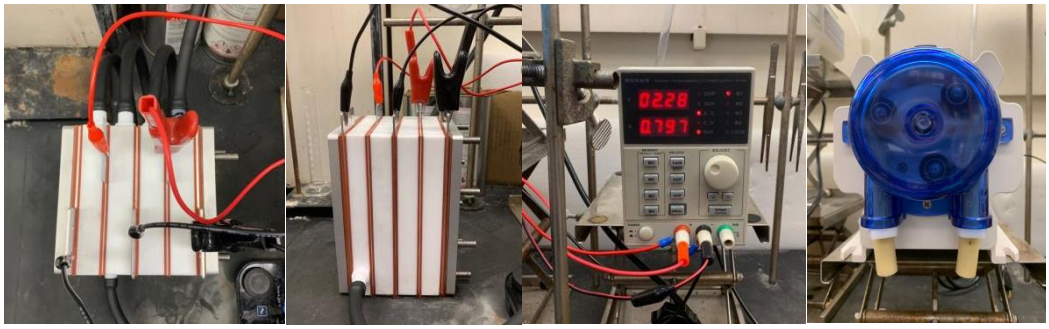
Recycle Flow Reactor Setup:

The flow reactor multi-plate/frame cell is comprised of the following components: 8 cap screws (made from 304 stainless steel, length: 20.0 cm), 2 stainless steel pressure plates, 2 bakelite plates (insulating plate), 10 fluororubber gaskets (with a space of 13 cm × 7 cm × 0.2 cm), 4 PTFE frames (with a channel size of 13 cm × 7 cm × 2 cm), 2 Zinc plates as anode and 3 stainless steel plates as cathode.

The reactor was assembled by placing four PTFE frames between anodes and cathodes. Gaskets were inserted between each electrode plate and PTFE frame. The two bakelite plates were placed on two ends of multi-plate/frame cell followed by two stainless-steel pressure plates (Figure 5). All plates and frames were threaded through and fastened by 8 cap screws to complete the cell assembly. Once assembled, the total volume of the cell is 730 mL. The assembled cell was connected, by fluororubber tube (1/4" ID, 3/8" OD), to a metering pump and a 5.0 L three neck round bottom as reservoir. The Teflon barbed fittings on the side of PTFE frames were connected via fluororubber tube to the fitting on the adjacent PTFE frame to allow the solution to flow between each cell. One of the two end fittings were connected to the pump by tubing serving as the flow inlet allowing the reaction solution to transfer from the reservoir to the cell; another fitting was connected directly to the reservoir by tubing functioning as the outlet of flow moving the solution from the cell back to the reservoir and thus forming a closed flow loop. The anode plate is connected through a wire to the positive terminal of a direct current power supply (maximum 5.0 A, 30.0 V), while the corresponding cathode plates are connected to the negative terminal.

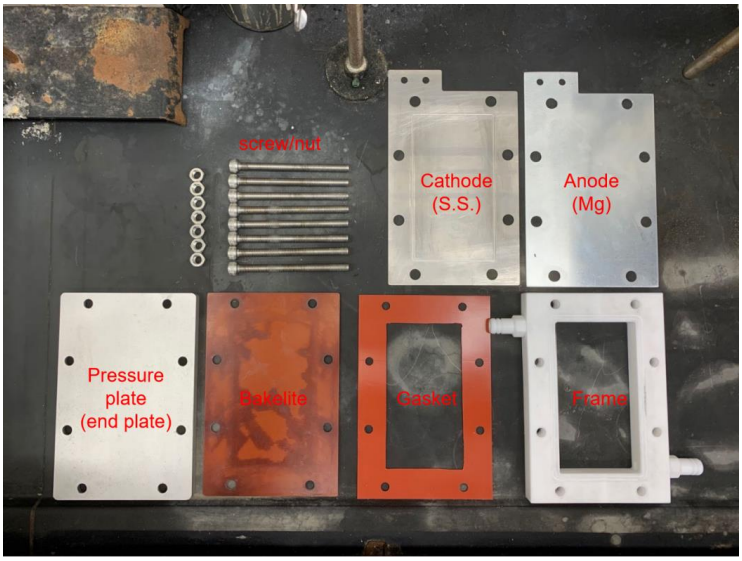
100 g ether substrate (0.71 mol, 1.0 equiv.), Cobalt catalyst (8.68g, 2 mol%), HFIP (300 ml, 2.86 mol, 4.0 equiv.), $TBABF_4$ (117.5 g, 0.35 mol, 0.5 equiv.) were charged to a 5.0 L three necked round bottom flask containing a stir bar as reaction reservoir. Acetone (4.7L, 0.15 M) was added to the round bottom flask, then connected it to multi-plate/frame cell via tubing. The reaction mixture was then stirred 20 min and pumped into cell with a flow rate of 420 mL/min until all cell chamber were filled and form a recirculating loop. The reservoir was vacuumed and backfilled with argon three times. The reaction was then electrolyzed under a constant current of 800 mA until all starting material was convert to product. After reaction finished, the reaction mixture was pumped out of cell and collected in a round bottom flask. The solvent was removed under reduced pressure, and the obtained crude residue was dissolved in Et_2O, transferred to a separatory funnel, and washed with H_2O (500 mL x 3) and brine (300 mL x 3). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated. The crude product was then purified by silica column chromatography with 10/1 Hexane/Ethyl Acetate to yield desired product as pale yellow oil (73%).

Graphical Guide

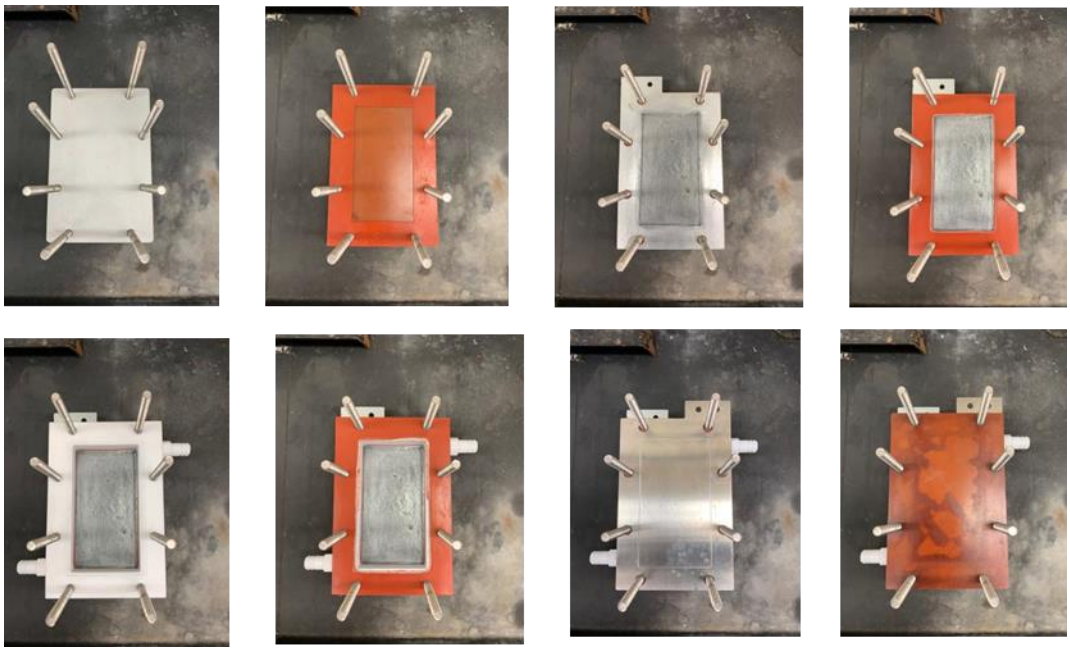


Left to right: top view of multicell; side view of multicell; DC power supply; peristaltic pump.

Left to right: 100g scale in recycle flow; top view of cell; side view of cell; cathode/anode after reaction.



Left to right: Component of flow cell



Construction of multicell with Stainless Steel and Zinc electrodes for flow set-up

GENERAL PROCEDURE E. 1 GRAM SCALE MONO-SUBSTITUTED ALKENE ISOMERIZATION REACTION IN RECYCLE FLOW

A clean and dry 20 ml reservoir equipped with a stir bar was charged with 4,4'-dimethoxy-2,2'-bipyridine (0.24 g, 1.1 mmol, 0.11 equiv.), 5-hexen-1-ol (1.0 g, 10.0 mmol, 1.00 equiv.), $CoBr_2$glyme (0.31 g, 1.0 mmol, 0.10 equiv.), $Et_3N.HBF_4$ (5.67 g, 30.0 mmol, 3.00 equiv.), and degassed MeCN (10 ml), under nitrogen atmosphere. The mixture was pumped through the flow cell by a peristaltic pump with 1 mL/min flow rate using a recirculation loop. The power supply was set to a constant current of 10 mA until complete consumption of 5-hexen-1-ol as judged by GC-FID. After 11h of electrolysis, 99% conversion was obtained with trans/cis ratio of 7/3. The yields of 92 % were calculated by weight assay via GC-FID.

(After electrolysis, the flow set-up was washed with water, acetone, and *tert*-butanol ; and the electrodes were washed with hydrochloric acid fuming 37 %, water, and acetone)

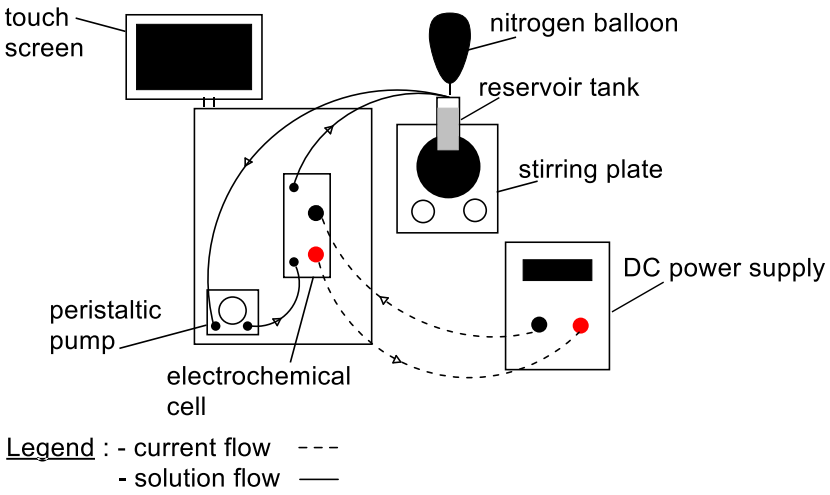
Frame Cell Setup:

The continuous flow cell assembly consists of (see below):

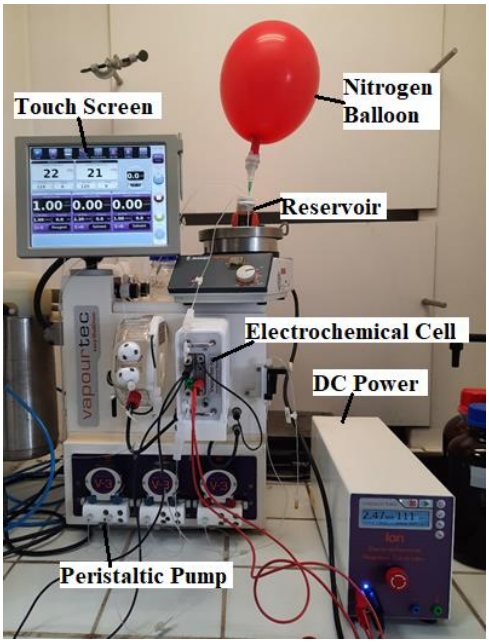
- Mg plate (length : 5 cm, width : 5 cm, thickness : 1 mm) used as anode
- Ni plate (length : 5 cm, width : 5 cm, thickness : 0.1 mm) used as cathode
- membrane with flow path (length : 5 cm, width : 5 cm, thickness : 1 mm)
- spacer (length : 5 cm, width : 5 cm, thickness : 1 mm)
- two electrodes carriers
- clamp plates
- hand wheel

In order to assembly the cell, the electrodes, spacer, and membrane are sandwiched between the electrode carriers. The two electrodes are separated by a membrane that creates a liquid flow path. The thickness of this membrane determines the volume of the reactor (1.2 ml) and the electrodes gap (1 mm). Additionally, the seals on the electrodes carriers allow to retain pressure up to 5 bar. A spacer is used to create a leak free seal by increasing the overall thickness of the membrane-electrodes assembly. When the assembly is completed, it is inserted into the clamp plates and tighten with the hand wheel (see below).

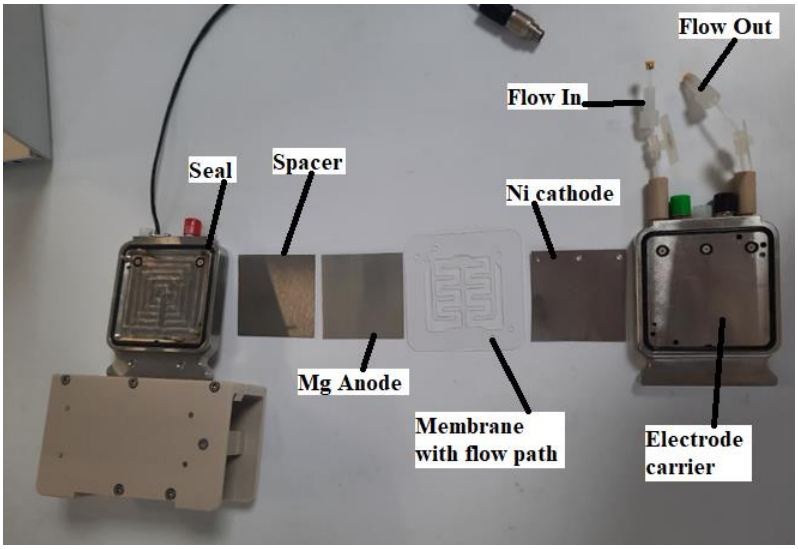
Graphical Guide



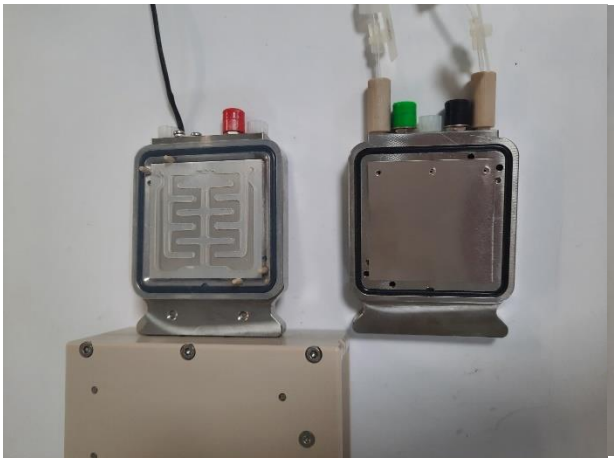
Scale up recycle flow diagram

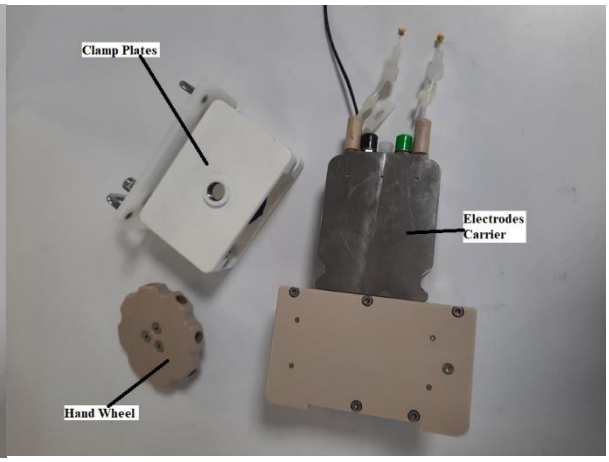


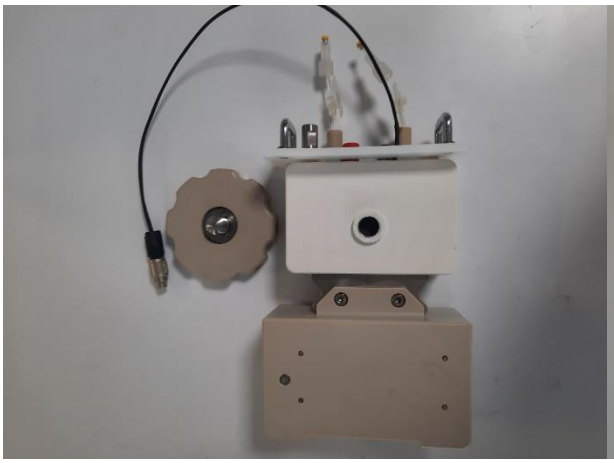
1 g scale in recycle flow setup

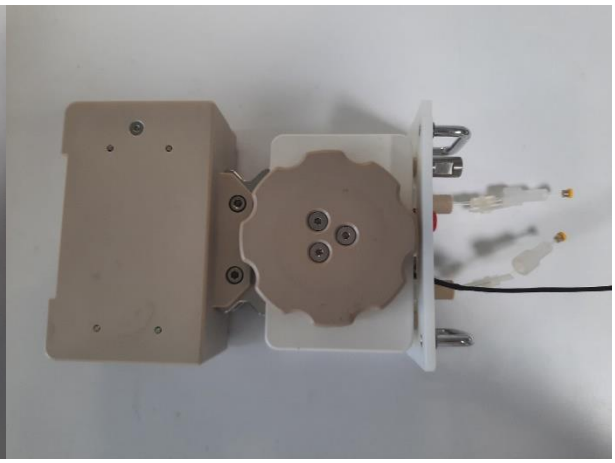


Component of flow cell

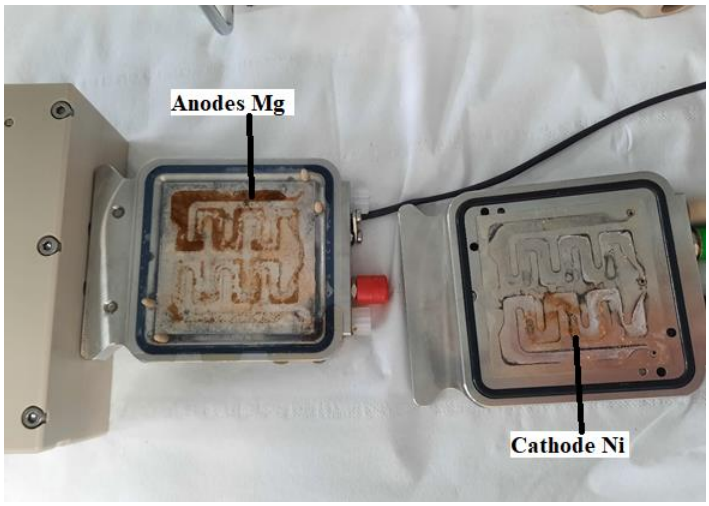




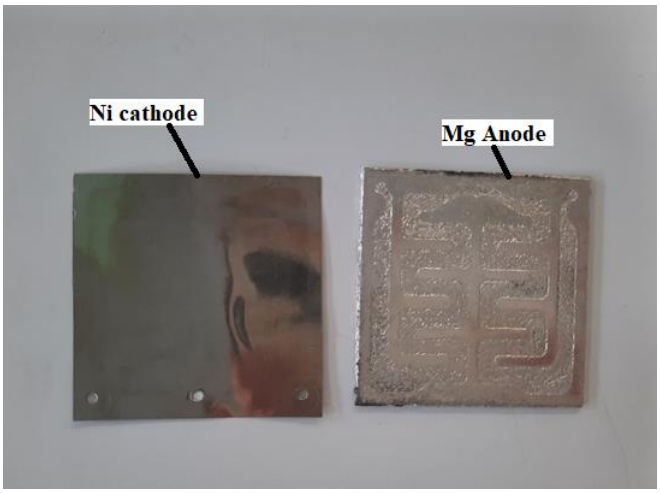




Construction of Cell

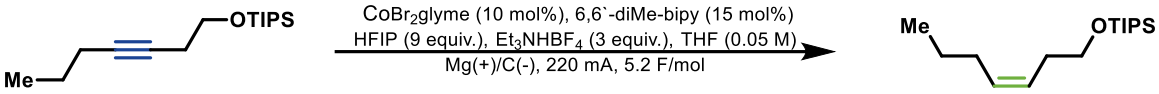


Anode and cathode after reaction



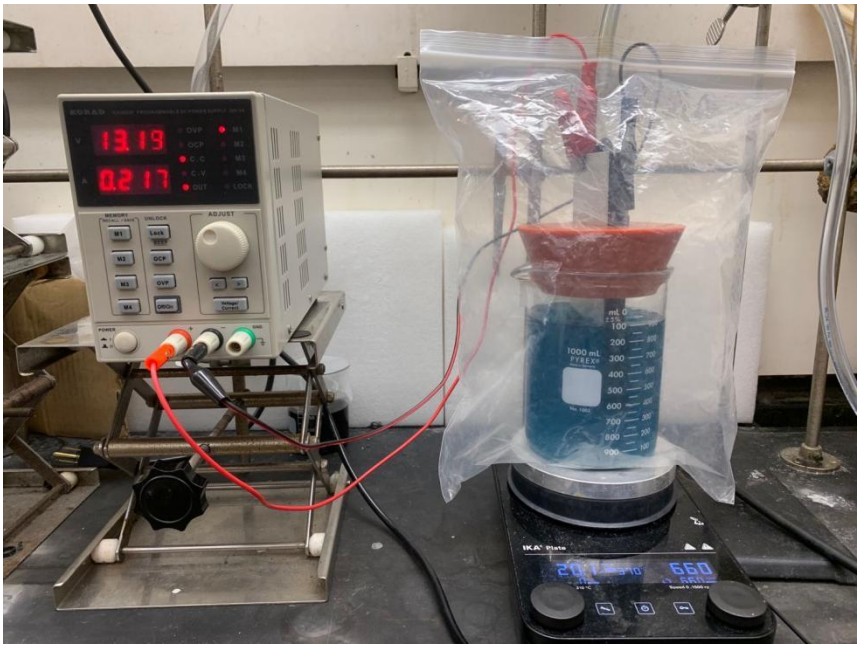
Anode and cathode after HCl, water, and acetone successive washes

GENERAL PROCEDURE F. 10 GRAM SCALE ALKYNE REDUCTION REACTION IN RECYCLE FLOW

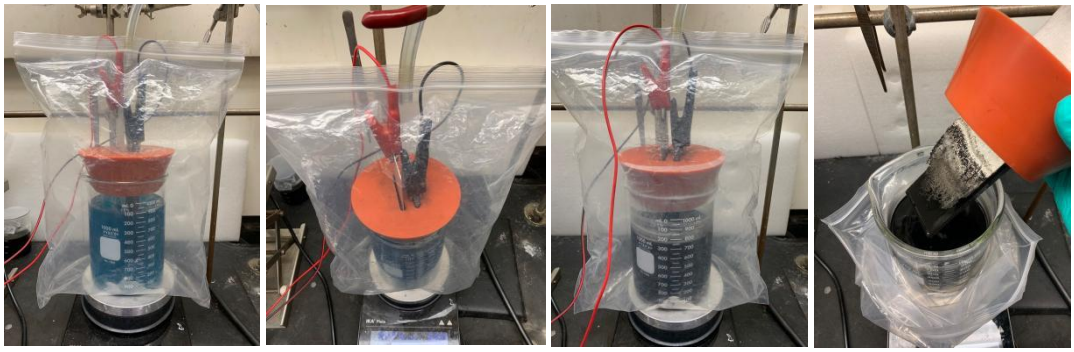


A clean and dry 2.0 L beaker with a stir bar was charged with substrate (10.0 g, 37.3 mmol), Cobalt catalyst (3.73 mmol, 10 mol%), 6,6-dimethylbipyridine (5.59 mmol, 15 mol%), Et_3NHBF_4 (21.2 g, 112 mmol, 3.0 equiv.) and THF (0.8 L, 0.05 M). The Mg anode and graphite cathode embedded a rubber cap with a distance of 1.8 cm between them, were inserted into the reaction mixture. The reaction mixture was deoxygenated with argon for 20 min, and then electrolyzed under a constant current of 220 mA from DC power until the complete consumption of alkyne as judged by GCMS. After reaction, the electrodes were taken out and rinsed with diethyl ether. The mixture was transferred to a 2.0 L round bottom and volatiles were removed under reduced pressure (>120 mbar, 40 °C water bath). 1.0 L of Et_2O was then added to dissolve the residue and 200 ml saturated Rochelle salt solution were added and stirred for 15 min. The biphase solution was poured to a separatory funnel, the organic layer was separated, and the aqueous layer was extracted twice with Et_2O (200 ml). The combined organic layers were washed with H_2O (500 ml x 2) and brine (300 ml x 2), dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was then purified by silica column chromatography with 10/1 Hexane/Ethyl Acetate to yield desired product as pale yellow oil (76%).

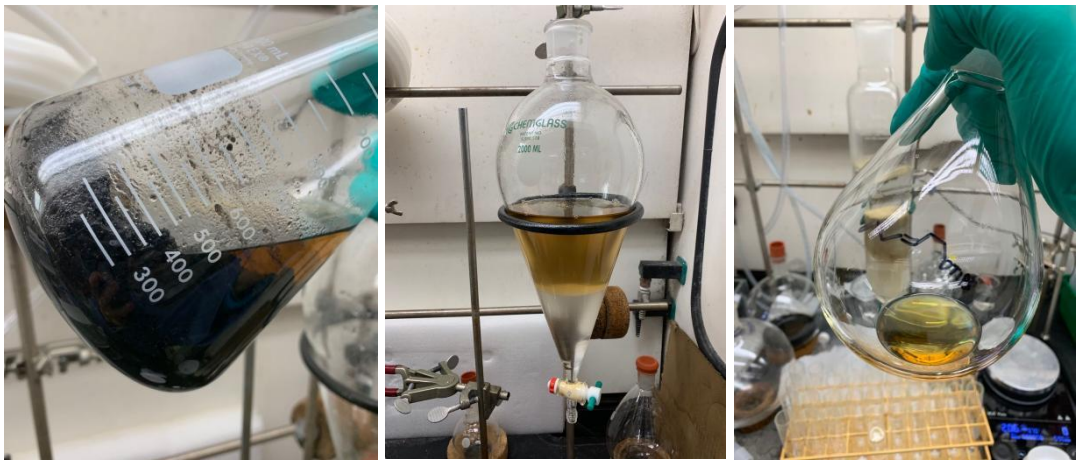
Graphical Guide



10 g batch scale-up of alkyne reduction



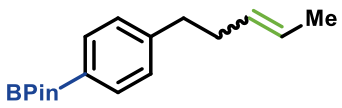
Left to right: side-view of batch reactor; top-view of batch reactor; reaction after 1h; after reaction.



Left to right: Rochelle salt wash reaction crude; brine wash in separatory funnel; column chromatography and isolated product.

CHARACTERIZATION DATA OF E-HAT PRODUCTS

Compound 2



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with zinc as anode and tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **2** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 39.2 mg (72%) as a mixture of isomers (4/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 5.58 – 5.39 (m, 2H), 2.72 – 2.60 (m, 2H), 2.42 – 2.26 (m, 2H), 1.70 – 1.55 (m, 3H), 1.35 (s, 12H).

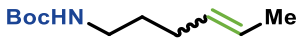
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 145.7, 134.9, 130.6, 128.1, 125.6, 83.7, 36.4, 34.4, 24.9, 18.0.

Physical State: colorless oil.

GC/MS (EI): 55 (40%), 118 (40%), 217 (100%), 272 (7%).

TLC: R_f = 0.38 (20:1 Hexanes: EtOAc).

Compound 3



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **3** purified by column chromatography (silica, 20:1 Hexanes: EtOAc) afforded 32.2 mg (81%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 5.51 – 5.29 (m, 2H), 4.54 (s, 1H), 3.09 (q, *J* = 7.2 Hz, 2H), 2.07 – 1.97 (m, 2H), 1.63 – 1.58 (m, 3H), 1.51 (p, *J* = 7.7 Hz, 2H), 1.42 (s, 9H).

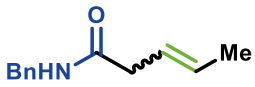
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 156.0, 130.4, 125.7, 79.1, 40.2, 29.9, 28.5, 18.0, 12.8.

Physical State: colorless oil.

GC/MS (EI): not found.

TLC: R_f = 0.21 (20:1 Hexanes: EtOAc).

Compound 4



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **4** purified by column chromatography (silica, 2:1 Hexanes: EtOAc) afforded 30.6 mg (81%) as a mixture of isomers (2/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.25 (m, 3H), 6.14 – 6.10 (m, 1H), 5.80 – 5.51 (m, 2H), 4.44 (d, *J* = 5.9 Hz, 2H), 3.09 – 2.98 (m, 2H), 1.73 – 1.66 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 171.4, 138.4, 131.2, 128.7, 127.8, 127.5, 123.7, 43.6, 40.5, 18.1.

Physical State: pale yellow oil.

GC/MS (EI): 91 (100%), 189 (4%).

TLC: R_f = 0.18 (2:1 Hexanes: EtOAc).

Compound 5

Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **5** purified by column chromatography (silica, 20:1 Hexanes: EtOAc) to afford 32.2 mg (81%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 5.51 – 5.29 (m, 2H), 4.54 (s, 1H), 3.09 (q, *J* = 7.2 Hz, 2H), 2.07 – 1.97 (m, 2H), 1.63 – 1.58 (m, 3H), 1.51 (p, *J* = 7.7 Hz, 2H), 1.42 (s, 9H).

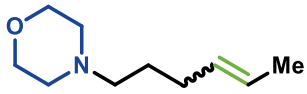
^{13}C NMR (151 MHz, $CDCl_3$, major isomers) δ 156.1, 130.4, 125.7, 79.1, 40.3, 29.9, 28.5, 18.0, 12.8.

Physical State: colorless oil.

GC/MS (EI): not found.

TLC: R_f = 0.21 (20:1 Hexanes: EtOAc).

Compound 6



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 μmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 μmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **6** purified by column chromatography (silica, 1:1 Hexanes: EtOAc) afforded 27.7 mg (82%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 5.50 – 5.32 (m, 2H), 3.71 (dd, *J* = 5.7, 3.7 Hz, 4H), 2.42 (brs, 4H), 2.35 – 2.28 (m, 2H), 2.09 – 1.96 (m, 2H), 1.67 – 1.59 (m, 3H), 1.57 – 1.50 (m, 2H).

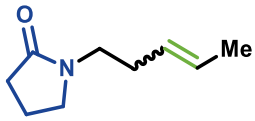
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 131.0, 125.3, 67.2, 58.7, 53.9, 30.6, 26.6, 18.0.

Physical State: colorless oil.

GC/MS (EI): 100 (100%), 126 (32%), 56 (13%), 142 (2%), 169 (0.4%).

TLC: R_f = 0.26 (Hex/EtOAc = 1:1)

Compound 7



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **7** purified by column chromatography (silica, 1:2 Hexanes: EtOAc) afforded 25.7 mg (84%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 5.55 – 5.45 (m, 1H), 5.38 – 5.33 (m, 1H), 3.40 – 3.35 (m, 2H), 3.31 – 3.27 (m, 2H), 2.38 – 2.34 (m, 2H), 2.30 – 2.16 (m, 2H), 2.02 – 1.94 (m, 2H), 1.65 – 1.59 (m, 3H).

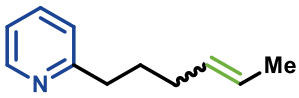
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 175.0, 127.6, 127.5, 47.4, 42.5, 31.2, 30.8, 25.3, 18.1.

Physical State: pale yellow oil.

GC/MS (EI): 70 (40%), 98 (100%), 153 (7%).

TLC: R_f = 0.23 (1:2 Hexanes: EtOAc).

Compound 8



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **8** purified by column chromatography (silica, 4:1 Hexanes: EtOAc) afforded 20.9 mg (65%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 8.51 (d, *J* = 3.8 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.14 – 7.12 (m, 1H), 7.11 – 7.04 (m, 1H), 5.50 – 5.37 (m, 2H), 2.81 – 2.76 (m, 2H), 2.13 – 2.01 (m, 2H), 1.82 – 1.74 (m, 2H), 1.66 – 1.55 (m, 3H).

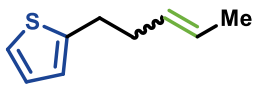
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 162.4, 149.3, 136.4, 131.0, 125.5, 122.9, 121.0, 37.9, 32.3, 29.8, 18.1.

Physical State: colorless oil.

GC/MS (EI): 93 (100%), 160 (8%), 161 (1%).

TLC: R_f = 0.23 (4:1 Hexanes: EtOAc).

Compound 9



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (12.4 mg, 40 µmol), 4,4'-dimethoxy-2,2'-bipyridine (9.6 mg, 44 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **9** purified by PTLC (silica, 40:1 Hexanes: EtOAc) afforded 23.1 mg (76%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 7.14 – 7.10 (m, 1H), 6.93 – 6.92 (m, 1H), 6.82 – 6.80 (m, 1H), 5.55 – 5.41 (m, 2H), 2.92 – 2.80 (m, 2H), 2.47 – 2.31 (m, 2H), 1.69 – 1.59 (m, 3H).

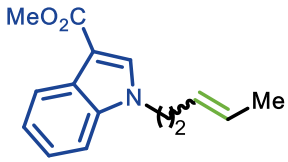
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 145.2, 130.1, 126.7, 126.2, 124.2, 123.0, 34.8, 30.2, 18.1.

Physical State: pale yellow oil.

GC/MS (EI): 97 (100%), 152 (11%).

TLC: R_f = 0.81 (40:1 Hexanes: EtOAc).

Compound 10



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **10** purified by PTLC (silica, 9:1 Hexanes: EtOAc) afforded 43.3 mg (89%) as a mixture of isomers (4/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 8.22 – 8.16 (m, 1H), 7.82 – 7.81 (m, 1H), 7.40 – 7.34 (m, 1H), 7.30 – 7.27 (m, 2H), 5.61 – 5.34 (m, 2H), 4.18 – 4.11 (m, 2H), 3.92 (s, 3H), 2.63 – 2.48 (m, 2H), 1.63 – 1.44 (m, 3H).

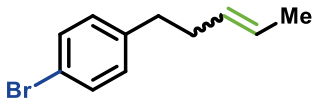
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 165.7, 136.5, 134.4, 129.0, 126.8, 126.3, 122.7, 121.9, 121.8, 110.1, 106.8, 51.0, 47.2, 33.1, 18.0.

Physical State: pale yellow oil.

GC/MS (EI): 188 (100%), 243 (17%).

TLC: R_f = 0.32 (9:1 Hexanes: EtOAc).

Compound 11



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **11** purified by PTLC (silica, Hexanes) to afford 36 mg (80%) as a mixture of isomers (4/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 11.0 Hz, 2H), 7.12 – 7.03 (m, 2H), 5.52 – 5.34 (m, 2H), 2.67 – 2.57 (m, 2H), 2.41 – 2.32 (m, 2H, *minor isomer*), 2.32 – 2.25 (m, 2H), 1.68 – 1.64 (m, 3H), 1.60 – 1.51 (m, 3H, *minor isomer*).

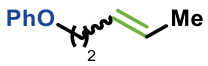
^{13}C NMR (151 MHz, $CDCl_3$): δ 141.2, 131.4, 130.4, 130.2 (*minor isomer*), 125.9, 125.0 (*minor isomer*), 119.6, 35.6, 35.3 (*minor isomer*), 34.4, 18.0.

Physical State: pale yellow oil.

GC/MS (EI): 169 (100%), 171 (100%)**,** 90 (48%), 182 (27%), 184 (27%), 145 (13%), 224 (9%), 226 (9%).

TLC: R_f = 0.8 (Hexanes).

Compound 12



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **12** purified by PTLC (silica, 50:1 Hexanes: Et_2O) afforded 29.5 mg (91%) as a mixture of isomers (4/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 7.30 – 7.26 (m, 2H), 7.00 – 6.87 (m, 3H), 5.66 – 5.46 (m, 2H), 3.99 – 3.96 (m, 2H), 2.59 – 2.45 (m, 2H), 1.70 – 1.67 (m, 3H).

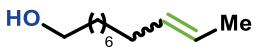
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 159.1, 129.5, 127.8, 126.9, 120.7, 114.7, 67.8, 32.7, 18.2.

Physical State: colorless oil.

GC/MS (EI): 69 (55%), 77 (42%), 94 (100%), 162 (15%).

TLC: R_f = 0.63 (30:1 Hexanes: Et_2O).

Compound 13



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **13** purified by PTLC (silica, 4:1 Hexanes: EtOAc) afforded 30.1 mg (88%) as a mixture of isomers (2/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 5.45 – 5.32 (m, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 2.06 – 1.91 (m, 2H), 1.85 (brs, 1H), 1.63 – 1.58 (m, 3H), 1.55 (p, *J* = 6.8 Hz, 2H), 1.34 – 1.22 (m, 10H).

^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 131.7, 124.7, 63.1, 32.9, 32.7, 29.7, 29.6, 29.5, 29.2, 25.8, 18.0.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 68 (60%), 81 (35%), 95 (20%), 109 (10%), 123 (5%), 152 (2%).

TLC: R_f = 0.42 (4:1 Hexanes: EtOAc).

Compound 14

Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (12.4 mg, 40 µmol), 4,4'-dimethoxy-2,2'-bipyridine (9.6 mg, 44 µmol), Et_3NHBF_4 (114 mg), and MeCN (2.5 mL), with zinc as anode and tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Due to the product volatility, the NMR yield is 86% determined by using CH_3NO_2 as internal standard.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 5.68 – 5.54 (m, 1H), 5.48 – 5.35 (m, 1H), 2.45 – 2.25 (m, 4H), 1.71 – 1.63 (m, 3H).

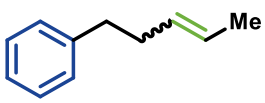
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 128.8, 126.9, 119.6, 28.5, 17.9, 17.8.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 94 (3%), 95 (3%).

TLC: R_f = 0.63 (4:1 Hexanes: Et_2O).

Compound 15



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compound **15** purified by PTLC (silica, Hexanes) to afford 26.5 mg (91%) as a mixture of isomers (7/2 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers): δ 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 5.54 – 5.43 (m, 2H), 2.70 – 2.67 (m, 2H), 2.42 – 2.28 (m, 2H), 1.70 – 1.56 (m, 3H).

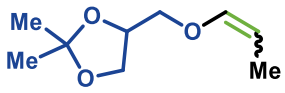
^{13}C NMR (151 MHz, $CDCl_3$, major isomer): δ 142.3, 130.7, 128.6, 128.4, 125.8, 125.5, 36.2, 34.6, 18.1.

Physical State: colorless oil.

GC/MS (EI): 91 (78%), 104 (100%), 146 (7%).

TLC: R_f = 0.50 (Hexanes).

Compound 16



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (12.4 mg, 40 µmol), 4,4'-dimethoxy-2,2'-bipyridine (9.6 mg, 44 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with magnesium as anode and in as cathode under the electrolysis of 2.5 mA for 4 F/mol. Due to the product volatility, the NMR yield is 76% determined by using CH_3NO_2 as internal standard.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 6.24 (dd, *J* = 12.6, 1.6 Hz, 1H), 5.96 (dq, *J* = 6.2, 1.7 Hz, 1H), 4.78 (dq, *J* = 12.4, 6.7 Hz, 1H), 4.44 – 4.37 (m, 1H), 4.34 – 4.23 (m, 2H), 4.07 (dd, *J* = 8.4, 6.4 Hz, 2H), 3.85 – 3.61 (m, 6H), 1.55 (ddd, *J* = 12.7, 6.8, 1.7 Hz, 6H), 1.45 – 1.40 (m, 6H), 1.36 (s, 6H).

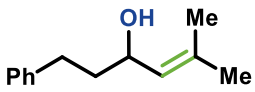
^{13}C NMR (151 MHz, $CDCl_3$, mixture of isomers) δ 146.4, 145.7, 109.7, 109.6, 101.8, 99.1, 74.6, 74.2, 72.4, 69.8, 66.8, 66.7, 26.9, 26.8, 25.6, 25.5, 12.6, 9.3.

Physical State: colorless oil.

GC/MS (EI): 57 (100%), 101 (36%), 115 (21%), 157 (14%), 172 (4%).

TLC: R_f = 0.68 (20:1 Hexanes: Et_2O).

Compound 17



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5

mA for 3 F/mol. Compound **17** purified by PTLC (silica, 4:1 Hexanes: EtOAc) to afforded 24.8 mg (65%) as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.17 (m, 3H), 5.22 (d, *J* = 8.7 Hz, 1H), 4.41 – 4.32 (m, 1H), 2.72 – 2.62 (m, 2H), 1.95 – 1.89 (m, 1H), 1.80 – 1.72 (m, 4H), 1.66 (s, 3H), (miss the OH proton).

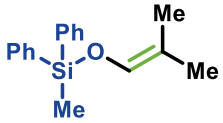
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 135.7, 128.5, 128.5, 128.0, 125.9, 68.3, 39.3, 31.9, 25.9, 18.4.

Physical State: brown oil.

GC/MS (EI): 91 (100%), 129 (18%), 157 (15%), 172 (12%), 190 (3%).

TLC: R_f = 0.40 (4:1 Hexanes: EtOAc).

Compound 18



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 1 F/mol. Compound **18** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afforded 46.1 mg (86%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 6.5, 1.4 Hz, 4H), 7.46 – 7.41 (m, 2H), 7.40 – 7.37 (td, *J* = 6.8, 1.2 Hz, 4H), 6.08 (hept, *J* = 1.5 Hz, 1H), 1.68 (s, 3H), 1.52 (s, 3H), 0.68 (s, 3H).

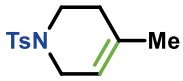
^{13}C NMR (151 MHz, $CDCl_3$) δ 135.6, 134.5, 133.0, 130.1, 128.0, 114.5, 19.4, 15.2, -2.8.

Physical State: colorless oil.

GC/MS (EI): not found.

TLC: R_f = 0.6 (20:1 Hexanes: EtOAc).

Compound 19



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **19** purified by column chromatography (silica, 7:1 Hexanes: EtOAc) to afforded 44.2 mg (88%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 1H), 3.51 (s, 2H), 3.15 (t, *J* = 5.8 Hz, 2H), 2.41 (s, 3H), 2.10 (s, 2H), 1.64 (s, 3H).

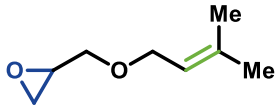
^{13}C NMR (151 MHz, $CDCl_3$): δ 143.5, 133.4, 132.8, 129.7, 127.8, 116.6, 44.9, 42.9, 30.0, 23.0, 21.6.

Physical State: white solid.

GC/MS (EI): 68 (100%), 91 (90%), 236 (40%), 251 (25%).

TLC: R_f = 0.47 (4:1 Hexanes: EtOAc).

Compound 20



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **20** purified by column chromatography (silica, 10:1 Hexanes: EtOAc) to afforded 16.7 mg (59%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of starting material and product) δ 5.35 (tp, *J* = 7.0, 1.4 Hz, 1H), 4.08 – 3.98 (m, 2H), 3.68 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.40 (ddd, *J* = 11.4, 5.8, 1.9 Hz, 1H), 3.15 (dtt, *J* = 5.6, 4.5, 2.9 Hz, 1H), 2.80 (dt, *J* = 4.4, 3.1 Hz, 1H), 2.61 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.75 (s, 3H), 1.68 (s, 3H).

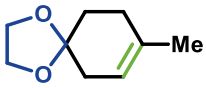
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 120.8, 70.8, 67.9, 51.0, 44.6, 25.9, 18.2.

Physical State: colorless oil.

GC/MS (EI): 57 (71%), 69 (85%), 85 (100%), 127 (37%), 142 (12%).

TLC: R_f = 0.4 (10:1 Hexanes: EtOAc).

Compound 21



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **21** purified by PTLC (silica, 8:1 Hexanes: EtOAc) to afford 25.8 mg (84%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.30 (tq, *J* = 3.5, 1.6 Hz, 1H), 3.98 (s, 4H), 2.23 (s, 2H), 2.19 – 2.14 (m, 2H), 1.76 (t, *J* = 6.6 Hz, 2H), 1.69 (s, 3H).

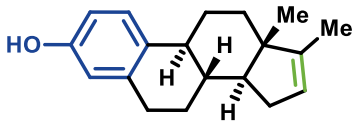
^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 118.6, 108.2, 64.5, 35.7, 31.3, 29.4, 23.3.

Physical State: colorless oil.

GC/MS (EI): 94 (100%), 139 (43%), 154 (18%).

TLC: R_f = 0.5 (8:1 Hexanes: EtOAc).

Compound 22



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **22** purified by PTLC (silica, 4:1 Hexanes: EtOAc) to afford 44.5 mg (83%) as a pale brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.67 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 5.37 (s, 1H), 4.98 (s, 1H), 2.97 – 2.82 (m, 2H), 2.37 (dtd, *J* = 13.4, 4.5, 2.4 Hz, 1H), 2.31 – 2.25 (m, 1H), 2.20 – 2.13 (m,

1H), 1.96 (ddt, *J* = 15.4, 9.1, 2.5 Hz, 2H), 1.87 (ddd, *J* = 12.3, 4.3, 2.5 Hz, 1H), 1.72 (s, 3H), 1.63-1.57 (m, 3H), 1.52-1.43 (m, 2H), 0.81 (s, 3H).

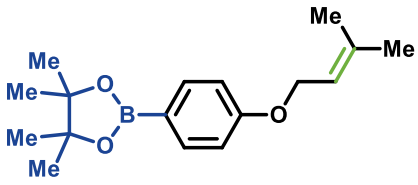
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.2, 151.6, 138.5, 133.4, 126.3, 122.7, 115.4, 112.7, 56.4, 46.7, 44.5, 37.6, 34.5, 31.0, 29.7, 27.9, 26.6, 15.3, 12.6.

Physical State: pale brown solid.

HRMS (ESI-TOF): calc'd for $C_{19}H_{25}O$ $[M+H]^+$: 269.1905; found 269.1915.

TLC: R_f = 0.37 (4:1 Hexanes: EtOAc).

Compound 23



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **23** purified by PTLC (silica, 8:1 Hexanes: EtOAc) to afford 45.5 mg (79%) as a pale colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of starting material and product) δ 7.76 – 7.70 (m, 2H), 6.93 – 6.87 (m, 2H), 5.49 (ddq, *J* = 8.1, 5.6, 1.4 Hz, 1H), 4.53 (d, *J* = 6.8 Hz, 2H), 1.79 (s, 3H), 1.74 (s, 3H), 1.33 (s, 12H).

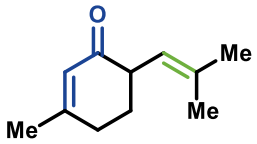
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 138.4, 136.6, 119.7, 114.2, 83.7, 64.7, 25.9, 25.0, 18.3.

Physical State: pale colorless solid.

GC/MS (EI): 69 (100%), 121 (100%), 134 (83%), 205 (81%), 220 (79%), 288 (2%).

TLC: R_f = 0.6 (8:1 Hexanes: EtOAc).

Compound 24



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **24** purified by PTLC (silica, 4:1 Hexanes: EtOAc) to afford 19.7 mg (60%) as pale yellow oil. *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (q, *J* = 1.5 Hz, 1H), 5.19 (dp, *J* = 8.8, 1.5 Hz, 1H), 3.11 (ddd, *J* = 10.6, 8.7, 4.8 Hz, 1H), 2.34 (q, *J* = 5.2, 4.7 Hz, 2H), 2.04 – 1.99 (m, 1H), 1.95 (s, 3H), 1.82 (dddd, *J* = 13.8, 10.7, 8.7, 5.6 Hz, 1H), 1.75 (d, *J* = 1.5 Hz, 3H), 1.66 (d, *J* = 1.4 Hz, 3H).

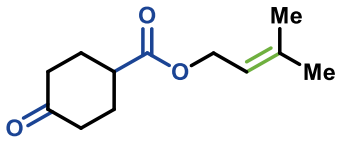
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.5, 161.7, 135.4, 126.5, 121.6, 45.7, 30.4, 29.6, 26.0, 24.4, 18.3.

Physical State: pale yellow oil.

GC/MS (EI): 82 (100%), 109 (20%), 164 (16%).

TLC: R_f = 0.36 (4:1 Hexanes: EtOAc).

Compound 25



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **25** purified by PTLC (silica, 4:1 Hexanes: EtOAc) to afforded 33.6 mg (80%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of starting material and product) δ 5.34 (tdt, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 2H), 2.74 (ttd, *J* = 9.8, 4.0, 1.9 Hz, 1H), 2.51 – 2.43 (m, 2H), 2.34 (ddd, *J* = 15.5, 11.0, 5.8 Hz, 2H), 2.24 – 2.15 (m, 2H), 2.09 – 1.98 (m, 2H), 1.76 (s, 3H), 1.71 (s, 3H).

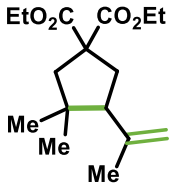
^{13}C NMR (151 MHz, $CDCl_3$) δ 210.5, 174.3, 139.6, 118.5, 61.8, 40.9, 39.9, 28.7, 25.9, 18.2.

Physical State: colorless oil.

GC/MS (EI): 69 (100%), 85 (69%), 143 (14%), 182 (7%).

TLC: R_f = 0.48 (4:1 Hexanes: EtOAc).

Compound 26



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 μmol), $TBABF_4$ (60 mg), HFIP (21 μL, 0.2 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 1.5 F/mol. Compound **26** purified by column chromatography (silica, 9:1 Hexanes: EtOAc) to afforded 49.1 mg (87%) as a yellow oil. *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.87 (s, 1H), 4.70 (s, 1H), 4.21 – 4.13 (m, 4H), 2.48 – 2.41 (m, 1H), 2.33 – 2.26 (m, 2H), 2.23 – 2.14 (m, 2H), 1.74 (s, 3H), 1.23 (td, *J* = 7.2, 3.0 Hz, 6H), 1.09 (s, 3H), 0.78 (s, 3H).

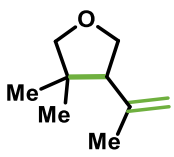
^{13}C NMR (151 MHz, $CDCl_3$): δ 173.2, 172.9, 143.7, 112.5, 61.5, 61.5, 57.2, 55.2, 49.0, 41.7, 37.7, 29.3, 23.7, 23.6, 14.2, 14.1.

Physical State: pale yellow oil.

GC/MS (EI): 122 (100%), 208 (42%), 282 (1.7%).

TLC: R_f = 0.56 (9:1 Hexanes: EtOAc).

Compound 27



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (21 µL, 0.2 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 1.5 F/mol. Compound **27** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 23.1 mg (82%) as a colorless oil. *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.90 (p, *J* = 1.5 Hz, 1H), 4.71 (s, 1H), 4.03 (dd, *J* = 8.6, 7.6 Hz, 1H), 3.90 (t, *J* = 8.4 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 2.46 (t, *J* = 7.9 Hz, 1H), 1.77 (s, 3H), 1.13 (s, 3H), 0.94 (s, 3H).

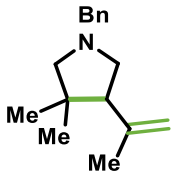
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 112.6, 81.3, 71.6, 55.8, 41.9, 26.9, 23.8, 21.6.

Physical State: colorless oil.

GC/MS (EI): 68 (100%), 95 (30%), 140 (2%).

TLC: R_f = 0.28 (20:1 Hexanes: EtOAc).

Compound 28



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 1.5 F/mol. Compound **28** purified by PTLC (silica, 4:1 Hexanes: EtOAc) to afford 35.3 mg (77%) as a colorless oil. *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.25 (t, *J* = 8.5 Hz, 1H), 4.85 (s, 1H), 4.72 (s, 1H), 3.68 (d, *J* = 13.1 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H), 2.86 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.63 (dt, *J* = 9.4, 4.9 Hz, 2H), 2.49 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.27 (d, *J* = 9.1 Hz, 1H), 1.77 (s, 3H), 1.17 (s, 3H), 0.91 (s, 3H).

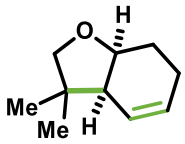
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 139.6, 128.7, 128.3, 126.9, 111.5, 69.5, 60.9, 58.2, 55.1, 40.5, 30.4, 24.5, 24.1.

Physical State: pale brown oil.

GC/MS (EI): 91 (100%), 132 (33%), 173 (22%), 229 (6%).

TLC: R_f = 0.40 (4:1 Hexanes: EtOAc).

Compound 29



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 0.9 F/mol. Compound **29** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 25.9 mg (85%) as a colorless oil. *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 10.3, 5.0, 2.5 Hz, 1H), 5.59 (ddt, *J* = 9.7, 3.4, 1.6 Hz, 1H), 4.40 (td, *J* = 6.1, 3.1 Hz, 1H), 3.47 – 3.42 (m, 2H), 2.25 (dq, *J* = 6.2, 2.3 Hz, 1H), 2.06 (dddd, *J* = 13.8, 9.0, 4.6, 2.3 Hz, 1H), 1.93 – 1.81 (m, 2H), 1.63 (dddd, *J* = 13.4, 10.2, 4.8, 3.1 Hz, 1H), 1.14 (s, 3H), 0.98 (s, 3H).

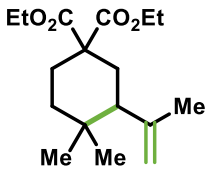
^{13}C NMR (151 MHz, $CDCl_3$) δ 129.1, 125.9, 79.4, 76.7, 47.9, 42.6, 27.4, 27.1, 22.3, 20.2.

Physical State: colorless oil.

GC/MS (EI): 80 (100%), 152 (8%).

TLC: R_f = 0.48 (20:1 Hexanes: EtOAc).

Compound 30



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 2.5 F/mol. Compound **30** purified by column chromatography (silica, 20:1 Hexanes: EtOAc) afforded 55.7

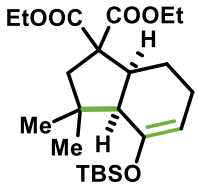
mg (6% starting material and 38% isomerization product and 50% desired product). The products were confirmed by the comparison with reported NMR spectrum of products (*J. Am. Chem. Soc.* 136, 16788-16791 (2014)).[15]

Physical State: pale yellow oil.

GC/MS (EI): 93 (59%), 136 (59%), 222 (100%), 296 (5%).

TLC: R_f = 0.36 (20:1 Hexanes: EtOAc).

Compound 31



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 5 mA for 1.5 F/mol. Compound **31** purified by PTLC (silica, 9:1 Hexanes: Et_2O) to afforded 79.2 mg (86%) as a dark oil. *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers) δ 4.79 (t, *J* = 3.9 Hz, 1H), 4.13 – 4.18 (m, 4H), 2.88 – 2.77 (m, 1H), 2.52 (d, *J* = 14.3 Hz, 1H), 2.49 (d, *J* = 6.7 Hz, 1H), 2.09 – 2.00 (m, 3H), 1.24 (dt, *J* = 14.7, 7.1 Hz, 8H), 1.09 (s, 3H), 1.06 (s, 3H), 0.90 (s, 9H), 0.14 (s, 6H)..

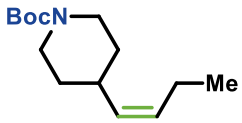
^{13}C NMR (151 MHz, $CDCl_3$, major isomer) δ 172.6, 170.2, 150.7, 102.2, 63.4, 61.3, 61.3, 51.9, 46.9, 45.8, 39.2, 33.8, 28.5, 25.9, 23.3, 21.5, 18.1, 14.3, 14.2, -4.2, -4.4.

Physical State: dark oil.

GC/MS (EI): 73 (100%), 211 (31%), 350 (15%), 424 (5%).

TLC: R_f = 0.48 (20:1 Hexanes: Et_2O).

Compound 32



Following the general procedure C on a 0.2 mmol scale and 6.5 F/mol. Compound **32** was isolated by p-TLC (Hex/EtOAc, 9:1) in 62% yield (29.7 mg, E/Z = 17:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 – 5.27 (m, 1H), 5.21 – 5.00 (m, 1H), 4.06 (brs, 2H), 2.74 (t, *J* = 12.8 Hz, 2H), 2.40 (dtd, *J* = 11.5, 8.2, 4.4 Hz, 1H), 2.06 (pd, *J* = 7.5, 1.5 Hz, 2H), 1.59 – 1.51 (m, 2H), 1.45 (s, 9H), 1.25 (d, *J* = 16.8 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

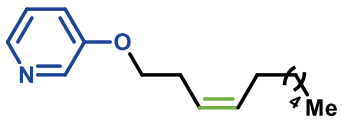
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 133.4, 131.3, 79.4, 34.5, 32.3, 28.6, 20.9, 14.7. The two carbon peaks next to the nitrogen atom are very broad and do not show up in the spectrum but they are visible through HSQC.

GC/MS (EI): 57 (100%), 126 (54%), 82 (43%), 183 (14%), 239 (0.4%).

Physical State: Yellow liquid.

***R*$_f$** = 0.60 (Hex/EtOAc, 9:1).

Compound 33



Following the general procedure C on a 0.2 mmol scale and 5 F/mol. Compound **33** was isolated by p-TLC (Hex/EtOAc, 3:1) in 82% yield (38.2 mg, E/Z = 17:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.22 (s, 1H), 7.24 (s, 2H), 5.60 – 5.31 (m, 2H), 4.01 (t, *J* = 6.9 Hz, 2H), 3.64 (t, *J* = 6.5 Hz, minor isomer), 2.56 (q, *J* = 6.9 Hz, 2H), 2.38 – 2.30 (m, minor isomer), 2.56 (qd, *J* = 7.3, 1.5 Hz, 2H), 1.40 – 1.21 (m, 8H), 0.88 (d, *J* = 17.1 Hz, 3H).

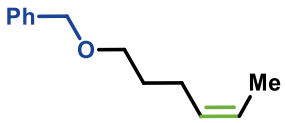
^{13}C NMR (126 MHz, $CDCl_3$): δ 141.6, 137.5, 133.4, 124.2, 121.9, 68.1, 31.9, 29.7, 29.1, 27.6, 27.5, 22.8, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 69 (50%), 83 (65%), 96 (30%), 108 (15%), 233 (10%).

TLC: R_f = 0.60 (3:1 Hexanes: EtOAc).

Compound 34



Following the general procedure C on a 0.2 mmol scale and 4.4 F/mol. Compound **34** was isolated by p-TLC (Hex/EtOAc, 40:1) in 67% yield (25.5 mg, E/Z = 17:1) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 4.3 Hz, 4H), 7.32 – 7.25 (m, 1H), 5.51 – 5.44 (m, 1H), 5.43 – 5.35 (m, 1H), 4.51 (s, 2H), 3.49 (t, J = 6.6 Hz, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.77 – 1.65 (m, 2H), 1.61 (d, *J* = 6.7 Hz, 3H).

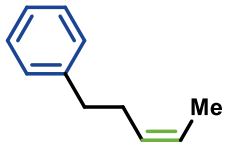
^{13}C NMR (151 MHz, $CDCl_3$): δ 138.8, 130.1, 128.5, 127.8, 127.6, 124.5, 73.1, 70.0, 29.7, 23.6, 12.9.

Physical State: colorless oil.

GC/MS (EI): 55 (20%), 81 (24%), 91 (100%), 107 (14%), 161 (6%), 190 (2%).

TLC: R_f = 0.71 (40:1 Hexanes: EtOAc).

Compound 35

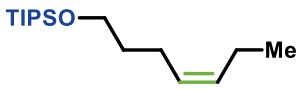


Following the general procedure C on a 0.2 mmol scale and 3.5 F/mol. Compound **35** was obtained in 80% NMR-yield with E/Z = 20:1. *Angew. Chem. Int. Ed.* 59, 6750-6755 (2020).

GC/MS (EI): 91 (100%), 65 (15%), 146 (5%), 104 (5%), 131 (4%).

R_f = 0.78 (Hex).

Compound 36



Following the general procedure C on a 0.2 mmol scale and 6.5 F/mol. Compound **36** was isolated by pTLC (Hex) in 78% yield (42.2 mg, *E/Z* = 20:1) as a yellow to red liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.49 – 5.32 (m, 2H), 3.71 (t, *J* = 6.5 Hz, 2H), 2.15 – 2.02 (m, 4H), 1.65 – 1.58 (m, 2H), 1.15 – 1.05 (m, 21H), 0.98 (t, *J* = 7.5 Hz, 3H).

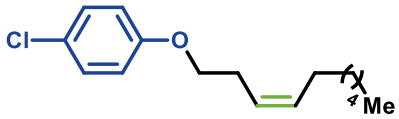
^{13}C NMR (151 MHz, $CDCl_3$): δ 132.1, 128.9, 63.0, 33.2, 23.6, 20.6, 18.2, 14.5, 12.2.

GC/MS (EI): 183 (100%), 155 (50%), 141 (6%), 270.0 (0.1%).

Physical State: orange oil.

***R*$_f$** = 0.46 (Hex)

Compound 37



Following the general procedure C on a 0.2 mmol scale and 5 F/mol. Compound **37** was isolated by pTLC (Hex) in 75% yield (39.9 mg, *E/Z* = 20:1) as a yellow to red liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.60 – 5.50 (m, 1H), 5.49 – 5.32 (m, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 2.53 (qd, *J* = 7.0, 1.5 Hz, 2H), 2.07 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.42 – 1.23 (m, 8H), 0.95 – 0.83 (m, 3H).

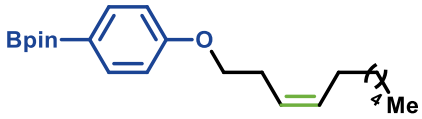
^{13}C NMR (126 MHz, $CDCl_3$): δ 157.7, 133.1, 129.4, 125.6, 124.5, 115.9, 67.9, 31.9, 29.7, 29.1, 27.5, 27.5, 22.8, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 69 (53%), 83 (77%), 97 (24%), 128 (82%), 266 (6%)

TLC: R_f = 0.81 (40:1 Hexanes: Et_2O).

Compound 38



Following the general procedure C on a 0.2 mmol scale and 5 F/mol. Compound **38** was isolated by pTLC (20:1 Hexanes: EtOAc) in 69% yield (49.4 mg, *E/Z* = 20:1) as a yellow to red liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.61 – 5.53 (m, 1H), 5.51 – 5.43 (m, 1H), 4.01 (t, *J* = 7.0 Hz, 2H), 2.56 (q, *J* = 7.1 Hz, 2H), 2.10 (q, *J* = 7.3 Hz, 2H), 1.40 – 1.21 (m, 20H), 0.91 (t, *J* = 7.1 Hz, 3H).

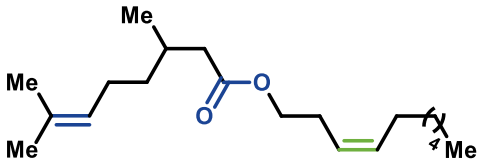
^{13}C NMR (151 MHz, $CDCl_3$): δ 161.3, 136.7, 133.7, 114.1, 83.7, 82.3, 75.8, 66.6, 31.5, 29.0, 28.7, 25.0, 22.7, 19.9, 18.9, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55(88%), 69 (53%), 83 (100%), 121 (56%), 134 (59%), 205 (72%), 220 (81%), 358 (11%).

TLC: R_f = 0.50 (20:1 Hexanes: EtOAc).

Compound 39



Following the general procedure C on a 0.2 mmol scale and 6.5 F/mol. Compound **39** was isolated by pTLC (40:1 Hexanes: EtOAc) in 70% yield (43.1 mg, 0.156 mmol, *E/Z* = 20:1) as a yellow to red liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.53 – 5.45 (m, 1H), 5.37 – 5.30 (m, 1H), 5.11 – 5.05 (m, 1H), 4.06 (t, *J* = 7.0 Hz, 2H), 2.37 (q, *J* = 7.2 Hz, 2H), 2.30 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.10 (dd, *J* = 14.7, 8.3 Hz, 1H), 2.07 – 1.89 (m, 5H), 1.68 (s, 3H), 1.59 (s, 3H), 1.38 – 1.16 (m, 10H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H).

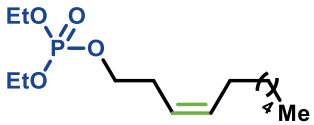
^{13}C NMR (151 MHz, $CDCl_3$): δ 173.4, 133.0, 131.6, 124.5, 124.4, 63.9, 41.8, 36.9, 31.9, 30.2, 29.7, 29.1, 27.5, 27.0, 25.8, 25.6, 22.8, 19.7, 17.8, 14.2.

Physical State: colorless oil.

GC/MS (EI): 55 (60%), 69 (100%), 83 (70%), 109 (40%), 138 (12%), 308 (0.5%).

TLC: R_f = 0.58 (40:1 Hexanes: EtOAc).

Compound 40



Following the general procedure C on a 0.2 mmol scale and 6.5 F/mol. Compound **40** was obtained in 64% NMR-yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62 – 5.45 (m, 1H), 5.42 – 5.20 (m, 1H), 4.24 – 4.05 (m, 4H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.48 – 2.38 (m, 2H), 2.09 – 1.95 (m, 2H), 1.37 – 1.25 (m, 14H), 0.92 – 0.84 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 133.5, 123.7, 67.1 (d, *J* = 6.0 Hz), 63.8 (d, *J* = 5.6 Hz), 31.9, 29.1, 28.6 (d, *J* = 7.1 Hz), 27.5, 22.8, 16.3, 16.3, 14.2.

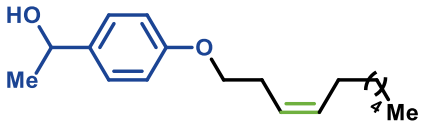
^{31}P NMR (162 MHz, CDCl3): δ – 0.96.

HRMS (ESI): calcd for $C_{14}H_{30}O_4P_1$ $[M+H]^+$ 293.1882, found 293.1870.

Physical State: Colorless oil.

***R*$_f$** = 0.38 (Hex/EtOAc, 1:1)

Compound 41



Following the general procedure C on a 0.2 mmol scale and 6.0 F/mol. Compound **41** was isolated by p-TLC (Hex:EtOAc, 1:1) in 69% yield (38.1 mg, E/Z = 20:1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.65 – 5.48 (m, 1H), 5.50 – 5.37 (m, 1H), 4.86 (q, *J* = 6.4 Hz, 1H), 3.95 (t, *J* = 7.0 Hz, 2H), 2.66 – 2.41 (m, 2H), 2.13 – 2.01 (m, 2H), 1.71 (s, 1H), 1.48 (d, *J* = 6.4 Hz, 3H), 1.40 – 1.23 (m, 8H), 0.97 – 0.73 (m, 3H).

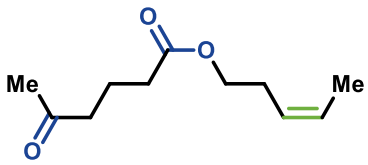
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 138.1, 133.0, 126.8, 124.7, 114.6, 70.2, 67.7, 31.9, 29.7, 29.1, 27.6, 27.5, 25.1, 22.8, 14.2.

HRMS (ESI): calcd for $C_{18}H_{29}O_2$ $[M\text{-}OH]^+$ 259.2062, found 259.2069.

Physical State: Colorless oil.

R_f = 0.76 (Hex/EtOAc, 1:1)

Compound 42



Following the general procedure C on a 0.2 mmol scale and 6.5 F/mol. Compound **42** was isolated by p-TLC (EtOAc/Hex, 7:3) in 59% yield (23.4 mg, E/Z = 14:1) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.63 – 5.57 (m, 1H), 5.43 – 5.34 (m, 1H), 4.10 (t, *J* = 6.9 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.44 – 2.37 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.16 (s, 3H), 1.91 (p, *J* = 7.2 Hz, 2H), 1.67 – 1.61 (m, 3H).

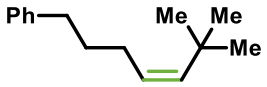
^{13}C NMR (151 MHz, $CDCl_3$): δ 208.2, 173.3, 127.0, 125.4, 63.9, 42.6, 33.4, 30.1, 26.6, 19.1, 12.9.

GC/MS (EI): 68 (100%), 131 (80%), 85 (53%), 198 (0.3%).

Physical State: colorless oil.

R_f = 0.49. (Hex/EtOAc, 7:3).

Compound 43



Following the general procedure C on a 0.2 mmol scale and 15 F/mol. Compound **43** was isolated by p-TLC (EtOAc/Hex, 7:3) in 88% yield (35.5 mg, E/Z = 18:1) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 3H), 5.54 – 5.42 (m, minor isomer), 5.37 (d, *J* = 17.0 Hz, 1H), 5.30 – 5.12 (m, 1H), 2.77 – 2.70 (m, minor isomer), 2.70 – 2.61 (m, 2H), 2.38 – 2.35 (m, minor isomer), 2.31 – 2.18 (m, 2H), 1.78 – 1.66 (m, 2H), 1.11 (s, 9H), 1.02 (s, minor isomer).

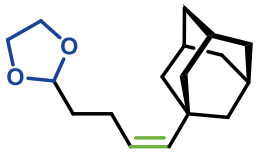
^{13}C NMR (151 MHz, $CDCl_3$): δ 142.6, 140.3, 128.6 (minor isomer), 128.6, 128.5, 128.4, 128.4 (minor isomer), 125.8, 35.7, 33.3 (minor isomer), 32.2, 31.6 (minor isomer), 31.3, 29.9 (minor isomer), 29.4, 28.1.

Physical State: colorless oil.

GC/MS (EI): 55 (33%), 83 (38%), 91 (75%), 104 (100%), 117 (21%), 131 (13%), 202 (8%).

TLC: R_f = 0.62 (40:1 Hexanes: EtOAc).

Compound 44



Following the general procedure C on a 0.2 mmol scale and 6.5 F/mol. Compound **44** was isolated by p-TLC (EtOAc/Hex, 9:1) in 60% yield (31.5 mg, 0.120 mmol, E/Z = 6:1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 – 5.04 (m, 2H), 4.87 (t, *J* = 4.8 Hz, 1H), 4.02 – 3.91 (m, 2H), 3.92 – 3.80 (m, 2H), 2.39 – 2.27 (m, 2H), 2.16 – 2.05 (m, minor isomer), 1.94 (s, 3H), 1.75 (d, *J* = 3.0 Hz, 5H), 1.75 – 1.60 (m, 8H), 1.57 – 1.41 (m, 1H).

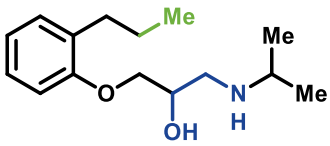
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 127.5, 104.3, 65.0, 43.0, 42.8 (minor isomer), 36.9, 35.8 (minor isomer), 34.8, 28.8, 23.6.

GC/MS (EI): 99 (100%), 73 (50%), 135 (25%), 262 (0.8%).

Physical State: Colorless oil.

R_f = 0.56 (Hex/EtOAc, 9:1).

Compound 45



Following the general procedure C on 0.1 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol), Et_3N*HBF_4 (114 mg), HFIP (300 µL), and THF (2.2 mL), with magnesium as anode and graphite as cathode under the electrolysis of 5 mA for 10 F/mol. Compound **45** purified by PTLC (silica, 9:1 DCM: MeOH) to afford 16.1 mg (64%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 – 7.10 (m, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 4.27 (s, 2H), 4.04 (dd, *J* = 9.4, 5.0 Hz, 1H), 3.94 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.08 (dd, *J* = 12.1, 4.2 Hz, 2H), 2.92 (dd, *J* = 12.3, 8.8 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.59 (h, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 6.2 Hz, 7H), 0.93 (t, *J* = 7.3 Hz, 3H).

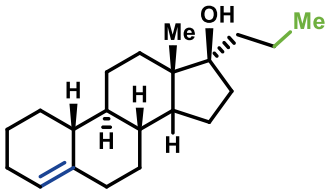
^{13}C NMR (151 MHz, $CDCl_3$): δ 156.4, 131.2, 130.2, 127.1, 120.9, 111.4, 70.3, 67.3, 49.9, 49.1, 32.5, 23.2, 21.4, 21.2, 14.3.

Physical State: colorless solid.

TLC: R_f = 0.2 (9:1 DCM: MeOH).

HRMS (ESI-TOF): calc'd for $C_{15}H_{26}NO_2$ $[M+H]^+$: 252.1964; found 252.1974.

Compound 46



Following the general procedure B on 0.2 mmol scale, using **Co(salen)-1** (12 mg, 20 µmol), $TBABF_4$ (100 mg), HFIP (63 µL, 0.4 mmol), and acetone (2.5 mL), with Zinc as anode and RVC as cathode under the electrolysis of 10 mA for 15 F/mol. Purification by column chromatography (silica, 20:1 to 10:1 Hexanes: EtOAc) afforded 54.4 mg (90%) of the title Compound **46.**

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.38 (s, 1H), 2.26 – 2.15 (m, 1H), 2.10 – 1.85 (m, 5H), 1.86 – 1.79 (m, 1H), 1.81 – 1.58 (m, 4H), 1.61 – 1.39 (m, 6H), 1.41 – 1.11 (m, 9H), 1.13 – 0.95 (m, 2H), 0.93 – 0.74 (m, 4H), 0.73 – 0.57 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.6, 120.0, 83.6, 50.4, 49.6, 46.7, 42.1, 42.0, 39.2, 35.7, 34.4, 32.0, 31.6, 28.9, 26.2, 25.6, 23.7, 22.2, 16.9, 15.0, 14.5.

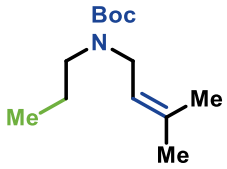
Physical State: pale yellow solid.

TLC: R_f = 0.44 (4:1 Hexanes: EtOAc).

HRMS (ESI-TOF): Not found.

$[\alpha]_D^{20}$ = +30.8 (*c* = 1.0, $CHCl_3$).

Compound 47



Following the general procedure C on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol), Et_3N*HBF_4 (114 mg), HFIP (300 µL), and THF (2.2 mL), with magnesium as anode and graphite as cathode under the electrolysis of 5 mA for 10 F/mol. Compound **47** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 36.4 mg (88%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.13 (s, 1H), 3.79 (s, 2H), 3.08 (s, 2H), 1.70 (s, 3H), 1.64 (s, 3H), 1.50 (q, *J* = 7.5 Hz, 2H), 1.44 (s, 9H), 0.85 (t, *J* = 7.5 Hz, 3H).

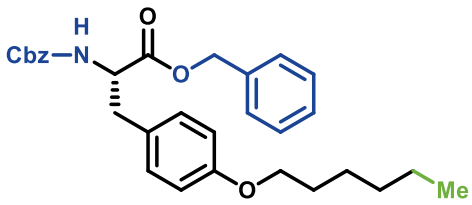
^{13}C NMR (151 MHz, $CDCl_3$): δ 155.8, 121.3, 79.2, 48.1, 44.7 (br), 28.6, 25.8, 21.7 (br), 17.9, 11.5.

Physical State: colorless oil.

GC/MS (EI): 57 (91%), 69 (80%), 116 (40%), 156 (100%), 171 (50%), 227 (0.5%).

TLC: R_f = 0.55 (20:1 Hexanes: EtOAc).

Compound 48



Following the general procedure C on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol), Et_3N*HBF_4 (114 mg), HFIP (300 µL), and THF (2.2 mL), with magnesium as anode and graphite as cathode under the electrolysis of 5 mA for 10 F/mol. Compound **48** purified by PTLC (silica, 4:1 Hexanes: EtOAc) to afford 68.1 mg (70%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.27 (m, 10H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 5.31 – 5.03 (m, 5H), 4.73 – 4.62 (m, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 3.05 (d, *J* = 5.9 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.50 – 1.42 (m, 2H), 1.39 – 1.33 (m, 4H), 0.96 – 0.87 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.6, 158.4, 155.8, 136.4, 135.2, 130.4, 128.7, 128.7, 128.6, 128.6, 128.3, 128.2, 127.3, 114.7, 68.0, 67.3, 67.1, 55.1, 37.4, 31.7, 29.4, 25.9, 22.7, 14.2.

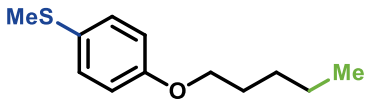
Physical State: white solid.

TLC: R_f = 0.62 (4:1 Hexanes: EtOAc).

HRMS (ESI-TOF): calc'd for $C_{30}H_{36}NO_5$ $[M+H]^+$: 490.2593; found 490.2598.

$[\alpha]_D^{20}$ = +4.6 (*c* = 1.0, $CHCl_3$).

Compound 49



Following the general procedure C on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol), Et_3N*HBF_4 (114 mg), HFIP (300 µL), and THF (2.2 mL), with magnesium as anode and graphite as cathode under the electrolysis of 5 mA for 15 F/mol. Compound **49** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 35.7 mg (85%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.82 – 1.74 (m, 2H), 1.48 – 1.33 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H).

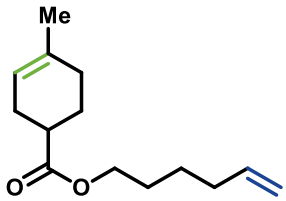
^{13}C NMR (151 MHz, $CDCl_3$): δ 157.9, 130.4, 128.6, 115.3, 68.3, 29.1, 28.3, 22.6, 18.3, 14.2.

Physical State: colorless oil.

GC/MS (EI): 125 (31%), 140 (100%), 210 (19%).

TLC: R_f = 0.42 (20:1 Hexanes: EtOAc).

Compound 51



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (147 µL, 1.4 mmol), and acetone (2.5 mL), with zinc as anode and nickel foam as cathode under the electrolysis of 2.5 mA for 0.6 F/mol. Afterwards Co(salen)-1 (3.0 mg, 5 µmol) and HFIP (147 µL, 1.4 mmol) were added and the reaction mixture was electrolyzed for 0.5 F/mol. Compound **51** purified by PTLC (silica, 10:1 Pentane: Et_2O) as colorless oil (59% yield), with 5% starting material residues.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.39 (tt, *J* = 3.4, 1.8 Hz, 1H), 5.08 – 4.95 (m, 2H), 4.10 (t, *J* = 6.6 Hz, 2H), 2.49 (dqt, *J* = 13.6, 6.7, 3.3 Hz, 1H), 2.24 (ddq, *J* = 7.9, 4.9, 2.3 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 2H), 2.06 – 1.94 (m, 2H), 1.78 – 1.56 (m, 6H), 1.48 (p, *J* = 7.6 Hz, 2H).

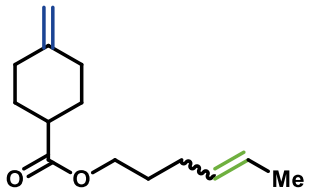
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 138.4, 133.7, 119.3, 114.8, 114.8, 64.2, 39.3, 33.3, 29.3, 28.1, 27.7, 25.5, 25.2, 23.5.

Physical State: colorless oil.

GC/MS (EI): 125 (31%), 140 (100%), 210 (19%).

TLC: R_f = 0.42 (20:1 Hexanes: Et_2O).

Compound 52



Following the general procedure A on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 4,4'-dimethoxy-2,2'-bipyridine (4.8 mg, 22 µmol), Et_3N*HBF_4 (114 mg), and MeCN (2.5 mL), with Magnesium as anode and Tin as cathode under the electrolysis of 2.5 mA for 4 F/mol. Compounds **52** purified by column chromatography (silica, 20:1 Hexanes: EtOAc) to afford 38.4 mg (92%) as a mixture of isomers (3/1 *E*/Z).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.63 – 5.28 (m, 2H), 4.66 (d, *J* = 1.9 Hz, 2H), 4.08 (q, *J* = 6.4 Hz, 2H), 2.46 (tq, *J* = 11.1, 4.0 Hz, 1H), 2.35 (dt, *J* = 13.7, 4.1 Hz, 2H), 2.16 – 1.97 (m, 6H), 1.75 – 1.54 (m, 7H).

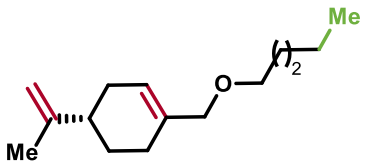
^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 147.7, 147.6, 129.9, 129.1, 125.8, 124.9, 107.9, 107.9, 107.9, 63.8, 63.8, 42.7, 33.6, 30.2, 28.9, 28.5, 23.2, 17.9, 12.7.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 67 (83%), 82 (83%), 95 (35%), 207 (9%), 208 (2%).

TLC: R_f = 0.36 (20:1 Hexanes: EtOAc).

Compound 54



Following the general procedure C on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol), Et_3N*HBF_4 (114 mg), HFIP (300 µL), and THF (2.2 mL), with magnesium as anode and graphite as cathode under the electrolysis of 5 mA for 5 F/mol. Compound **54** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 42.2 mg (95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.71 (dd, *J* = 4.6, 2.4 Hz, 1H), 4.74 (d, *J* = 5.8 Hz, 2H), 3.85 (s, 2H), 3.38 (t, *J* = 6.8 Hz, 2H), 2.25 – 2.04 (m, 4H), 2.03 – 1.94 (m, 1H), 1.86 (ddq, *J* = 12.7, 4.9, 2.4 Hz, 1H), 1.76 (s, 3H), 1.60 (dd, *J* = 9.3, 4.7 Hz, 2H), 1.50 (qd, *J* = 11.7, 5.8 Hz, 1H), 1.39 – 1.30 (m, *J* = 6.1, 5.7 Hz, 4H), 0.92 (dt, *J* = 8.4, 4.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 134.9, 123.9, 108.6, 75.1, 70.0, 41.2, 30.5, 29.5, 28.4, 27.5, 26.4, 22.6, 20.8, 14.1.

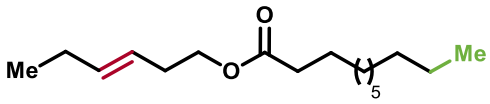
Physical State: colorless oil.

GC/MS (EI): 55 (42%), 67 (53%), 79 (61%), 93 (100%), 119 (48%), 134 (26%), 222 (7%).

TLC: R_f = 0.51 (20:1 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = -42.7 (*c* = 1.0, $CHCl_3$).

Compound 56



Following the general procedure C on 0.2 mmol scale, using $CoBr_2$*glyme (6.2 mg, 20 µmol), 6,6'-dimethyl-2,2'-bipyridine (5.5 mg, 30 µmol), Et_3N*HBF_4 (114 mg), HFIP (300 µL), and THF (2.2 mL), with magnesium as anode and graphite as cathode under the electrolysis of 5 mA for 8 F/mol. Compound **56** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 43.4 mg (81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.57 (dt, *J* = 15.5, 6.4 Hz, 1H), 5.39 (tt, *J* = 15.8, 14.1, 5.7 Hz, 1H), 4.08 (t, *J* = 7.0 Hz, 2H), 2.31 (dt, *J* = 17.7, 7.3 Hz, 4H), 2.02 (p, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H), 1.35 – 1.22 (m, 16H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H).

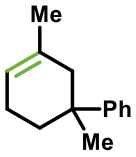
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 135.0, 124.1, 63.9, 34.4, 32.0, 31.9, 29.6, 29.5, 29.3, 29.2, 29.2, 25.6, 25.0, 22.7, 14.1, 13.7.

Physical State: colorless oil.

GC/MS (EI): 55 (39%), 67 (55%), 82 (100%), 266 (0.1%).

TLC: R_f = 0.50 (20:1 Hexanes: EtOAc).

Compound 58



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **58** purified by column chromatography (silica, 40:1 Hexanes: EtOAc) to afford 33.3 mg (89%)**.** *J. Am. Chem. Soc.* 140, 6873−6882 (2018).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.22 (tt, *J* = 6.8, 1.9 Hz, 1H), 5.40 (dd, *J* = 3.7, 1.9 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.11 – 2.00 (m, 2H), 1.92 (dt, *J* = 12.2, 5.5 Hz, 1H), 1.85 – 1.77 (m, 4H), 1.72 (dt, *J* = 12.7, 6.4 Hz, 1H), 1.31 (s, 3H).

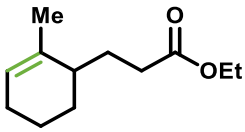
^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 132.7, 128.0, 125.7, 125.5, 120.6, 42.4, 36.9, 34.7, 28.9, 23.8, 23.3.

Physical State: colorless oil.

GC/MS (EI): 118 (100%), 186 (10%).

TLC: R_f = 0.56 (40:1 Hexanes: EtOAc).

Compound 60



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **60** purified by column chromatography (silica, 20:1 Hexanes: EtOAc) afforded 31.0 mg (79%) as a mixture of isomer (7/1, ratio determined by GCMS)**.**

^{1}H NMR (600 MHz, $CDCl_3$, mixture of regioisomers) δ 5.45 (dq, *J* = 3.9, 2.0 Hz, 1H), 4.14 (p, *J* = 7.2 Hz, 2H), 2.44 – 2.25 (m, 3H), 2.00 – 1.89 (m, 5H), 1.71 – 1.67 (m, 3H), 1.66 – 1.39 (m, 4H), 1.28 (td, *J* = 7.2, 3.5 Hz, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 136.3, 123.1, 60.2, 37.9, 33.1, 32.1, 31.8, 29.1, 28.9, 27.6, 27.1, 25.5, 23.4, 23.3, 22.1, 19.6, 14.3.

Physical State: pale yellow oil.

GC/MS (EI): 55 (36%), 67 (50%), 79 (55%), 93 (91%), 108 (100%), 196 (18%).

TLC: R_f = 0.37 (20:1 Hexanes: EtOAc).

Compound 62

Following the general procedure E on 10 mmol scale.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54 – 5.28 (m, 2H), 3.62 (td, J = 6.5, 2.4 Hz, 2H), 2.05 (tdd, J = 8.2, 3.4, 1.7 Hz, 2H), 1.69 – 1.52 (m, 5H).

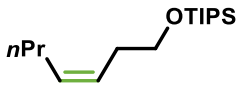
^{13}C NMR (151 MHz, $CDCl_3$) δ 131.1, 125.8, 62.9, 32.8, 29.3, 18.3.

Physical State: colorless oil.

GC/MS (EI): 100 (5%).

TLC: R_f = 0.3 (2:1 Hexanes: EtOAc).

Compound 64



Following the general procedure F on 37.4 mmol scale. *Nat. Chem.* 5, 718-723 (2013).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.45 (tdd, *J* = 18.2, 11.3, 6.9 Hz, 2H), 3.70 (t, *J* = 7.1 Hz, 2H), 2.34 (q, *J* = 7.0 Hz, 2H), 2.06 (p, *J* = 7.6 Hz, 2H), 1.40 (h, *J* = 7.3 Hz, 2H), 1.18 – 1.09 (m, 21H), 0.92 (dt, *J* = 10.9, 7.3 Hz, 3H).

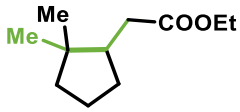
^{13}C NMR (151 MHz, $CDCl_3$) δ 131.5, 125.8, 63.3, 31.3, 29.4, 22.9, 17.7, 13.8, 12.0.

Physical State: colorless oil.

GC/MS (EI): 185 (78%), 227 (100%), 239 (0.1%), 270 (0.1%).

TLC: R_f = 0.7 (exanes).

Compound 67



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (147 µL, 1.4 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **67** purified by column chromatography (silica, 20:1 Hexanes: EtOAc) to afford 22.5 mg (61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (q, *J* = 7.1 Hz, 2H), 2.37 (dd, *J* = 14.5, 4.1 Hz, 1H), 2.06 (dd, *J* = 14.5, 10.4 Hz, 1H), 1.98 – 1.81 (m, 2H), 1.68 – 1.55 (m, 2H), 1.50 – 1.41 (m, 2H), 1.39 – 1.34 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.01 (s, 3H), 0.77 (s, 3H).

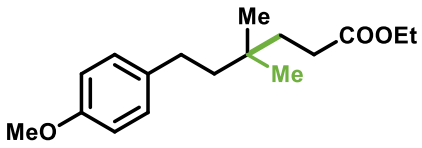
^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 60.2, 45.9, 41.4, 40.6, 35.6, 30.4, 27.7, 21.8, 21.1, 14.3.

Physical State: colorless oil.

GC/MS (EI): 55 (100%), 68 (100%), 95 (73%), 110 (62%), 138 (87%), 184 (2%).

TLC: R_f = 0.45 (20:1 Hexanes: EtOAc).

Compound 69



Following the general procedure B on 0.2 mmol scale, using Co(salen)-2 (2.2 mg, 4 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 5 mA for 3 F/mol. Compound **69** purified by column chromatography (silica, 8:1 Hexanes: EtOAc) to afford 27.8 mg (50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 2H), 6.88 – 6.81 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.57 – 2.48 (m, 2H), 2.35 – 2.26 (m, 2H), 1.69 – 1.60 (m, 2H), 1.53 – 1.44 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 6H).

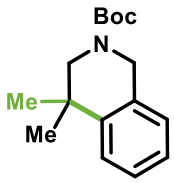
^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 157.6, 135.2, 129.1, 113.8, 60.3, 55.3, 44.3, 36.4, 32.6, 29.7, 29.6, 26.7, 14.2.

Physical State: colorless oil.

GC/MS (EI): 121 (100%), 175 (3%), 278 (5%).

TLC: R_f = 0.4 (8:1 Hexanes: EtOAc).

Compound 71a



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (102 µL, 1.2 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 4 F/mol. Compound **71a** purified by PTLC (silica, 9:1 Hexanes: EtOAc) to afford 39.4 mg (75%). *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (q, *J* = 7.8 Hz, 1H), 7.20 (dt, *J* = 25.7, 7.3 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 4.65 (d, *J* = 15.8 Hz, 2H), 3.45 (d, *J* = 6.7 Hz, 2H), 1.52 (s, 9H), 1.30 (s, 7H).

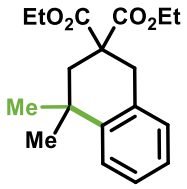
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 143.9, 143.4, 132.4, 126.6, 126.3, 126.0, 125.5, 53.9, 46.7, 35.1, 28.5, 27.7, 27.6.

Physical State: colorless oil.

GC/MS (EI): 57 (100%), 132 (53%), 204 (50%).

TLC: R_f = 0.61 (9:1 Hexanes: EtOAc).

Compound 71b



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 2.5 F/mol. Compound **71b** purified by PTLC (silica, 20:1 Hexanes: EtOAc) afforded 51.8 mg (85%). *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 1H), 7.18 (td, *J* = 7.8, 7.1, 2.1 Hz, 1H), 7.15 – 7.09 (m, 2H), 4.19 – 4.13 (m, 4H), 3.23 (s, 2H), 2.33 (s, 2H), 1.28 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 6H).

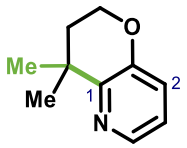
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 143.6, 132.8, 128.9, 126.7, 126.0, 125.9, 61.5, 52.7, 42.7, 35.5, 33.8, 32.5, 14.1.

Physical State: colorless oil.

GC/MS (EI): 143 (100%), 215 (44%), 230 (31%), 304 (6%).

TLC: R_f = 0.33 (20:1 Hexanes: EtOAc).

Compound 73



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (6.0 mg, 10 µmol), $TBABF_4$ (60 mg), HFIP (126 µL, 1.2 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 5 F/mol. Compound **73** purified by PTLC (silica, 2:1 Hexanes: EtOAc) afforded 13.8 mg (43%, r.r. 1:1). *Org. Lett.* 19, 2290–2293 (2017).

^{1}H NMR (600 MHz,) δ 8.17 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.11 (s, 1H), 8.05 (d, *J* = 5.2 Hz, 1H), 7.18 (d, *J* = 5.2 Hz, 1H), 7.09 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.03 (dd, *J* = 8.2, 4.5 Hz, 1H), 4.27 – 4.20 (m, 4H), 1.98 – 1.94 (m, 2H), 1.90 – 1.85 (m, 2H), 1.41 (s, 6H), 1.35 (s, 6H).

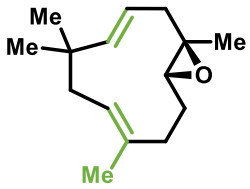
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.5, 140.8, 140.2, 139.8, 137.6, 124.0, 122.3, 121.9, 121.2, 118.9, 65.1, 63.2, 63.2, 37.4, 30.2, 29.2.

Physical State: colorless oil.

GC/MS (EI): 120 (29%), 133 (44%), 148 (100%), 163 (56%).

TLC: R_f = 0.63 (2:1 Hexanes: EtOAc).

Compound 75



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (84 µL, 0.8 mmol), and acetone (2.5 mL), with Zinc as anode and Nickel foam as cathode under the electrolysis of 5 mA for 1.0 F/mol. Compound **75** purified by PTLC (silica, 20:1 Hexanes: EtOAc) to afford 38.2 mg (87%). *J. Am. Chem. Soc.* 136, 16788-16791 (2014).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.27 (ddd, *J* = 15.5, 10.1, 5.2 Hz, 1H), 5.15 (d, *J* = 15.8 Hz, 1H), 5.01 – 4.96 (m, 1H), 2.60 – 2.50 (m, 2H), 2.23 (dd, *J* = 11.9, 5.9 Hz, 1H), 2.13 (dddd, *J* = 36.3, 12.1, 9.4, 4.9 Hz, 2H), 1.99 (dd, *J* = 13.7, 9.2 Hz, 1H), 1.86 (dd, *J* = 14.2, 5.9 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.56 (s, 3H), 1.40 – 1.32 (m, 1H), 1.30 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 132.0, 125.8, 122.2, 63.3, 62.1, 42.7, 40.3, 36.7, 36.6, 29.1, 24.9, 17.3, 15.2.

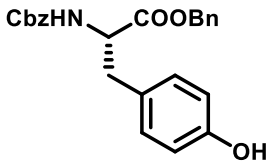
Physical State: pale yellow oil.

GC/MS (EI): 55 (57%), 69 (64%), 79 (100%), 93 (70%), 107 (45%), 220 (3%).

TLC: R_f = 0.32 (20:1 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = -89.8 (*c* = 1.0, $CHCl_3$).

Compound 77



Following the general procedure B on 0.2 mmol scale, using Co(salen)-1 (4.8 mg, 8 µmol), $TBABF_4$ (60 mg), HFIP (42 µL, 0.4 mmol), and acetone (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 5 mA for 1.0 F/mol. Compound **77** purified by PTLC (silica, 1:1 Hexanes: EtOAc) to afford 60.7 mg (75%). *Bio. Med. Chem. 15*, 97-103 (2007).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.26 (m, 10H), 6.90 – 6.83 (m, 2H), 6.69 – 6.60 (m, 2H), 5.68 (s, 1H), 5.34 – 5.27 (m, 1H), 5.23 – 5.07 (m, 4H), 4.75 – 4.65 (m, 1H), 3.05 (qd, *J* = 14.0, 5.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 155.8, 155.0, 136.1, 135.0, 130.5, 128.7, 128.7, 128.7, 128.6, 128.6, 128.6, 128.2, 128.1, 127.7, 127.2, 127.1, 115.5, 67.3, 67.1, 55.0, 37.4.

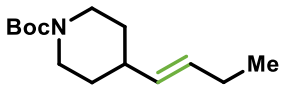
Physical State: white solid.

HRMMS (ESI): calcd for $C_{24}H_{24}NO_5$ $[M+H]^+$ 406.1654, found 406.1658

TLC: R_f = 0.35 (1:1 Hexanes: EtOAc).

$[\alpha]_D^{20}$ = +4.5 (*c* = 1.0, $CHCl_3$).

Compound 79



Following the general procedure B on 0.2 mmol scale, using Co(salen)-2 (2.2 mg, 4 µmol), $TBABF_4$ (60 mg), HFIP (210 µL, 2.0 mmol), and acetone (2.5 mL), with Zinc as anode and Tin as cathode under the electrolysis of 5 mA for 5 F/mol. Compound **79** purified by column chromatography (silica, 8:1 Hexanes: EtOAc) to afford 28.8 mg (60%)**.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (dtd, *J* = 15.5, 6.3, 1.2 Hz, 1H), 5.35 (ddt, *J* = 15.5, 6.6, 1.5 Hz, 1H), 4.08 (m, 2H), 2.74 (m, 2H), 2.12 – 2.01 (m, 2H), 1.66 (d, *J* = 12.3 Hz, 2H), 1.48 (s, 9H), 1.33 – 1.21 (m, 2H), 0.99 (td, *J* = 7.5, 5.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 133.2, 130.7, 79.2, 38.8, 32.1, 28.5, 28.5, 25.6, 13.9.

Physical State: colorless oil.

GC/MS (EI): 57 (100%), 82 (43%), 126 (57%), 183 (29%), 239 (1%).

TLC: R_f = 0.6 (8:1 Hexanes: EtOAc).

KINETIC STUDIES

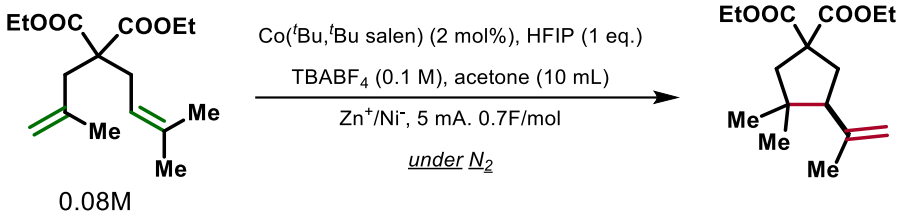
Kinetics for the Cycloisomerization with the Co(t-Bu,t-Bu Salen) Catalyst

All FTIR spectra were taken with a Mettler Toledo ReactIR 15 equipped with a LN_2 MCT detector and a 9.5 mm AgX Fibre DiComp probe at 4 cm^{-1} resolution. The spectra were recorded every 1 min. The product was monitored using the height of the signal at 1263 cm^{-1}.

Procedure for cycloisomerization Co(t-Bu,t-Bu Salen)

To a three necked 25 mL round-bottom flask was added alkene substrate **30** (225.6 mg, 0.8 mmol) and $TBABF_4$ (329.3 mg, 1.0 mmol). The flask was inserted with an IR probe, anode (Zinc), and cathode (Nickel). The flask was then connected to a Schlenk line and vacuumed and refilled with N_2 (X3). A 25 mL volumetric flask was charged with Co(t-Bu, t-Bu Salen) (30.2 mg, 0.05 mmol) and acetone (25 mL) to prepare a 25 mL Co stock solution (0.002 M). HFIP (336.1 mg, 2.0 mmol) and dodecane (340.7 mg, 2.0 mmol, as internal standard) were added to a 5 mL volumetric flask and dissolved in acetone (5 mL) to prepare a 5 mL HFIP and dodecane stock solution. To the three necked 25 mL round flask was added 8 mL of Co stock solution, which was then vacuumed and refilled with N_2(X3). This was followed by adding 2 mL of HFIP and dodecane stock solution and also vacuumed and refilled with N_2 (X3). After pre-stirring for 5 minutes under N_2, the reaction mixture was electrolyzed under a constant current of 5 mA for 0.7 F/mol. React IR data collection was immediately started when the current was turned on.

At the end of the reaction, the mmol of the product was determined by calibrated GC-FID using dodecane as the internal standard.



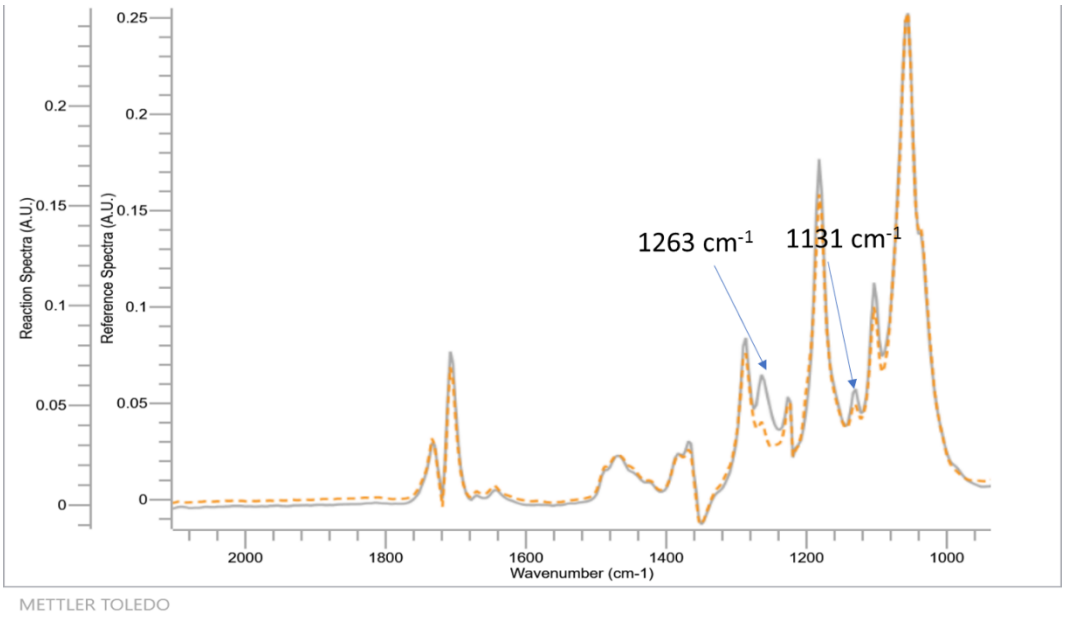


Figure S1. Orange: **[30]=0.08M**, [$TBABF_4$]=0.1M, [HFIP]=0.08M. Gray: **[sub]=0.04M, [pro]=0.04M**, [$TBABF_4$]=0.1M, [HFIP]=0.08M

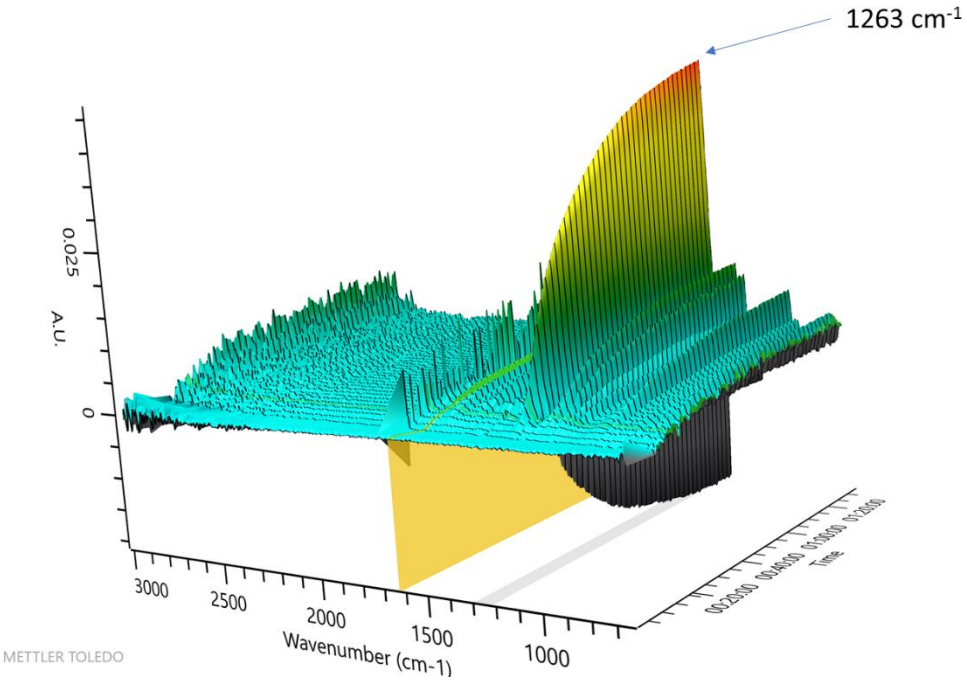


Figure S2. 3D surface for reaction under standard conditions: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=5 mA, 10 mL acetone.

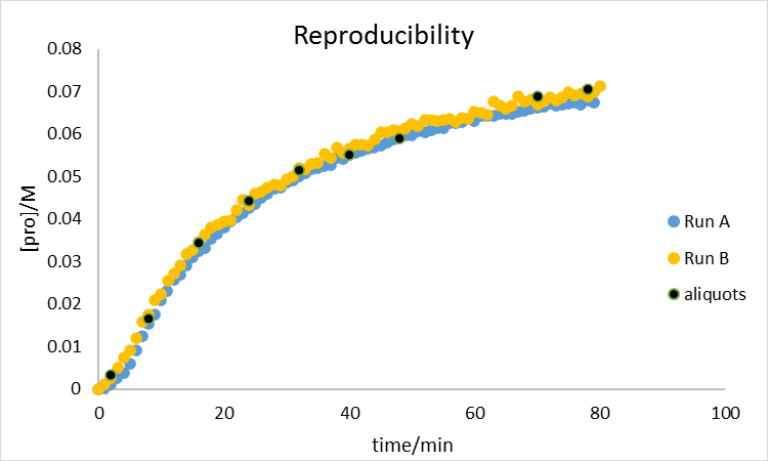


Figure S3. Reaction probed by React IR vs. reaction probed by taking aliquots under standard conditions. Time adjusted: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=5 mA, 10 mL acetone.

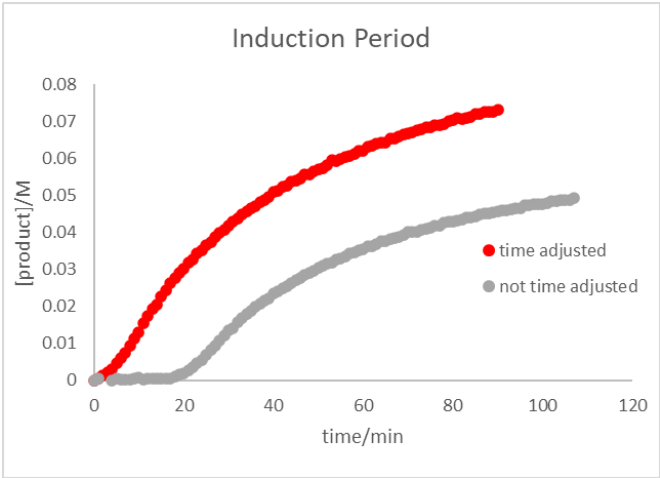


Figure S4. Reaction under standard conditions. gray: whole reaction data with induction period; red: data after time-adjusting to remove induction period: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=5 mA, 10 mL acetone.

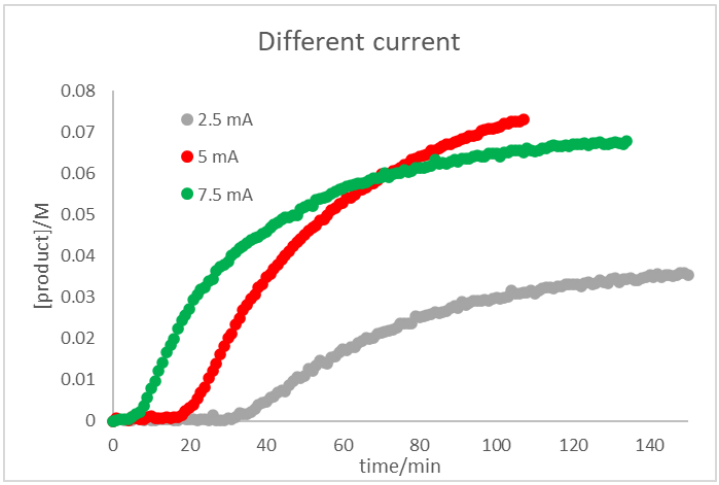


Figure S5a. Reactions with different current. Not time adjusted to show induction period. Grey: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=2.5 mA, 10 mL acetone; Red: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=5 mA, 10 mL acetone; Green: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=7.5 mA, 10 mL acetone.

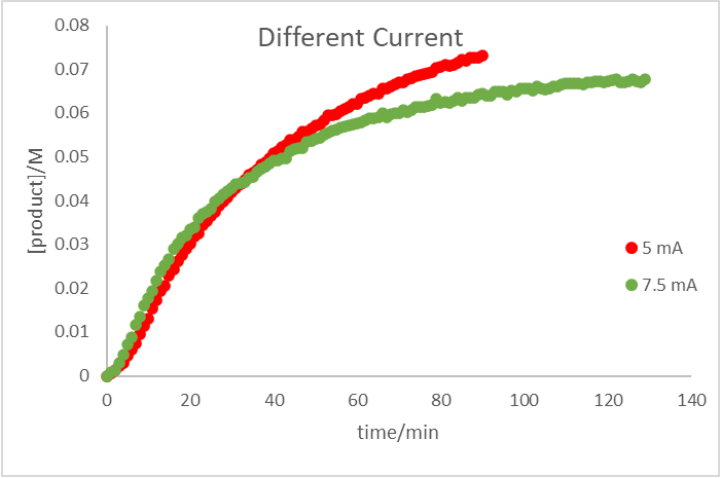


Figure S5b. Reactions with different current. Time adjusted. Data taken from figure S5a.

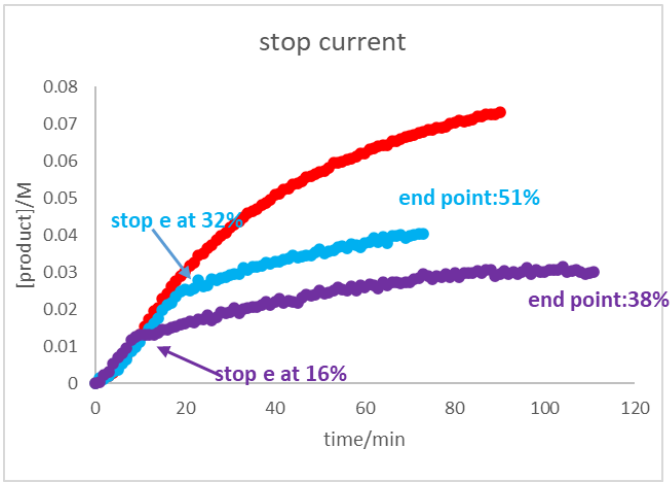


Figure S6. Stopped electricity at different time points. Time adjusted. Red/Blue/Purple: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=2.5 mA, 10 mL acetone.

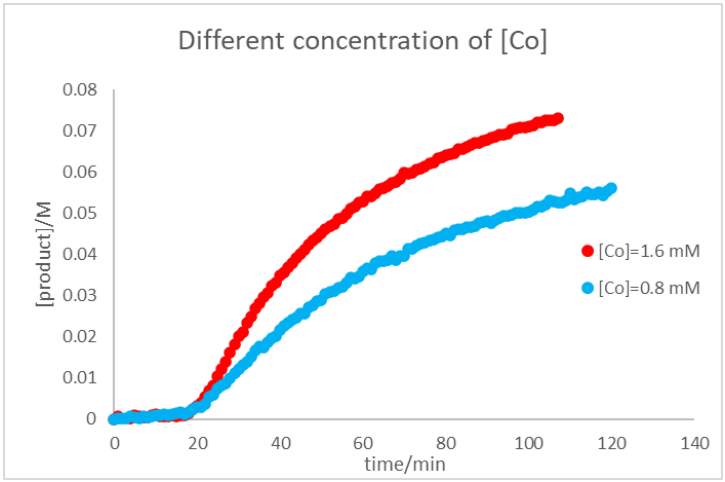


Figure S7a. Reaction with different concentrations of [Co] showing induction period. Not time adjusted. blue: [30]=0.08M, [Co]=0.8 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=5 mA, 10 mL acetone; red: [sub]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current=5 mA, 10 mL acetone

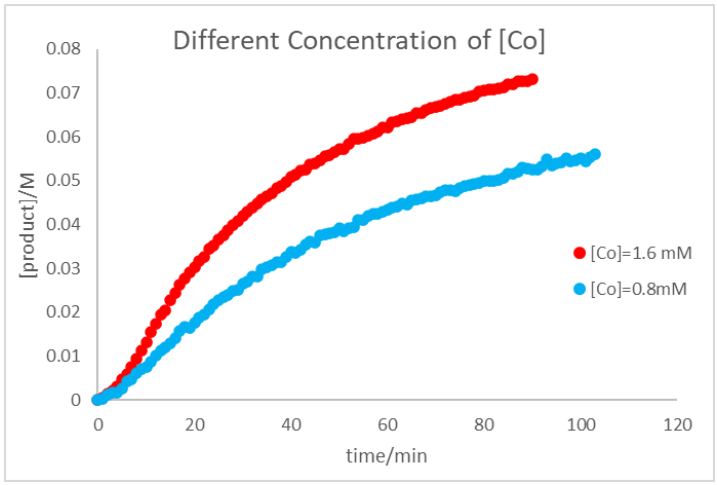


Figure S7b. Reaction with different concentrations of [Co] with time adjustment. Data taken from Figure S7a

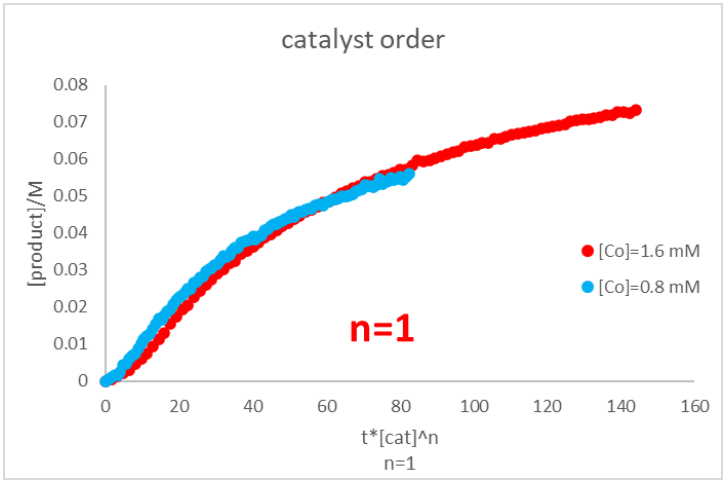


Figure S7c. Reaction with different concentrations of [Co] using the Burés method for determining reaction order. Data taken from Figure S7a

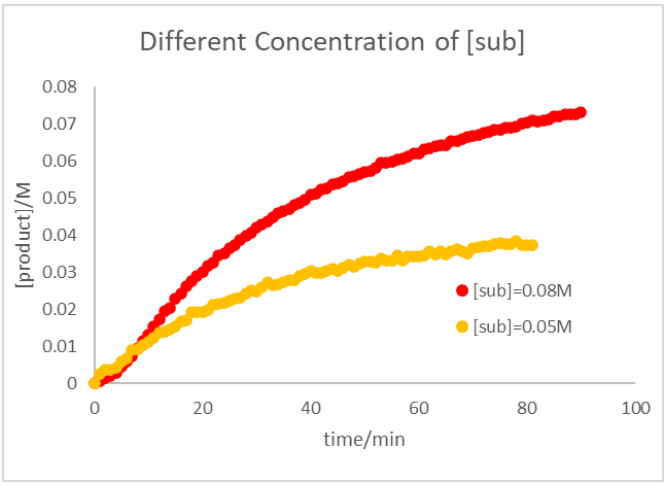


Figure S8. Reactions with different concentrations of [30]. Time adjusted. red: [sub]=0.08M, [Co]=0.8 mM, [HFIP]=1.6M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone; yellow: [sub]=0.05M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone

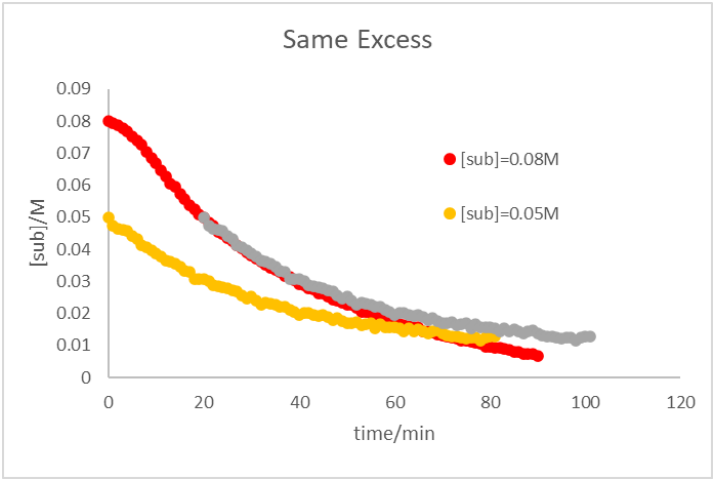


Figure S9. Reactions with different concentrations of [sub]. Time adjusted. red: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone; yellow: [30]=0.05M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone

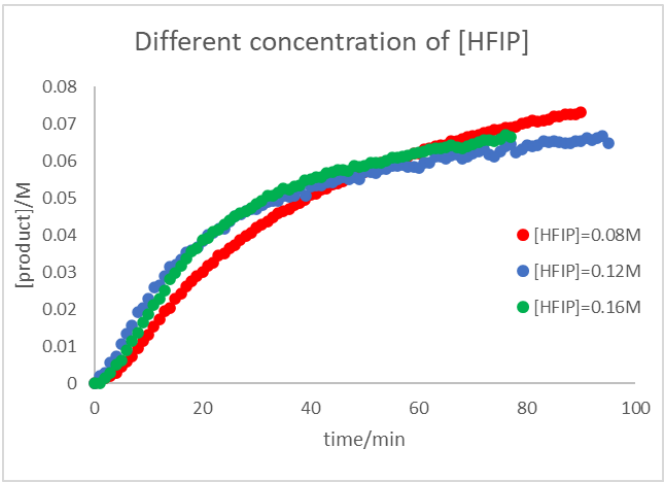
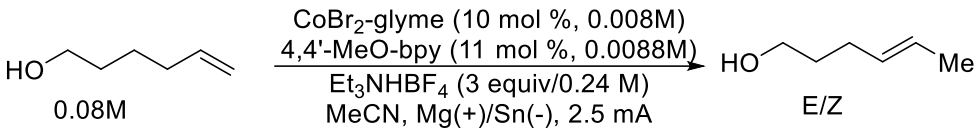


Figure S10. Reactions with different concentrations of [HFIP]. Time adjusted. red: [30]=0.08M, [Co]=1.6 mM, [HFIP]=0.08M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone; blue: [30]=0.05M, [Co]=1.6 mM, [HFIP]=0.12M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone; green: [30]=0.05M, [Co]=1.6 mM, [HFIP]=0.16M, [$TBABF_4$]=0.1M, current =5 mA, 10 mL acetone

Kinetics for the isomerization of terminal alkenes using the $COBr_2$-glyme/4,4'-MeO-bpy catalyst

Analysis: The concentrations at a given time were determined based on quantitative ^1H NMR. The T1 was determined for the trans isomer of 4-hexene-1-ol (5.76 s) and the relaxation delay was set to 5*T1 (28.8 s). All ^1H NMRs were taken at 400 MHz on a Joel spectrometer with 16 scans. Automatic baseline correction was applied prior to integration. Note that the cis and trans isomers were not differentiated by this method due to peak overlap. As such, the product formation represents the overall rate of formation of the trans plus cis isomers. The concentrations of the product and starting material were determined by comparison to the anisole internal standard. When the catalyst was not pre-activated, an induction period was observed. The data has not been time adjusted.



Representative Standard Procedure with OH substrate

A 25 mL volumetric flask was charged with 5-hexene-1-ol (**61**, 200 mg, 2.00 mmol) and anisole (internal standard, 213 mg, 1.97 mmol) and the flask was evacuated and backfilled with argon (X3). The flask was then charged with dry and degassed MeCN (25 mL) to prepare a substrate stock solution (0.080 M)

A 10 mL ElectraSyn vial was equipped with a magnetic stir bar, wrapped with Teflon tape on the screw thread, and charged with $CoBr_2$-glyme (24.6 mg, 79.8 μmol), 4,4'-dimethoxy-2,2'-bypyridine (4,4'-MeO-bpy, 19.1 mg, 88.1 μmol), and Et_3NHBF_4 (453 mg, 2.40 mmol) The vial was sealed with the cap carrying a magnesium anode and a tin cathode and evacuated and backfilled with argon (X3). The vial was charged with an aliquot of the MeCN stock solution of substrate (10 mL) and evacuated and backfilled with argon (X1). The vial was stirred at rt for approximately 1 min until the catalyst dissolved. The vial was electrolyzed with 2.5 mA. At the indicated time, aliquots (0.15 mL) were taken using a syringe pre-rinsed with argon. The aliquots were filtered through a short plug of silica gel (approximately 1 cm) and the silica gel was rinsed with CD_3CN (0.5 mL). The resulting solution was analyzed by ^1H NMR.

The integration of anisole was determined from the peak at 6.95-6.85 (3H). The integration of the starting material was determined by averaging the peaks at 5.87 – 5.75 (1H) and 5.02 – 4.88 (2H). The integration of the product was determined by integrating the peak at 5.48-5.32 (2H).

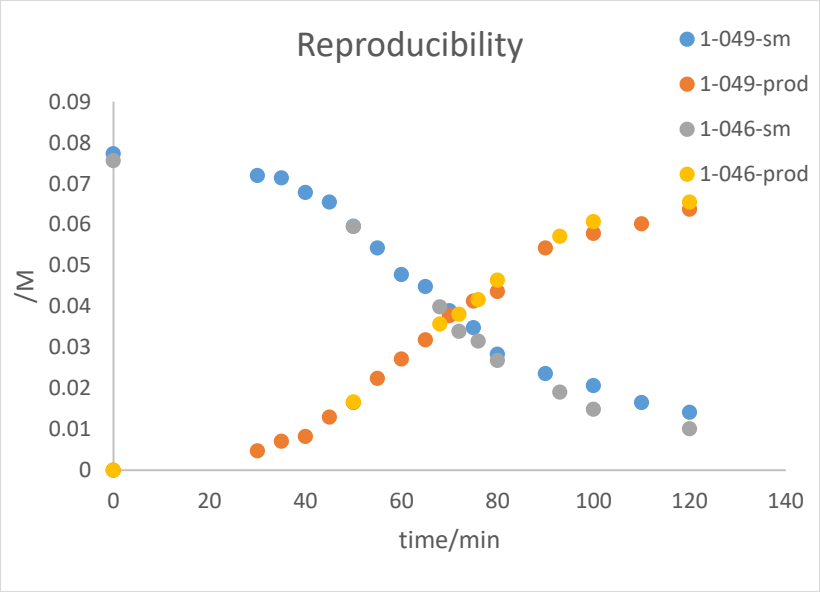


Figure S11. Reactions to probe reproducibility; [61]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN.

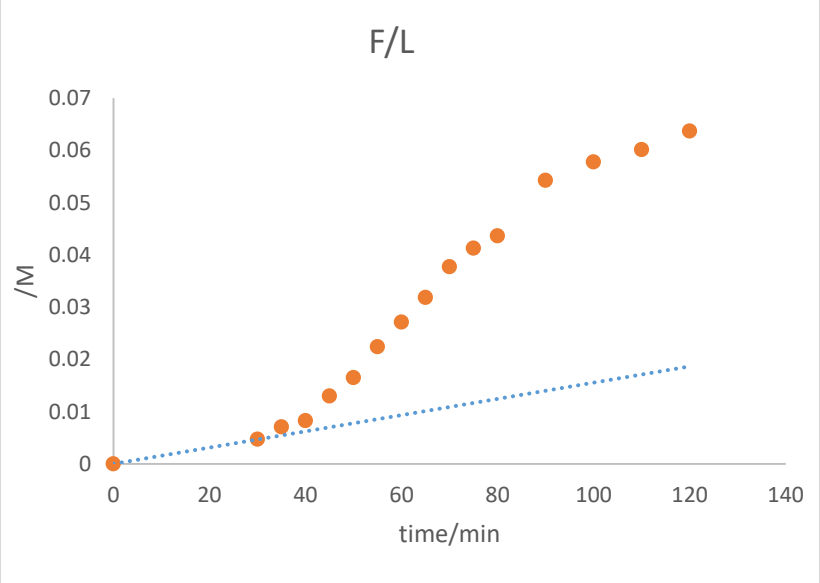


Figure S12. Reaction with F/mol overlayed; orange: [61]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN; Blue: F/L based 2.5 mA of current.

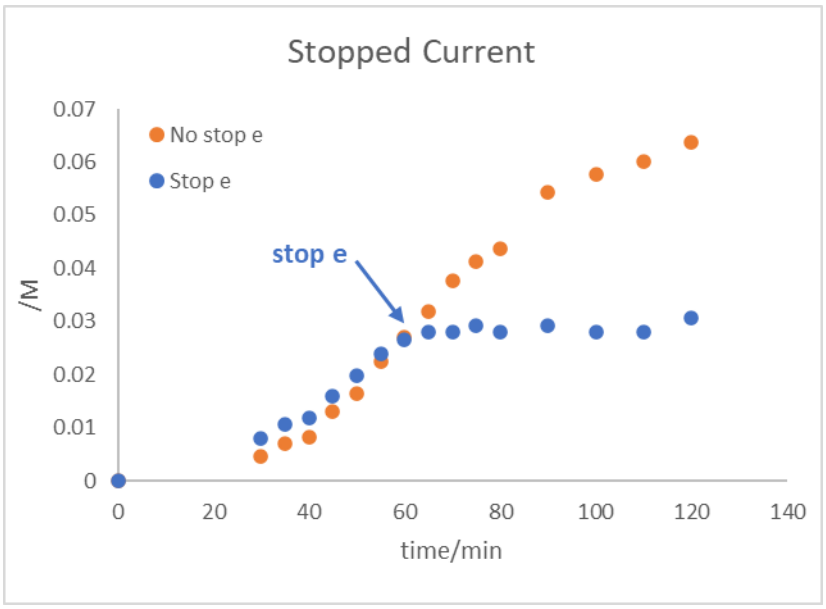


Figure S13. Reaction with stopped current; orange: [61]=0.080M, [Co]=8.0mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN; Blue: [61]=0.08M, [Co]=8.0 mM, [4,4-MeO-bpy]=8.8mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL, current stopped at 62.5 min/0.12 F/mol.

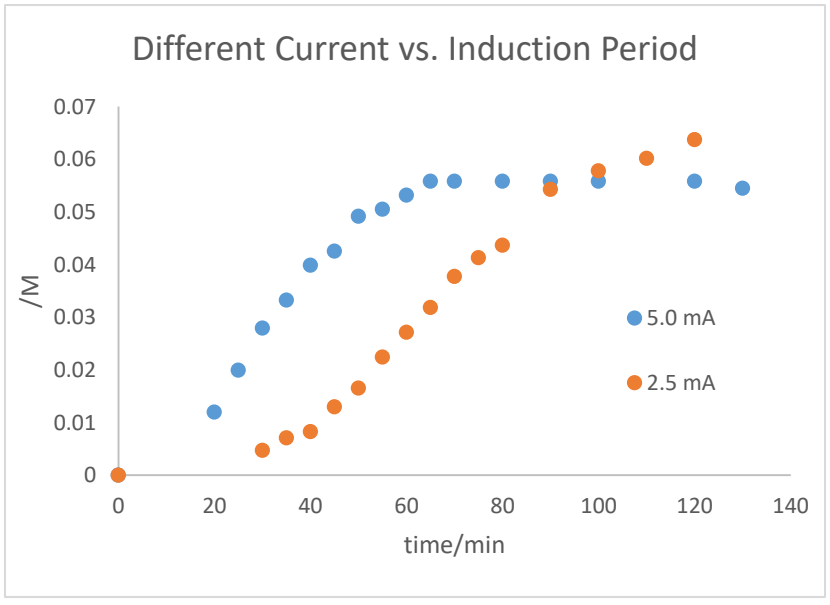
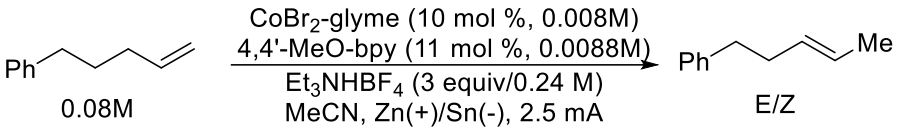


Figure S14. Reactions with different current; orange: [61]=0.080M, [Co]=8.0mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN; Blue: [61]=0.08M, [Co]=8.0 mM, [4,4-MeO-bpy]=8.8mM, [Et_3NHBF_4]=0.24M, current =5.0 mA, 10 mL.



Representative Standard Procedure with Ph substrate (**15a**) – No catalyst pre-activation:

A 25 mL volumetric flask was charged with 5-phenyl-1-pentene (**15a**) (292 mg, 2.00 mmol) and anisole (internal standard, 215 mg, 1.99 mmol) and the flask was evacuated and backfilled with argon (X3). The flask was then charged with dry and degassed MeCN (25 mL) to prepare a stock solution of substrate (0.080 M)

A 10 mL ElectraSyn-vial was equipped with a magnetic stir bar, wrapped with Teflon tape on the screw thread, and charged with $CoBr_2$-glyme (24.7 mg, 80.1 µmol), 4,4'-dimethoxy-2,2'-bypyridine (4,4'-MeO-bpy, 19.1 mg, 88.1 µmol), and Et_3NHBF_4 (454 mg, 2.40 mmol) The vial was sealed with the cap carrying a magnesium anode and a tin cathode and evacuated and backfilled with argon (X3). The vial was charged with an aliquot of the MeCN solution of starting material (10 mL) and evacuated and backfilled with argon (X1). The vial was stirred at rt for approximately 1 min until the catalyst dissolved. The vial was electrolyzed with 2.5 mA. At the indicated time, aliquots (0.15 mL) were taken using a syringe pre-rinsed with argon. The aliquots were filtered through a short plug of silica gel (approximately 1 cm) and the silica gel was rinsed with CD_3CN (0.5 mL). The resulting solution was analyzed by ^1H NMR.

The integration of anisole was determined from the peak at 6.95-6.85 (3H). The integration of the starting material was determined by averaging the peaks at 5.90 – 5.77 (1H) and 5.04 – 4.89 (2H). The integration of the product was determined by integrating the peak at 5.49-5.36 (2H).

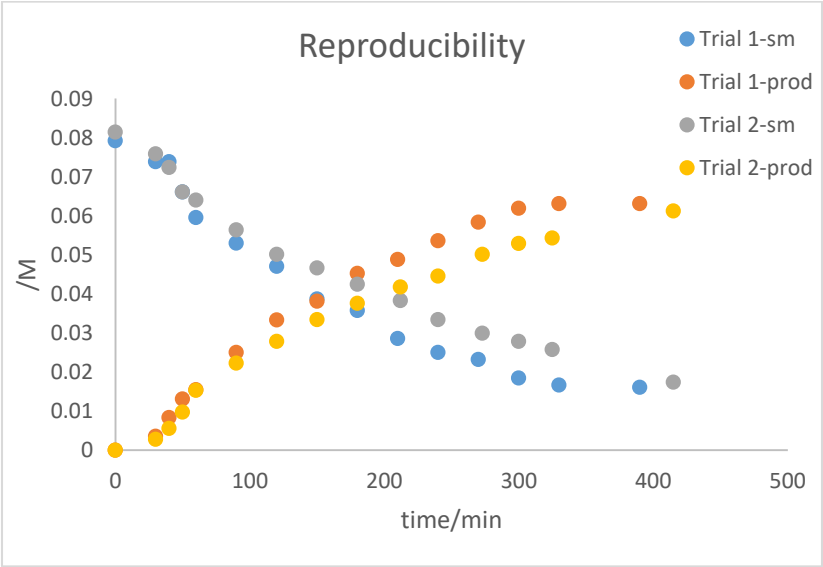


Figure S15. Reactions to probe reproducibility; [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN.

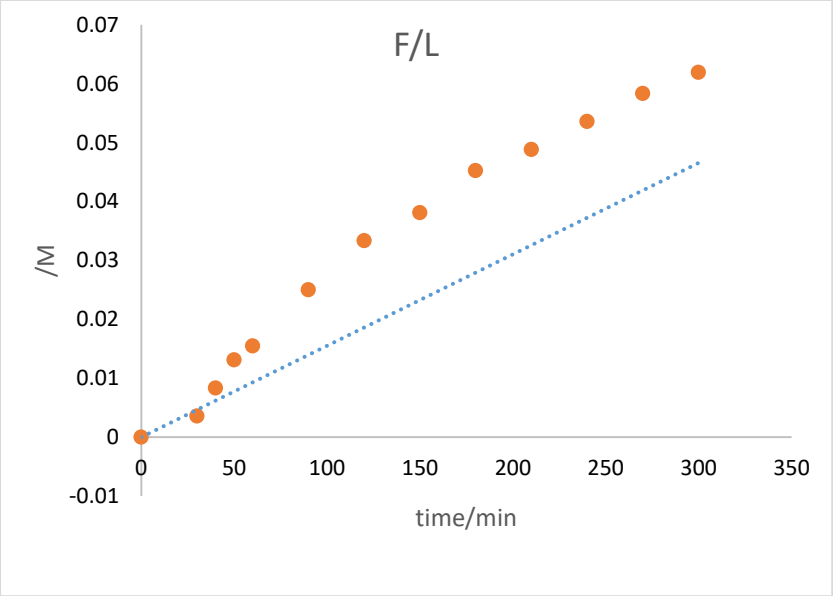


Figure S16. Reaction overlayed with F/mol; orange: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN. Blue: (F/mol)/L based on and 2.5 mA of current.

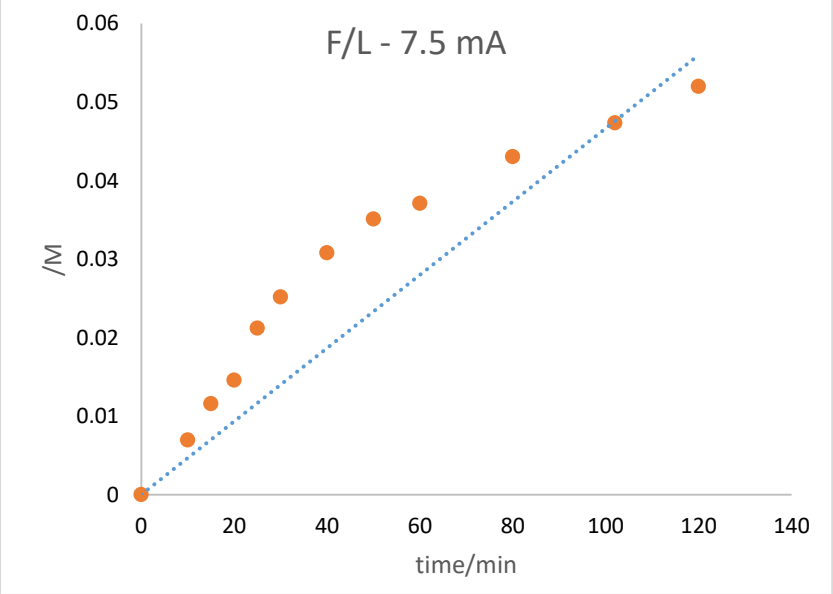


Figure S17. Reaction overlayed with F/mol; orange: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN. Blue: (F/mol)/L based on 7.5 mA of current.

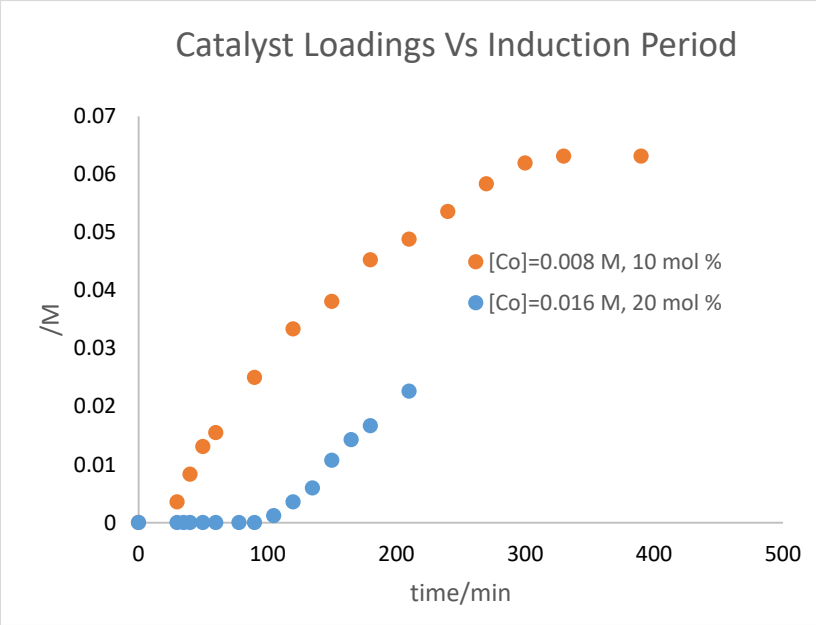
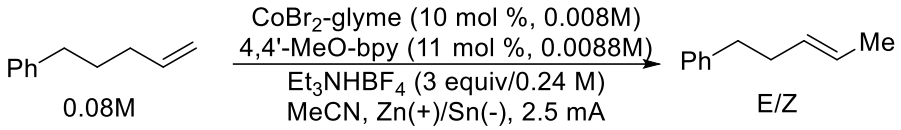


Figure S18. Reactions with different concentrations of [Co]; orange: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24 M, current =2.5 mA, 10 mL MeCN; Blue: [15a]=0.08 M, [Co]=16 mM, [4,4'-MeO-bpy]=17.6 mM, [Et_3NHBF_4]=0.24 M, current =2.5 mA, 10 mL MeCN.



Representative Standard Procedure with Ph substrate (**15a**) – with catalyst pre-activation

A 5 mL volumetric flask was charged with 5-phenyl-1-pentene (**15a**, 293 mg, 2.01 mmol) and anisole (internal standard, 66.2 mg, 0.612 mmol) and the flask was evacuated and backfilled with argon (X3). The flask was then charged with dry and degassed MeCN (5 mL) to prepare a stock solution of substrate (0.40 M).

A 10 mL Electrasyn-vial was equipped with a magnetic stir bar, wrapped with Teflon tape on the screw thread, and charged with $CoBr_2$-glyme (24.6 mg, 79.8 μmol), 4,4'-dimethoxy-2,2'-bypyridine (4,4'-MeO-bpy, 19.1 mg, 88.1 μmol), and Et_3NHBF_4 (453 mg, 2.40 mmol). The vial was sealed with the cap carrying a magnesium anode and a tin cathode and evacuated and backfilled with argon (X3). The vial was charged with dry and degassed MeCN (8 mL) and evacuated and backfilled with argon. The vial was stirred for approximately 1 min until the catalyst dissolved. The vial was electrolyzed with 2.5 mA. After 59 min (0.12 F/mol), the vial was charged with an aliquot of the MeCN solution of starting material (2 mL) and evacuated and backfilled with argon (X1) to give a final substrate concentration of 0.080 M. On the subsequent graphs, the substrate injection time represents time = 0 min. At the indicated time, aliquots (0.15 mL) were taken using a syringe pre-rinsed with argon. The aliquots were filtered through a short plug of silica gel (approximately 1 cm) and the silica gel was rinsed with CD_3CN (0.5 mL). The resulting solution was analyzed by ^1H NMR.

This method gave the product in a 74% yield based on anisole as the internal standard with 5 mA and 10 mol % catalyst after 135 min (not including induction time) and a 87% yield with 2.5 mA and 10 mol % catalyst after approximately 13 hours (1.5 F/mol).

The integration of anisole was determined from the peak at 6.95-6.85 (3H). The integration of the starting material was determined by averaging the peaks at 5.90 – 5.77 (1H) and 5.04 – 4.89 (2H). The integration of the product was determined by integrating the peak at 5.49-5.36 (2H).

Note: The induction period/substrate injection time was estimated to be after 1.2 equiv of electrons/1.0 equiv of catalyst. The F/mol given are based on the substrate and, as such, 1.2 equiv of electrons represents 0.12 F/mol with 10 mol % catalyst and 0.24 F/mol with 20 mol % catalyst.

Entry	Standard Conditions:			Order in:			
	Current (mA)	Catalyst (M)	Substrate (M)	Catalyst	Substrate	Current	Et_3NHBF_4
1	2.5	0.008	0.08	0	0	1	0
2	7.5	0.008	0.08	1	0	0	n.d.
3	7.5	0.008	0.16	1	0	n.d.	n.d.
4	7.5	0.004	0.08	1	0	0	n.d.
5	10	0.008	0.08	1	n.d.	0	0

Figure S19. Summary of reaction orders for the Ph substrate with catalyst pre-activation, n.d. = not determined

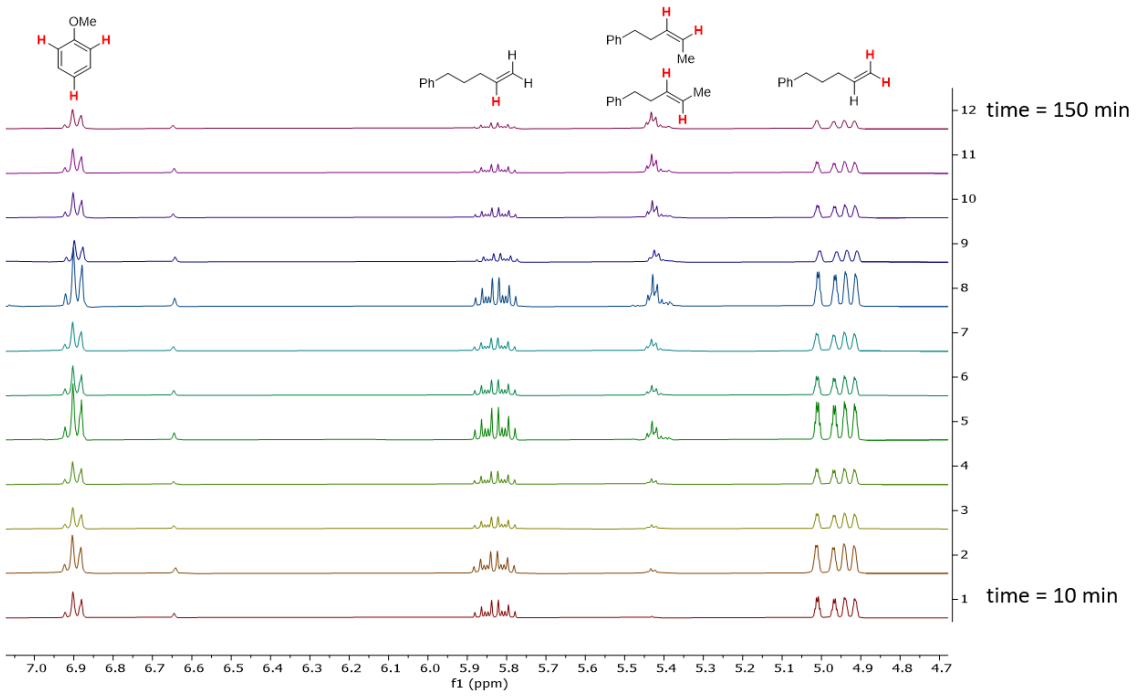


Figure S20. Sample ^{1}H NMR spectra under standard conditions: [sub]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure).

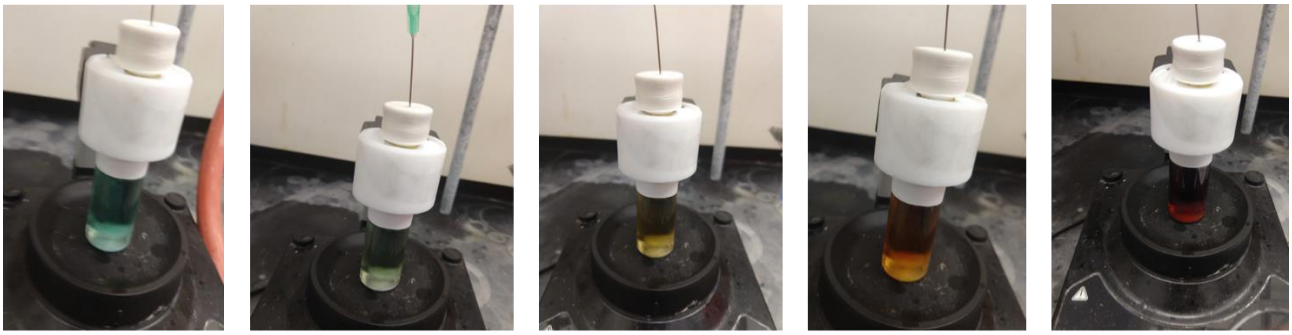


Figure S21. Example color changes prior to substrate injection. [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN, Time zero represents when the current was turned on.

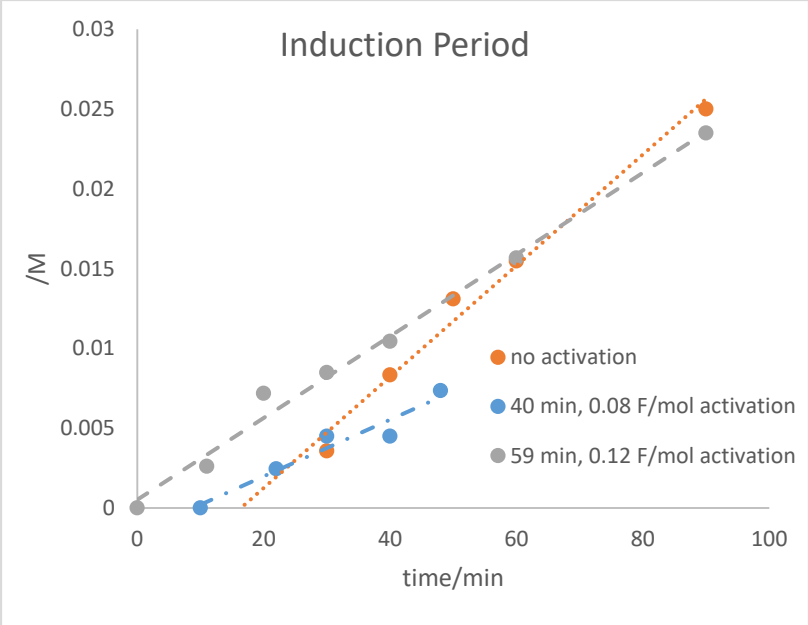


Figure S22. Reactions to show effect of catalyst activation period on induction period; [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN; Orange: no pre-activation. The substrate was injected prior to the electricity being turned on; Blue: substrate injection at time=40 min/0.08 F/mol (time zero in figure); Grey: substrate injection at time=59 min/0.12 F/mol (time zero in figure)

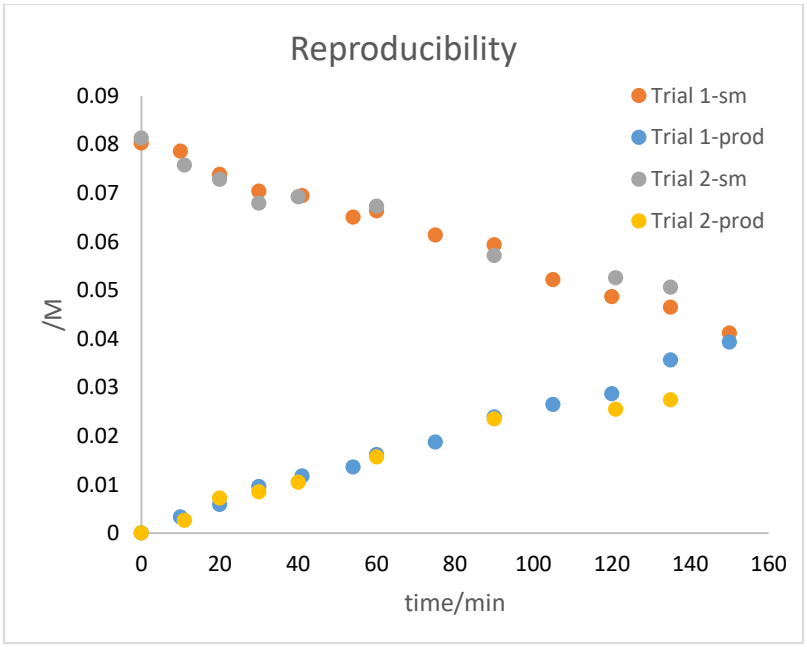


Figure S23. Reactions to probe reproducibility; [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure).

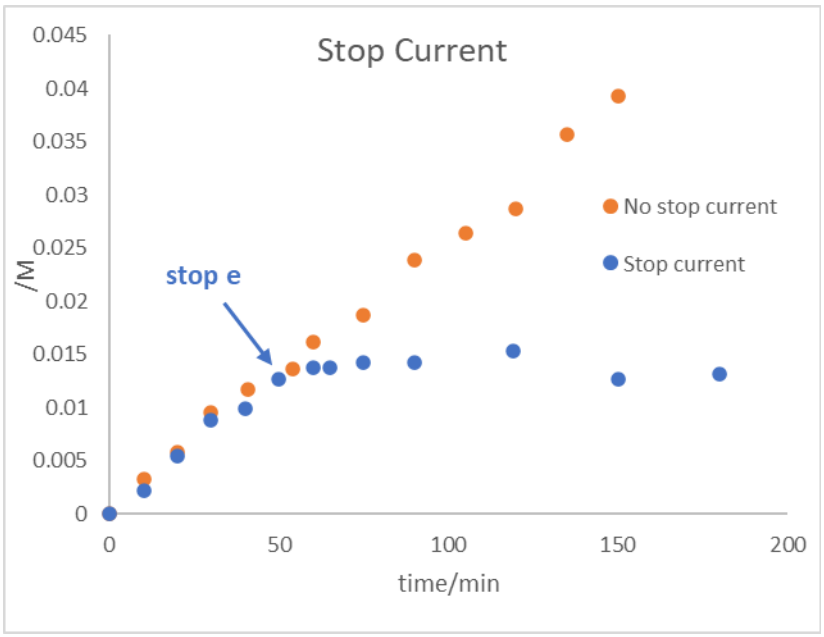


Figure S24. Reaction with stopped current; orange: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol; Blue: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN, substrate injection at time=60 min/0.12 F/mol (time zero in figure); Blue: current stopped 60 minutes (0.12 F/mol) after substrate injection.

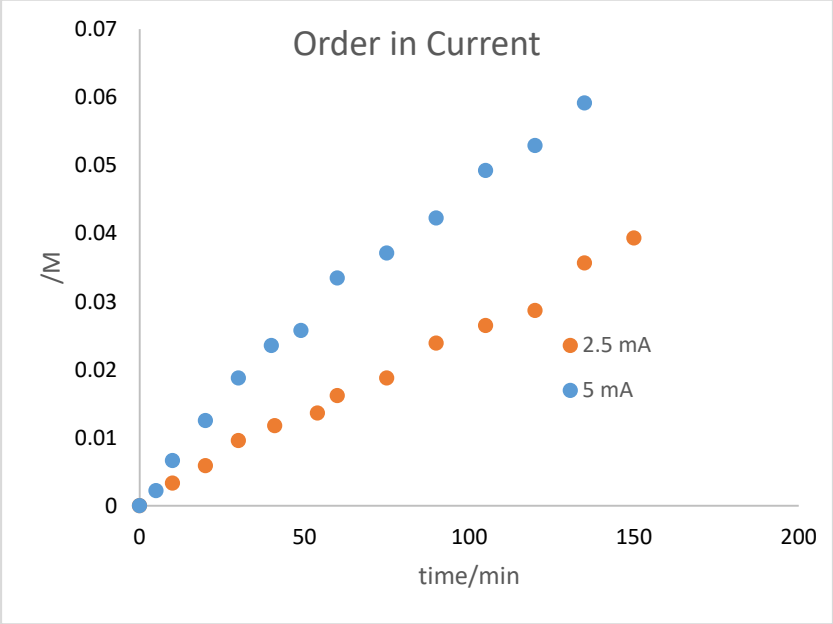


Figure S25a. Reactions with different current; orange: [15a]=0.080 M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol; Blue: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current=5.0 mA, 10 mL MeCN, substrate injection at time=30 min/0.12 F/mol (time zero in figure).

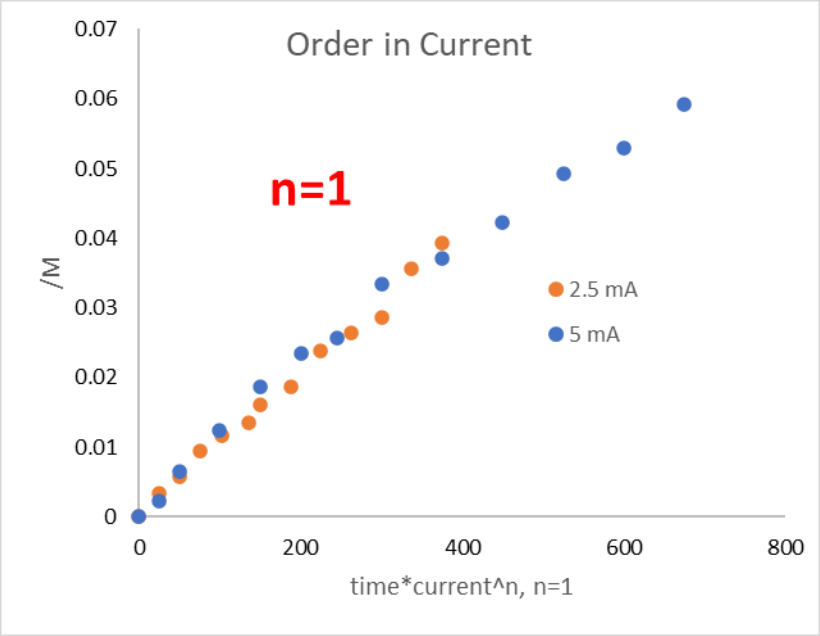


Figure S25b. Reactions with different current using the Burés method for determining reaction order. Data taken from figure S25a.

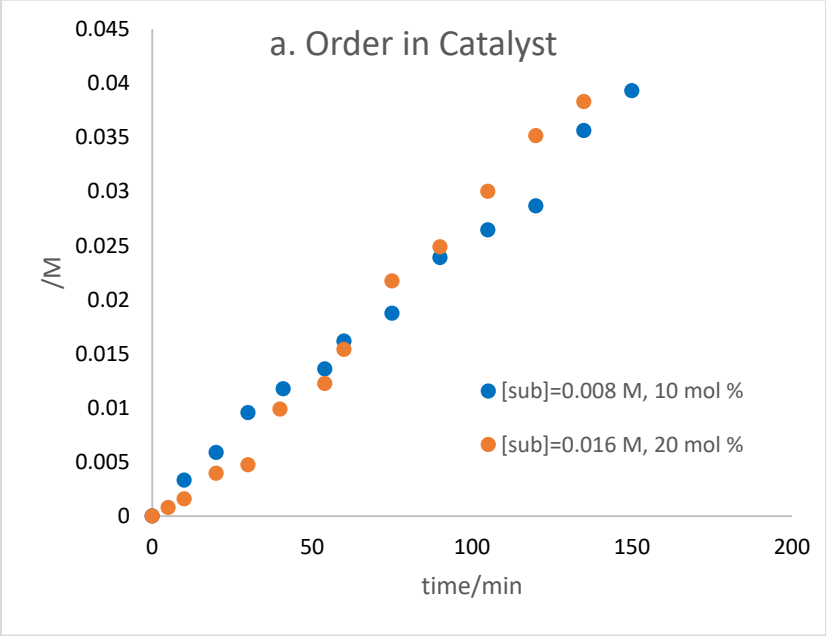


Figure S26a. Reactions with different concentrations of [Co]; Orange: [15a]=0.080 M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24 M, current=2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure); Blue: [15a]=0.080 M, [Co]=16 mM, [4,4'-MeO-bpy]=18 mM, [Et_3NHBF_4]=0.24 M, current=2.5 mA, 10 mL MeCN, substrate injection at time=121 min/0.24 F/mol (time zero in figure).

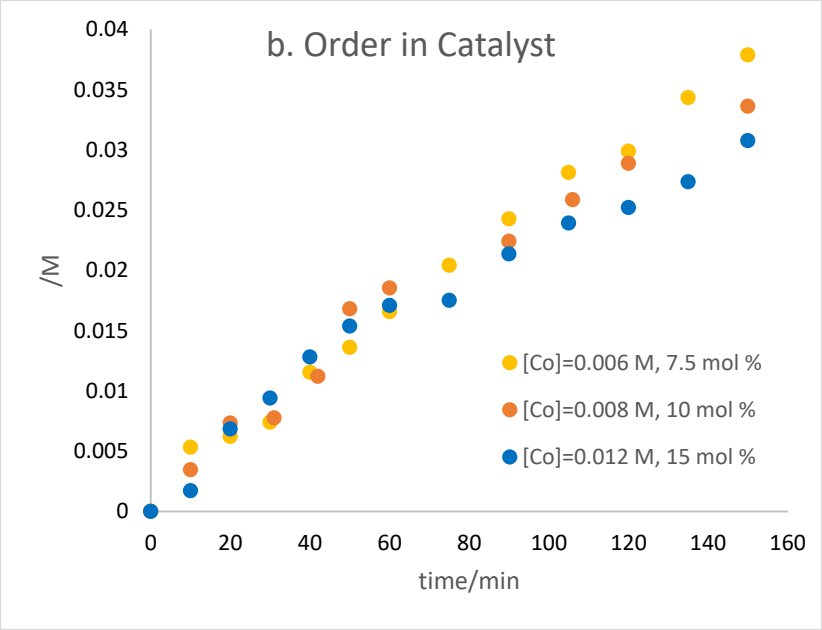


Figure S26b. Reactions with different concentrations of [Co]; Yellow: [15a]=0.080 M, [Co]=6.0 mM, [4,4'-MeO-bpy]=6.7 mM, [Et_3NHBF_4]=0.24 M, current =2.5 mA, 10 mL MeCN, substrate injection at time=45 min/0.09 F/mol (time zero in figure); Orange: [15a]=0.080 M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24 M, current =2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure); Blue: [15a]=0.080 M, [Co]=12 mM, [4,4'-MeO-bpy]=13 mM, [Et_3NHBF_4]=0.24 M, current=2.5 mA, 10 mL MeCN, substrate injection at time=90 min/0.18 F/mol (time zero in figure).

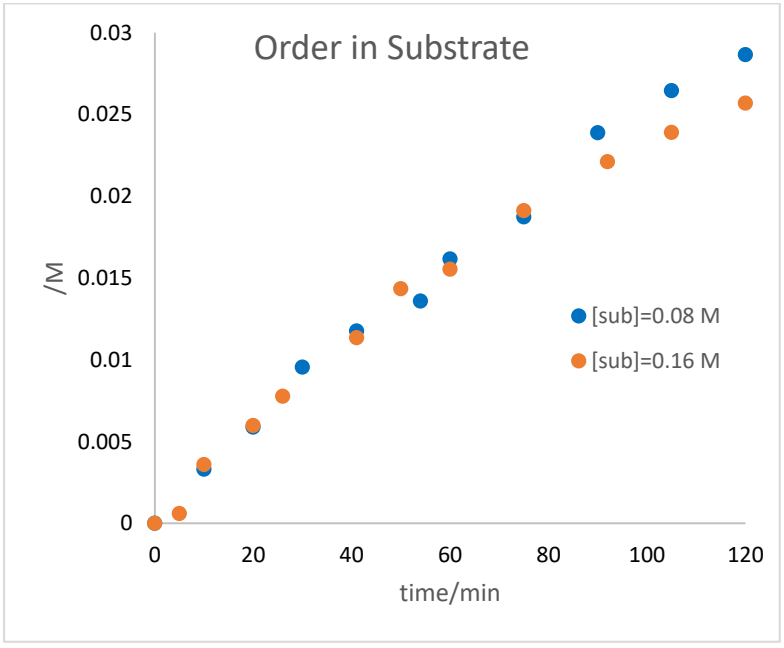


Figure S27. Reactions with different concentrations of substrate; orange: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure); Blue: [15a]=0.16M, [Co]=8.0mM, [4,4'-MeO-bpy]=8.8mM, [Et_3NHBF_4]=0.24M, current=2.5 mA, 10 mL MeCN, substrate injection at time=60 min/0.06 F/mol (time zero in figure).

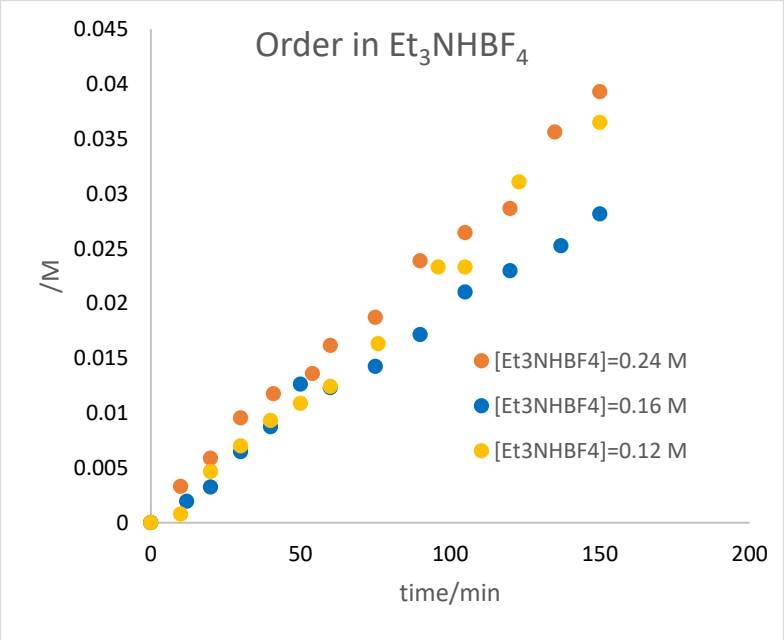


Figure S28. Reactions with different concentrations of Et_3NHBF_4; orange: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure); Blue: [15a]=0.080M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.16M, current=2.5 mA, 10 mL MeCN, substrate injection at time=59 min/0.12 F/mol (time zero in figure); Yellow: [15a]=0.080 M, [Co]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.12 M, current =2.5 mA, 10 mL MeCN, substrate injection at time=60 min/0.12 F/mol (time zero in figure).

Data with 7.5 mA current and 10 mol % catalyst: The standard procedure with catalyst pre-activation was followed, except the reactions were run at 7.5 mA instead of 2.5 mA. The induction time was adjusted.

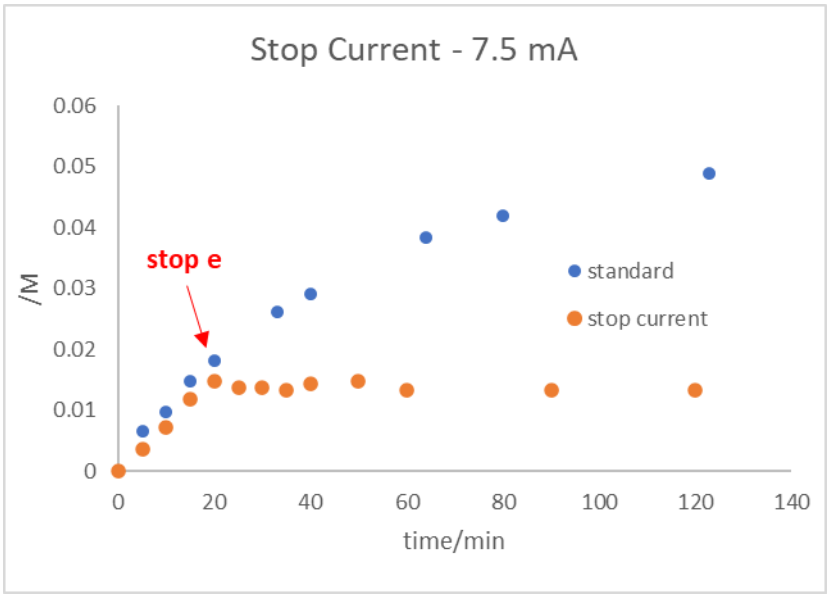


Figure S29. Reactions to probe catalyst order; blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time= 23 min/0.12 F/mol (time zero

in figure); blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0mM, [4,4'-MeO-bpy]=8.8mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time= 23 min/0.12 F/mol (time zero in figure), current stopped 20 min after substrate injection.

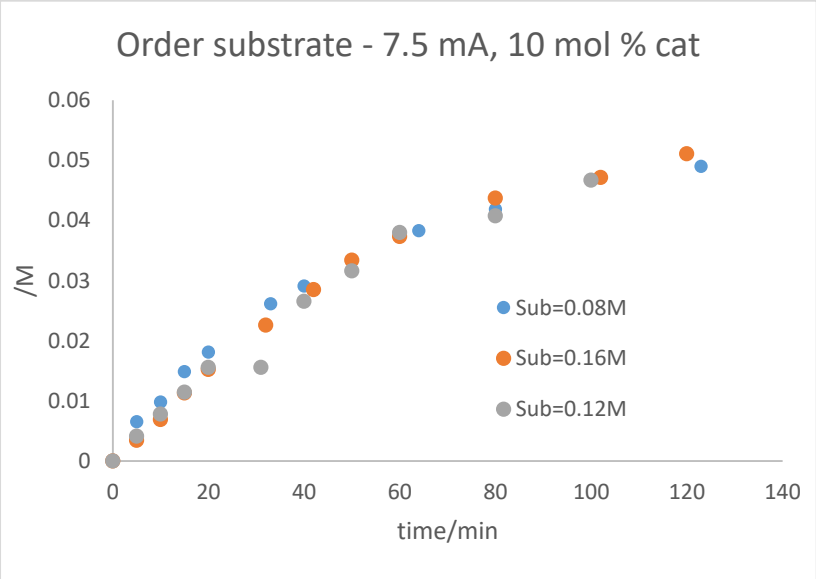


Figure S30. Reactions to probe catalyst order; blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time= 23 min/0.12 F/mol (time zero in figure); orange: [sub]=0.16M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.12M, current =7.5 mA, 10 mL MeCN, substrate injection at time=23 min/0.09 F/mol (time zero in figure); grey: [sub]=0.12M, [$CoBr_2$-glyme]=8.0mM, [4,4'-MeO-bpy]=8.8mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time=23 min/0.06 F/mol (time zero in figure).

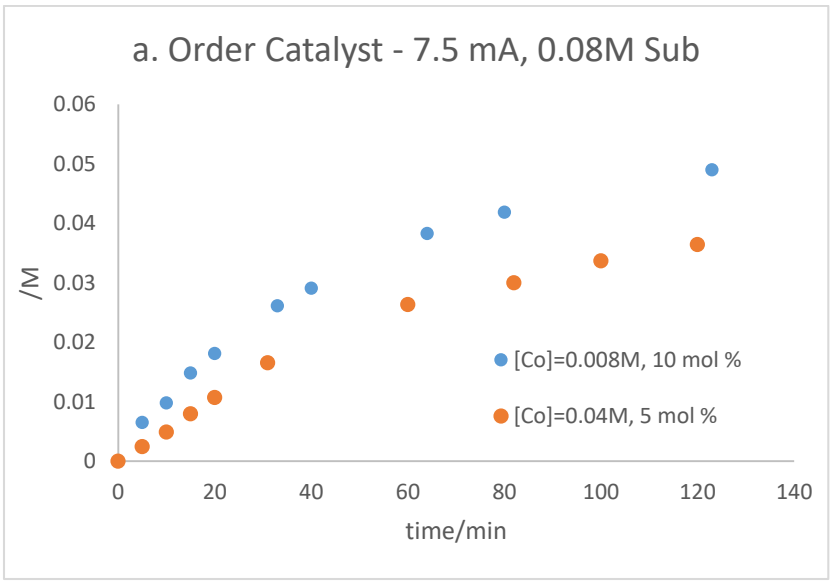


Figure S31a. Reactions to probe catalyst order; blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time=23 min/0.12 F/mol (time zero in figure); orange: [sub]=0.080M, [$CoBr_2$-glyme]=4.0mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time=8 min/0.06 F/mol (time zero in figure).

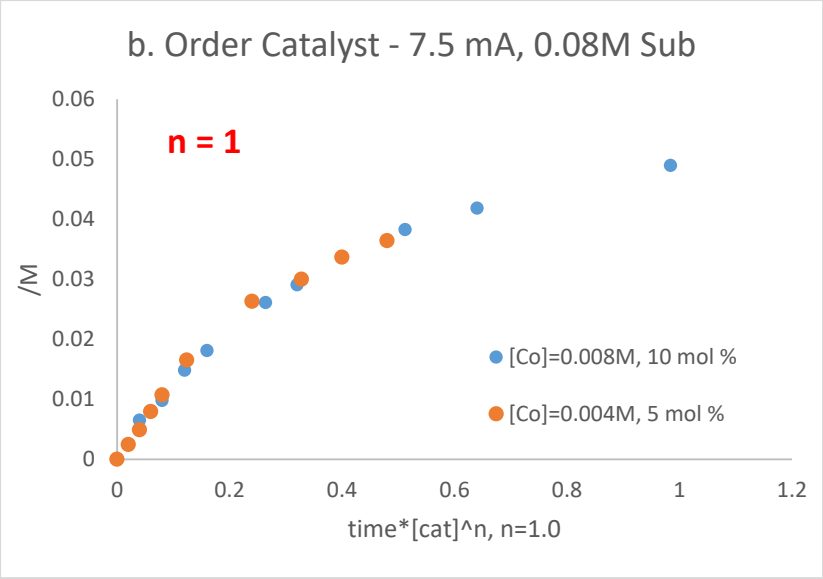


Figure S31b. Reactions with different catalyst loadings using the Burés method for determining reaction order. Data taken from figure S31a.

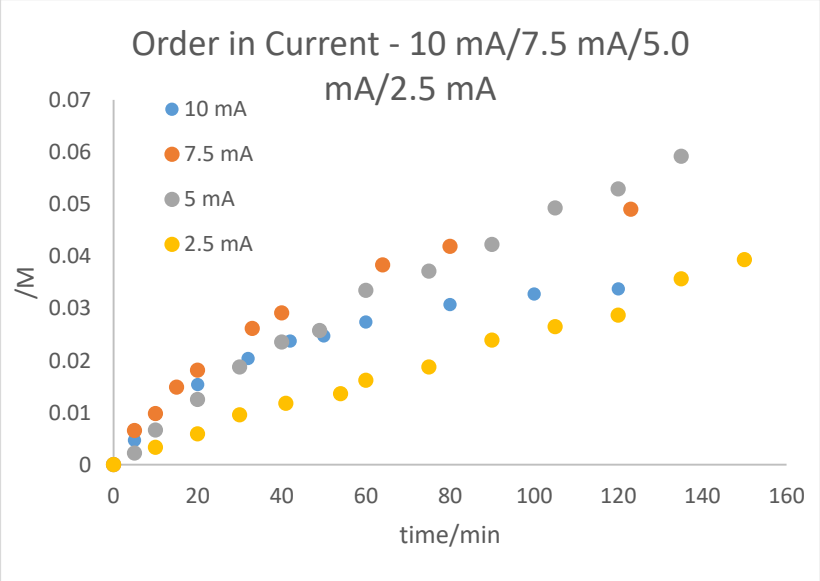


Figure S32. Reactions to probe catalyst order; blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =10 mA, 10 mL MeCN, substrate injection at time=15 min/0.12 F/mol (time zero in figure); orange: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time=23 min/0.12 F/mol (time zero in figure); grey: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =5.0 mA, 10 mL MeCN, substrate injection at time=30 min/0.12 F/mol (time zero in figure); yellow: [sub]=0.080M, yellow: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =2.5 mA, 10 mL MeCN, substrate injection at time=60 min/0.12 F/mol (time zero in figure).

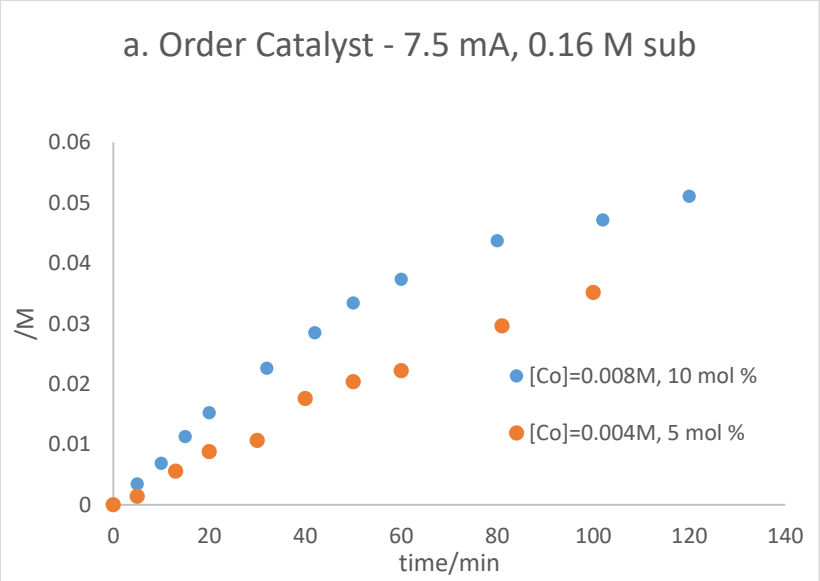


Figure S33a. Reactions to probe catalyst order; blue: [sub]=0.16M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time= 23 min/0.12 F/mol (time zero in figure); orange: [sub]=0.16M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time=12 min/0.06 F/mol (time zero in figure).

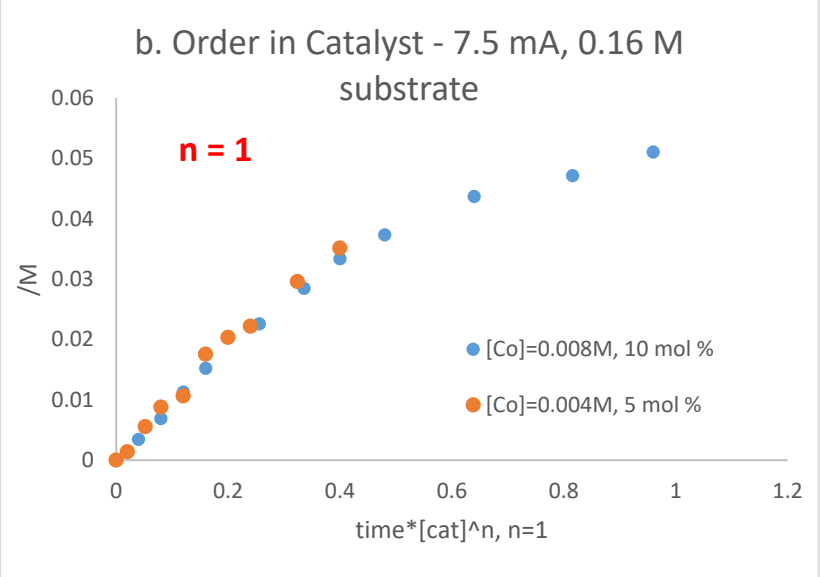


Figure S33b. Reactions with different catalyst loadings using the Burés method for determining reaction order. Data taken from figure S33a.

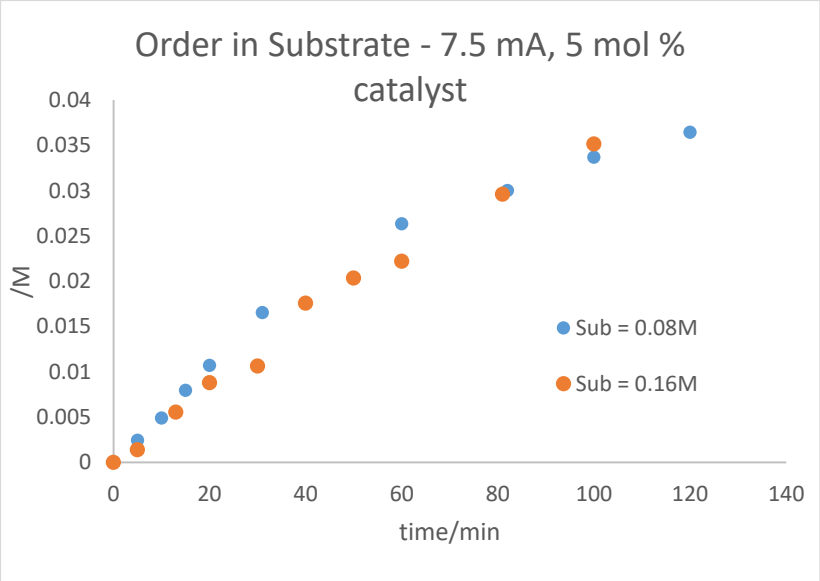


Figure S34. Reactions to probe order in substrate; blue: [sub]=0.080M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time= 12 min/0.06 F/mol (time zero in figure); orange: [sub]=0.16M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =7.5 mA, 10 mL MeCN, substrate injection at time= 12 min/0.03 F/mol (time zero in figure).

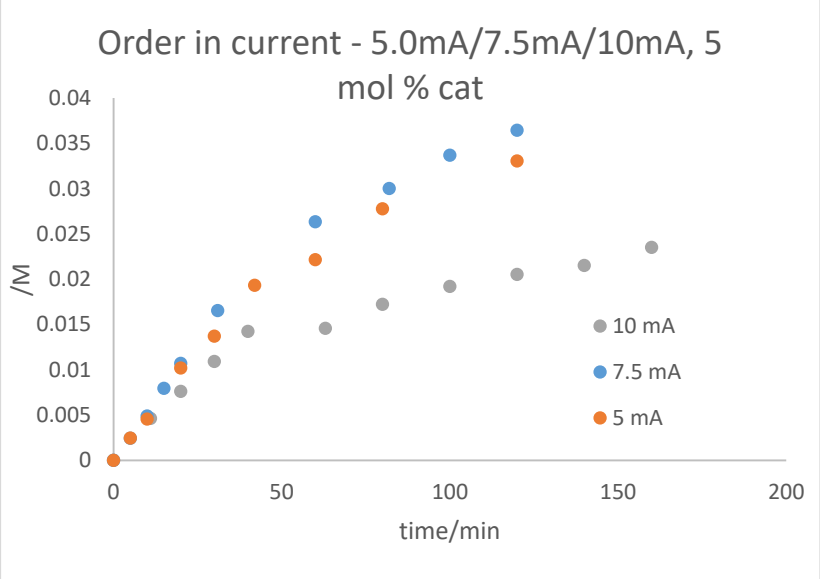


Figure S35. Reactions to probe order in current; grey: [sub]=0.080M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =10 mA, 10 mL MeCN, substrate injection at time= 9 min/0.06 F/mol (time zero in figure); orange: [sub]=0.080M, blue: [sub]=0.080M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =5.0 mA, 10 mL MeCN, substrate injection at time= 12 min/0.06 F/mol (time zero in figure); orange: [sub]=0.080M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =5.0 mA, 10 mL MeCN, substrate injection at time= 15 min/0.06 F/mol (time zero in figure).

Data with 10 mA current: The standard procedure with catalyst pre-activation, except the reactions were run at 10.0 mA instead of 2.5 mA. The induction time was adjusted accordingly.

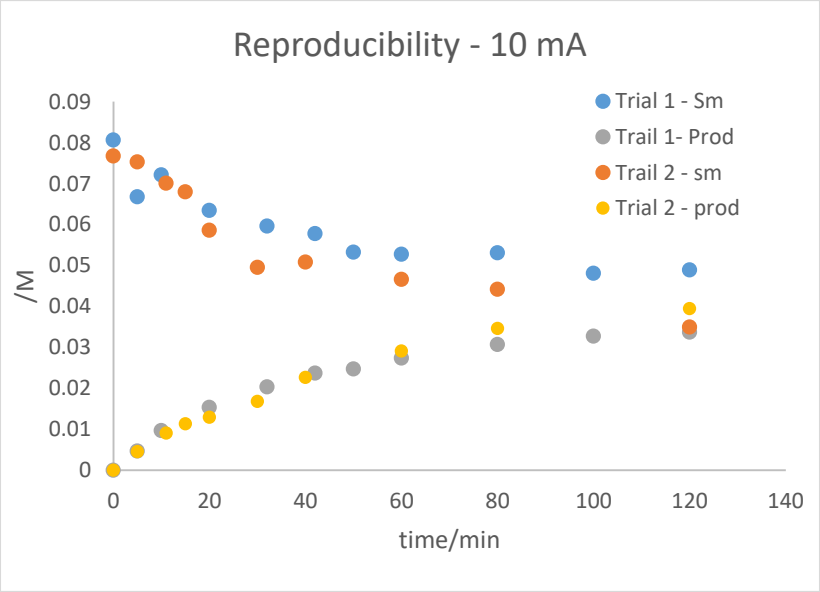


Figure S36. Reactions to probe reproducibility; [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =10 mA, 10 mL MeCN, substrate injection at time=15 min/0.12 F/mol (time zero in figure).

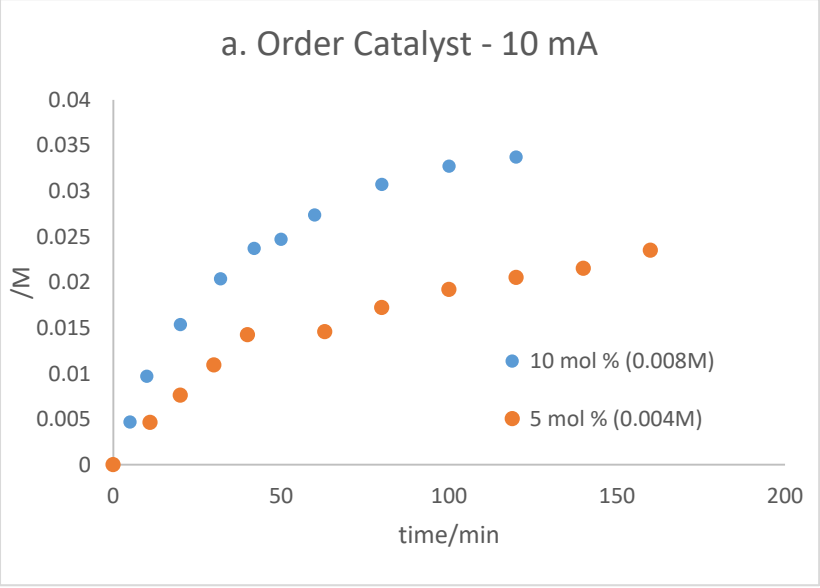


Figure S37a. Reactions to probe catalyst order; blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =10 mA, 10 mL MeCN, substrate injection at time=15 min/0.12 F/mol (time zero in figure); orange: [sub]=0.080M, [$CoBr_2$-glyme]=4.0 mM, [4,4'-MeO-bpy]=4.4 mM, [Et_3NHBF_4]=0.24M, current =10 mA, 10 mL MeCN, substrate injection at time=10 min/0.08 F/mol (time zero in figure).

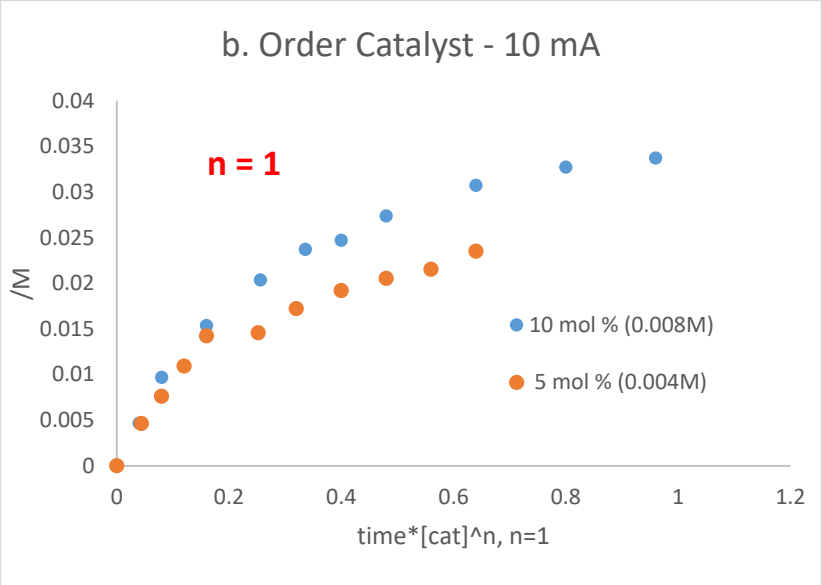


Figure S37b. Reactions with different catalyst loadings using the Burés method for determining reaction order. Data taken from figure S37a.

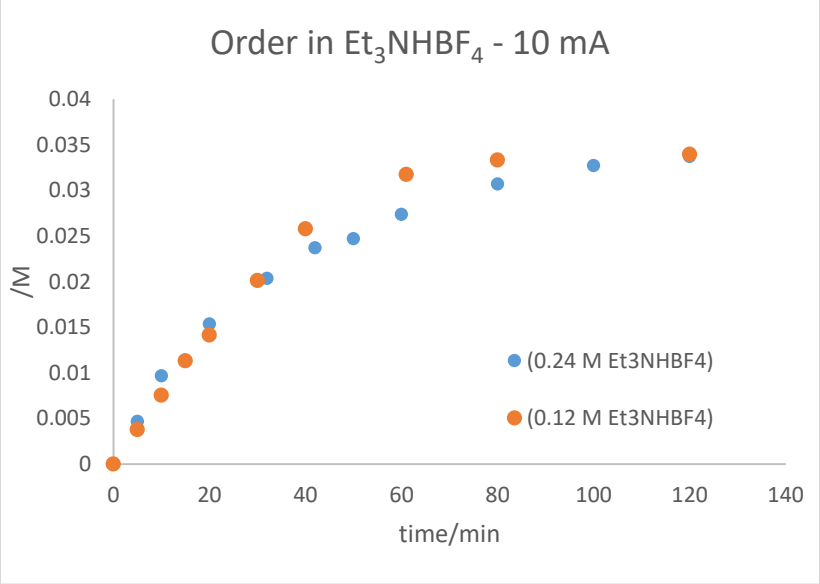


Figure S38. Reactions to probe order in Et_3NHBF_4; blue: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.8 mM, [Et_3NHBF_4]=0.24M, current =10 mA, 10 mL MeCN, substrate injection at time=15 min/0.12 F/mol (time zero in figure); orange: [sub]=0.080M, [$CoBr_2$-glyme]=8.0 mM, [4,4'-MeO-bpy]=8.4 mM, [Et_3NHBF_4]=0.12M, current =10 mA, 10 mL MeCN, substrate injection at time=15 min/0.12 F/mol (time zero in figure).

CYCLIC VOLTAMMETRY CO(SALEN)-1 SYSTEM

General Reagent Information

Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (98%, Acros) was purified by recrystallization from ethanol three times and dried under reduced pressure at room temperature for 48 hours. Acetonitrile (MeCN) (HPLC Grade) was purchased from Fisher Chemical and dried over activated 4 Å molecular sieves (Mallinckrodt Chemicals) for at least two days before use. Acetone (Ultra Resi-Analyzed) was purchased from J. T. Baker kept dry over activated 4 Å molecular sieves (Mallinckrodt Chemicals) for at most two weeks before new acetone was aquired. Microcloth PSA (polishing paper) was purchased from Buehler.

Cyclic Voltammetry Procedures

Benchtop cyclic voltammetry experiments were performed in a three-compartment glass cell with medium porosity glass frits separating the compartments. A homemade Ag/AgCl reference electrode (-0.45 V *vs.* ferrocene in MeCN; -0.54 V *vs.* ferrocene in acetone) and a coiled Pt wire counter electrode were used. All 3-mm glassy carbon (GC) electrodes were purchased from CH Instruments. Prior to the experiment, electrodes were polished using diamond paste and MetaDi Fluid (Buehler). Before beginning electrochemical testing, the solution was purged with Ar gas for at least 20 minutes to remove any oxygen from the solution.

For the experiments run in acetone, the Ar gas was first bubbled through a round bottem flask containing acetone and then into the electrolyte solution in order to presaturate the Ar gas with acetone vapor and prevent evaporation and subsequent concentration changes occuring in the anaylte solution.

Cyclic voltammetry experiments were conducted using a Biologic SP150 potentiostat. The CV scans were conducted with varying sweep rates to probe the system for coupled chemical reactions.

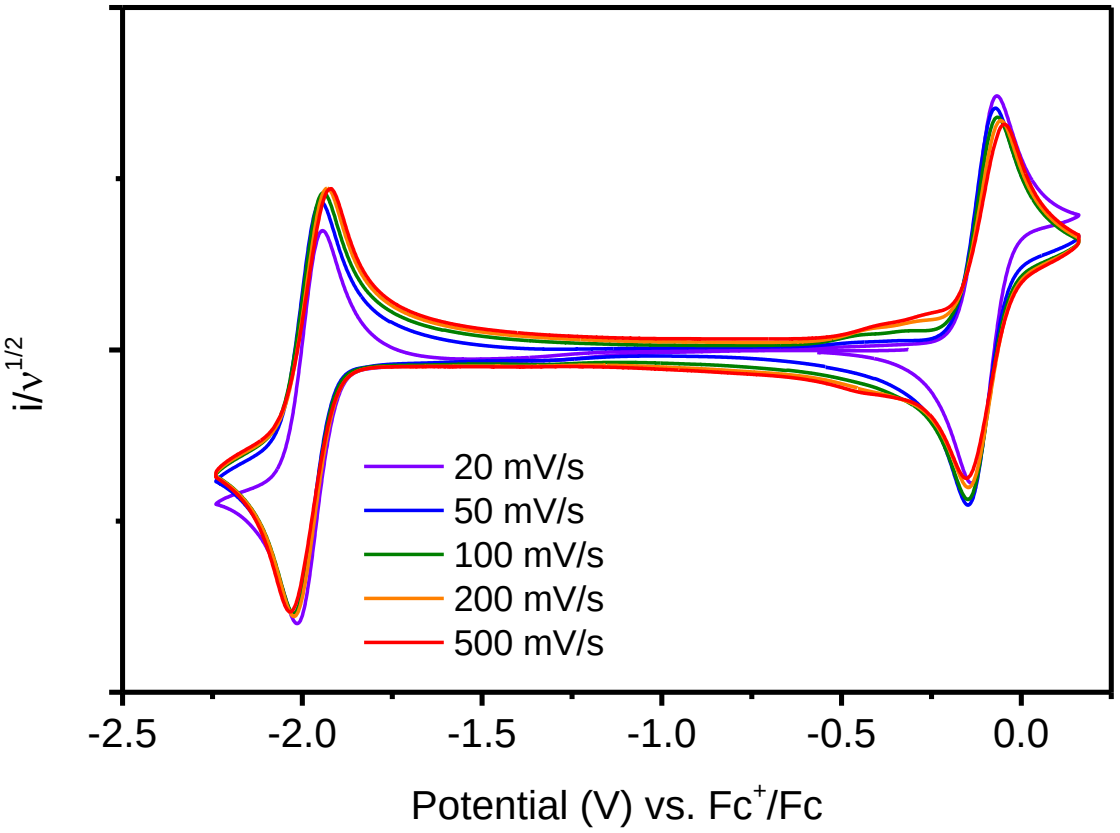


Figure S39. Cyclic voltametric profiles of 3.2 mM Co(Salen) in 0.1 M $TBAPF_6$ in acetone at varied sweep rates with the current normalized to the square root of scan rate. No coupled chemical reactions are observed, implying both redox couples are reversible. The redox couple at -1.98 V *vs.* Fc^+/Fc corresponds to the Co(II/I) redox couple and the redox couple at -0.10 V *vs.* Fc^+/Fc corresponds to the Co(III/II) redox couple.

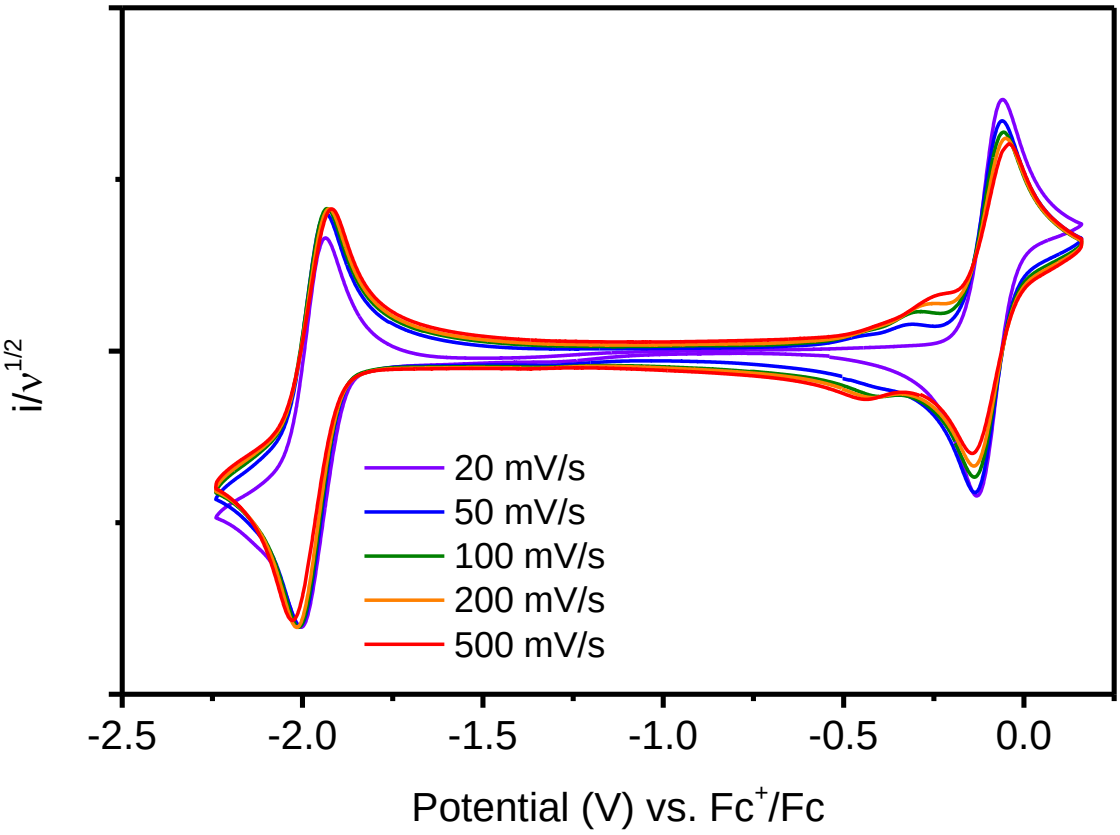


Figure S40. Cyclic voltametric profiles of 3.2 mM Co(Salen) with 80 mM secondary alkene in 0.1 M $TBAPF_6$ in acetone at varied sweep rates with the current normalized to the square root of scan rate. No coupled chemical reactions are observed, implying both redox couples are reversible. No catalysis or chemical reactions are observed between the Co catalyst and the alkene in the absence of a proton source.

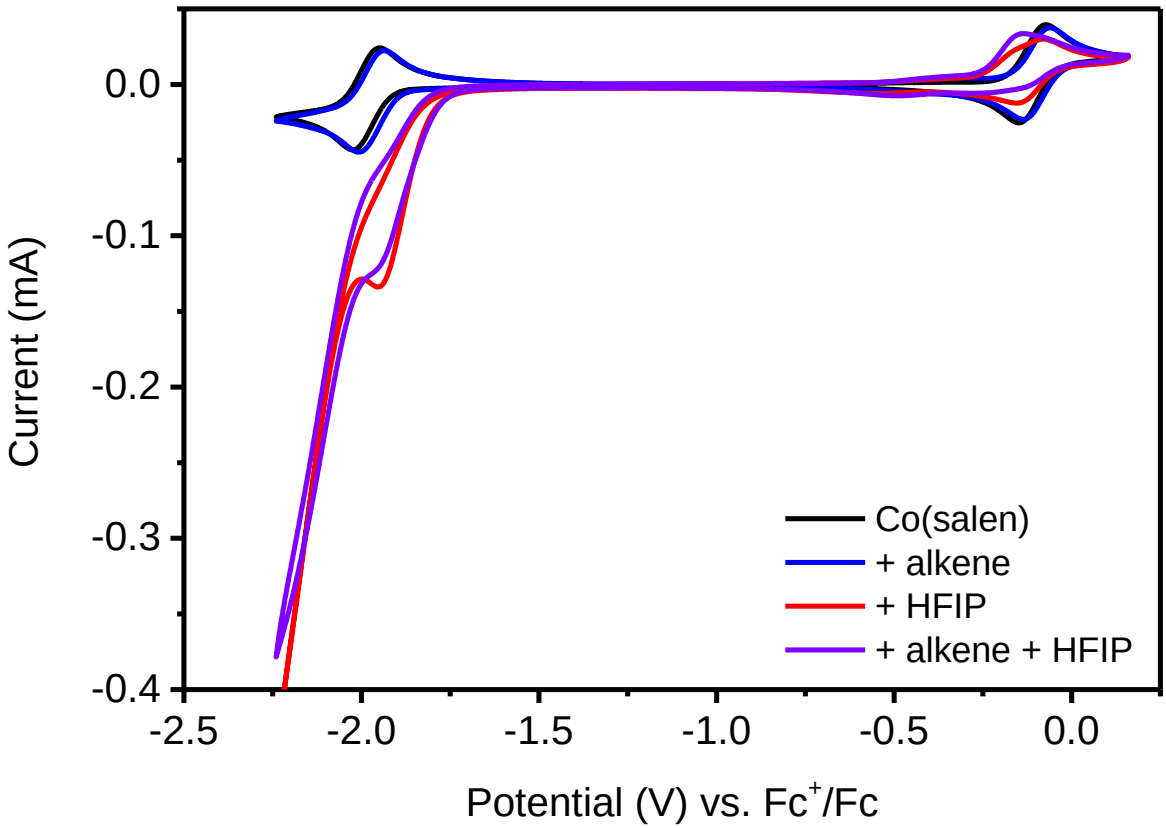


Figure S41. Cyclic voltametric profiles of 3.2 mM Co(Salen) in 0.1 M $TBAPF_6$ in acetone with the addition of (blue) 80 mM secondary alkene **19a**, (red) 320 mM HFIP, and (purple) 80 mM alkene and 320 mM HFIP at 50 mV/s. No coupled chemical reactions are observed between the Co catalyst and the alkene in the absence of a proton source. The addition of the HFIP to the Co(Salen) solution results in the observation of catalytic current. This is expected to arise from the $ECEC_{cat}$ process corresponding to the generation of H_2. The addition of both HFIP and alkene to the Co(salen) catalyst solution results in a slight dampening of the catalytic current. This could indicate that the alkene is reacting with the Co-H species to catalyze the isomerization reaction, diverting the catalyst from the H_2 generation cycle.

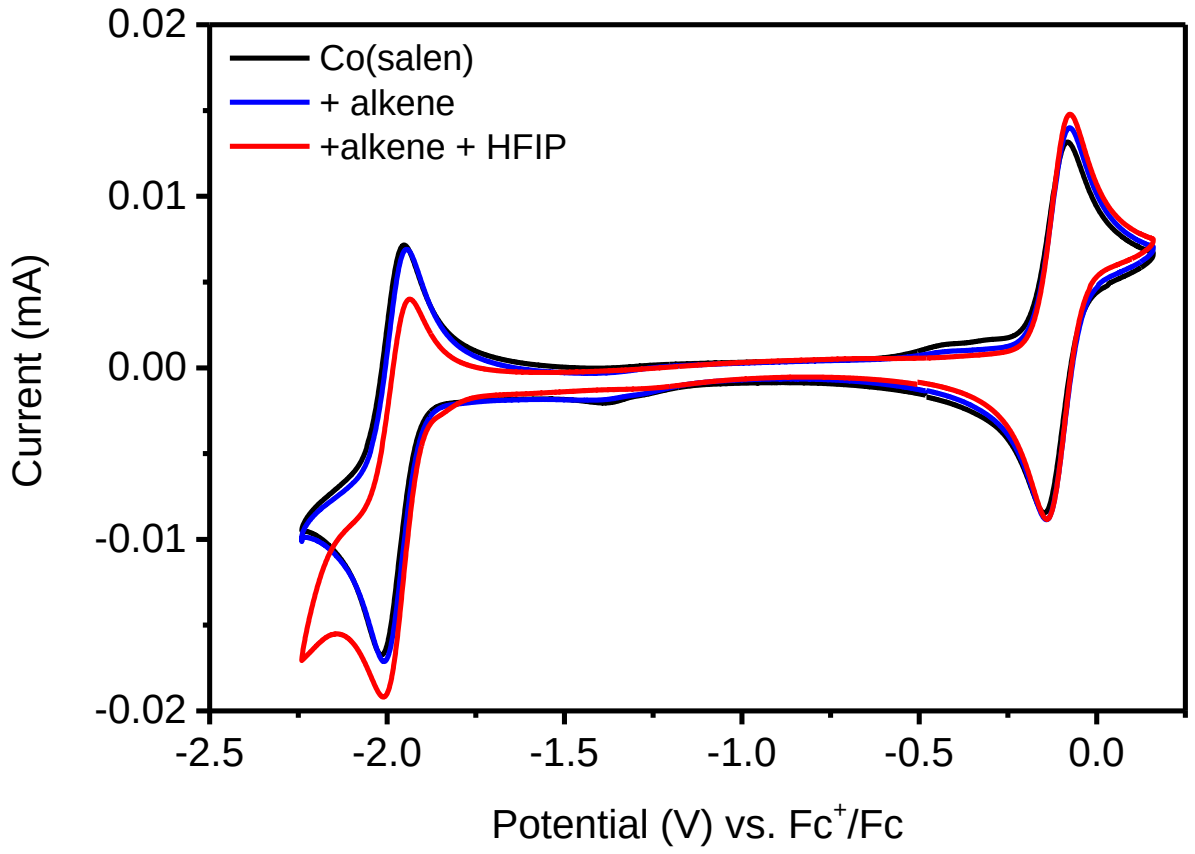


Figure S42. Cyclic voltametric profiles of 1 mM Co(Salen) in 0.1 M TBAPF6 in acetone with the addition of (blue) 1 mM secondary alkene, (red) 1 mM HFIPand 1mM alkene **19a** at 50 mV/s. No coupled chemical reactions are observed between the Co catalyst and the alkene in the absence of a proton source. The addition of the HFIP to the Co(Salen) solution results in the observation of catalytic current. This is expected to arise from the ECECcat process corresponding to the generation of H_2.

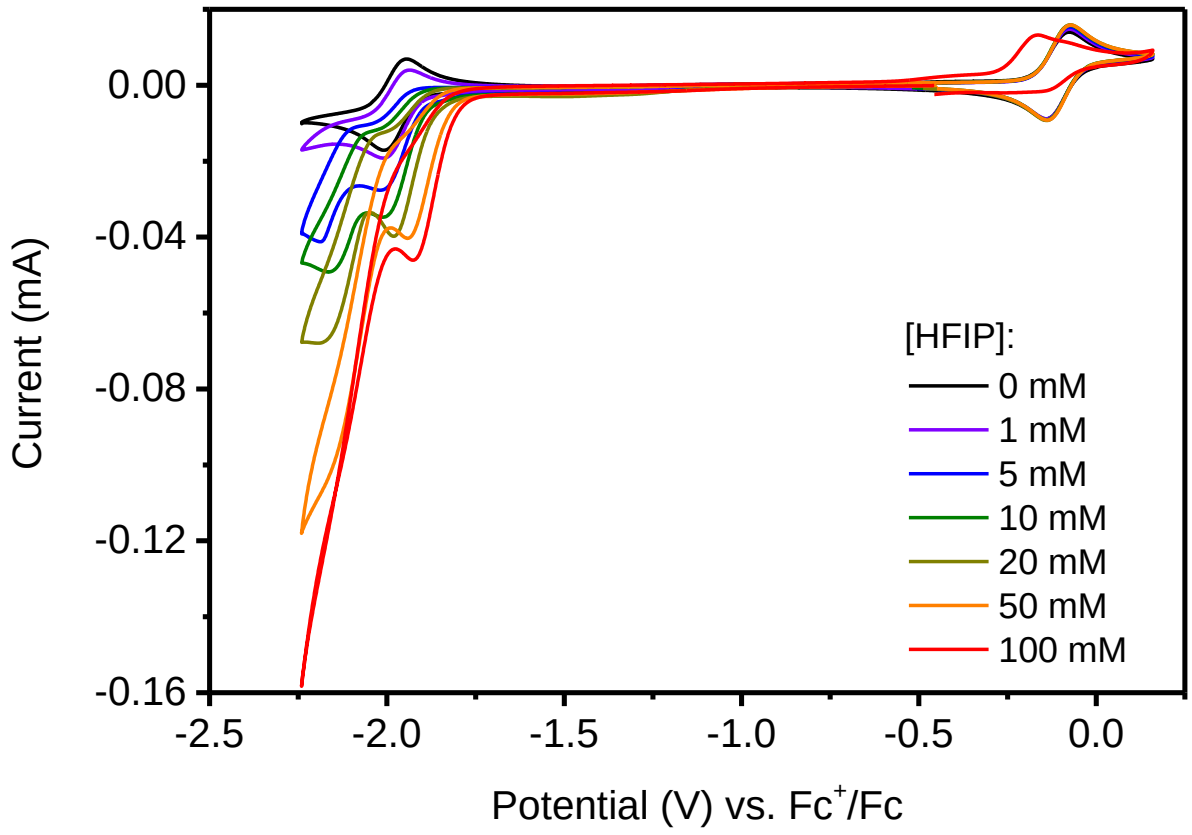


Figure S43. Cyclic voltametric profiles of 1 mM Co(Salen) and 1 mM secondary alkene **19a** in 0.1 M $TBAPF_6$ in acetone with varied concentrations of HFIP at 50 mV/s. By increasing the concentration of HFIP the catalytic current increases, supporting the $ECEC_{cat}$ process corresponding to the generation of H_2.

Considering the proposed $ECEC_{cat}$ process containing a high concentration of HFIP (100 mM), an anodic shift of ~100 mV is reasonable. We have found that the magnitude of the shift is a strong function of the proton concentration, as evidenced by the plot presented below (Figure S44a), as would be expected the proposed process. Analysis of the reduction peak corresponding the reduction of Co^{II} to Co^{I} with increasing proton concentration resulted in a slope (E_{red}/log[HFIP]) of 66 mV (Figure S44b), suggesting a hydrogen atom transfer or proton coupled electron transfer process. A second reduction peak is observed at lower concentrations of HFIP, corresponding to the reduction of the Co-H species, which disappears in favor of the observation of catalytic current at concentrations of HFIP higher than 50 mM.

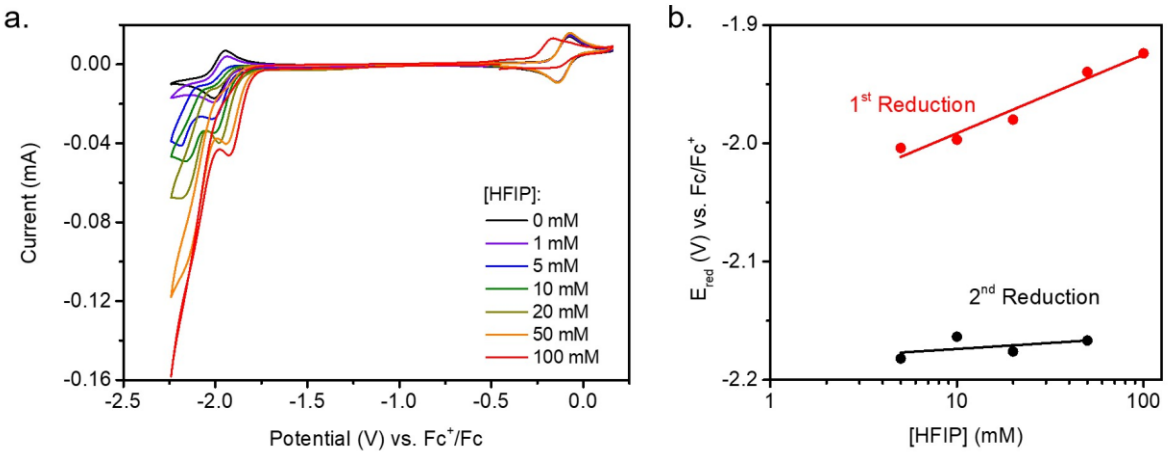


Figure S44: a) Cyclic voltametric profiles at 50 mV/s of 1 mM Co(Salen) and 1 mM secondary alkene in 0.1 M $TBAPF_6$ in acetone at various concentrations of HFIP. The catalytic current increases with increasing concentration of HFIP, supporting the $ECEC_{cat}$ process corresponding to the generation of H_2. (b.) Corresponding peak reduction potential of the first (red) and second (black) reduction of Co(Salen) in the presence of varying concentrations of HFIP.

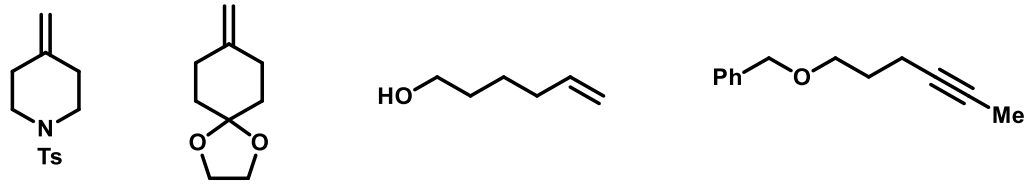
CYCLIC VOLTAMMETRY $CoBr_2$/4,4-MEO-BIPY SYSTEMS

Mechanistic studies using cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed with a Biologic (Model SP-150) with a $Ag/AgNO_3$ as reference electrode. Voltammograms were calibrated to Fc/Fc+ couple. A 3.0 mm diameter glassy carbon was used as working electrode, and a Pt mesh was used as the counter electrode. Experiments were performed in 100 mM $TBAPF_6$ in acetonitrile or THF. Total volume of solutions was 2.0 mL unless specified otherwise. All experiments were performed in a drybox under argon.

Ligation study by CV analysis of $CoBr_2$ with increasing concentration of 4,4'-dimethoxybipyridine in acetonitrile. Scan rate = 100 mV/s, 1 mM $CoBr_2$, 1 to 3 mM 4,4'-dimethoxybipyridine in 100 mM $TBAPF_6$ acetonitrile. CV studies for the addition of Et_3NHBF_4 (1 mM) and alkene (1 mM). Scan rate = 100 mV/s.

Ligation study by CV analysis of CoBr2 with increasing concentration of 6,6'-dimethylbipyridine in acetonitrile. Scan rate = 50 mV/s, 3 mM CoBr2, 3 to 9 mM 6,6'-dimethylbipyridine in 100 mM $TBAPF_6$ THF. CV studies for the addition of Et_3NHBF_4 (3 mM) and alkyne (3 mM). Scan rate = 50 mV/s.

Structures of Co(salen)-1 and Co(salen)-2



19a **21a** **61** **34a**

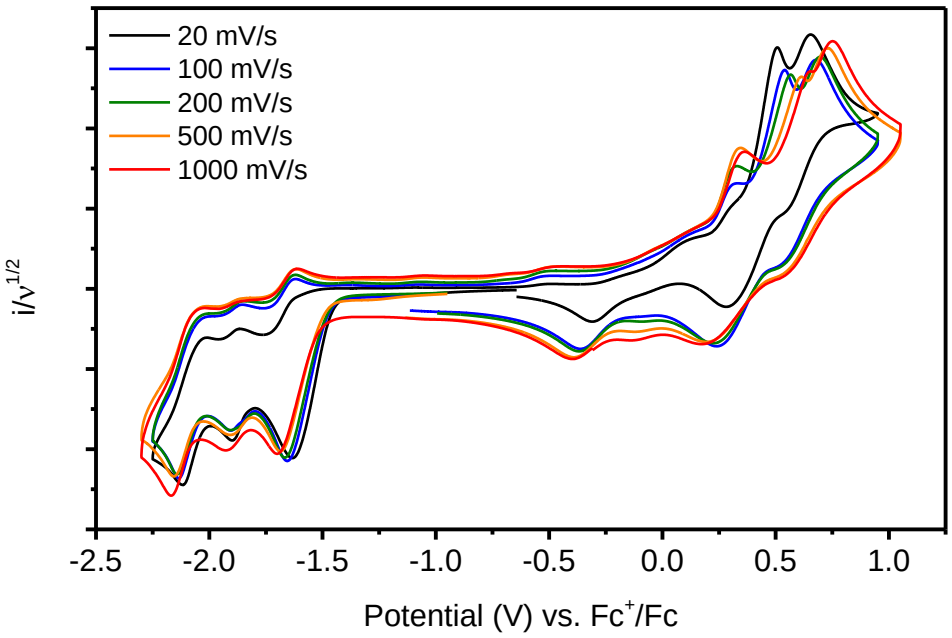


Figure S45. Cyclic voltametric profiles of 4 mM $CoBr_2$*glyme and 4.4 mM 4,4'-diMeO-2,2'-bpy in an electrolyte solution of 0.1 M $TBAPF_6$ in MeCN at various sweep rates. The peak at 0.33 V *vs.* Fc^+/Fc represents Br^- oxidation and grows in with increasing sweep rate. This likely means that Br^- is generated upon reduction(s) of the $CoBr_2$ (glyme/bpy/MeCN) complex. The disappearance of the Br^- oxidation peak at slow sweep rate is likely due to its diffusion away from the electrode at long times (slow sweep rates).

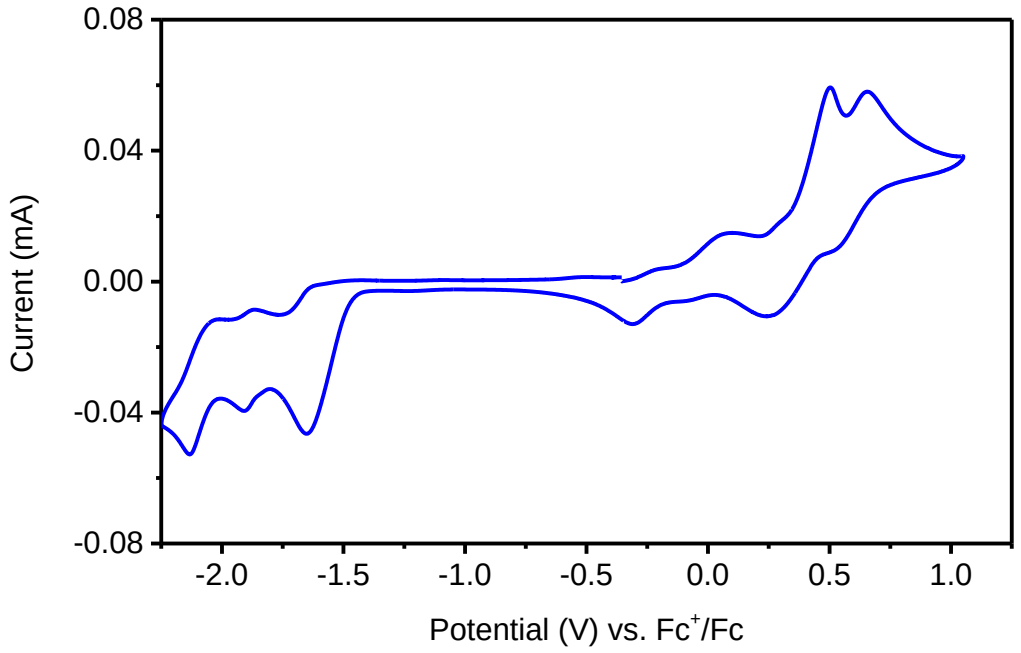


Figure S46. Cyclic voltammogram taken on the initial scan of a solution of 4 mM $CoBr_2$*glyme and 4.4 mM 4,4'-diMeO-2,2'-bpy in an electrolyte solution of 0.1 M $TBAPF_6$ in MeCN at 50 mV/s. The CV was initiated by an anodic sweep to determine the initial form of the $CoBr_2$ catalyst. **No Br^- oxidation peak was observed, indicating the catalyst remains coordinated to Br^- in solution until it is reduced.**

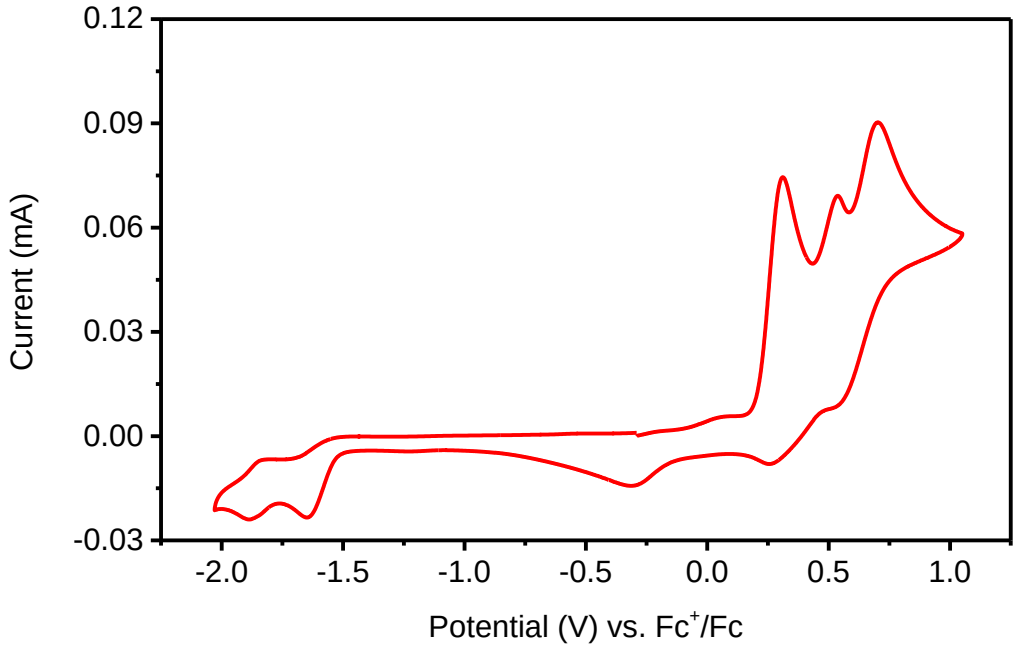


Figure S47. Cyclic voltammogram of a solution of 1 mM $CoBr_2$*glyme and 1.1 mM 4,4'-diMeO-2,2'-bpy in an electrolyte solution of 0.1 M $TBAPF_6$ in MeCN at 50 mV/s to which 5 mM TBABr has been added. **The new peak at 0.79 V *vs.* Ag/AgCl is attributed to Br^- oxidation.**

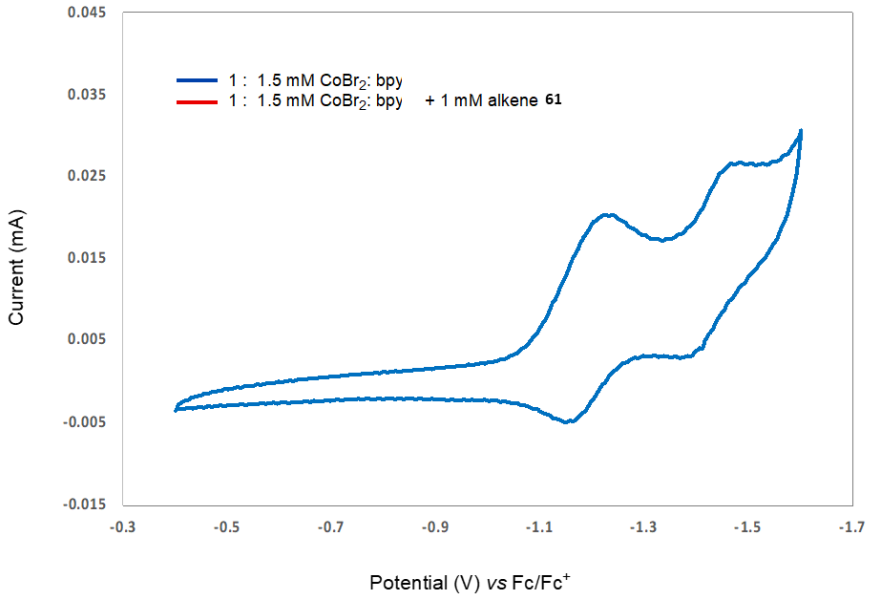


Figure S48. CV analysis of 1 mM $CoBr_2$ and 1.5 mM 4,4'-dimethoxybipyridine in 100 mM $TBAPF_6$ in THF (blue), and the addition of 1 mM alkene **61** (red). Scan rate = 100 mV/s, 3 mm glassy carbon was used as working electrode and Pt mesh as counter electrode. Potentials were calibrated to Fc/Fc^+ couple.

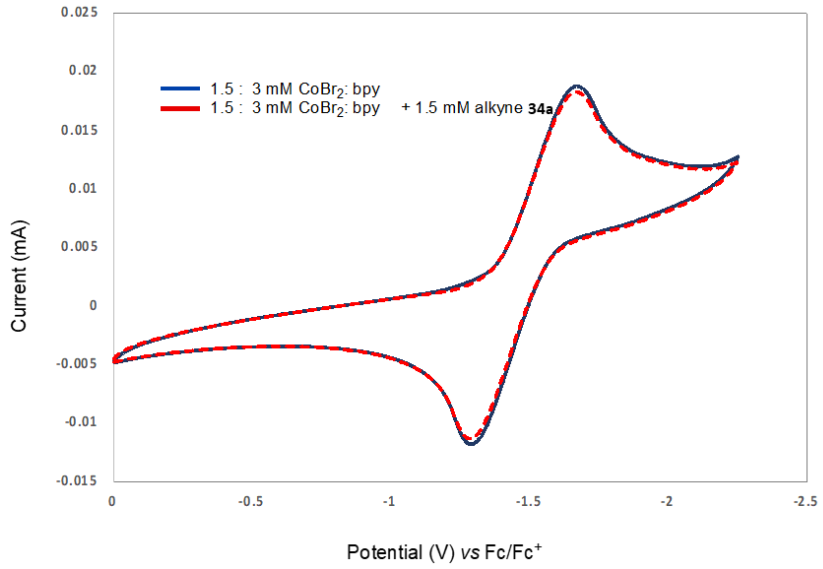


Figure S49. CV analysis of 1.5 mM $CoBr_2$ and 1.5 mM 6,6'-dimethylbipyridine in 100 mM $TBAPF_6$ in THF (blue), and the addition of 1 mM alkyne **34a** (red). Scan rate = 50 mV/s, 3 mm glassy carbon was used as working electrode and Pt mesh as counter electrode. Potentials were calibrated to Fc/Fc^+ couple.

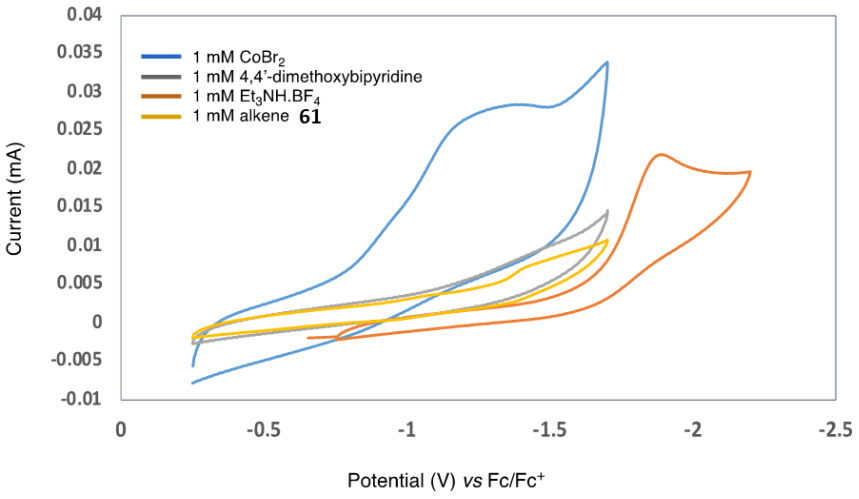


Figure S50. Control CV analysis of 1 mM $CoBr_2$ (light blue), 1 mM 4,4'-dimethoxybipyridine (grey), 1 mM Et3N.HBF4 (orange), and 1m= mM alkene **61** (yellow) in 100 mM $TBAPF_6$ in THF. Scan rate = 100 mV/s, 3 mm glassy carbon was used as working electrode and Pt mesh as counter electrode. Potentials were calibrated to Fc/Fc^+ couple.

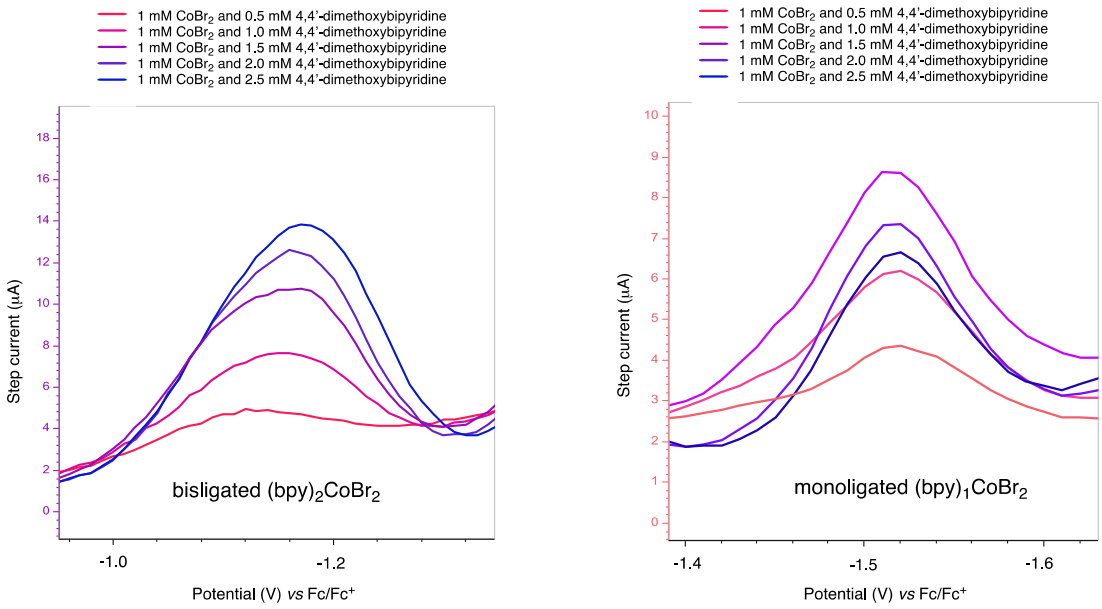


Figure S51. SWV analysis of 1.0 mM $CoBr_2$ and increasing concentration of (0.5 to 2.5 mM 4,4'-dimethoxybipyridine in 100 mM $TBAPF_6$ in THF. SWVs were performed with pulse height = 20 mV, pulse width = 20 ms, and a step height = 2 mV. A 3 mm glassy carbon was used as working electrode and Pt mesh as counter electrode. Potentials were calibrated to Fc/Fc^+ couple.

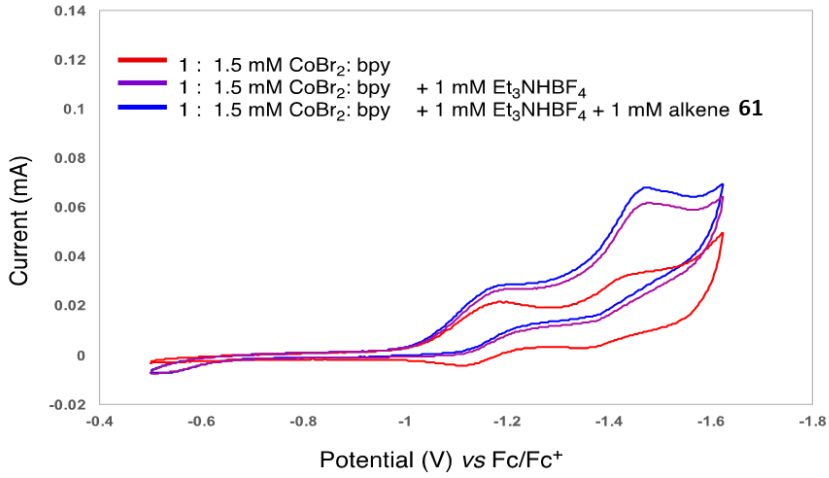


Figure S52. CV analysis of 1 mM $CoBr_2$ and 1.5 mM 4,4'-dimethoxybipyridine in 100 mM $TBAPF_6$ in THF (red), and the addition of 1 mM $Et_3N.HBF_4$ (purple), and addition of 1 mM alkene **61** (red). Scan rate = 100 mV/s, 3 mm glassy carbon was used as working electrode and Pt mesh as counter electrode, in 100 mM $TBAPF_6$ in THF. Potentials were calibrated to Fc/Fc^+ couple.

UV-VIS SPECECELCTROCHEMISTRY

General Details for Electroanalytical Studies

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)], a 0.01 M $Ag^{+/0}$ ($AgNO_3$) in MeCN non-aqueous reference electrode, and a Pt wire counter electrode. A Gamry Reference 600 potentiostat was used for all room temperature voltammetry. All voltammetry was 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 $Fc^{+/0}$. Measurements were recorded using a Hamamatsu L1179 deuterium light source coupled to an OceanOptics 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

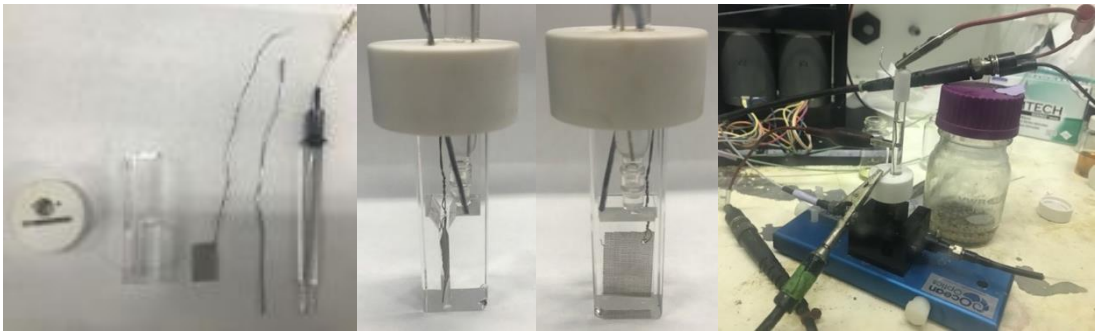


Figure S53. (**Left**) Individual components of spectroelectrochemical cell from left to right: PTFE cap, spectroelectrochemical cuvette, custom Ni-mesh working electrode, metal wire counter electrode, reference electrode. (**Middle**) Assembled spectroelectrochemical cell side profile. (**Middle**) Assembled spectroelectrochemical cell front on profile. (**Right**) Assembled spectroelectrochemical cell placed inside cuvette holder connected to both optics and potentiostat cables inside of a glovebox.

UV-Vis Spectroelectrochemical Studies

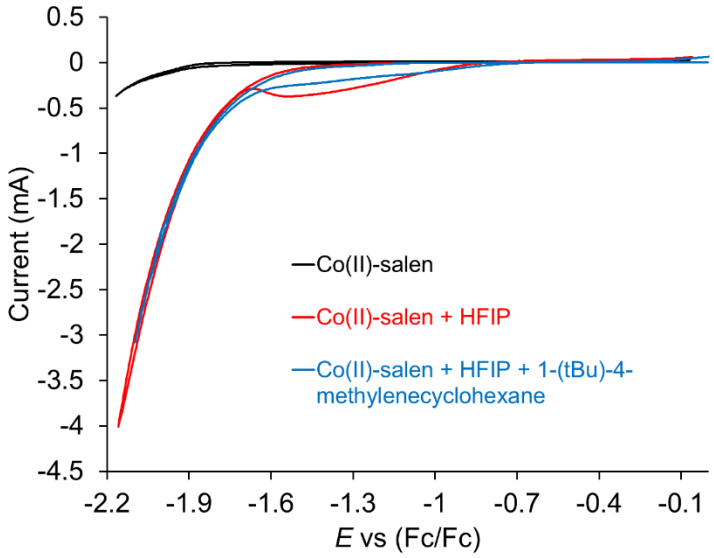


Figure S54. Cyclic voltammetry of Co-salen, Co-salen + HFIP, and Co-salen+HFIP+1-(tert-butyl)-4-methylenecyclohexane: (Co-salen) [N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II):] = 0.25 mM. (**Co-salen + HFIP**) [N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II):] = 0.25 mM, [HFIP] = 0.2 M. (**Co-salen + HFIP + 1-(tert-butyl)-4-methylenecyclohexane**) [N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II):] = 0.25 mM, [HFIP] = 0.2 M, [1-(tert-butyl)-4-methylenecyclohexane] = 50 mM. All CV experiments were run in acetone with [$TBAPF_6$] = 0.1 M and acquired with a scan rate of 25 mV/s, a Ni-mesh working electrode, and a platinum counter electrode. All potentials referenced to $Fc^{+/0}$.

Prior to conducting UV-vis spectroelectrochemical chronoamperometry experiments, a CV for each mixture of interest was acquired to ensure its voltammetry properties agreed with the trends observed from our analytical voltammetry experiments.

Ni-mesh working electrode, and platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials are referenced against an Ag+/Ag acetonitrile pseudo-reference electrode. The indicated chronoamperometric potentials were held for 3 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5 point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

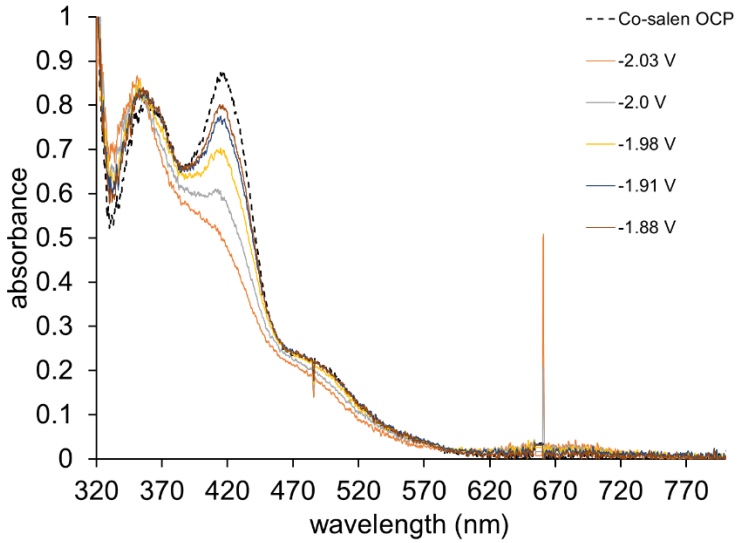


Figure S55. UV-vis spectroelectrochemical chronoamperometry of *N,N′*-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II): [N,N′-Bis(3,5-di-tert-butylsalicylidene) -1,2-cyclo-hexanediamino-cobalt(II):] = 0.25 mM in acetone with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 3 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5 point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

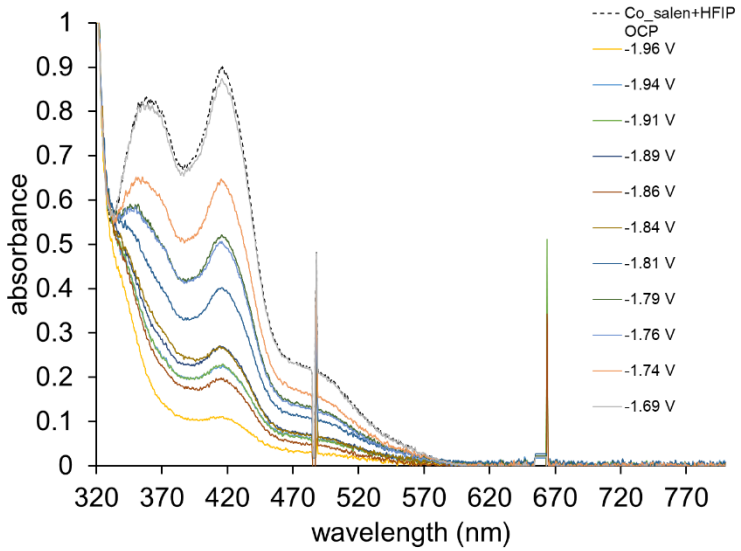


Figure S56. UV-vis spectroelectrochemical chronoamperometry from -1.69 V vs Fc/Fc^+ to -1.96 V vs Fc/Fc^+ of *N,N′*-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) and HFIP: [N,N′-Bis(3,5-di-tert-

butylsalicylidene) -1,2-cyclo-hexanediamino-cobalt(II):] = 0.25 mM, [HFIP] = 0.2 M in acetone with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 3 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

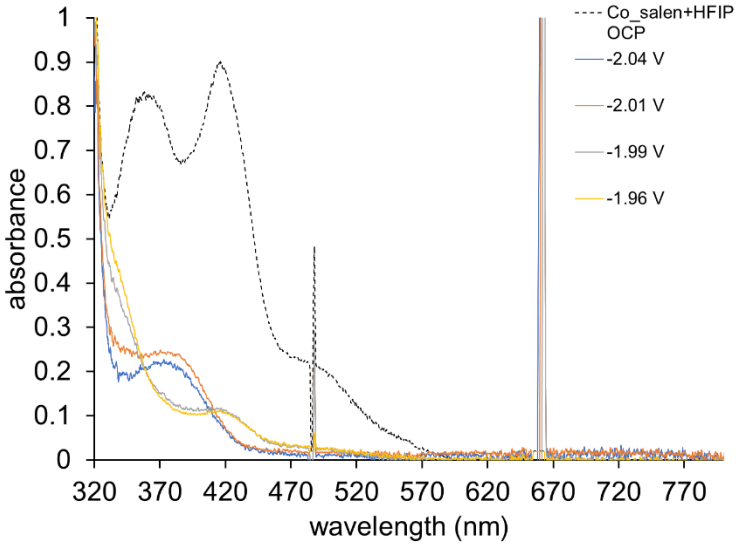


Figure S57. UV-vis spectroelectrochemical chronoamperometry from -1.96 V vs Fc/Fc^+ to -2.04 V vs Fc/Fc^+ of *N,N′*-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) and HFIP: [N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclo-hexanediamino-cobalt(II):] = 0.25 mM, [HFIP] = 0.2 M in acetone with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 3 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

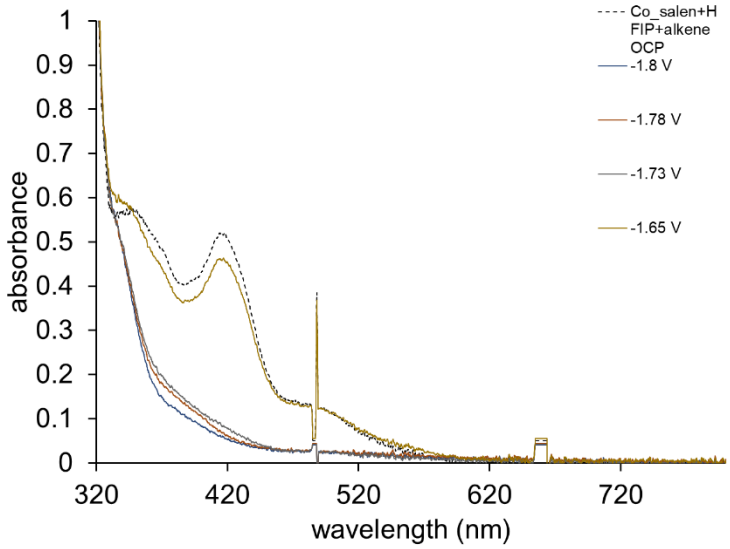


Figure S58. UV-vis spectroelectrochemical chronoamperometry from -1.65 V vs Fc/Fc^+ to -1.8 V vs Fc/Fc^+ of *N,N′*-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II), HFIP, and 1-(tert-butyl)-4-methylenecyclohexane : [N,N′-Bis(3,5-di-tert-butylsalicylidene) -1,2-cyclo-hexanediamino-cobalt(II):] = 0.25 mM, [HFIP] = 0.2 M, [1-(tert-butyl)-4-methylenecyclohexane] = 50 mM in acetone with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 3 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

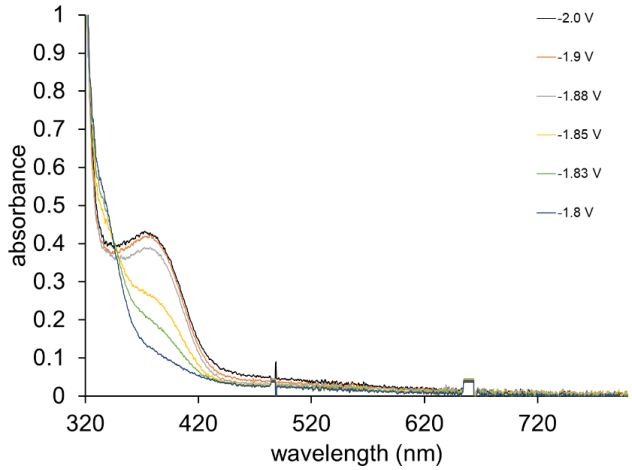


Figure S59. UV-vis spectroelectrochemical chronoamperometry from -1.8 V vs Fc/Fc^+ to -2.0 V vs Fc/Fc^+ of *N,N′*-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II), HFIP, and 1-(tert-butyl)-4-

methylenecyclohexane : [N,N′-Bis(3,5-di-tert-butylsalicylidene) -1,2-cyclo-hexanediamino-cobalt(II):] = 0.25 mM, [HFIP] = 0.2 M, [1-(tert-butyl)-4-methylenecyclohexane] = 50 mM in acetone with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 3 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

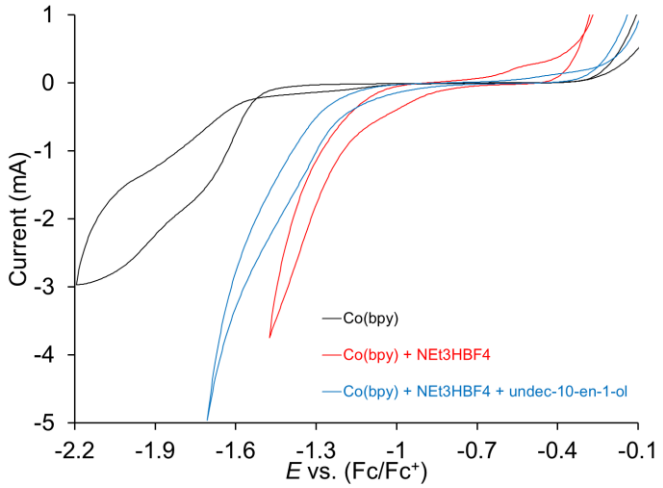


Figure S60. Cyclic voltammetry of Co(bpy), Co(bpy)+ NEt_3HBF_4, Co(bpy)+ NEt_3HBF_4+ undec-10-en-1-ol: (Cobpy) [$CoBr_2$•DME] = 8 mM, [4,4'-dimethoxy-2,2'-bipyridine] = 9.6 mM. **(Cobpy + NEt_3HBF_4)** [$CoBr_2$•DME] = 8 mM, [4,4'-dimethoxy-2,2'-bipyridine] = 9.6 mM, [NEt_3HBF_4] = 128 mM. **(Cobpy + NEt_3HBF_4 + 1-(tert-butyl)-4-methylenecyclohexane)** [$CoBr_2$•DME] = 8 mM, [4,4'-dimethoxy-2,2'-bipyridine] = 9.6 mM, [NEt_3HBF_4] = 128 mM, [undec-10-en-1-ol] = 66 mM. All CV experiments were run in acetonitrile with [$TBAPF_6$] = 0.1 M and acquired with a scan rate of 25 mV/s, a Ni-mesh working electrode, and a platinum counter electrode. All potentials referenced to $Fc^{+/0}$.

Prior to conducting UV-vis spectroelectrochemical chronoamperometry experiments, a CV for each mixture of interest was acquired to ensure its voltammetry properties agreed with the trends observed from our analytical voltammetry experiments. A restricted electrochemical window was utilized for the CV of **Cobpy + NEt_3HBF_4** and **Cobpy + NEt_3HBF_4 + 1-(tert-butyl)-4-methylenecyclohexane** to prevent the potentiostat from exceeding its compliance voltage.

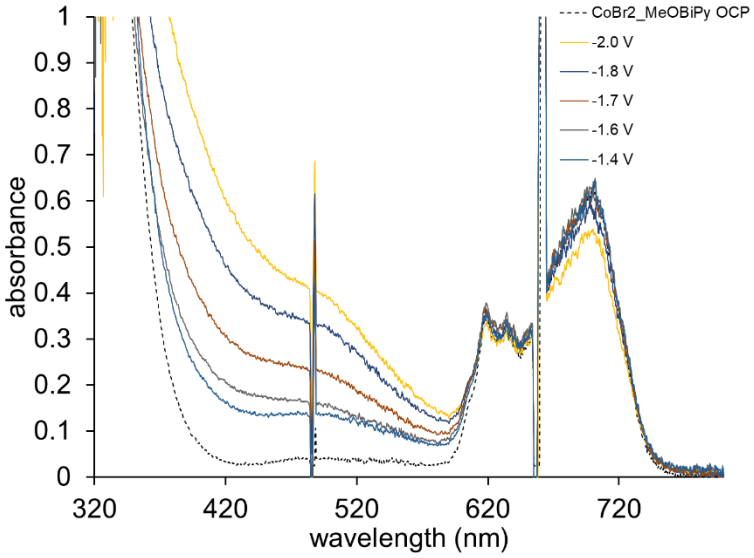


Figure S61. UV-vis spectroelectrochemical chronoamperometry from -1.4 V vs Fc/Fc^+ to -2.0 V vs Fc/Fc^+ of Co(bpy): [$CoBr_2$•DME] = 8 mM, [4,4'-dimethoxy-2,2'-bipyridine] = 9.6 mM in acetonitrile with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 2 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

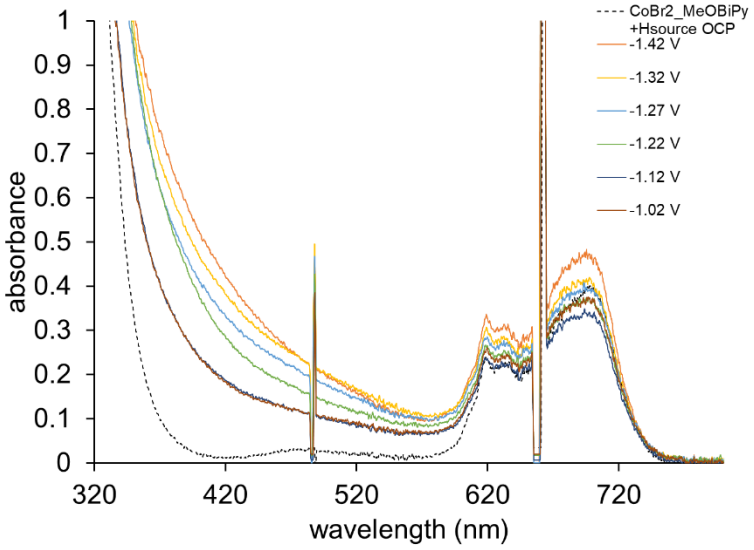


Figure S62. UV-vis spectroelectrochemical chronoamperometry from -1.02 V vs Fc/Fc^+ to -1.42 V vs Fc/Fc^+ of Co(bpy) and NEt_3HBF_4: [$CoBr_2$•DME] = 8 mM, [4,4'-dimethoxy-2,2'-bipyridine] = 9.6 mM, [NEt_3HBF_4] = 128 mM in acetonitrile with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for

2 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

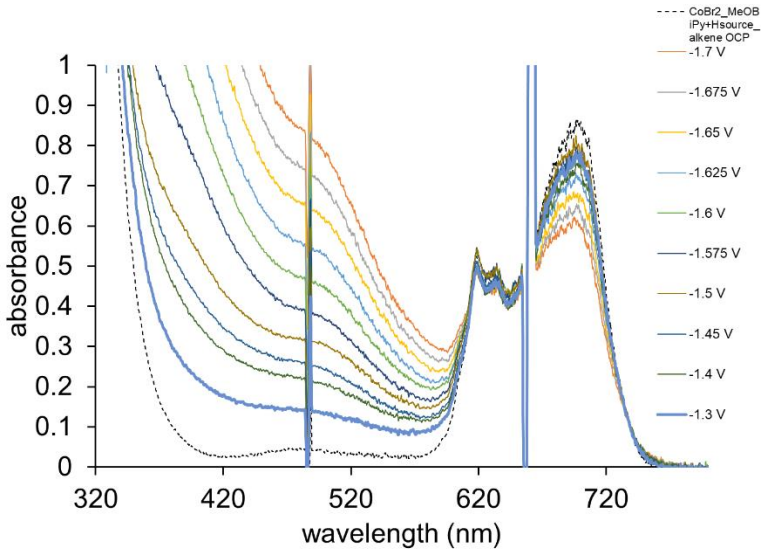


Figure S63. UV-vis spectroelectrochemical chronoamperometry from -1.02 V vs Fc/Fc^+ to -1.42 V vs Fc/Fc^+ of Co(bpy), NEt_3HBF_4, and undec-10-en-1-ol: [$CoBr_2$•DME] = 8 mM, [4,4'-dimethoxy-2,2'-bipyridine] = 9.6 mM, [NEt_3HBF_4] = 128 mM in acetonitrile with [$TBAPF_6$] = 0.1 M, a Ni-mesh working electrode, and a platinum counter electrode. SEC cell has path length of 0.17 cm. All potentials referenced to $Fc^{+/0}$. The indicated chronoamperometric potentials were held for 2 minutes and applied rapidly in succession. Absorbance data are smoothed using a 5-point moving average and then baseline corrected by zeroing the absorbance at 800 nm. The asterisk indicates portions of the UV−vis absorbance data that have signal saturation inherent to the detector/light source used for these experiments.

The gradual increase of cathodic potential to a Co(II)-bpy solution found the appearance of a small shoulder for an absorbance feature past the UV-vis solvent cut off as well as minor changes to the electronic spectra of the parent Co(II)-bpy catalyst. The reduction of this Co(II)-bpy in the presence of $HNEt_3BF_4$ solution lead to the slightly blue-shift, broadening, and decrease in intensity for the Co(II)-bpy absorbance at 700 nm as well as the persistence of a shoulder feature within the UV-vis window akin to that observed for the Co(II)-bpy. The spectroelectrochemical features of the Co(II)-bpy $HNEt_3BF_4$ solution increase in intensity upon introduction of olefin to the reaction mixture. By analogy to our hypothesis for the Co-salen system, we suggest that these changes in signal intensity for the Co-bpy system could reflect a difference in catalyst speciation between the Co-bpy promoted HER versus the Co-bpy catalyzed olefin migration.

In conclusion, spectroelectrochemical studies of both Co-catalyzed olefin migration chemistries find that the catalyst resting state in these systems is neither the parent metal catalyst added at the beginning of the reaction nor the product

of direct reduction of the Co catalyst. In the Co-salen system we speculate that the dramatic changes to the spectroelectrochemial features during active olefin migration electrocatalysis arise from the formation of a persistent Co(III)-hydride catalyst resting state. Our spectroelectrochemical studies of the Co-bpy system could support a similar mechanistic hypothesis; however, further investigation is needed to substantiate this interpretation.

DIFFERENTIAL ELECTROCHEMICAL MASS SPECTROMETRY (DEMS) STUDY FOR H_2 DETECTION

General Reagent Information

Tetrabutylammonium hexafluorophosphate (TBAPF6) (98%, Acros) was purified by recrystallization from ethanol three times and dried under reduced pressure at room temperature for 48 hours. Acetonitrile (MeCN) (HPLC Grade) was purchased from Fisher Chemical and dried over activated 4 Å molecular sieves (Mallinckrodt Chemicals) for at least two days before use. Carbon cloth was purchased from FuelCellStore and Mg foil was purchased from Sigma-Aldrich.

DEMS Measurement Procedures

The DEMS measurement for H_2 monitoring was performed at room temperature with a home-made DEMS cell. A detailed description of the DEMS setup can be found in our previous publication (Ref. *ACS Catal*. 2021, 11, 3, 1136–1178). Specifically, a piece of carbon cloth (1 cm*1 cm) was employed as a working electrode and sandwiched between a porous PTFE membrane and PTFE gasket. A Mg stripe (0.5 cm * 7 cm) tailored from Mg foil was used as counter electrode. The porous membrane supported by a stainless-steel frit served as an interface separating the electrolyte and vacuum chamber. With this configuration, any gases or volatile species generated in the vicinity of working electrode can transport through the porous membrane to the vacuum chamber and be analyzed by a quadrupole mass spectrometer with a response time of less than 1 s. Prior to the experiment, the electrochemical cell was sealed by a plastic zip-lock bag and purged with ultra-high purity Ar for at least 20 minutes. 3 mL Ar-saturated electrolyte solution was then quickly transferred to the electrochemical cell and purged with Ar for another 20 minutes to remove any residual oxygen from the solution. A specific current was applied to the system with a potentiostat from Pine Instrument while a home-made LabVIEW program was used to record the ionic current of hydrogen (m/z =2) from the mass spectrometer. The collected ionic current after stopping the applied current was processed by subtracting the background signals and fitted with an exponential decay function.

Differential electrochemical mass spectrometry (DEMS) enables *operando* measurement with gaseous or volatile products (Ref. *ACS Catal*. 2021, 11, 3, 1136–1178) and was employed to further investigate the isomerization mechanism in the Co-bipyridine system. The transient response behaviors of H_2 mass spectrometric signals were studied after removing the applied current. With only proton source, the hydrogen formation was terminated and hydrogen signals displayed an obvious exponential decay with similar relaxation time (8-10 s), independent of the applied currents (**Figure S64**). Therefore, the larger relation time with addition of Co catalyst and alkene compared with only proton source suggested extra hydrogen release from Co-H intermediate after the current was stopped. This DEMS observation served as compelling evidence for the existence of Co hydride intermediate and its conversion back to Co(II).

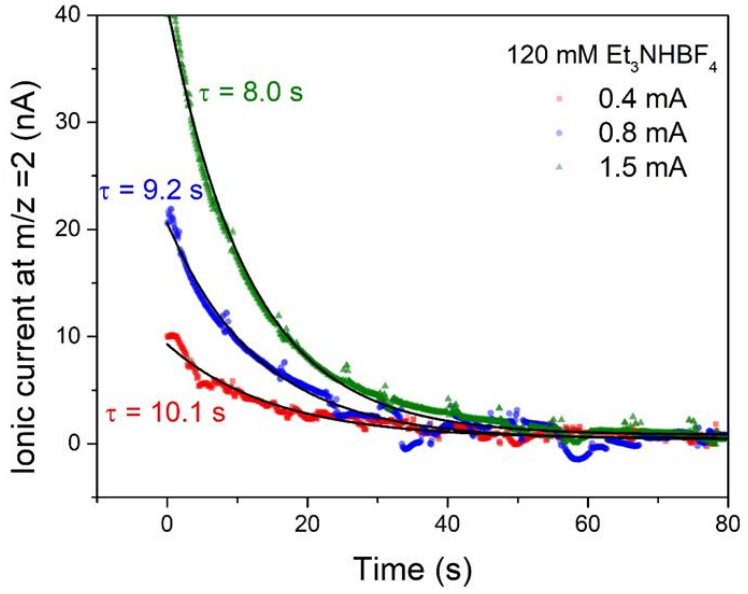


Figure S64. The effect of applied current on the transient response of H_2 mass spectrometric signals in electrolyte containing 120 mM Et_3NHBF_4. The current was applied to the system for 2 minutes to reach steady state and removed at 0 s. The decay of H_2 signals was fitted with an exponential decay function and different relaxation times (τ).

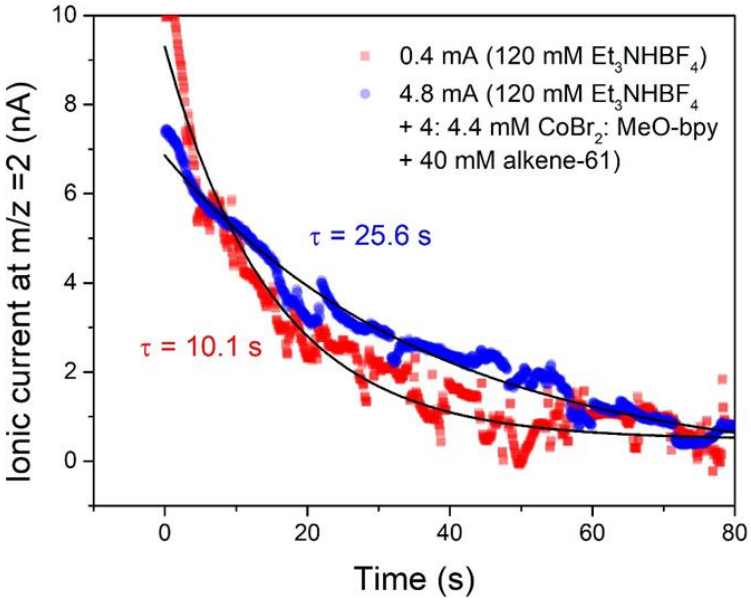
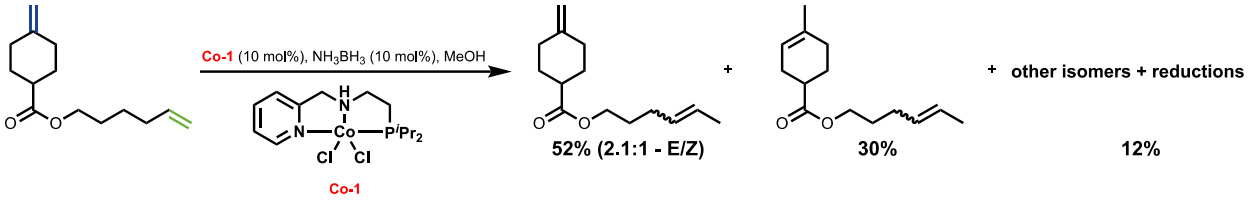


Figure S65. A comparison of transient response of H_2 mass spectrometric signals under different reaction conditions. The slower decay with presence of Co catalyst and alkene indicates gradual release of H_2 after stopping applied current.

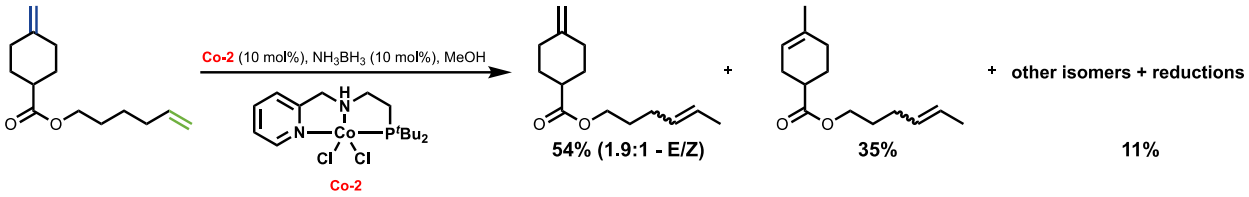
ISOMERIZATION COMPARISON:

Liu isomerization - *JACS 2018, 140, 6873*:

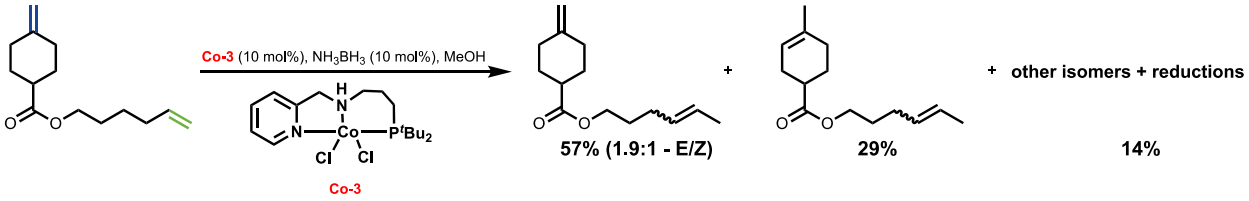
Co-1 catalyst:

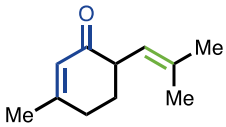


Co-2 catalyst:



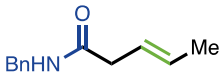
Co-3 catalyst:





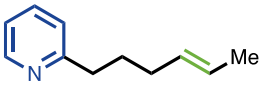
e-HAT - 60%

Liu - 21%



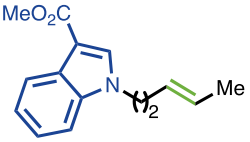
e-HAT - 81%

Liu - N.D.



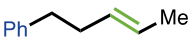
e-HAT - 65%

Liu - 30%



e-HAT- 78%

Liu - 20%



e-HAT - 78%

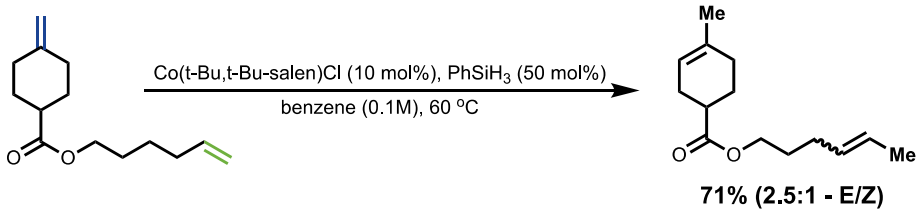
Liu - 10%

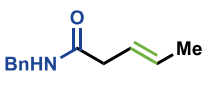
(80% chain-walking, 10% reduction)

e-HAT - 78%

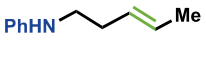
Liu - 60% + 35% reduction

Shenvi isomerization - *JACS 2014, 136, 16788*:

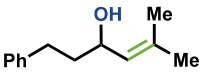




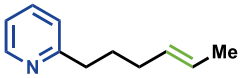
e-HAT - 81%
Shenvi - 45%



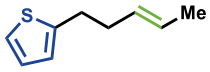
e-HAT - 78%
Shenvi - 20%



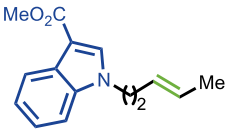
e-HAT - 65%
Shenvi - 12%



e-HAT - 65%
Shenvi - 12%

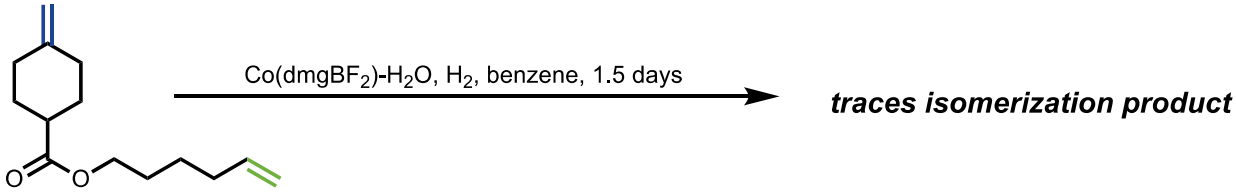


e-HAT - 76%
Shenvi - 15%



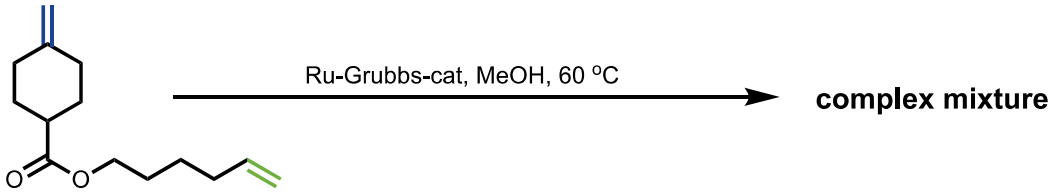
e-HAT- 78%
Shenvi - ND

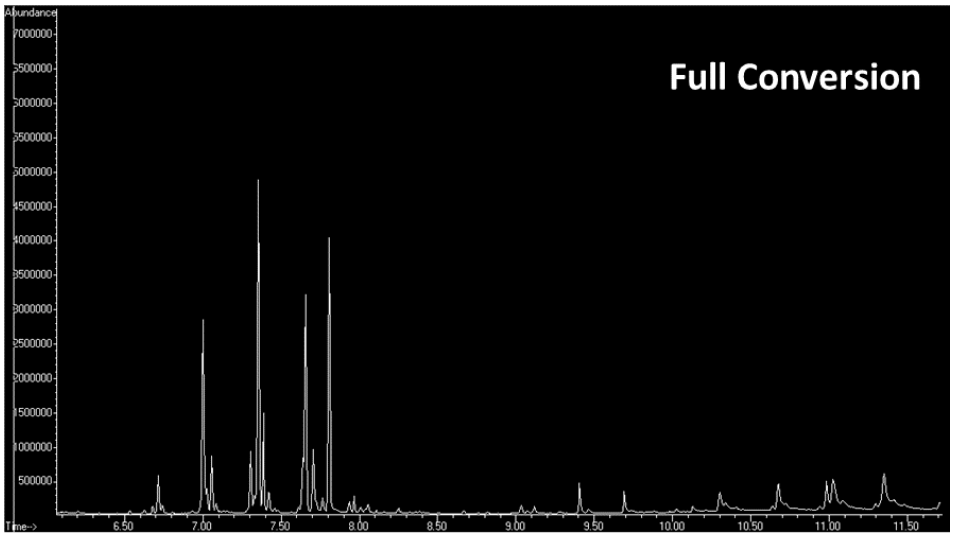
Norton isomerization - *JACS 2016, 138, 7698*:



Other metals isomerization

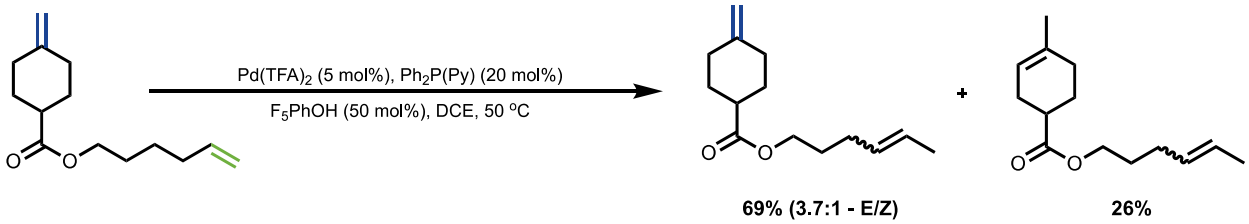
Ruthenium - Larsson isomerization - *Org. Lett. 2006, 8, 5481*:



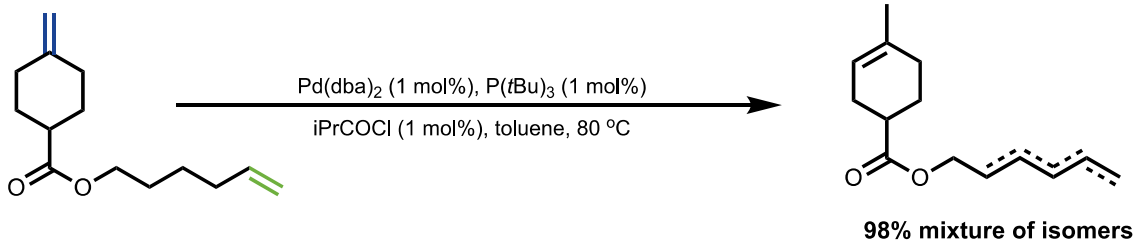


GCMS trace

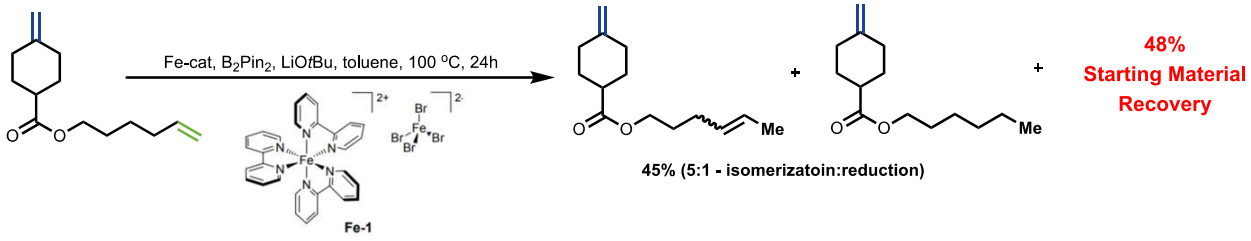
Palladium - Shi isomerization - *Org. Lett. 2020, 22, 1868*:



Palladium - Skrydstrup isomerization - *J. Am. Chem. Soc. 2010, 132, 7998*:

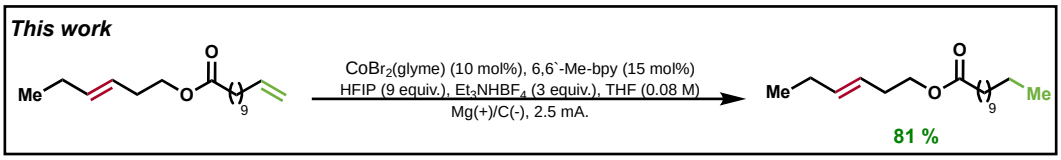


Iron - Koh isomerization - *JACS 2020, 142, 18223*:

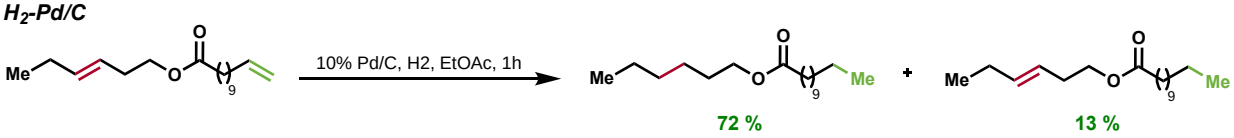


REDUCTION COMPARISON:

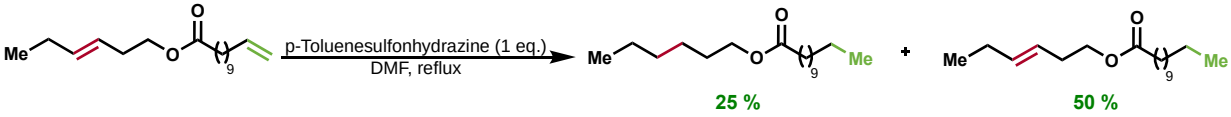
This work



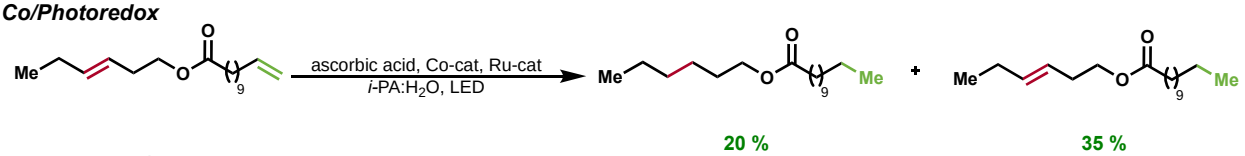
H_2-Pd/C



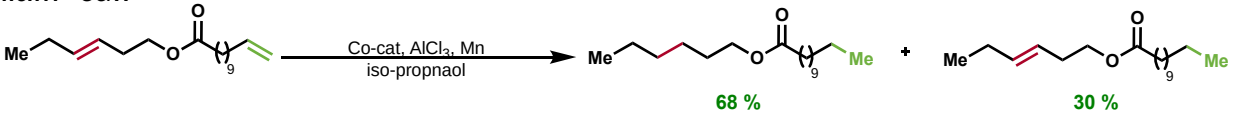
Diimide reductoin



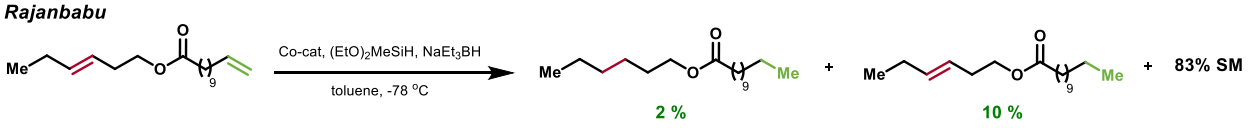
Co/Photoredox

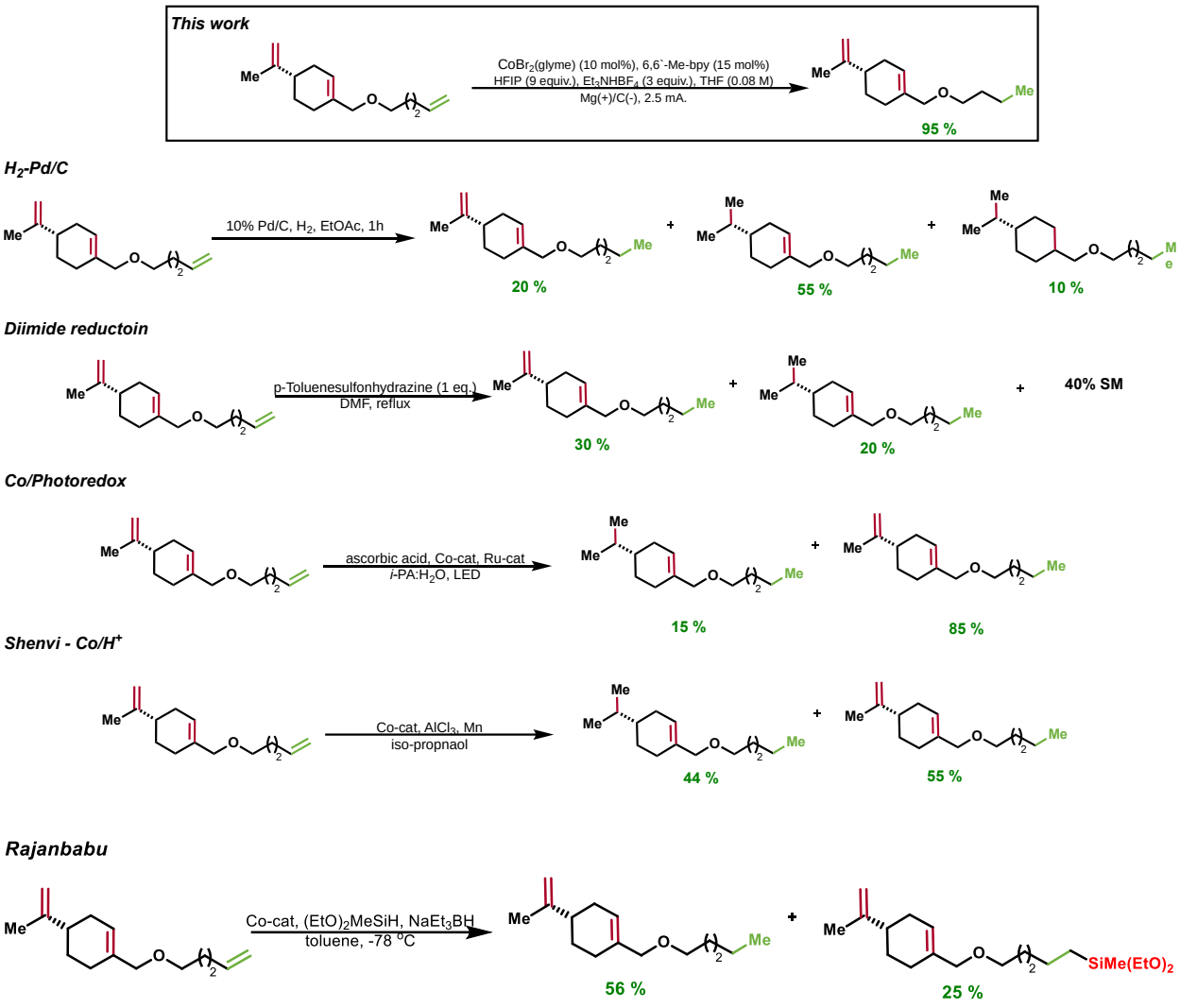


Shenvi - Co/H^+



Rajanbabu





PROCEDURES USED FOR THE CONTROL COMPARISON:

Shenvi isomerizatio procedure:

A small vial was flame dried under vacuum and degassed under an argon atmosphere for 5 minutes and then charged with the starting material. Another small test tube, also flame dried under vacuum, was charged with catalyst (10 mol%) and degassed for 10 minutes. Benzene was added to the starting material and the Co(SalentBu,tBu)Cl pre-catalyst so that the total concentration relative to substrate was 0.1 M. The resulting dark green solution of precatalyst was syringed or cannulated into the small vial and phenylsilane (50 mol%) was then added. The reaction rapidly formed a clear red-orange solution and was stirred at 60 °C for overnight. The resulting mixture was removed from the oil bath, cooled to 23 °C and ^{1}H-NMR yield was determined.[15]

Shenvi alkene reduction:

The olefin (0.2 mmol), Mn powder (33 mg, 0.3 mmol), $Co(OAc)_2 \bullet 4H_2O$ (14.2 mg, 30 mol%) and $AlCl_3$ (26.6 mg, 0.2 mmol) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A cap is placed on the reaction vessel and *i*-PrOH (2 mL) is added. The reaction is stirred vigorously for 20 h at rt. Upon completion, yield was determined by ^{1}H-NMR.[28]

Pd/C hydrogenation:

The olefin (0.2 mmol) was dissolved in EtOAc (2 mL) and one drop of acetic acid was added. After 5 min stirring, catalytic amount of 10% Pd/C was added to the reaction mixture, and the reaction was stirred for 1 hour under balloon of H_2. Upon completion, yield was determined by ^{1}H-NMR.

Diimide reduction:

A 25 mL three neck flask equipped with a condenser was charged with the alkene (1 eq., 0.2 mmol) and DMF (40 mL/mmol). *p*-Toluenesulfonhydrazine (1 eq.) was added and the mixture was refluxed. Then an aqueous solution (1 M) of potassium acetate (2 eq.) was slowly added. After 8 h the mixture was cooled down to room temperature and water was added (10 mL/mmol). The aqueous phase was extracted with DCM (3 x 50 mL/mmol), the organic phases were united and dried over Na_2SO_4, filtered and volatiles were removed under reduced pressure. The crude was analyzed by ^{1}H NMR and GCMS.

Norton Isomerization:

A solution of $Co(dmgBF_2)_2(THF)_2$ (7 mol %) and 8 mL benzene were prepared in a Fischer−Porter reactor, and the substrate **1** (0.5 mmol) was added. The vessel was sealed and then pressurized to 6 atm, and then placed in an oil bath at 50 °C. After stirring for the amount of time indicated in the reaction conditions, the reaction was allowed to return to room temperature, the H_2 pressure was vented, and NMR yield was determined.[29]

Photoredox Reduction:

In an argon-filled glove box, a flame dried reaction vial was charged with an alkene (0.20 mmol), ascorbic acid (0.60 mmol), Co(phenyl-salen) (20 µmol), tricyclohexylphosphine (40 µmol) and $Ru(bpy)_3Cl2 \bullet 6H_2O$ (4.0 µmol) The vial was capped and removed from the glove box. A mixed solvent (2-propanol/H_2O = 3:1, 1 mL) was added to the vial via syringe, and the syringe hole was carefully sealed with a vinyl tape. The reaction vial was placed in front of the light source (ca. 3 cm from two blue LED panels) in a cold room (4 °C) so that the temperature of the reaction mixture was kept approximately at 25 °C. After stirring for the indicated time, the reaction mixture was cooled in an ice bath and sat. aq. NaHCO3 was added. Organic material was extracted with EtOAc (x 3) and the combined organic layer was washed with brine. The organic layer was concentrated under reduced pressure and NMR yield was determined.[30]

Liu Isomerization - JACS 2018, 140, 6873:

In glovebox, cobalt complex (0.025 mmol, 10 mol%), ammonia borane (0.775 mg, 0.025 mmol, 10 mol%), alkene substrate (0.25 mmol) and methanol (1 mL) were added sequentially to a 25 mL Schleck tube equipped with a magnetic stir bar. The reaction was stirred for 3 hours at room temperature. The resulting solution was concentrated in vacuum and yield was determined by ^{1}H-NMR.

Larsson isomerization - Org. Lett. 2006, 8, 5481:

To a solution of the olefin (1 equiv.) in MeOH (0.075M) was added Grubbs-cat. (10 mol %) at room temperature. The suspension was then heated at 60 o C. After a few minutes, the insoluble catalyst (purple) dissolved completely and the resulting orangebrown solution was stirred at 60 ^{o}C until completion. Upon completion, yield was determined by ^{1}H-NMR.

Shi isomerization - Org. Lett. 2020, 22, 1868:

To a mixture of $Pd(TFA)_2$ (0.0083 g, 0.025 mmol) and ligand L1 (0.0263 g, 0.10 mmol) in a vial (2.0 mL) were added 2-fluoroethanol or F_5PhOH (0.016 g, 0.25 mmol), alkene (0.0842 g, 0.50 mmol), and dry DCE (0.30 mL) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at room temperature or 50 ^{o}C for 24 h. Upon completion, yield was determined by ^{1}H-NMR.

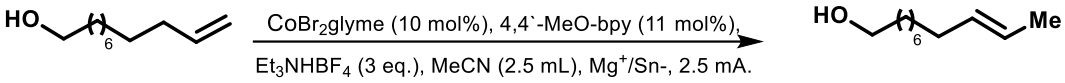
Skrydstrup isomerization - J. Am. Chem. Soc. 2010, 132, 7998:

The olefin (0.4 mmol) was dissolved in toluene (1.0 mL) in a glovebox under an argon atmosphere. $Pd(dba)_2$ from a 0.01 mg.µL-1 stock solution in toluene (1.0 mol%), $P(tBu)_3$ from a 0.02 mg.µL-1 stock solution in toluene (1.0 mol%), isobutyryl chloride from a 0.01 mg.µL-1 stock solution in toluene (1.0 mol%) were added. The sample vial was fitted with a Teflon-sealed screwcap and removed from the glovebox. The reaction mixture was heated at 80 °C for the time stated. Upon completion, yield was determined by ^{1}H-NMR.

Koh isomerization - JACS 2020, 142, 18223

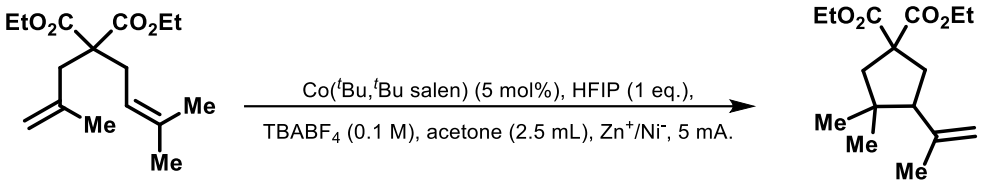
In a N_2-filled glove box, an ovendried 4 mL vial equipped with a magnetic stir bar was charged with Fe-cat (0.002 mmol, 0.01 eq), LiOt-Bu (0.04 mmol, 0.2 eq), $B_2(pin)_2$ (0.04 mmol, 0.2 eq) and toluene (0.5 mL). Then, the alkene substrate (0.20 mmol, 1.0 eq) was sequentially added to the system via syringe and the reaction mixture was allowed to stir at 100 °C for 24 h. Upon completion, yield was determined by ^{1}H-NMR and GCMS.

Moreover, to outline the value of electroreductive approach for both isomerization and cycloisomerization compared to simple chemical reductants, we replaced the electricity with three different types of metal reductants; Mn, Zn, and Mg. Results are summarized below.



Entry	Conditions	Results
1	**Mg turning *instead* of e-chem**	traces
2	**Zn* *instead* of e-chem**	traces
3	**Mn *instead* of e-chem**	traces
4	**w/o e-chem**	traces

* Zn dust, activated Zn, Zn nanopowder.

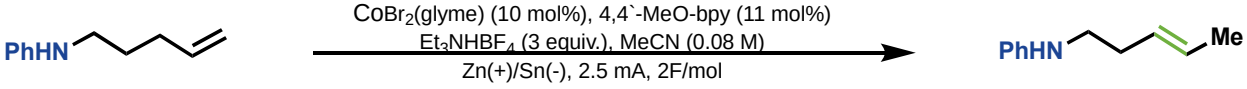


Entry	Conditions	Results
1	**Mg turning *instead* of e-chem**	N.D.
2	**Zn* *instead* of e-chem**	traces
3	**Mn *instead* of e-chem**	traces
4	**w/o e-chem**	traces

* Zn dust, activated Zn, Zn nanopowder.

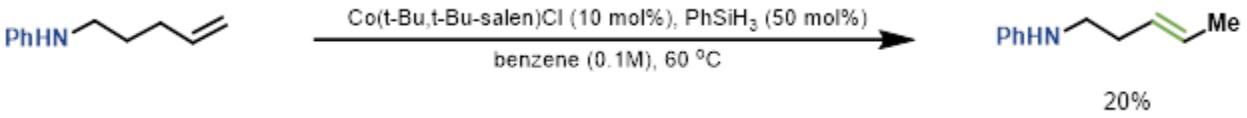
Isomerization:

This work:

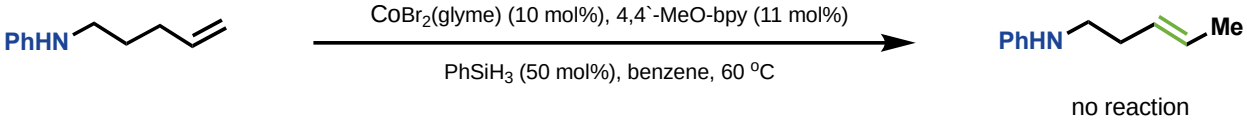


78%

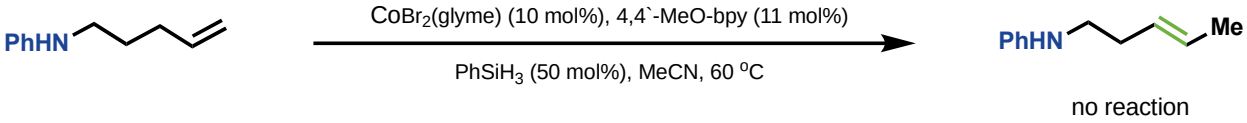
Shenvi conditions - JACS 2014, 136, 16788:



Shenvi conditions with $CoBr_2$/bpy:

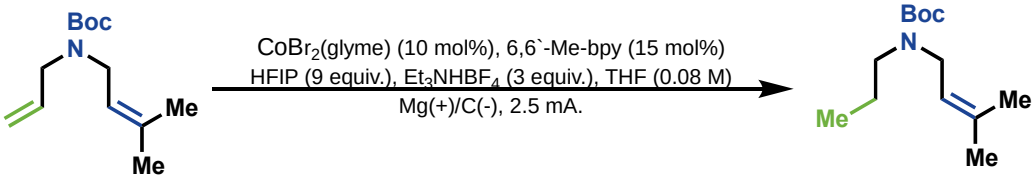


Shenvi conditions with $CoBr_2$/bpy:

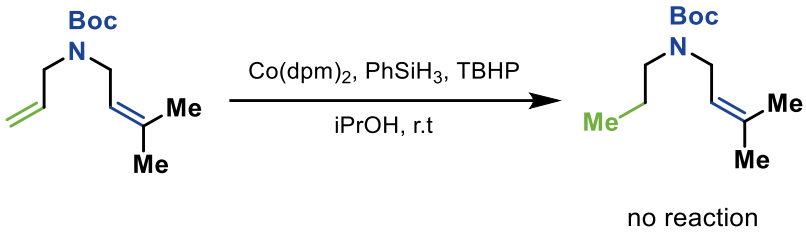


Alkene reduction:

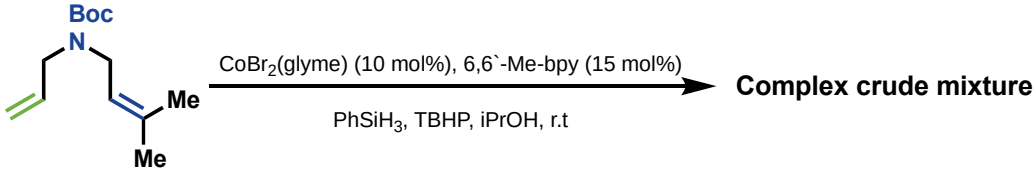
This work:



Shenvi conditions - J. Am. Chem. Soc. 2014, 136, 1300:



Shenvi conditions with $CoBr_2$/bpy:



COMPUTATIONAL CALCULATIONS

Computational Details

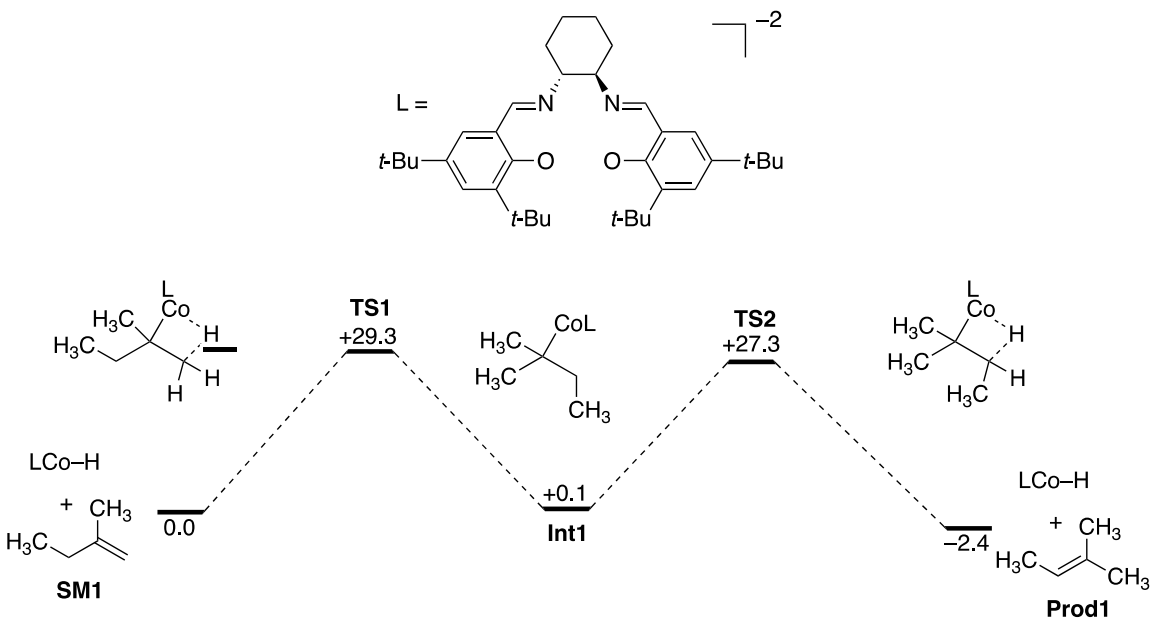
DFT calculations were undertaken using Gaussian 16 (Revision A.03).[31] DFT optimizations were carried out using unrestricted spin, B3LYP[32] density functional, GD3BJ empirical dispersion correction (as implemented in Gaussian Revision A.03), and basis functions LANL2DZ for Co or 6-31+G(d,p) for all others atoms. All ground states (zero imaginary frequencies) were verified as stationary points by frequency analysis. A relaxed scan for bond association between two fragments was performed to map the potential energy surface of bond formation and to provide initial guesses for transition states. Transition state structures were obtained using using a Berny (TS) optimization and confirmed by frequency analysis to show a single negative frequency. Intrinsic reaction coordinate (IRC) calculations were used to verify the transition state and local minima.

Transition State Analysis

Migratory Insertion / Beta-hydride Elimination Mechanism (Olefin Isomerization):

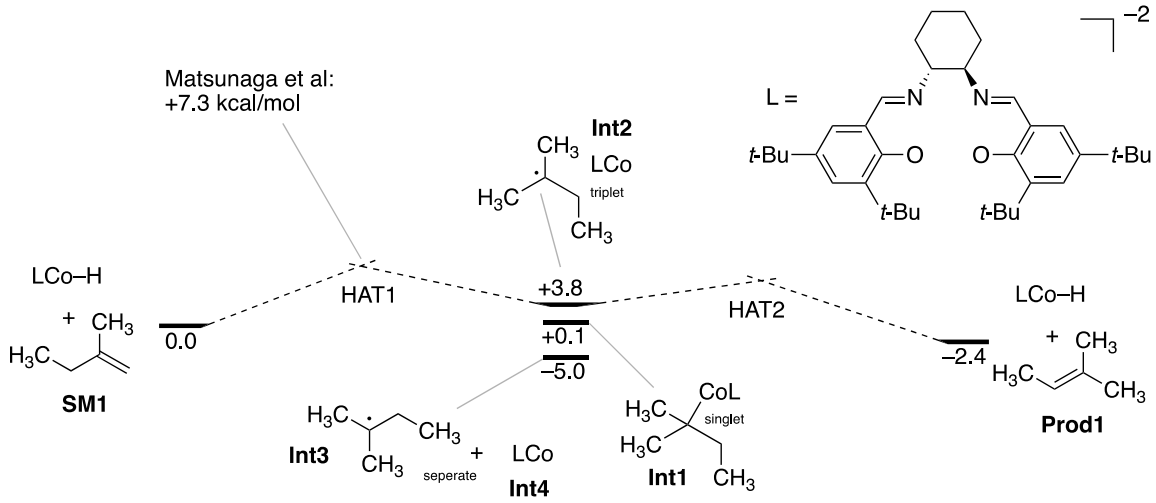
We hypothesized this pathway would be unfavorable for the Co(^{t}Bu,^{t}Bu-Salen) complex because partial dissociation of the ligand is required for an inner-sphere transition states like TS1 and TS2. Indeed we've found this pathway requires two high energy transition states (TS1 = 29.3 kcal/mol, TS2 = 27.3 kcal/mol) making it highly unlikely to proceed at a productive rate at room temperature.

While we believe this is the operating mechanism for Co(4,4-MeO-bpy) complexes, the exact intermediate species are unknown. Electrochemical conditions create a complex environment of coordinating ions and oxidation states that, when combine with a dative ligand, makes implicating specific intermediate species impossible.

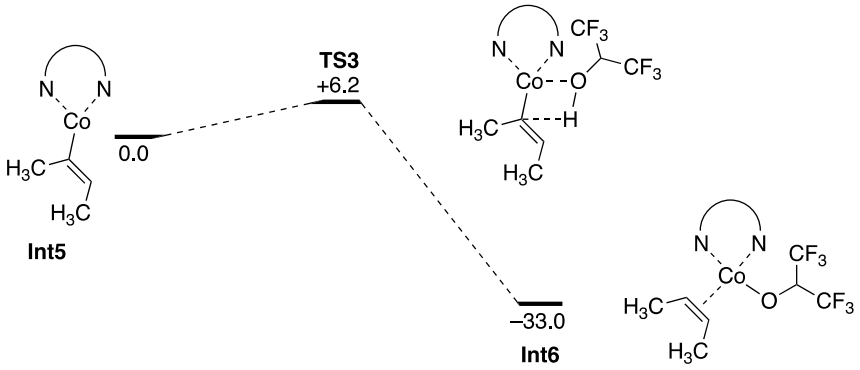


Sequential H-atom Transfer (HAT) Mechanism (Olefin Isomerization):

Because the Co(salen) complex cannot undergo inner-sphere insertion or elimination easily, we've proposed that these processes are instead achieved by outer-sphere HAT mechanisms. The first HAT process (HAT1) transfers an H-atom from the cobalt(III) hydride complex to terminal carbon of the alkene. Multiple possibilities for the intermediate common to HAT1 and HAT2, including the triplet diradical, singlet diradical, and separately calculated radicals, are shown. Overall the conversion of SM1 to Int1, Int2, or Int3+4 is relatively thermoneutral. Attempts to estimate the transition state energy for this process proved difficult as the potential energy scans of the forming bond were barrierless. Conversely, Matsunaga and coworkers[30] have published a very similar transition state analysis that asserts a +7.3 kcal/mol barrier to the forming Co(II)/tertiary radical pair. Both of these analyses demonstrate that an outer-sphere mechanism is much more feasible than the migratory insertion shown above. Attempts to locate a local maxima in the course of HAT2 also proved difficult as the potential energy surface was also barrierless. Because this transition involves the combination of two open shell species, a low or nonexistent energy barrier is feasible.

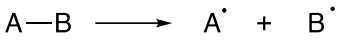


Protodemetalation Mechanism (Alkyne Reduction):

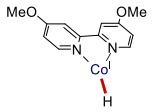
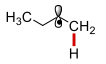
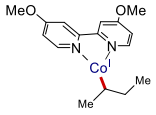
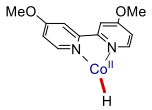
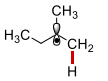
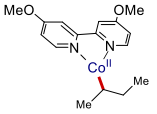
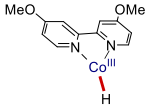
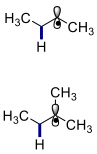
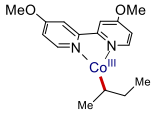
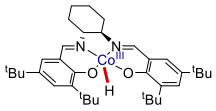
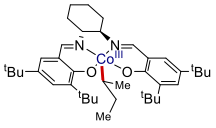
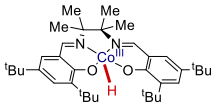
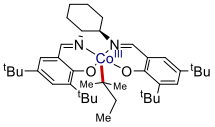
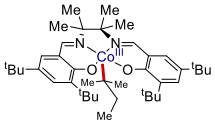


Tabulated Bond Dissociation Energies

Bond dissociation energies (BDEs) were calculated using the following equation:



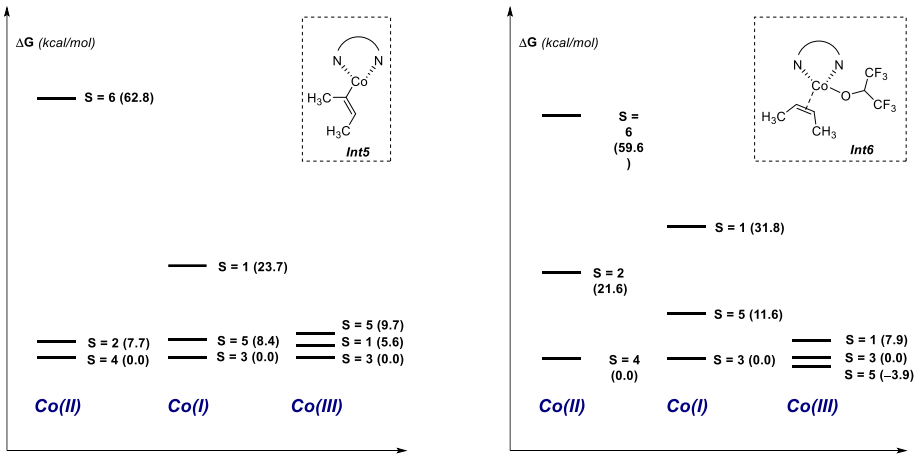
$$\text{BDE} = (E_{A^{\cdot}} + E_{B^{\cdot}}) - E_{A-B}$$

Co–H BDE (*kcal/mol*)		C–H BDE (*kcal/mol*)		Co–C BDE (*kcal/mol*)		Co–C BDE (*kcal/mol*)	
	*75.8*		*46.7*		*53.4*		
	*54.7*		*44.8*		*42.8*		
	*28.6*		*41.8* *43.0*		*61.9*		
	*41.9*				*27.3*		
	*41.9*				*19.6*		*16.6*

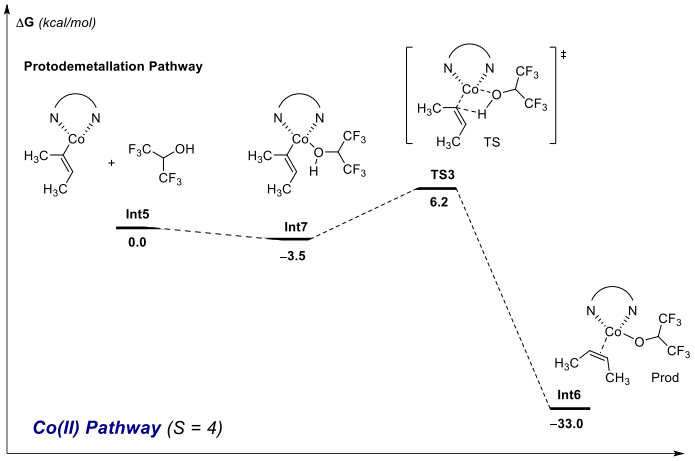
Transition State Analysis

Discussion on the spin and oxidation states for Co-complexes

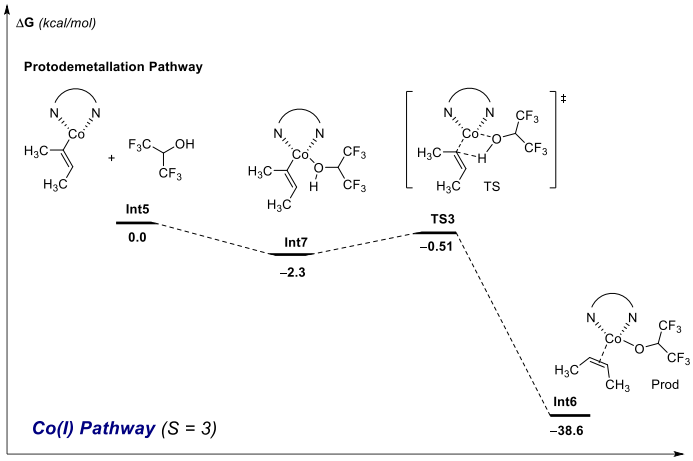
DFT computation was conducted on both the alkenyl-Co(6,6'-dimethylbipyridine) (SM) and alkoxyl- Co(6,6'-dimethylbipyridine) complexes (Prod), where three possible spin states for each oxidation state (Co(I), Co(II), or Co(III)) were considered for the SM and Prod complexes. The relative energies for each complex are tabulated below. For both SM and Prod, Co(II) complexes with spin state (S = 4) and Co(I) complexes with spin state (S = 3) have the lowest energy. However, for Co(III), it is more difficult to determine the spin state since different spin states are energetically preferable for SM and Prod.



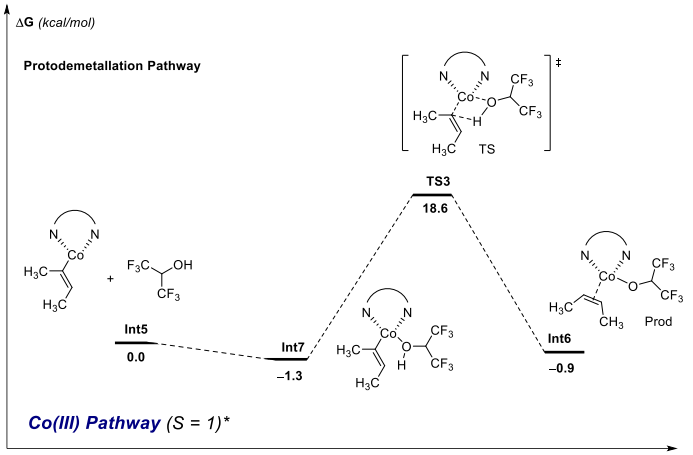
The influence of cobalt's oxidation states was also investigated. As a result of the analysis above, we conducted the transition state computation for Co(II) pathway with a spin state (S = 4), Co(I) pathway with a spin state (S = 3), and Co(III) pathway with all possible spin states. Shown below are the Co(II) pathway, where the transition state was found with an energy barrier of 9.7 kcal/mol from the Int1 complex. This suggests a protodemetallation via a Co(II) pathway is feasible.



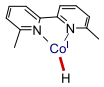
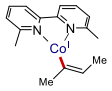
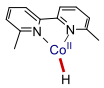
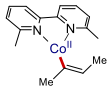
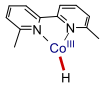
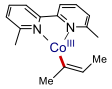
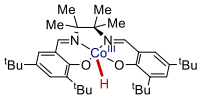
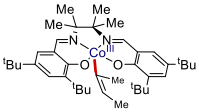
As for Co(I) pathway, the transition state was located with an energy barrier of 1.8 kcal/mol. This suggests that, if it exists, the Co(I)-alkenyl complex could proceed a protodemetallation step to afford the alkyne reduction product, despite the possibility that the generation of this low-valent complex is unlikely under these reaction conditions.



Multiple spin states (S = 1, 3, and 5) were considered in the transition state search for Co(III) pathway. However, a transition state with sping S = 3 and S = 5 could not be located, possibly due to high energy barriers in both cases. When S = 1, we found a transition state with 19.9 kcal/mol as the energy barrier, which is much higher than the Co(II) and Co(I) pathway. Additionally, in the cyclic voltammetic study of Co(6,6'-dimethylbipyridine)Br_2 with proton sources (Figure 3.B.8), the proposed Co(III)-H complex has a similar reduction potential as the Co(6,6'-dimethylbipyridine)Br_2 complex, which suggests the Co(III) complex might be reduced by the applied potential during the constant current electrolysis. As a result, we argue the Co(III) pathway is an unlikely pathway for the protodemetallation compared to the more likely Co(II) and Co(I) pathways.

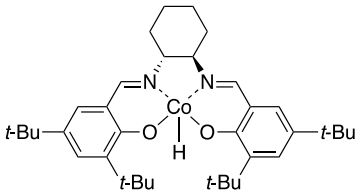


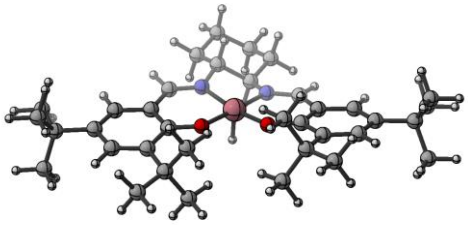
Tabulated Bond Dissociation Energies

	Co–H BDE (*kcal/mol*)		C–H BDE (*kcal/mol*)		Co–C BDE (*kcal/mol*)
	*77.2*		44.0		*71.3*
	*53.2*		113.5		*55.5*
	*25.1*		114.0		*70.0*
	*42.4*				*37.8*

Molecular Coordinates of Optimized Structures

Co(^{t}Bu,^{t}Bu-Salen)–H (E_{uB3LYP} = -1809.155211 Hartree)





Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

Solvation: None

G_{298}: -1808.400437 Hartree

Molecular Coordinates:

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N	1.27232700	2.12524000	-0.15839400
O	-1.27891600	-0.61944700	0.10840500
N	-1.27773300	2.11451100	0.23192700
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C	-4.68355700	0.77338700	0.12458100
C	-4.74292700	-1.59350500	-0.11696200
C	-5.44530100	-0.36567900	0.00714600
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C	4.67763300	0.77764300	-0.21211900
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C	-0.66015900	5.93261200	0.48593100
C	0.64072300	5.94448700	-0.32468700
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H	-4.32669800	-4.33776600	0.43495700
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H	-2.48556200	-2.86868100	-2.47320400
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C	1.90319900	-2.99134500	1.75732300
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H	-7.14292300	-2.26209500	1.09985000
H	-7.16228900	-0.82240600	2.12510300
C	-7.55835200	1.04558700	0.14034400
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H	-7.24514500	1.69687800	-0.68212900
H	-8.65189300	1.00095500	0.13040300
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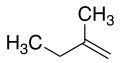
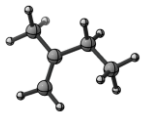
H	-7.12842700	-0.36628000	-2.18617200
H	-7.12644600	-1.98877900	-1.48477300
H	-8.57563500	-0.98249200	-1.36304100
C	6.97538700	-0.36466800	-0.17452900
C	7.42809200	-1.26107500	-1.34781900
H	8.52169300	-1.28642100	-1.41227500
H	7.07682900	-2.29004900	-1.22906400
H	7.03668900	-0.88245300	-2.29731500
C	7.55419500	-0.91881300	1.14571900
H	7.20958500	-1.93802500	1.34241000
H	8.64910800	-0.93827300	1.10667500
H	7.25189100	-0.29491300	1.99280900
C	7.54695900	1.04469600	-0.39676300
H	7.18842800	1.48166500	-1.33441900
H	7.28113500	1.72146200	0.42184900
H	8.63928800	0.99862400	-0.44783000
H	-0.14270900	0.79602700	-1.44200500

SM1 (E_{uB3LYP} = -196.579965 Hartree)





Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

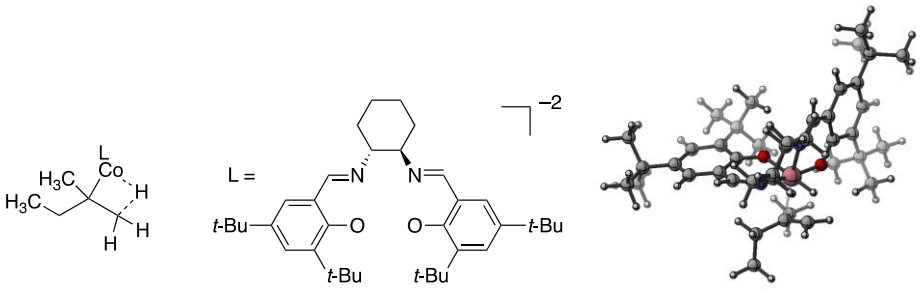
Solvation: None

G_{298}: -196.472786 Hartree

Molecular Coordinates:

C	0.54048200	0.11993800	-0.00006700
C	-0.69375500	-0.75616000	-0.00022700
H	-0.63433700	-1.42485700	0.87160500
C	-2.04363900	-0.03896400	0.00016300
H	-2.86237500	-0.76534700	0.00017600
H	-2.15851100	0.59481600	0.88571100
C	0.50151400	1.45866600	-0.00006700
H	1.41554100	2.04579600	-0.00001400
H	-0.43129100	2.01224700	-0.00009900
H	-2.15889200	0.59527800	-0.88498800
C	1.84736300	-0.63421400	0.00011700
H	1.92287700	-1.28574500	0.88042200
H	1.92328100	-1.28549300	-0.88028200
H	2.70640300	0.04201100	0.00046700
H	-0.63449100	-1.42430600	-0.87251200

TS1 (E_{uB3LYP} = -2005.711466 Hartree)



Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 1 (-383.94 cm^{-1})

Solvation: none

G_{298}: -2004.826598 Hartree

Molecular Coordinates:

Co	-0.09233300	1.28769400	0.88382000
O	-0.69488900	-0.41797900	0.11528000
N	-1.68033600	2.15802500	0.21187400
O	1.54837600	0.39096000	1.34541000
N	0.65358800	2.06274100	-0.71061100
C	2.54053600	0.13516900	0.54423400
C	2.61695400	0.63472200	-0.80045000
C	3.65815500	-0.66415000	0.99894400
C	3.67438300	0.26334300	-1.66737600
C	4.65083600	-0.98867600	0.09014300
C	4.69210000	-0.56726700	-1.26054000
H	3.65570000	0.66579200	-2.67518100
H	5.46579100	-1.61108200	0.43608400
C	-1.88286200	-0.76777200	-0.23587000
C	-2.14728200	-2.13581000	-0.62878000
C	-2.97913100	0.16127200	-0.31478300

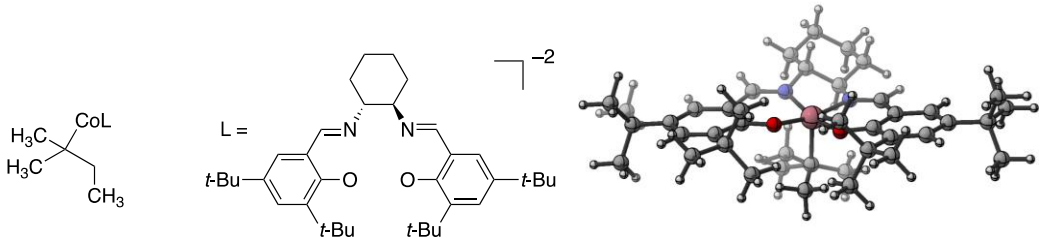
C	-3.45108000	-2.49374400	-0.90826400
C	-4.28798600	-0.27991500	-0.64380000
C	-4.56000200	-1.60191100	-0.90461600
H	-3.64924600	-3.52576900	-1.16979200
H	-5.07349700	0.46840200	-0.68165600
C	-2.74175300	1.56416300	-0.25460300
H	-3.51835100	2.19351100	-0.69642500
C	1.70190200	1.60554600	-1.30976300
H	1.94852500	2.01448600	-2.29438200
C	-0.16419800	3.12161000	-1.31705200
C	0.58133100	4.39461700	-1.72499300
C	-0.41527300	5.40974800	-2.31072400
C	-1.59473500	5.68850100	-1.36487300
C	-2.30506700	4.39263100	-0.93471000
C	-1.27238000	3.46408000	-0.29869300
H	0.10236400	6.34475700	-2.54977300
H	1.07991400	4.80864000	-0.83926400
H	1.36409300	4.17283100	-2.45772600
H	-0.66716300	2.70008600	-2.20195800
H	-1.22703500	6.20785500	-0.46997600
H	-2.30916500	6.36406300	-1.84698400
H	-3.11271200	4.61025100	-0.22669500
H	-2.75992700	3.91850800	-1.81348100
H	-0.80156200	3.99850800	0.53492900
H	-0.80400500	5.01654900	-3.25988700
C	3.73140800	-1.18415000	2.44411000
C	2.63286200	-2.24835400	2.64564500
H	1.65803400	-1.86129300	2.36304800

H	2.83793100	-3.12540200	2.02324700
H	2.59438100	-2.57407700	3.69197200
C	5.08332700	-1.85044100	2.76307500
H	5.92364600	-1.16519700	2.60925200
H	5.09040100	-2.15695700	3.81391800
H	5.25566700	-2.74940100	2.16279300
C	3.56290100	-0.02008600	3.44639800
H	4.38333800	0.69744300	3.33499900
H	2.62540500	0.50742400	3.28333200
H	3.58534700	-0.40211300	4.47328300
C	-0.98502500	-3.13334900	-0.75355100
C	0.03456600	-2.60096300	-1.78886500
H	0.43719600	-1.63649500	-1.47834300
H	0.86638900	-3.30720900	-1.89111400
H	-0.43783900	-2.48909100	-2.77114900
C	-0.27685400	-3.31403500	0.60511900
H	0.15537700	-2.37109700	0.93089600
H	-0.97993400	-3.66782800	1.36777000
H	0.52626200	-4.05440900	0.51645700
C	-1.46171700	-4.51667200	-1.22831700
H	-2.15658100	-4.97737400	-0.51776600
H	-1.95077700	-4.46925100	-2.20715000
H	-0.59787800	-5.18201700	-1.32186900
C	5.83921400	-1.02587700	-2.16577700
C	5.83111400	-2.56749500	-2.25825100
H	6.64923000	-2.92014700	-2.89659900
H	5.95124800	-3.03046200	-1.27446200
H	4.88646500	-2.92381100	-2.68101300

C	5.71035200	-0.45750700	-3.58800700
H	4.77791400	-0.77571100	-4.06530900
H	5.74058800	0.63703400	-3.58886800
H	6.54001100	-0.81288000	-4.20731500
C	7.18712600	-0.55585500	-1.57691800
H	7.21899800	0.53616100	-1.50748200
H	7.35261600	-0.95865900	-0.57351600
H	8.01932700	-0.88448300	-2.20974200
C	-5.95834400	-2.13970600	-1.22400000
C	-6.33957700	-3.22009600	-0.18831500
H	-7.33364500	-3.62770900	-0.40448500
H	-5.62913400	-4.05177500	-0.19293200
H	-6.35333300	-2.79891600	0.82198500
C	-5.96668400	-2.76185500	-2.63762700
H	-5.25023200	-3.58390300	-2.72257500
H	-6.95960500	-3.15866900	-2.87770000
H	-5.70519600	-2.01210000	-3.39114000
C	-7.02432400	-1.03338600	-1.17942400
H	-7.07475400	-0.56295600	-0.19212200
H	-6.82706100	-0.25300000	-1.92166000
H	-8.00960400	-1.45715900	-1.39794800
C	-1.05477400	0.79540100	2.93943500
C	-2.56474700	0.92699800	2.92029200
H	-2.84511700	1.87758400	2.46114600
H	-3.00114000	0.13483900	2.30558000
C	-3.16998500	0.86092800	4.33445600
H	-2.75066900	1.64163900	4.97834500
H	-4.25446100	1.00352100	4.29069900

H	-2.98345600	-0.10441600	4.81333100
C	-0.27116600	1.93866400	3.02803400
H	-0.75711200	2.90730100	3.11871200
H	0.73953500	1.87484200	3.41746800
H	0.37929100	2.49707000	1.56254500
C	-0.52030600	-0.55310800	3.33743600
H	0.56417200	-0.54990100	3.38554900
H	-0.91178000	-0.83360200	4.32352700
H	-0.83373800	-1.32099100	2.62678700

Int1 (E_{uB3LYP} = -2005.765596 Hartree)



Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -2004.873020 Hartree

Molecular Coordinates:

Co	-0.02717700	0.62330400	0.05553900
O	-1.35209500	-0.73440200	0.06938300
N	-1.31647700	2.01508500	-0.12082500
O	1.23173800	-0.75847800	-0.22312200
N	1.23105100	1.94275900	-0.50633000
C	2.52688000	-0.68577400	-0.26812200
C	3.22242300	0.56522500	-0.34513900
C	3.32280200	-1.89003800	-0.29784800
C	4.63893300	0.61940900	-0.31265100
C	4.69817600	-1.75803800	-0.23742100
C	5.39893400	-0.52301300	-0.21687000
H	5.10505400	1.59818100	-0.36273900
H	5.29293900	-2.66221300	-0.22311700
C	-2.64278300	-0.63538200	-0.03244200
C	-3.45669300	-1.82493800	-0.13772600
C	-3.31681700	0.62830000	-0.07882700

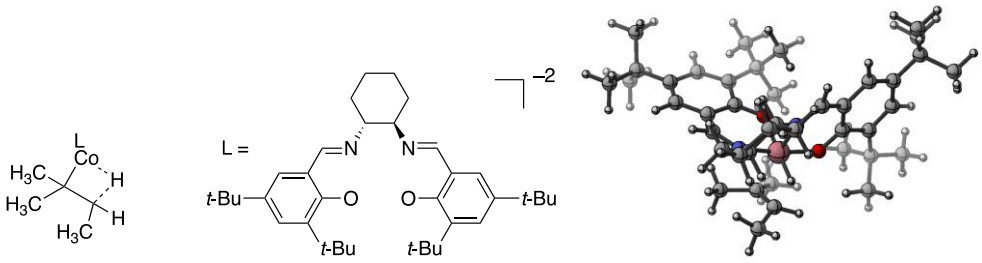
C	-4.83065100	-1.67102300	-0.17443200
C	-4.73298000	0.70269700	-0.12316000
C	-5.51463100	-0.42773300	-0.15032900
H	-5.43760200	-2.56497100	-0.23545300
H	-5.18172600	1.69079100	-0.14010600
C	-2.60569700	1.86061700	-0.15009600
H	-3.23024700	2.74847000	-0.25340600
C	2.51683800	1.77943200	-0.59264500
H	3.13071700	2.62447400	-0.90785500
C	0.57617300	3.15496700	-1.03123100
C	1.40738300	4.43932000	-1.09507900
C	0.55276400	5.58981900	-1.64750300
C	-0.73570600	5.77718600	-0.83954300
C	-1.55800700	4.48170700	-0.77368800
C	-0.70325100	3.34604400	-0.20722400
H	1.13759900	6.51559700	-1.65233300
H	1.77560300	4.69245100	-0.09314500
H	2.28427200	4.30074000	-1.73511600
H	0.25293000	2.91153000	-2.05567800
H	-0.48075400	6.09249400	0.18114800
H	-1.34255400	6.57941700	-1.27234000
H	-2.44271200	4.64627800	-0.15040300
H	-1.91338600	4.20830600	-1.77615700
H	-0.40131700	3.62430600	0.81057700
H	0.29588300	5.37546000	-2.69358000
C	2.65691800	-3.26440600	-0.47142900
C	1.92245700	-3.27334300	-1.83224600
H	1.17821300	-2.47812300	-1.87699700

H	2.63458300	-3.13550800	-2.65312300
H	1.41202500	-4.23139100	-1.98042300
C	3.68556400	-4.40885400	-0.48427100
H	4.23667100	-4.47468800	0.46014000
H	3.16119400	-5.35868800	-0.62675000
H	4.40859100	-4.30683400	-1.30028600
C	1.64931600	-3.55264000	0.65993700
H	2.14282100	-3.52115000	1.63767700
H	0.84216100	-2.82588900	0.65081400
H	1.22115000	-4.55298400	0.53071700
C	-2.81266900	-3.21830900	-0.22316400
C	-1.81072500	-3.26010300	-1.39855700
H	-1.02449200	-2.51940400	-1.26614700
H	-1.34924800	-4.25187800	-1.46093600
H	-2.32374400	-3.06564100	-2.34711500
C	-2.08317600	-3.54479000	1.09623800
H	-1.27663800	-2.83901500	1.27682400
H	-2.77835900	-3.50944100	1.94207300
H	-1.65207100	-4.55121400	1.05118200
C	-3.85596700	-4.32471000	-0.46326000
H	-4.56646900	-4.41127400	0.36572700
H	-4.42069200	-4.16249100	-1.38740700
H	-3.34114100	-5.28610000	-0.55367600
C	6.92849800	-0.52558200	-0.13204600
C	7.51496300	-1.28322400	-1.34339300
H	8.60947600	-1.29820100	-1.29339400
H	7.16926900	-2.32024100	-1.37895800
H	7.22070800	-0.80075900	-2.28085200

C	7.50647100	0.89860600	-0.12914100
H	7.25874800	1.43666100	-1.04998500
H	7.13561500	1.48167900	0.72001600
H	8.59754200	0.85654200	-0.05360900
C	7.36564200	-1.22837900	1.17174700
H	6.97074800	-0.70175100	2.04632100
H	7.00630700	-2.26057800	1.21377200
H	8.45852200	-1.25085800	1.24842000
C	-7.04618100	-0.40757300	-0.17933100
C	-7.59185700	-1.16429100	1.05134700
H	-8.68765400	-1.16992800	1.04476000
H	-7.25268300	-2.20400400	1.06895500
H	-7.25636200	-0.68822000	1.97814700
C	-7.54901500	-1.09557200	-1.46730500
H	-7.21347100	-2.13475400	-1.52859900
H	-8.64433700	-1.09610600	-1.50018600
H	-7.17906000	-0.57247700	-2.35483300
C	-7.60296400	1.02475900	-0.14977600
H	-7.29303200	1.55866600	0.75441100
H	-7.27510300	1.60302400	-1.01979800
H	-8.69710100	0.99844600	-0.16234100
C	0.18071400	0.73014900	2.09604600
C	1.49637400	1.38966900	2.53456100
H	1.67687600	1.02577300	3.55930100
H	2.32177300	0.98154600	1.94519100
C	1.59872900	2.91399800	2.58208000
H	0.82185000	3.35775700	3.21248500
H	2.56610800	3.20971700	3.00208000

H	1.52716200	3.36126300	1.59153000
C	0.21741100	-0.72500500	2.55880200
H	1.10723400	-1.24294700	2.20464100
H	0.23169500	-0.74225900	3.65967300
H	-0.65873300	-1.27402100	2.22534900
C	-1.04863200	1.40571400	2.69312800
H	-1.14728400	2.45886400	2.42522400
H	-1.96572500	0.88926200	2.40098600
H	-0.97948300	1.35785300	3.79119200

TS2 (E_{uB3LYP} = -2005.715692 Hartree)



Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 1 (-354.16 cm^{-1})

Solvation: none

G_{298}: -2004.829655 Hartree

Molecular Coordinates:

Co	-0.12948900	1.31997200	0.82555200
O	-0.72369500	-0.44511500	0.20640200
N	-1.74689500	2.11854400	0.13204400
O	1.54184000	0.48663500	1.30505400
N	0.55268800	1.94545600	-0.86615300
C	2.49909400	0.15340100	0.49003900
C	2.51180800	0.51095300	-0.90129000
C	3.64293400	-0.59083600	0.97300200
C	3.52809300	0.04925700	-1.77383300
C	4.59260400	-1.01037900	0.05716900
C	4.56679900	-0.73580000	-1.33113200
H	3.46012500	0.34399100	-2.81620500
H	5.42630300	-1.59249900	0.42774900
C	-1.91569800	-0.83757200	-0.07647600
C	-2.16911100	-2.23701500	-0.34730200
C	-3.02864400	0.06766500	-0.19666200

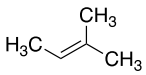
C	-3.47433000	-2.63424400	-0.55703500
C	-4.33915500	-0.41734200	-0.44959800
C	-4.59687800	-1.75976600	-0.59358200
H	-3.66373200	-3.68688500	-0.72669000
H	-5.13770200	0.31423200	-0.52437800
C	-2.81193100	1.47328500	-0.25459800
H	-3.60915000	2.05414000	-0.72556700
C	1.57264300	1.42751400	-1.46406600
H	1.77335000	1.73437300	-2.49536700
C	-0.29427800	2.93742300	-1.53953200
C	0.42710400	4.16948000	-2.09147800
C	-0.59655500	5.12406400	-2.72968900
C	-1.74020000	5.48744300	-1.76852700
C	-2.42633700	4.23542500	-1.19373600
C	-1.36454600	3.37143700	-0.51645300
H	-0.09368700	6.03376200	-3.07458900
H	0.95615700	4.66462600	-1.26714400
H	1.18338600	3.88255400	-2.82948200
H	-0.82562900	2.43259900	-2.36209700
H	-1.34088900	6.08749300	-0.94009700
H	-2.47612000	6.11455200	-2.28272700
H	-3.20659000	4.51587200	-0.47693300
H	-2.91339500	3.68258700	-2.00670000
H	-0.86366800	3.98236400	0.24236600
H	-1.01974300	4.64366900	-3.62233300
C	3.78877200	-0.95412000	2.45980300
C	2.71429900	-2.00050900	2.82189000
H	1.72312000	-1.65437900	2.54400100

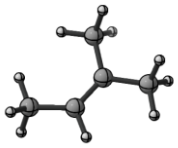
H	2.90530300	-2.93670400	2.28731100
H	2.72562300	-2.21346200	3.89753100
C	5.16217000	-1.57240600	2.78401800
H	5.98601200	-0.90224800	2.51655000
H	5.22218100	-1.76256600	3.86039200
H	5.31699800	-2.53028700	2.27743000
C	3.65288700	0.30873900	3.34025300
H	4.46516800	1.01088900	3.12191500
H	2.70770700	0.81646300	3.15931200
H	3.71759900	0.03691500	4.39995100
C	-0.99399900	-3.22416800	-0.42684400
C	-0.02057700	-2.76732300	-1.53990400
H	0.37550300	-1.77405900	-1.32711800
H	0.81997600	-3.46698700	-1.61145700
H	-0.52854200	-2.74715100	-2.51053800
C	-0.23468200	-3.27767700	0.91546500
H	0.20008600	-2.30668900	1.14027500
H	-0.90542300	-3.56723100	1.73235600
H	0.57212300	-4.01743200	0.86237300
C	-1.46250400	-4.64993800	-0.76433500
H	-2.12556500	-5.05713900	0.00673000
H	-1.98450800	-4.69413900	-1.72615200
H	-0.59113500	-5.30870500	-0.83032400
C	5.66949000	-1.29138500	-2.23710000
C	5.66109000	-2.83399600	-2.16297000
H	6.44752600	-3.25538600	-2.79947800
H	5.83101600	-3.18881100	-1.14226400
H	4.69754000	-3.23108400	-2.49760100

C	5.46915300	-0.87891000	-3.70412400
H	4.51511400	-1.24414200	-4.09772200
H	5.49631100	0.20909900	-3.82438200
H	6.26820300	-1.30106100	-4.32178200
C	7.04340900	-0.76422700	-1.76914000
H	7.07568300	0.32881900	-1.81971100
H	7.25877700	-1.05676500	-0.73739500
H	7.84460600	-1.16143000	-2.40268400
C	-5.99477600	-2.34132700	-0.82676200
C	-6.32880700	-3.33882300	0.30401300
H	-7.32166400	-3.77681300	0.15090700
H	-5.60516000	-4.15797700	0.34615000
H	-6.32121300	-2.83684200	1.27676600
C	-6.03288800	-3.07679600	-2.18439900
H	-5.30648300	-3.89355100	-2.22325900
H	-7.02586700	-3.50487600	-2.36249900
H	-5.80416300	-2.38756300	-3.00349700
C	-7.07692800	-1.25005200	-0.84077200
H	-7.10702000	-0.70132800	0.10610800
H	-6.91335000	-0.53028000	-1.64947300
H	-8.06098200	-1.70388700	-0.99496500
C	-1.00014000	0.98173500	2.90332200
C	-2.51048400	0.95078000	2.92488300
H	-2.97255300	1.80732900	2.43739800
H	-2.89123300	0.04321900	2.45293500
C	-0.29442900	2.18492600	2.91534800
H	0.73206700	2.13154500	3.27043100
H	0.36085600	2.58348000	1.37517800

C	-0.37117800	-0.27618300	3.44190300
H	0.70783200	-0.18562200	3.52260400
H	-0.78264300	-0.48402900	4.44009300
H	-0.60230500	-1.13355200	2.80690600
H	-2.84552400	0.93761500	3.97205600
C	-0.95942500	3.53632000	3.05236600
H	-0.26293300	4.34803400	2.82585600
H	-1.82516300	3.63182700	2.39428100
H	-1.31124800	3.66777800	4.08312300

Prod1 (E_{uB3LYP} = -196.582471 Hartree)





Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

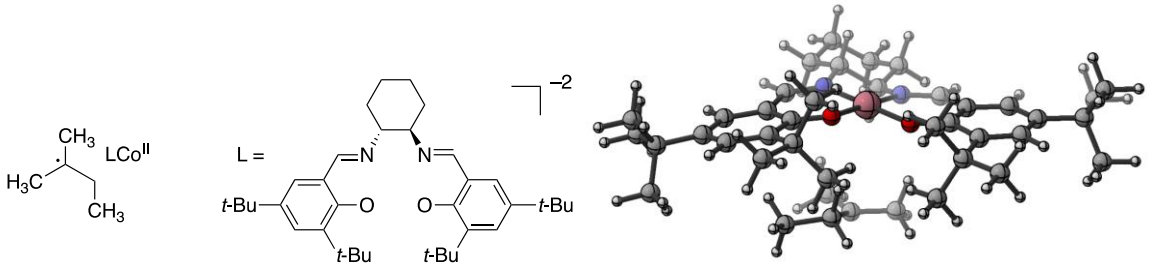
Solvation: none

G_{298}: -196.476539 Hartree

Molecular Coordinates:

C	-0.44951300	-0.04206500	0.00011000
C	0.73421900	-0.67687800	0.00000200
H	0.71146400	-1.76738400	-0.00010400
C	2.11251900	-0.07796300	-0.00001000
H	2.67992400	-0.40642500	-0.88039000
H	2.10521600	1.01436500	0.00093100
C	-0.62354800	1.45610500	-0.00000700
H	-1.19780400	1.77582900	0.87953400
H	0.32151300	2.00165600	0.00017200
H	-1.19732800	1.77564100	-0.87995300
H	2.68046000	-0.40791500	0.87947000
C	-1.74473400	-0.81779800	-0.00002200
H	-2.35222300	-0.56812800	-0.88025000
H	-1.57254800	-1.89788100	-0.00000800
H	-2.35232400	-0.56816400	0.88016400

Int2 (E_{uB3LYP} = -2005.748804 Hartree)



Charge: 0

Spin Multiplicity: 3

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -2004.867093 Hartree

Molecular Coordinates:

Co	-0.12871400	0.69878600	-0.56386400
O	-1.39224100	-0.63665800	-0.33566400
N	-1.39375400	2.07580300	-0.33657900
O	1.15029100	-0.64034700	-0.74302500
N	1.14138300	2.07250900	-0.77314400
C	2.44714900	-0.55780700	-0.65633300
C	3.13039600	0.69603300	-0.57249400
C	3.24177100	-1.75969900	-0.64419200
C	4.53645100	0.74845500	-0.38735600
C	4.60364100	-1.63079200	-0.44377400
C	5.29011000	-0.39722700	-0.28906700
H	4.99689600	1.72820900	-0.31305200
H	5.19750800	-2.53466400	-0.40368100
C	-2.68987600	-0.56195900	-0.25607400
C	-3.46726700	-1.76819300	-0.13179500
C	-3.38649500	0.68657500	-0.26616400

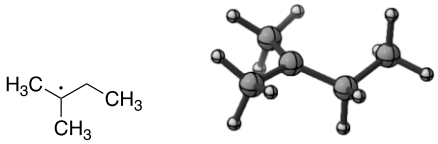
C	-4.84404400	-1.65012200	-0.09689800
C	-4.80453400	0.72845300	-0.21435000
C	-5.55538500	-0.42123600	-0.14631900
H	-5.42863600	-2.55762400	-0.01668200
H	-5.27841300	1.70456100	-0.22833200
C	-2.68717300	1.92489200	-0.26082700
H	-3.30708500	2.81583700	-0.15783700
C	2.43504600	1.93026900	-0.70021700
H	3.05925100	2.82300600	-0.74398400
C	0.50999200	3.38036000	-1.00511900
C	1.35676200	4.62810700	-0.75057000
C	0.52253700	5.88917400	-1.02226700
C	-0.77430300	5.90064200	-0.20502600
C	-1.60879100	4.63149100	-0.43678800
C	-0.76145700	3.39136300	-0.14607900
H	1.11759700	6.78173300	-0.80255900
H	1.70844100	4.62344900	0.28965900
H	2.24295600	4.63263800	-1.39337900
H	0.18733800	3.38829900	-2.05732100
H	-0.52813800	5.97488300	0.86265400
H	-1.37011700	6.78587200	-0.45084000
H	-2.49226300	4.65932600	0.20854500
H	-1.96519000	4.59393600	-1.47479600
H	-0.43814700	3.43069100	0.90449900
H	0.27720200	5.93140200	-2.09189600
C	2.58454300	-3.13215000	-0.85471600
C	1.86910100	-3.14851500	-2.22531900
H	1.11050000	-2.36813000	-2.28046000

H	2.59043100	-2.99588700	-3.03566500
H	1.38233700	-4.11743900	-2.38196600
C	3.61712900	-4.27290800	-0.85290100
H	4.13645200	-4.35526300	0.10793700
H	3.10162900	-5.22184900	-1.02947100
H	4.36672400	-4.15171100	-1.64213400
C	1.56691000	-3.41759300	0.26948300
H	2.05974500	-3.41767800	1.24761500
H	0.77665200	-2.67156900	0.27583300
H	1.11190100	-4.40309900	0.12001400
C	-2.76672400	-3.12766900	0.00063100
C	-1.87493800	-3.39830800	-1.23198600
H	-1.11140900	-2.63132800	-1.34308400
H	-1.38128200	-4.37096700	-1.12857900
H	-2.48333300	-3.42398700	-2.14300200
C	-1.91646000	-3.12004800	1.29258900
H	-1.19000200	-2.30860800	1.28174900
H	-2.56114800	-2.99779100	2.16990600
H	-1.37652600	-4.06740600	1.39643300
C	-3.77107700	-4.28815200	0.11092900
H	-4.41736500	-4.19248700	0.98986000
H	-4.40577700	-4.36672900	-0.77830000
H	-3.22120400	-5.22928500	0.20820300
C	6.79978800	-0.40448200	-0.03040500
C	7.52565400	-1.10818300	-1.19753600
H	8.60659000	-1.12930100	-1.01959100
H	7.18862700	-2.14130500	-1.32095800
H	7.34336800	-0.58244200	-2.14018200

C	7.36747700	1.01749900	0.10328900
H	7.21717900	1.59977400	-0.81172000
H	6.90571200	1.55873700	0.93540800
H	8.44421800	0.97088200	0.29371100
C	7.08255200	-1.16461000	1.28413300
H	6.57748600	-0.68081500	2.12611700
H	6.73112600	-2.19922900	1.23535000
H	8.15809400	-1.18569800	1.49260700
C	-7.08690300	-0.43681200	-0.10136200
C	-7.55774900	-1.10128400	1.21088300
H	-8.65223000	-1.12667400	1.25685700
H	-7.19675000	-2.13016700	1.29604200
H	-7.19037700	-0.54558700	2.07943000
C	-7.62705100	-1.23990900	-1.30473500
H	-7.26407900	-2.27162100	-1.29803300
H	-8.72219300	-1.27063900	-1.28508700
H	-7.31326200	-0.78177700	-2.24801500
C	-7.67919100	0.98015100	-0.16295800
H	-7.35527000	1.59013800	0.68659400
H	-7.39425800	1.49624900	-1.08551300
H	-8.77202900	0.92709300	-0.13538800
C	0.51320100	0.63147100	3.10756900
C	1.24969400	-0.62842600	2.75010100
H	0.83974000	-1.45782200	3.34582100
H	1.01603700	-0.89416500	1.70727000
C	2.77351200	-0.58928700	2.90866200
H	3.06367200	-0.36013200	3.94026300
H	3.21156400	-1.55474400	2.63975400

H	3.22765100	0.15876100	2.25286000
C	-0.98221600	0.56326300	3.13533300
H	-1.33311100	-0.36348000	3.60570000
C	1.17503000	1.96702200	2.97321400
H	1.32978100	2.24853400	1.91718900
H	0.56933500	2.75754700	3.43159100
H	2.16621800	1.98910900	3.44051600
H	-1.42056400	1.40990300	3.67750200
H	-1.41318900	0.57007300	2.12079000

Int3 (E_{uB3LYP} = -197.151329 Hartree)



Charge: 0

Spin Multiplicity: 2

Number of Imaginary Frequencies: 0

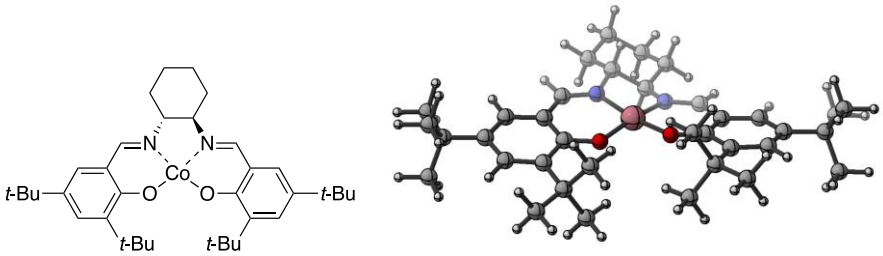
Solvation: none

G_{298}: -197.037743 Hartree

Molecular Coordinates:

C	0.50836700	-0.00220300	-0.11739300
C	1.78141300	-0.78973600	-0.10823700
H	2.57255400	-0.29118400	-0.68035800
H	2.17222300	-0.92115500	0.91899300
H	1.64071700	-1.79586400	-0.52005800
C	0.60136700	1.48111100	0.06453300
H	1.49552200	1.88742500	-0.42051300
H	-0.27004300	2.00895600	-0.33660600
H	0.66794600	1.75462100	1.13517000
C	-0.75626100	-0.72076300	0.25892100
H	-0.72262300	-1.73726000	-0.15536100
H	-0.78293200	-0.85931500	1.35890800
C	-2.06328400	-0.04103800	-0.17272400
H	-2.92508800	-0.66629800	0.08229700
H	-2.20087800	0.92570900	0.32174900
H	-2.07700700	0.13013900	-1.25481700

Int4 (E_{uB3LYP} = -1808.588838 Hartree)



Charge: 0

Spin Multiplicity: 2

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1807.843464 Hartree

Molecular Coordinates:

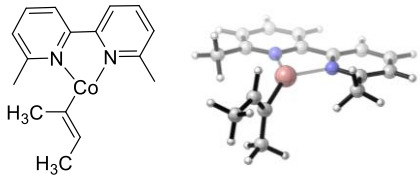
Co	0.00000100	0.73180800	-0.00001300
O	1.29351900	-0.60573000	0.09880300
N	1.27452800	2.11277300	-0.21166500
O	-1.29352000	-0.60572700	-0.09883400
N	-1.27452300	2.11277500	0.21164700
C	3.27240400	0.72776200	-0.12792000
C	-2.59090700	-0.51702700	-0.05680100
C	-3.27240100	0.72776500	0.12792600
C	-3.38858500	-1.70771800	-0.20682000
C	-4.68987500	0.77788000	0.18331800
C	-4.76362900	-1.58013300	-0.14036800
C	-5.45704200	-0.35654000	0.05735600
H	-5.15176600	1.74897100	0.32972800
H	-5.36164200	-2.47623900	-0.24645700
C	2.59090600	-0.51703100	0.05678800
C	3.38858100	-1.70772300	0.20681000

C	4.76362700	-1.58014000	0.14038200
C	4.68988000	0.77787600	-0.18328800
C	5.45704300	-0.35654500	-0.05732000
H	5.36163700	-2.47624600	0.24647300
H	5.15177300	1.74896800	-0.32968400
C	2.56723400	1.95907100	-0.25509500
H	3.18922400	2.84323600	-0.40012900
C	-2.56722800	1.95907300	0.25509600
H	-3.18921600	2.84323700	0.40014100
C	-0.63564600	3.42024300	0.43171400
C	-1.48086800	4.66818900	0.16912300
C	-0.64445100	5.93304100	0.41470500
C	0.64446100	5.93303800	-0.41474300
C	1.48087700	4.66818600	-0.16915300
C	0.63565300	3.42024100	-0.43173600
H	-1.24216800	6.82212300	0.18808100
H	-1.84431000	4.64805900	-0.86685800
H	-2.36070000	4.68469300	0.81990500
H	-0.30601200	3.43722500	1.48260300
H	0.38864400	5.99096800	-1.48119500
H	1.24217900	6.82212100	-0.18812400
H	2.36070900	4.68468500	-0.81993500
H	1.84431900	4.64806300	0.86682800
H	0.30601900	3.43721800	-1.48262500
H	-0.38863400	5.99097700	1.48115700
C	-2.71097800	-3.06612500	-0.44194900
C	-1.77340400	-3.39976000	0.74031700
H	-0.99837200	-2.64394300	0.84986900

H	-2.34252200	-3.46050400	1.67464400
H	-1.29267400	-4.37022400	0.57340400
C	-3.73409600	-4.20891600	-0.56365000
H	-4.41770300	-4.06215100	-1.40673200
H	-3.20140200	-5.14993300	-0.73186500
H	-4.32973700	-4.32542400	0.34812800
C	-1.90493100	-3.01639500	-1.76021700
H	-2.57266900	-2.83275900	-2.60926000
H	-1.15310200	-2.22852500	-1.72964400
H	-1.39888200	-3.97368700	-1.92721800
C	2.71096700	-3.06613100	0.44191300
C	1.90490400	-3.01641500	1.76017100
H	1.15308000	-2.22854000	1.72960100
H	1.39884700	-3.97370600	1.92715200
H	2.57263200	-2.83279600	2.60922500
C	1.77340800	-3.39974800	-0.74037000
H	0.99837400	-2.64393300	-0.84991500
H	2.34253600	-3.46047300	-1.67469200
H	1.29268000	-4.37021700	-0.57347900
C	3.73408000	-4.20892700	0.56361200
H	4.32972900	-4.32542700	-0.34816200
H	4.41768000	-4.06217200	1.40670200
H	3.20138100	-5.14994400	0.73181200
C	-6.98827200	-0.36078200	0.11614100
C	-7.45516000	-1.25689400	1.28408300
H	-8.54943800	-1.28013500	1.33687600
H	-7.10472400	-2.28652100	1.16867900
H	-7.07322100	-0.87940500	2.23789200

C	-7.56039100	1.04925100	0.33264500
H	-7.21316700	1.48476900	1.27522300
H	-7.28307900	1.72637800	-0.48182300
H	-8.65335200	1.00479100	0.36993500
C	-7.55350500	-0.91352500	-1.21055700
H	-7.24131700	-0.28951800	-2.05396800
H	-7.20785300	-1.93298400	-1.40409700
H	-8.64880700	-0.93171700	-1.18335100
C	6.98827500	-0.36078700	-0.11607600
C	7.45518700	-1.25689000	-1.28401500
H	8.54946600	-1.28012900	-1.33678700
H	7.10475000	-2.28651800	-1.16862600
H	7.07326600	-0.87939500	-2.23782900
C	7.55348000	-0.91354000	1.21062900
H	7.20782100	-1.93299900	1.40415600
H	8.64878300	-0.93173600	1.18344400
H	7.24127800	-0.28953700	2.05403800
C	7.56039800	1.04924700	-0.33255800
H	7.21319200	1.48477300	-1.27513900
H	7.28307100	1.72636800	0.48191000
H	8.65336000	1.00478800	-0.36982800

Int5 (E_{uB3LYP} = -875.687853 Hartree)



Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 0

Solvation: none

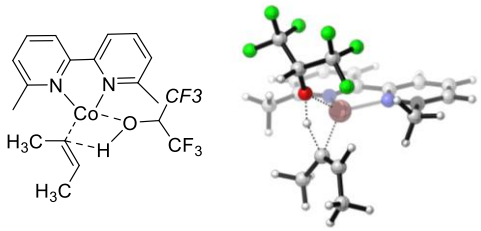
G_{298}: -875.430875 Hartree

Molecular Coordinates:

N	-0.71040500	-1.34415300	-0.13730400
C	-0.59647000	-2.68794900	-0.15042700
C	-1.73237800	-3.49368300	-0.01217500
C	-3.08042300	-1.50471900	0.13903400
C	-1.92021600	-0.74446400	0.00297000
N	-0.71040100	1.34415400	-0.13730500
C	-0.59646100	2.68795000	-0.15042900
C	-1.73236700	3.49368700	-0.01217700
C	-3.08041800	1.50472800	0.13903400
C	-1.92021300	0.74446900	0.00296900
H	-1.62766100	-4.57236400	-0.01969200
H	-4.04773100	-1.03379300	0.25182200
H	-1.62764600	4.57236800	-0.01969500
H	-4.04772800	1.03380500	0.25182300
Co	0.84713400	-0.00000200	-0.19134900
C	2.64548300	-0.00000200	0.46242100
C	3.51227300	-0.00000800	-0.57422700

H	3.10803000	-0.00001400	-1.59492900
C	3.01354800	0.00000500	1.92175800
H	2.59868800	-0.87861800	2.43103500
H	2.59868500	0.87863100	2.43102800
C	5.01901600	-0.00000800	-0.54203500
H	5.41740100	0.00000200	0.47380900
H	5.41234400	-0.87997600	-1.06521000
H	5.41234400	0.87994800	-1.06522800
H	4.09492100	0.00000800	2.09691200
C	0.77531700	3.26758600	-0.34168200
H	1.52105900	2.72292400	0.24450700
H	1.07094200	3.20065800	-1.39550400
H	0.80042200	4.32018600	-0.05447300
C	0.77530600	-3.26759000	-0.34167900
H	1.07093000	-3.20066800	-1.39550200
H	1.52105100	-2.72292800	0.24450700
H	0.80040800	-4.32018900	-0.05446500
C	-2.97949900	2.89609500	0.13222600
H	-3.87067500	3.50528400	0.24053800
C	-2.97950900	-2.89608700	0.13222800
H	-3.87068700	-3.50527300	0.24053900

TS3 (E_{uB3LYP} = -1665.559961 Hartree)



Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 1 (−1178.48 cm^{-1})

Solvation: none

G_{298}: -1665.255667 Hartree

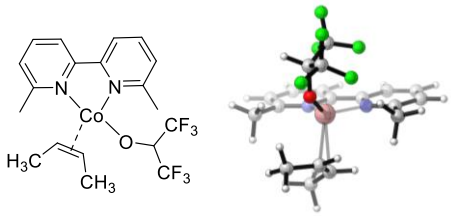
Molecular coordinates:

N	-1.70998200	-1.21120300	-0.56150100
C	-1.65190700	-2.48157900	-1.01734000
C	-2.68688600	-3.00178200	-1.80082600
C	-3.83267200	-0.89651400	-1.62390500
C	-2.77453800	-0.41833000	-0.85281100
N	-1.68949300	1.27380800	0.49000400
C	-1.55538900	2.51107100	1.01380300
C	-2.50944000	3.49857300	0.74071100
C	-3.71368300	1.91750900	-0.61265100
C	-2.74024400	0.96686900	-0.31221100
H	-2.62156100	-4.02151600	-2.16139600
H	-4.68516600	-0.27048100	-1.84930700
H	-2.38783600	4.48791200	1.16584200
H	-4.54631700	1.68037000	-1.26077300
C	0.50709000	-1.00233500	2.45352800
C	1.08541400	-2.22999700	2.41794200

H	1.50539500	-2.56154800	1.46654100
C	-0.05393200	-0.38792600	3.71953800
H	-1.08092200	-0.03073400	3.57497800
H	0.54183100	0.48328900	4.01691900
C	1.29173800	-3.21399600	3.53156200
H	0.83503700	-2.90851200	4.47337800
H	0.88495300	-4.19300000	3.24903100
H	2.36484400	-3.36682600	3.70211600
H	-0.07110300	-1.07558000	4.57047000
C	-0.37659300	2.77992000	1.90015600
H	-0.26080000	3.85053000	2.07508900
H	-0.51452000	2.29128400	2.86998400
H	0.54480300	2.39504000	1.45825800
C	-0.45832800	-3.30594900	-0.64176600
H	0.46999900	-2.79390500	-0.90599200
H	-0.44955400	-3.48739600	0.43751100
H	-0.47367900	-4.26988200	-1.15231300
C	-3.59294700	3.19883600	-0.07570900
H	-4.33790100	3.95478500	-0.30064900
C	-3.78417800	-2.20414800	-2.10342900
H	-4.59761200	-2.59308400	-2.70678300
Co	-0.35211800	-0.27622900	0.65523800
C	2.71524000	0.44904000	-0.25850300
H	3.63528500	0.37092600	0.33240100
C	2.73717800	-0.70244700	-1.27920600
C	2.70868900	1.84850800	-0.90403200
F	3.78714000	-0.64715200	-2.10468700
F	2.79617200	-1.88089200	-0.60513600

F	1.60668000	-0.73652600	-2.02446200
F	1.58463500	2.05814400	-1.62371000
F	3.76680800	2.04093400	-1.70625700
F	2.74594900	2.78185000	0.07127300
O	1.57996500	0.35460900	0.54731700
H	1.43448700	-0.25777900	1.54292600

Int6 (E_{uB3LYP} = -1665.628122 Hartree)



Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.318071 Hartree

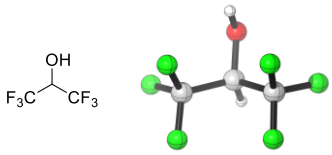
Molecular coordinates:

N	1.87691900	-0.73230800	-0.67686300
C	2.19280300	-1.82441900	-1.39829500
C	3.32332800	-1.82056500	-2.22249800
C	3.76253900	0.44883400	-1.54391300
C	2.62386900	0.39805200	-0.74217600
N	1.01023000	1.34912300	0.78630700
C	0.48231600	2.32630400	1.55014600
C	1.09796300	3.58133500	1.60993700
C	2.79664900	2.78152800	0.10196200
C	2.14399300	1.55094700	0.06876500
H	3.56769300	-2.70289300	-2.80263000
H	4.36584300	1.34486100	-1.60244800
H	0.66115600	4.36292700	2.22044400
H	3.70029400	2.95119300	-0.46806900
Co	0.21382400	-0.51429600	0.48793500
C	-0.75592400	2.00299000	2.33348400
H	-1.49670100	1.49332500	1.71299200

H	-0.50963900	1.34973300	3.17915800
H	-1.21091100	2.90854300	2.73754300
C	1.29896100	-3.02305600	-1.26658200
H	1.58324000	-3.61330400	-0.38835700
H	0.25355800	-2.72423600	-1.14716900
H	1.38057300	-3.67128300	-2.14101900
C	4.11354400	-0.67800500	-2.28826900
H	4.99393300	-0.65625600	-2.92189600
C	2.26021100	3.80731800	0.88073300
H	2.74912100	4.77523900	0.91418300
C	-0.22125200	-1.87208400	2.51064100
C	1.06932600	-1.46179000	2.61764300
H	1.24214300	-0.46867300	3.03285500
C	2.30866100	-2.27881500	2.38376900
H	3.04457800	-1.72652900	1.79103200
H	2.78115800	-2.50106300	3.34814900
H	2.10343300	-3.22949600	1.88957200
C	-0.72311200	-3.22503900	2.10546500
H	0.06029200	-3.87463900	1.71100200
H	-1.15975500	-3.72037700	2.98128200
H	-1.51722900	-3.12177900	1.36134700
H	-0.99511100	-1.17193900	2.82527500
O	-1.51484300	-0.95519400	0.01270300
C	-2.37039300	-0.47183900	-0.94968400
H	-2.54897800	-1.20382000	-1.75332400
C	-3.74770700	-0.21513600	-0.29974700
C	-1.81665300	0.78247700	-1.65908200
F	-4.25240300	-1.38162500	0.14742900

F	-4.62814600	0.31399400	-1.17159400
F	-3.65774200	0.62187700	0.75951300
F	-0.52463500	0.52957200	-2.03855700
F	-2.50067400	1.10793000	-2.76102100
F	-1.76394900	1.87003800	-0.85529000

HFIP (E_{uB3LYP} = -789.860962 Hartree)



Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

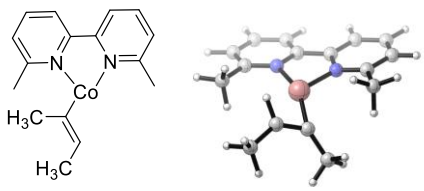
Solvation: none

G_{298}: -789.834679 Hartree

Molecular coordinates:

C	0.00000000	0.53112700	-0.53186300
H	0.00000000	0.47262000	-1.62367700
C	-1.29302000	-0.15125500	-0.04207000
C	1.29302000	-0.15125500	-0.04207100
F	-1.42585000	-0.03824500	1.30042700
F	-1.33887000	-1.45913000	-0.35825500
F	-2.35914500	0.44683700	-0.60817900
F	1.33887200	-1.45912900	-0.35825900
F	1.42584700	-0.03824900	1.30042800
F	2.35914500	0.44684000	-0.60817500
O	0.00000000	1.88632100	-0.18419700
H	0.00000000	1.97478900	0.78140200

Int5-Co(I)-S1 (E_{uB3LYP} = -875.841575 Hartree)



Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

Solvation: none

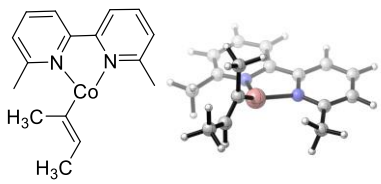
G_{298}: -875.577272 Hartree

Molecular Coordinates:

N	-0.65656200	-1.20174300	-0.14743600
C	-0.66197400	-2.55450300	-0.33590300
C	-1.83569100	-3.29281600	-0.21269700
C	-3.05264700	-1.28480400	0.23790000
C	-1.85623500	-0.57471900	0.09074400
N	-0.50165800	1.33946900	-0.18065900
C	-0.30062600	2.68893000	-0.20172600
C	-1.33011600	3.58084700	0.07813900
C	-2.81468200	1.73592000	0.43248900
C	-1.75577500	0.87430800	0.12508500
H	-1.79518000	-4.36607100	-0.36386600
H	-3.97558200	-0.75491800	0.43993900
H	-1.12921500	4.64606900	0.04024100
H	-3.78580400	1.33218500	0.69244500
Co	0.82388300	-0.05574800	-0.18038500
C	2.40529200	-0.82245700	0.39208700

C	2.92469300	0.28322000	-0.17570800
H	2.25800300	0.79051900	-0.93529600
C	3.10463100	-1.78123300	1.29879200
H	3.42399400	-2.66723600	0.73323200
H	2.44367800	-2.13374000	2.09775800
C	4.25146000	0.98284800	-0.03438900
H	4.82424900	0.55965400	0.79655100
H	4.85801300	0.88114500	-0.94355100
H	4.12904500	2.05697700	0.15097800
H	4.00665600	-1.35646800	1.76274500
C	1.07957400	3.18091700	-0.52137100
H	1.79070500	2.84396900	0.24024700
H	1.42188100	2.78743100	-1.48489000
H	1.10164100	4.27222300	-0.56285700
C	0.62617900	-3.23855500	-0.68565300
H	1.18950300	-2.65477900	-1.41639200
H	1.26169900	-3.34243700	0.19740200
H	0.42397200	-4.23538600	-1.08709800
C	-2.60637800	3.10666100	0.40727200
H	-3.41187000	3.79553900	0.63860300
C	-3.04641300	-2.66376700	0.09911300
H	-3.96043600	-3.23834600	0.20581600

Int5-Co(I)-S3 (E_{uB3LYP} = -875.871501 Hartree)



Charge: 0

Spin Multiplicity: 3

Number of Imaginary Frequencies: 0

Solvation: none

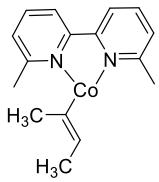
G_{298}: -875.615046 Hartree

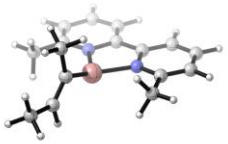
Molecular Coordinates:

N	-0.72338100	-1.30835700	-0.28177800
C	-0.63683200	-2.65962000	-0.38512900
C	-1.71617400	-3.47739400	-0.07739100
C	-3.01904100	-1.51854600	0.43386700
C	-1.90841500	-0.72926100	0.09037700
N	-0.72331100	1.30836500	-0.28176400
C	-0.63669500	2.65962800	-0.38513100
C	-1.71599600	3.47745500	-0.07740200
C	-3.01896300	1.51867700	0.43387600
C	-1.90838200	0.72933200	0.09038500
H	-1.61543100	-4.55375200	-0.16295700
H	-3.94358500	-1.05399700	0.75473500
H	-1.61520600	4.55380700	-0.16298600
H	-3.94353100	1.05418100	0.75475400
Co	0.82527300	0.00001000	-0.24248000
C	2.63830200	-0.00007600	0.52871500

C	3.68059900	-0.00005200	-0.33400100
H	3.46493700	-0.00005600	-1.40770000
C	2.82730200	-0.00011900	2.03193500
H	2.34004100	-0.87650300	2.47980500
H	2.34017400	0.87632600	2.47983100
C	5.16501300	-0.00007400	-0.04023200
H	5.38842100	-0.00018100	1.02908000
H	5.65078400	-0.88044400	-0.48292400
H	5.65077000	0.88039900	-0.48273800
H	3.87296000	-0.00020300	2.36820200
C	0.68425200	3.20627700	-0.84496400
H	1.50153900	2.76251000	-0.26401000
H	0.86234500	2.94499400	-1.89460200
H	0.71923300	4.29427000	-0.75209400
C	0.68407800	-3.20633100	-0.84500300
H	0.86207500	-2.94517300	-1.89469000
H	1.50141000	-2.76248900	-0.26417300
H	0.71906700	-4.29431300	-0.75201300
C	-2.92343000	2.89804800	0.35075400
H	-3.77179100	3.52357300	0.60888200
C	-2.92357800	-2.89792200	0.35075400
H	-3.77197400	-3.52340300	0.60888000

Int5-Co(I)-S5 (E_{uB3LYP} = -875.857875 Hartree)





Charge: 0

Spin Multiplicity: 5

Number of Imaginary Frequencies: 0

Solvation: none

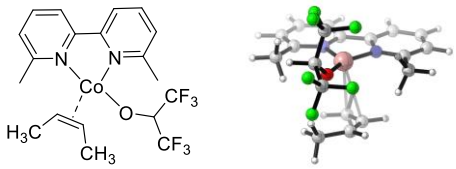
G_{298}: -875.601619 Hartree

Molecular Coordinates:

N	-0.69001600	-1.33966400	-0.09462700
C	-0.59719500	-2.69503600	-0.09429400
C	-1.71853200	-3.49893500	-0.00199000
C	-3.09682800	-1.51576000	0.08734600
C	-1.92940400	-0.71743300	0.00386500
N	-0.69002700	1.33966200	-0.09462500
C	-0.59721700	2.69503400	-0.09429000
C	-1.71856000	3.49892400	-0.00198600
C	-3.09684000	1.51573800	0.08734800
C	-1.92941000	0.71742000	0.00386600
H	-1.61193400	-4.57742300	0.00086600
H	-4.06952600	-1.04377100	0.15406900
H	-1.61197100	4.57741300	0.00087200
H	-4.06953400	1.04374100	0.15406900
Co	0.79974600	0.00000500	-0.23122800

C	2.65866300	0.00000600	0.35081400
C	3.58614700	0.00001700	-0.63171600
H	3.24089000	0.00002700	-1.67113600
C	2.99133400	-0.00000800	1.82440800
H	2.55323800	-0.87692400	2.31914500
H	2.55324100	0.87690000	2.31916100
C	5.09176300	0.00001800	-0.51300300
H	5.43503800	0.00000700	0.52382200
H	5.52020700	-0.88046900	-1.00981200
H	5.52020400	0.88051900	-1.00979200
H	4.06536800	-0.00001200	2.04799200
C	0.79051300	3.26583400	-0.19768400
H	1.42045300	2.91287000	0.62571200
H	1.27438500	2.94408700	-1.12754600
H	0.76838400	4.35765100	-0.17945300
C	0.79053900	-3.26582500	-0.19768900
H	1.27441000	-2.94406900	-1.12754800
H	1.42047500	-2.91285900	0.62571000
H	0.76841900	-4.35764200	-0.17946200
C	-2.99627900	2.88877400	0.08685700
H	-3.88962100	3.50146000	0.15449800
C	-2.99625500	-2.88879500	0.08685400
H	-3.88959300	-3.50148800	0.15449500

Int6-Co(I)-S1 (E_{uB3LYP} = -1665.768834 Hartree)



Charge: 0

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.462171Hartree

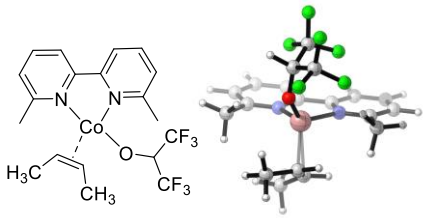
Molecular coordinates:

N	1.51738300	-1.29459300	-0.25242500
C	1.30342800	-2.61601700	-0.00743800
C	2.32742400	-3.54468700	-0.18243700
C	3.80625100	-1.78411100	-0.86410600
C	2.75843200	-0.88481600	-0.66597500
N	1.65331800	1.16853300	-0.53120600
C	1.54215100	2.51863600	-0.63115700
C	2.62458300	3.28602900	-1.05069100
C	3.94380000	1.28743100	-1.27174800
C	2.83270200	0.55777600	-0.84396800
H	2.12525100	-4.59084000	0.01899900
H	4.77371900	-1.42542000	-1.19534600
H	2.51172400	4.36200600	-1.12512200
H	4.86915000	0.77997500	-1.51789500
Co	0.25622900	0.05278400	-0.00705200
C	0.20682200	3.10389900	-0.27826700

H	-0.58191700	2.66764200	-0.90134700
H	-0.04881100	2.88128100	0.76291100
H	0.20387800	4.18718900	-0.41578200
C	-0.07196500	-3.02890200	0.42493700
H	-0.42088300	-2.42138700	1.26371400
H	-0.78148900	-2.87684500	-0.39500500
H	-0.08432300	-4.08343900	0.70881100
C	3.59107900	-3.13464000	-0.61864400
H	4.38804200	-3.85679700	-0.75991200
C	3.83966400	2.66970000	-1.37486000
H	4.68613000	3.26254600	-1.70465700
C	0.26234500	0.94862600	3.06970800
C	1.55748500	1.13841200	2.77508800
H	1.85949300	2.13554700	2.45569800
C	2.66704600	0.12884600	2.83501000
H	3.21016400	0.09428900	1.88371200
H	3.39892100	0.39823800	3.60757900
H	2.30760200	-0.87993700	3.04955100
C	-0.40419100	-0.31551200	3.52623800
H	0.28544500	-1.16219700	3.57525600
H	-0.84422700	-0.18222100	4.52265300
H	-1.21898800	-0.56570500	2.83870000
H	-0.40551900	1.80392700	2.97042000
O	-1.51241100	-0.17057900	0.41571400
C	-2.69012500	-0.54412900	-0.15191200
H	-2.93171800	-1.61114700	0.00825600
C	-3.84021800	0.23467400	0.52684800
C	-2.68844300	-0.36615700	-1.68903000

F	-3.80657100	0.01329400	1.86144300
F	-5.06395000	-0.15594200	0.09450300
F	-3.74997900	1.56878800	0.33628500
F	-1.76209100	-1.19383000	-2.23552400
F	-3.87627100	-0.68163900	-2.25812700
F	-2.37725500	0.89097700	-2.07265500

Int6-Co(I)-S3 (E_{uB3LYP} = -1665.820342 Hartree)



Charge: 0

Spin Multiplicity: 3

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.512801 Hartree

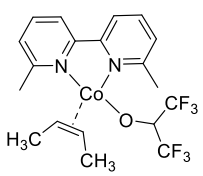
Molecular coordinates:

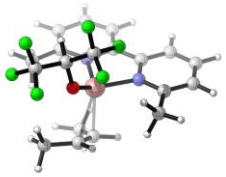
N	1.78048500	-0.77914800	-0.61196400
C	2.05379000	-1.92453000	-1.27537200
C	3.05850200	-1.97690200	-2.24122700
C	3.48267300	0.35775900	-1.87171100
C	2.46567200	0.35442100	-0.90906000
N	0.97824200	1.39233900	0.65457500
C	0.49976400	2.44605300	1.35426000
C	1.08098100	3.70907100	1.24616500
C	2.66509600	2.80567600	-0.31528900
C	2.04068500	1.56038400	-0.17448900
H	3.25545700	-2.90902300	-2.75953500
H	4.01758600	1.26887000	-2.10799700
H	0.66996100	4.53741400	1.81279800
H	3.51444700	2.92664600	-0.97573600
Co	0.22225400	-0.52288200	0.69629700
C	-0.67787700	2.18446300	2.24770400

H	-1.44073300	1.61064400	1.71526000
H	-0.37462100	1.59894600	3.12329500
H	-1.11870100	3.11880700	2.60247900
C	1.21572800	-3.12136300	-0.92896300
H	1.53838800	-3.55566900	0.02321100
H	0.16753000	-2.82640100	-0.81507400
H	1.29744500	-3.89443400	-1.69668700
C	3.78669400	-0.82262400	-2.53862300
H	4.56839400	-0.84181400	-3.29108700
C	2.17979400	3.89133300	0.40334600
H	2.64547500	4.86663400	0.30606000
C	0.19554600	-1.43915600	2.67986200
C	1.47828300	-0.94663100	2.63271200
H	1.63304600	0.07735000	2.96558600
C	2.73939300	-1.72668600	2.38044900
H	3.41660700	-1.17633700	1.71915100
H	3.27561900	-1.90009100	3.32377100
H	2.54752400	-2.70145000	1.92751500
C	-0.23070200	-2.87837900	2.53197900
H	0.54839700	-3.50376600	2.09025900
H	-0.47275700	-3.30123700	3.51617400
H	-1.12612800	-2.94772700	1.90730900
H	-0.57580600	-0.77934400	3.07853900
O	-1.51657400	-1.09379600	0.08733800
C	-2.42919700	-0.67254900	-0.81862500
H	-2.75499900	-1.47313400	-1.51206000
C	-3.72805000	-0.23437300	-0.09785700
C	-1.90009800	0.44044000	-1.75723800

F	-4.23657000	-1.28022400	0.59235800
F	-4.69855500	0.18460400	-0.95015500
F	-3.52362500	0.76706500	0.79253900
F	-0.73907900	0.03401100	-2.33171500
F	-2.75473800	0.72818300	-2.76849500
F	-1.63316100	1.60441900	-1.11657300

Int6-Co(I)-S5 (E_{uB3LYP} = -1665.799630 Hartree)





Charge: 0

Spin Multiplicity: 5

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.494376 Hartree

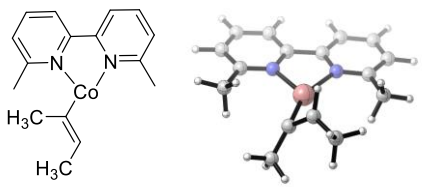
Molecular coordinates:

N	1.45699100	-1.21825900	-0.67605100
C	1.26133400	-2.49942500	-1.07741800
C	2.17126300	-3.15319600	-1.88820400
C	3.53845600	-1.15773900	-1.90969700
C	2.58892900	-0.51211800	-1.07692400
N	1.70439200	1.30579200	0.22802700
C	1.73794000	2.56857600	0.71920700
C	2.77077500	3.43732600	0.41365600
C	3.78867800	1.70209600	-0.93041000
C	2.71448900	0.83526500	-0.60353800
H	1.98729300	-4.17621500	-2.19410200
H	4.42621100	-0.62510500	-2.22817100
H	2.76962600	4.44378800	0.81480400
H	4.58430200	1.35566700	-1.57852900
Co	0.32253500	-0.10634400	0.54617000
C	0.59949500	2.95954900	1.62123800

H	-0.36406300	2.78048000	1.13517900
H	0.61919000	2.36991500	2.54622900
H	0.65964700	4.01465000	1.89553000
C	-0.00006700	-3.16178800	-0.59664800
H	-0.05864500	-3.14478100	0.49640500
H	-0.88730900	-2.63895900	-0.96757700
H	-0.04957200	-4.20086400	-0.92822200
C	3.33616200	-2.45857100	-2.30970500
H	4.06375100	-2.95212800	-2.94608800
C	3.81619300	2.98465600	-0.43199600
H	4.63539300	3.64948400	-0.68708800
C	-0.01596200	-0.76809600	2.95708500
C	1.31967900	-0.83362900	2.73948500
H	1.87997500	0.09919200	2.79101000
C	2.15450000	-2.06460800	2.52515000
H	2.81210500	-1.93968700	1.65981900
H	2.79533100	-2.23074100	3.40004100
H	1.55480900	-2.96312800	2.37011100
C	-0.99245300	-1.90466300	3.03312800
H	-0.53430000	-2.87363600	2.82485700
H	-1.42559300	-1.94671600	4.03993200
H	-1.81275800	-1.73781600	2.32911800
H	-0.44217500	0.21543700	3.15507300
O	-1.55194400	-0.05037200	0.49574400
C	-2.32353800	0.09179600	-0.62442900
H	-1.91455600	-0.40033900	-1.52585800
C	-3.68665800	-0.58758500	-0.37872100
C	-2.45721400	1.58055000	-1.01214800

F	-3.48362600	-1.90216600	-0.10966300
F	-4.49804400	-0.52739800	-1.46097500
F	-4.35591200	-0.06217900	0.66501200
F	-1.21641000	2.07305700	-1.27134800
F	-3.19876700	1.77242400	-2.12597600
F	-2.98649100	2.33655800	-0.02966000

Int5-Co(II)-S2 (E_{uB3LYP} = -875.682192 Hartree)



Charge: 1

Spin Multiplicity: 2

Number of Imaginary Frequencies: 0

Solvation: none

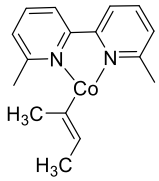
G_{298}: -875.41854 Hartree

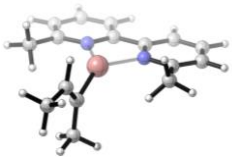
Molecular Coordinates:

N	0.51508200	1.38066600	-0.00113600
C	0.27558300	2.70889000	0.02729800
C	1.33512700	3.61872900	0.11431600
C	2.87649400	1.77440600	0.14246300
C	1.78565500	0.91100400	0.05159700
N	0.72776300	-1.24550200	-0.07600700
C	0.73585600	-2.59537000	-0.17745500
C	1.94752700	-3.29823900	-0.18663900
C	3.13194500	-1.22240000	-0.00479700
C	1.90552400	-0.56252700	-0.00354100
H	1.12508300	4.68170300	0.13687900
H	3.88840100	1.39446800	0.19051300
H	1.92962900	-4.37852200	-0.26815700
H	4.05858800	-0.66724100	0.05400700
Co	-0.86438100	-0.08428600	0.01946100
C	-2.53406100	-0.82127300	0.20953100

C	-2.98862200	0.12249200	-0.65685100
H	-2.39901500	0.31404000	-1.57000500
C	-3.27341400	-1.57681100	1.25796900
H	-2.67894800	-1.73297700	2.16253500
H	-3.54274700	-2.56526300	0.86469800
C	-4.27431600	0.91073500	-0.59229700
H	-4.78427100	0.77493100	0.36374800
H	-4.08482500	1.98018400	-0.73284400
H	-4.95387000	0.59527400	-1.39257600
H	-4.21287600	-1.08296400	1.53456600
C	-0.56607600	-3.33332700	-0.27484100
H	-1.10468500	-3.28515200	0.67557800
H	-1.21010500	-2.89402300	-1.03963500
H	-0.39013000	-4.38295700	-0.51609200
C	-1.15206300	3.16779000	-0.04939900
H	-1.56476300	2.97047700	-1.04463800
H	-1.77343000	2.63553900	0.67635500
H	-1.22722700	4.23933600	0.14253200
C	3.15137800	-2.61202700	-0.09329600
H	4.09448800	-3.14803800	-0.09718100
C	2.64263900	3.14786700	0.17406400
H	3.47399800	3.84112000	0.24552800

Int5-Co(II)-S4 (E_{uB3LYP} = -875.687853 Hartree)





Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 0

Solvation: none

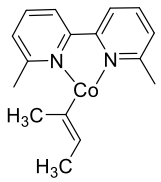
G_{298}: -875.430881 Hartree

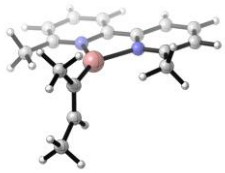
Molecular Coordinates:

N	0.71029300	1.34411200	-0.13711400
C	0.59604400	2.68788900	-0.15030400
C	1.73176900	3.49390100	-0.01221500
C	3.08030100	1.50528400	0.13902300
C	1.92026900	0.74473900	0.00306800
N	0.71076600	-1.34393100	-0.13712700
C	0.59697700	-2.68776900	-0.15037300
C	1.73298300	-3.49337400	-0.01237000
C	3.08084300	-1.50429900	0.13886200
C	1.92052200	-0.74415400	0.00301300
H	1.62679800	4.57255600	-0.01981800
H	4.04770600	1.03453800	0.25177200
H	1.62841300	-4.57206900	-0.01999300
H	4.04808300	-1.03320100	0.25154600
Co	-0.84725400	-0.00021400	-0.19117500
C	-2.64563700	-0.00038400	0.46250600
C	-3.51214700	-0.00006900	-0.57439300

H	-3.10763400	0.00033500	-1.59498900
C	-3.01412400	-0.00095100	1.92172500
H	-2.59918200	0.87733500	2.43151300
H	-2.59962900	-0.87989600	2.43074100
C	-5.01891000	-0.00027700	-0.54263200
H	-5.41757000	-0.00046500	0.47310300
H	-5.41223200	0.87968600	-1.06580700
H	-5.41196300	-0.88024200	-1.06601300
H	-4.09554300	-0.00075400	2.09657800
C	-0.77473700	-3.26759200	-0.34152500
H	-1.52062000	-2.72267300	0.24424400
H	-1.07019500	-3.20128700	-1.39543200
H	-0.79981800	-4.32003700	-0.05373600
C	-0.77587100	3.26724200	-0.34145900
H	-1.07152400	3.20035700	-1.39527700
H	-1.52148300	2.72236000	0.24468900
H	-0.80120000	4.31980700	-0.05415000
C	2.98009000	-2.89565500	0.13193700
H	3.87133000	-3.50478000	0.24006100
C	2.97906400	2.89661900	0.13214500
H	3.87009700	3.50603200	0.24034400

Int5-Co(II)-S6 (E_{uB3LYP} = -875.585850 Hartree)





Charge: 1

Spin Multiplicity: 6

Number of Imaginary Frequencies: 0

Solvation: none

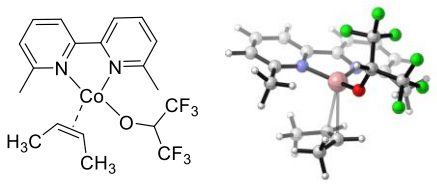
G_{298}: -875.330762 Hartree

Molecular Coordinates:

N	0.68671100	1.32963300	0.06485900
C	0.60879300	2.65218300	0.08182400
C	1.77032000	3.47383500	-0.05089200
C	3.13499000	1.50472200	-0.21707600
C	1.93666300	0.69360600	-0.08082300
N	0.68553700	-1.32989900	0.06477100
C	0.60648100	-2.65238600	0.08158900
C	1.76729400	-3.47502300	-0.05129000
C	3.13367900	-1.50708800	-0.21719900
C	1.93604800	-0.69494600	-0.08088400
H	1.65698700	4.55125100	-0.03694400
H	4.09907700	1.02768500	-0.33038900
H	1.65301600	-4.55234200	-0.03754100
H	4.09818200	-1.03086800	-0.33041200
Co	-0.87755900	0.00053000	0.24037300

C	-2.79654700	0.00053500	0.26875700
C	-3.26966600	0.00162100	-1.00143300
H	-2.54086600	0.00222500	-1.82316600
C	-3.65521700	-0.00044700	1.50712500
H	-3.44166600	0.87668000	2.13068200
H	-3.44148000	-0.87842700	2.12941900
C	-4.69493900	0.00214400	-1.48450100
H	-5.41795600	0.00153100	-0.66729500
H	-4.88580900	0.88184800	-2.11150900
H	-4.88595600	-0.87648800	-2.11296600
H	-4.73054900	-0.00041300	1.29867600
C	-0.73382300	-3.29772500	0.25785100
H	-1.54904700	-2.57438200	0.18284500
H	-0.88070200	-4.08137500	-0.49220600
H	-0.78467300	-3.78200200	1.24074100
C	-0.73095500	3.29863100	0.25825000
H	-0.87735700	4.08222300	-0.49196200
H	-1.54678800	2.57593300	0.18357300
H	-0.78123200	3.78317900	1.24103500
C	3.03398300	-2.87527500	-0.19984700
H	3.92032100	-3.49186400	-0.30096100
C	3.03647900	2.87299900	-0.19954000
H	3.92335500	3.48882900	-0.30056400

Int6-Co(II)-S2 (E_{uB3LYP} = -1665.596162 Hartree)



Charge: 1

Spin Multiplicity: 2

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.283639 Hartree

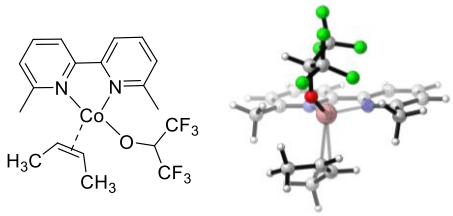
Molecular coordinates:

N	1.98660300	-0.62555500	-0.60676700
C	2.41337400	-1.77127100	-1.17135700
C	3.64230300	-1.80232400	-1.84047800
C	3.94059400	0.53622700	-1.35100500
C	2.71311200	0.51890000	-0.69627400
N	0.87455000	1.41407300	0.52459700
C	0.20886000	2.36754500	1.20582900
C	0.74187400	3.66330700	1.29018800
C	2.64901100	2.94756400	0.01635000
C	2.08301600	1.68041700	-0.04651900
H	3.97813400	-2.72935000	-2.29120100
H	4.51888100	1.44848200	-1.42198400
H	0.18918500	4.42272700	1.83167400
H	3.60708200	3.15055400	-0.44484100
Co	0.24420800	-0.42465500	0.21673000
C	-1.07025200	2.01833500	1.90459800

H	-1.45131800	1.04522900	1.60335600
H	-0.90422800	2.01125800	2.98832300
H	-1.83806900	2.76753600	1.69638800
C	1.54686200	-2.99122300	-1.05032600
H	1.91348700	-3.64328200	-0.25099600
H	0.50864100	-2.73552300	-0.82229900
H	1.56319000	-3.56591300	-1.97939400
C	4.41025300	-0.64603000	-1.92486500
H	5.36378500	-0.65803700	-2.44193700
C	1.95710400	3.95740400	0.68852500
H	2.37210000	4.95799200	0.74599800
C	0.13250700	-1.66561600	2.44295300
C	1.34624700	-1.06555300	2.47912600
H	1.37226100	-0.01714000	2.77080100
C	2.68988700	-1.72028100	2.33195600
H	3.37111700	-1.10752000	1.73410700
H	3.15069100	-1.83098100	3.32105100
H	2.63199300	-2.71434600	1.88526000
C	-0.16677900	-3.11787800	2.22099300
H	0.70096000	-3.69362700	1.89394500
H	-0.52315200	-3.55945900	3.15951400
H	-0.97438000	-3.22937900	1.49179700
H	-0.73428600	-1.05720300	2.69072600
O	-1.53324800	-0.95055600	0.25832300
C	-2.48936100	-0.68973400	-0.70269000
H	-2.66655300	-1.57354700	-1.33494700
C	-3.84610400	-0.39111100	-0.02934600
C	-2.05601700	0.42660600	-1.67763400

F	-4.25312100	-1.47996800	0.64931800
F	-4.79372700	-0.08433800	-0.93862300
F	-3.76751100	0.63237900	0.84900300
F	-0.74899400	0.17873400	-2.05160100
F	-2.78169400	0.46699000	-2.79692900
F	-2.05319300	1.65624000	-1.12323400

Int6-Co(II)-S4 (E_{uB3LYP} = -1665.628122 Hartree)



Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.318071 Hartree

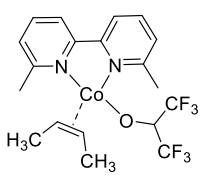
Molecular coordinates:

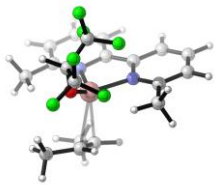
N	1.87691900	-0.73230800	-0.67686300
C	2.19280300	-1.82441900	-1.39829500
C	3.32332800	-1.82056500	-2.22249800
C	3.76253900	0.44883400	-1.54391300
C	2.62386900	0.39805200	-0.74217600
N	1.01023000	1.34912300	0.78630700
C	0.48231600	2.32630400	1.55014600
C	1.09796300	3.58133500	1.60993700
C	2.79664900	2.78152800	0.10196200
C	2.14399300	1.55094700	0.06876500
H	3.56769300	-2.70289300	-2.80263000
H	4.36584300	1.34486100	-1.60244800
H	0.66115600	4.36292700	2.22044400
H	3.70029400	2.95119300	-0.46806900
Co	0.21382400	-0.51429600	0.48793500
C	-0.75592400	2.00299000	2.33348400
H	-1.49670100	1.49332500	1.71299200

H	-0.50963900	1.34973300	3.17915800
H	-1.21091100	2.90854300	2.73754300
C	1.29896100	-3.02305600	-1.26658200
H	1.58324000	-3.61330400	-0.38835700
H	0.25355800	-2.72423600	-1.14716900
H	1.38057300	-3.67128300	-2.14101900
C	4.11354400	-0.67800500	-2.28826900
H	4.99393300	-0.65625600	-2.92189600
C	2.26021100	3.80731800	0.88073300
H	2.74912100	4.77523900	0.91418300
C	-0.22125200	-1.87208400	2.51064100
C	1.06932600	-1.46179000	2.61764300
H	1.24214300	-0.46867300	3.03285500
C	2.30866100	-2.27881500	2.38376900
H	3.04457800	-1.72652900	1.79103200
H	2.78115800	-2.50106300	3.34814900
H	2.10343300	-3.22949600	1.88957200
C	-0.72311200	-3.22503900	2.10546500
H	0.06029200	-3.87463900	1.71100200
H	-1.15975500	-3.72037700	2.98128200
H	-1.51722900	-3.12177900	1.36134700
H	-0.99511100	-1.17193900	2.82527500
O	-1.51484300	-0.95519400	0.01270300
C	-2.37039300	-0.47183900	-0.94968400
H	-2.54897800	-1.20382000	-1.75332400
C	-3.74770700	-0.21513600	-0.29974700
C	-1.81665300	0.78247700	-1.65908200
F	-4.25240300	-1.38162500	0.14742900

F	-4.62814600	0.31399400	-1.17159400
F	-3.65774200	0.62187700	0.75951300
F	-0.52463500	0.52957200	-2.03855700
F	-2.50067400	1.10793000	-2.76102100
F	-1.76394900	1.87003800	-0.85529000

Int6-Co(II)-S6 (E_{uB3LYP} = -1665.527482 Hartree)





Charge: 1

Spin Multiplicity: 6

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.223065 Hartree

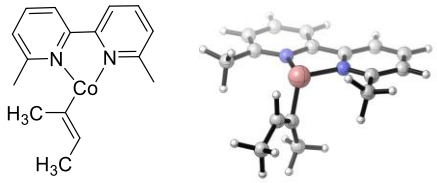
Molecular coordinates:

N	1.88330500	-0.73891100	-0.64567900
C	2.25446200	-1.79716600	-1.34357900
C	3.46232500	-1.80598500	-2.10476200
C	3.90236500	0.45262900	-1.40585000
C	2.65896300	0.43926100	-0.65494900
N	0.94434800	1.37255400	0.73208000
C	0.40426700	2.37844900	1.39646800
C	1.03993200	3.65912900	1.46195500
C	2.84618100	2.82035000	0.11580600
C	2.17068500	1.53277800	0.05258600
H	3.73044300	-2.69537900	-2.66231700
H	4.52211900	1.33881500	-1.40914000
H	0.55934700	4.45838800	2.01322900
H	3.79220600	2.95884300	-0.38940100
Co	0.19932900	-0.50386500	0.46619600
C	-0.89863400	2.16519300	2.09918100

H	-1.29430300	1.16250300	1.93483000
H	-0.77903000	2.34140600	3.17442800
H	-1.64218100	2.88266400	1.73643900
C	1.37723900	-3.01093900	-1.32527800
H	1.91726100	-3.86399100	-0.89910800
H	0.46317400	-2.84315000	-0.75268300
H	1.09905000	-3.28823300	-2.34779500
C	4.28308400	-0.66013800	-2.11358700
H	5.20763000	-0.65802700	-2.68047600
C	2.27404900	3.85598800	0.80993000
H	2.76591600	4.82139300	0.85692600
C	-0.15395500	-1.88256400	2.51162700
C	1.11872600	-1.41809700	2.59758000
H	1.25593100	-0.42341200	3.02162600
C	2.38452100	-2.18111000	2.32416500
H	3.11205900	-1.56383600	1.78907100
H	2.84796000	-2.46684500	3.27635400
H	2.21347900	-3.09445300	1.75177200
C	-0.60230200	-3.25259000	2.10017200
H	0.20027100	-3.85743200	1.67343700
H	-0.98629400	-3.78233600	2.98061900
H	-1.42423900	-3.17874400	1.38310400
H	-0.95072100	-1.22127000	2.85098800
O	-1.54809700	-0.96938300	0.08000600
C	-2.42012800	-0.53230700	-0.88922800
H	-2.60113500	-1.29680000	-1.66152100
C	-3.79233900	-0.26230900	-0.23427400
C	-1.89027300	0.69953500	-1.65597400

F	-4.28915700	-1.41692100	0.25106300
F	-4.68225000	0.23745700	-1.11510300
F	-3.69750500	0.60595600	0.79807500
F	-0.58627100	0.46310500	-2.00627600
F	-2.56761100	0.94531000	-2.78303800
F	-1.87883300	1.83100100	-0.91410500

Int5-Co(III)-S1 (E_{uB3LYP} = -875.308904 Hartree)



Charge: 2

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

Solvation: none

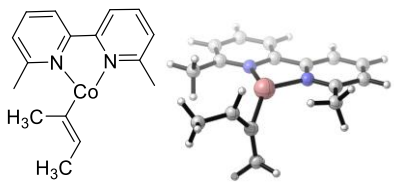
G_{298}: -875.044406 Hartree

Molecular Coordinates:

N	-1.27103800	0.51805200	-0.25893400
C	-2.60880700	0.33712200	-0.35461300
C	-3.45812600	1.41770800	-0.08768900
C	-1.53923900	2.81396100	0.35340300
C	-0.72638400	1.72456300	0.07871400
N	1.27579100	0.50675500	-0.25882600
C	2.61190700	0.31399000	-0.35437900
C	3.47075200	1.38697400	-0.08727800
C	1.56428000	2.80017600	0.35364300
C	0.74182800	1.71803800	0.07879400
H	-4.52975500	1.27664200	-0.16964100
H	-1.11006300	3.77228200	0.61857900
H	4.54109600	1.23640600	-0.16911900
H	1.14357100	3.76225400	0.61877400
Co	-0.00351300	-0.81567300	-0.55756700
C	-0.00878200	-1.91778200	0.82960100

C	-0.01293000	-2.94115100	-0.04517400
H	-0.01121100	-2.71436500	-1.13836200
C	-0.00869000	-1.72853200	2.28866200
H	0.87765100	-1.17171900	2.60979300
H	-0.01129600	-2.69847100	2.80001100
C	-0.01986300	-4.42190700	0.22187100
H	-0.02162700	-4.62985300	1.29225400
H	-0.90344400	-4.87847200	-0.23746000
H	0.86022500	-4.88652500	-0.23609800
H	-0.89231300	-1.16713500	2.60931400
C	3.12087800	-1.04557700	-0.73421300
H	3.03785300	-1.74157700	0.10771400
H	2.56992900	-1.46058400	-1.58493500
H	4.17229400	-0.99298200	-1.02012900
C	-3.12976000	-1.01794100	-0.73429100
H	-2.58269900	-1.43776300	-1.58515400
H	-3.05254800	-1.71463100	0.10762300
H	-4.18076900	-0.95616400	-1.01985600
C	2.94990000	2.62589200	0.27267900
H	3.61462200	3.45756900	0.48199200
C	-2.92634200	2.65197700	0.27225200
H	-3.58367300	3.48954100	0.48142600

Int5-Co(III)-S3 (E_{uB3LYP} = -875.311646 Hartree)



Charge: 2

Spin Multiplicity: 3

Number of Imaginary Frequencies: 0

Solvation: none

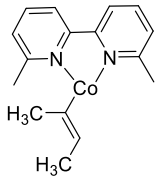
G_{298}: -875.053391 Hartree

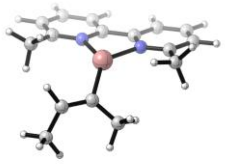
Molecular Coordinates:

N	-1.20433300	-0.93008900	-0.18113000
C	-1.74175100	-2.16700300	-0.26352500
C	-3.12391200	-2.33468800	-0.12408600
C	-3.35130100	0.04808700	0.18078900
C	-1.97648400	0.17900900	0.03090200
N	0.09299700	1.42786200	-0.10151300
C	0.84178800	2.55528500	-0.11187200
C	0.23261300	3.80128400	0.05941200
C	-1.90512900	2.70049300	0.23942700
C	-1.26093500	1.48015100	0.06620400
H	-3.55109000	-3.32865300	-0.19573200
H	-3.97785800	0.91408200	0.34832500
H	0.83931600	4.69919300	0.04915300
H	-2.97785200	2.75314700	0.37012800
Co	0.69823100	-0.47304200	-0.27817700
C	2.14707800	-1.46529700	0.55608100

C	2.95579500	-1.31487500	-0.50464100
H	2.55430500	-1.48334600	-1.51627900
C	2.21914200	-1.85761500	1.97112200
H	1.55654000	-1.28223900	2.62078000
H	3.25754900	-1.75497500	2.32127600
C	4.41183100	-0.92473500	-0.45735000
H	4.75153800	-0.72122600	0.55838700
H	4.99394200	-1.75637600	-0.87567900
H	4.59488300	-0.05153200	-1.09072000
H	1.96936600	-2.92343400	2.06373700
C	2.32222100	2.40923400	-0.31281000
H	2.77066500	1.82446200	0.49775100
H	2.53715100	1.91102400	-1.26504500
H	2.81249200	3.38321400	-0.33155100
C	-0.82961000	-3.33396500	-0.50043900
H	0.19256800	-3.00929500	-0.72814300
H	-0.79041100	-3.98163700	0.38202500
H	-1.18390100	-3.94247600	-1.33734200
C	-1.14555800	3.87275800	0.23795800
H	-1.63147500	4.83356300	0.37222400
C	-3.92748600	-1.22419800	0.10418800
H	-5.00041900	-1.33932100	0.21784700

Int5-Co(III)-S5 (E_{uB3LYP} = -875.296470 Hartree)





Charge: 2

Spin Multiplicity: 5

Number of Imaginary Frequencies: 0

Solvation: none

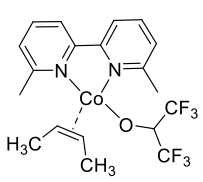
G_{298}: -875.037675 Hartree

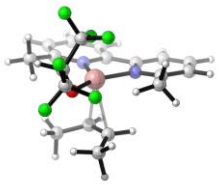
Molecular Coordinates:

N	-1.30787900	-0.87228400	-0.18571000
C	-1.92463900	-2.06918200	-0.29934700
C	-3.27843300	-2.19284400	0.03337500
C	-3.33106100	0.16010500	0.55888600
C	-1.98833600	0.24325400	0.21340100
N	0.07320300	1.43058200	-0.23582500
C	0.84070900	2.53715600	-0.36432700
C	0.32411900	3.79201300	-0.03219100
C	-1.76645000	2.74273000	0.54903000
C	-1.22008800	1.51350800	0.19562300
H	-3.76613200	-3.15643200	-0.06334000
H	-3.88177200	1.03554100	0.87650600
H	0.94512800	4.67309300	-0.14573200
H	-2.78829700	2.81882800	0.89624200
Co	0.62806100	-0.47823500	-0.47824400
C	2.31270300	-1.48569800	0.11373200

C	3.53537300	-0.86479900	0.01747100
H	3.75552900	-0.29333700	-0.88694100
C	2.05906700	-2.77819300	0.82055600
H	1.08554100	-2.81279800	1.31458400
H	2.85027600	-2.99951000	1.54724100
C	4.60990400	-0.87356100	1.04390100
H	4.31563700	-1.32350800	1.99141100
H	5.45603800	-1.44099200	0.61703600
H	4.99986800	0.13674400	1.21280700
H	2.08488300	-3.59548700	0.08461600
C	2.24705400	2.36223500	-0.85741900
H	2.90978300	2.07134500	-0.03408400
H	2.29887600	1.60330800	-1.64631200
H	2.63423500	3.29375700	-1.27395000
C	-1.12824100	-3.24213500	-0.79005100
H	-0.16838700	-2.93433600	-1.21837600
H	-0.93541900	-3.95258000	0.02098200
H	-1.67765800	-3.77978300	-1.56777700
C	-0.98157600	3.89256400	0.43739900
H	-1.39518900	4.85940700	0.70460500
C	-3.97849900	-1.07731800	0.47548100
H	-5.02750300	-1.15799800	0.74070400

Int6-Co(III)-S1 (E_{uB3LYP} = -1665.200000 Hartree)





Charge: 2

Spin Multiplicity:1

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1664.880483 Hartree

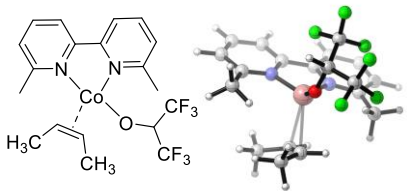
Molecular coordinates:

N	1.74315400	-1.13989100	-0.15308700
C	1.68791600	-2.48512000	-0.27203600
C	2.87581400	-3.18952700	-0.51532500
C	4.09943300	-1.11661700	-0.57019700
C	2.90649600	-0.44937500	-0.33028500
N	1.42494000	1.37064900	-0.11395300
C	1.03719800	2.66163000	-0.18192900
C	2.00441300	3.65228900	-0.40670200
C	3.71010500	1.95473300	-0.52338700
C	2.72394400	1.00326700	-0.30693500
H	2.83207900	-4.26917500	-0.60385300
H	5.02197600	-0.56565100	-0.70542000
H	1.68986900	4.68901700	-0.45686000
H	4.74178700	1.66046500	-0.67169200
Co	0.20795500	-0.07385500	0.24963100
C	-0.41560100	3.01406300	-0.04473600

H	-1.02527000	2.18816700	0.32405500
H	-0.54274800	3.86581500	0.62901800
H	-0.81662800	3.30953300	-1.02019800
C	0.36738700	-3.19543800	-0.20899200
H	0.50865600	-4.23263000	0.09875800
H	-0.33023500	-2.72006800	0.47957300
H	-0.08289100	-3.21056000	-1.20900700
C	4.08182200	-2.51144800	-0.64869000
H	5.00076300	-3.05914700	-0.82989000
C	3.33994200	3.30285400	-0.56397600
H	4.09041100	4.06843900	-0.73082800
C	0.04097300	0.80981500	2.54933300
C	0.83943600	-0.31910000	2.40189500
H	1.89595300	-0.12985400	2.22708700
C	0.48280000	-1.67697200	2.92484400
H	1.10789300	-2.45505400	2.48540500
H	0.68293900	-1.68630000	4.00546500
H	-0.56998700	-1.92555500	2.78502400
C	-1.31685700	0.86078000	3.12900200
H	-1.82551900	-0.10068900	3.15273100
H	-1.18635700	1.20753200	4.16944500
H	-1.94646600	1.60879600	2.64067000
H	0.51083100	1.76712900	2.33347200
O	-1.46469100	-0.53639000	0.61769600
C	-2.39190800	-0.76588300	-0.40273000
H	-2.55881200	-1.84242400	-0.53561500
C	-3.74526600	-0.14974600	0.02621900
C	-1.90347800	-0.21592000	-1.76477000

F	-4.20531100	-0.80703500	1.09746300
F	-4.63229900	-0.24501400	-0.97159300
F	-3.59532200	1.14925000	0.35914500
F	-0.45669500	-0.25001000	-1.69670700
F	-2.22891300	-0.96707000	-2.79371400
F	-2.19474500	1.05281500	-2.00829200

Int6-Co(III)-S3 (E_{uB3LYP} = -1665.204025 Hartree)



Charge: 2

Spin Multiplicity: 3

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1664.893032 Hartree

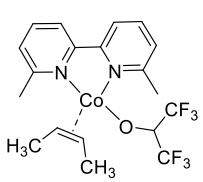
Molecular coordinates:

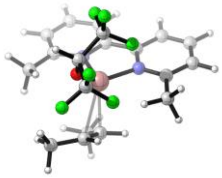
N	1.90928800	-0.58131200	-0.65689700
C	2.28166500	-1.66584500	-1.36723100
C	3.45397200	-1.60349800	-2.13170800
C	3.77766000	0.68390000	-1.42673200
C	2.61657000	0.58872100	-0.67415600
N	0.89281700	1.30791900	0.81196300
C	0.25238200	2.15767100	1.64418900
C	0.76226900	3.45356900	1.80899600
C	2.56946400	2.93047200	0.29920800
C	2.03913900	1.65791100	0.15160200
H	3.75953300	-2.47546200	-2.69951400
H	4.34838300	1.60396800	-1.44922300
H	0.24313400	4.13991700	2.46838100
H	3.47371100	3.21688700	-0.22337700
Co	0.29920200	-0.47506800	0.36638500
C	-0.95114800	1.68401100	2.40056200

H	-1.54821900	0.97210200	1.83022800
H	-0.63813400	1.21433600	3.34147600
H	-1.59470600	2.52679700	2.65840500
C	1.40708200	-2.88297400	-1.34926300
H	2.01045500	-3.79159400	-1.28347900
H	0.70033200	-2.87583100	-0.51675900
H	0.83117300	-2.93877600	-2.28025400
C	4.20073800	-0.43134300	-2.15950400
H	5.10870500	-0.37671500	-2.75128200
C	1.91319100	3.84143300	1.13439800
H	2.30683600	4.84516400	1.25732600
C	-0.12111100	-2.00399000	2.32295500
C	1.18984400	-1.60858200	2.37293700
H	1.39088200	-0.63203600	2.81649800
C	2.39616700	-2.45681300	2.10902100
H	3.19230100	-1.88744800	1.62181600
H	2.79994000	-2.78850800	3.07494200
H	2.17851400	-3.35079200	1.52365200
C	-0.65053000	-3.34868500	1.95260100
H	0.09476100	-4.00776800	1.50562600
H	-1.01333100	-3.83440700	2.86909900
H	-1.51730900	-3.26116100	1.29118500
H	-0.86468200	-1.29955800	2.69598500
O	-1.36404200	-0.90322900	-0.08046100
C	-2.30314700	-0.43621800	-0.99653600
H	-2.39682600	-1.16834500	-1.81268100
C	-3.68499500	-0.38417400	-0.29277100
C	-1.85581000	0.89730400	-1.63478200

F	-4.02826000	-1.62834300	0.07080400
F	-4.61154600	0.11436300	-1.11131400
F	-3.62538300	0.37642000	0.82061600
F	-0.54094800	0.75737600	-2.00294000
F	-2.56231600	1.20298600	-2.71137800
F	-1.89896100	1.92146500	-0.76077900

Int6-Co(III)-S5 (E_{uB3LYP} = -1665.207758 Hartree)





Charge: 2

Spin Multiplicity: 5

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1664.899234 Hartree

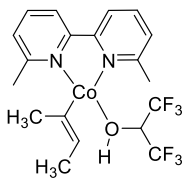
Molecular coordinates:

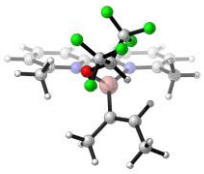
N	1.86556600	-0.88079900	-0.61285600
C	2.10500600	-2.05319800	-1.24187500
C	3.29976100	-2.22663300	-1.95278100
C	3.96427500	0.00669300	-1.34442700
C	2.76621000	0.14362600	-0.65458500
N	1.18253000	1.31016600	0.73561600
C	0.70335300	2.36077700	1.44188500
C	1.44593200	3.54318200	1.50901600
C	3.14269900	2.52712200	0.12415700
C	2.38018400	1.36767100	0.07995000
H	3.48119000	-3.16702400	-2.46085300
H	4.68445300	0.81376700	-1.37677000
H	1.05876300	4.38318200	2.07508500
H	4.08901800	2.59146700	-0.39669600
Co	0.19665600	-0.37077600	0.41227100
C	-0.60910100	2.21428800	2.15142500

H	-1.11771900	1.28054200	1.89845700
H	-0.46494600	2.24978400	3.23687600
H	-1.28507800	3.03132200	1.88448800
C	1.09472600	-3.15714900	-1.14460600
H	1.35436900	-3.83356400	-0.32169800
H	0.08500700	-2.77800400	-0.98213600
H	1.09313600	-3.75512100	-2.05842200
C	4.23081300	-1.19696800	-2.00328200
H	5.15840900	-1.32180700	-2.55214400
C	2.66602500	3.62589200	0.84704800
H	3.24935800	4.53997800	0.88798300
C	-0.83443100	-1.82344800	2.31193000
C	0.42819200	-1.32680400	2.57895100
H	0.46659800	-0.34023400	3.04348200
C	1.70846600	-2.10621000	2.59496800
H	2.56101000	-1.48642200	2.30481100
H	1.90006700	-2.43078300	3.62754500
H	1.68097200	-2.99856800	1.96891400
C	-1.18676500	-3.21305900	1.92825900
H	-0.33398100	-3.82003800	1.62555900
H	-1.63909300	-3.68903800	2.81269300
H	-1.96049500	-3.22892400	1.15604200
H	-1.67537500	-1.15205800	2.48731800
O	-1.25353000	-0.82138700	-0.48568000
C	-2.33765000	-0.27728500	-1.17505400
H	-2.61570900	-0.93682800	-2.00615100
C	-3.54443500	-0.23635200	-0.20006000
C	-1.94156500	1.09354100	-1.76828400

F	-3.82651400	-1.49548800	0.18274100
F	-4.61299200	0.30462000	-0.77043100
F	-3.23387600	0.46592300	0.91702900
F	-0.82898400	0.92528100	-2.51790300
F	-2.90520100	1.60624200	-2.51974300
F	-1.62335400	1.97461700	-0.78673600

Int7-Co(I) (E_{uB3LYP} = -1665.757716 Hartree)





Charge: 0

Spin Multiplicity: 3

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.453461 Hartree

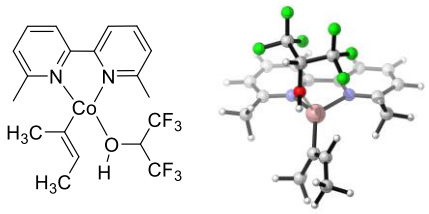
Molecular coordinates:

N	-2.37134200	-1.16761600	-0.16397500
C	-2.43139300	-2.51161100	-0.33033300
C	-3.60339200	-3.13517700	-0.75283200
C	-4.67208300	-0.98603400	-0.84993900
C	-3.46427600	-0.40586600	-0.44225000
N	-2.01337900	1.42773200	0.06925800
C	-1.71493800	2.74629000	0.14901200
C	-2.67762300	3.72178000	-0.11591400
C	-4.27211800	1.98474700	-0.56286500
C	-3.26450500	1.04623000	-0.30563500
H	-3.62182300	-4.21249500	-0.87473000
H	-5.54050700	-0.37140100	-1.05051100
H	-2.40877300	4.76956000	-0.04162300
H	-5.26837000	1.66531700	-0.84133400
C	0.51172200	-0.33999400	2.21668400
C	1.25931800	-1.47403200	2.25870100

H	1.26706200	-2.11757300	1.37375900
C	0.45333200	0.59307800	3.41530300
H	-0.58386900	0.87158800	3.63823400
H	0.97799400	1.53322600	3.19575200
C	2.11199400	-2.02573100	3.37896600
H	2.10538600	-1.39940100	4.27296100
H	1.77123900	-3.02915300	3.66781800
H	3.15725700	-2.13356500	3.05863300
H	0.89081300	0.19188700	4.33828400
C	-0.31426900	3.11393600	0.53762700
H	-0.19380900	4.19859400	0.58503100
H	-0.06890300	2.68738500	1.51479000
H	0.41117500	2.70800700	-0.17226500
C	-1.18284600	-3.28541000	-0.02402200
H	-0.36975500	-2.98495600	-0.69240900
H	-0.85245200	-3.07685100	0.99971600
H	-1.34614700	-4.35967300	-0.13595700
C	-3.97393500	3.33740800	-0.46526400
H	-4.73664800	4.08367800	-0.66325100
C	-4.74238800	-2.36432300	-1.00582800
H	-5.66691400	-2.83439900	-1.32485400
Co	-0.84509700	-0.16947800	0.73995300
C	2.91144400	-0.00754000	-0.34857300
H	2.97347900	-0.86027300	0.34025300
C	2.33115200	-0.56045100	-1.66554800
C	4.33811200	0.54263800	-0.49313000
F	2.99967000	-1.65110700	-2.10174600
F	1.04331700	-0.94939700	-1.45089100

F	2.31268900	0.34162400	-2.66238300
F	4.39447500	1.65065600	-1.25516400
F	5.17257500	-0.37488100	-1.03824100
F	4.82500000	0.85635100	0.72637800
O	2.09929100	1.00411800	0.14524000
H	1.47050800	0.59381400	0.80753200

Int7-Co(II) (E_{uB3LYP} = -1665.579602 Hartree)



Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1665.271098 Hartree

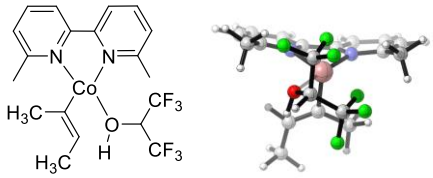
Molecular coordinates:

N	-0.76141200	-1.16639100	-1.35712500
C	-0.14817200	-1.76120400	-2.40082300
C	-0.79946000	-1.87074300	-3.63430200
C	-2.70879100	-0.75694200	-2.68477400
C	-2.01973200	-0.67330100	-1.47563100
N	-1.85921800	-0.14205200	0.87581900
C	-2.30396000	0.37110200	2.04005800
C	-3.55153600	0.99977600	2.10655800
C	-3.85826900	0.55248800	-0.23779700
C	-2.60872400	-0.06649500	-0.25104700
H	-0.29544000	-2.35248600	-4.46397600
H	-3.71475100	-0.37141100	-2.78228300
H	-3.89535400	1.41017600	3.04881200
H	-4.45518200	0.62589800	-1.13691100
C	1.00701700	-2.31510300	1.59618100
C	2.34304000	-2.37062800	1.39685200

H	2.78812200	-1.73871000	0.61881600
C	0.27788300	-3.19962700	2.58236700
H	-0.72412500	-3.45839700	2.22104300
H	0.14164000	-2.68623600	3.54342900
C	3.35274600	-3.26391100	2.07517700
H	2.91085200	-3.87546100	2.86350300
H	3.82783900	-3.93378500	1.34734500
H	4.15791000	-2.66939600	2.52365600
H	0.79953500	-4.14039000	2.79043900
C	-1.41745700	0.22358200	3.24177900
H	-1.81872000	0.77171900	4.09555400
H	-1.32758800	-0.83108300	3.52071800
H	-0.41244700	0.59861900	3.02898300
C	1.23908000	-2.28874400	-2.18216700
H	1.94728700	-1.46174500	-2.06787000
H	1.28518300	-2.89431700	-1.27225700
H	1.56469300	-2.89587900	-3.02831700
C	-4.32996500	1.09281800	0.95760000
H	-5.29770700	1.58232700	0.98812500
C	-2.08537000	-1.36113400	-3.77584000
H	-2.60551100	-1.43816600	-4.72483100
Co	-0.00353400	-0.98889300	0.54641100
C	1.86410700	1.83295000	0.41848000
H	2.57218500	2.33227200	1.08683100
C	2.58665900	1.58680200	-0.92033200
C	0.62481000	2.73744300	0.31209000
F	3.12743500	2.71047000	-1.40194600
F	3.57782900	0.68988000	-0.70694400

F	1.76353100	1.06704000	-1.85329100
F	-0.33779700	2.17825500	-0.45112400
F	0.94420300	3.92769800	-0.20960800
F	0.10837000	2.93100400	1.54194700
O	1.42734400	0.60172000	0.96617300
H	2.13707500	0.11801800	1.42797900

Int7-Co(III) (E_{uB3LYP} = -1665.197704 Hartree)



Charge: 2

Spin Multiplicity: 1

Number of Imaginary Frequencies: 0

Solvation: none

G_{298}: -1664.877044 Hartree

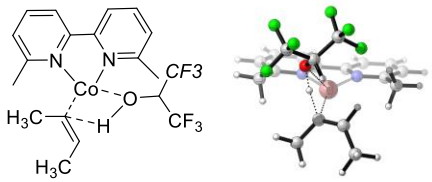
Molecular coordinates:

N	1.29891300	1.33620300	-0.63100200
C	1.09132400	2.63506500	-0.95440200
C	2.19208800	3.49490600	-1.07799800
C	3.67746100	1.66302700	-0.62699500
C	2.56611900	0.83816400	-0.53205800
N	1.38557300	-1.22501500	-0.49187900
C	1.28691000	-2.56687900	-0.66856200
C	2.45372100	-3.34395800	-0.68976200
C	3.78665800	-1.36698100	-0.45008700
C	2.61431100	-0.62481900	-0.44846700
H	2.01466000	4.53186500	-1.33953500
H	4.67757100	1.26012400	-0.53250100
H	2.35905600	-4.41401900	-0.83409800
H	4.74976000	-0.87550000	-0.40203800
C	0.61356900	0.17034900	1.81111500
C	0.84391500	-0.96979500	2.46550100

H	0.83730000	-1.91528100	1.92460600
C	0.70769000	1.58653700	2.28622700
H	-0.08150600	2.23419500	1.90144900
H	1.67202200	2.02851500	2.01764800
C	1.18258300	-1.09605700	3.93256800
H	1.11007300	-0.15124900	4.47113000
H	0.52253100	-1.82421600	4.41454700
H	2.20621000	-1.47390400	4.03767400
H	0.62530500	1.60035500	3.37841400
C	-0.04033200	-3.23051500	-0.88395400
H	-0.56053300	-3.42579100	0.05728900
H	-0.68841600	-2.63046400	-1.51981900
H	0.11658700	-4.19246700	-1.37388500
C	-0.29355400	3.15076100	-1.21156800
H	-0.93189900	2.39389300	-1.66881300
H	-0.76751000	3.50733800	-0.29196400
H	-0.24019500	4.00018500	-1.89485600
C	3.70277800	-2.75593600	-0.54261000
H	4.60198000	-3.36294200	-0.53934600
C	3.48241500	3.02306200	-0.87814100
H	4.33210300	3.69340800	-0.95368000
Co	0.02028200	0.03928500	-0.02888400
C	-2.81942600	-0.69435300	0.29471500
H	-3.59463700	-1.31082300	0.75881500
C	-2.87592700	0.72867100	0.86812600
C	-2.97113400	-0.77431000	-1.23869200
F	-3.90532200	1.45360700	0.49756300
F	-2.78731000	0.68693300	2.19909100

F	-1.71198600	1.38084000	0.41985700
F	-1.85921700	-0.21599200	-1.82668600
F	-4.04244000	-0.12251800	-1.66292000
F	-3.03119700	-2.04905200	-1.62234300
O	-1.50905700	-1.19533100	0.58889700
H	-1.39679800	-1.35557600	1.54703600

TS3-Co(I) (E_{uB3LYP} = -1665.751134 Hartree)



Charge: 0

Spin Multiplicity: 3

Number of Imaginary Frequencies: 1 (−757.81 cm^{-1})

Solvation: none

G_{298}: -1665.45054 Hartree

Molecular coordinates:

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C	0.64966100	-0.35255000	2.26464900
C	1.00669500	-1.66342600	2.33064600

H	1.16632400	-2.18941200	1.38635500
C	0.50326400	0.50265600	3.50693600
H	-0.50912200	0.91864000	3.58817800
H	1.18176600	1.36314600	3.44383400
C	1.25315100	-2.53143800	3.53942800
H	1.01472200	-2.03262600	4.48094400
H	0.65401900	-3.44957700	3.48310200
H	2.30353000	-2.84958000	3.58199800
H	0.72311200	-0.01463600	4.44871600
C	-0.09447500	3.06867900	0.84532800
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H	-0.01618800	2.67334000	1.86227800
H	0.67845800	2.56966100	0.25467500
C	-1.28016800	-3.28448800	-0.08002900
H	-0.40227900	-3.00276400	-0.66801600
H	-1.01540000	-3.15739800	0.97512300
H	-1.50391000	-4.33735400	-0.26567700
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H	-4.25943800	4.32497000	-0.88615000
C	-4.70115200	-2.09384900	-1.23278000
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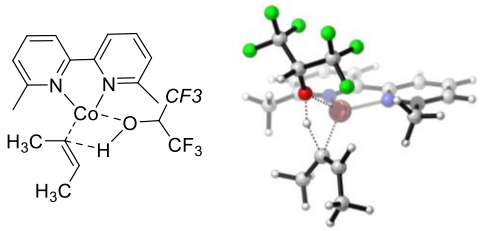
C	2.60600800	-0.99700100	-1.57193600
C	3.90620000	0.94001700	-0.50083800
F	3.73508100	-1.67366500	-1.89126500
F	1.65302400	-1.93525900	-1.30938200

F	2.20830200	-0.32688300	-2.66922700
F	3.68078200	1.80896300	-1.50783900
F	5.11326900	0.36212100	-0.72560800
F	4.02061900	1.66119600	0.63906400
O	1.59575600	0.54187100	-0.04507700
H	1.18230100	0.22687900	1.01936200

TS3-Co(II) (E_{uB3LYP} = -1665.559961 Hartree)



Charge: 1

Spin Multiplicity: 4

Number of Imaginary Frequencies: 1 (−1178.48 cm^{-1})

Solvation: none

G_{298}: -1665.255667 Hartree

Molecular coordinates:

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C	-3.83267200	-0.89651400	-1.62390500
C	-2.77453800	-0.41833000	-0.85281100
N	-1.68949300	1.27380800	0.49000400
C	-1.55538900	2.51107100	1.01380300
C	-2.50944000	3.49857300	0.74071100
C	-3.71368300	1.91750900	-0.61265100
C	-2.74024400	0.96686900	-0.31221100
H	-2.62156100	-4.02151600	-2.16139600
H	-4.68516600	-0.27048100	-1.84930700
H	-2.38783600	4.48791200	1.16584200
H	-4.54631700	1.68037000	-1.26077300
C	0.50709000	-1.00233500	2.45352800
C	1.08541400	-2.22999700	2.41794200

H	1.50539500	-2.56154800	1.46654100
C	-0.05393200	-0.38792600	3.71953800
H	-1.08092200	-0.03073400	3.57497800
H	0.54183100	0.48328900	4.01691900
C	1.29173800	-3.21399600	3.53156200
H	0.83503700	-2.90851200	4.47337800
H	0.88495300	-4.19300000	3.24903100
H	2.36484400	-3.36682600	3.70211600
H	-0.07110300	-1.07558000	4.57047000
C	-0.37659300	2.77992000	1.90015600
H	-0.26080000	3.85053000	2.07508900
H	-0.51452000	2.29128400	2.86998400
H	0.54480300	2.39504000	1.45825800
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H	-0.47367900	-4.26988200	-1.15231300
C	-3.59294700	3.19883600	-0.07570900
H	-4.33790100	3.95478500	-0.30064900
C	-3.78417800	-2.20414800	-2.10342900
H	-4.59761200	-2.59308400	-2.70678300
Co	-0.35211800	-0.27622900	0.65523800
C	2.71524000	0.44904000	-0.25850300
H	3.63528500	0.37092600	0.33240100
C	2.73717800	-0.70244700	-1.27920600
C	2.70868900	1.84850800	-0.90403200
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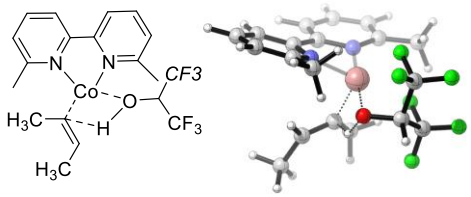
F	2.79617200	-1.88089200	-0.60513600

F	1.60668000	-0.73652600	-2.02446200
F	1.58463500	2.05814400	-1.62371000
F	3.76680800	2.04093400	-1.70625700
F	2.74594900	2.78185000	0.07127300
O	1.57996500	0.35460900	0.54731700
H	1.43448700	-0.25777900	1.54292600

TS3-Co(III) (E_{uB3LYP} = -1665.164975 Hartree)



Charge: 2

Spin Multiplicity: 1

Number of Imaginary Frequencies: 1 (−917.27 cm^{-1})

Solvation: none

G_{298}: -1664.849502 Hartree

Molecular coordinates:

N	1.20826600	1.36567500	-0.66837500
C	0.99318900	2.66027200	-1.00283100
C	2.08575100	3.53644600	-1.09560200
C	3.58281400	1.72537400	-0.60570000
C	2.47940300	0.88640800	-0.53939600
N	1.33344800	-1.20804900	-0.48915200
C	1.25865300	-2.55460900	-0.66184600
C	2.44573100	-3.30200700	-0.70602300
C	3.73749500	-1.29573100	-0.48946300
C	2.54952200	-0.57773200	-0.46434500
H	1.90143500	4.57021000	-1.36518100
H	4.58615600	1.33732100	-0.48657700
H	2.37309600	-4.37408400	-0.84602500
H	4.69016800	-0.78281500	-0.46402900
C	0.45238000	0.13406200	1.83416100
C	0.97090000	-0.96758800	2.46693400

H	0.95758400	-1.92022400	1.94052400
C	0.48633400	1.53101800	2.40026600
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H	1.50838200	1.91955500	2.36964100
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H	0.92622900	-1.78070700	4.43458100
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H	0.15041800	1.52958100	3.44280200
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H	-0.67865300	-3.20774200	0.03465100
H	-0.60666100	-2.79260700	-1.67771400
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C	-0.38768200	3.15528900	-1.31871500
H	-1.00681300	2.37812400	-1.76750000
H	-0.89333800	3.53916300	-0.42749000
H	-0.31789100	3.98167000	-2.02855200
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H	4.21847700	3.76493400	-0.91457700
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H	-3.43542400	-1.38278900	0.84544400
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C	-2.84140100	-0.87231300	-1.16922800
F	-3.90492500	1.35505200	0.44643100
F	-2.75500800	0.76323700	2.18622000

F	-1.70306300	1.38320400	0.35719700
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F	-3.89520600	-0.22990300	-1.65020200
F	-2.89386800	-2.15127900	-1.53192000
O	-1.38008700	-1.15653100	0.71621300
H	-0.65449300	-0.56609300	1.78048700

TROUBLESHOOTING AND FREQUENTLY ASKED QUESTIONS

Q. What can I do when the yield of the reaction does not match the one reported in the paper?

A. Check if the vial is properly sealed and that no oxygen is present in the vial. If the conversion is low, you may resubmit the crude to the reaction conditions.

Q. Where can I get the electrode materials?

A. We purchased a graphite electrode from IKA but could be obtained from multiple suppliers since this material is very common. See "electrode materials/dimensions" section for details in this Supporting Information.

Q. Is the pre-stirring and degassing described in the General Procedures prior to electrolysis is essential?

A. We conducted control reaction without pre-stirring and without bubbling argon through the solution of the starting material, the reaction will typically work very similarly if the solvent is oxygen-free.

Q. What are the suitable current values for reactions on different scales?

A. *For isomerization with Co(salen):*

We typically use 5 mA on 0.2 mmol scales and gives us an operational voltage of approximately 1.5–2.5 V. The submerged exterior surface area of electrode is approximately W7 × D1.5 × H20 mm. The current values and exterior area of electrodes may be adjusted proportionally for other scales to maintain similar levels of current density (mA/cm^2).

For isomerization with $CoBr_2$ and 4,4-MeO-bpy:

We use 2.5 mA or 1.3 mA on 0.2 mmol scales and gives us an operational voltage of approximately 0.0–1.0 V with a magnesium anode and 0.5–2.0 V with a zinc anode. The submerged exterior surface area of electrode is approximately W7 × D1.5 × H20 mm. The current values and exterior area of electrodes may be adjusted proportionally for other scales to maintain similar levels of current density (mA/cm^2).

For reduction with $CoBr_2$ and 6,6-Me-bpy:

We use 5 mA on 0.2 mmol scales and gives us an operational voltage of approximately 2.0–20.0 V. In some cases, the voltage starts at 2-5 V then increases to 15-20 V and then decreases to 1-5 V. The submerged exterior surface area of electrode is approximately W7 × D1.5 × H20 mm. The current values and exterior area of electrodes may be adjusted proportionally for other scales to maintain similar levels of current density (mA/cm^2).

Q. We notice that Co(cyclohexyl-tBu-salen) catalyst is not completely soluble in acetone. Can we electrolyze this heterogeneous solution as is?

A. Yes—Our preliminary experiments showed that solubility of Co(cyclohexyl-tBu-salen) in acetone varies on its manufacturer, batch number, and crystal shape/size, etc. Qualitatively, 0.002-0.004 M Co(cyclohexyl-tBu-salen) gives a homogeneous system whereas Co(cyclohexyl-tBu-salen) remained insoluble at higher concentrations. Even on the latter case, Co(cyclohexyl-tBu-salen) dissolves gradually during electrolysis so you can electrolyze it as is.

Q. We notice that a starting material which we plan to use is not soluble in reaction solvent. Can we electrolyze this heterogeneous solution as is?

A. *For isomerization with Co(salen):* You may use a small amount of THF as a co-solvent to dissolve your starting material. As discussed in Supplementary Table 7 (optimization table), our preliminary studies showed a comparable result when we used a THF as a solvent.

For isomerization with $CoBr_2$ and 4,4-MeO-bpy: You may use a small amount of THF or toluene as a co-solvent to dissolve your starting material.

For reduction with $CoBr_2$ and 6,6-Me-bpy: The reaction works only with THF as a solvent.

Q. Is this reaction sensitive to water?

A. *For isomerization with Co(salen):* The reaction seems not to be sensitive to water but we recommend the use of anhydrous acetone.

For isomerization with $CoBr_2$ and 4,4-MeO-bpy: The reaction is typically not sensitive to the presence of water. Even hydrate salts have been used without diminishing the yield.

For reduction with $CoBr_2$ and 6,6-Me-bpy: The reaction is typically not sensitive to the presence of water. Even hydrate salts have been used without diminishing the yield.

Q. How air sensitive is the reaction?

A. The reaction is not particularly air sensitive as it proceeds without freeze-pump-thaw. However, evacuation-argon backfill cycle is still required as running the reaction under air results in much lower yield.

Q. Is this reaction sensitive to stirring rate?

A. Stirring rate (400–1,500 rpm) unlikely to affect the outcome significantly. However, we noticed that with some specific substrates, especially with the reduction protocol, a turbid reaction mixture and a buildup can be formed on the cathode surface after electrolysis. Thus, we usually applied a faster stirring at a rate of 1,500 rpm.

Q. How can I optimize the reaction if lots of homocoupling dimer or dehalogenation byproducts were detected at the end of the reaction?

A. One can try to increase the amount of proton source to enhance the cobalt hydride formation. Alternatively, using higher loading of the catalyst and ligand (15-20 mol%) can help in particular cases.

Q. Would it affect the yield if the electrolysis is conducted for longer, after the consumption of starting materials?

A. *For isomerization with Co(salen):*

In some cases, we observed reduction of the double bond, although a lot of additional Faradays/mol have to be ran for that.

For isomerization with $CoBr_2$ and 4,4-MeO-bpy:

In some cases, we observed reduction of the double bond, although a lot of additional Faradays/mol have to be ran for that.

For reduction with $CoBr_2$ and 6,6-Me-bpy:

Over-reduction of alkynes is a common problem, the reaction has to be carefully monitored. Please note that the starting material (alkyne) is typically separable from the alkene product while the over-reduced alkane is not.

Q. What are typical byproducts for this protocol?

A. *For isomerization with Co(salen):* There are typically no side products in these reactions. Occasionally unreacted starting material is observed.

For isomerization with $CoBr_2$ and 4,4-MeO-bpy: There are typically no side products in these reactions. Occasionally unreacted starting material is observed.

For reduction with $CoBr_2$ and 6,6-Me-bpy: The typical side product is the over-reduced product when the alkyne is semi-reduced to the alkene (*i.e.* the corresponding alkane).

Q. What can I do if a significant amount of starting materials remains after electrolysis?

A. Resubmit to reaction conditions with more equivalents of HFIP and more Faradays/mol.

Q. Can I reuse the electrodes, if yes, how should I wash them for the next reaction?

A. After the isomerization/reduction, if graphite/tin/nickel-foam/zinc/magnesium electrodes used are not very dirty so you can reuse them after a simple cleaning as follows:

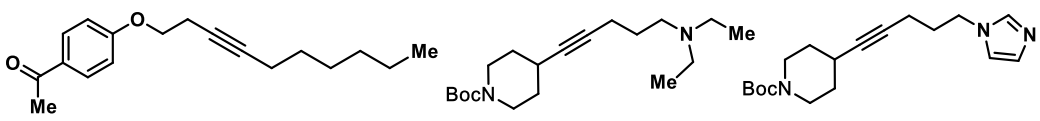
1. Wash vigorously with water and soap.
2. Wash the surfaces of the electrode three times with acetone and three times with DCM.
3. Heat the electrode to 150 ^{o}C, using hot plate for 5 min on each side.
4. Scratch the electrode surface to get a clean dark gray color.

Q. Can I leave the reaction mixture overnight after electrolysis?

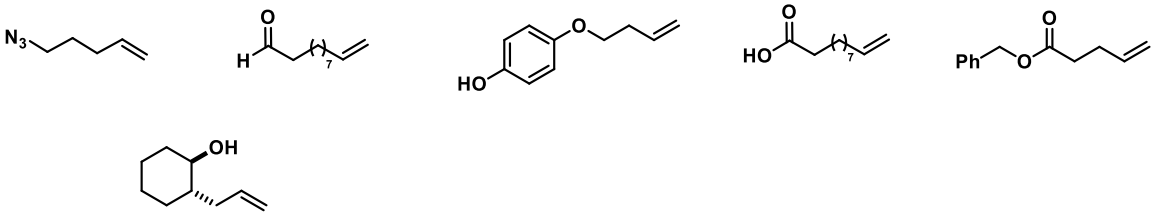
A. In some cases, we observed low mass balance and side products formation by leaving the reaction mixture overnight. Accordingly, it will be better to work up the reaction mixture after the electrolysis is over, and the crude mixture can be left overnight.

UNSUCCESSFUL AND LOW CONVERSION SUBSTRATES FOR ISOMERIZATION AND REDUCTION

Alkyne Reduction



Alkene Isomerization



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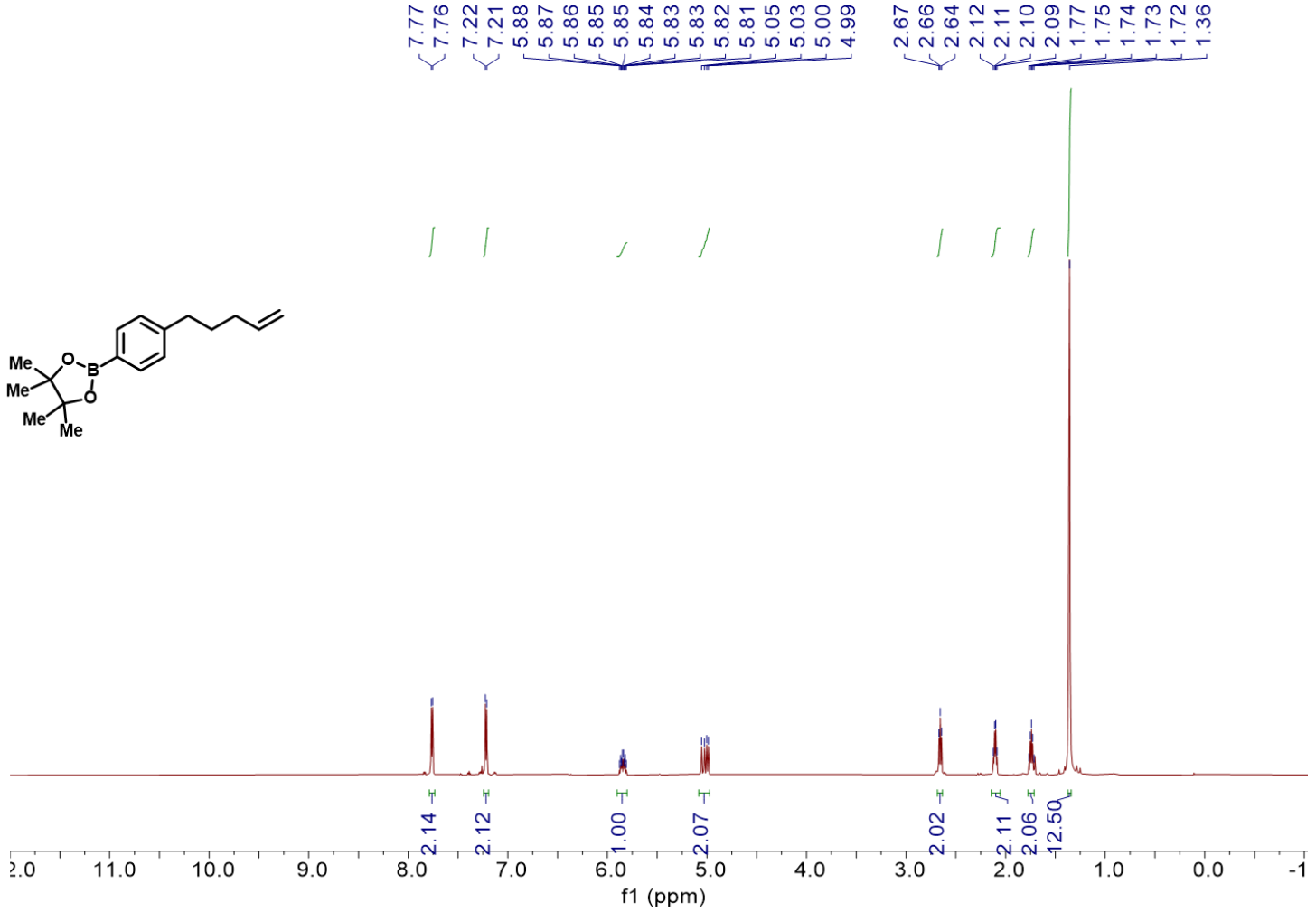
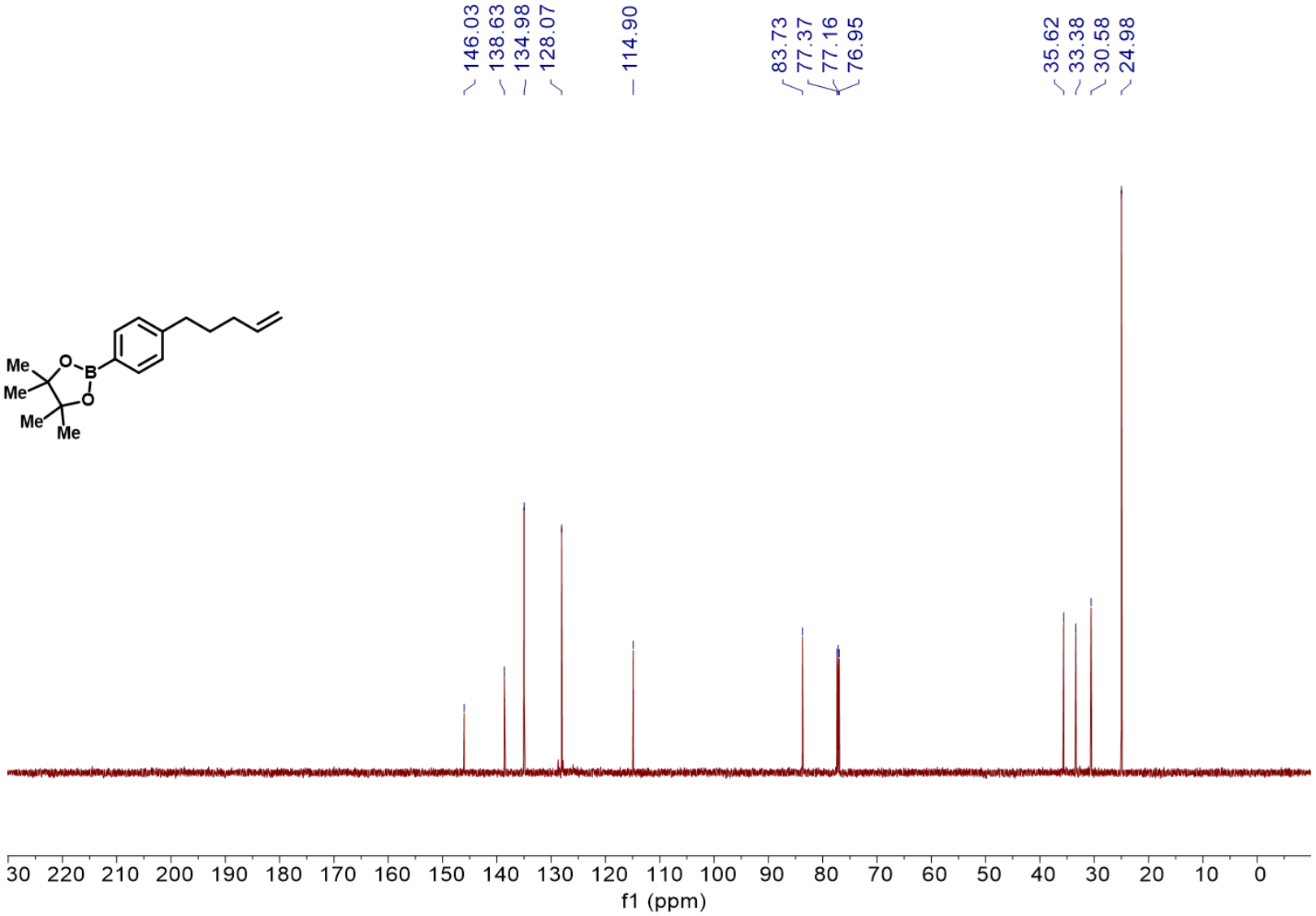
NMR SPECTRA

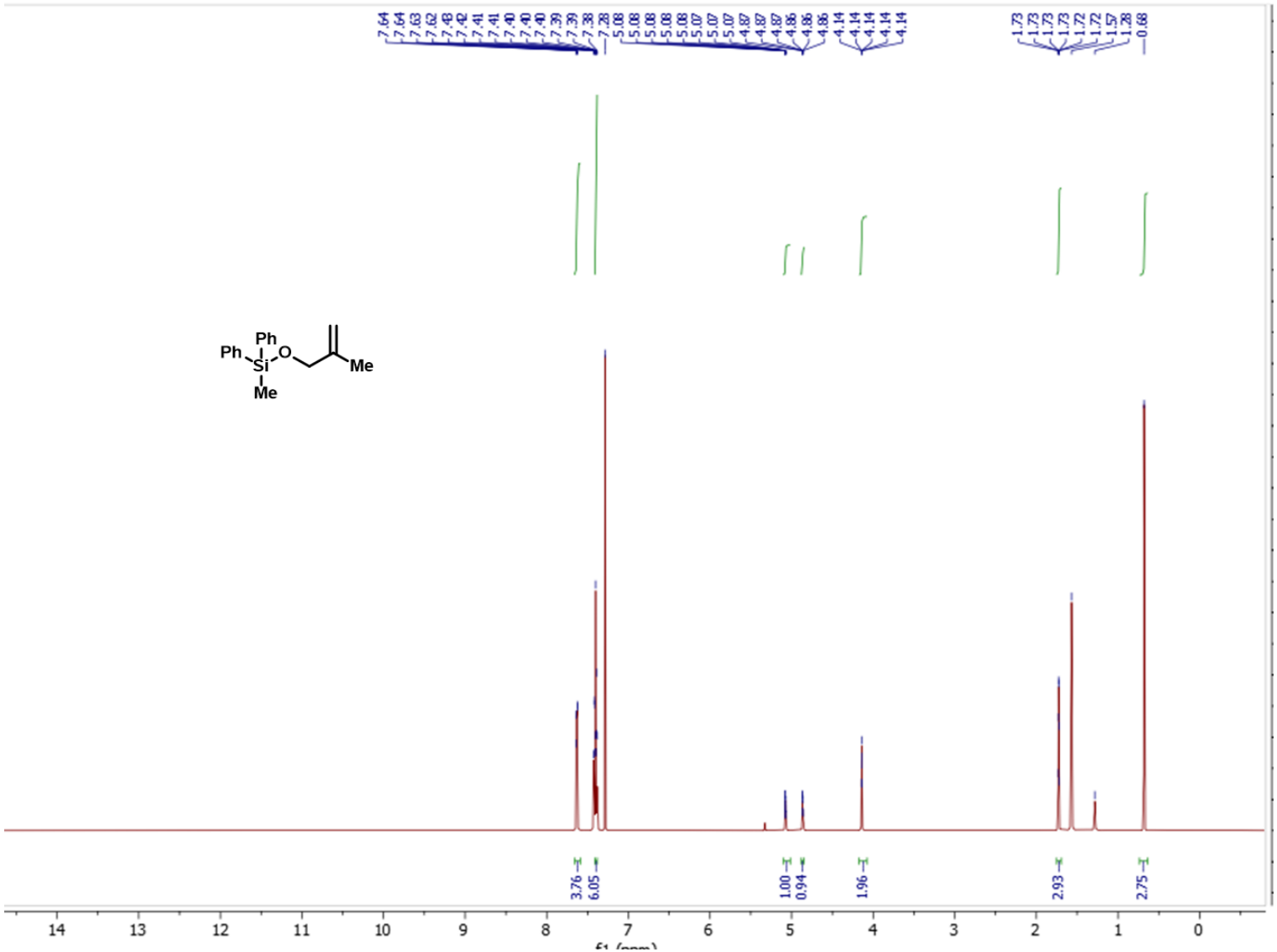
^{1}H NMR (600 MHz, $CDCL_3$) OF COMPOUND **1**



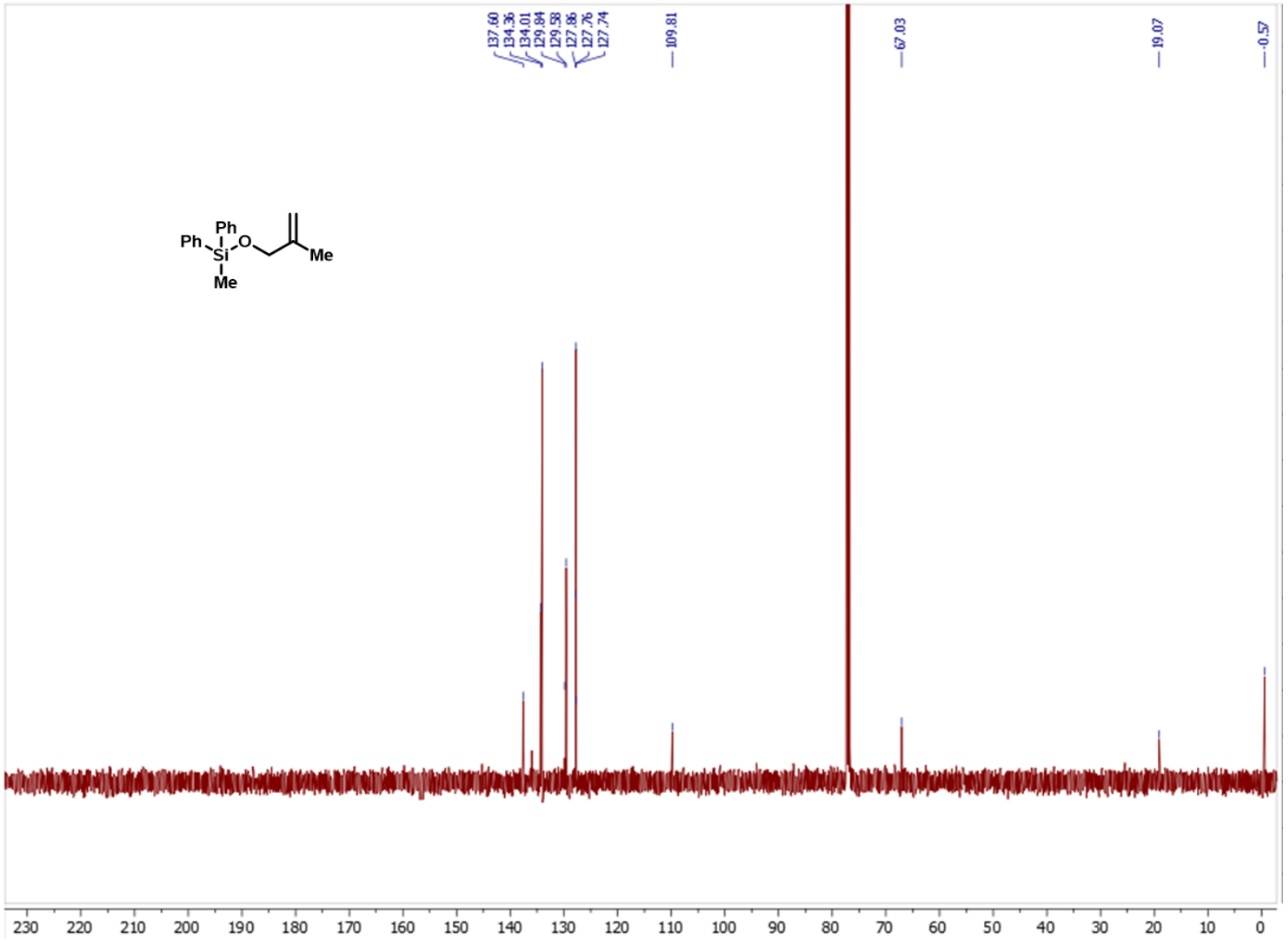
^{13}C NMR (151 MHz, $CDCL_3$) OF COMPOUND **1**



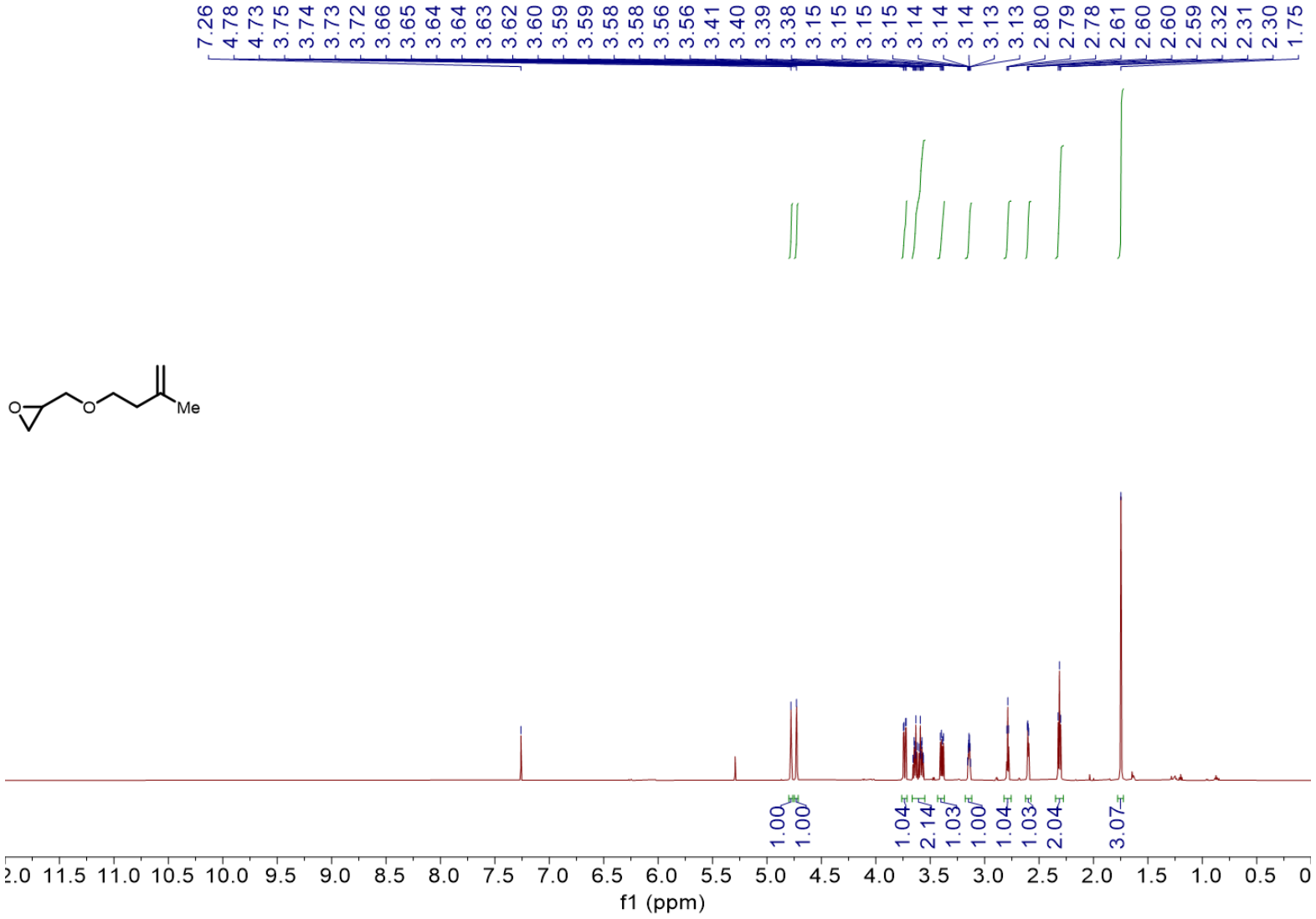
^{1}H NMR (500 MHz, $CDCl_3$) OF COMPOUND **S1**



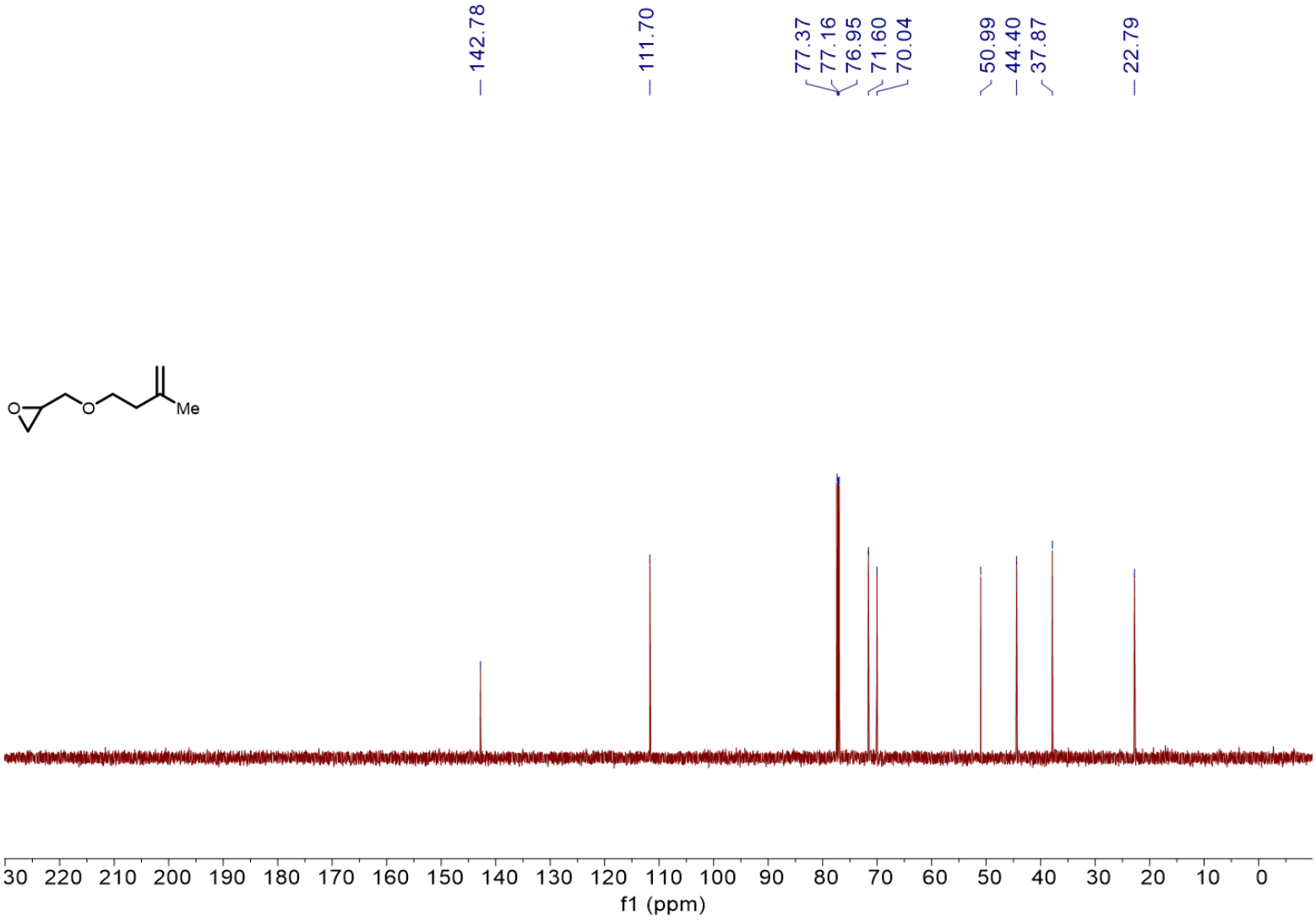
^{13}C NMR (126 MHz, $CDCl_3$) OF COMPOUND **S1**



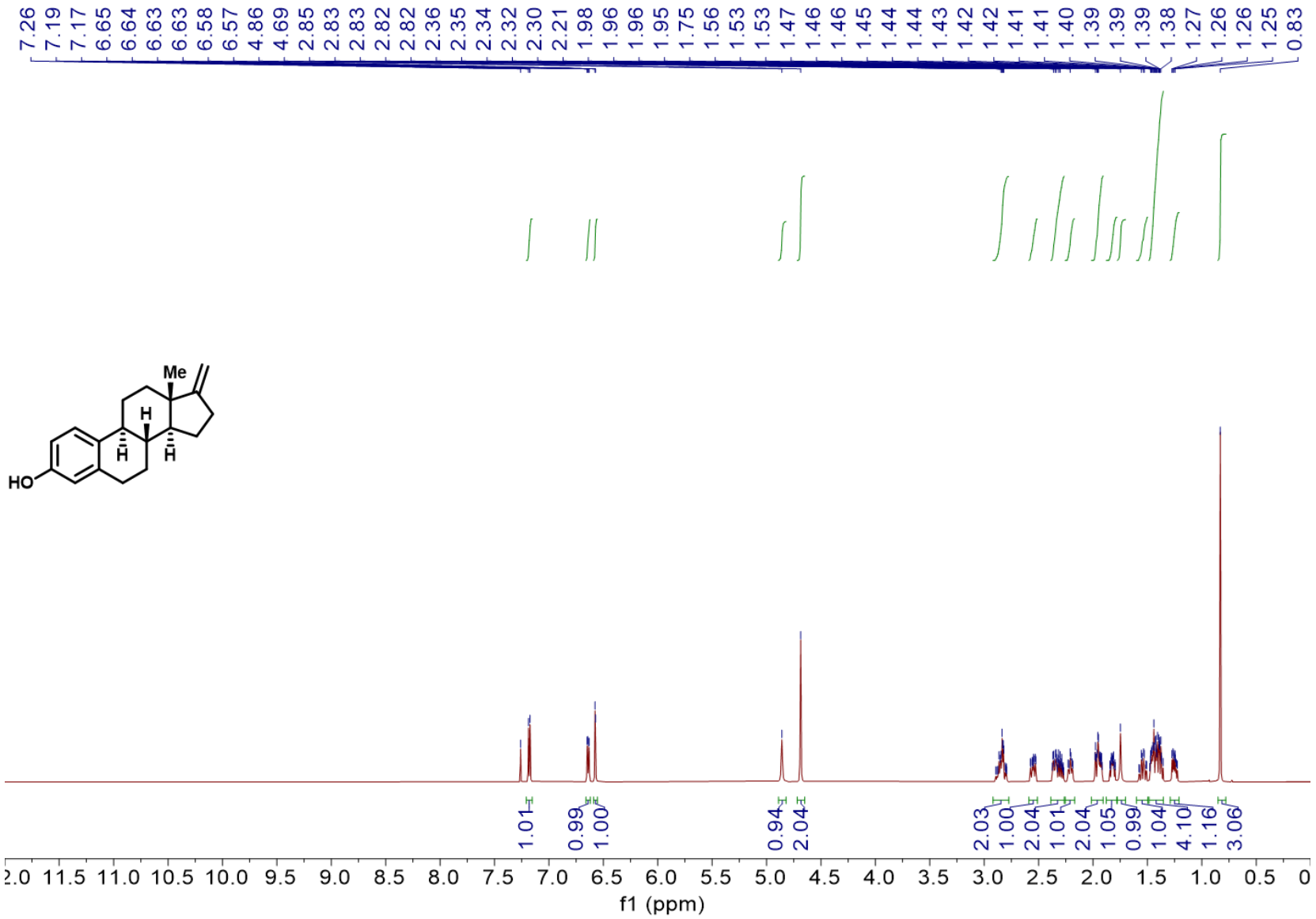
^{1}H NMR (600 MHz, $CDCl_3$) OF COMPOUND **S2**



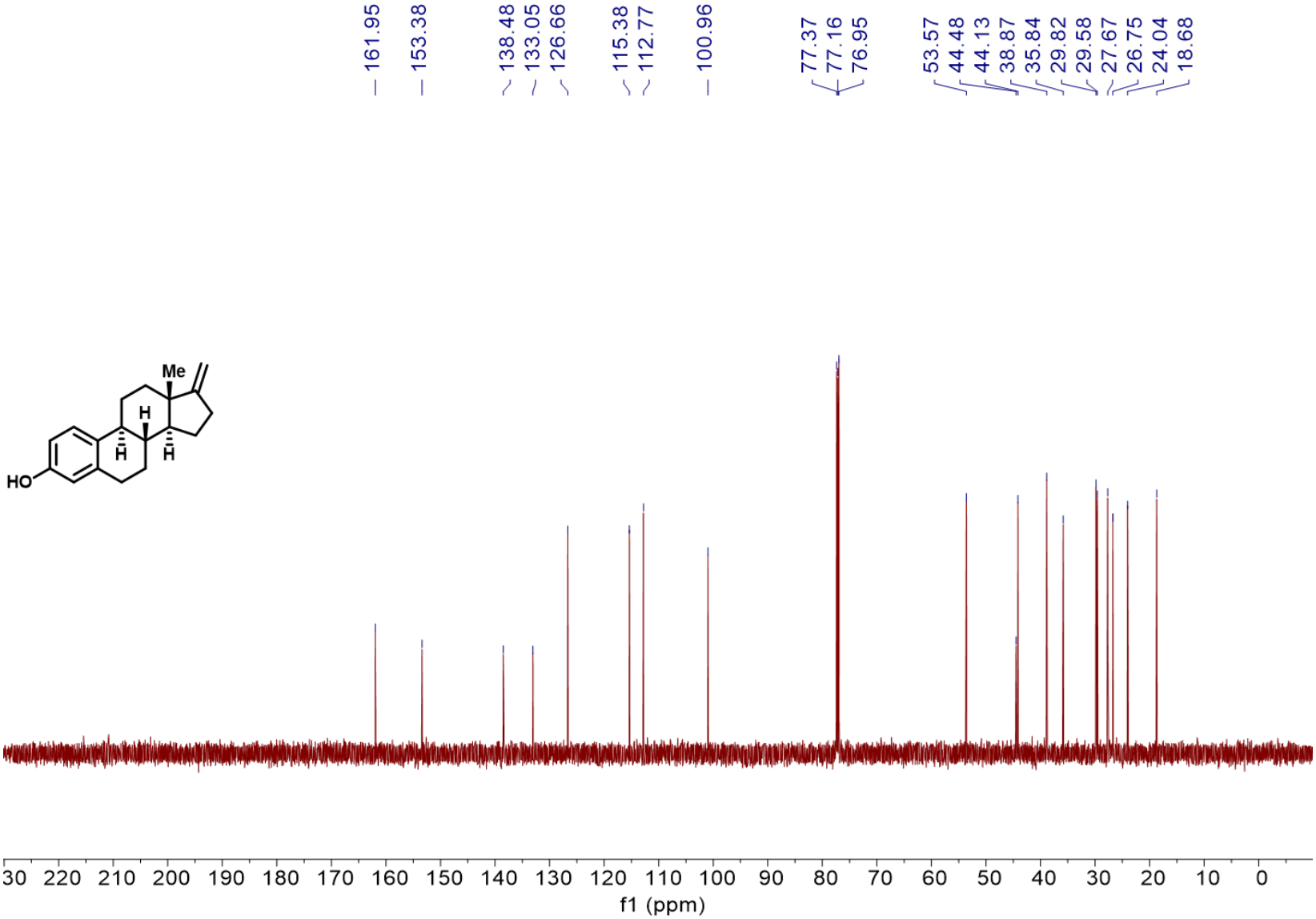
^{13}C NMR (151 MHz, $CDCL_3$) OF COMPOUND **S2**



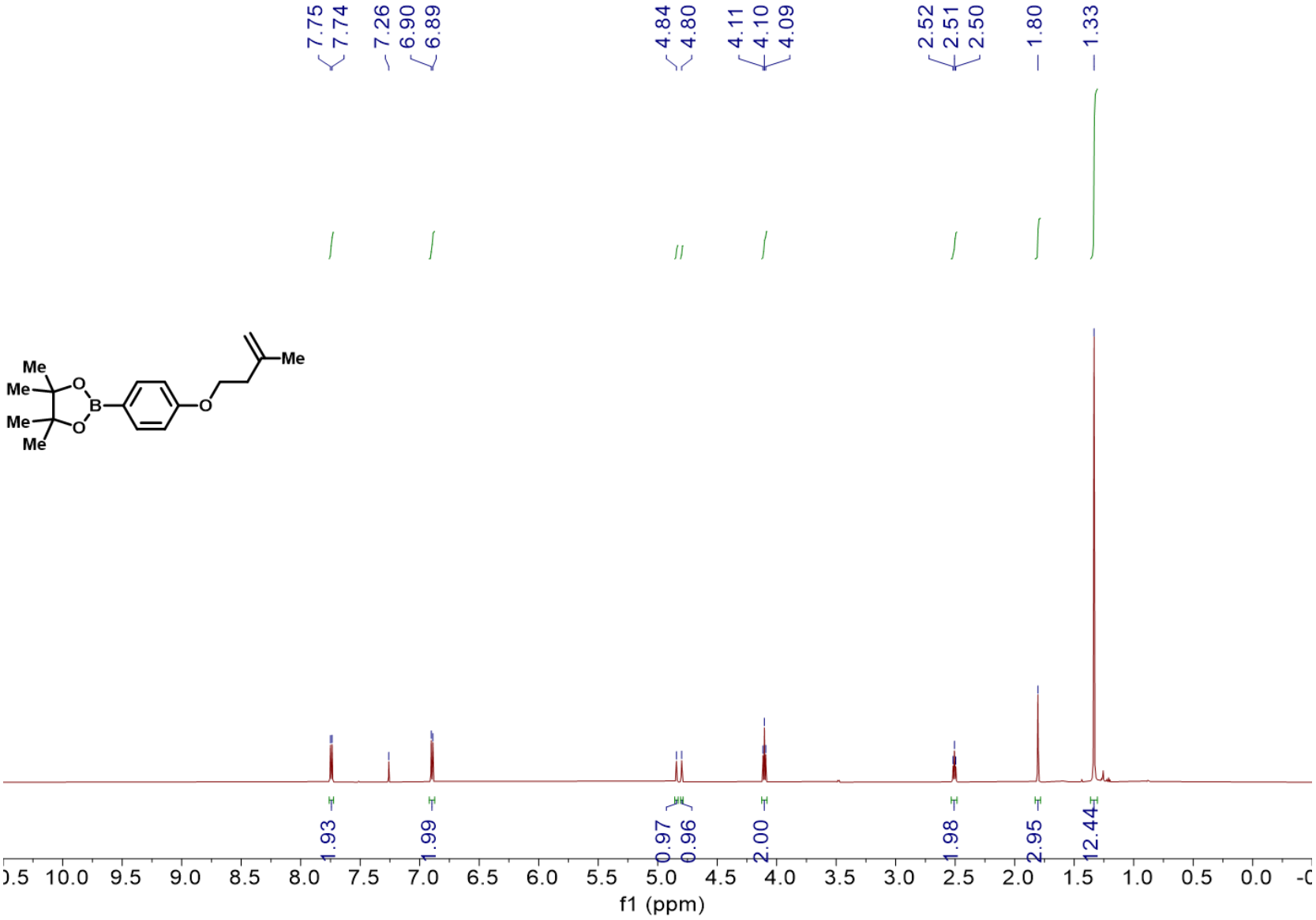
^{1}H NMR (600 MHz, $CDCl_3$) OF COMPOUND **S3**



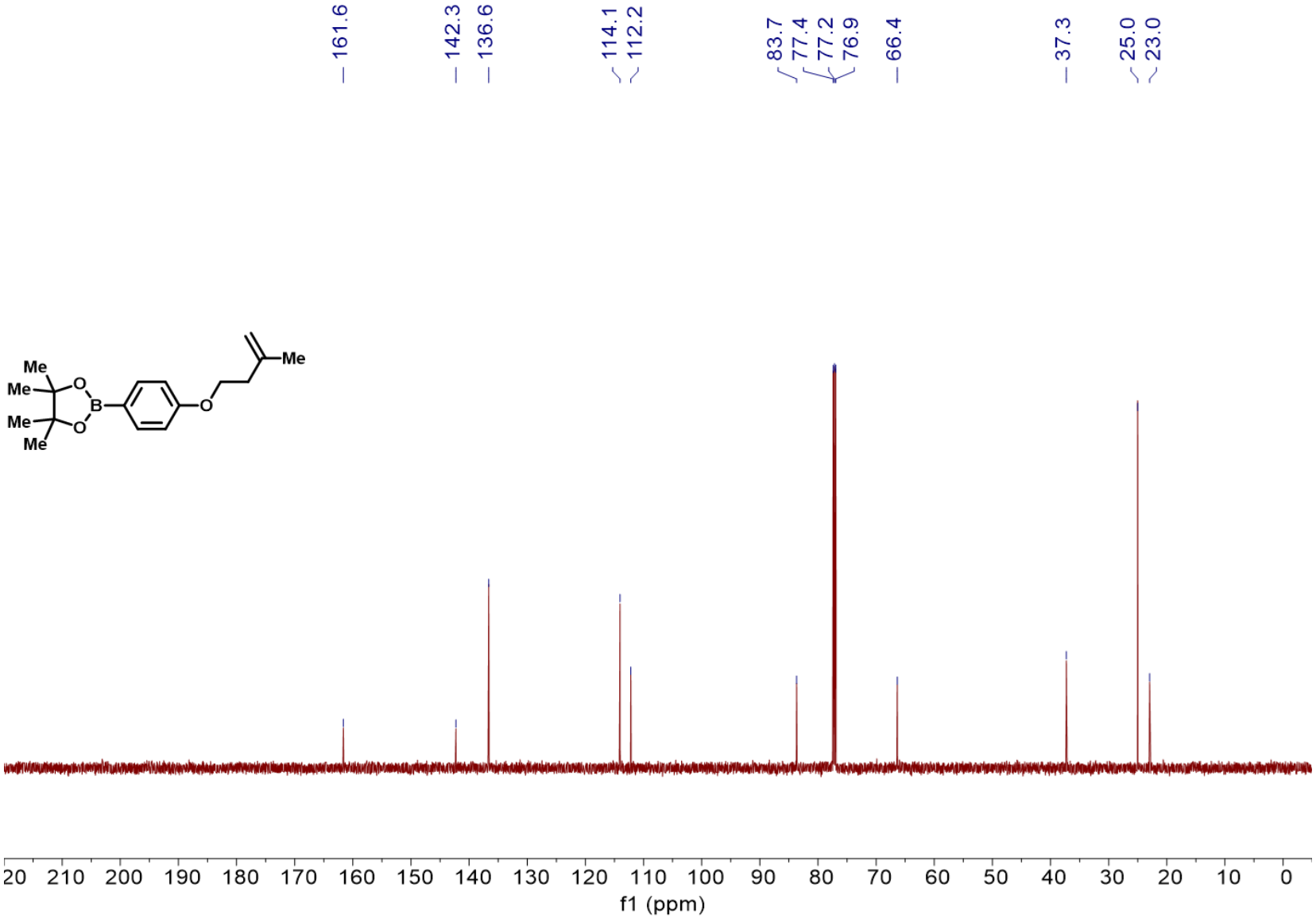
^{13}C NMR (151 MHz, $CDCl_3$) OF COMPOUND **S3**



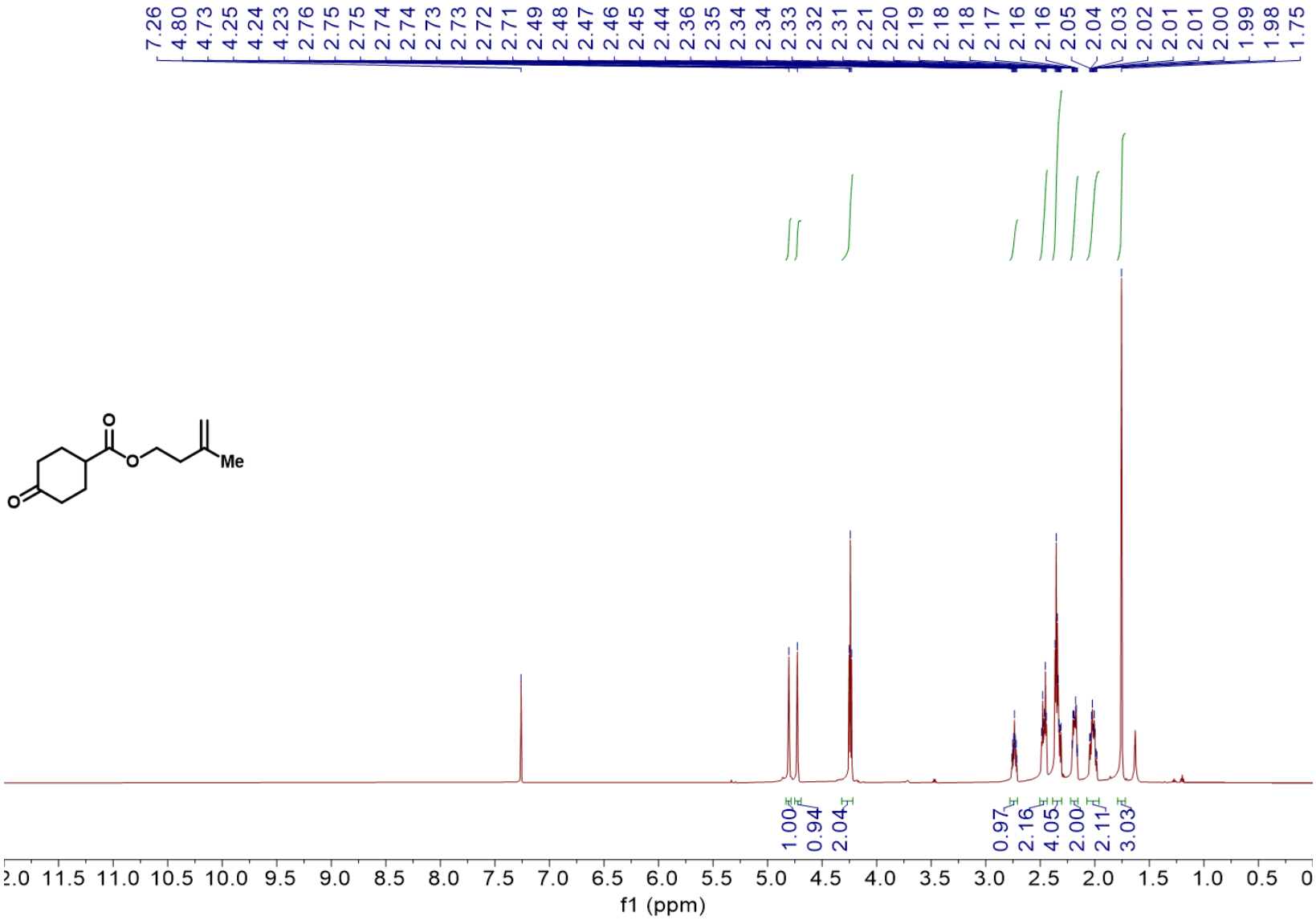
^{1}H NMR (600 MHz, $CDCL_3$) OF COMPOUND **S4**



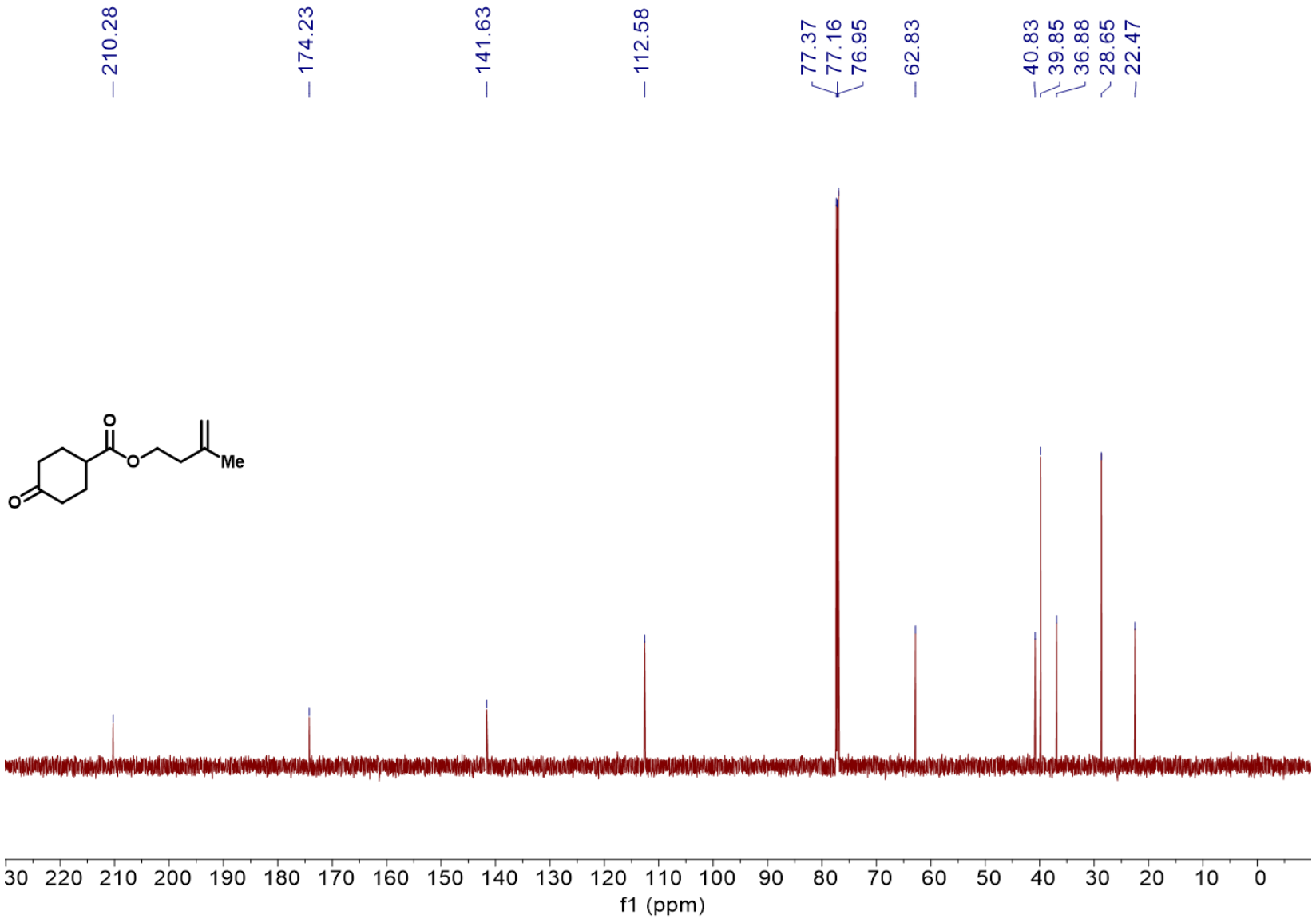
^{13}C NMR (151 MHz, $CDCl_3$) OF COMPOUND **S4**



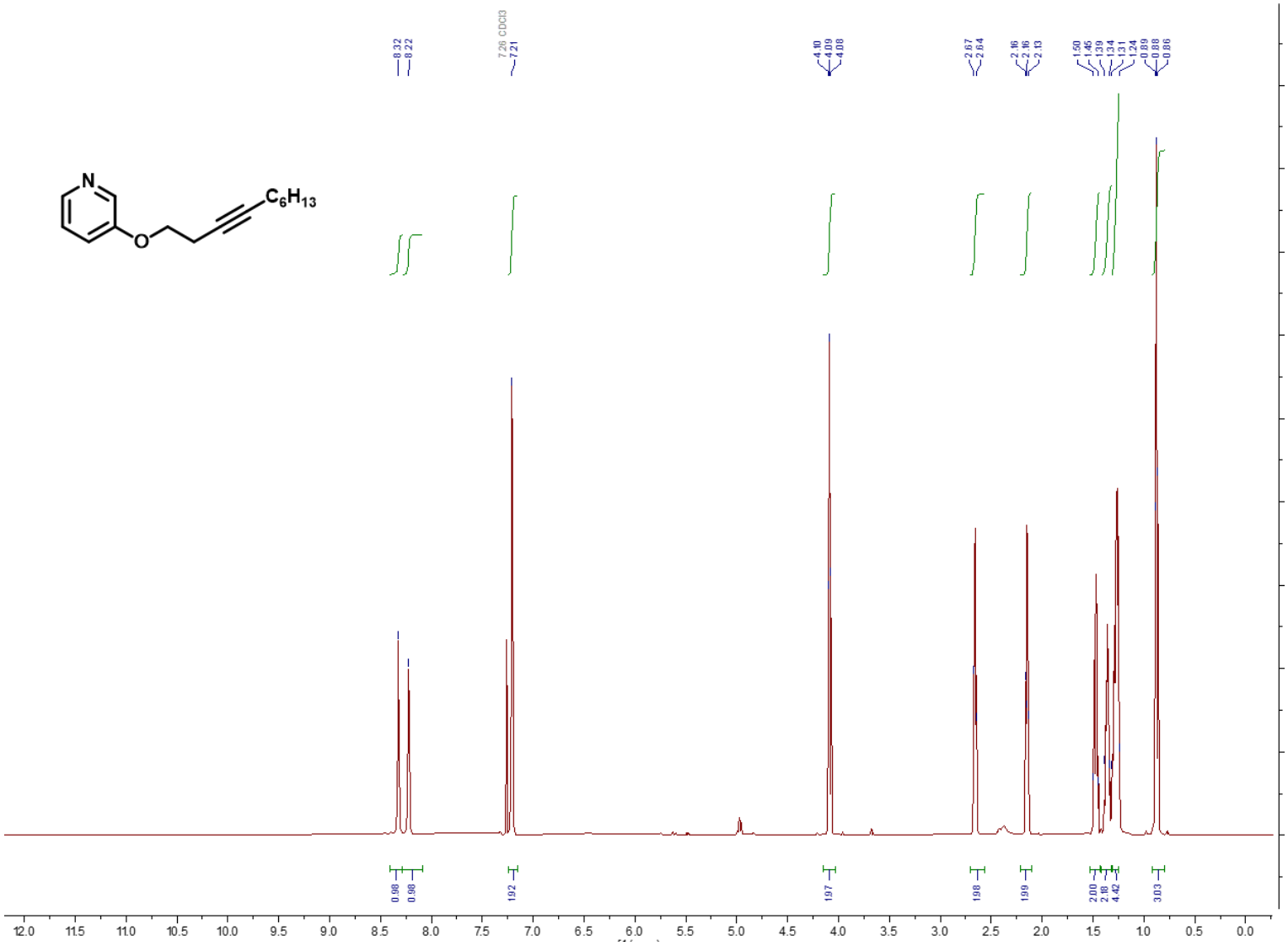
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S5**



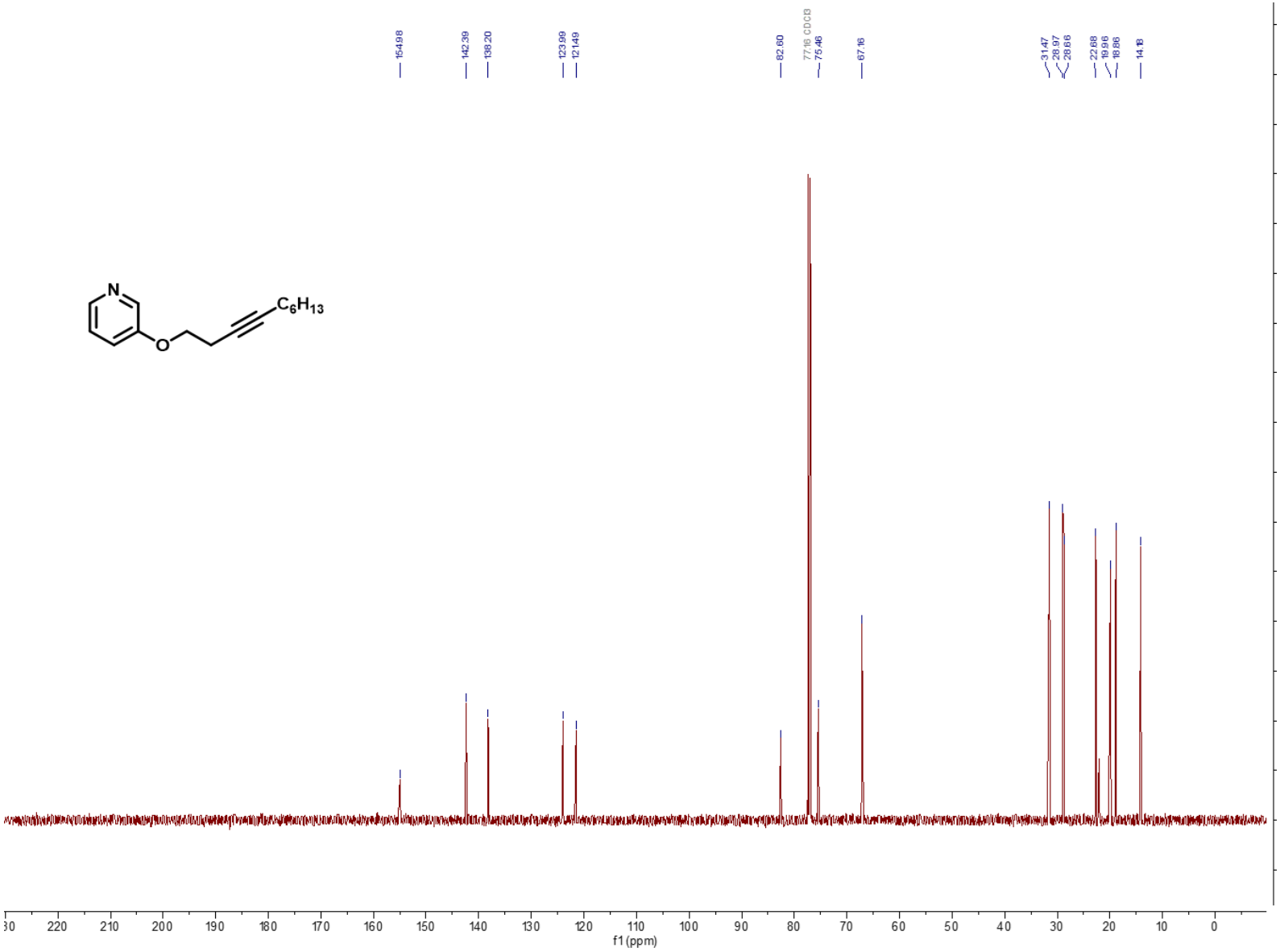
^{13}C NMR (151 MHz, $CDCl_3$) OF COMPOUND **S5**



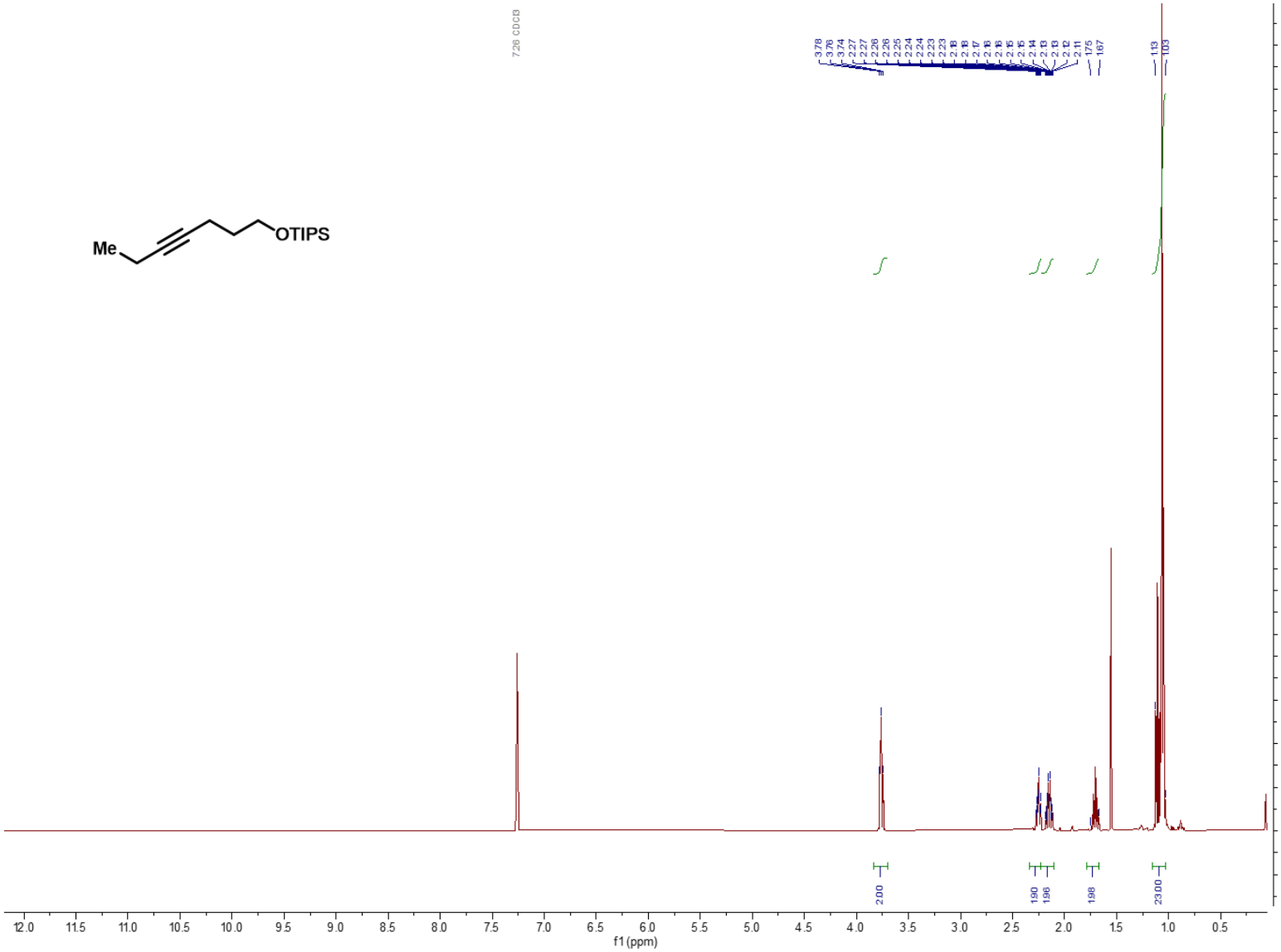
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S6**



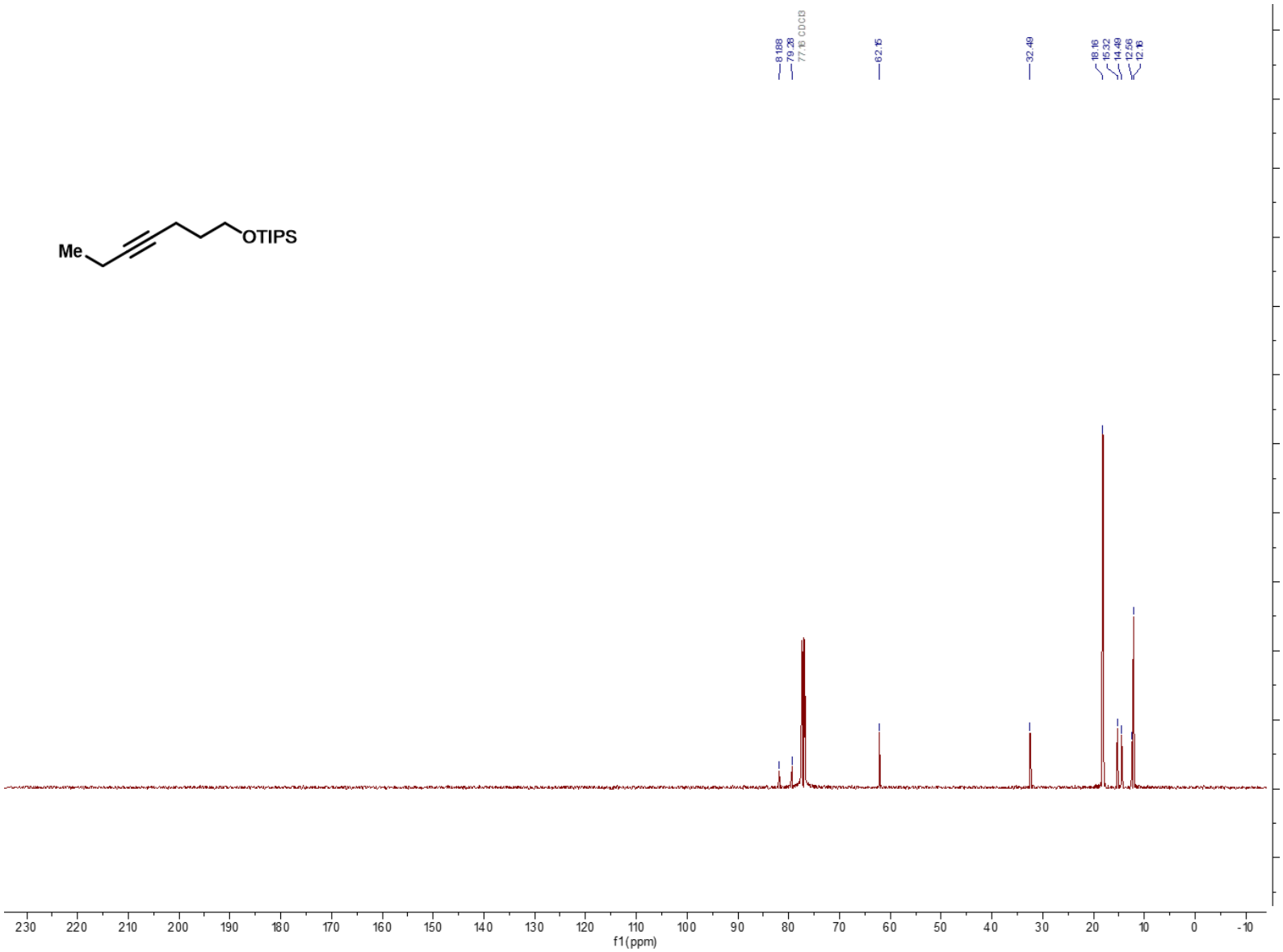
^{13}C NMR (151 MHz, $CDCL_3$) OF COMPOUND **S6**



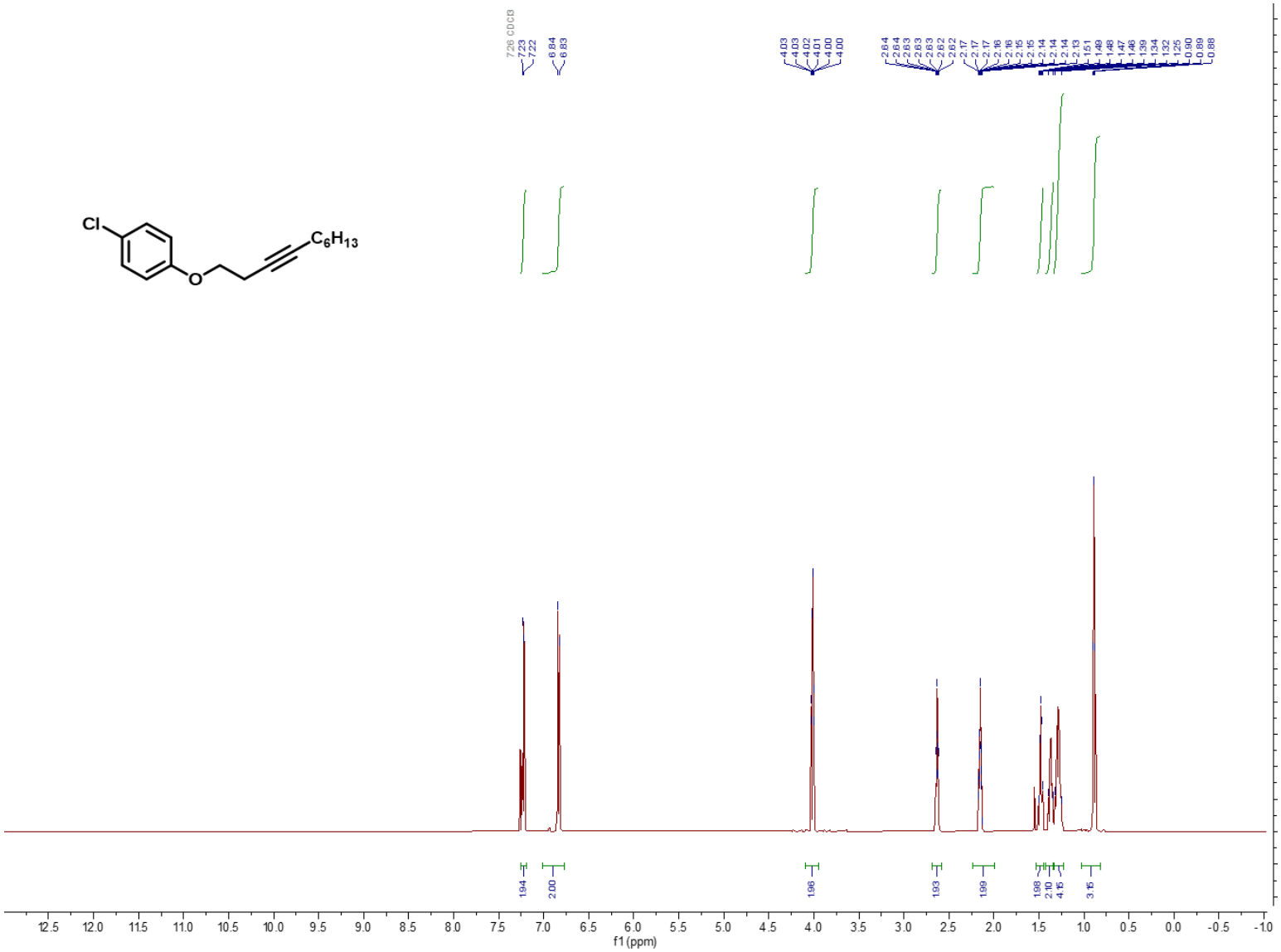
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S7**



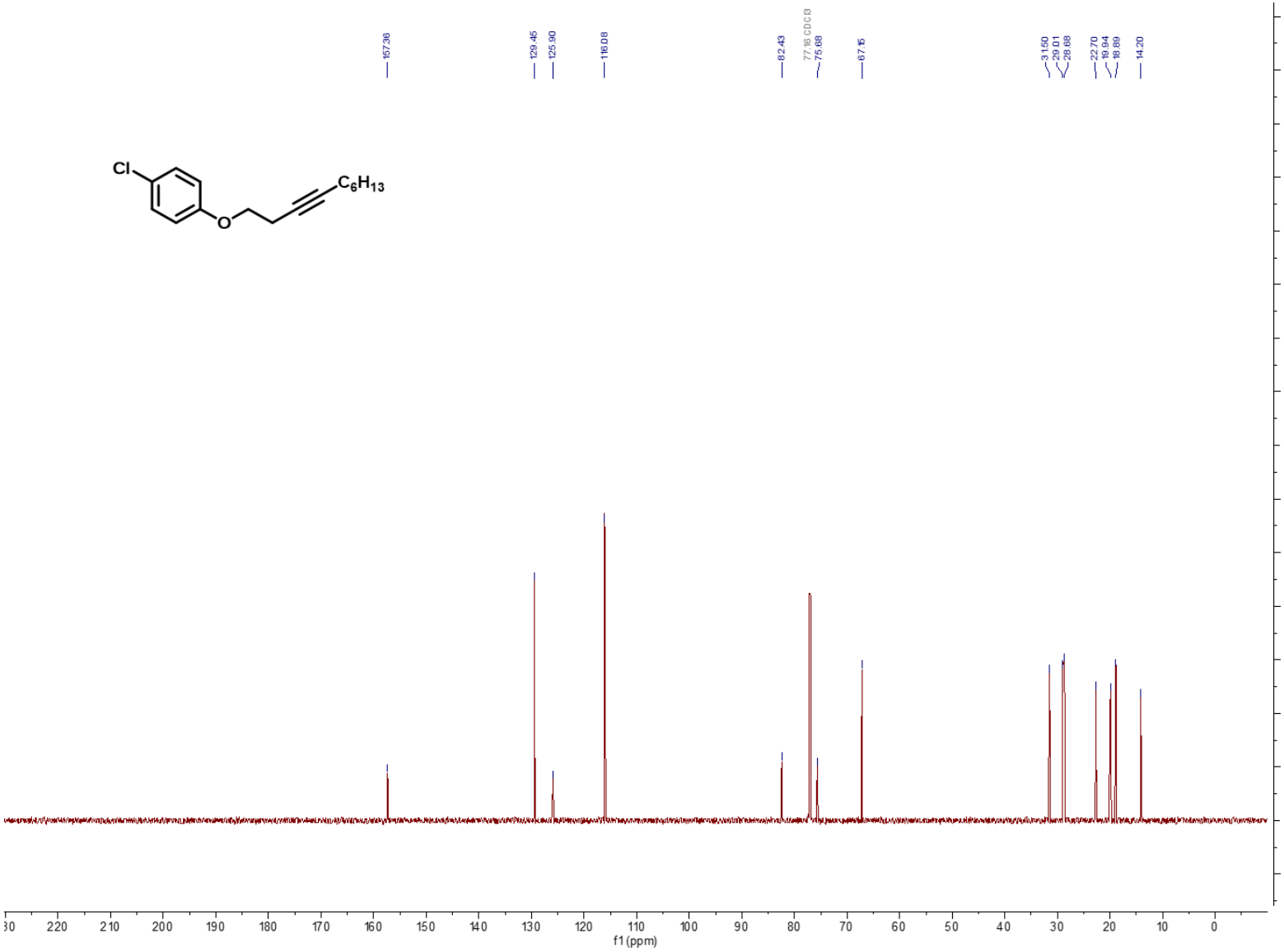
^{13}C NMR (126 MHz, $CDCL_3$) OF COMPOUND **S7**



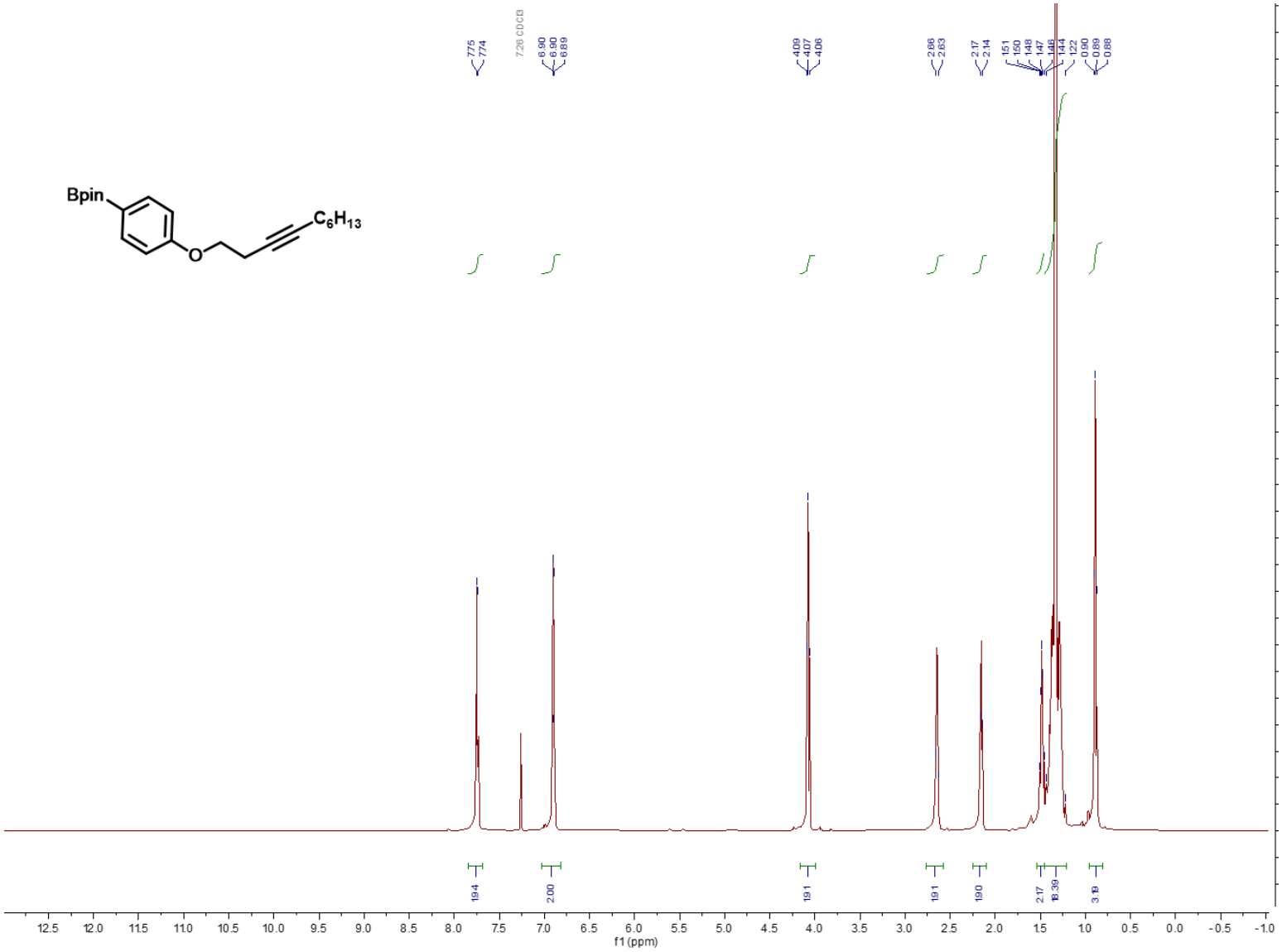
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S8**



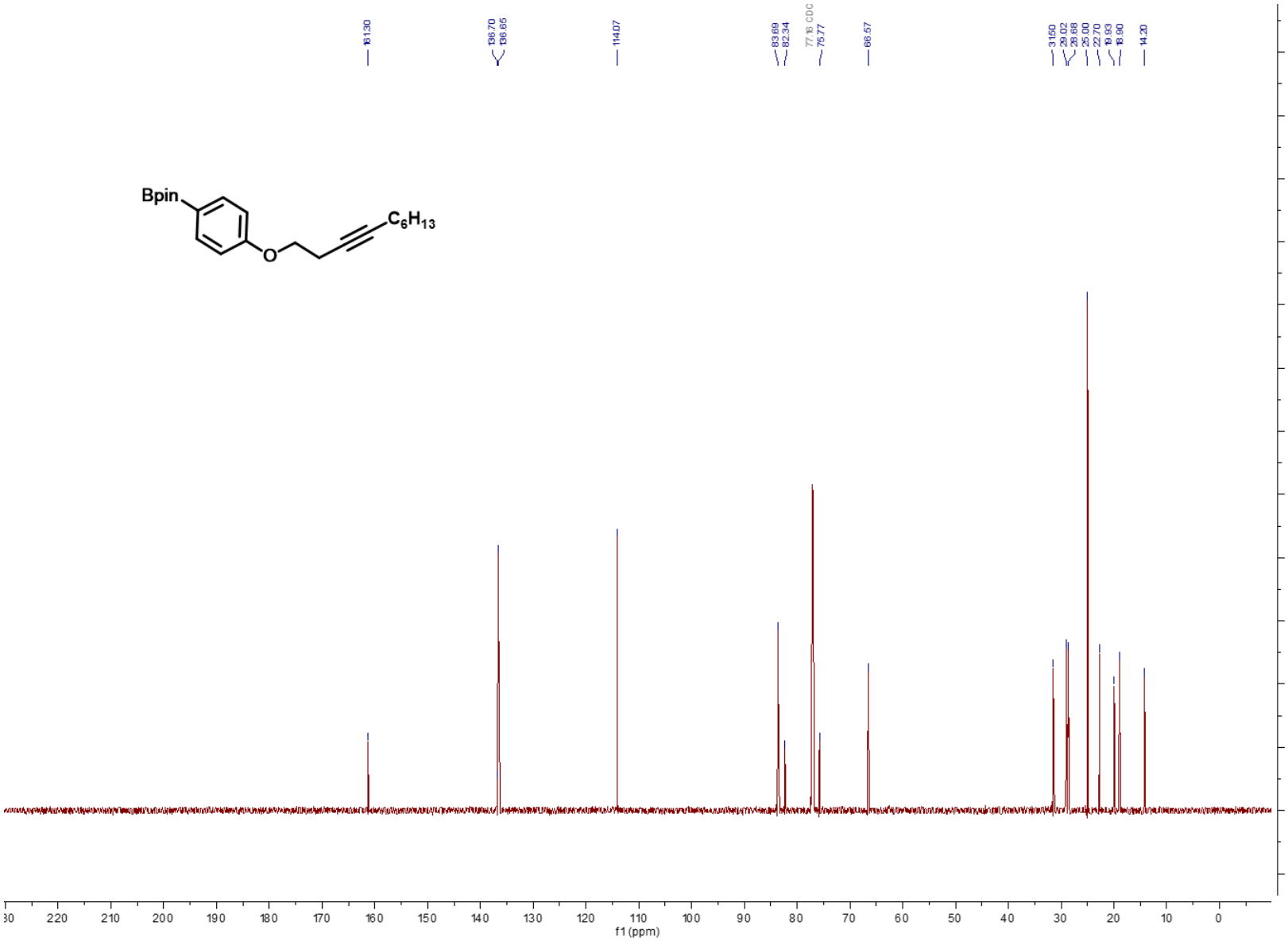
^{13}C NMR (151 MHz, $CDCl_3$) OF COMPOUND **S8**



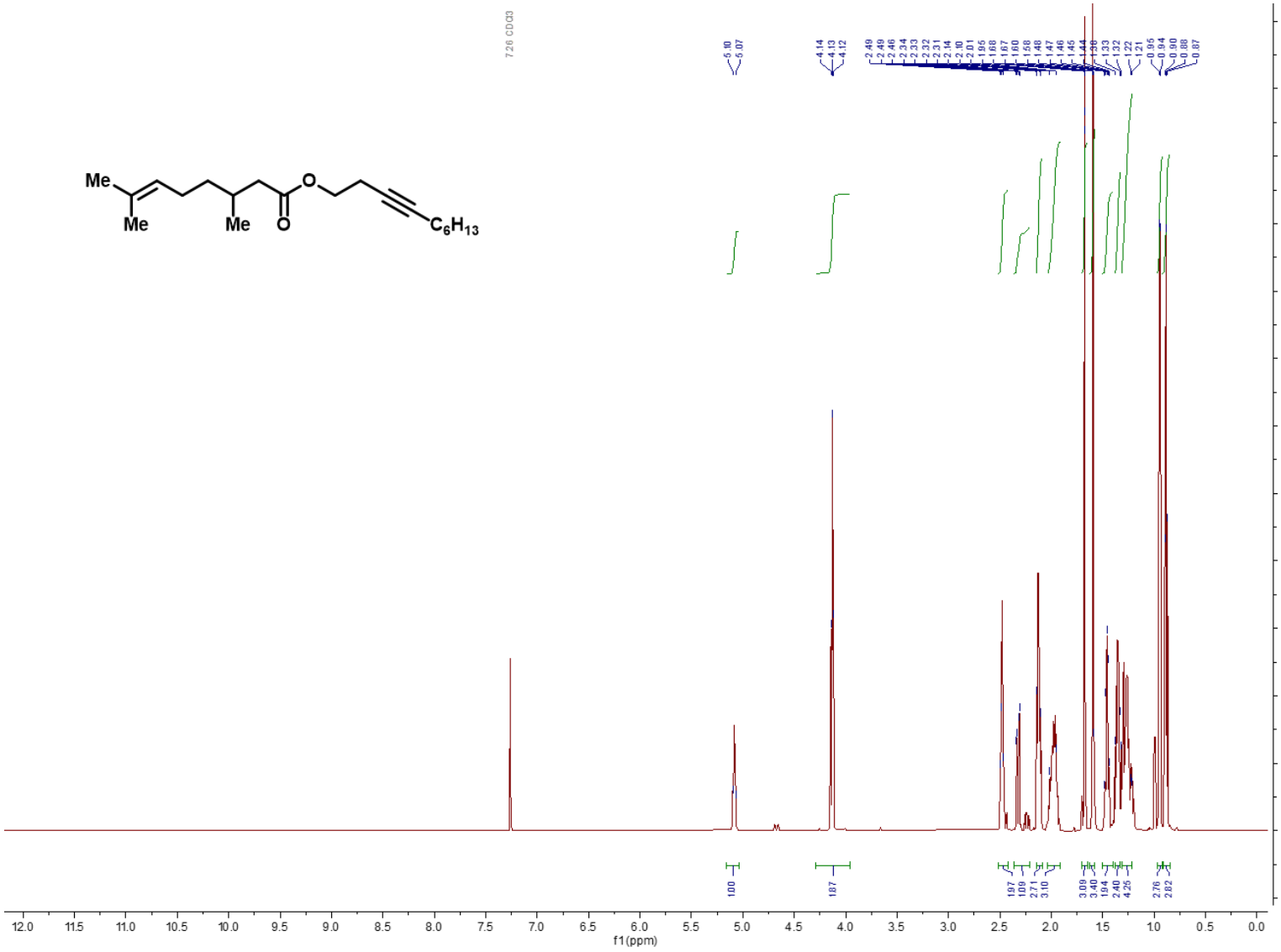
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S9**



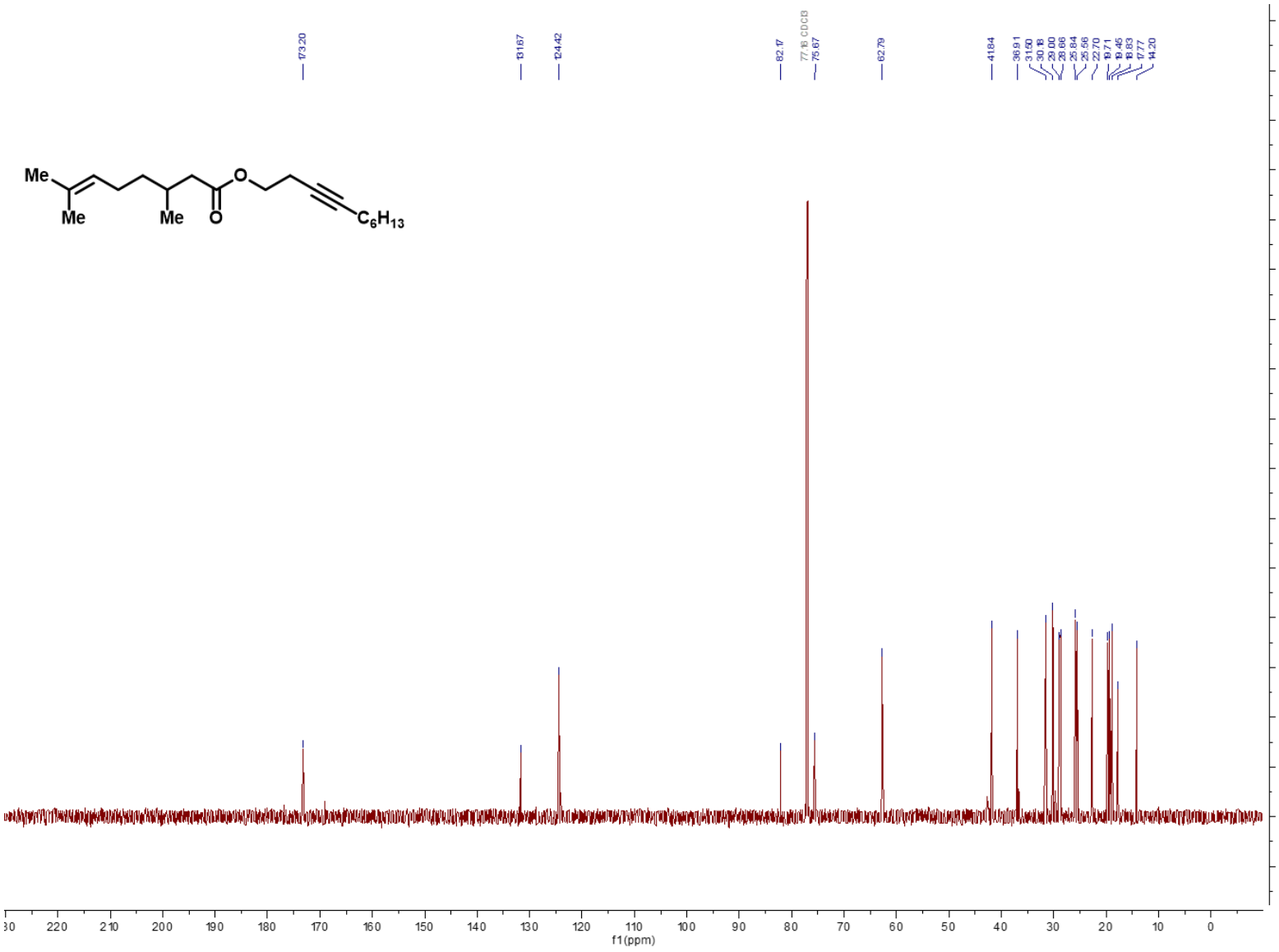
^{13}C NMR (151 MHz, $CDCL_3$) OF COMPOUND **S9**



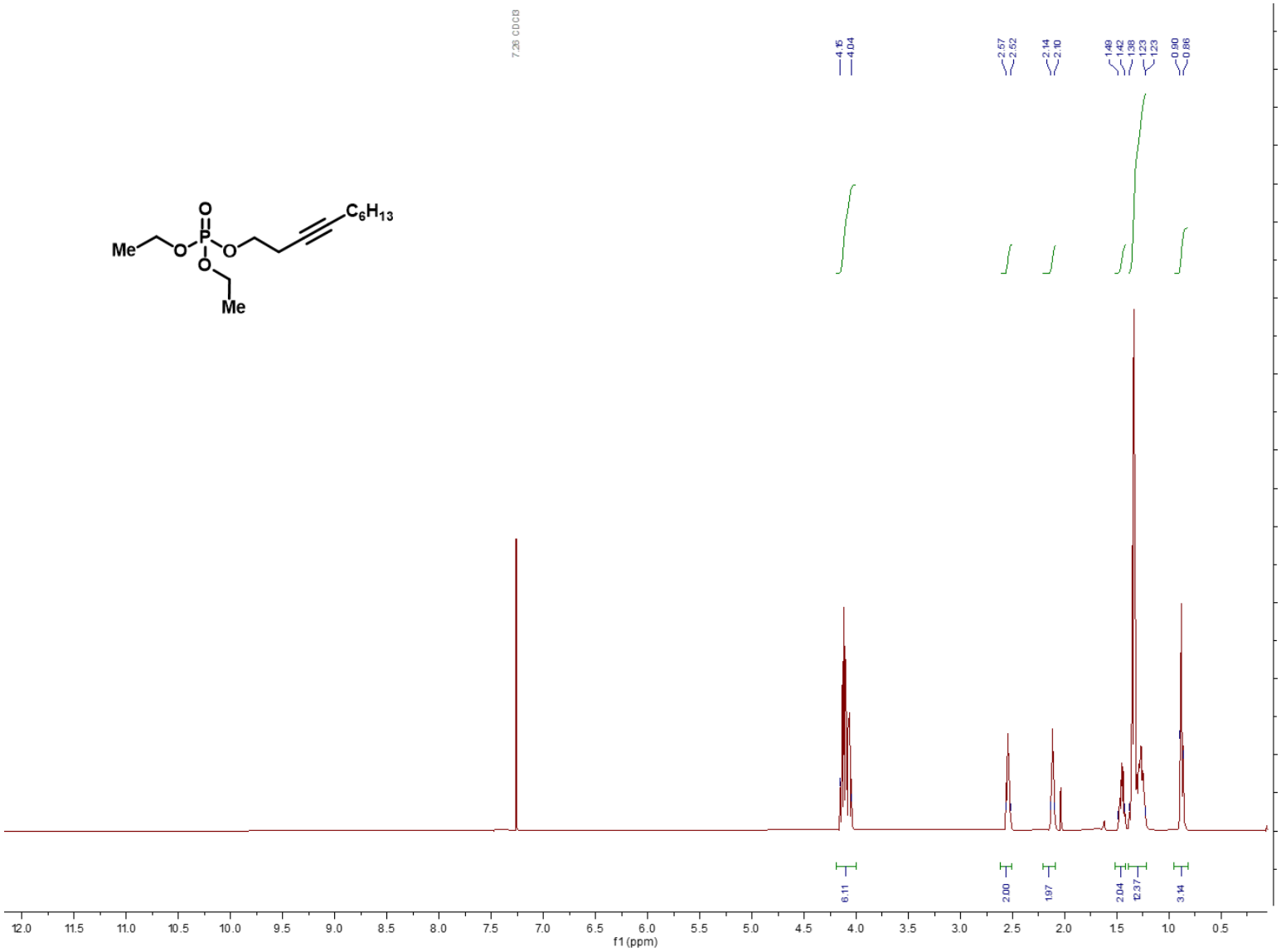
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S10**



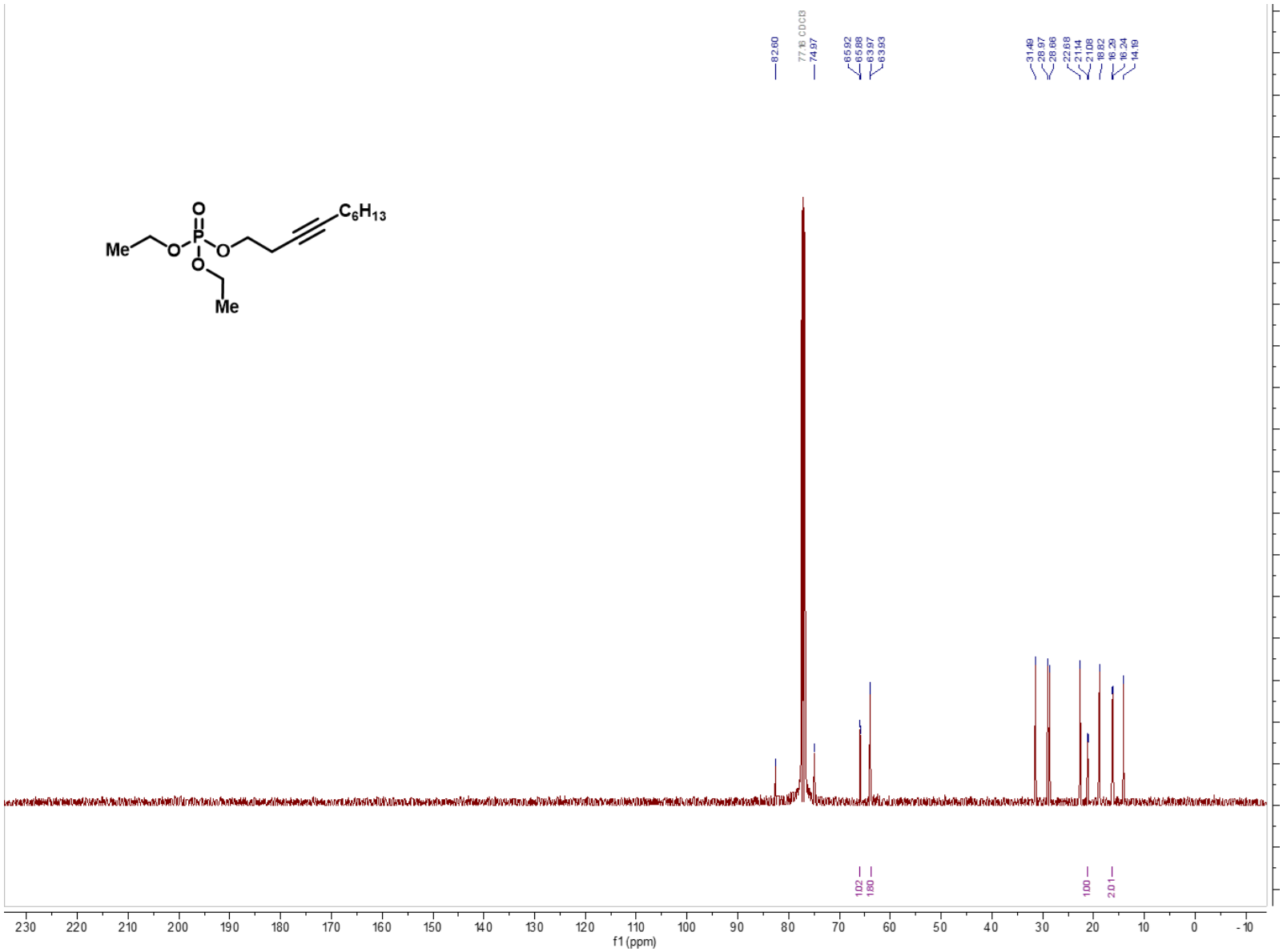
^{13}C NMR (151 MHz, $CDCL_3$) OF COMPOUND **S10**



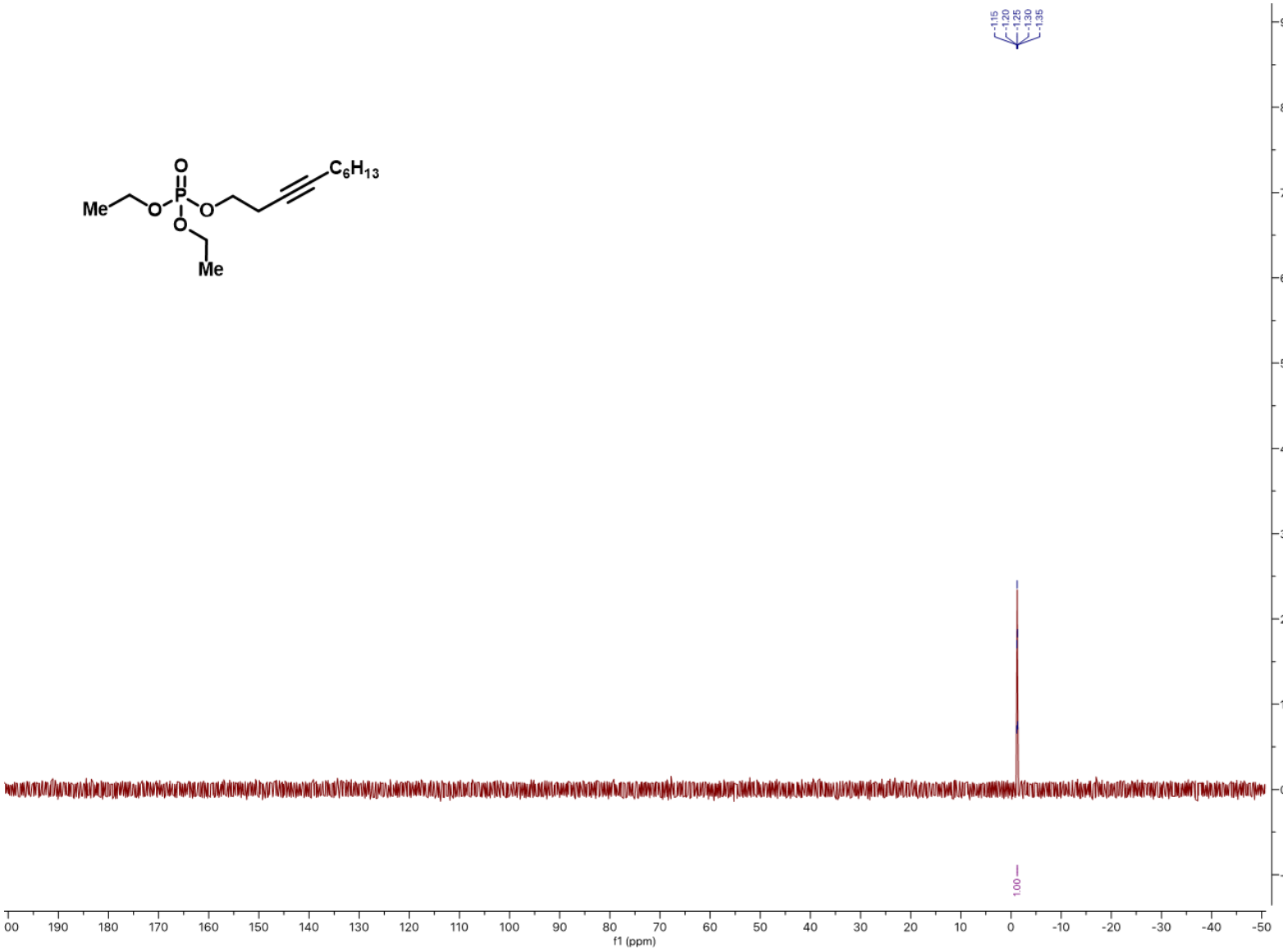
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S11**



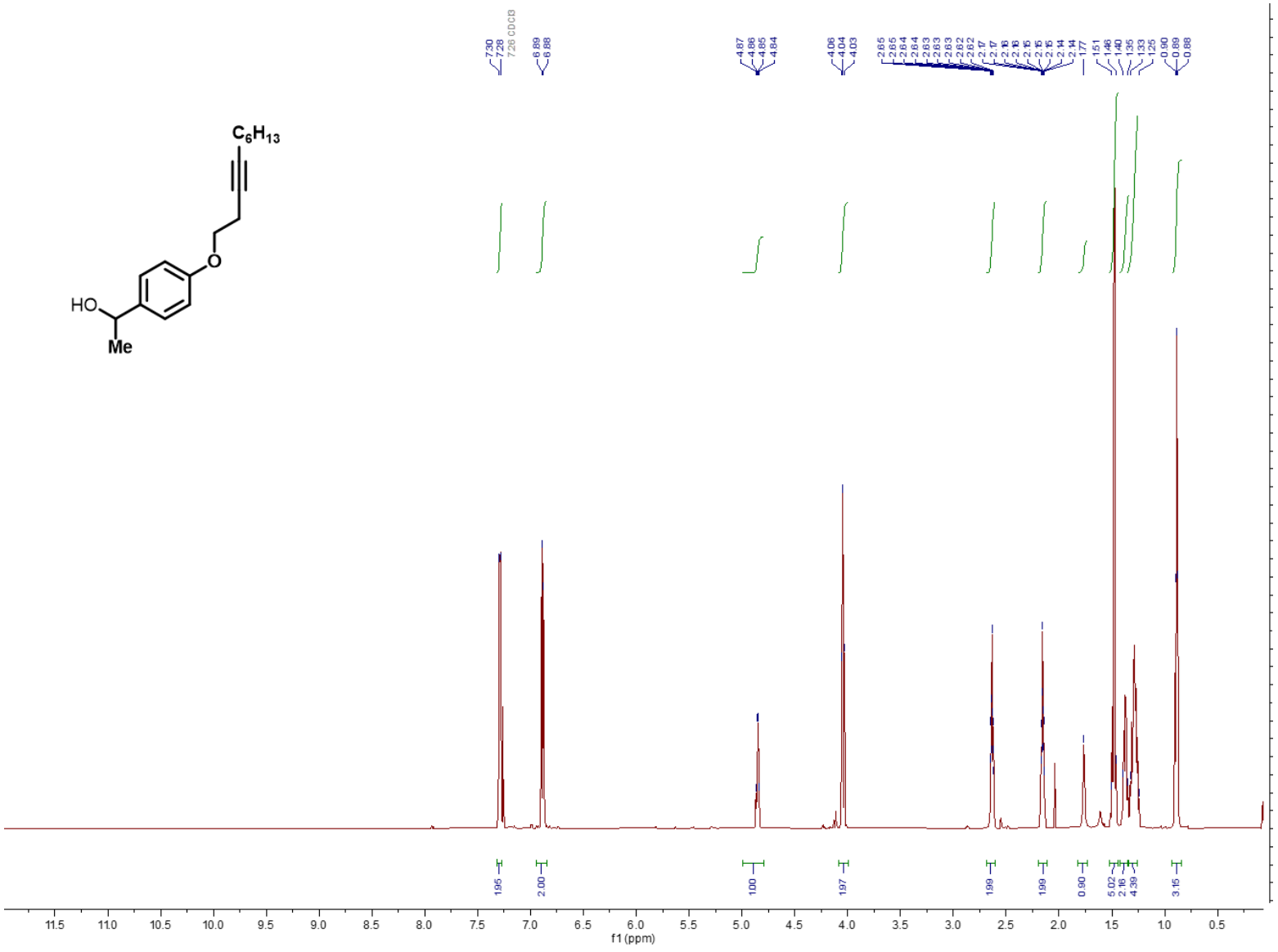
^{13}C NMR (126 MHz, $CDCl_3$) OF COMPOUND **S11**



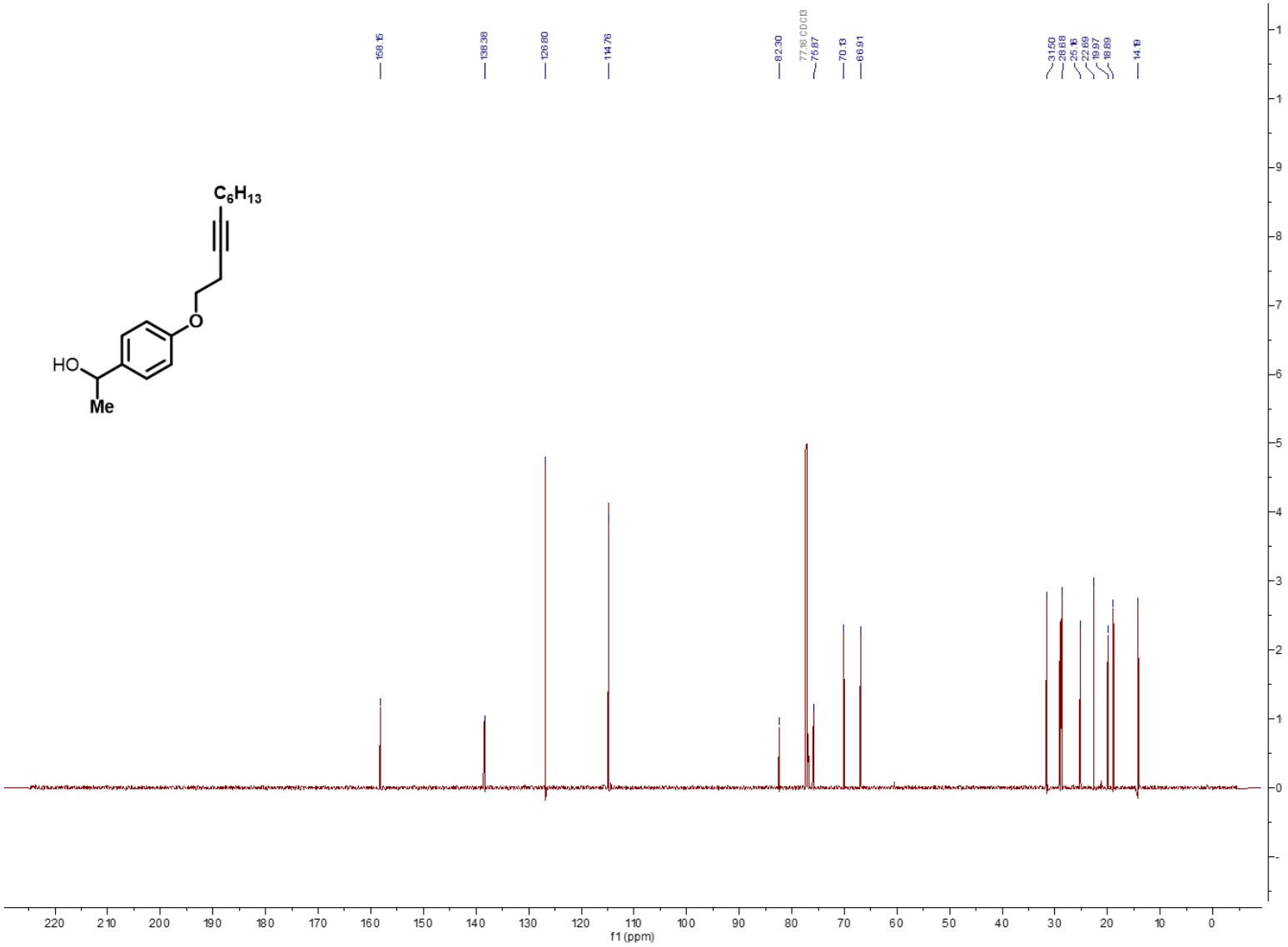
^{31}P NMR (162 MHz, $CDCl_3$) of compound **S11**



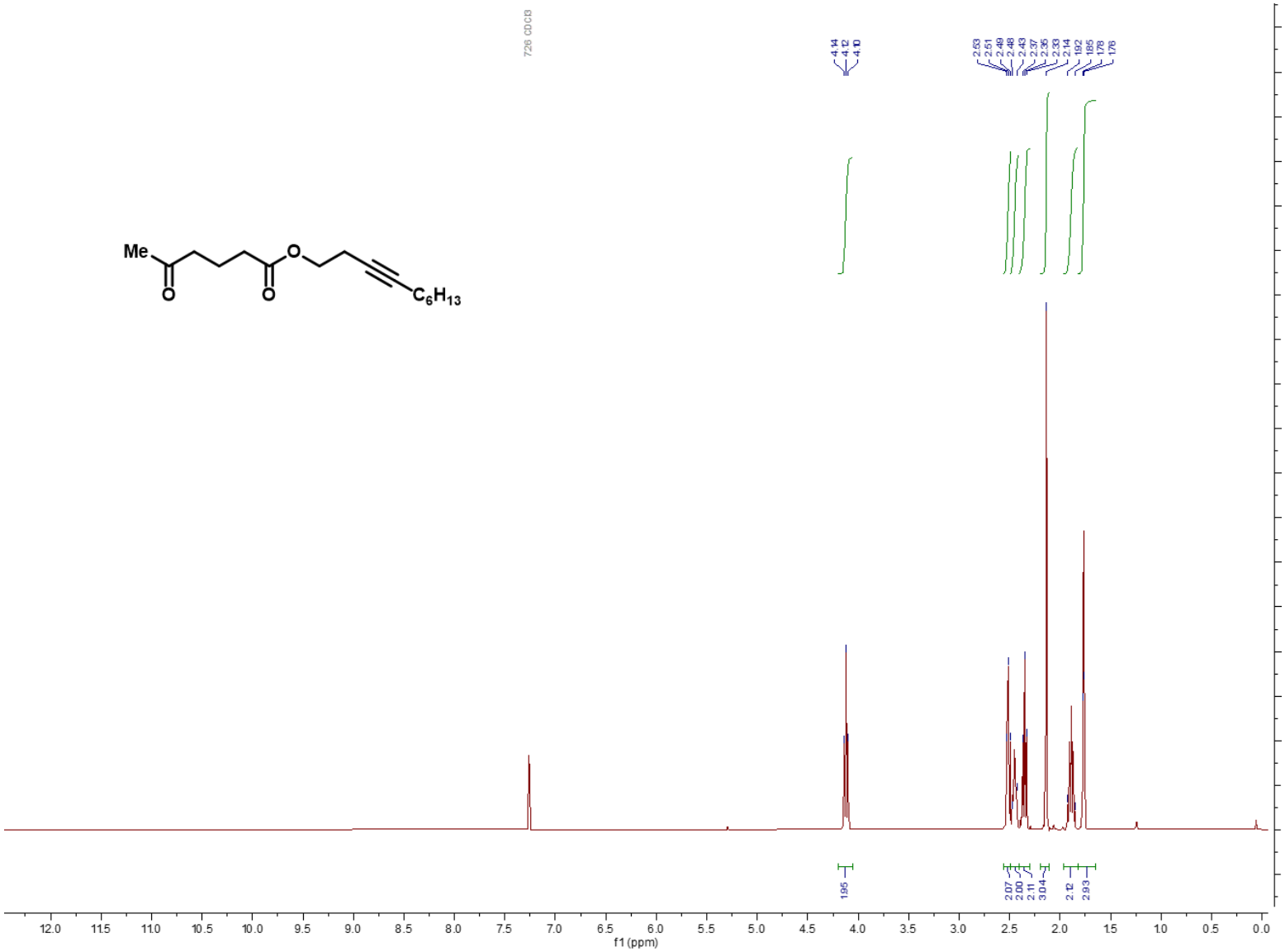
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S12**



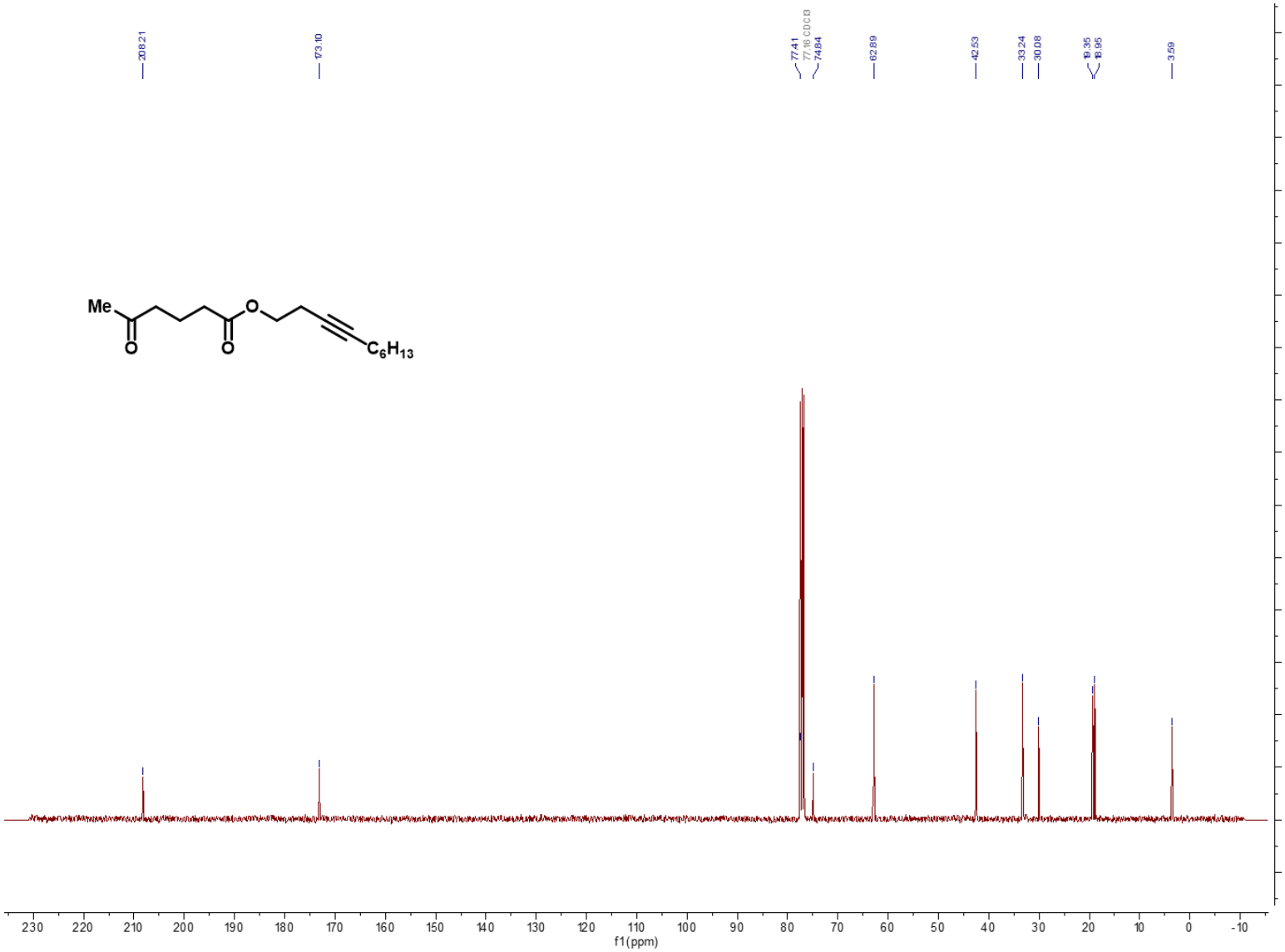
^{13}C NMR (151 MHz, $CDCl_3$) of compound **S12**



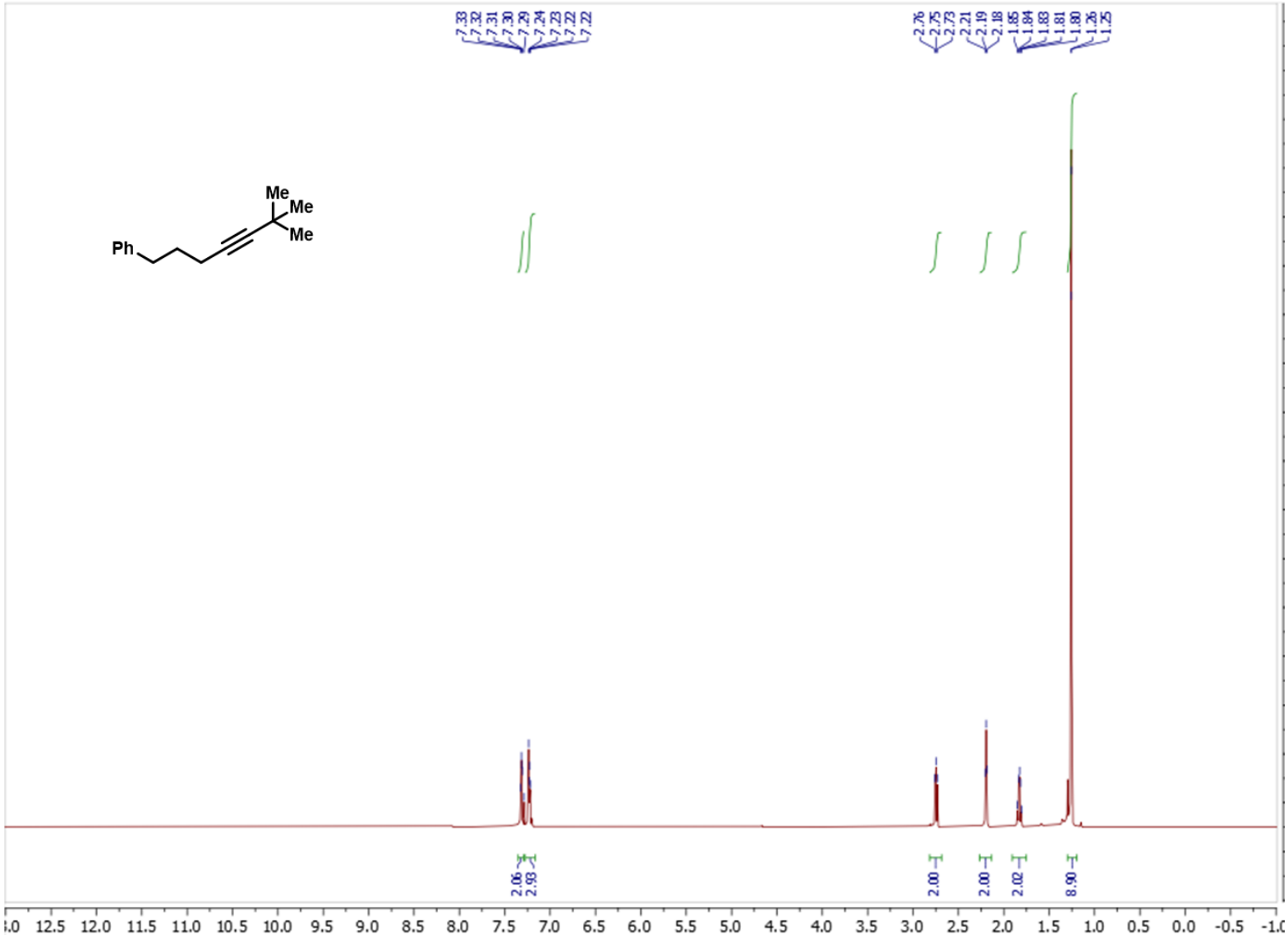
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S13**



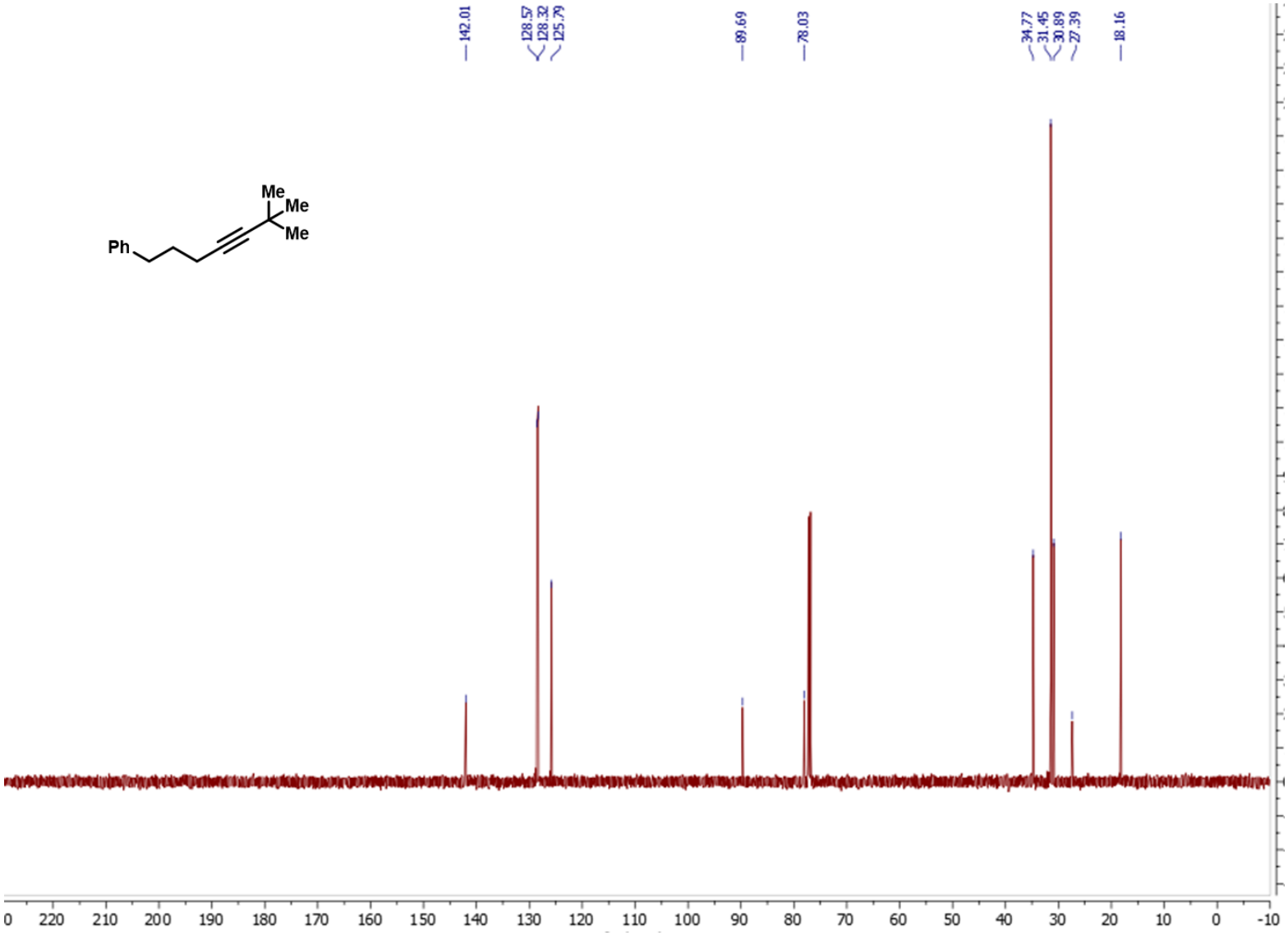
^{13}C NMR (101 MHz, $CDCl_3$) of compound **S13**



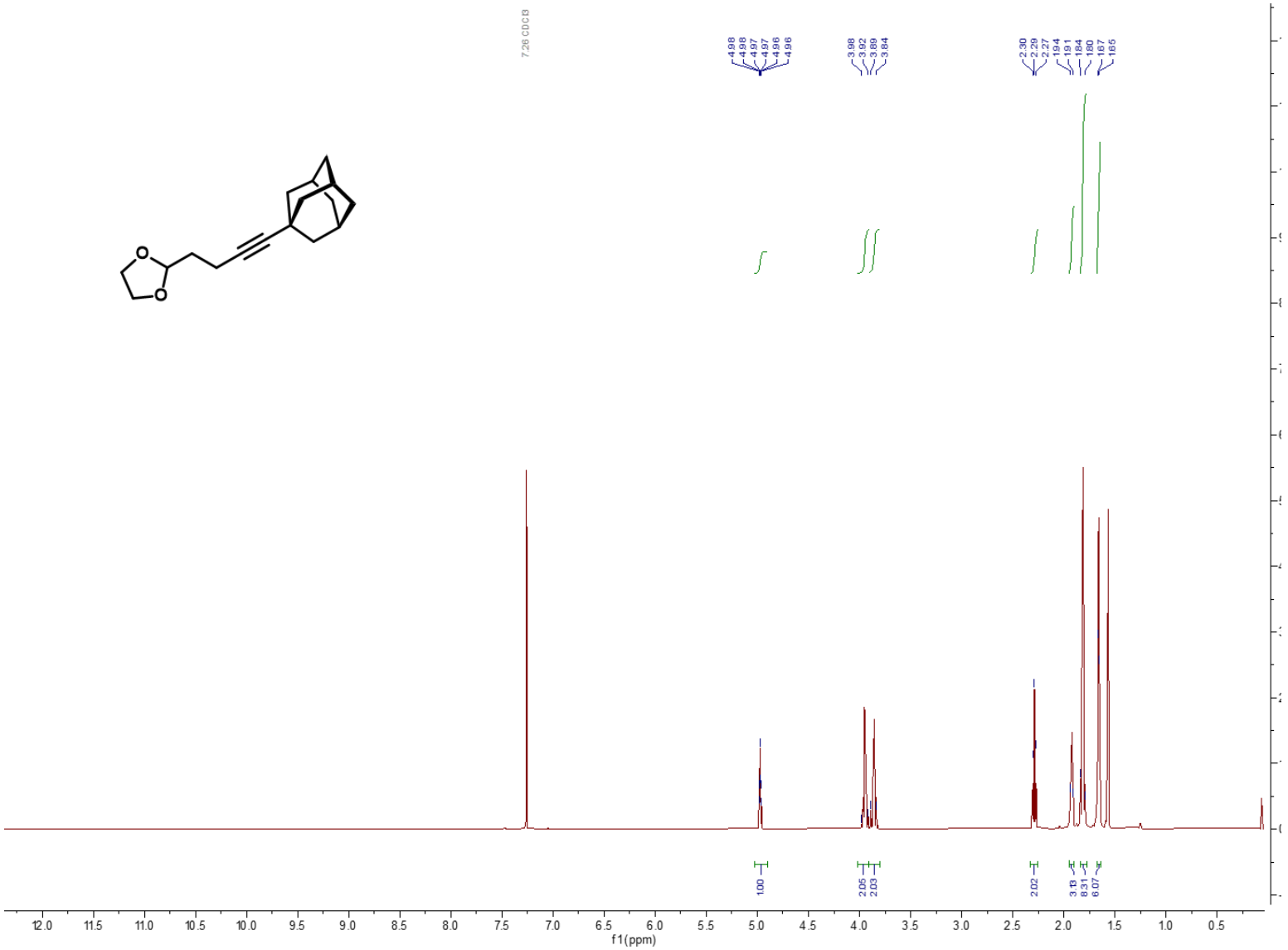
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S14**



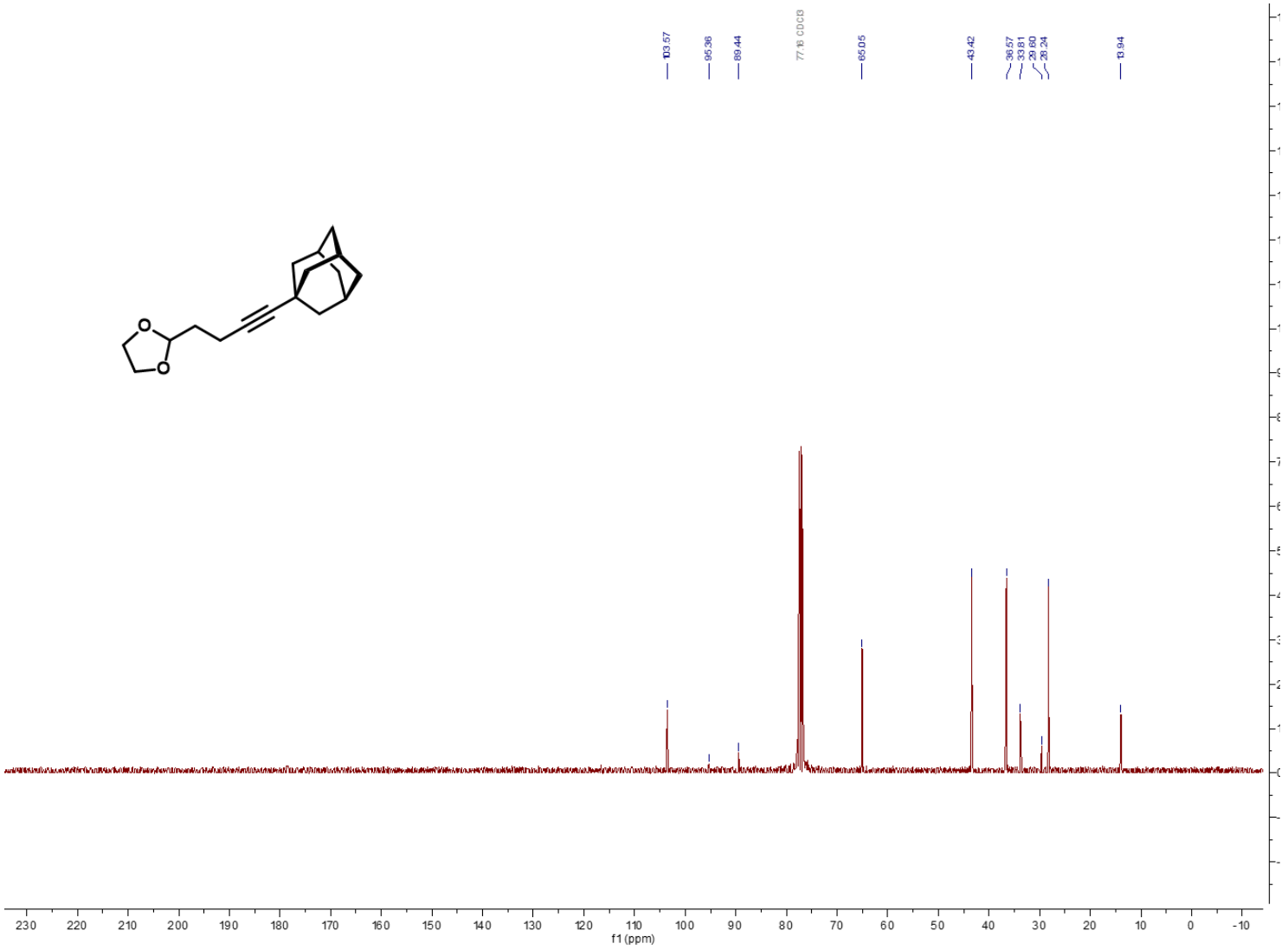
^{13}C NMR (151 MHz, $CDCl_3$) of compound **S14**



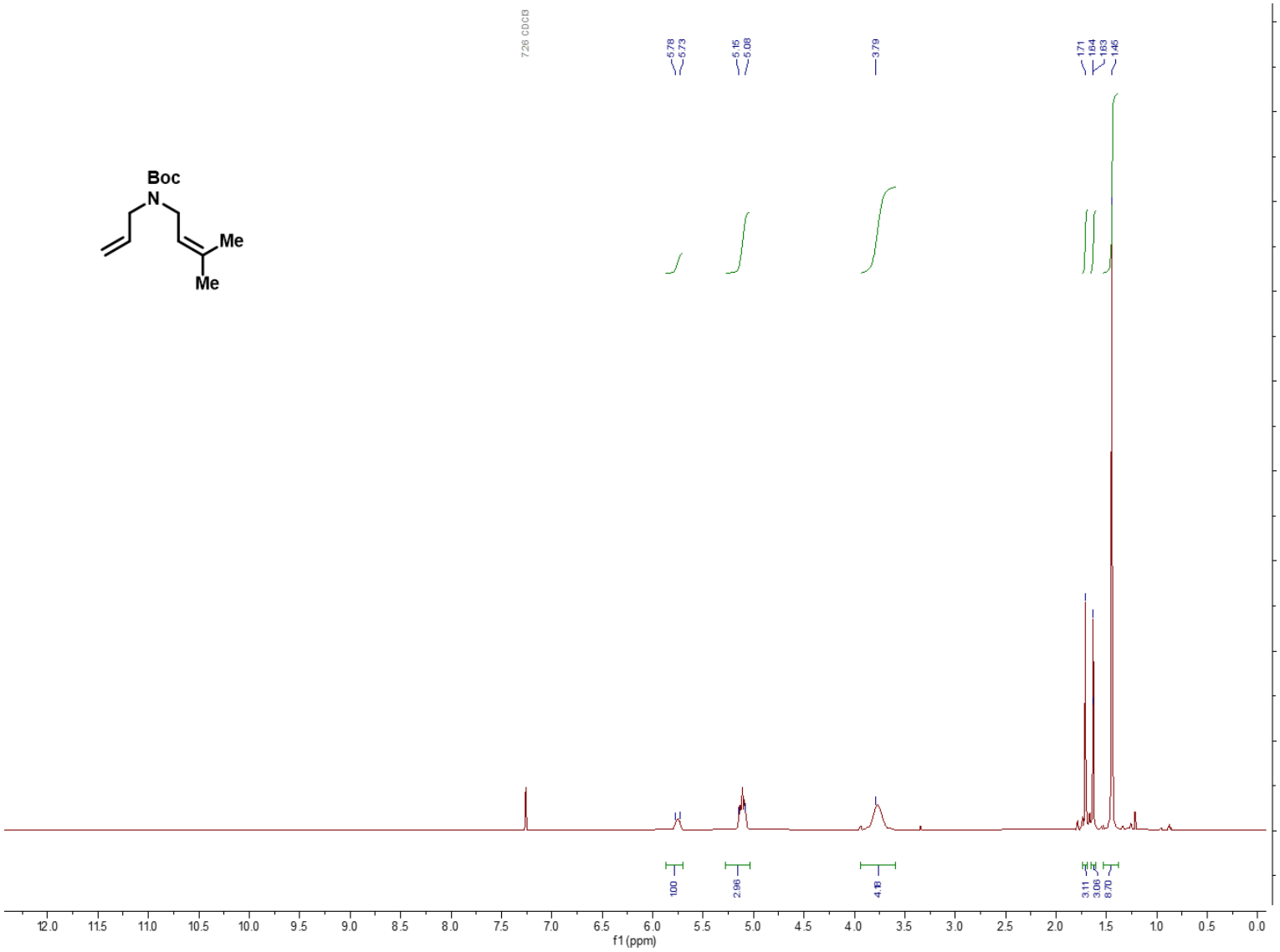
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S15**



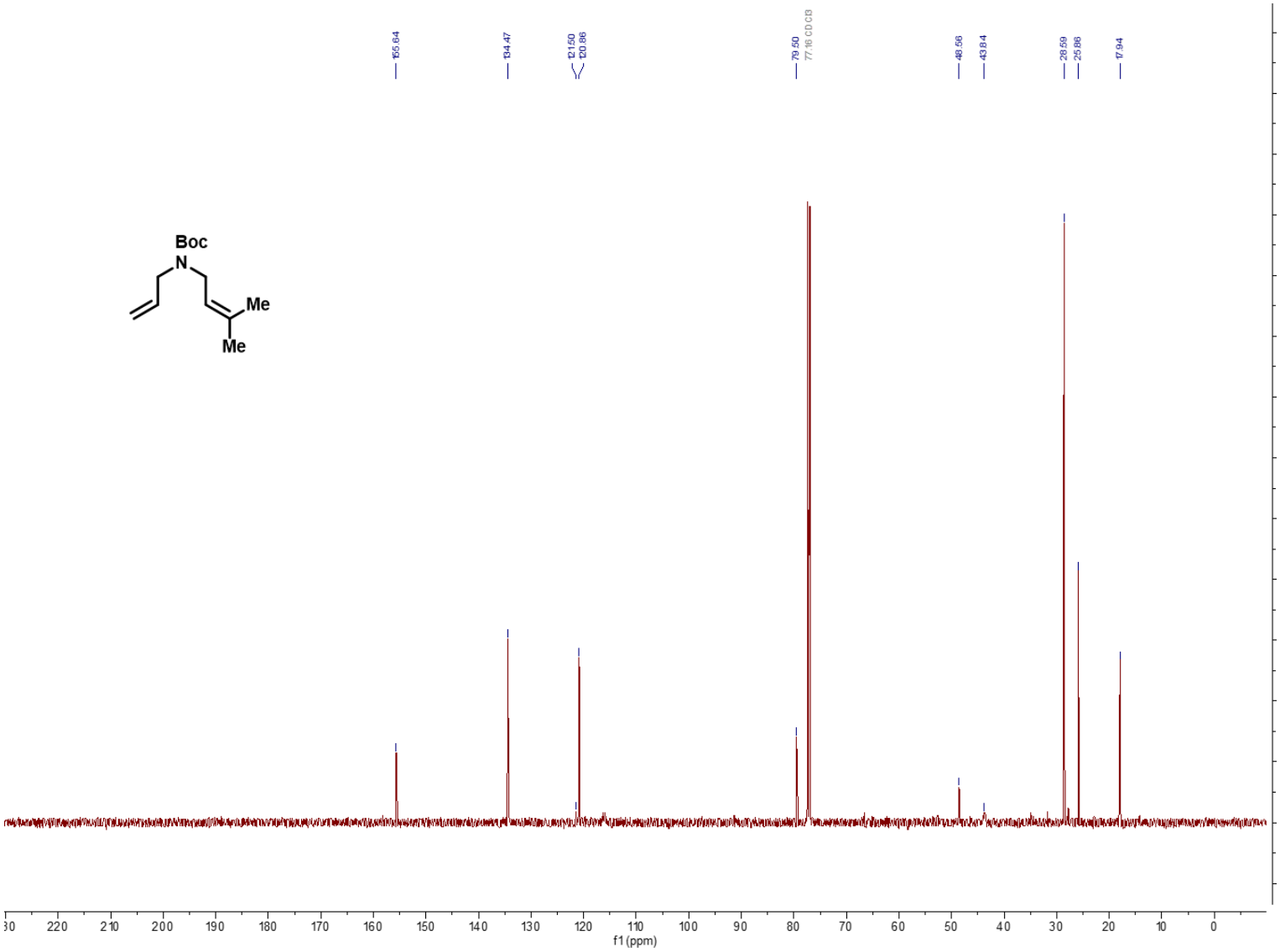
^{13}C NMR (126 MHz, $CDCl_3$) of compound **S15**



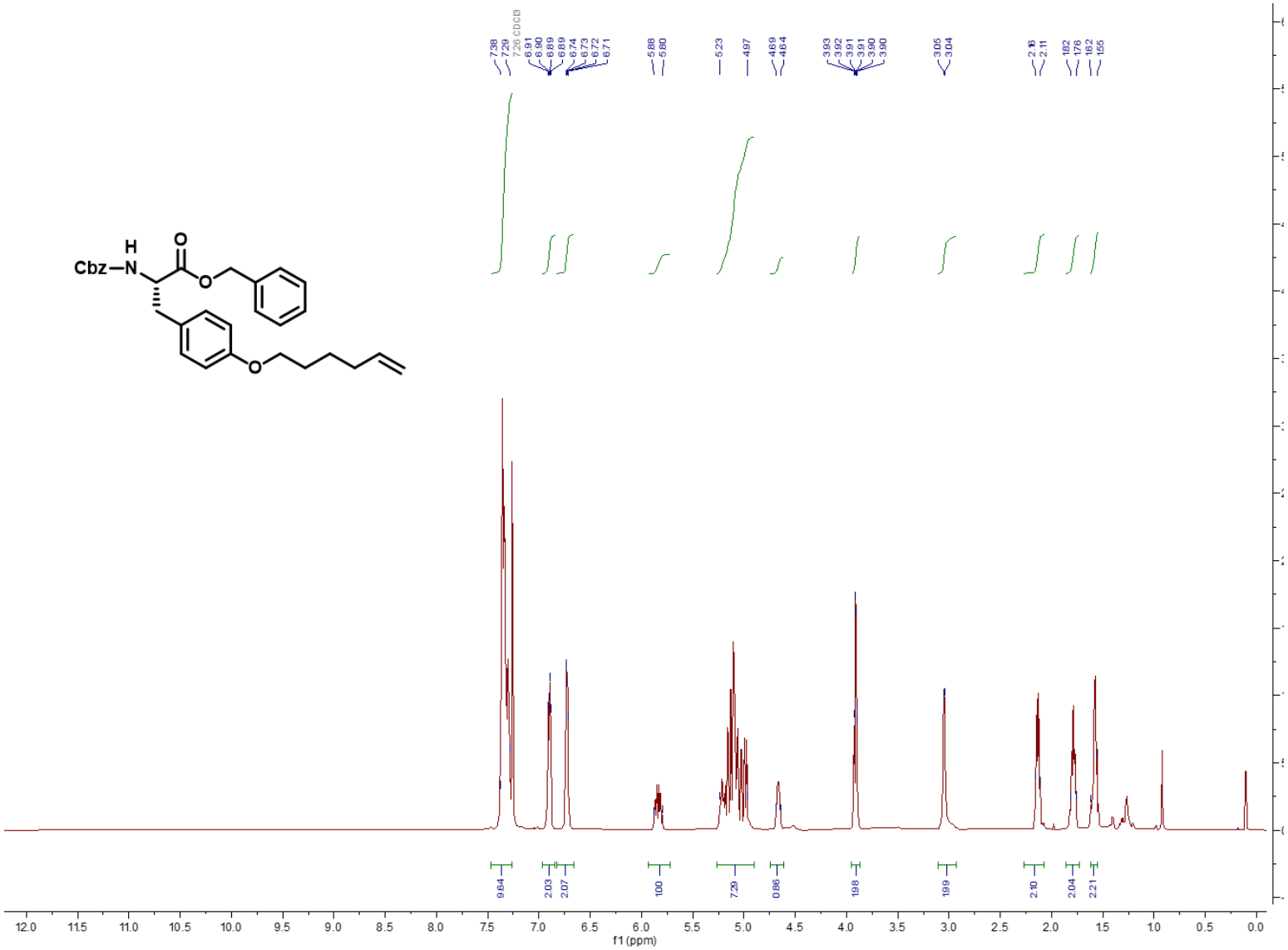
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S16**



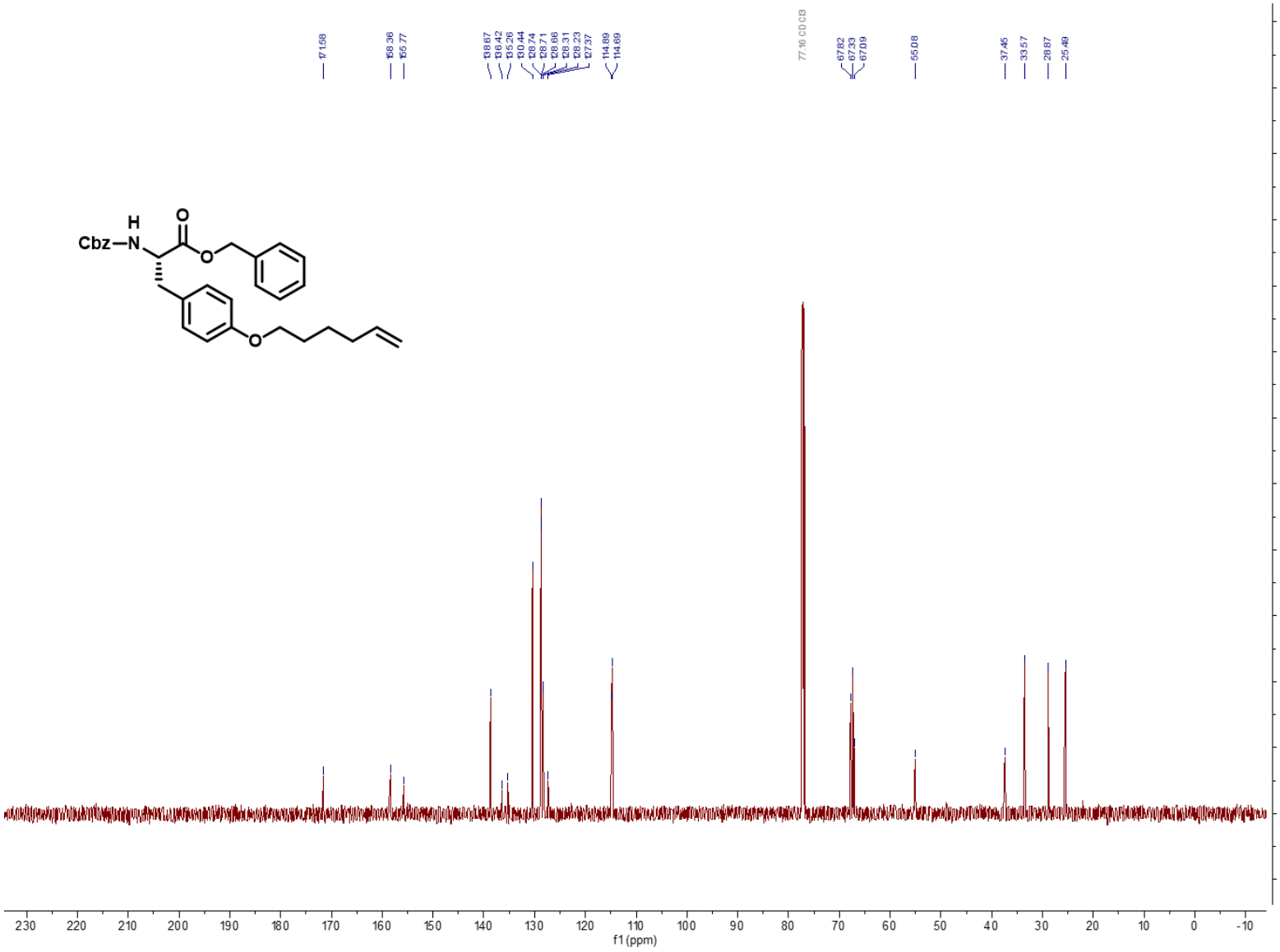
^{13}C NMR (151 MHz, $CDCl_3$) of compound **S16**



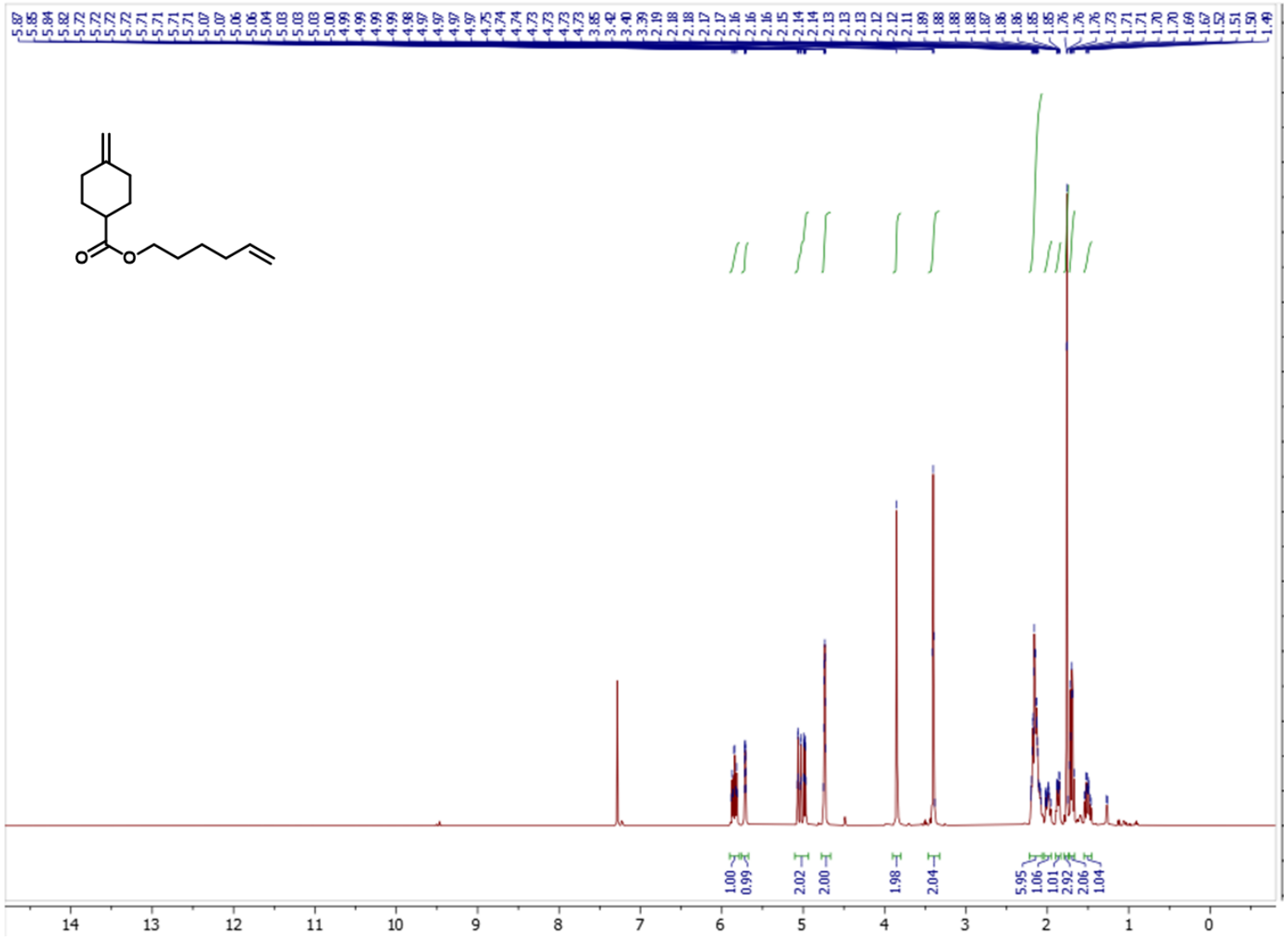
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S17**



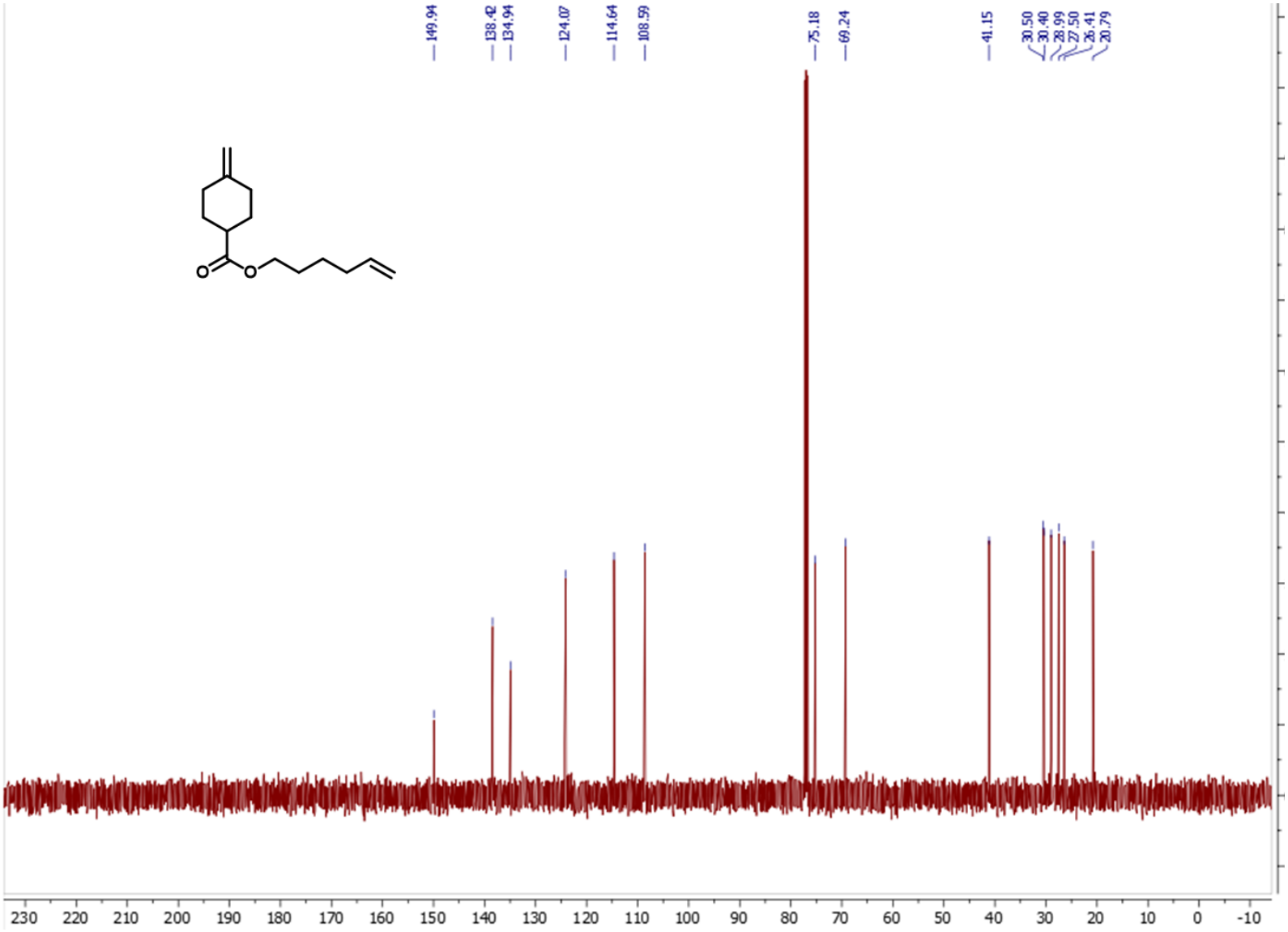
^{13}C NMR (126 MHz, $CDCl_3$) of compound **S17**



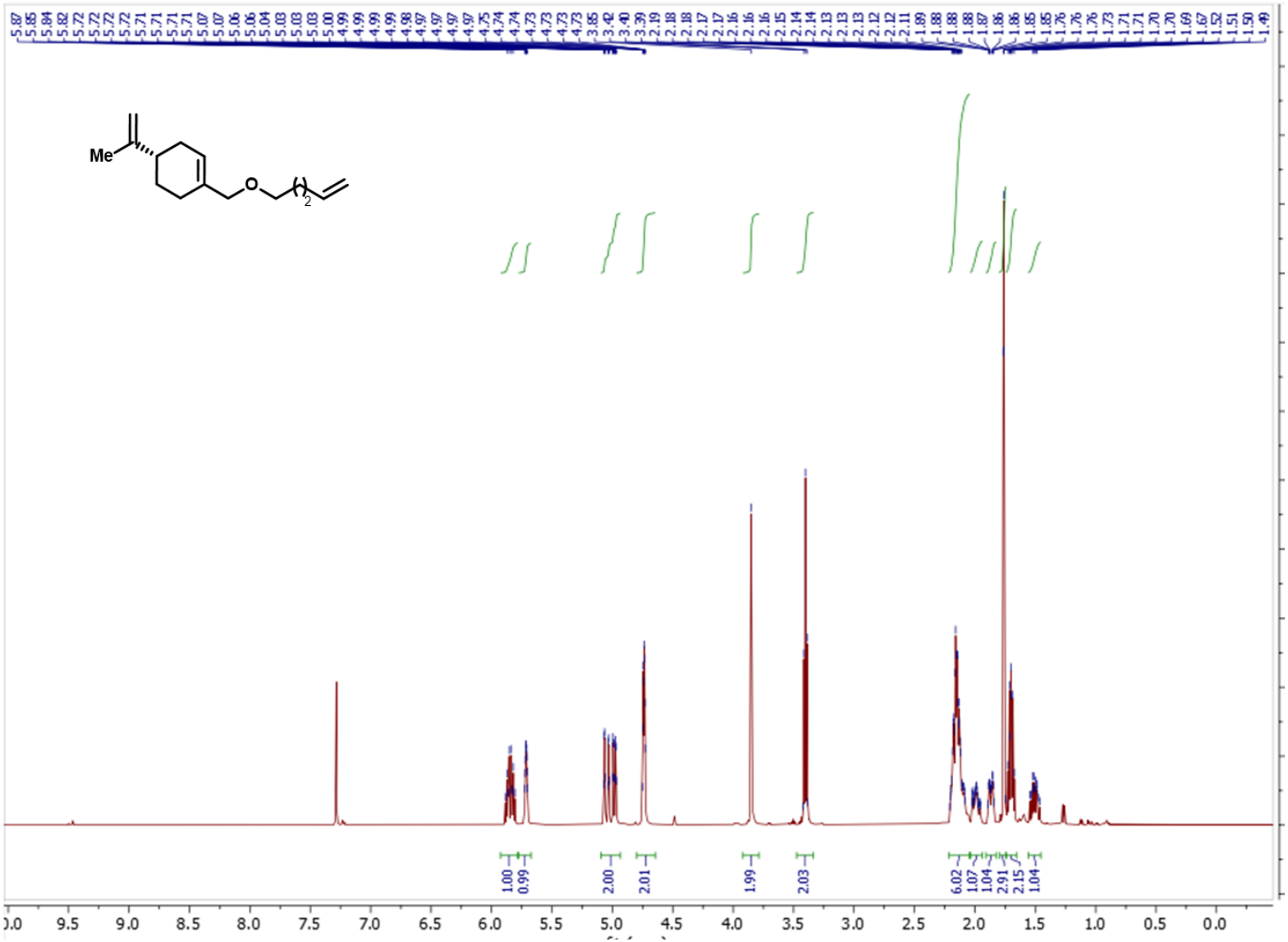
^{1}H NMR (500 MHz, $CDCl_3$) of compound **50**



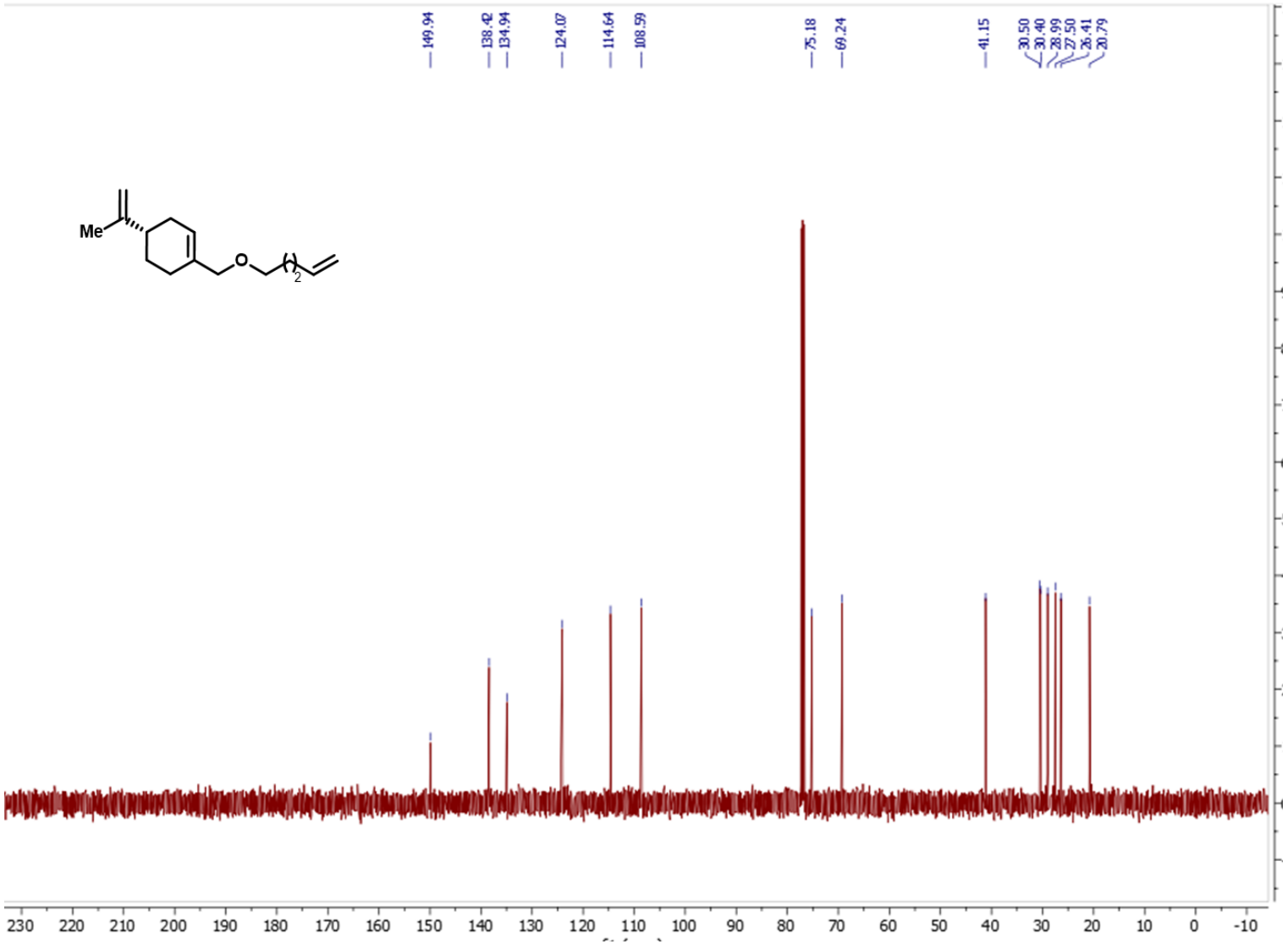
^{13}C NMR (126 MHz, $CDCl_3$) of compound **50**



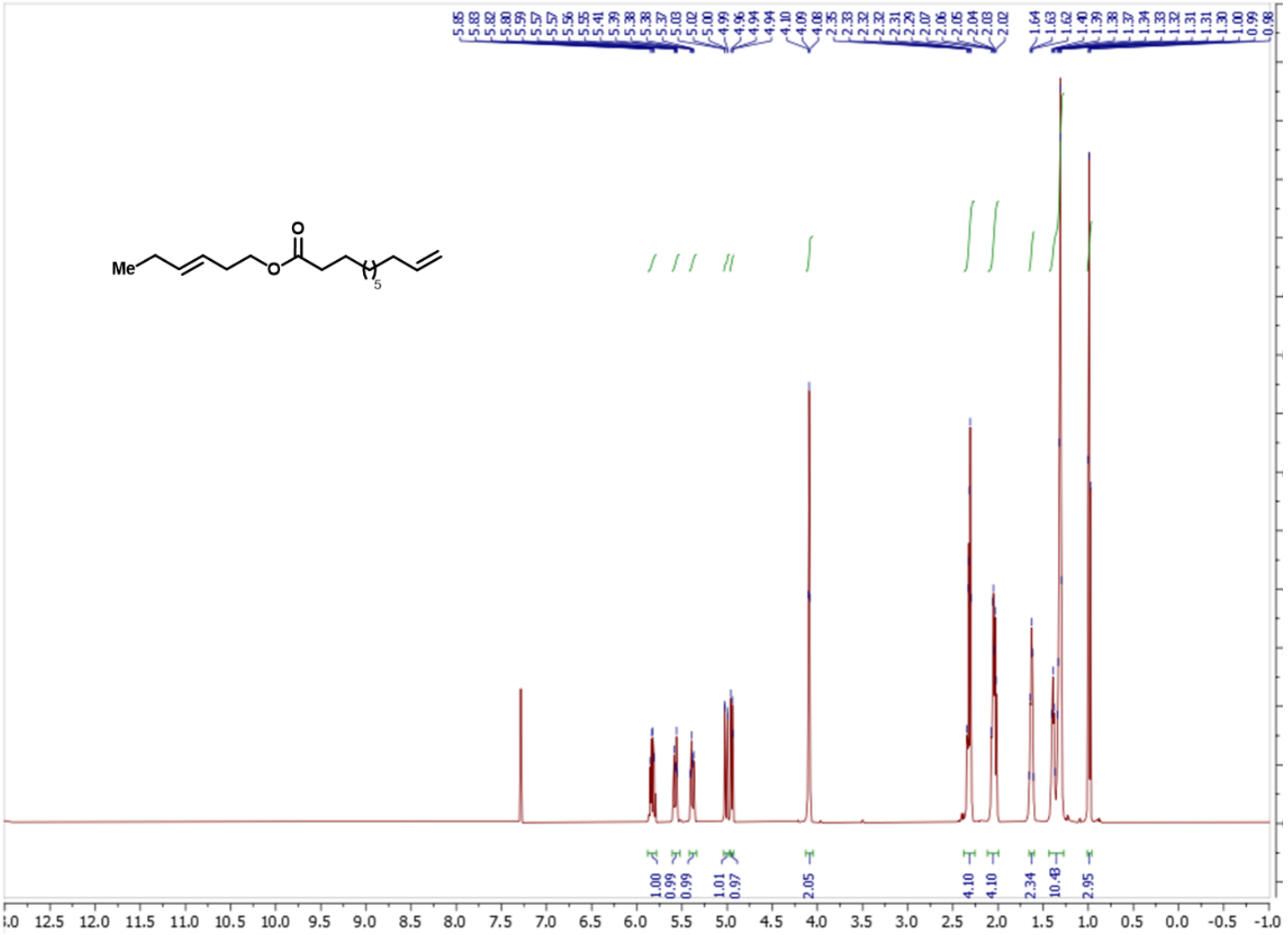
^{1}H NMR (500 MHz, $CDCl_3$) of compound **53**



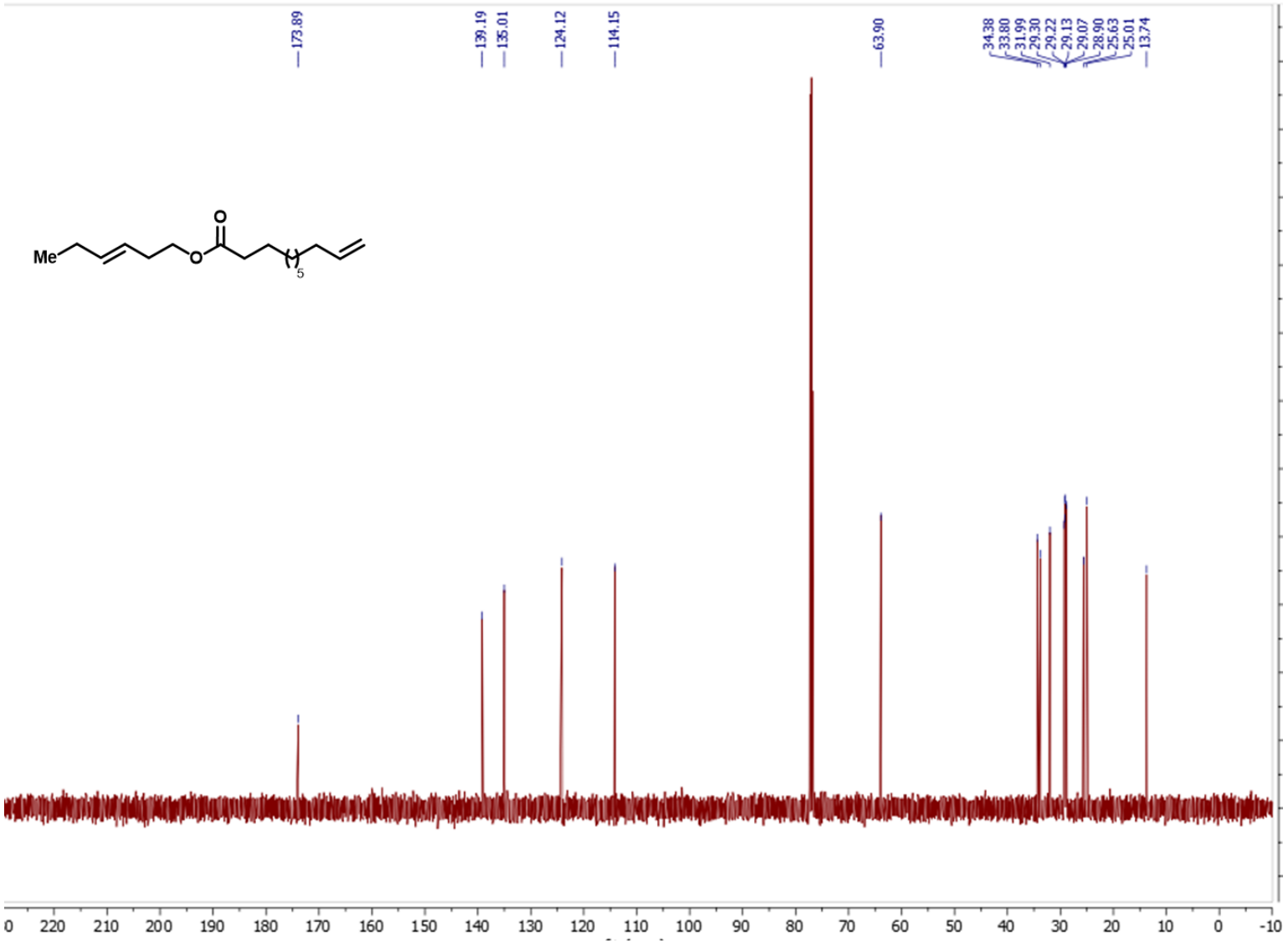
^{13}C NMR (126 MHz, $CDCl_3$) of compound **53**



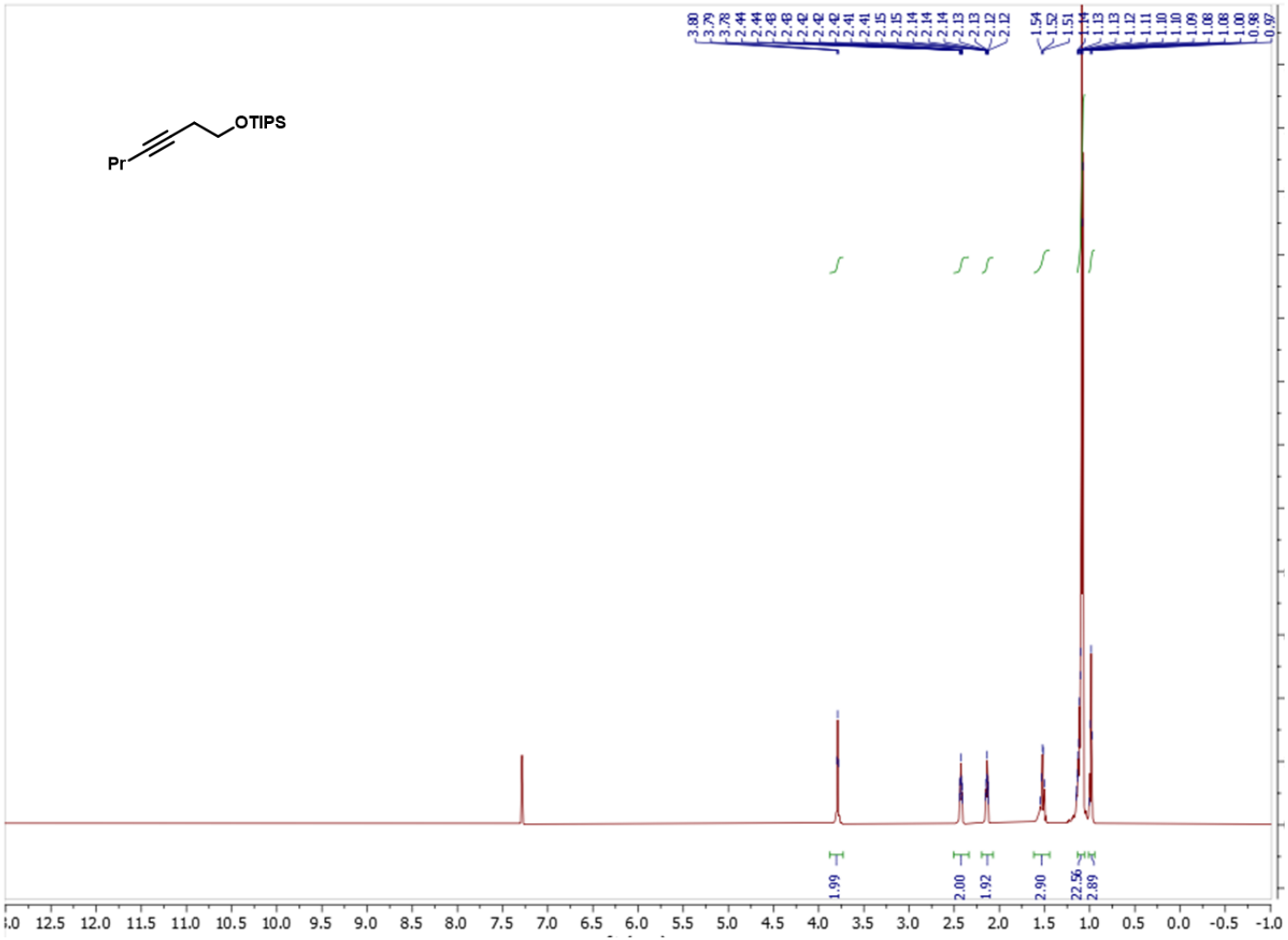
^{1}H NMR (600 MHz, $CDCl_3$) of compound **55**



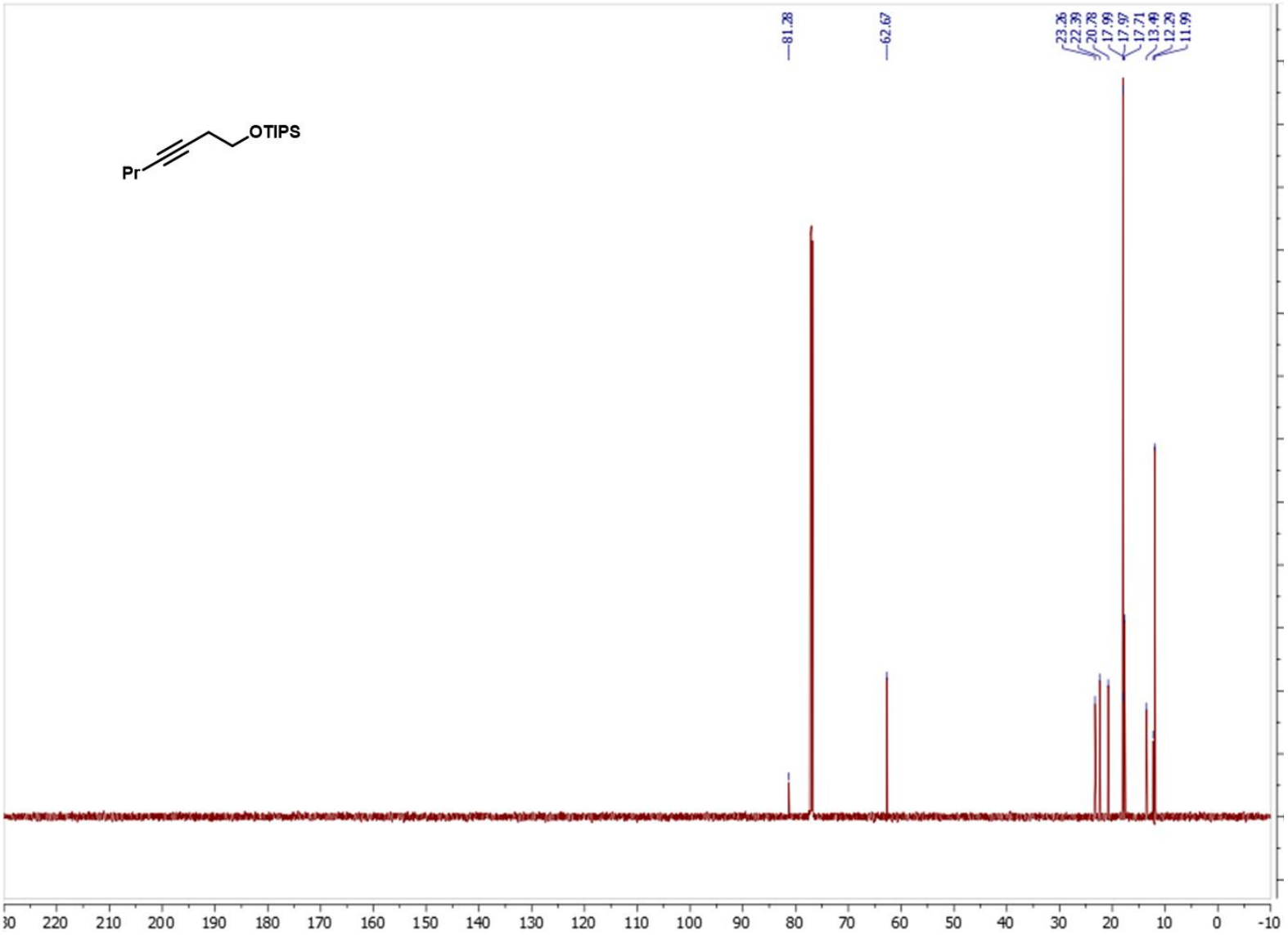
^{13}C NMR (151 MHz, $CDCl_3$) of compound **55**



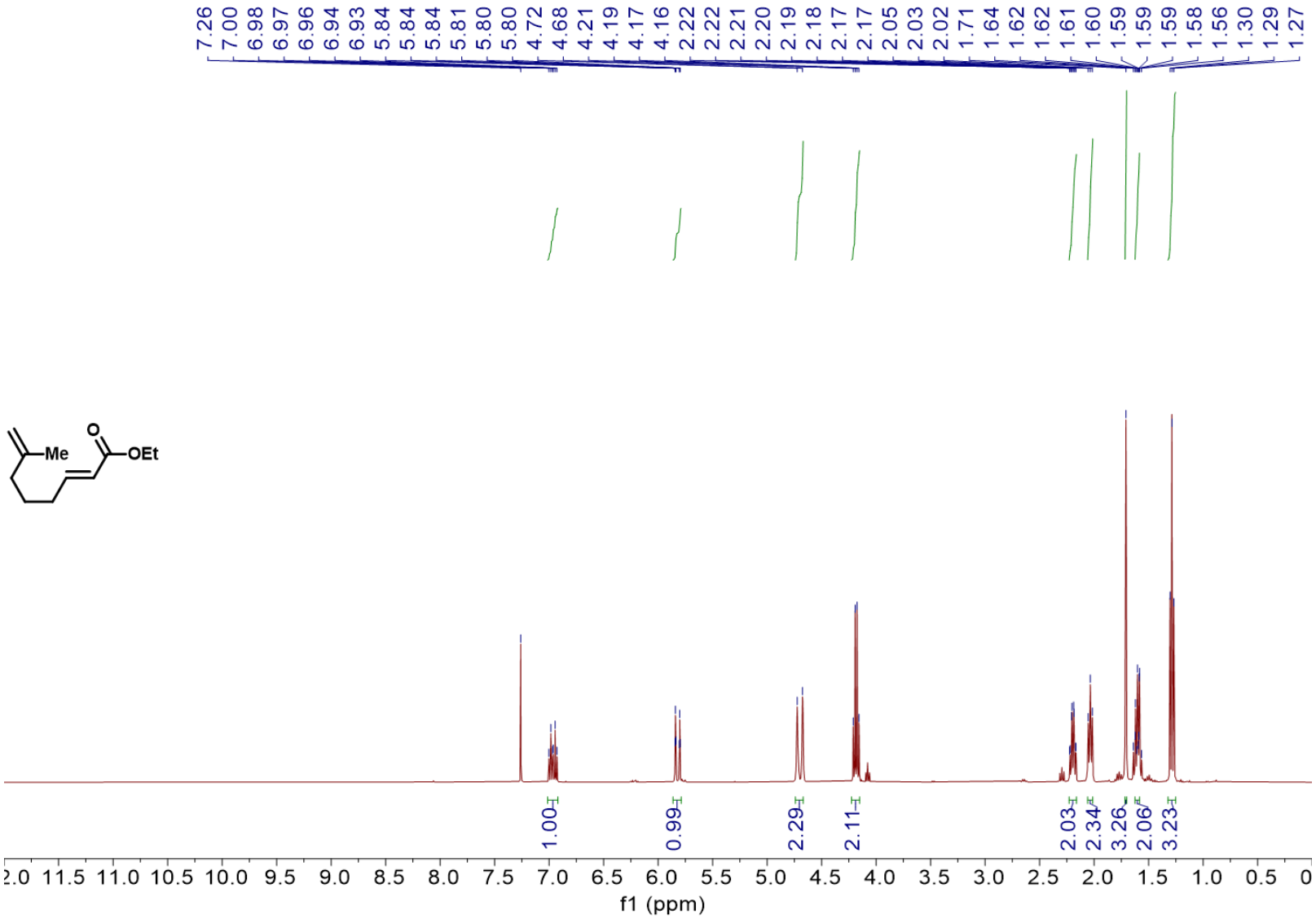
^{1}H NMR (600 MHz, $CDCl_3$) of compound **63**



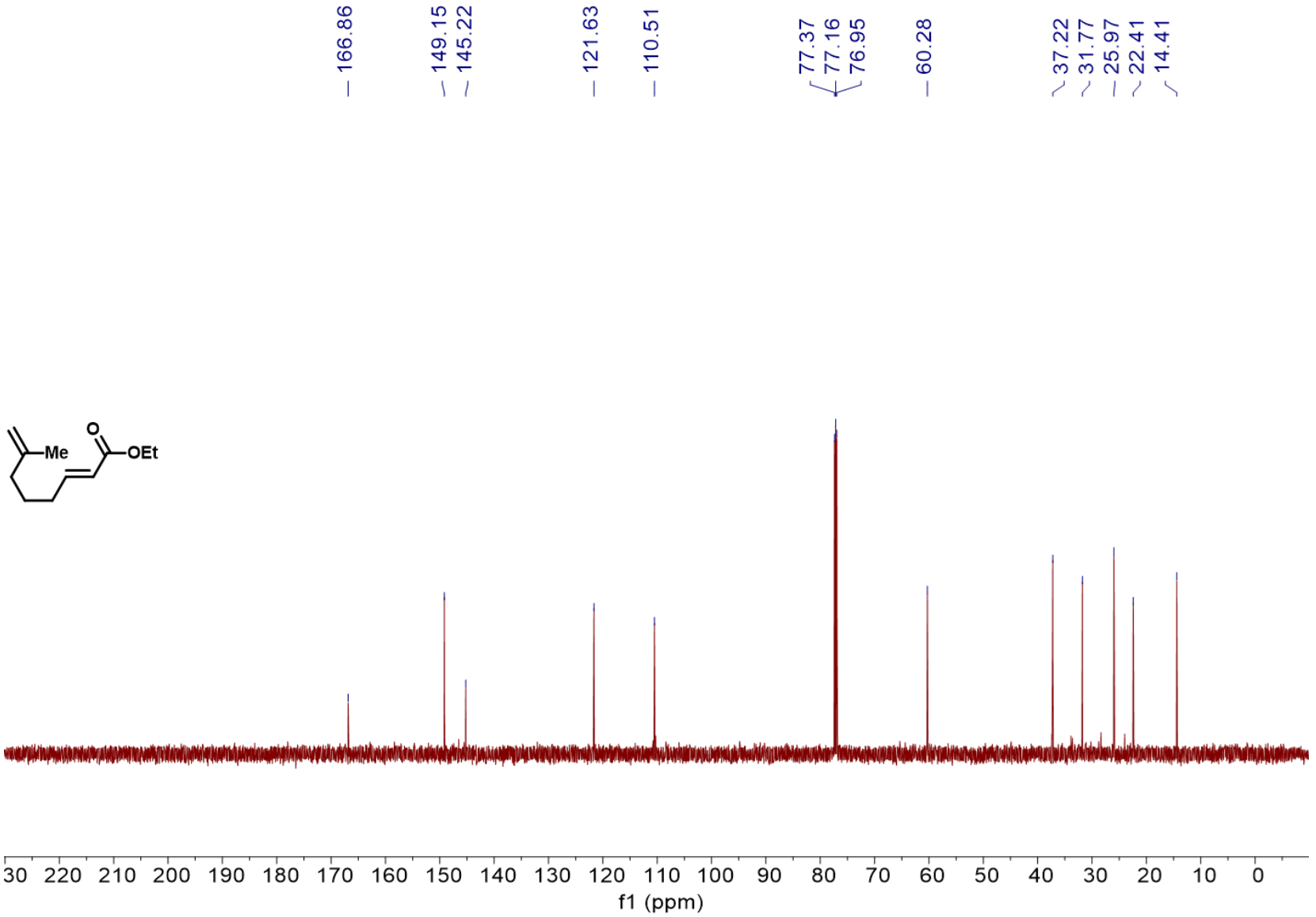
^{13}C NMR (151 MHz, $CDCl_3$) of compound **63**



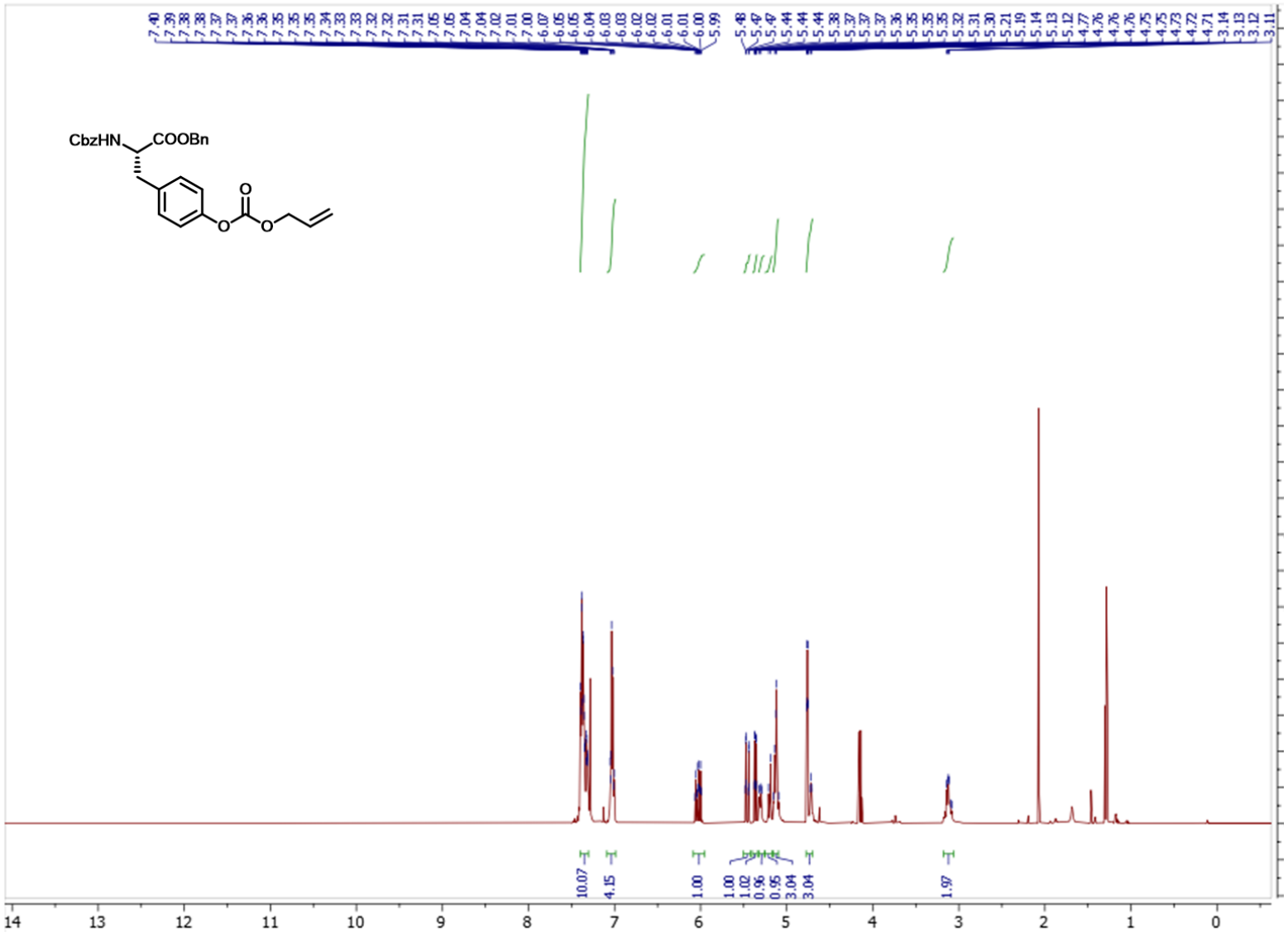
^{1}H NMR (400 MHz, $CDCl_3$) of compound **66**



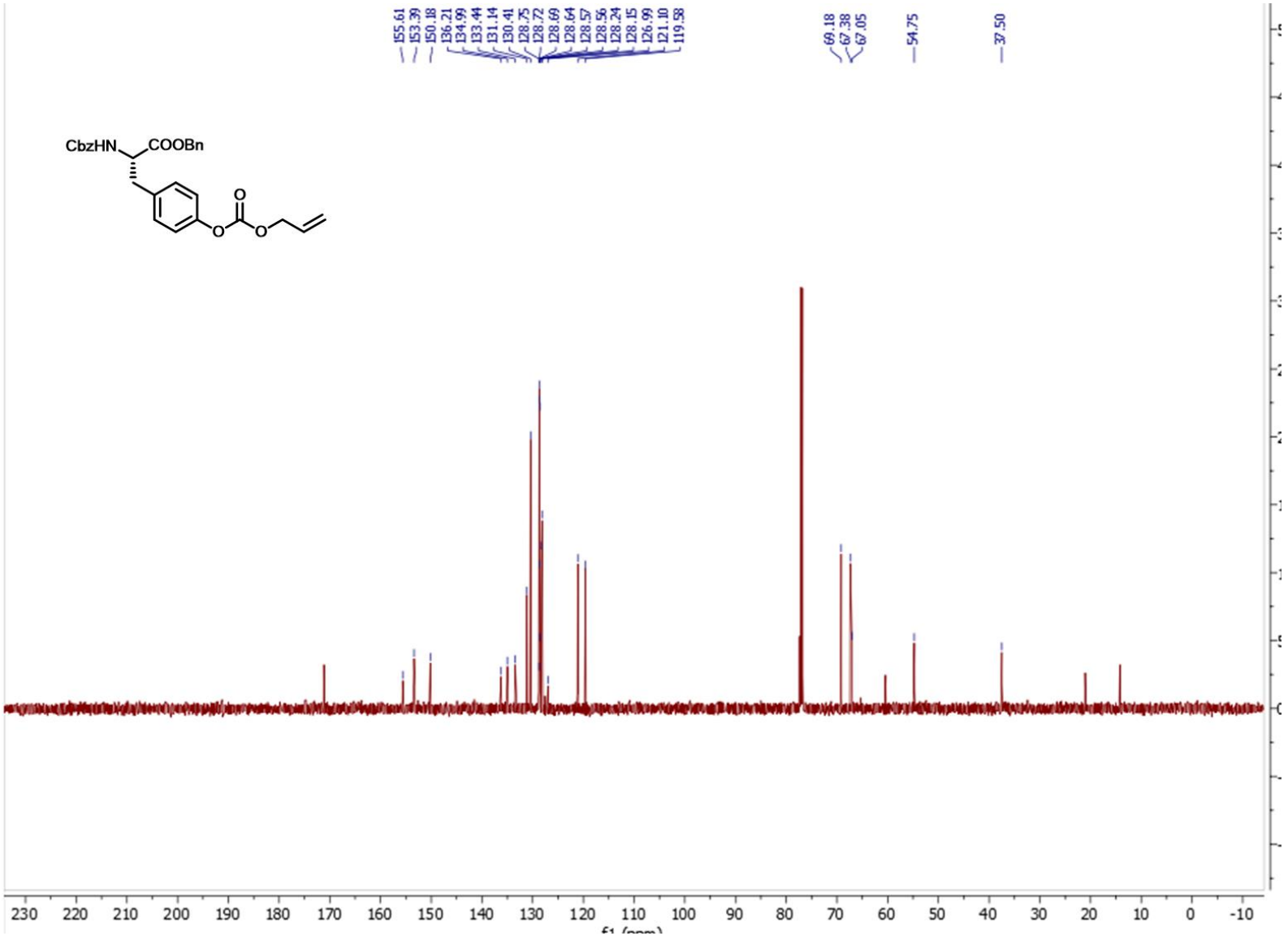
^{13}C NMR (151 MHz, $CDCl_3$) of compound **66**



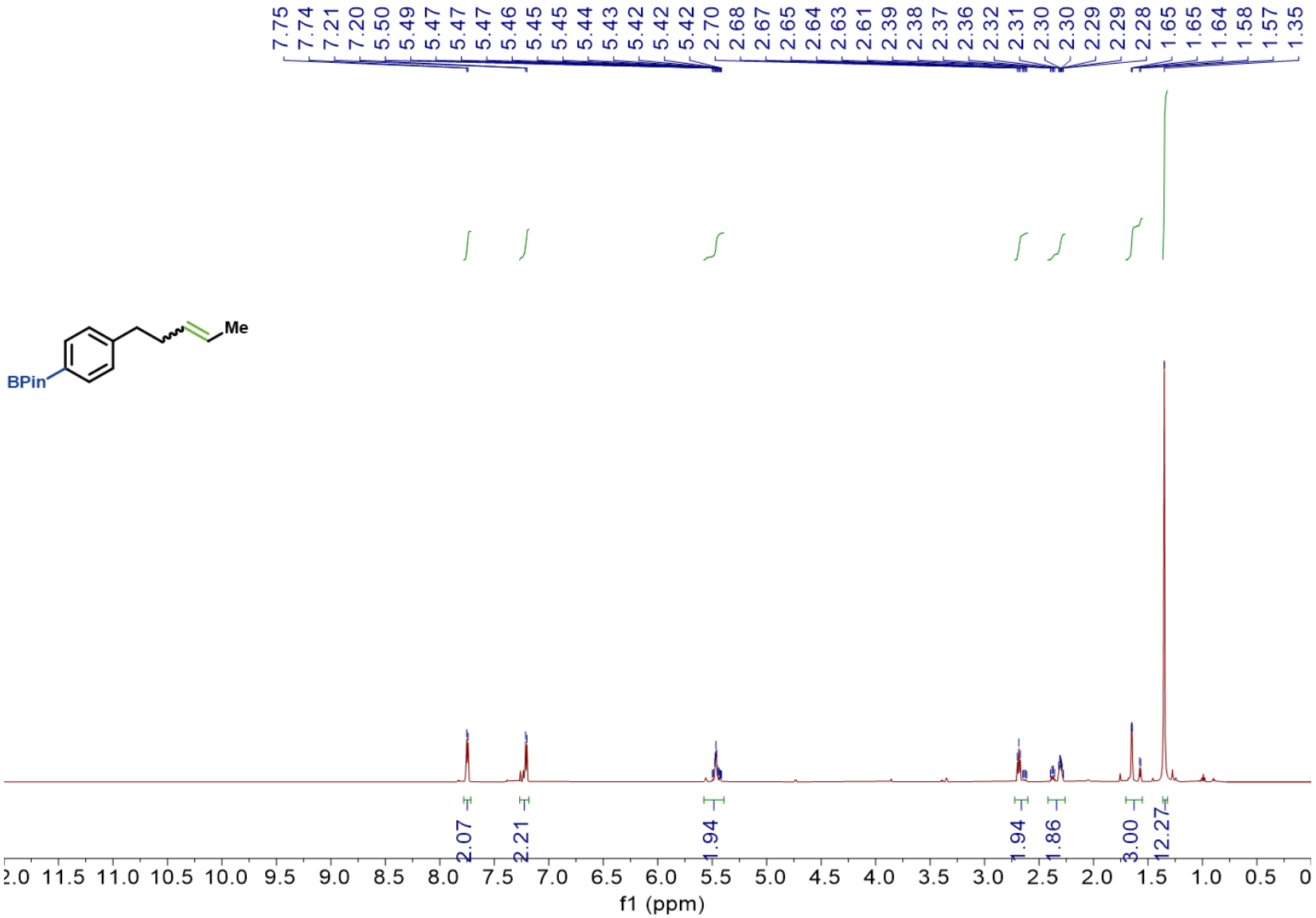
^{1}H NMR (500 MHz, $CDCl_3$) of compound **76**



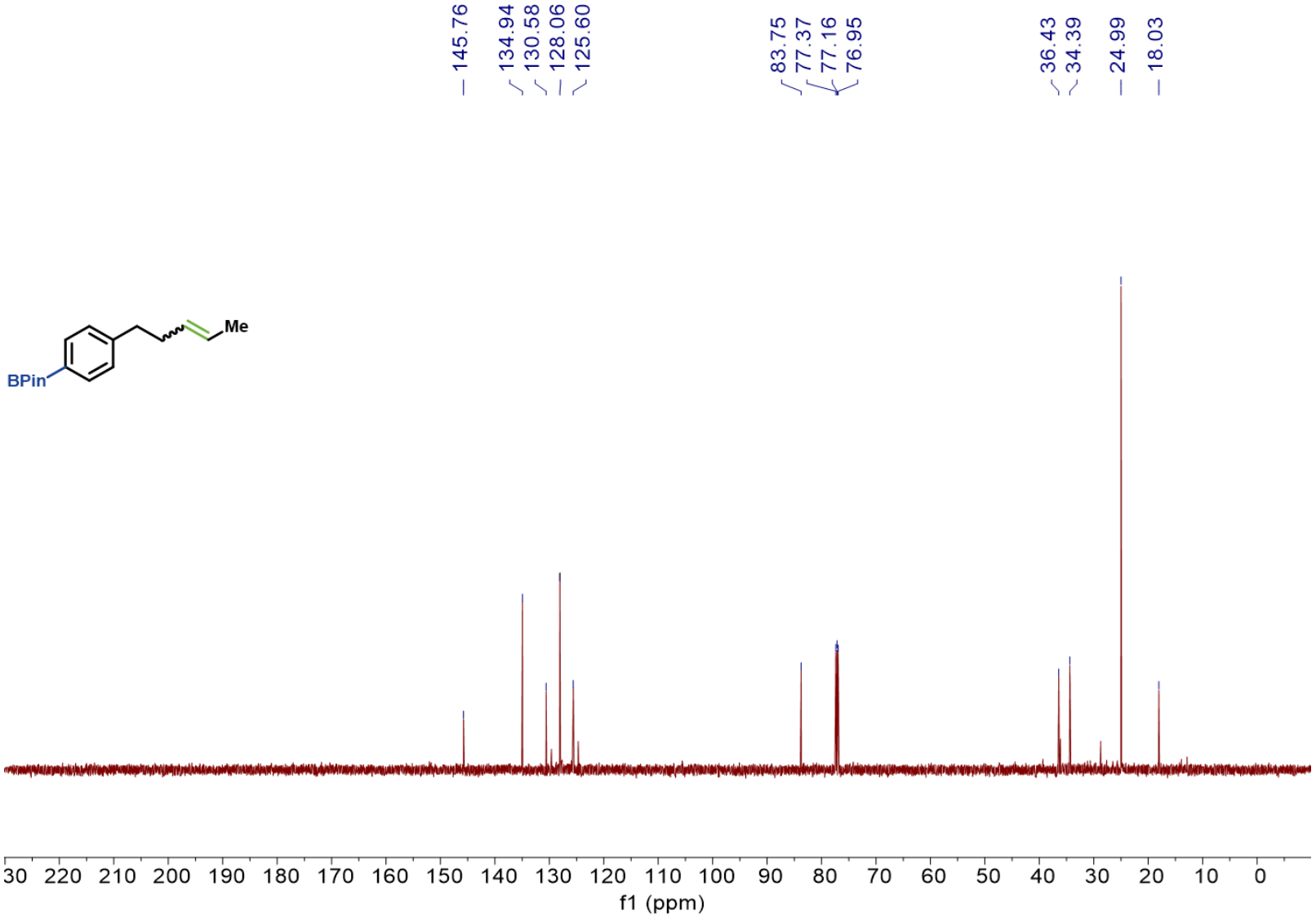
^{13}C NMR (126 MHz, $CDCl_3$) of compound **76**



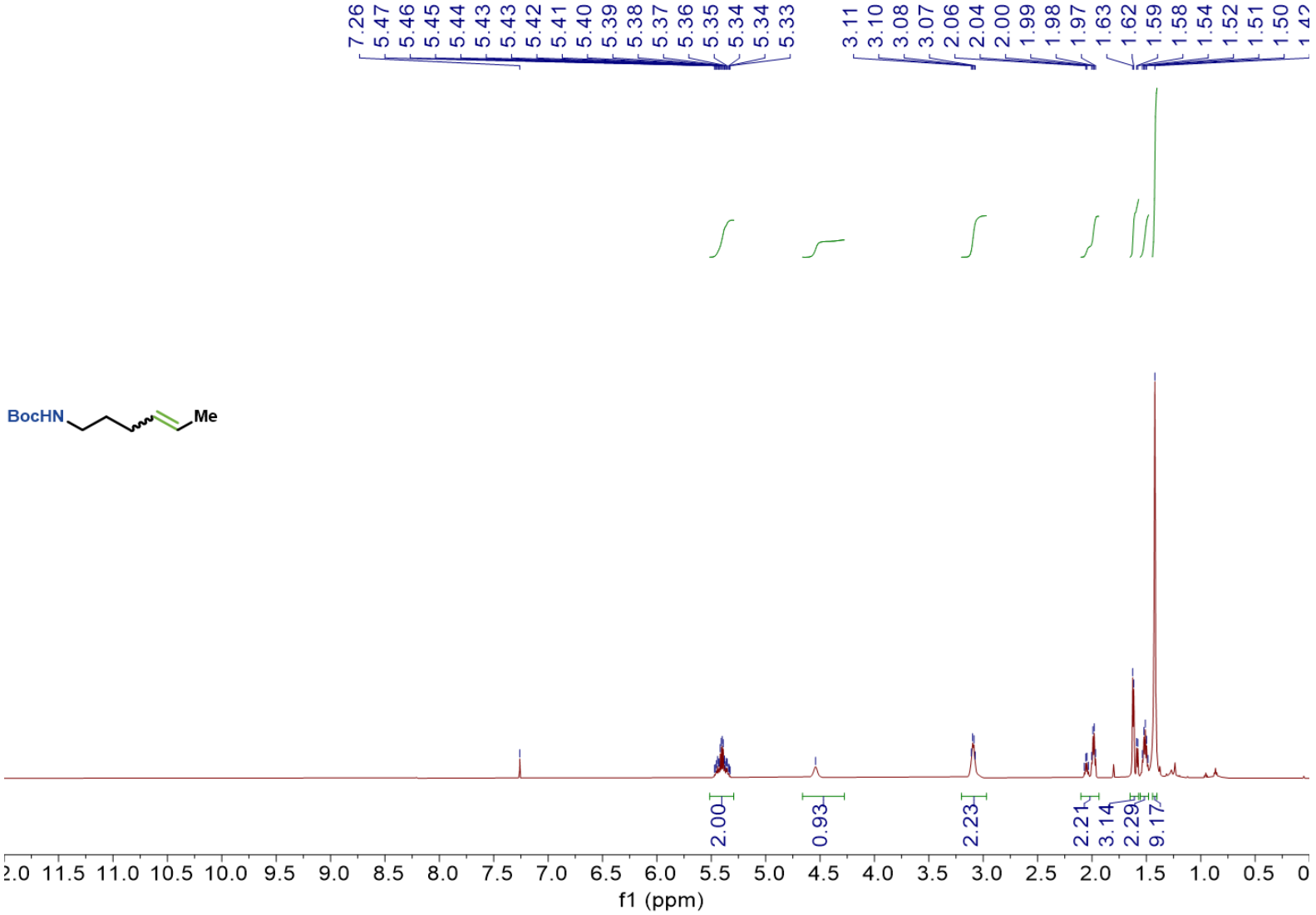
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2**



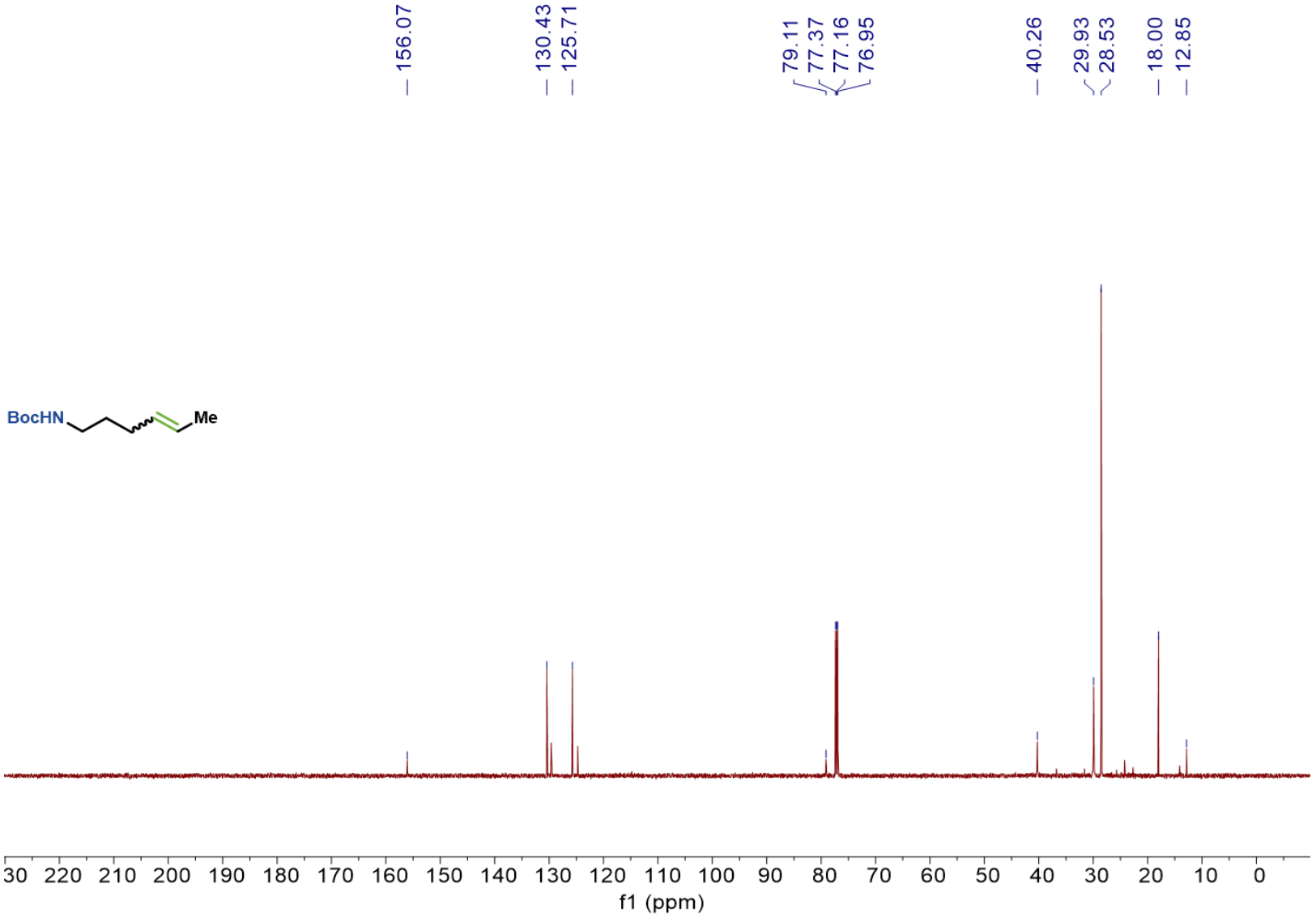
^{13}CNMR (151 MHz, $CDCl_3$) of compound **2**



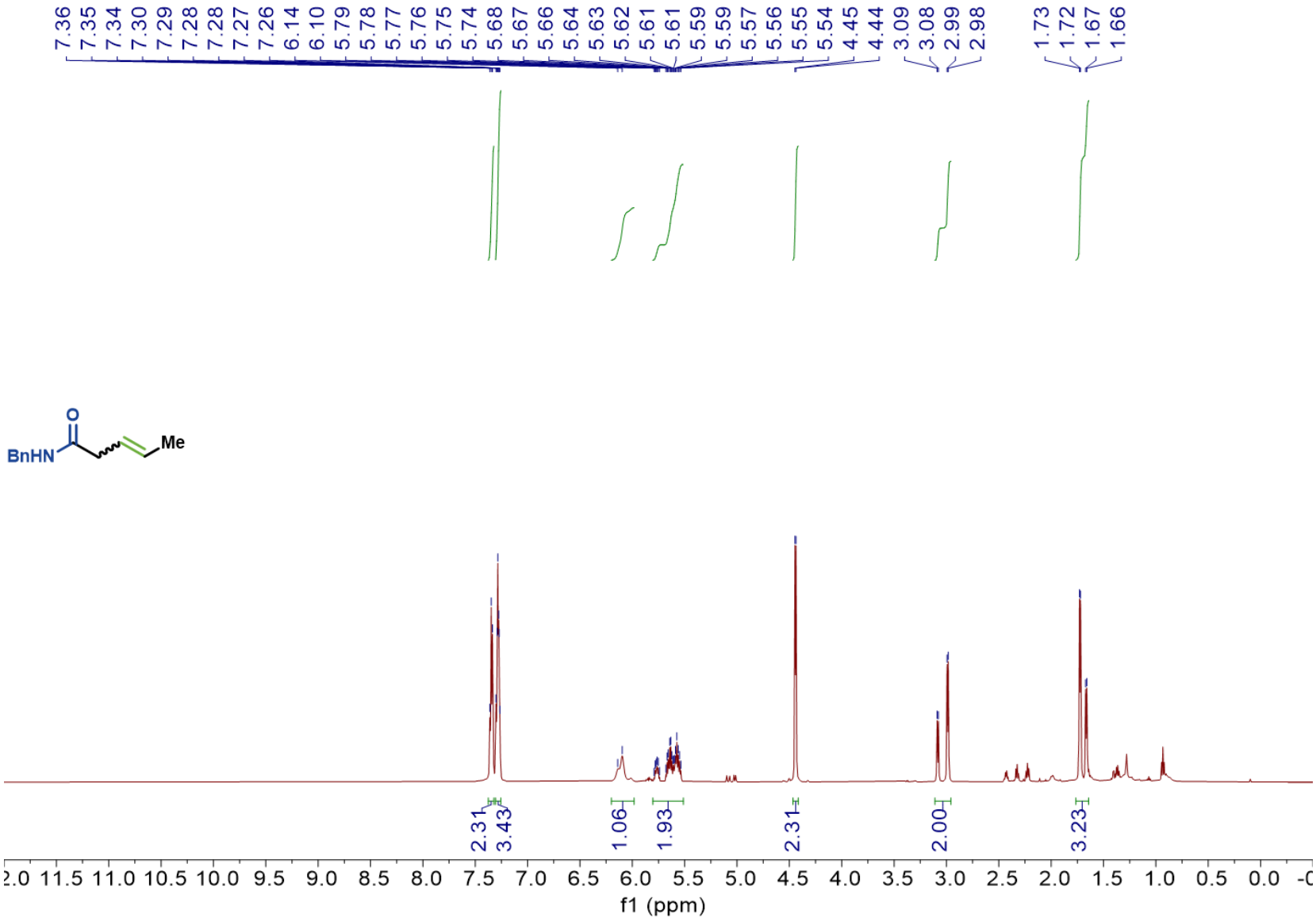
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3**



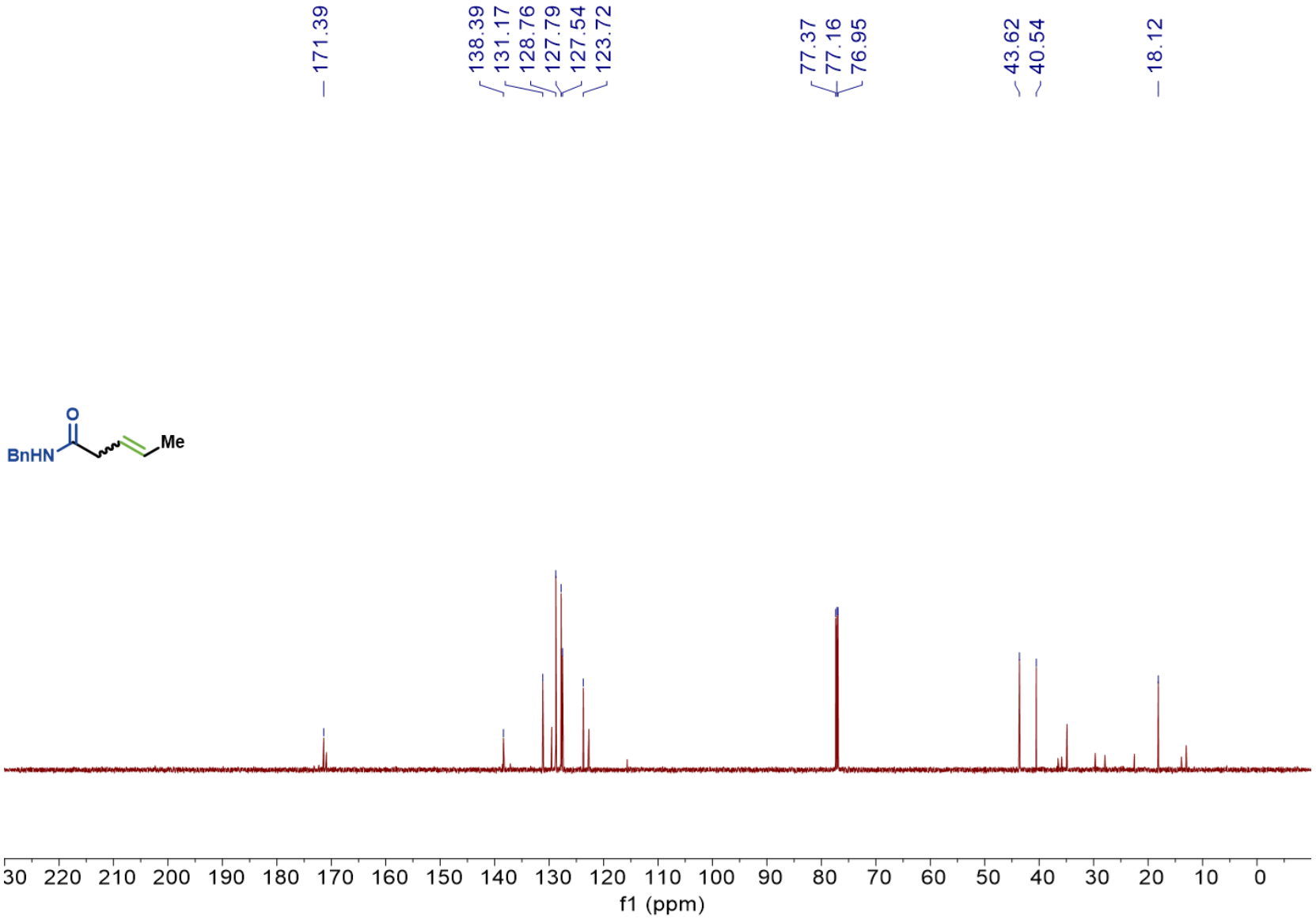
^{13}CNMR (151 MHz, $CDCl_3$) of compound **3**



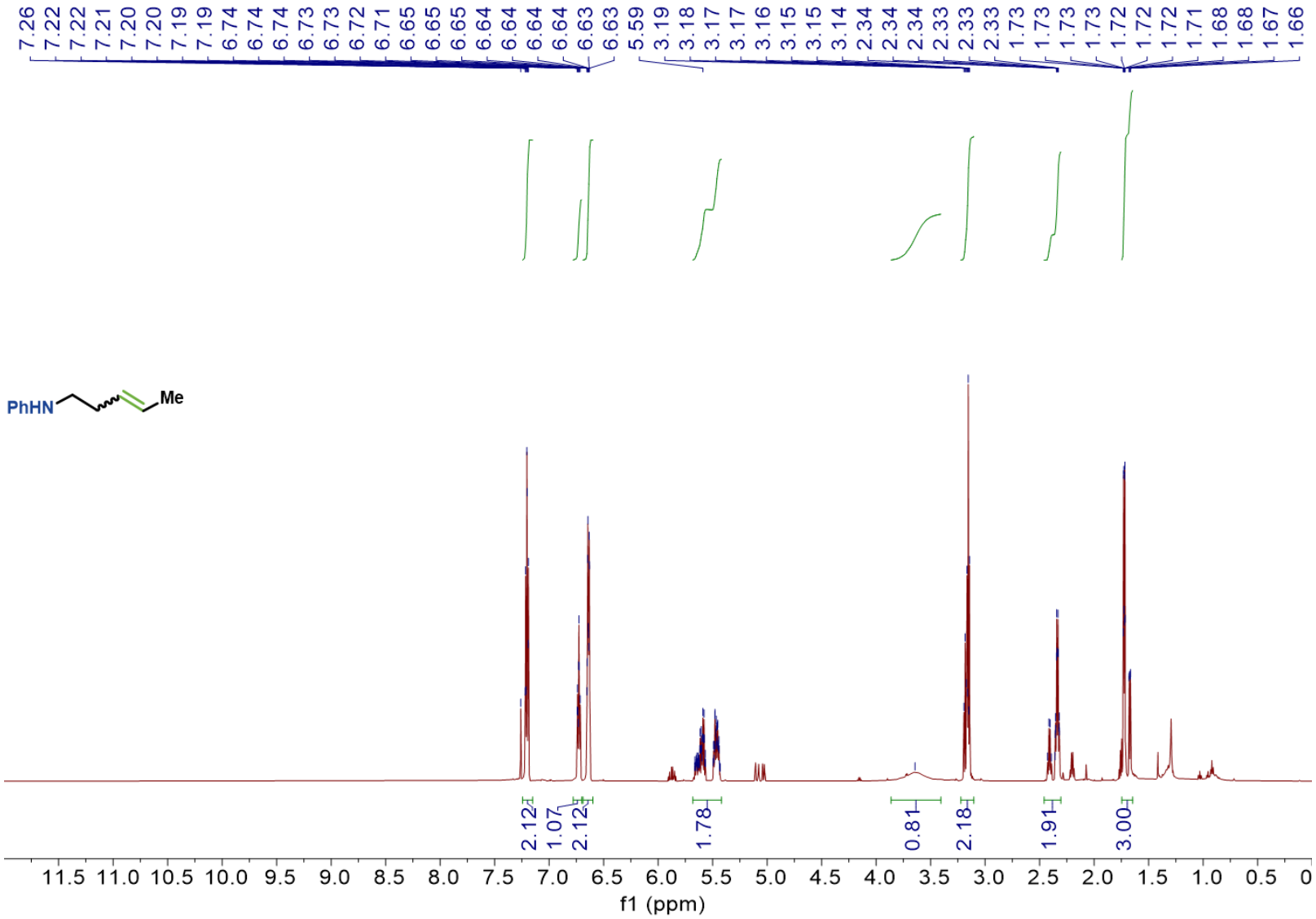
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4**



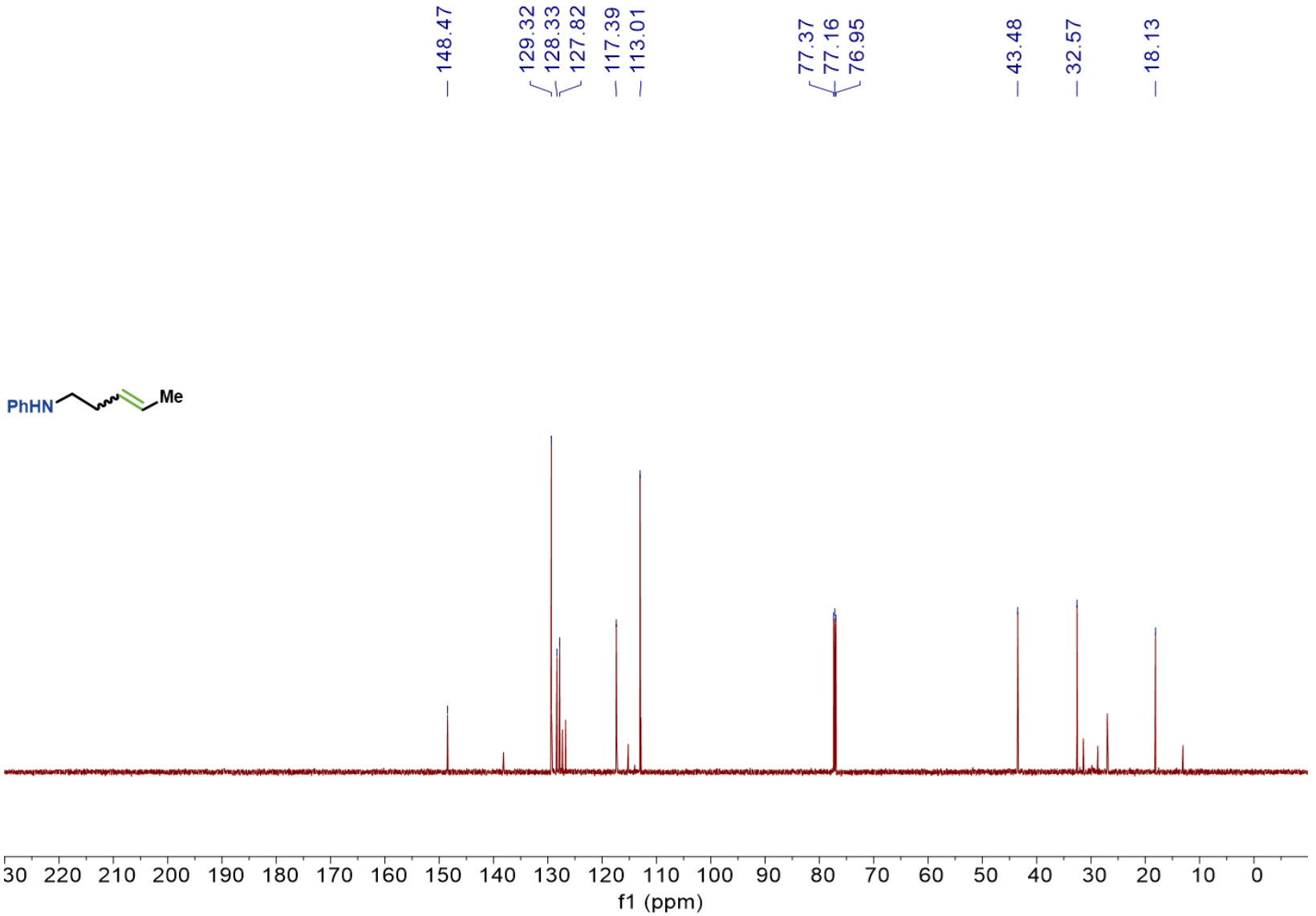
^{13}CNMR (151 MHz, $CDCl_3$) of compound **4**



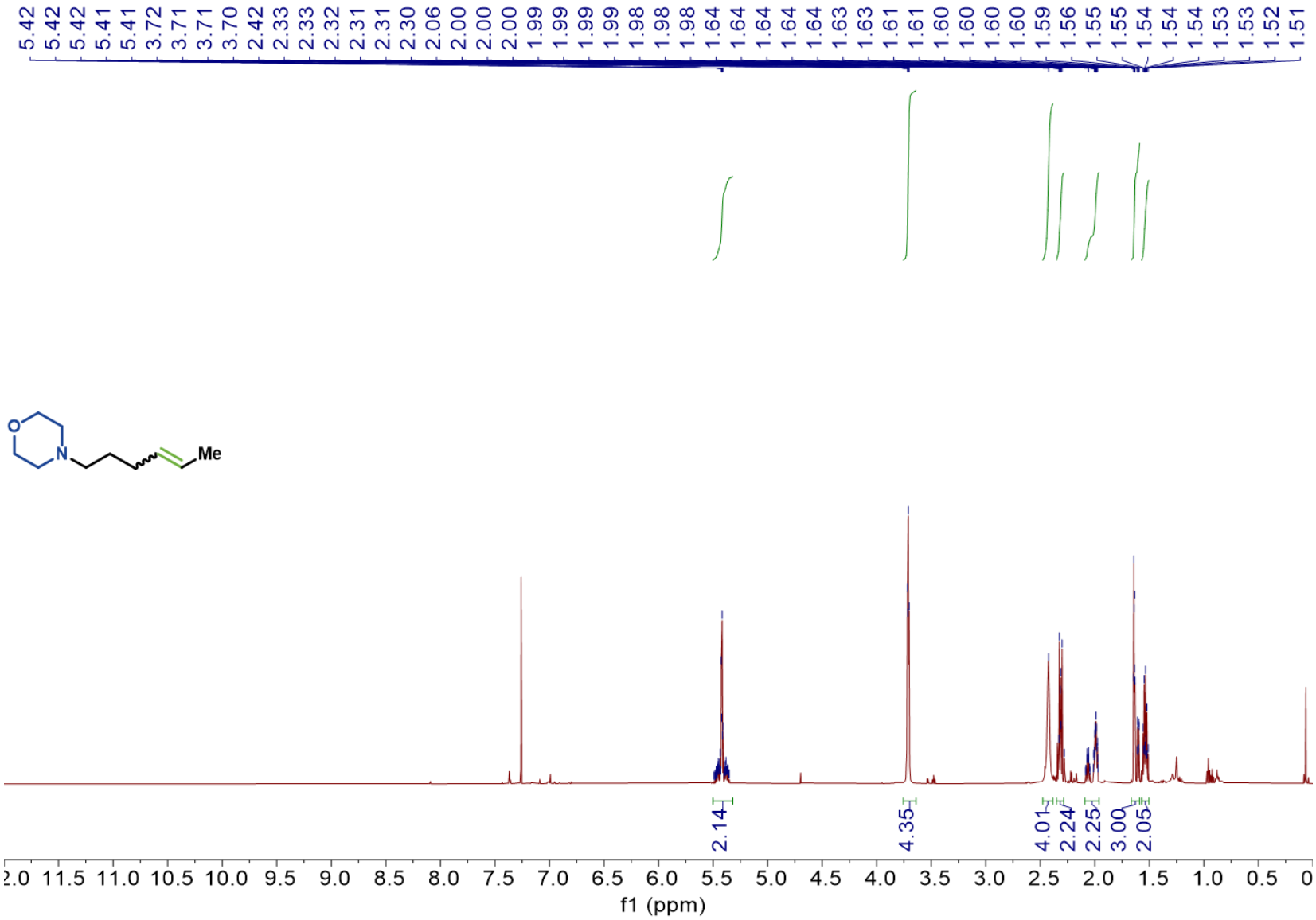
^{1}H NMR (600 MHz, $CDCl_3$) of compound **5**



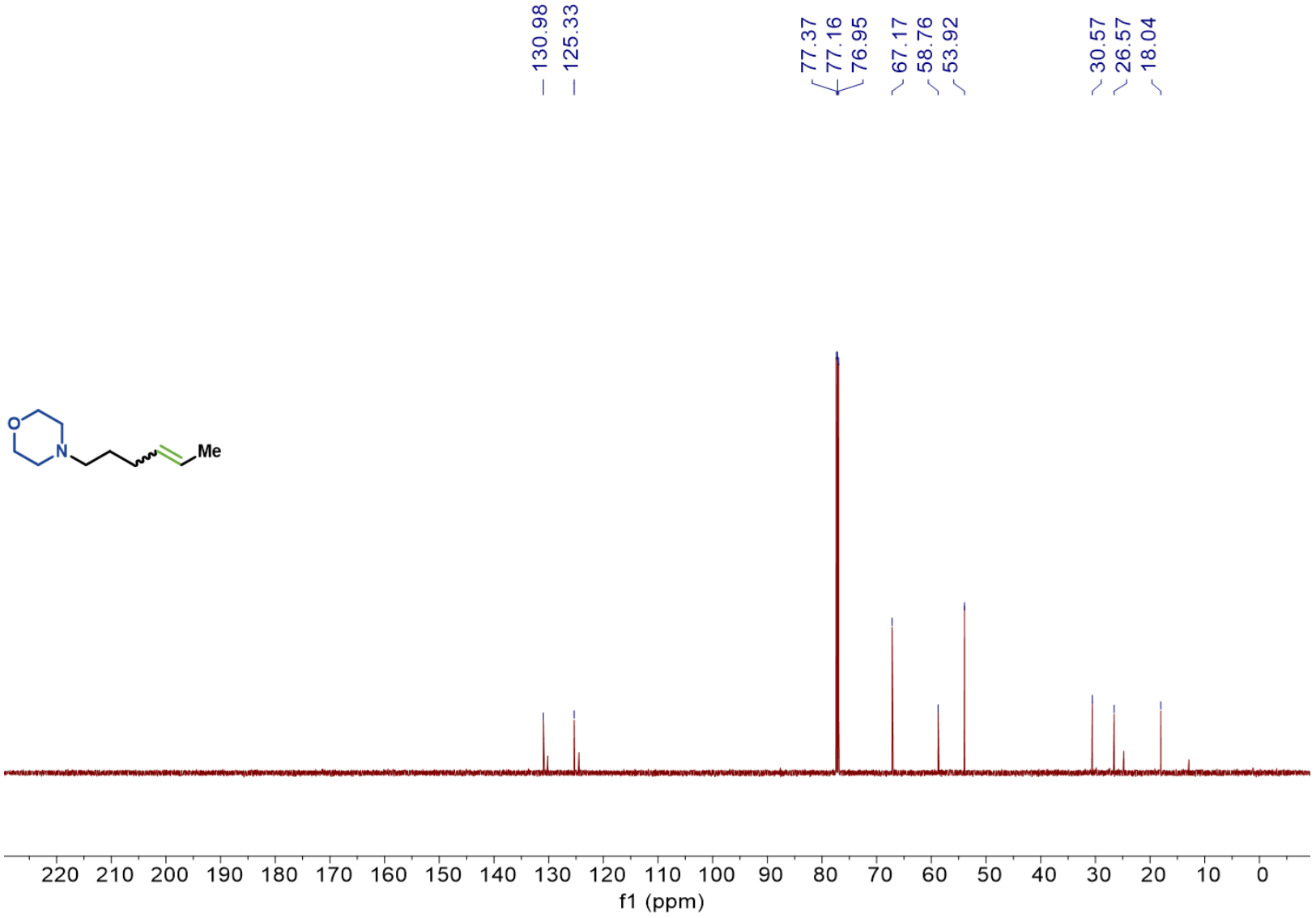
^{13}C NMR (151 MHz, $CDCl_3$) of compound **5**



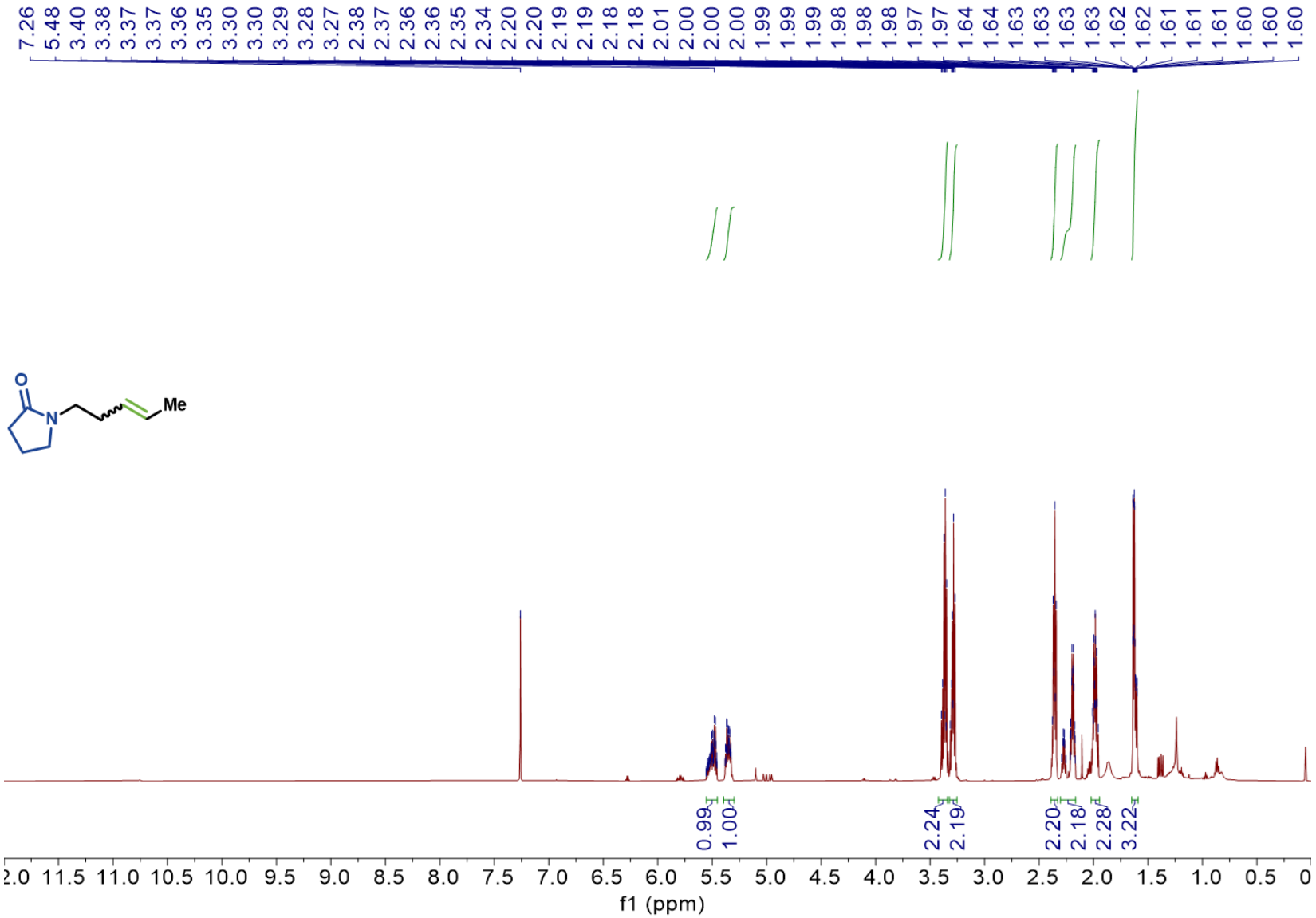
^{1}H NMR (460 MHz, $CDCl_3$) of compound **6**



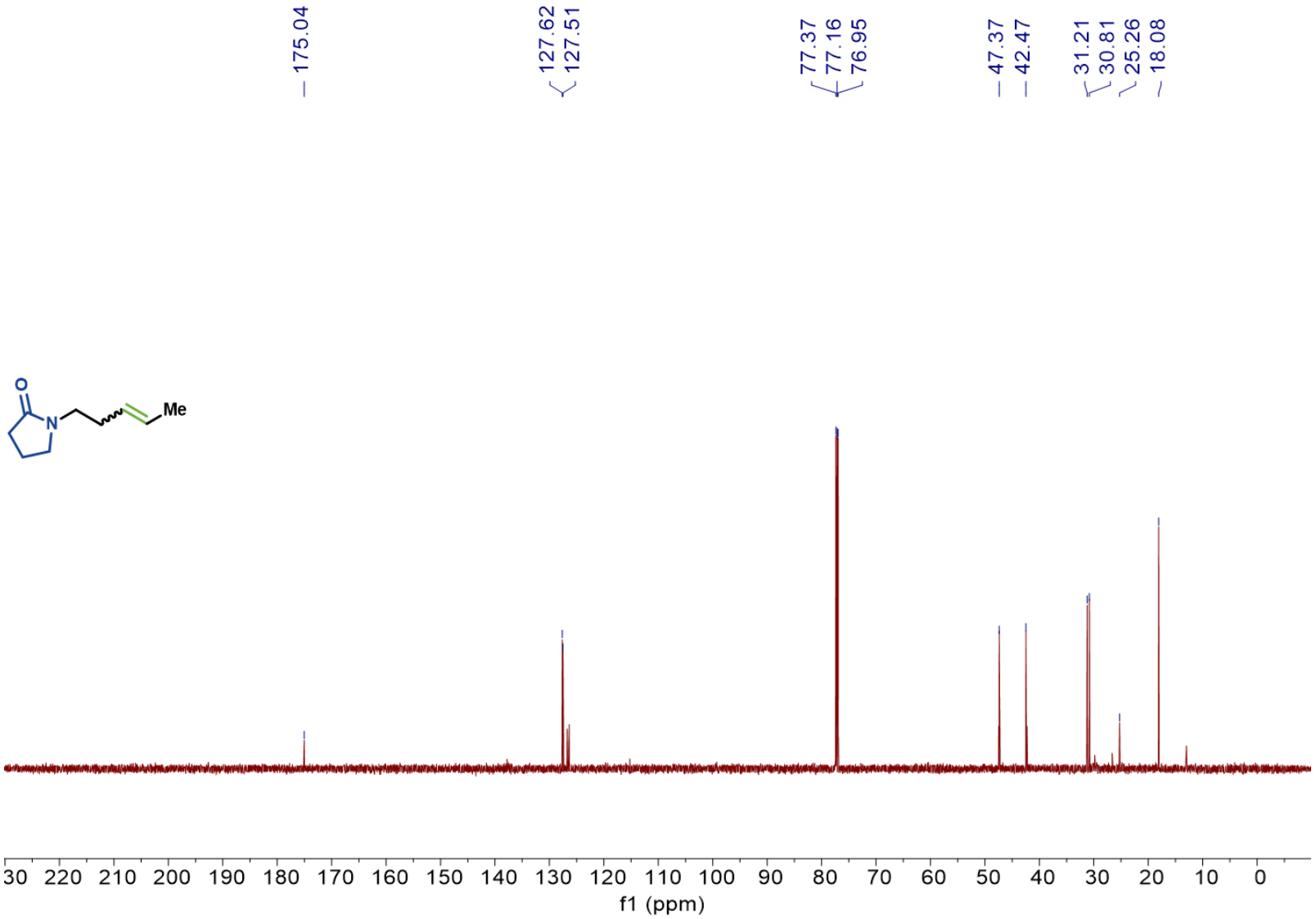
^{13}CNMR (151 MHz, $CDCl_3$) of compound **6**



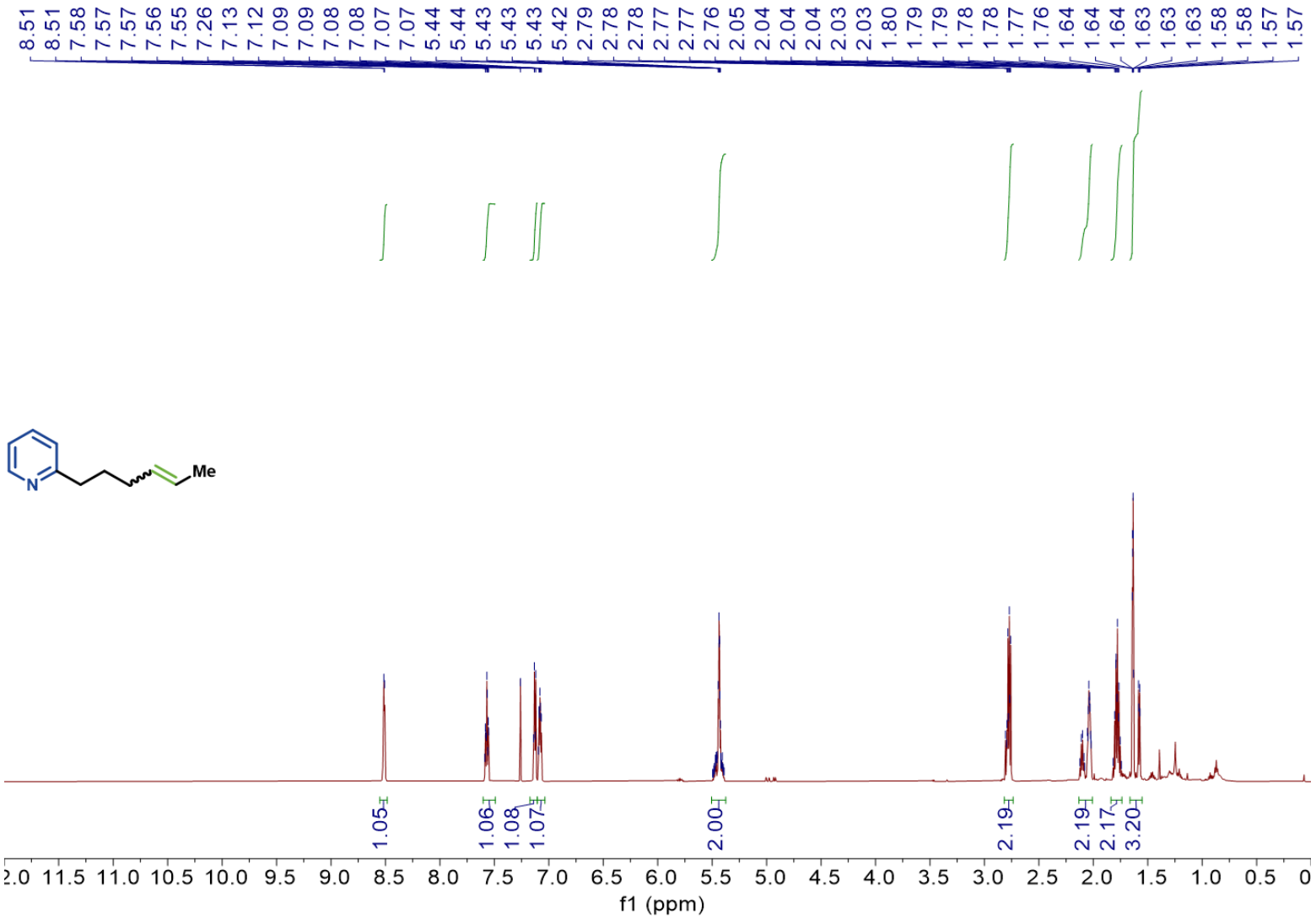
^{1}H NMR (600 MHz, $CDCl_3$) of compound **7**



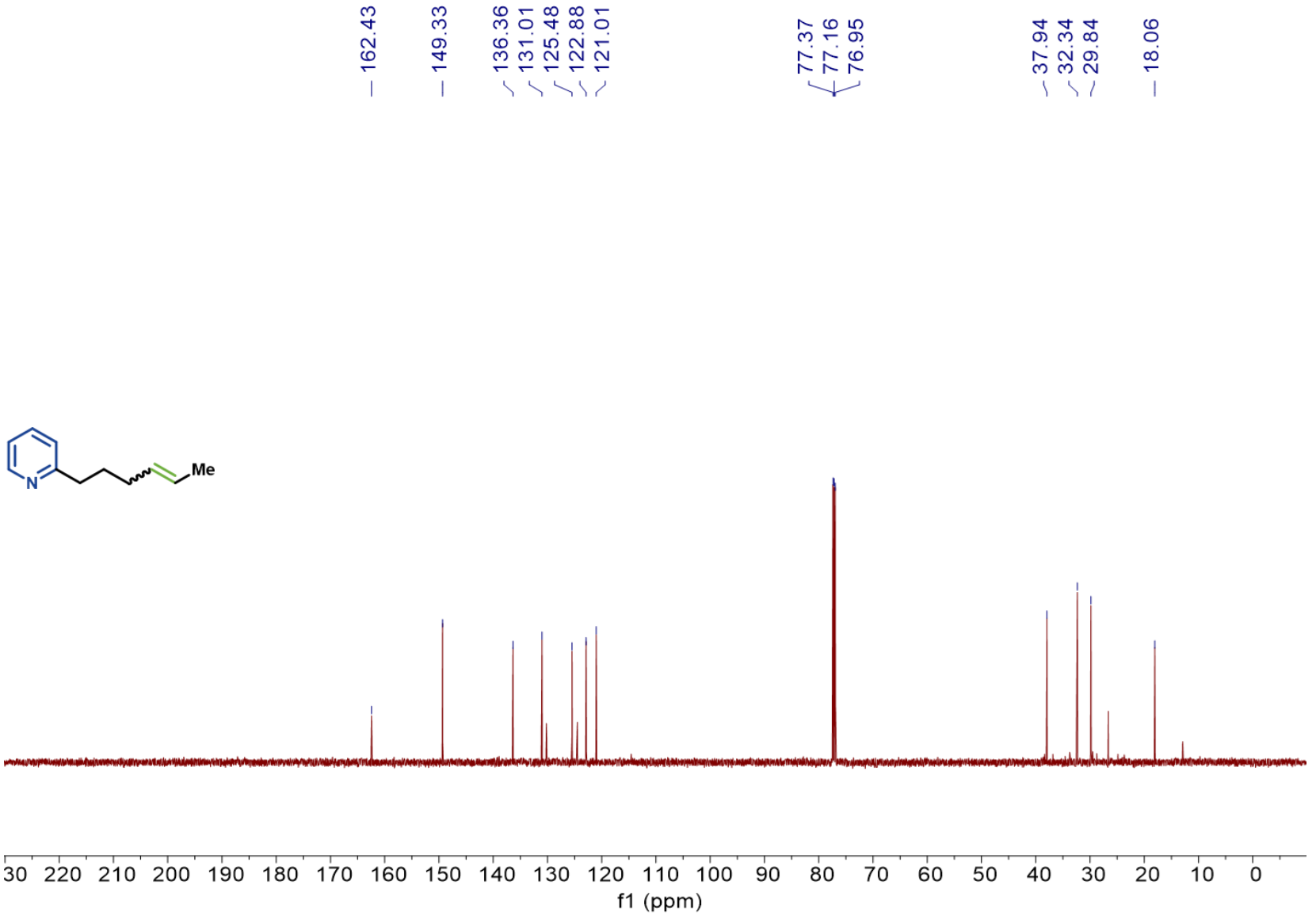
^{13}CNMR (151 MHz, $CDCl_3$) of compound **7**



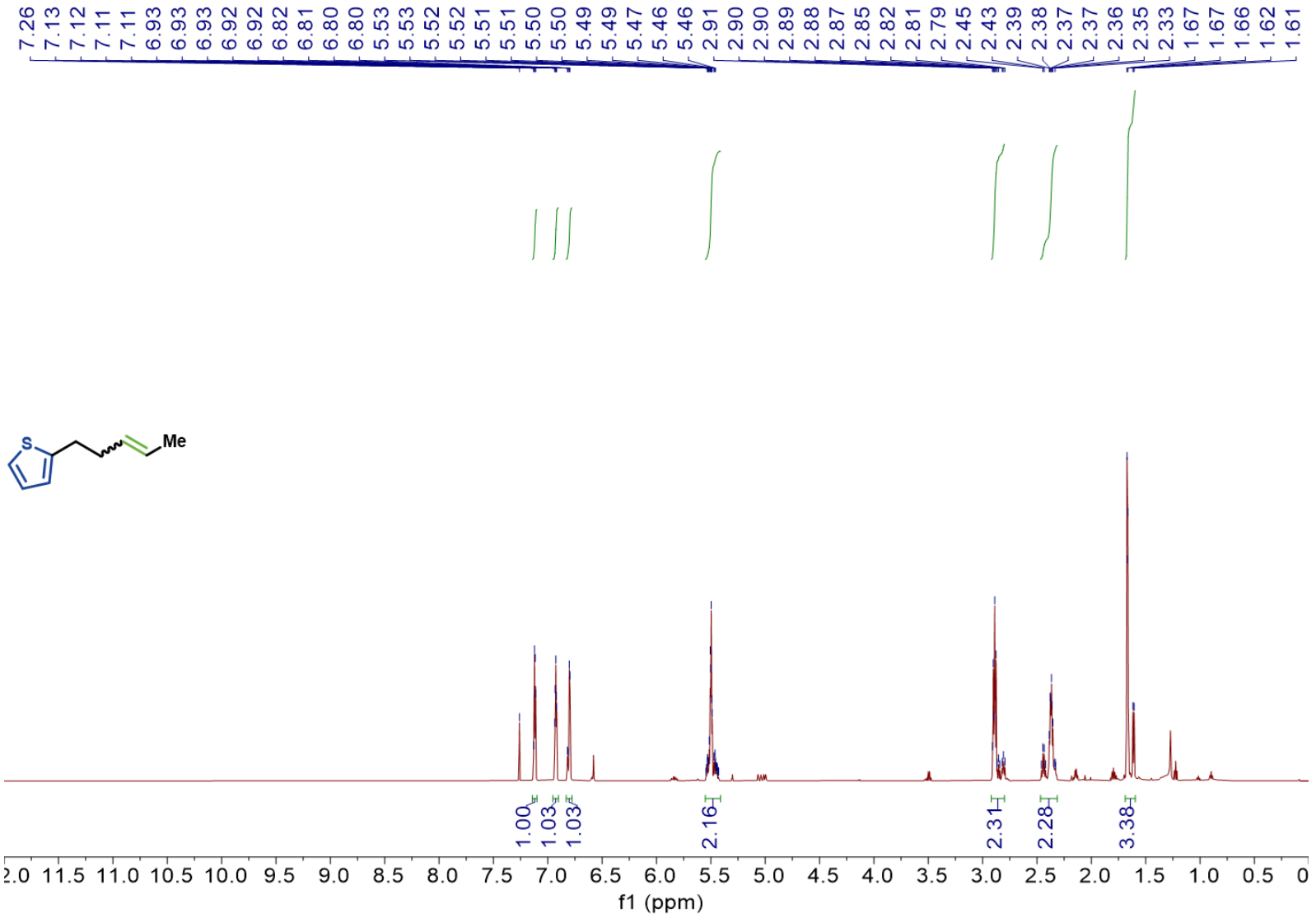
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8**



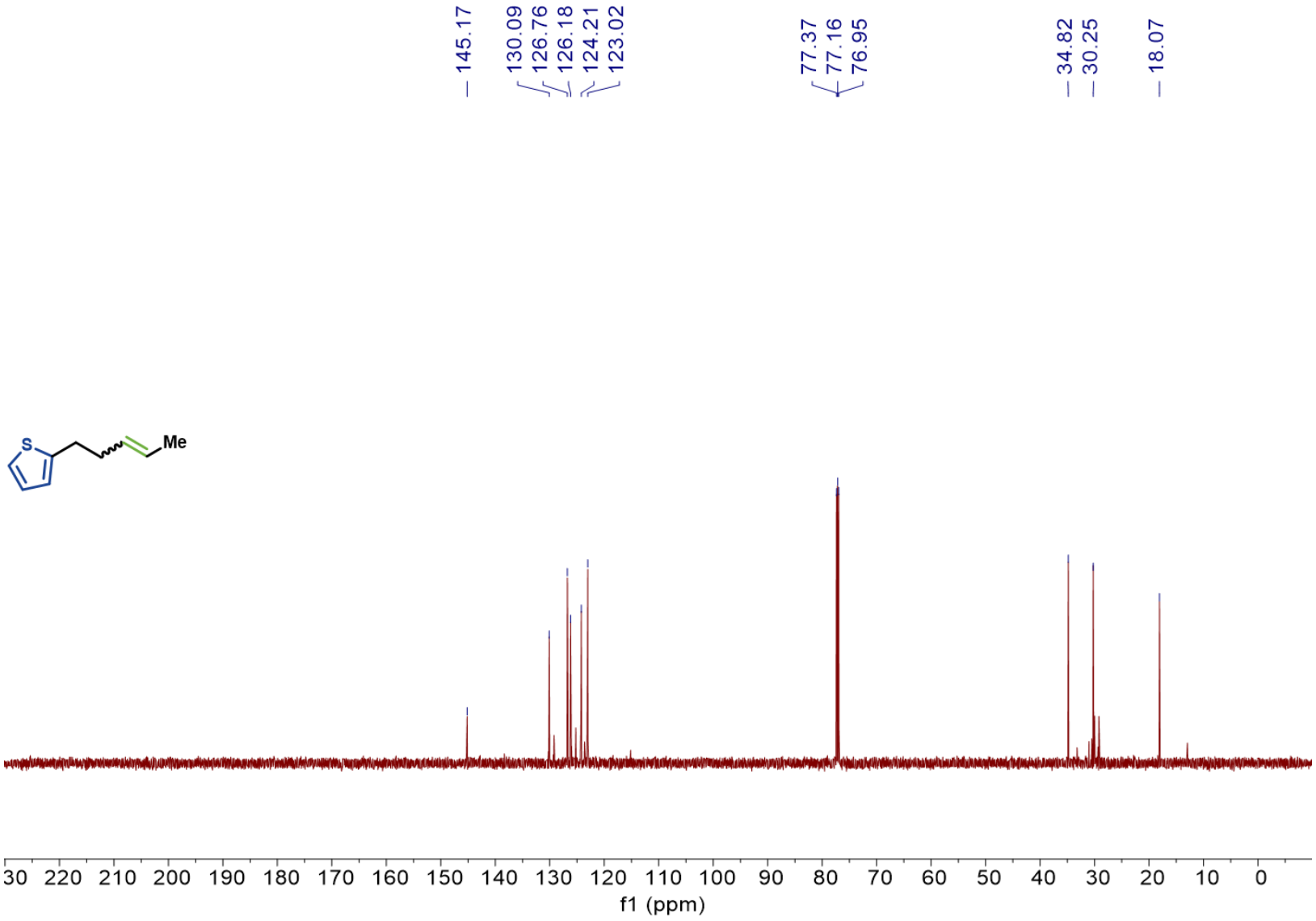
^{13}C NMR (151 MHz, $CDCl_3$) of compound **8**



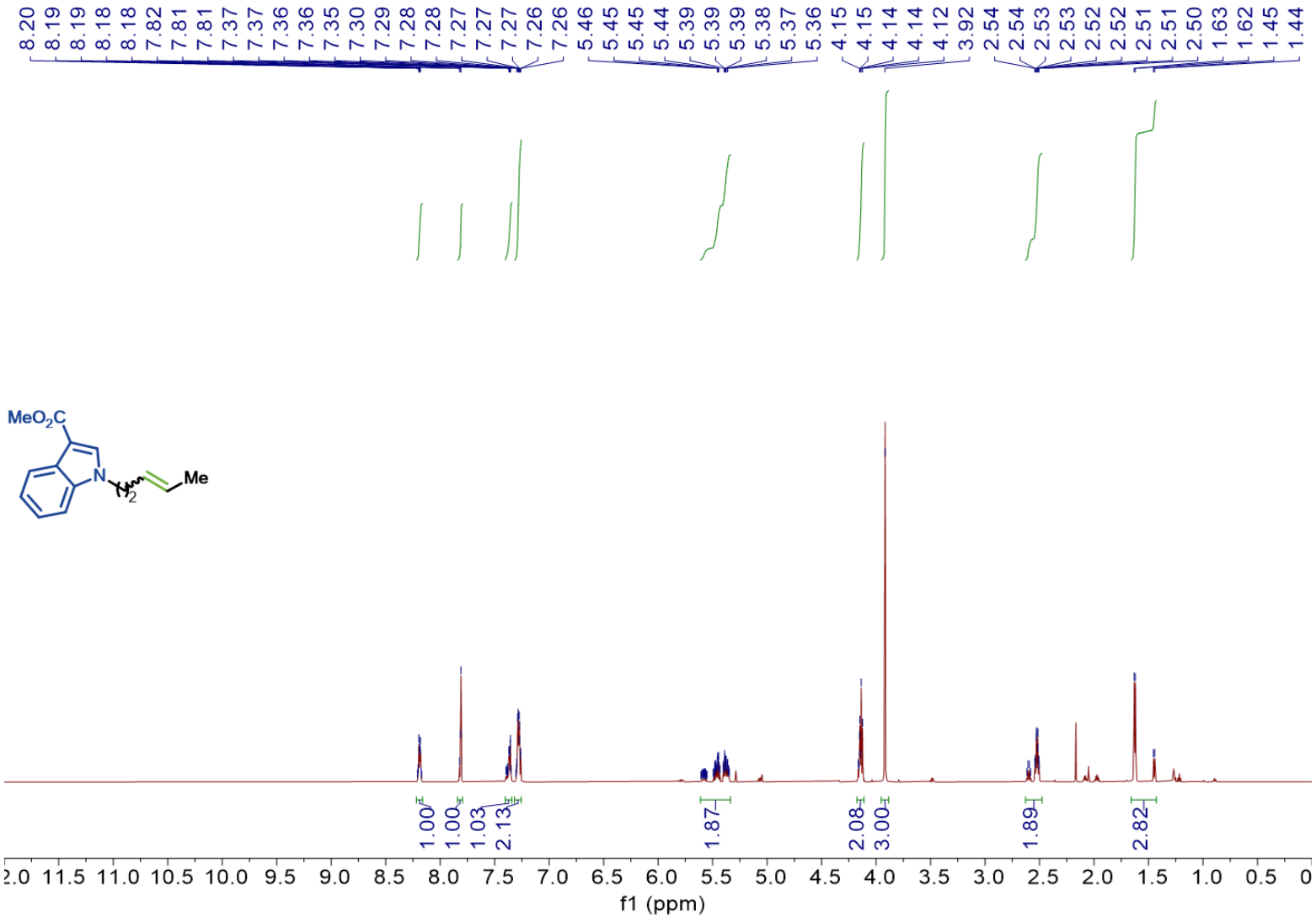
^{1}H NMR (600 MHz, $CDCl_3$) of compound **9**



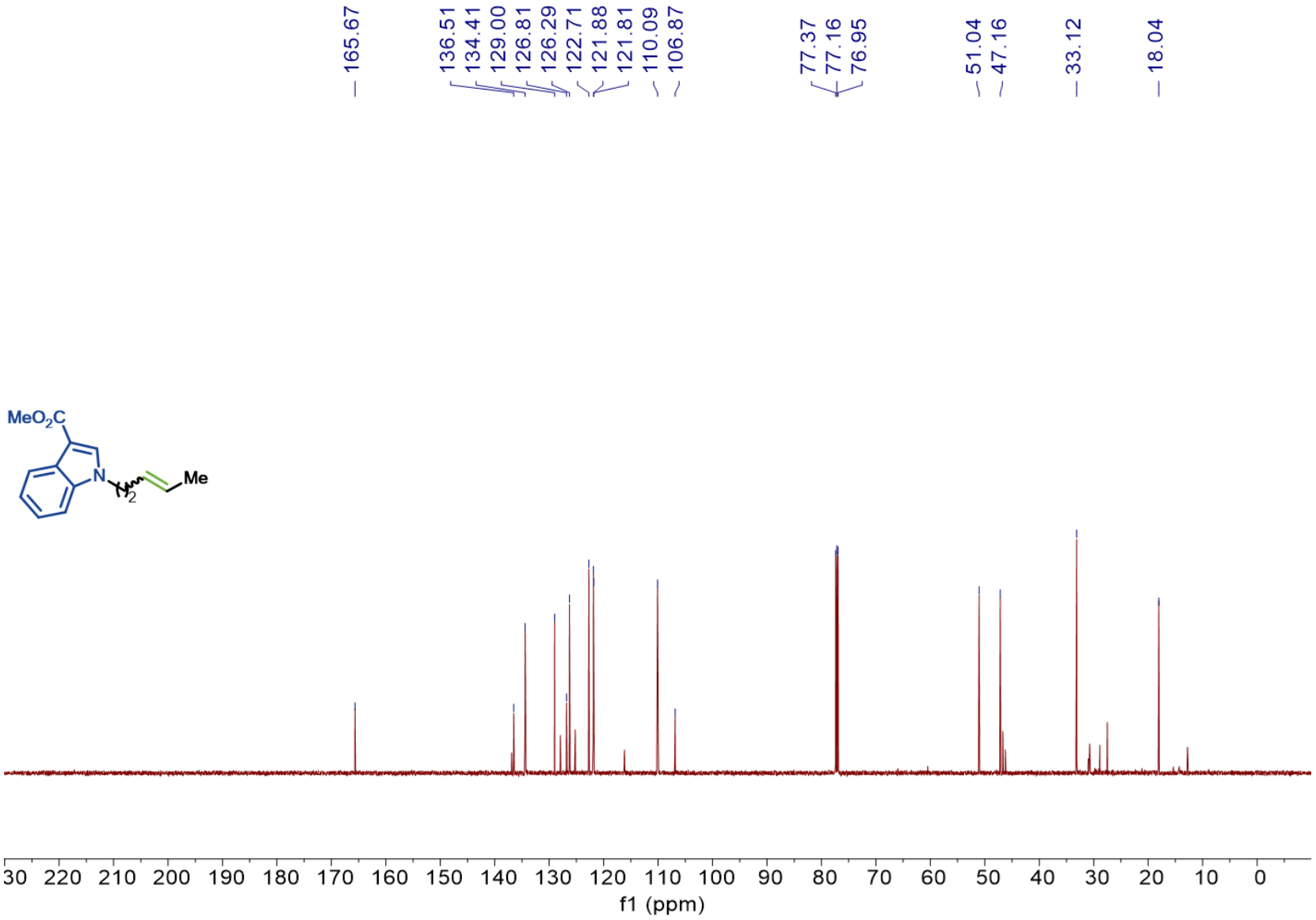
^{13}C NMR (151 MHz, $CDCl_3$) of compound **9**



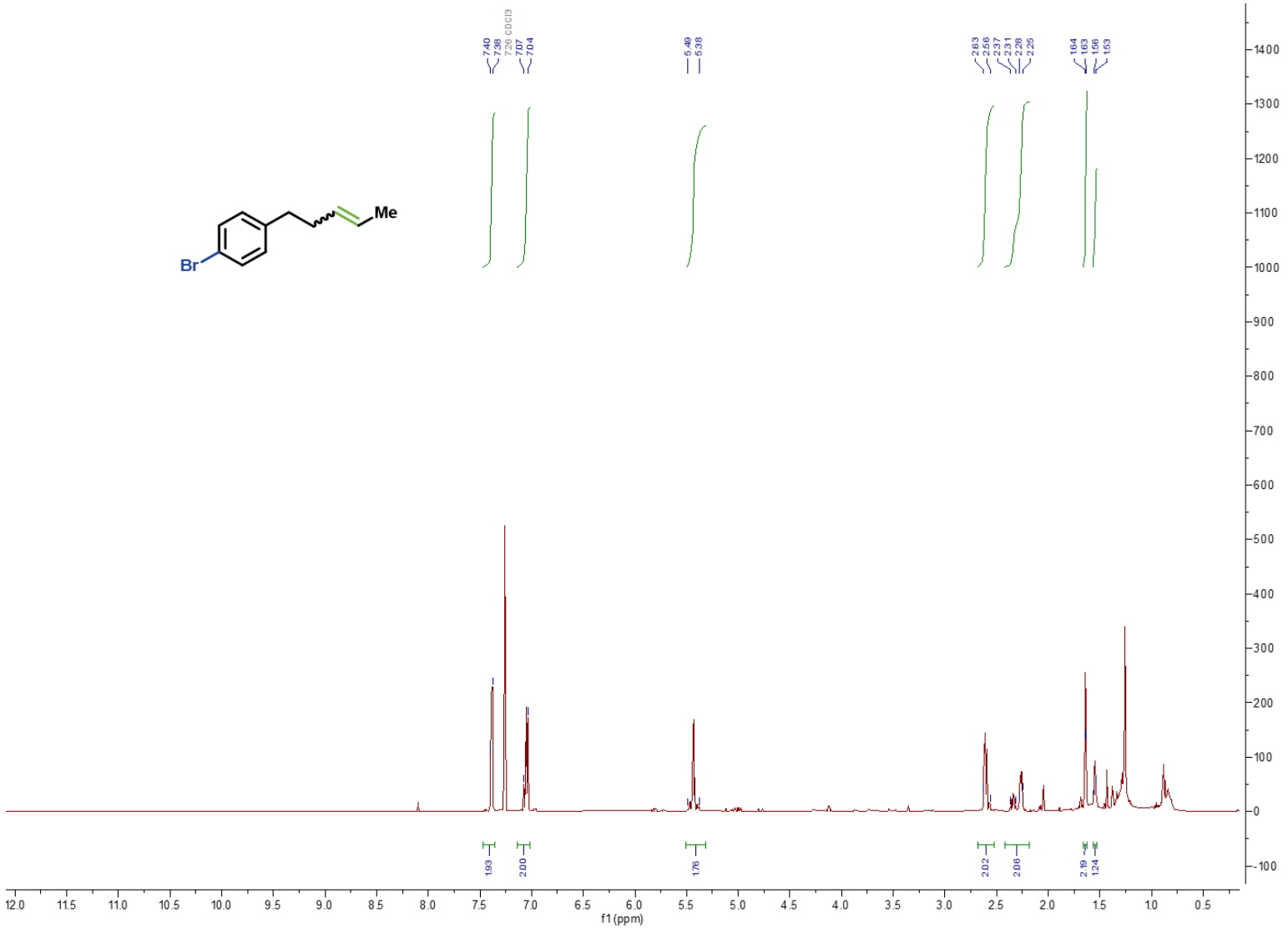
^{1}H NMR (600 MHz, $CDCl_3$) of compound **10**



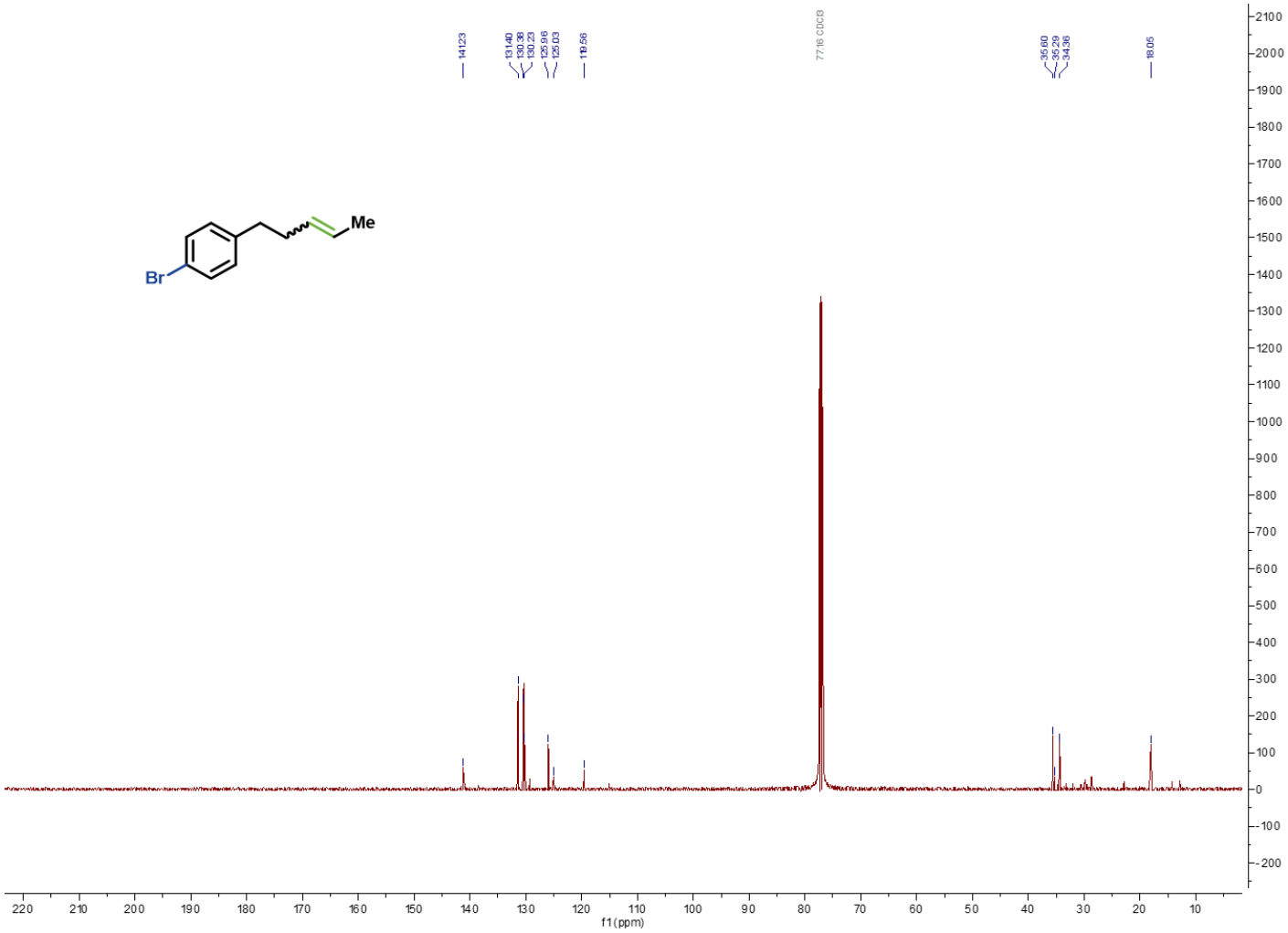
^{13}C NMR (151 MHz, $CDCl_3$) of compound **10**



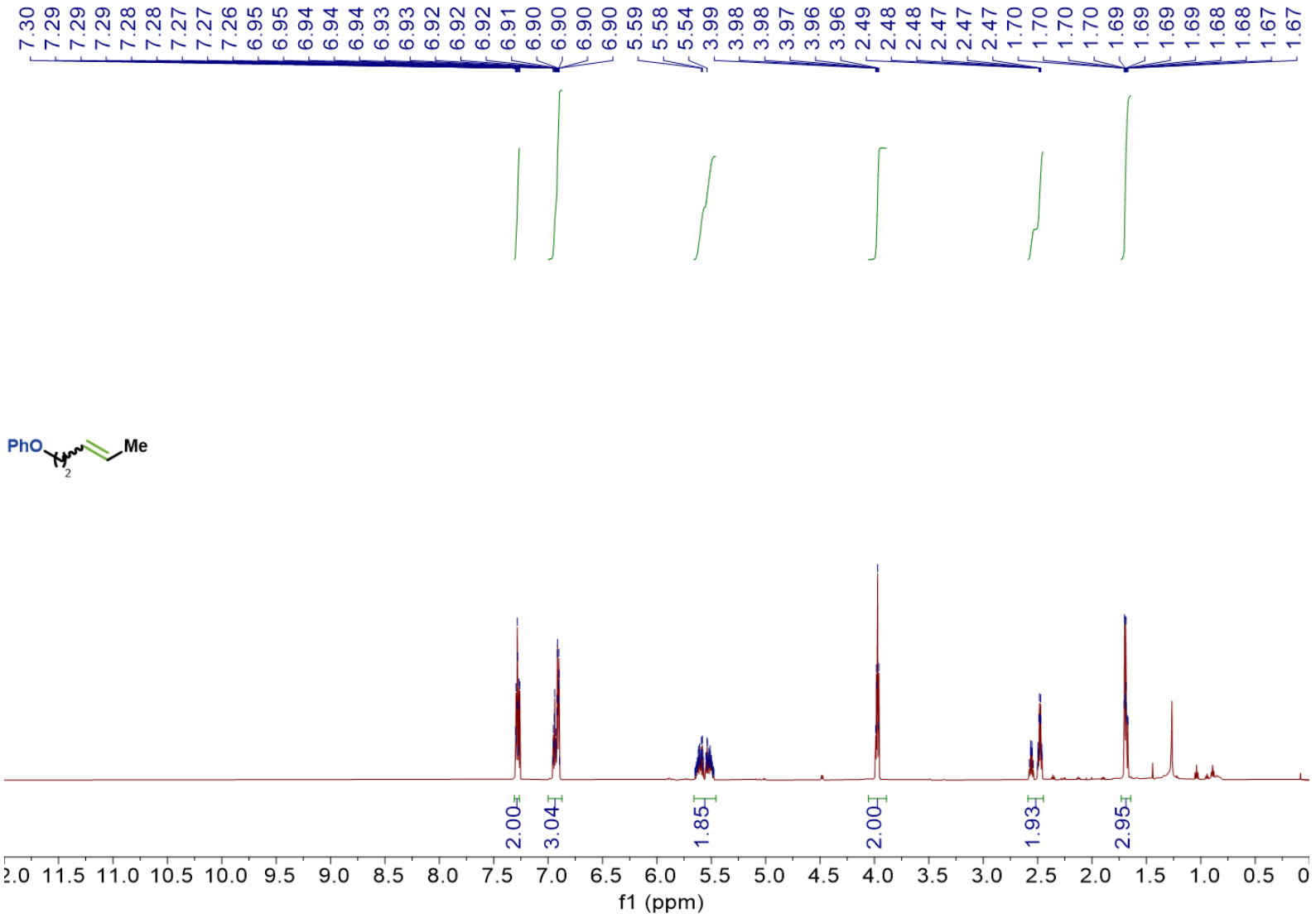
^{1}H NMR (600 MHz, $CDCl_3$) of compound **11**



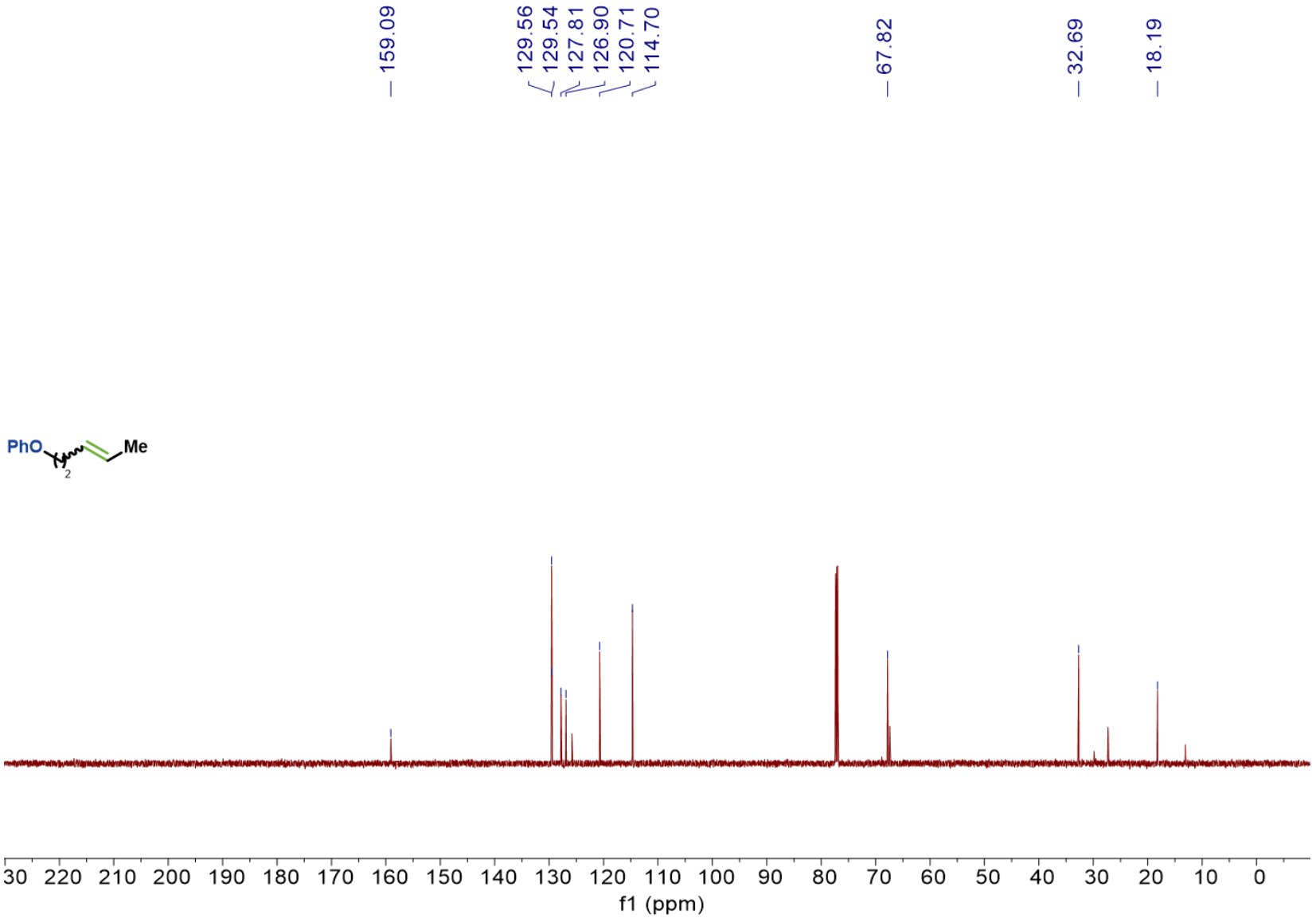
^{13}C NMR (151 MHz, $CDCl_3$) of compound **11**



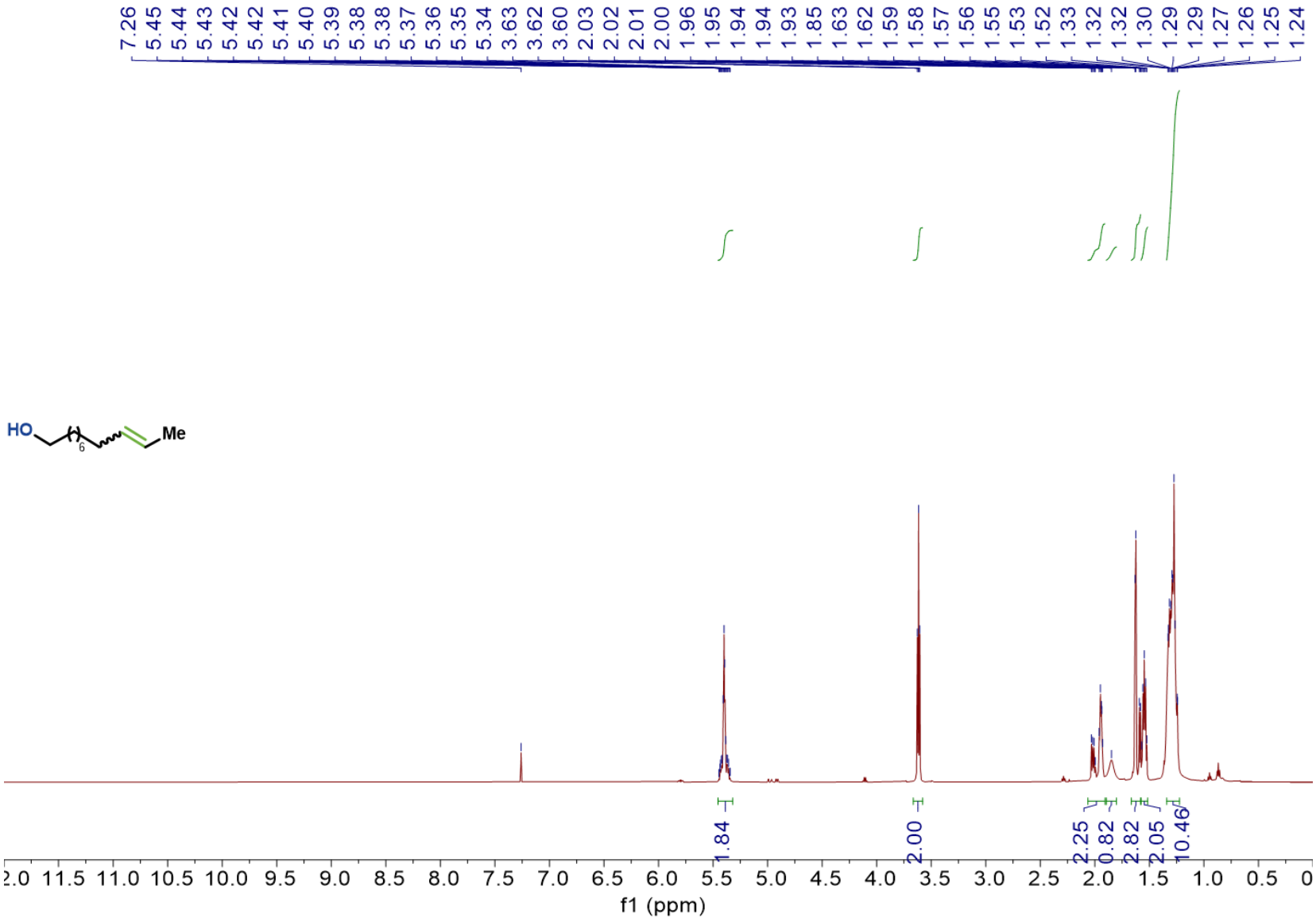
^{1}H NMR (600 MHz, $CDCl_3$) of compound **12**



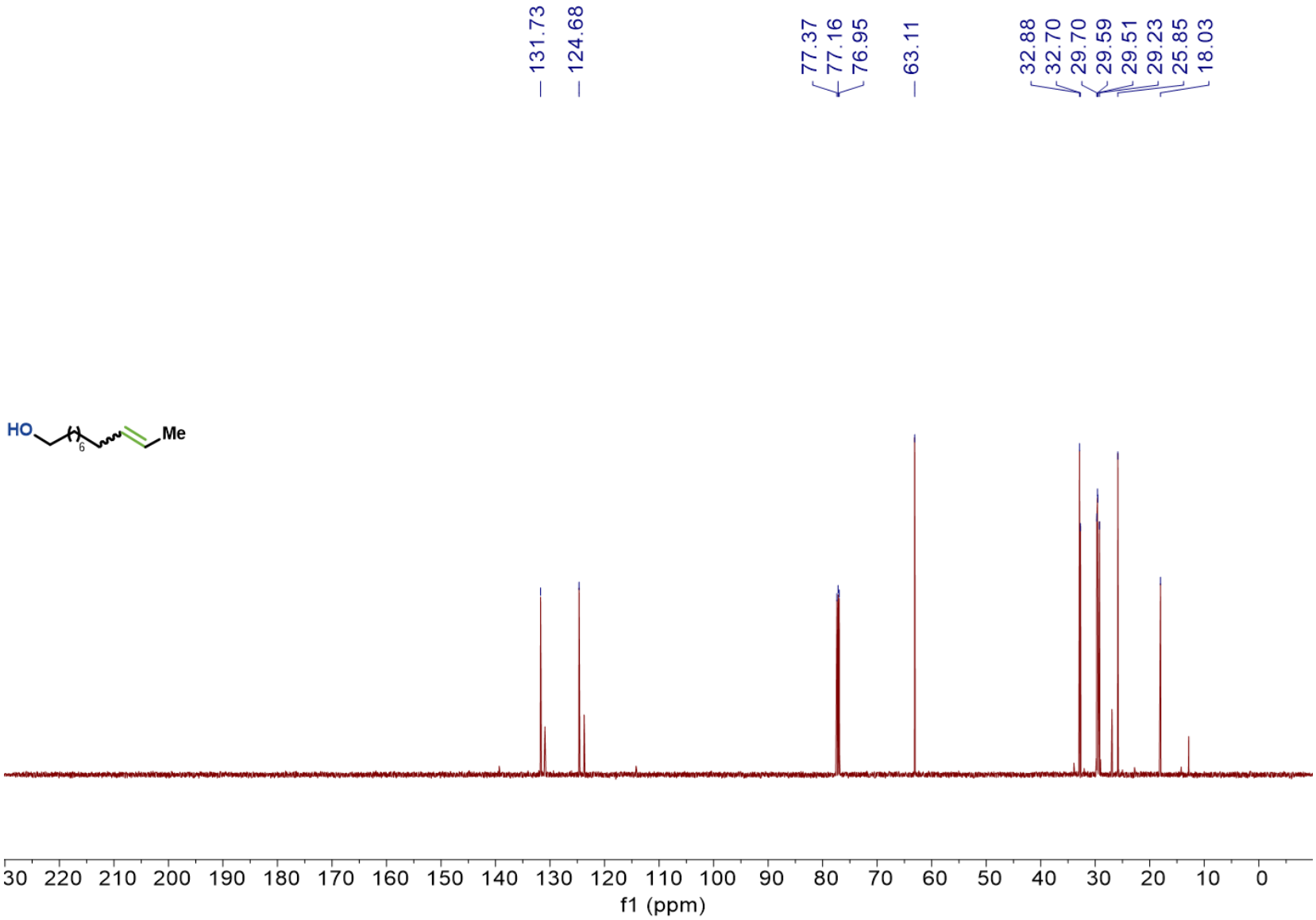
^{13}C NMR (151 MHz, $CDCl_3$) of compound **12**



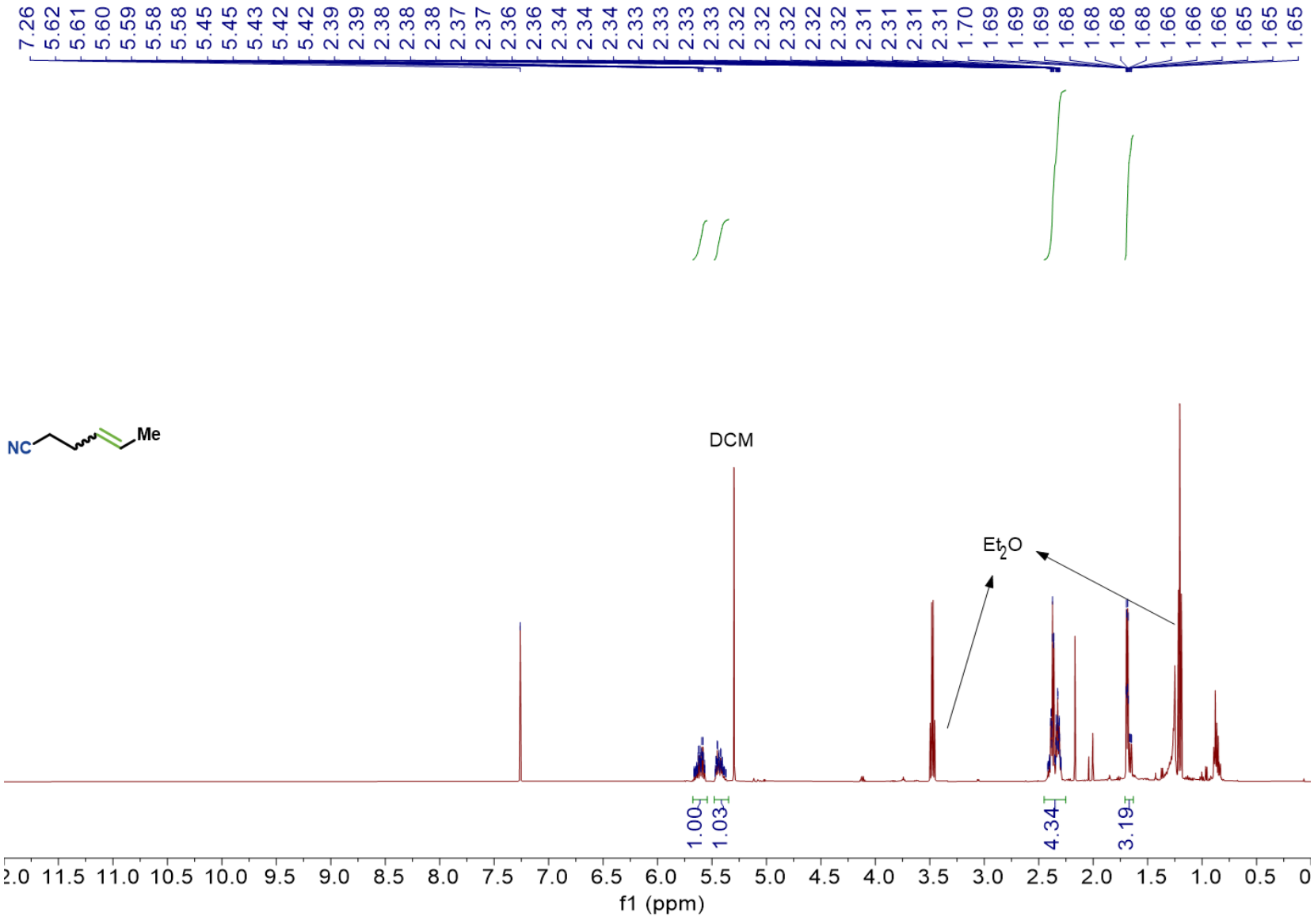
^{1}H NMR (600 MHz, $CDCl_3$) of compound **13**



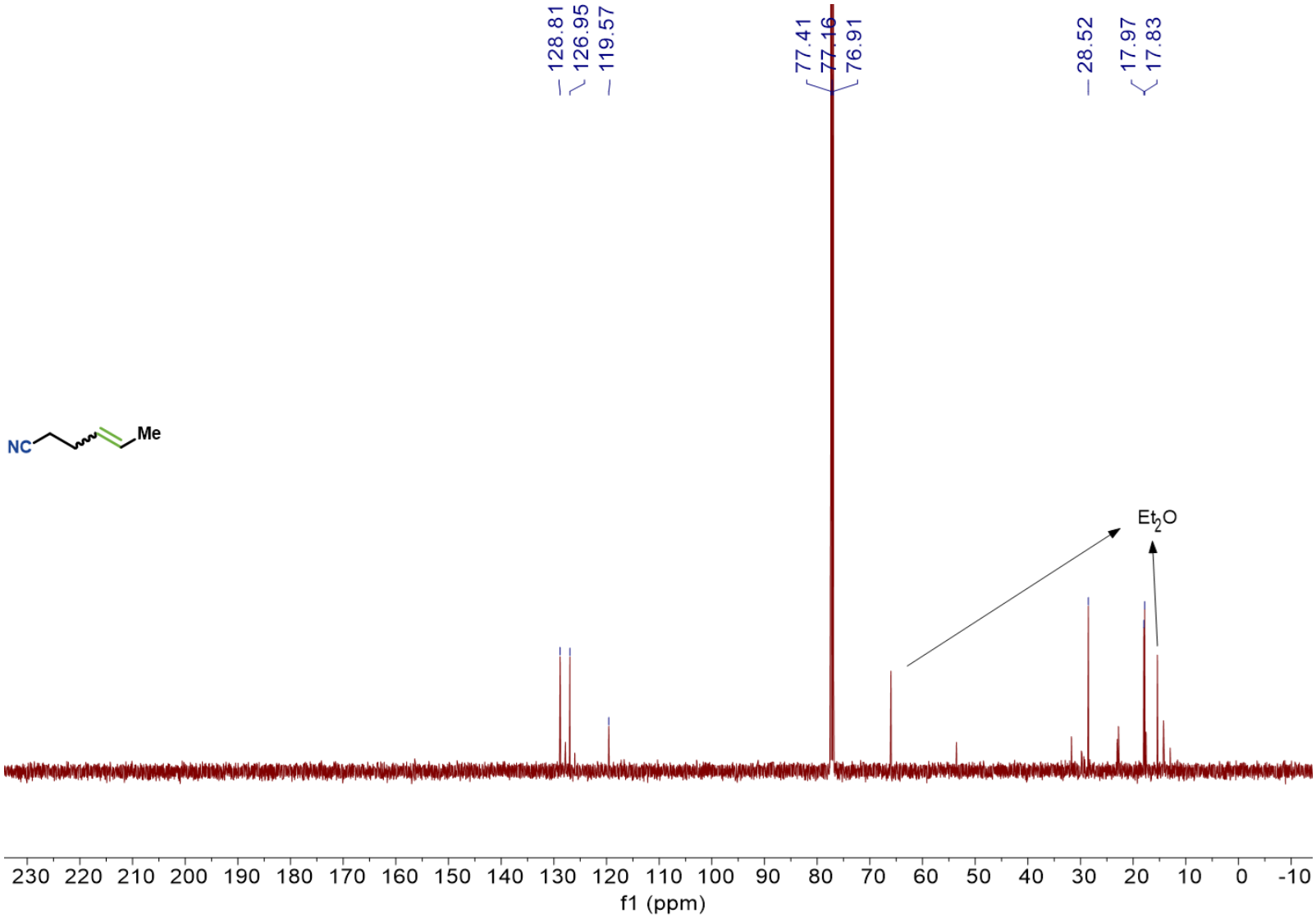
^{13}C NMR (151 MHz, $CDCl_3$) of compound **13**



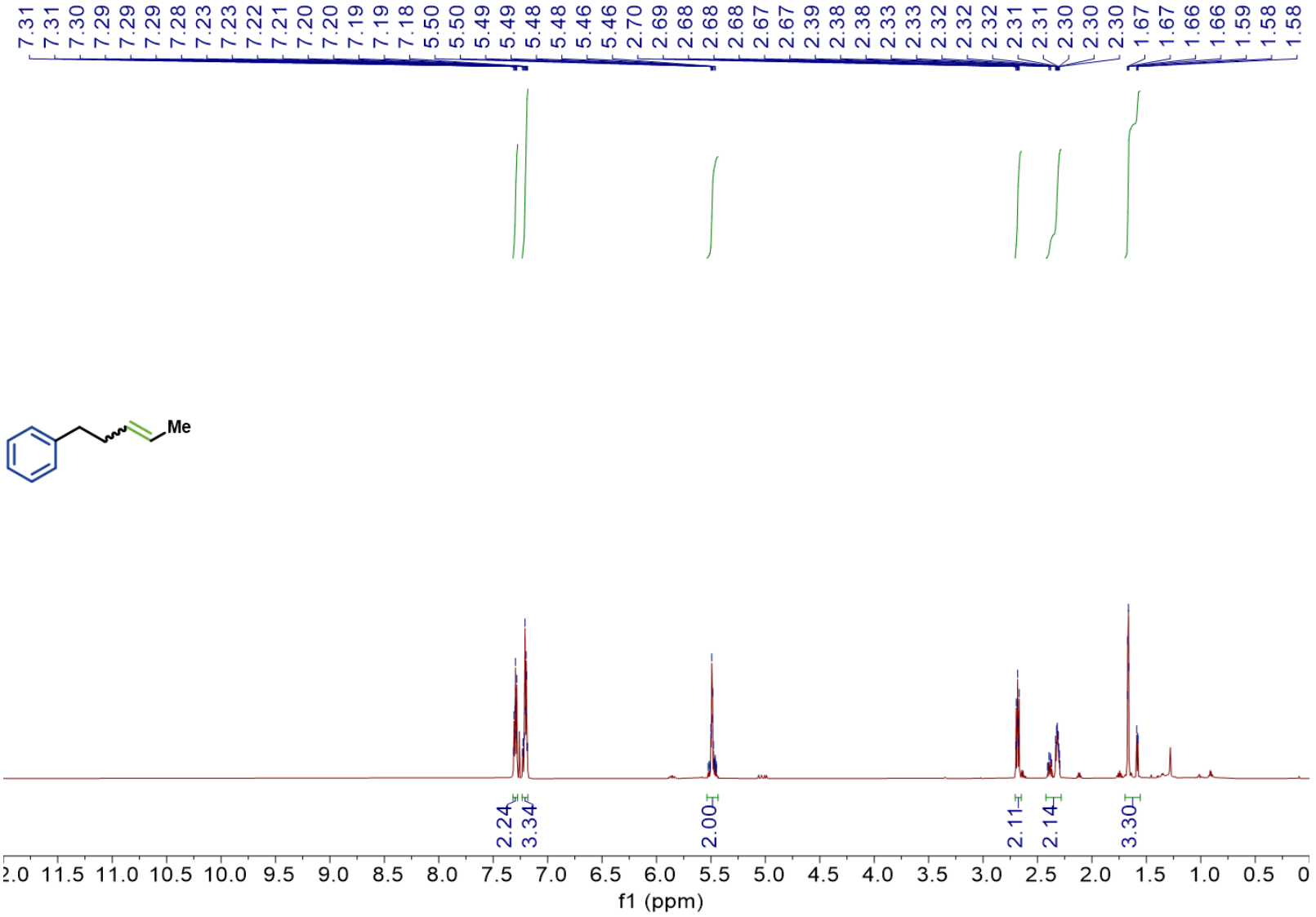
^{1}H NMR (600 MHz, $CDCl_3$) of compound **14**



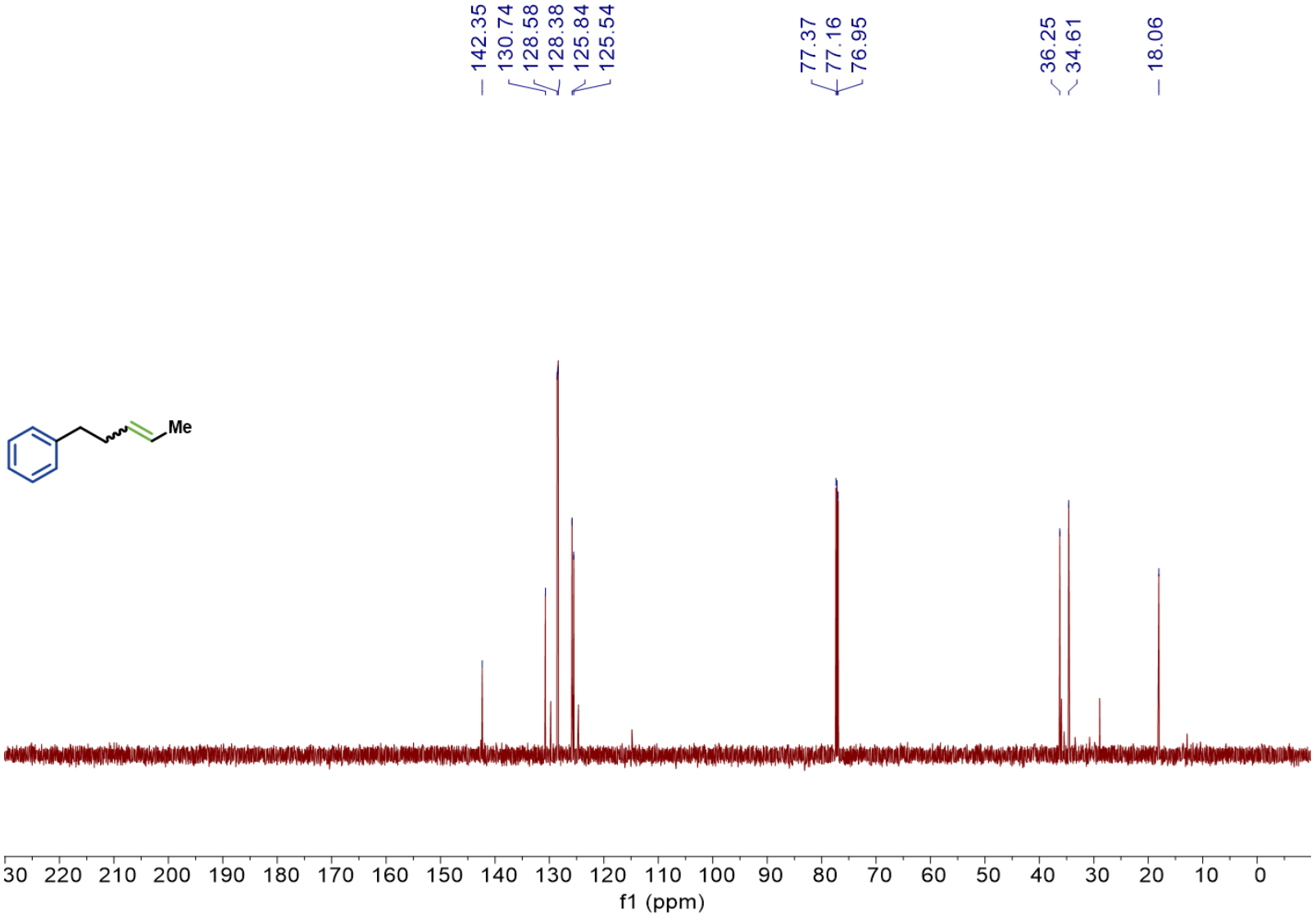
^{13}C NMR (151 MHz, $CDCl_3$) of compound **14**



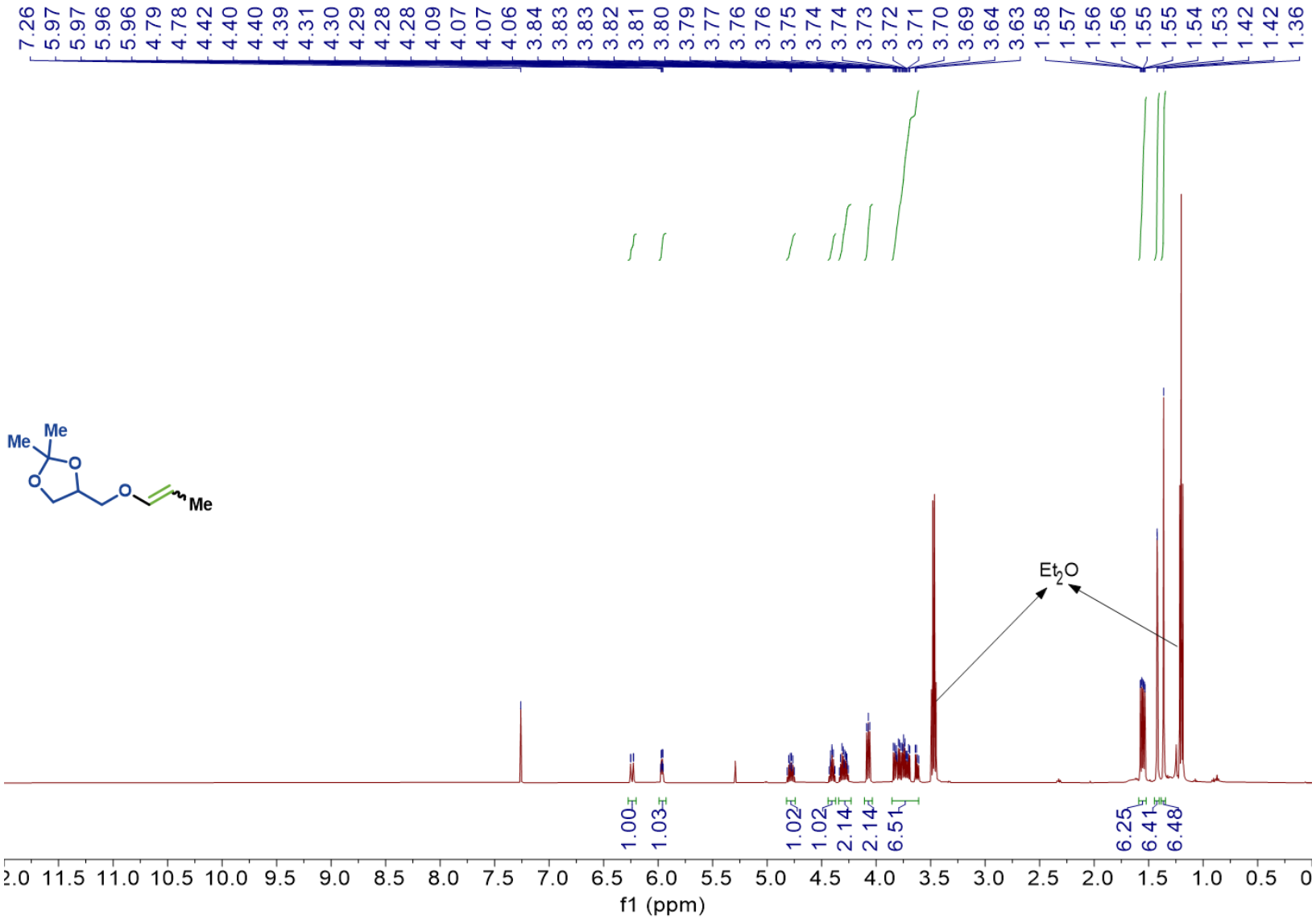
^{1}H NMR (600 MHz, $CDCl_3$) of compound **15**



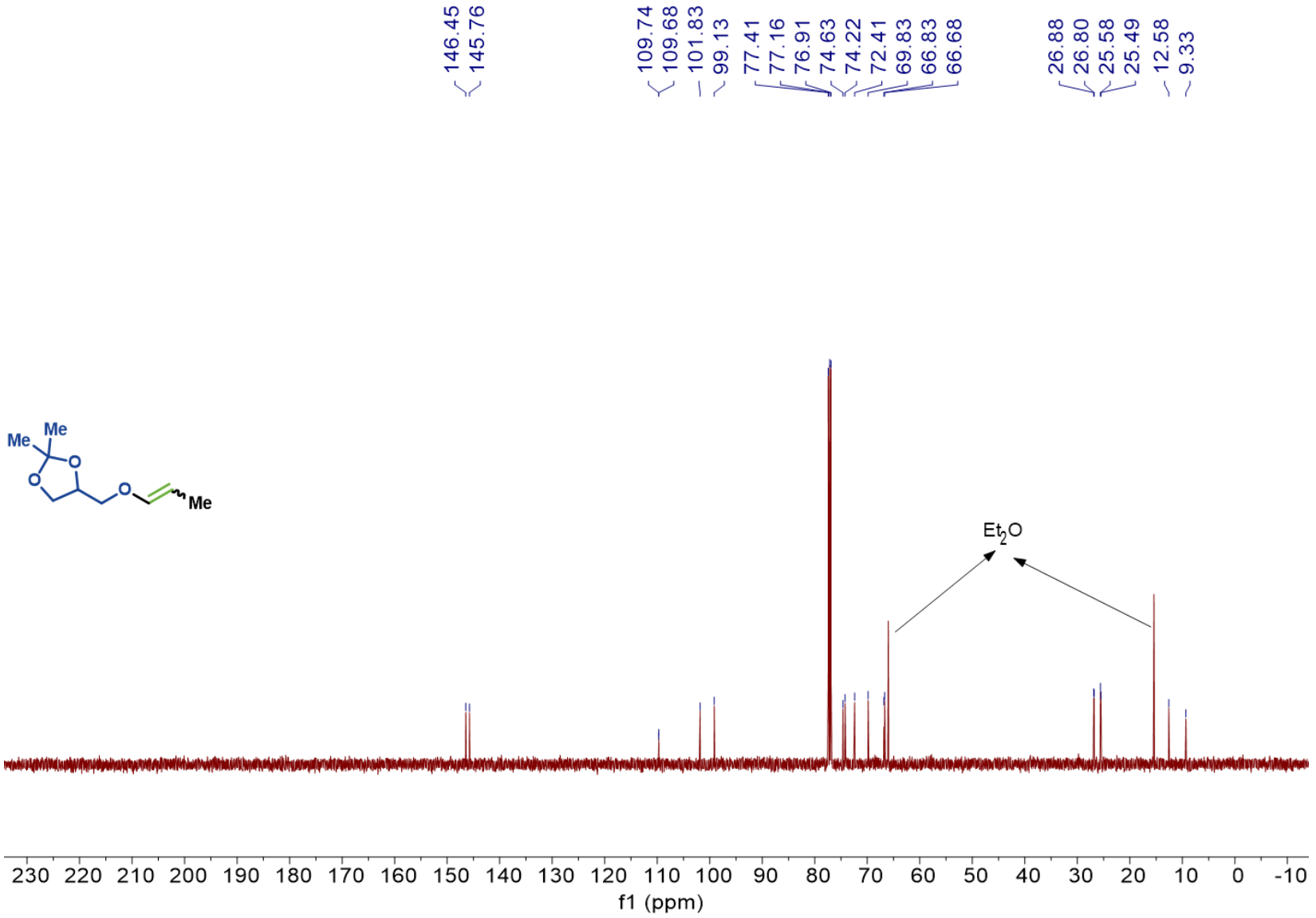
^{13}C NMR (151 MHz, $CDCl_3$) of compound **15**



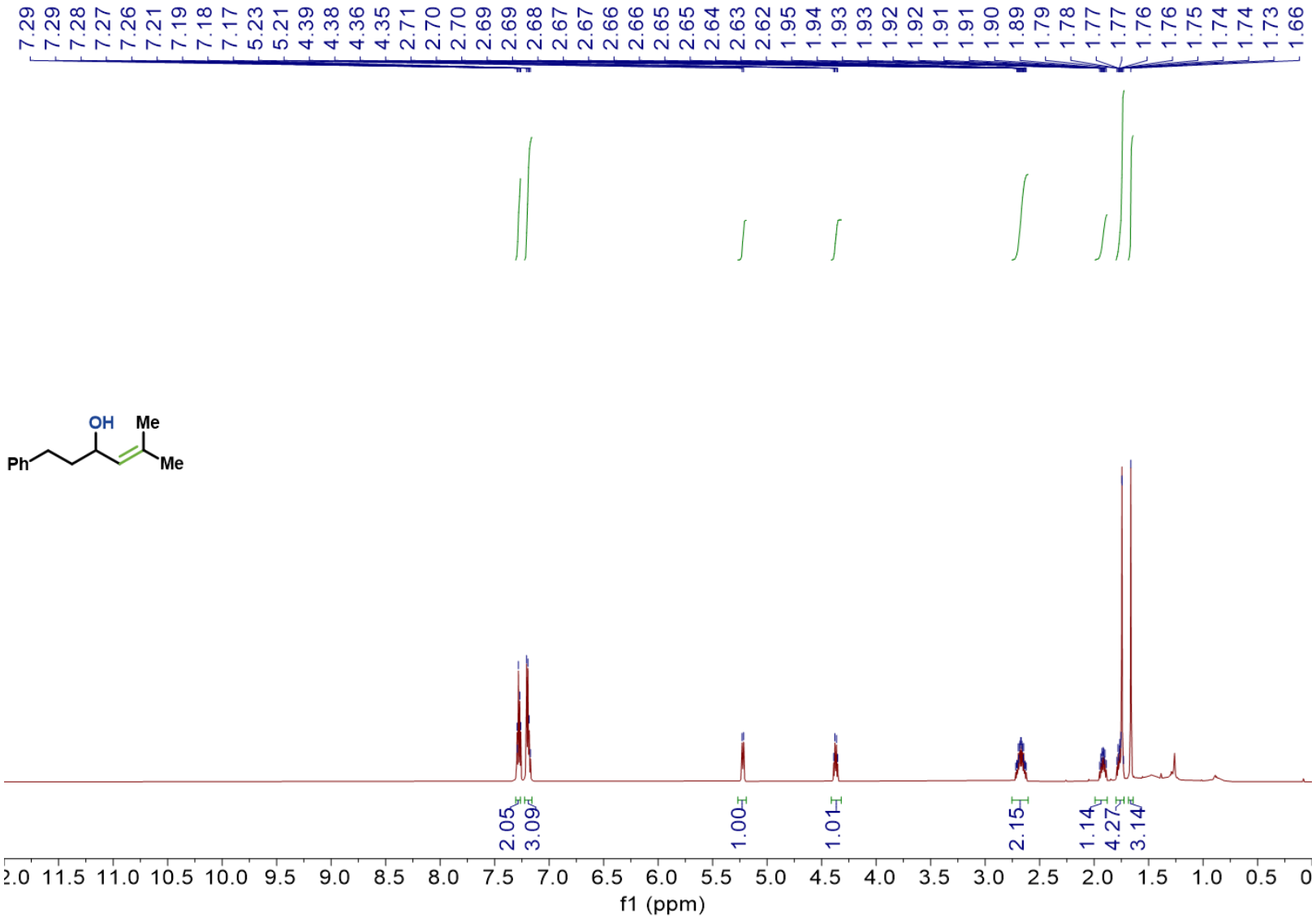
^{1}H NMR (600 MHz, $CDCl_3$) of compound **16**



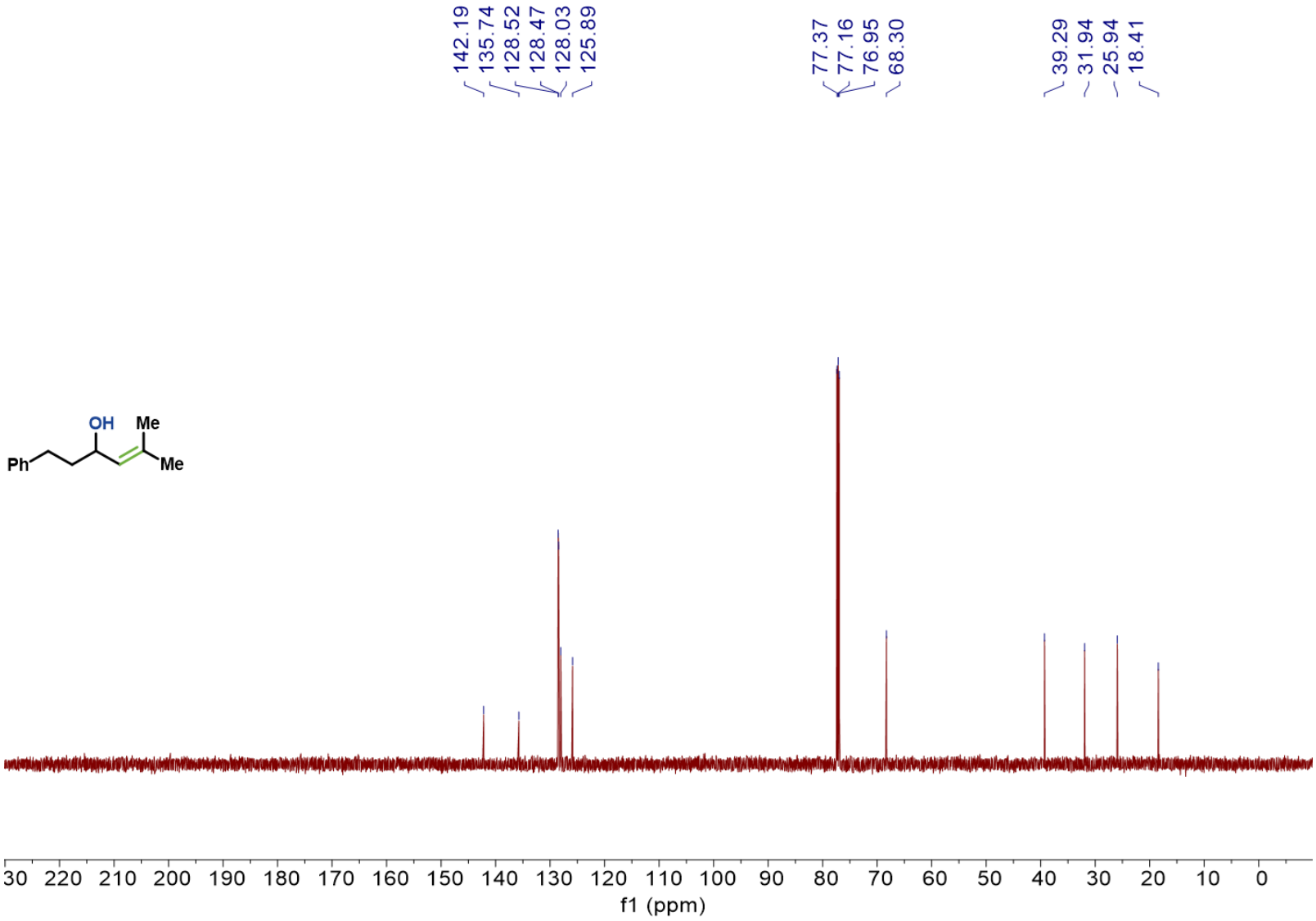
^{13}C NMR (151 MHz, $CDCl_3$) of compound **16**



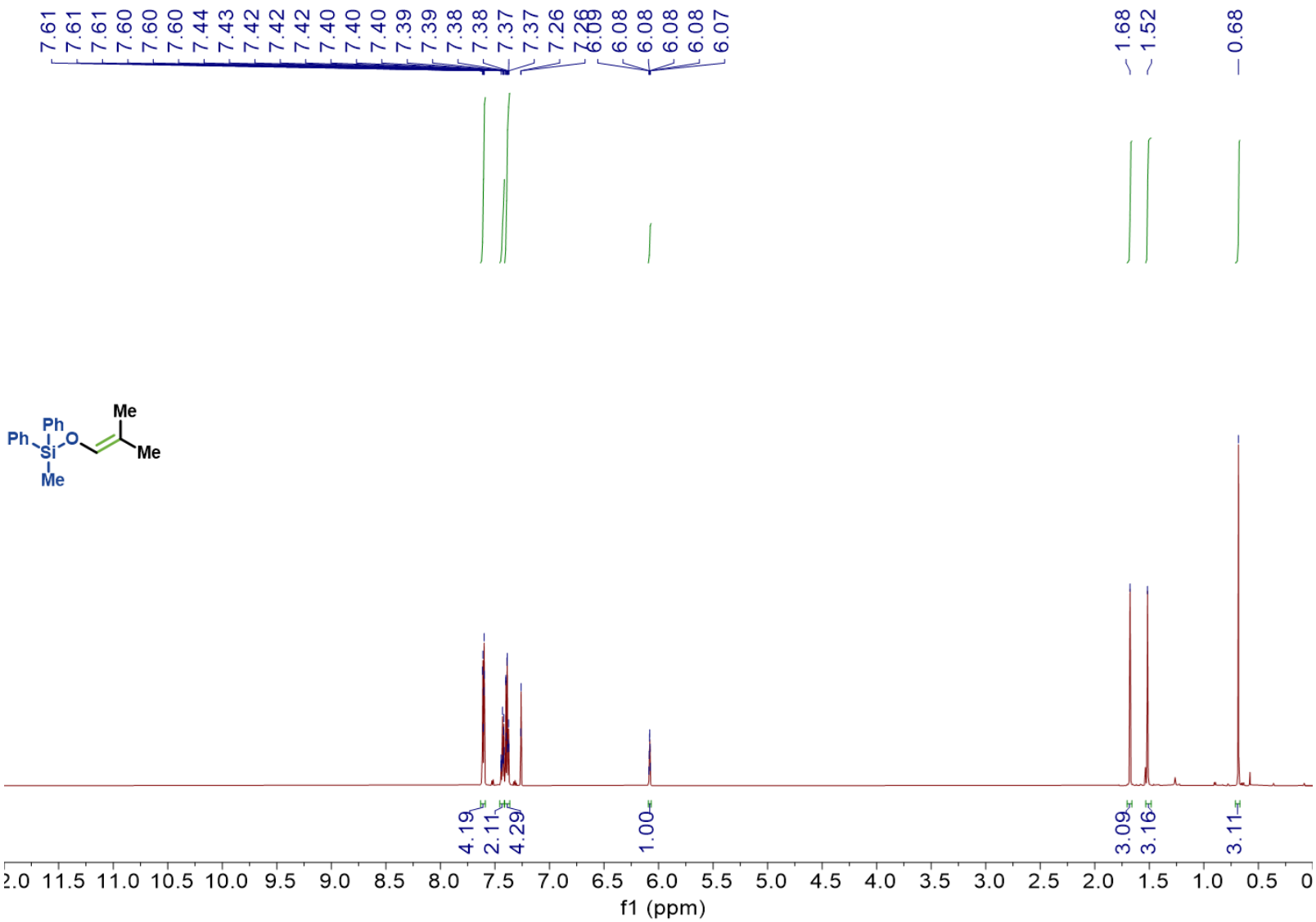
^{1}H NMR (600 MHz, $CDCl_3$) of compound **17**



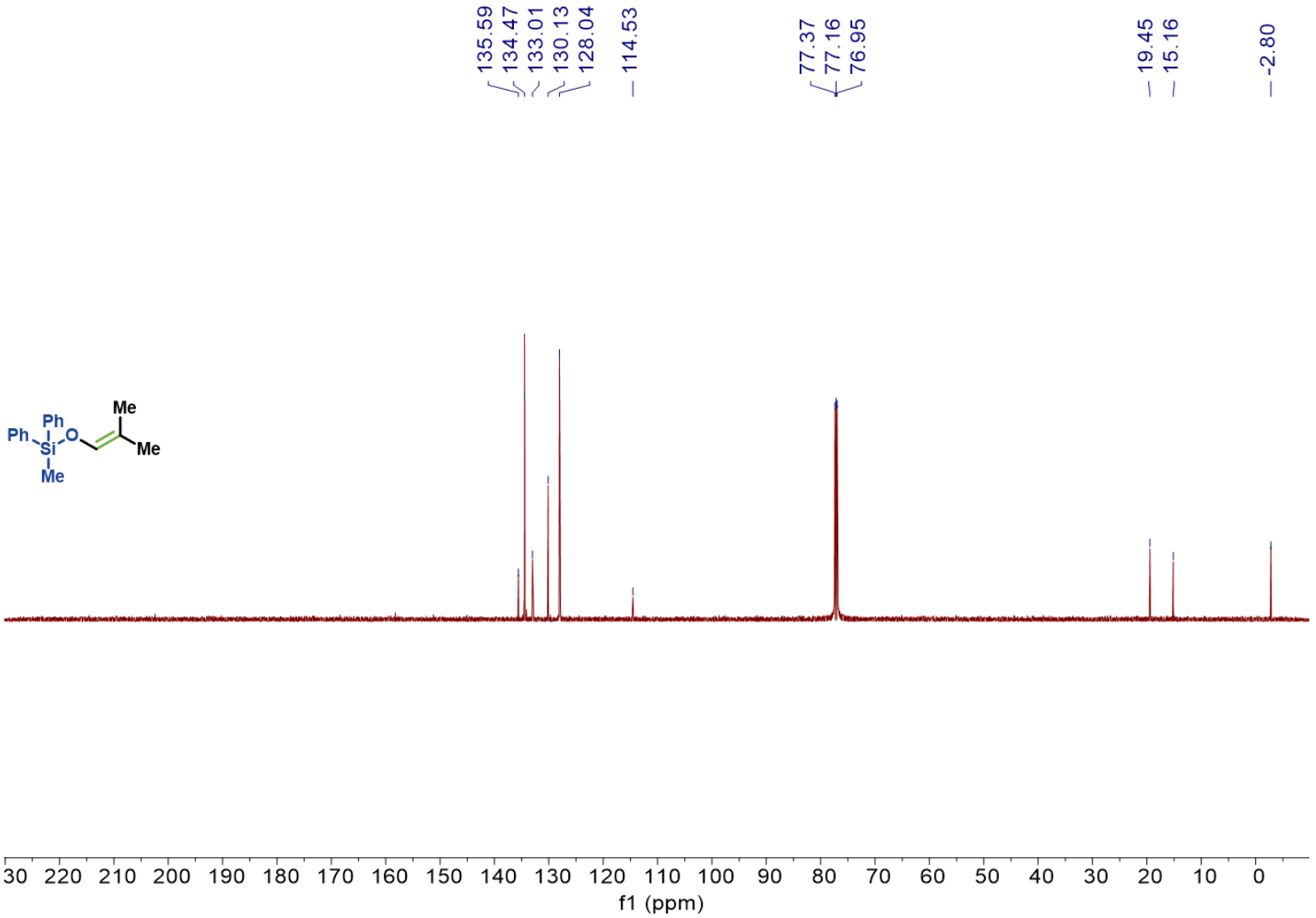
^{13}C NMR (151 MHz, $CDCl_3$) of compound **17**



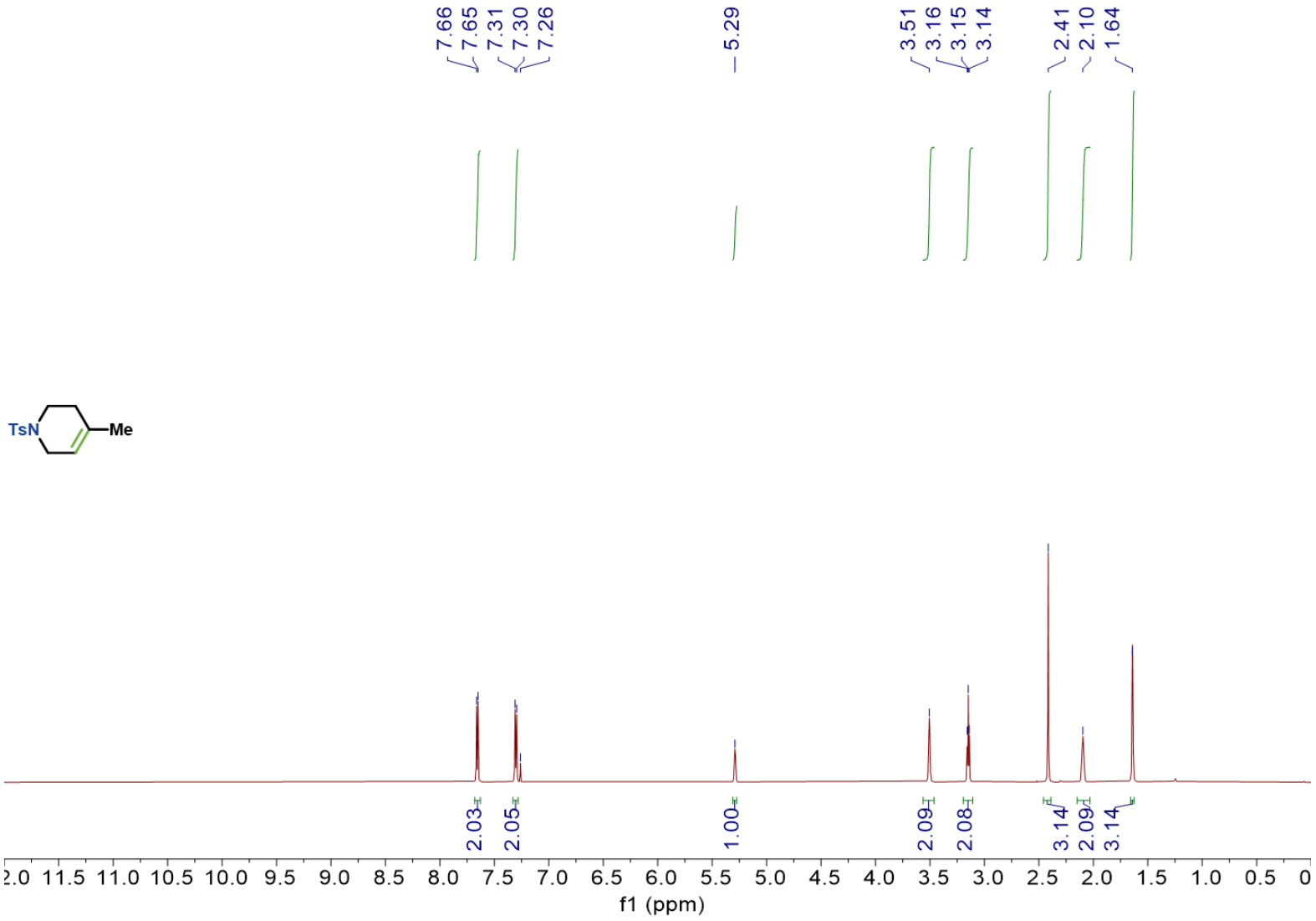
^{1}H NMR (600 MHz, $CDCl_3$) of compound **18**



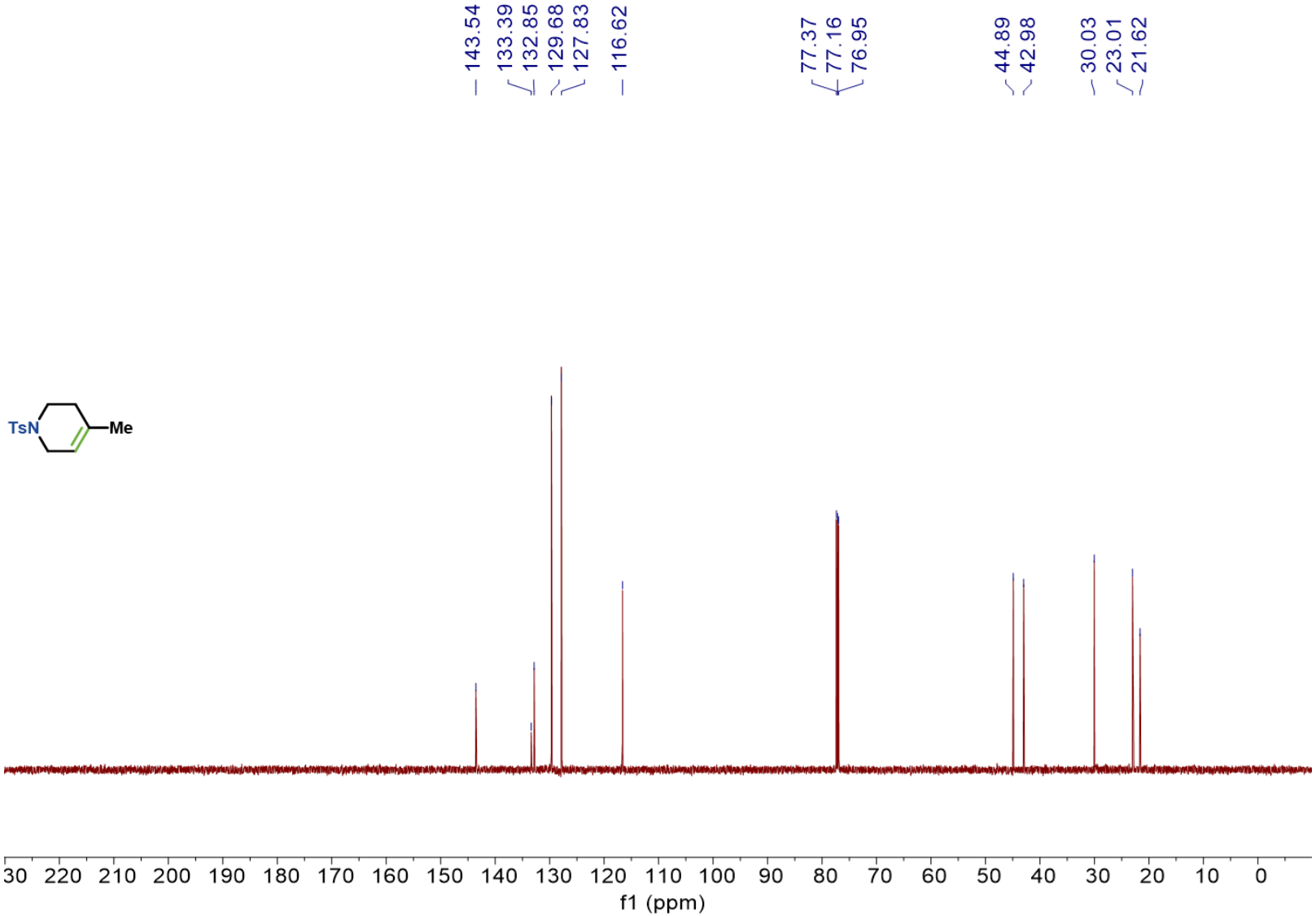
^{13}C NMR (151 MHz, $CDCl_3$) of compound **18**



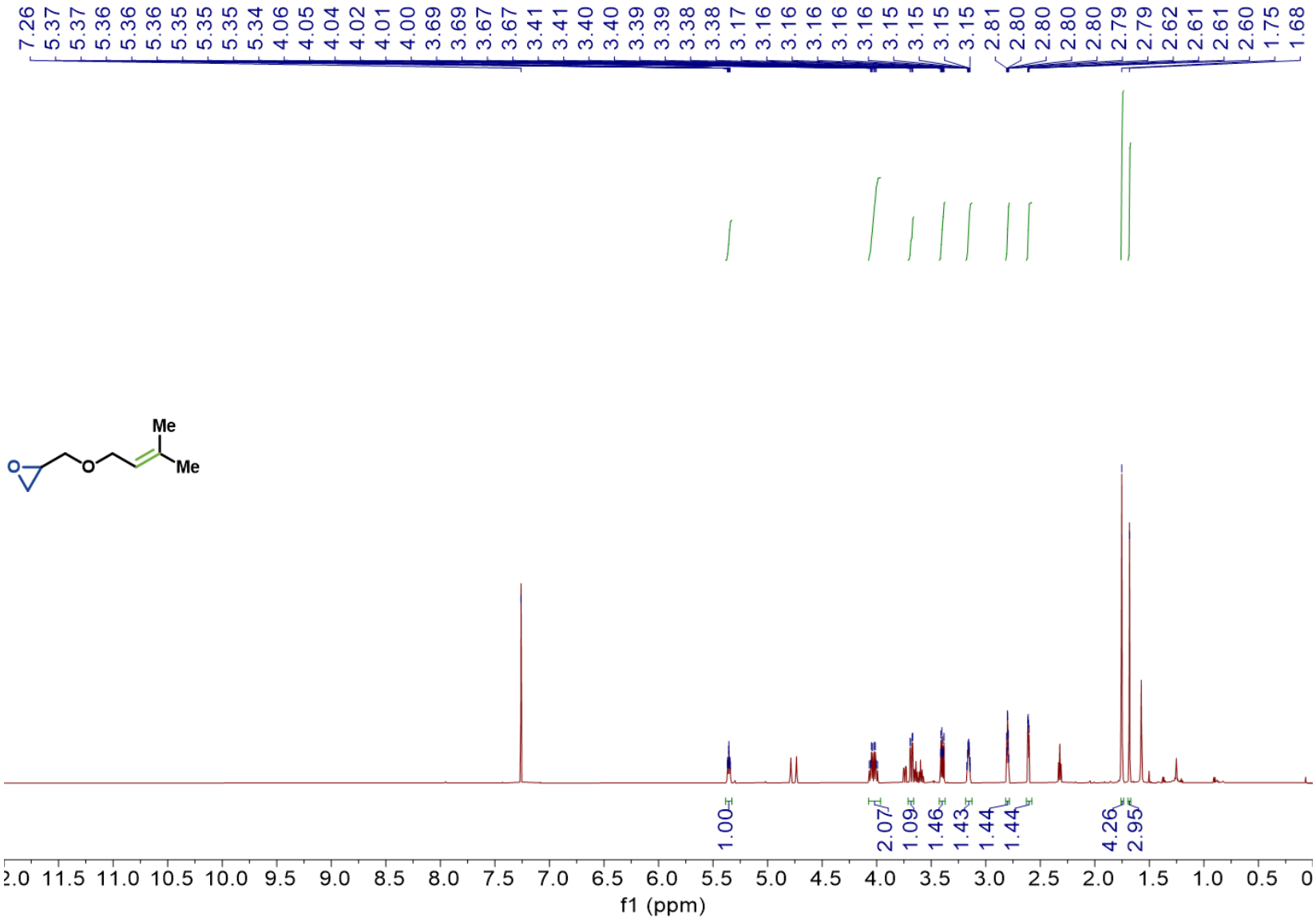
^{1}H NMR (600 MHz, $CDCl_3$) of compound **19**



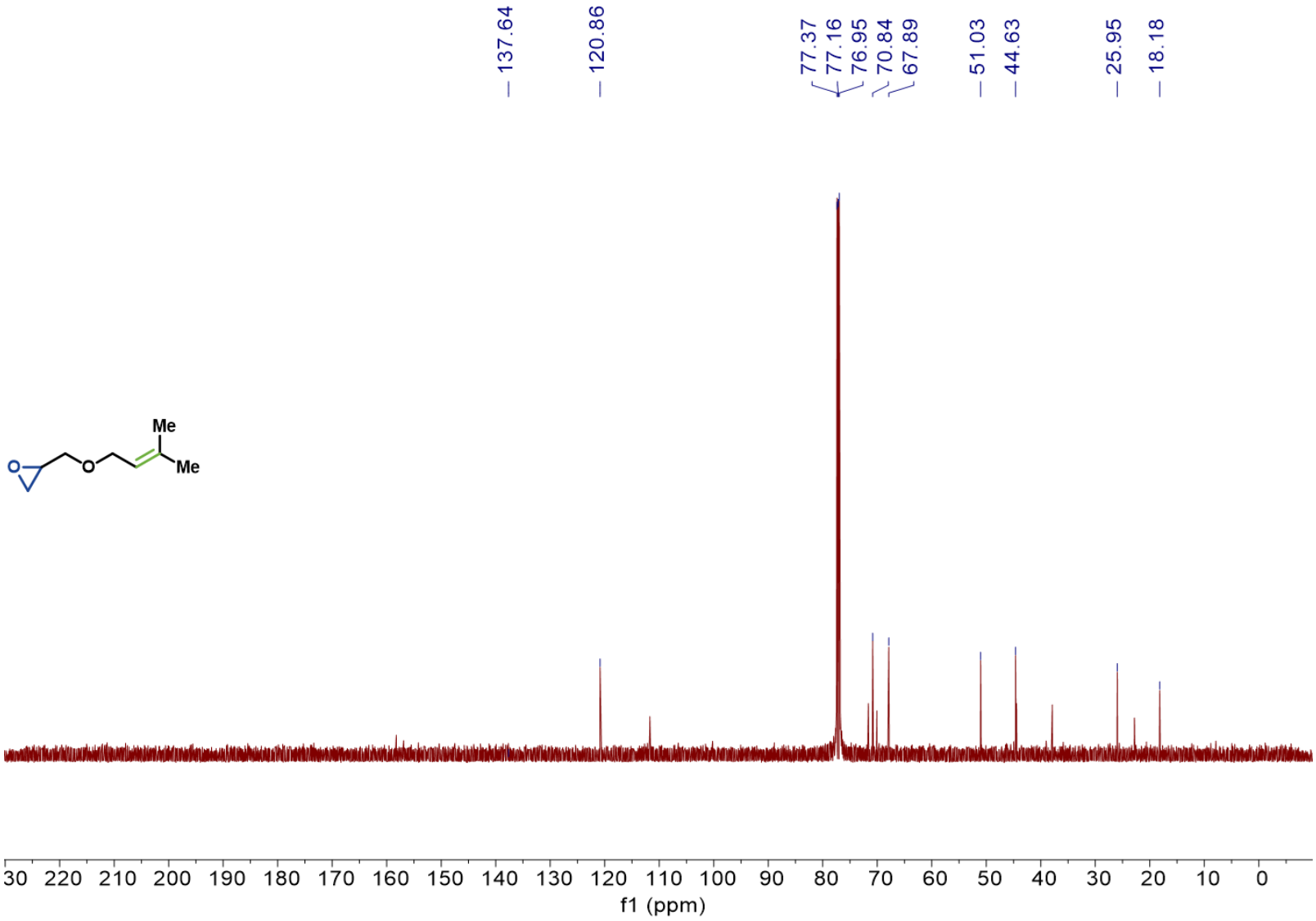
^{13}C NMR (151 MHz, $CDCl_3$) of compound **19**



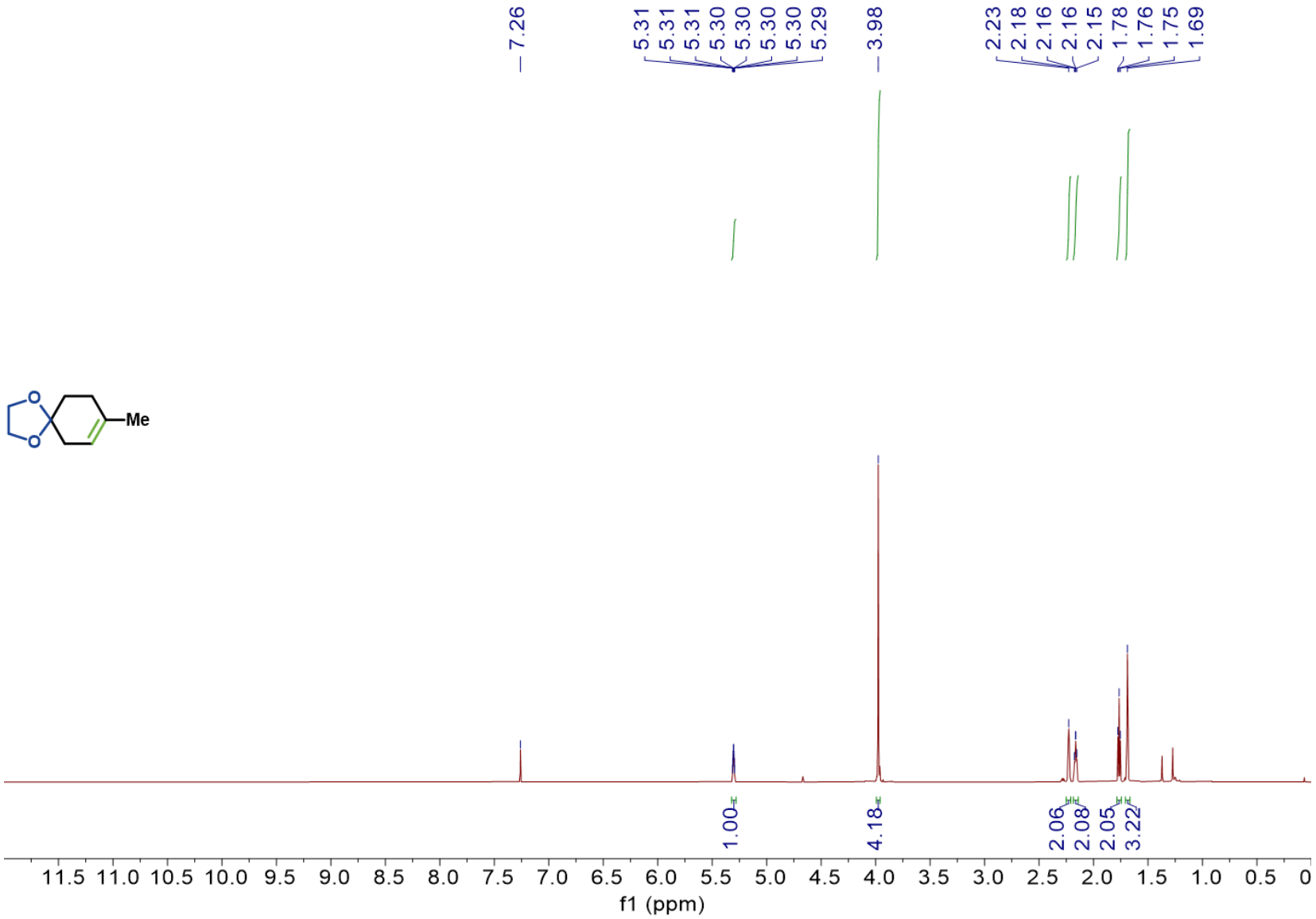
^{1}H NMR (600 MHz, $CDCl_3$) of compound **20 (mixture of product and inseparable SM)**



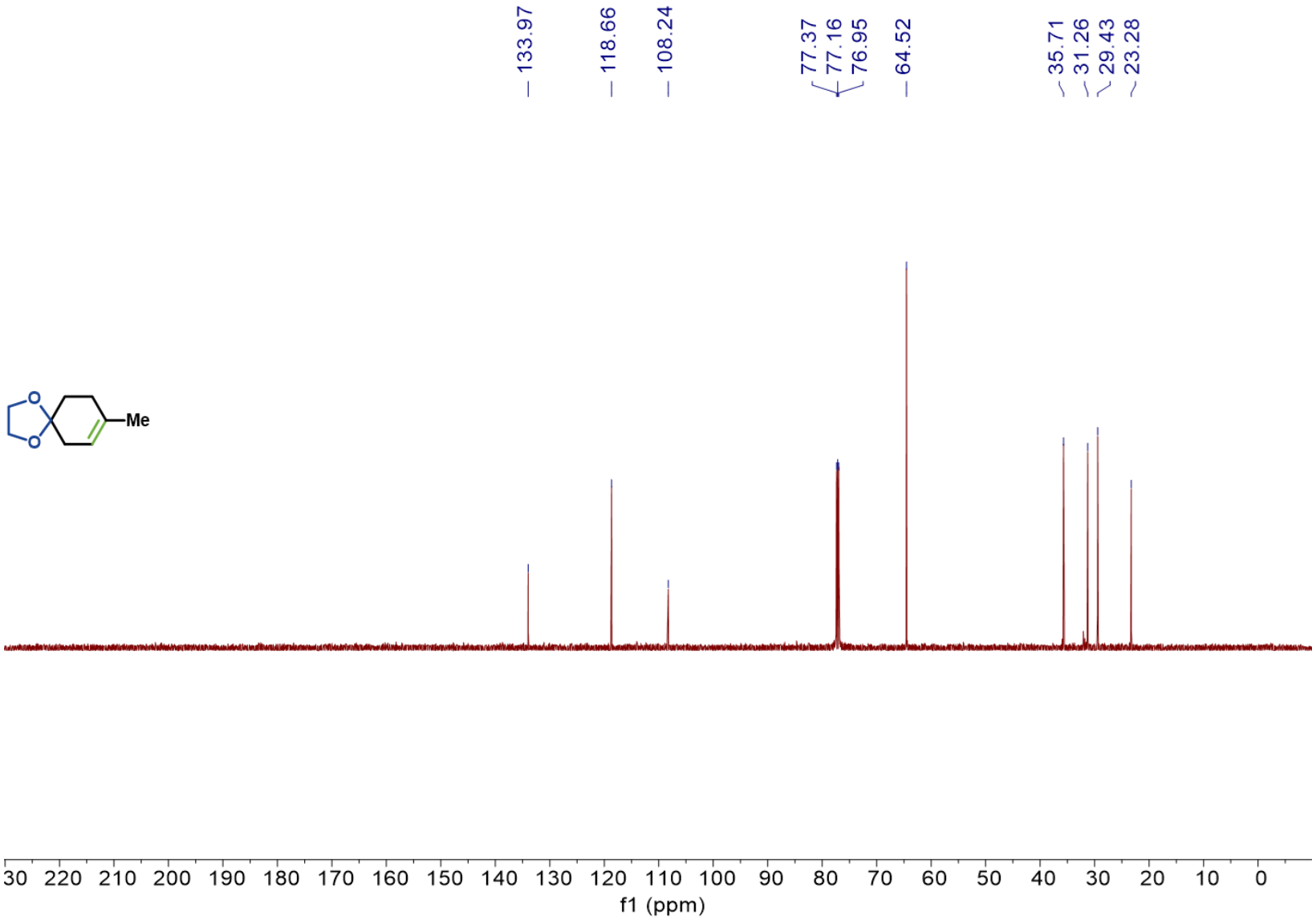
^{13}C NMR (151 MHz, $CDCl_3$) of compound **20 (mixture of product and inseparable SM)**



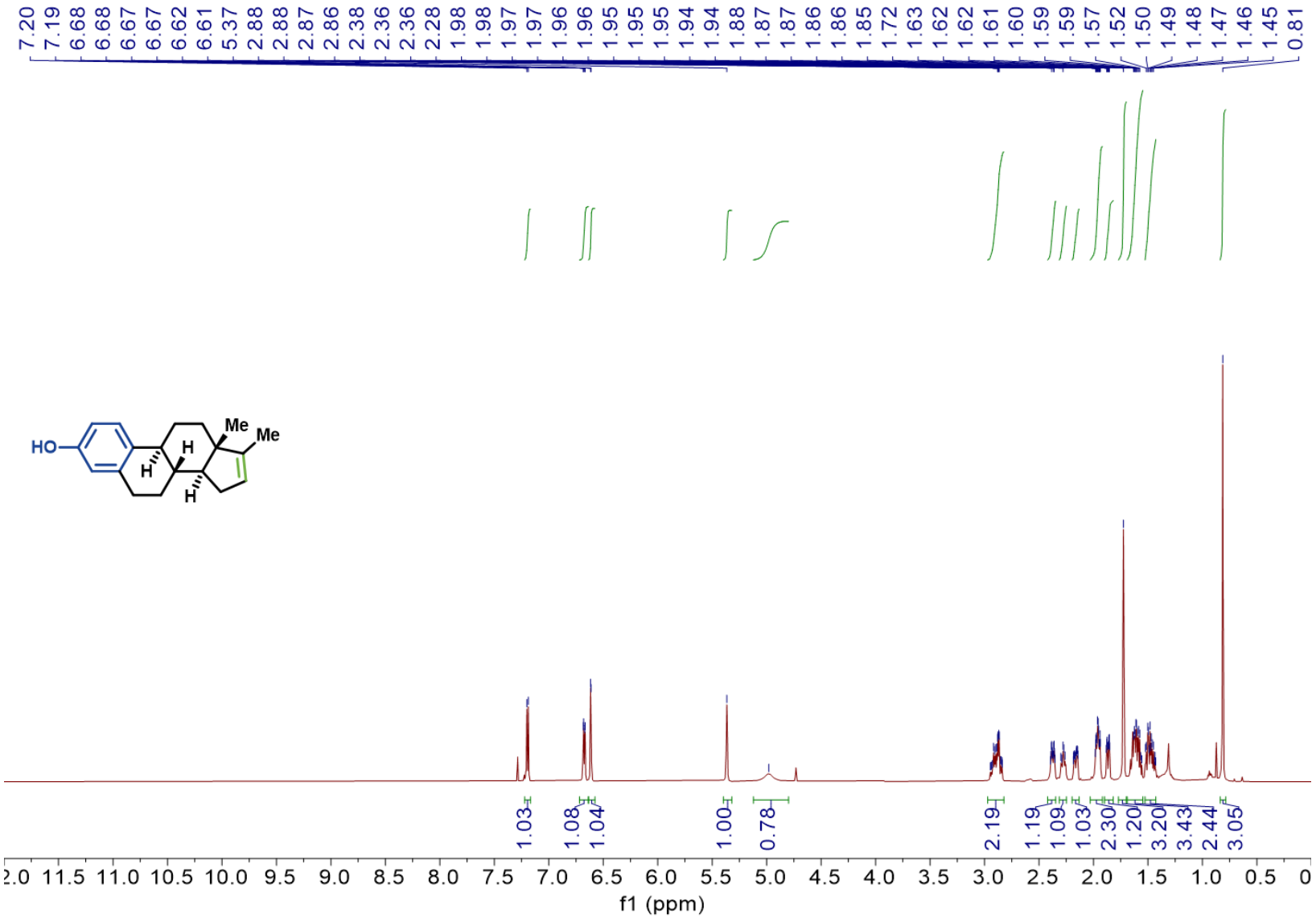
^{1}H NMR (600 MHz, $CDCl_3$) of compound **21**



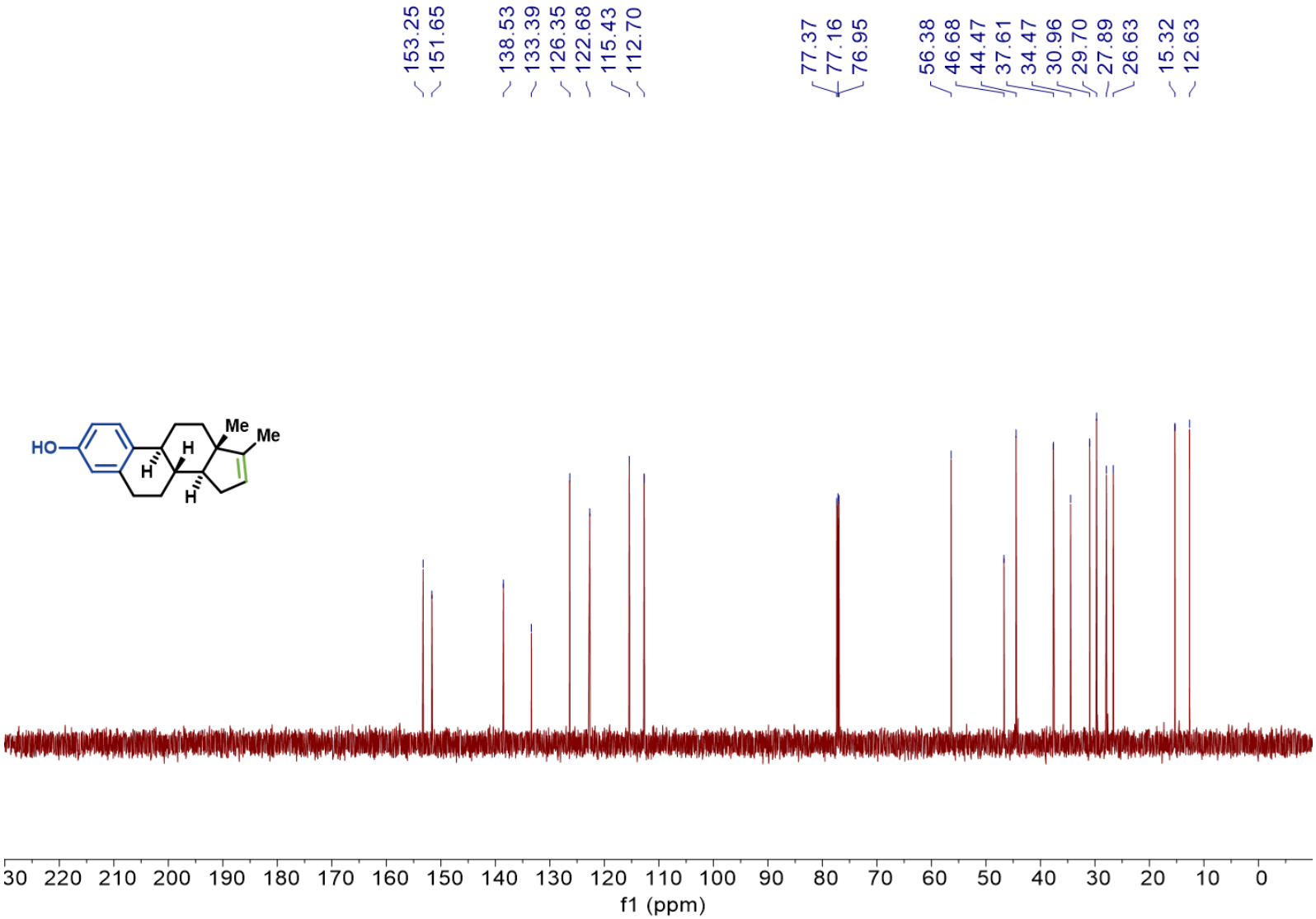
^{13}C NMR (151 MHz, $CDCl_3$) of compound **21**



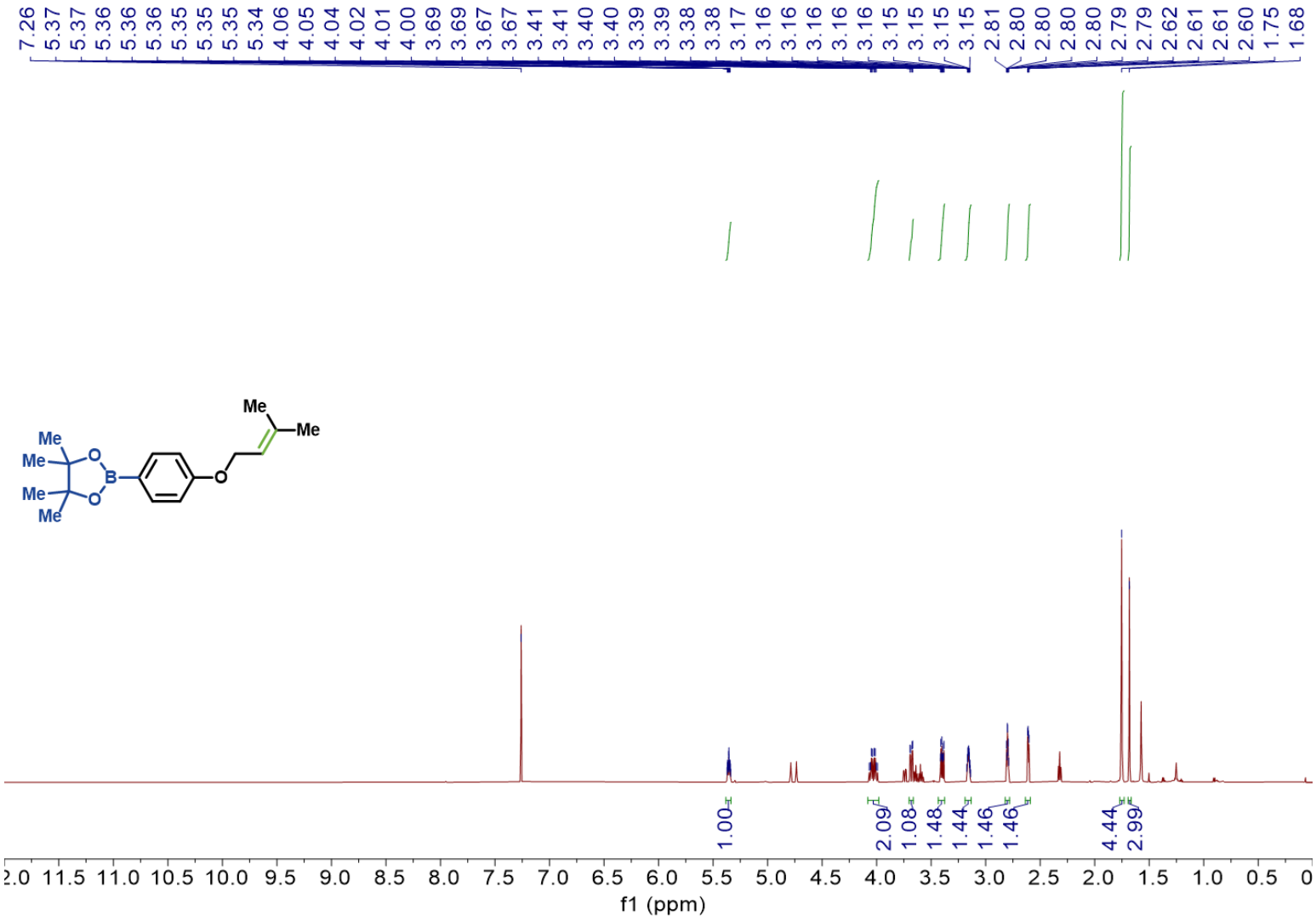
^{1}H NMR (600 MHz, $CDCl_3$) of compound **22**



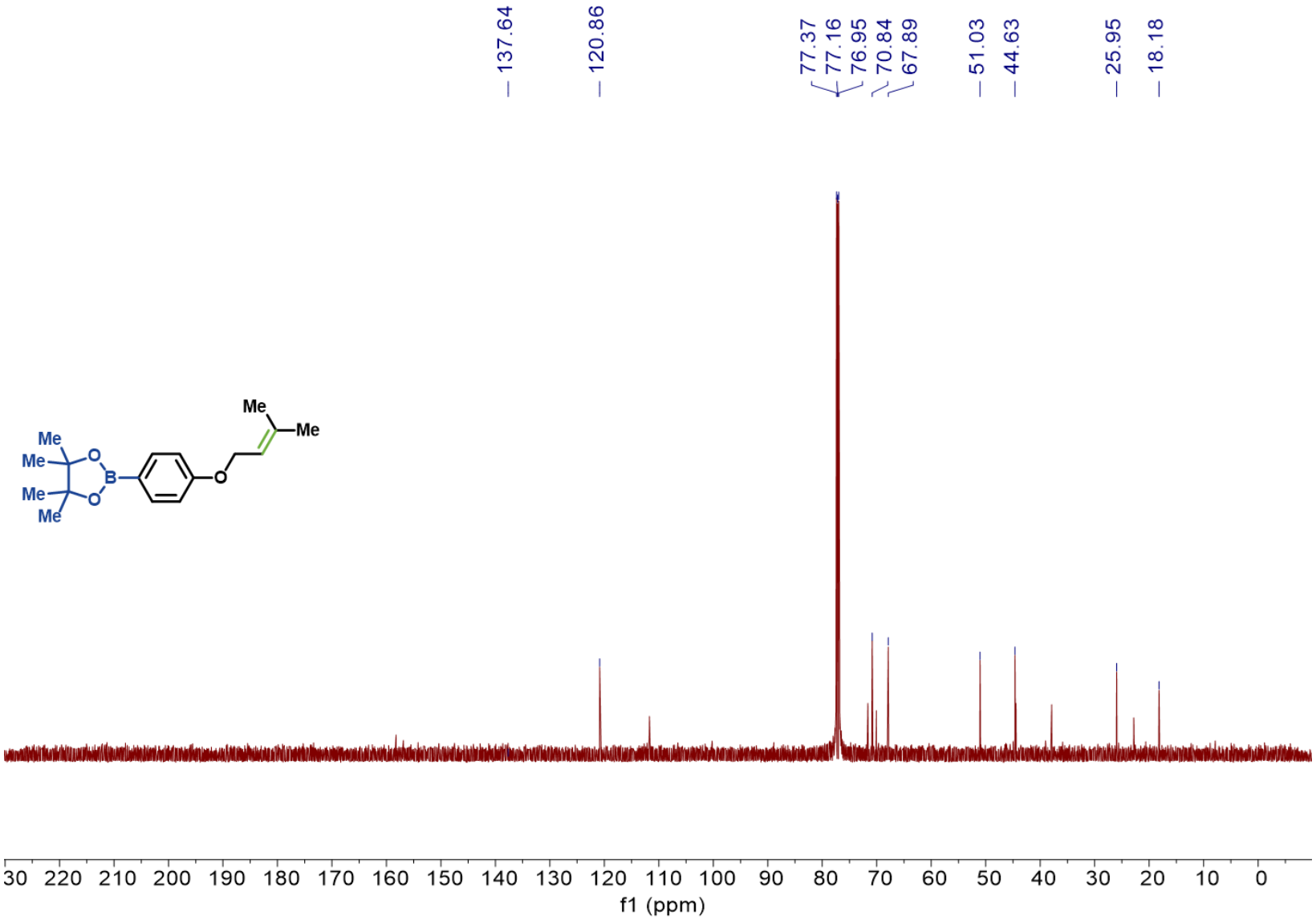
^{13}C NMR (151 MHz, $CDCl_3$) of compound **22**



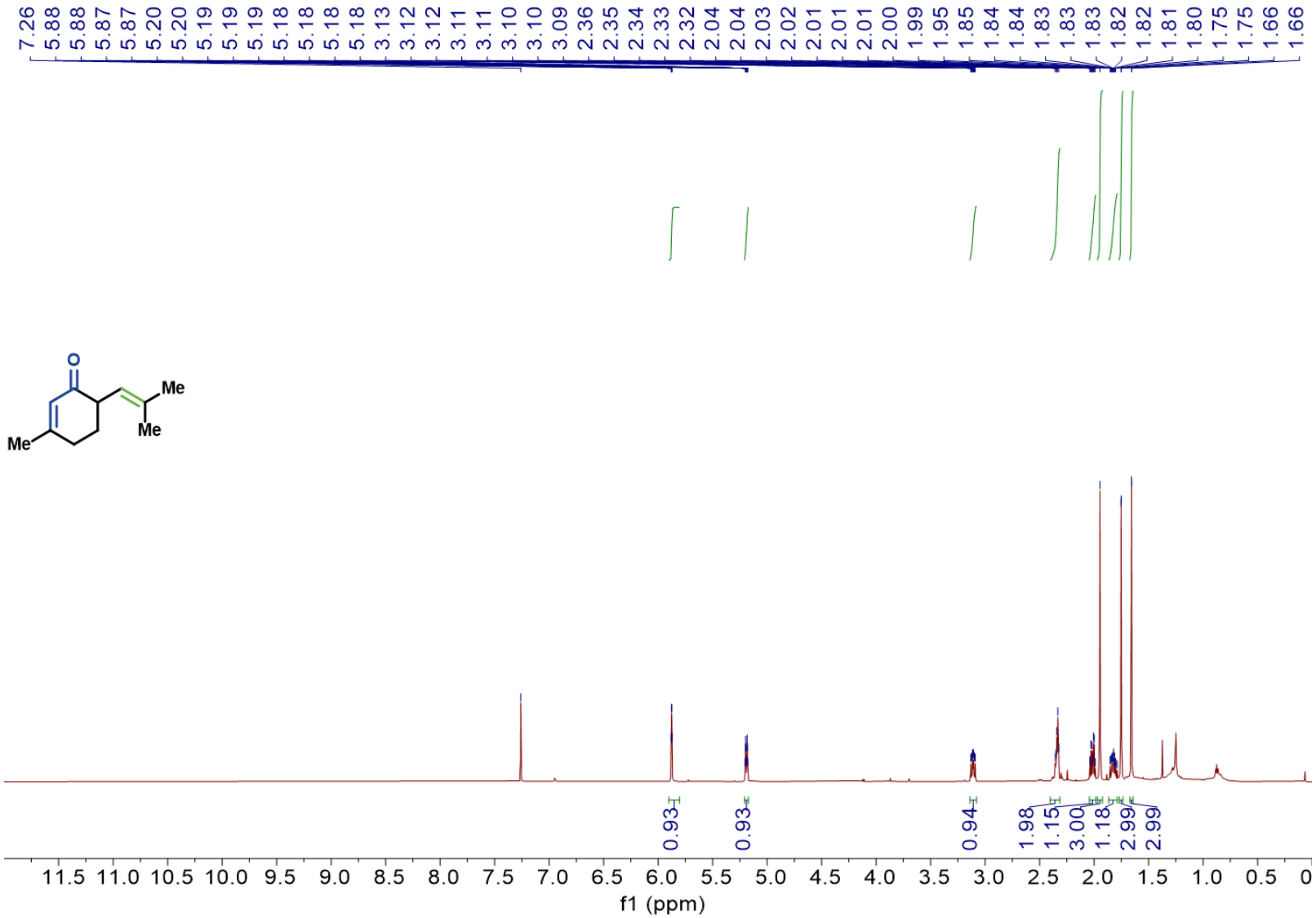
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23 (4:1 mixture of Product:SM)**



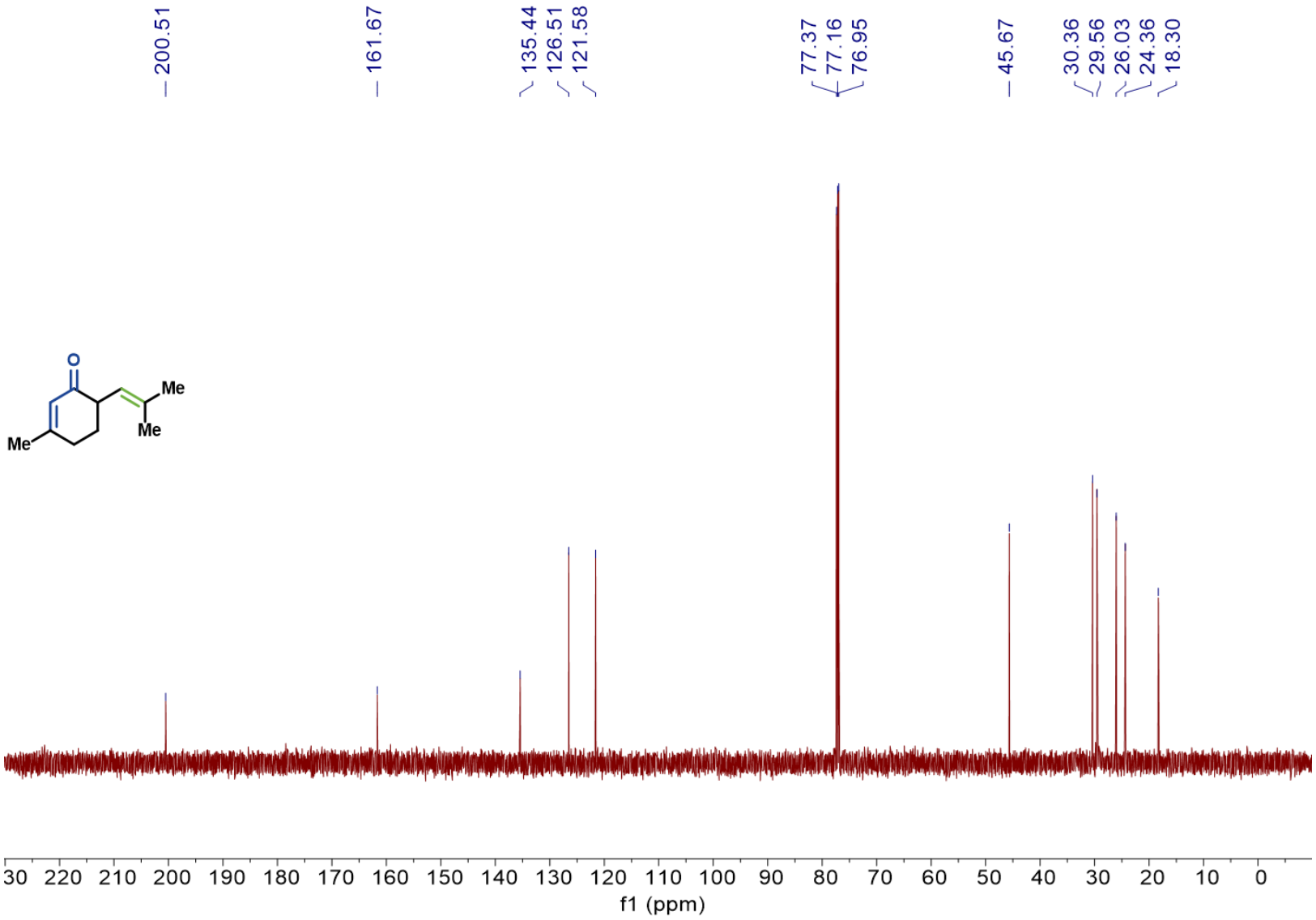
^{13}C NMR (126 MHz, $CDCl_3$) of compound **23 (4:1 mixture of Product:SM)**



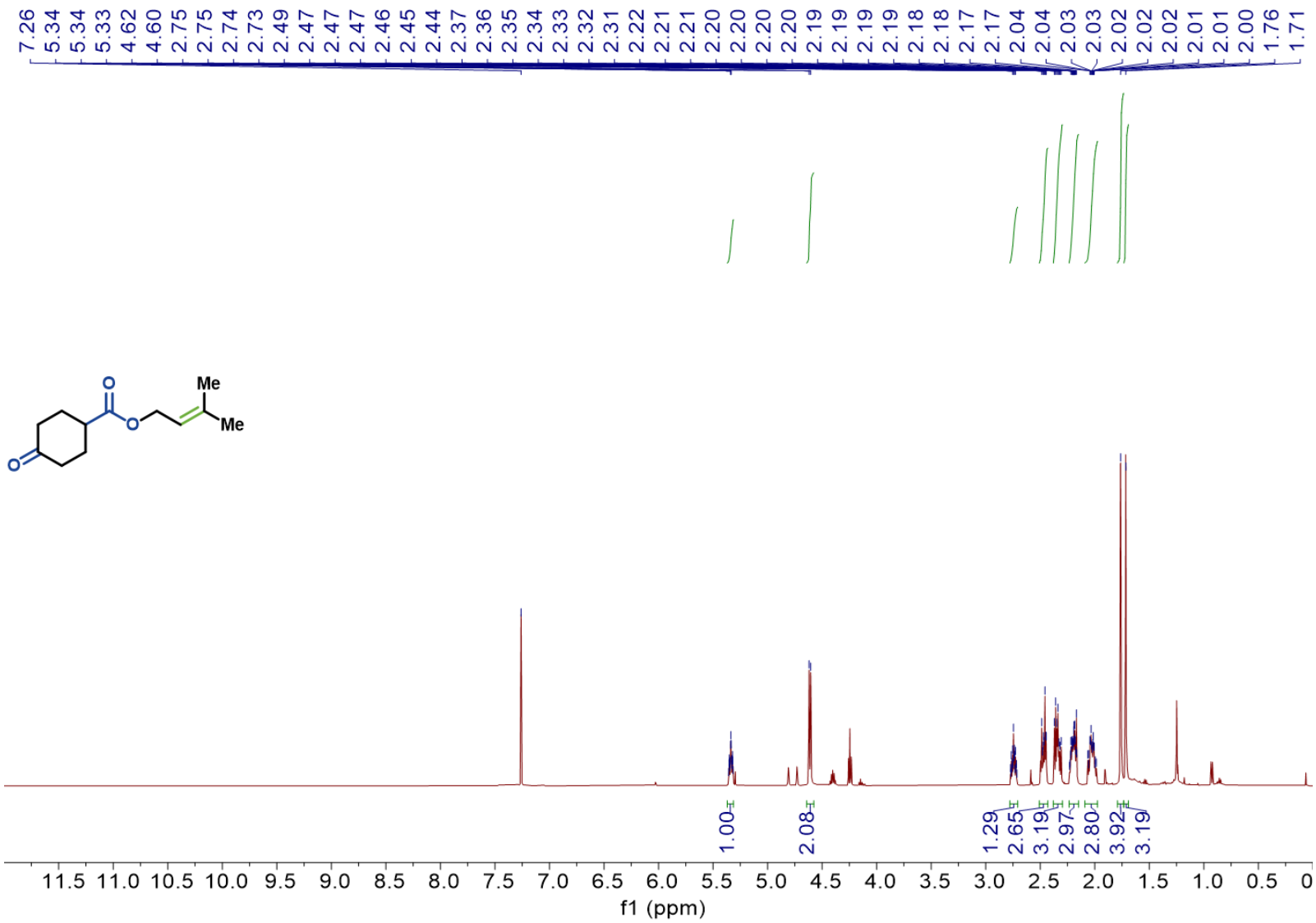
^{1}H NMR (600 MHz, $CDCl_3$) of compound **24**



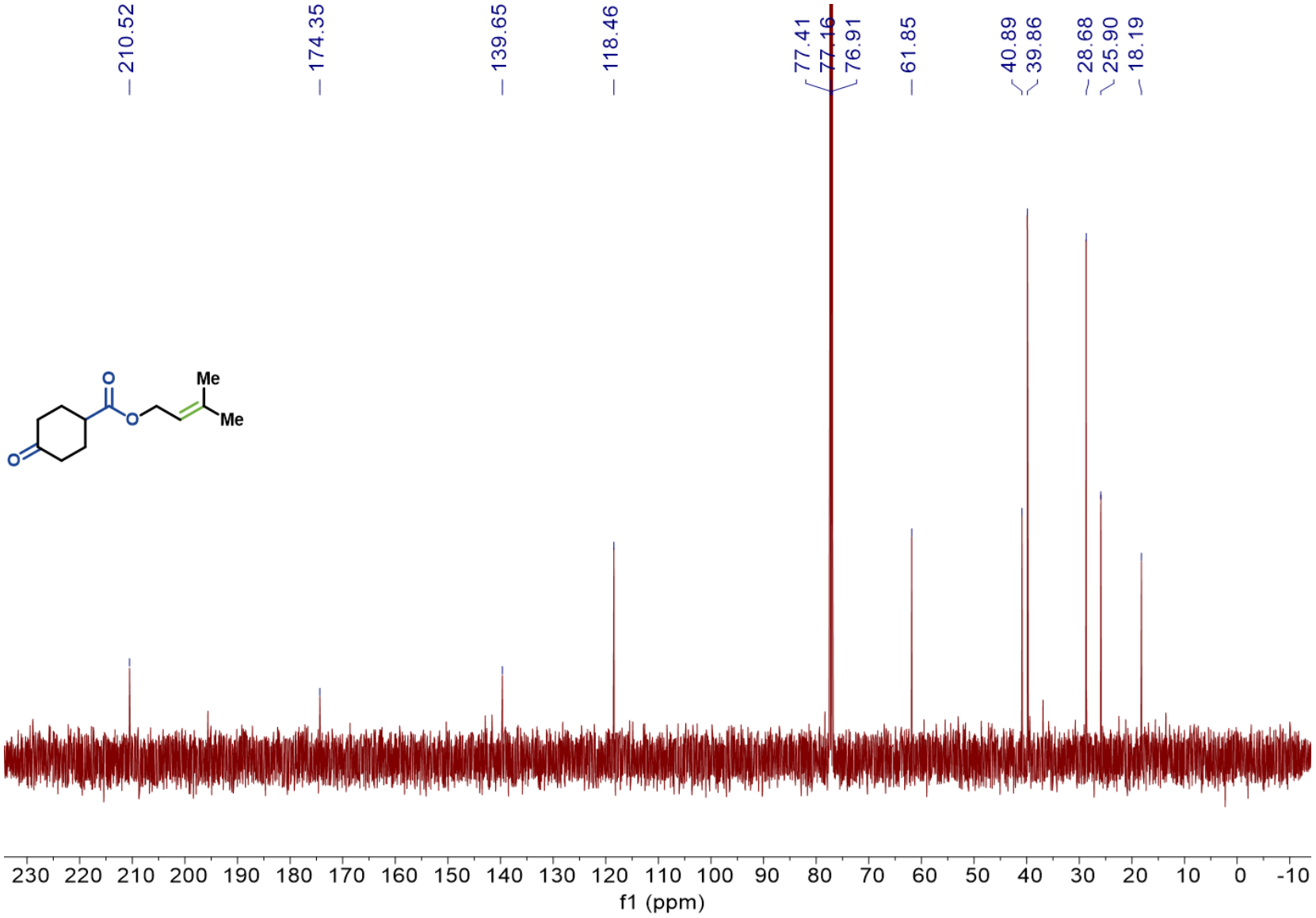
^{13}C NMR (151 MHz, $CDCl_3$) of compound **24**



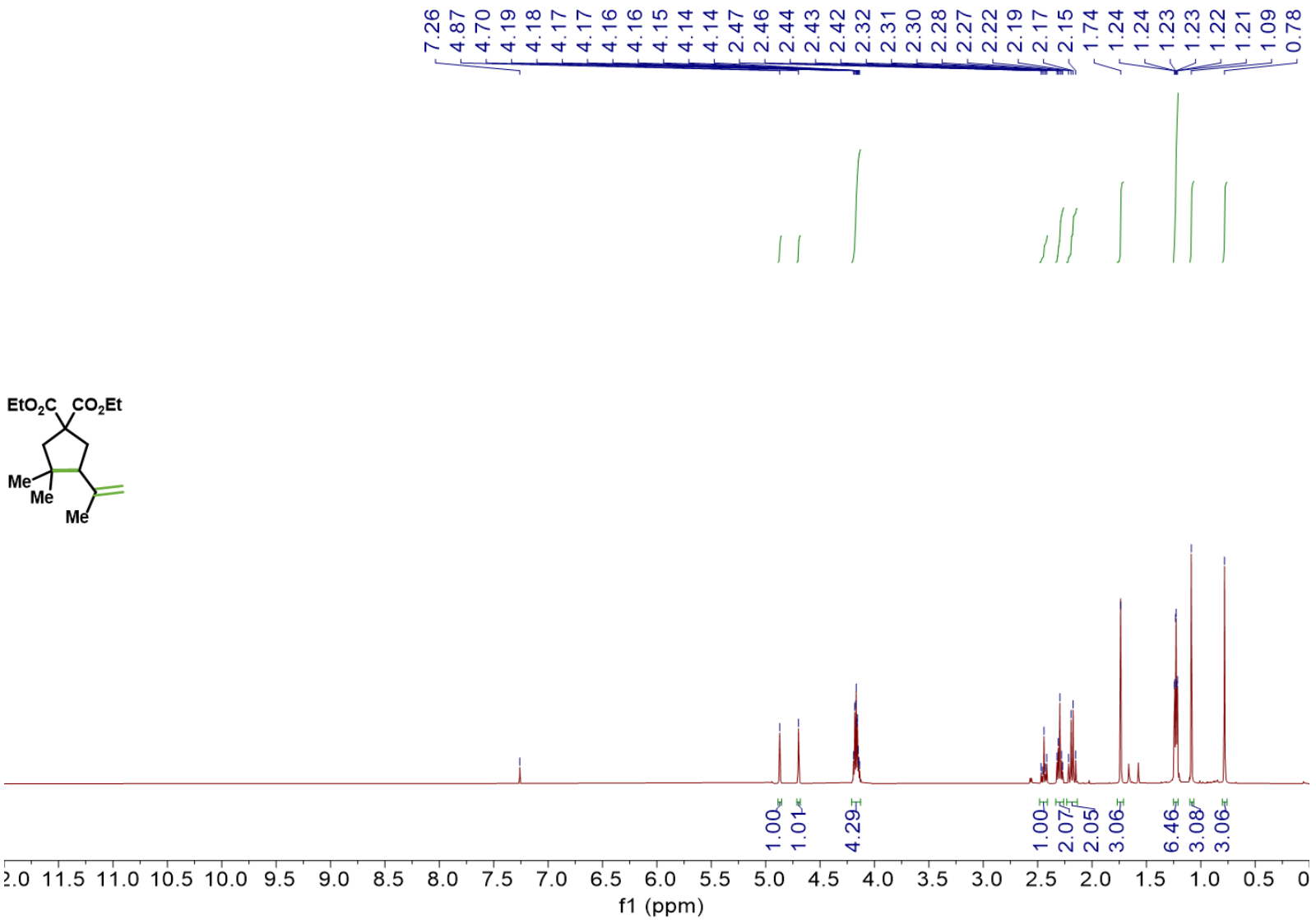
^{1}H NMR (600 MHz, $CDCl_3$) of compound **25**



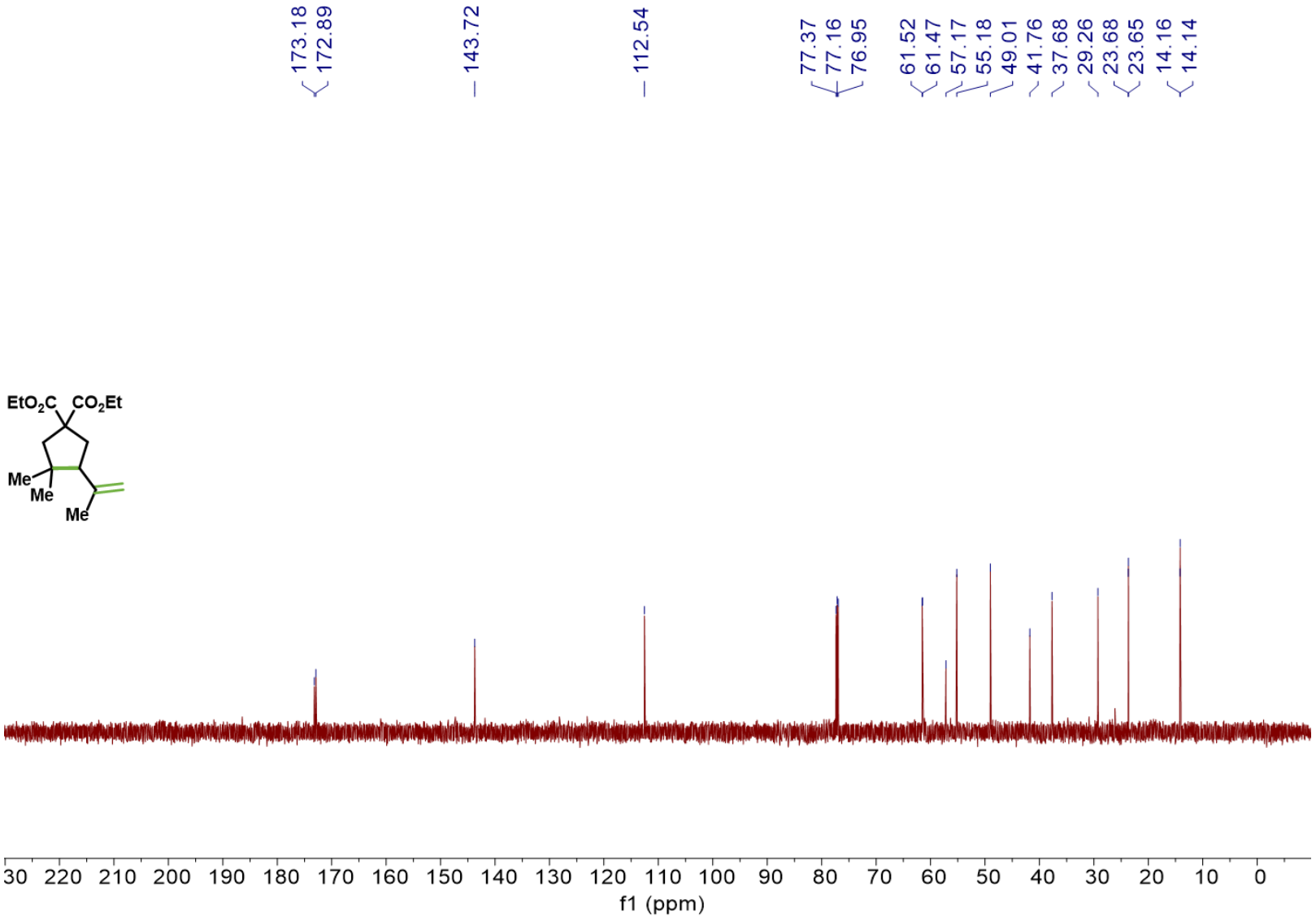
^{13}C NMR (151 MHz, $CDCl_3$) of compound **25**



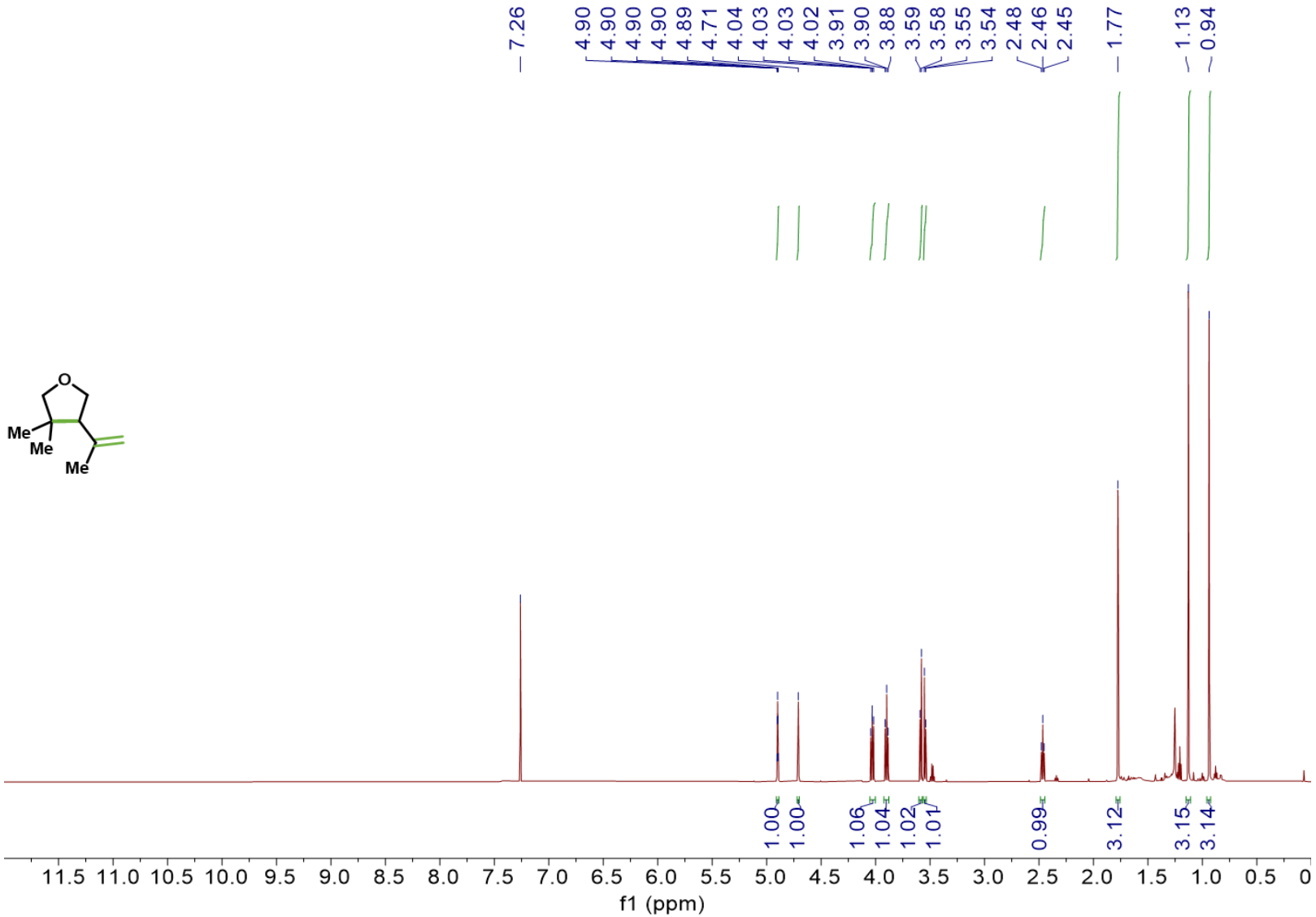
^{1}H NMR (600 MHz, $CDCl_3$) of compound **26**



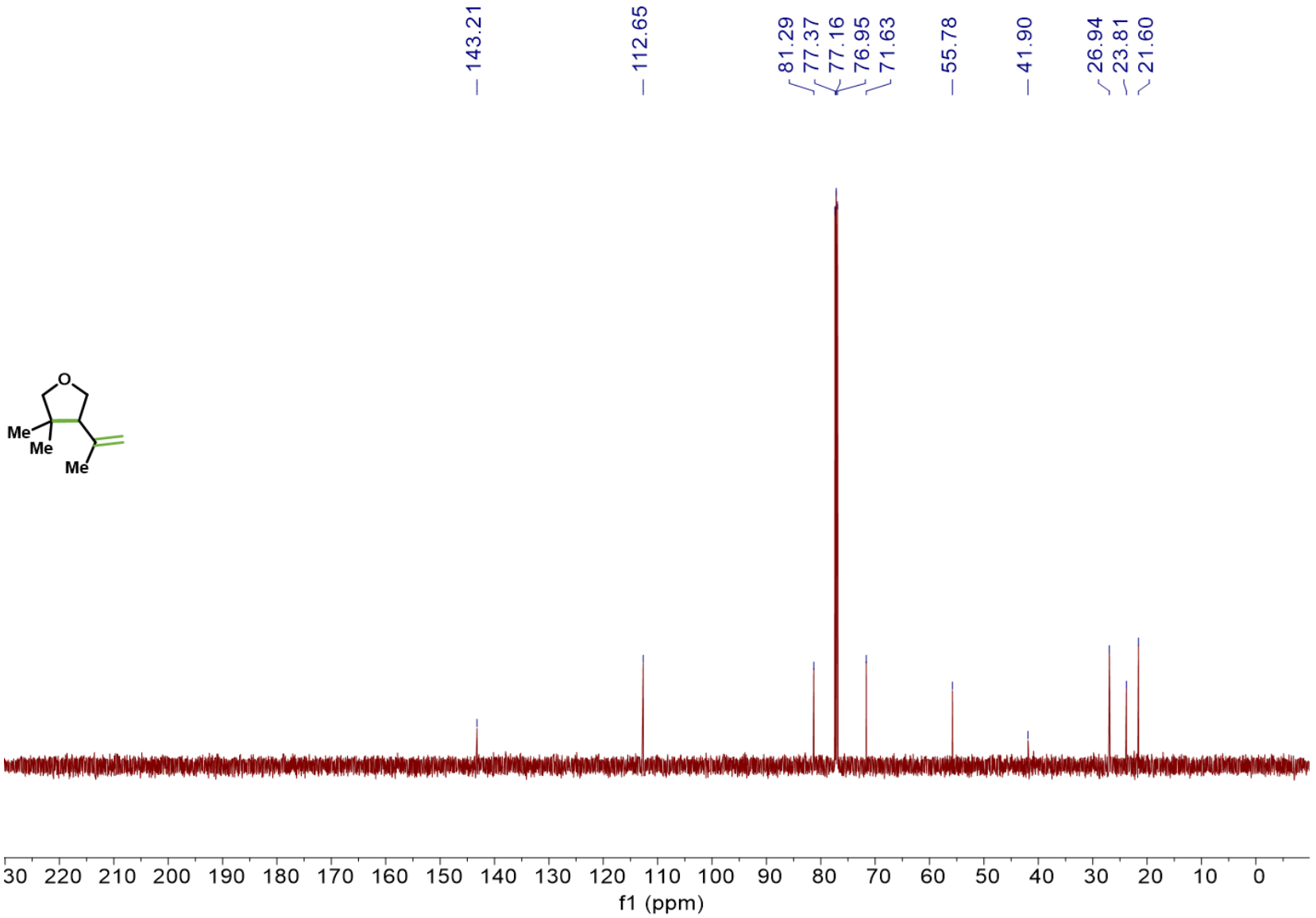
^{13}C NMR (151 MHz, $CDCl_3$) of compound **26**



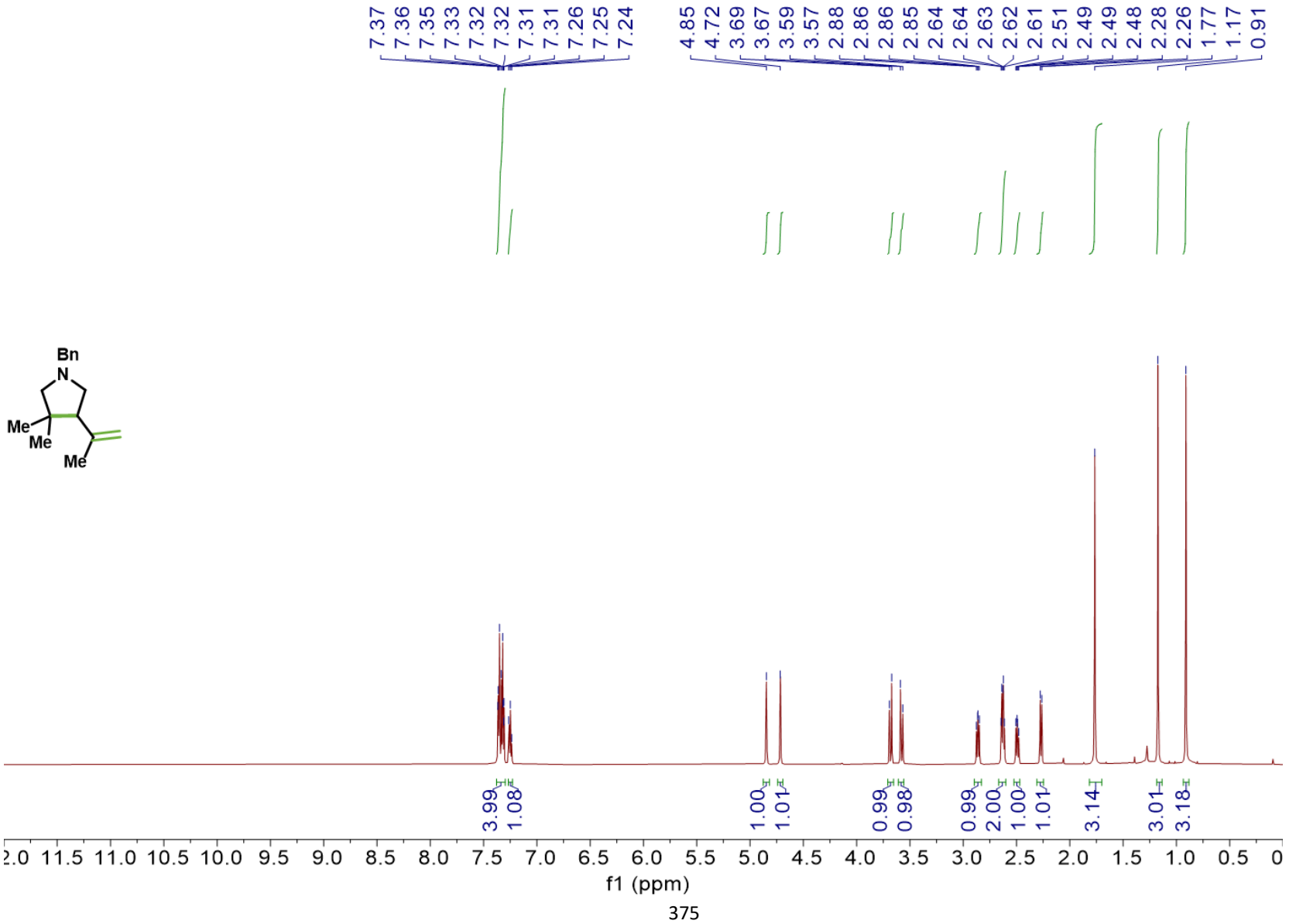
^{1}H NMR (600 MHz, $CDCl_3$) of compound **27**



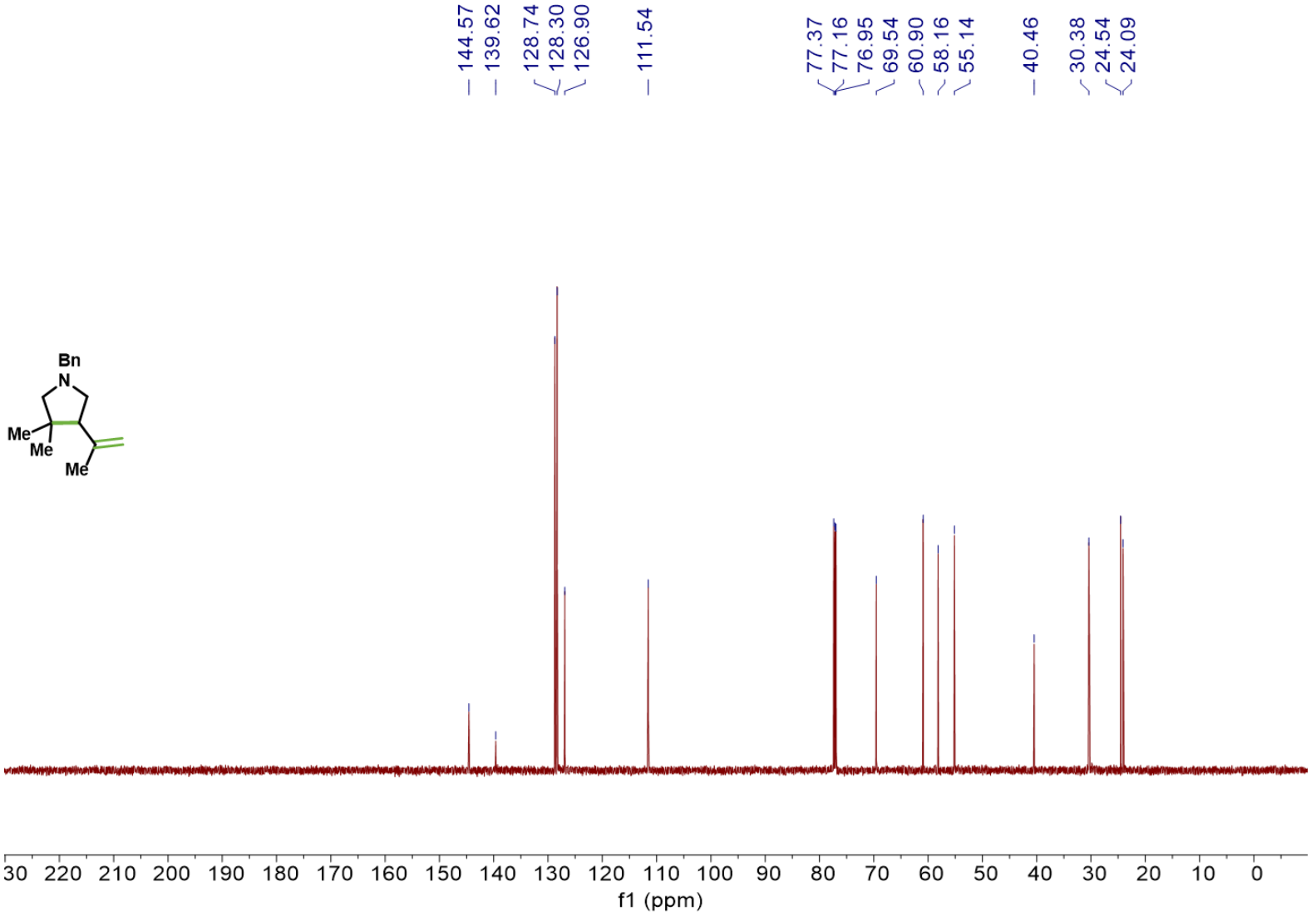
^{13}C NMR (151 MHz, $CDCl_3$) of compound **27**



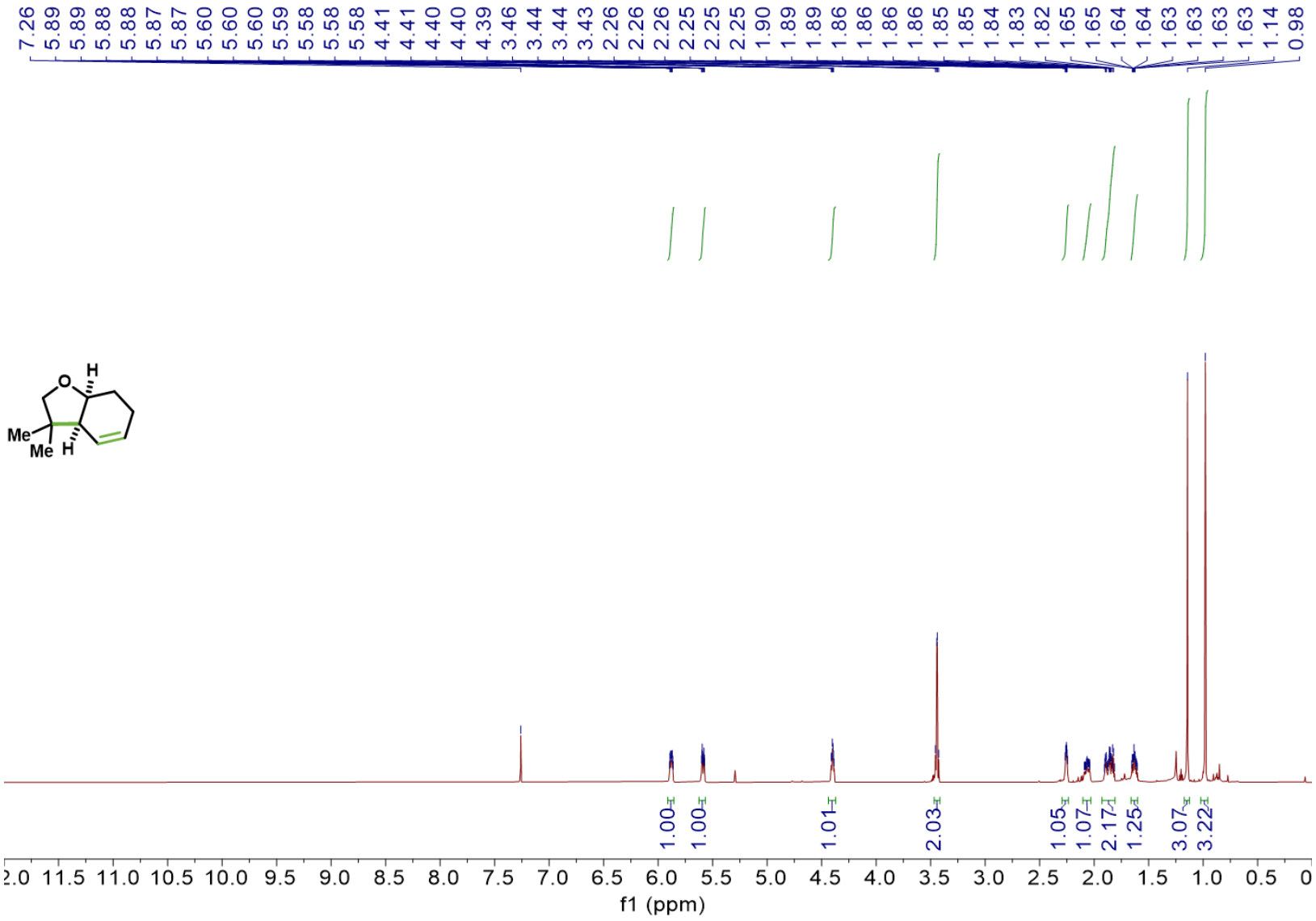
^{1}H NMR (600 MHz, $CDCl_3$) of compound **28**



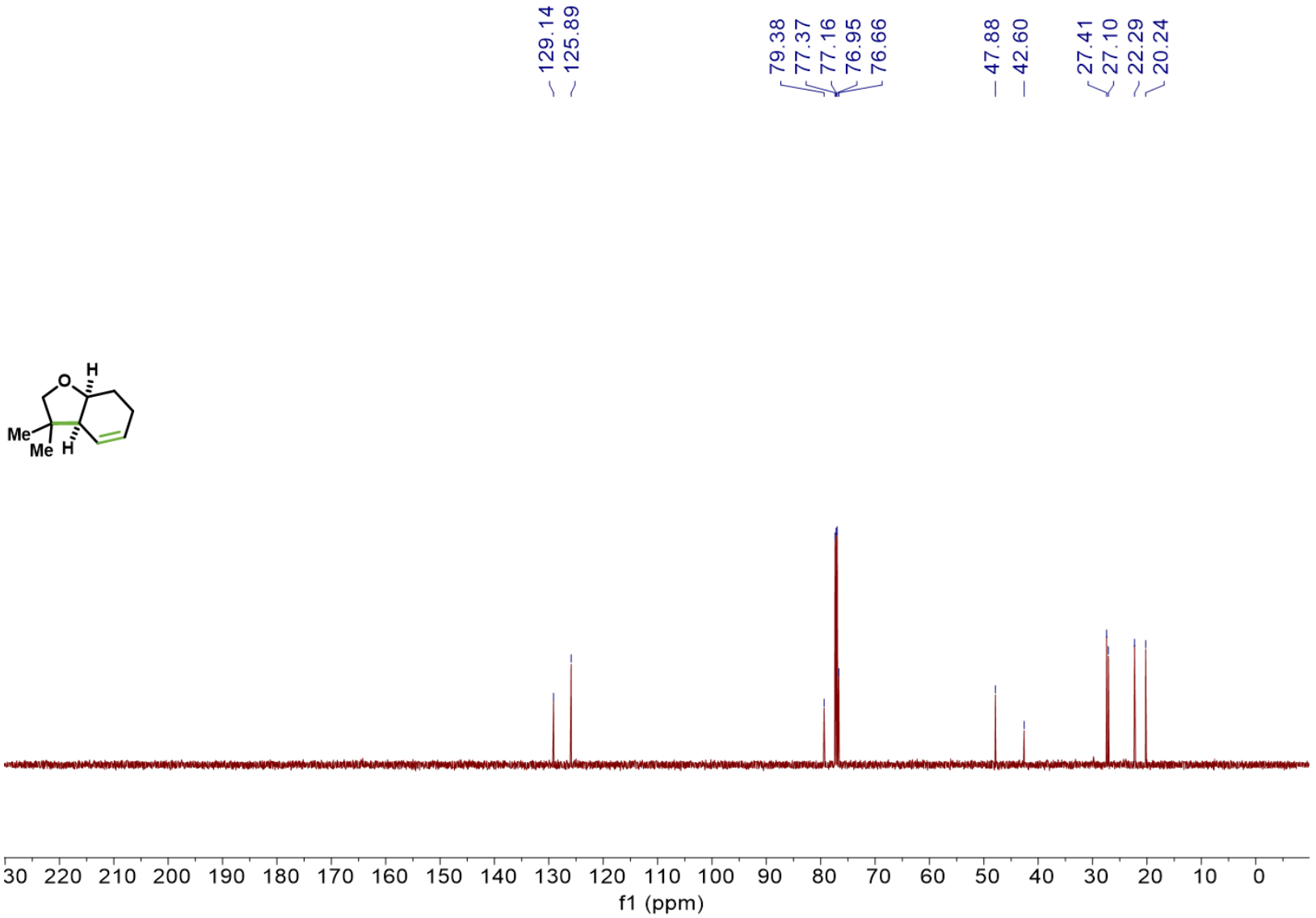
^{13}C NMR (151 MHz, $CDCl_3$) of compound **28**



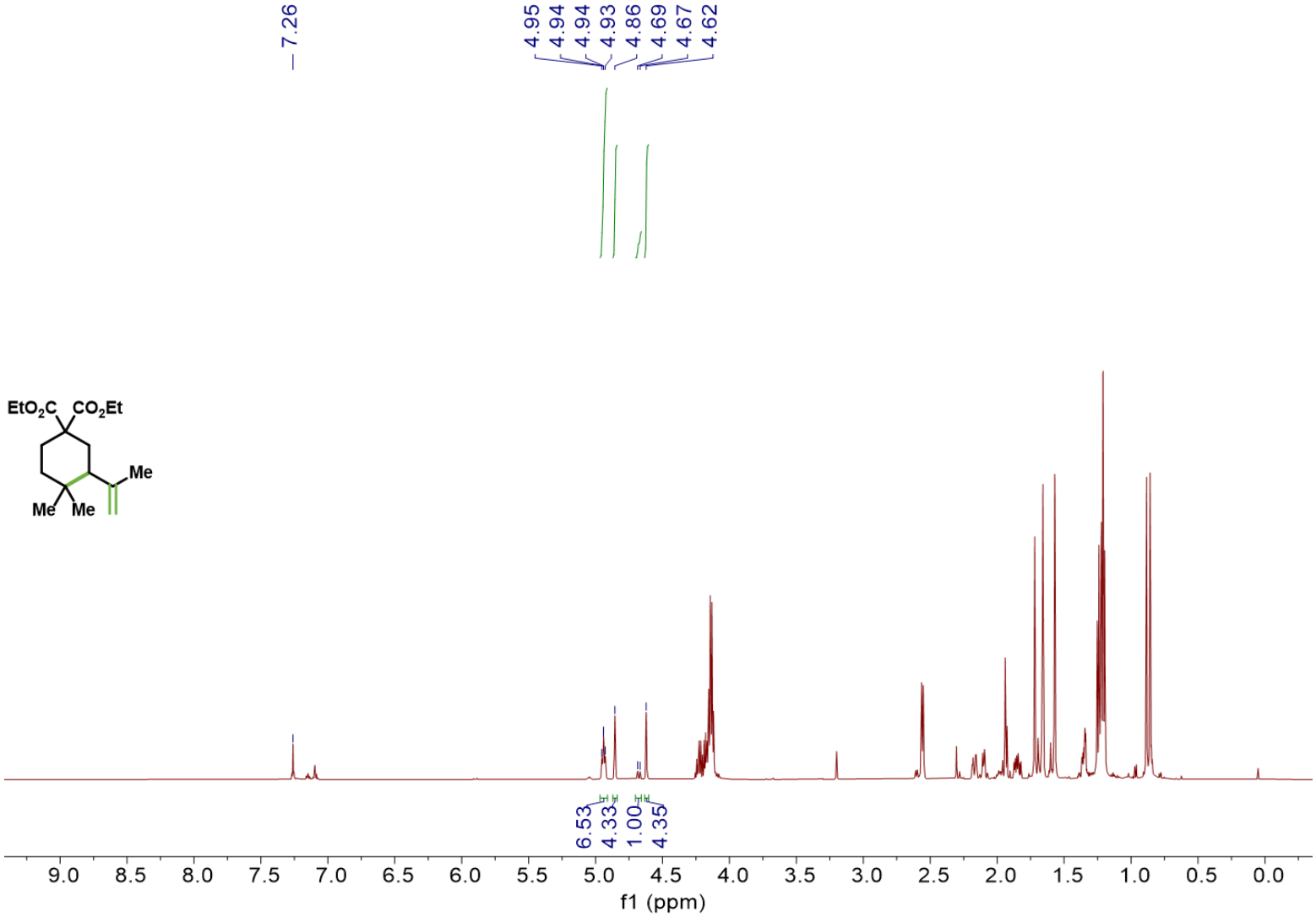
^{1}H NMR (600 MHz, $CDCl_3$) of compound **29**



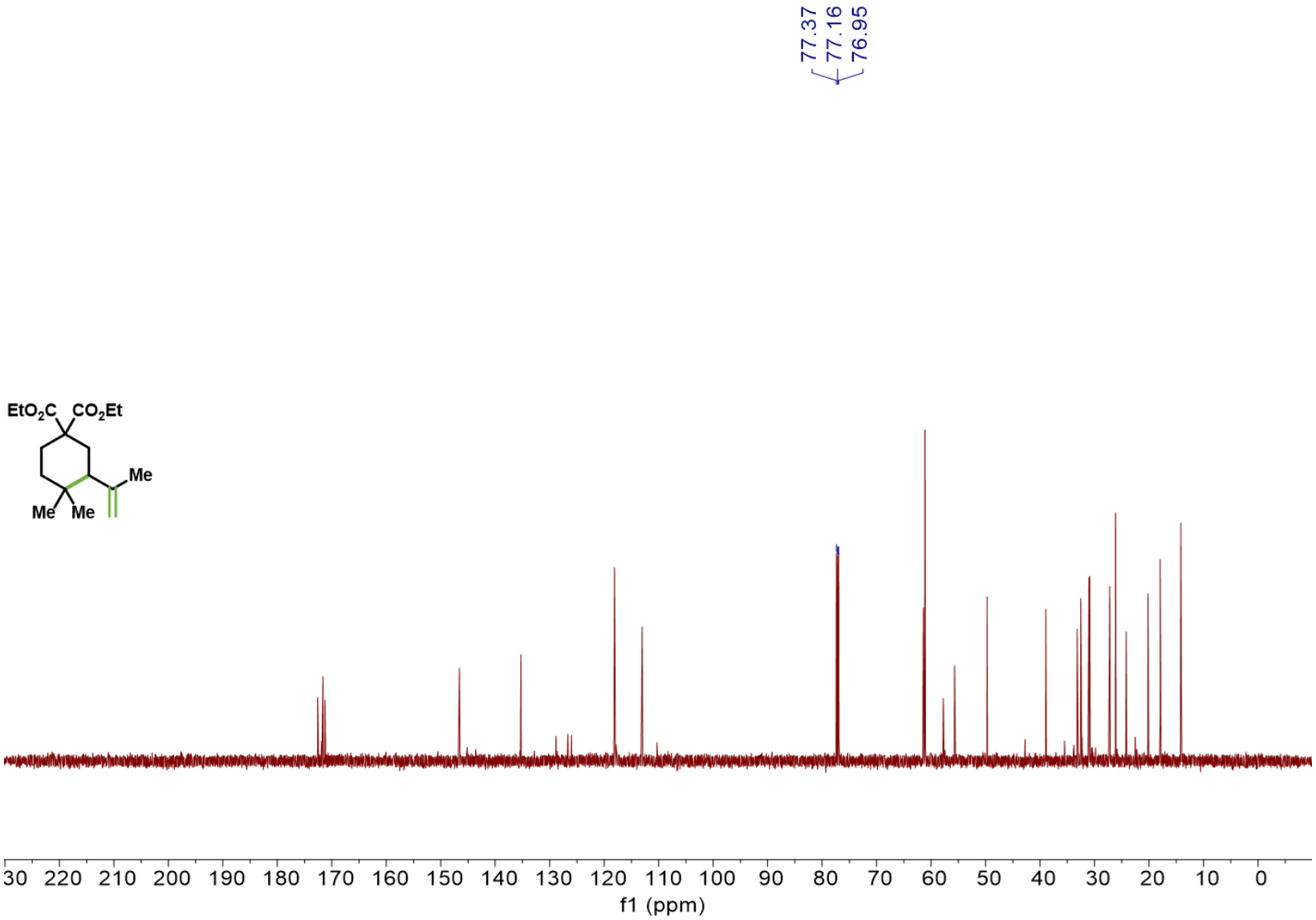
^{13}C NMR (151 MHz, $CDCl_3$) of compound **29**



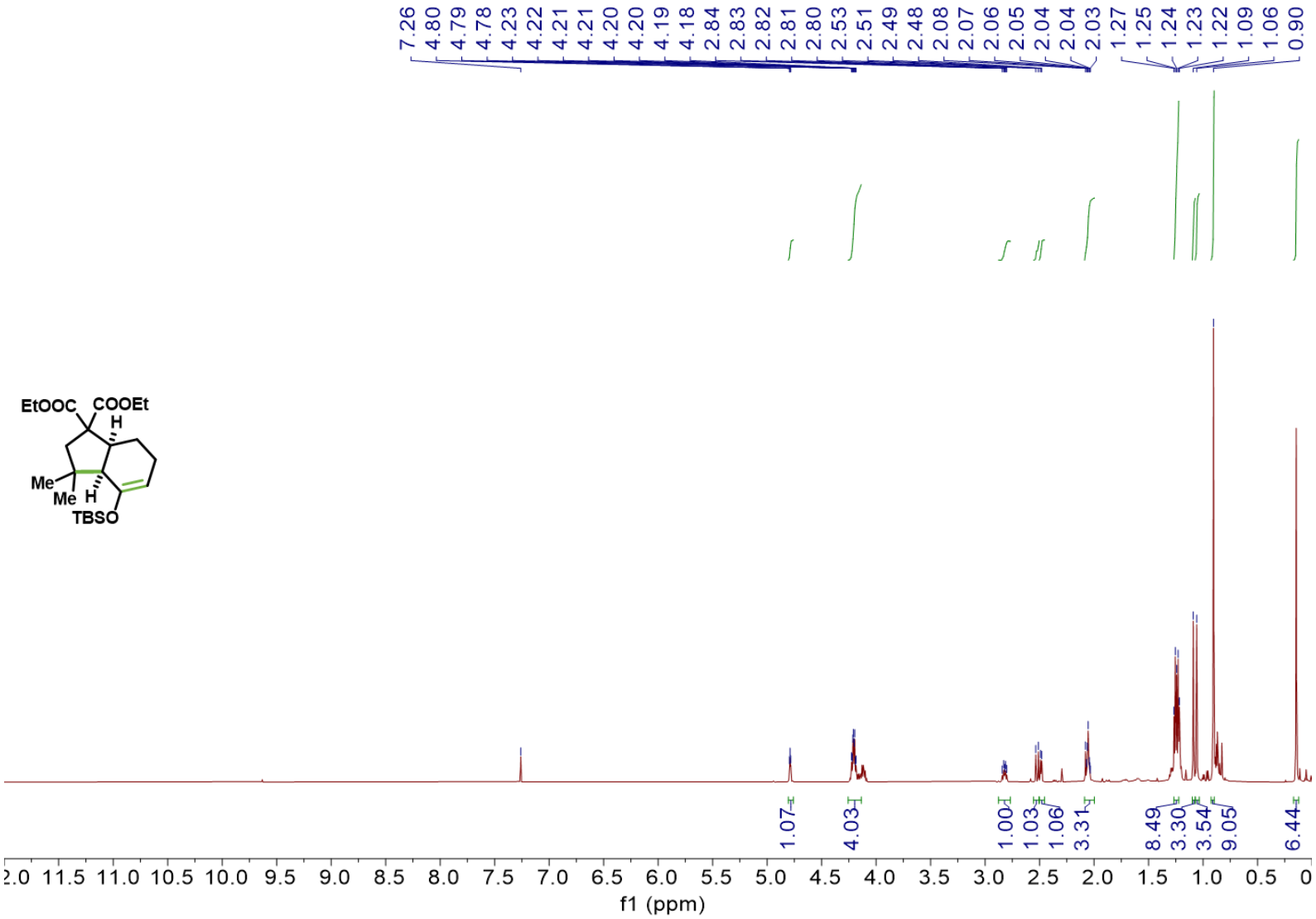
^{1}H NMR (600 MHz, $CDCl_3$) of compound **30**



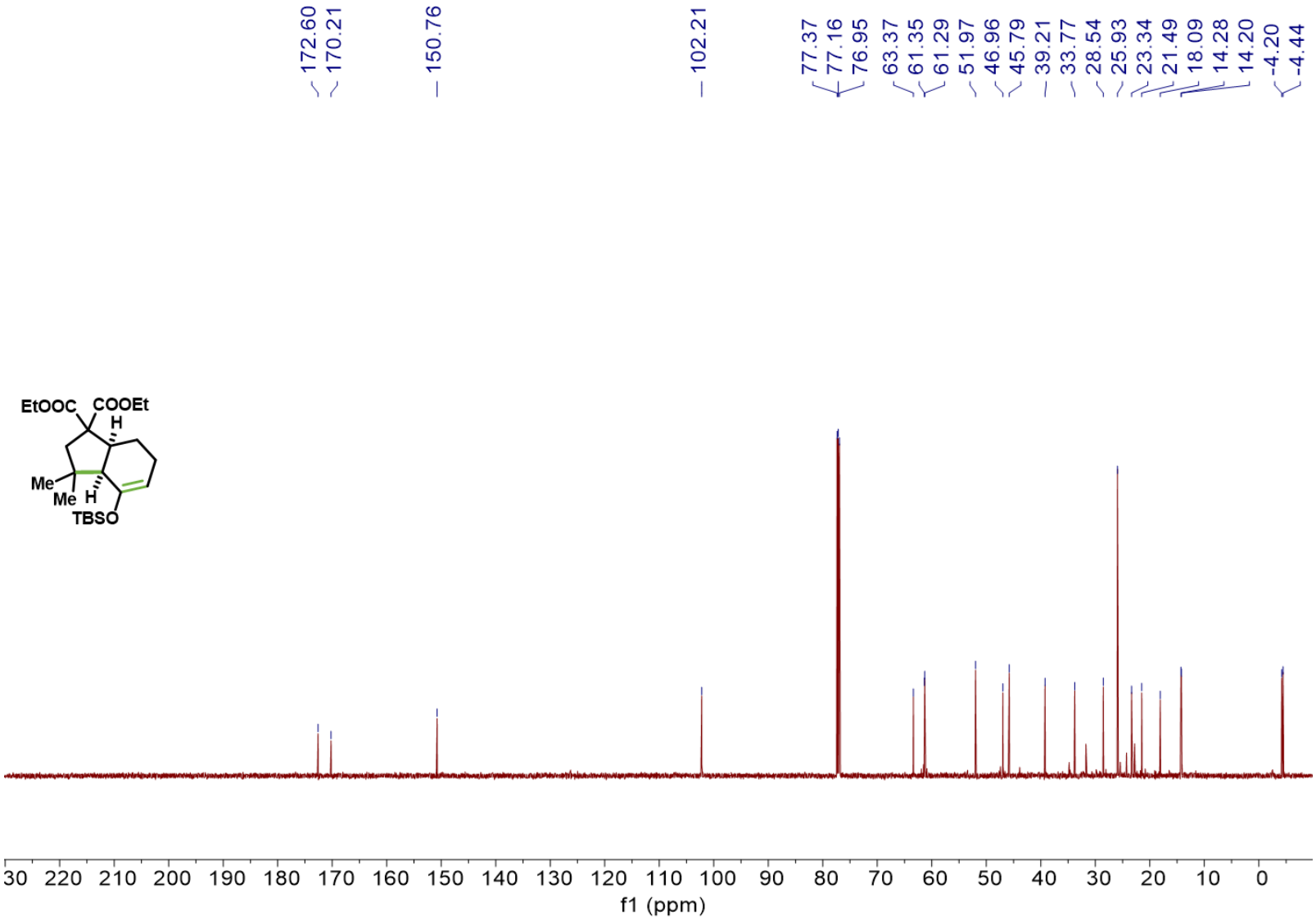
^{13}C NMR (151 MHz, $CDCl_3$) of compound **30**



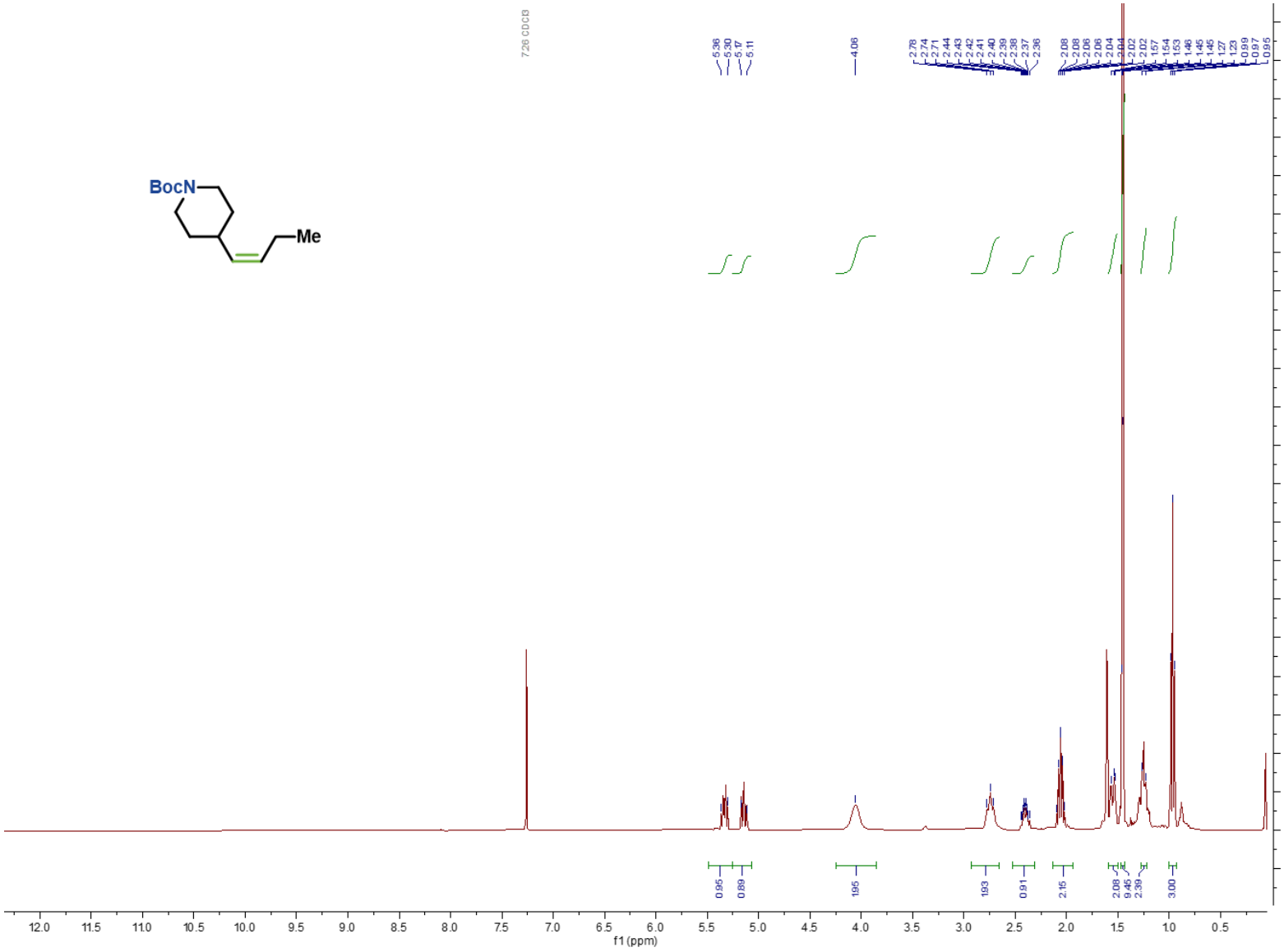
^{1}H NMR (600 MHz, $CDCl_3$) of compound **31**



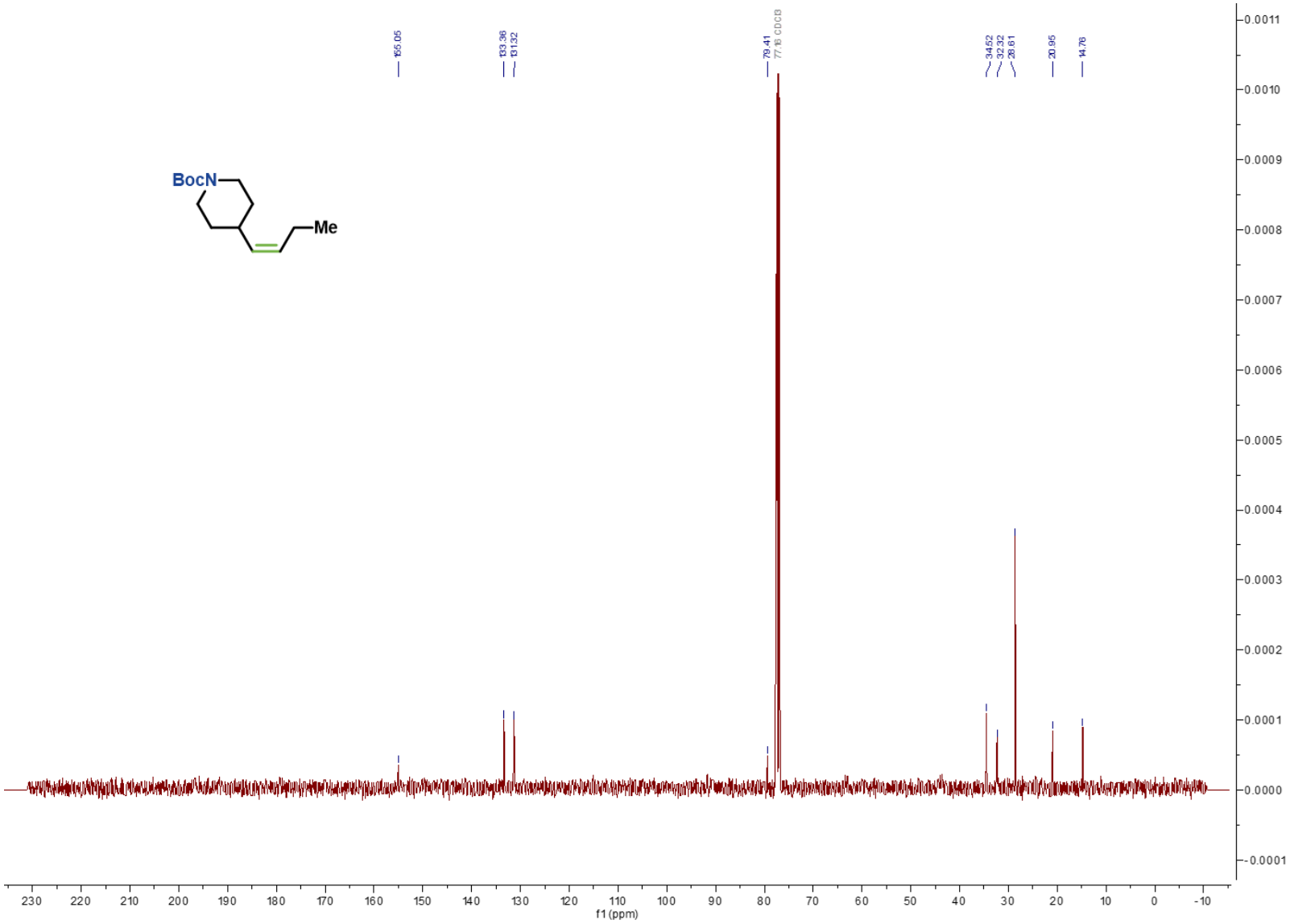
^{13}C NMR (151 MHz, $CDCl_3$) of compound **31**



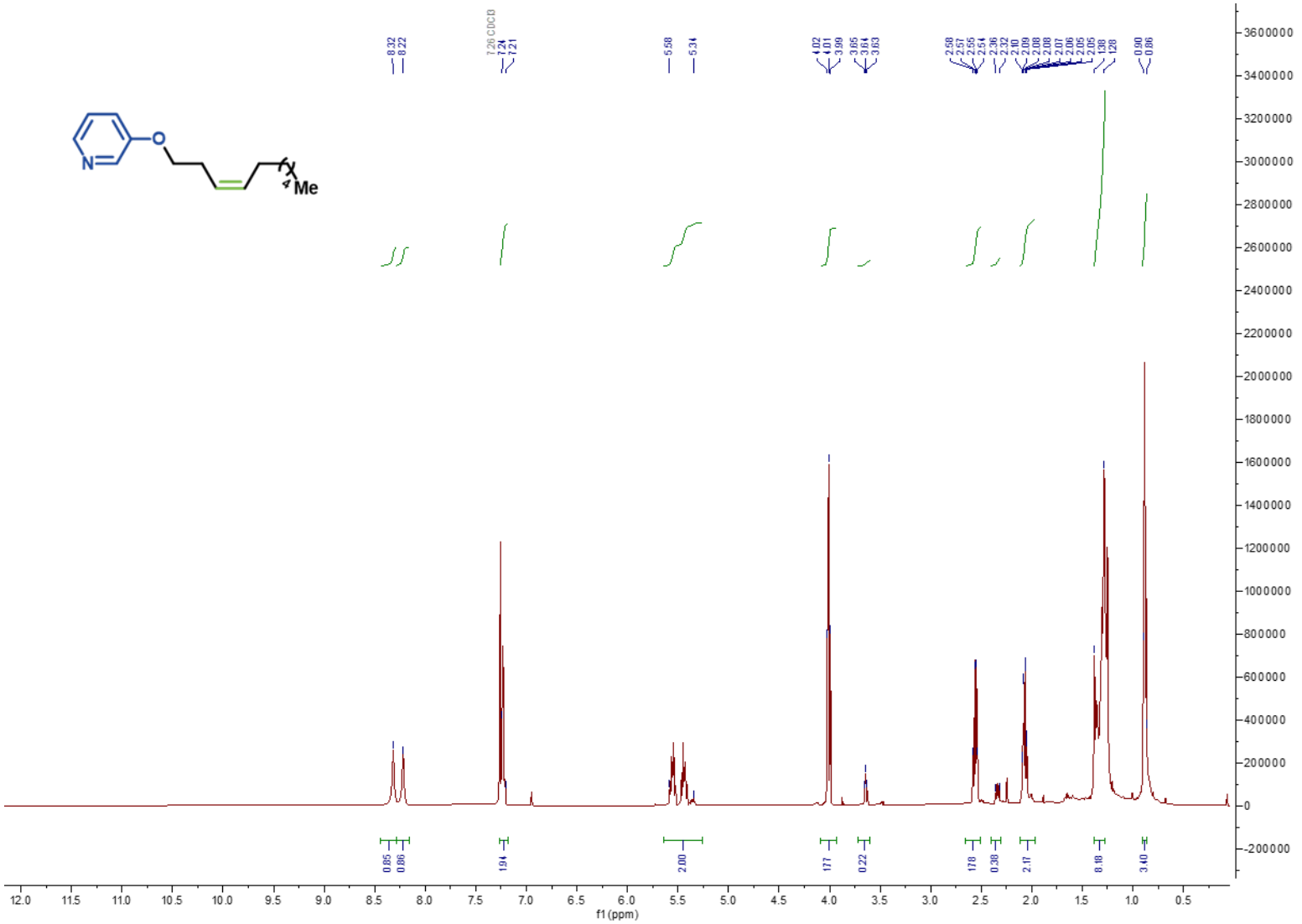
^{1}H NMR (400 MHz, $CDCl_3$) of compound **32**



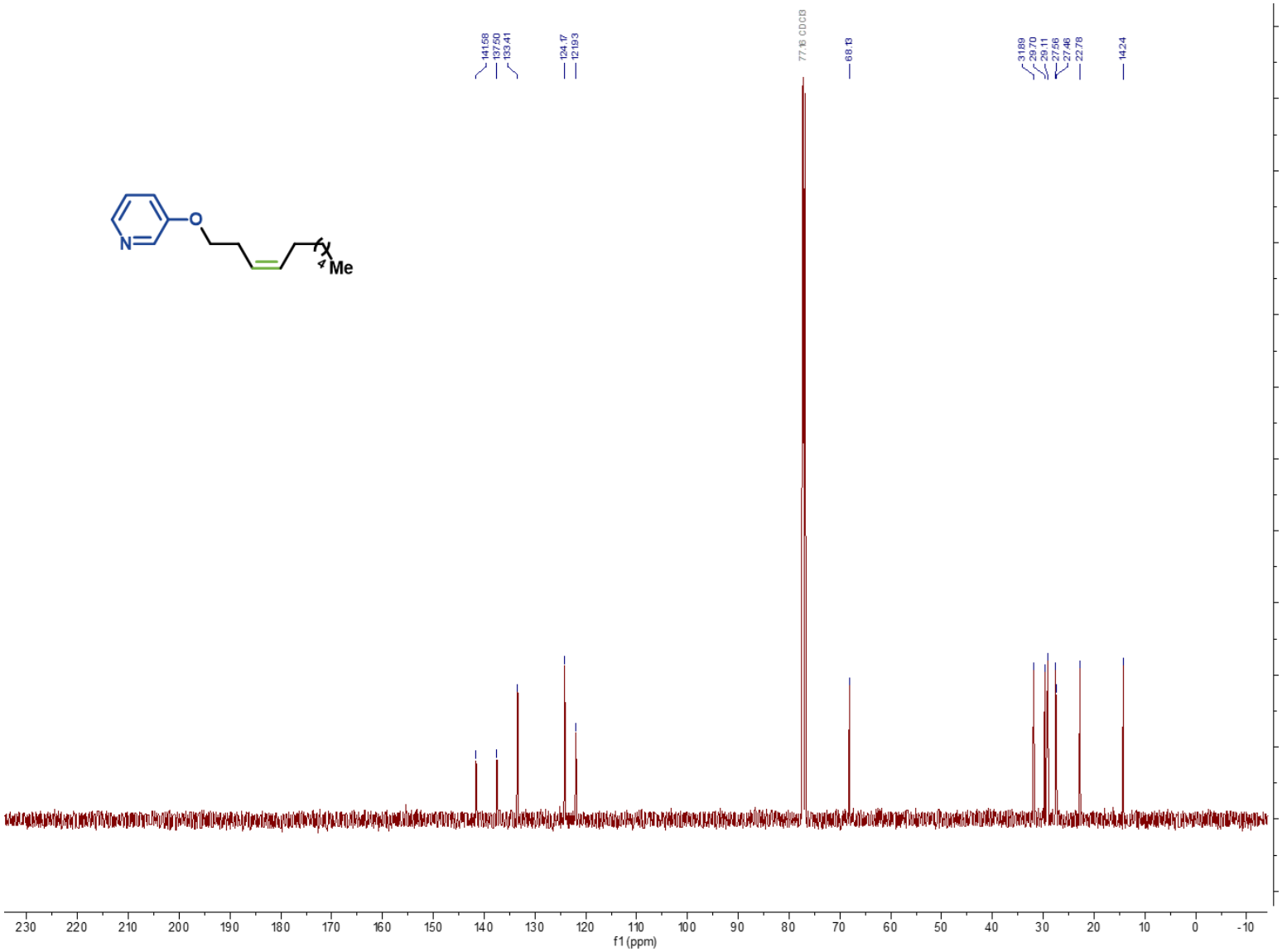
^{13}C NMR (100 MHz, $CDCl_3$) of compound **32**



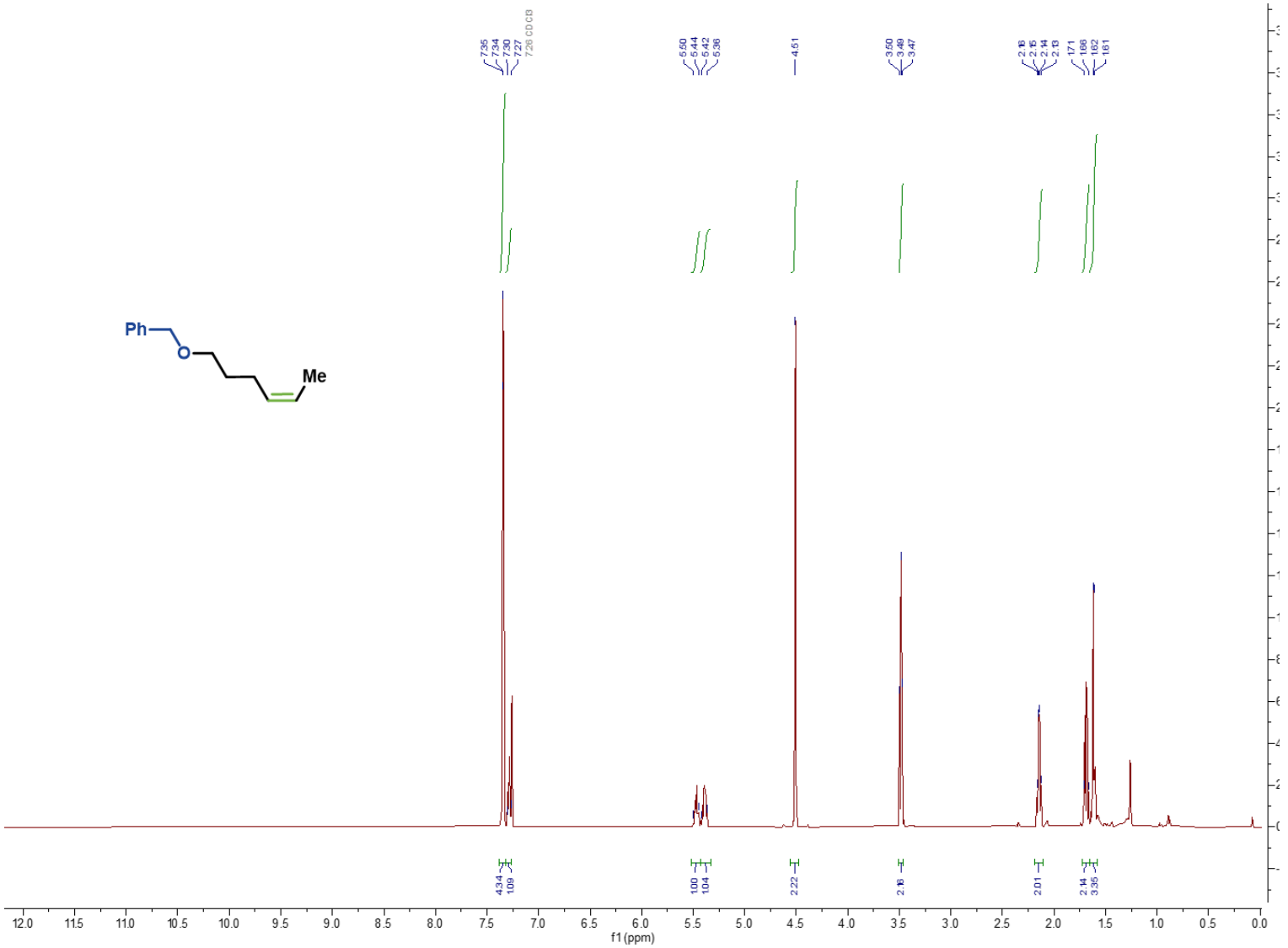
^{1}H NMR (500 MHz, $CDCl_3$) of compound **33**



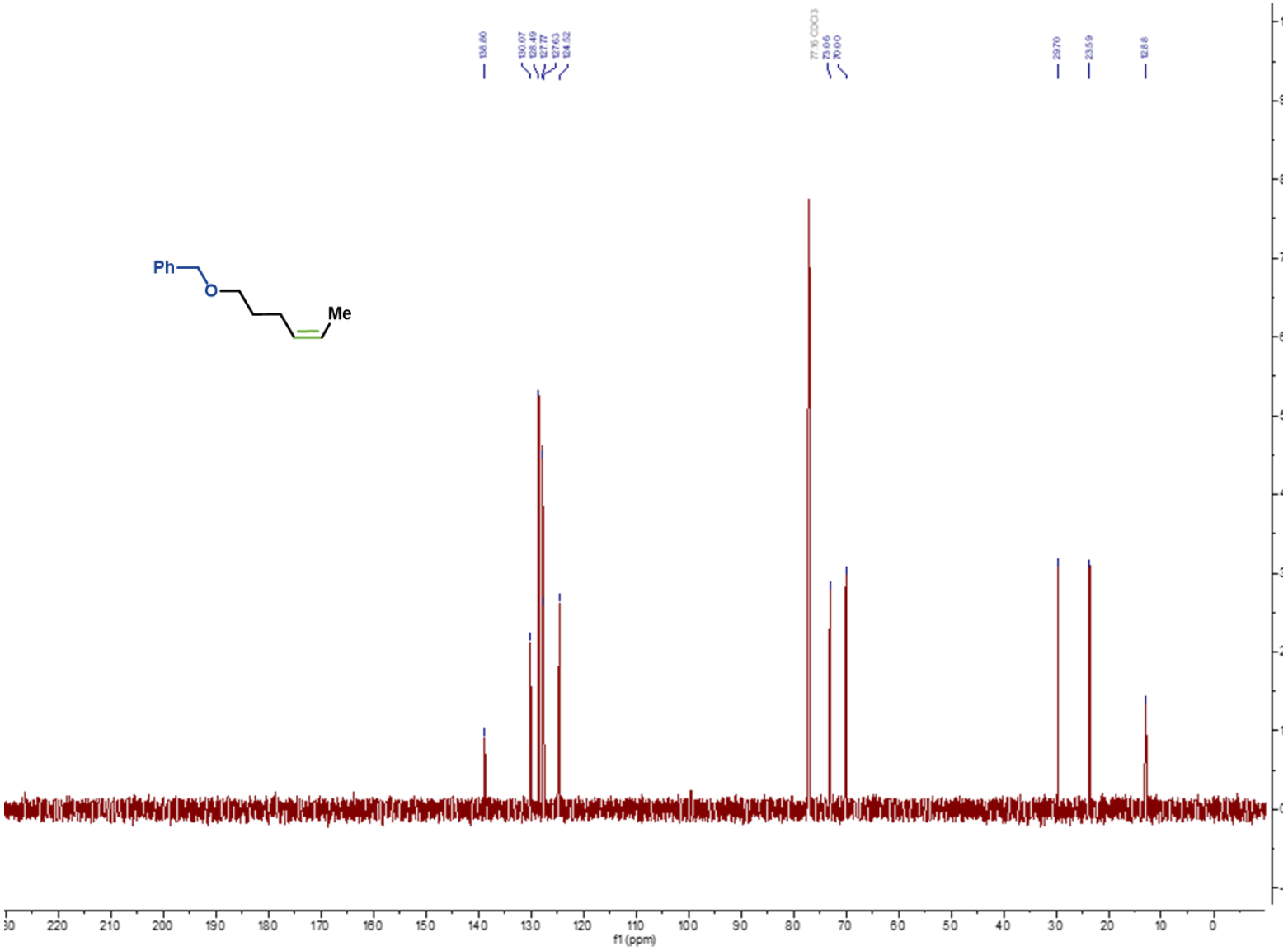
^{13}C NMR (126 MHz, $CDCl_3$) of compound **33**



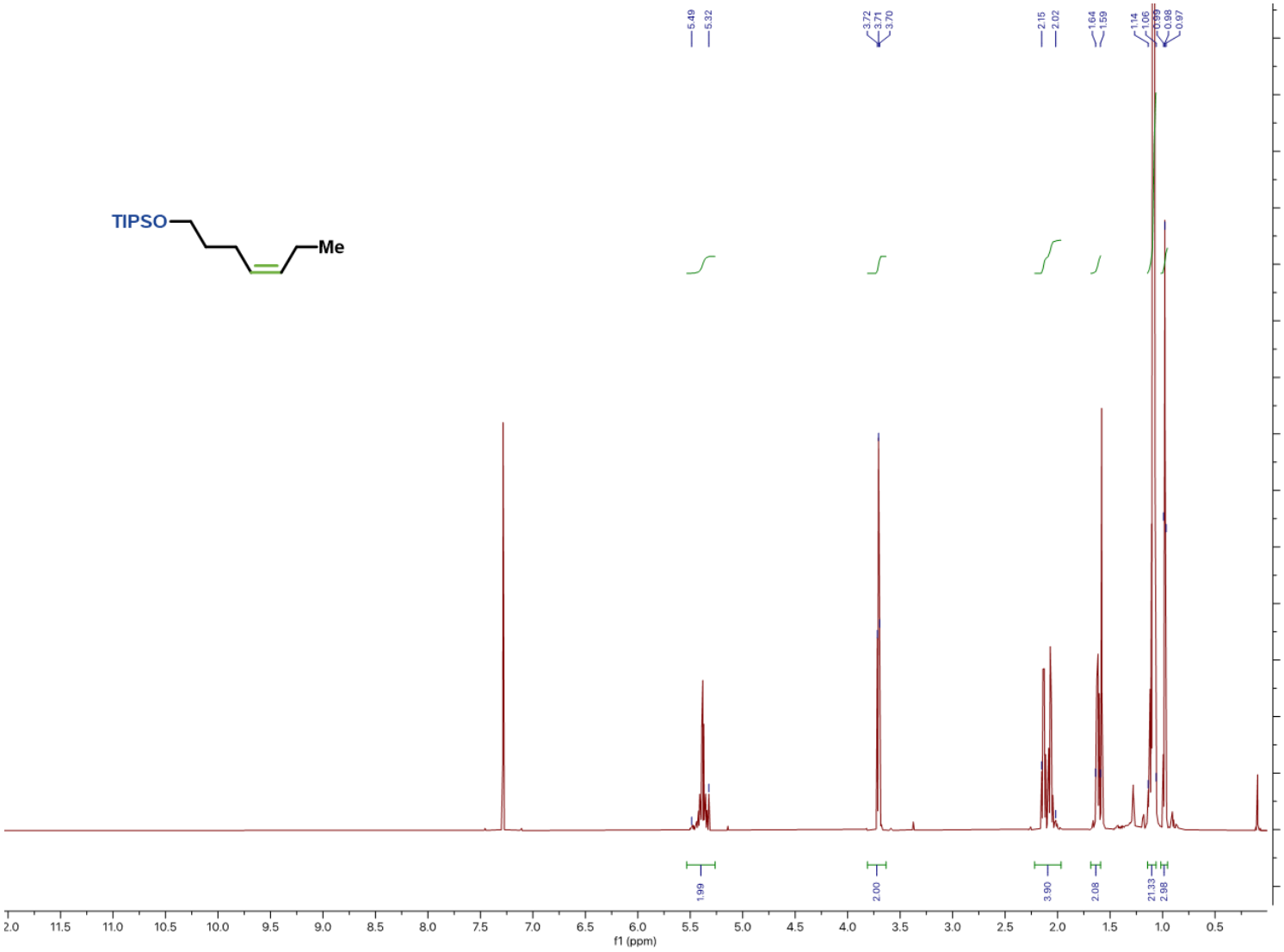
^{1}H NMR (600 MHz, $CDCl_3$) of compound **34**



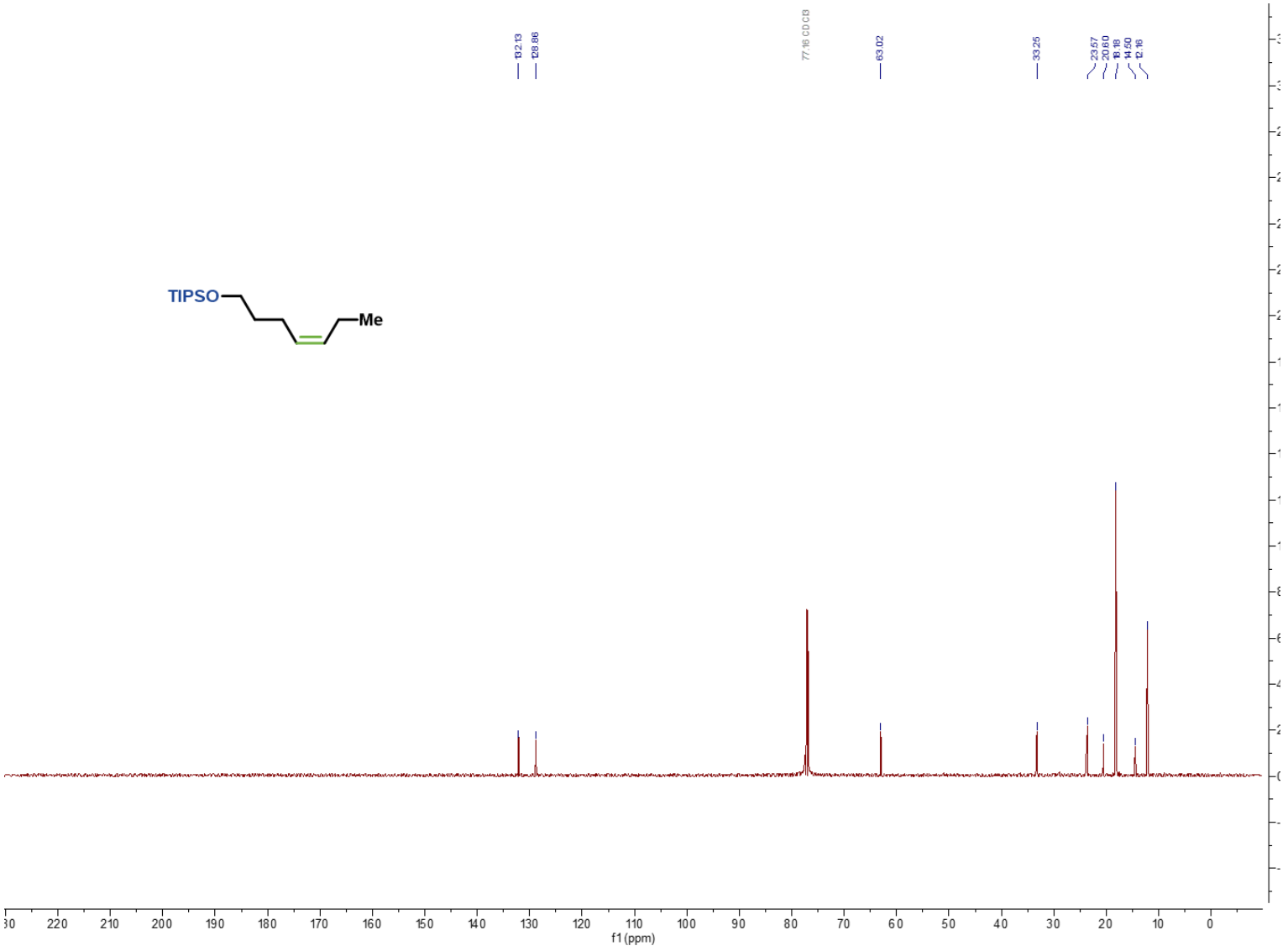
^{13}C NMR (151 MHz, $CDCl_3$) of compound **34**



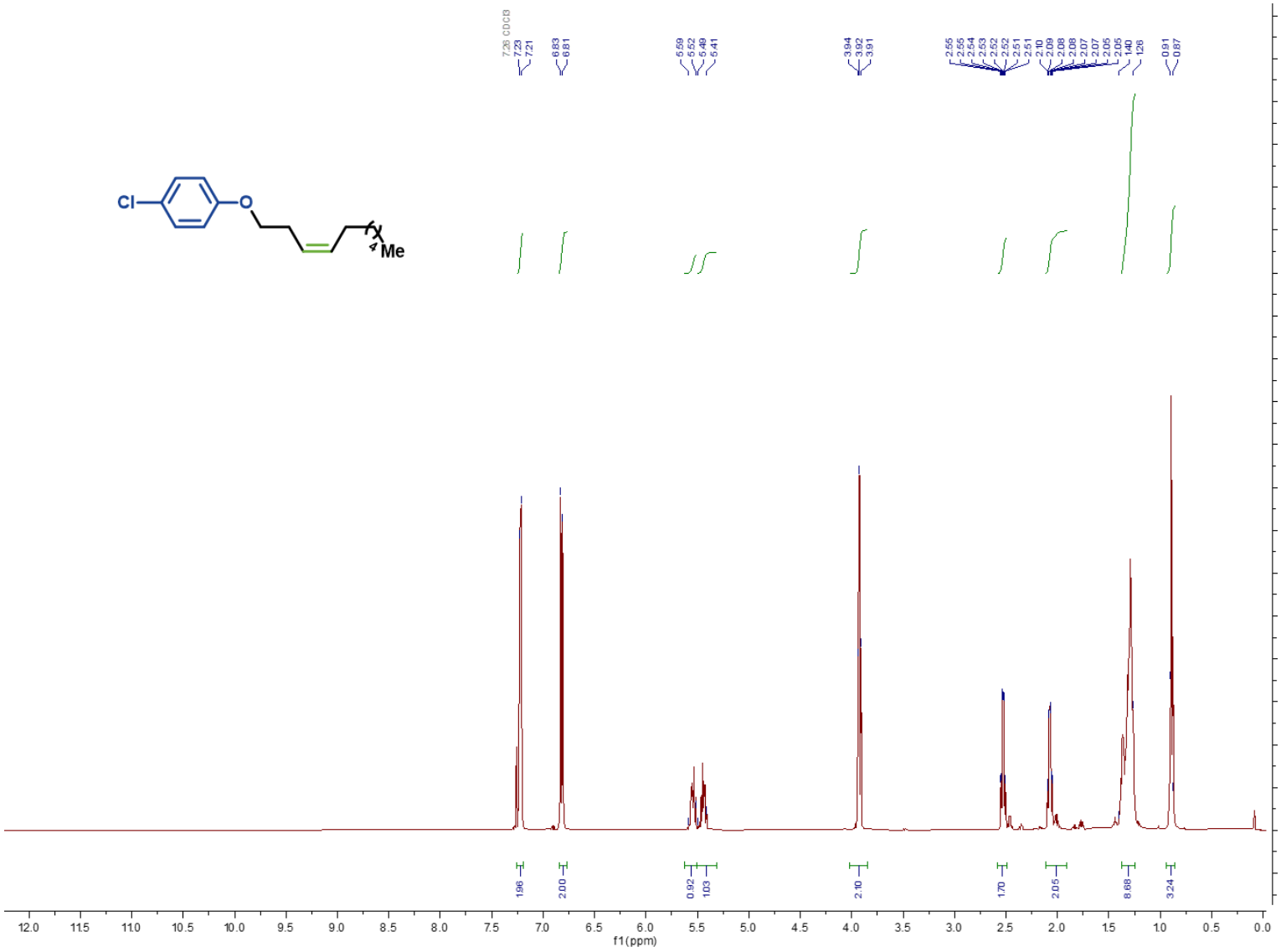
^{1}H NMR (600 MHz, $CDCl_3$) of compound **36**



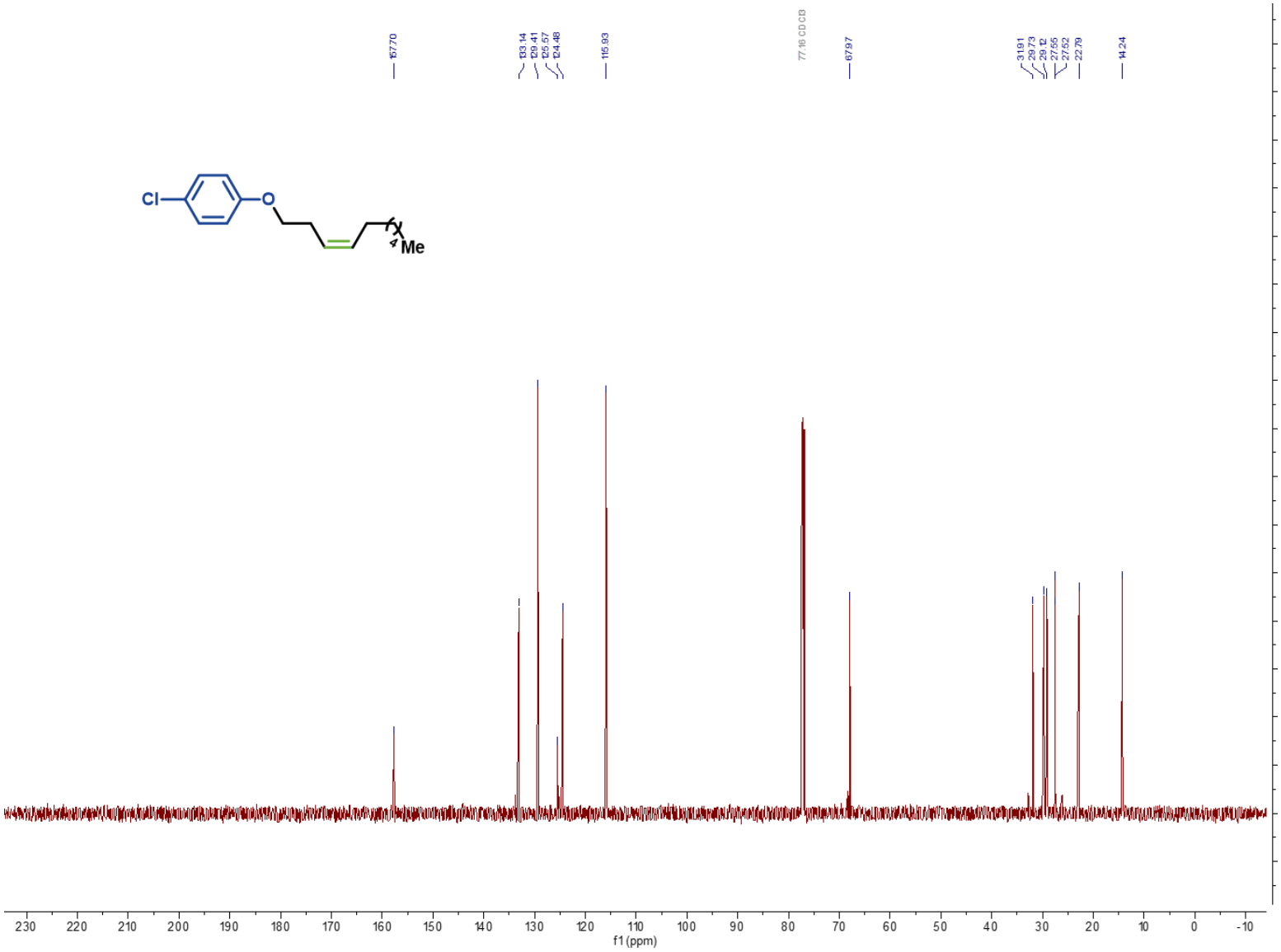
^{13}C NMR (151 MHz, $CDCl_3$) of compound **36**



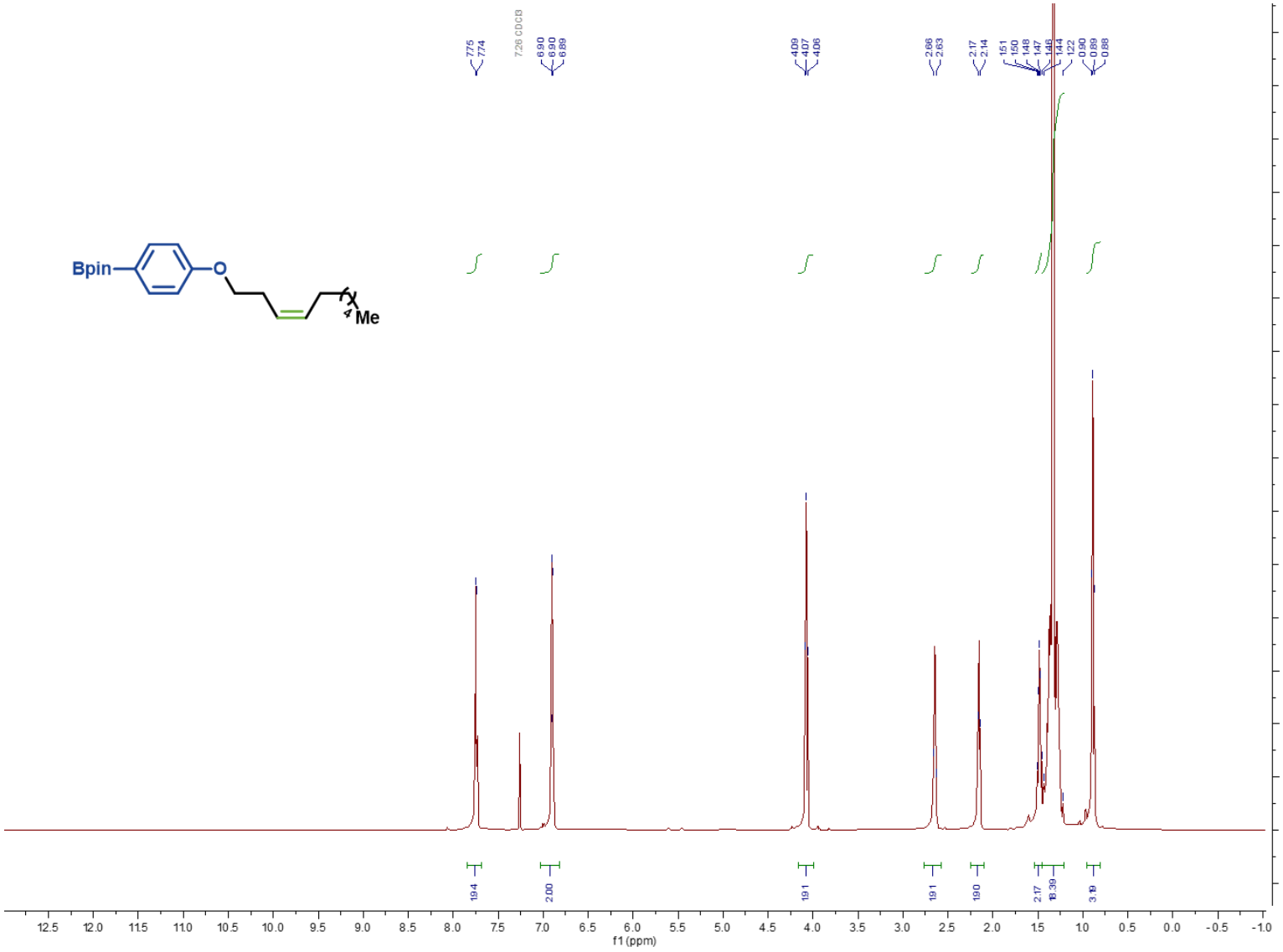
^{1}H NMR (500 MHz, $CDCl_3$) of compound **37**



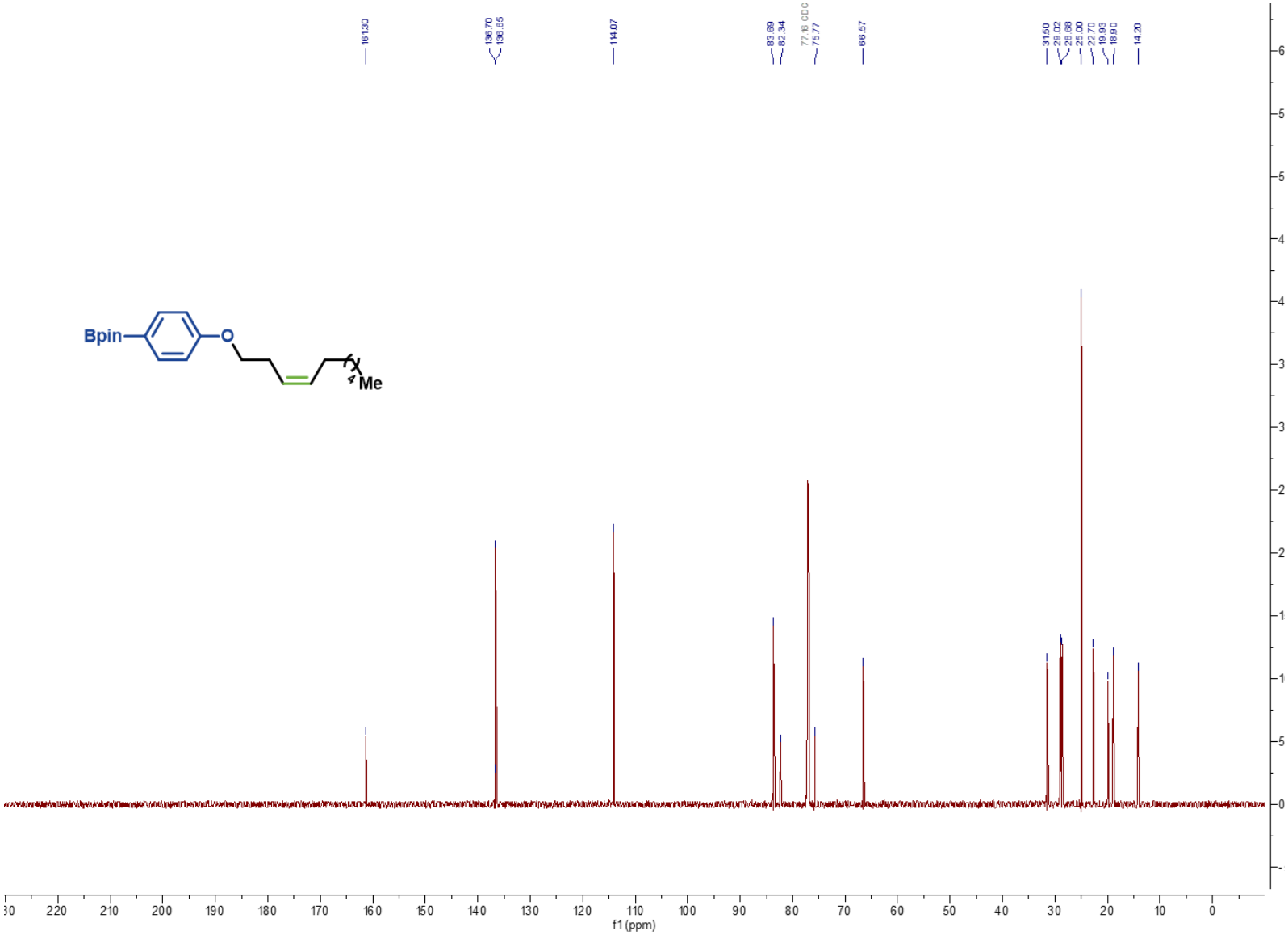
^{13}C NMR (126 MHz, $CDCl_3$) of compound **37**



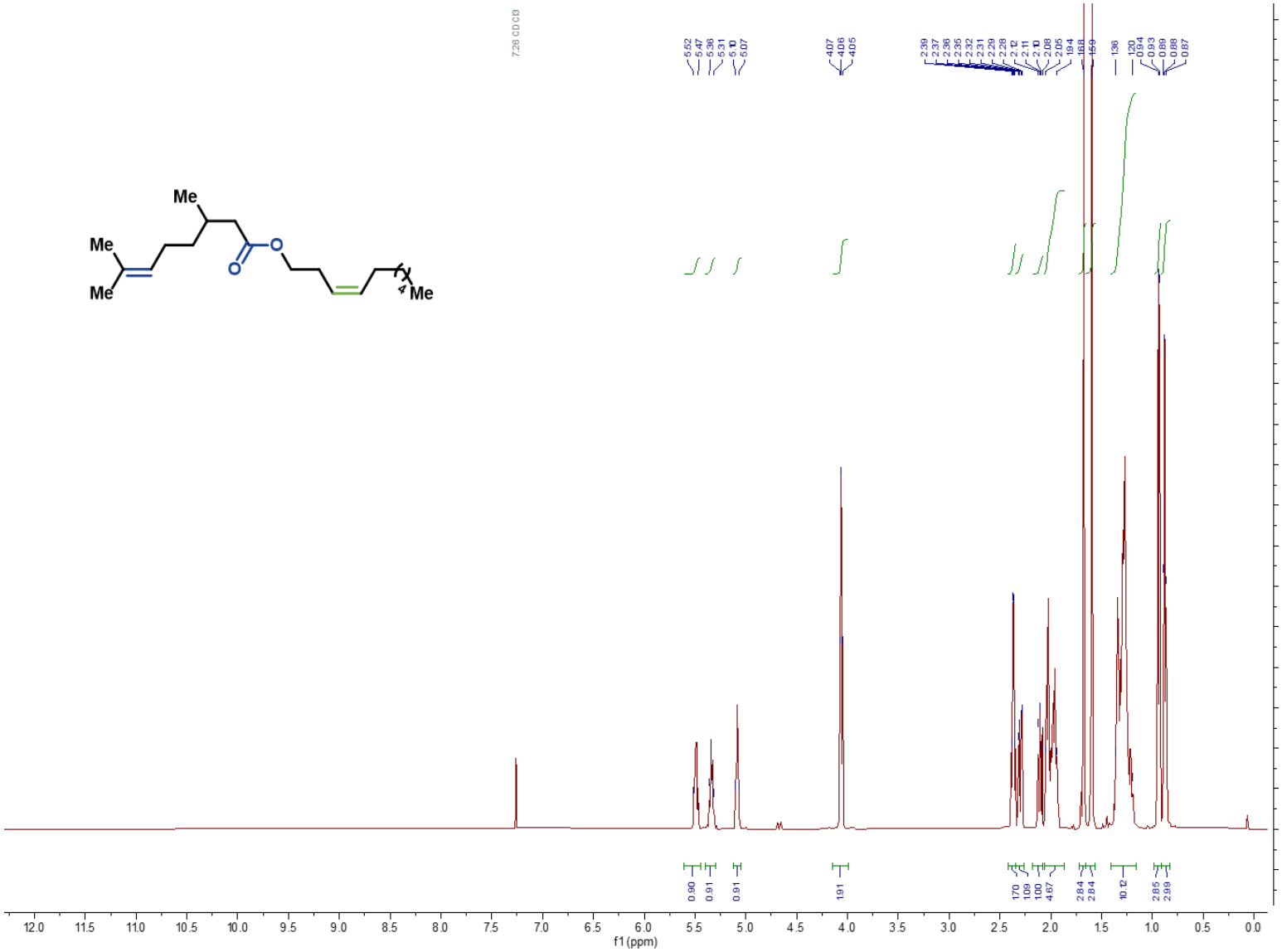
^{1}H NMR (600 MHz, $CDCl_3$) of compound **38**



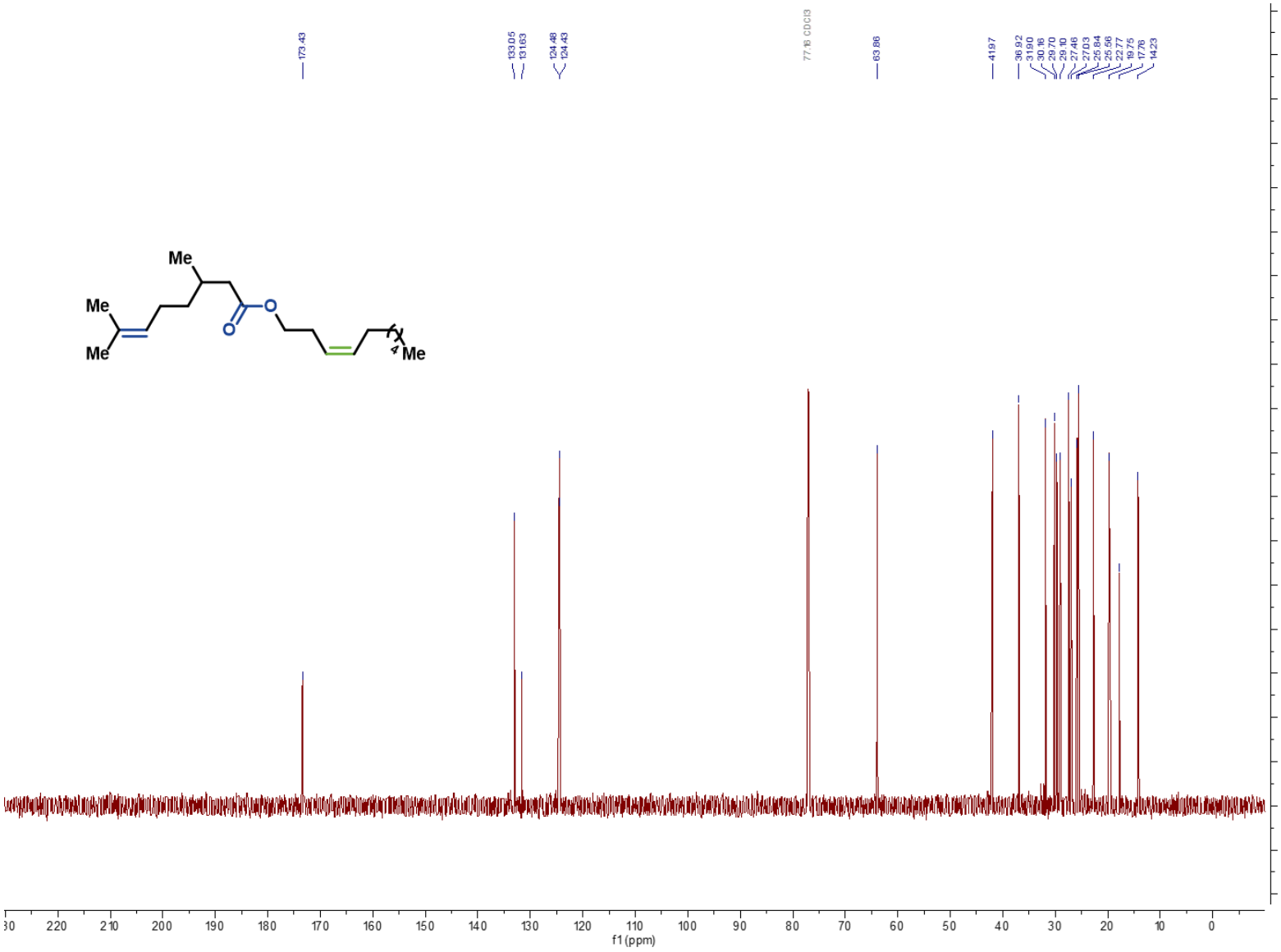
^{13}C NMR (151 MHz, $CDCl_3$) of compound **38**



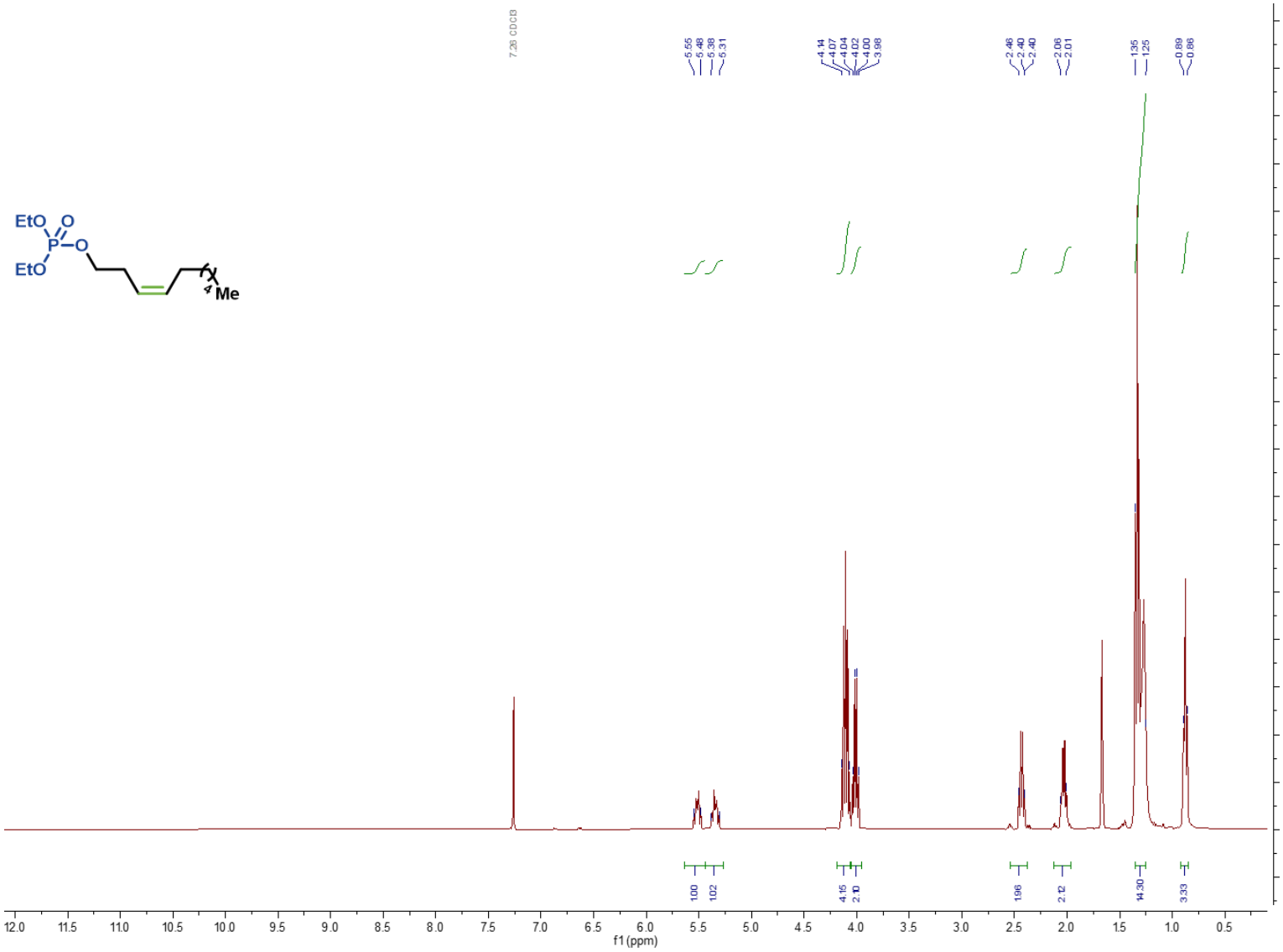
^{1}H NMR (600 MHz, $CDCl_3$) of compound **39**



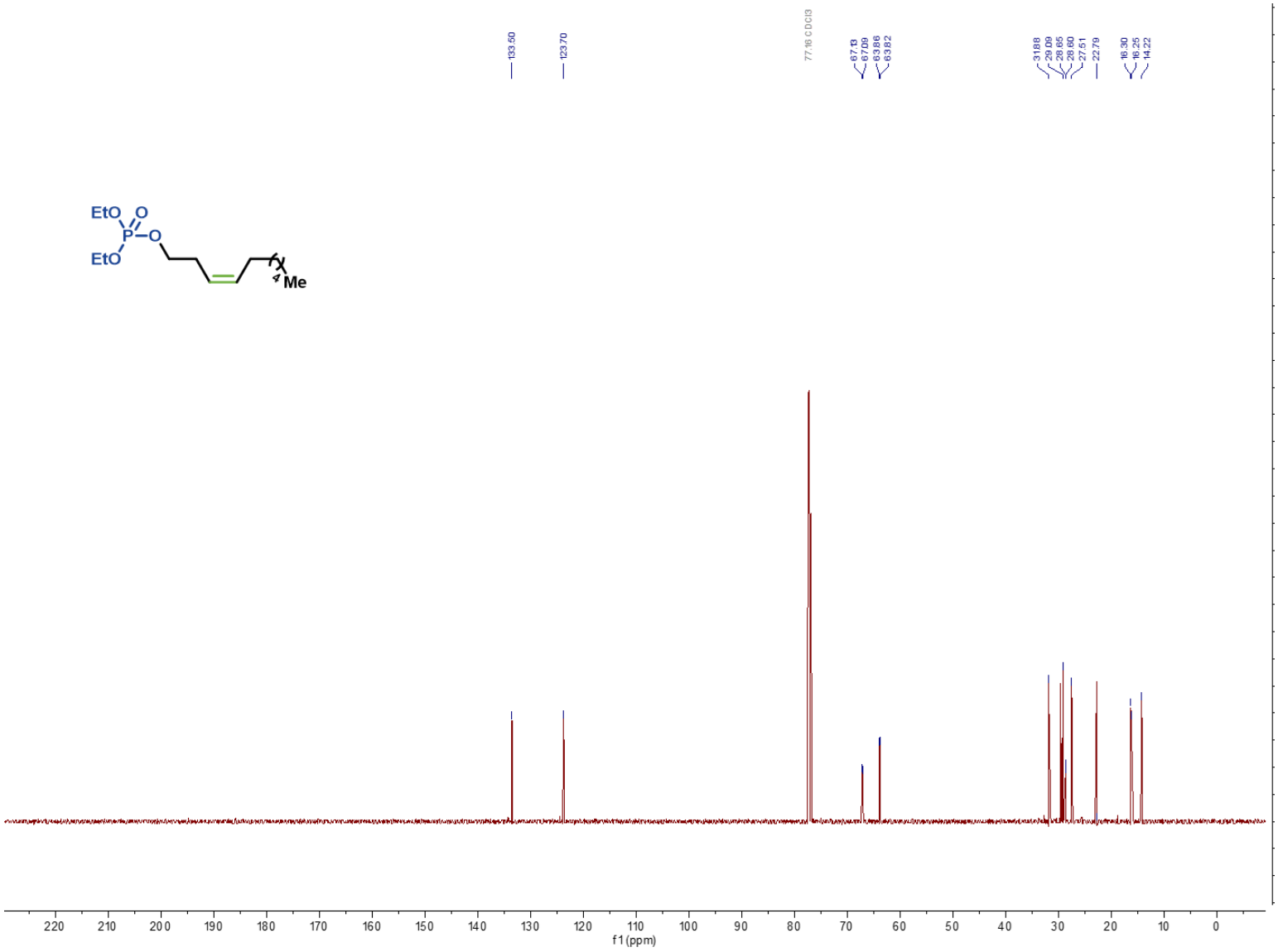
^{13}C NMR (151 MHz, $CDCl_3$) of compound **39**



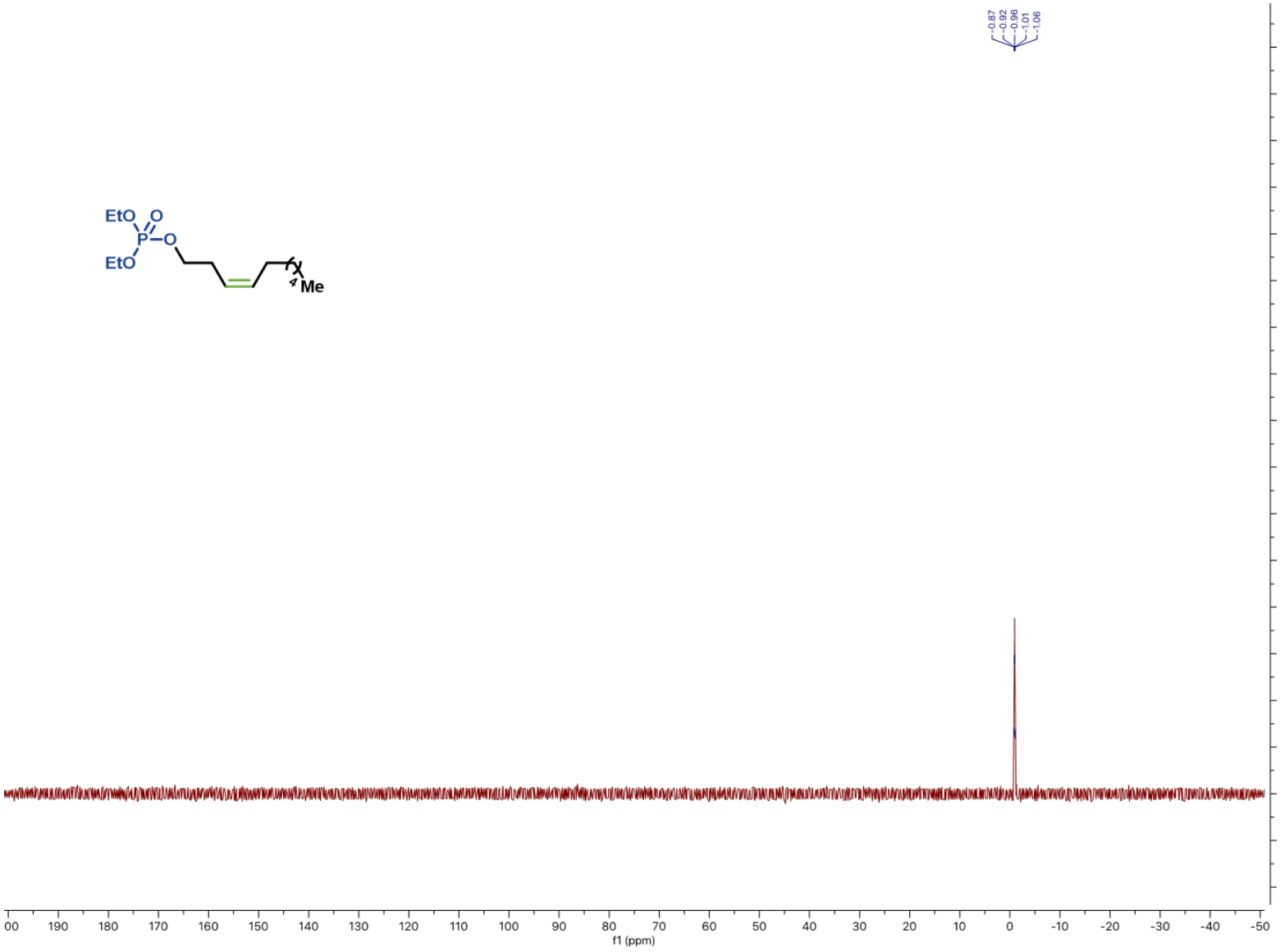
^{1}H NMR (400 MHz, $CDCl_3$) of compound **40**



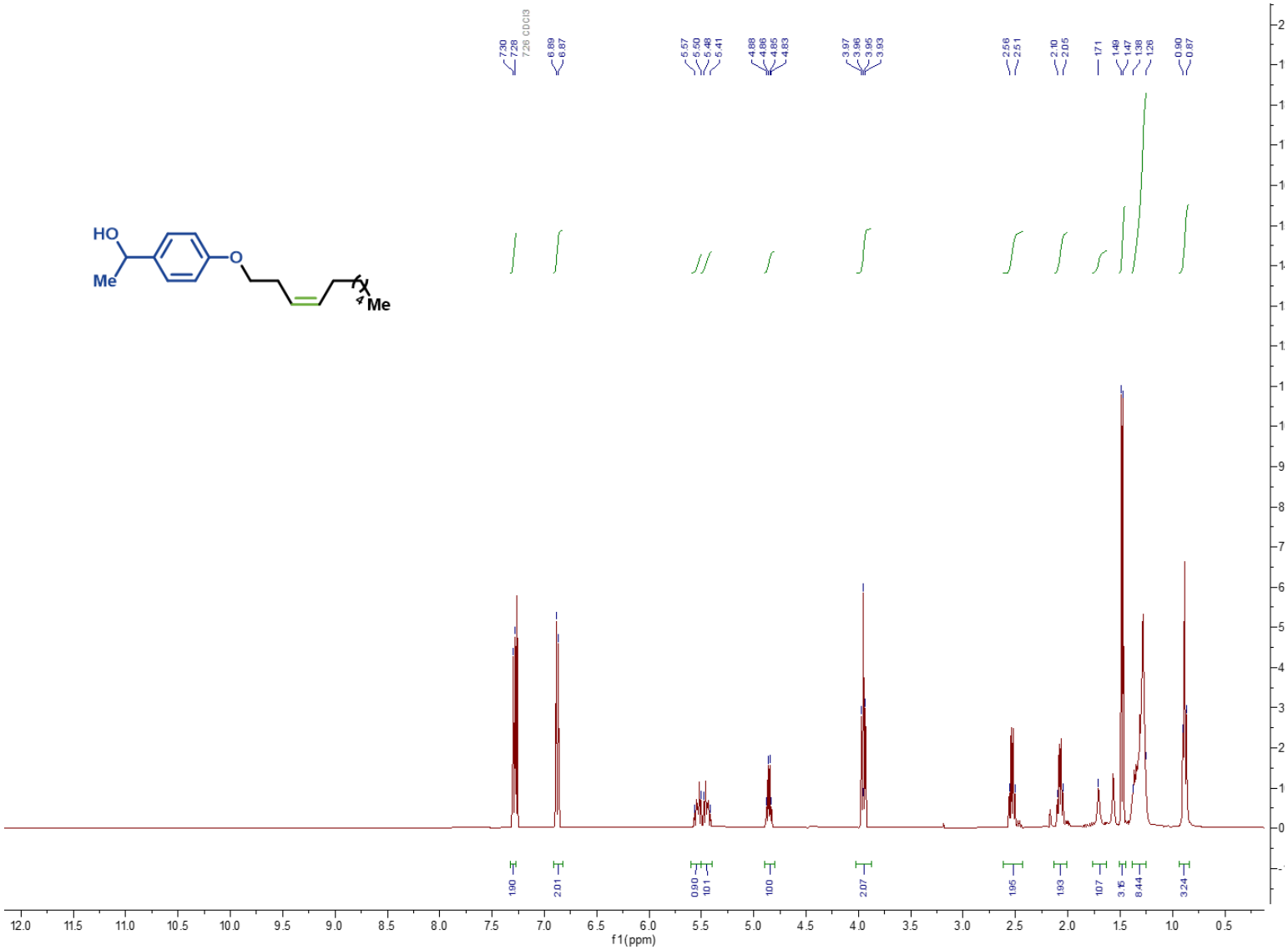
^{13}C NMR (151 MHz, $CDCl_3$) of compound **40**



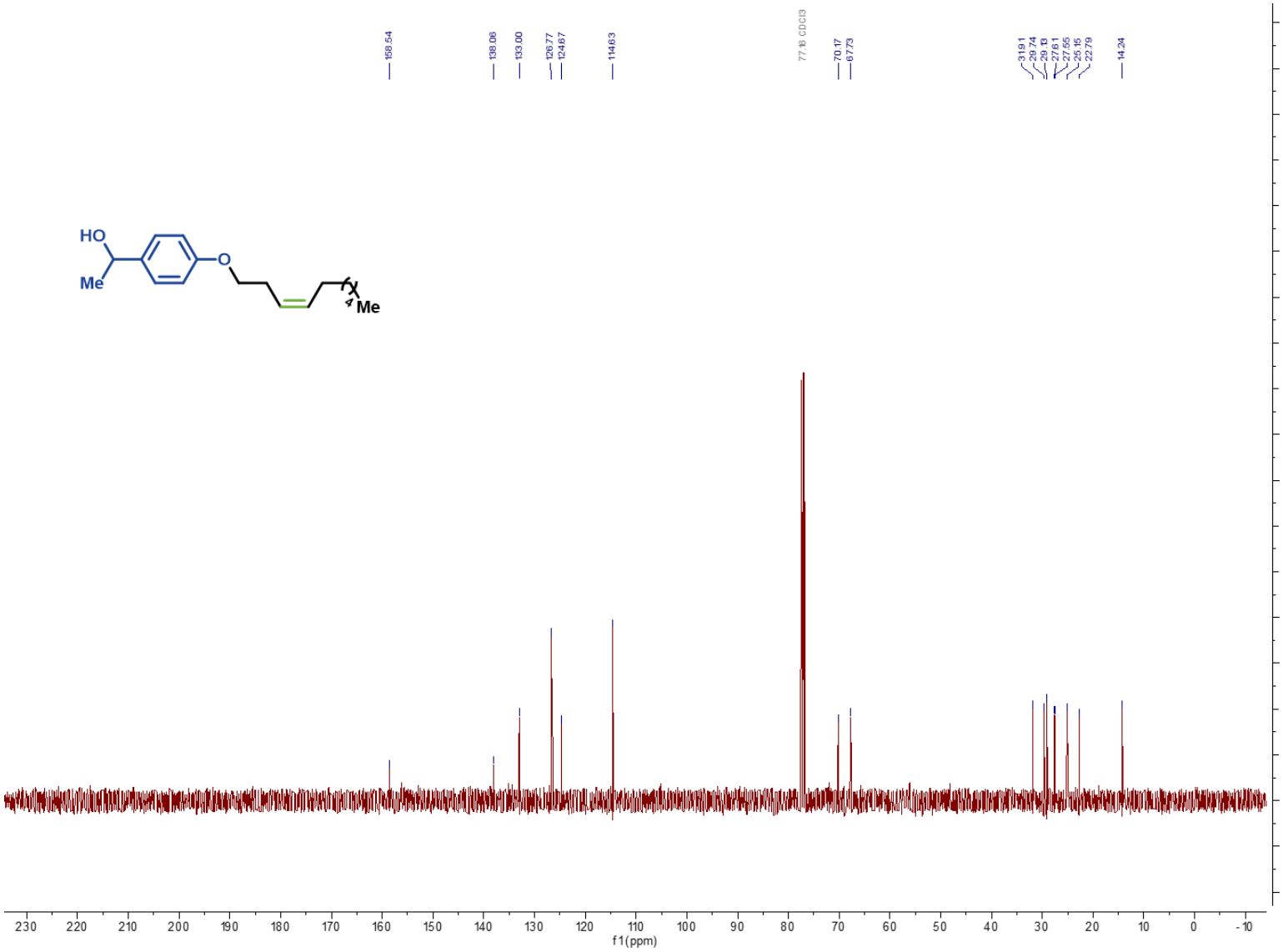
^{1}P NMR (162 MHz, $CDCl_3$) of compound **40**



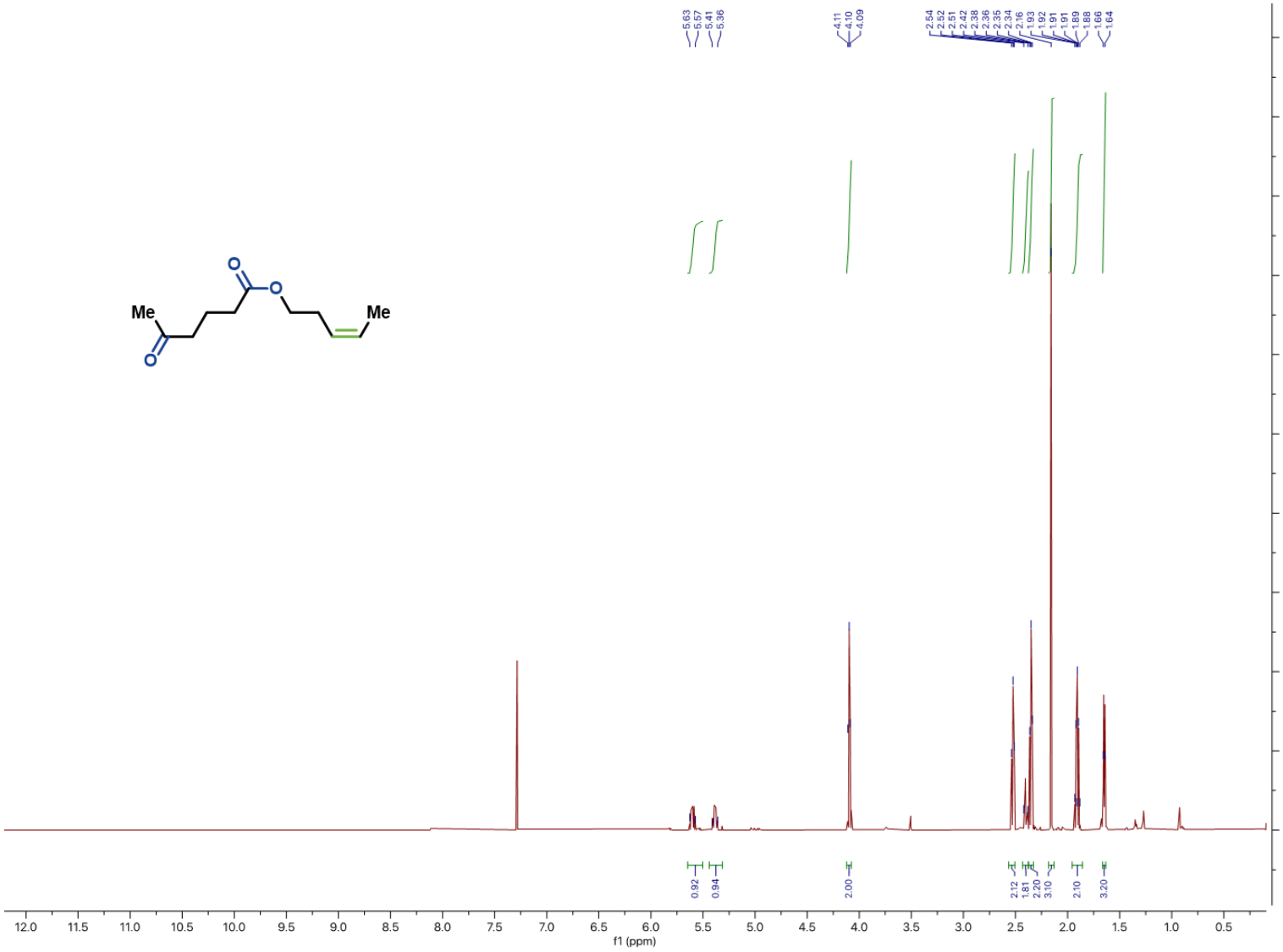
^{1}H NMR (400 MHz, $CDCl_3$) of compound **41**



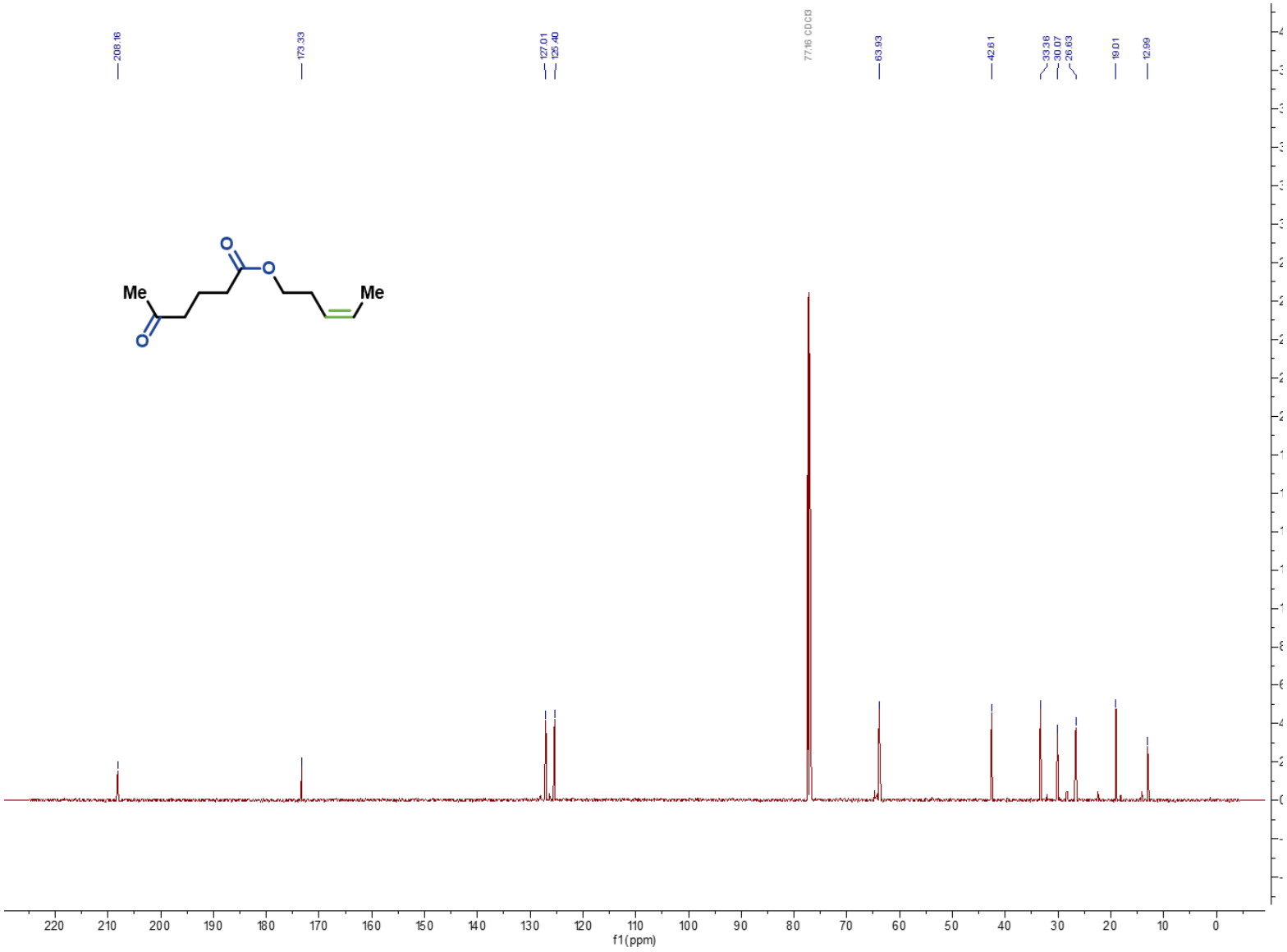
^{13}C NMR (126 MHz, $CDCl_3$) of compound **41**



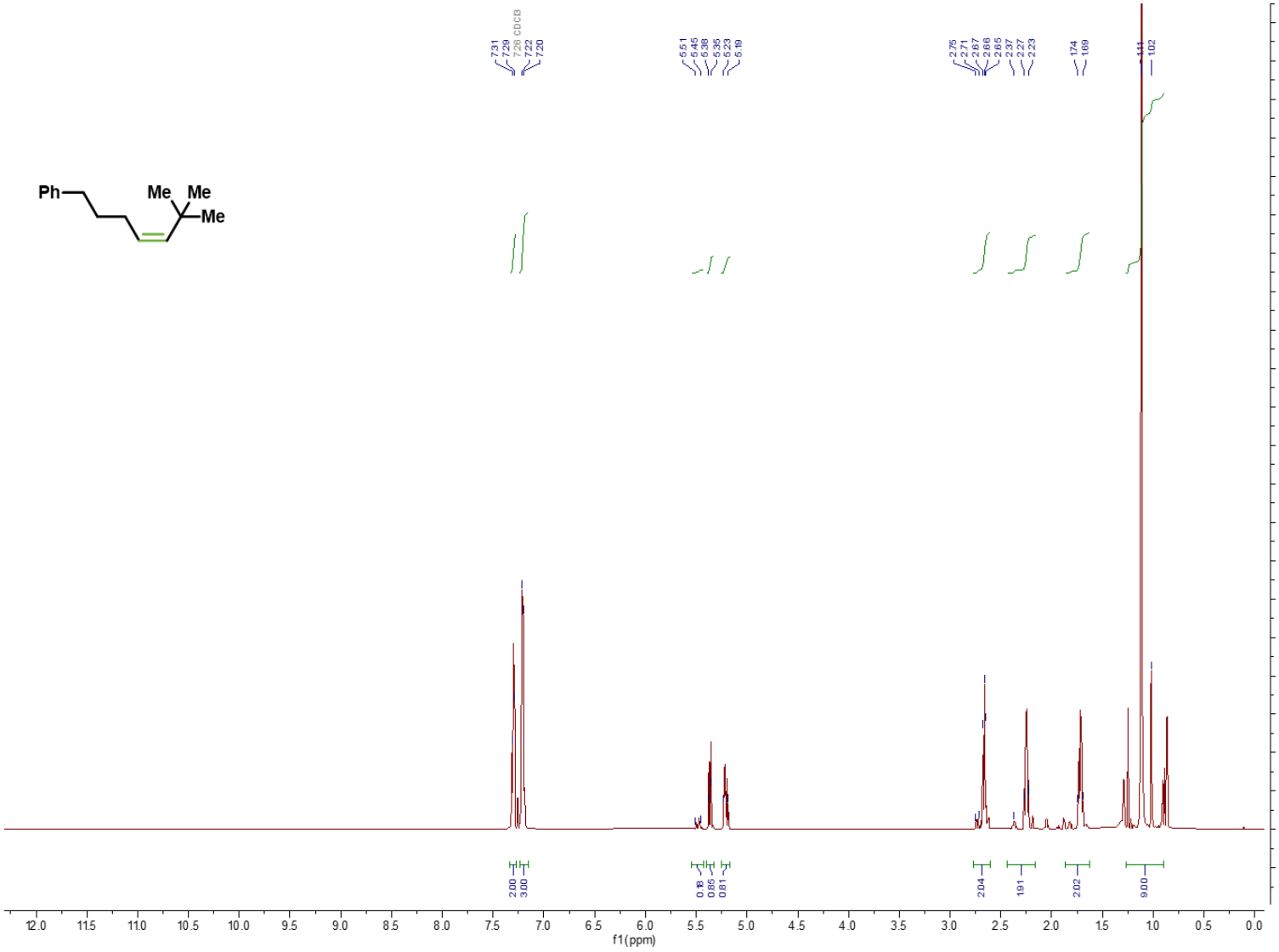
^{1}H NMR (600 MHz, $CDCl_3$) of compound **42**



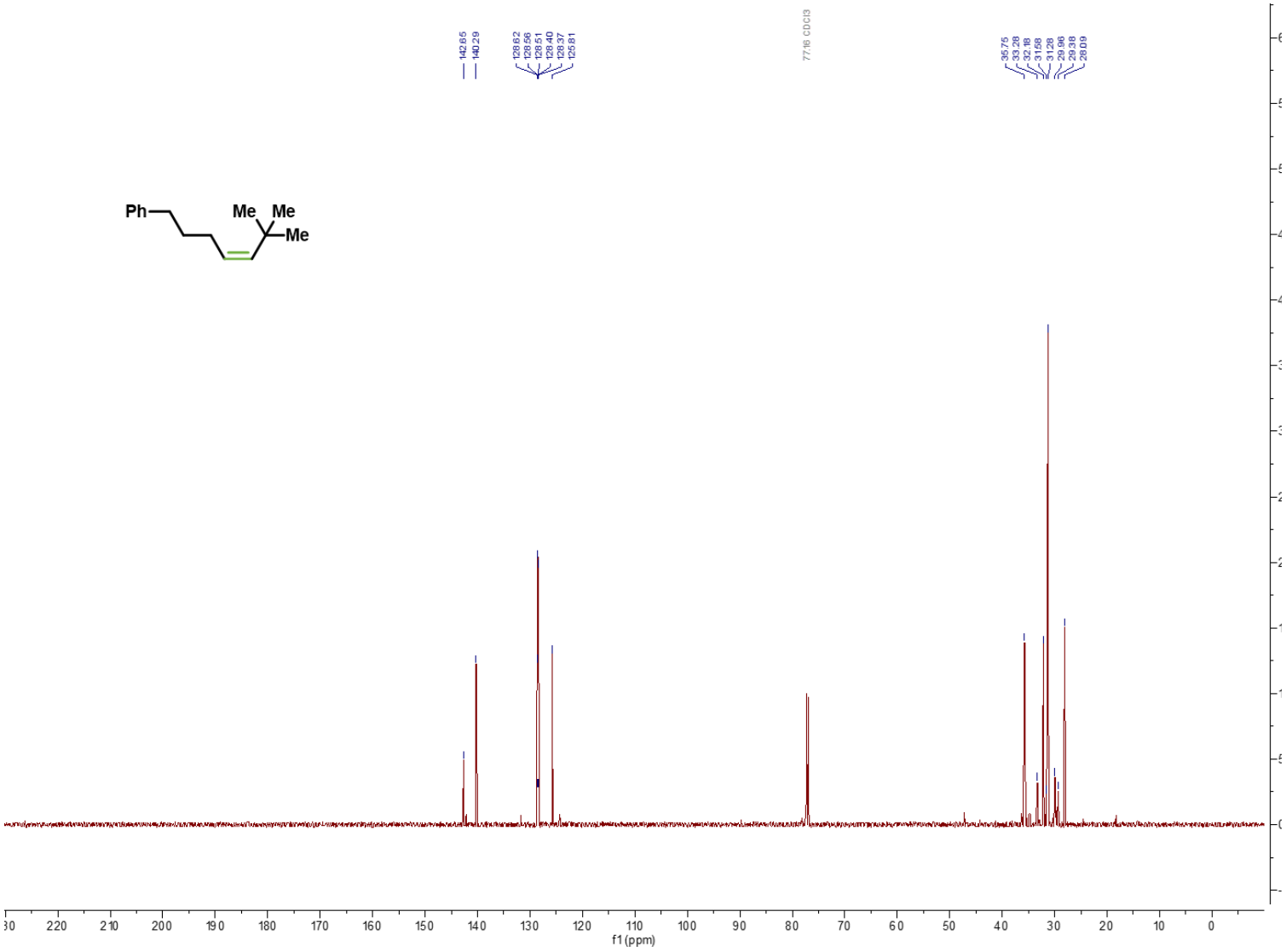
^{13}C NMR (151 MHz, $CDCl_3$) of compound **42**



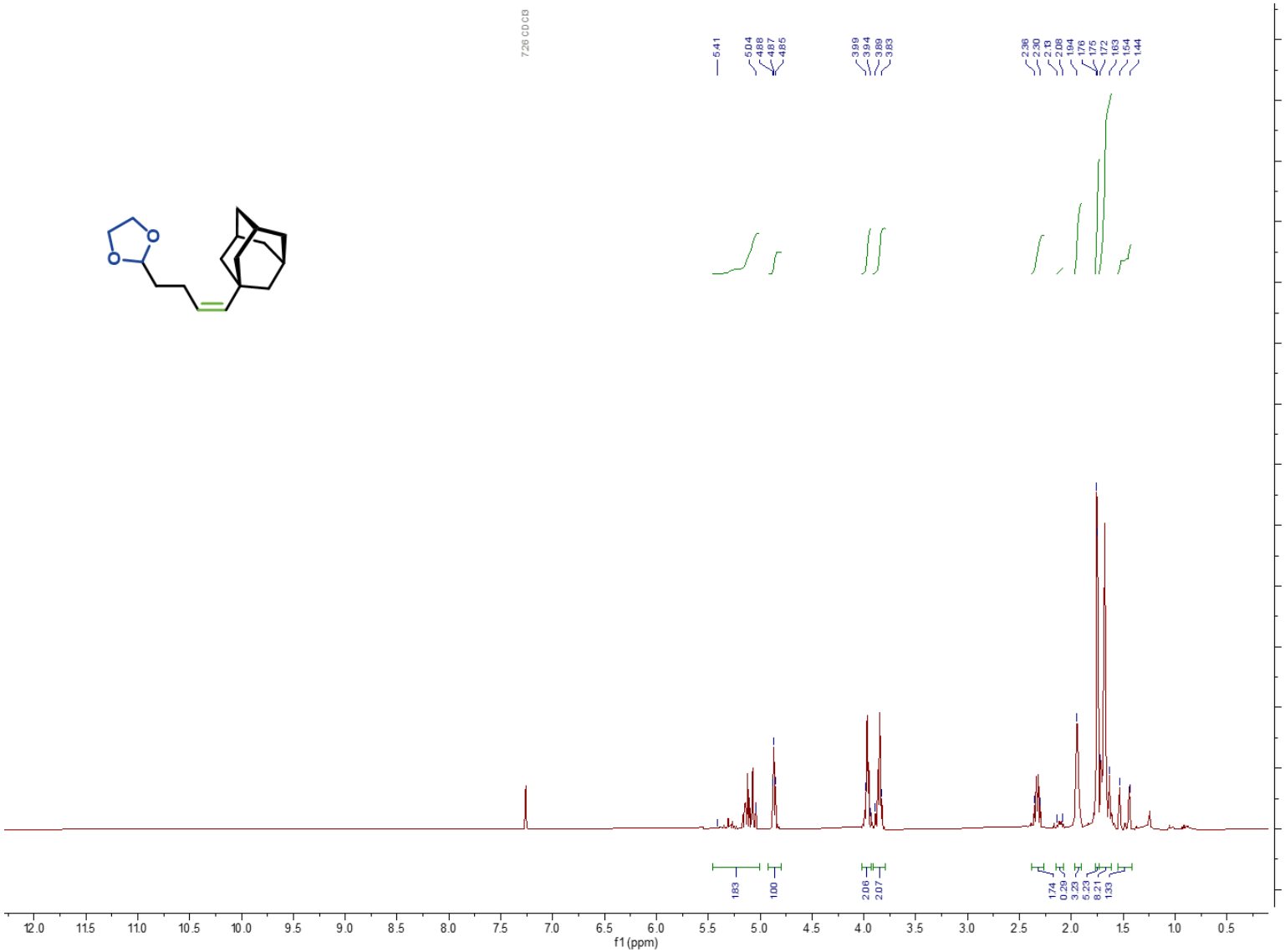
^{1}H NMR (600 MHz, $CDCl_3$) of compound **43**



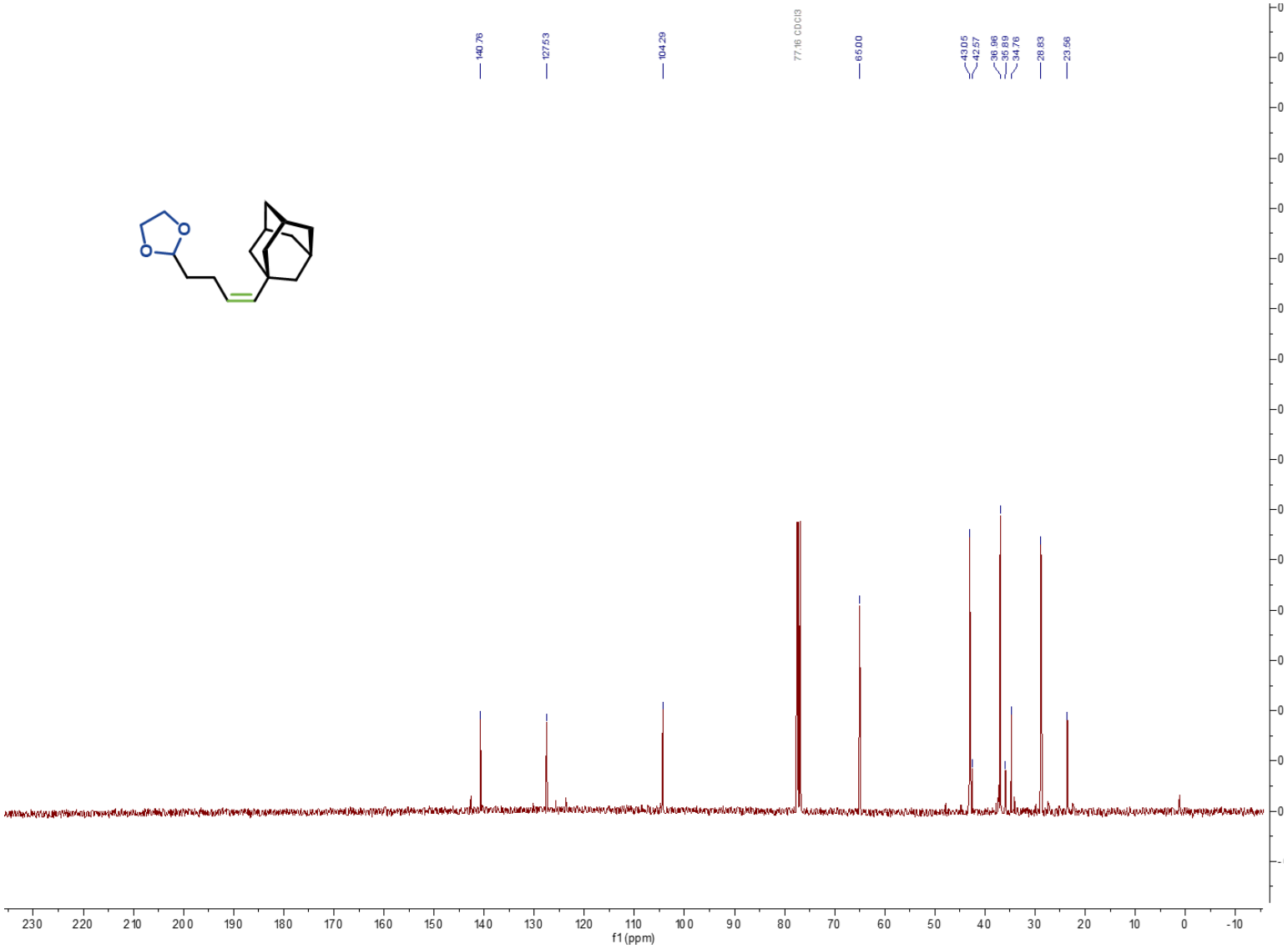
^{13}C NMR (151 MHz, $CDCl_3$) of compound **43**



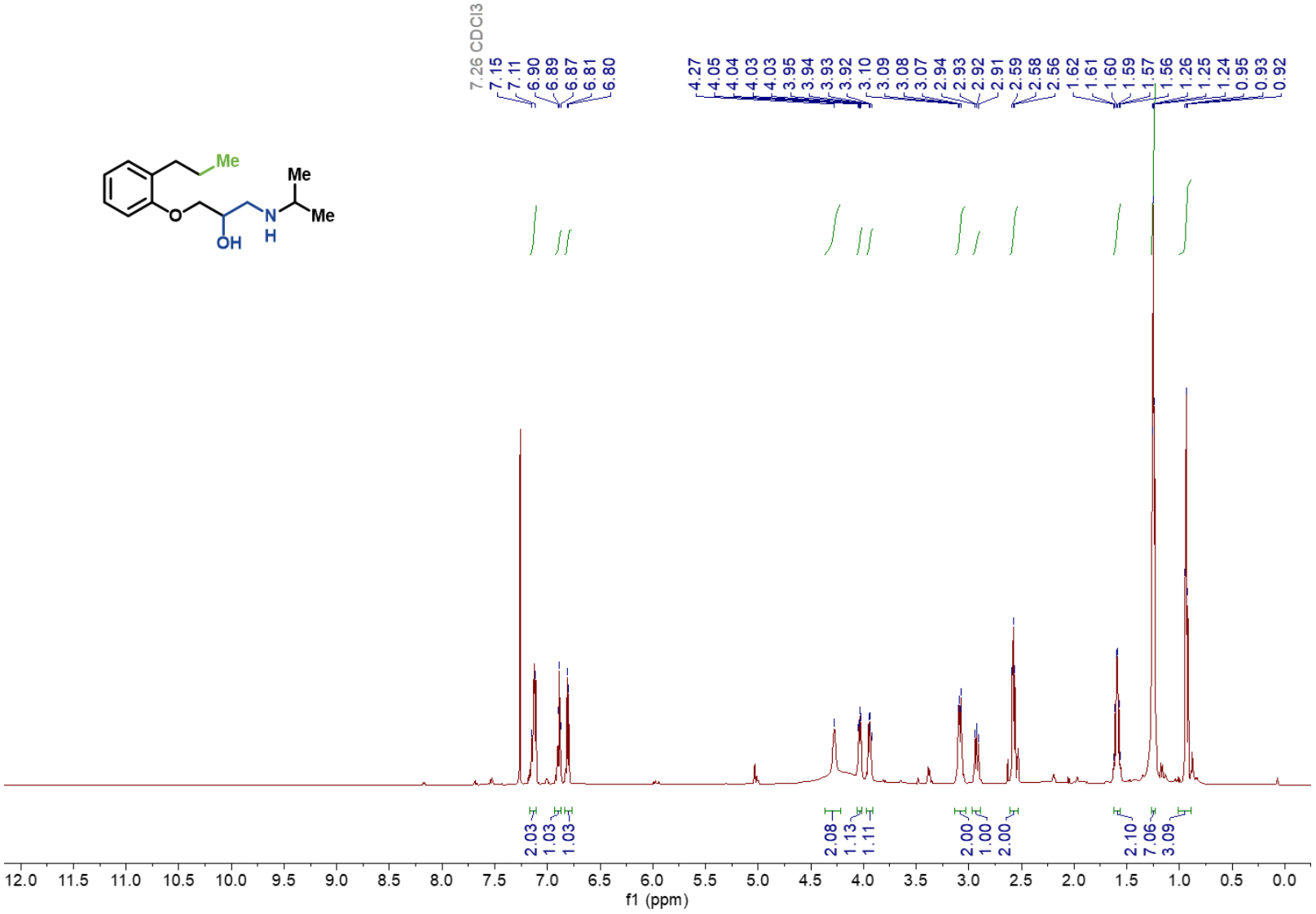
^{1}H NMR (400 MHz, $CDCl_3$) of compound **44**



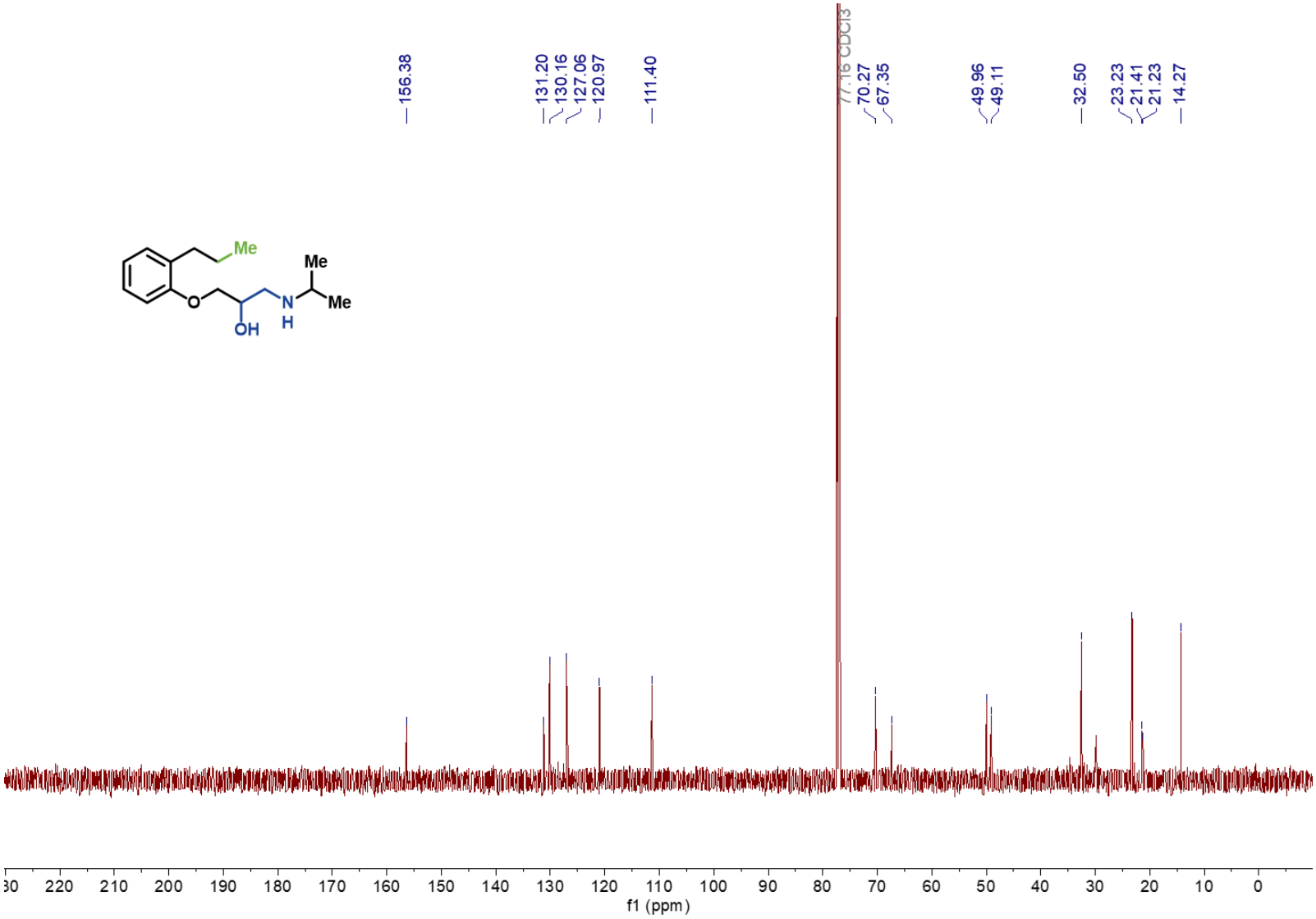
^{13}C NMR (100 MHz, $CDCl_3$) of compound **44**



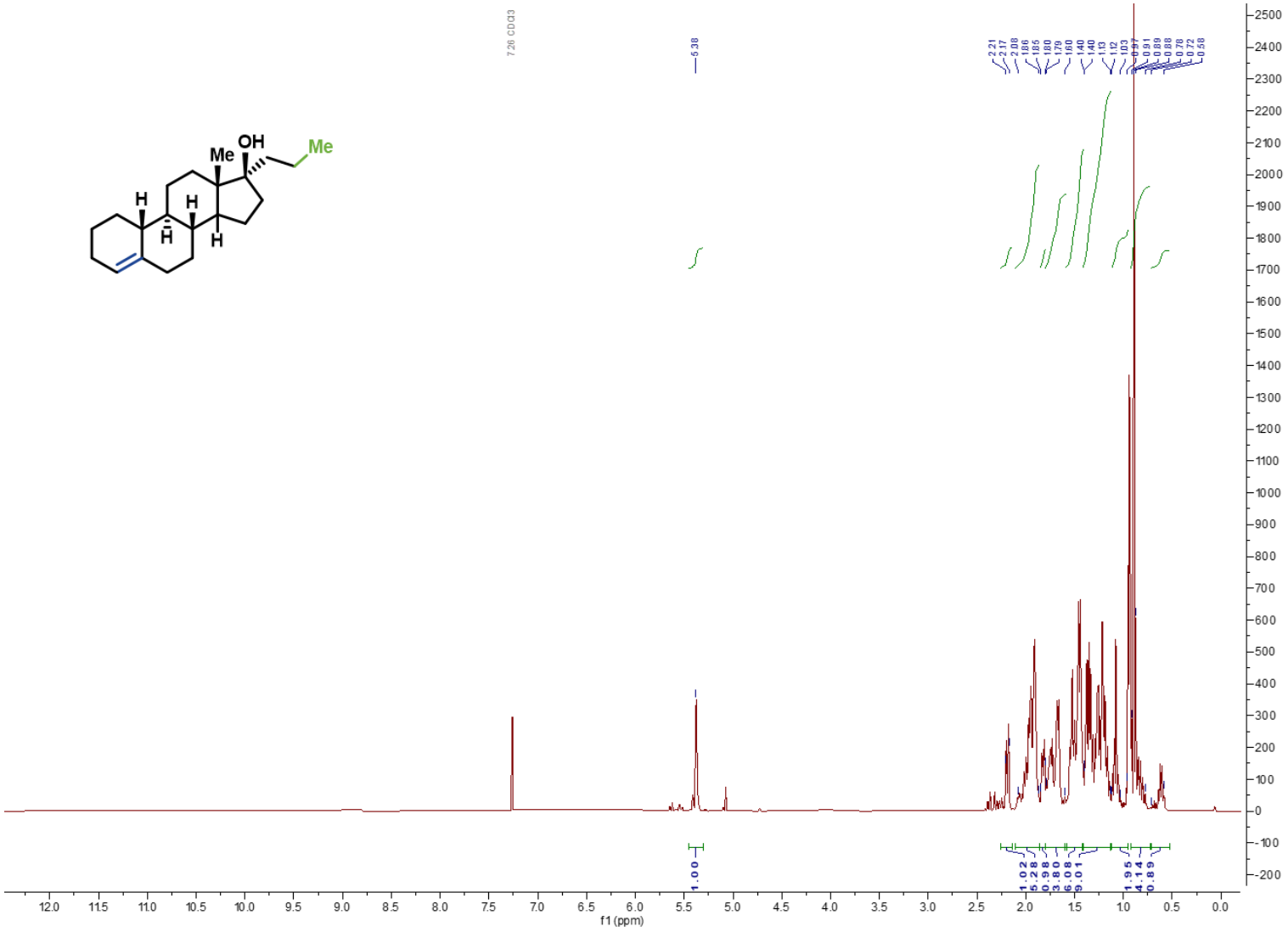
^{1}H NMR (600 MHz, $CDCl_3$) of compound **45**



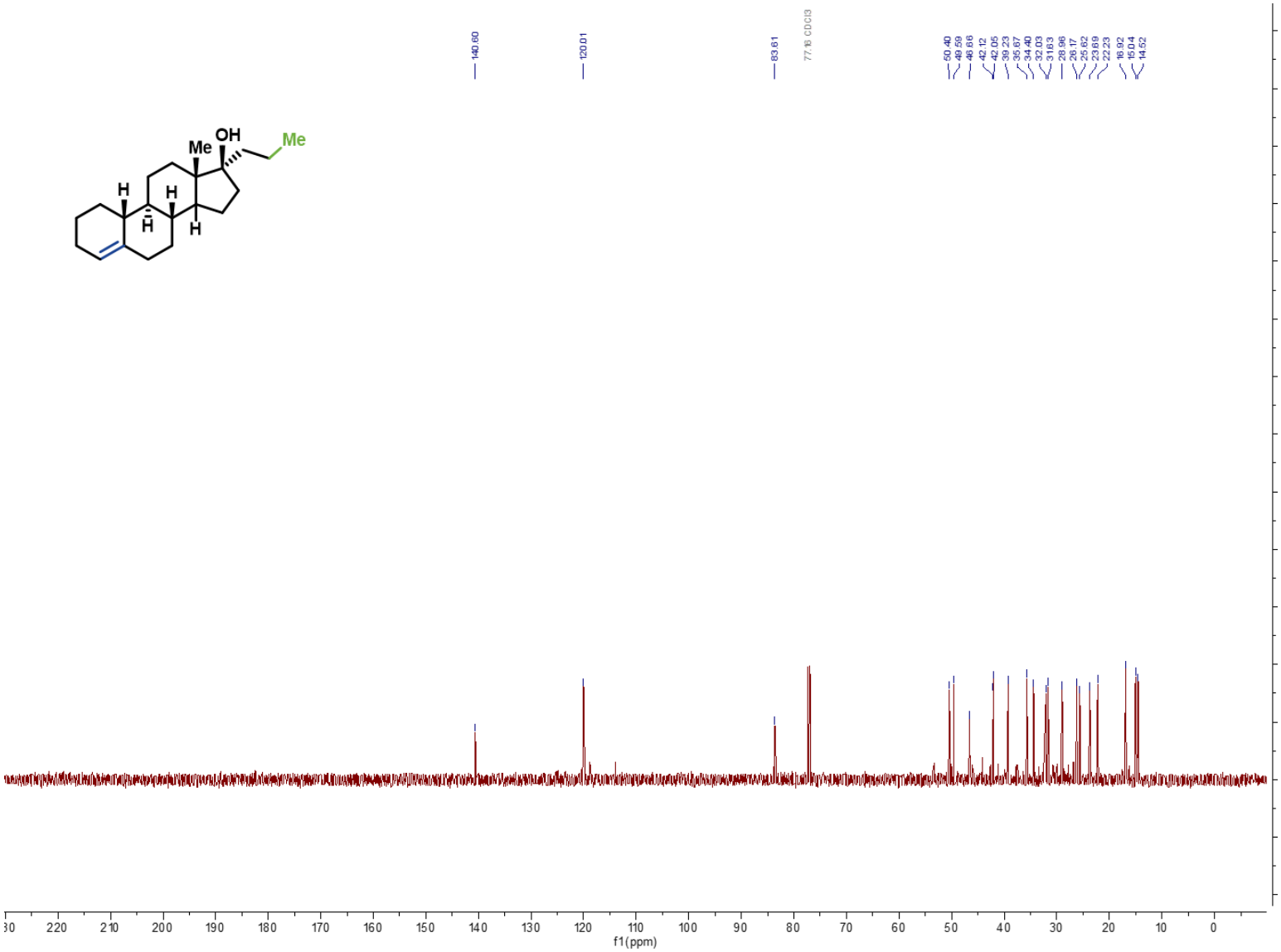
^{13}C NMR (151 MHz, $CDCl_3$) of compound **45**



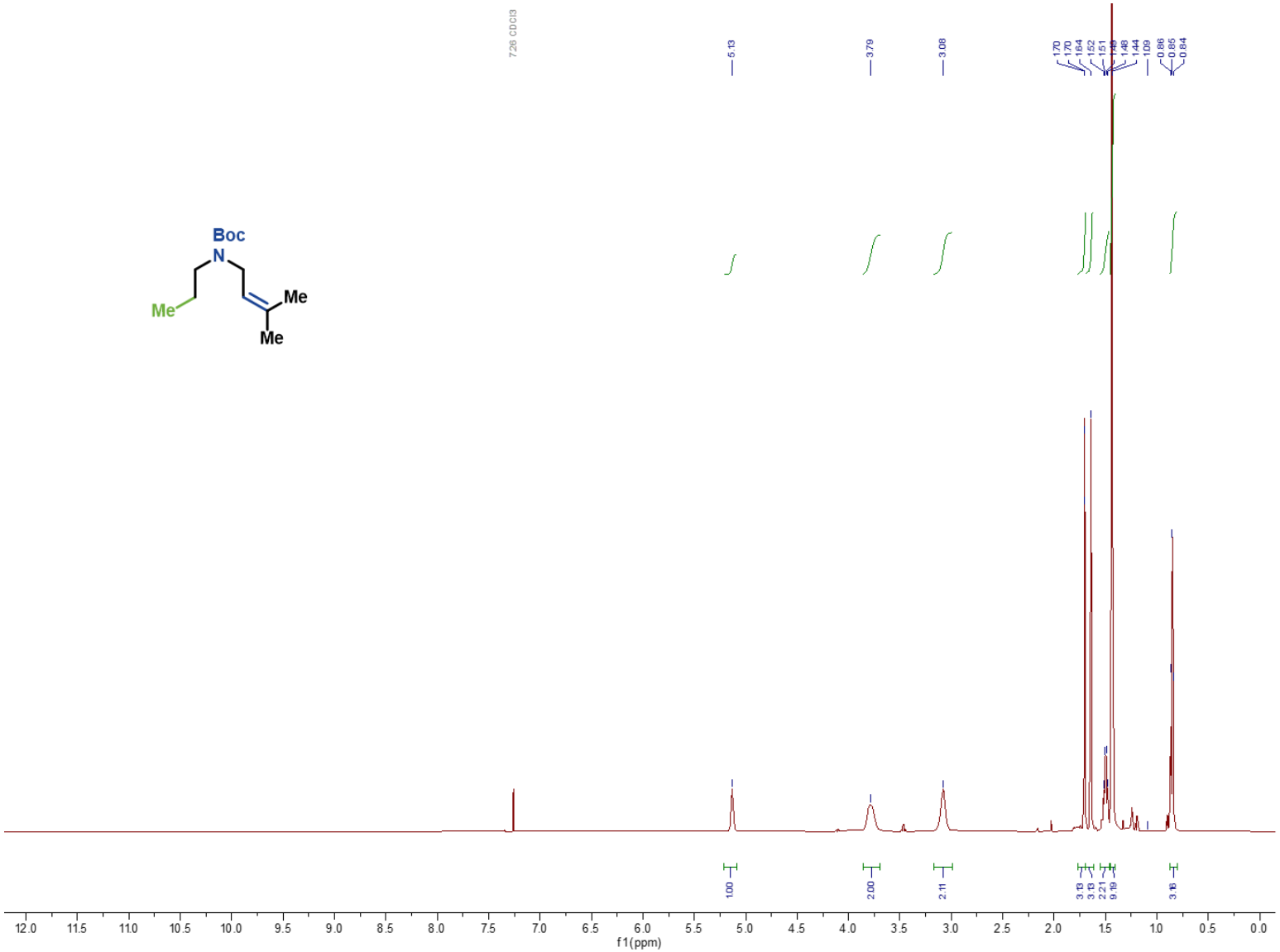
^{1}H NMR (600 MHz, $CDCl_3$) of compound **46**



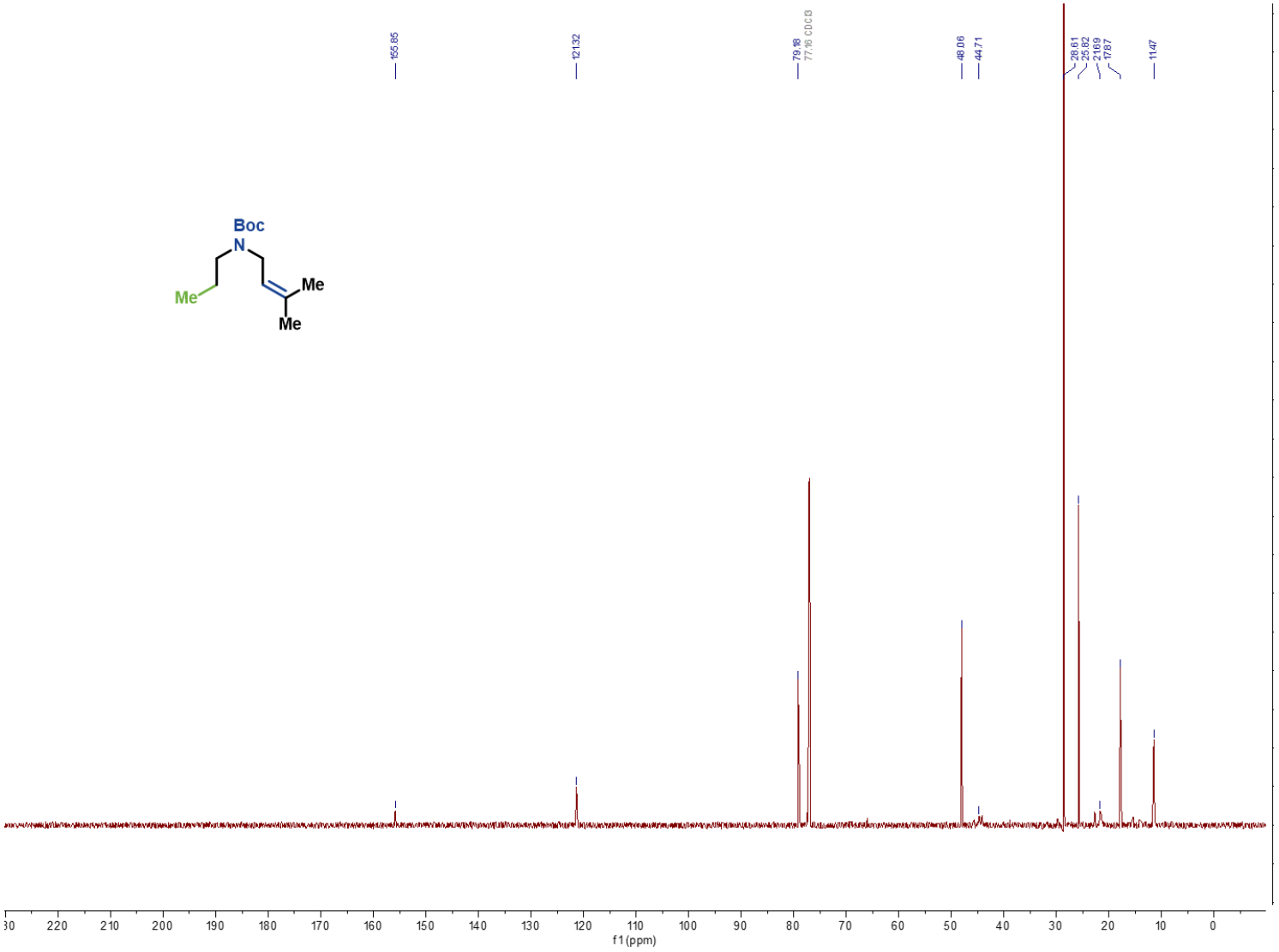
^{13}C NMR (151 MHz, $CDCl_3$) of compound **46**



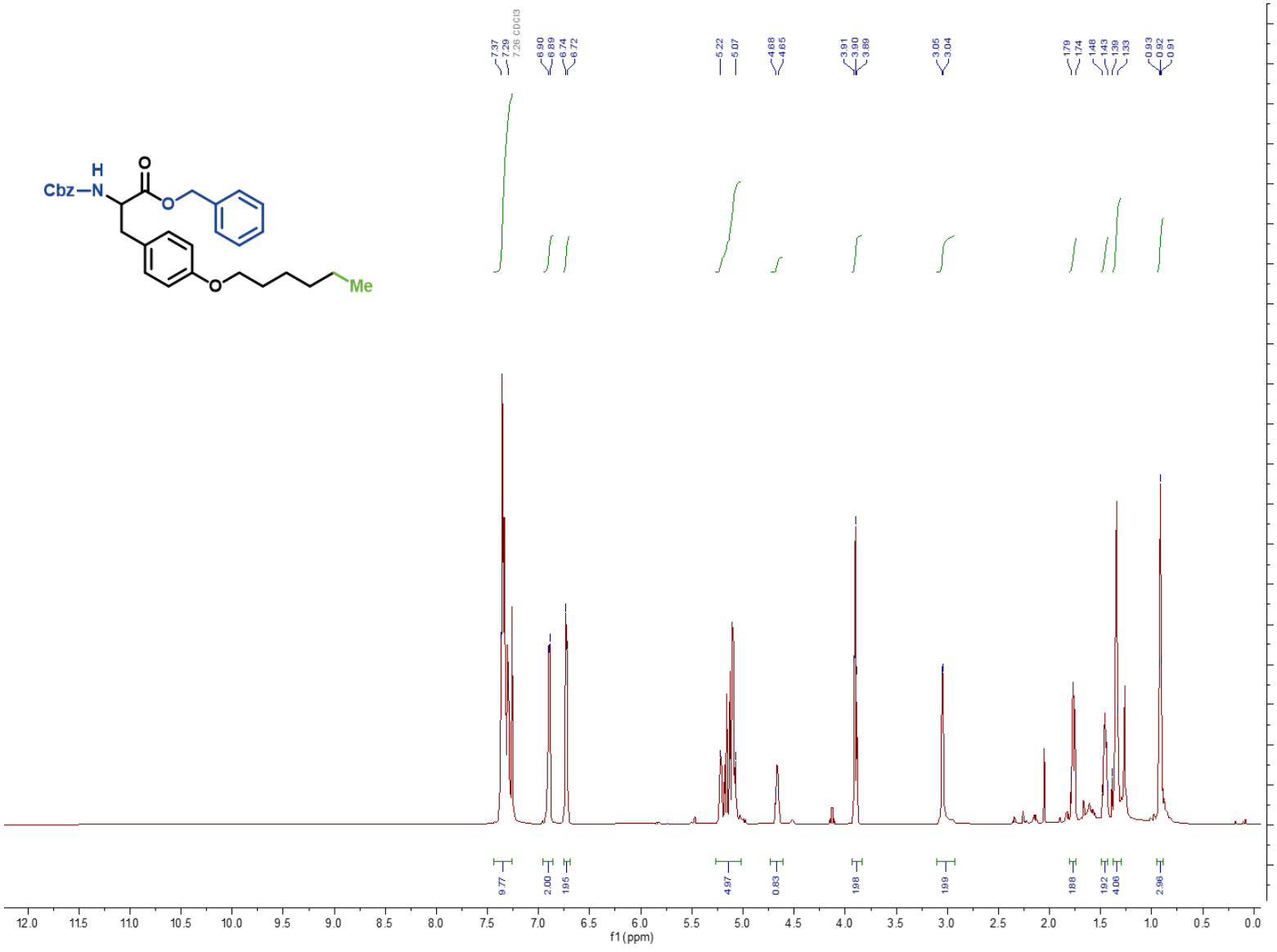
^{1}H NMR (600 MHz, $CDCl_3$) of compound **47**



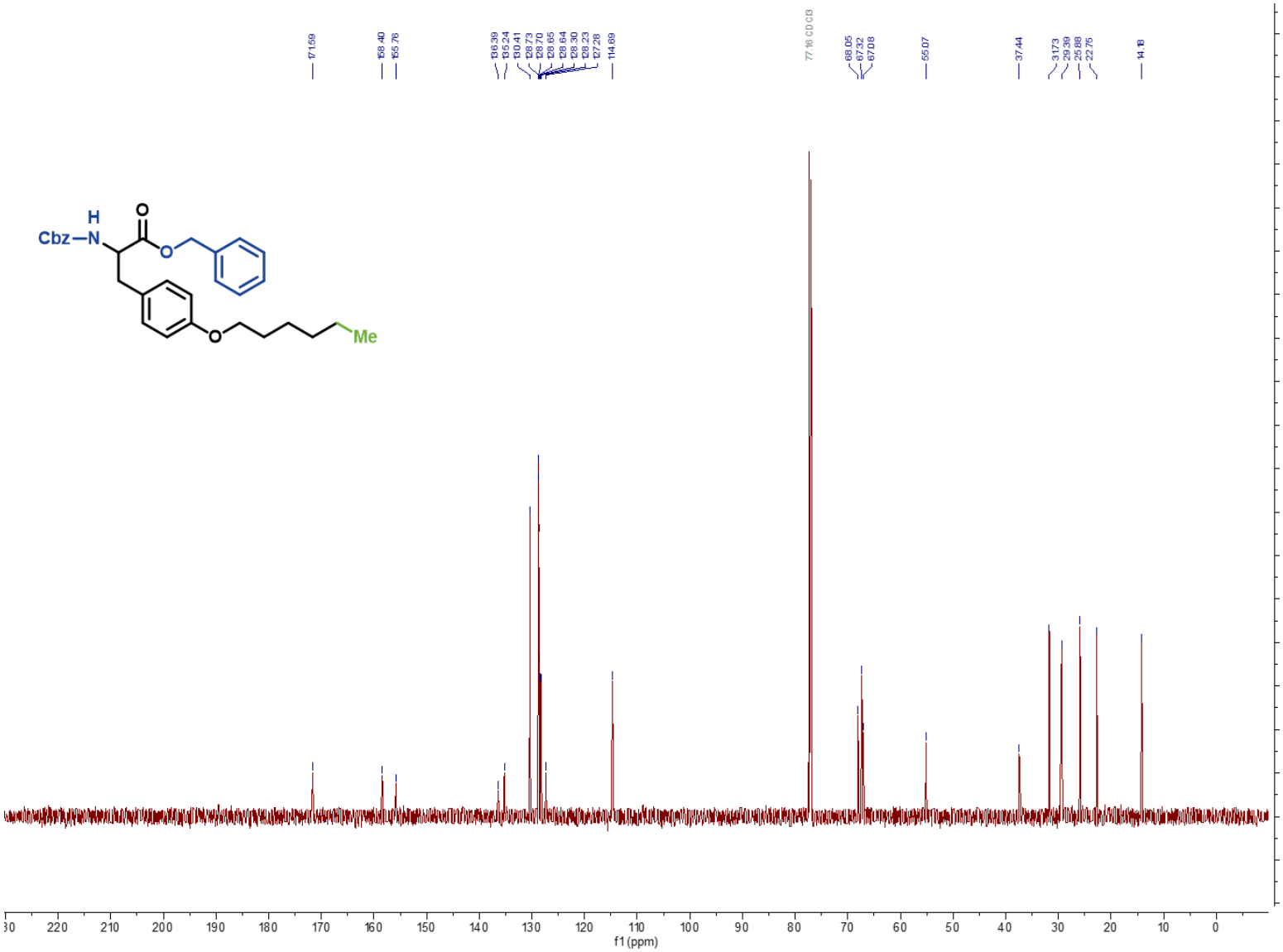
^{13}C NMR (151 MHz, $CDCl_3$) of compound **47**



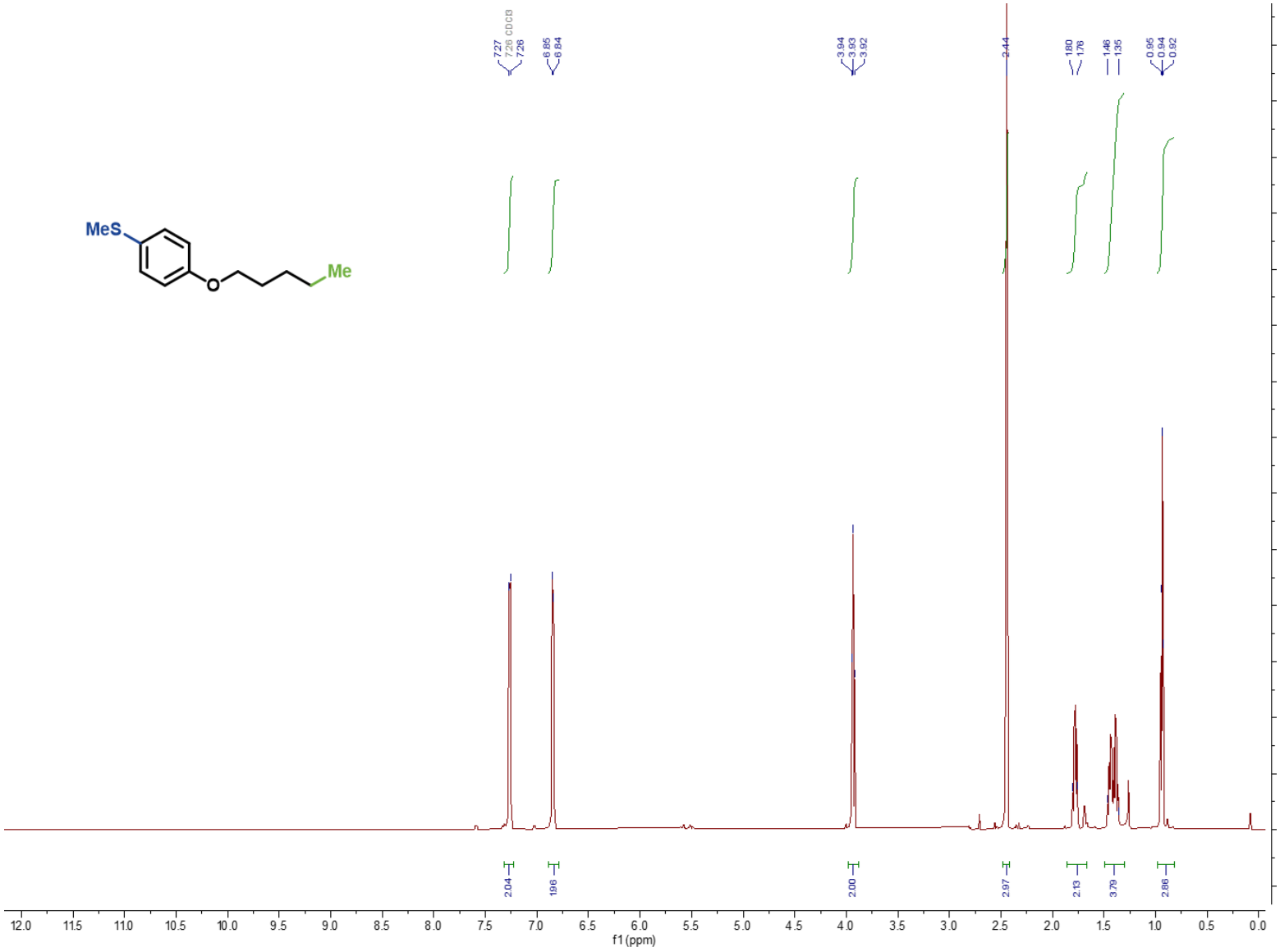
^{1}H NMR (600 MHz, $CDCl_3$) of compound **48**



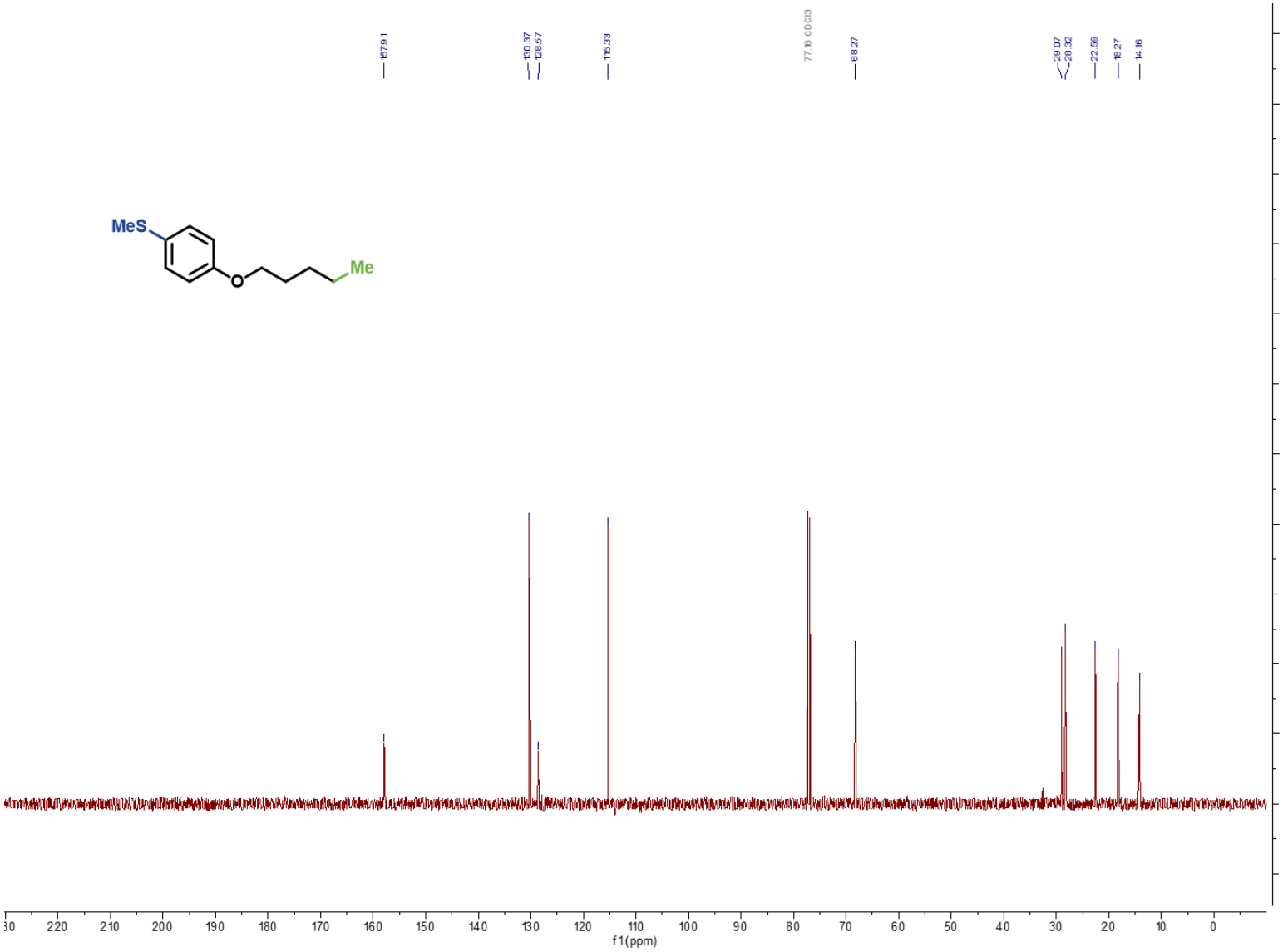
^{13}C NMR (151 MHz, $CDCl_3$) of compound **48**



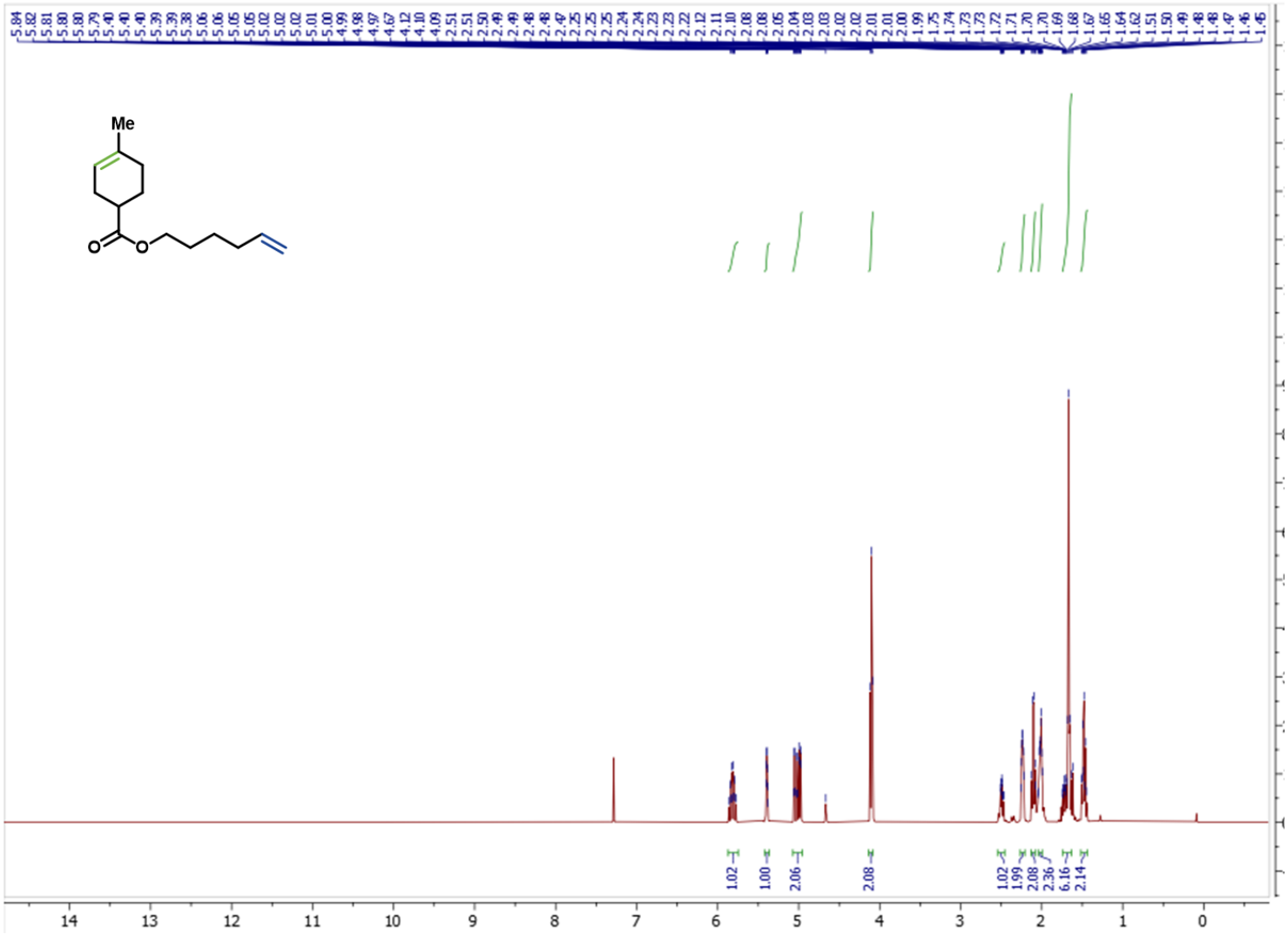
^{1}H NMR (600 MHz, $CDCl_3$) of compound **49**



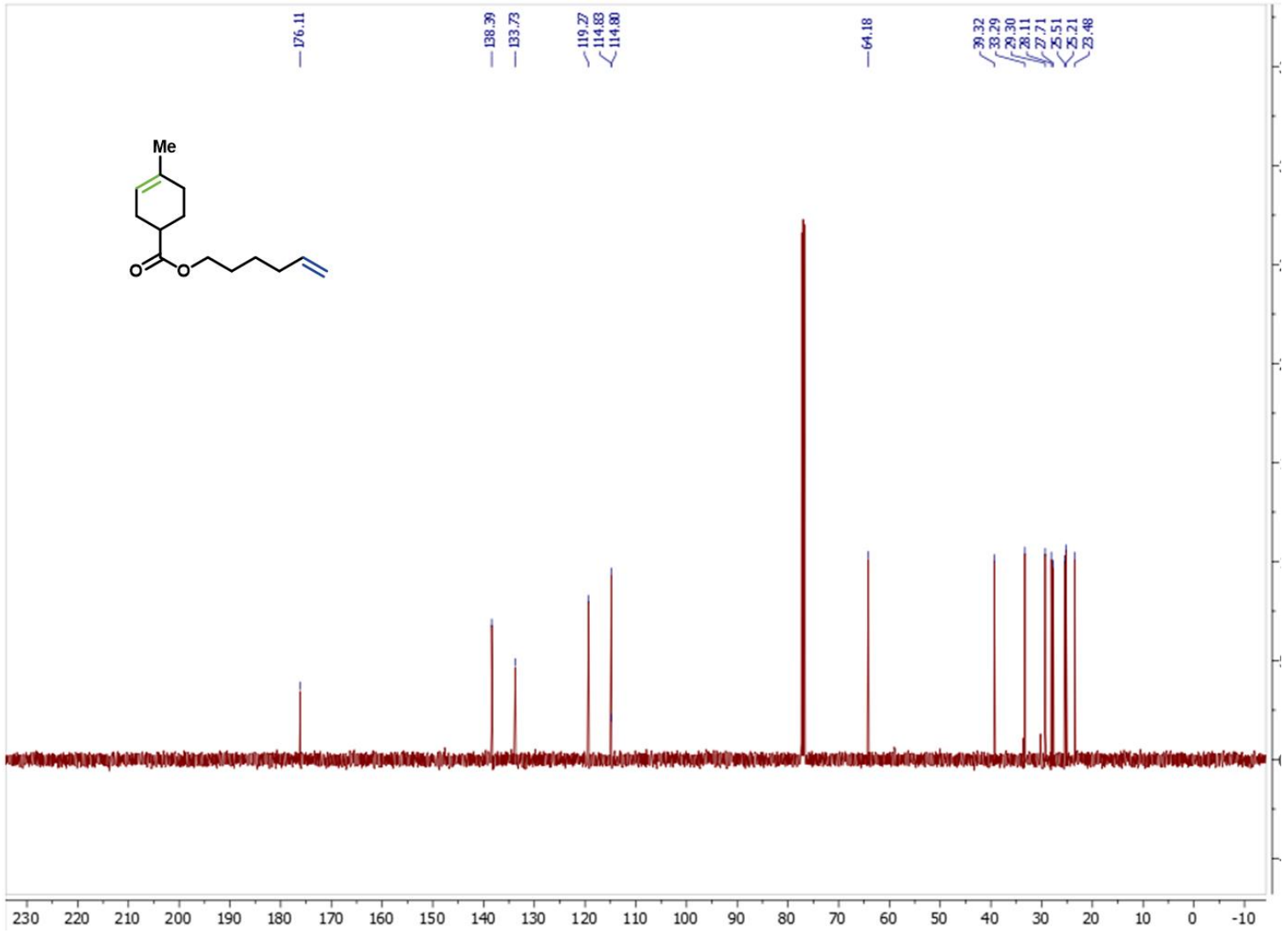
^{13}C NMR (151 MHz, $CDCl_3$) of compound **49**



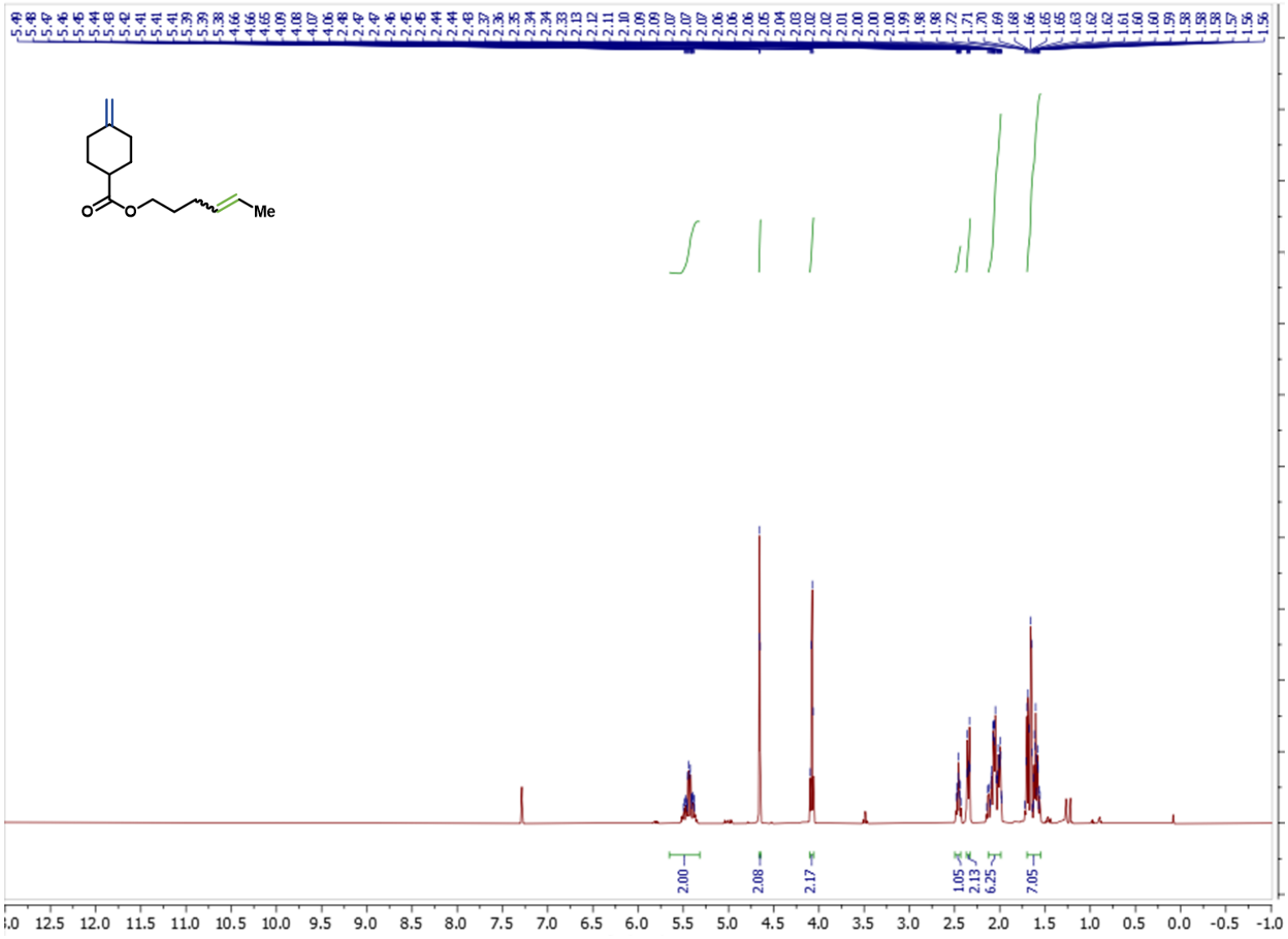
^{1}H NMR (500 MHz, $CDCl_3$) of compound **51**



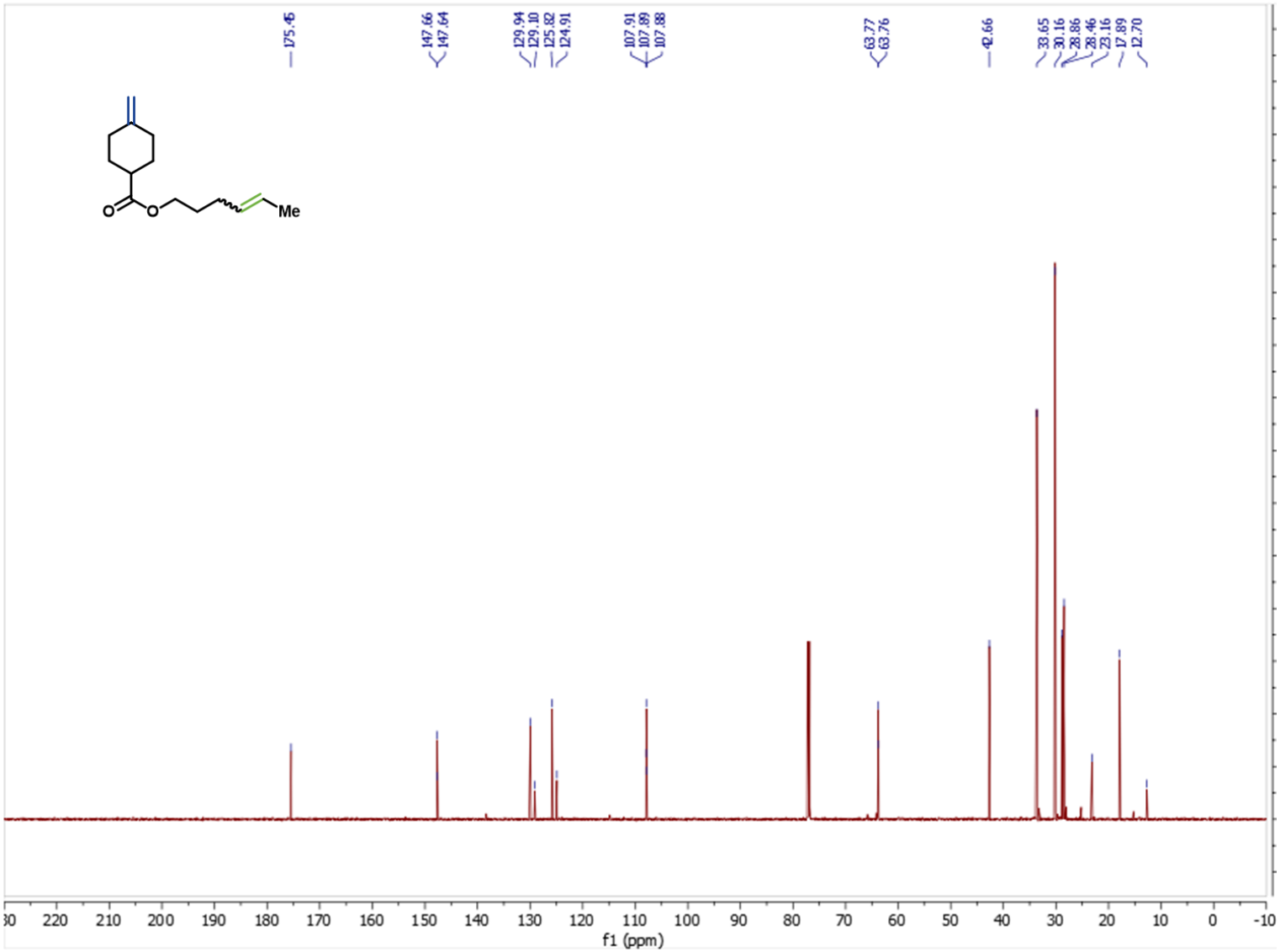
^{13}C NMR (151 MHz, $CDCl_3$) of compound **51**



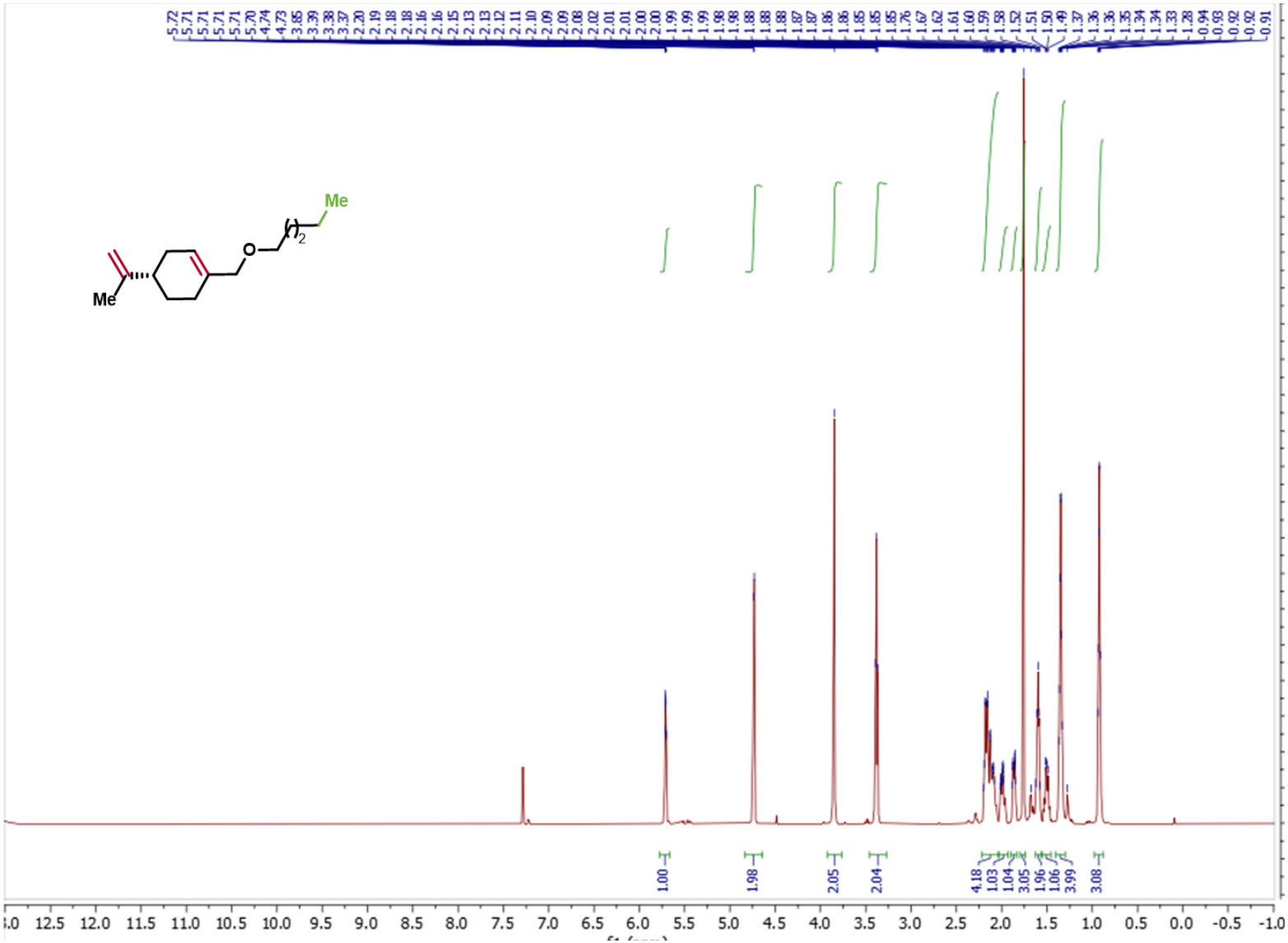
^{1}H NMR (600 MHz, $CDCl_3$) of compound **52**



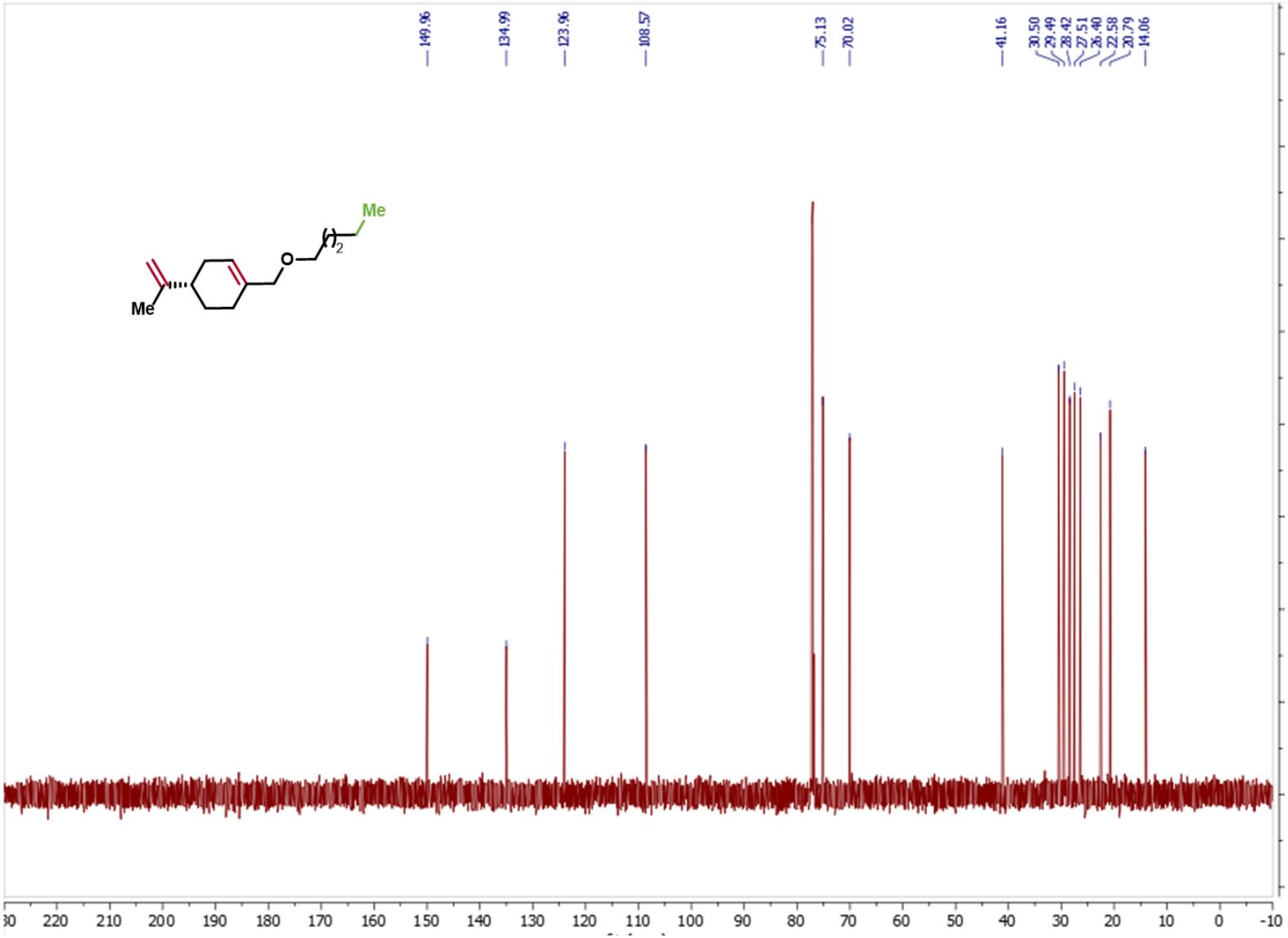
^{13}C NMR (151 MHz, $CDCl_3$) of compound **52**



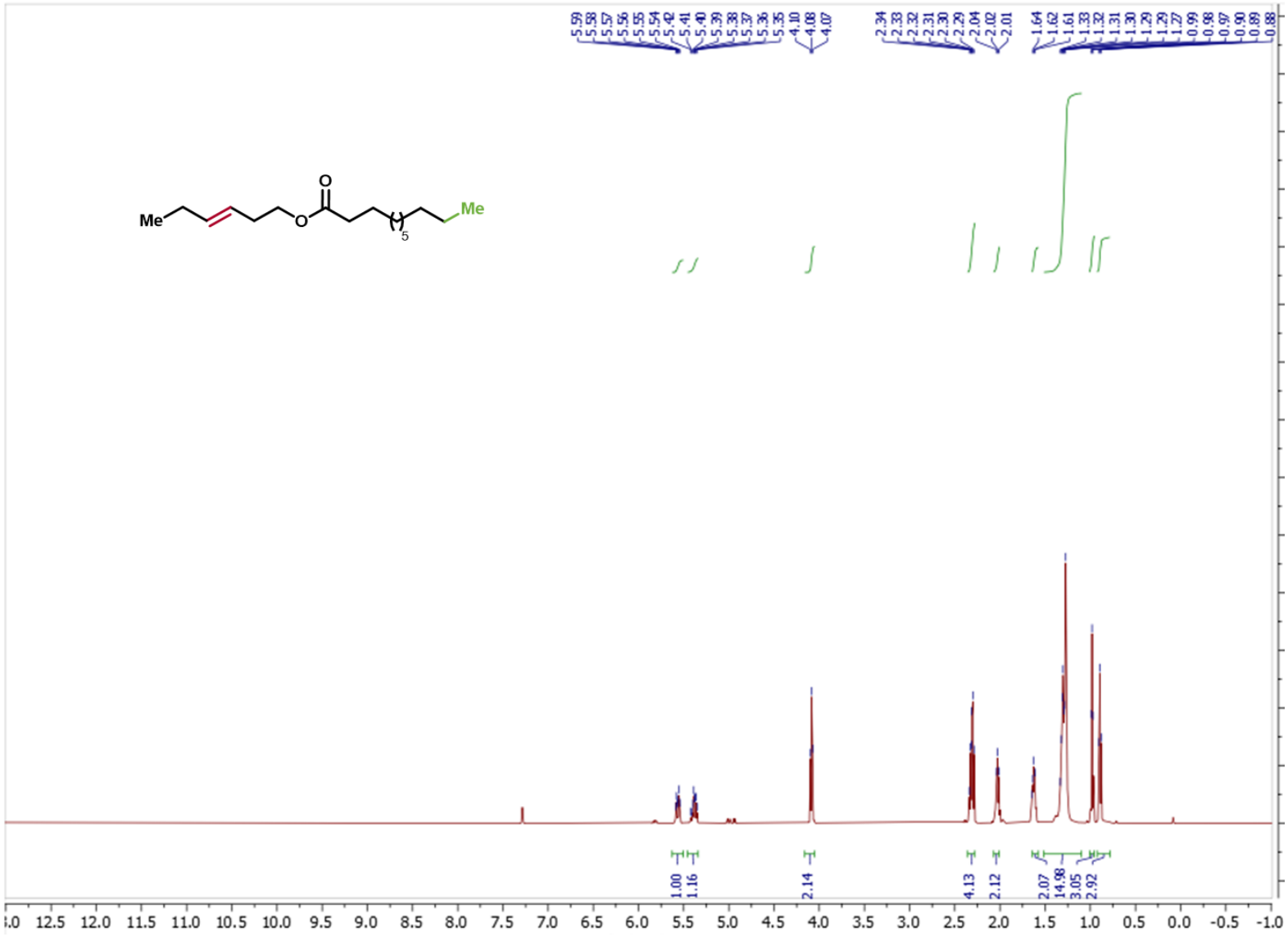
^{1}H NMR (600 MHz, $CDCl_3$) of compound **54**



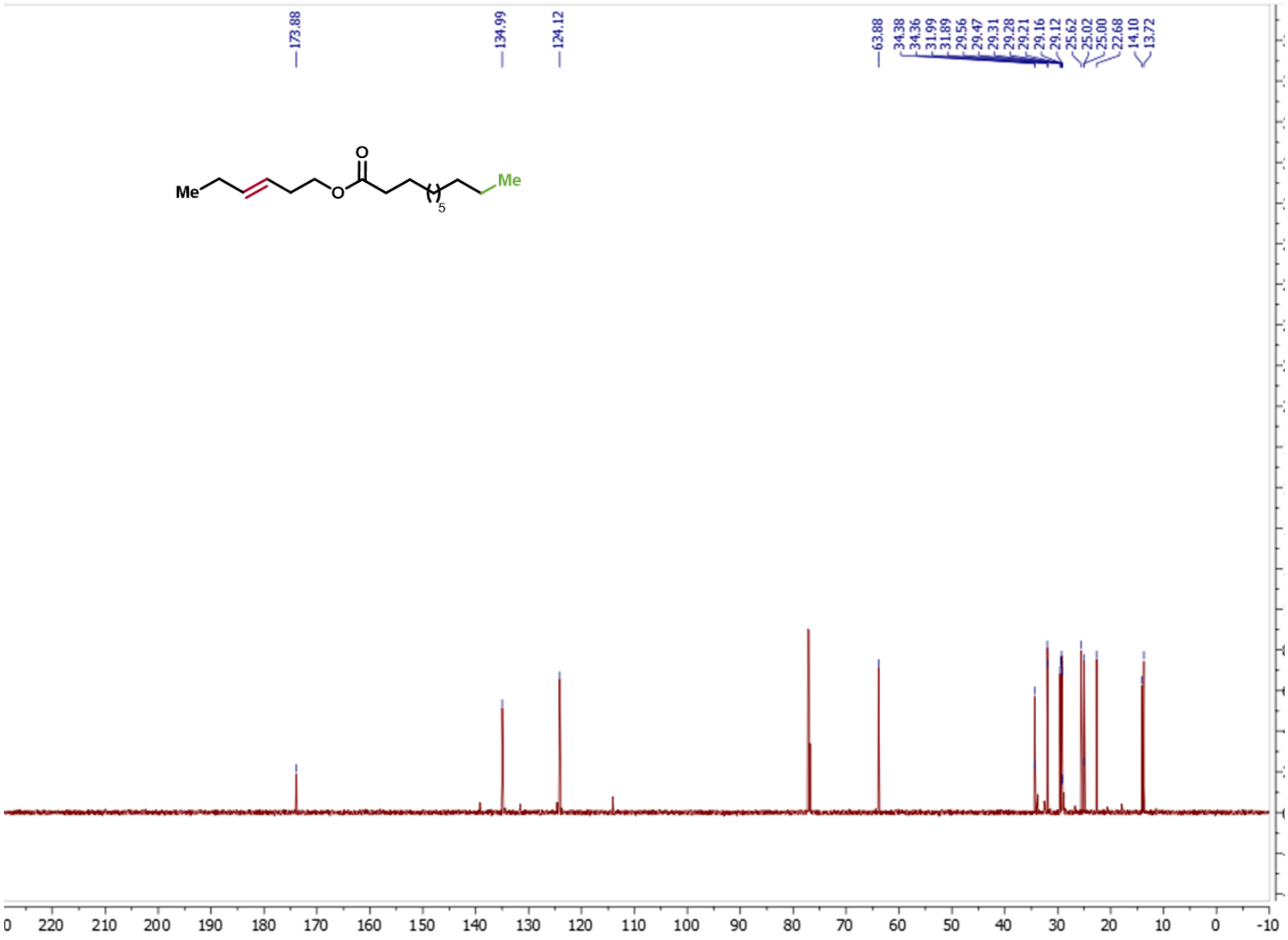
^{13}C NMR (151 MHz, $CDCl_3$) of compound **54**



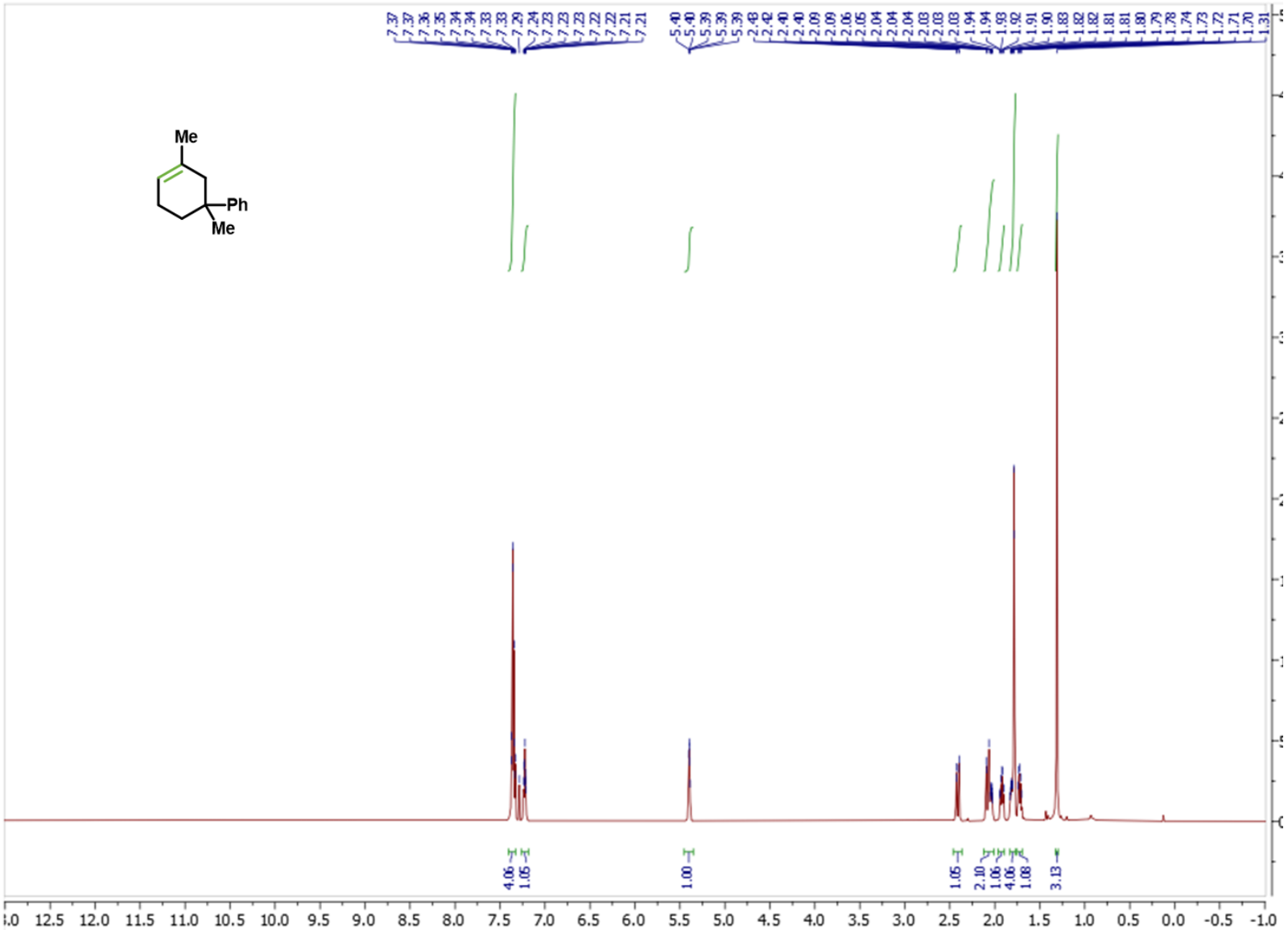
^{1}H NMR (600 MHz, $CDCl_3$) of compound **56**



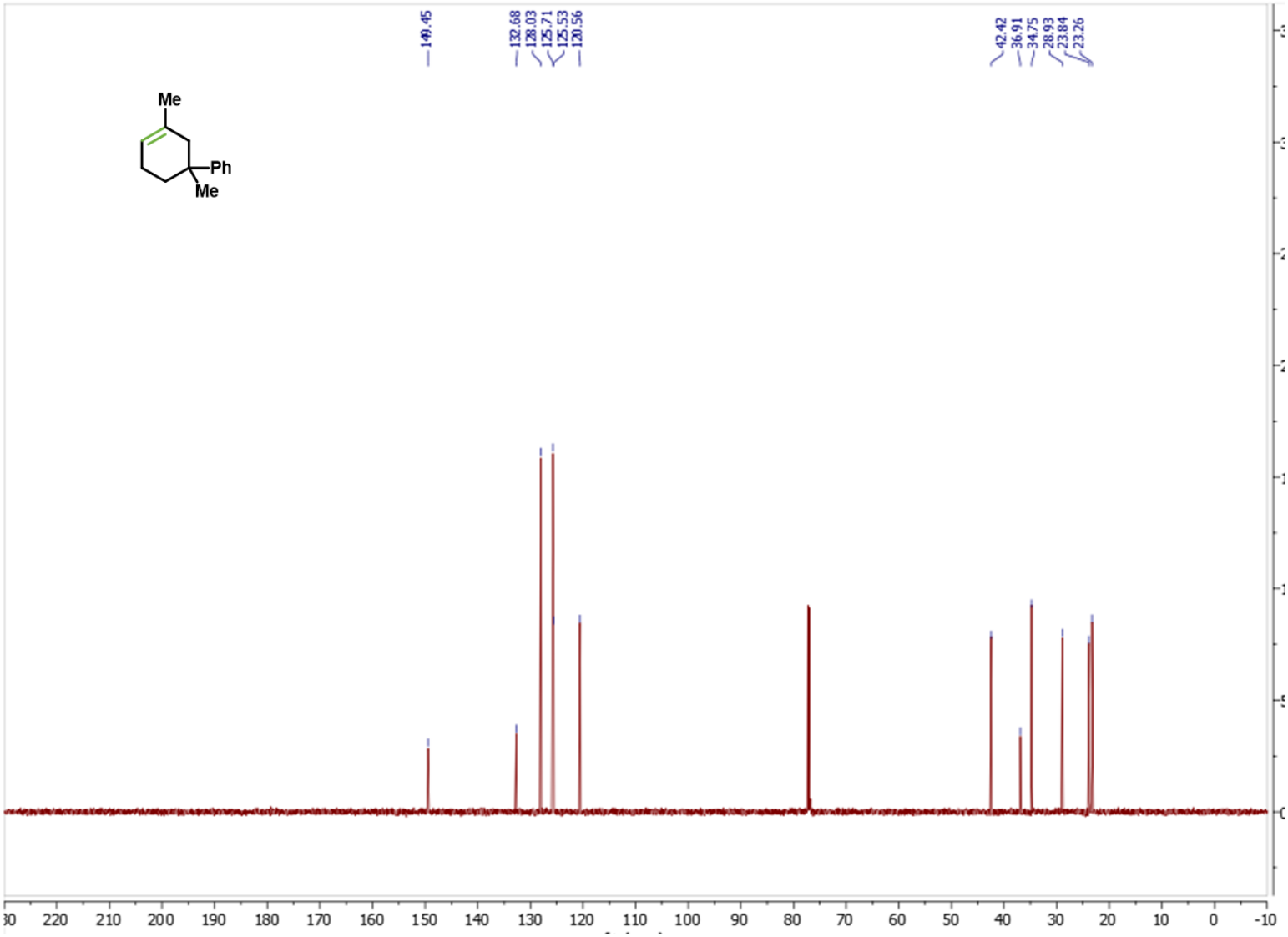
^{13}C NMR (151 MHz, $CDCl_3$) of compound **56**



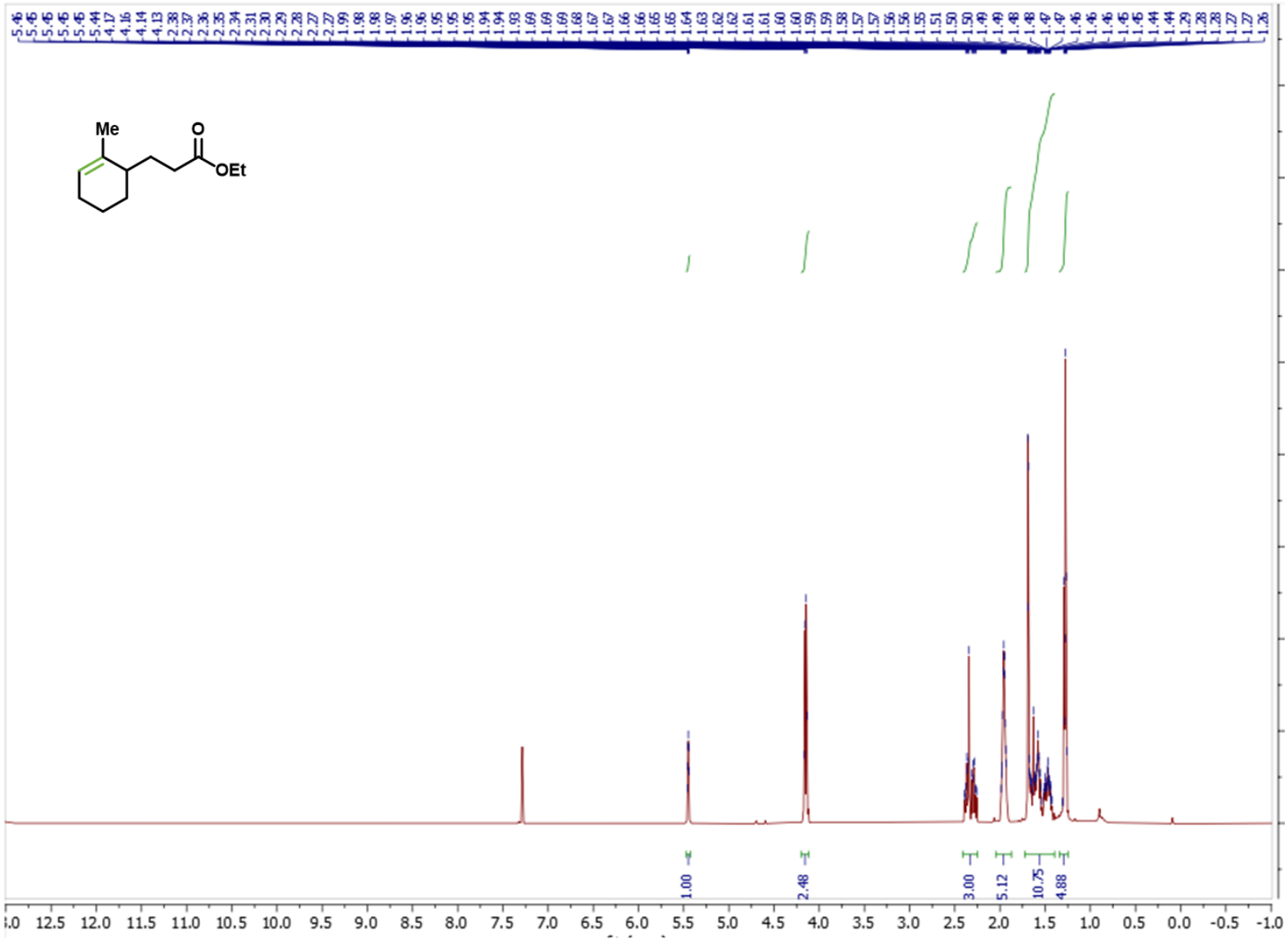
^{1}H NMR (600 MHz, $CDCl_3$) of compound **58**



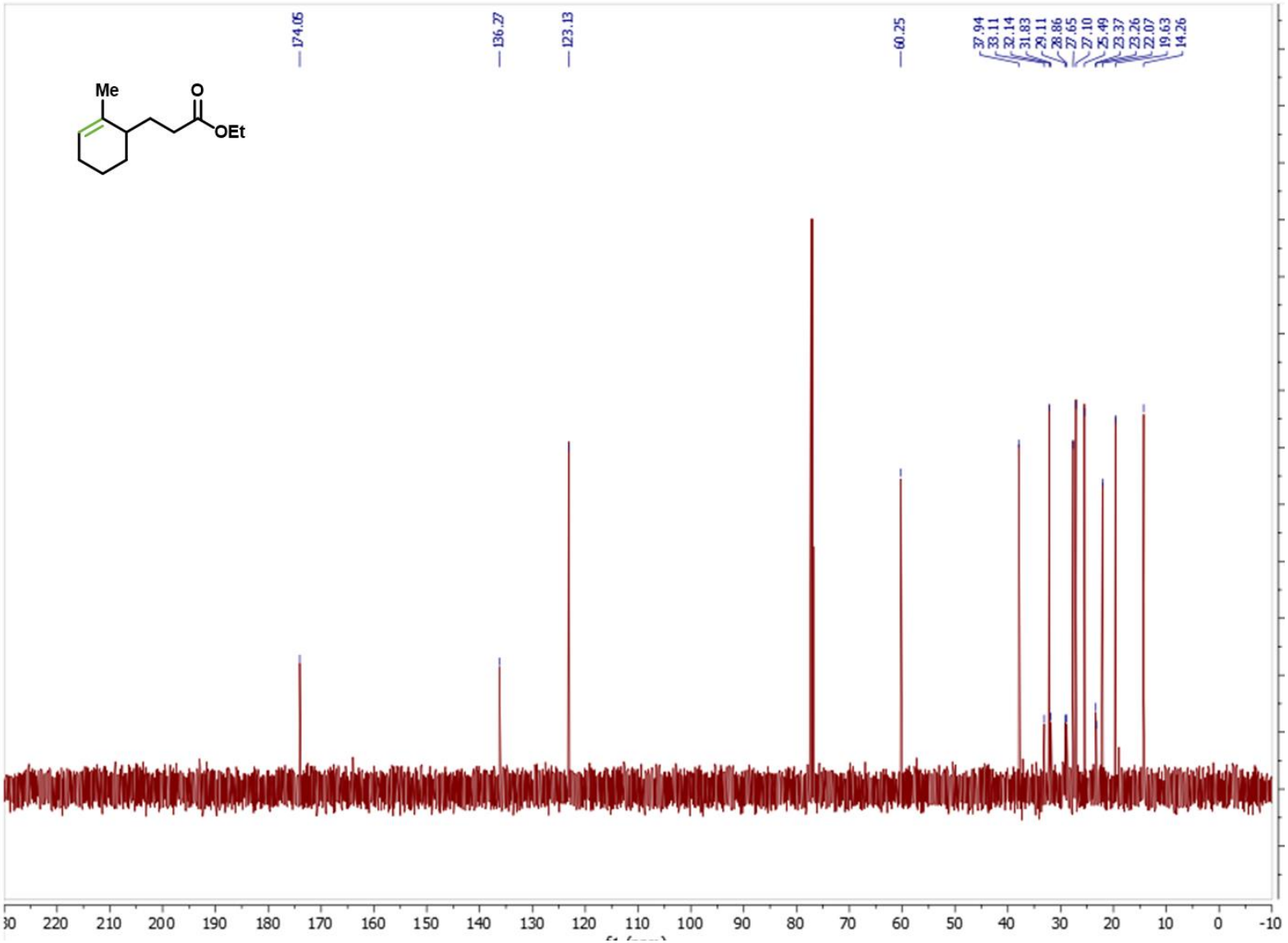
^{13}C NMR (151 MHz, $CDCl_3$) of compound **58**



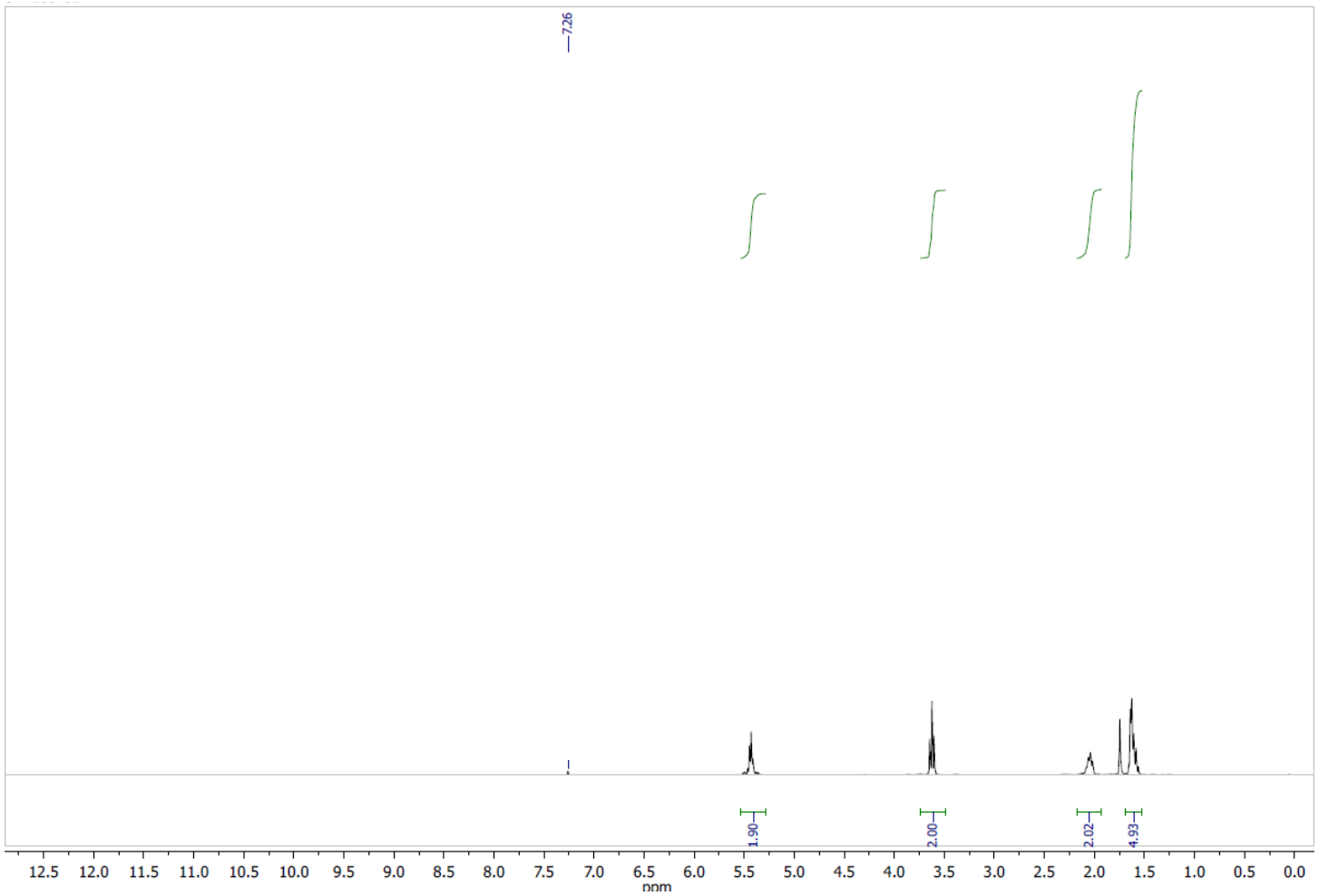
^{1}H NMR (600 MHz, $CDCl_3$) of compound **60**



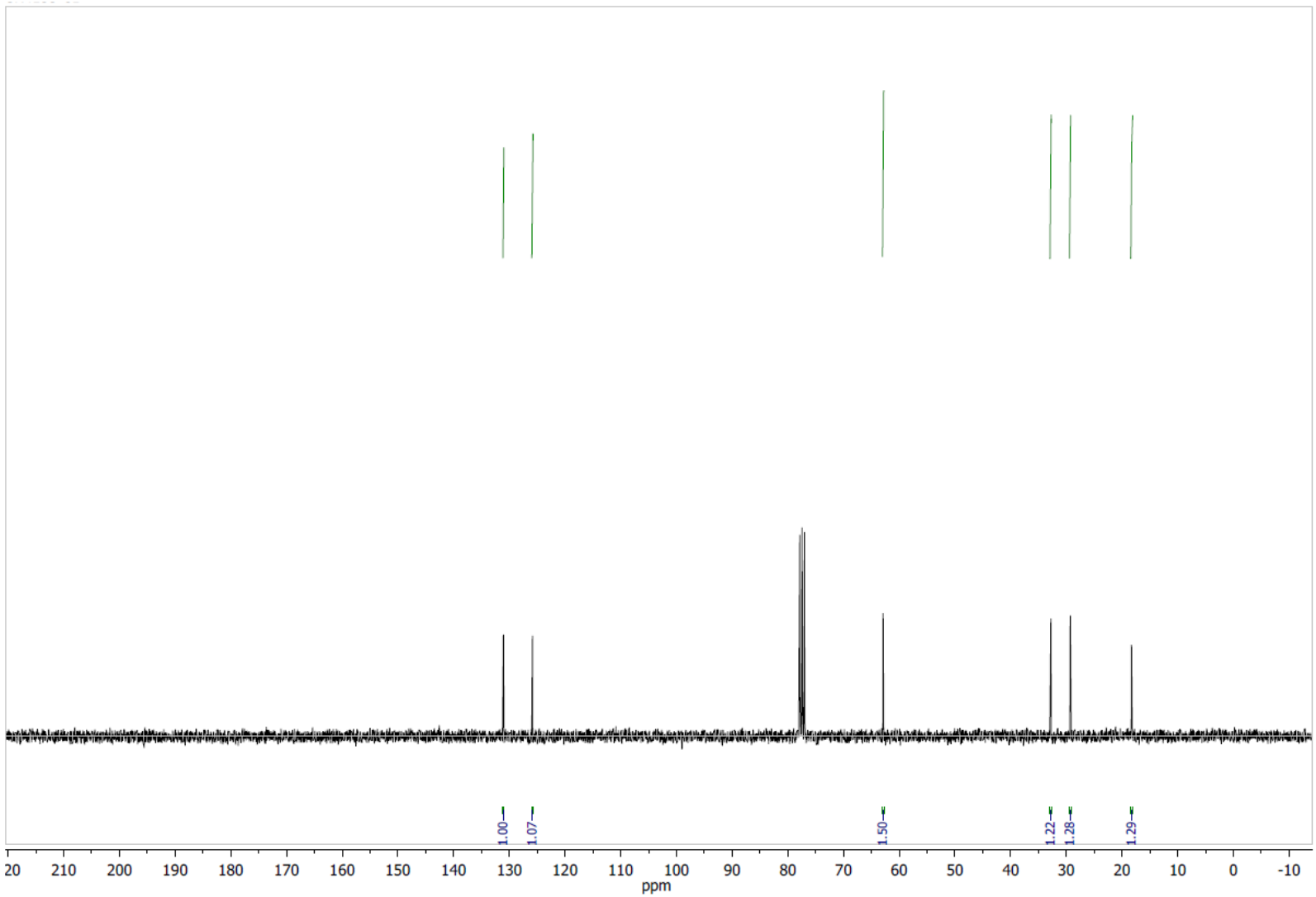
^{13}C NMR (151 MHz, $CDCl_3$) of compound **60**



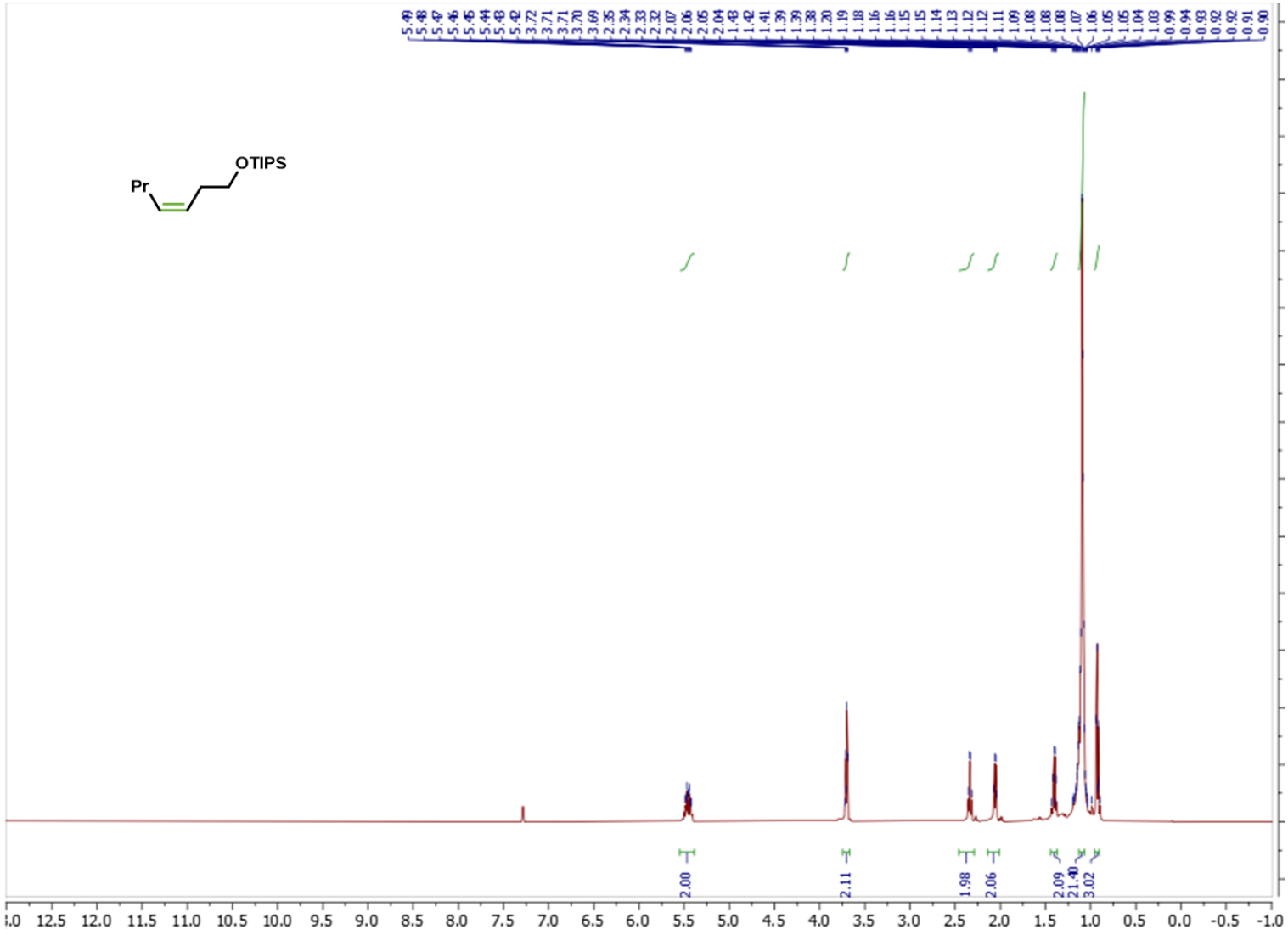
^{1}H NMR (300 MHz, $CDCl_3$) of compound **62**



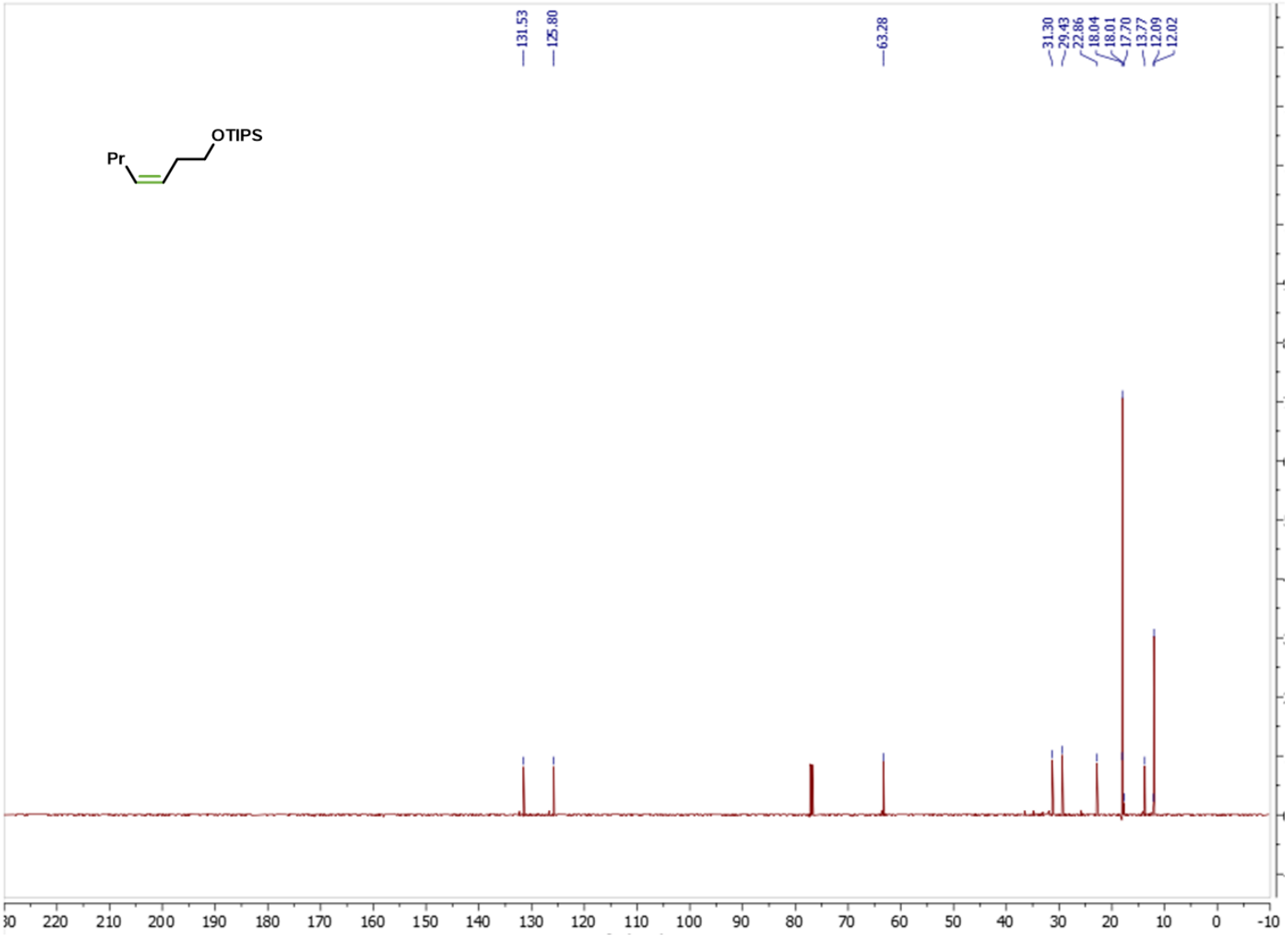
^{13}C NMR (75 MHz, $CDCl_3$) of compound **62**



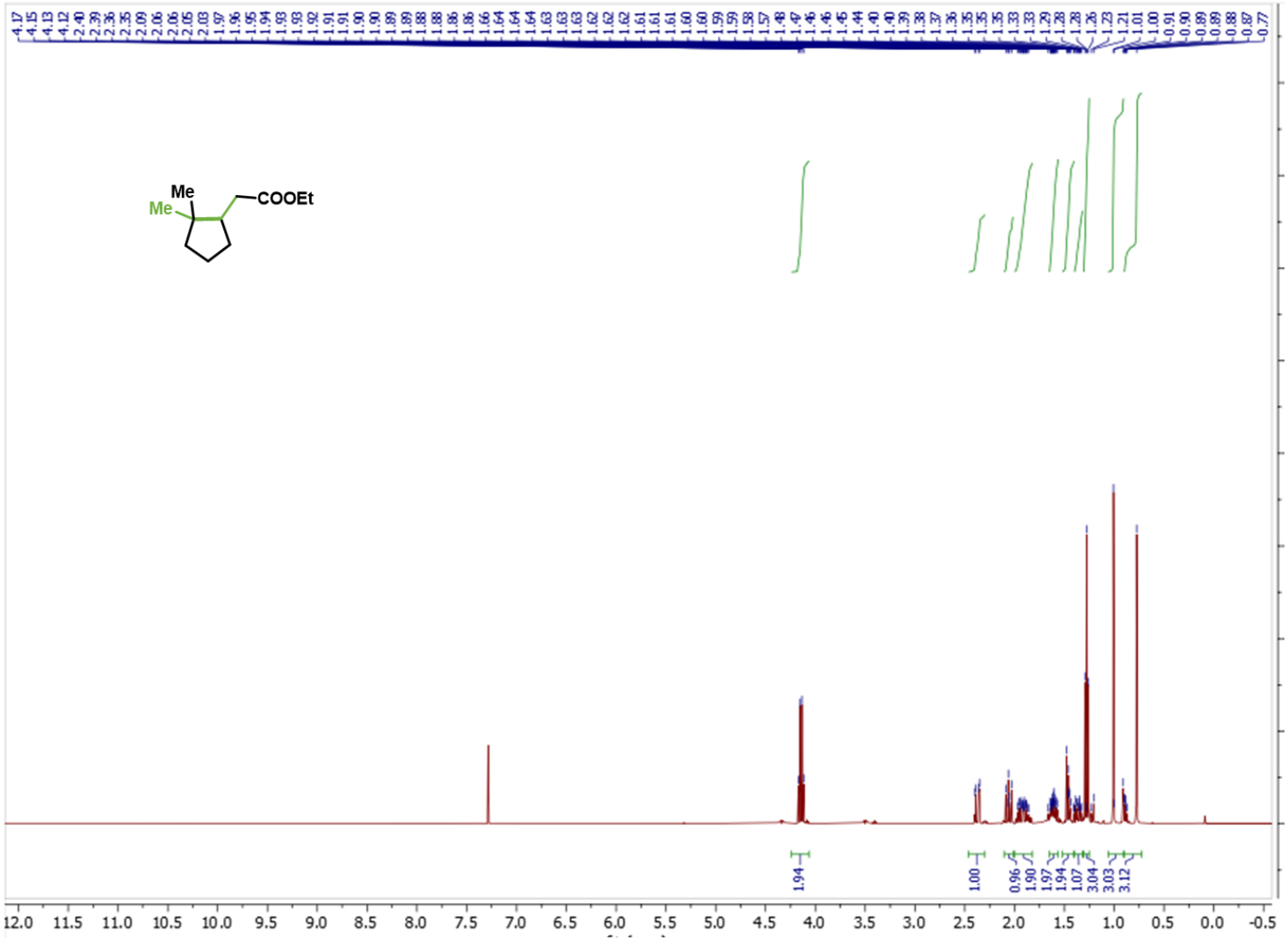
^{1}H NMR (600 MHz, $CDCl_3$) of compound **64**



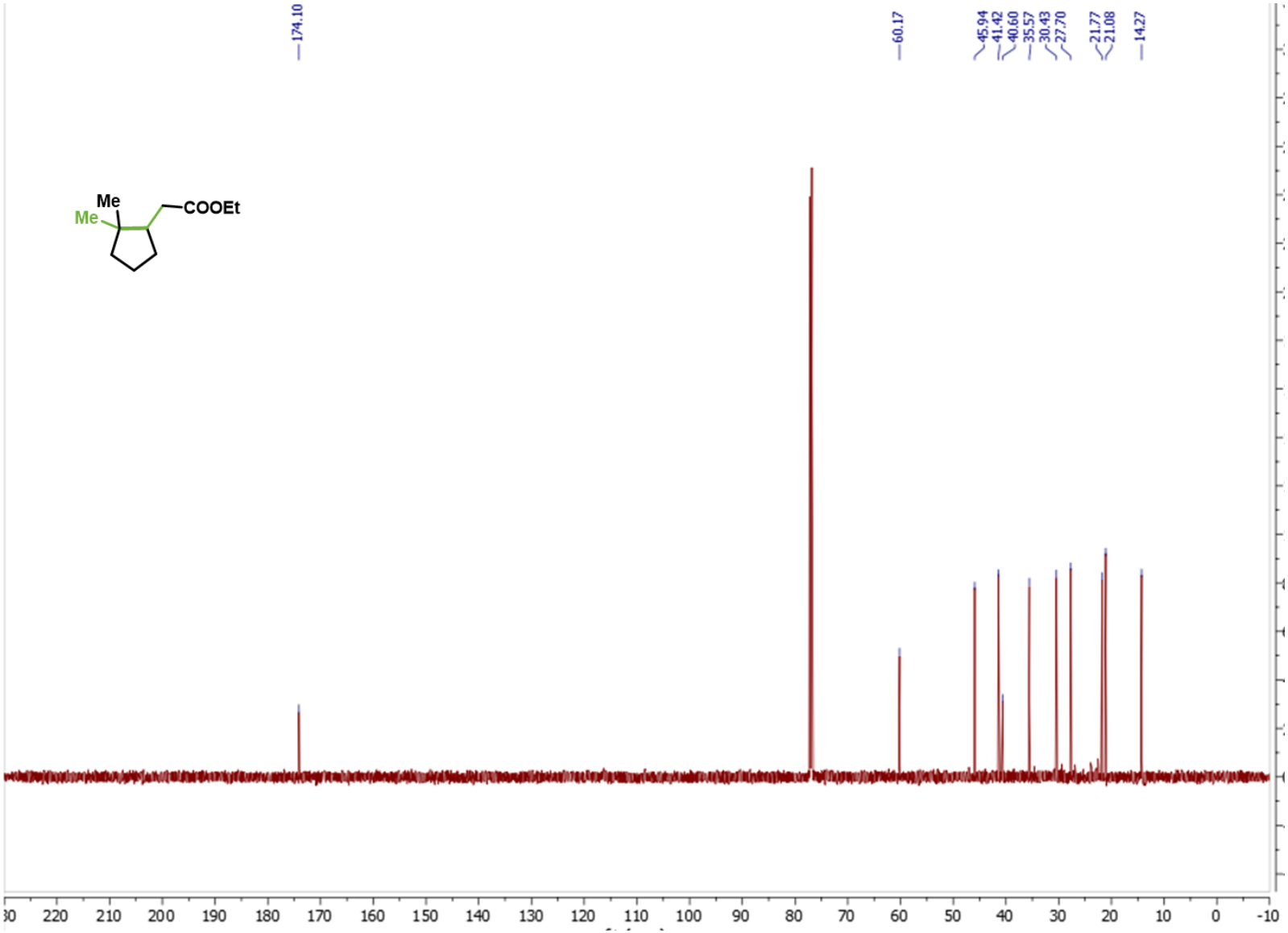
^{13}C NMR (151 MHz, $CDCl_3$) of compound **64**



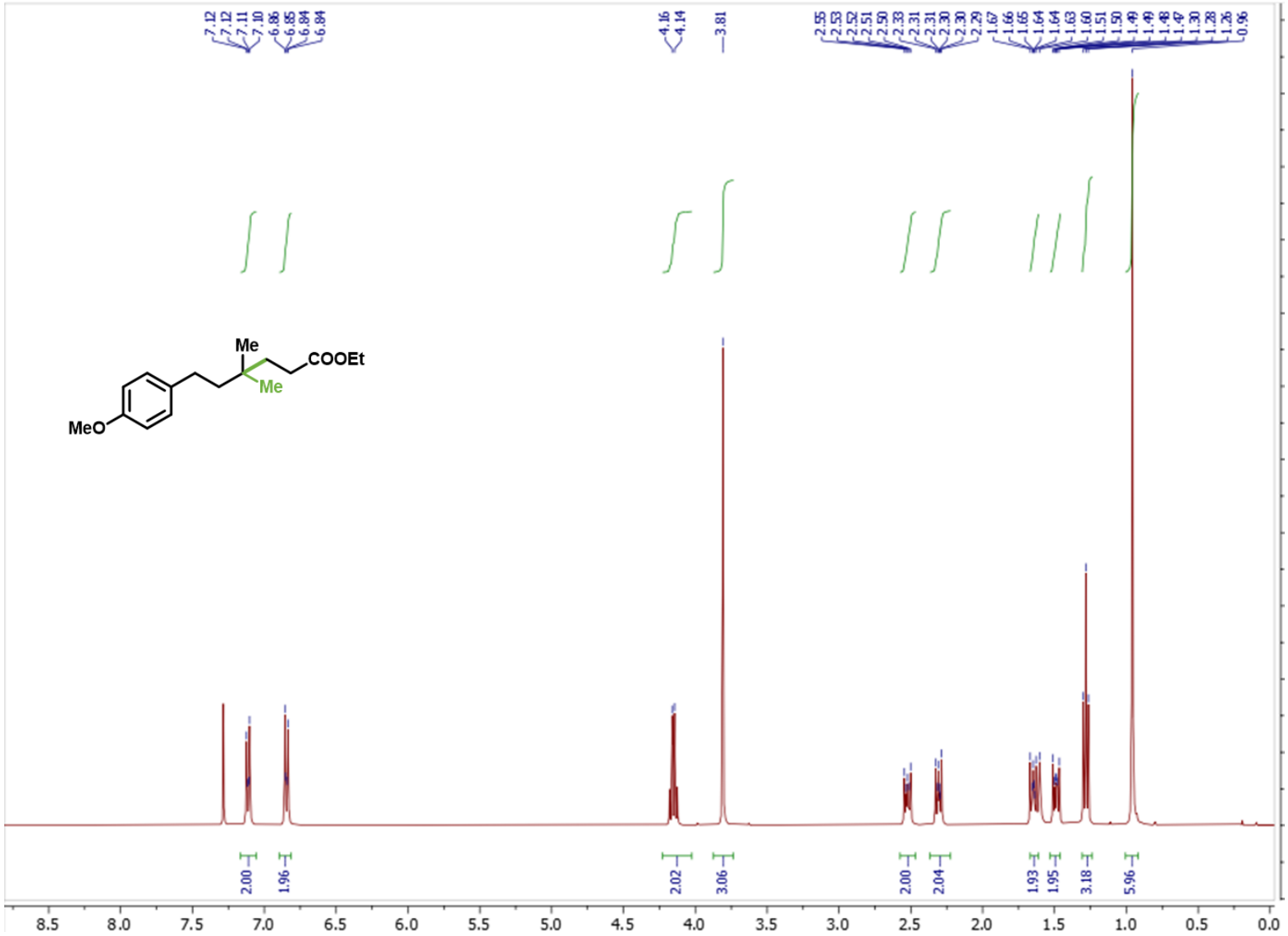
^{1}H NMR (400 MHz, $CDCl_3$) of compound **67**



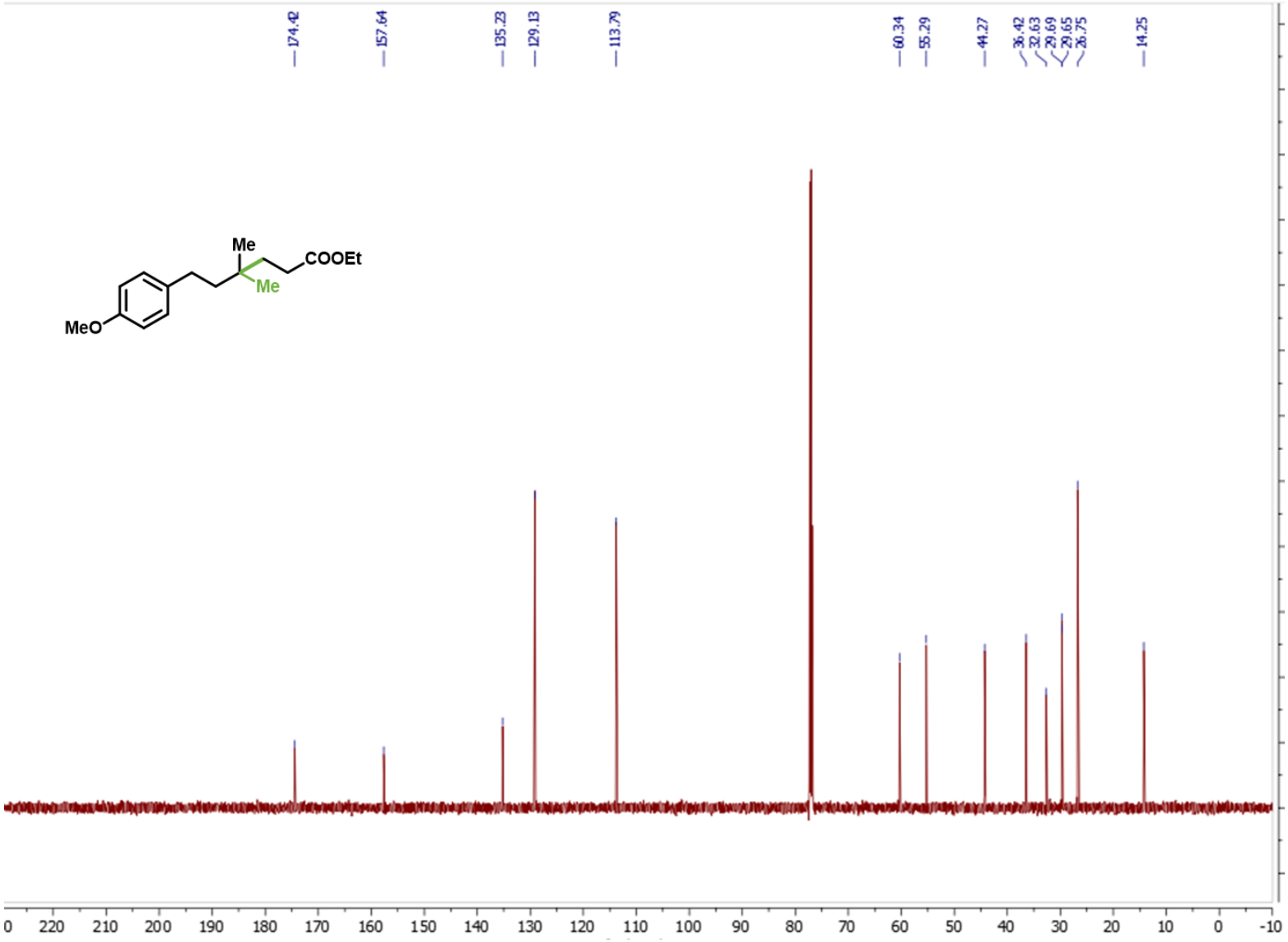
^{13}C NMR (151 MHz, $CDCl_3$) of compound **67**



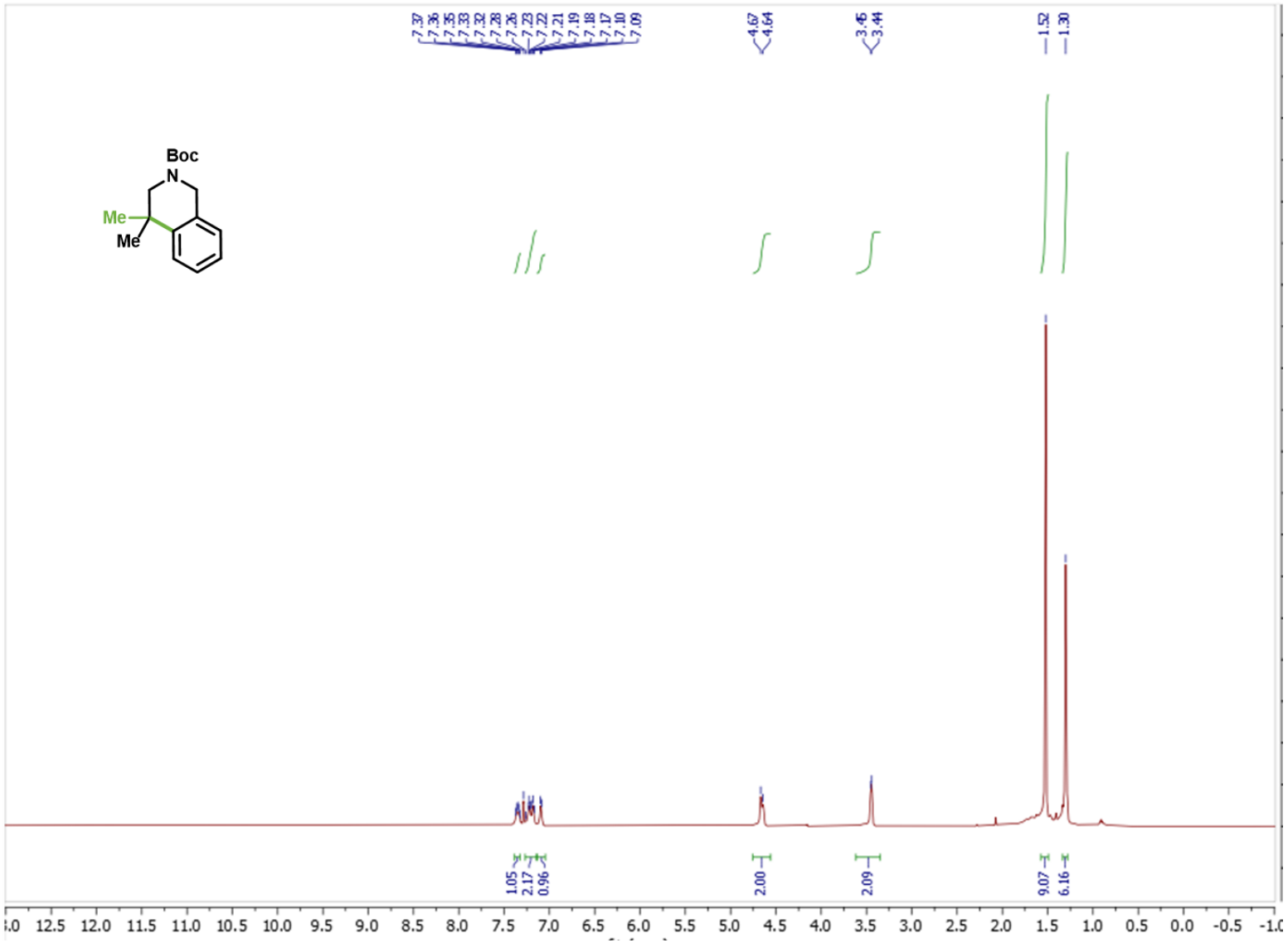
^{1}H NMR (400 MHz, $CDCl_3$) of compound **69**



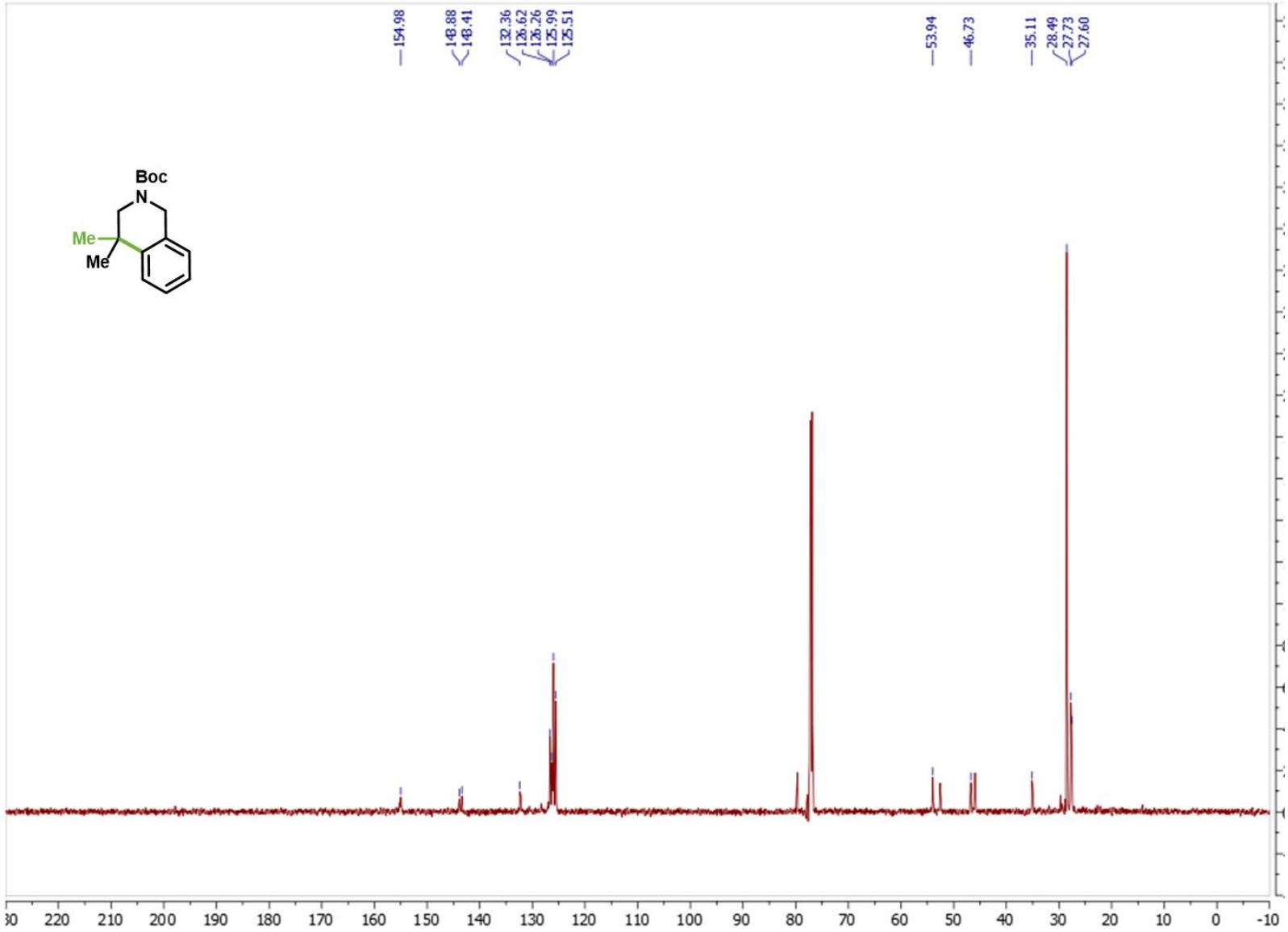
^{13}C NMR (151 MHz, $CDCl_3$) of compound **69**



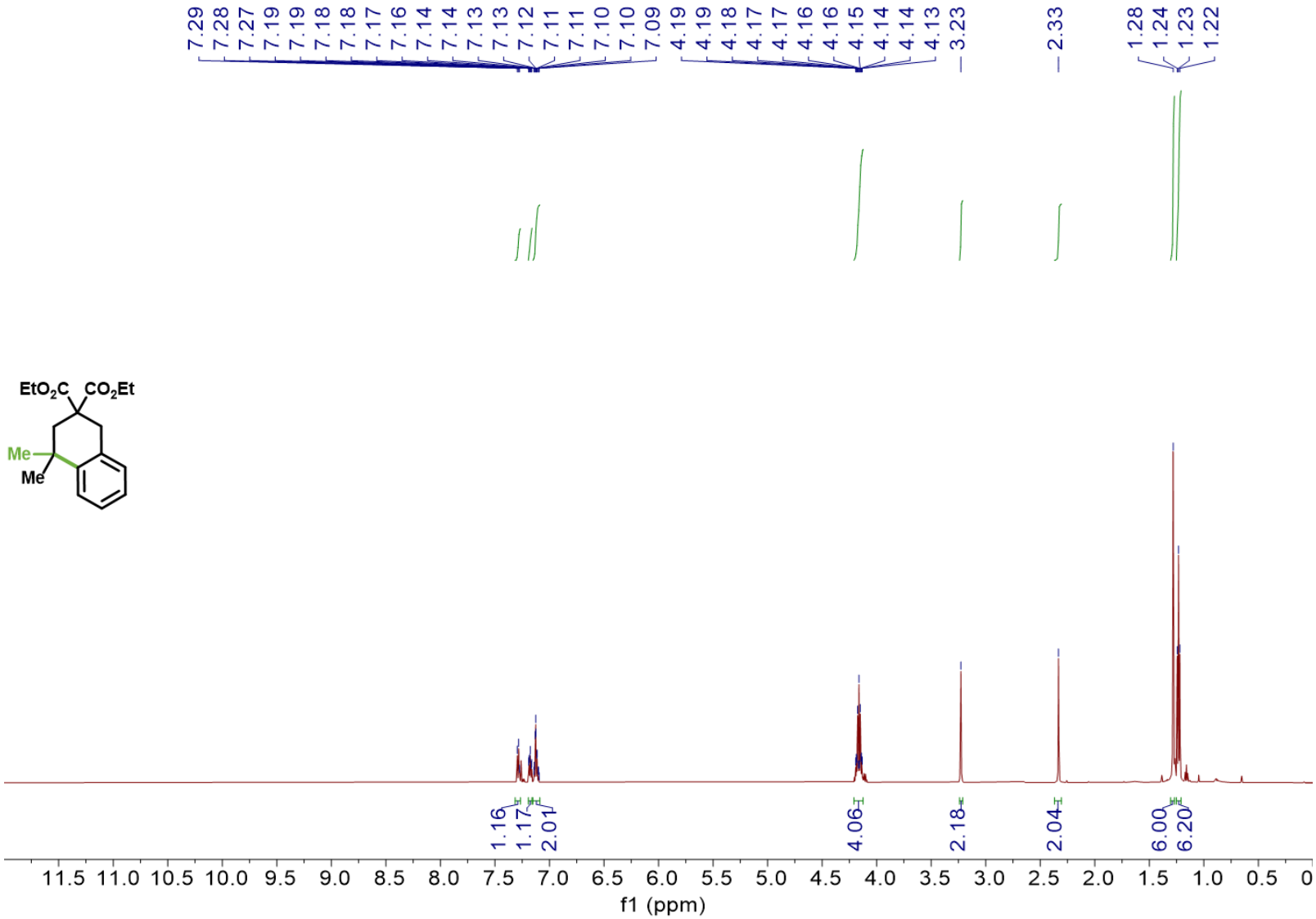
^{1}H NMR (600 MHz, $CDCl_3$) of compound **71a**



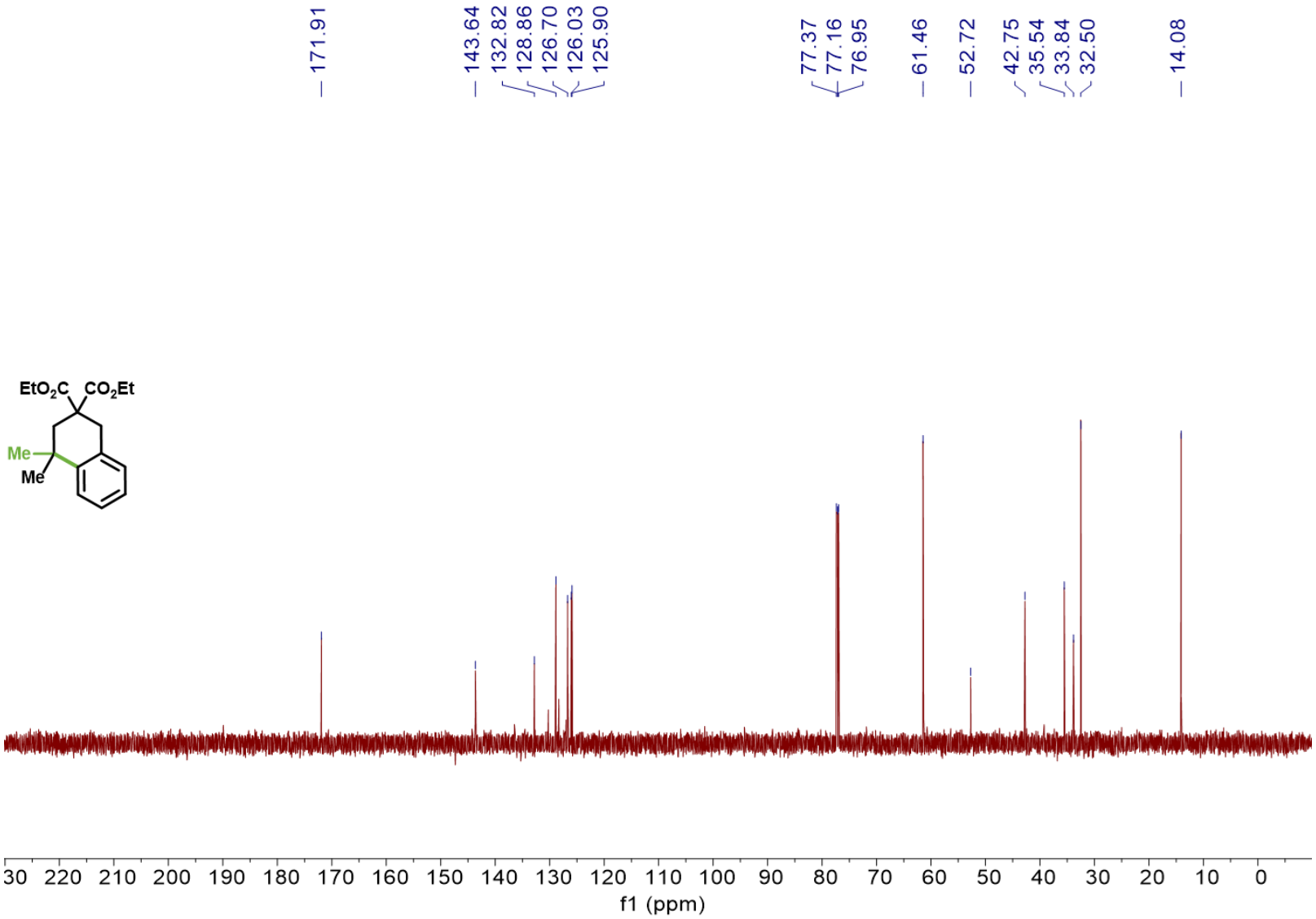
^{13}C NMR (151 MHz, $CDCl_3$) of compound **71a**



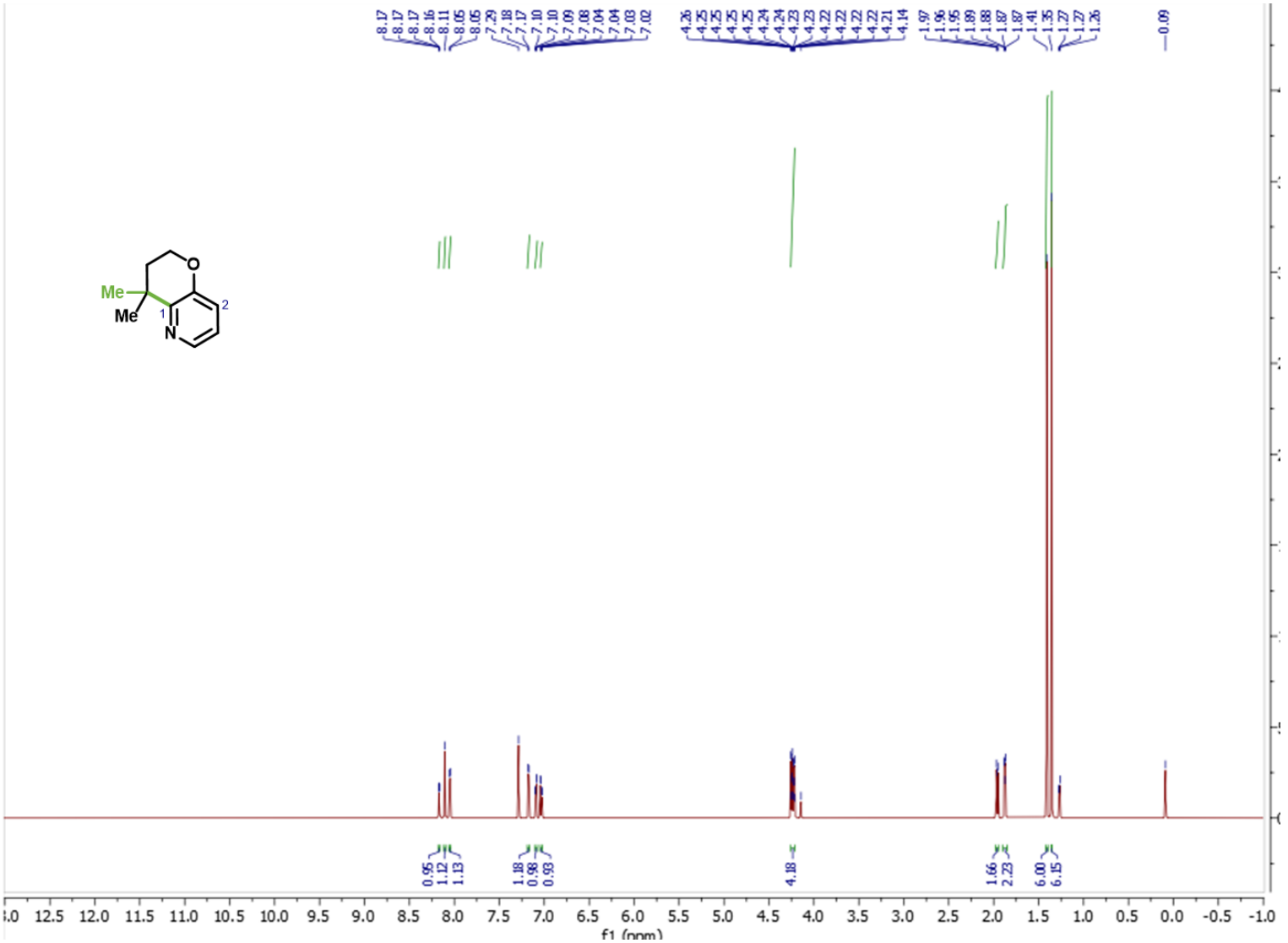
^{1}H NMR (600 MHz, $CDCl_3$) of compound **71b**



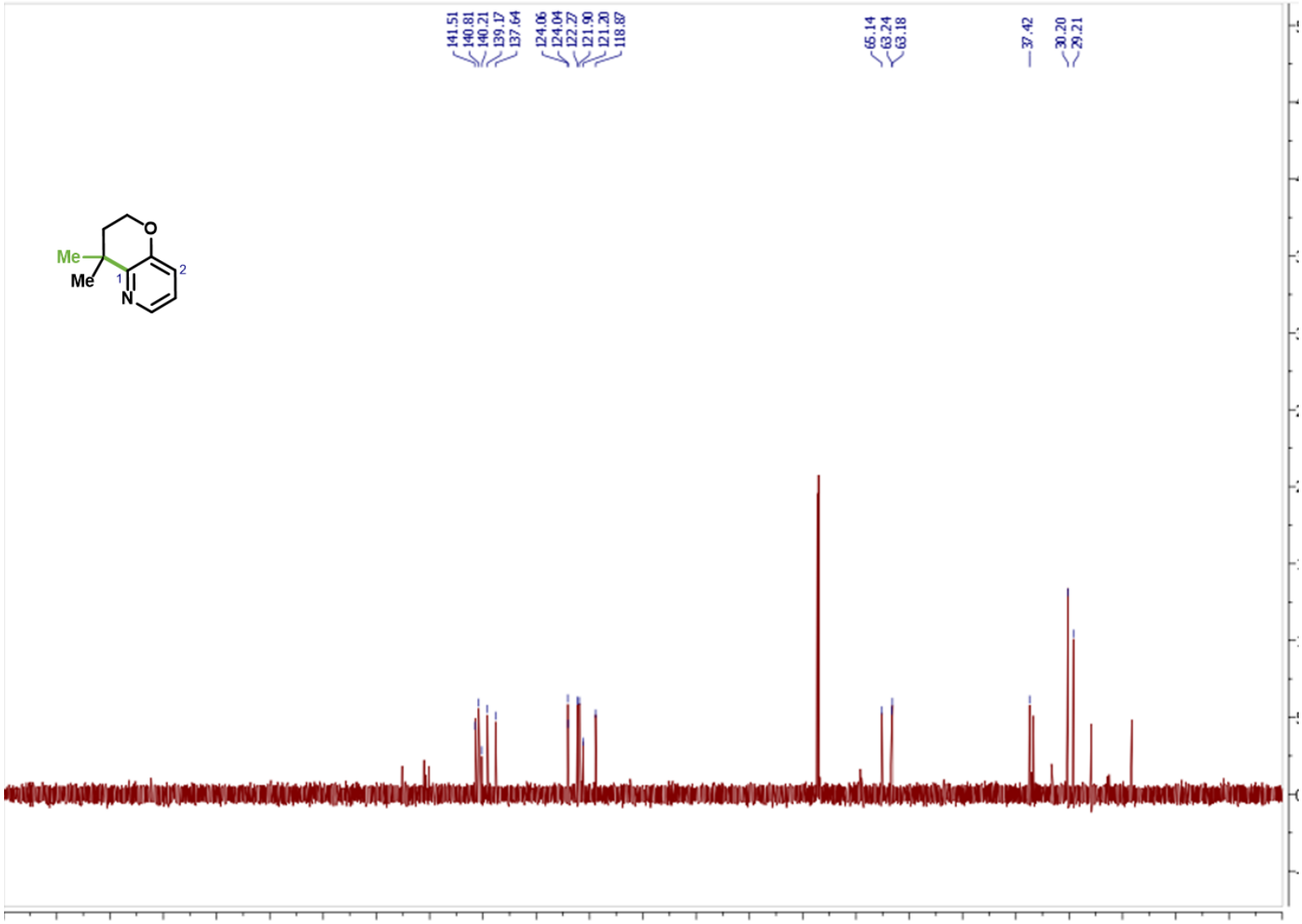
^{13}C NMR (151 MHz, $CDCl_3$) of compound **71b**



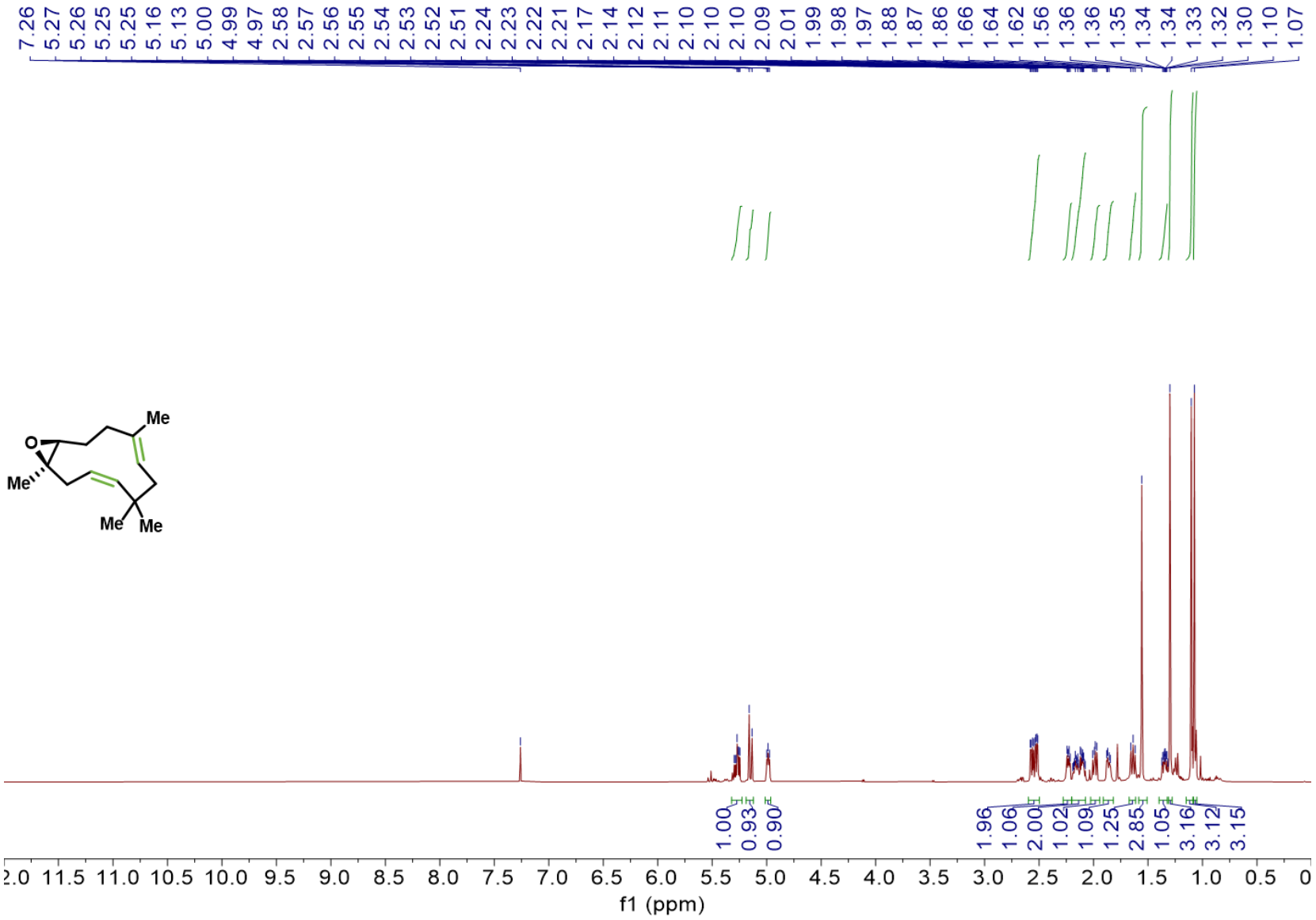
^{1}H NMR (600 MHz, $CDCl_3$) of compound **73**



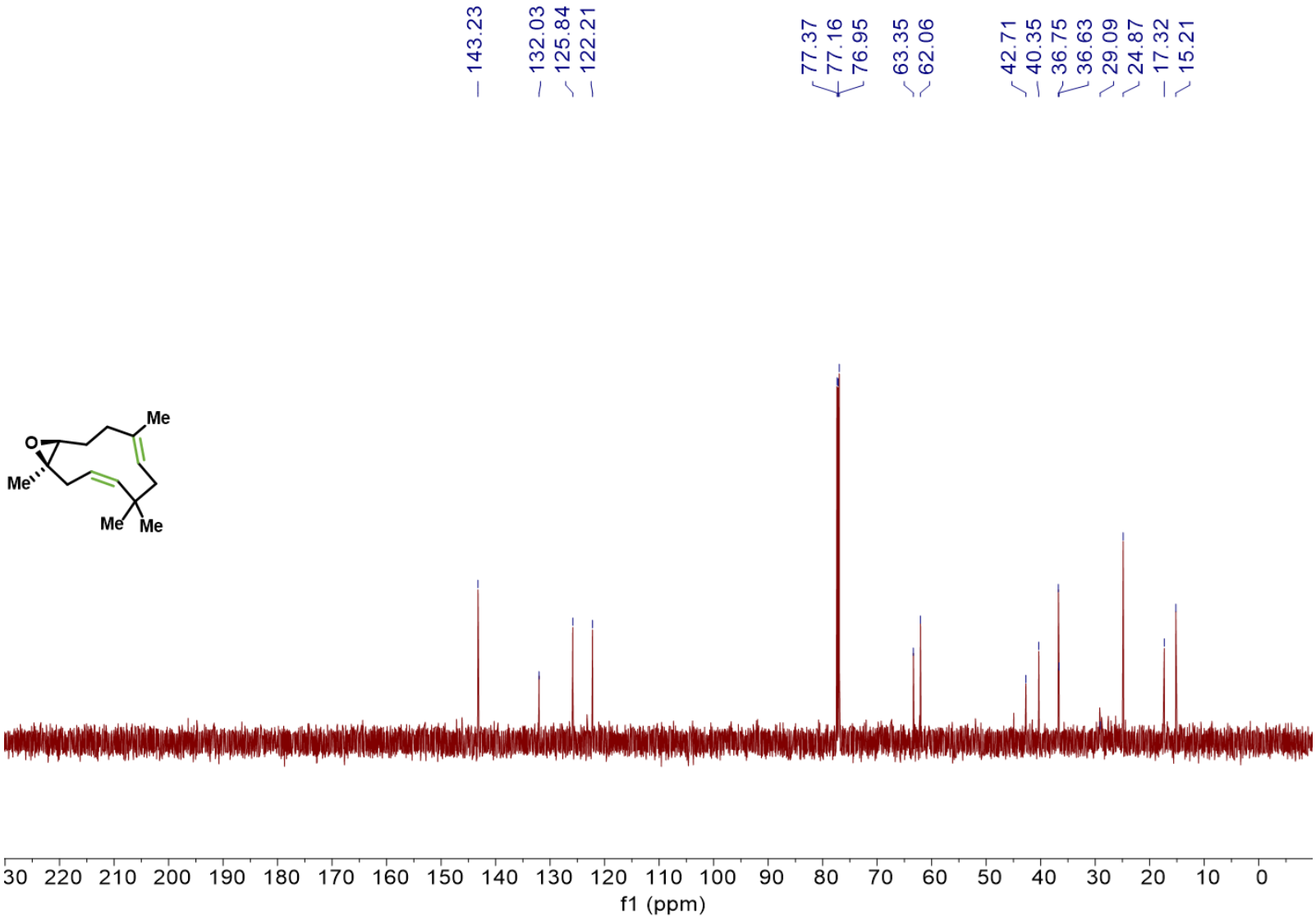
^{13}C NMR (151 MHz, $CDCl_3$) of compound **73**



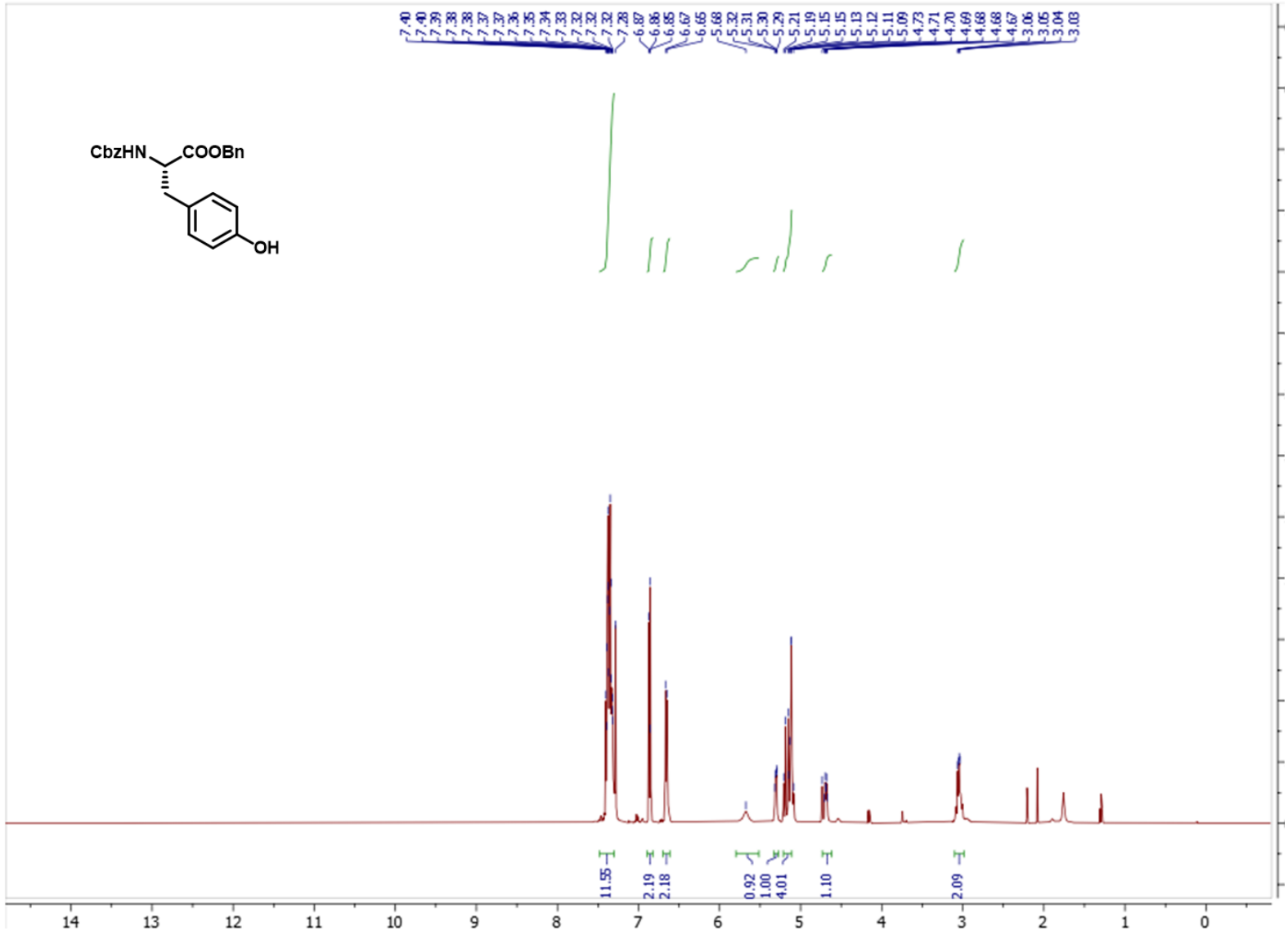
^{1}H NMR (600 MHz, $CDCl_3$) of compound **75**



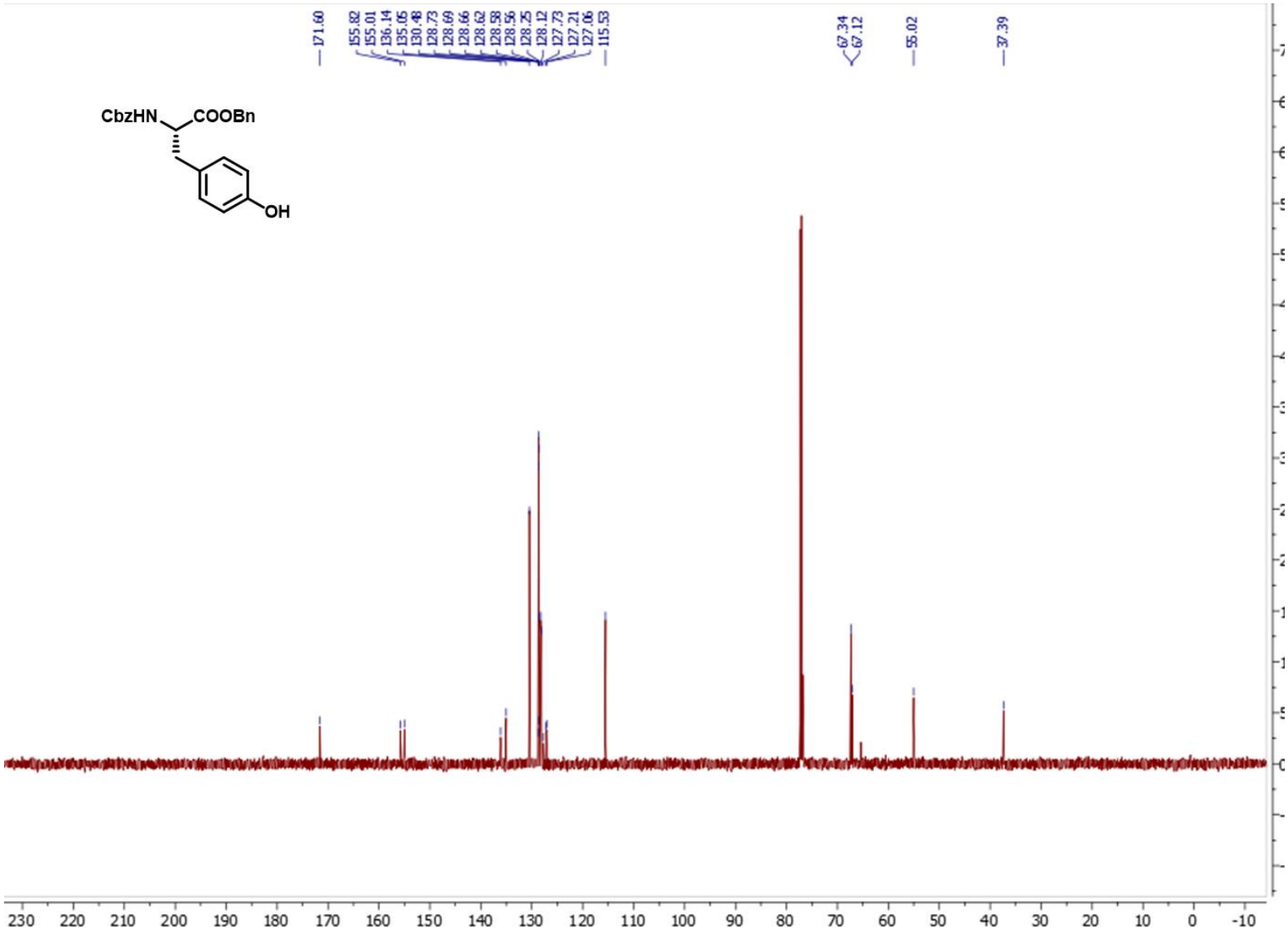
^{13}C NMR (151 MHz, $CDCl_3$) of compound **75**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **77**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **77**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **79**

^{13}C NMR (151 MHz, $CDCl_3$) of compound **79**