

Catalytic Asymmetric Synthesis of Sterically Hindered Tertiary α -Aryl Ketones

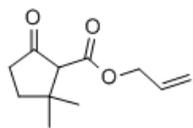
Robert Doran and Patrick J. Guiry*

*Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University
College Dublin, Belfield, Dublin 4, Ireland.*

Supporting Information

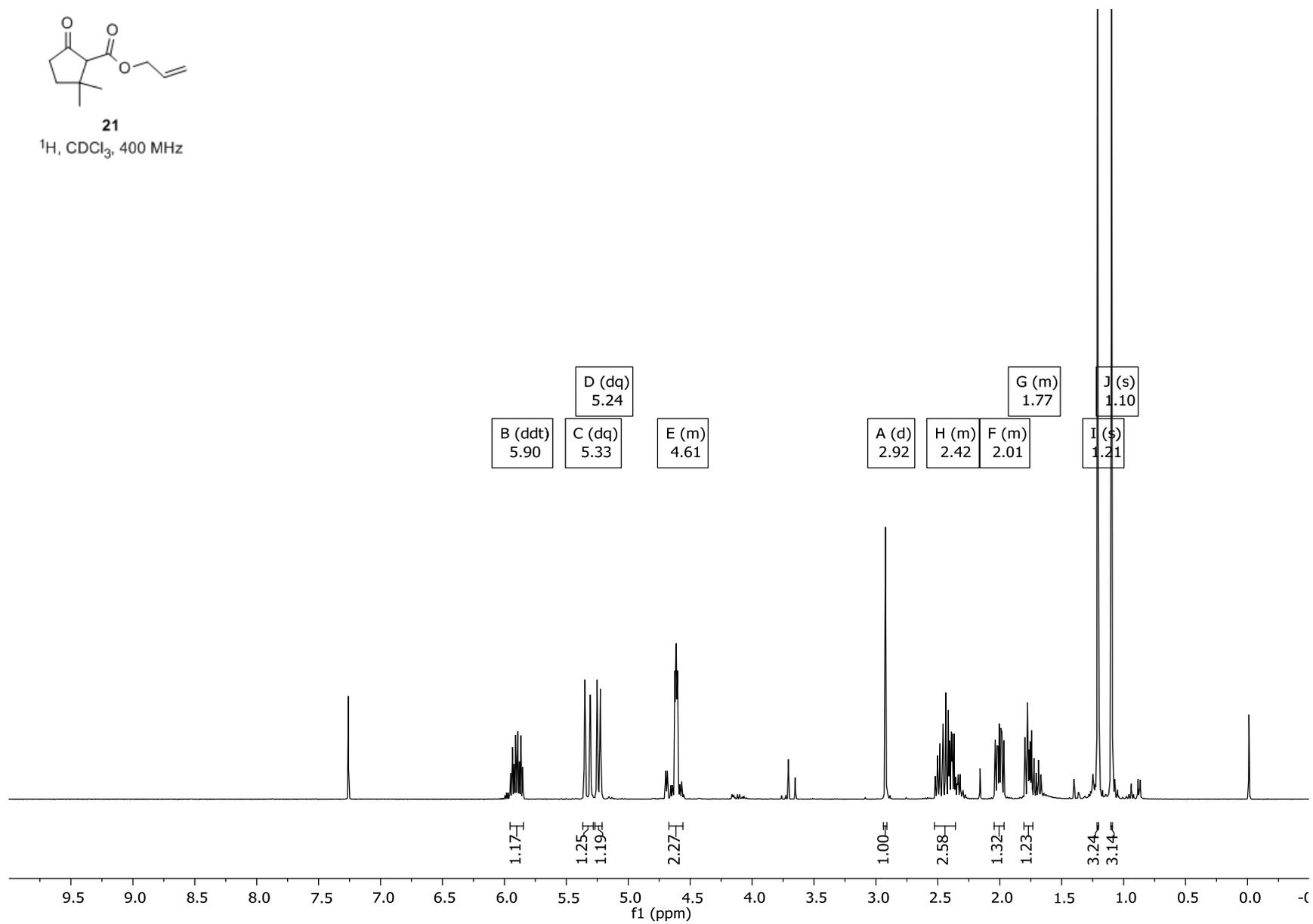
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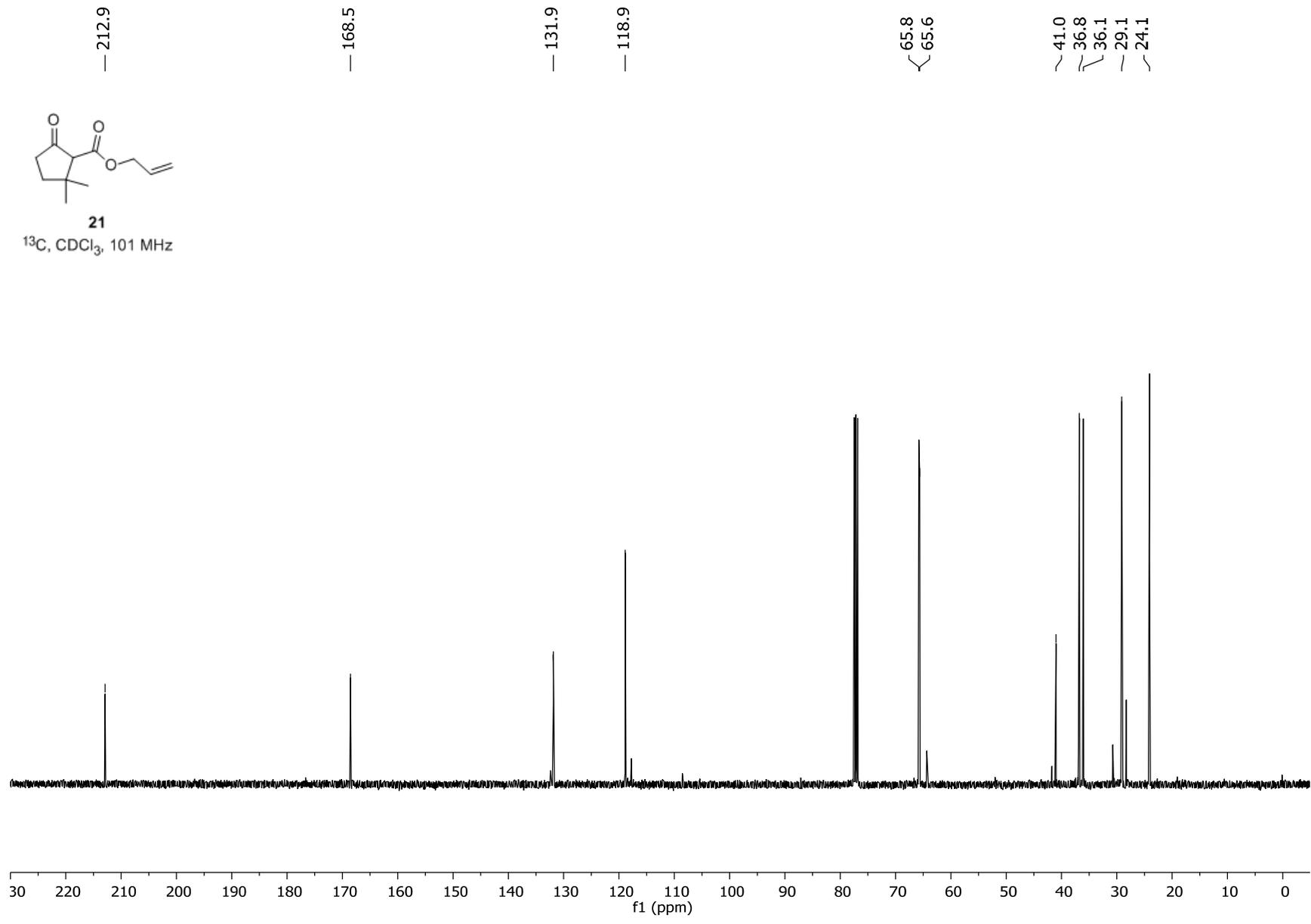
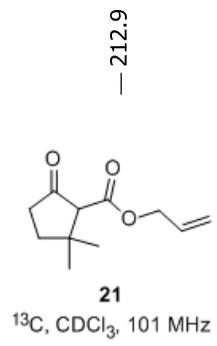
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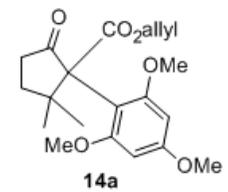


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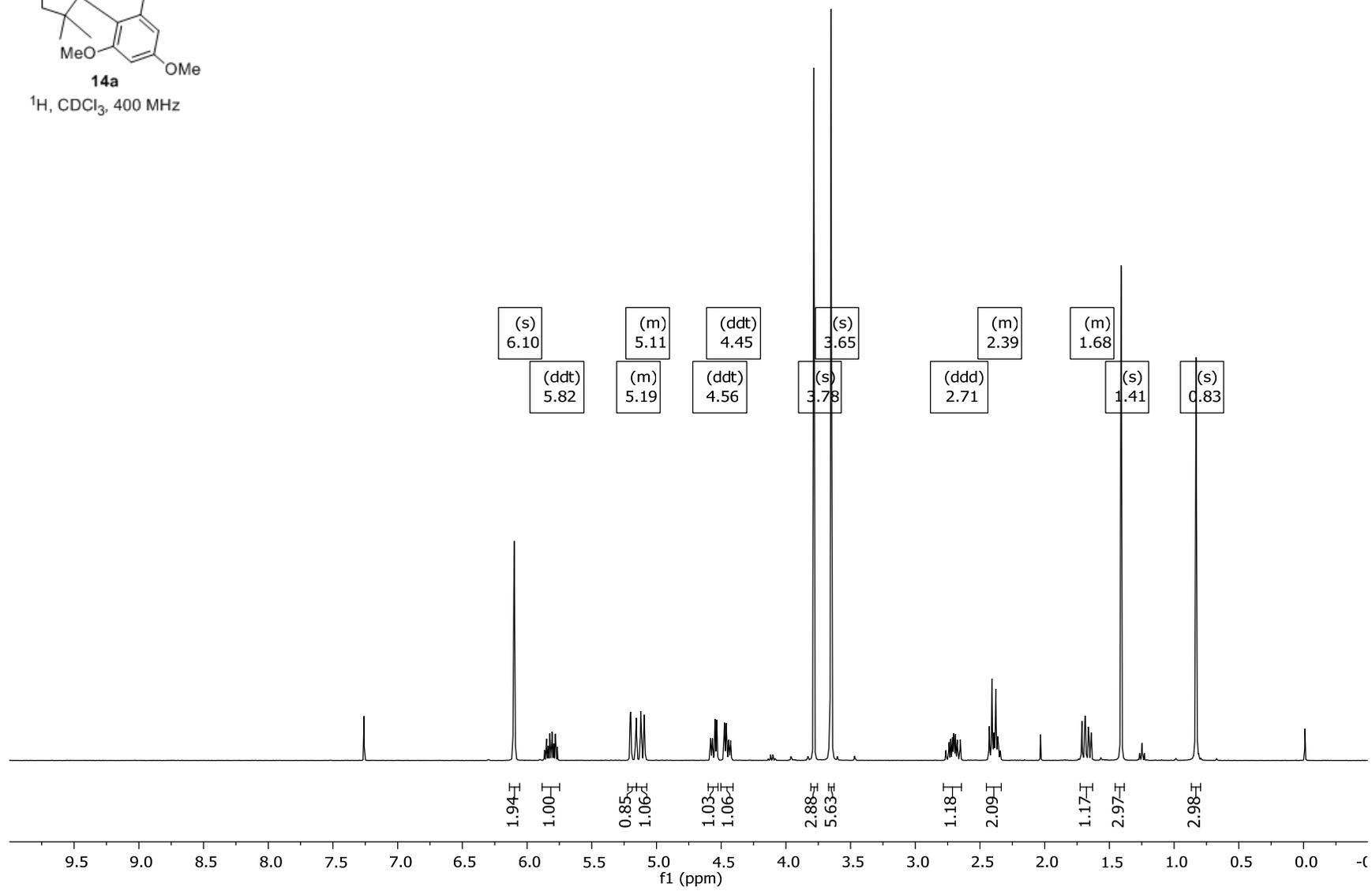
¹H, CDCl₃, 400 MHz

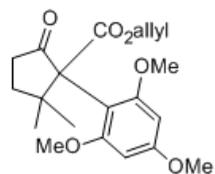






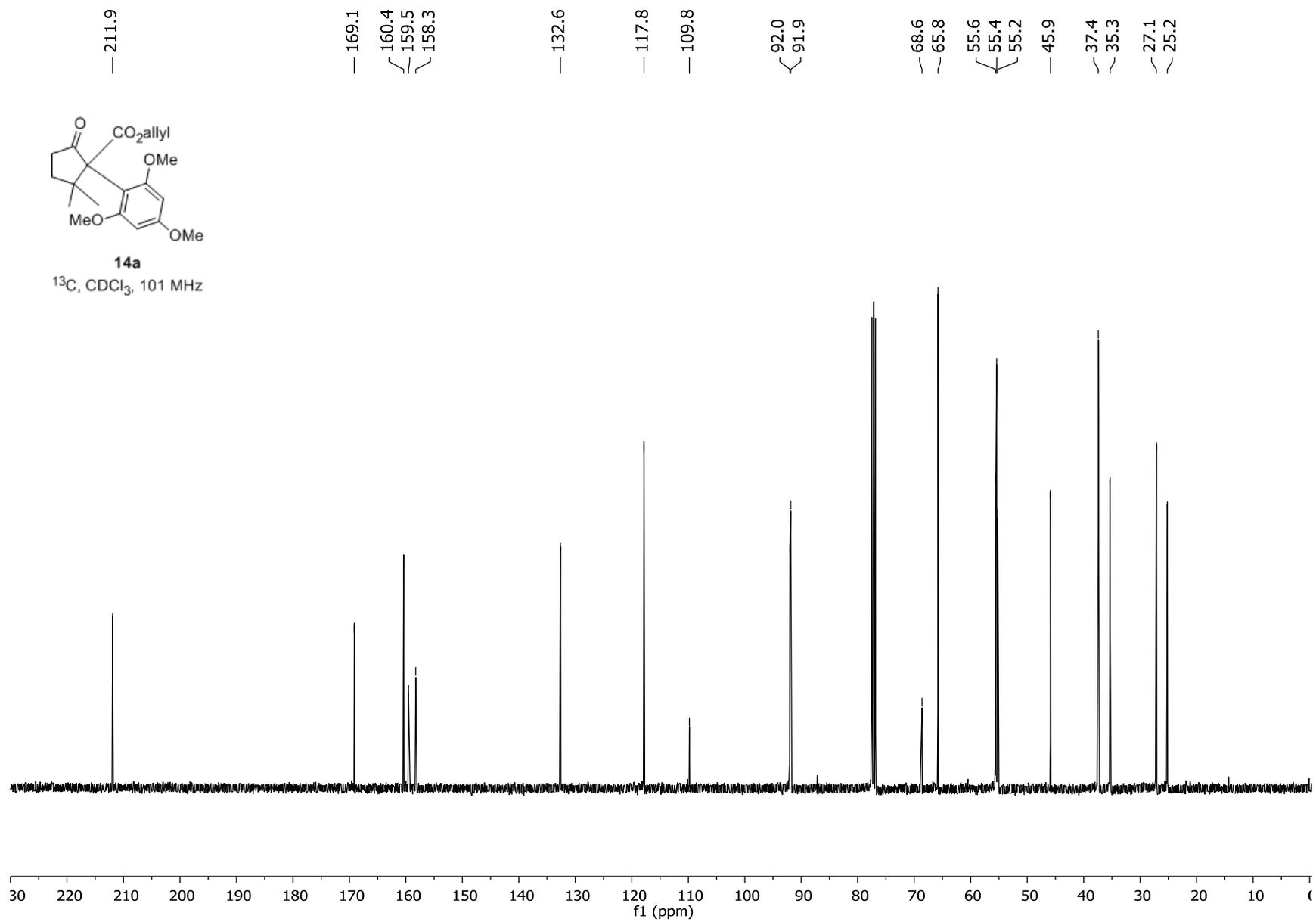
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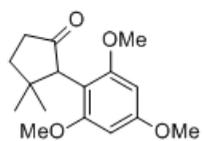




14a

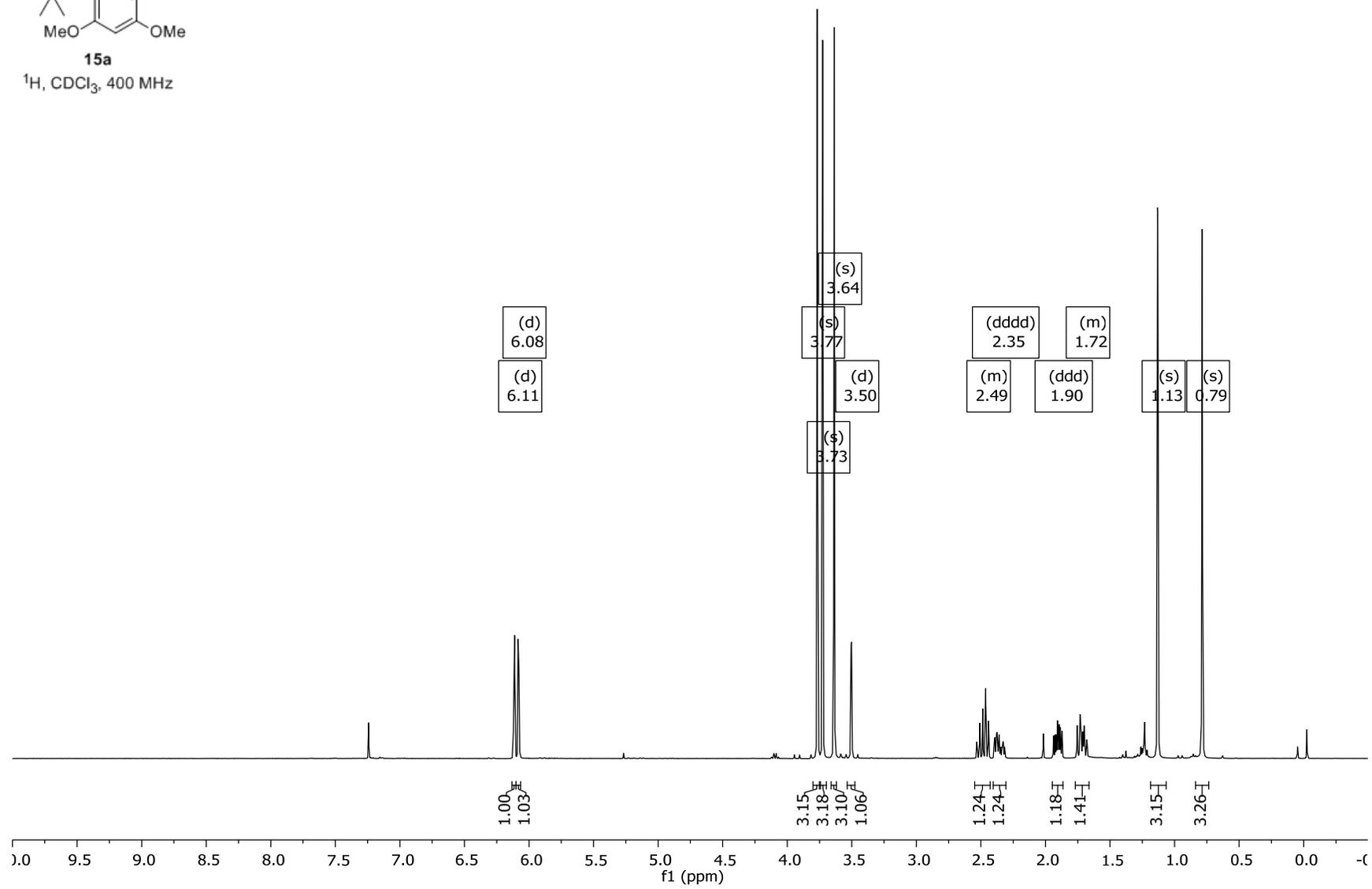
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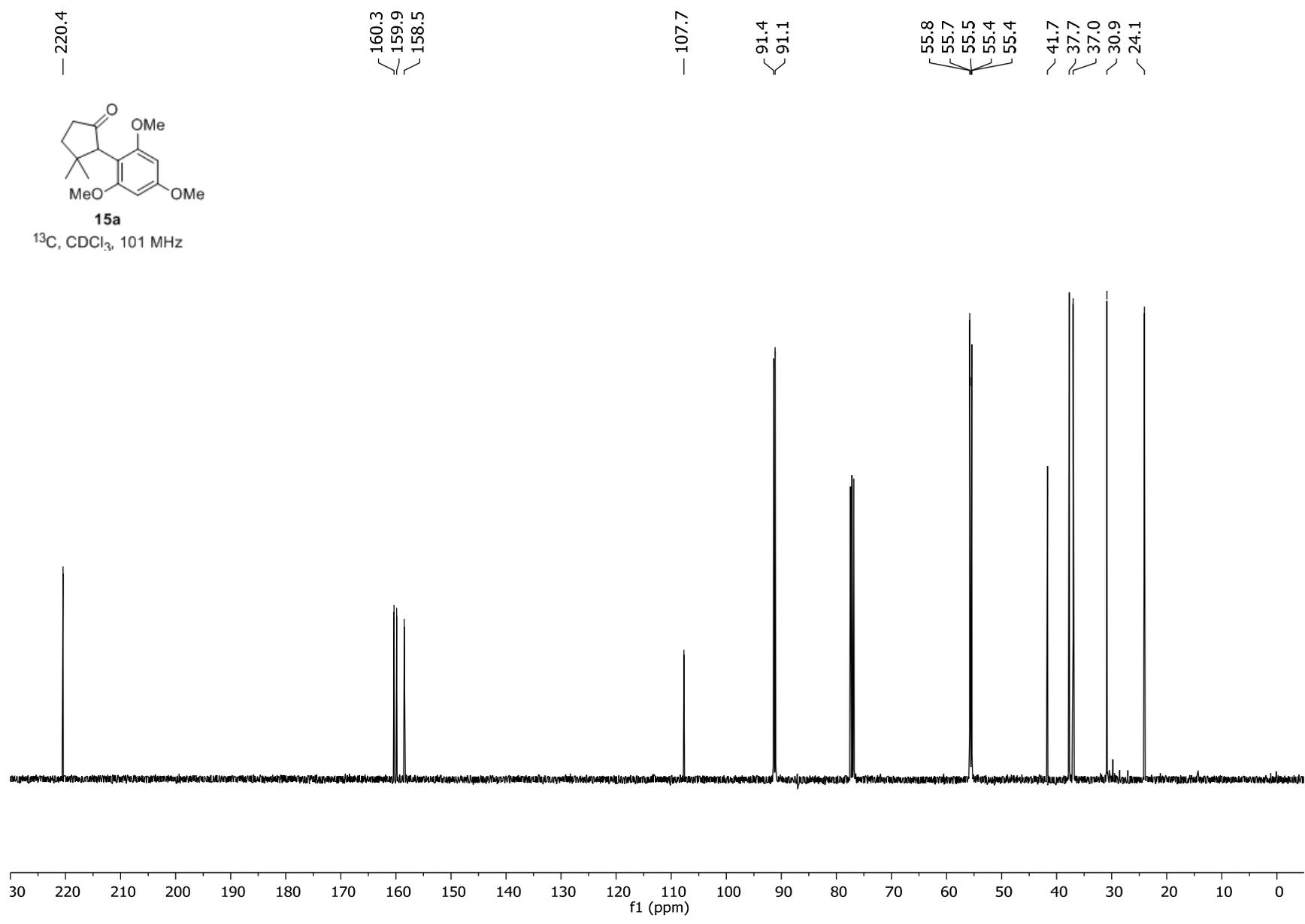


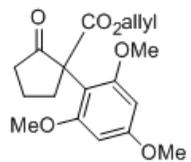


15a

^1H , CDCl_3 , 400 MHz

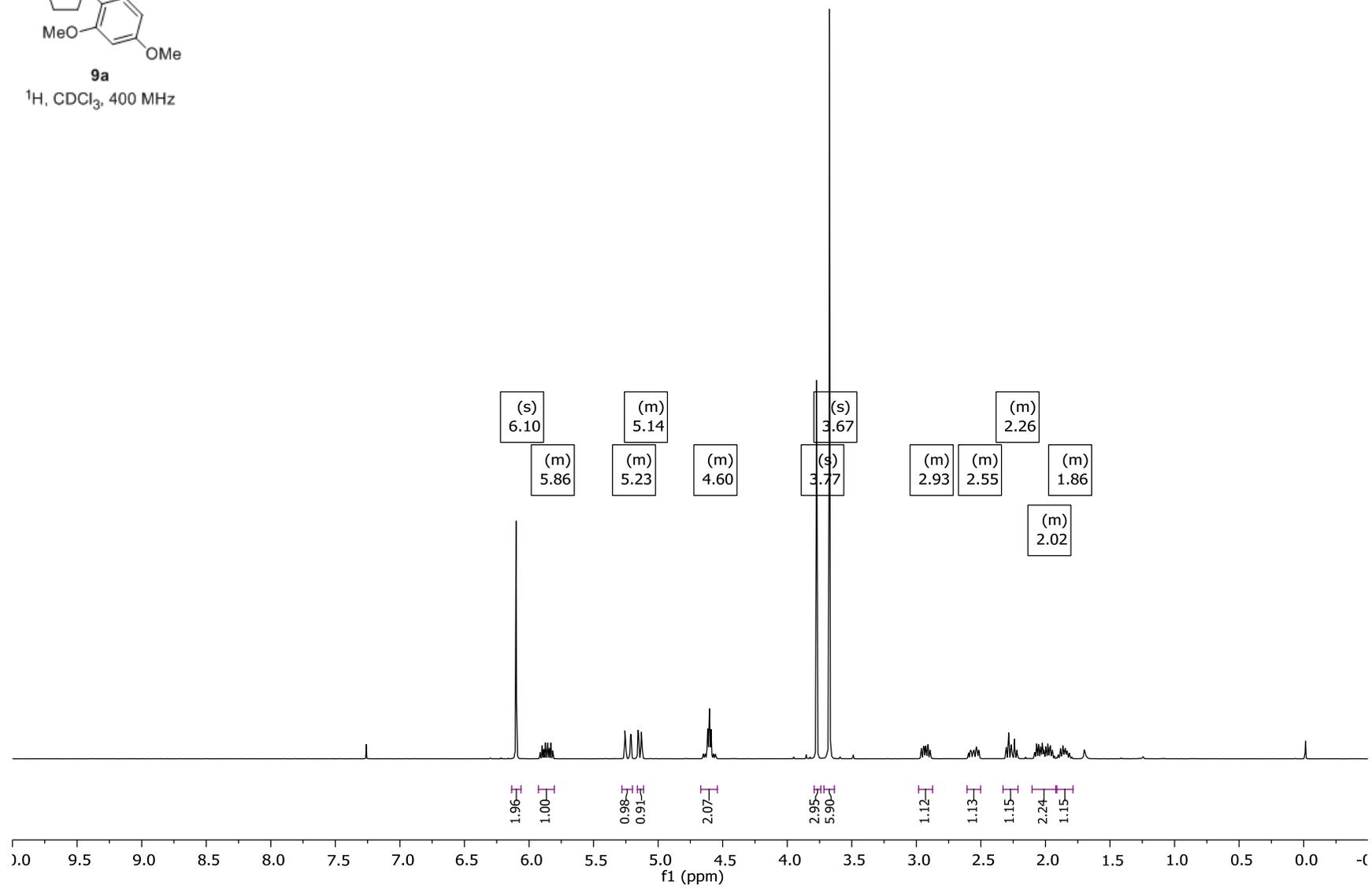


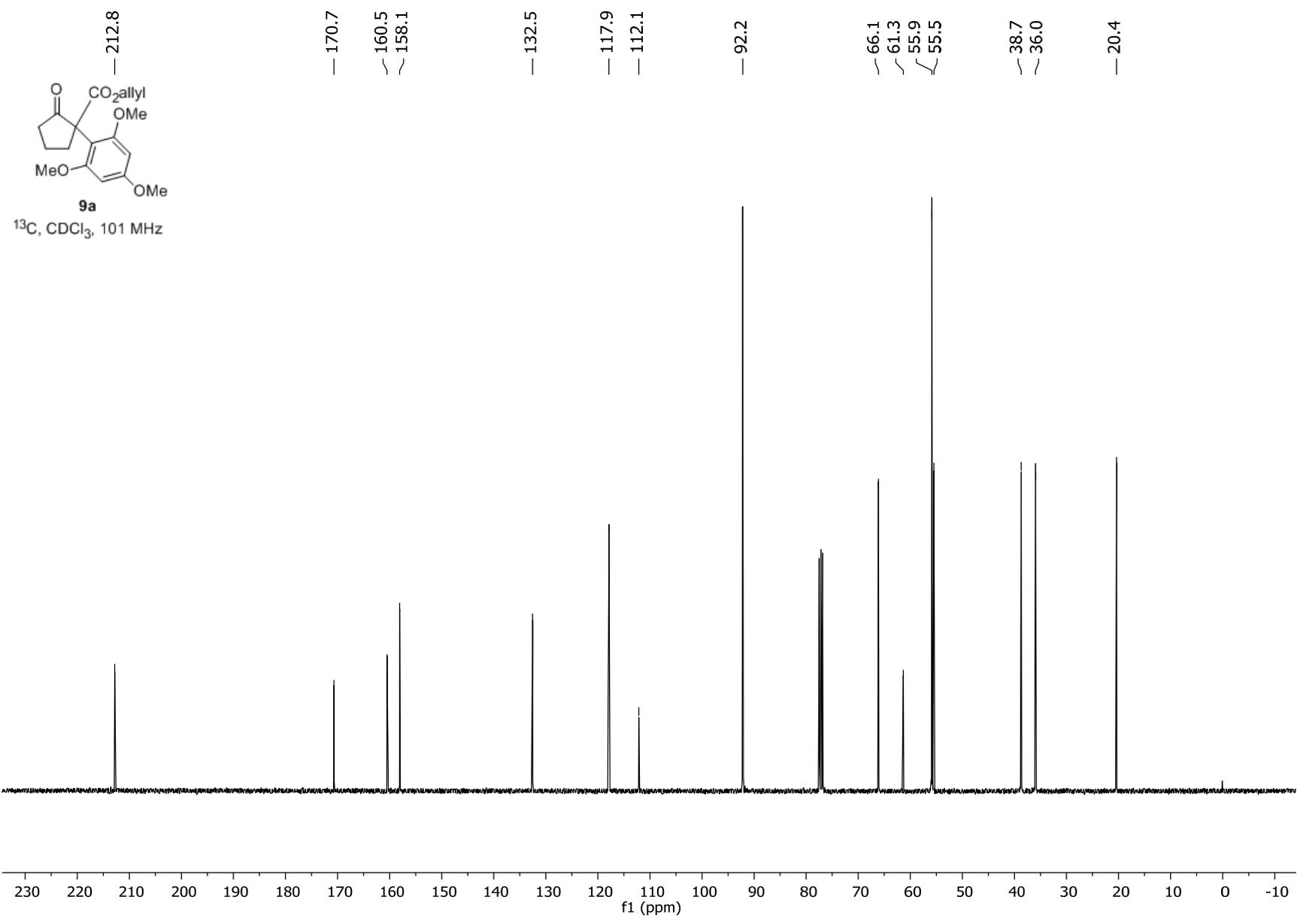


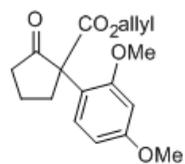


9a

^1H , CDCl_3 , 400 MHz

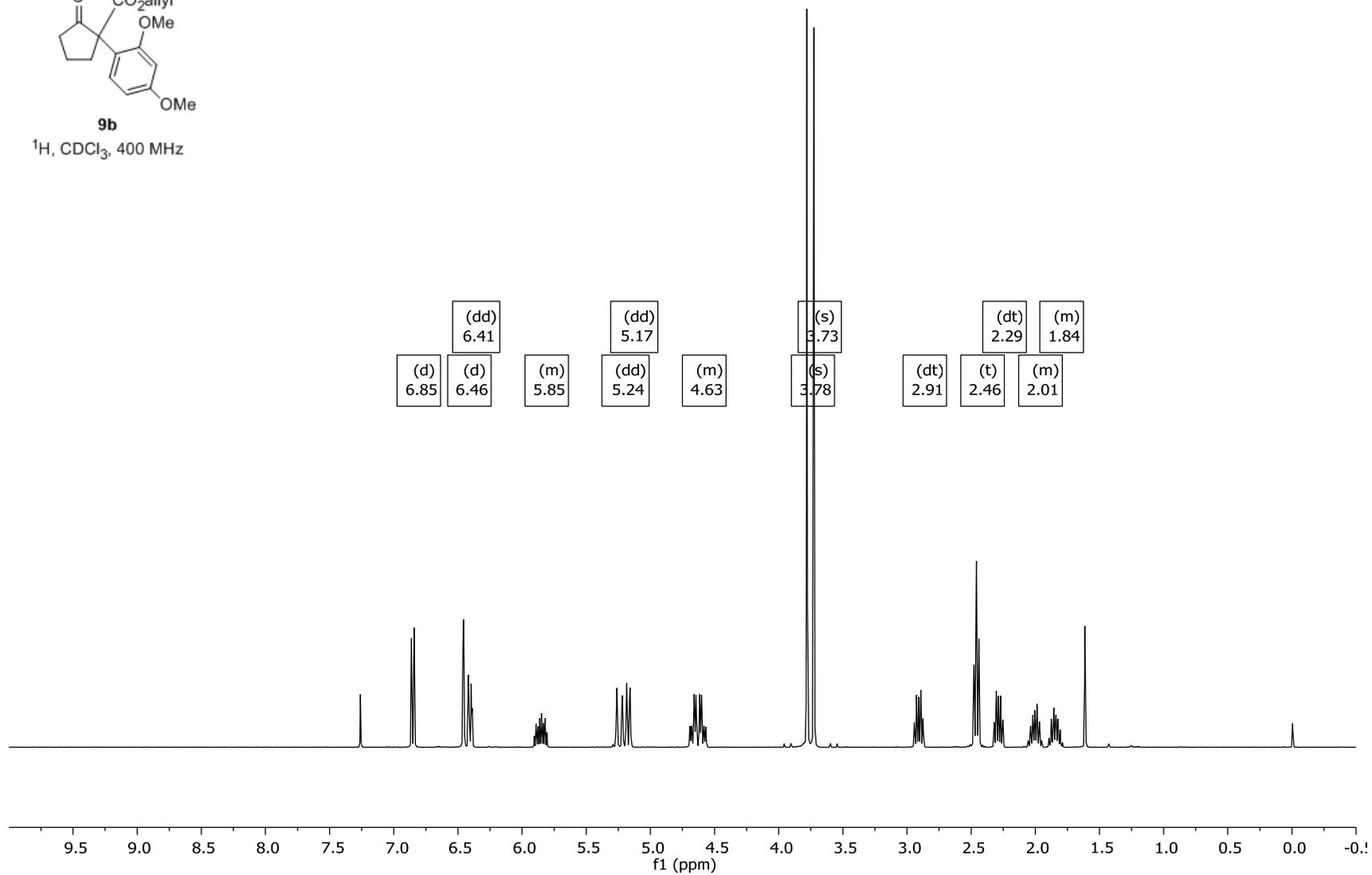


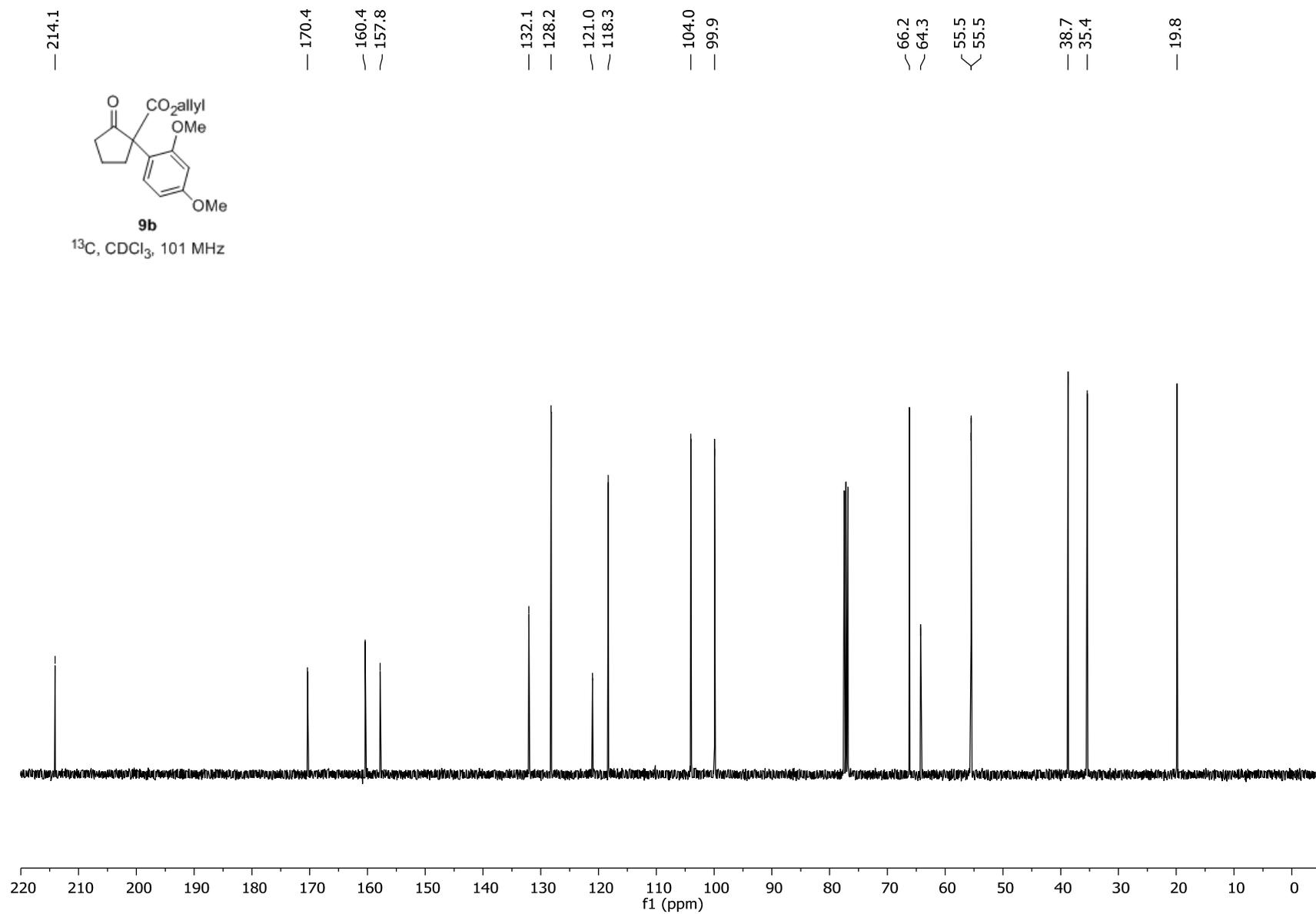


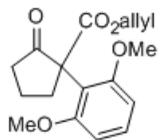


9b

¹H, CDCl₃, 400 MHz

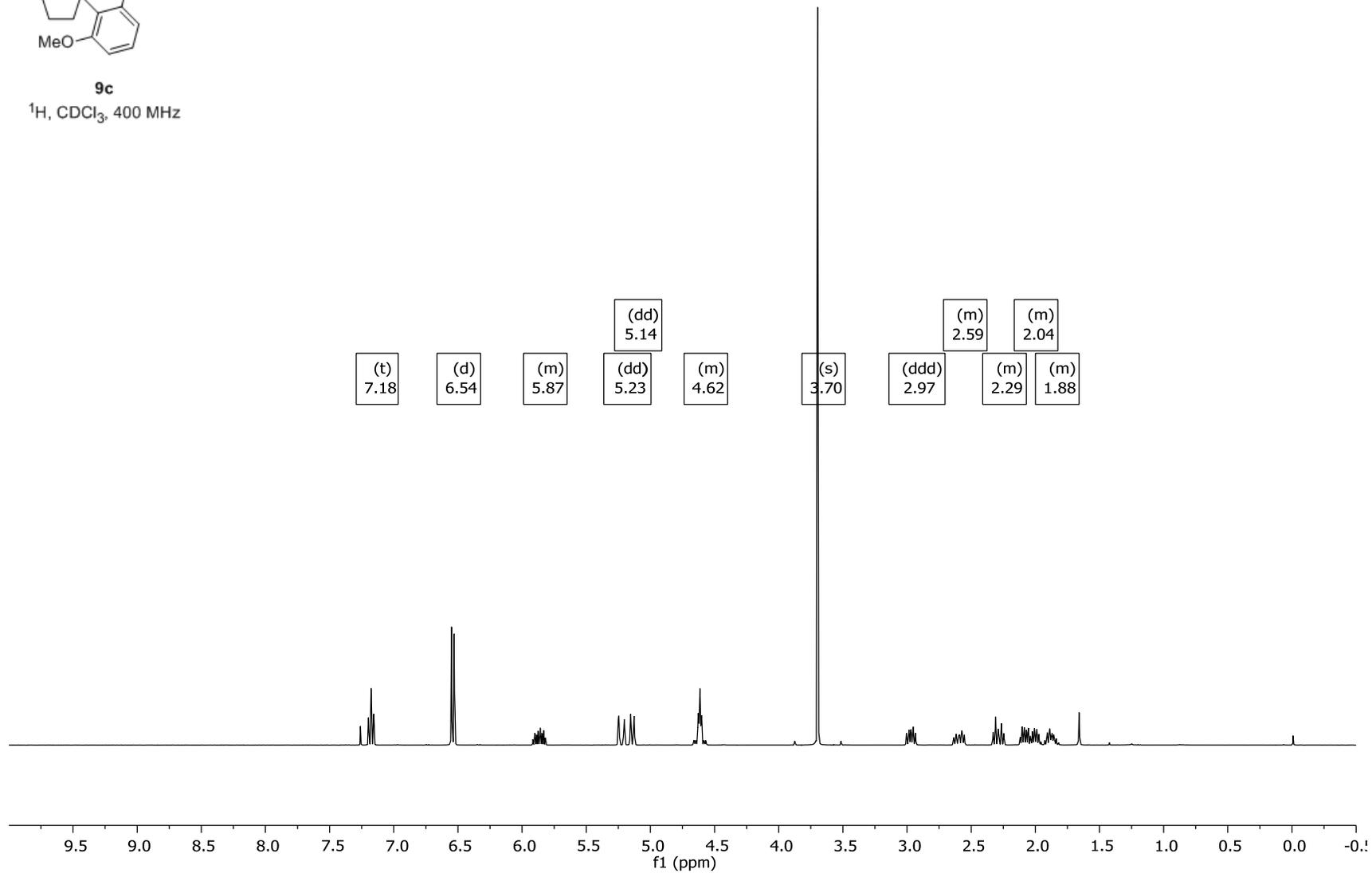


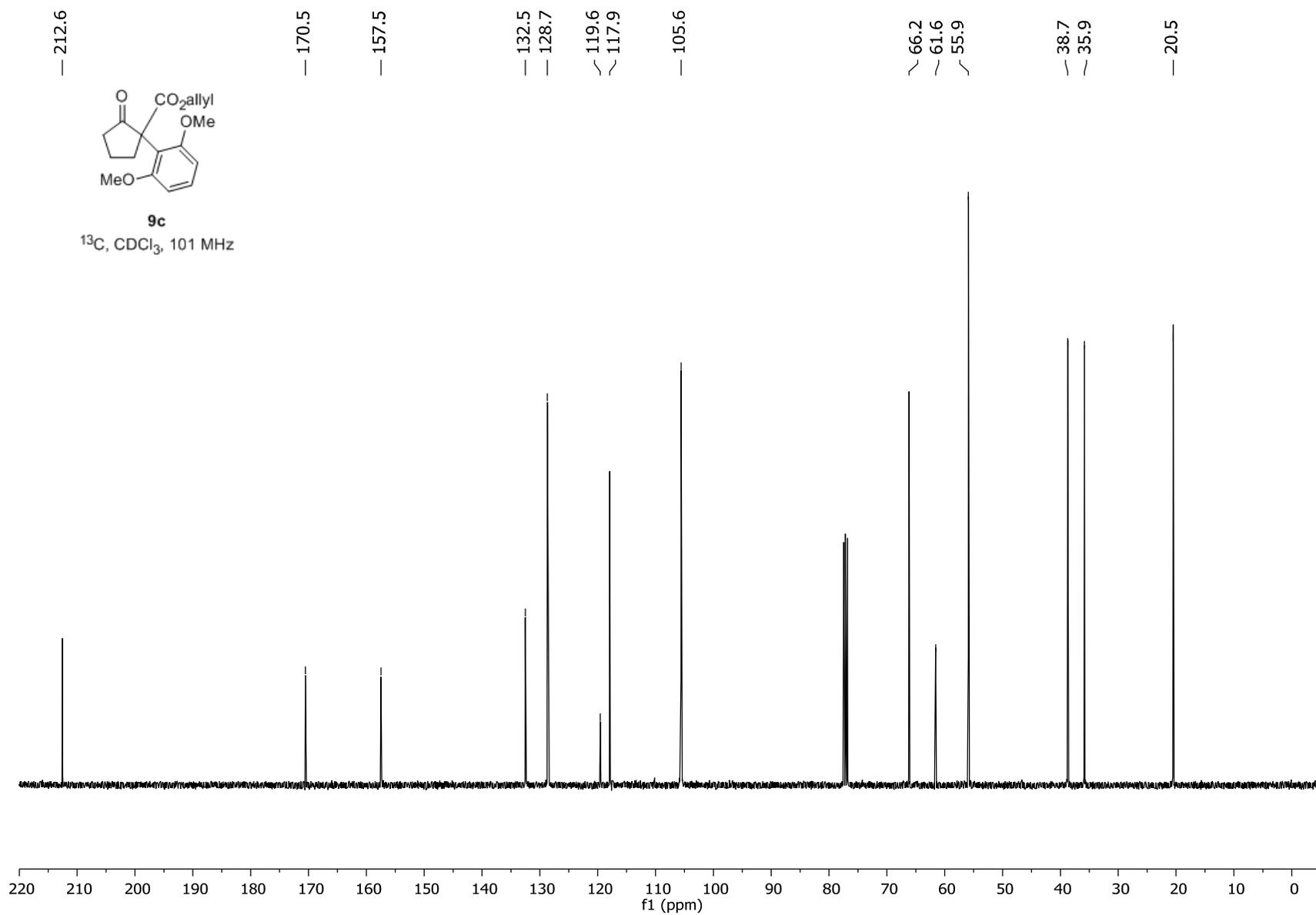


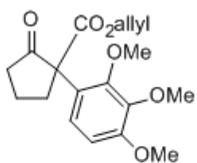


9c

^1H , CDCl_3 , 400 MHz

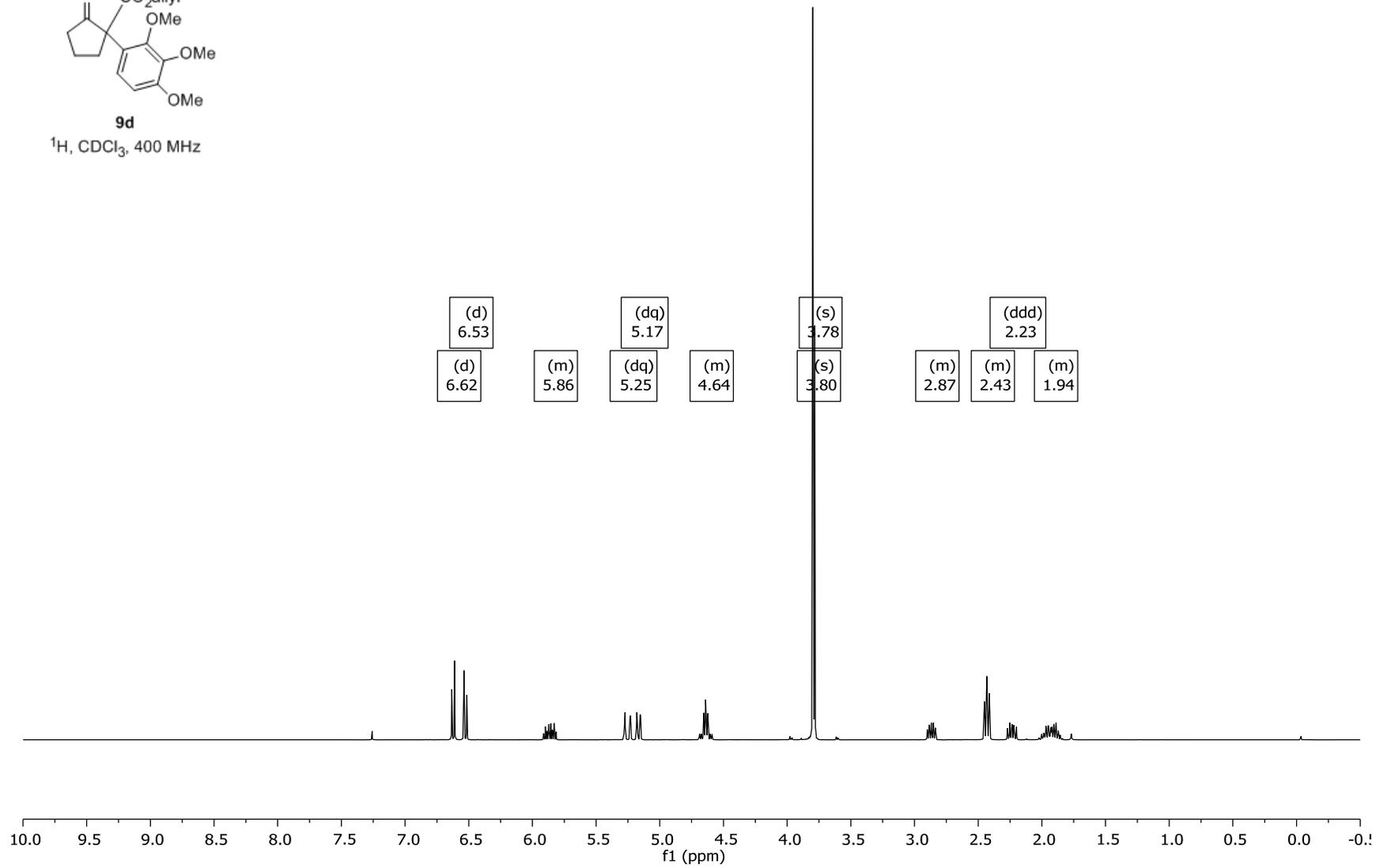


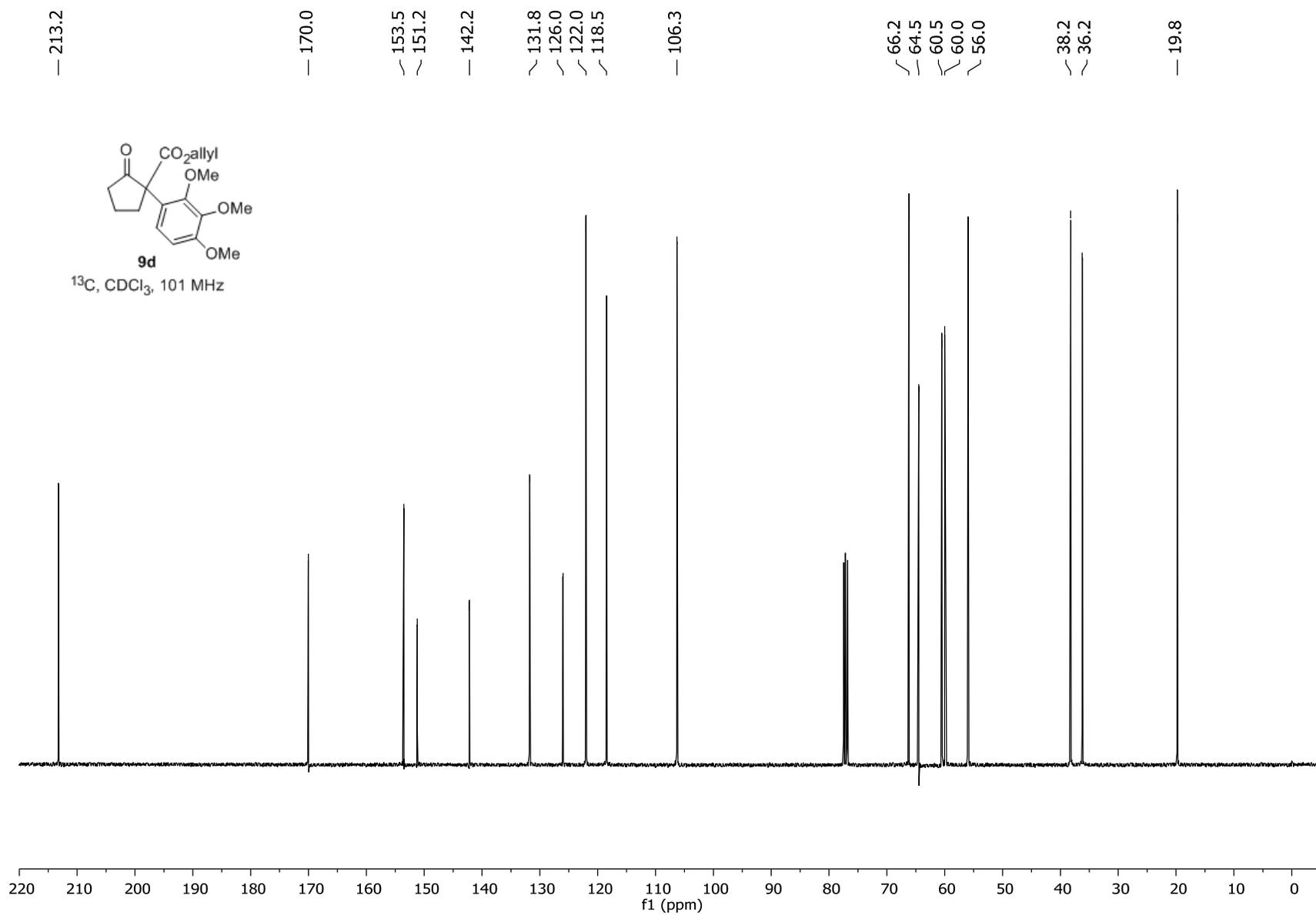


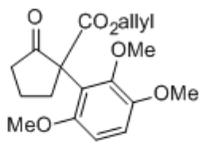


9d

^1H , CDCl_3 , 400 MHz

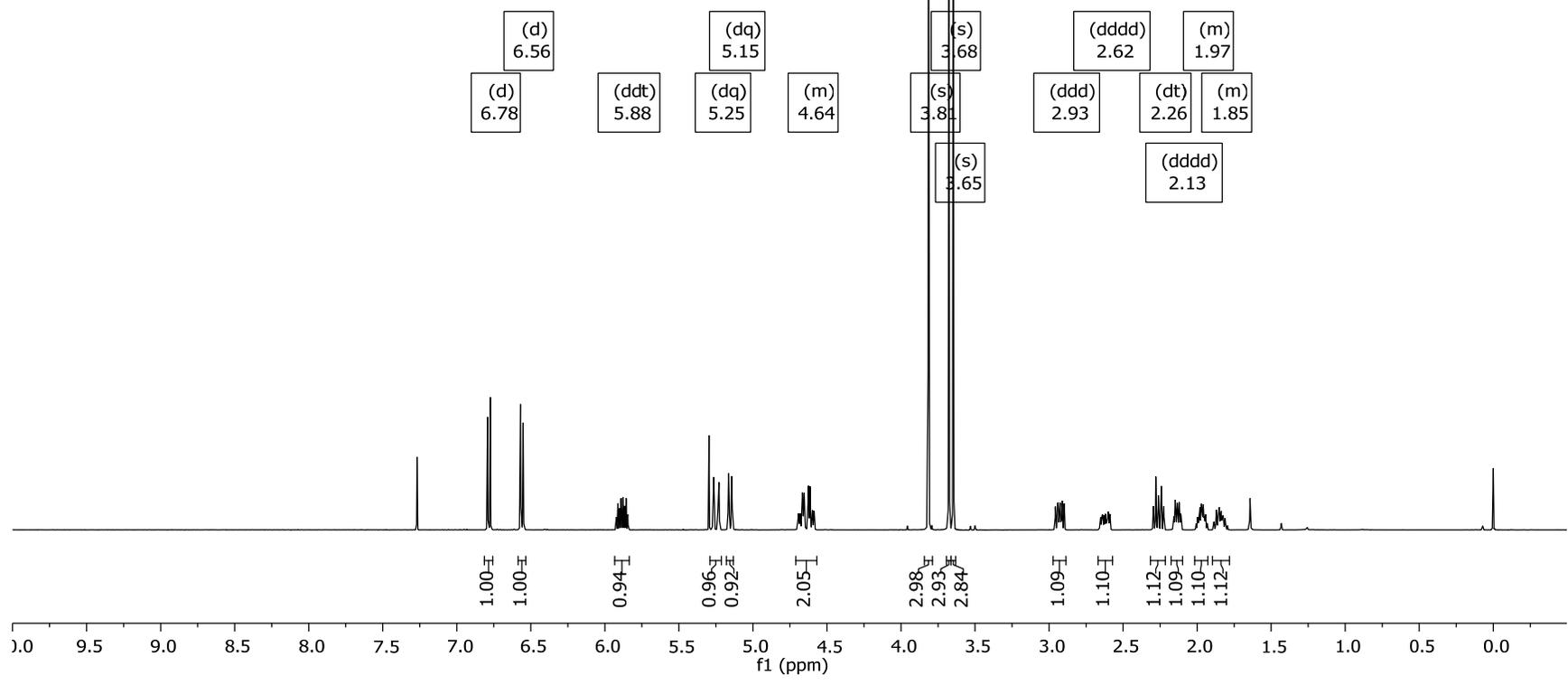


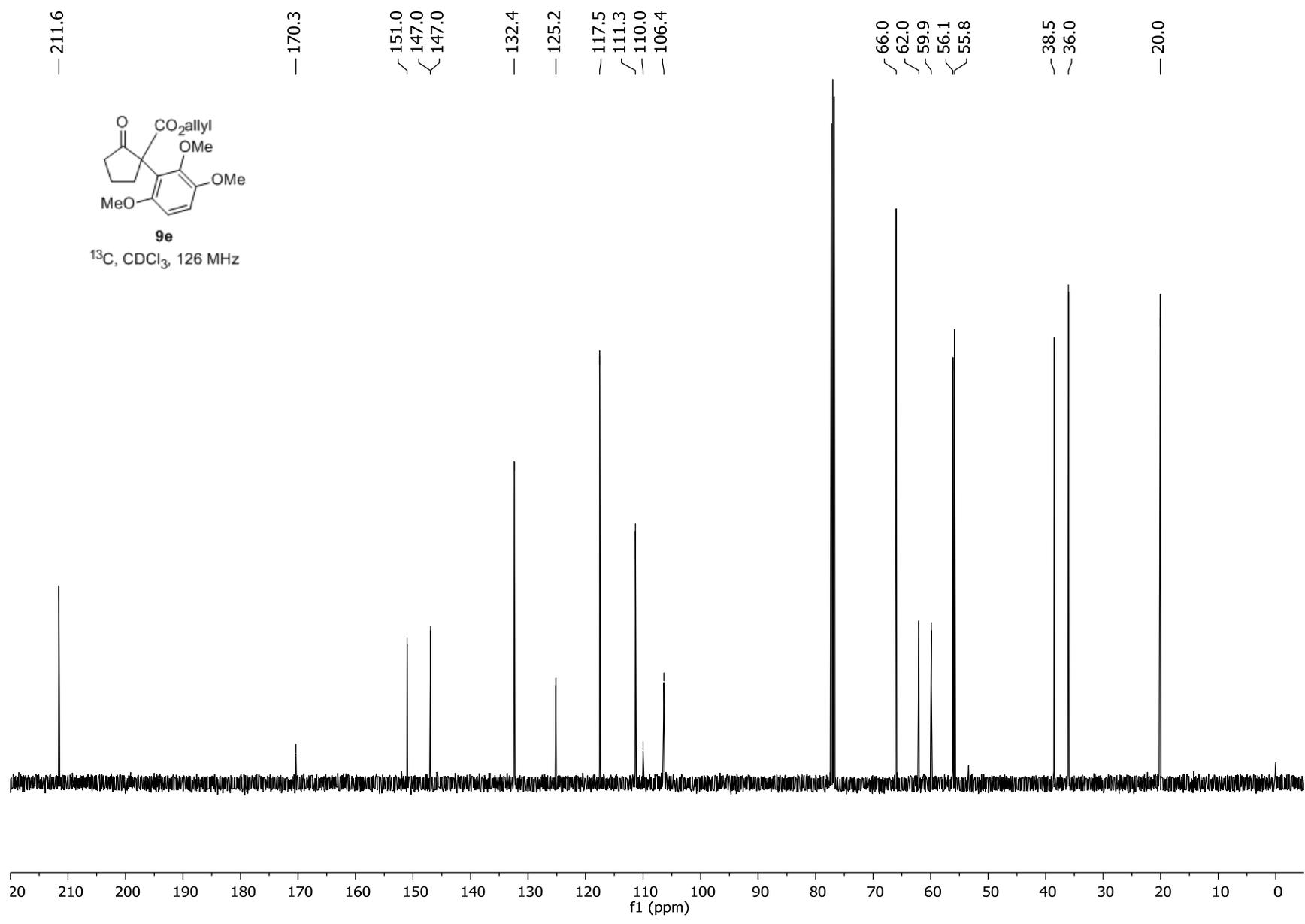


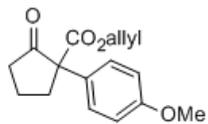


9e

¹H, CDCl₃, 400 MHz

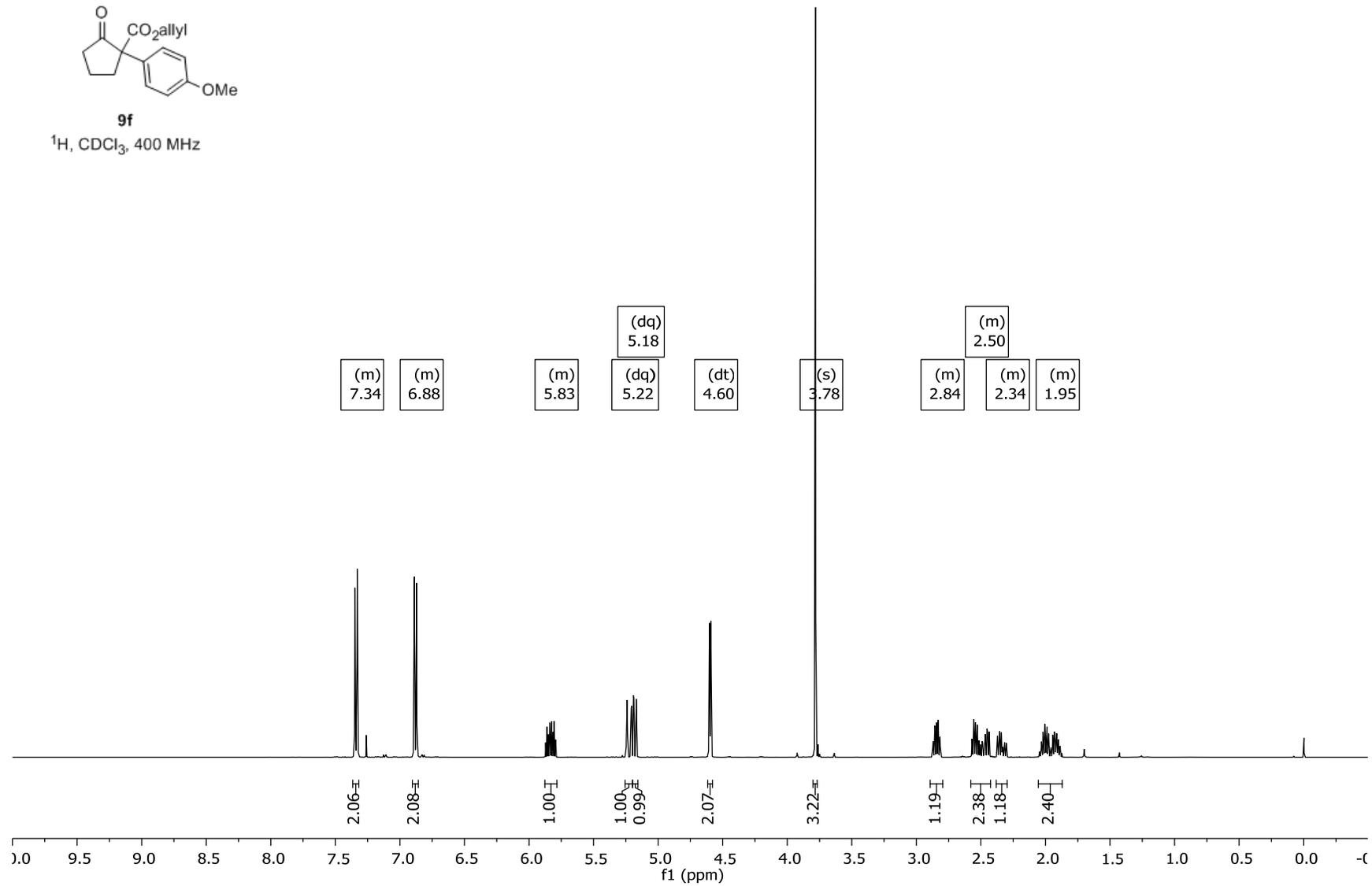


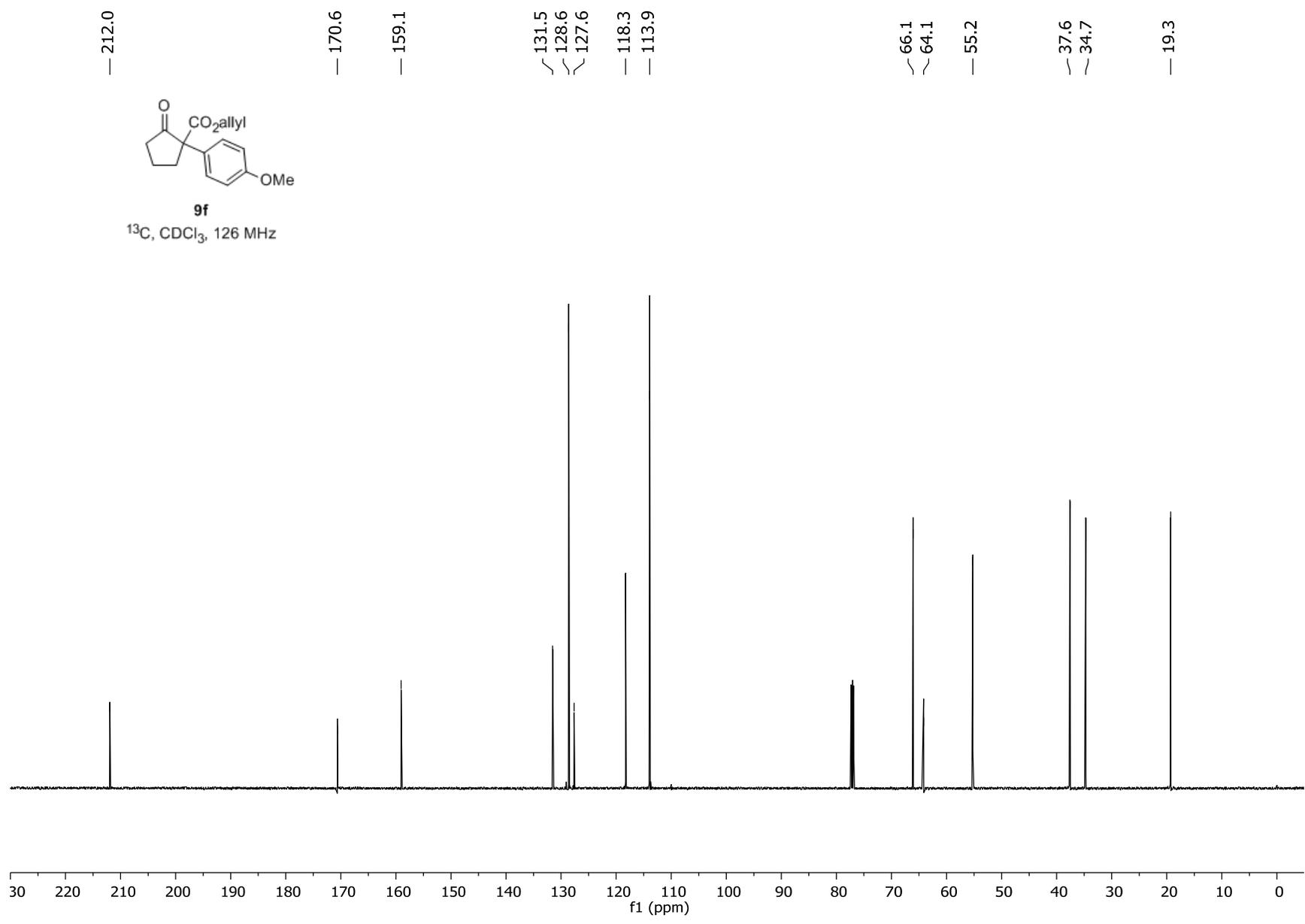


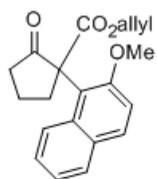


9f

¹H, CDCl₃, 400 MHz

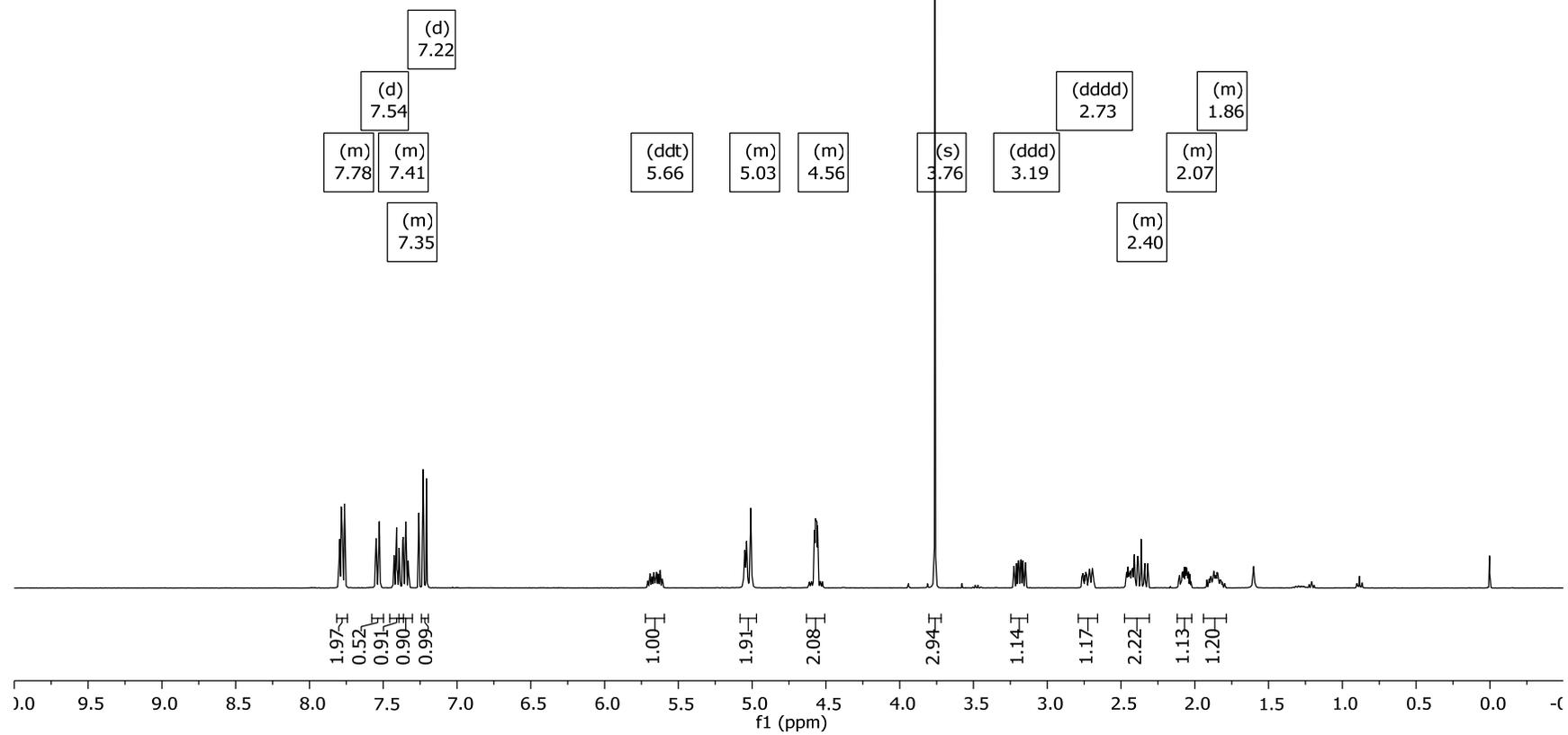


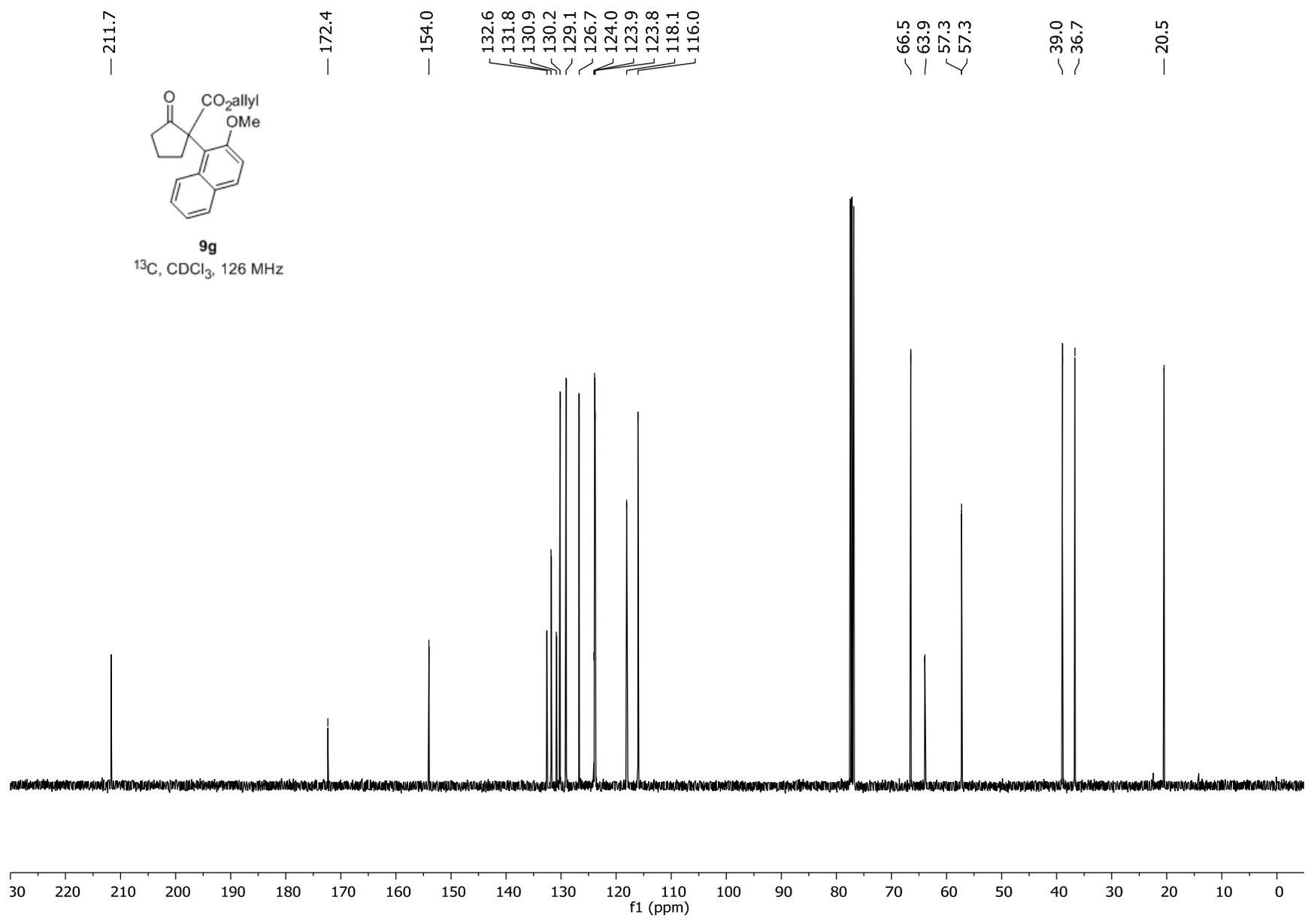


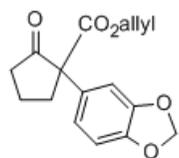


9g

¹H, CDCl₃, 400 MHz

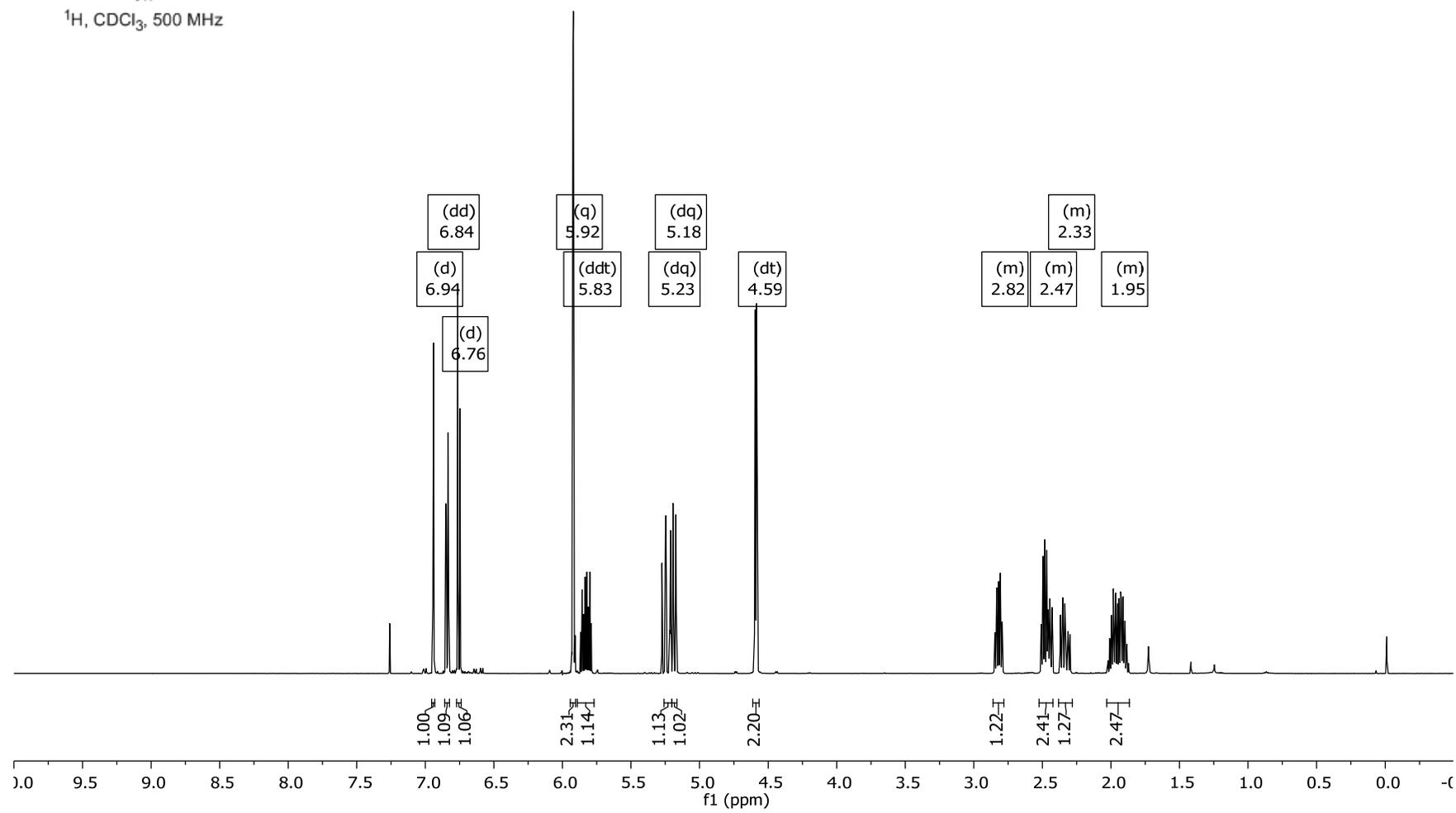






9h

^1H , CDCl_3 , 500 MHz



— 211.6

— 170.4

147.1
147.1

131.5
129.4

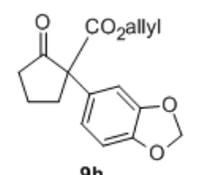
120.7
118.4

108.3
108.1
101.2

66.2
64.4

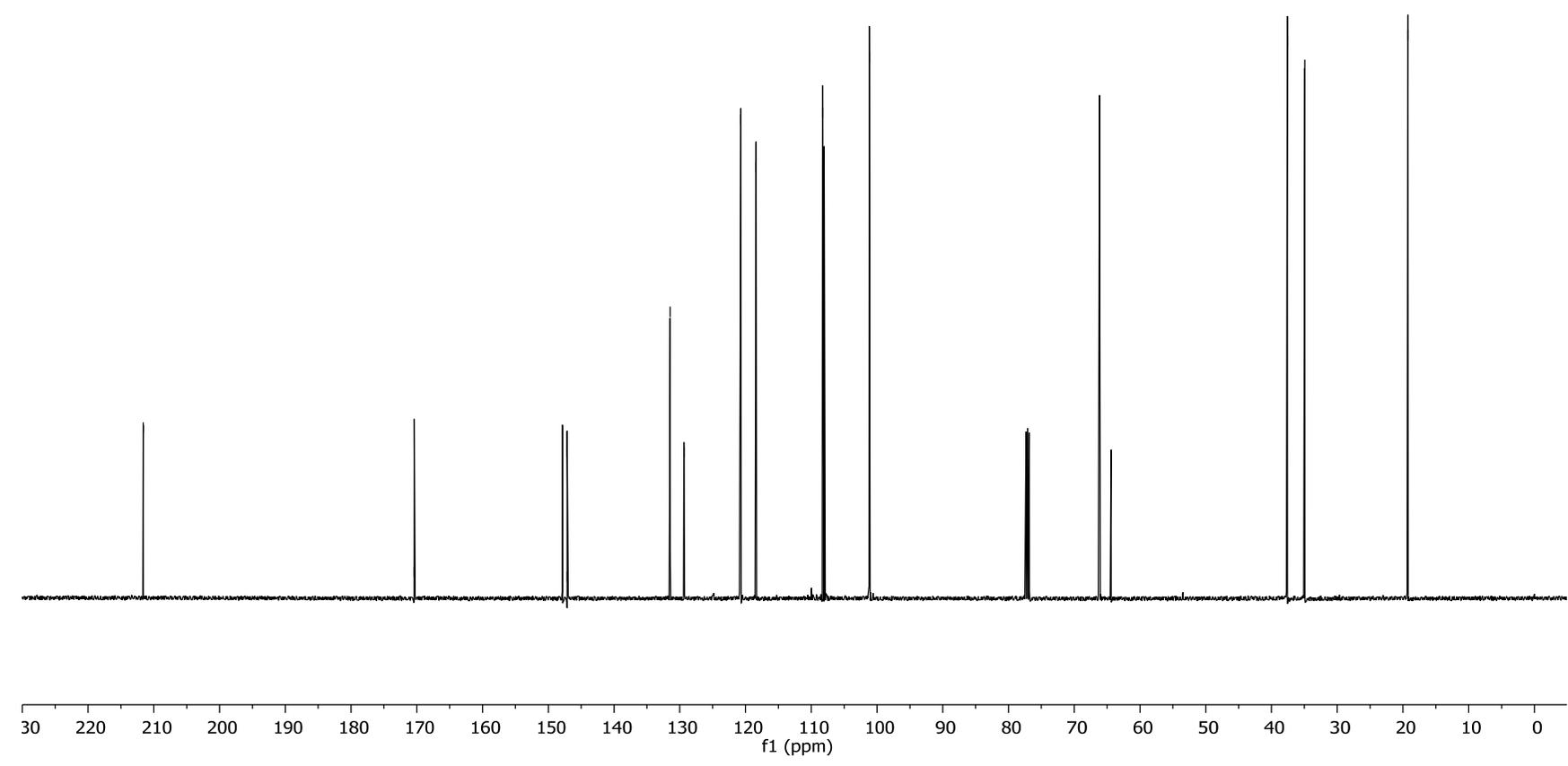
37.6
34.9

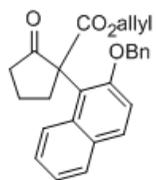
— 19.2



9h

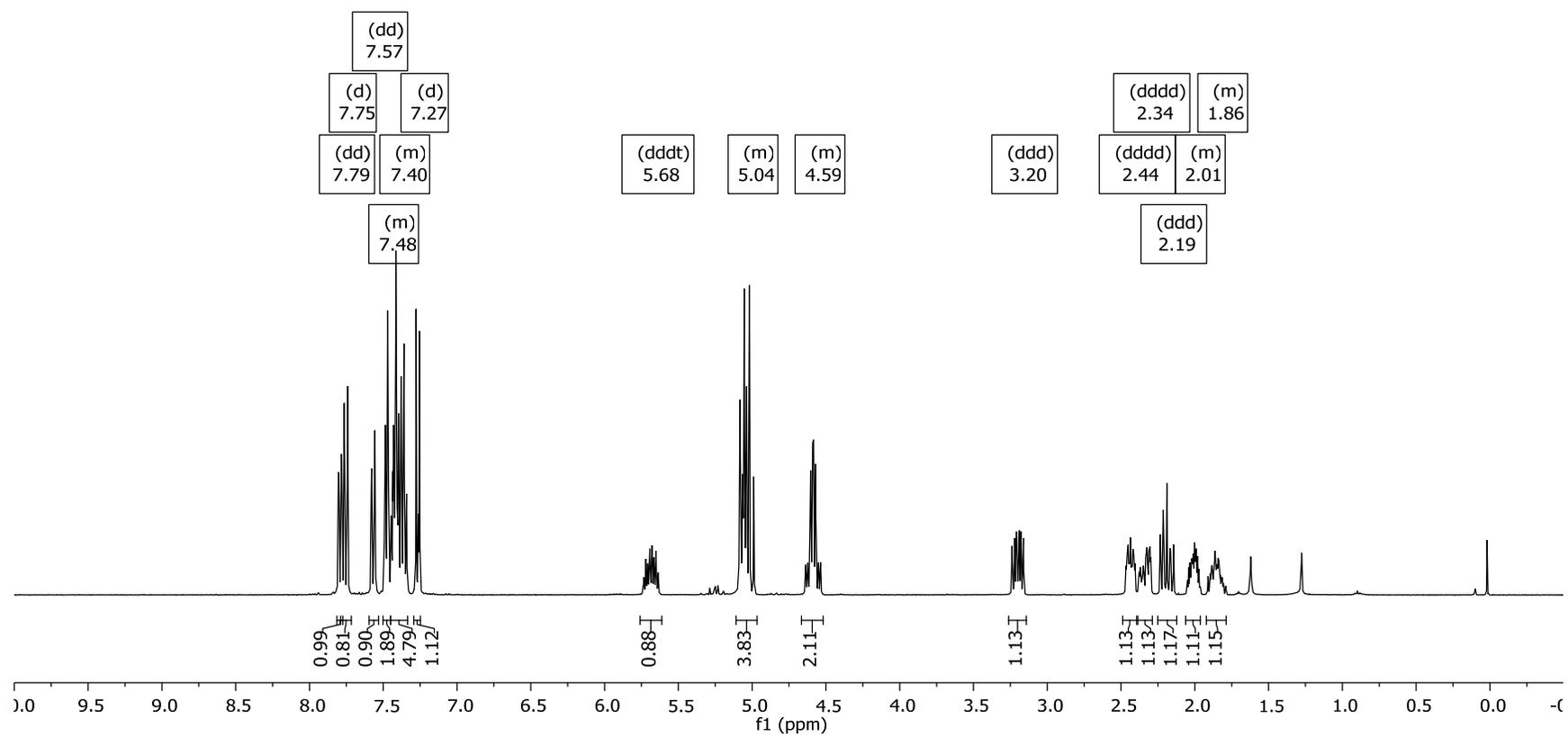
¹³C, CDCl₃, 126 MHz

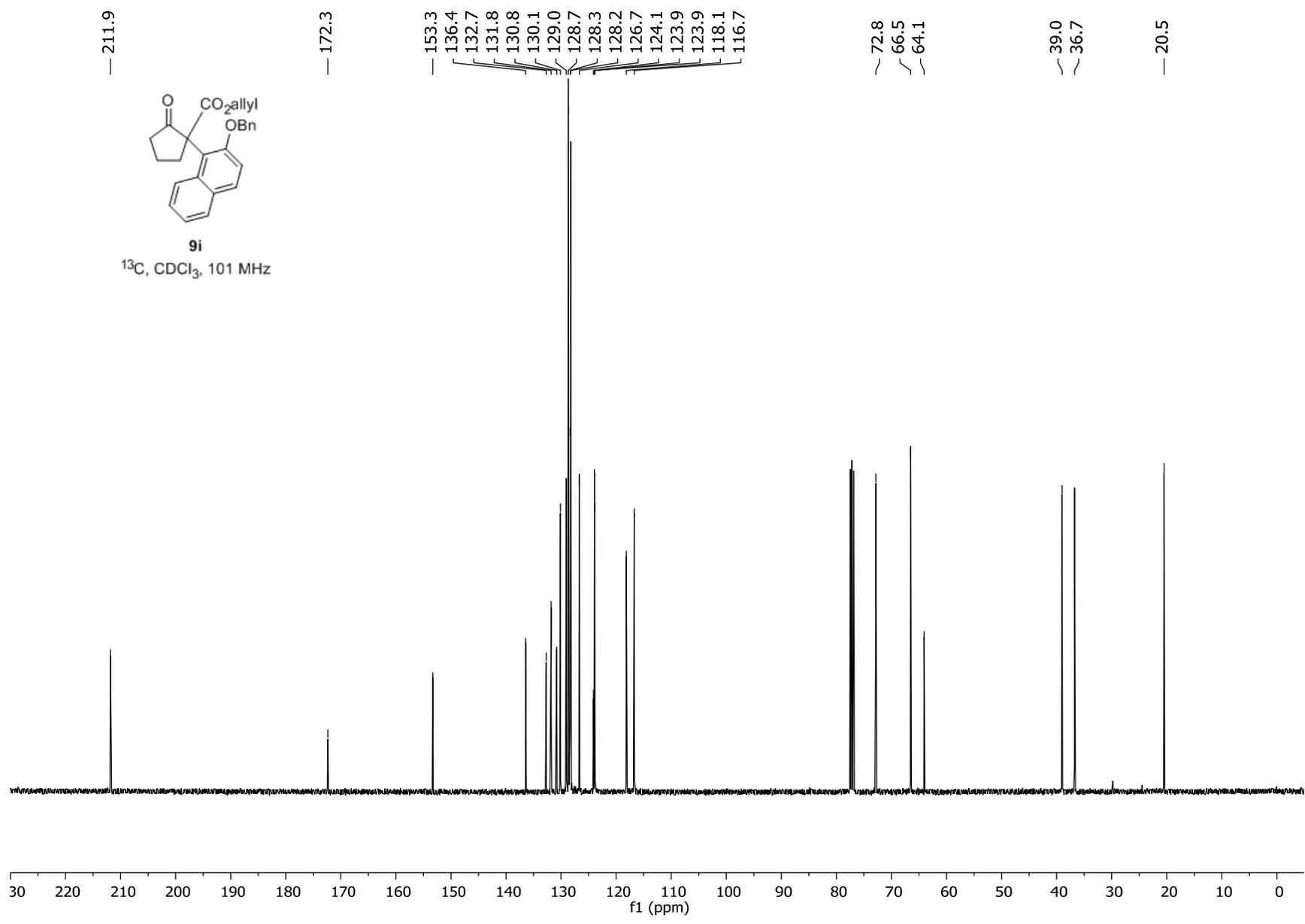


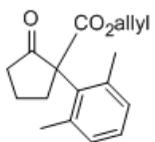


9i

¹H, CDCl₃, 400 MHz

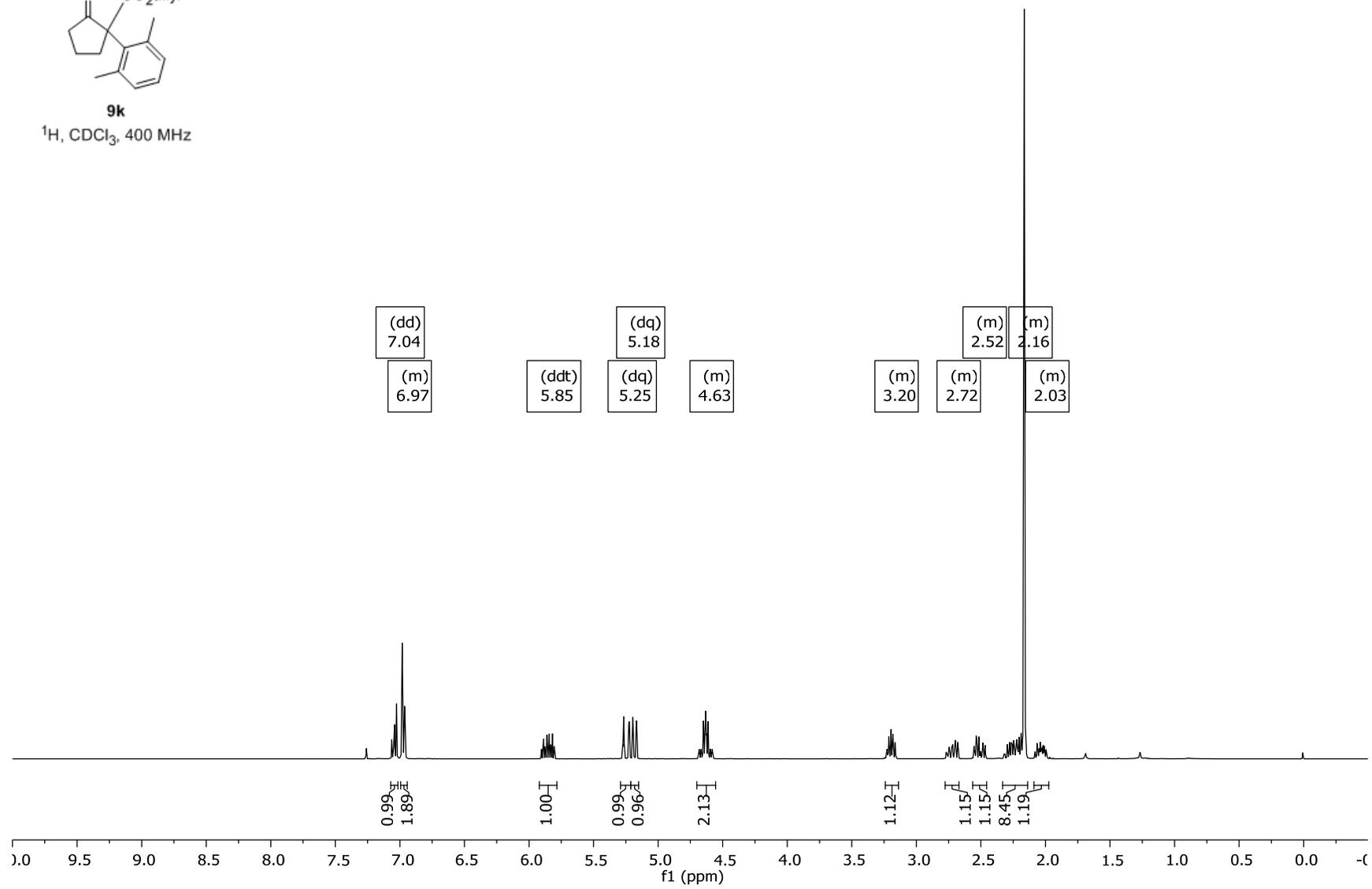


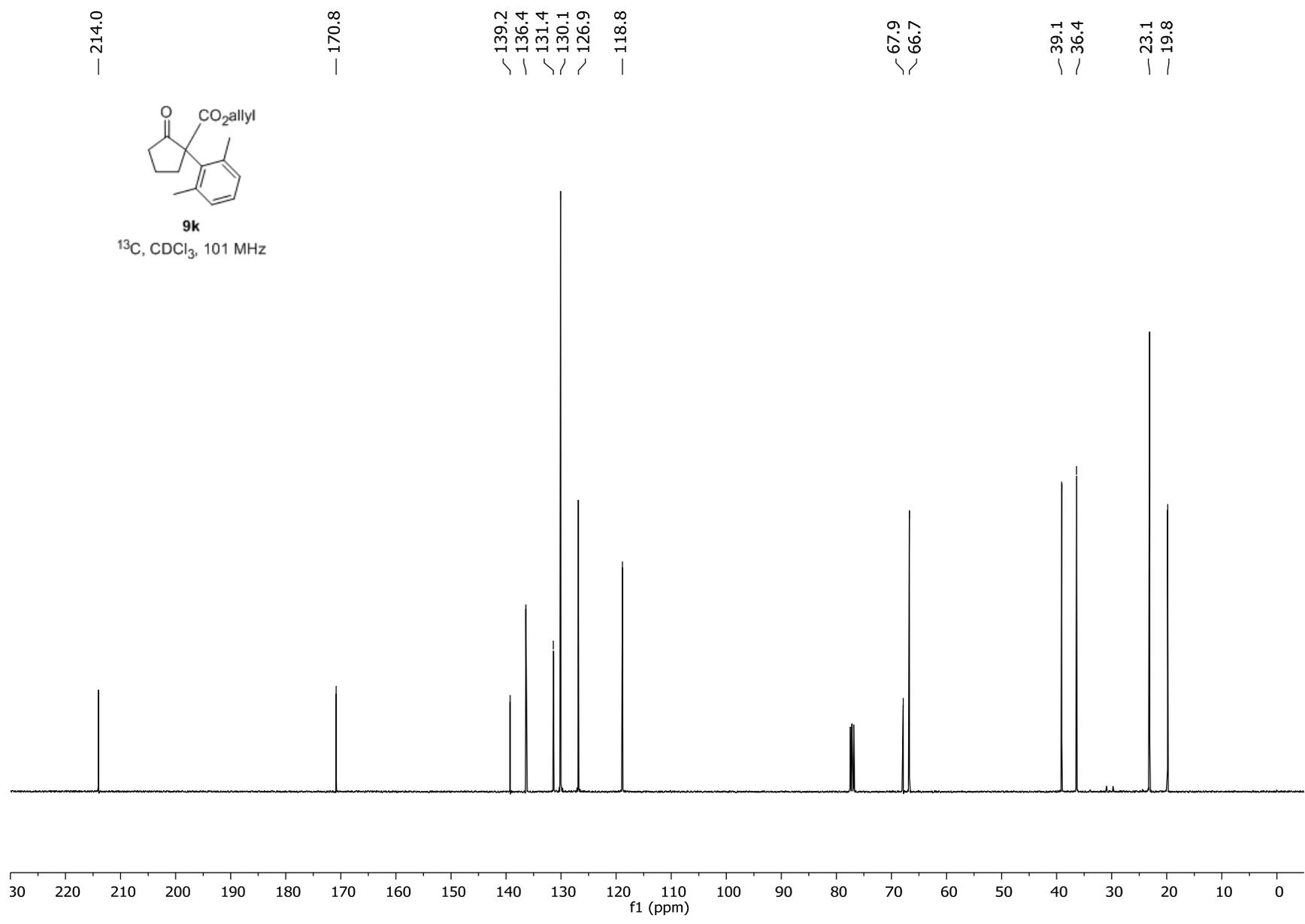


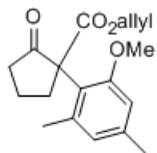


9k

^1H , CDCl_3 , 400 MHz

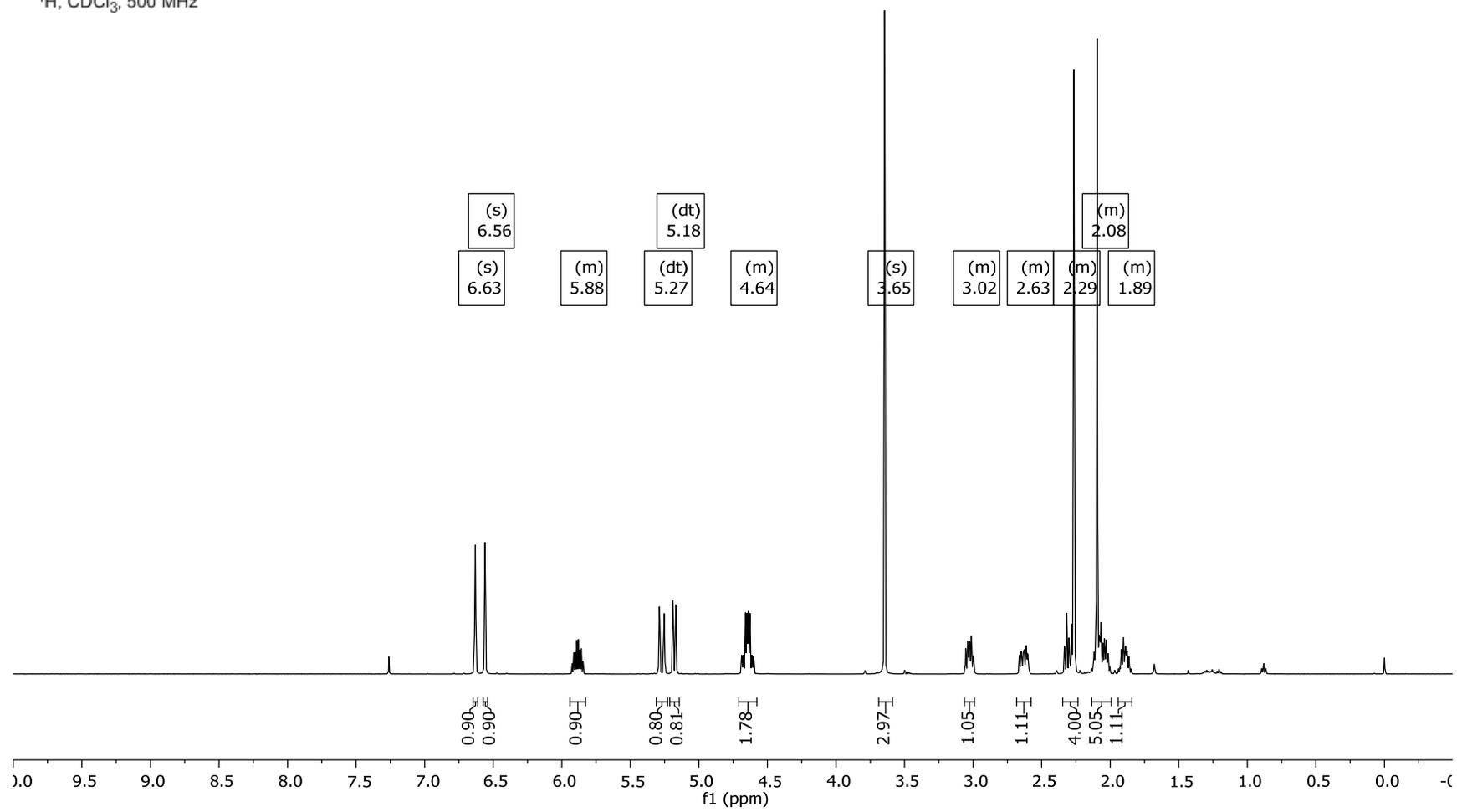






9j

¹H, CDCl₃, 500 MHz



— 211.9

— 171.2

— 156.4

— 137.8
— 137.7

— 131.9

— 127.3

— 126.1

— 118.6

— 111.9

— 66.5

— 64.0

— 55.9

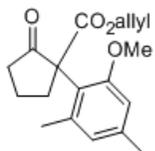
— 38.7

— 36.4

— 21.2

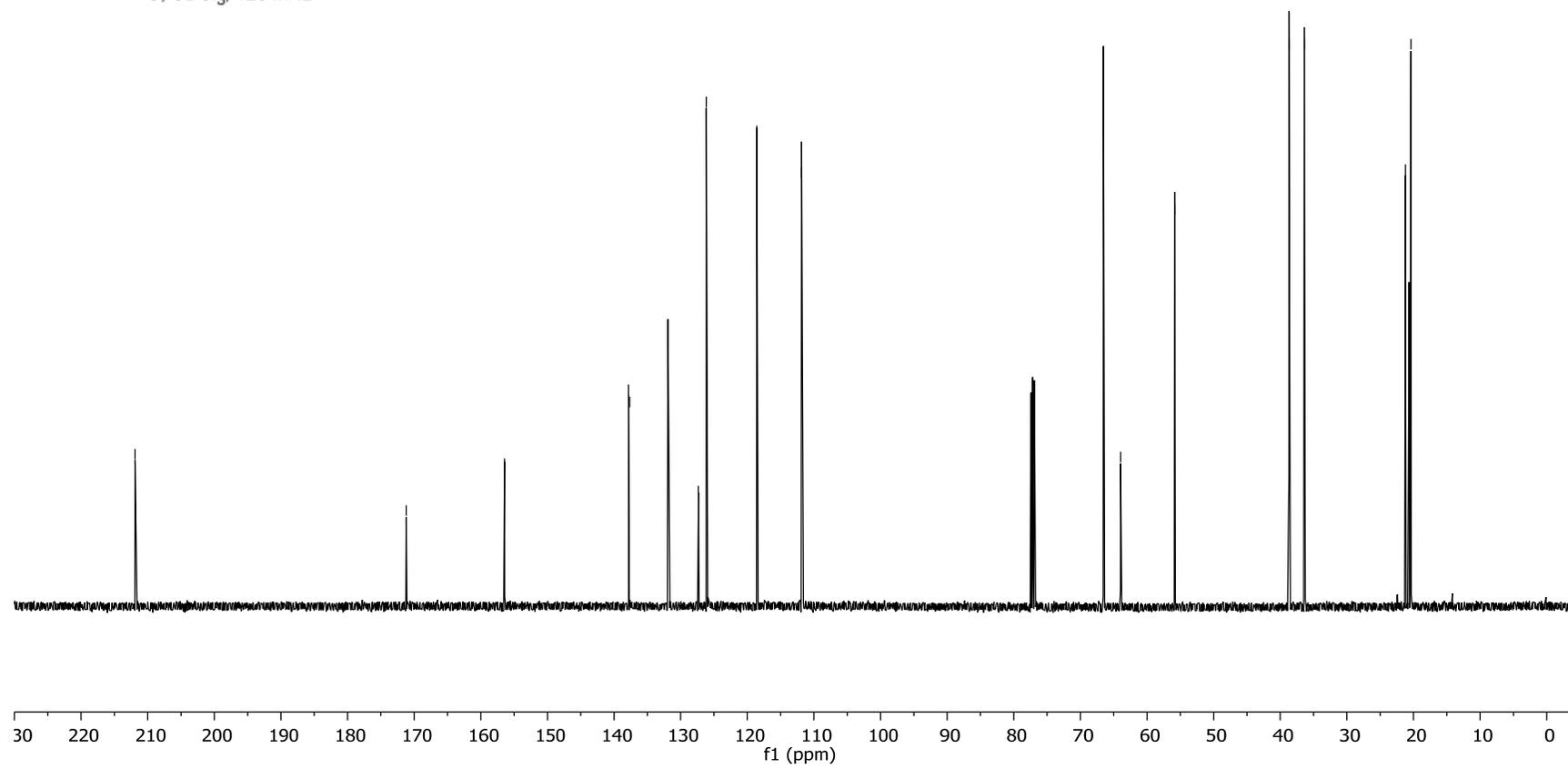
— 20.7

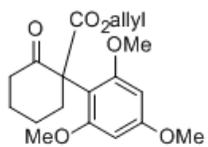
— 20.4



9j

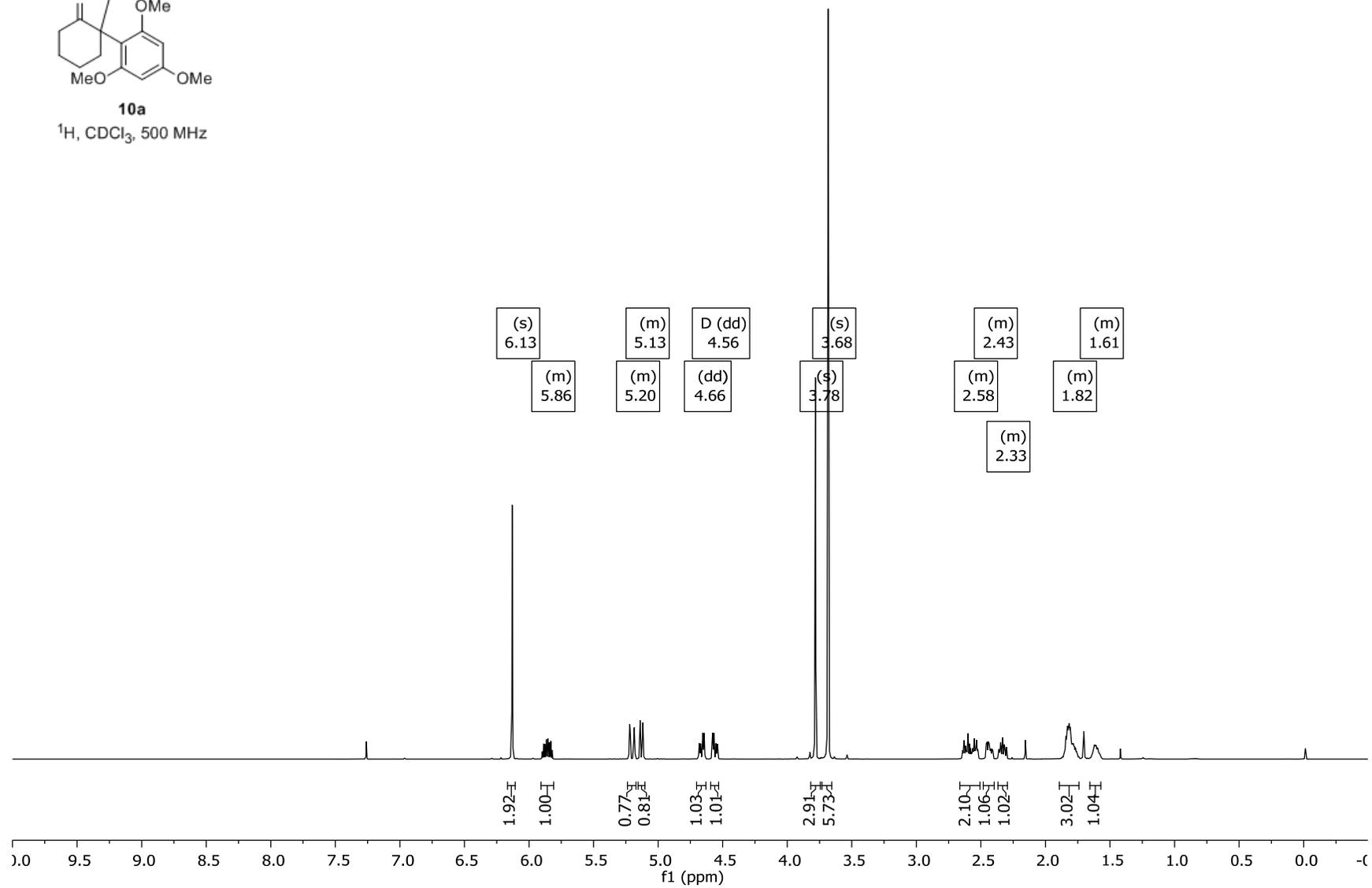
¹³C, CDCl₃, 126 MHz

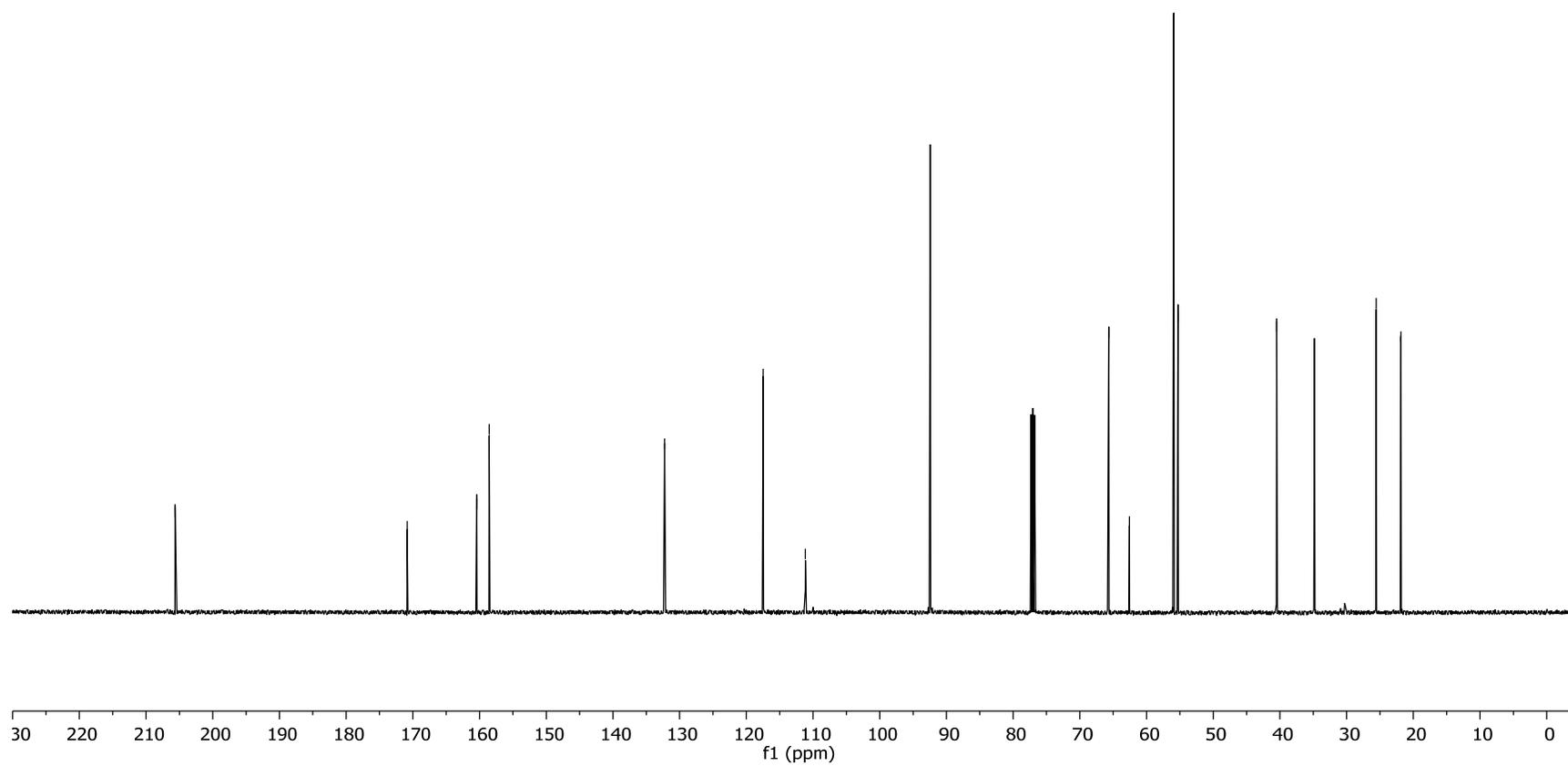
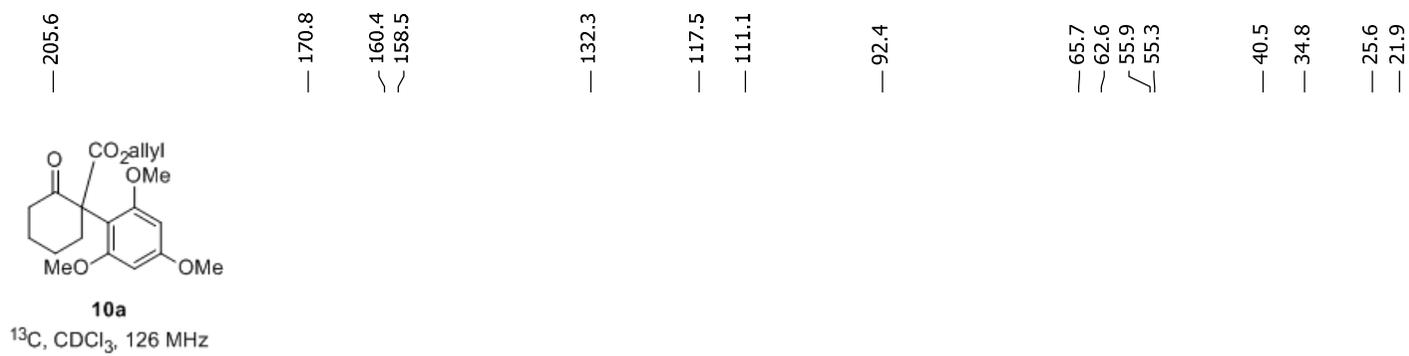


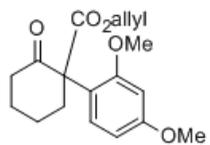


10a

^1H , CDCl_3 , 500 MHz

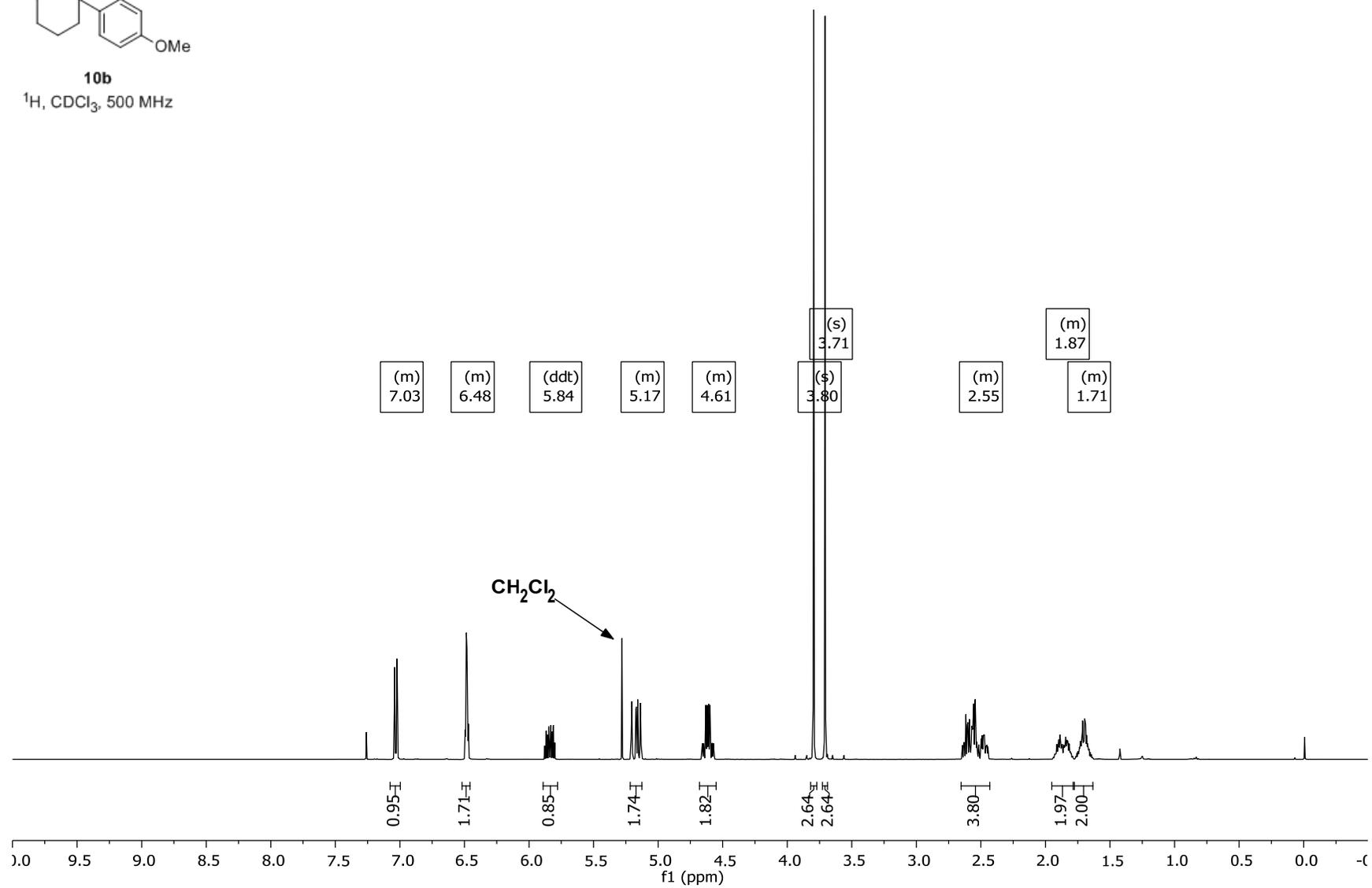


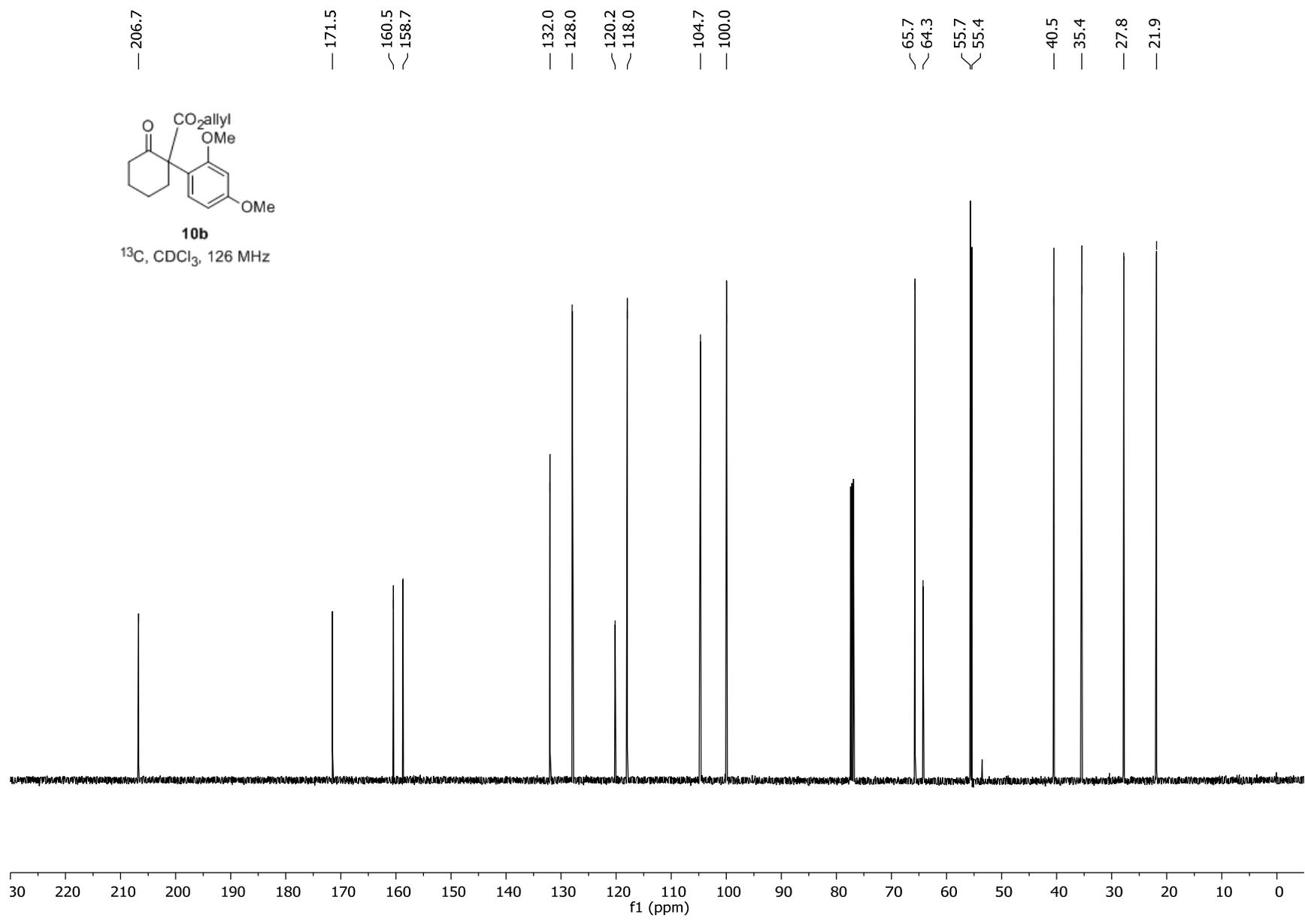


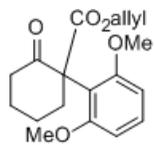


10b

^1H , CDCl_3 , 500 MHz

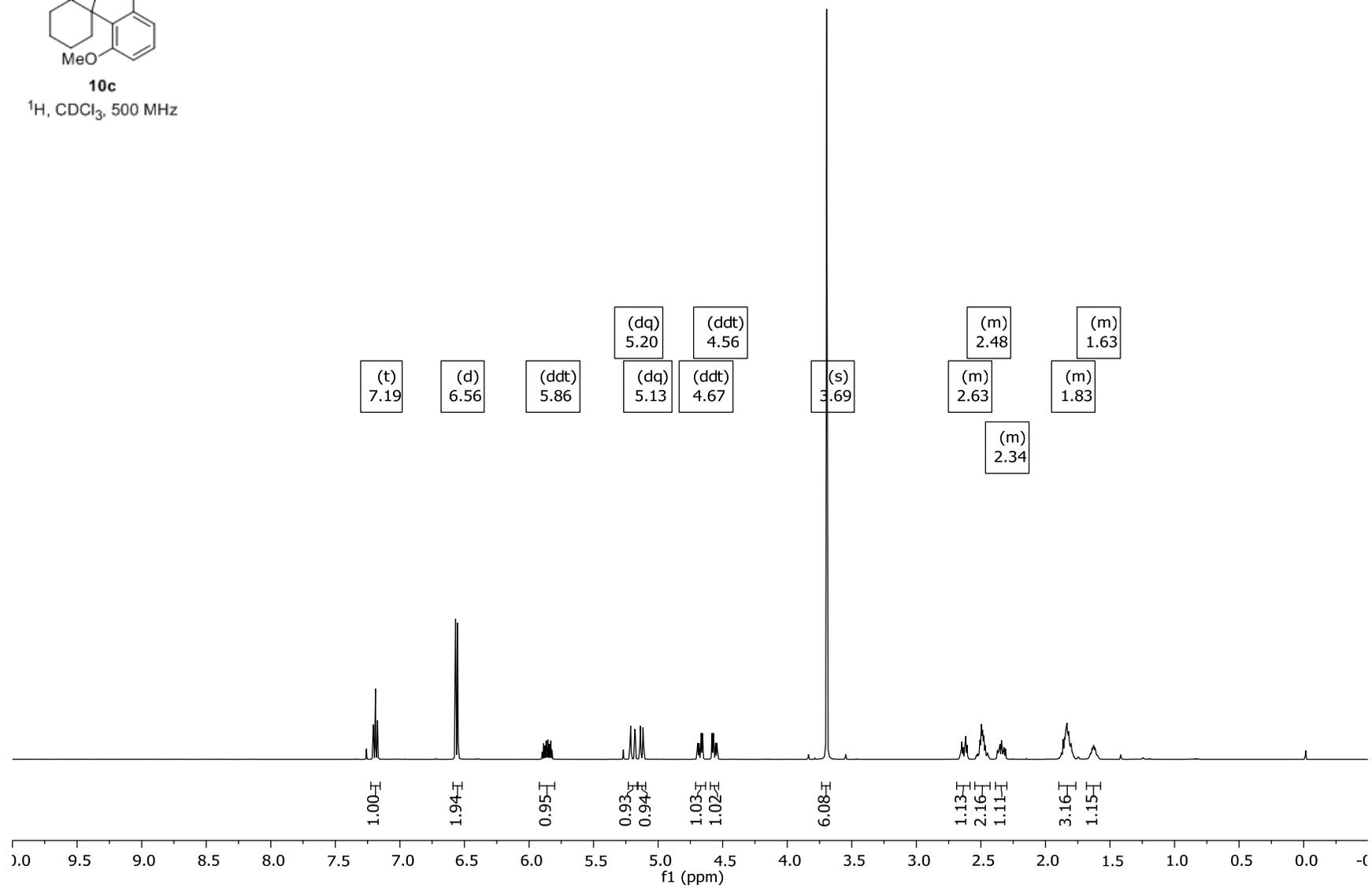


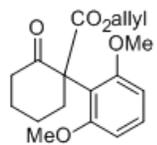




10c

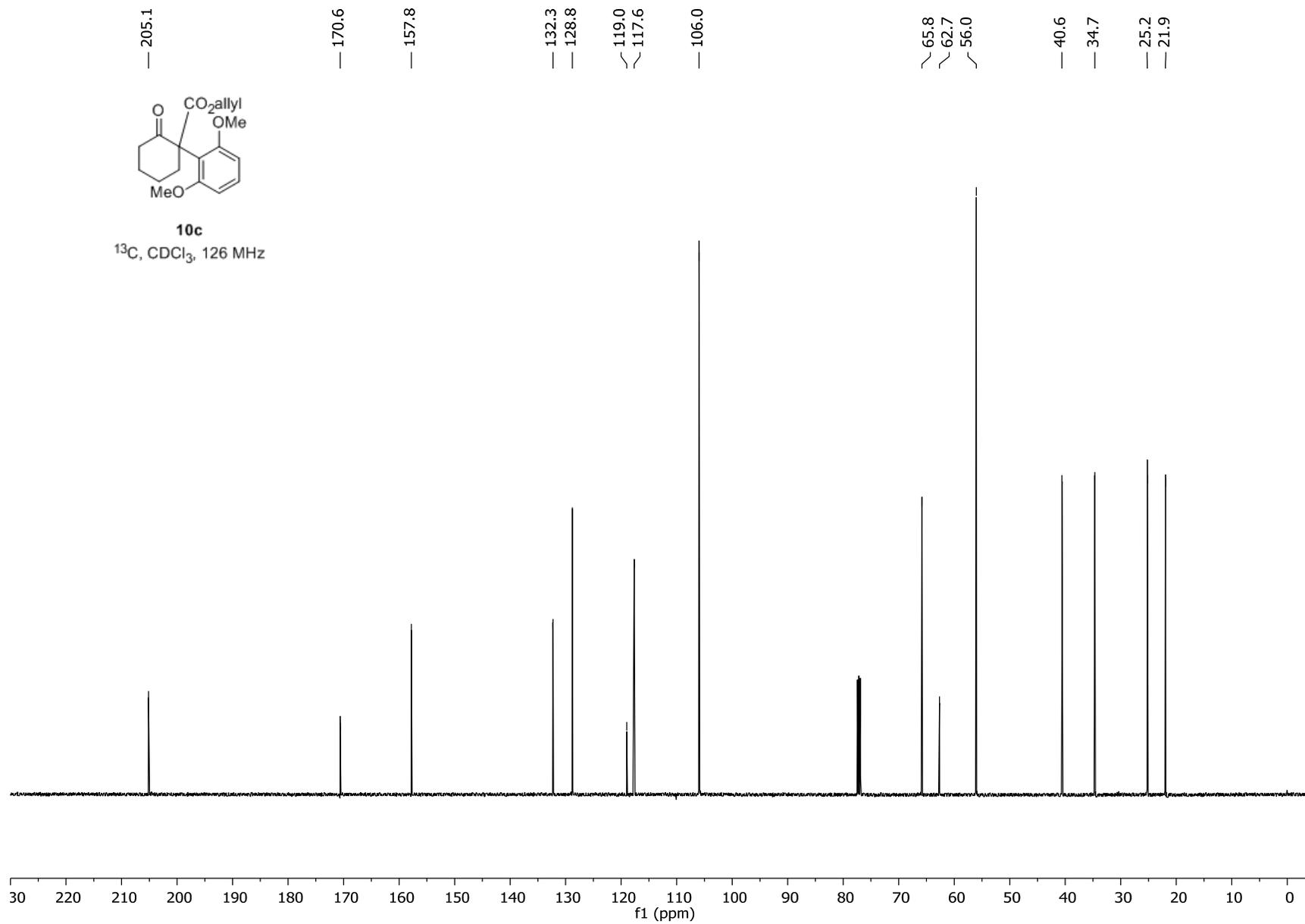
¹H, CDCl₃, 500 MHz

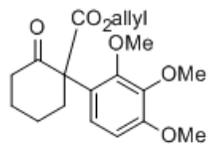




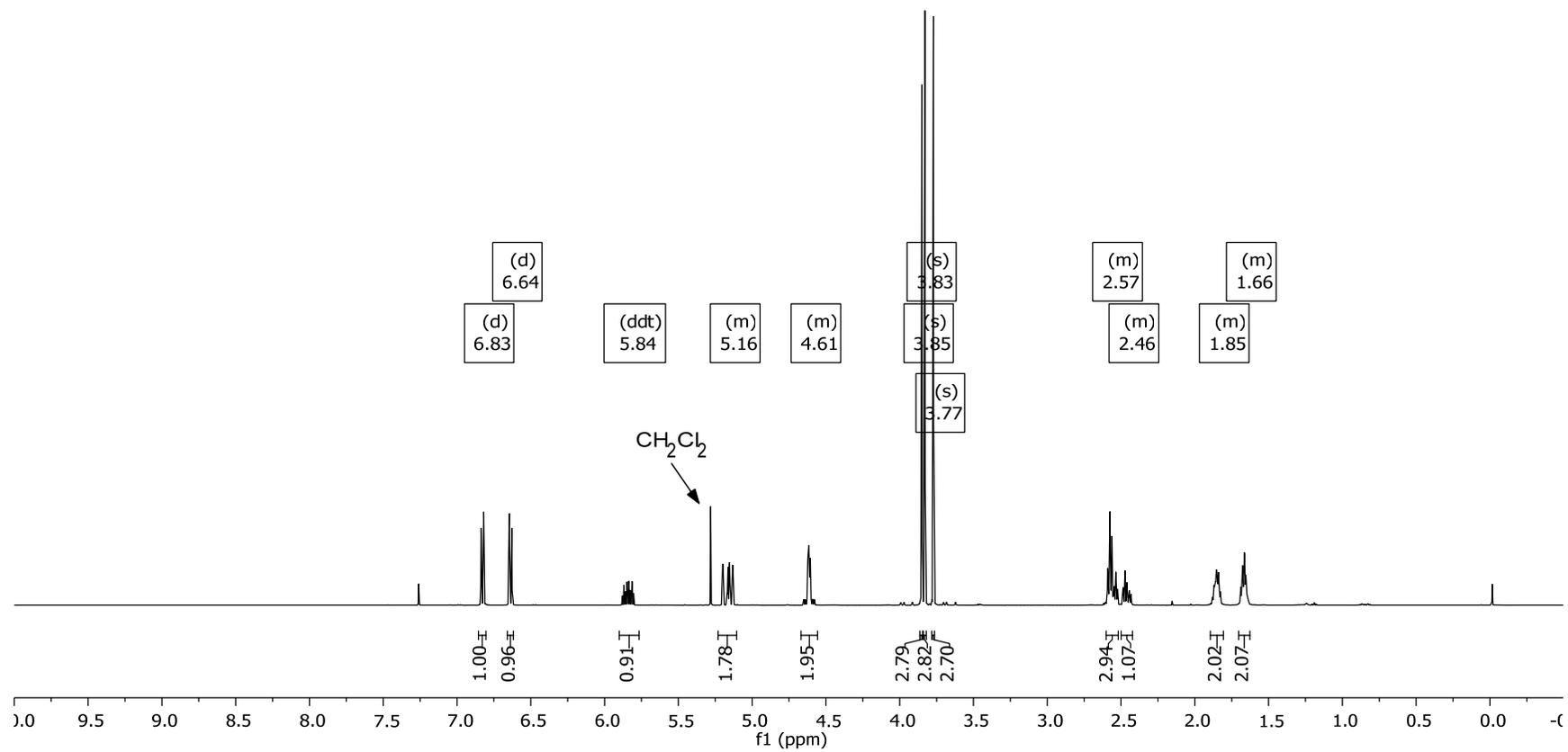
10c

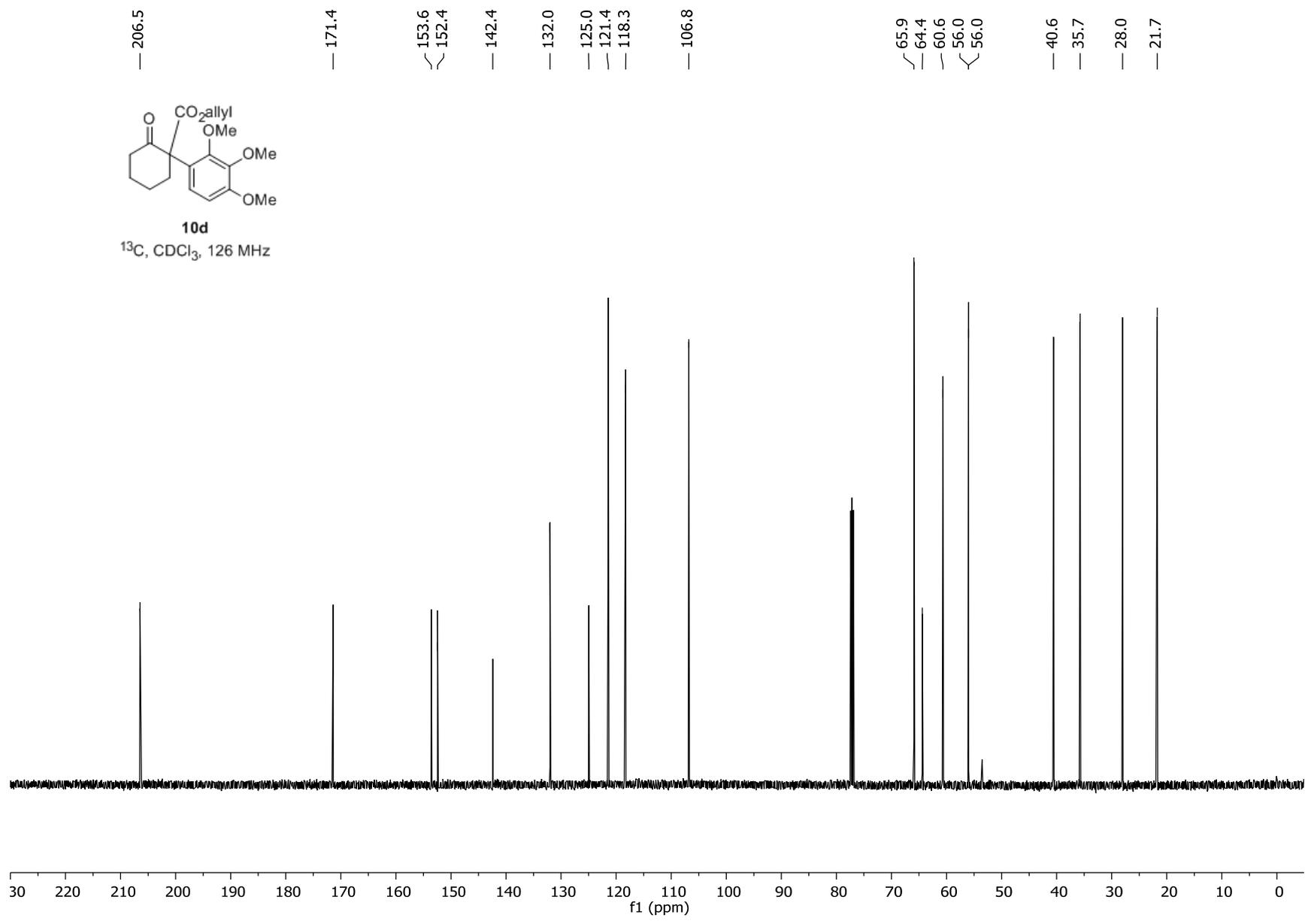
^{13}C , CDCl_3 , 126 MHz

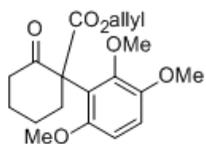




10d
 ^1H , CDCl_3 , 500 MHz

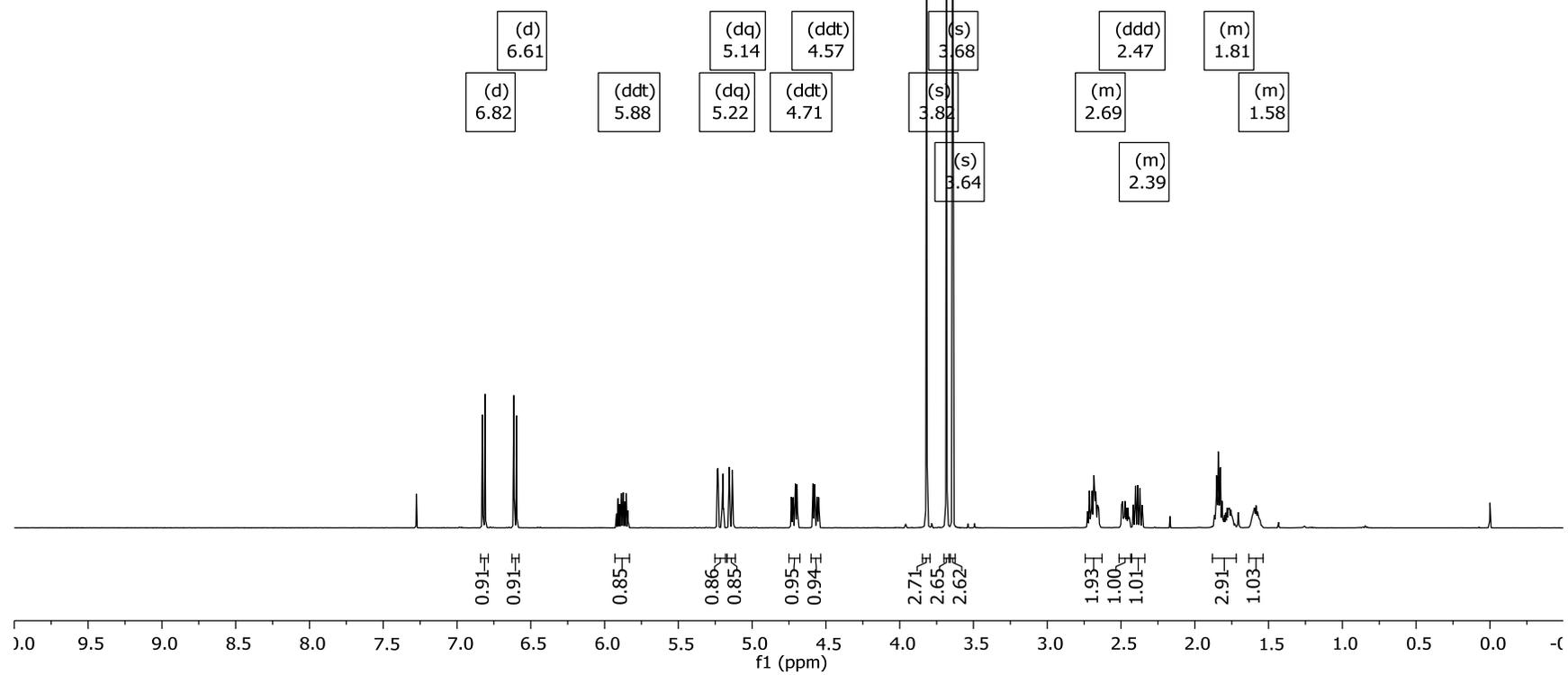


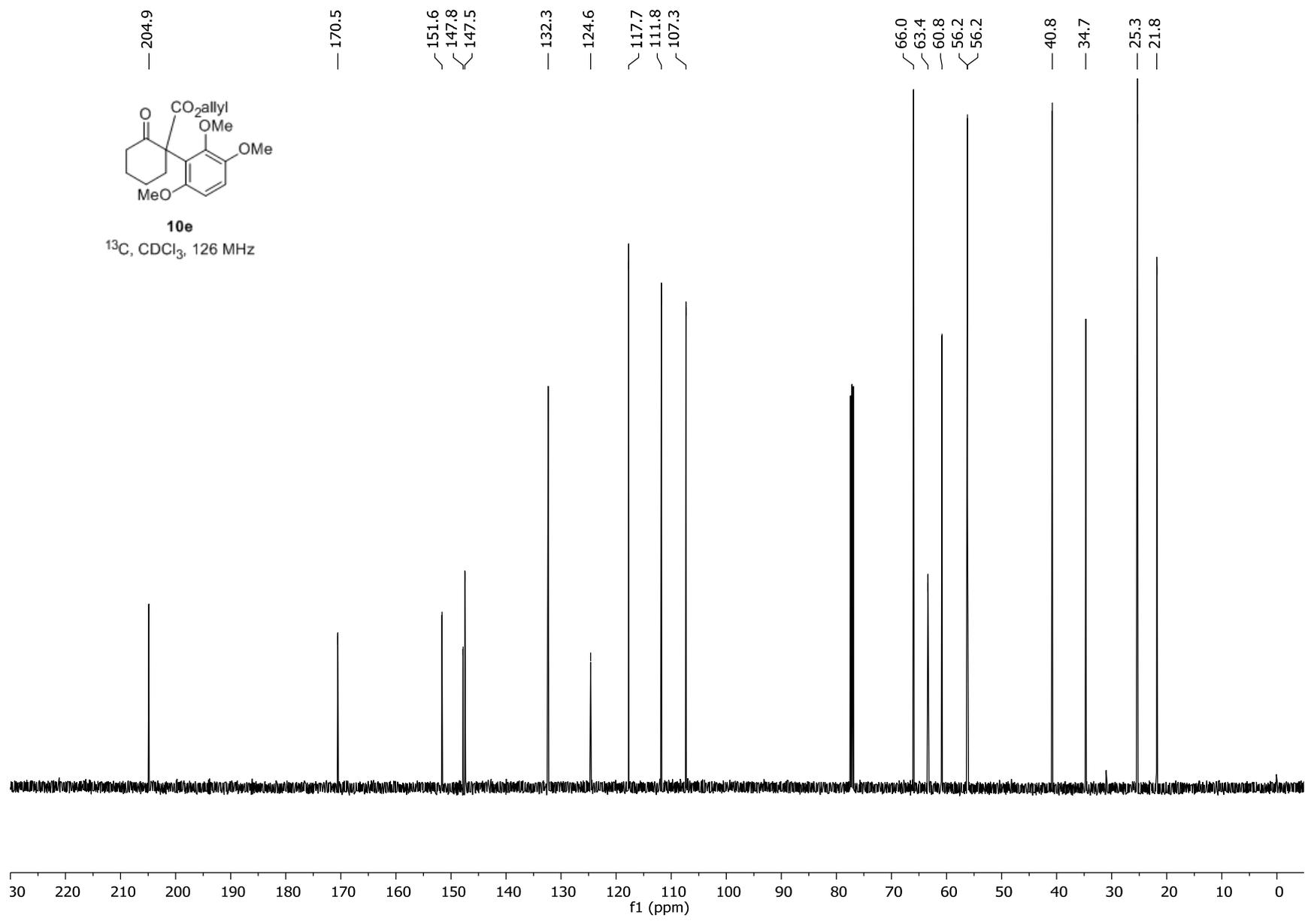


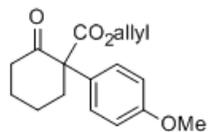


10e

¹H, CDCl₃, 500 MHz

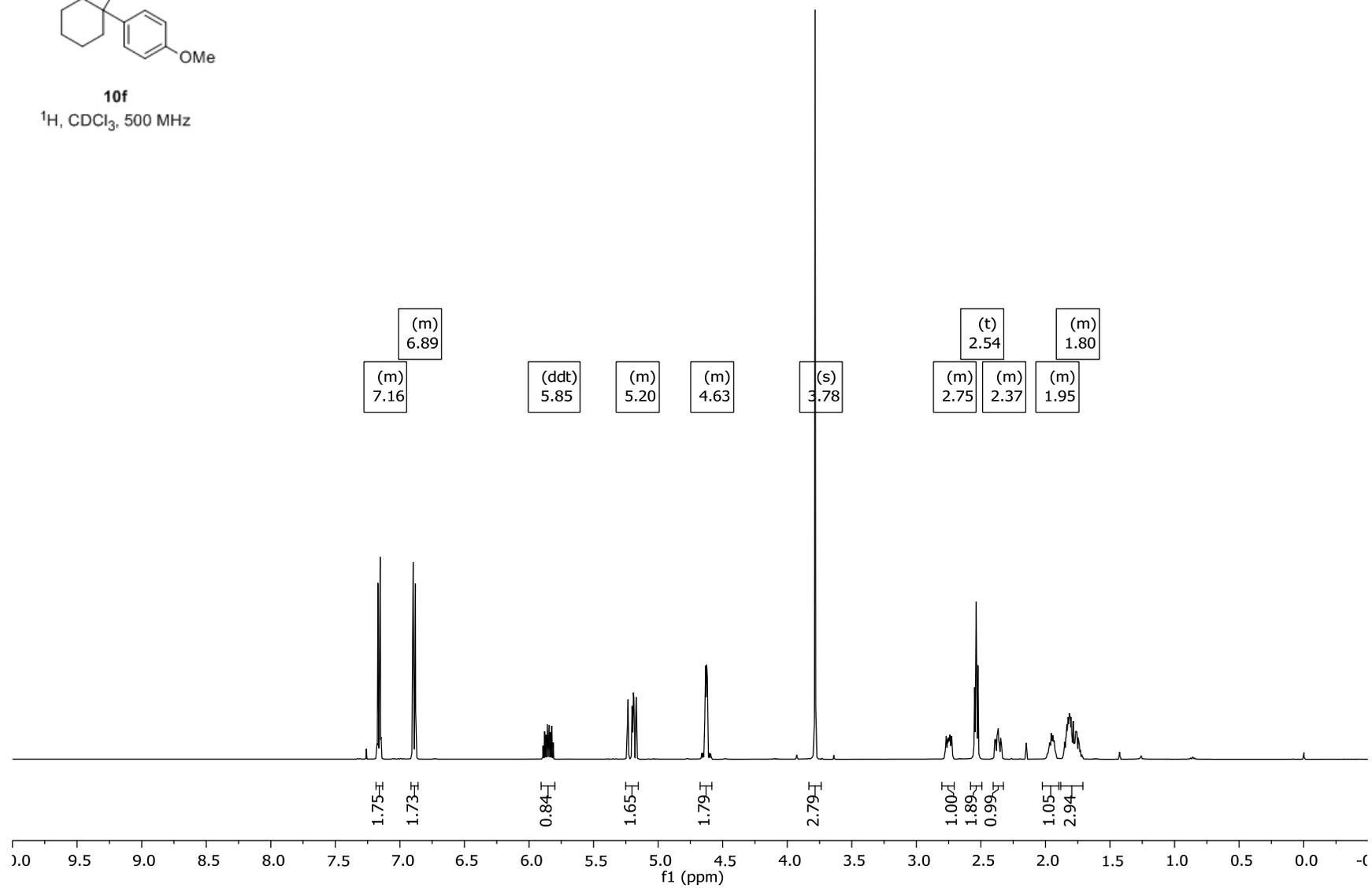


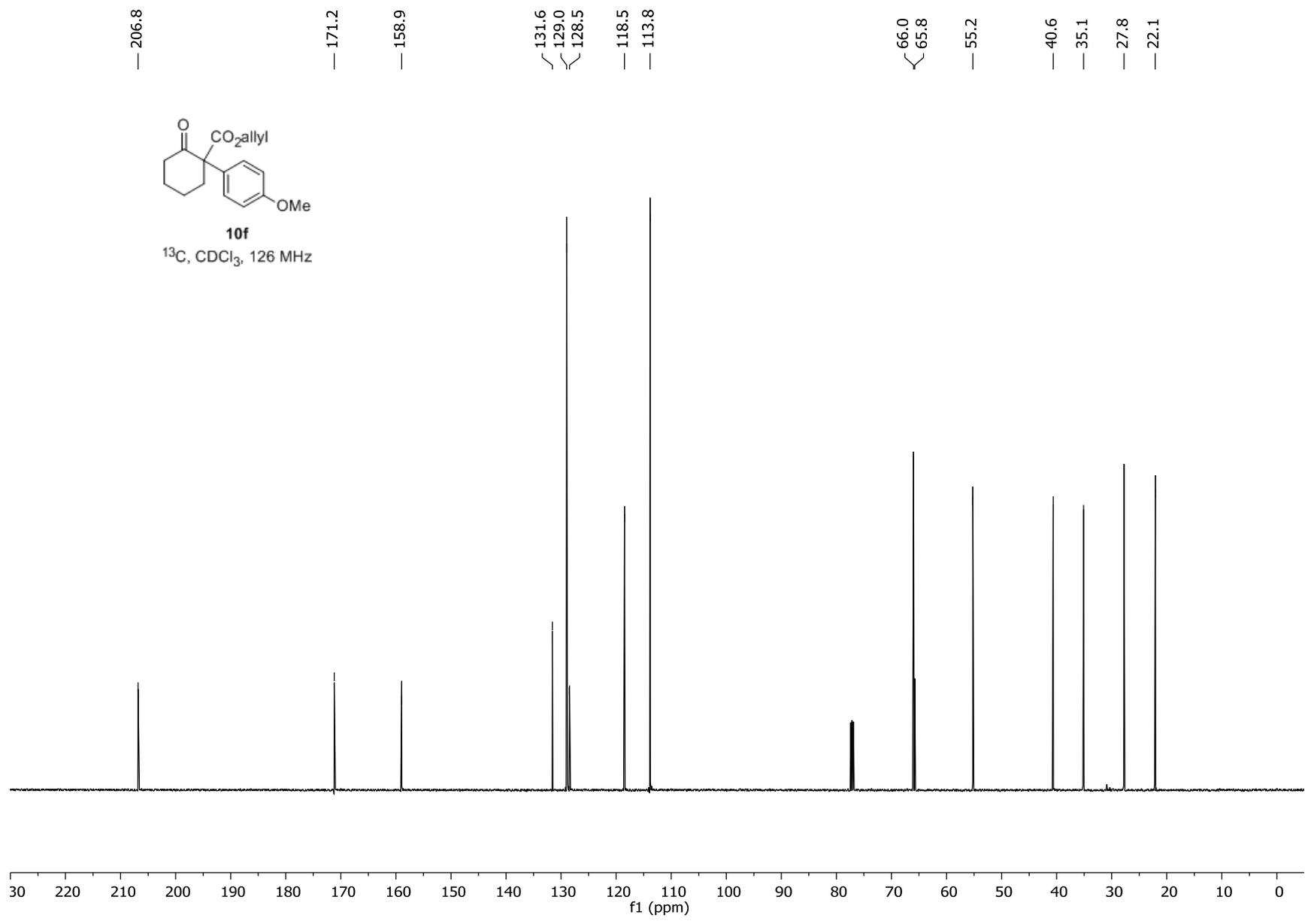


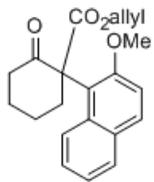


10f

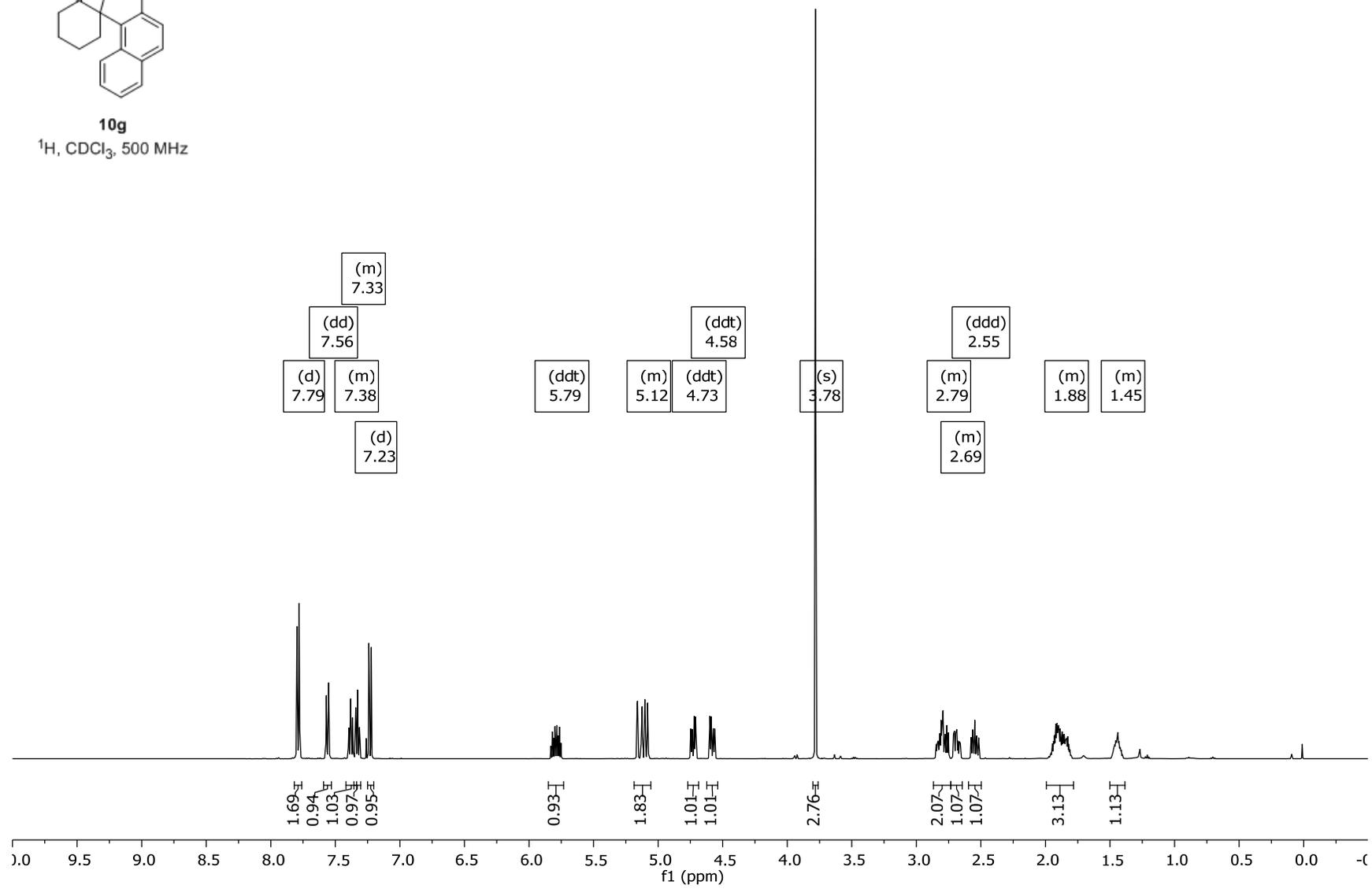
¹H, CDCl₃, 500 MHz







10g
 ^1H , CDCl_3 , 500 MHz



— 205.8

— 171.9

— 154.7

132.0
131.9
130.8
130.4
129.2
126.0
124.4
123.6
123.2
118.1
115.9

77.4
77.2
76.9

66.2
64.6

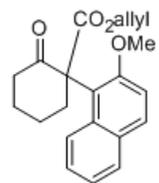
— 57.5

— 40.7

— 35.3

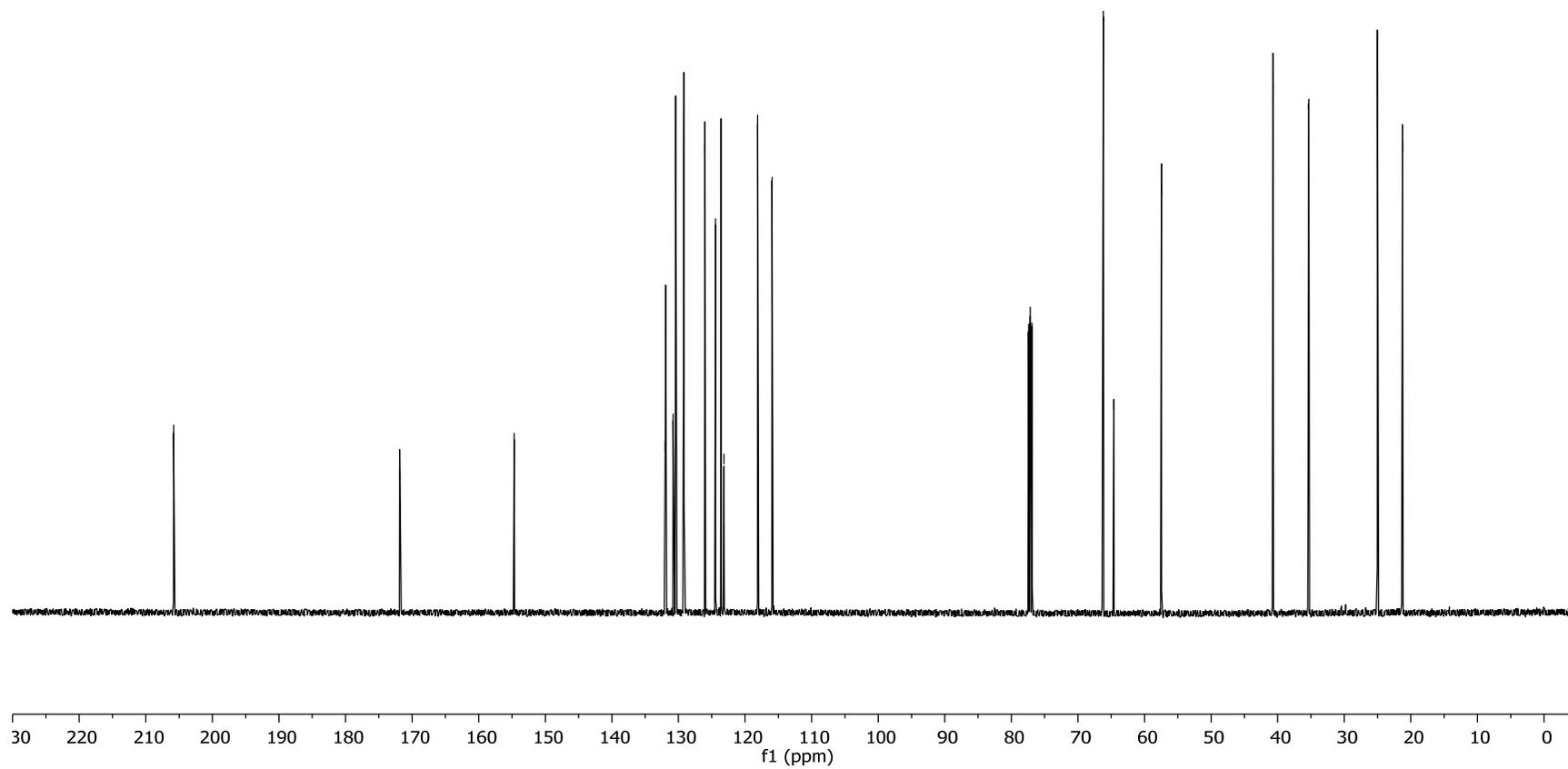
— 25.0

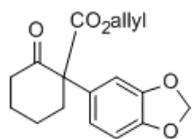
— 21.3



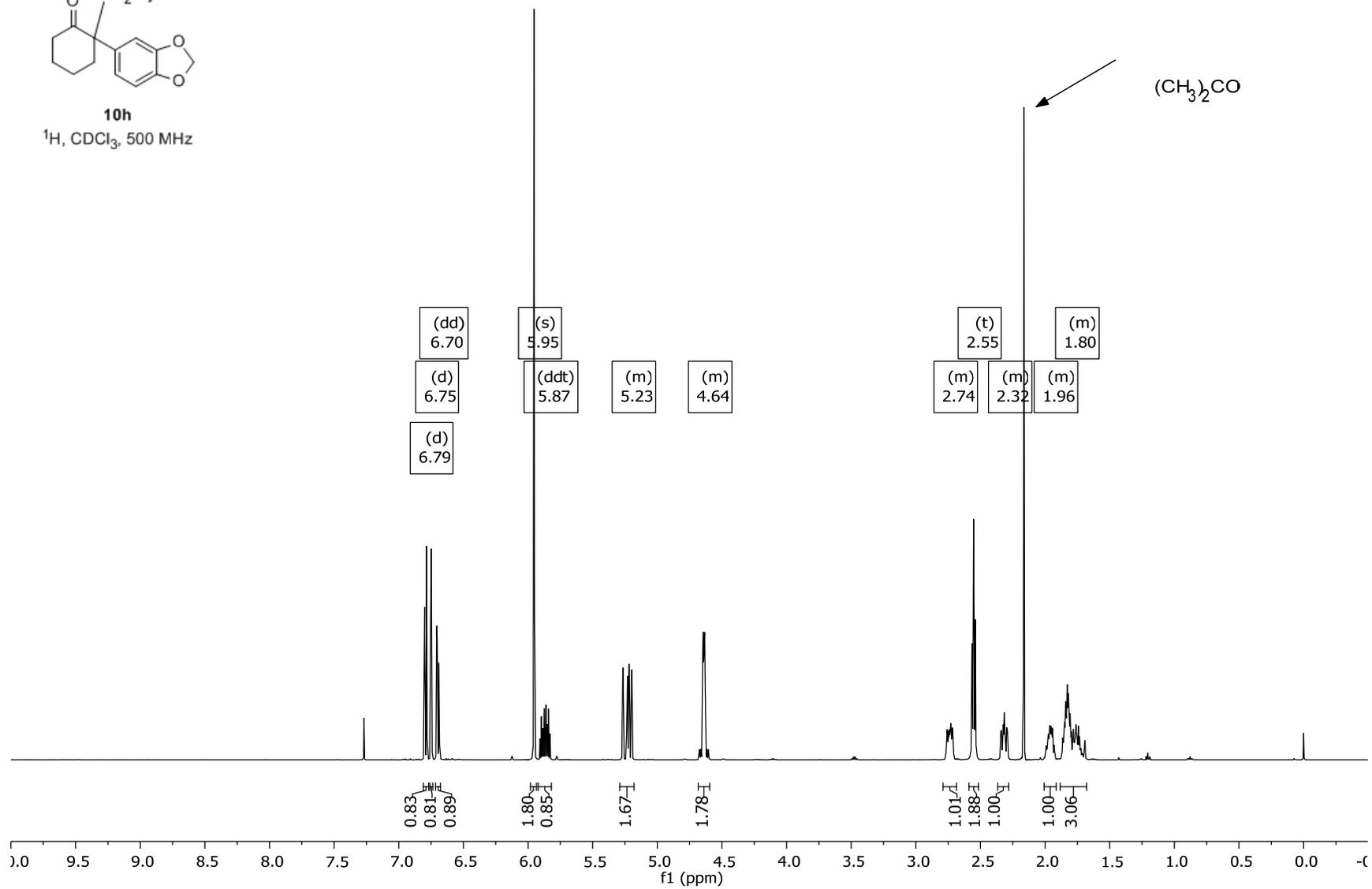
10g

¹³C, CDCl₃, 126 MHz





10h
¹H, CDCl₃, 500 MHz



— 206.7

— 171.1

— 147.9
— 147.1

— 131.6
— 130.2

— 121.2
— 118.8

— 108.7
— 108.2

— 101.3

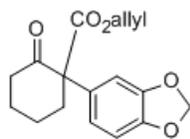
— 66.2
— 66.1

— 40.7

— 35.3

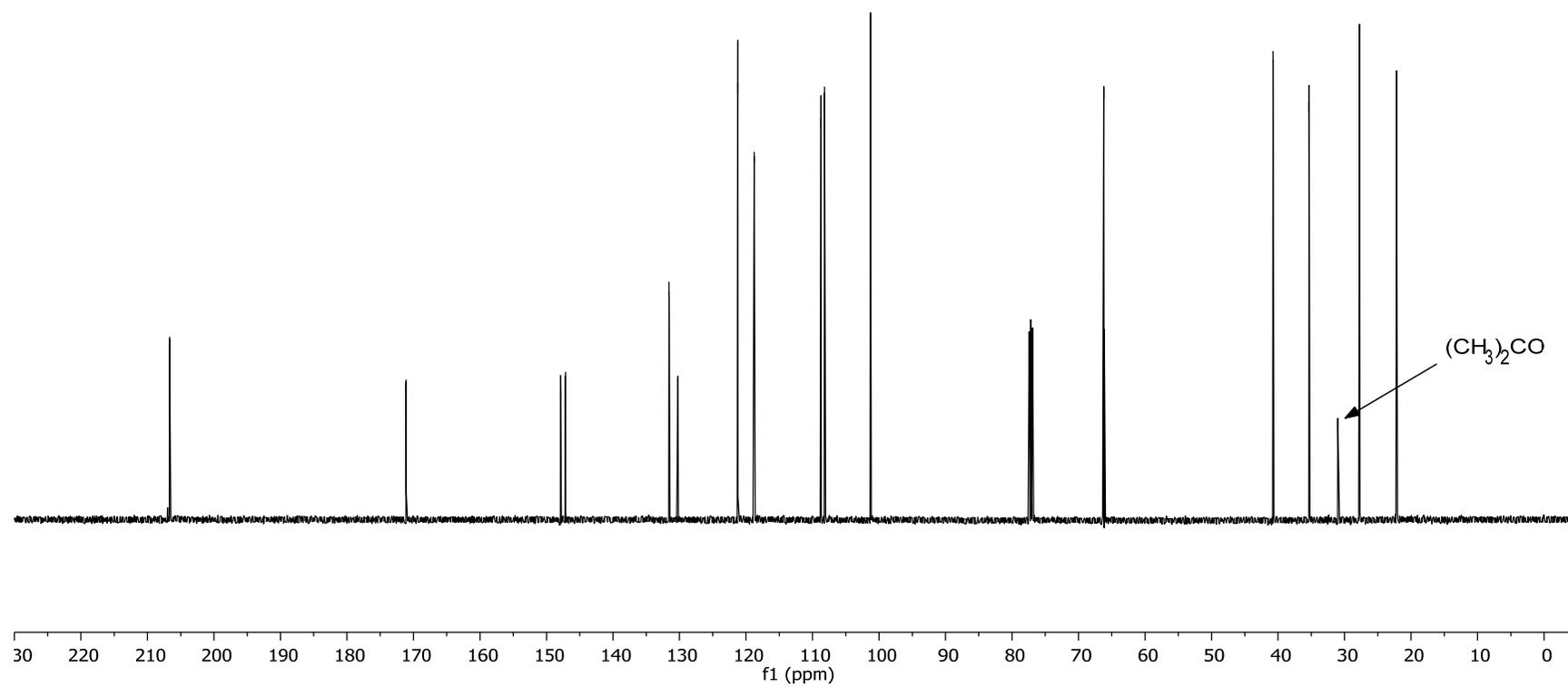
— 27.7

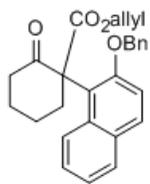
— 22.2



10h

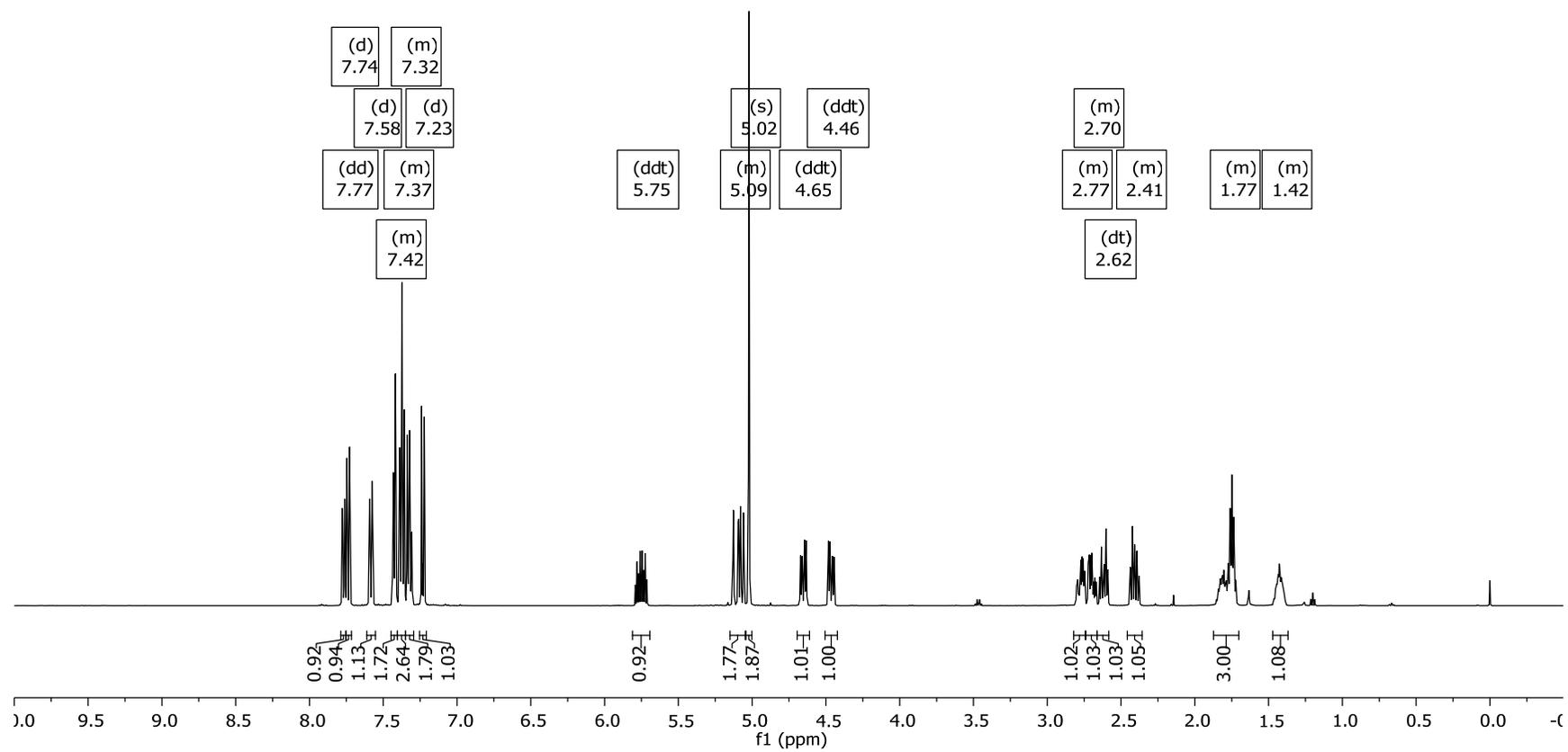
¹³C, CDCl₃, 126 MHz





10u

¹H, CDCl₃, 500 MHz



— 205.7

— 171.9

— 154.1
— 136.6
— 132.1
— 131.9
— 130.9
— 130.3
— 129.1
— 128.6
— 128.2
— 128.1
— 126.1
— 124.4
— 123.8
— 123.7
— 118.3
— 117.2

— 73.3

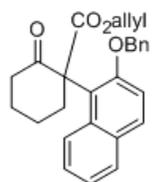
— 66.2
— 64.8

— 40.9

— 35.4

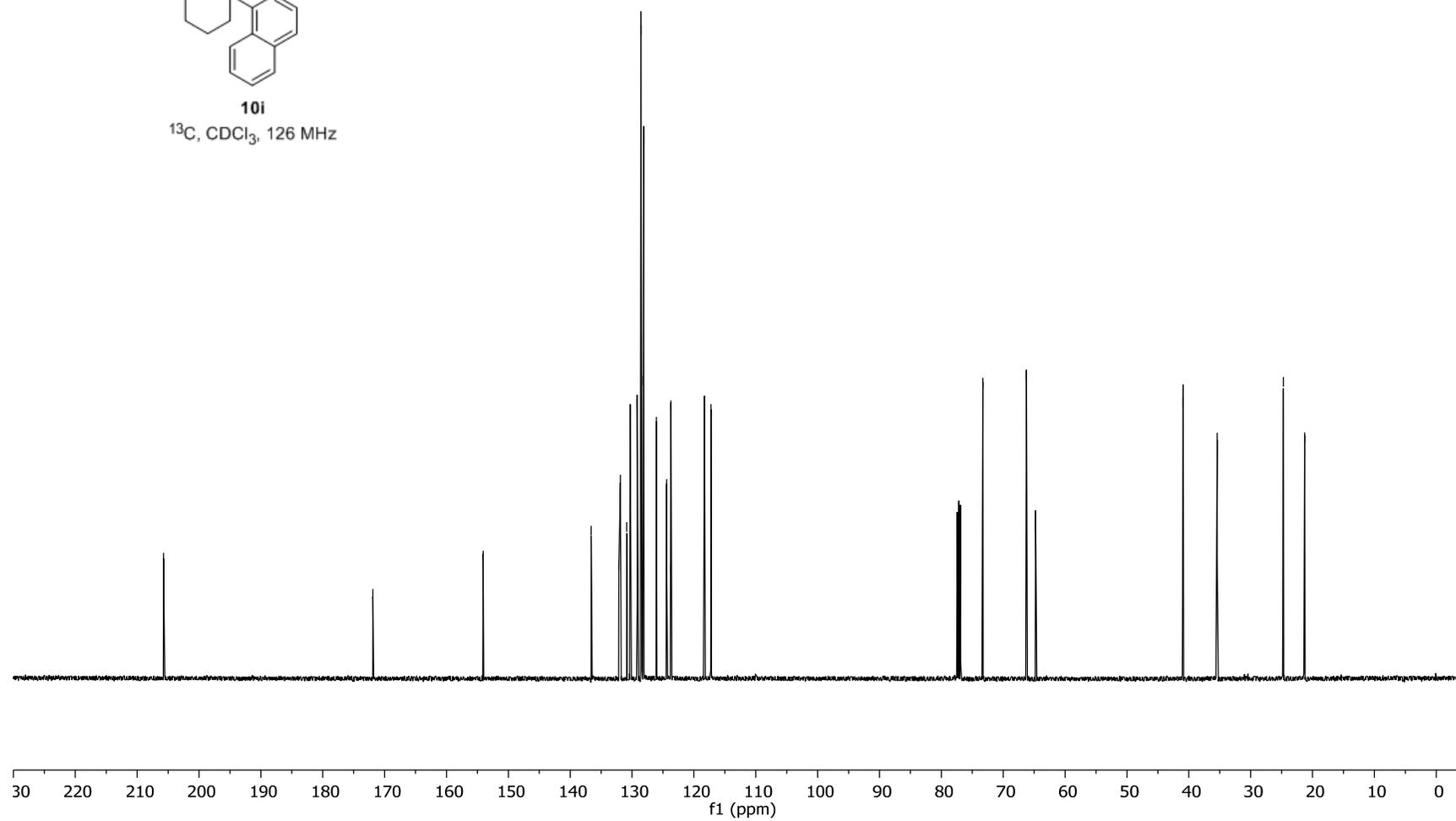
— 24.7

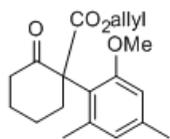
— 21.3



10i

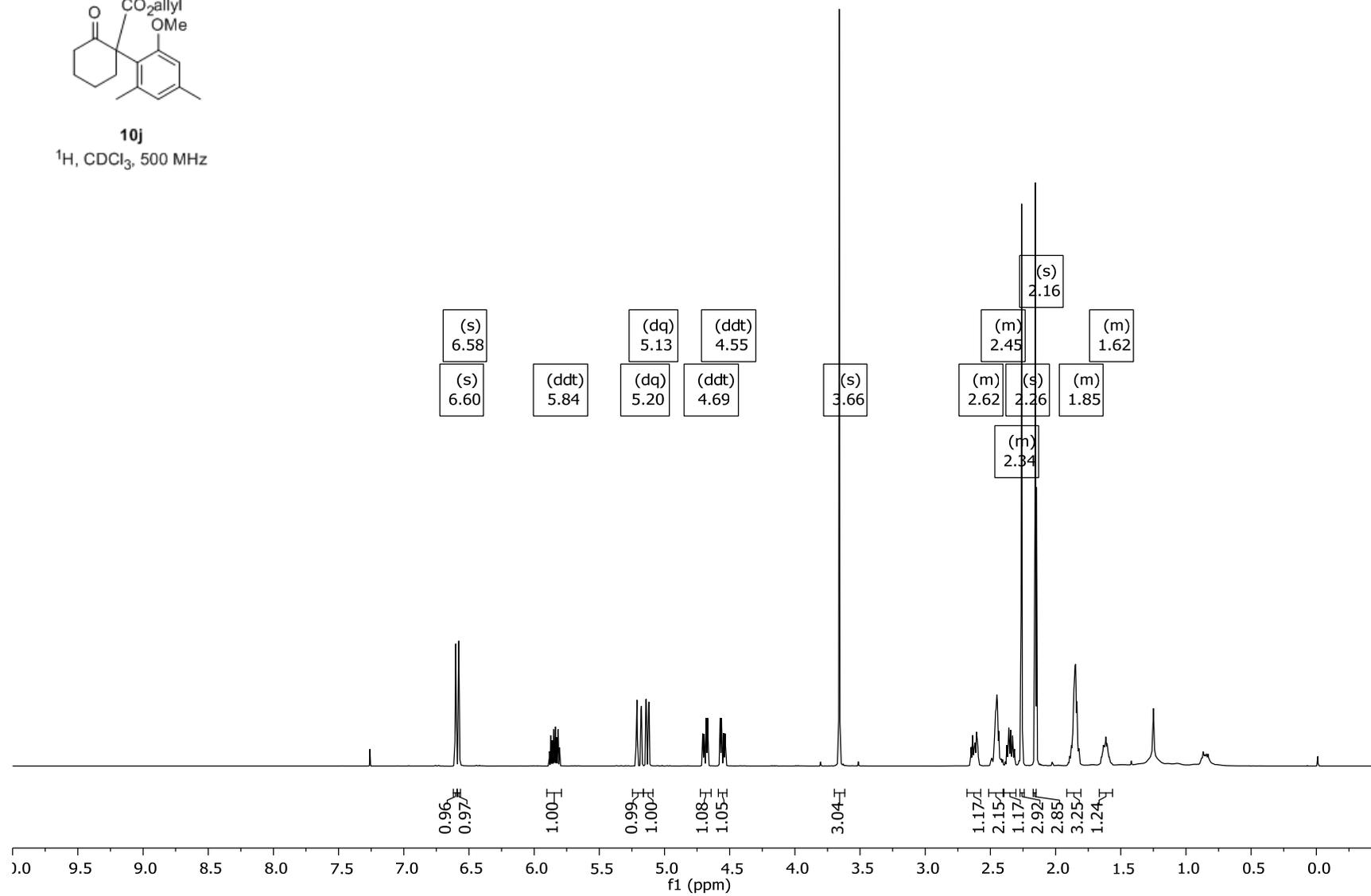
¹³C, CDCl₃, 126 MHz



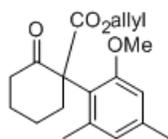


10j

¹H, CDCl₃, 500 MHz

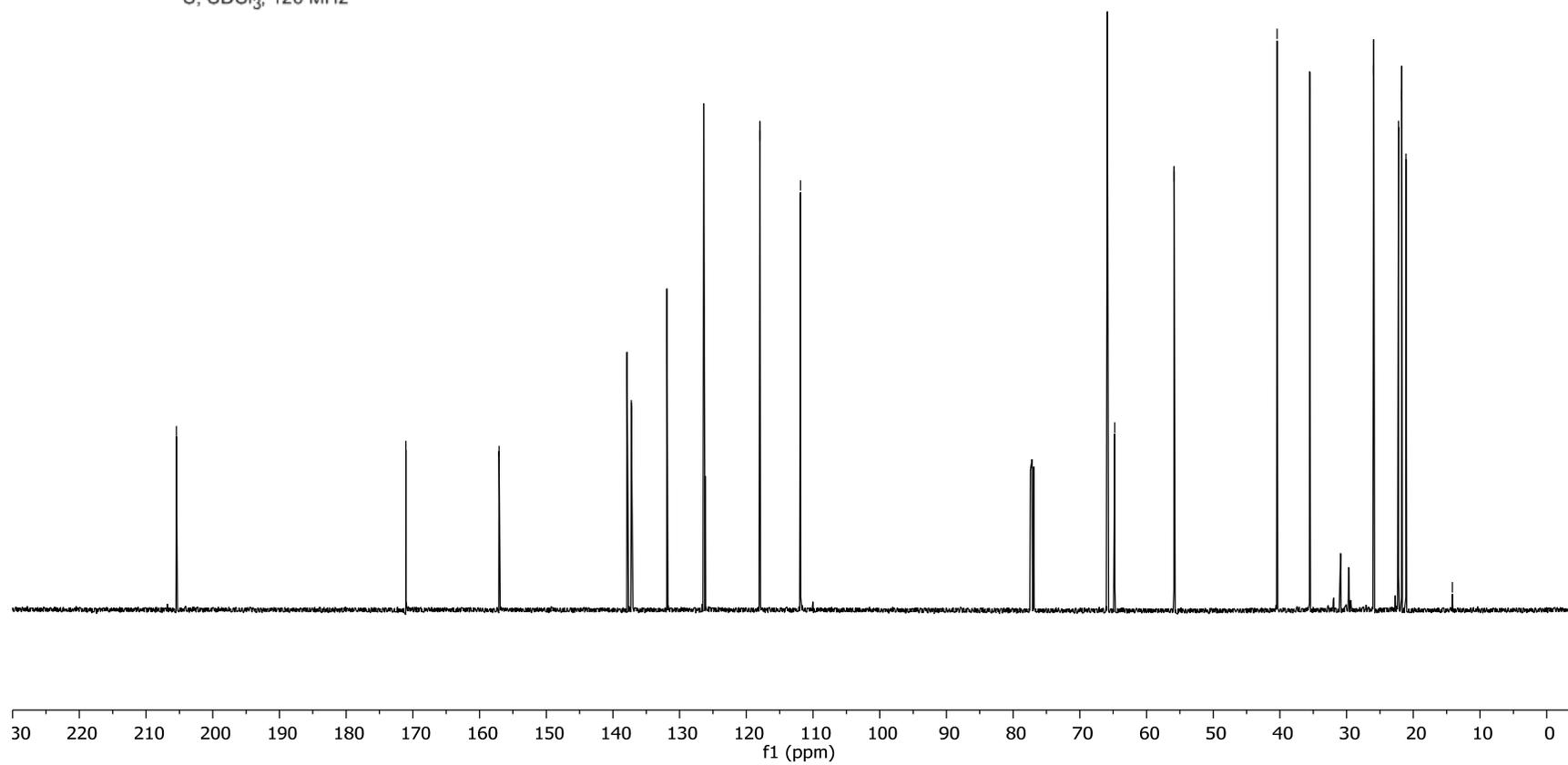


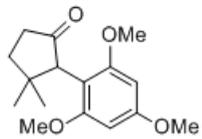
— 205.4
— 171.0
— 157.1
— 137.3
— 137.2
— 118.0
— 111.9
— 65.9
— 64.8
— 55.9
— 40.4
— 35.5
— 25.9
— 22.2
— 21.7
— 21.1
— 14.1



10j

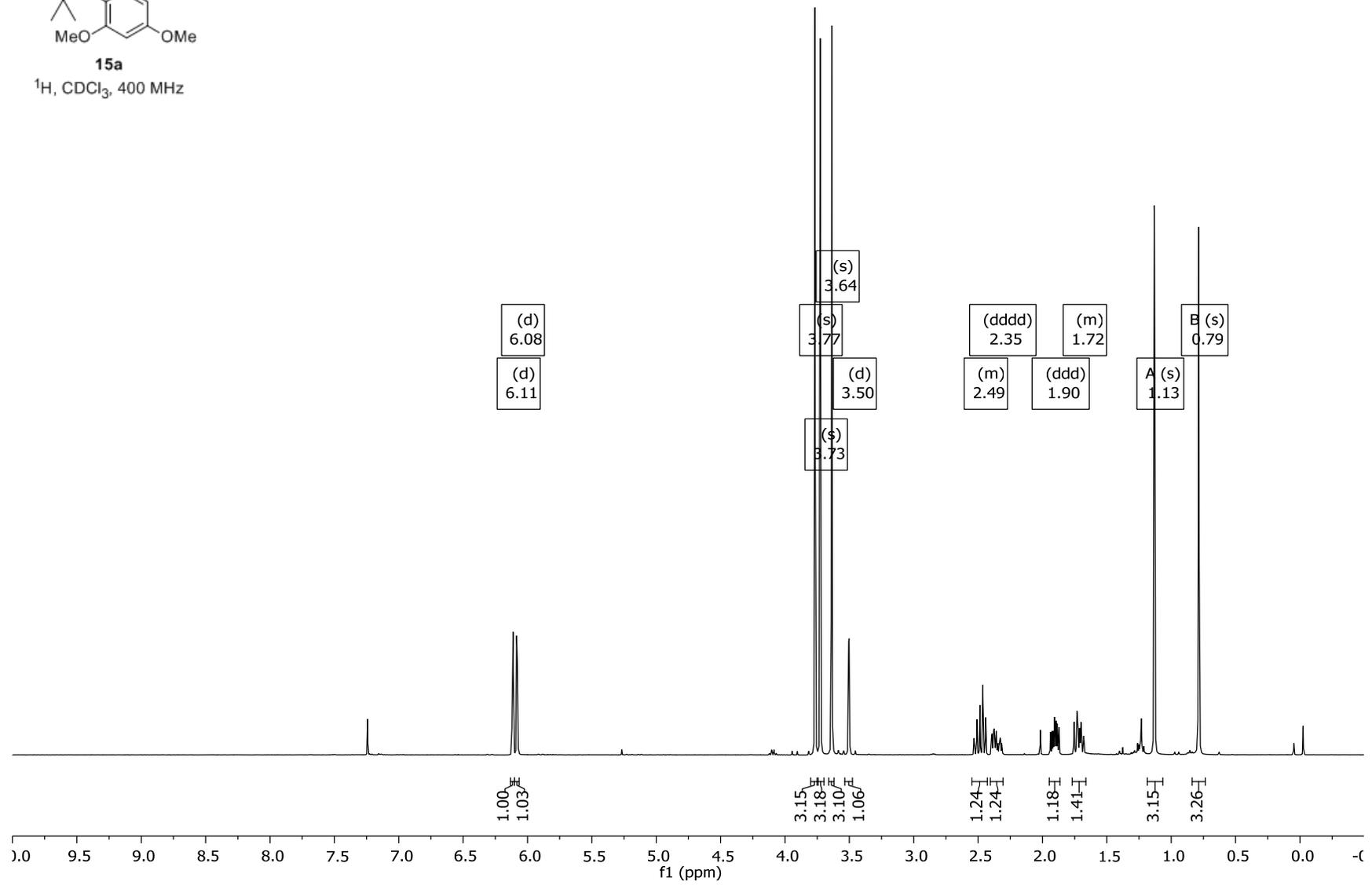
^{13}C , CDCl_3 , 126 MHz

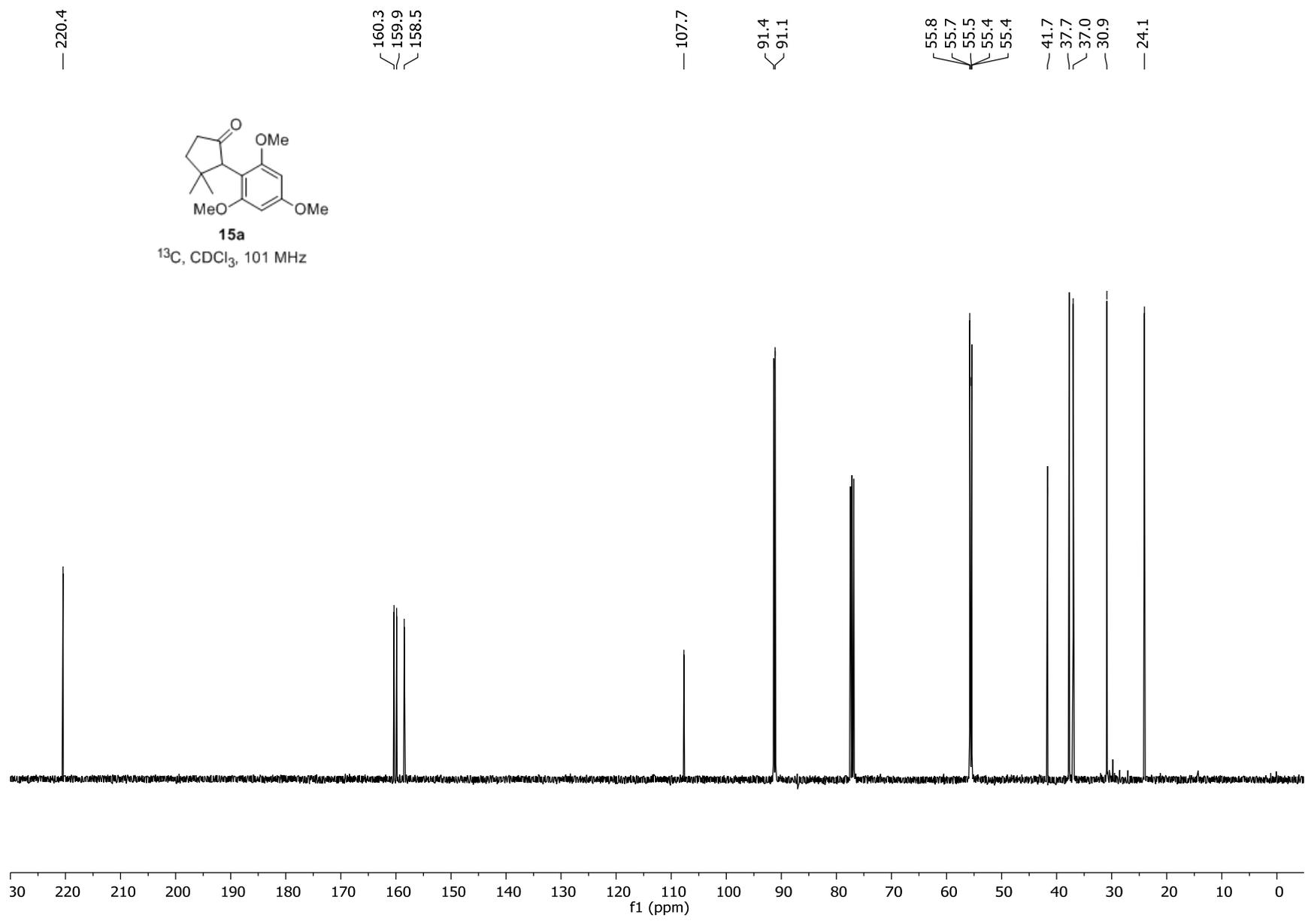


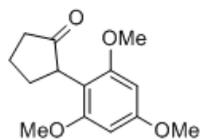


15a

¹H, CDCl₃, 400 MHz

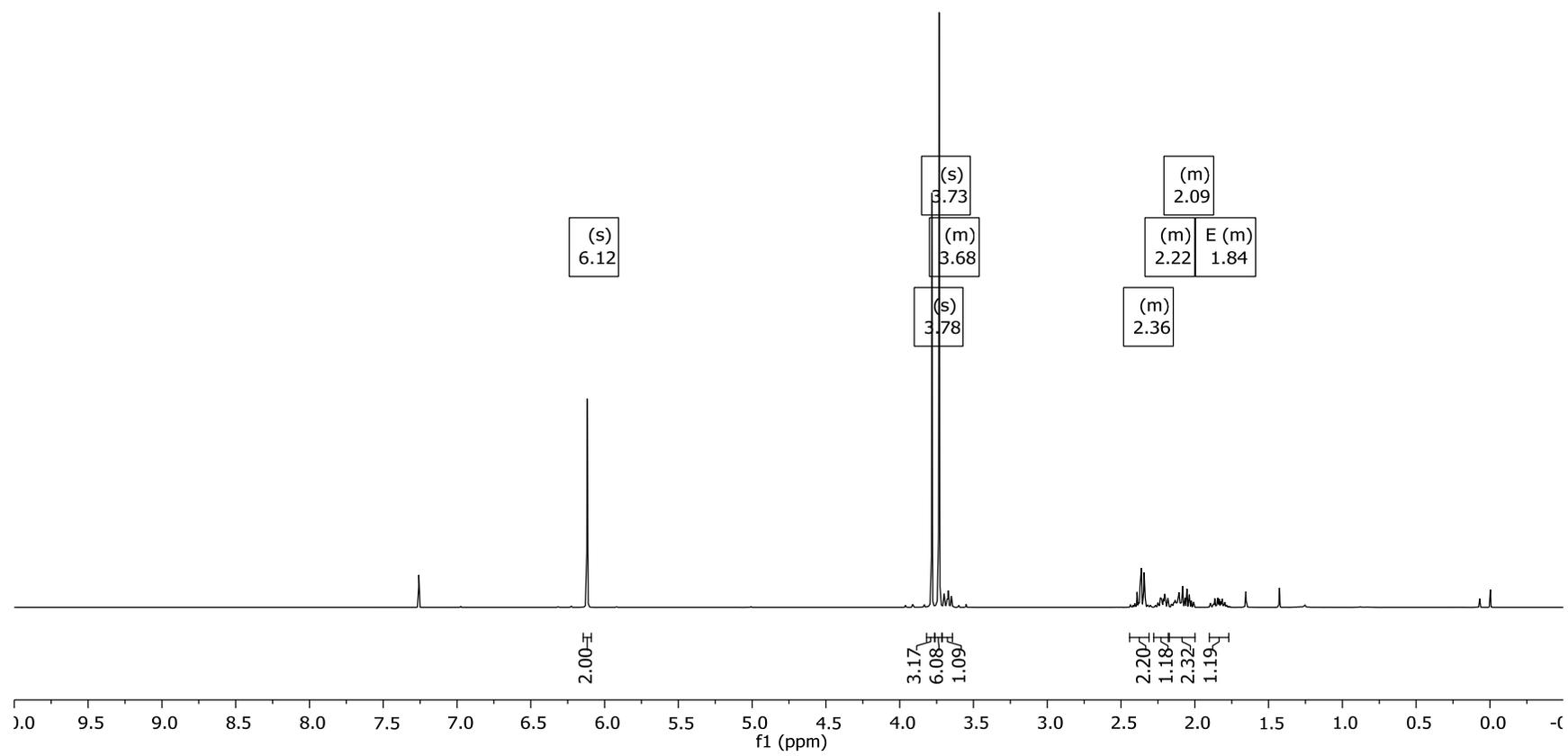


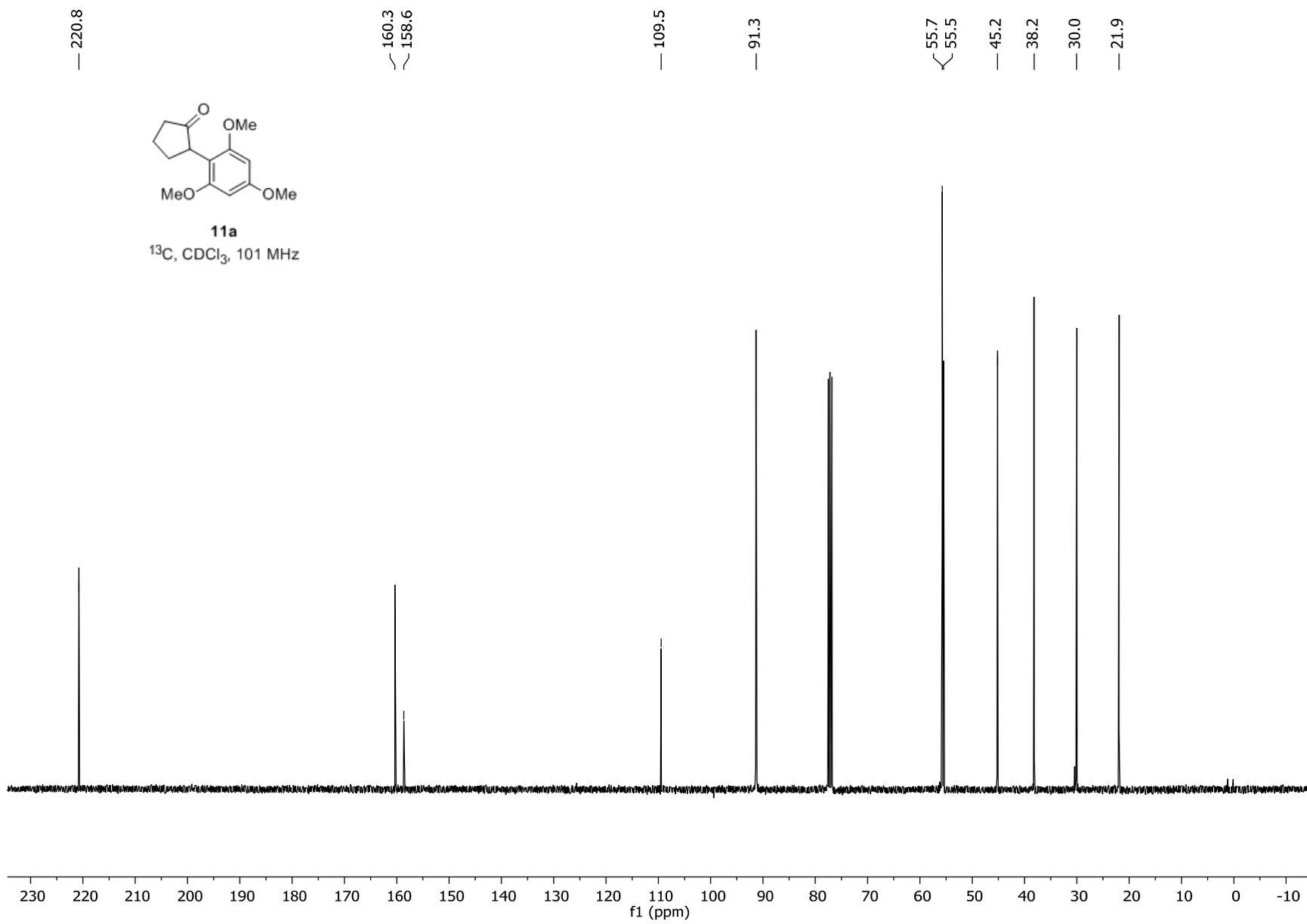


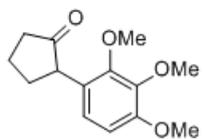


11a

¹H, CDCl₃, 400 MHz

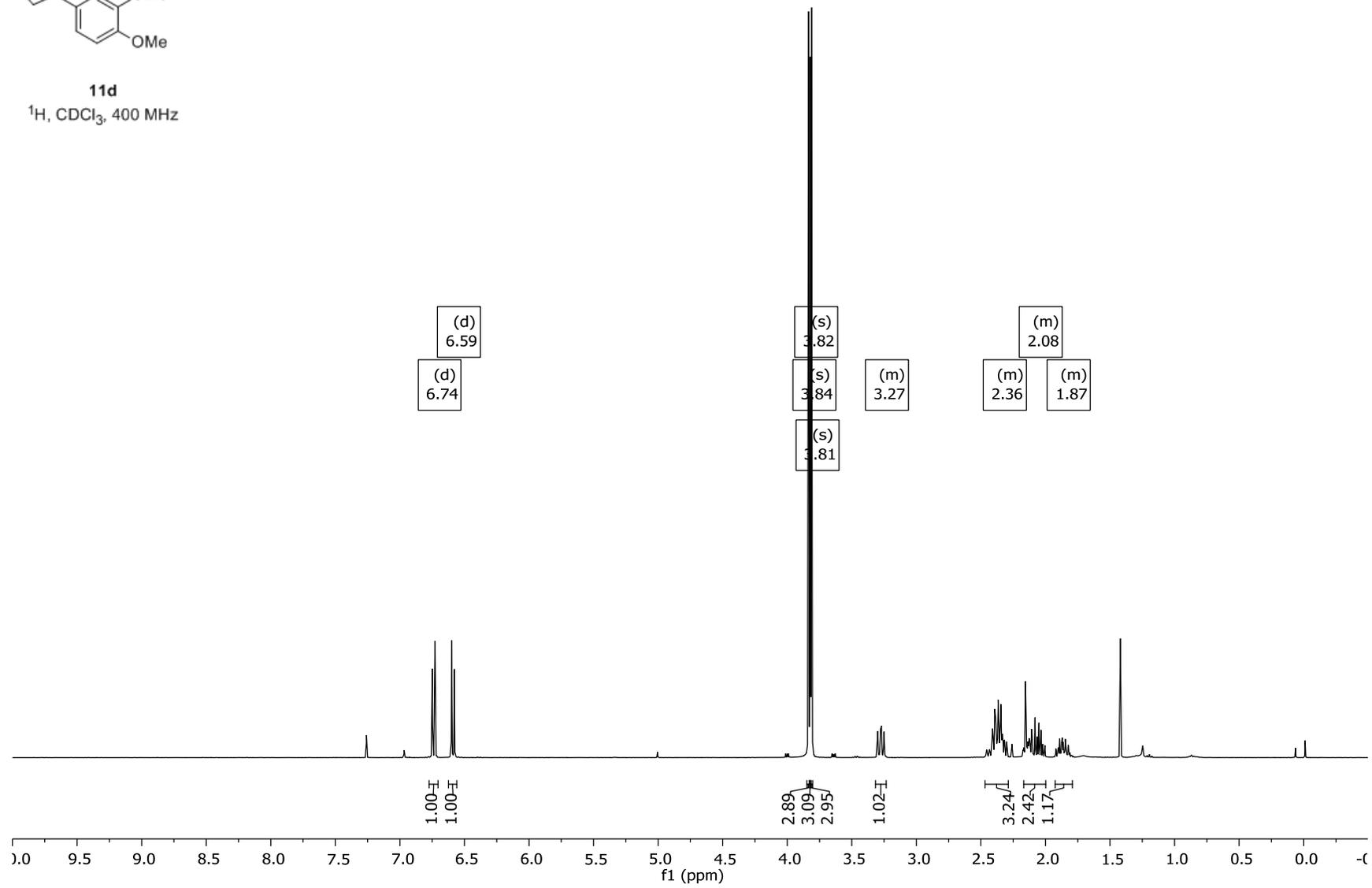






11d

^1H , CDCl_3 , 400 MHz



— 219.7

~ 153.2
~ 151.5

— 142.3

~ 126.2
~ 124.4

— 107.2

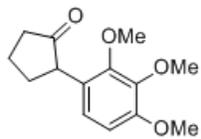
~ 60.7
~ 60.2

~ 56.1
~ 52.2

— 38.2

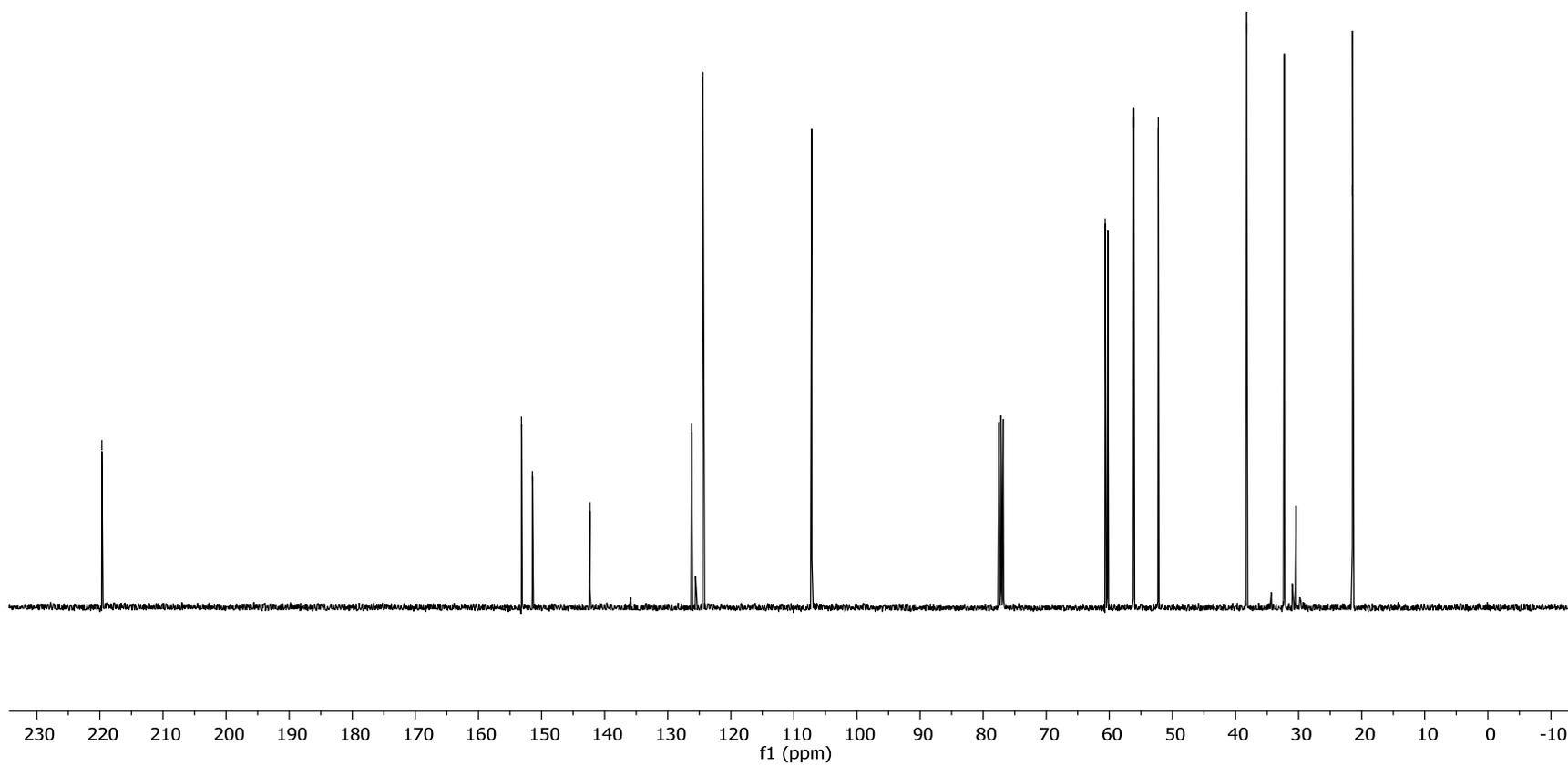
— 32.3

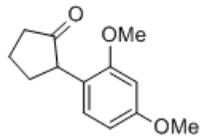
— 21.4



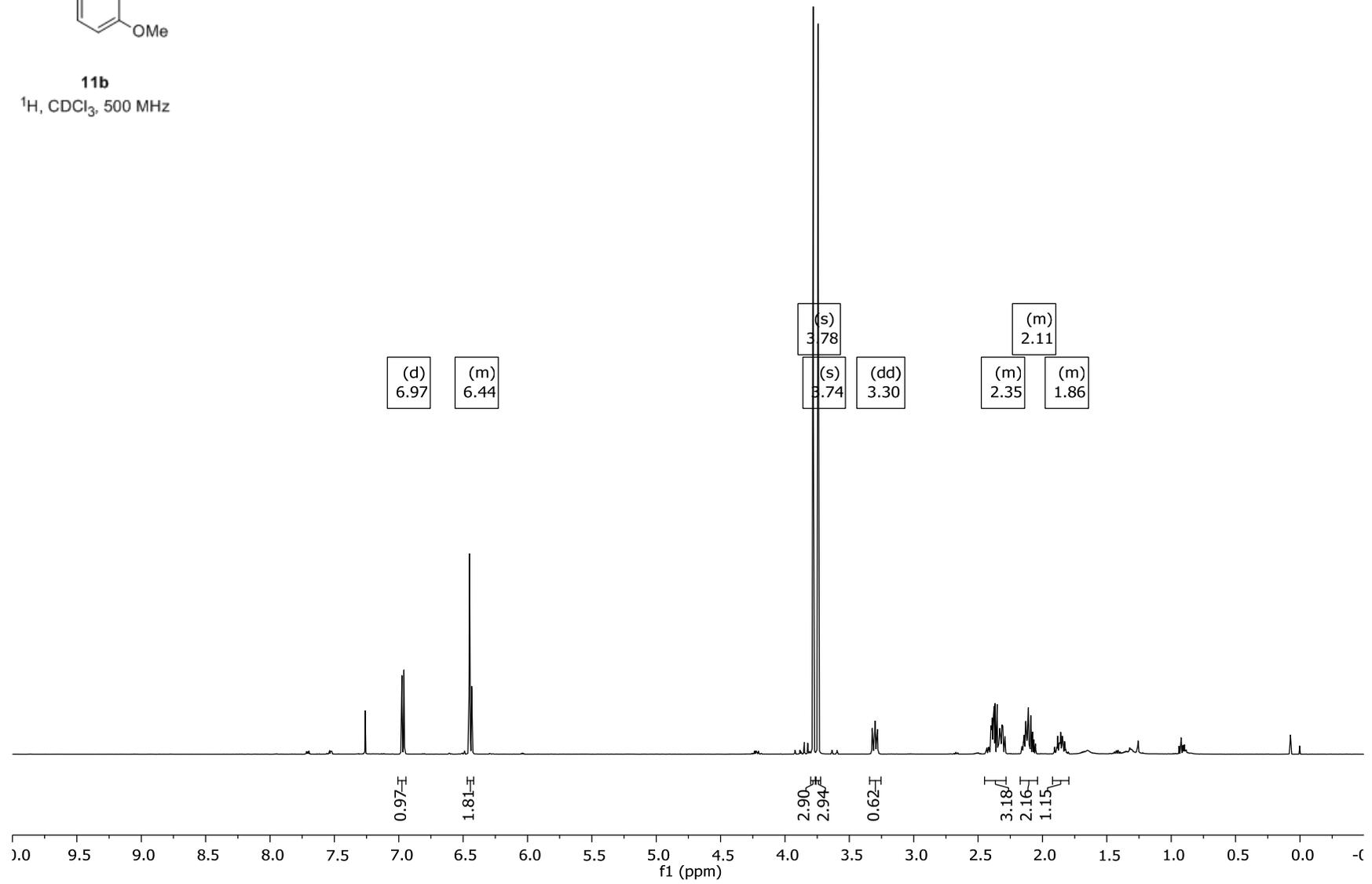
11d

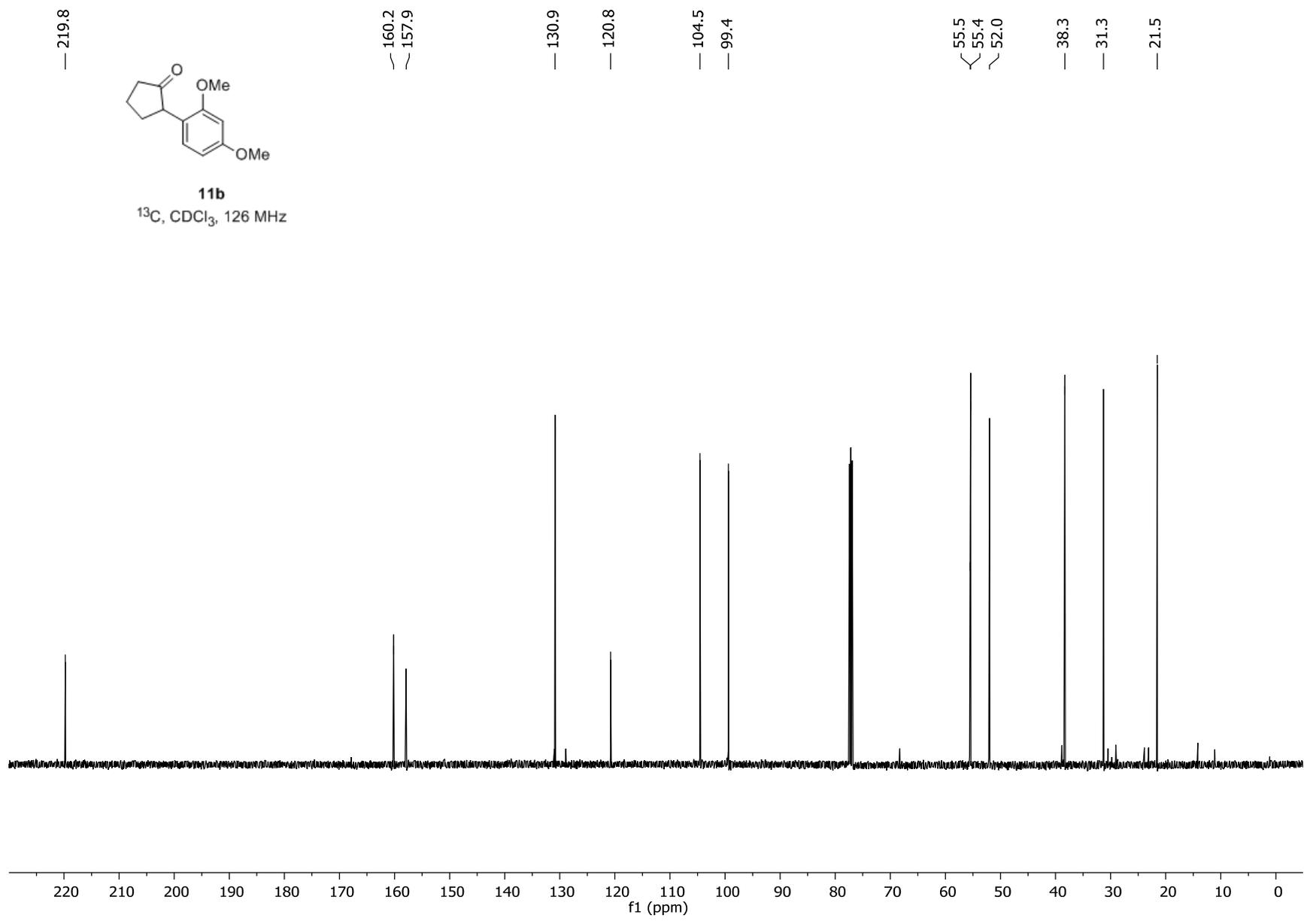
¹³C, CDCl₃, 101 MHz

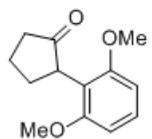




11b
 ^1H , CDCl_3 , 500 MHz

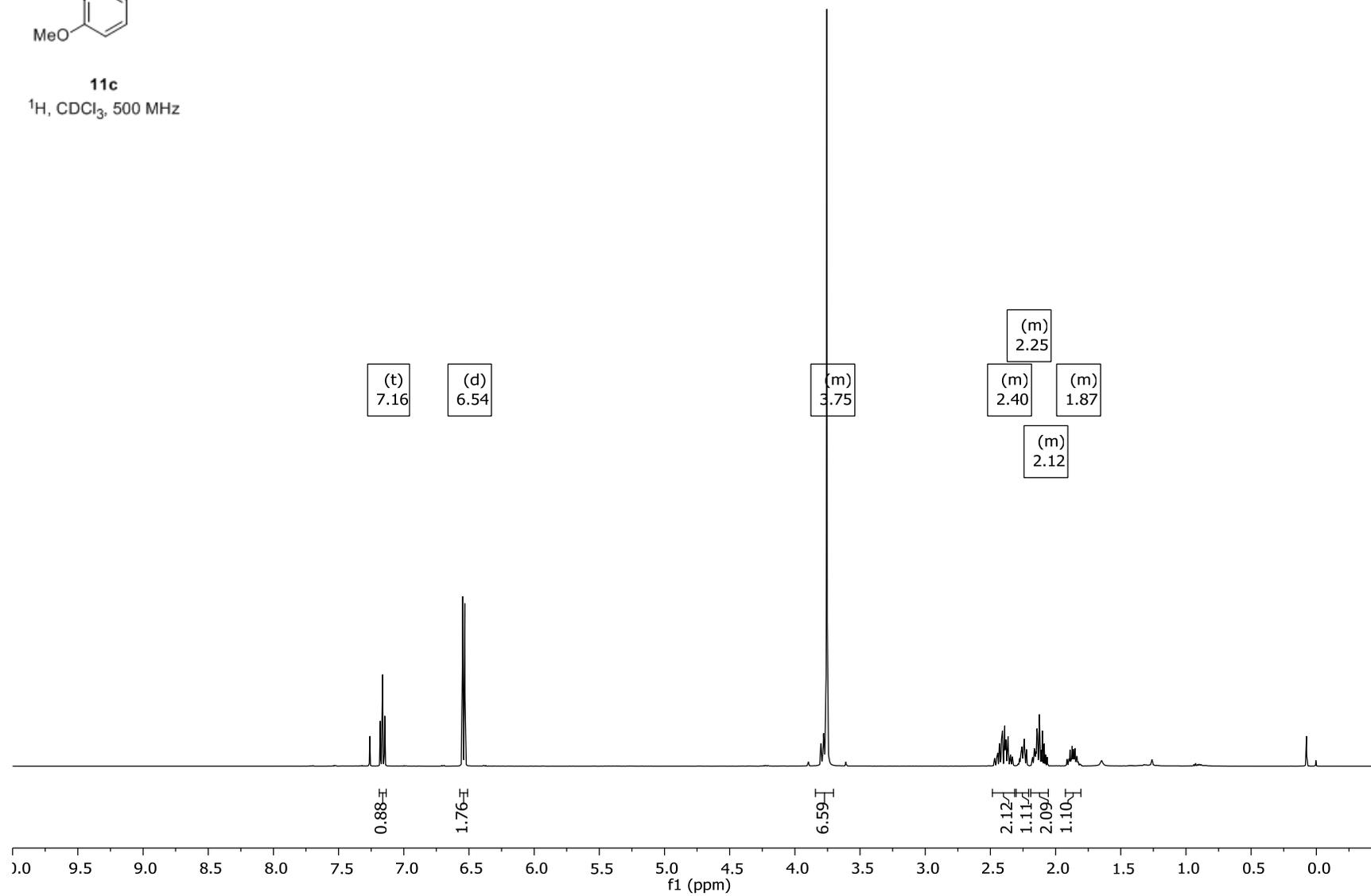


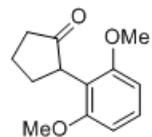




11c

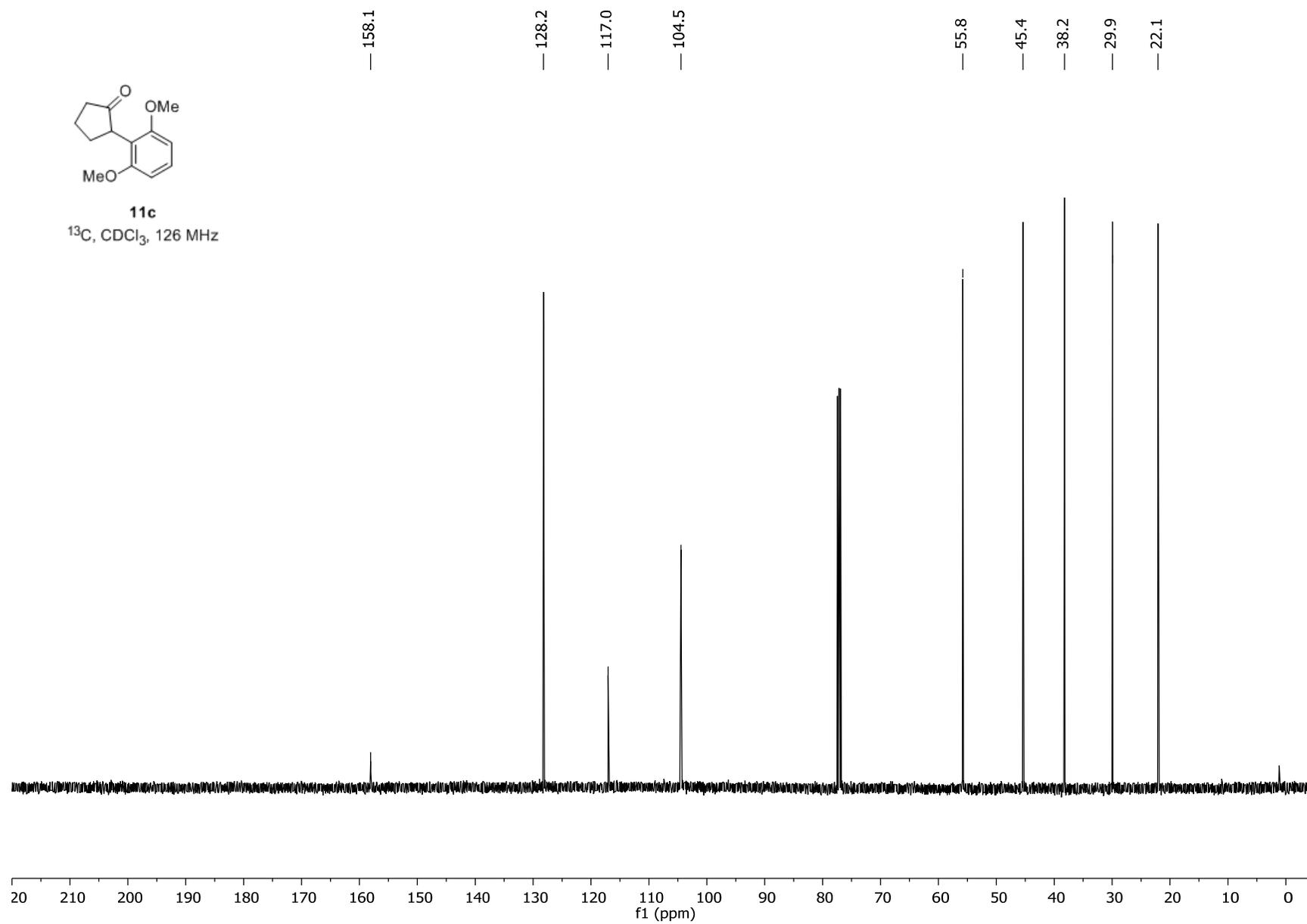
^1H , CDCl_3 , 500 MHz

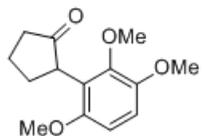




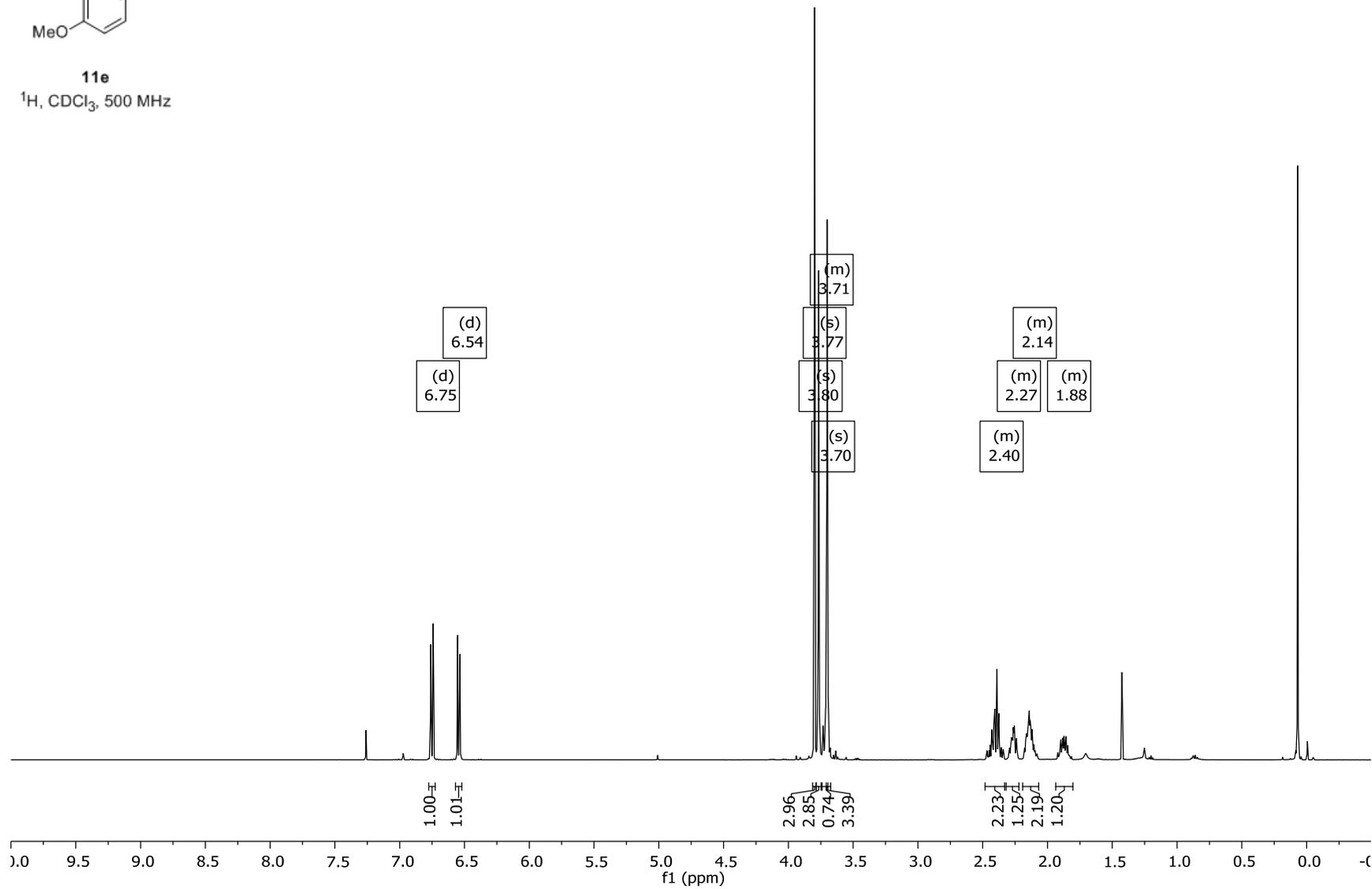
11c

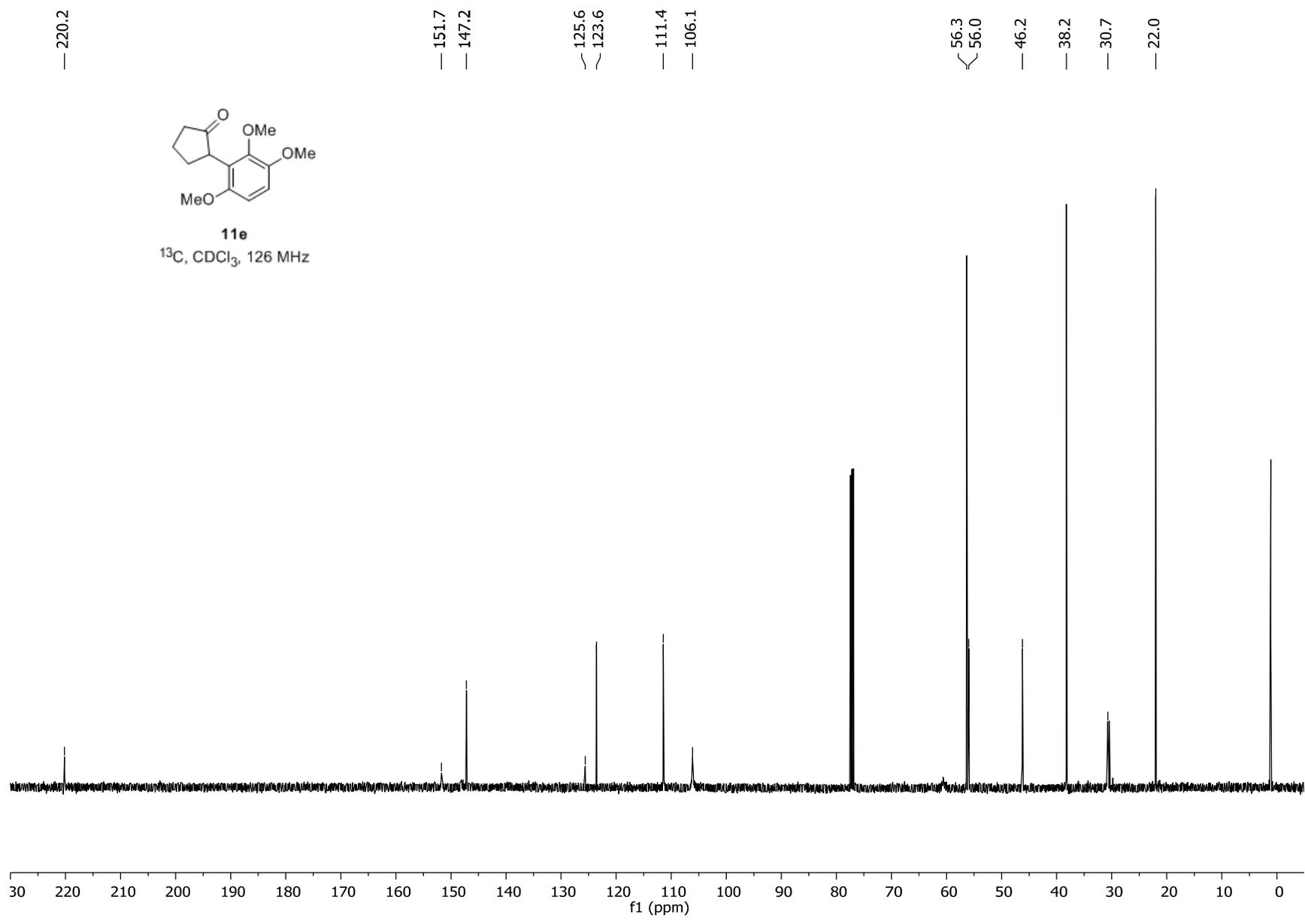
^{13}C , CDCl_3 , 126 MHz

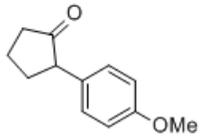




11e
¹H, CDCl₃, 500 MHz

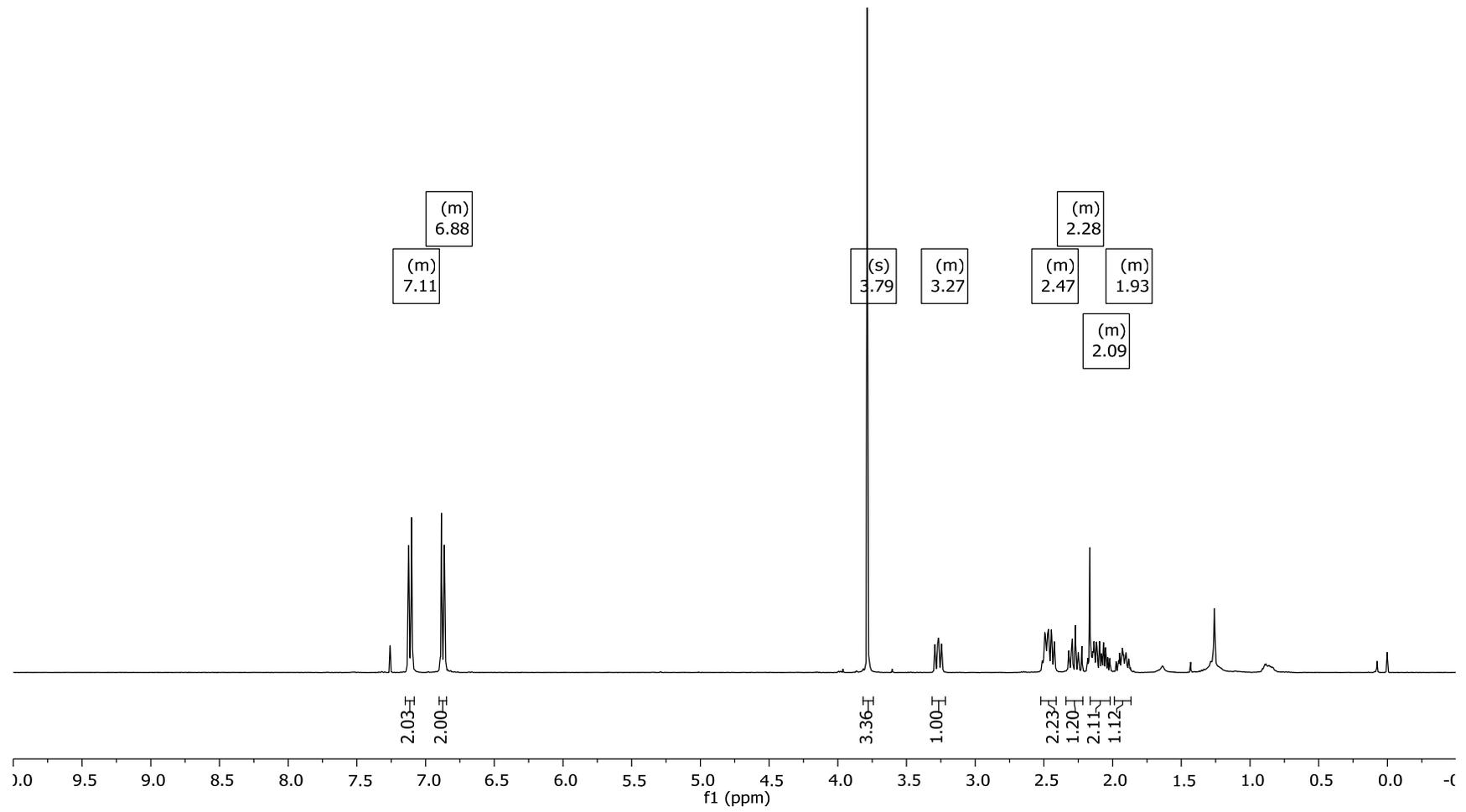






11f

¹H, CDCl₃, 400 MHz



— 218.5

— 158.6

~ 130.5
~ 129.2

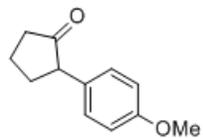
— 114.2

~ 55.4
~ 54.7

— 38.4

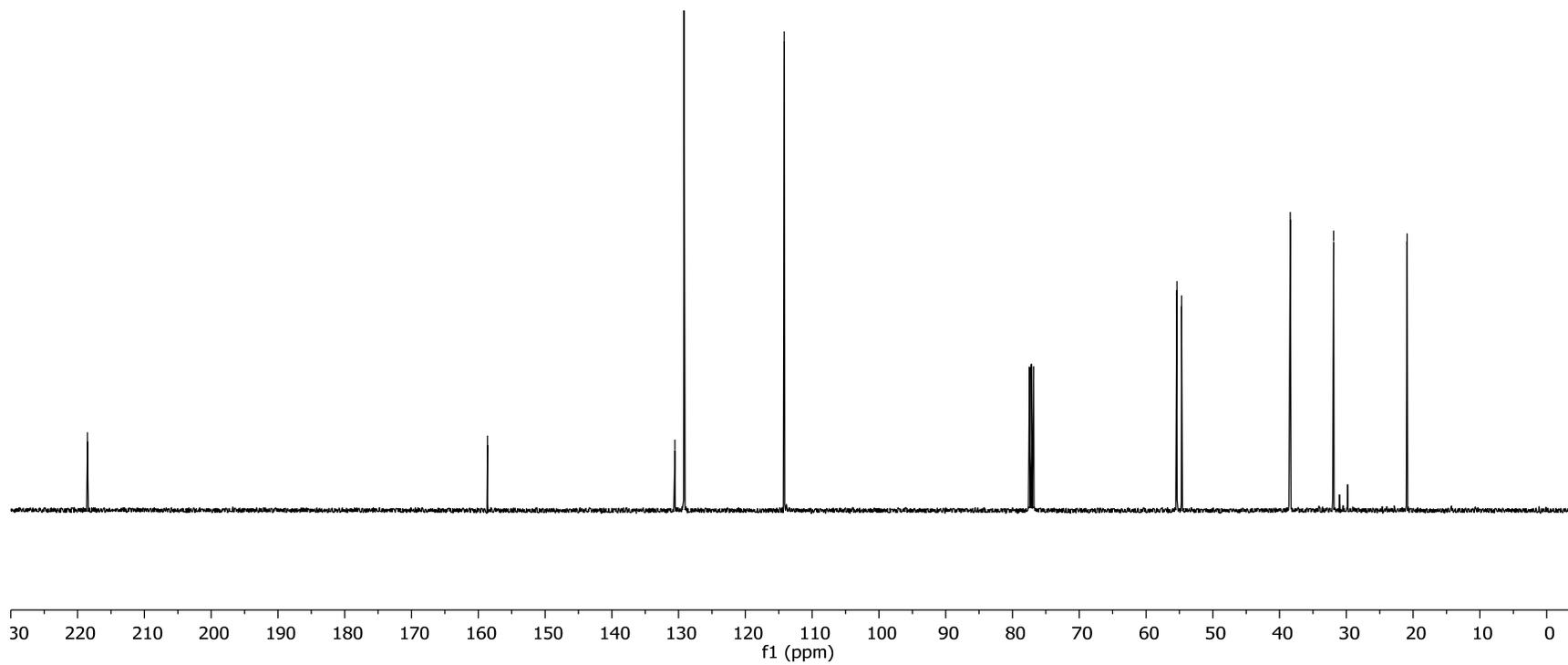
— 31.9

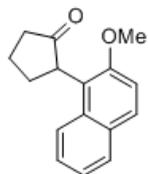
— 20.9



11f

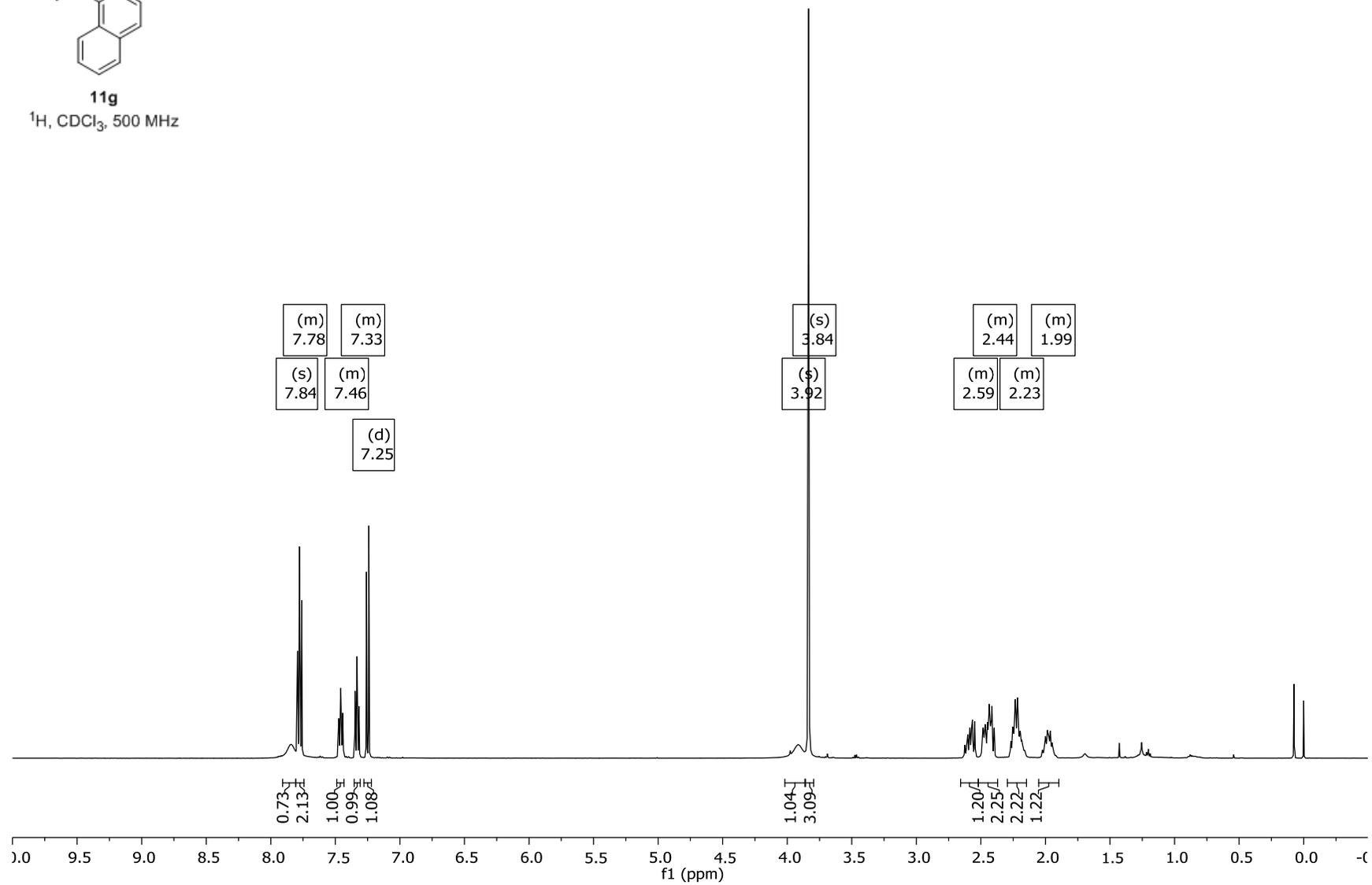
¹³C, CDCl₃, 101 MHz



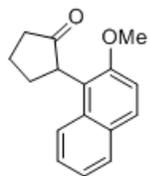


11g

¹H, CDCl₃, 500 MHz



— 219.9



11g

^{13}C , CDCl_3 , 126 MHz

129.7
129.1
128.8
126.8
123.6
122.6
— 114.2

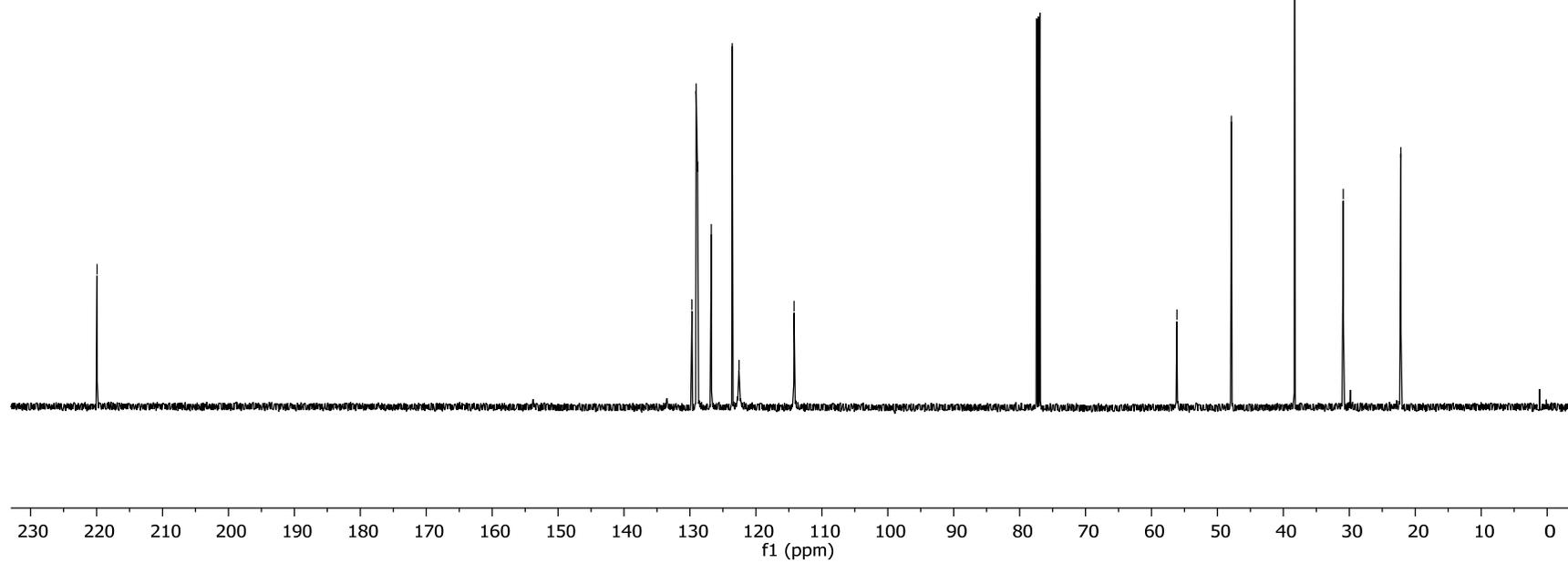
— 56.2

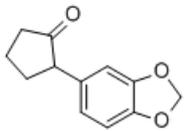
— 47.9

— 38.3

— 30.9

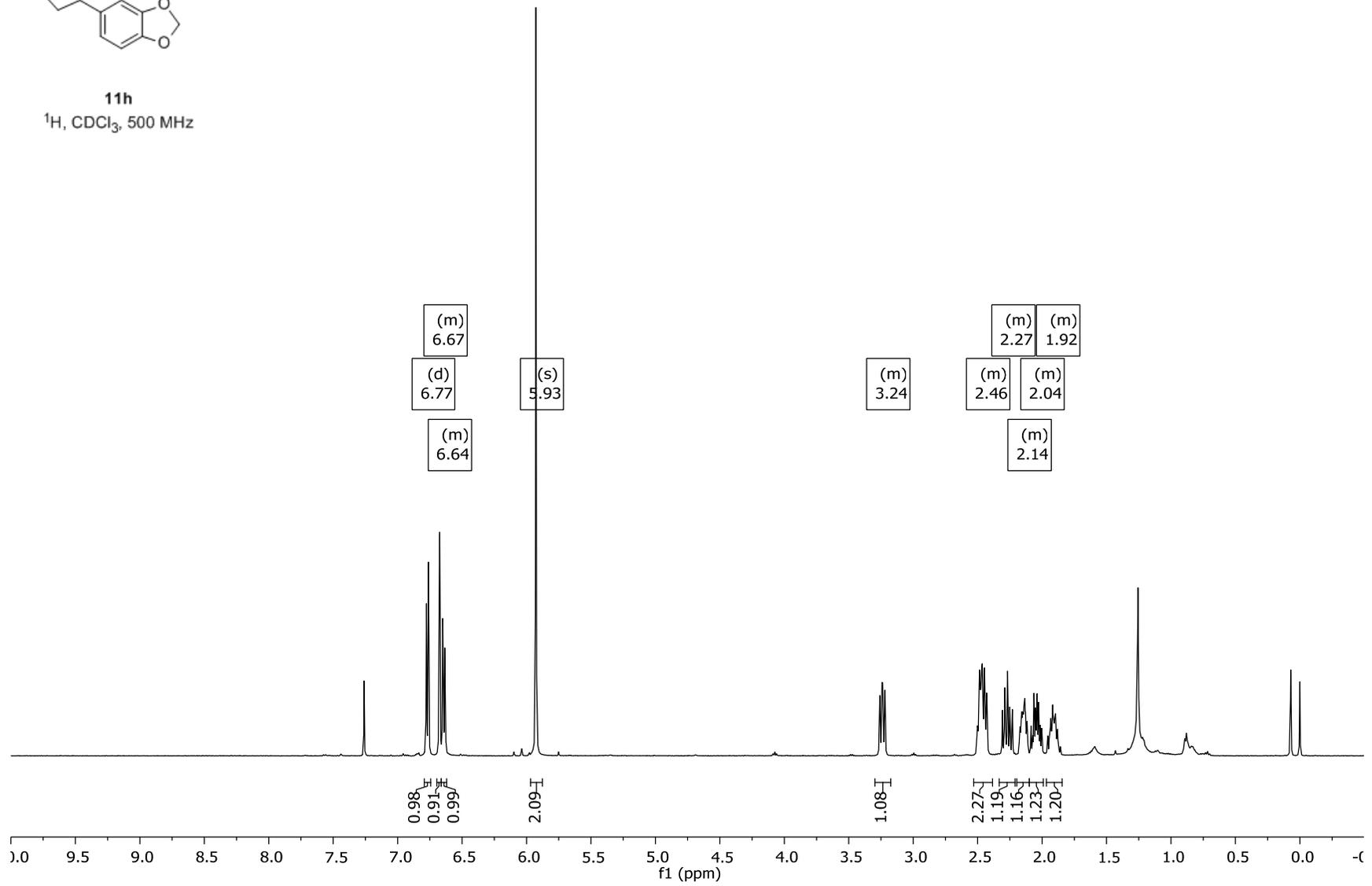
— 22.2



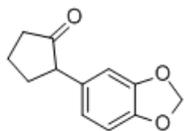


11h

¹H, CDCl₃, 500 MHz



— 218.2



11h

^{13}C , CDCl_3 , 126 MHz

— 147.9
— 146.6

— 132.2
— 132.2

— 121.4

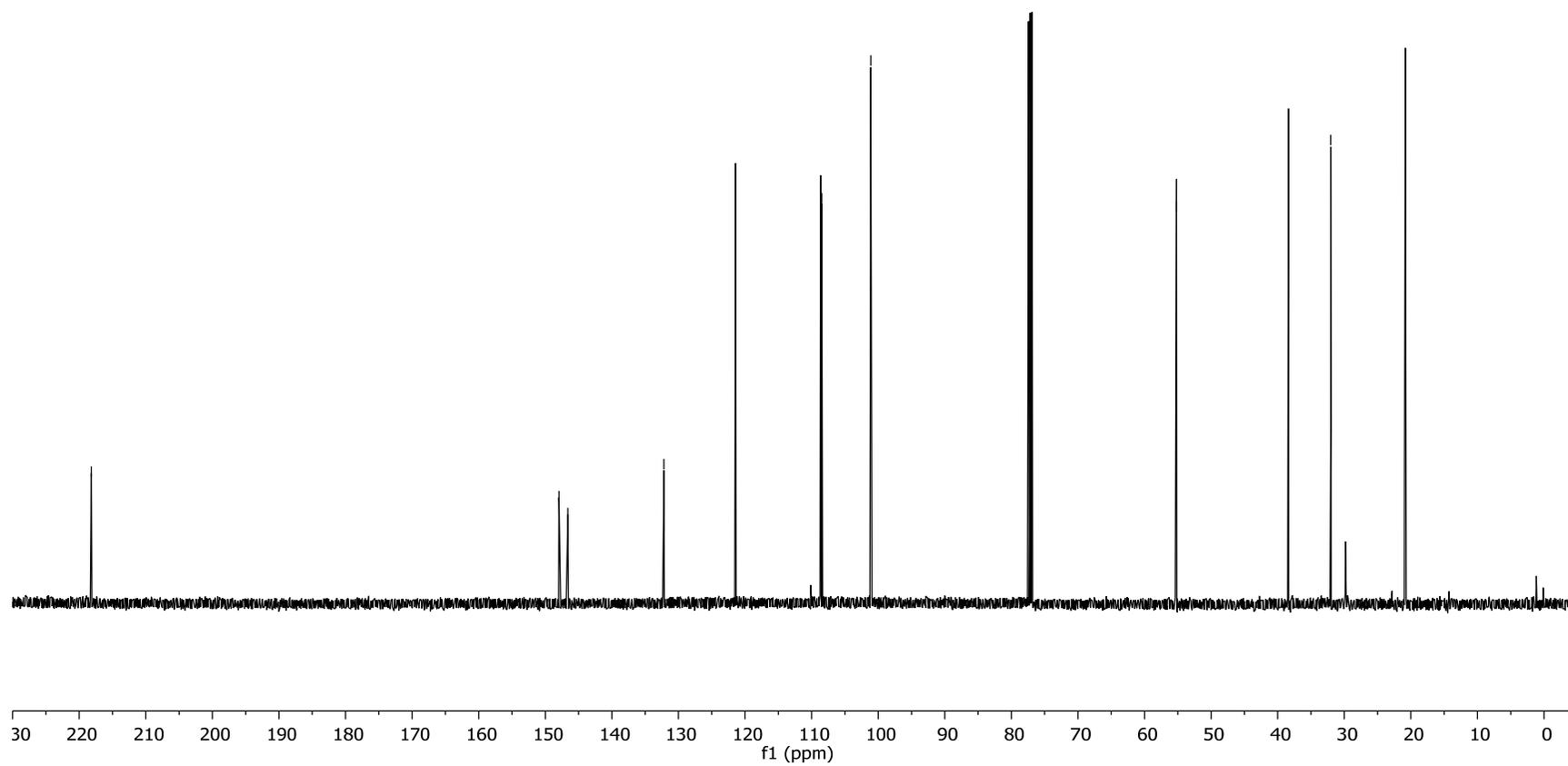
— 108.7
— 108.5
— 101.1

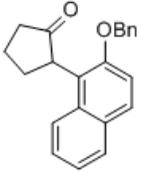
— 55.2

— 38.4

— 32.0

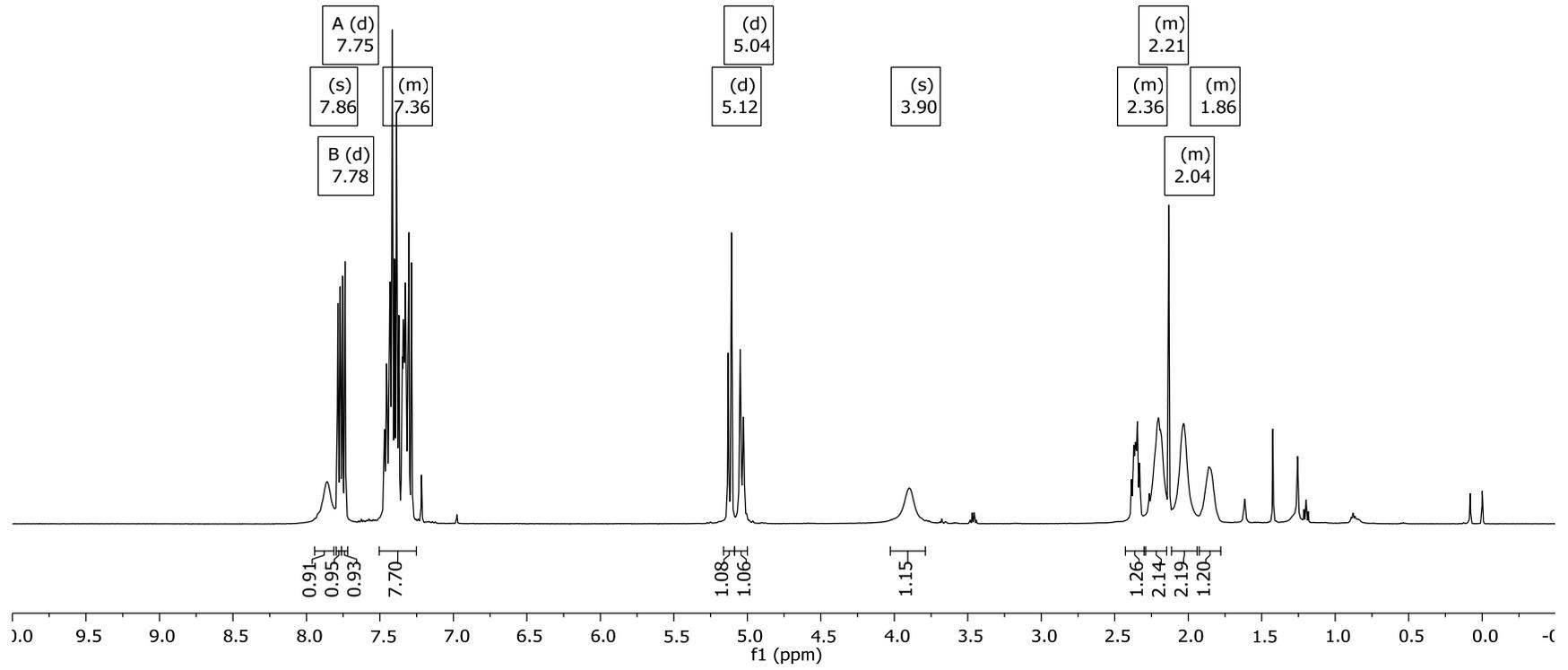
— 20.8



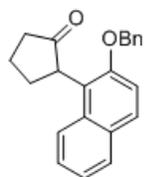


11i

¹H, CDCl₃, 500 MHz



— 219.8



11i

¹³C, CDCl₃, 101 MHz

153.1
136.6
133.6
129.7
129.0
128.8
128.7
128.4
128.3
126.8
123.6
122.5
— 114.6

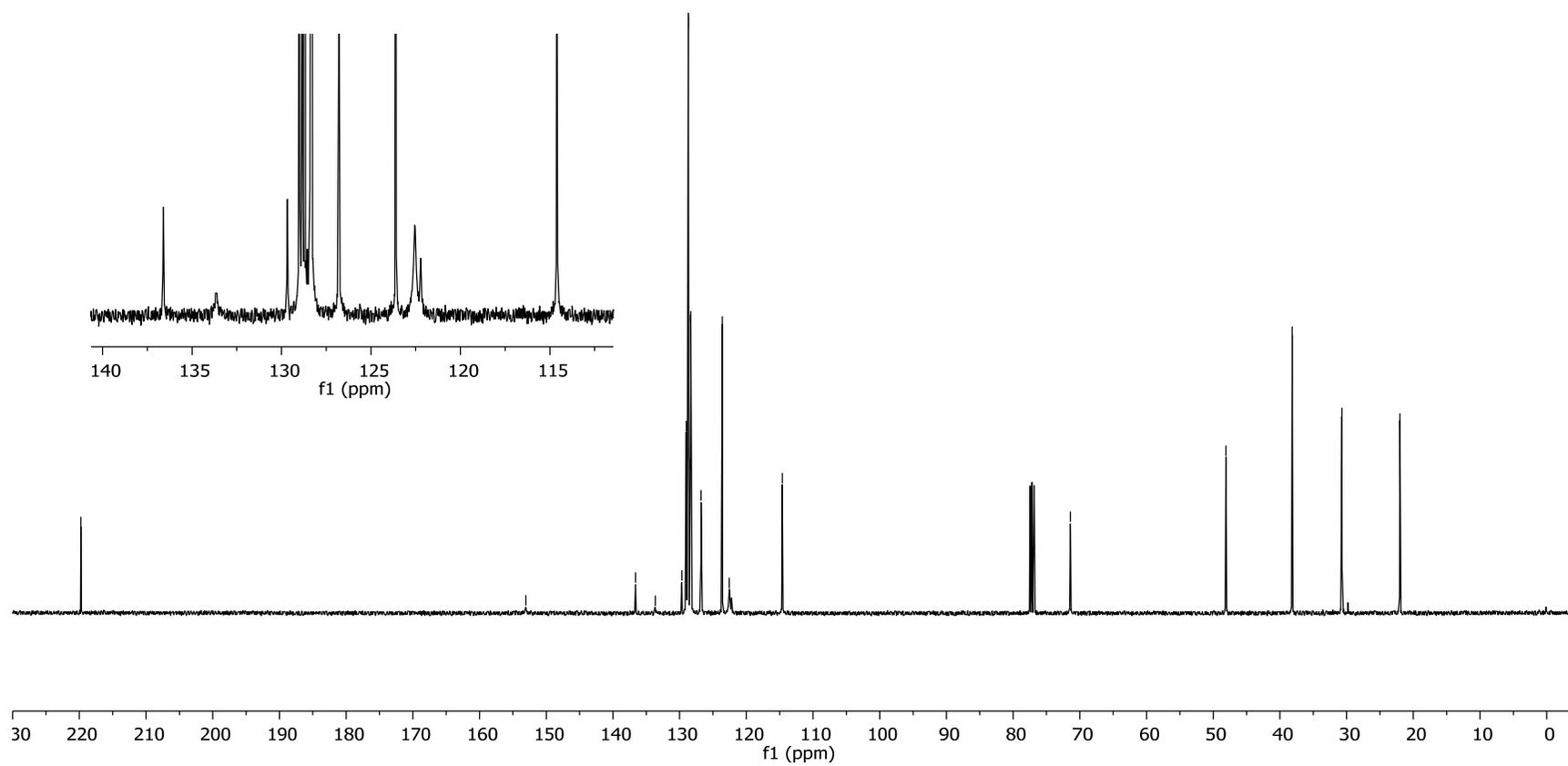
— 71.4

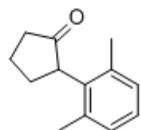
— 48.1

— 38.2

— 30.7

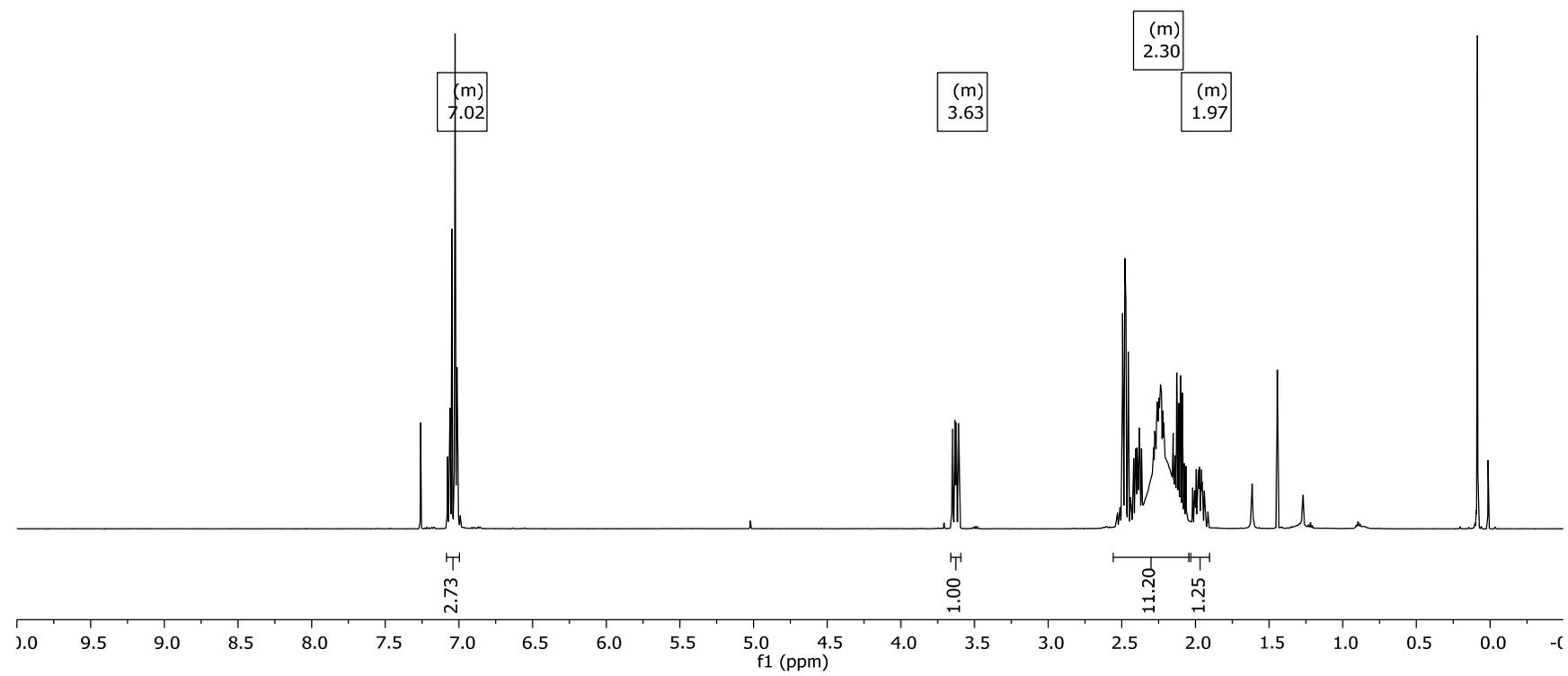
— 22.0

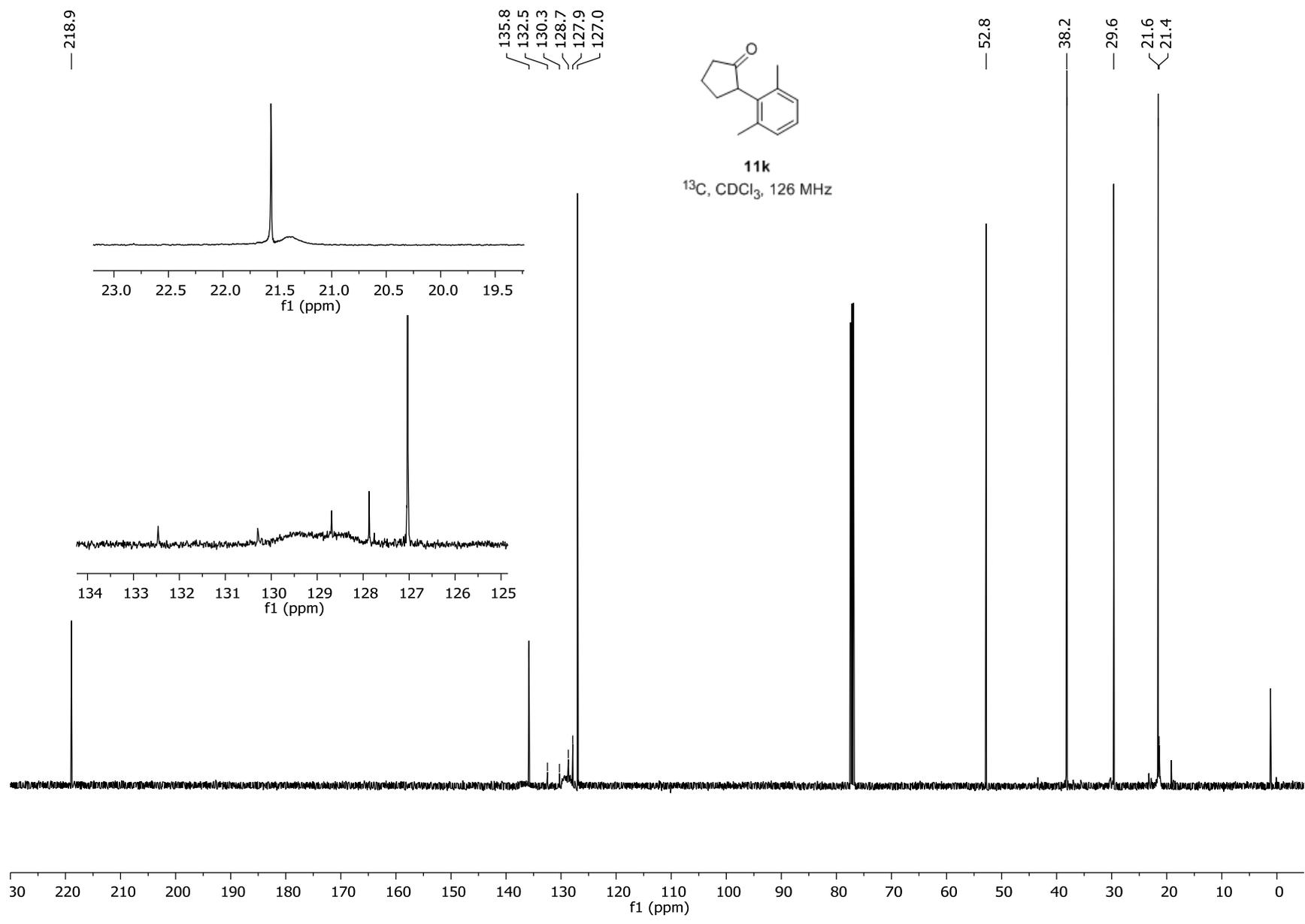


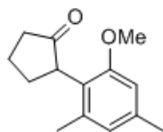


11k

^1H , CDCl_3 , 500 MHz

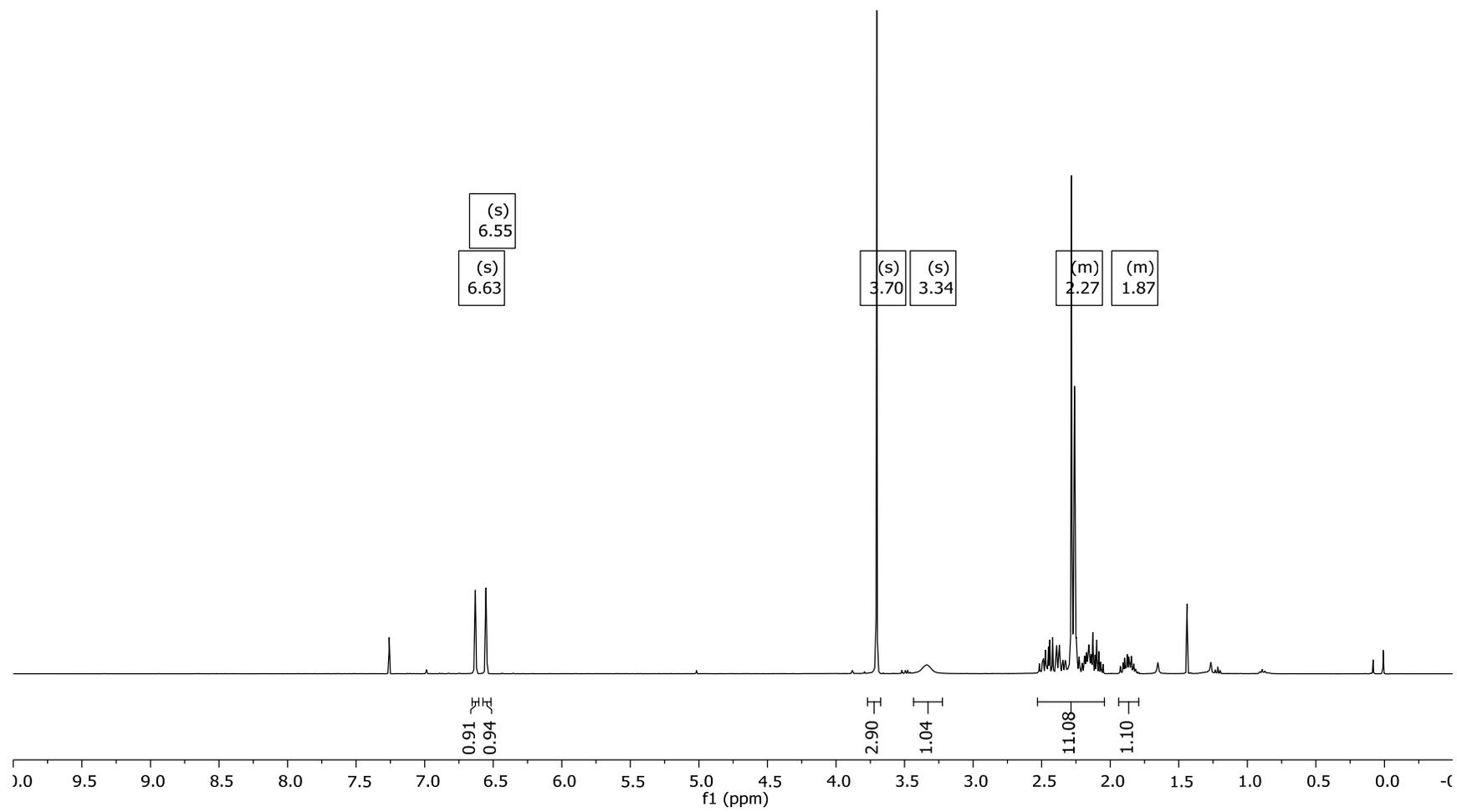






11j

¹H, CDCl₃, 400 MHz



— 220.2

— 156.6

— 137.8
— 137.5

— 123.9

— 110.4

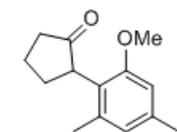
— 55.3

— 49.0

— 38.0

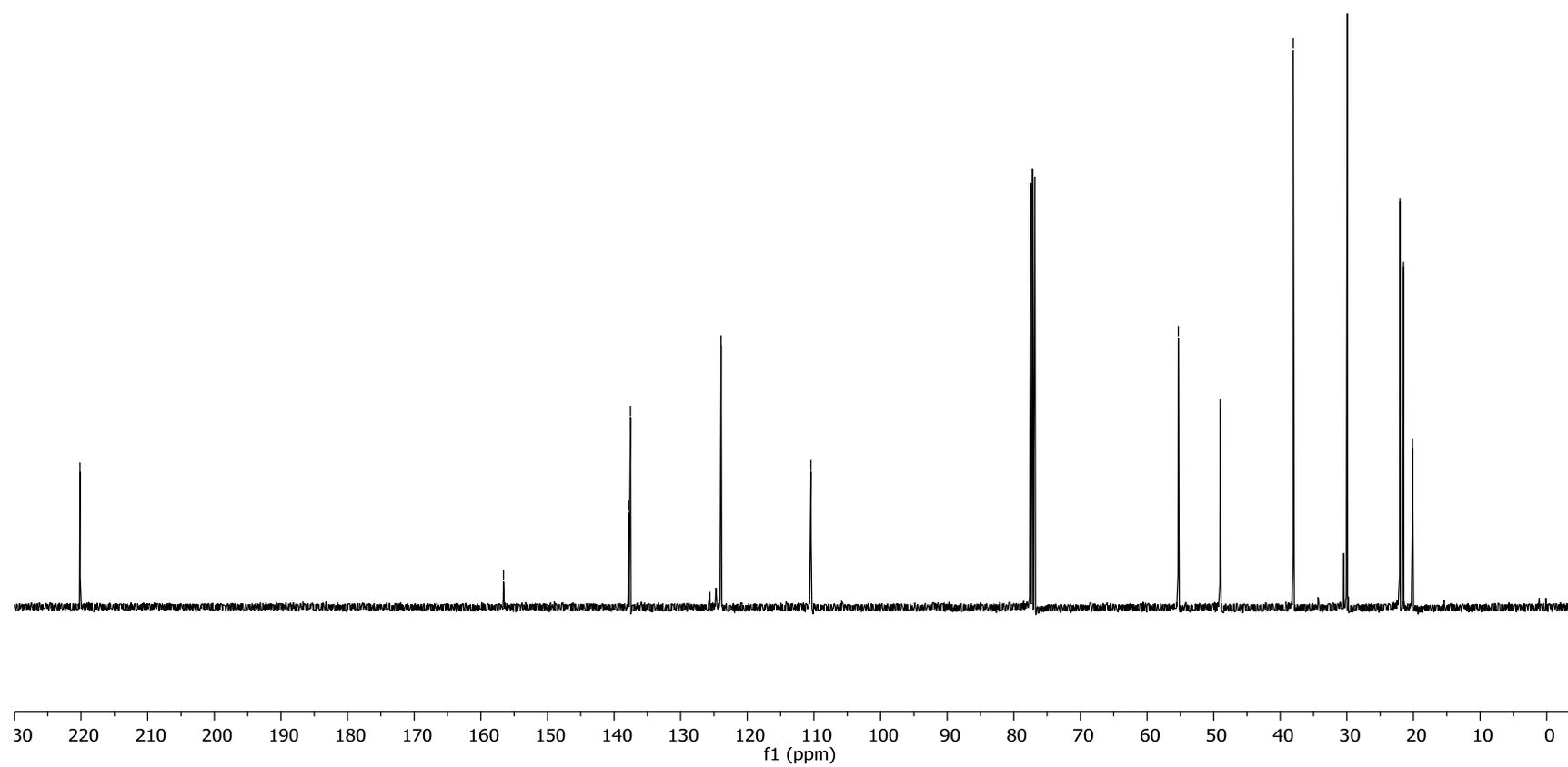
— 29.9

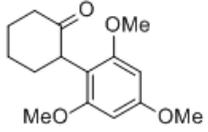
— 22.0
— 21.5
— 20.1



11j

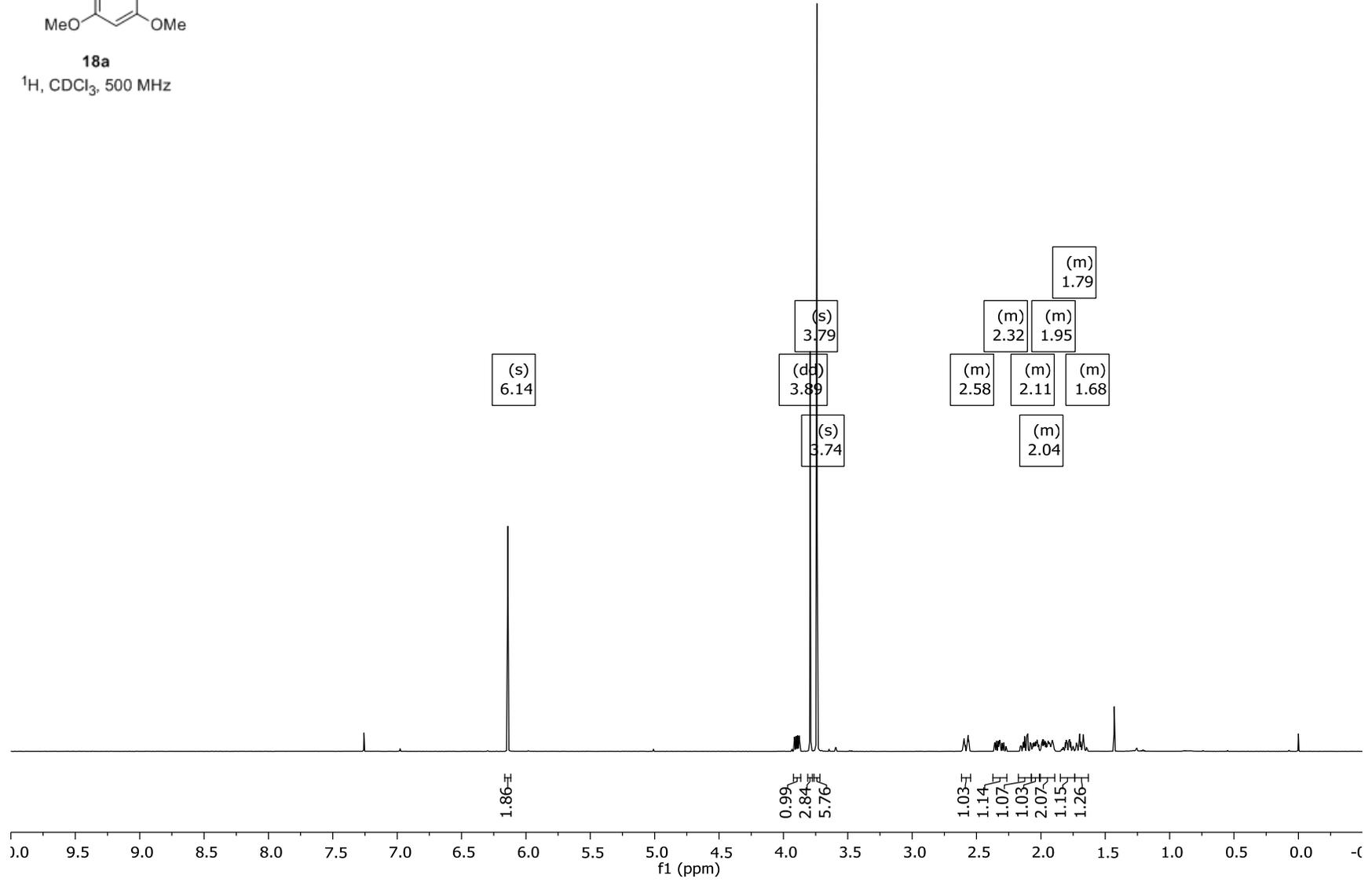
¹³C, CDCl₃, 101 MHz

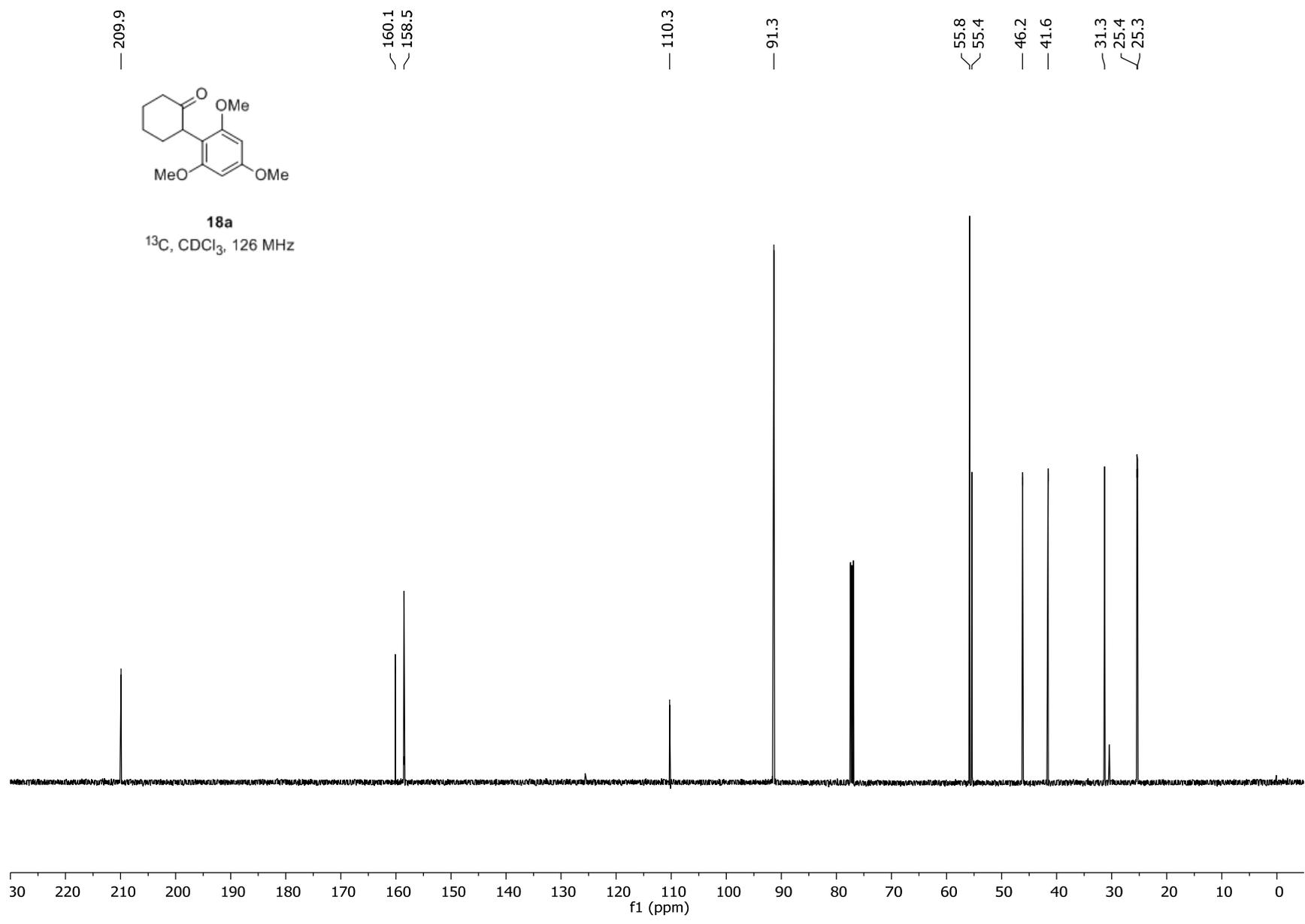


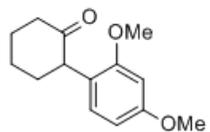


18a

¹H, CDCl₃, 500 MHz

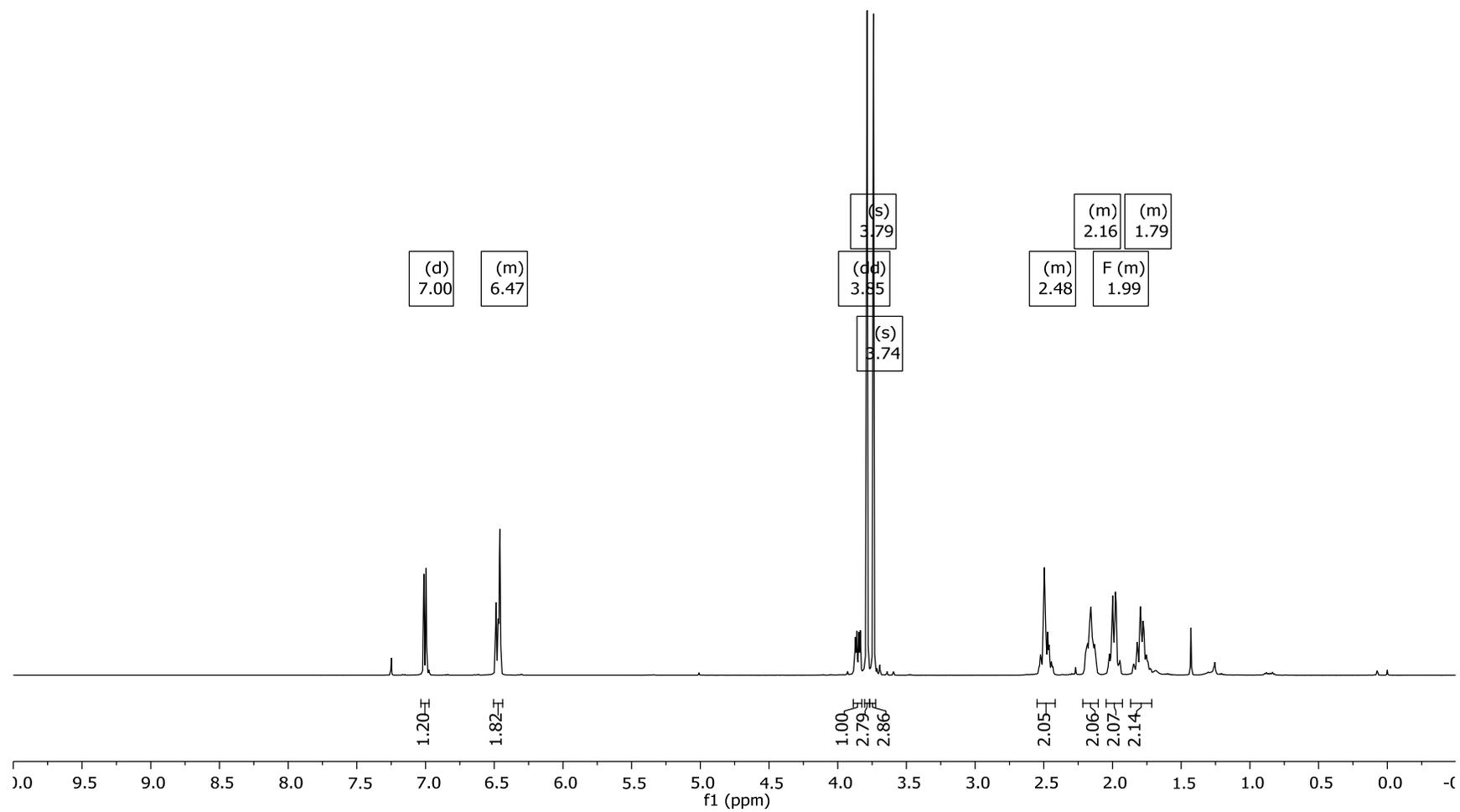






18b

^1H , CDCl_3 , 500 MHz



— 210.3

~ 159.8
~ 157.9

— 129.1

— 120.4

— 104.2

— 98.7

~ 55.5

~ 55.4

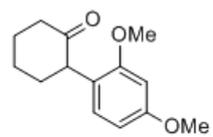
~ 50.6

— 42.4

~ 33.7

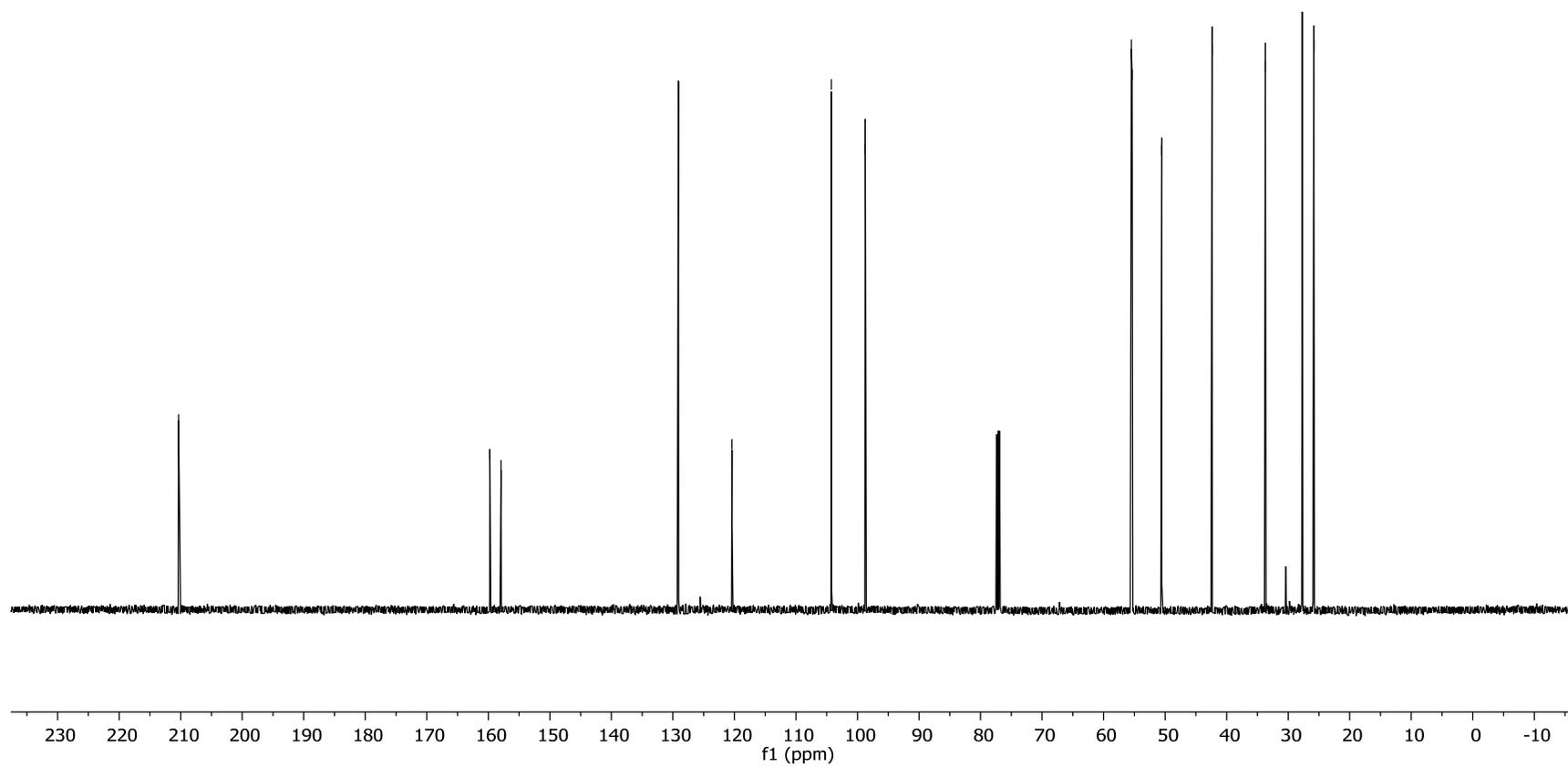
~ 27.7

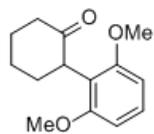
~ 25.9



18b

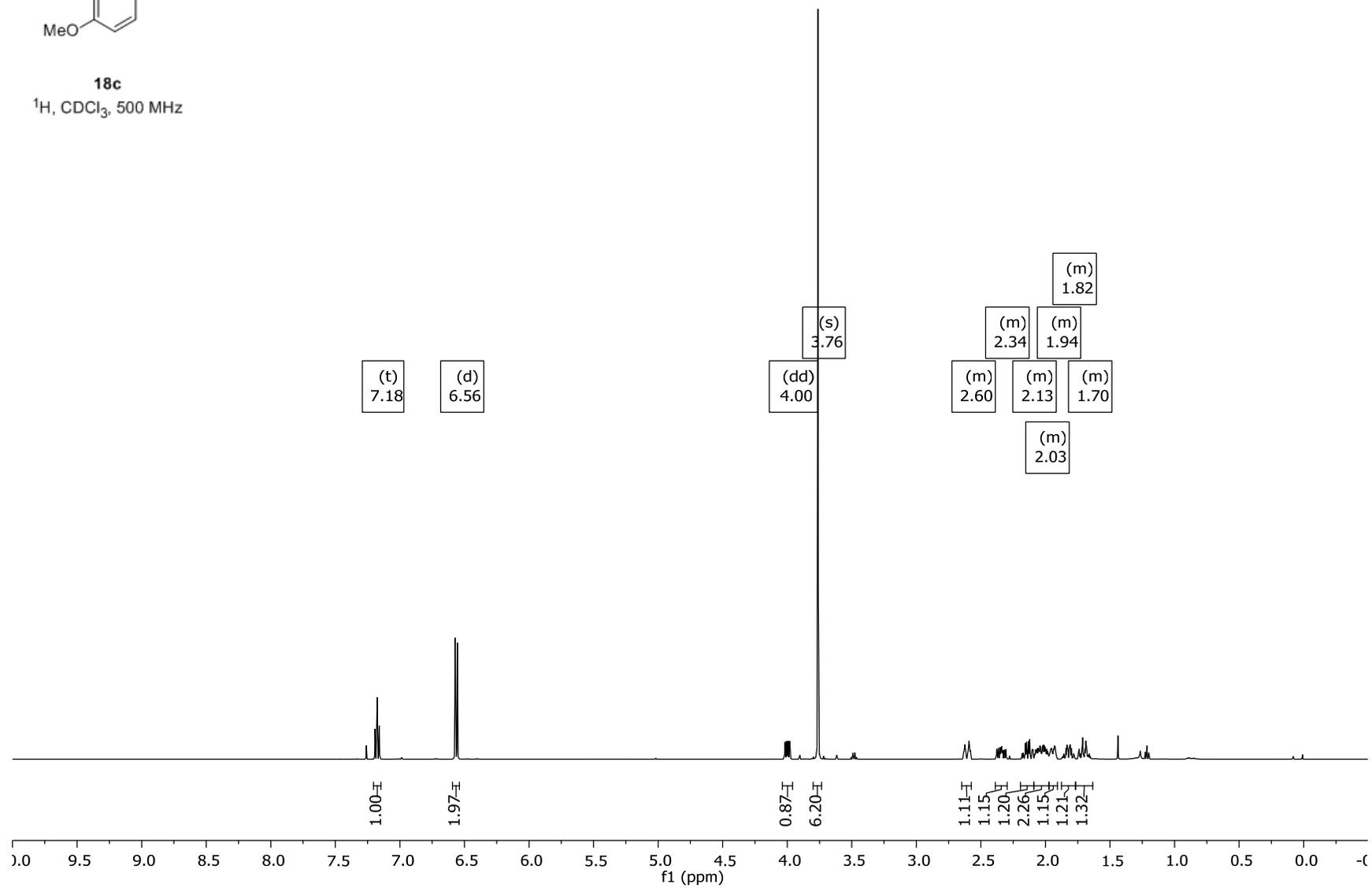
¹³C, CDCl₃, 126 MHz

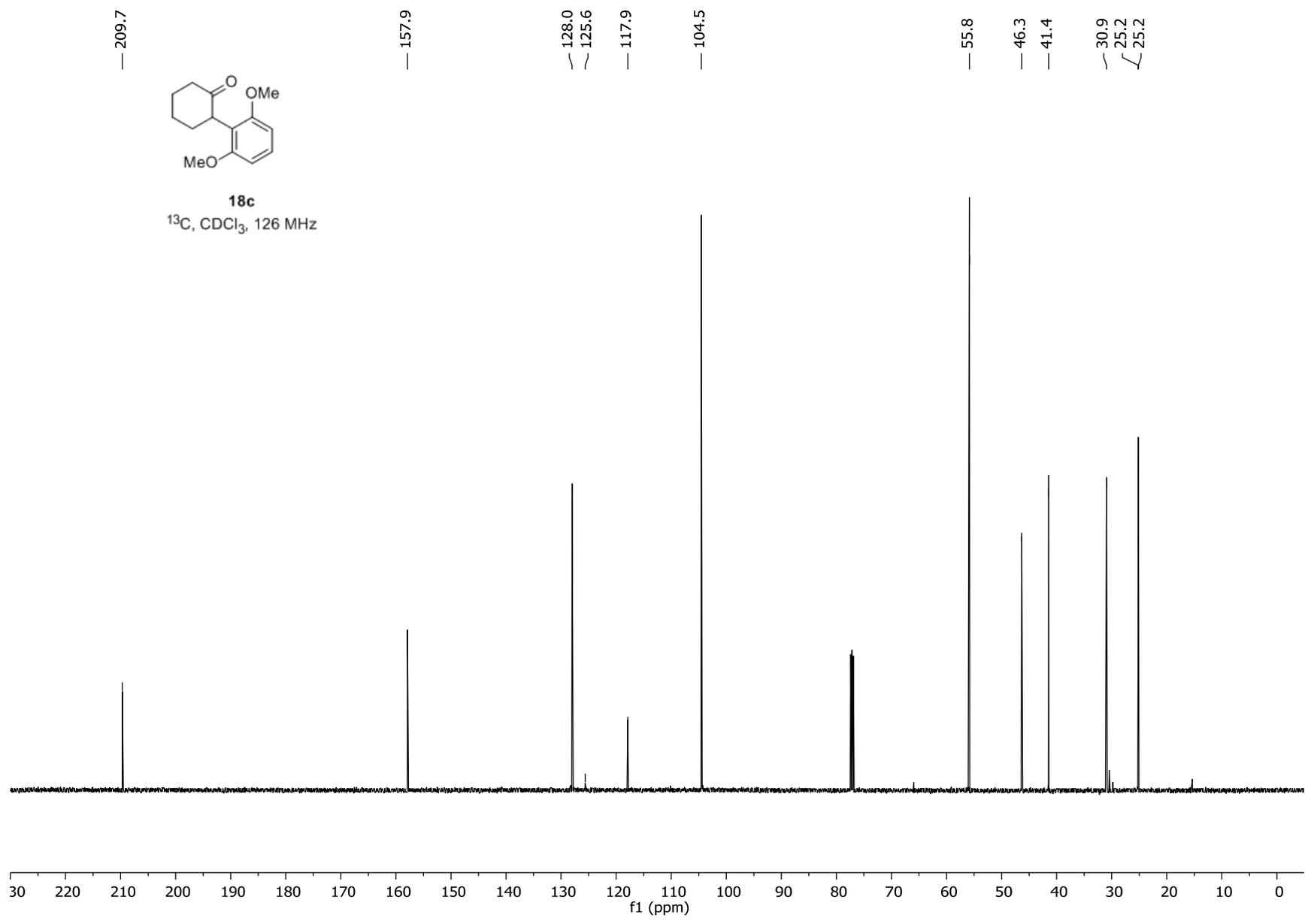


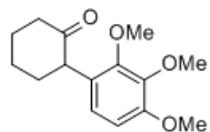


18c

^1H , CDCl_3 , 500 MHz

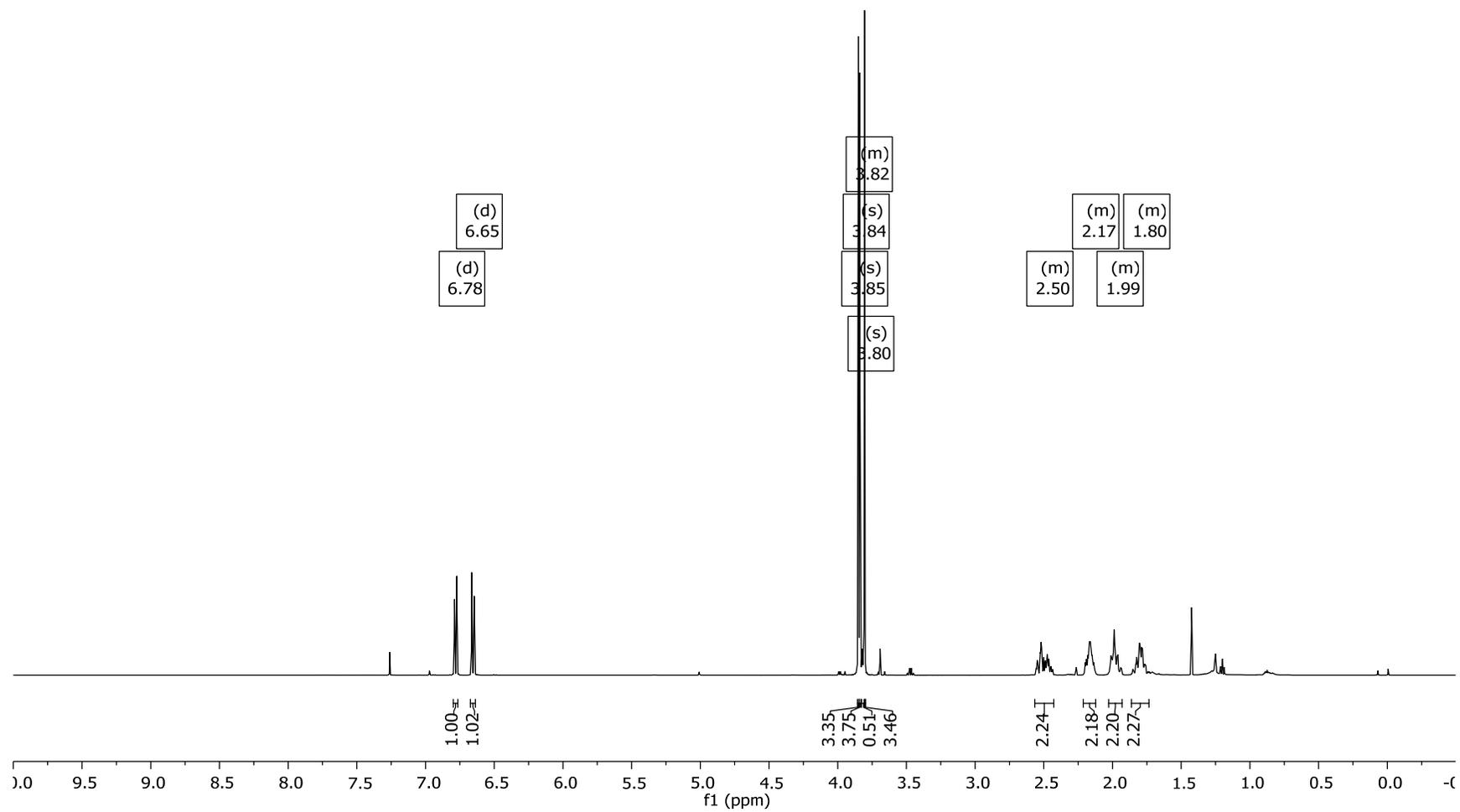


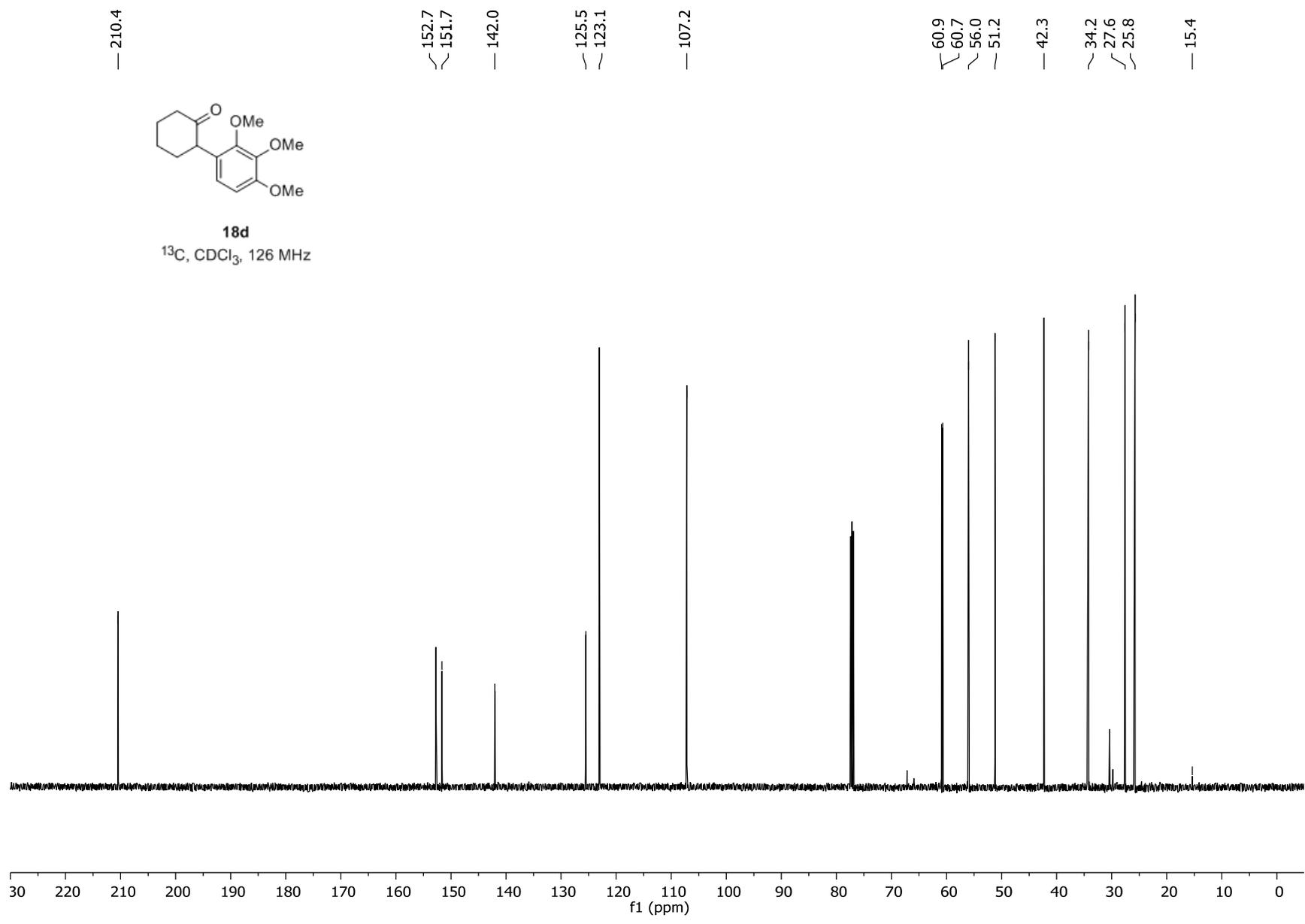


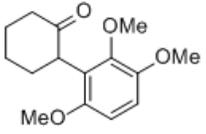


18d

¹H, CDCl₃, 500 MHz

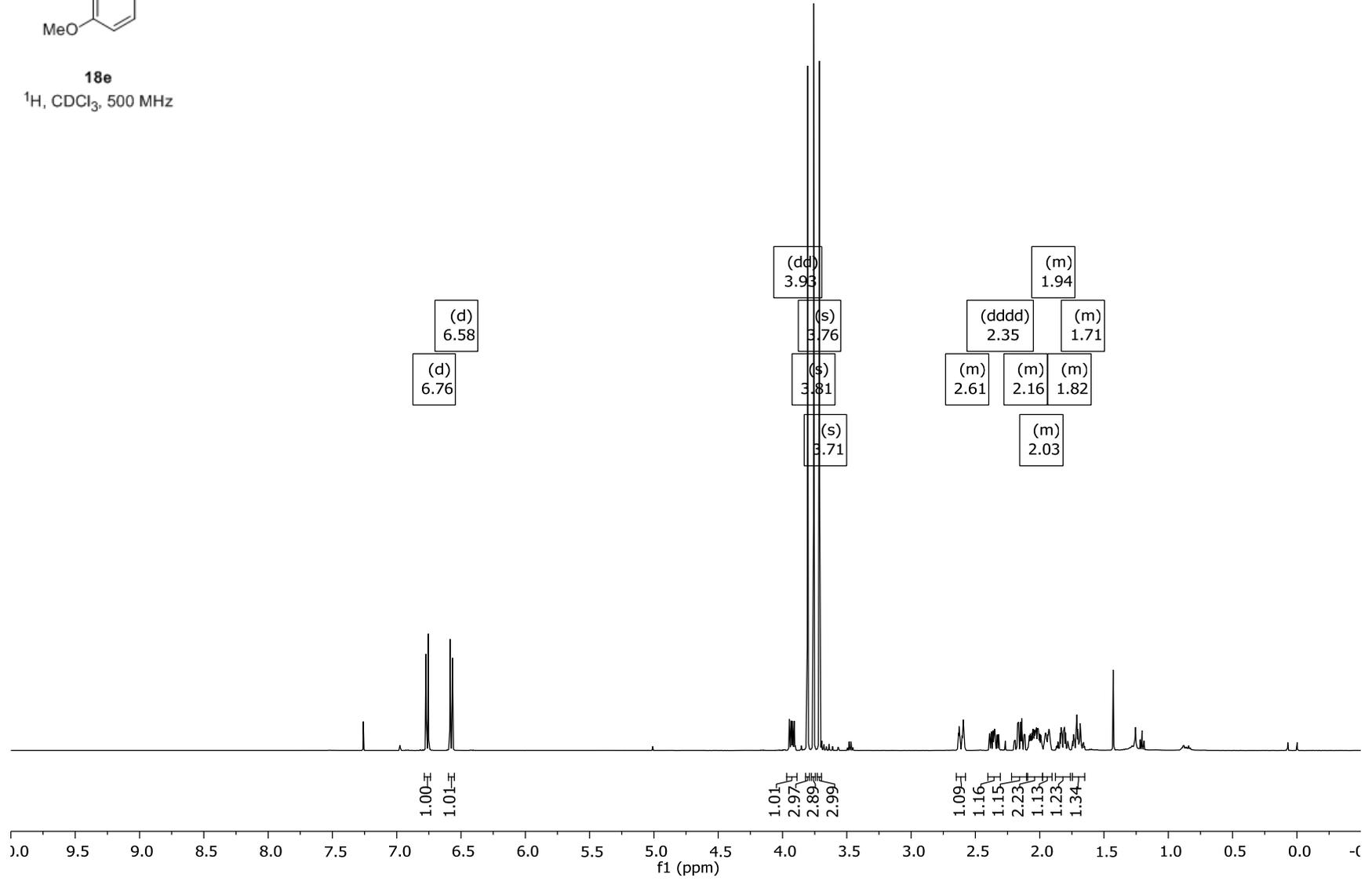






18e

¹H, CDCl₃, 500 MHz



— 209.8

✓ 151.7
✓ 147.8
✓ 147.2

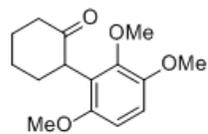
— 124.2

— 111.2
— 106.3

✓ 60.7
✓ 56.3
✓ 56.1

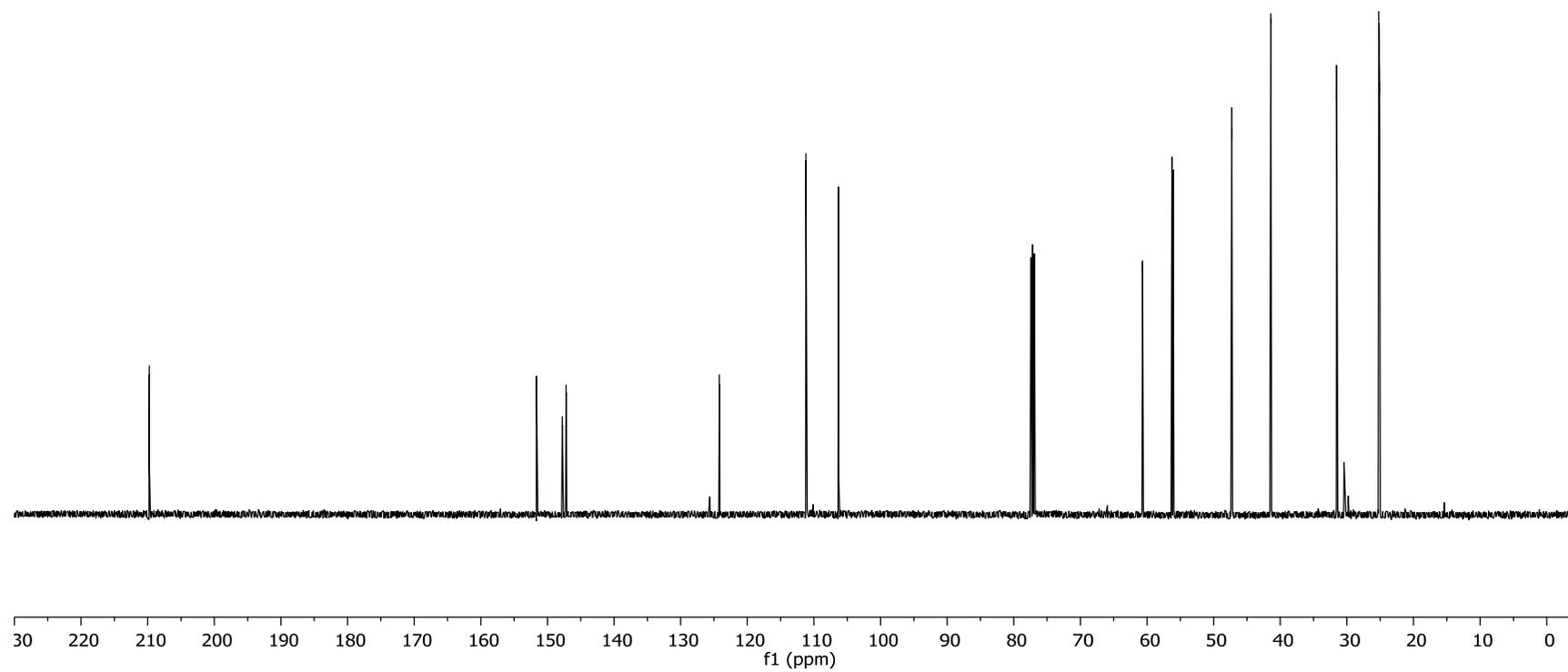
— 47.3
— 41.4

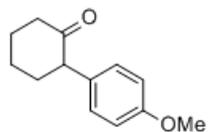
— 31.5
✓ 25.2
✓ 25.1



18e

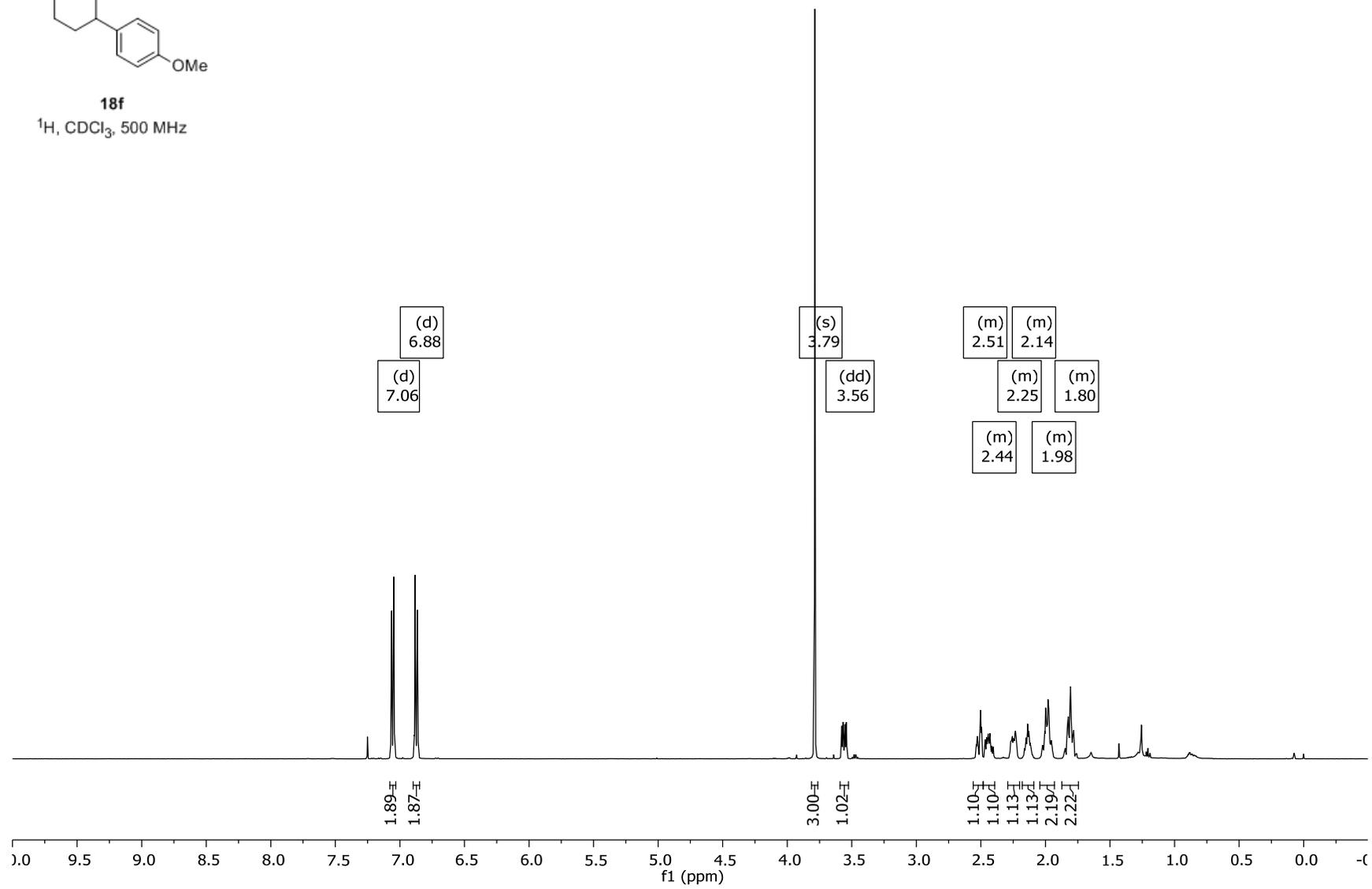
¹³C, CDCl₃, 126 MHz

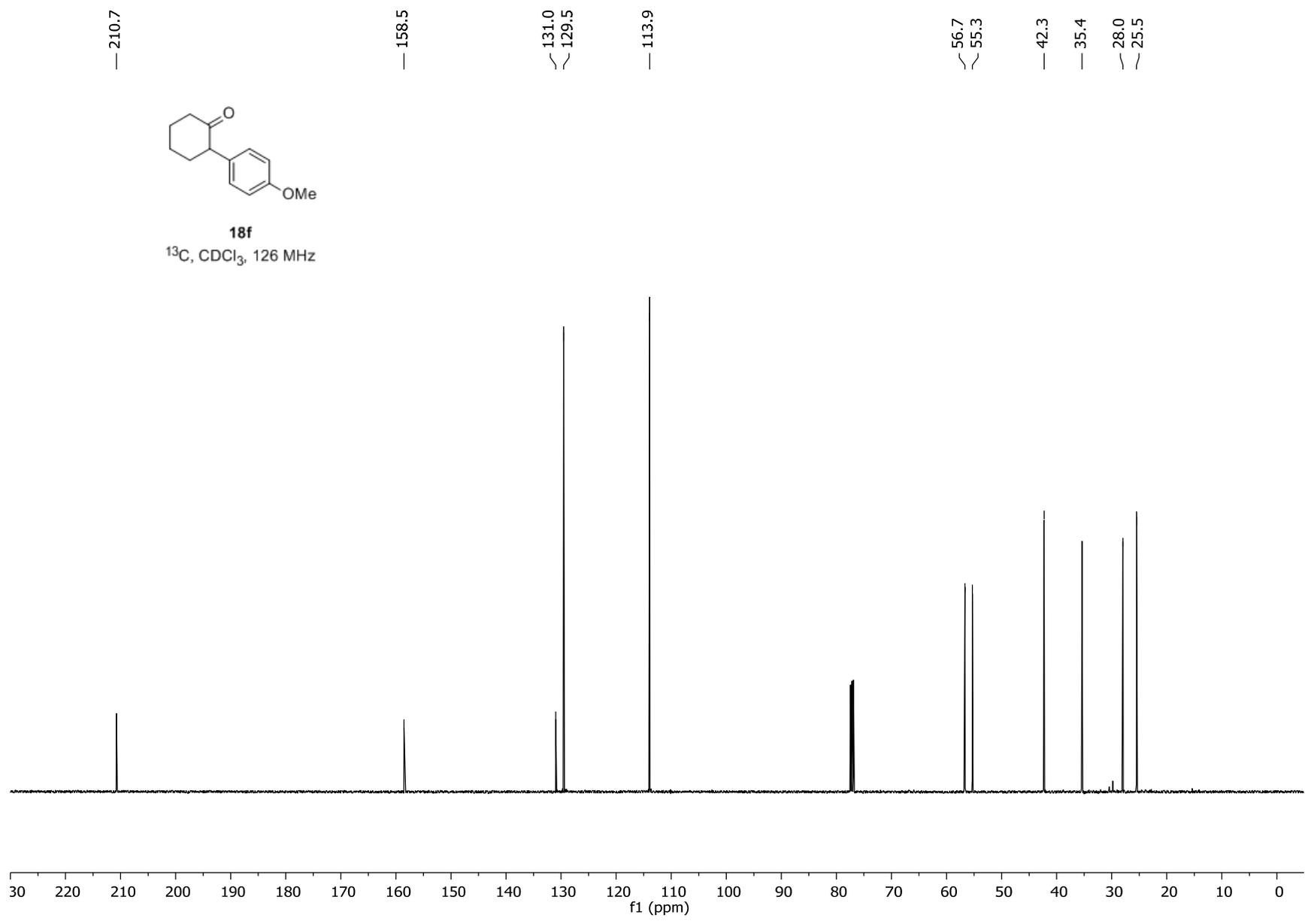


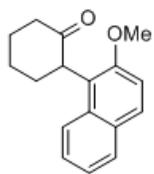


18f

¹H, CDCl₃, 500 MHz

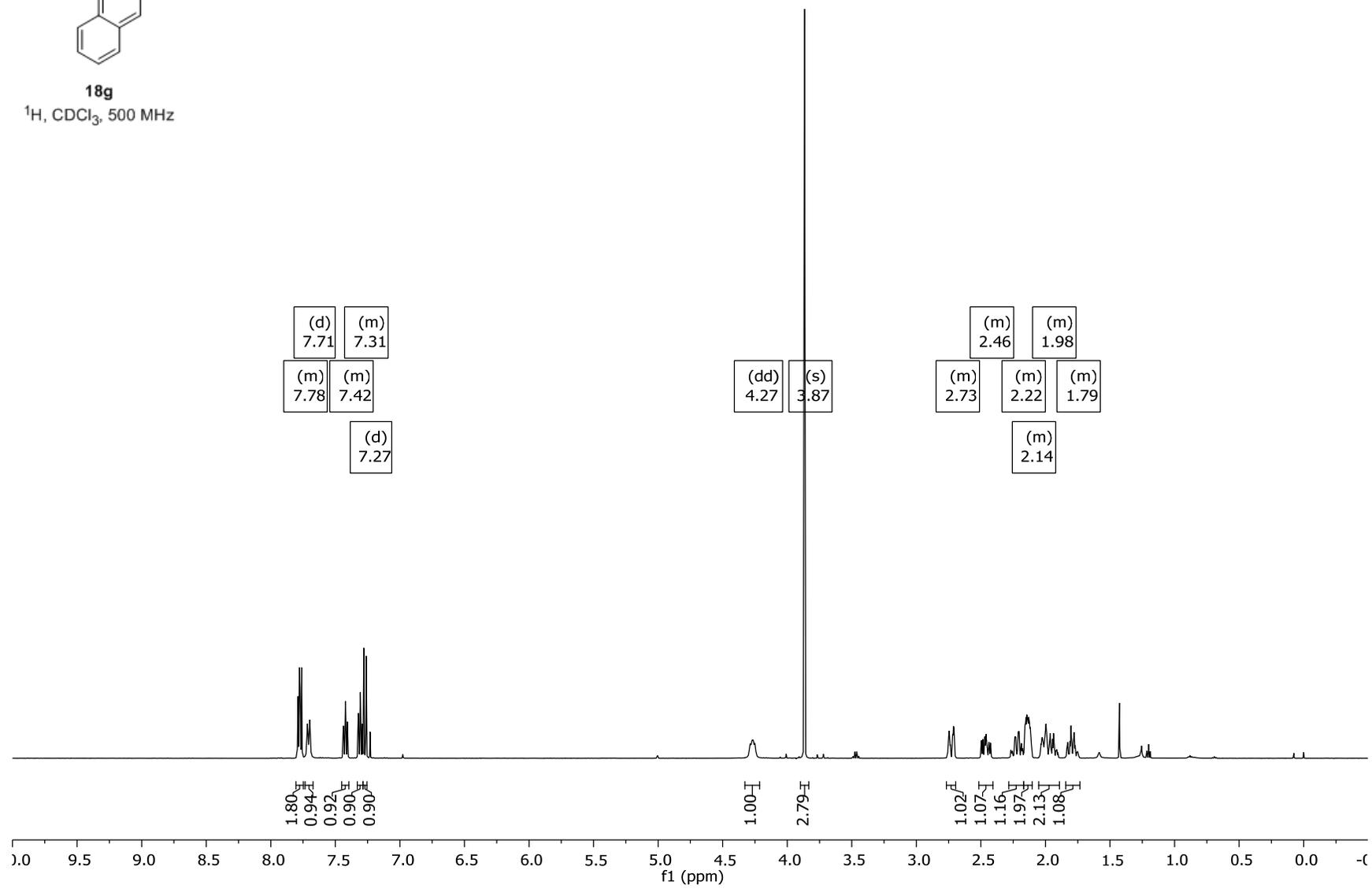




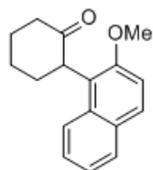


18g

^1H , CDCl_3 , 500 MHz



— 209.8



18g

¹³C, CDCl₃, 126 MHz

— 154.1

132.4
129.8
128.9
128.9
126.4
123.3
123.1
— 114.0

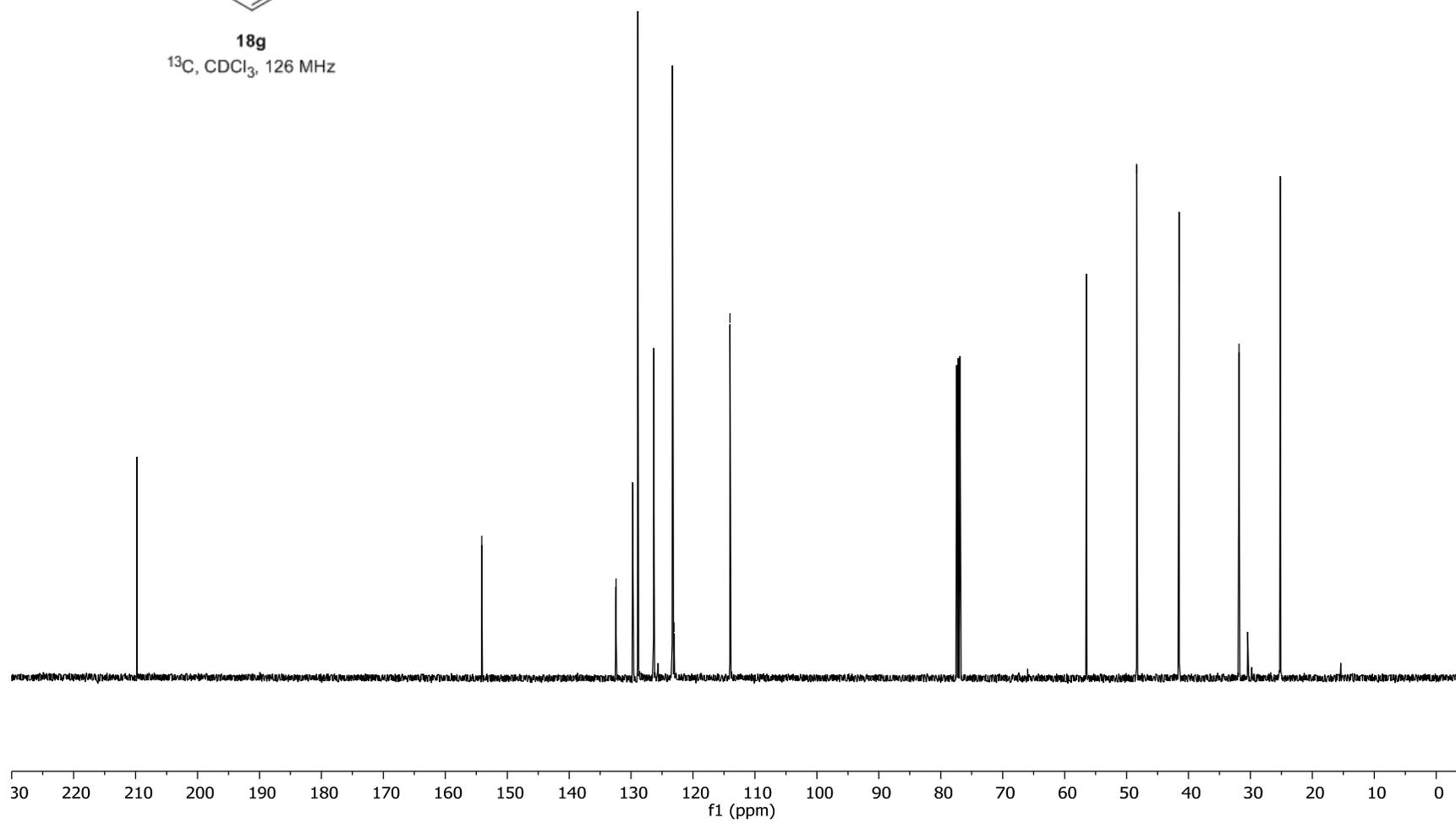
— 56.5

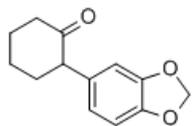
— 48.4

— 41.5

— 31.8

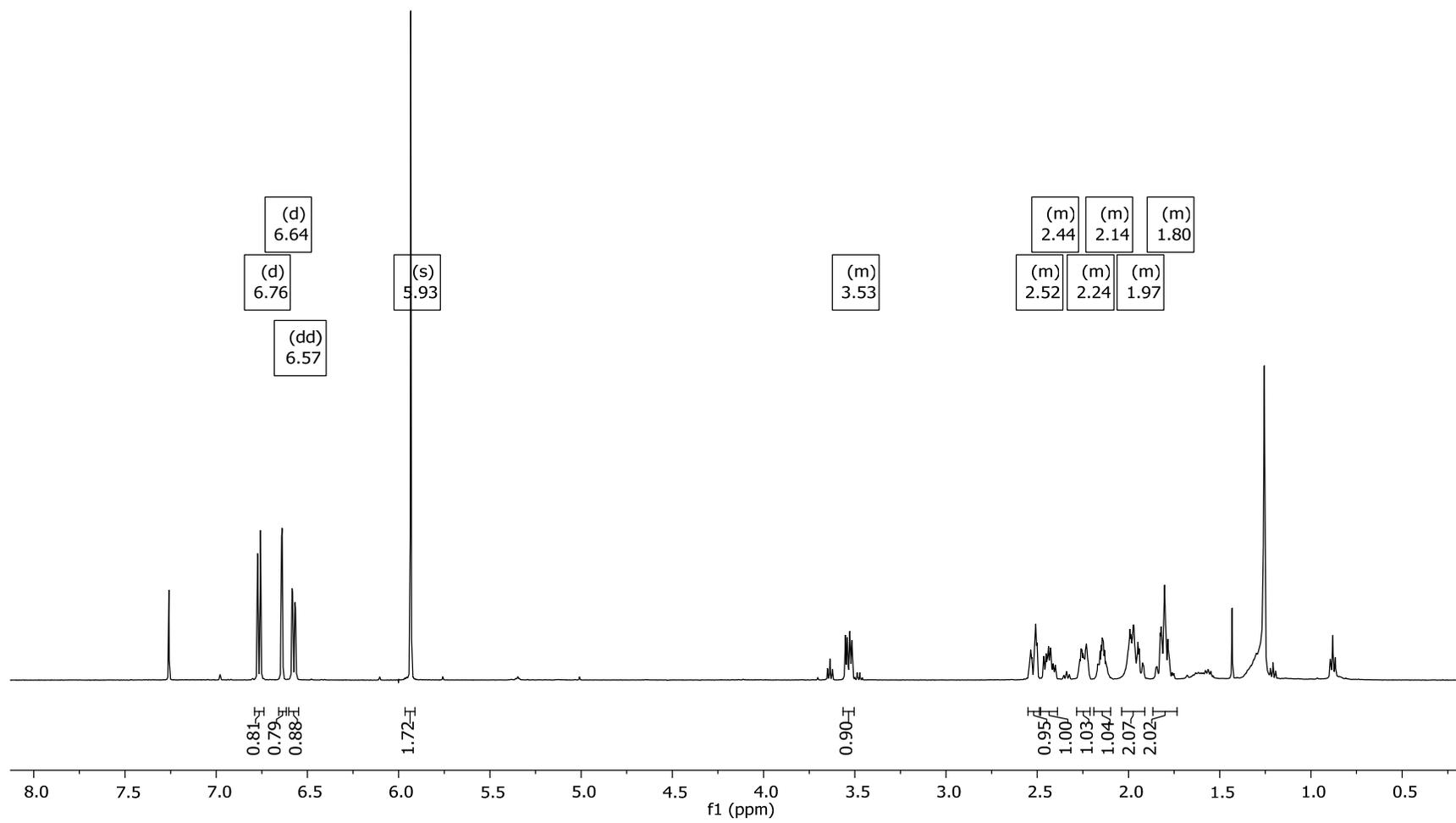
25.2
25.1

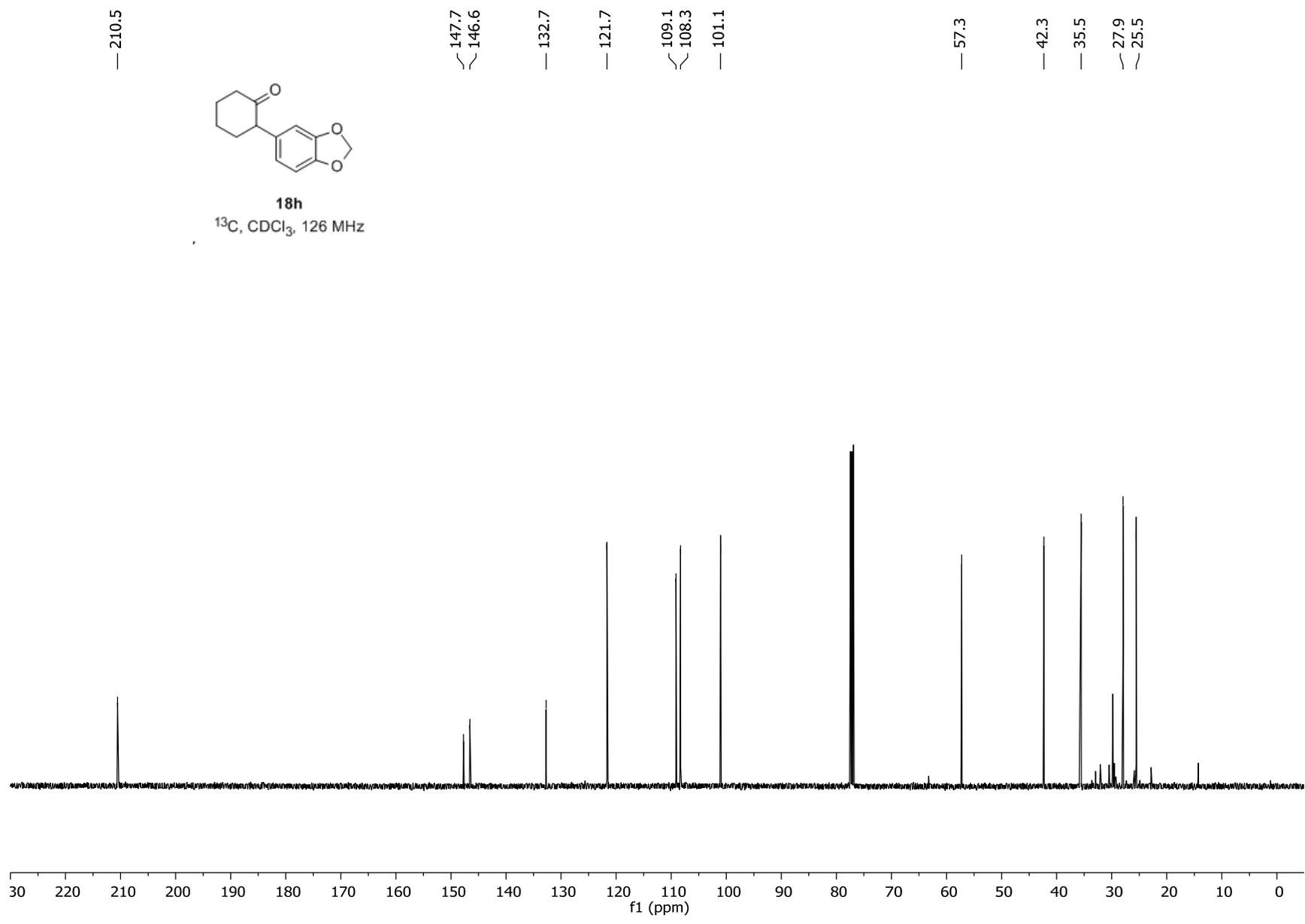


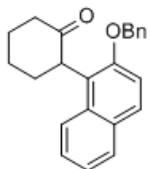


18h

¹H, CDCl₃, 500 MHz

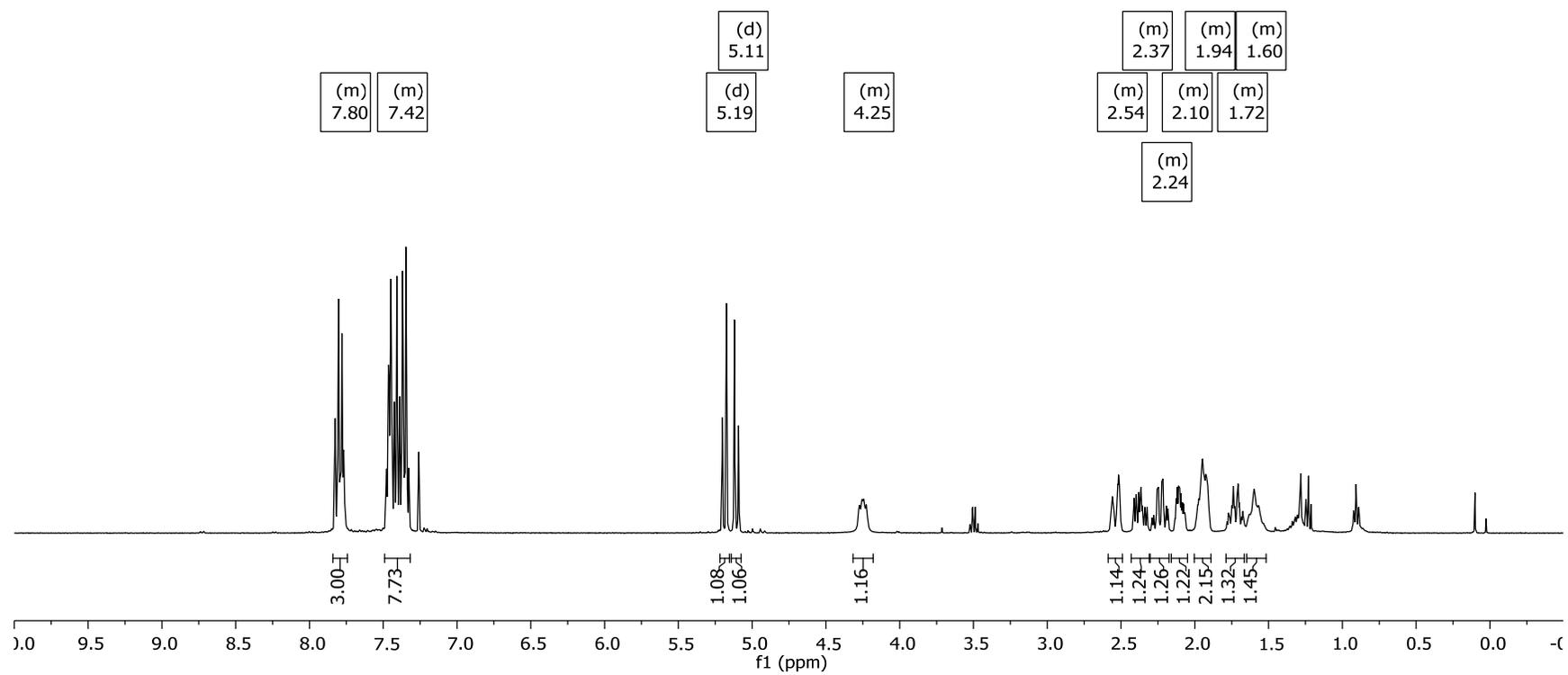




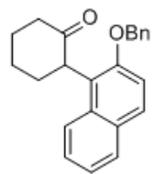


18i

¹H, CDCl₃, 400 MHz



— 209.7



18i

^{13}C , CDCl_3 , 101 MHz

153.4
137.1
132.6
129.9
129.0
128.9
128.6
128.2
128.2
126.5
123.5
123.4
123.1
115.0

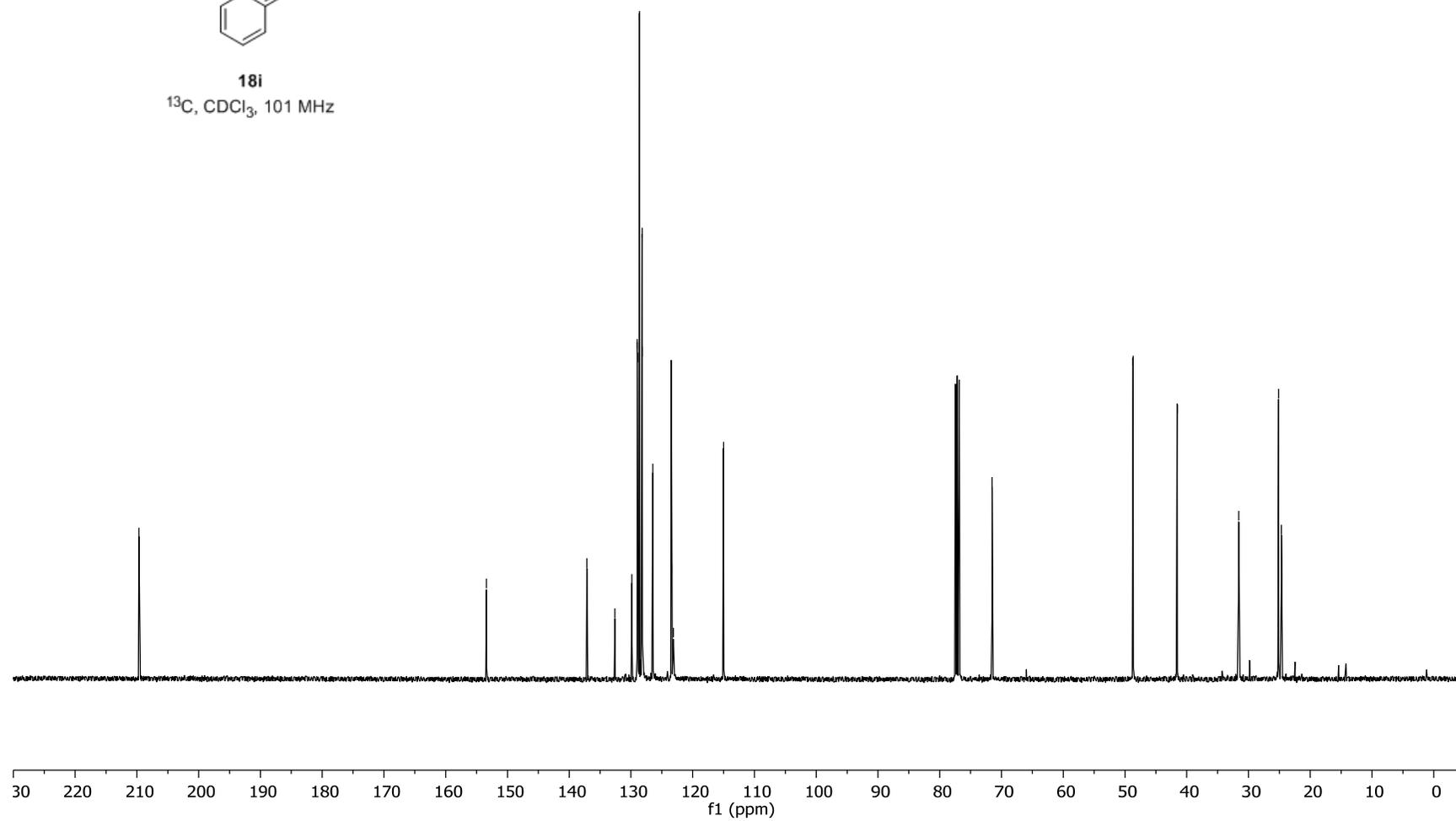
— 71.5

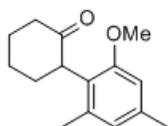
— 48.7

— 41.6

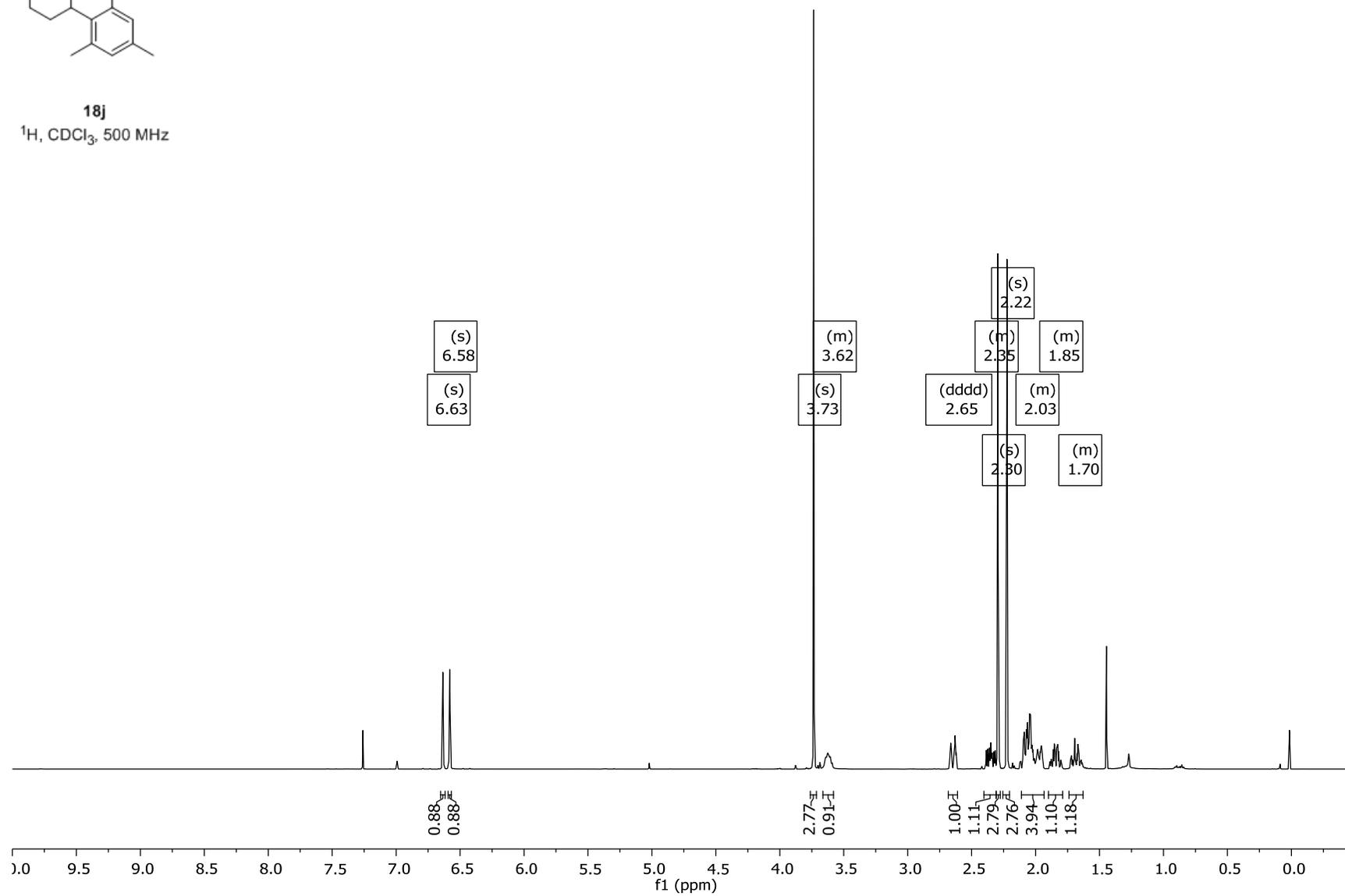
— 31.6

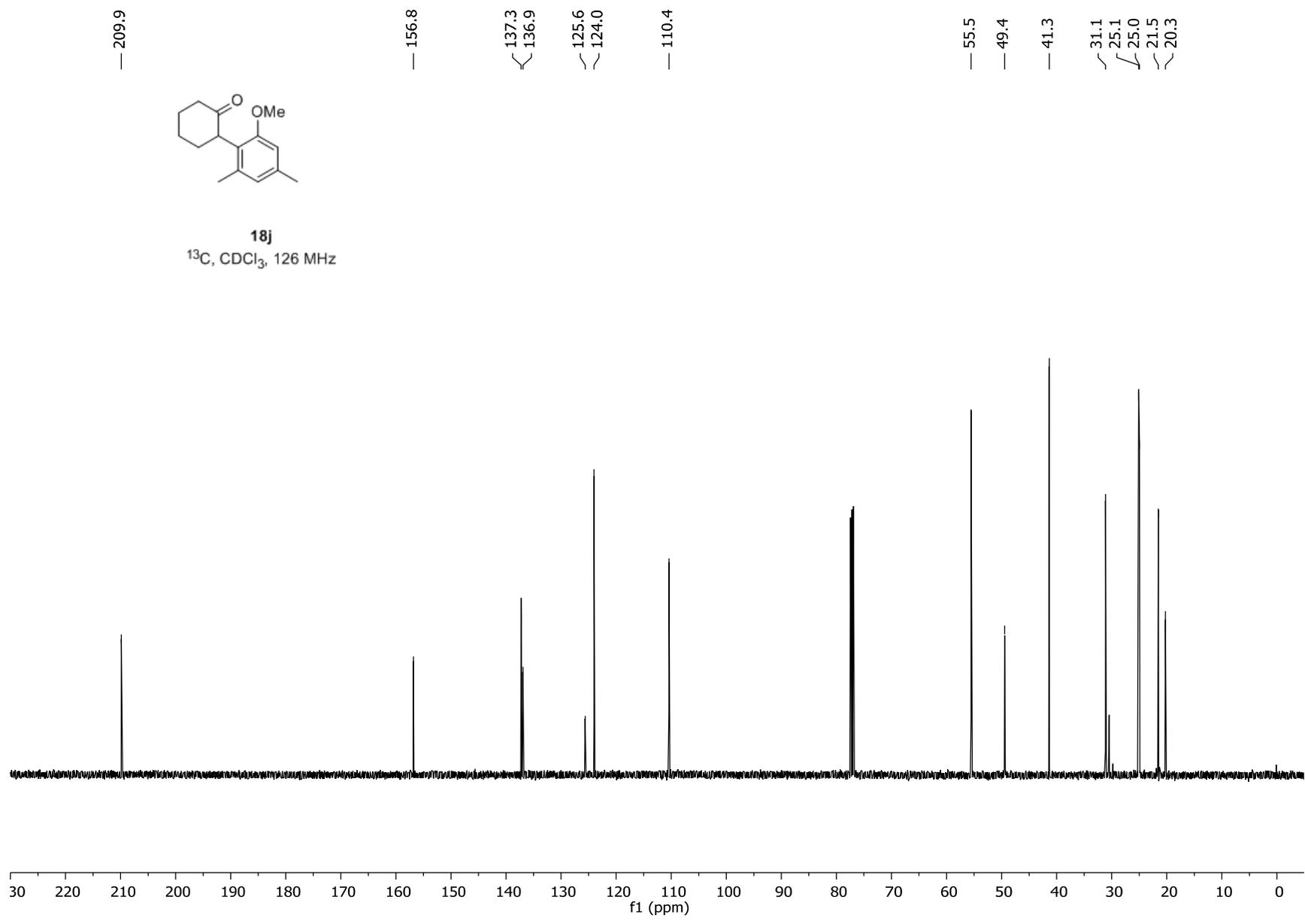
25.1
24.7

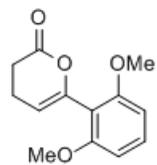




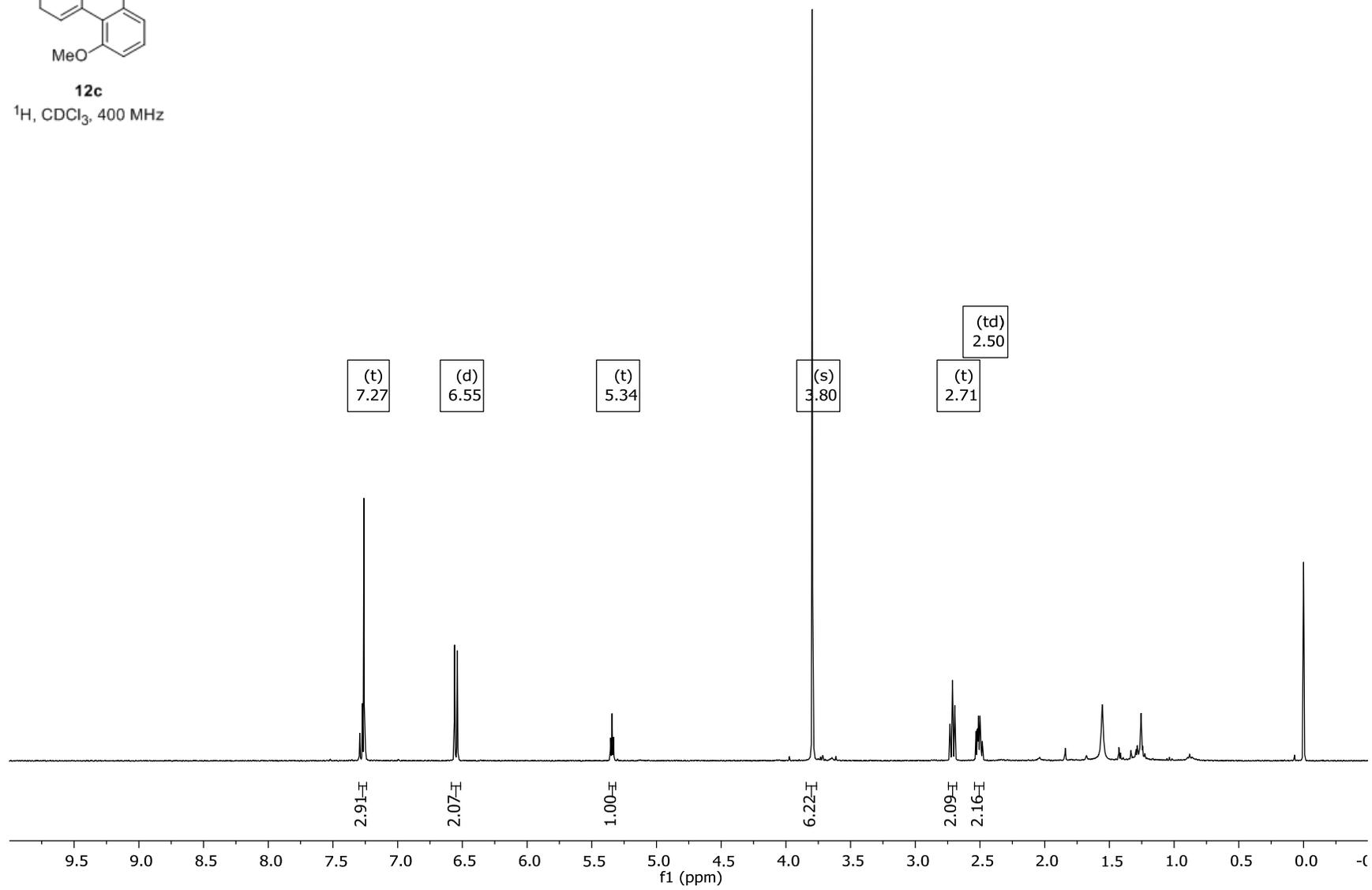
18j
 ^1H , CDCl_3 , 500 MHz

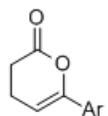






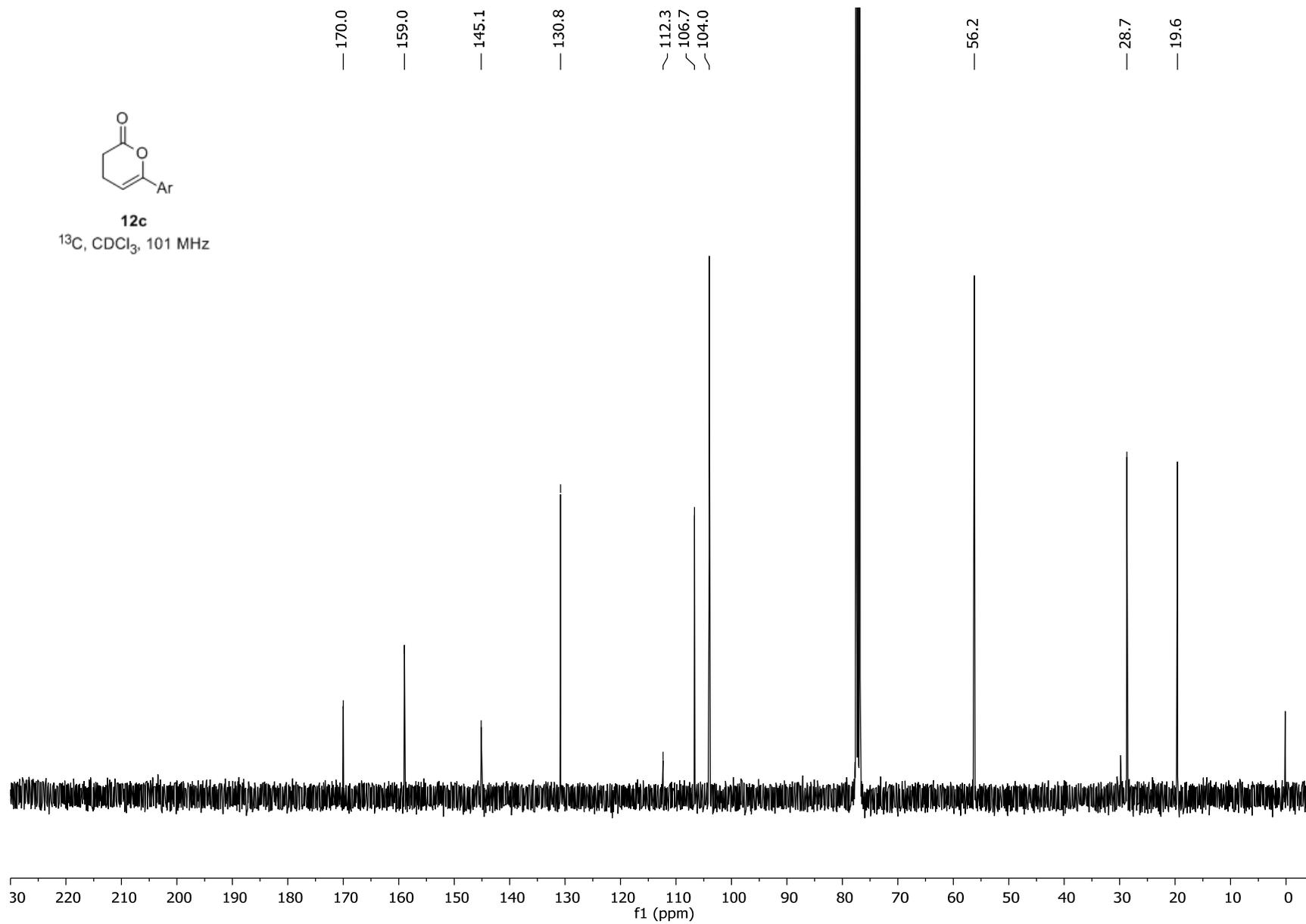
12c
 ^1H , CDCl_3 , 400 MHz

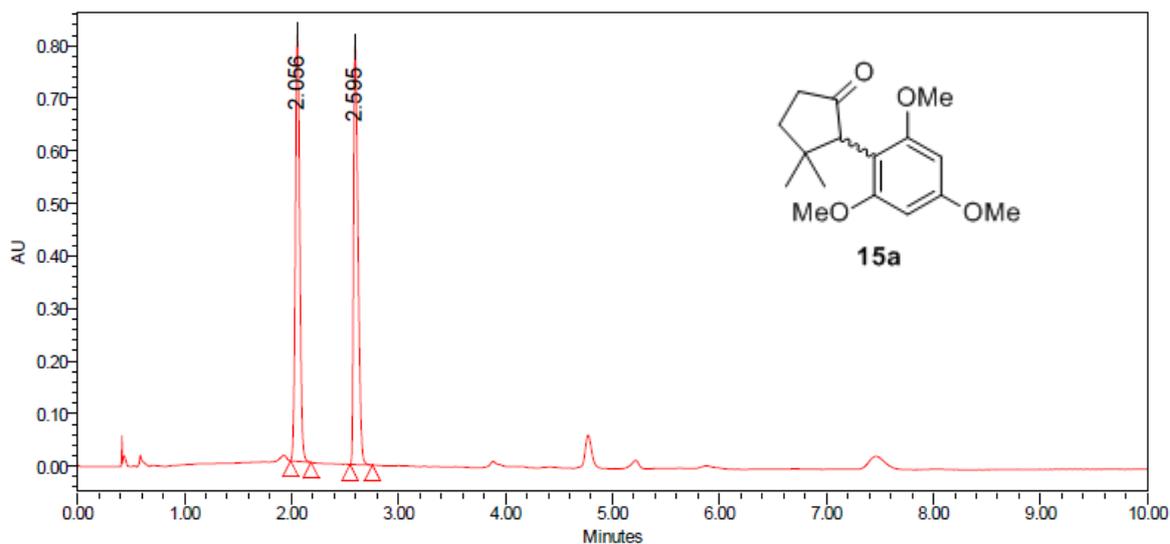




12c

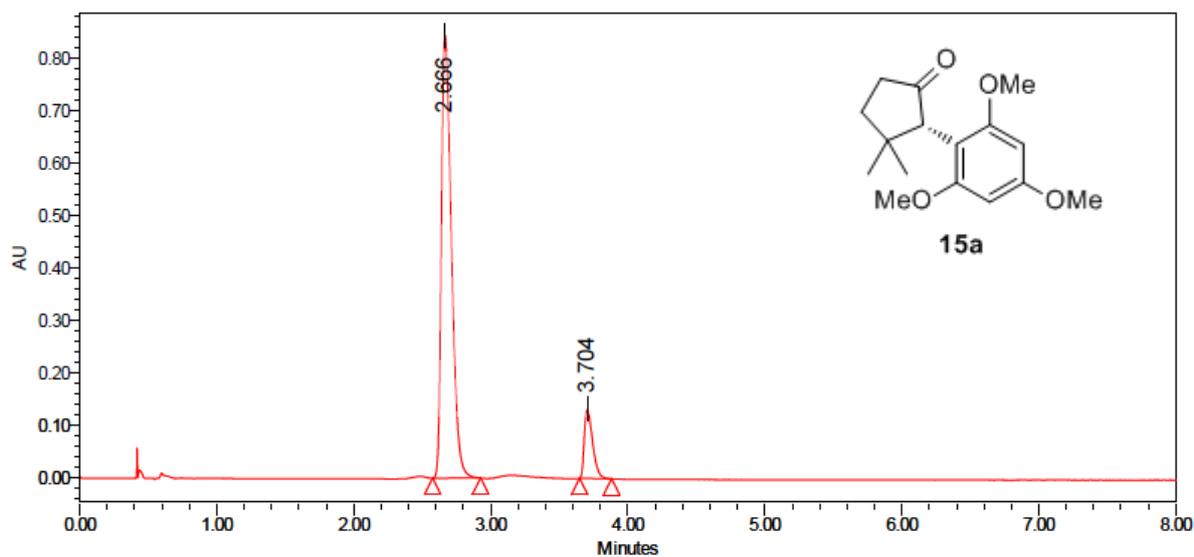
^{13}C , CDCl_3 , 101 MHz





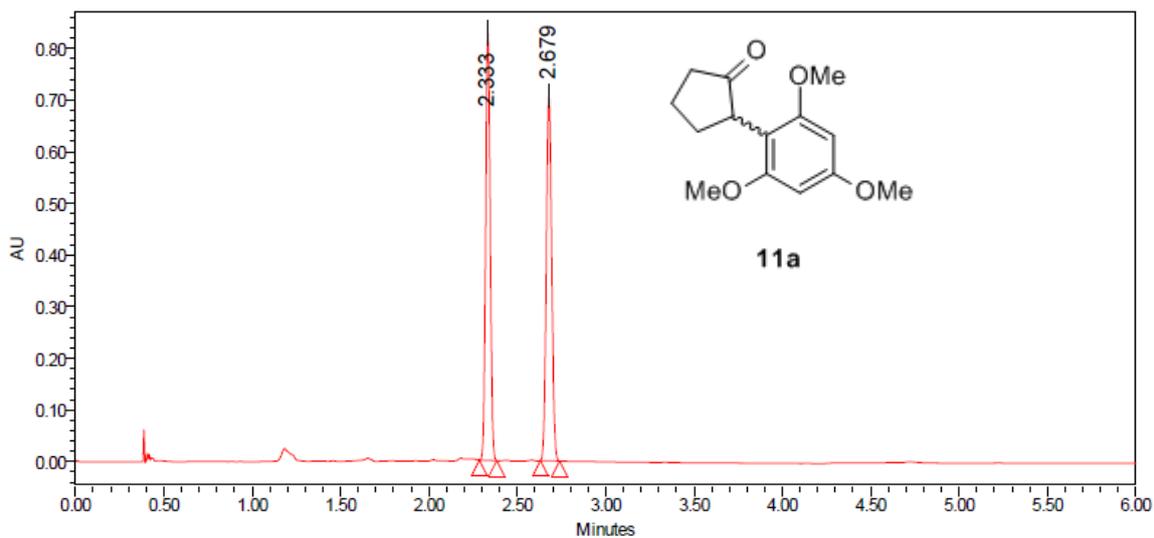
Peak Results

Name	RT	Area	Height	% Area
1	2.056	2307137	812392	50.19
2	2.595	2289515	796290	49.81



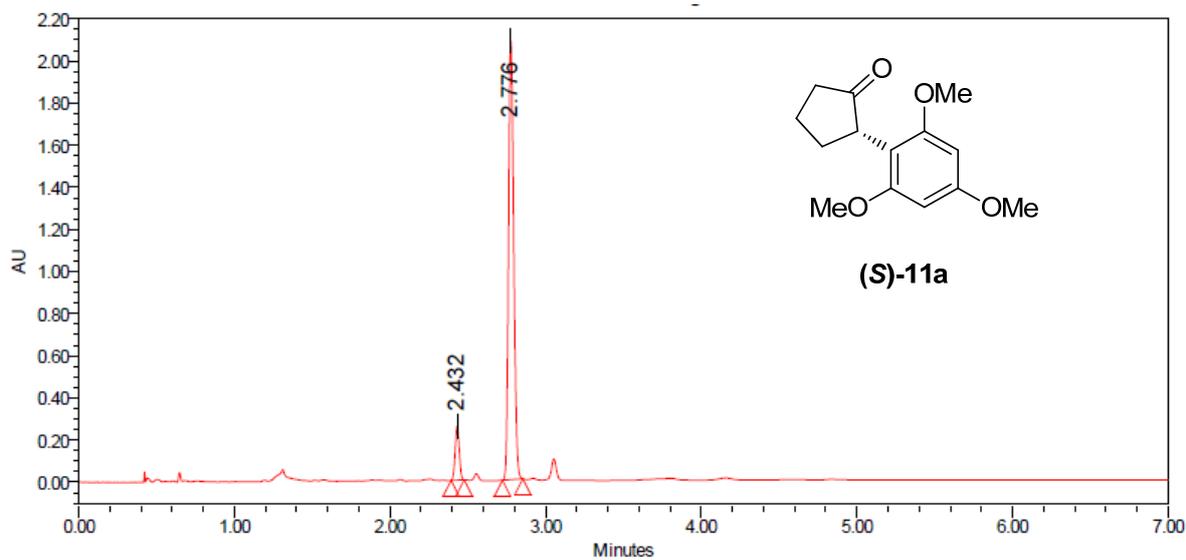
Peak Results

Name	RT	Area	Height	% Area
1	2.666	4292278	844570	88.47
2	3.704	559537	132358	11.53



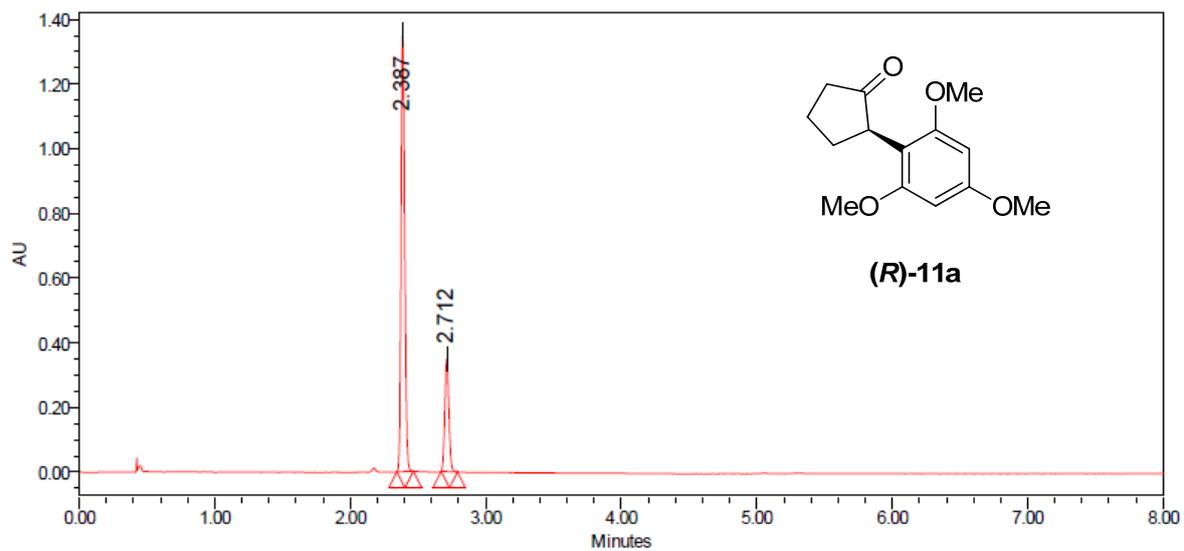
Peak Results

Name	RT	Area	Height	% Area
1	2.333	1484909	827475	49.79
2	2.679	1497159	707369	50.21



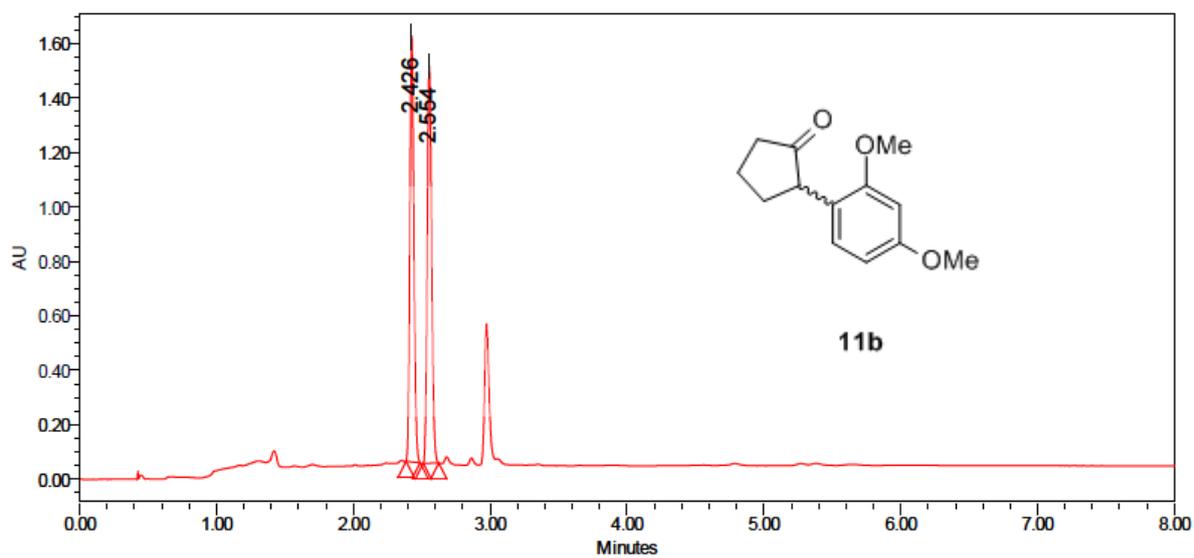
Peak Results

Name	RT	Area	Height	% Area
1	2.432	473131	255784	8.87
2	2.776	4860381	2084739	91.13



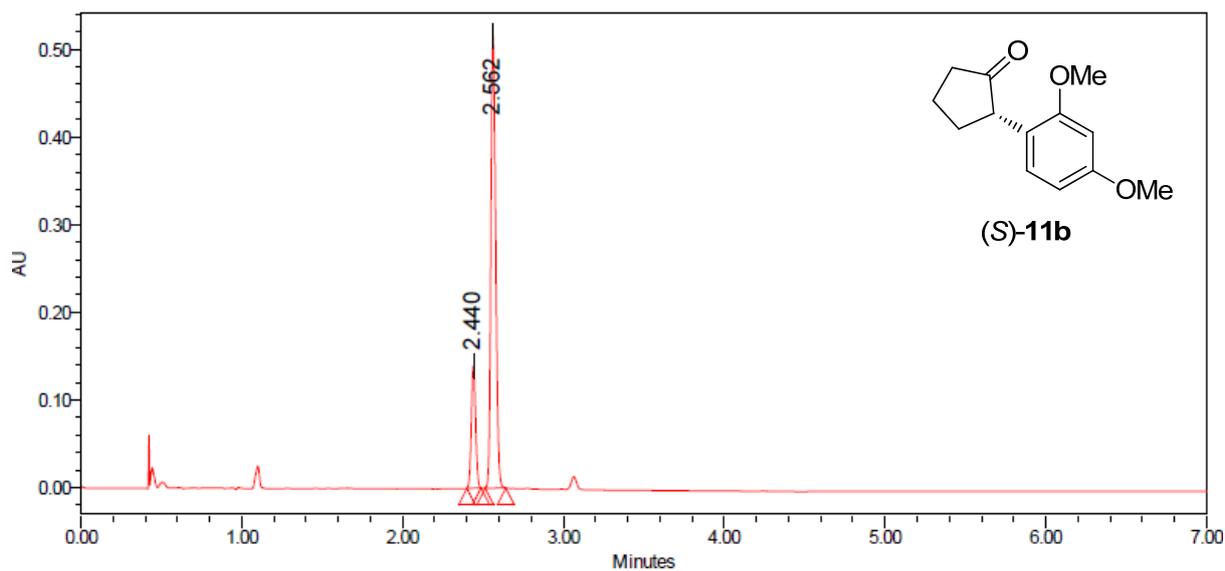
Peak Results

Name	RT	Area	Height	% Area
1	2.387	2542635	1351059	77.71
2	2.712	729207	347387	22.29



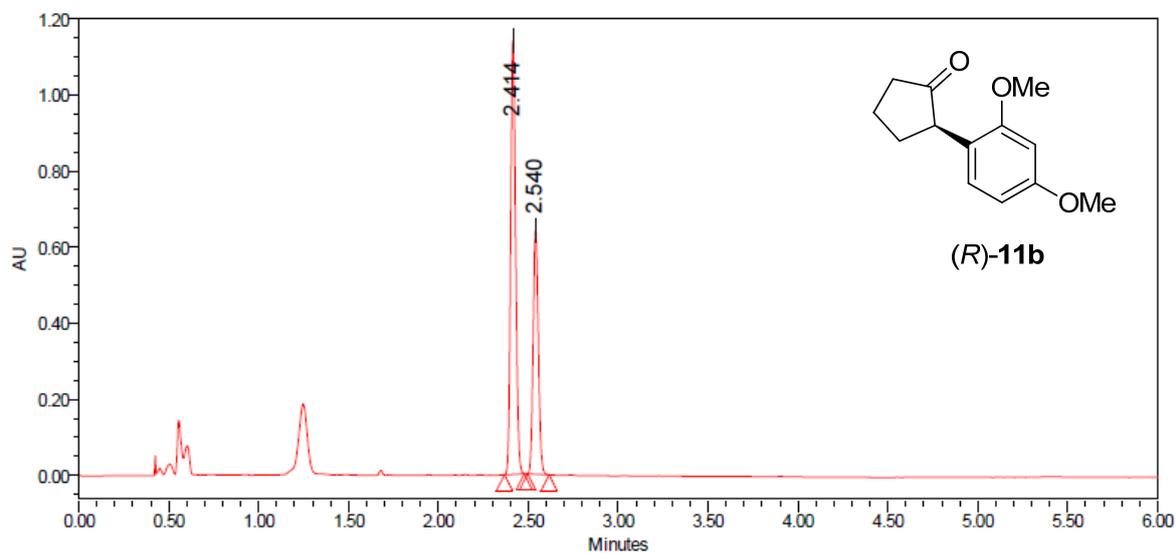
Peak Results

Name	RT	Area	Height	% Area
1	2.426	3227508	1564432	49.81
2	2.554	3251526	1458388	50.19



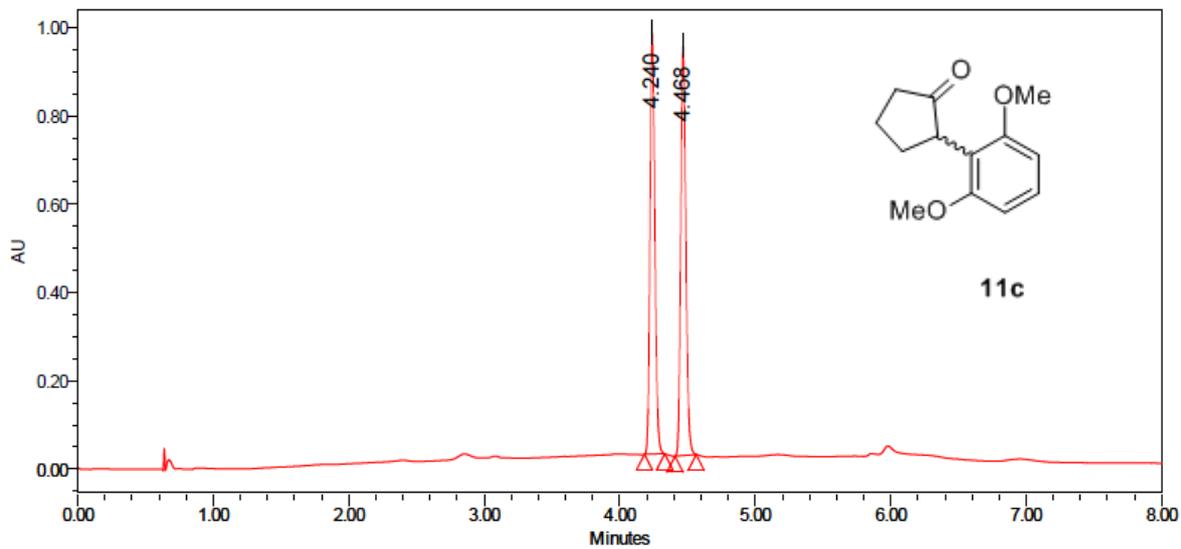
Peak Results

Name	RT	Area	Height	% Area
1	2.440	258312	139471	19.62
2	2.562	1058246	516027	80.38



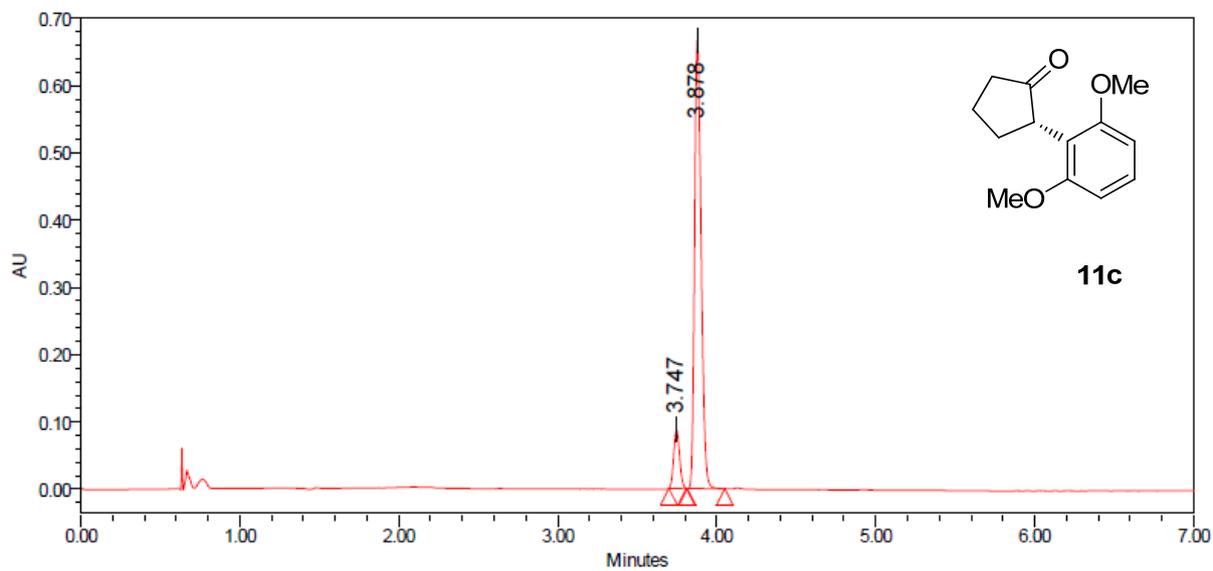
Peak Results

Name	RT	Area	Height	% Area
1	2.414	2191516	1140118	62.90
2	2.540	1292704	643273	37.10



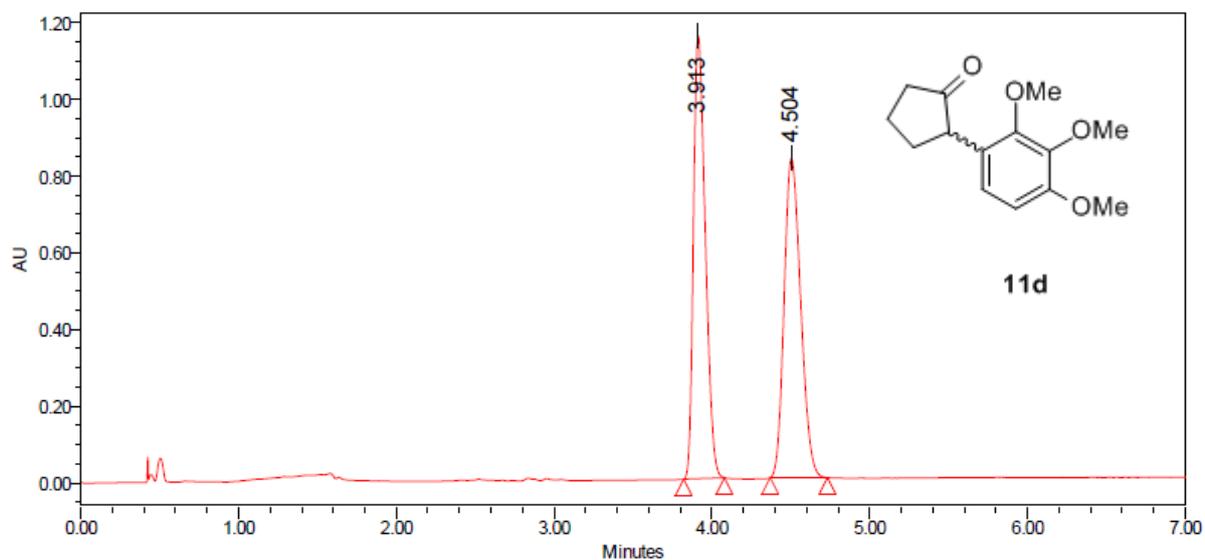
Peak Results

Name	RT	Area	Height	% Area
1	4.240	2388341	955757	49.67
2	4.468	2419814	929259	50.33



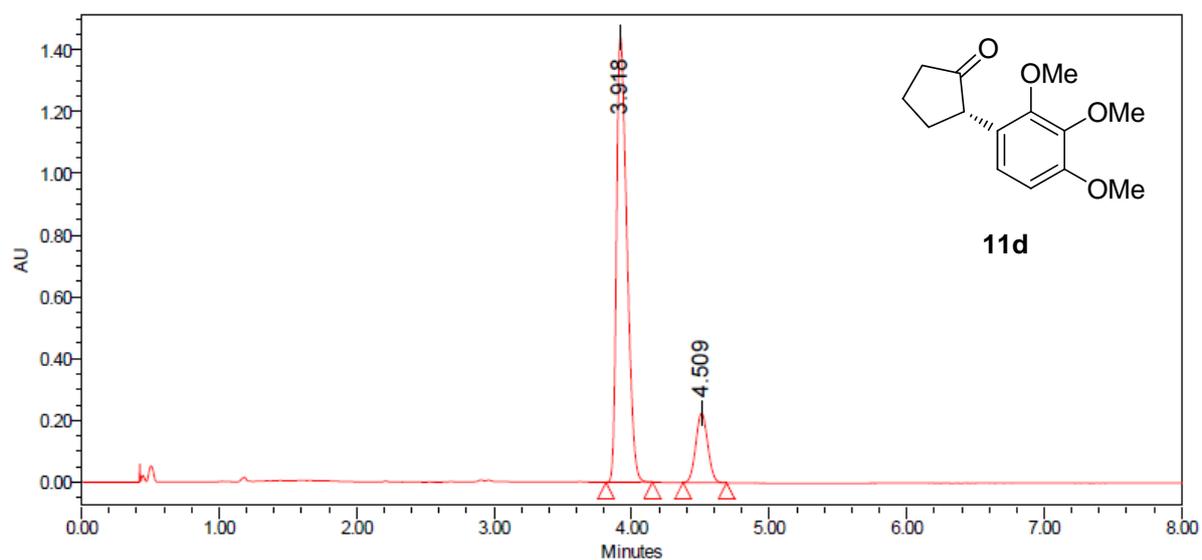
Peak Results

Name	RT	Area	Height	% Area
1	3.747	222745	87111	10.41
2	3.878	1916728	666154	89.59



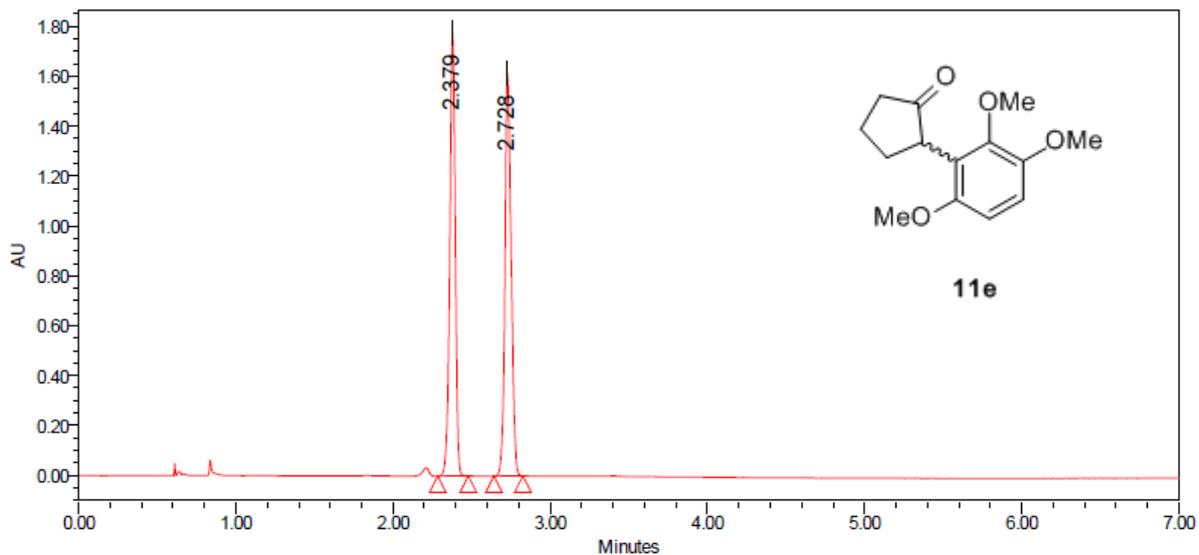
Peak Results

Name	RT	Area	Height	% Area
1	3.913	6015515	1154736	49.77
2	4.504	6072072	832291	50.23



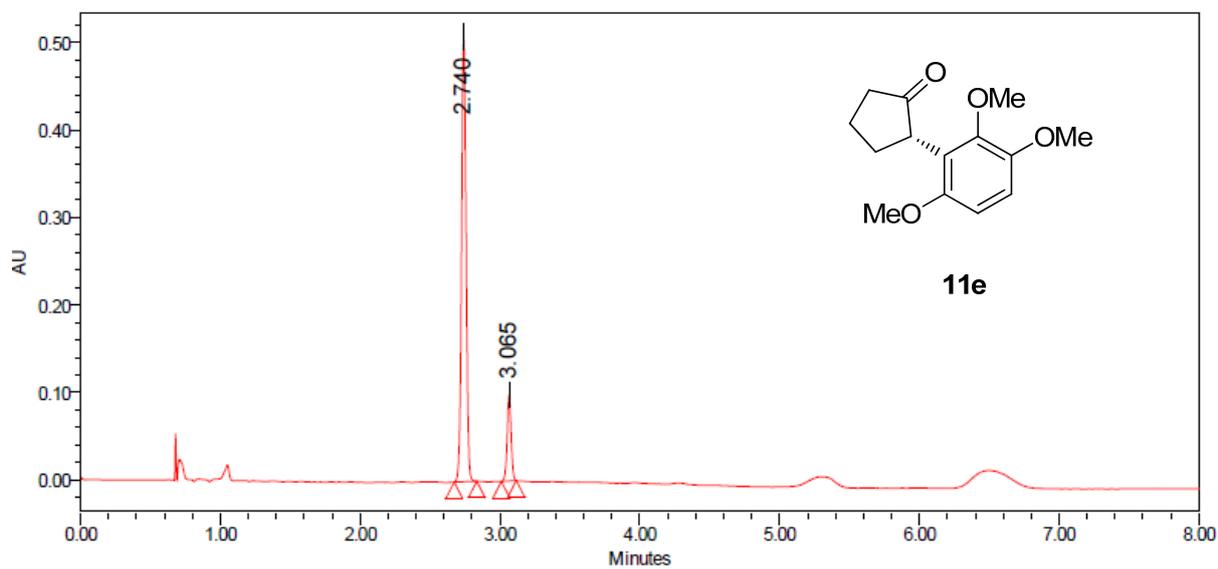
Peak Results

Name	RT	Area	Height	% Area
1	3.918	7547631	1440871	84.74
2	4.509	1358857	225651	15.26



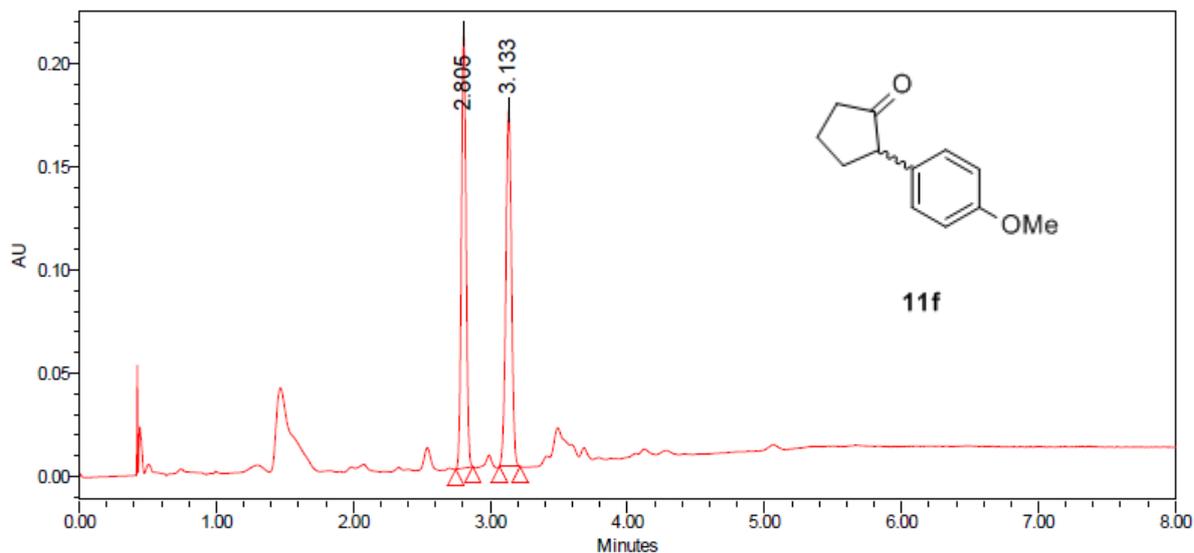
Peak Results

Name	RT	Area	Height	% Area
1	2.379	4326202	1778184	49.31
2	2.728	4447016	1614045	50.69



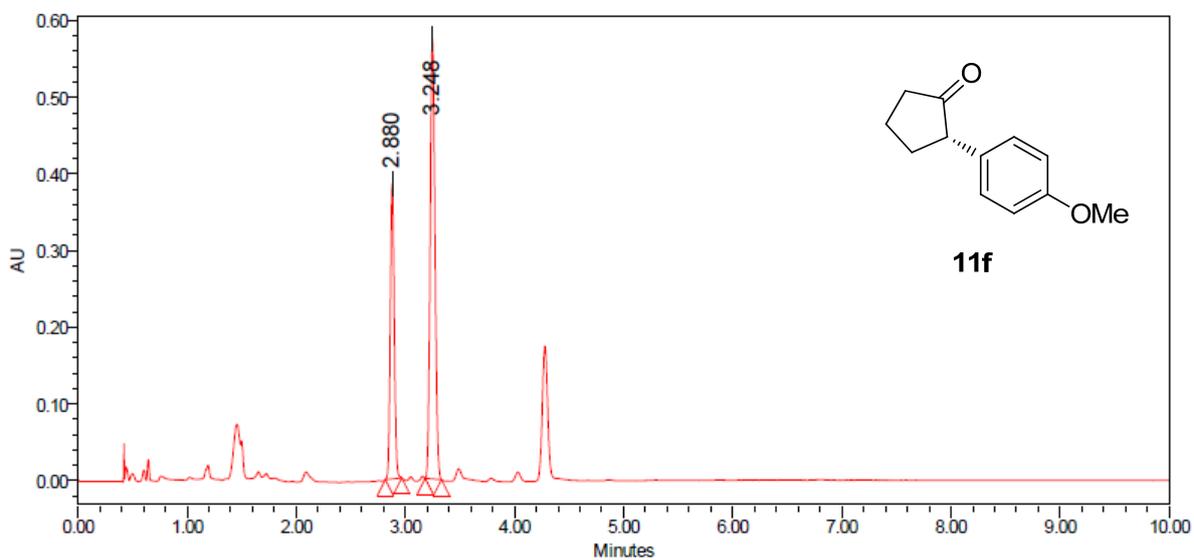
Peak Results

Name	RT	Area	Height	% Area
1	2.740	1139639	509582	85.39
2	3.065	194993	98270	14.61



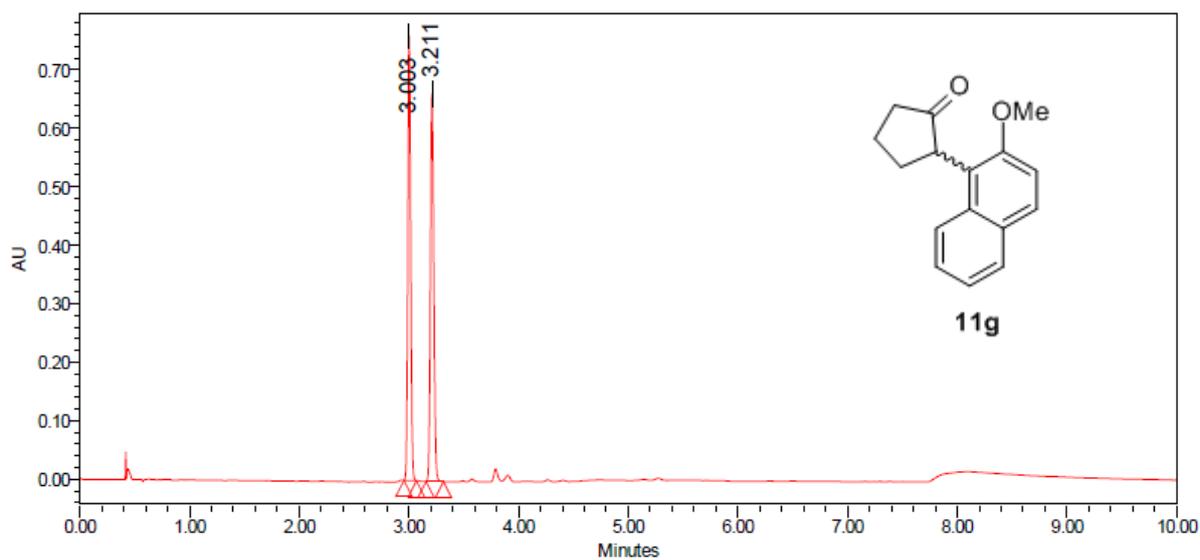
Peak Results

Name	RT	Area	Height	% Area
1	2.805	495364	210248	50.04
2	3.133	494637	172425	49.96



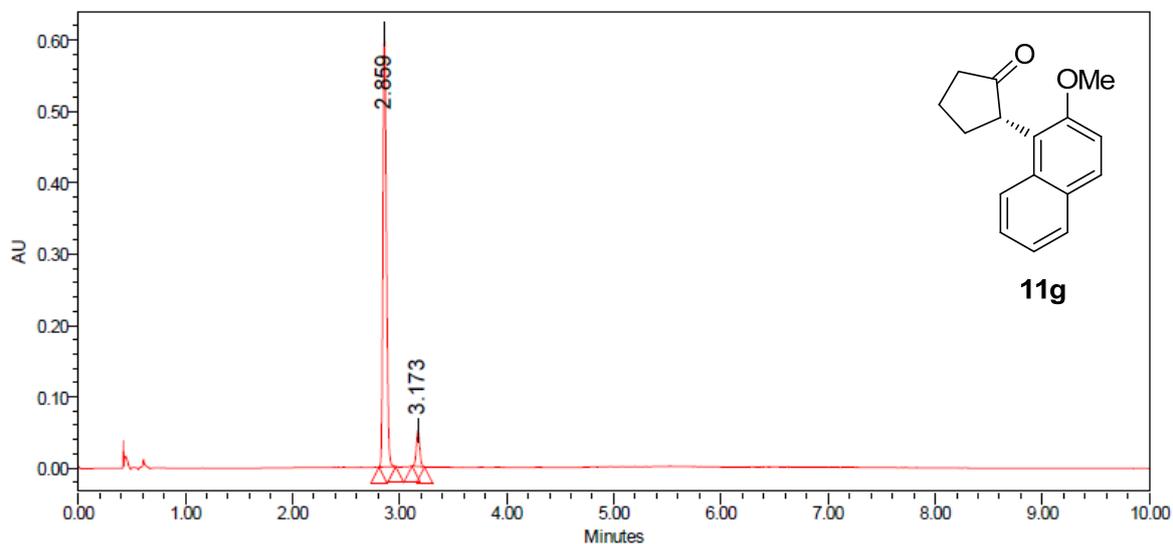
Peak Results

Name	RT	Area	Height	% Area
1	2.880	969018	384415	35.49
2	3.248	1761002	574381	64.51



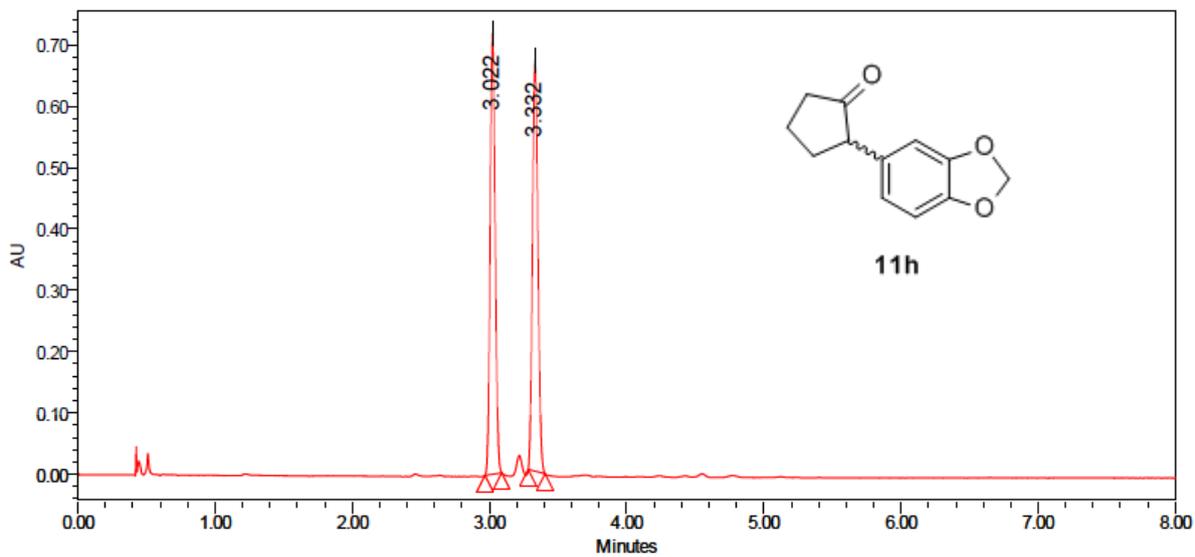
Peak Results

Name	RT	Area	Height	% Area
1	3.003	1385772	759795	49.68
2	3.211	1403658	662807	50.32



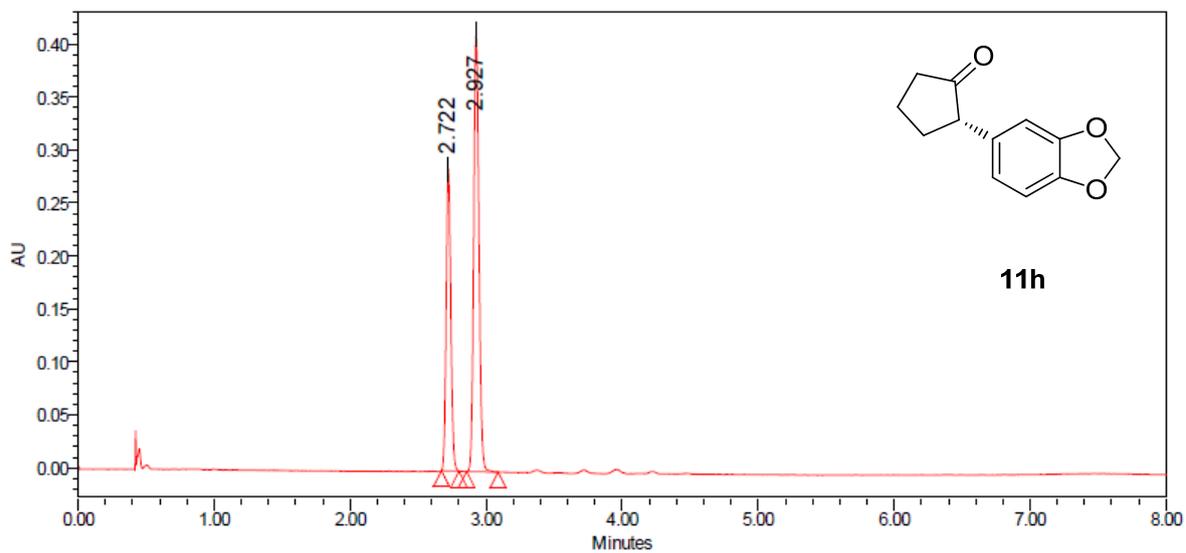
Peak Results

Name	RT	Area	Height	% Area
1	2.859	1377375	607215	92.53
2	3.173	111191	50695	7.47



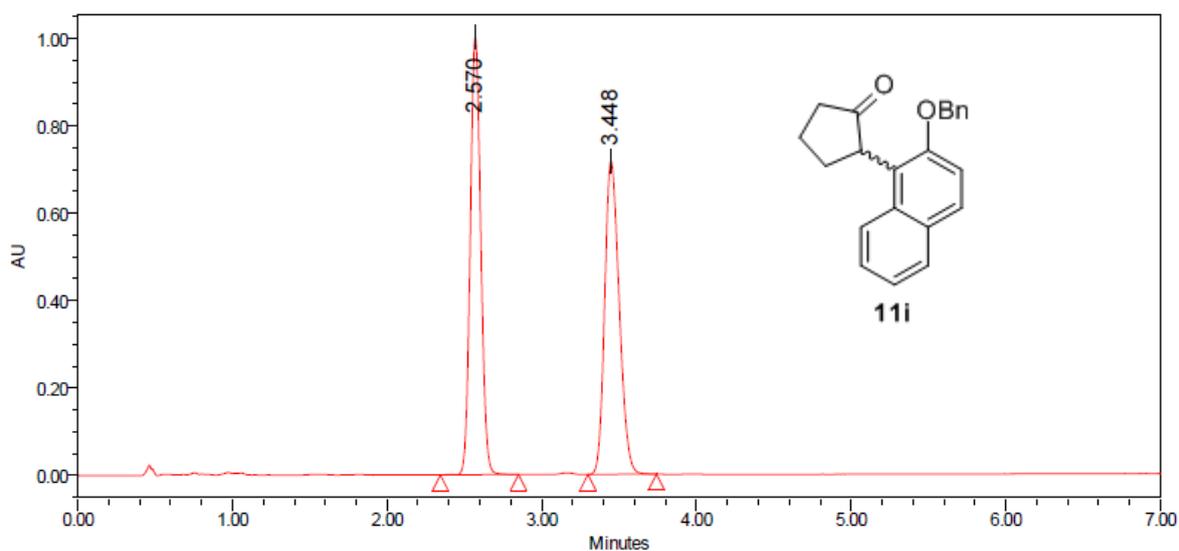
Peak Results

Name	RT	Area	Height	% Area
1	3.022	1824206	719056	49.51
2	3.332	1860323	670136	50.49



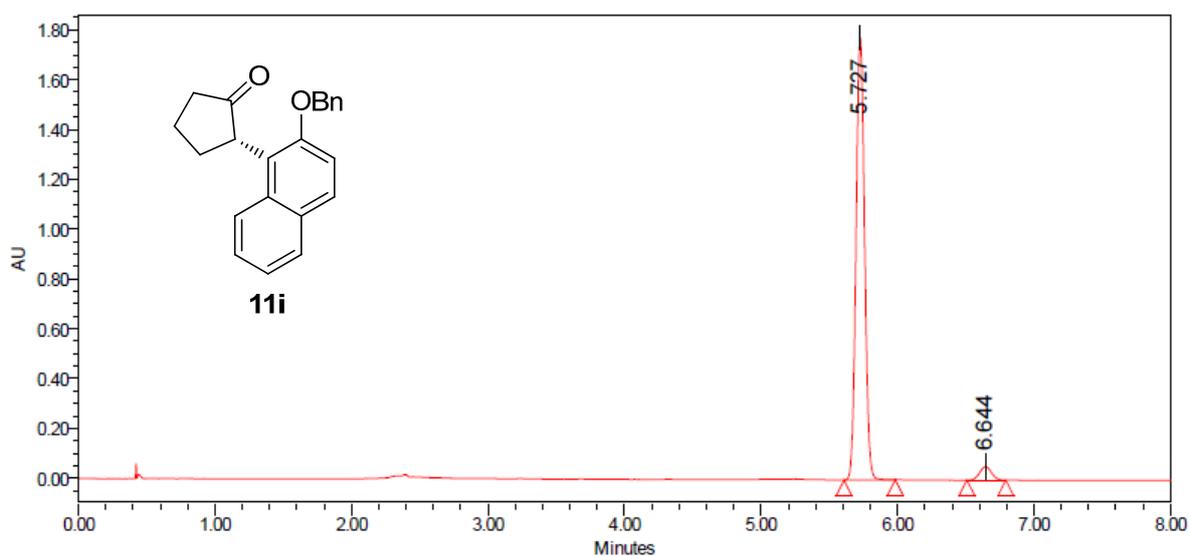
Peak Results

Name	RT	Area	Height	% Area
1	2.722	676156	284763	37.95
2	2.927	1105513	413049	62.05



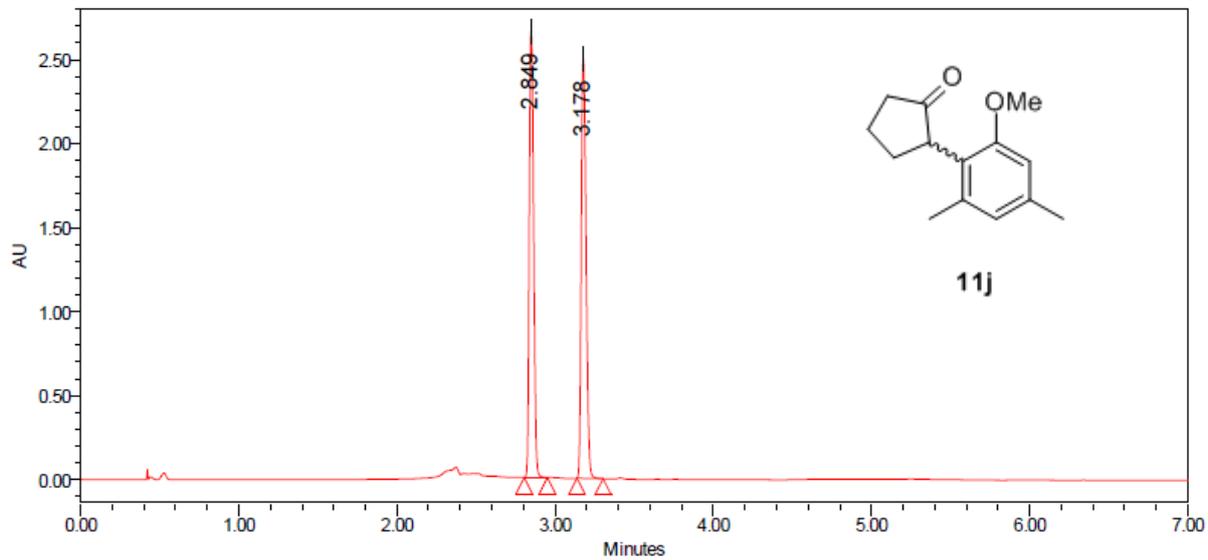
Peak Results

Name	RT	Area	Height	% Area
1	2.570	4718399	1002948	50.18
2	3.448	4684880	717641	49.82



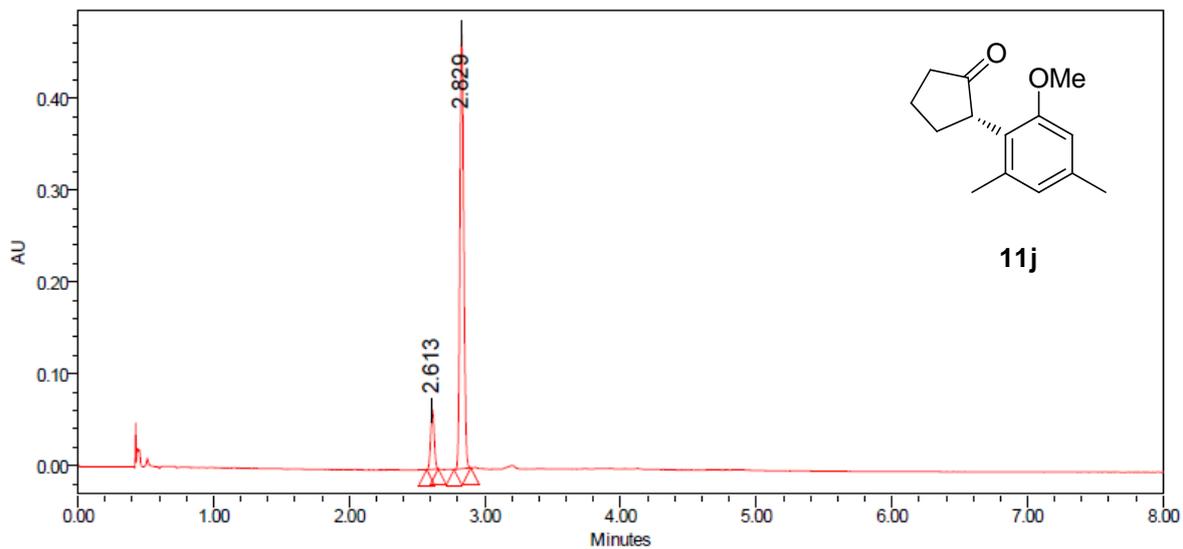
Peak Results

Name	RT	Area	Height	% Area
1	5.727	7722744	1776728	95.92
2	6.644	328319	54465	4.08



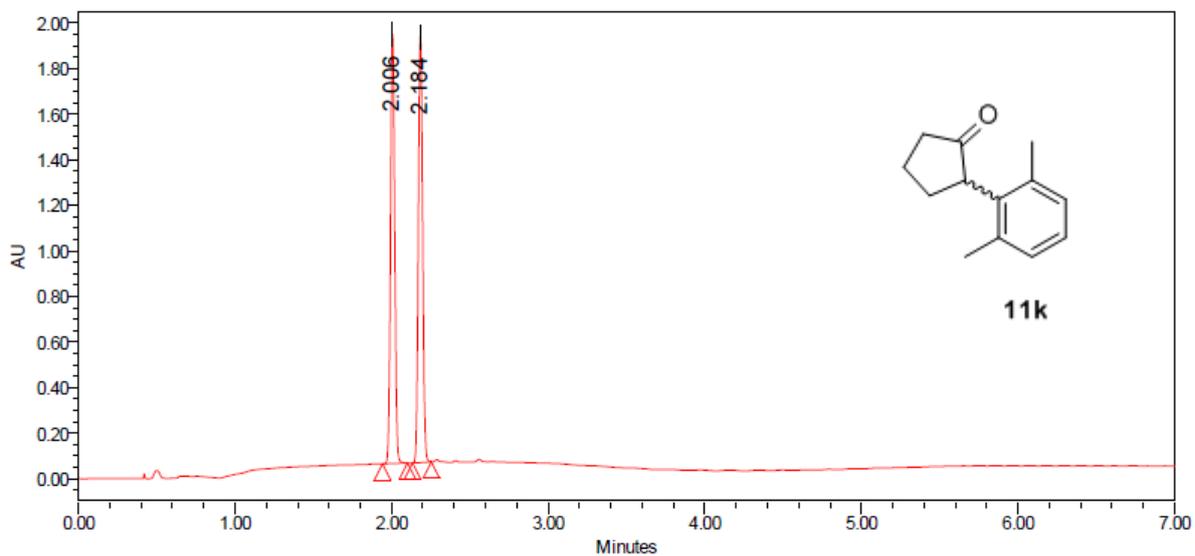
Peak Results

Name	RT	Area	Height	% Area
1	2.849	5104841	2656960	49.15
2	3.178	5280734	2496124	50.85



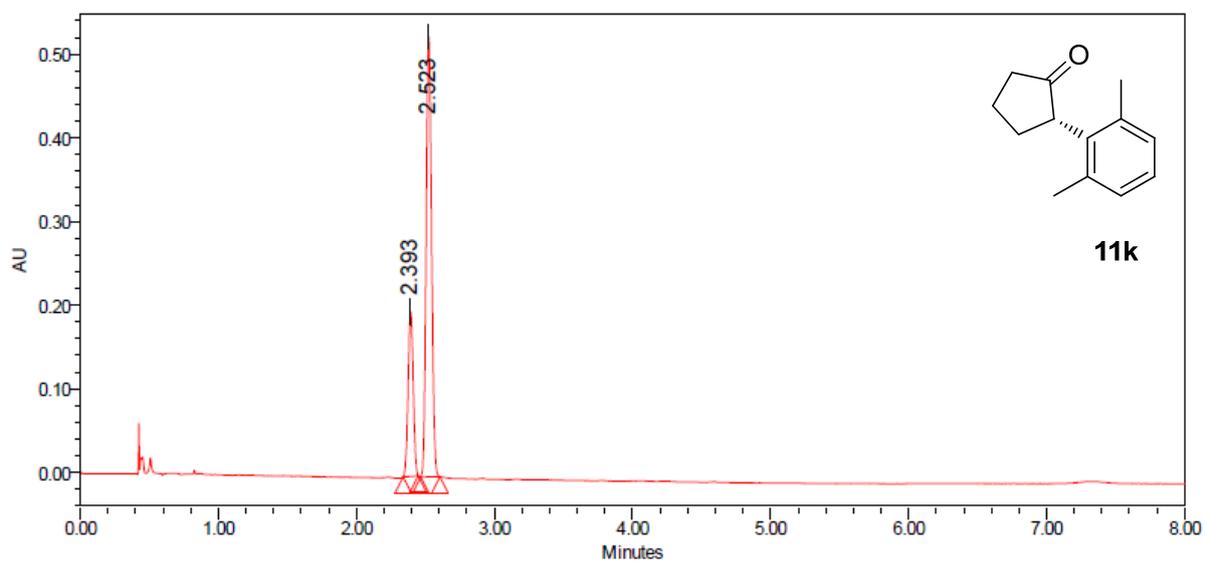
Peak Results

Name	RT	Area	Height	% Area
1	2.613	118750	64820	11.32
2	2.829	930219	475164	88.68



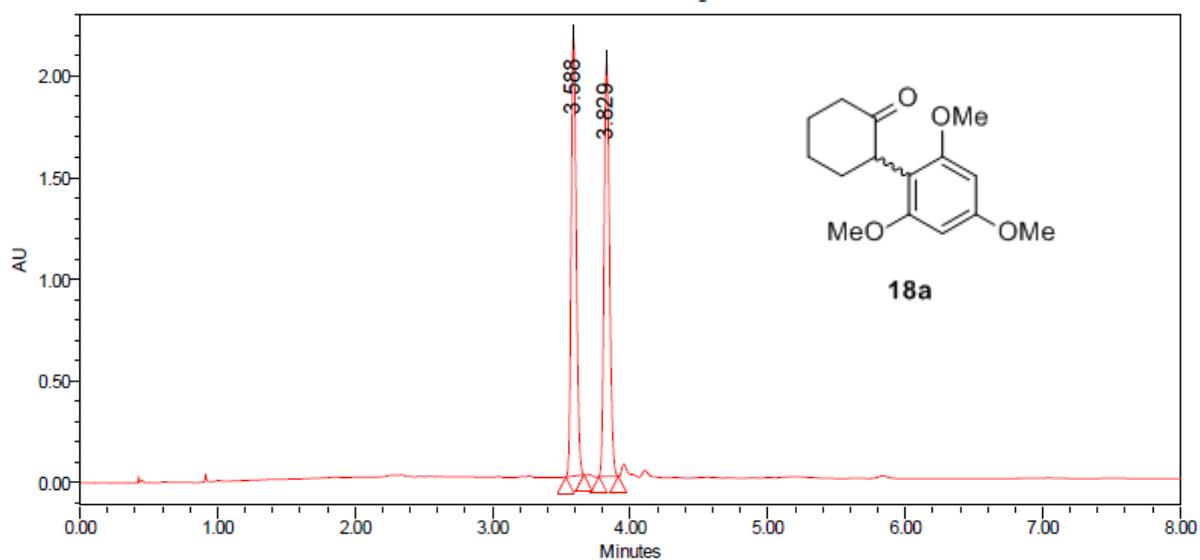
Peak Results

Name	RT	Area	Height	% Area
1	2.006	3532335	1884155	49.79
2	2.184	3562428	1867990	50.21



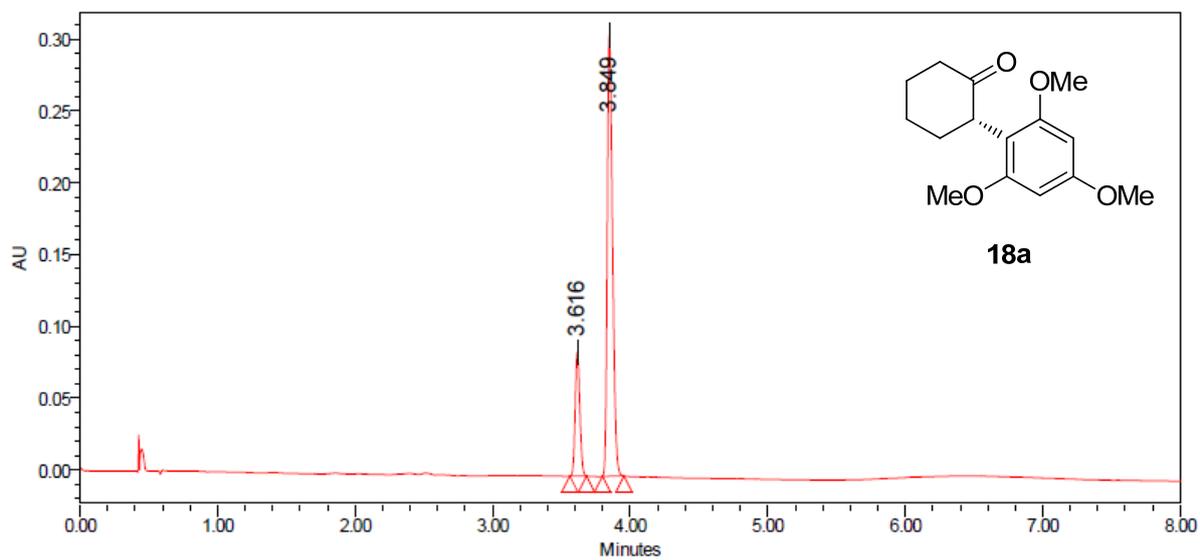
Peak Results

Name	RT	Area	Height	% Area
1	2.393	508019	196835	26.27
2	2.523	1425912	526368	73.73



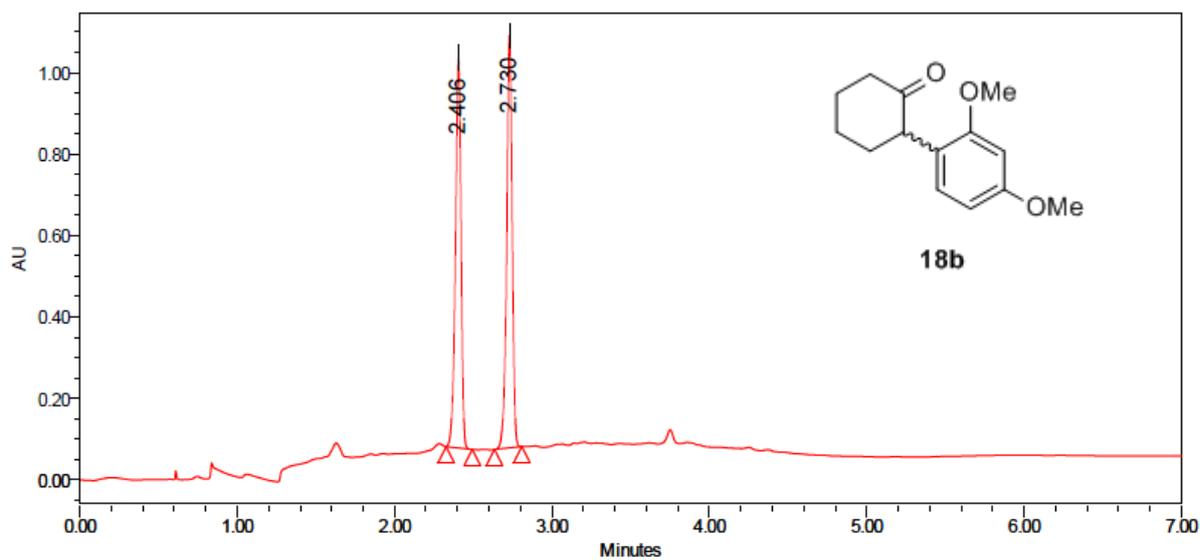
Peak Results

Name	RT	Area	Height	% Area
1	3.588	5555013	2160035	49.68
2	3.829	5626121	2037253	50.32



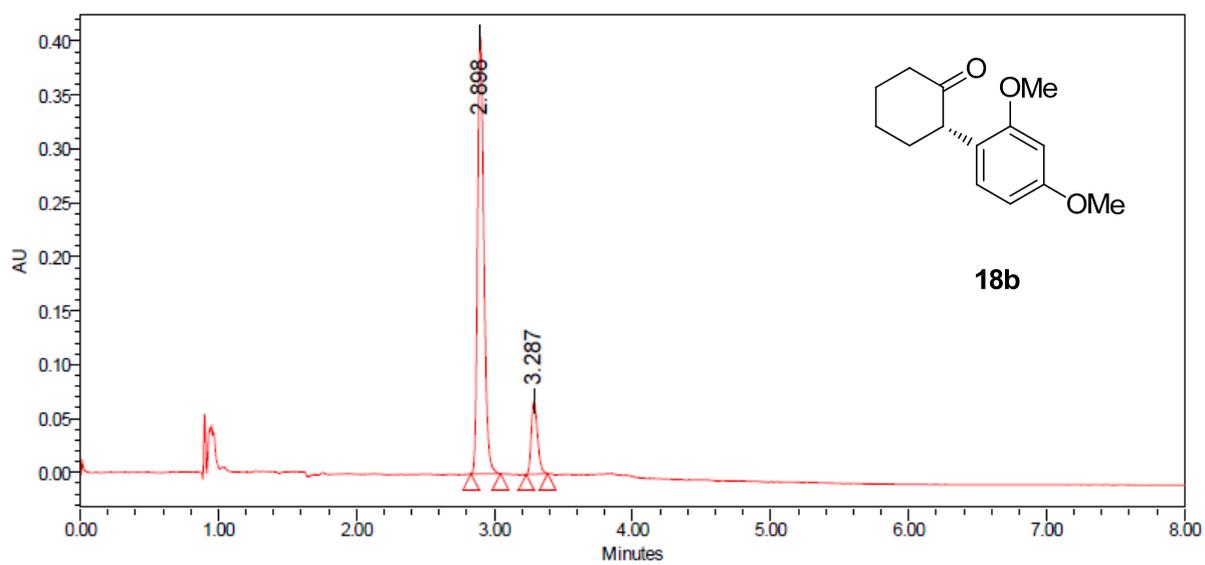
Peak Results

Name	RT	Area	Height	% Area
1	3.616	203064	86076	19.86
2	3.849	819388	307287	80.14



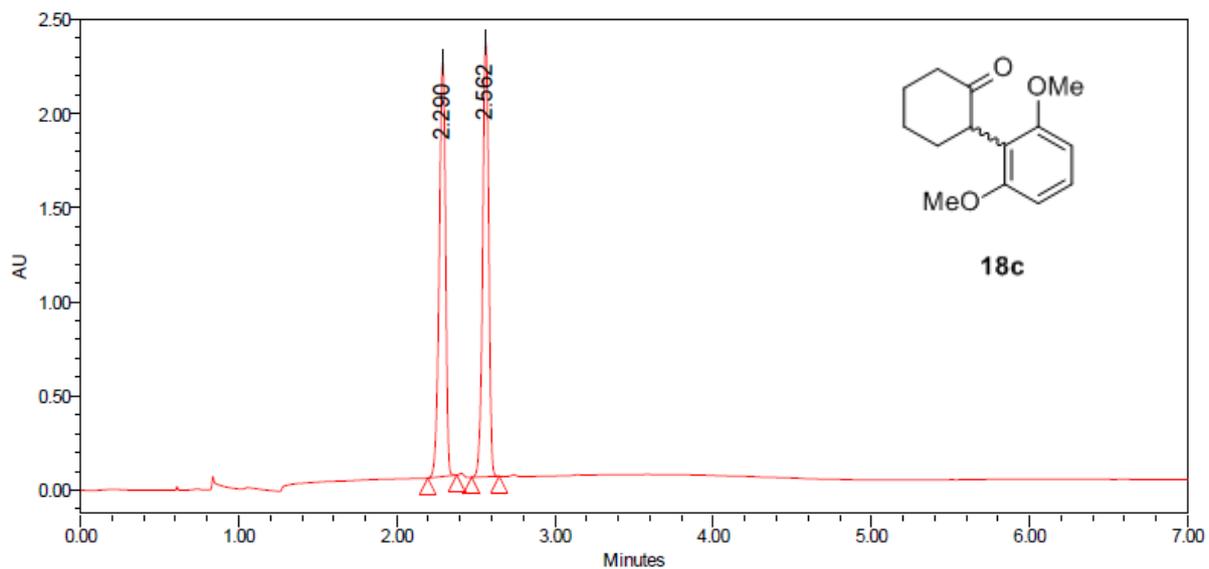
Peak Results

Name	RT	Area	Height	% Area
1	2.406	2364787	960001	49.12
2	2.730	2449755	1012738	50.88



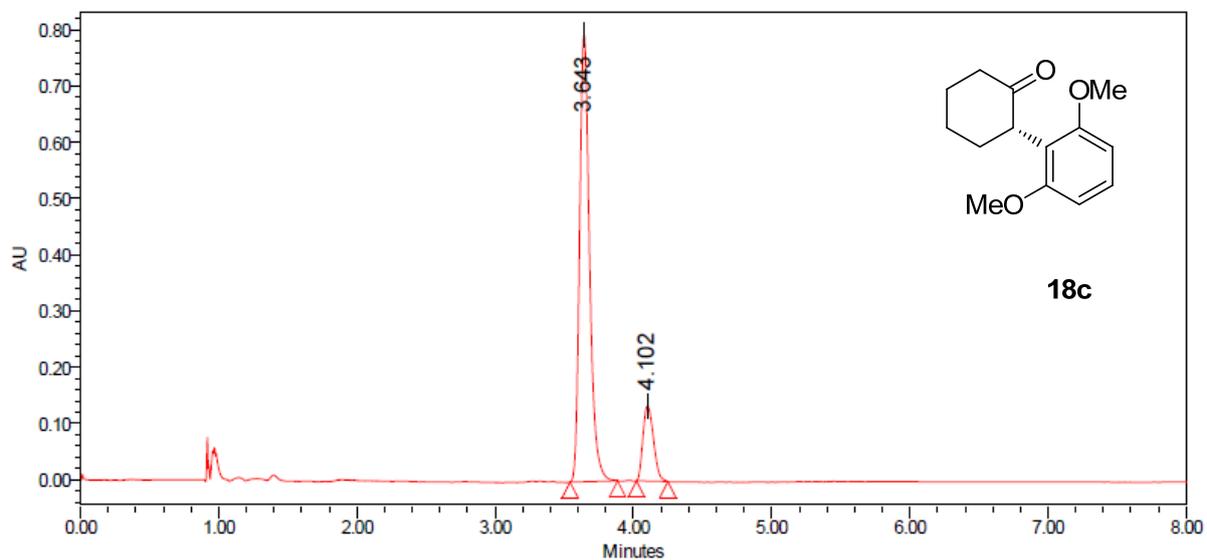
Peak Results

Name	RT	Area	Height	% Area
1	2.898	1286571	404764	85.95
2	3.287	210394	67520	14.05



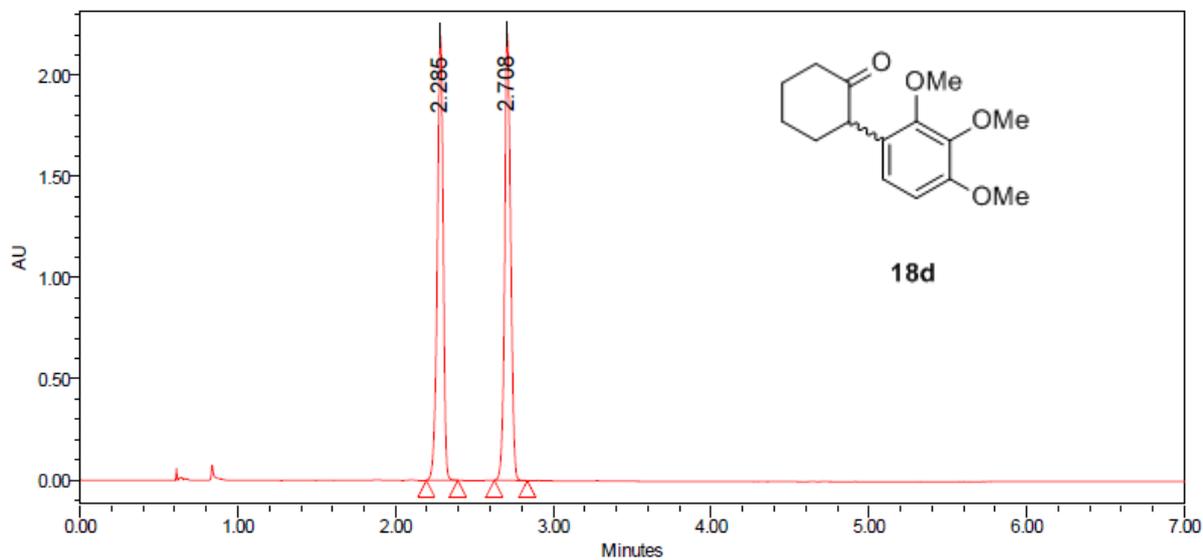
Peak Results

Name	RT	Area	Height	% Area
1	2.290	6097028	2200910	49.83
2	2.562	6138928	2309054	50.17



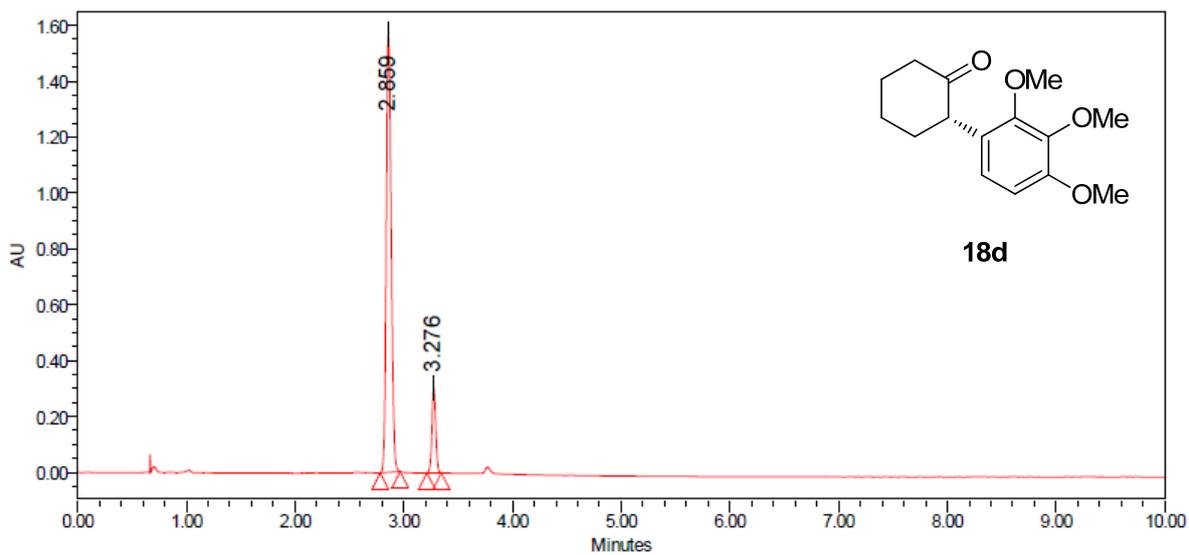
Peak Results

Name	RT	Area	Height	% Area
1	3.643	3976881	795406	84.87
2	4.102	708837	133236	15.13



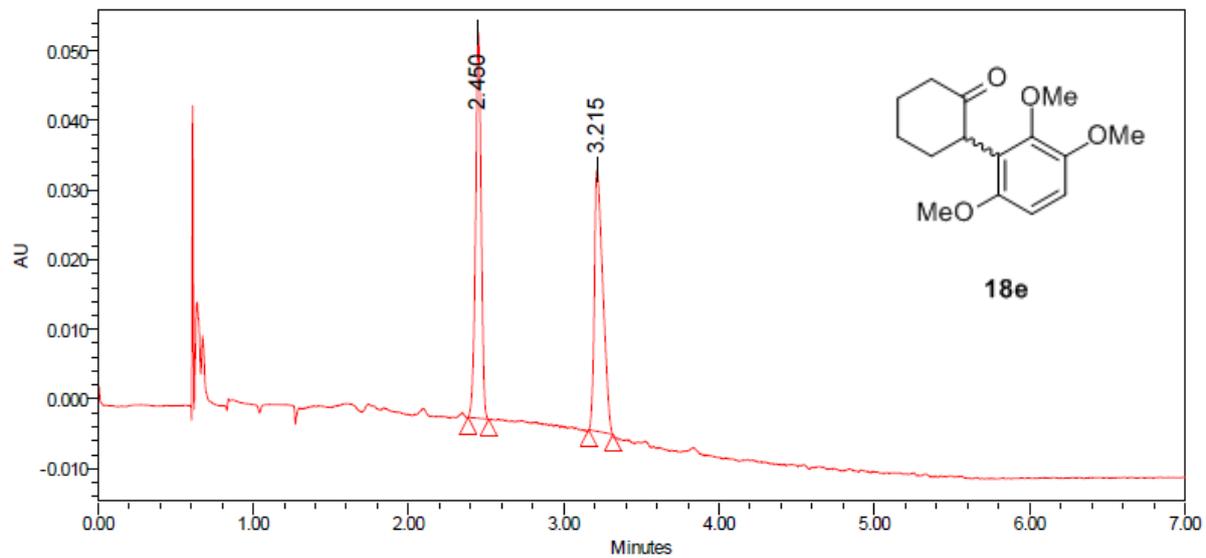
Peak Results

Name	RT	Area	Height	% Area
1	2.285	5675899	2196814	49.40
2	2.708	5813733	2206249	50.60



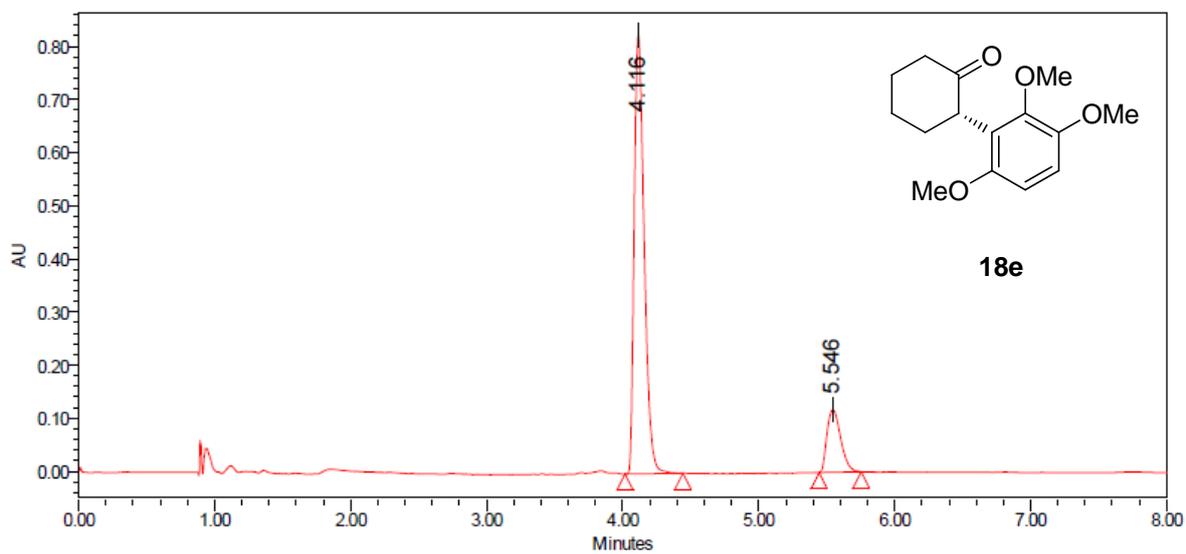
Peak Results

Name	RT	Area	Height	% Area
1	2.859	4953590	1569075	87.15
2	3.276	730086	305250	12.85



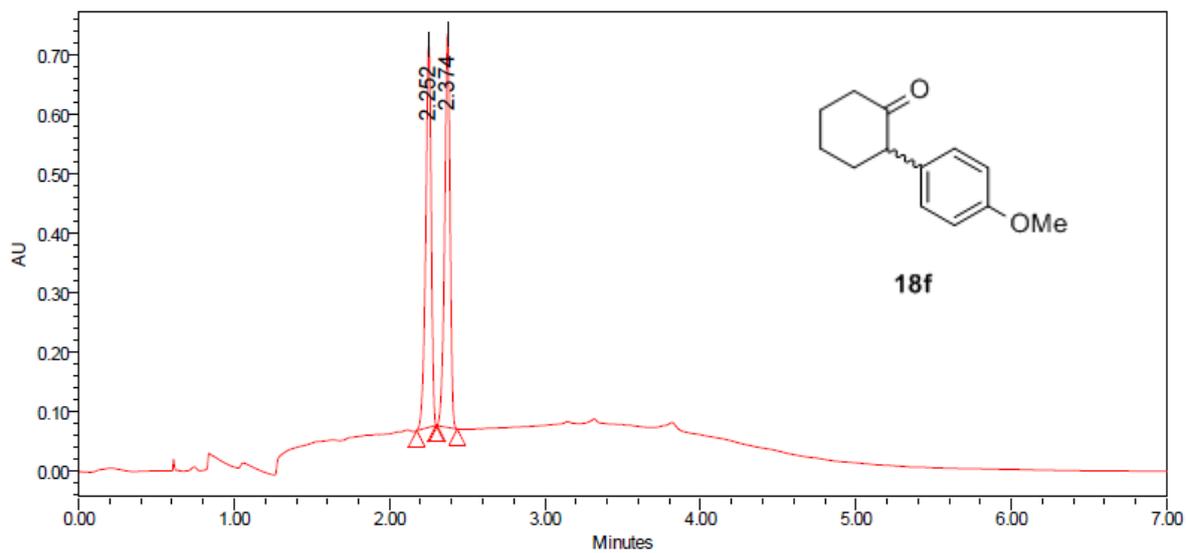
Peak Results

Name	RT	Area	Height	% Area
1	2.450	138310	55425	49.35
2	3.215	141965	37535	50.65



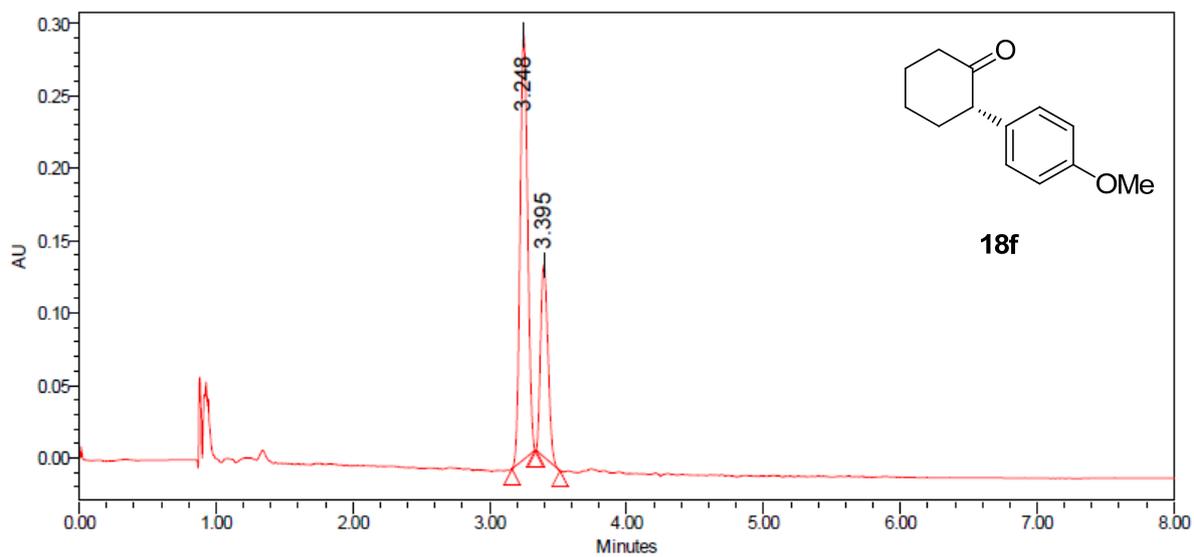
Peak Results

Name	RT	Area	Height	% Area
1	4.116	4208274	825954	83.61
2	5.546	824890	117506	16.39



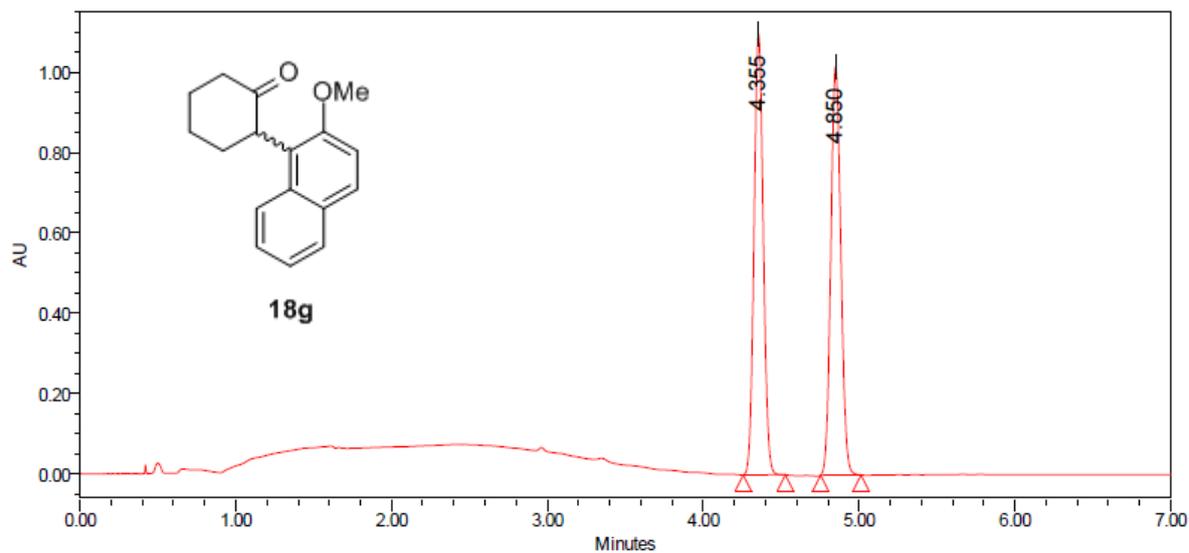
Peak Results

Name	RT	Area	Height	% Area
1	2.252	1584821	644605	49.79
2	2.374	1598249	662081	50.21



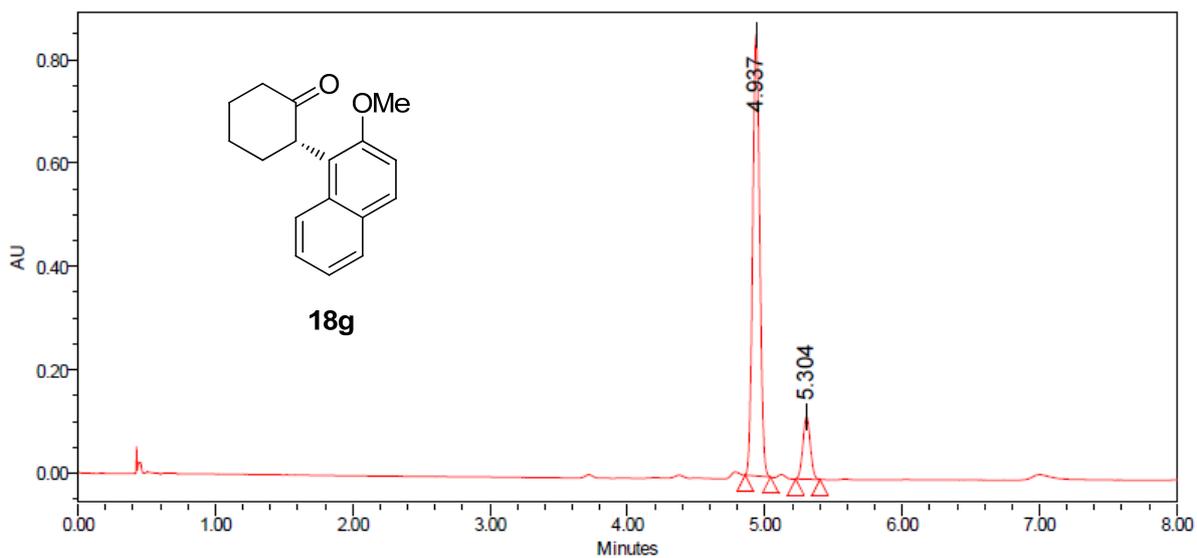
Peak Results

Name	RT	Area	Height	% Area
1	3.248	1120841	293018	69.19
2	3.395	499144	132342	30.81



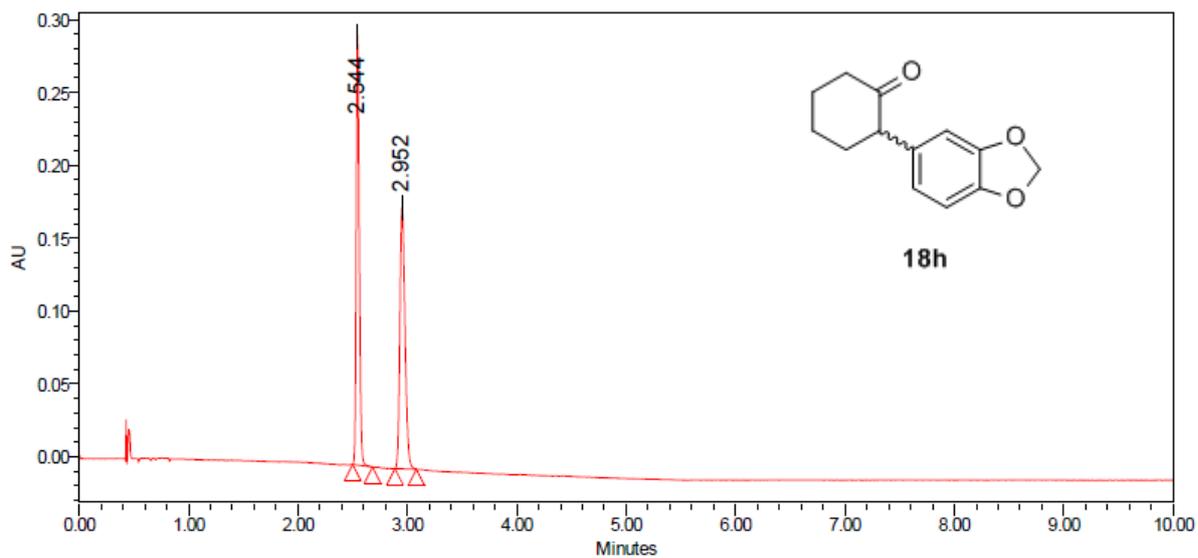
Peak Results

Name	RT	Area	Height	% Area
1	4.355	4533643	1097873	50.02
2	4.850	4529224	1017153	49.98



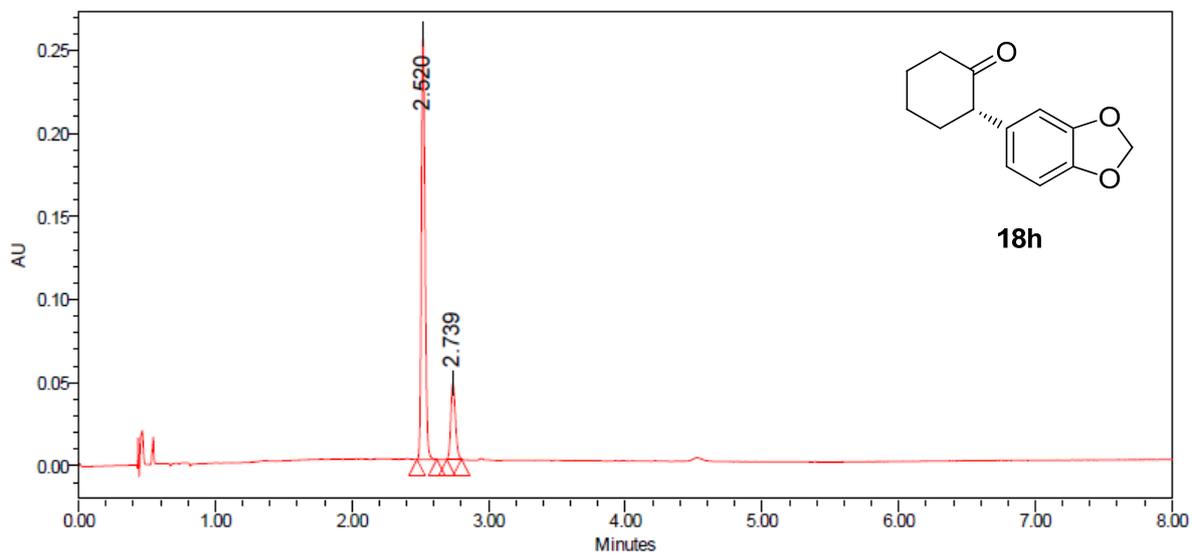
Peak Results

Name	RT	Area	Height	% Area
1	4.937	3066597	854002	87.04
2	5.304	455061	120651	12.96



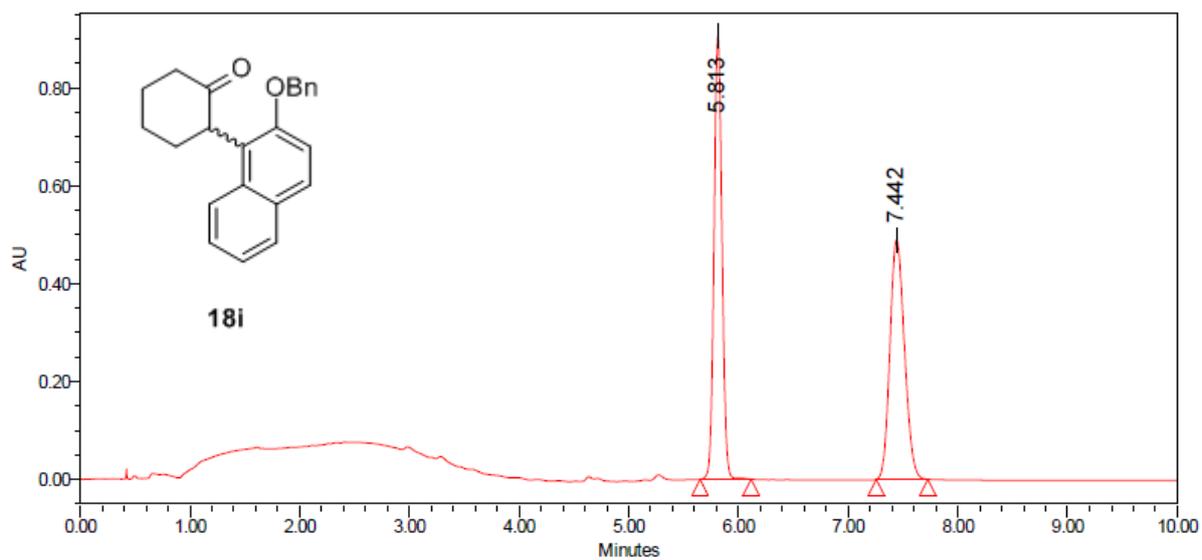
Peak Results

Name	RT	Area	Height	% Area
1	2.544	579278	294985	49.71
2	2.952	586084	179417	50.29



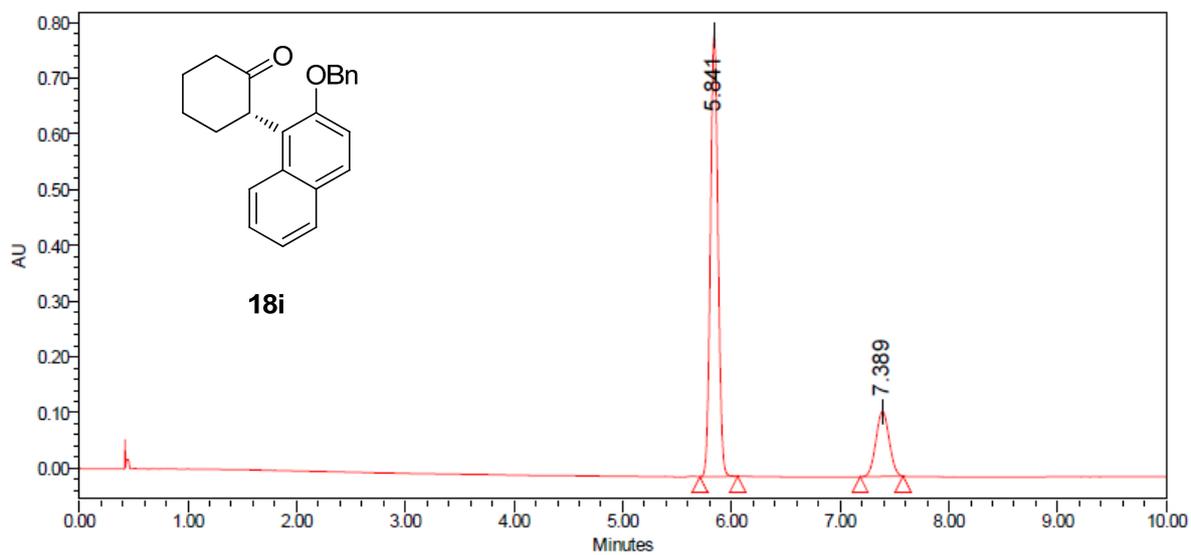
Peak Results

Name	RT	Area	Height	% Area
1	2.520	467742	256088	81.58
2	2.739	105642	45756	18.42



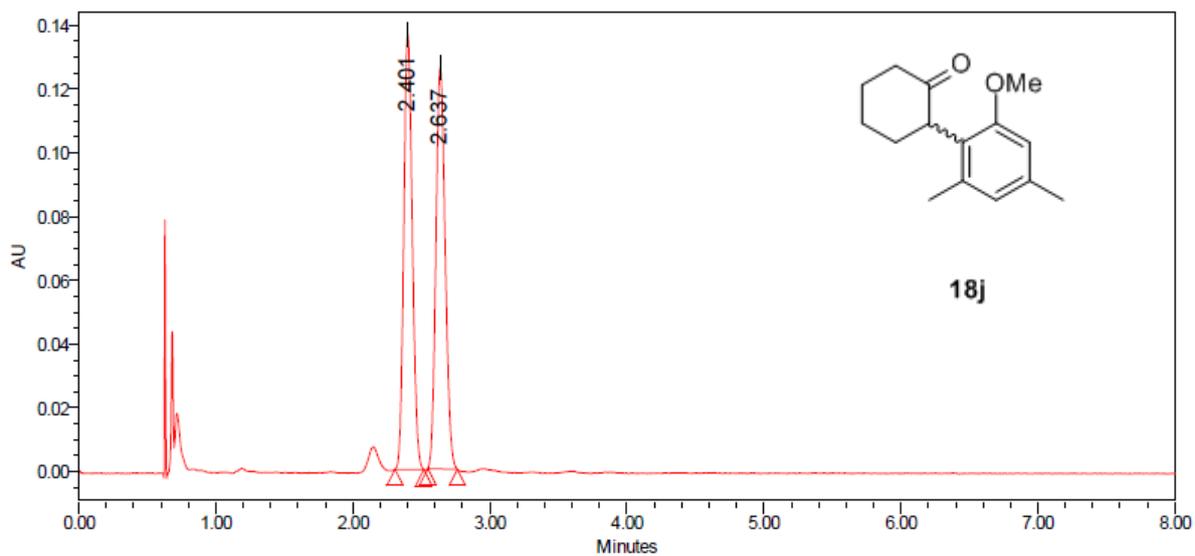
Peak Results

Name	RT	Area	Height	% Area
1	5.813	4580576	907041	50.37
2	7.442	4513677	490086	49.63



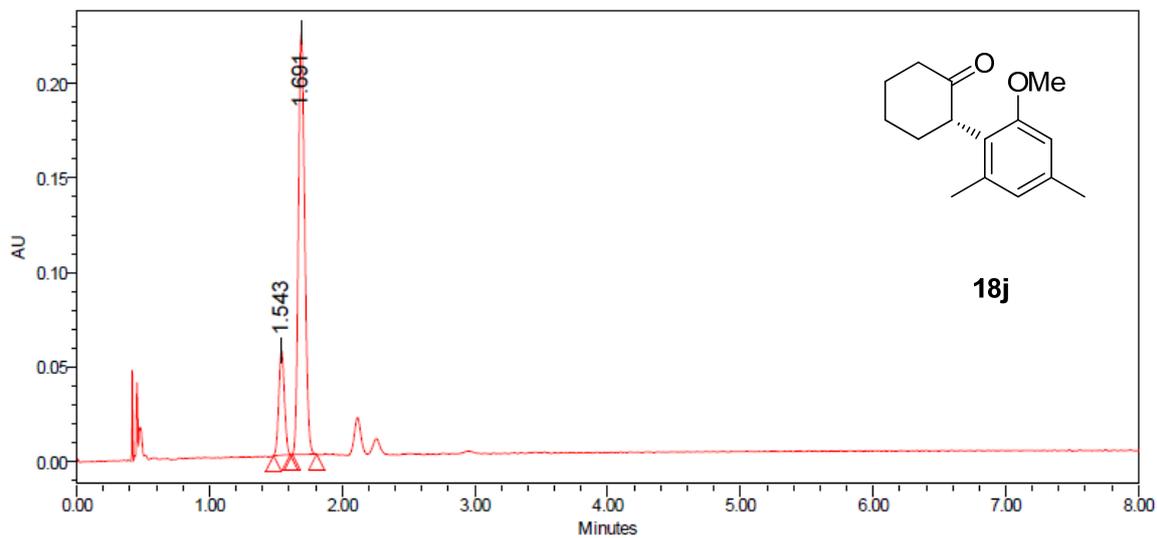
Peak Results

Name	RT	Area	Height	% Area
1	5.841	3856596	792497	79.56
2	7.389	990672	116645	20.44



Peak Results

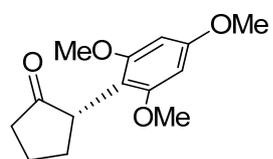
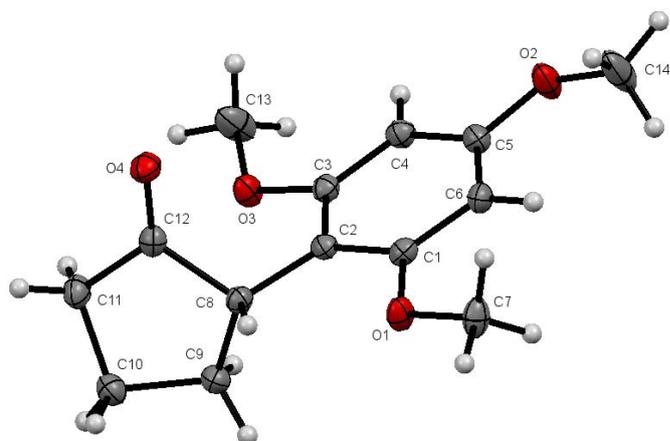
Name	RT	Area	Height	% Area
1	2.401	59114E	136444	49.88
2	2.637	594062	125815	50.12



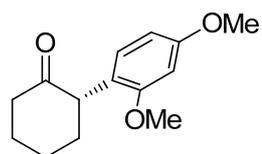
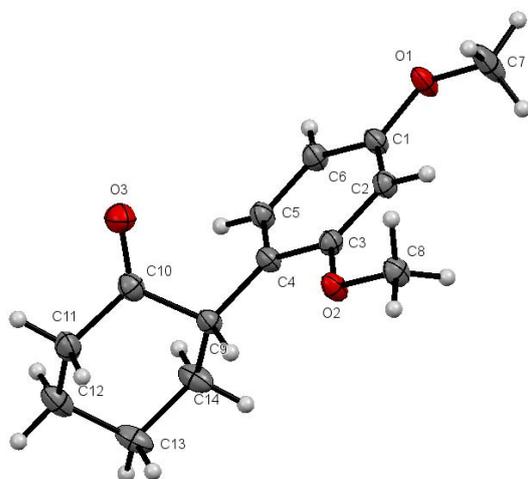
Peak Results

Name	RT	Area	Height	% Area
1	1.543	163677	55261	18.08
2	1.691	741722	223030	81.92

X-Ray Crystal Structures



11a



18b