

Supporting Information

Enantioselective Phase-transfer Catalytic α -Alkylation of 2-Methylbenzyl *tert*-Butyl Malonates

Min Woo Ha, Suckchang Hong, Cheongyoung Park, Yohan Park, Jihye Lee, Mi-hyun Kim, Jihoon Lee, and Hyeung-geun Park*

*Research Institute of Pharmaceutical Sciences and College of Pharmacy,
Seoul National University, Seoul 151-742, Korea,*

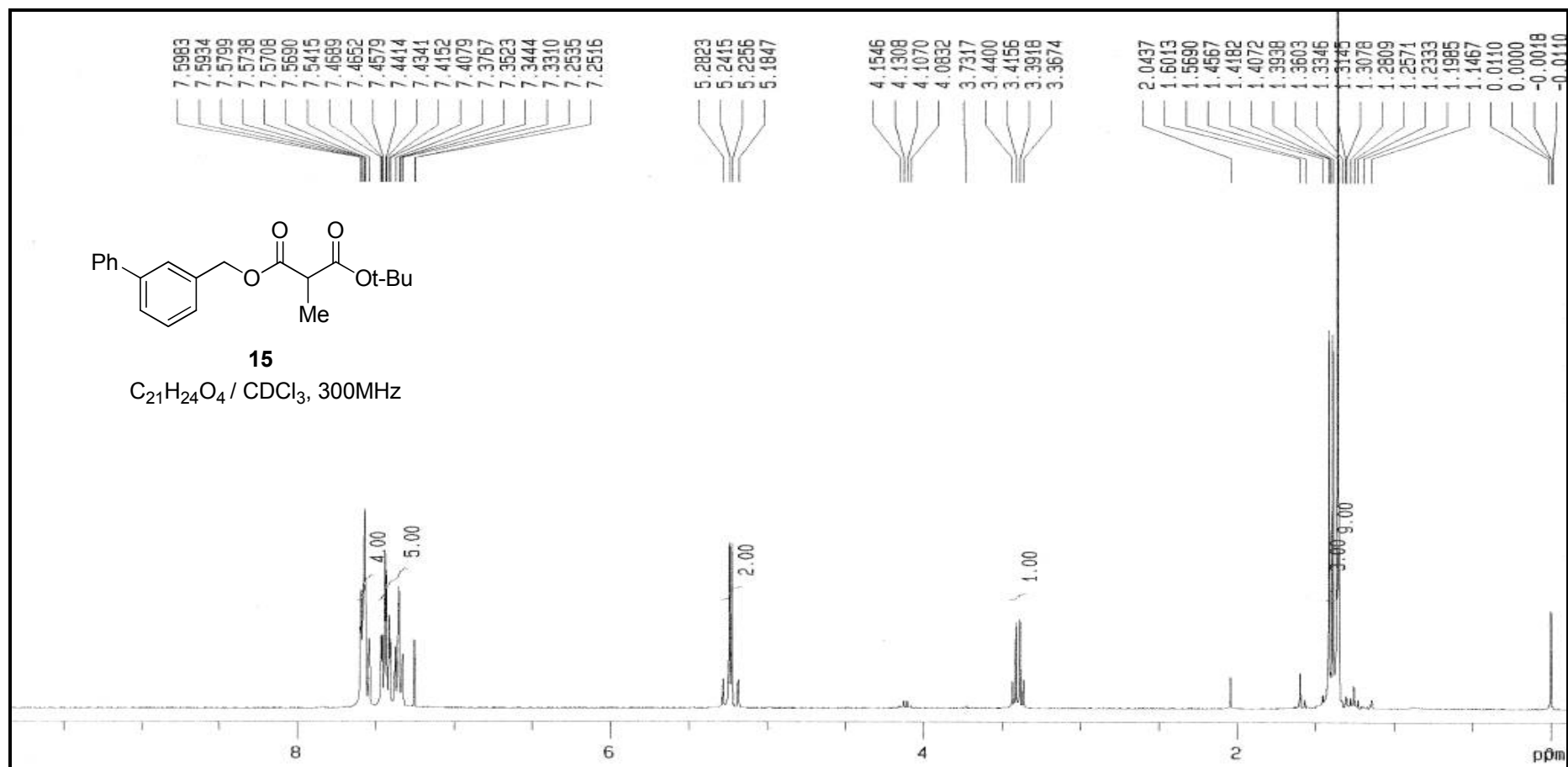
hgpk@snu.ac.kr

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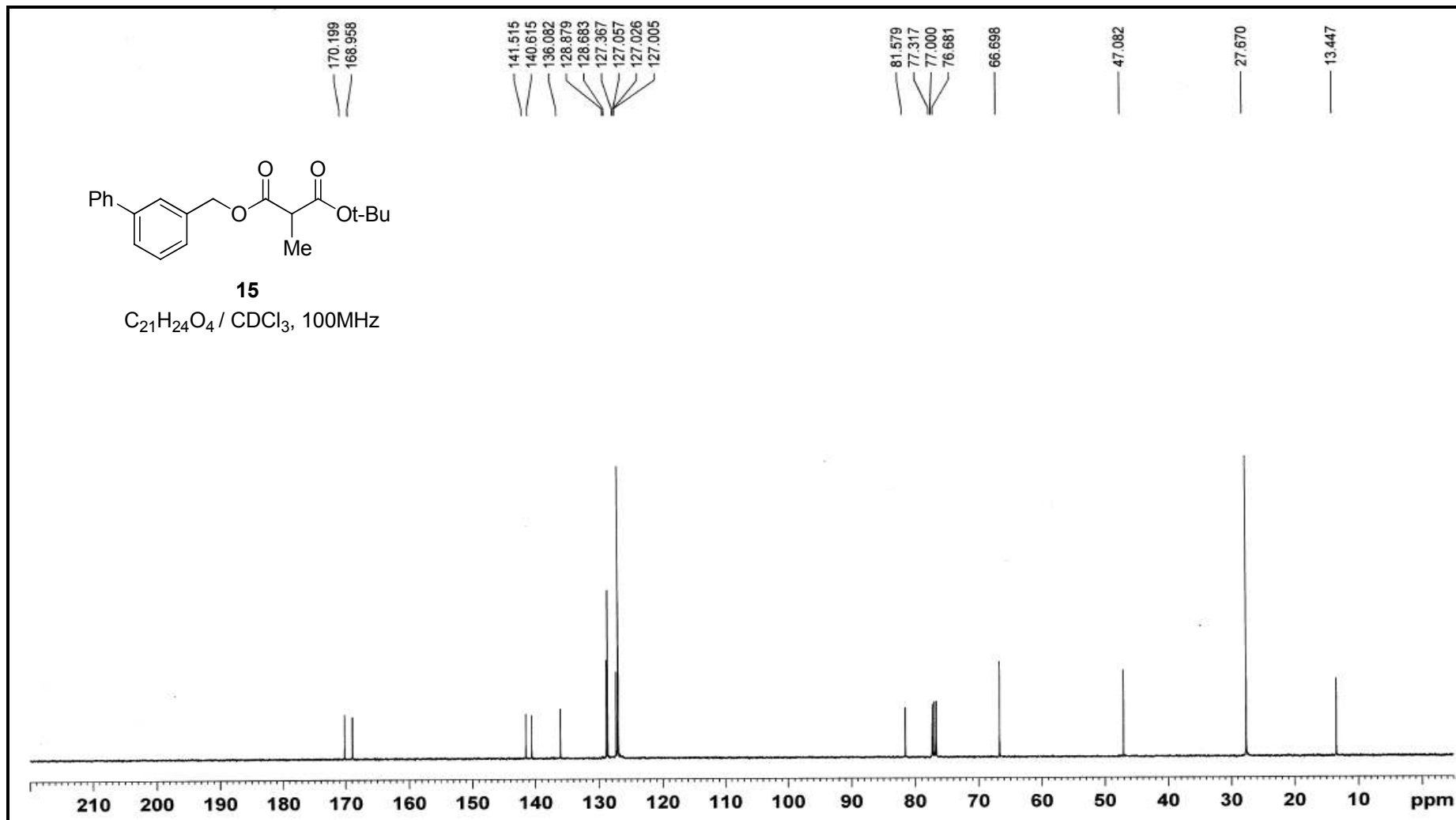
(1) ^1H & ^{13}C NMR Spectra -----	S2
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(1) ^1H & ^{13}C NMR Spectra

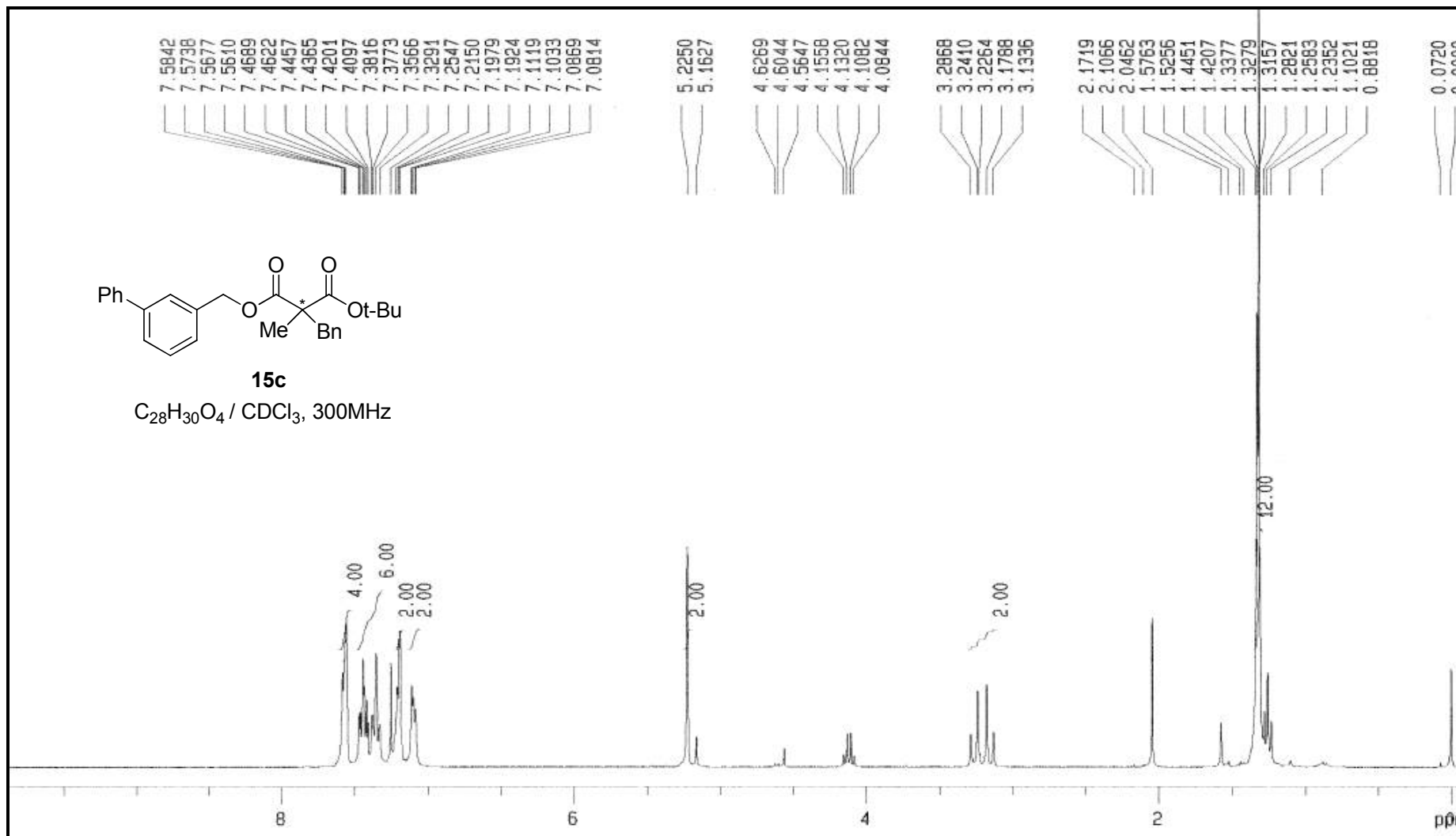
^1H -NMR of compound (15)



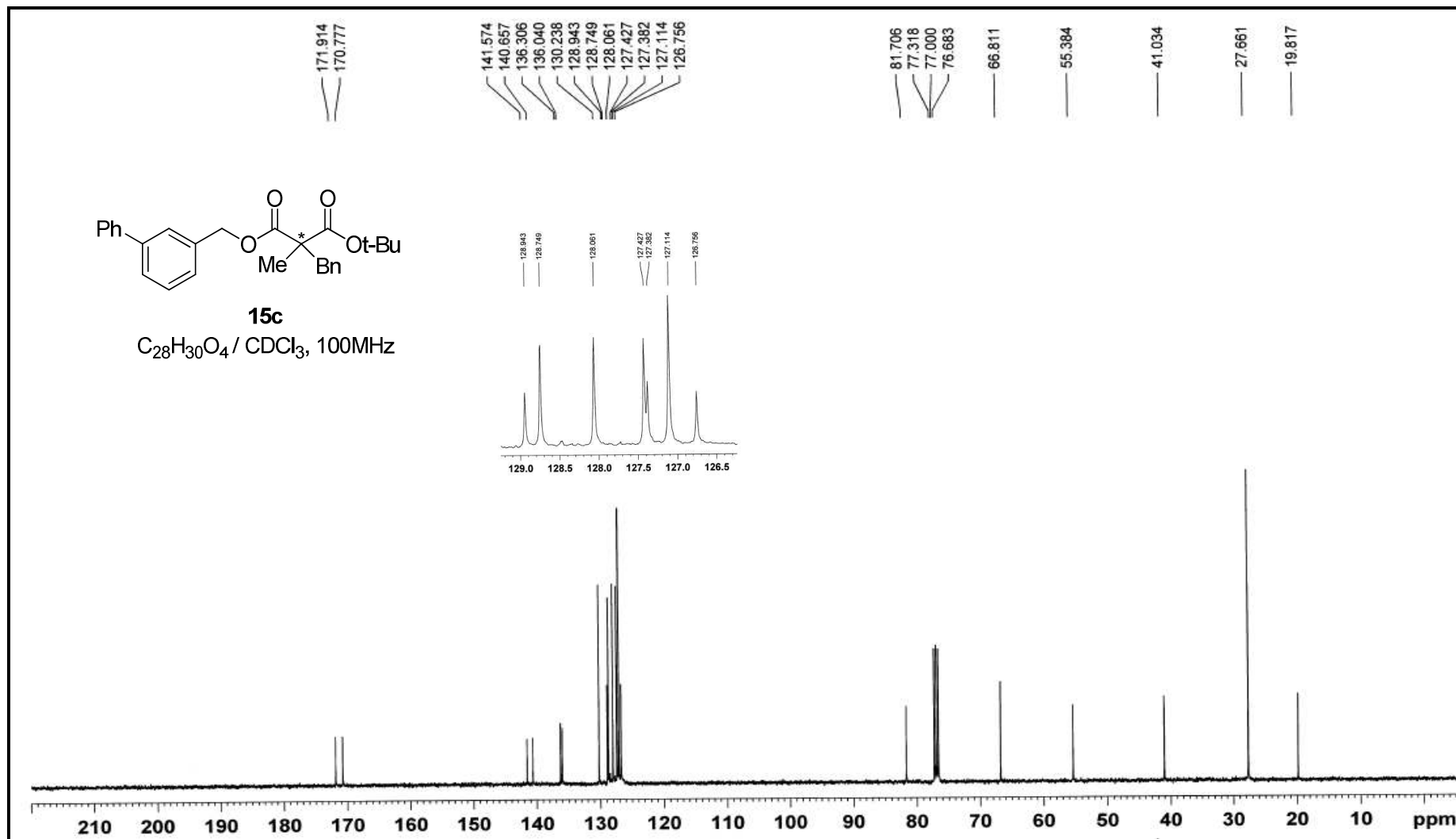
$^{13}\text{C-NMR}$ of compound (**15**)



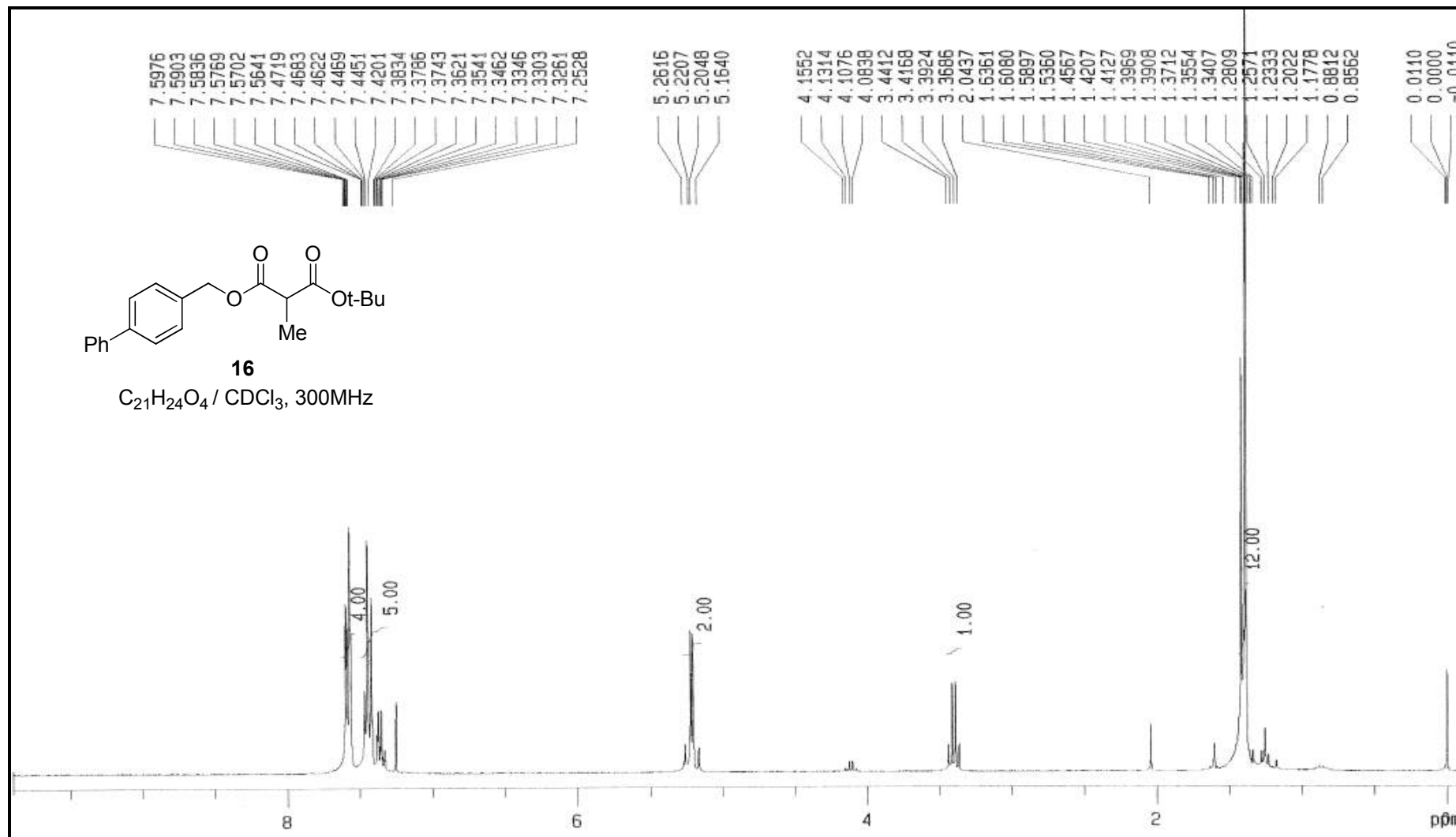
¹H-NMR of compound (15c)



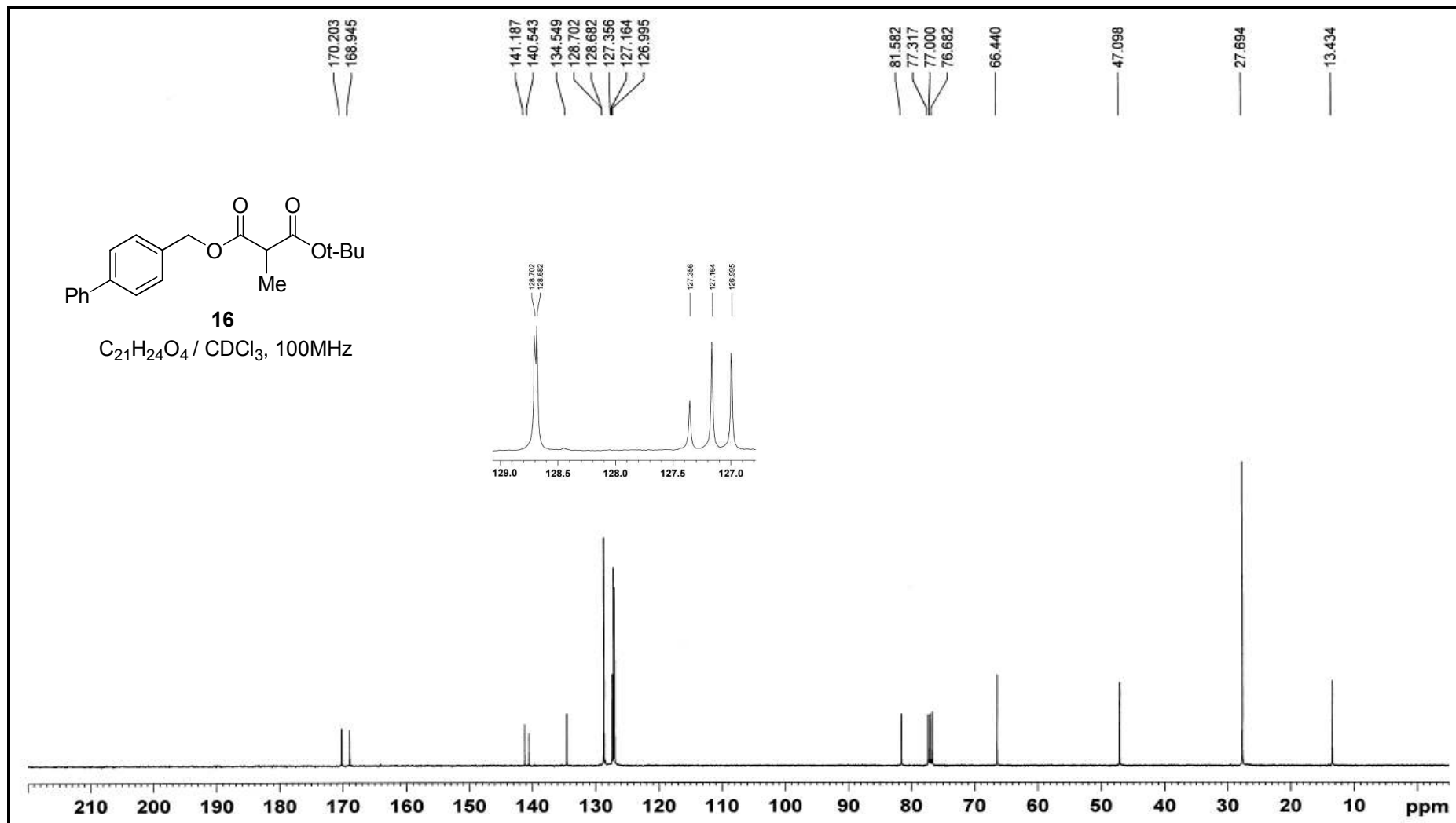
$^{13}\text{C-NMR}$ of compound (**15c**)



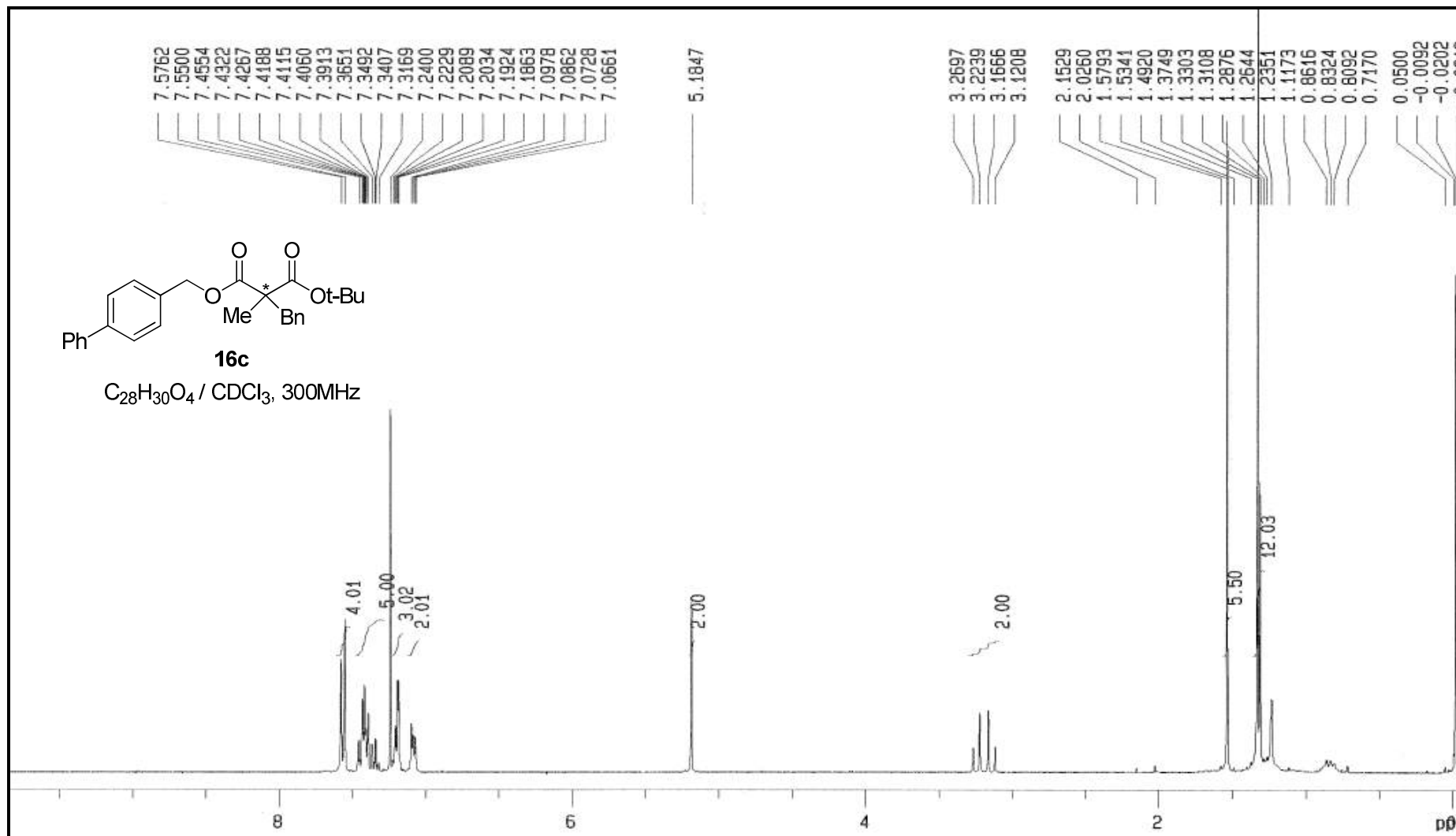
¹H-NMR of compound (16)



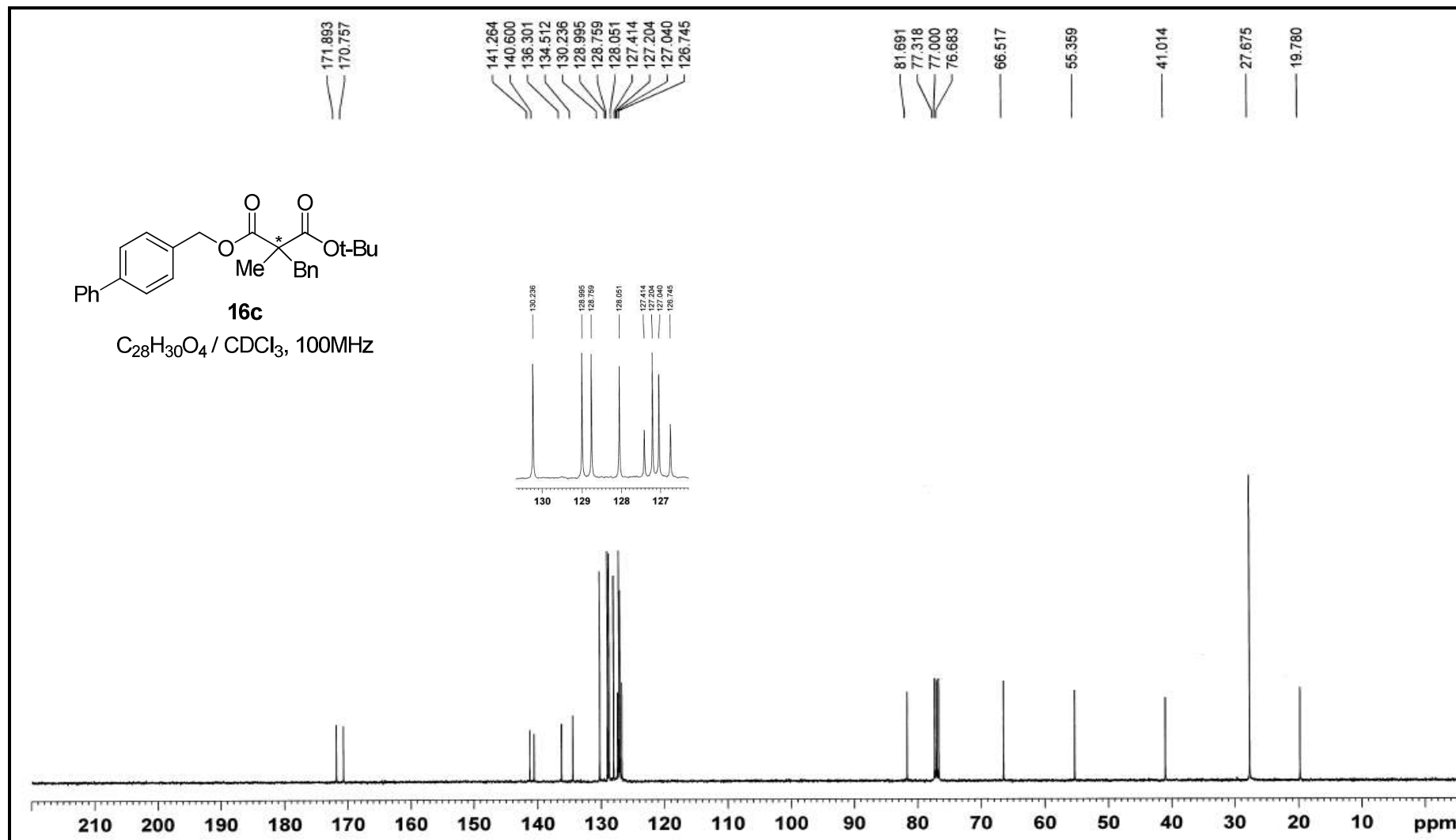
$^{13}\text{C-NMR}$ of compound (**16**)



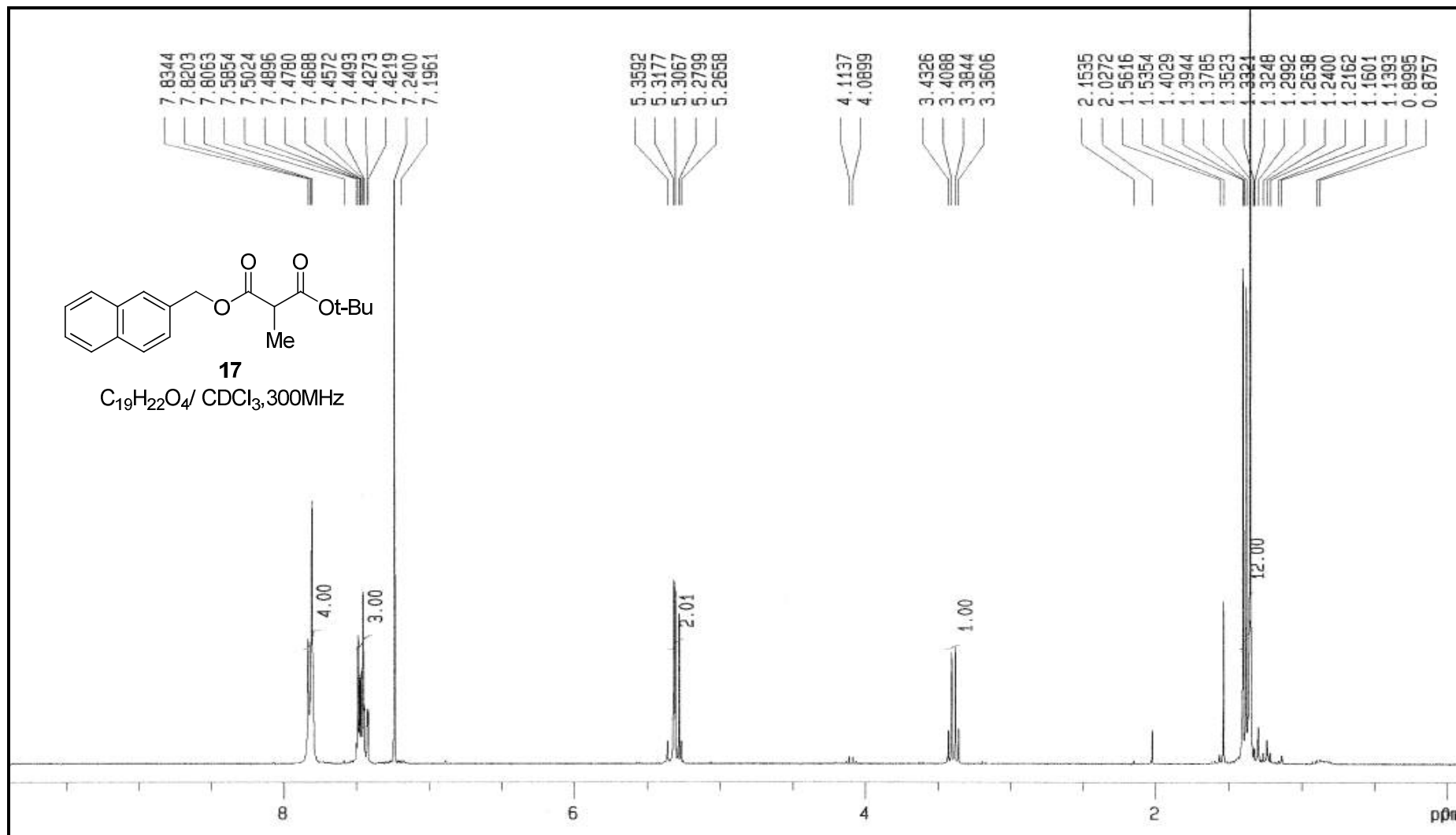
¹H-NMR of compound (16c)



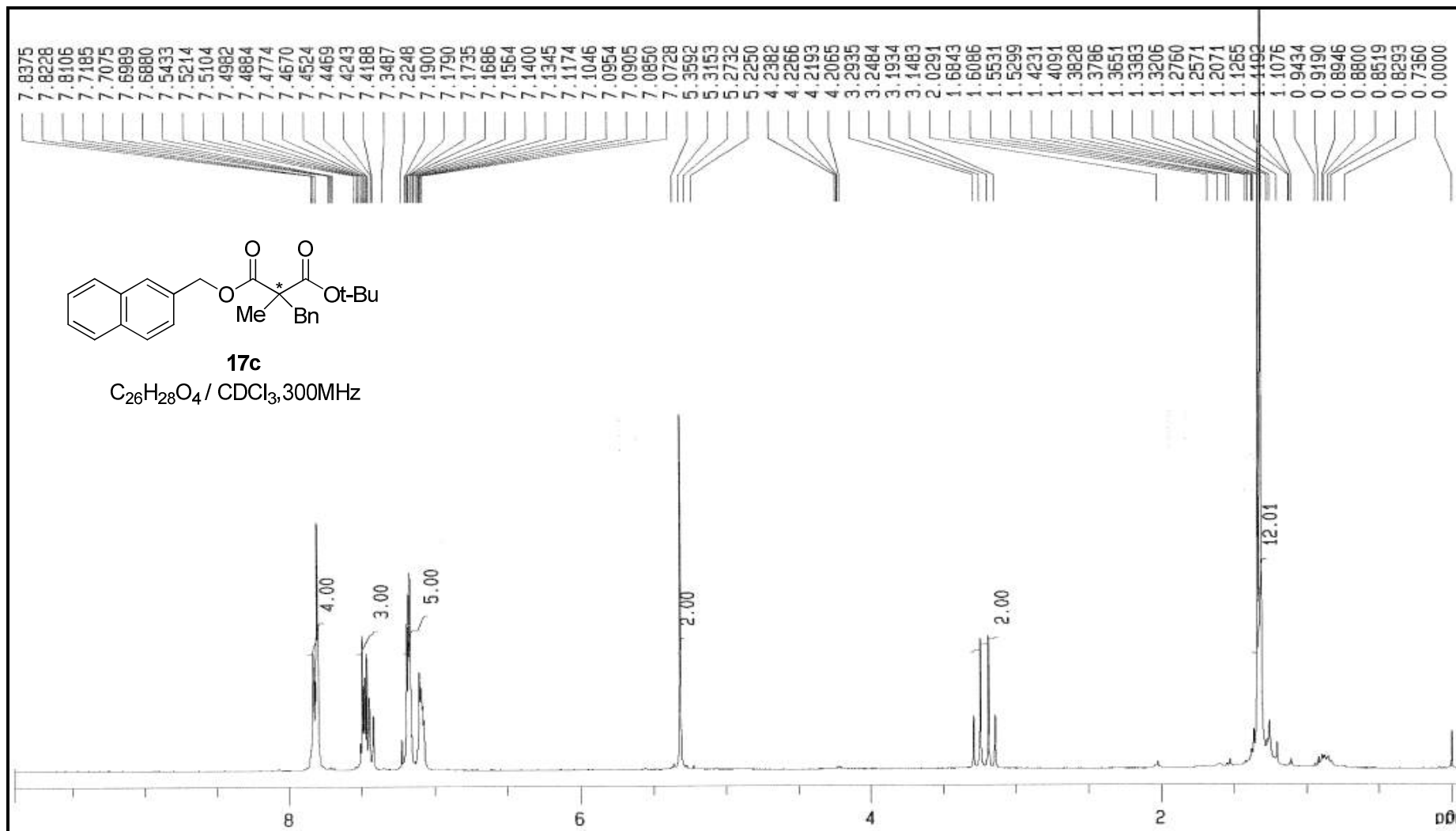
$^{13}\text{C-NMR}$ of compound (**16c**)



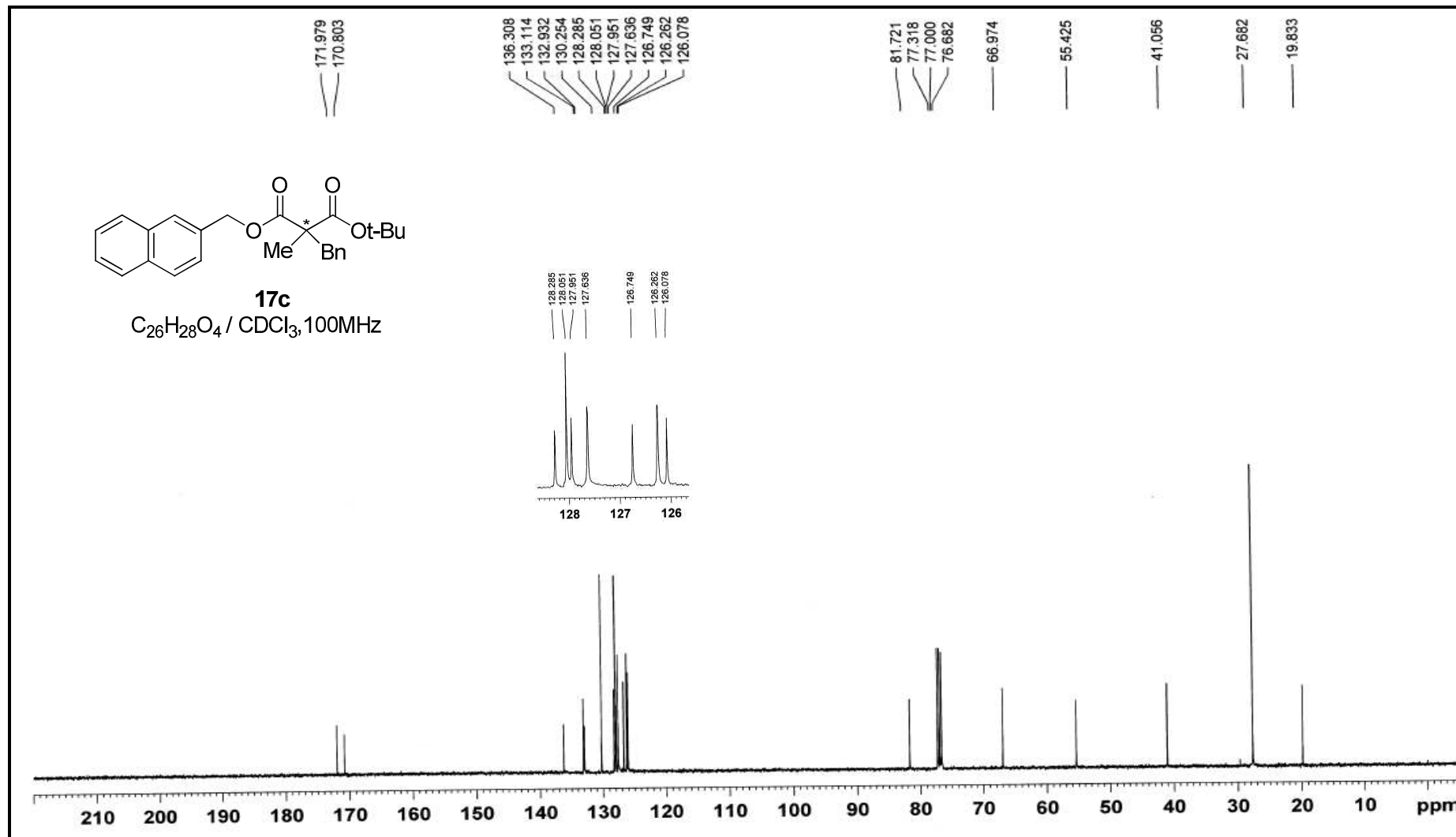
¹H-NMR of compound (17)



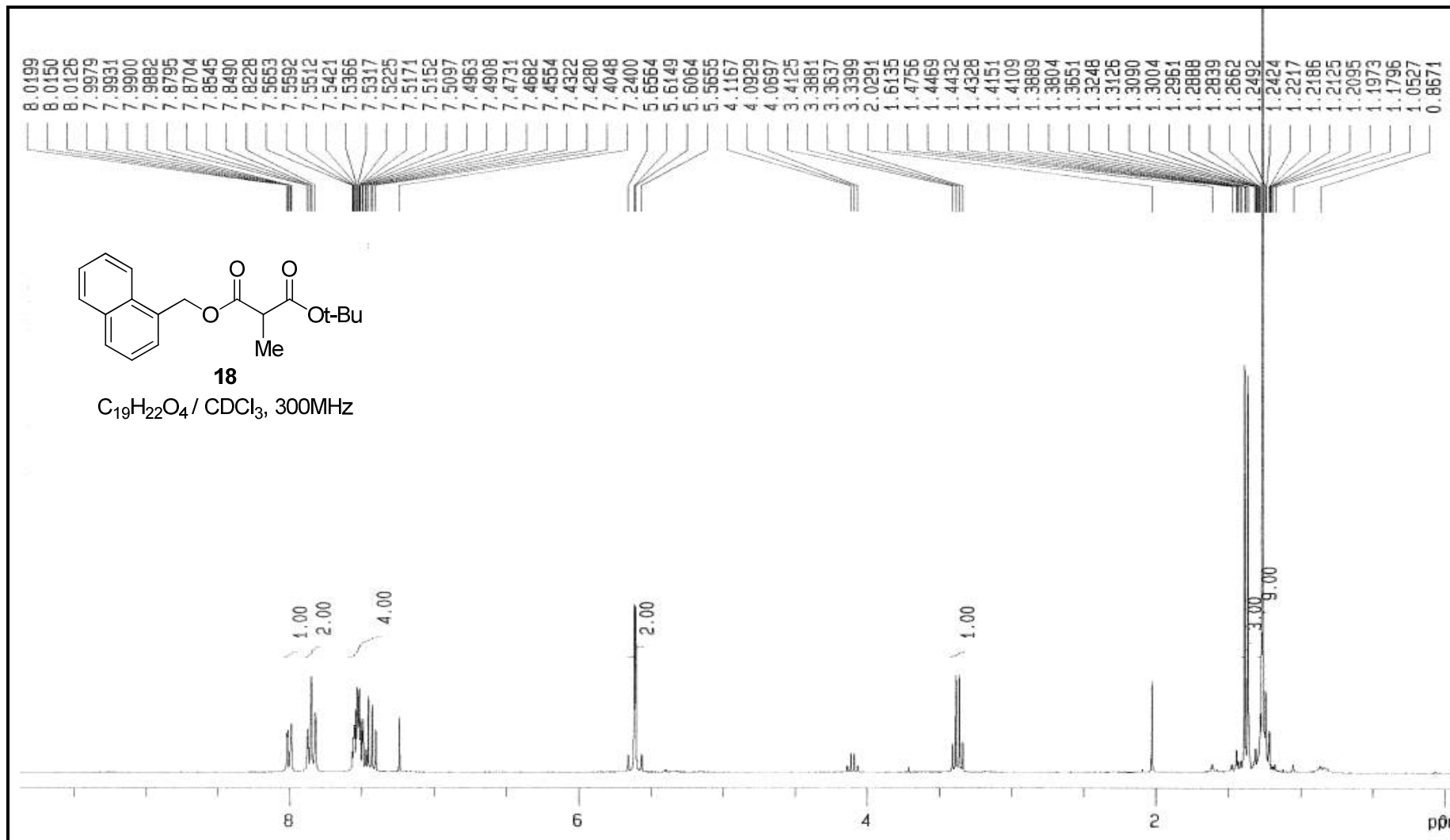
¹H-NMR of compound (17c)



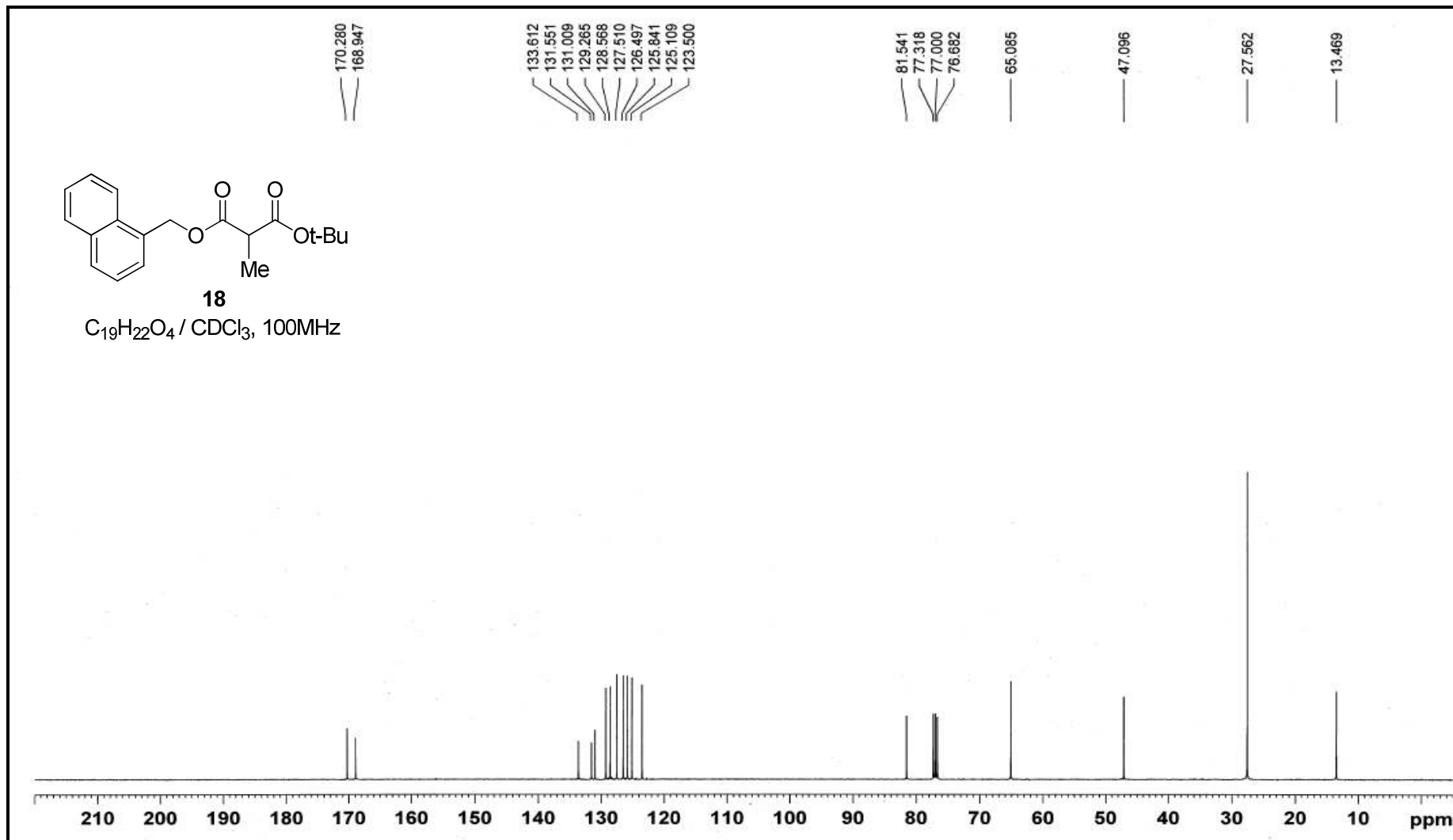
$^{13}\text{C-NMR}$ of compound (**17c**)



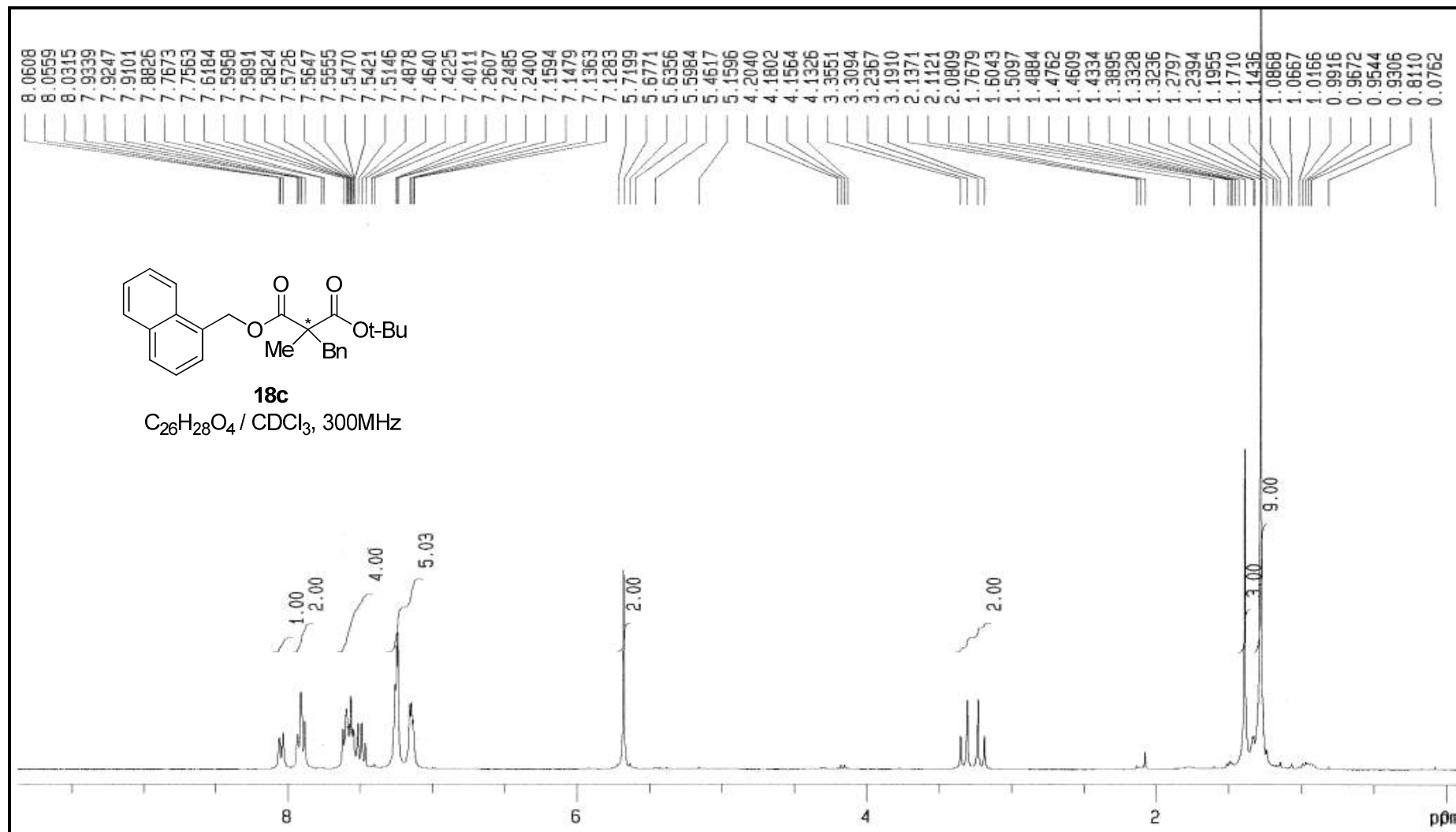
¹H-NMR of compound (18)



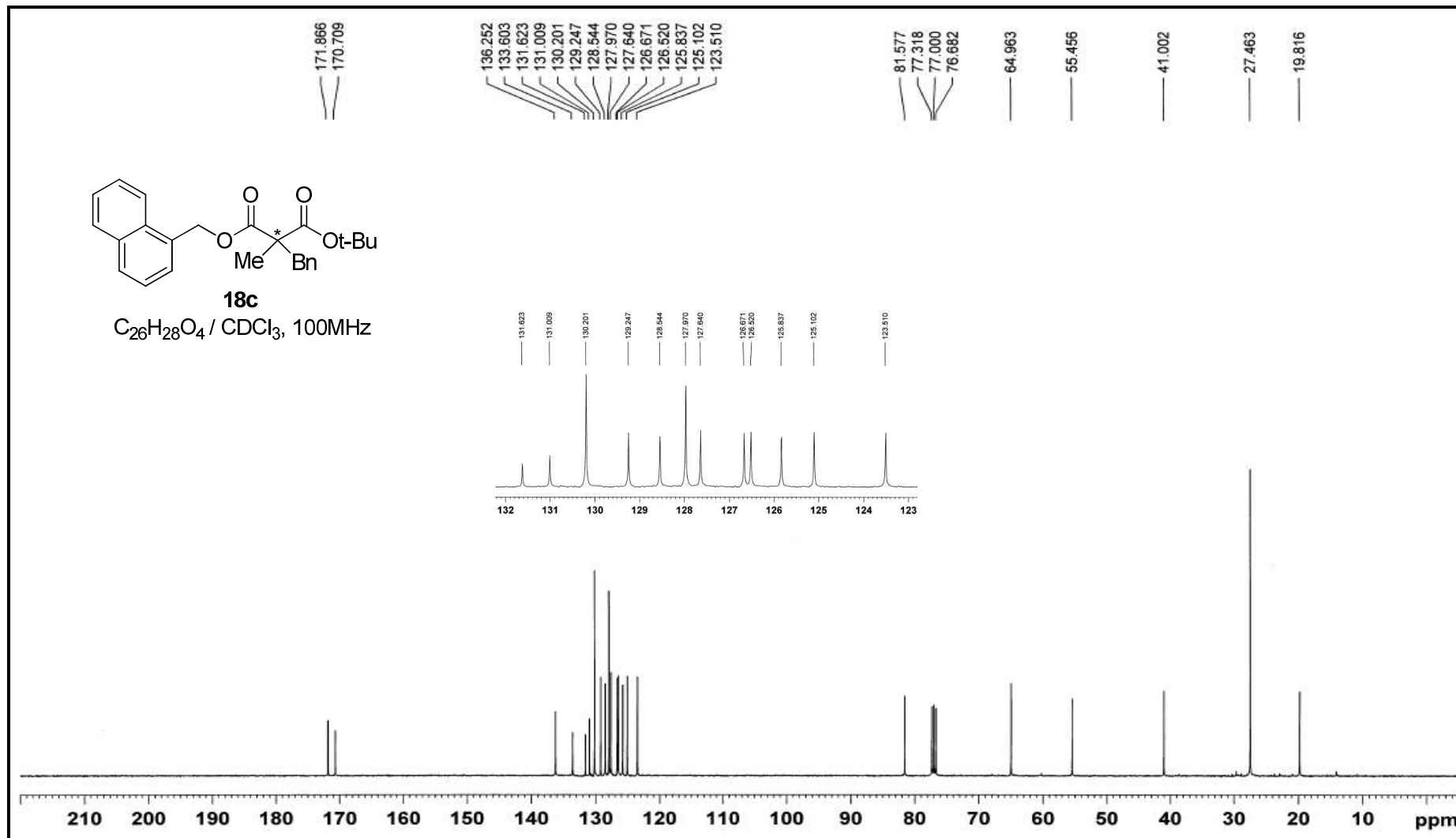
$^{13}\text{C-NMR}$ of compound (**18**)



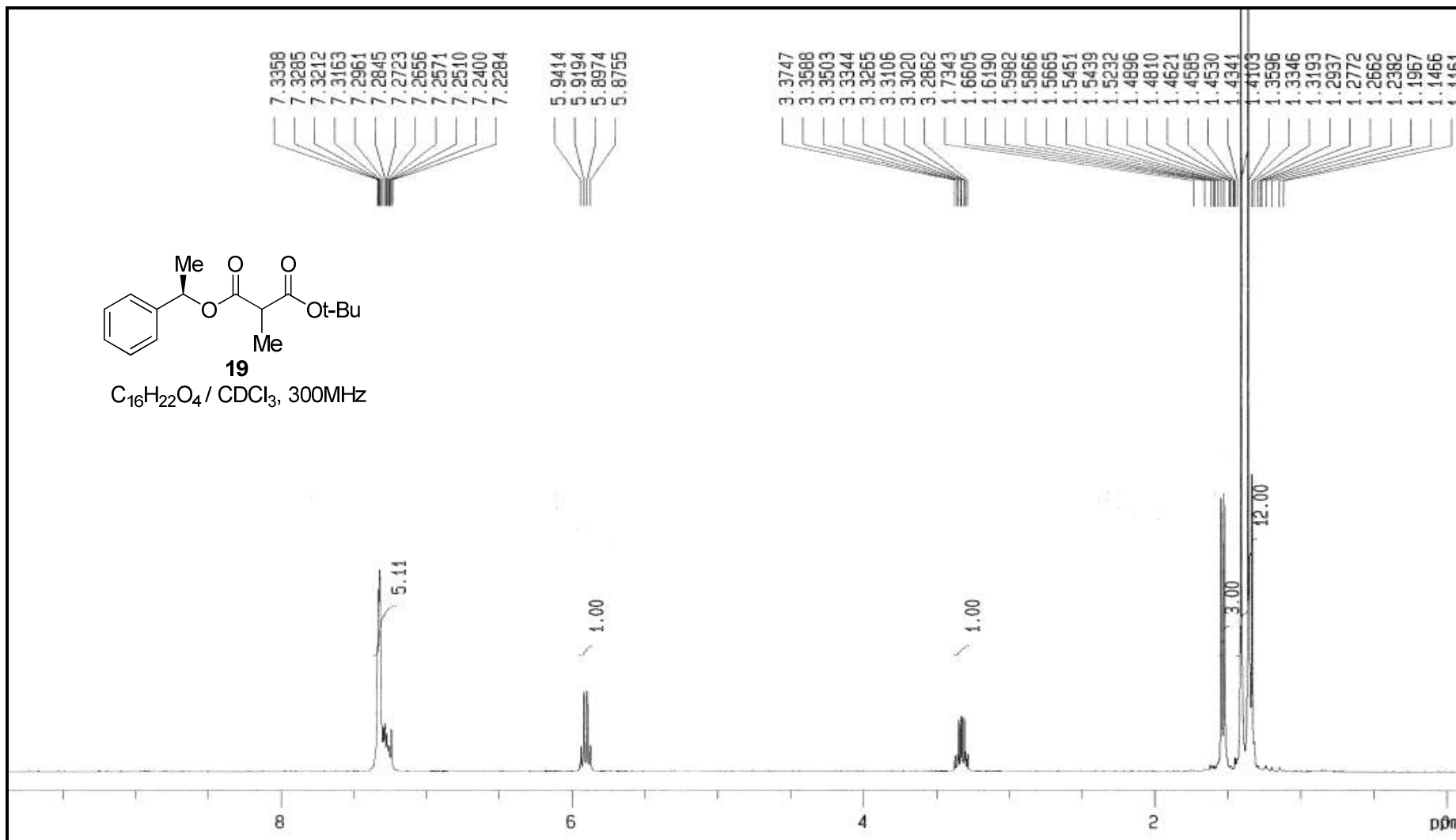
¹H-NMR of compound (18c)



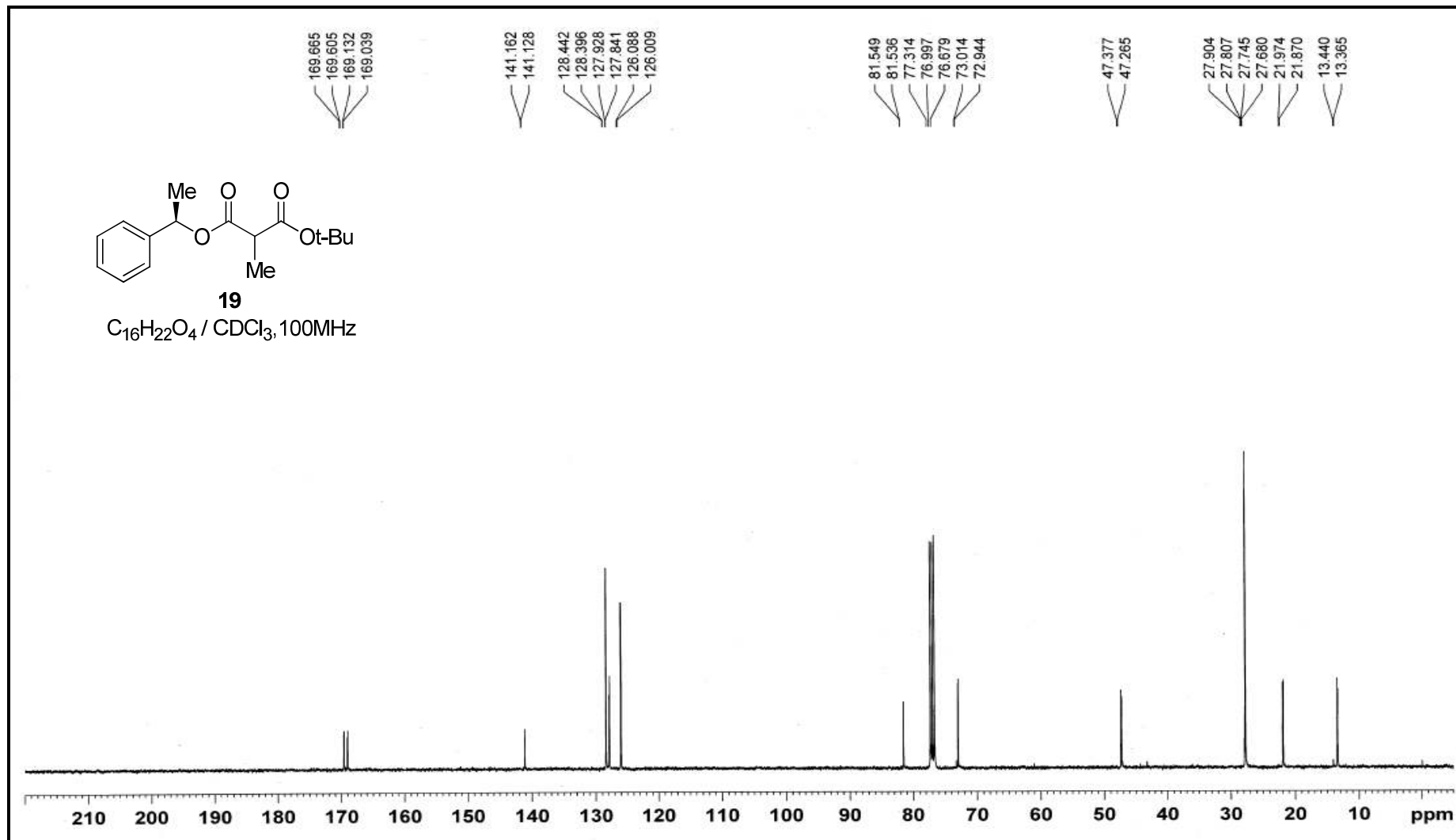
$^{13}\text{C-NMR}$ of compound (**18c**)



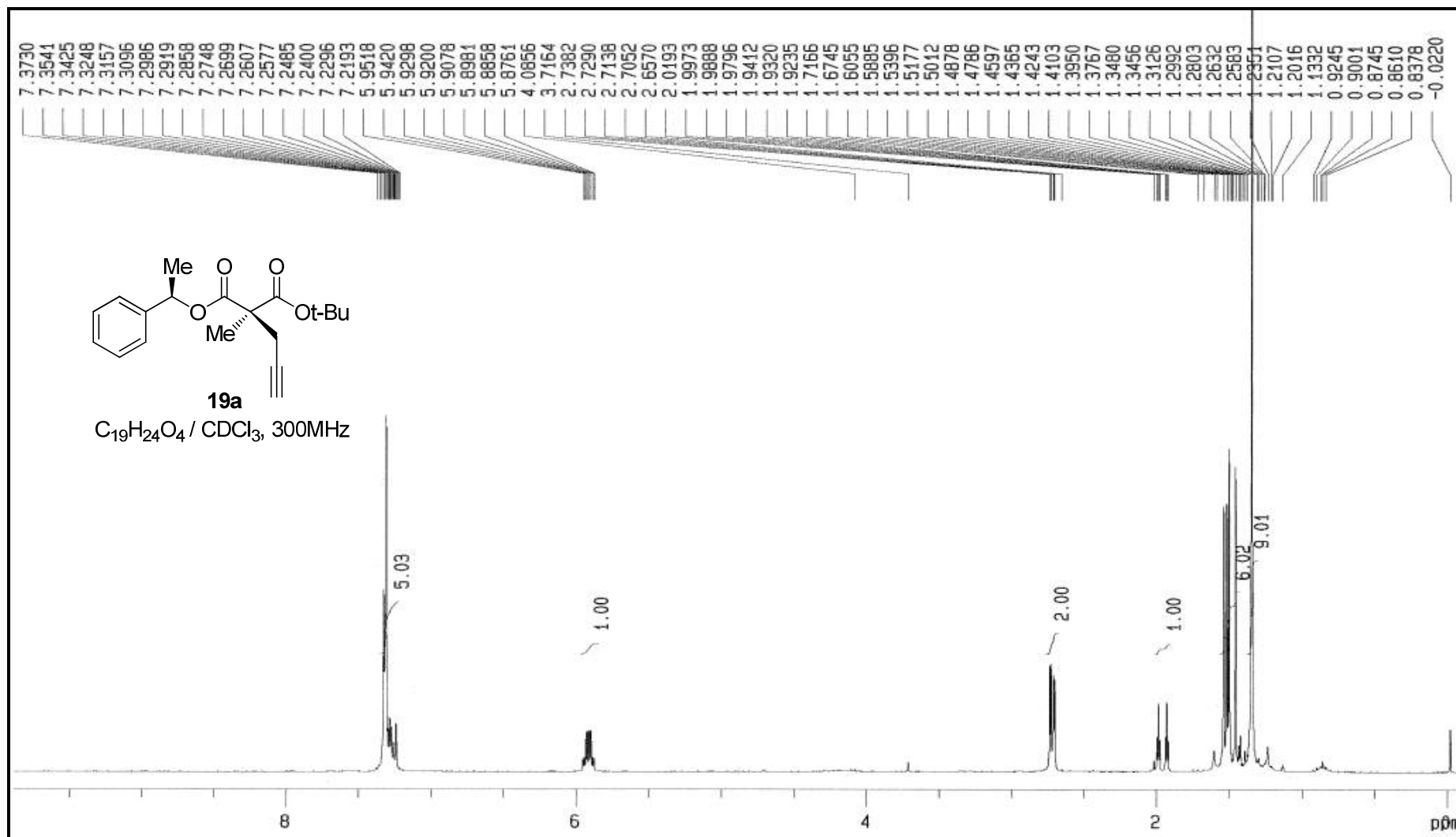
¹H-NMR of compound (19)



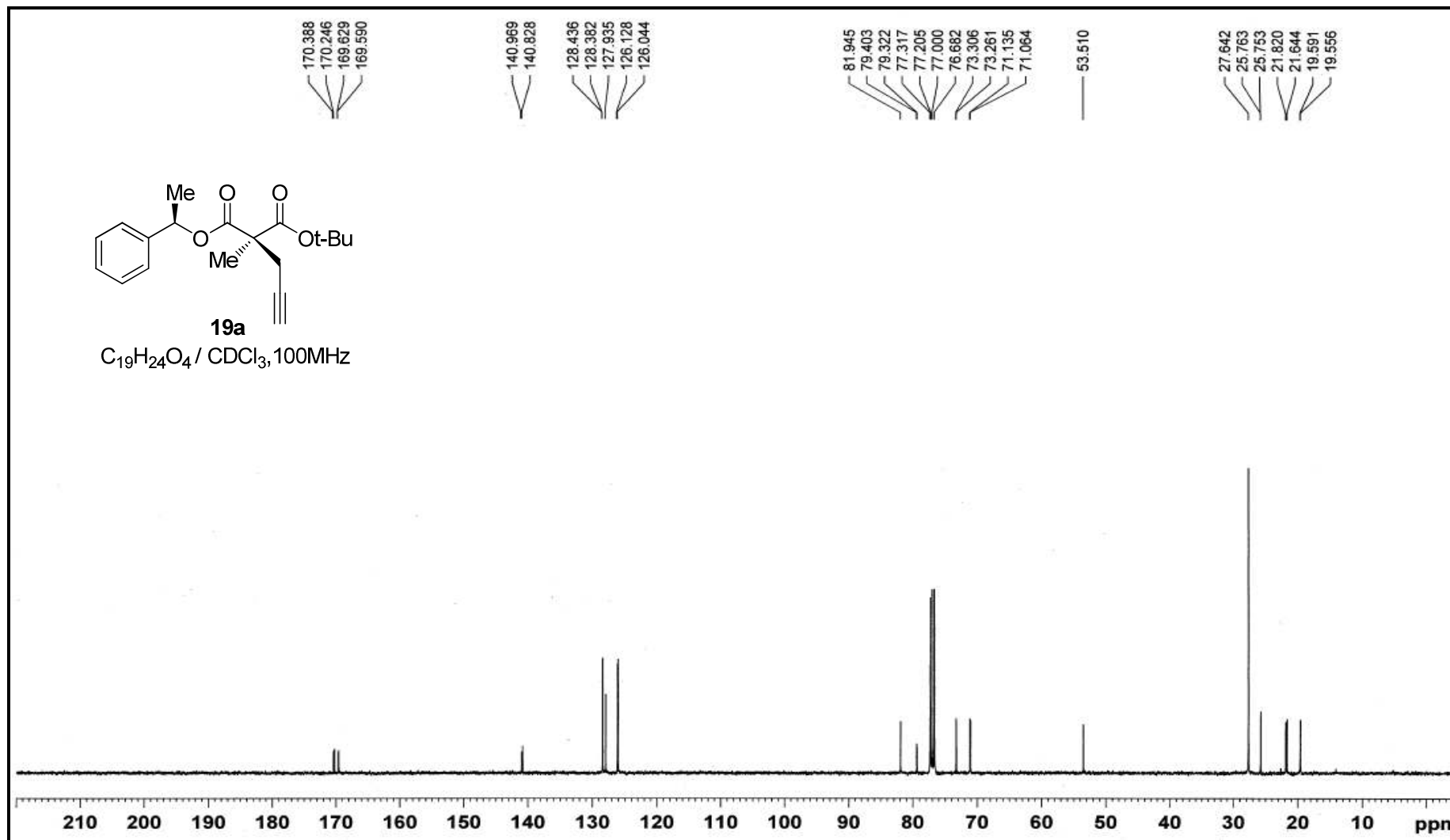
$^{13}\text{C-NMR}$ of compound (**19**)



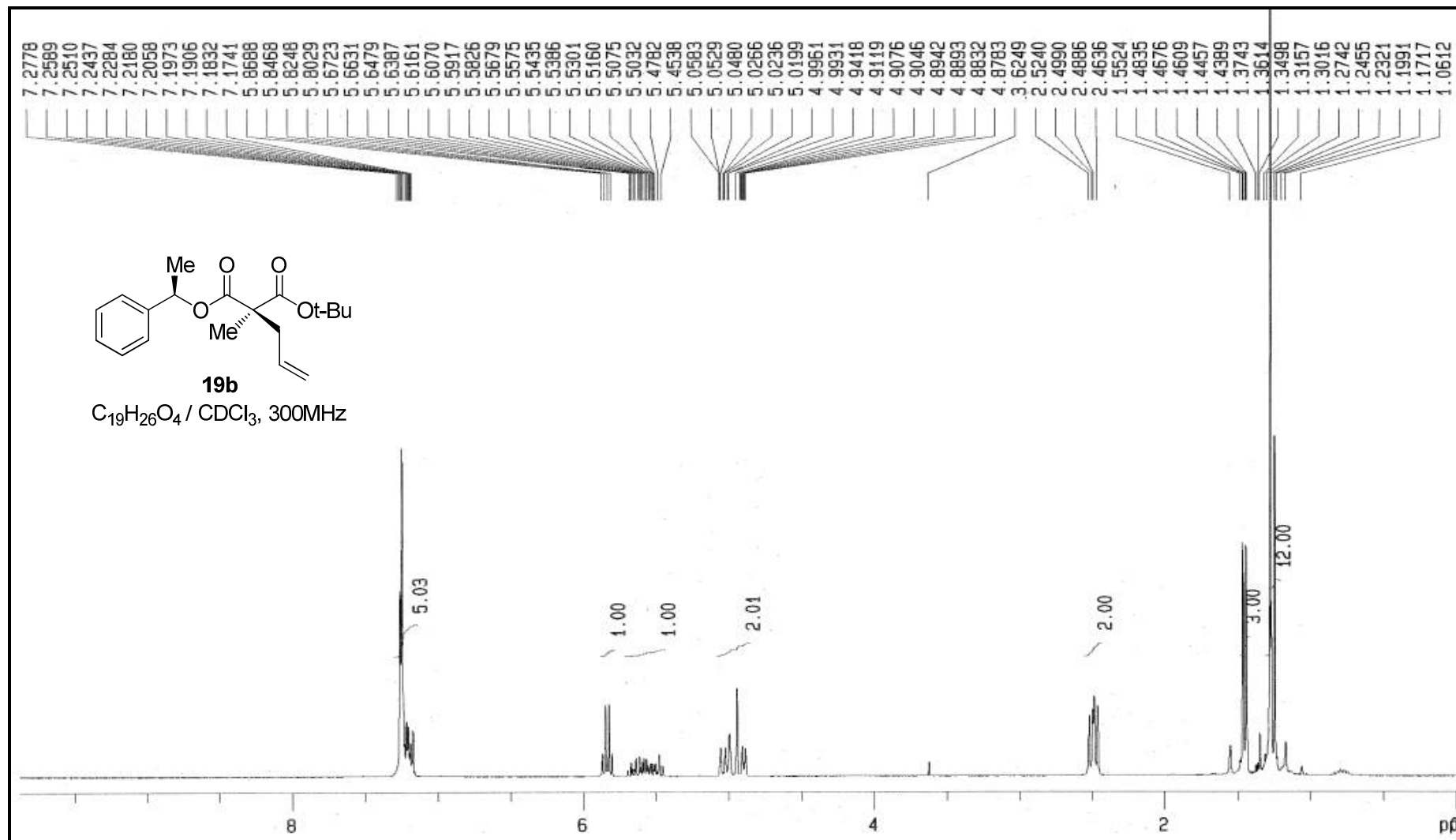
¹H-NMR of compound (19a)



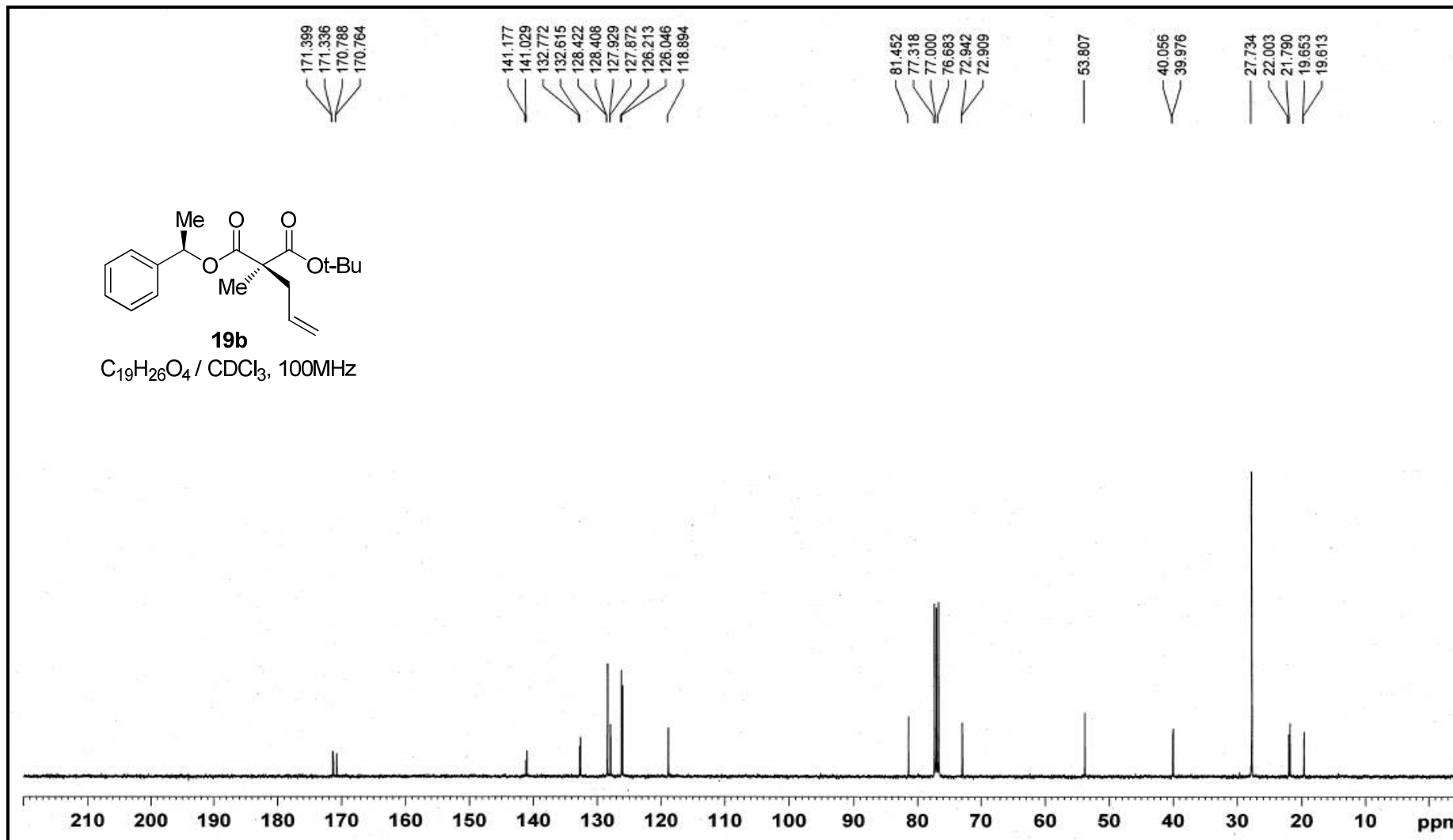
¹³C-NMR of compound (19a)



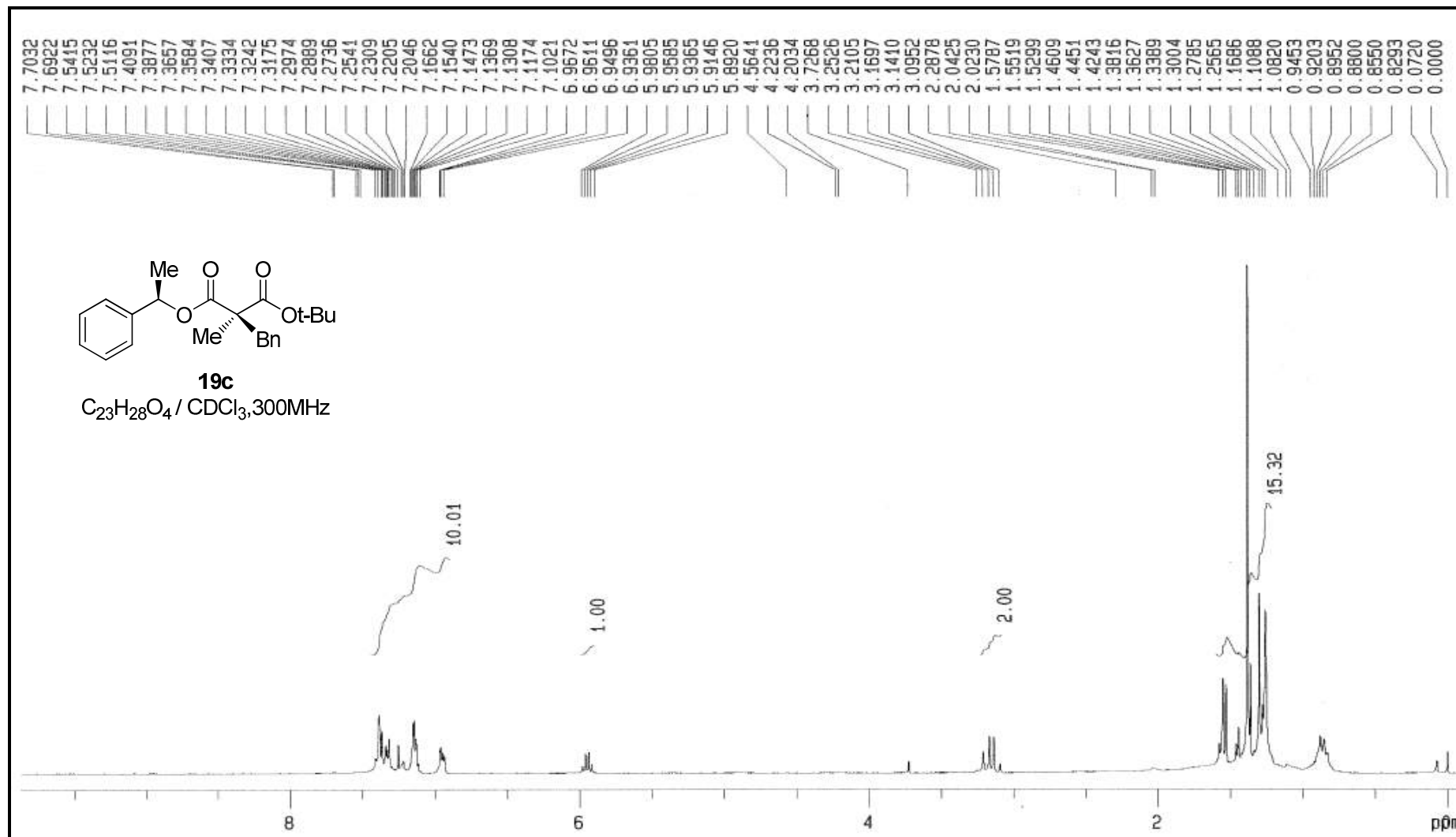
¹H-NMR of compound (19b)



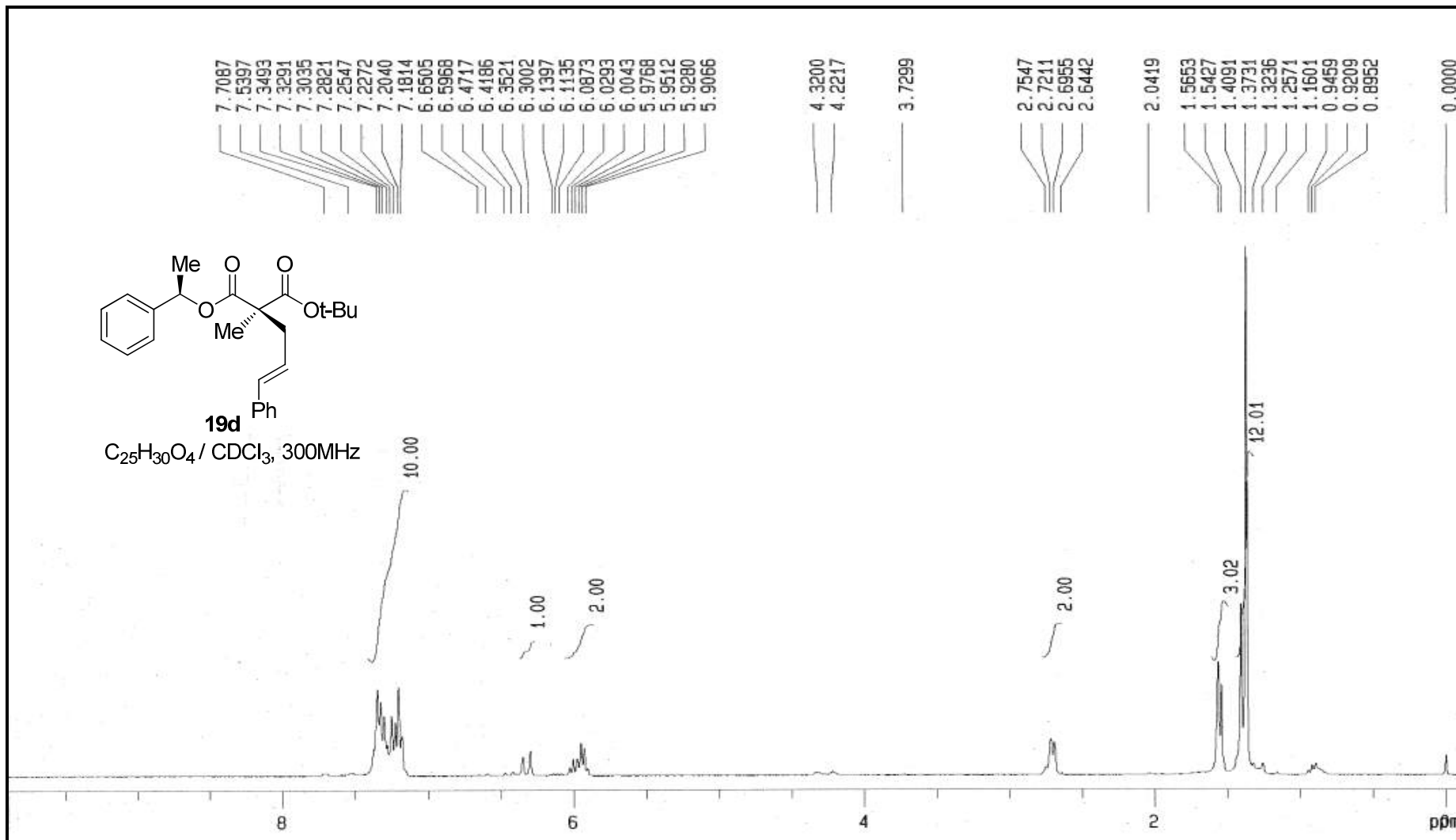
$^{13}\text{C-NMR}$ of compound (**19b**)



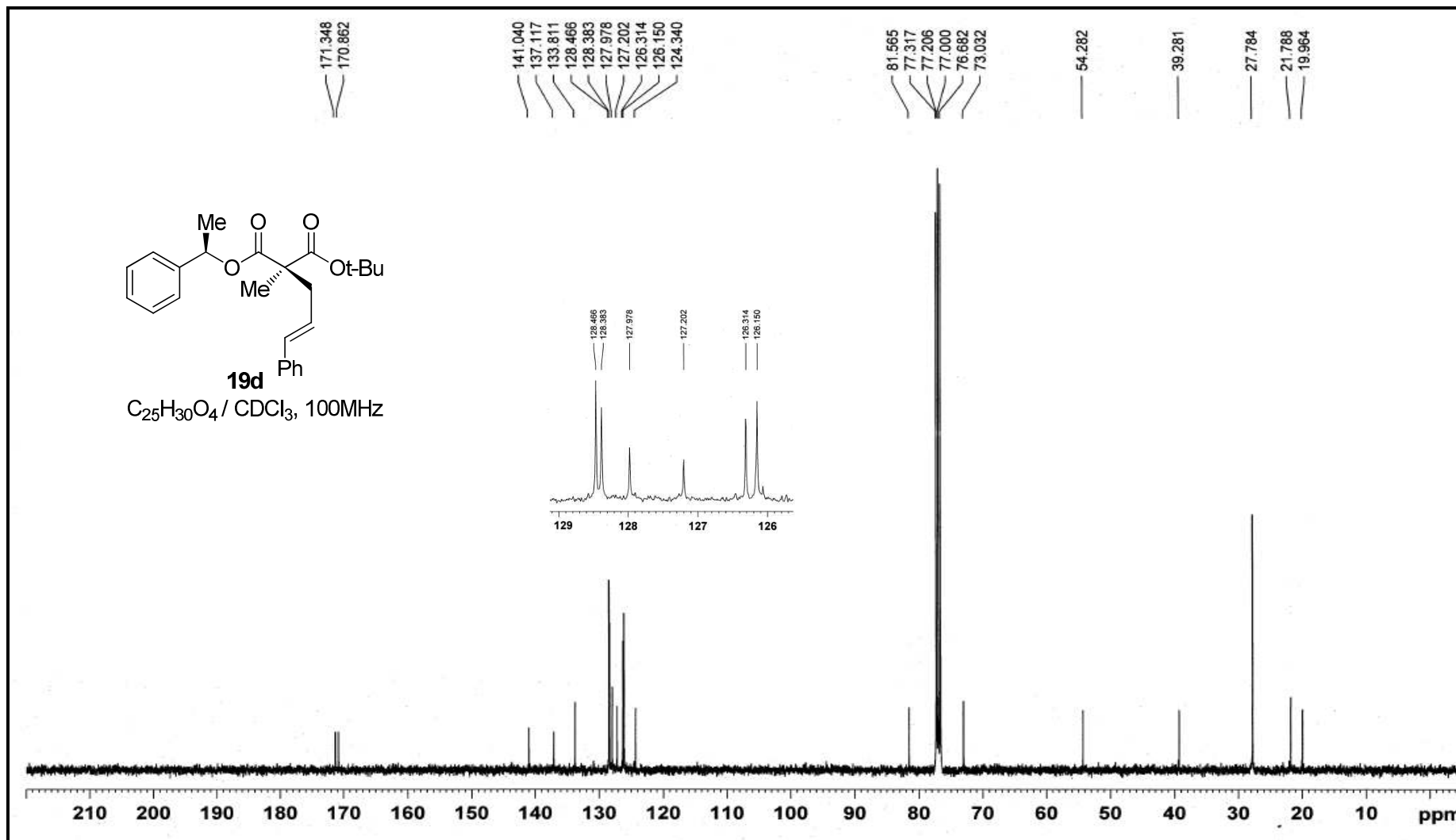
¹H-NMR of compound (19c)



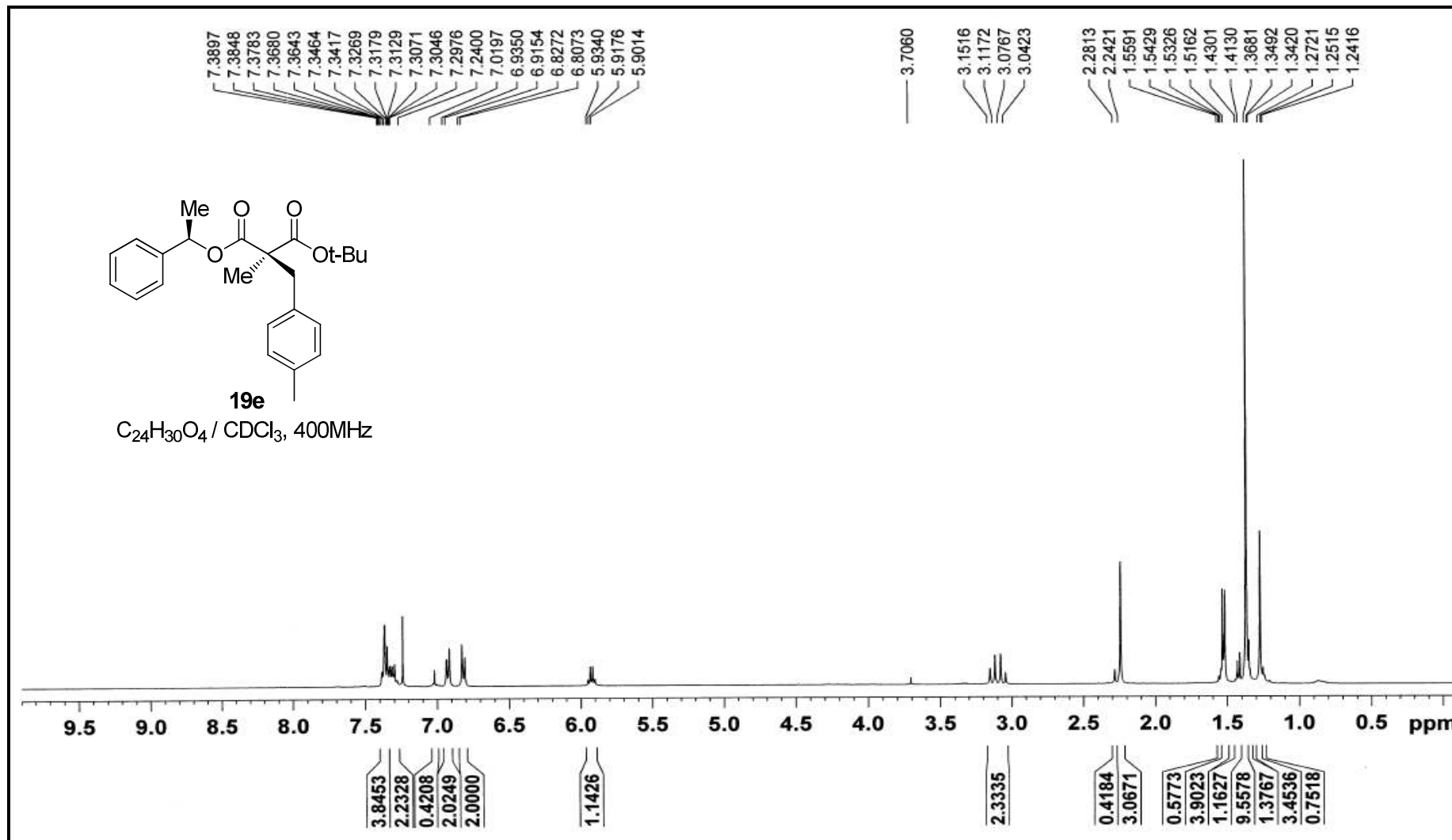
¹H-NMR of compound (19d)



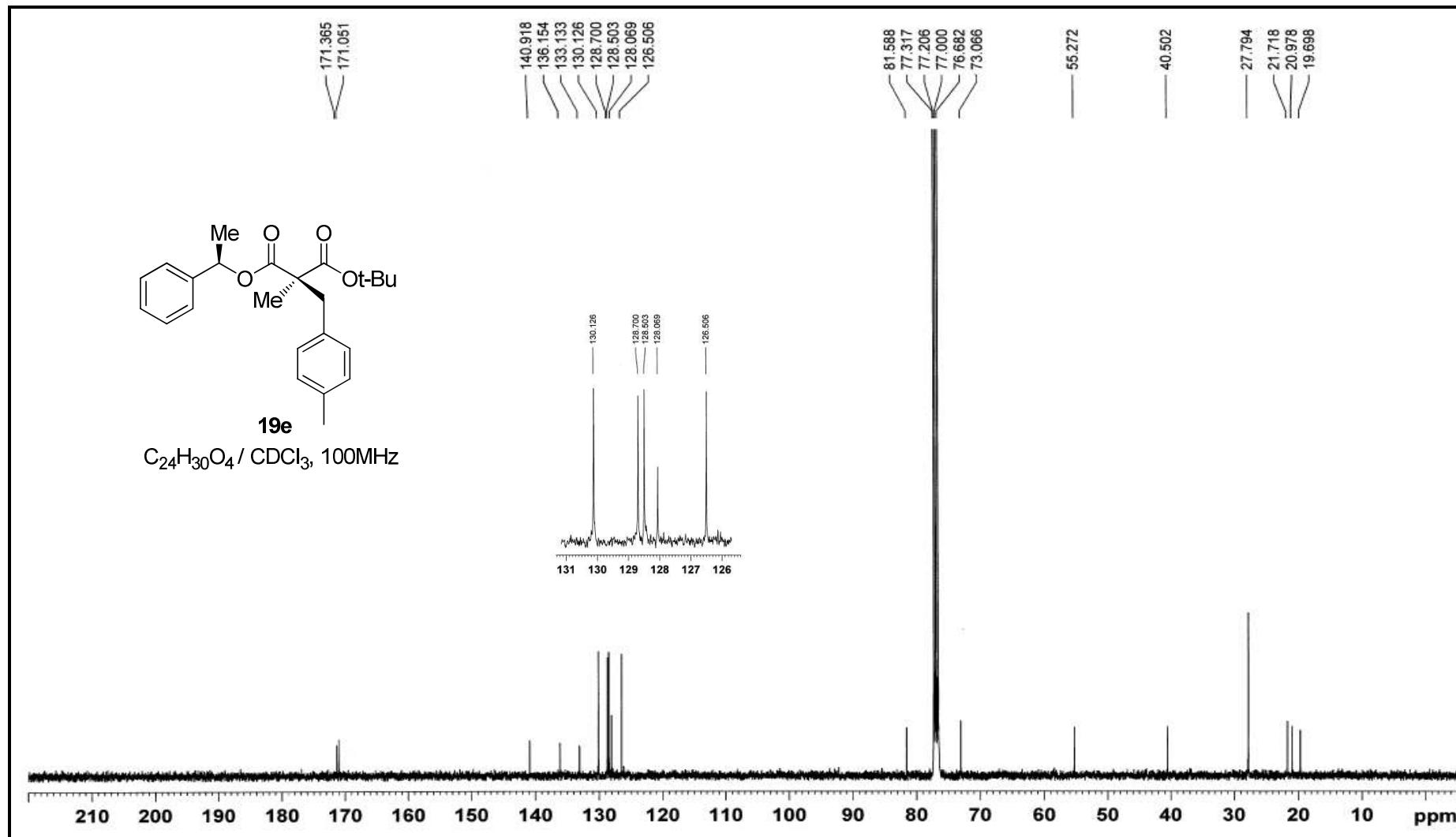
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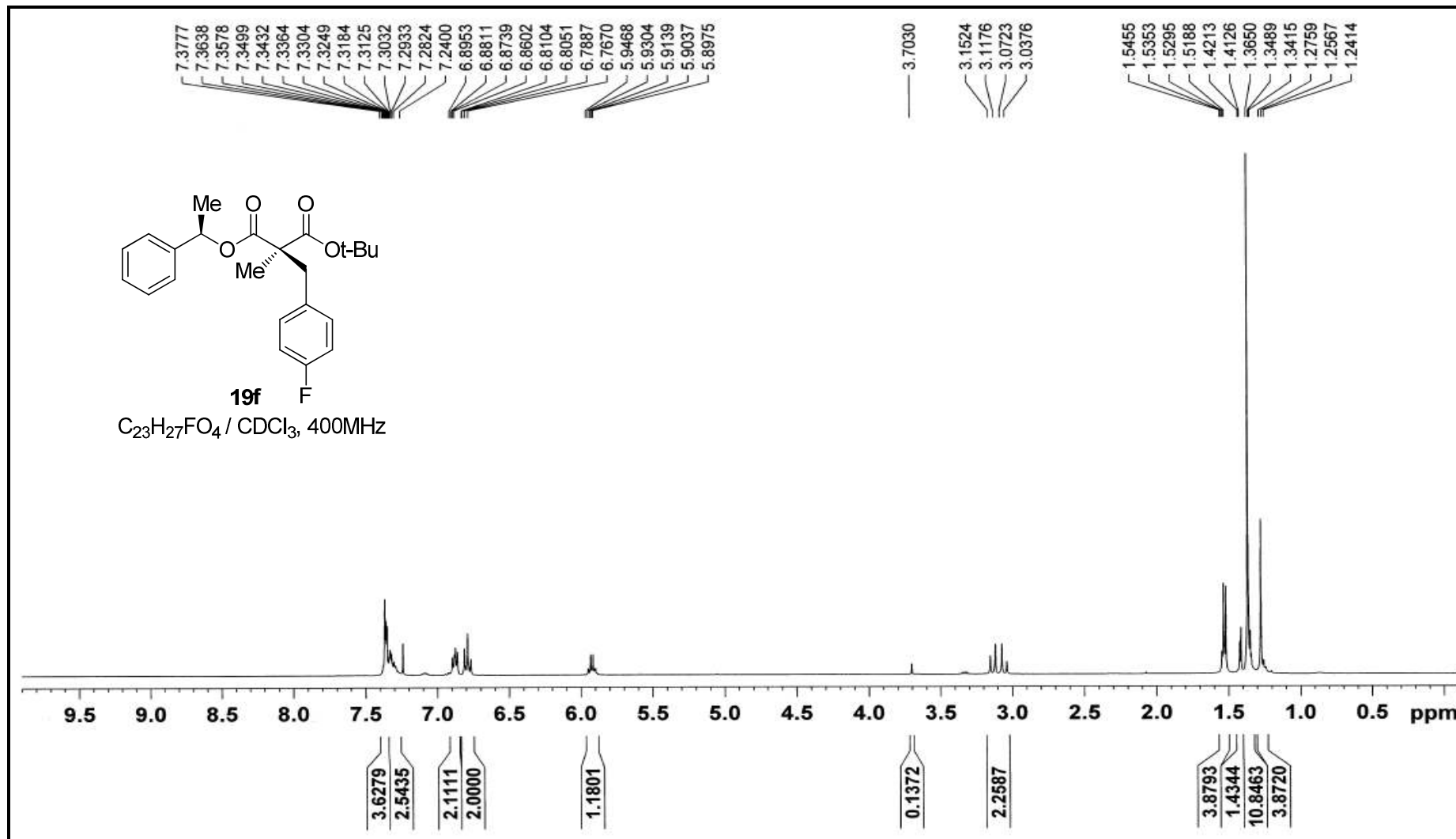
¹H-NMR of compound (19e)



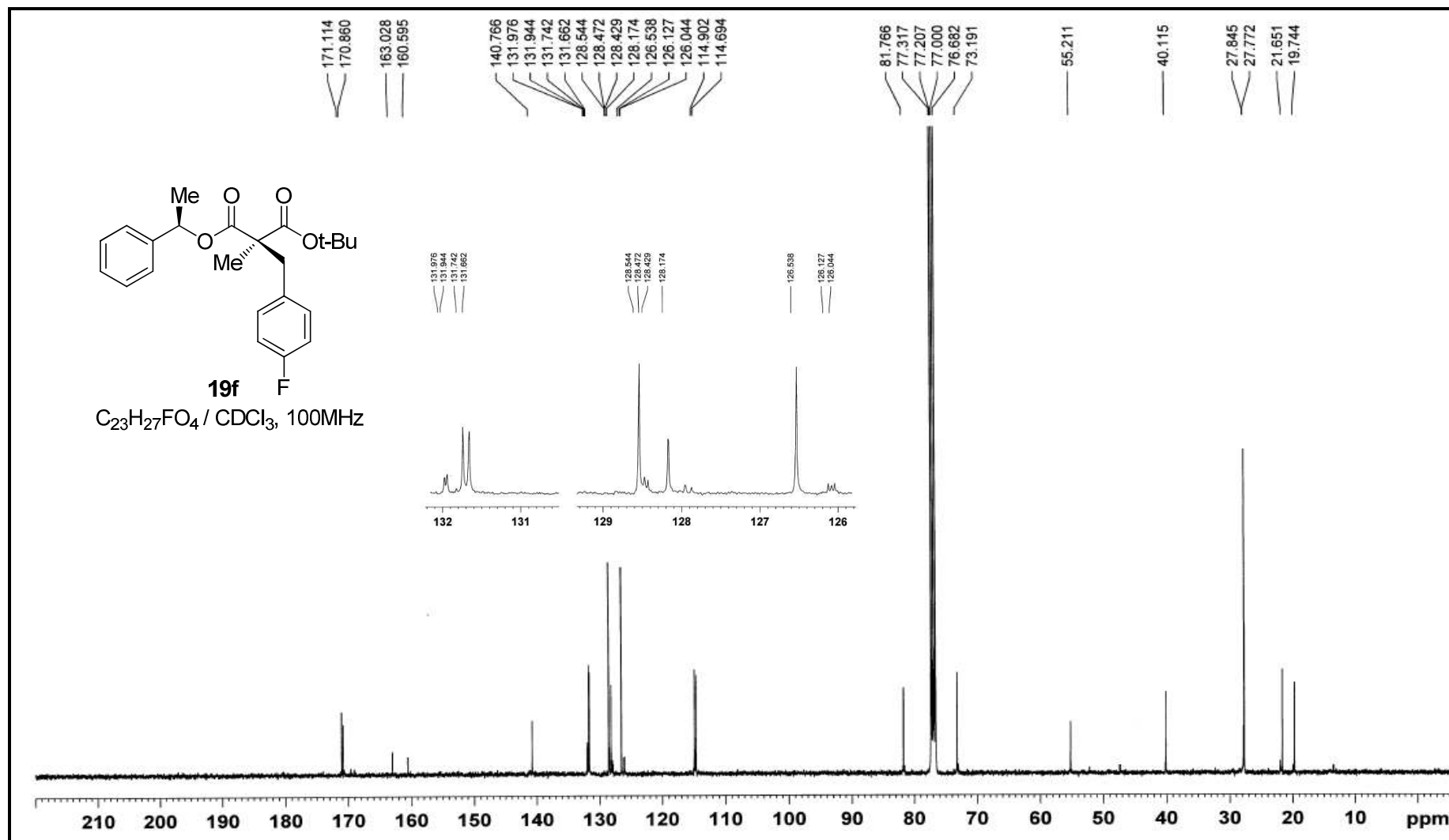
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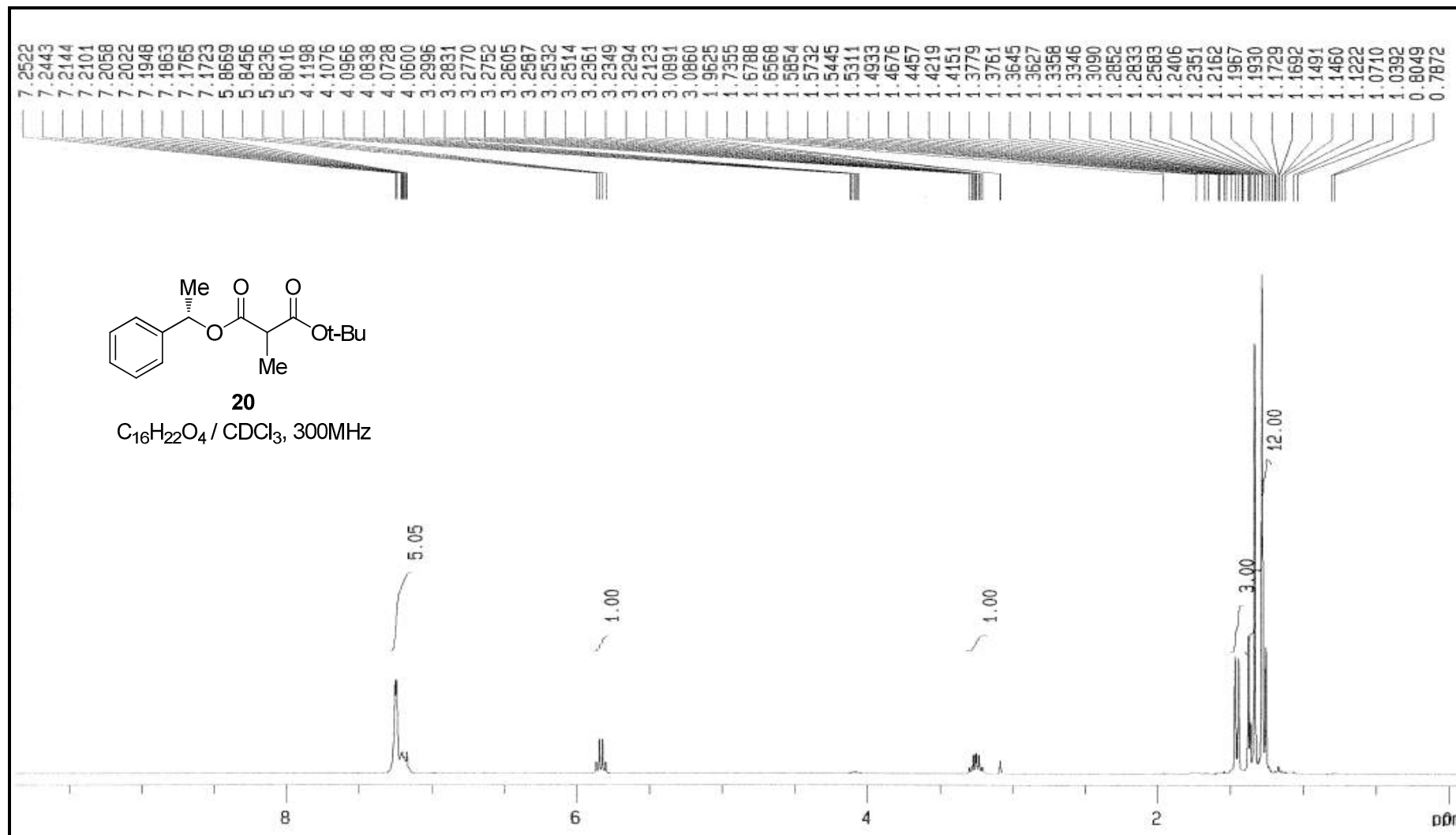
¹H-NMR of compound (19f)



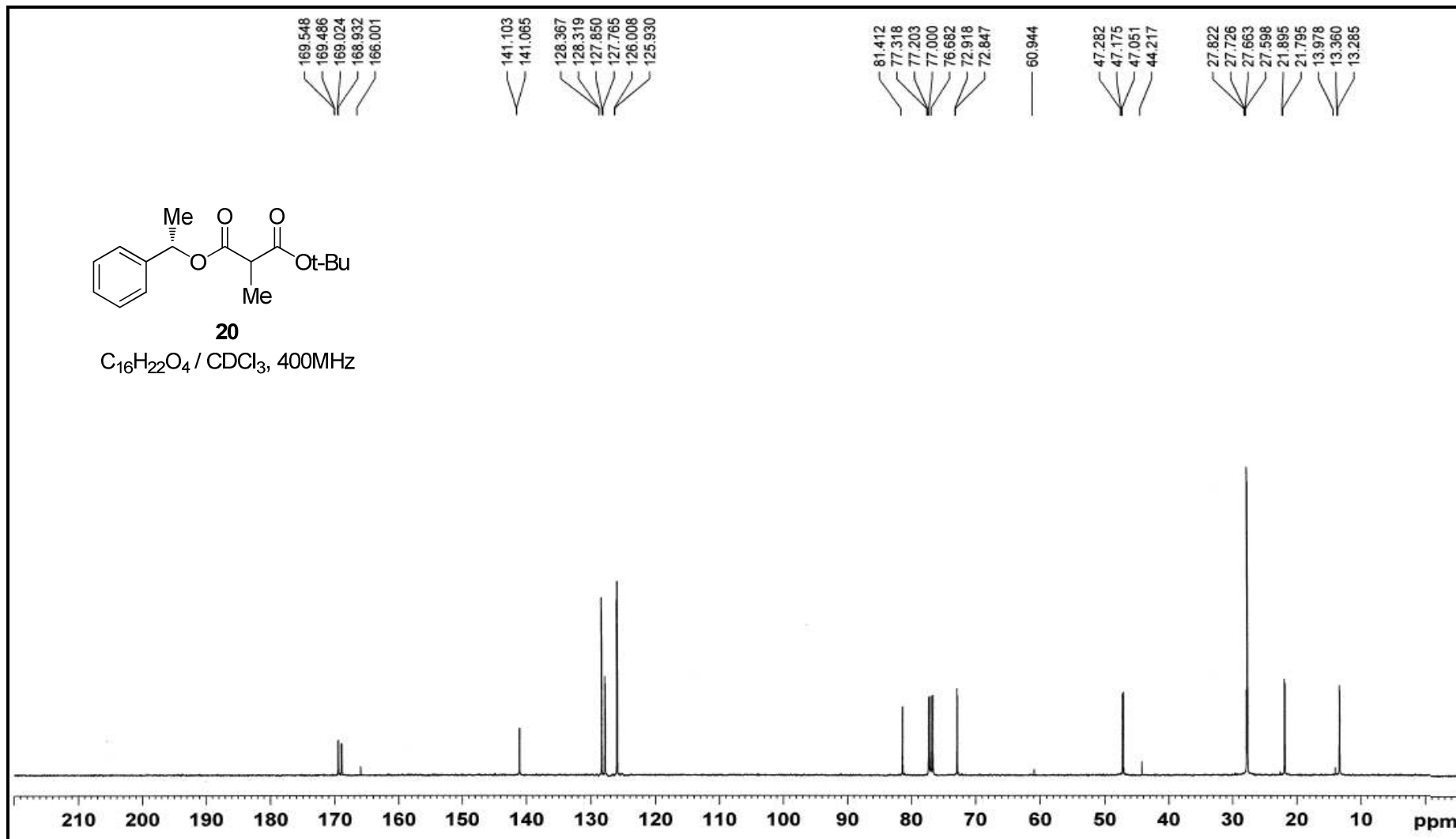
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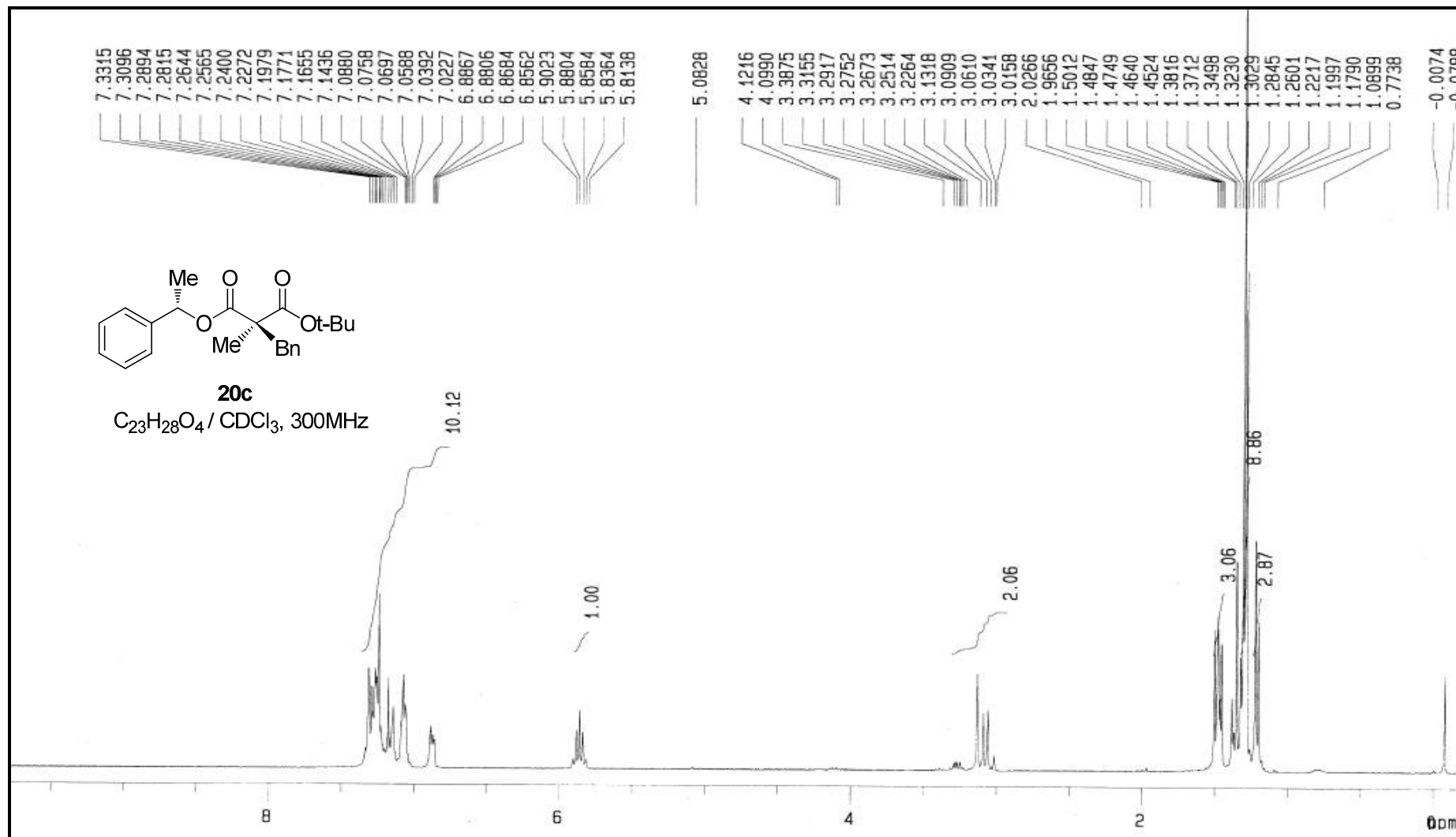
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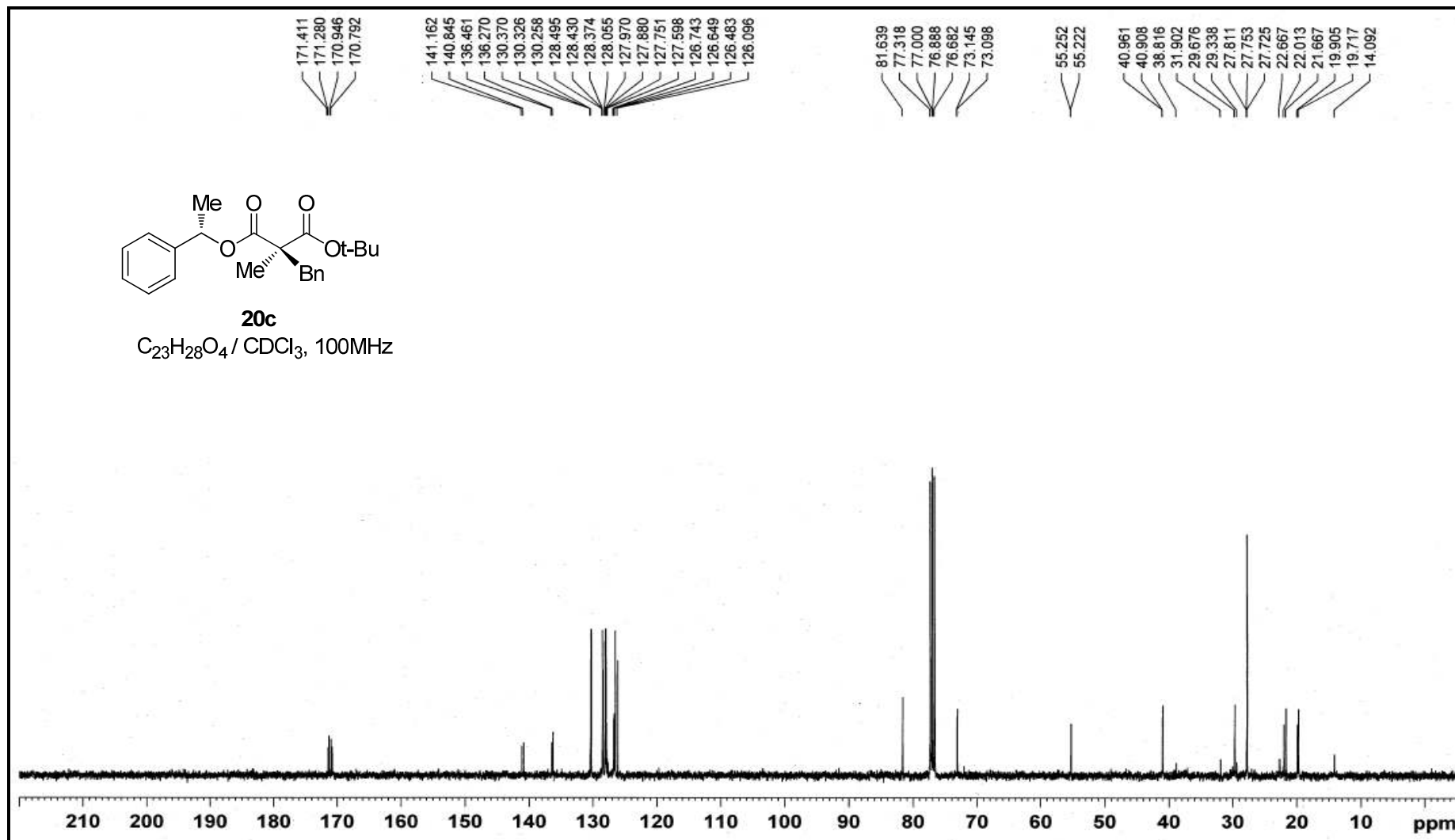
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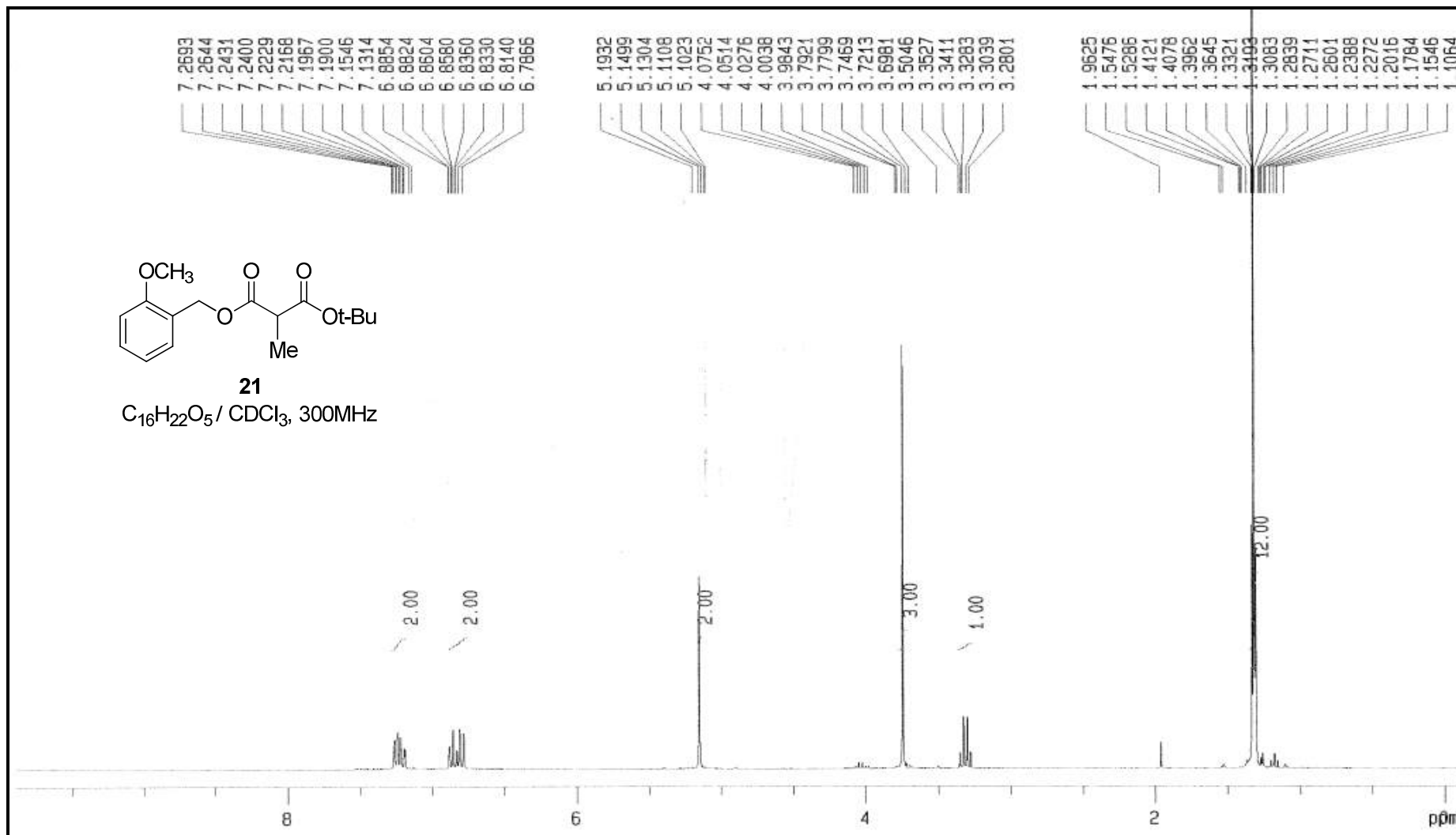
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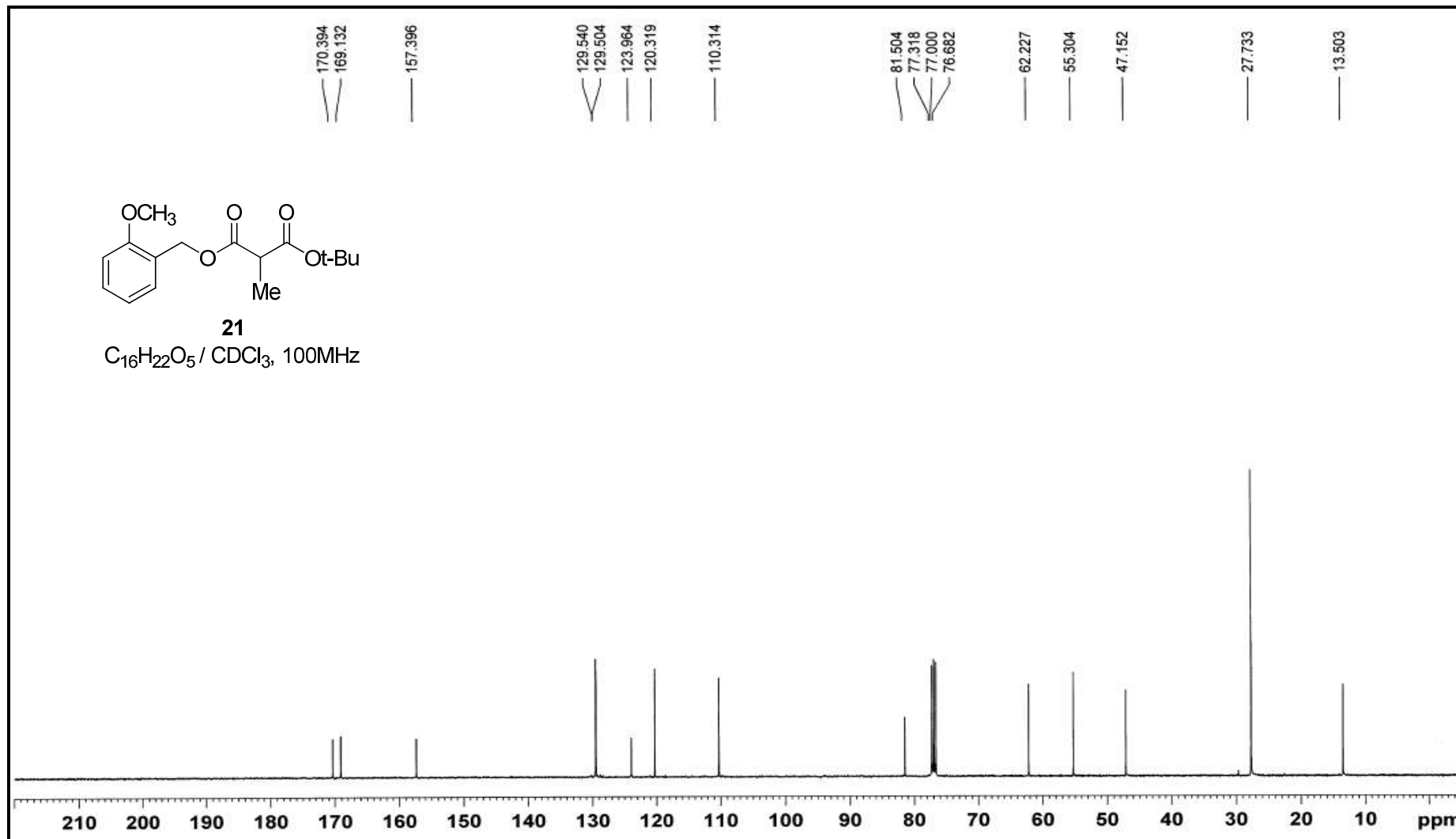
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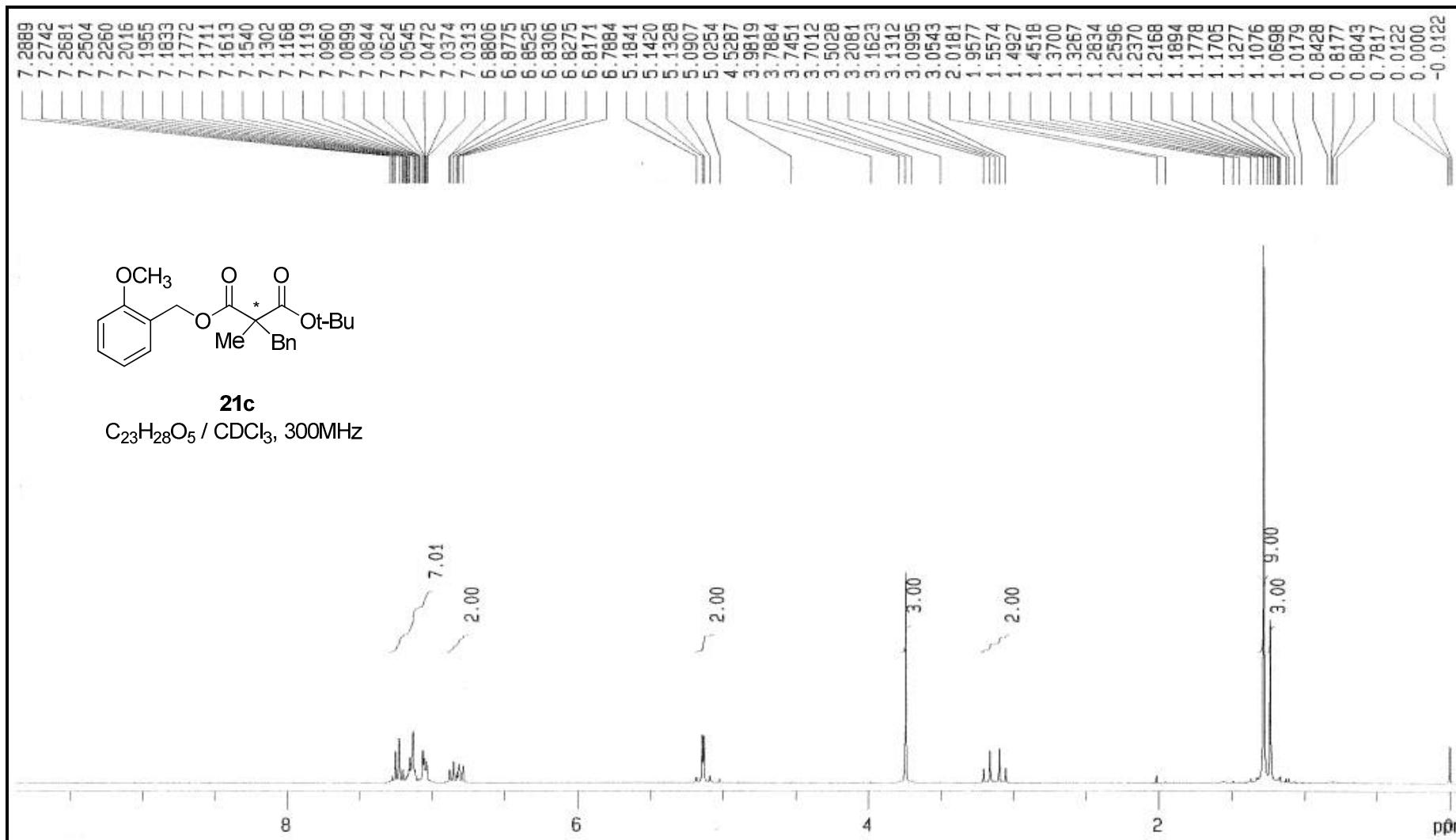
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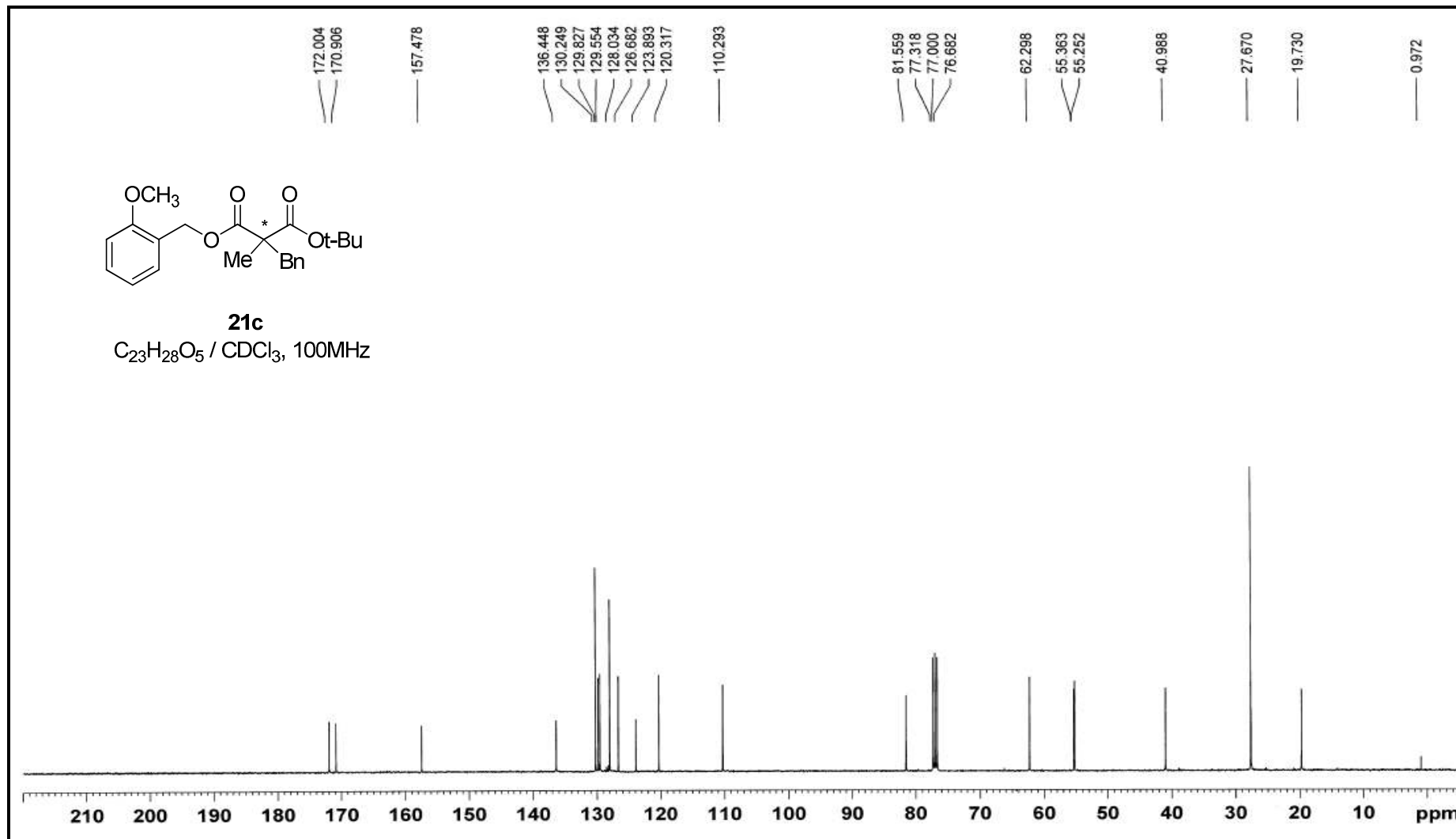
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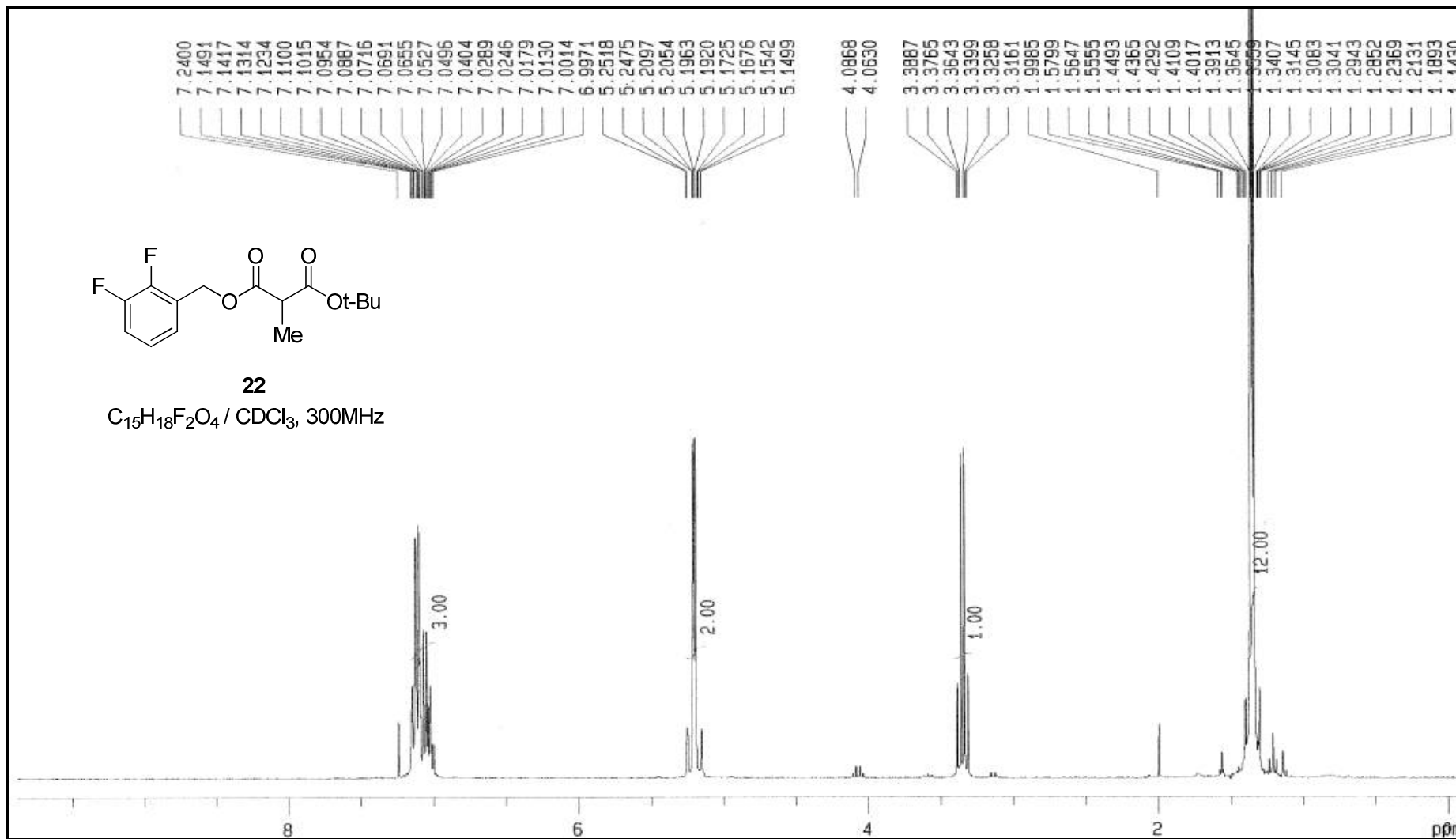
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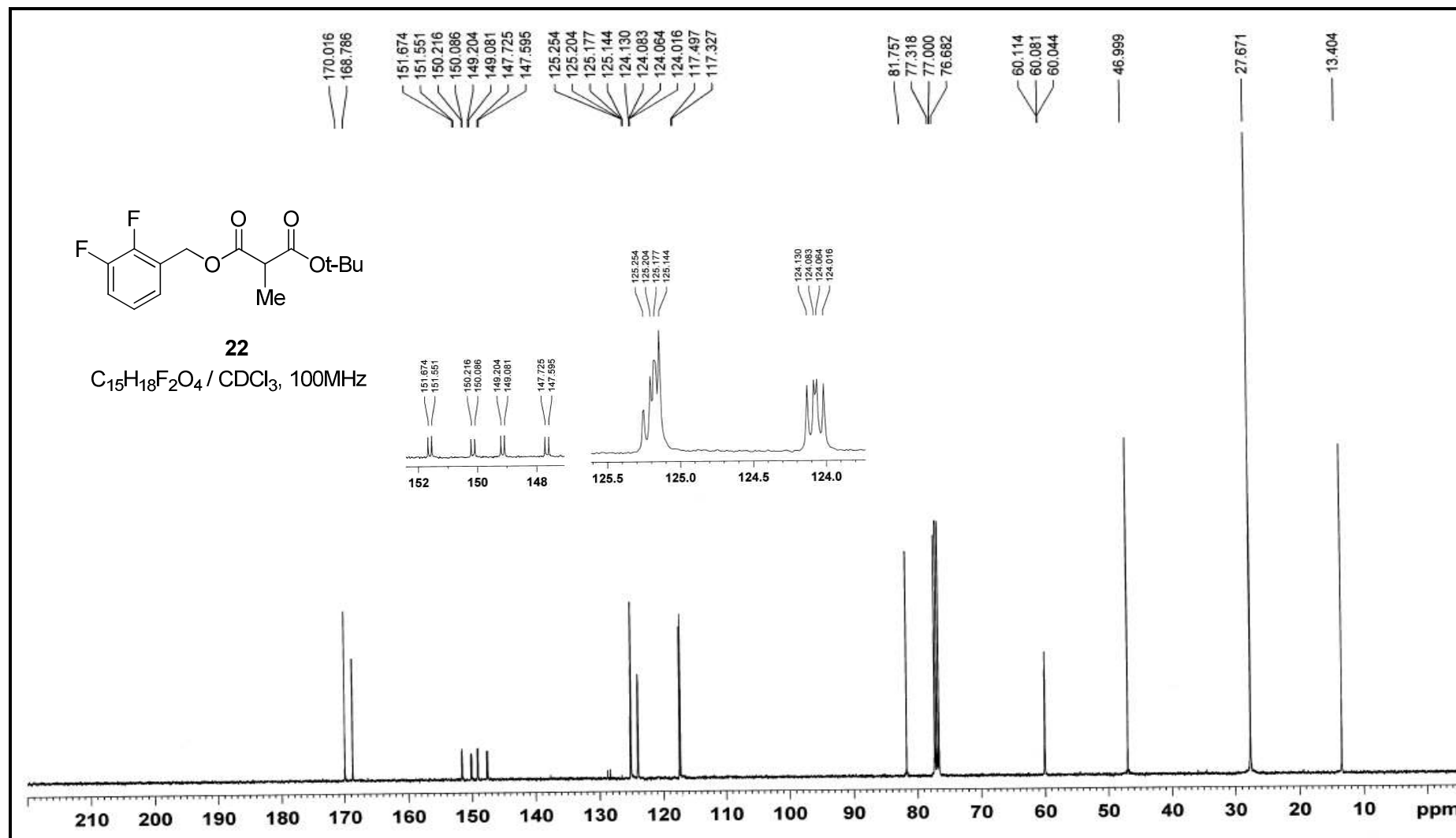
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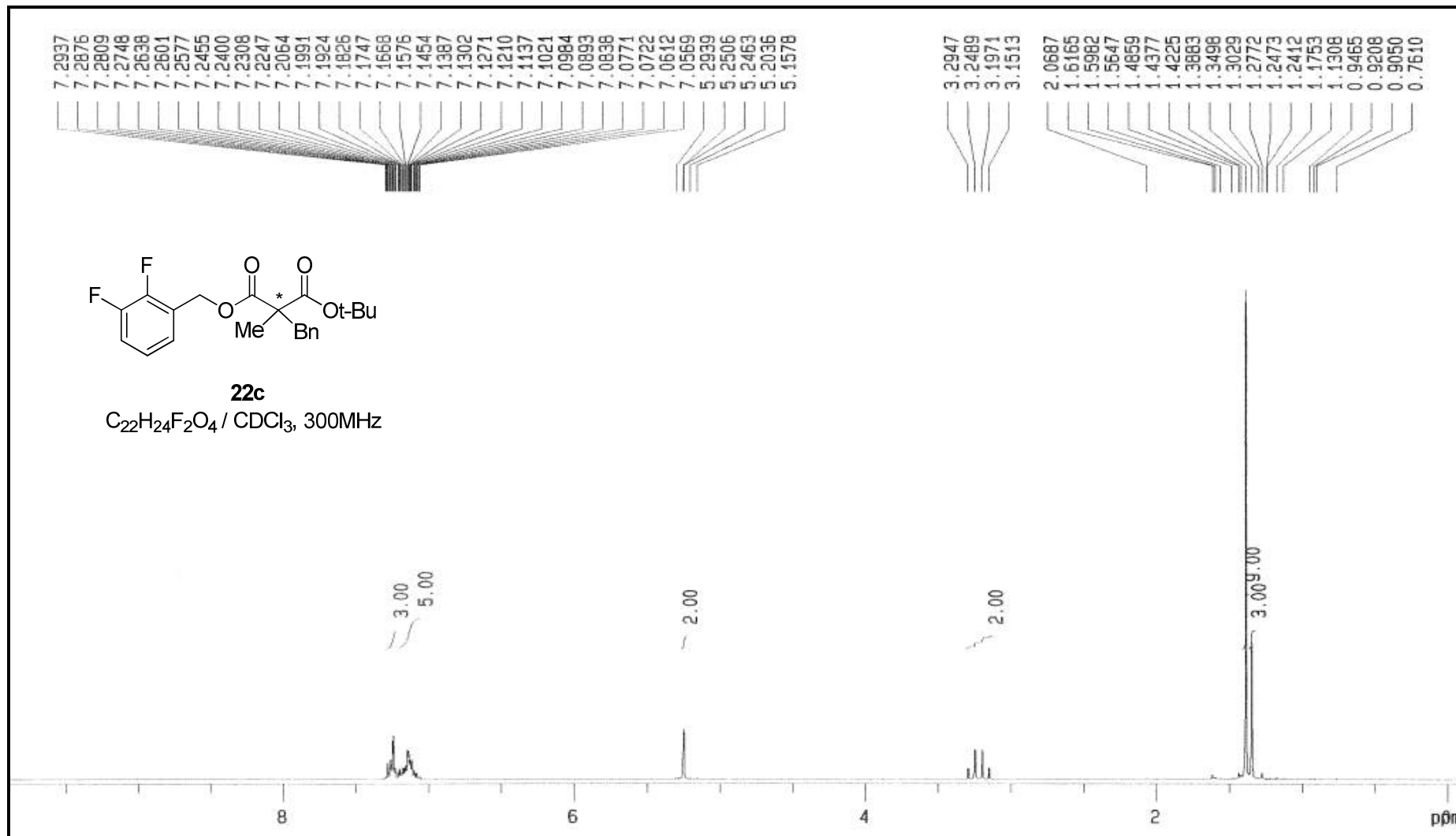
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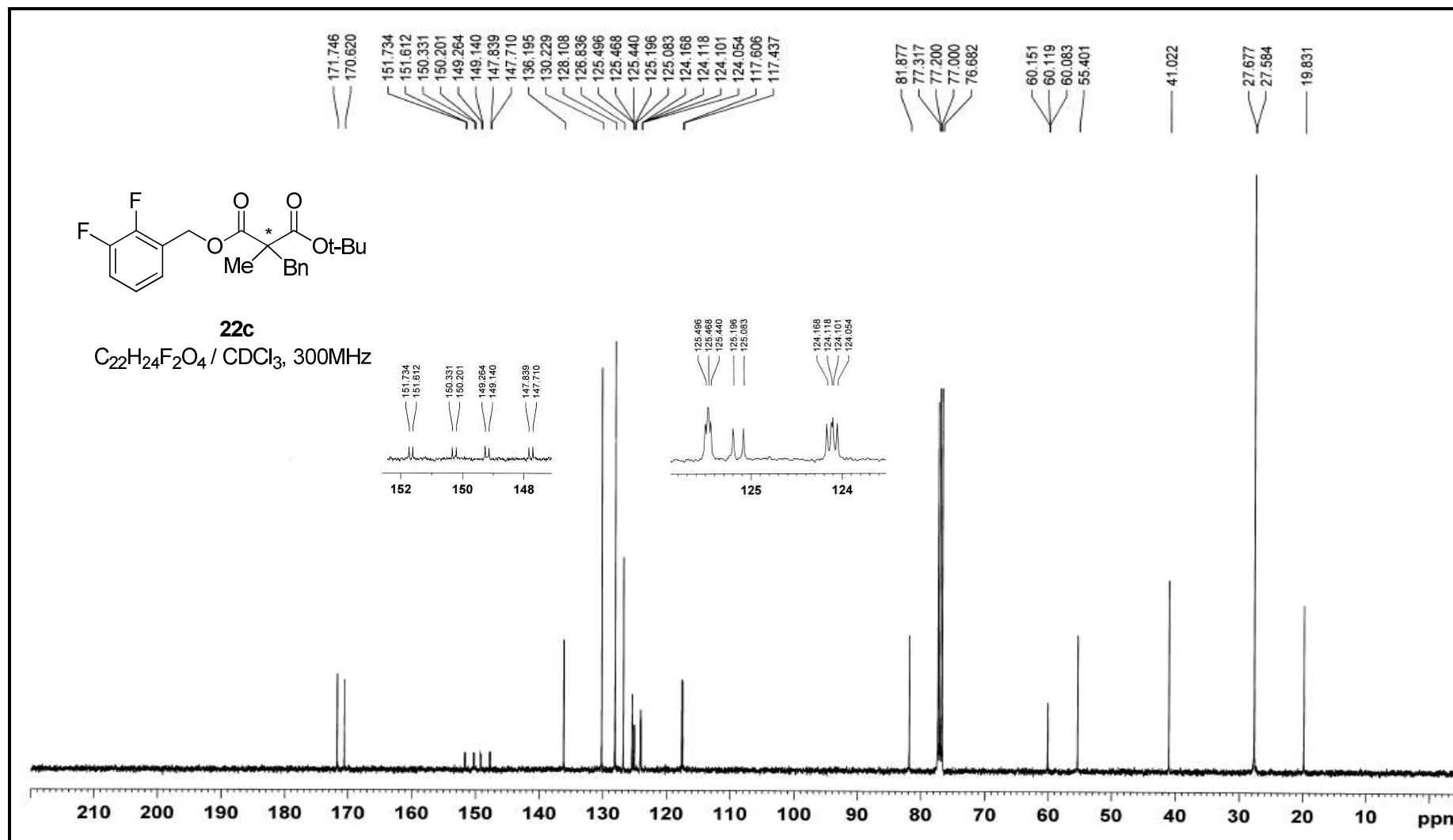
^{13}C -NMR of compound (**22**)



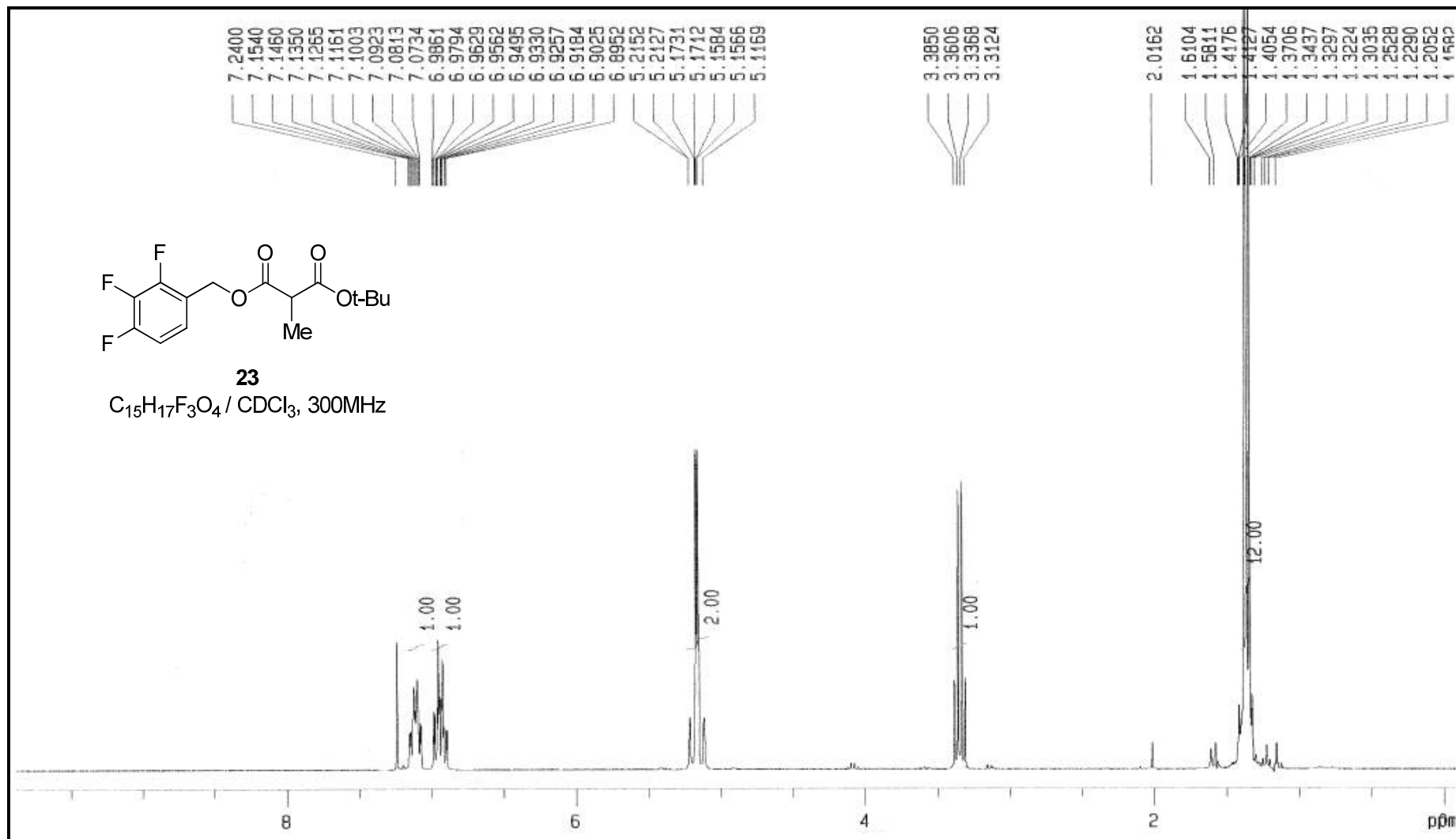
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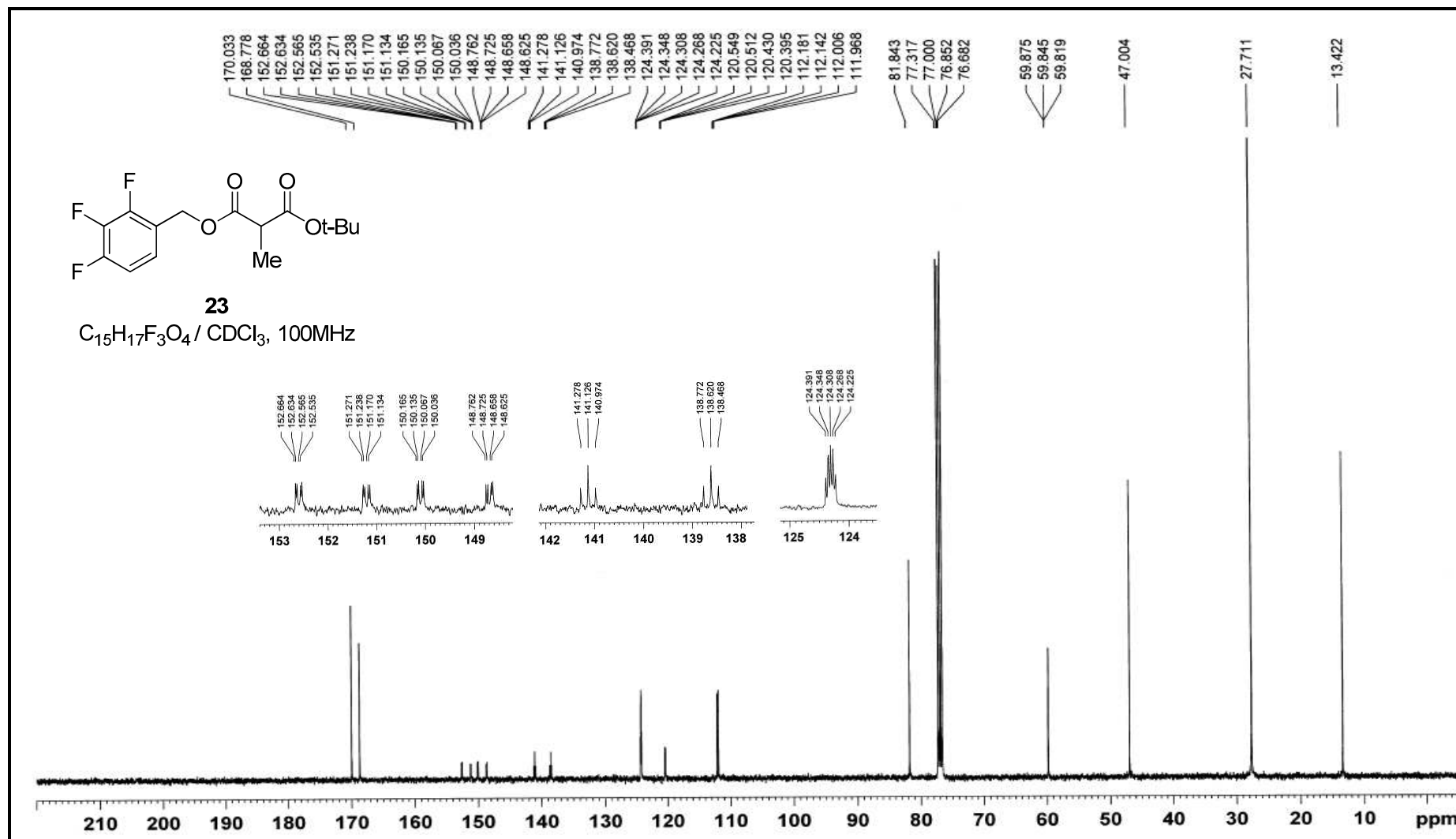
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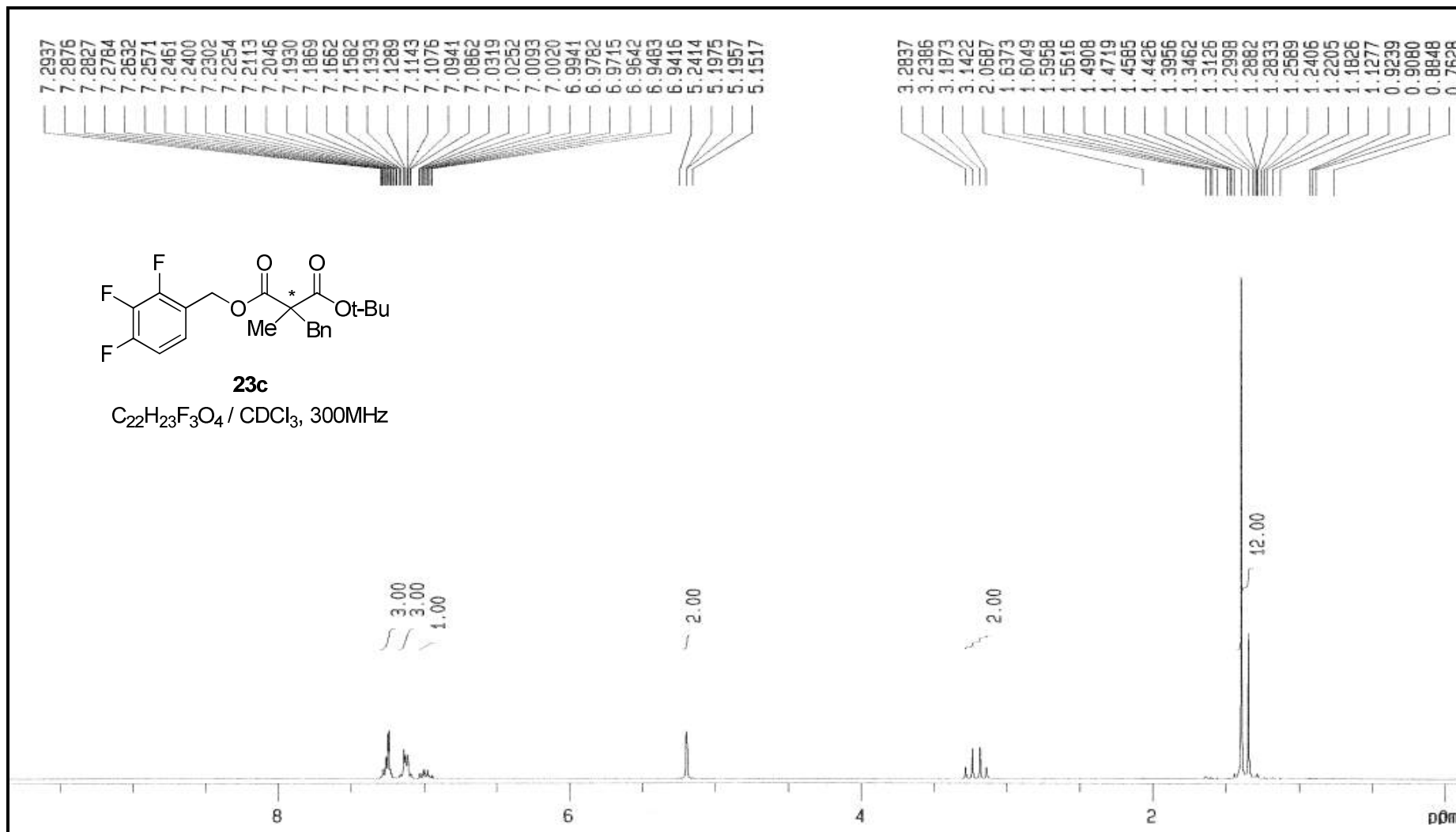
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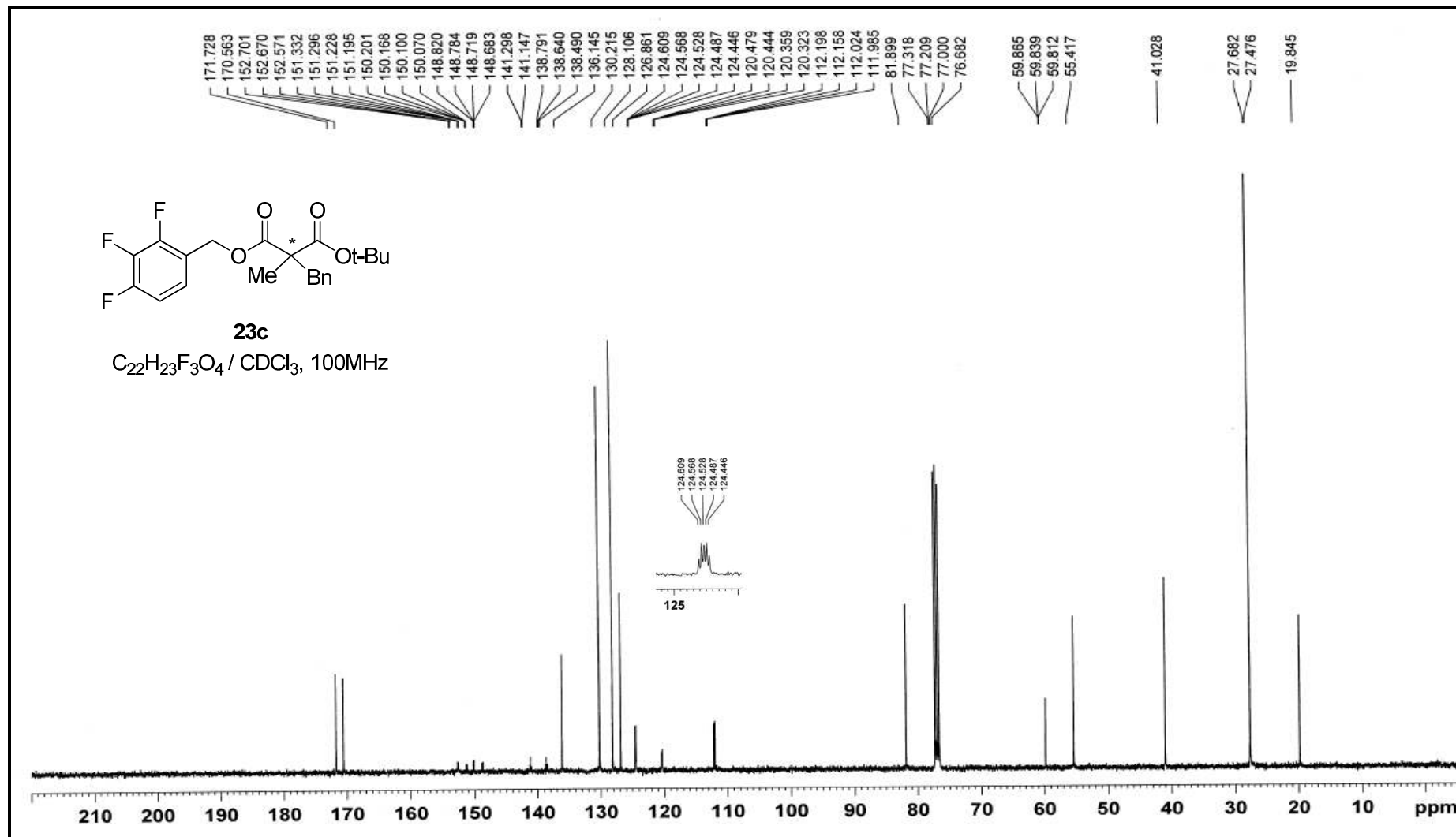
$^{13}\text{C-NMR}$ of compound (**23**)



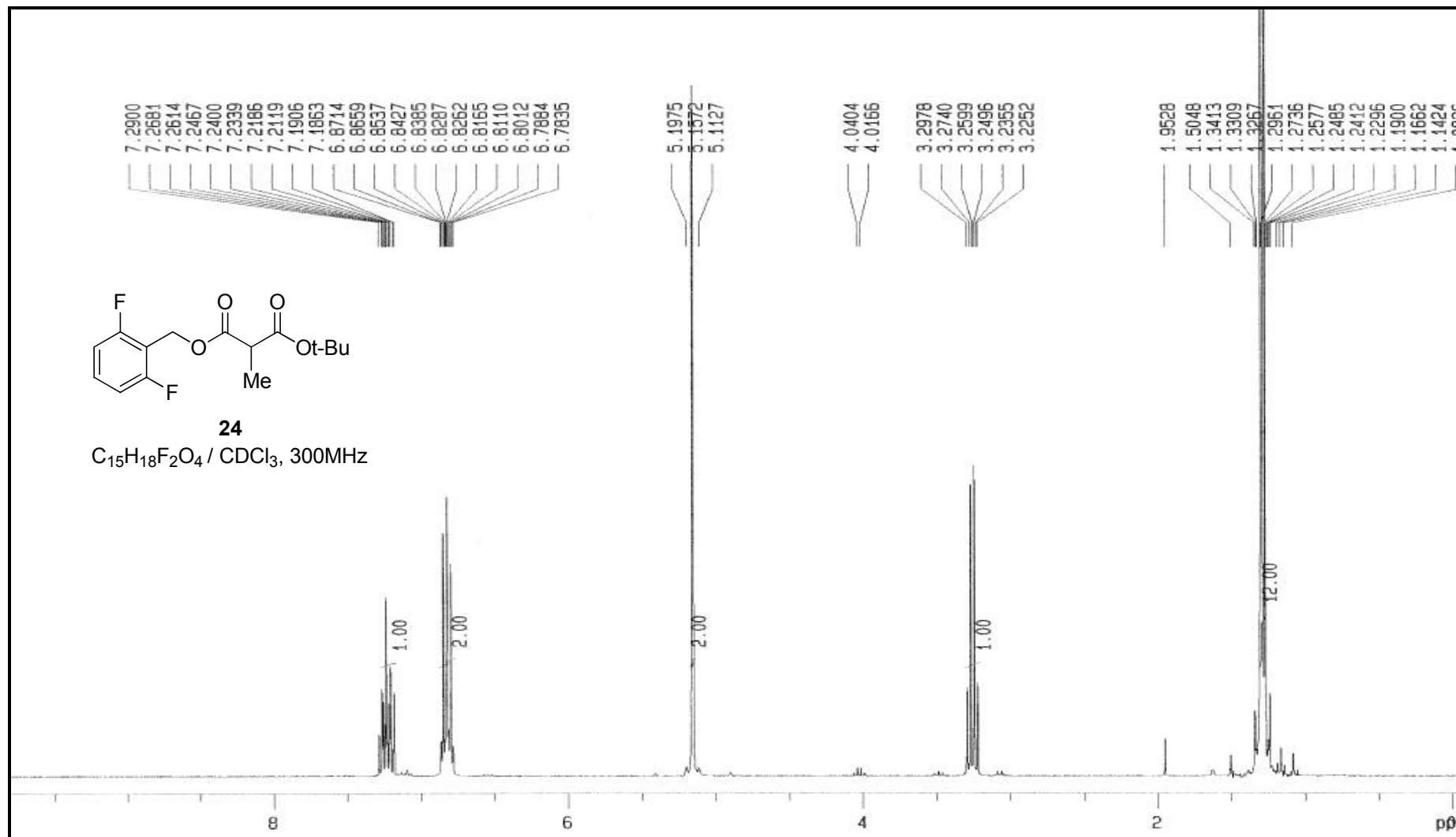
¹H-NMR of compound (23c)



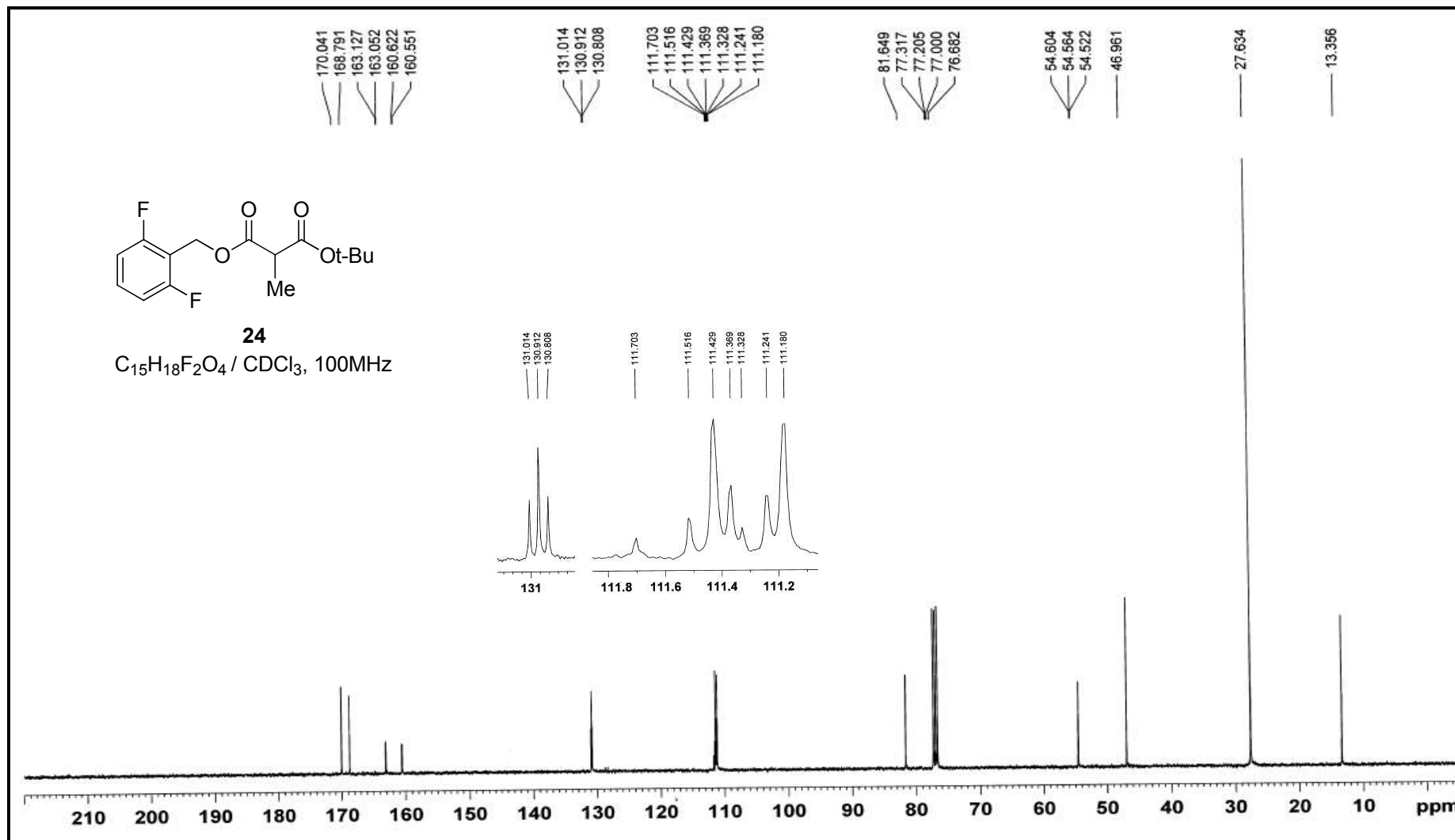
^{13}C -NMR of compound (**23c**)



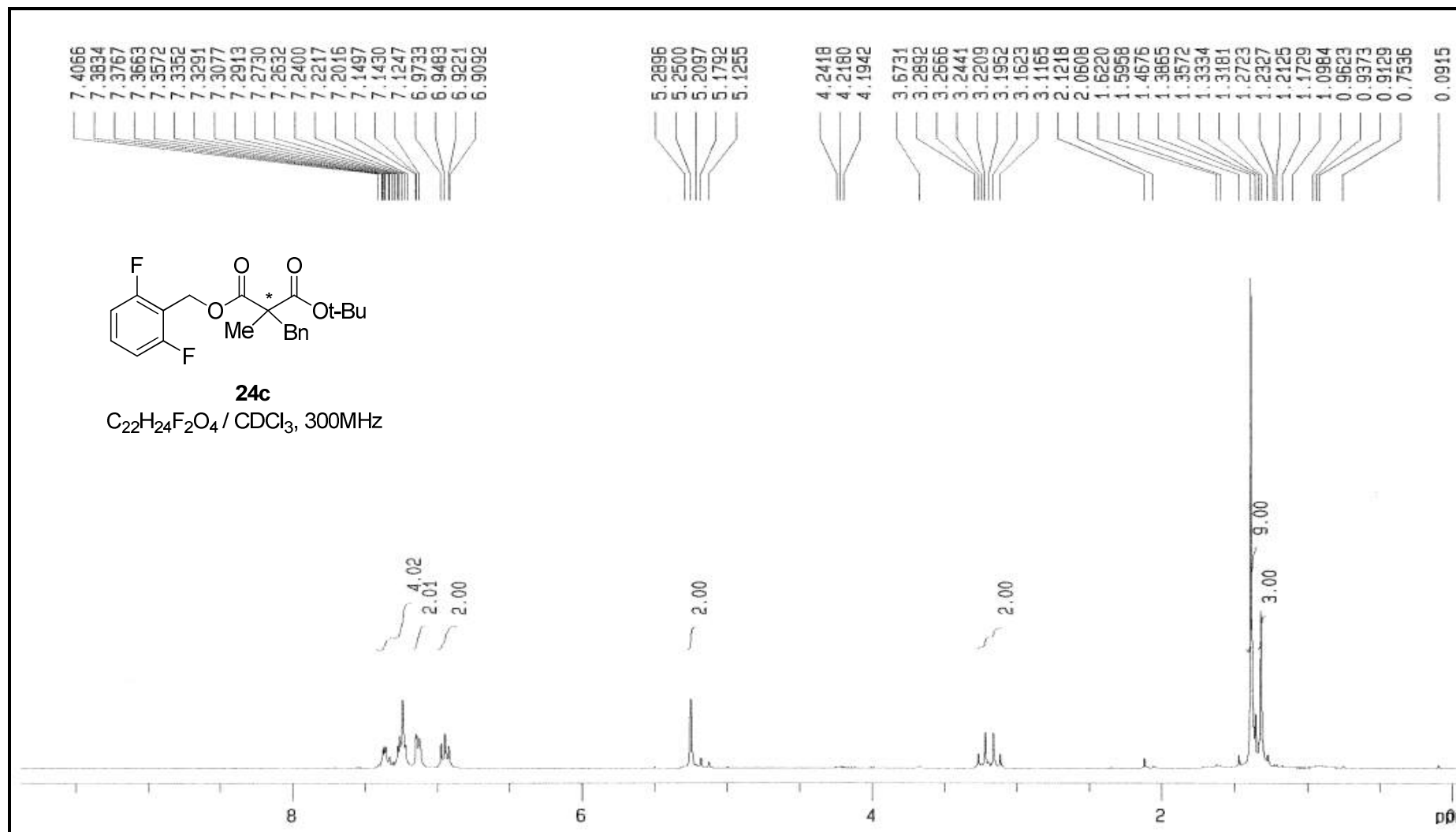
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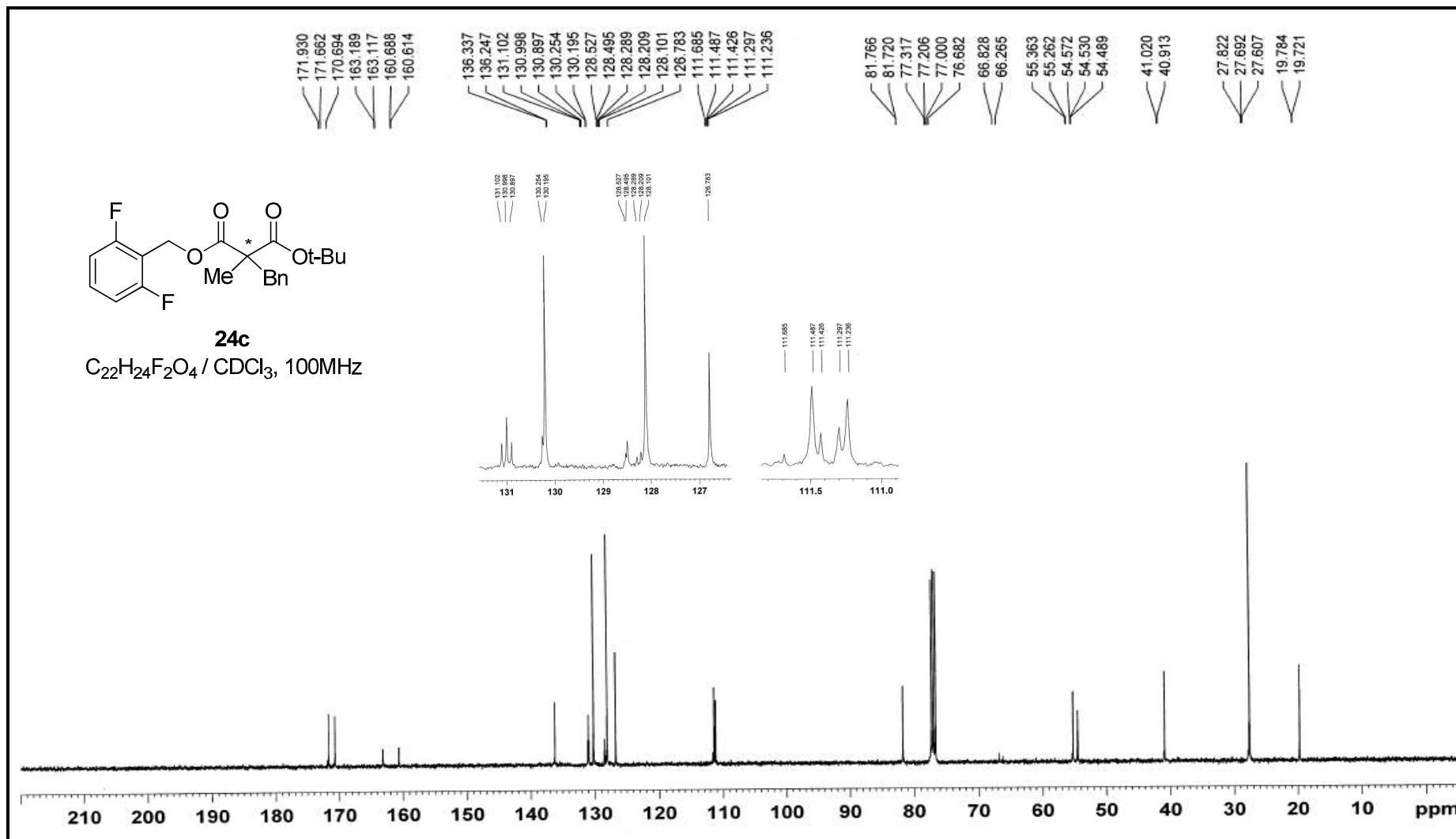
$^{13}\text{C-NMR}$ of compound (**24**)



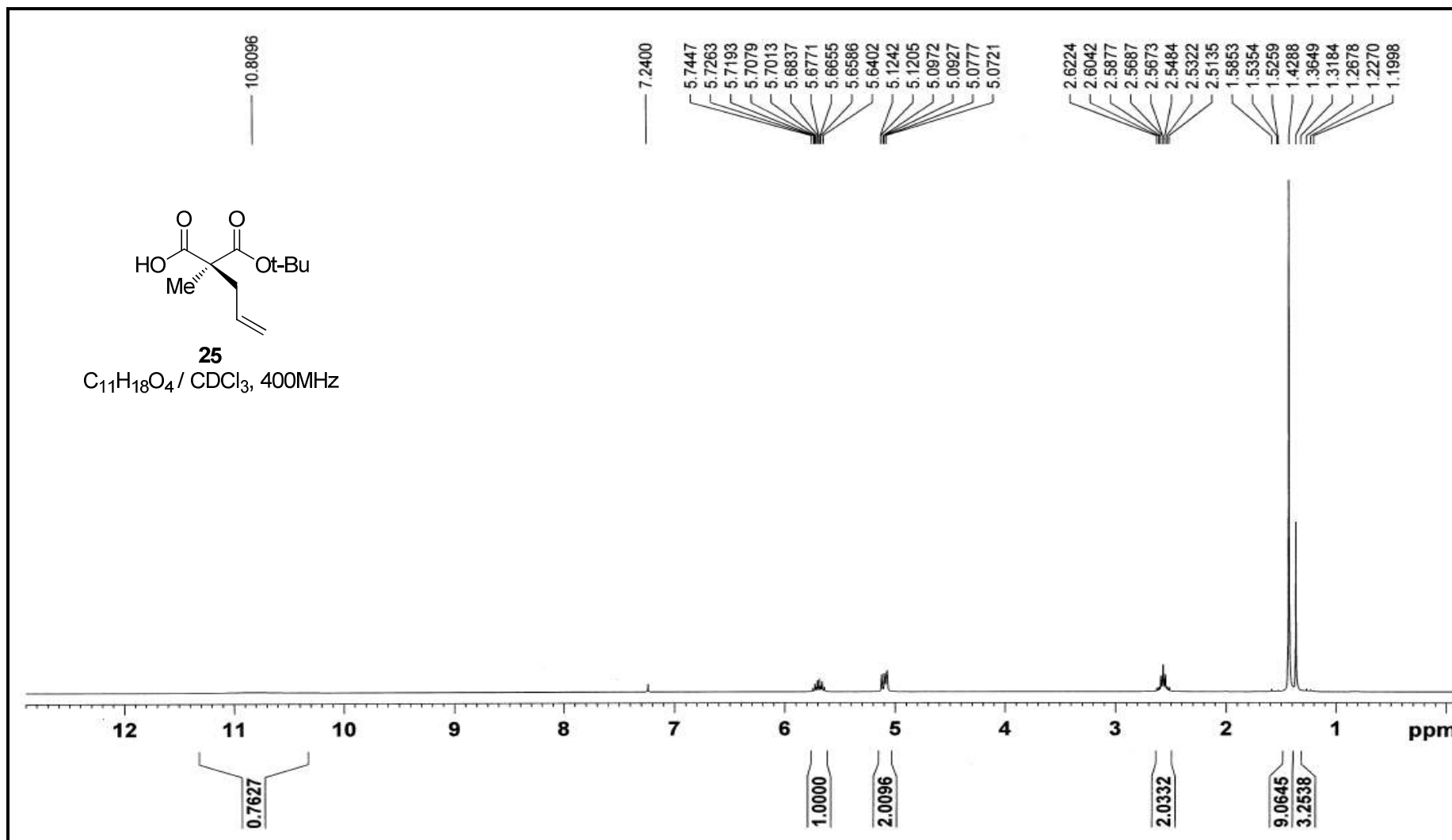
¹H-NMR of compound (24c)



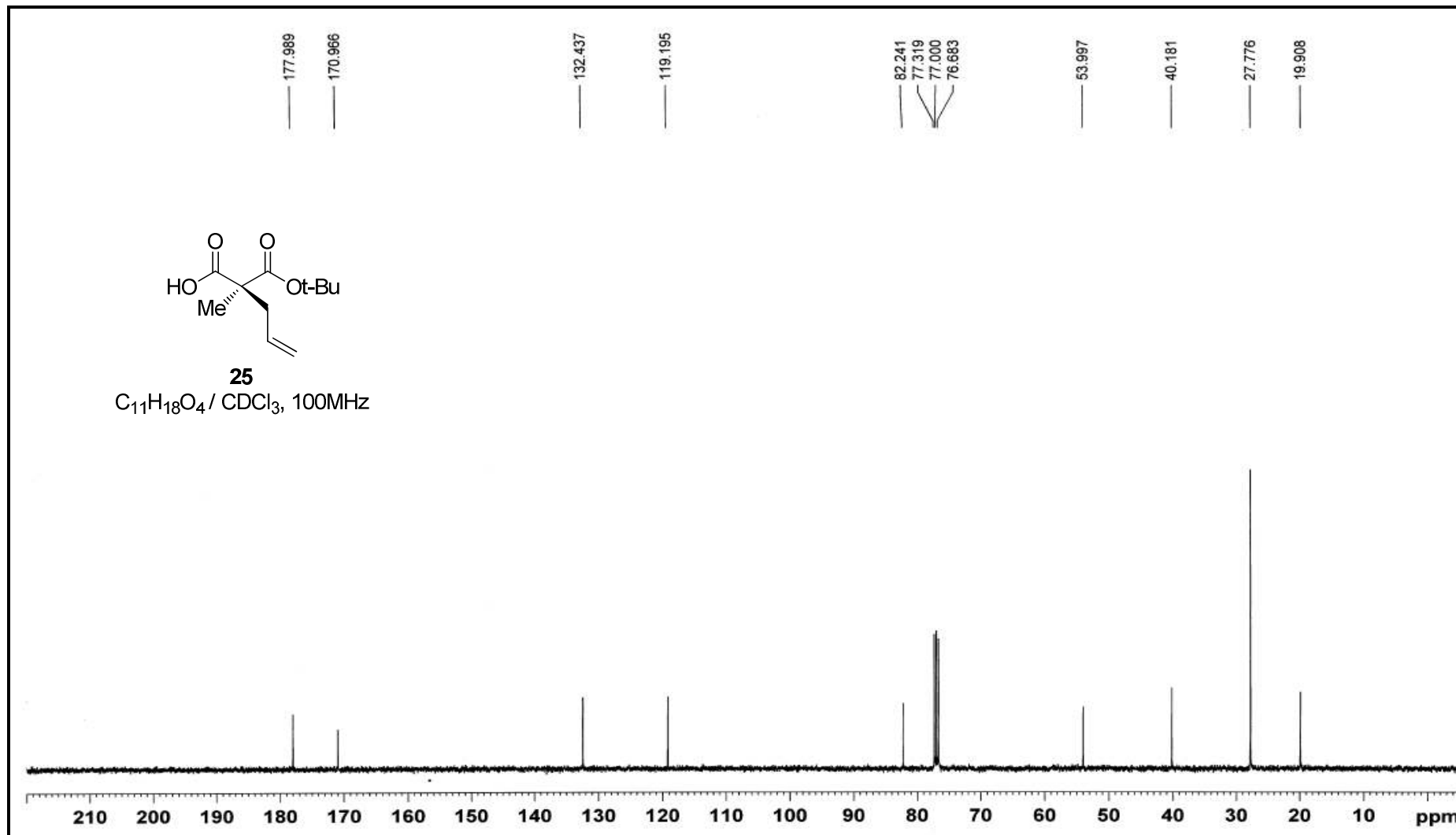
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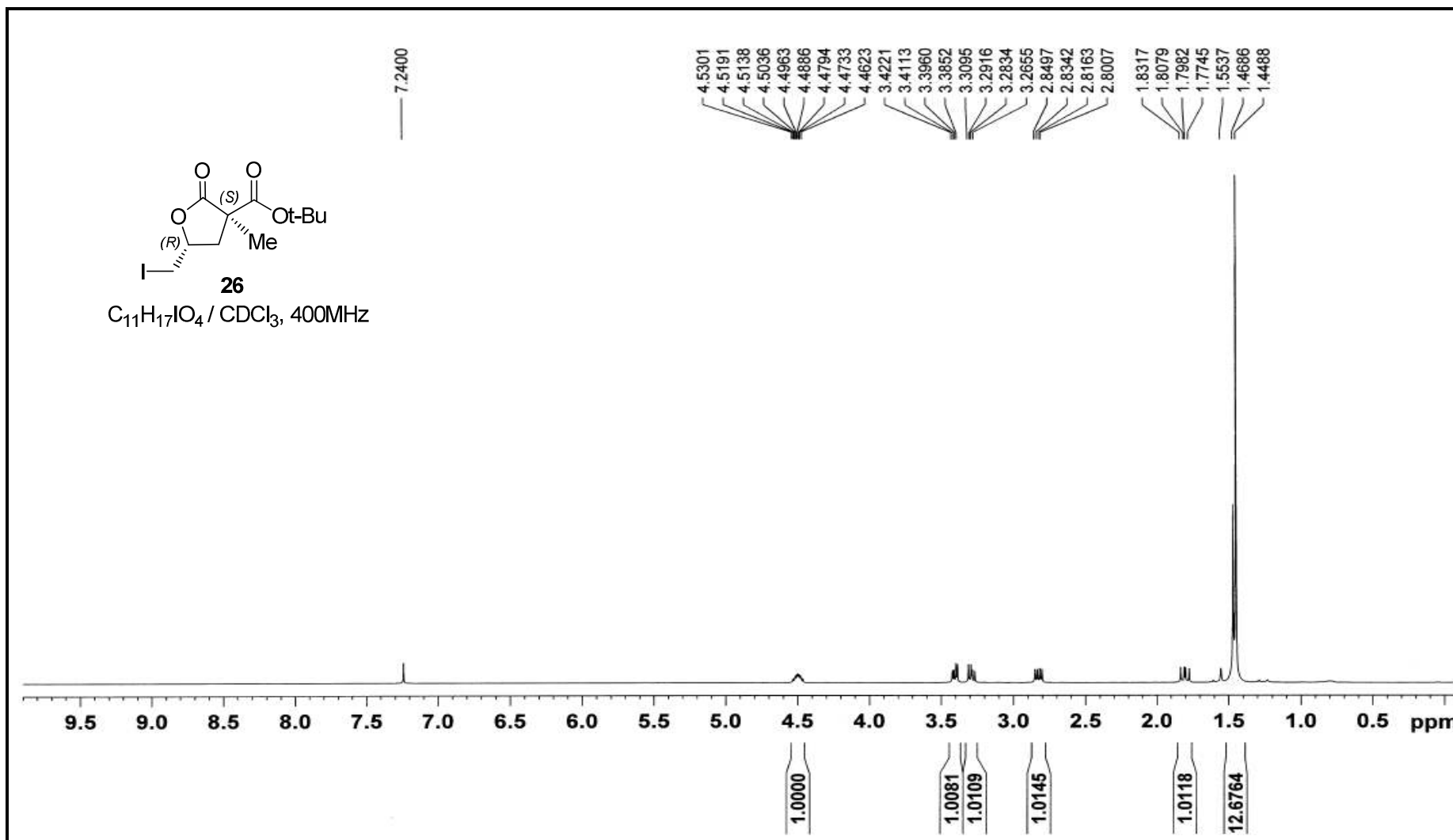
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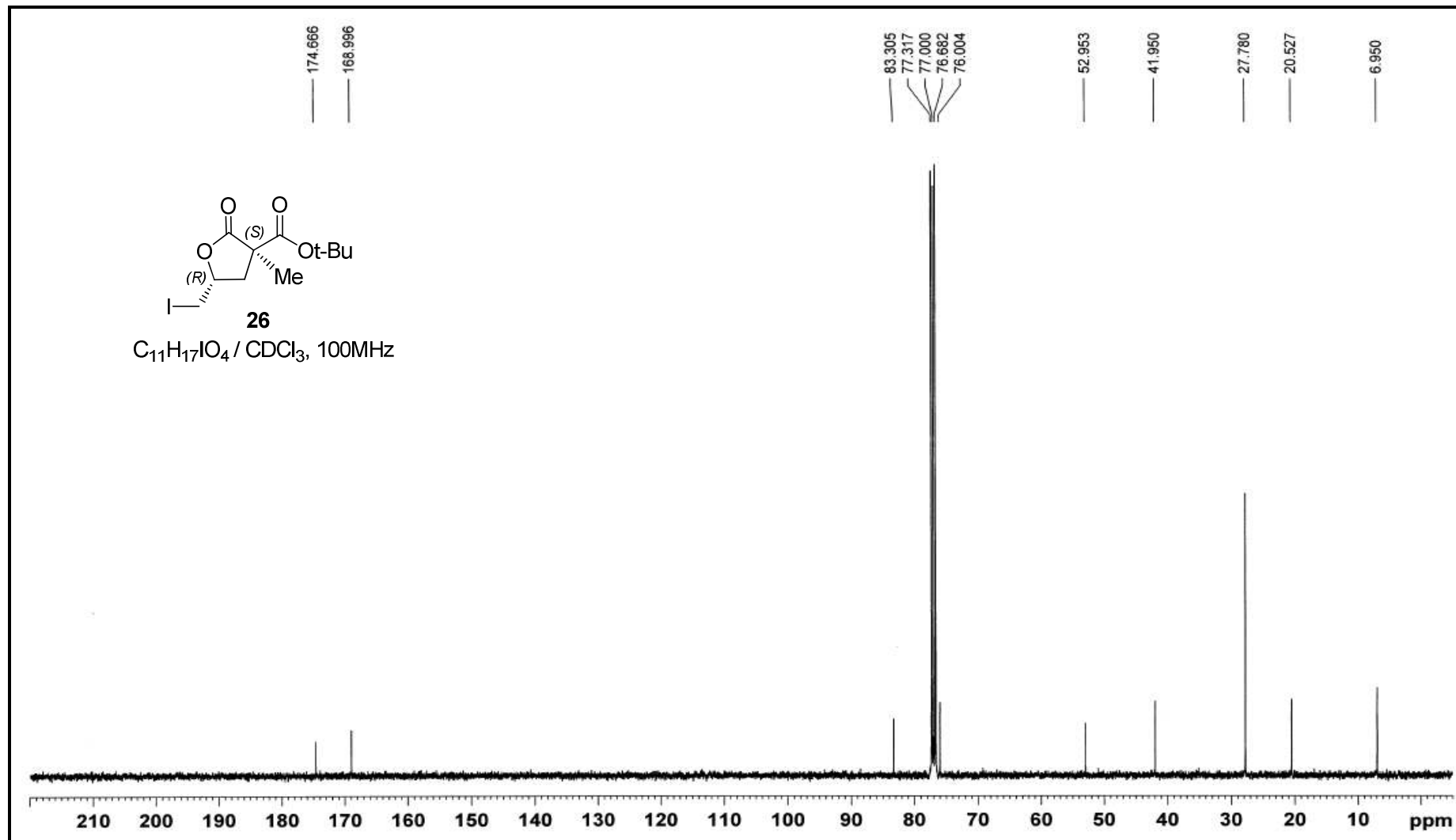
$^{13}\text{C-NMR}$ of compound (**25**)



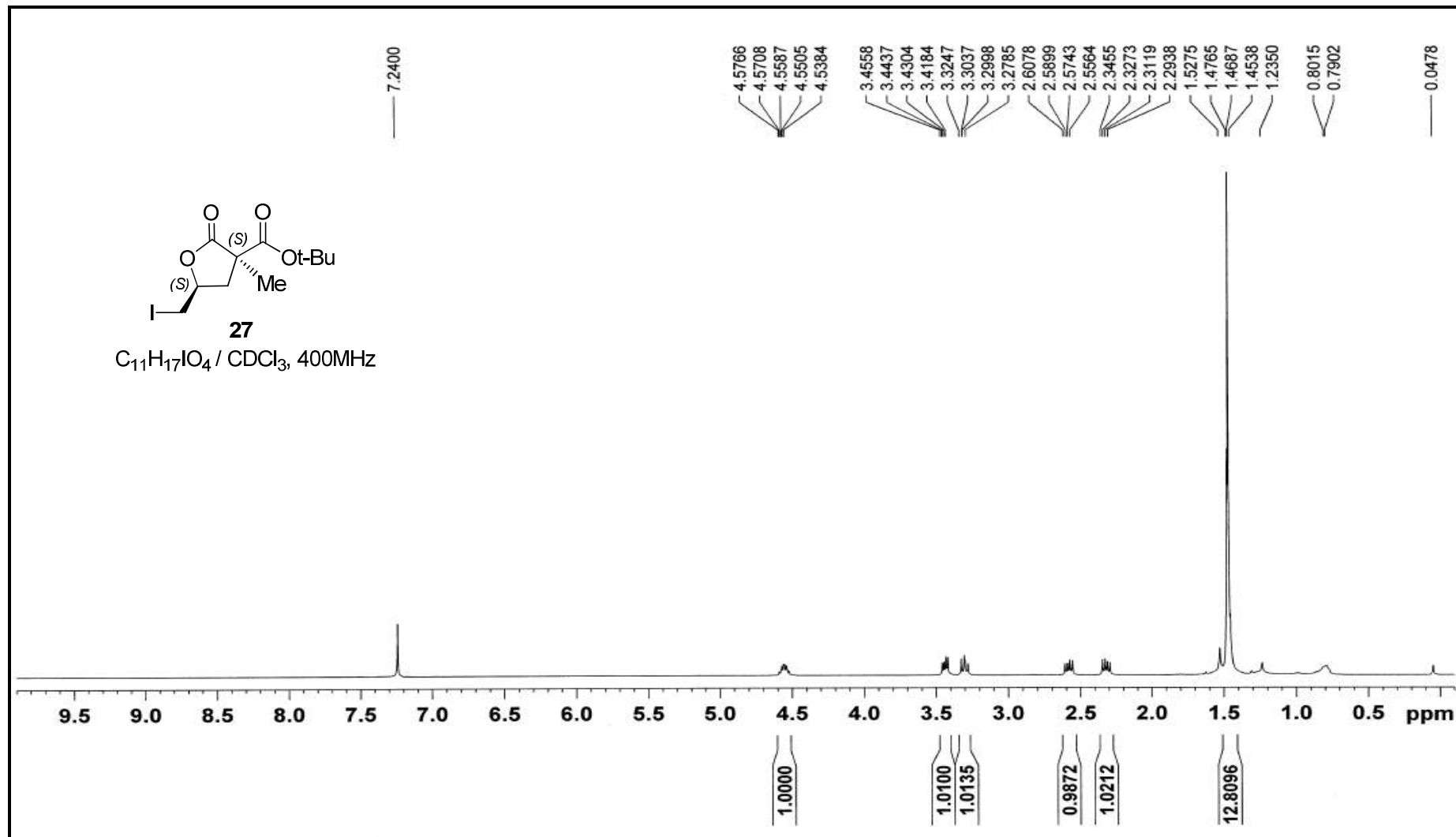
¹H-NMR of compound (26)



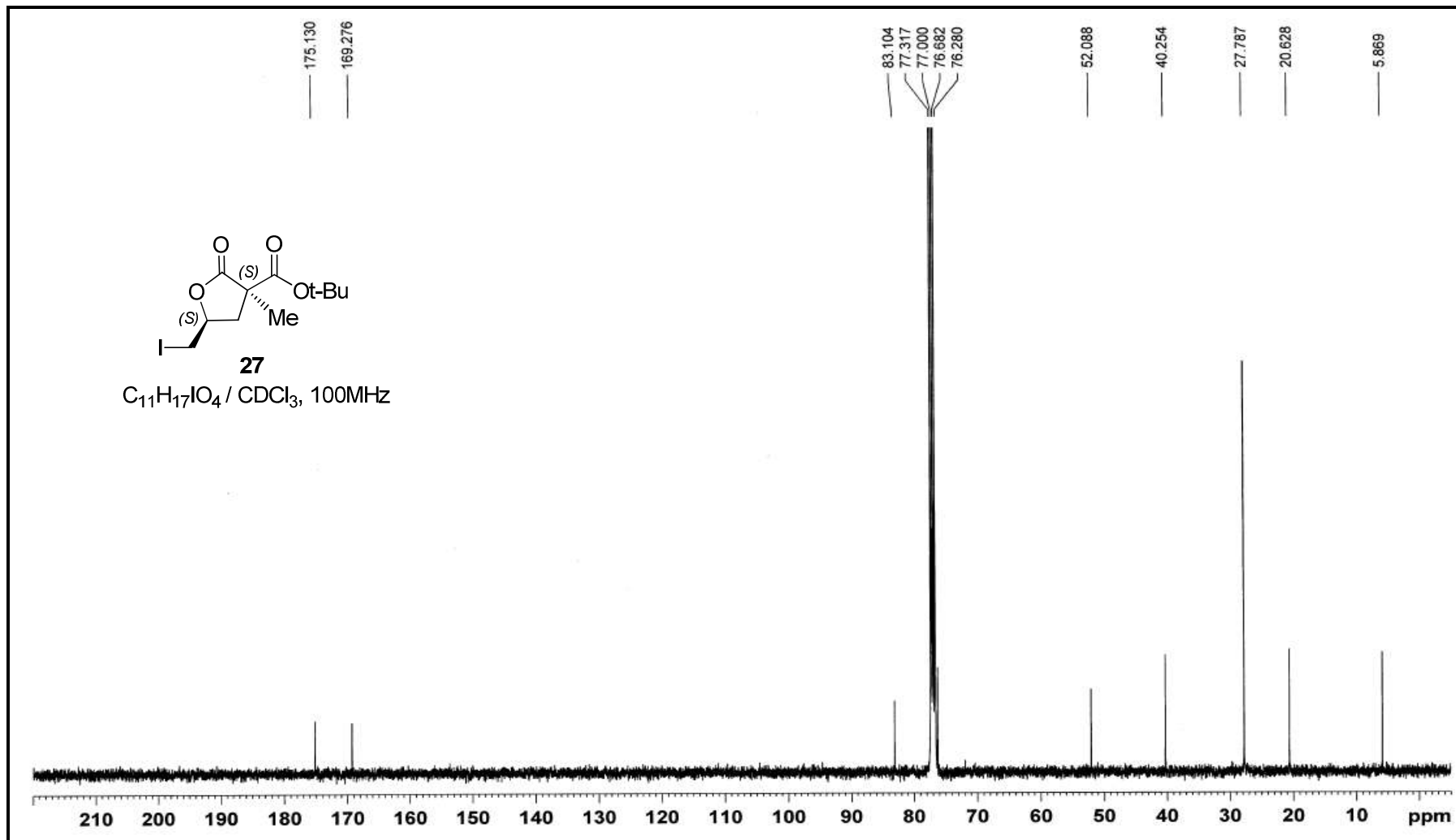
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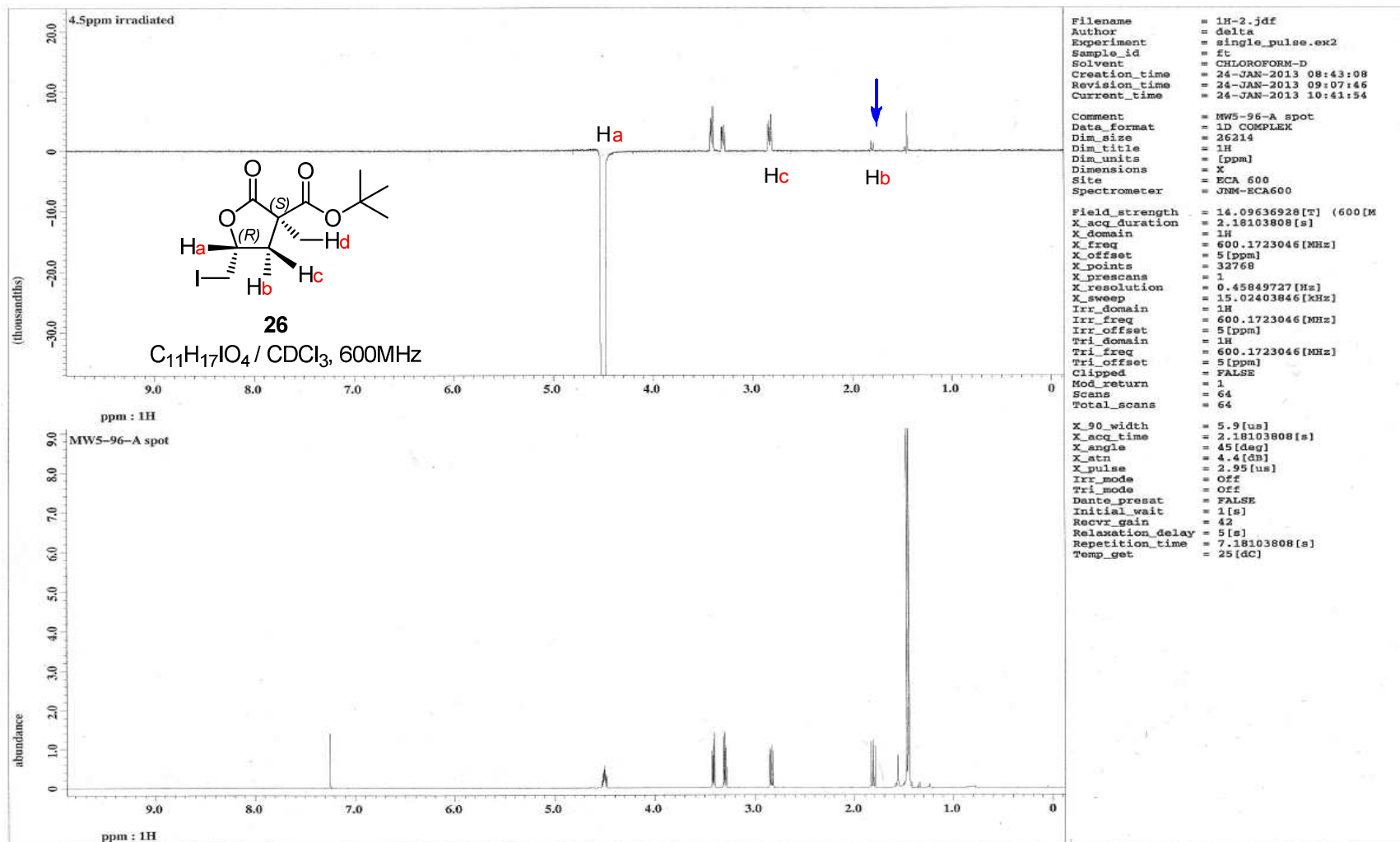
$^1\text{H-NMR}$ of compound (**27**)

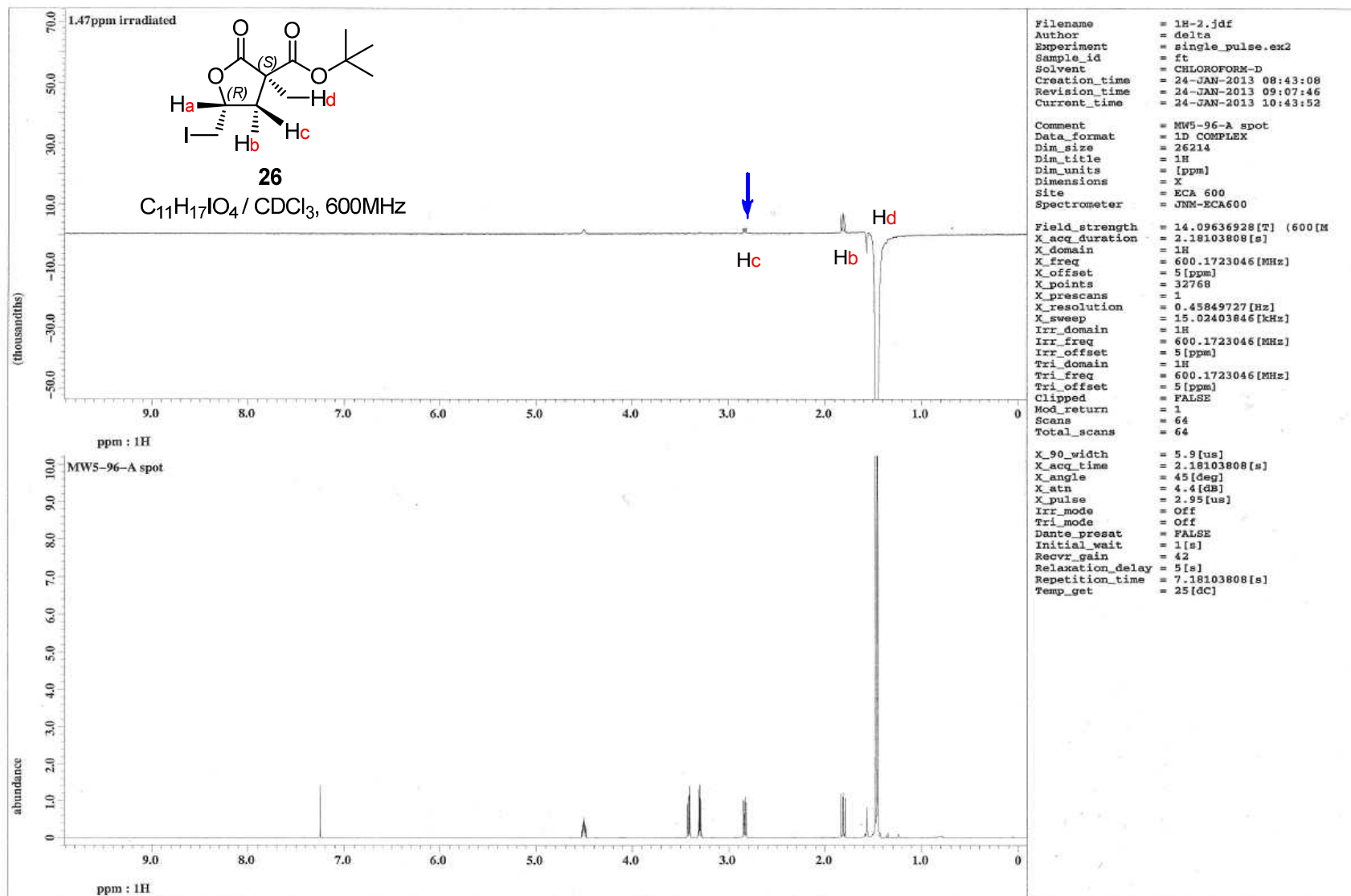


$^{13}\text{C-NMR}$ of compound (**27**)

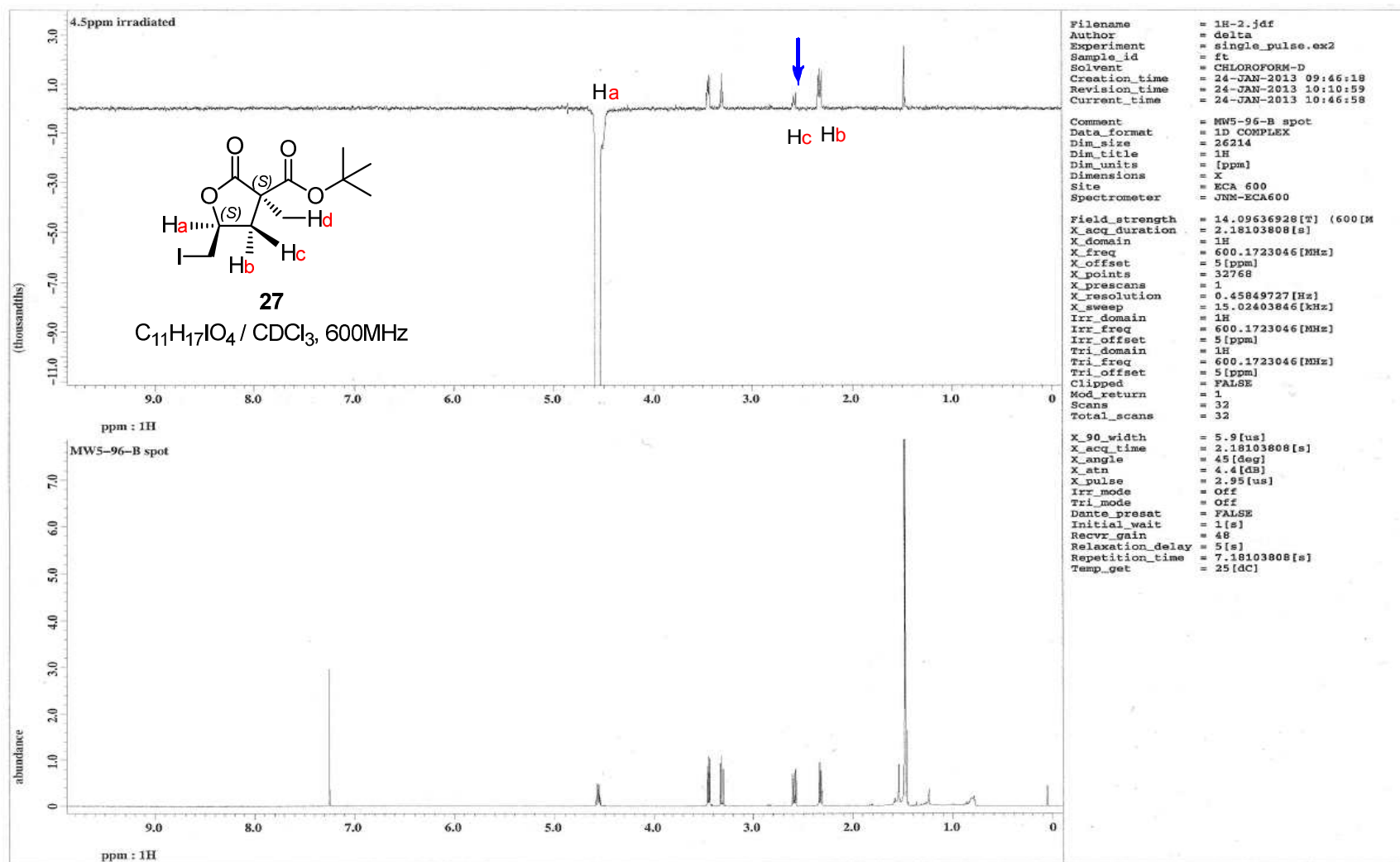


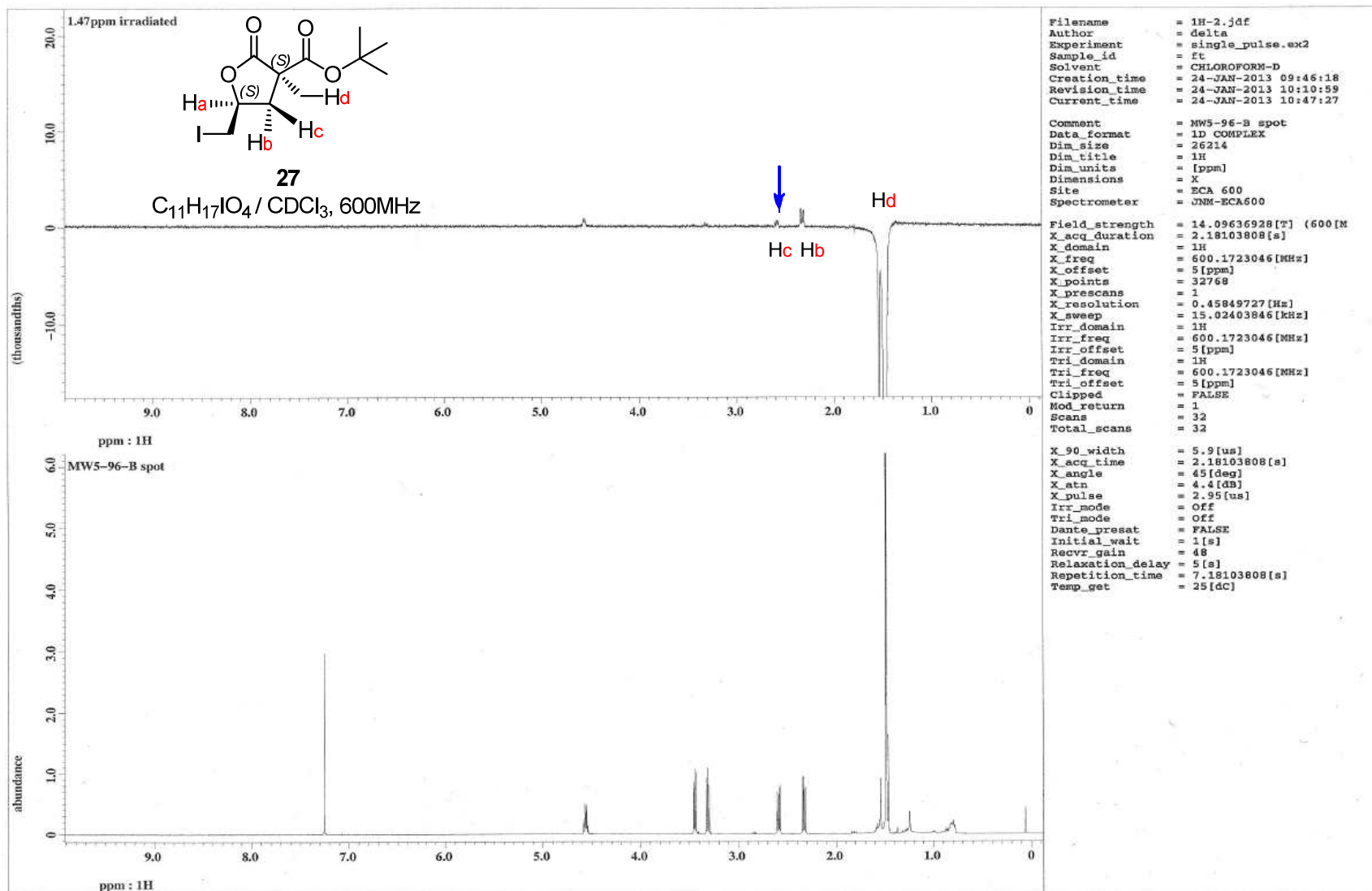
nOe of compound (26)



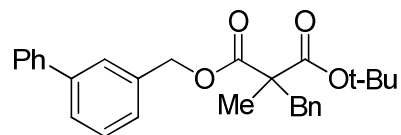


nOe of compound (27)

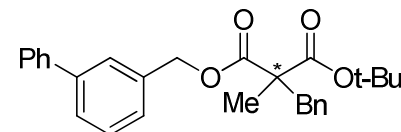




(2) Chiral HPLC Chromatogram



rac-15c

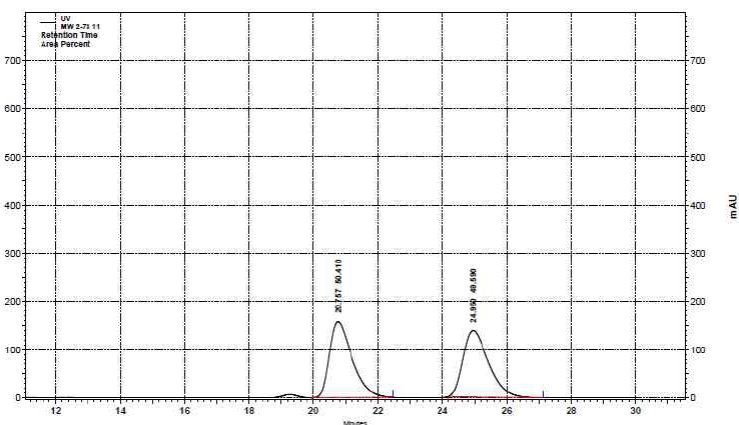


chiral-15c

Area Percent Report

Instrument Name: L-2000
 Software Version: Version LaChrom 8908800-07
 Acquisition Method: Diacel OD-H, Hexane : 2-Propanol = 99.5 : 0.5,
 λ = 254nm, flow rate = 1mL/min

Sample ID: *rac-15c*



UV Results

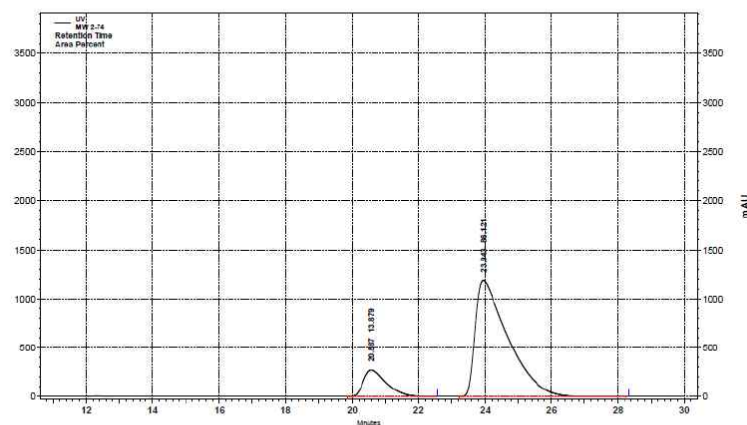
Name	Retention Time	Area	Area Percent	Integration Codes
1	20.757	30792063	50.410	BI
2	24.950	30290609	49.590	II

Totals		61082672	100.000	
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Area Percent Report

Instrument Name: L-2000
 Software Version: Version LaChrom 8908800-07
 Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99.5 : 0.5,
 λ = 254nm, flow rate = 1mL/min

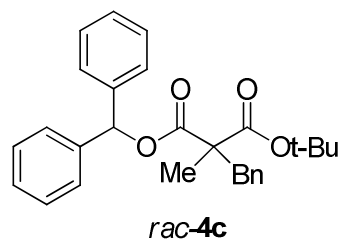
Sample ID: *chiral-15c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	20.587	52407515	13.879	II
2	23.943	325190306	86.121	II

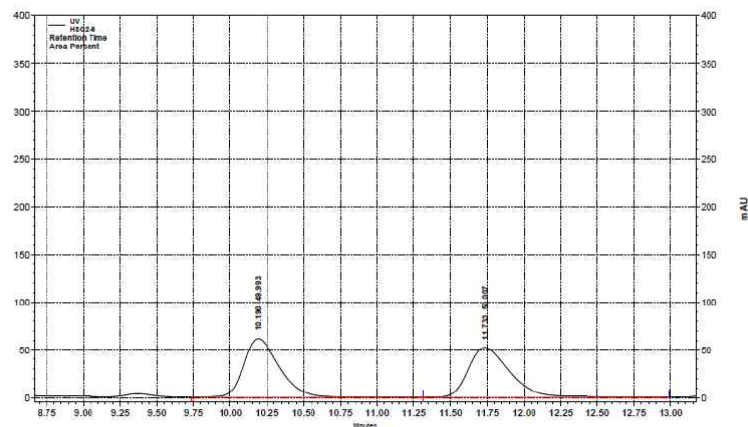
Totals		377597821	100.000	
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Area Percent Report

Instrument Name: L-2000
 Software Version: Version LaChrom 8908800-07
 Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 98 : 2,
 $\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-4c*



UV Results

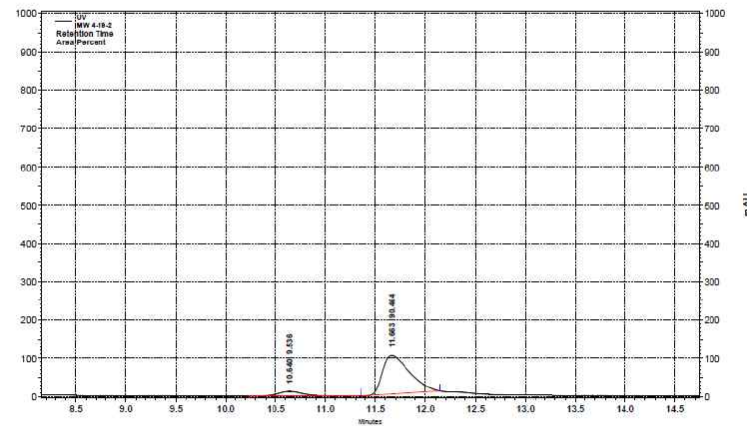
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1	10.867	10415588	49.876	IB
2	12.577	10467229	50.124	BI

Totals		20882817	100.000	
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Area Percent Report

Instrument Name: L-2000
 Software Version: Version LaChrom 8908800-07
 Acquisition Method: Diapak AD-H, Hexane : 2-Propanol = 98 : 2,
 $\lambda = 254\text{nm}$, flow rate = 1mL/min

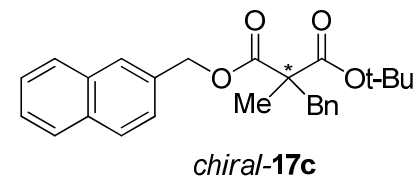
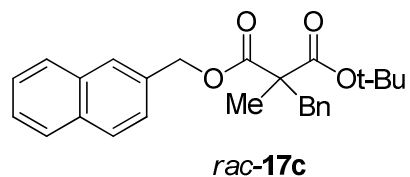
Sample ID: *chiral-4c* (Modification of *chiral-16c*)



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	10.640	759562	9.078	IB
2	11.663	7607273	90.922	IB

Totals		8366835	100.000	
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Area Percent Report

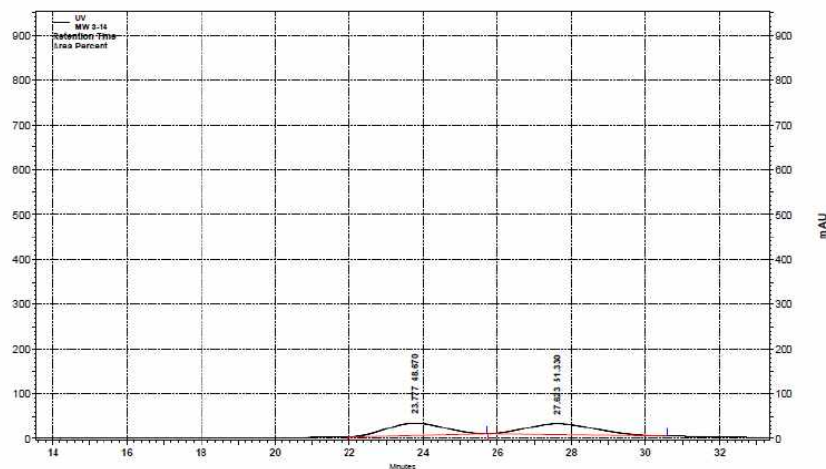
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 95 : 5,

λ = 254nm, flow rate = 1mL/min

Sample ID: *rac-17c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
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	27.623	12985424	51.330	mm

Totals

25298075 100.000

Area Percent Report

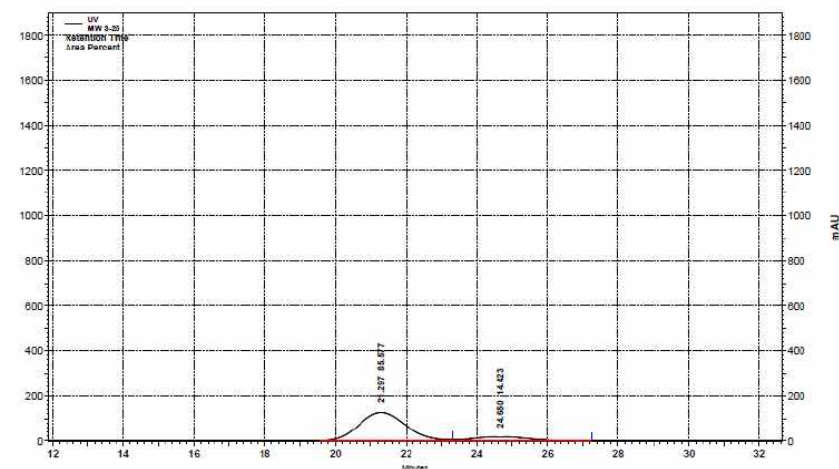
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 95 : 5,

λ = 254nm, flow rate = 1mL/min

Sample ID: *chiral-17c*

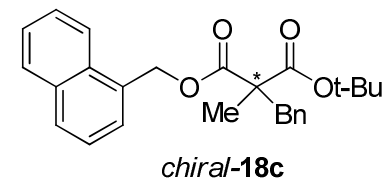
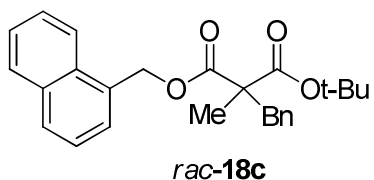


UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
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	24.650	7780377	14.423	VI

Totals

53945991 100.000



Area Percent Report

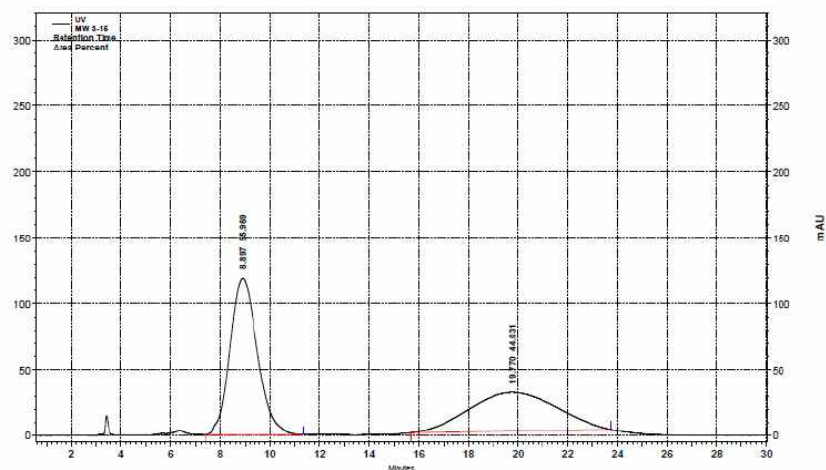
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 80 : 20,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: **rac-18c**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	8.897	36407380	55.969	BB
2	19.770	28641926	44.031	mm

Totals

63049306 100.000

Area Percent Report

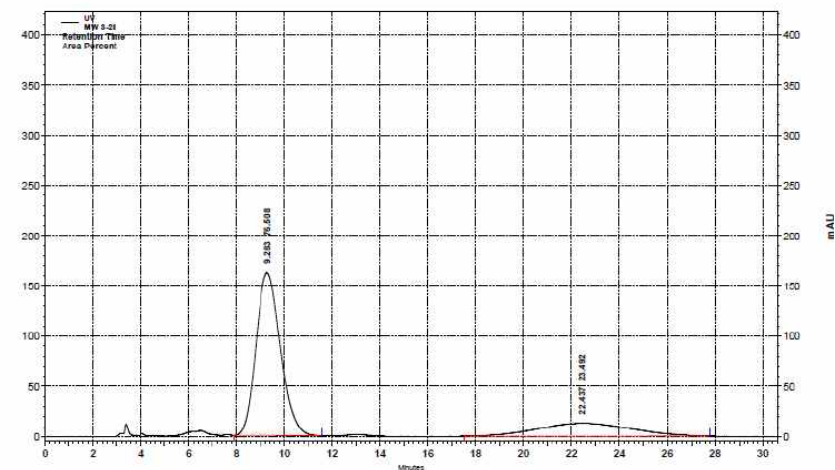
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 80 : 20,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: **chiral-18c**

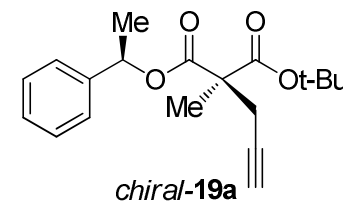
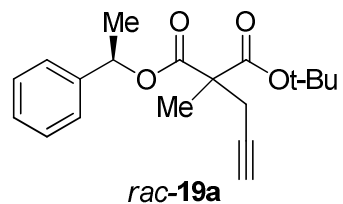


UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	9.283	46046631	76.508	BI
2	22.437	14138972	23.492	mm

Totals

60185603 100.000



Area Percent Report

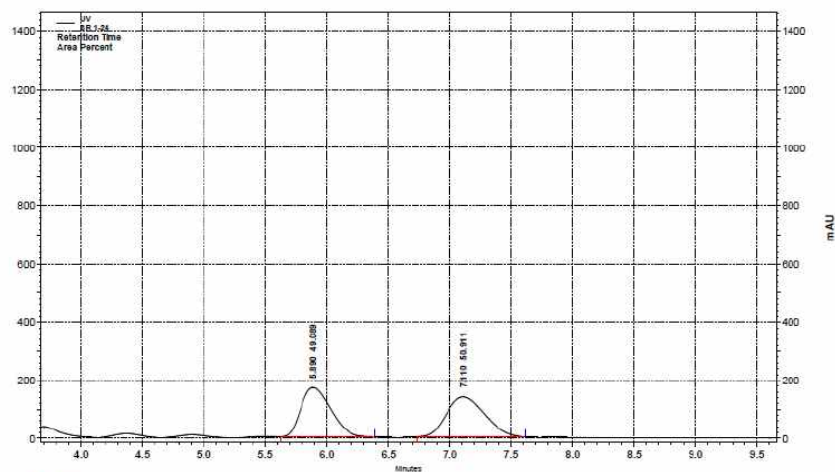
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 210\text{nm}$, flow rate = 1mL/min

Sample ID: **rac-19a**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	5.890	11435030	49.089	mm
	7.110	11859389	50.911	mm

Totals	Area	Area Percent
	23294419	100.000

Area Percent Report

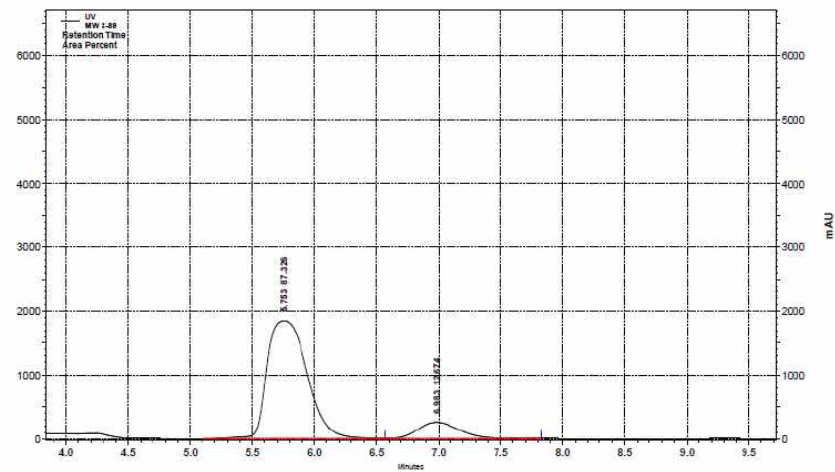
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 210\text{nm}$, flow rate = 1mL/min

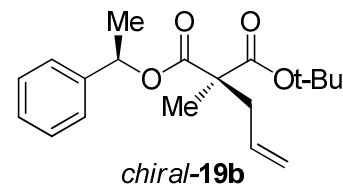
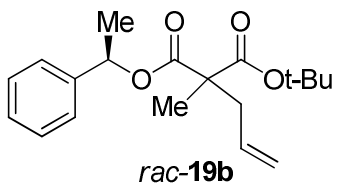
Sample ID: **chiral-19a**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	5.753	164188170	87.326	BV
	6.983	23829377	12.674	VI

Totals	Area	Area Percent
	188017547	100.000



Area Percent Report

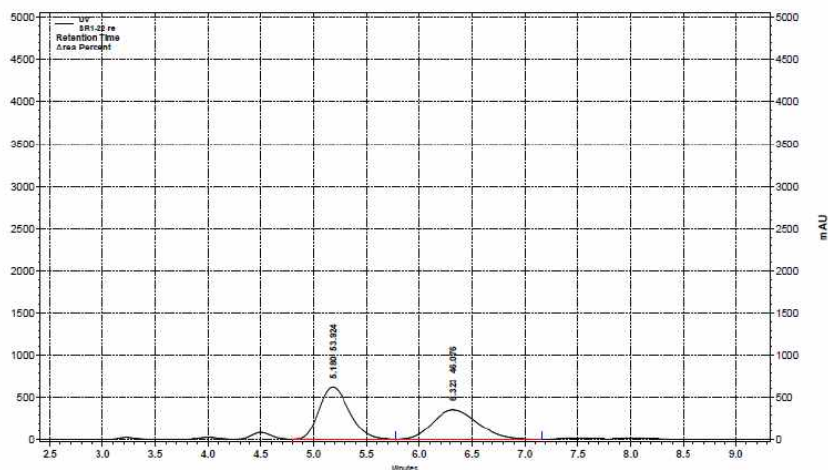
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 210\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-19b*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	5.180	49517203	53.924	mm
	6.323	42310784	46.076	mm

Totals	Area	Area Percent
	91827987	100.000

Area Percent Report

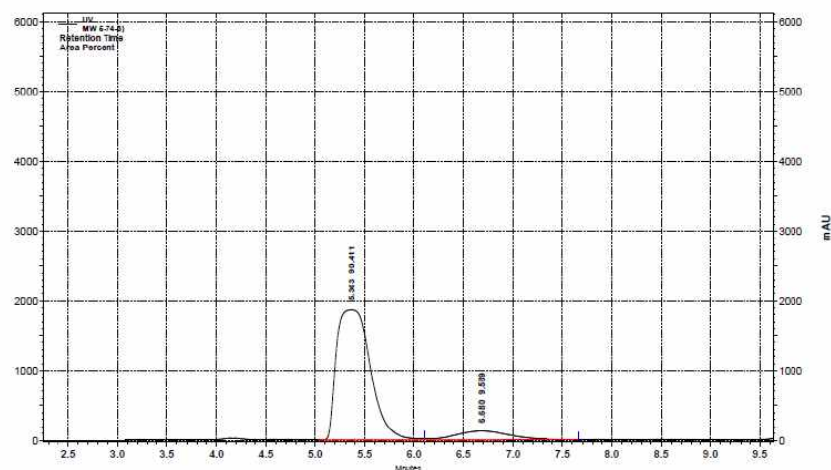
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 210\text{nm}$, flow rate = 1mL/min

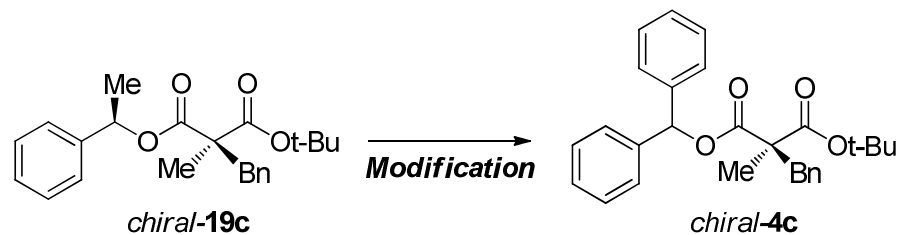
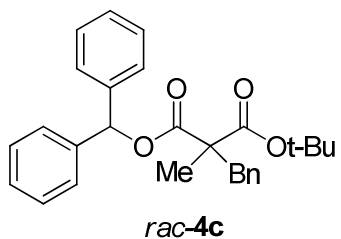
Sample ID: *chiral-19b*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	5.363	179072241	90.411	BV
2	6.680	18992371	9.589	VB

Totals	Area	Area Percent
	198064612	100.000



Area Percent Report

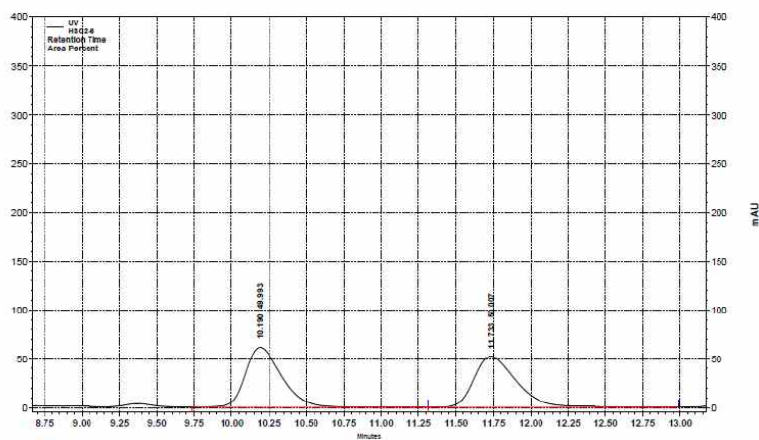
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diapak chiralpak AD-H, Hexane : 2-Propanol = 98 : 2,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-4c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	10.867	10415388	49.876	IB
	11.777	10467229	50.124	BI

Totals		20882817	100.000	
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Area Percent Report

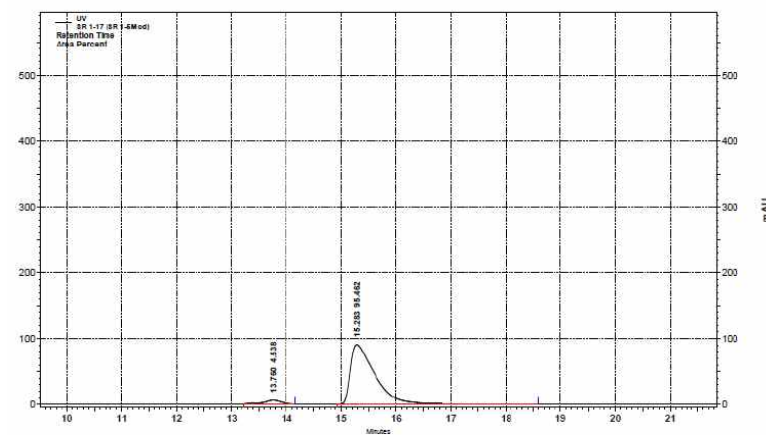
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diapak AD-H, Hexane : 2-Propanol = 98 : 2,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

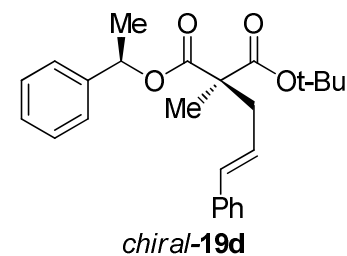
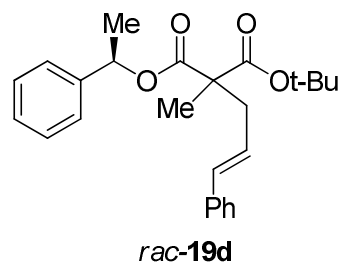
Sample ID: *chiral-4c* (Modification of *chiral-19c*)



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	13.760	537094	4.538	nm
	15.283	11297513	95.462	nm

Totals		11834607	100.000	
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Area Percent Report

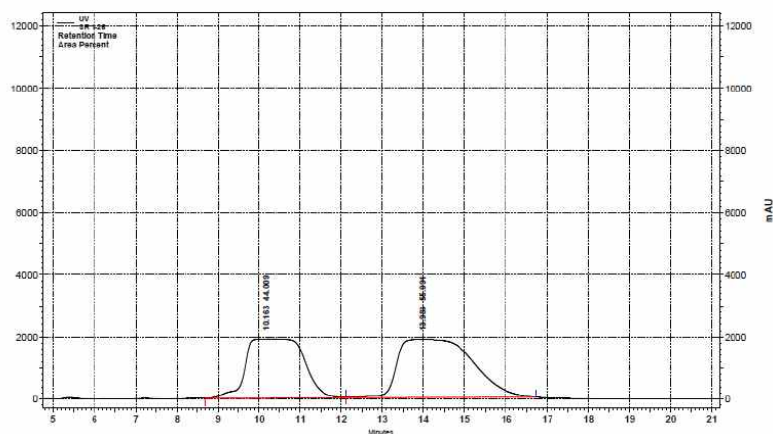
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 210\text{nm}$, flow rate = 1mL/min

Sample ID: **rac-19d**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	10.163	738732571	44.009	mm
	13.983	939857505	55.991	mm

Totals		Area	Area Percent
		1678590076	100.000

Area Percent Report

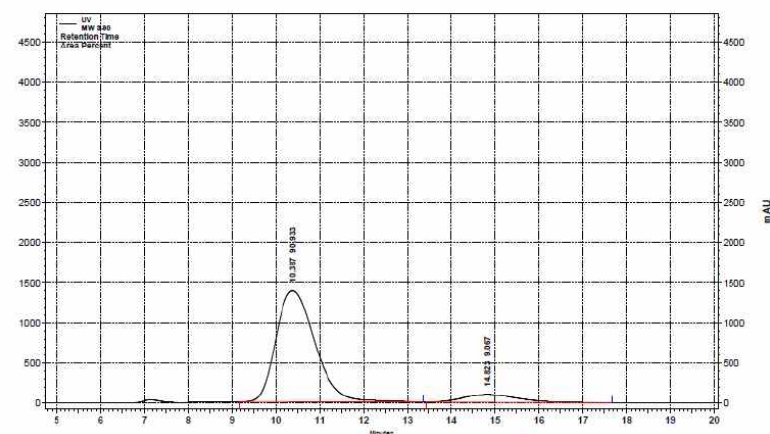
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OJ-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 210\text{nm}$, flow rate = 1mL/min

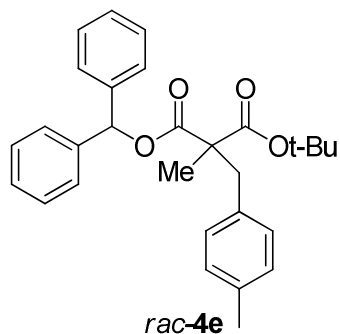
Sample ID: **chiral-19d**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	10.387	342649151	90.933	mm
	14.823	34164954	9.067	BB

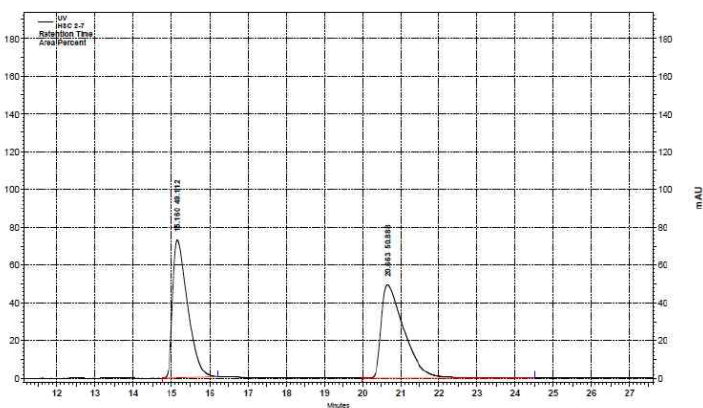
Totals		Area	Area Percent
		376814105	100.000



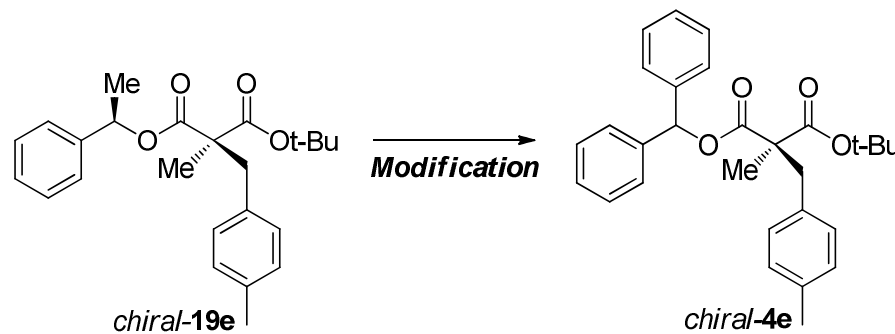
Area Percent Report

Instrument Name: L-2000
 Software Version: Version LaChrom 8908800-07
 Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 98 : 2,
 $\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-4e*



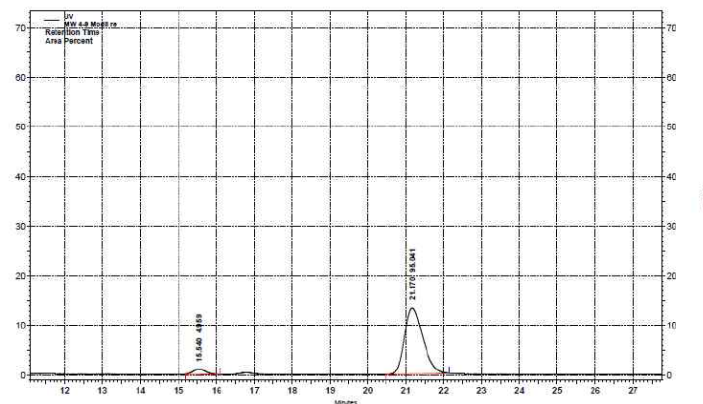
UV Results				
Name	Retention Time	Area	Area Percent	Integration Codes
	15.160	7875112	49.112	BI
	20.663	8159894	50.888	BI
Totals		16035006	100.000	



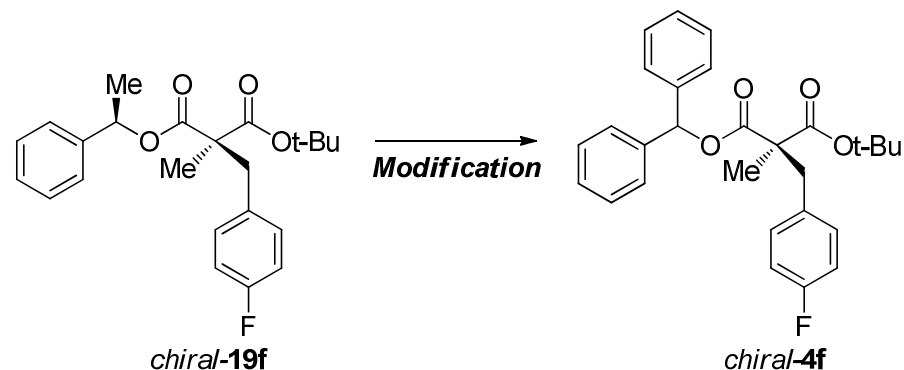
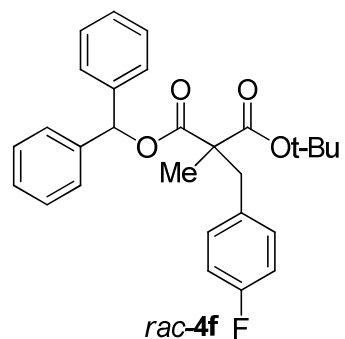
Area Percent Report

Instrument Name: L-2000
 Software Version: Version LaChrom 8908800-07
 Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 98 : 2,
 $\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *chiral-4e* (Modification of *chiral-19e*)



UV Results				
Name	Retention Time	Area	Area Percent	Integration Codes
	15.540	93204	4.959	BI
2	21.170	1786140	95.041	BI
Totals		1879344	100.000	



Area Percent Report

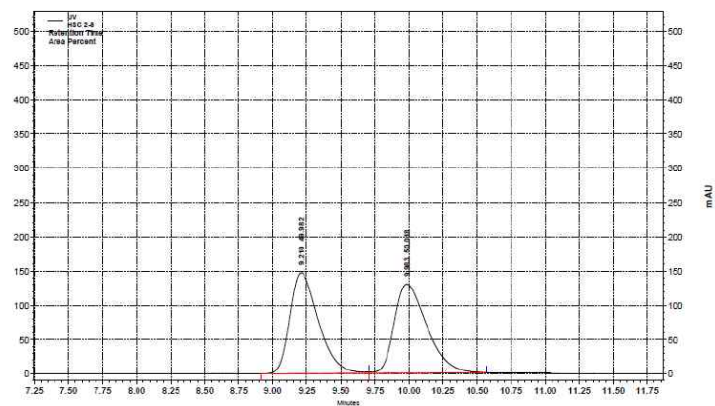
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 95 : 5,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-4f*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	9.210	8609656	49.982	BV
	9.983	8615763	50.018	VI

Totals	Area	Area Percent
	17225419	100.000

Area Percent Report

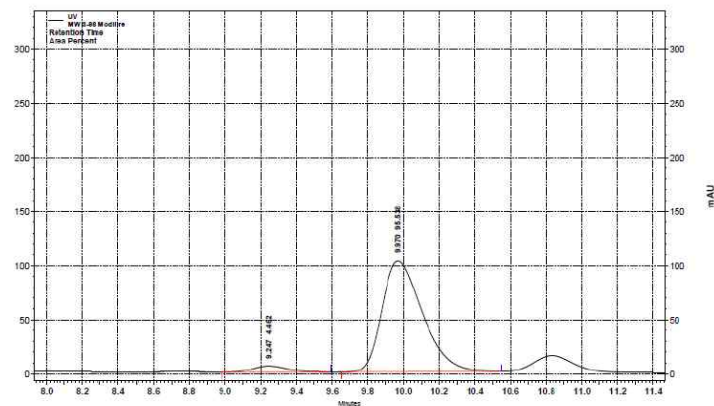
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 95 : 5,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

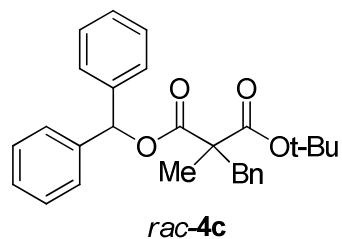
Sample ID: *chiral-4f* (Modification of *chiral-19f*)



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	9.247	301195	4.462	BB
	9.970	6449021	95.538	BB

Totals	Area	Area Percent
	6750216	100.000



Area Percent Report

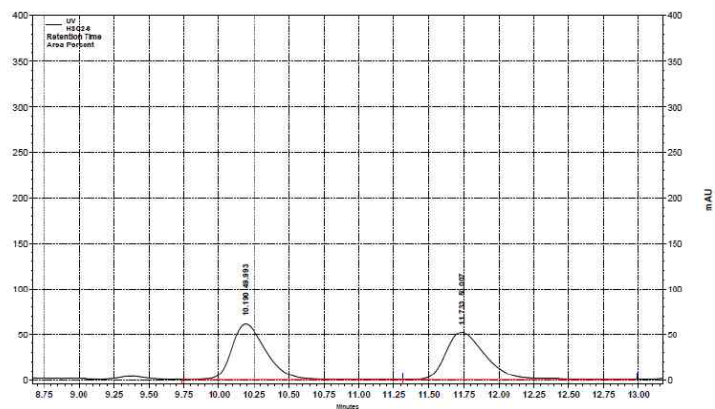
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 98 : 2,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-4c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	10.867	10415588	49.876	IB
2	12.577	10467229	50.124	BI

Totals		20882817	100.000	
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Area Percent Report

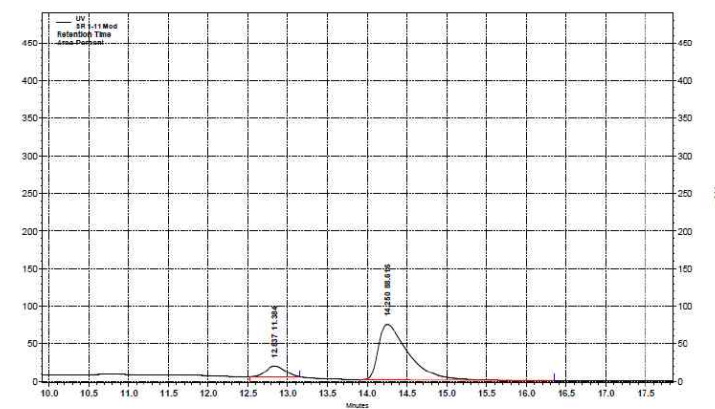
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diapak AD-H, Hexane : 2-Propanol = 98 : 2,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

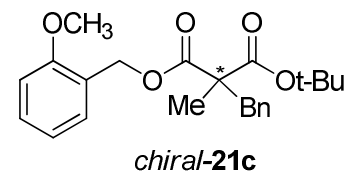
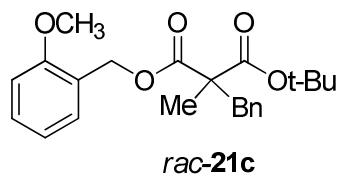
Sample ID: *chiral-4c* (Modification of *chiral-20c*)



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	12.837	998414	11.384	mm
2	14.250	7771971	88.616	BI

Totals		8770385	100.000	
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Area Percent Report

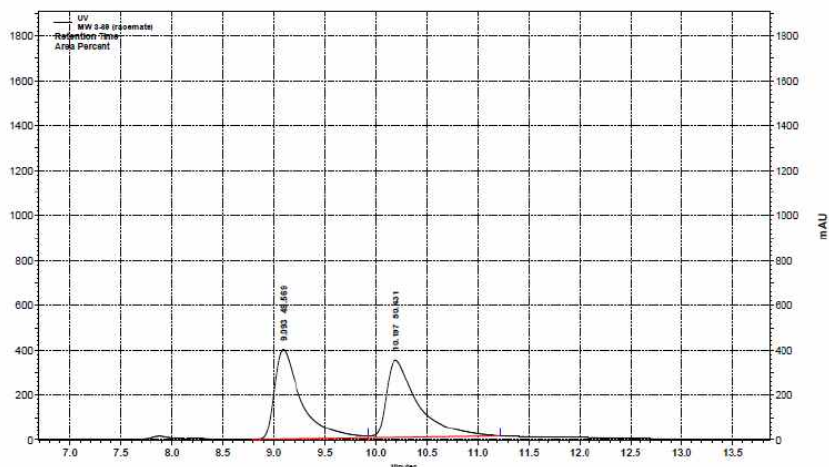
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: rac-21c



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	9.093	29185587	49.569	mm
2	10.197	29693304	50.431	mm

Totals	Area	Area Percent
	58878891	100.000

Area Percent Report

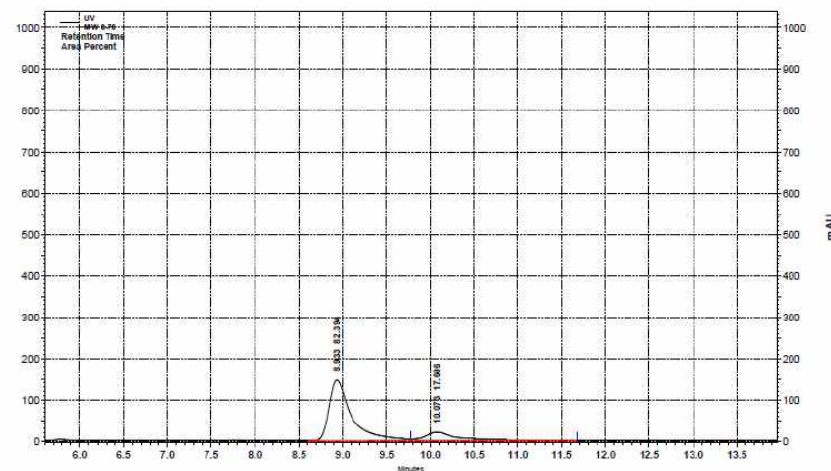
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralpak AD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

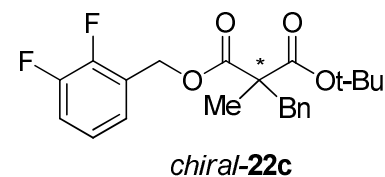
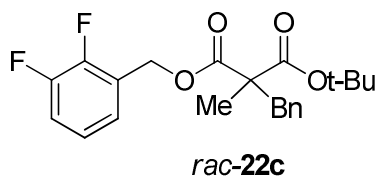
Sample ID: chiral-21c



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	8.933	10504148	82.394	BV
	10.073	2244587	17.606	VI

Totals	Area	Area Percent
	12748735	100.000



Area Percent Report

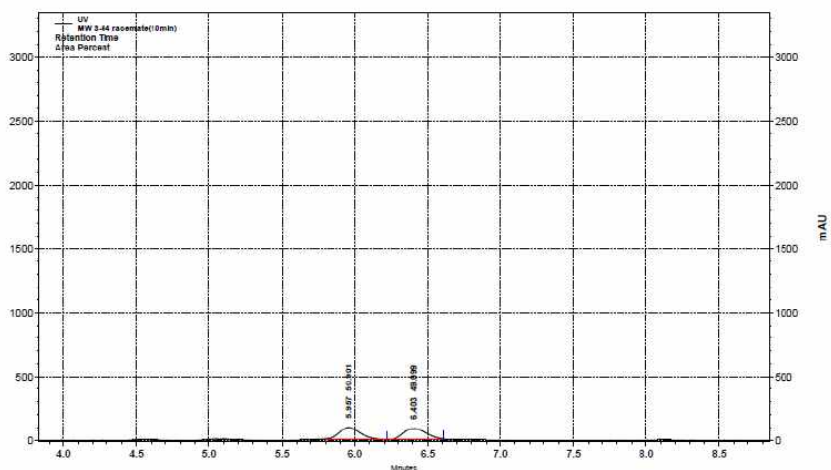
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-22c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	5.957	3445121	50.901	mm
2	6.403	3323208	49.099	mm

Totals	Area	Area Percent
	6768329	100.000

Area Percent Report

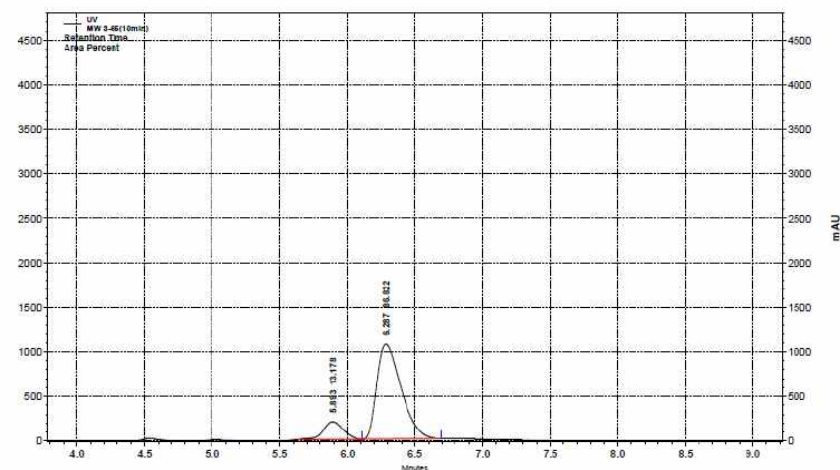
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

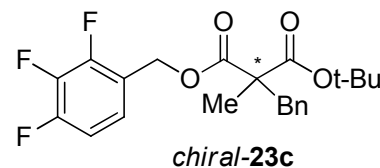
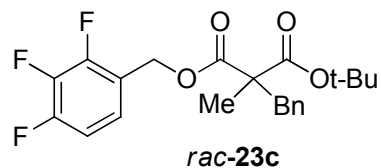
Sample ID: *chiral-22c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	5.893	7957665	13.178	mm
2	6.287	52430213	86.822	mm

Totals	Area	Area Percent
	60387878	100.000



Area Percent Report

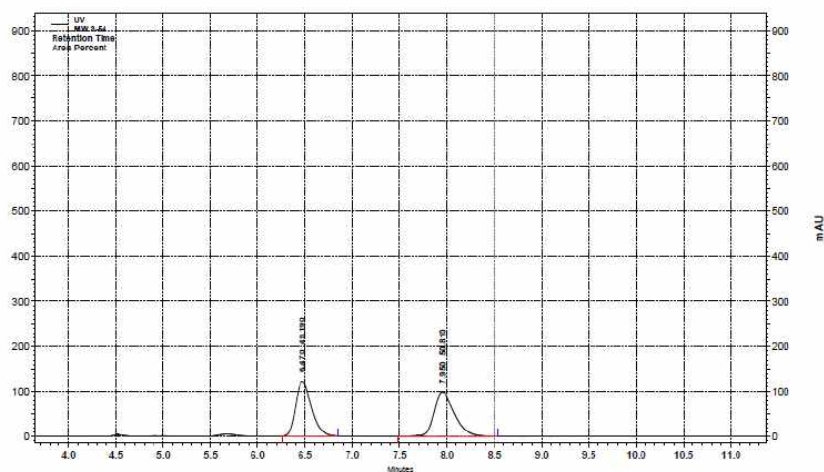
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: **rac-23c**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	6.470	5833615	49.190	II
	7.950	6025810	50.810	II

Totals		11859425	100.000	
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Area Percent Report

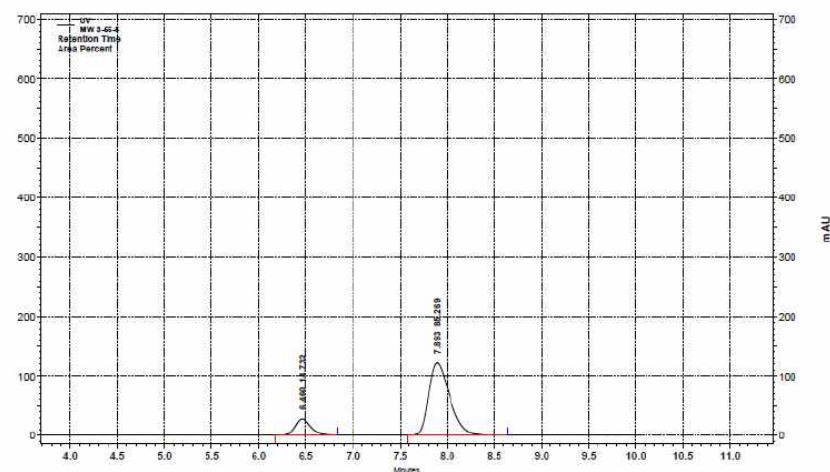
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

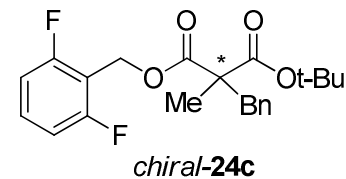
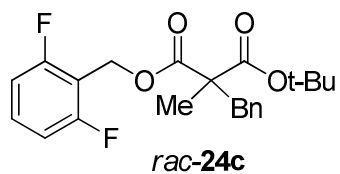
Sample ID: **chiral-23c**



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
2	6.460	1303016	14.732	II
	7.893	7542084	85.269	BI

Totals		8845100	100.000	
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Area Percent Report

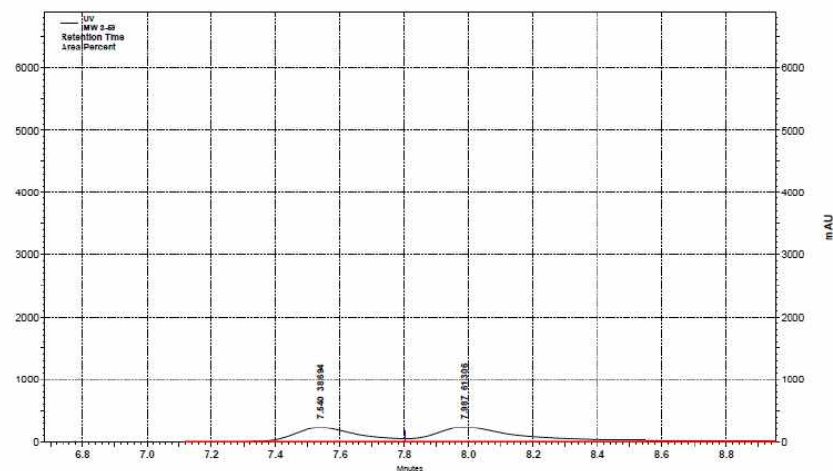
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *rac-24c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	7.540	11997039	38.694	BV
	7.987	19007497	61.306	VI

Totals	Area	Area Percent
	31004536	100.000

Area Percent Report

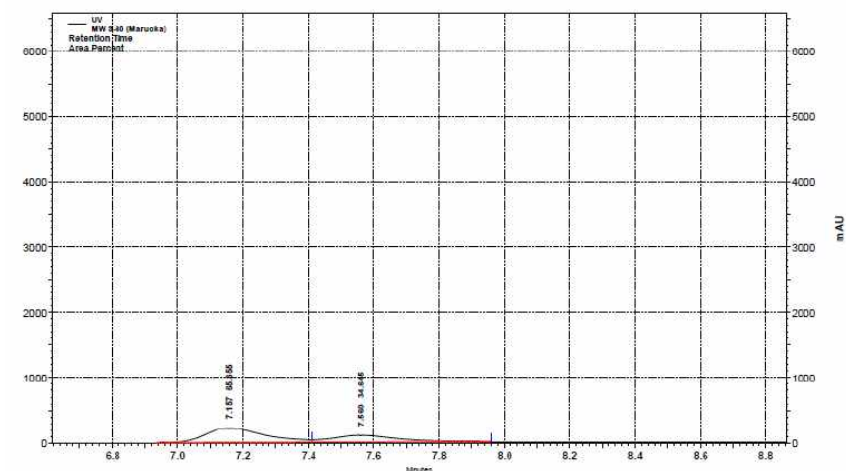
Instrument Name: L-2000

Software Version: Version LaChrom 8908800-07

Acquisition Method: Diacel chiralcel OD-H, Hexane : 2-Propanol = 99 : 1,

$\lambda = 254\text{nm}$, flow rate = 1mL/min

Sample ID: *chiral-24c*



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
1	7.157	11324610	65.355	BV
	7.560	6003174	34.645	VI

Totals	Area	Area Percent
	17327784	100.000