Supplementary Information (SI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

Experimental verification of halomethyl carbinols synthesis from carbonyl compounds using a $TiCl_4$-Mg bimetallic complex promoter

Olga Michalak, *[a] Sylwia Żurawicka, [a] Marek Kubiszewski, [b] Piotr Krzeczyński, [a] Andrzej Leś, [c] Sławomir Filipek, [d] Marcin Cybulski [a]

[a] *Pharmacy, Cosmetic Chemistry and Biotechnology Research Group, Łukasiewicz Research Network-Industrial Chemistry Institute, Rydygiera 8, 01–793 Warsaw, Poland.*
[b] *Pharmaceutical Analysis Laboratory, Łukasiewicz Research Network-Industrial Chemistry Institute, Rydygiera 8, 01–793 Warsaw, Poland.*
[c] *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.*
[d] *Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.*
** Correspondence: Łukasiewicz Research Network-Industrial Chemistry Institute, Rydygiera 8, 01–793 Warsaw, Poland; o.michalak@ichp.lukasiewicz.gov.pl ; Tel. +48 453 056 175*

Table of Content

[S.1] Modeling of the Mg powder and reagents

The chemical reaction occurring in the course of synthesis can be analysed with the stoichiometric equations and the Gibbs free energies (ΔG), enthalpies (ΔH) and the sum of electronic and nuclear energies (ΔE) estimated with the quantum mechanical calculations.

A theoretical model of the Mg powder becomes a challenge from the quantum mechanical point of view. The metallic Mg powder is composed of small metallic particles which should have an internal molecular structure close to the Mg crystals with irregular structure at the particle surface. In a more advanced modeling one should consider clusters of the Mg atoms, e.g. Mg_n, $n \gg 1$.

At first approximation, one can represent the Mg powder by a single Mg atom in the singlet ground state.

The reagents (including solvents) can be represented by the corresponding chemical molecules.

[S.2] Reaction of Mg powder with CH_2Br_2

One can suggest the following reaction (SE.1):

$$Mg + CH_2Br_2 \rightarrow CH_2Br_2{::}Mg \qquad \text{(SE.1)}$$

ΔG = –51.6 kcal/mol
ΔH = –58.0 kcal/mol
ΔE = –57.4 kcal/mol

From these calculations, one can predict that the reaction of Mg (powder) with dibromomethane is spontaneous and exothermic. It is expected that this reaction will require intensive cooling.

The reaction product, i.e. CH_2Br_2::Mg magnesium complex can be viewed as a Br analogue of the Grignard reagent of a general formula alkyl–Mg–Br.

An interesting molecular structure of the CH_2Br_2::Mg product was obtained theoretically. The Mg atom is bound to Br and the bromomethylene unit, as shown in Figure S1.

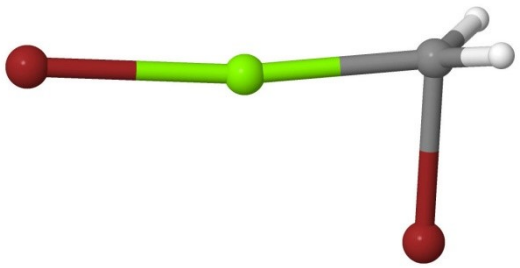


Figure S1. The optimized molecular structure of the $MgCH_2Br_2$ magnesium complex. Colour codes: dark red: Br; green: Mg; grey: C; white: H.

[S.3] Reaction of Mg powder with $Mg::CH_2Br_2$ complex and TiCl4

The suggested stoichiometric reaction (SE.3) corresponds to the formation of the Ti/Mg bimetallic catalyst:

$$Mg + 2\ TiCl_4 + 2\ Mg::CH_2Br_2 \rightarrow 2\ [TiCl_3::MgCH_2Br_2]^{\bullet} + MgCl_2$$

$\Delta G = -68.9$ kcal/mol (SE.3)
$\Delta H = -86.2$ kcal/mol
$\Delta E = -87.5$ kcal/mol

An interesting feature of the $[TiCl_3::MgCH_2Br_2]^{\bullet}$ complex is a split of the $MgCH_2Br_2$ unit into $[MgBr]^{\bullet}$ and $[CH_2Br]^{\bullet}$ radicals. The $[CH_2Br]^{\bullet}$ unit is coordinated to the Ti cation. The Mg atom of $[MgBr]^{\bullet}$ unit is bound simultaneously to two chlorine atoms of $TiCl_3$. The optimized molecular geometry of the titanium/magnesium complex in the form of the $[TiCl_3::MgCH_2Br_2]^{\bullet}$ radical is presented in Figure S2.

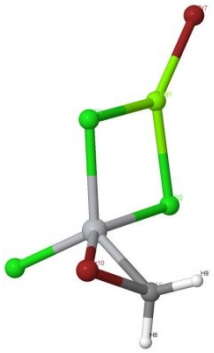


Figure S2. The optimized molecular structure of the $TiCl_3MgCH_2Br_2$ magnesium complex. Color codes: light grey: Ti; dark red: Br; green: Cl; light green: Mg; dark grey: C; white: H.

[S.4] A model of reactions of the solvent molecules with the Ti/Mg catalyst

[S.4.A] Inclusion of DBE in the $TiCl_3::MgBr_2$ bimetallic catalyst

(DBE means the dibutylether)

$$2\ TiCl_4 + Mg + 2\ Mg::CH_2Br_2 + 2\ DBE \rightarrow \rightarrow 2\ [TiCl_3::MgCH_2Br_2::DBE]^{\bullet} + MgCl_2$$

$\Delta G = -60.4$ kcal/mol (SE.4)
$\Delta H = -101.8$ kcal/mol
$\Delta E = -106.9$ kcal/mol

It is clear that the above reactions should be spontaneous and exothermic.

A hypothetical $[TiCl_3{:}MgCH_2Br_2::DBE]^{\bullet}$ complex may have the molecular structure presented in the Figure S4:

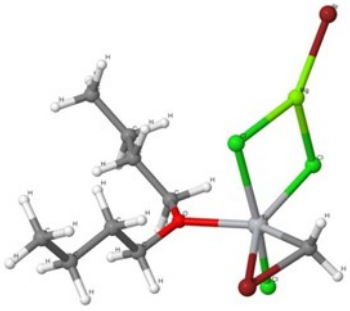


Figure S3. The optimized geometry of the $TiCl_3::MgCH_2Br_2::DBE$ complex. Color codes: light gray: Ti; green; Cl; dark red: Br; light green: Mg; red: O; dark gray: C; white: H. The atoms O–Ti–C , Cl(up) and Cl(down) , Br–Ti–Cl belong to one plane (approximately). Also, Ti–Cl–Cl–Cl belong to another plane (perpendicular to the former plane). The Mg atom is coordinated by two Cl atoms and one Br atom. The oxygen atom from DBE occupies one coordination site of Ti.

The Ti-containing radical is reactive species and likely it should attack aldehyde/ketone present in the reaction soup.

[S.4.B] Inclusion of DEE to the $TiCl_3::MgBr_2$ bimetallic catalyst

An interesting though rather hypothetical formation of a Ti/Mg bimetallic complex with the bidentate ligand 1,2-dimethoxyethene (DEE),) as the result of interactions of with dimethoxyethane reagent (DME), was presented below in the Figure S4.

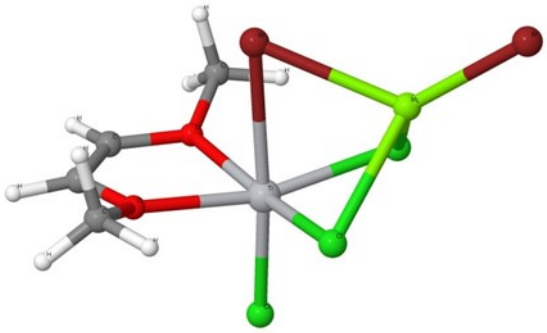


Figure S4. The octahedral molecular geometry of the $DEETiCl_3MgBr_2LB$ complex of $TiCl_3::MgBr_2::$2,5-dimethoxyethene. Colour codes: light gray: Ti; green; Cl; dark red: Br; light green: Mg; red: O; dark gray: C; white: H. The atoms O–Ti–Br, Cl(up) and

Cl(down) belong to one plane (approximately). Also Ti–Cl–Cl–Cl belong to another plane (perpendicular to the former plane). The Mg atom is coordinated to two Cl atoms, and two Br atoms.

$TiCl_3^{\bullet}$ + $MgBr_2$ + DEE → $[DEE::TiCl_3::MgBr_2]^{\bullet}$

A energy output suggests rather strong ligand binding to the $TiCl_3$ core:

ΔG = -32.8 kcal/mol
ΔH = -55.5 kcal/mol
ΔE = -58.5 kcal/mol

[S.4.C] Inclusion of 2,5-dihydrofuran to the $TiCl_3::MgCH_2Br_2$ bimetallic catalyst

Below is an analogical model reaction of furan (THF) in place of DME. A possible stoichrometric reaction including $TiCl_4$ (original, not reduced to $TiCl_3$), $MgCH_2Br_2$ and furan can read as follows:

2 $TiCl_4$ + Mg + 2 THF + 2 $MgCH_2Br_2$ + 4 benzaldehyde → 2 $[DHF::TiCl_3::MgCH_2Br_2]^{\bullet}$ + $MgCl_2$ + 2 [hydrobenzoin] (SE.5)

ΔG = -6.1 kcal/mol
ΔH = -71.3 kcal/mol
ΔE = -80.2 kcal/mol

The product ($[2,5\text{-}DHF::TiCl_3::MgCH_2Br_2]^{\bullet}$) is presented in the Figure S5.

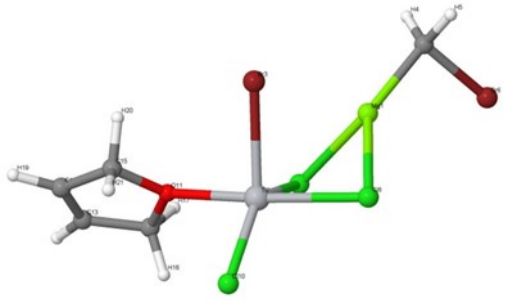


Figure S5. The molecular structure of the $[2,5\text{-}DHF::TiCl_3::MgCH_2Br_2]^{\bullet}$. Colour codes: light gray: Ti; green; Cl; dark red: Br; light green: Mg; red: O; dark gray: C; white: H.

[S.5] A model of 1,2-dichloroethane reaction with magnesium powder

The addition of 1,2-dichloroethane ($Cl–CH_2–CH_2–Cl$, DCE) to the reaction mixture causes production of heat. It is reasonable to assume that the heat is a result of the reaction of the Mg powder with DCE. The following stoichiometric reactions were designed (SE.6):

$Mg + Cl–CH_2–CH_2–Cl \rightarrow CH_2=CH_2 + MgCl_2$ (SE.6)

ΔG = –86.9 kcal/mol
ΔH = –85.1 kcal/mol
ΔE = –82.7 kcal/mol

The Mg powder can be better represented with the Mg_7 cluster powder (simulated by a single Mg atom or the Mg_7 cluster). The corresponding reaction with DCE is shown as the R.8 reaction in the main part:

$Mg_7 + Cl–CH_2–CH_2–Cl \rightarrow CH_2=CH_2::Mg_7::Cl_2$ (SE.7)

ΔG = –74.2 kcal/mol
ΔH = –94.1 kcal/mol
ΔE = –84.2 kcal/mol

It is predicted that the Mg powder should react efficiently with DCE spontaneously and exothermic. It is likely that the ΔG estimation for the Reaction R.8 can be even more negative because in the calculations, the geometry of the Mg_7 cluster was kept fixed (not optimized), see Figure S6.

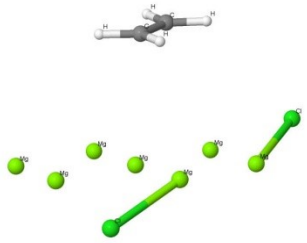


Figure S6. The molecular structure of the $CH_2=CH_2::Mg_7::Cl_2$ complex supposed to be the result of the reaction of the Mg_7 cluster with the 1,2-dichloroethane. The geometry of the Mg_7 cluster was assumed to be fixed. Color codes: light green: Mg; dark green : Cl, grey: C, white: H.

An interesting feature of the R.7 and R.8 reaction products is the C–Cl bond split in 1,2-dichloroethane and formation of the $[MgCl]^{\bullet}$ radicals. Either reaction producs, i.e. ethylene and the $[MgCl]^{\bullet}$ radicals are higly reactive species that can influence other reactions occuring in the reaction soup.

[S.6] A model of the reaction of benzaldehyde with Ti/Mg catalyst

Due to a large size of the molecular complexes, we select here the $[TiCl_3]^{\bullet}$ radical as the active form of the $[TiCl_3::MgCH_2Br_2]^{\bullet}$ catalyst. A first step of the reaction is the formation of an intermediate molecular structure composed from one benzaldehyde molecule and one $TiCl_3$ unit as it is shown in the reaction SE.8:

$[TiCl_3]^{\bullet}$ + benzaldehyde → $[TiCl_3]$–O–$HC^{\bullet}$–phenyl (SE.8)

ΔG = –18.5 kcal/mol
ΔH = –28.4 kcal/mol
ΔE = –29.3 kcal/mol

The molecular geometry of the reaction's product is shown in Figure S7.

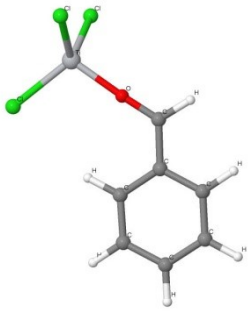


Figure S7. The molecular structure of the $[TiCl_3]$–O–$HC^{\bullet}$–phenyl complex. Color codes: light gray: Ti; dark green : Cl, grey: C, white: H.

Next, two $[TiCl_3]$–O–$HC^{\bullet}$–phenyl complexes couple together via the carbon–carbon bond as it is shown in the reaction (SE9):

2 $[TiCl_3]$–O–$HC^{\bullet}$–phenyl →
→ { $[TiCl_3]$–O–HC–phenyl–phenyl–CH–O–$[TiCl_3]$ }

ΔG = –15.2 kcal/mol (SE.9)
ΔH = –30.9 kcal/mol
ΔE = –34.4 kcal/mol

The product of the SE.9 reaction can be viewed as a precursor of hydrobenzoin. In the present modeling the $TiCl_3$ units are bound to the oxygen atoms while the carbon–carbon bond links the neighboring benzaldehyde residues, see Figure S8.

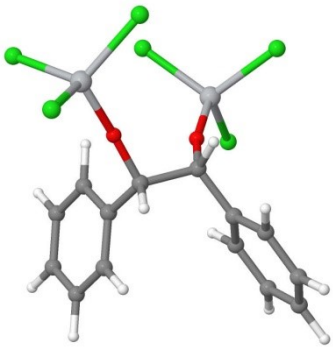


Figure S8. The molecular geometry of the {$[TiCl_3]$–O–HC–phenyl–phenyl–CH–O–$[TiCl_3]$} titanium–benzaldehyde (pinacol-like) hydrobenzoin complex. Titanium atoms are shown in light-grey, oxygen atoms in red.

[S.7] Hydrobenzoin formation promoted by the Ti/Mg catalyst

A subsequent formation of hydrobenzoin in water can be represented by the following stoichiometric reaction (SE.10):

[($TiCl_3$–O)–phenyl–phenyl–(O–$TiCl_3$)] + Mg + 2CH_2Br_2 +2 DBE +2H_2O →
→ hydrobenzoin + 2 [$TiCl3^{\bullet}$::$MgCH_2Br_2$::DBE] + $Mg(OH)_2$

ΔG = –19.6 kcal/mol (SE.10)
ΔH = –59.8 kcal/mol
ΔE = –64.8 kcal/mol

The molecular geometry of hydrobenzoin is given in Figure S9:

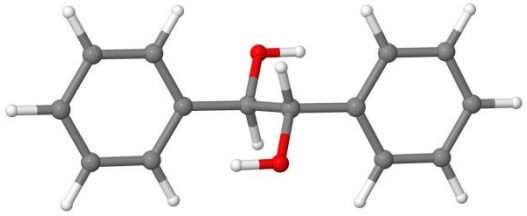


Figure S9. The molecular geometry of the hydrobenzoin. Titanium atoms are shown in light-grey, oxygen atoms in red.

The $[TiCl_3^{\bullet}$::$MgCH_2Br_2$::DHF] complex is shown on Figure S5:
A more efficient reaction can occur when the $KHCO_3$ aqueous solution is used:

[($TiCl_3$–O-CH-)–phenyl–phenyl–(-HC-O–$TiCl_3$)] + Mg + 2 Mg::CH_2Br_2 + 2 DBE + 2 $KHCO_3$ →
→ hydrobenzoin + 2 [$TiCl3^{\bullet}$::$MgCH_2Br_2$::DBE] + $Mg(KCO_3)_2$

(SE.11)

ΔG = –59.3 kcal/mol
ΔH = –103.8 kcal/mol
ΔE = –108.5 kcal/mol

An additional energy gain is expected when two [$TiCl_3^{\bullet}$::$MgCH_2Br_2$::DBE] radicals will form a dimeric complex.

The molecular geometry of $K_2Mg(CO_3)_2$ is given in Figure S10:

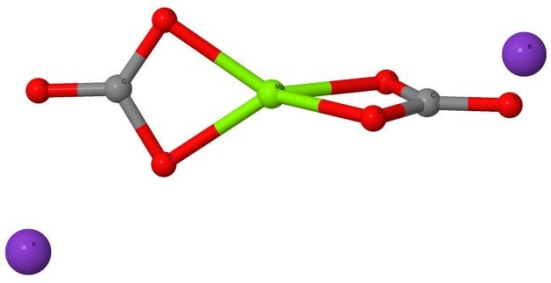


Figure S10. The molecular geometry of the $K_2Mg(CO_3)_2$. Potassium atoms are shown in violet, oxygen atoms in red, magnessium in light-green and carbon in dark gray: C.

[S.8] A possible formation of 1-bromomethyl)benzyl alcohol

A possible formation of (1-bromomethyl)benzylalcohol will likely not occur (SE.13):

4 { $[CH_2Br]^{\bullet}$ ::$[MgBr]^{\bullet}$} + $TiCl_4$ + 4 benzaldehyde + 2 H_2O → 4 { α-(bromomethyl)benzylalcohol} + TiO_2 + 4 MgClBr

ΔG = –6.8 kcal/mol (SE.13)
ΔH = –44.5 kcal/mol
ΔE = –56.7 kcal/mol

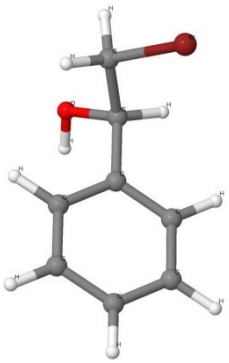


Figure S11. The optimized molecular geometry of (1-bromomethyl)benzyl alcohol. Color codes: Bromine atom is shown in dark red, the oxygen atom in red, carbon atoms are in dark grey and hydrogen atmos are in light grey.

[S.9] A cumulative stoichiometric reaction of hydrobenzoin formation

Reaction with water :

2 Mg + 2 $TiCl_4$ + 2 benzaldehyde + 2 $MgCH_2Br_2$ + 2 DBE + 2H_2O
→hydrobenzoin + 2 [$TiCl_3MgCH_2Br_2$DBE] + $Mg(OH)_2$ + $MgCl_2$

(SE.14)

ΔG = –87.6 kcal/mol
ΔH = –157.4 kcal/mol
ΔE = –166.6 kcal/mol

Reaction with $KHCO_3$:

2 Mg + 2 $TiCl_4$ + 2 benzaldehyde + 2 $MgCH_2Br_2$ + 2 DBE + 2$KHCO_3$
→hydrobenzoin + 2 [$TiCl_3MgCH_2Br_2$DBE] + $Mg(KCO_3)_2$ + MgCl2

(SE. 15)

ΔG = –127.3 kcal/mol
ΔH = –201.4 kcal/mol
ΔE = –210.3 kcal/mol

[S.10] The solvent effect on the output of the reaction (E.5) in the main text

Four solvents were considered, i.e. DBE, THF, 2,5-dihydrofuran, and DEE.

The output of the reaction (E.5, manuscript) is presented in the table below, in kcal/mol.

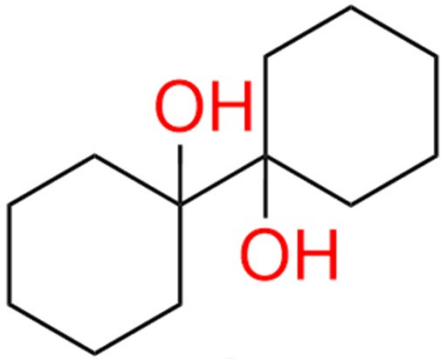
Quantity	DBE	THF	2,5-dihydrofuran	DEE[1)]
ΔG	-59.3	-59.9	-59.6	-80.4
ΔH	-103.8	-102.1	-102.1	-123.0
ΔE	-108.4	-106.4	-106.4	-127.4

Footnote [1)] : In the reaction (E.5, manuscript) the $MgCH_2Br_2$ was used.

In the reaction with DEE we used the $MgBr_2$.

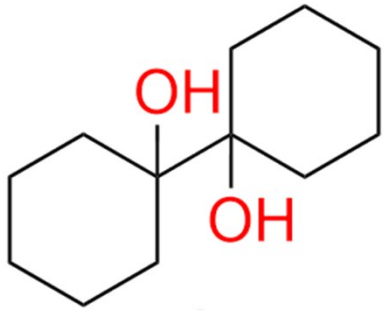
[S.11] NMR spectra

(



1a

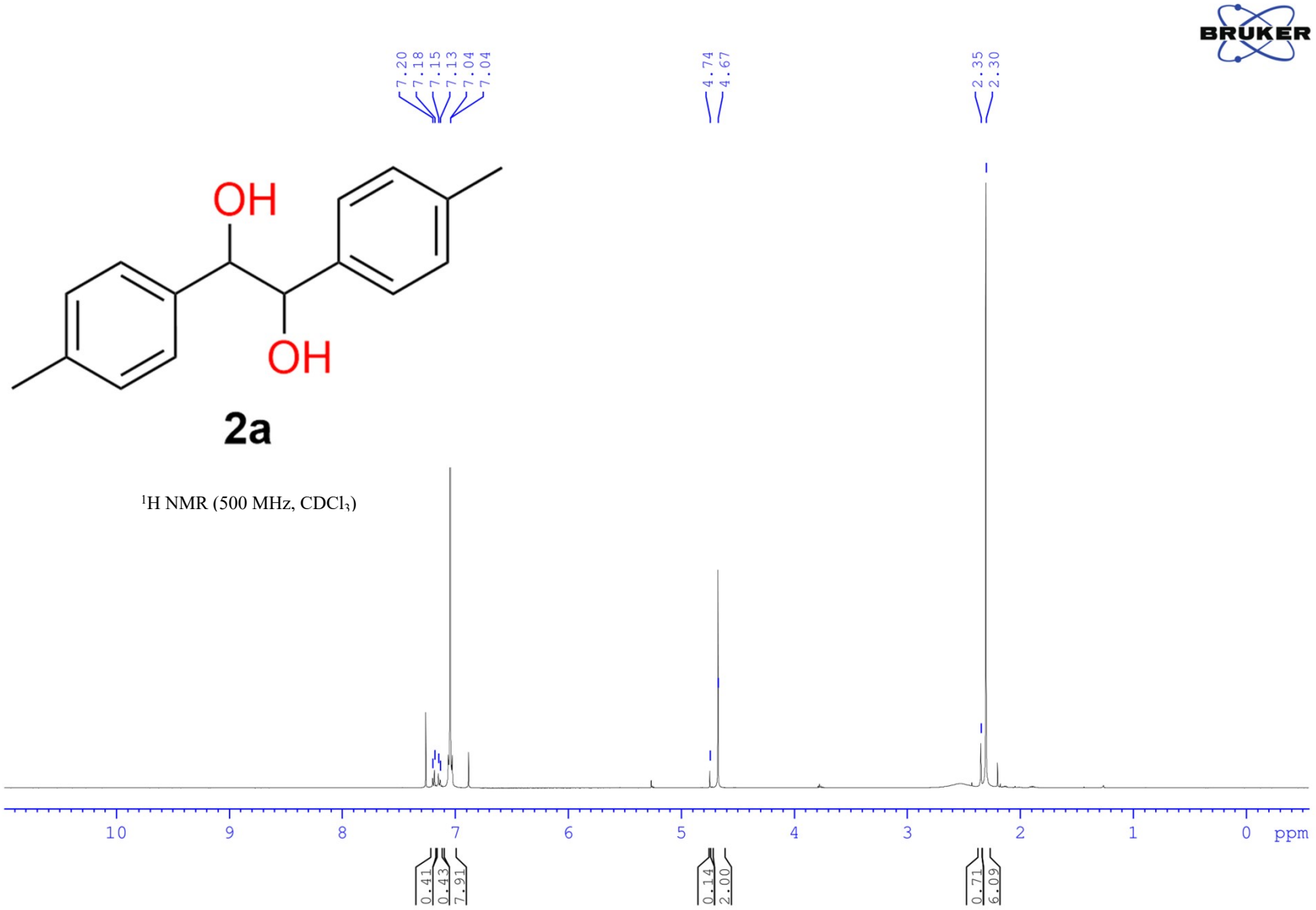
^{1}H NMR (500 MHz, $CDCl_3$)



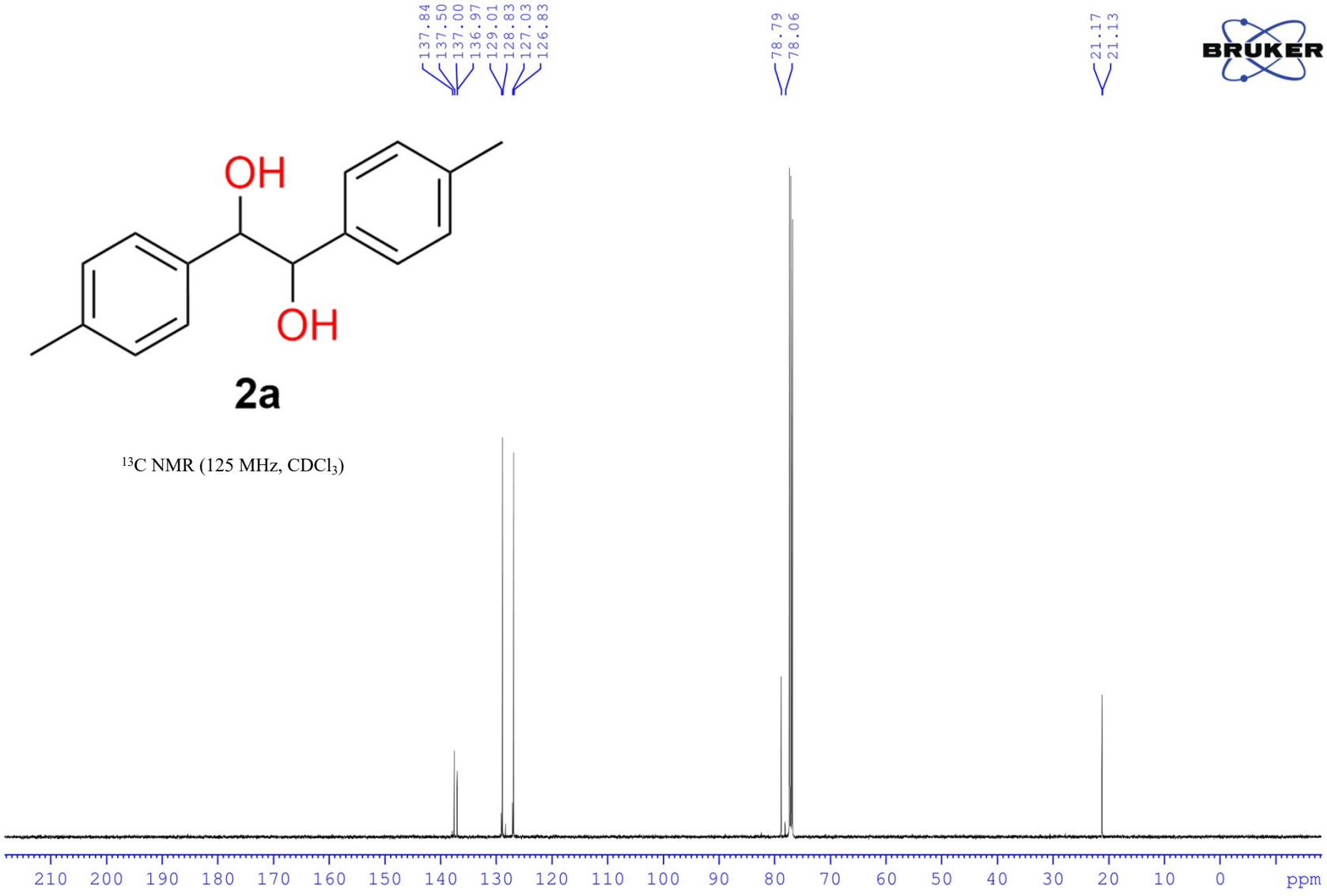
1a

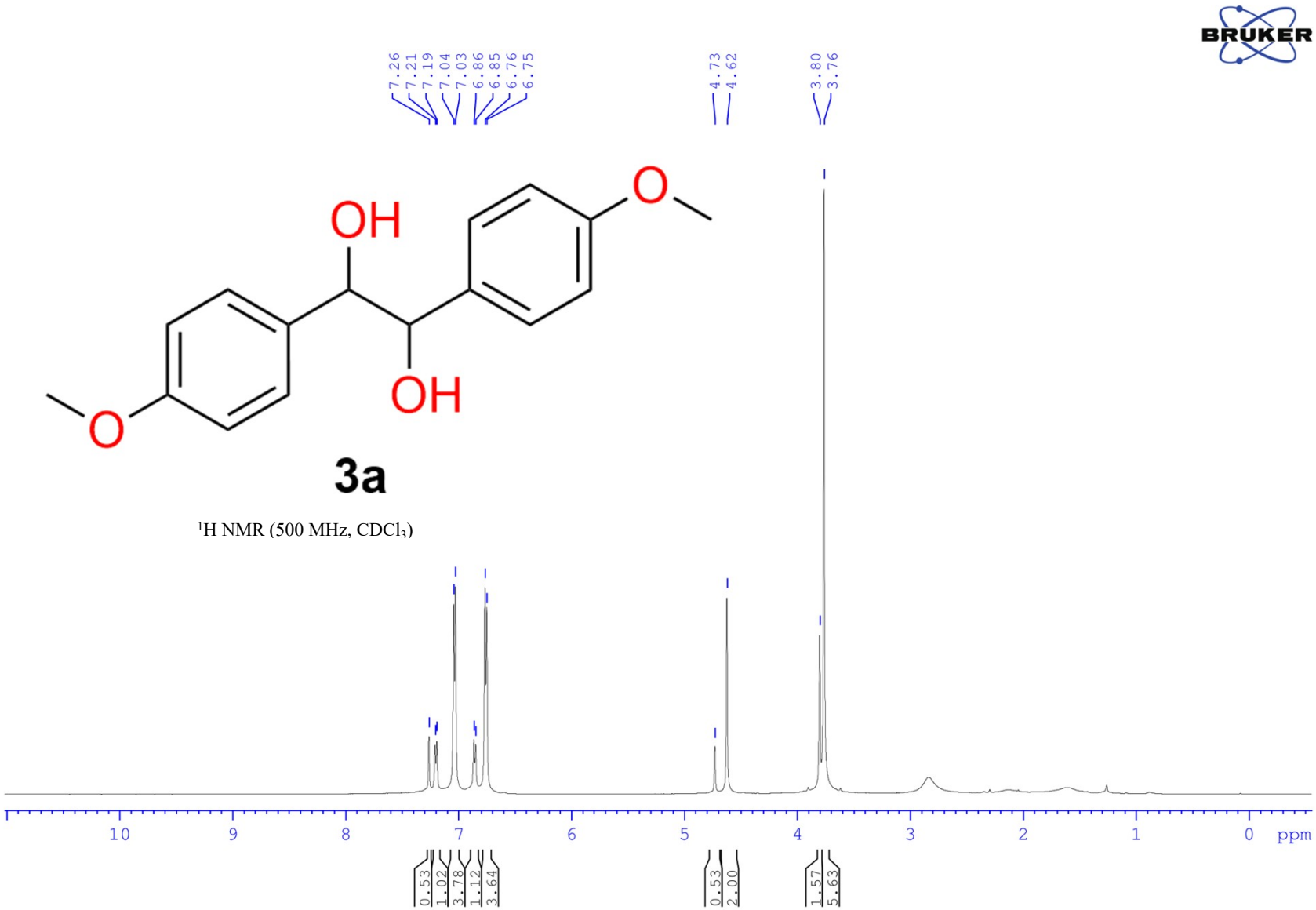
^{13}C NMR (125 MHz, $CDCl_3$)

13C NMR (125 MHz, CDCl3)

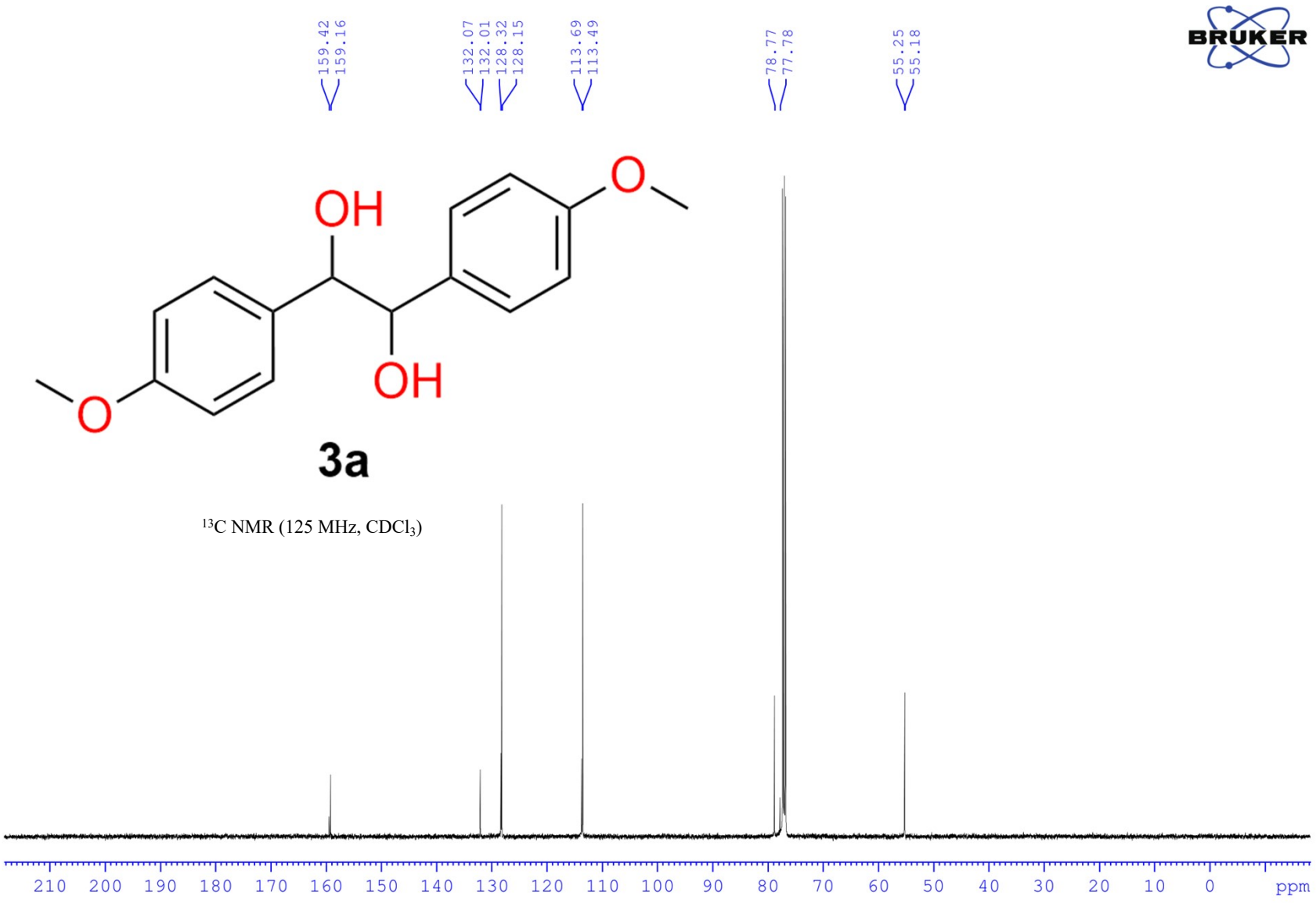


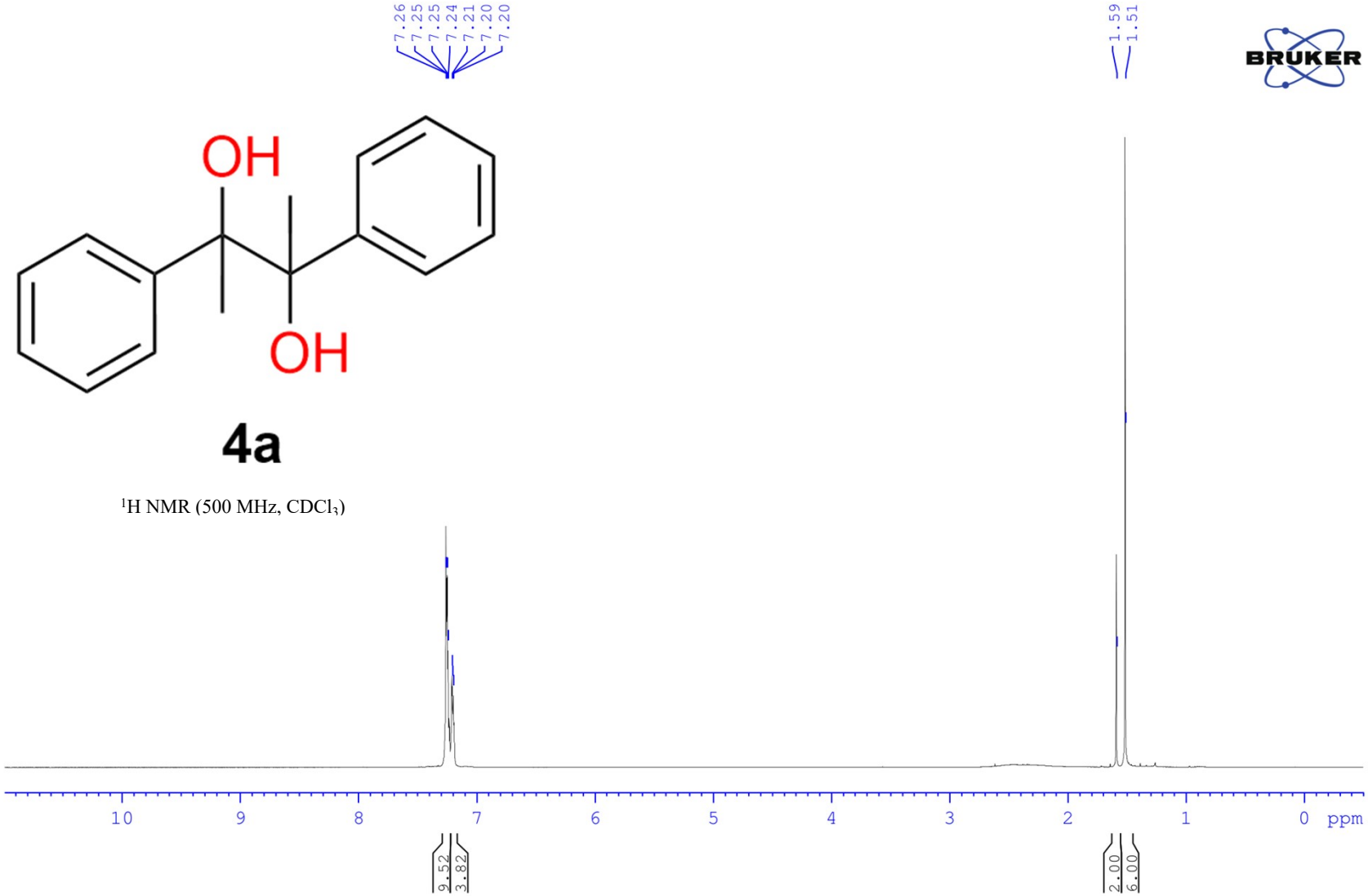
^{1}H NMR (500 MHz, $CDCl_3$)

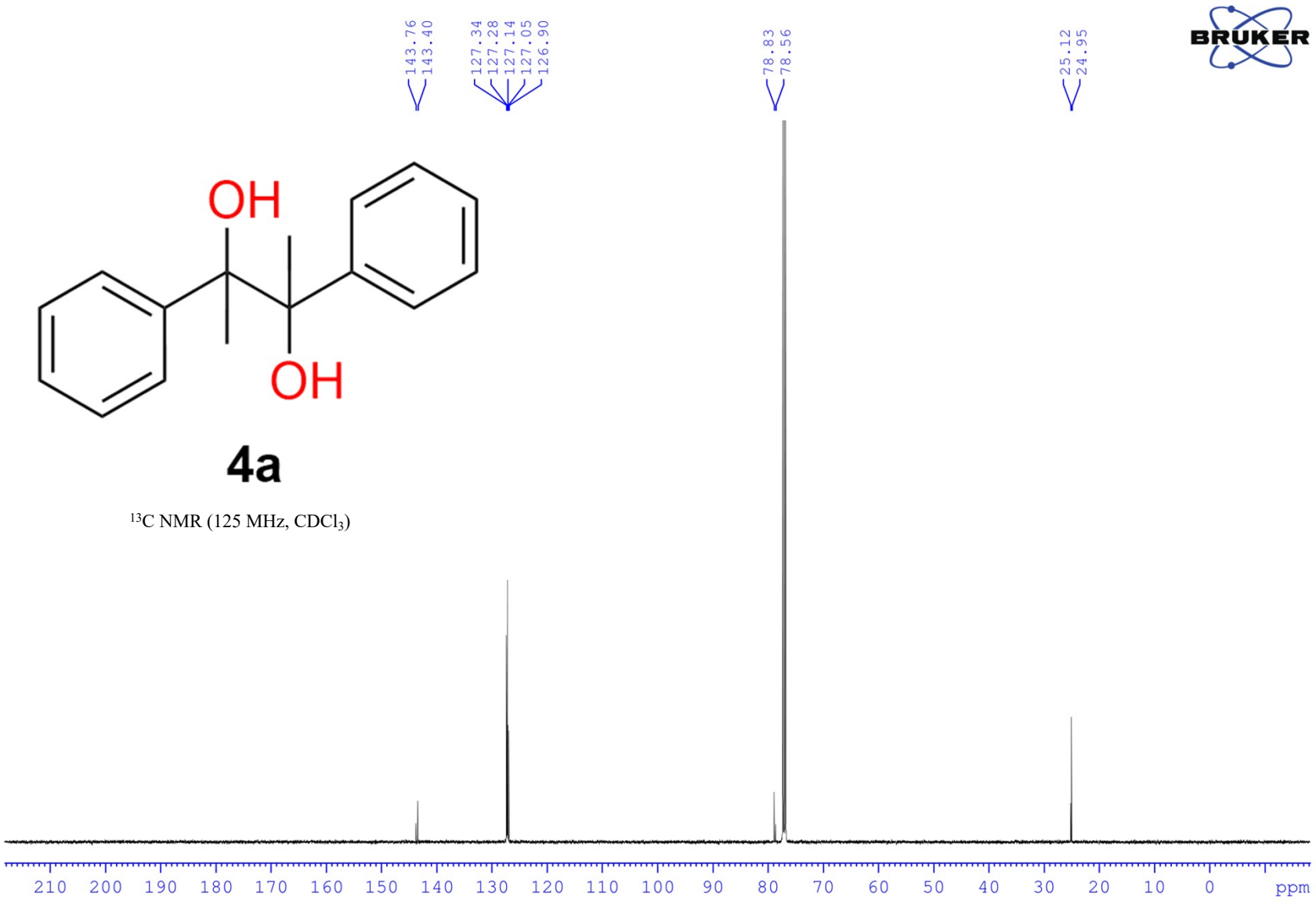

137.84
137.50
137.00
136.97
129.01
128.83
127.03
126.83
78.79
78.06
21.17
21.13
BRUKER
OH
OH
2a
^{13}C NMR (125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



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

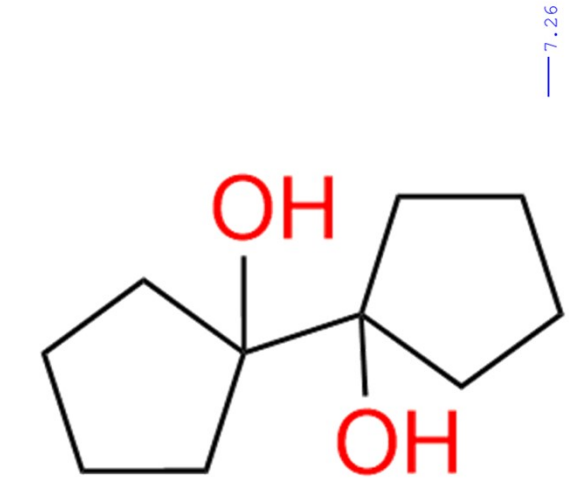

159.42
159.16
132.07
132.01
128.32
128.15
113.69
113.49
78.77
77.78
55.25
55.18
OH
OH
O
O
3a
^{13}C NMR (125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.26
7.25
7.25
7.24
7.21
7.20
7.20
1.59
1.51
OH
OH
4a
^{1}H NMR (500 MHz, $CDCl_3$)
10
9
8
7
6
5
4
3
2
1
0 ppm
9.52
3.82
2.00
6.00



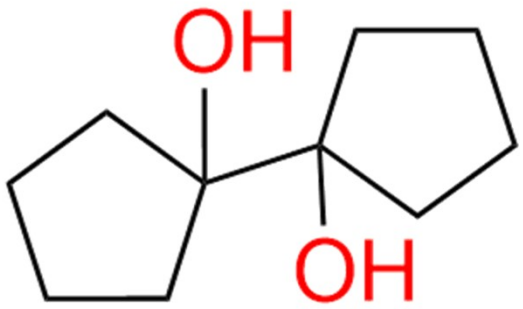
4a

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



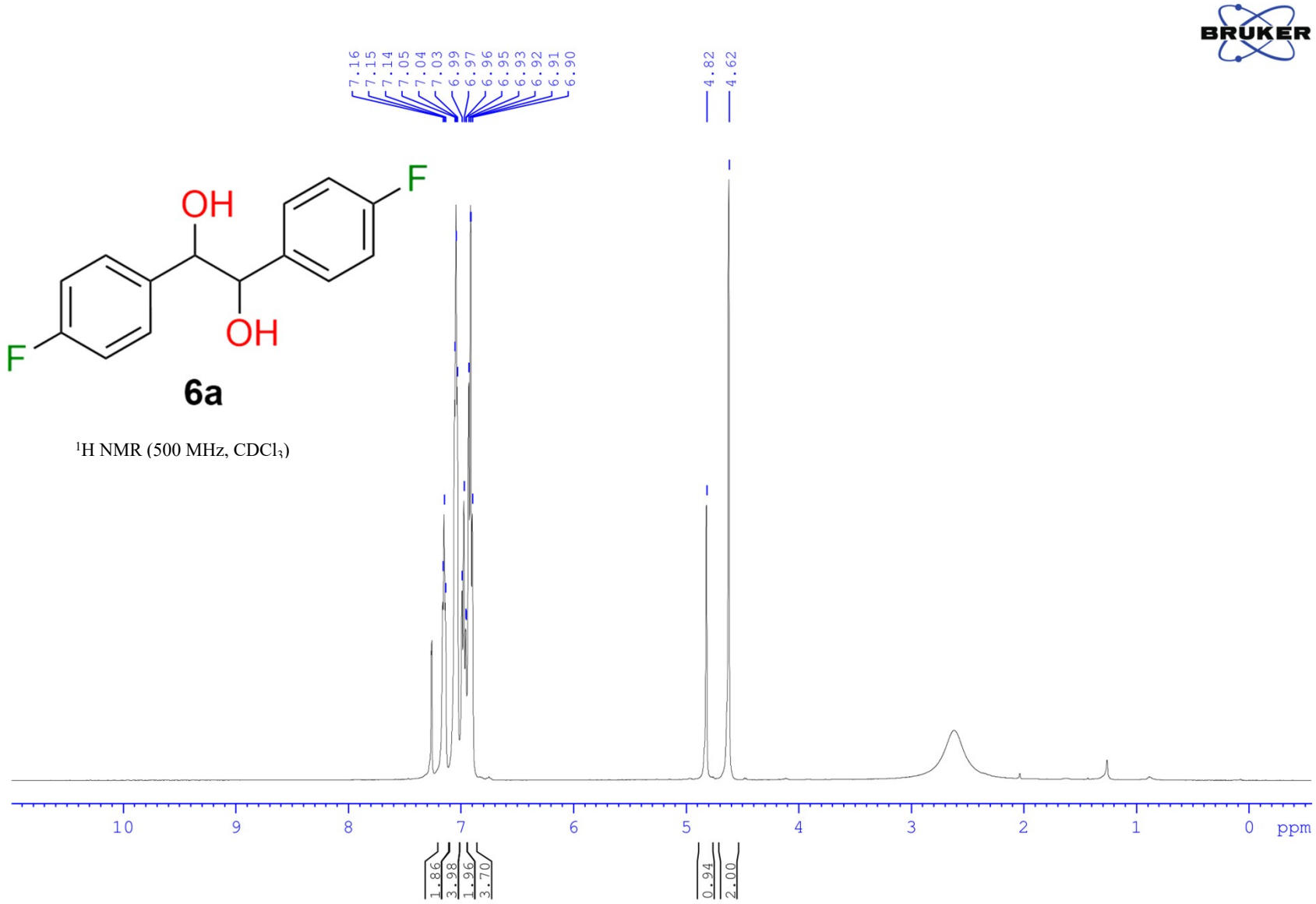
5a

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

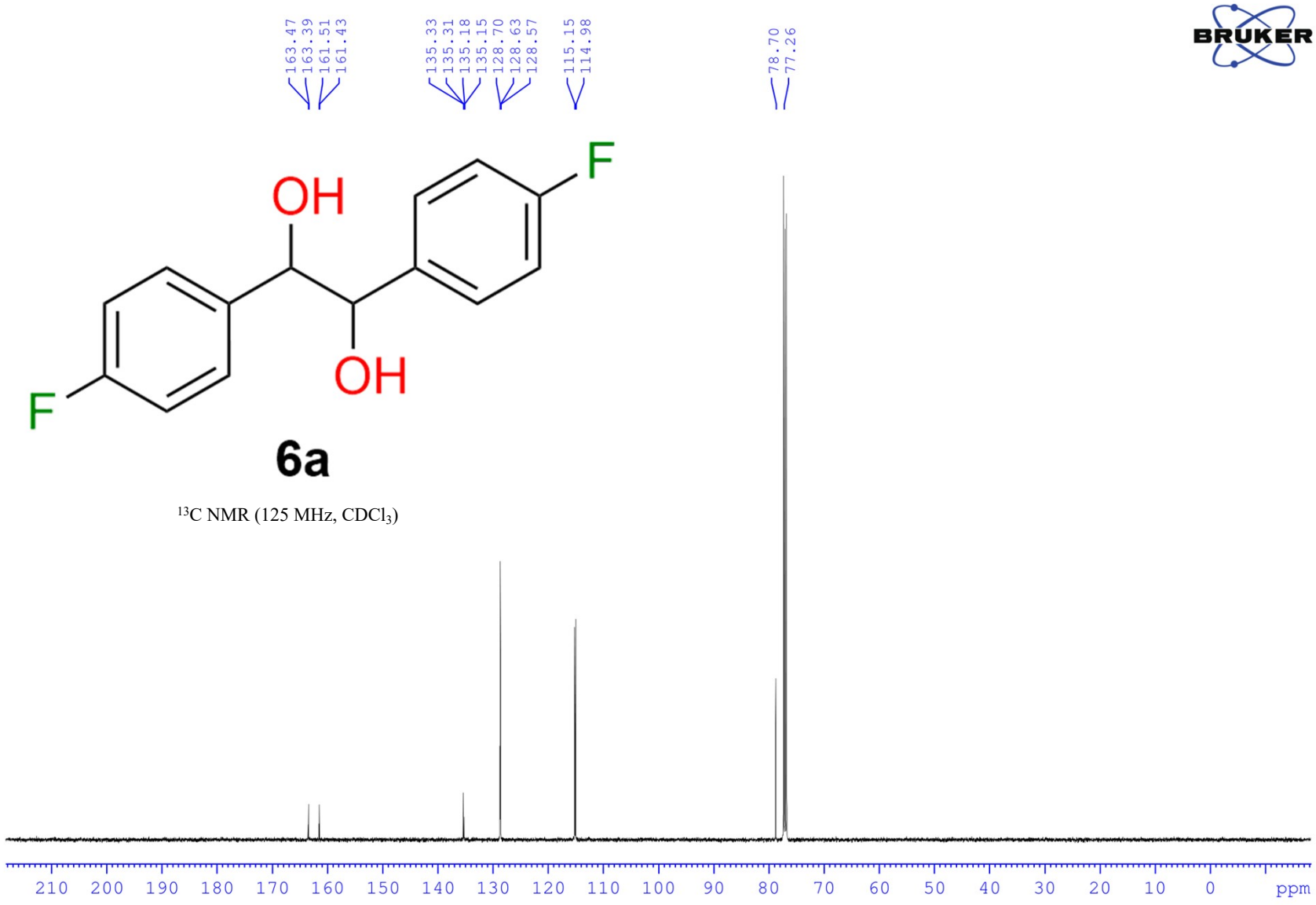


5a

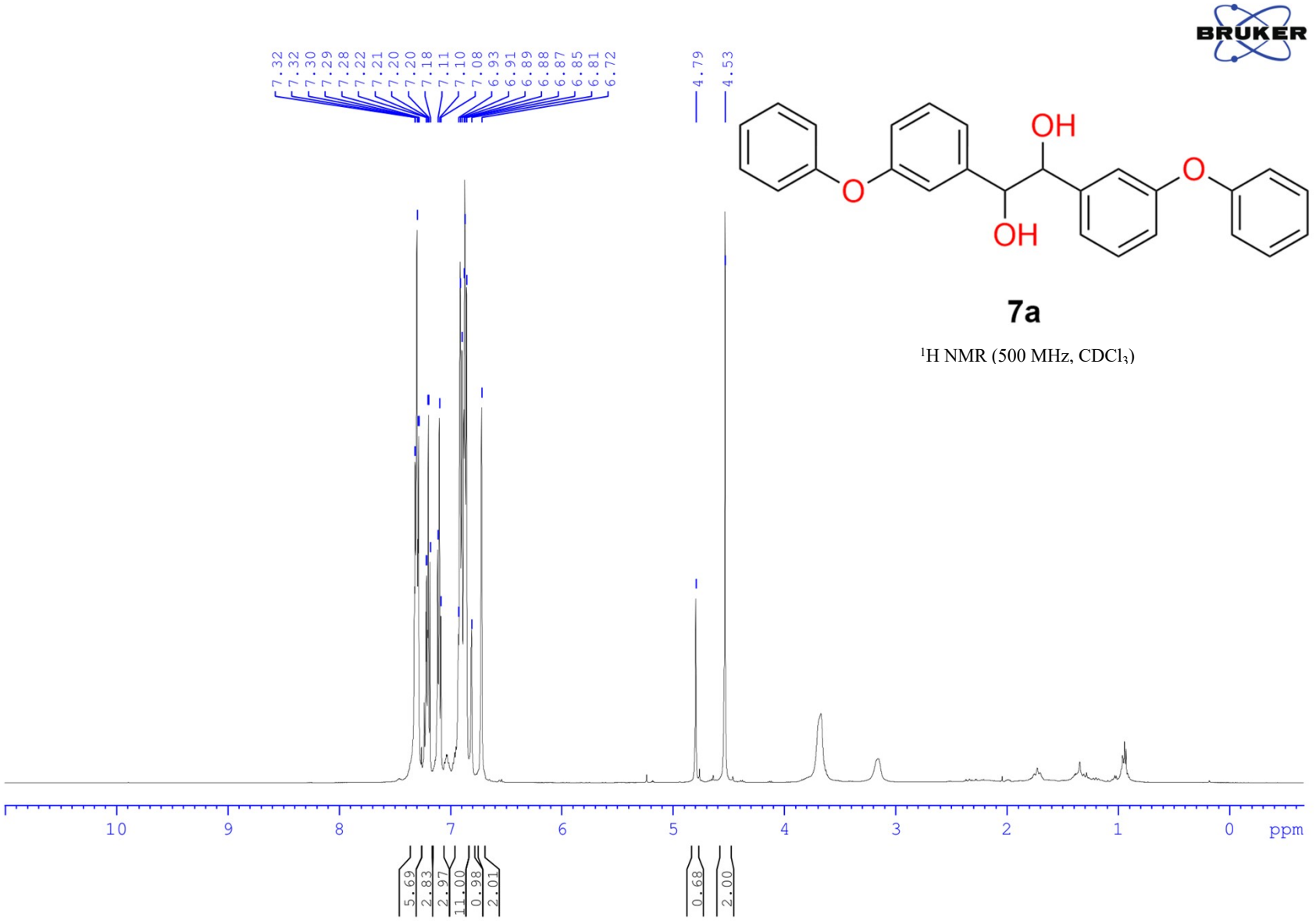
^{13}C NMR (125 MHz, $CDCl_3$)



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

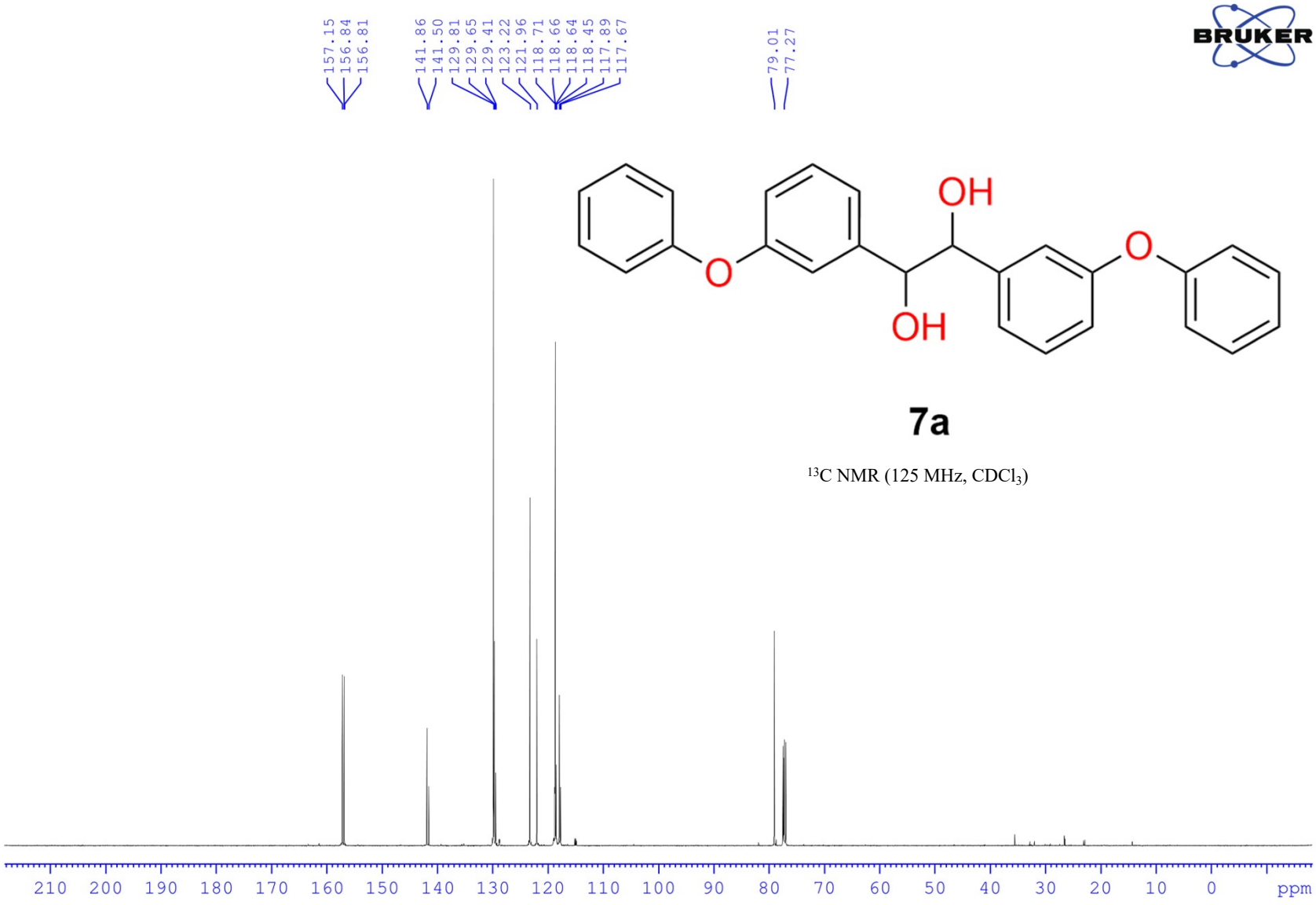


^{13}C NMR (125 MHz, $CDCl_3$)



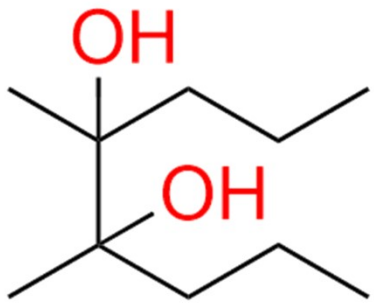
7a

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



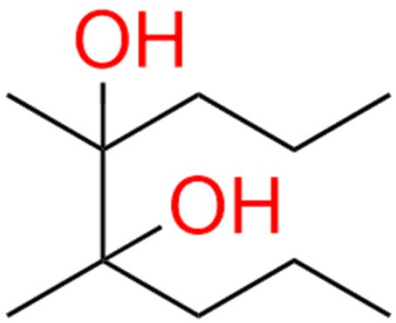
7a

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



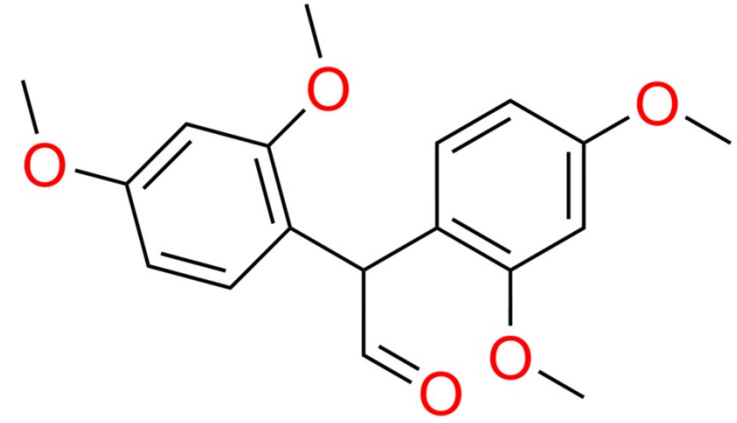
8a

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



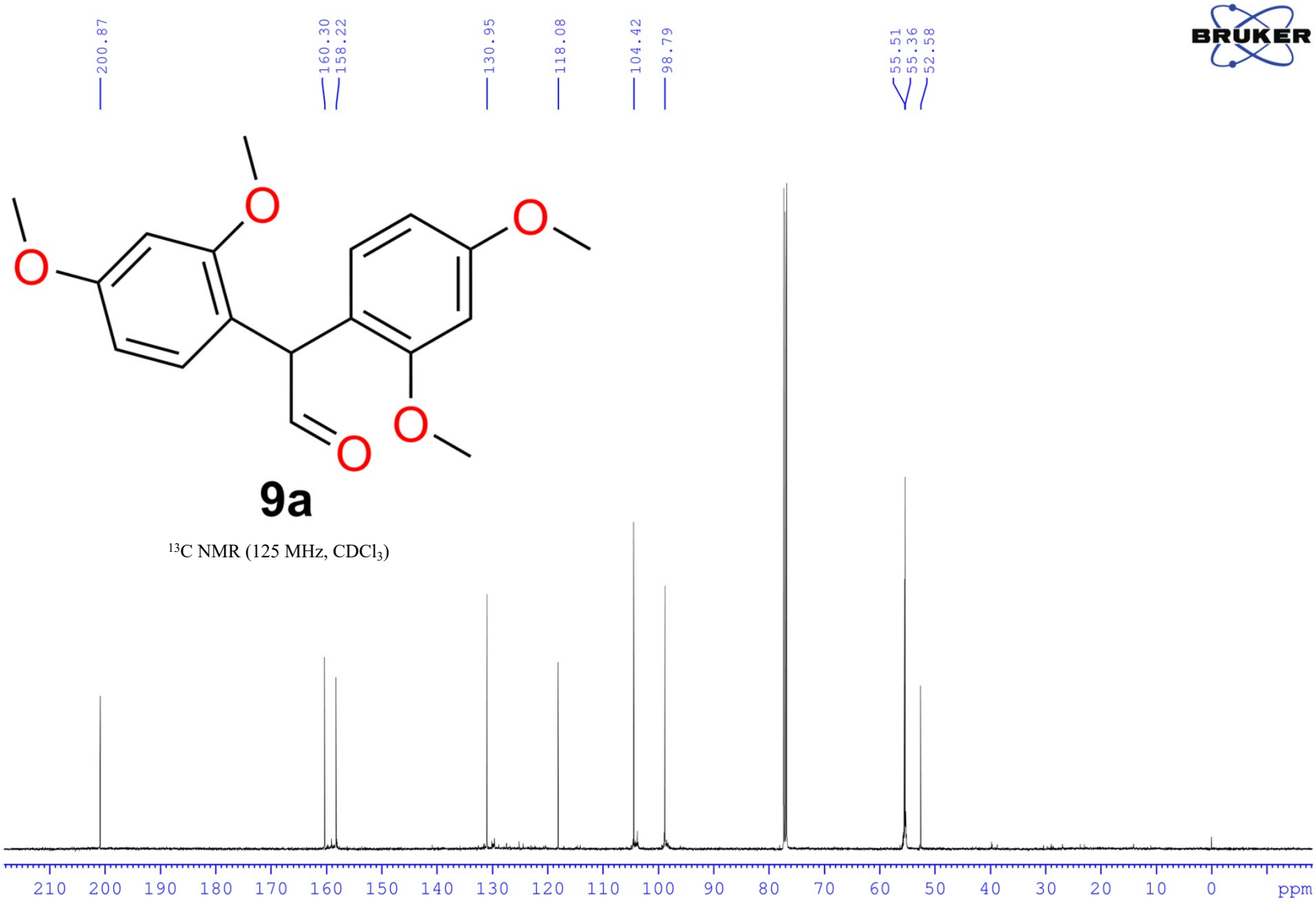
8a

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

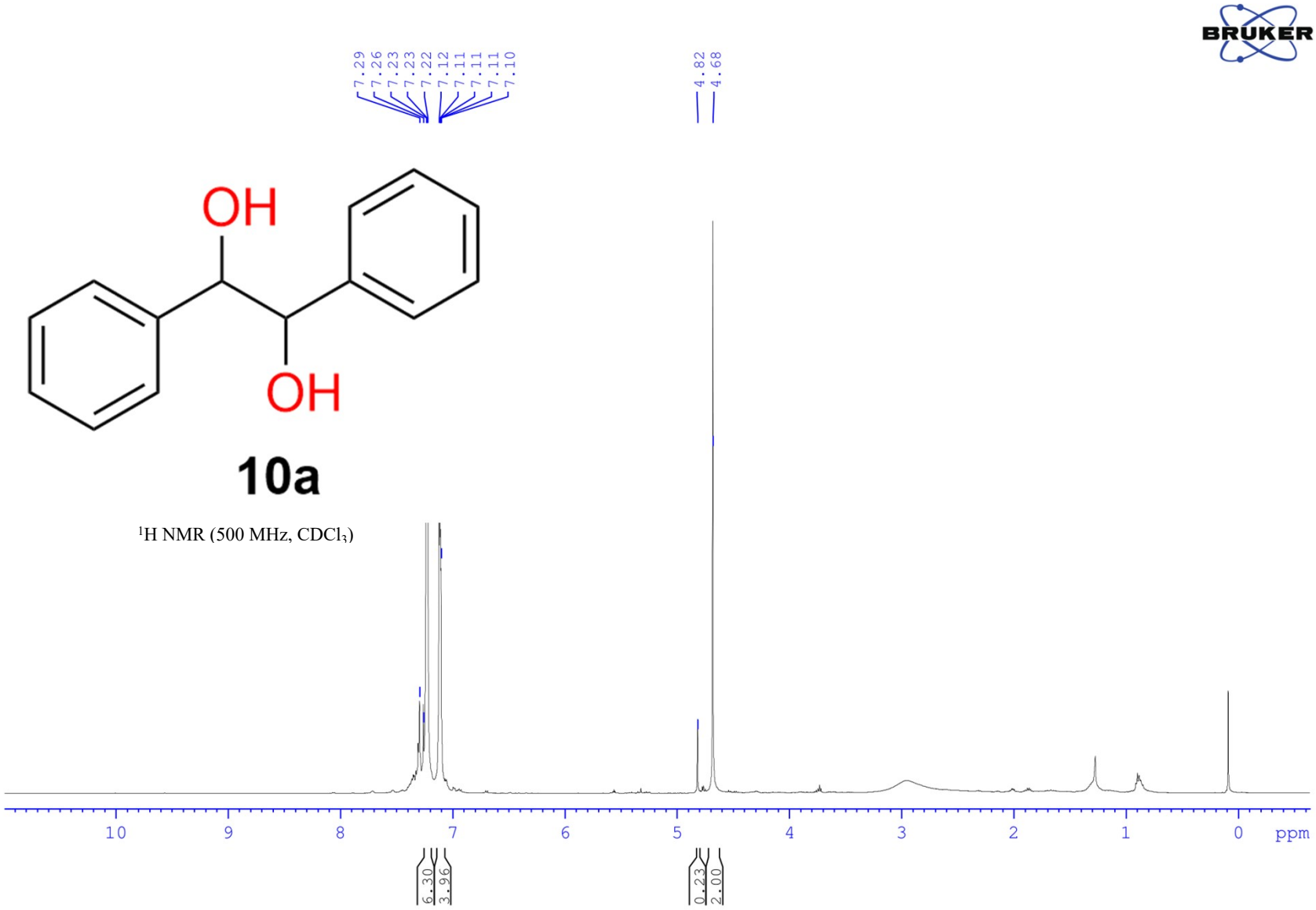


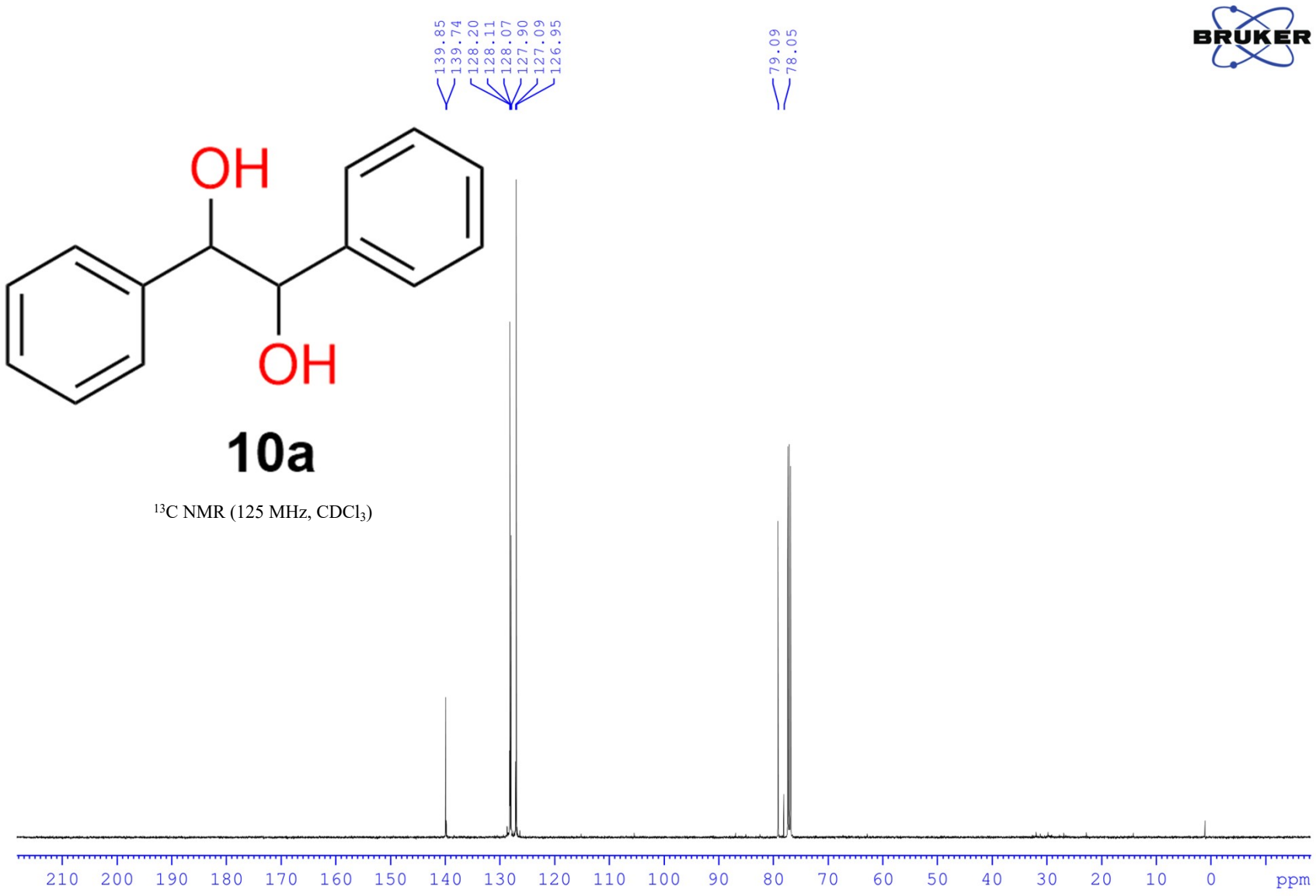
9a

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



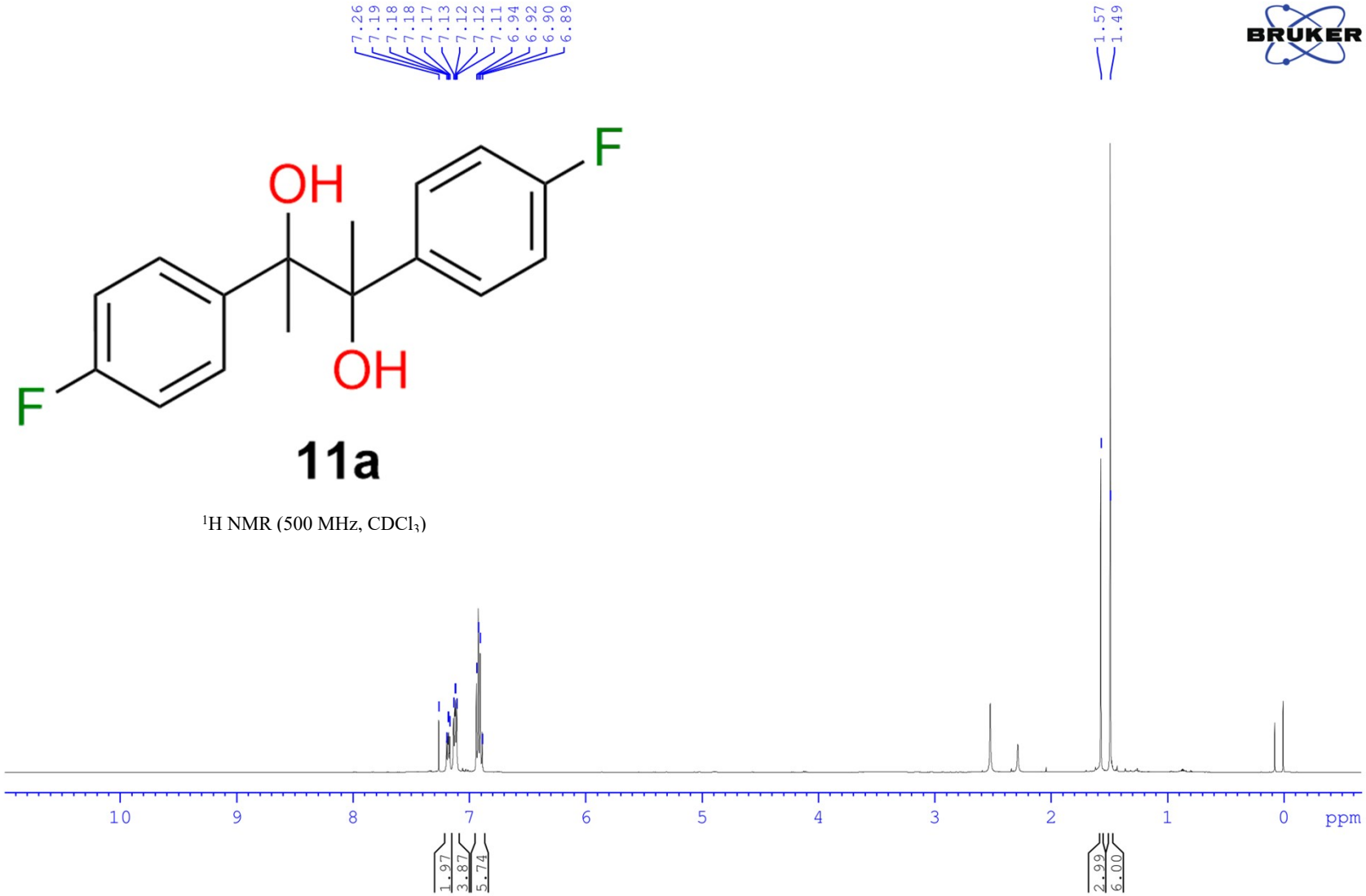
^{13}C NMR (125 MHz, $CDCl_3$)


7.29
7.26
7.23
7.23
7.22
7.12
7.11
7.11
7.11
7.10
4.82
4.68
OH
OH
10a
^{1}H NMR (500 MHz, $CDCl_3$)
10
9
8
7
6
5
4
3
2
1
0
ppm
6.30
3.96
0.23
2.00

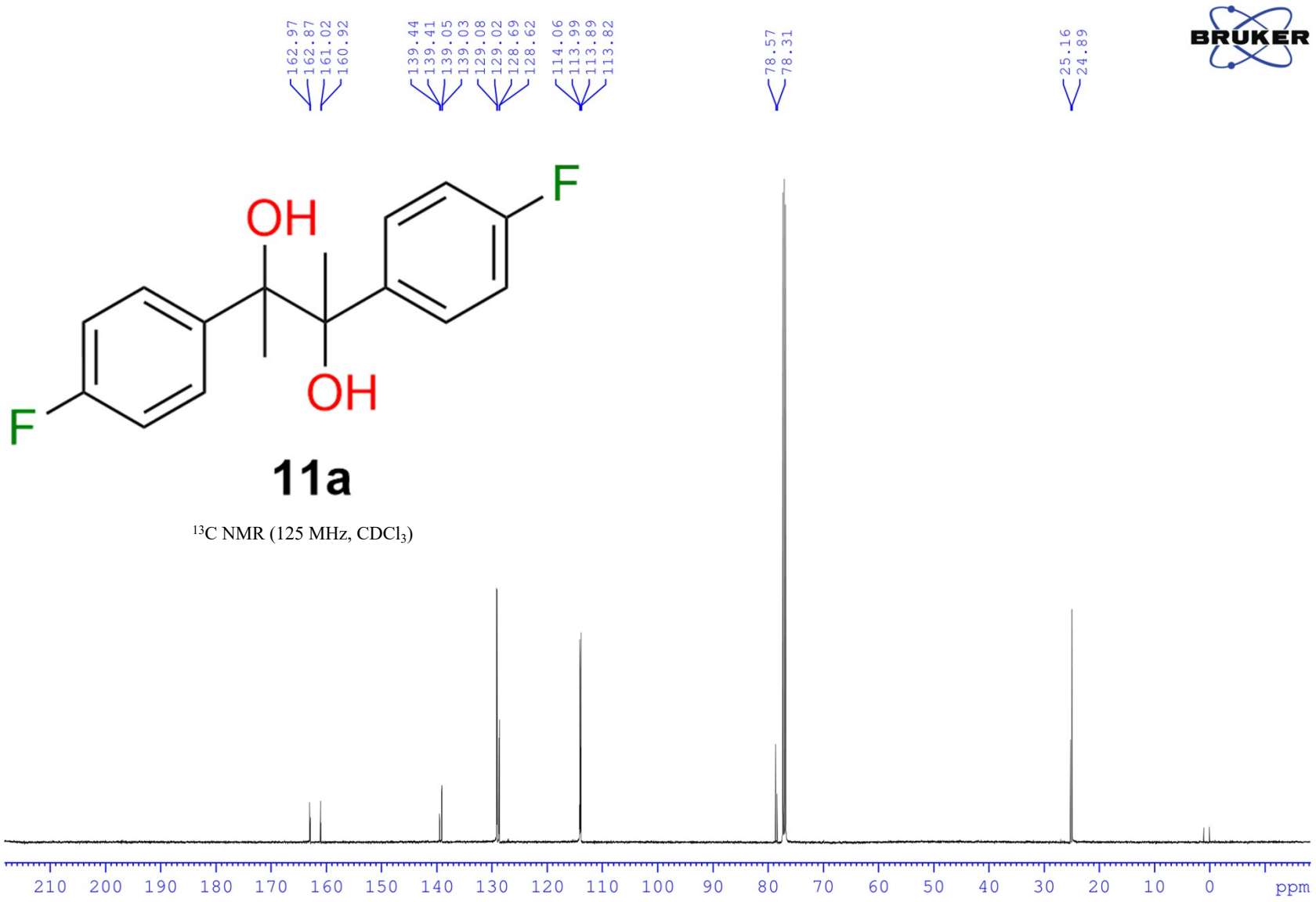


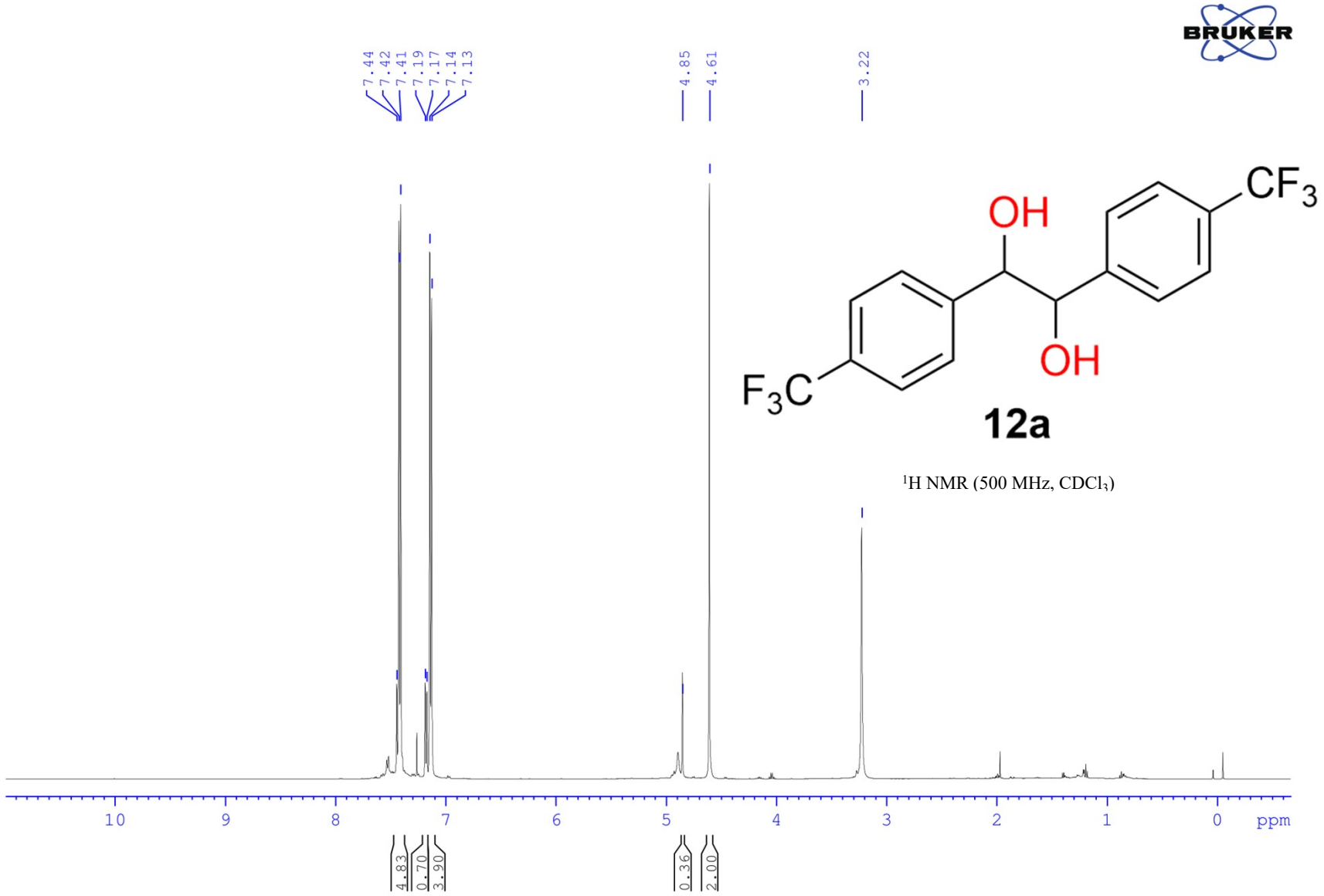
10a

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

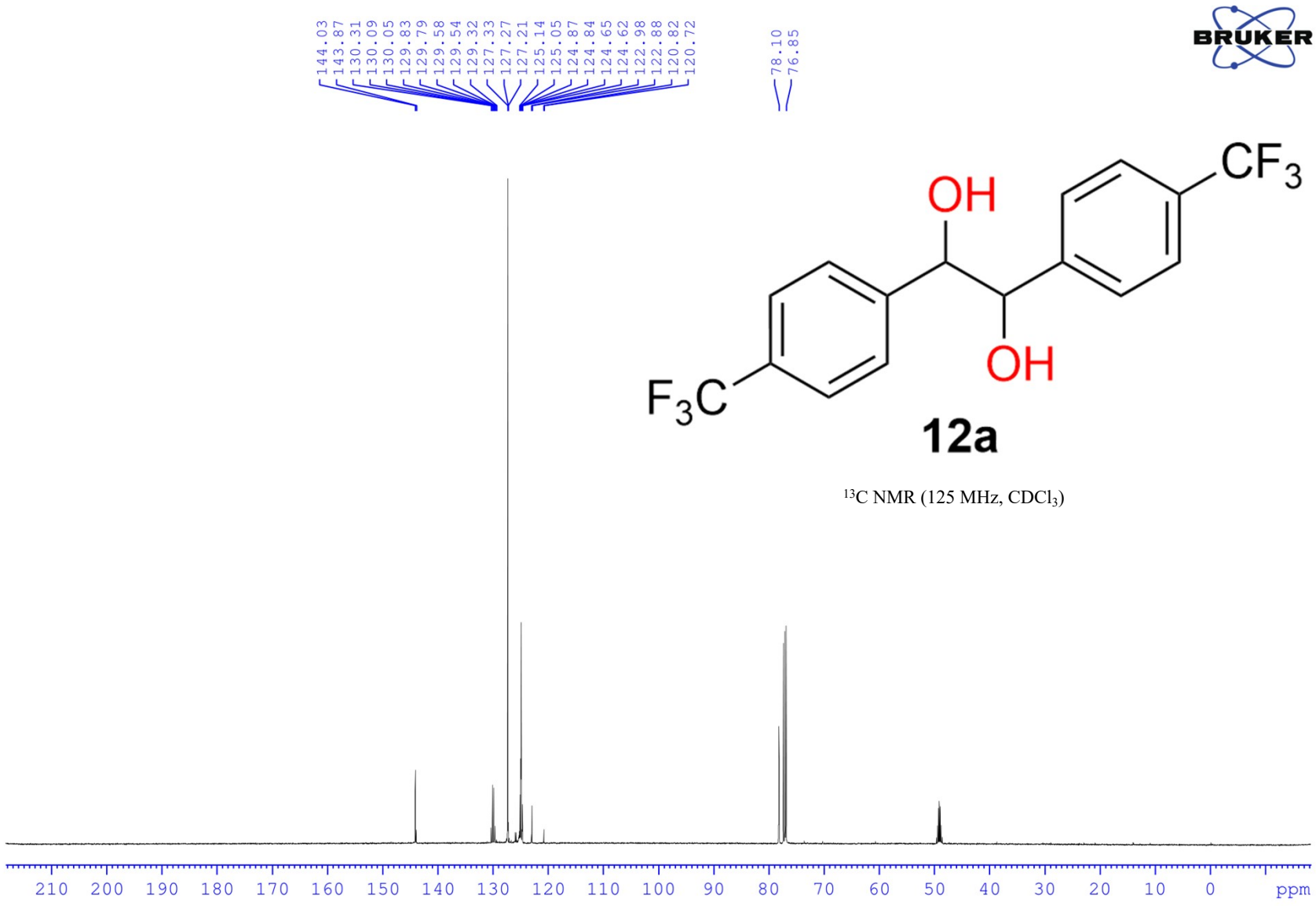


^{1}H NMR (500 MHz, $CDCl_3$)


162.97
162.87
161.02
160.92
139.44
139.41
139.05
139.03
129.08
129.02
128.69
128.62
114.06
113.99
113.89
113.82
78.57
78.31
25.16
24.89
BRUKER
OH
OH
F
F
11a
^{13}C NMR (125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



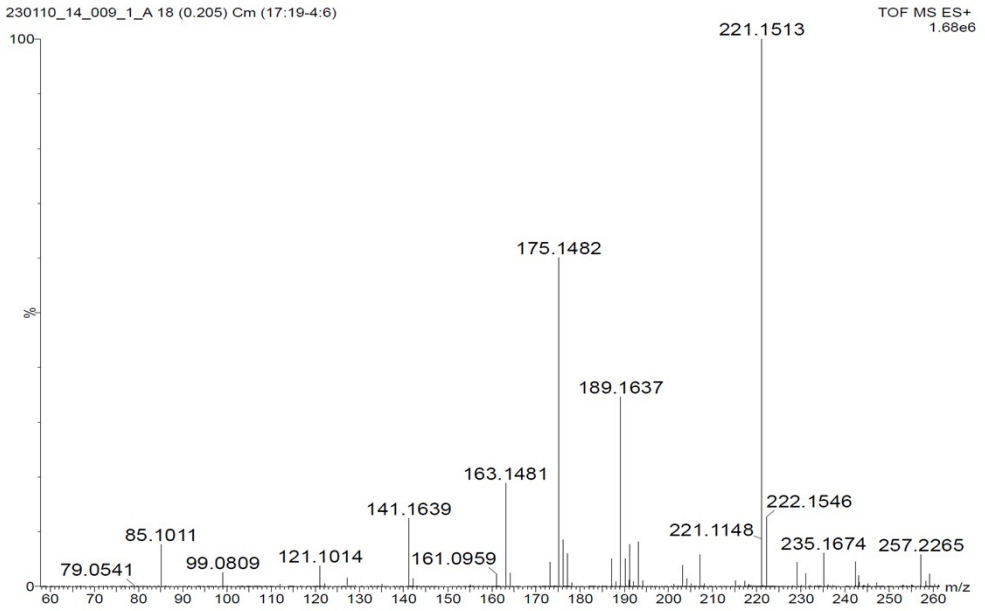
^{1}H NMR (500 MHz, $CDCl_3$)



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

[S.12] HRMS spectra

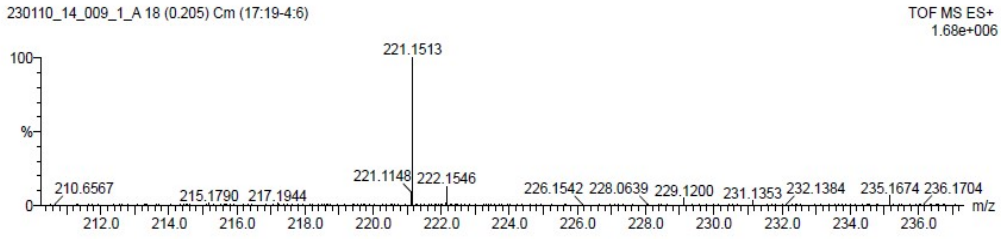
Compound 1a



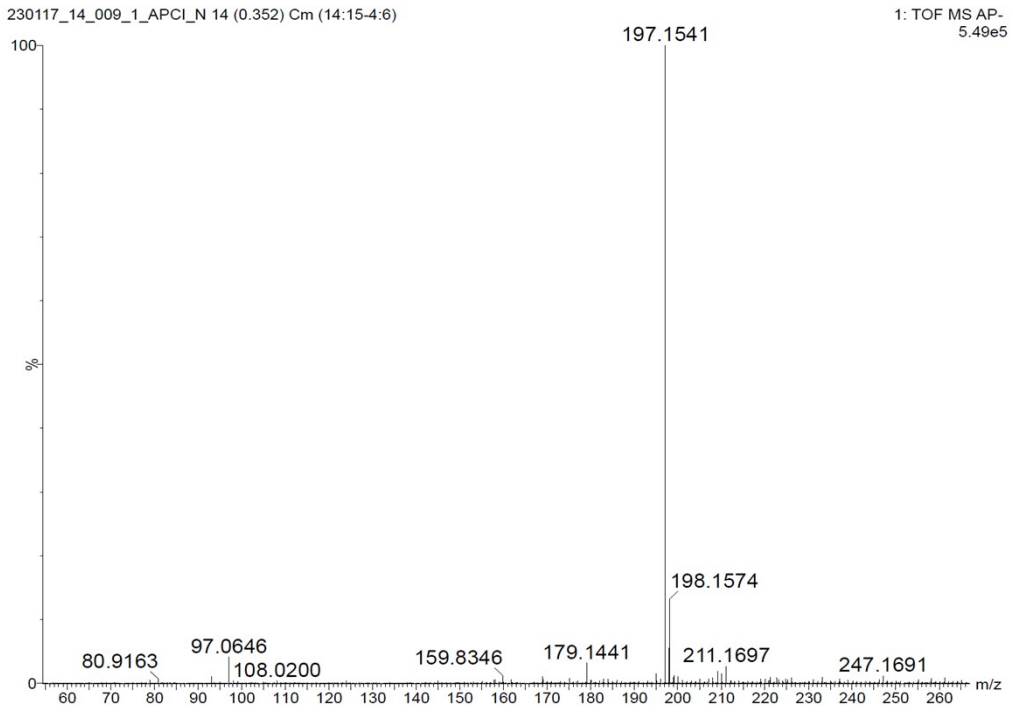
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
38 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1



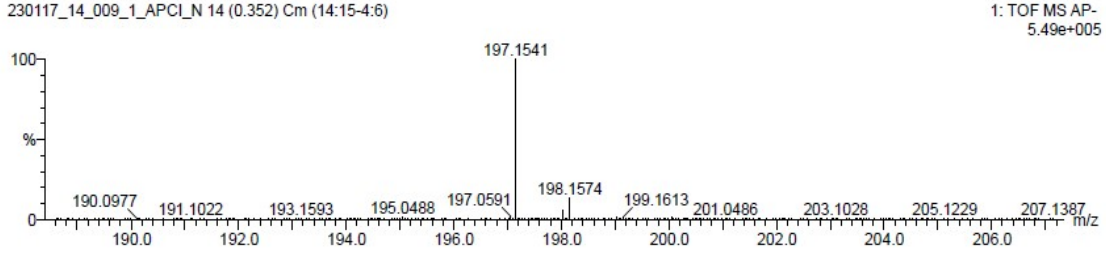
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
221.1513	221.1517	-0.4	-1.8	1.5	507.1	n/a	n/a	C12 H22 O2 Na



Elemental Composition Report **Page 1**

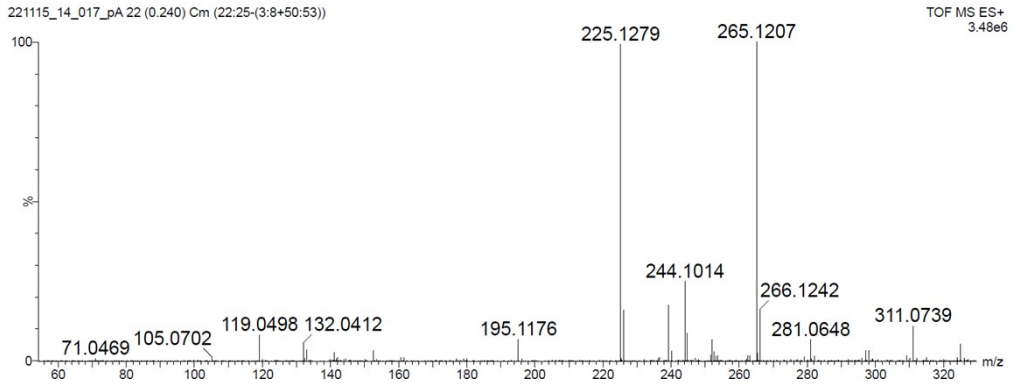
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Odd and Even Electron Ions
36 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
197.1541	197.1542	-0.1	-0.5	2.5	1141.9	n/a	n/a	C12 H21 O2

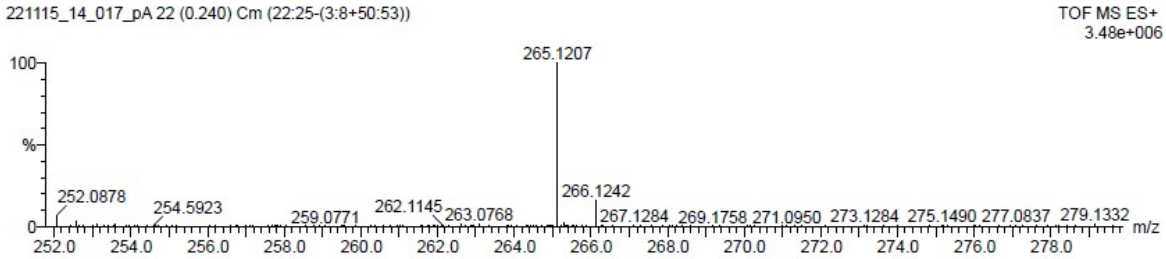
Compound 2a



Elemental Composition Report **Page 1**

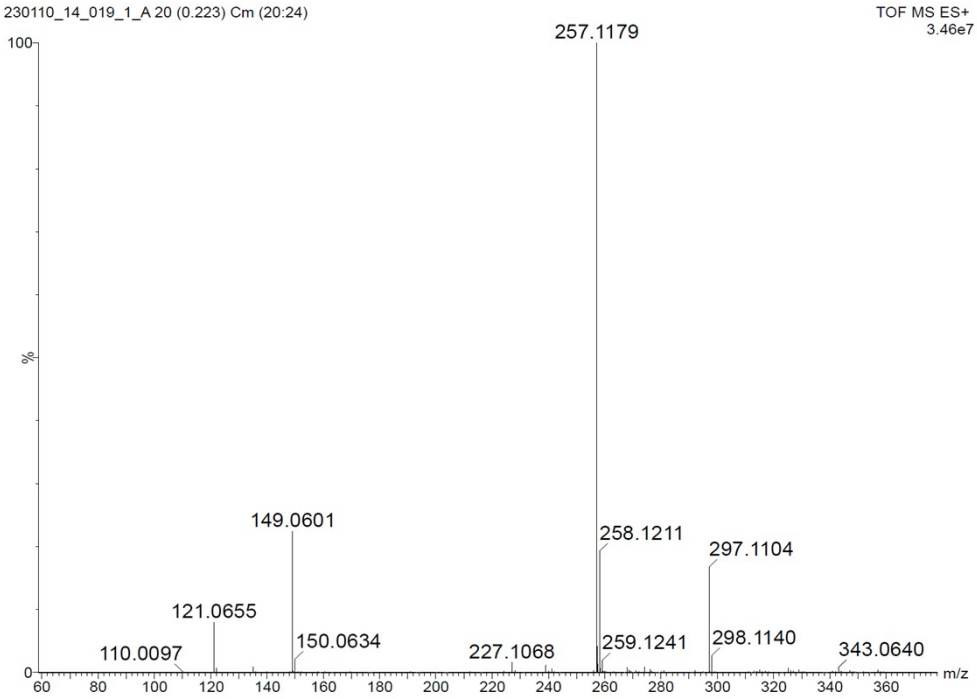
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 90.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-20 O: 0-10 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	10.0	90.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
265.1207	265.1204	0.3	1.1	7.5	403.9	n/a	n/a	C16 H18 O2 Na

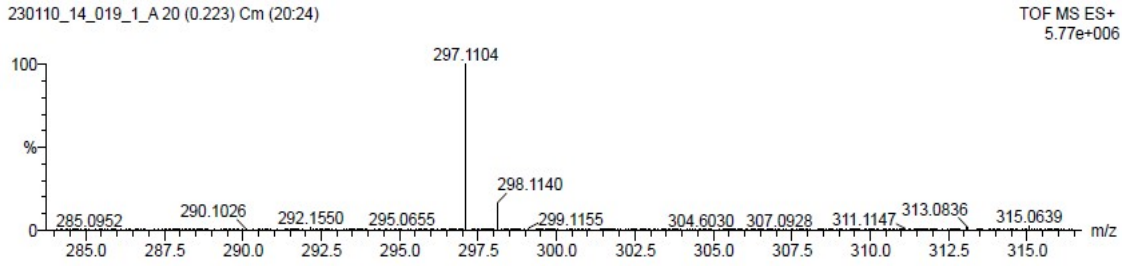
Compound 3a



Elemental Composition Report **Page 1**

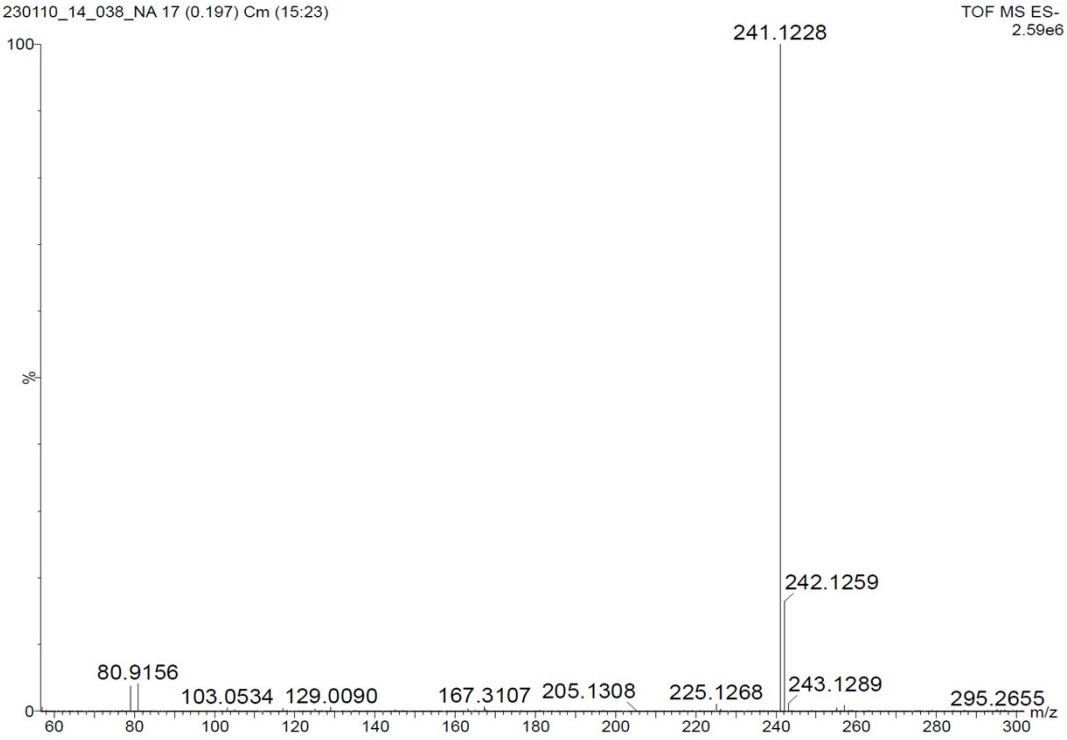
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
39 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
297.1104	297.1103	0.1	0.3	7.5	1241.0	n/a	n/a	C16 H18 O4 Na

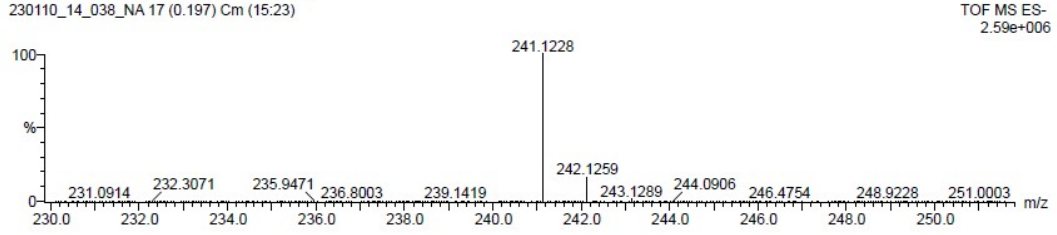
Compound 4a



Elemental Composition Report **Page 1**

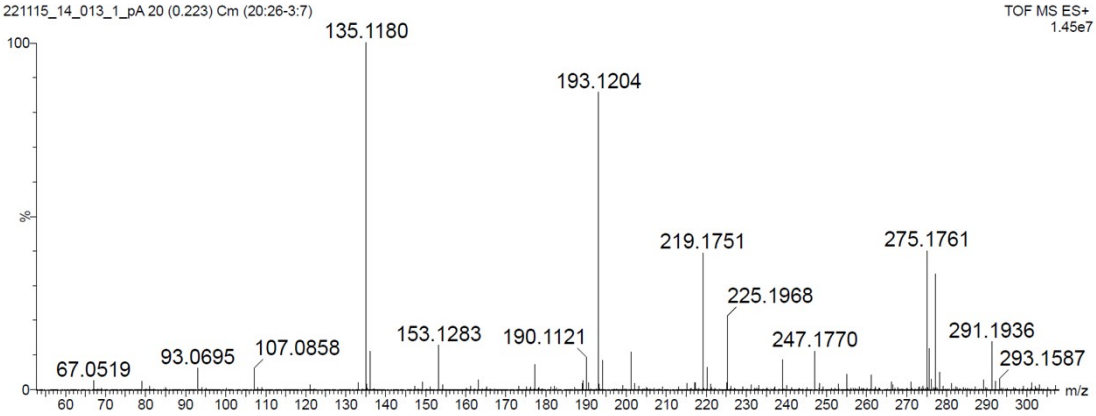
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
39 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
241.1228	241.1229	-0.1	-0.4	8.5	1197.9	n/a	n/a	C16 H17 O2

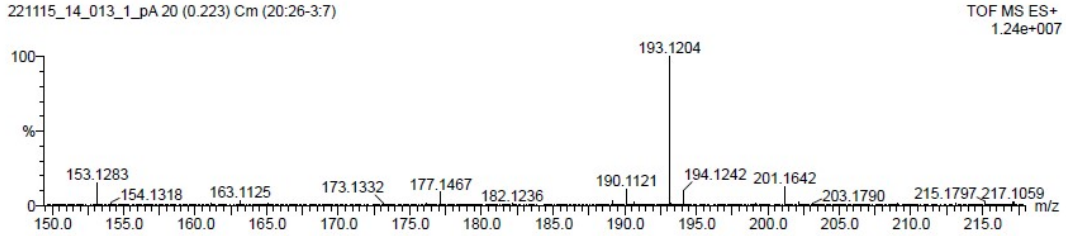
Compound 5a



Elemental Composition Report **Page 1**

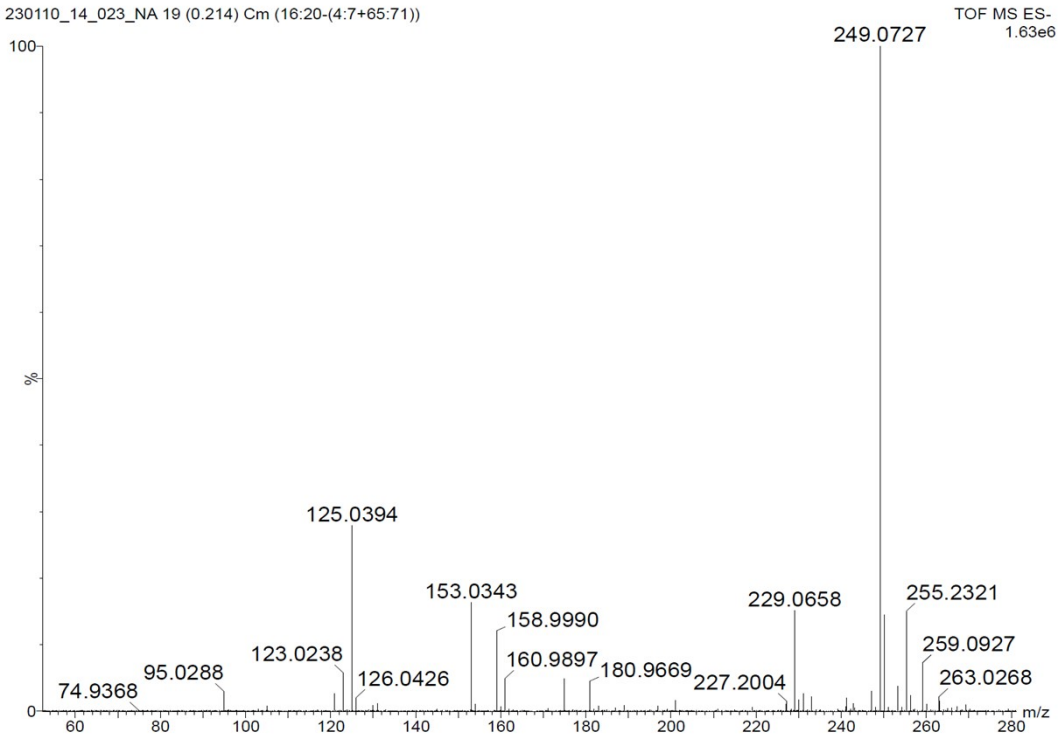
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 90.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-20 O: 0-10 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	10.0	90.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
193.1204	193.1204	0.0	0.0	1.5	1538.8	n/a	n/a	C10 H18 O2 Na

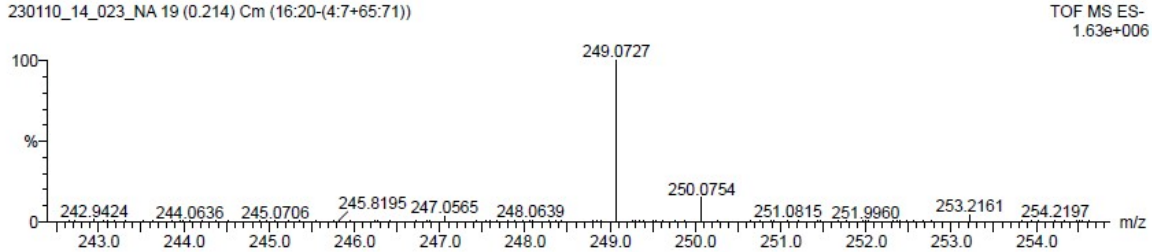
Compound 6a



Elemental Composition Report **Page 1**

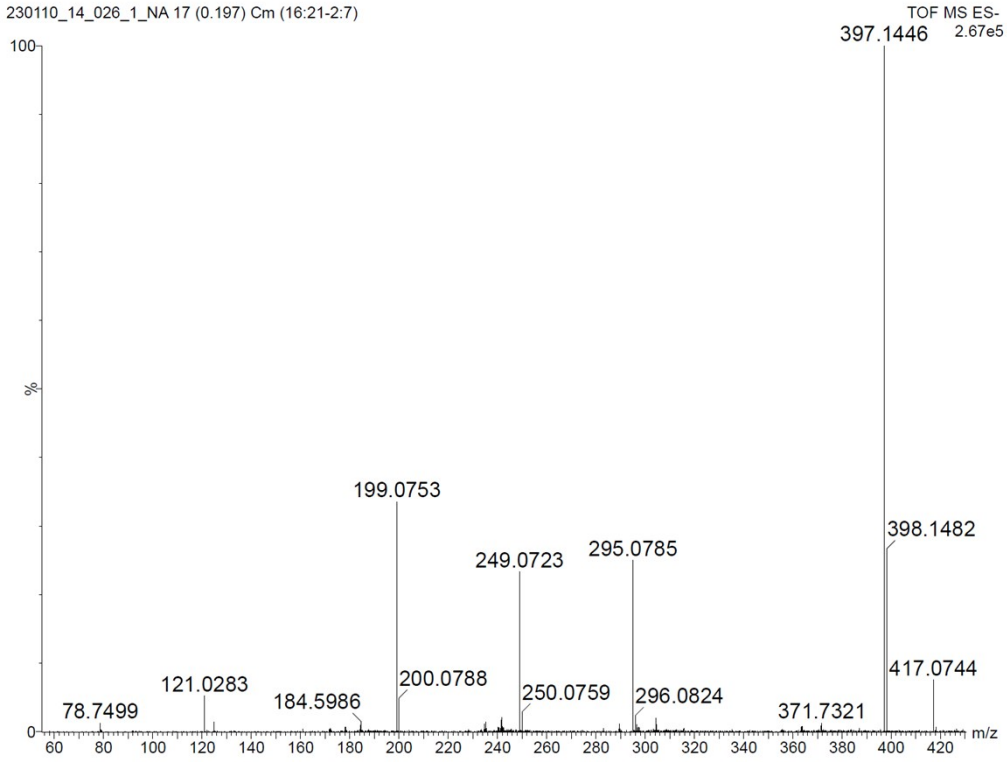
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
116 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1 F: 0-2



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%) Formula
249.0727	249.0727	0.0	0.0	8.5	439.9	0.048	95.34 C14 H11 O2 F2

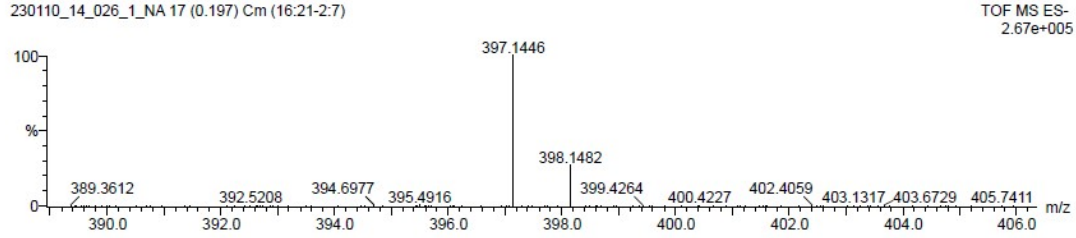
Compound 7a



Elemental Composition Report **Page 1**

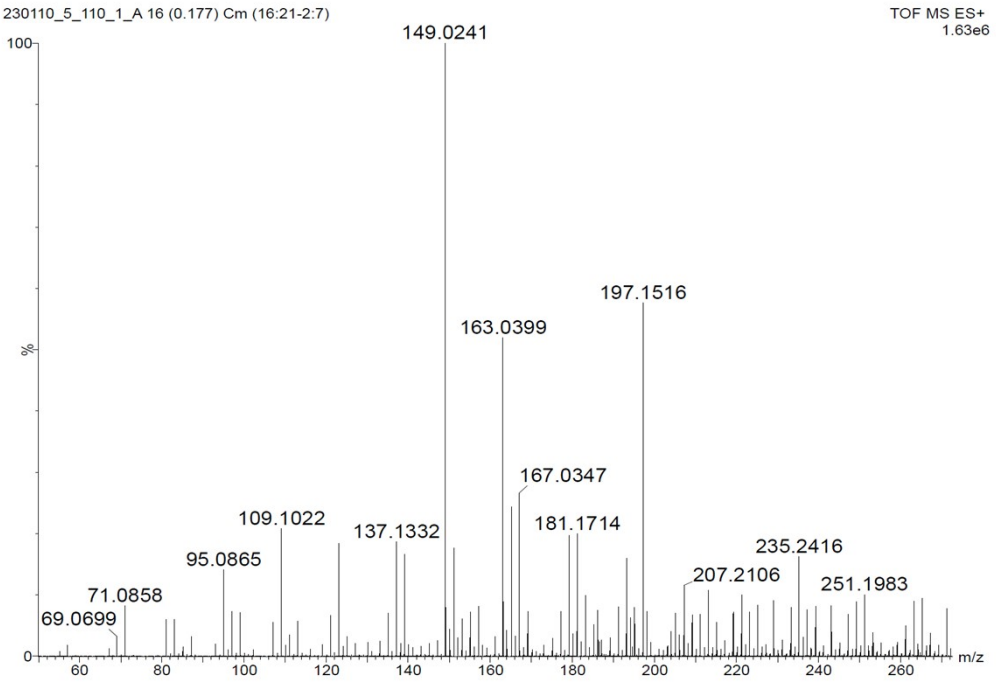
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
397.1446	397.1440	0.6	1.5	16.5	441.8	n/a	n/a	C26 H21 O4

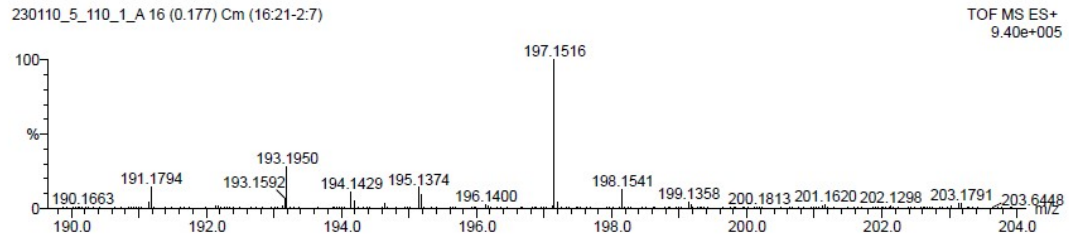
Compound 8a



Elemental Composition Report **Page 1**

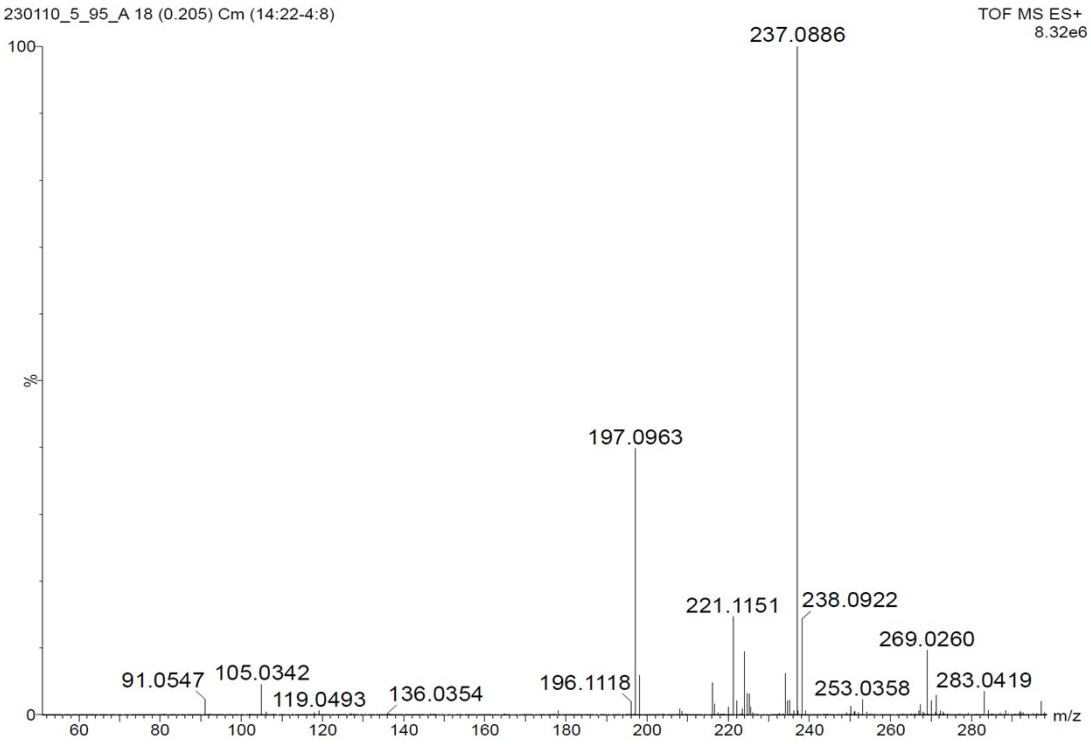
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
36 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
197.1516	197.1517	-0.1	-0.5	-0.5	928.4	n/a	n/a	C10 H22 O2 Na

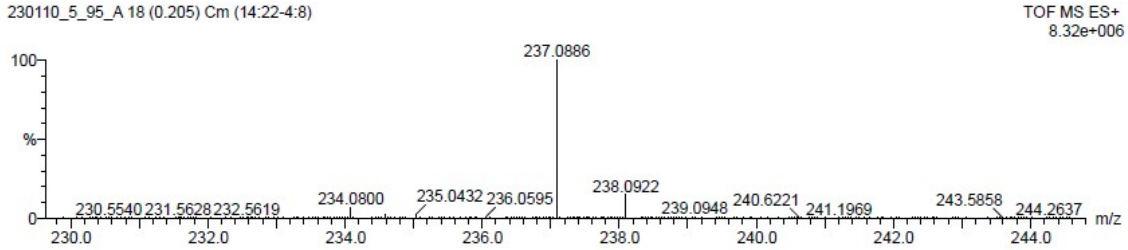
Compound 10a



Elemental Composition Report **Page 1**

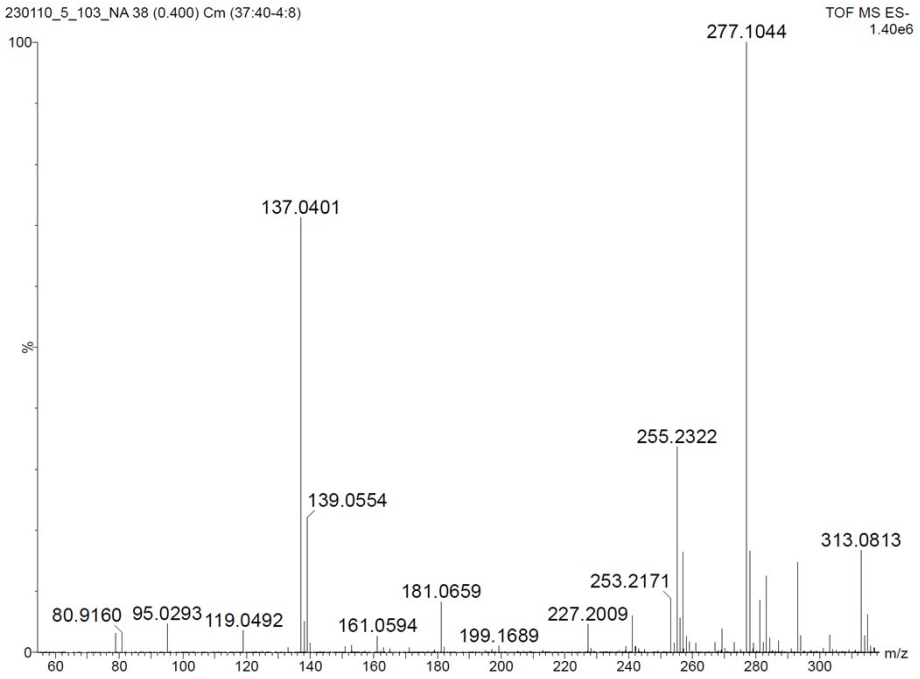
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-20 H: 0-20 O: 0-8 Na: 0-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
237.0886	237.0891	-0.5	-2.1	7.5	1218.2	n/a	n/a	C14 H14 O2 Na

Compound 11a

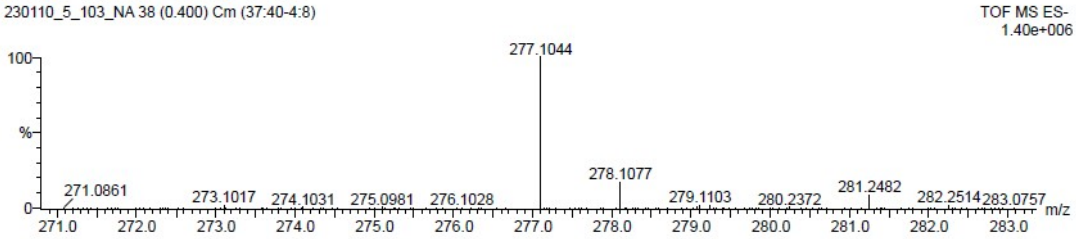


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

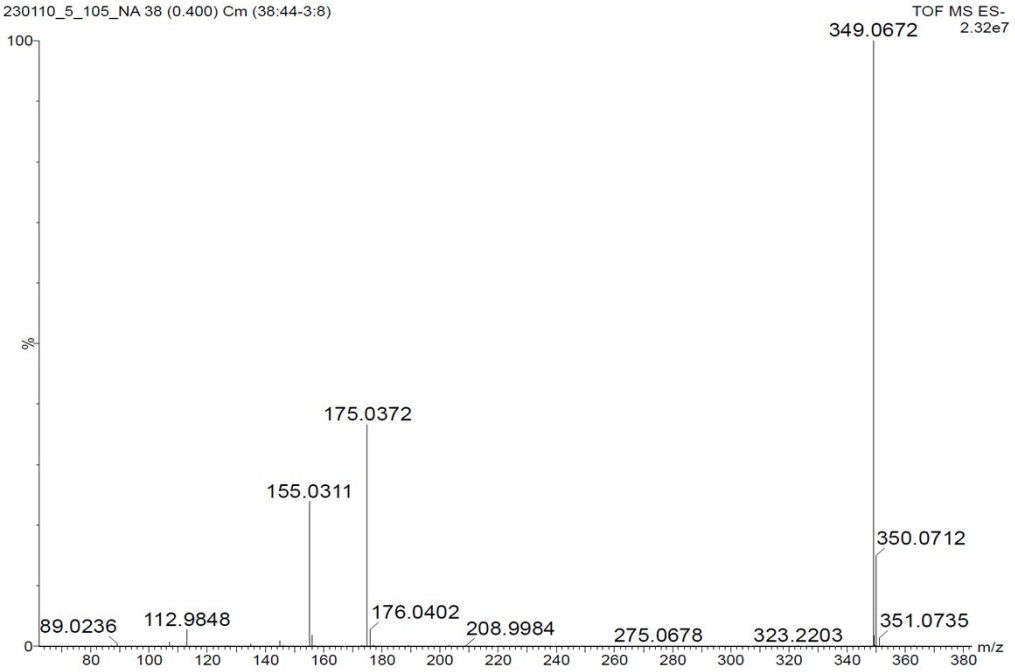
Monoisotopic Mass, Even Electron Ions
131 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 F: 0-6

230110_5_103_NA 38 (0.400) Cm (37:40-4:8)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
277.1044	277.1040	0.4	1.4	8.5	777.3	0.563	56.95	C16 H15 O2 F2

Compound 12a

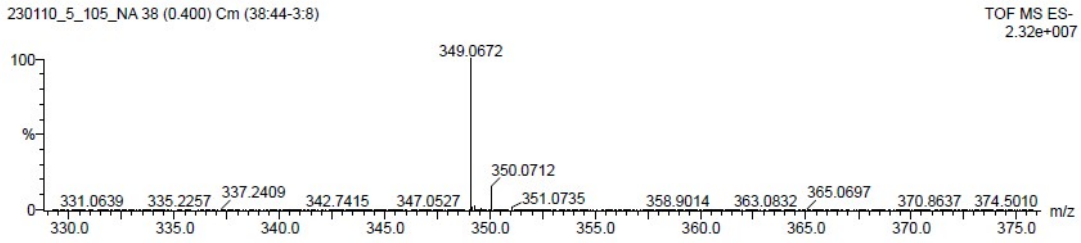


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
140 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-25 O: 0-8 F: 0-6

230110_5_105_NA 38 (0.400) Cm (38:44-3:8)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
349.0672	349.0663	0.9	2.6	8.5	1865.1	0.000	99.95	C16 H11 O2 F6