

Catalytic Asymmetric Synthesis of Sterically Hindered Tertiary α -Aryl Ketones

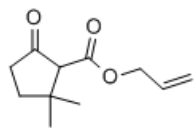
Robert Doran and Patrick J. Guiry*

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

Supporting Information

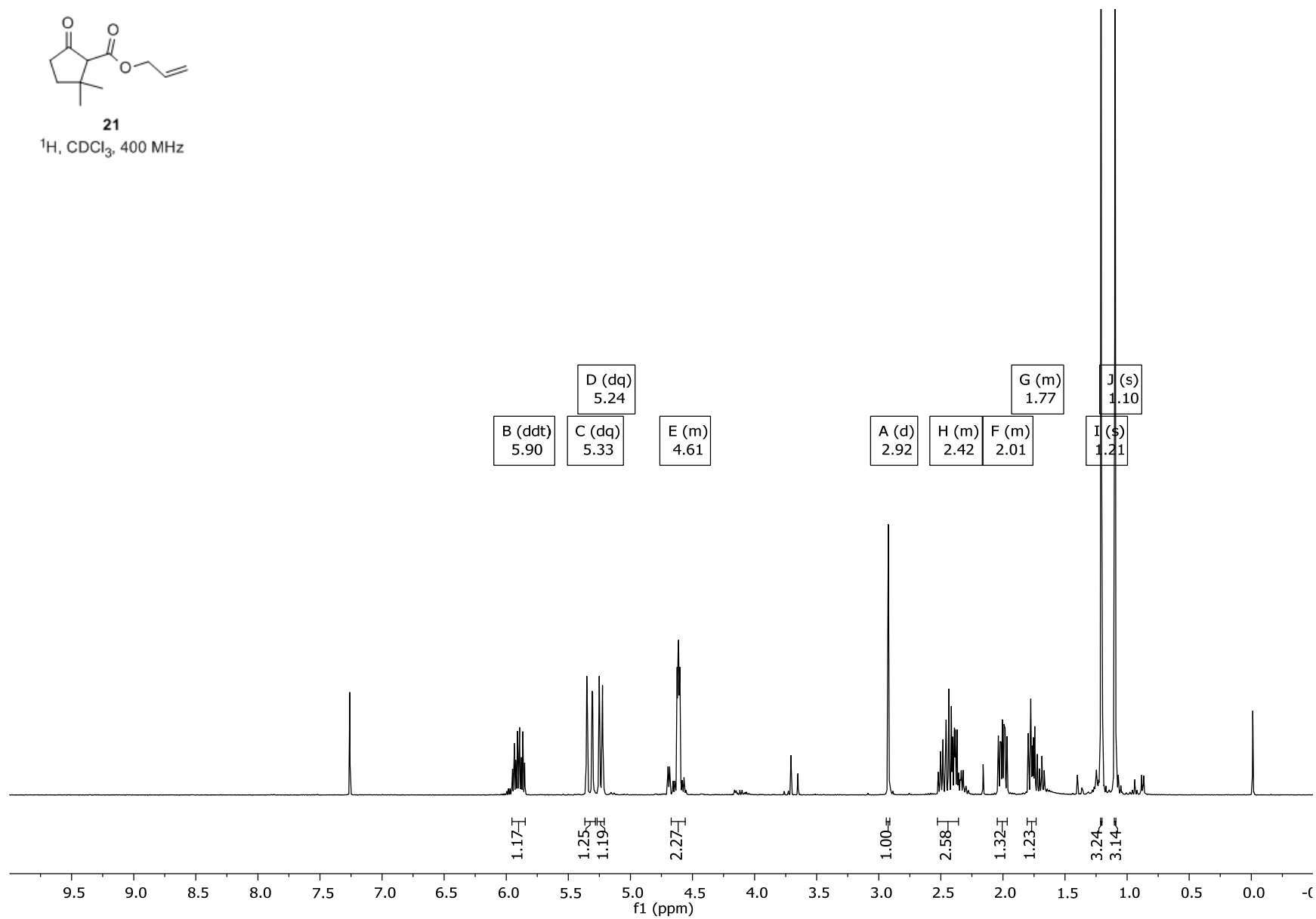
Table of Contents

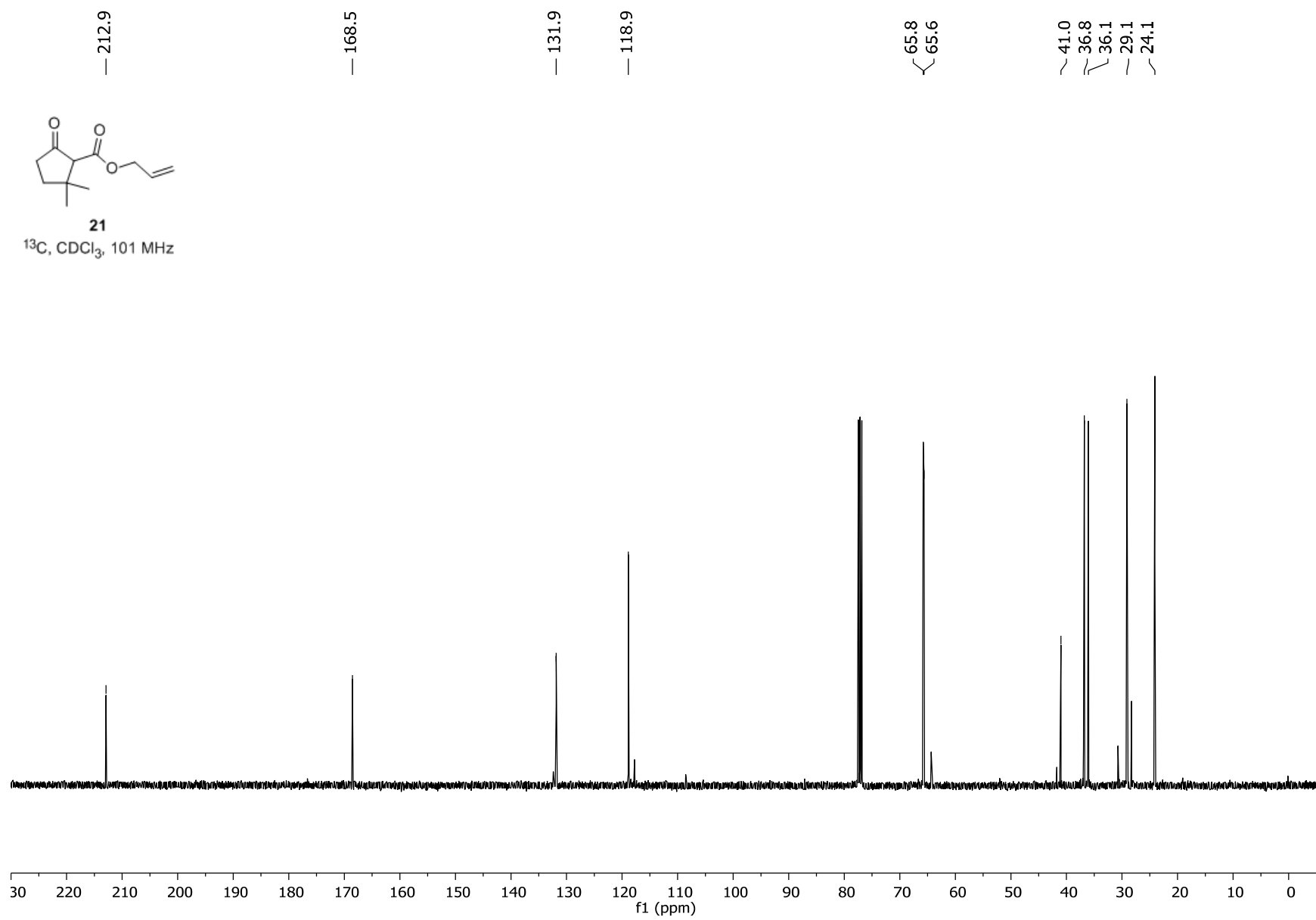
¹ H NMR and ¹³ C NMR Spectra of all new compounds	2
SFC chromatograms of all racemic and enantioenriched compounds	96
X-Ray Crystal Structures	119

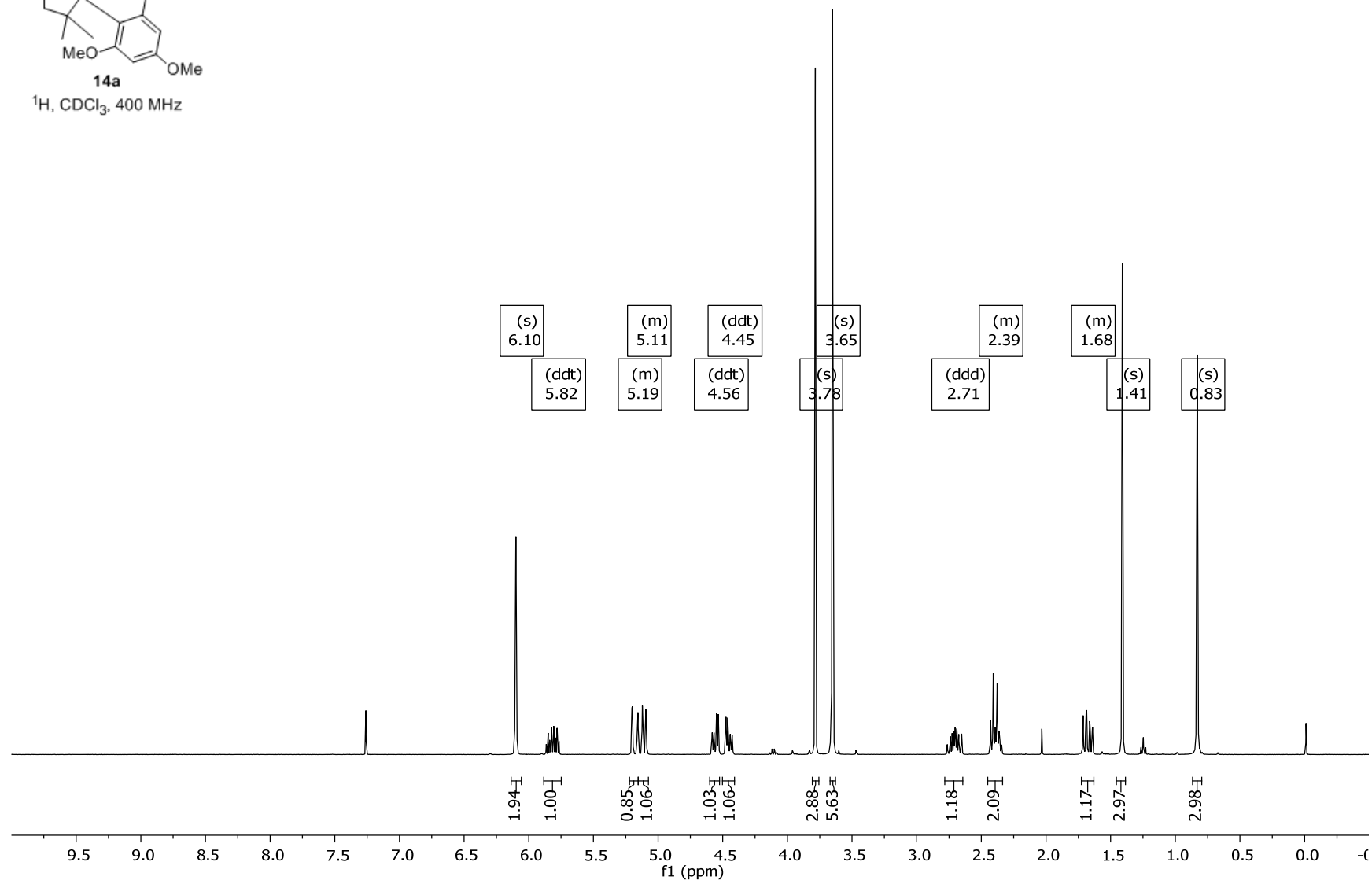
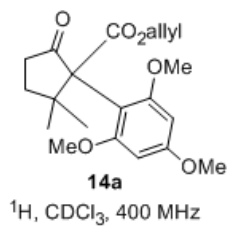


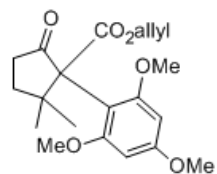
21

¹H, CDCl₃, 400 MHz



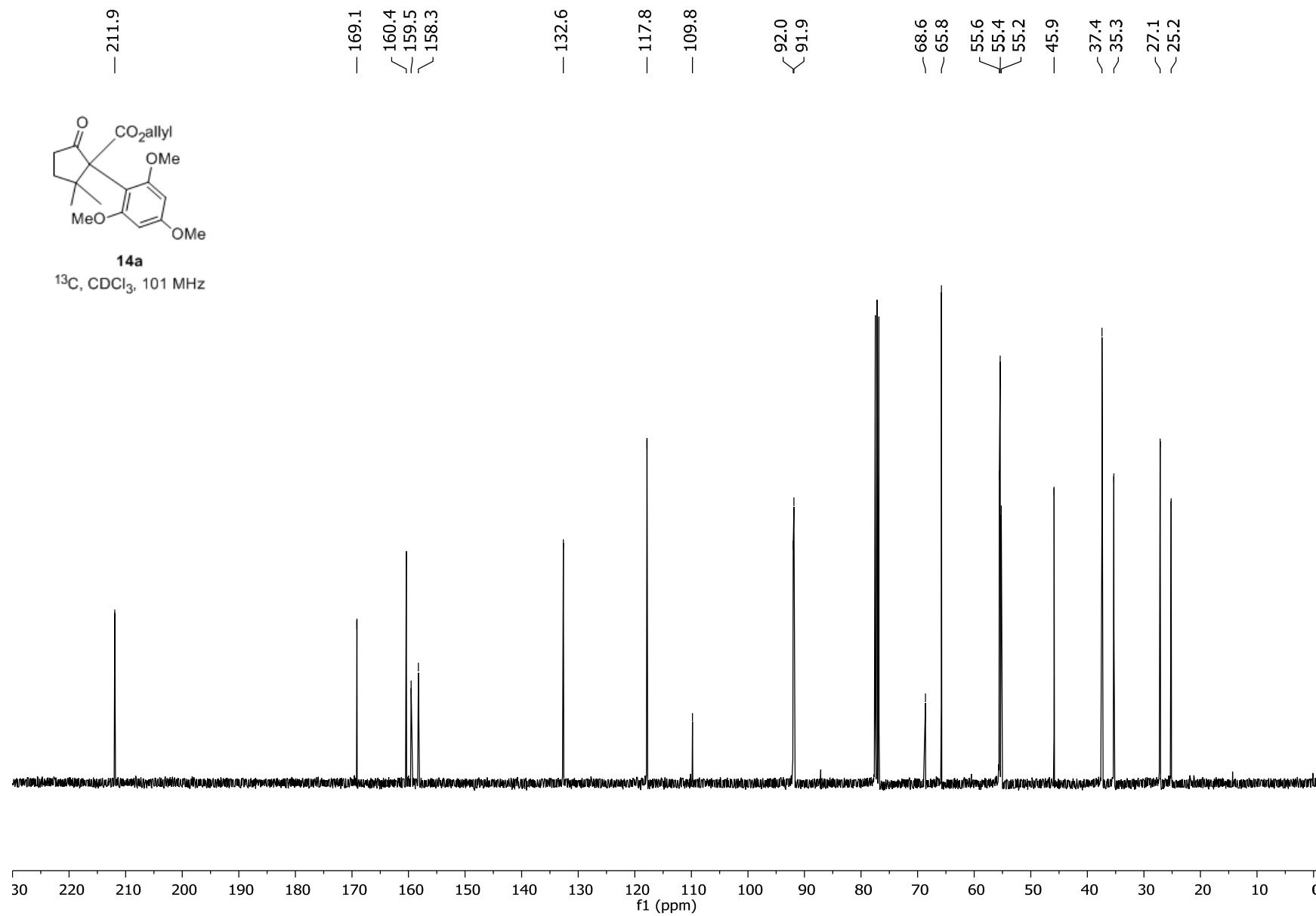


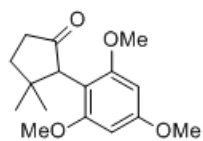




14a

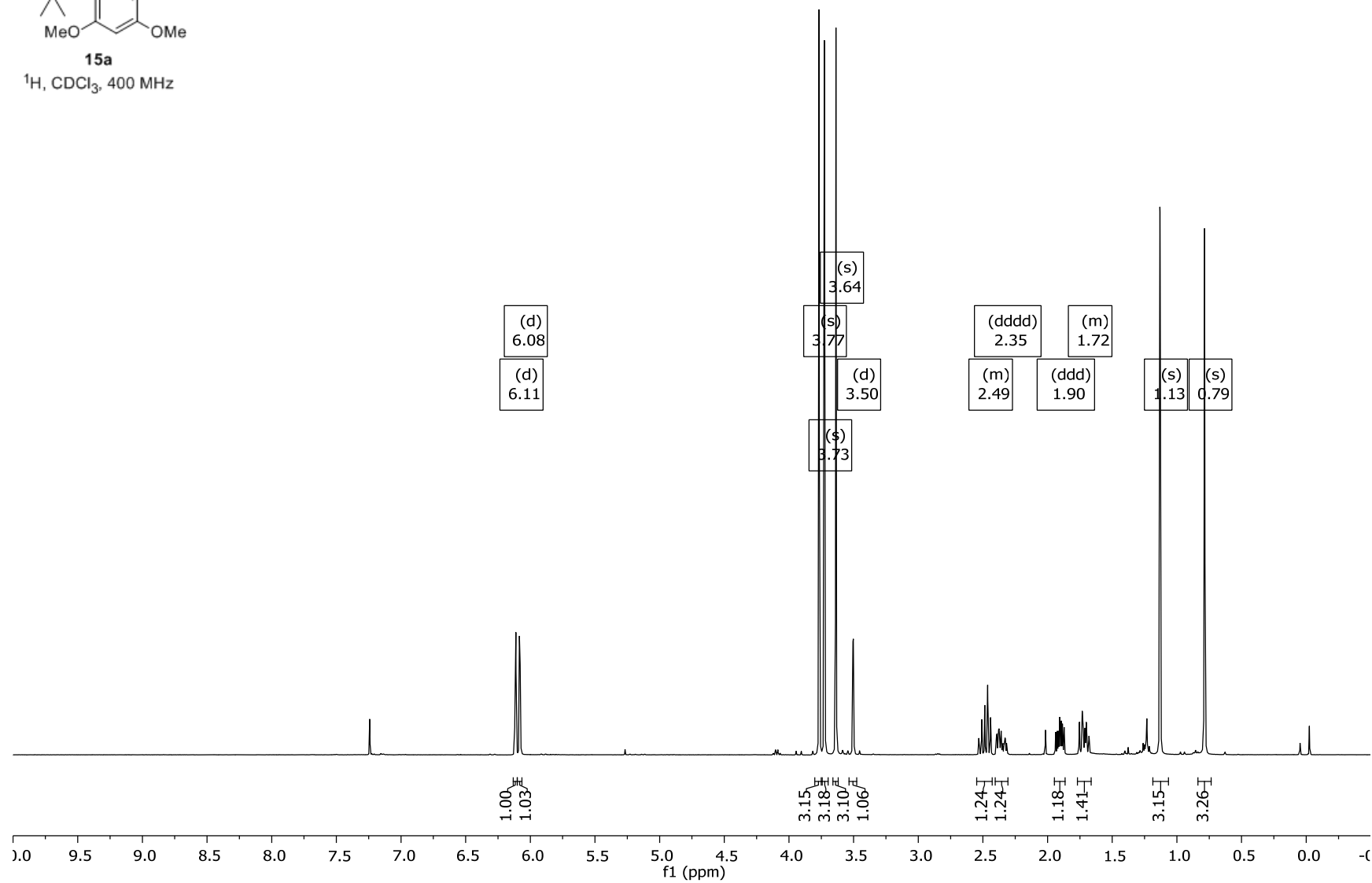
^{13}C , CDCl_3 , 101 MHz

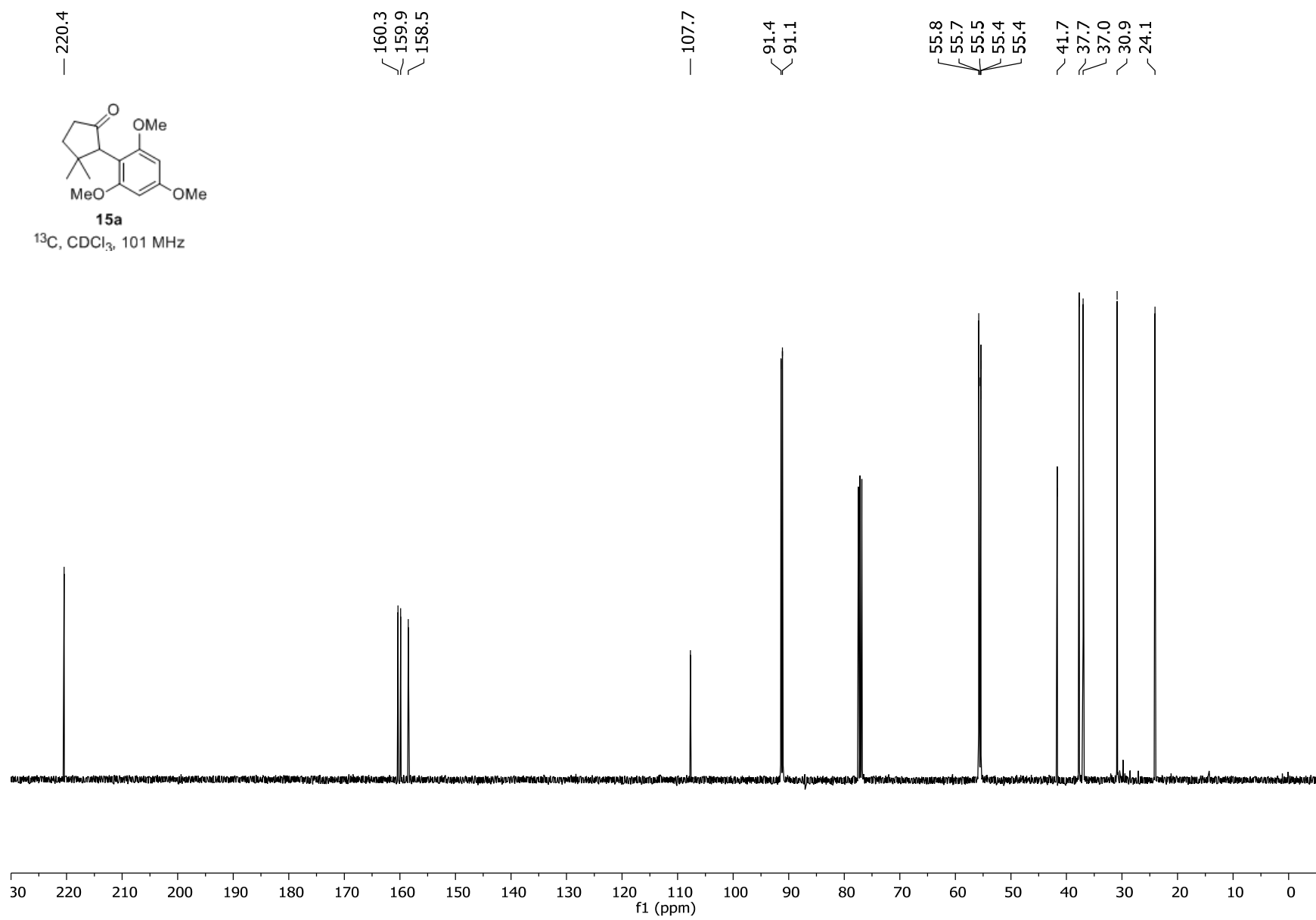


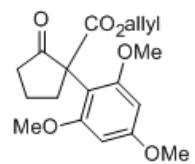


15a

^1H , CDCl_3 , 400 MHz

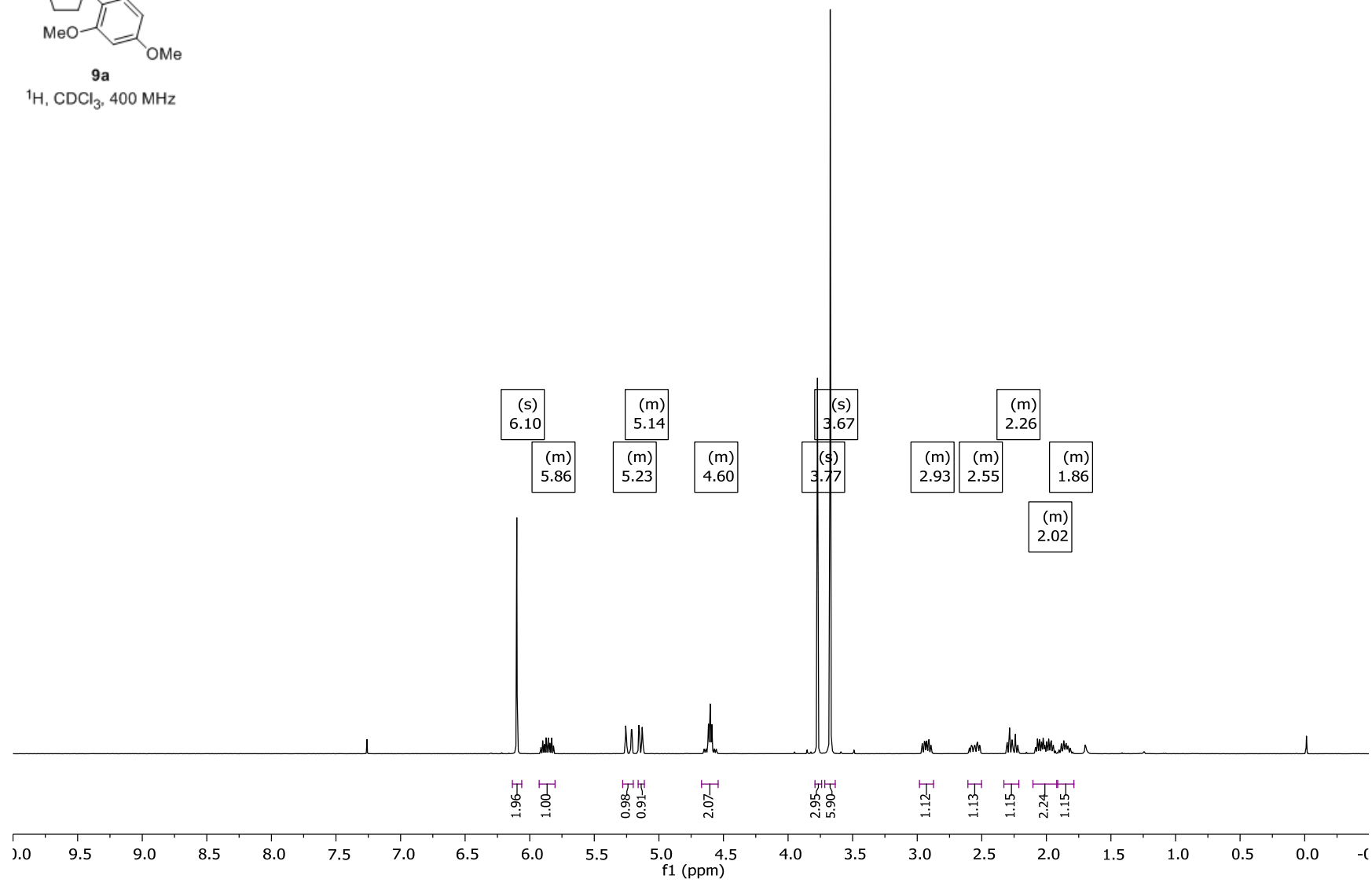


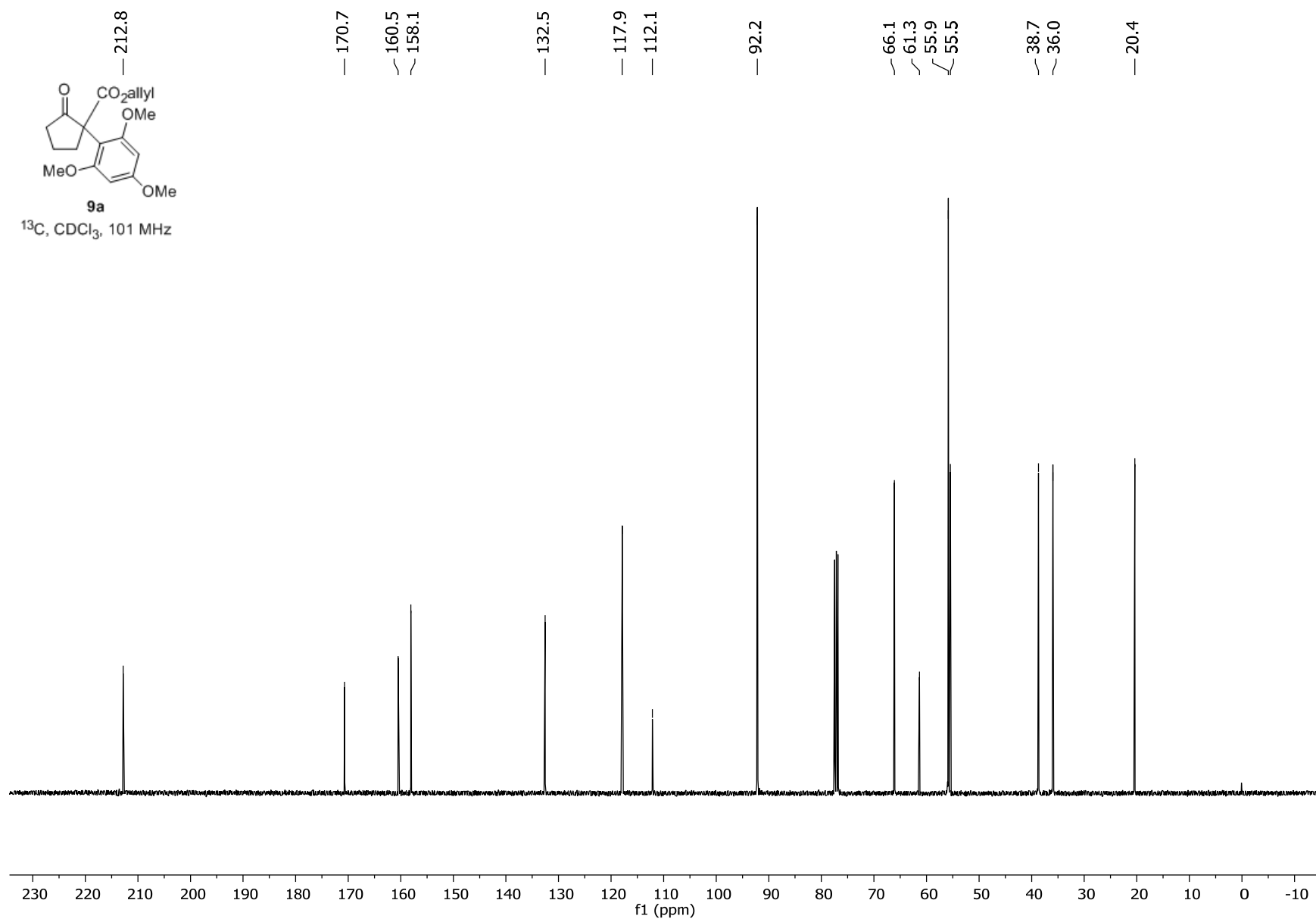


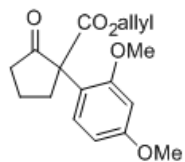


9a

^1H , CDCl_3 , 400 MHz

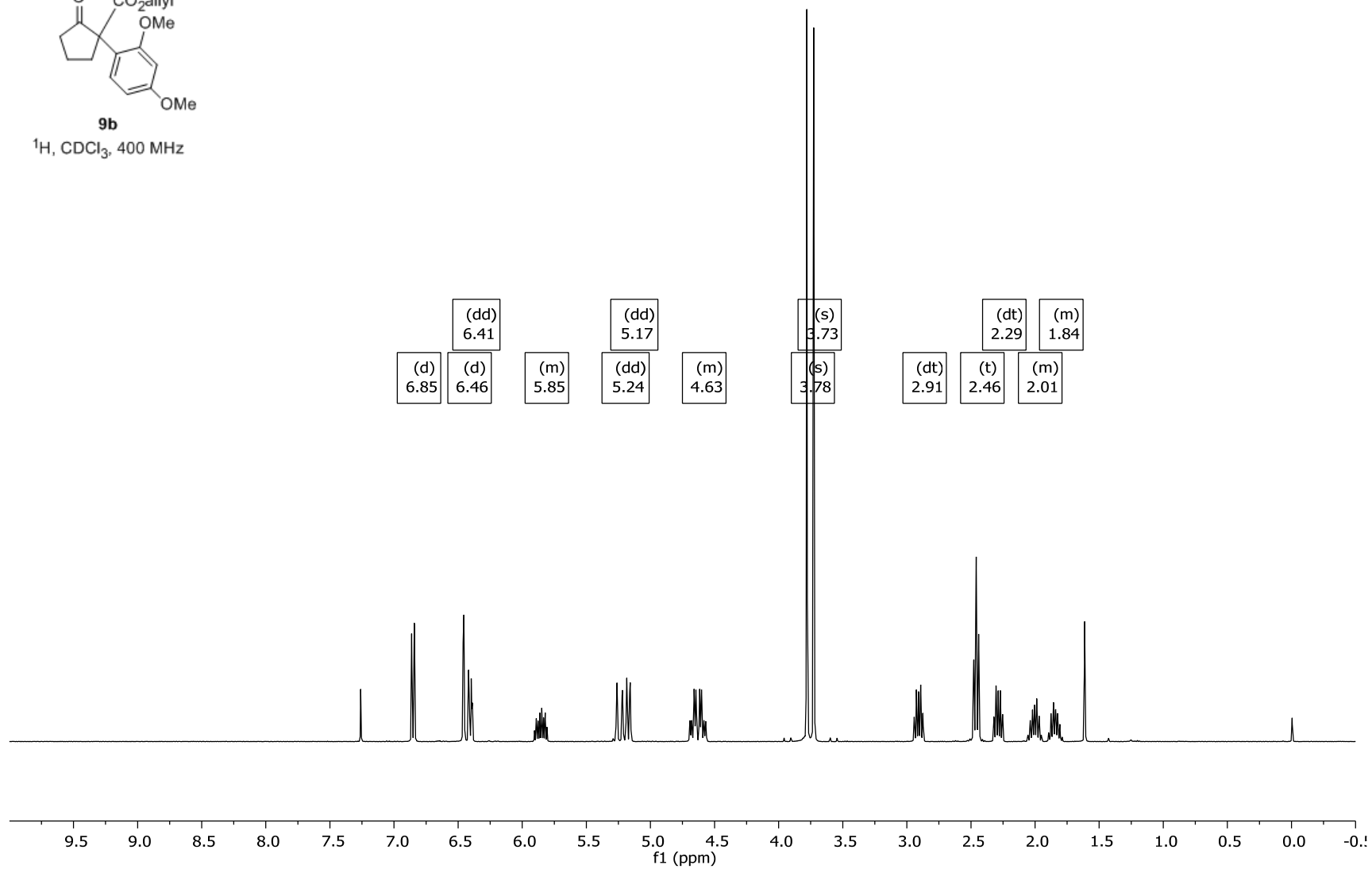


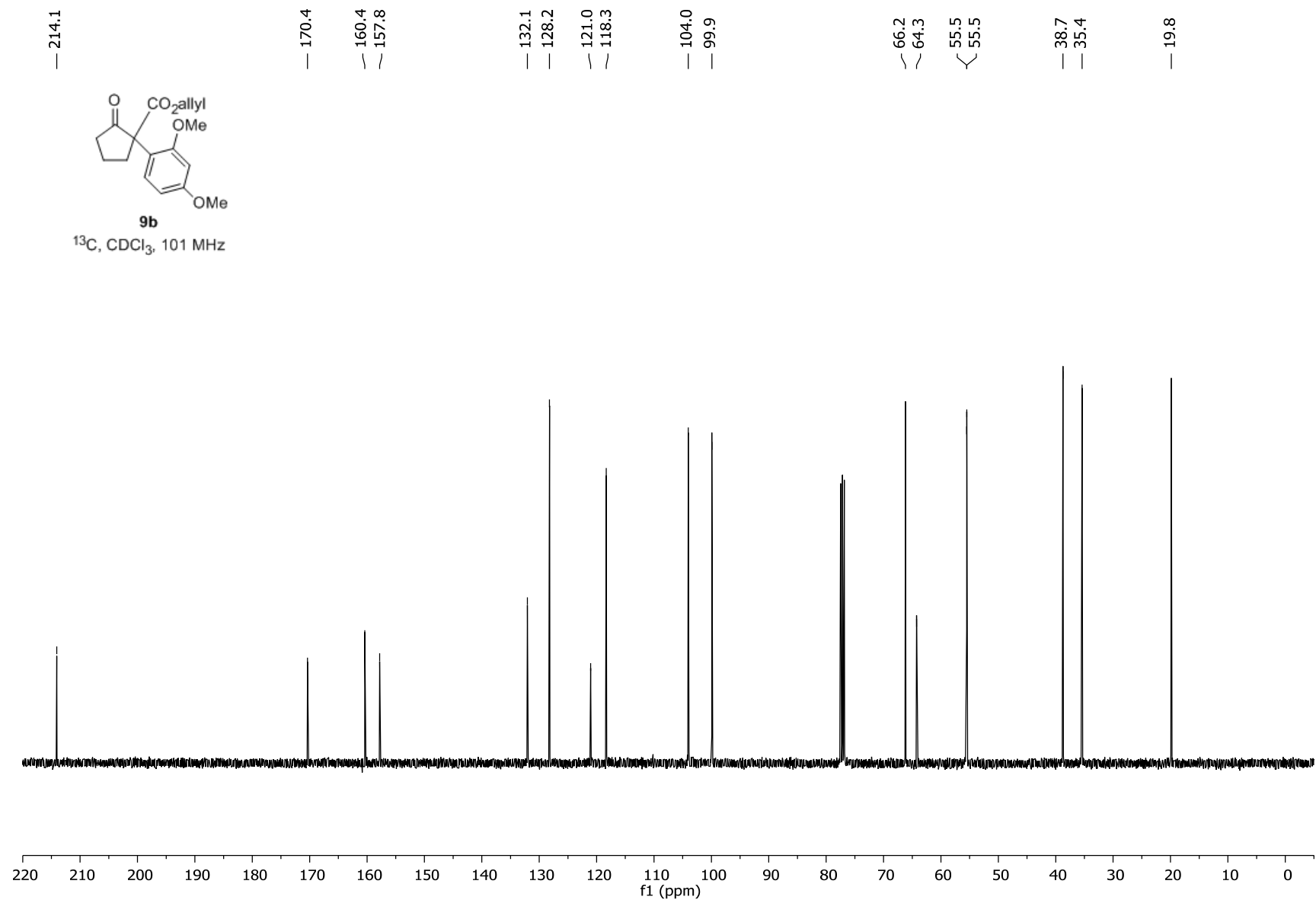


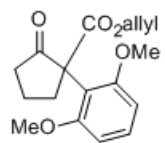


9b

^1H , CDCl_3 , 400 MHz

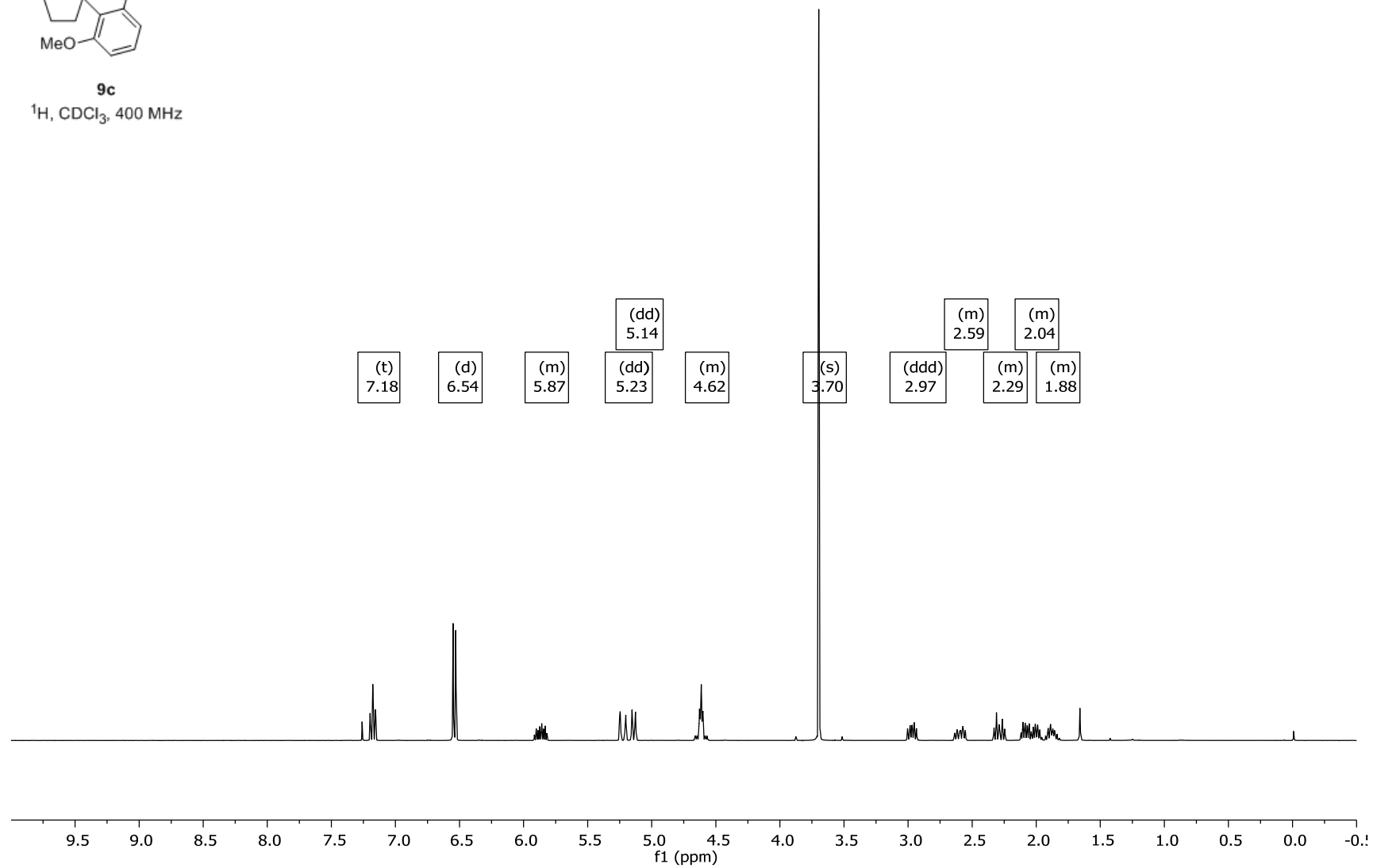


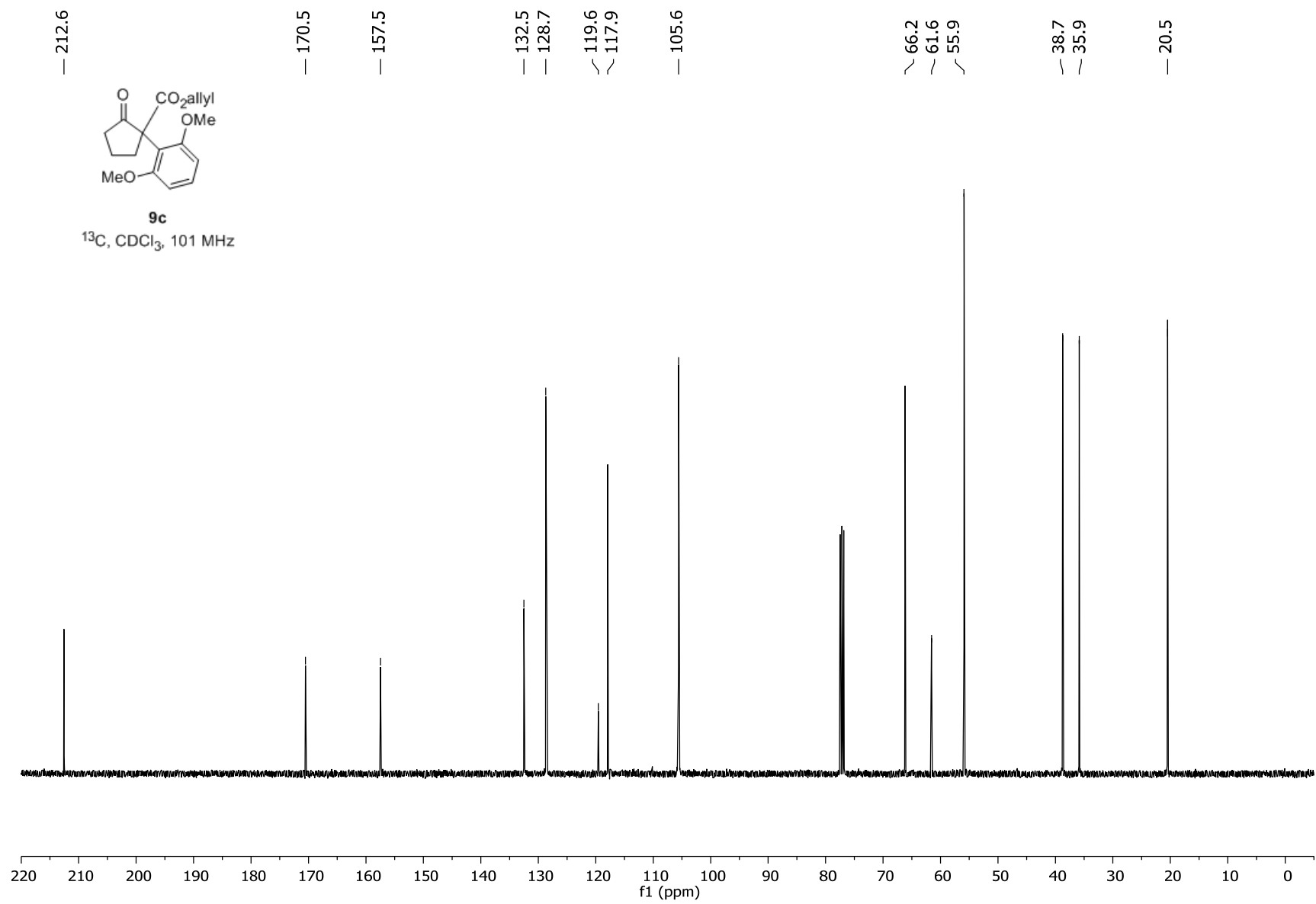


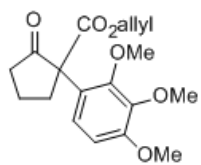


9c

^1H , CDCl_3 , 400 MHz

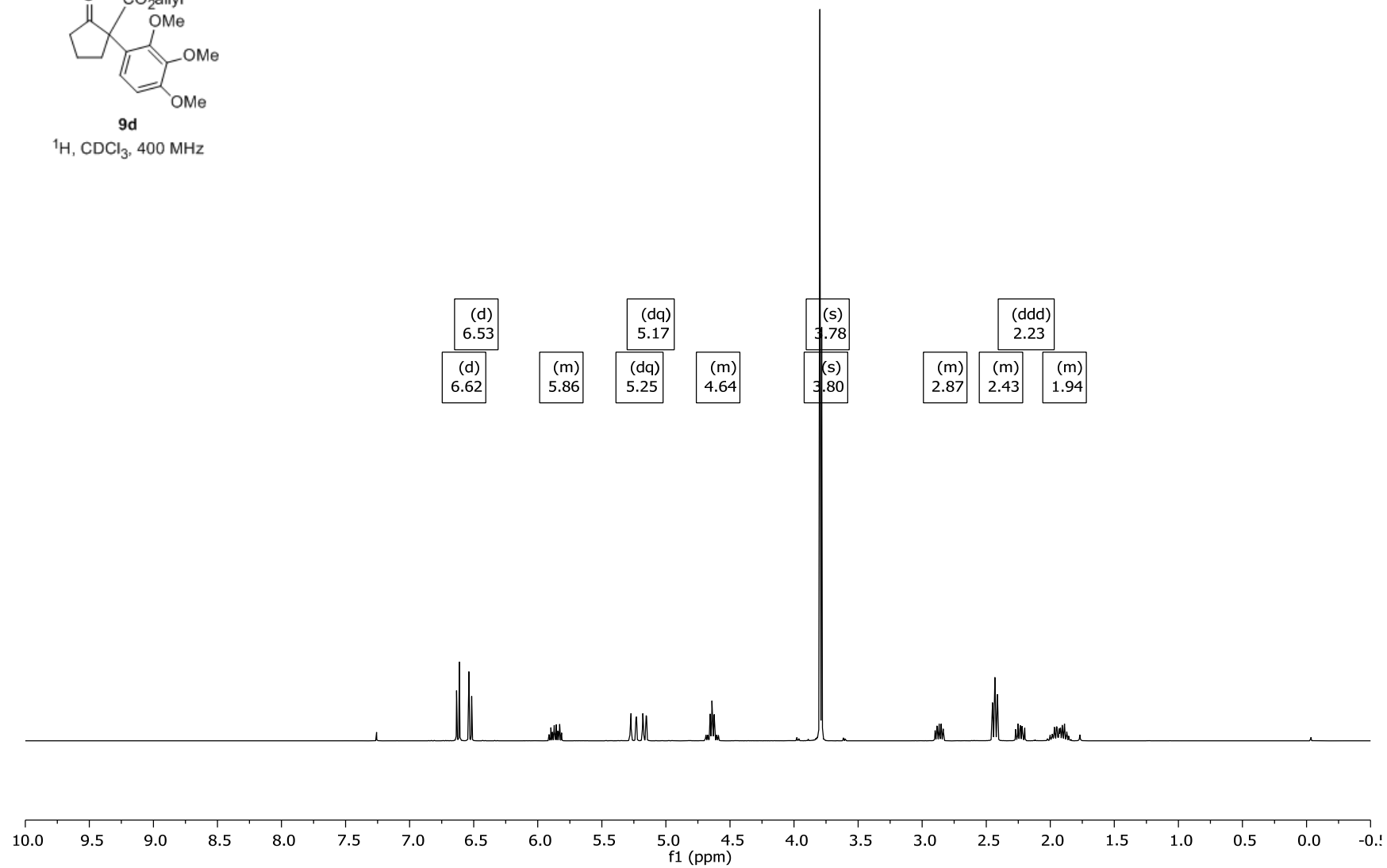


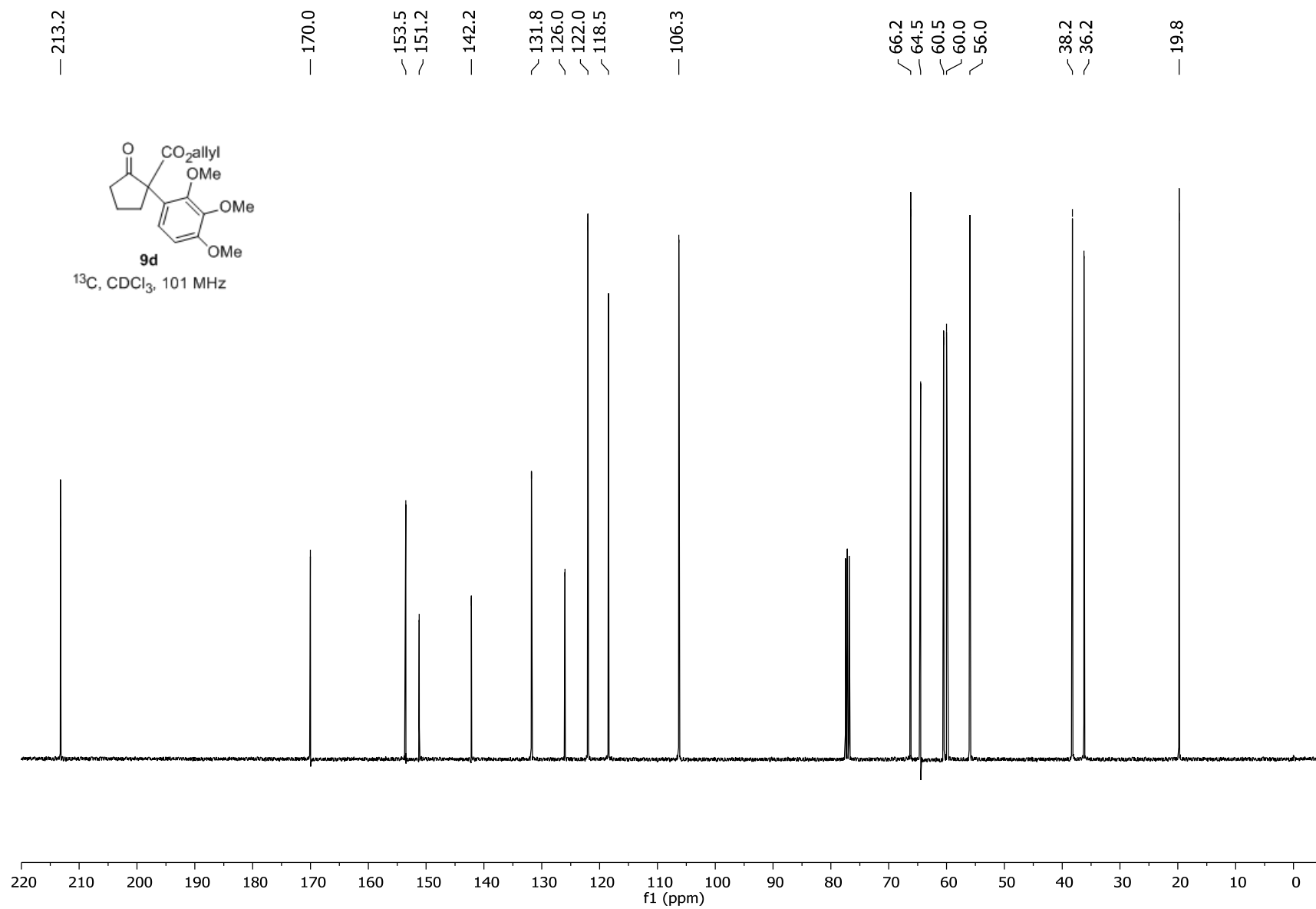


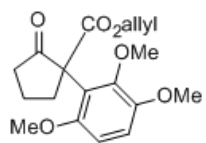


9d

^1H , CDCl_3 , 400 MHz

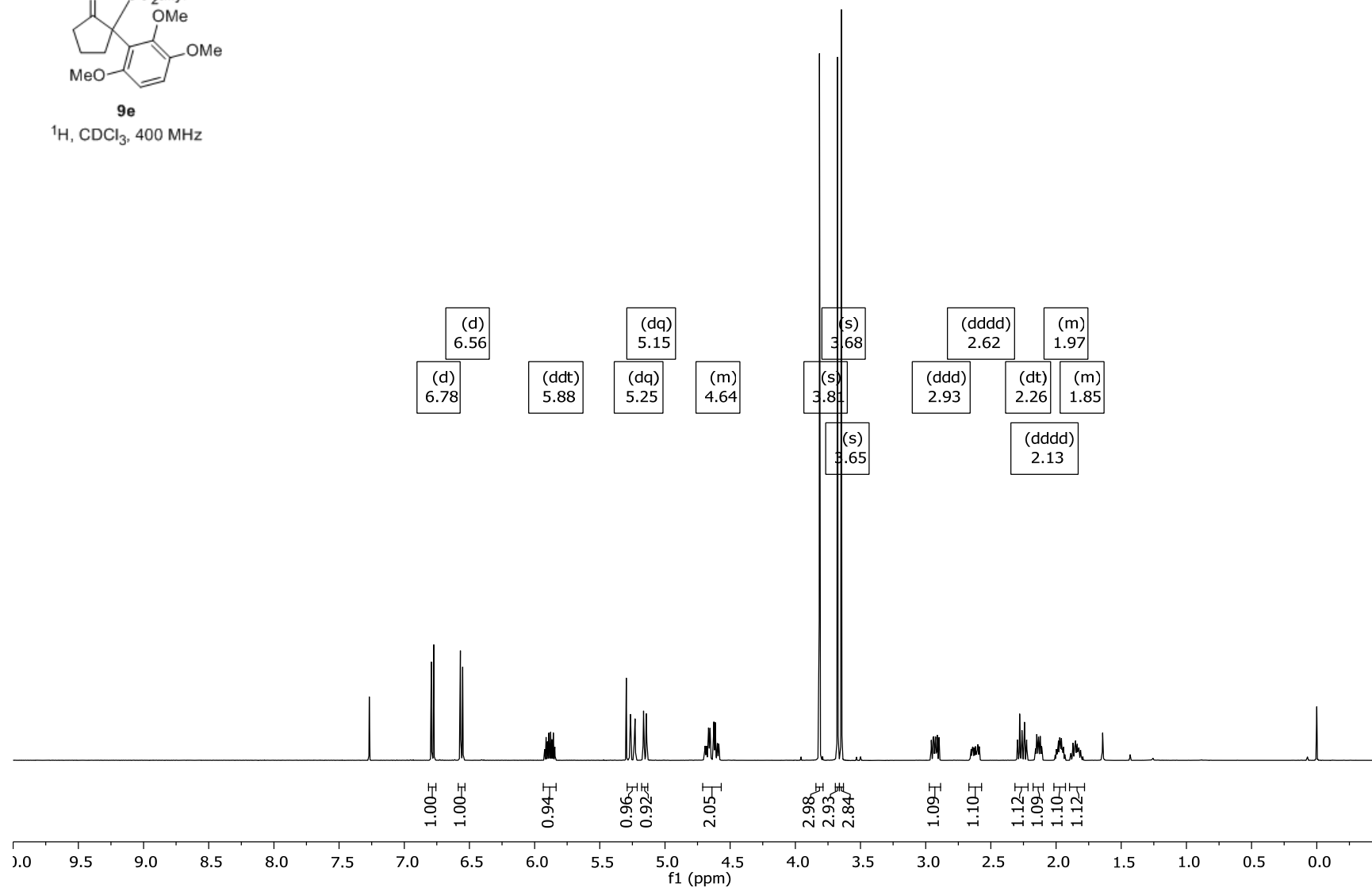


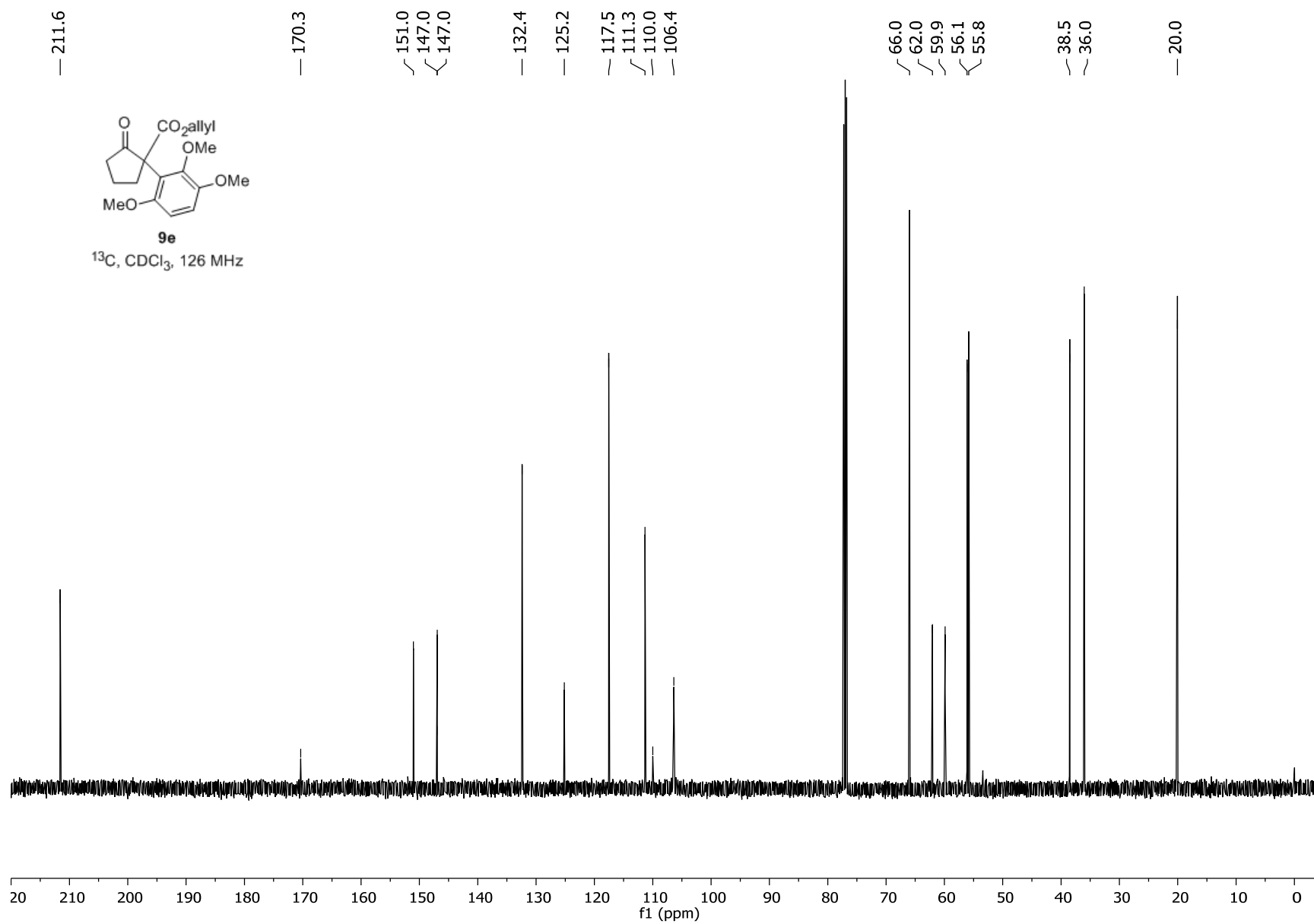


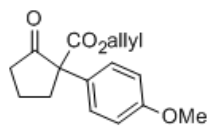


9e

^1H , CDCl_3 , 400 MHz

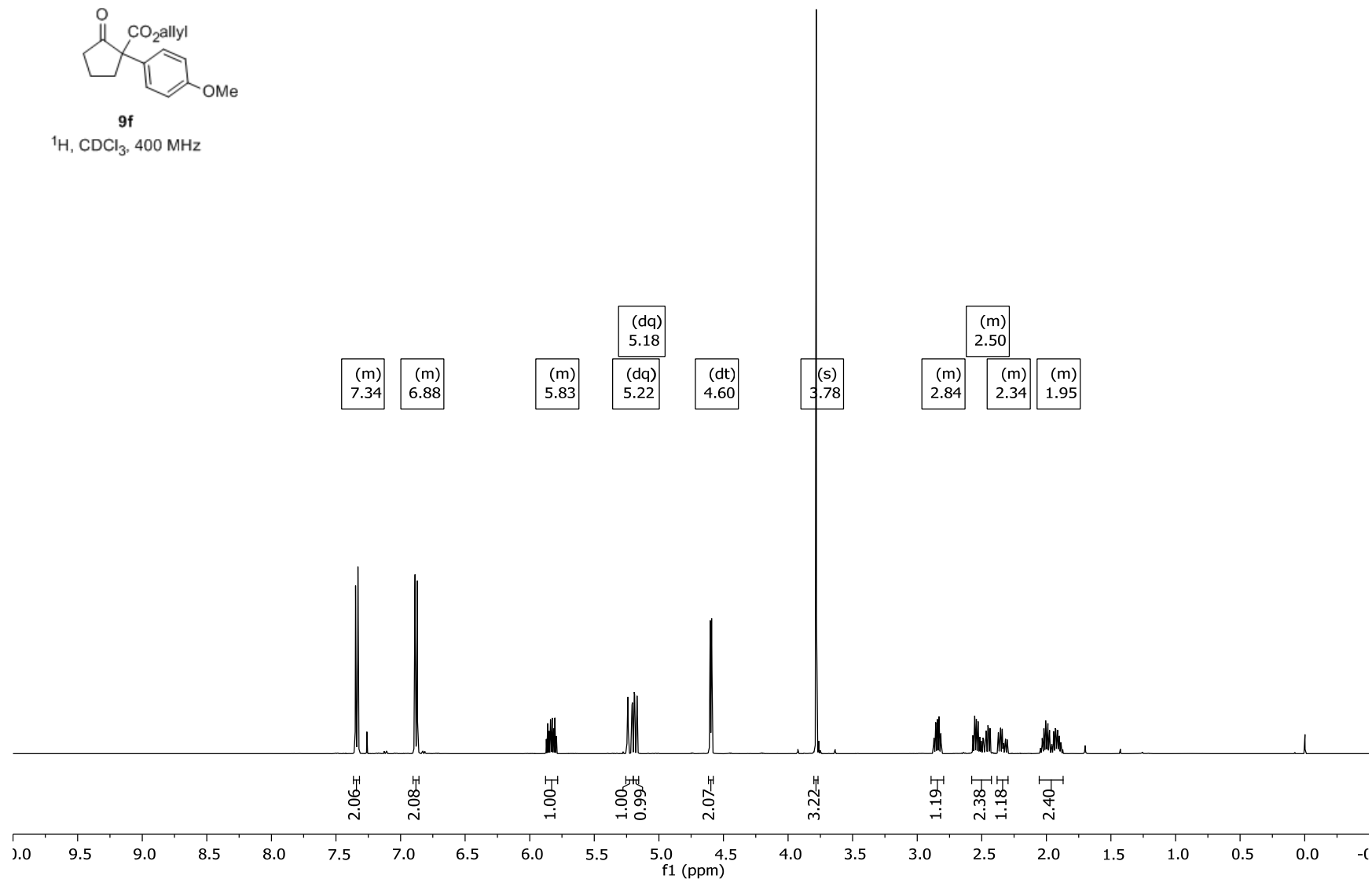


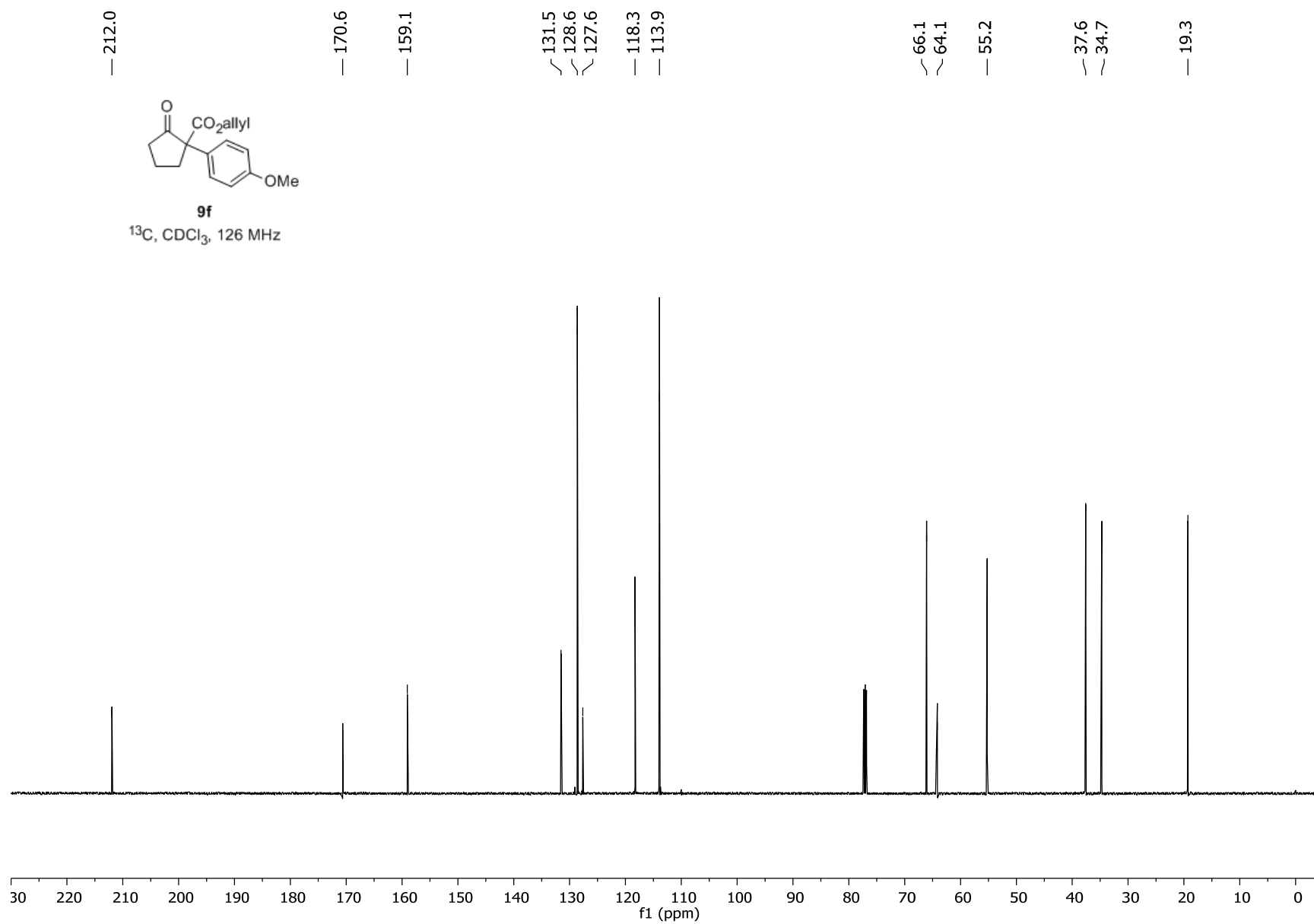


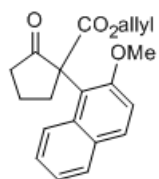


9f

^1H , CDCl_3 , 400 MHz

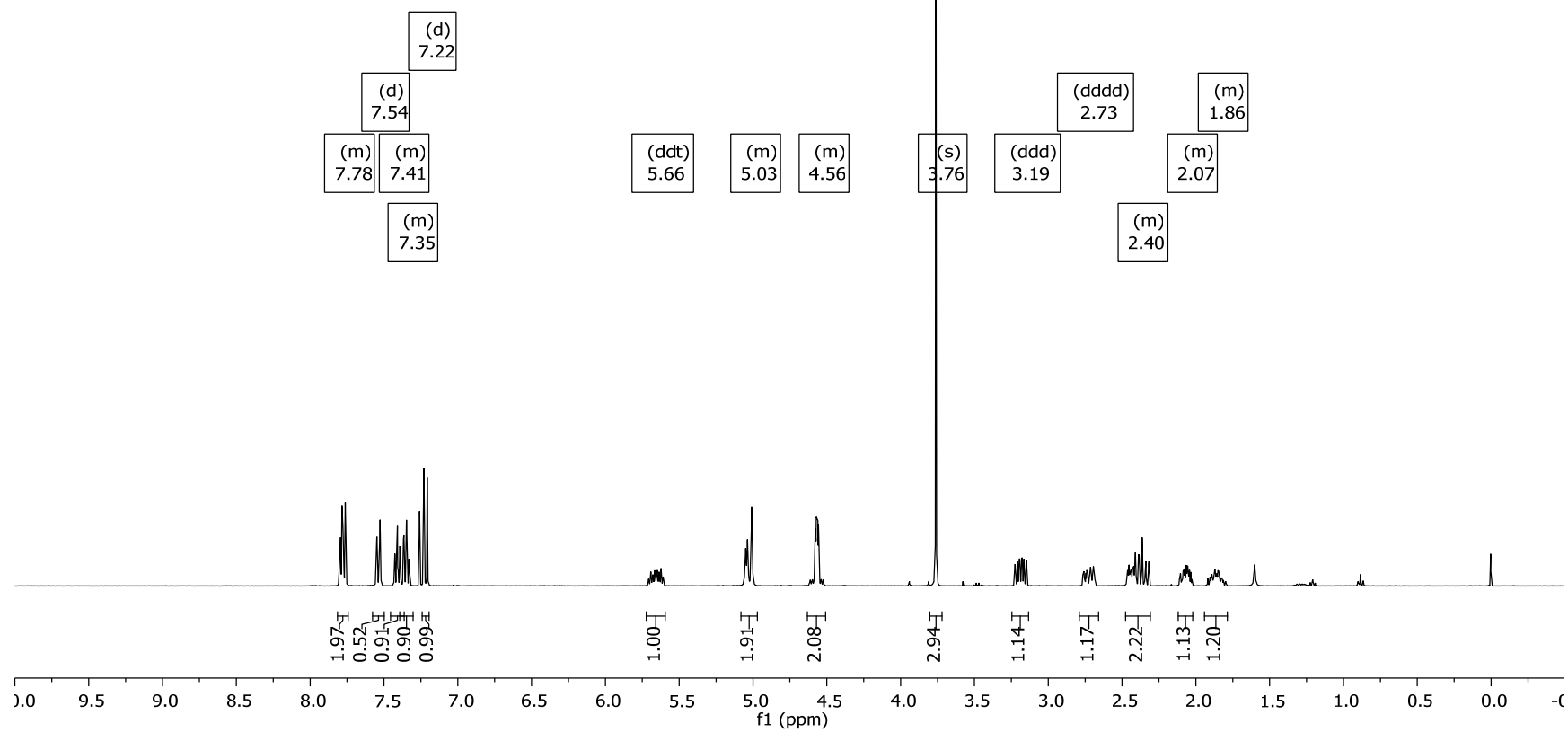


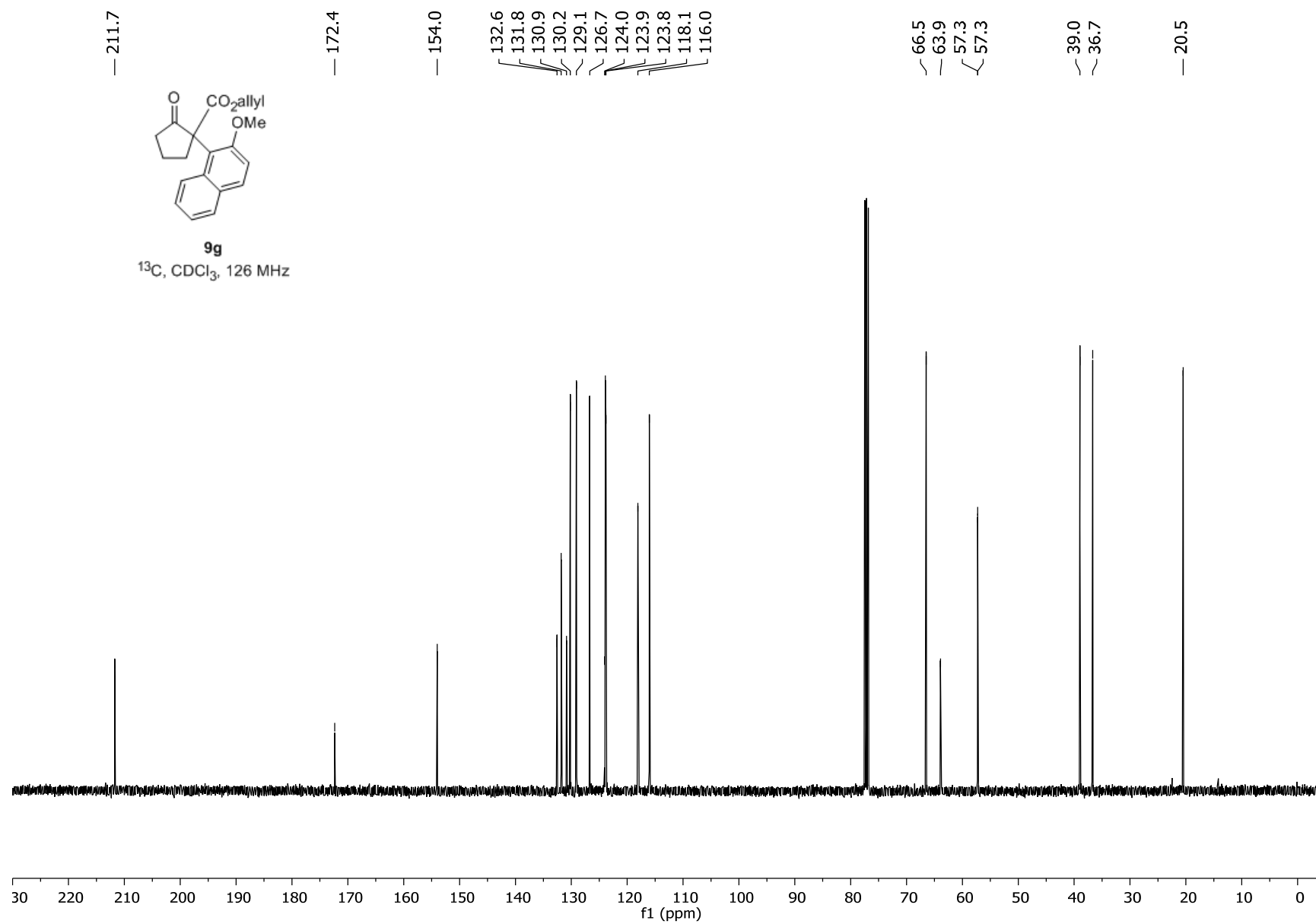


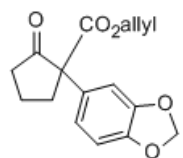


9g

^1H , CDCl_3 , 400 MHz

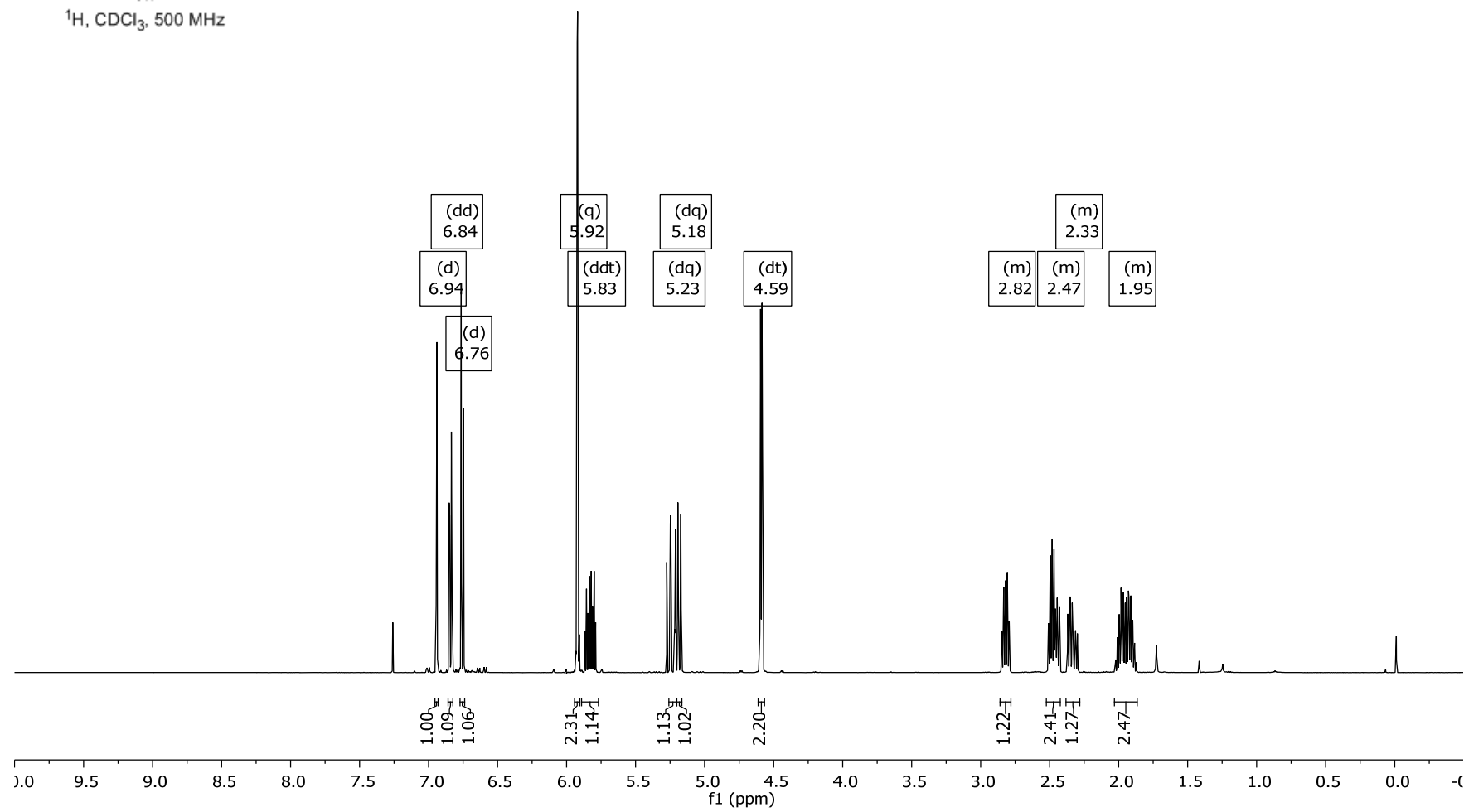


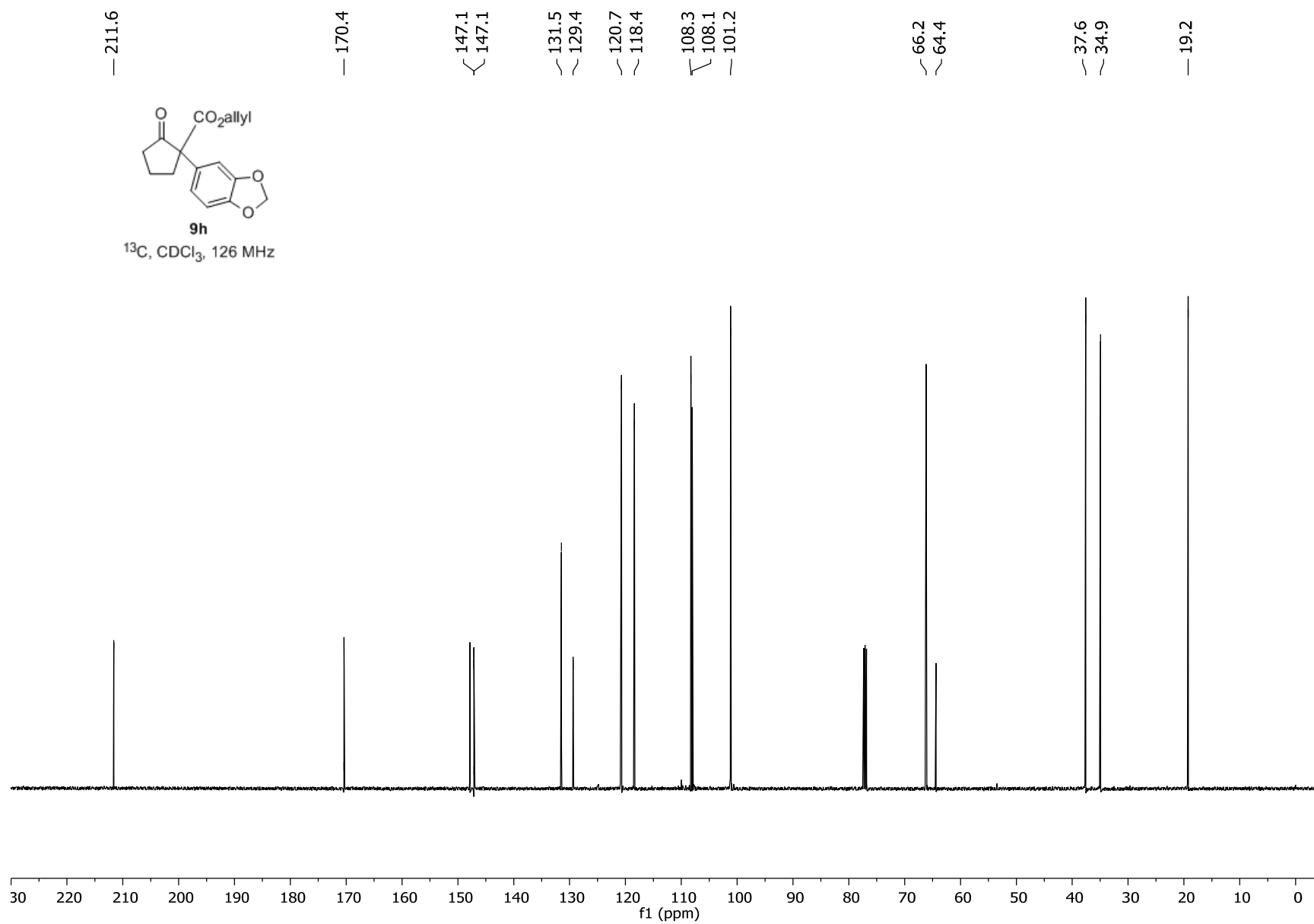


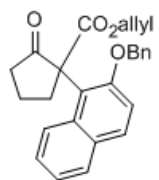


9h

^1H , CDCl_3 , 500 MHz

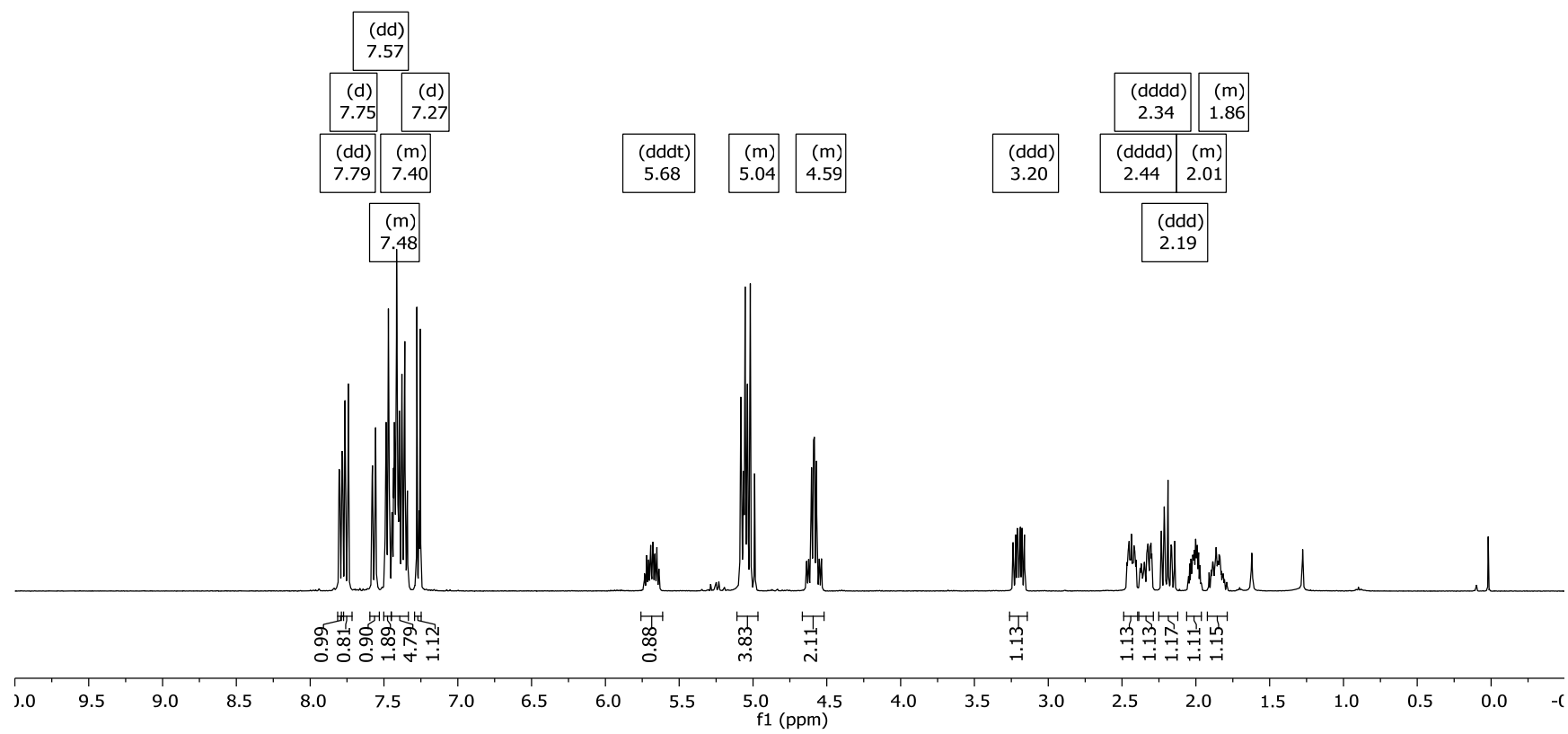


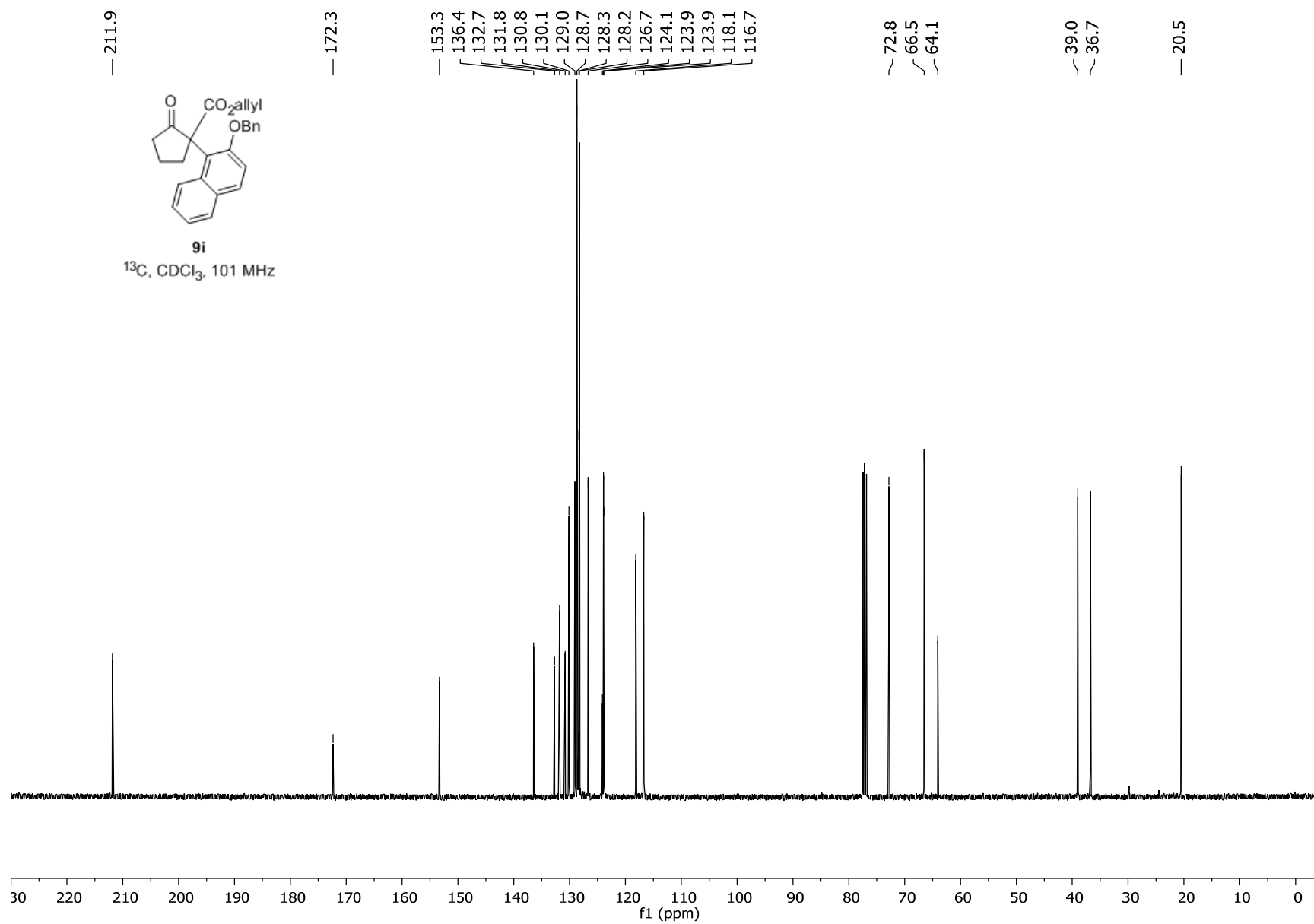


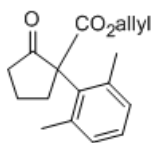


9i

^1H , CDCl_3 , 400 MHz

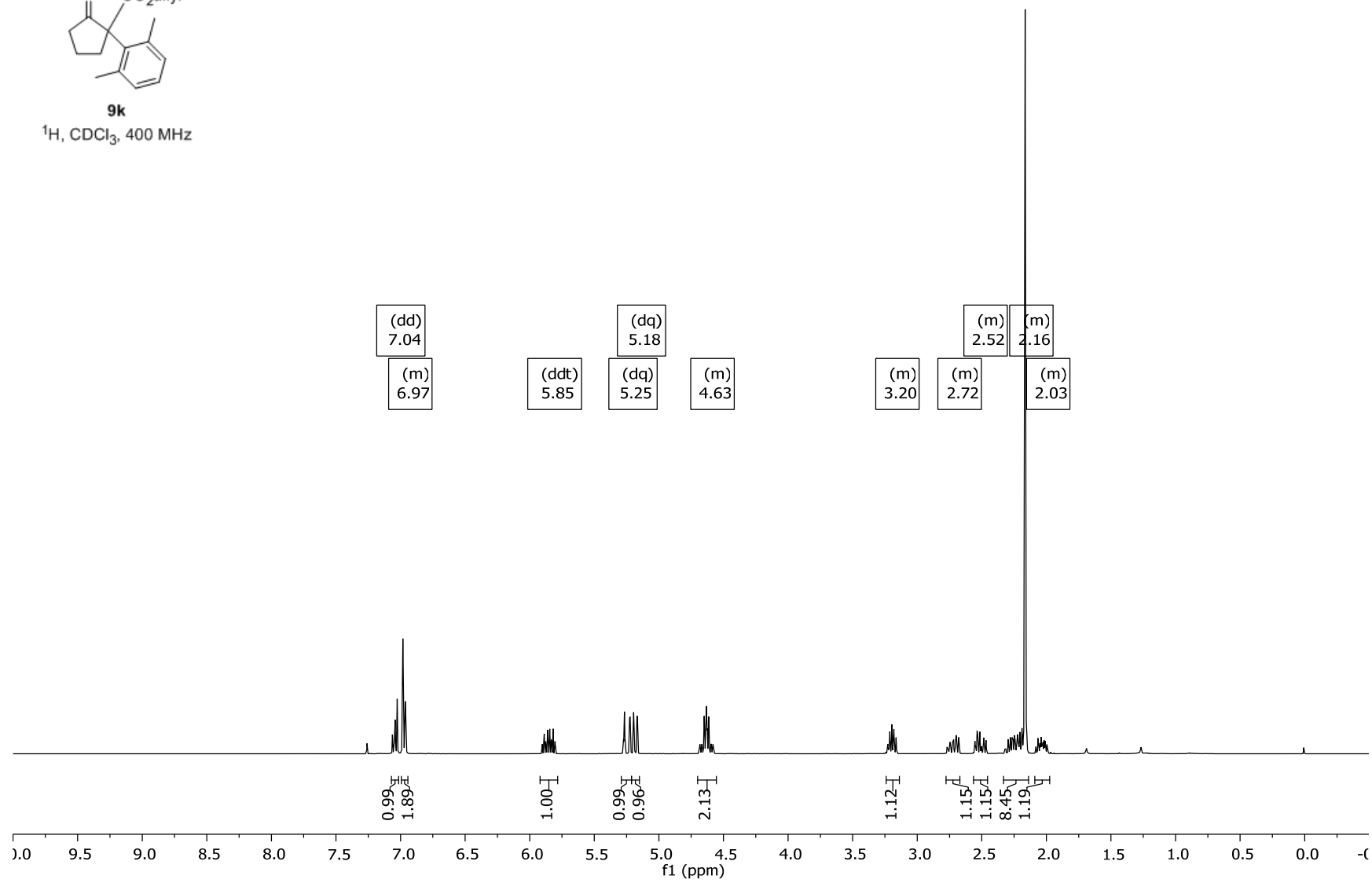


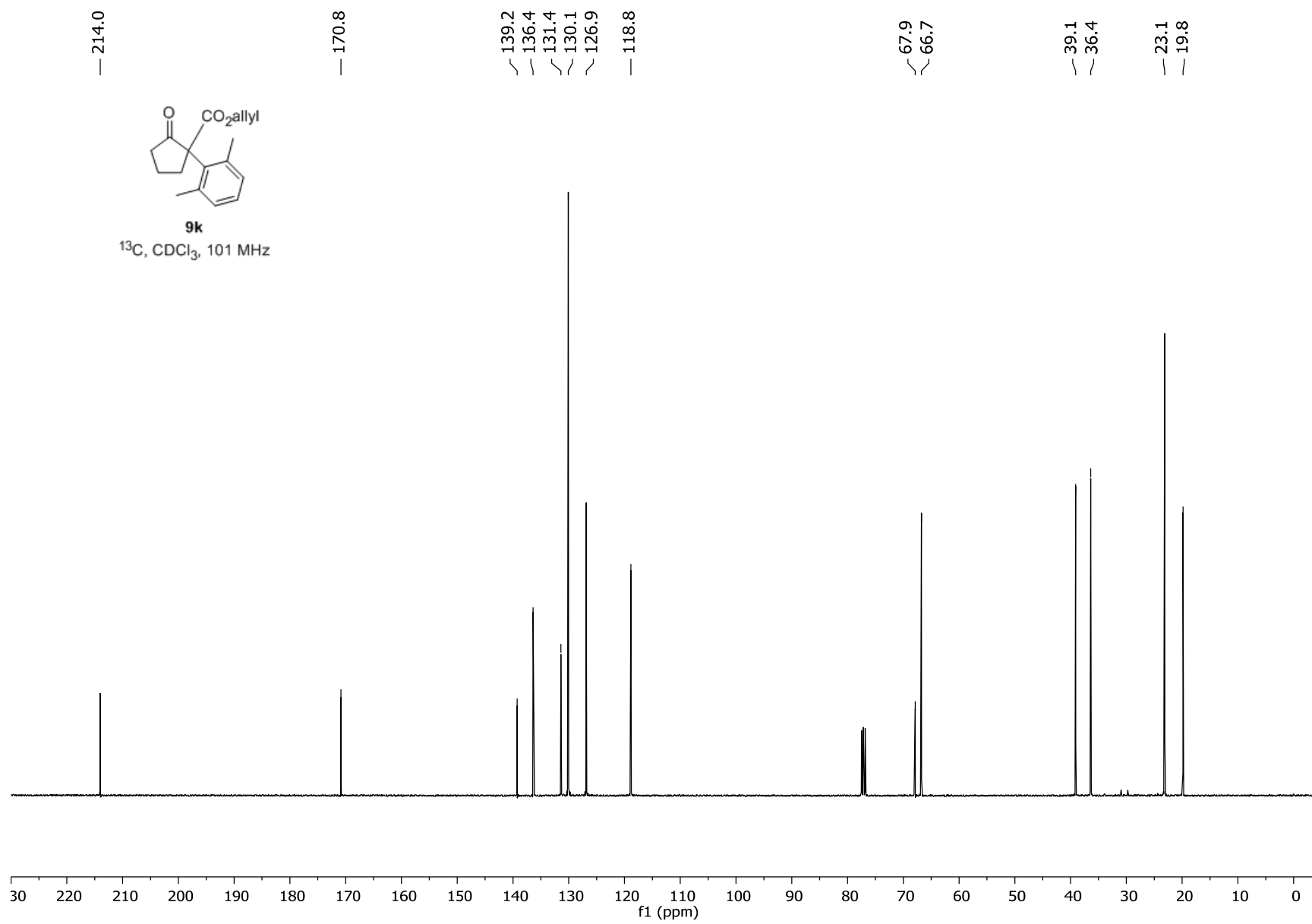


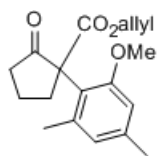


9k

^1H , CDCl_3 , 400 MHz

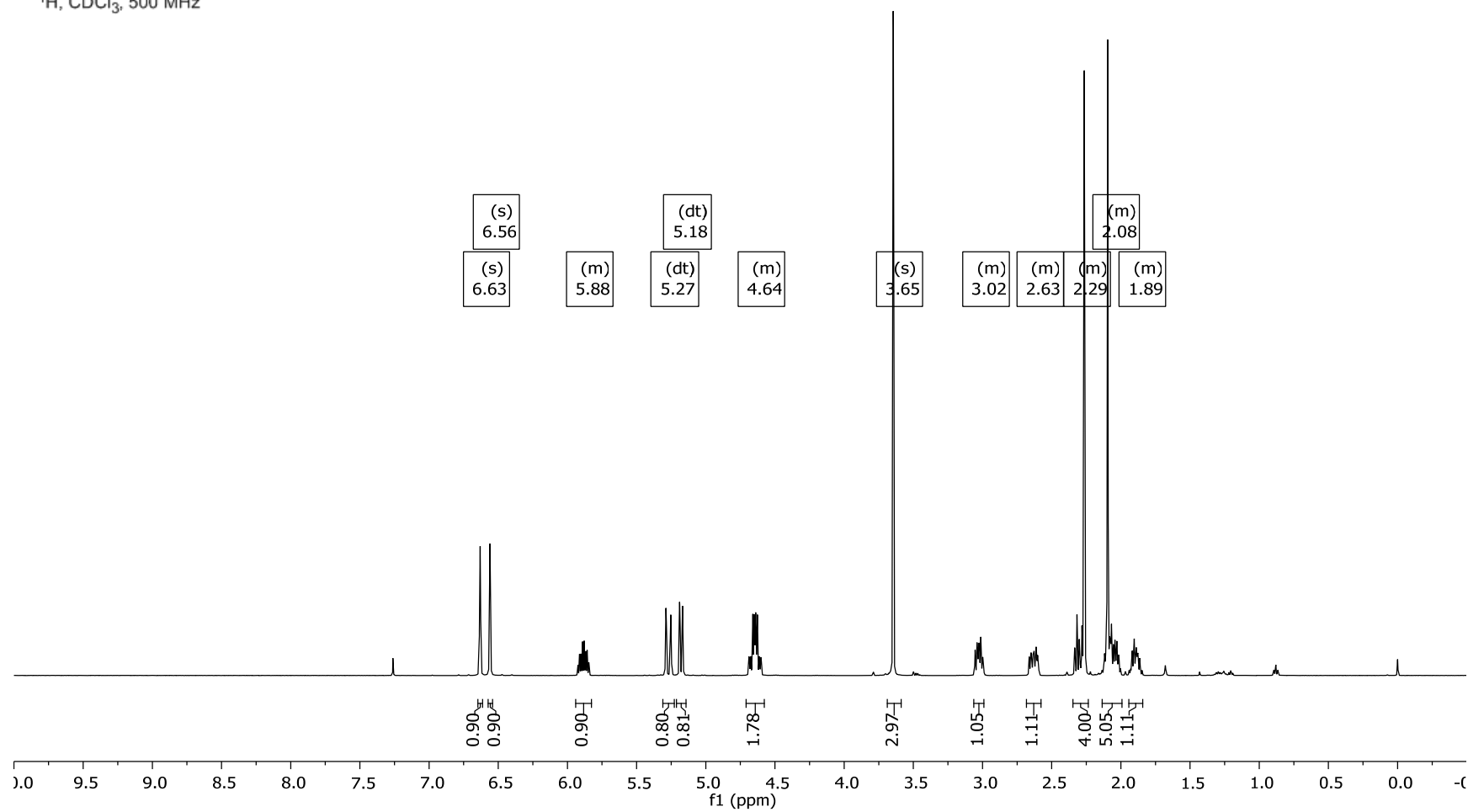


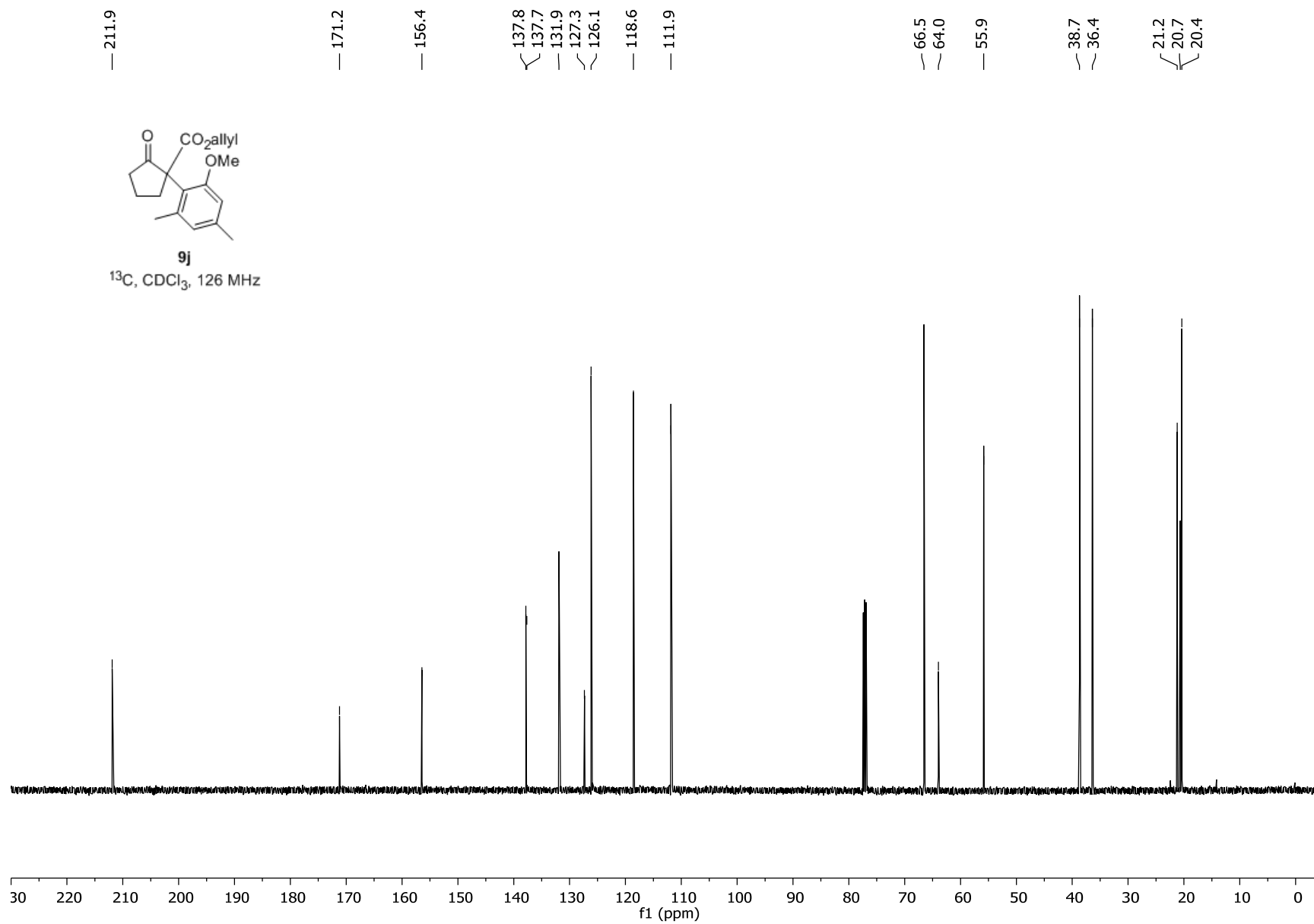


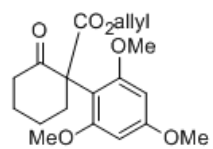


9j

^1H , CDCl_3 , 500 MHz

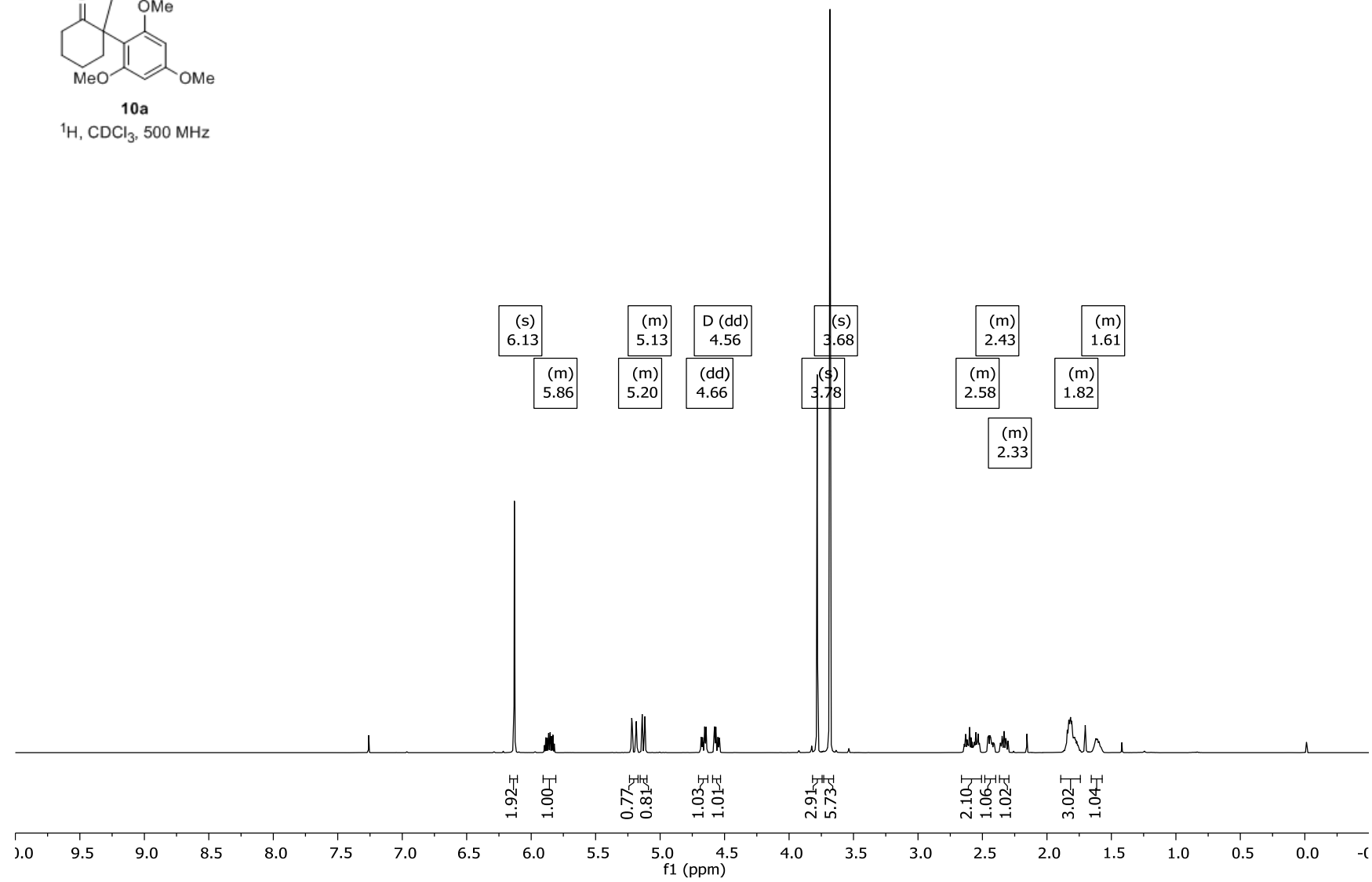


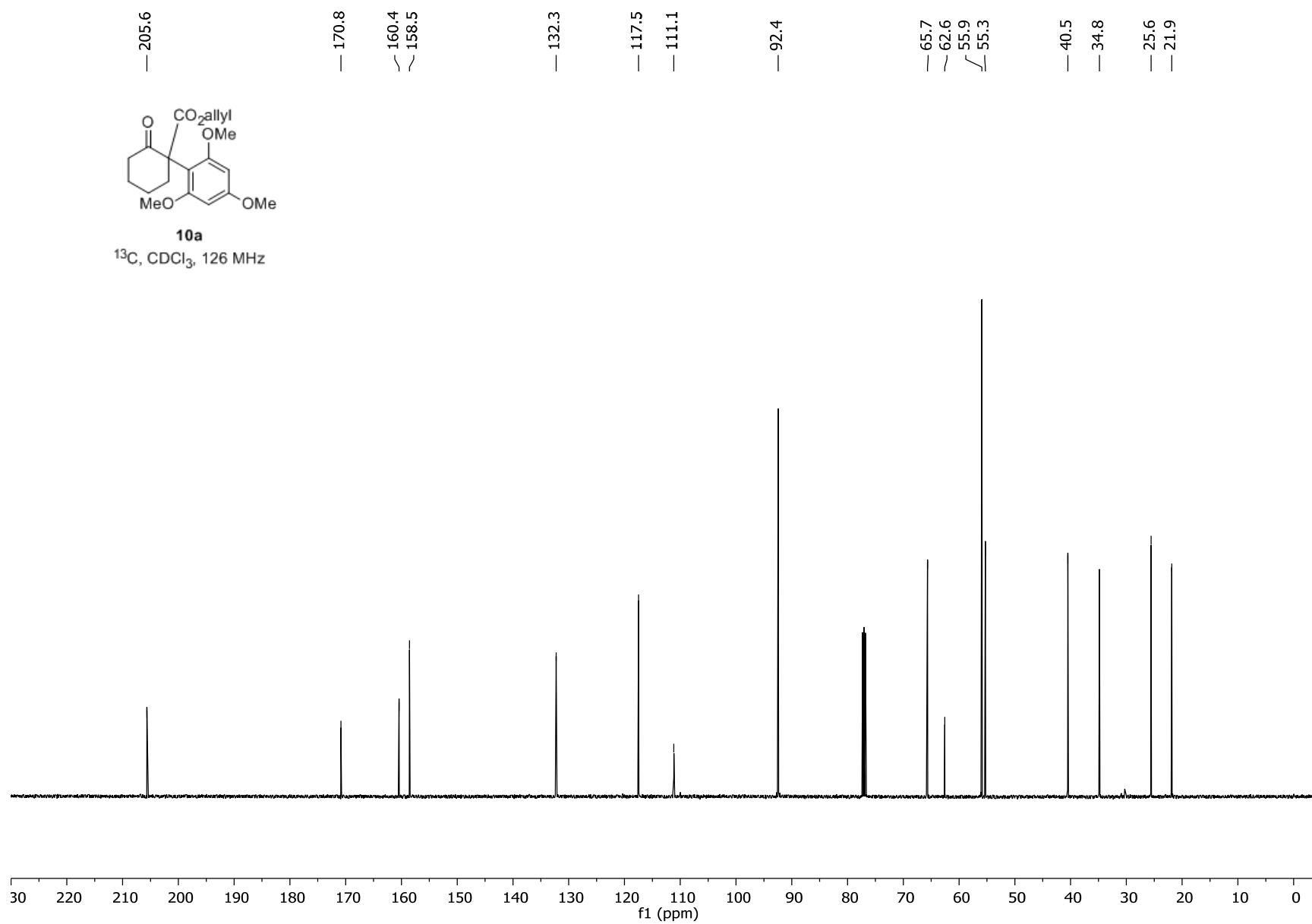


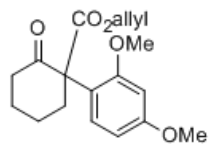


10a

^1H , CDCl_3 , 500 MHz

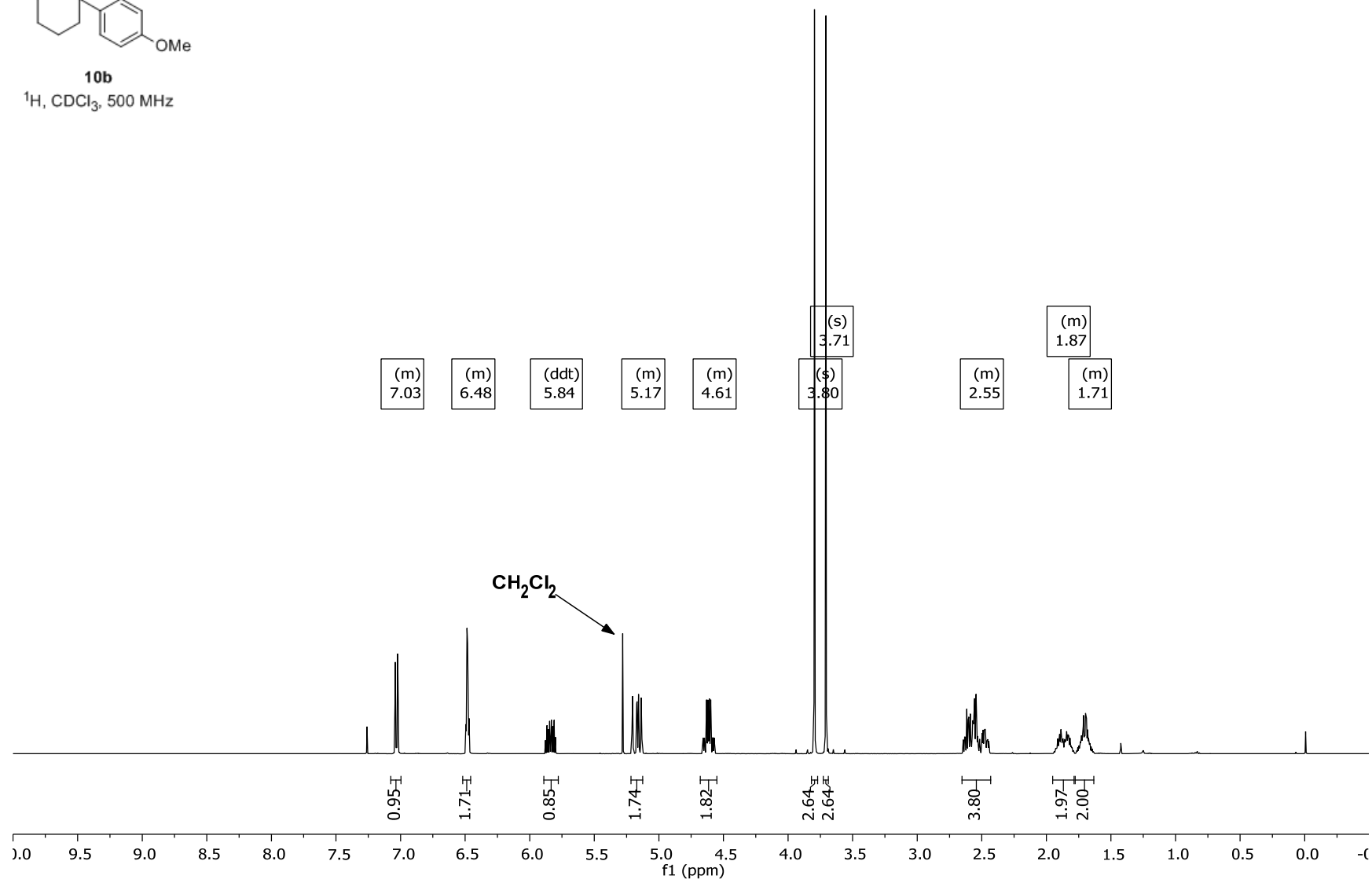


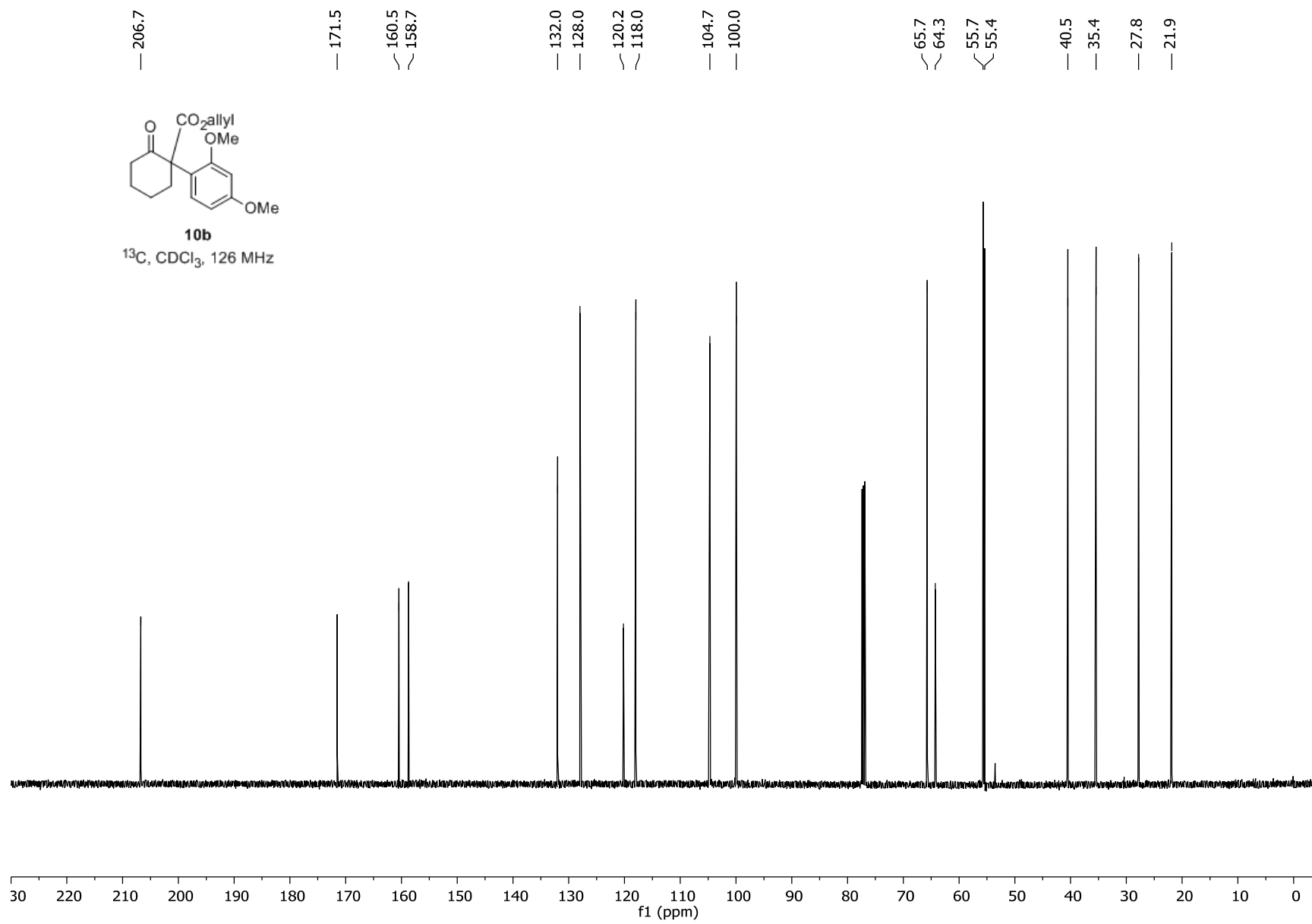


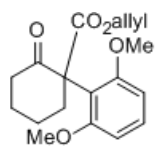


10b

^1H , CDCl_3 , 500 MHz

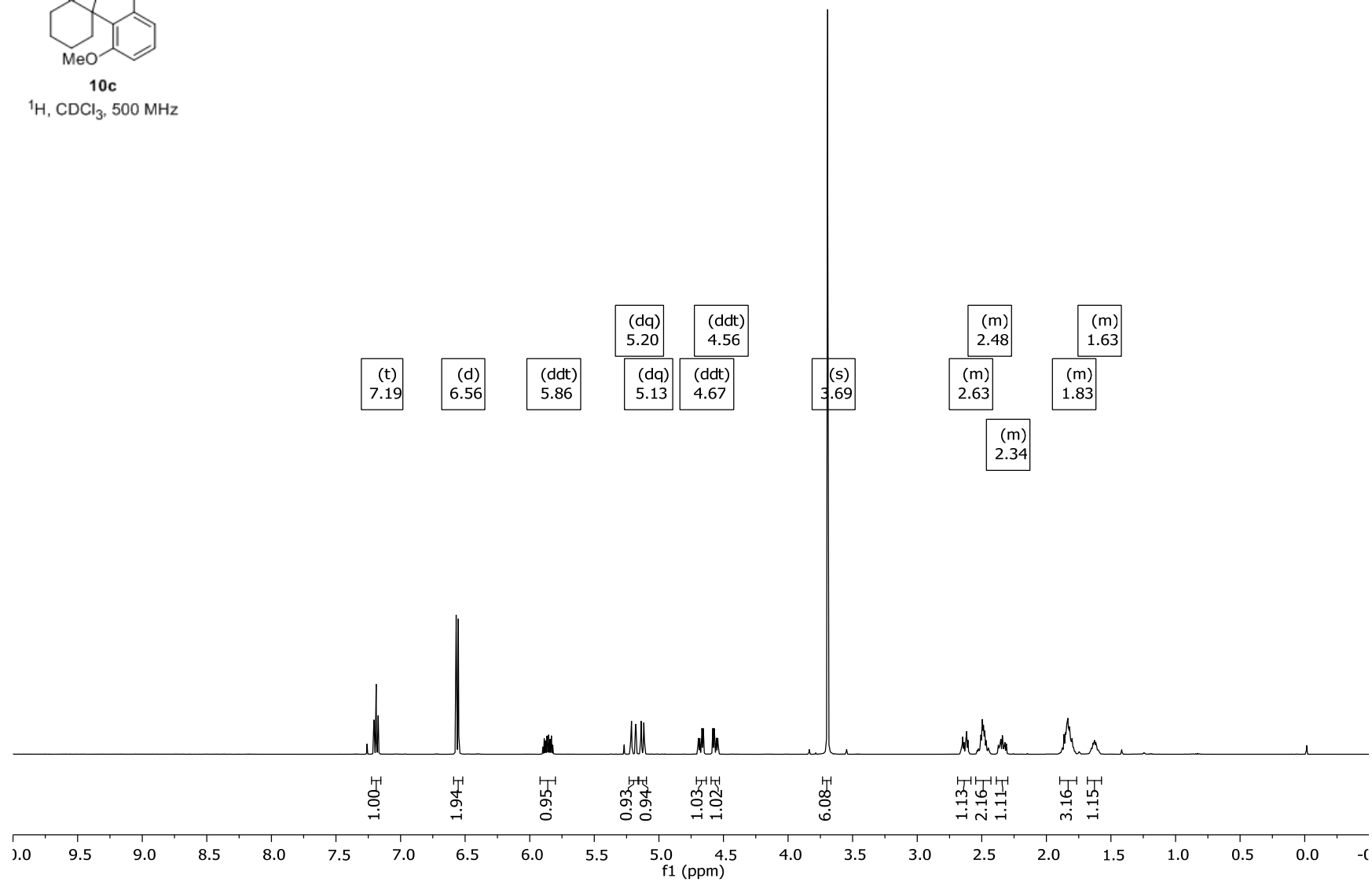


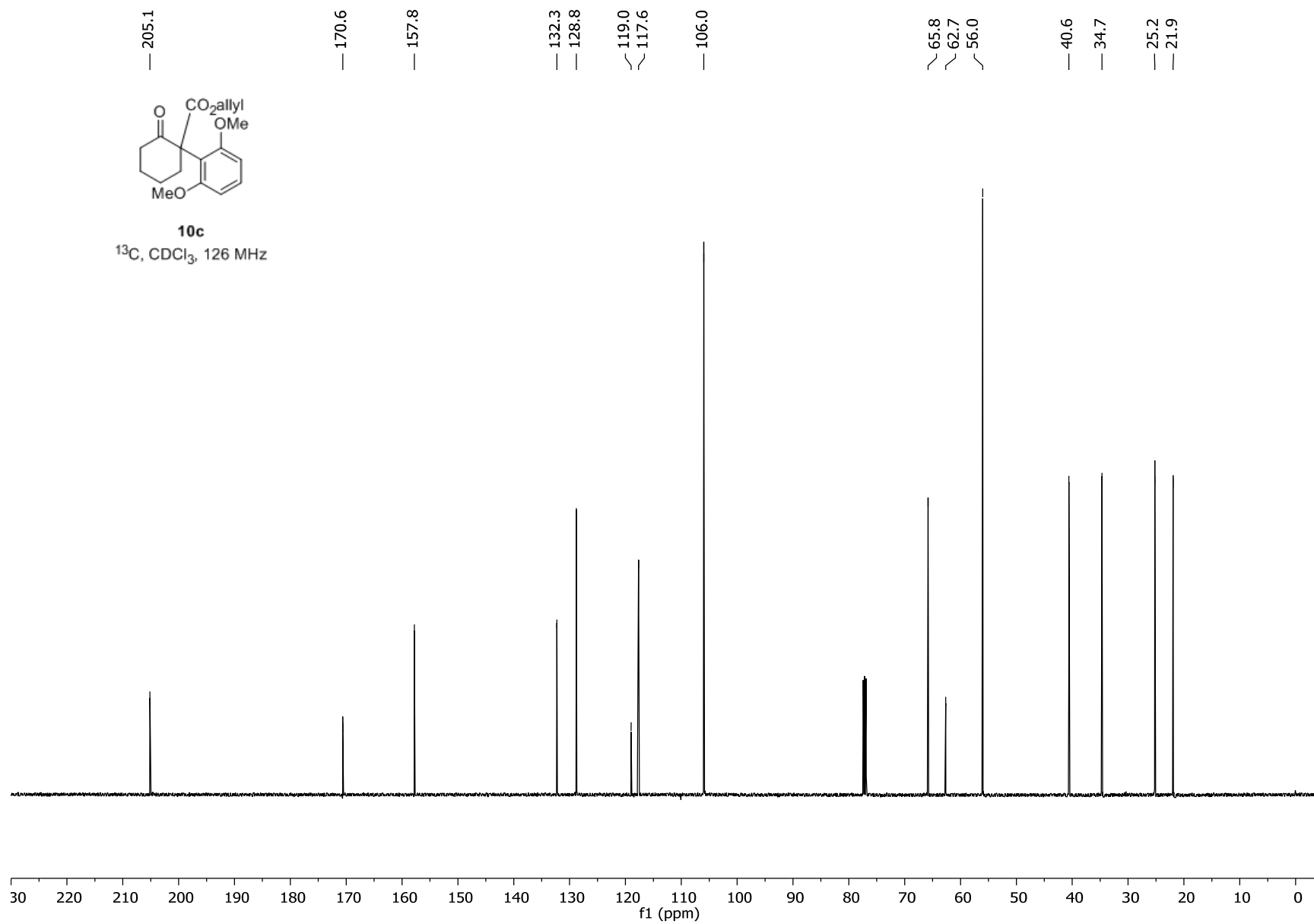


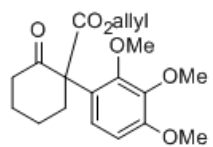


10c

^1H , CDCl_3 , 500 MHz

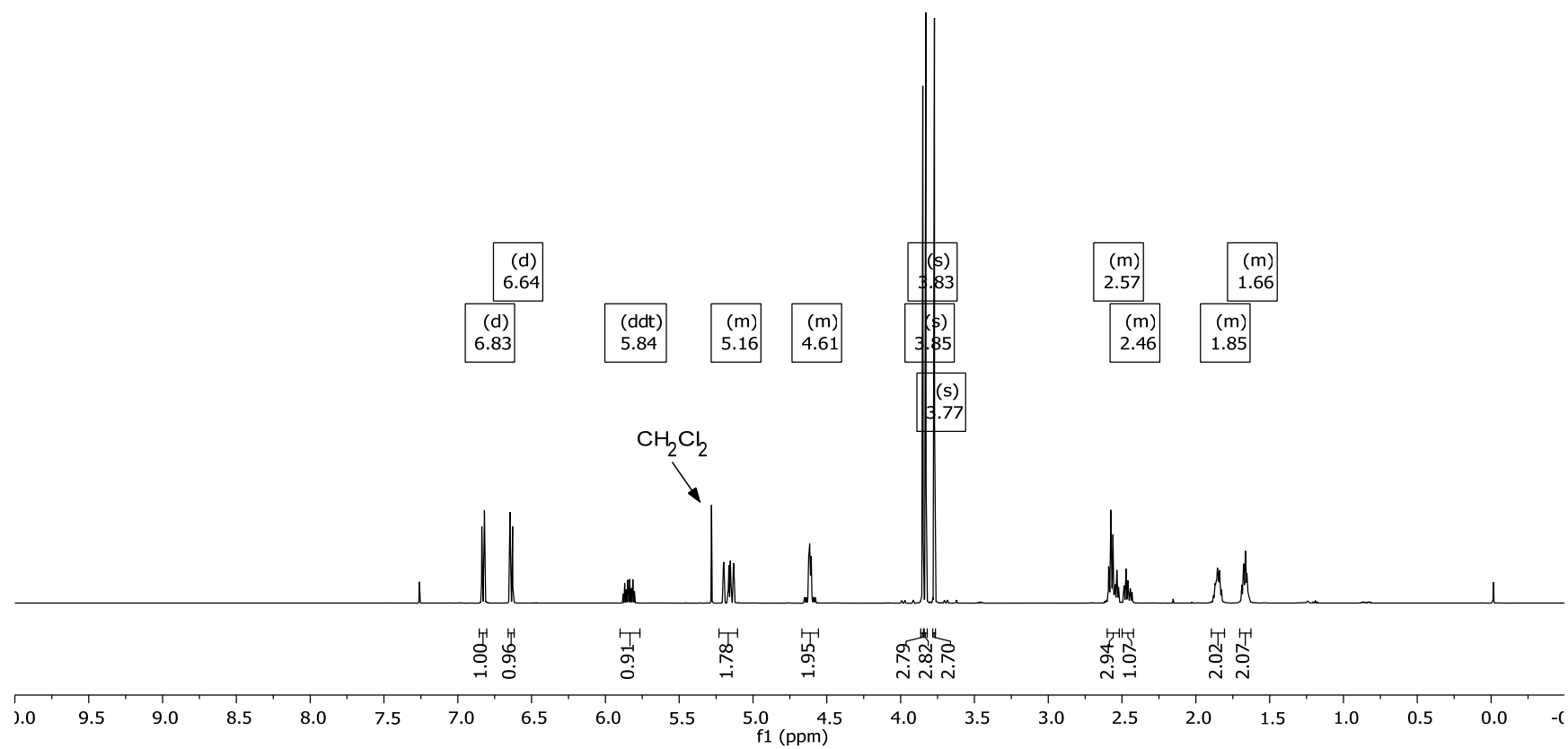


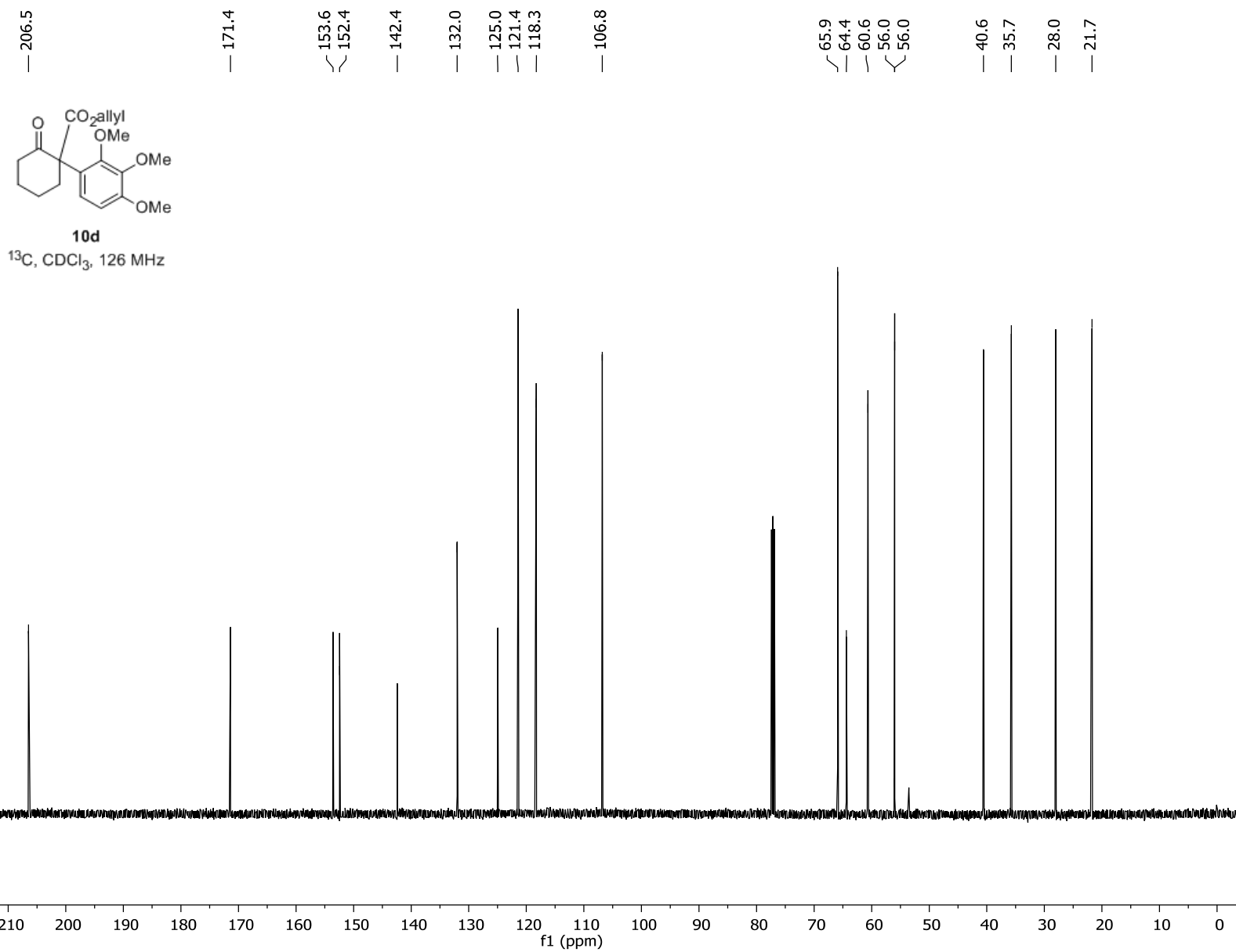


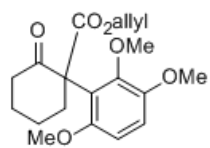


10d

^1H , CDCl_3 , 500 MHz

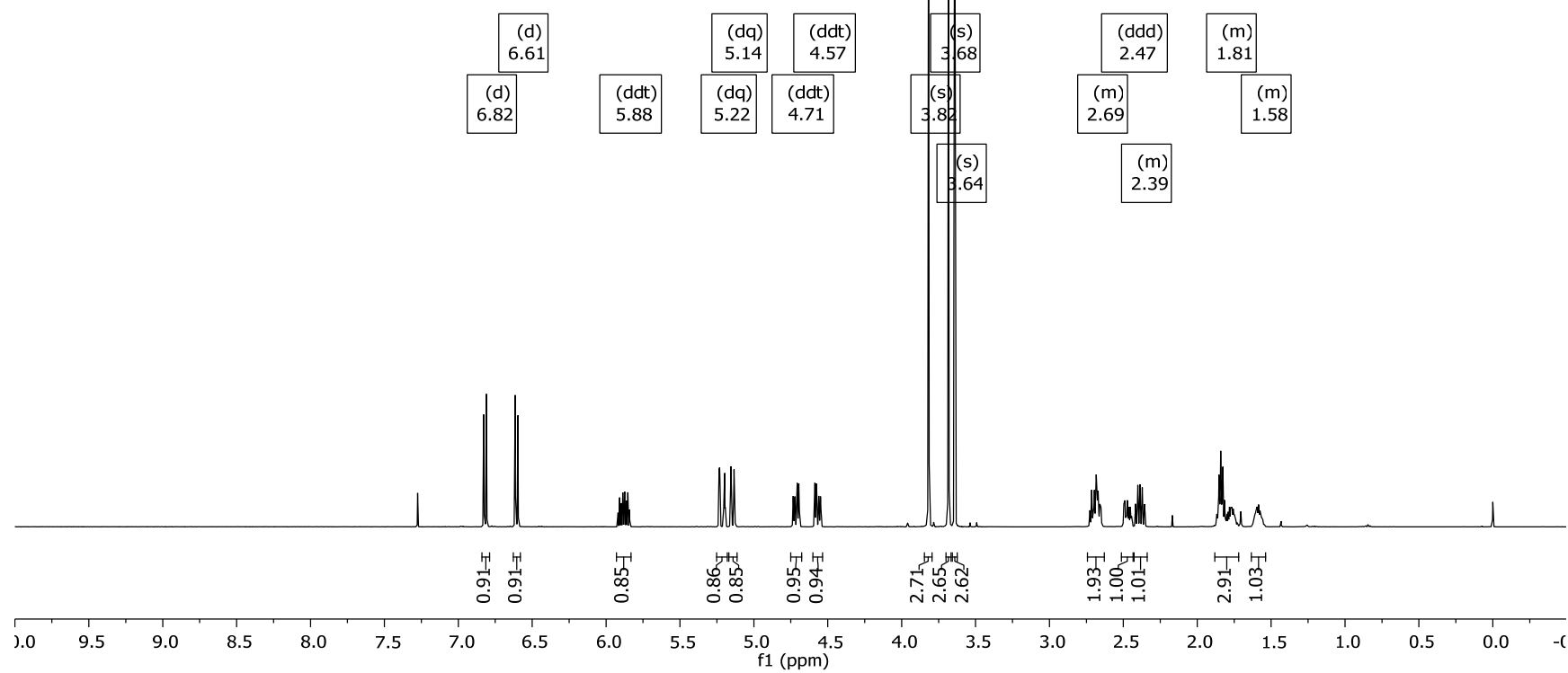


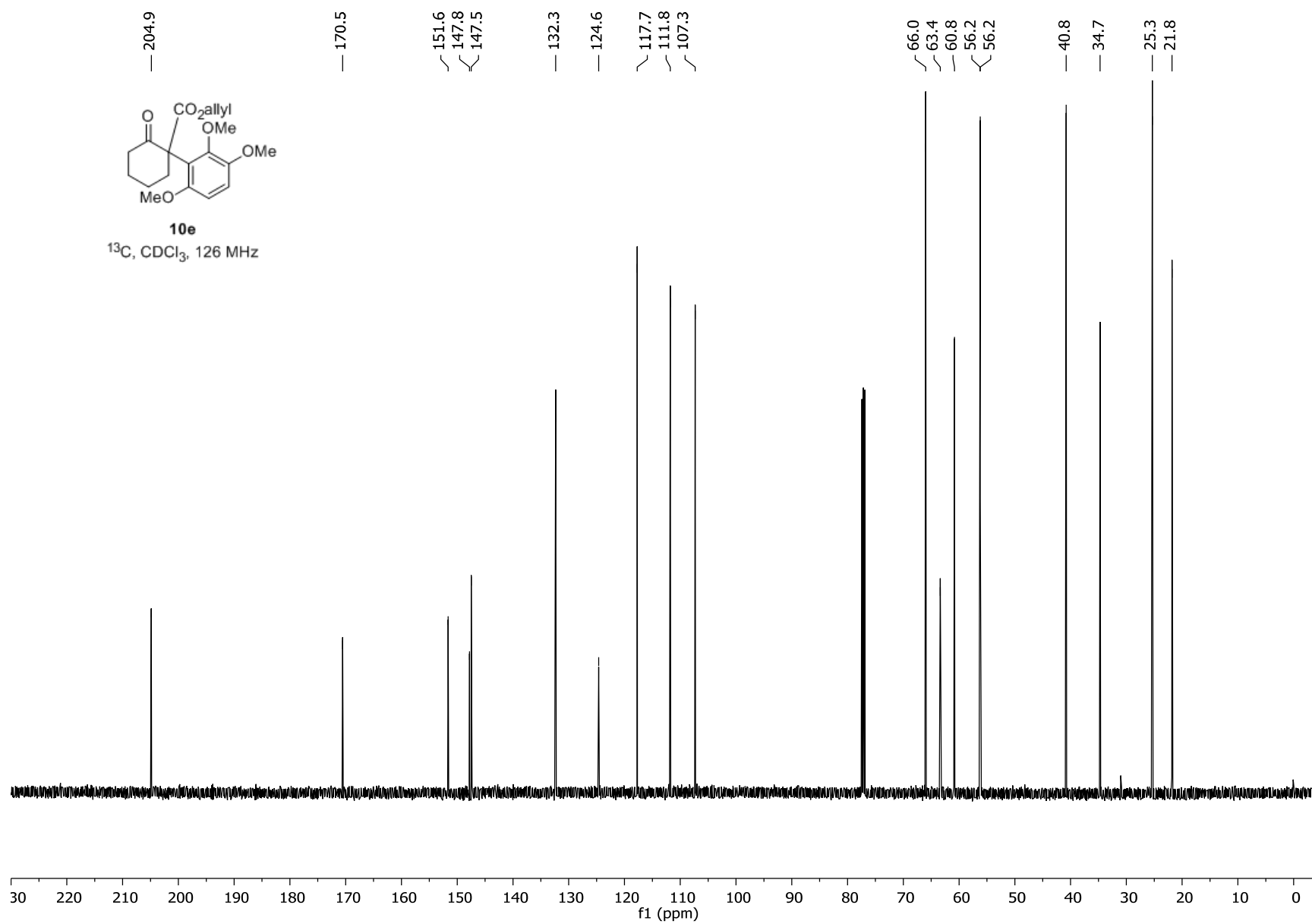


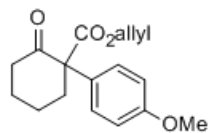


10e

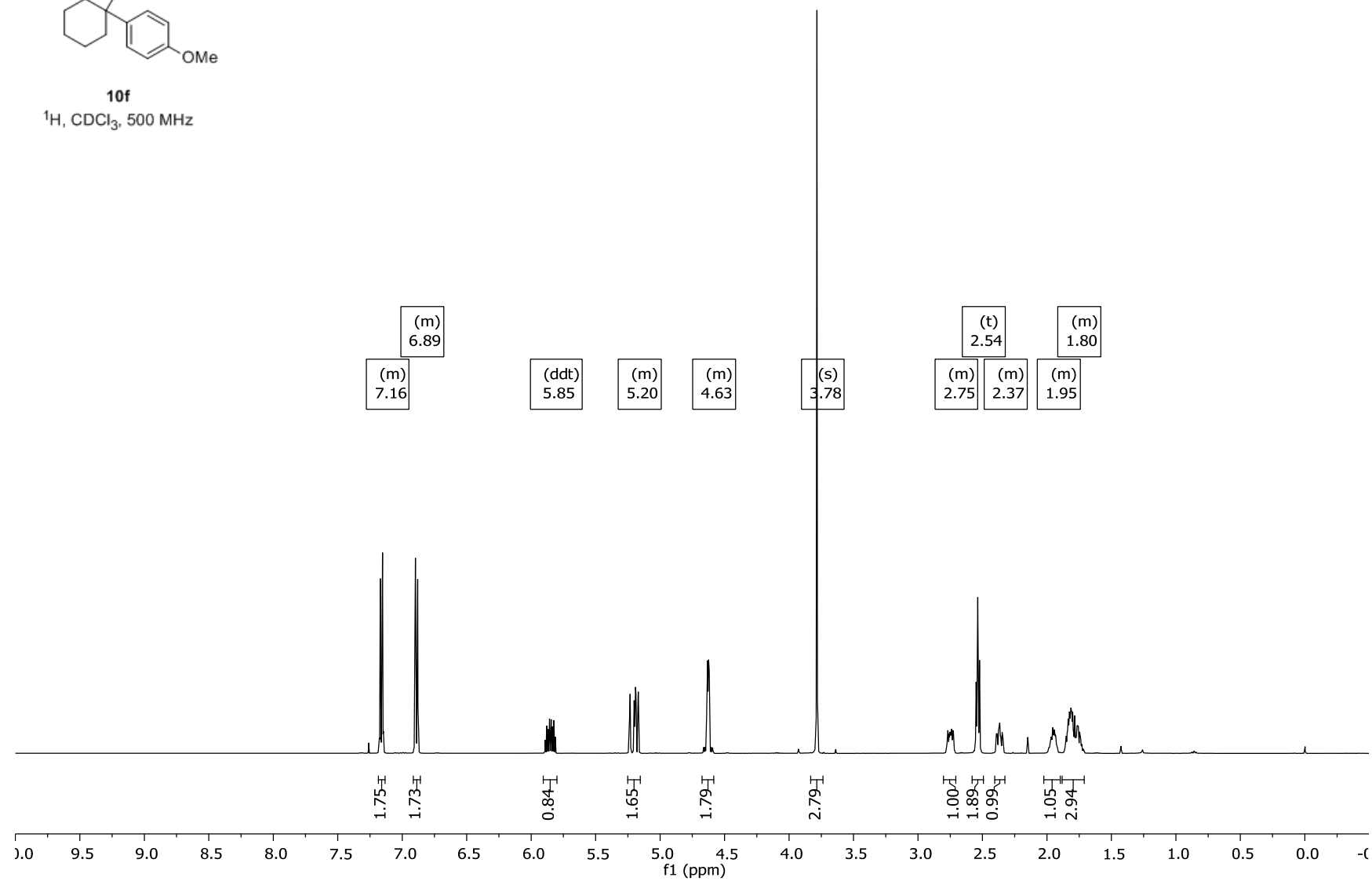
^1H , CDCl_3 , 500 MHz

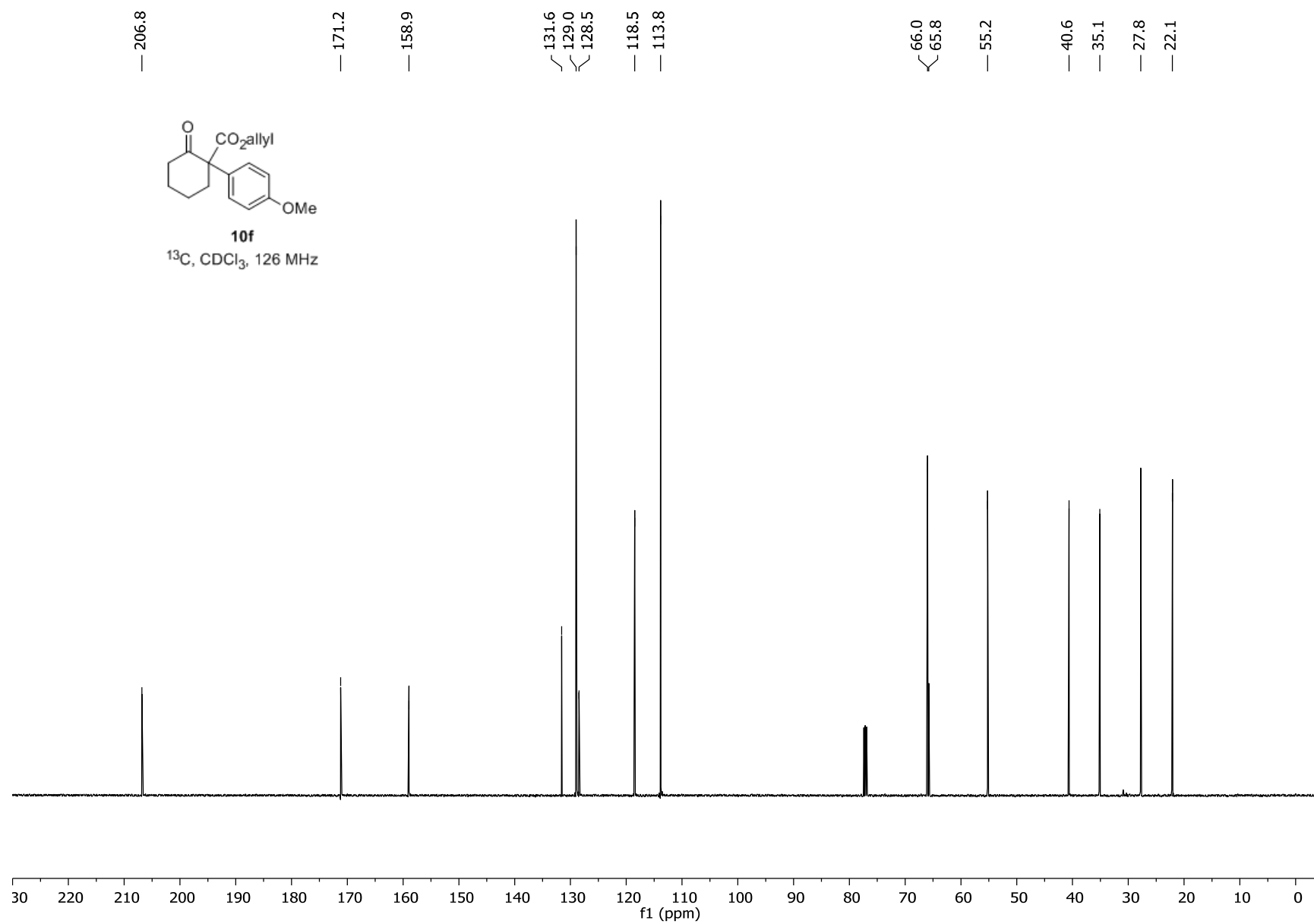


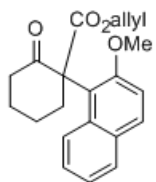




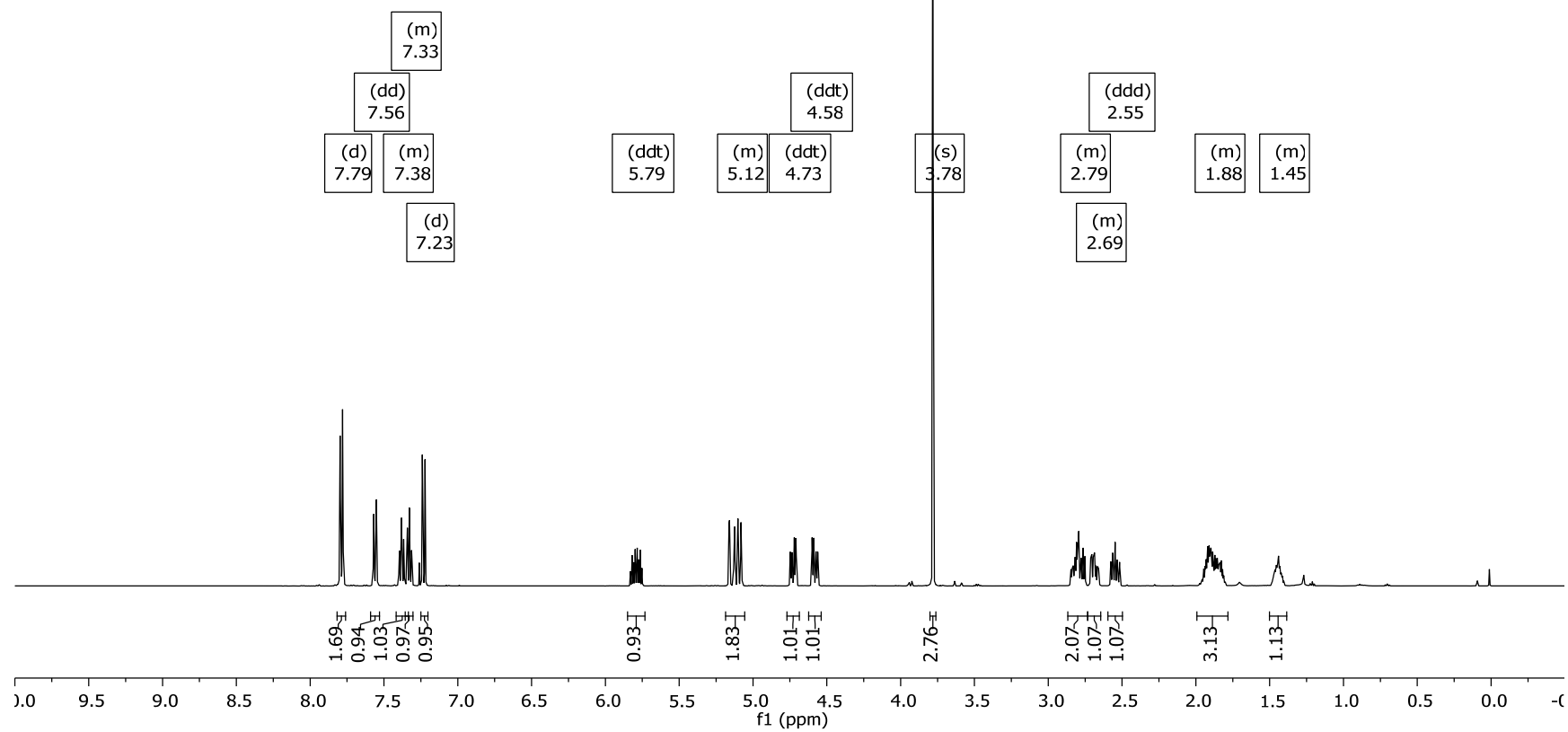
10f
 ^1H , CDCl_3 , 500 MHz

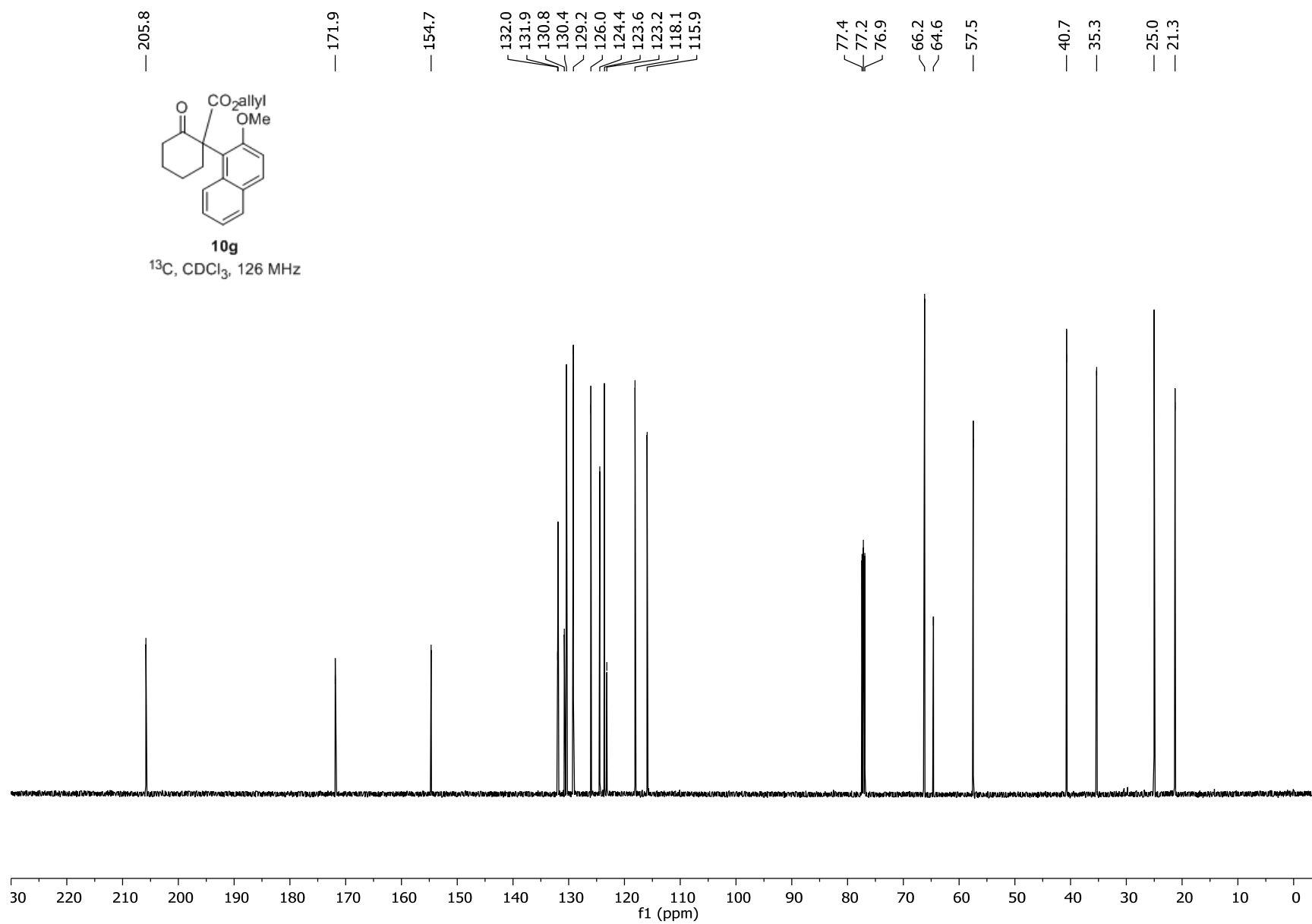


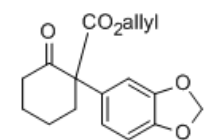




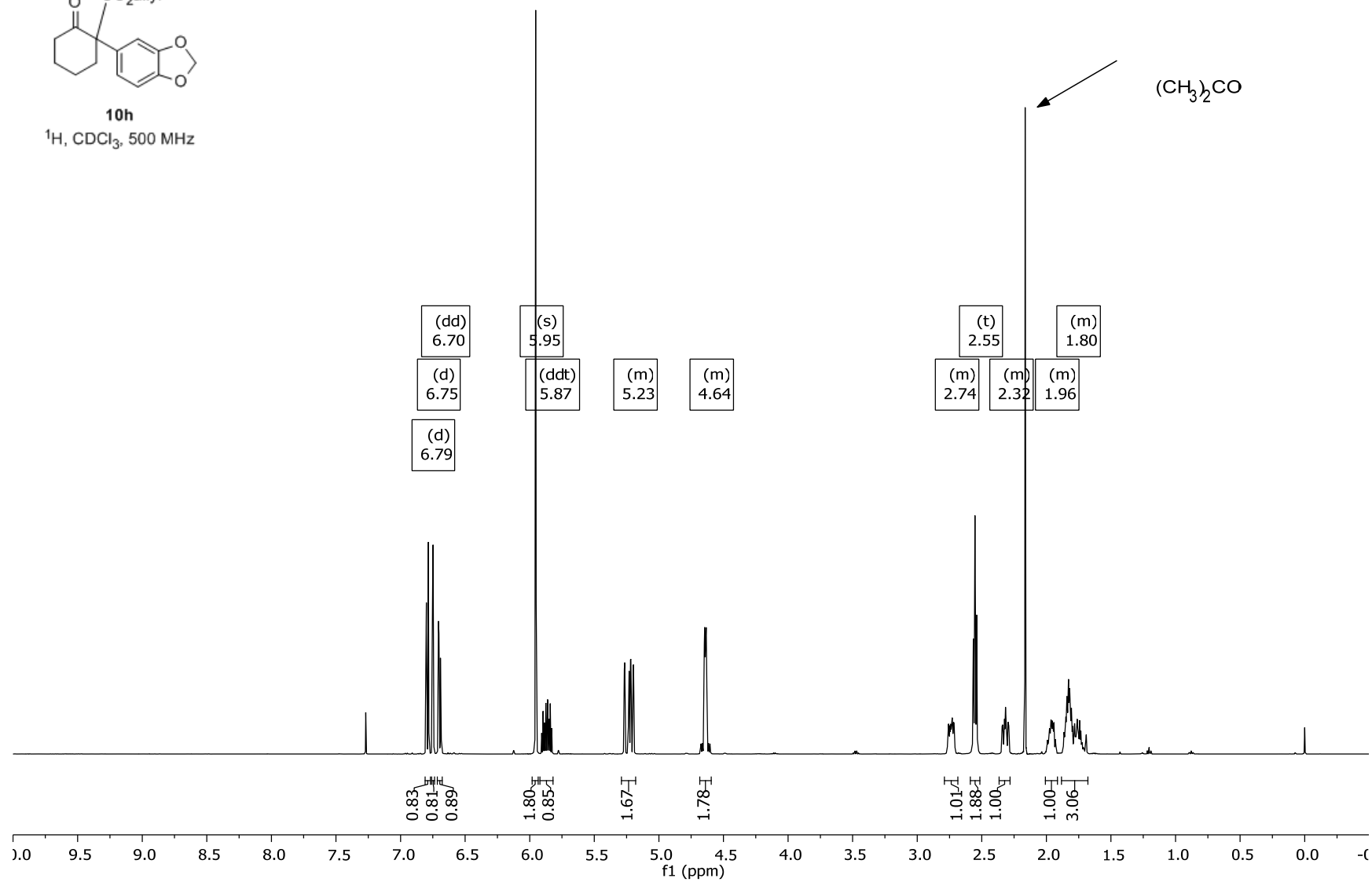
10g
 ^1H , CDCl_3 , 500 MHz

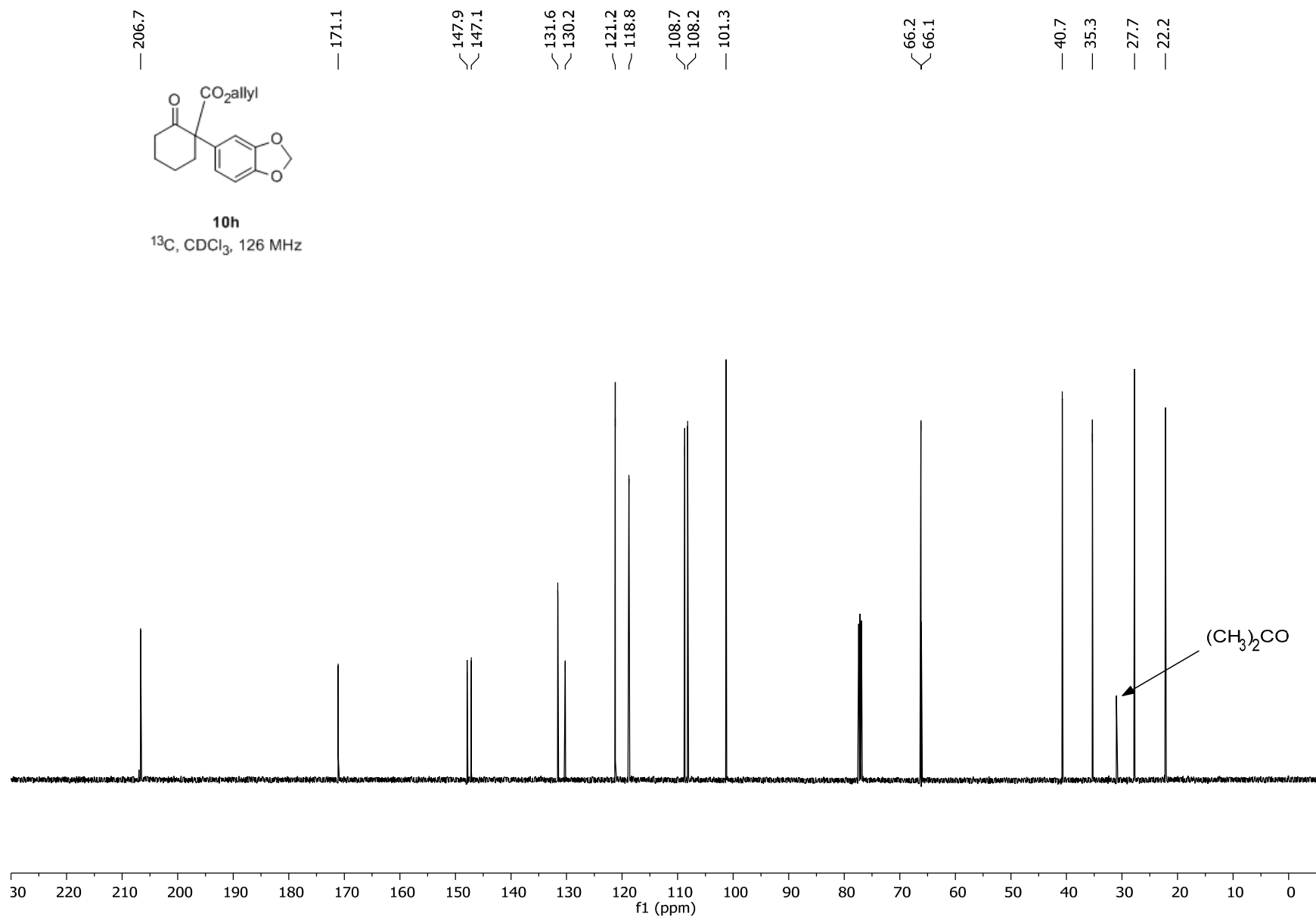


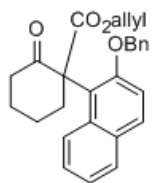




10h
 ^1H , CDCl_3 , 500 MHz

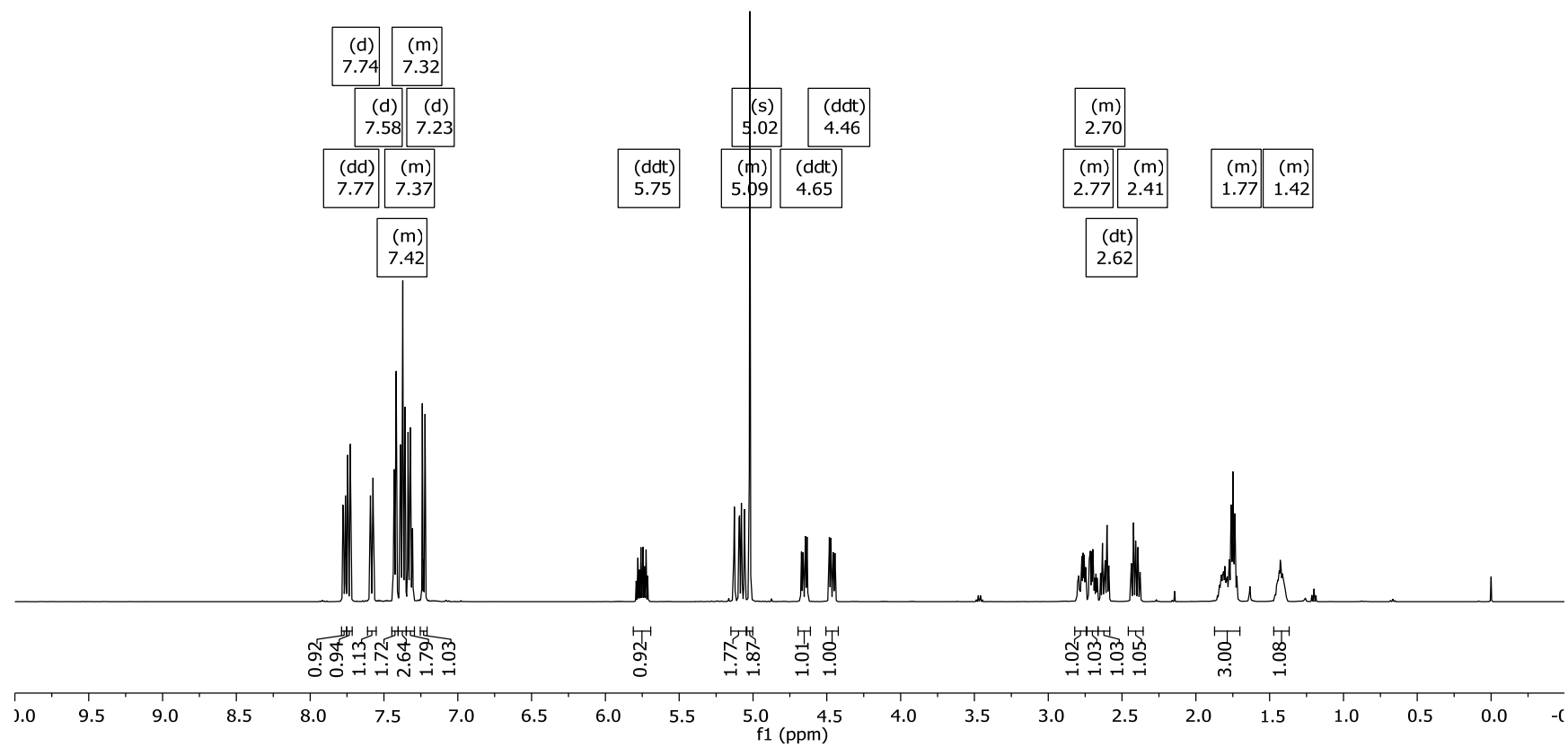


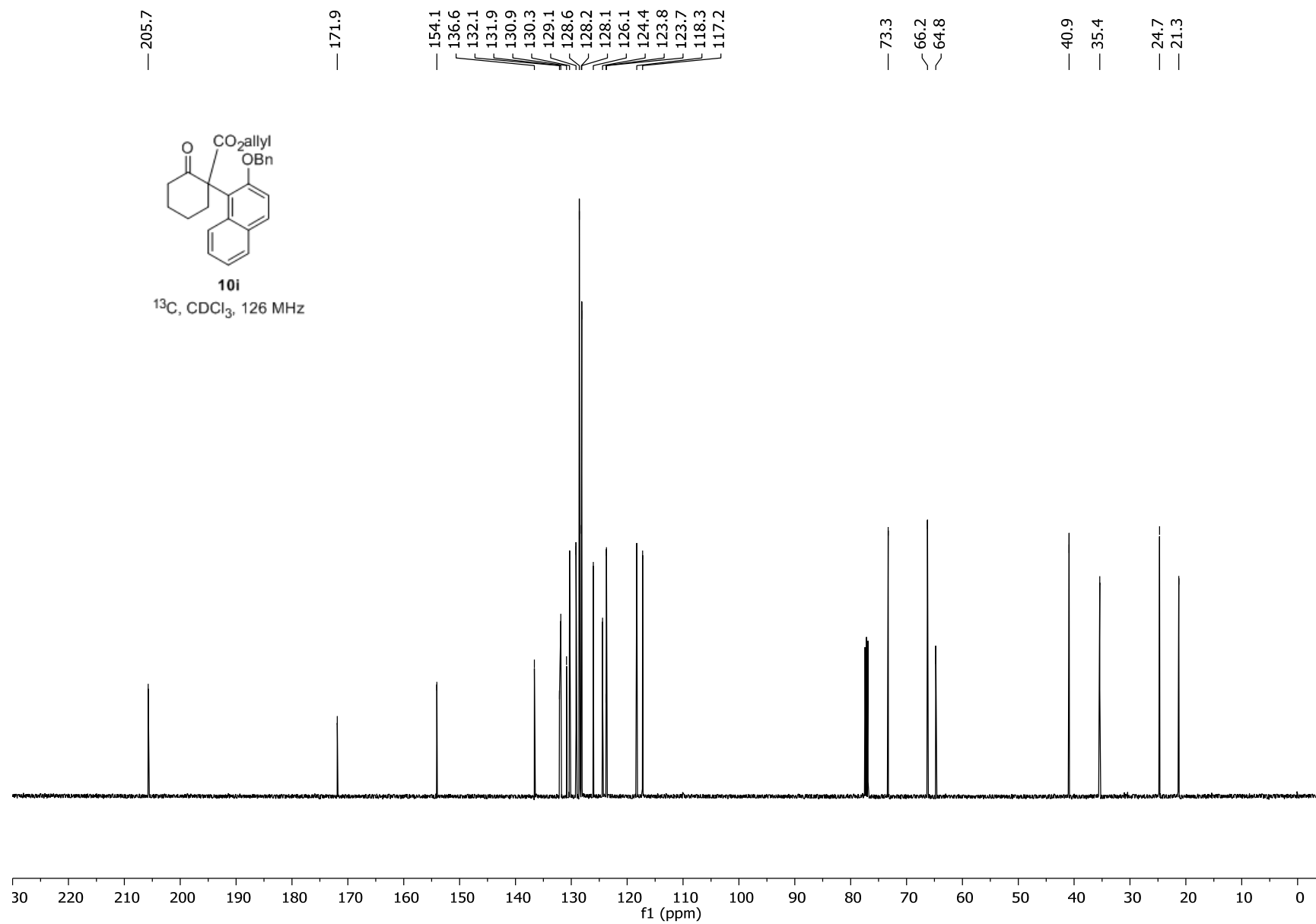


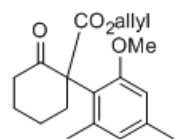


10u

^1H , CDCl_3 , 500 MHz

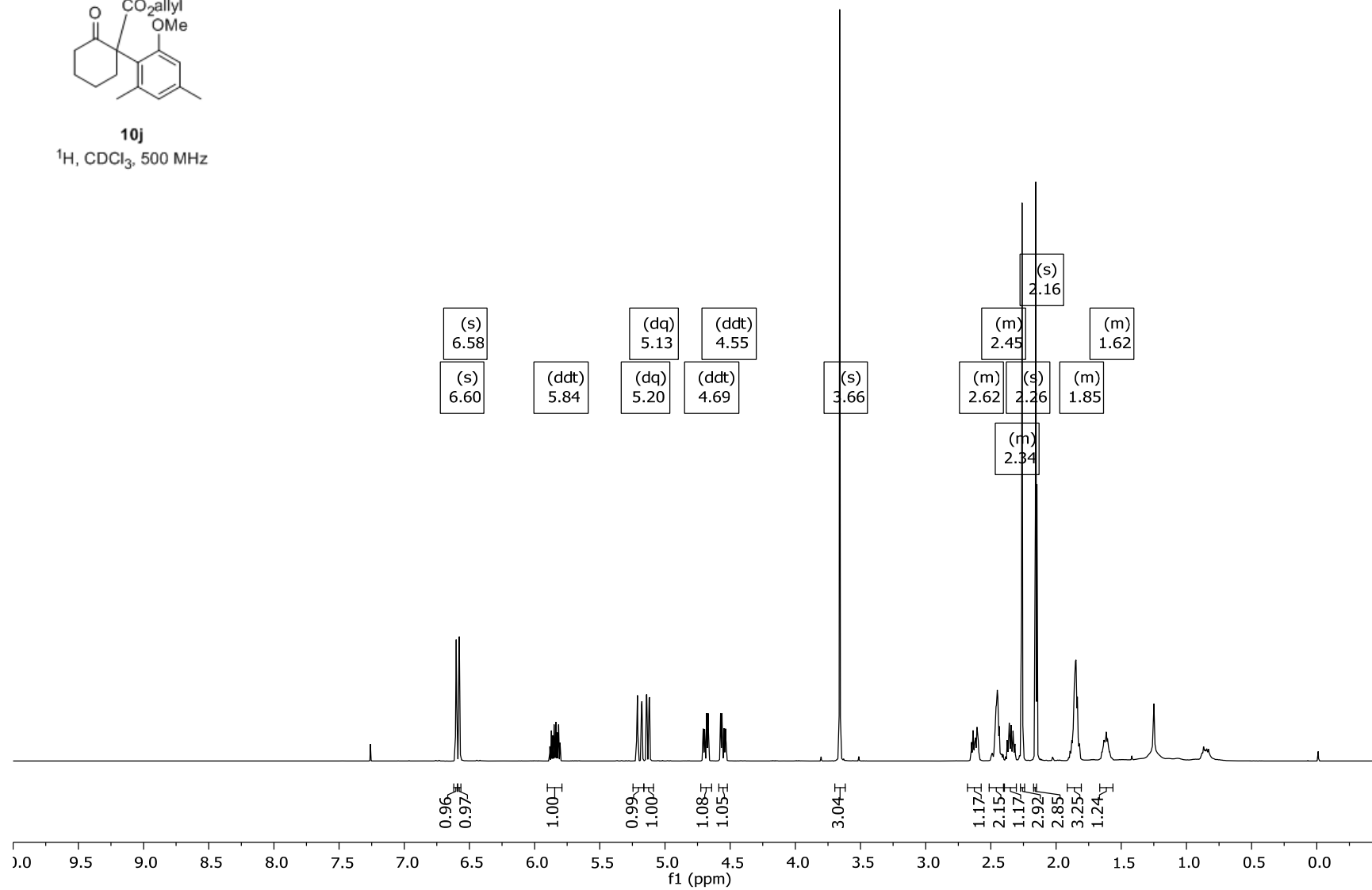




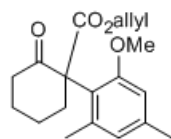


10j

¹H, CDCl₃, 500 MHz

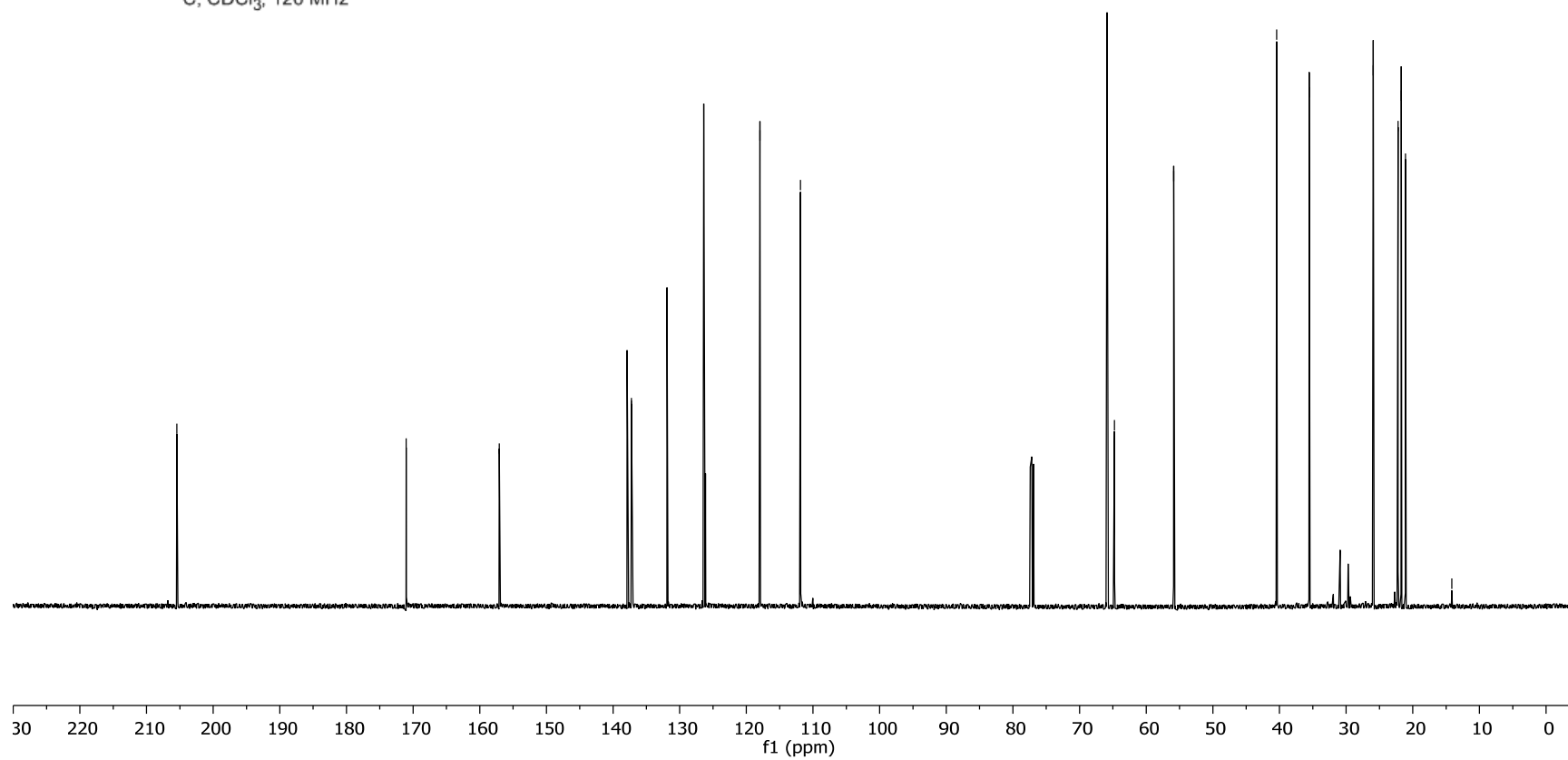


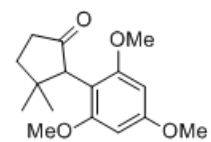
— 205.4
 — 171.0
 — 157.1
 137.3
 137.2
 — 118.0
 — 111.9
 65.9
 64.8
 — 55.9
 — 40.4
 — 35.5
 25.9
 22.2
 21.7
 21.1
 — 14.1



10j

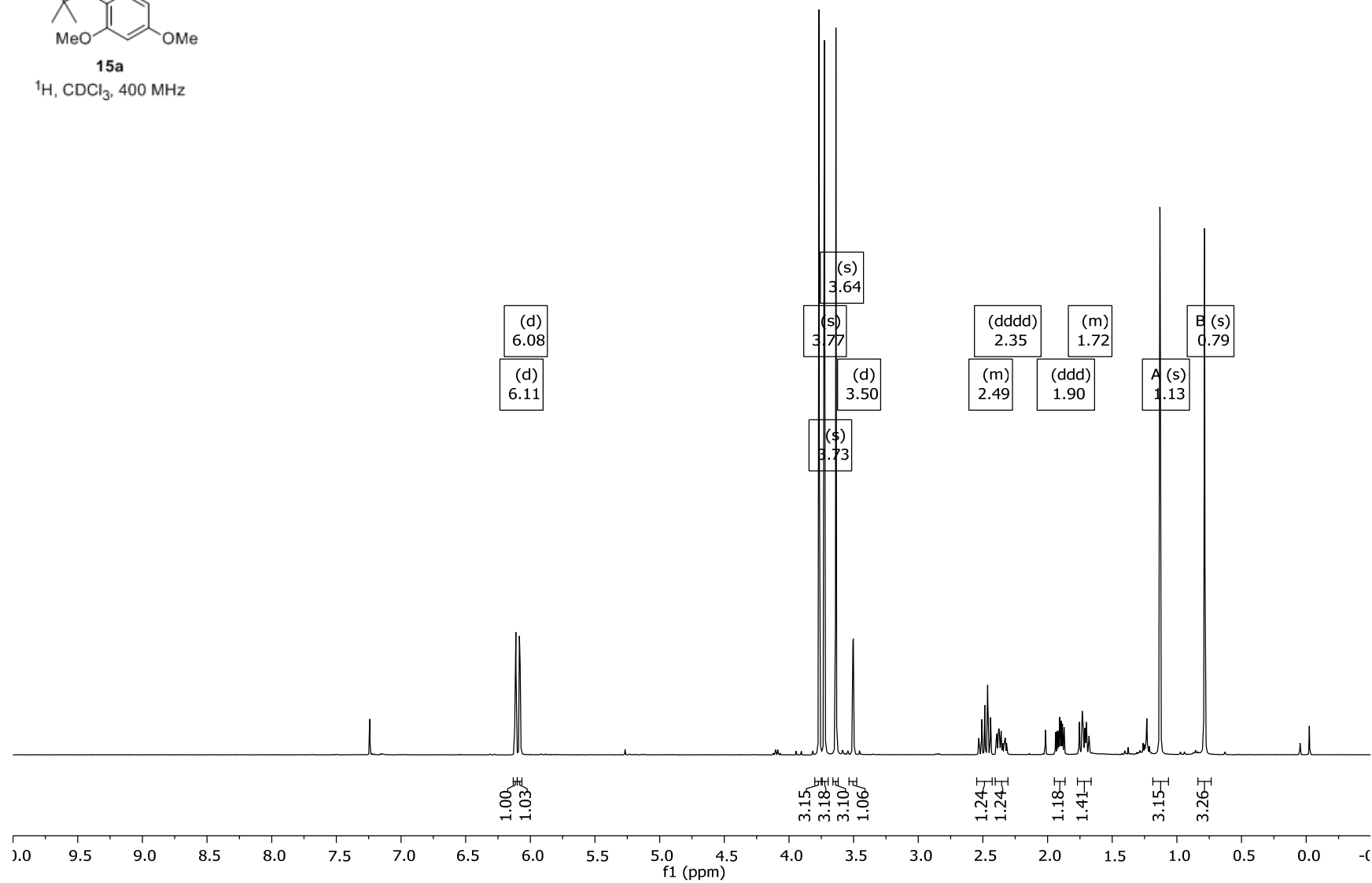
^{13}C , CDCl_3 , 126 MHz

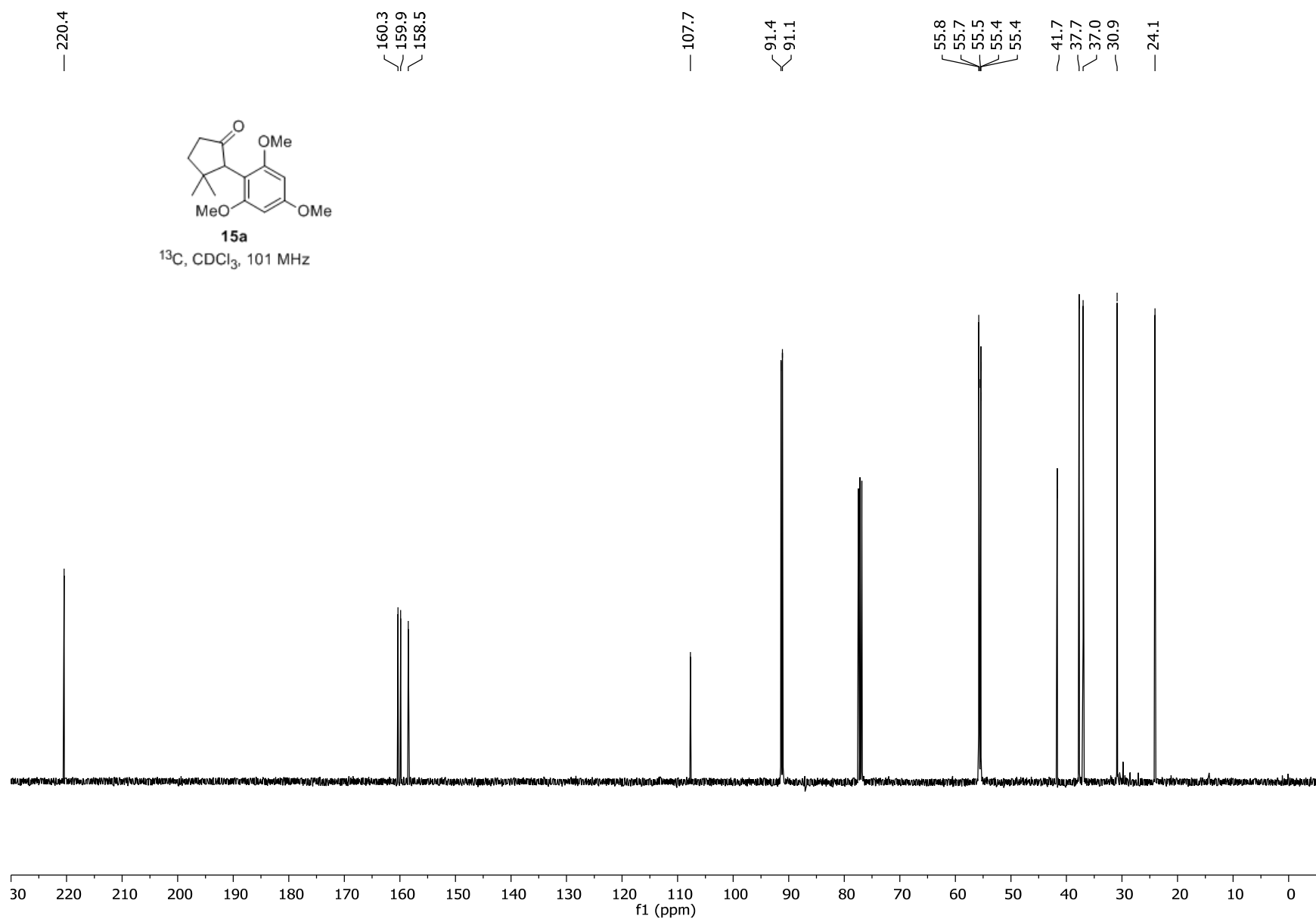


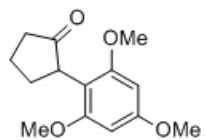


15a

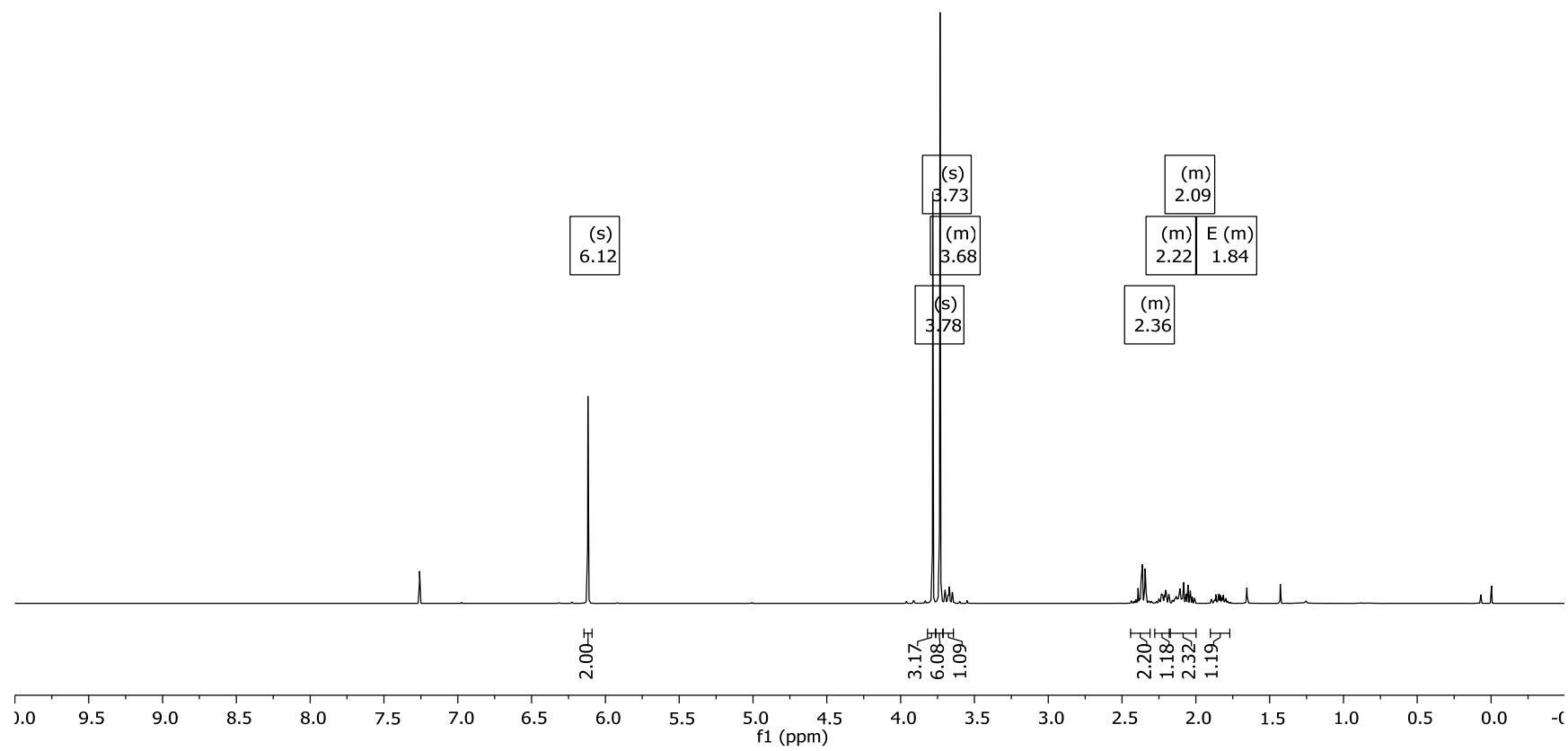
^1H , CDCl_3 , 400 MHz

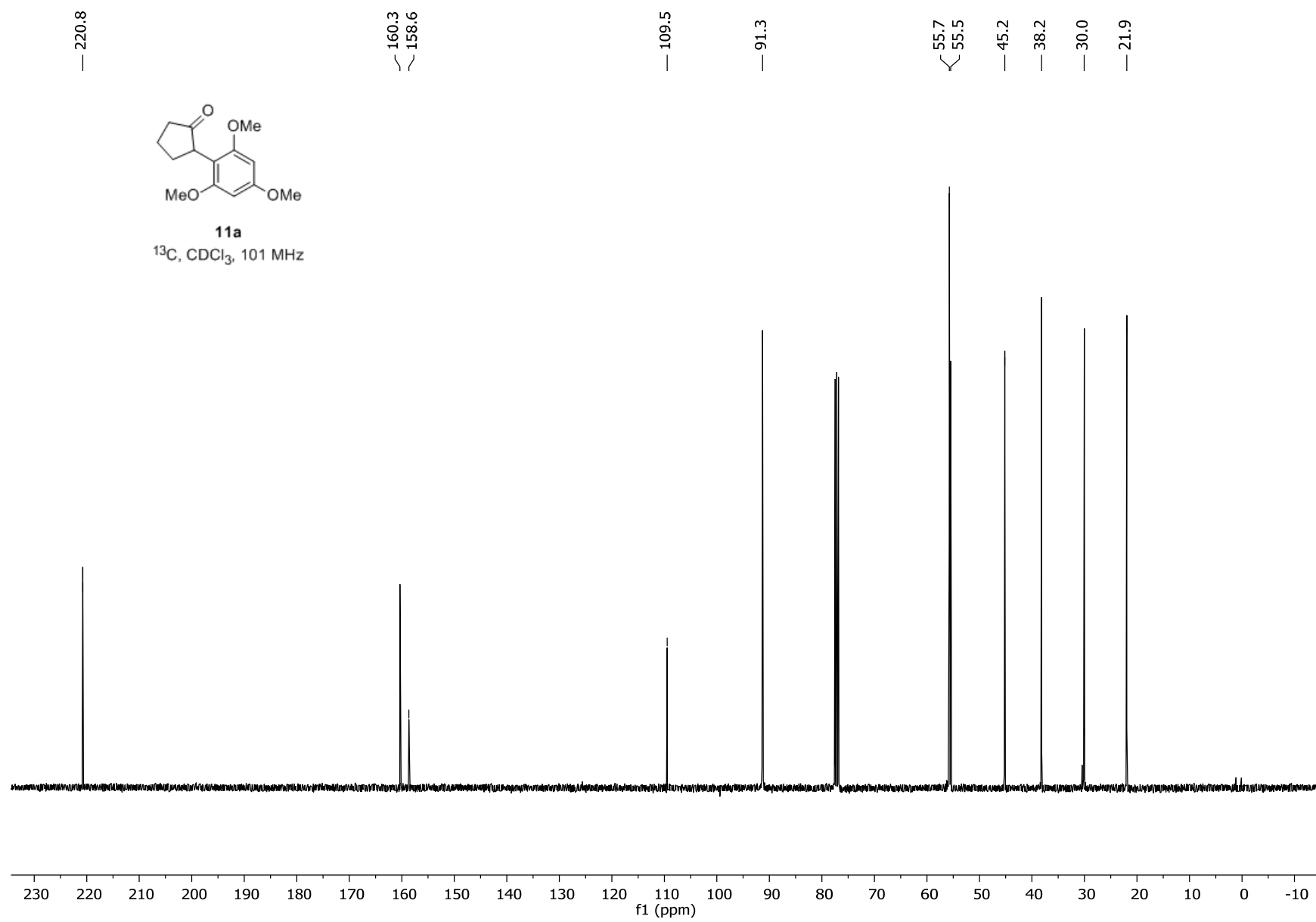


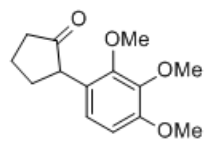




11a
 ^1H , CDCl_3 , 400 MHz

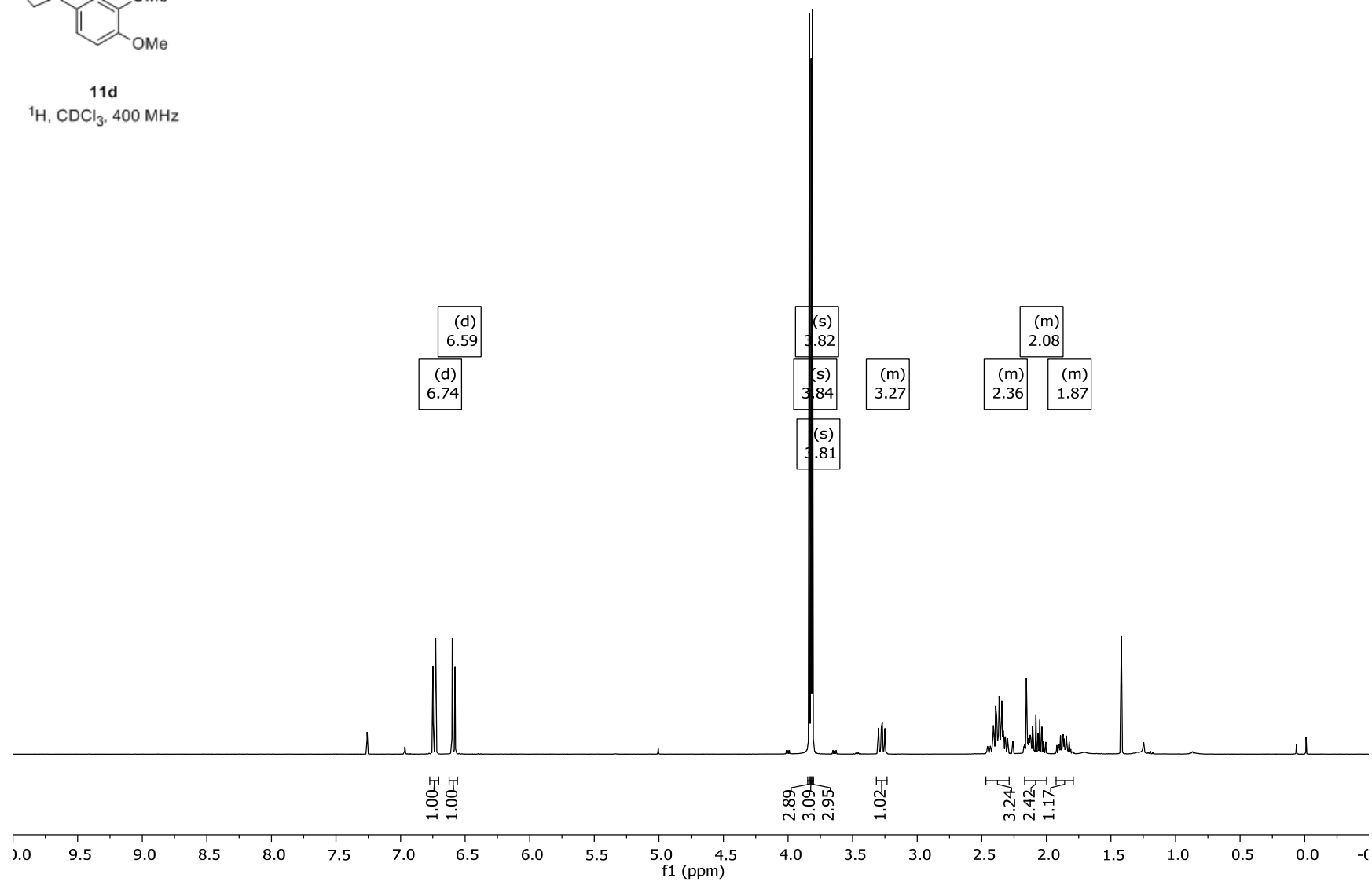


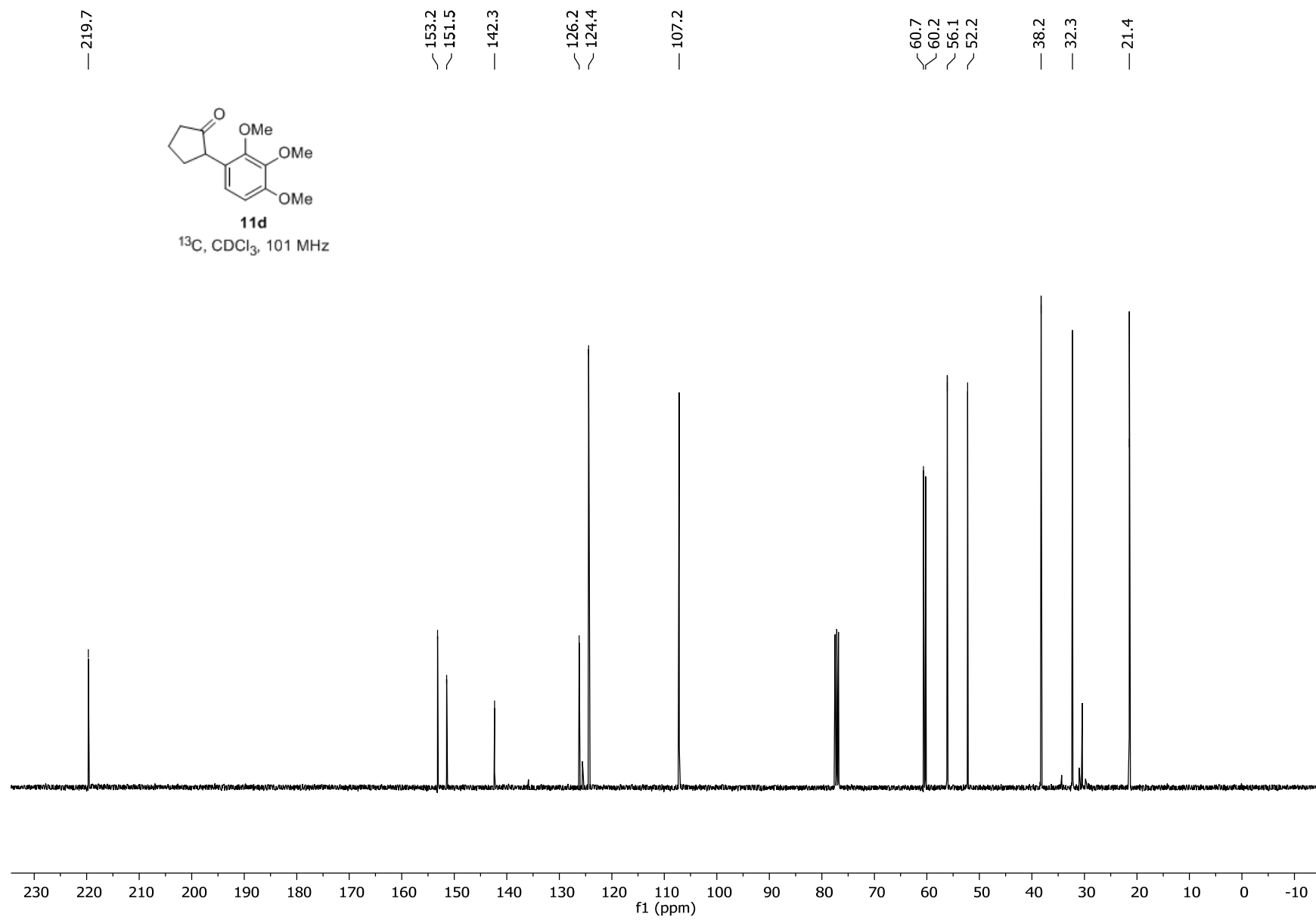


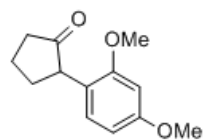


11d

^1H , CDCl_3 , 400 MHz

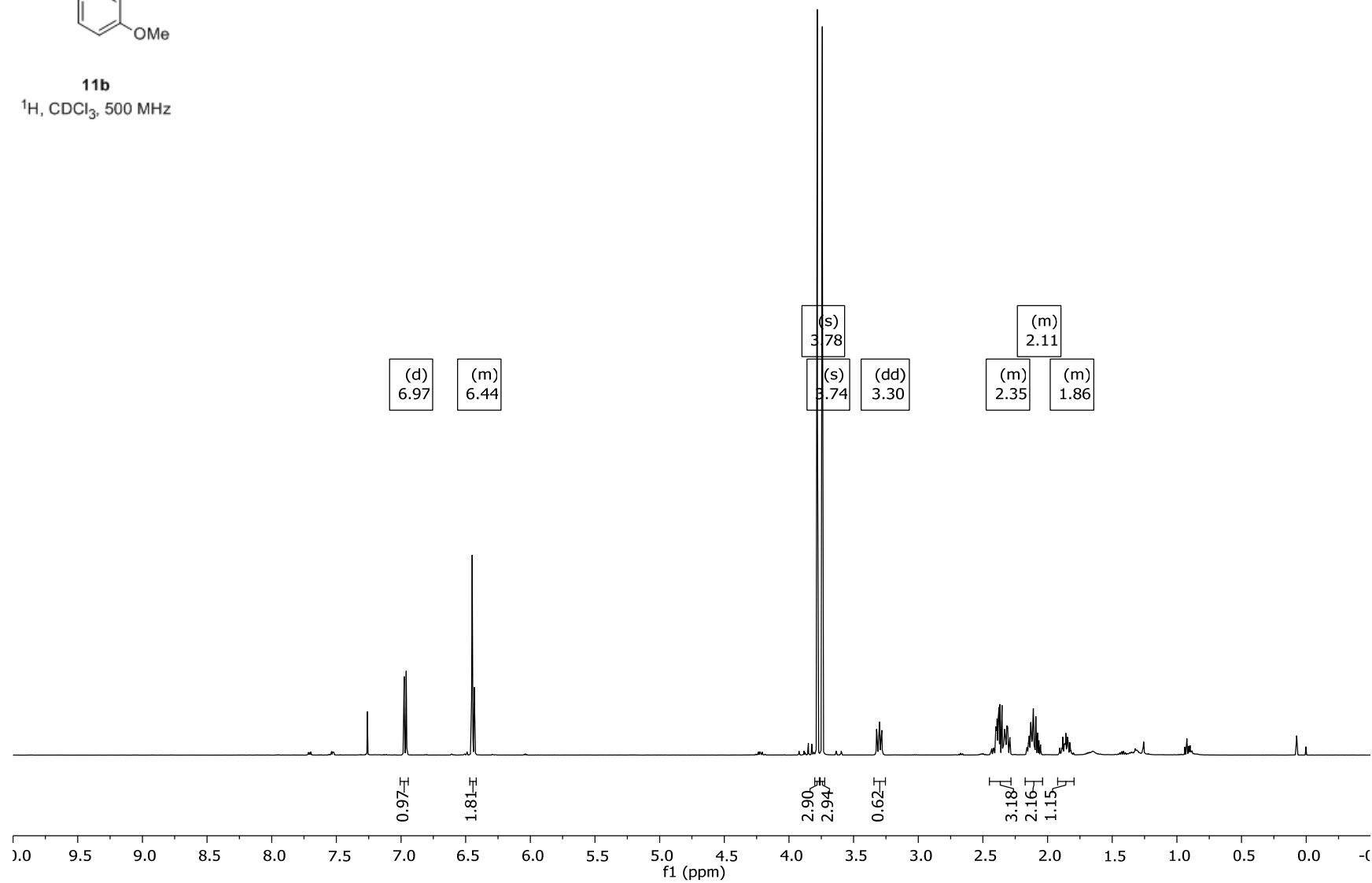


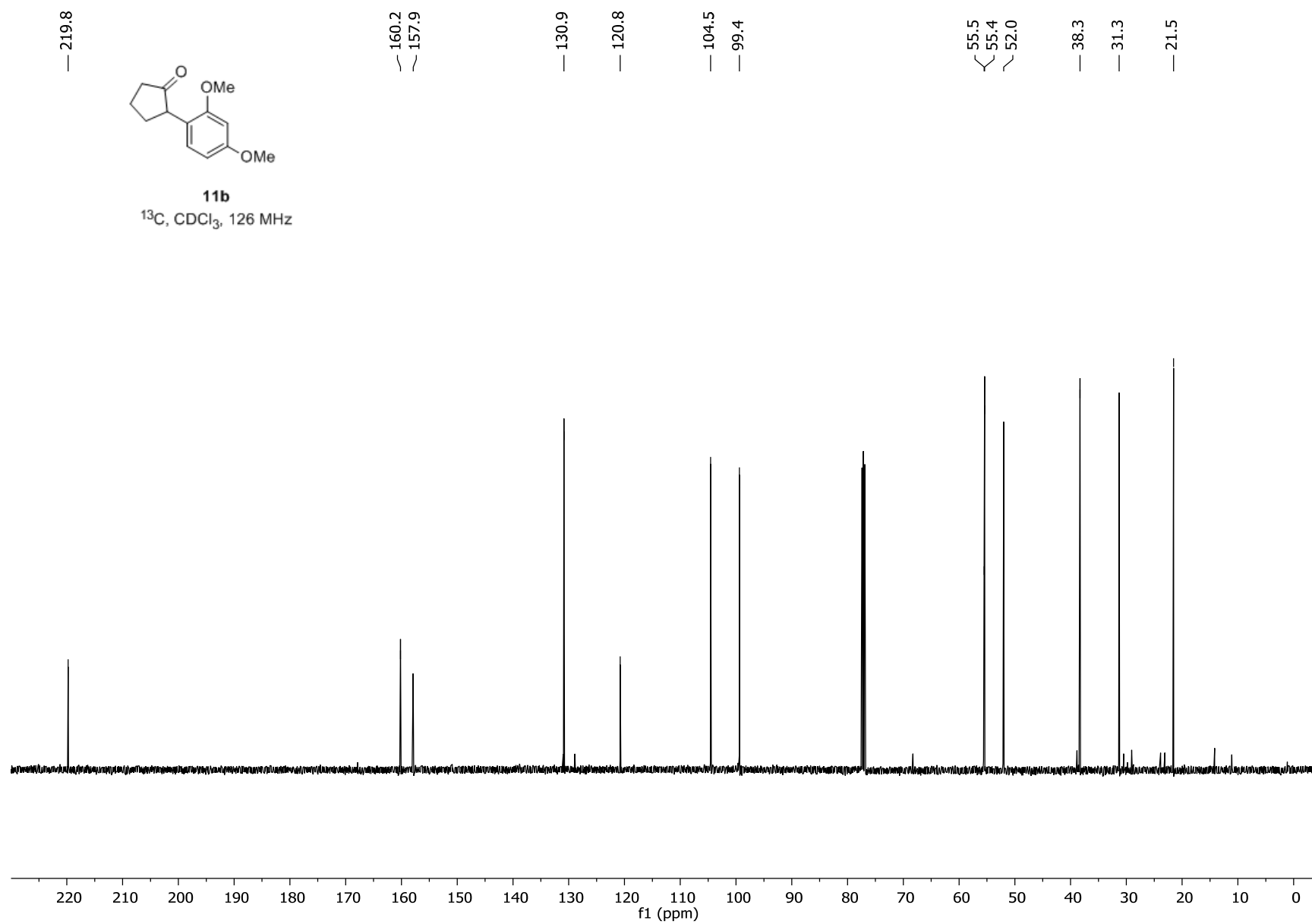


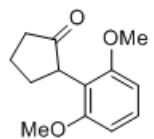


11b

^1H , CDCl_3 , 500 MHz

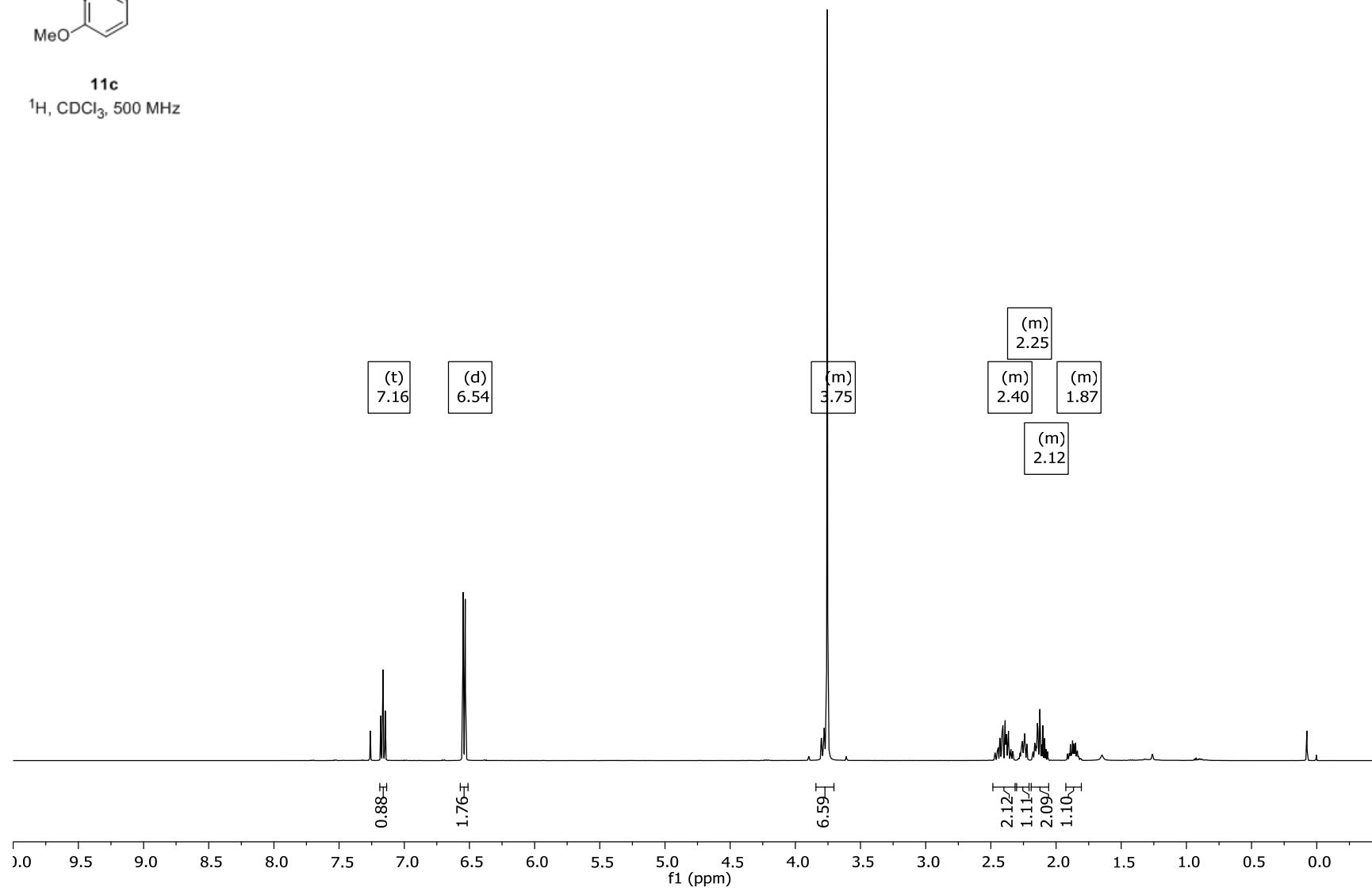


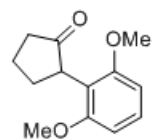




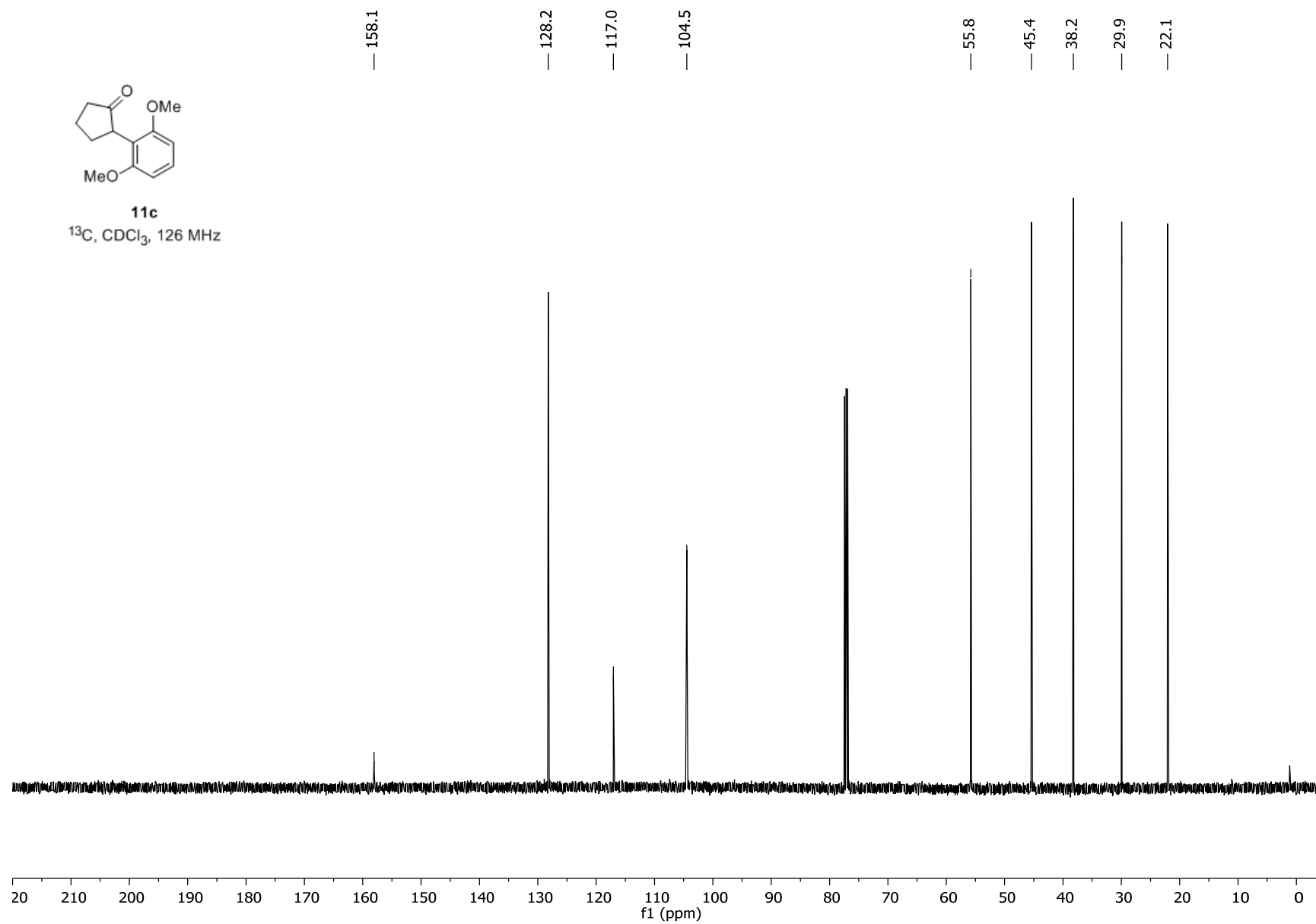
11c

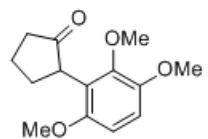
^1H , CDCl_3 , 500 MHz



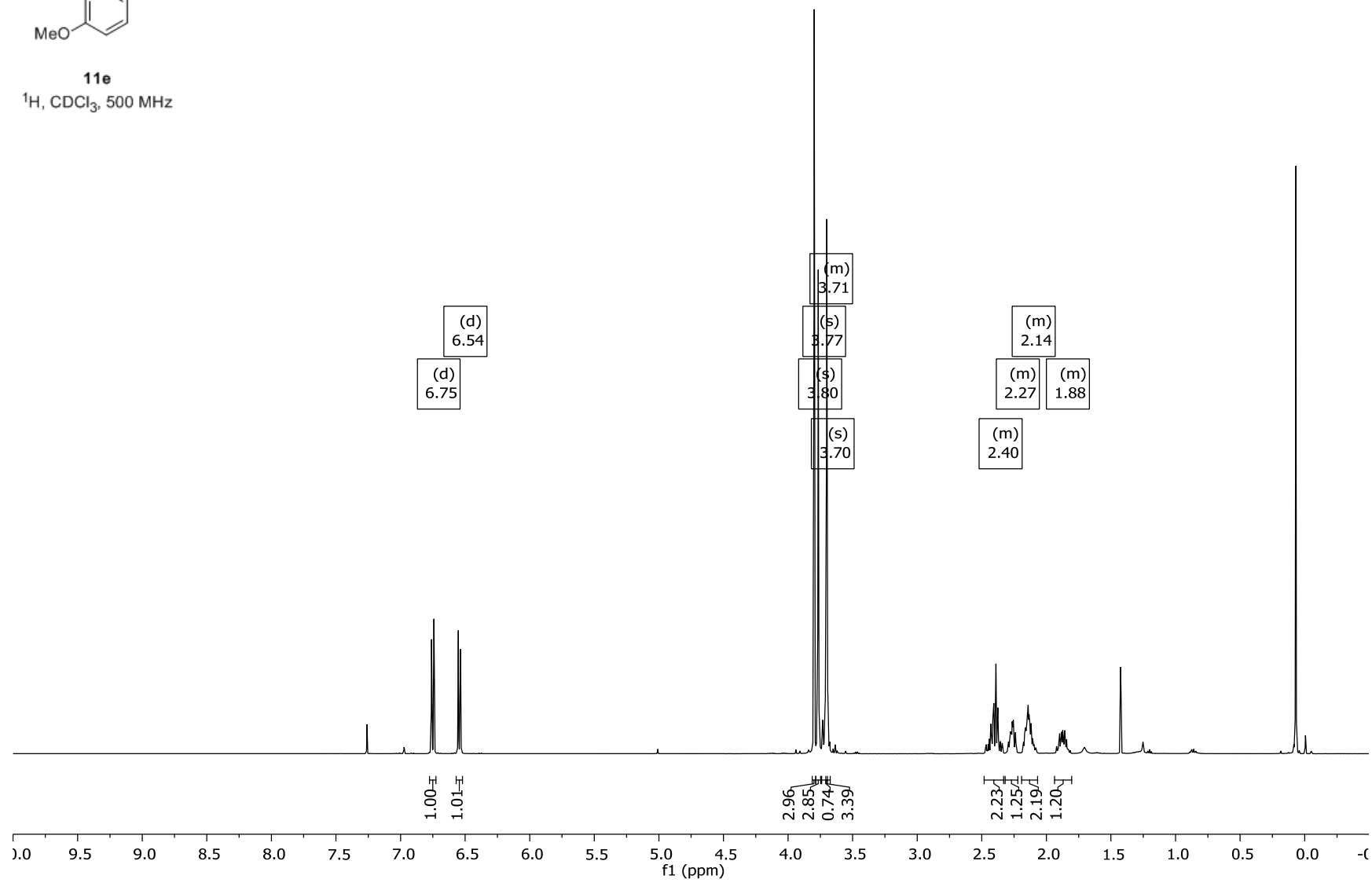


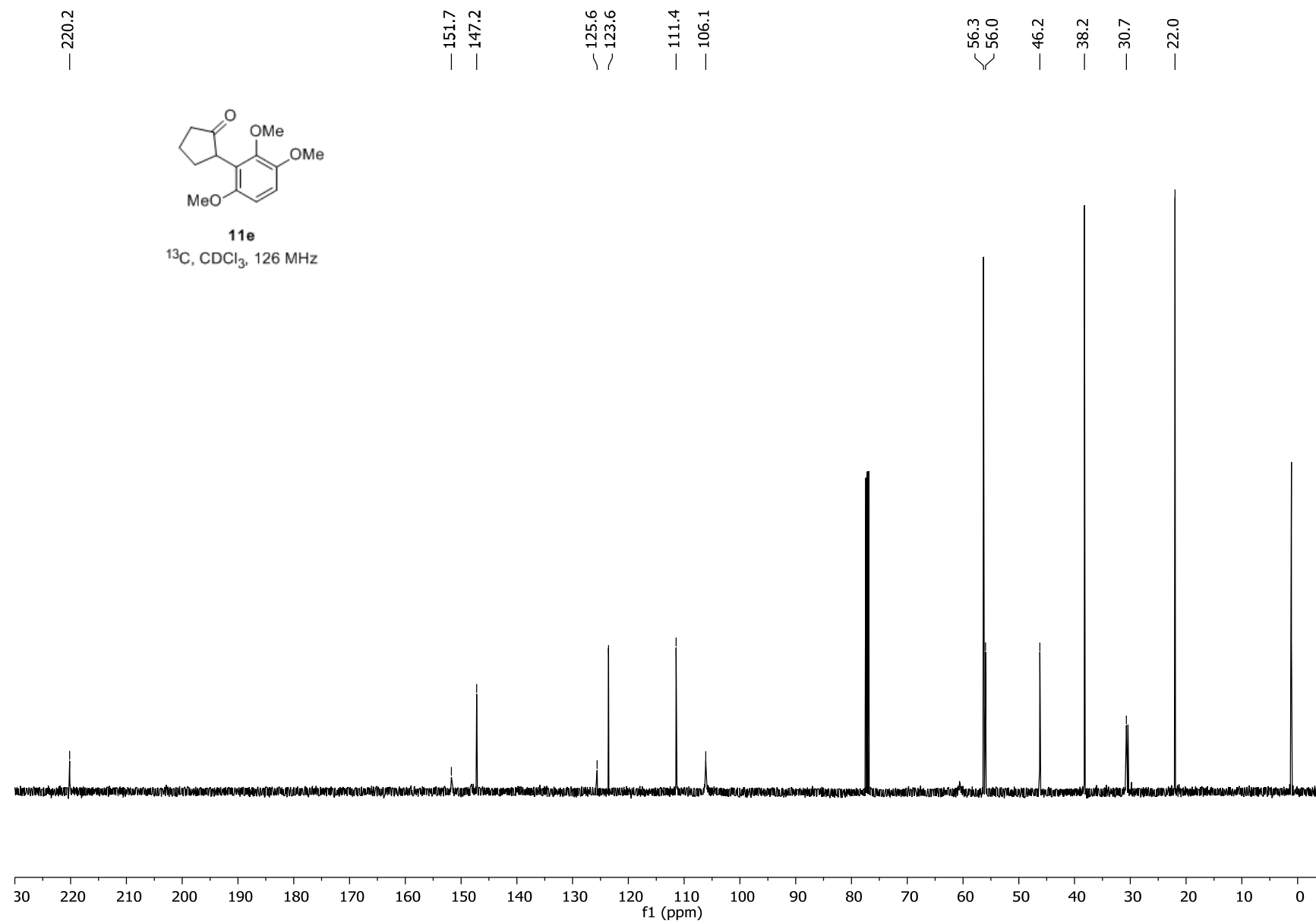
11c
 ^{13}C , CDCl_3 , 126 MHz

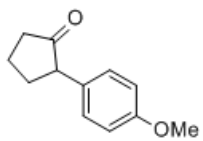




11e
¹H, CDCl₃, 500 MHz

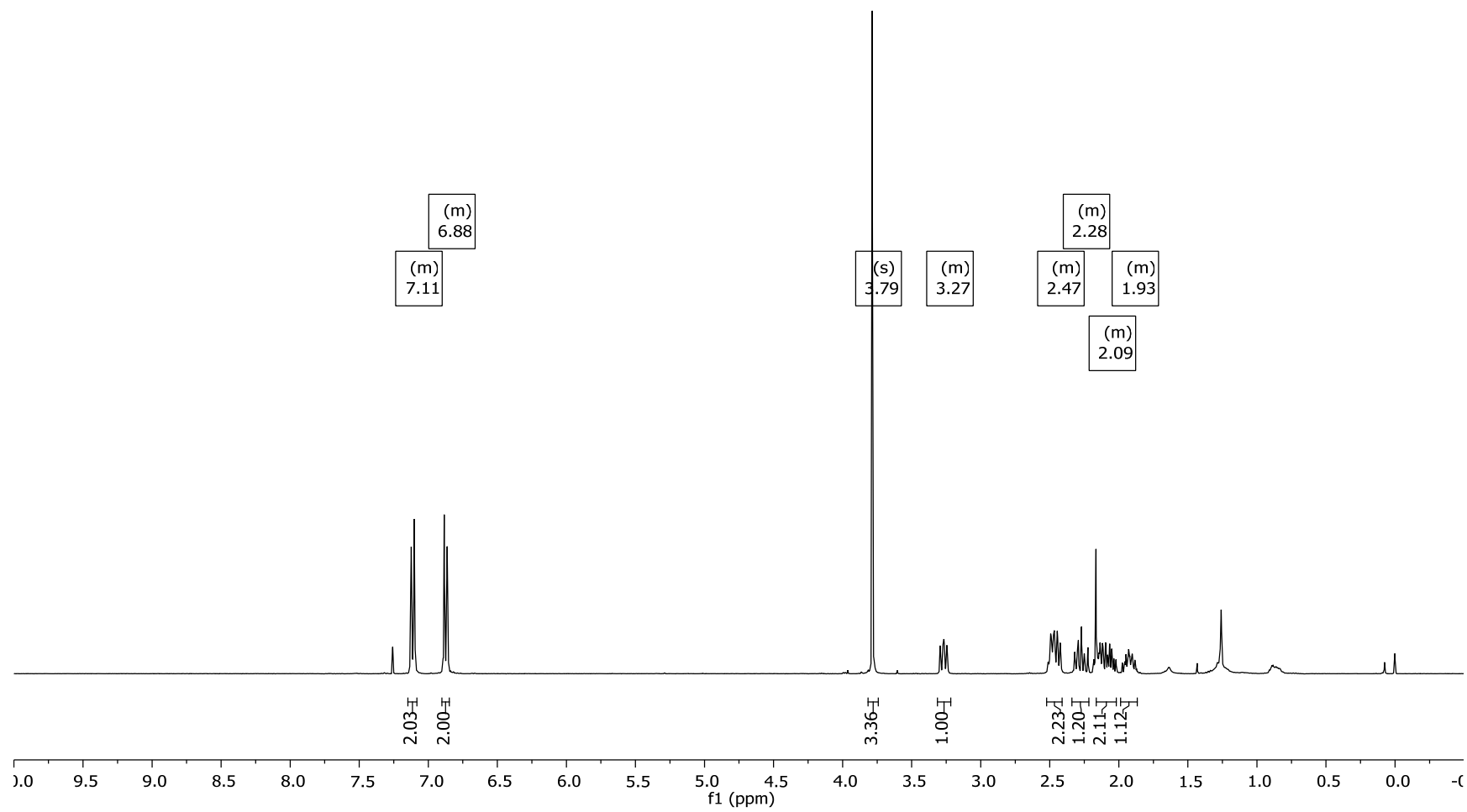


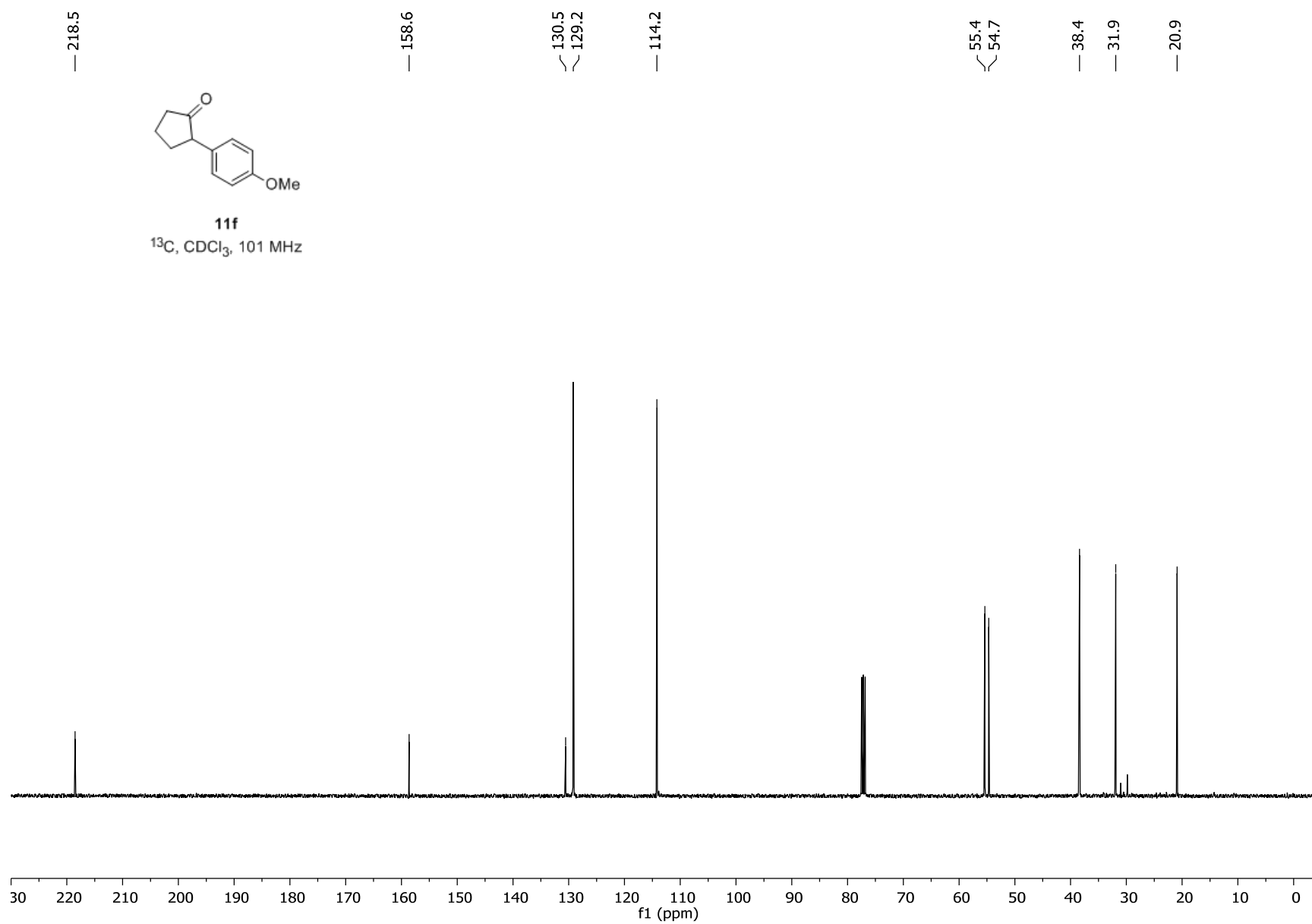


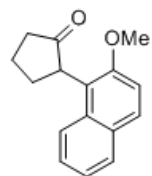


11f

^1H , CDCl_3 , 400 MHz

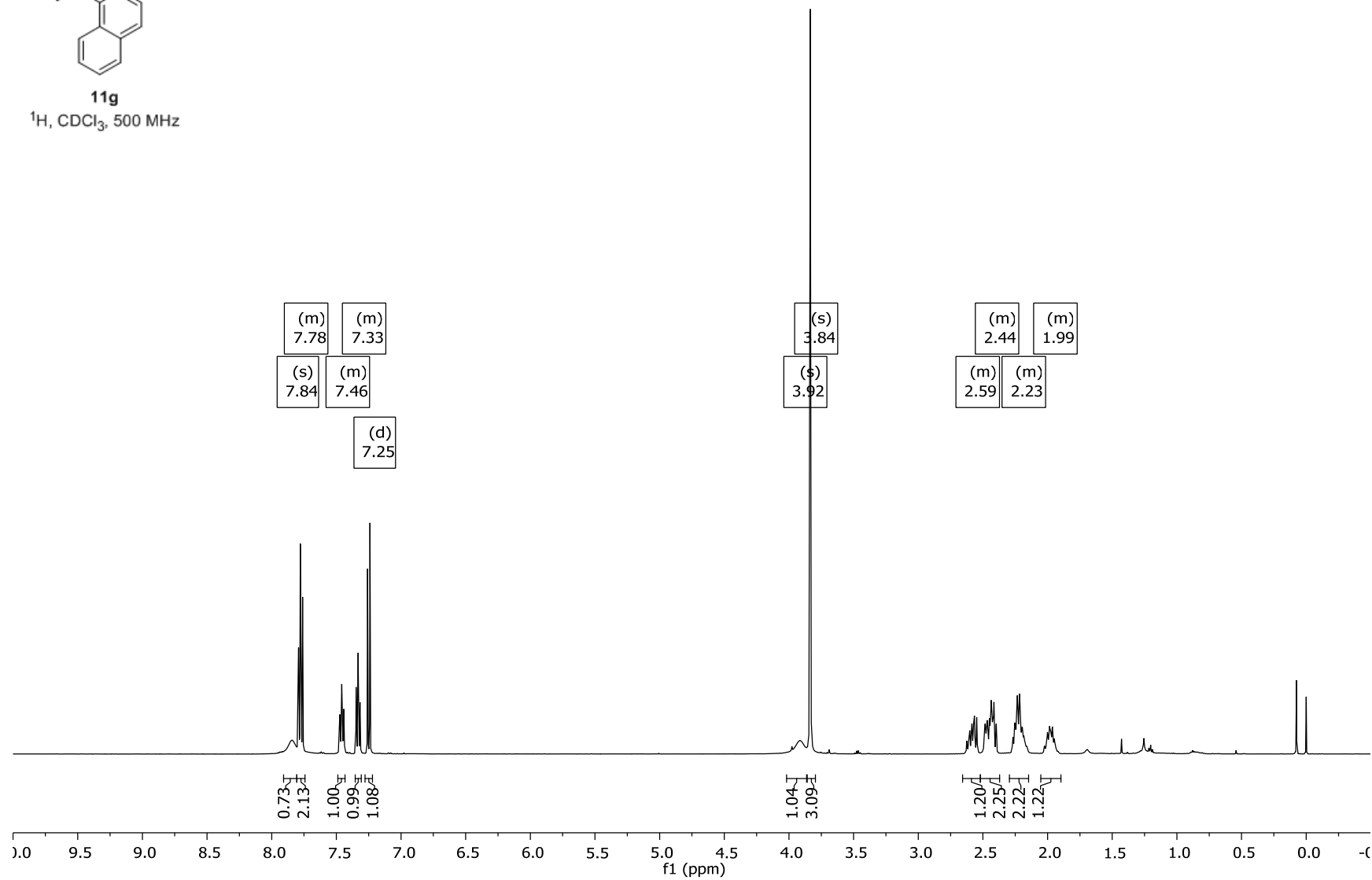


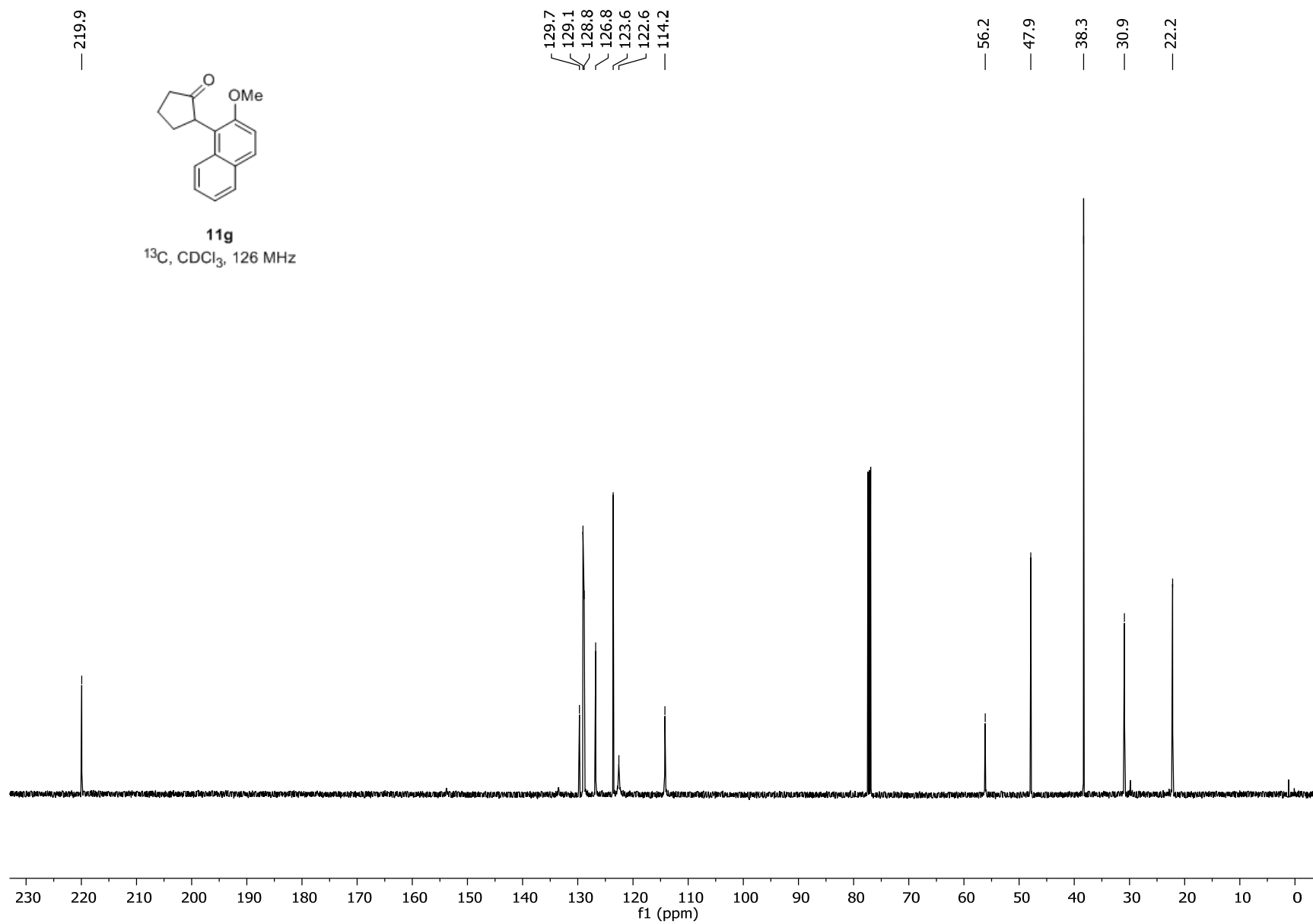


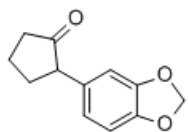


11g

¹H, CDCl₃, 500 MHz

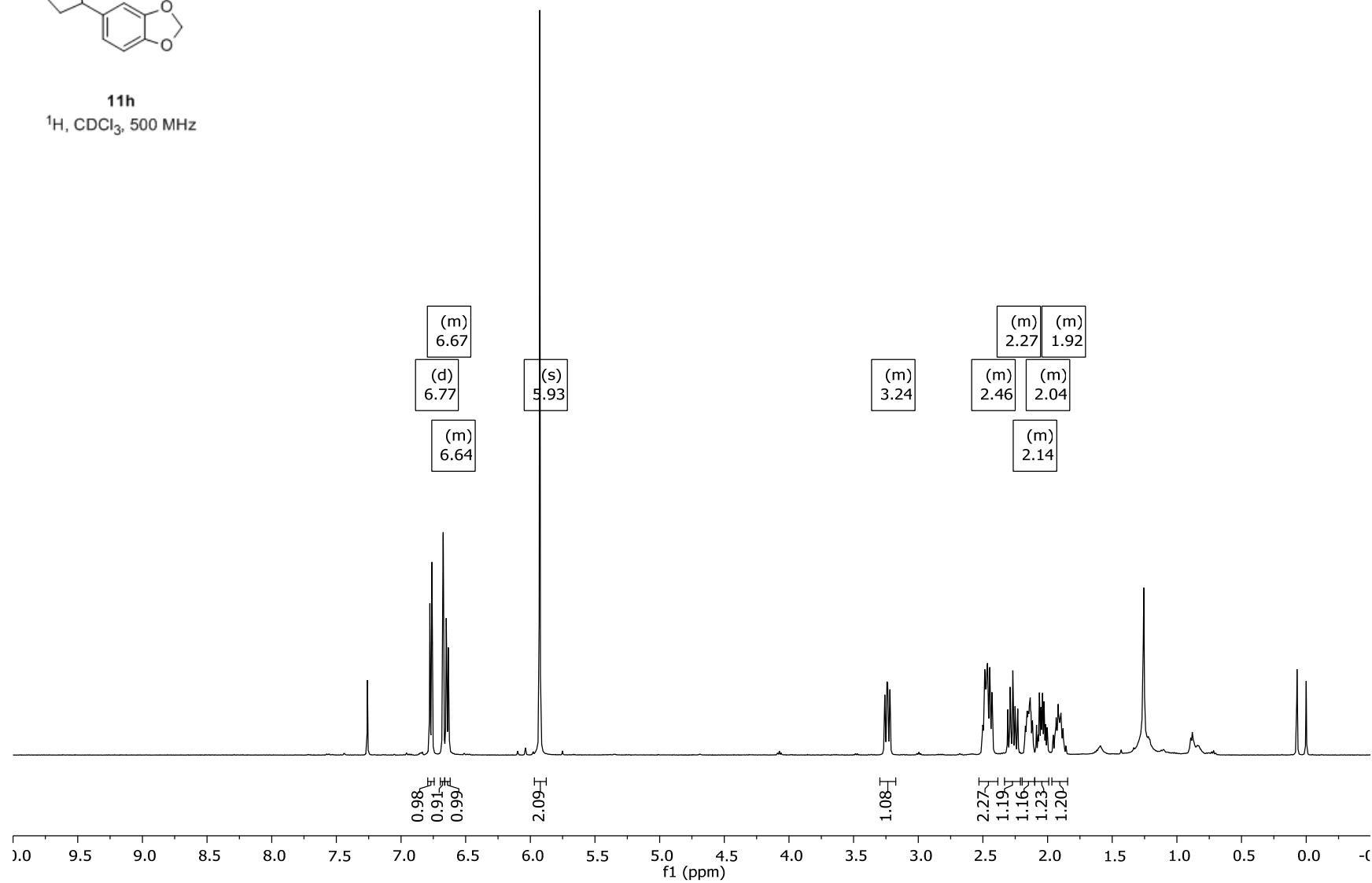




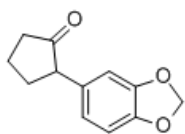


11h

^1H , CDCl_3 , 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

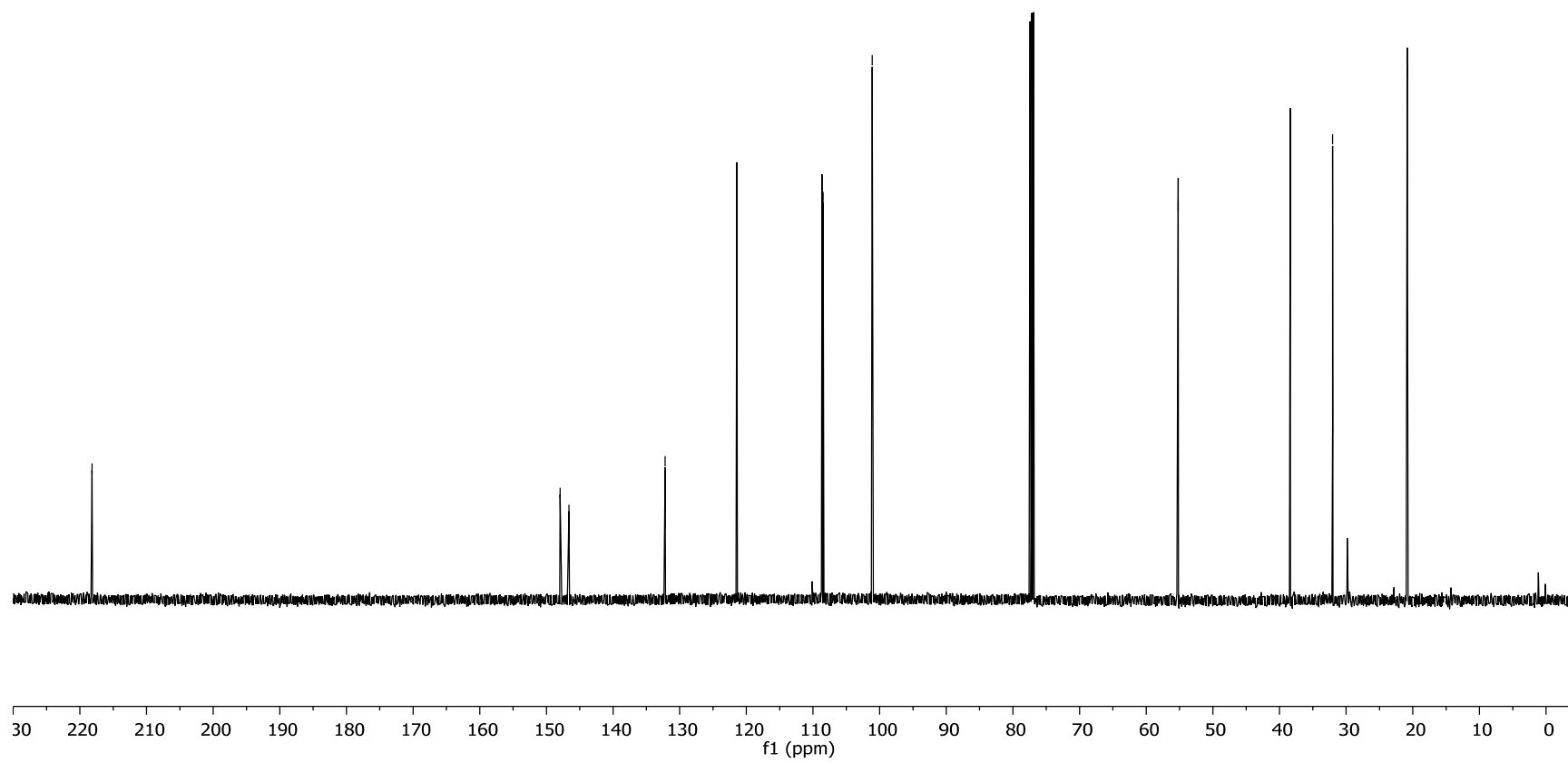
— 101.1

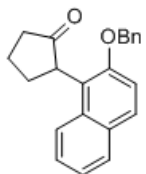
— 55.2

— 38.4

— 32.0

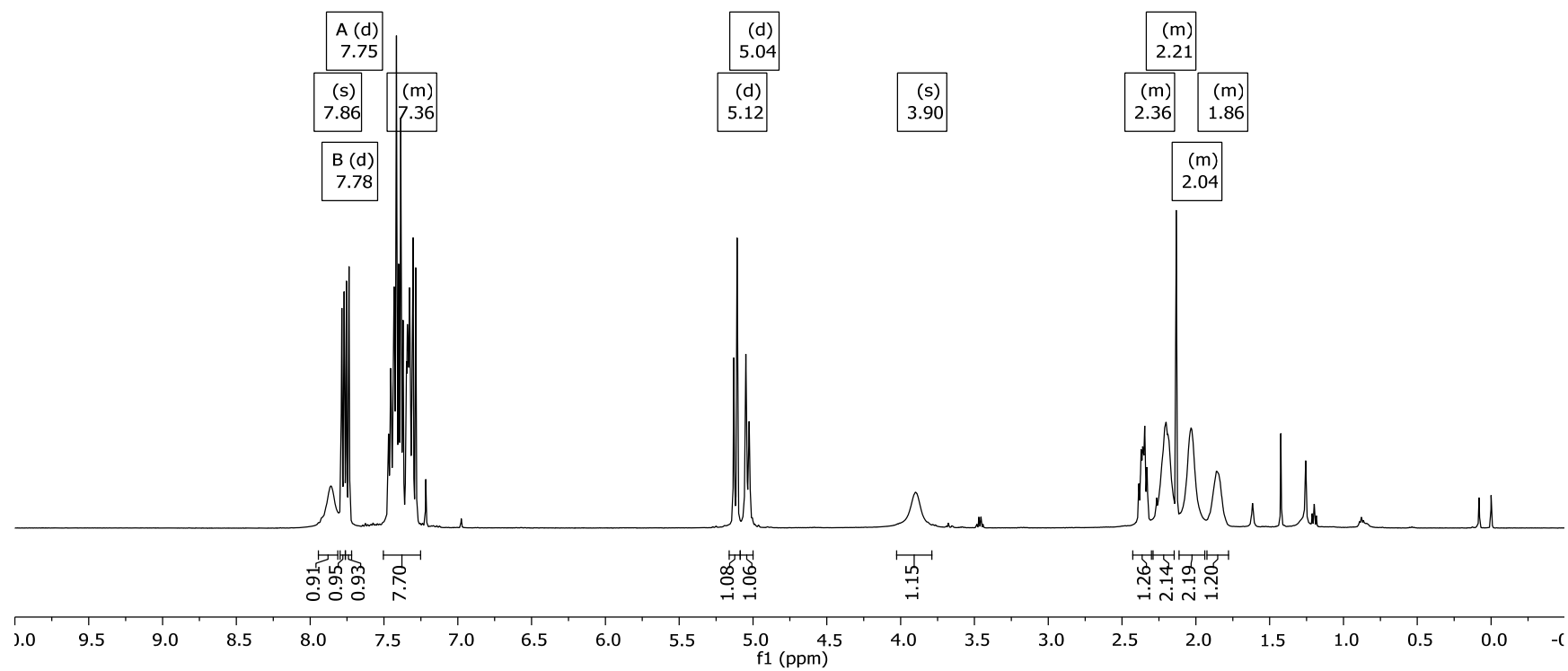
— 20.8

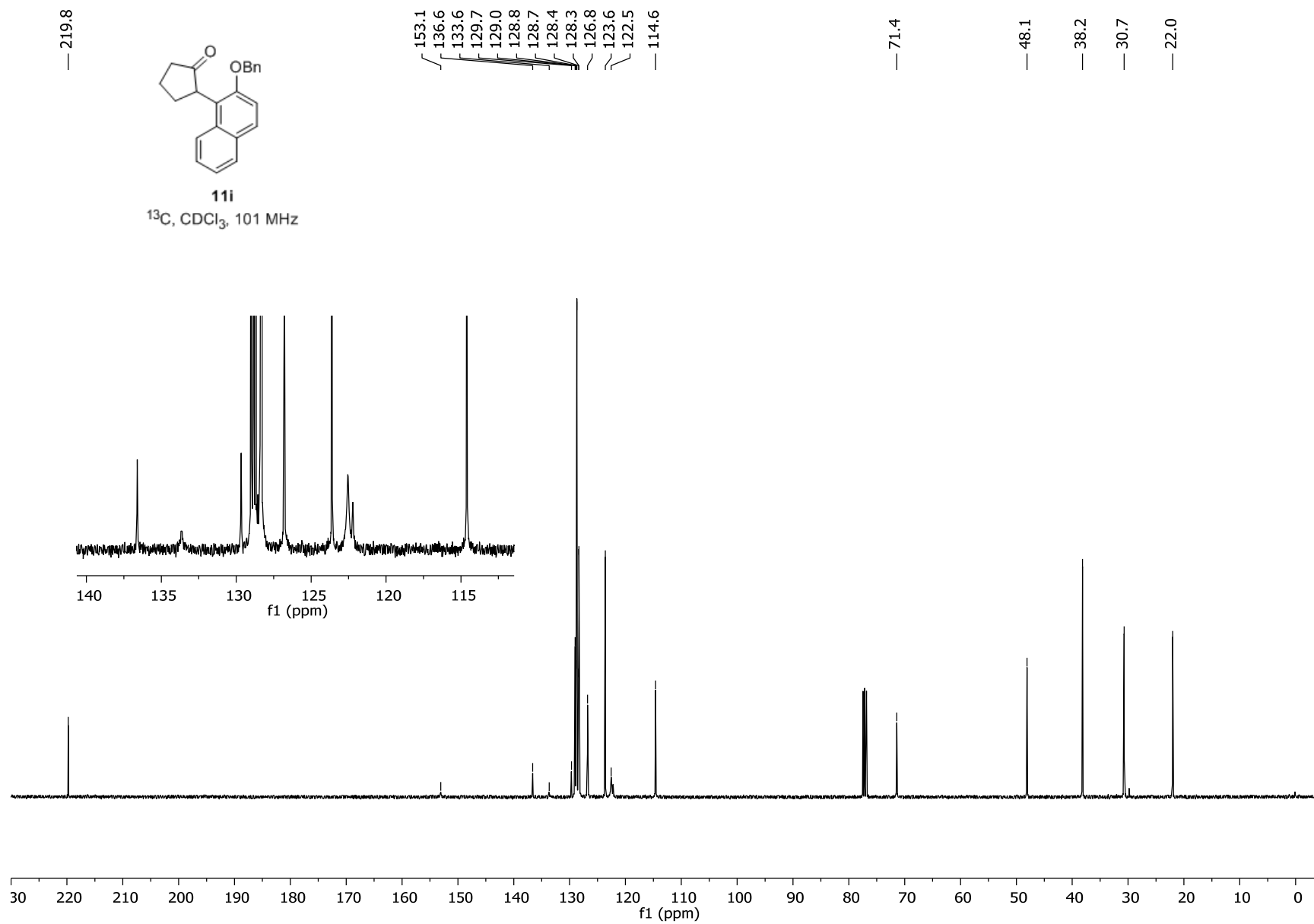


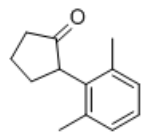


11i

^1H , CDCl_3 , 500 MHz

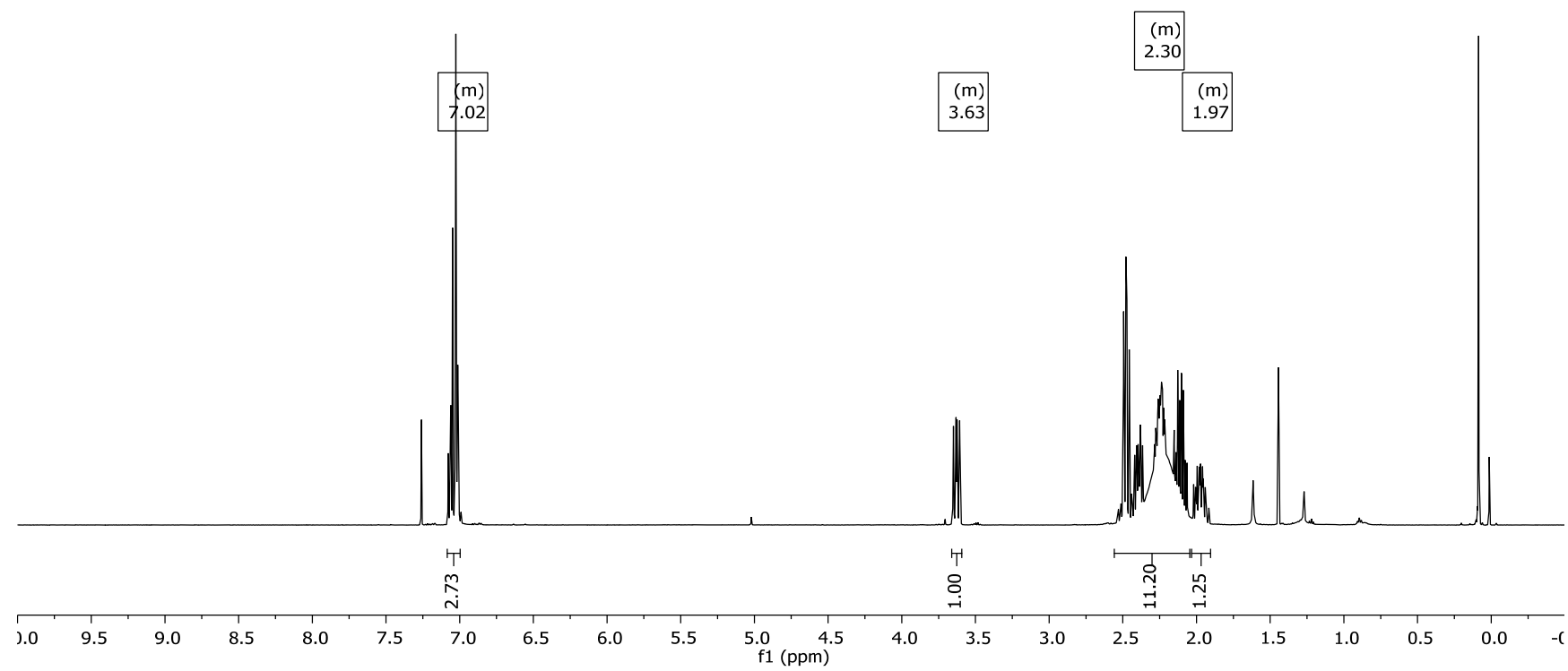


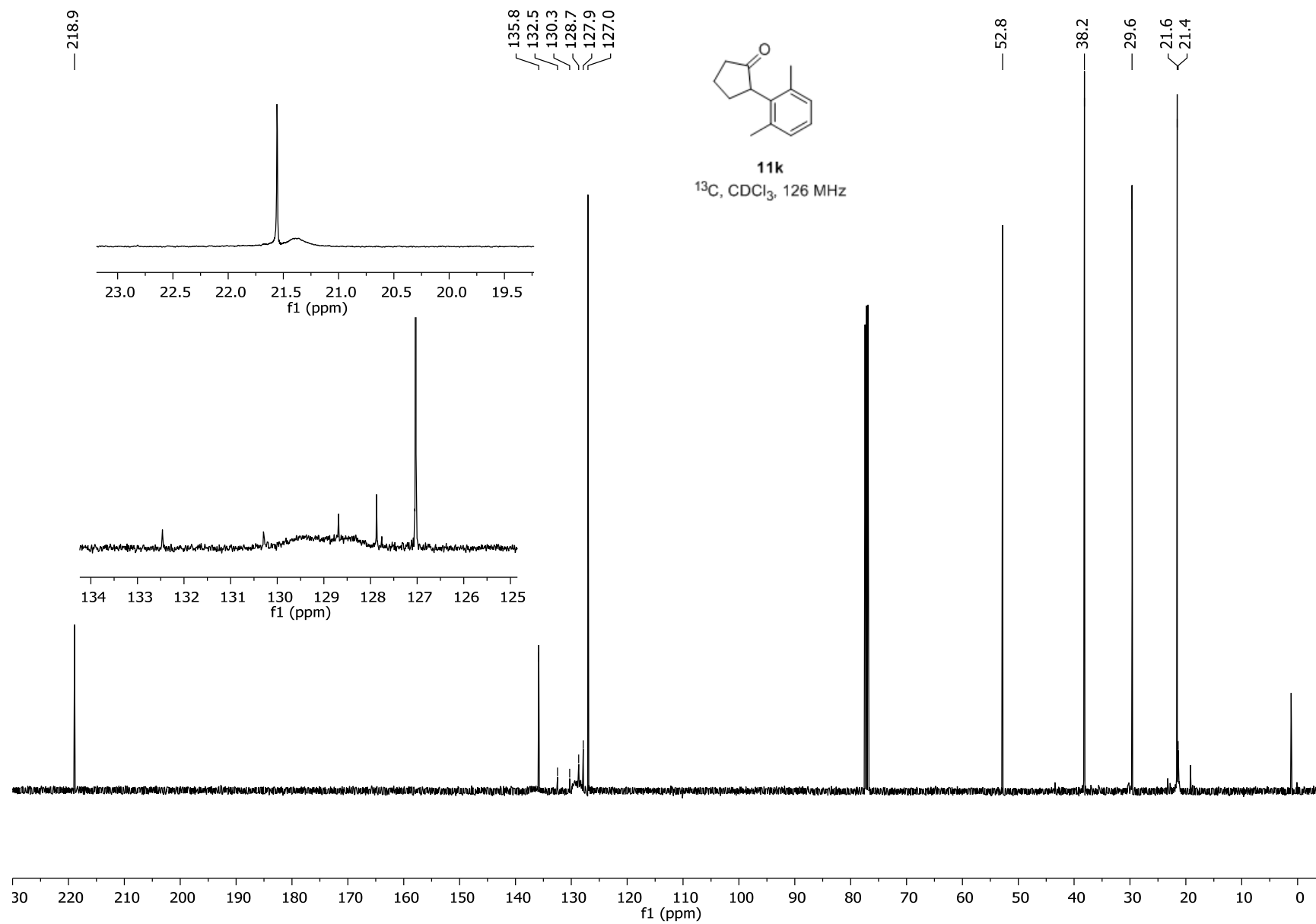


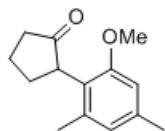


11k

^1H , CDCl_3 , 500 MHz

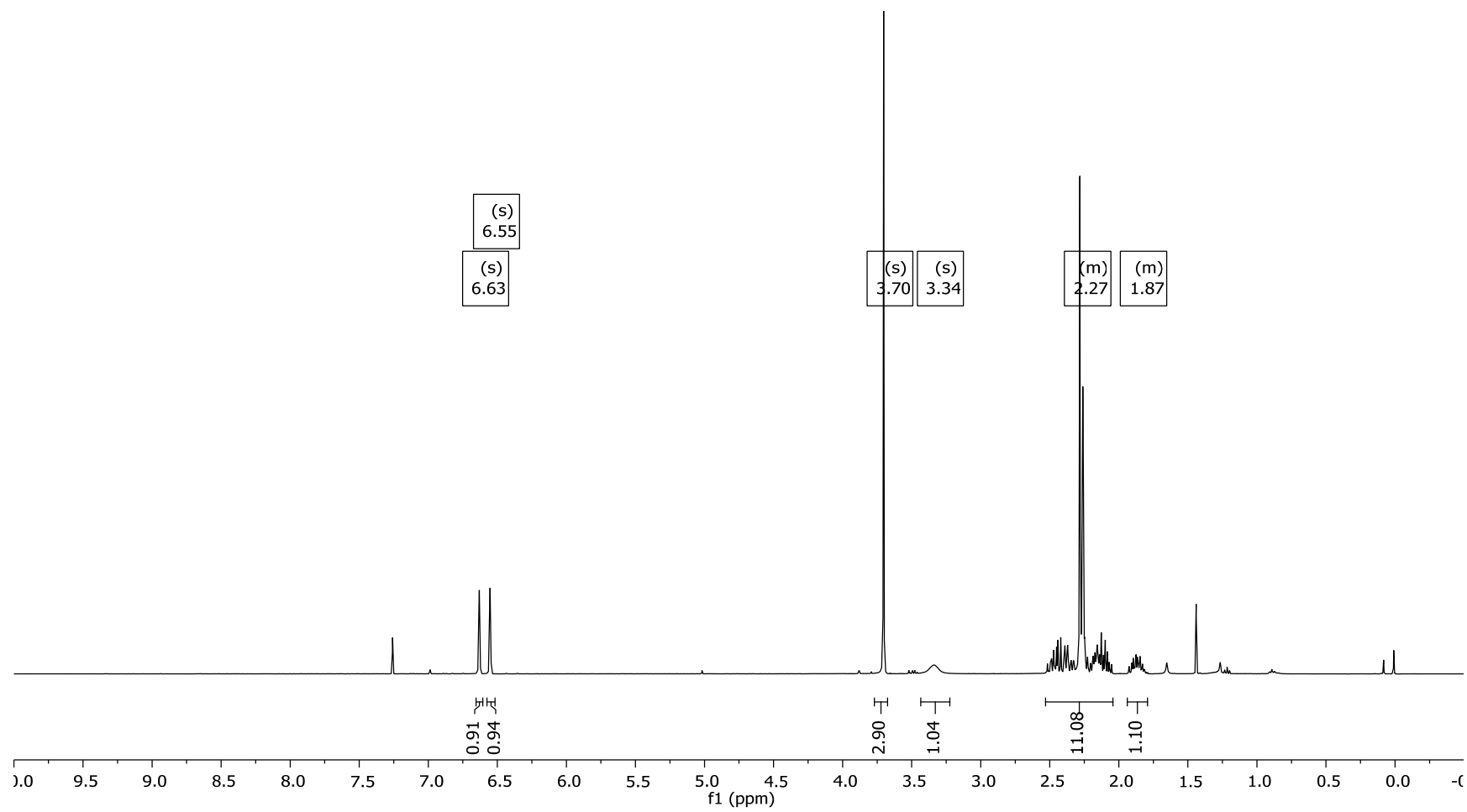


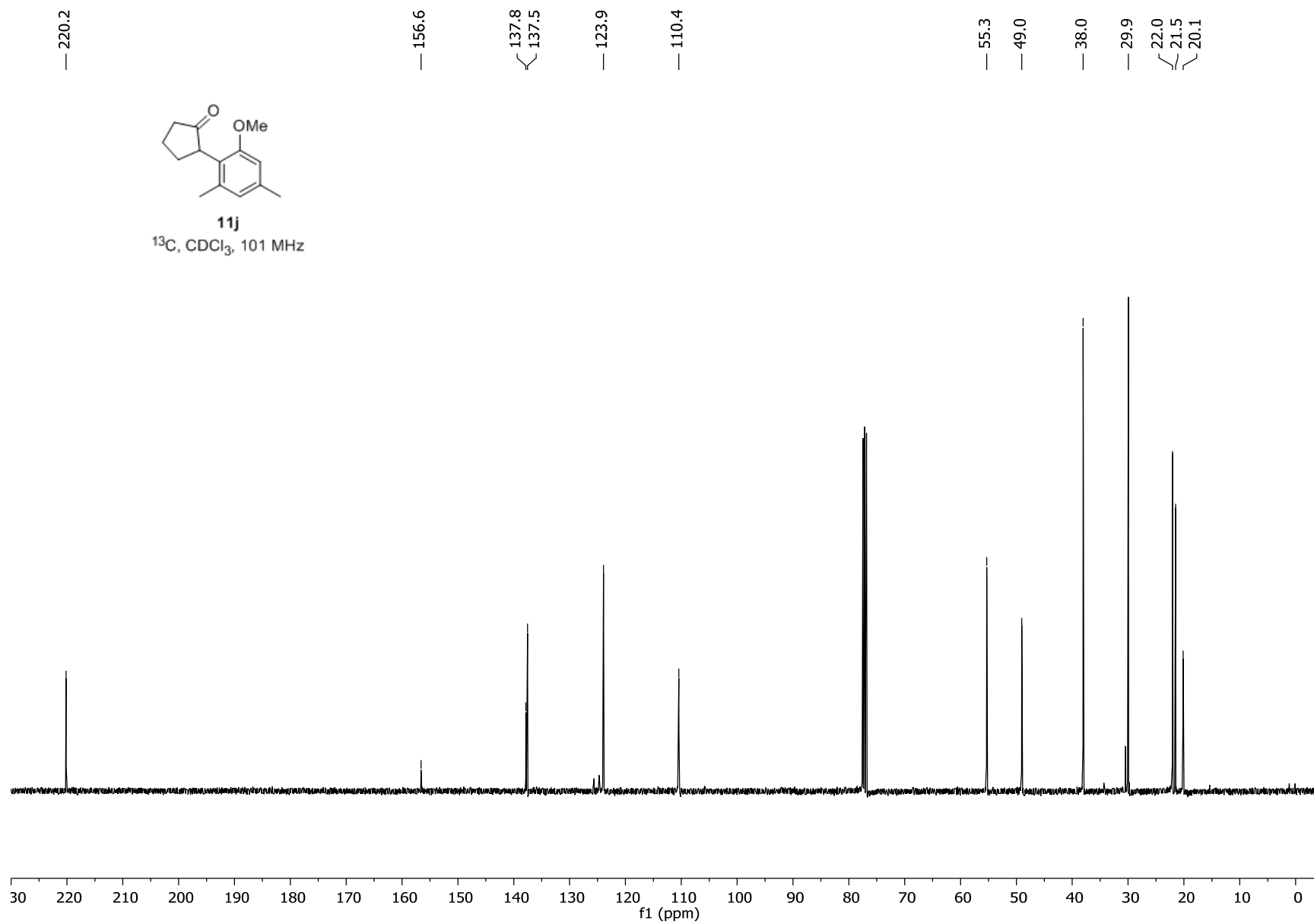


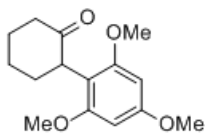


11j

^1H , CDCl_3 , 400 MHz

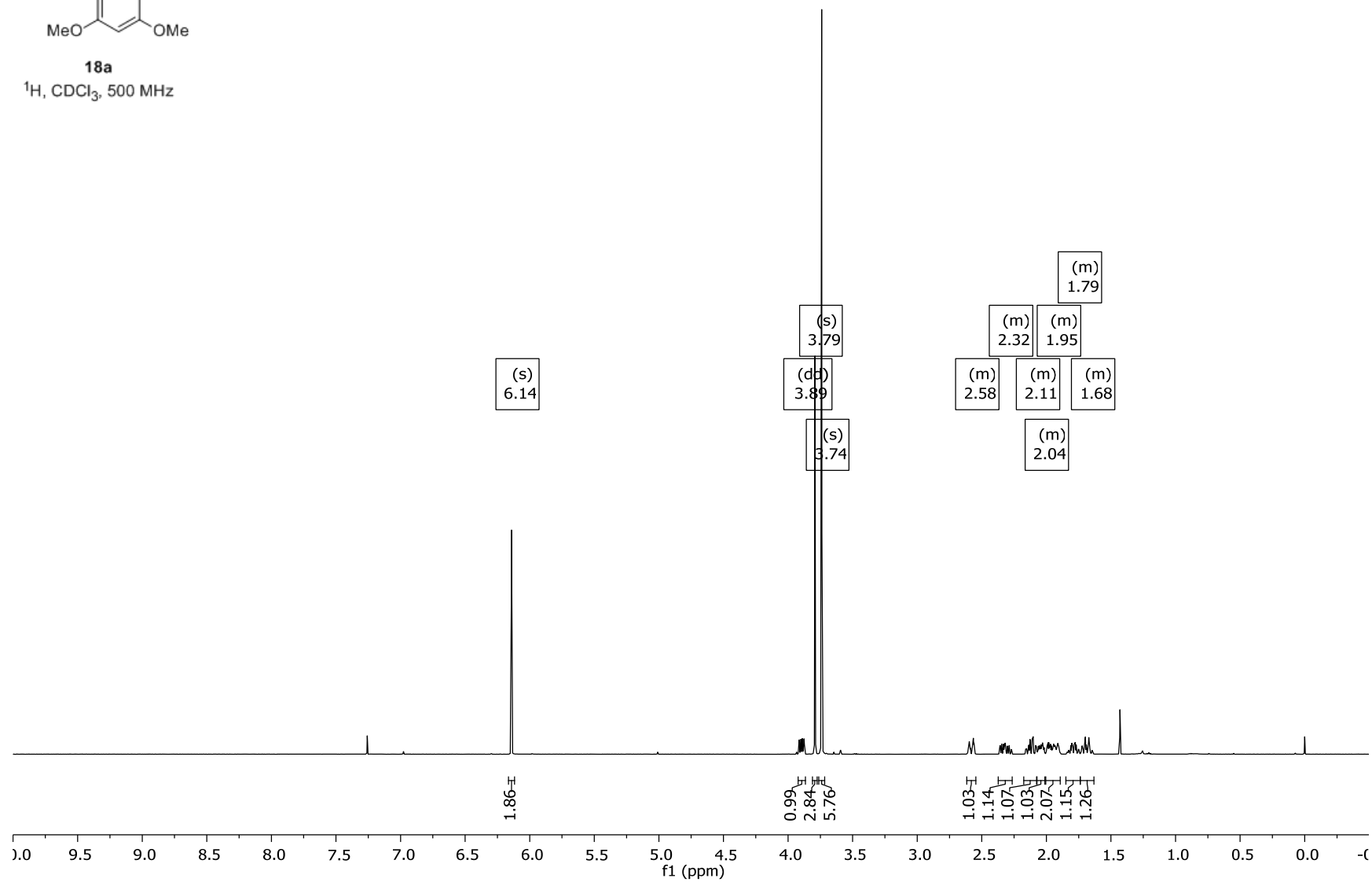


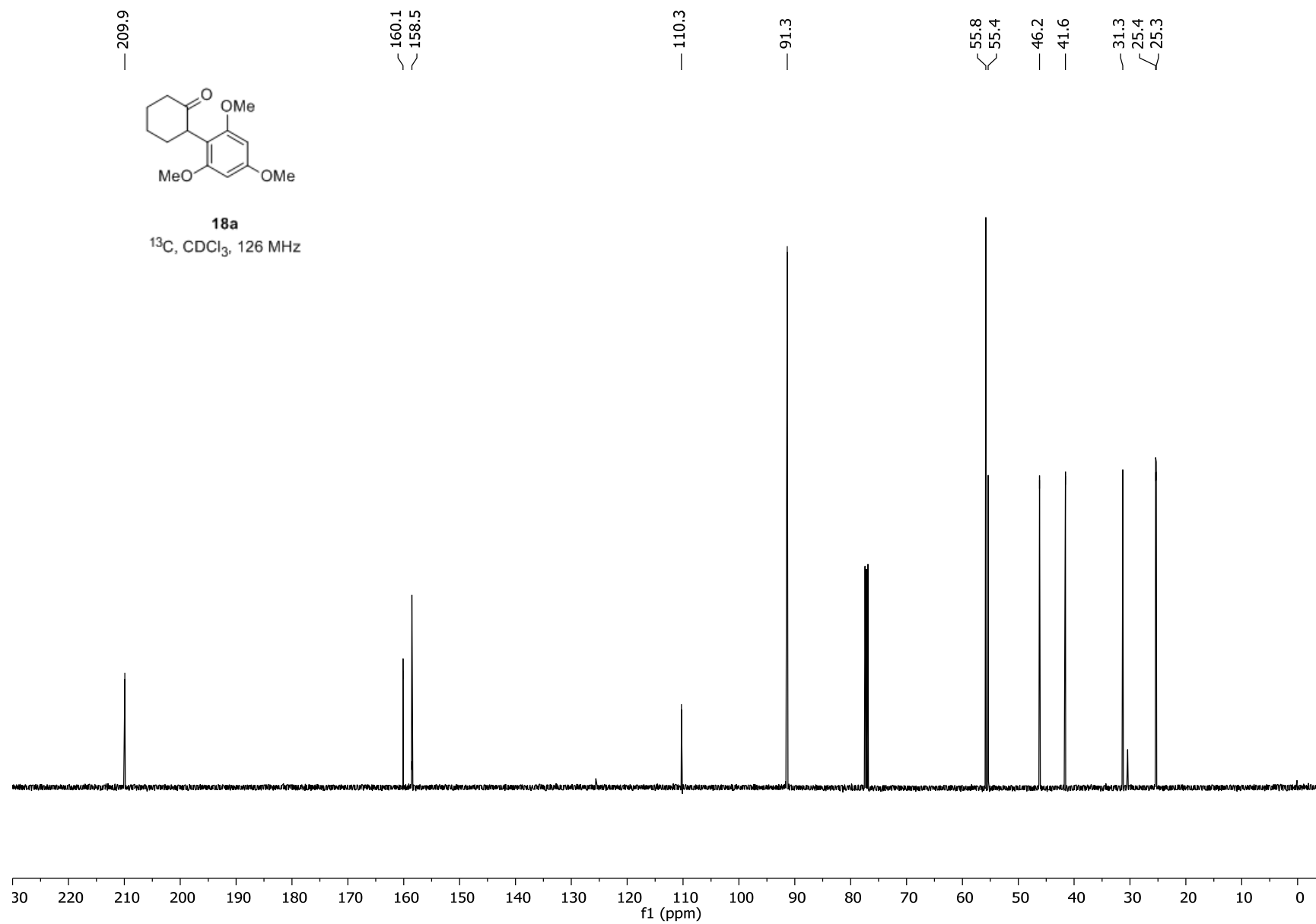


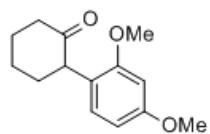


18a

^1H , CDCl_3 , 500 MHz

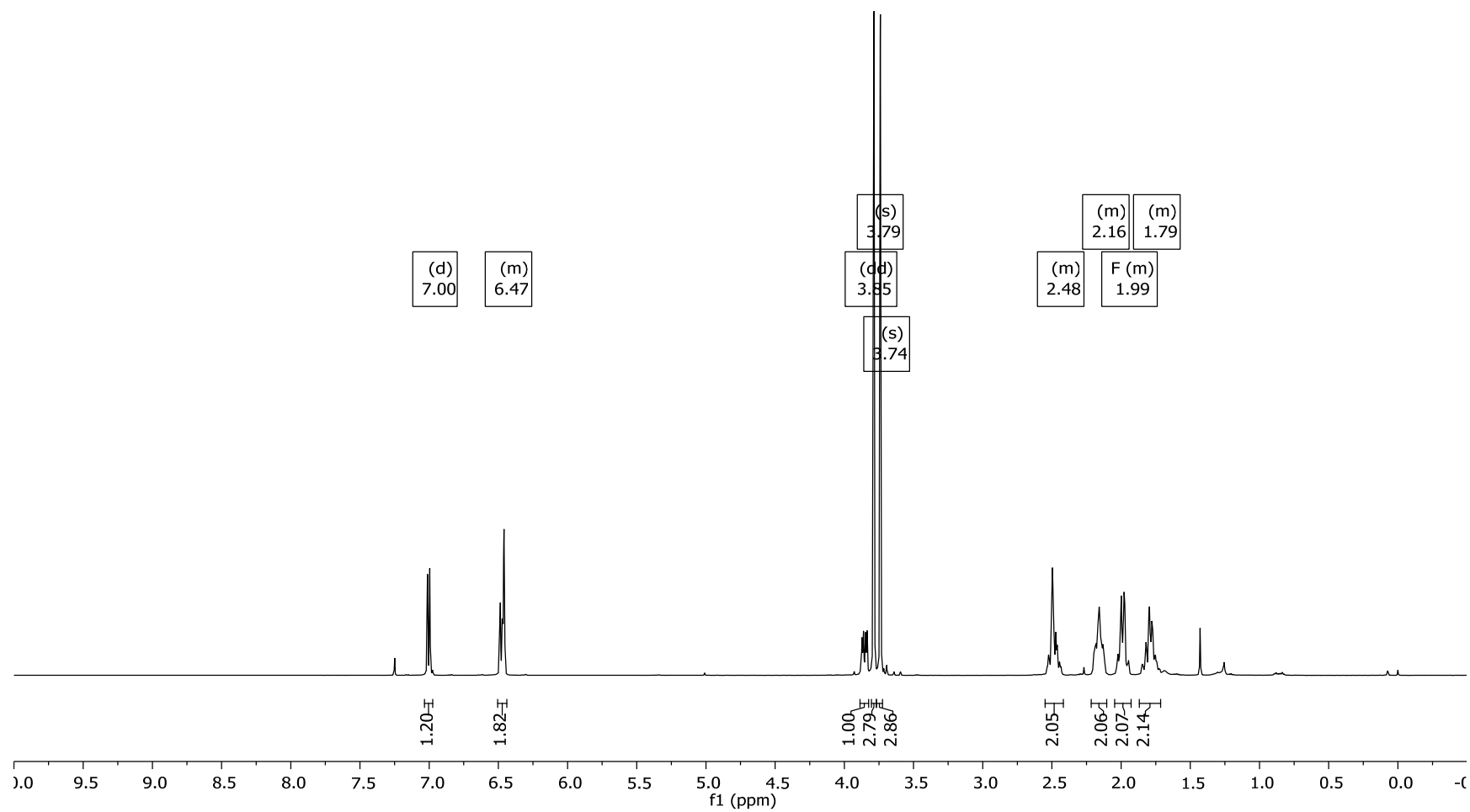


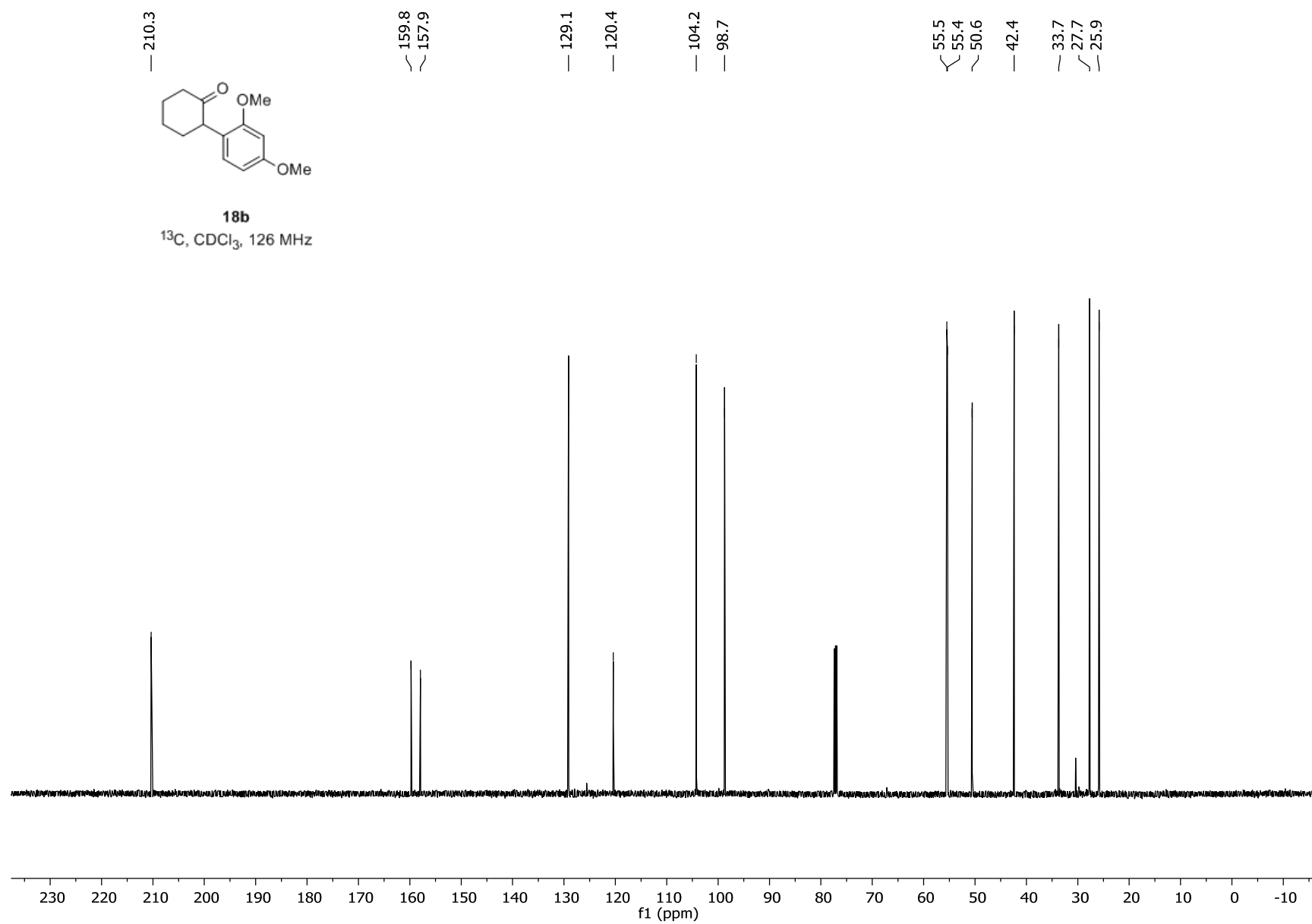


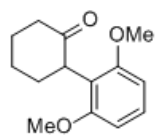


18b

^1H , CDCl_3 , 500 MHz

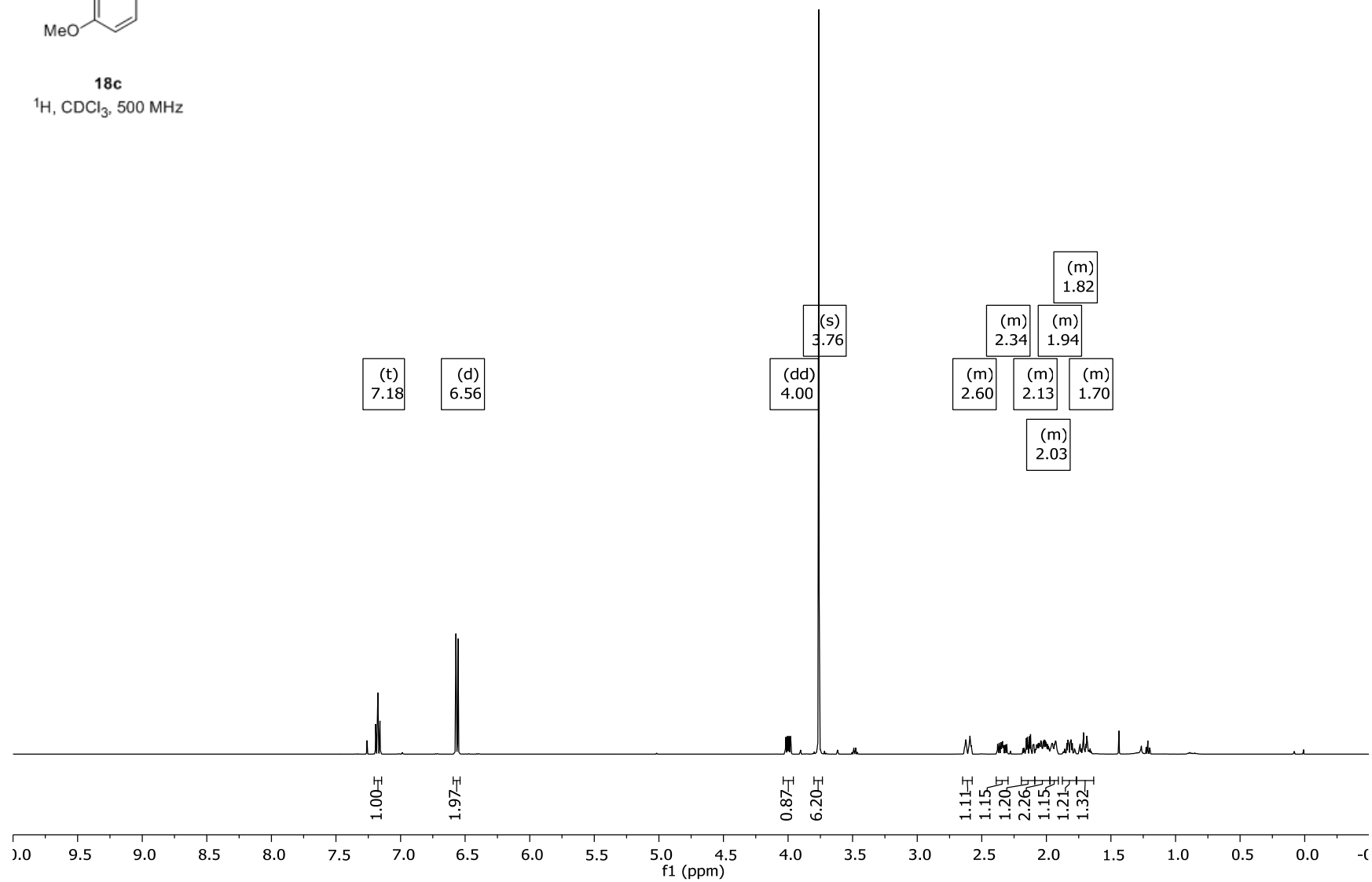


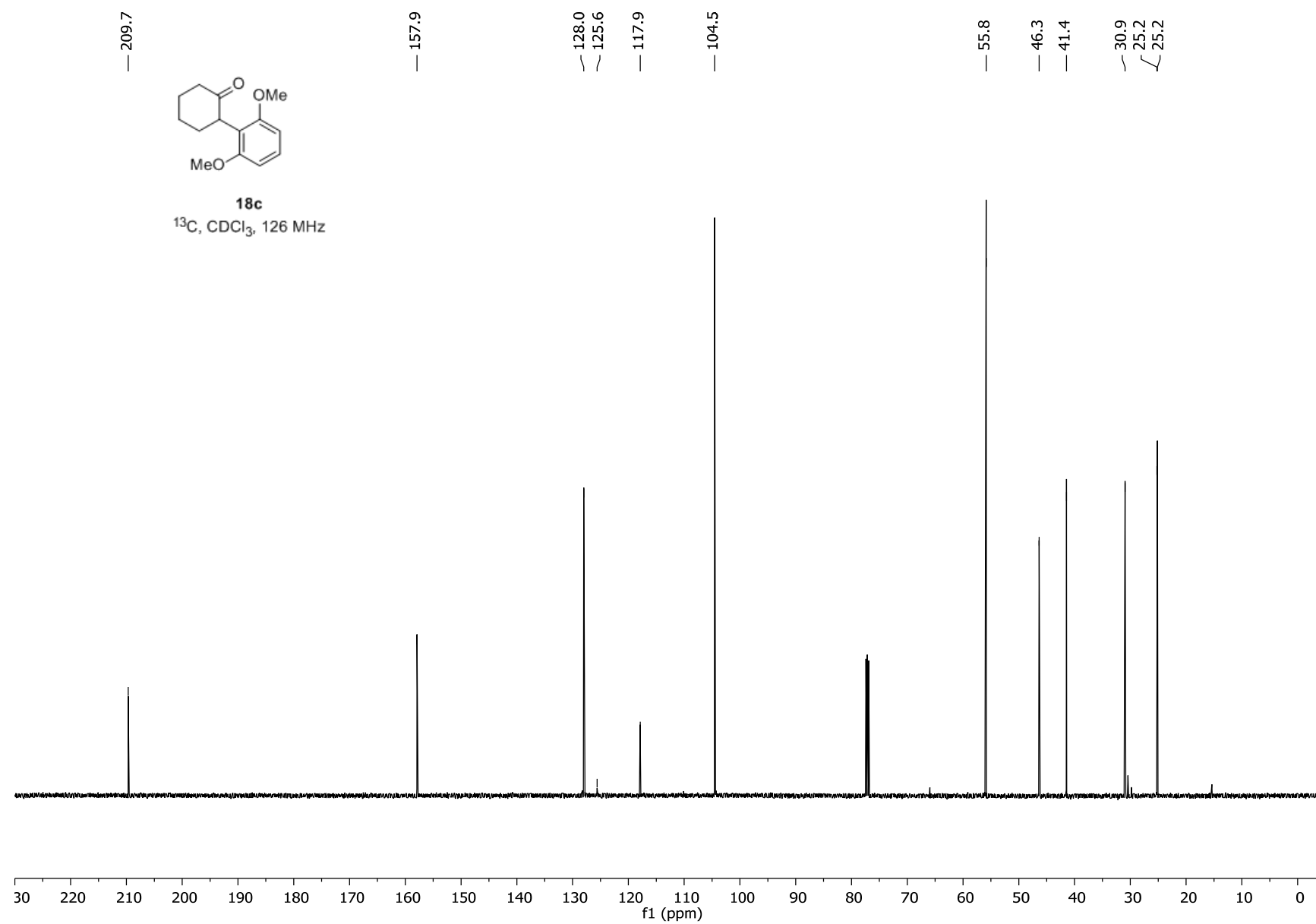


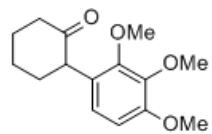


18c

¹H, CDCl₃, 500 MHz

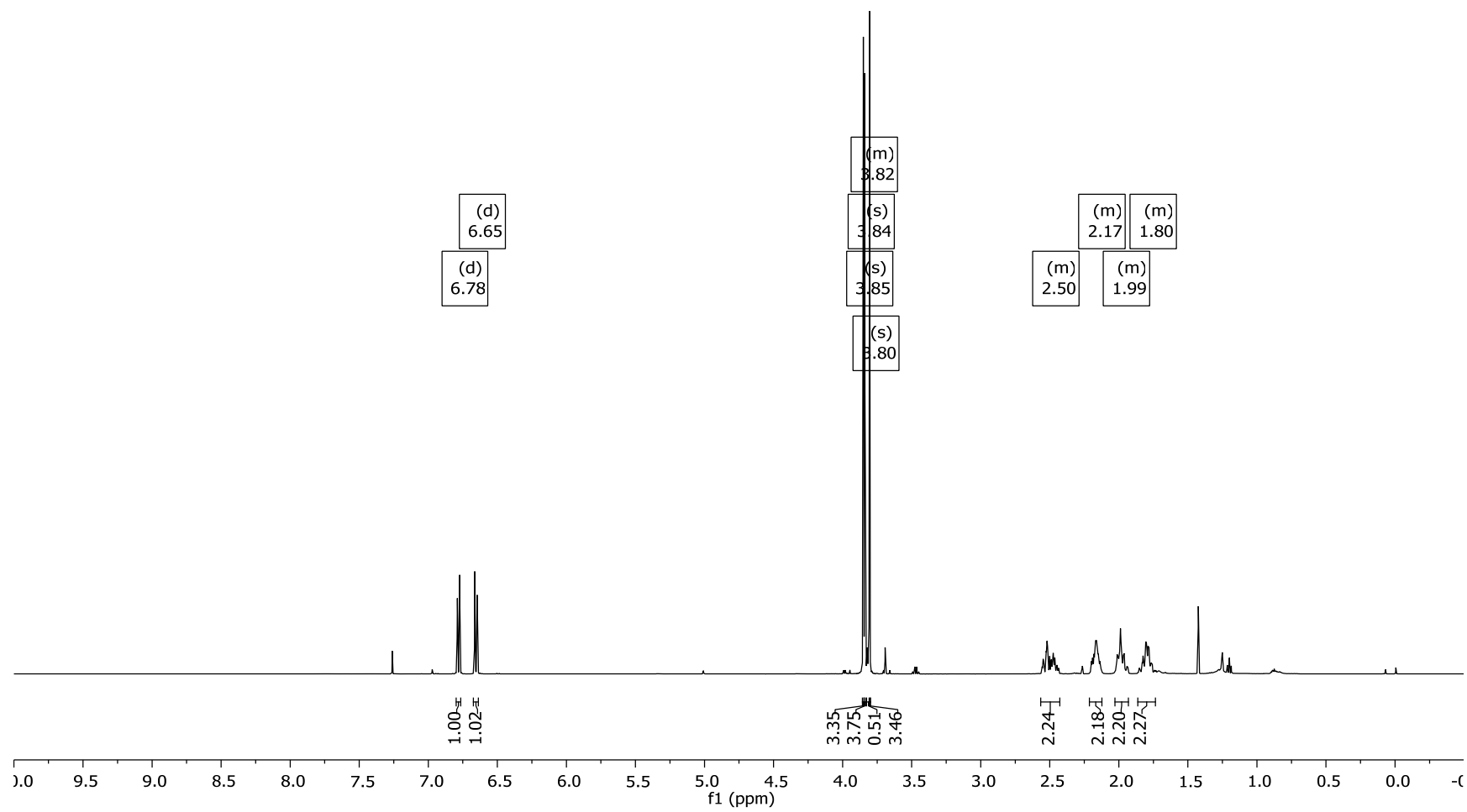


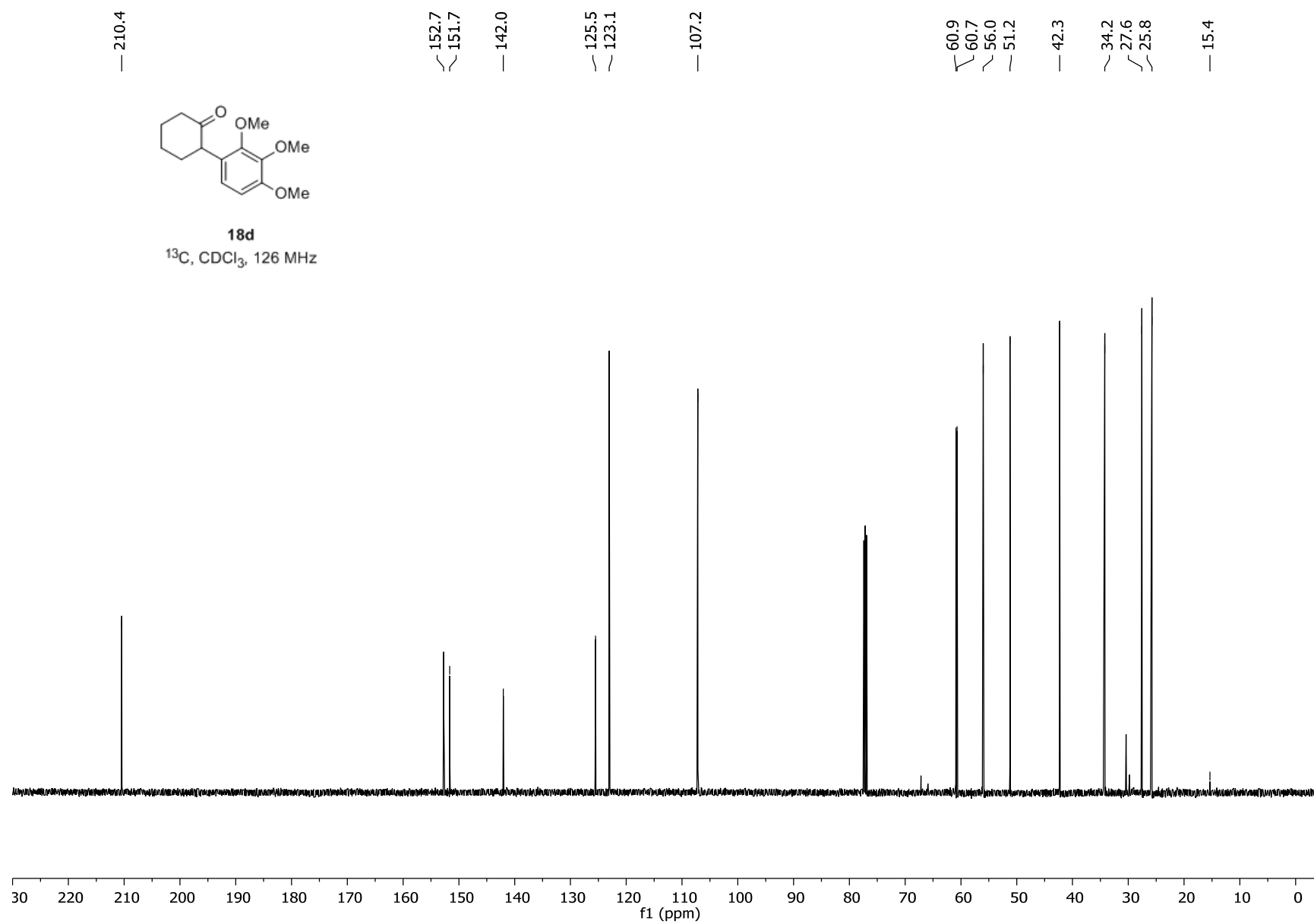


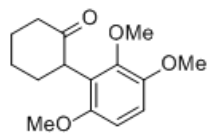


18d

^1H , CDCl_3 , 500 MHz

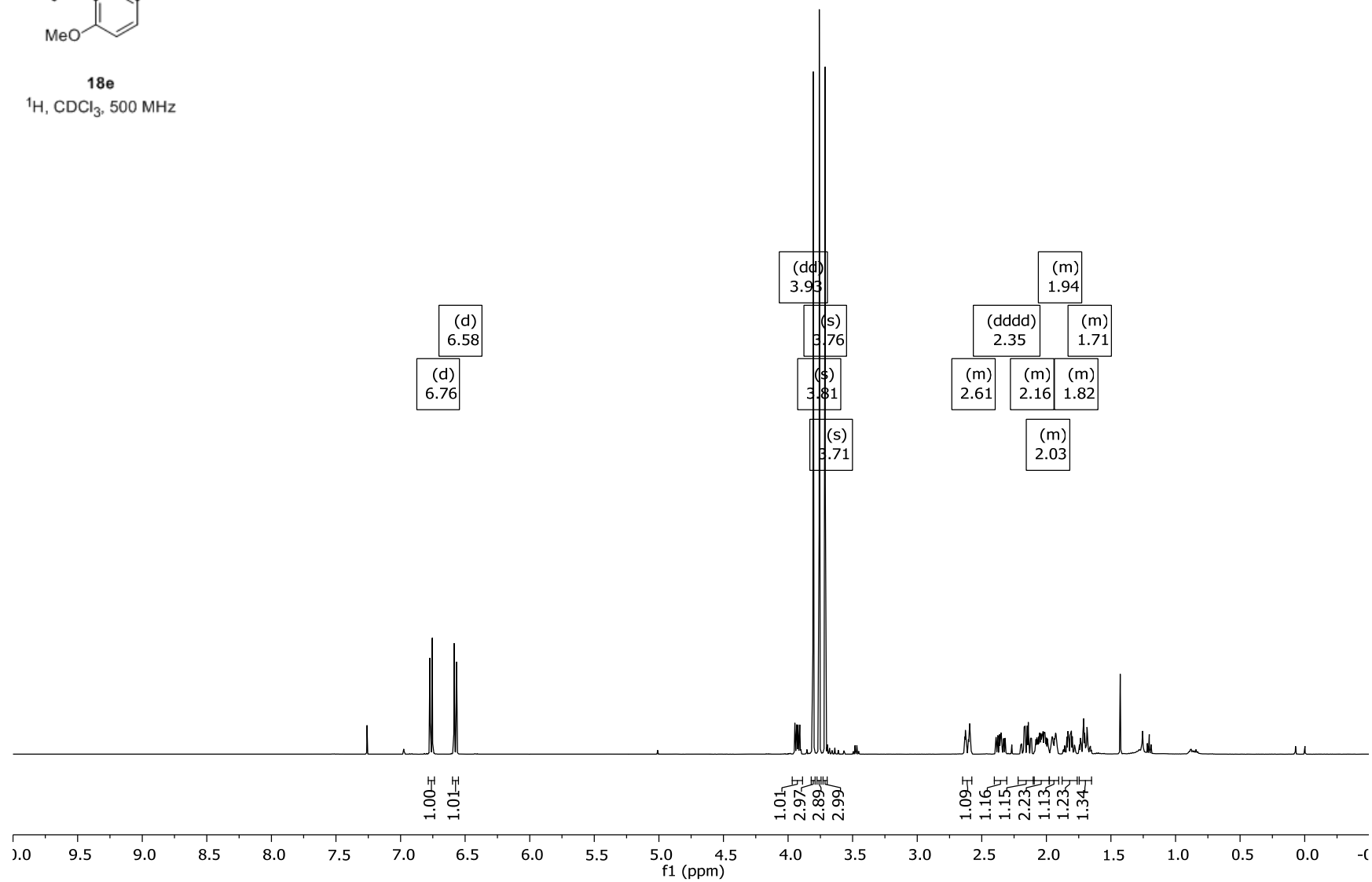


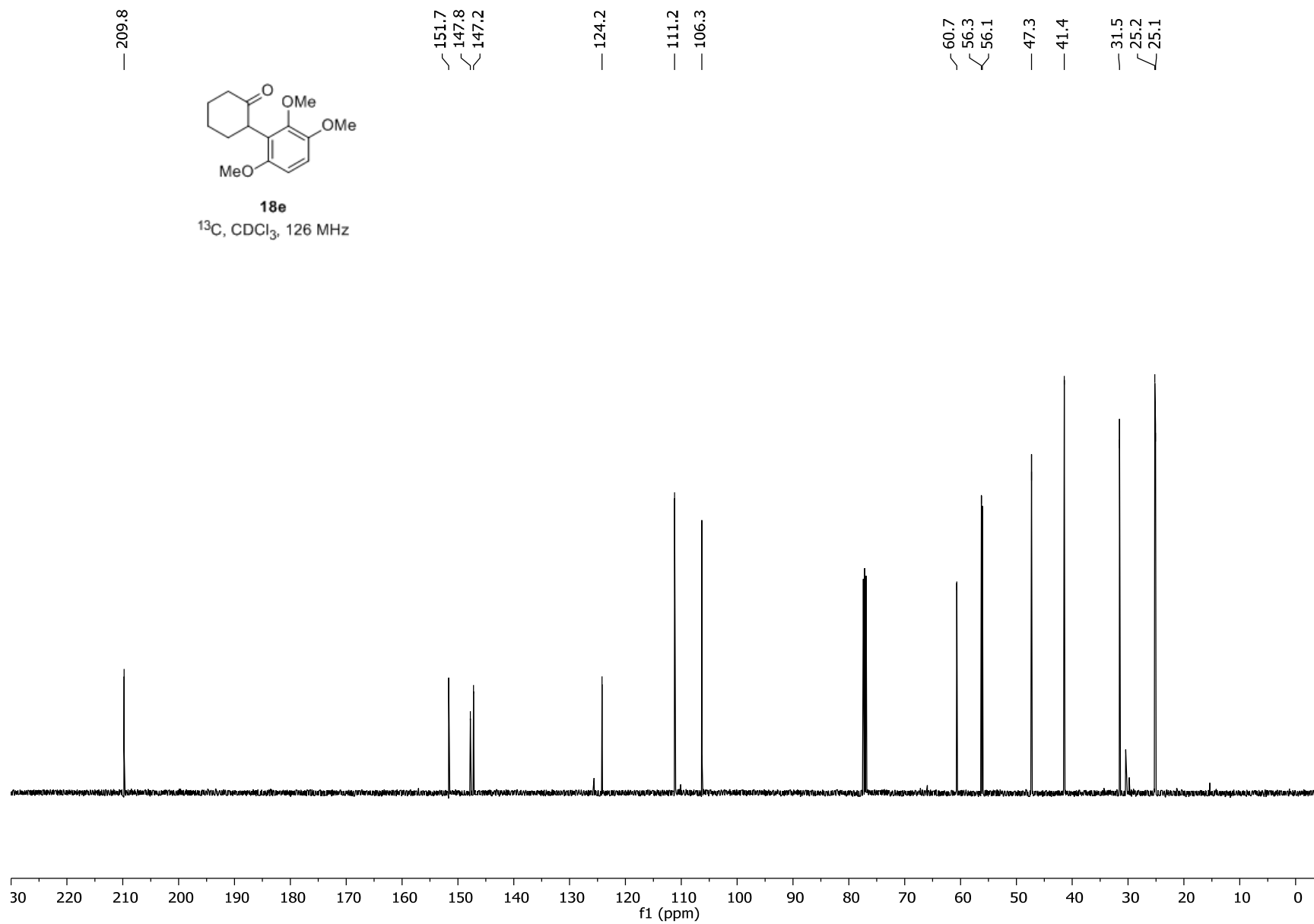


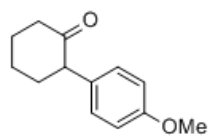


18e

¹H, CDCl₃, 500 MHz

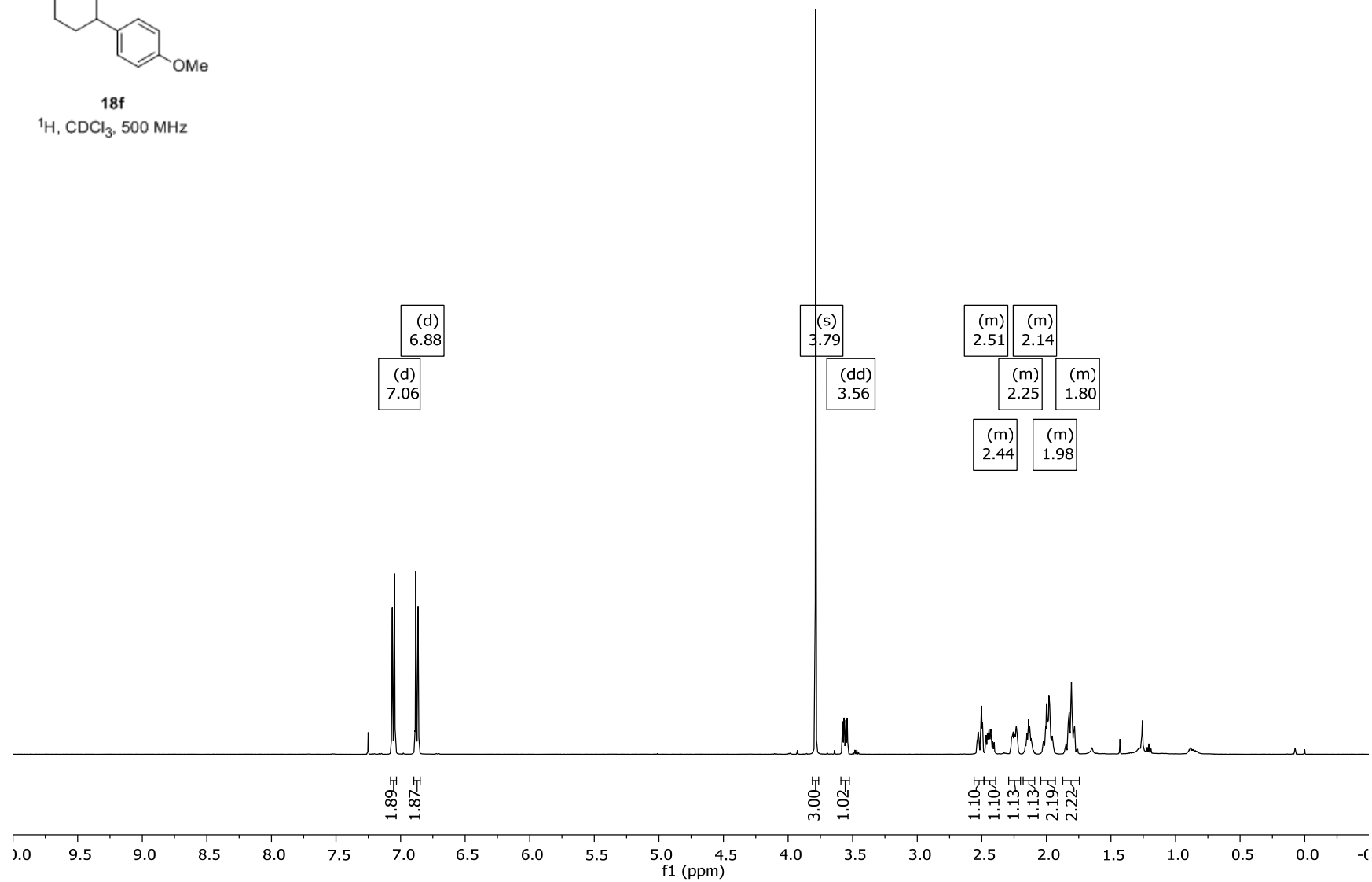


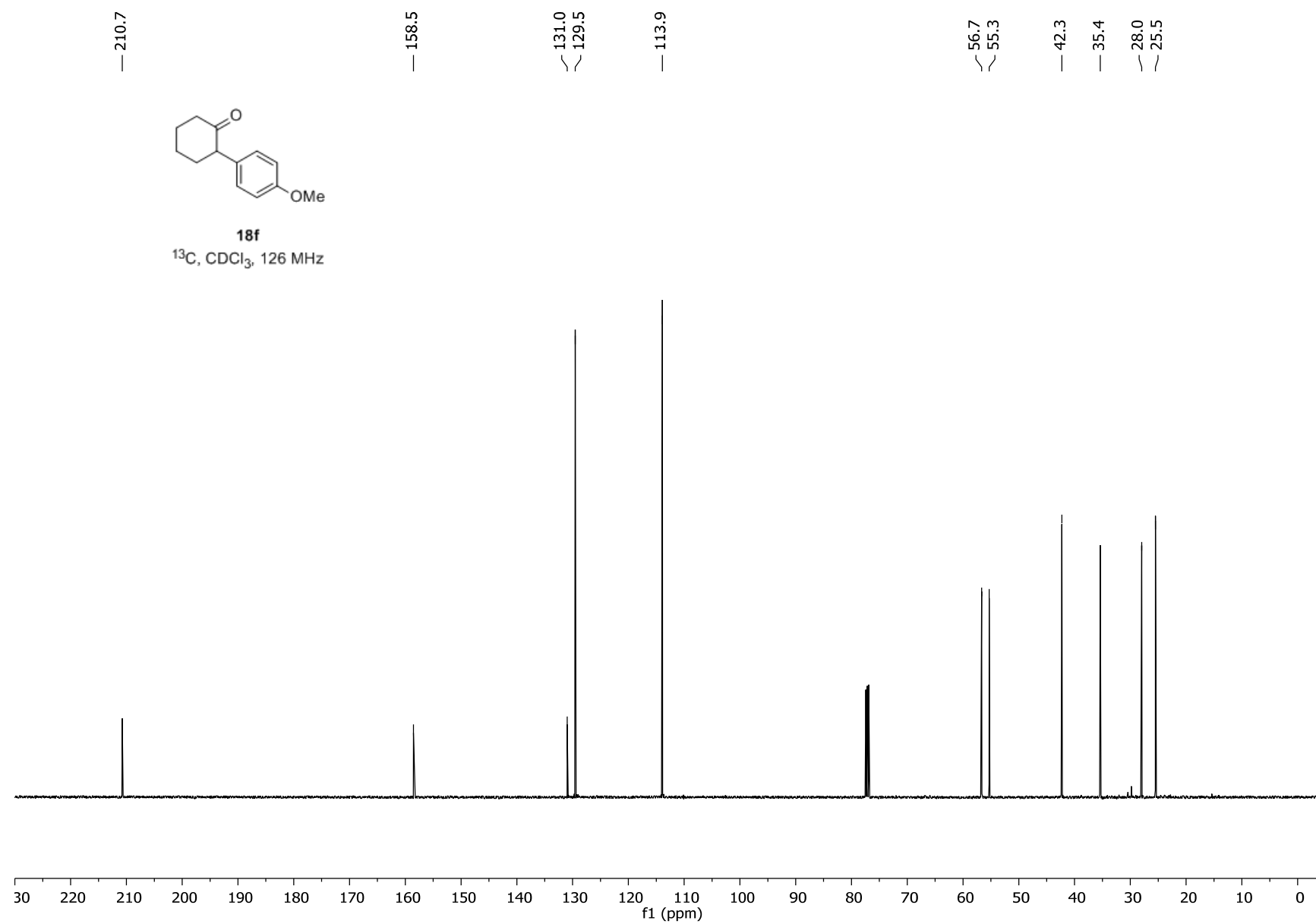


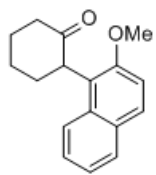


18f

^1H , CDCl_3 , 500 MHz

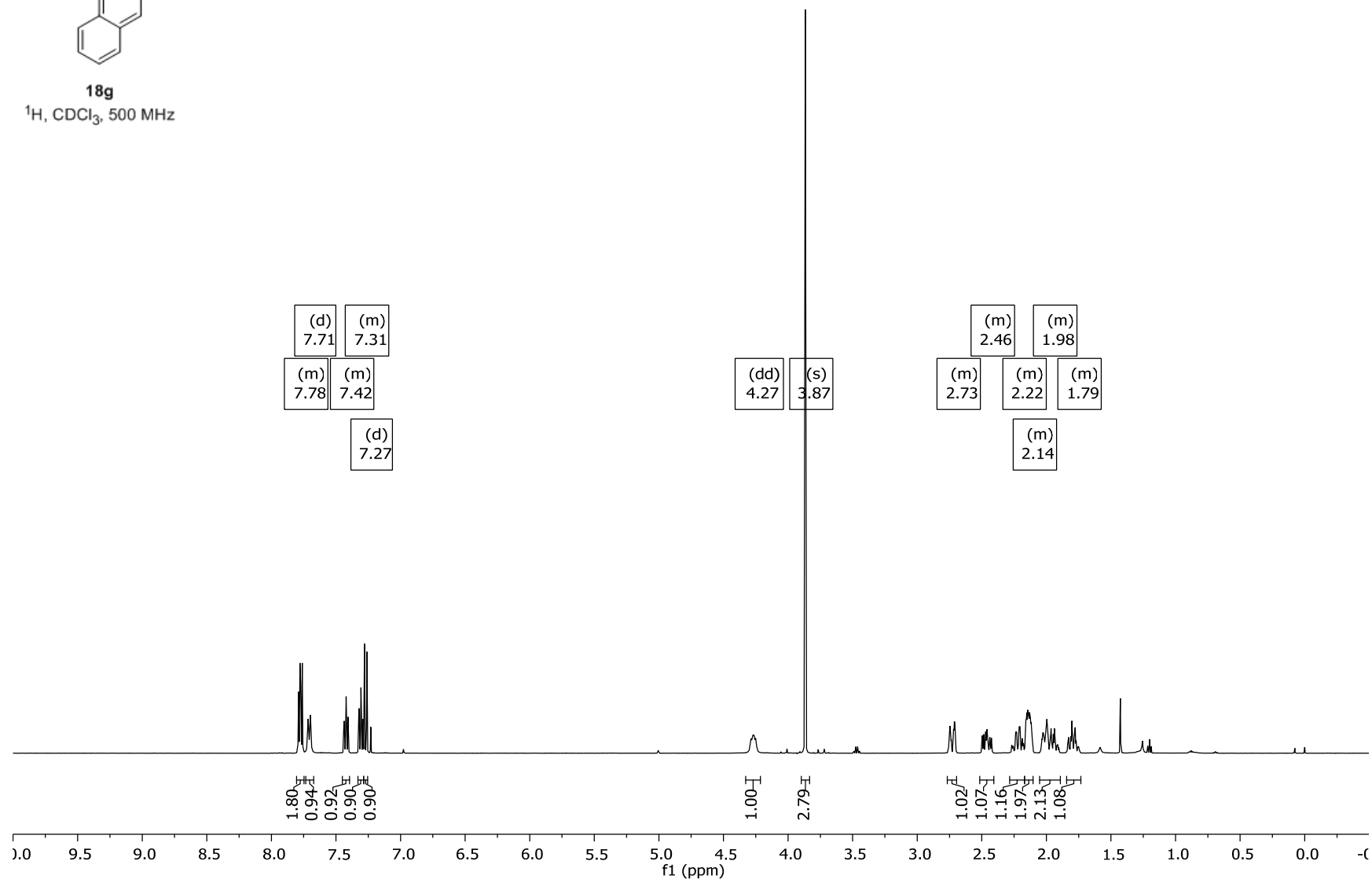


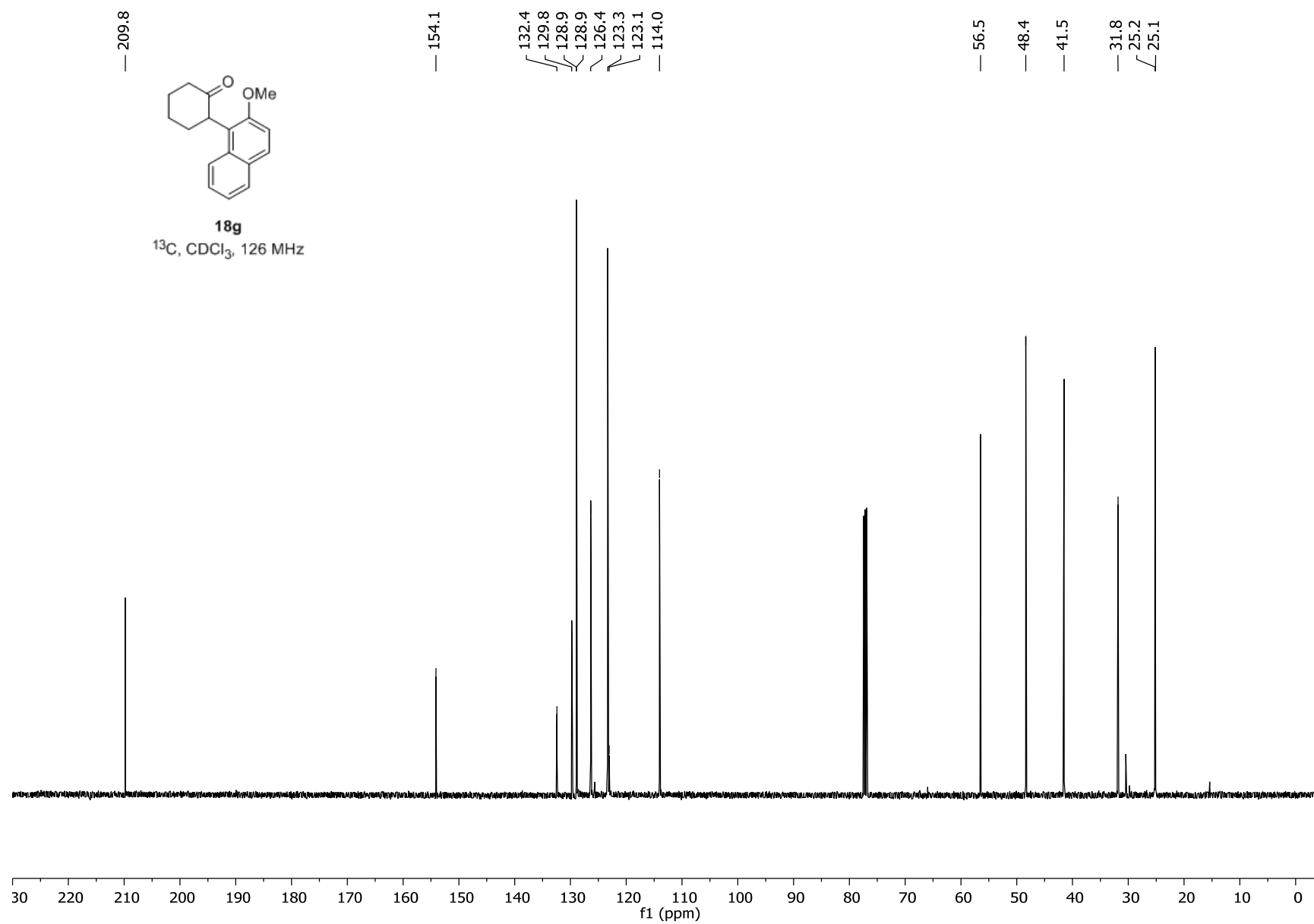


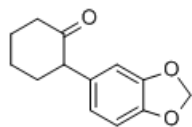


18g

¹H, CDCl₃, 500 MHz

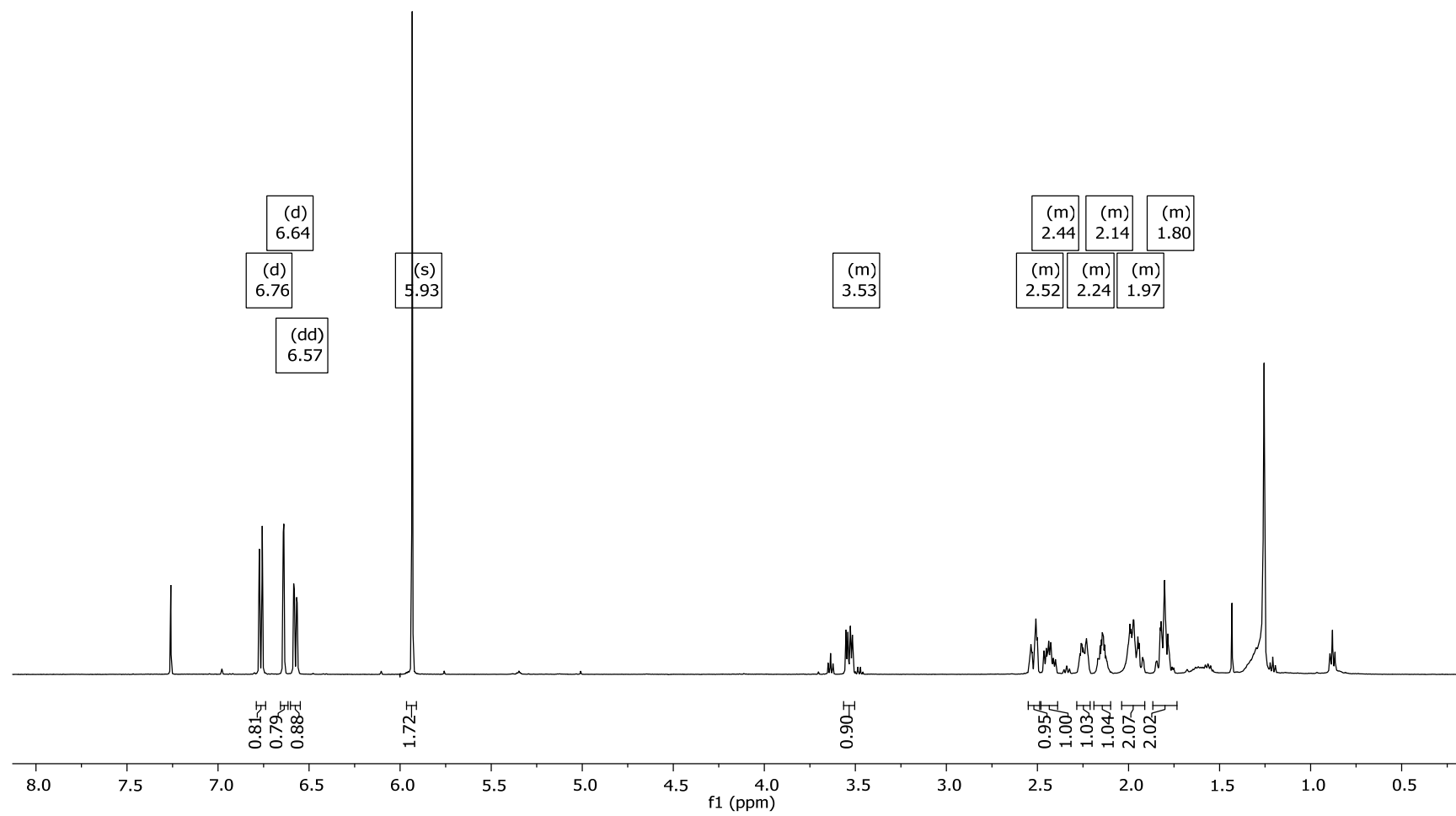


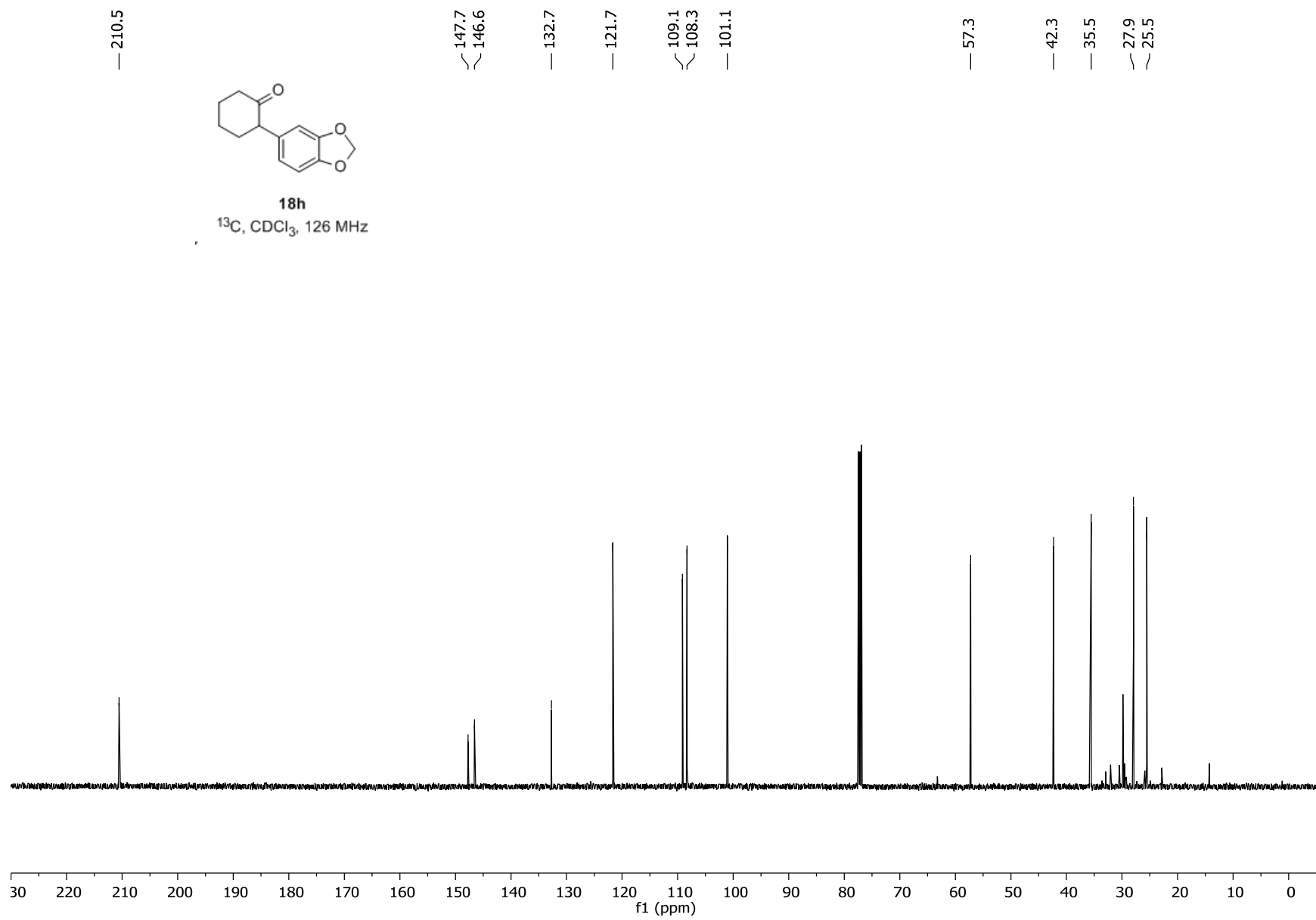


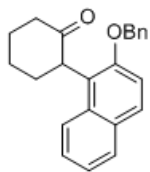


18h

¹H, CDCl₃, 500 MHz

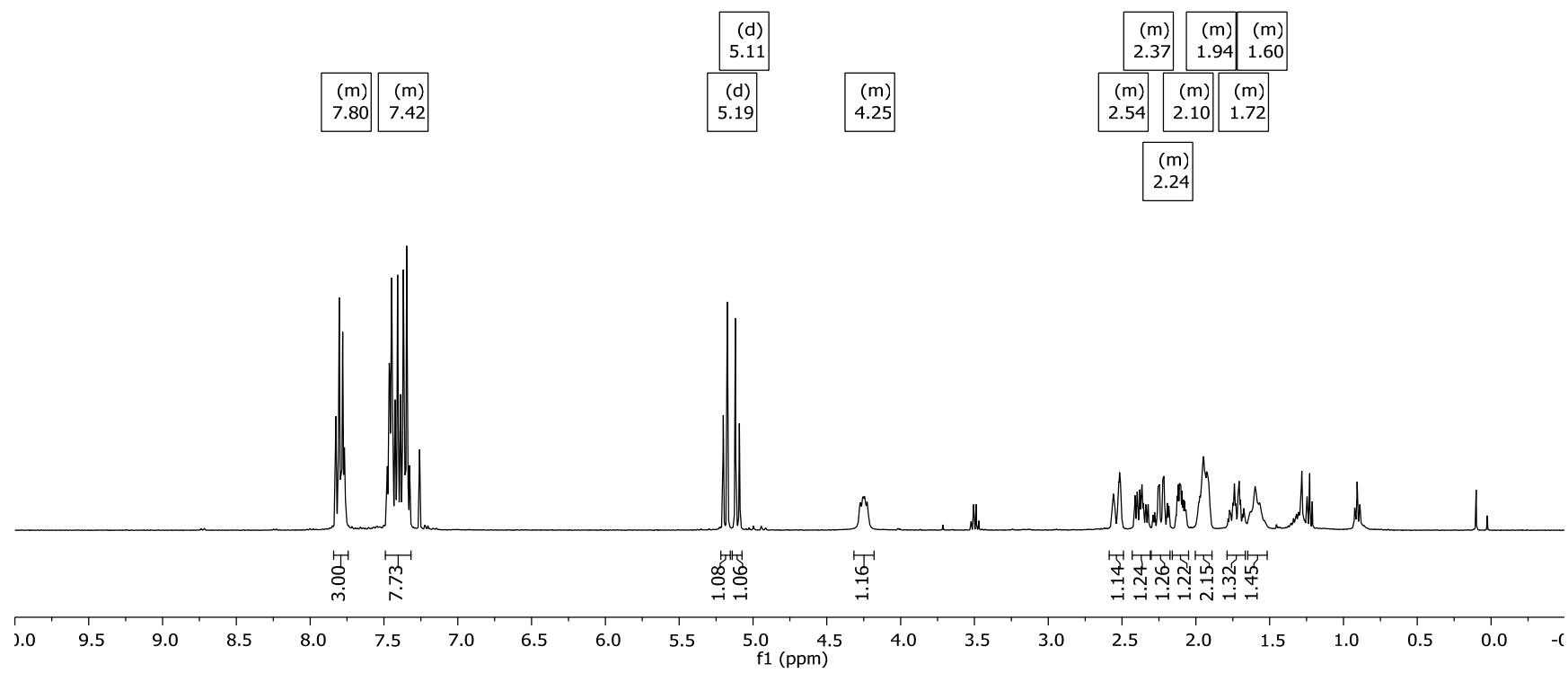


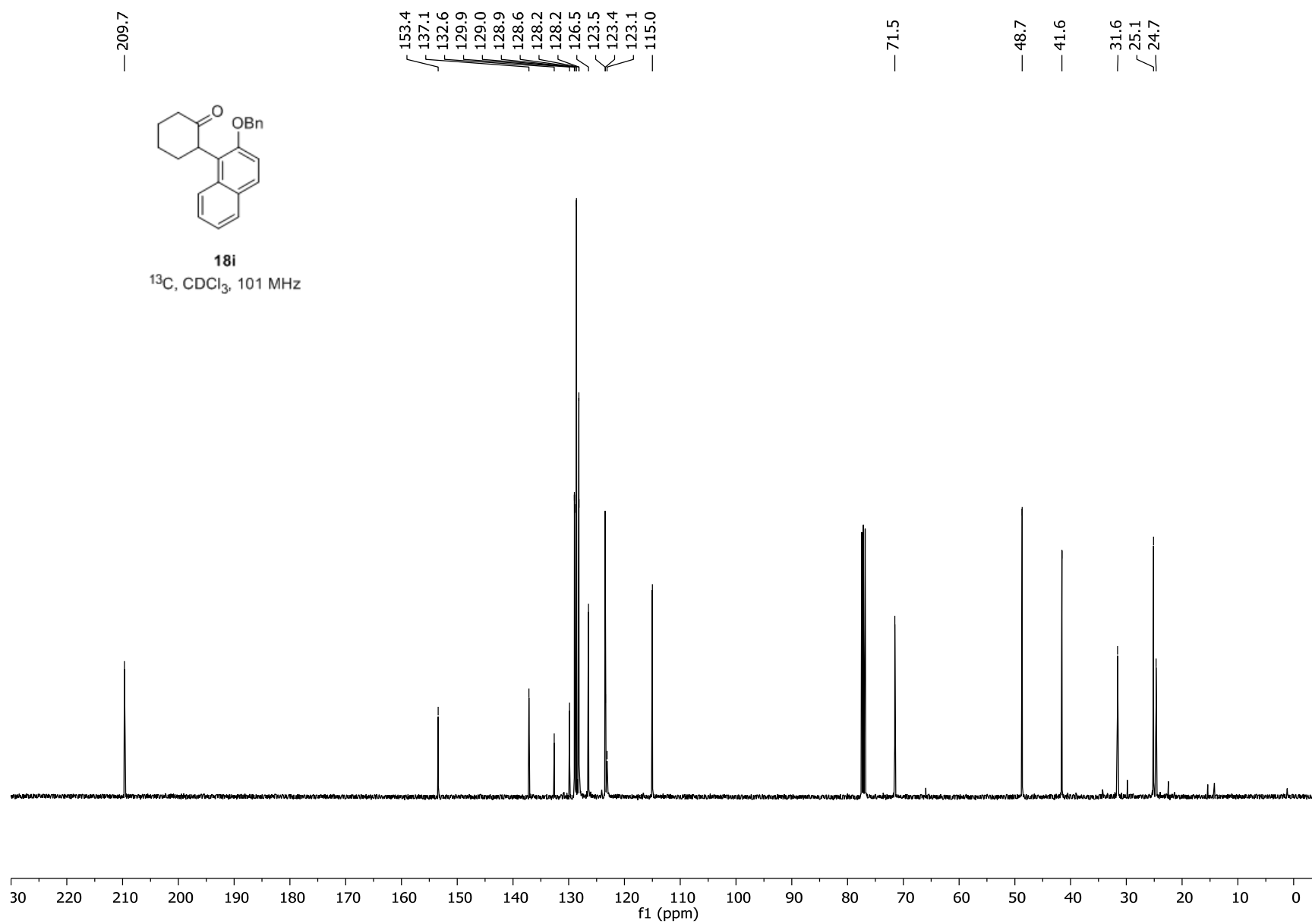


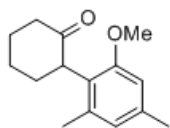


18i

^1H , CDCl_3 , 400 MHz

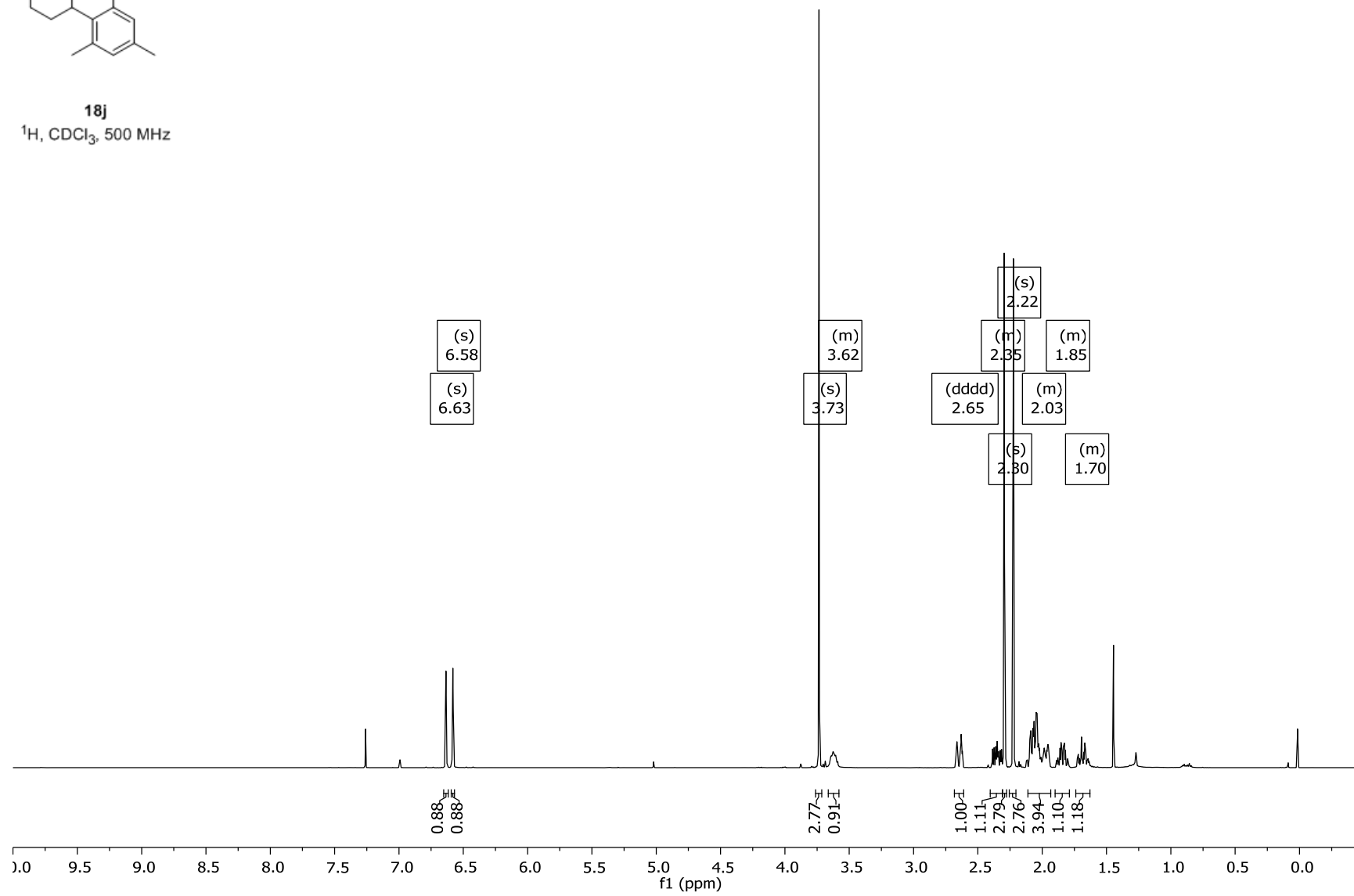


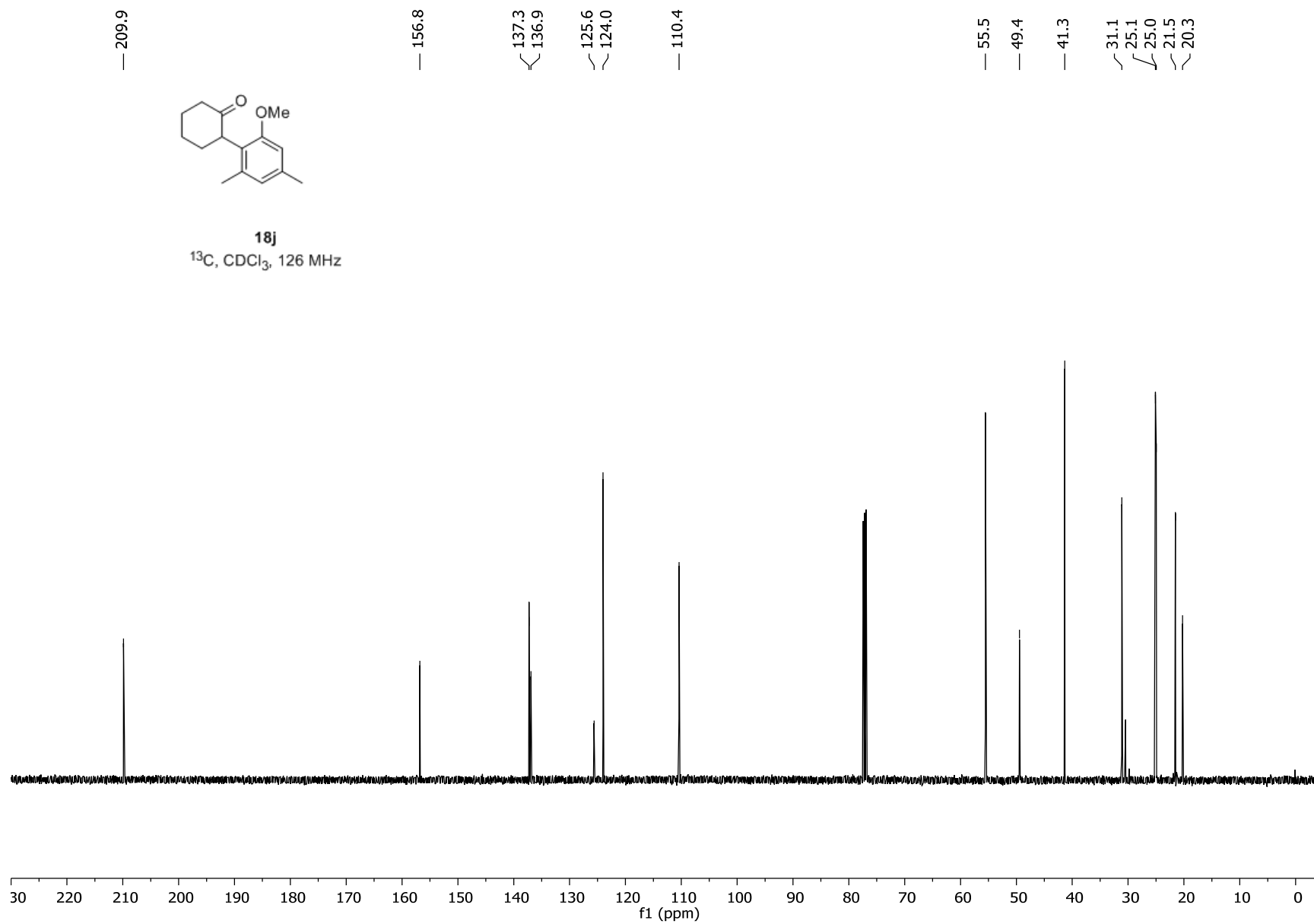


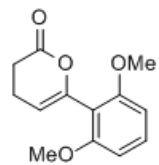


18j

¹H, CDCl₃, 500 MHz

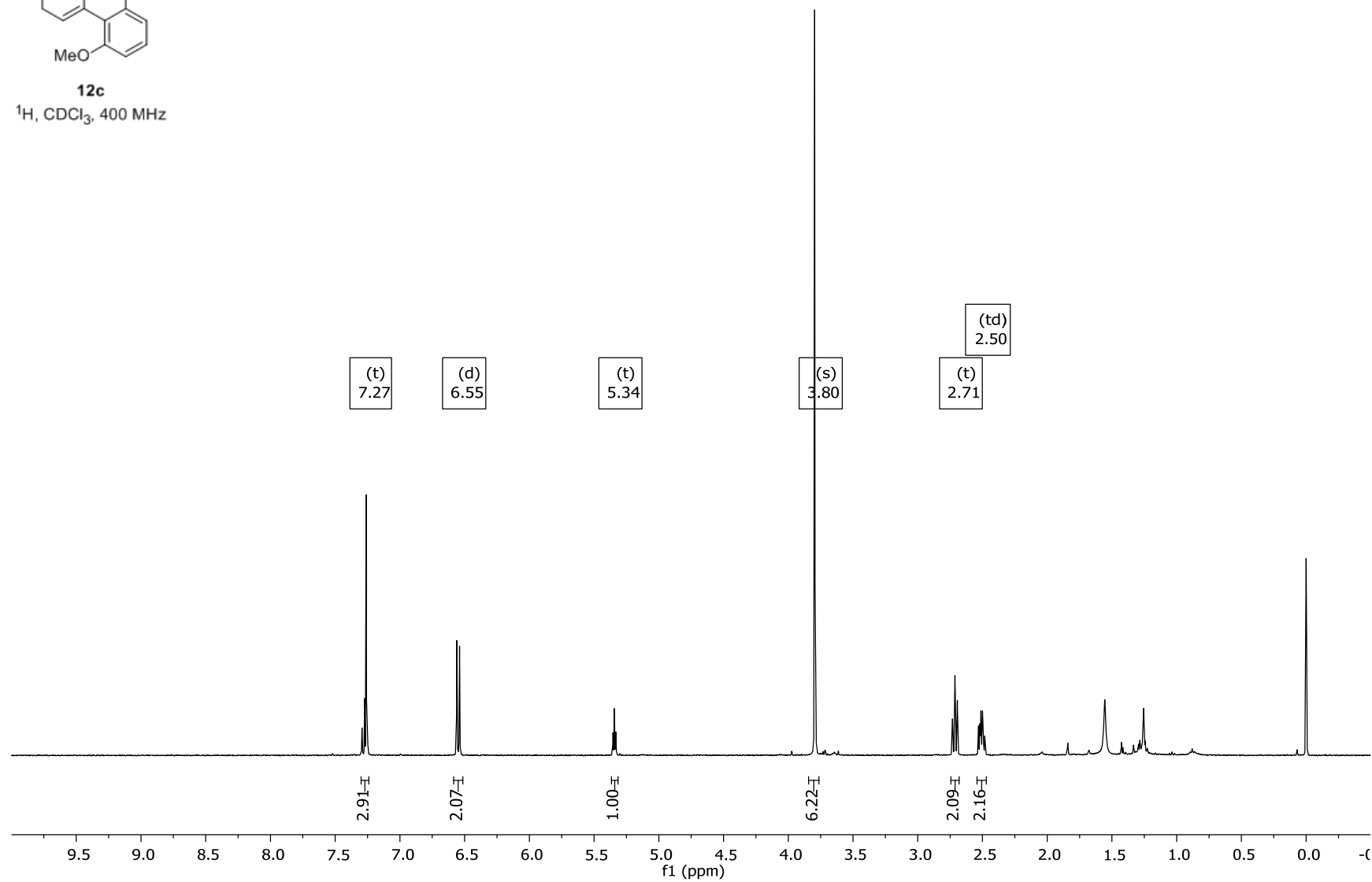


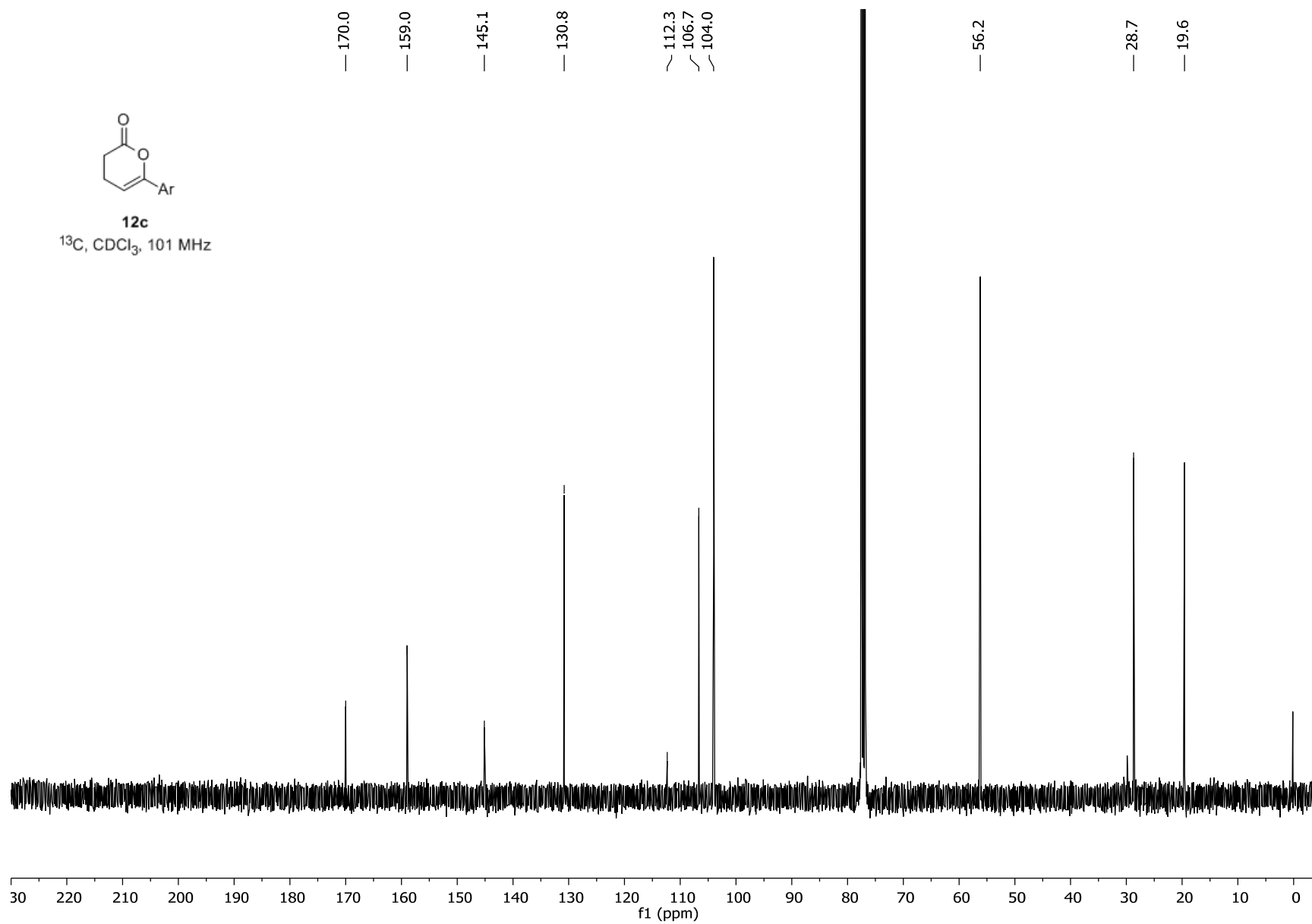


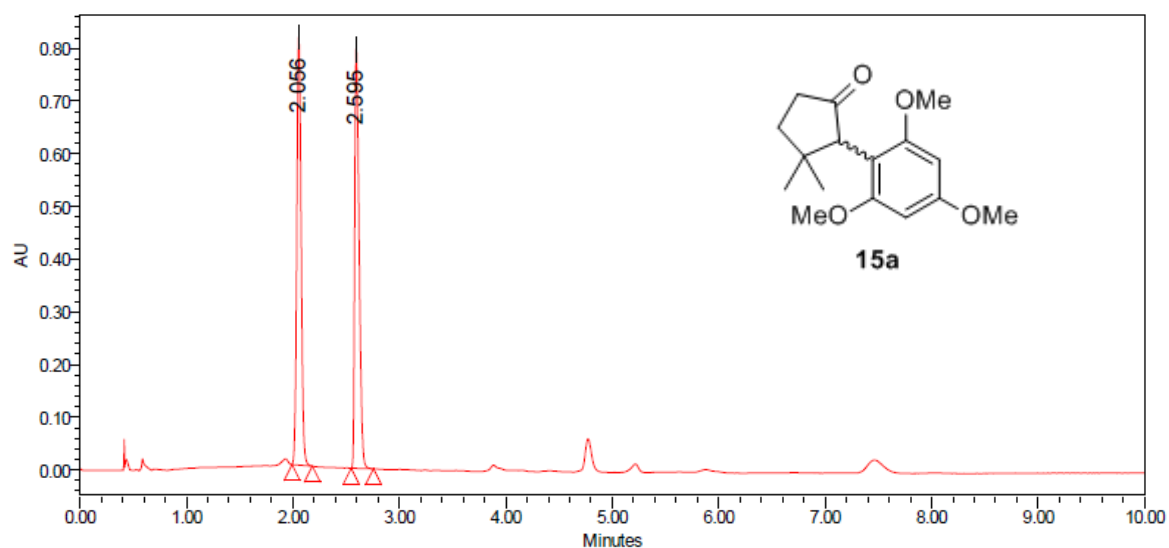


12c

¹H, CDCl₃, 400 MHz

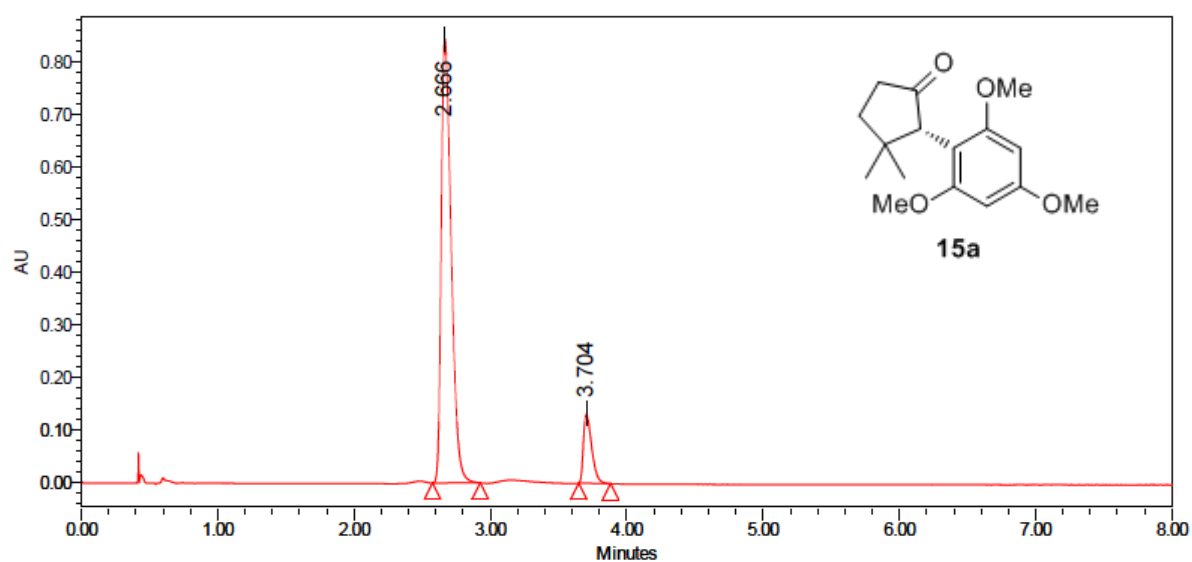






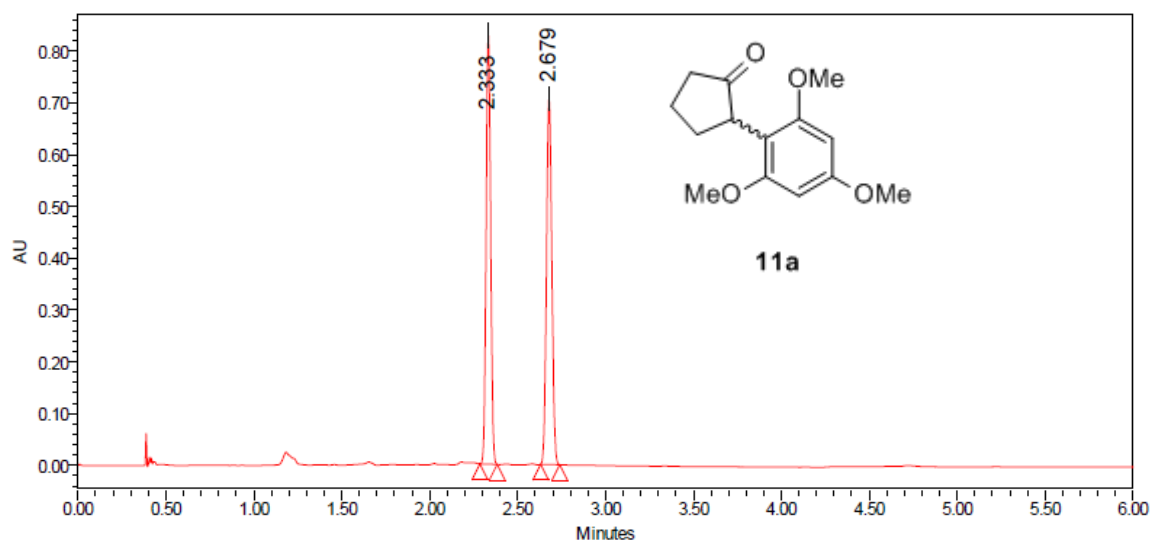
Peak Results

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



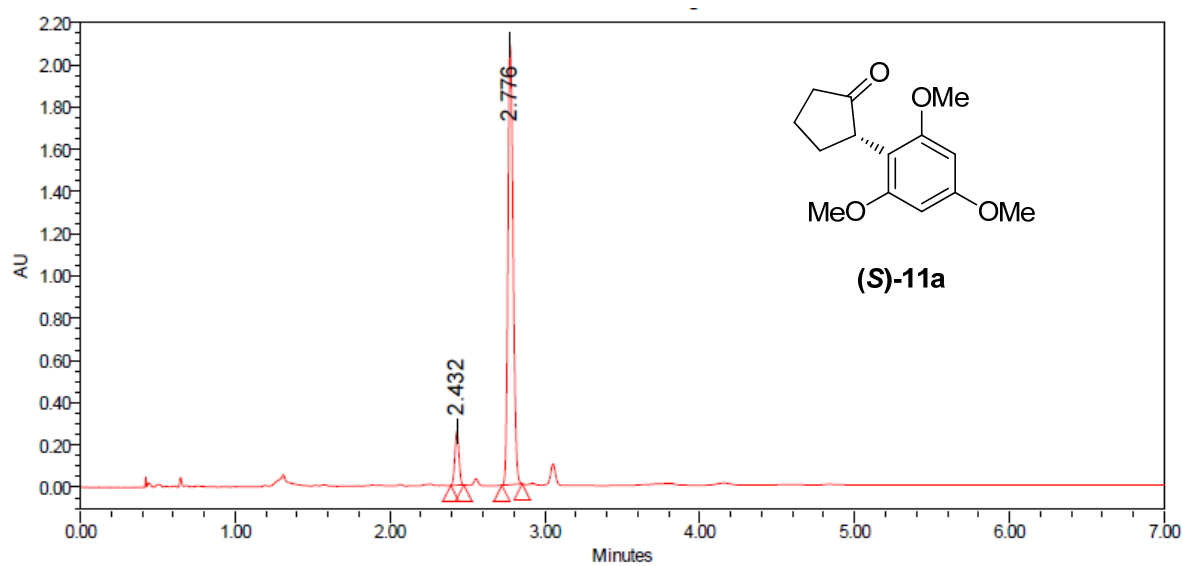
Peak Results

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



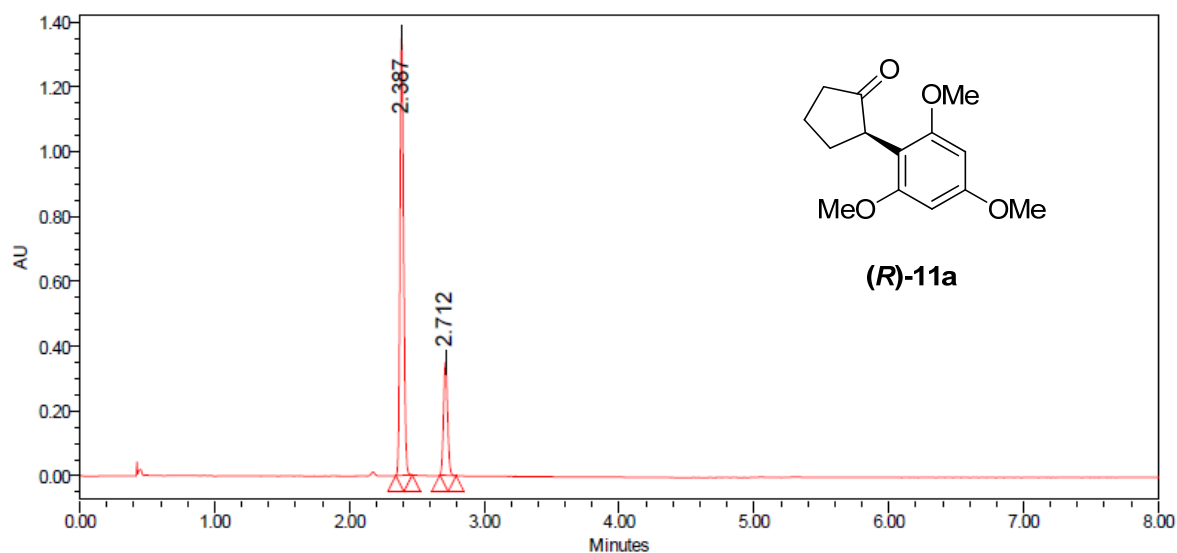
Peak Results

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



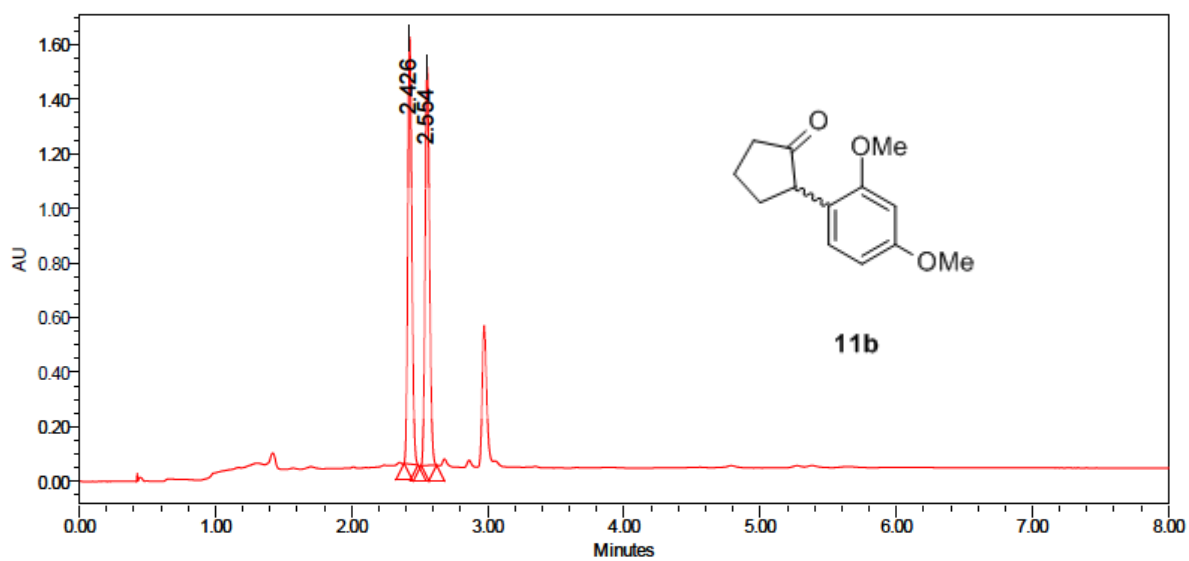
Peak Results

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



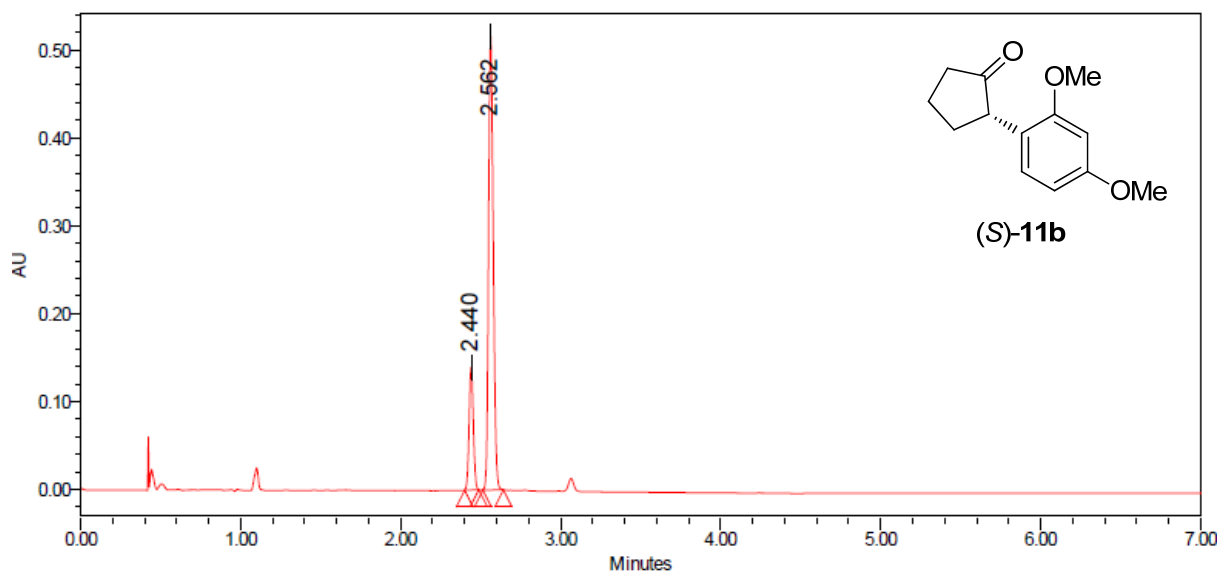
Peak Results

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



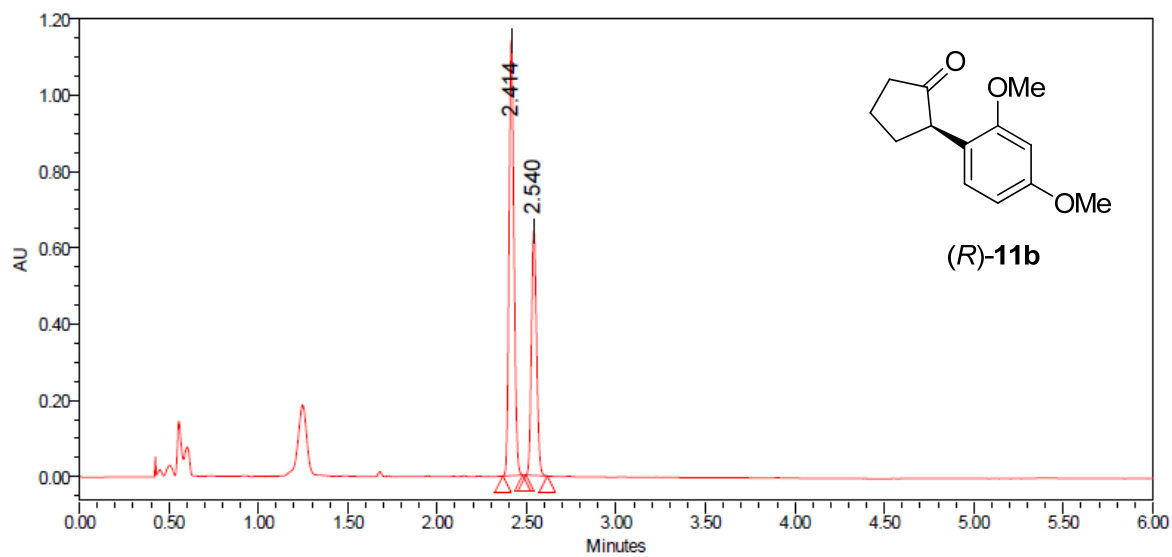
Peak Results

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



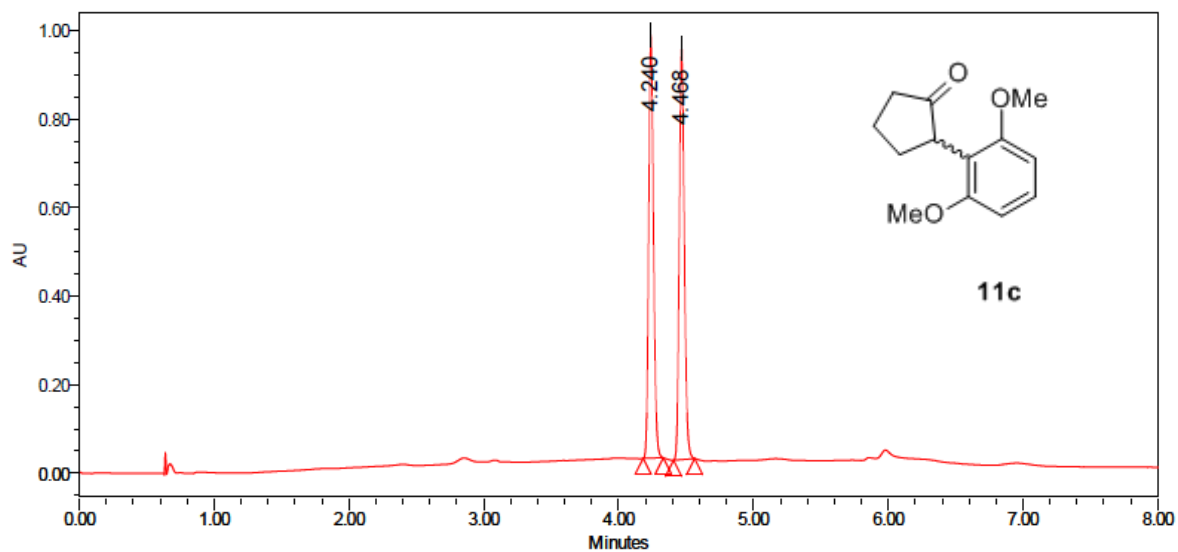
Peak Results

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



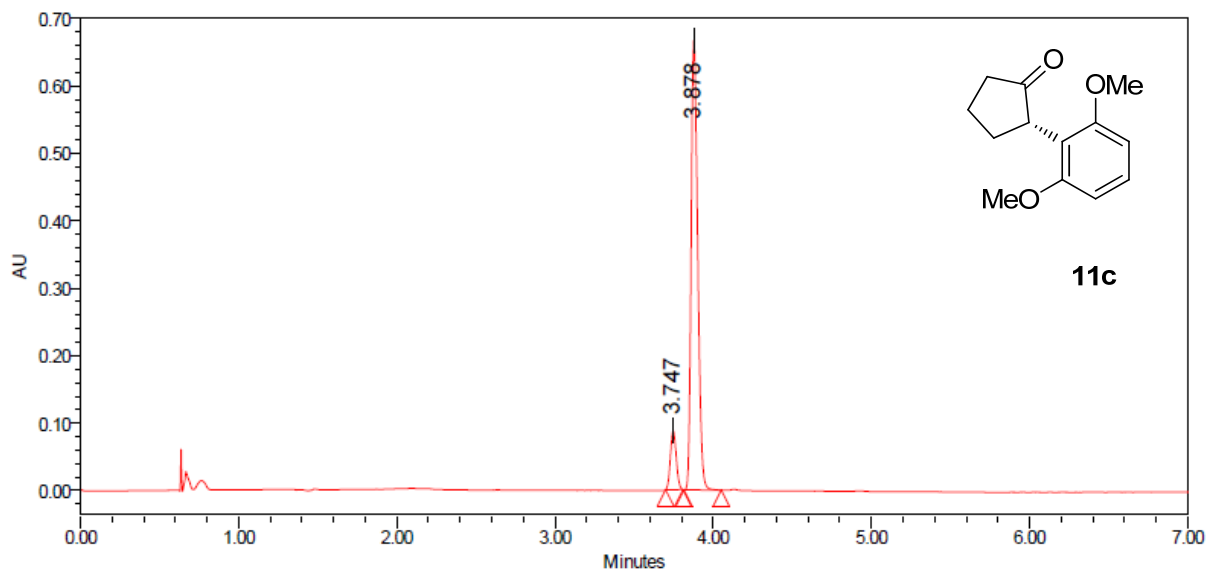
Peak Results

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



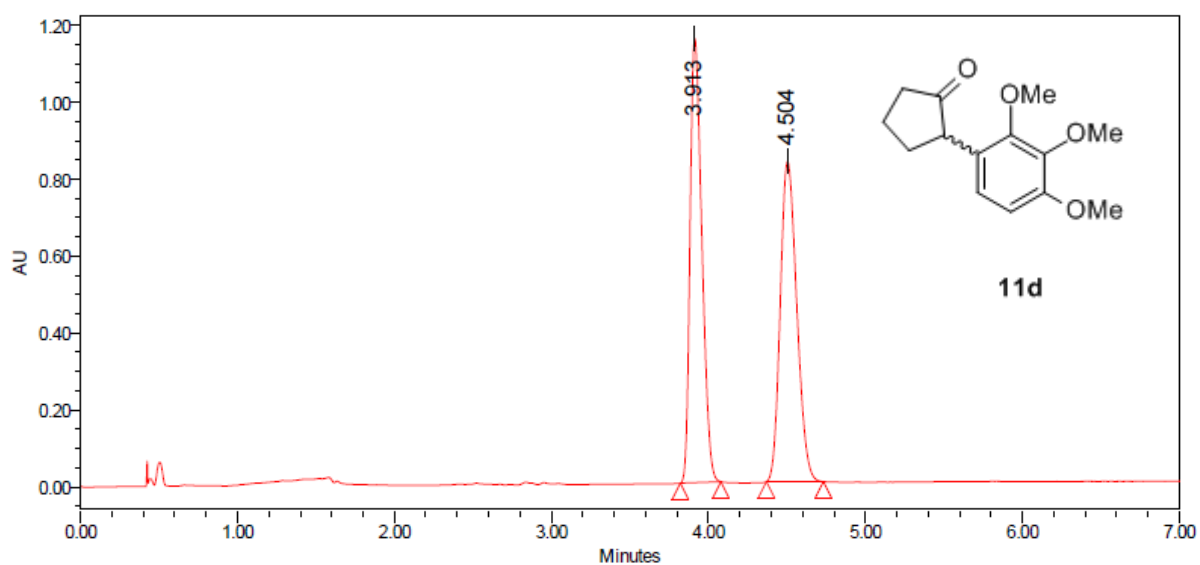
Peak Results

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



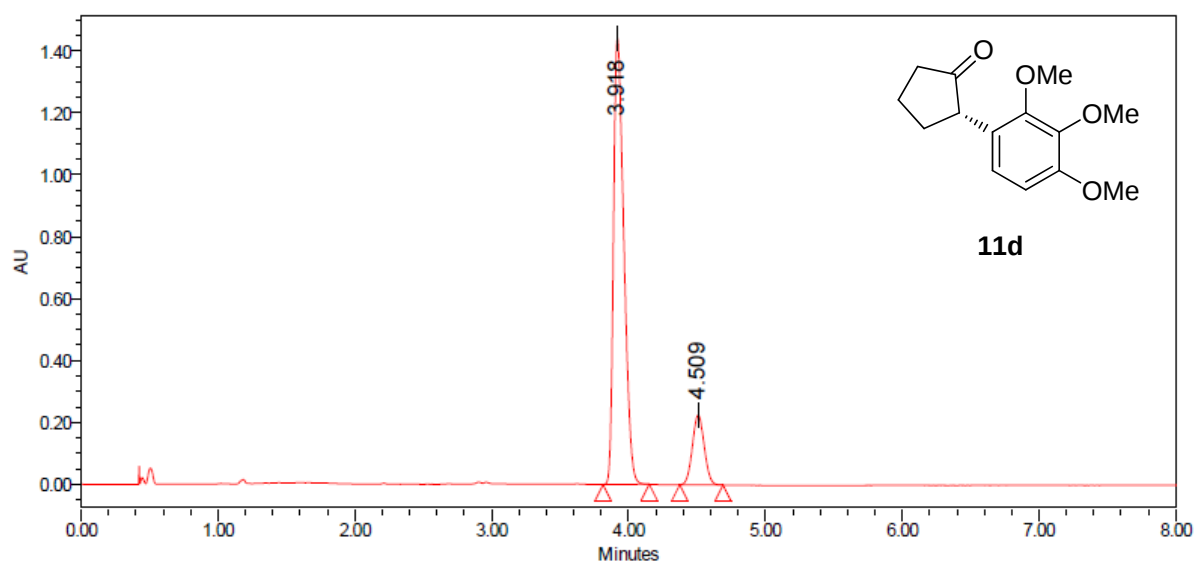
Peak Results

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



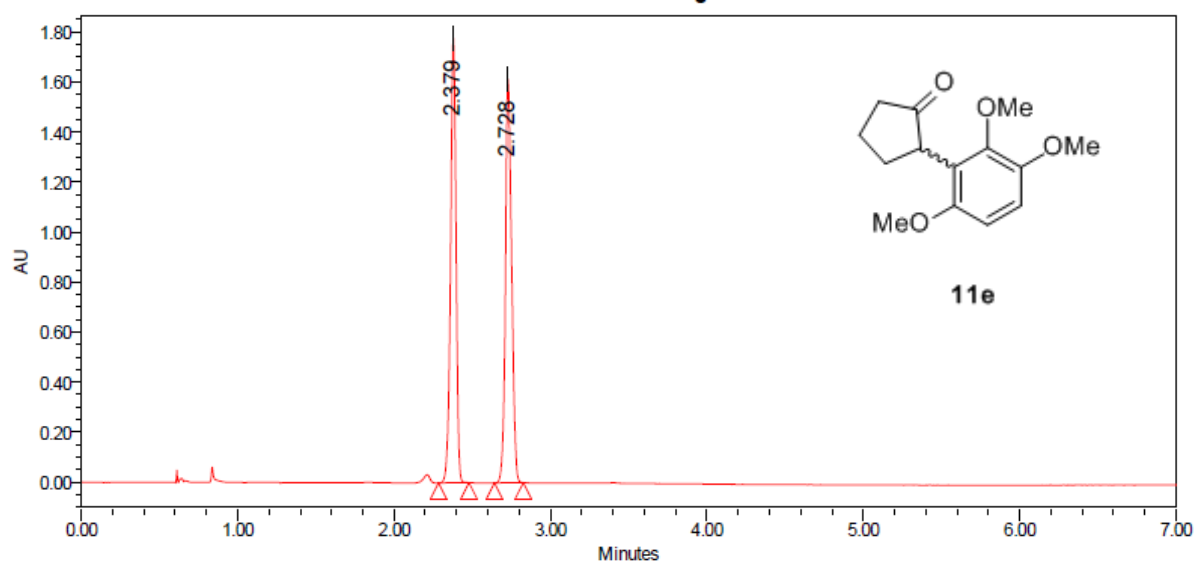
Peak Results

	Name	RT	Area	Height	% Area
1		3.913	6015515	1154739	49.77
2		4.504	6072072	832291	50.23



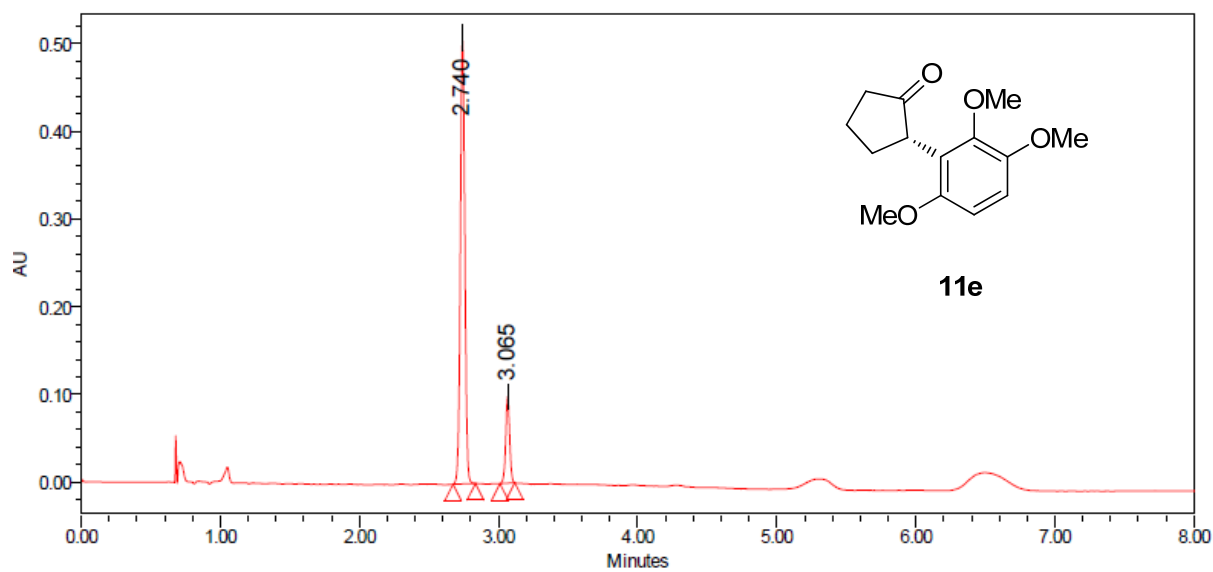
Peak Results

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



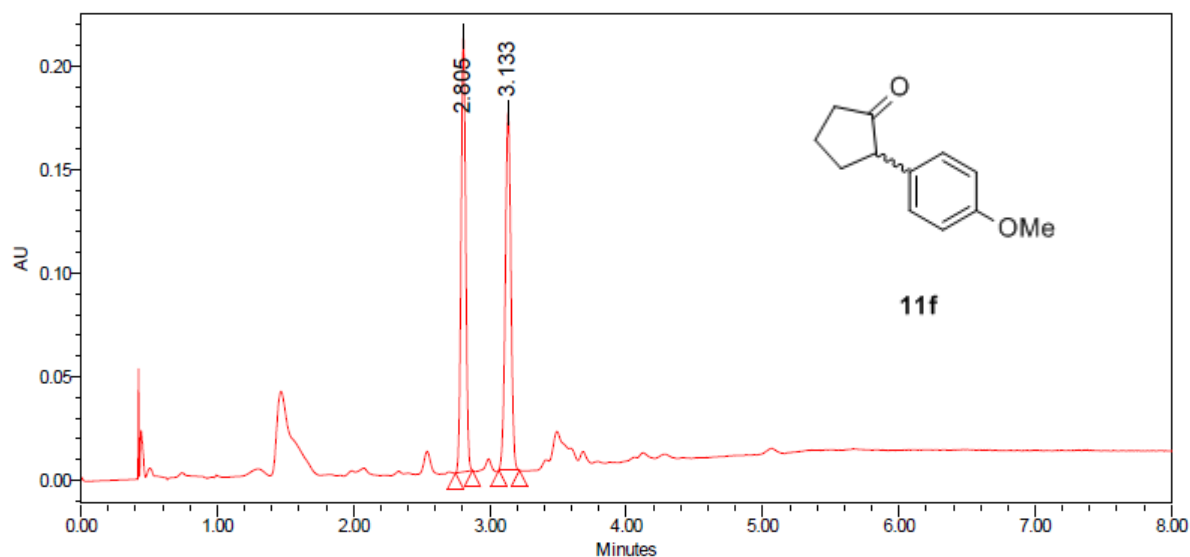
Peak Results

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



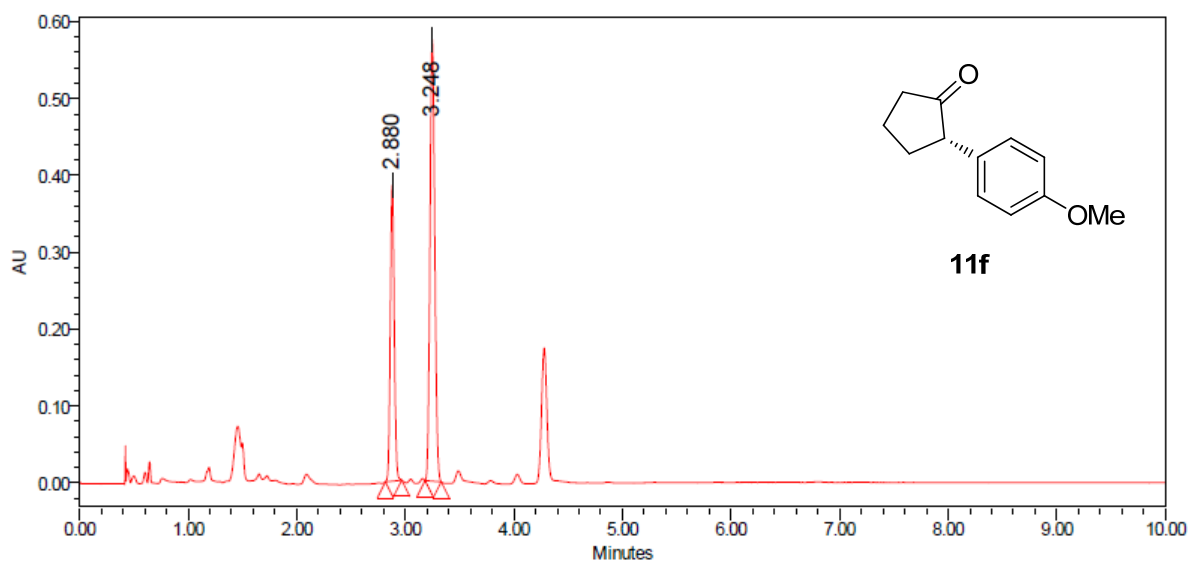
Peak Results

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



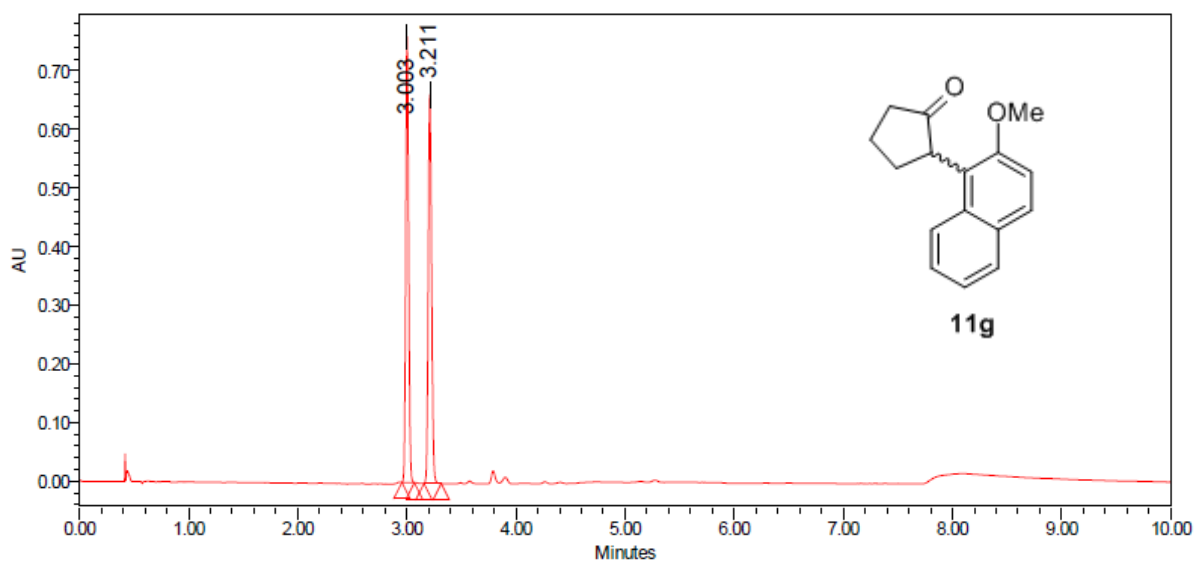
Peak Results

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



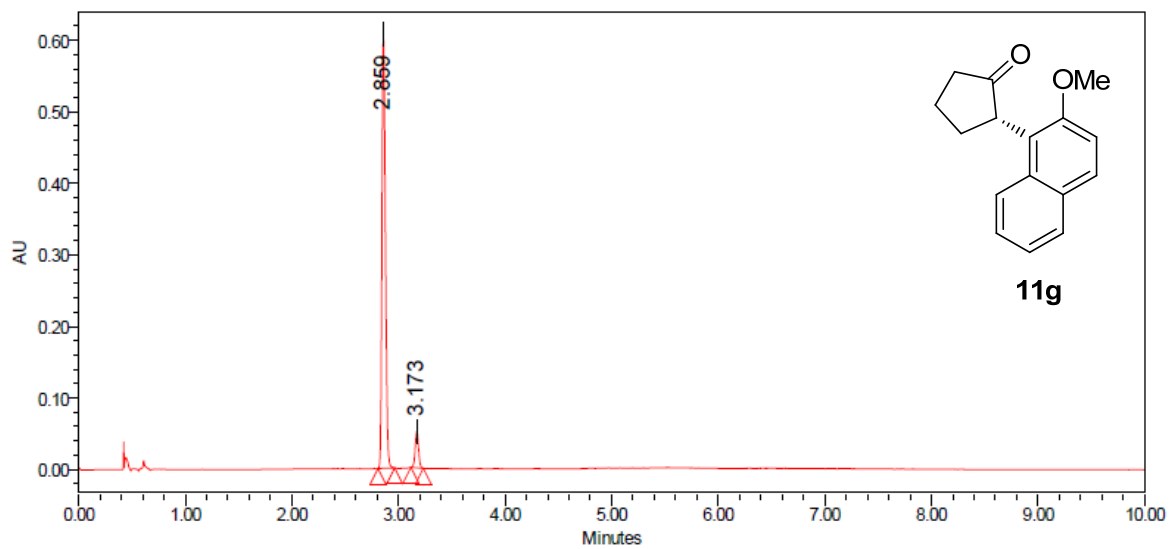
Peak Results

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



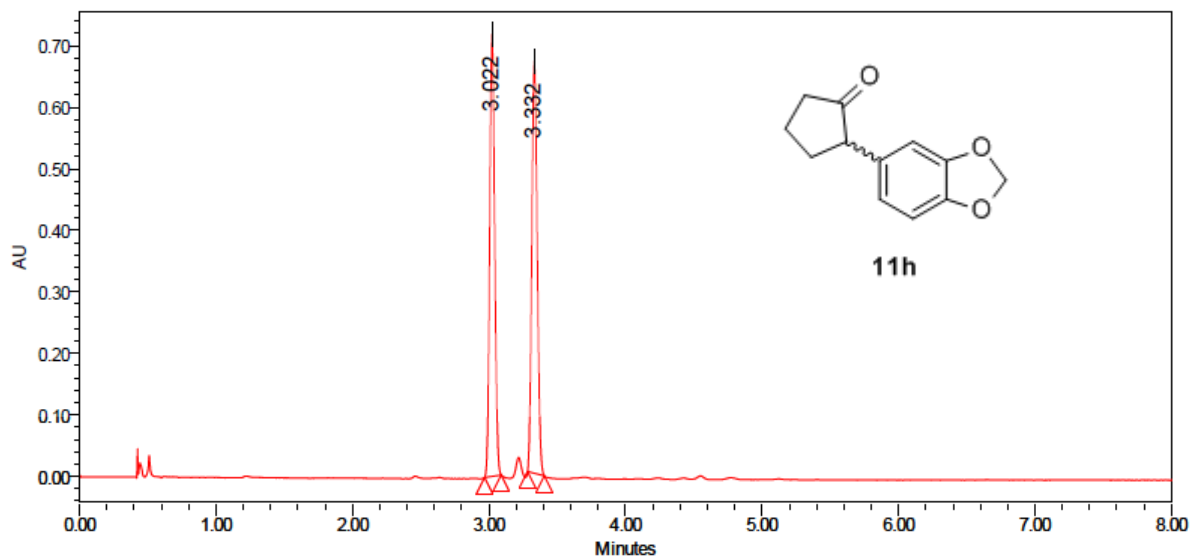
Peak Results

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



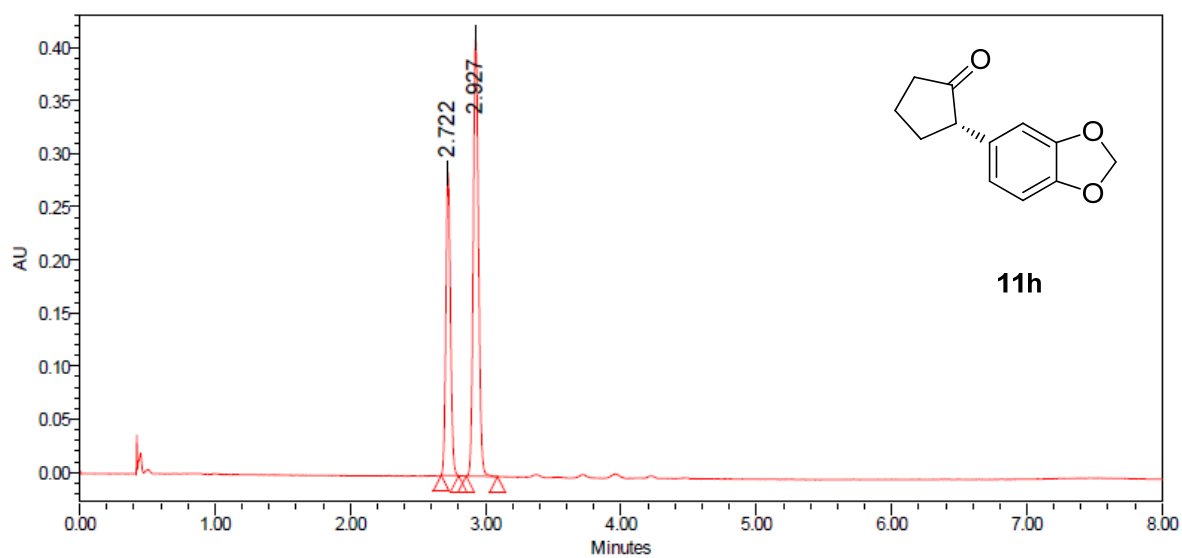
Peak Results

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



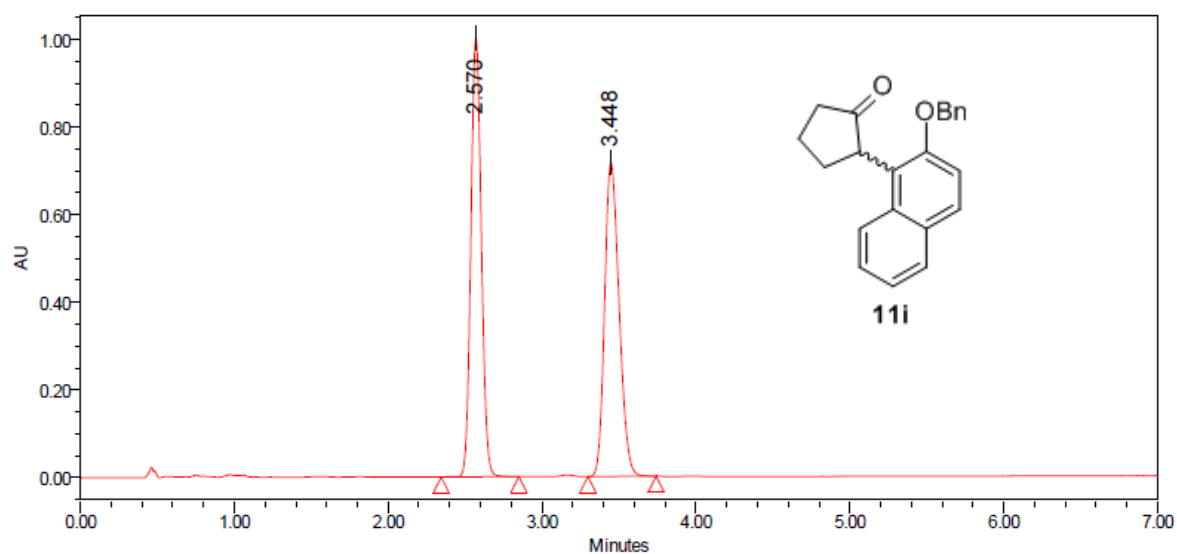
Peak Results

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



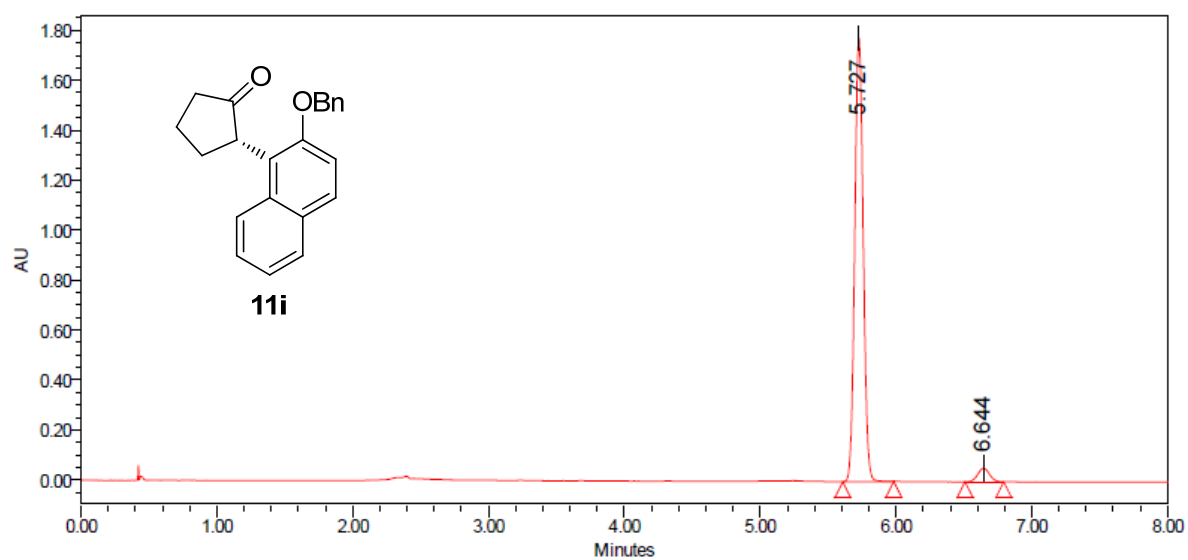
Peak Results

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



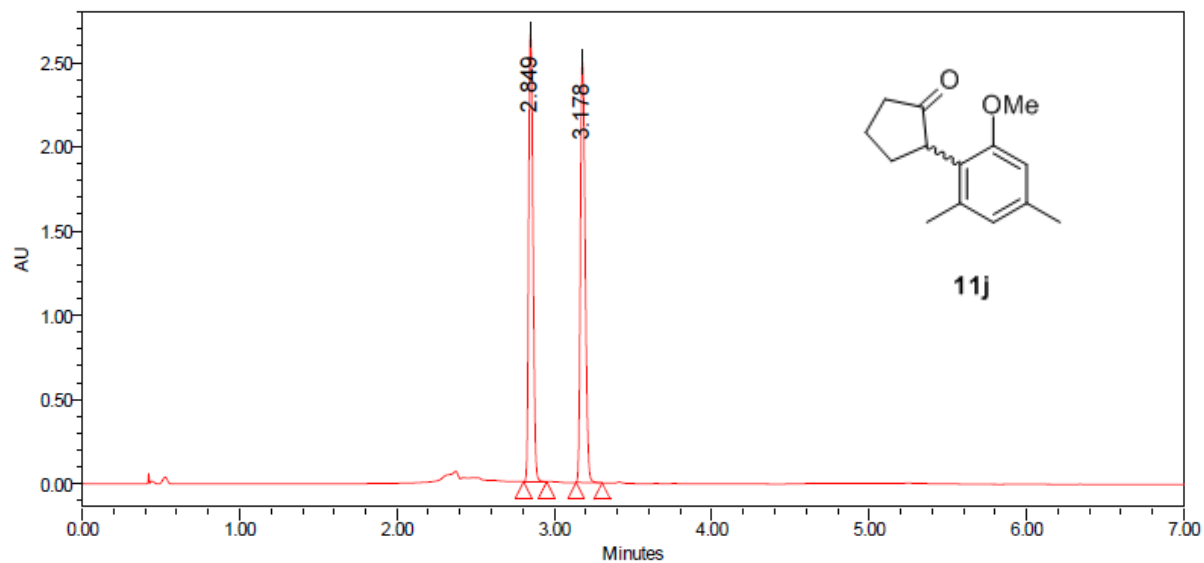
Peak Results

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



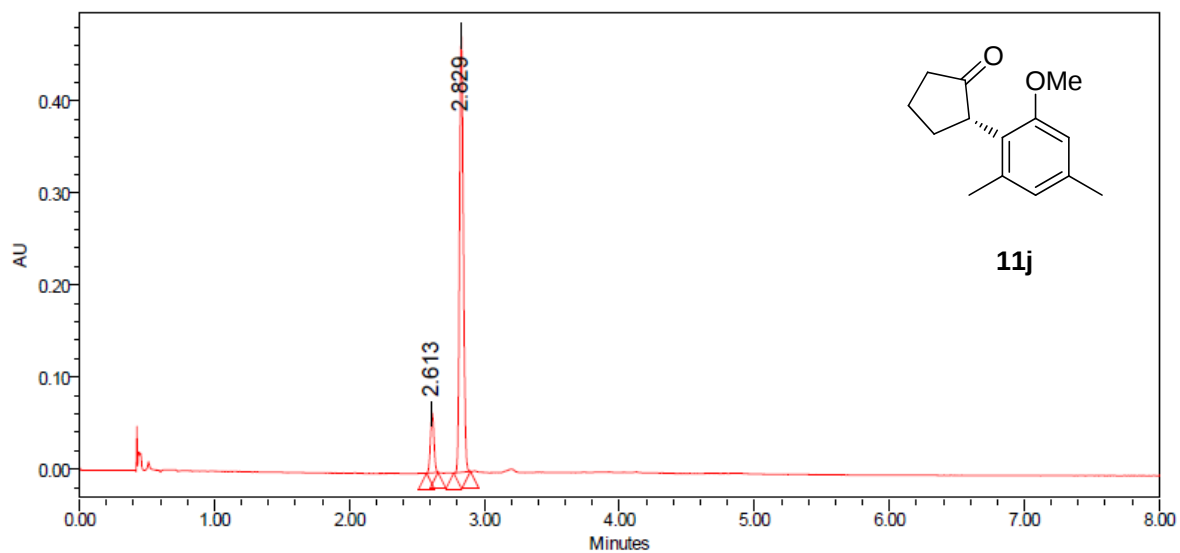
Peak Results

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



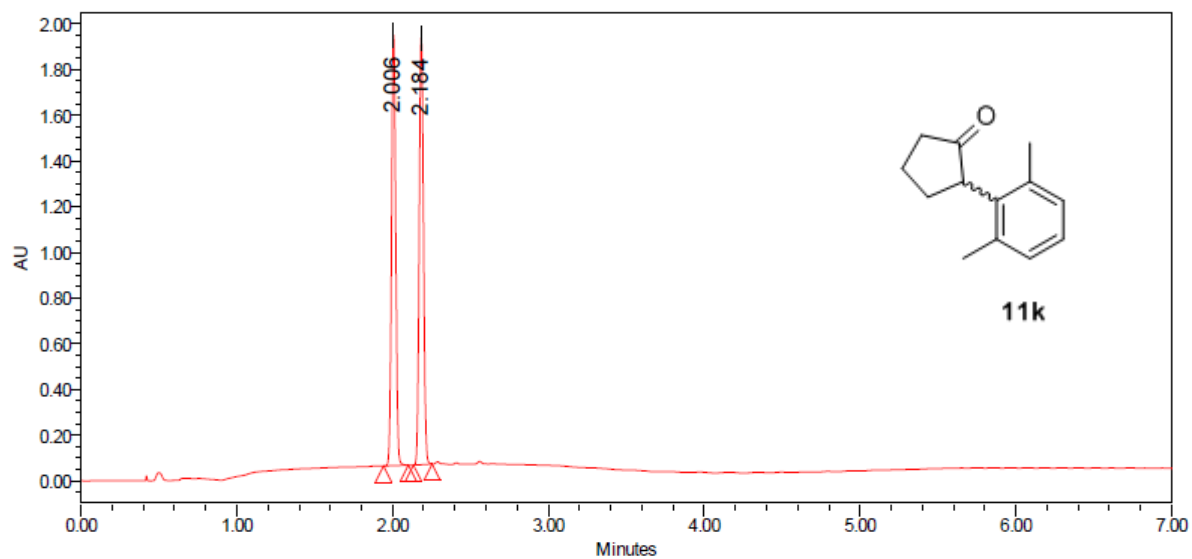
Peak Results

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



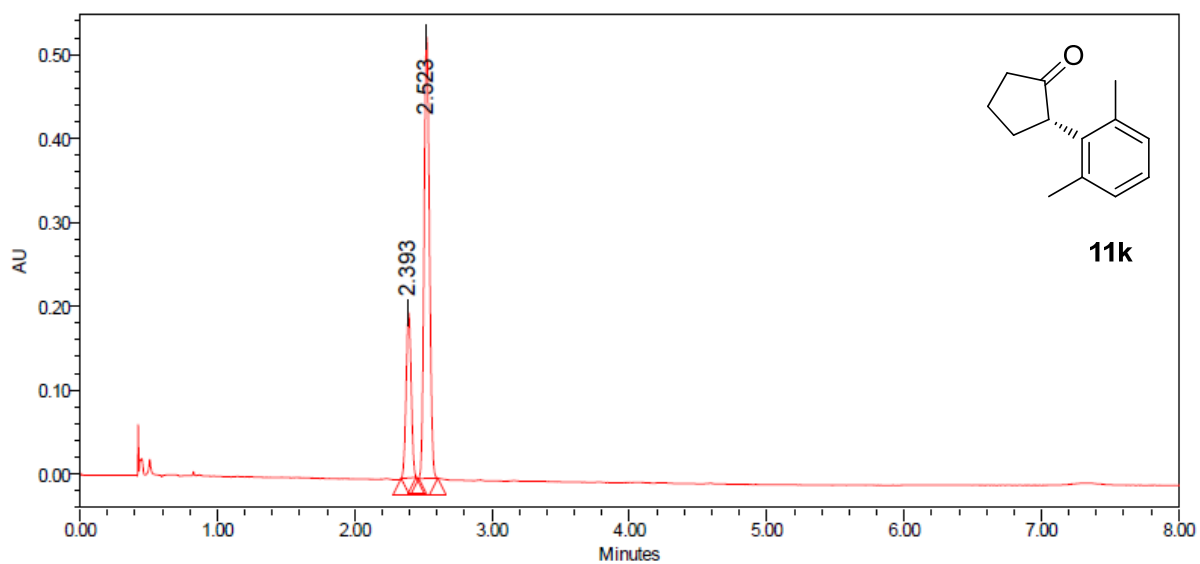
Peak Results

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



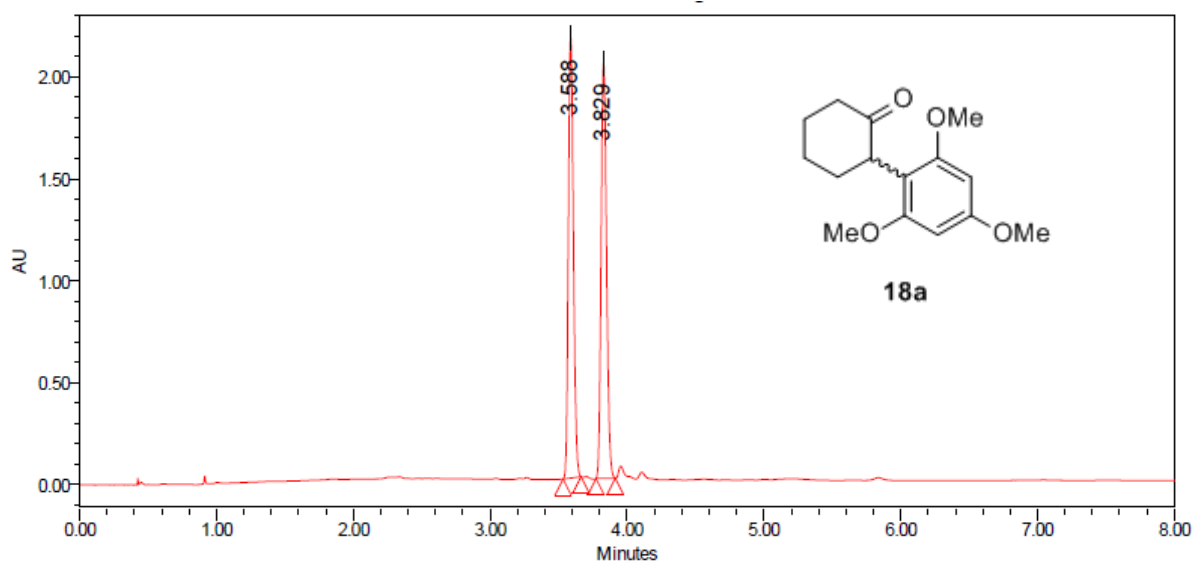
Peak Results

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



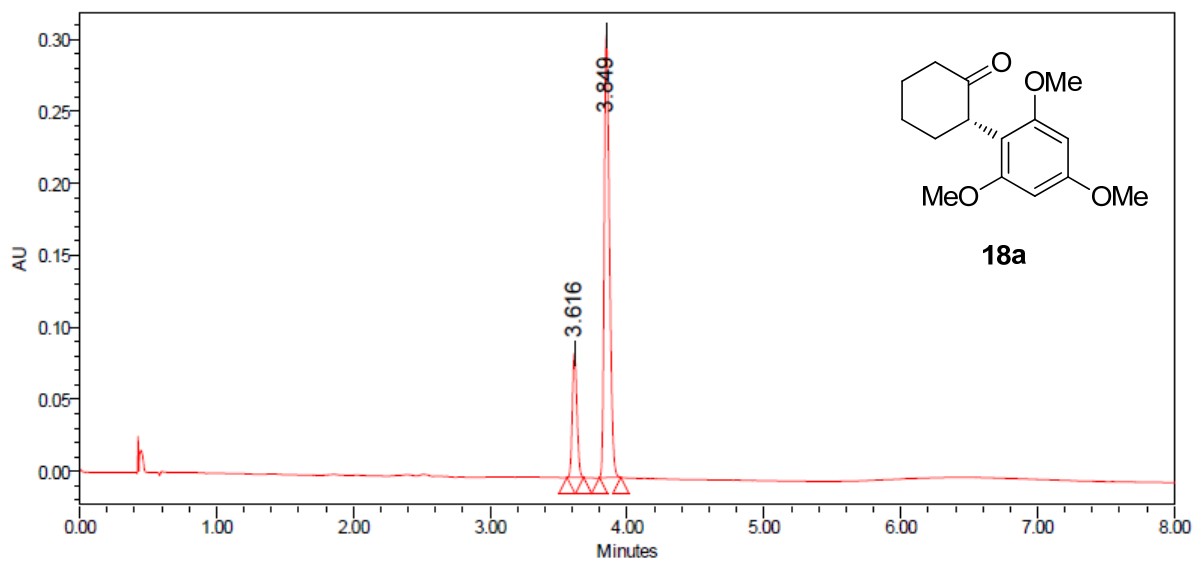
Peak Results

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



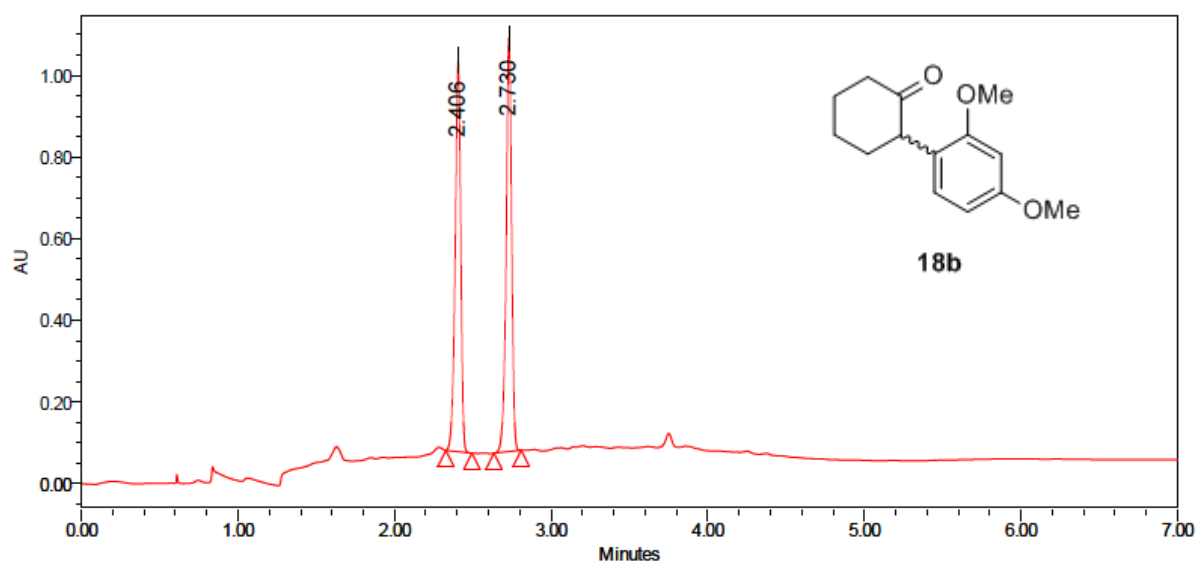
Peak Results

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



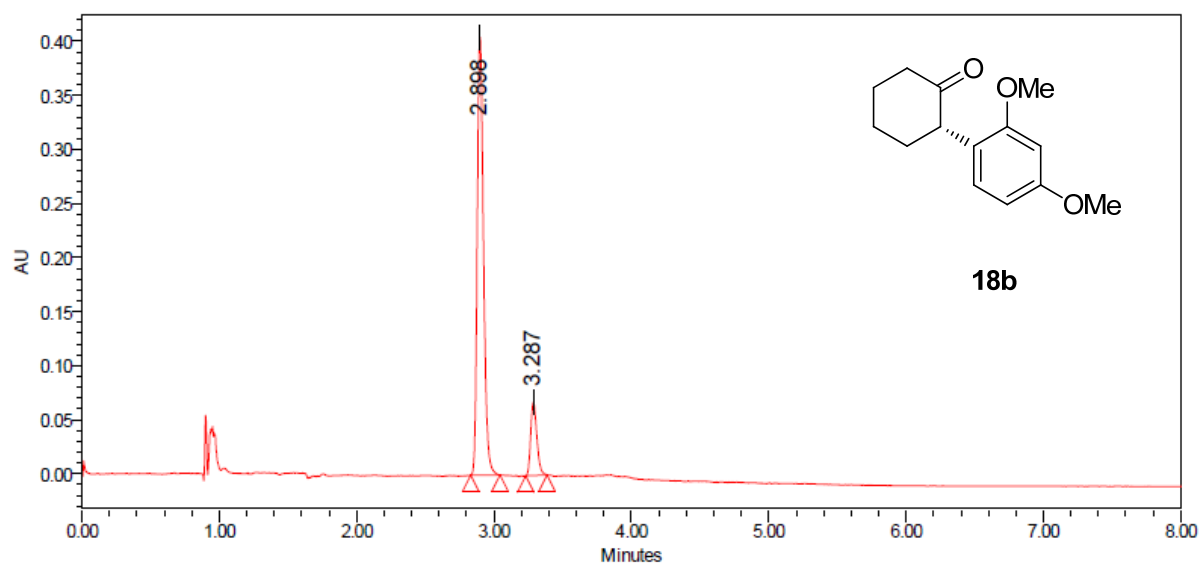
Peak Results

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



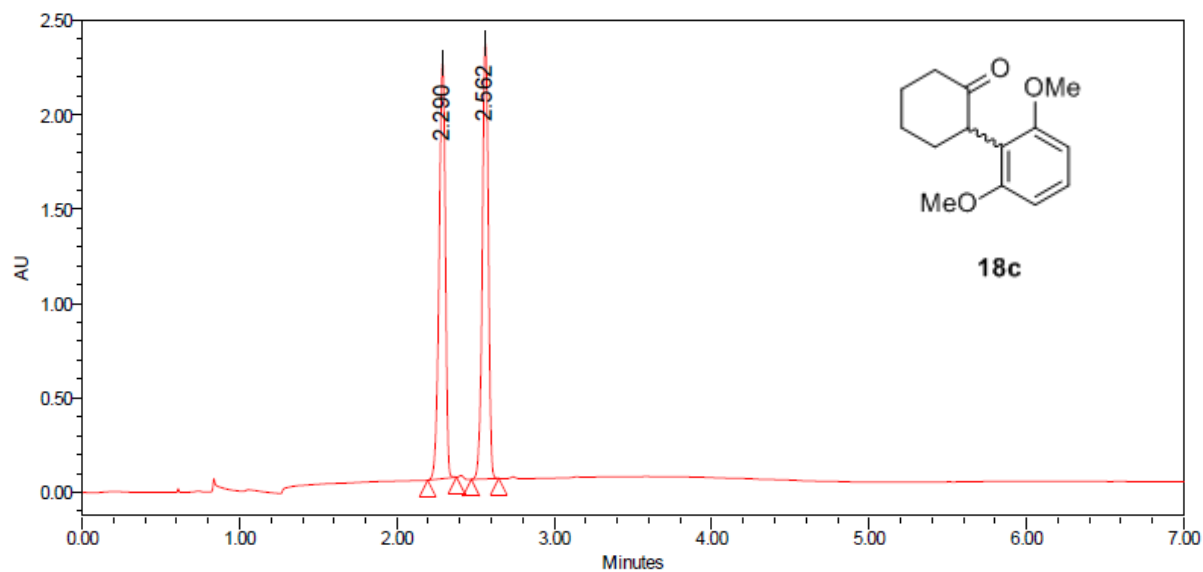
Peak Results

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



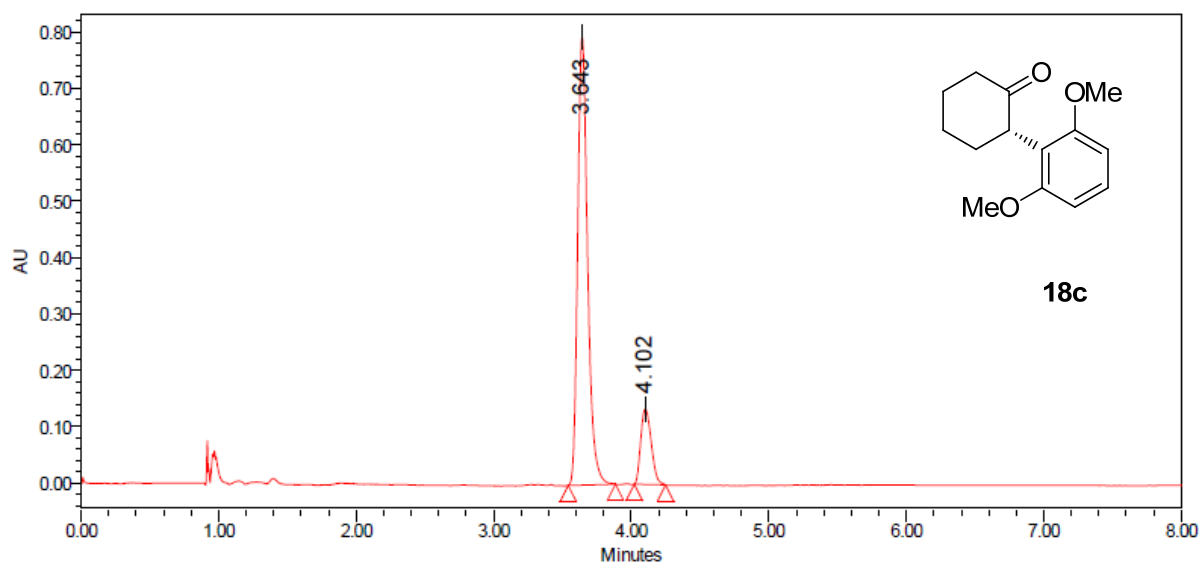
Peak Results

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



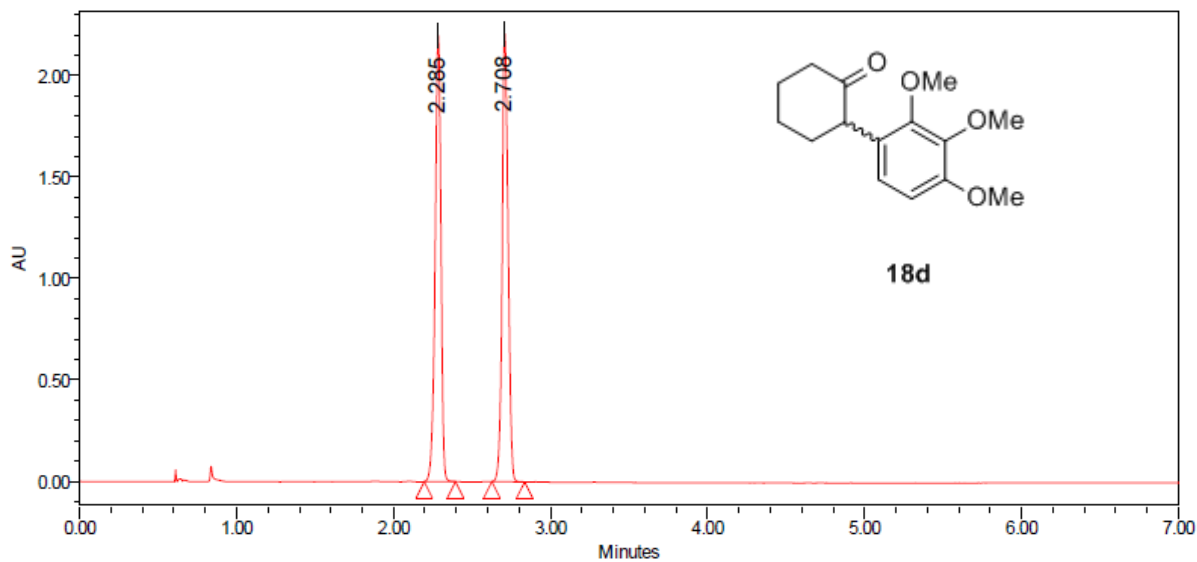
Peak Results

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



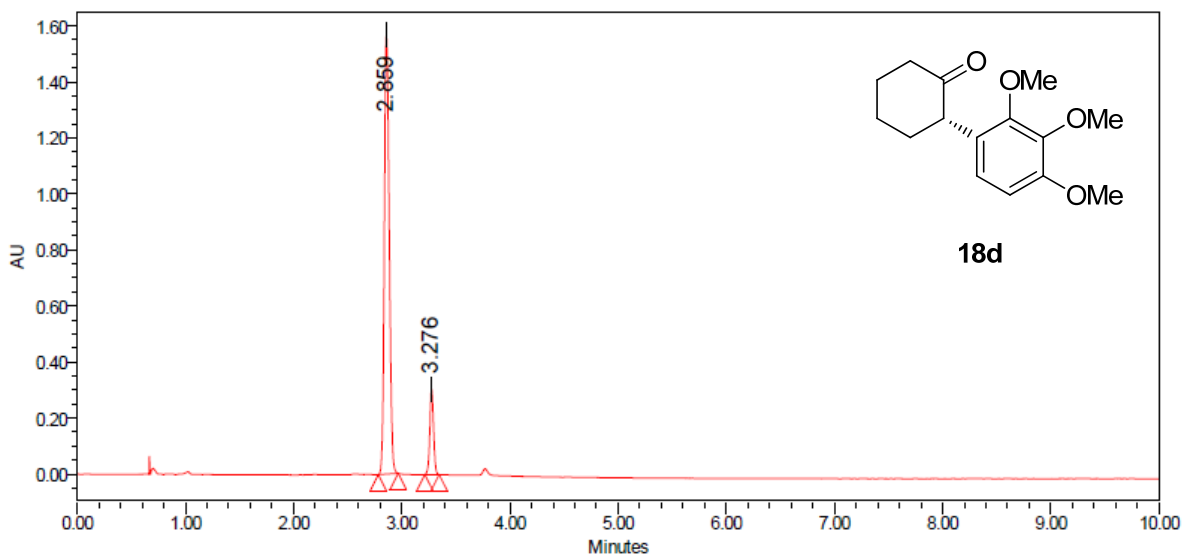
Peak Results

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



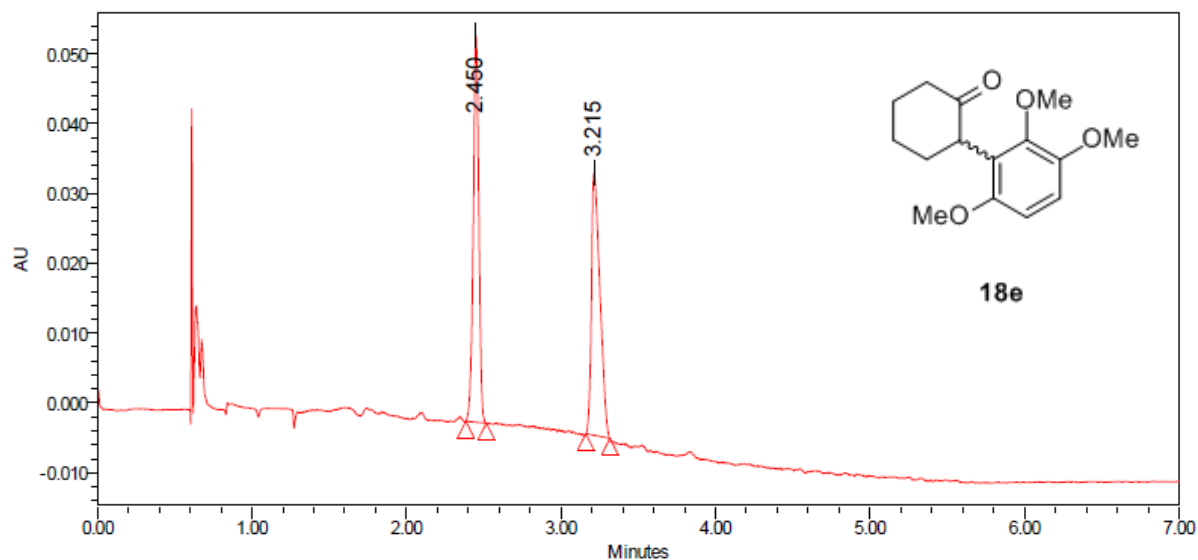
Peak Results

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



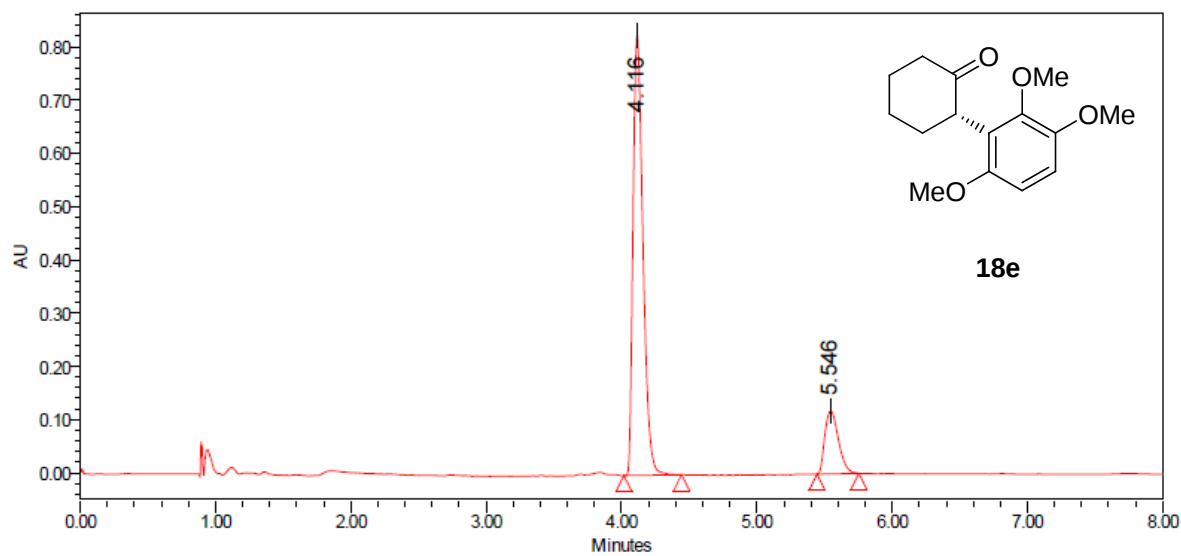
Peak Results

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



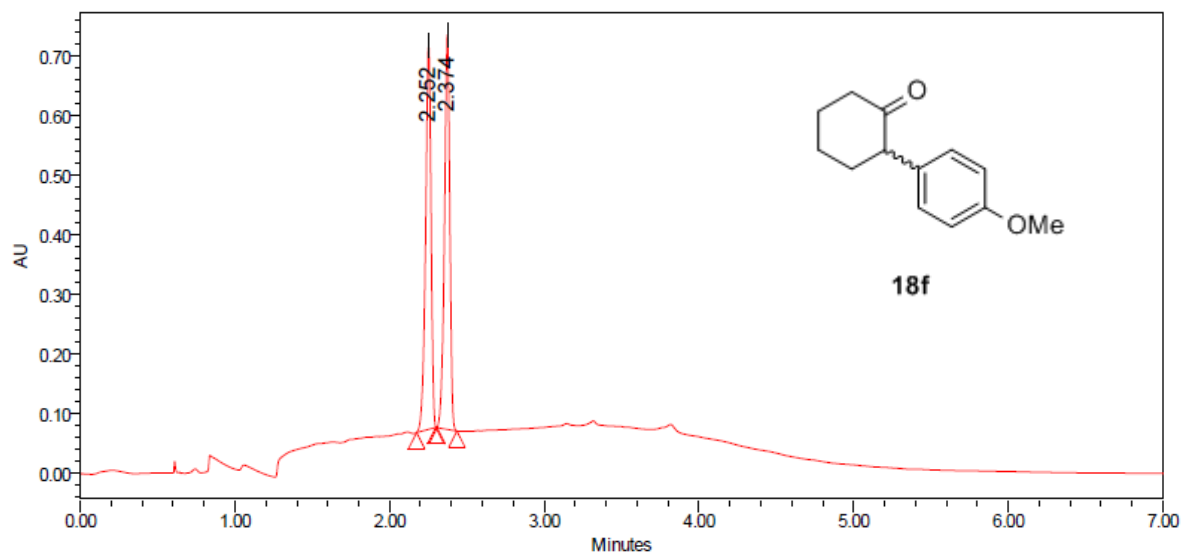
Peak Results

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



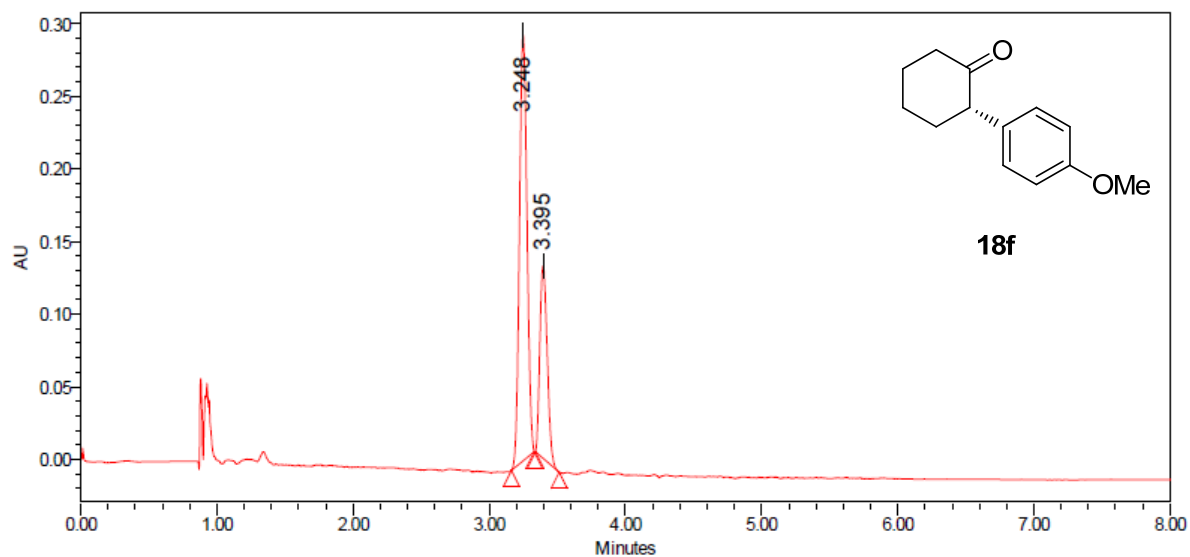
Peak Results

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



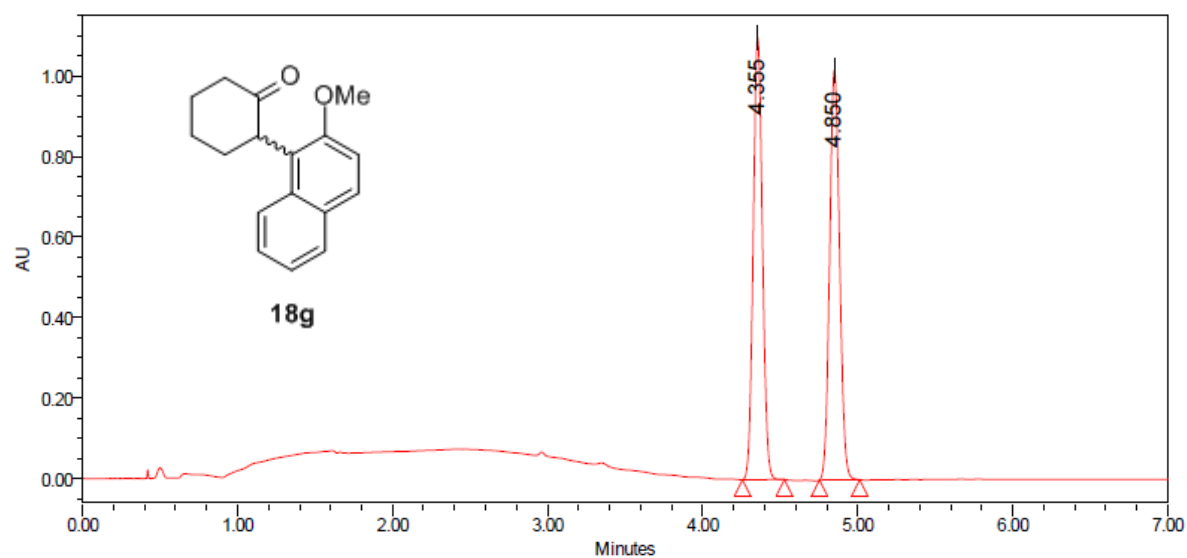
Peak Results

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



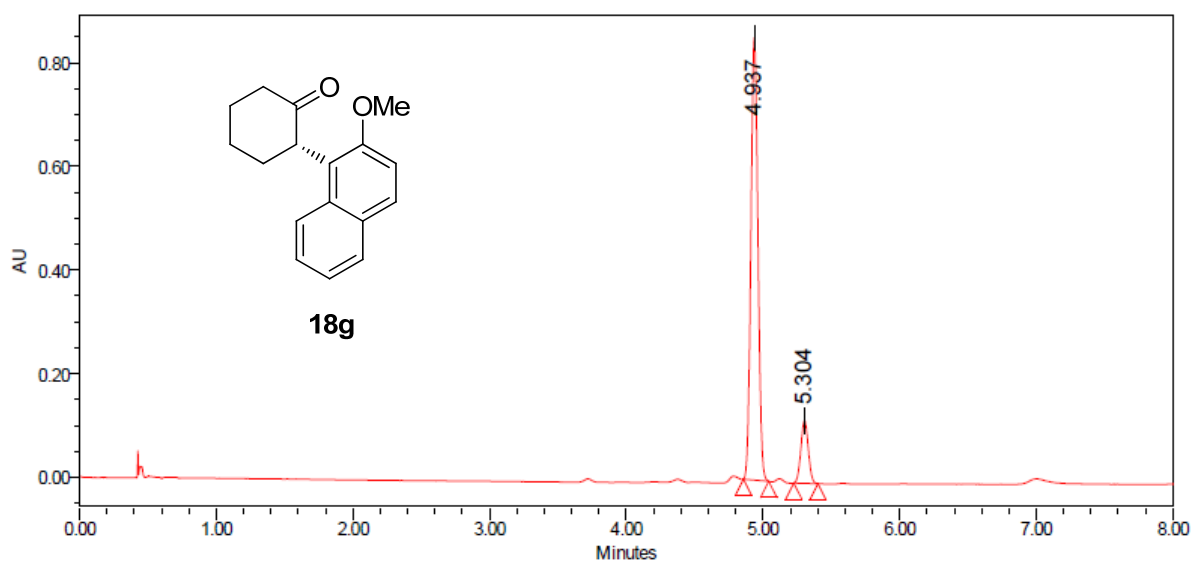
Peak Results

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



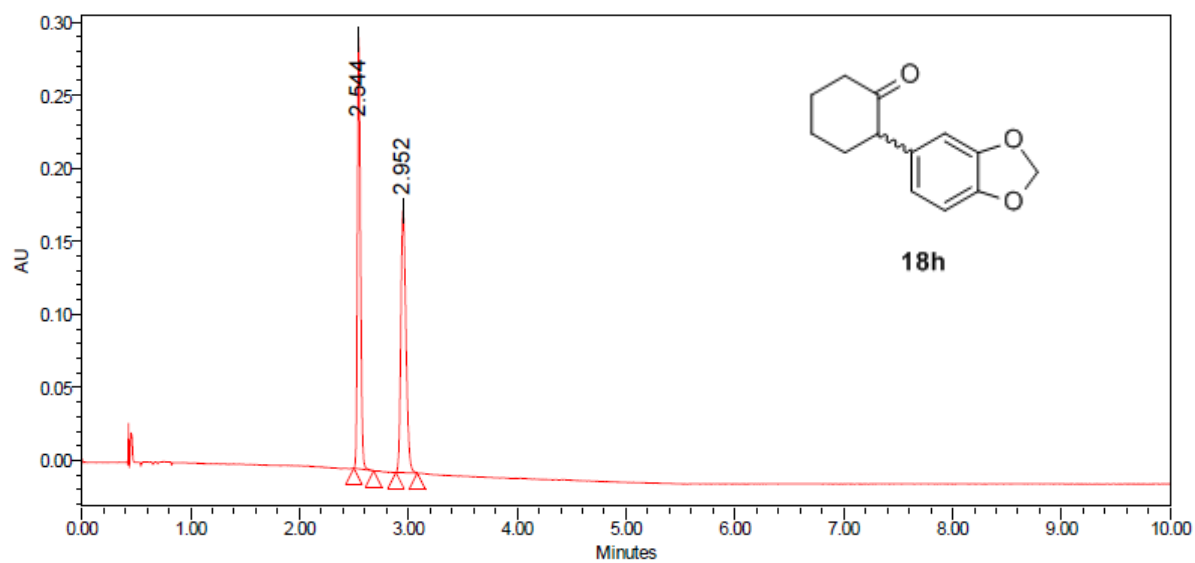
Peak Results

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



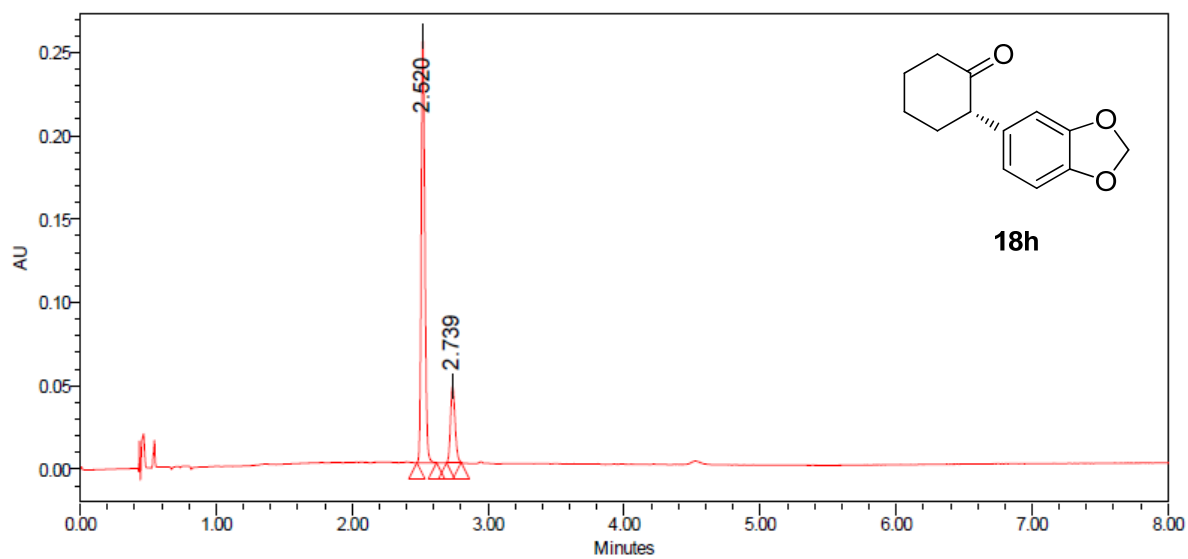
Peak Results

	Name	RT	Area	Height	% Area
1		4.937	3056597	854002	87.04
2		5.304	455061	120651	12.96



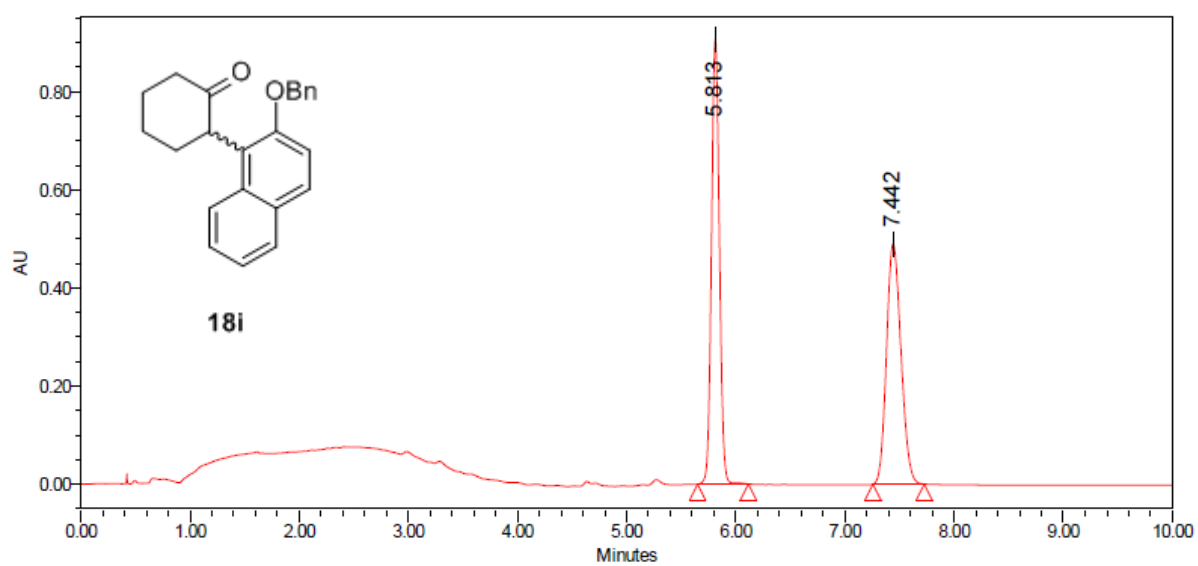
Peak Results

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



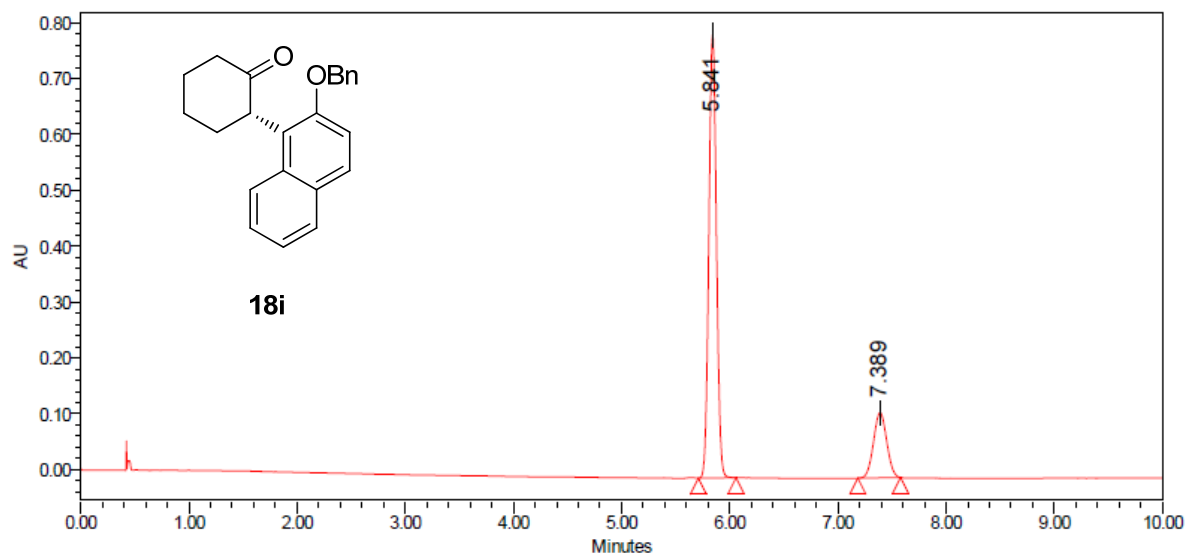
Peak Results

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



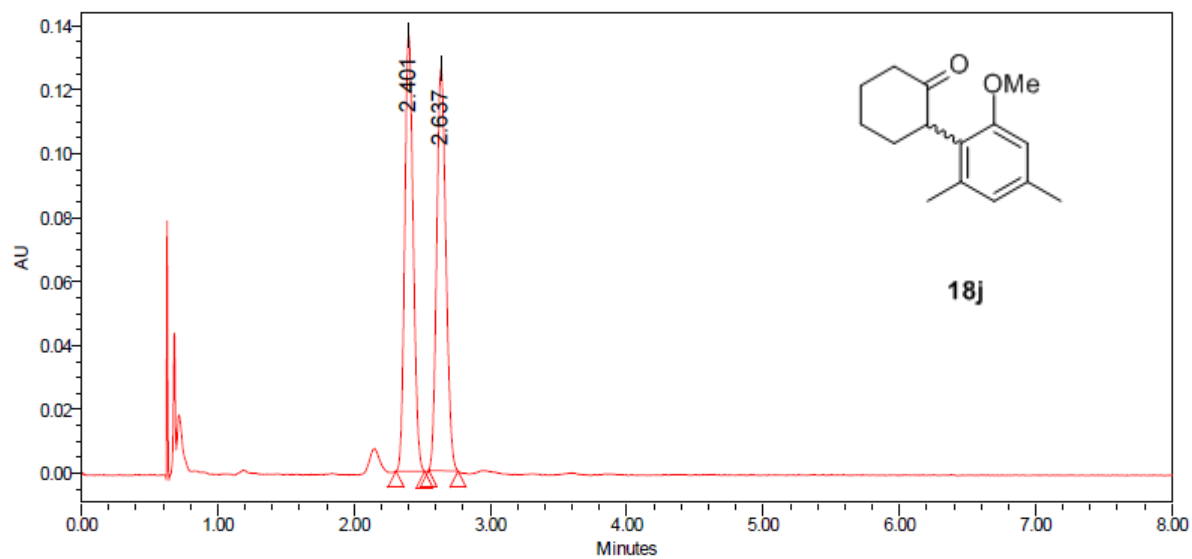
Peak Results

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

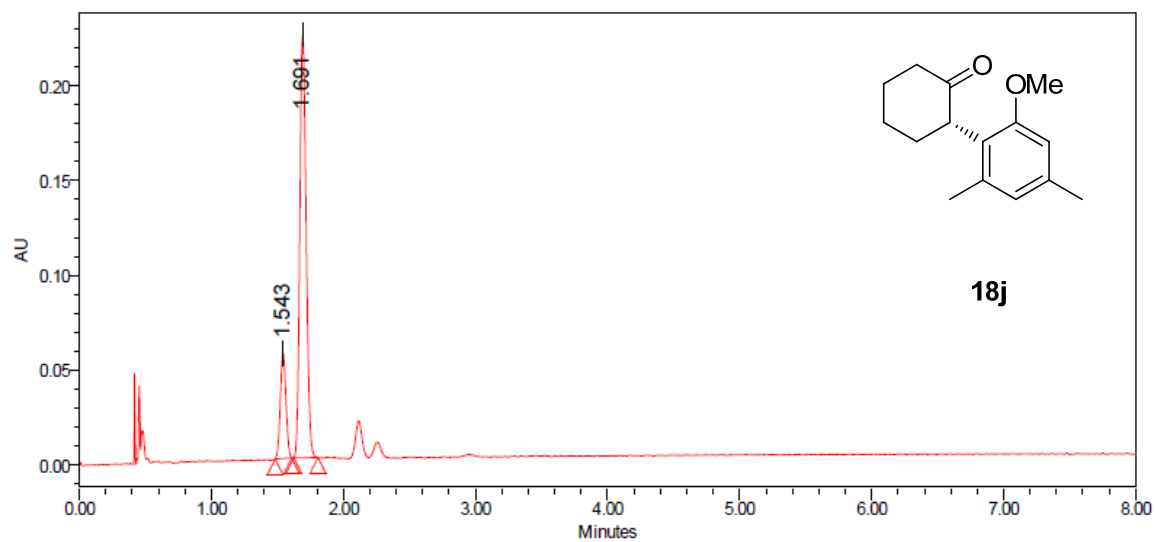


Peak Results

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



Name	RT	Area	Height	% Area
1	2.401	591146	136444	49.88
2	2.637	594062	125815	50.12



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

X-Ray Crystal Structures

