Supporting Information for

Natural products inspired [3 + 2] cycloaddition enables efficient construction of hydroxylated tetrahydronfuran acetals and concise syntheses of lignans

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Table of Contents

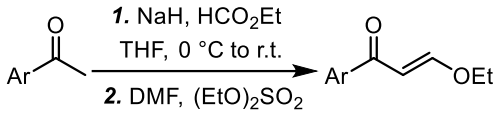
General Experimental

Unless otherwise stated, all reactions were carried out under anhydrous conditions. Super-dried solvents and reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) or LC/MS. TLC was performed using precoated silica gel 60 F254 (Merck), using short-wave UV light as the visualizing agent, and cerium molybdate (CAM or Hanessian's stain), phosphomolybdic acid (PMA), or KMnO4 and heat as developing agents. Flash silica gel chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). NMR data were obtained on Bruker AVANCE III 400, AVANCE III 500, Ascend 600 and/or Ascend 800 NMR spectrometers referenced to deuterated solvent peaks (δ_H 7.26 in $CDCl_3$ or 1.94 in acetonitrile-d_3, δ_C 77.16 in $CDCl_3$, 118.3 in acetonitrile-d_3 or 49.00 in CD_3OD).

The X-ray diffraction analysis was performed on a Bruker SMART CCD detector employing graphite monochromated Cu-Kα radiation. Melting points were recorded on an SGM X-4 apparatus. ESIMS and HRESIMS were implemented on a Bruker Daltonics Esquire 3000 plus and Waters-Micromass Q-TOF Ultima Global mass spectrometer, respectively.

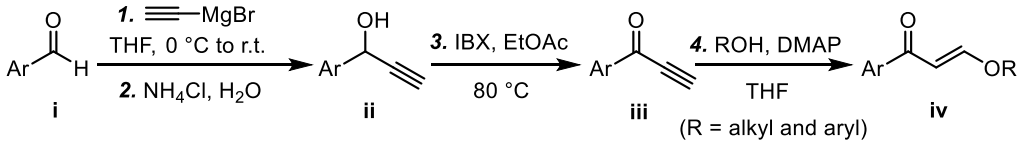
General Procedures for the Synthesis of *β*-Keto Enol Ethers

General Procedure A



In air, a 100 mL round-bottom flask equipped with a magnetic stir-bar was charged with NaH (60% in oil, 0.24 g, 6 mmol, 1.2 eq.), which was suspended in 15 mL of super-dried THF. Ethyl formate (571 μL, 6 mmol, 1.2 eq.) was added to the suspension. Then, aromatic methyl ketone (5 mmol, 1 eq.) was added dropwise at 0 ℃. The mixture was stirred for at least 1 hour until the solution gave an orange or pink precipitate. The solvent was removed under reduced pressure, and the remaining reaction mixture was dissolved in 15 mL of super-dried DMF. Diethyl sulfate (786 μL, 6 mmol, 1.2 eq.) was added dropwise to the red solution. The mixture was stirred for another 2 hours at room temperature before being quenched with water (20 mL). The aqueous phase was extracted with ethyl acetate (20 mL × 3) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (gradient 5%→15% EtOAc in petroleum ether) afforded the desired ethyl *β*-keto enol ether.

General Procedure B

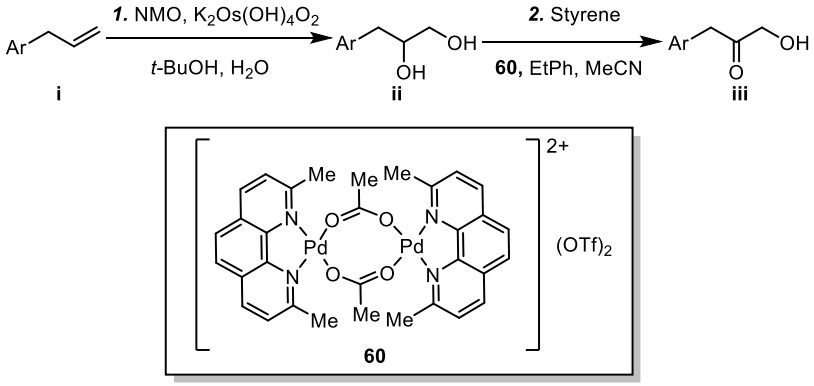


To a 100 mL round-bottom flask equipped with a magnetic stir-bar and aromatic aldehyde (**i**, 5 mmol, 1 eq.) was added 10 mL of super-dried THF under Ar atmosphere. Then 15 mL of 0.5 M ethynylmagnesium bromide solution in THF was added dropwise at 0 ℃. The mixture was stirred until the aldehyde was completely consumed, as monitored by TLC. Then the reaction was quenched with saturated ammonia chloride

solution (5 mL). Another 20 mL of water was added, the aqueous phase was extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (gradient 15%→33% EtOAc in petroleum ether) afforded the alcohol (**ii**). The alcohol (**ii**) was then dissolved in 25 mL of super-dried ethyl acetate. IBX (2.8 g, 10 mmol, 2 eq.) was added to the solution. The mixture was stirred for 4 hours at 80 ℃, and was then filtered to remove the excess IBX. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (gradient 10%→ 25% EtOAc in petroleum ether) to afford the acetylenic ketone (**iii**). Then, the acetylenic ketone (**iii**, 4 mmol, 1 eq.) was dissolved in 40 mL of super-dried THF. To the solution was added alcohol (4.8 mmol, 1.2 eq.) and DMAP (0.4 mmol, 0.1 eq.). The mixture was stirred for 4 hours until all the starting materials were consumed. Then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (gradient 5%→20% EtOAc in petroleum ether) to afford the desired *β*-keto enol ether (**iv**) (For details of procedure for step 4, see the following reference).

Reference: Shi, Y.; Bai, T.; Bai, W.; Wang, Z.; Chen, M.; Yao, B.; Sun, J. Z.; Qin, A.; Ling, J.; Tang, B. Z. *Chem. Eur. J.* **2017**, *23*, 10725–10731.

General Procedure for the Synthesis of *α*-Hydroxyphenylacetone



The allylbenzene (**i**, 5 mmol, 1 eq.) was dissolved in 90 mL of 1∶1(v/v) *t*-

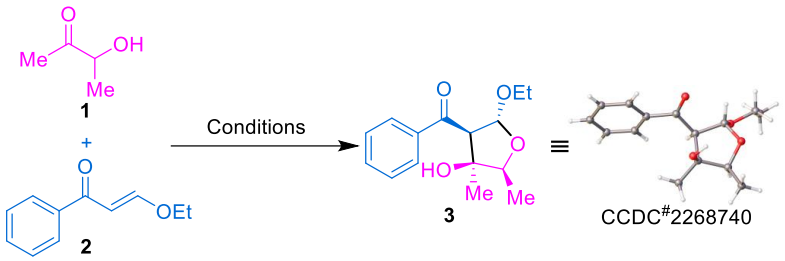
BuOH/water in a 250 mL round-bottom flask equipped with a magnetic stir-bar. NMO (1.76 g, 15 mmol, 3 eq.) and catalytic amount of $K_2Os(OH)_4O_2$ (9.2 mg, 0.5 mol%) were sequentially added to the solution. The reaction mixture was stirred overnight and turned dark yellow. The mixture was diluted with 10 mL of saturated $Na_2S_2O_3$ solution. The aqueous phase was extracted with ethyl acetate (20 mL × 3), and the combined organic layers were washed with saturated $Na_2S_2O_3$ solution and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (gradient 50%→100% EtOAc in petroleum ether) afforded the diol (**ii**). The diol (**ii**, 4.93 mmol, 1 eq.), styrene (847 μL, 7.39 mmol, 1.5 eq.) and dimethylsulfone (46.4 mg, 0.493 mmol, 0.1 eq.) were dissolved in 16 mL of 1:1(v/v) MeCN/EtPh in a 50 mL round-bottom flask equipped with a magnetic stir-bar. The Pd catalyst (10.3 mg, 0.4 mol% Pd) was dissolved in 1 mL of super-dried MeCN, and the resulting solution was added dropwise to the reaction mixture. The mixture was stirred for about 2 days in open air until the diol (**ii**) was completely consumed, as monitored by TLC. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (gradient 33%→50% EtOAc in Petroleum ether) to afford the α-hydroxyketone (For details of procedure for step 2, see the following reference).

Reference: Ho, W. C.; Chung, K.; Ingram, A. J.; Waymouth, R. M. *J. Am. Chem. Soc.* **2018**, *140*, 748–757.

Optimization of the Reaction Conditions of 1 and 2

Tables S1 to S3 provide the full details of the optimization processes.

Table S1. Optimization: For Catalyst

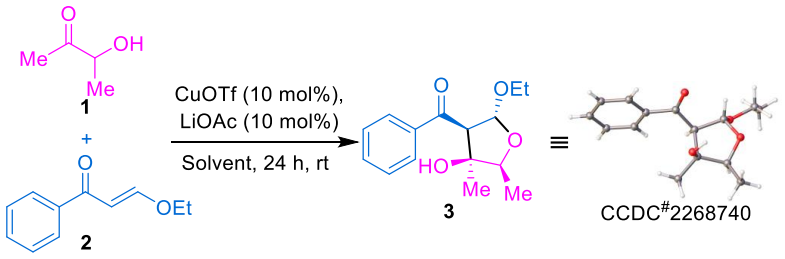


entry	Condition	Time	yield (%)[e]
1	$Pd(OAc)_2$, THF, reflux[a]	2 weeks	48
2	Bis(dibenzylideneacetone)palladium (0), DCM, rt[b]	5 days	53
3	Tris(dibenzylideneacetone)dipalladium (0)-chloroform adduct, DCM, rt[b]	1 week	33
4	Bis(tri-tert-butylphosphine) palladium (0), DCM, rt[b]	1 week	33
5	$[RhCp^*Cl_2]_2$, $AgBF_4$, BINAP, THF, rt[c]	20 hours	53
6	CuOTf, LiOAc, THF, rt[d]	24 hours	80 (89)
7	$Cu(OTf)_2$, LiOAc, THF, rt[d]	24 hours	68 (82)
8	CuCl, LiOAc, THF, rt[d]	24 hours	66 (74)
9	CuBr, LiOAc, THF, rt[d]	24 hours	73 (84)
10	CuI, LiOAc, THF, rt[d]	24 hours	46 (95)
11	CuOAc, THF, rt[d]	24 hours	44
12	CuOAc, LiOTf, THF, rt[d]	24 hours	43
13	$Ni(OTf)_2$, LiOAc, THF, rt[d]	24 hours	15
14	$Co(OTf)_2$, LiOAc, THF, rt[d]	24 hours	24
15	$Fe(OTf)_3$, LiOAc, THF, rt[d]	24 hours	decomposed

16	$Zn(OTf)_2$, LiOAc, THF, rt[d]	24 hours	57
17	$Mg(OTf)_2$, LiOAc, THF, rt[d]	24 hours	trace
18	$Ga(OTf)_3$, LiOAc, THF, rt[d]	24 hours	not detected

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), THF (1 mL), reflux, 2 weeks; [b]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), [Pd] (10 mol %), DCM (1 mL), rt, 5 days; [c]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgBF_4$ (10 mol %), BINAP (10 mol %), THF (1 mL), rt, 20 h; [d]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), [M] (10 mol %), lithium salt (10 mol %), THF (1 mL), rt, 24 h; [e]Yields of isolated products. The yields in parentheses are those obtained based on recovery of starting materials. Abbreviations: THF = tetrahydrofuran; DCM = dichloromethane.

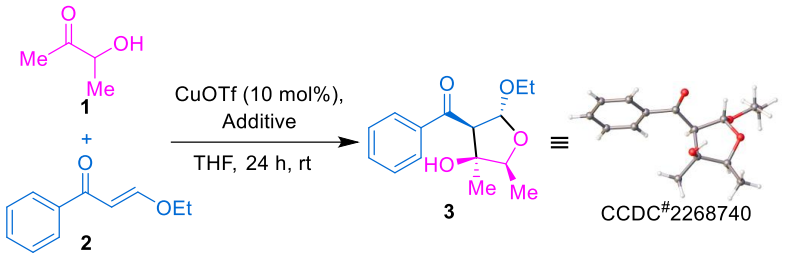
Table S2. Optimization: For Solvent



entry	Solvent	yield (%)[b]
1	MeCN	44 (75)
2	HFIP	17
3	DCM	53 (88)
4	MTBE	56 (80)
5	DME	66 (77)
6	DMF	23
7	THF	80 (89)

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), cuprous triflate (10 mol %), lithium acetate (10 mol %), solvent (1 mL), rt, 24 h; [b]Yields of isolated products. The yields in parentheses are those obtained based on recovery of starting materials. Abbreviations: THF = tetrahydrofuran; HFIP = hexafluoroisopropanol; DCM = dichloromethane; MTBE = methyl *tert*-butyl ether; DME = 1,2-dimethoxyethane; DMF = *N*,*N*-dimethylformamide.

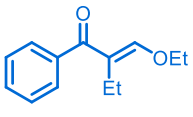
Table S3. Optimization: For Additive



entry	Additive	yield (%)[b]
1	none	64
2	without [Cu]	n.d.
3	LiOAc	80 (89)
4	NaOAc	trace
5	KOAc	trace

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), cuprous triflate (10 mol %), additive (10 mol %), THF (1 mL), rt, 24 h; [b]Yields of isolated products. The yields in parentheses are those obtained based on recovery of starting materials. Abbreviations: THF = tetrahydrofuran.

Limited Substrates



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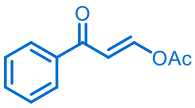

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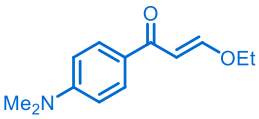

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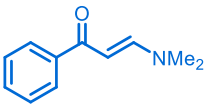

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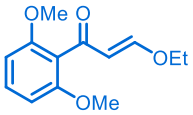

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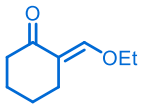

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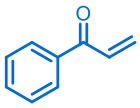

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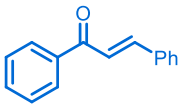

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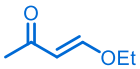

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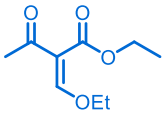

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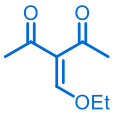

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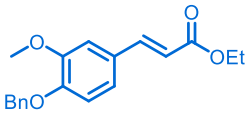

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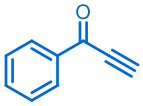

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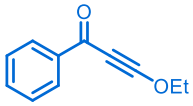

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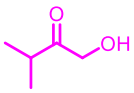

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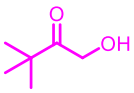

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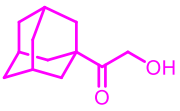

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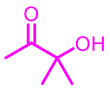

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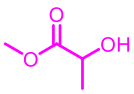

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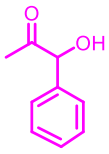

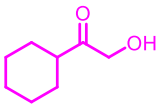

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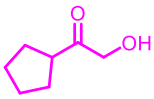

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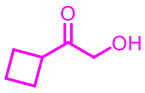

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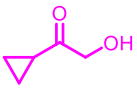

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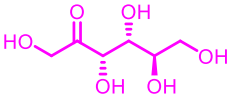

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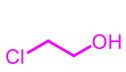

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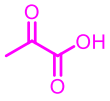

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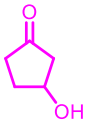

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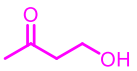

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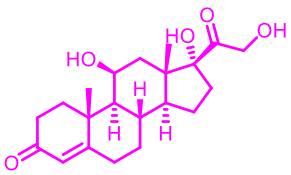

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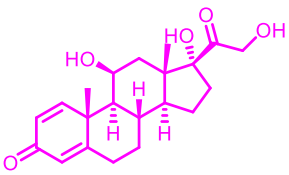

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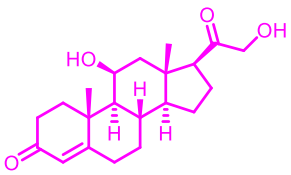
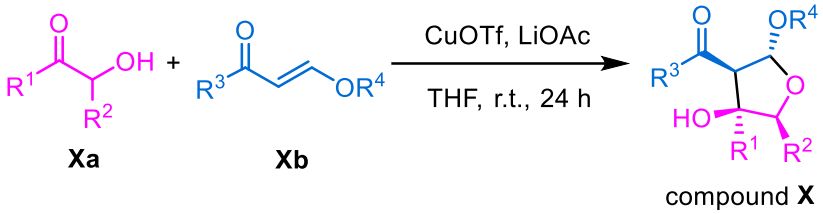


Trace, MS detected

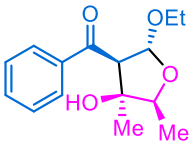
General Procedure for Cu-Catalyzed [3 + 2] Cycloaddition of *α*-Hydroxyketone with *β*-Keto Enol Ethers



The *α*-hydroxyketone (**Xa**, 0.2 mmol. 1 eq.) and *β*-keto enol ethers (**Xb**, 0.2 mmol, 1 eq.) were dissolved in 1 mL of super-dried THF. CuOTf (10 mol%) and LiOAc (10 mol%) was added to the solution. The mixture was stirred for 24 hours until the starting materials were consumed, as monitored by TLC. The reaction mixture turned green or blue. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (gradient 5%→25% EtOAc in petroleum ether) to afford the desired tetrahydrofuran derivatives (compound **X**).

Synthetic Procedures and Characterization Data

Compound 3:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 80% yield (42 mg).

Physical State: white solid;

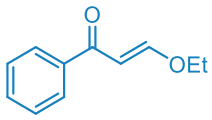
TLC: R_f = 0.40 (PE∶EtOAc = 9∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.98 (m, 2H), 7.65 – 7.57 (m, 1H), 7.49 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.38 (d, *J* = 4.4 Hz, 1H), 4.07 (q, *J* = 6.3 Hz, 1H), 4.05(d, *J* =4.4 Hz, 1H), 3.80 (dq, *J* = 9.6, 7.1 Hz, 1H), 3.45 (dq, *J* = 9.6, 7.1 Hz, 1H), 1.26 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.0, 137.5, 134.0, 129.1, 128.8, 104.5, 82.0, 80.7, 64.4, 63.0, 22.2, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{15}H_{20}NaO_4$ $[M + Na]^+$: 287.1254, found: 287.1253.

Compound 3a:

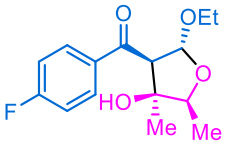


(E)-3-ethoxy-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 42% yield (0.37g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org*. *Lett*. **2022**, *24*, 6716–6721.

Compound 4:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(4-fluorophenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 71% yield (40 mg).

Physical State: colorless crystal;

TLC: R_f = 0.66 (PE∶EtOAc = 4∶1);

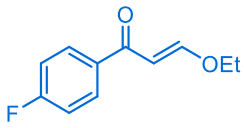
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 – 8.03 (m, 2H), 7.19 – 7.13 (m, 2H), 5.35 (d, *J* = 4.4 Hz, 1H), 4.06 (q, *J* = 6.3 Hz, 1H), 3.97 (d, *J* = 4.4 Hz, 1H), 3.80 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.44 (dq, *J* = 9.7, 7.1 Hz, 1H), 1.26 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.3, 166.3(d, *J* = 256.5 Hz), 133.9 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 9.5 Hz), 116.0 (d, *J* = 25.8 Hz), 104.3, 82.0, 80.7, 64.4, 62.9, 22.2, 15.3, 12.0;

^{19}F NMR (753 MHz, $CDCl_3$): δ −103.70;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}FNaO_4$ $[M + Na]^+$: 305.1160, found: 305.1163.

Compound 4b:

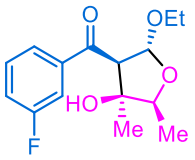


(E)-3-ethoxy-1-(4-fluorophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 60% yield (0.58 g). Identified as a known compound according to the following reference.

Reference: Ryu, H.; Seo, S.; Lee, J.-Y.; Ha, T.-H.; Lee, S.; Jung, A.; Ann, J.; Kim, S.-E.; Yoon, S.; Hong, M.; Blumberg, P. M.; Frank-Foltyn, R.; Bahrenberg, G.; Schiene, K.; Stockhausen, H.; Christoph, T.; Frormann, S.; Lee, J. *Eur. J. Med. Chem.* **2015**, *93*, 101–108.

Compound 5:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(3-

fluorophenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 59% yield (33 mg).

Physical State: white solid;

TLC: R_f = 0.21 (PE∶EtOAc = 5∶1);

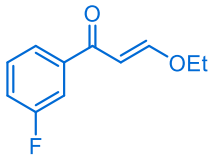
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.71 (ddd, *J* = 9.5, 2.7, 1.6 Hz, 1H), 7.48 (td, *J* = 8.0, 5.5 Hz, 1H), 7.34 – 7.28 (m, 1H), 5.37 (d, *J* = 4.3 Hz, 1H), 4.07 (q, *J* = 6.2 Hz, 1H), 3.96 (d, *J* = 4.3 Hz, 1H), 3.81 (dq, *J* = 9.4, 7.1 Hz, 1H), 3.45 (dq, *J* = 9.4, 7.0 Hz, 1H), 1.27 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.5, 162.9 (d, *J* = 248.3 Hz), 139.6 (d, *J* = 6.3 Hz), 130.4 (d, *J* = 7.6 Hz), 124.9 (d, *J* = 3.1 Hz), 121.0 (d, *J* = 21.5 Hz), 115.8 (d, *J* = 22.6 Hz), 104.0, 81.9, 80.8, 64.4, 63.5, 22.2, 15.3, 12.0;

^{19}F NMR (753 MHz, $CDCl_3$): δ −111.50;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}FNaO_4$ $[M + Na]^+$: 305.1160, found: 305.1166.

Compound 5b:



(E)-3-ethoxy-1-(3-fluorophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 55% yield (0.53 g).

Physical State: yellow oil;

TLC: R_f = 0.55 (PE∶EtOAc = 4∶1);

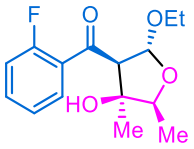
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 12.1 Hz, 1H), 7.63 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.56 (ddd, *J* = 9.5, 2.7, 1.5 Hz, 1H), 7.39 (td, *J* = 7.9, 5.6 Hz, 1H), 7.19 (tdd, *J* = 8.2, 2.7, 1.1 Hz, 1H), 6.28 (d, *J* = 12.2 Hz, 1H), 4.04 (q, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 189.2 (d, J = 2.5 Hz), 164.7, 162.9 (d, J = 247.5 Hz), 141.0 (d, J = 6.5 Hz), 130.1 (d, J = 7.5 Hz), 123.7 (d, J = 3.0 Hz), 119.2 (d, J = 21.6 Hz), 114.8 (d, J = 22.6 Hz), 101.8, 68.1, 14.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ −112.31;

HRMS(ESI-TOF): calc'd for $C_{11}H_{12}FO_2$ $[M + H]^+$: 195.0816, found: 195.0818.

Compound 6:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(2-fluorophenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 48% yield (27 mg).

Physical State: yellow solid;

TLC: R_f = 0.37 (PE∶EtOAc = 4∶1);

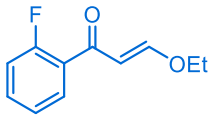
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (td, J = 7.6, 1.8 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.25 – 7.22 (m, 1H), 7.17 – 7.11 (m, 1H), 5.51 (d, J = 4.0 Hz, 1H), 4.09 (d, J = 4.0 Hz, 1H), 4.04 (q, J = 6.3 Hz, 1H), 3.78 (dq, J = 9.6, 7.1 Hz, 1H), 3.48 (dq, J = 9.6, 7.0 Hz, 1H), 1.20 (s, 3H), 1.19 (d, J = 4.5 Hz, 3H)1.17 (t, J = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 197.4, 161.3 (d, J = 254.9 Hz), 134.9 (d, J =8.97 Hz), 131.0 (d, J = 1.6 Hz), 127.0 (d, J = 11.6 Hz), 124.7 (d, J = 3.5 Hz), 116.8 (d, J = 23.3 Hz), 103.7, 81.6, 80.9, 67.8, 67.8, 64.2, 21.6, 15.3, 12.0;

^{19}F NMR (753 MHz, $CDCl_3$): δ −111.16;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}FNaO_4$ $[M + Na]^+$: 305.1160, found: 305.1165.

Compound 6b:



(E)-3-ethoxy-1-(2-fluorophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 48% yield (0.46 g).

Physical State: yellow oil;

TLC: R_f = 0.33 (PE∶EtOAc = 9∶1);

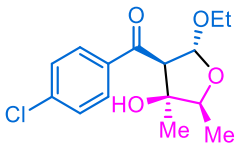
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.70 (m, 2H), 7.46 (dddd, *J* = 8.3, 7.1, 5.1, 1.9 Hz, 1H), 7.21 (td, *J* = 7.5, 1.2 Hz, 1H), 7.10 (ddd, *J* = 10.9, 8.3, 1.2 Hz, 1H), 6.22 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.0 (d, *J* = 2.3 Hz), 164.5, 160.9 (d, *J* = 252.0 Hz), 133.4 (d, *J* = 8.7 Hz), 130.7 (d, *J* = 3.2 Hz), 127.7 (d, *J* = 13.6 Hz), 124.5 (d, *J* = 3.5 Hz), 116.5 (d, *J* = 23.4 Hz), 106.4 (d, *J* = 6.9 Hz), 67.7, 14.6;

^{19}F NMR (471 MHz, $CDCl_3$): δ −111.93;

HRMS(ESI-TOF): calc'd for $C_{11}H_{12}FO_2$ $[M + H]^+$: 195.0816, found: 195.0818.

Compound 7:



(±)-(4-chlorophenyl)((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 68% yield (41 mg).

Physical State: yellow solid;

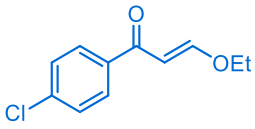
TLC: R_f = 0.34 (PE∶EtOAc = 9∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.5 Hz, 2H), 7.56 – 7.40 (d, J = 8.8 Hz, 2H), 5.36 (d, J = 4.3 Hz, 1H), 4.06 (q, J = 6.3 Hz, 1H), 3.96 (d, J = 4.3 Hz, 1H), 3.80 (dq, J = 9.7, 7.1 Hz, 1H), 3.45 (dq, J = 9.7, 7.1 Hz, 1H), 1.25 (s, 3H), 1.23 (d, J = 6.3 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 140.6, 135.9, 130.5, 129.1, 104.2, 81.9, 80.7, 64.4, 63.1, 22.2, 15.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}ClNaO_4[M + Na]^+$: 321.0864, found: 321.0861.

Compound 7b:

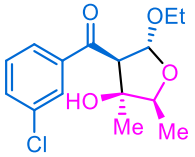


(E)-3-ethoxy-1-(4-chlorophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 52% yield (0.58g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 8:



(±)-(3-chlorophenyl)((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 59% yield (35 mg).

Physical State: yellow solid;

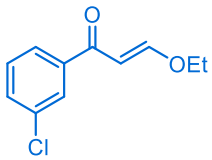
TLC: R_f = 0.57 (PE∶EtOAc = 4∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 5.36 (d, *J* = 4.3 Hz, 1H), 4.06 (q, *J* = 6.2 Hz, 1H), 3.95 (d, *J* = 4.4 Hz, 1H), 3.81 (dq, *J* = 9.3, 7.1 Hz, 1H), 3.45 (dq, *J* = 9.5, 7.0 Hz, 1H), 1.26 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 139.1, 135.2, 133.8, 130.1, 129.2, 127.2, 104.1, 81.9, 80.7, 64.4, 63.5, 22.2, 15.2, 12.0;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}ClNaO_4$ $[M + Na]^+$: 321.0864, found: 321.0863.

Compound 8b:

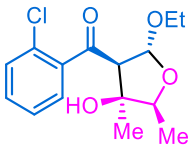


(E)-3-ethoxy-1-(3-chlorophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 51% yield (0.54 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 9:



(±)-(2-chlorophenyl)((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 50% yield (30 mg).

Physical State: yellow solid;

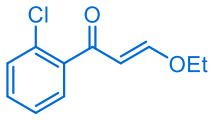
TLC: R_f = 0.46 (PE：EtOAc = 4∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.46 (m, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 5.51 (d, *J* = 4.1 Hz, 1H), 4.02 – 3.97 (m, 2H), 3.78 (dq, *J* = 9.6, 7.0 Hz, 1H), 3.49 (dq, *J* = 9.6, 7.1 Hz, 1H), 1.18 (d, *J* = 6.1 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.11 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 201.2, 139.6, 132.0, 131.0, 130.6, 129.4, 127.0, 103.2, 81.5, 80.7, 68.0, 64.4, 21.7, 15.3, 11.8;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}ClNaO_4$ $[M + Na]^+$: 321.0864, found: 321.0866.

Compound 9b:

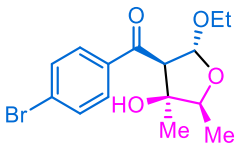


(E)-3-ethoxy-1-(2-chlorophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 48% yield (0.51 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 10:



(±)-(4-bromophenyl)((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 62% yield (42 mg).

Physical State: yellow solid;

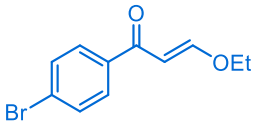
TLC: R_f = 0.35 (PE∶EtOAc = 9∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 – 7.84 (m, 2H), 7.64 – 7.59 (m, 2H), 5.36 (d, *J* = 4.3 Hz, 1H), 4.05 (q, *J* = 6.3 Hz, 1H), 3.95 (d, *J* = 4.3 Hz, 1H), 3.79 (dq, *J* = 9.6, 7.1 Hz, 1H), 3.44 (dq, *J* = 9.7, 7.0 Hz, 1H), 1.24 (s, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.7, 136.2, 132.1, 130.6, 129.3, 104.1, 81.9, 80.7, 64.3, 63.1, 22.2, 15.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{15}H_{19}BrNaO_4$ $[M + Na]^+$: 365.0359, found: 365.0355.

Compound 10b:



(E)-3-ethoxy-1-(4-bromophenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 53% yield (0.67 g).

Physical State: white solid;

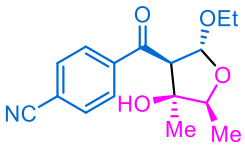
TLC: R_f = 0.43 (PE∶EtOAc = 9∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 – 7.73 (m, 3H), 7.61 – 7.56 (m, 2H), 6.30 (d, *J* = 12.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.6, 164.7, 137.6, 131.8, 129.7, 127.3, 101.8, 68.2, 14.8;

HRMS(ESI-TOF): calc'd for $C_{11}H_{12}BrO_2$ $[M + H]^+$: 255.0015, found: 255.0014.

Compound 11:



(±)-4-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-carbonyl)benzonitrile

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 72% yield (42 mg).

Physical State: yellow solid;

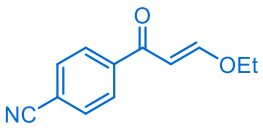
TLC: R_f = 0.15 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.04 (m, 2H), 7.82 – 7.76 (m, 2H), 5.40 (d, J = 4.1 Hz, 1H), 4.07 (q, J = 6.2 Hz, 1H), 3.98 (d, J = 4.1 Hz, 1H), 3.80 (dq, J = 9.6, 7.1 Hz, 1H), 3.45 (dq, J = 9.6, 7.0 Hz, 1H), 1.24 (s, 3H), 1.22 (d, J = 6.3 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 140.6, 132.6, 129.4, 117.9, 117.0, 103.8, 81.8, 80.8, 64.3, 64.0, 22.2, 15.3, 11.9;

HRMS(ESI-TOF): calc'd for $C_{16}H_{19}NNaO_4$ $[M + Na]^+$: 312.1206, found: 312.1204.

Compound 11b:



(E)-4-(3-ethoxyacryloyl)benzonitrile

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 43% yield (0.43 g).

Physical State: white solid;

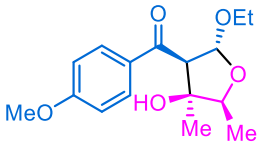
TLC: R_f = 0.79 (PE∶EtOAc = 1∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.91 (m, 2H), 7.78 (d, J = 12.1 Hz, 1H), 7.75 – 7.70 (m, 2H), 6.29 (d, J = 12.1 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 165.6, 142.3, 132.5, 128.5, 118.3, 115.5, 101.8, 68.5, 14.7;

HRMS(ESI-TOF): calc'd for $C_{12}H_{12}NO_2$ $[M + H]^+$: 202.0863, found: 202.0861.

Compound 12:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(4-methoxyphenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 82% yield (48 mg).

Physical State: yellow solid;

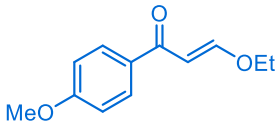
TLC: R_f = 0.21 (PE∶EtOAc = 5∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 – 7.97 (m, 2H), 7.03 – 6.88 (m, 2H), 5.32 (d, J = 4.6 Hz, 1H), 4.06 (q, J = 6.3 Hz, 1H), 3.97 (d, J = 4.6 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 1H), 3.79 (dq, J = 9.8, 7.1 Hz, 1H), 3.44 (dq, J = 9.7, 7.1 Hz, 1H), 1.25 (s, 3H), 1.24 (d, J = 6.3 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.5, 164.4, 131.7, 130.5, 114.0, 104.7, 82.1, 80.6, 64.4, 62.1, 55.7, 22.3, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{16}H_{22}NaO_5$ $[M + Na]^+$: 317.1359, found: 317.1357.

Compound 12b:

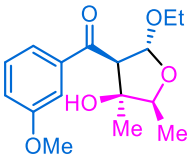


(E)-3-ethoxy-1-(4-methoxyphenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 62% yield (0.64 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 13:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(3-methoxyphenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 60% yield (35 mg).

Physical State: white solid;

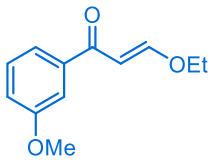
TLC: R_f = 0.35 (PE∶EtOAc = 5∶1);

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.60 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.54 (t, *J* = 2.1 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 8.3, 2.7 Hz, 1H), 5.37 (d, *J* = 4.3 Hz, 1H), 4.07 (q, *J* = 6.3 Hz, 1H), 4.02 (d, *J* = 4.3 Hz, 1H), 3.87 (s, 3H), 3.81 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.46 (dq, *J* = 9.5, 7.0 Hz, 1H), 1.27 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): *δ* 199.8, 160.1, 138.9, 129.8, 121.9, 120.8, 113.0, 104.5, 82.0, 80.8, 64.4, 63.1, 55.6, 22.2, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{16}H_{22}NaO_5$ $[M + Na]^+$: 317.1359, found: 317.1357.

Compound 13b:

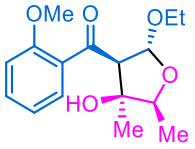


(E)-3-ethoxy-1-(3-methoxyphenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 57% yield (0.58 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 14:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(2-methoxyphenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 45% yield (26 mg).

Physical State: yellow solid;

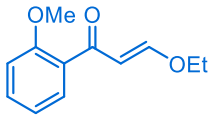
TLC: R_f = 0.18 (PE∶EtOAc = 5∶1);

^{1}H NMR (500MHz, $CDCl_3$): *δ* 7.54 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.95 (dd, *J* = 8.4, 0.9 Hz, 1H), 5.42 (d, *J* = 4.3 Hz, 1H), 4.24 (d, *J* = 4.3 Hz, 1H), 4.00 (q, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.75 (dq, *J* = 9.8, 7.1 Hz, 1H), 3.45 (dq, *J* = 9.8, 7.0 Hz, 1H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.15 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 202.0, 158.2, 133.7, 130.4, 129.5, 121.0, 111.6, 104.3, 81.7, 80.7, 67.3, 64.2, 55.7, 22.0, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{16}H_{22}NaO_5$ $[M + Na]^+$: 317.1359, found: 317.1358.

Compound 14b:

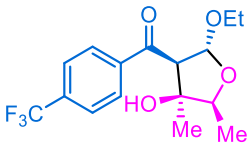


(E)-3-ethoxy-1-(2-methoxyphenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 54% yield (0.56 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 15:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(4-(trifluoromethyl)phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 43% yiled (30 mg).

Physical State: yellow solid;

TLC: R_f = 0.35 (PE∶EtOAc = 5∶1);

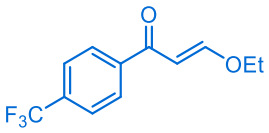
^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.11 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 5.41 (d, *J* = 4.2 Hz, 1H), 4.08 (q, *J* = 6.3 Hz, 1H), 4.02 (d, *J* = 4.2 Hz, 1H), 3.82 (dq, *J* = 9.6, 7.1 Hz, 1H), 3.46 (dq, *J* = 9.6, 7.0 Hz, 1H), 1.26 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): *δ* 198.8, 140.2, 135. 0 (q, *J* = 32.9 Hz), 129.4, 125.9 (q, *J* = 3.7 Hz), 123.6 (d, *J* = 272.8 Hz), 104.0, 81.9, 80.8, 64.4, 63.8, 22.2, 15.3, 12.0;

^{19}F NMR (471 MHz, $CDCl_3$): *δ* −63.20;

HRMS(ESI-TOF): calc'd for $C_{16}H_{19}ClF_3O_4$ $[M + Cl]^-$: 367.0929, found: 367.0928.

Compound 15b:



(E)-3-ethoxy-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 46% yield (0.56 g).

Physical State: yellow oil;

TLC: R_f = 0.53 (PE∶EtOAc = 9∶1);

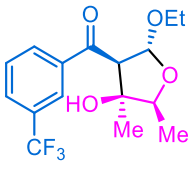
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dt, J = 8.1, 0.9 Hz, 2H), 7.78 (d, J = 12.1 Hz, 1H), 7.71 (dt, J = 8.2, 0.7 Hz, 2H), 6.32 (d, J = 12.2 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 165.2, 141.8, 133.7 (d, J = 32.5 Hz), 128.4, 125.6 (q, J = 3.9 Hz), 123.6 (d, J = 273.8 Hz), 102.1, 68.4, 14.8;

^{19}F NMR (471 MHz, $CDCl_3$): δ −62.98;

HRMS(ESI-TOF): calc'd for $C_{12}H_{12}F_3O_2$ $[M + H]^+$: 245.0784, found: 245.0785.

Compound 16:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(3-(trifluoromethyl)phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 58% yield (40 mg).

Physical State: yellow solid;

TLC: R_f = 0.38 (PE∶EtOAc = 5∶1);

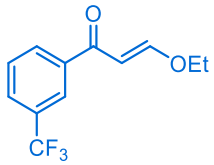
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 2.0 Hz, 1H), 8.20 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 5.38 (d, J = 4.3 Hz, 1H), 4.09 (q, J = 6.3 Hz, 1H), 3.99 (d, J = 4.3 Hz, 1H), 3.82 (dq, J = 9.7, 7.1 Hz, 1H), 3.46 (dq, J = 9.6, 7.0 Hz, 1H), 1.28 (s, 3H), 1.24 (d, J = 6.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 138.0, 132.2, 131.5 (q, J = 33.1 Hz), 130.3 (q, J = 3.6 Hz), 129.5, 126.1 (q, J = 3.8 Hz), 123.8 (q, J = 272.7 Hz), 103.9, 81.9, 80.8, 64.4, 63.5, 22.2, 15.2, 11.9;

^{19}F NMR (471 MHz, $CDCl_3$): δ −62.83;

HRMS(ESI-TOF): calc'd for $C_{16}H_{19}ClF_3O_4$ $[M + Cl]^-$: 367.0929, found: 367.0928.

Compound 16b:



(E)-3-ethoxy-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 42% yield (0.51 g).

Physical State: yellow oil;

TLC: R_f = 0.48 (PE∶EtOAc = 9∶1);

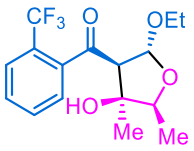
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.69 (d, J = 7.9 Hz, 1H), 7.57 (td, J = 7.4, 1.0 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 12.8 Hz, 1H), 5.88 (d, J = 12.8 Hz, 1H), 3.97 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H);

^{13}C NMR (200 MHz, $CDCl_3$): δ 194.4, 166.5, 139.5, 131.7, 129.6, 128.1, 127.6 (q, J = 32.0 Hz), 126.7 (q, J = 4.8 Hz), 123.8 (q, J = 273.9 Hz), 107.9, 67.6, 14.4.

^{19}F NMR (753 MHz, $CDCl_3$): δ −58.15;

HRMS(ESI-TOF): calc'd for $C_{12}H_{12}F_3O_2$ $[M + H]^+$: 245.0784, found: 245.0785.

Compound 17:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(2-(trifluoromethyl)phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 27% yield (18 mg).

Physical State: yellow solid;

TLC: R_f = 0.69 (PE∶EtOAc = 2∶1);

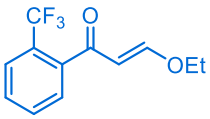
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 – 7.71 (m, 1H), 7.66 – 7.58 (m, 3H), 5.43 (d, J = 4.3 Hz, 1H), 4.01 (q, J = 6.3 Hz, 1H), 3.77 (dq, J = 9.7, 7.1 Hz, 1H), 3.73 (d, J = 4.3 Hz, 1H), 3.45 (dq, J = 9.8, 7.1 Hz, 1H), 1.21 (d, J = 6.3 Hz, 3H), 1.16 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 202.3, 139.7, 132.0, 130.8, 128.4, 127.3 (q, J = 32.4 Hz), 126.9 (q, J = 4.9 Hz), 123.7 (d, J = 273.8 Hz), 103.5, 81.7, 80.6, 68.5, 64.5, 21.9, 15.2, 11.9;

^{19}F NMR (471 MHz, $CDCl_3$): δ −57.31;

HRMS(ESI-TOF): calc'd for $C_{16}H_{19}F_3NaO_4$ $[M + Na]^+$: 355.1128, found: 355.1125.

Compound 17b:



(E)-3-ethoxy-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 39% yield (0.47 g).

Physical State: yellow oil;

TLC: $\mathbf{R_f}$ = 0.44 (PE∶EtOAc = 9∶1);

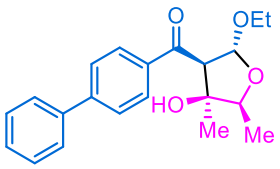
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.67 (m, 1H), 7.61 – 7.48 (m, 2H), 7.40 – 7.35 (m, 2H), 7.25 (d, *J* = 12.8 Hz, 1H), 5.88 (d, *J* = 12.8 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 166.5, 139.5, 131.7, 129.6, 127.6 (d, *J* = 32.0 Hz), 126.7 (q, *J* = 4.8 Hz), 123.8 (d, *J* = 274.0 Hz), 107.9, 67.6, 14.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ −58.14;

HRMS(ESI-TOF): calc'd for $C_{12}H_{12}F_3O_2$ $[M + H]^+$: 245.0784, found: 245.0786.

Compound 18:



(±)-[1,1'-biphenyl]-4-yl((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 83% yield (56 mg).

Physical State: white solid;

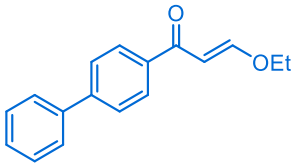
TLC: R_f = 0.26 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.08 (m, 2H), 7.75 – 7.69 (m, 2H), 7.67 – 7.61 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.37 (m, 1H), 4.14 – 4.06 (m, 2H), 3.83 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.58 (s, 1H), 3.48 (dq, *J* = 9.7, 7.1 Hz, 1H), 1.30 (s, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 146.7, 139.7, 136.2, 129.8, 129.1, 128.6, 127.4, 104.5, 82.0, 80.8, 64.4, 62.9, 22.3, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{21}H_{24}NaO_4$ $[M + Na]^+$: 363.1567, found: 363.1563.

Compound 18b:



(E)-1-([1,1'-biphenyl]-4-yl)-3-ethoxyprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 50% yield (0.63 g).

Physical State: yellow solid;

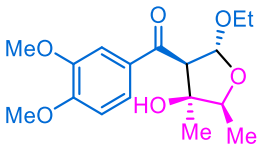
TLC: R_f = 0.35 (PE∶EtOAc = 9∶1);

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.00 – 7.95 (m, 2H), 7.80 (d, *J* = 12.1 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.66 – 7.61 (m, 2H), 7.50 – 7.43 (m, 1H), 7.42 – 7.36 (m, 1H), 6.41 (d, *J* = 12.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 190.3, 164.2, 145.1, 140.2, 137.6, 129.1, 128.7, 128.2, 127.4, 127.3, 102.2, 68.0, 14.8;

HRMS(ESI-TOF): calc'd for $C_{17}H_{17}O_2$ $[M + H]^+$: 253.1223, found: 253.1223.

Compound 19:



(±)-(3,4-dimethoxyphenyl)((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 60% yield (39 mg).

Physical State: yellow solid;

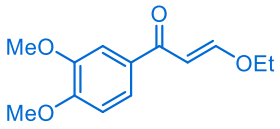
TLC: R_f = 0.18 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J = 8.5, 2.1 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 5.31 (d, J = 4.5 Hz, 1H), 4.03 (q, J = 6.2 Hz, 1H), 3.96 (d, J = 4.6 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.81 – 3.71 (m, 1H), 3.42 (dq, J = 9.7, 7.0 Hz, 1H), 1.23 (s, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 154.2, 149.2, 130.6, 124.5, 110.7, 110.0, 104.6, 82.0, 80.6, 64.3, 62.0, 56.2, 56.0, 22.2, 15.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{17}H_{24}NaO_6$ $[M + Na]^+$: 347.1465, found: 347.1461.

Compound 19b:



(E)-1-(3,4-dimethoxyphenyl)-3-ethoxyprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 56% yield (0.66 g).

Physical State: colorless oil;

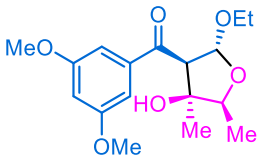
TLC: R_f = 0.31 (PE∶EtOAc = 2∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 12.1 Hz, 1H), 7.52 (s, 1H), 7.50 (d, J = 8.3 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.37 (d, J = 12.1 Hz, 1H), 4.05 (q, J = 7.0 Hz, 2H), 3.93 (s, 6H), 1.38 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.1, 163.6, 152.8, 149.1, 131.9, 122.3, 110.5, 110.0, 101.7, 68.0, 56.1, 56.1, 14.8;

HRMS(ESI-TOF): calc'd for $C_{13}H_{17}O_4$ $[M + H]^+$: 237.1121, found: 237.1122.

Compound 20:



(±)-(3,5-dimethoxyphenyl)((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 80% yield (52 mg).

Physical State: white solid;

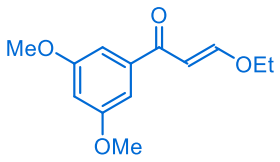
TLC: R_f = 0.33 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 2.3 Hz, 2H), 6.66 (t, J = 2.3 Hz, 1H), 5.35 (d, J = 4.3 Hz, 1H), 4.03 (q, J = 6.0 Hz, 1H), 3.94 (d, J = 4.3 Hz, 1H), 3.80 (s, 6H), 3.79 – 3.71 (m, 1H), 3.47 – 3.37 (m, 1H), 1.24 (s, 3H), 1.20 (d, J = 6.2 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 161.0, 139.4, 106.8, 106.3, 104.3, 81.9, 80.7, 64.2, 63.1, 55.6, 22.2, 15.2, 12.0;

HRMS(ESI-TOF): calc'd for $C_{17}H_{24}NaO_6$ $[M + Na]^+$: 347.1465, found: 347.1463.

Compound 20b:



(E)-1-(3,5-dimethoxyphenyl)-3-ethoxyprop-2-en-1-one

Experimental: Prepared according to the general procedure B for the synthesis of β-keto enol ethers, 48% yield (0.57 g).

Physical State: yellow solid;

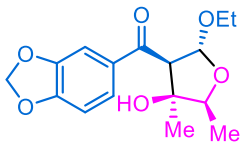
TLC: R_f = 0.38 (PE∶EtOAc = 9∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 12.2 Hz, 1H), 7.02 (d, J = 2.3 Hz, 2H), 6.61 (t, J = 2.3 Hz, 1H), 6.28 (d, J = 12.2 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.83 (s, 6H), 1.38 (t, J = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 164.4, 160.9, 141.0, 106.0, 104.6, 102.3, 68.0, 55.7, 14.8;

HRMS(ESI-TOF): calc'd for $C_{13}H_{17}O_4$ $[M + H]^+$: 237.1121, found: 237.1125.

Compound 21:



(±)-benzo[d][1,3]dioxol-5-yl((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 55% yield (34 mg).

Physical State: white solid;

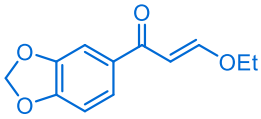
TLC: R_f = 0.26 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J = 8.2, 1.8 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 5.32 (d, J = 4.5 Hz, 1H), 4.05 (q, J = 6.2 Hz, 1H), 3.92 (d, J = 4.5 Hz, 1H), 3.80 (dq, J = 9.5, 7.1 Hz, 1H), 3.44 (dq, J = 9.5, 7.0 Hz, 1H), 1.26 (s, 3H), 1.24 (d, J = 6.3 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 152.8, 148.5, 132.3, 126.2, 108.6, 108.0, 104.6, 102.2, 82.0, 80.7, 64.4, 62.4, 22.3, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{16}H_{20}NaO_6$ $[M + Na]^+$: 331.1152, found: 331.1151.

Compound 21b:

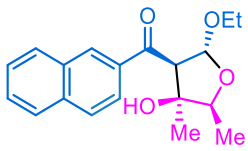


(E)-1-(benzo[d][1,3]dioxol-5-yl)-3-ethoxyprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 46% yield (0.51 g). Identified as a known compound according to the following reference.

Reference: Stern, E.; Millet, R.; Depreux, P.; Hénichart, J.-P. *Tetrahedron Lett.* **2004**, *45*, 9257–9259.

Compound 22:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(naphthalen-2-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 93% yield (58 mg).

Physical State: yellow solid;

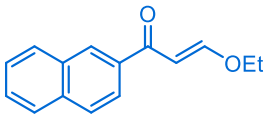
TLC: R_f = 0.35 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.07 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 5.43 (d, *J* = 4.4 Hz, 1H), 4.20 (d, *J* = 4.4 Hz, 1H), 4.13 (q, *J* = 6.0 Hz, 1H), 3.85 (dq, *J* = 8.7, 7.1 Hz, 1H), 3.70 (s, 1H), 3.47 (dq, *J* = 8.8, 7.0 Hz, 1H), 1.30 (s, 3H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 136.0, 134.8, 132.5, 131.7, 129.9, 129.1, 128.7, 127.9, 127.1, 124.2, 104.5, 82.1, 80.8, 64.5, 62.9, 22.3, 15.3, 12.1;

HRMS(ESI-TOF): calc'd for $C_{19}H_{22}NaO_4$ $[M + Na]^+$: 337.1410, found: 337.1411.

Compound 22b:

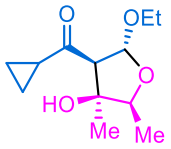


(E)-3-ethoxy-1-(naphthalen-2-yl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 66% yield (0.75 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 23:



(±)-cyclopropyl((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 30% yield (14 mg).

Physical State: white solid;

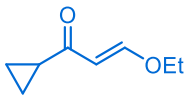
TLC: R_f = 0.20 (PE∶EtOAc = 9∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (d, J = 4.8 Hz, 1H), 3.97 (q, J = 6.3 Hz, 1H), 3.82 (dq, J = 9.7, 7.1 Hz, 1H), 3.52 (dq, J = 9.6, 7.0 Hz, 1H), 3.28 (d, J = 4.8 Hz, 1H), 3.20 (s, 1H), 2.06 (tt, J = 7.7, 4.5 Hz, 1H), 1.37 (s, 3H), 1.21 (t, J = 7.1 Hz, 2H), 1.20 (d, J = 6.3 Hz, 3H), 1.17 – 1.12 (m, 2H), 1.02 – 0.93 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 209.6, 103.3, 81.6, 79.7, 68.4, 64.3, 22.3, 21.9, 15.4, 12.1, 11.9, 11.8;

HRMS(ESI-TOF): calc'd for $C_{12}H_{20}NaO_4$ $[M + Na]^+$: 251.1254, found: 251.1254.

Compound 23b:



(E)-1-cyclopropyl-3-ethoxyprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 60% yield (0.42 g).

Physical State: colorless oil;

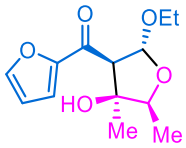
TLC: R_f = 0.48 (PE∶EtOAc = 9∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 12.6 Hz, 1H), 5.72 (d, J = 12.6 Hz, 1H), 3.93 (q, J = 7.1 Hz, 2H), 1.89 (tt, J = 7.8, 4.6 Hz, 1H), 1.33 (t, J = 7.0 Hz, 3H), 1.03 (dt, J = 4.3, 3.2 Hz, 2H), 0.83 (dt, J = 7.9, 3.4 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 161.5, 106.2, 67.1, 19.8, 14.6, 10.4;

HRMS(ESI-TOF): calc'd for $C_8H_{13}O_2$ $[M + H]^+$: 141.0910, found: 141.0908.

Compound 24:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(furan-2-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 75% yield (38 mg).

Physical State: colorless crystal;

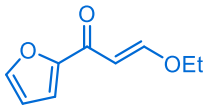
TLC: R_f = 0.18 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J = 1.7, 0.7 Hz, 1H), 7.33 (dt, J = 3.6, 0.6 Hz, 1H), 6.58 (dd, J = 3.6, 1.7 Hz, 1H), 5.39 (d, J = 4.3 Hz, 1H), 4.05 (q, J = 6.2 Hz, 1H), 3.84 – 3.73 (m, 2H), 3.45 (dq, J = 9.7, 7.1 Hz, 1H), 1.30 (s, 3H), 1.22 (d, J = 6.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8, 153.0, 147.8, 119.9, 112.9, 103.9, 81.9, 81.1, 64.3, 63.9, 22.0, 15.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{13}H_{18}NaO_5$ $[M + Na]^+$: 277.1046, found: 277.1046.

Compound 24b:

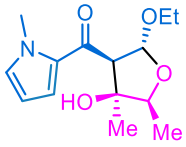


(E)-3-ethoxy-1-(furan-2-yl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 45% yield (0.37 g). Identified as a known compound according to the following reference.

Reference: Szychowski, J.; Leniewski, A.; Wróbel, J. T.; Glinka, T. *Collect. Czechoslov. Chem. Commun.* **1992**, *57,* 1072–1080.

Compound 25:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(1-methyl-1H-pyrrol-2-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 30% yield (16 mg).

Physical State: colorless crystal;

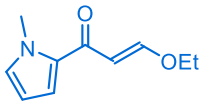
TLC: R_f = 0.75 (PE∶EtOAc = 1∶1);

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.09 (dd, *J* = 4.2, 1.7 Hz, 1H), 6.89 (t, *J* = 2.1 Hz, 1H), 6.17 (dd, *J* = 4.2, 2.5 Hz, 1H), 5.33 (d, *J* = 4.5 Hz, 1H), 4.02 (q, *J* = 6.2 Hz, 1H), 3.96 (s, 3H), 3.79 (dq, *J* = 9.6, 7.1 Hz, 1H), 3.71 (d, *J* = 4.5 Hz, 1H), 3.46 (dq, *J* = 9.6, 7.0 Hz, 1H), 1.27 (s, 3H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 188.8, 133.1, 131.8, 122.5, 108.8, 104.9, 82.1, 80.7, 64.3, 63.4, 38.1, 22.2, 15.3, 12.2;

HRMS(ESI-TOF): calc'd for $C_{14}H_{21}NNaO_4$ $[M + Na]^+$: 290.1363, found: 290.1364.

Compound 25b:



(E)-3-ethoxy-1-(1-methyl-1H-pyrrol-2-yl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 45% yield (0.4 g).

Physical State: brown oil;

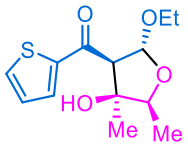
TLC: R_f = 0.47 (PE∶EtOAc = 9∶1);

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.63 (d, *J* = 12.1 Hz, 1H), 6.89 – 6.84 (m, 1H), 6.79 (t, *J* = 2.2 Hz, 1H), 6.20 (d, *J* = 12.2 Hz, 1H), 6.13 – 6.04 (m, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 1.2 Hz, 3H), 1.38 – 1.34 (m, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 181.1, 161.3, 131.7, 130.8, 118.0, 107.9, 103.3, 67.5, 37.8, 14.8;

HRMS(ESI-TOF): calc'd for $C_{10}H_{14}NO_2$ $[M + H]^+$: 180.1019, found: 180.1018.

Compound 26:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(thiophen-2-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 46% yield (25 mg).

Physical State: colorless crystal;

TLC: R_f = 0.78 (PE∶EtOAc = 1∶1);

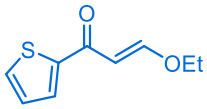
^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.85 (d, *J* = 3.8 Hz, 1H), 7.74 (d, *J* = 4.9 Hz, 1H), 7.17 (t, *J* = 4.4 Hz, 1H), 5.37 (d, *J* = 4.4 Hz, 1H), 4.05 (q, *J* = 6.3 Hz, 1H), 3.84 – 3.77 (m,

2H), 3.50 – 3.42 (m, 1H), 1.31 (s, 3H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 191.9, 145.0, 135.9, 134.4, 128.6, 104.3, 82.0, 80.7, 64.4, 64.3, 22.2, 15.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{13}H_{18}NaO_4S$ $[M + Na]^+$: 293.0818, found: 293.0816.

Compound 26b:

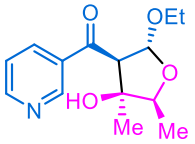


(E)-3-ethoxy-1-(thiophen-2-yl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 40% yield (0.36 g). Identified as a known compound according to the following reference.

Reference: Li, X.-M.; Yang, J.-K. *Eur. J. Org. Chem.* **2022**, *47*, e202201163.

Compound 27:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(pyridin-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 72% yield (35 mg).

Physical State: white solid;

TLC: R_f = 0.35 (PE∶EtOAc = 1∶1);

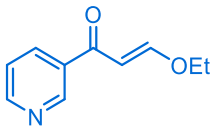
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.19 (d, *J* = 2.6 Hz, 1H), 8.80 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.27 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.44 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H), 5.42 (d, *J* = 4.2 Hz,

1H), 4.08 (q, *J* = 6.3 Hz, 1H), 3.99 (d, *J* = 4.2 Hz, 1H), 3.80 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.45 (dq, *J* = 9.6, 7.1 Hz, 1H), 1.27 (s, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.2, 154.0, 150.3, 136.4, 132.9, 123.8, 103.8, 81.8, 80.8, 64.3, 64.0, 22.2, 15.2, 11.9;

HRMS(ESI-TOF): calc'd for $C_{14}H_{20}NO_4$ $[M + H]^+$: 266.1387, found: 266.1387.

Compound 27b:

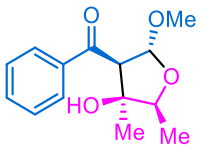


(E)-3-ethoxy-1-(pyridin-3-yl)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 39% yield (0.8 g). Identifed as a known compound according to the following reference.

Reference: Sakamoto, T.; Yasuhara, A.; Kondo, Y.; Yamanaka, H. *Chem. Pharm. Bull.* **1992**, *40,* 1137–1139.

Compound 28:



(±)-((2R,3R,4S,5S)-4-hydroxy-2-methoxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 60% yield (30 mg).

Physical State: yellow solid;

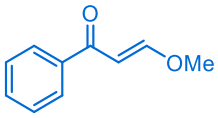
TLC: R_f = 0.48 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.96 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 5.28 (d, J = 4.2 Hz, 1H), 4.10 – 4.00 (m, 2H), 3.39 (s, 3H), 1.27 – 1.22 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 137.5, 134.0, 129.0, 128.9, 105.8, 82.1, 80.8, 62.9, 56.1, 22.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{16}H_{22}NaO_4$ $[M + Na]^+$: 273.1097, found: 273.1093.

Compound 28b:

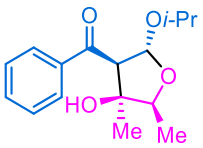


(E)-3-methoxy-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 70% yield (0.57 g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org*. *Lett*. **2022**, *24*, 6716–6721.

Compound 29:



(±)-((2R,3R,4S,5S)-4-hydroxy-2-isopropoxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 53% yield (29 mg).

Physical State: white solid;

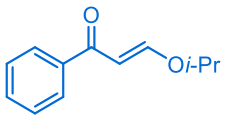
TLC: R_f = 0.77 (PE∶EtOAc = 2∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 8.00 (m, 2H), 7.64 – 7.58 (m, 1H), 7.50 – 7.47 (m, 2H), 5.46 (d, *J* = 4.5 Hz, 1H), 4.08 (q, *J* = 6.3 Hz, 1H), 4.01 (d, *J* = 4.5 Hz, 1H), 3.87 (hept, *J* = 6.1 Hz, 1H), 1.26 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.4, 137.6, 134.0, 129.2, 128.8, 102.9, 81.8, 80.7, 70.7, 63.1, 23.8, 22.3, 21.9, 12.1;

HRMS(ESI-TOF): calc'd for $C_{16}H_{22}NaO_4$ $[M + Na]^+$: 301.1410, found: 301.1408.

Compound 29b:

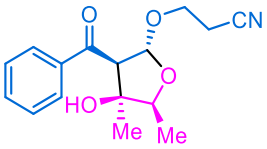


(E)-3-isopropoxy-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 68% yield (0.65 g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org*. *Lett*. **2022**, *24*, 6716–6721.

Compound 30:



(±)-3-(((2R,3R,4S,5S)-3-benzoyl-4-hydroxy-4,5-dimethyltetrahydrofuran-2-yl)oxy)propanenitrile

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 47% yield (27 mg).

Physical State: yellow solid;

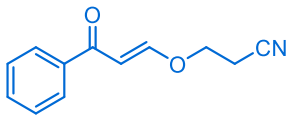
TLC: R_f = 0.38 (PE∶EtOAc = 2∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 – 7.97 (m, 2H), 7.65 – 7.58 (m, 1H), 7.50 (t, J = 7.8 Hz, 2H), 5.41 (d, J = 4.1 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.93 (ddd, J = 10.1, 6.6, 5.5 Hz, 1H), 3.67 (ddd, J = 10.1, 7.4, 5.3 Hz, 1H), 2.72 – 2.54 (m, 2H), 1.27 (s, 3H), 1.23 (d, J = 6.3 Hz, 3H);

^{13}C NMR (125MHz, $CDCl_3$): δ 199.3, 137.3, 134.1, 129.0, 128.9, 117.9, 104.7, 82.4, 80.6, 63.1, 62.9, 22.2, 19.3, 11.9;

HRMS(ESI-TOF): calc'd for $C_{16}H_{19}NNaO_4$ $[M + Na]^+$: 312.1206, found: 312.1202.

Compound 30b:

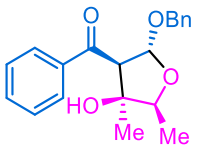


(E)-3-((3-oxo-3-phenylprop-1-en-1-yl)oxy)propanenitrile

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 56% yield (0.56 g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org*. *Lett*. **2022**, *24*, 6716–6721.

Compound 31:



(±)-((2R,3R,4S,5S)-2-(benzyloxy)-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 62% yield (40 mg).

Physical State: white solid;

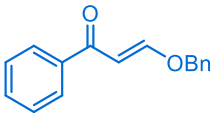
TLC: R_f = 0.53 (PE∶EtOAc = 5∶1);

^{1}H NMR (500MHz, $CDCl_3$): δ 8.04 – 7.99 (m, 2H), 7.65 – 7.59 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.35 – 7.25 (m, 5H), 5.52 (d, J = 4.1 Hz, 1H), 4.82 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.18 – 4.10 (m, 2H), 1.30 – 1.26 (m, 6H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 137.7, 137.4, 134.0, 129.1, 128.8, 128.5, 128.1, 127.9, 104.1, 82.1, 80.8, 70.6, 62.9, 22.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{20}H_{22}NaO_4$ $[M + Na]^+$: 349.1410, found: 349.1407.

Compound 31b:

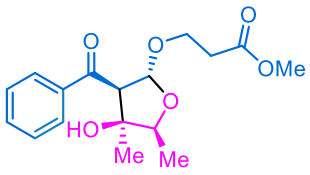


(E)-3-(benzyloxy)-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of β-keto enol ethers, 72% yield (0.86 g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org*. *Lett*. **2022**, *24*, 6716–6721.

Compound 32:



(±)-methyl 3-(((2R,3R,4S,5S)-3-benzoyl-4-hydroxy-4,5-dimethyltetrahydrofuran-2-yl)oxy)propanoate

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 75% yield (48 mg).

Physical State: white solid;

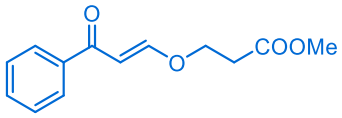
TLC: R_f = 0.58 (PE∶EtOAc = 2∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 – 7.96 (m, 2H), 7.64 – 7.57 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 5.37 (d, *J* = 4.3 Hz, 1H), 4.07 – 3.95 (m, 3H), 3.72 (ddd, *J* = 10.2, 7.2, 5.8 Hz, 1H), 3.60 (s, 3H), 2.64 – 2.51 (m, 2H), 1.25 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 171.9, 137.4, 134.0, 129.1, 128.9, 104.7, 82.1, 80.7, 64.2, 62.8, 51.8, 35.2, 22.3, 12.0;

HRMS(ESI-TOF): calc'd for $C_{17}H_{22}NaO_6$ $[M + Na]^+$: 345.1309, found: 345.1306.

Compound 32b:

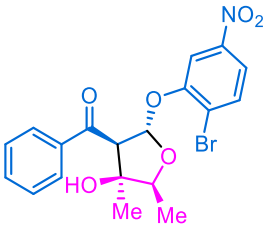


methyl (E)-3-((3-oxo-3-phenylprop-1-en-1-yl)oxy)propanoate

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 60% yield (0.7 g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org*. *Lett*. **2022**, *24*, 6716–6721.

Compound 33:



(±)-((2S,3R,4S,5S)-2-(2-bromo-5-nitrophenoxy)-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 53% yield (46 mg).

Physical State: yellow solid;

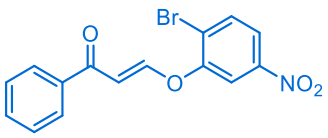
TLC: R_f = 0.77 (PE∶EtOAc = 2∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 – 8.06 (m, 3H), 7.76 (dd, J = 8.7, 2.5 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.56 – 7.50 (m, 2H), 6.14 (d, J = 4.2 Hz, 1H), 4.52 (d, J = 4.2 Hz, 1H), 4.28 (q, J = 6.2 Hz, 1H), 1.38 (s, 3H), 1.31 (d, J = 6.3 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 198.8, 154.2, 148.1, 137.1, 134.5, 133.7, 129.2, 129.1, 120.7, 118.0, 111.7, 104.1, 84.2, 80.8, 62.4, 22.3, 12.0.

HRMS(ESI-TOF): calc'd for $C_{19}H_{18}BrNNaO_6$ $[M + Na]^+$: 458.0210, found: 458.0211.

Compound 33b:



(E)-3-(2-bromo-5-nitrophenoxy)-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure B for the synthesis of β-keto enol ethers, 49% yield (0.85 g).

Physical State: colorless oil;

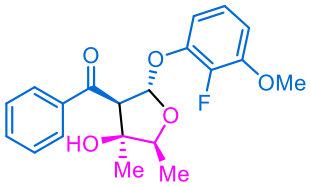
TLC: R_f = 0.54 (PE∶EtOAc = 6∶1);

^{1}H NMR (800 MHz, $CDCl_3$): δ 8.04 (d, J = 2.5 Hz, 1H), 7.98 (dd, J = 8.7, 2.5 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.87 (d, J = 11.7 Hz, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 6.86 (d, J = 11.8 Hz, 1H);

^{13}C NMR (200 MHz, $CDCl_3$): δ 189.7, 157.6, 153.3, 148.2, 137.8, 134.8, 133.3, 128.8, 128.4, 121.8, 120.9, 114.1, 109.1;

HRMS(ESI-TOF): calc'd for $C_{15}H_{11}BrNO_4$ $[M + H]^+$: 347.9866, found: 347.9865.

Compound 34:



(±)-((2S,4S)-2-(2-fluoro-3-methoxyphenoxy)-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 56% yield (40 mg).

Physical State: yellow solid;

TLC: R_f = 0.53 (PE∶EtOAc = 3∶1);

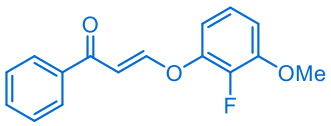
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.05 (m, 2H), 7.66 – 7.58 (m, 1H), 7.51 (dd, *J* = 8.3, 7.0 Hz, 2H), 6.95 (td, *J* = 8.4, 2.1 Hz, 1H), 6.85 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 6.63 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 5.99 (d, *J* = 4.2 Hz, 1H), 4.45 (d, *J* = 4.2 Hz, 1H), 4.27 (q, *J* = 6.2 Hz, 1H), 3.85 (s, 3H), 1.35 (s, 3H), 1.27 (t, *J* = 6.8 Hz, 3H);

^{13}C NMR (150MHz, $CDCl_3$): δ 199.4, 148.7 (d, *J* = 8.6 Hz), 145.8 (d, *J* = 8.5 Hz), 143.5 (d, *J* = 244.6 Hz), 137.2, 134.3, 129.2, 129.0, 123.4 (d, *J* = 5.2 Hz), 110.4, 107.3, 104.1, 83.3, 80.8, 62.7, 56.6, 22.3, 11.9;

^{19}F NMR (471 MHz, $CDCl_3$): δ −156.63;

HRMS(ESI-TOF): calc'd for $C_{20}H_{21}FNaO_5$ $[M + Na]^+$: 383.1265, found: 383.1263.

Compound 34b:



(E)-3-(2-fluoro-3-methoxyphenoxy)-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure B for the synthesis of *β*-keto enol ethers, 61% yield (0.83 g).

Physical State: colorless oil;

TLC: R_f = 0.38 (PE∶EtOAc = 6∶1);

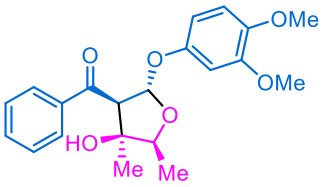
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.96 – 7.84 (m, 3H), 7.58 – 7.53 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.07 (td, *J* = 8.4, 2.1 Hz, 1H), 6.84 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 6.79 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 6.69 (d, *J* = 11.8 Hz, 1H), 3.92 (s, 3H);

^{13}C NMR (200 MHz, $CDCl_3$): δ 190.4, 160.5, 149.2 (d, *J* = 8.3 Hz), 144.3 (d, *J* = 9.2 Hz), 143.7 (d, *J* = 249.3 Hz), 138.3, 132.9, 128.7, 128.3, 124.0 (d, *J* = 5.2 Hz), 112.0, 110.2, 107.1, 56.7;

^{19}F NMR (753 MHz, $CDCl_3$): δ −153.96;

HRMS(ESI-TOF): calc'd for $C_{16}H_{14}FO_3$ $[M + H]^+$: 273.0921, found: 273.0922.

Compound 35:



(±)-((2S,3R,4S,5S)-2-(3,4-dimethoxyphenoxy)-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 74% yield (55 mg).

Physical State: yellow foam;

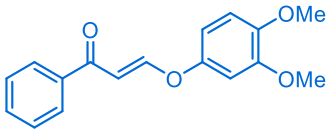
TLC: R_f = 0.34 (PE∶EtOAc = 3∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.62 – 6.55 (m, 2H), 5.97 (d, *J* = 4.3 Hz, 1H), 4.35 (d, *J* = 4.3 Hz, 1H), 4.23 (q, *J* = 6.3 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 1.33 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 199.2, 151.5, 149.7, 144.6, 137.3, 134.2, 129.1, 128.9, 111.9, 107.6, 103.7, 102.3, 83.1, 80.7, 62.9, 56.4, 56.0, 22.2, 12.0;

HRMS(ESI-TOF): calc'd for $C_{21}H_{24}NaO_6$ $[M + Na]^+$: 395.1465, found: 395.1462.

Compound 35b:



(E)-3-(3,4-dimethoxyphenoxy)-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure B for the synthesis of *β*-keto enol ethers, 64% yield (0.84 g).

Physical State: white solid;

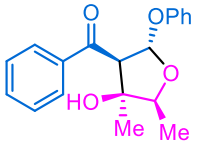
TLC: R_f = 0.29 (PE∶EtOAc = 6∶1);

^{1}H NMR (800MHz, $CDCl_3$): *δ* 7.93 (d, *J* = 11.8 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.68 – 6.64 (m, 3H), 3.87 (s, 3H), 3.87 (s, 3H);

^{13}C NMR (200 MHz, $CDCl_3$): *δ* 190.4, 161.2, 150.2, 150.0, 146.6, 138.4, 132.7, 128.6, 128.1, 111.6, 109.2, 106.2, 103.0, 56.3, 56.2;

HRMS(ESI-TOF): calc'd for $C_{17}H_{17}O_4$ $[M + H]^+$: 285.1121, found: 285.1124.

Compound 36:



(±)-((2S,3R,4S,5S)-4-hydroxy-4,5-dimethyl-2-phenoxytetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 98% yield (61 mg).

Physical State: colorless oil;

TLC: R_f = 0.39 (PE∶EtOAc = 8∶1);

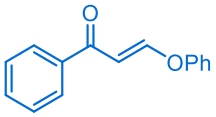
^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.08 – 8.05 (m, 2H), 7.68 – 7.60 (m, 1H), 7.54 – 7.50 (m, 2H), 7.29 – 7.25 (m, 2H), 7.07 – 7.02 (m, 2H), 6.99 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.06

(d, *J* = 4.3 Hz, 1H), 4.40 (d, *J* = 4.3 Hz, 1H), 4.24 (q, *J* = 6.3 Hz, 1H), 1.35 (s, 3H), 1.29 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (100 MHz, CDCl$_3$): δ 199.2, 157.0, 137.3, 134.2, 129.6, 129.1, 128.9, 122.2, 116.6, 102.9, 83.1, 80.7, 62.8, 22.2, 12.0;

HRMS(ESI-TOF): calc'd for $C_{19}H_{20}NaO_4$ $[M + Na]^+$: 335.1254, found: 335,1251.

Compound 36b:

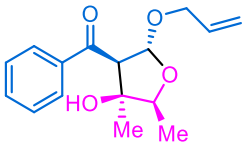


(E)-3-phenoxy-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 70 % yield (0.78 g). Identified as a known compound according to the following reference.

Reference: Li, M.; Liu, Y.; Zhang, Y. J. *Org. Lett*. **2022**, *24*, 6716–6721.

Compound 37:



(±)-((2R,3R,4S,5S)-2-(allyloxy)-4-hydroxy-4,5-dimethyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 63% yield (35 mg).

Physical State: yellow solid;

TLC: R_f = 0.45 (PE∶EtOAc = 5∶1);

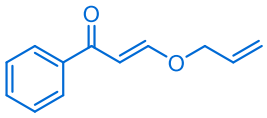
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.04 – 7.98 (m, 2H), 7.65 – 7.57 (m, 1H), 7.49 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.93 – 5.78 (m, 1H), 5.42 (d, *J* = 4.2 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7

Hz, 1H), 5.14 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.25 (ddt, *J* = 12.7, 5.4, 1.6 Hz, 1H), 4.14 – 4.03 (m, 2H), 3.98 (ddt, *J* = 12.9, 6.1, 1.5 Hz, 1H), 1.26 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 137.5, 134.2, 134.0, 129.1, 128.8, 117.5, 104.0, 82.1, 80.8, 69.5, 62.9, 22.2, 12.0;

HRMS(ESI-TOF): calc'd for $C_{16}H_{20}NaO_4$ $[M + Na]^+$: 299.1254, found: 299.1252.

Compound 37b:



(E)-3-(allyloxy)-1-phenylprop-2-en-1-one

Experimental: Prepared according to the general procedure B for the synthesis of *β*-keto enol ethers, 66% yield (0.62 g).

Physical State: yellow oil;

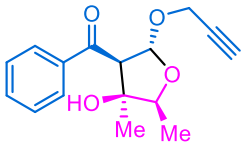
TLC: R_f = 0.40 (PE∶EtOAc = 8∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.84 (m, 2H), 7.73 (d, *J* = 12.1 Hz, 1H), 7.50 (td, *J* = 7.3, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.5, 6.9 Hz, 2H), 6.39 (d, *J* = 12.2 Hz, 1H), 6.02 – 5.88 (m, 1H), 5.38 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.31 (dt, *J* = 10.5, 1.3 Hz, 1H), 4.49 (dd, *J* = 5.5, 1.6 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 163.6, 138.7, 132.3, 131.8, 128.5, 128.0, 119.1, 102.7, 72.6;

HRMS(ESI-TOF): calc'd for $C_{12}H_{13}O_2$ $[M + H]^+$: 189.0910, found: 189.0909.

Compound 38:



(±)-((2R,3R,4S,5S)-4-hydroxy-4,5-dimethyl-2-(prop-2-yn-1-yloxy)tetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 83% yield (45 mg).

Physical State: yellow solid;

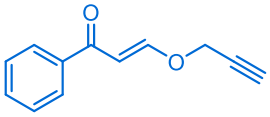
TLC: R_f = 0.42 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.95 (m, 2H), 7.64 – 7.56 (m, 1H), 7.49 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.55 (d, *J* = 3.9 Hz, 1H), 4.32 (dd, *J* = 15.5, 2.4 Hz, 1H), 4.21 (dd, *J* = 15.5, 2.4 Hz, 1H), 4.11 (d, *J* = 4.0 Hz, 1H), 4.06 (q, *J* = 6.3 Hz, 1H), 2.37 (t, *J* = 2.4 Hz, 1H), 1.26 (s, 3H), 1.23 (d, *J* = 6.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 137.4, 134.0, 129.1, 128.9, 103.2, 82.3, 80.8, 79.2, 74.6, 63.0, 55.3, 22.2, 11.9;

HRMS(ESI-TOF): calc'd for $C_{16}H_{18}NaO_4$ $[M + Na]^+$: 297.1097, found: 297.1095.

Compound 38b:



(E)-1-phenyl-3-(prop-2-yn-1-yloxy)prop-2-en-1-one

Experimental: Prepared according to the general procedure A for the synthesis of *β*-keto enol ethers, 46% yield (0.43 g).

Physical State: yellow oil;

TLC: R_f = 0.43 (PE∶EtOAc = 9∶1);

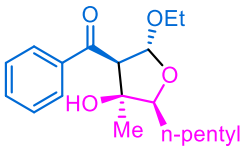
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.87 (m, 2H), 7.73 (d, *J* = 12.1 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.46 (m, 2H), 6.49 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 2.4 Hz, 2H), 2.64 (t, *J* = 2.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 162.1, 138.6, 132.6, 128.7, 128.2, 103.9, 59.0;

^{13}C NMR (125 MHz, CD_3OD): δ 192.7, 164.2, 139.6, 133.9, 129.7, 129.7, 129.2, 104.5, 78.5, 78.2, 60.1;

HRMS(ESI-TOF): calc'd for $C_{12}H_{11}O_2$ $[M + H]^+$: 187.0754, found: 187.0753.

Compound 39:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4-methyl-5-pentyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 66% (42 mg).

Physical State: colorless crystal;

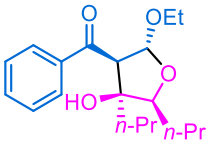
TLC: R_f = 0.72 (PE∶EtOAc = 5∶1);

^{1}H NMR (500MHz, $CDCl_3$): δ 8.04 – 7.98 (m, 2H), 7.64 – 7.56 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 5.38 (d, *J* = 4.1 Hz, 1H), 4.03 (d, *J* = 4.2 Hz, 1H), 3.86 (dd, *J* = 9.3, 2.3 Hz, 1H), 3.79 (dq, *J* = 9.7, 7.0 Hz, 1H), 3.52 – 3.40 (m, 2H), 1.69 – 1.49 (m, 2H), 1.33 (dt, *J* = 7.4, 3.2 Hz, 6H), 1.28 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.93 – 0.86 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 137.5, 133.9, 129.1, 128.8, 104.3, 86.2, 80.9, 64.2, 63.2, 32.1, 27.3, 26.6, 22.7, 22.4, 15.4, 14.2;

HRMS(ESI-TOF): calc'd for $C_{19}H_{28}NaO_4$ $[M + Na]^+$: 343.1880, found: 343.1879.

Compound 40:



(±)-((2R,3R,4S,5S)-2-ethoxy-4-hydroxy-4,5-dipropyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 29% yield (18 mg).

Physical State: colorless crystal;

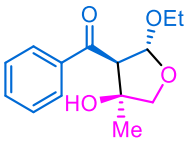
TLC: R_f = 0.61 (PE∶EtOAc = 5∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 8.01 (m, 2H), 7.66 – 7.57 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 5.20 (d, *J* = 4.5 Hz, 1H), 4.00 (d, *J* = 4.5 Hz, 1H), 3.90 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.78 (dq, *J* = 9.8, 7.1 Hz, 1H), 3.43 (dq, *J* = 9.8, 7.0 Hz, 1H), 1.78 – 1.35 (m, 8H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (100MHz, $CDCl_3$): δ 202.4, 137.4, 134.1, 129.1, 128.8, 105.0, 85.7, 84.3, 64.3, 60.0, 39.4, 29.8, 20.2, 18.5, 15.3, 14.7, 14.3;

HRMS(ESI-TOF): calc'd for $C_{19}H_{28}NaO_4$ $[M + Na]^+$: 343.1880, found: 343.1880.

Compound 41:



(±)-((2R,3R,4S)-2-ethoxy-4-hydroxy-4-methyltetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 64% yield (32 mg).

Physical State: white solid;

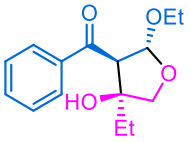
TLC: R_f = 0.48 (PE∶EtOAc = 3∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.61 (td, *J* = 7.4, 1.3 Hz, 1H), 7.52 – 7.47 (m, 2H), 5.45 (d, *J* = 4.2 Hz, 1H), 3.96 (d, *J* = 4.3 Hz, 1H), 3.93 (d, *J* = 9.1 Hz, 1H), 3.86 (d, *J* = 9.1 Hz, 1H), 3.79 (dq, *J* = 9.8, 7.1 Hz, 1H), 3.46 (dq, *J* = 9.7, 7.1 Hz, 1H), 1.39 (s, 3H), 1.17 (dd, *J* = 7.5, 6.5 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.9, 137.5, 134.1, 129.1, 128.8, 106.6, 80.6, 78.9, 64.5, 61.9, 23.0, 15.3;

HRMS(ESI-TOF): calc'd for $C_{14}H_{18}NaO_4$ $[M + Na]^+$: 273.1097, found: 273.1095.

Compound 42:



(±)-((2R,3R,4S)-2-ethoxy-4-ethyl-4-hydroxytetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 63% yield (33 mg).

Physical State: yellow solid;

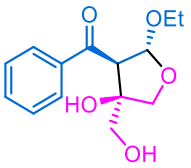
TLC: R_f = 0.46 (PE∶EtOAc = 5∶1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (dd, J = 8.2, 1.4 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 5.37 (d, J = 4.6 Hz, 1H), 3.96 – 3.92 (m, 2H), 3.89 (d, J = 9.1 Hz, 1H), 3.79 (dq, J = 9.7, 7.1 Hz, 1H), 3.44 (dq, J = 9.7, 7.0 Hz, 1H), 1.69 (qd, J = 7.2, 3.8 Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 201.2, 137.4, 134.1, 129.1, 128.8, 106.9, 84.1, 77.8, 64.5, 60.3, 30.4, 15.2, 9.2;

HRMS(ESI-TOF): calc'd for $C_{15}H_{20}NaO_4$ $[M + Na]^+$: 287.1254, found: 287.1254.

Compound 43:



(±)-((2R,3R,4R)-2-ethoxy-4-hydroxy-4-(hydroxymethyl)tetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 62% yield (33 mg).

Physical State: yellow solid;

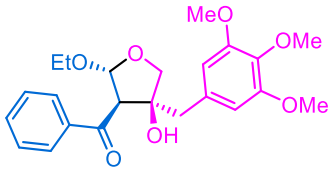
TLC: R_f = 0.45 (PE∶EtOAc = 1∶1);

^{1}H NMR (500MHz, $CDCl_3$): δ 8.04 – 8.00 (m, 2H), 7.62 – 7.55 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 5.34 (d, J = 3.8 Hz, 1H), 4.08 (d, J = 3.8 Hz, 1H), 4.01 (d, J = 9.4 Hz, 1H), 3.89 (d, J = 9.4 Hz, 1H), 3.76 (dq, J = 9.8, 7.1 Hz, 1H), 3.71 – 3.63 (m, 2H), 3.43 (dq, J = 9.7, 7.1 Hz, 1H), 1.15 (t, J = 7.0 Hz, 3H);

^{13}C NMR (125MHz, $CDCl_3$): δ 200.6, 137.1, 134.1, 129.1, 128.8, 106.6, 83.9, 75.7, 66.4, 64.4, 57.5, 15.2;

HRMS(ESI-TOF): calc'd for $C_{14}H_{18}NaO_5$ $[M + Na]^+$: 289.1046, found: 289.1043.

Compound 44:



(±)-((2R,3R,4S)-2-ethoxy-4-hydroxy-4-(3,4,5-trimethoxybenzyl)tetrahydrofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 28% yield (23 mg).

Physical State: yellow foem;

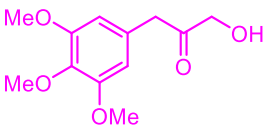
TLC: R_f = 0.29 (PE∶EtOAc = 3∶1);

^{1}H NMR (600MHz, $CDCl_3$): δ 7.82 – 7.78 (m, 2H), 7.56 (tt, J = 7.3, 1.3 Hz, 1H), 7.43 – 7.38 (m, 2H), 6.26 (s, 2H), 5.27 (d, J = 5.2 Hz, 1H), 4.05 (d, J = 9.0 Hz, 1H), 3.98 (d, J = 5.2 Hz, 1H), 3.94 (d, J = 8.9 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.72 (s, 3H), 3.54 (s, 6H), 3.44 (dq, J = 9.7, 7.1 Hz, 1H), 2.95 (d, J = 13.6 Hz, 1H), 2.71 (d, J = 13.6 Hz, 1H), 1.17 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 152.9, 137.5, 136.8, 134.0, 132.7, 128.6, 128.6, 107.2, 106.8, 85.1, 78.4, 64.9, 60.8, 58.1, 55.8, 43.7, 15.2.

HRMS(ESI-TOF): calc'd for $C_{23}H_{28}NaO_7$ $[M + Na]^+$: 439.1727, found: 439.1727.

Compound 44a:

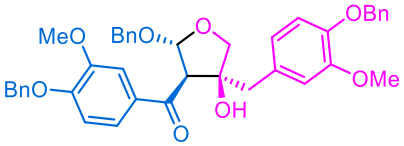


1-hydroxy-3-(3,4,5-trimethoxyphenyl)propan-2-one

Experimental: Prepared according to the general procedure for the synthesis of *α*-hydroxyphenylacetone, 65% yield (0.78 g). Identified as a known compound according to the following reference.

Reference: Rosowsky, A.; Chen, H.; Fu, H.; Queener, S. F. *Bioorg. Med. Chem.* **2003**, *11*, 59–67.

Compound 45:



(±)-(4-(benzyloxy)-3-methoxyphenyl)((2R,3R,4S)-2-(benzyloxy)-4-(4-(benzyloxy)-3-methoxybenzyl)-4-hydroxytetrahydrofuran-3-yl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 54% yield (71 mg).

Physical State: white solid;

TLC: R_f = 0.61 (PE∶EtOAc = 2∶1);

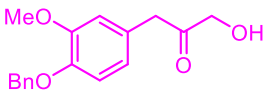
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49 – 7.19 (m, 17H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 6.56 (d, *J* = 2.5 Hz, 2H), 5.41 (d, *J* = 4.9 Hz, 1H), 5.23 (s, 2H), 5.00 (s, 2H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.10 (d, *J* = 8.9 Hz, 1H), 4.00 (d, *J* = 5.0 Hz, 1H), 3.96 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 3.61 (s, 3H), 2.96 (d, *J* = 13.7 Hz, 1H), 2.80 (d, *J* = 13.7 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 199.6, 153.2, 149.4, 149.2, 147.0, 137.3, 137.2, 136.1, 130.7, 130.0, 128.7, 128.6, 128.5, 128.4, 128.4, 128.2, 128.0, 127.8, 127.8, 127.3, 127.2,

123.8, 122.1, 113.5, 113.5, 111.8, 110.9, 106.7, 84.9, 78.1, 70.9, 70.9, 70.8, 57.5, 55.9, 55.5, 42.9;

HRMS(ESI-TOF): calc'd for $C_{41}H_{41}O_8$ $[M + H]^+$: 661.2796, found: 661.2797.

Compound 45a:



1-(4-(benzyloxy)-3-methoxyphenyl)-3-hydroxypropan-2-one

Experimental: Eugenol (820 mg, 5 mmol, 1 eq.) was dissolved in 15 mL of super-dried MeCN. NaH (240 mg, 6 mmol, 60% in oil,1.2 eq.) was added in ice bath. Then, benzylbromide (1 g, 6 mmol, 1.2 eq.) was added dropwise to the mixture. The reaction mixture was stirred for 2 h at room temperature before being quenched with saturated NH_4Cl (5 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product then followed the general procedure for the synthesis of *α*-hydroxyphenylacetone, 62% yield (0.89 g) over three steps.

Physical State: yellow oil;

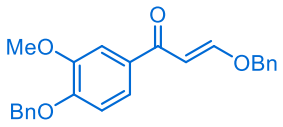
TLC: R_f = 0.21 (PE∶EtOAc = 2∶1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.45 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.33 – 7.27 (m, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.13 (s, 2H), 4.27 (s, 2H), 3.87 (s, 3H), 3.64 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 207.7, 150.0, 147.7, 137.1, 128.7, 128.0, 127.4, 125.8, 121.6, 114.4, 112.9, 71.2, 67.6, 56.1, 45.5;

HRMS(ESI-TOF): calc'd for $C_{17}H_{18}NaO_4$ $[M + Na]^+$: 309.1097, found: 309.1098.

Compound 45b:



(E)-3-(benzyloxy)-1-(4-(benzyloxy)-3-methoxyphenyl)prop-2-en-1-one

Experimental: Prepared according to the general procedure B for the synthesis of *β*-keto enol ethers, 66% yield (1.23 g).

Physical State: white solid;

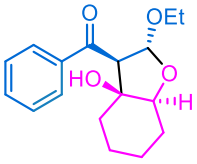
TLC: R_f = 0.45 (PE∶EtOAc = 4∶1);

^{1}H NMR (800 MHz, $CDCl_3$): *δ* 7.83 (d, *J* = 12.1 Hz, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.46 – 7.30 (m, 11H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 12.1 Hz, 1H), 5.21 (s, 2H), 5.01 (s, 2H), 3.93 (s, 3H);

^{13}C NMR (200 MHz, $CDCl_3$): *δ* 188.9, 163.1, 152.0, 149.6, 136.5, 135.4, 131.9, 128.9, 128.7, 128.7, 128.1, 127.8, 127.3, 122.1, 112.2, 111.0, 102.5, 73.9, 70.8, 56.1;

HRMS(ESI-TOF): calc'd for $C_{24}H_{23}O_4$ $[M + H]^+$: 375.1591, found: 375.1595.

Compound 51:



(±)-((2R,3R,3aS,7aS)-2-ethoxy-3a-hydroxyoctahydrobenzofuran-3-yl)(phenyl)methanone

Experimental: Prepared according to the general procedure for [3 + 2] cycloaddition, 5% yield (3 mg).

Physical State: white solid;

TLC: R_f = 0.51 (PE∶EtOAc = 9∶1);

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 8.04 – 7.93 (m, 2H), 7.62 – 7.56 (m, 1H), 7.54 – 7.44 (m, 2H), 5.60 (d, *J* = 4.4 Hz, 1H), 3.91 (d, *J* = 4.4 Hz, 1H), 3.87 – 3.78 (m, 2H), 3.50

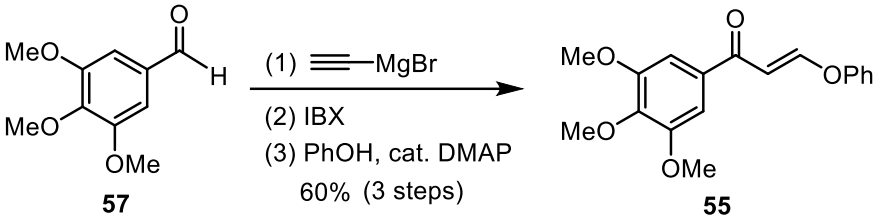
(dq, *J* = 9.6, 7.0 Hz, 1H), 1.88 – 1.76 (m, 4H), 1.29 – 1.22 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 137.6, 133.8, 129.0, 128.8, 104.9, 83.5, 79.6, 64.8, 62.9, 33.8, 24.4, 23.6, 20.7, 15.3;

HRMS(ESI-TOF): calc'd for $C_{17}H_{22}NaO_4$ $[M + Na]^+$: 313.1410, found: 313.1412;

Total Synthesis of (±)-*β*-Apopicropodophyllin

Compound 55



Experimental: Prepared according to the general procedure B for the synthesis of *β*-keto enol ethers, 60% yield (0.94 g).

Physical State: white solid;

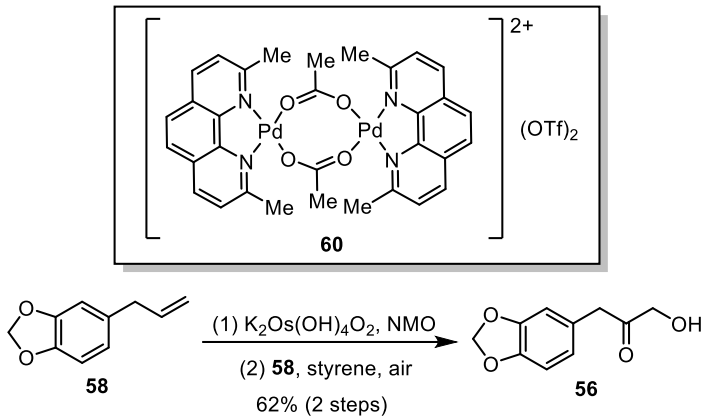
TLC: R_f = 0.52 (PE∶EtOAc = 4∶1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.32 – 7.23 (m, 2H), 7.15 (s, 2H), 7.06 – 6.96 (m, 3H), 6.65 (d, *J* = 1.6 Hz, 1H), 6.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 5.96 (d, *J* = 4.8 Hz, 1H), 5.83 (dt, *J* = 15.4, 1.3 Hz, 2H), 4.27 (d, *J* = 4.8 Hz, 1H), 4.17 (d, *J* = 9.3 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 3.95 (d, *J* = 0.9 Hz, 3H), 3.90 (d, *J* = 1.0 Hz, 6H), 3.01 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 188.9, 159.7, 156.2, 153.0 142.2, 133.5, 130.0, 125.0, 117.6, 106.5, 105.5, 60.9, 56.2;

HRMS(ESI-TOF): calc'd for $C_{18}H_{19}O_5$ $[M + H]^+$: 315.2227, found: 315.2228.

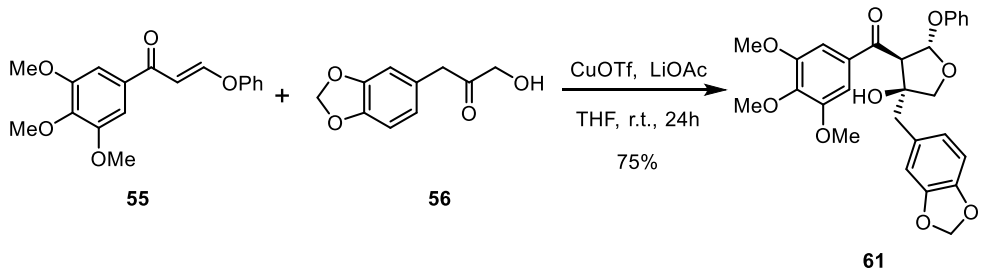
Compound 56



Experimental: Prepared according to the general procedure for the synthesis of α-hydroxyphenylacetone, 62% yield (0.6 g). Identified as a known compound according to the following reference.

Reference: Dobbelaar, Peter H.; Franklin, Christopher L.; Goodman, A.; Guo, Cheng; Guzzo, Peter R.; Hadden, M.; He, Shuwen; Henderson, Alan J.; Jian, Tianying; Lin, Linus S.; Liu, Jian; Nargund, Ravi P.; Ruenz M.; Sargent, Bruce J.; Sebhat, Iyassu K.; Yet L. Preparation of substituted imidazoles as bombesin receptor subtype-3 modulators. WO2008051405A12007.

Compound 61



Experimental: Compound **61** was synthesized according to the general procedure of [3 + 2] cycloaddition. To the solution of **55** (1 mmol, 314 mg, 1 eq.) in 5 mL of super-dried THF was added **56** (194 mg, 1 mmol, 1 eq.). Then, CuOTf (21 mg, 10 mol%) and LiOAc (6.6 mg, 10 mol%) were added to the mixture, which was stirred for 20 h. The

slovent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (gradient 5%→35% EtOAc in petroleum ether) to afford **61** (381 mg, 75%).

Physical State: yellow foam;

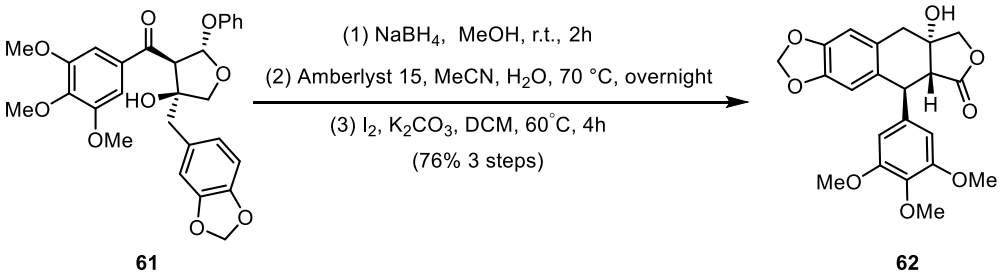
TLC: R_f = 0.67 (PE∶EtOAc = 2∶1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 2H), 7.15 (s, 2H), 7.06 – 6.96 (m, 3H), 6.65 (d, *J* = 1.6 Hz, 1H), 6.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 5.96 (d, *J* = 4.8 Hz, 1H), 5.83 (dt, *J* = 15.4, 1.3 Hz, 2H), 4.27 (d, *J* = 4.8 Hz, 1H), 4.17 (d, *J* = 9.3 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 3.95 (d, *J* = 0.9 Hz, 3H), 3.90 (d, *J* = 1.0 Hz, 6H), 3.01 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 156.6, 152.9, 147.4, 146.4, 143.5, 132.2, 130.3, 129.5, 123.0, 122.4, 116.4, 110.5, 107.9, 106.2, 105.2, 100.9, 84.7, 78.8, 60.9, 57.8, 56.2, 42.9;

HRMS(ESI-TOF): calc'd for $C_{28}H_{29}O_9$ $[M + H]^+$: 509.1806, found: 509.1801.

Compound 62



61 **62**

Experimental: To the solution of **61** (100 mg, 0.2 mmol, 1 eq.) in 2 mL of super-dried methanol was added $NaBH_4$ (0.4 mmol, 15 mg, 2 eq.). The reaction mixture was stirred for 2 h before being quenched with saturated NH_4Cl (5 mL) and extracted with DCM (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. Without further purification, the residue was dissolved in 6 mL of MeCN and 0.3 mL of water. Amberlyst 15 (40 mg) was then added to the solution. The mixture was stirred overnight at 70℃ before being filtered. The organic phase was then concentrated under reduced pressure. The residue was dissolved

in 4 mL of super-dried DCM. I_2 (0.4 mmol, 101 mg) and K_2CO_3 (0.4 mmol, 55 mg) were then added to the solution. The mixture was stirred at 60℃ for 4 h before being quenched with saturated $Na_2S_2O_3$ (5 mL) and extracted with DCM (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. And the residue was purified by flash column chromatography on silica gel (gradient 0%→6% methanol in DCM) to afford **62** (63 mg, 76%). (For details, see the following reference)

Physical State: white solid**;**

TLC: R_f = 0.48 (DCM∶MeOH = 19∶1);

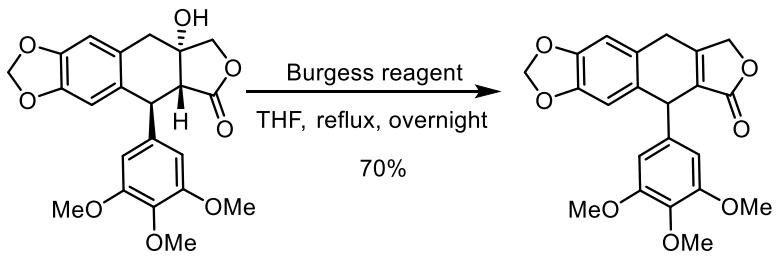
^{1}H NMR (500 MHz, acetonitrile-*d*$_3$): δ 6.65 (s, 1H), 6.53 (s, 2H), 6.26 (s, 1H), 5.86 (s, 2H), 4.32 (d, *J* = 9.3 Hz, 1H), 4.26 (d, *J* = 9.3 Hz, 1H), 4.07 (d, *J* = 11.8 Hz, 1H), 3.76 (s, 6H), 3.71 (s, 3H), 3.29 (d, *J* = 15.6 Hz, 1H), 3.07 (d, *J* = 11.8 Hz, 1H), 2.95 (d, *J* = 16.4 Hz, 1H);

^{13}C NMR (125 MHz, acetonitrile-*d*$_3$): δ 175.8, 154.2, 147.3, 142.6, 139.9, 137.5, 133.2, 127.4, 109.9, 109.8, 107.8, 102.2, 77.8, 75.7, 60.7, 56.7, 51.0, 42.9, 39.1;

HRMS(ESI-TOF): calc'd for $C_{22}H_{23}O_8$ $[M + H]^+$: 415.1387, found: 415.1390.

Reference: (a) Fusaro, M. B.; Chagnault, V.; Josse, S.; Postel, D. *Tetrahedron* **2013**, *69*, 5880–5883;(Step 2) (b) Hébert, M.; Bellavance, G.; Barriault, L. *J. Am. Chem. Soc.* **2022**, *144*, 17792–17796. (Step 3)

Compound 53



62 **53**

Experimental: To the solution of **62** (0.1 mmol, 41 mg, 1 eq.) in 2 mL of super-dried THF was added Burgess reagent (48 mg, 0.2 mmol, 2 eq.). The reaction mixture was

stirred overnight at 70℃ before being quenched with water (2 mL) and extracted with DCM (5 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by HPLC to afford **53** (27.6 mg, 70%).

Physical State: white solid;

TLC: R_f = 0.70 (PE∶DCM = 1∶1);

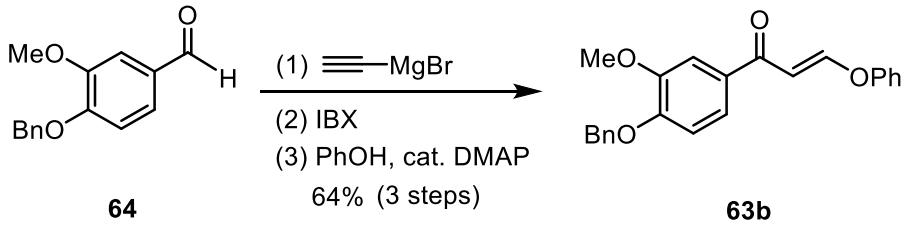
^{1}H NMR (800 MHz, $CDCl_3$): δ 6.72 (s, 1H), 6.63 (s, 1H), 6.37 (s, 2H), 5.95 (d, *J* = 8.4, 2H), 4.89 (d, *J* = 16.7 Hz, 1H), 4.83 – 4.81 (m, 1H), 3.85 (dd, *J* = 22.5, 4.4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 6H), 3.65 (dd, *J* = 22.3, 3.9 Hz, 1H);

^{13}C NMR (200 MHz, $CDCl_3$): δ 172.4, 157.4, 153.4, 147.4, 147.2, 138.4, 137.2, 129.8, 128.3, 123.9, 109.7, 107.9, 105.7, 101.5, 71.1, 60.9, 56.3, 42.9, 29.4;

HRMS(ESI-TOF): calc'd for $C_{22}H_{19}O_7$ $[M-H]^-$: 395.1136, found: 395.1138.

Total Synthesis of (±)-Cycloolivil

Compound 63b



64 **63b**

Experimental: Prepared according to the general procedure B for the synthesis of *β*-keto enol ethers.

Physical State: white solid;

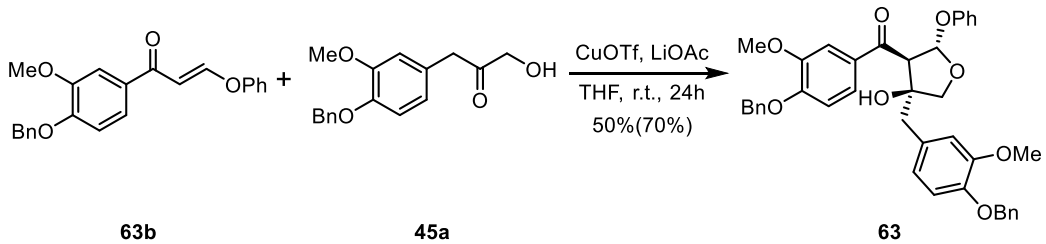
TLC: R_f = 0.57 (PE∶EtOAc = 4∶1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.98 (d, *J* = 11.7 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.47 – 7.34 (m, 8H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 11.7 Hz, 1H), 5.21 (s, 2H), 3.94 (s, 3H);

NMR (100 MHz, $CDCl_3$): *δ* 188.6, 159.3, 156.2, 152.2, 149.6, 136.3, 131.6, 130.0, 128.7, 128.1, 127.2, 125.0, 122.4, 117.8, 112.2, 110.8, 106.4, 70.8, 56.0;

HRMS(ESI-TOF): calc'd for $C_{23}H_{21}O_4$ $[M + H]^+$: 361.1434, found: 361.1432.

Compound 63



63b **45a** **63**

Experimental: Compound **63** was synthesized according to the general procedure of [3 + 2] cycloaddition. To the solution of **63b** (360 mg, 1 mmol, 1 eq.) in 5 mL of super-dried THF was added **45a** (286 mg, 1 mmol, 1 eq.). Then, CuOTf (21 mg, 10 mol%)

and LiOAc (6.6 mg, 10 mol%) were added to the solution. The reaction mixture was stirred for 20 h. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (gradient 5%→25% EtOAc in petroleum ether) to afford **63** (373 mg, 50%).

Physical State: white solid;

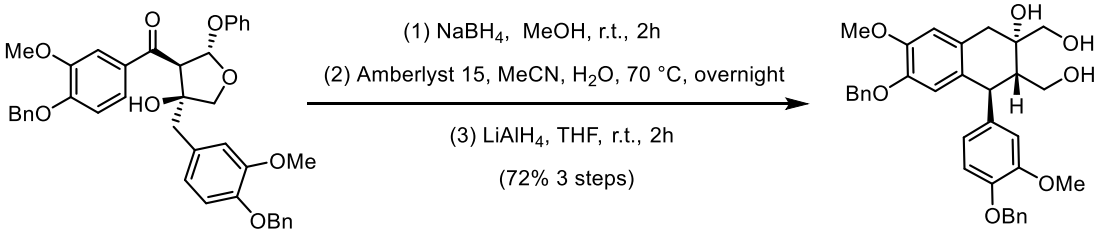
TLC: R_f = 0.68 (PE∶EtOAc = 2∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.5, 2.1 Hz, 1H), 7.40 – 7.24 (m, 11H), 7.21 – 7.17 (m, 2H), 6.93 (dd, J = 8.0, 5.4 Hz, 3H), 6.83 (d, J = 8.5 Hz, 1H), 6.64 (d, J = 1.4 Hz, 1H), 6.52 (d, J = 1.5 Hz, 2H), 5.84 (d, J = 5.0 Hz, 1H), 5.33 (s, 1H), 5.18 (d, J = 2.5 Hz, 2H), 4.96 (s, 2H), 4.18 (d, J = 5.1 Hz, 1H), 4.12 (d, J = 9.0 Hz, 1H), 3.96 (d, J = 9.0 Hz, 1H), 3.84 (s, 3H), 3.59 (s, 3H), 2.95 (d, J = 13.8 Hz, 1H), 2.81 (d, J = 13.8 Hz, 1H);

^{13}C NMR (200 MHz, $CDCl_3$): δ 199.2, 156.9, 153.5, 149.6, 149.3, 147.3, 137.2, 136.1, 130.7, 129.9, 129.7, 128.8, 128.6, 128.4, 127.9, 127.4, 127.3, 124.0, 122.5, 122.2, 116.6, 113.6, 113.6, 112.0, 110.9, 105.6, 84.7, 78.8, 71.0, 70.9, 57.3, 56.1, 55.7, 43.0;

HRMS(ESI-TOF): calc'd for $C_{40}H_{39}O_8$ $[M + H]^+$: 647.2639, found: 647.2640.

Compound 66



63 **66**

Experimental: To the solution of **63** (130 mg, 0.2 mmol, 1 eq.) in 2 mL of super-dried methanol was added $NaBH_4$ (15 mg, 0.4 mmol, 2 eq.). The reaction mixture was stirred for 2 h before being quenched with saturated NH_4Cl (5 mL) and extracted with DCM (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. Without further purification, the residue was dissolved in 6 mL of MeCN and 0.3 mL of water. Amberlyst 15 (40 mg) was then added

to the solution. The mixture was stirred overnight at 70℃ before being filtered. The solution was then concentrated under reduced pressure. The residue was dissolved in 2 mL of super-dried THF. $LiAlH_4$ (11 mg, 0.3 mmol, 1.5 eq.) was then added to the solution. The mixture was stirred at room temperature for 2 h before being quenched with water (5 mL). 1 M HCl was then added to adjust pH to 2. The mixture was then extracted with DCM (10 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (gradient 0%→6% methanol in DCM) to afford **66** (80 mg, 72%).

Physical State: white solid;

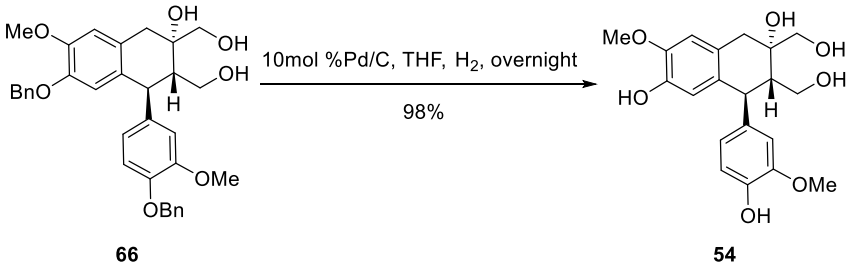
TLC: R_f = 0.71 (DCM∶MeOH = 10∶1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.43 (m, 2H), 7.38 (ddd, *J* = 7.8, 6.4, 1.3 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.21 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.18 – 7.12 (m, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.62 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.59 (s, 1H), 6.50 (d, *J* = 2.1 Hz, 1H), 6.21 (d, *J* = 0.8 Hz, 1H), 3.95 (d, *J* = 11.6 Hz, 1H), 3.85 (s, 3H), 3.83 – 3.76 (m, 2H), 3.74 (s, 3H), 3.68 (d, *J* = 11.0 Hz, 1H), 3.60 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.07 (d, *J* = 16.6 Hz, 1H), 2.73 (d, *J* = 16.8 Hz, 1H), 1.95 (ddd, *J* = 11.6, 5.3, 2.4 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 148.3, 147.0, 146.5, 137.7, 137.4, 137.3, 131.0, 128.7, 128.5, 128.0, 127.7, 127.5, 127.4, 125.6, 122.0, 115.7, 113.9, 112.5, 112.1, 73.2, 71.2, 71.0, 69.3, 61.0, 56.1 (×2), 48.1, 44.0, 39.7;

HRMS(ESI-TOF): calc'd for $C_{34}H_{35}O_7$ $[M-H]^-$: 555.2388, found: 555.2386.

Compound 54



66 **54**

Experimental: To the solution of **66** (55.6 mg, 0.1 mmol) was in 10 mL of super-dried

THF was added Pd/C (10 mol%). The mixture was stirred overnight at room temperature under 1 atm H_2 atmosphere before being filtered. The organic phase was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (gradient 0%→10% methanol in DCM) to afford **54** (37 mg, 98%).

Physical State: white solid;

TLC: R_f = 0.12 (DCM∶MeOH = 9∶1);

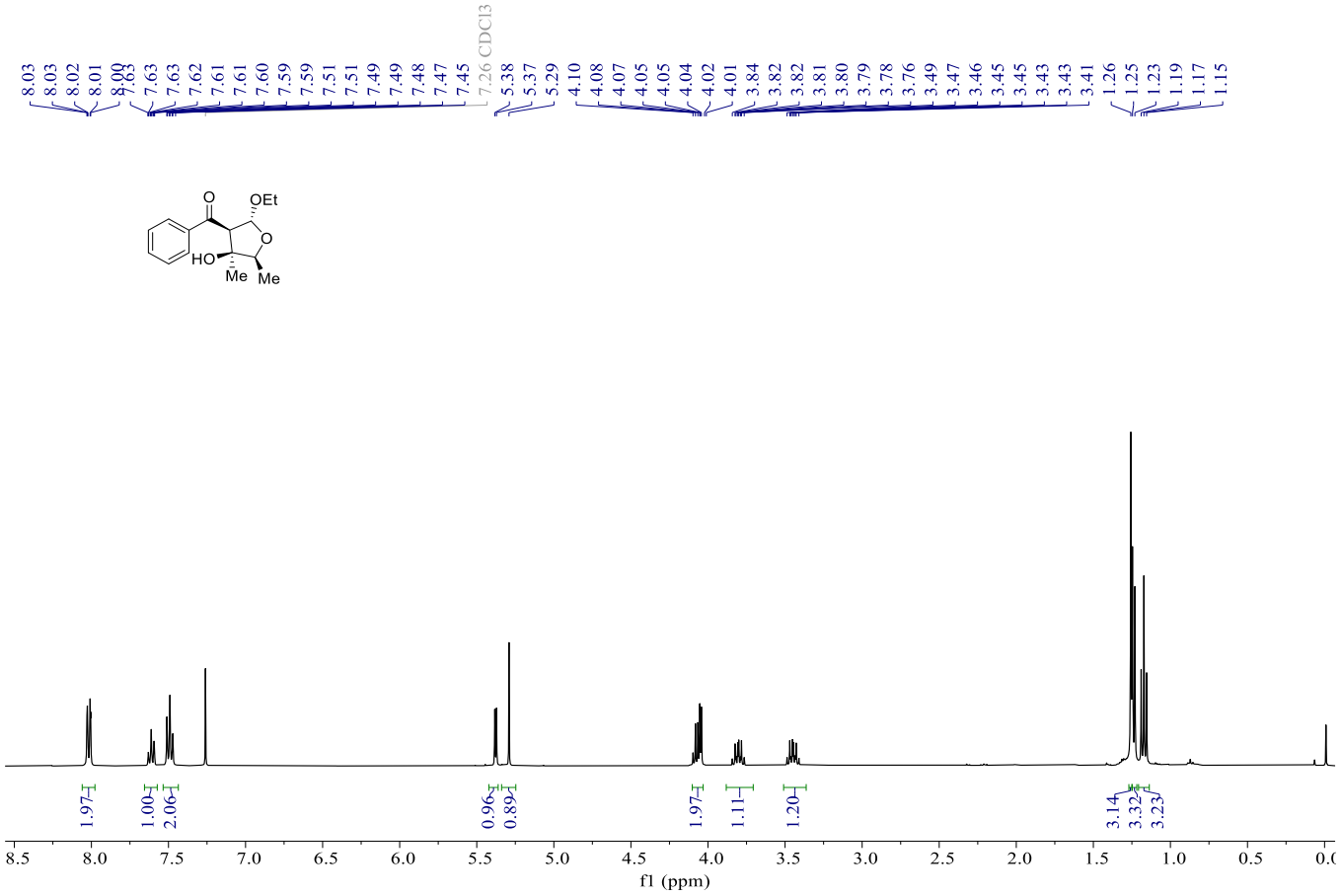
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (d, J = 8.1 Hz, 1H), 6.68 (dd, J = 8.1, 2.0 Hz, 1H), 6.61 (d, J = 2.0 Hz, 1H), 6.57 (s, 1H), 6.34 – 6.28 (m, 1H), 3.97 (d, J = 11.4 Hz, 1H), 3.85 (s, 3H), 3.83 (d, J = 2.0 Hz, 3H), 3.83 – 3.79 (m, 2H), 3.69 (d, J = 11.3 Hz, 1H), 3.65 (dd, J = 11.1, 5.5 Hz, 1H), 3.09 (d, J = 16.3 Hz, 1H), 2.74 (d, J = 16.5 Hz, 1H), 2.00 (ddd, J = 11.4, 5.4, 2.6 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 146.9, 145.4, 144.5, 144.1, 136.6, 132.1, 124.5, 122.6, 115.6, 114.5, 111.7, 111.0, 73.3, 69.3, 61.0, 56.1, 56.0, 48.3, 44.2, 39.8;

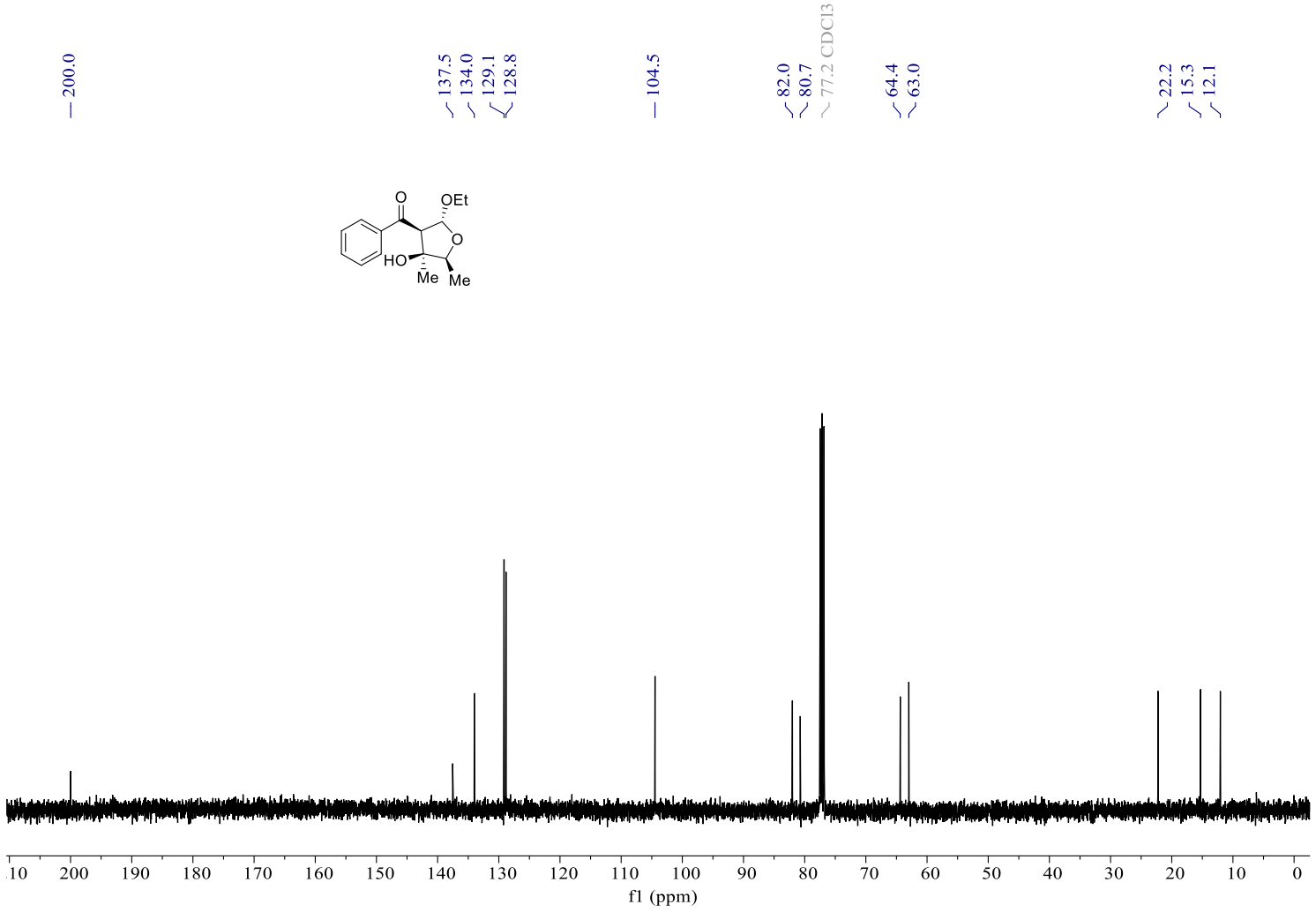
HRMS(ESI-TOF): calc'd for $C_{22}H_{23}O_7$ $[M - H]^-$: 375.1449, found: 375.1448.

NMR Spectra

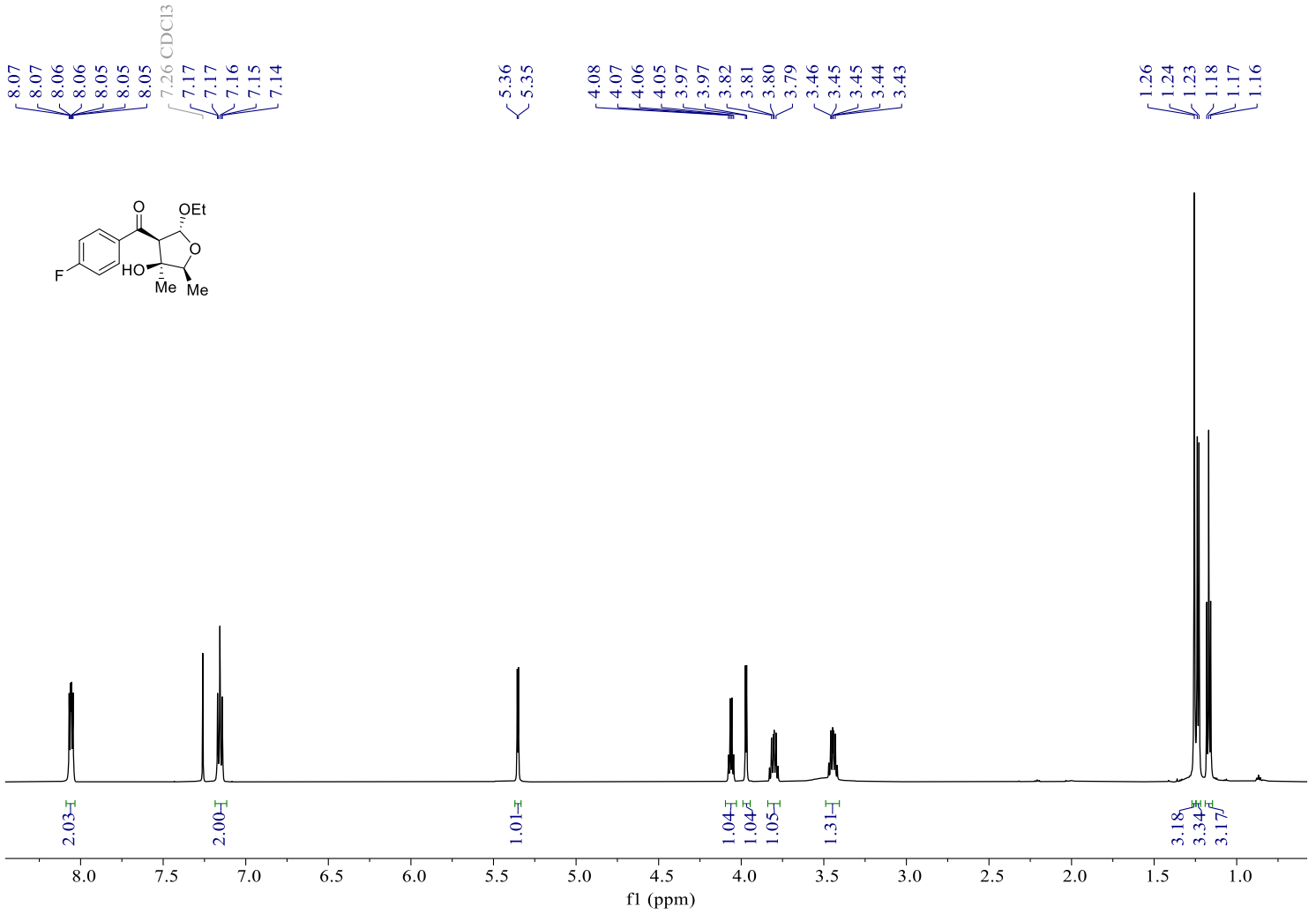
Compound 3 ^{1}H NMR (400 MHz, $CDCl_3$)



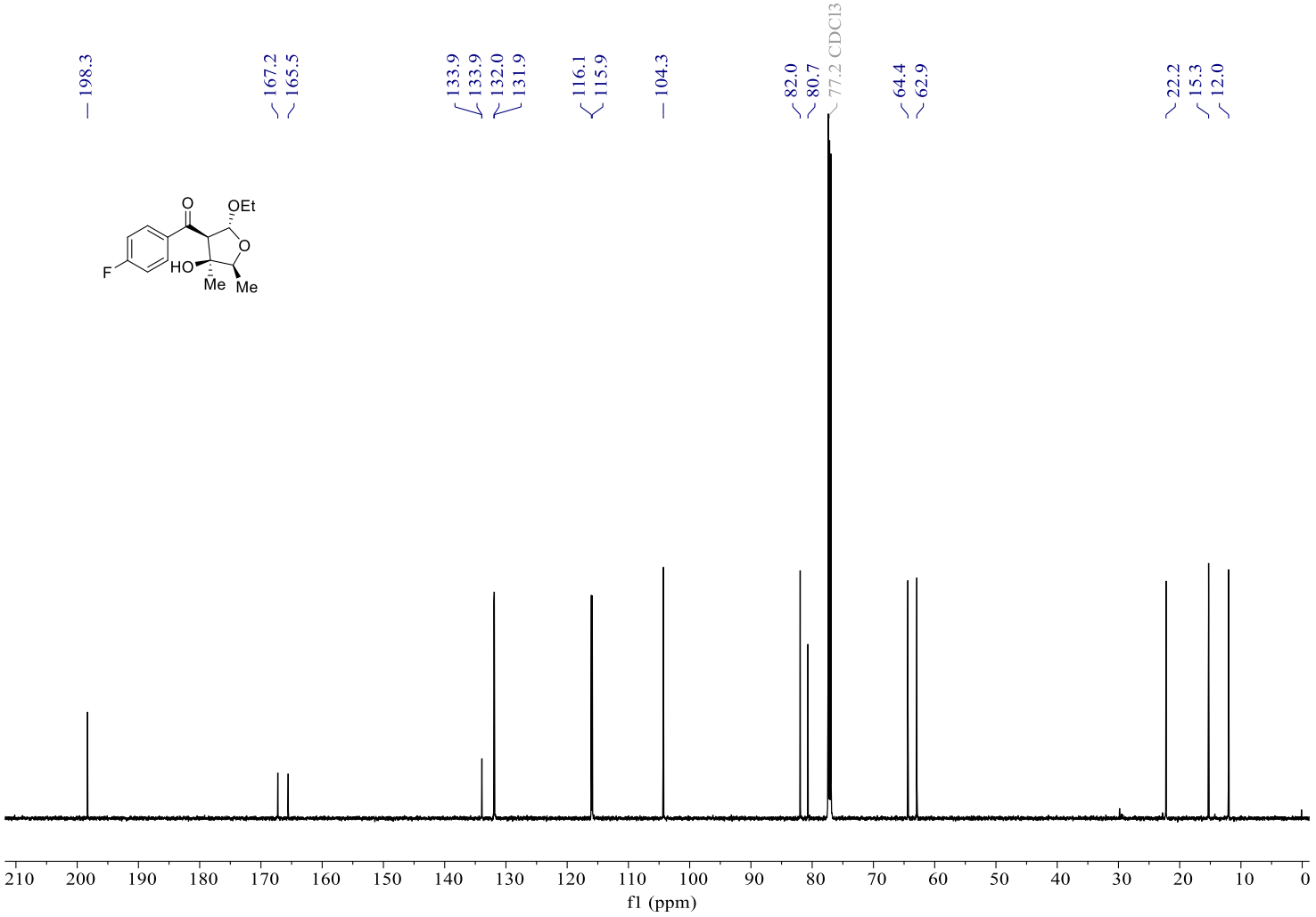
Compound 3 ^{13}C NMR (100 MHz, $CDCl_3$)



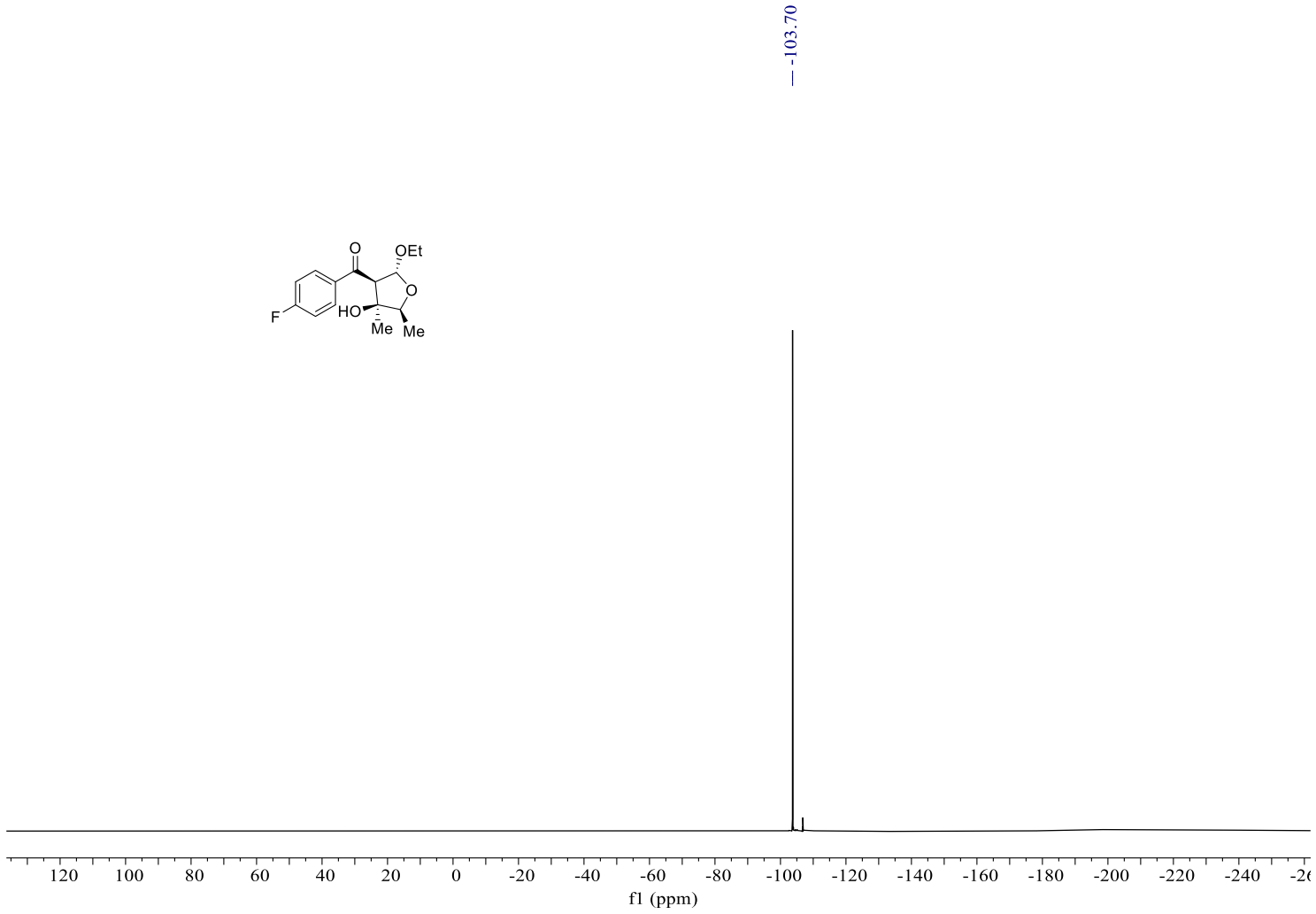
Compound 4 ^{1}H NMR (600 MHz, $CDCl_3$)



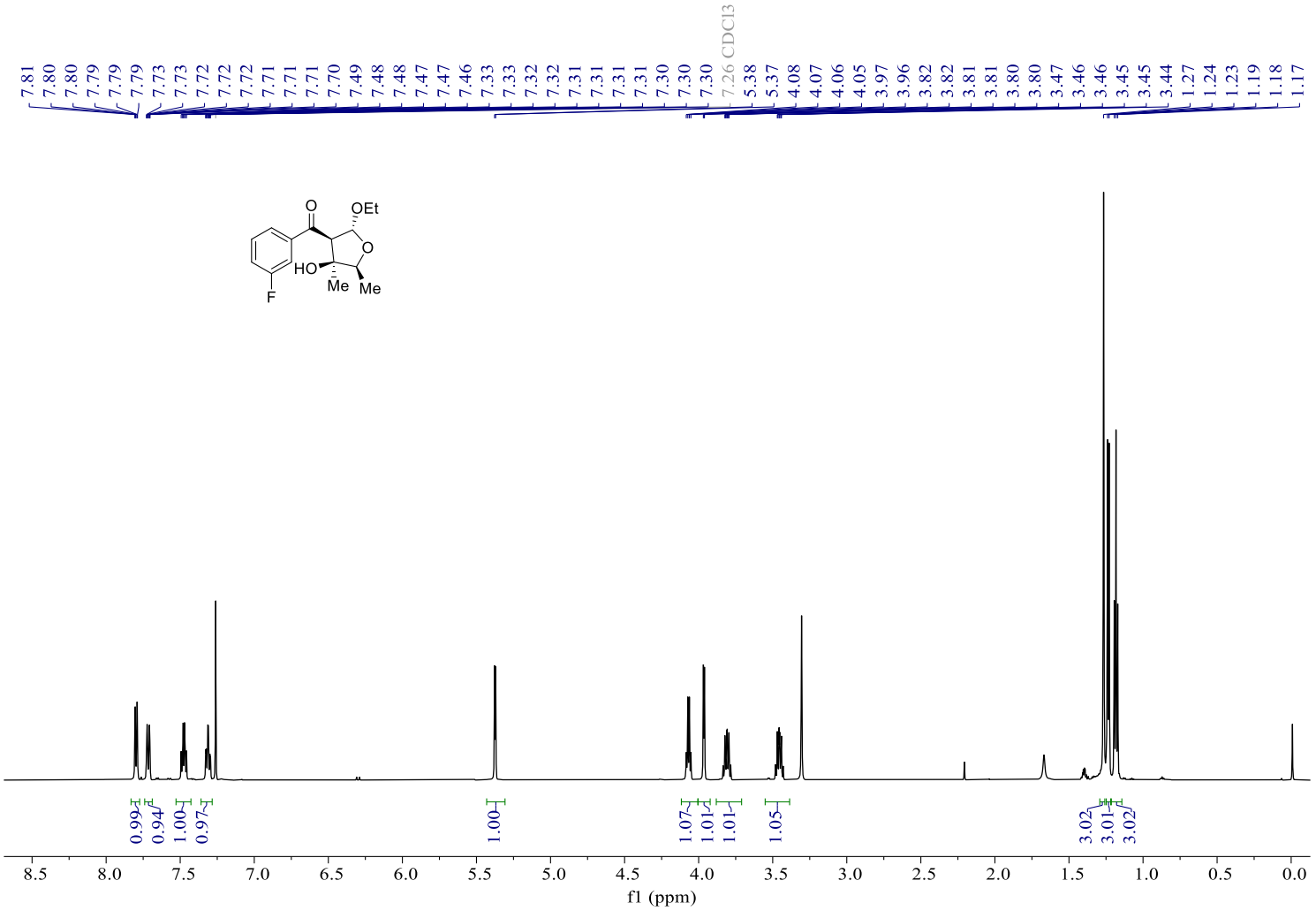
Compound 4 ^{13}C NMR (150 MHz, $CDCl_3$)



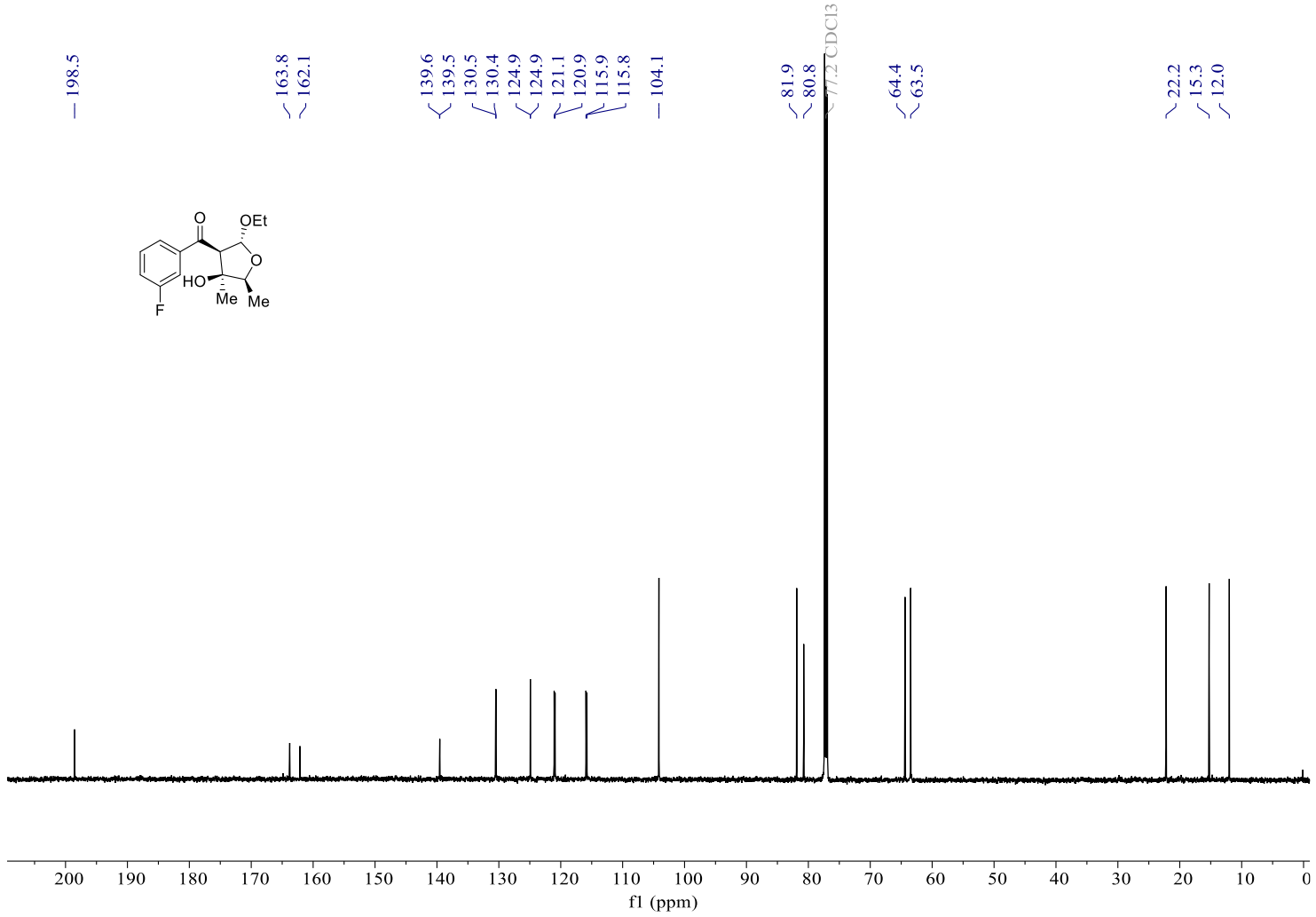
Compound 4 ^{19}F NMR (753 MHz, $CDCl_3$)



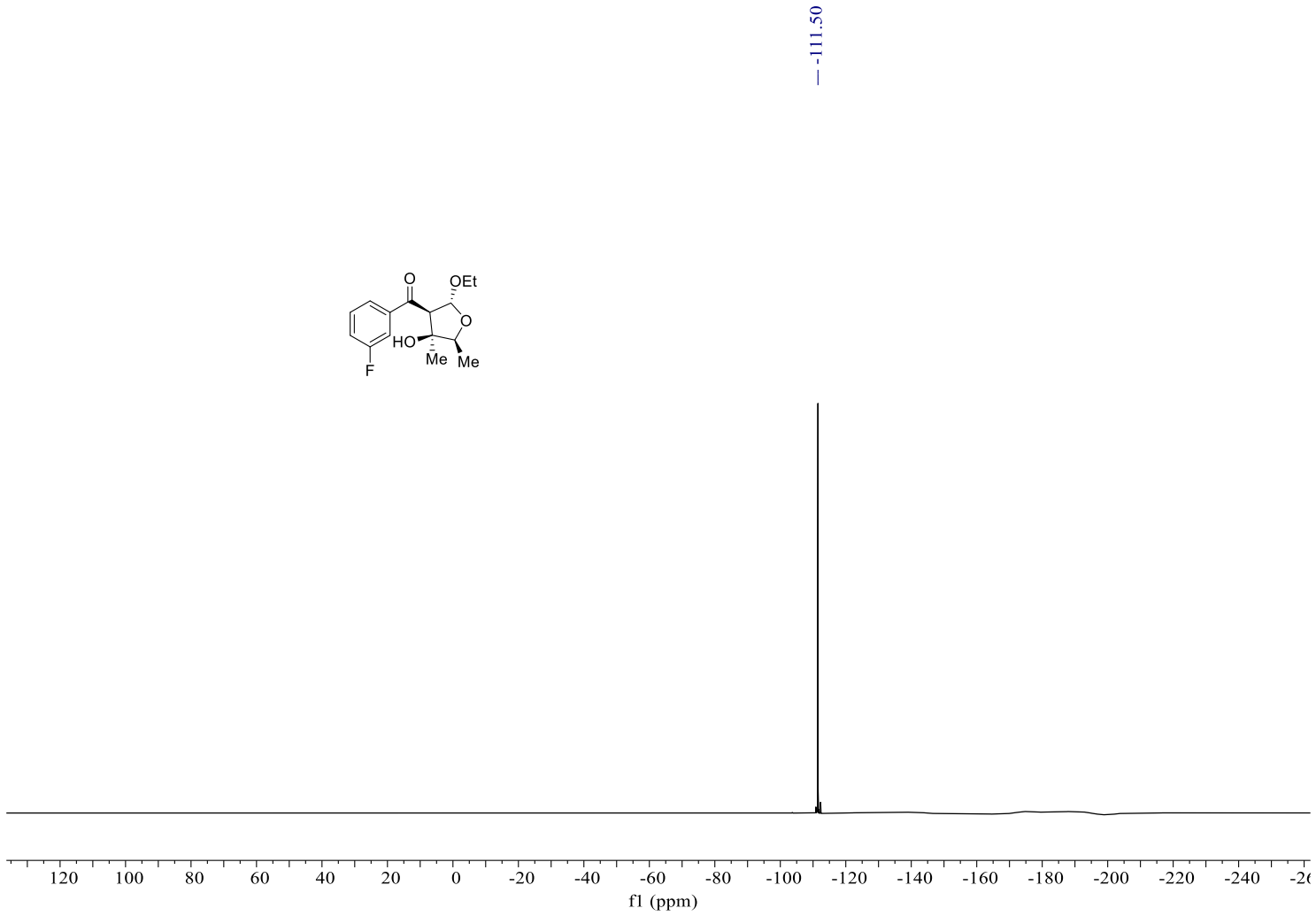
Compound 5 ^{1}H NMR (600 MHz, $CDCl_3$)



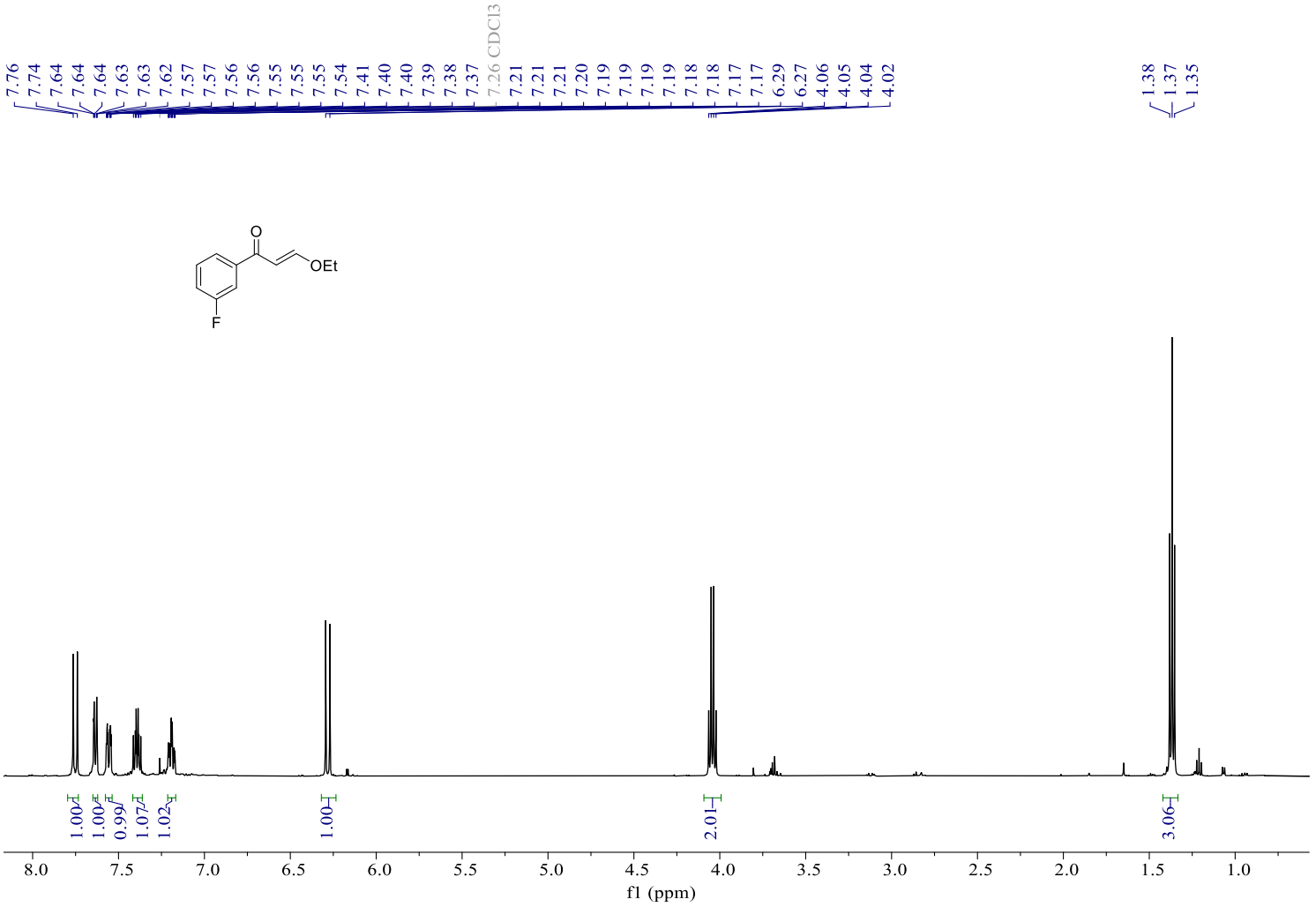
Compound 5 ^{13}C NMR (150 MHz, $CDCl_3$)



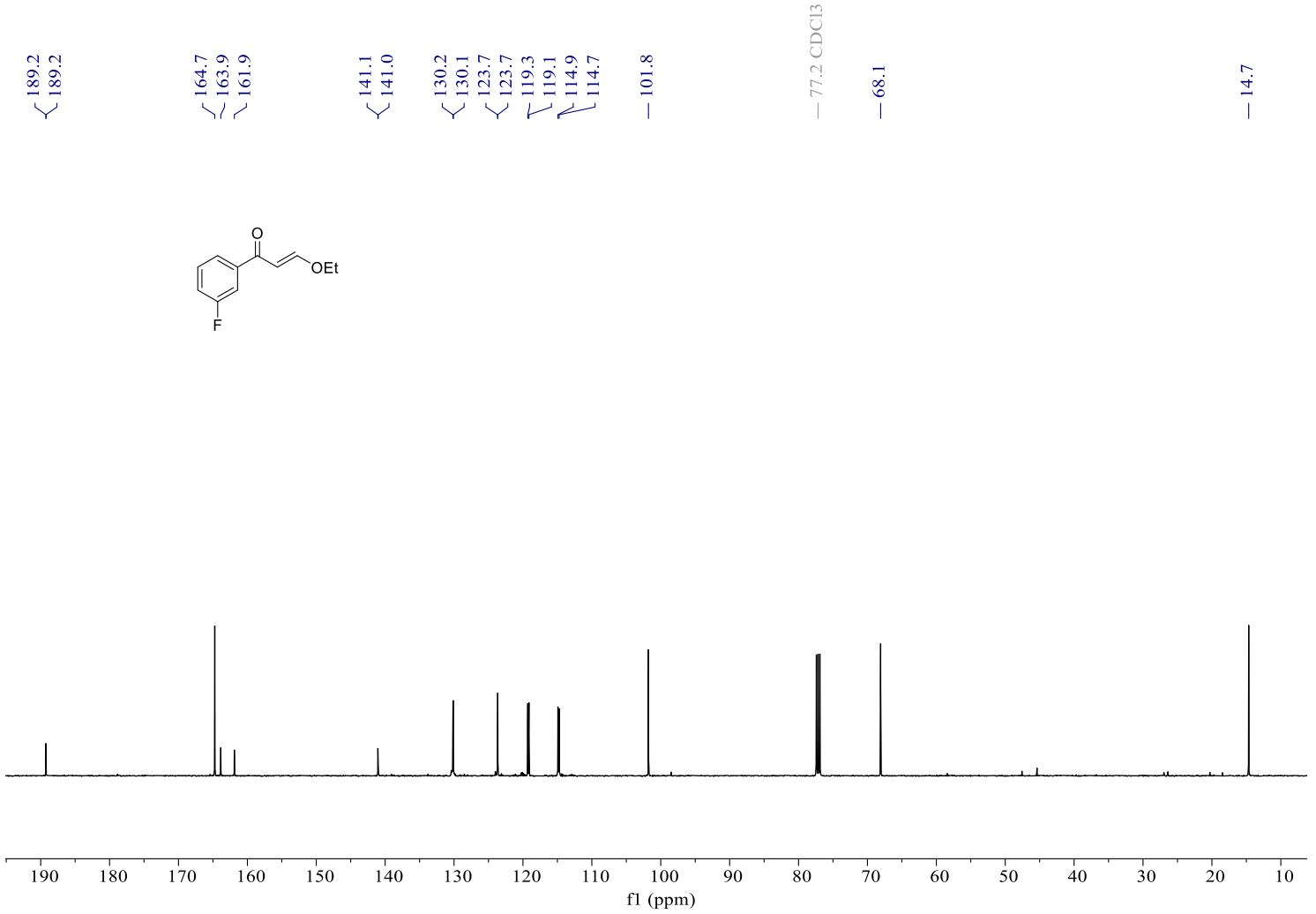
Compound 5 ^{19}F NMR (753 MHz, $CDCl_3$)



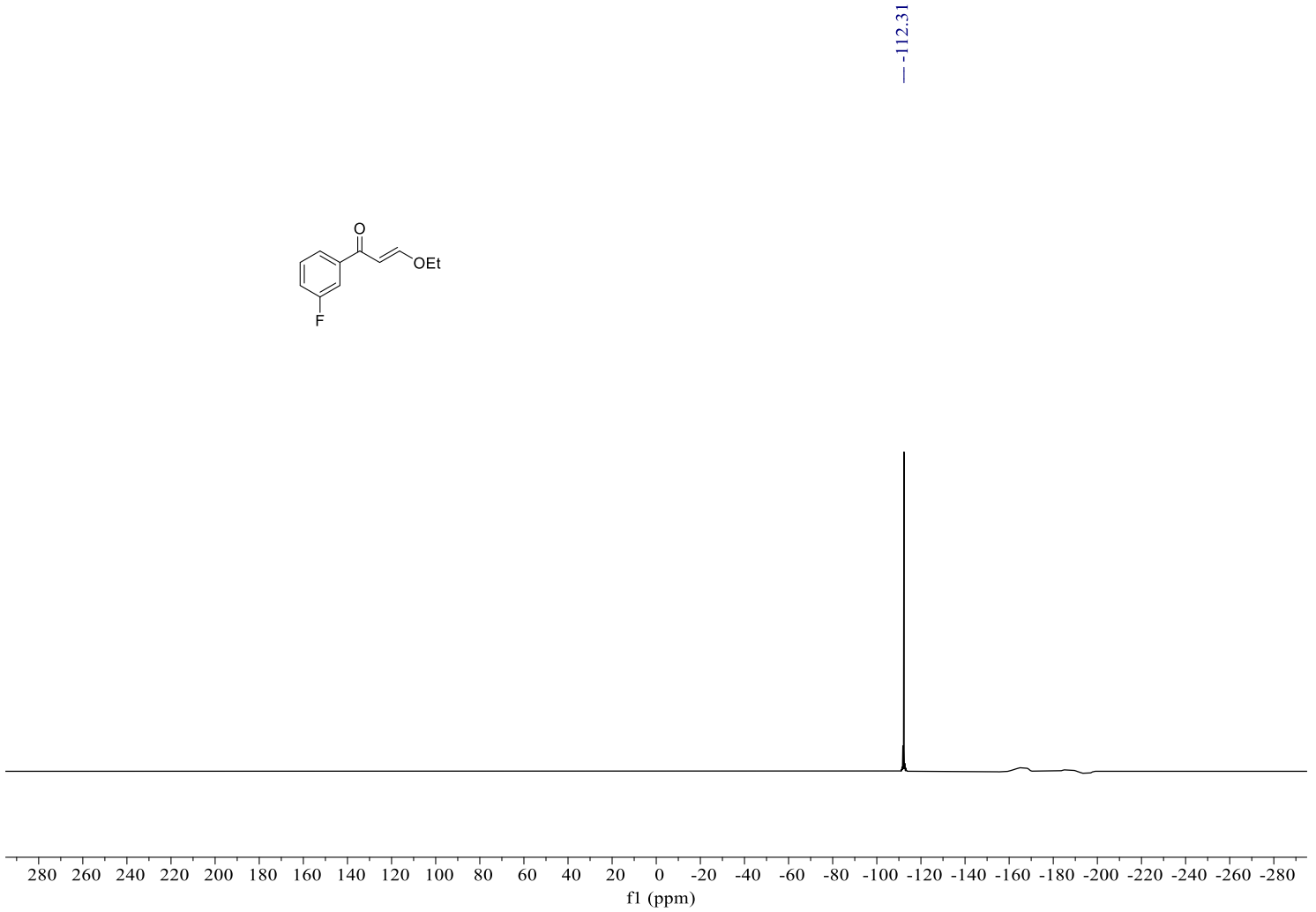
Compound 5b ^{1}H NMR (500 MHz, $CDCl_3$)



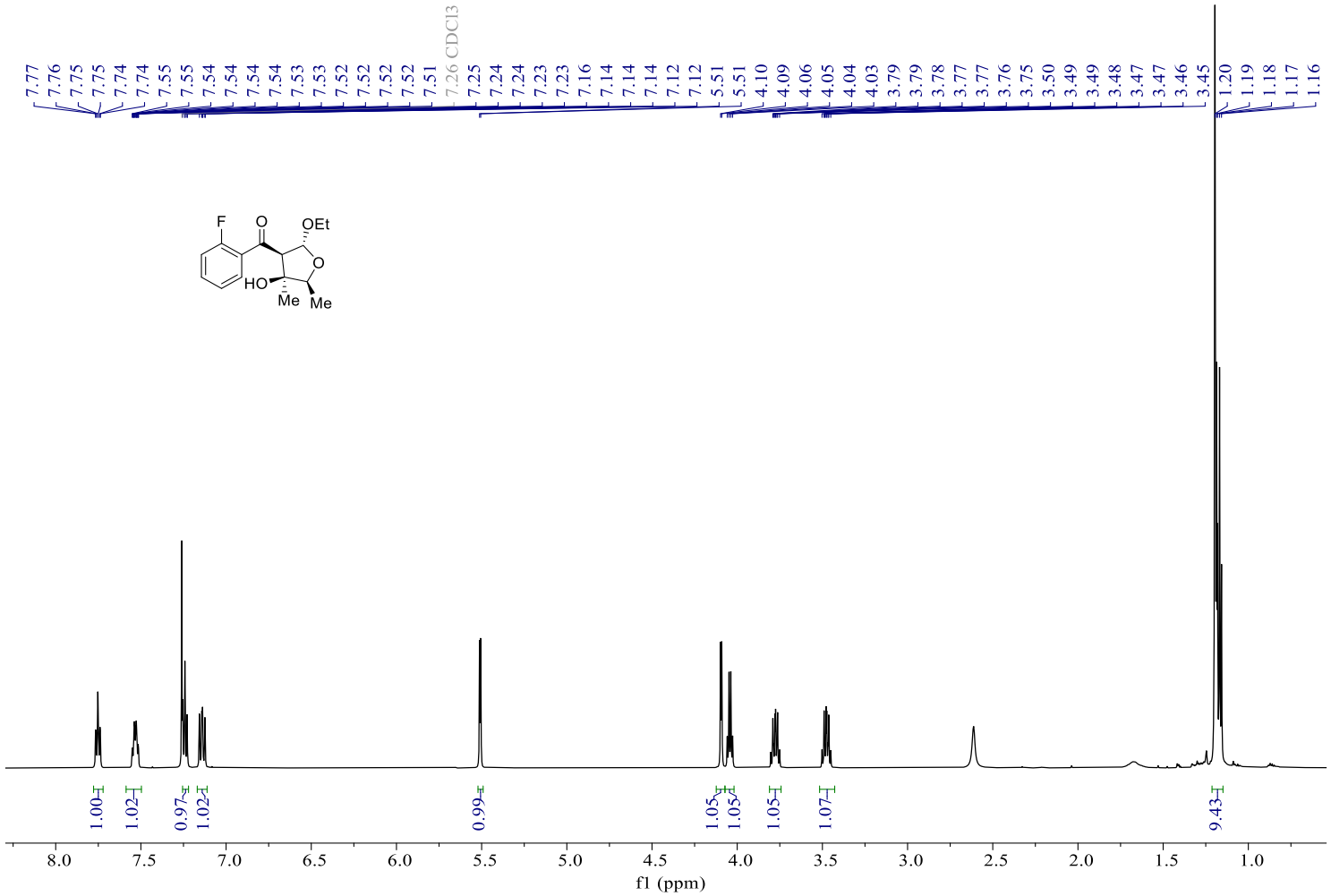
Compound 5b ^{13}C NMR (150 MHz, $CDCl_3$)



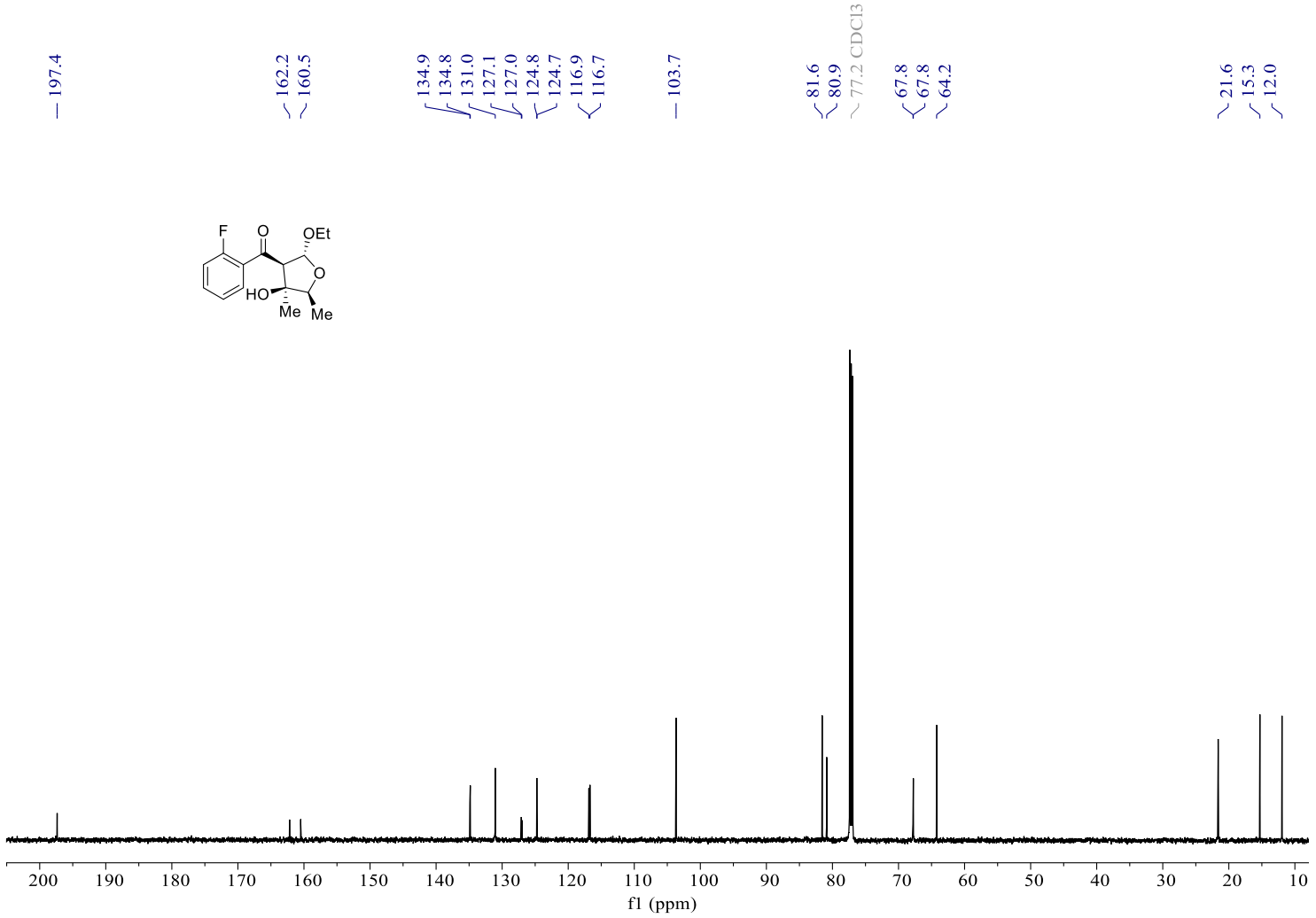
Compound 5b ^{19}F NMR (471 MHz, $CDCl_3$)



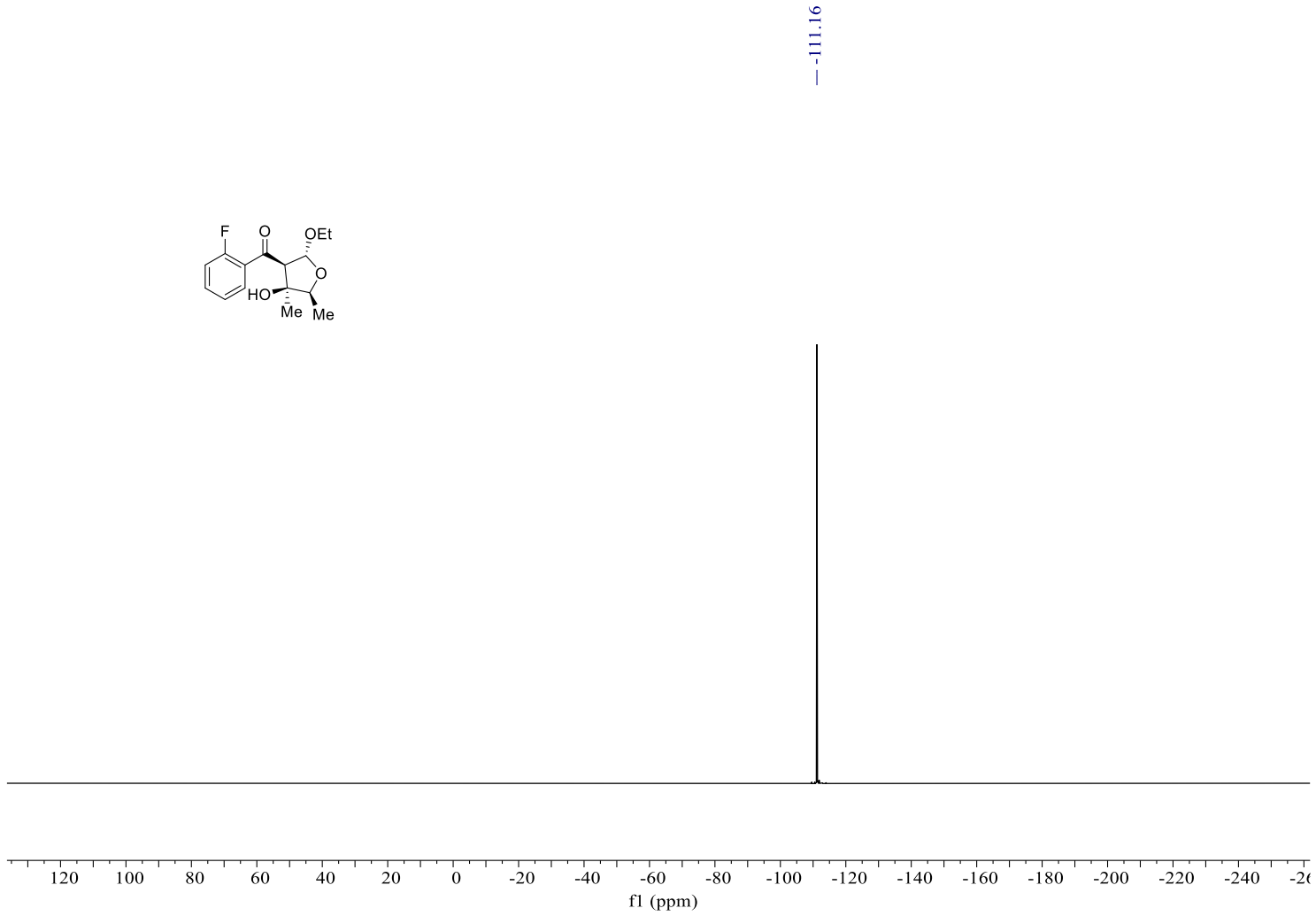
Compound 6 ^{1}H NMR (600 MHz, $CDCl_3$)



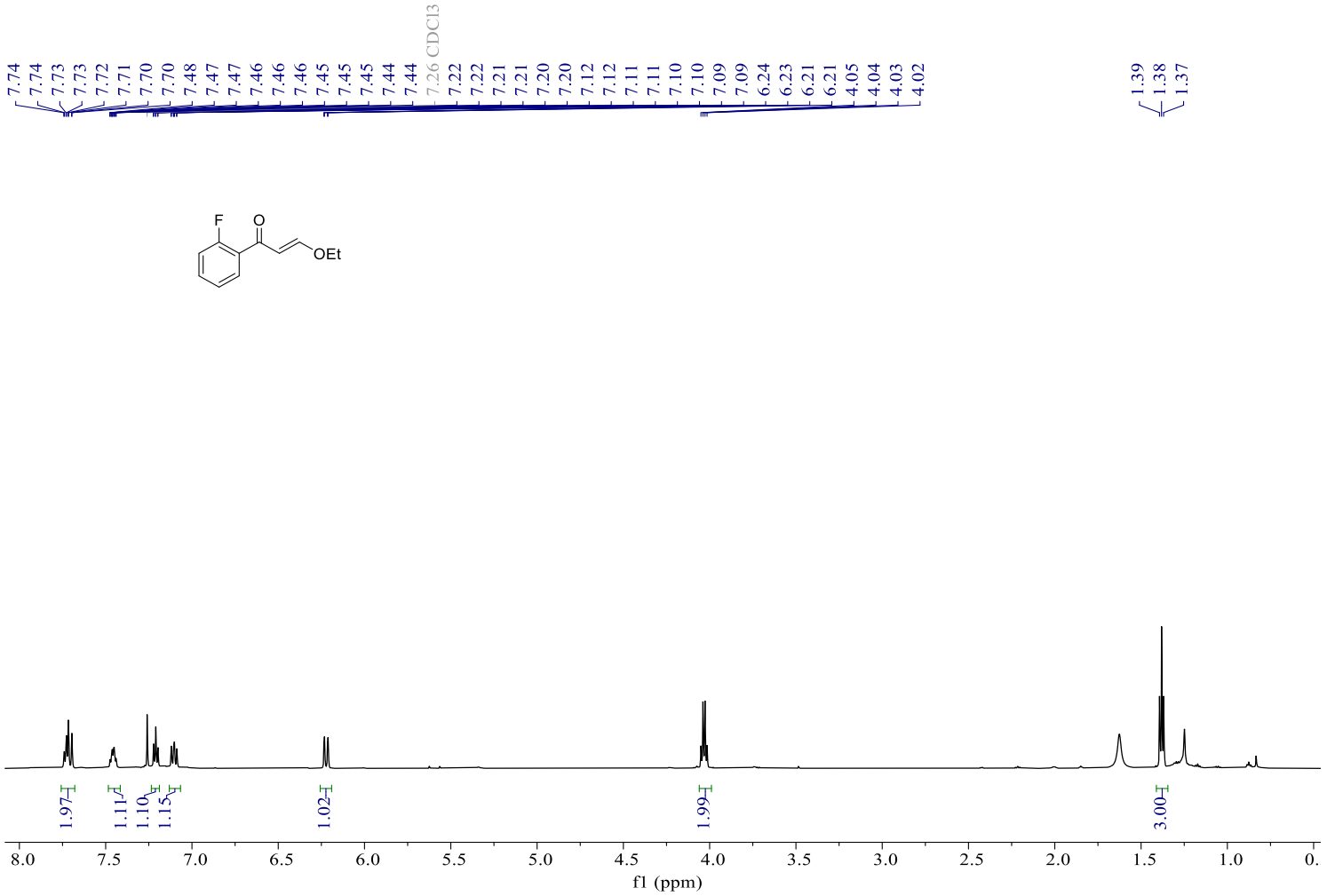
Compound 6 ^{13}C NMR (150 MHz, $CDCl_3$)



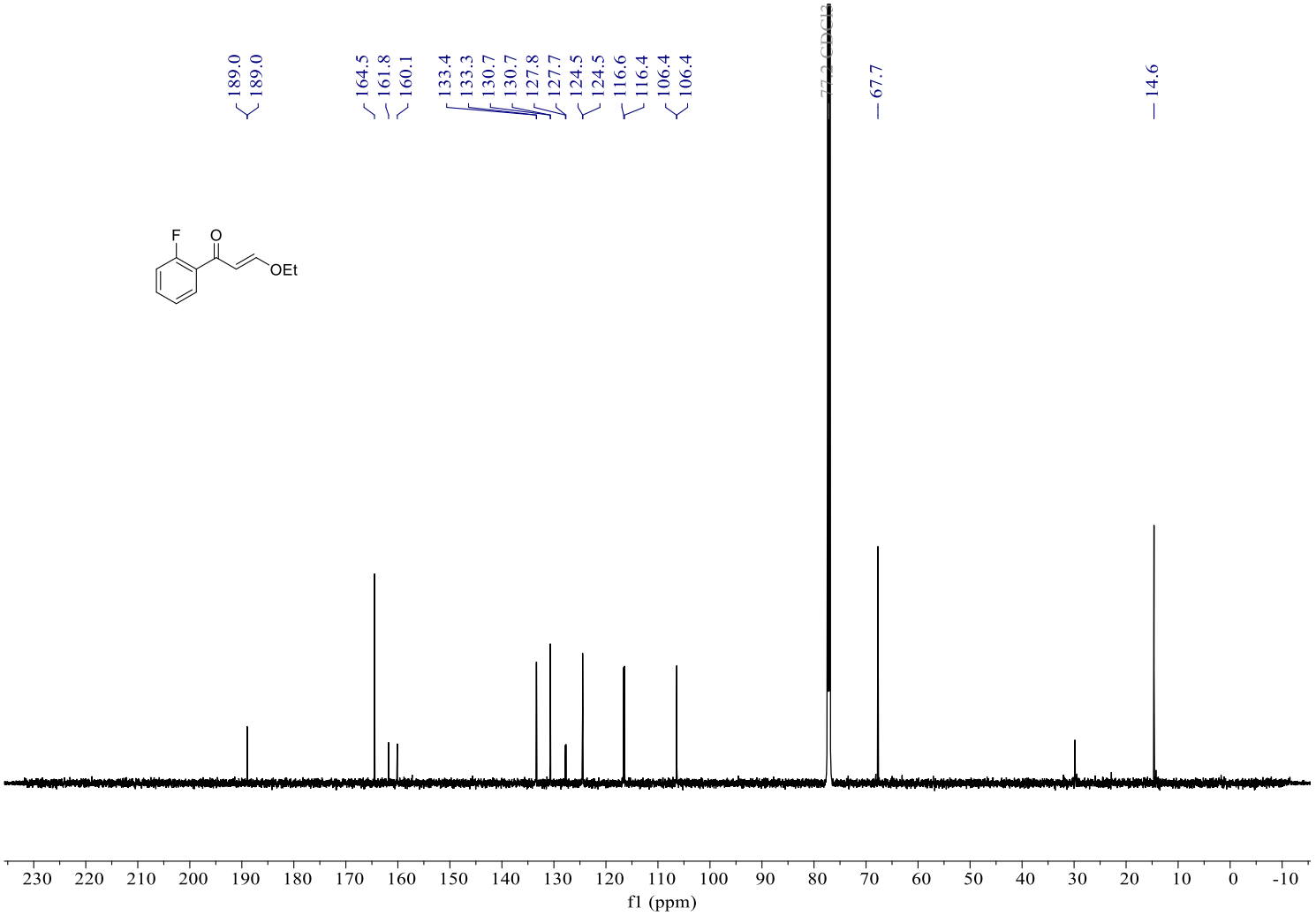
Compound 6 ^{19}F NMR (753 MHz, $CDCl_3$)



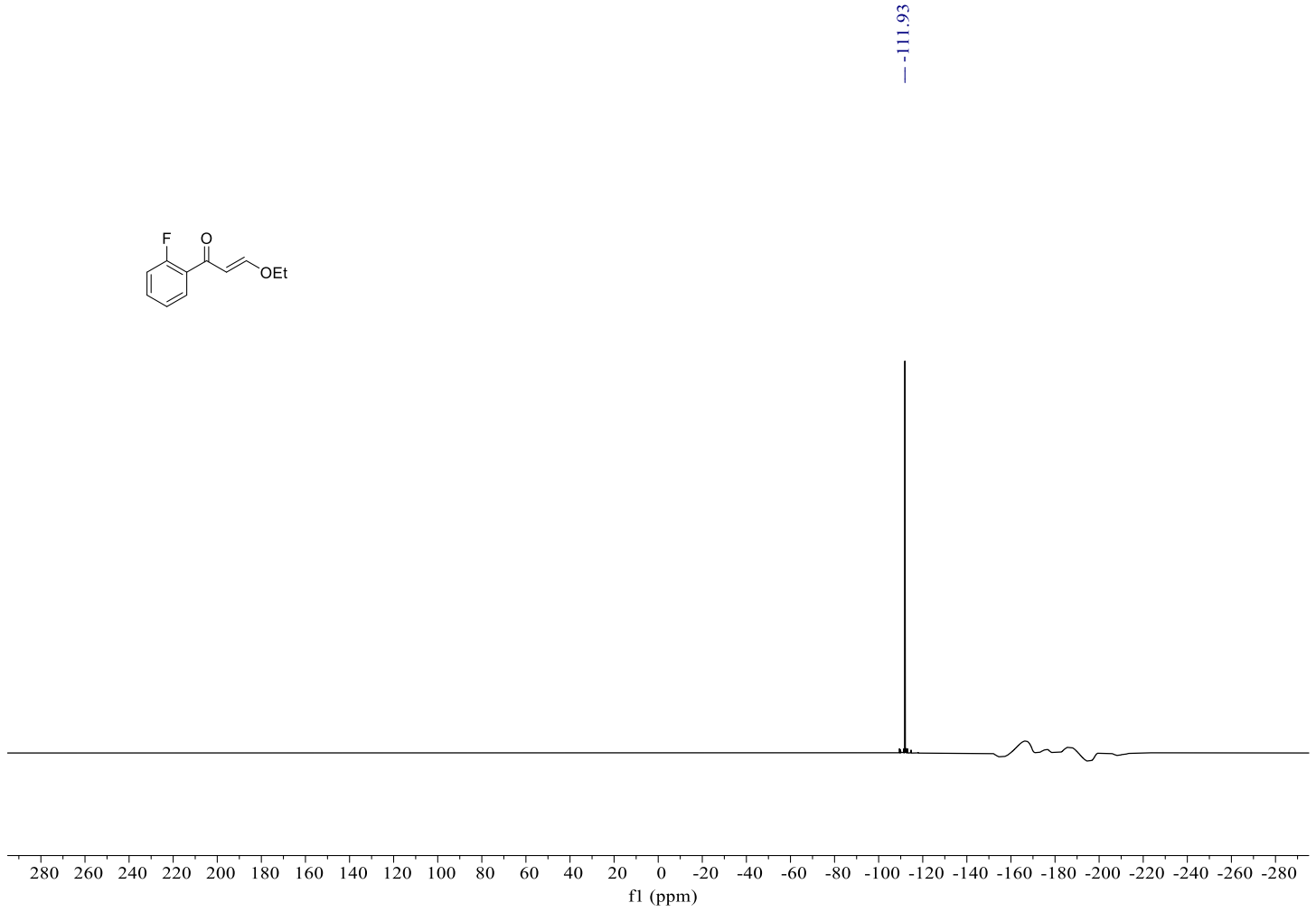
Compound 6b ^{1}H NMR (600 MHz, $CDCl_3$)



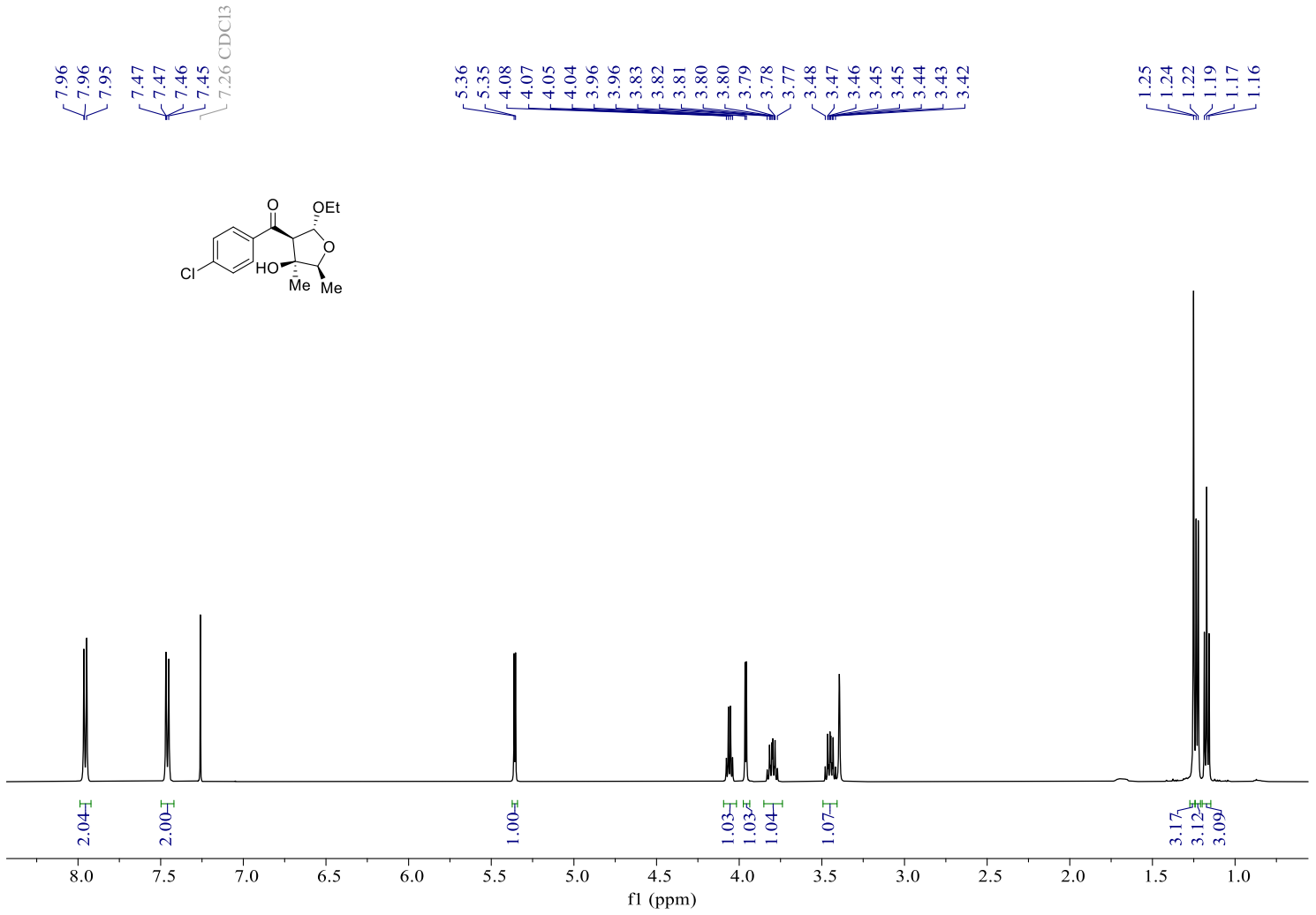
Compound 6b ^{13}C NMR (150 MHz, $CDCl_3$)



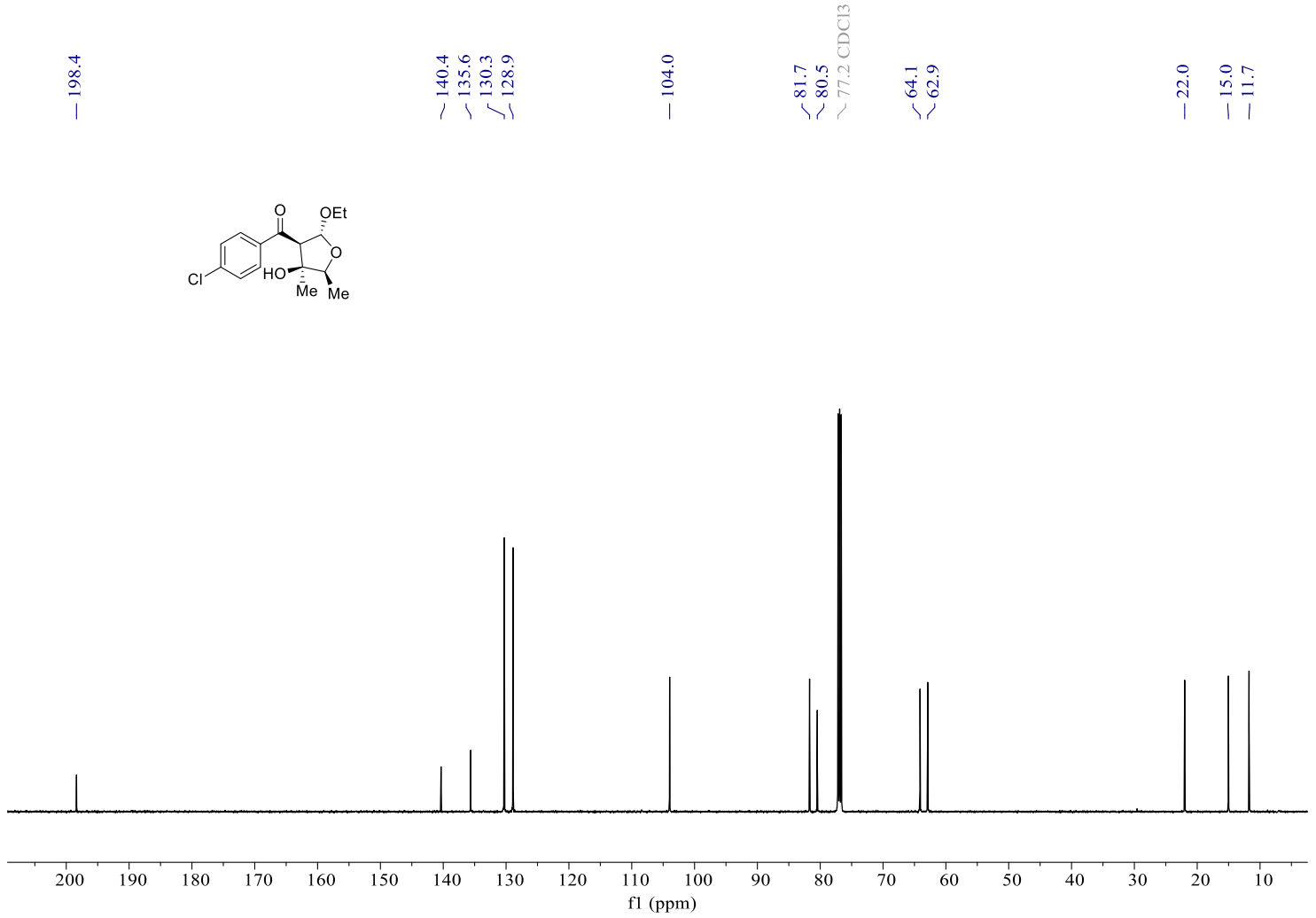
Compound 6b ^{19}F NMR (471 MHz, $CDCl_3$)



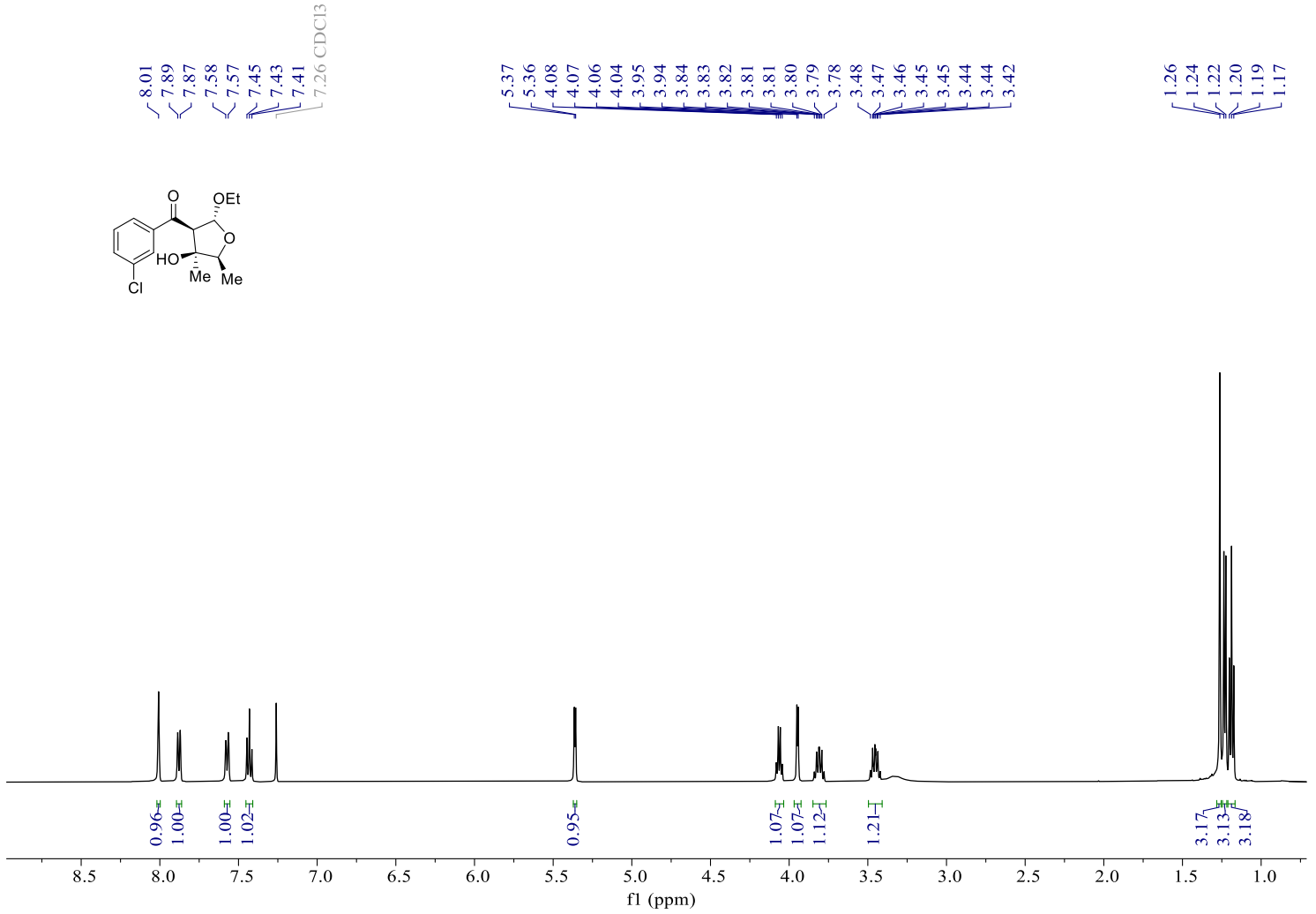
Compound 7 ^{1}H NMR (500 MHz, $CDCl_3$)



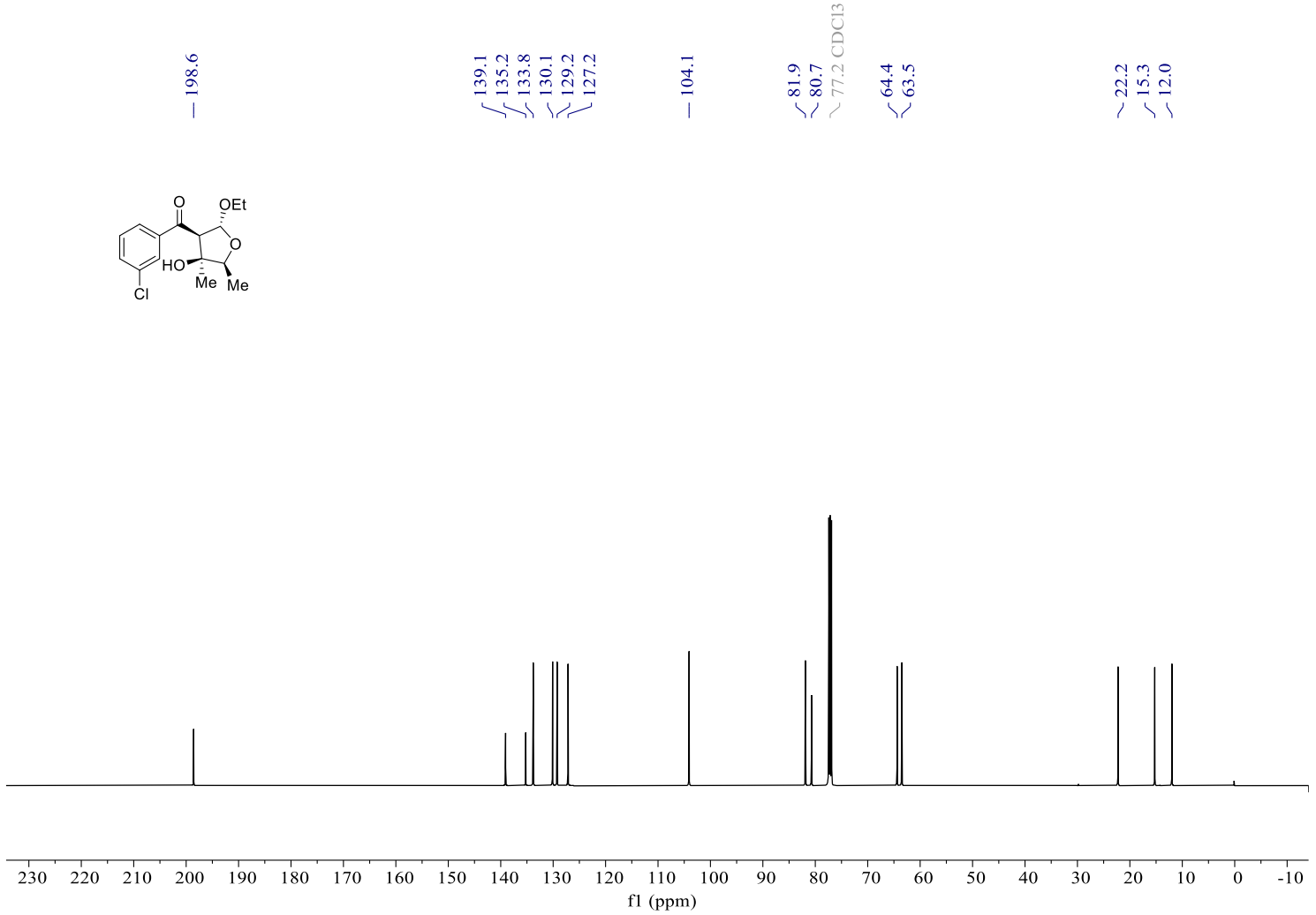
Compound 7 ^{13}C NMR (125 MHz, $CDCl_3$)



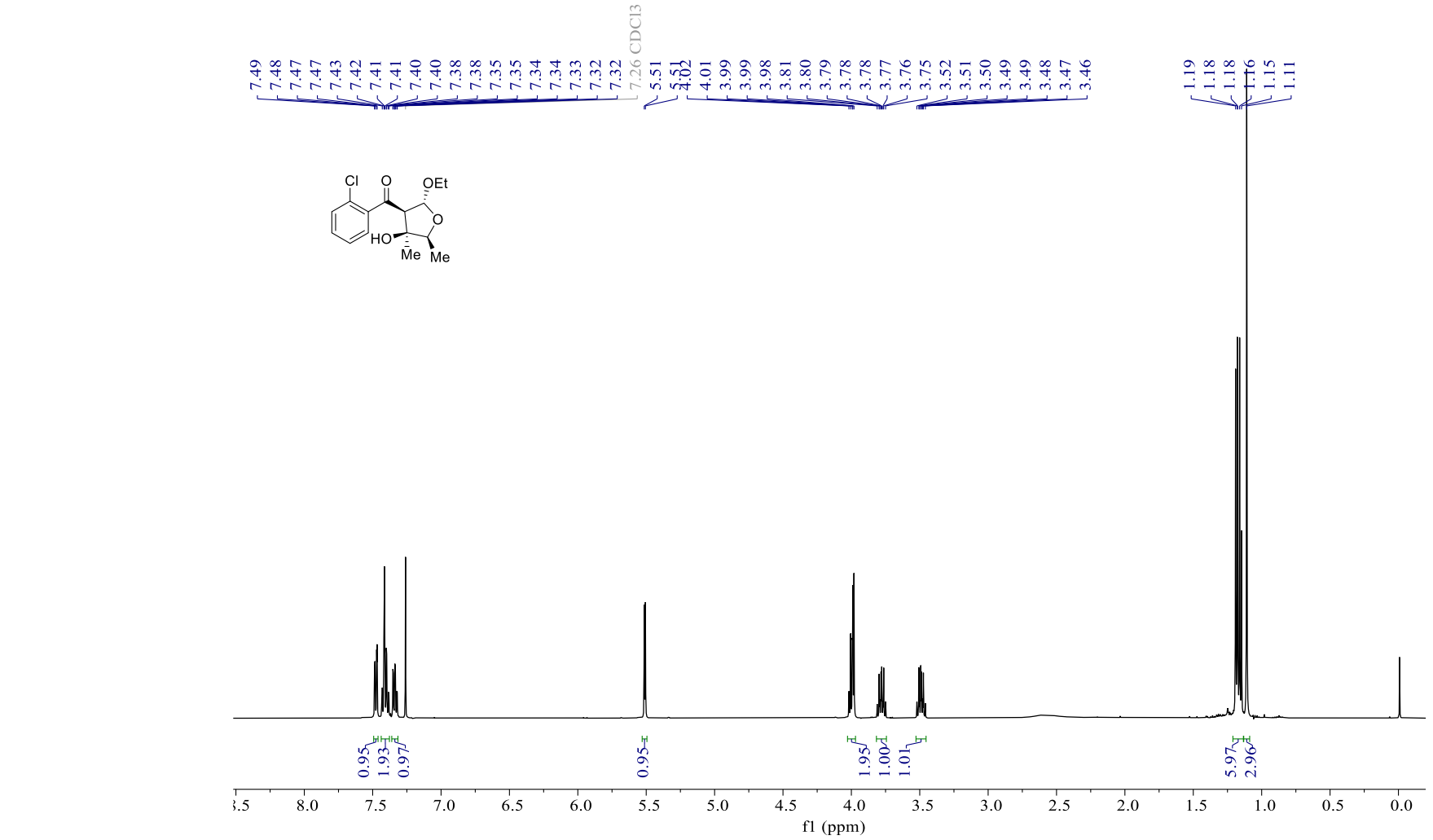
Compound 8 ^{1}H NMR (500 MHz, $CDCl_3$)



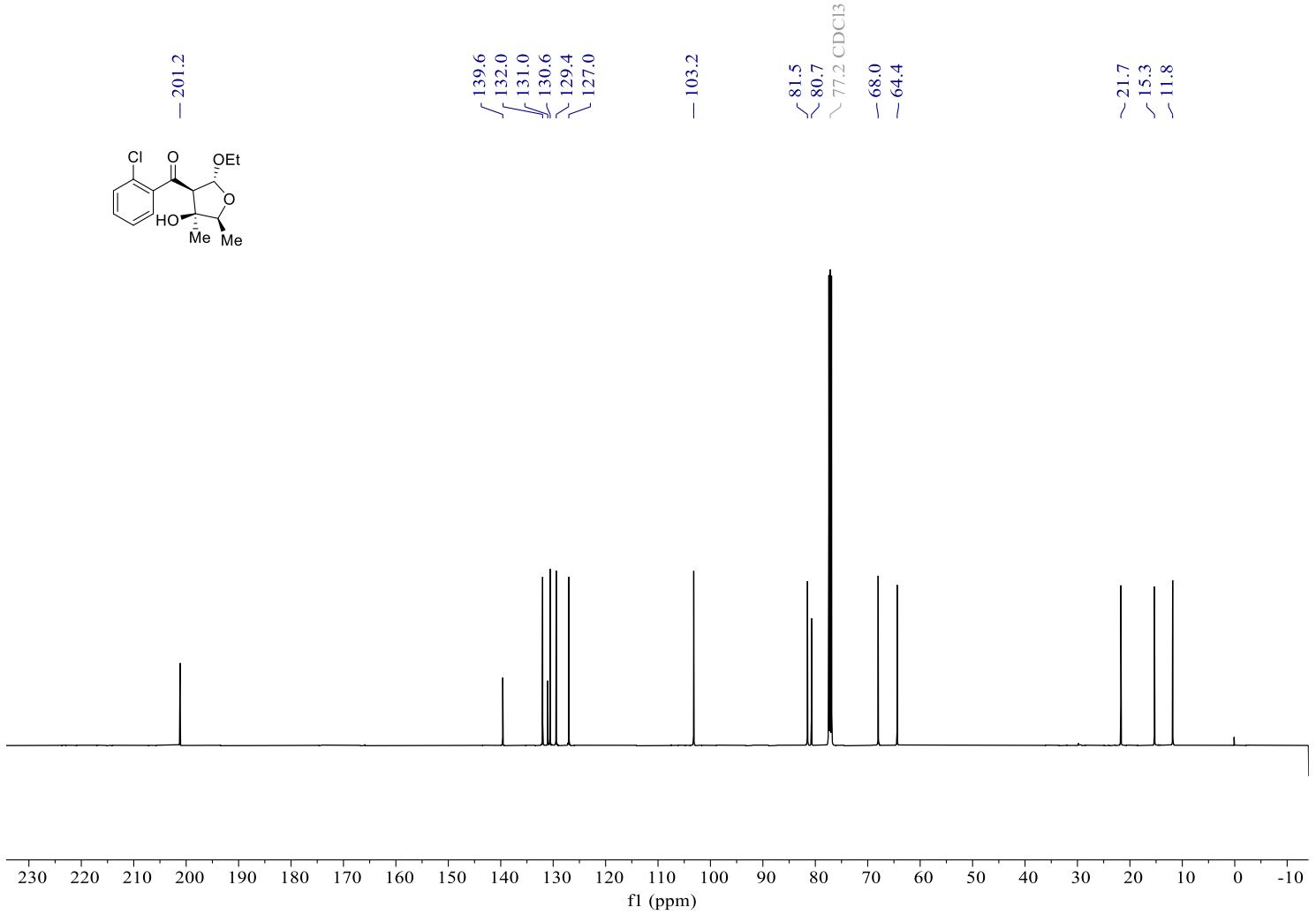
Compound 8 ^{13}C NMR (125 MHz, $CDCl_3$)



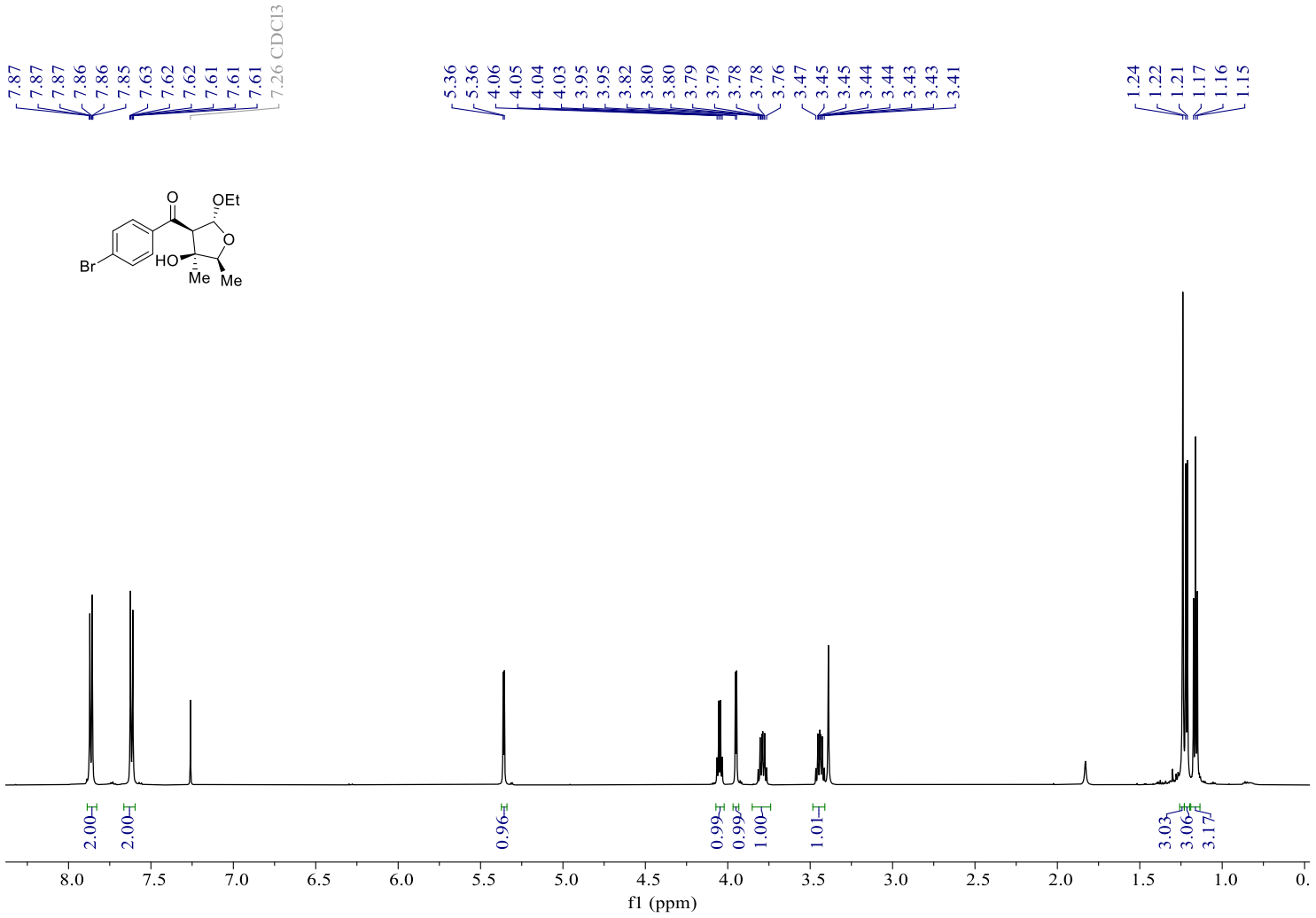
Compound 9 ^{1}H NMR (500 MHz, $CDCl_3$)



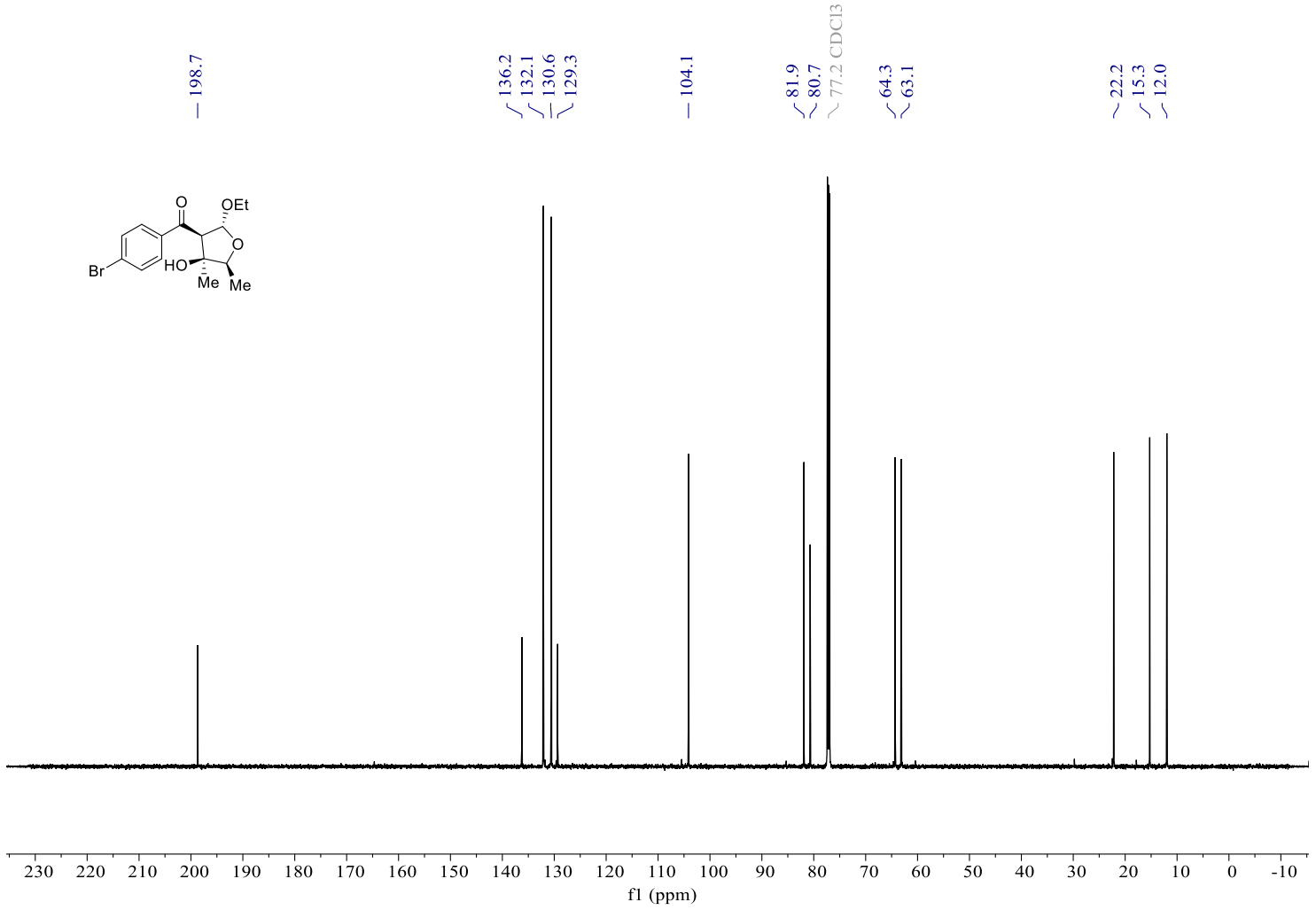
Compound 9 ^{13}C NMR (125 MHz, $CDCl_3$)



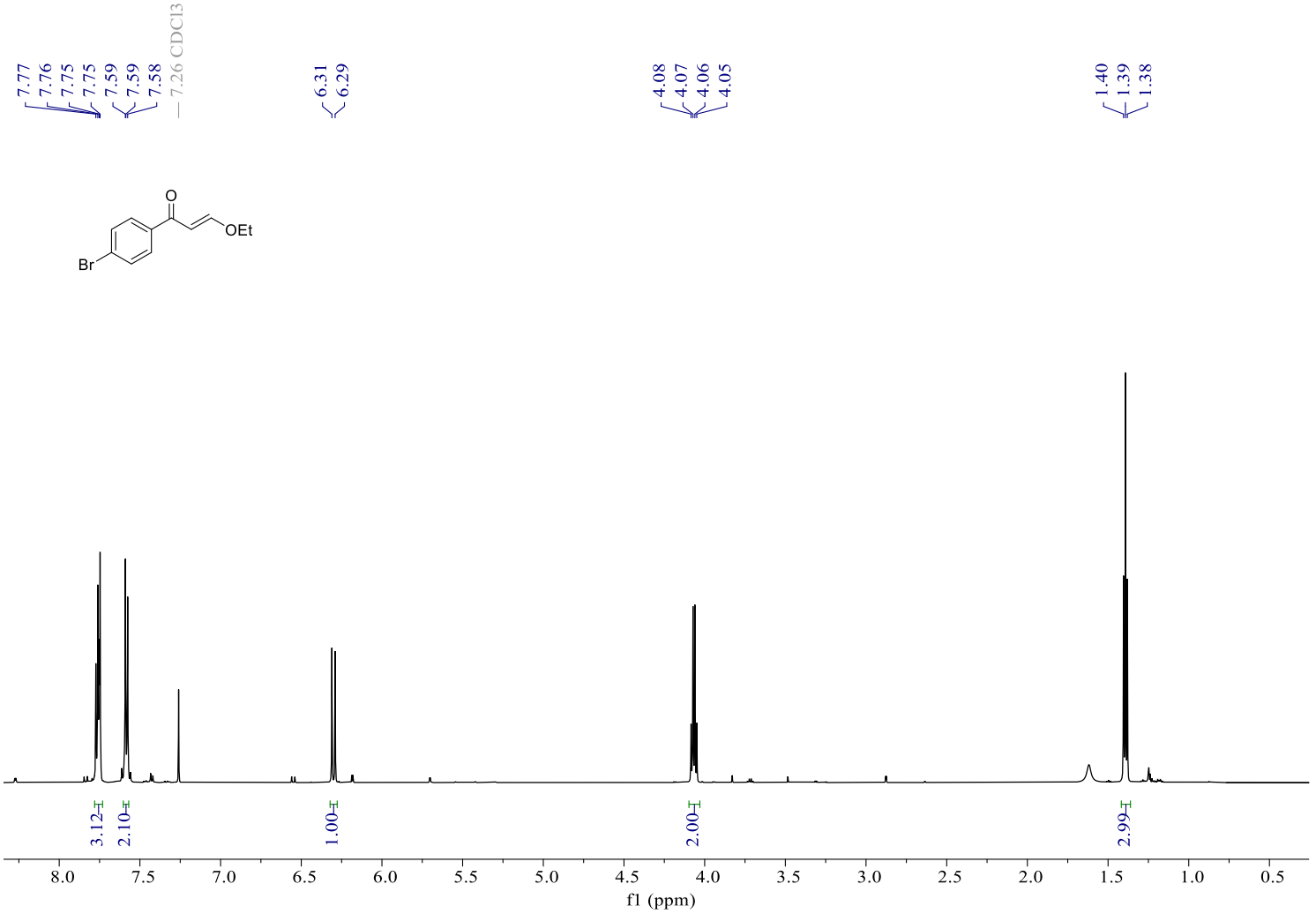
Compound 10 ^{1}H NMR (600 MHz, $CDCl_3$)



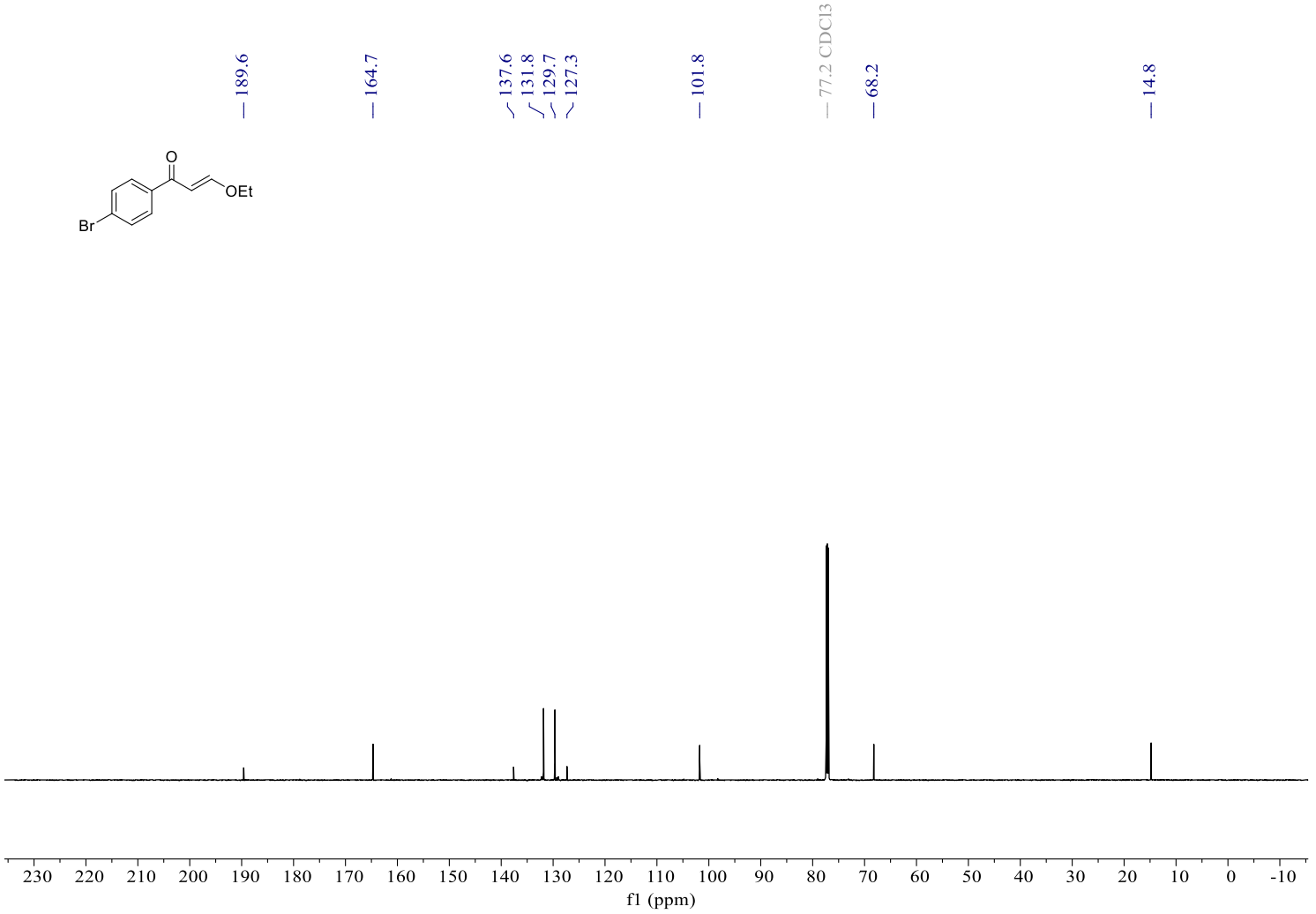
Compound 10 ^{13}C NMR (150 MHz, $CDCl_3$)



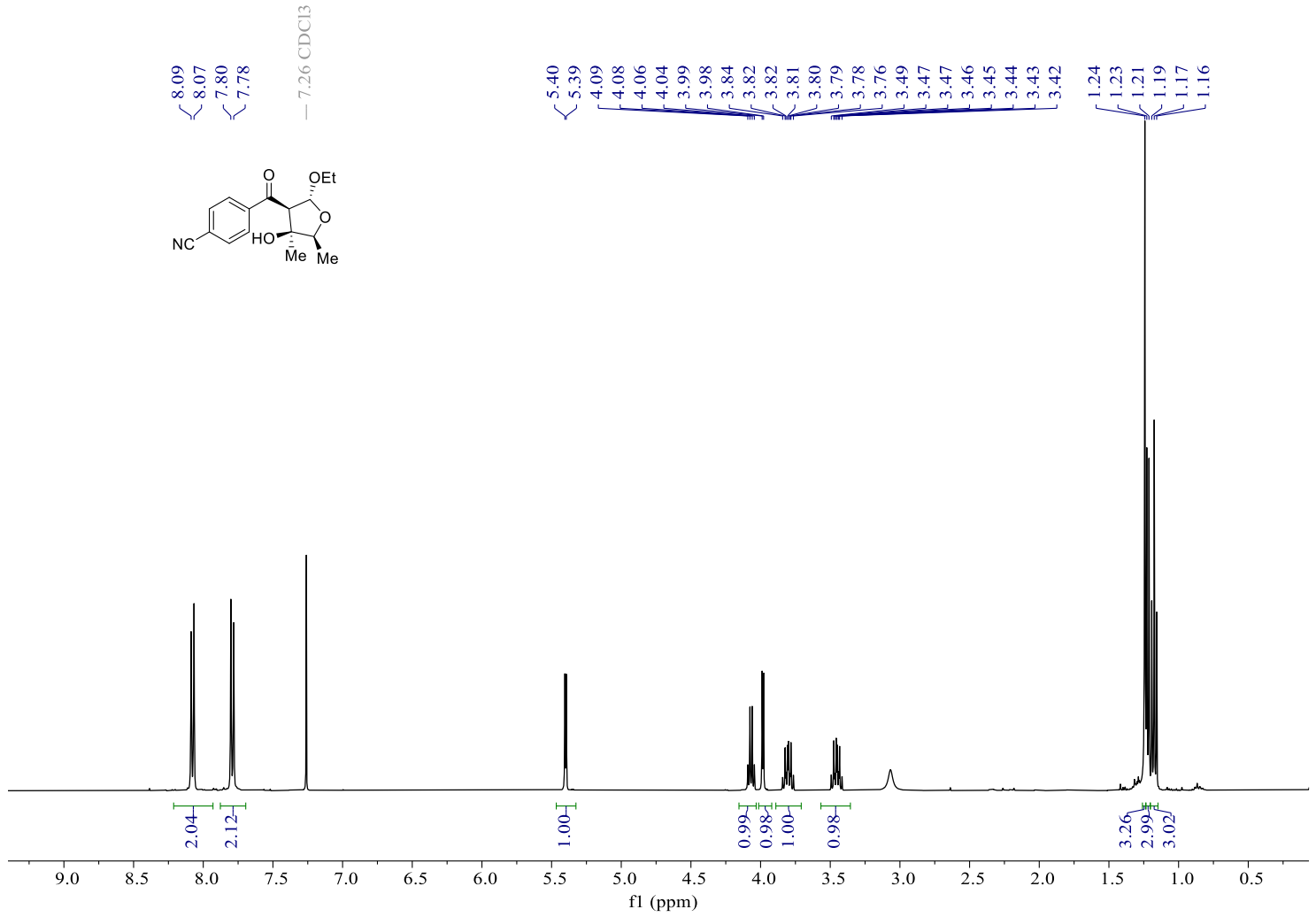
Compound 10b ^{1}H NMR (600 MHz, $CDCl_3$)



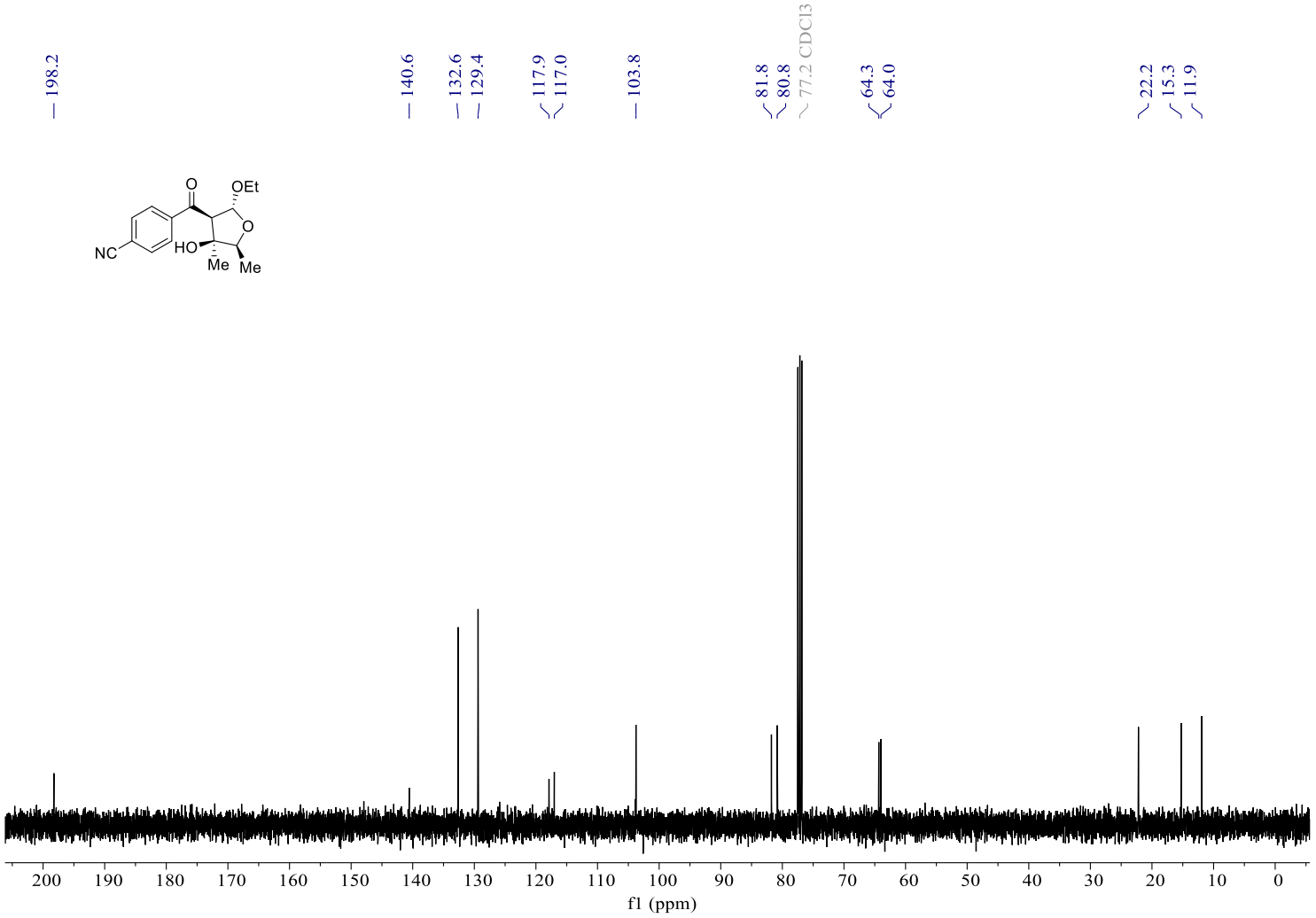
Compound 10b ^{13}C NMR (150 MHz, $CDCl_3$)



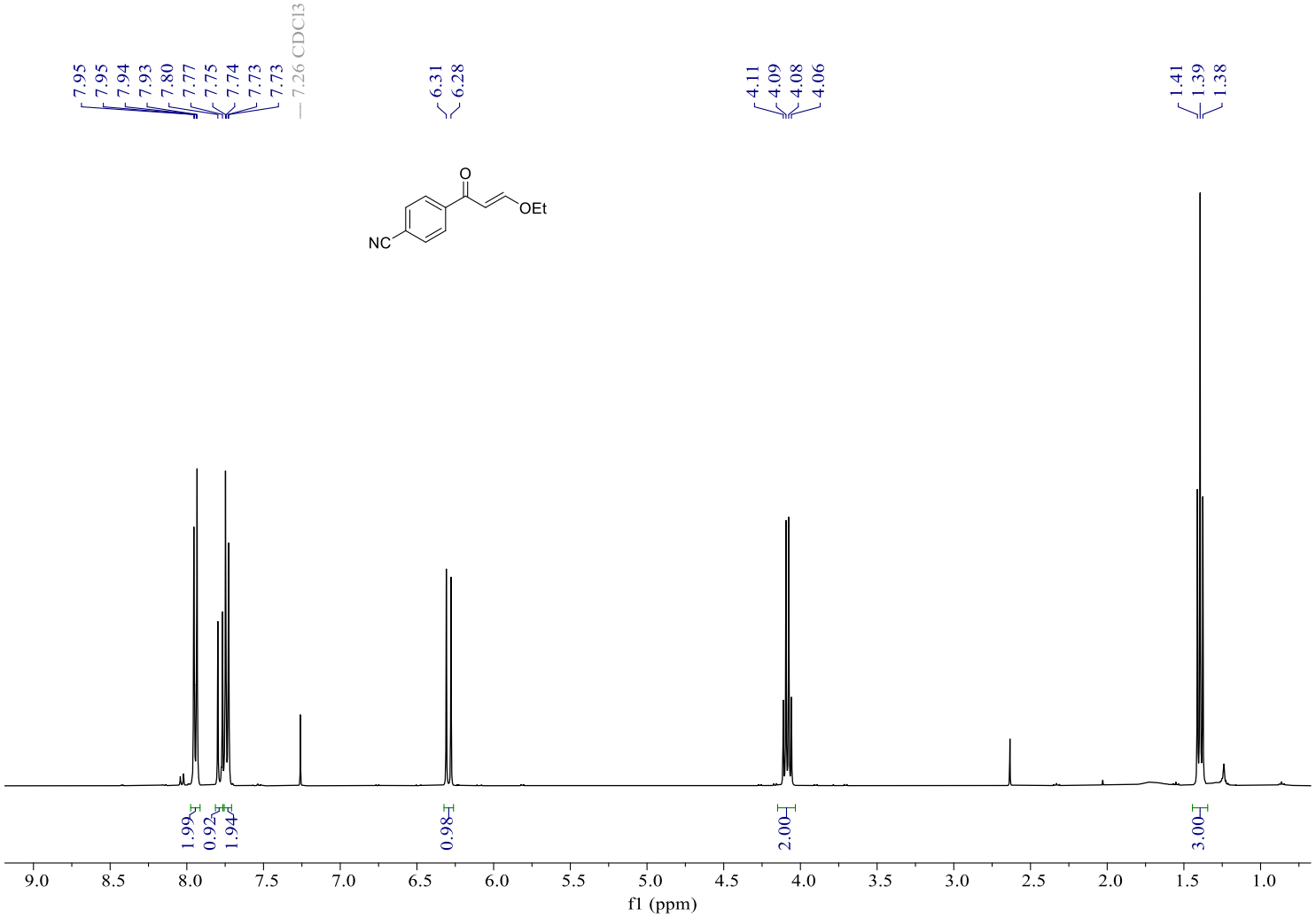
Compound 11 ^{1}H NMR (400 MHz, $CDCl_3$)



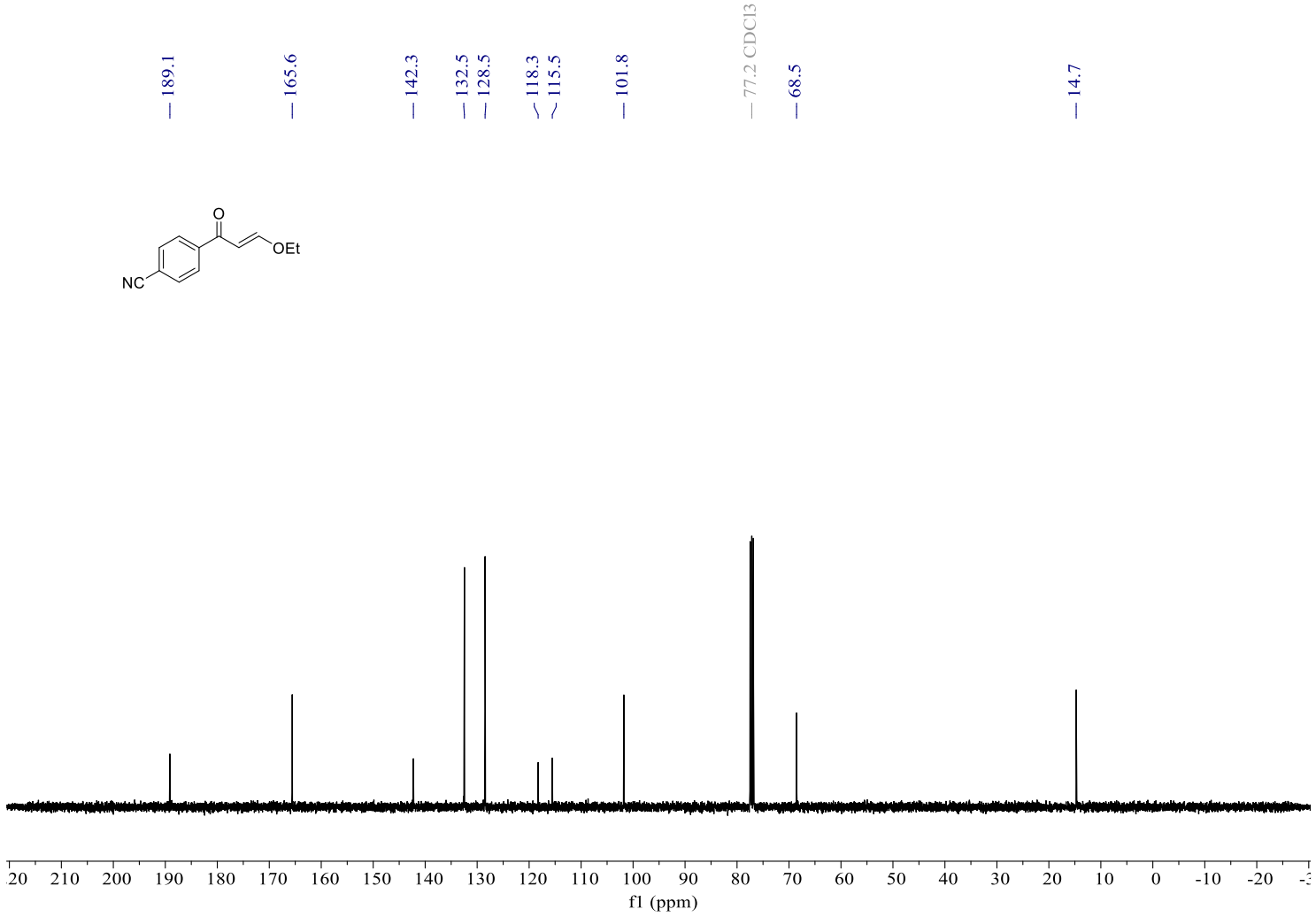
Compound 11 ^{13}C NMR (100 MHz, $CDCl_3$)



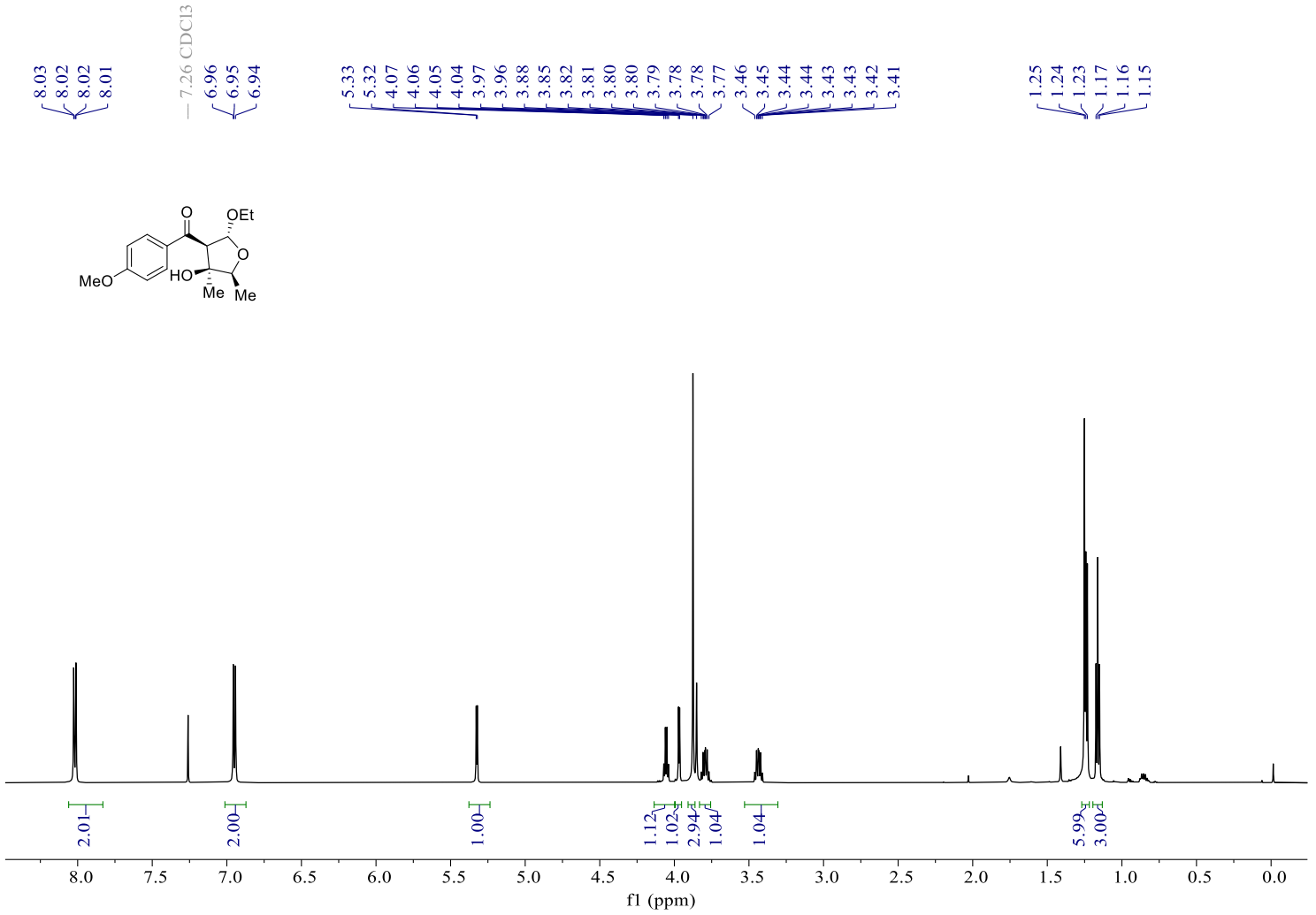
Compound 11b ^{1}H NMR (400 MHz, $CDCl_3$)



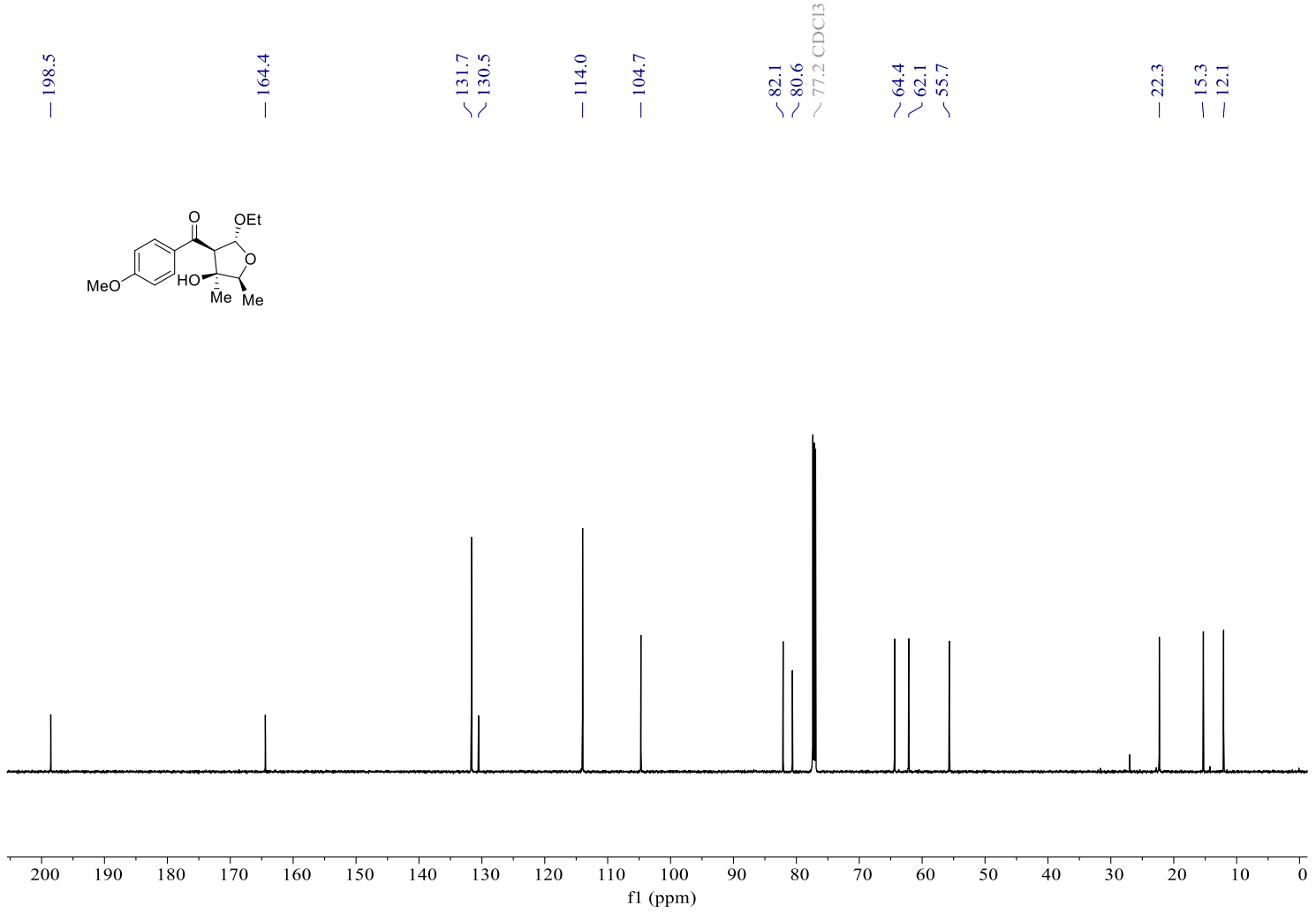
Compound 11b ^{13}C NMR (100 MHz, $CDCl_3$)



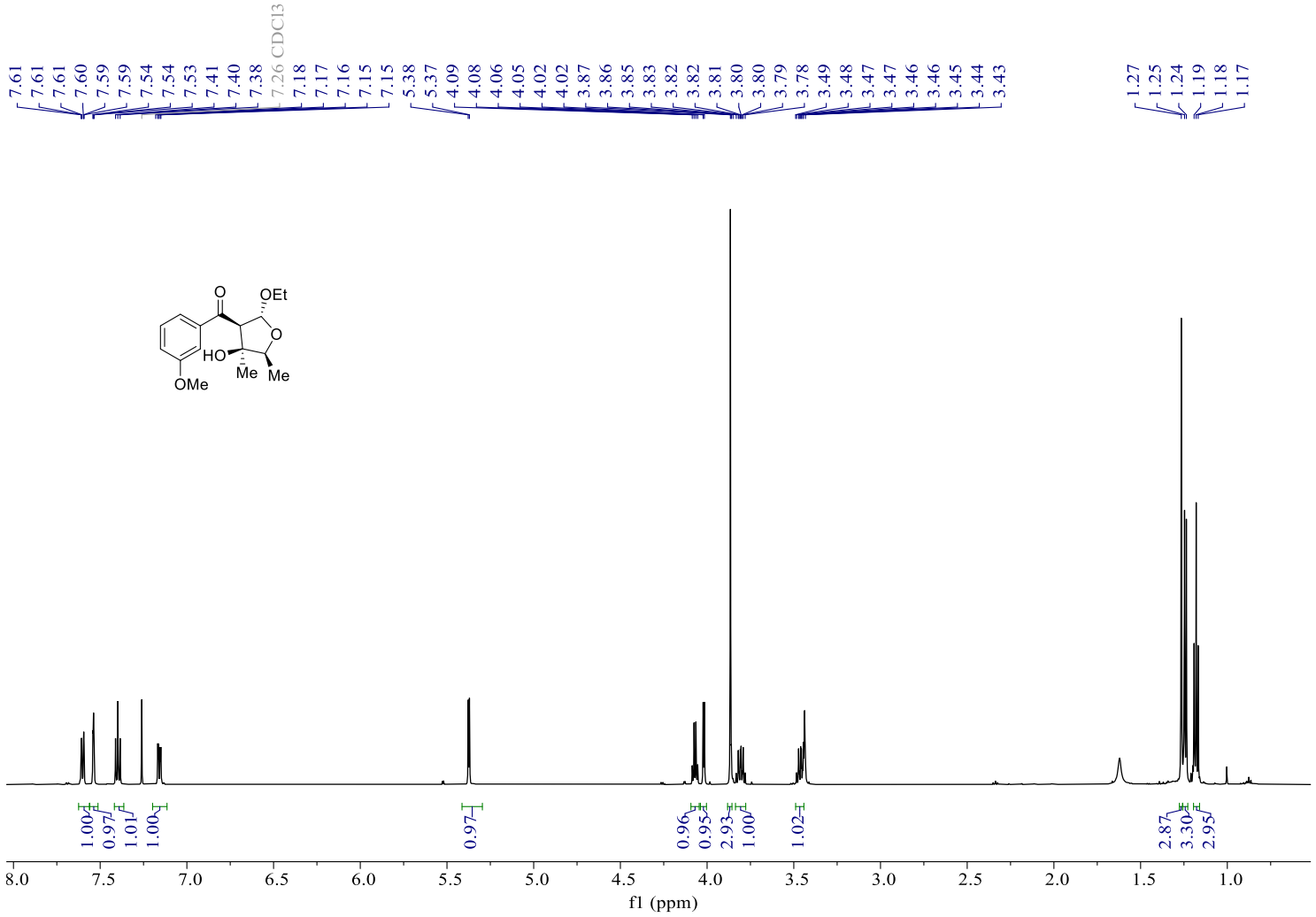
Compound 12 ^{1}H NMR (600 MHz, $CDCl_3$)



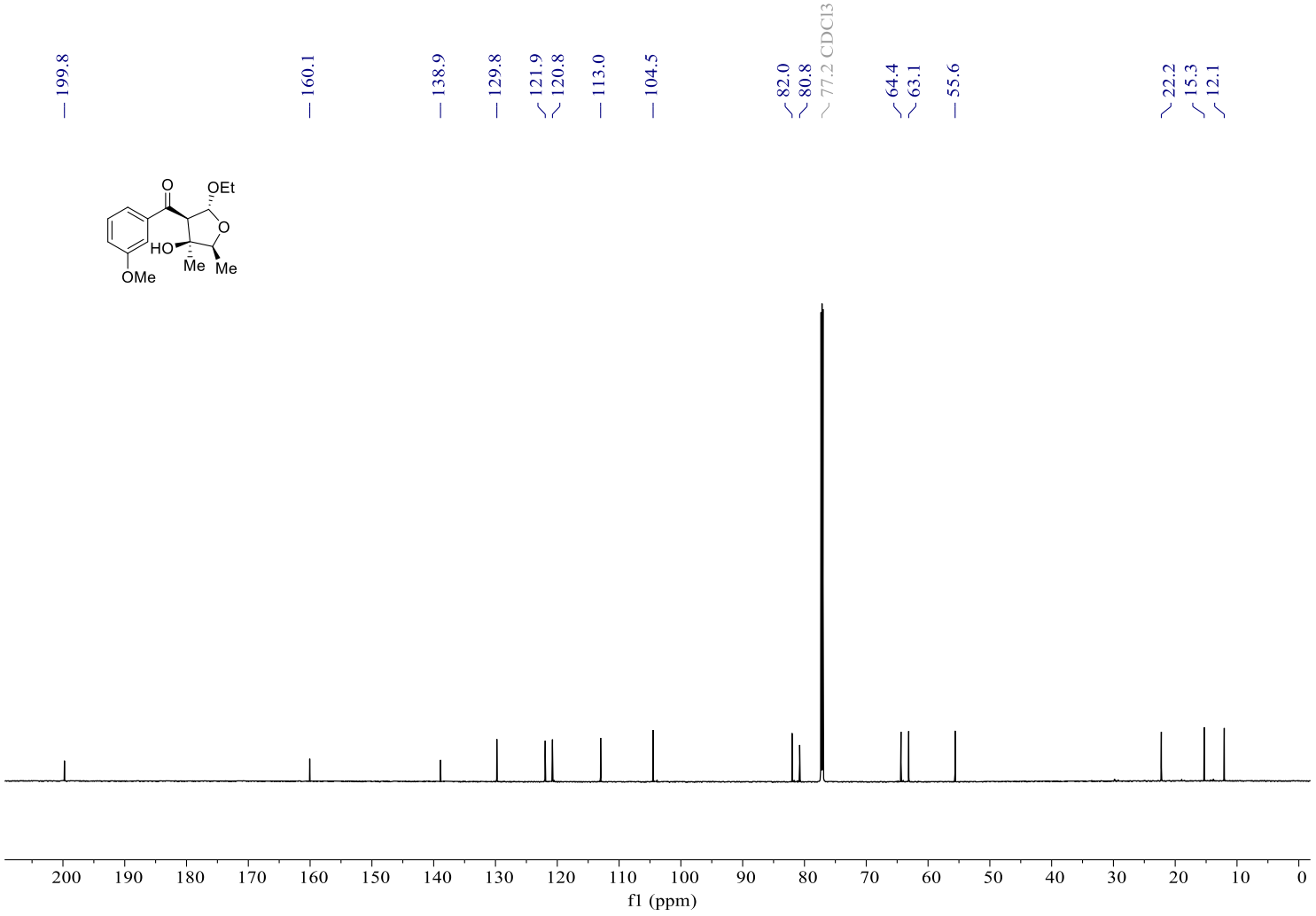
Compound 12 ^{13}C NMR (150 MHz, $CDCl_3$)



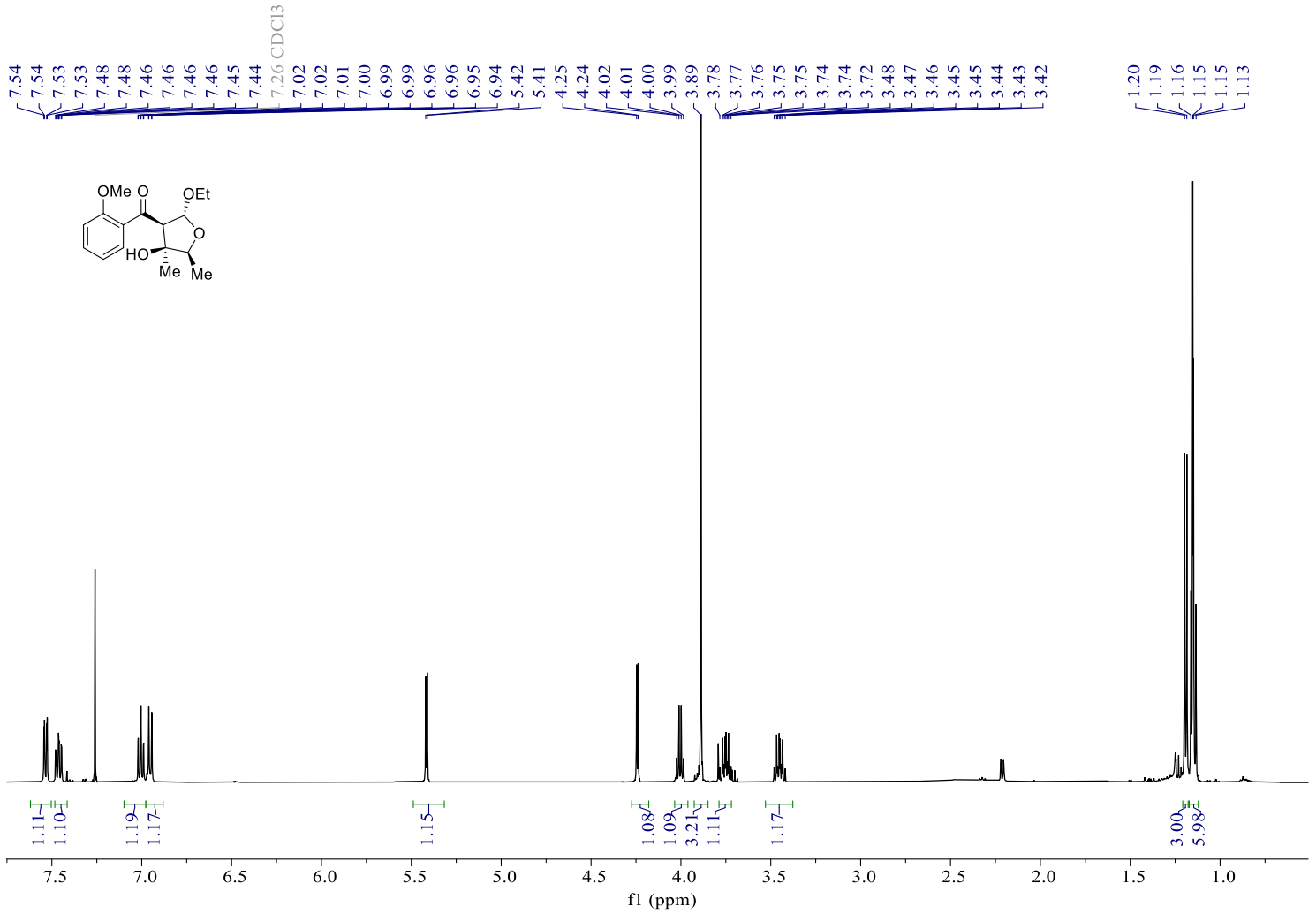
Compound 13 ^{1}H NMR (600 MHz, $CDCl_3$)



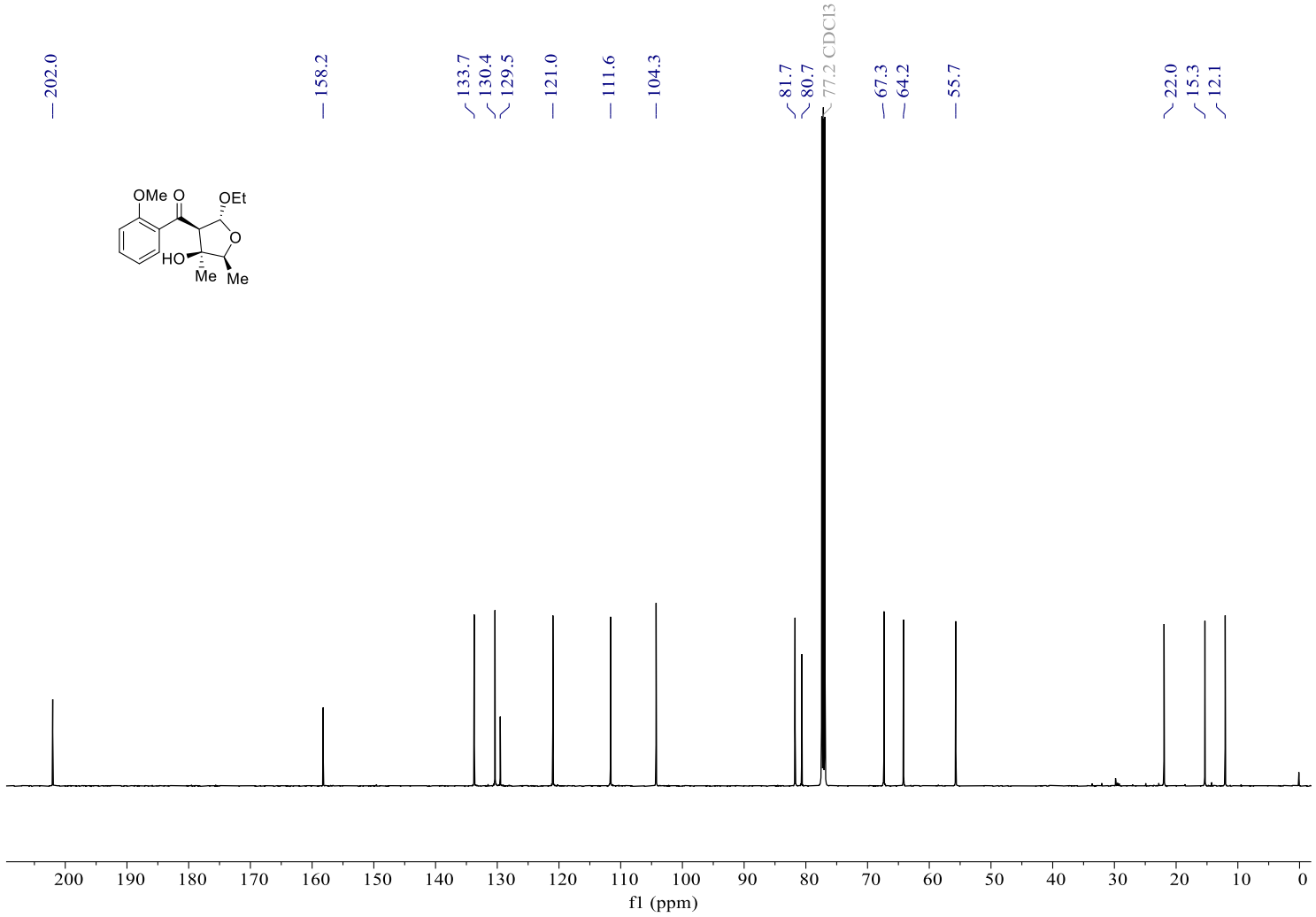
Compound 13 ^{13}C NMR (200 MHz, $CDCl_3$)



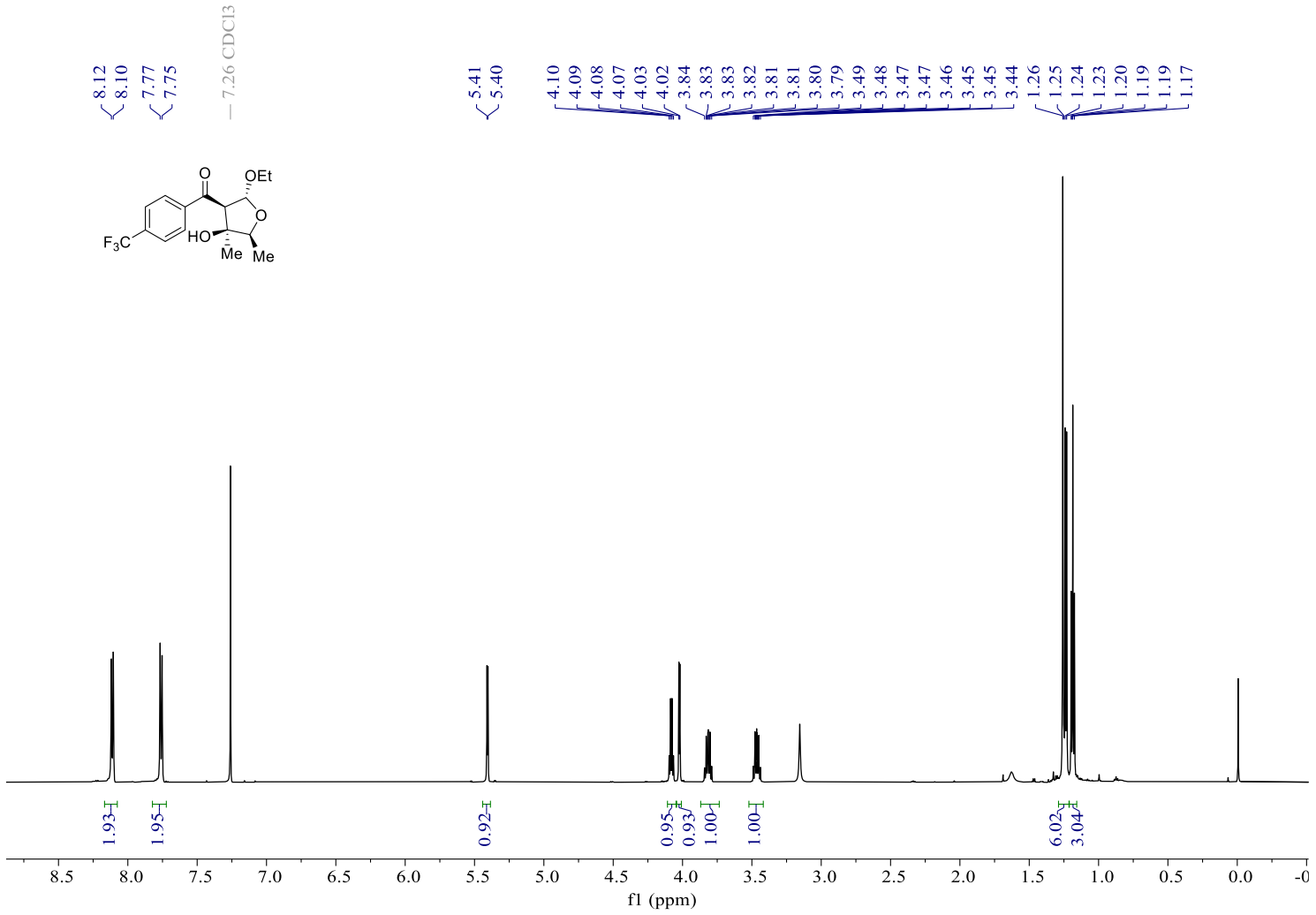
Compound 14 ^{1}H NMR (500 MHz, $CDCl_3$)



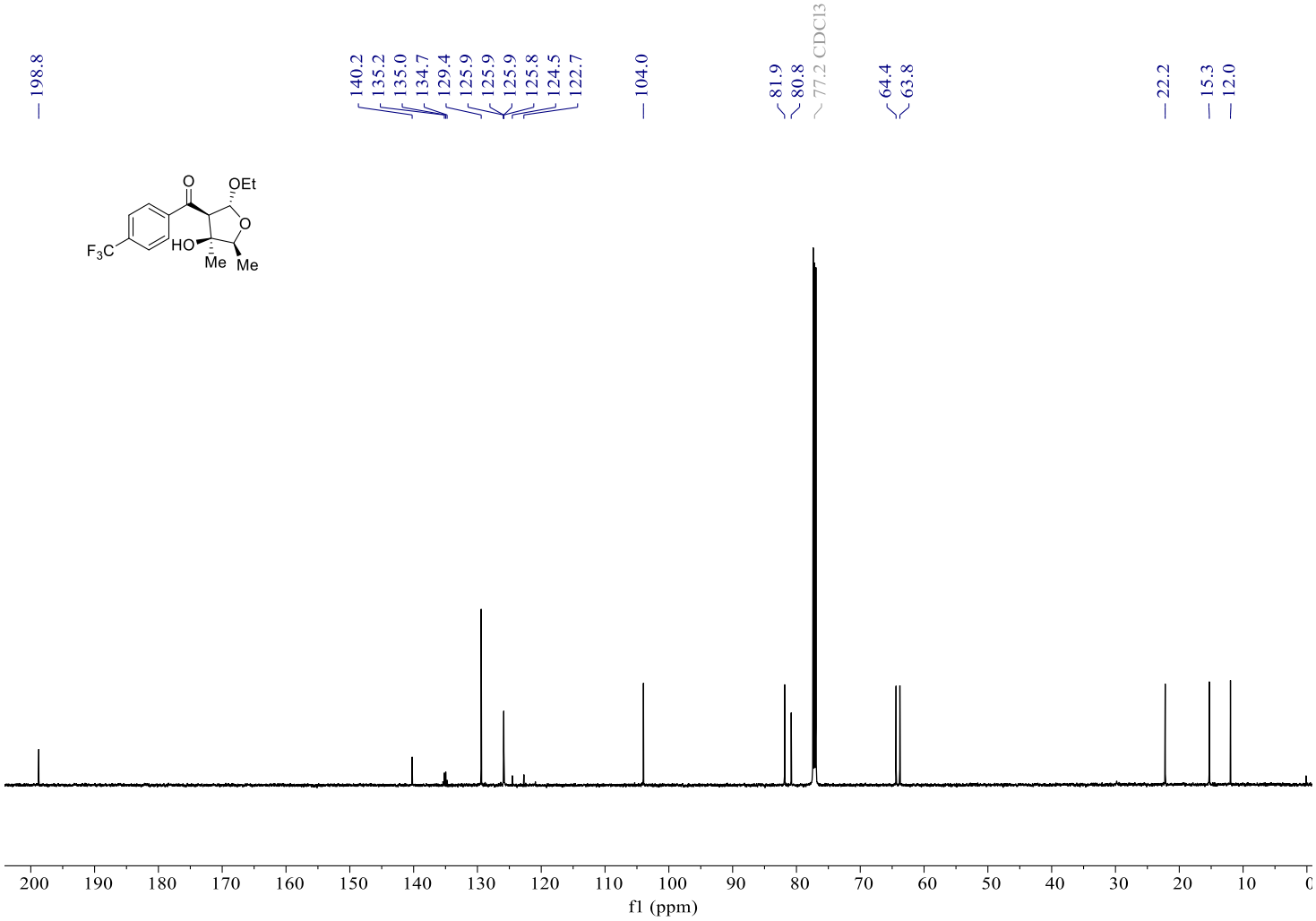
Compound 14 ^{13}C NMR (125 MHz, $CDCl_3$)



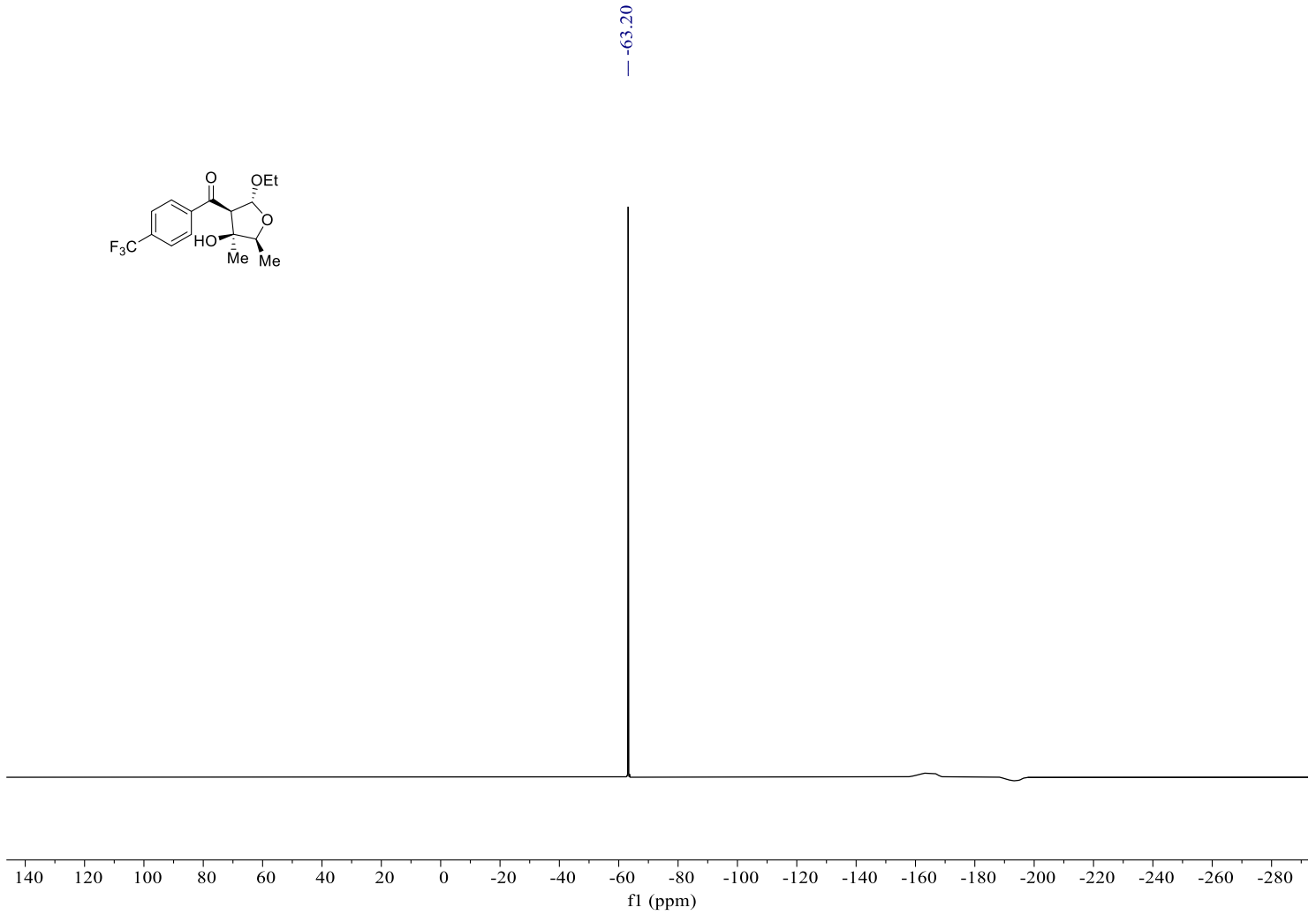
Compound 15 ^{1}H NMR (600 MHz, $CDCl_3$)



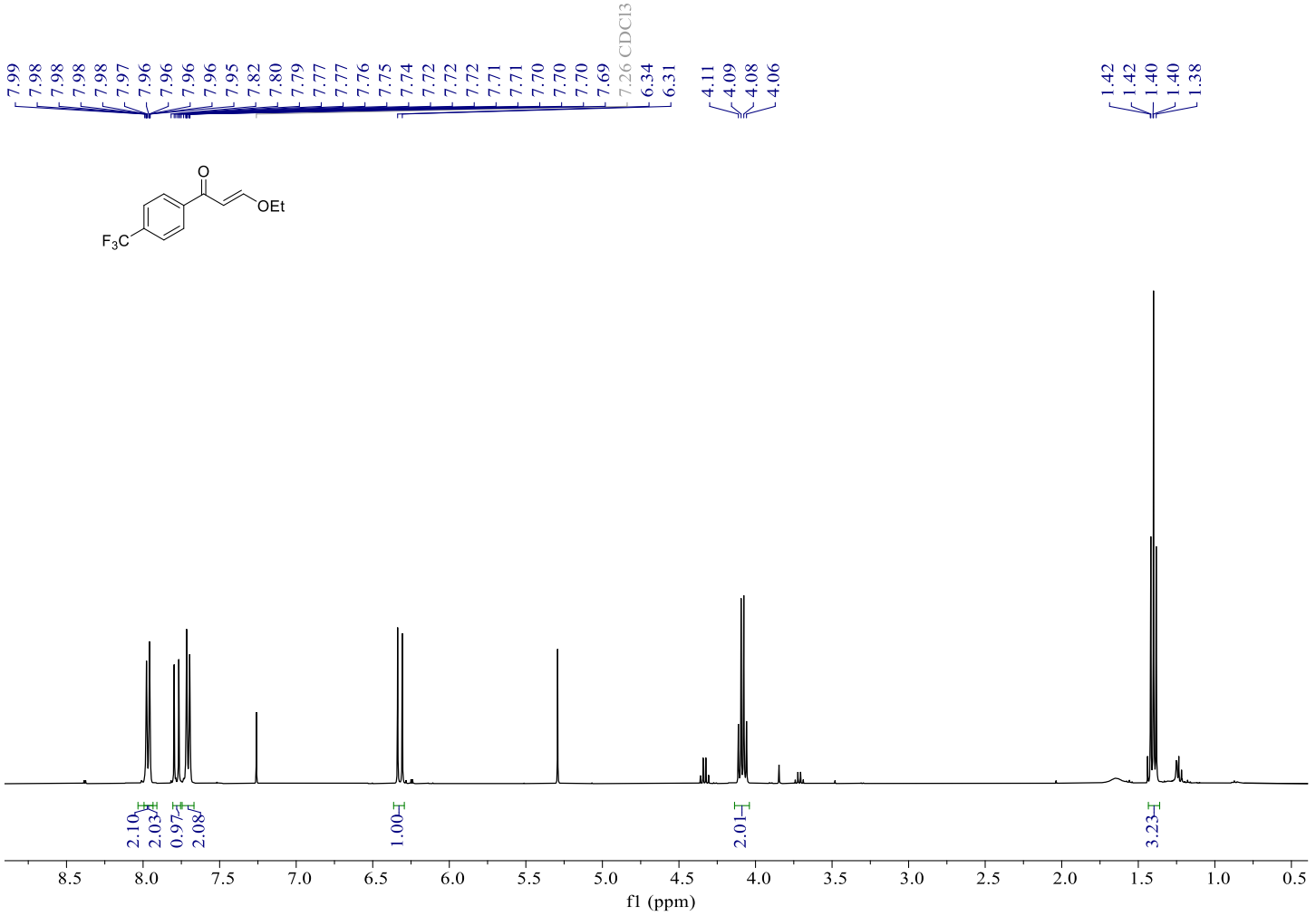
Compound 15 ^{13}C NMR (150 MHz, $CDCl_3$)



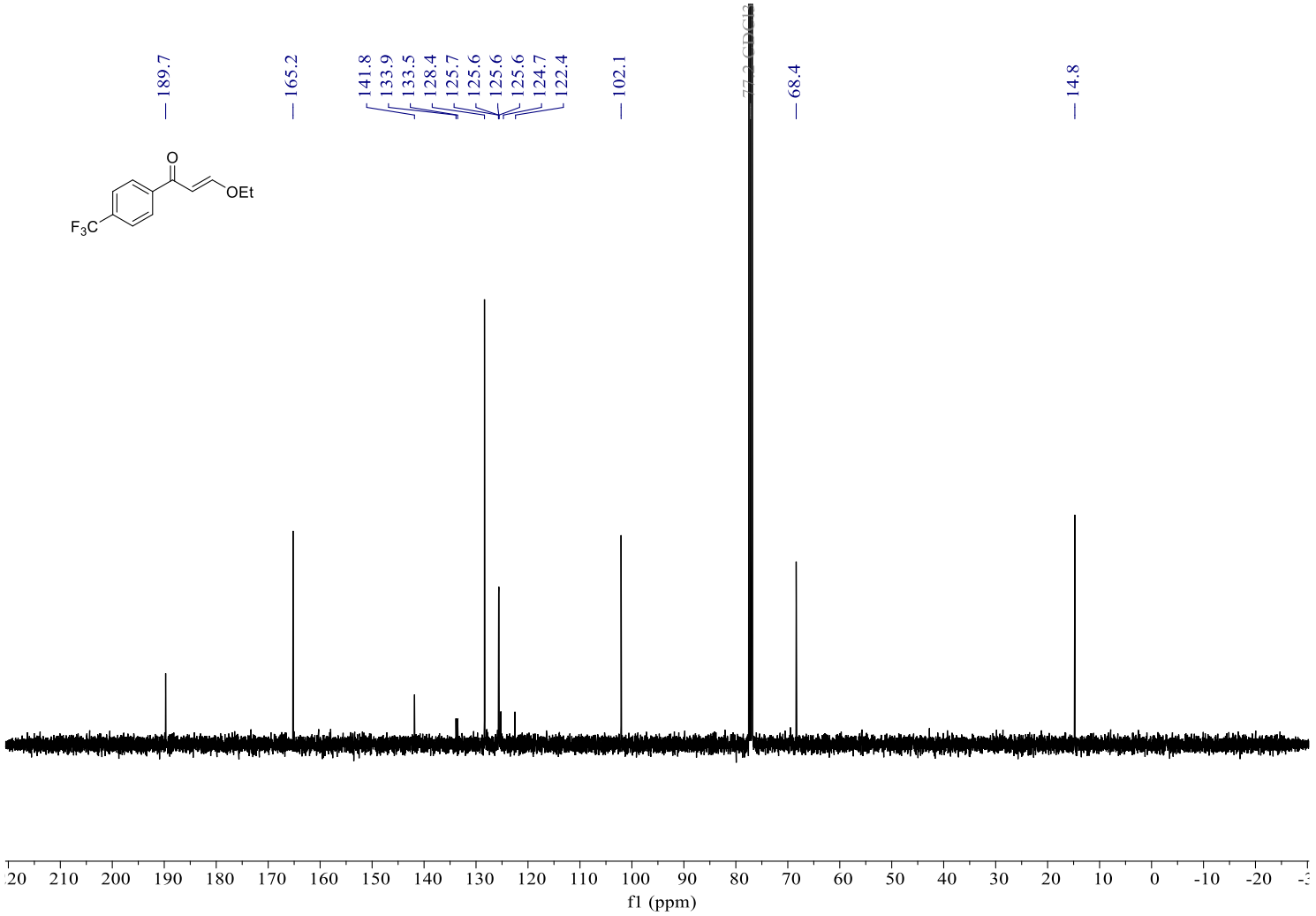
Compound 15 ^{19}F NMR (753 MHz, $CDCl_3$)



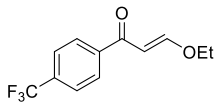
Compound 15b ^{1}H NMR (400 MHz, $CDCl_3$)



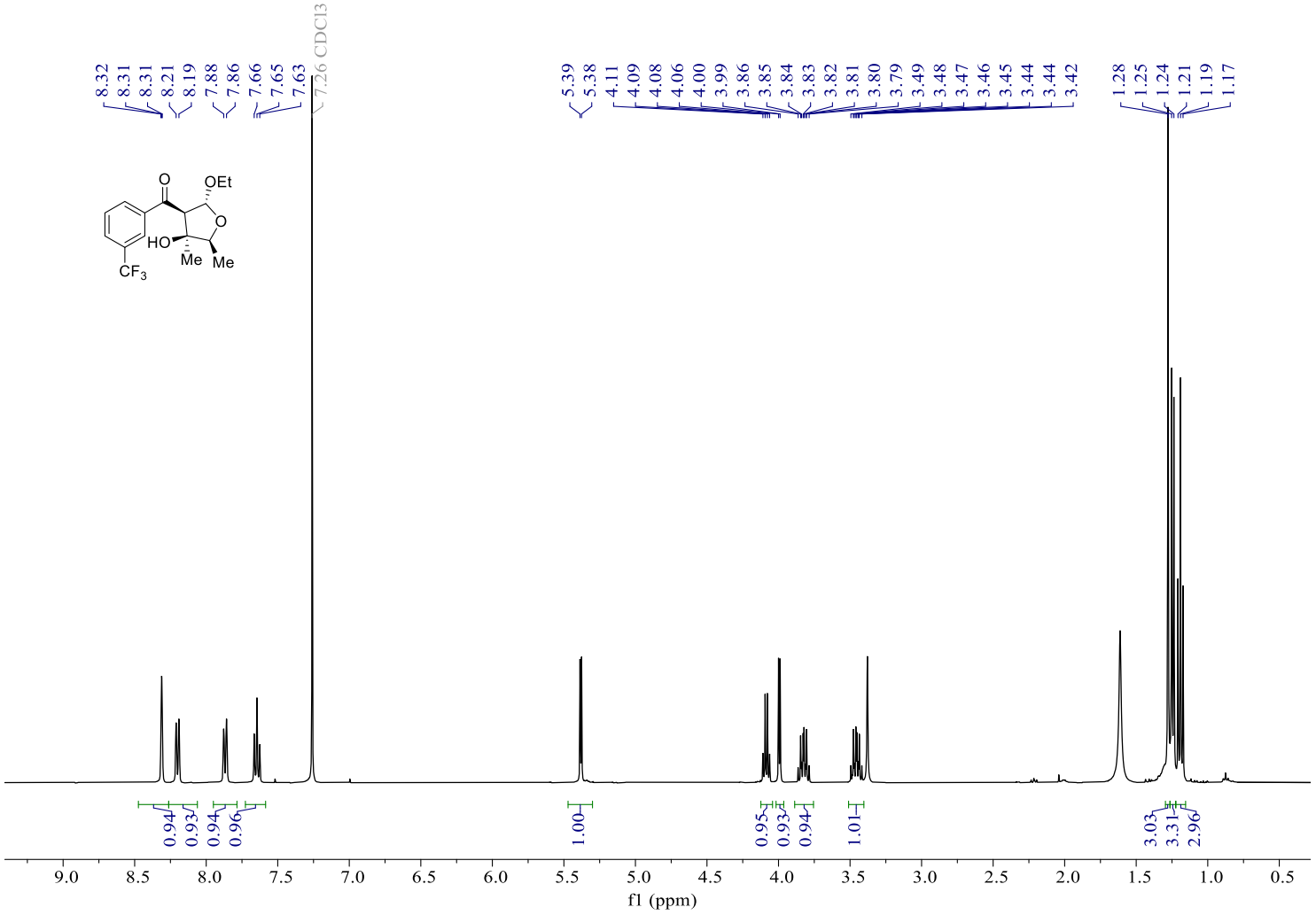
Compound 15b ^{13}C NMR (100 MHz, $CDCl_3$)



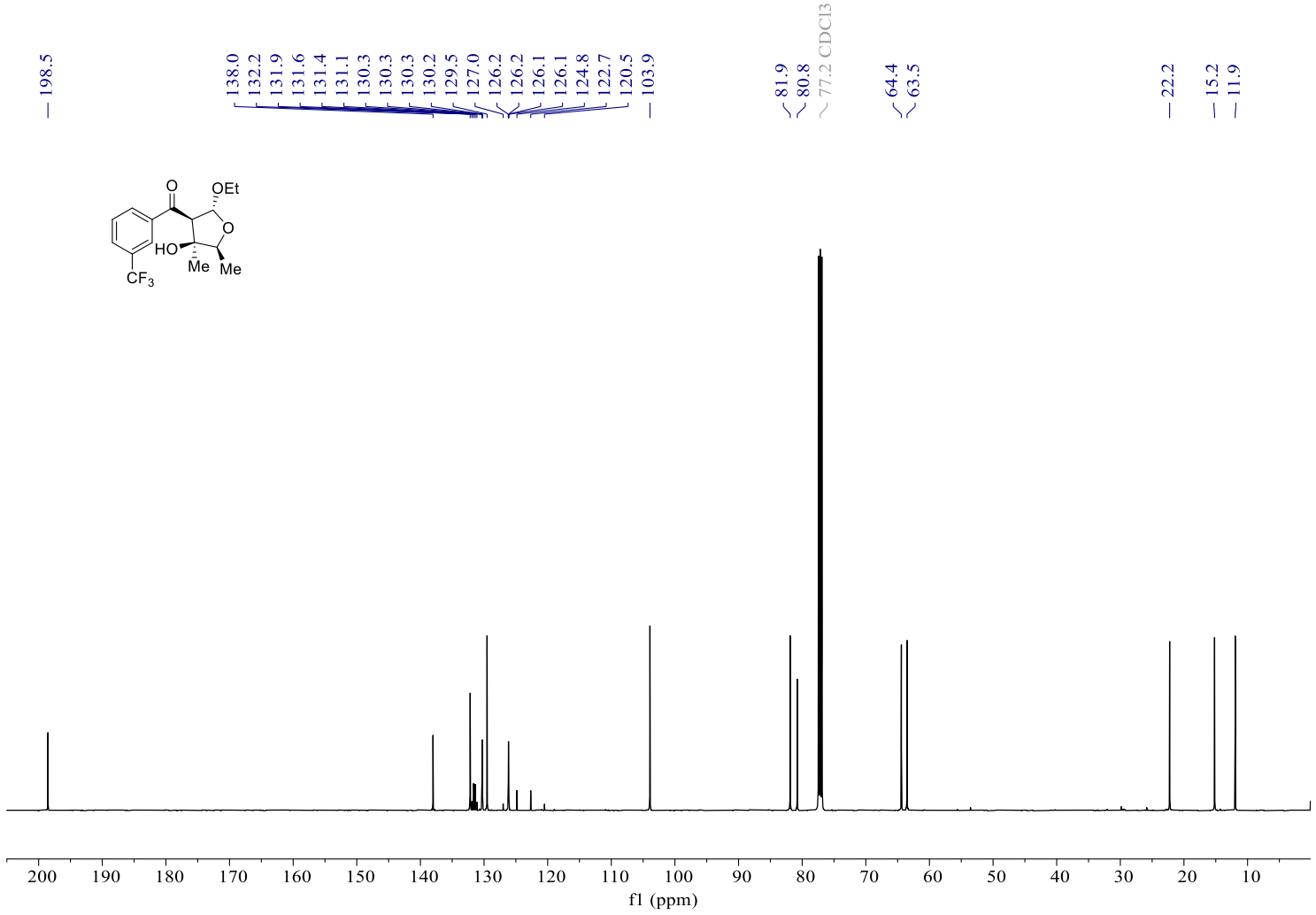
Compound 15b ^{19}F NMR (753 MHz, $CDCl_3$)



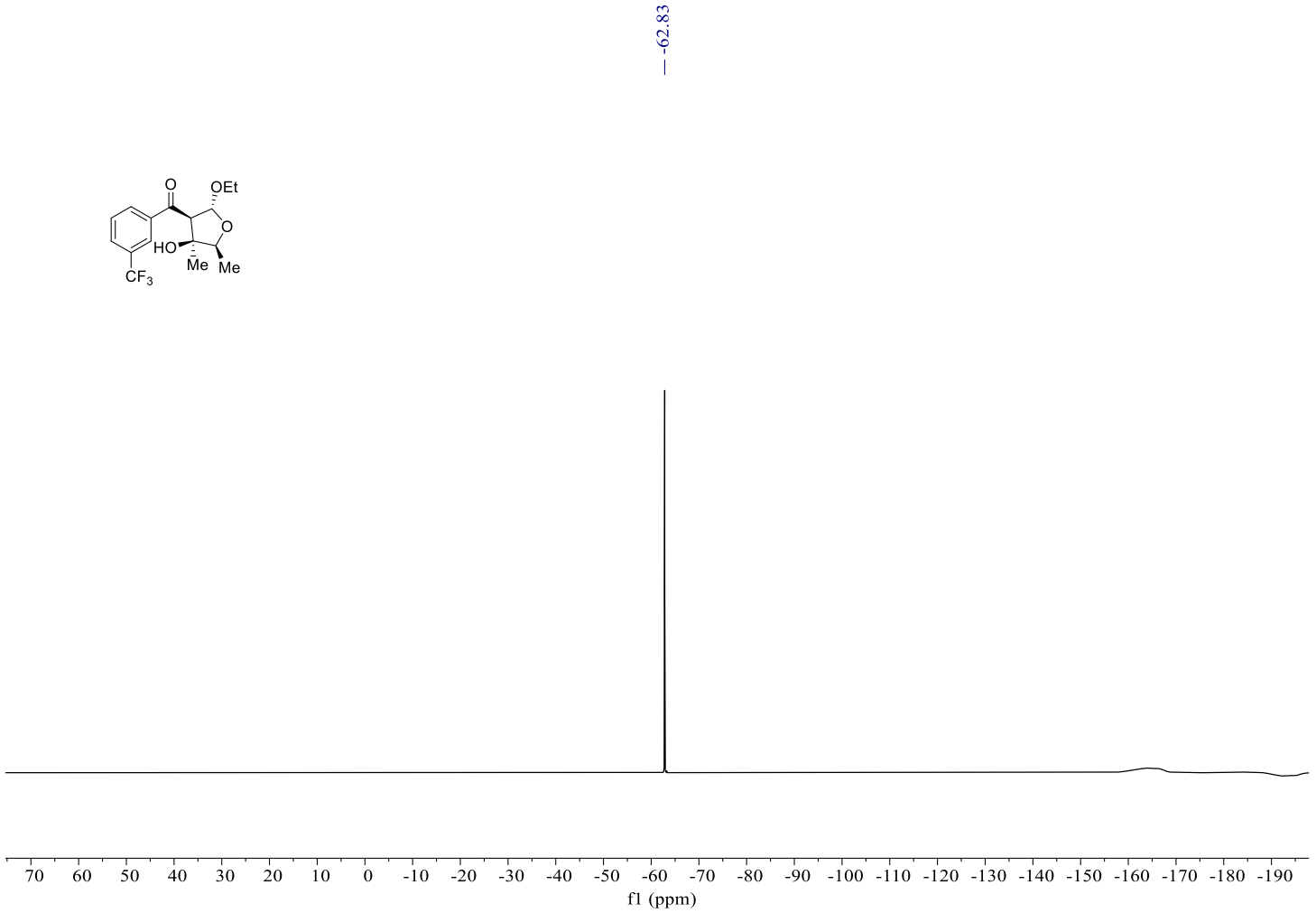
Compound 16 ^{1}H NMR (400 MHz, $CDCl_3$)



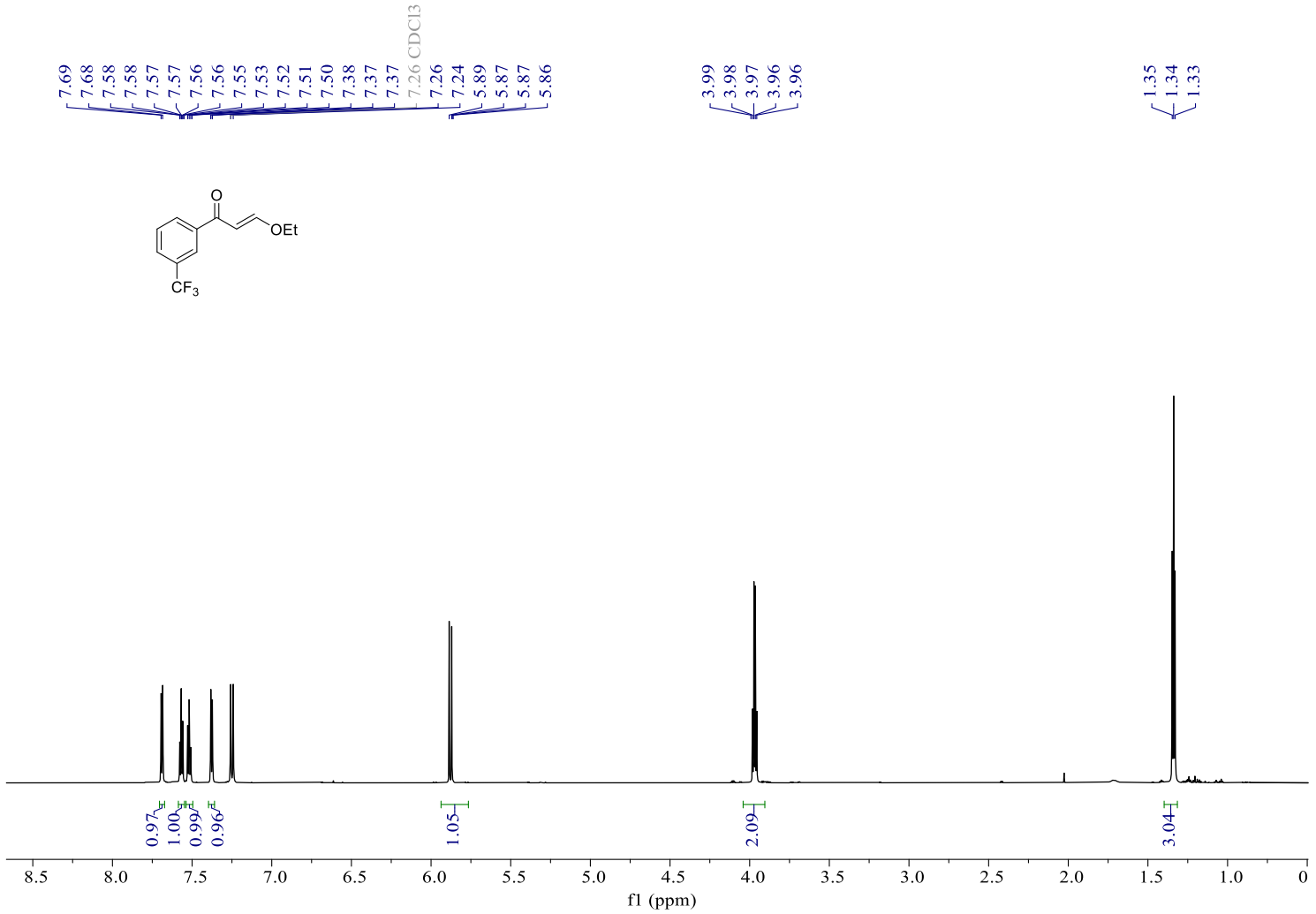
Compound 16 ^{13}C NMR (125 MHz, $CDCl_3$)



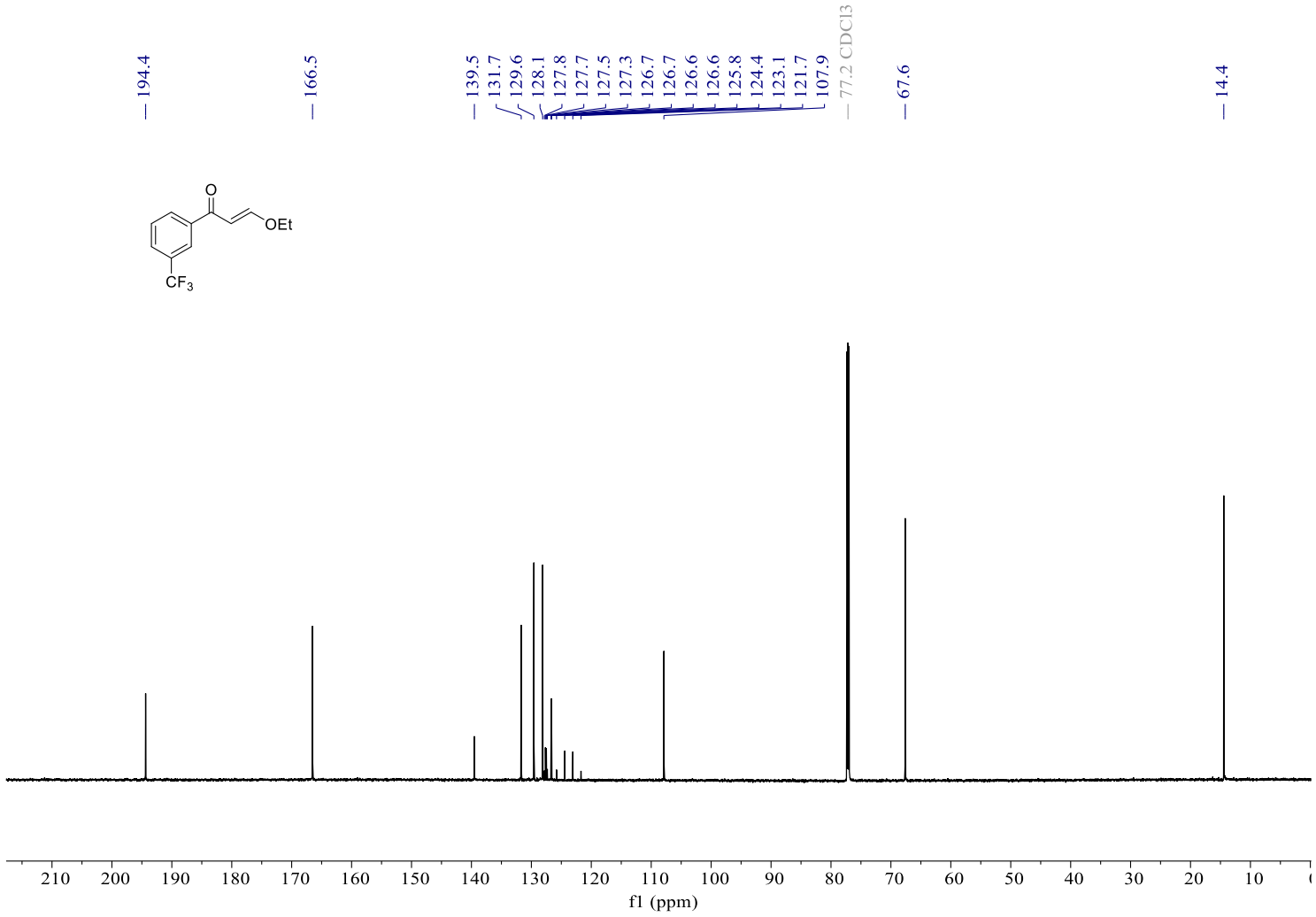
Compound 16 ^{19}F NMR (471 MHz, $CDCl_3$)



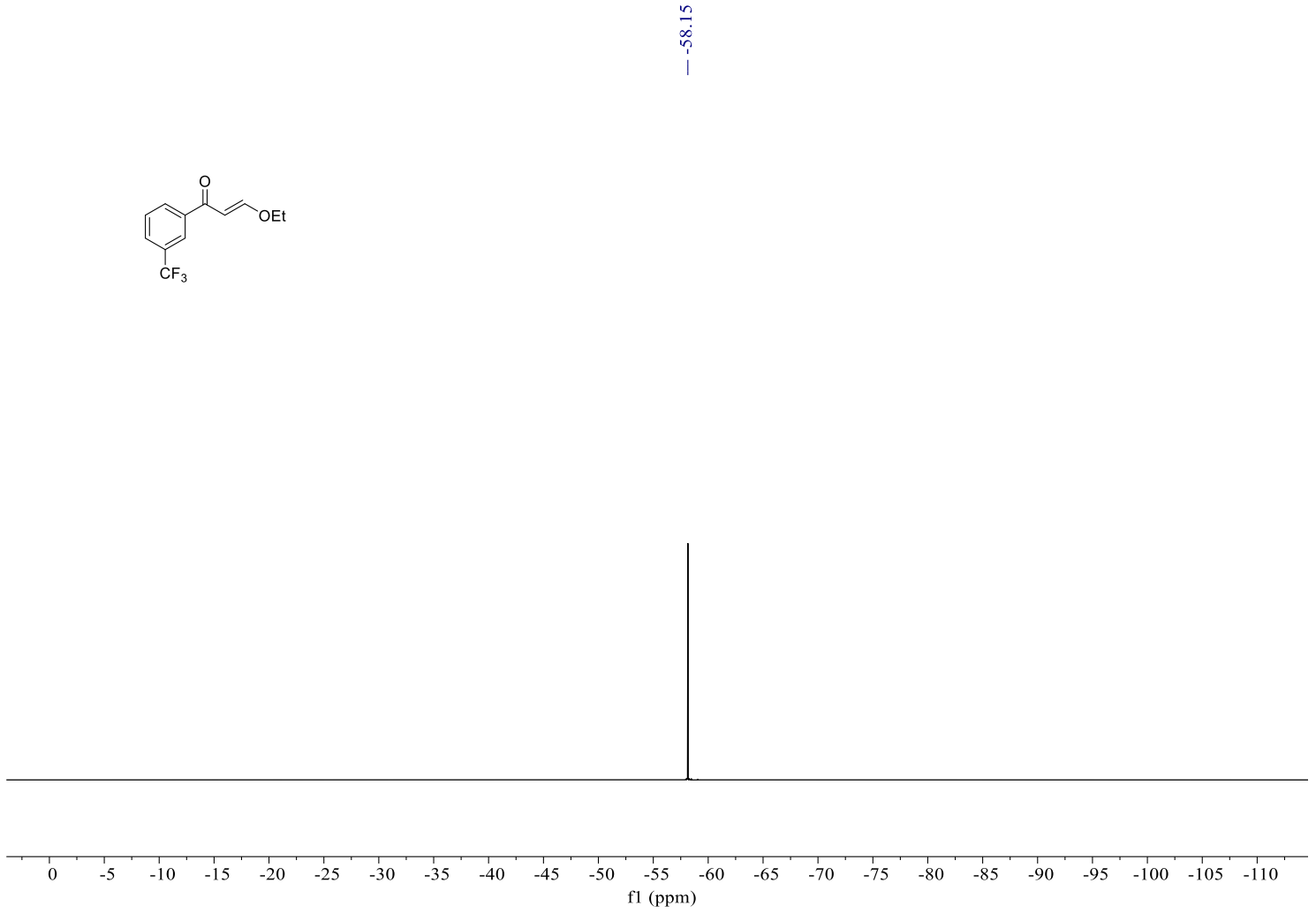
Compound 16b ^{1}H NMR (800 MHz, $CDCl_3$)



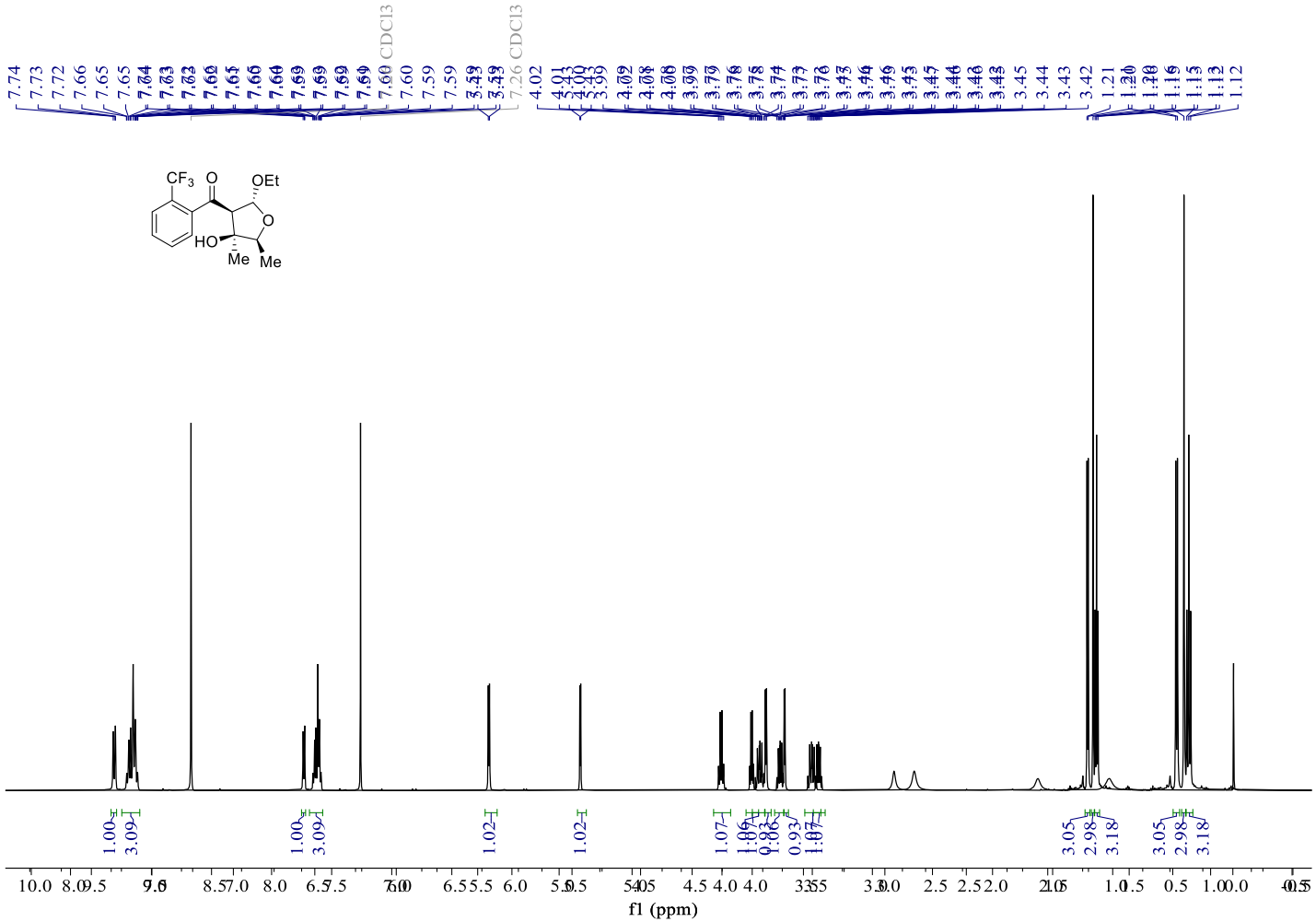
Compound 16b ^{13}C NMR (200 MHz, $CDCl_3$)



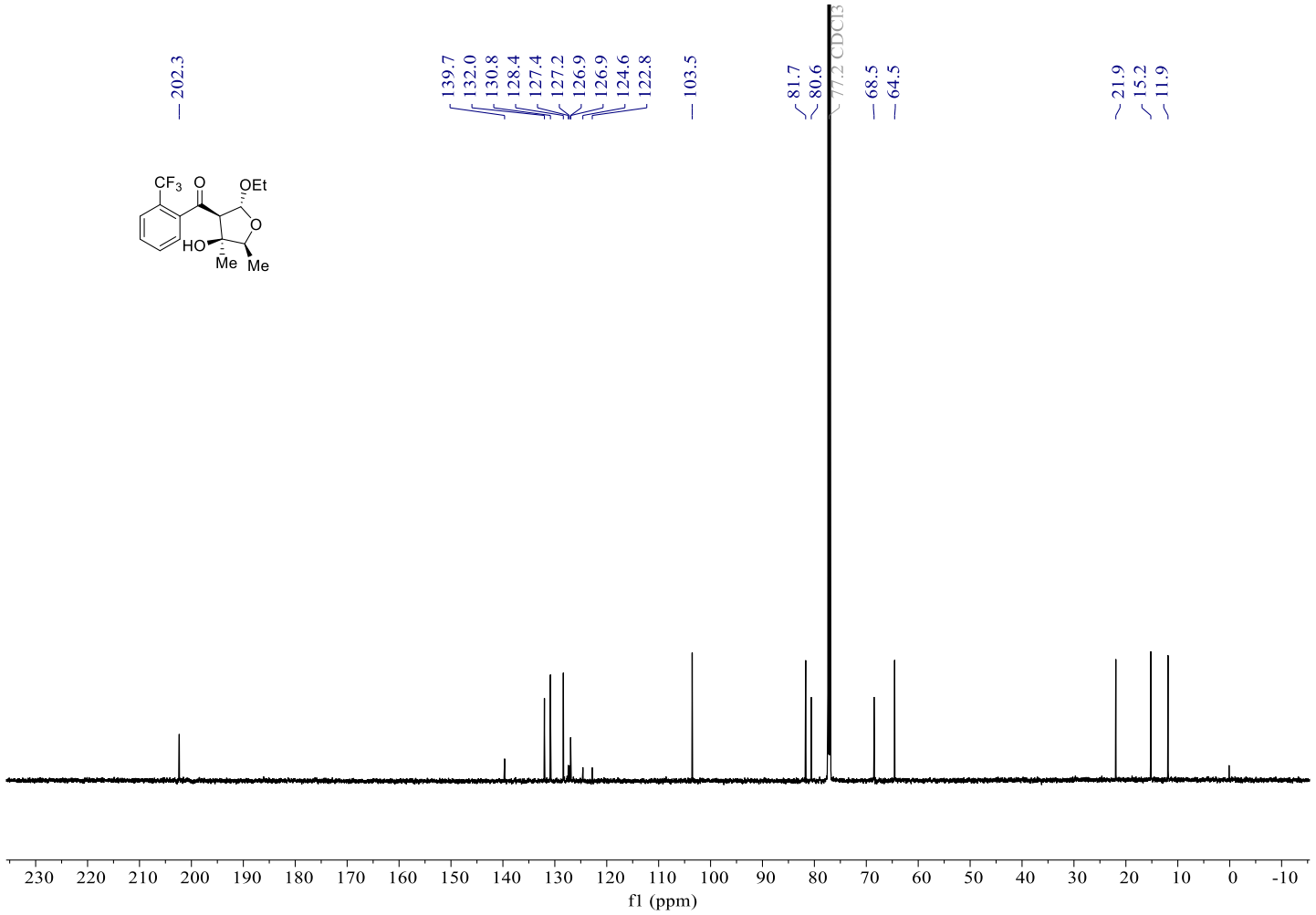
Compound 16b ^{19}F NMR (753 MHz, $CDCl_3$)



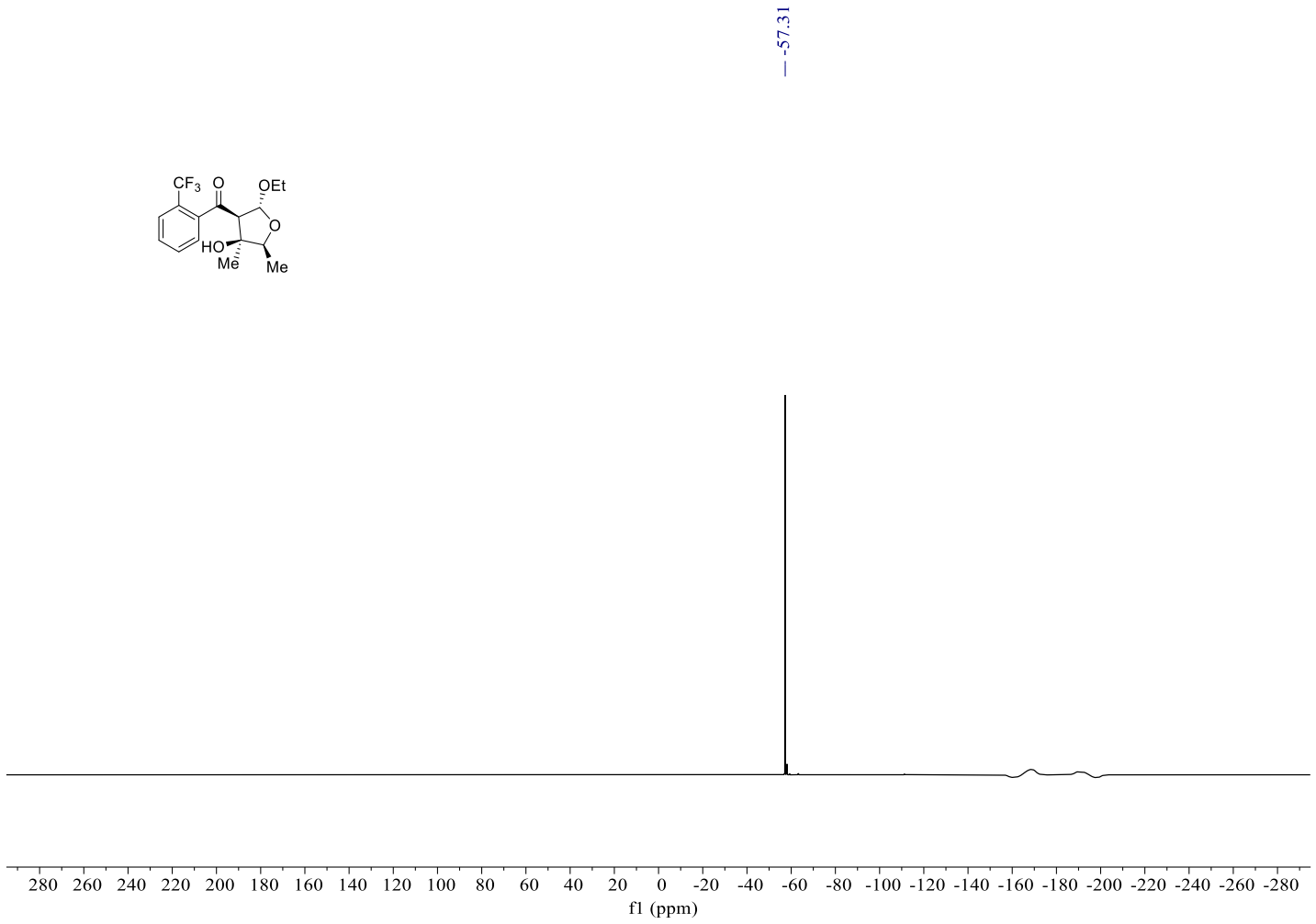
Compound 17 ^{1}H NMR (600 MHz, $CDCl_3$)



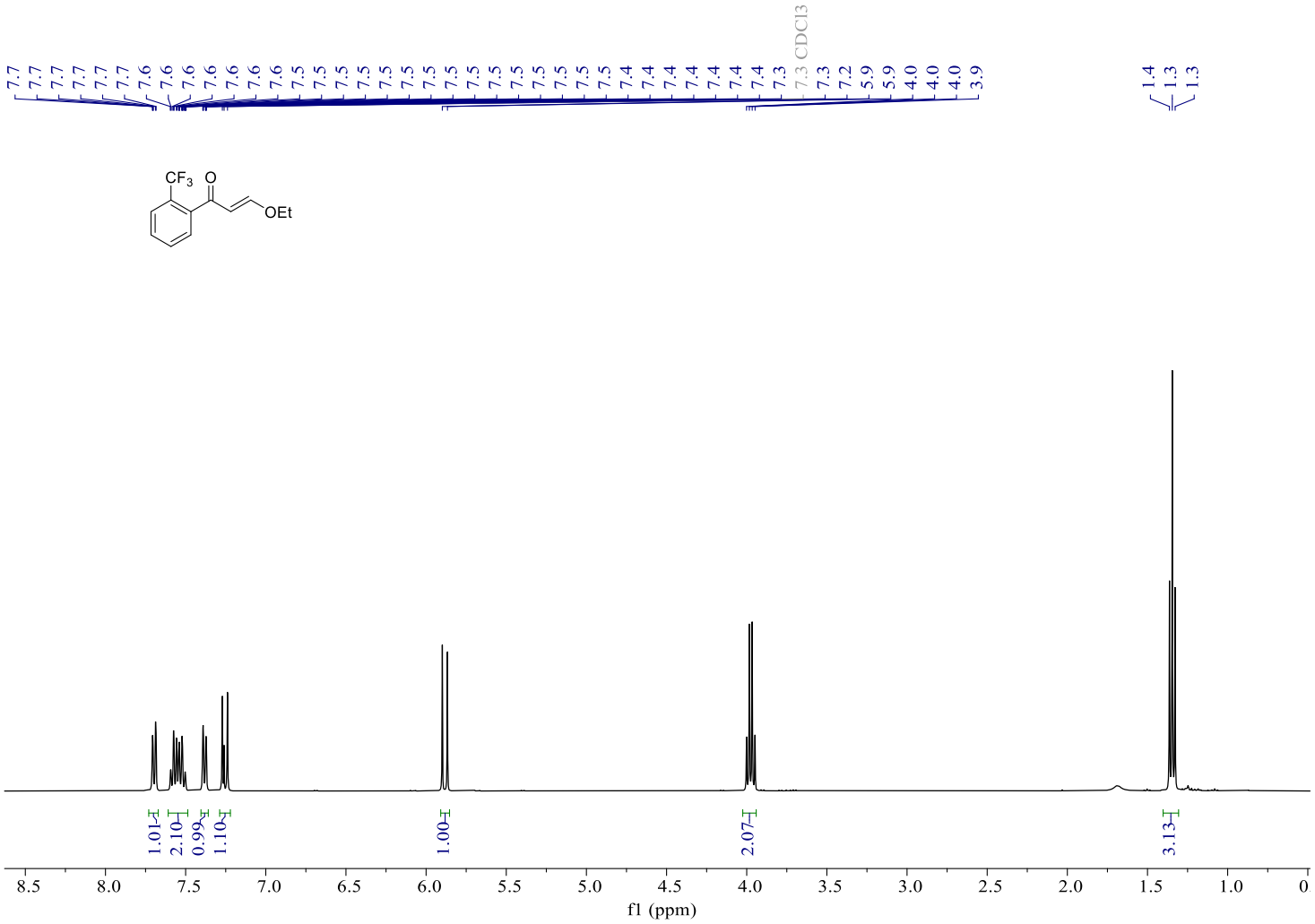
Compound 17 ^{13}C NMR (150 MHz, $CDCl_3$)



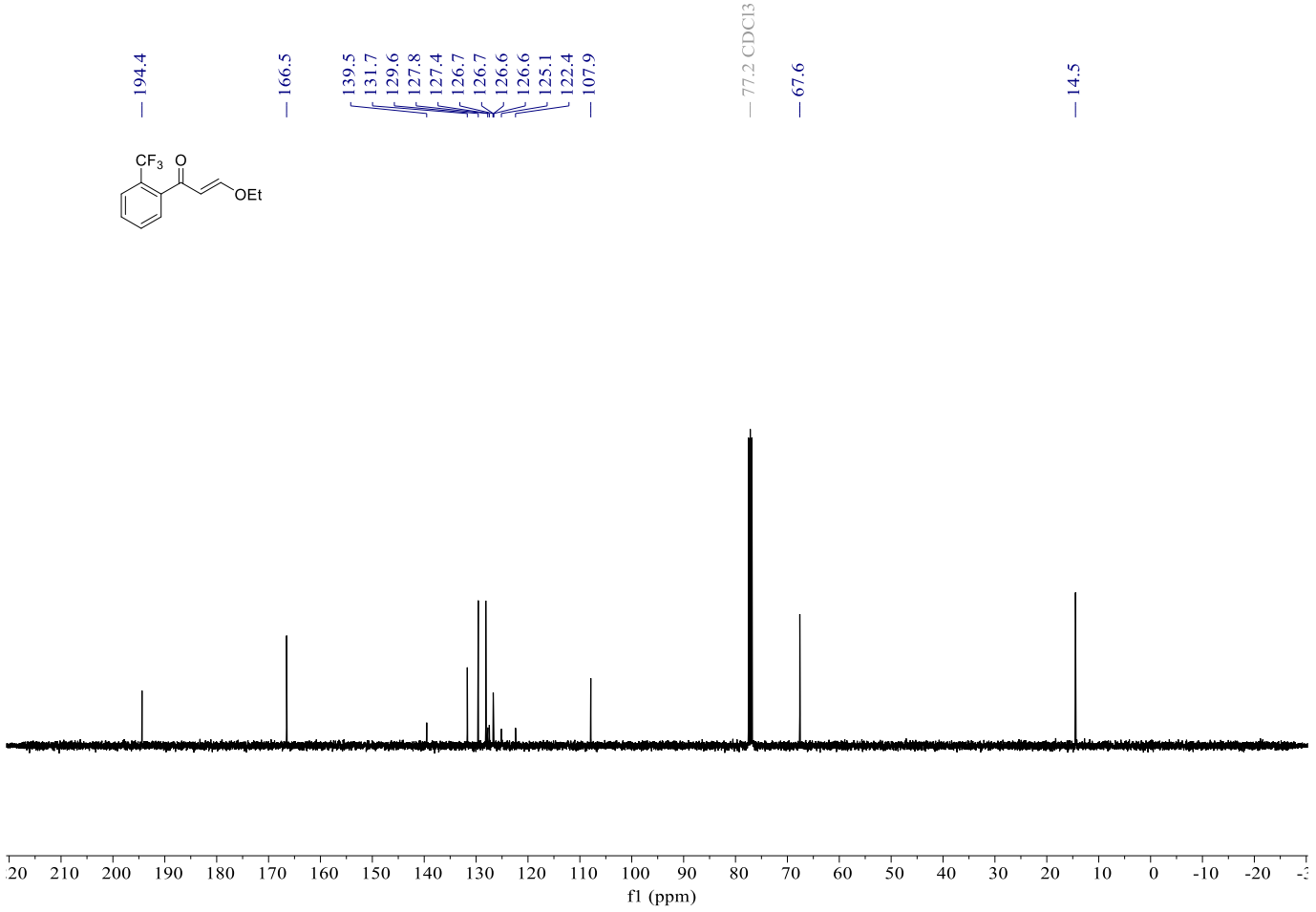
Compound 17 ^{19}F NMR (471 MHz, $CDCl_3$)



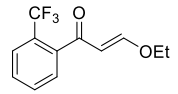
Compound 17b ^{1}H NMR (400 MHz, $CDCl_3$)



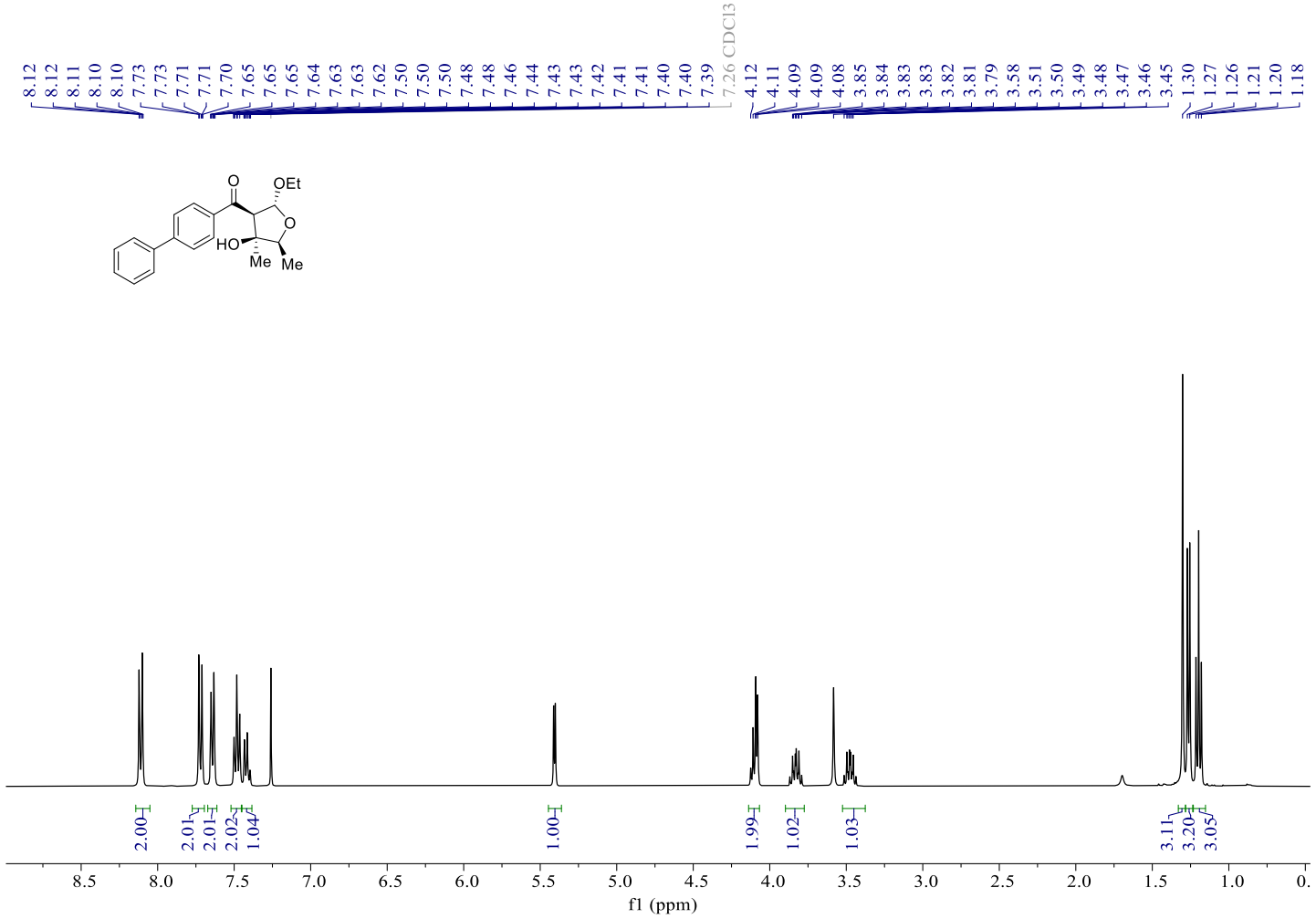
Compound 17b ^{13}C NMR (100 MHz, $CDCl_3$)



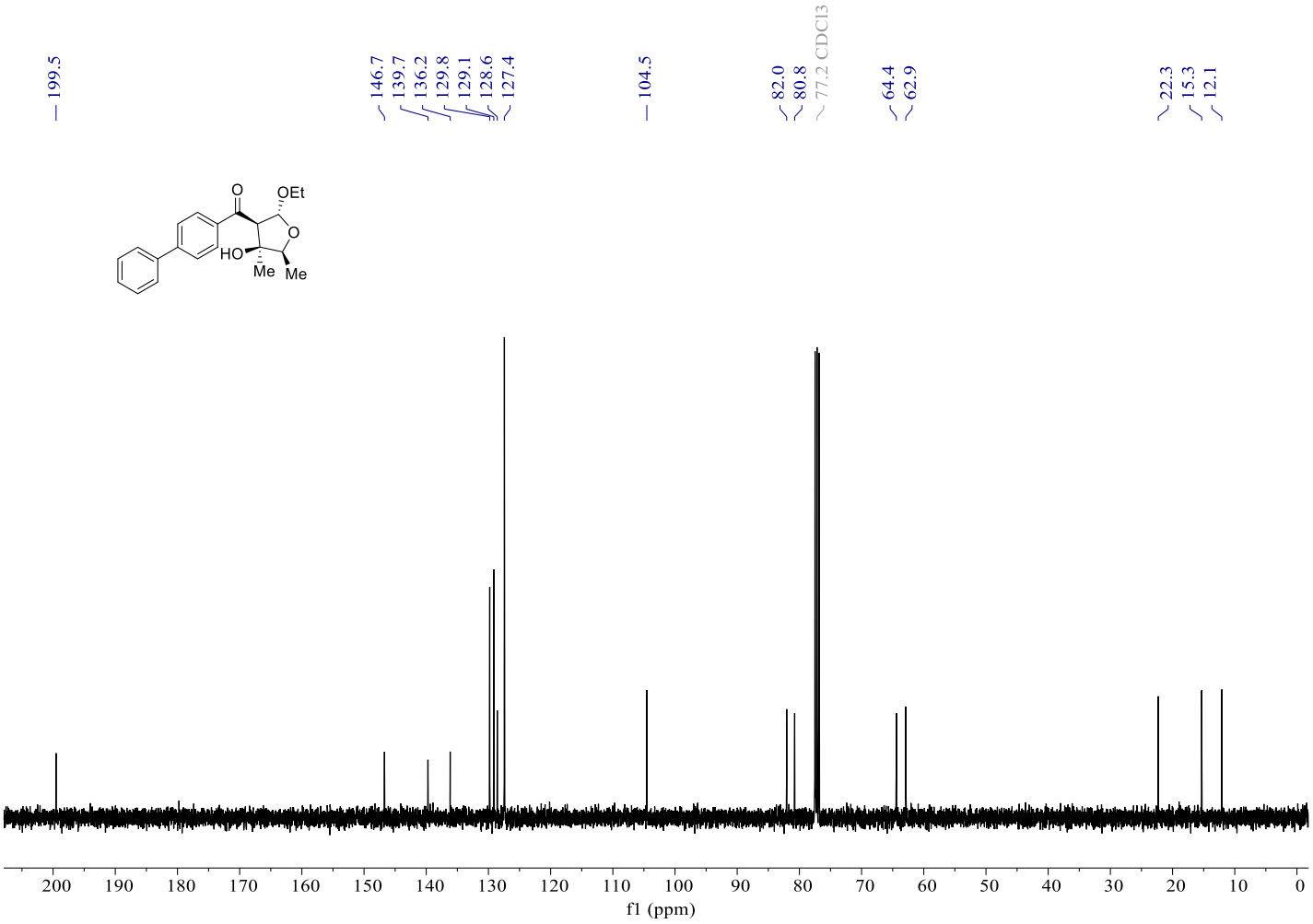
Compound 17b ^{19}F NMR (471 MHz, $CDCl_3$)



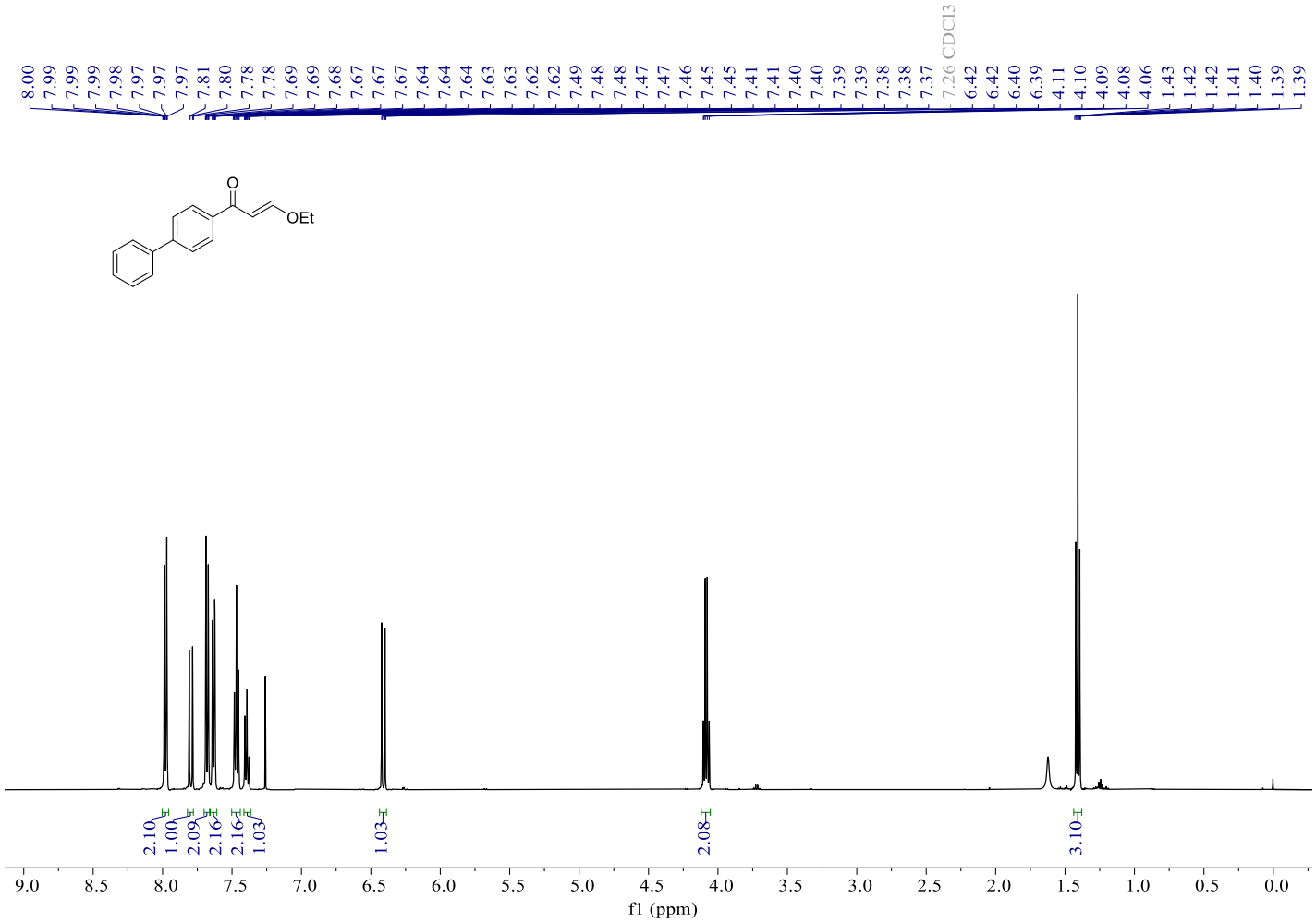
Compound 18 ^{1}H NMR (400 MHz, $CDCl_3$)



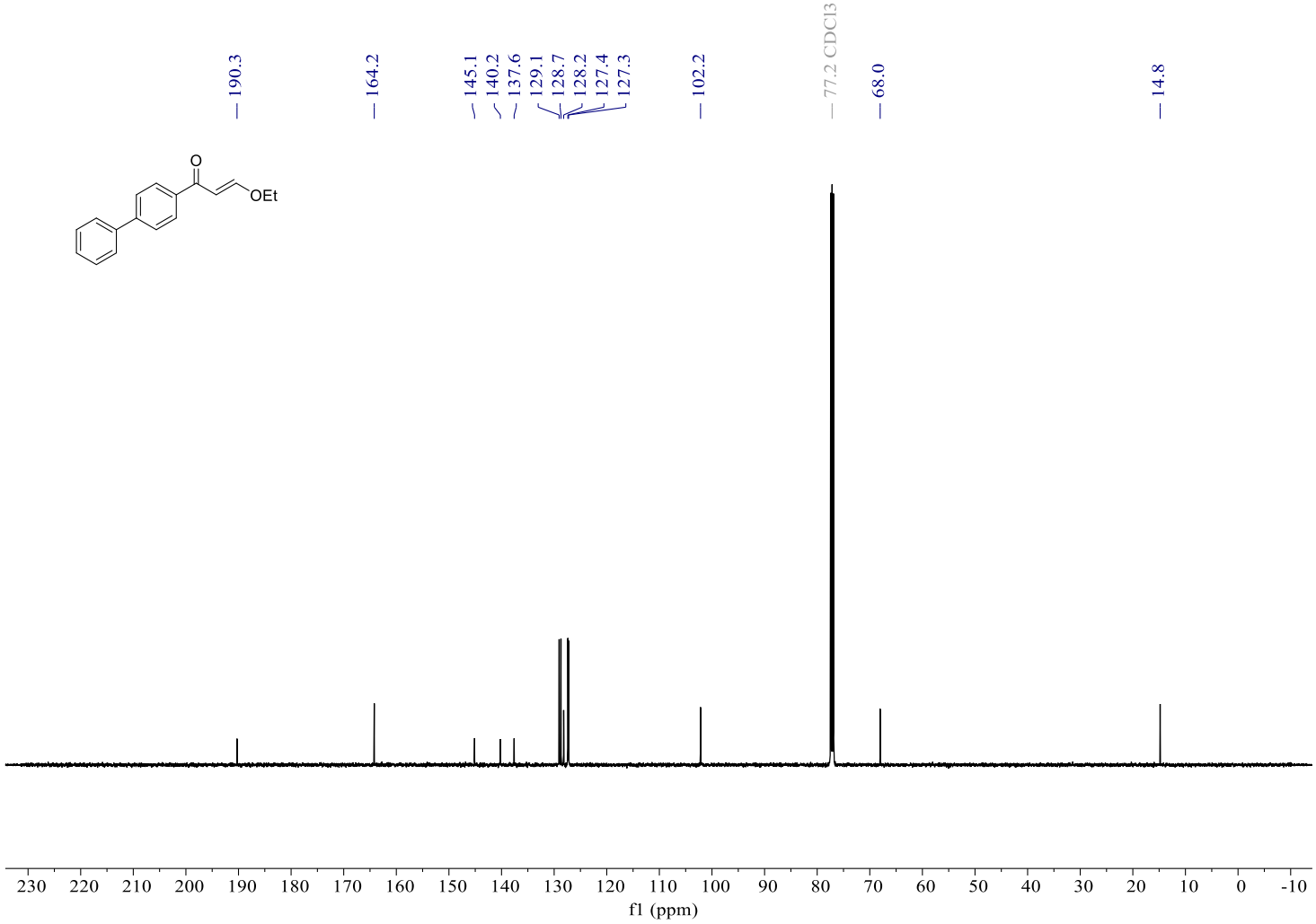
Compound 18 ^{13}C NMR (100 MHz, $CDCl_3$)



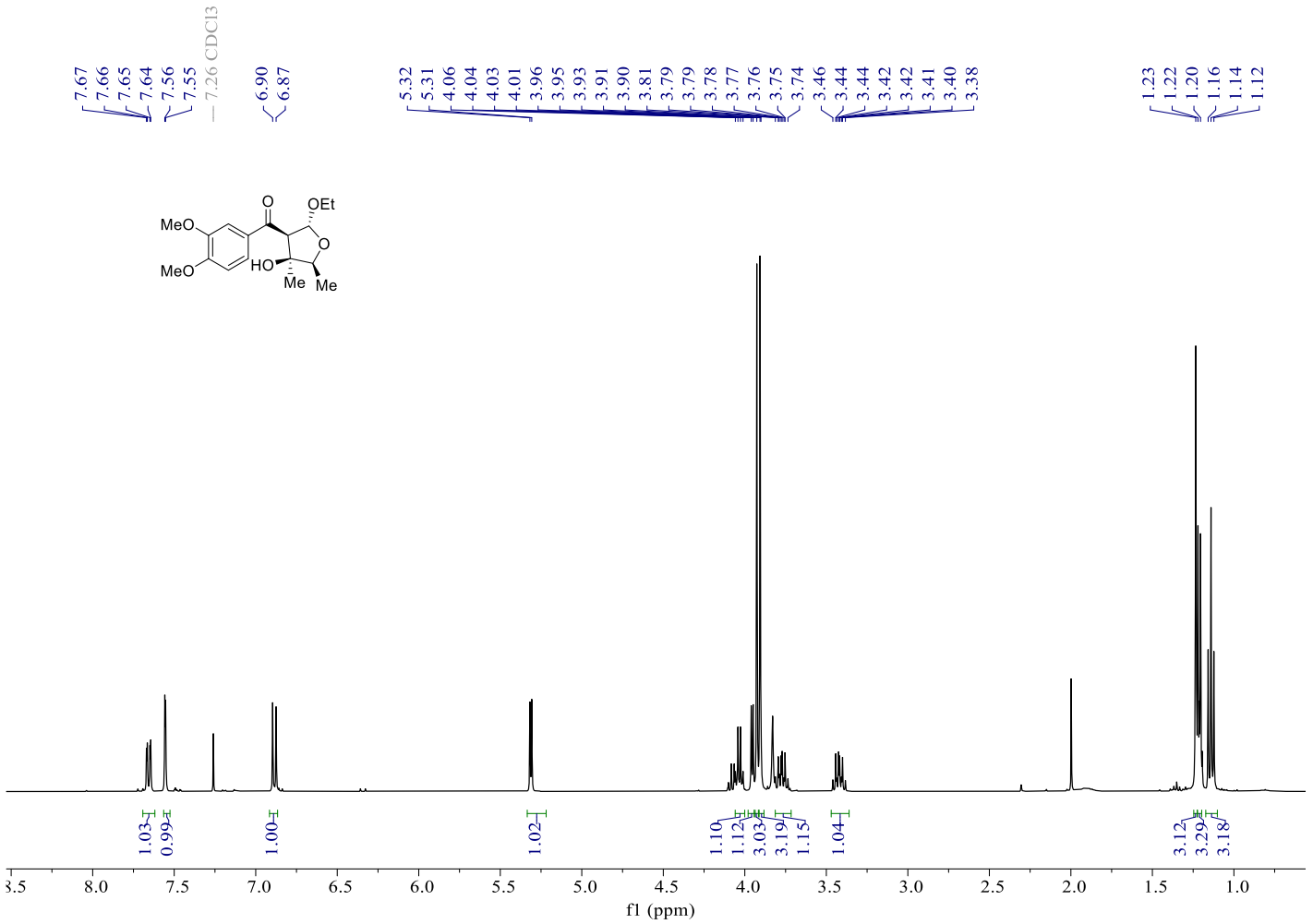
Compound 18b ^{1}H NMR (500 MHz, $CDCl_3$)



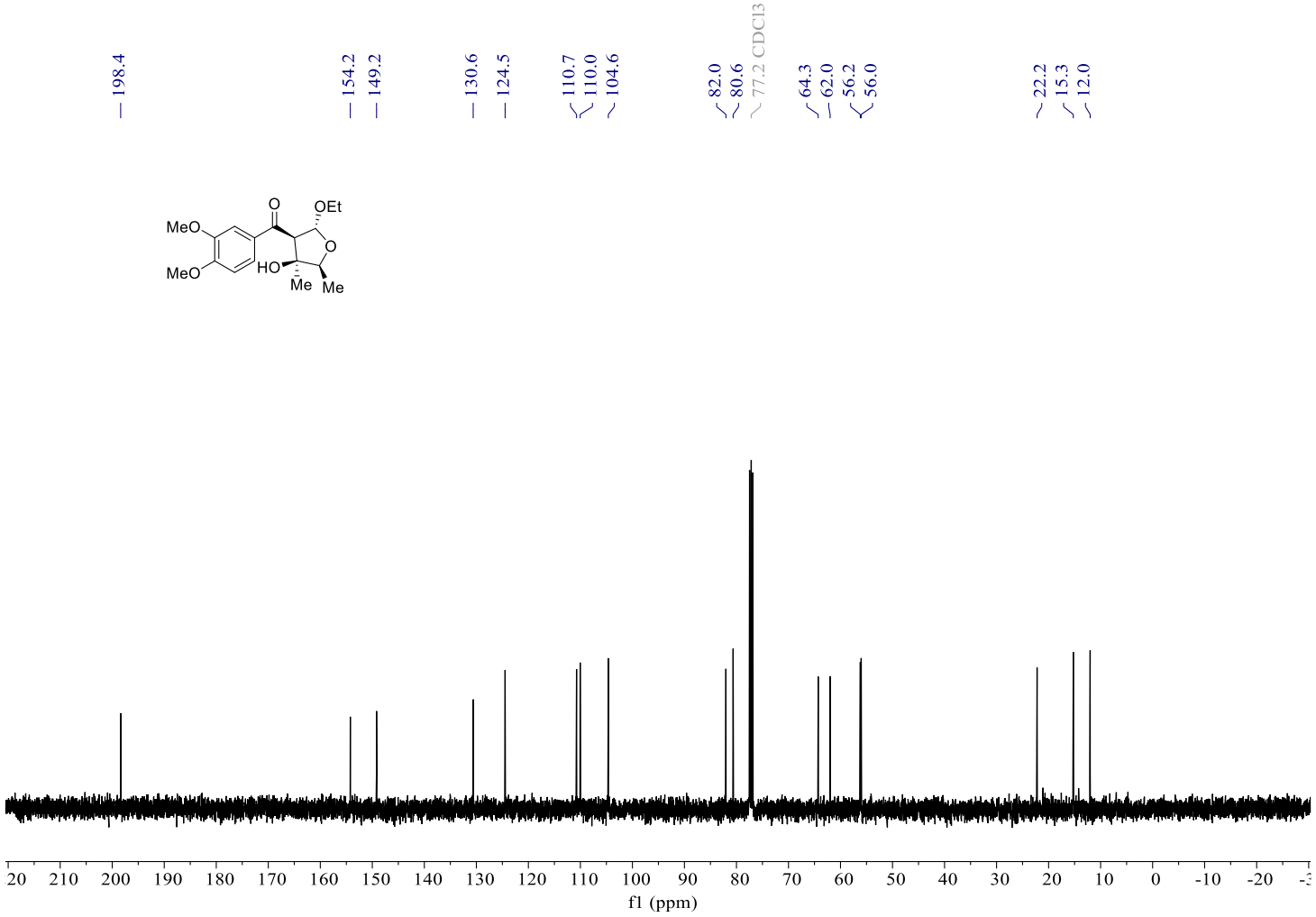
Compound 18b ^{13}C NMR (125 MHz, $CDCl_3$)



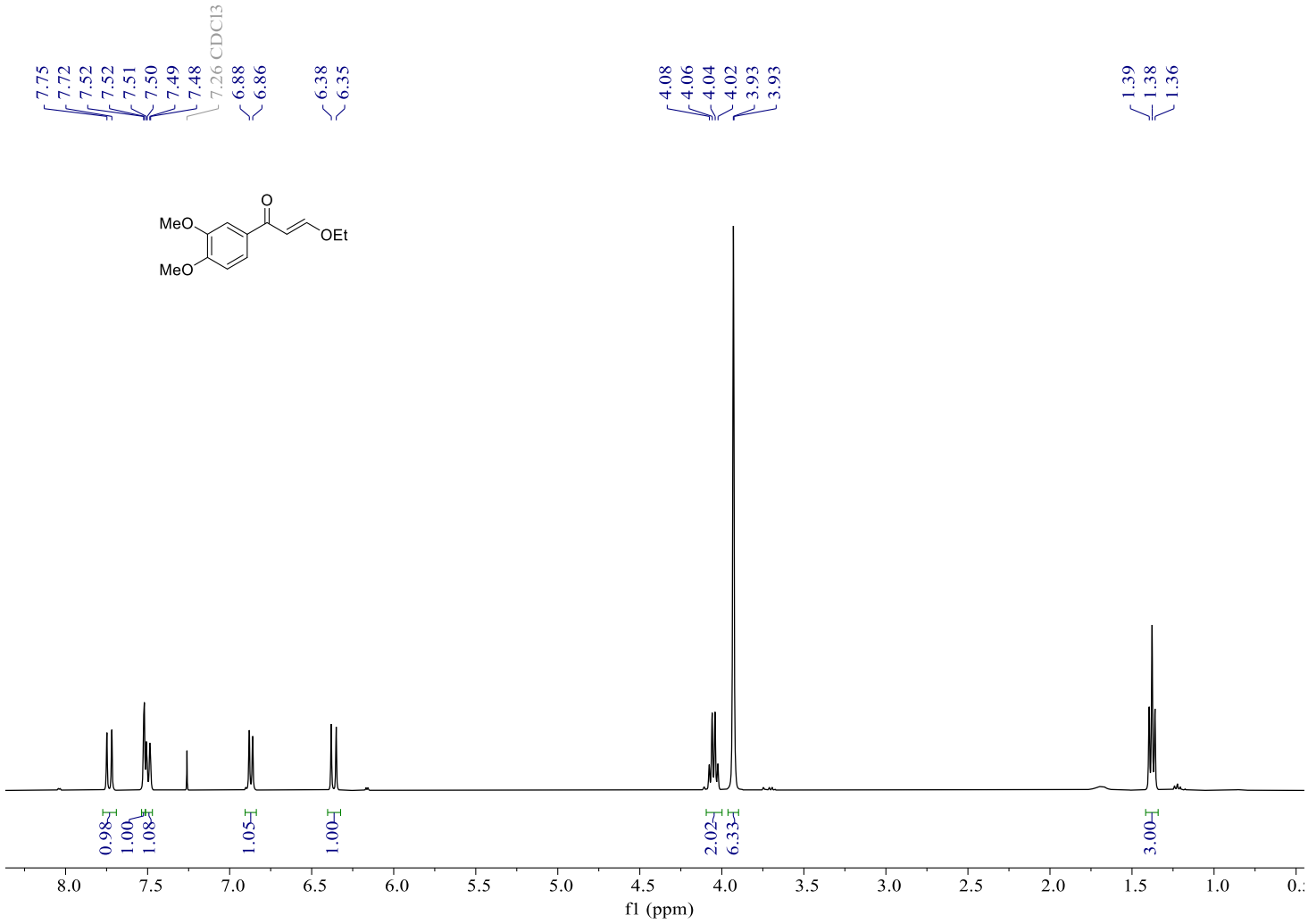
Compound 19 ^{1}H NMR (400 MHz, $CDCl_3$)



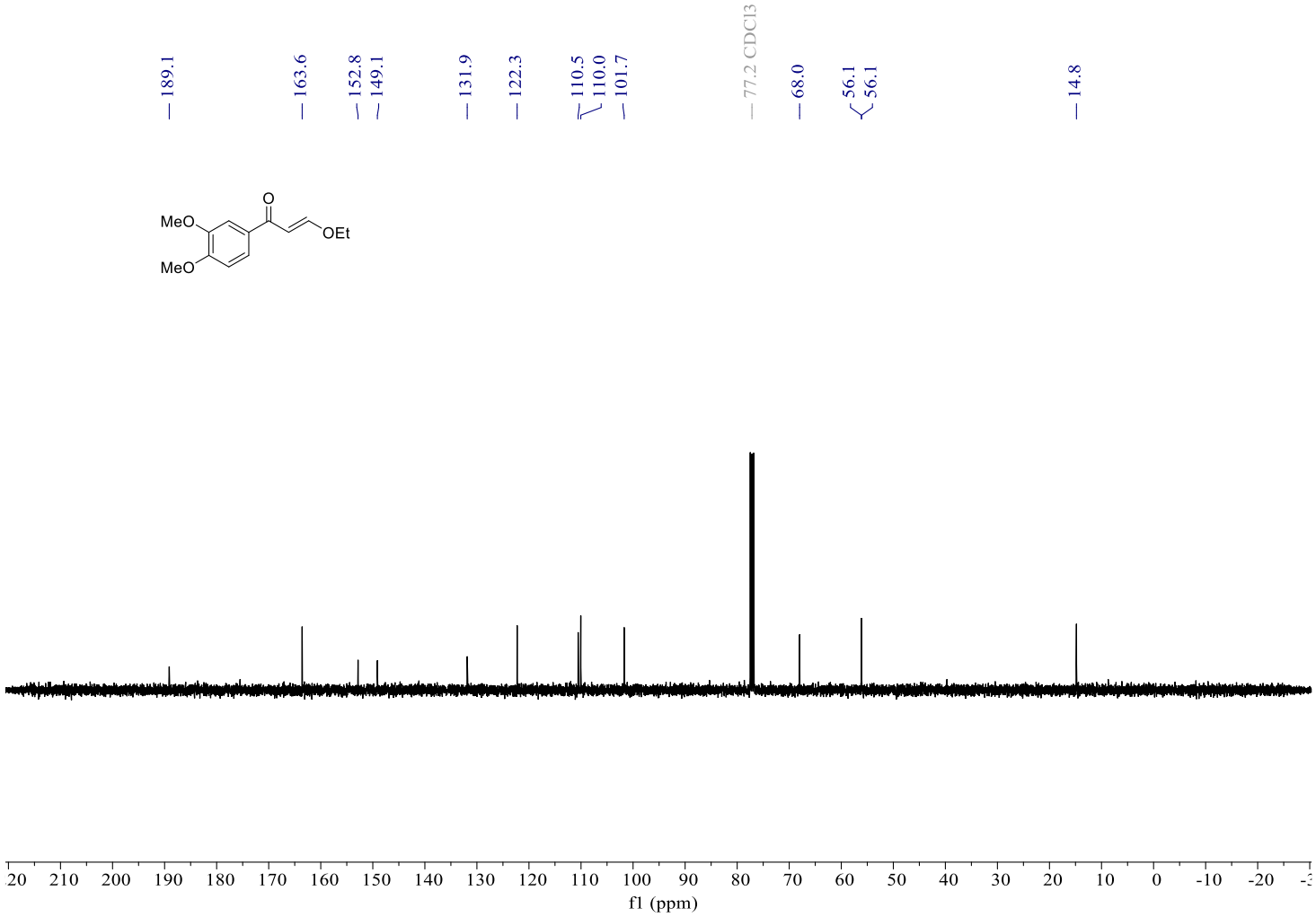
Compound 19 ^{13}C NMR (100 MHz, $CDCl_3$)



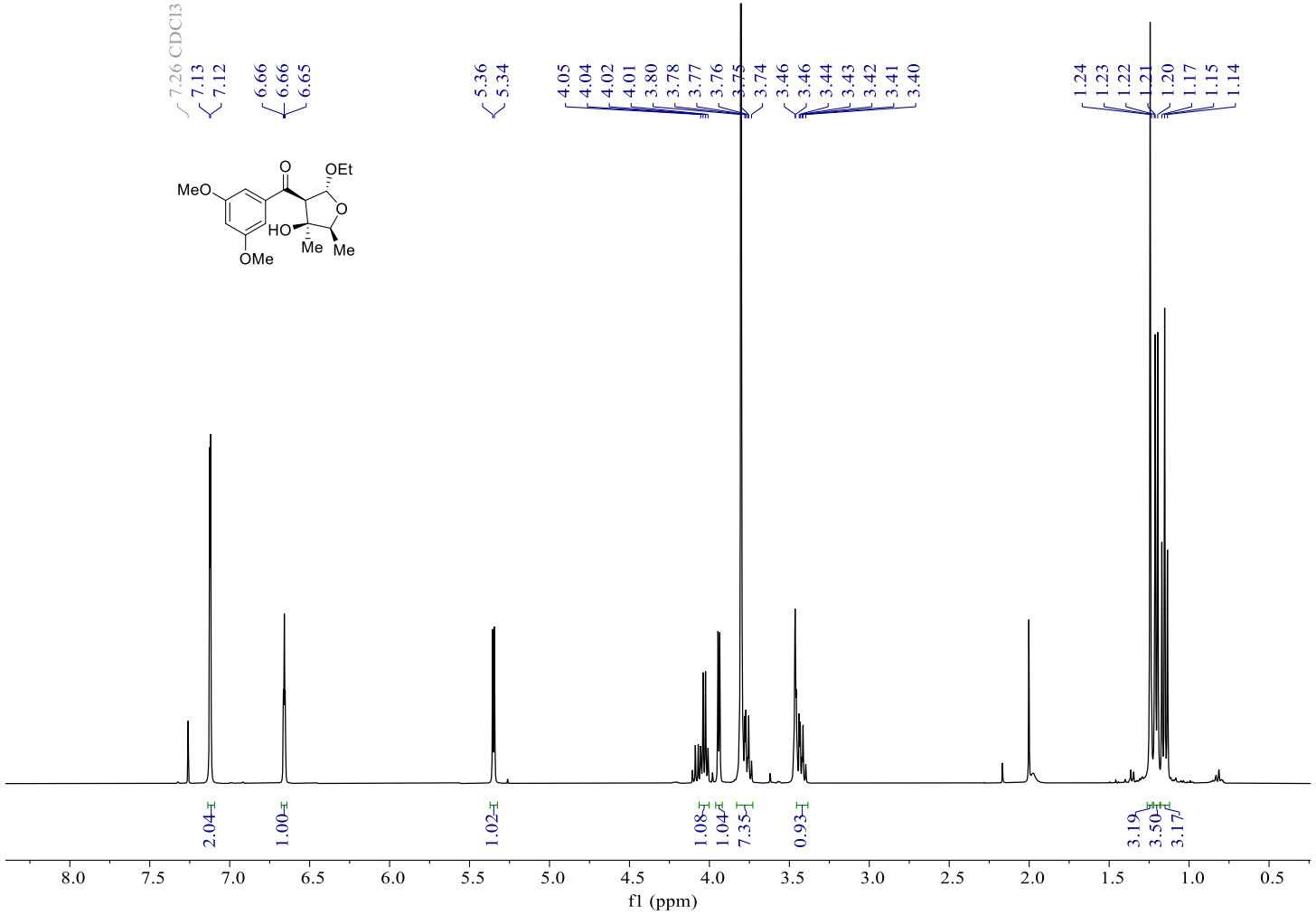
Compound 19b ^{1}H NMR (400 MHz, $CDCl_3$)



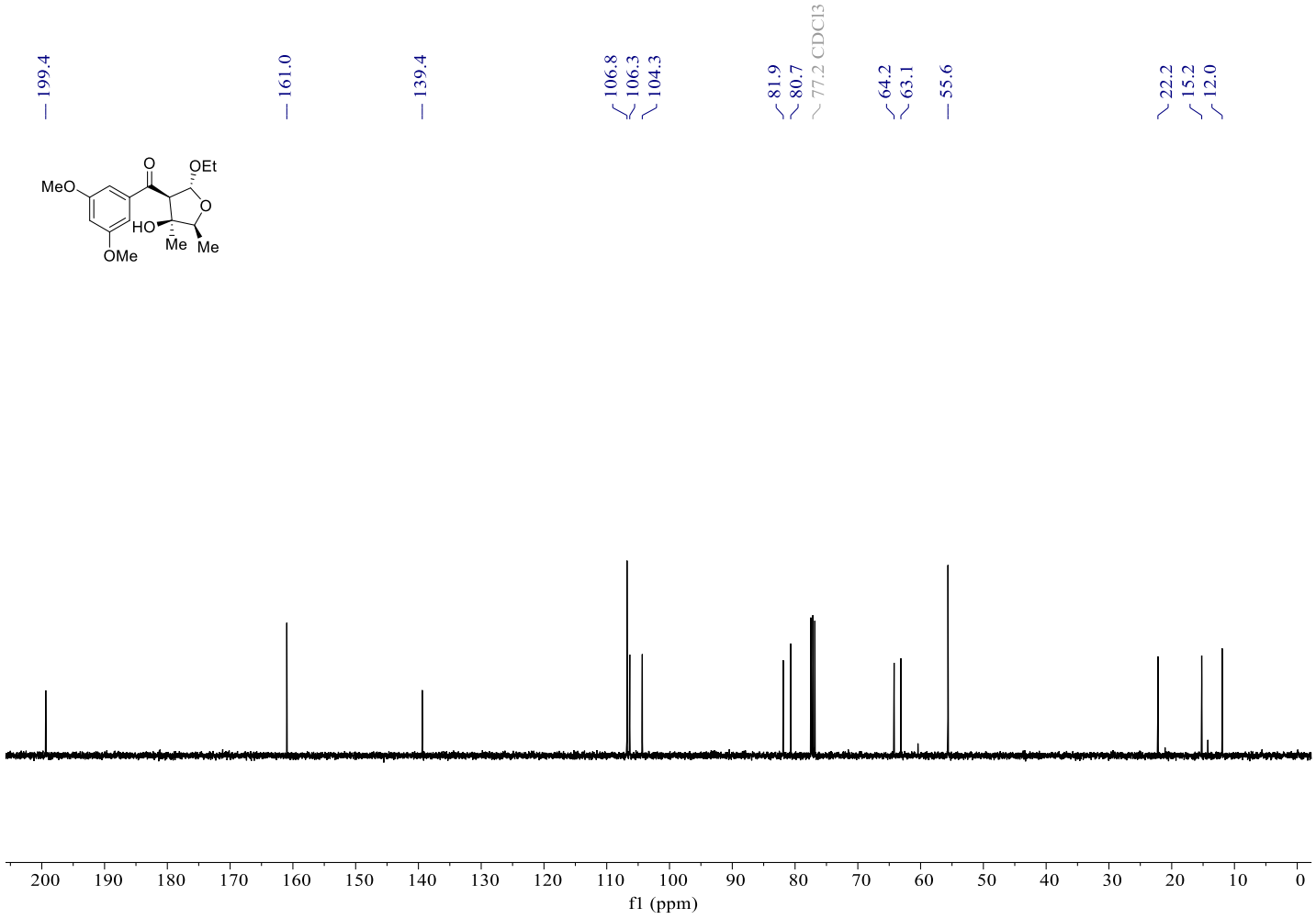
Compound 19b ^{13}C NMR (100 MHz, $CDCl_3$)



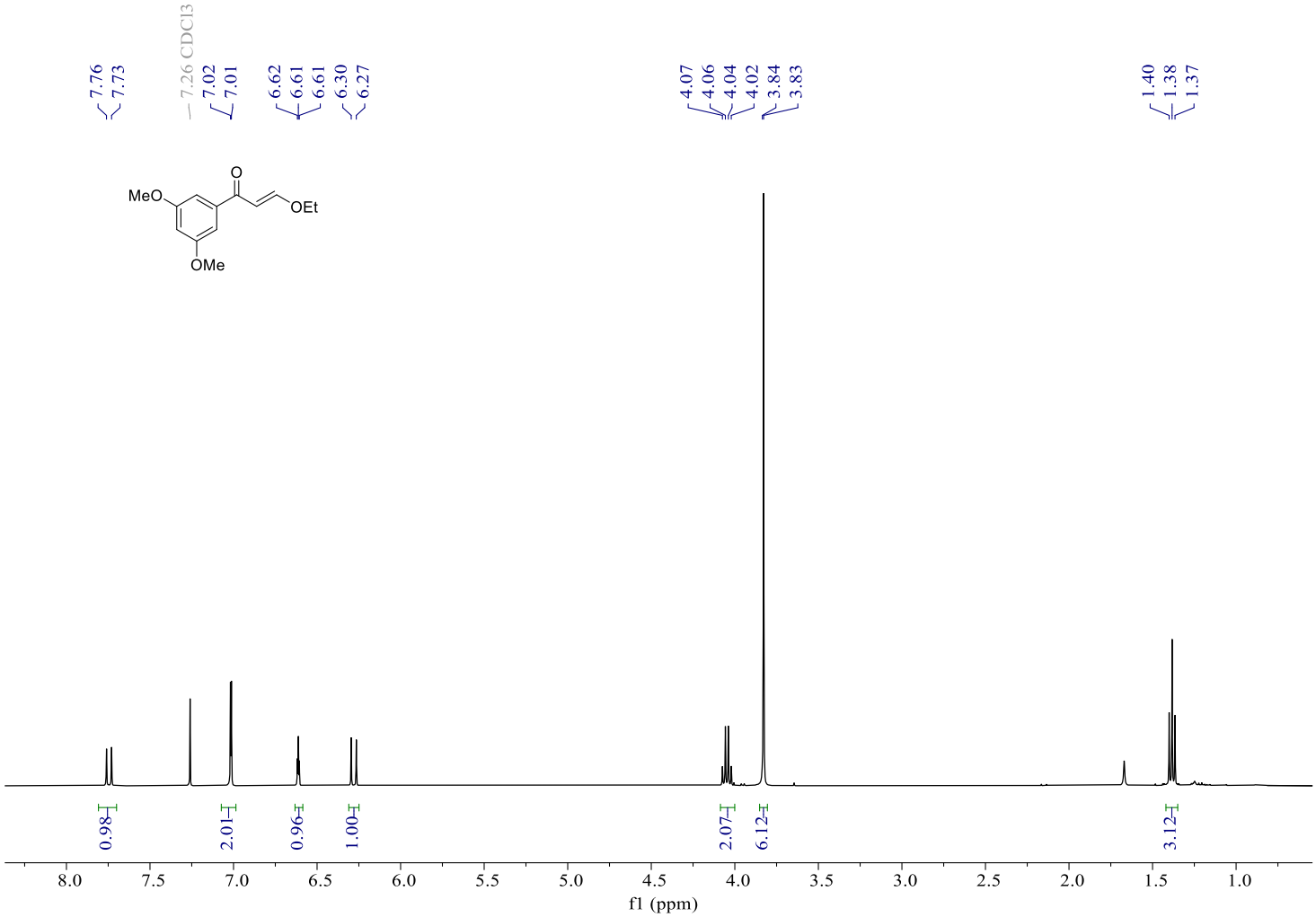
Compound 20 ^{1}H NMR (400 MHz, $CDCl_3$)



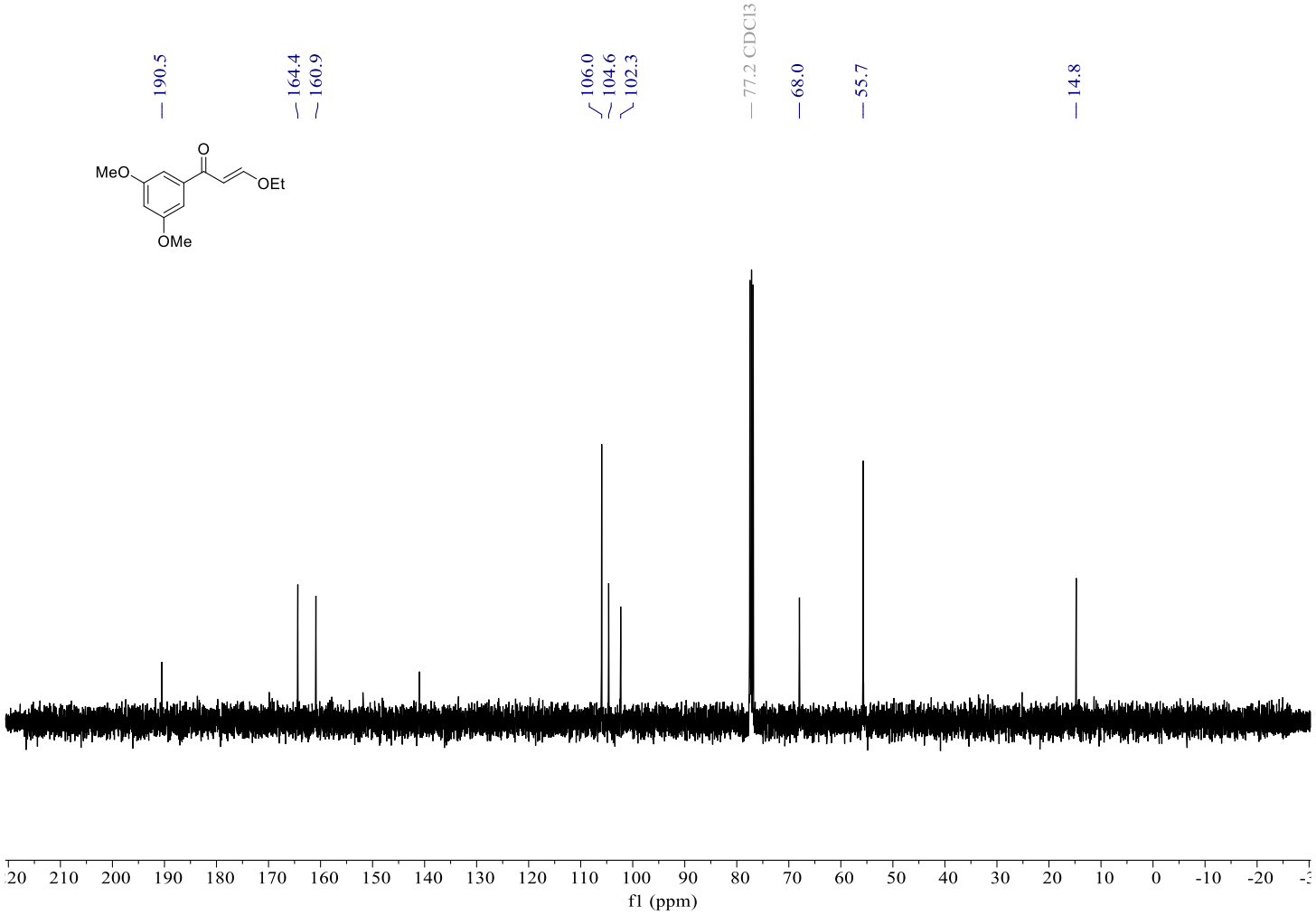
Compound 20 ^{13}C NMR (100 MHz, $CDCl_3$)



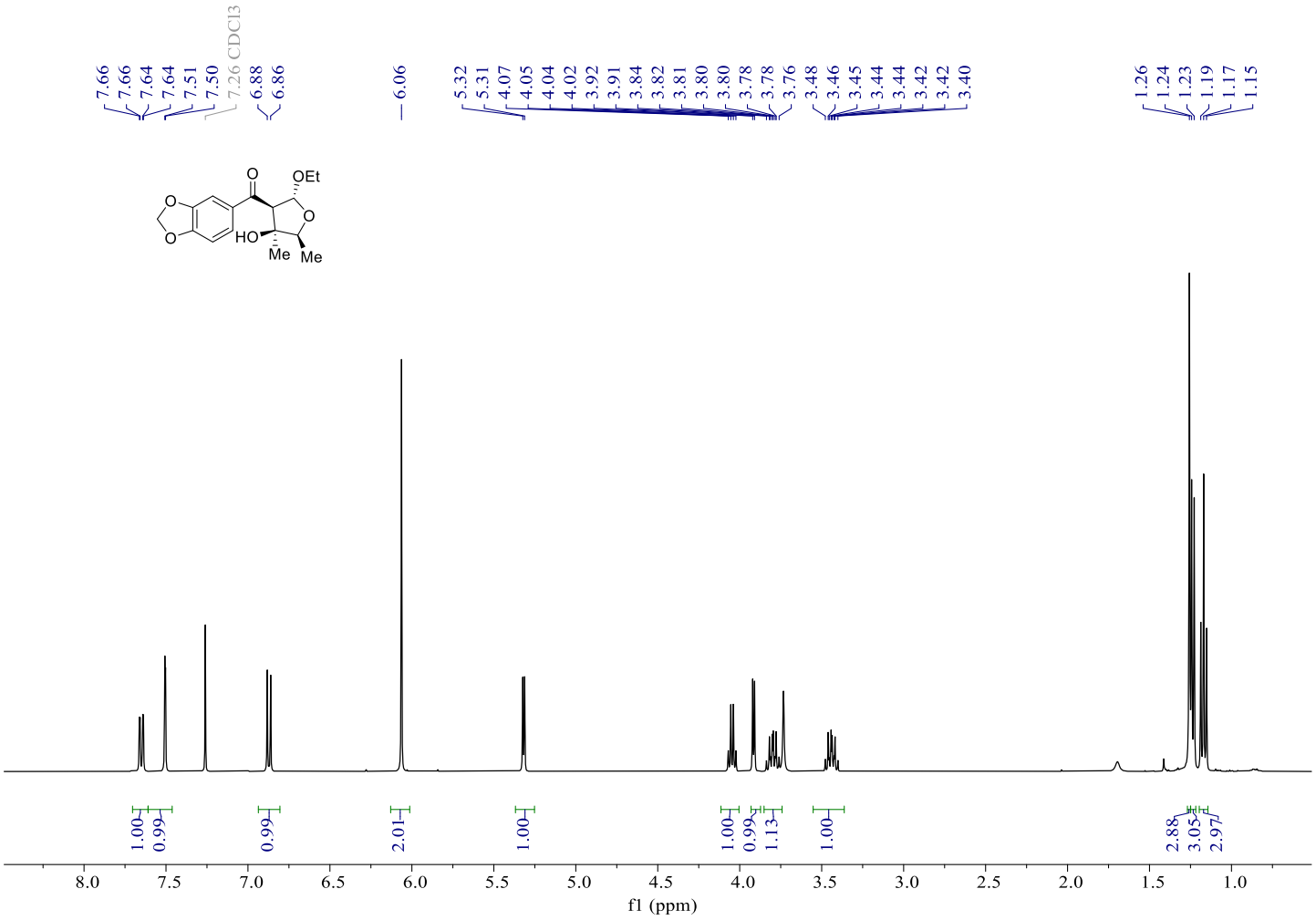
Compound 20b ^{1}H NMR (400 MHz, $CDCl_3$)



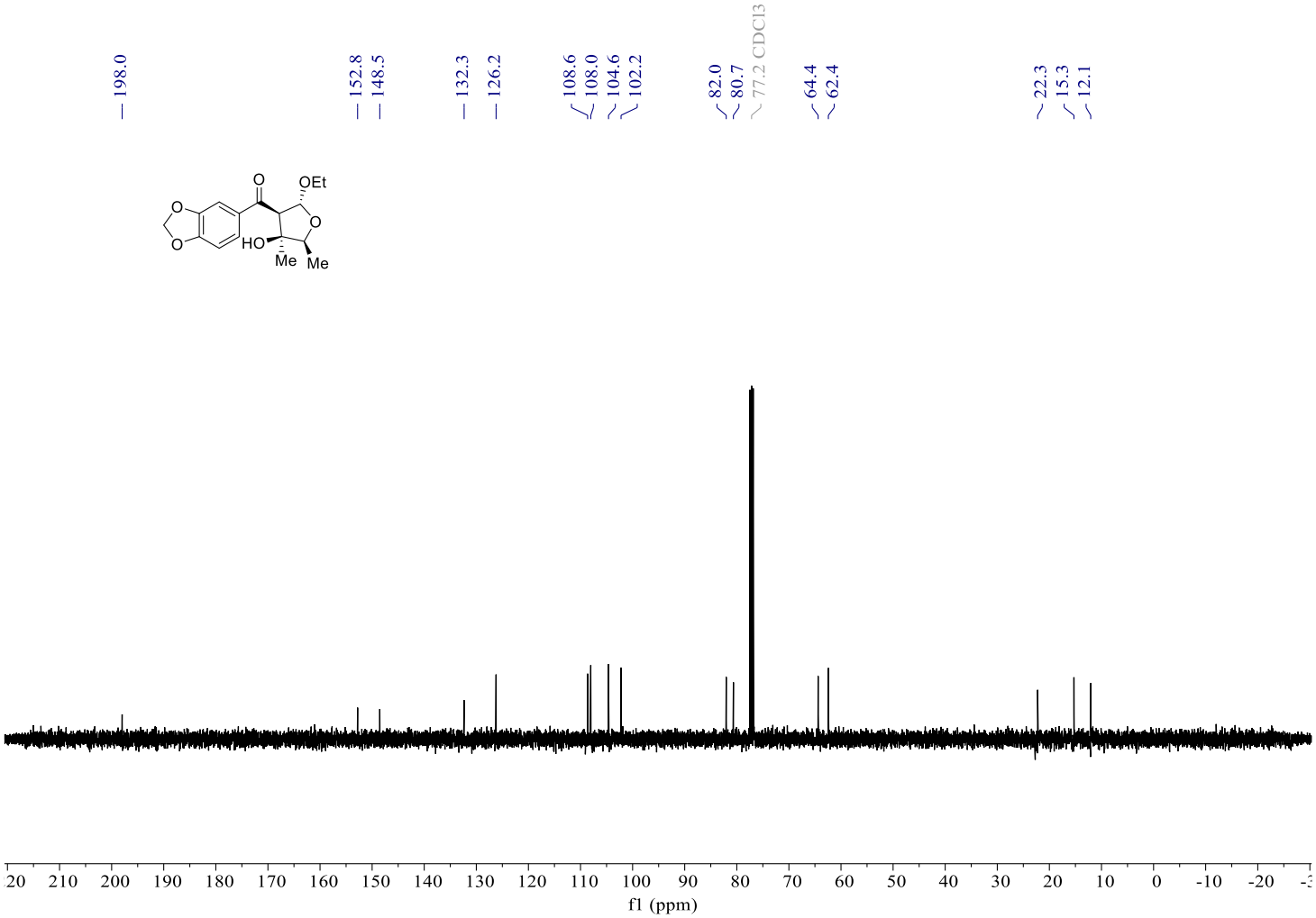
Compound 20b ^{13}C NMR (100 MHz, $CDCl_3$)



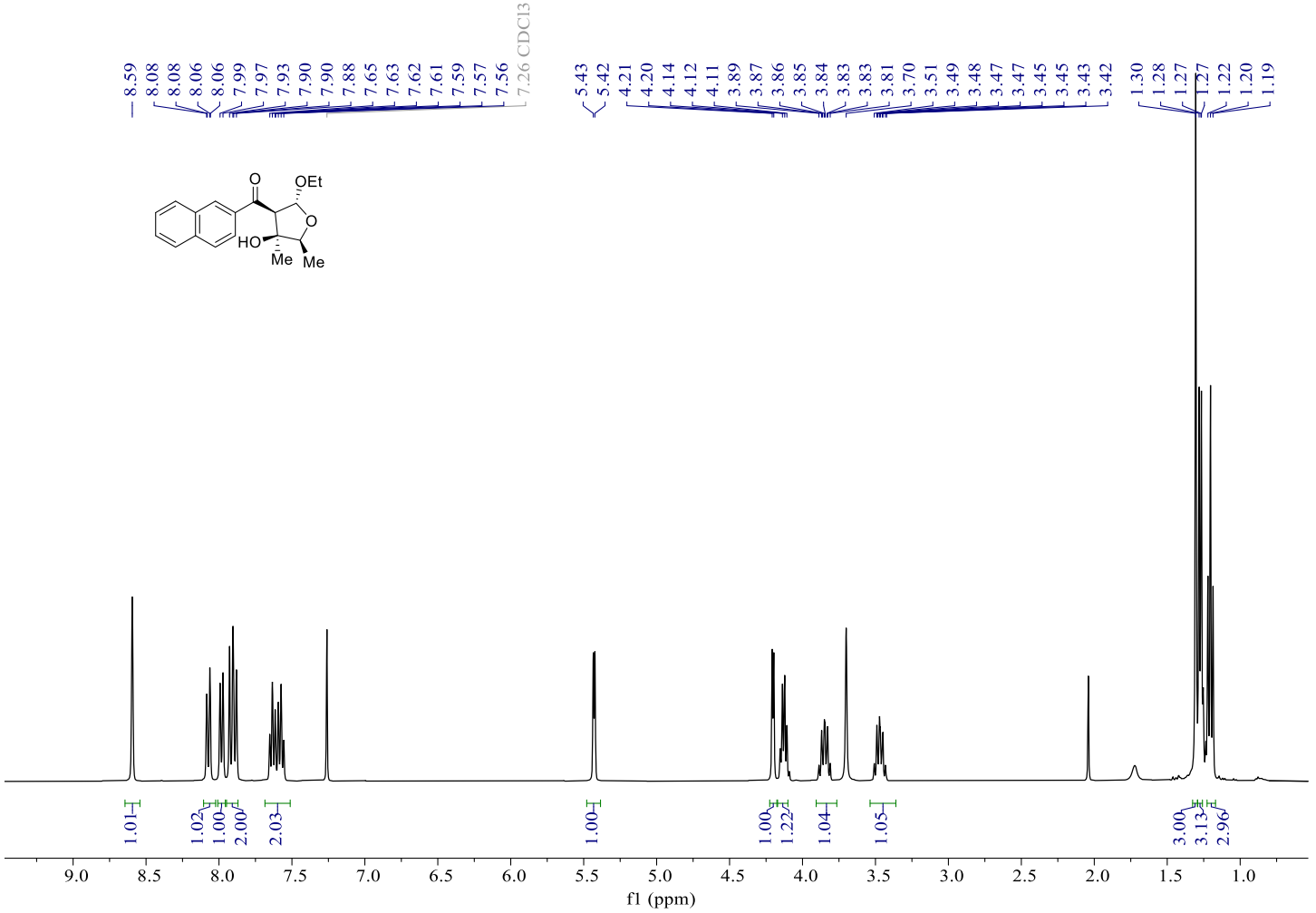
Compound 21 ^{1}H NMR (400 MHz, $CDCl_3$)



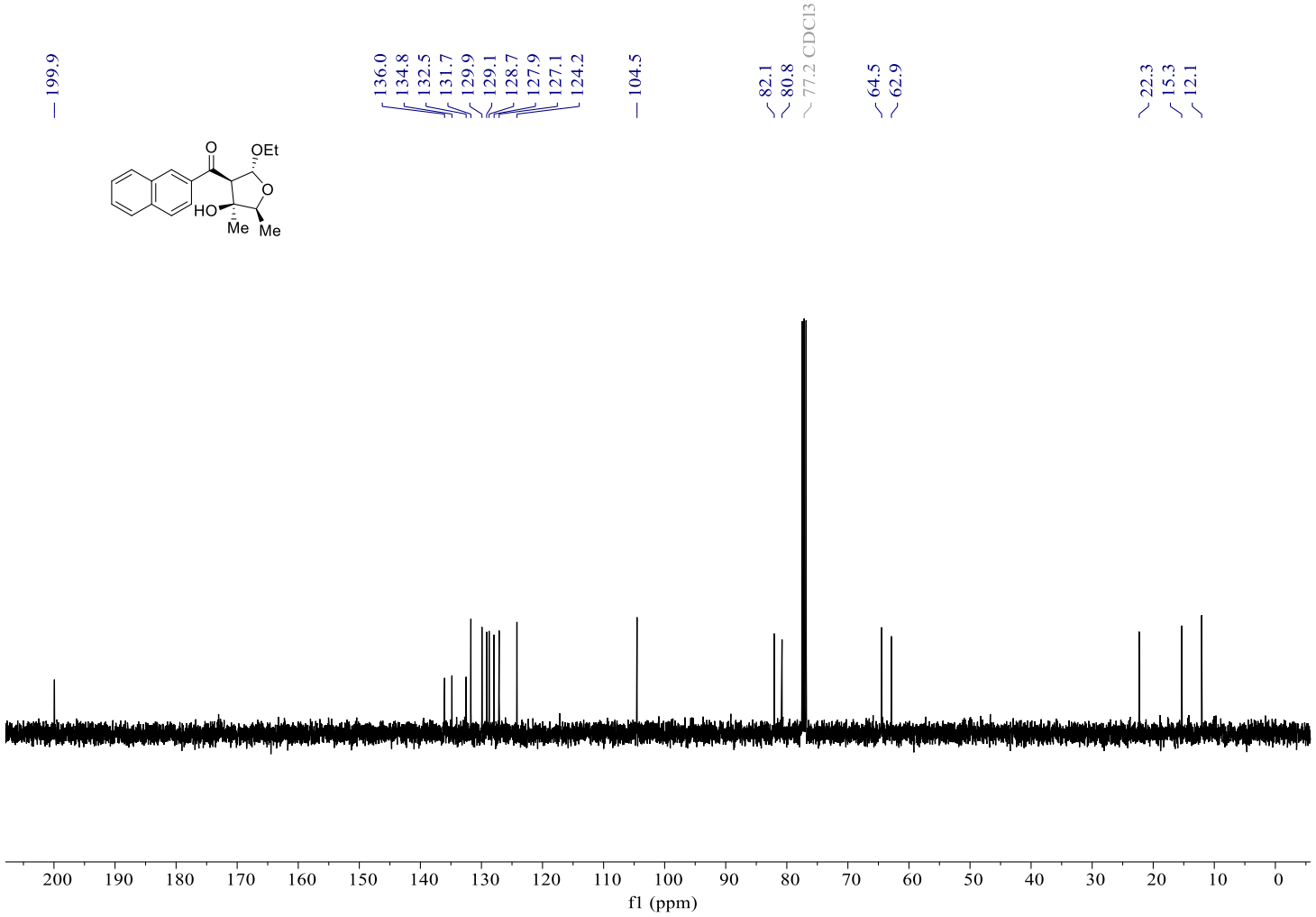
Compound 21 ^{13}C NMR (100 MHz, $CDCl_3$)



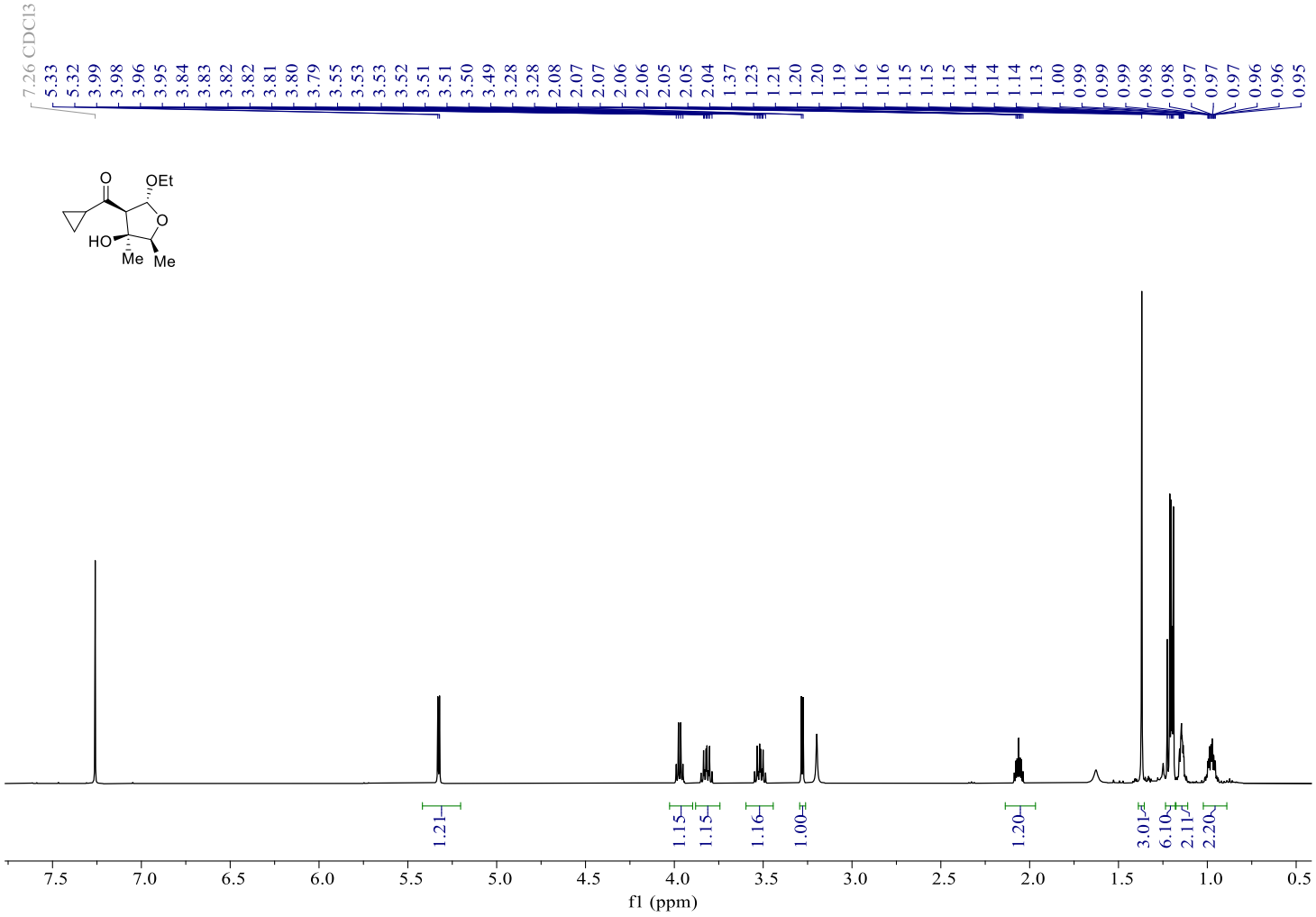
Compound 22 ^{1}H NMR (400 MHz, $CDCl_3$)



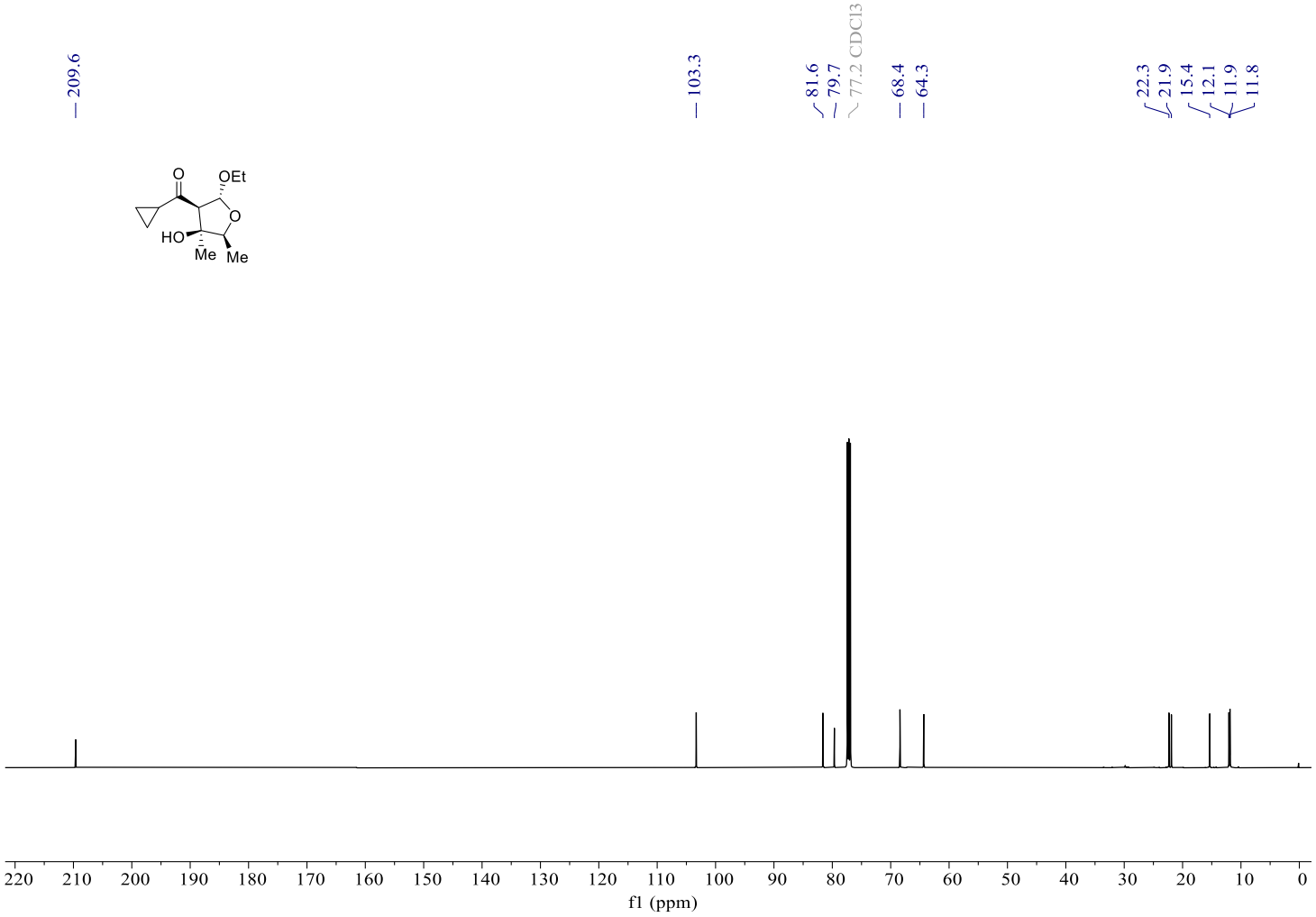
Compound 22 ^{13}C NMR (100 MHz, $CDCl_3$)



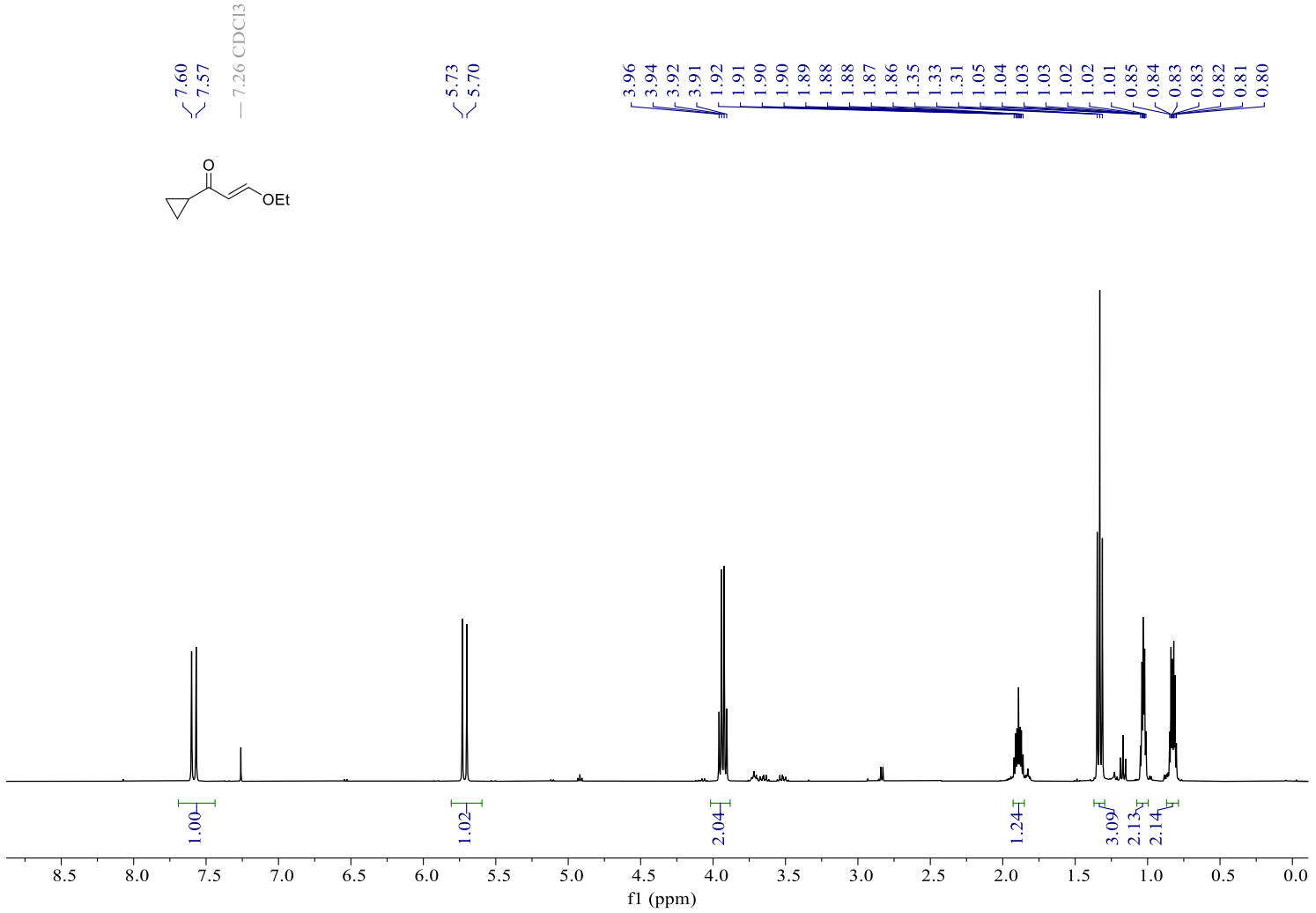
Compound 23 ^{1}H NMR (500 MHz, $CDCl_3$)



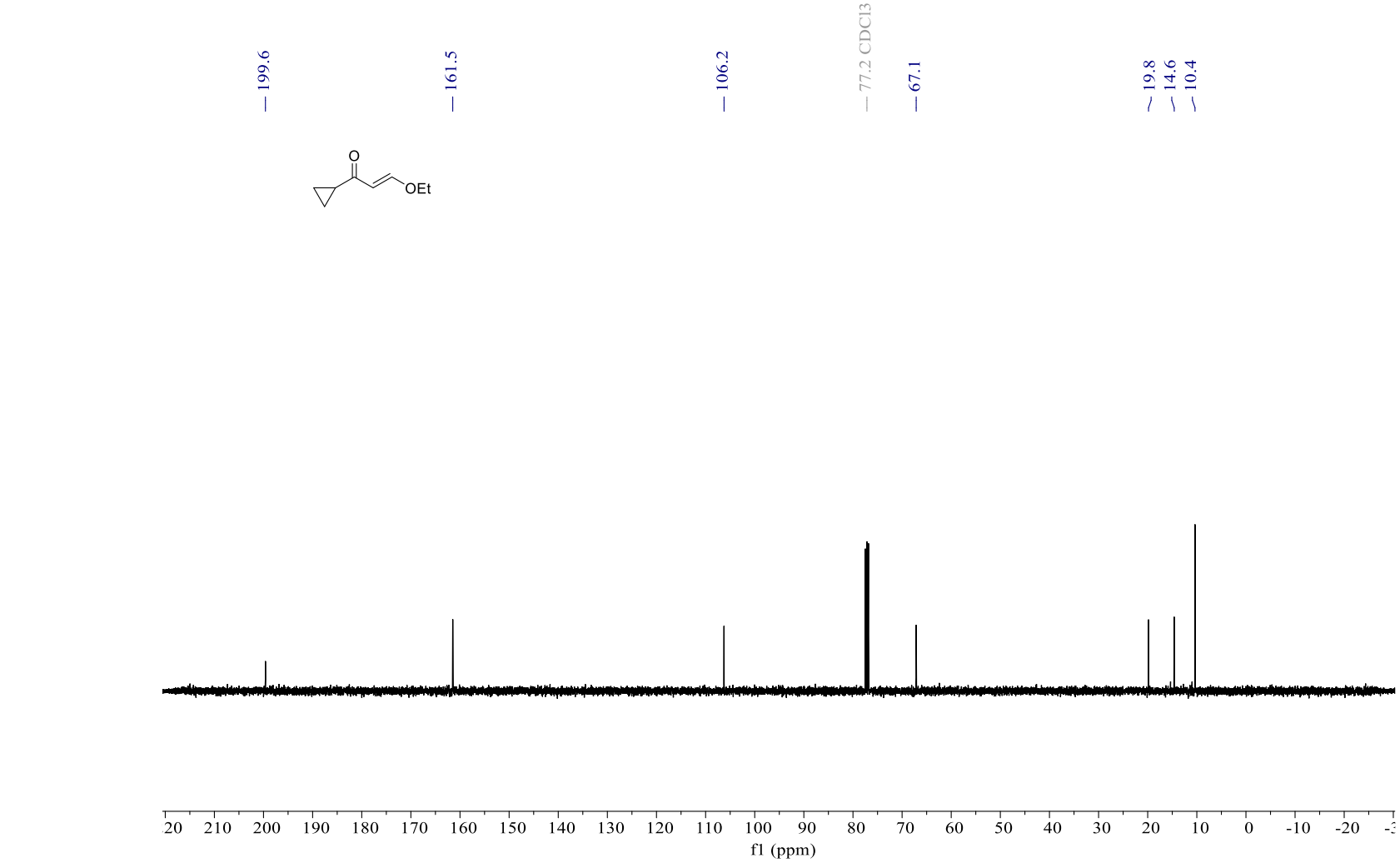
Compound 23 ^{13}C NMR (125 MHz, $CDCl_3$)



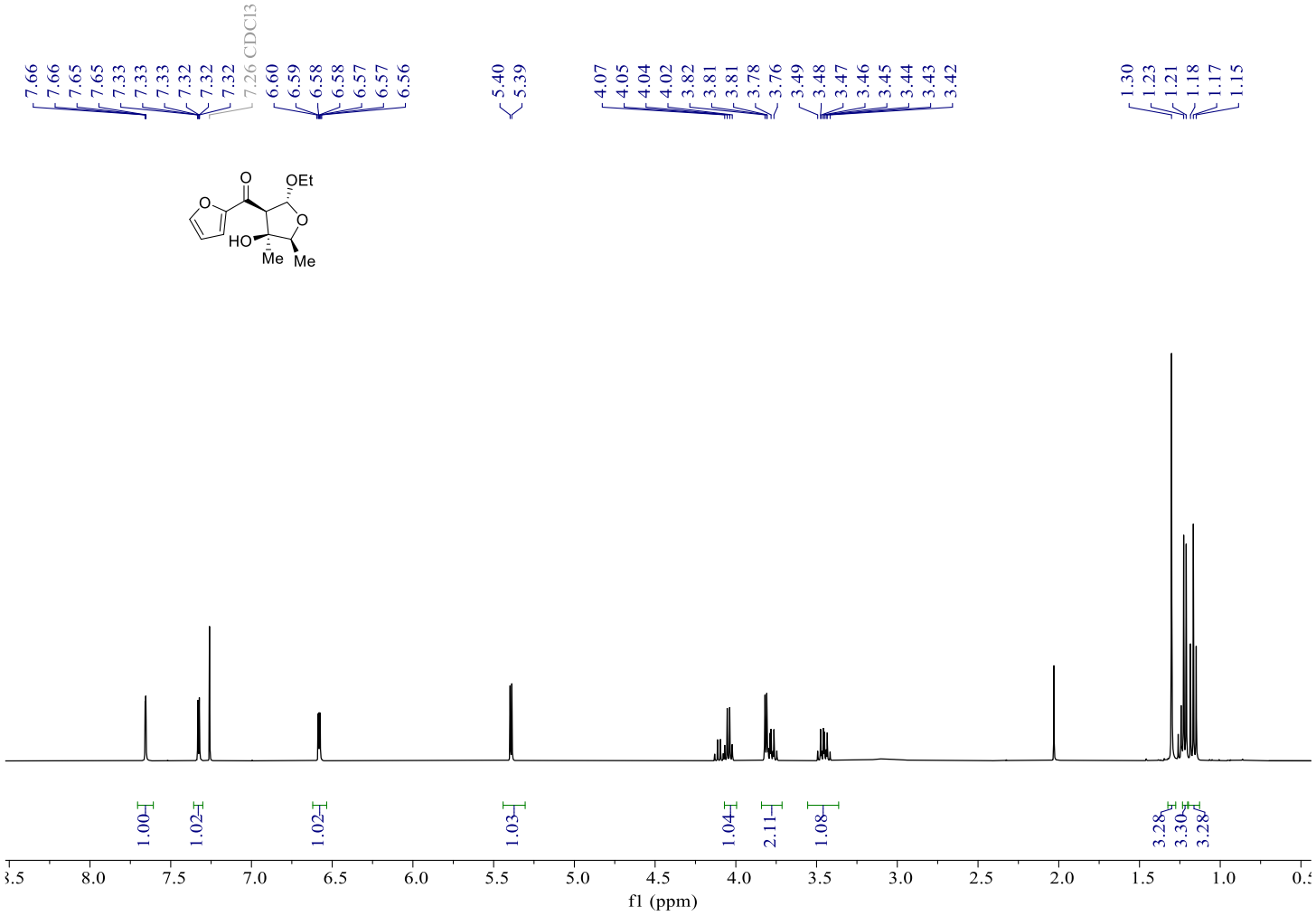
Compound 23b ^{1}H NMR (400 MHz, $CDCl_3$)



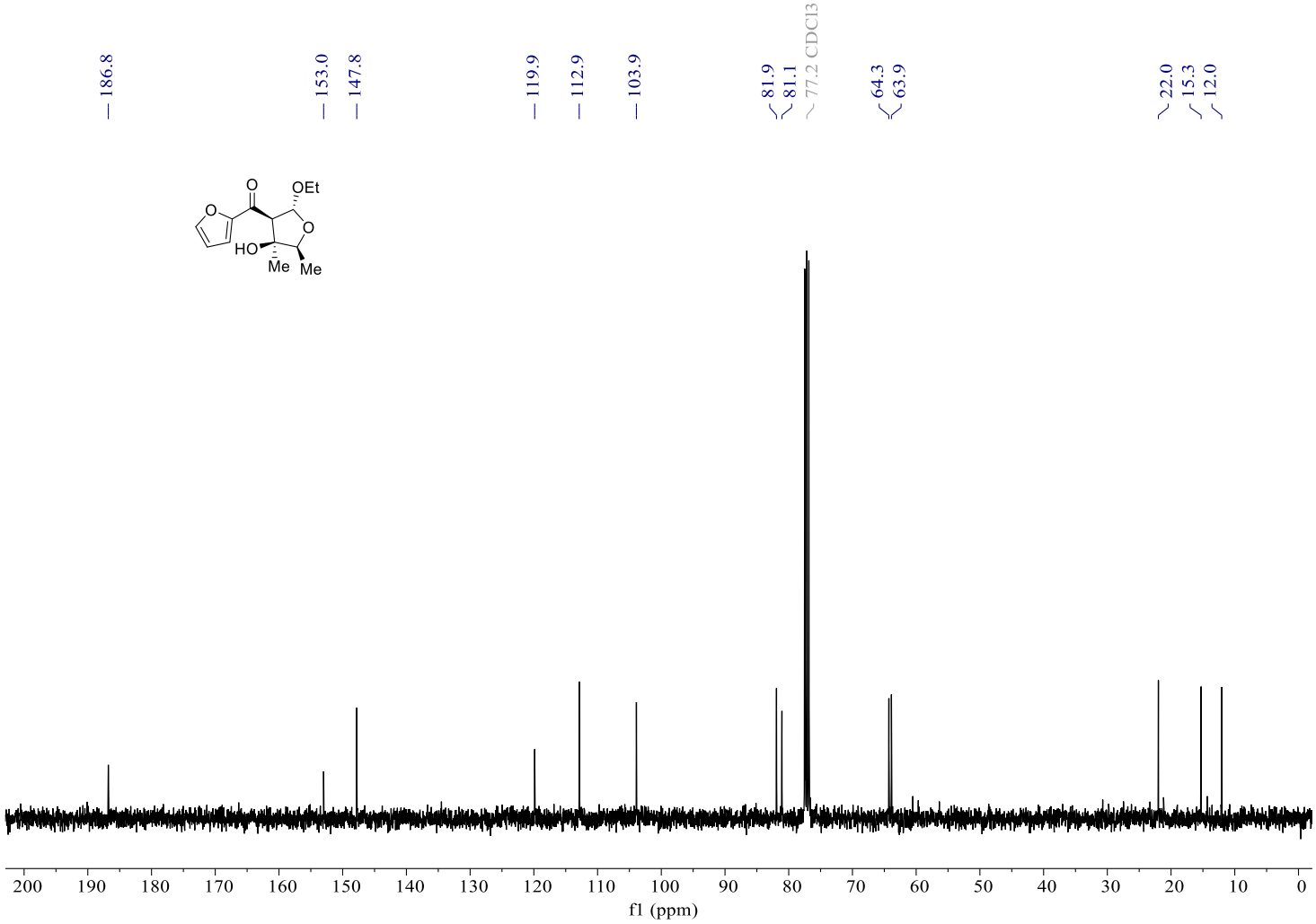
Compound 23b ^{13}C NMR (100 MHz, $CDCl_3$)



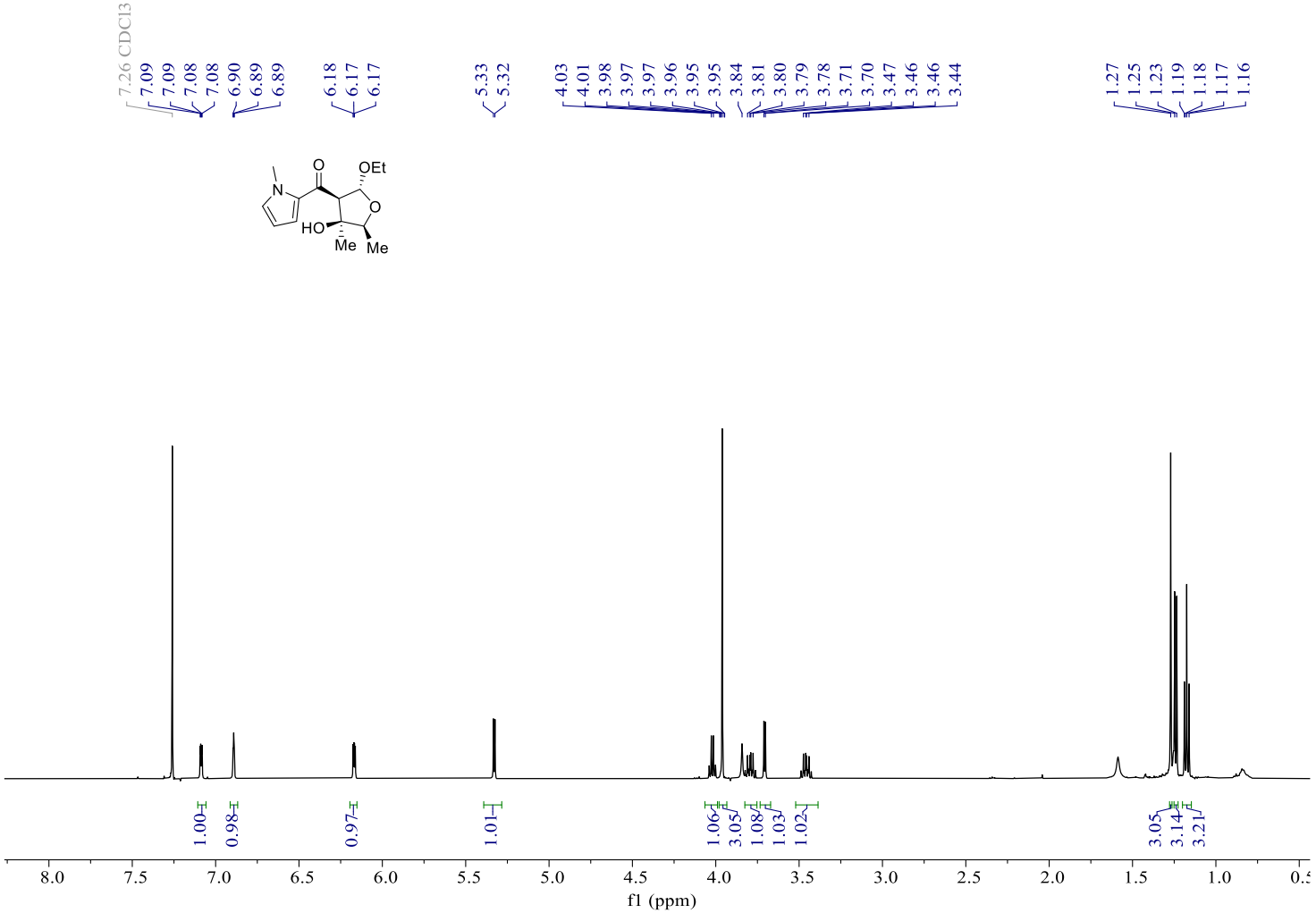
Compound 24 ^{1}H NMR (400 MHz, $CDCl_3$)



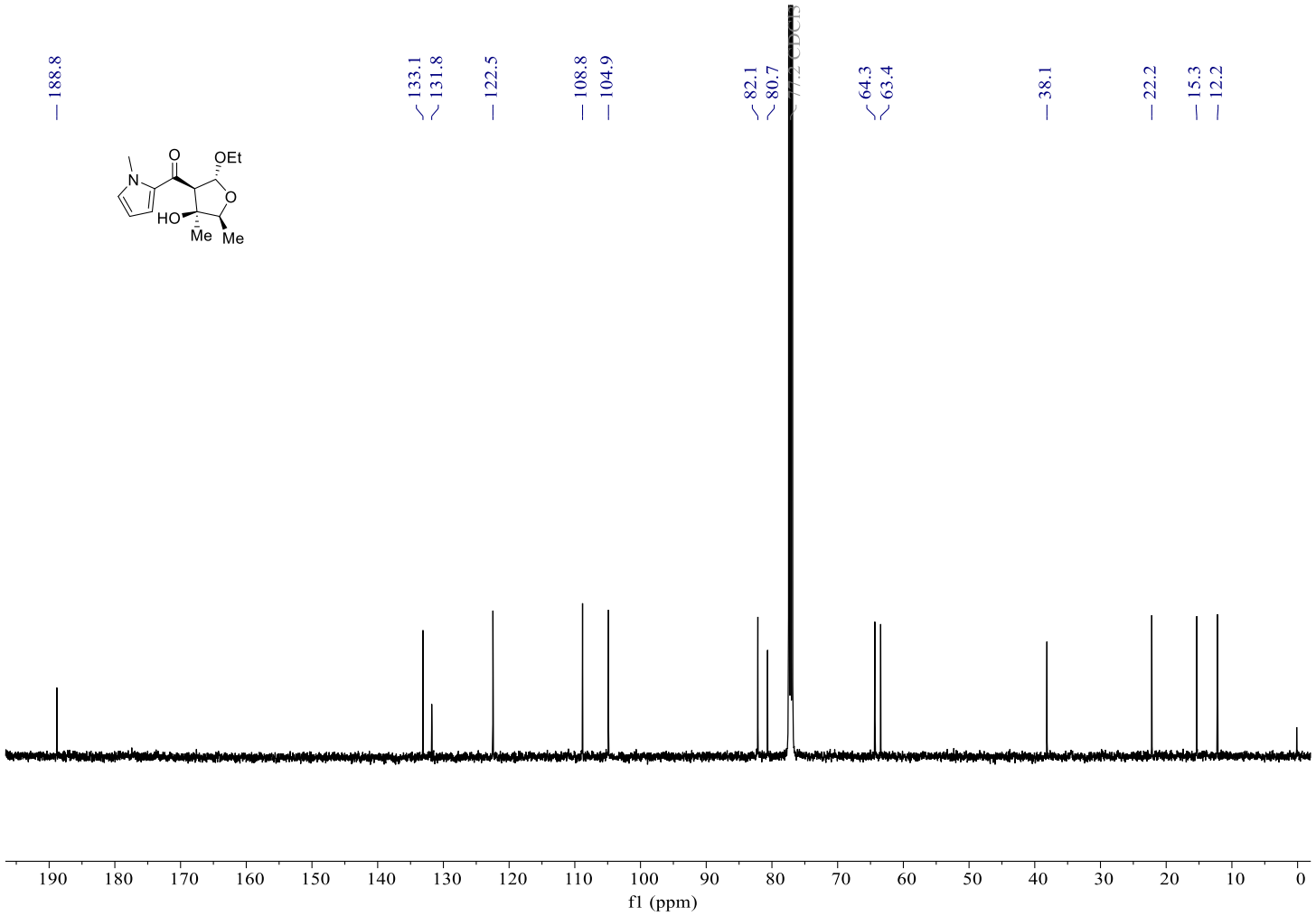
Compound 24 ^{13}C NMR (100 MHz, $CDCl_3$)



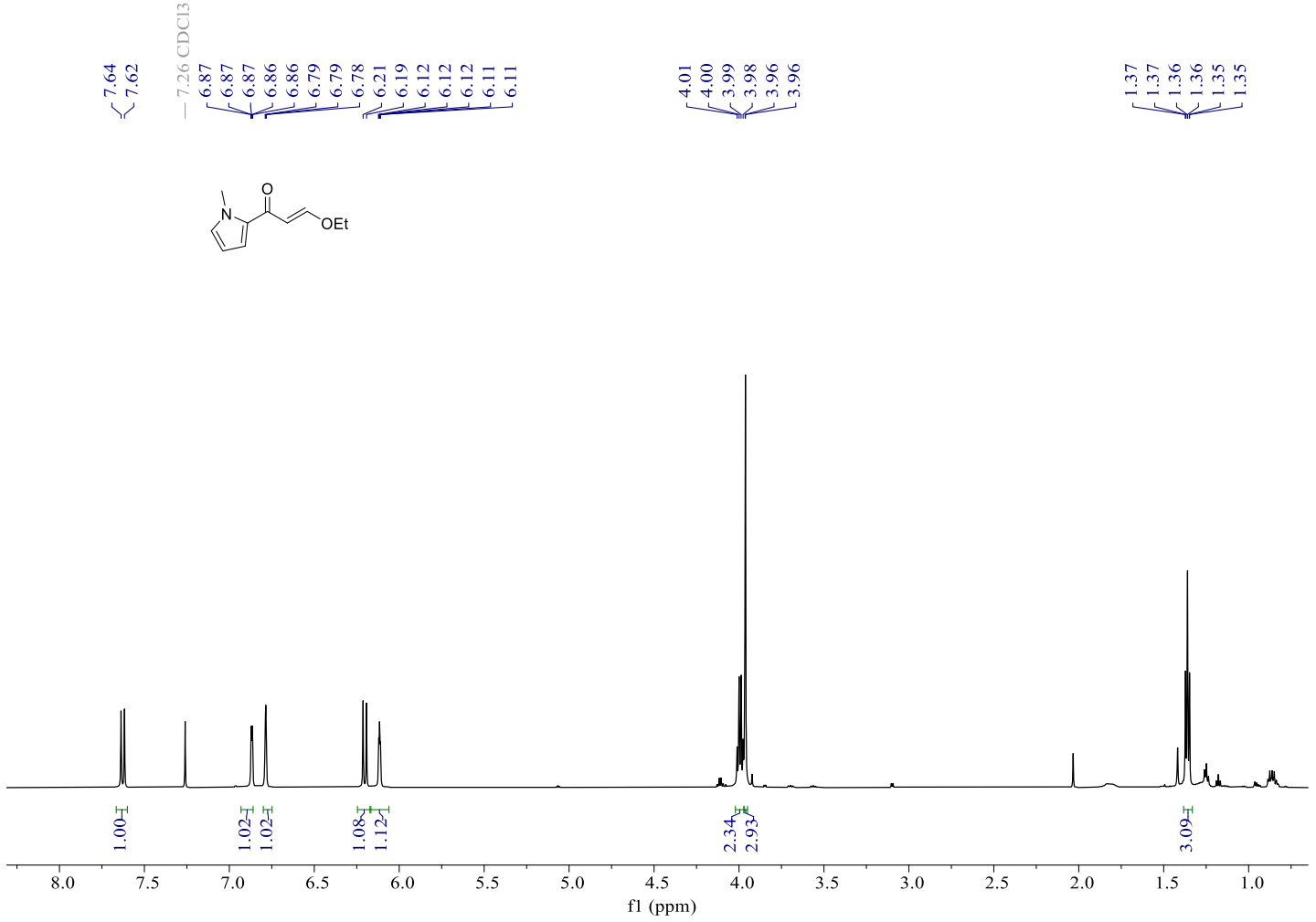
Compound 25 ^{1}H NMR (400 MHz, $CDCl_3$)



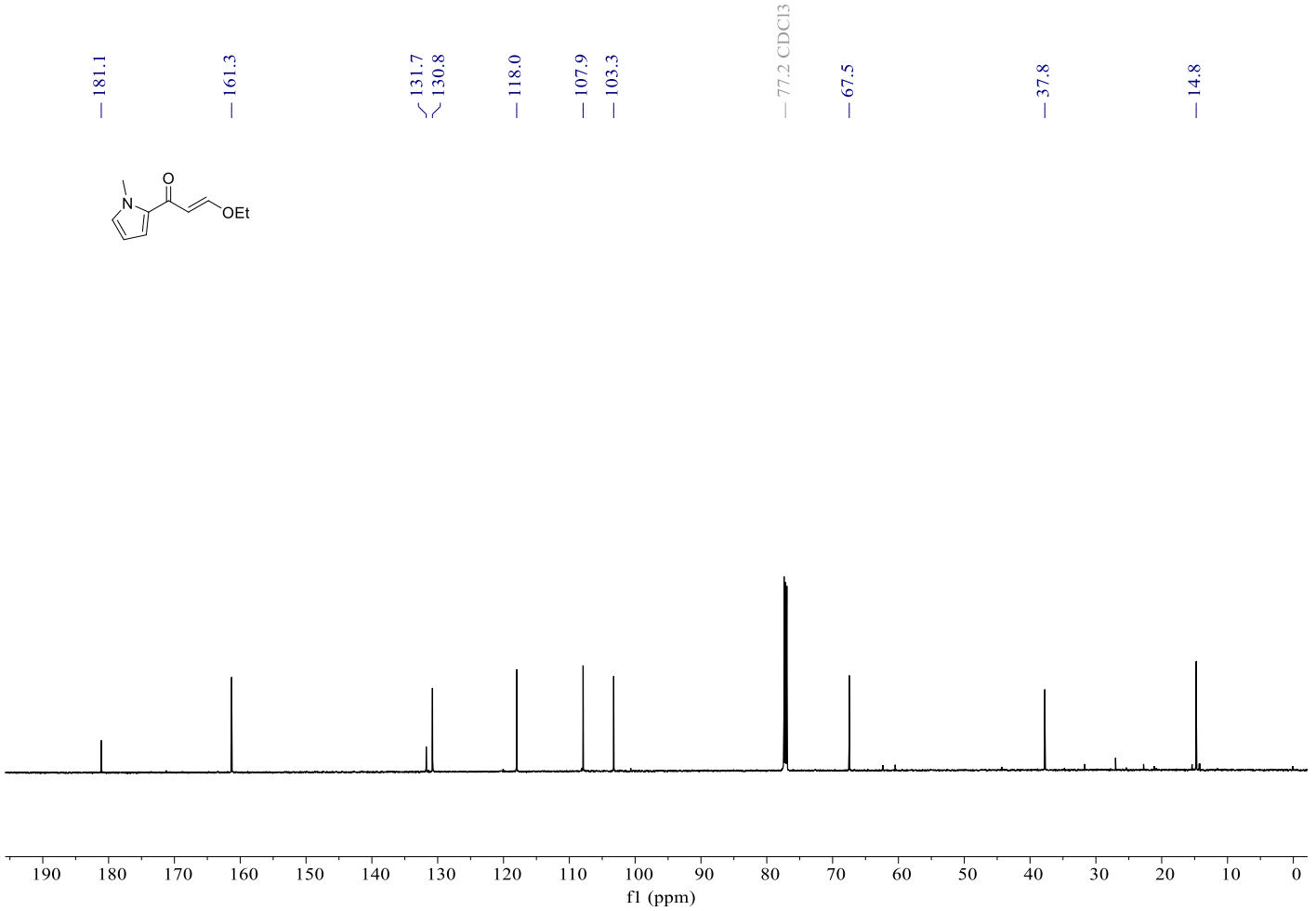
Compound 25 ^{13}C NMR (100 MHz, $CDCl_3$)



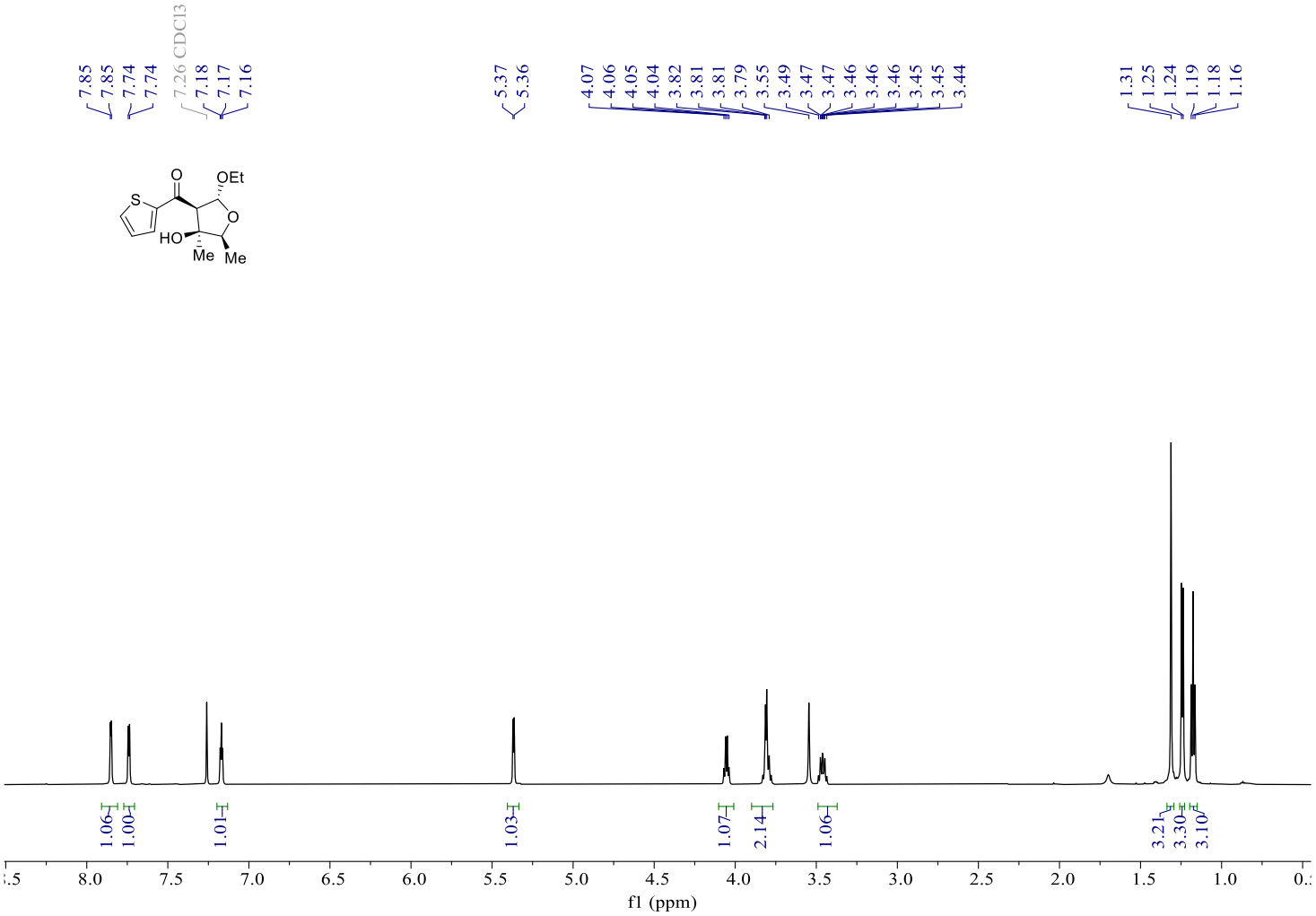
Compound 25b ^{1}H NMR (600 MHz, $CDCl_3$)



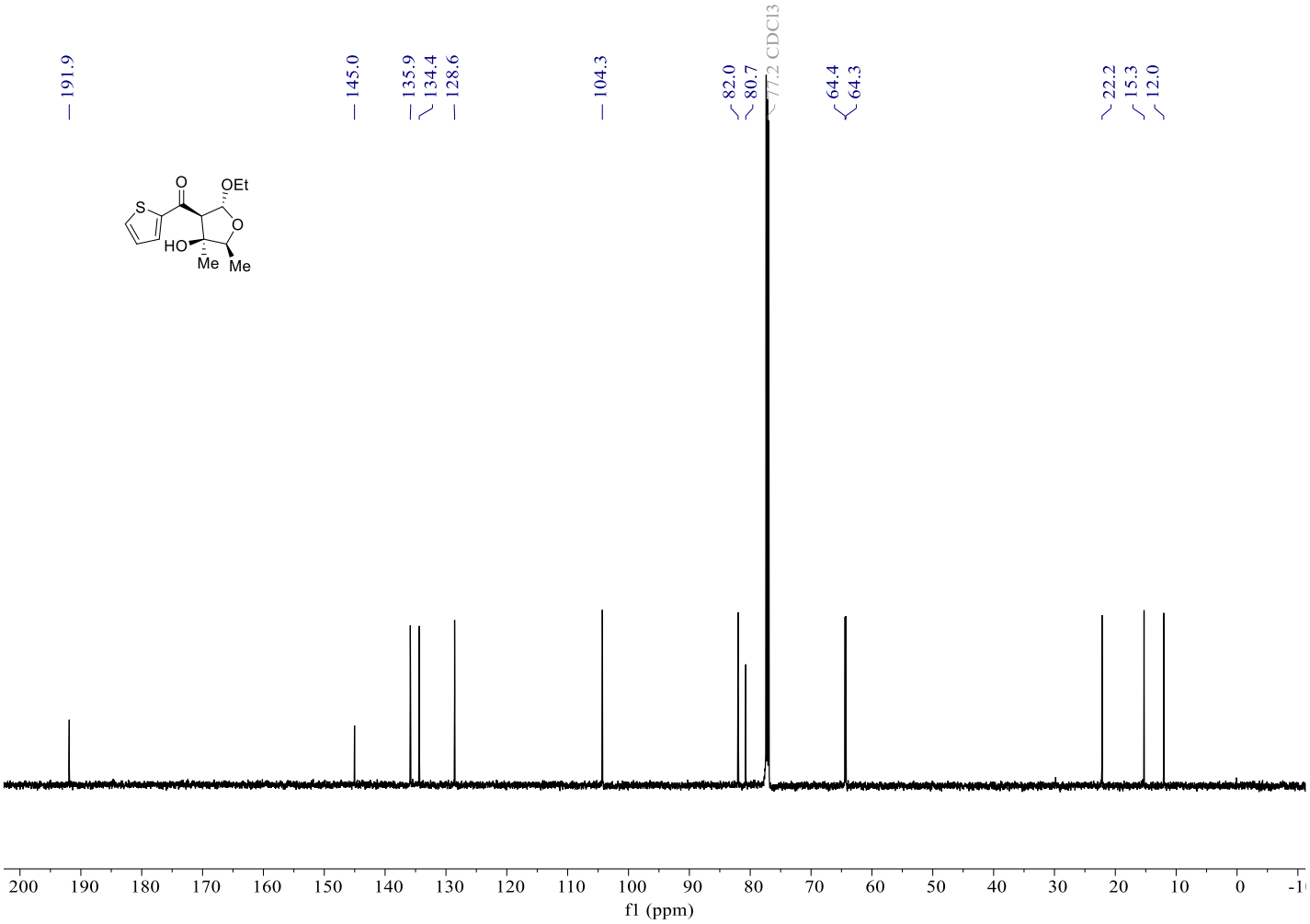
Compound 25b ^{13}C NMR (150 MHz, $CDCl_3$)



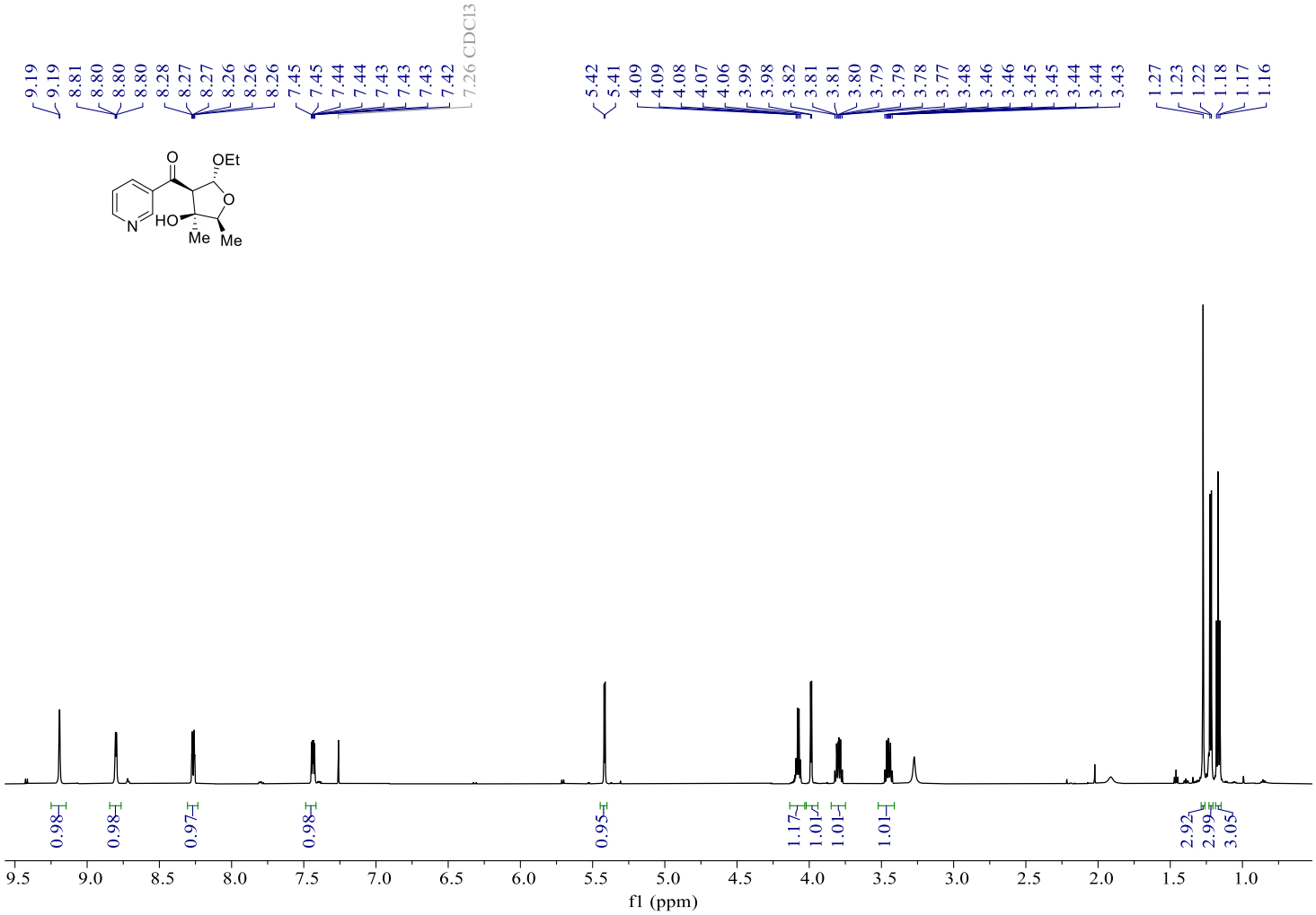
Compound 26 ^{1}H NMR (600 MHz, $CDCl_3$)



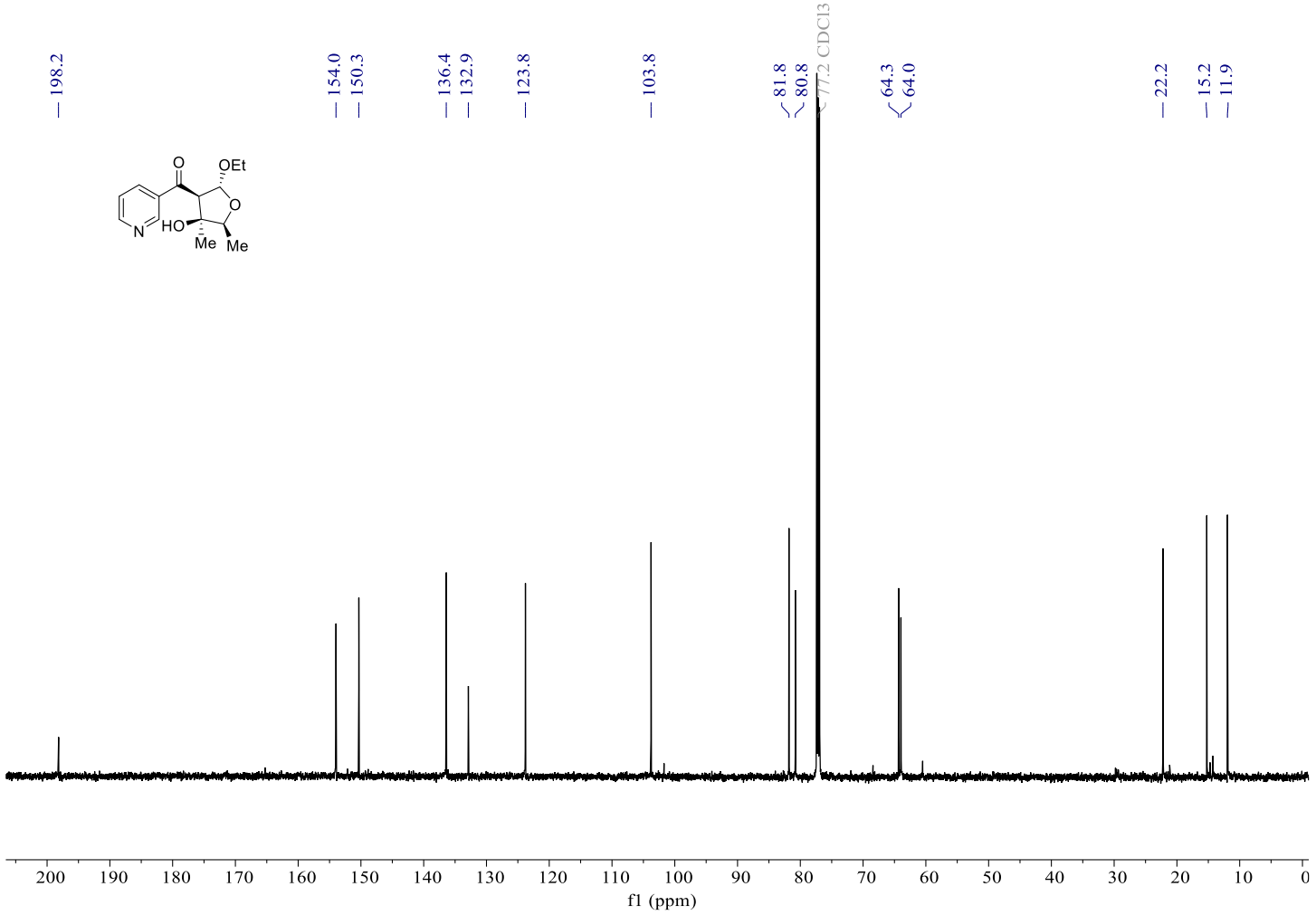
Compound 26 ^{13}C NMR (150 MHz, $CDCl_3$)



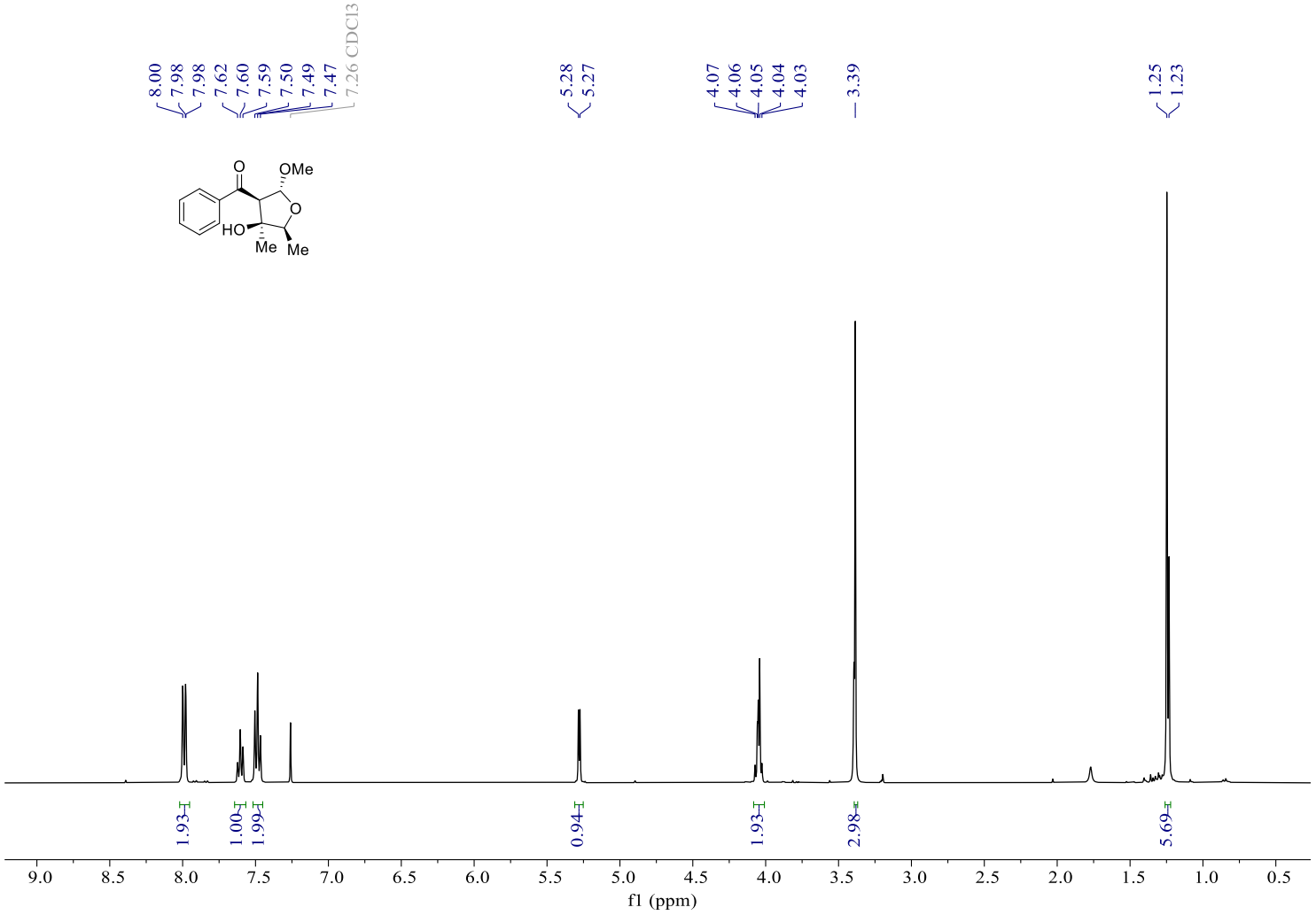
Compound 27 ^{1}H NMR (400 MHz, $CDCl_3$)



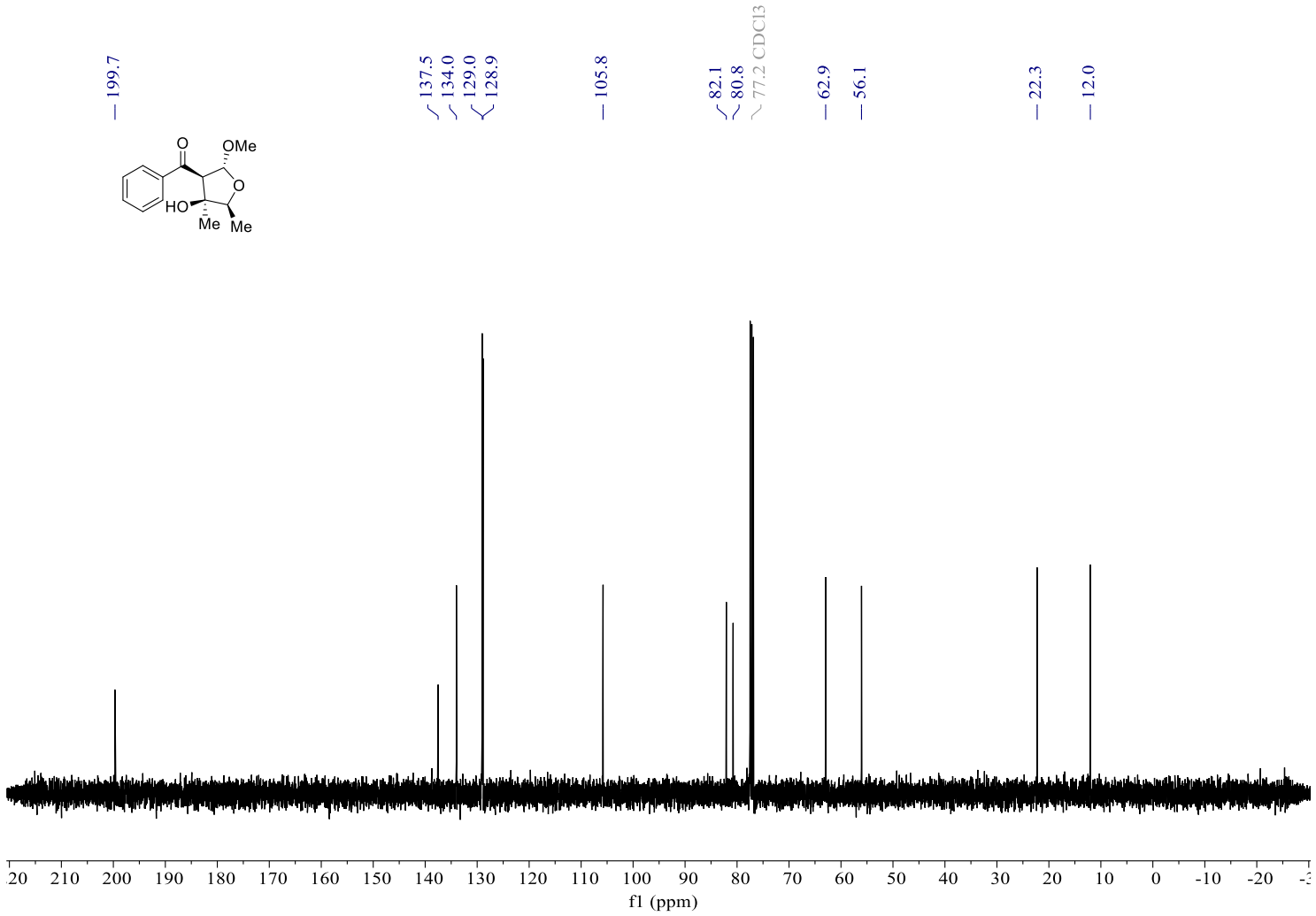
Compound 27 ^{13}C NMR (150 MHz, $CDCl_3$)



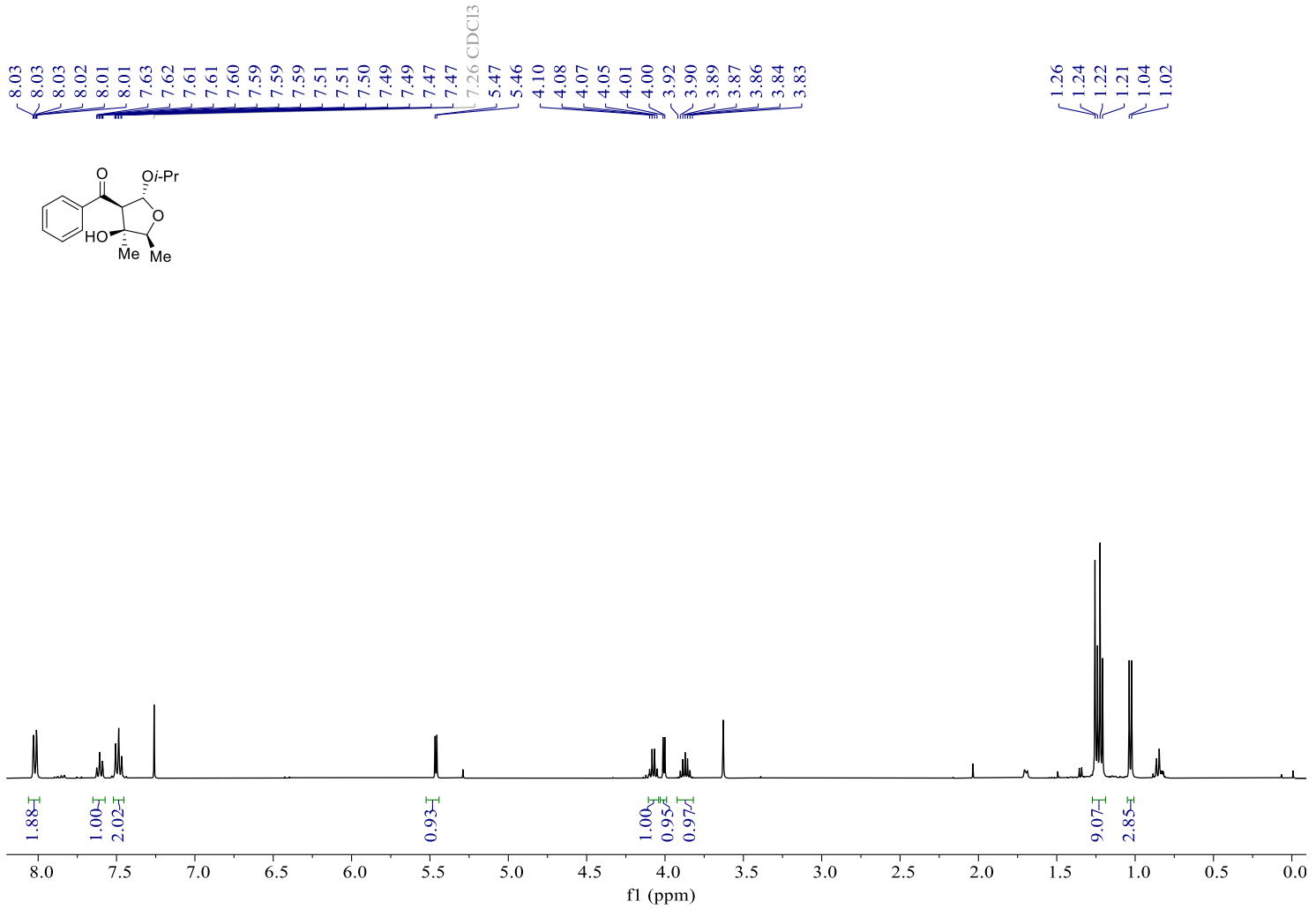
Compound 28 ^{1}H NMR (400 MHz, $CDCl_3$)



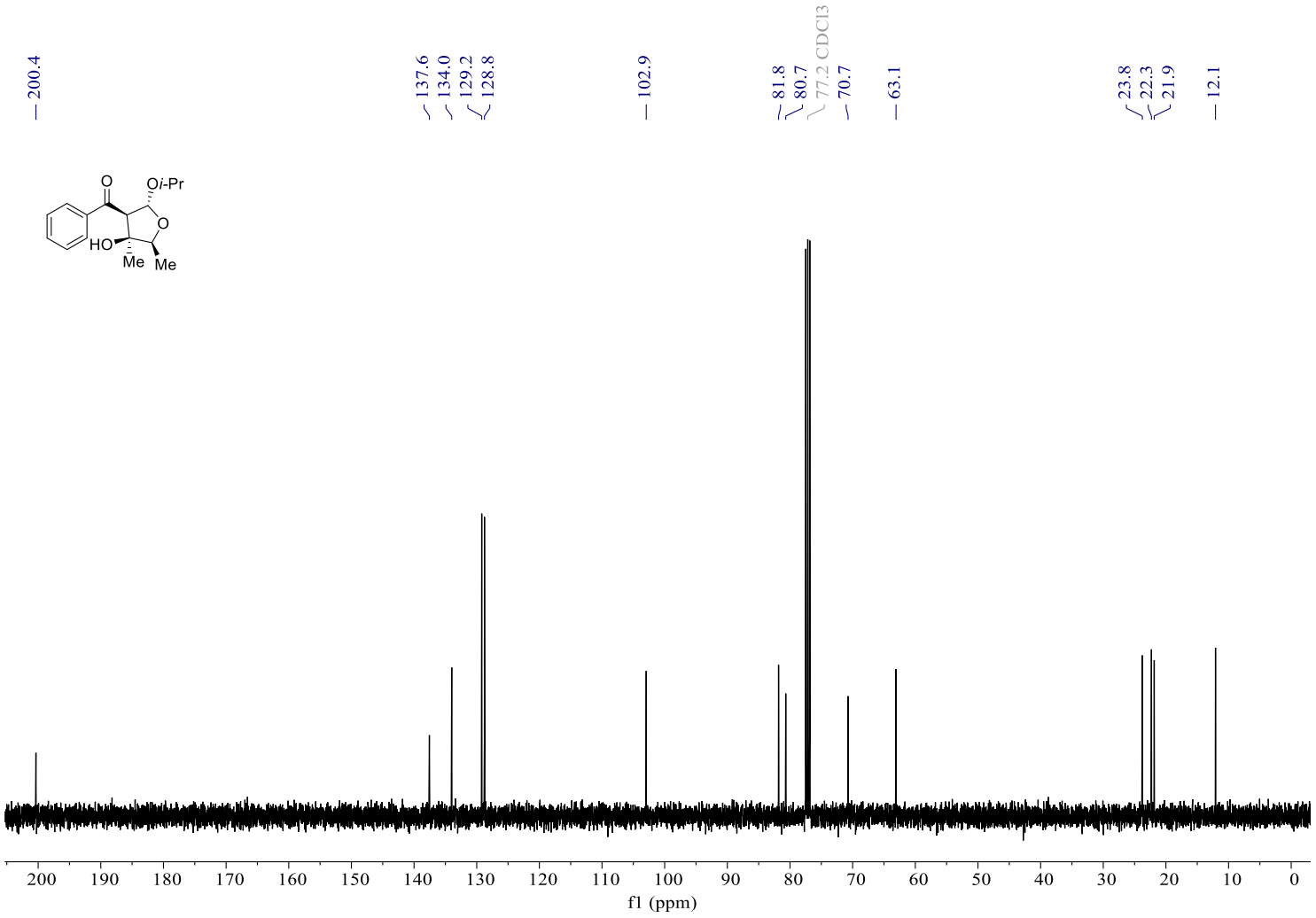
Compound 28 ^{13}C NMR (100 MHz, $CDCl_3$)



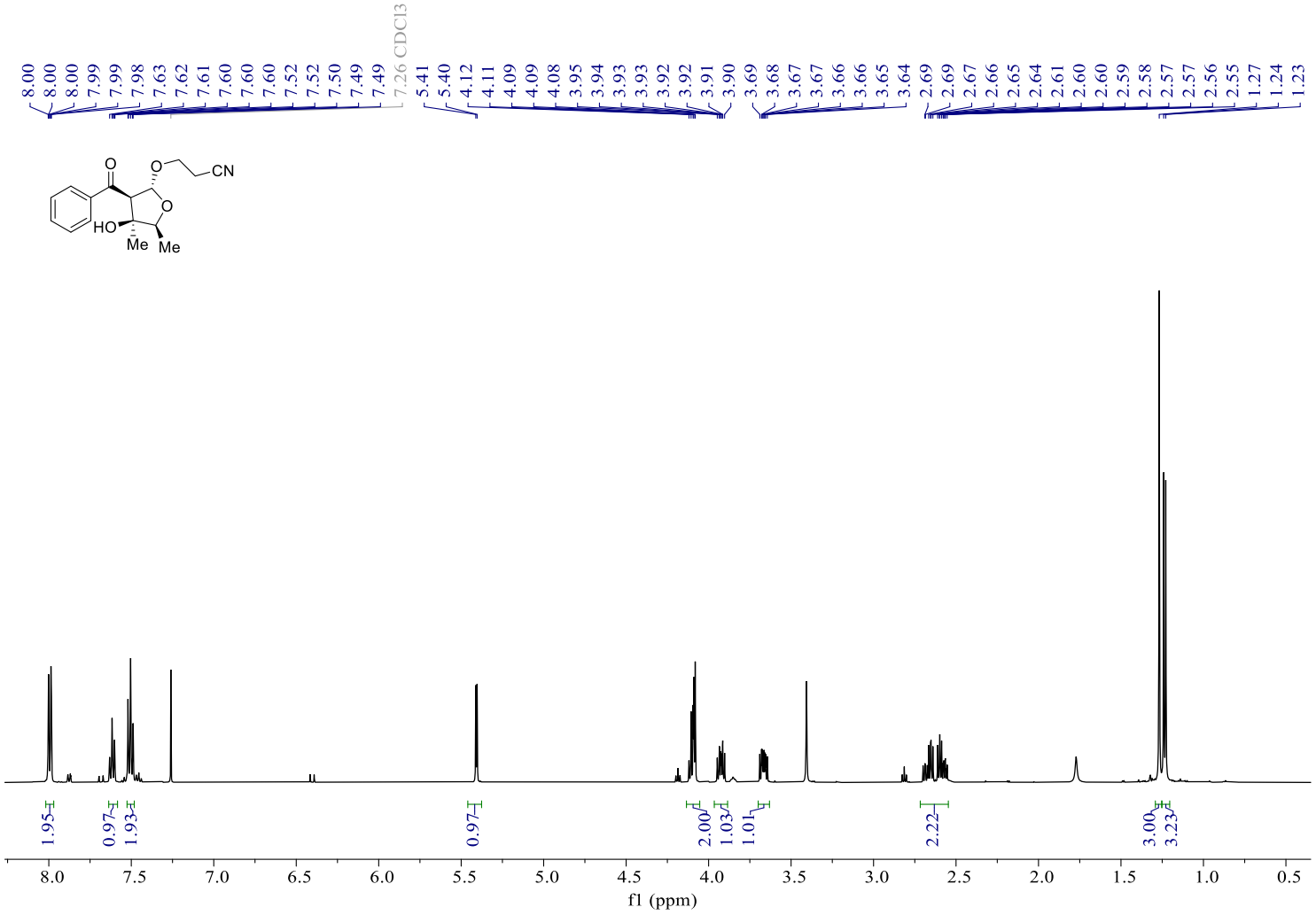
Compound 29 ^{1}H NMR (400 MHz, $CDCl_3$)



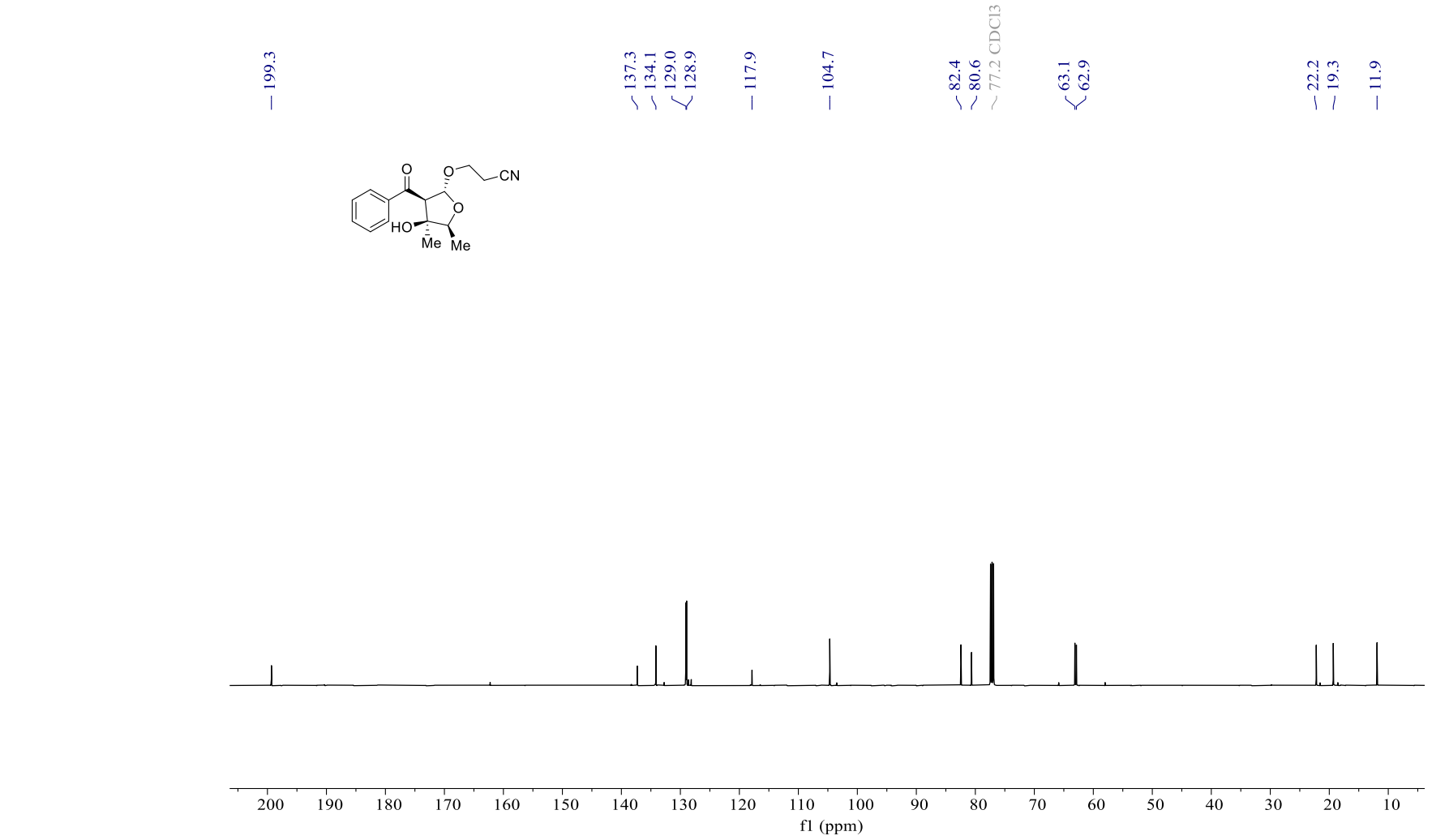
Compound 29 ^{13}C NMR (100 MHz, $CDCl_3$)



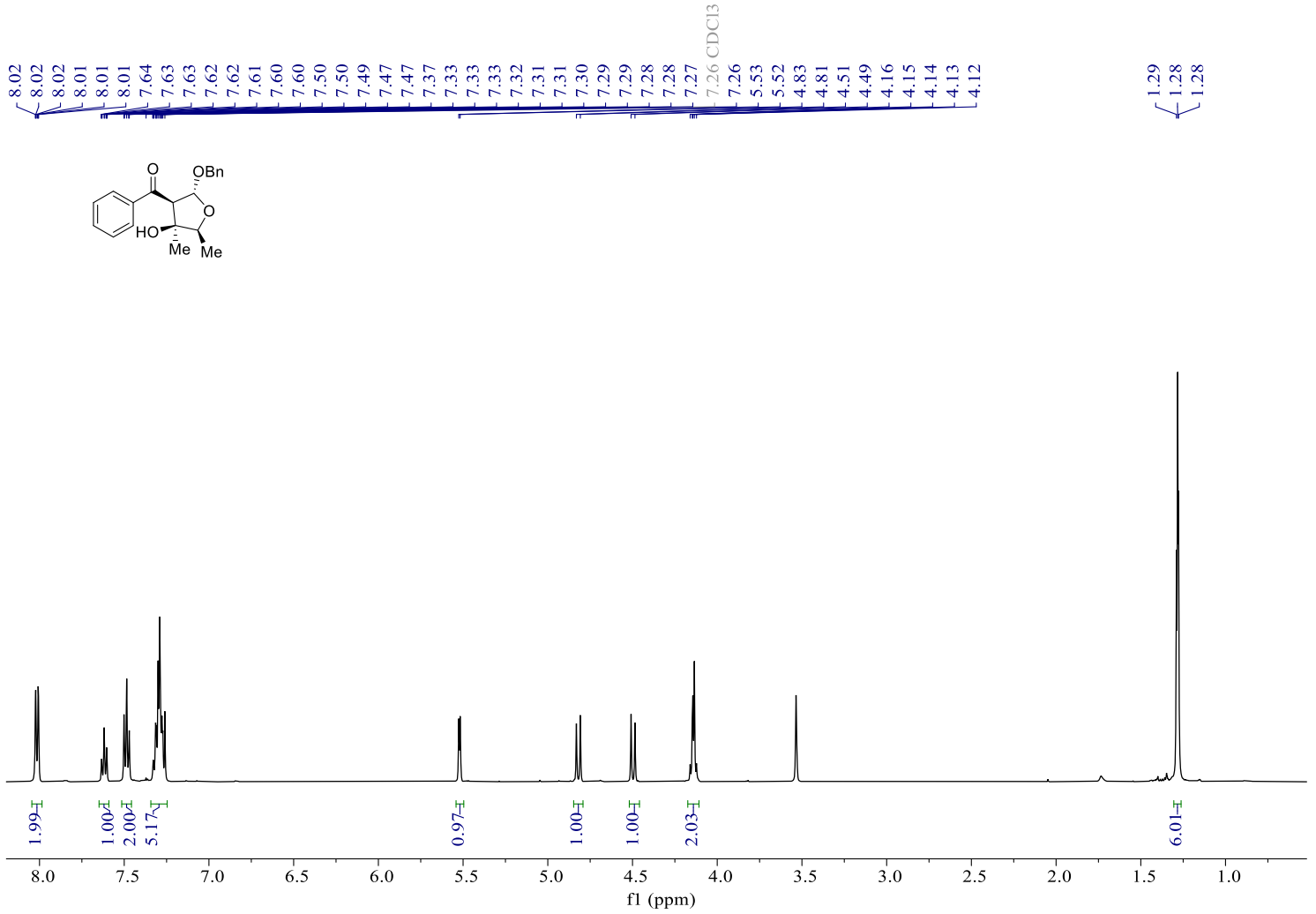
Compound 30 ^{1}H NMR (500 MHz, $CDCl_3$)



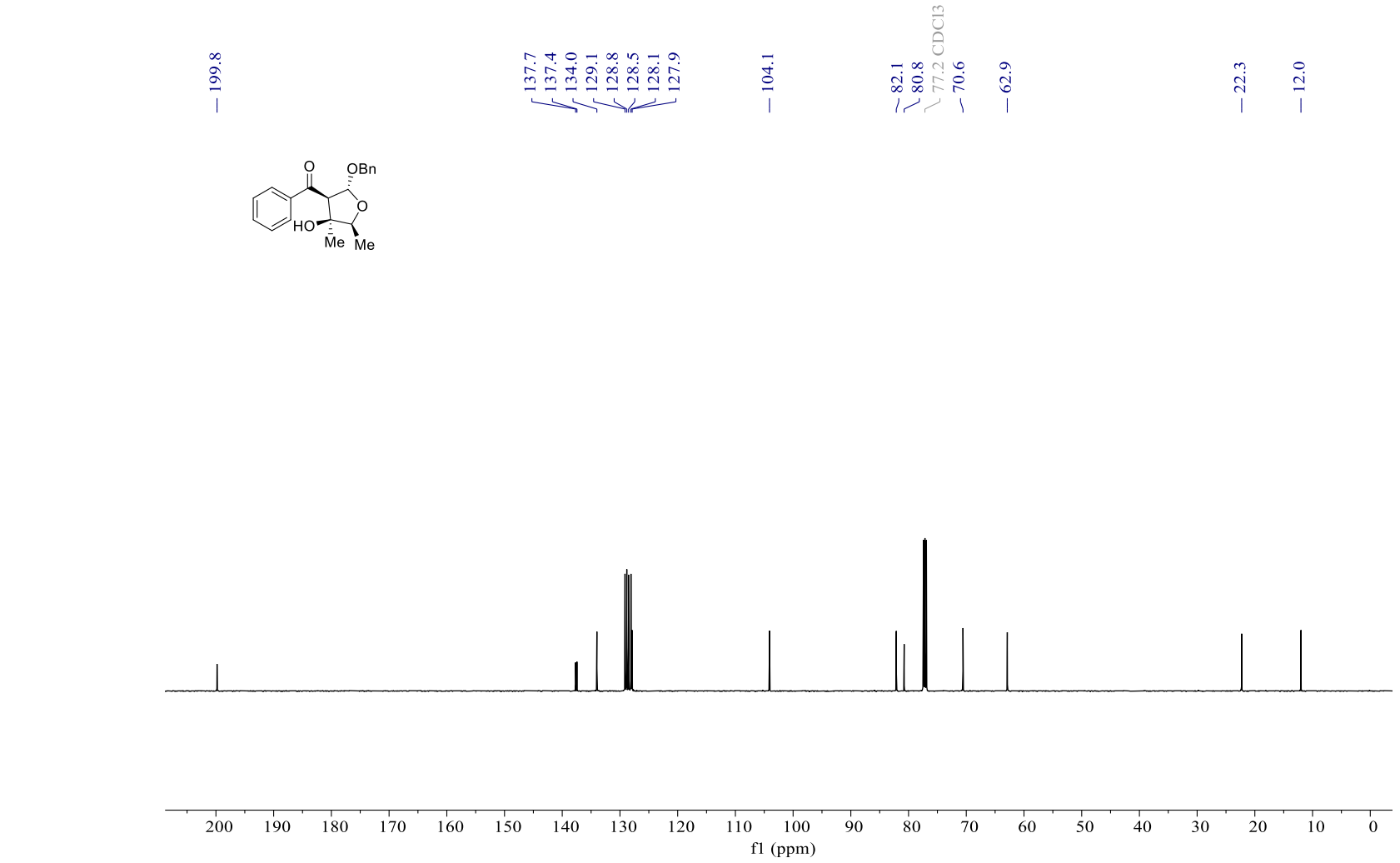
Compound 30 ^{13}C NMR (125 MHz, $CDCl_3$)



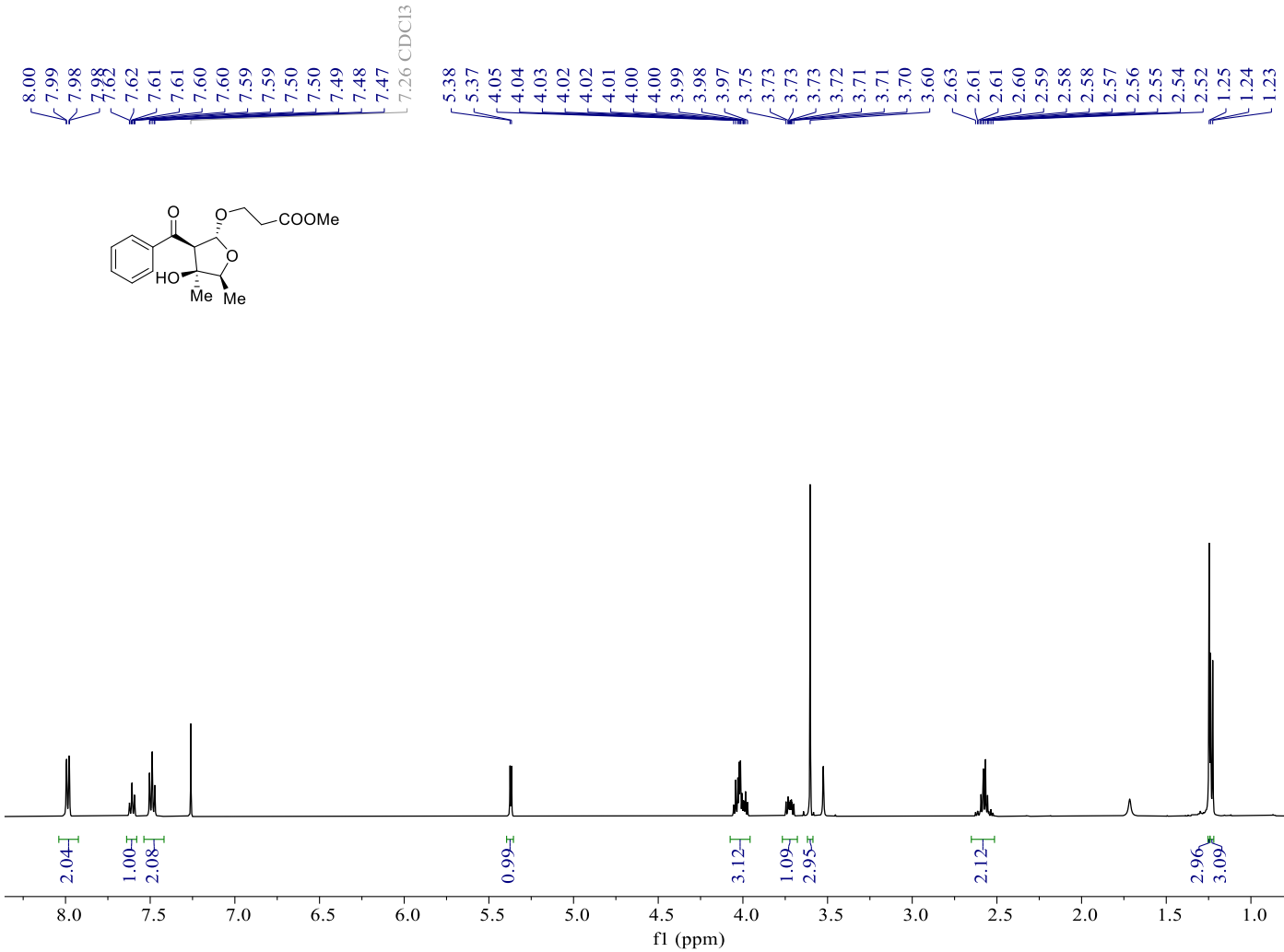
Compound 31 ^{1}H NMR (500 MHz, $CDCl_3$)



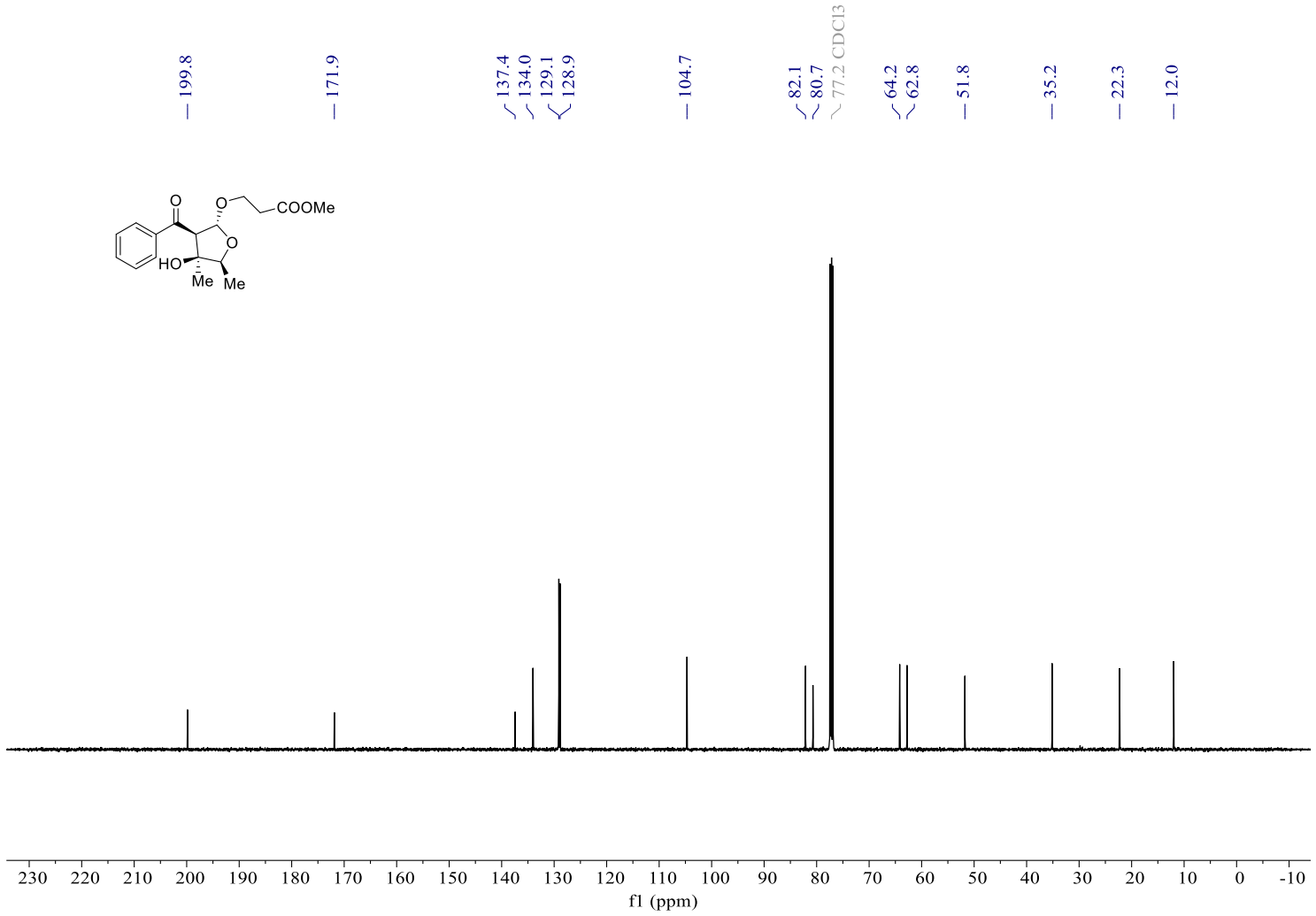
Compound 31 ^{13}C NMR (125 MHz, $CDCl_3$)



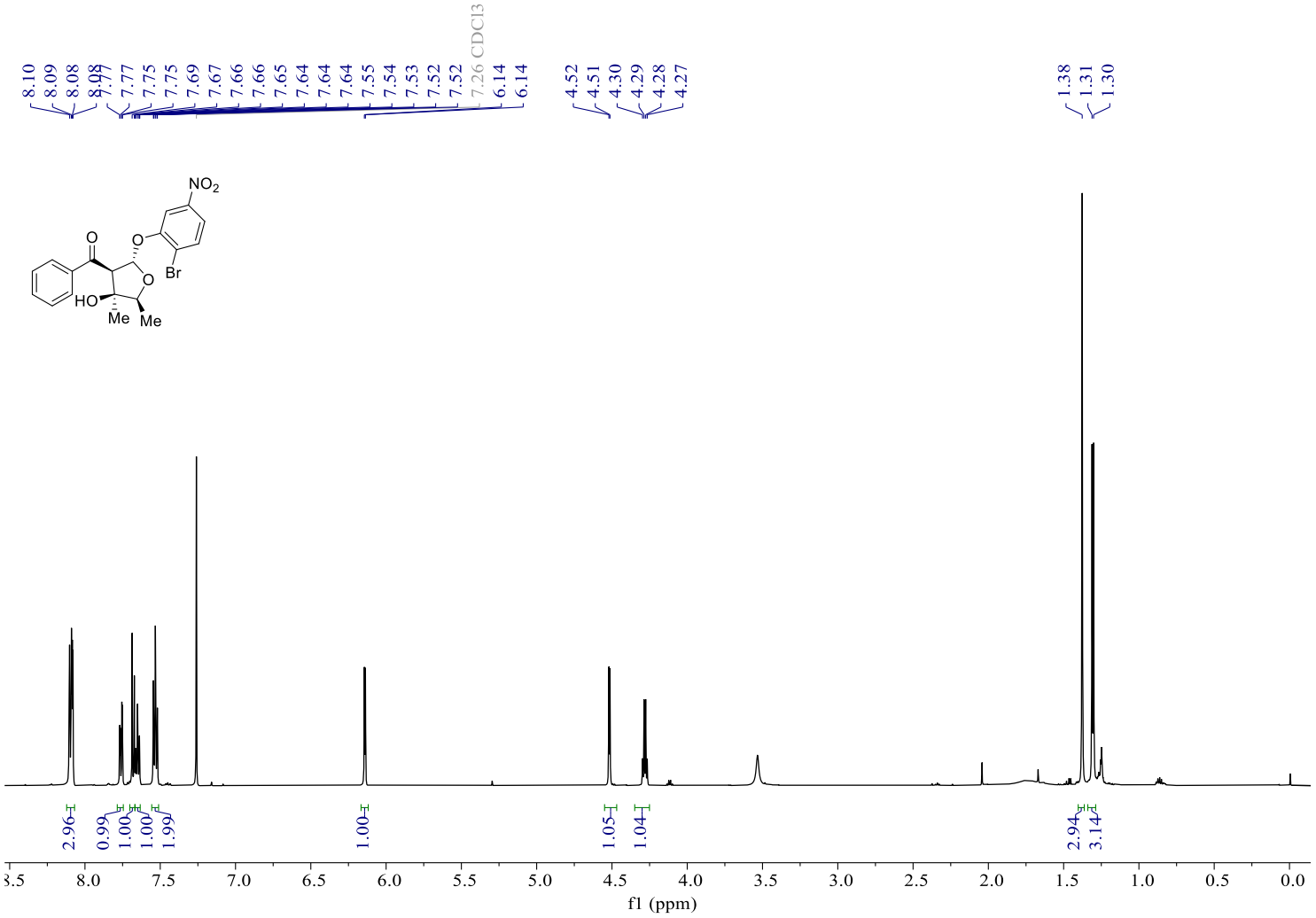
Compound 32 ^{1}H NMR (MHz, $CDCl_3$)



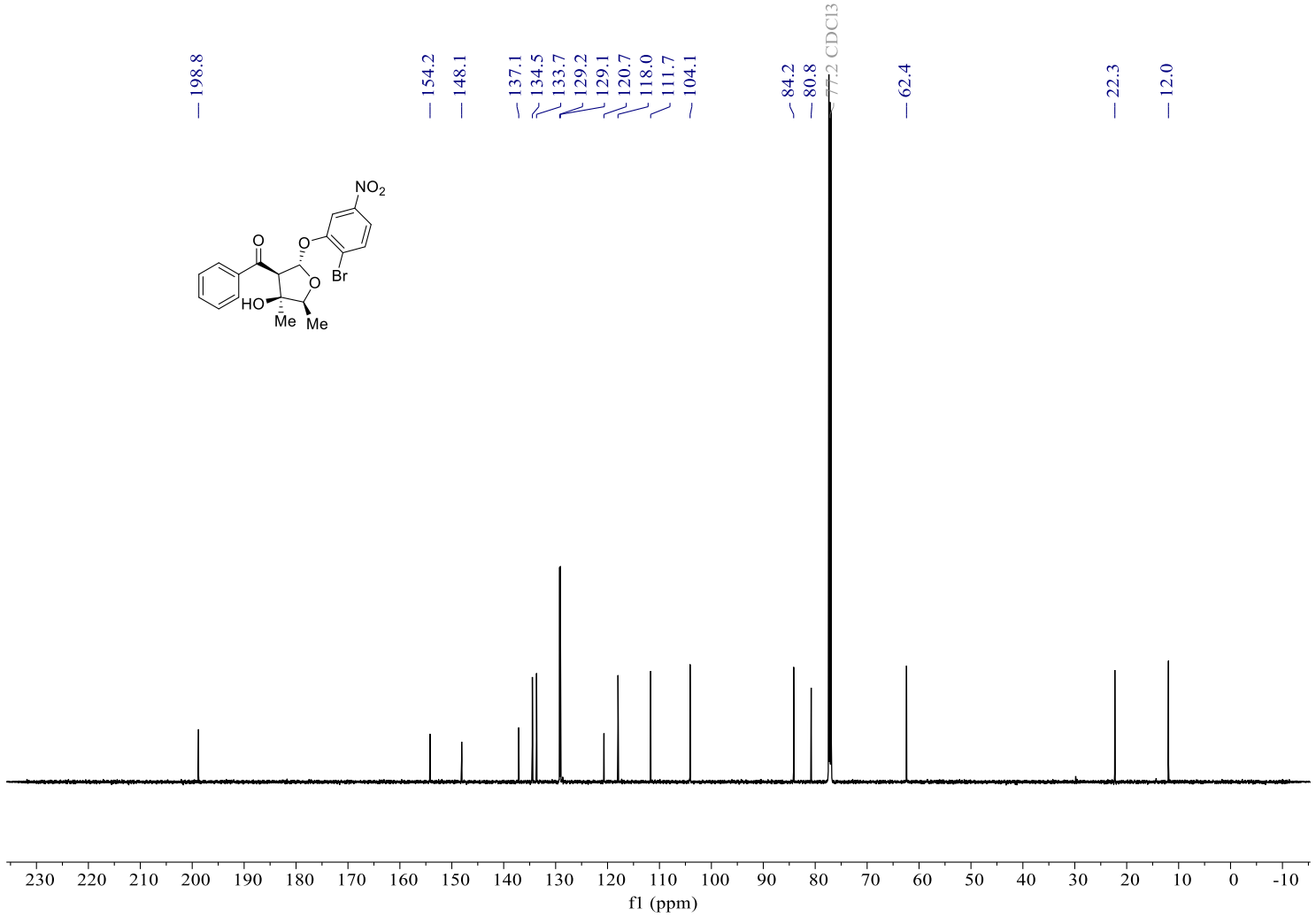
Compound 32 ^{13}C NMR (125 MHz, $CDCl_3$)



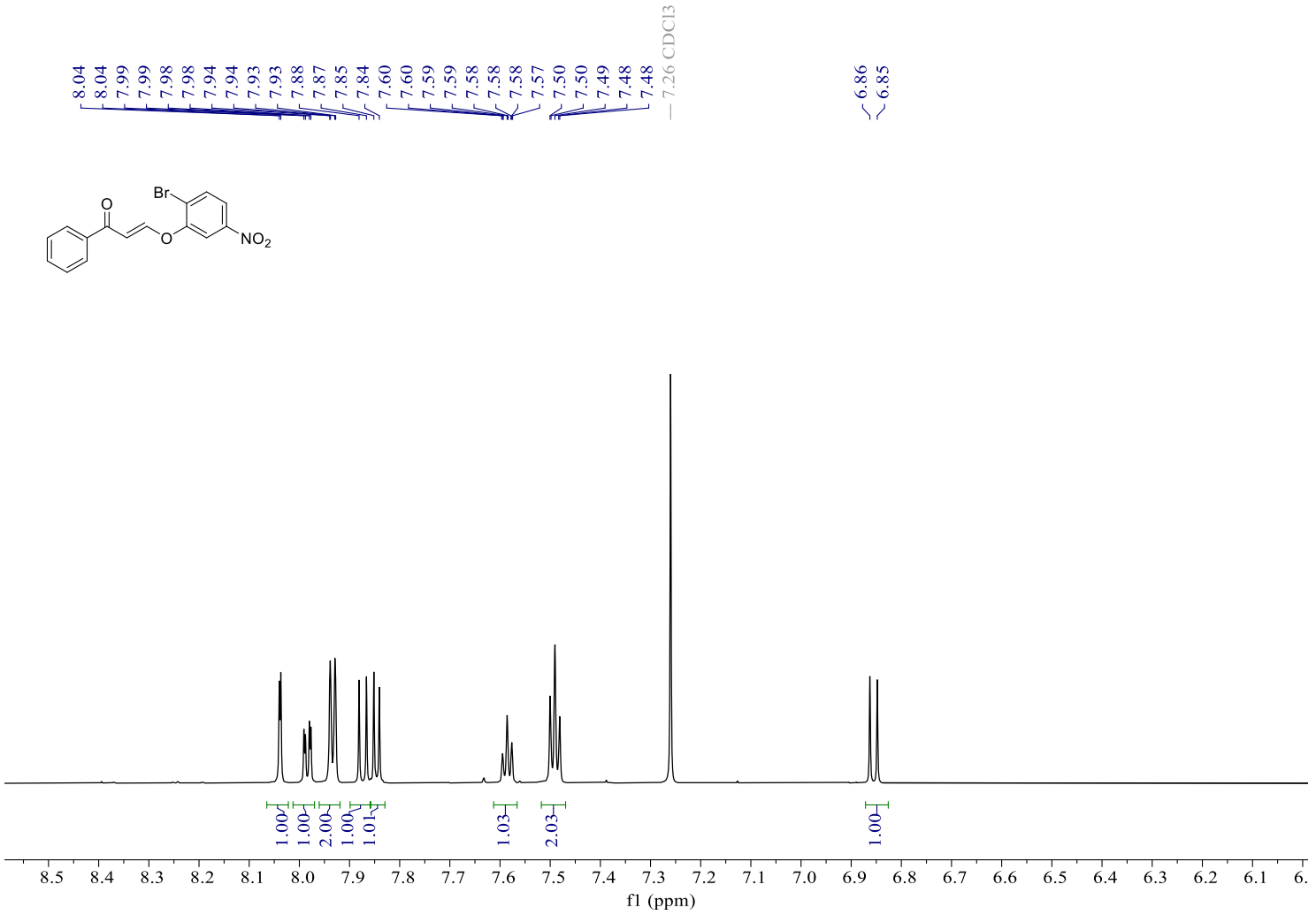
Compound 33 ^{1}H NMR (400 MHz, $CDCl_3$)



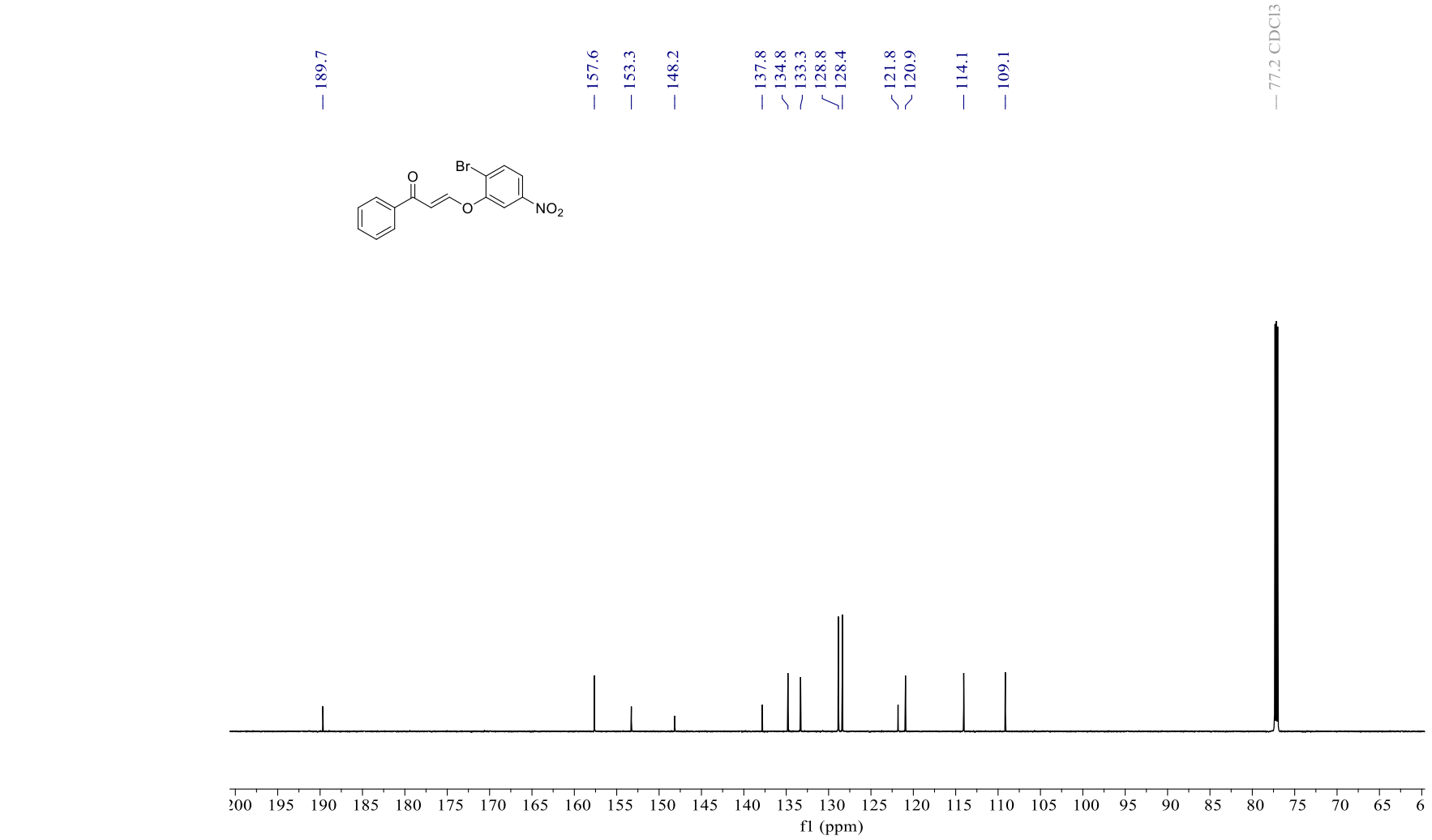
Compound 33 ^{13}C NMR (150 MHz, $CDCl_3$)



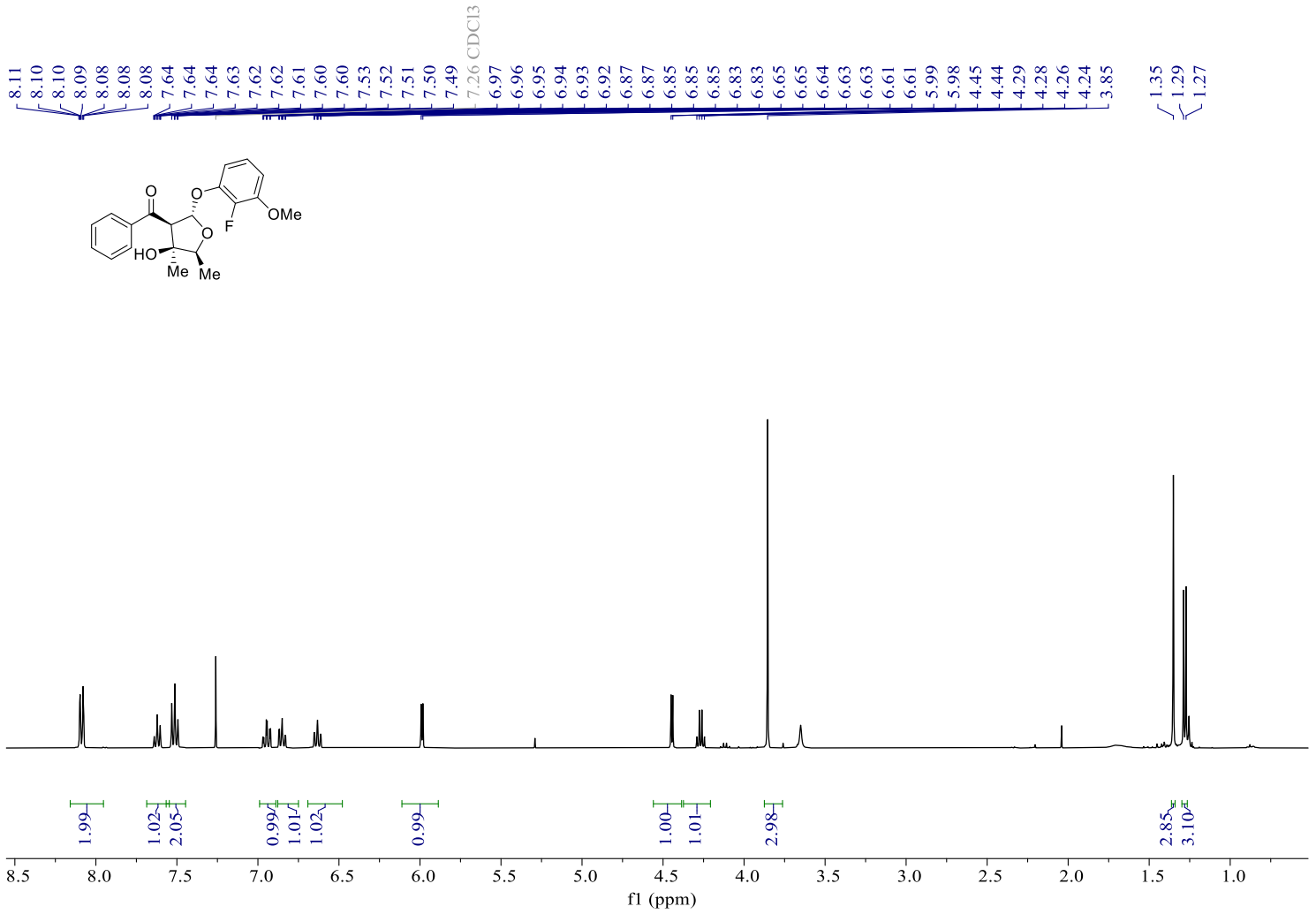
Compound 33b ^{1}H NMR (800 MHz, $CDCl_3$)



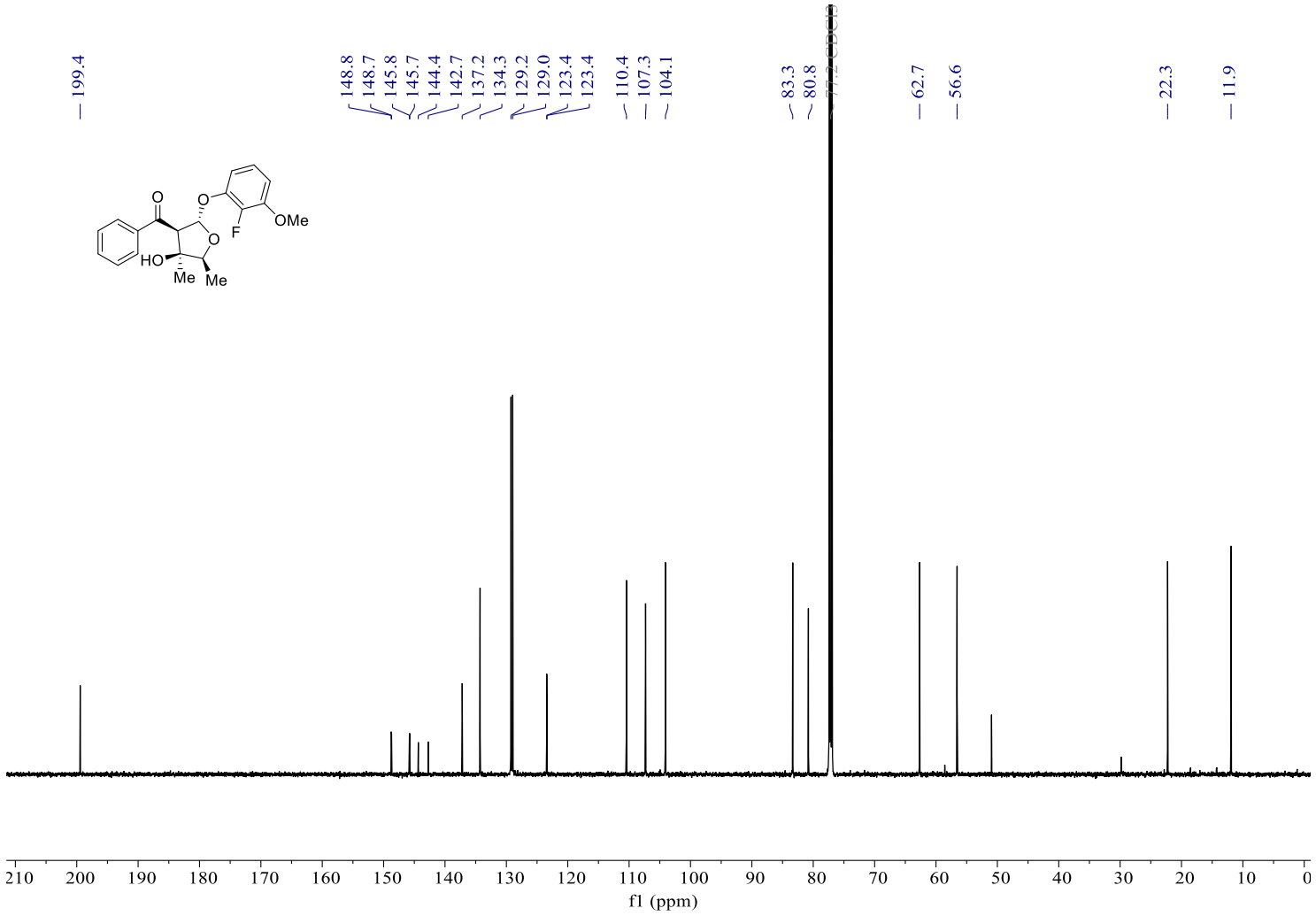
Compound 33b ^{13}C NMR (200 MHz, $CDCl_3$)



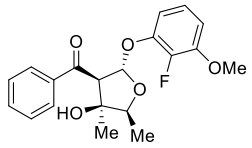
Compound 34 ^{1}H NMR (400 MHz, $CDCl_3$)



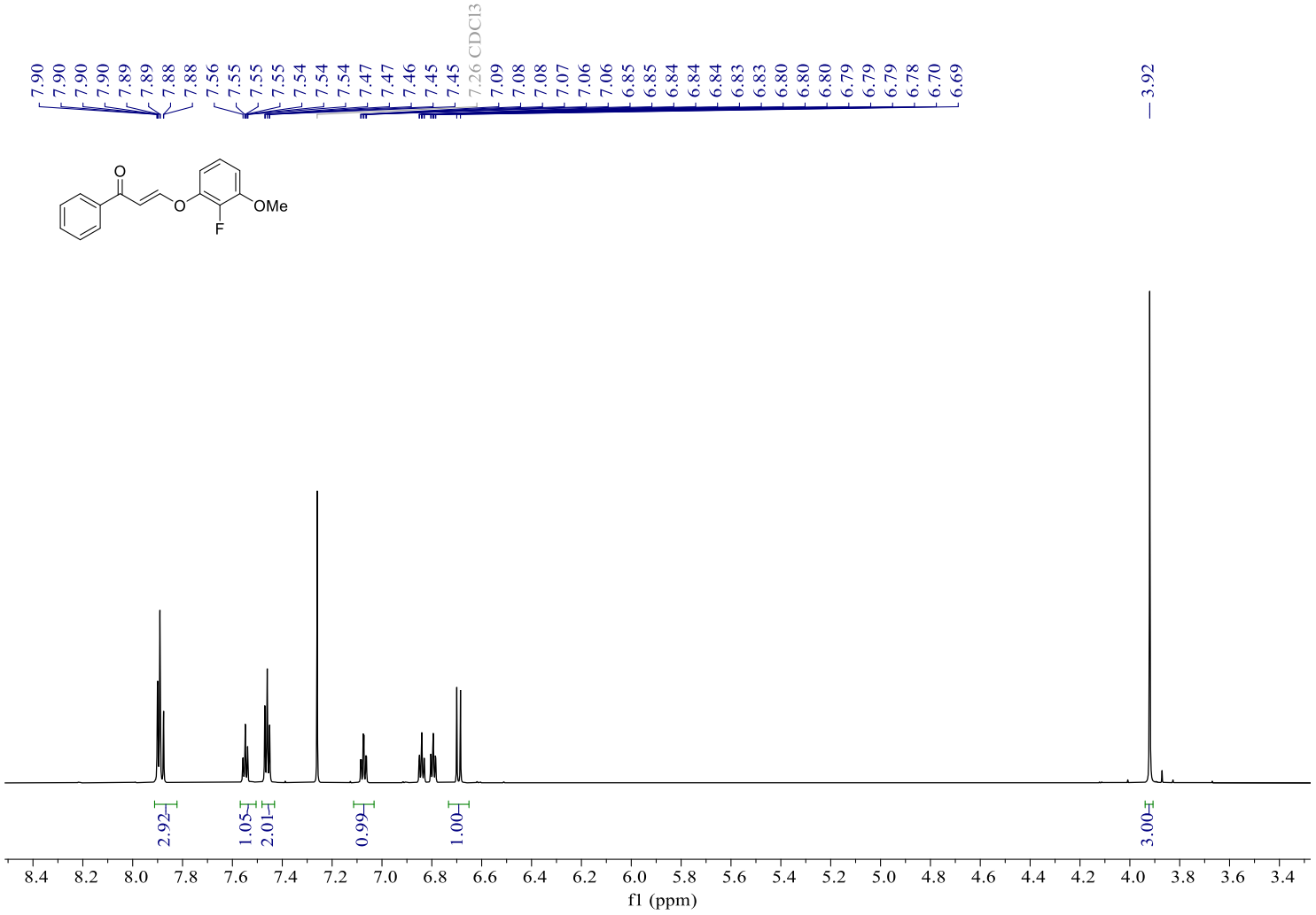
Compound 34 ^{13}C NMR (150 MHz, $CDCl_3$)



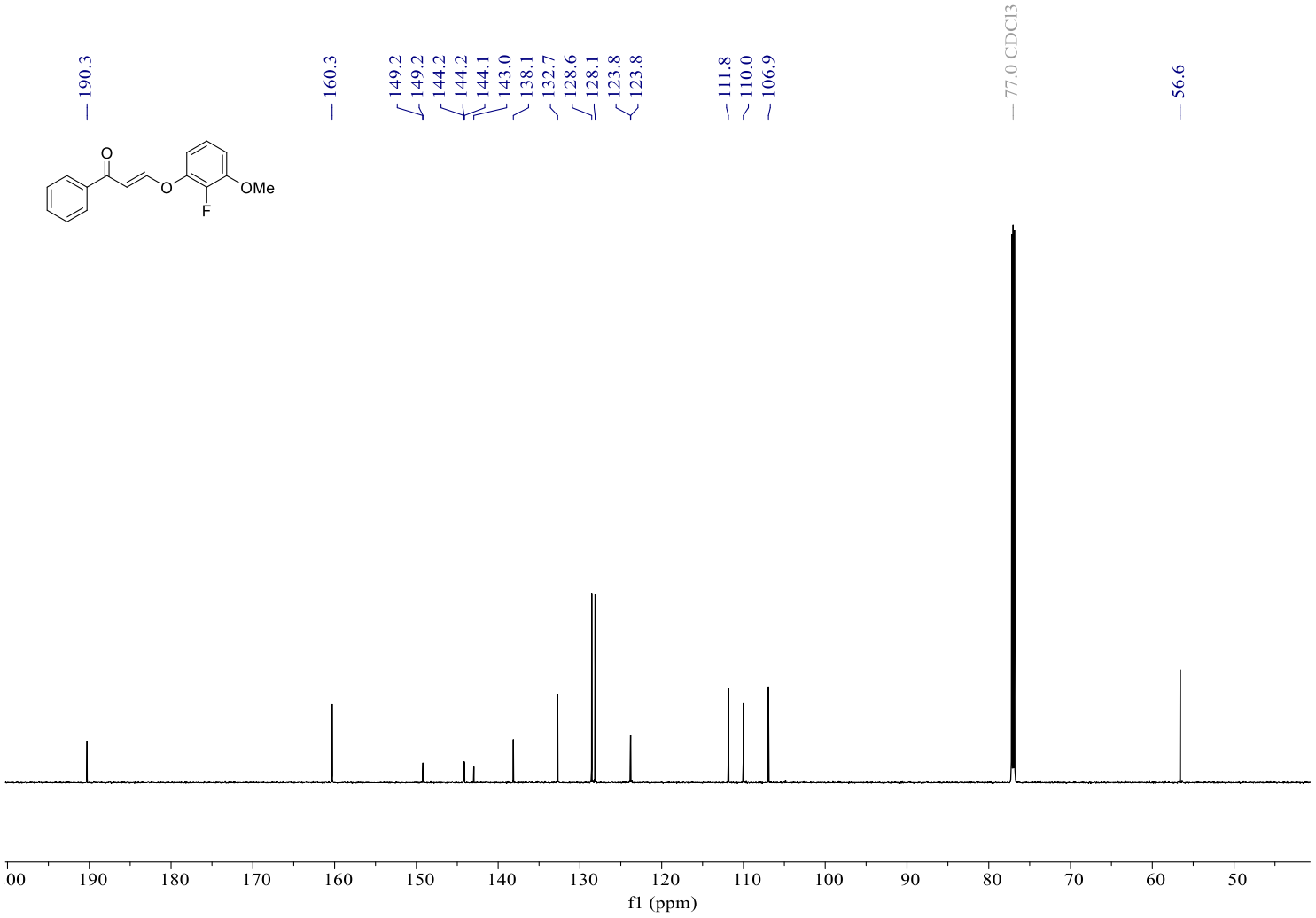
Compound 34 ^{19}F NMR (476 MHz, $CDCl_3$)



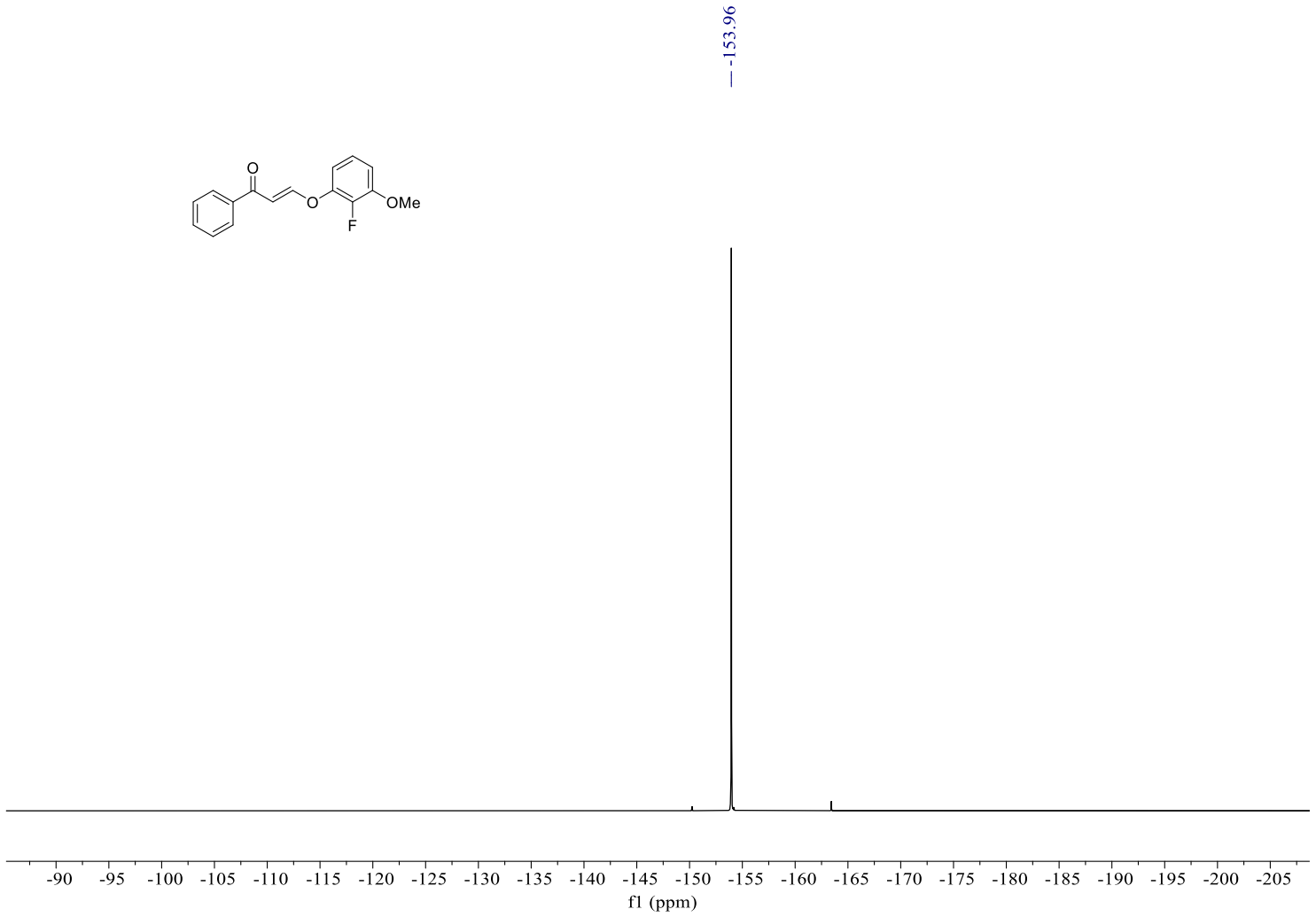
Compound 34b ^{1}H NMR (800 MHz, $CDCl_3$)



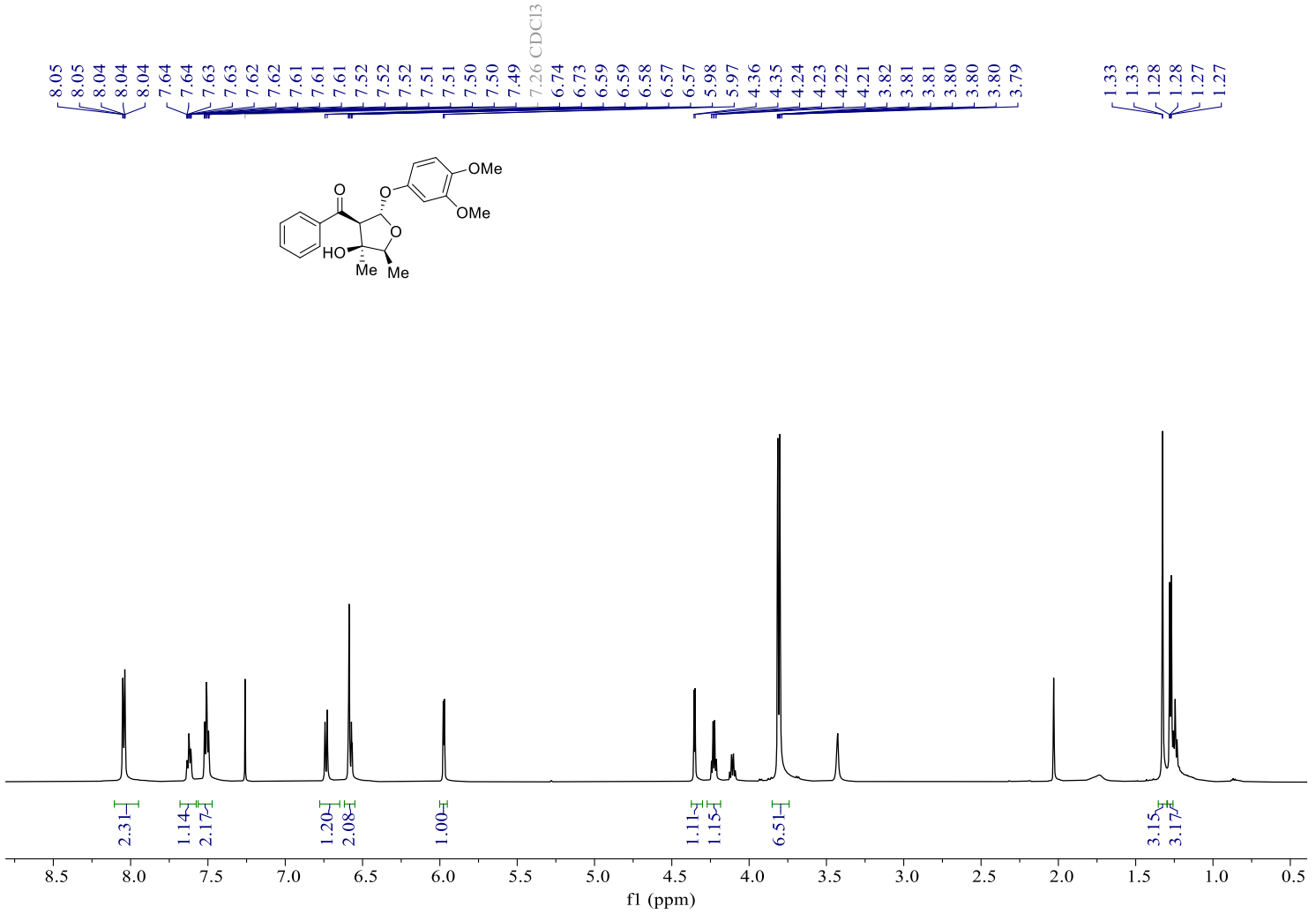
Compound 34b ^{13}C NMR (200 MHz, $CDCl_3$)



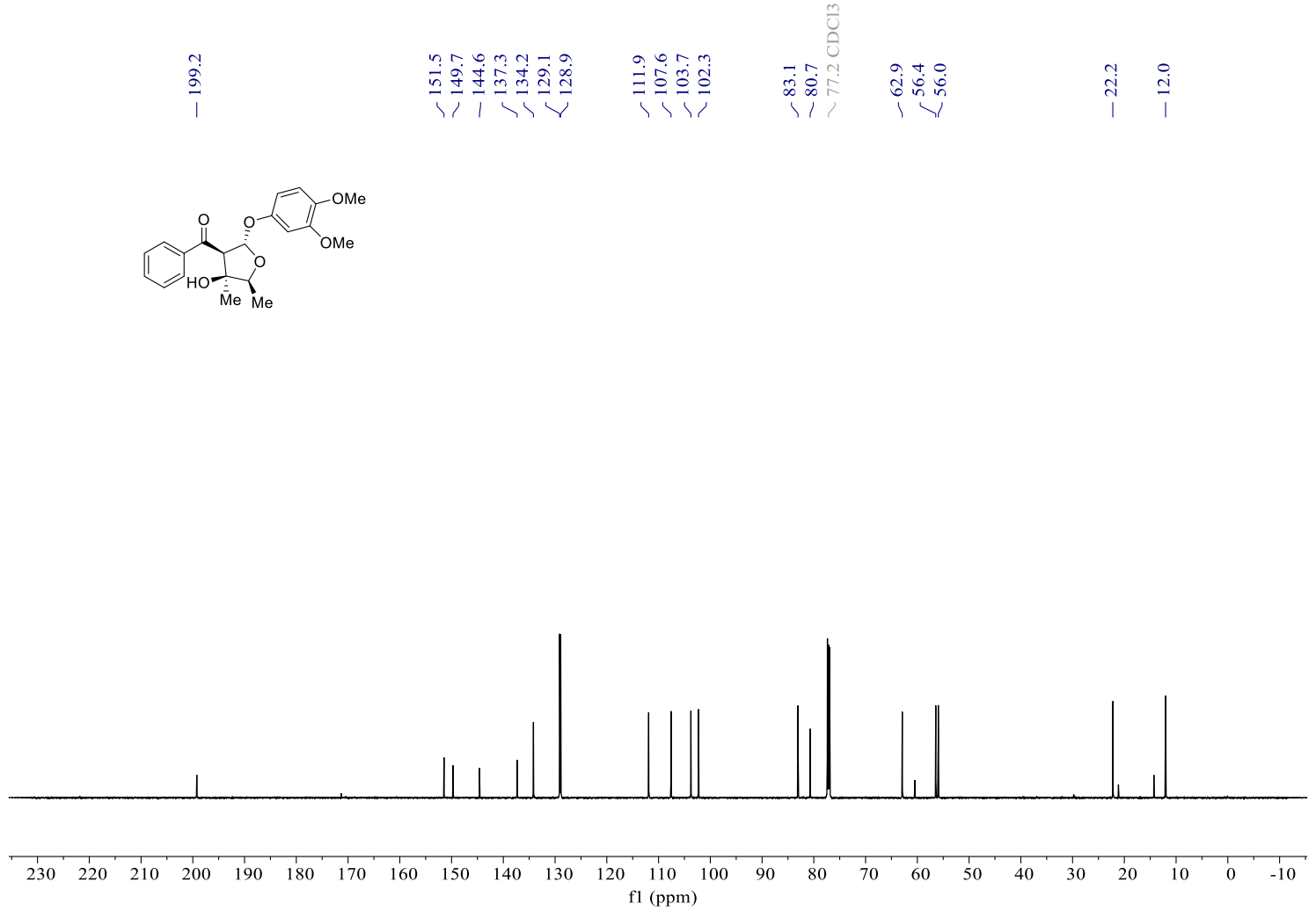
Compound 34b ^{19}F NMR (753 MHz, $CDCl_3$)



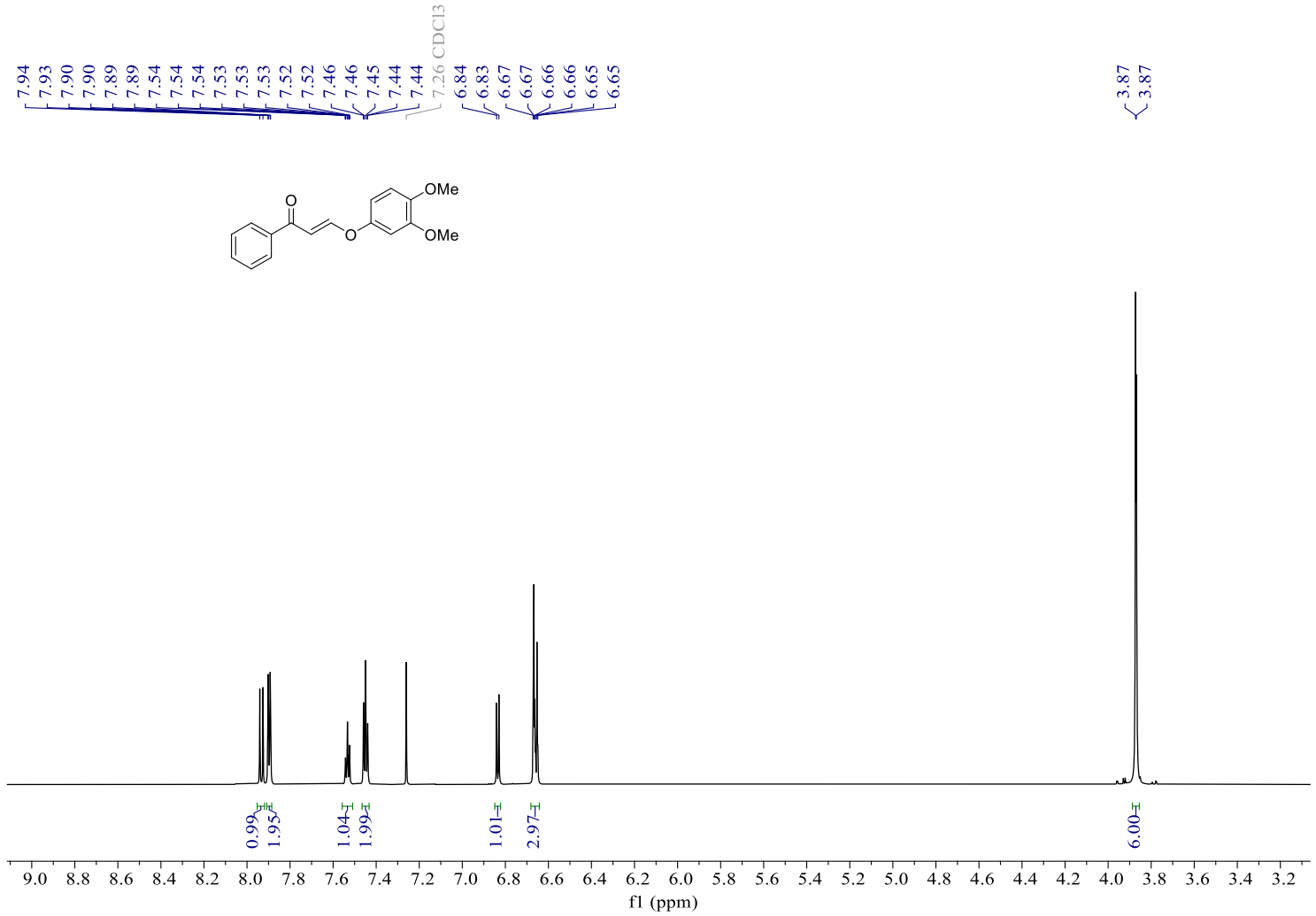
Compound 35 ^{1}H NMR (400 MHz, $CDCl_3$)



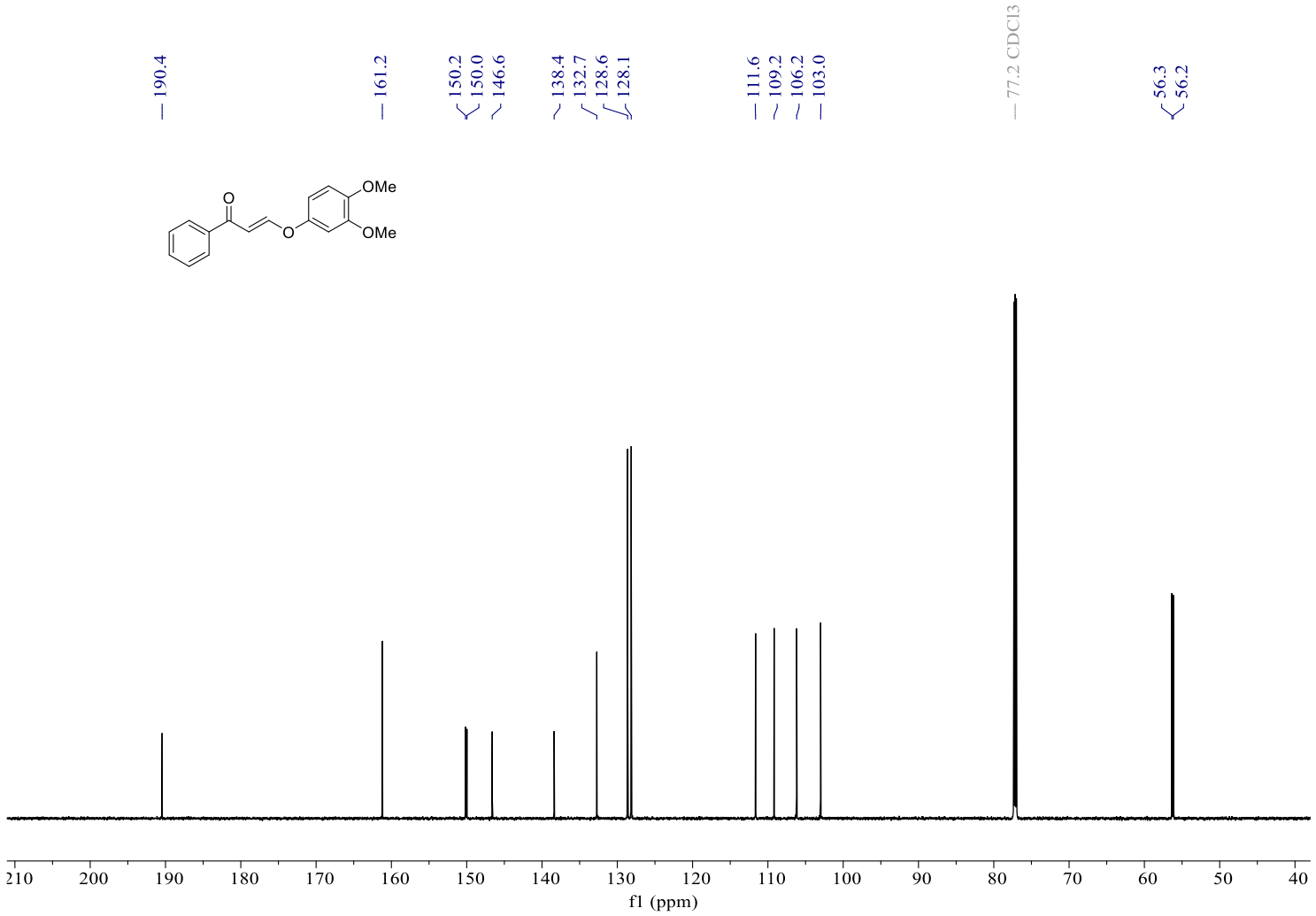
Compound 35 ^{13}C NMR (150 MHz, $CDCl_3$)



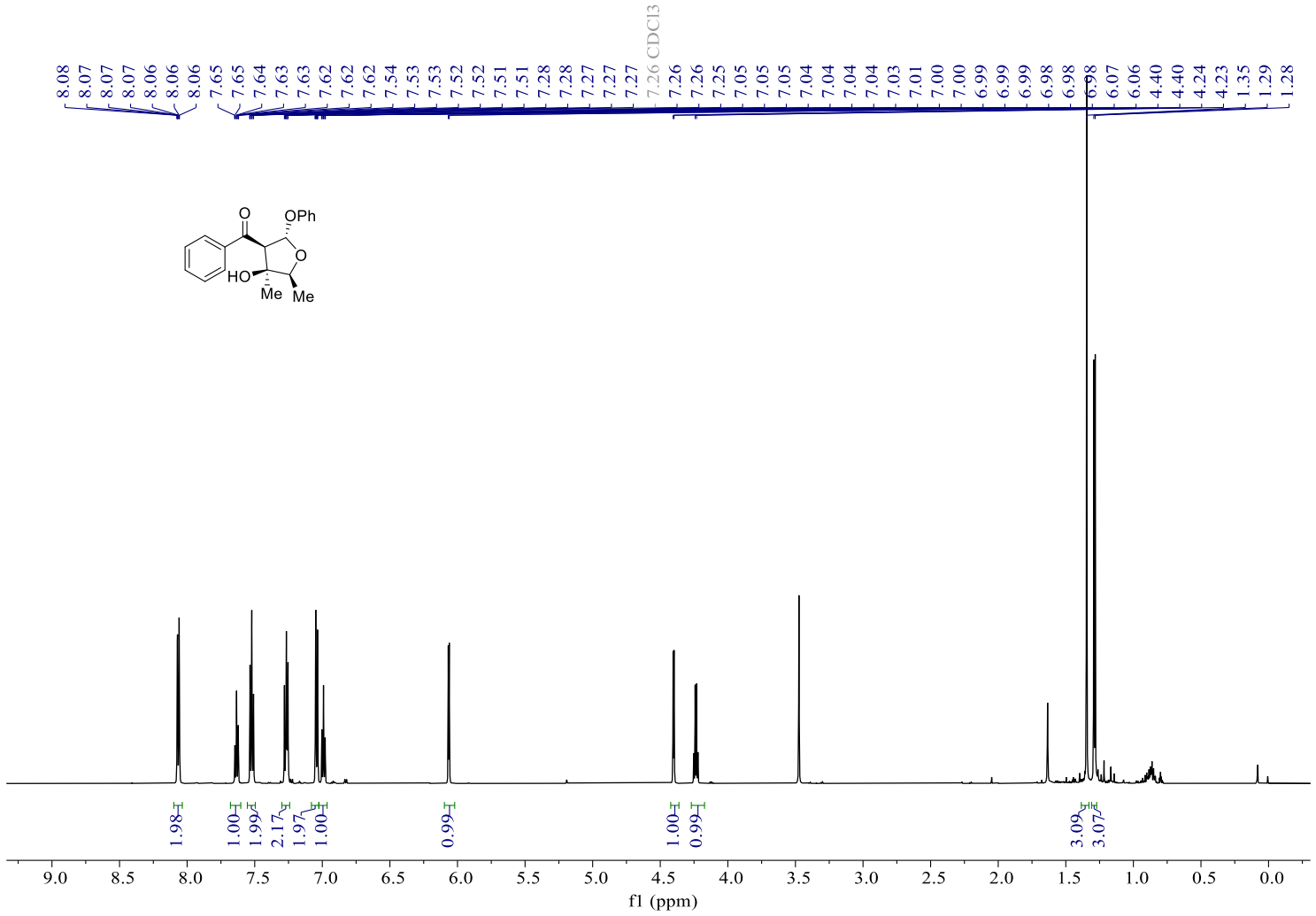
Compound 35b ^{1}H NMR (800 MHz, $CDCl_3$)



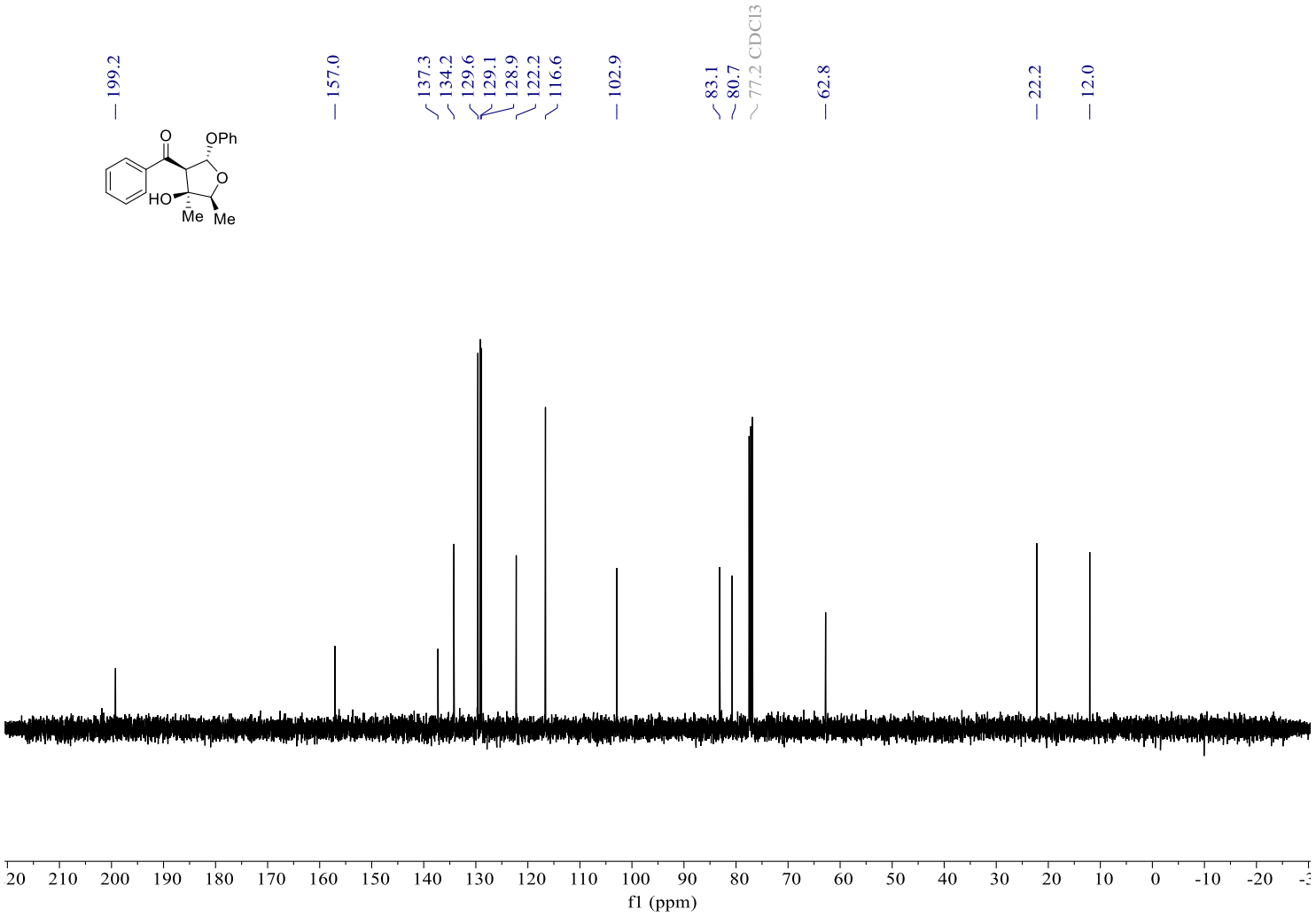
Compound 35b ^{13}C NMR (200 MHz, $CDCl_3$)



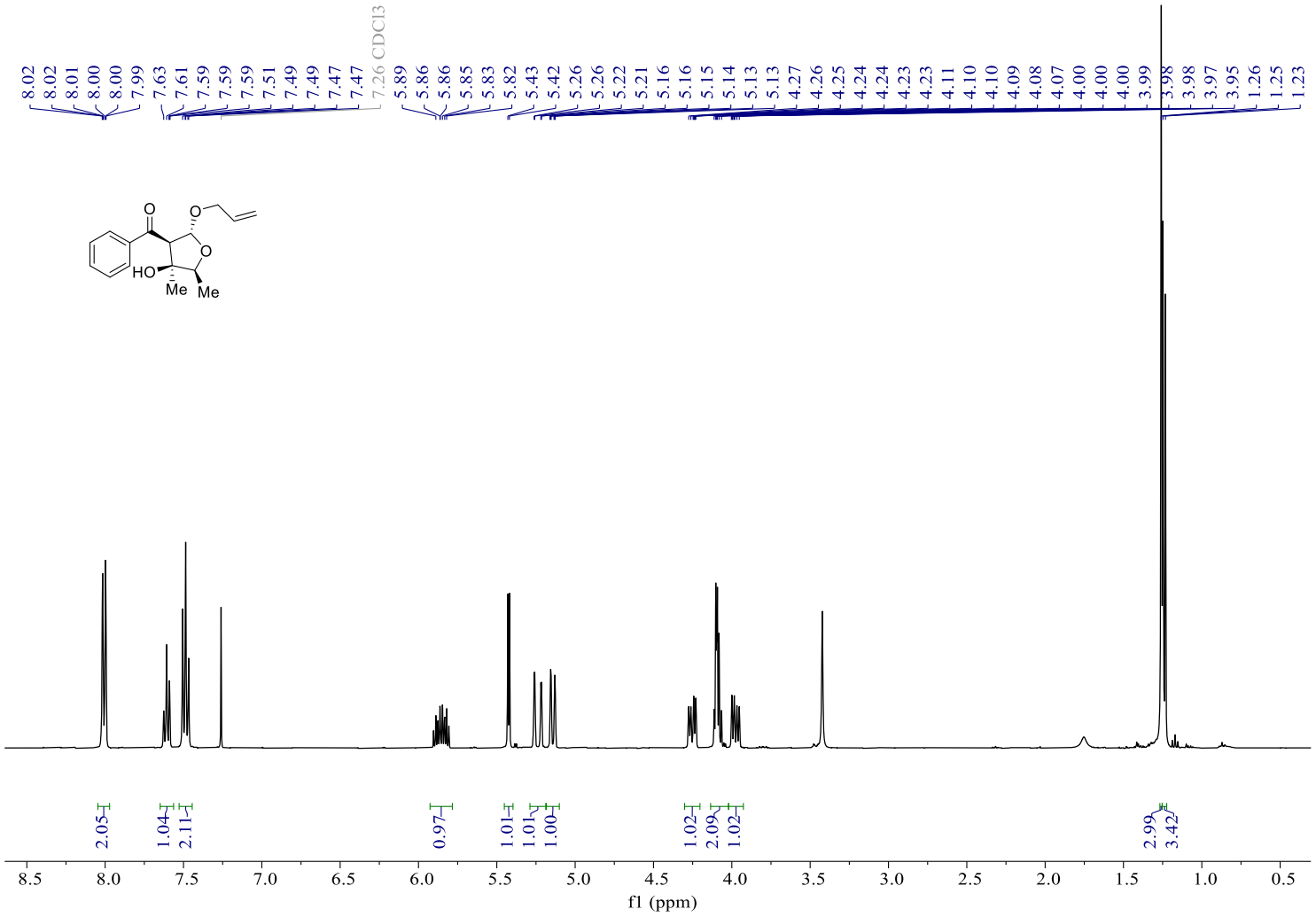
Compound 36 ^{1}H NMR (600 MHz, $CDCl_3$)



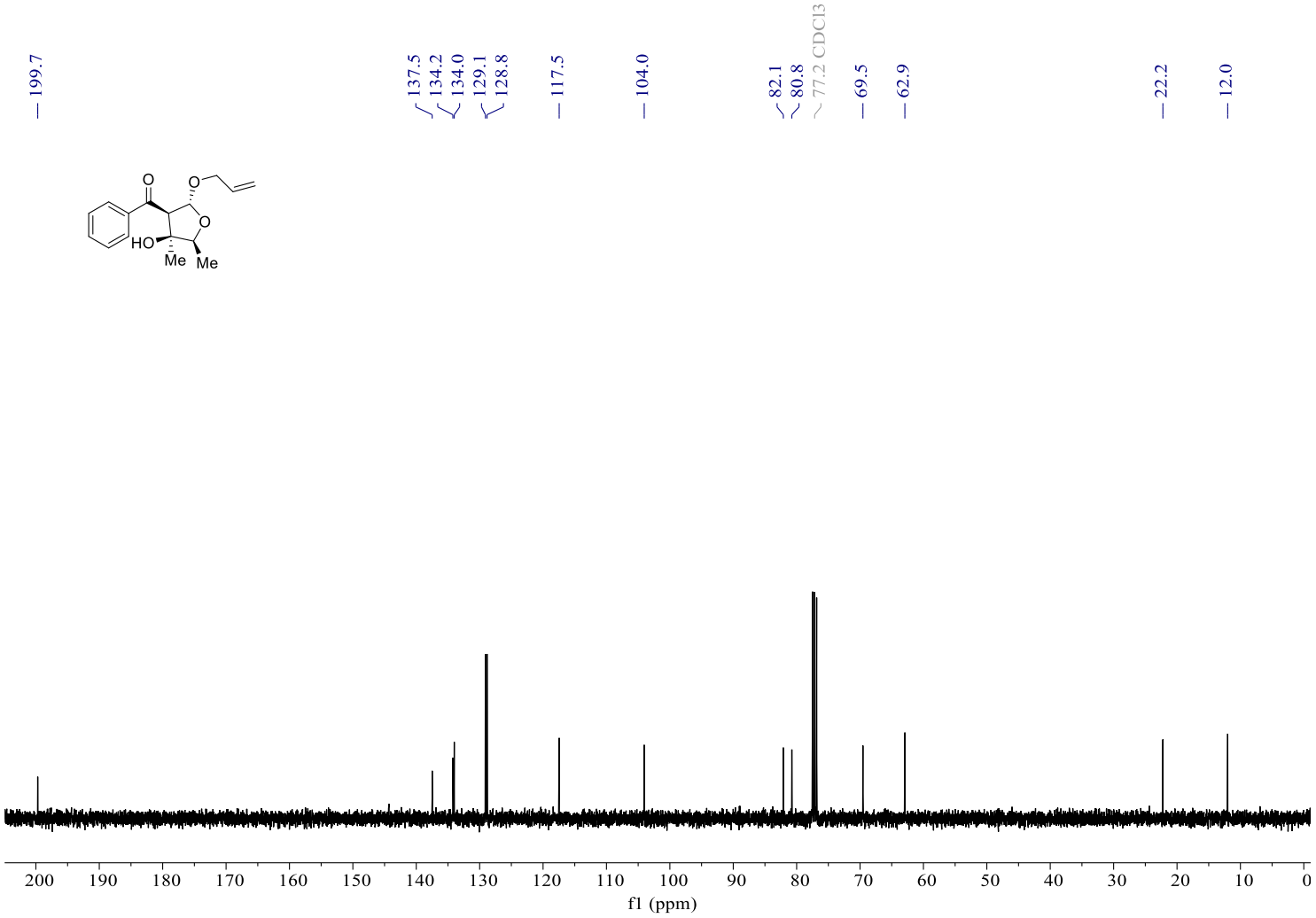
Compound 36 ^{13}C NMR (100 MHz, $CDCl_3$)



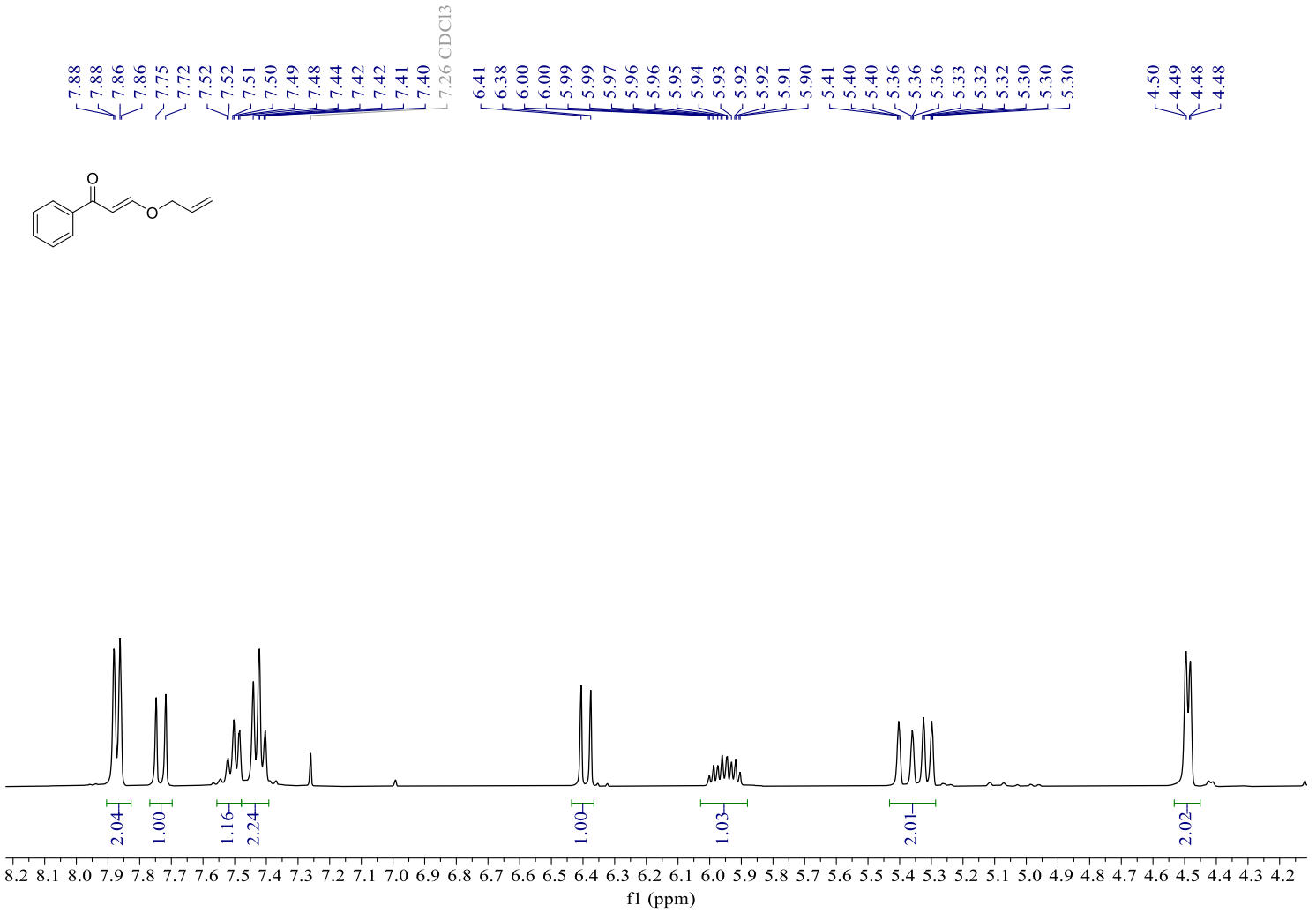
Compound 37 ^{1}H NMR (400 MHz, $CDCl_3$)



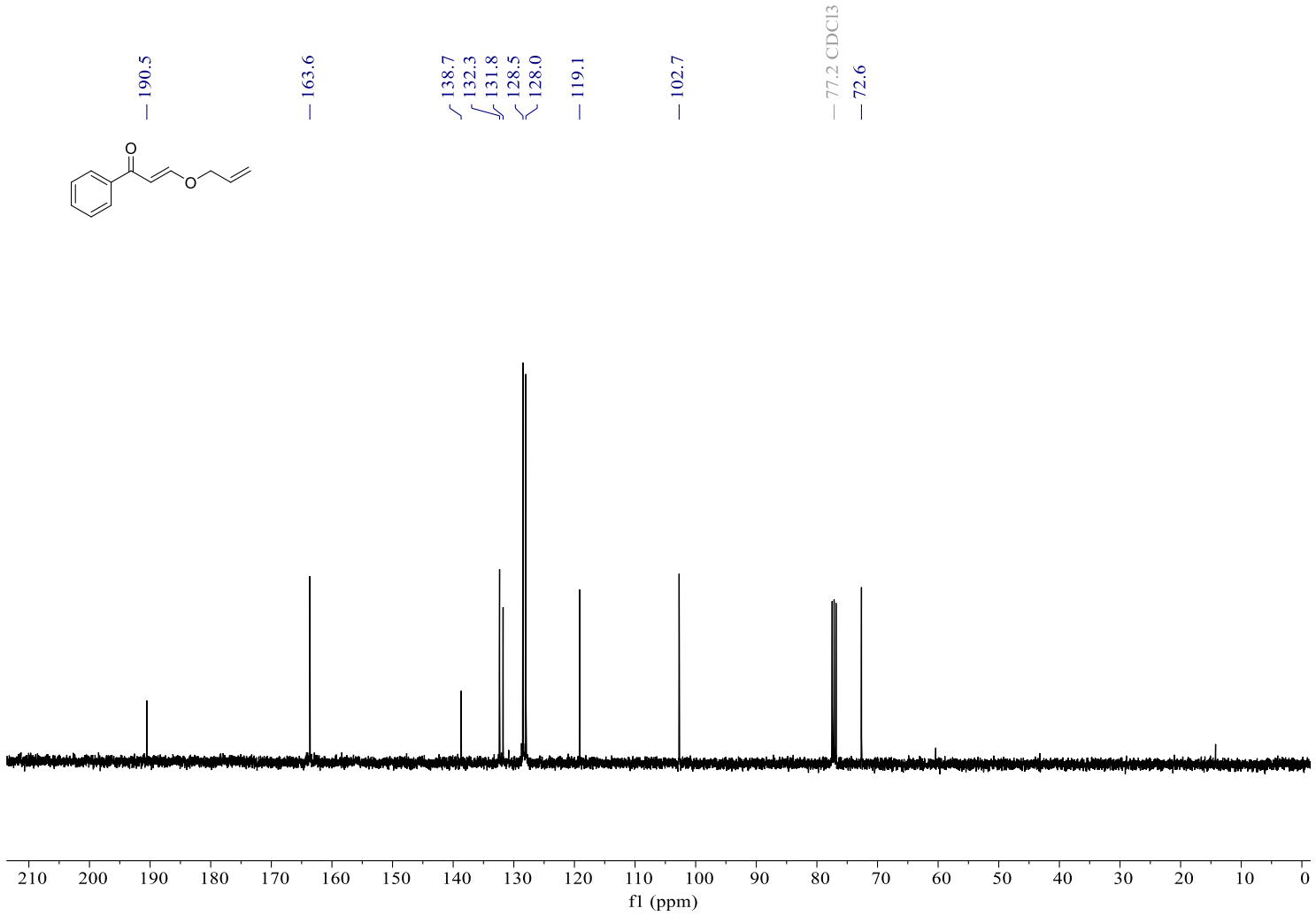
Compound 37 ^{13}C NMR (100 MHz, $CDCl_3$)



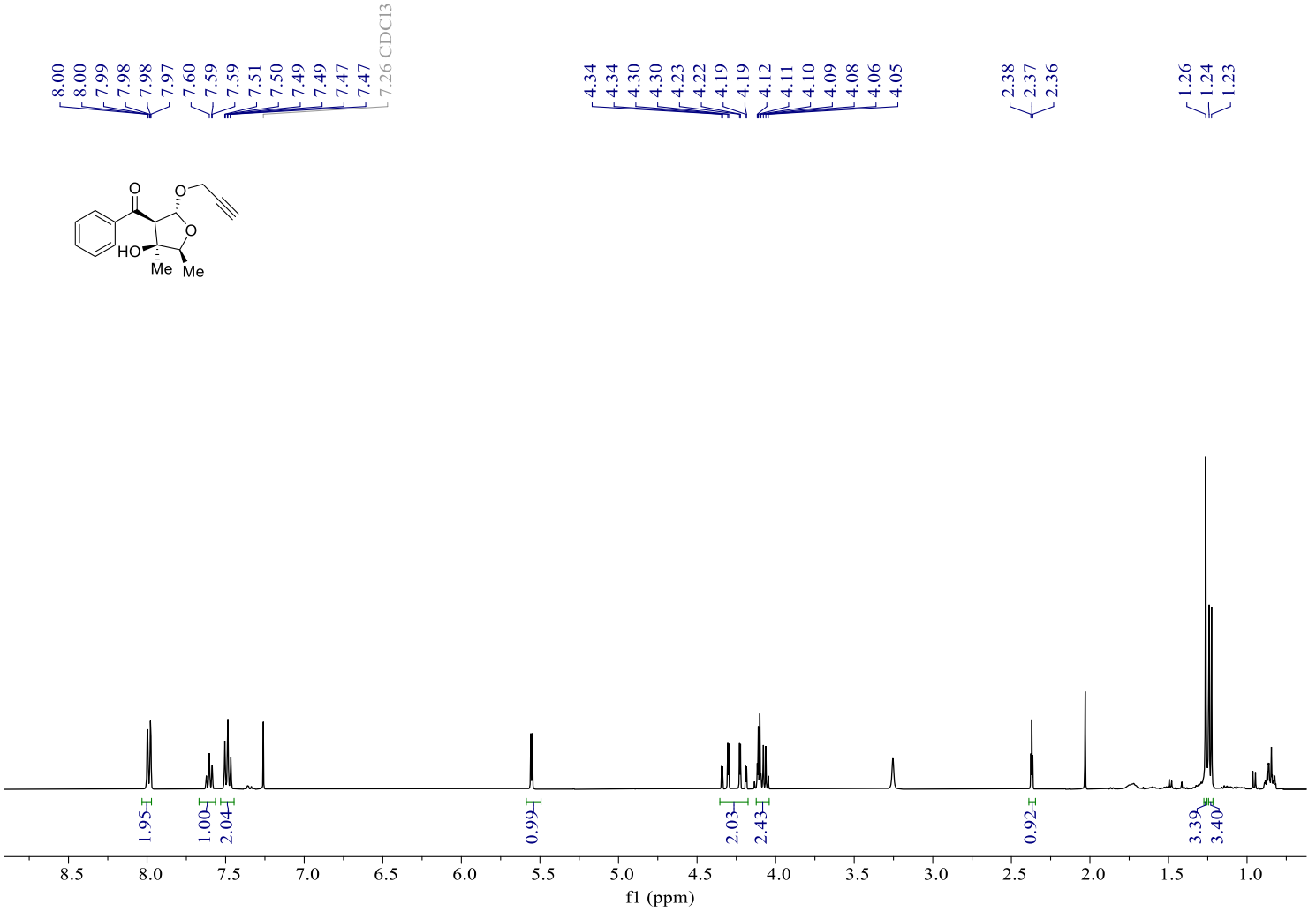
Compound 37b ^{1}H NMR (400 MHz, $CDCl_3$)



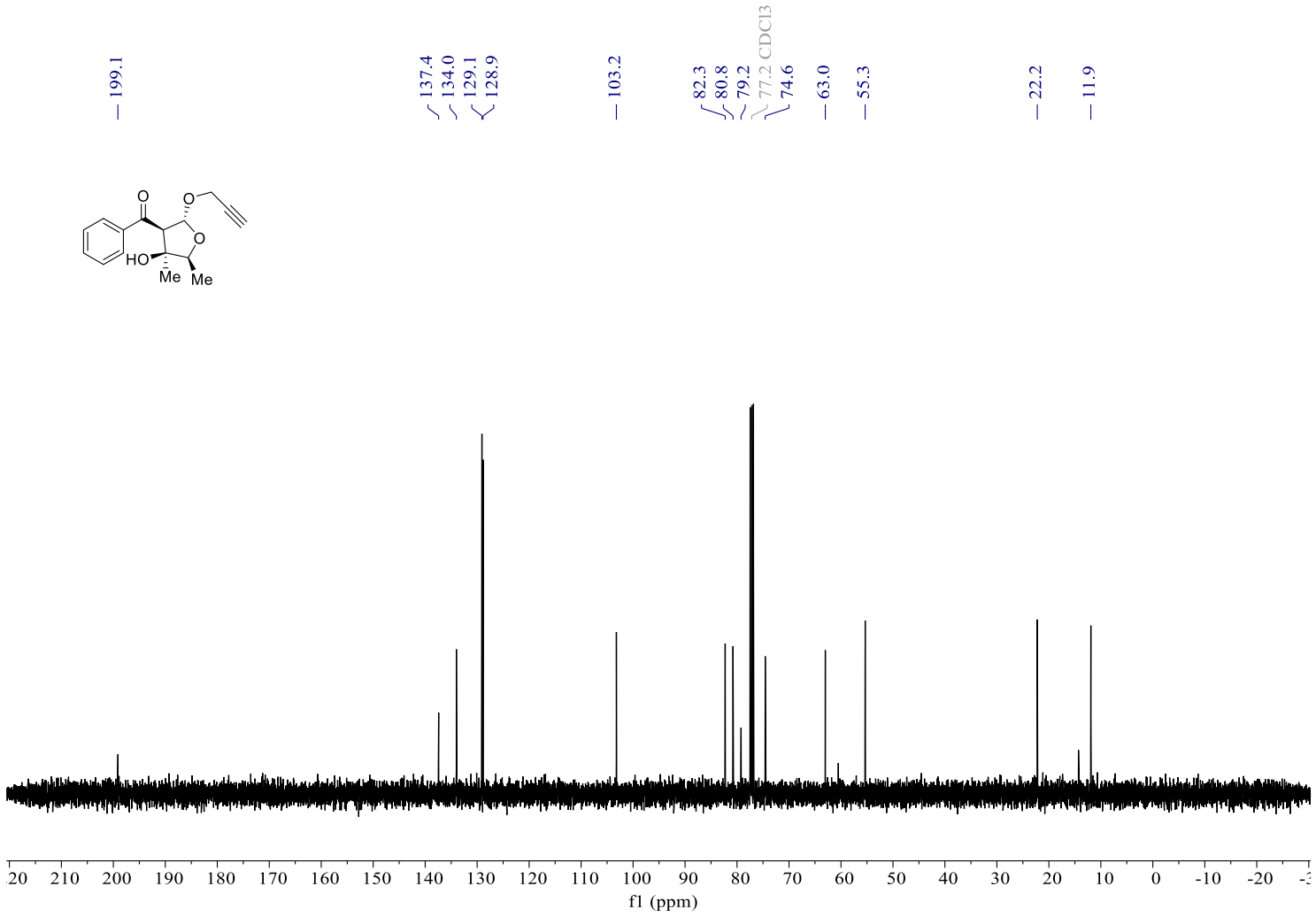
Compound 37b ^{13}C NMR (100 MHz, $CDCl_3$)



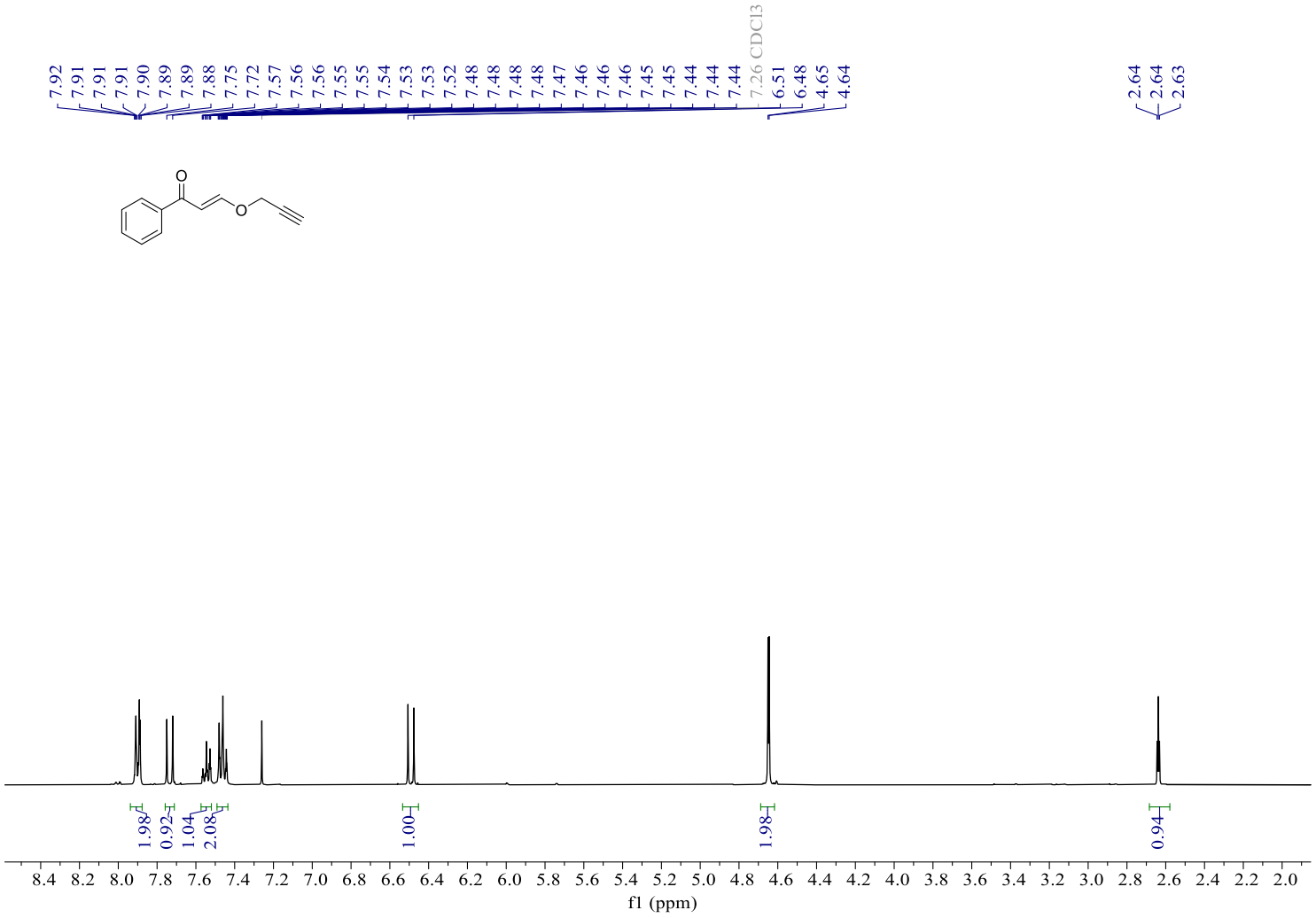
Compound 38 ^{1}H NMR (400 MHz, $CDCl_3$)



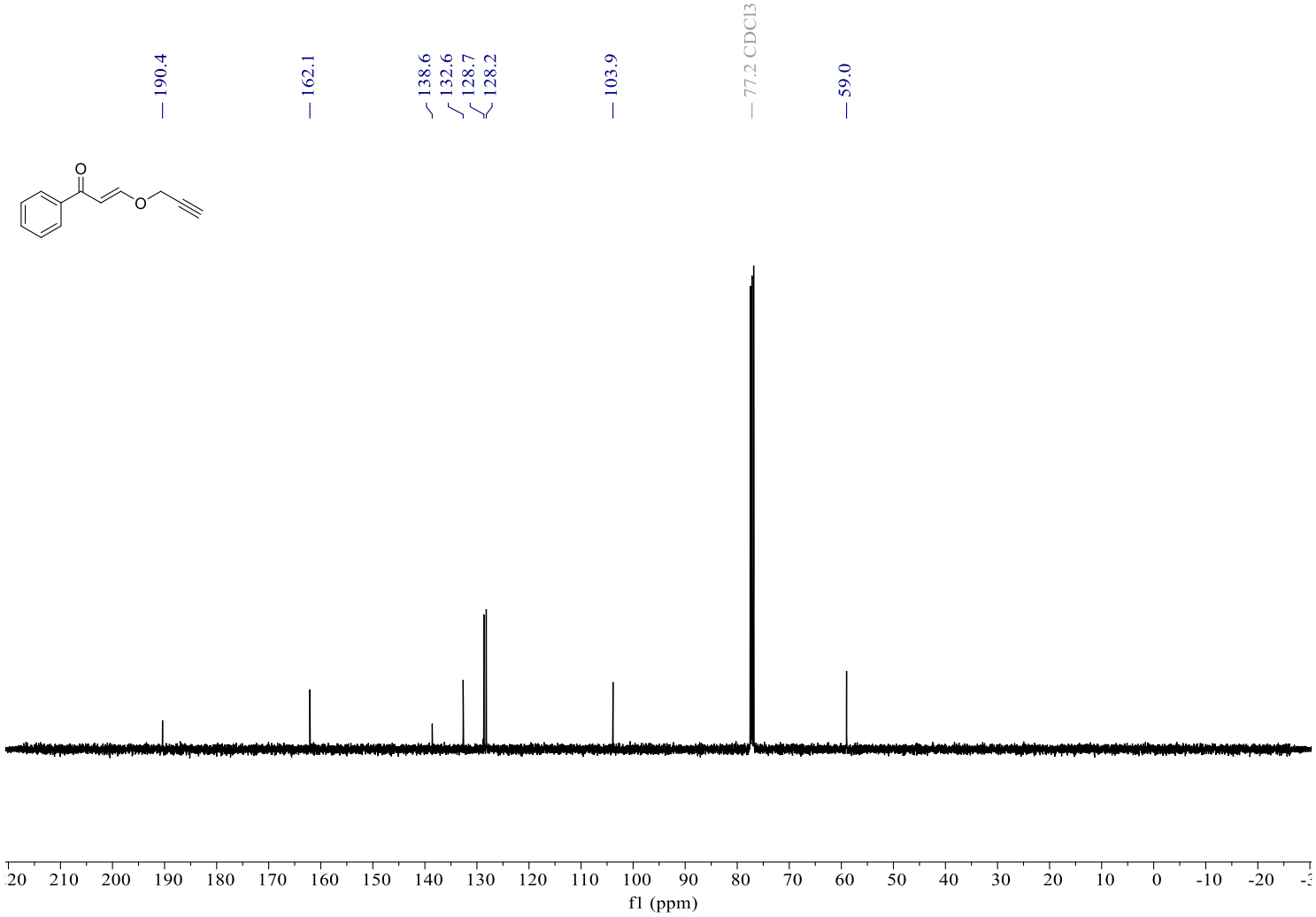
Compound 38 ^{13}C NMR (100 MHz, $CDCl_3$)



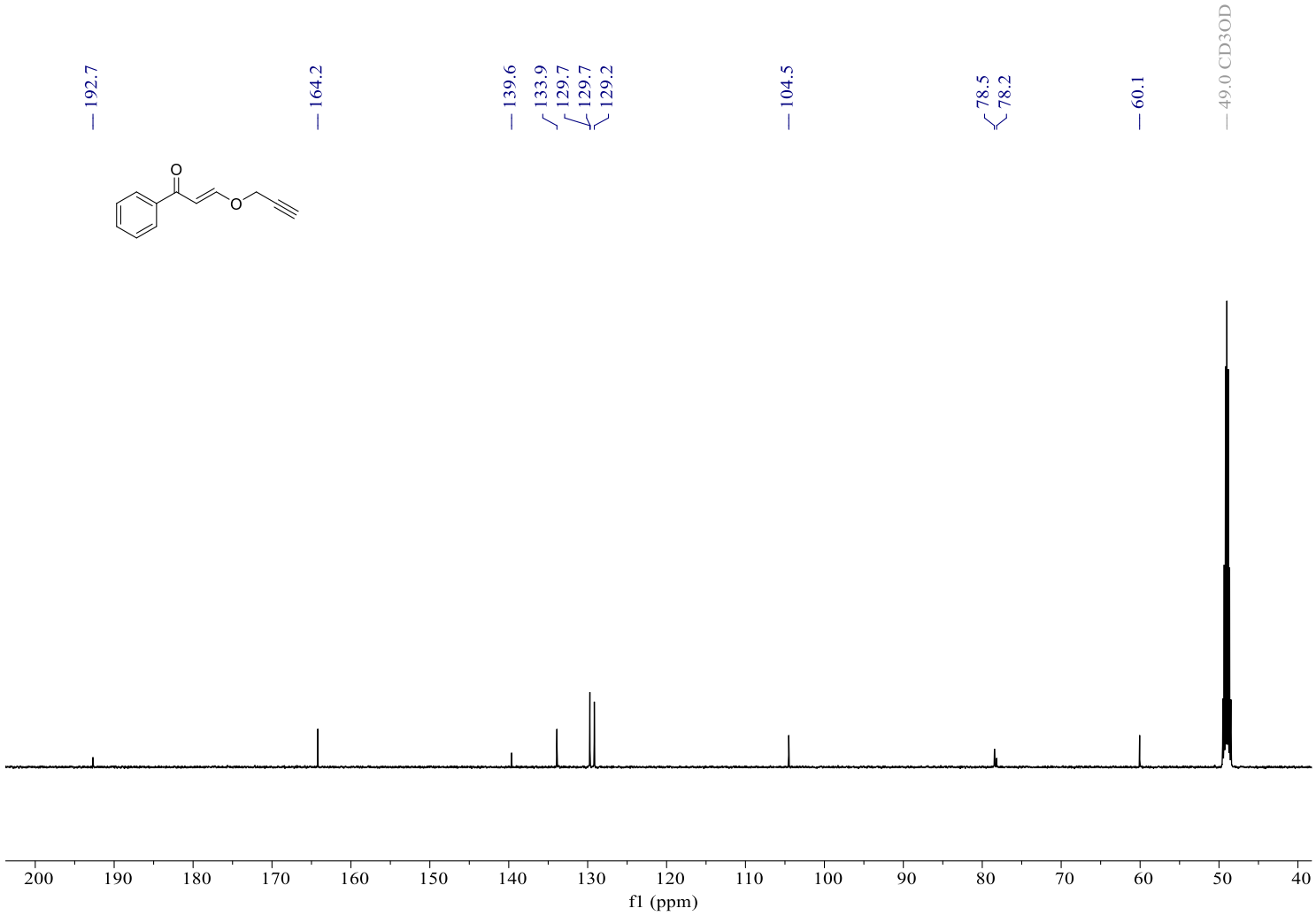
Compound 38b ^{1}H NMR (400 MHz, $CDCl_3$)



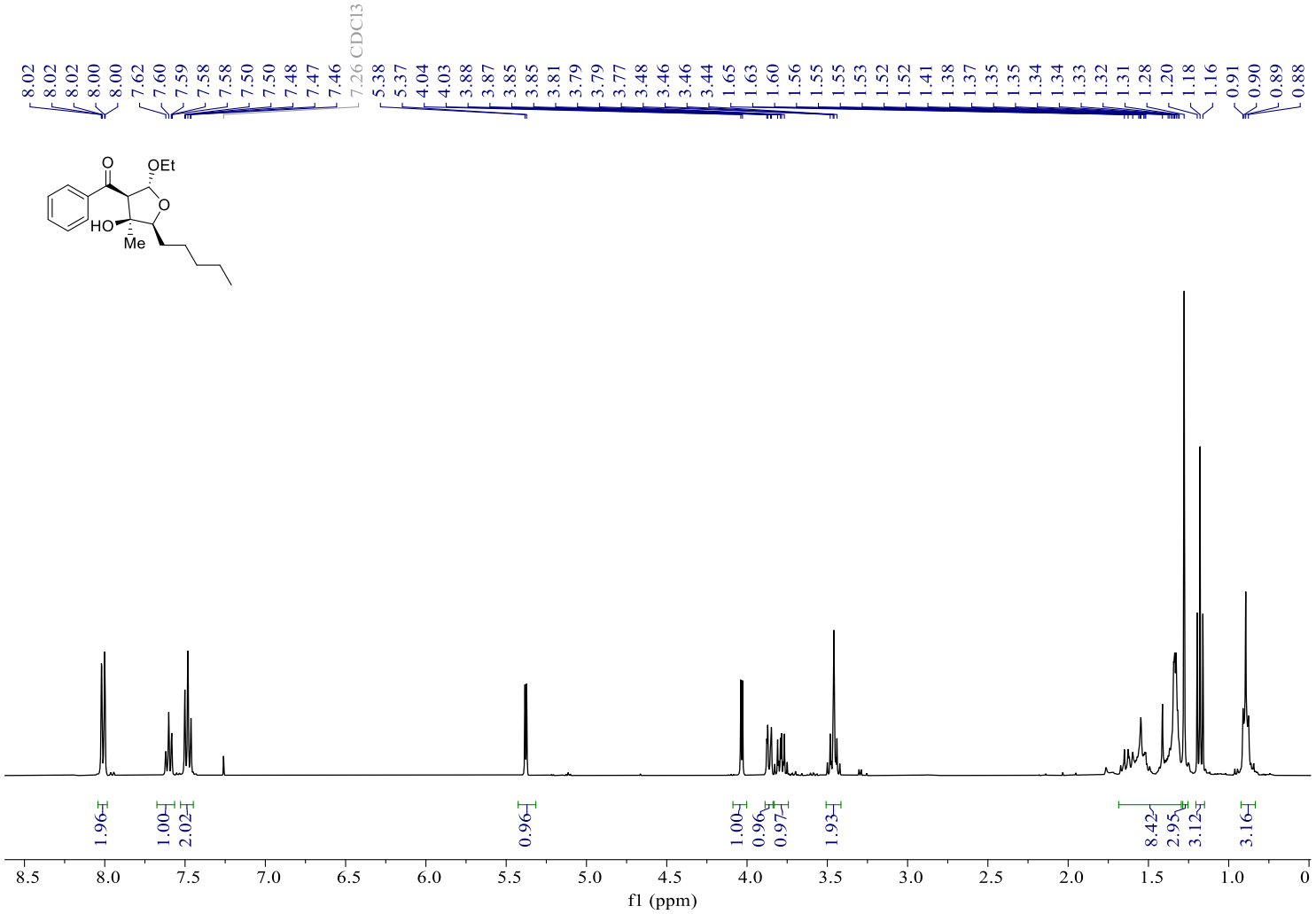
Compound 38b ^{13}C NMR (100 MHz, $CDCl_3$)



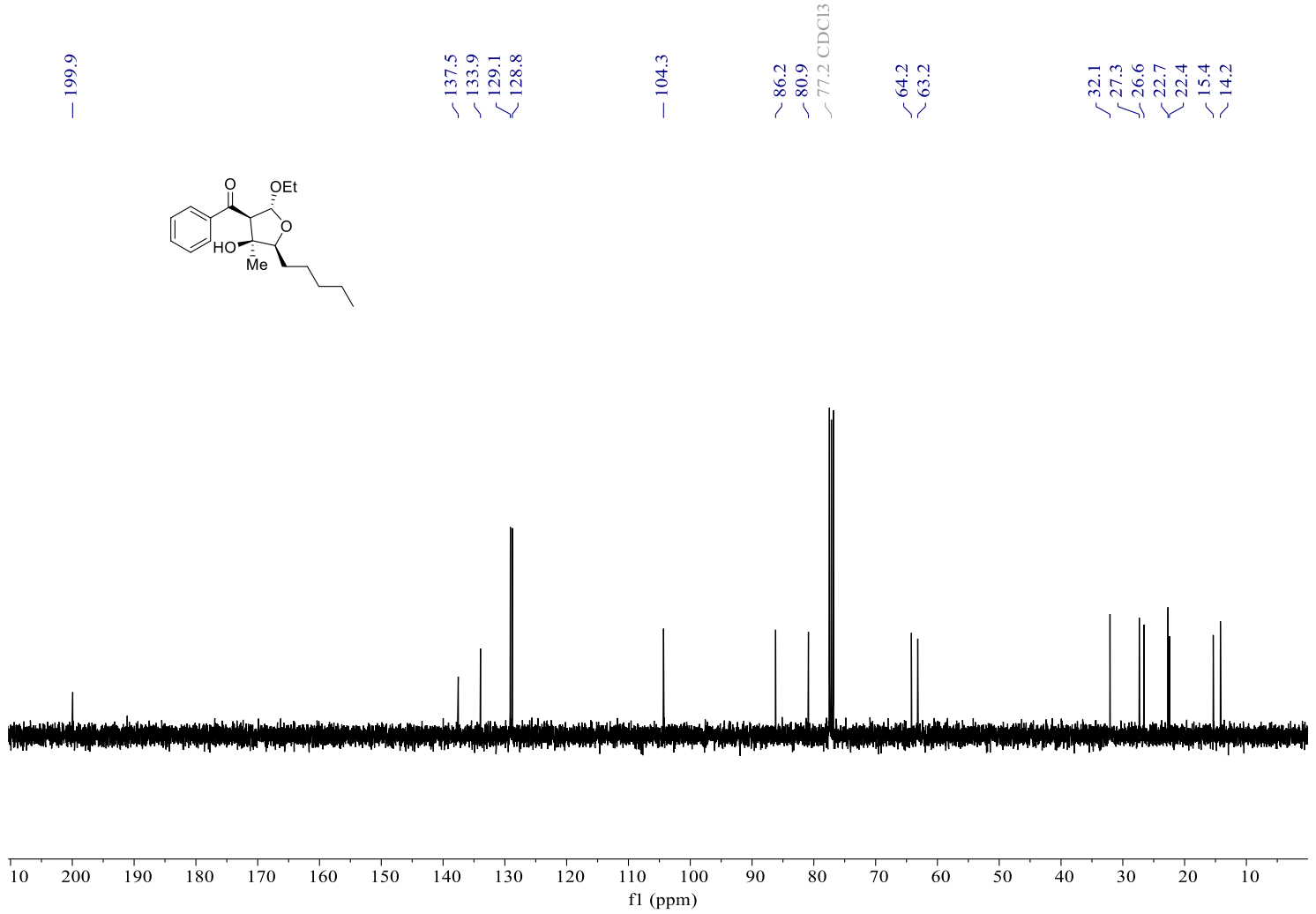
Compound 38b ^{13}C NMR (125 MHz, CD_3OD)



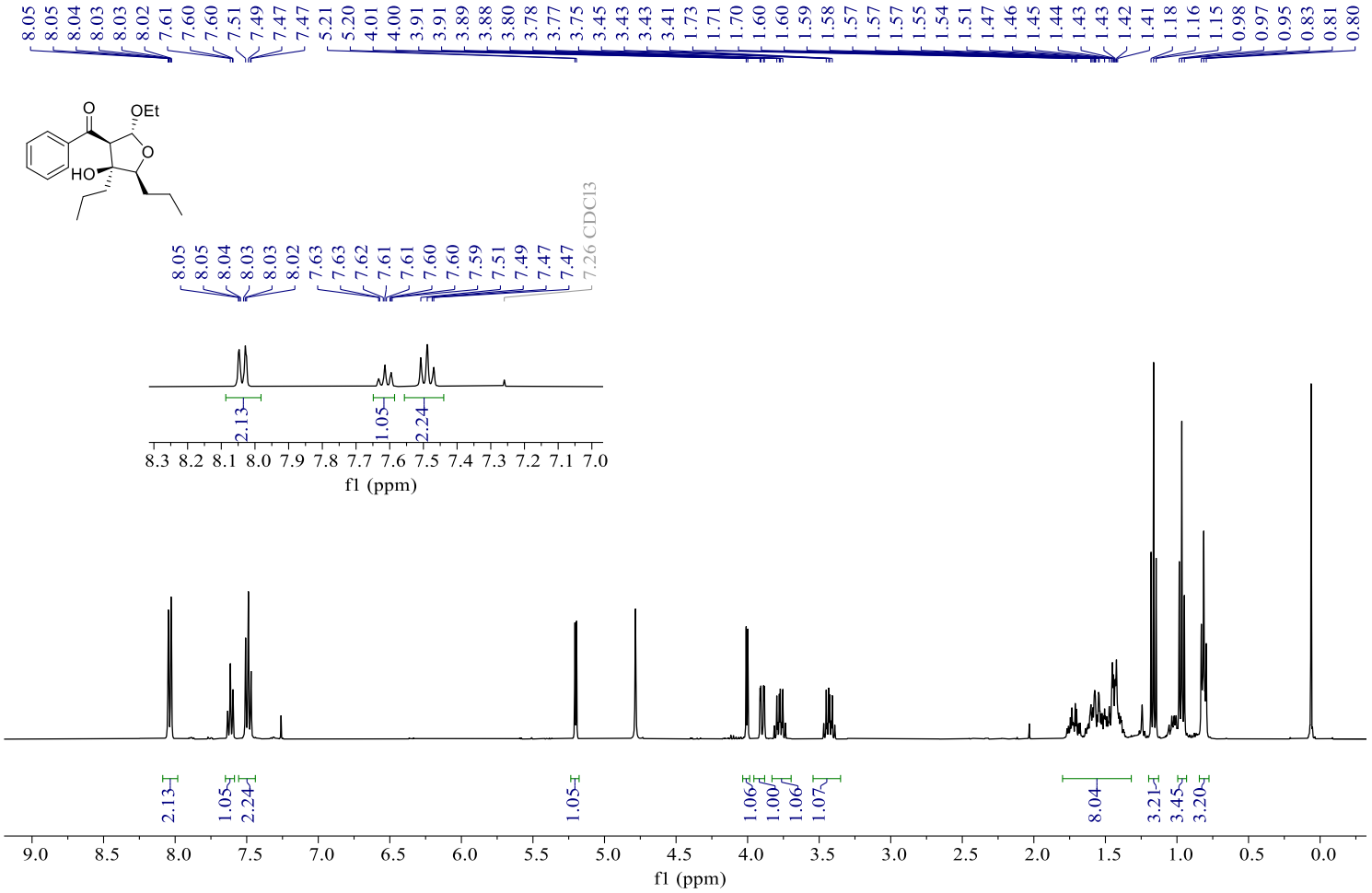
Compound 39 ^{1}H NMR (400 MHz, $CDCl_3$)



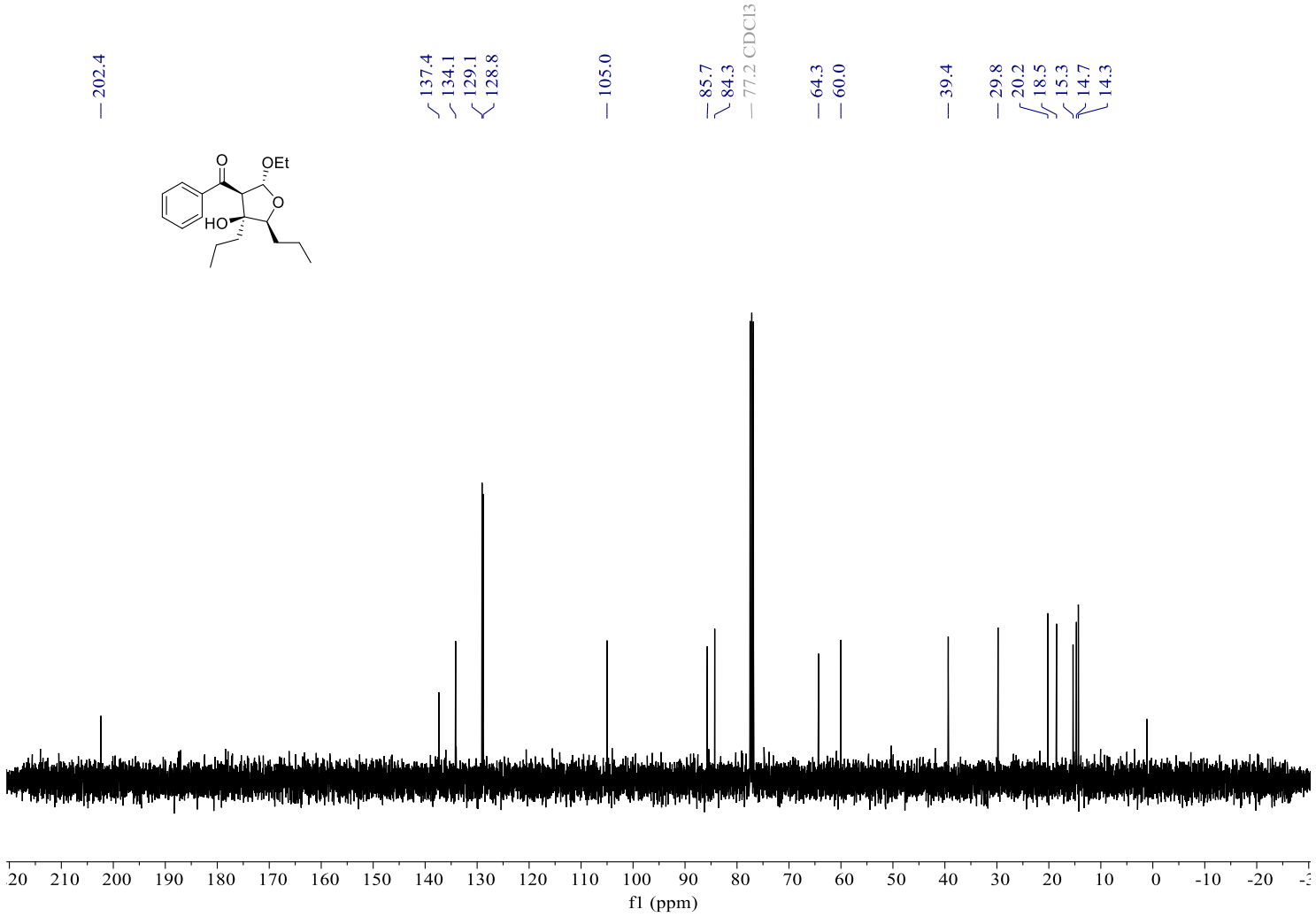
Compound 39 ^{13}C NMR (100 MHz, $CDCl_3$)



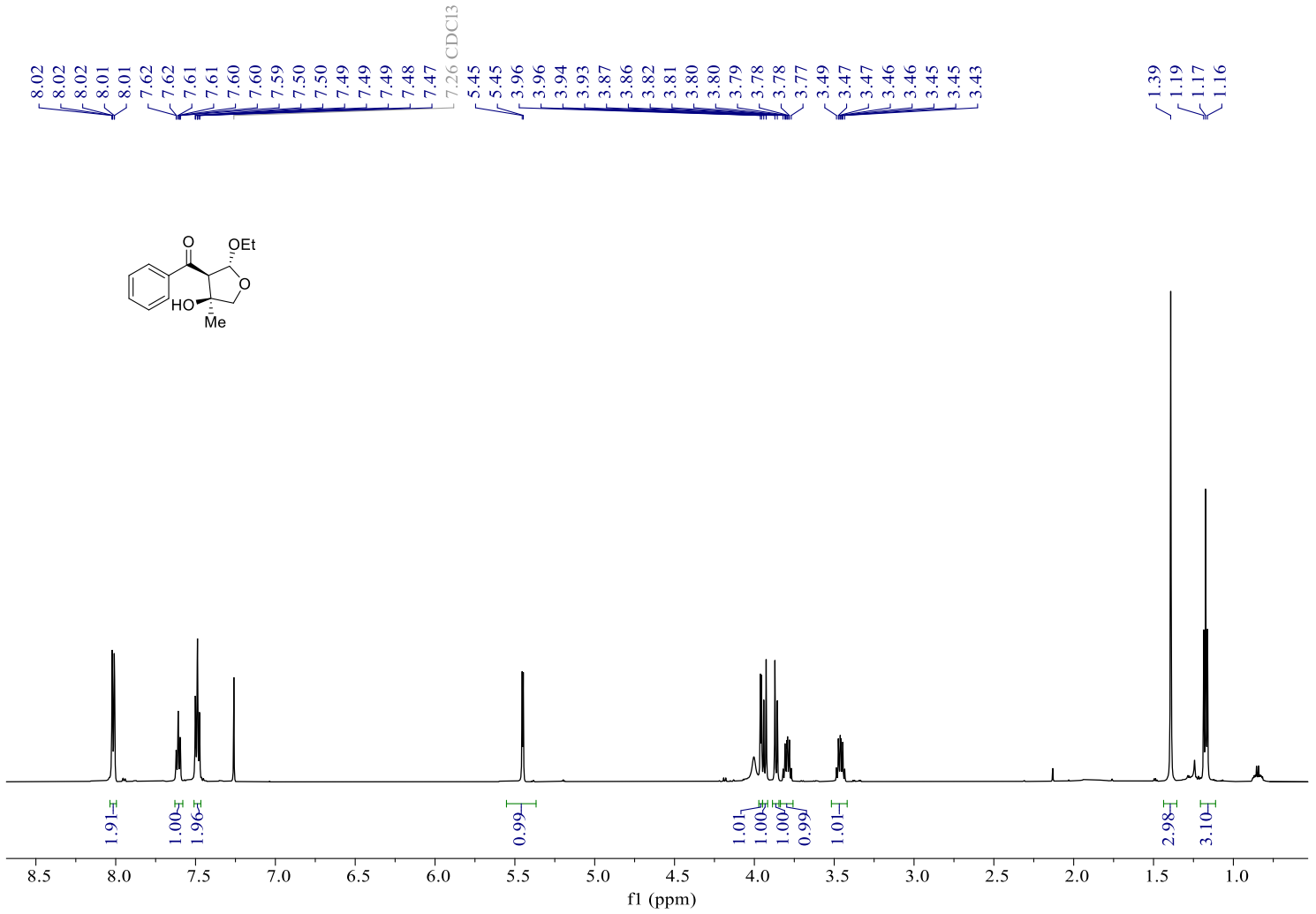
Compound 40 ^{1}H NMR (400 MHz, $CDCl_3$)



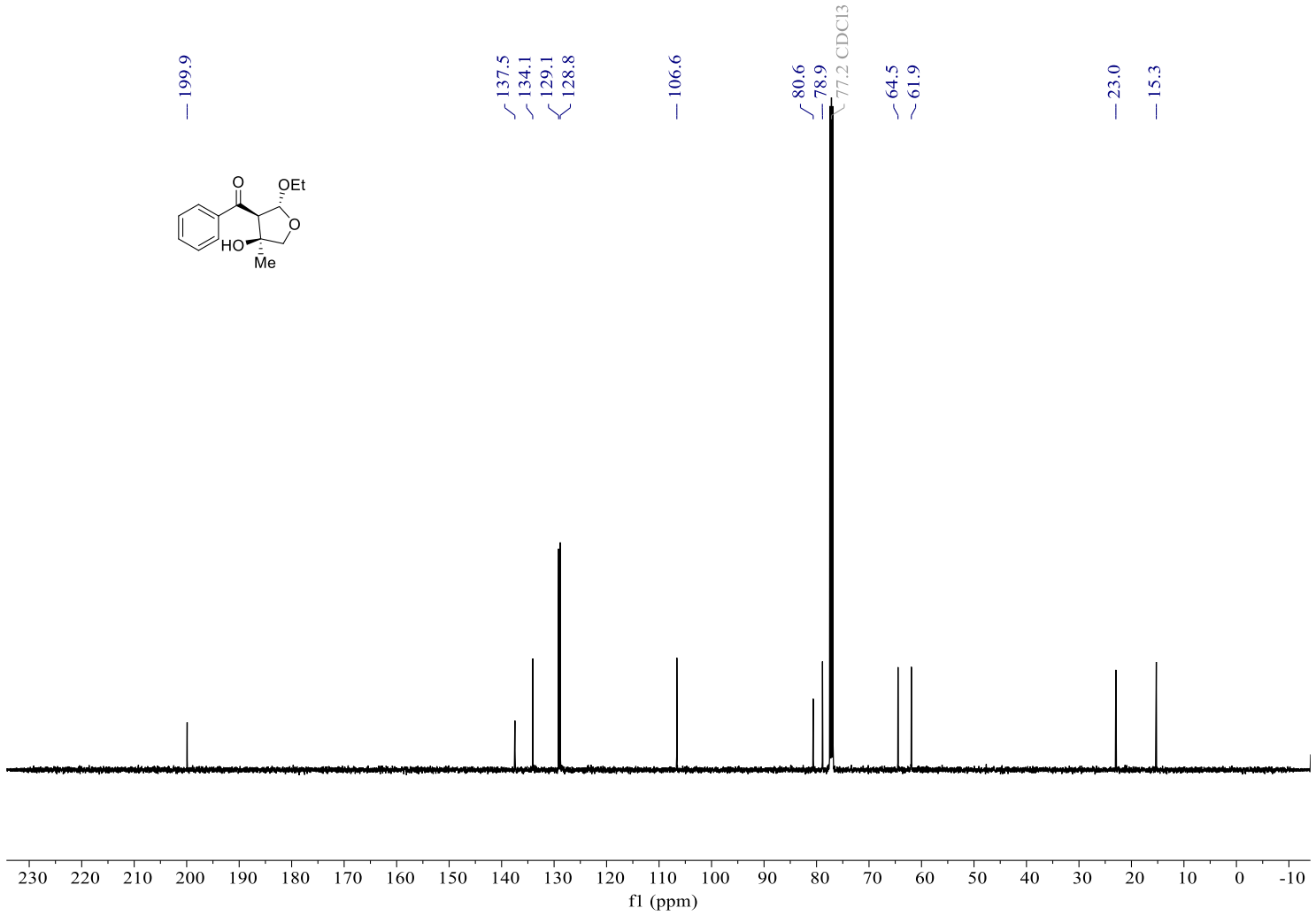
Compound 40 ^{13}C NMR (100 MHz, $CDCl_3$)



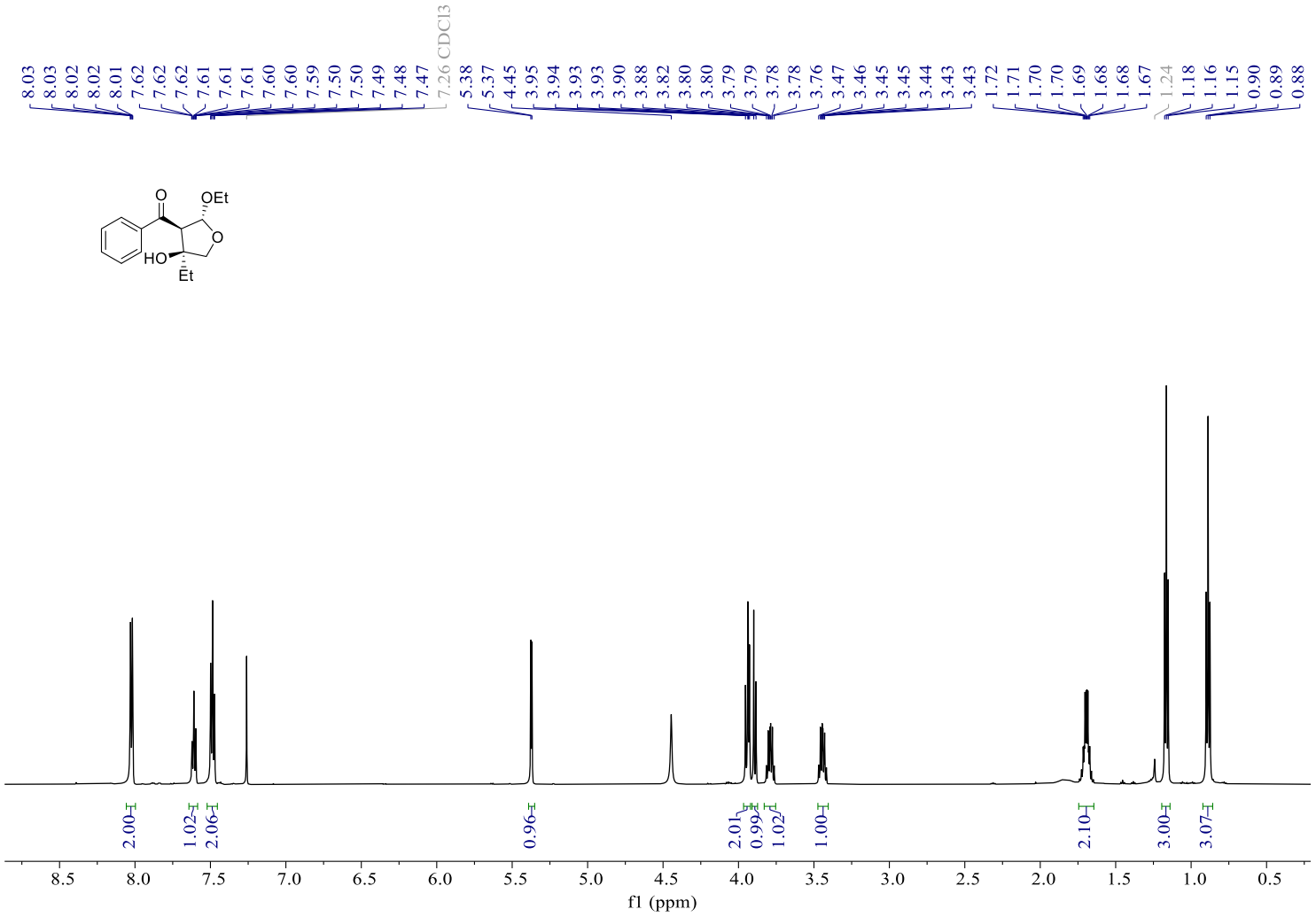
Compound 41 ^{1}H NMR (600 MHz, $CDCl_3$)



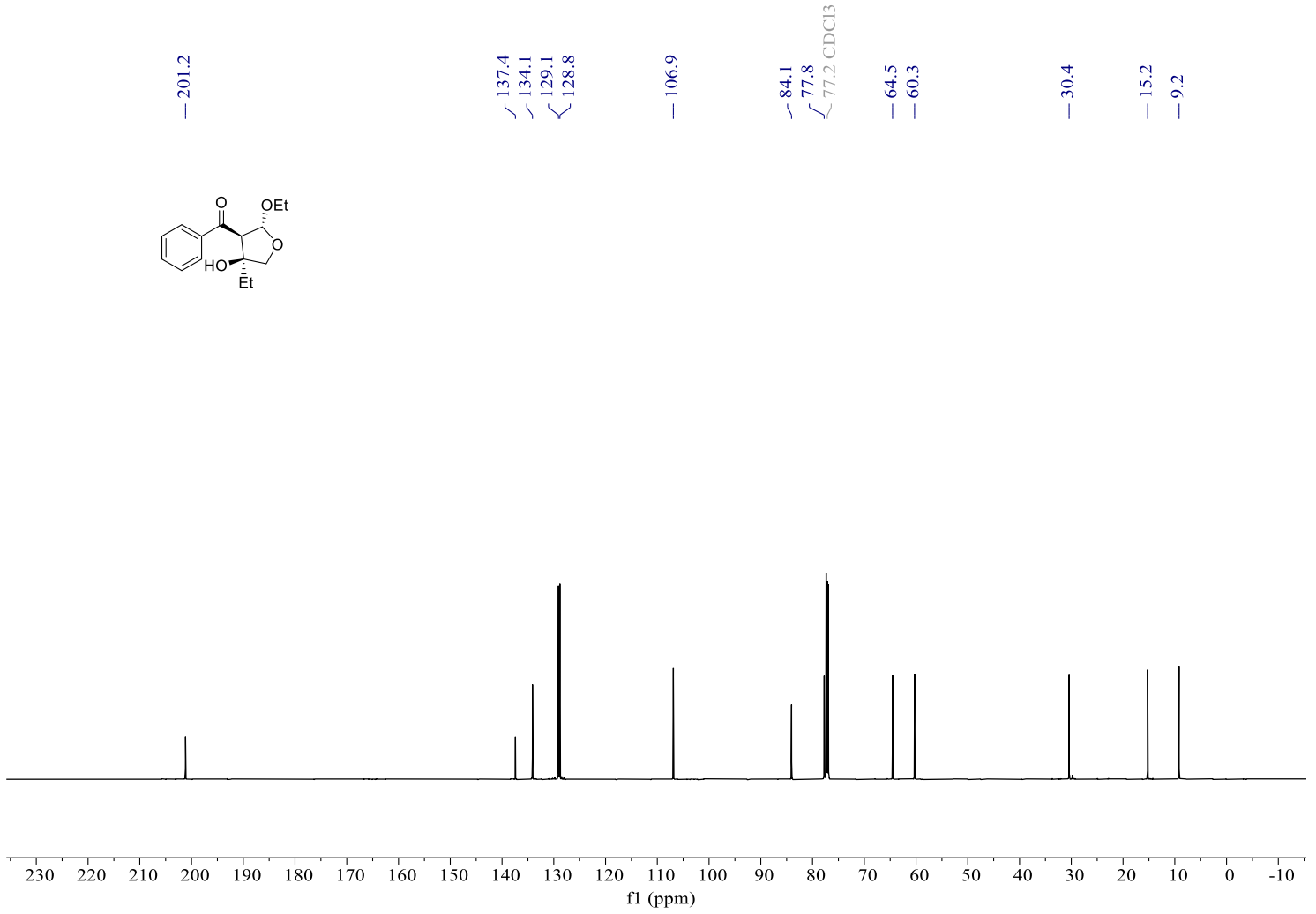
Compound 41 ^{13}C NMR (125 MHz, $CDCl_3$)



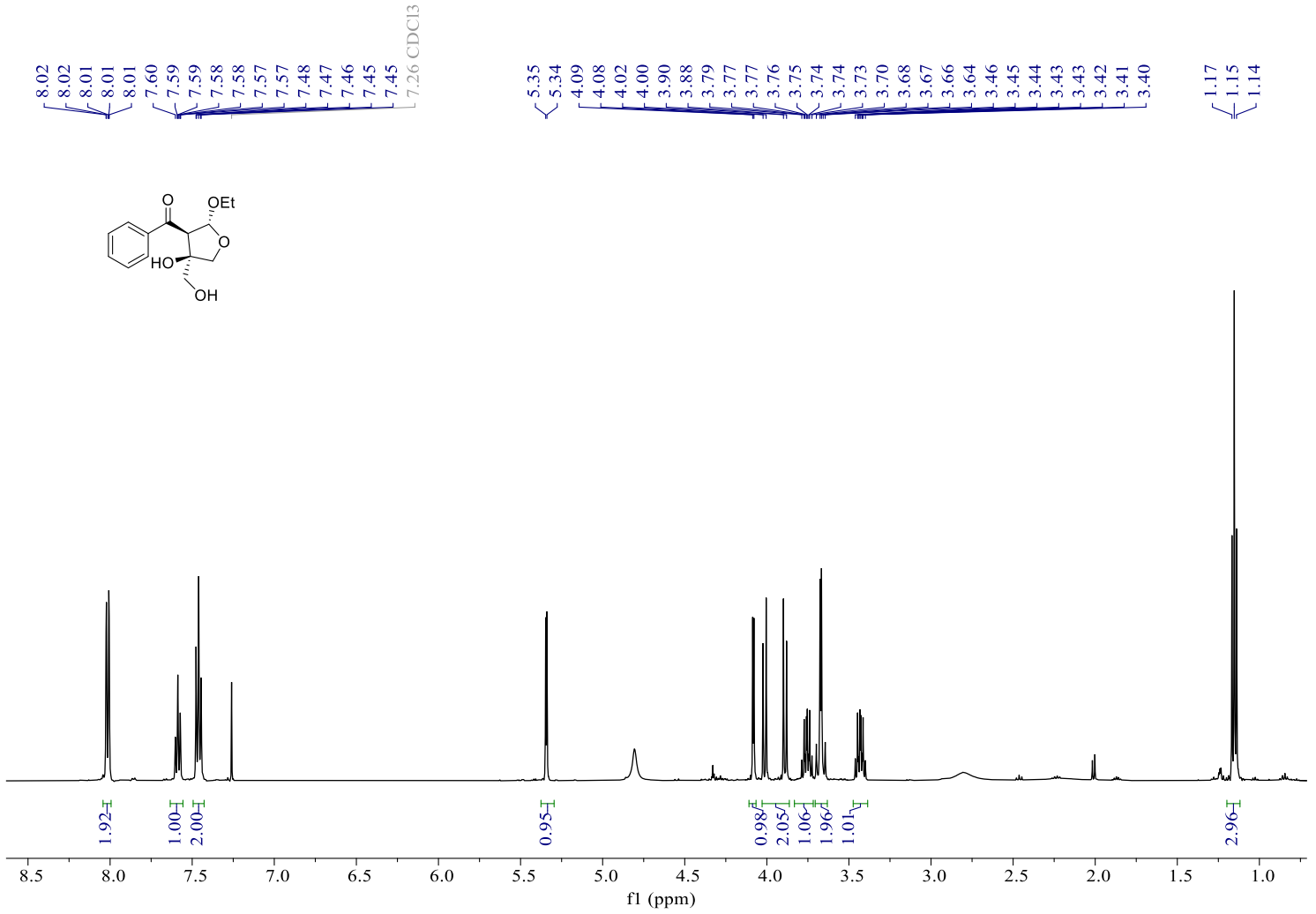
Compound 42 ^{1}H NMR (600 MHz, $CDCl_3$)



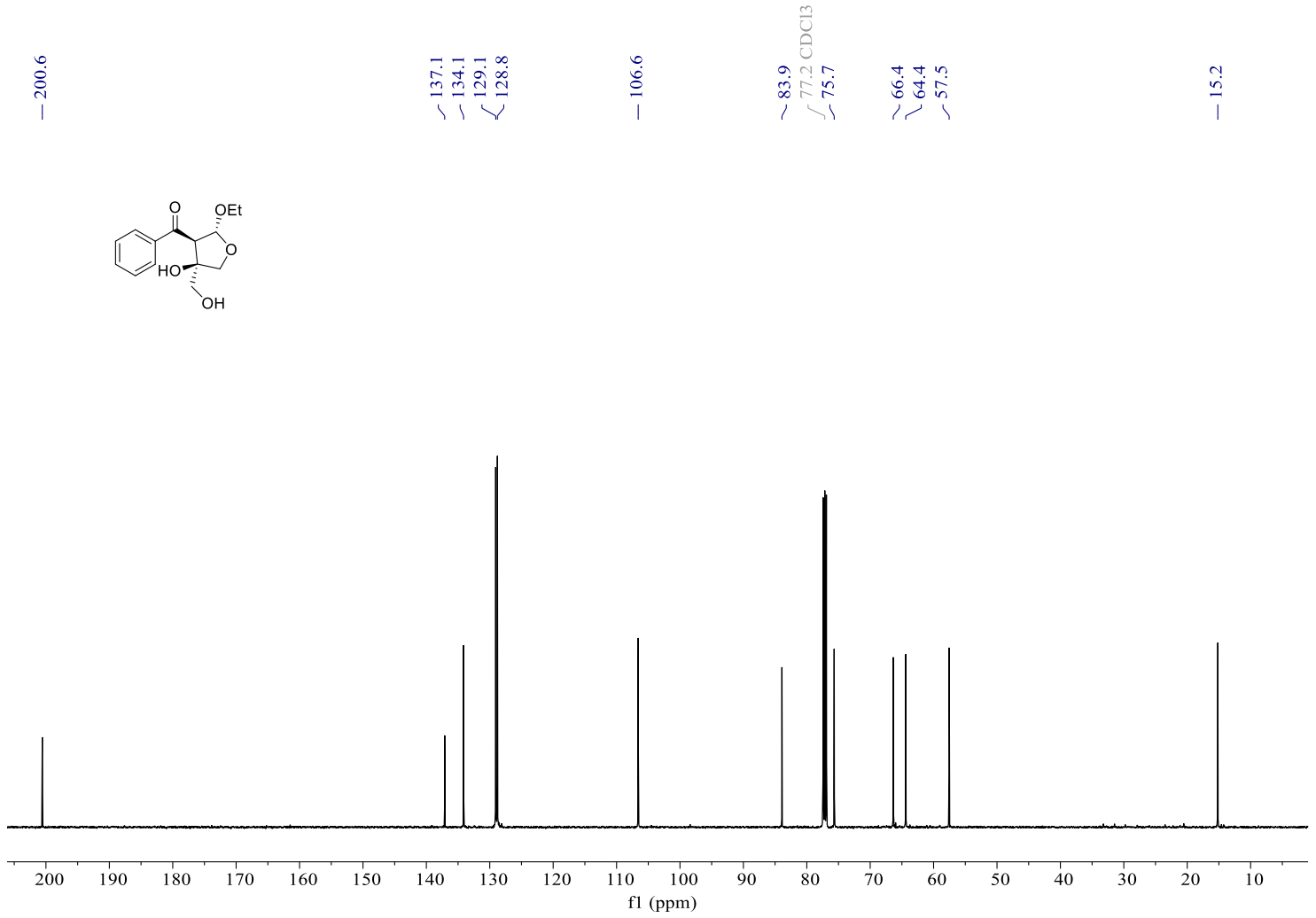
Compound 42 ^{13}C NMR (150 MHz, $CDCl_3$)



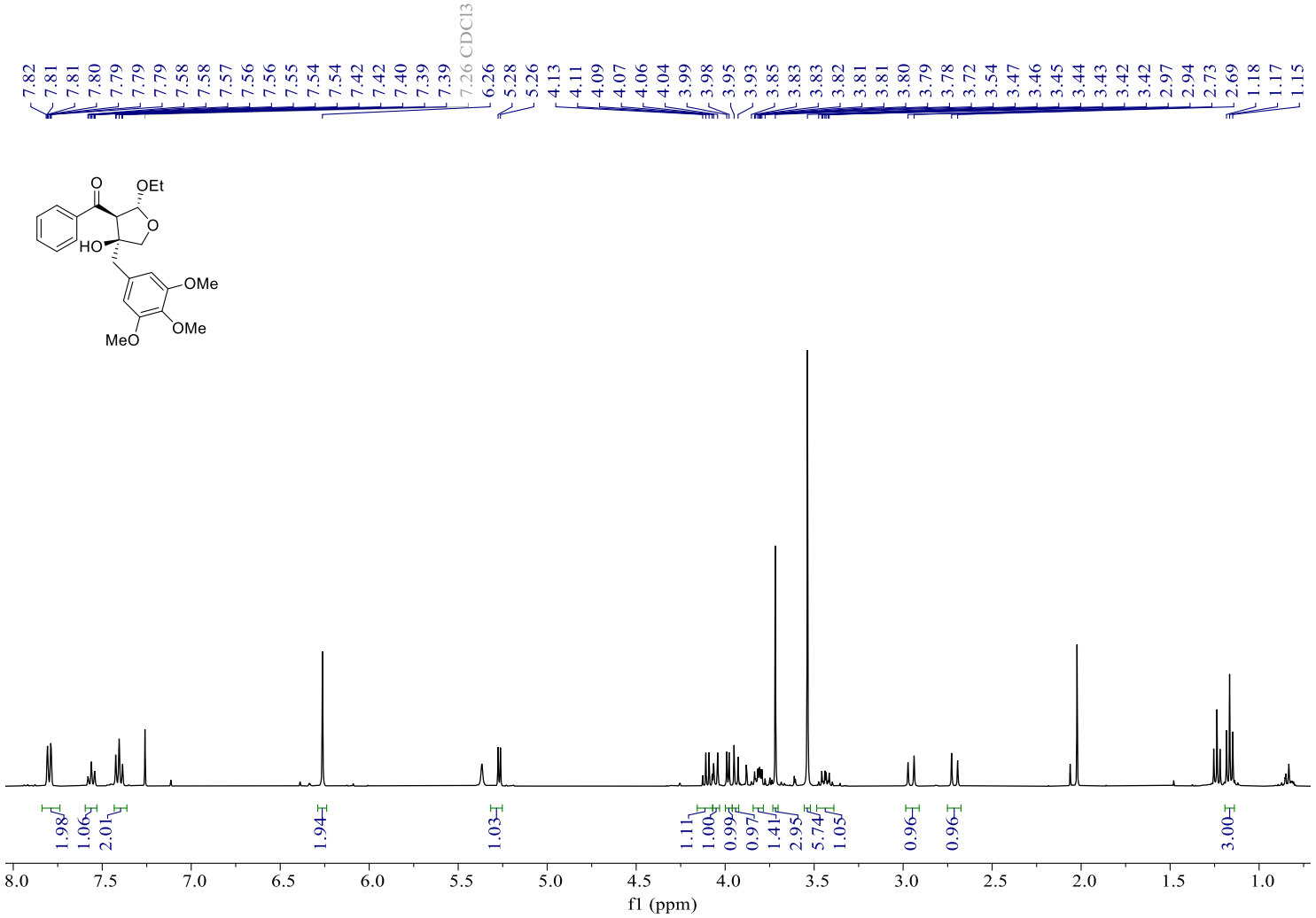
Compound 43 ^{1}H NMR (500 MHz, $CDCl_3$)



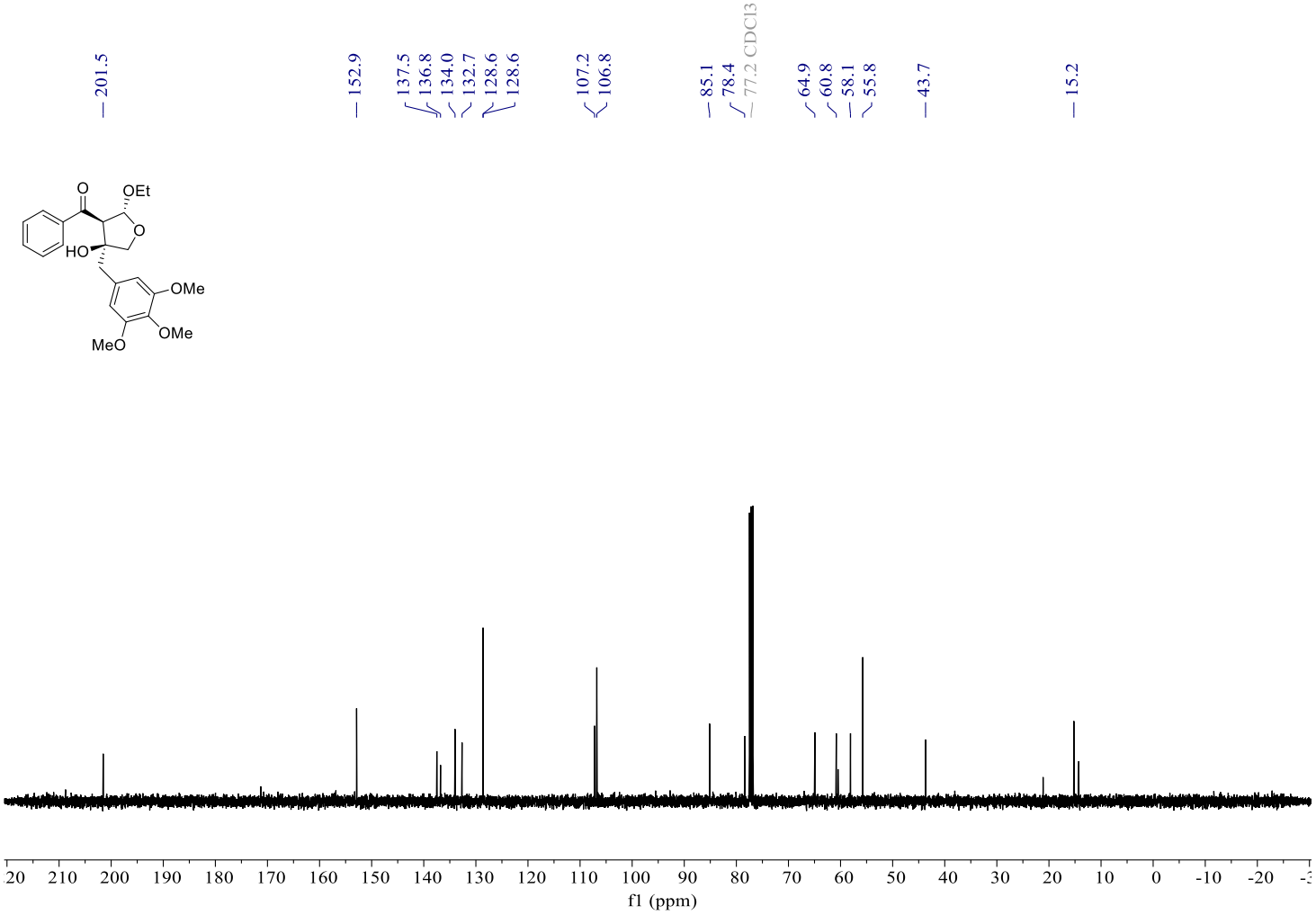
Compound 43 ^{13}C NMR (125 MHz, $CDCl_3$)



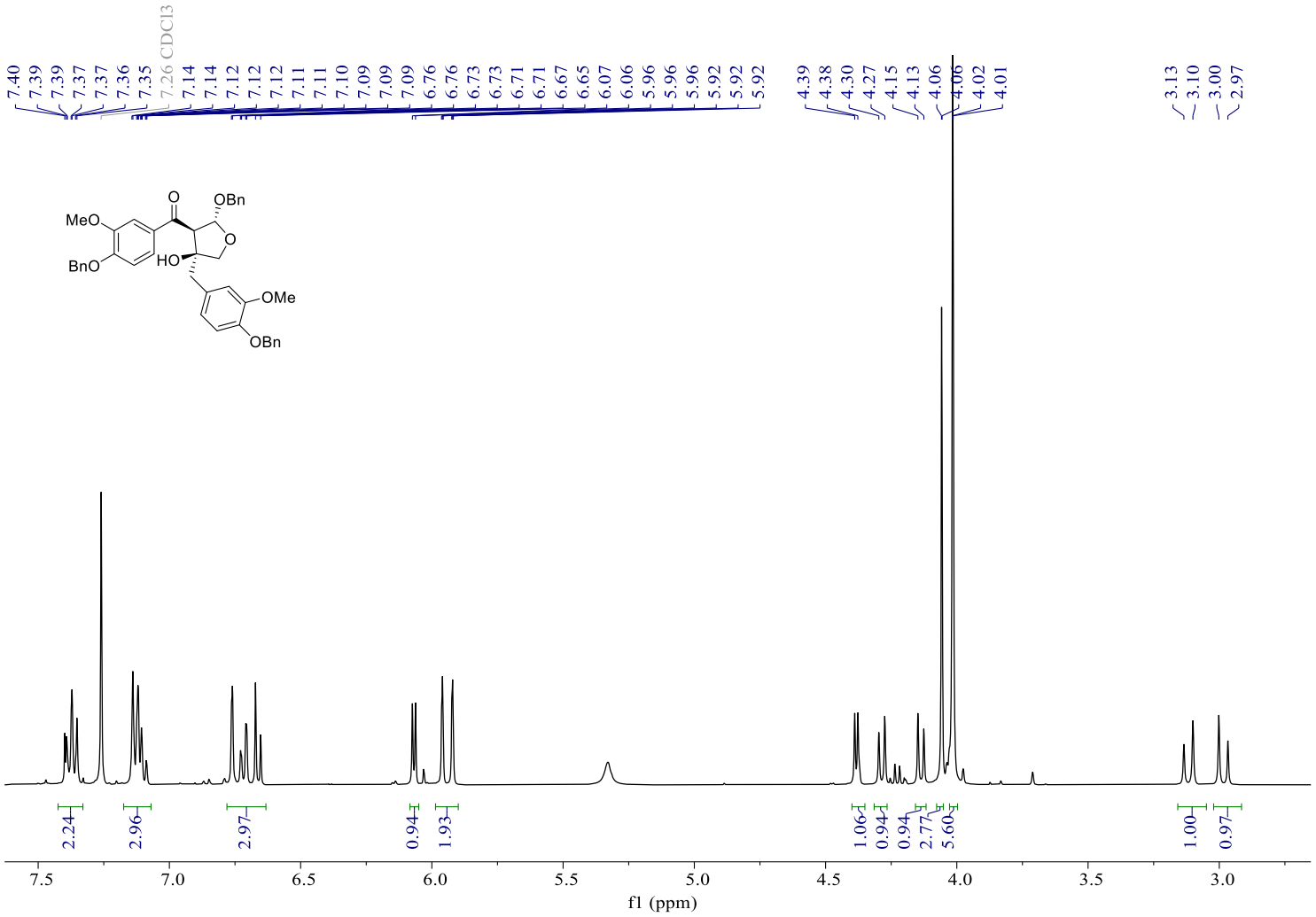
Compound 44 ^{1}H NMR (400 MHz, $CDCl_3$)



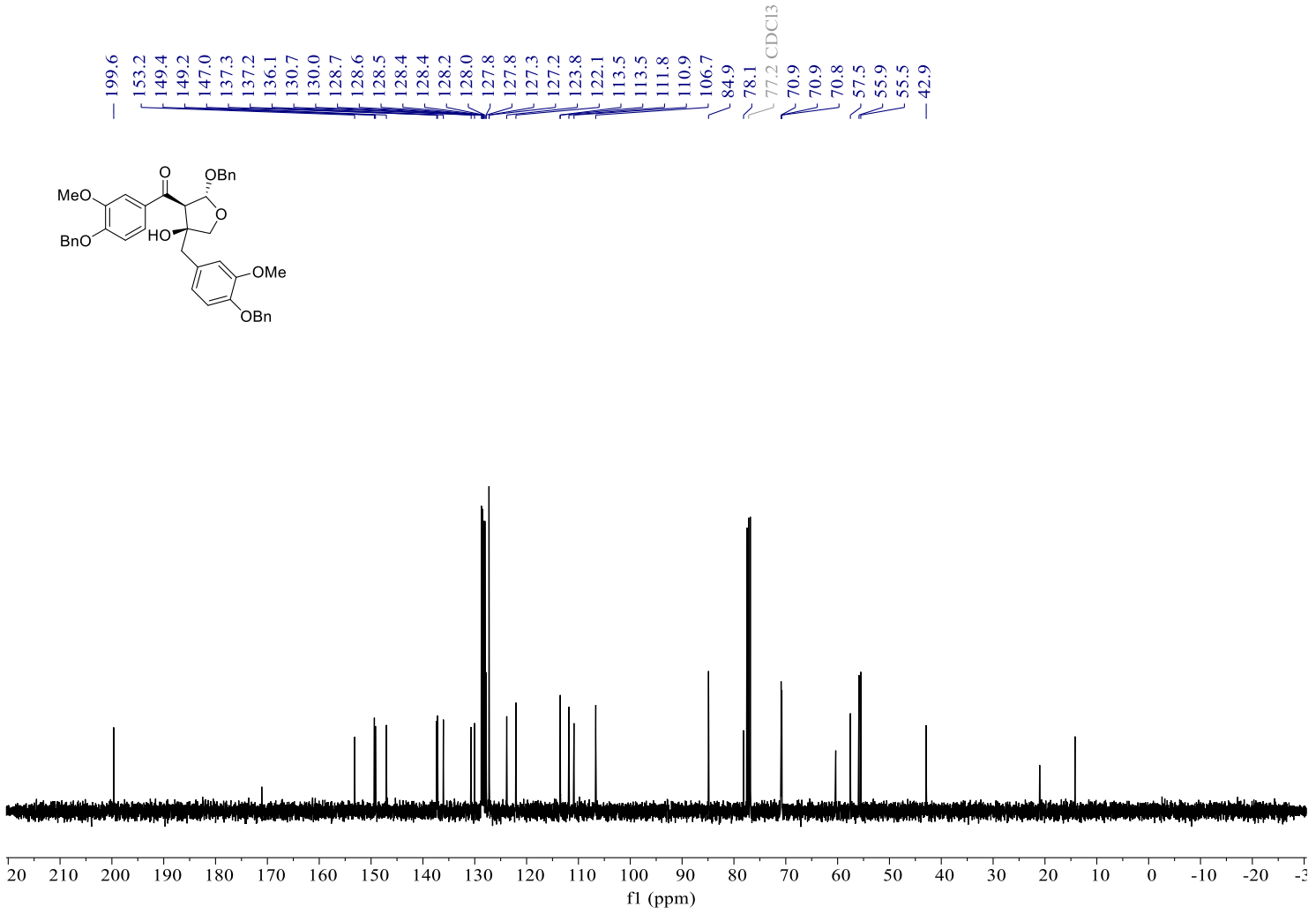
Compound 44 ^{13}C NMR (100 MHz, $CDCl_3$)



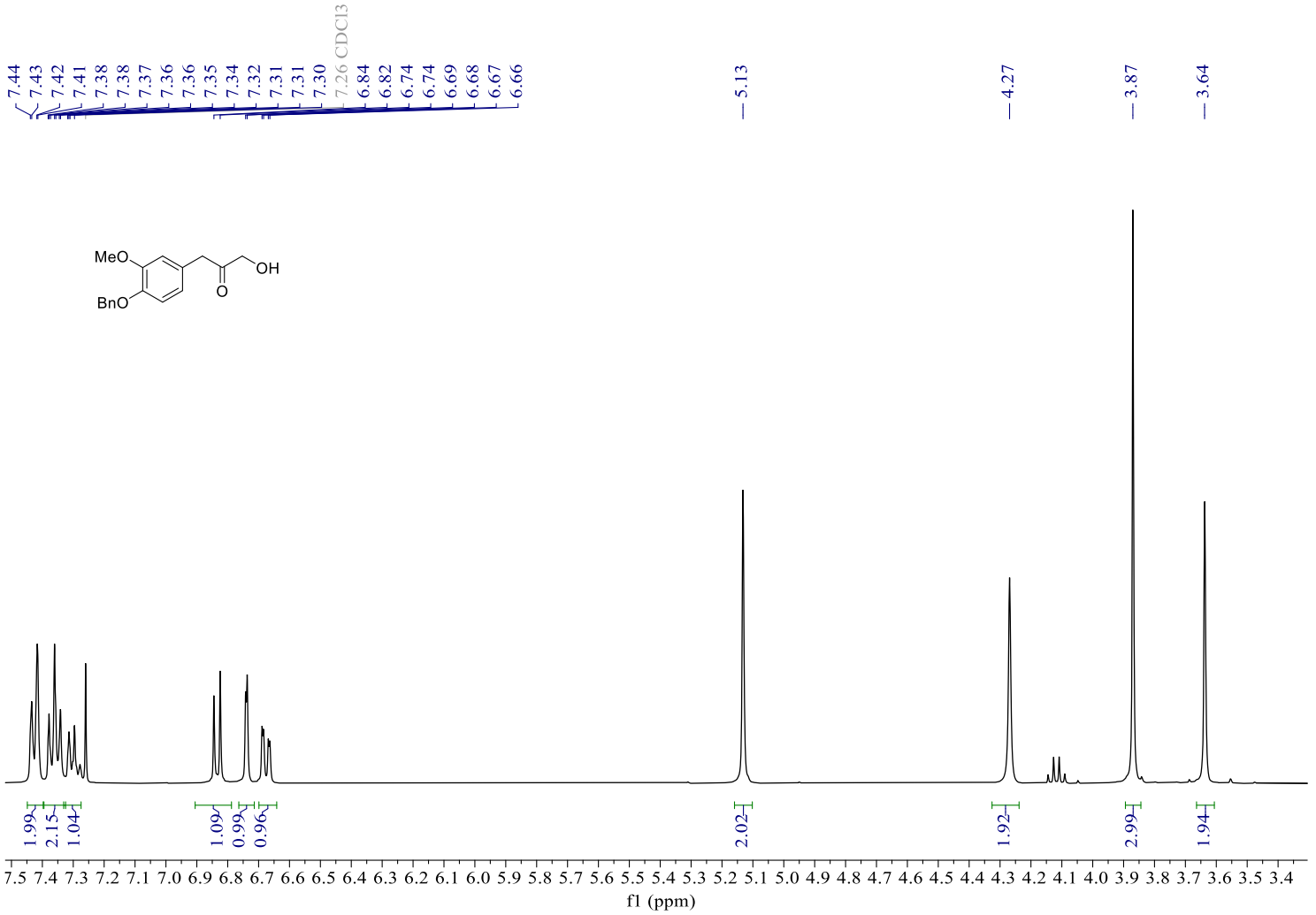
Compound 45 ^{1}H NMR (400 MHz, $CDCl_3$)



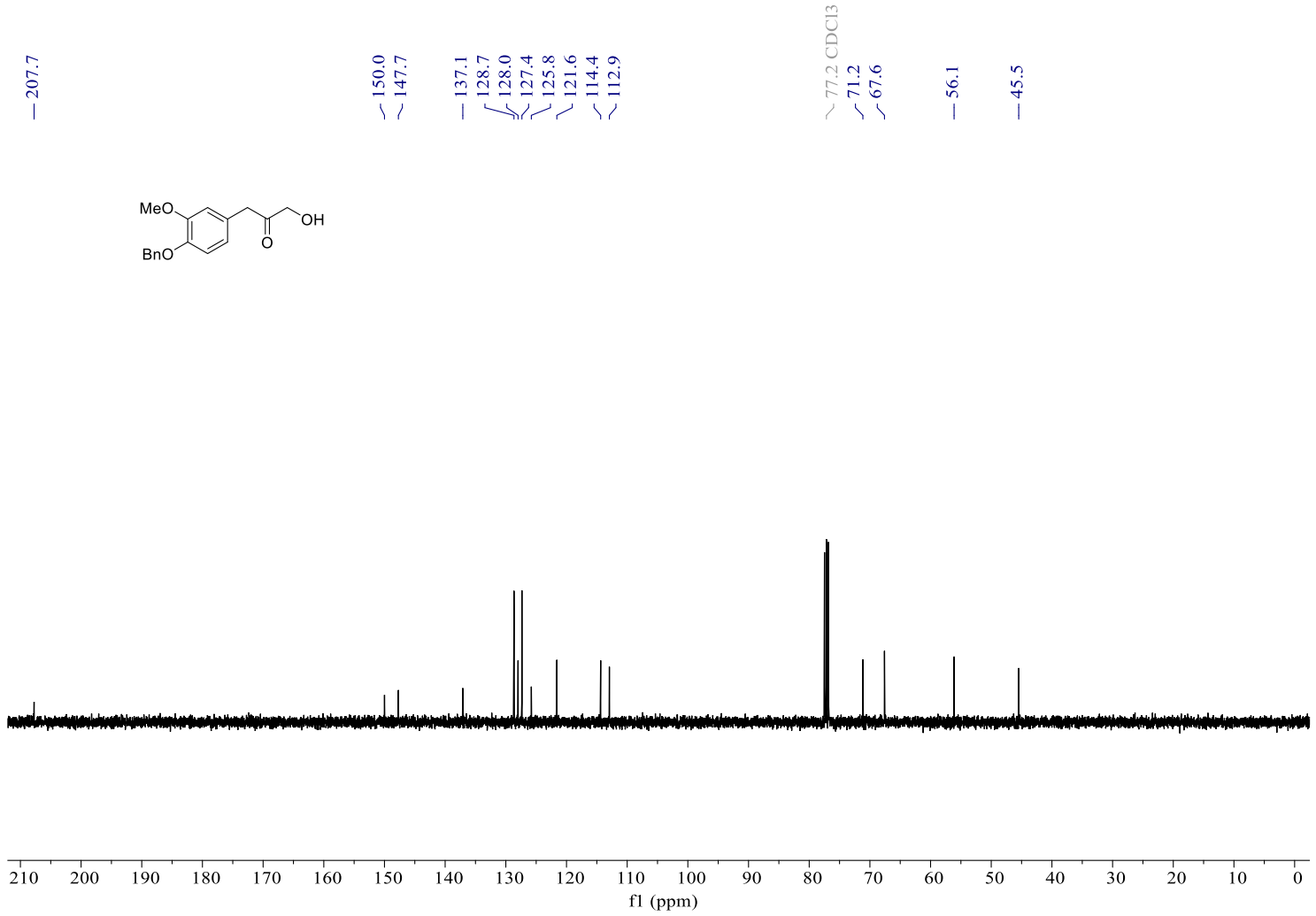
Compound 45 ^{13}C NMR (100 MHz, $CDCl_3$)



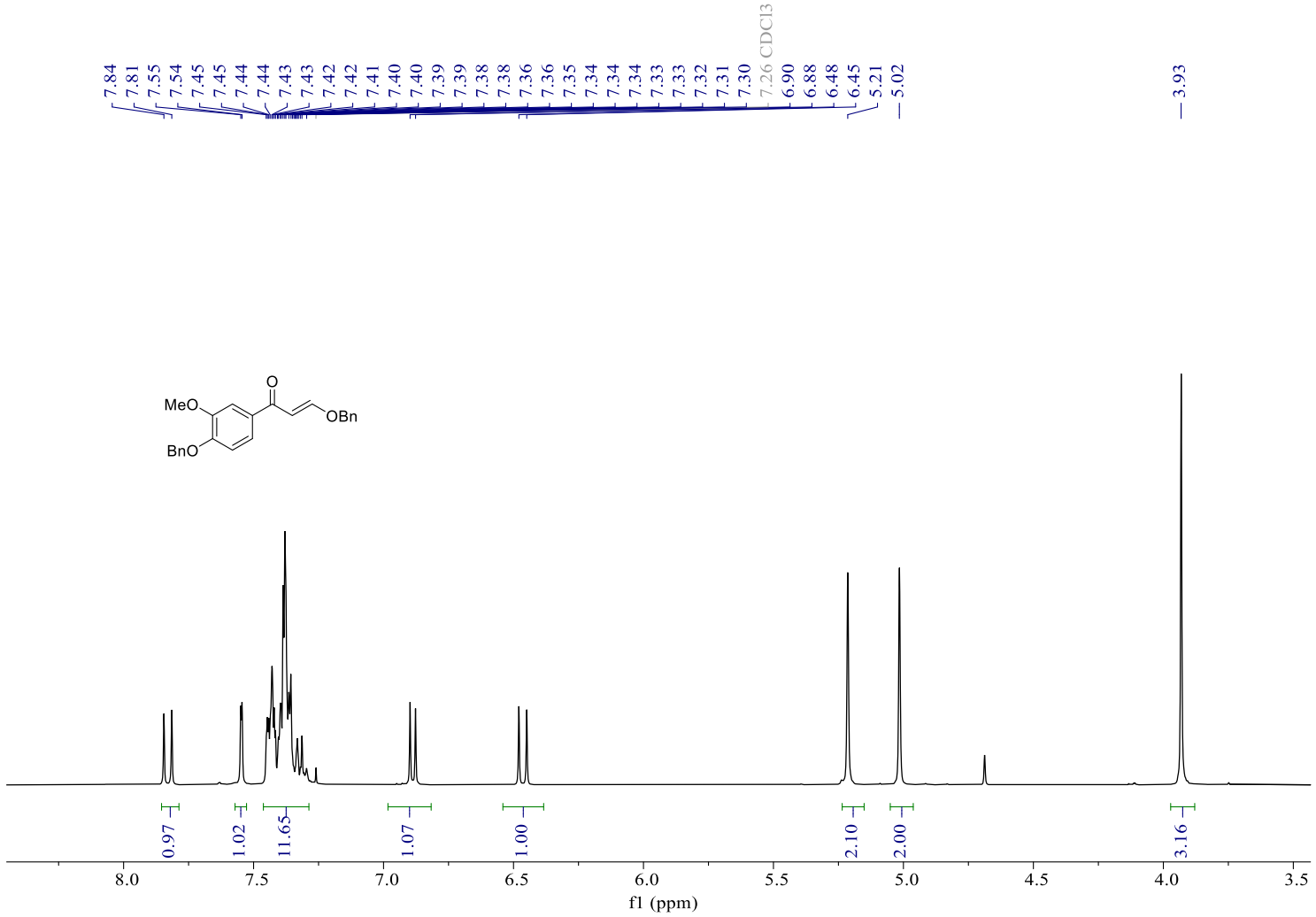
Compound 45a ^{1}H NMR (400 MHz, $CDCl_3$)



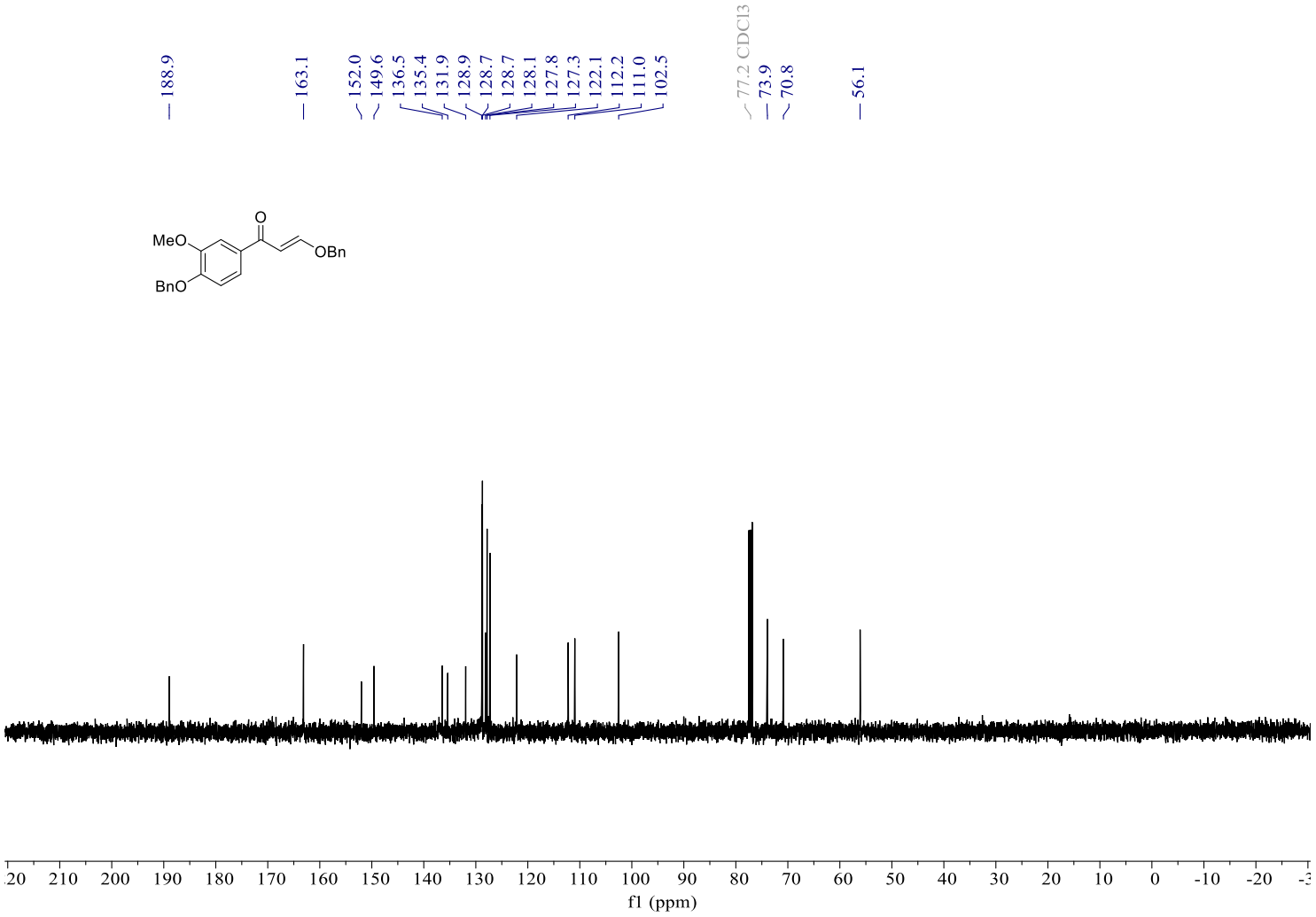
Compound 45a ^{13}C NMR (100 MHz, $CDCl_3$)



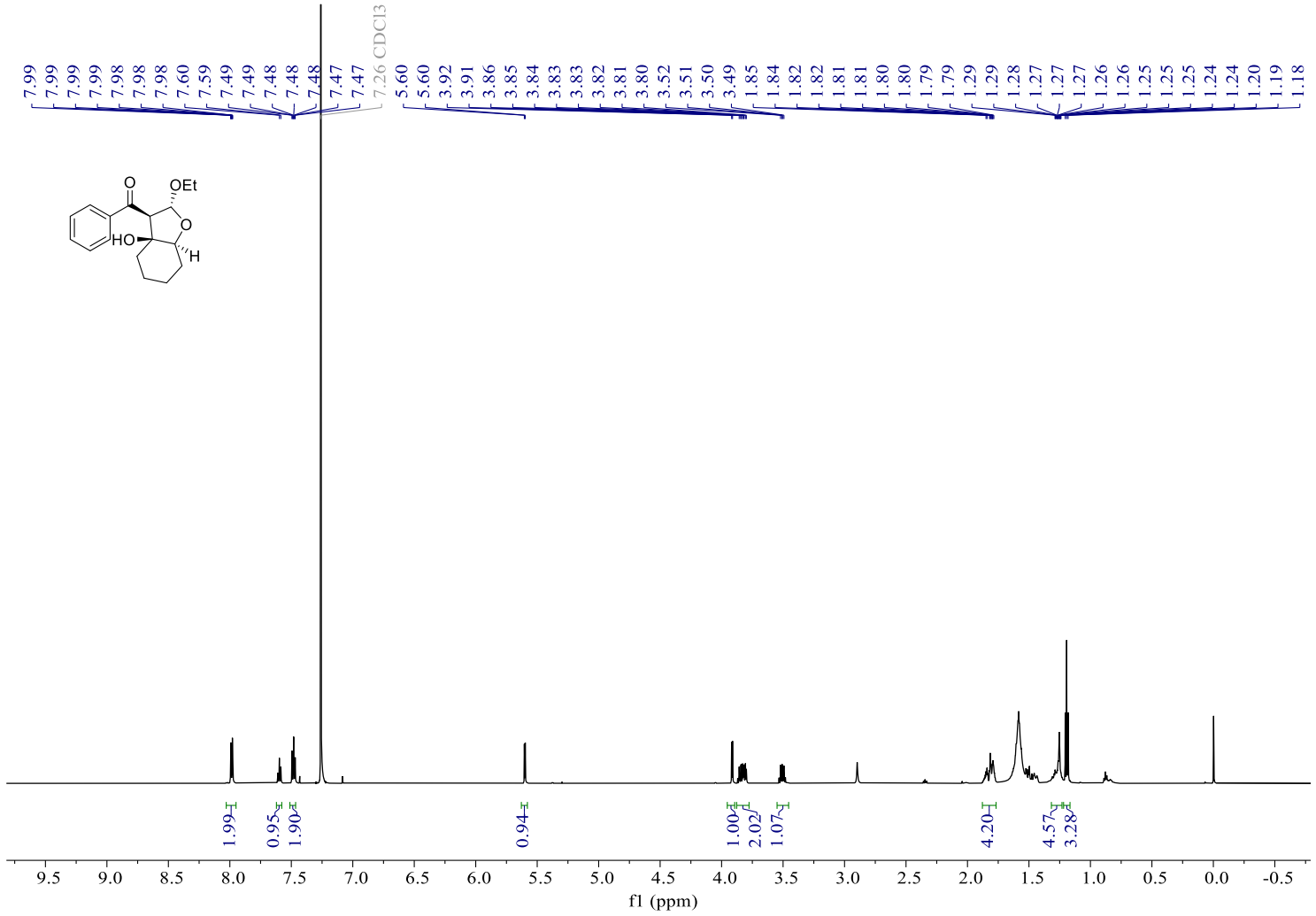
Compound 45b ^{1}H NMR (800 MHz, $CDCl_3$)



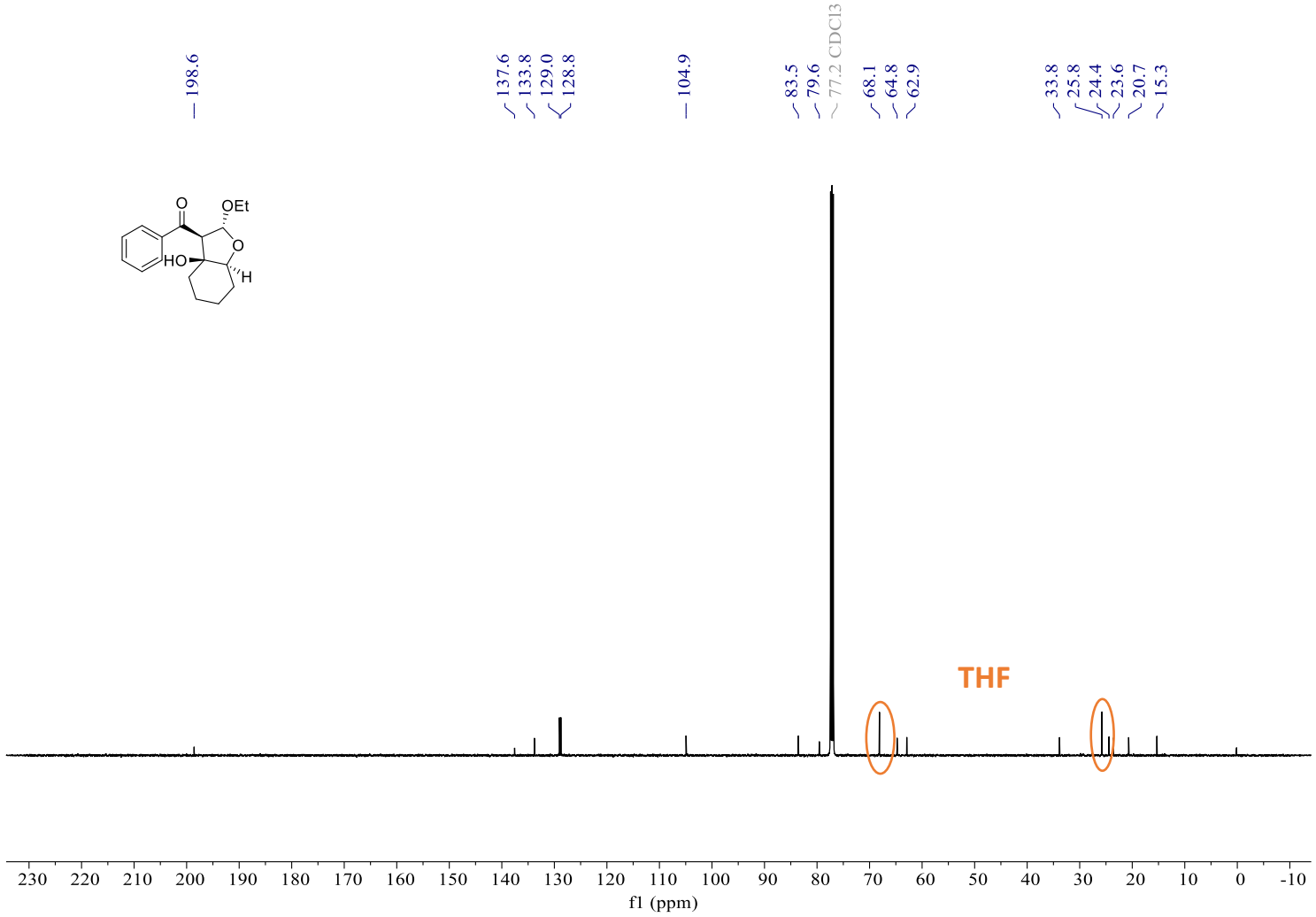
Compound 45b ^{13}C NMR (100 MHz, $CDCl_3$)



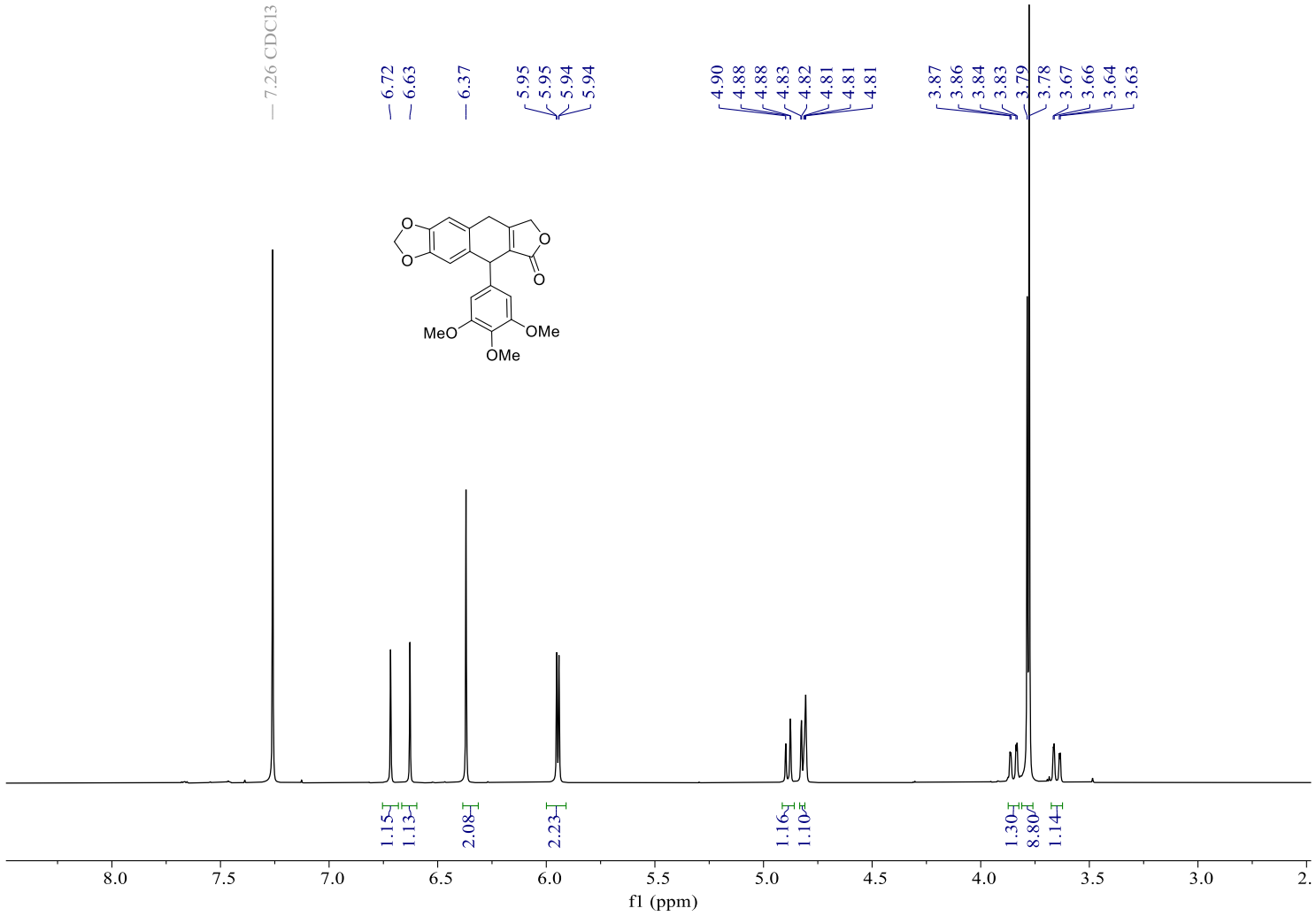
Compound 51 ^{1}H NMR (600 MHz, $CDCl_3$)



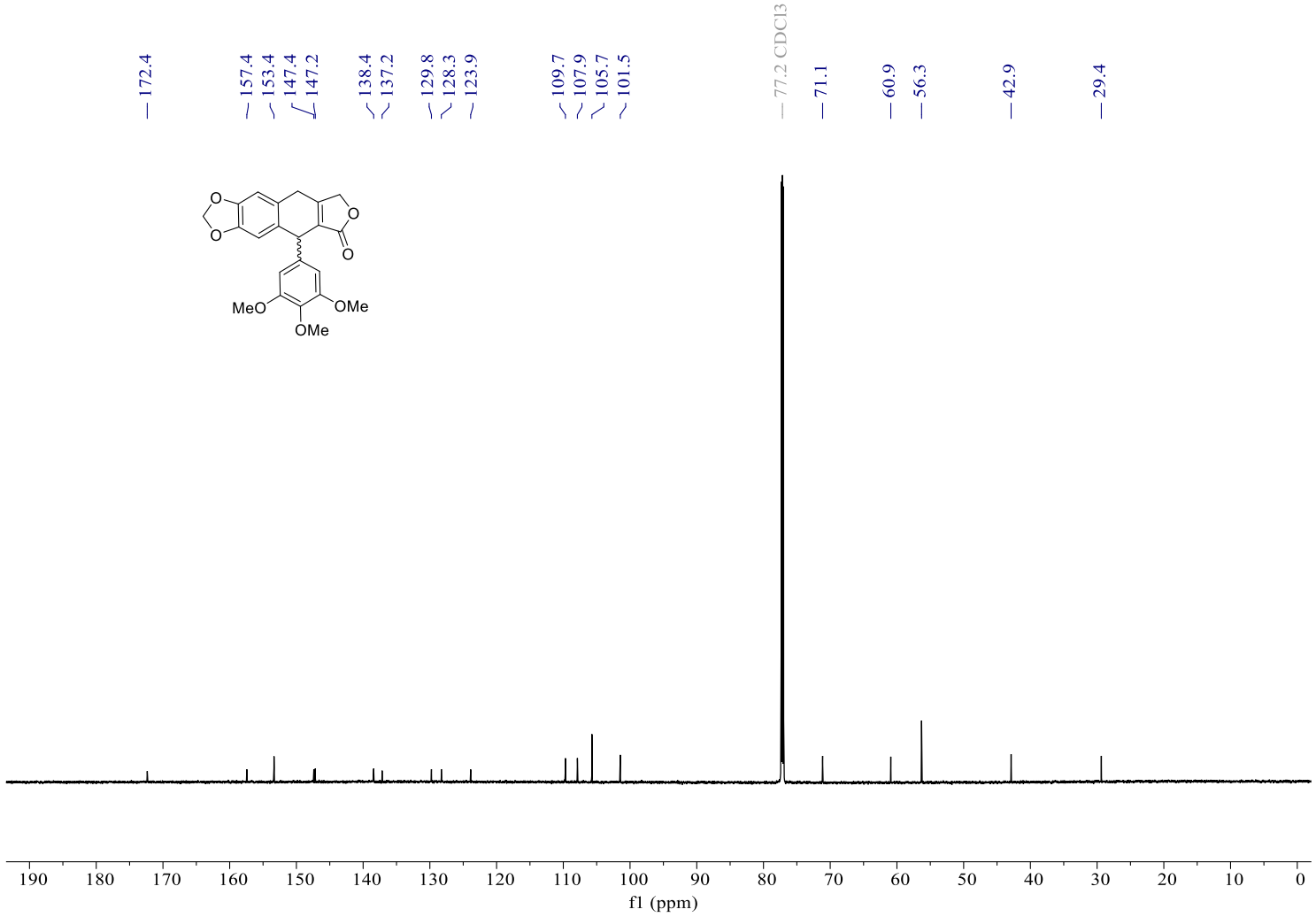
Compound 51 ^{13}C NMR (125 MHz, $CDCl_3$)



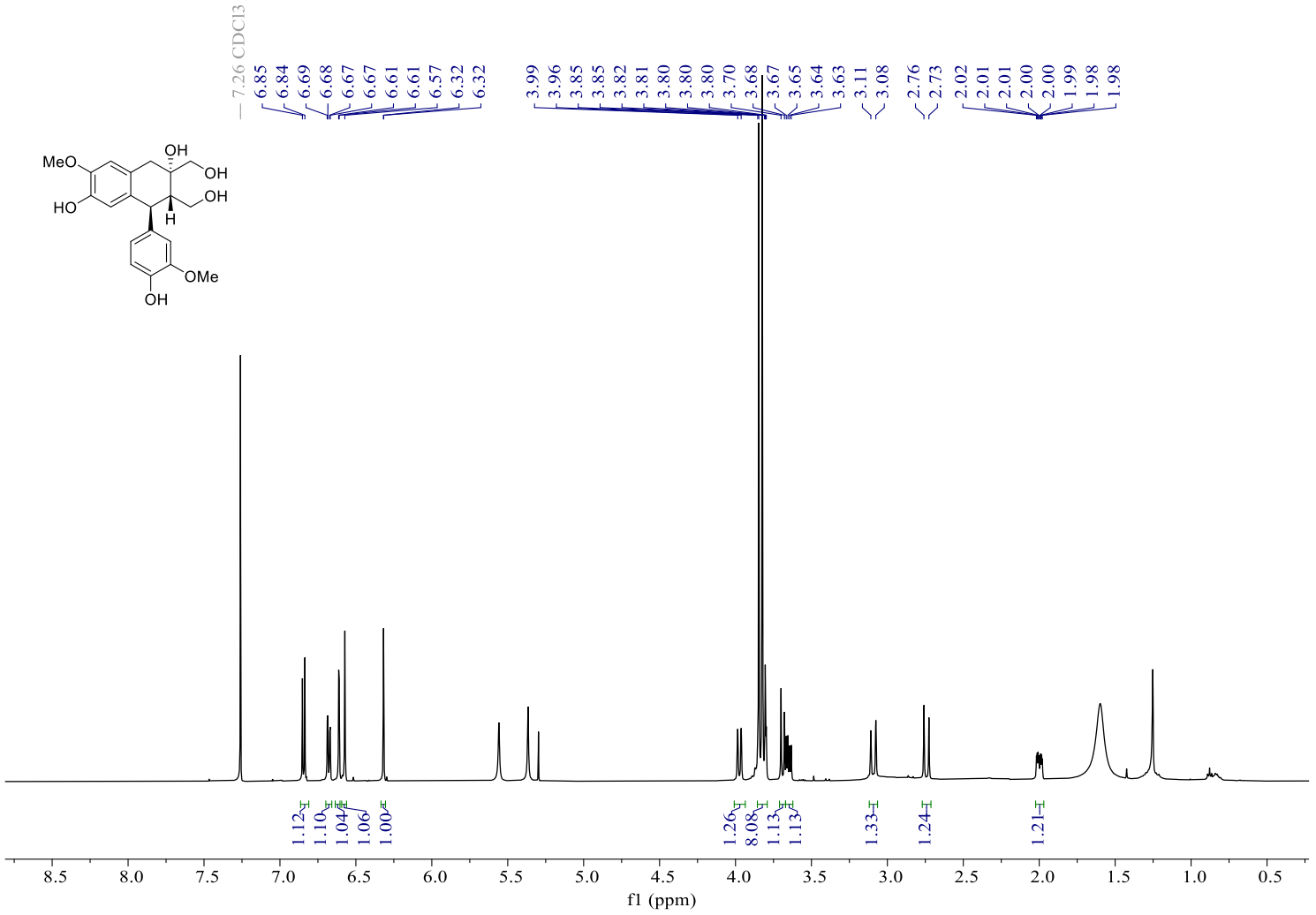
Compound 53 ^{1}H NMR (800 MHz, $CDCl_3$)



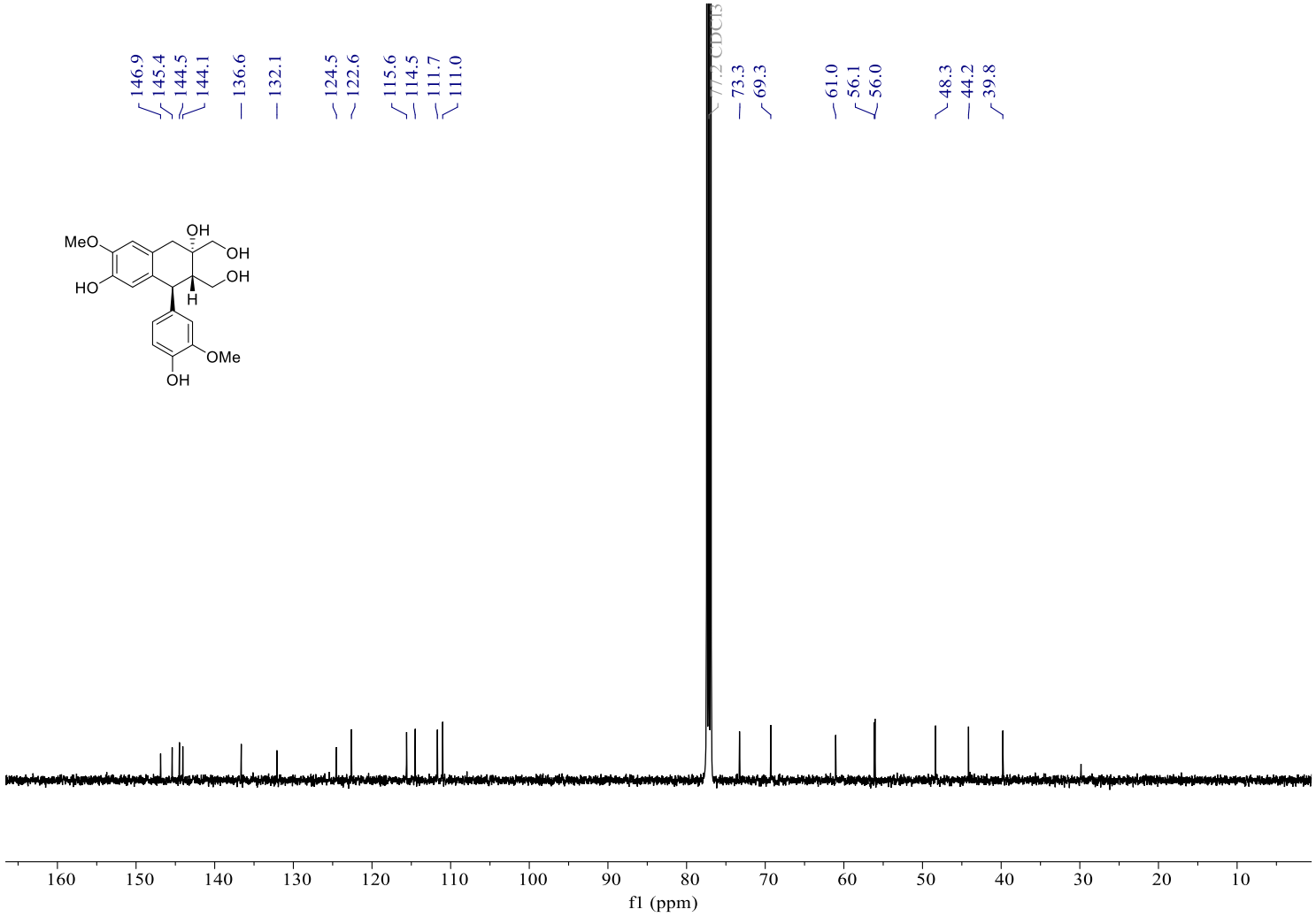
Compound 53 ^{13}C NMR (200 MHz, $CDCl_3$)



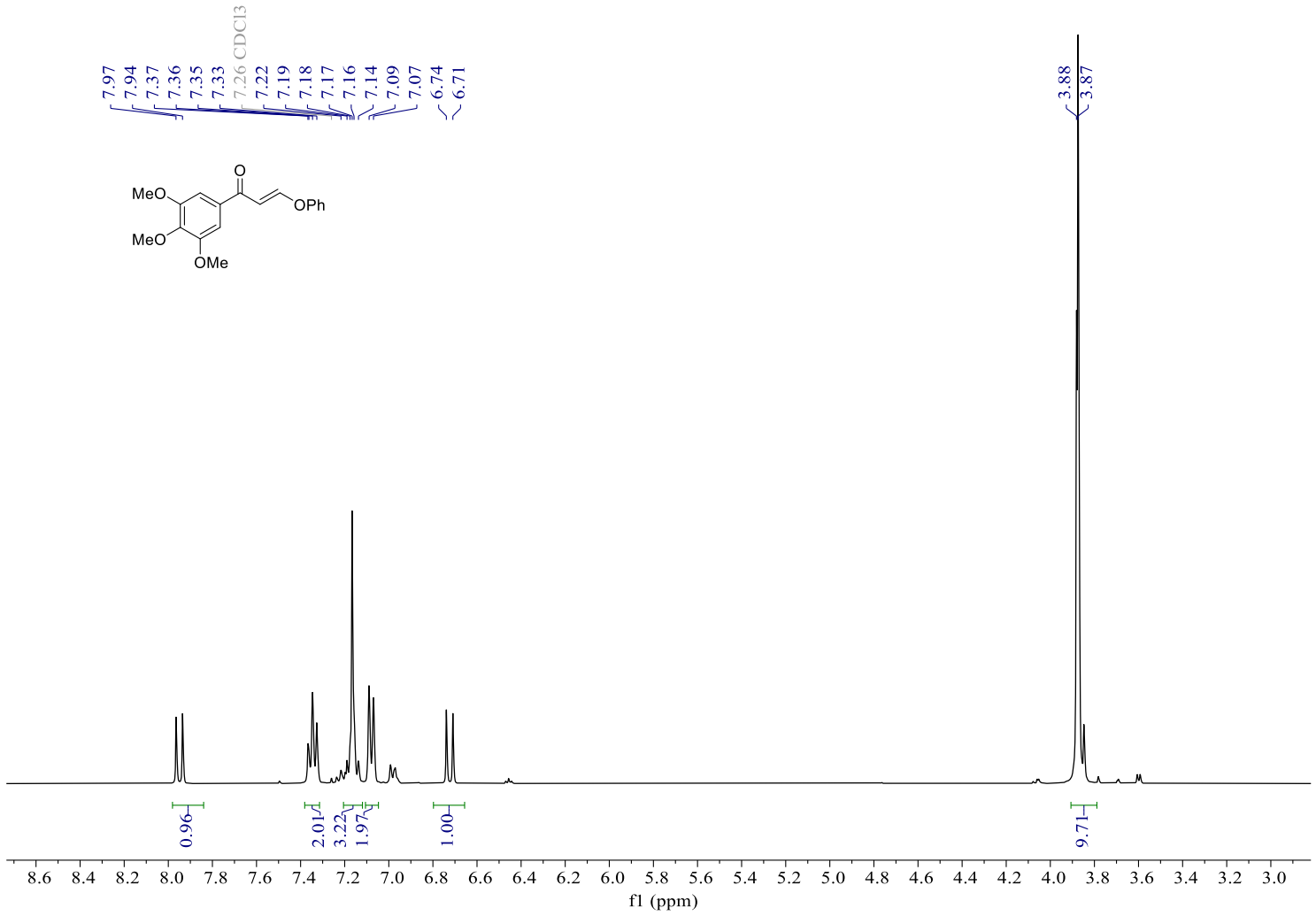
Compound 54 ^{1}H NMR (500 MHz, $CDCl_3$)



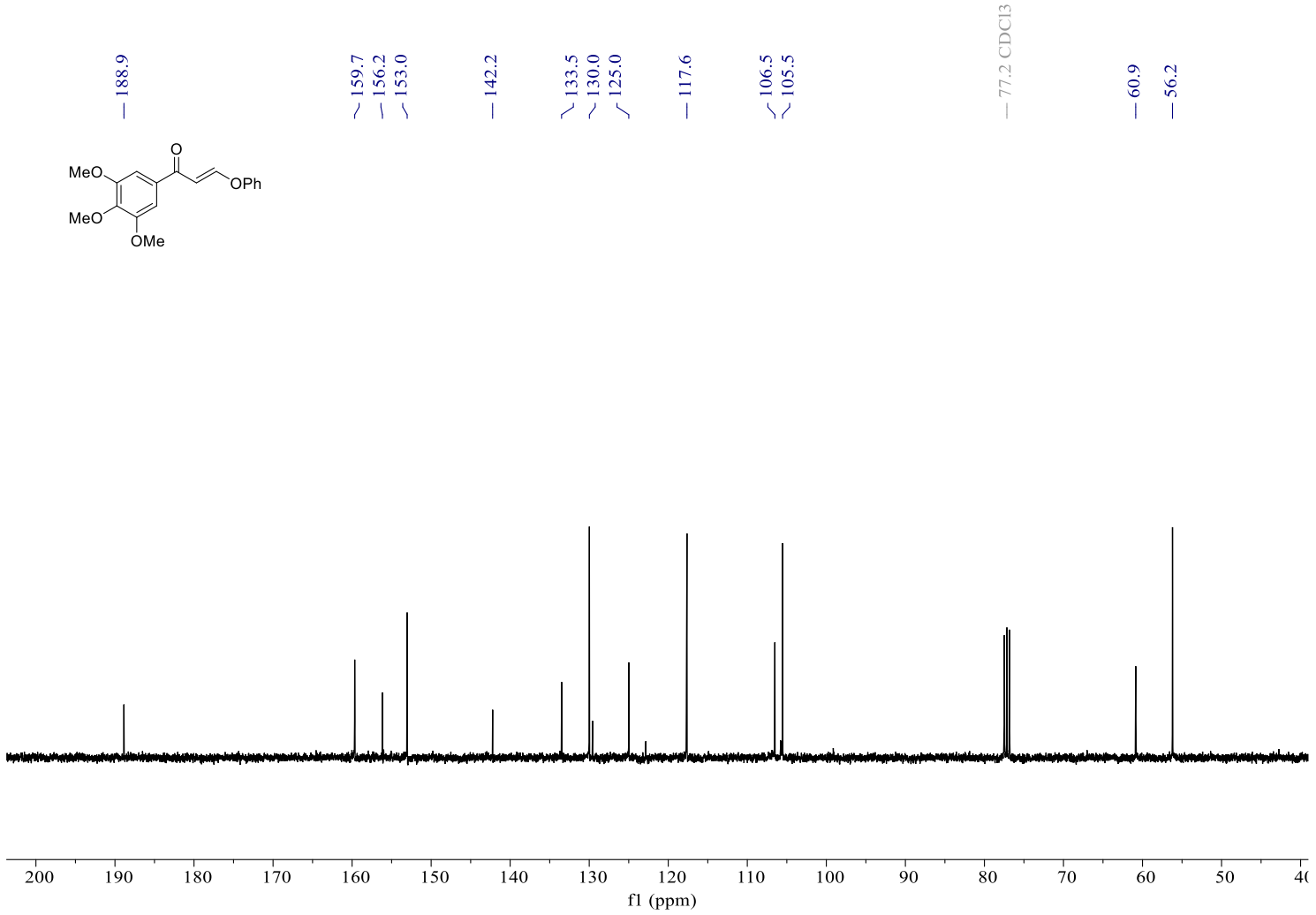
Compound 54 ^{13}C NMR (125 MHz, $CDCl_3$)



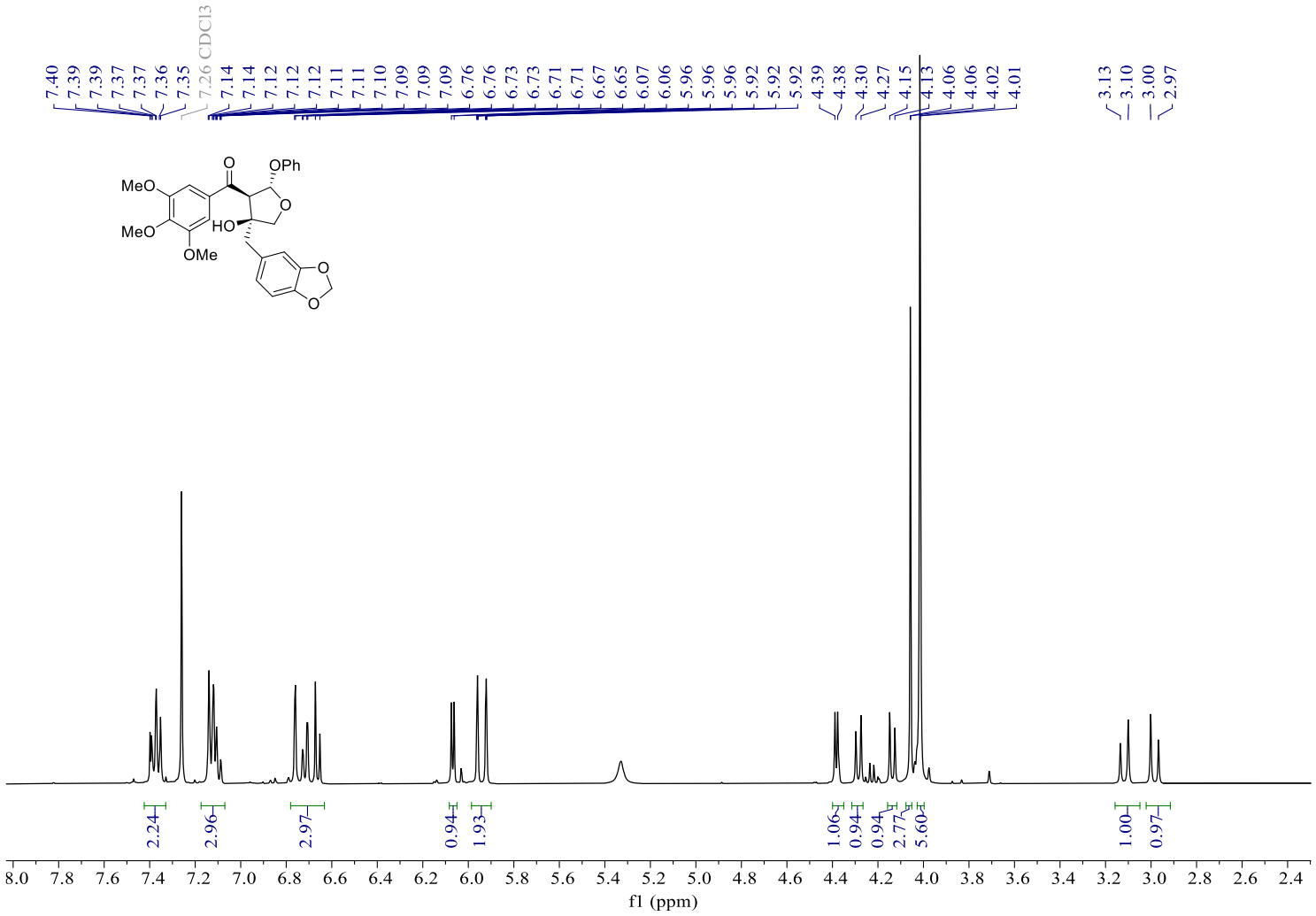
Compound 55 ^{1}H NMR (400 MHz, $CDCl_3$)



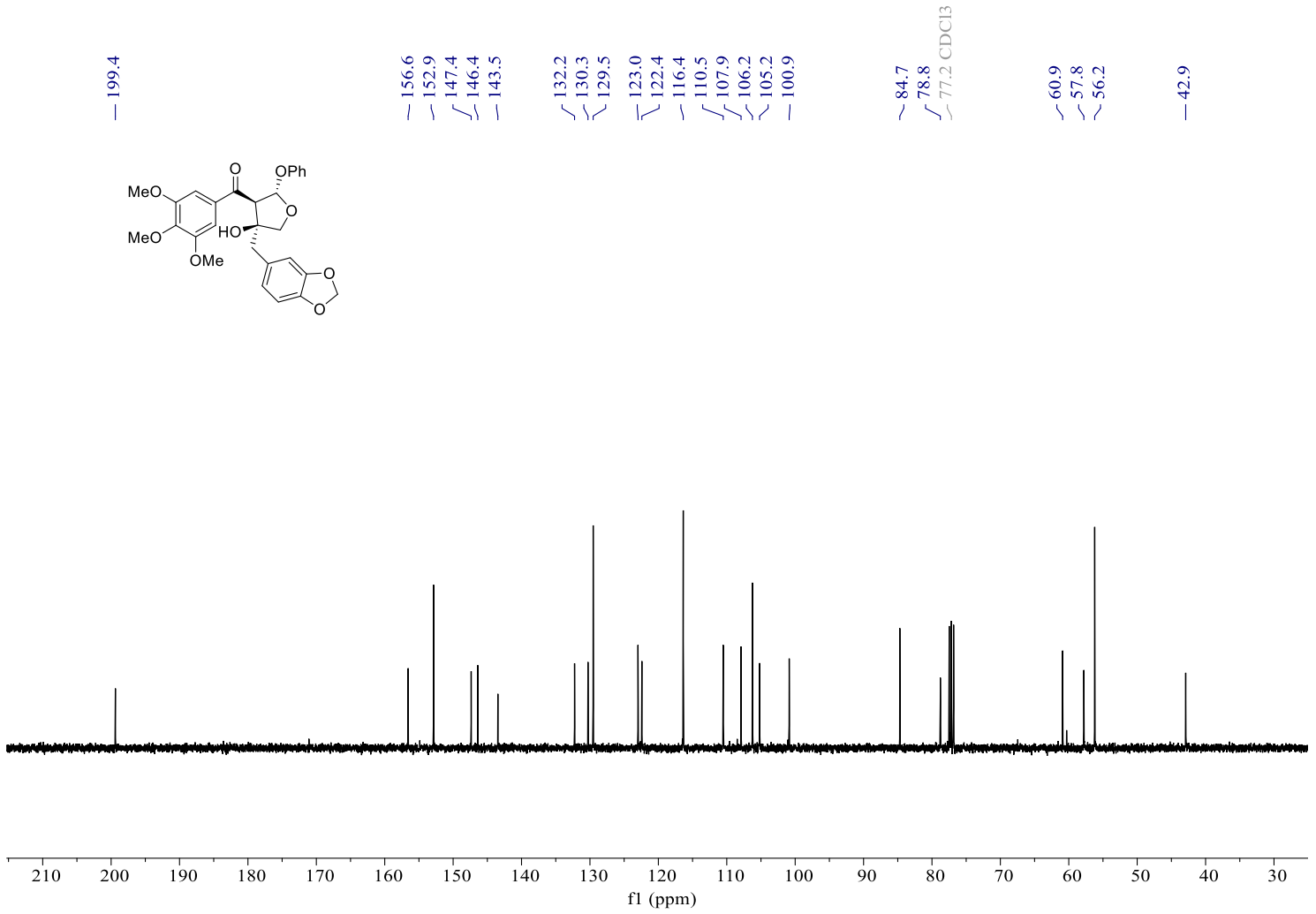
Compound 55 ^{13}C NMR (100 MHz, $CDCl_3$)



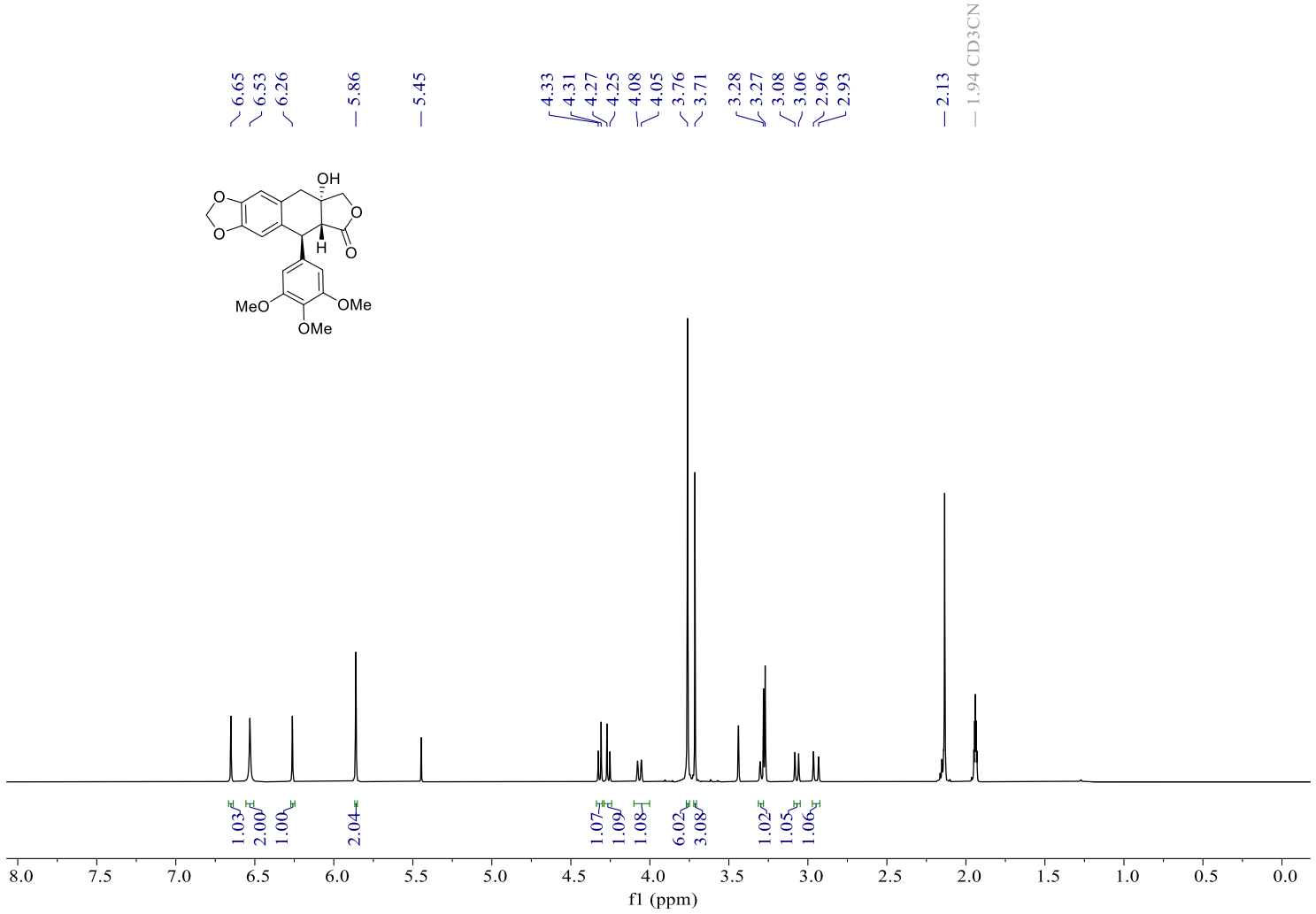
Compound 61 ^{1}H NMR (400 MHz, $CDCl_3$)



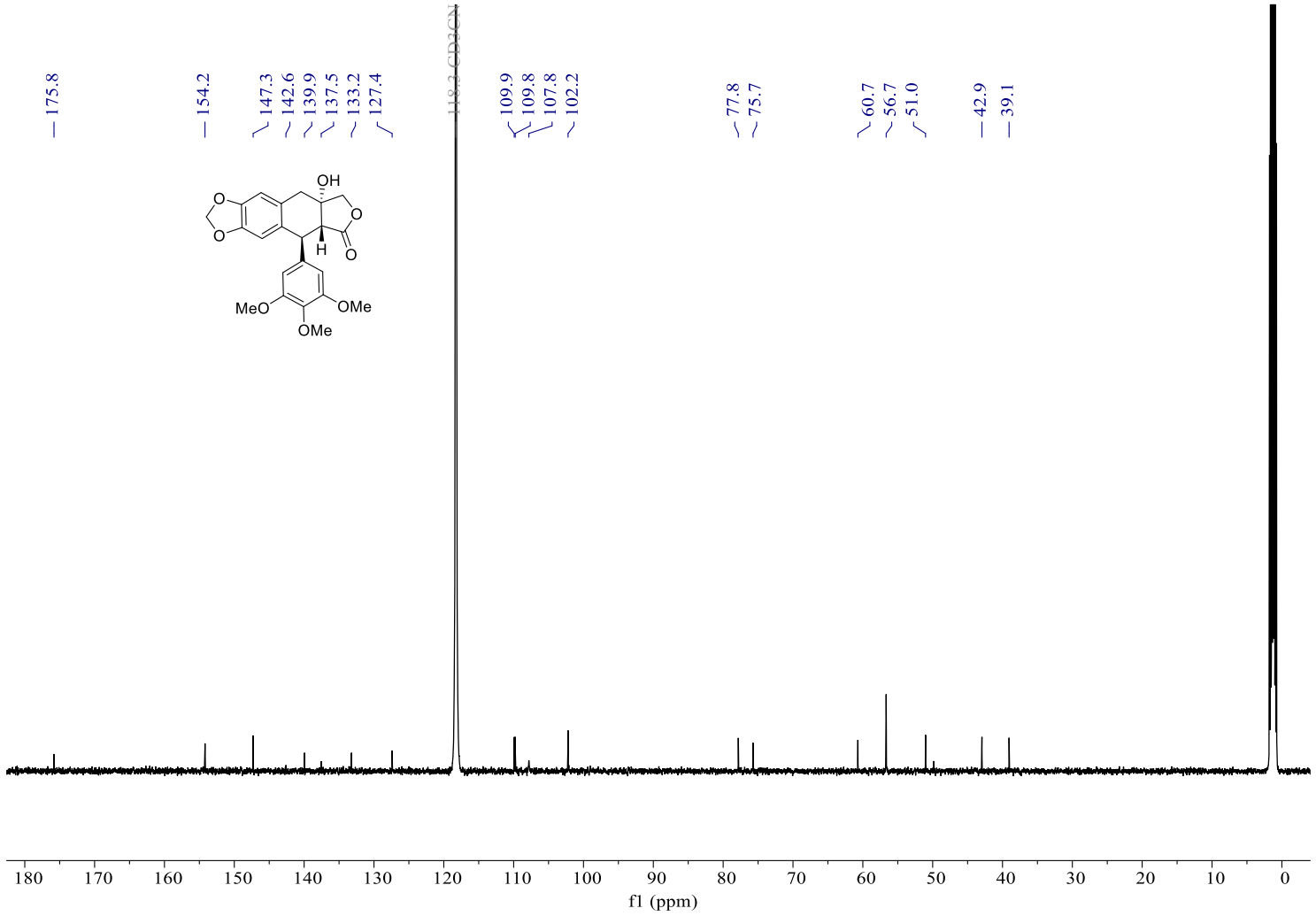
Compound 61 ^{13}C NMR (100 MHz, $CDCl_3$)



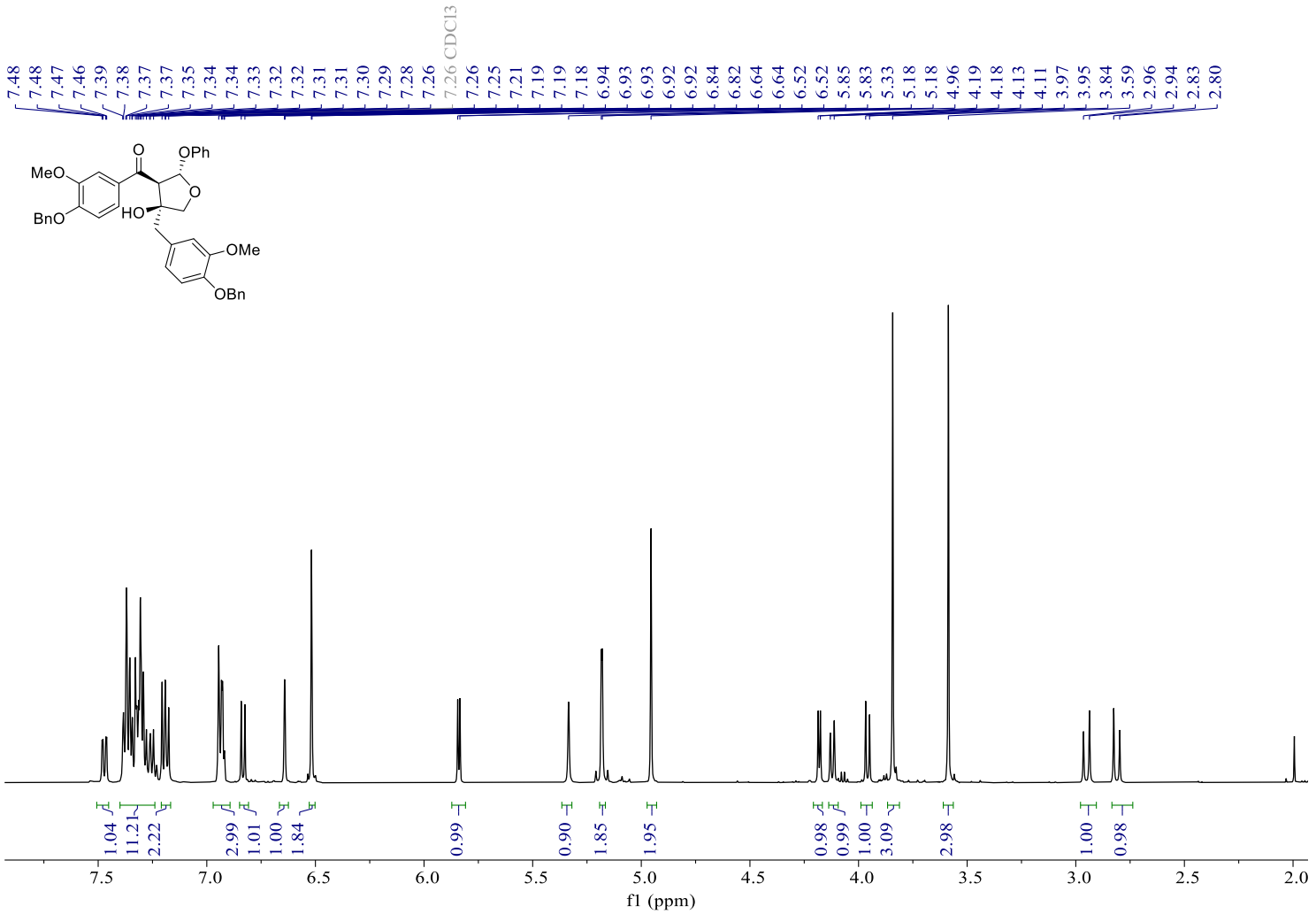
Compound 62 ^{1}H NMR (500 MHz, acetonitrle-*d*$_3$)



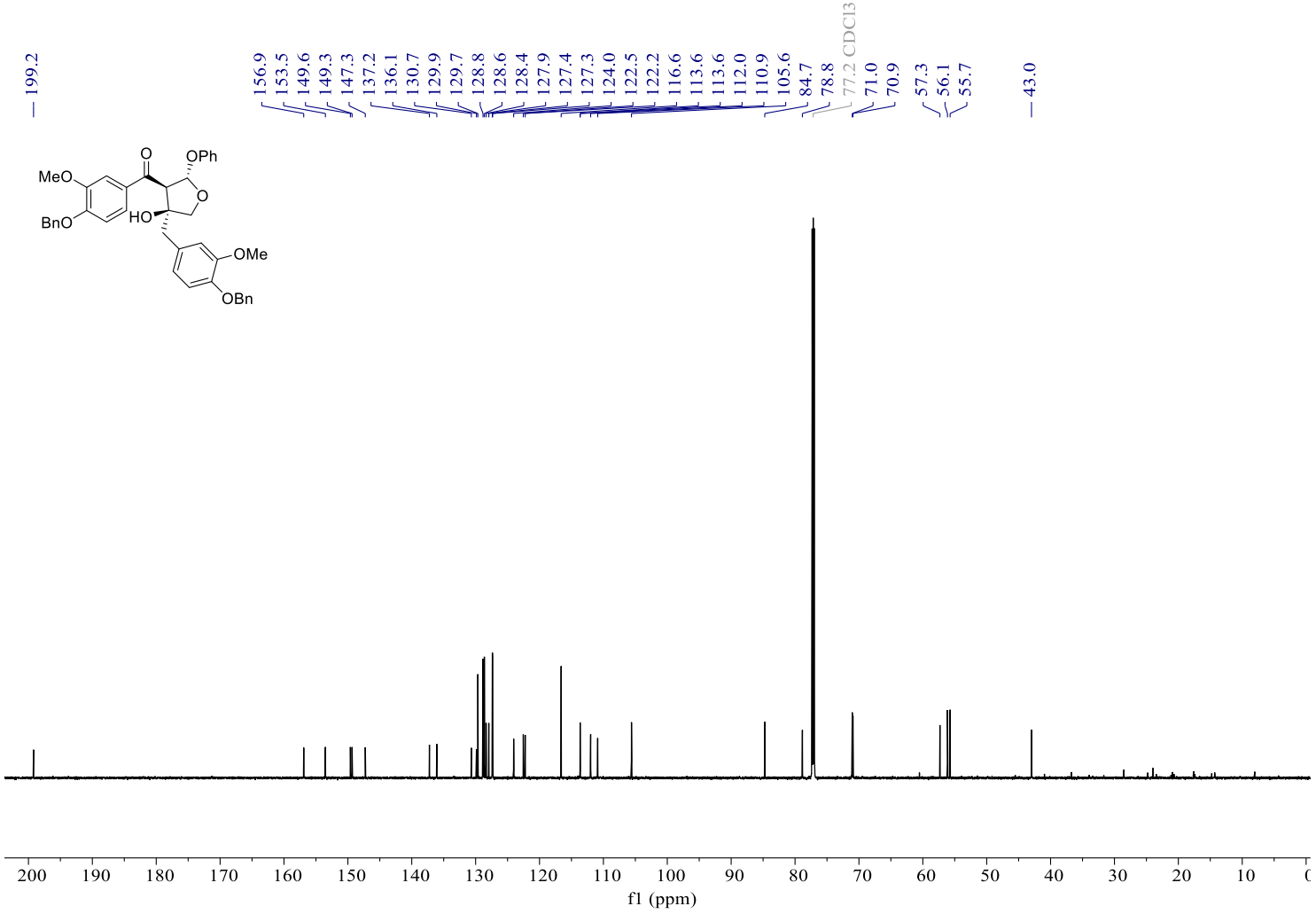
Compound 62 ^{13}C NMR (100 MHz, acetonitrle-*d*$_3$)



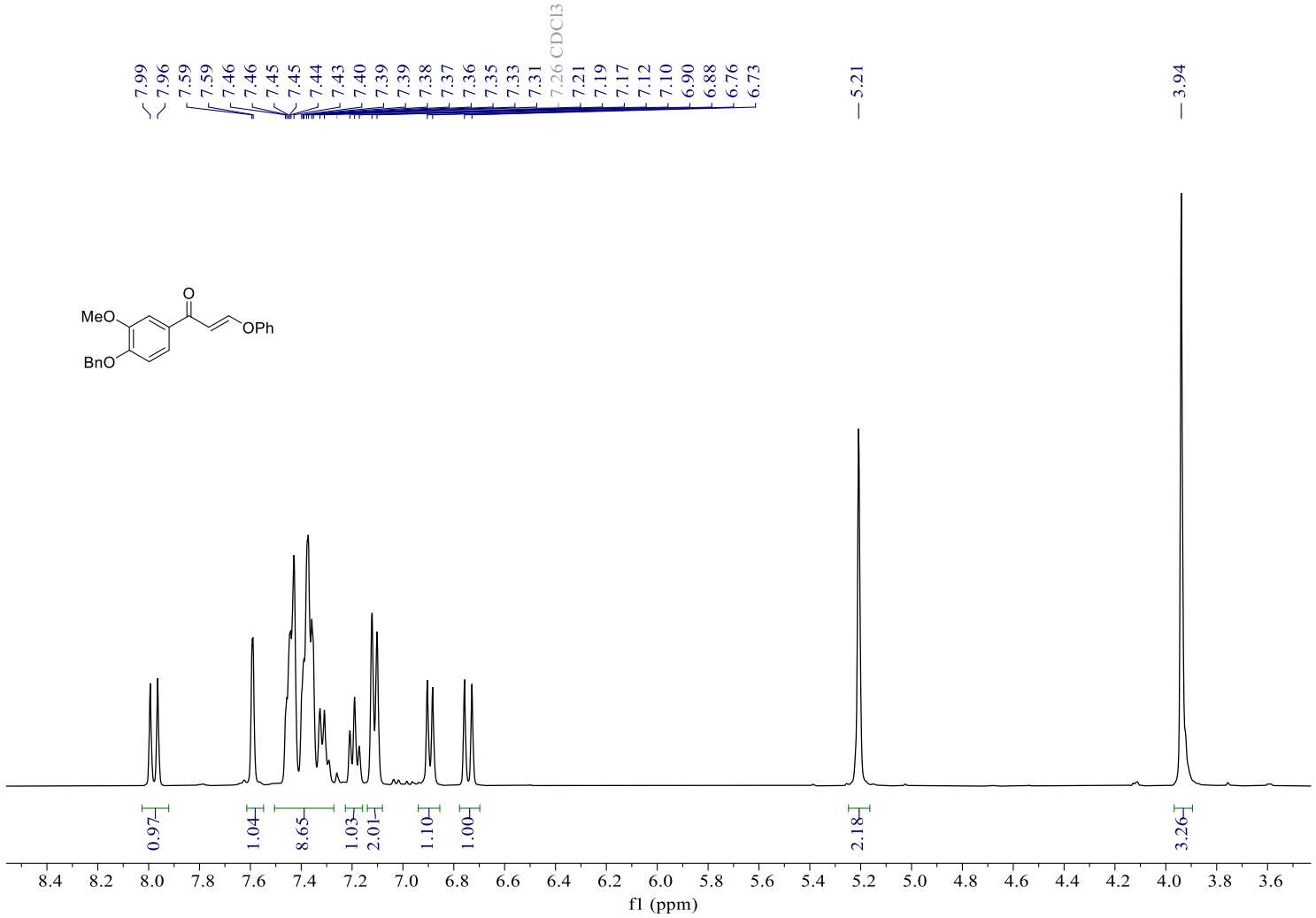
Compound 63 ^{1}H NMR (500 MHz, $CDCl_3$)



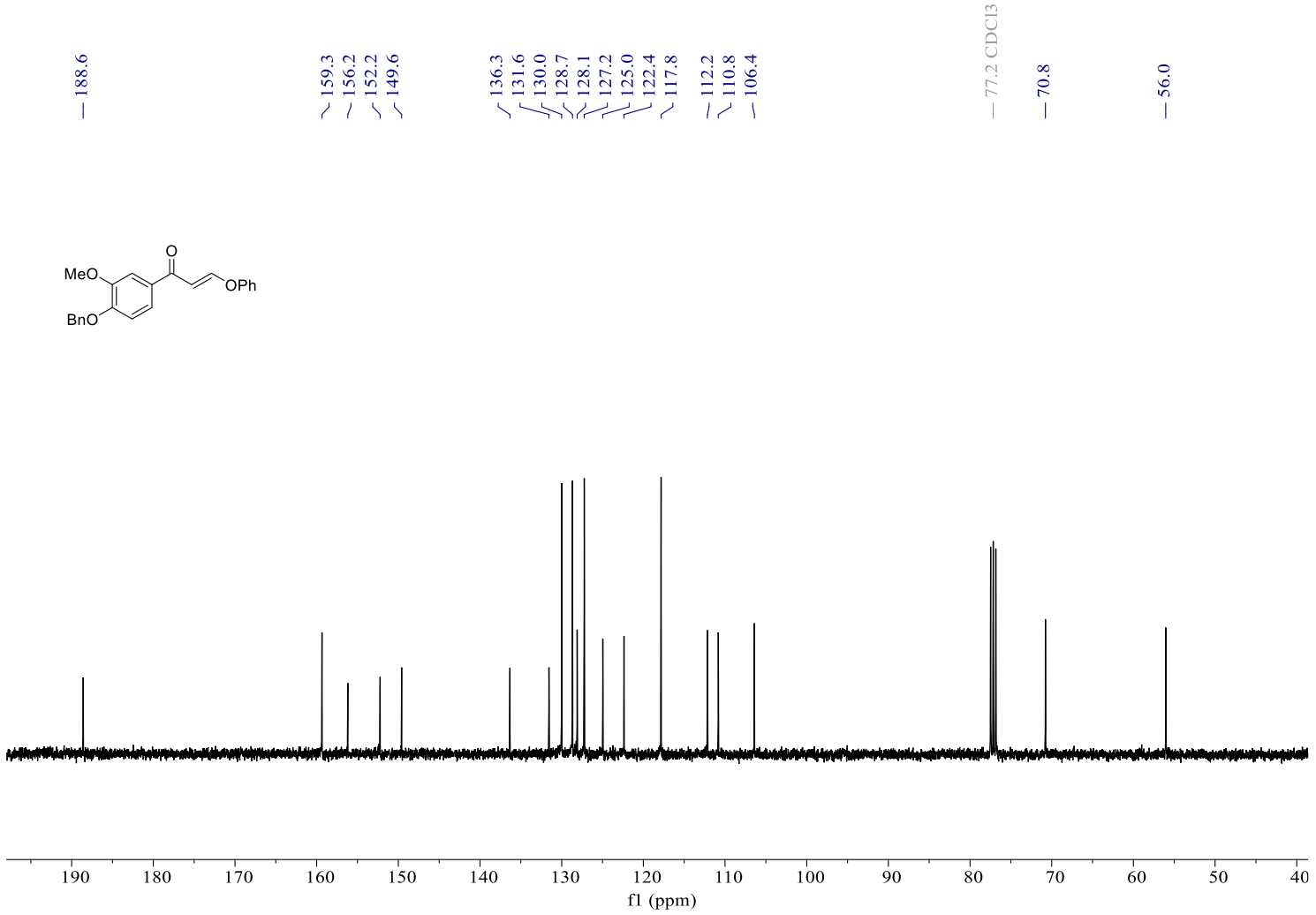
Compound 63 ^{13}C NMR (200 MHz, $CDCl_3$)



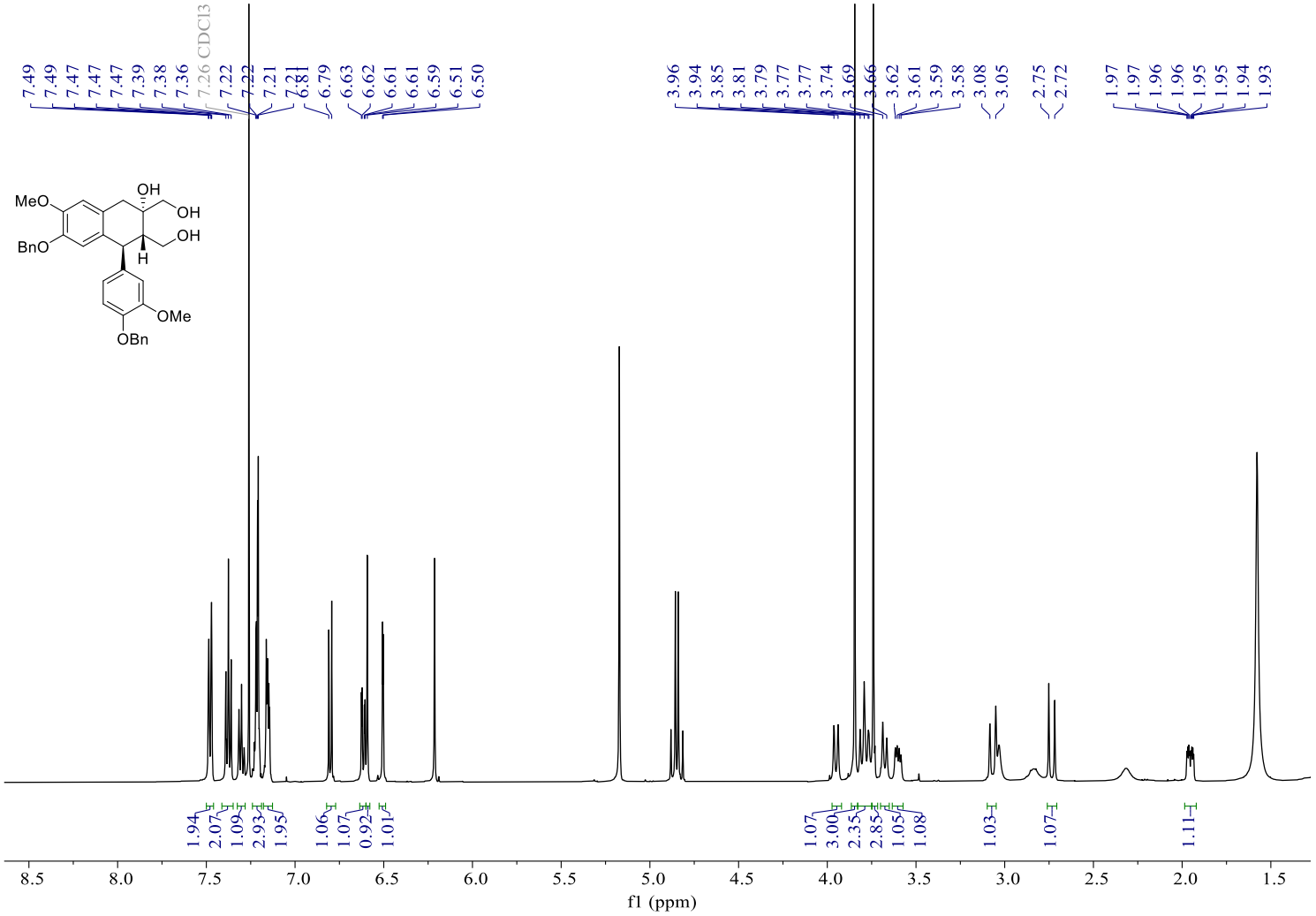
Compound 63b ^{1}H NMR (400 MHz, $CDCl_3$)



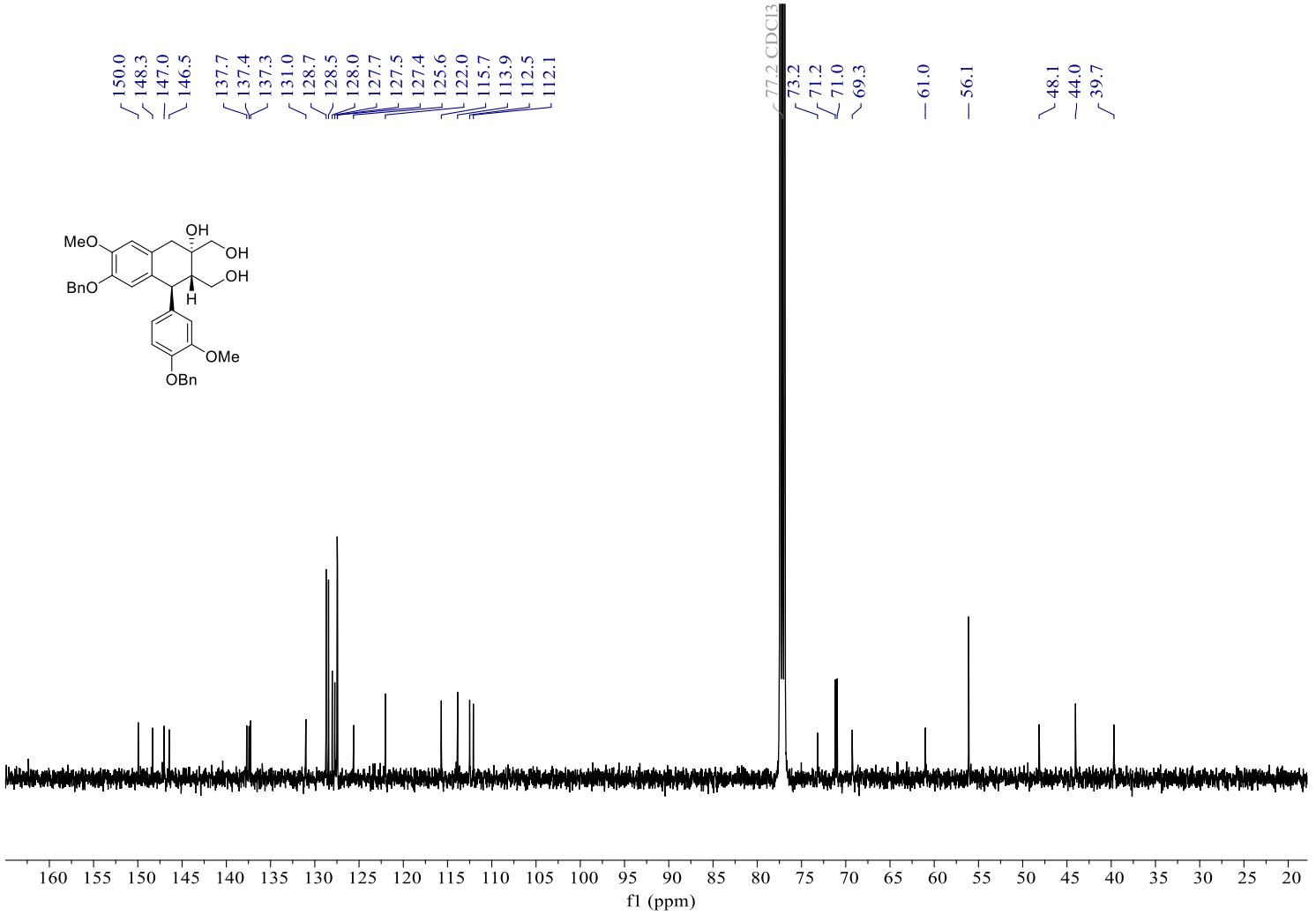
Compound 63b ^{13}C NMR (100 MHz, $CDCl_3$)



Compound 66 ^{1}H NMR (500 MHz, $CDCl_3$)



Compound 66 ^{13}C NMR (125 MHz, $CDCl_3$)



X-Ray Crystallography Data

Compound 3

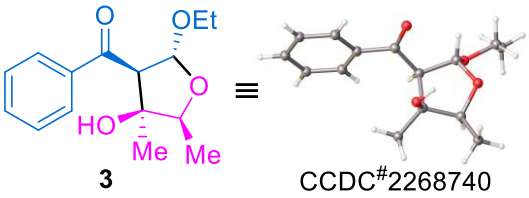


Table S4 Crystal data and structure refinement for Compound 3 (CCDC 2268740)	
Identification code	Compound 3
Empirical formula	$C_{15}H_{20}O_4$
Formula weight	264.31
Temperature/K	170.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.4596(8)
b/Å	10.3025(6)
c/Å	20.3754(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2825.4(3)
Z	8
ρ_{calc}g/cm^3	1.243
μ/mm^{-1}	0.730
F(000)	1136.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.892 to 144.776
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 11, -25 ≤ l ≤ 25
Reflections collected	18371
Independent reflections	2790 [R_{int} = 0.0432, R_{sigma} = 0.0256]
Data/restraints/parameters	2790/0/176
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.0948
Largest diff. peak/hole / e Å^{-3}	0.20/-0.19

Compound 37

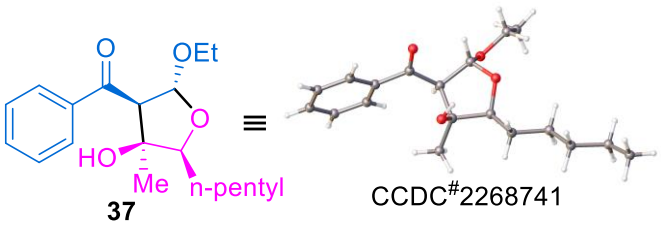


Table S5 Crystal data and structure refinement for Compound 37 (CCDC 2268741)	
Identification code	Compound 37
Empirical formula	$C_{19}H_{28}O_4$
Formula weight	320.41
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2843(4)
b/Å	13.2289(5)
c/Å	30.1700(11)
α/°	90
β/°	99.459(2)
γ/°	90
Volume/Å^3	4048.8(3)
Z	8
ρ_{calc}g/cm^3	1.051
μ/mm^{-1}	0.581
F(000)	1392.0
Crystal size/mm^3	0.15 × 0.07 × 0.06
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.312 to 130.434
Index ranges	-11 ≤ h ≤ 12, -15 ≤ k ≤ 15, -34 ≤ l ≤ 35
Reflections collected	27212
Independent reflections	6861 [R_{int} = 0.0671, R_{sigma} = 0.0604]
Data/restraints/parameters	6861/0/423
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0695, wR_2 = 0.1936
Final R indexes [all data]	R_1 = 0.0747, wR_2 = 0.1981
Largest diff. peak/hole / e Å^{-3}	0.38/-0.36

Computational Study of [3 + 2] Cyloaddition Mechanism

Computational Methods

All DFT calculations were carried out with *ORCA* 5.0.4 program package[1–3]. Geometry optimization were performed at PBE0-D4/def2-TZVP(-f) level[4–7] with CPCM solvation model of THF[8]. Frequency analysis was carried out to check the nature of each intermediate or transition state. Thermal correction to Gibbs free energy at 298.15 K and 1 M (12.23 M was used for concentration of THF) was acquired with Grimme's quasi-RRHO correction[9] as implemented in *ORCA*. Single point energy at ωB97M-V/def2-QZVPP/SMD(DCM)[10,11] level was to identify the conformer with lowest free energy for each intermediate or transition state. Default RIJCOSX approximation[12] along with the def2/J auxiliary basis set[13] were used to save computation time for all DFT calculations. Conformational search was performed for all stationary points and transition states with *crest* 2.12[14] and *xtb* 6.5.0, at xTB-GFN2/GBSA(THF) level.[6] An energy window of 3 kcal/mol was utilized for conformation searching.

Other Pathway of [3 + 2] Cycloaddition Mechanism

Open Michael Addition

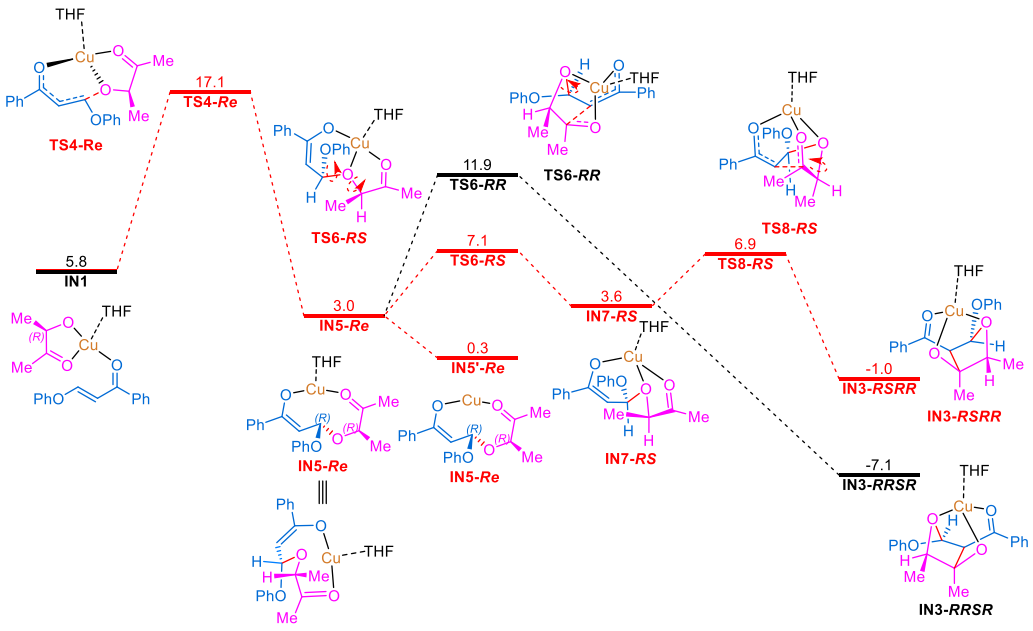


Figure S1. Computed reaction mechanism for open Michael mechanism.

The further transformation after another open Michael addition via for **TS4-*Re*** was studied, though this pathway was unfavoured because **TS4-*Re*** is higher in terms of free energy than **TS2-*Re***. The addition product **IN5-*Re***, which may dissociate a THF molecule to give **IN5'-*Re***, can undergo direct intramoleclar aldol condensation through **TS6-*RR*** ($\Delta G^{\neq}$ = 8.9 kcal/mol) to give **IN3-*RRSR*** which is identical with the main concerted pathway. It is interesting to find that, in this disfavored pathway, the steps of conformation change (through **TS6-*RS***) and aldol condensation (on the opposite diastereo face through **TS8-*RS***) are easy with low activation Gibbs energies of 4.1 and 3.9 kcal/mol, respectively.

Addition to *cis*-enone

The *trans* to *cis* isomerization for the C=C bond in **IN1** was also considered. The isomerization is endergonic by 5.1 kcal/mol and the following Michael additions through **TS2-*cis*-*Si*** and **TS2-*cis*-*Re*** are neither favored, compared to the original **TS2-*Re*** which has a relative free energy of 11.8 kcal/mol.

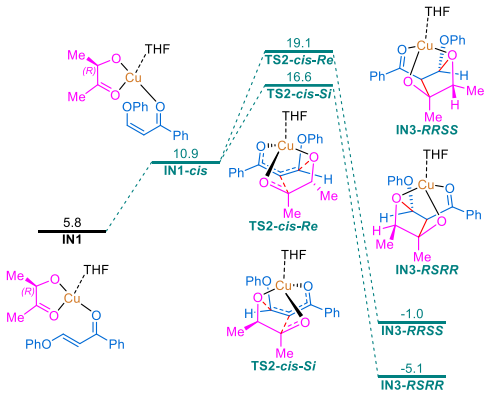


Figure S2. Pathway involving *cis*-enone.

Effect of THF coordination

The effect of different amount of coordinating THF molecules was investigated for pathway involving **TS2-*Re*** and for **1-Cu**. The results were shown in **Figure S3**. Losing one THF molecule for **IN1** to form **IN1-0THF** is exergonic, but the following **TS2-*Re*-0THF** is much more unfavored than **TS2-*Re*** by 9.8 kcal/mol. For **IN3-*RRSR*** and **1-Cu**, having no or more THF molecule coordinating to Cu is thermodynamically unfavored as well.

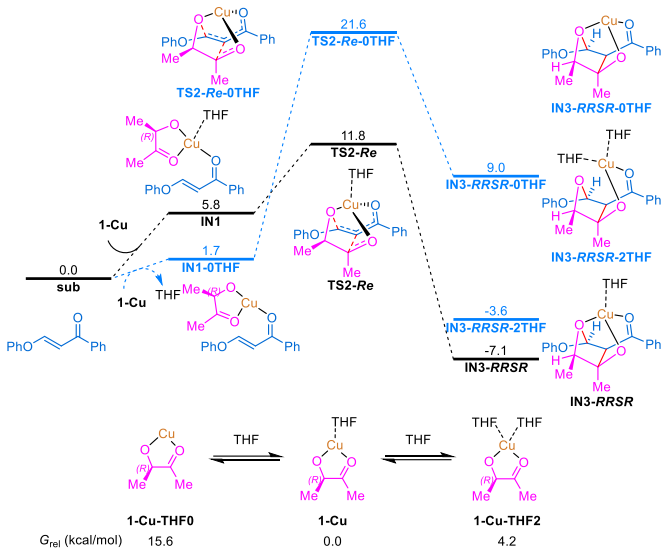


Figure S3. Other intermediate and transition states with different THF coordination.

Summarized Energies and Optimized Cartesian Coordinates

Thermal corrections to Gibbs energy, high-level DFT electronic energy and Gibbs energy

Name	*TCG*/Ha	E_{ele}/Ha	*G*/Ha
THF	0.089823	-232.452414	-232.357205
1	0.086715	-307.720536	-307.630801
36b	0.188599	-729.311548	-729.119929
36b-*cis*	0.189121	-729.308001	-729.115860
1-Cu	0.182045	-2180.092630	-2179.907565
1-Cu-0THF	0.072189	-1947.600685	-1947.525476
1-Cu-2THF	0.291724	-2412.552846	-2412.258102
IN1	0.395399	-2909.416735	-2909.018316
IN1-0THF	0.285521	-2676.956106	-2676.667565
IN1-*cis*	0.396323	-2909.409515	-2909.010172
TS2-*Re*	0.397249	-2909.408908	-2909.008639
TS2-*Re*-0THF	0.287149	-2676.925980	-2676.635810
TS2-*Si*	0.400043	-2909.402065	-2908.999003
TS2-*cis*-*Re*	0.398797	-2909.398902	-2908.997084
TS2-*cis*-*Si*	0.397974	-2909.402094	-2909.001100
IN3-*RRSR*	0.405483	-2909.447281	-2909.038778
IN3-*RRSR*-0THF	0.292808	-2676.951751	-2676.655923
IN3-*RRSR*-2THF	0.515412	-3141.908858	-3141.390426
IN3-*RSRS*	0.404780	-2909.438257	-2909.030458

IN3-*RSRR*	0.405153	-2909.443733	-2909.035560
IN3-*RRSS*	0.405659	-2909.437781	-2909.029102
TS4-*Re*	0.398051	-2909.401350	-2909.000278
TS4-*Si*	0.395869	-2909.403261	-2909.004373
IN5-*Re*	0.399417	-2909.425203	-2909.022766
IN5'-*Re*	0.289983	-2676.962821	-2676.669818
IN5-*Si*	0.401689	-2909.429963	-2909.025254
IN5'-*Si*	0.290039	-2676.962882	-2676.669823
TS6-*RR*	0.400810	-2909.420042	-2909.016212
TS6-*RS*	0.400500	-2909.412119	-2909.008599
IN7-*RS*	0.400356	-2909.425202	-2909.021825
TS8-*RS*	0.402857	-2909.422439	-2909.016561
36	0.306995	-1037.067811	-1036.757796

Optimized Cartesian coordinates

THF

C	1.159982	0.133857	0.422091
O	0.000000	0.000000	1.246037
C	-1.159982	-0.133857	0.422091
C	-0.725536	0.232235	-0.986001
C	0.725536	-0.232235	-0.986001
H	1.515417	1.170917	0.466351
H	1.944879	-0.517308	0.814912
H	-1.515417	-1.170917	0.466351
H	-1.944879	0.517308	0.814912
H	-1.337305	-0.249571	-1.749642
H	-0.777929	1.314547	-1.132440
H	0.777929	-1.314547	-1.132440
H	1.337305	0.249571	-1.749642

1

C	0.700696	0.362135	-0.215993
C	-0.750808	-0.043322	-0.052250
O	1.376050	-0.598841	-0.985128
H	0.687537	1.324065	-0.751889
O	-1.131554	-1.076789	-0.565420
C	1.386162	0.560999	1.127162
H	0.924104	1.372773	1.691107
H	1.339171	-0.356229	1.718486
H	2.433882	0.813478	0.958437
C	-1.650813	0.843302	0.742213
H	-1.409043	1.895907	0.586331
H	-2.691312	0.645015	0.490158
H	-1.499569	0.627808	1.804816
H	0.698312	-1.256175	-1.218115

36b

O	1.297059	1.712427	-0.650384
C	1.541908	0.577136	-0.255802
C	2.957952	0.149434	-0.063030
C	3.943468	1.136531	-0.041717
C	3.333713	-1.186400	0.072262
C	5.274500	0.798675	0.123554

H	3.643619	2.171408	-0.152664
C	4.669439	-1.526426	0.223286
H	2.592496	-1.974803	0.040010
C	5.640548	-0.535976	0.254821
H	6.031027	1.574598	0.148805
H	4.952087	-2.568596	0.316959
H	6.683758	-0.803255	0.380191
C	0.484945	-0.382376	0.054169
C	-0.792092	-0.037707	-0.148477
H	0.717464	-1.357076	0.460056
H	-1.065602	0.937439	-0.539803
O	-1.788852	-0.895195	0.090637
C	-3.086499	-0.424227	0.070725
C	-3.423093	0.830784	0.553000
C	-4.050240	-1.296430	-0.409095
C	-4.755013	1.221252	0.528097
H	-2.664552	1.489130	0.959362
C	-5.376202	-0.895127	-0.420344
H	-3.751223	-2.272952	-0.770866
C	-5.732536	0.365191	0.042532
H	-5.026397	2.200819	0.904316
H	-6.134250	-1.571390	-0.798135
H	-6.770364	0.676032	0.030539

36b-*cis*

O	3.263539	-1.983497	0.533339
C	2.216382	-1.469424	0.165018
C	2.149750	-0.002284	-0.070414
C	2.953119	0.836095	0.698427
C	1.354510	0.539649	-1.076907
C	2.939924	2.203881	0.482387
H	3.576459	0.403235	1.471917
C	1.360222	1.905081	-1.308914
H	0.741165	-0.112021	-1.688016
C	2.145558	2.739307	-0.523891
H	3.552276	2.854757	1.095788
H	0.749291	2.320726	-2.101890
H	2.140334	3.809355	-0.698285
C	1.041107	-2.315342	-0.076485
C	-0.243385	-1.995010	0.112436
H	1.252979	-3.348386	-0.325346
H	-1.036430	-2.716806	-0.064896
O	-0.637487	-0.812198	0.612815
C	-1.913455	-0.377027	0.345649
C	-2.482427	0.470995	1.284127
C	-2.583604	-0.712456	-0.820871
C	-3.751421	0.975549	1.055831
H	-1.926081	0.721398	2.179463
C	-3.859664	-0.206115	-1.030783
H	-2.112879	-1.343027	-1.565594
C	-4.446945	0.635609	-0.098522
H	-4.201060	1.636829	1.787440
H	-4.388851	-0.465452	-1.940487
H	-5.440147	1.032041	-0.272547

1-Cu

Cu	0.067371	0.966172	0.046716
O	1.914246	0.451749	0.275145
O	-1.636877	1.674290	-0.120322
C	2.263612	-0.887546	0.687702

C	3.024194	1.068655	-0.421994
C	-2.695383	0.810524	-0.163336
C	3.774379	-0.912296	0.651393
H	1.827473	-1.599079	-0.018869
H	1.833802	-1.048290	1.676267
C	4.074653	-0.018512	-0.546874
H	2.664879	1.440883	-1.381225
H	3.367020	1.907979	0.187616
C	-3.494179	0.814989	1.151472
C	-2.343861	-0.632780	-0.483220
H	-3.404327	1.093860	-0.968957
H	4.185342	-0.481863	1.567804
H	4.162081	-1.924516	0.536279
H	3.938496	-0.575373	-1.476788
H	5.084394	0.391611	-0.533891
H	-2.861467	0.456334	1.968235
H	-4.395671	0.199776	1.104696
H	-3.787427	1.842970	1.370149
C	-3.469019	-1.598931	-0.706594
O	-1.185909	-1.009977	-0.538466
H	-4.386377	-1.098678	-1.016958
H	-3.173816	-2.344695	-1.444974
H	-3.668694	-2.118899	0.235794

1-Cu-0THF

Cu	1.595225	0.155448	-0.473923
O	0.586256	0.561435	1.091491
C	-0.753824	0.418100	0.876158
C	-1.347592	-0.734224	1.704634
C	-1.162950	0.203071	-0.573263
H	-1.310803	1.337348	1.158715
H	-2.434468	-0.804065	1.623407
H	-0.905411	-1.683005	1.388466
H	-1.087801	-0.565958	2.750686
C	-2.619506	0.153399	-0.903628
O	-0.328279	0.057644	-1.459249
H	-2.941048	-0.892964	-0.880584
H	-3.218699	0.704669	-0.179155
H	-2.787962	0.536002	-1.910195

1-Cu-2THF

Cu	-0.460262	-0.762979	-1.033055
O	1.414805	-1.202435	-0.954527
O	1.770360	1.599131	1.363673
C	2.047352	-1.671841	0.259098
C	2.401679	-0.920345	-1.967939
O	-2.215667	-0.218878	-1.294588
C	2.185240	2.366713	0.233634
C	0.346050	1.658363	1.484182
C	3.528452	-1.443988	0.043776
H	1.803297	-2.730862	0.374581
H	1.637290	-1.105478	1.094136
C	3.668407	-1.580951	-1.468500
H	2.033039	-1.319975	-2.912606
H	2.512736	0.164107	-2.052165
C	-3.172915	-0.645090	-0.416595
C	0.934151	2.623245	-0.584373
H	2.629121	3.309567	0.578071
H	2.951124	1.804945	-0.306829
C	-0.125575	2.719854	0.505724

H	0.090550	1.883132	2.522855
H	-0.075037	0.677451	1.226005
H	3.805221	-0.437399	0.364385
H	4.133418	-2.163203	0.595903
H	3.688320	-2.634271	-1.758307
H	4.561577	-1.095077	-1.861342
C	-3.881947	0.538063	0.261294
C	-2.689686	-1.596803	0.664451
H	-3.960962	-1.233695	-0.934528
H	0.721763	1.769238	-1.235754
H	1.012186	3.520238	-1.199907
H	-1.135507	2.525756	0.143104
H	-0.105682	3.709090	0.970841
H	-3.170426	1.092754	0.878945
H	-4.252429	1.205133	-0.518552
H	-4.725430	0.228723	0.881974
C	-3.707123	-2.164216	1.608132
O	-1.511401	-1.892086	0.774485
H	-4.698840	-2.214758	1.158021
H	-3.390821	-3.151196	1.945358
H	-3.769436	-1.509610	2.483377

IN1

C	-1.742826	2.417140	-2.588127
C	-0.400501	3.096669	-2.794295
O	-1.677825	1.207011	-1.957677
H	-2.315202	3.153230	-1.984092
Cu	0.005160	0.425480	-1.716121
O	0.643454	2.531309	-2.513712
C	-2.448773	2.318835	-3.949679
H	-3.430645	1.868903	-3.794247
H	-2.585148	3.290639	-4.429422
H	-1.875070	1.670757	-4.617782
C	-0.385403	4.480101	-3.370022
H	-0.239035	4.400572	-4.452018
H	-1.323032	5.008070	-3.195854
H	0.451614	5.043875	-2.957918
O	1.455646	-0.783623	-1.484253
C	1.544223	-1.843100	-0.829345
C	2.783356	-2.633396	-0.970496
C	3.157802	-3.587349	-0.023984
C	3.605512	-2.405482	-2.075221
C	4.336020	-4.298518	-0.179694
H	2.540994	-3.759536	0.849466
C	4.774094	-3.127036	-2.235947
H	3.308410	-1.664809	-2.807021
C	5.142359	-4.073529	-1.287122
H	4.626449	-5.029790	0.565441
H	5.401697	-2.954223	-3.102433
H	6.060157	-4.636937	-1.411533
C	0.495576	-2.344317	0.021551
C	-0.452897	-1.518792	0.499976
H	0.489368	-3.389932	0.299553
H	-0.421429	-0.442697	0.339633
O	-1.433415	-1.972519	1.273551
C	-2.413212	-1.075444	1.674288
C	-2.921123	-1.255978	2.949661
C	-2.886423	-0.082610	0.832533
C	-3.920196	-0.408029	3.401003

H	-2.525085	-2.047117	3.574942
C	-3.883786	0.759914	1.303926
H	-2.495244	0.059106	-0.170969
C	-4.401800	0.604545	2.581281
H	-4.318870	-0.537469	4.400422
H	-4.258178	1.543690	0.655436
H	-5.181166	1.267912	2.937121
C	1.418022	1.087856	1.963437
O	0.562488	1.483934	0.901637
C	-0.304627	2.468038	1.451853
C	-0.591017	2.025611	2.890738
C	0.512493	0.992665	3.184791
H	1.889317	0.144888	1.682714
H	2.201469	1.843855	2.109987
H	0.196923	3.444171	1.434110
H	-1.191674	2.517803	0.819990
H	-0.551069	2.874078	3.574815
H	-1.579623	1.574074	2.972871
H	1.052636	1.201033	4.109055
H	0.087831	-0.009815	3.263565

IN1-0THF

C	2.301709	2.583034	0.839947
C	2.275406	1.995972	-0.560049
O	1.159072	2.416168	1.571000
H	3.162579	2.063564	1.314015
Cu	-0.310490	1.573197	0.827046
O	1.265134	1.491396	-1.021184
C	2.686012	4.066823	0.733867
H	2.750178	4.476278	1.743017
H	3.645062	4.223379	0.235464
H	1.909932	4.611460	0.189646
C	3.531864	2.054836	-1.374498
H	3.591834	1.178828	-2.020338
H	3.490304	2.944436	-2.011161
H	4.422645	2.127714	-0.750725
O	-1.970207	0.771452	0.424193
C	-2.357032	-0.395624	0.210221
C	-3.812098	-0.613500	0.080414
C	-4.680706	0.369315	0.559039
C	-4.339183	-1.760305	-0.514494
C	-6.049227	0.202458	0.455534
H	-4.266214	1.256295	1.021260
C	-5.710221	-1.918865	-0.628421
H	-3.683023	-2.523802	-0.913261
C	-6.566678	-0.942014	-0.139506
H	-6.717053	0.964330	0.840179
H	-6.111484	-2.807419	-1.101330
H	-7.639688	-1.072092	-0.222466
C	-1.477860	-1.533022	0.116706
C	-0.152592	-1.382469	-0.049647
H	-1.894170	-2.529695	0.169921
H	0.317953	-0.408598	-0.167707
O	0.650609	-2.437343	-0.132931
C	2.018360	-2.210073	-0.158743
C	2.608324	-1.241118	0.635801
C	2.767089	-3.031677	-0.982806
C	3.984769	-1.078787	0.574491
H	2.008708	-0.625726	1.296815

C	4.142232	-2.862743	-1.025990
H	2.269330	-3.783648	-1.583115
C	4.753391	-1.883080	-0.254510
H	4.455405	-0.319633	1.188258
H	4.736854	-3.497443	-1.672506
H	5.828093	-1.751686	-0.294461

IN1-*cis*

C	-2.485507	-2.400300	-0.333093
C	-1.731397	-2.020779	-1.598743
O	-2.320644	-1.529472	0.708106
H	-3.548635	-2.449751	-0.646702
Cu	-0.730611	-0.510794	0.732618
O	-0.810660	-1.223451	-1.574142
C	-2.062101	-3.833505	0.036497
H	-2.632646	-4.139999	0.915127
H	-2.244615	-4.555774	-0.763037
H	-0.999789	-3.842624	0.291217
C	-2.178825	-2.631330	-2.891808
H	-2.874475	-1.926044	-3.359433
H	-1.331535	-2.766923	-3.564212
H	-2.710626	-3.571177	-2.746423
O	0.608556	0.792703	1.148434
C	1.449734	1.351389	0.417155
C	2.797422	1.591950	0.982416
C	2.935911	1.602791	2.371211
C	3.928993	1.770589	0.185863
C	4.176788	1.790818	2.951625
H	2.055245	1.466211	2.985862
C	5.174432	1.937380	0.769285
H	3.854557	1.746448	-0.893822
C	5.301266	1.951830	2.151383
H	4.271161	1.807439	4.031207
H	6.049999	2.054668	0.141564
H	6.276171	2.088612	2.605229
C	1.169643	1.782712	-0.926767
C	-0.053641	1.906380	-1.481290
H	1.992145	2.075906	-1.562183
H	-0.155558	2.212547	-2.518009
O	-1.178867	1.677893	-0.820929
C	-2.394013	1.900826	-1.448378
C	-3.414544	1.023353	-1.122160
C	-2.593845	2.971209	-2.303941
C	-4.662246	1.214514	-1.694439
H	-3.210462	0.206897	-0.432738
C	-3.849271	3.143141	-2.871368
H	-1.797098	3.674515	-2.514045
C	-4.882798	2.267369	-2.573704
H	-5.467828	0.531133	-1.451344
H	-4.017486	3.978190	-3.541500
H	-5.860395	2.410185	-3.018708
C	1.331180	-2.841302	2.207702
O	1.161545	-2.395162	0.868504
C	2.454209	-2.109435	0.333045
C	3.414097	-1.959741	1.521427
C	2.489860	-2.022680	2.737910
H	0.388176	-2.680051	2.732139
H	1.567177	-3.914748	2.222602
H	2.762525	-2.924071	-0.331189

H	2.368033	-1.198668	-0.263660
H	4.127445	-2.785970	1.539582
H	3.979383	-1.028763	1.476610
H	2.964299	-2.473164	3.610791
H	2.139550	-1.024624	3.006705

TS2-*Re*

C	-0.996075	-0.774520	2.107902
C	0.462195	-0.797581	2.525484
O	-1.261504	0.083567	1.063725
H	-1.239320	-1.813010	1.824910
Cu	0.151077	1.362477	0.623919
O	1.235736	0.072426	2.163092
C	-1.840702	-0.423731	3.337295
H	-1.681857	-1.126590	4.158196
H	-2.893966	-0.452044	3.054710
H	-1.598584	0.584075	3.683025
C	0.915295	-1.891427	3.440994
H	1.914370	-2.219045	3.150976
H	0.227207	-2.736392	3.446305
H	0.977908	-1.488956	4.456737
O	1.159193	0.342916	-1.067111
C	1.160698	-0.908286	-0.911435
C	2.473741	-1.613098	-0.913245
C	3.626554	-0.877143	-0.645753
C	2.592389	-2.978100	-1.172345
C	4.868191	-1.490956	-0.622032
H	3.529778	0.182918	-0.446839
C	3.835433	-3.591473	-1.161277
H	1.710671	-3.563584	-1.404512
C	4.976645	-2.851152	-0.881527
H	5.755456	-0.908374	-0.400545
H	3.914734	-4.651506	-1.374776
H	5.947835	-3.332907	-0.868766
C	-0.009444	-1.652541	-0.675493
C	-1.225801	-0.992429	-0.627756
H	0.031056	-2.698820	-0.407017
H	-1.357441	-0.050871	-1.144737
O	-2.314210	-1.758124	-0.459311
C	-3.571991	-1.210478	-0.548312
C	-3.836193	0.151537	-0.533414
C	-4.604050	-2.134076	-0.645104
C	-5.153403	0.578772	-0.635474
H	-3.038747	0.869652	-0.409567
C	-5.912673	-1.691667	-0.739997
H	-4.365656	-3.191171	-0.649382
C	-6.194431	-0.331594	-0.739633
H	-5.362231	1.642530	-0.621695
H	-6.715559	-2.415740	-0.817908
H	-7.218166	0.015312	-0.814760
C	-0.001112	4.189705	-0.330825
O	0.854263	3.199590	0.274981
C	2.209274	3.353213	-0.213863
C	2.139416	4.428216	-1.281239
C	0.940658	5.259112	-0.836670
H	-0.556834	3.725812	-1.151494
H	-0.701659	4.529522	0.432638
H	2.829767	3.655102	0.633874

H	2.544020	2.387347	-0.590028
H	3.063451	5.003522	-1.340859
H	1.946887	3.980631	-2.259293
H	1.219416	5.937113	-0.026037
H	0.499946	5.843629	-1.644559

TS2-*Re*-0THF

C	2.051872	-2.205322	-1.602166
C	2.711559	-2.647512	-0.305958
O	0.753934	-1.819485	-1.424745
H	2.701599	-1.350246	-1.900406
Cu	0.457304	-1.375107	0.595452
O	2.140975	-2.475162	0.768445
C	2.196331	-3.278186	-2.685116
H	1.758710	-2.896096	-3.608314
H	3.237317	-3.542016	-2.881930
H	1.651378	-4.179814	-2.394461
C	4.066740	-3.264605	-0.336282
H	3.964590	-4.317305	-0.619470
H	4.696587	-2.788525	-1.089441
H	4.532213	-3.207897	0.646570
O	-0.904912	-0.027589	0.892051
C	-1.543384	0.364840	-0.125963
C	-2.928328	0.847614	0.100402
C	-3.574390	1.674727	-0.817436
C	-3.588211	0.491076	1.276032
C	-4.859704	2.128303	-0.568429
H	-3.060375	1.980408	-1.720893
C	-4.874728	0.939323	1.522133
H	-3.079418	-0.147340	1.987513
C	-5.513353	1.759264	0.599877
H	-5.351169	2.776795	-1.284499
H	-5.383222	0.649158	2.434502
H	-6.519655	2.113347	0.793494
C	-1.052087	0.326813	-1.448559
C	0.253053	0.204763	-1.892706
H	-1.788805	0.249004	-2.237965
H	0.409169	-0.024426	-2.937934
O	1.361345	0.759382	-1.384803
C	1.343976	1.539991	-0.241420
C	2.192448	1.178786	0.790041
C	0.587956	2.698343	-0.183968
C	2.256925	1.977174	1.923076
H	2.796037	0.284446	0.697633
C	0.654714	3.483115	0.957193
H	-0.048578	2.973573	-1.014752
C	1.481326	3.123829	2.013991
H	2.916074	1.696483	2.736312
H	0.061503	4.388442	1.014908
H	1.528463	3.743665	2.901584

TS2-*Si*

C	-1.062512	-0.222924	2.083642
C	0.351201	-0.307933	2.647523
O	-1.120629	-0.481044	0.723970
H	-1.534360	-1.077043	2.615425
Cu	0.469860	-1.538903	0.088945
O	1.182710	-1.006954	2.087347
C	-1.831833	1.019742	2.515995
H	-1.351599	1.936518	2.175327
H	-2.835556	0.980084	2.091524

H	-1.925952	1.059487	3.602391
C	0.676482	0.375969	3.932996
H	1.676071	0.099788	4.264178
H	0.617004	1.459086	3.795204
H	-0.058308	0.114512	4.698751
O	1.784423	-0.047715	-0.769446
C	1.674340	1.071207	-0.193974
C	2.914101	1.710321	0.327576
C	3.002099	3.077317	0.588512
C	4.029321	0.907855	0.562427
C	4.178353	3.627269	1.073337
H	2.153923	3.722420	0.392684
C	5.201441	1.454168	1.058811
H	3.956050	-0.152676	0.355565
C	5.280074	2.817023	1.315309
H	4.237012	4.693501	1.261004
H	6.057892	0.816224	1.246527
H	6.198206	3.247465	1.699079
C	0.438893	1.705854	0.018195
C	-0.713171	1.096550	-0.453940
H	0.359488	2.608490	0.606786
H	-0.637497	0.360249	-1.244737
O	-1.848901	1.807015	-0.405646
C	-2.983491	1.335597	-1.019234
C	-3.986029	2.278141	-1.203893
C	-3.160129	0.020921	-1.425731
C	-5.171783	1.904908	-1.814407
H	-3.820435	3.295826	-0.870338
C	-4.351883	-0.335551	-2.042125
H	-2.399793	-0.721139	-1.232017
C	-5.359428	0.596488	-2.241705
H	-5.951577	2.643775	-1.959394
H	-4.492024	-1.363356	-2.357930
H	-6.286697	0.305164	-2.720561
C	1.113150	-2.776516	-2.449804
O	0.934098	-3.154732	-1.073367
C	-0.093288	-4.158782	-1.117268
C	-1.115840	-3.640645	-2.122743
C	-0.298383	-2.684779	-3.015747
H	1.669553	-1.841938	-2.464549
H	1.693042	-3.563986	-2.943490
H	0.363300	-5.094045	-1.459753
H	-0.475092	-4.290350	-0.106533
H	-1.561709	-4.460510	-2.686306
H	-1.917904	-3.104708	-1.613975
H	-0.322988	-2.969666	-4.067823
H	-0.674880	-1.664101	-2.931961

TS2-*cis*-*Re*

C	0.015388	0.571200	-2.926703
C	1.136581	1.461263	-2.398557
O	-0.801377	0.077363	-1.924643
H	-0.563788	1.310861	-3.518976
Cu	-0.781474	1.153283	-0.263795
O	0.986486	2.057249	-1.344357
C	0.473727	-0.496750	-3.913164
H	-0.396127	-1.067184	-4.243886
H	0.933800	-0.049125	-4.795274
H	1.191634	-1.186299	-3.467275

C	2.359916	1.672245	-3.228130
H	2.085110	1.953876	-4.247865
H	2.988399	2.441631	-2.783081
H	2.917930	0.734305	-3.298951
O	0.669684	0.166502	1.117973
C	1.527844	-0.468174	0.455833
C	2.965639	-0.260655	0.798923
C	3.322207	0.884539	1.508745
C	3.960225	-1.173699	0.452102
C	4.643223	1.120812	1.852155
H	2.543208	1.585778	1.782802
C	5.281697	-0.943484	0.802713
H	3.698661	-2.083178	-0.075737
C	5.627984	0.206353	1.499995
H	4.908032	2.020017	2.397248
H	6.043696	-1.667096	0.535595
H	6.661897	0.386535	1.772185
C	1.214402	-1.308404	-0.632480
C	-0.082785	-1.580540	-1.044202
H	2.001736	-1.637670	-1.295570
H	-0.235142	-2.194764	-1.922985
O	-1.060053	-1.644270	-0.122721
C	-2.320412	-2.061248	-0.467247
C	-2.789656	-2.158304	-1.768981
C	-3.138915	-2.383422	0.608088
C	-4.089786	-2.597771	-1.981882
H	-2.171335	-1.854402	-2.600862
C	-4.434855	-2.812896	0.379610
H	-2.743802	-2.294915	1.613308
C	-4.917072	-2.925867	-0.918445
H	-4.459235	-2.670505	-2.998629
H	-5.069687	-3.063049	1.221957
H	-5.931554	-3.261298	-1.098307
C	-2.139607	1.289434	2.343753
O	-1.666007	2.129252	1.262714
C	-0.964658	3.265977	1.804605
C	-1.481328	3.397877	3.219064
C	-1.639052	1.936119	3.622939
H	-3.230924	1.273755	2.286066
H	-1.750691	0.282621	2.192877
H	0.110855	3.063955	1.789744
H	-1.181342	4.119927	1.162146
H	-0.790634	3.947446	3.859067
H	-2.447501	3.908801	3.226089
H	-0.670157	1.516915	3.903759
H	-2.332430	1.790328	4.451451

TS2-*cis*-*Si*

C	-0.111557	-0.059506	2.727798
C	0.913121	1.027965	2.451502
O	-0.925227	-0.350217	1.660909
H	0.487842	-0.943269	3.016139
Cu	-0.829076	0.870520	0.130540
O	0.839344	1.728827	1.457146
C	-0.929486	0.355970	3.957140
H	-1.636358	-0.441617	4.190329
H	-1.493208	1.266903	3.741205
H	-0.300337	0.529100	4.833118
C	1.996514	1.244567	3.461709

H	2.920344	1.525529	2.955289
H	2.157124	0.365541	4.085687
H	1.703439	2.075864	4.110625
O	0.525655	-0.034919	-1.319822
C	1.400778	-0.707613	-0.719826
C	2.831739	-0.424210	-1.025502
C	3.166930	0.811831	-1.574716
C	3.843577	-1.353619	-0.789457
C	4.485060	1.120547	-1.866490
H	2.375435	1.526553	-1.762547
C	5.162061	-1.050637	-1.091791
H	3.597053	-2.328538	-0.385484
C	5.487579	0.189258	-1.625525
H	4.733724	2.090093	-2.283432
H	5.938442	-1.786002	-0.913093
H	6.519522	0.427329	-1.857572
C	1.109279	-1.658424	0.284985
C	-0.171636	-2.000735	0.670577
H	1.905144	-2.001149	0.930781
H	-0.304026	-2.634104	1.541212
O	-1.162065	-2.035020	-0.231388
C	-2.405781	-2.492510	0.129189
C	-2.833091	-2.655838	1.439182
C	-3.248110	-2.789764	-0.934115
C	-4.112920	-3.141729	1.671461
H	-2.200618	-2.368146	2.265921
C	-4.524244	-3.266148	-0.685835
H	-2.887257	-2.646880	-1.945870
C	-4.962477	-3.449626	0.619624
H	-4.448805	-3.267152	2.694739
H	-5.177713	-3.498514	-1.518900
H	-5.960783	-3.822998	0.814735
C	-1.206685	3.637995	-0.795695
O	-1.644185	2.298425	-1.067710
C	-1.501482	2.121532	-2.490066
C	-0.319809	2.999489	-2.917435
C	0.027373	3.806527	-1.656458
H	-2.002534	4.331642	-1.091676
H	-1.030684	3.719940	0.275647
H	-1.346388	1.060384	-2.669958
H	-2.433267	2.443844	-2.964112
H	0.524530	2.395640	-3.248385
H	-0.610167	3.653860	-3.740118
H	0.891477	3.376809	-1.146565
H	0.239917	4.854439	-1.869634

IN3-*RRSR*

C	-0.427242	-0.404916	2.577568
C	1.033535	-0.336603	2.070828
O	-1.216804	-0.062097	1.430875
H	-0.652947	-1.441332	2.863487
Cu	0.625620	2.106663	0.836565
O	1.511258	0.940906	1.960524
C	-0.765063	0.533291	3.699319
H	-1.825335	0.465640	3.951116
H	-0.185438	0.276936	4.588592
H	-0.528078	1.559349	3.411724
C	1.960008	-1.159271	2.951887
H	2.966559	-1.173870	2.530466

H	2.017230	-0.697776	3.940579
H	1.612320	-2.189080	3.065667
O	1.610949	0.395418	-1.013773
C	1.804178	-0.601909	-0.334288
C	3.095401	-1.327042	-0.432167
C	3.263774	-2.635040	0.019356
C	4.175955	-0.665336	-1.017610
C	4.487811	-3.270614	-0.119377
H	2.439527	-3.174535	0.467794
C	5.400981	-1.294222	-1.141657
H	4.036834	0.351235	-1.364388
C	5.557974	-2.601551	-0.695455
H	4.606054	-4.291504	0.224605
H	6.237572	-0.768294	-1.587053
H	6.516406	-3.098061	-0.796869
C	0.789035	-1.042379	0.666071
C	-0.634357	-0.649007	0.302142
H	0.816641	-2.119294	0.822879
H	-0.678801	0.068386	-0.519232
O	-1.319376	-1.826738	-0.090718
C	-2.481100	-1.667788	-0.782972
C	-2.959414	-2.797000	-1.442513
C	-3.188313	-0.471299	-0.854794
C	-4.129241	-2.725574	-2.178493
H	-2.396169	-3.720559	-1.374305
C	-4.356025	-0.412599	-1.604960
H	-2.850368	0.403811	-0.317520
C	-4.833946	-1.530759	-2.269864
H	-4.489668	-3.610483	-2.690969
H	-4.899281	0.524567	-1.656855
H	-5.747598	-1.475621	-2.849592
C	-0.185152	3.224660	-1.747097
O	-0.366545	3.294547	-0.308108
C	-1.770232	3.497012	0.004100
C	-2.439916	3.780107	-1.324823
C	-1.571727	2.997793	-2.303406
H	0.234594	4.179871	-2.073812
H	0.517671	2.420286	-1.955423
H	-2.149736	2.584017	0.467596
H	-1.833775	4.318439	0.718159
H	-3.481778	3.459274	-1.324922
H	-2.405002	4.847911	-1.553227
H	-1.822509	1.934606	-2.275238
H	-1.661090	3.350766	-3.330906

IN3-*RRSR*-0THF

C	-0.766188	1.895287	1.452528
C	0.662674	1.593124	0.936205
O	-1.627986	1.373517	0.436195
H	-0.935173	1.335636	2.383049
Cu	0.753478	1.941200	-1.836722
O	1.052810	2.452772	-0.039341
C	-1.074459	3.350461	1.655816
H	-2.114224	3.482127	1.962245
H	-0.433963	3.761815	2.438810
H	-0.896401	3.903272	0.733250
C	1.676889	1.574408	2.070807
H	1.786343	2.586332	2.467981

H	1.376252	0.910006	2.884793
H	2.651681	1.254573	1.696910
O	1.129810	-0.057558	-1.770314
C	1.276752	-0.413154	-0.587891
C	2.437763	-1.248009	-0.232699
C	2.605888	-1.809816	1.034561
C	3.408371	-1.481460	-1.211823
C	3.718443	-2.585789	1.314314
H	1.869479	-1.654263	1.811591
C	4.519297	-2.252822	-0.929566
H	3.275124	-1.043184	-2.192671
C	4.676413	-2.808293	0.335429
H	3.836914	-3.018886	2.300486
H	5.267905	-2.423571	-1.694394
H	5.546668	-3.415549	0.557220
C	0.349008	0.084361	0.449216
C	-1.107638	0.155442	0.002465
H	0.384416	-0.534049	1.342706
H	-1.238164	0.088631	-1.080016
O	-1.766239	-0.946534	0.606503
C	-3.010735	-1.266868	0.155616
C	-3.771712	-0.462507	-0.687047
C	-3.517766	-2.486309	0.597491
C	-5.028075	-0.897807	-1.091000
H	-3.407720	0.502932	-1.011457
C	-4.773447	-2.902410	0.192175
H	-2.910311	-3.097488	1.254982
C	-5.537352	-2.111979	-0.658756
H	-5.615456	-0.265849	-1.747791
H	-5.156801	-3.854633	0.541390
H	-6.520167	-2.438910	-0.976696

IN3-*RRSR*-2THF

C	-1.170633	-0.310118	2.758306
C	0.044171	-0.946766	2.040351
O	-1.894825	0.352576	1.715655
H	-1.799898	-1.113978	3.164026
Cu	0.750411	1.454397	0.755328
O	1.054772	-0.066243	1.784057
C	-0.836979	0.686329	3.829692
H	-1.747462	1.118549	4.249729
H	-0.284355	0.199884	4.636245
H	-0.218613	1.484485	3.414476
C	0.580926	-2.126412	2.836933
H	0.974220	-1.764494	3.790418
H	-0.189782	-2.874806	3.038380
H	1.401676	-2.603114	2.298220
O	0.286180	-0.389493	-1.133952
C	0.194995	-1.400950	-0.453555
C	1.063215	-2.569836	-0.741481
C	2.139908	-2.386450	-1.610286
C	0.850036	-3.829554	-0.183734
C	2.993713	-3.433000	-1.903912
H	2.294973	-1.406234	-2.043063
C	1.698708	-4.882717	-0.487924
H	0.017681	-4.003610	0.485326
C	2.774020	-4.685587	-1.341924
H	3.833932	-3.276262	-2.570656
H	1.520568	-5.859673	-0.053934

H	3.441073	-5.508578	-1.572399
C	-0.717388	-1.437122	0.725518
C	-1.900383	-0.486313	0.601462
H	-1.102318	-2.439029	0.905196
H	-1.860684	0.134002	-0.294463
O	-3.073541	-1.287790	0.556781
C	-4.240662	-0.681333	0.210894
C	-4.400510	0.693920	0.066512
C	-5.324466	-1.530596	-0.001922
C	-5.639981	1.200259	-0.305192
H	-3.580867	1.372034	0.260453
C	-6.554065	-1.010439	-0.364831
H	-5.182067	-2.598477	0.118088
C	-6.720685	0.360571	-0.523006
H	-5.756007	2.272877	-0.414877
H	-7.388572	-1.683241	-0.528211
H	-7.683745	0.767607	-0.807138
C	3.506740	1.508771	-1.141319
O	3.311787	1.928301	0.214799
C	4.098610	1.112253	1.091287
C	4.534538	-0.083348	0.267183
C	4.668145	0.530416	-1.120911
H	2.587322	1.028051	-1.494635
H	3.697169	2.392260	-1.756111
H	4.962215	1.692579	1.437965
H	3.478130	0.838960	1.945745
H	5.459441	-0.529480	0.634892
H	3.753014	-0.846854	0.271982
H	5.618910	1.062535	-1.211677
H	4.606279	-0.202105	-1.927083
C	1.066274	4.232138	-0.400641
O	0.271433	3.032978	-0.266797
C	-0.702481	2.950458	-1.331496
C	-0.662334	4.305103	-2.007536
C	0.789795	4.723876	-1.804337
H	0.727025	4.948079	0.353833
H	2.104283	3.965911	-0.210949
H	-0.404716	2.143774	-2.004805
H	-1.666735	2.706817	-0.883451
H	-0.949996	4.241984	-3.057067
H	-1.333971	5.004853	-1.504223
H	1.439120	4.213766	-2.520524
H	0.943911	5.798941	-1.898570

IN3-*RSRS*

C	-0.138958	2.486504	-2.109960
C	0.901703	1.383541	-1.786835
O	-1.064177	2.524411	-1.009449
H	0.374996	3.455815	-2.135316
Cu	-0.183656	-1.186894	-1.111728
O	0.514451	0.149692	-2.200057
C	-0.898319	2.271632	-3.388959
H	-0.212746	2.300377	-4.239192
H	-1.389266	1.298592	-3.372463
H	-1.645709	3.056160	-3.525907
C	2.258363	1.737373	-2.388581
H	2.174399	1.733896	-3.478315
H	2.619307	2.718356	-2.069539
H	2.997009	0.983787	-2.109030

O	1.167401	-0.600459	0.658126
C	1.654370	0.512921	0.485027
C	3.077619	0.741981	0.842832
C	3.917560	-0.370631	0.916884
C	3.600299	2.005122	1.117325
C	5.254002	-0.222357	1.239745
H	3.504388	-1.348676	0.702523
C	4.935441	2.150657	1.460368
H	2.966662	2.882851	1.088442
C	5.765965	1.040447	1.514596
H	5.901344	-1.090979	1.277281
H	5.328906	3.135444	1.683902
H	6.812641	1.158110	1.771233
C	0.912463	1.594958	-0.207498
C	-0.553984	1.857209	0.107131
H	1.411301	2.550057	-0.048225
H	-0.673469	2.498306	0.986598
O	-1.260805	0.659927	0.348962
C	-2.516401	0.745157	0.864895
C	-3.070542	-0.456731	1.299246
C	-3.246502	1.924728	0.968344
C	-4.344007	-0.478040	1.838354
H	-2.484788	-1.362239	1.206167
C	-4.521134	1.888033	1.521335
H	-2.843773	2.859754	0.603407
C	-5.078504	0.696283	1.956989
H	-4.764341	-1.420118	2.172593
H	-5.085082	2.810898	1.599341
H	-6.075940	0.679662	2.379774
C	-2.076474	-3.526258	-0.980841
O	-1.006020	-2.779192	-0.361483
C	-0.518553	-3.466668	0.808705
C	-1.609731	-4.456099	1.149971
C	-2.132333	-4.842094	-0.229687
H	-2.996290	-2.946814	-0.866675
H	-1.847476	-3.634841	-2.041134
H	0.420324	-3.966859	0.553766
H	-0.329950	-2.718571	1.577853
H	-1.228082	-5.305734	1.716191
H	-2.393961	-3.970205	1.736237
H	-1.469771	-5.575737	-0.694829
H	-3.141627	-5.252892	-0.206763

IN3-*RSRR*

C	-0.411588	0.699285	2.737004
C	0.971463	0.470146	2.081926
O	-1.345024	0.389294	1.693191
H	-0.550060	-0.064911	3.505099
Cu	0.414567	-2.058253	0.946093
O	1.283162	-0.863224	2.046413
C	-0.679547	2.073056	3.314507
H	-1.727055	2.143570	3.615293
H	-0.479366	2.867305	2.592309
H	-0.059843	2.243138	4.196910
C	2.097333	1.225894	2.770770
H	3.038749	1.019004	2.258891
H	2.190067	0.872338	3.800767
H	1.938317	2.305527	2.783847
O	1.136272	-0.561925	-0.953839

C	1.495216	0.472343	-0.404461
C	2.825871	1.049828	-0.710618
C	3.776620	0.223442	-1.311870
C	3.156806	2.375755	-0.433818
C	5.034160	0.708342	-1.620098
H	3.512599	-0.805557	-1.522417
C	4.411837	2.865855	-0.758491
H	2.434641	3.041235	0.021314
C	5.353157	2.033604	-1.347084
H	5.770102	0.055283	-2.074664
H	4.655492	3.900966	-0.549566
H	6.336893	2.416854	-1.593549
C	0.650209	1.095416	0.650850
C	-0.838939	0.846169	0.473922
H	0.814115	2.168816	0.712725
H	-1.058164	0.098727	-0.290134
O	-1.428492	2.076671	0.079917
C	-2.702024	2.041894	-0.397032
C	-3.172094	3.228121	-0.956235
C	-3.527800	0.922240	-0.351399
C	-4.453915	3.291544	-1.472888
H	-2.515088	4.089886	-0.981508
C	-4.809808	0.999698	-0.881955
H	-3.193696	0.003544	0.111377
C	-5.282232	2.175418	-1.443119
H	-4.807213	4.220442	-1.906528
H	-5.447029	0.123159	-0.842051
H	-6.285878	2.225611	-1.848158
C	-1.287143	-2.984873	-1.236883
O	-0.438348	-3.404114	-0.135256
C	0.228832	-4.642471	-0.468869
C	-0.621780	-5.243912	-1.562879
C	-1.055739	-4.003817	-2.336534
H	-2.315684	-2.992051	-0.869727
H	-1.005657	-1.971177	-1.520455
H	1.239281	-4.417152	-0.821309
H	0.284060	-5.237217	0.442589
H	-0.060347	-5.952766	-2.171567
H	-1.486508	-5.756842	-1.134934
H	-0.252649	-3.672485	-2.998834
H	-1.953068	-4.162744	-2.934403

IN3-*RRSS*

C	0.722602	-2.517279	1.023409
C	-0.533906	-1.628992	1.353212
O	1.194827	-2.163662	-0.290964
H	1.477608	-2.205390	1.751470
Cu	0.461109	0.877757	1.947809
O	-0.274068	-0.828076	2.423786
C	0.556832	-4.012917	1.062683
H	0.245516	-4.333184	2.058696
H	1.507925	-4.498993	0.833874
H	-0.187115	-4.349831	0.338302
C	-1.810281	-2.423198	1.612646
H	-2.053396	-3.119273	0.806757
H	-2.644579	-1.728711	1.734287
H	-1.705656	-2.986614	2.542016
O	-0.939977	1.400782	0.505332
C	-1.436097	0.392357	-0.011230

C	-2.835858	0.457056	-0.486515
C	-3.635176	1.511056	-0.035630
C	-3.378804	-0.468218	-1.379104
C	-4.946892	1.628660	-0.454874
H	-3.210381	2.228868	0.654826
C	-4.689254	-0.340024	-1.810714
H	-2.780809	-1.283795	-1.764623
C	-5.477005	0.703525	-1.347158
H	-5.560527	2.443466	-0.088444
H	-5.095778	-1.058717	-2.512560
H	-6.503882	0.797888	-1.681640
C	-0.693002	-0.886895	-0.073017
C	0.723340	-0.904276	-0.619255
H	-1.224166	-1.596117	-0.703310
H	0.770561	-0.795273	-1.705136
O	1.494802	0.132342	-0.027721
C	2.726229	0.413058	-0.545767
C	3.370065	-0.369708	-1.496528
C	3.335030	1.563995	-0.056020
C	4.619079	0.024004	-1.961804
H	2.923740	-1.285150	-1.859669
C	4.581544	1.938948	-0.524480
H	2.812942	2.157193	0.687822
C	5.230962	1.172126	-1.484723
H	5.118696	-0.589080	-2.703448
H	5.046779	2.839103	-0.139056
H	6.206813	1.465837	-1.852441

TS4-*Re*

C	2.969660	0.817323	1.112056
C	3.530410	1.825558	0.127087
O	1.676062	0.472997	0.761296
H	3.629838	-0.063445	1.040197
Cu	0.567640	1.550079	-0.338309
O	2.824122	2.326193	-0.728161
C	3.068278	1.376901	2.531860
H	4.097733	1.619279	2.801410
H	2.699644	0.632690	3.238771
H	2.455277	2.276832	2.622158
C	4.972156	2.200937	0.263592
H	5.042264	3.064813	0.932469
H	5.371443	2.491312	-0.707728
H	5.563416	1.393853	0.696984
O	-1.579139	0.426050	1.872317
C	-1.454211	-0.435749	0.974002
C	-2.634332	-0.681584	0.072555
C	-2.535593	-1.325337	-1.160280
C	-3.882812	-0.218623	0.482179
C	-3.656559	-1.507317	-1.956153
H	-1.574264	-1.672730	-1.518502
C	-5.007168	-0.406576	-0.305843
H	-3.951756	0.291577	1.435246
C	-4.897701	-1.053340	-1.529927
H	-3.559553	-2.001406	-2.916486
H	-5.972095	-0.046332	0.033382
H	-5.773859	-1.198272	-2.151975
C	-0.291184	-1.199298	0.752494
C	0.836473	-0.975979	1.547501
H	-0.244059	-1.918857	-0.049564

H	0.691872	-0.470127	2.492603
O	1.849667	-1.871325	1.655326
C	2.188186	-2.673451	0.587649
C	2.320848	-2.182848	-0.704299
C	2.475831	-3.997298	0.880220
C	2.738789	-3.042719	-1.709160
H	2.097350	-1.143552	-0.905215
C	2.899392	-4.844380	-0.133143
H	2.366127	-4.349272	1.899183
C	3.029669	-4.371744	-1.431613
H	2.843587	-2.663925	-2.719666
H	3.123738	-5.879896	0.095739
H	3.358731	-5.034546	-2.223249
C	-1.426351	1.974087	-2.505244
O	-0.907158	2.432214	-1.231886
C	-1.964976	3.038589	-0.449450
C	-3.048262	3.356565	-1.454158
C	-2.923816	2.197374	-2.436490
H	-0.950719	2.573851	-3.285108
H	-1.151332	0.927091	-2.632762
H	-2.293884	2.317860	0.302609
H	-1.540739	3.913941	0.042833
H	-4.030786	3.409249	-0.984612
H	-2.846305	4.309469	-1.949572
H	-3.420971	1.310252	-2.040758
H	-3.343001	2.422307	-3.417464

TS4-*Si*

C	-2.300143	-1.414671	0.746850
C	-1.831601	-2.746857	0.185467
O	-1.331237	-0.432880	0.726882
H	-3.158112	-1.116546	0.119969
Cu	0.518881	-1.053723	0.831771
O	-0.656230	-2.946579	-0.061656
C	-2.822672	-1.636752	2.169024
H	-3.637920	-2.362610	2.199269
H	-2.012417	-1.987346	2.813603
H	-3.190272	-0.686322	2.558164
C	-2.859661	-3.816017	-0.019607
H	-3.855896	-3.399858	-0.171479
H	-2.577126	-4.448500	-0.861095
H	-2.888941	-4.441169	0.878674
O	1.466561	0.096830	-0.708491
C	1.004761	1.275730	-0.726393
C	1.978005	2.402165	-0.617731
C	3.282018	2.120096	-0.214497
C	1.640146	3.723004	-0.913251
C	4.222925	3.130187	-0.096846
H	3.541788	1.092359	0.005706
C	2.580730	4.734445	-0.799694
H	0.640407	3.966842	-1.251222
C	3.874676	4.442474	-0.388293
H	5.231676	2.894552	0.223538
H	2.303614	5.755309	-1.037496
H	4.609226	5.234897	-0.298704
C	-0.364889	1.564175	-0.817175
C	-1.267096	0.525233	-1.011393
H	-0.733316	2.565699	-0.654649

H	-0.932022	-0.390319	-1.479502
O	-2.572426	0.730404	-1.265870
C	-3.214303	1.832691	-0.735447
C	-4.013370	2.565394	-1.596383
C	-3.133089	2.142577	0.614004
C	-4.744421	3.634159	-1.097438
H	-4.056949	2.292310	-2.644086
C	-3.865541	3.216149	1.097518
H	-2.503195	1.540687	1.256752
C	-4.671438	3.964012	0.248578
H	-5.371308	4.211276	-1.767417
H	-3.809308	3.465290	2.151142
H	-5.242940	4.799202	0.636169
C	1.857609	-3.118592	2.554390
O	2.073672	-1.939385	1.747257
C	3.353086	-2.020633	1.085707
C	4.106856	-3.106752	1.821565
C	2.985307	-4.067010	2.200666
H	1.892780	-2.814727	3.604469
H	0.867136	-3.512567	2.326296
H	3.191099	-2.277882	0.035370
H	3.818746	-1.036883	1.143643
H	4.873193	-3.566194	1.196923
H	4.584250	-2.701509	2.717367
H	2.708512	-4.684449	1.342542
H	3.241595	-4.724144	3.031893

IN5-*Re*

C	2.119674	0.580021	-2.648581
C	3.099222	0.005082	-1.640247
O	0.787887	0.202998	-2.383801
H	2.221887	1.672419	-2.637172
Cu	0.986546	-1.361640	-0.376947
O	2.838099	-0.978310	-0.959610
C	2.484302	0.038844	-4.024699
H	3.520173	0.262050	-4.281935
H	2.340972	-1.043186	-4.045427
H	1.832986	0.495841	-4.769816
C	4.422757	0.673437	-1.532863
H	4.294872	1.508902	-0.833738
H	5.170419	-0.007608	-1.130034
H	4.748109	1.096801	-2.483347
O	-0.921394	-1.473473	-0.334425
C	-1.696685	-0.544304	-0.796866
C	-3.156801	-0.846325	-0.668016
C	-3.562208	-2.178450	-0.600232
C	-4.133016	0.147111	-0.595038
C	-4.903669	-2.511034	-0.489183
H	-2.804875	-2.951596	-0.638396
C	-5.474365	-0.182425	-0.475299
H	-3.841438	1.190629	-0.609946
C	-5.867094	-1.513650	-0.426998
H	-5.198714	-3.553942	-0.448472
H	-6.216809	0.605393	-0.410570
H	-6.916162	-1.770978	-0.333351
C	-1.327282	0.631657	-1.389375
C	0.058512	1.104406	-1.582940
H	-2.099121	1.282408	-1.774817
H	0.074895	2.095512	-2.054394

O	0.836715	1.204386	-0.369192
C	0.635137	2.252475	0.465065
C	-0.387732	3.185714	0.325834
C	1.536281	2.361663	1.523345
C	-0.490858	4.224680	1.243858
H	-1.111420	3.101784	-0.472692
C	1.416424	3.398077	2.430912
H	2.319968	1.619364	1.619467
C	0.402322	4.340472	2.296590
H	-1.290593	4.947925	1.128722
H	2.122872	3.471567	3.250238
H	0.310072	5.152671	3.007747
C	2.130344	-2.487036	2.401112
O	1.614545	-1.269978	1.867838
C	0.506370	-0.934948	2.704026
C	-0.181432	-2.259506	3.033122
C	0.903649	-3.318455	2.755975
H	2.775511	-2.936799	1.646242
H	2.728129	-2.263277	3.294020
H	0.882997	-0.444621	3.609965
H	-0.122700	-0.236192	2.154998
H	-0.523555	-2.277714	4.068418
H	-1.044251	-2.411769	2.385355
H	1.091712	-3.964434	3.614262
H	0.617426	-3.950815	1.914157

IN5'-*Re*

C	2.671730	-1.157474	-1.057840
C	3.341620	-1.063167	0.300402
O	1.274324	-1.308199	-0.942080
H	2.916675	-0.235781	-1.599047
Cu	0.804928	-1.278549	1.422463
O	2.730994	-1.224157	1.351077
C	3.223517	-2.355991	-1.818004
H	4.302642	-2.278052	-1.950689
H	2.997290	-3.279565	-1.281582
H	2.752710	-2.393871	-2.800231
C	4.808347	-0.821987	0.323329
H	5.127363	-0.217809	-0.526441
H	5.092131	-0.351975	1.263737
H	5.317649	-1.789086	0.254607
O	-1.053106	-1.138204	1.251531
C	-1.576275	-0.855146	0.091964
C	-3.062908	-1.000224	0.046150
C	-3.755393	-1.302824	-1.126038
C	-3.791789	-0.831124	1.222324
C	-5.137027	-1.416729	-1.124581
H	-3.208394	-1.472451	-2.045963
C	-5.174617	-0.932956	1.223342
H	-3.257413	-0.611802	2.138292
C	-5.854400	-1.225751	0.049021
H	-5.655835	-1.663069	-2.044492
H	-5.724385	-0.784841	2.146387
H	-6.935093	-1.312926	0.049027
C	-0.934521	-0.419039	-1.031774
C	0.511922	-0.139696	-1.166922
H	-1.531353	-0.193367	-1.903844
H	0.744771	0.246948	-2.166472
O	1.026622	0.805362	-0.208000

C	0.728414	2.119978	-0.348165
C	1.284988	2.967293	0.608774
C	-0.067654	2.647352	-1.360605
C	1.053950	4.329421	0.547683
H	1.897213	2.537503	1.393335
C	-0.286549	4.019246	-1.410237
H	-0.528444	2.007662	-2.100065
C	0.266777	4.867093	-0.464815
H	1.493059	4.977038	1.298373
H	-0.907572	4.421582	-2.202902
H	0.085224	5.934222	-0.511308

IN5-*Si*

C	0.201255	1.285204	2.022012
C	-0.156836	0.234343	3.054171
O	0.519244	0.645570	0.811143
H	-0.719911	1.874542	1.889741
Cu	-0.461058	-1.472219	0.405756
O	-0.261008	-0.938612	2.759759
C	1.332155	2.196093	2.477769
H	1.544110	2.930300	1.698825
H	1.065042	2.739046	3.384849
H	2.238301	1.616551	2.666904
C	-0.394002	0.715994	4.449949
H	-0.914249	1.675634	4.456748
H	-0.958488	-0.030513	5.005790
H	0.572621	0.866656	4.940820
O	-2.144885	-0.685618	-0.036817
C	-2.342365	0.570685	-0.276822
C	-3.783542	0.961738	-0.370297
C	-4.223271	2.041281	-1.135996
C	-4.731406	0.211133	0.323490
C	-5.569190	2.369166	-1.193754
H	-3.509325	2.618464	-1.711569
C	-6.077011	0.542385	0.274570
H	-4.394683	-0.637992	0.905435
C	-6.502265	1.624227	-0.484580
H	-5.892372	3.205895	-1.803336
H	-6.797969	-0.047930	0.829538
H	-7.554719	1.880768	-0.530945
C	-1.394467	1.547512	-0.421488
C	0.064455	1.326321	-0.371827
H	-1.714695	2.565870	-0.587820
H	0.600285	2.280158	-0.451694
O	0.470460	0.486318	-1.435771
C	1.785094	0.430914	-1.781778
C	2.827333	0.969741	-1.034967
C	2.057838	-0.226255	-2.979431
C	4.131343	0.849710	-1.499998
H	2.635064	1.458073	-0.090476
C	3.361435	-0.342911	-3.426622
H	1.231701	-0.637541	-3.547865
C	4.410058	0.195717	-2.689647
H	4.938655	1.270349	-0.910708
H	3.559333	-0.858365	-4.359785
H	5.431335	0.103444	-3.039379
C	1.629410	-3.260983	-0.803972
O	1.173050	-2.591471	0.394787
C	2.302720	-2.210179	1.209623

C	3.455166	-3.038353	0.688042
C	3.138049	-3.118688	-0.800554
H	1.313226	-4.305732	-0.739349
H	1.150636	-2.791575	-1.663289
H	2.479301	-1.139790	1.079034
H	2.040946	-2.409207	2.248255
H	4.417578	-2.569562	0.895327
H	3.447578	-4.033658	1.139556
H	3.432295	-2.194590	-1.302584
H	3.626032	-3.955860	-1.300202

IN5'-*Si*

C	-2.854599	-0.662632	0.494640
C	-3.275419	-1.715566	-0.512971
O	-1.481618	-0.781551	0.817214
H	-3.043086	0.293541	-0.015864
Cu	-0.580960	-2.070906	-1.085395
O	-2.461950	-2.379396	-1.148855
C	-3.678717	-0.705564	1.769783
H	-3.348136	0.102278	2.421331
H	-3.531421	-1.656561	2.285292
H	-4.741022	-0.574602	1.565029
C	-4.727874	-1.914571	-0.747565
H	-4.885335	-2.461077	-1.675128
H	-5.252325	-0.957296	-0.765714
H	-5.141963	-2.491490	0.085840
O	1.205430	-1.581881	-0.969701
C	1.576234	-0.746930	-0.033076
C	3.044300	-0.730771	0.227923
C	3.808990	-1.844949	-0.114434
C	3.691859	0.376578	0.776892
C	5.178517	-1.861500	0.103713
H	3.312672	-2.700178	-0.555564
C	5.060311	0.362492	0.994157
H	3.124281	1.268332	1.014642
C	5.810187	-0.758330	0.660703
H	5.755956	-2.739593	-0.163868
H	5.546292	1.235985	1.414575
H	6.881626	-0.767155	0.826519
C	0.760090	0.070664	0.686227
C	-0.672712	0.308050	0.399656
H	1.174829	0.668954	1.485138
H	-0.867753	0.481800	-0.671618
O	-1.152663	1.431967	1.125841
C	-0.912500	2.673921	0.630521
C	-0.089537	2.940348	-0.459760
C	-1.546465	3.721212	1.296066
C	0.079921	4.255312	-0.878031
H	0.438452	2.142507	-0.964710
C	-1.361248	5.024392	0.871532
H	-2.180487	3.493146	2.145178
C	-0.548423	5.301455	-0.222288
H	0.723719	4.455664	-1.727284
H	-1.858586	5.830825	1.398780
H	-0.404028	6.322778	-0.553915

TS6-*RR*

C	-0.629178	1.845220	-0.365221
C	-0.221187	1.653164	1.086569
O	-0.520239	0.642380	-1.092043

H	-1.647766	2.239792	-0.385625
Cu	1.933732	-0.026394	-0.283695
O	0.638938	0.846936	1.388169
C	0.291708	2.863389	-1.014176
H	-0.032809	3.039724	-2.040389
H	0.259036	3.809753	-0.471136
H	1.319901	2.498433	-1.022844
C	-0.897744	2.513480	2.096528
H	-0.396592	2.451387	3.060530
H	-0.938557	3.549280	1.749409
H	-1.934214	2.174872	2.196284
O	1.346732	-1.697591	-0.930482
C	0.220882	-2.248490	-0.575314
C	0.342262	-3.703342	-0.228815
C	-0.535156	-4.357411	0.636780
C	1.400379	-4.433855	-0.768426
C	-0.371960	-5.701427	0.935791
H	-1.342991	-3.804996	1.102383
C	1.560221	-5.780979	-0.479640
H	2.097862	-3.924960	-1.421931
C	0.674092	-6.422514	0.374641
H	-1.059846	-6.186000	1.620152
H	2.384272	-6.331804	-0.920252
H	0.802352	-7.473159	0.609768
C	-1.020345	-1.697581	-0.533206
C	-1.527216	-0.344443	-0.877415
H	-1.842229	-2.364374	-0.302932
H	-2.118343	-0.390271	-1.800143
O	-2.413356	0.040125	0.171180
C	-3.566759	0.701061	-0.134591
C	-3.807196	1.354989	-1.339053
C	-4.528934	0.722681	0.871560
C	-5.016888	2.012499	-1.528154
H	-3.064274	1.370835	-2.126224
C	-5.724160	1.390326	0.672373
H	-4.322262	0.206894	1.802059
C	-5.978570	2.037186	-0.531364
H	-5.197234	2.517565	-2.470412
H	-6.465978	1.399690	1.463022
H	-6.916831	2.555750	-0.687936
C	3.641737	2.150906	1.067142
O	3.328832	1.382967	-0.112552
C	4.209537	1.744443	-1.197918
C	5.264632	2.638888	-0.578652
C	4.503812	3.290768	0.570890
H	2.703969	2.467000	1.521755
H	4.181096	1.505417	1.766509
H	4.607386	0.826152	-1.630811
H	3.618519	2.271485	-1.952512
H	6.094440	2.040885	-0.194763
H	5.659328	3.358599	-1.295896
H	5.157256	3.679213	1.352225
H	3.877559	4.107150	0.202234

TS6-*RS*

C	1.658965	-0.688849	2.534855
C	2.950009	0.004669	2.156868
O	0.792583	-0.581682	1.425676
H	1.870200	-1.743367	2.751613

Cu	1.034411	1.320265	0.135420
O	2.958029	0.884340	1.318381
C	1.099301	0.005853	3.772714
H	1.798174	-0.065856	4.607455
H	0.909455	1.057904	3.552223
H	0.163492	-0.463796	4.077185
C	4.185010	-0.425821	2.869952
H	4.963196	0.329890	2.780349
H	3.983024	-0.653227	3.917783
H	4.530188	-1.354667	2.402537
O	-0.745332	1.754327	0.717569
C	-1.691870	0.940645	1.073124
C	-3.050505	1.572020	1.099067
C	-4.060293	1.162352	1.969215
C	-3.316861	2.627022	0.226994
C	-5.304209	1.775215	1.954344
H	-3.865018	0.368793	2.681053
C	-4.562461	3.235908	0.203611
H	-2.529436	2.960501	-0.437612
C	-5.563269	2.812028	1.067575
H	-6.072492	1.447884	2.646331
H	-4.752926	4.046904	-0.491004
H	-6.535701	3.291473	1.055996
C	-1.617316	-0.387654	1.378142
C	-0.432654	-1.262841	1.541032
H	-2.546190	-0.899994	1.595339
H	-0.472237	-1.756486	2.517728
O	-0.408104	-2.412066	0.681345
C	-0.519468	-2.301210	-0.668264
C	-0.621854	-3.513874	-1.348917
C	-0.521058	-1.110715	-1.388322
C	-0.724036	-3.537610	-2.728785
H	-0.619575	-4.433309	-0.774508
C	-0.633630	-1.148971	-2.772423
H	-0.439786	-0.153859	-0.888472
C	-0.733963	-2.351922	-3.453326
H	-0.800773	-4.490871	-3.240038
H	-0.640769	-0.213712	-3.321130
H	-0.818353	-2.367593	-4.533509
C	1.889260	1.928185	-2.723089
O	2.247286	1.263839	-1.497513
C	3.011465	0.071627	-1.786022
C	3.000243	-0.069409	-3.296234
C	2.838666	1.373385	-3.762129
H	0.847965	1.693974	-2.964059
H	1.985775	3.001628	-2.557199
H	4.020087	0.222376	-1.393216
H	2.547115	-0.770390	-1.271248
H	3.910477	-0.541053	-3.667081
H	2.144088	-0.668436	-3.614141
H	3.795281	1.900530	-3.724931
H	2.434706	1.455502	-4.771518

IN7-*RS*

C	1.143145	2.090178	0.543175
C	2.327762	2.070644	-0.408221
O	0.585115	0.797999	0.508494
H	1.514464	2.305932	1.556067
Cu	0.255524	-0.629862	-1.320512

O	2.377405	1.285824	-1.328371
C	0.206484	3.213717	0.108739
H	-0.619395	3.318916	0.810552
H	0.752935	4.158283	0.079381
H	-0.200942	3.006204	-0.881474
C	3.410960	3.066760	-0.141724
H	4.065492	2.641568	0.627213
H	3.995722	3.243881	-1.042801
H	3.017551	4.003662	0.254359
O	-1.373706	0.273726	-1.640569
C	-2.127734	0.785933	-0.711464
C	-3.458242	1.264043	-1.198508
C	-4.047089	0.635638	-2.294817
C	-4.135595	2.327360	-0.601768
C	-5.288676	1.037654	-2.763721
H	-3.517542	-0.179534	-2.772540
C	-5.373265	2.736746	-1.073801
H	-3.680703	2.853476	0.229174
C	-5.959058	2.089396	-2.153592
H	-5.735847	0.527603	-3.610006
H	-5.879852	3.570990	-0.600903
H	-6.927552	2.408384	-2.522220
C	-1.848918	0.924349	0.615321
C	-0.579459	0.565703	1.285788
H	-2.614425	1.326680	1.264467
H	-0.481543	1.099852	2.241199
O	-0.575519	-0.833528	1.546005
C	0.331266	-1.349708	2.418161
C	1.374999	-0.637695	3.000324
C	0.160810	-2.698743	2.724573
C	2.233764	-1.282609	3.882188
H	1.537898	0.404799	2.768272
C	1.024605	-3.328259	3.602342
H	-0.660838	-3.236770	2.265952
C	2.070975	-2.624587	4.187550
H	3.045969	-0.719220	4.328077
H	0.878948	-4.378186	3.830517
H	2.749886	-3.118065	4.872608
C	2.870595	-1.710414	-0.367273
O	1.655180	-1.977866	-1.112597
C	1.252360	-3.351421	-0.919873
C	2.511463	-4.060140	-0.478391
C	3.185006	-2.993224	0.378092
H	3.641635	-1.447526	-1.094463
H	2.690282	-0.862395	0.290031
H	0.479590	-3.388288	-0.147290
H	0.840257	-3.704750	-1.865115
H	2.291236	-4.974382	0.073437
H	3.129515	-4.313899	-1.343241
H	2.739066	-2.970721	1.374242
H	4.259447	-3.145268	0.482679

TS8-*RS*

C	0.162807	1.996011	-1.584266
C	-0.378843	2.994524	-0.570262
O	0.456287	0.787590	-0.917745
H	1.128910	2.432720	-1.887966
Cu	-0.028818	0.524237	1.399741
O	-0.446787	2.723697	0.610629

C	-0.702358	1.908487	-2.833024
H	-0.753637	2.892398	-3.299098
H	-0.258212	1.228856	-3.560149
H	-1.711111	1.569362	-2.601018
C	-0.774287	4.340865	-1.086275
H	-0.088047	4.687693	-1.861392
H	-1.766884	4.266011	-1.541401
H	-0.815658	5.053715	-0.264779
O	-1.733712	-0.279057	1.115887
C	-2.201424	-0.583813	-0.052982
C	-3.676682	-0.835031	-0.082220
C	-4.486230	-0.203911	0.861192
C	-4.279195	-1.685220	-1.009614
C	-5.859951	-0.394126	0.862729
H	-4.019858	0.443712	1.593322
C	-5.651451	-1.883963	-1.004787
H	-3.666347	-2.214497	-1.729774
C	-6.449439	-1.235094	-0.071579
H	-6.473710	0.114866	1.598031
H	-6.099529	-2.556741	-1.727878
H	-7.522441	-1.391058	-0.067746
C	-1.509153	-0.671411	-1.227468
C	-0.056459	-0.463309	-1.401135
H	-2.053429	-0.902914	-2.132029
H	0.215062	-0.573421	-2.455455
O	0.665445	-1.422502	-0.647952
C	1.998497	-1.570166	-0.873835
C	2.739384	-0.827804	-1.788001
C	2.624635	-2.556859	-0.115197
C	4.096081	-1.087554	-1.936874
H	2.279576	-0.042814	-2.371190
C	3.977517	-2.800414	-0.270196
H	2.030329	-3.125983	0.590460
C	4.725169	-2.066504	-1.183824
H	4.665979	-0.502925	-2.650605
H	4.450975	-3.570930	0.328039
H	5.785008	-2.255913	-1.304784
C	2.791667	1.530021	1.392979
O	1.789739	0.799811	2.138962
C	2.413763	-0.251808	2.907904
C	3.886426	0.093573	2.924833
C	4.072702	0.738748	1.556183
H	2.457029	1.605569	0.359360
H	2.865460	2.530153	1.828654
H	1.944260	-0.262730	3.892002
H	2.230516	-1.206182	2.407749
H	4.103274	0.808979	3.722084
H	4.508997	-0.789601	3.070440
H	4.954776	1.376958	1.498613
H	4.144767	-0.027635	0.781342
36			
H	0.473112	0.033985	1.118008
C	0.473317	0.292313	0.060632
C	-0.969668	0.229702	-0.439822
C	0.848810	1.801430	-0.068460
C	1.414657	-0.587398	-0.721167
O	-1.738938	-0.339245	0.600284
O	-1.363381	1.542827	-0.723896

H	-1.086813	-0.362618	-1.347534
C	1.820873	2.287777	0.977250
C	-0.550409	2.418141	0.064506
O	1.422112	2.088760	-1.328082
C	2.664225	-1.065277	-0.077563
O	1.175051	-0.854994	-1.883430
C	-3.013447	-0.728389	0.311038
H	1.973200	3.363171	0.867130
H	1.440398	2.087415	1.979813
H	2.786939	1.794405	0.863567
C	-0.710105	3.828849	-0.426525
H	-0.856642	2.344775	1.116257
H	0.808476	1.810553	-2.019543
C	3.675264	-1.557457	-0.905080
C	2.862359	-1.050140	1.302496
C	-3.675295	-0.432489	-0.875992
C	-3.656516	-1.464123	1.302799
H	-0.088793	4.503363	0.165519
H	-0.417928	3.914051	-1.473774
H	-1.749354	4.144937	-0.322329
C	4.861818	-2.017103	-0.365683
H	3.512866	-1.565482	-1.975819
C	4.048003	-1.522342	1.843578
H	2.093233	-0.684744	1.970242
C	-4.973891	-0.891379	-1.061965
H	-3.203400	0.164050	-1.644688
C	-4.951989	-1.907741	1.105309
H	-3.123199	-1.682917	2.220696
C	5.049305	-2.001747	1.011958
H	5.644780	-2.388777	-1.016371
H	4.189493	-1.515021	2.917913
C	-5.619690	-1.626936	-0.081097
H	-5.484239	-0.657270	-1.989596
H	-5.442009	-2.481535	1.883884
H	5.978105	-2.365462	1.436678
H	-6.633748	-1.975740	-0.235771

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