Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Organocatalytic Vinylogous Mannich Reaction of Trimethylsiloxyfuran with Isatin-derived Benzhydryl-Ketimines

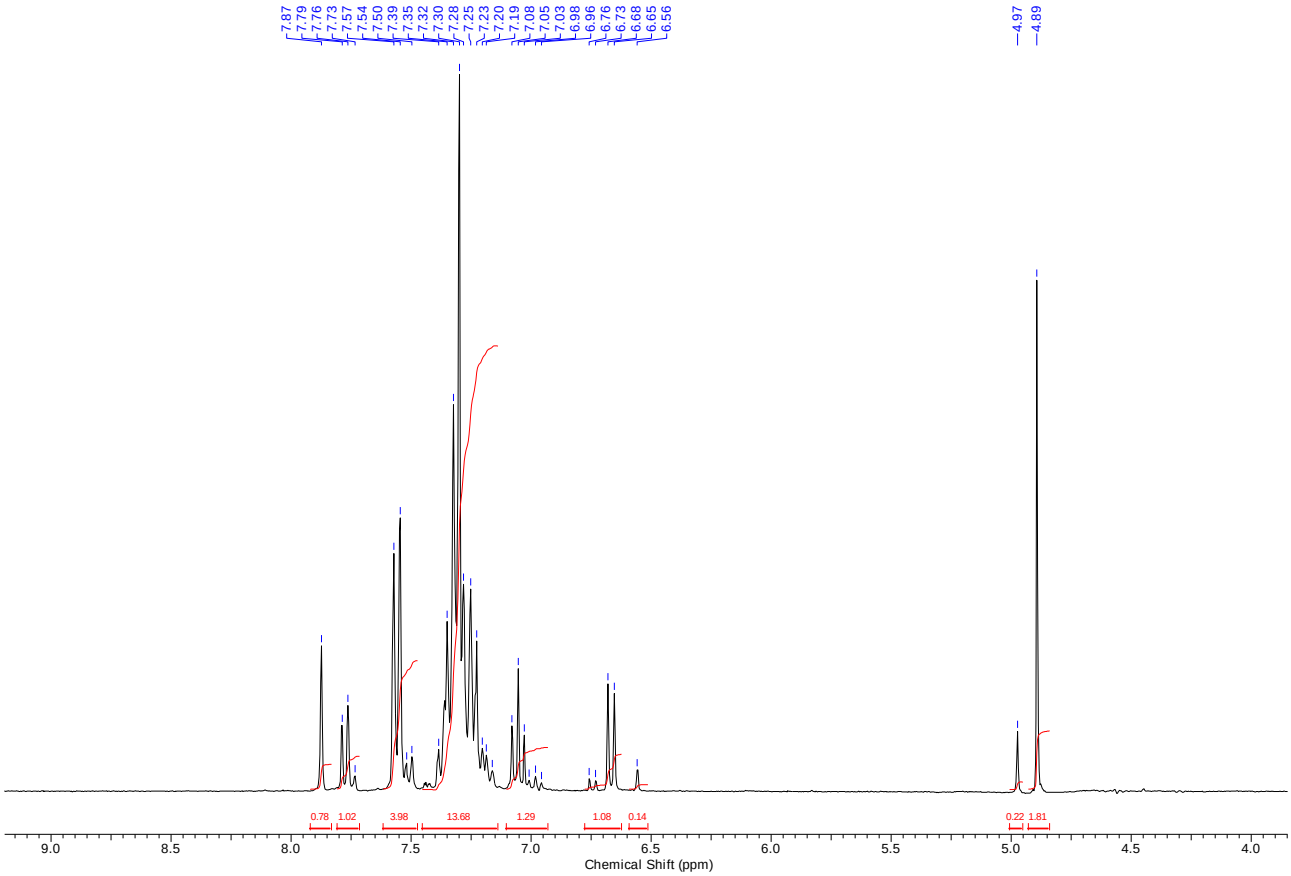
Giulia Rainoldi,[a] Alessandro Sacchetti,[b] Alessandra Silvani[*,a] and Giordano Lesma[a]*

[a]Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, Milano, 20133, Italy.
[b]Dipartimento di Chimica, Materiali ed Ing. Chimica 'Giulio Natta', Politecnico di Milano, p.zza Leonardo da Vinci 32, Milano, 20133, Italy.

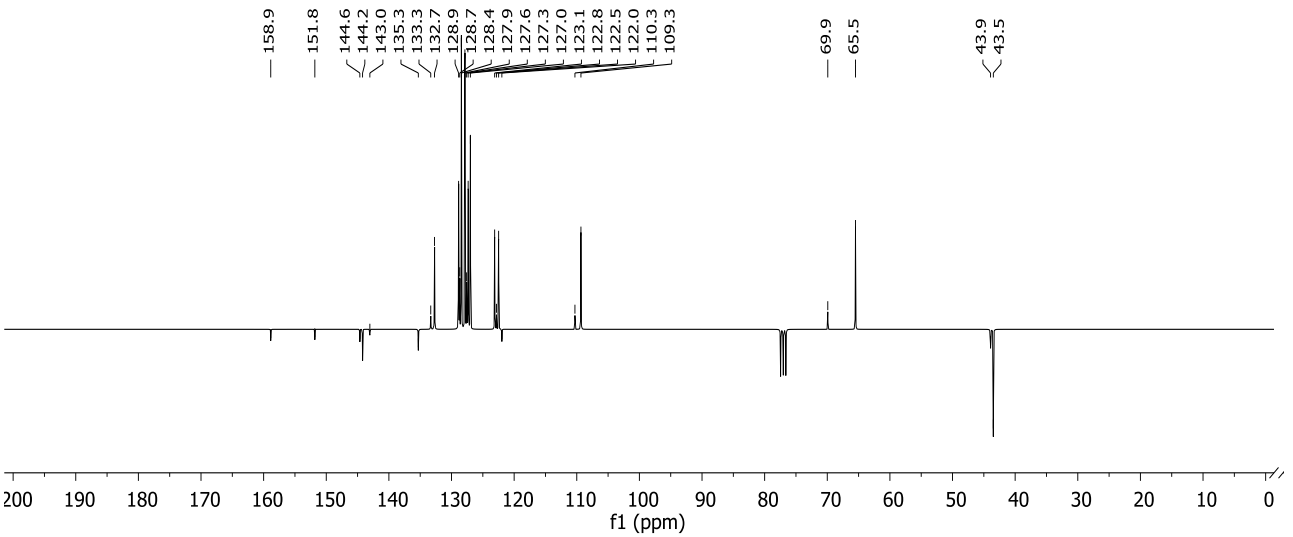
E-mail: alessandra.silvani@unimi.it

Table of contents

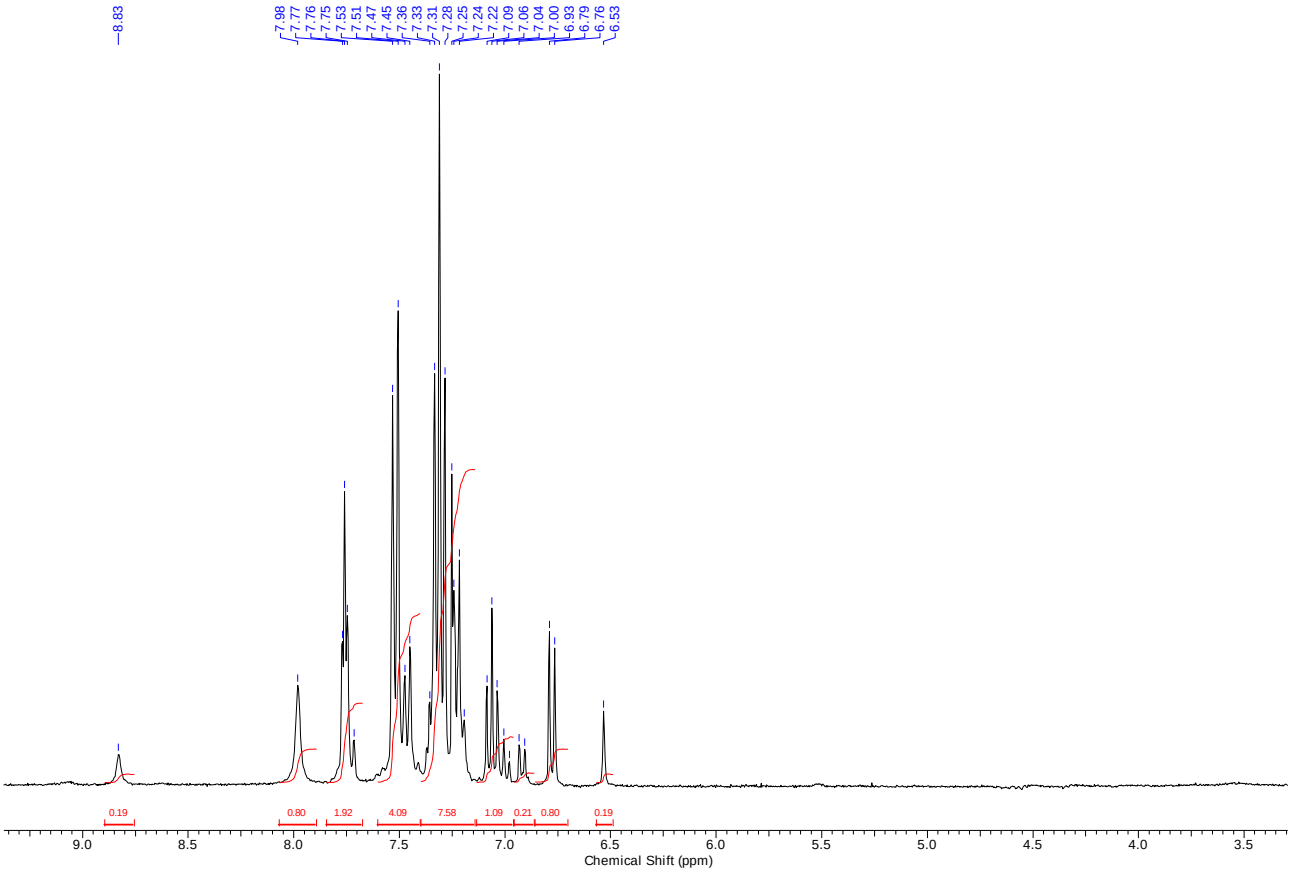
Compound 1a: ^{1}H NMR (300 MHz, $CDCl_3$)



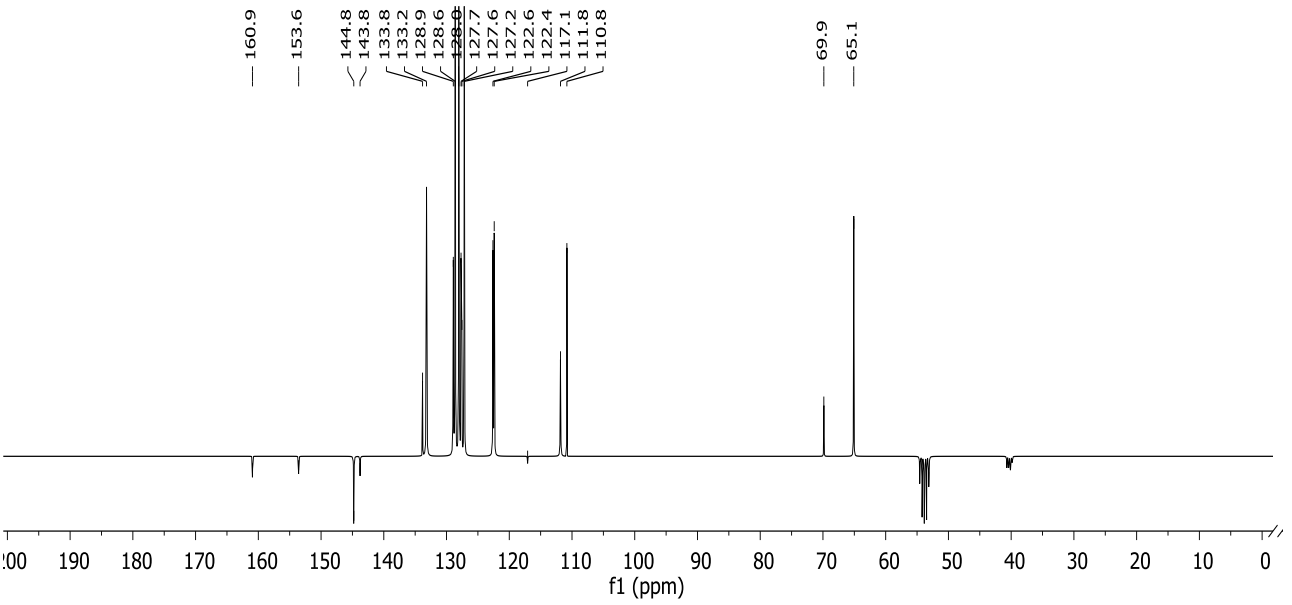
Compound 1a: ^{13}C NMR (75 MHz, $CDCl_3$)



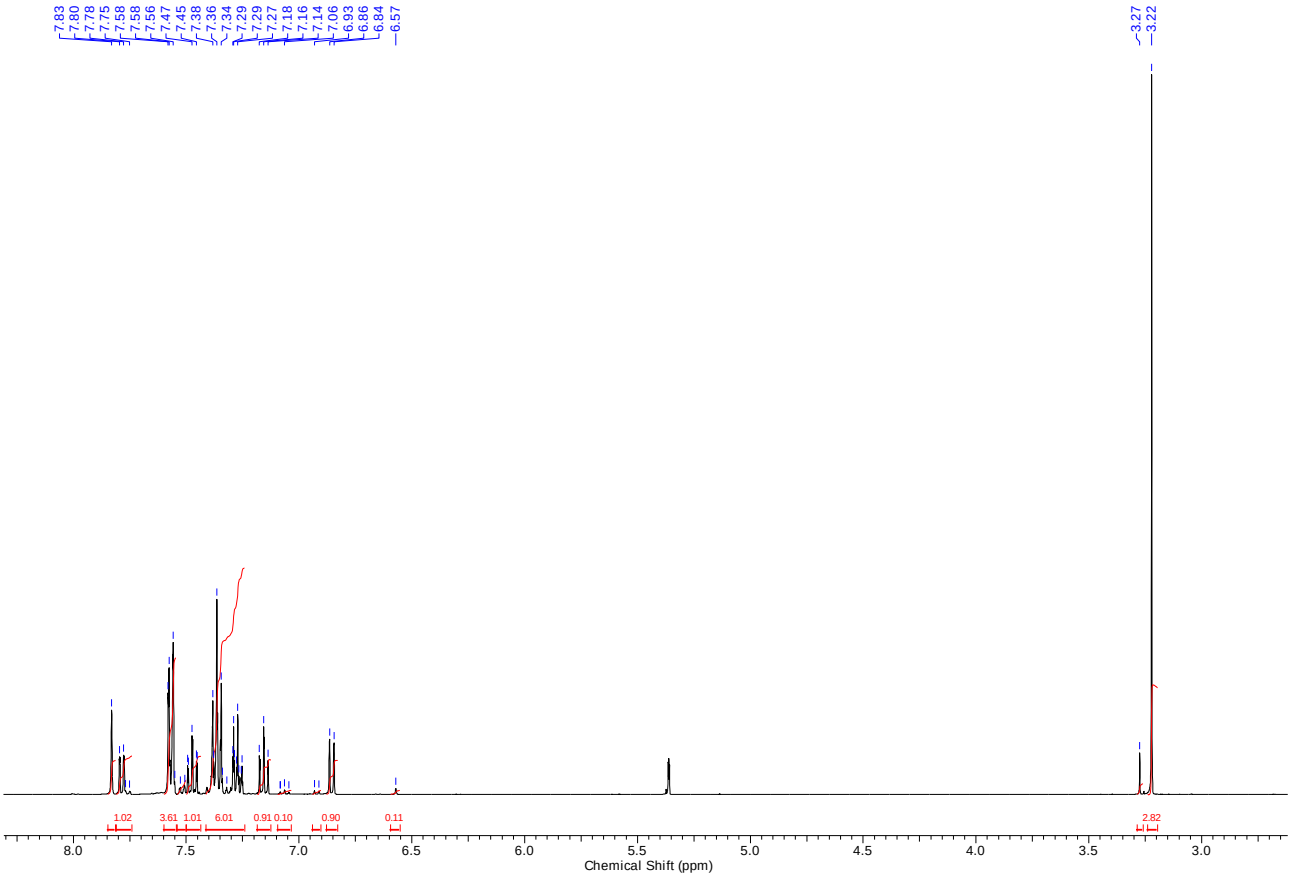
Compound 1b: ^{1}H NMR (300 MHz, $CDCl_3$)



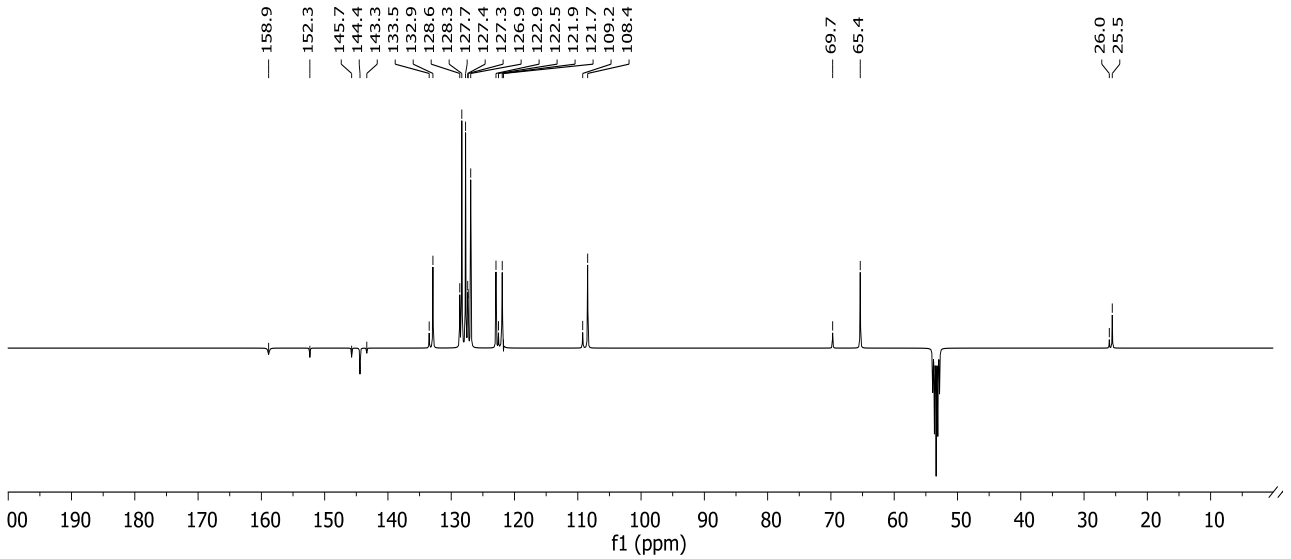
Compound 1b: ^{13}C NMR (75 MHz, CD_2Cl_2+1%DMSO-d_6)



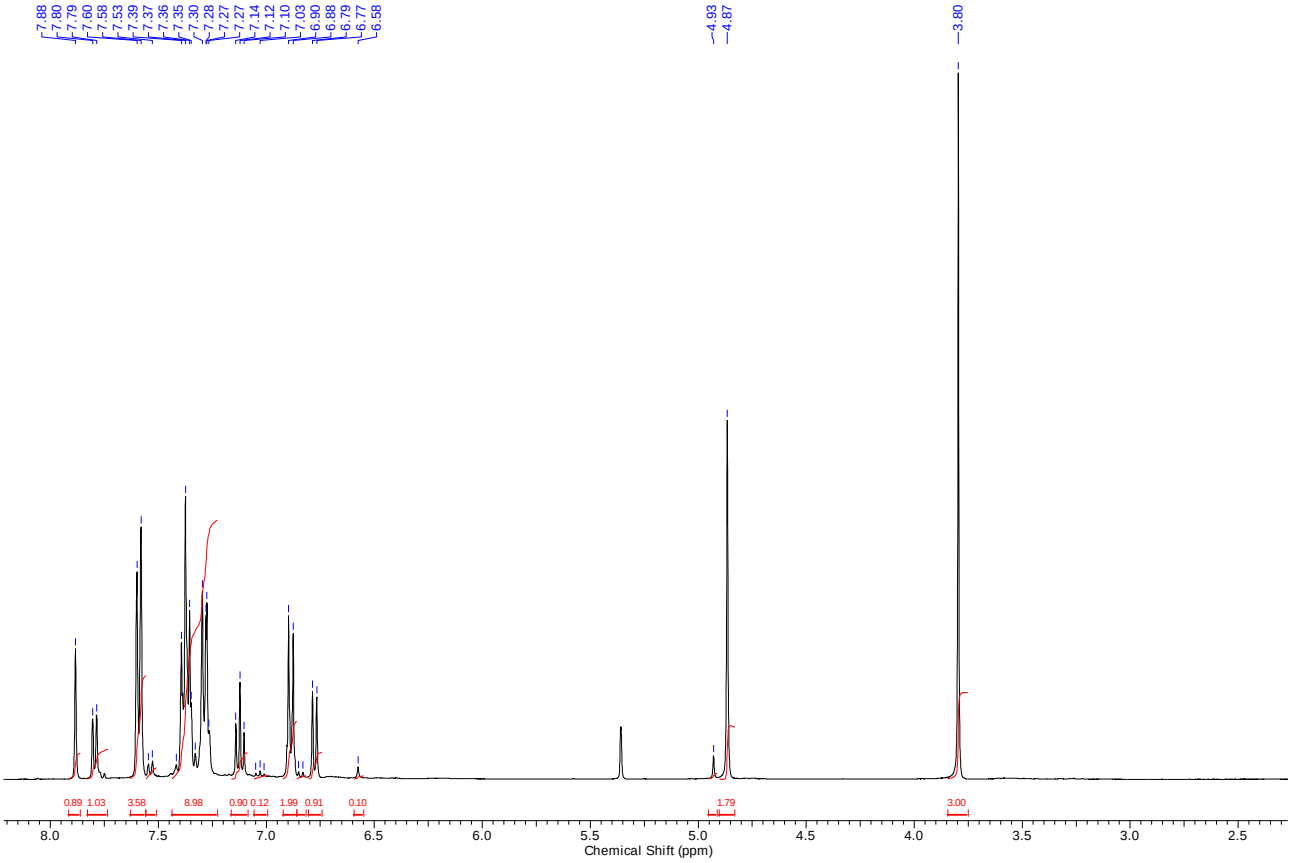
Compound 1c: ^{1}H NMR (400 MHz, CD_2Cl_2)



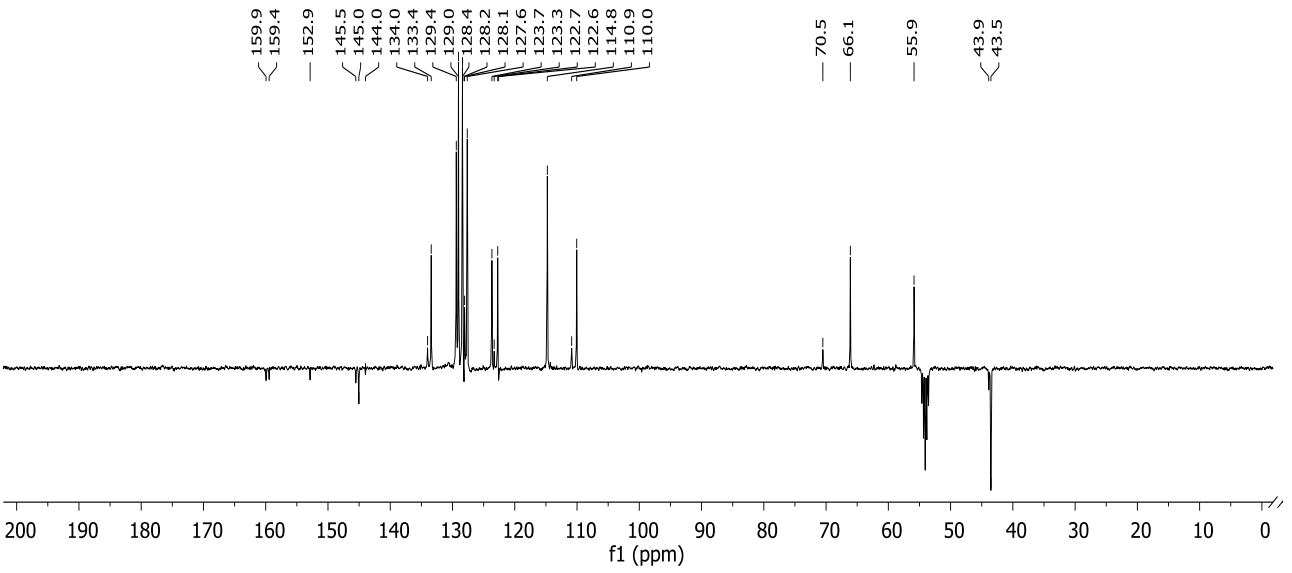
Compound 1c: ^{13}C NMR (101 MHz, CD_2Cl_2)



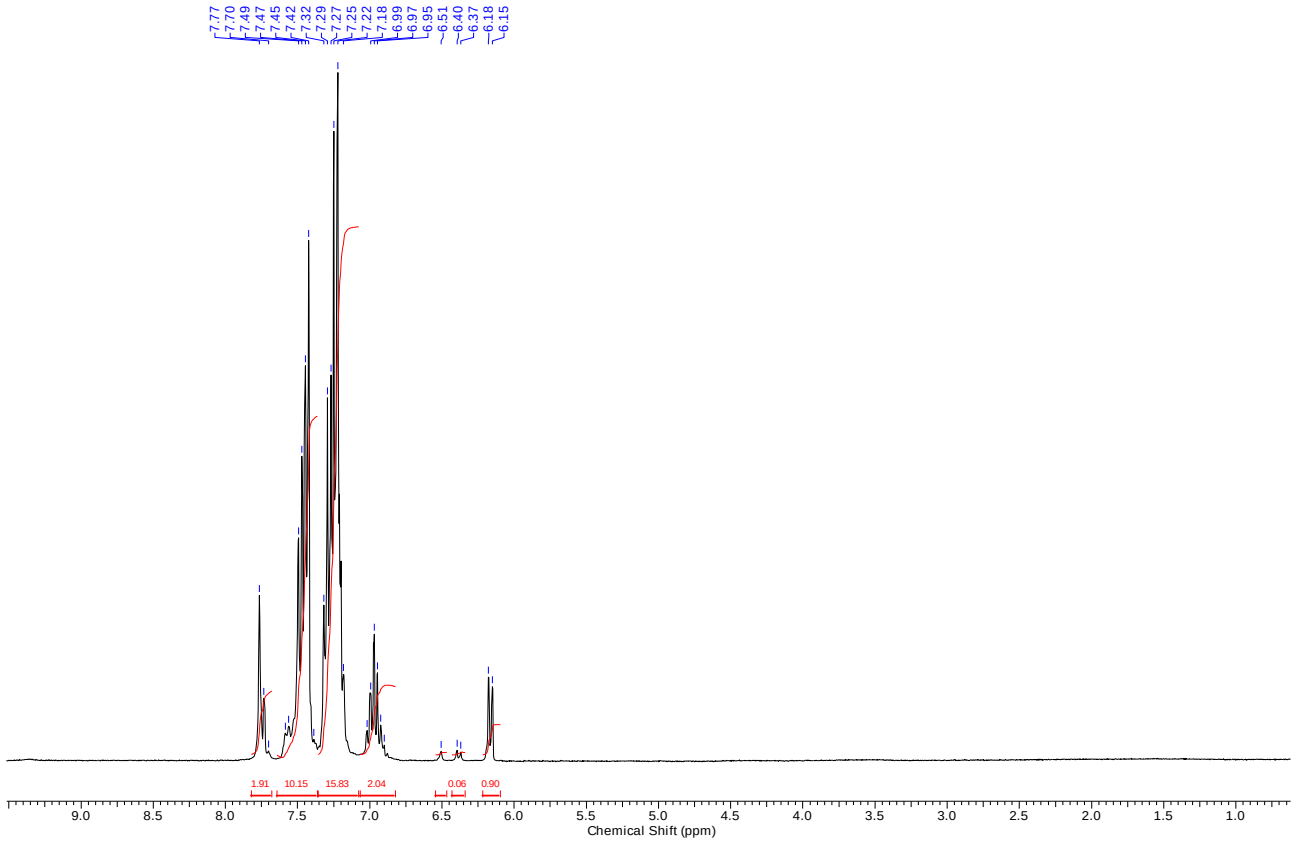
Compound 1d: ^{1}H NMR (400 MHz, CD_2Cl_2)



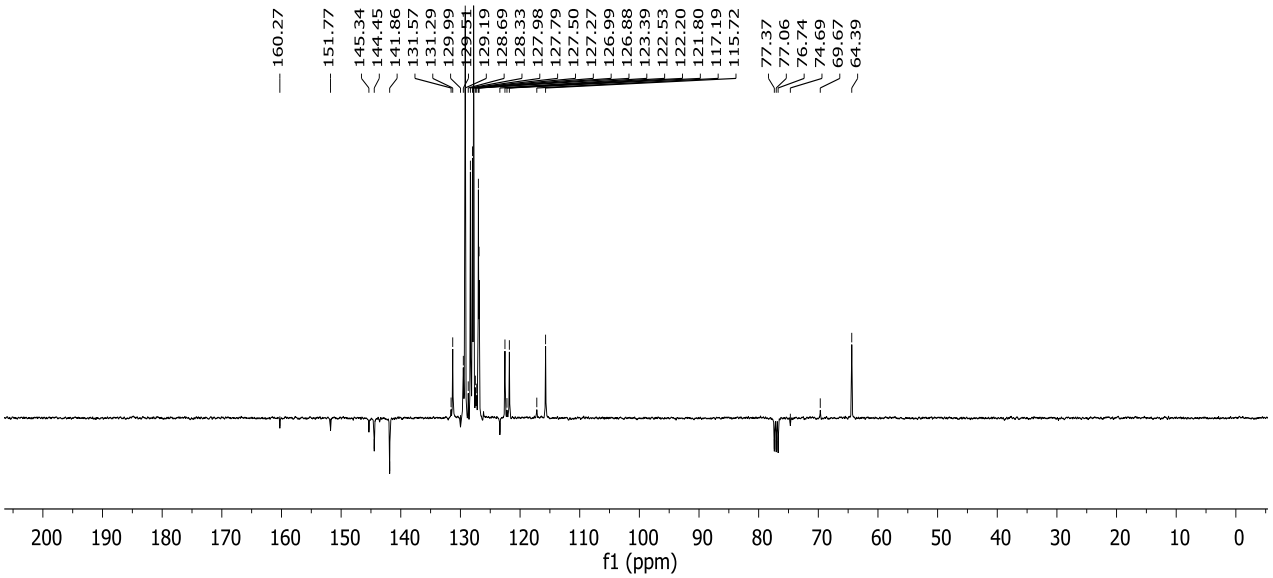
Compound 1d: ^{13}C NMR (101 MHz, CD_2Cl_2)



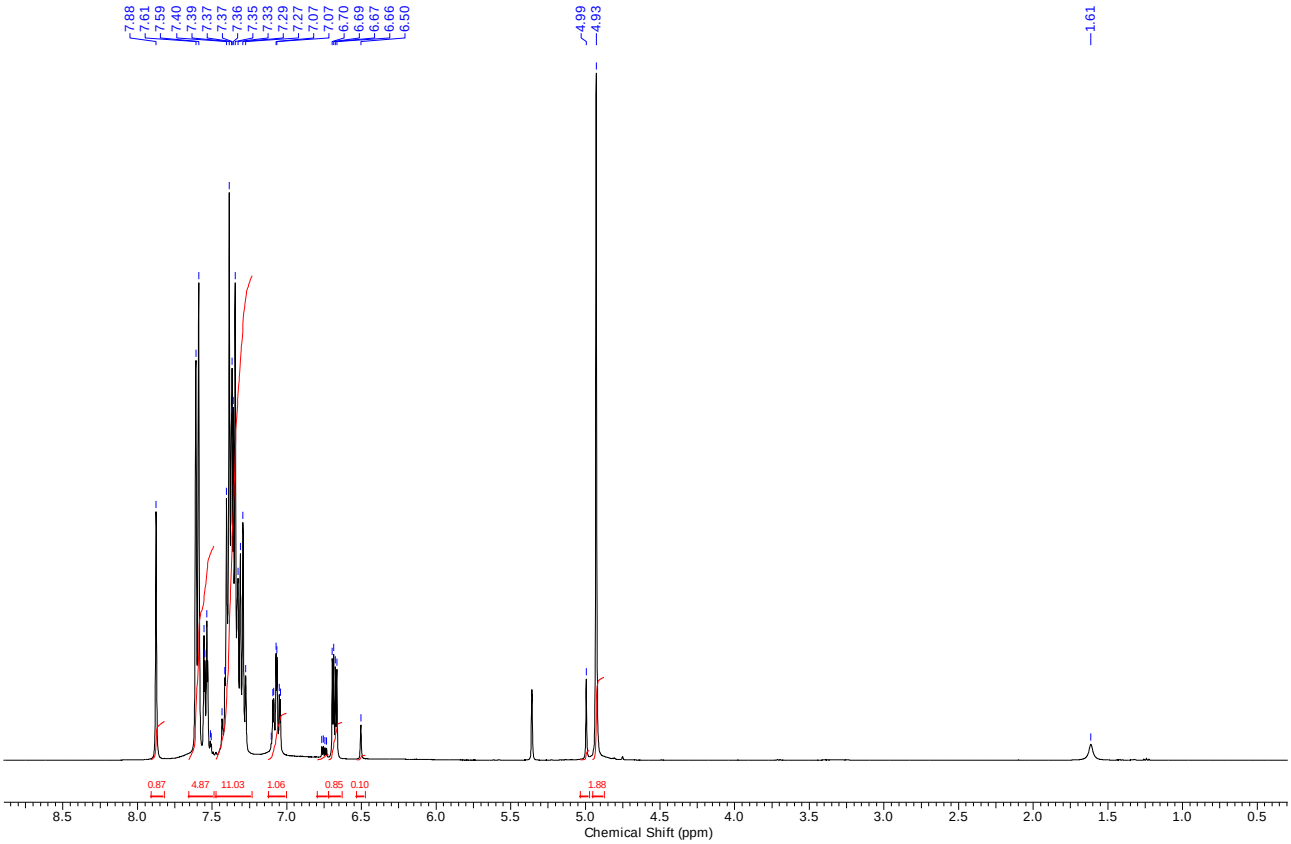
Compound **1e:** ^{1}H NMR (400 MHz, $CDCl_3$)



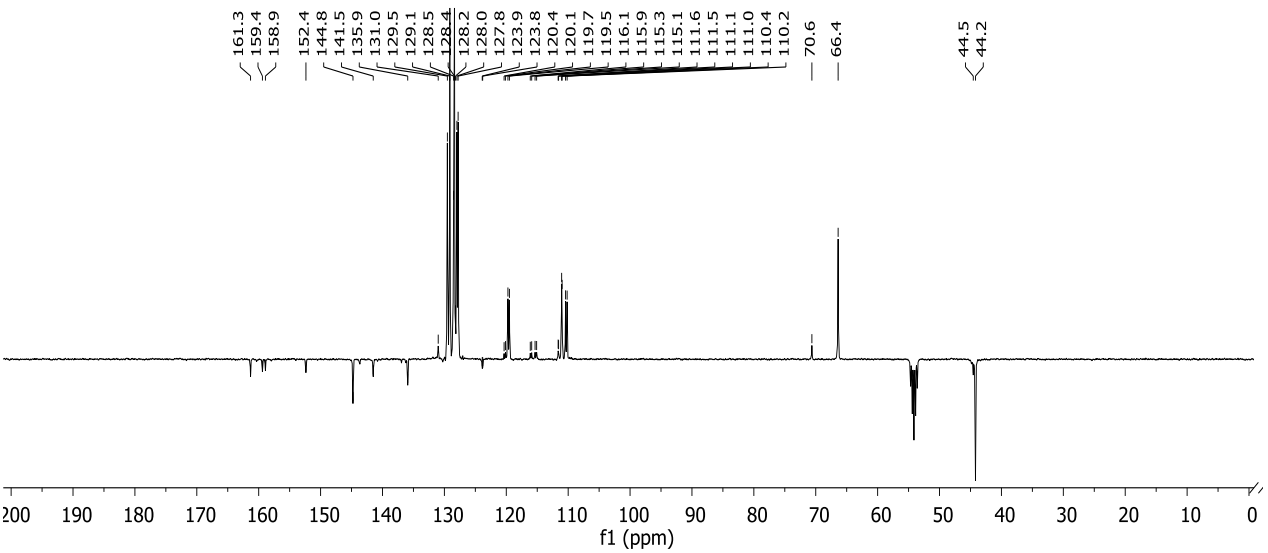
Compound **1e:** ^{13}C NMR (101 MHz, $CDCl_3$)



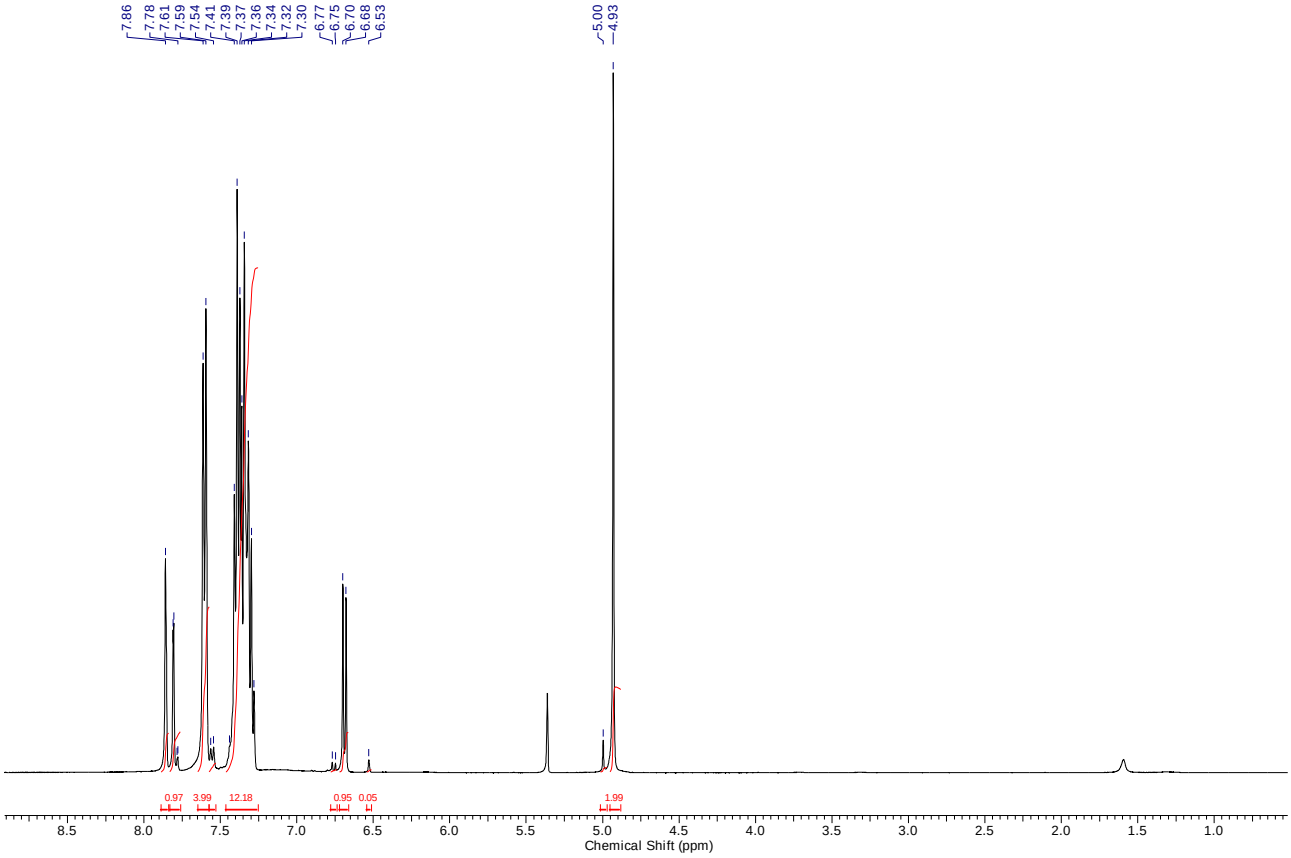
Compound 1f: ^{1}H NMR (400 MHz, CD_2Cl_2)



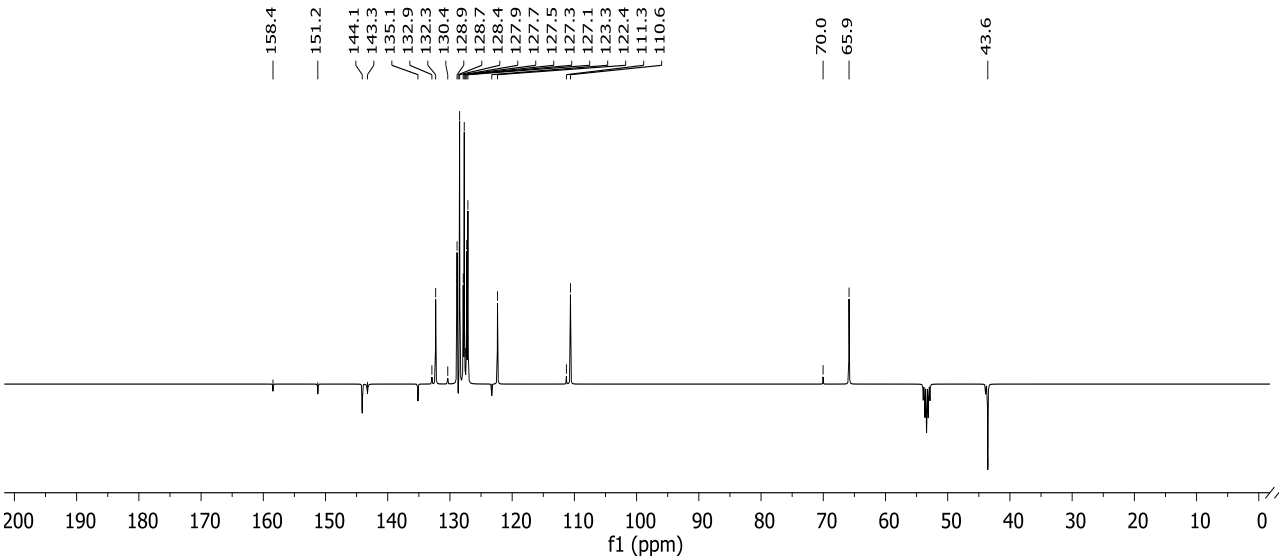
Compound 1f: ^{13}C NMR (101 MHz, CD_2Cl_2)



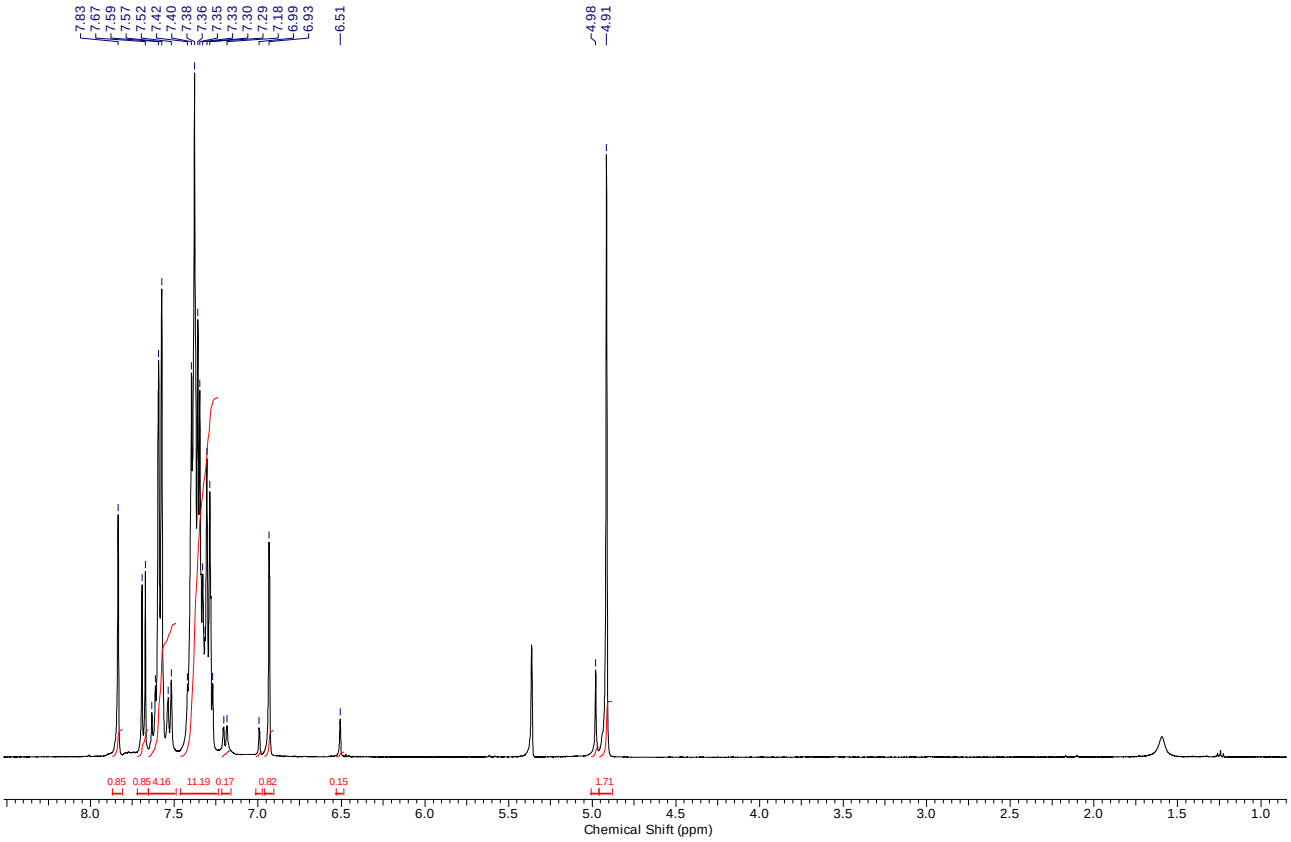
Compound 1g: ^{1}H NMR (400 MHz, CD_2Cl_2)



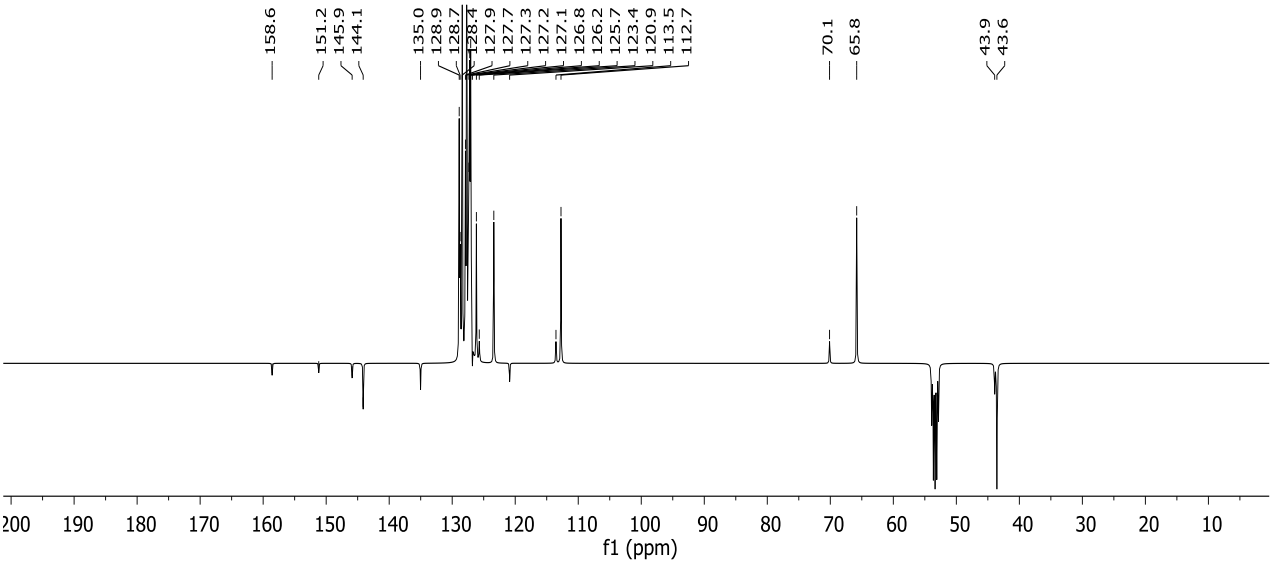
Compound 1g: ^{13}C NMR (101 MHz, CD_2Cl_2)



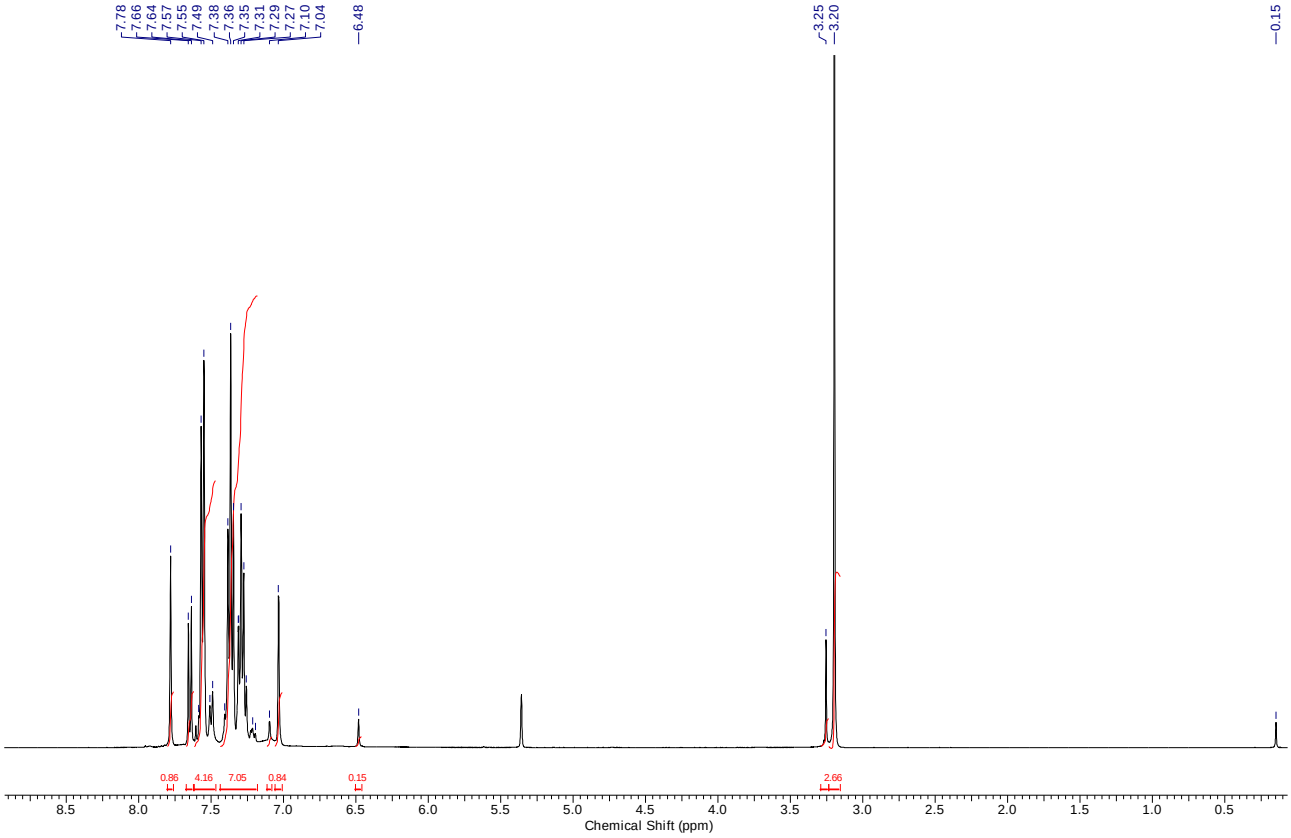
Compound 1h: ^{1}H NMR (400 MHz, CD_2Cl_2)



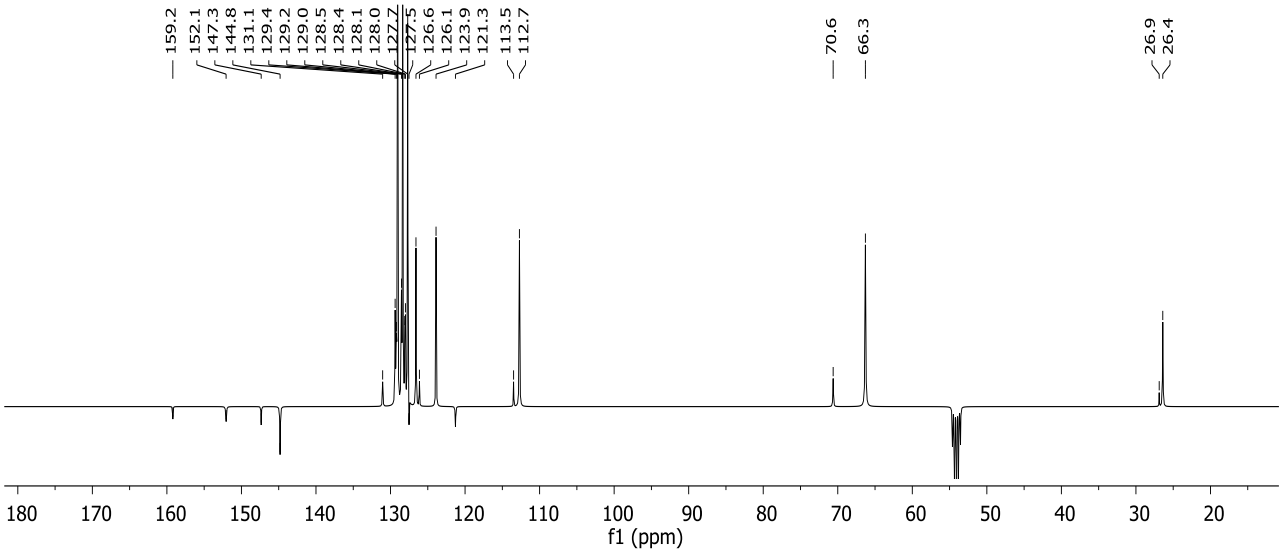
Compound 1h: ^{13}C NMR (101 MHz, CD_2Cl_2)



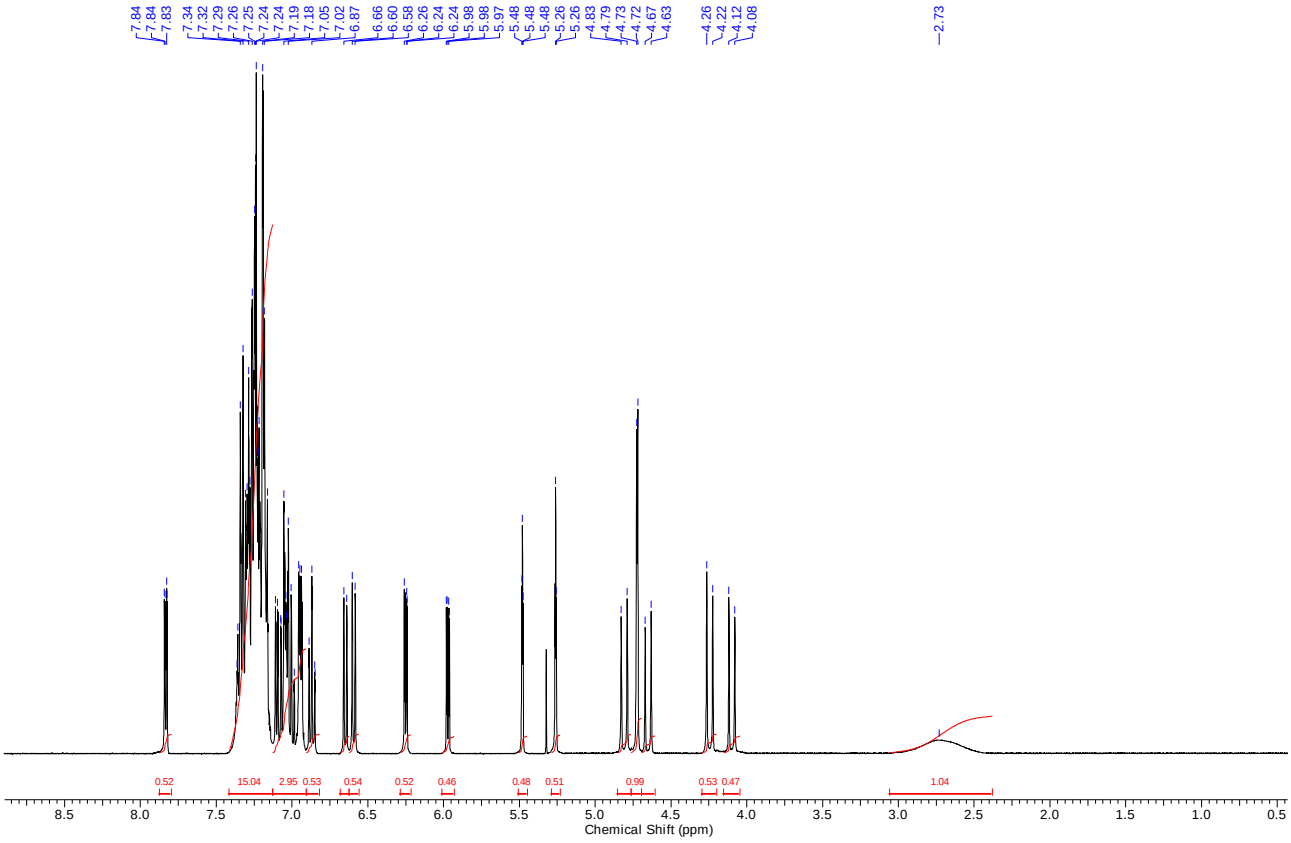
Compound 1i: ^{1}H NMR (400 MHz, CD_2Cl_2)



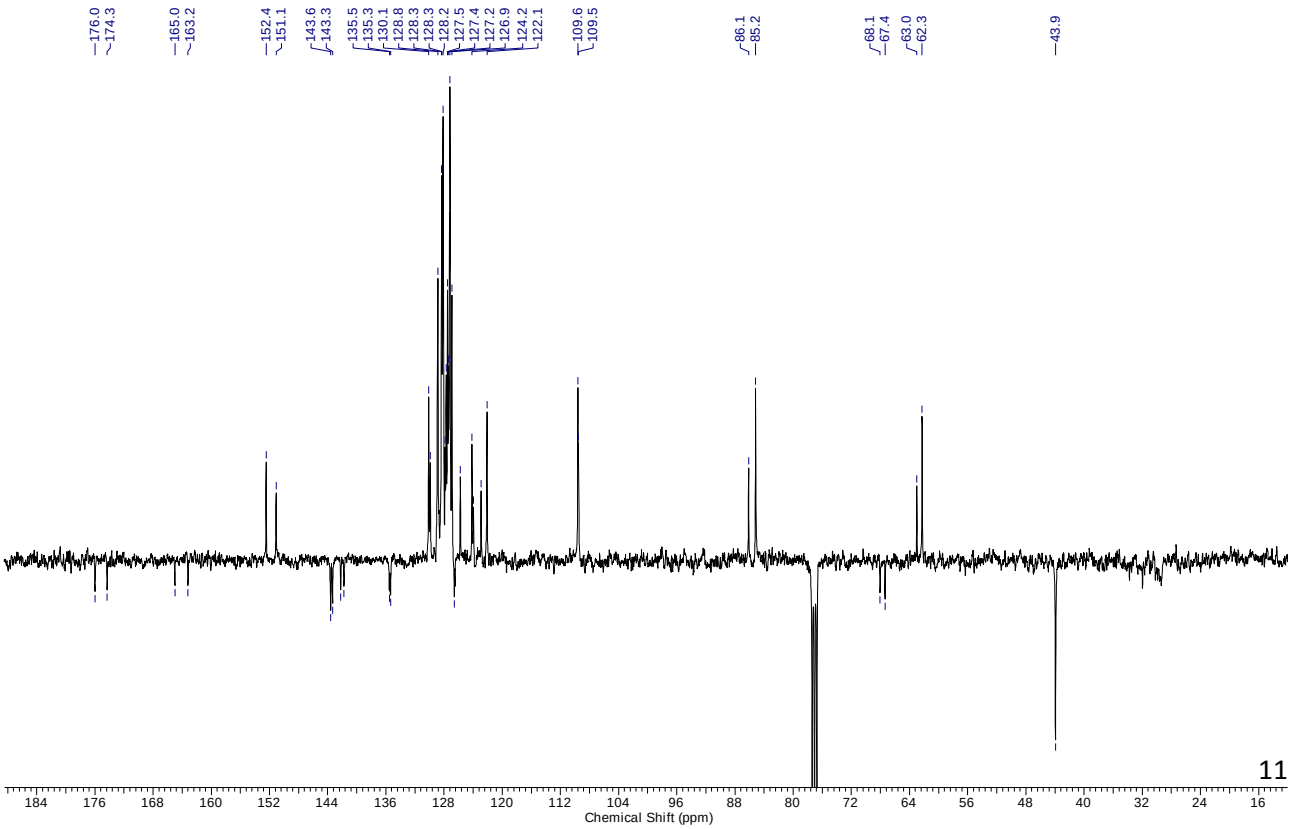
Compound 1i: ^{13}C NMR (101 MHz, CD_2Cl_2)



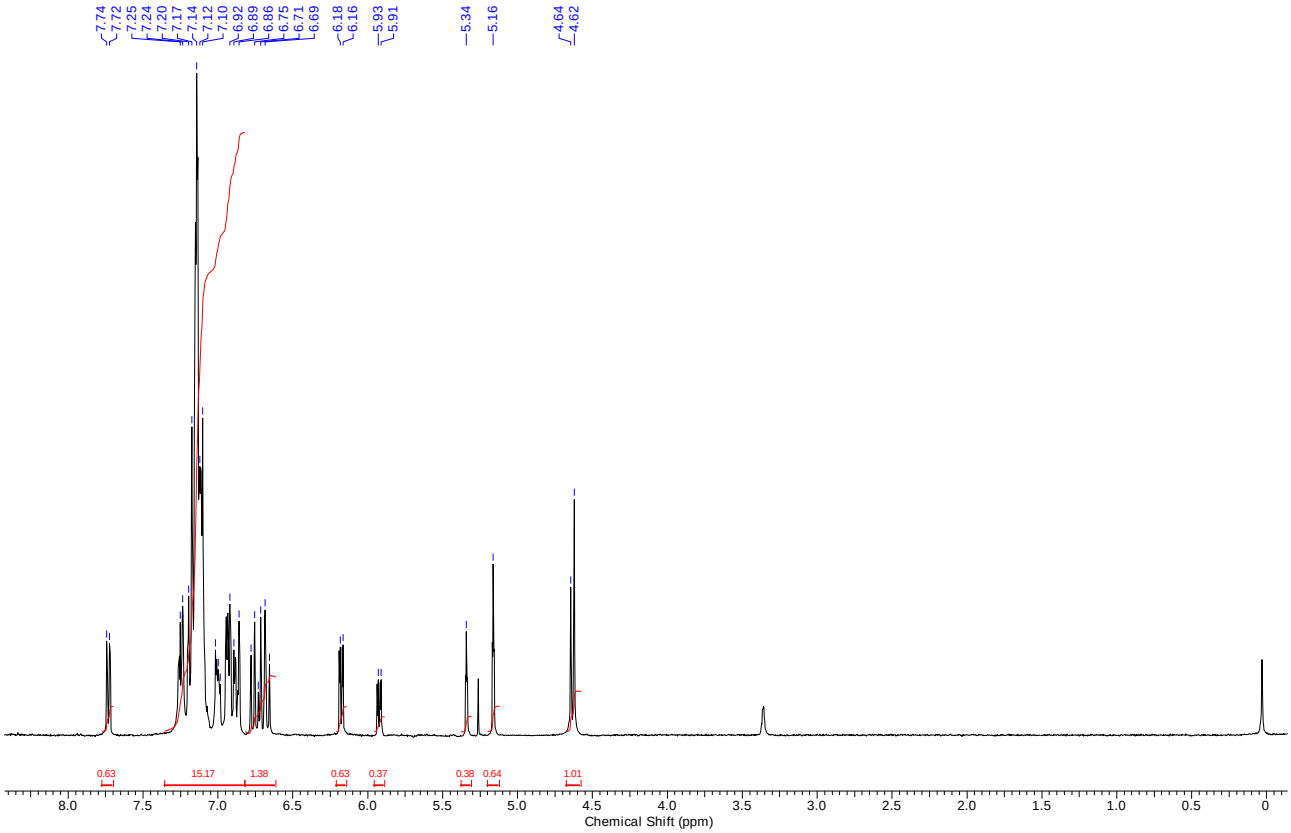
Compound 5a,b: ^{1}H NMR (400MHz, $CDCl_3$)



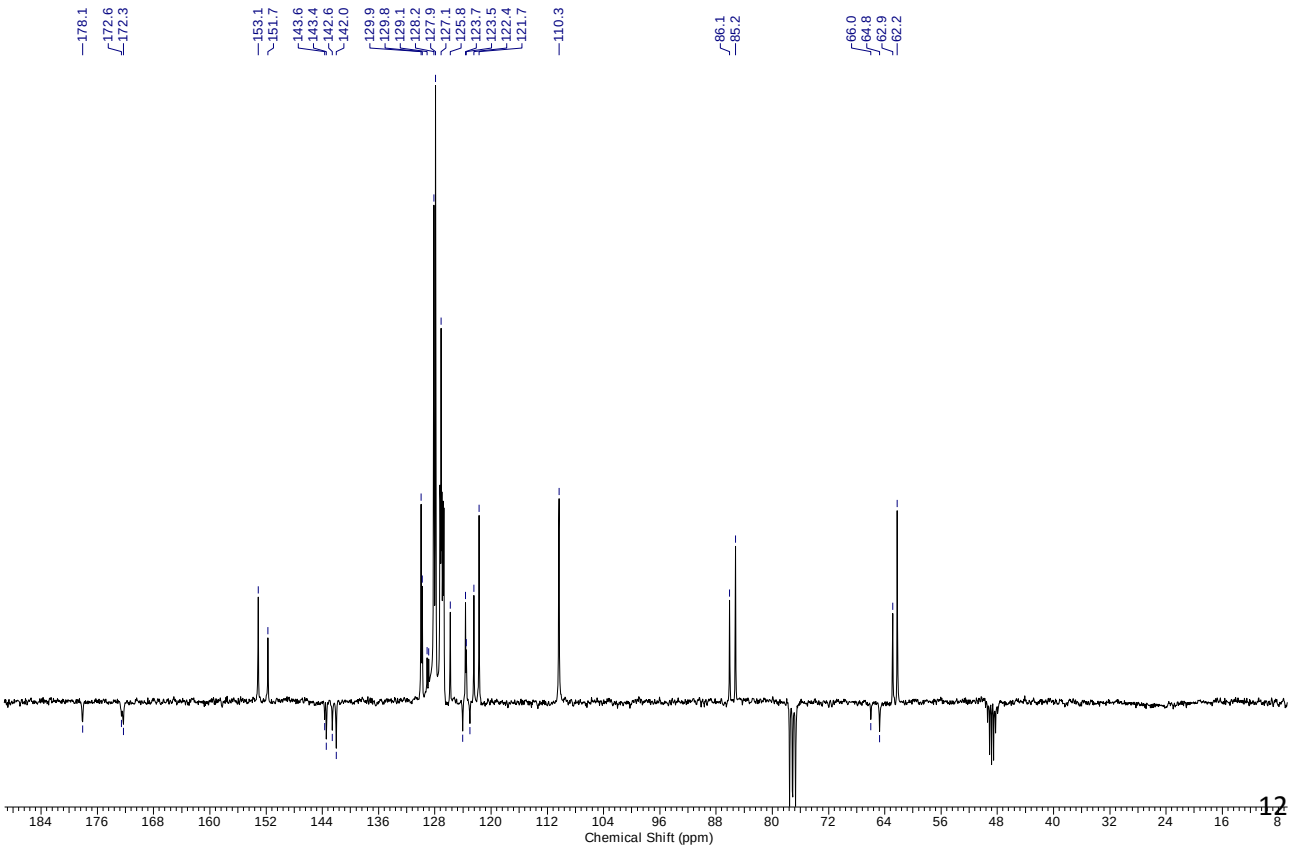
Compound 5a,b: ^{13}C NMR (101 MHz, $CDCl_3$)



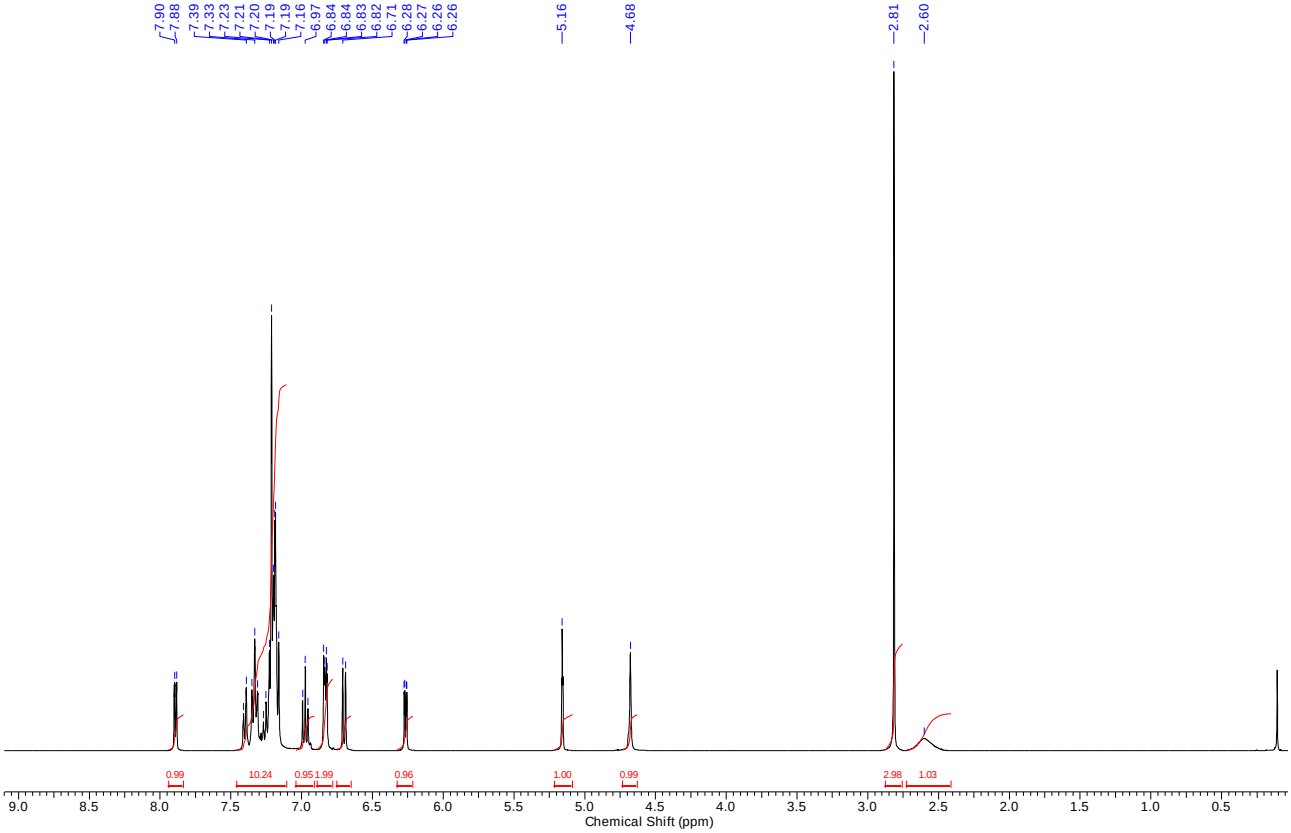
Compound 6a,b: ^{1}H NMR (300 MHz, $CDCl_3$+1% CD_3OD)



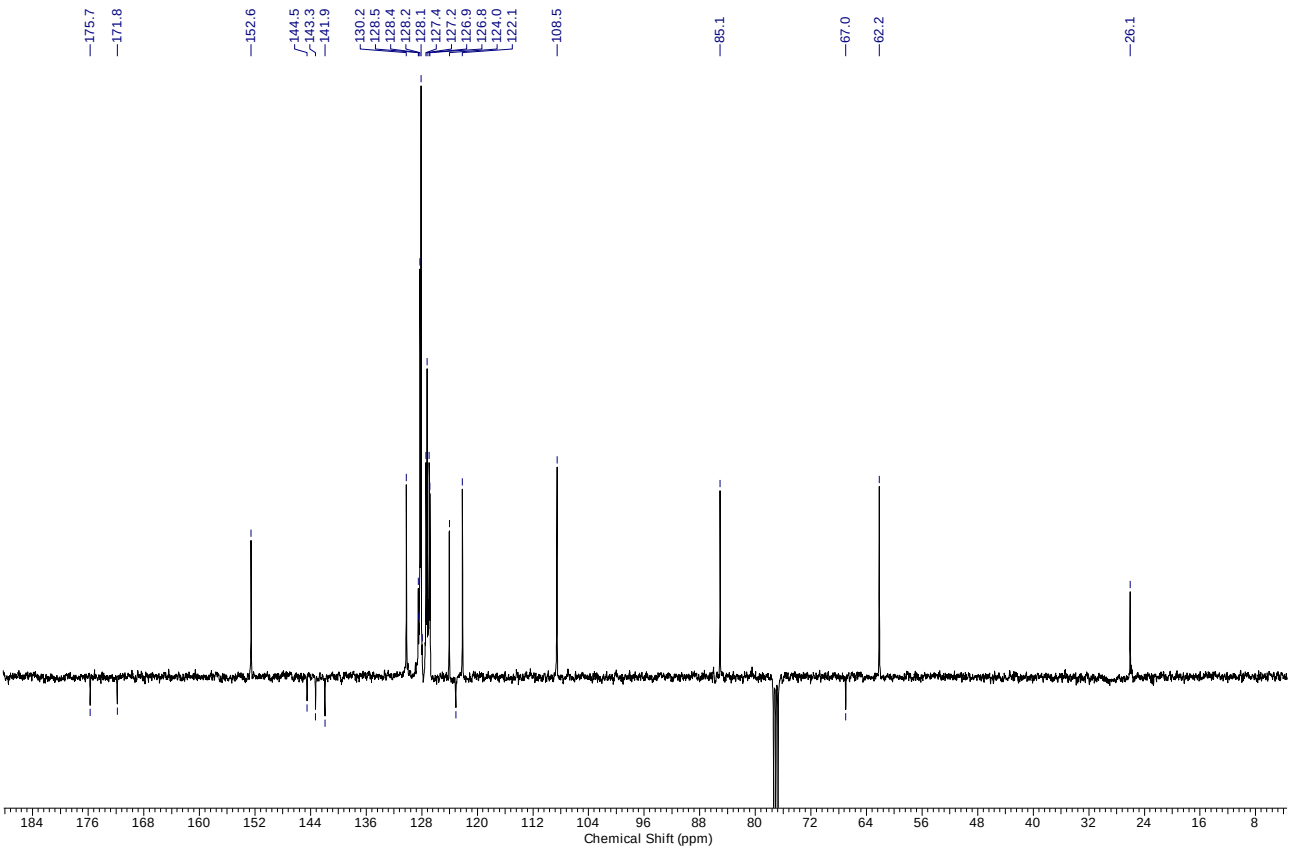
Compound 6a,b: ^{13}C NMR (75 MHz, $CDCl_3$+1% CD_3OD)



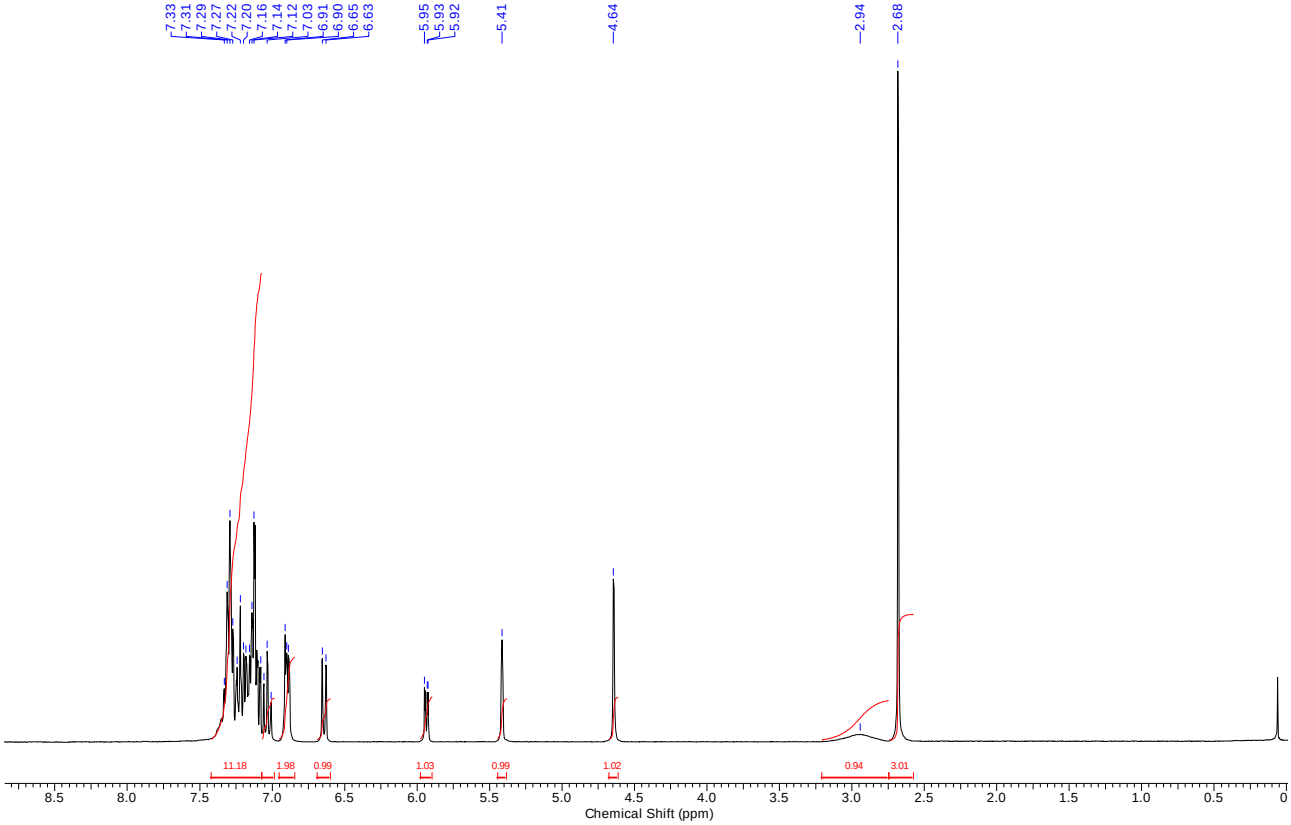
Compound 7a: ^{1}H NMR (400MHz, $CDCl_3$)



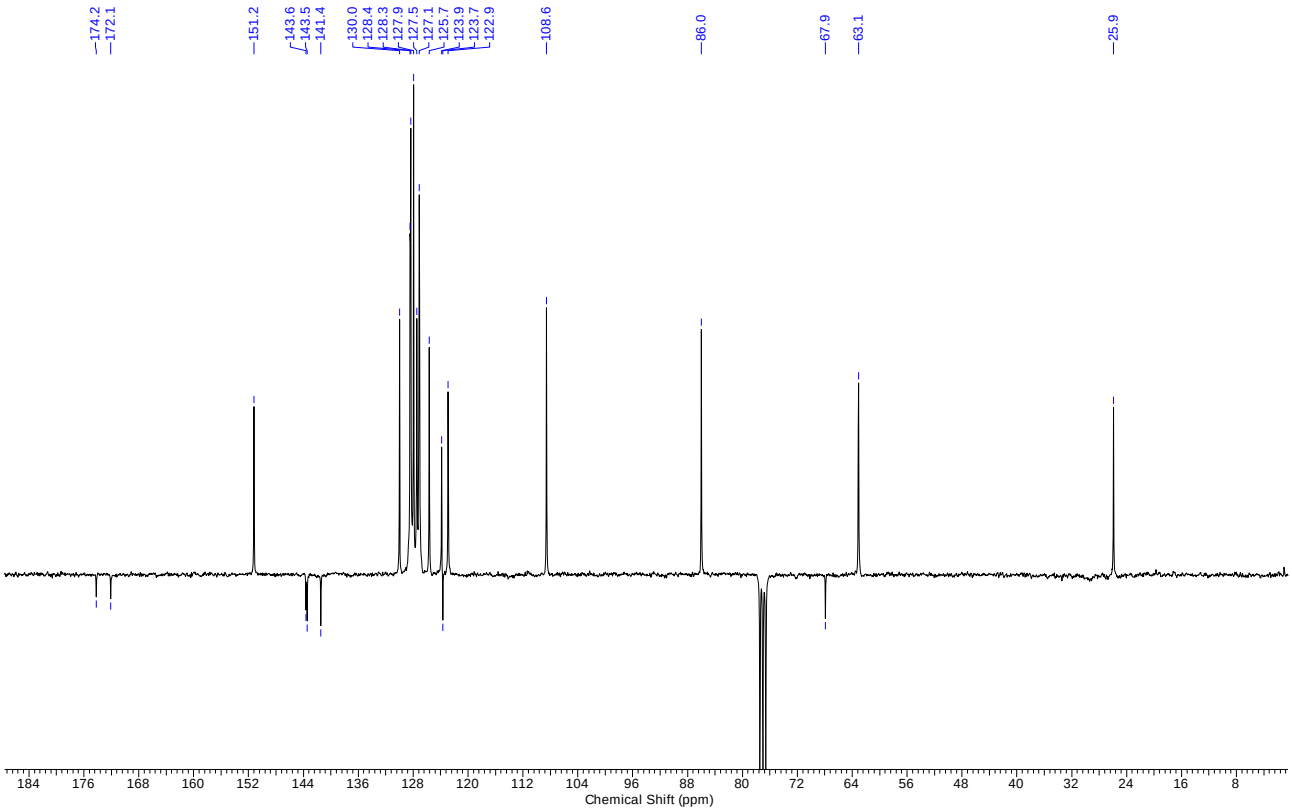
Compound 7a: ^{13}C NMR (101 MHz, $CDCl_3$)



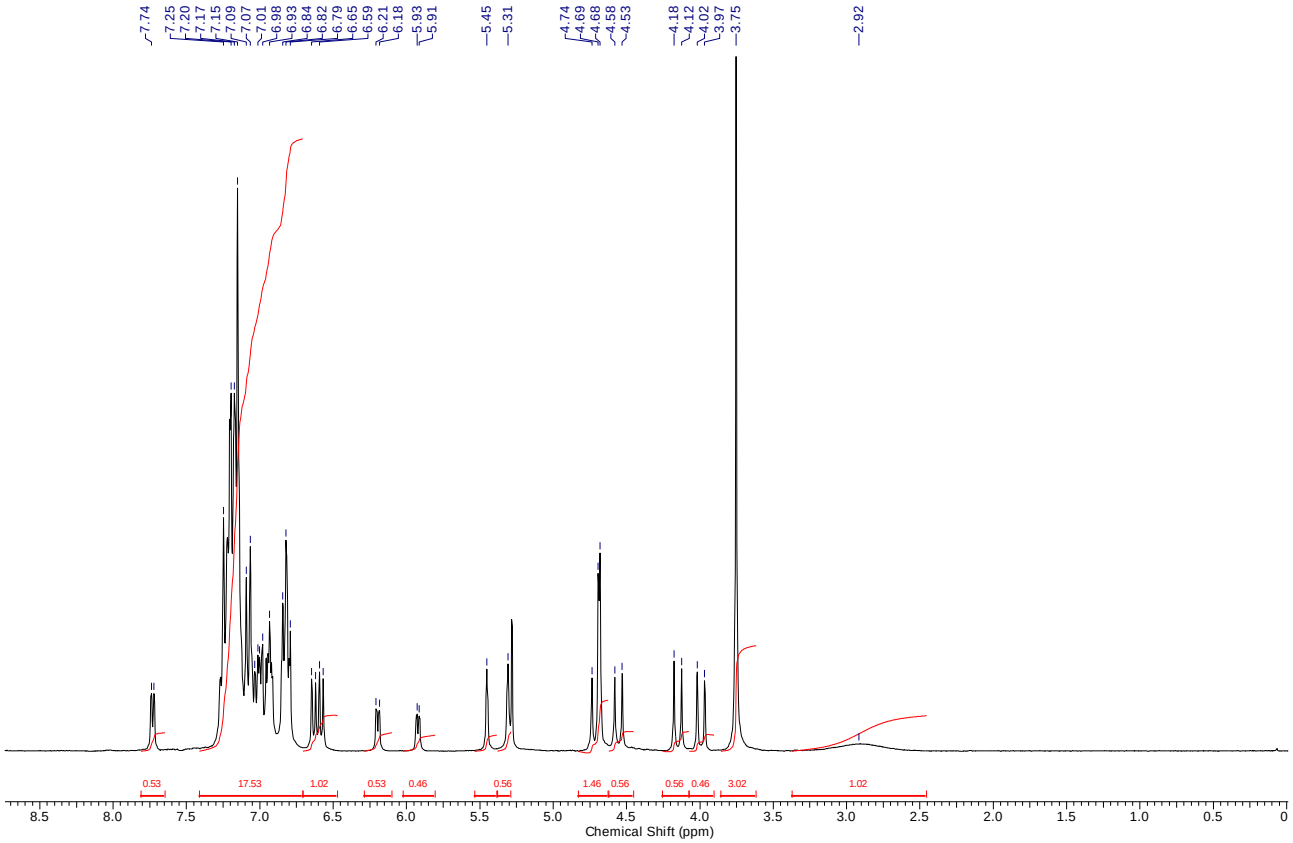
Compound 7b: ^{1}H NMR (300MHz, $CDCl_3$)



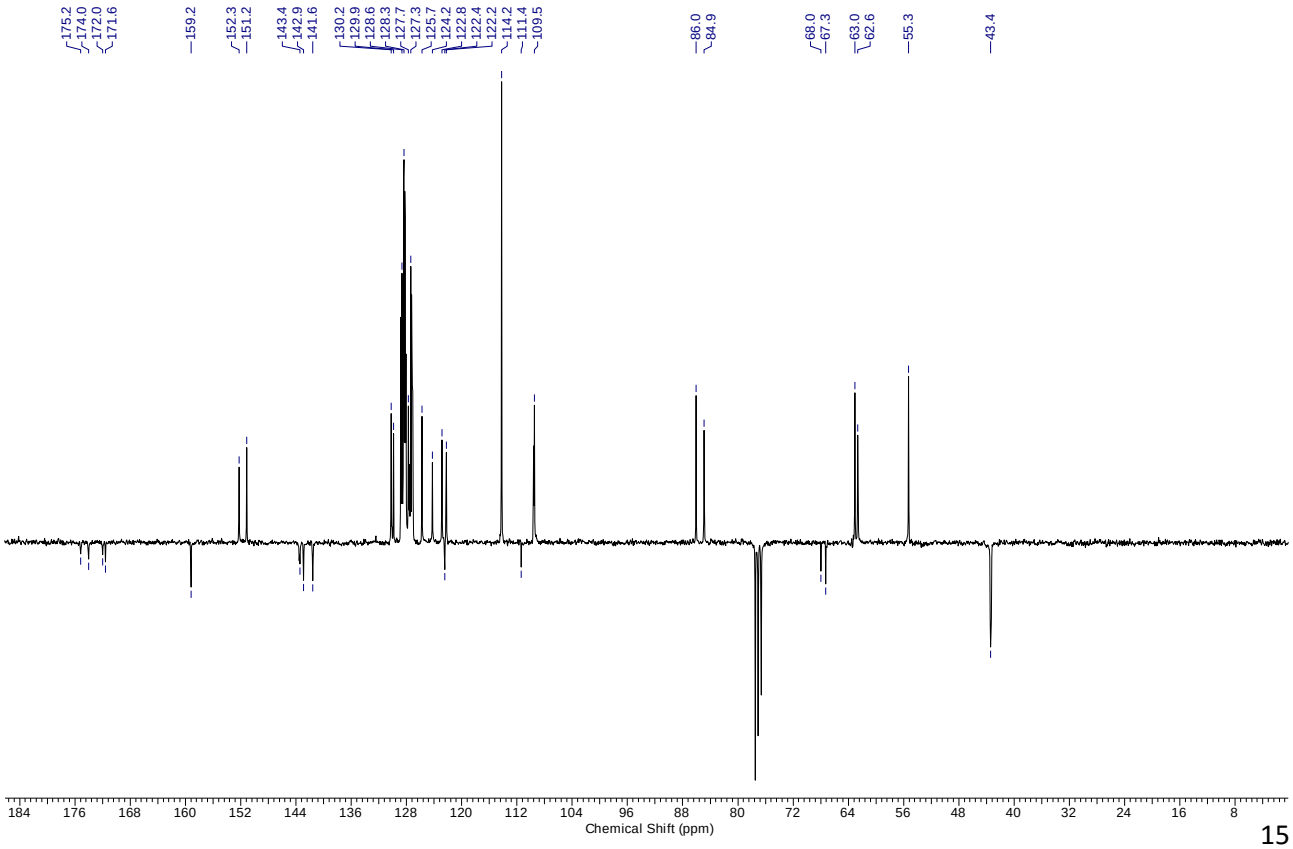
Compound 7b:^{13}C NMR (75 MHz, $CDCl_3$)



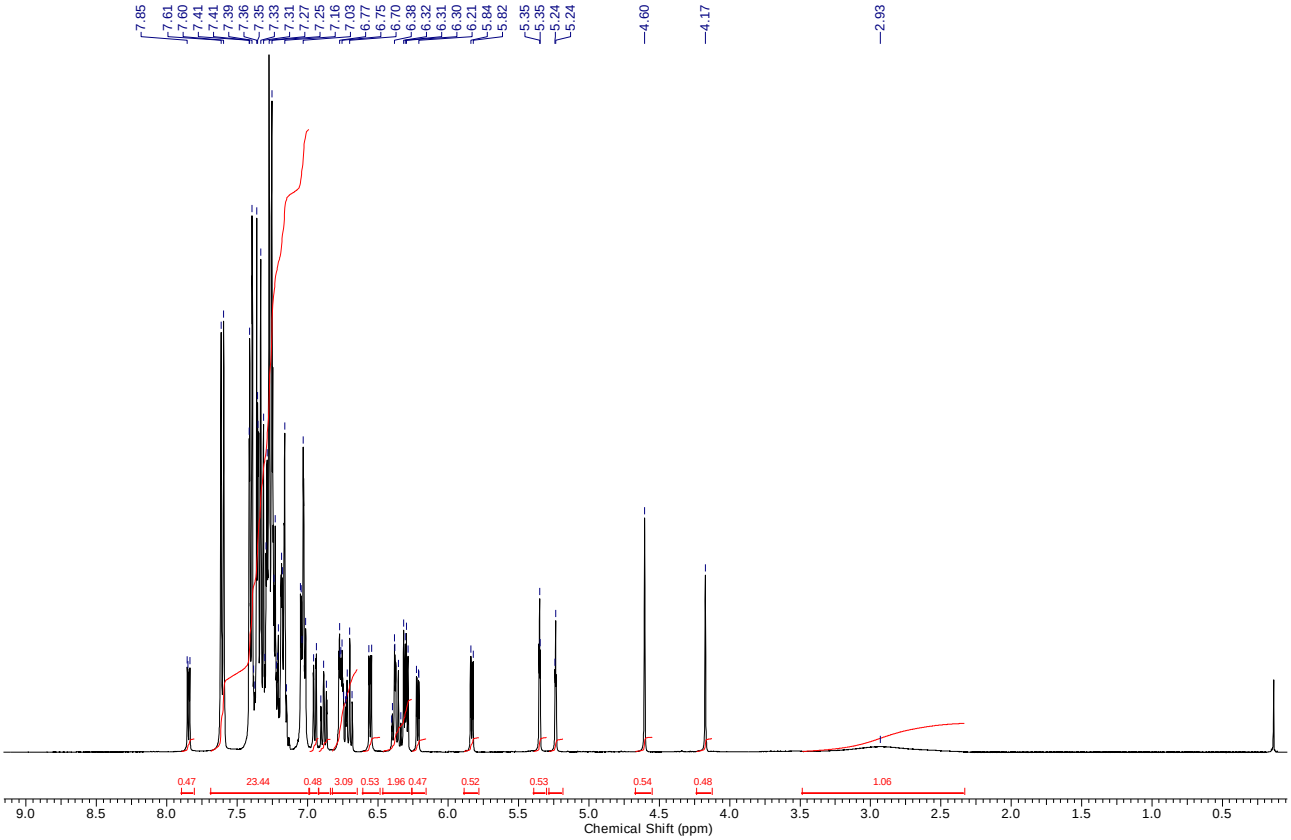
Compound 8ab: ^{1}H NMR (300MHz, $CDCl_3$)



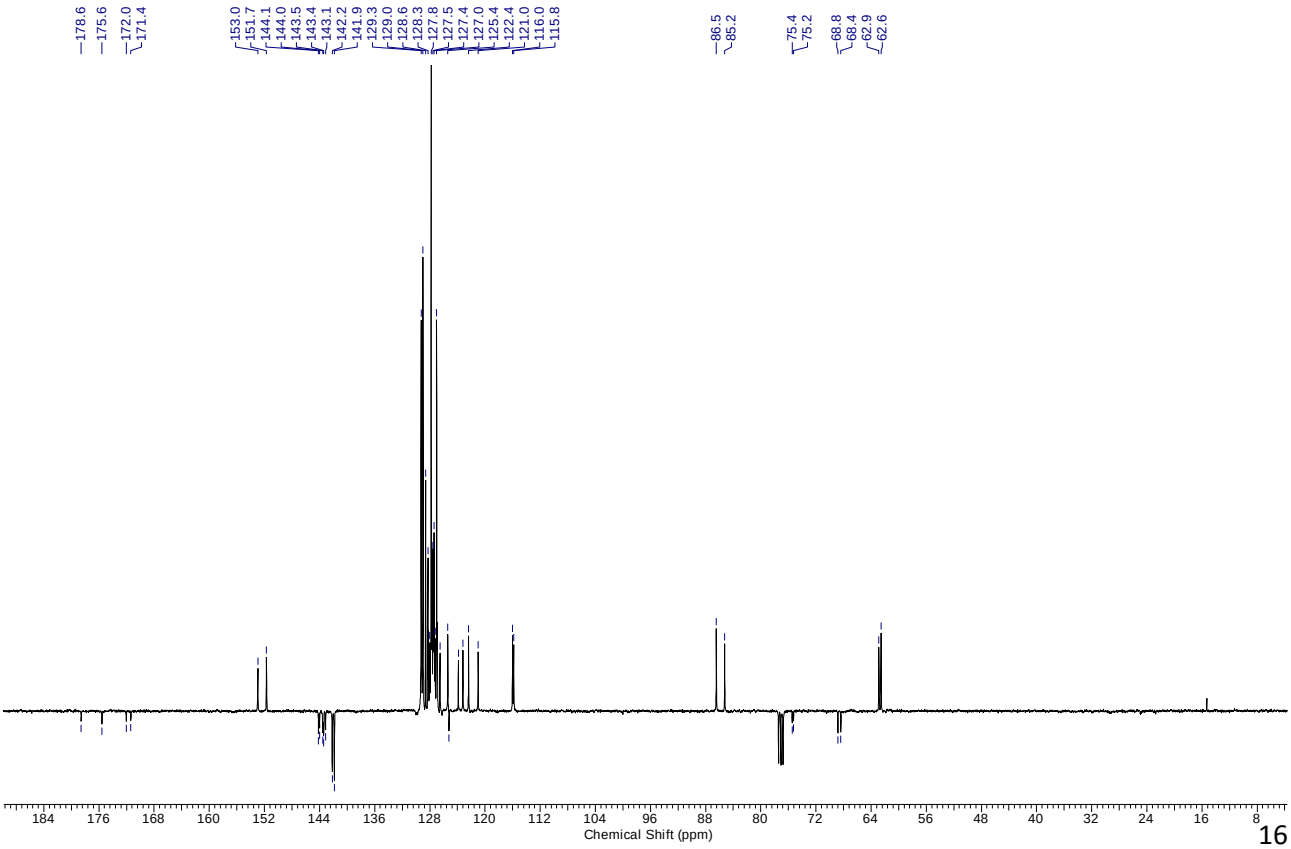
Compound 8ab: ^{13}C NMR (75 MHz, $CDCl_3$)



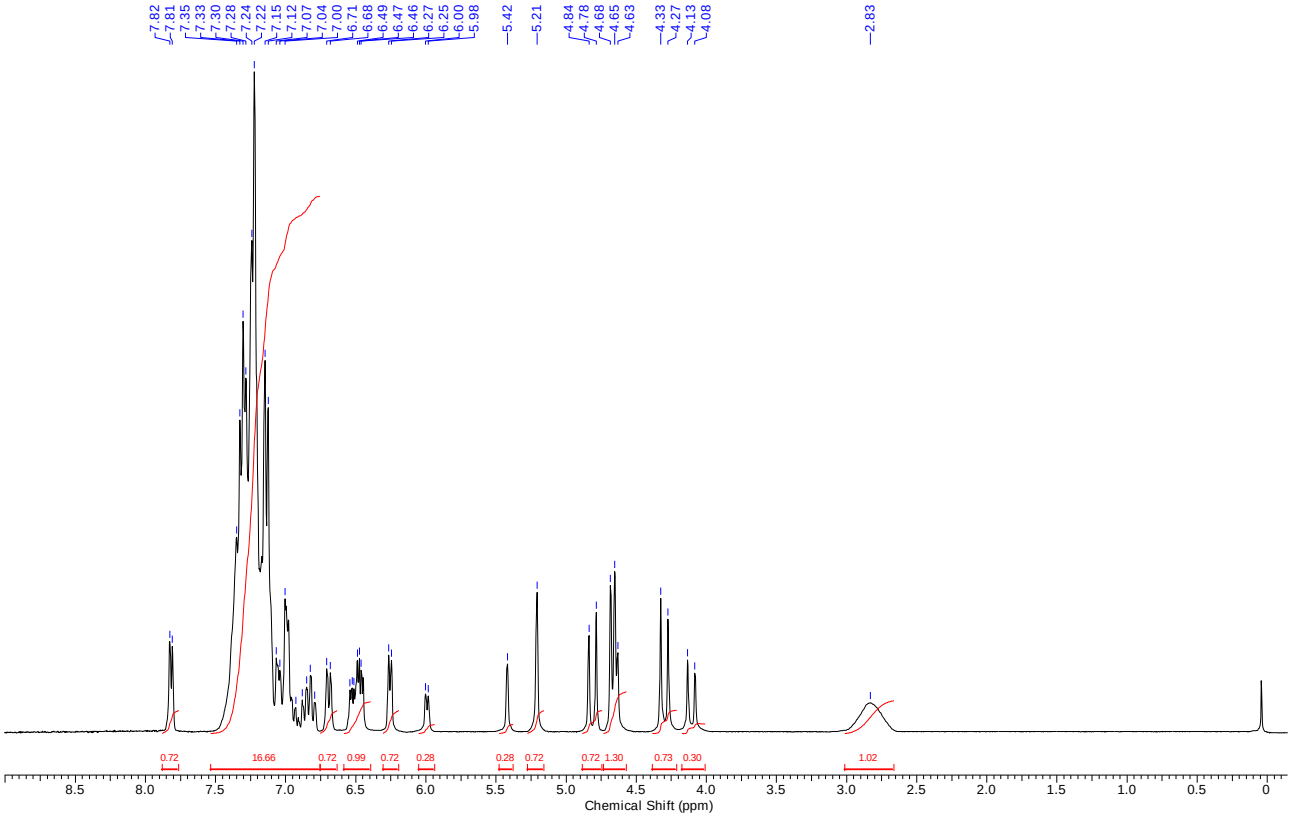
Compound 9ab: ^{1}H NMR (400MHz, $CDCl_3$) -



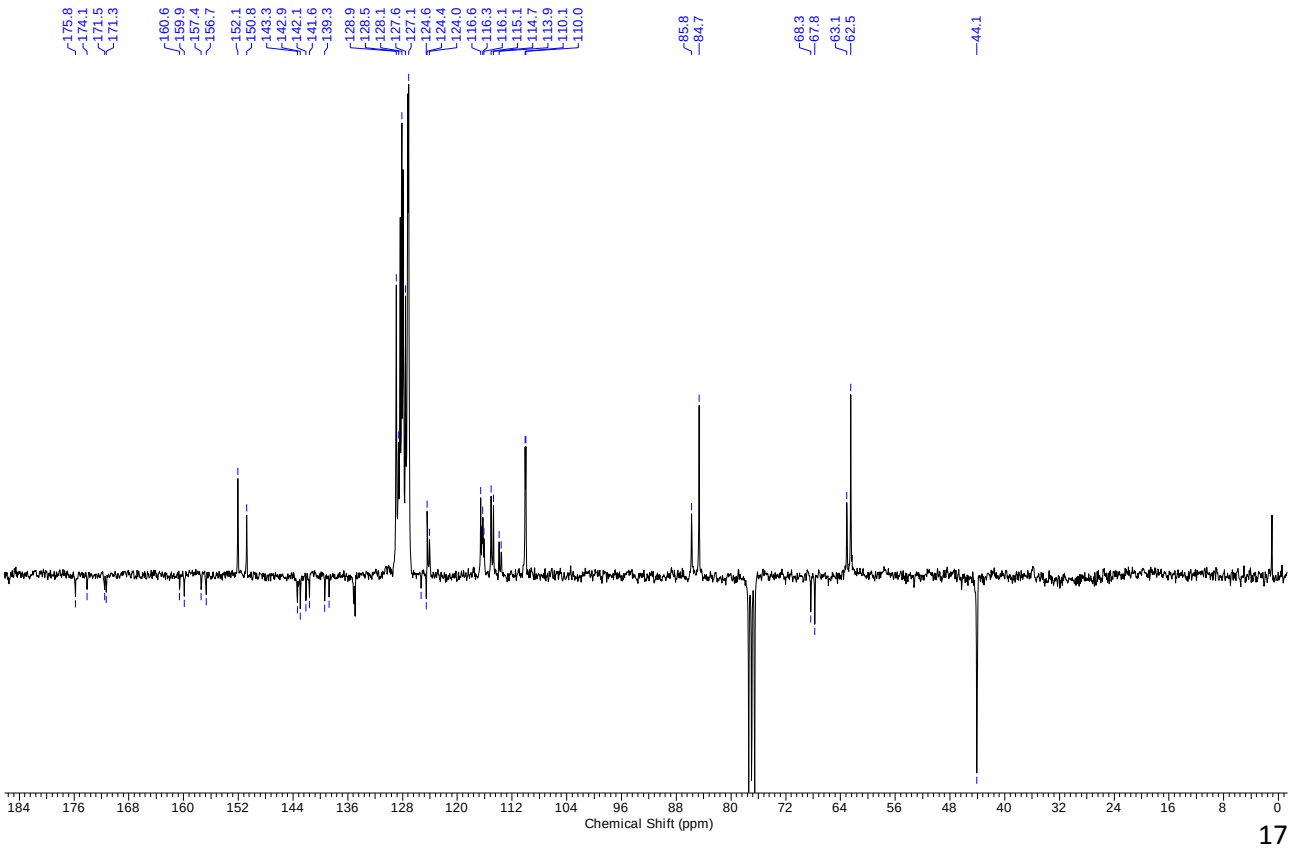
Compound 9ab: ^{13}C NMR (101 MHz, $CDCl_3$)



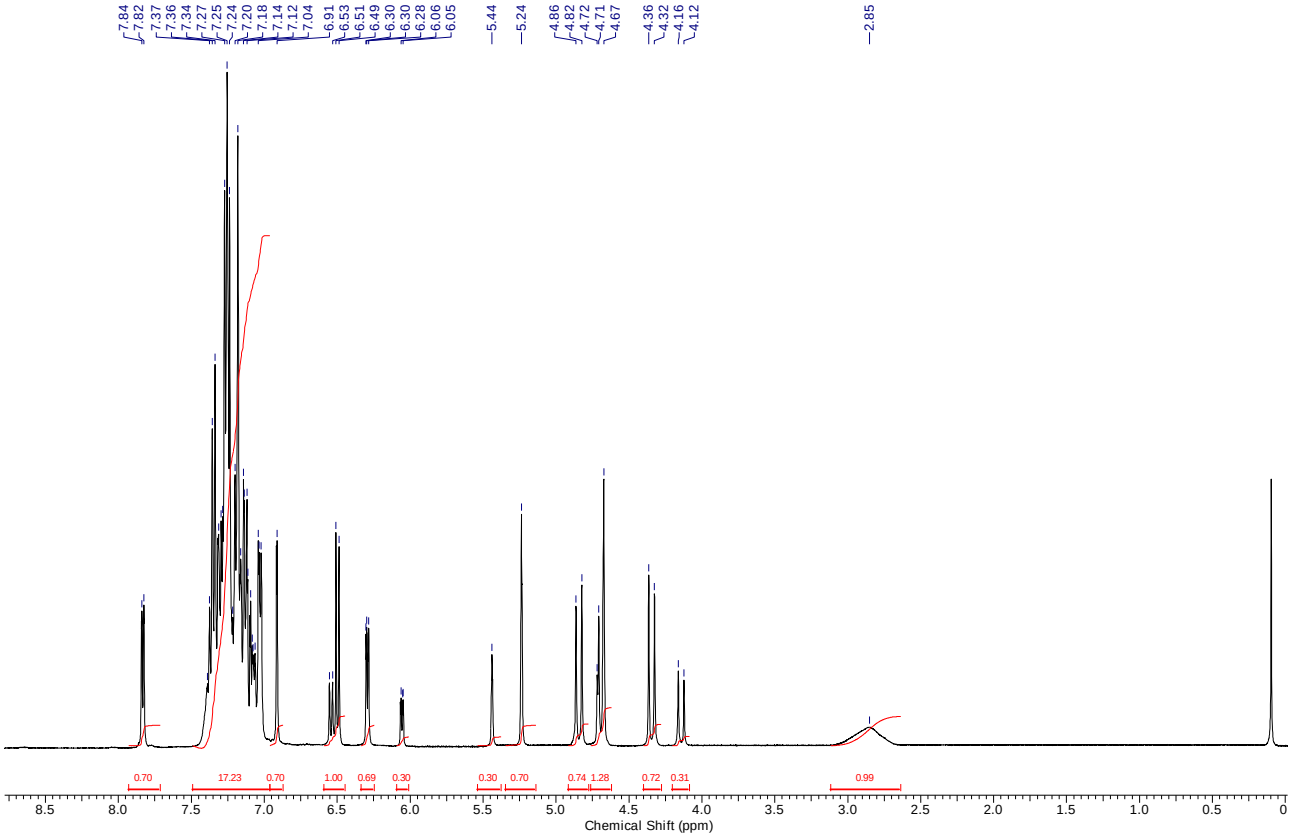
Compound 10ab: ^{1}H NMR (300MHz, $CDCl_3$)



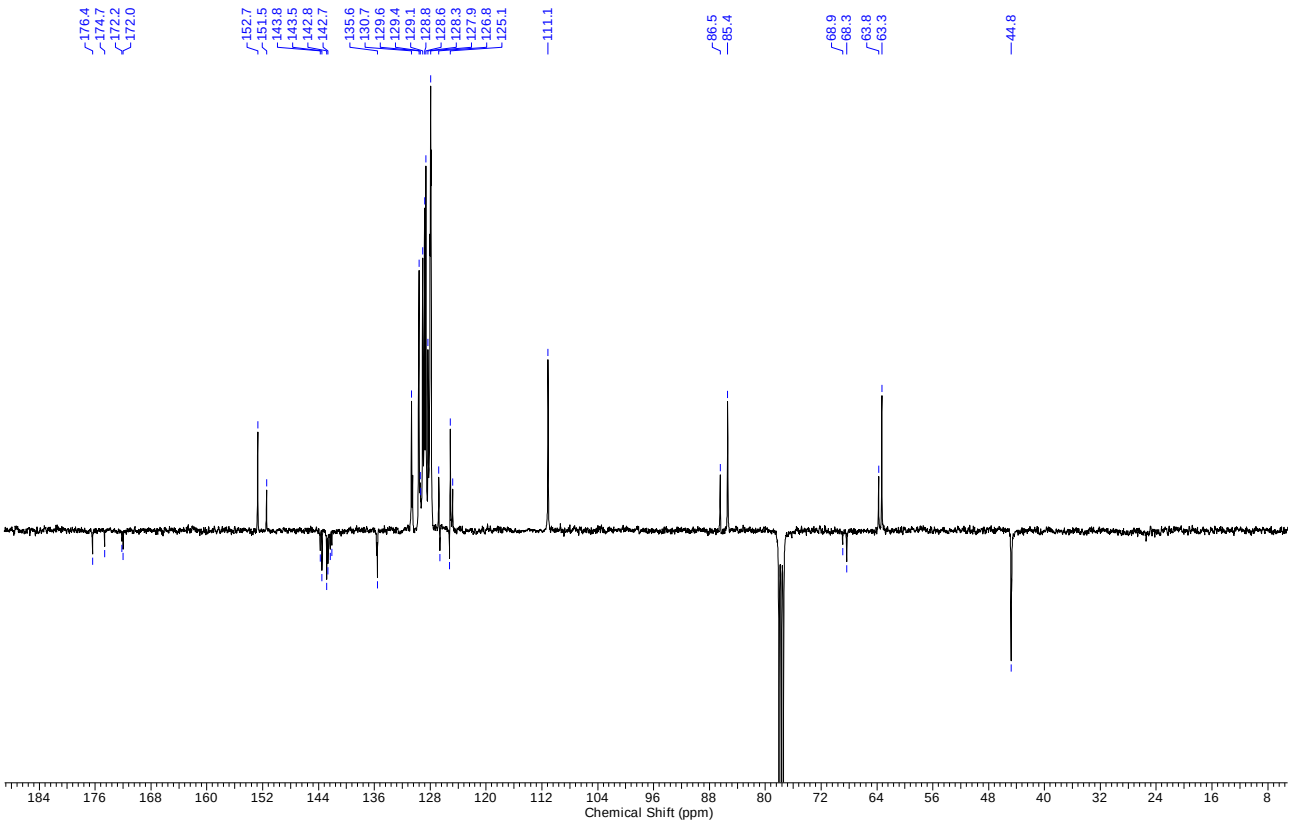
Compound 10ab: ^{13}C NMR (75 MHz, $CDCl_3$)



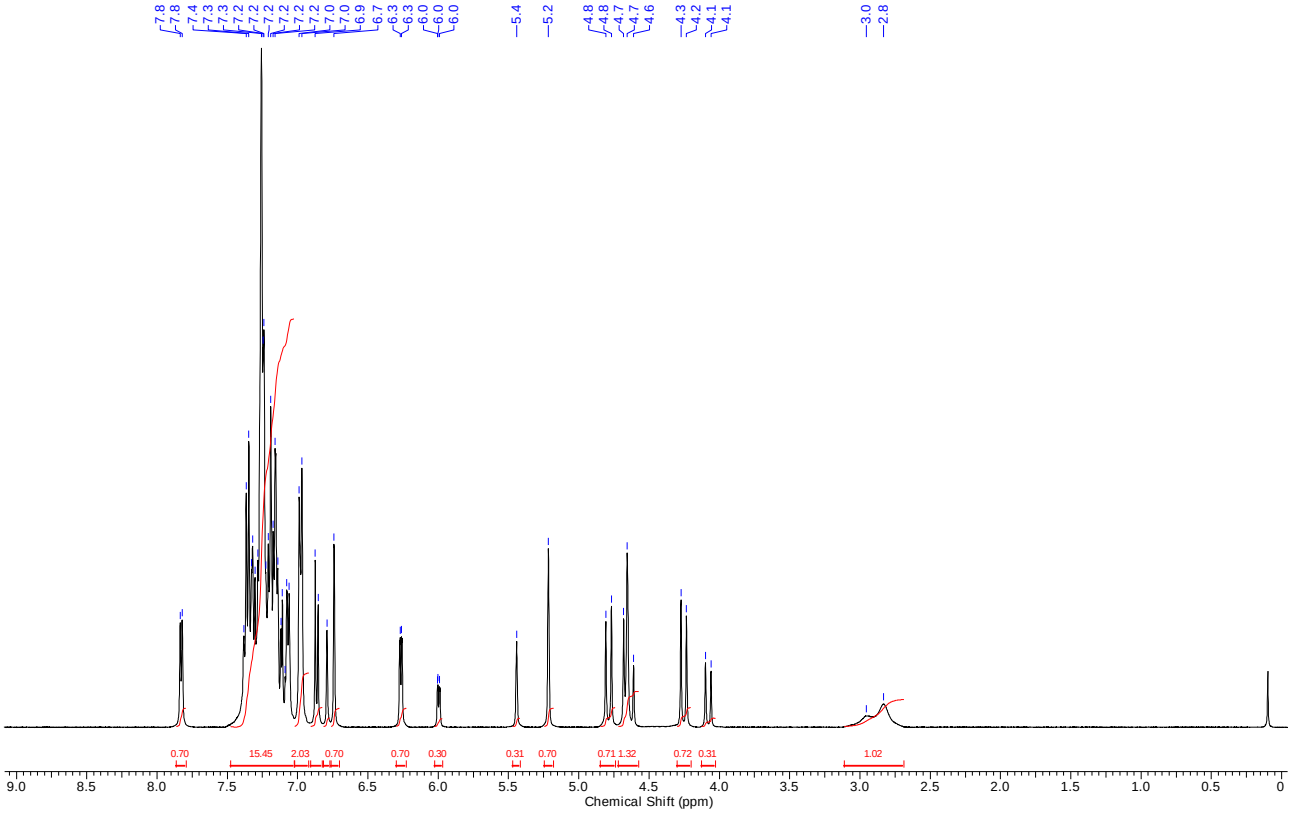
Compound 11ab: ^{1}H NMR (400MHz, $CDCl_3$)



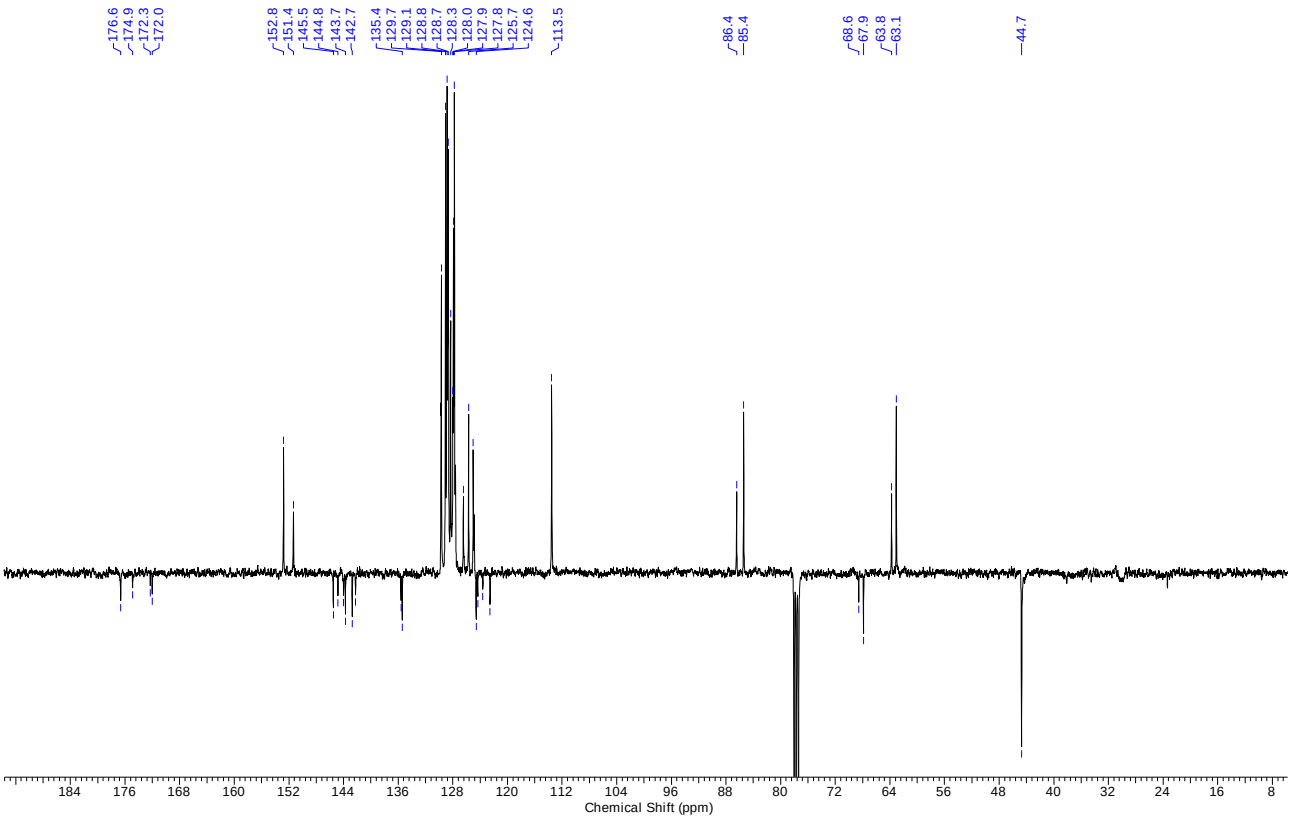
Compound 11ab: ^{13}C NMR (101 MHz, $CDCl_3$)



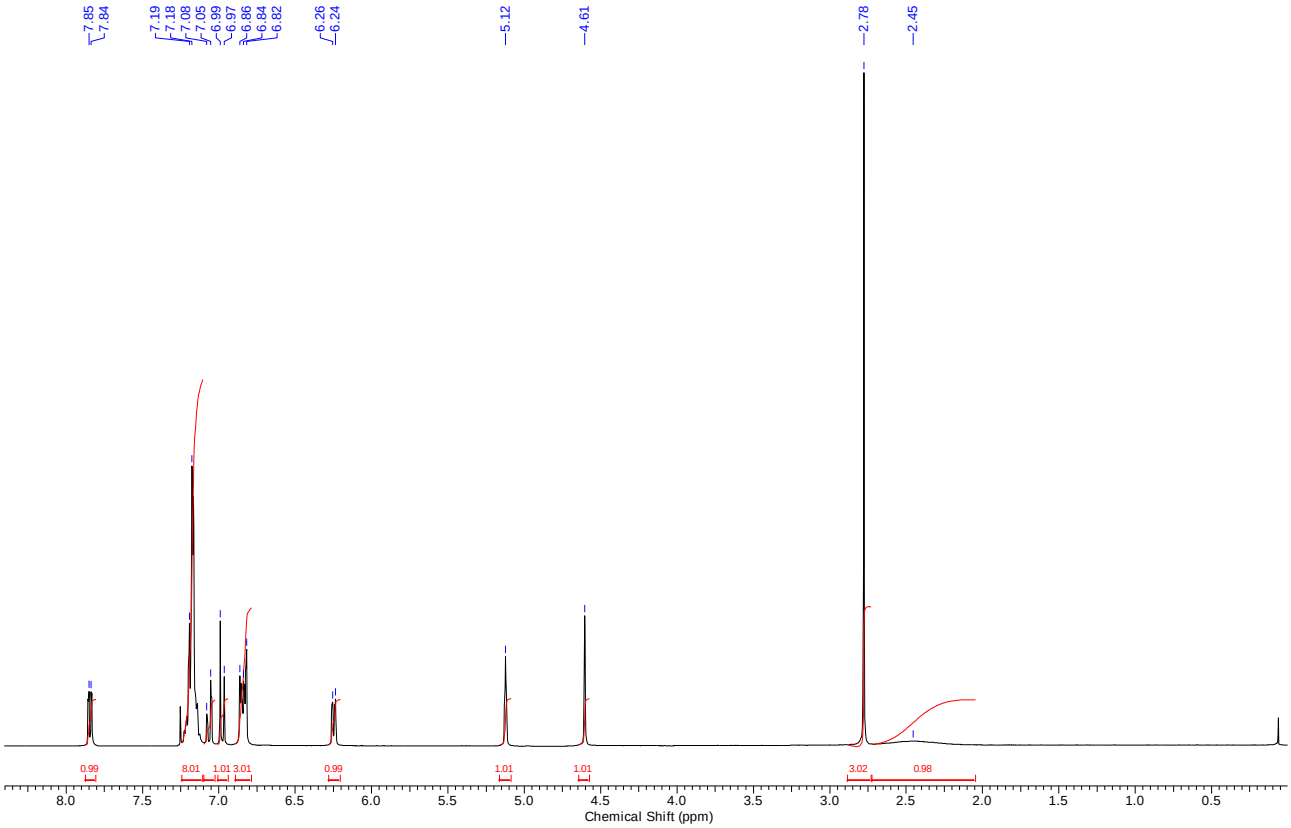
Compound 12ab: ^{1}H NMR (400MHz, $CDCl_3$)



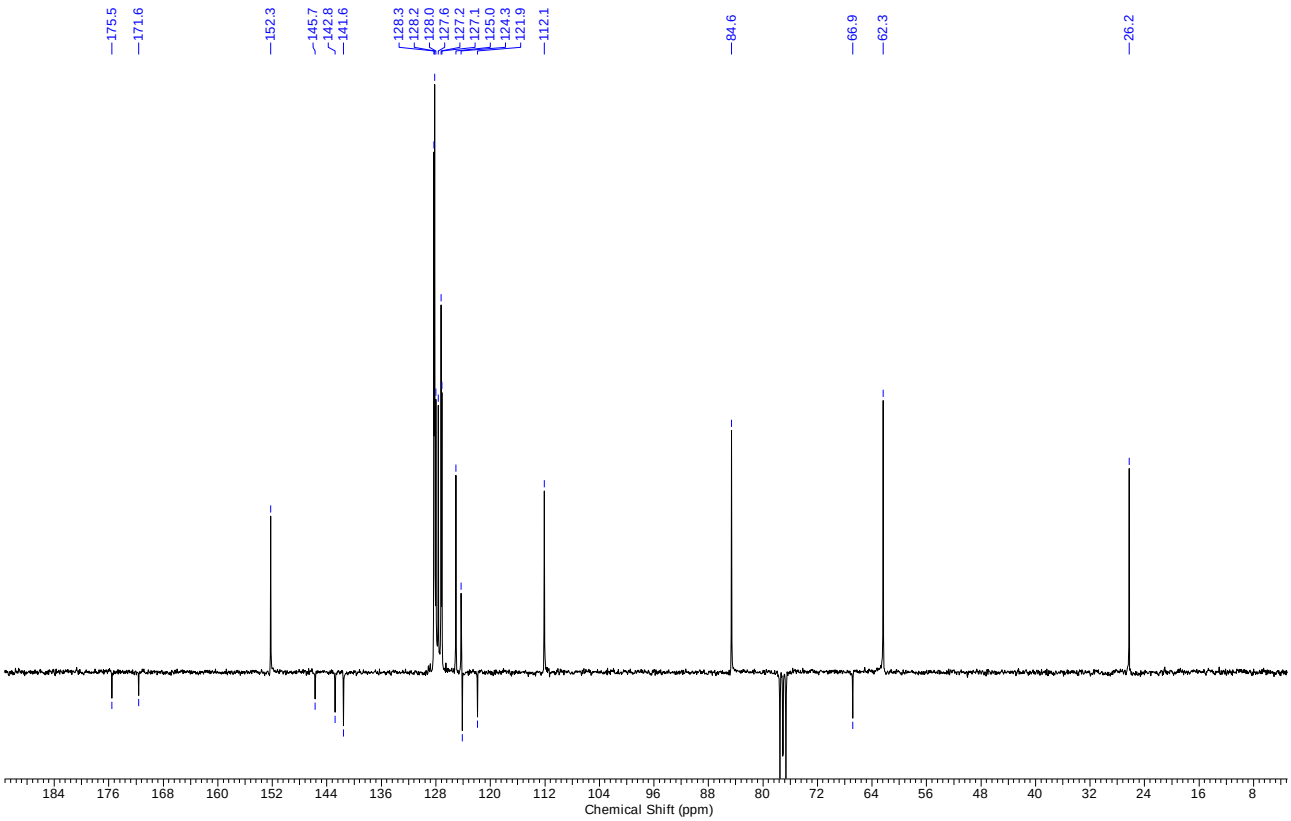
Compound 12ab: ^{13}C NMR (101 MHz, $CDCl_3$)



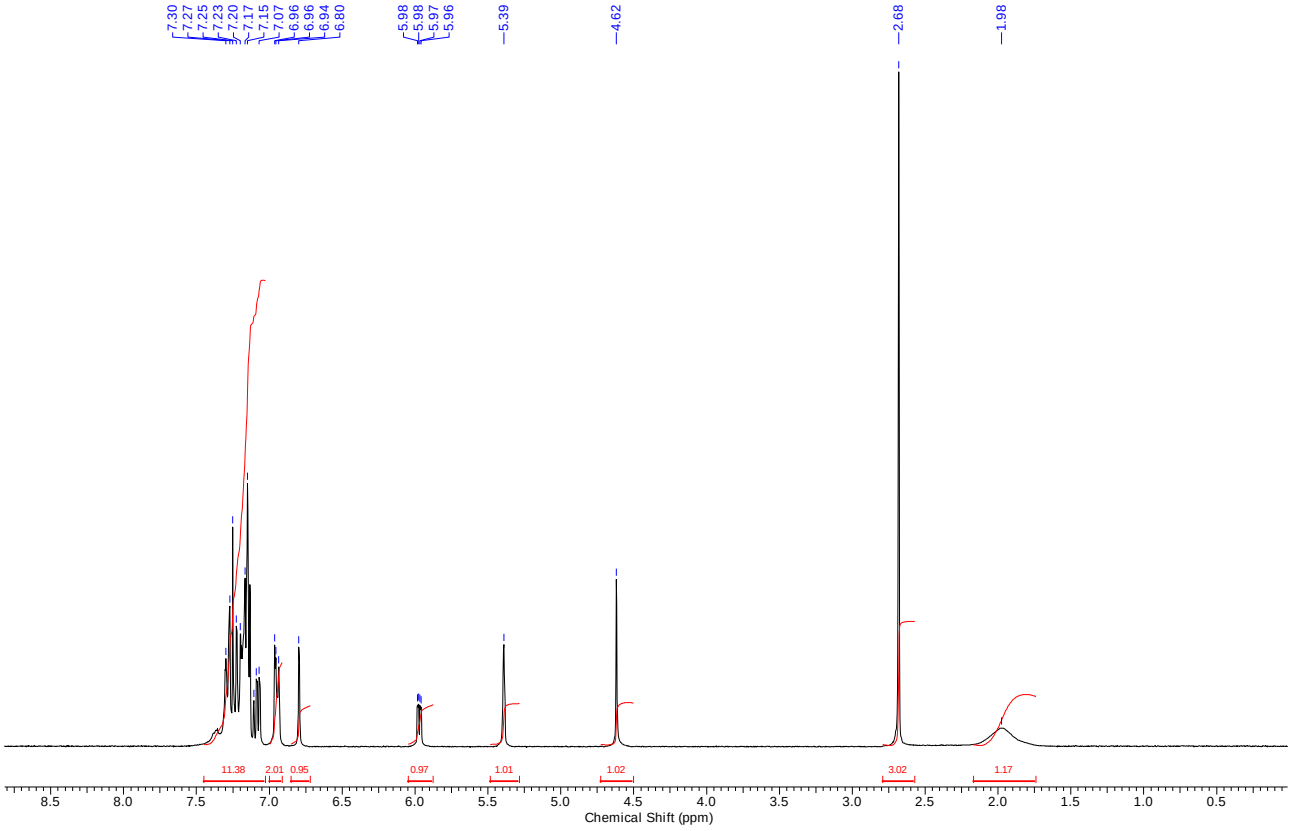
Compound 13a: ^{1}H NMR (300MHz, $CDCl_3$)



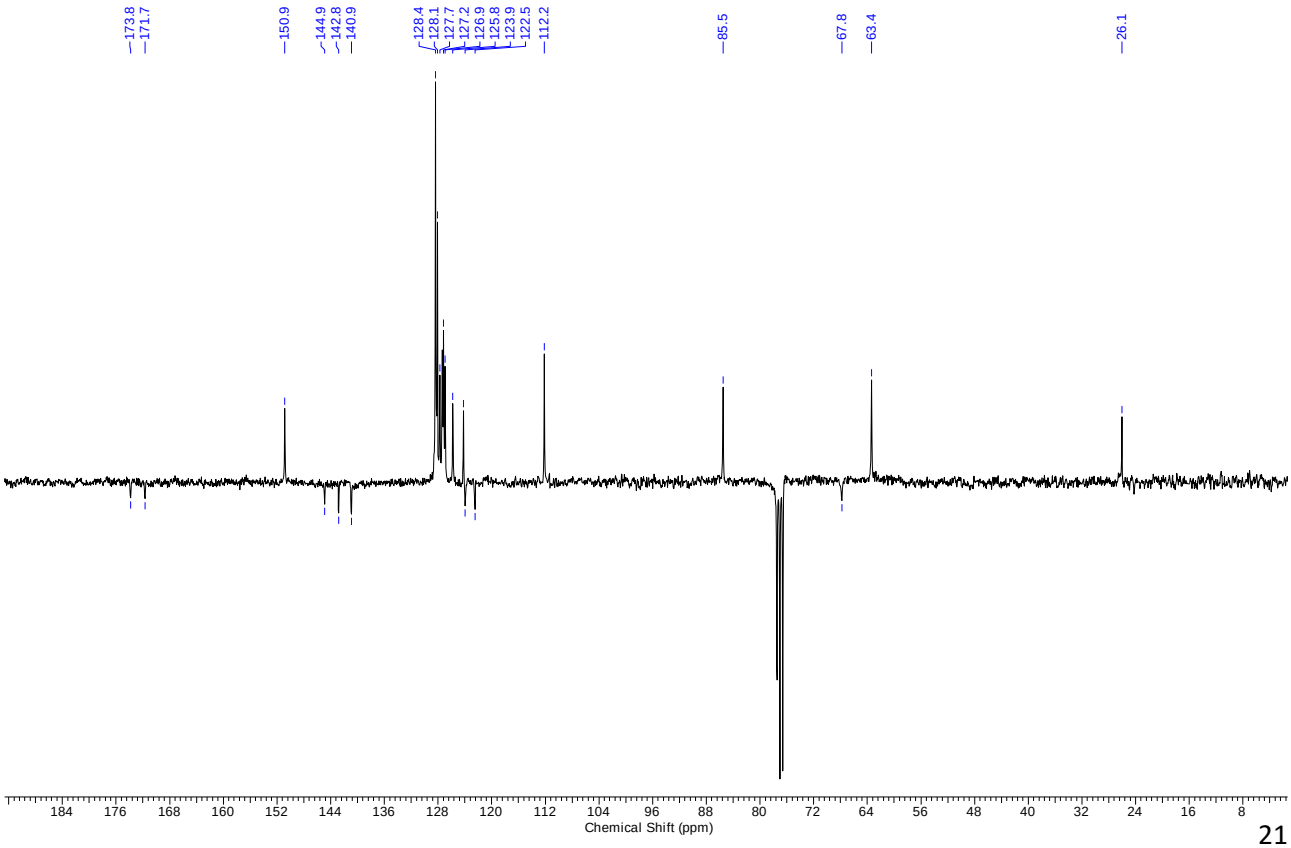
Compound 13a: ^{13}C NMR (75 MHz, $CDCl_3$)



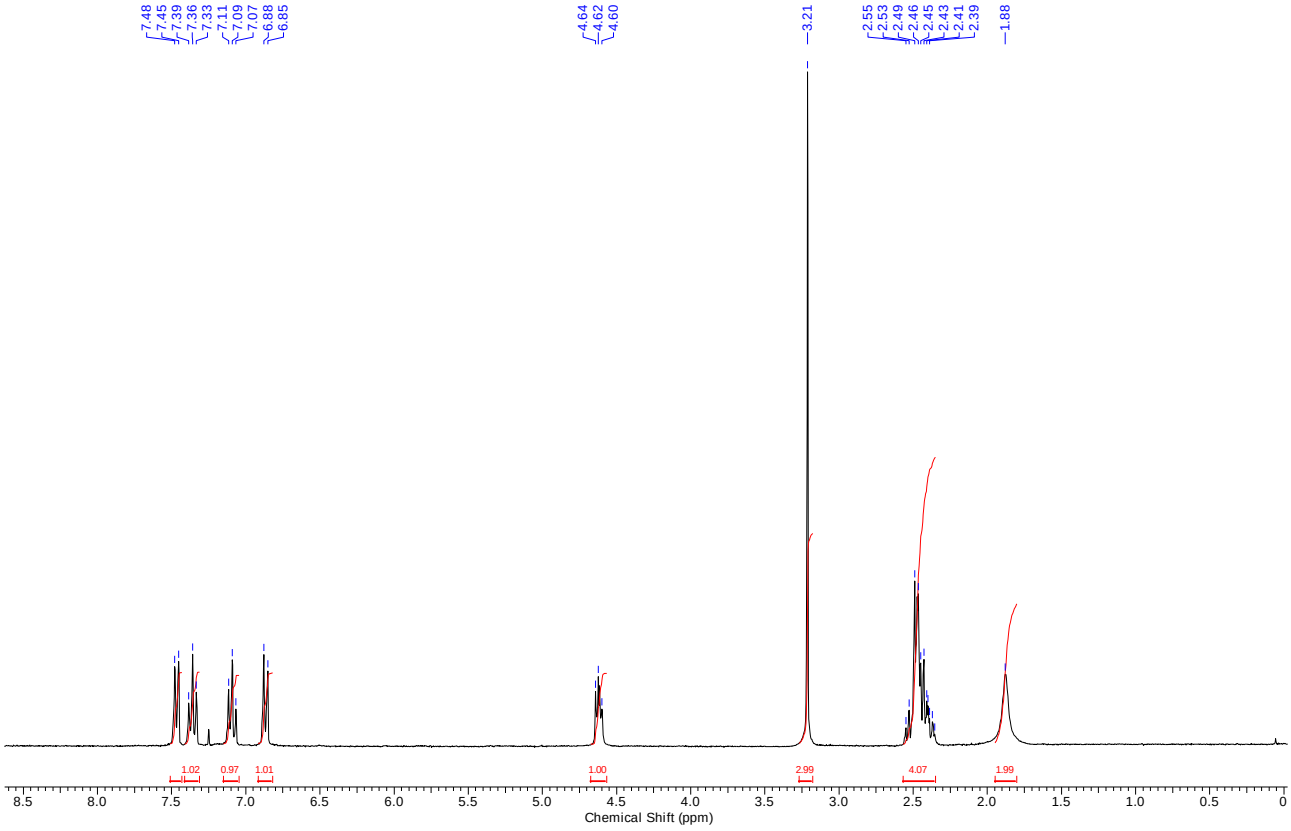
Compound 13b: ^{1}H NMR (300MHz, $CDCl_3$)



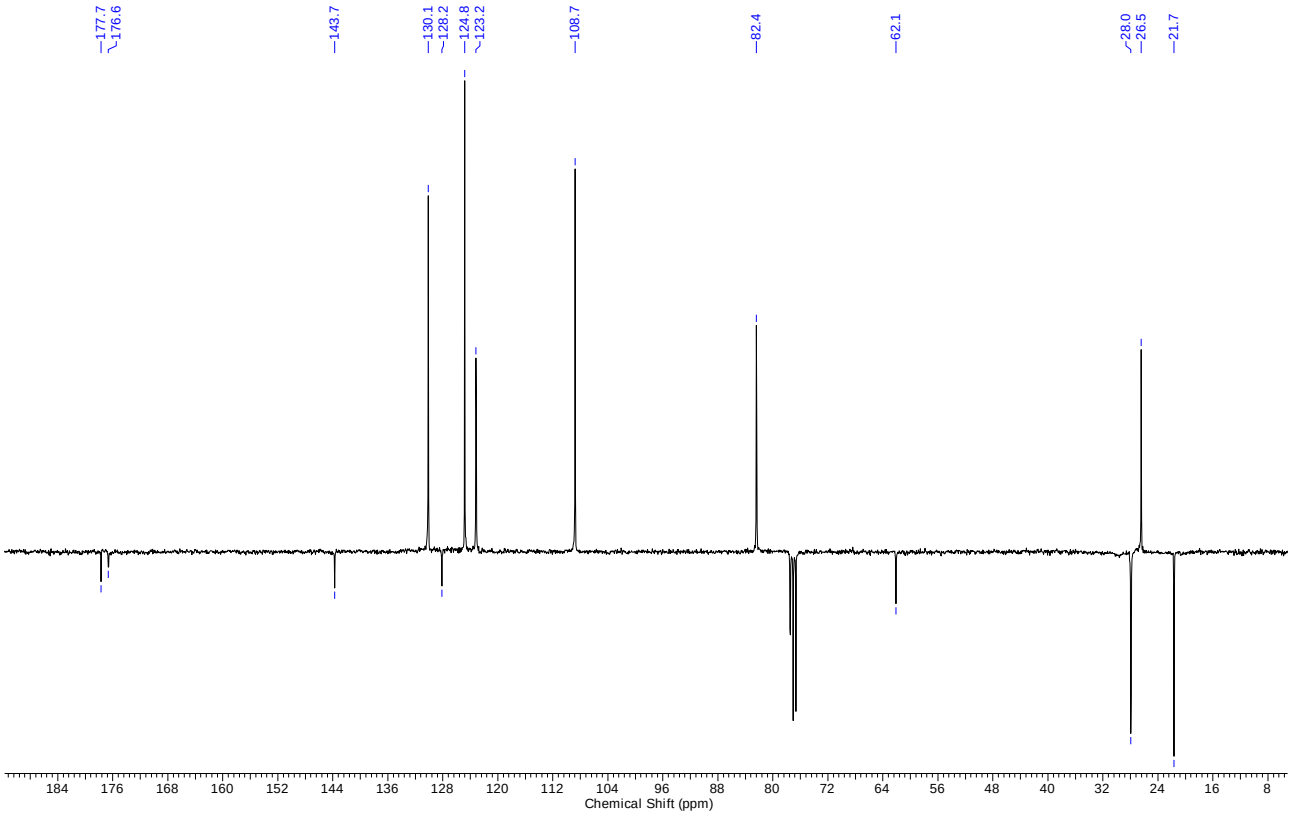
Compound 13b: ^{13}C NMR (75 MHz, $CDCl_3$)



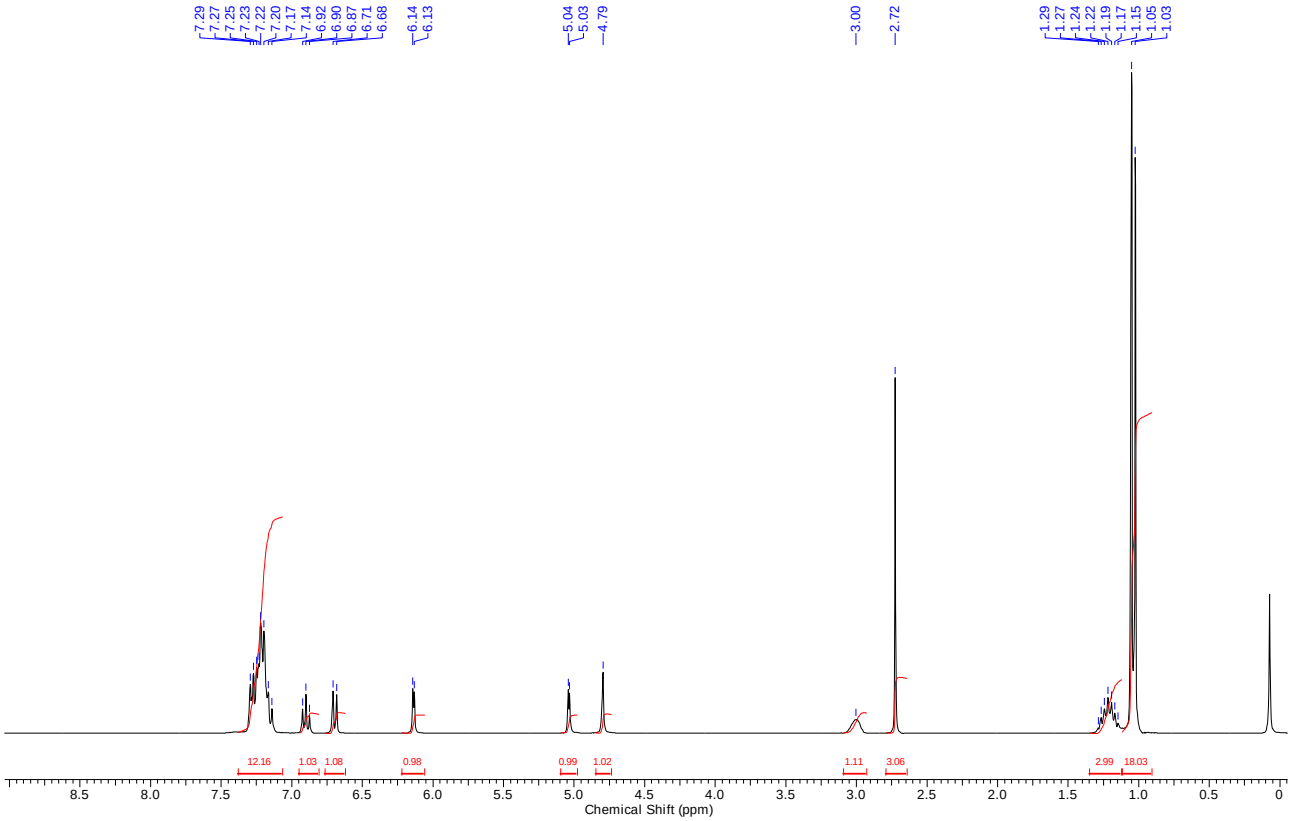
Compound 15': ^{1}H NMR (300MHz, $CDCl_3$)



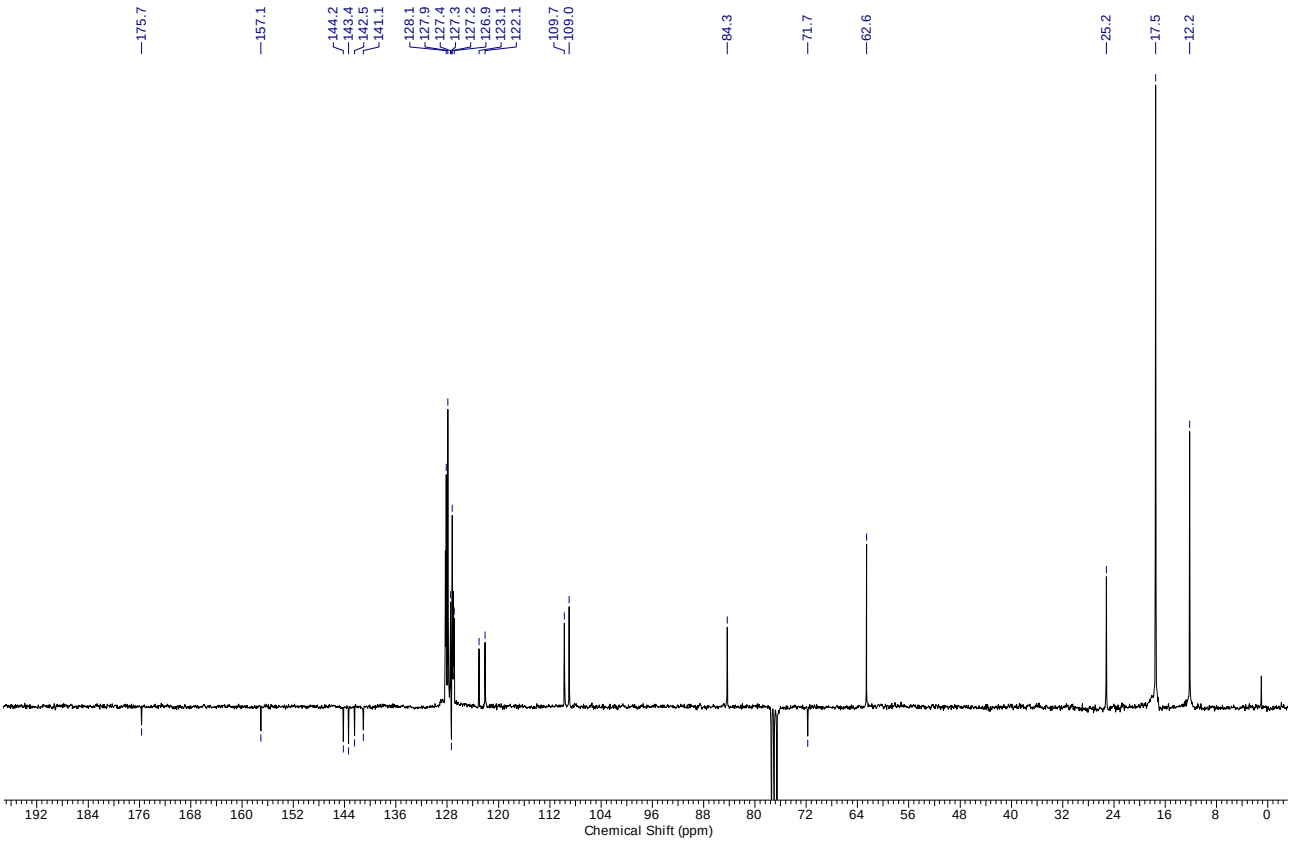
Compound 15': ^{13}C NMR (75 MHz, $CDCl_3$)



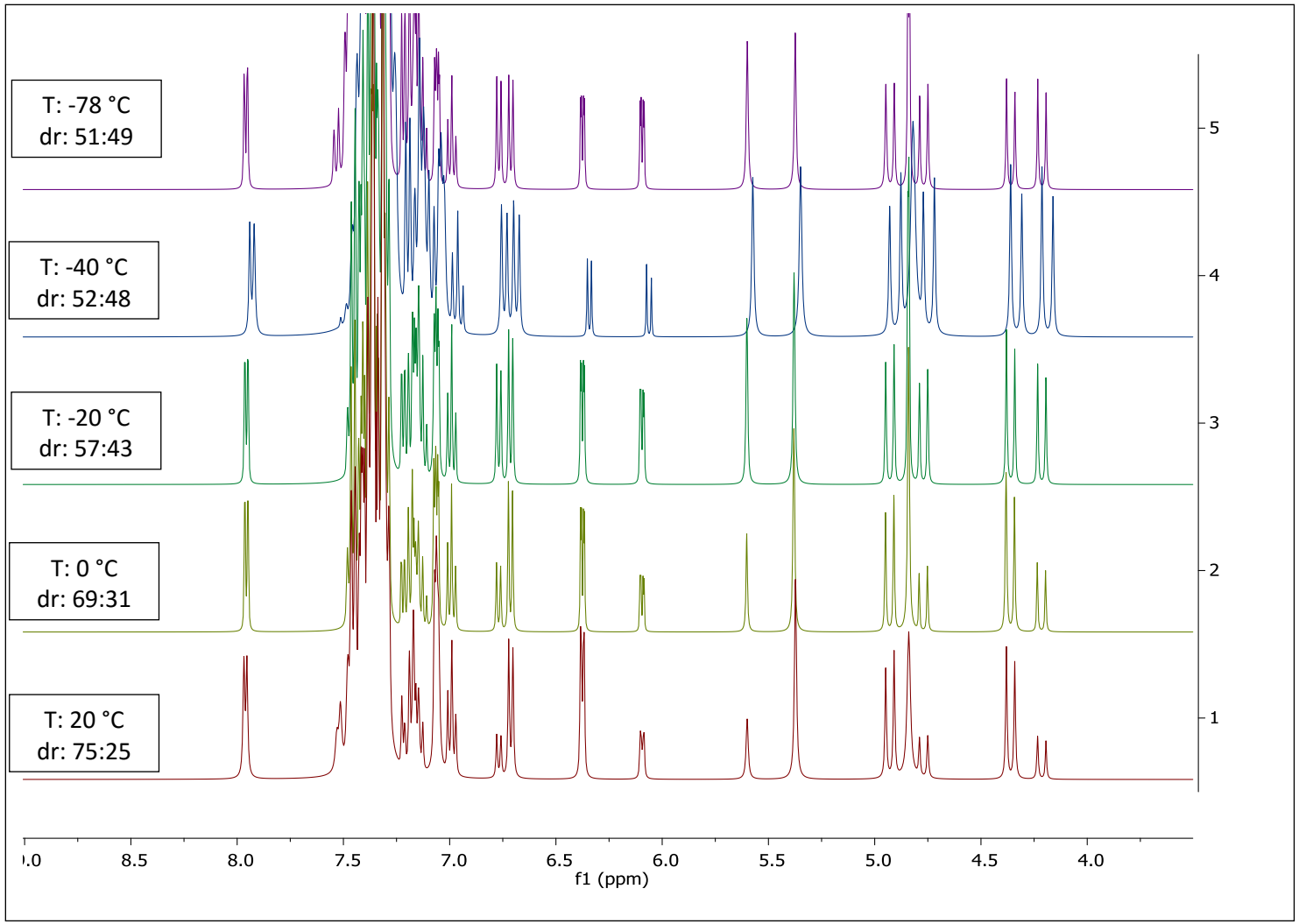
Compound 16: ^{1}H NMR (300MHz, $CDCl_3$)



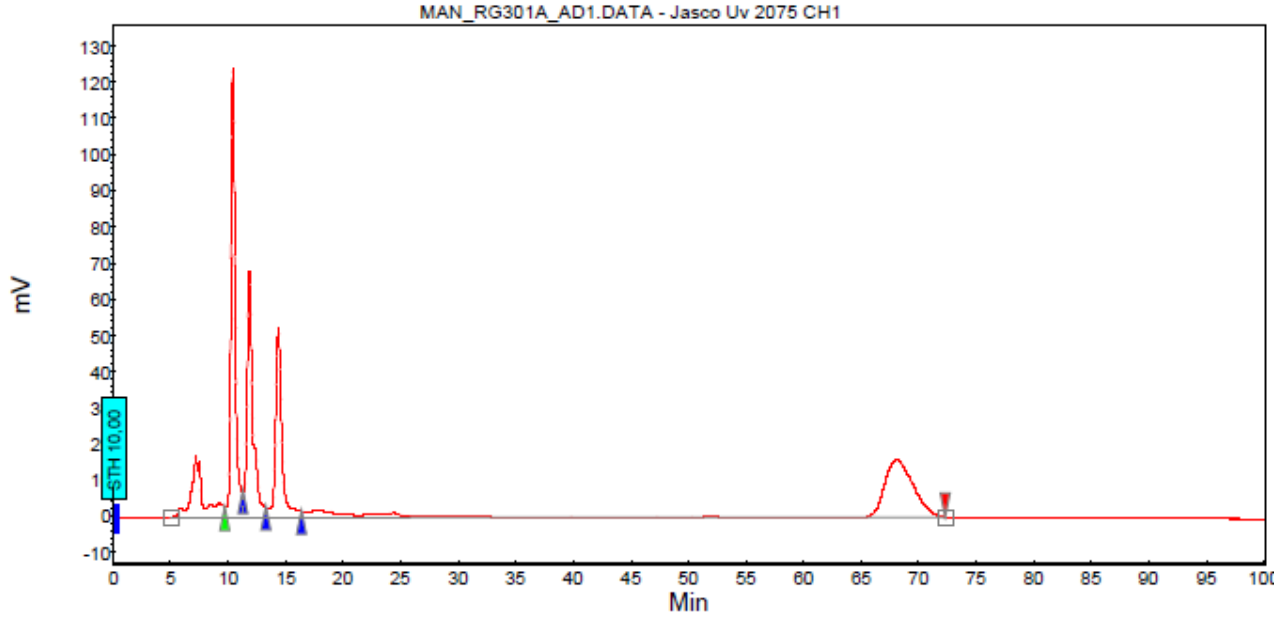
Compound 16: ^{13}C NMR (75 MHz, $CDCl_3$)



Compound 5a,b: ^{1}H NMR (400MHz, $CDCl_3$) Screening of reaction's temperature

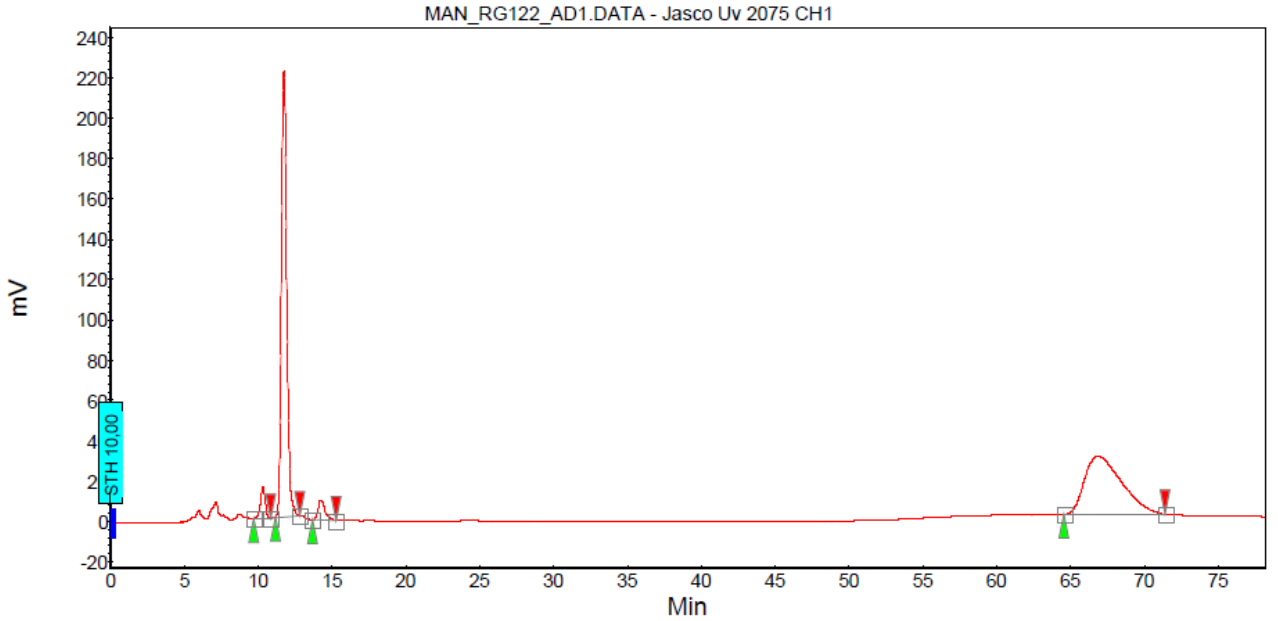


Compound 5a,b (racemic mixture)



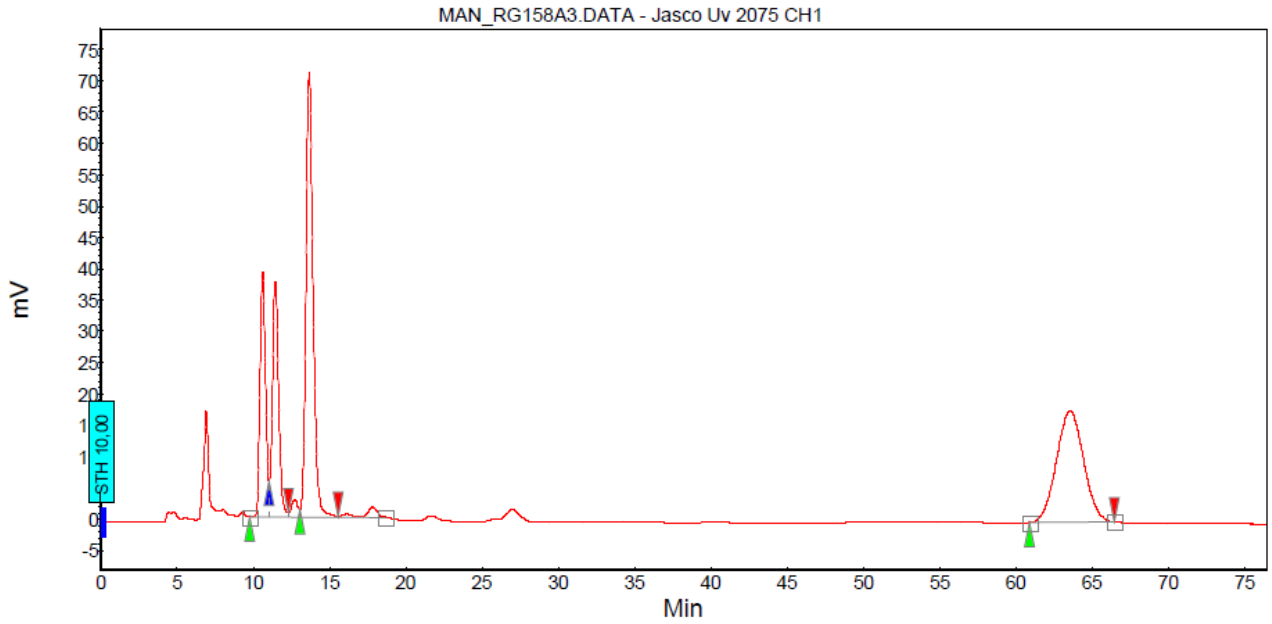
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	9,716	10,400	11,256	0,000	29,58	123,9	54,4	29,578
2	UNKNOWN	11,256	11,833	13,270	0,000	22,17	68,1	40,8	22,168
3	UNKNOWN	13,270	14,358	16,351	0,000	18,01	52,2	33,1	18,008
4	UNKNOWN	16,351	68,075	72,275	0,000	30,25	15,7	55,6	30,246
Total						100,00	259,9	184,0	100,000

Compound 5a,b (enantioenriched)



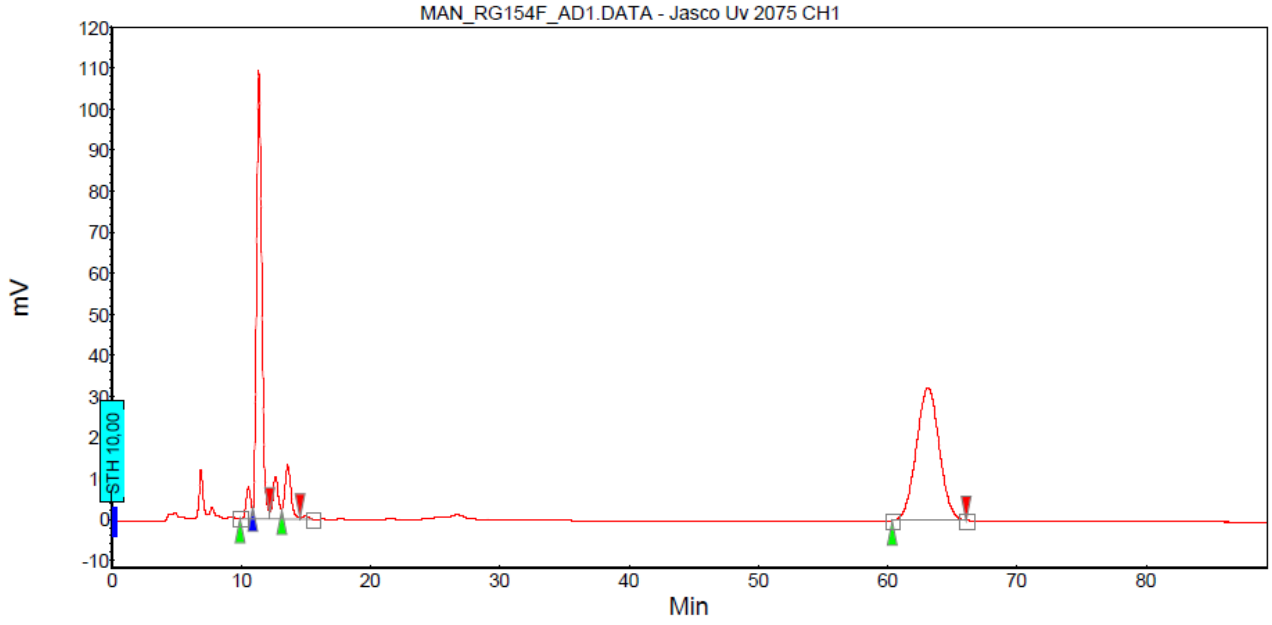
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	9,700	10,325	10,850	0,000	2,48	15,7	4.6	2,479
2	UNKNOWN	11,183	11,750	12,842	0,000	49,92	220,9	93,1	49,920
3	UNKNOWN	13,700	14,267	15,292	0,000	2,15	10,0	4,0	2,149
4	UNKNOWN	64,567	66,850	71,383	0,000	45,45	28,8	84,8	45,452
Total						100,00	275,3	186,6	100,000

Compound 6a,b (racemic mixture)



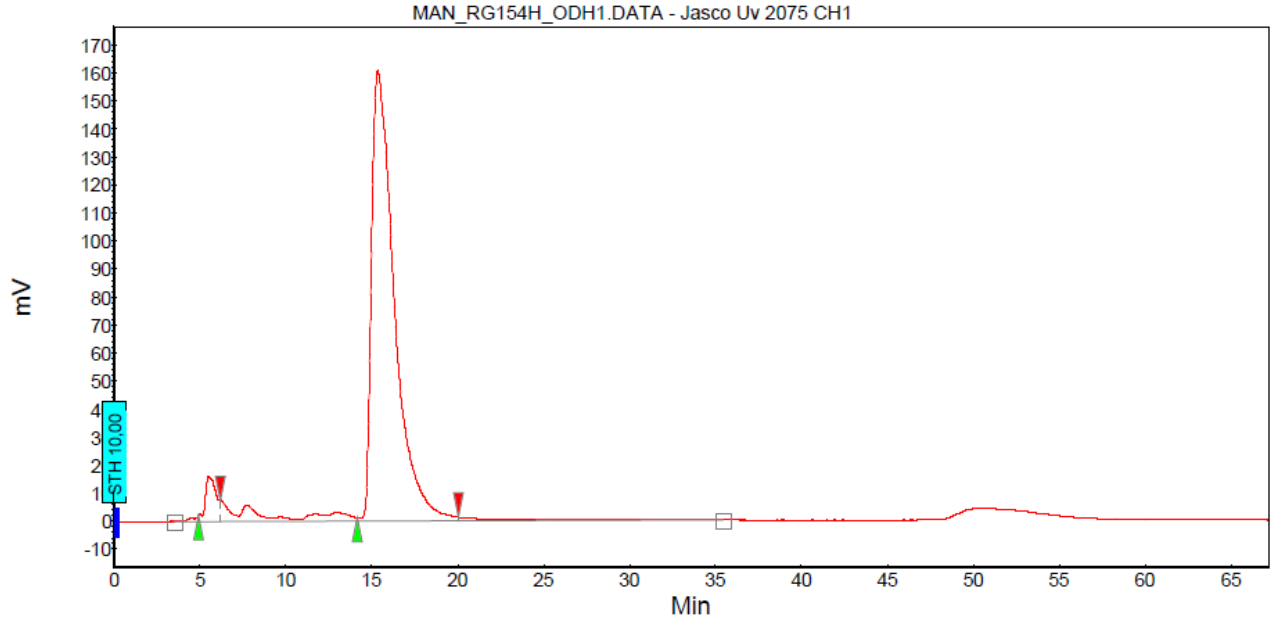
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	9,775	10,608	11,050	0,000	15,10	39,2	16,6	15,099
2	UNKNOWN	11,050	11,442	12,300	0,000	16,45	37,6	18,0	16,455
3	UNKNOWN	13,067	13,658	15,550	0,000	34,98	70,9	38,4	34,982
4	UNKNOWN	60,883	63,542	66,433	0,000	33,46	17,7	36,7	33,464
Total						100,00	165,4	109,6	100,000

Compound 6a,b (enantioenriched)



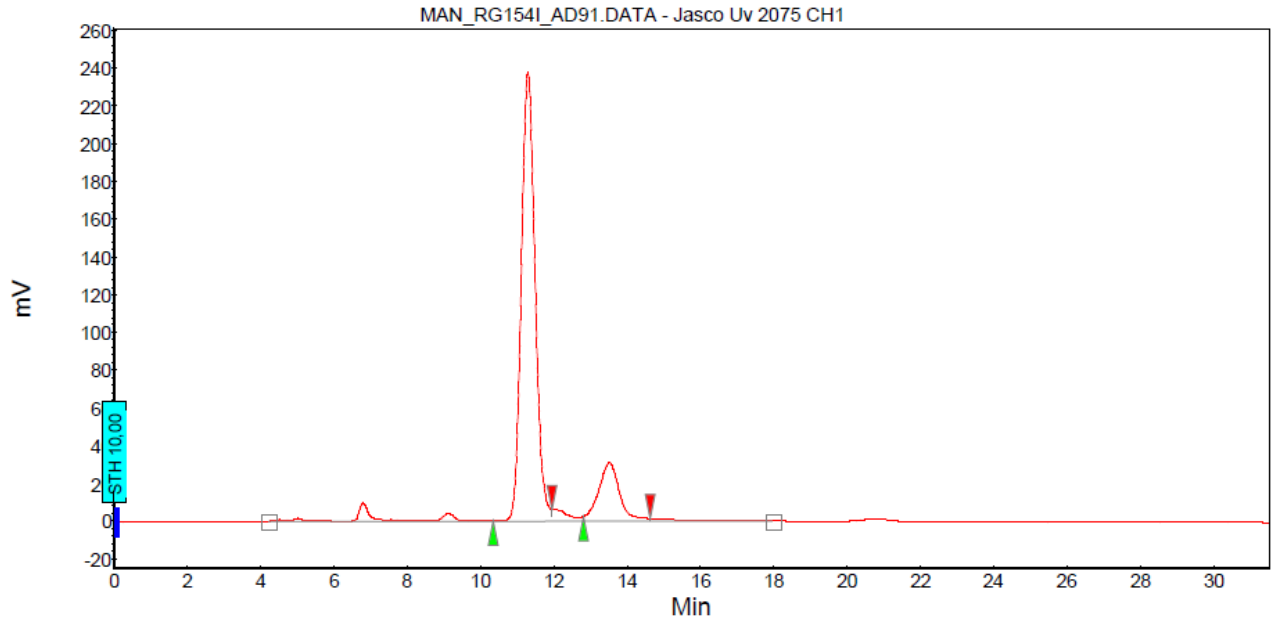
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	9,933	10,575	10,900	0,000	2,50	7,7	3,2	2,500
2	UNKNOWN	10,900	11,383	12,233	0,000	39,79	109,0	50,9	39,787
3	UNKNOWN	13,150	13,608	14,583	0,000	5,70	13,2	7,3	5,697
4	UNKNOWN	60,383	63,133	66,083	0,000	52,02	32,3	66,5	52,016
Total						100,00	162,2	127,9	100,000

Compound 7a (enantioenriched)



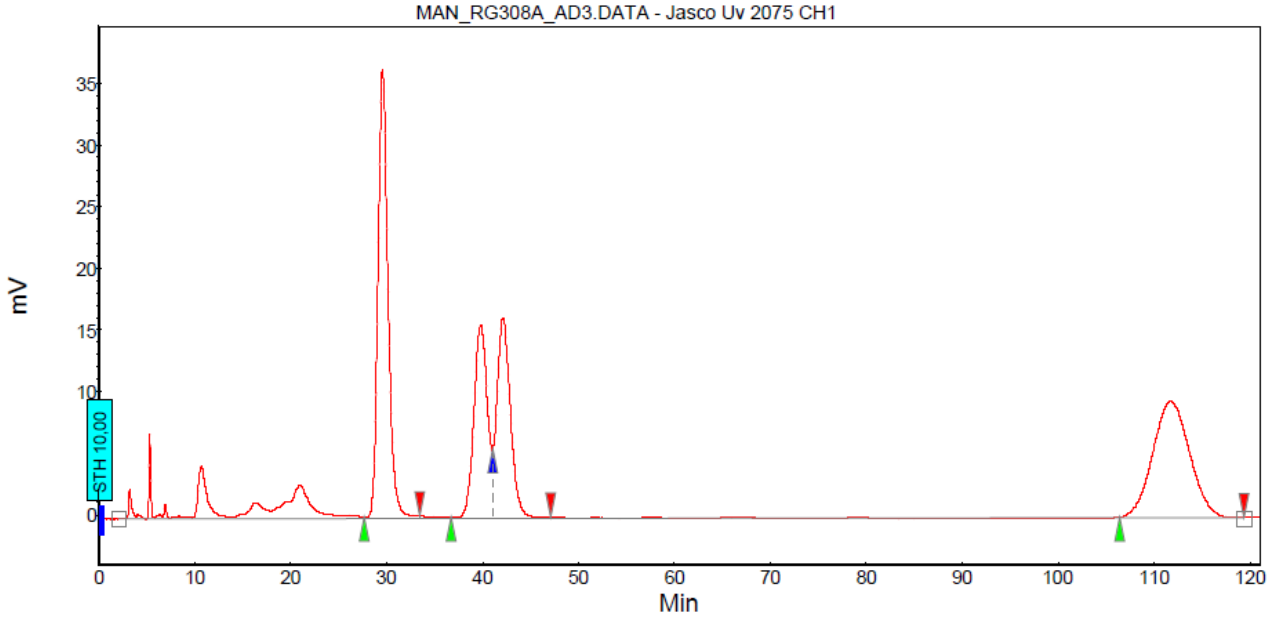
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	4,930	5,508	6,202	0,000	4,57	15,9	11,8	4,565
2	UNKNOWN	14,153	15,342	20,037	0,000	95,43	160,6	246,9	95,435
Total						100,00	176,5	258,7	100,000

Compound 7b (enantioenriched)



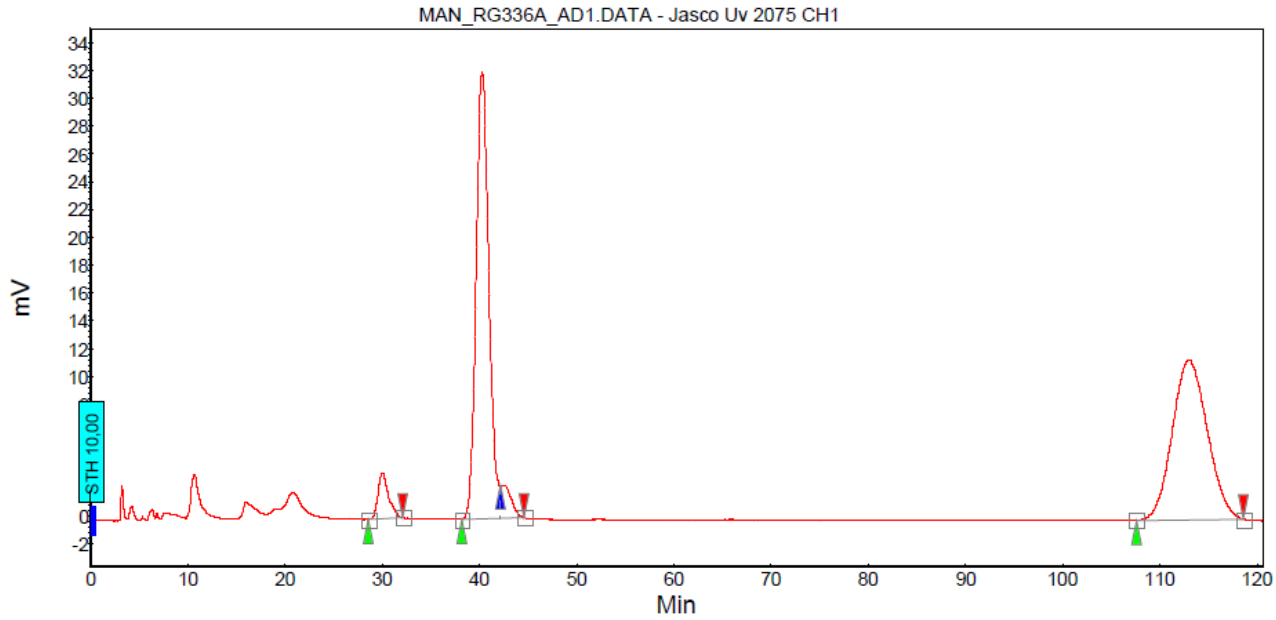
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	10,330	11,283	11,934	0,000	83,60	237,6	104,5	83,599
2	UNKNOWN	12,791	13,508	14,619	0,000	16,40	30,9	20,5	16,401
Total						100,00	268,5	125,0	100,000

Compound 8a,b (racemic mixture)



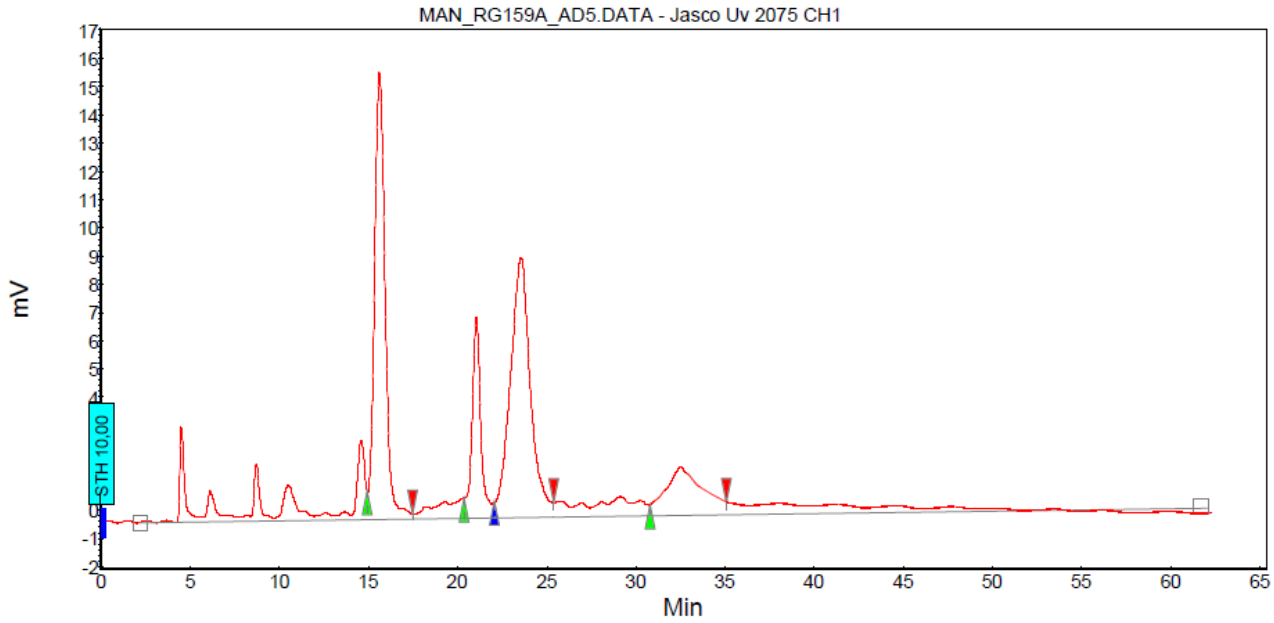
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	27,679	29,542	33,416	0,000	31,89	36,3	44,6	31,893
2	UNKNOWN	36,715	39,792	41,017	0,000	18,52	15,7	25,9	18,522
3	UNKNOWN	41,017	42,092	47,041	0,000	19,38	16,2	27,1	19,379
4	UNKNOWN	106,415	111,650	119,322	0,000	30,21	9,4	42,2	30,205
Total						100,00	77,7	139,7	100,000

Compound 8a,b (enantioenriched)



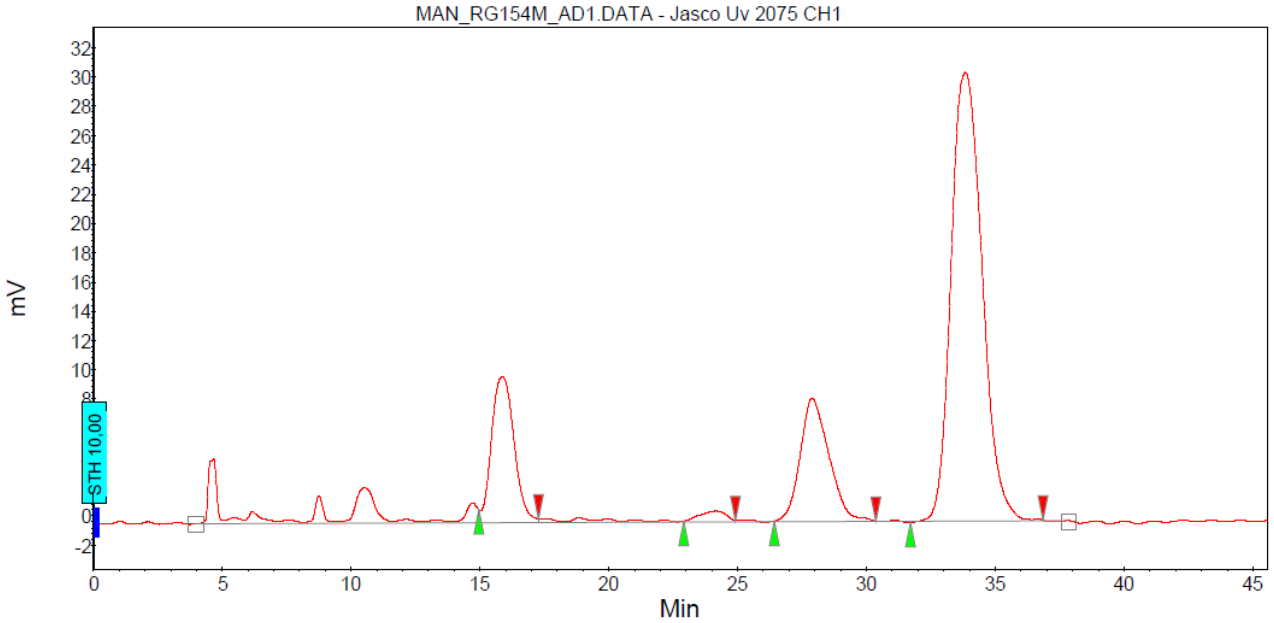
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	28,533	29,992	32,075	0,000	3,99	3,3	4,1	3,988
2	UNKNOWN	38,133	40,250	42,142	0,000	47,05	32,0	48,6	47,048
3	UNKNOWN	42,142	42,458	44,567	0,000	2,80	2,3	2,9	2,795
4	UNKNOWN	107,617	112,892	118,583	0,000	46,17	11,4	47,7	46,168
Total						100,00	49,1	103,3	100,000

Compound 9a,b (racemic mixture)



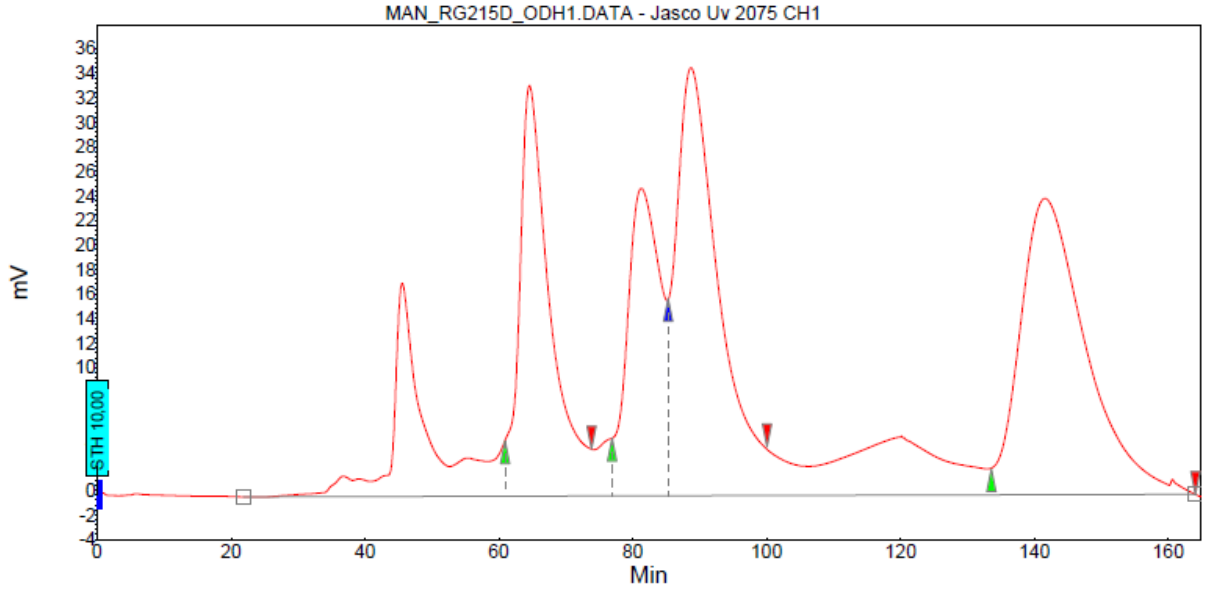
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	14,934	15,625	17,488	0,000	34,52	15,8	10,9	34,521
2	UNKNOWN	20,351	21,050	22,053	0,000	12,89	7,1	4,1	12,889
3	UNKNOWN	22,053	23,558	25,380	0,000	38,23	9,2	12,1	38,233
4	UNKNOWN	30,797	32,517	35,208	0,000	14,36	1,7	4,5	14,356
Total						100,00	33,9	31,7	100,000

Compound 9a,b (enantioenriched)



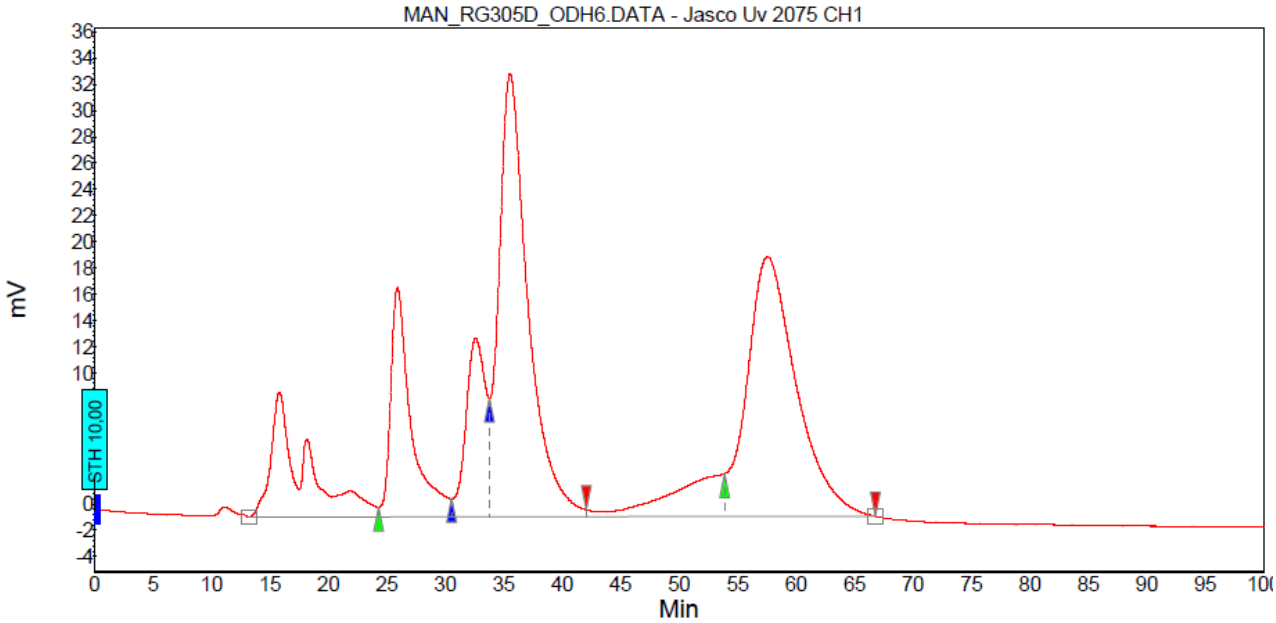
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	14,941	15,850	17,261	0,000	21,01	9,9	13,5	21,010
2	UNKNOWN	22,924	24,133	24,920	0,000	1,12	0,7	0,7	1,121
3	UNKNOWN	26,430	27,900	30,368	0,000	22,77	8,5	14,6	22,767
4	UNKNOWN	31,716	33,825	36,841	0,000	55,10	30,7	35,6	55,102
Total						100,00	49,8	64,4	100,000

Compound 10a,b (racemic mixture)



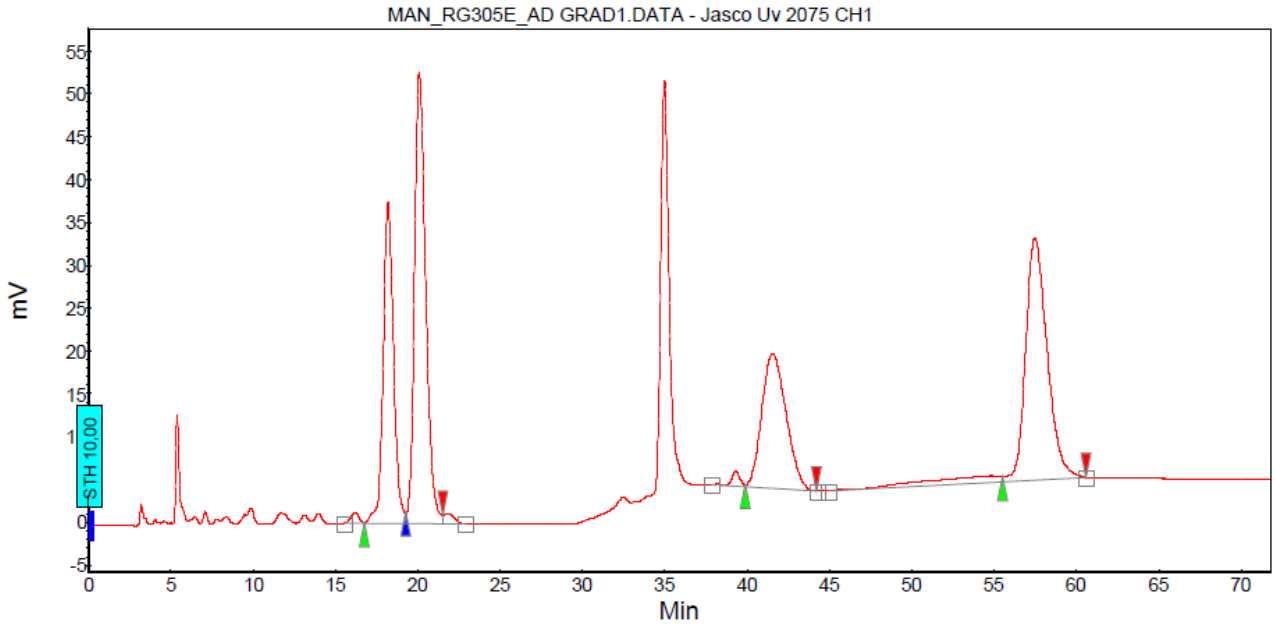
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	60,915	64,567	70,287	0,000	19,97	33,4	160,9	19,966
2	UNKNOWN	76,925	81,275	84,930	0,000	17,08	25,0	137,7	17,083
3	UNKNOWN	84,930	88,683	98,987	0,000	32,09	34,9	258,6	32,088
4	UNKNOWN	134,840	141,517	164,002	0,000	30,86	24,1	248,7	30,864
Total						100,00	117,5	805,9	100,000

Compound 10a,b (enantioenriched)



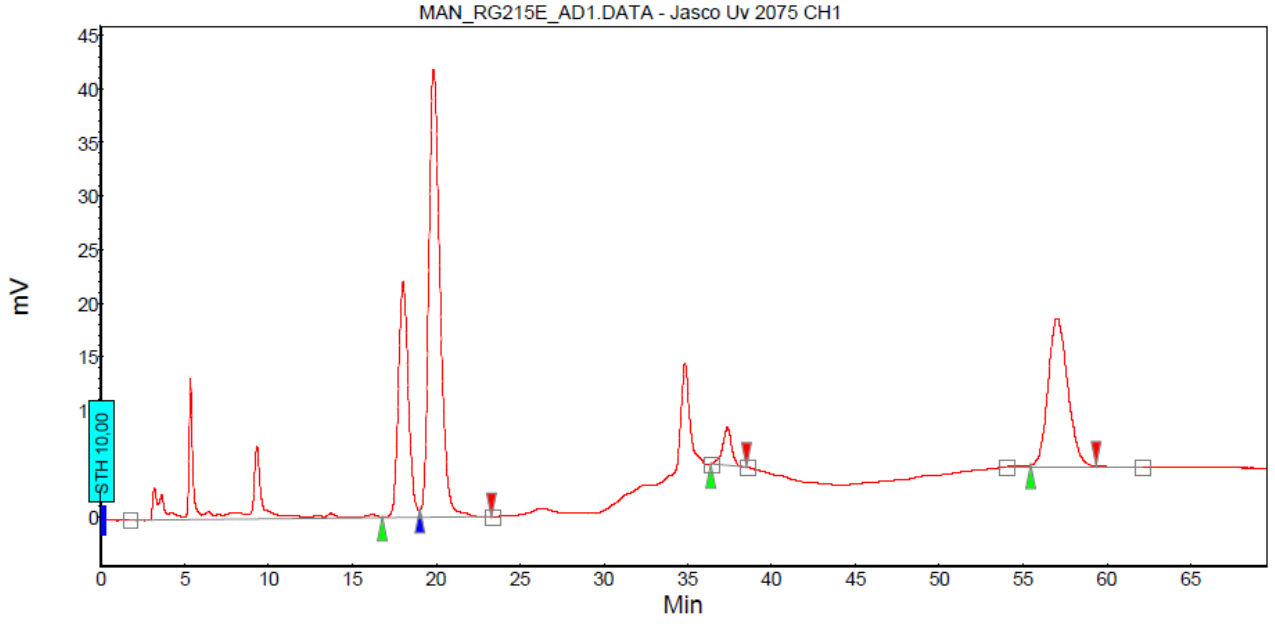
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	24,292	25,908	30,542	0,000	13,91	17,5	35,7	13,908
2	UNKNOWN	30,542	32,600	33,783	0,000	10,41	13,6	26,7	10,406
3	UNKNOWN	33,783	35,533	42,062	0,000	38,25	33,8	98,2	38,248
4	UNKNOWN	53,910	57,558	66,783	0,000	37,44	19,8	96,2	37,438
Total						100,00	84,7	256,9	100,000

Compound 11a,b (racemic mixture)



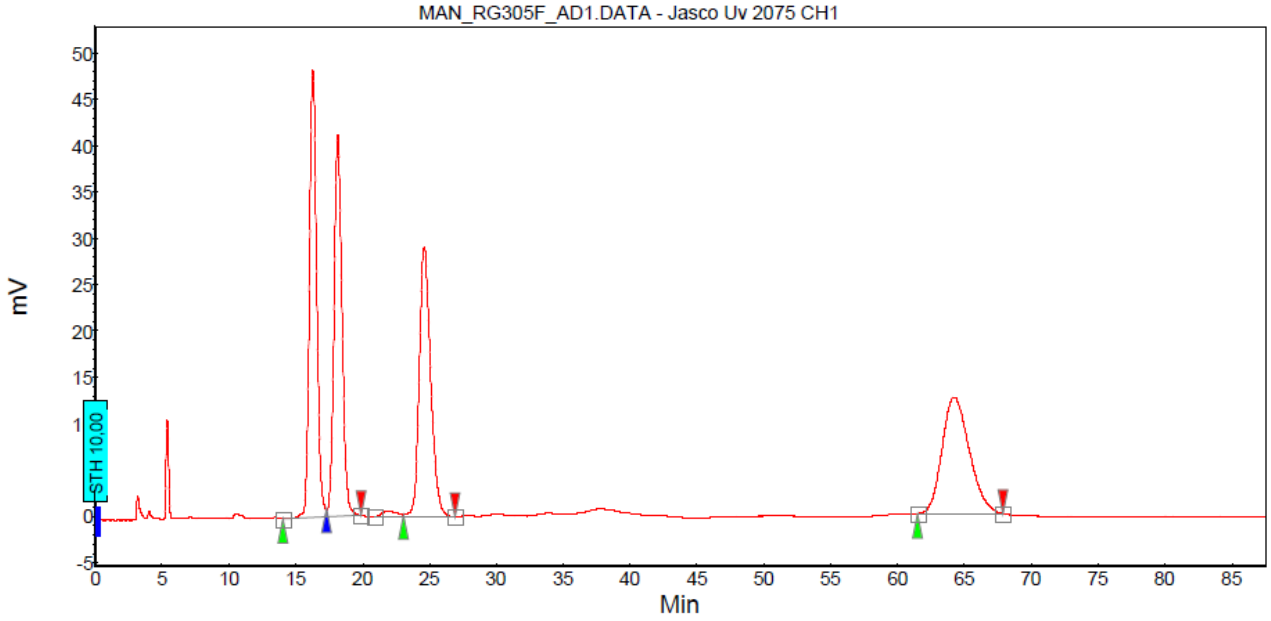
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	16,742	18,175	19,233	0,000	19,71	37,5	27,3	19,708
2	UNKNOWN	19,233	20,067	21,492	0,000	30,05	52,5	41,6	30,046
3	UNKNOWN	39,892	41,558	44,208	0,000	19,37	15,7	26,8	19,366
4	UNKNOWN	55,533	57,475	60,583	0,000	30,88	28,3	42,8	30,879
Total						100,00	134,1	138,6	100,000

Compound 11a,b (enantioenriched)



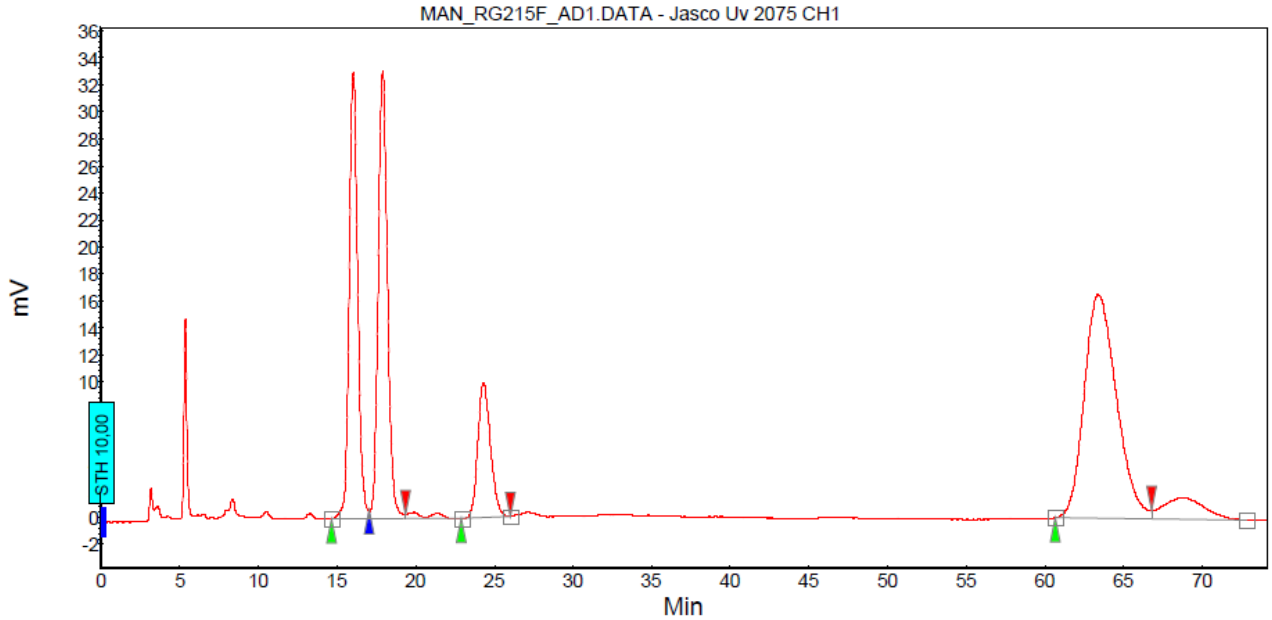
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	16,786	18,017	19,008	0,000	22,04	22,1	15,2	22,037
2	UNKNOWN	19,008	19,842	23,287	0,000	47,24	41,7	32,6	47,239
4	UNKNOWN	36,371	37,375	38,510	0,000	3,23	3,6	2,2	3,233
3	UNKNOWN	55,461	57,017	59,329	0,000	27,49	13,9	18,9	27,491
Total						100,00	81,3	68,9	100,000

Compound 12a,b (racemic mixture)



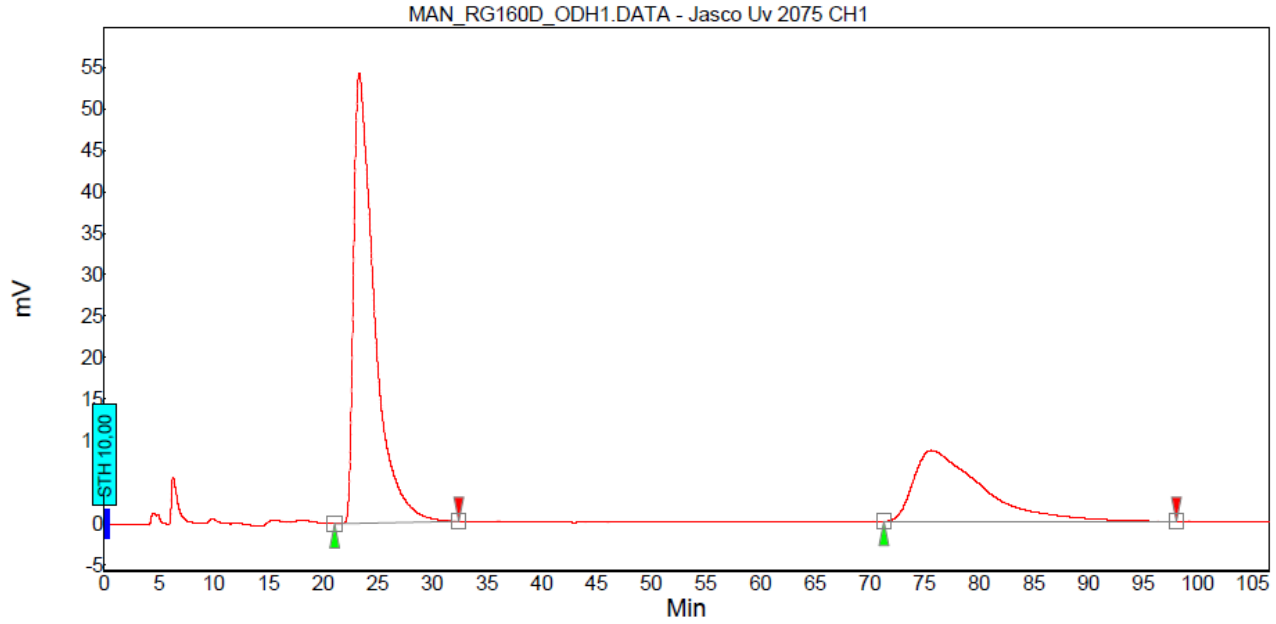
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	14,042	16,275	17,300	0,000	25,79	48,2	30,3	25,789
2	UNKNOWN	17,300	18,142	19,867	0,000	24,27	41,1	28,5	24,269
3	UNKNOWN	23,042	24,600	26,883	0,000	24,62	29,1	28,9	24,616
4	UNKNOWN	61,500	64,225	67,883	0,000	25,33	12,6	29,7	25,326
Total						100,00	131,0	117,4	100,000

Compound 12a,b (enantioenriched)



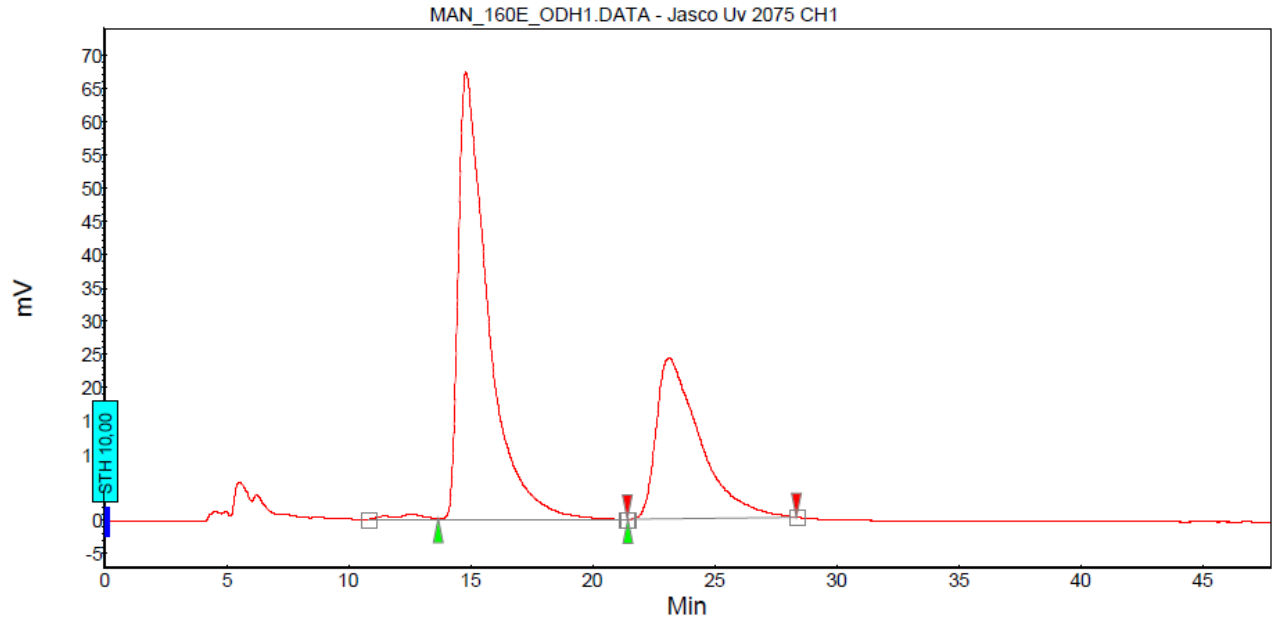
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	14,667	16,042	17,067	0,000	22,46	33,0	20,7	22,457
2	UNKNOWN	17,067	17,908	19,367	0,000	24,62	33,1	22,7	24,615
3	UNKNOWN	22,917	24,308	26,008	0,000	10,11	9,9	9,3	10,107
4	UNKNOWN	60,633	63,350	66,760	0,000	42,82	16,6	39,4	42,821
Total						100,00	92,5	92,0	100,000

Compound 13a (enantioenriched)



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	21,073	23,325	32,430	0,000	65,96	54,3	119,4	65,963
2	UNKNOWN	71,294	75,675	98,046	0,000	34,04	8,6	61,6	34,037
Total						100,00	62,9	181,0	100,000

Compound 13b (enantioenriched)



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[mV]	[mV.Min]	[%]
1	UNKNOWN	13,667	14,808	21,400	0,000	65,26	67,1	94,3	65,258
2	UNKNOWN	21,425	23,125	28,350	0,000	34,74	24,1	50,2	34,742
Total						100,00	91,2	144,4	100,000

Computational study

Structures **1c, 4a** and 2-hydroxyfuran were first submitted to a Monte Carlo conformational search with MM (MMFF94 force field) minimization. The global minima were then submitted to a geometry optimization with DFT at the B3LYP/6-31G(d) level. For imine **1c** the Z geometry was found to be the most stable. All the minima were confirmed by frequency calculation. Transition state search was first attempted with HF/3-21G on a simplified model (figure) then refined on the complete model. Single point calculation at the B3LYP/6-31G(d) level was then performed on the complete TS structures. TS were confirmed by analysis of the imaginary frequencies.

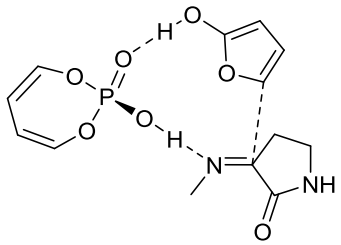
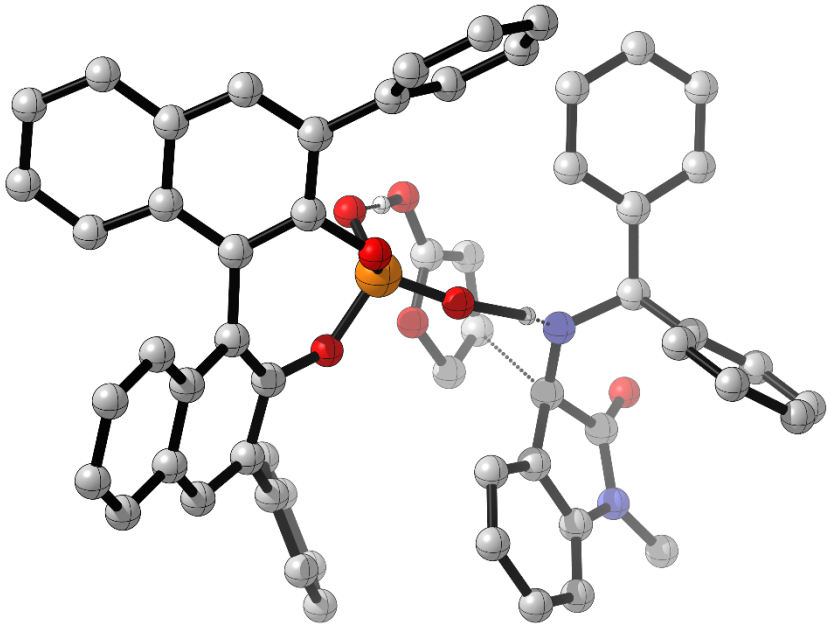


Figure. Simplified model for the transition state search

Computational data for the two transition states

TS-C



Energy = -3213.54148 au

G^0 (233K) = -3212.71793

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C1	2.8639811	-3.9266354	-0.4492690
2	C	C2	3.4553109	-3.5989563	0.7465567
3	C	C3	2.6258347	-2.6990314	1.4173958
4	O	O1	1.4439299	-2.6371477	0.6865148
5	C	C4	1.6132304	-3.2973267	-0.4253411
6	C	C5	3.3505661	-0.6524255	0.8265120
7	N	N1	2.9484731	-0.5242032	-0.4161859
8	H	H1	3.2367914	-4.5177731	-1.2565987
9	H	H2	4.4203747	-3.9091930	1.0915069
10	H	H3	2.4815500	-2.6018189	2.4712726
11	P	P1	-1.0997779	-0.4029072	-0.5322803
12	O	O3	-1.2725267	-1.7300348	-1.1578230

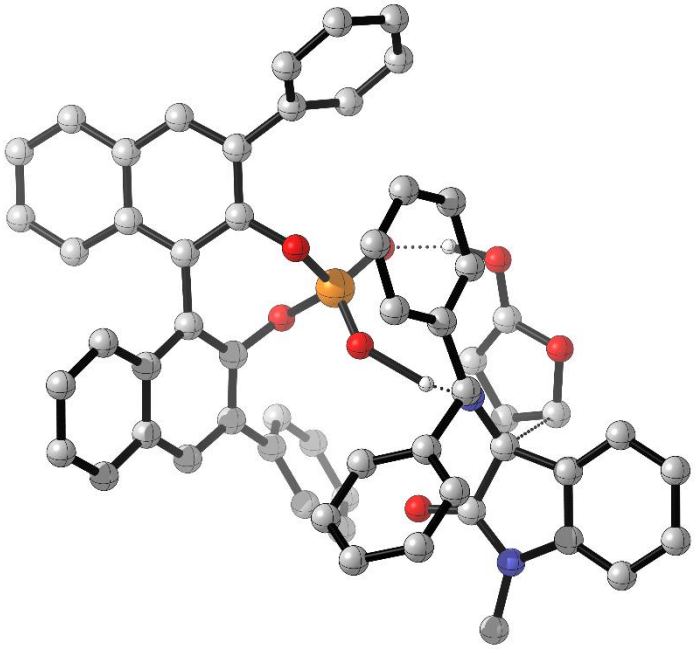
13	O	O4	0.2115508	0.2745454	-0.5634933
14	O	O2	0.7079270	-3.3485328	-1.3142430
15	H	H10	-0.0670058	-2.7264498	-1.2026930
16	H	H8	1.9896953	-0.2171821	-0.5408318
17	O	O5	-2.0799254	0.7541050	-1.1202815
18	O	O6	-1.4315058	-0.4741573	1.0400251
19	C	C6	-3.3549128	0.3301090	-1.3901209
20	C	C7	-4.1304242	-0.1285203	-0.3146942
21	C	C8	-4.9722821	-0.4303410	-2.9843644
22	C	C9	-5.2882394	-0.9155093	-0.6133785
23	C	C10	-3.7781246	0.2528834	-2.7248793
24	C	C11	-5.7056991	-1.0470622	-1.9616902
25	C	C12	-6.0584653	-1.5906288	0.3666619
26	H	H12	-7.1770503	-1.8895335	-3.3138744
27	H	H13	-5.3065275	-0.5232700	-4.0170787
28	C	C13	-7.1951384	-2.3321693	0.0371860
29	H	H14	-5.7661436	-1.5580814	1.4145843
30	H	H15	-7.7567942	-2.8370358	0.8184285
31	C	C14	-7.5966602	-2.4275748	-1.2867417
32	H	H16	-8.4771181	-3.0062747	-1.5507166
33	C	C15	-6.8553407	-1.7904398	-2.2790195
34	C	C16	-2.5676889	-0.0862685	1.7044996
35	C	C17	-3.7837036	0.2746207	1.0835161
36	C	C18	-3.4283891	0.6212585	3.8528887
37	C	C19	-4.7441892	1.0253724	1.8531149
38	C	C20	-2.4152990	-0.0044709	3.1101938
39	C	C21	-4.5540431	1.1789038	3.2449483
40	C	C22	-5.8988372	1.6441572	1.3036623
41	H	H18	-5.3509969	1.9738628	5.1015914
42	H	H19	-3.3261658	0.6843567	4.9355153
43	C	C23	-6.8230765	2.3408193	2.0865638

44	H	H20	-6.0915382	1.6008180	0.2328388
45	H	H21	-7.6931050	2.7954336	1.6205742
46	C	C24	-6.6237778	2.4487560	3.4530089
47	H	H22	-7.3382623	2.9859762	4.0700221
48	C	C25	-5.4950598	1.8715581	4.0277304
49	C	C26	-3.0293467	0.8577557	-3.8374002
50	C	C27	-1.6298933	2.0417541	-5.9754415
51	C	C28	-3.5778497	1.9364975	-4.5540898
52	C	C29	-1.7684369	0.3800412	-4.2216235
53	C	C30	-1.0717537	0.9717672	-5.2790480
54	C	C31	-2.8850109	2.5239518	-5.6151516
55	H	H7	-4.5524069	2.3331959	-4.2766547
56	H	H9	-1.3207500	-0.4614761	-3.6955133
57	H	H11	-0.0898275	0.5983449	-5.5559005
58	H	H23	-3.3236126	3.3602574	-6.1524343
59	H	H24	-1.0825473	2.5004365	-6.7940229
60	C	C32	-1.2659896	-0.5990098	3.8361766
61	C	C33	0.8346893	-1.7910781	5.3049011
62	C	C34	-0.8784743	-1.9308077	3.6058550
63	C	C35	-0.5711638	0.1166206	4.8268473
64	C	C36	0.4723511	-0.4699830	5.5503703
65	C	C37	0.1567150	-2.5230279	4.3347805
66	H	H17	-1.3970302	-2.5278509	2.8562156
67	H	H25	-0.8354143	1.1502699	5.0390726
68	H	H26	0.9962833	0.1070358	6.3073359
69	H	H27	0.4236042	-3.5585493	4.1406381
70	H	H28	1.6375301	-2.2516845	5.8734390
71	C	C45	3.9817477	-0.2928883	-1.4277352
72	H	H6	4.8124765	-0.9773157	-1.2594455
73	C	C46	3.5126870	-0.6456692	-2.8361300
74	C	C47	2.7954178	-1.3937377	-5.4625041

75	C	C48	4.4504619	-0.6183944	-3.8885526
76	C	C49	2.2069859	-1.0427783	-3.1393821
77	C	C50	1.8558341	-1.4282113	-4.4368370
78	C	C51	4.0947249	-0.9820857	-5.1895274
79	H	H4	5.4779709	-0.3148954	-3.6970517
80	H	H34	1.4309433	-1.0860319	-2.3830683
81	H	H35	0.8401672	-1.7641627	-4.6355328
82	H	H36	4.8349987	-0.9525675	-5.9843177
83	H	H37	2.5133961	-1.6920104	-6.4681308
84	C	C52	4.4260902	1.1567073	-1.3085489
85	C	C53	5.2437934	3.8257920	-1.0290633
86	C	C54	5.7817802	1.4727354	-1.1297706
87	C	C55	3.4872259	2.1996441	-1.3546288
88	C	C56	3.8954603	3.5258797	-1.2123789
89	C	C57	6.1870823	2.8007083	-0.9902300
90	H	H29	6.5305164	0.6835946	-1.0985040
91	H	H38	2.4290313	1.9859858	-1.5023702
92	H	H39	3.1583522	4.3241944	-1.2499976
93	H	H40	7.2393435	3.0371422	-0.8565303
94	H	H41	5.5588802	4.8606465	-0.9246562
95	C	C38	4.8681923	-0.8141359	1.2530910
96	N	N2	5.1493030	0.0167944	2.3076155
97	C	C39	2.9231627	0.4120698	1.8543788
98	C	C40	2.7070180	2.3991045	3.7781415
99	C	C41	1.7089331	1.0299121	2.0236689
100	C	C42	4.0206640	0.7635530	2.6521731
101	C	C43	3.9312606	1.7491603	3.6217599
102	C	C44	1.6073252	2.0429842	2.9834884
103	H	H32	0.8380064	0.7528948	1.4583893
104	H	H42	4.7786497	2.0316904	4.2358332
105	H	H43	0.6542714	2.5519305	3.1179665

106	H	H44	2.5992930	3.1877571	4.5195081
107	O	O7	5.5970813	-1.6016799	0.6768447
108	C	C58	6.4454971	0.1707286	2.9058666
109	H	H5	7.1526022	-0.5440372	2.4751394
110	H	H30	6.3740677	-0.0063428	3.9829428
111	H	H31	6.8122182	1.1842927	2.7180202

TS-D



Energy = -3213.53879 au

G^0 (233K) = -3212.71716

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C1	-1.8207565	0.5344703	3.3627390
2	C	C2	-3.1046345	0.0045966	3.2953042
3	C	C3	-3.9499164	0.9577267	2.7690644
4	O	O1	-3.1973461	2.1531176	2.6455767
5	C	C4	-1.9108381	1.8526075	2.9506226
6	C	C5	-3.6960601	0.4155475	0.5309359
7	N	N1	-2.5484856	0.9057555	0.1664235
8	H	H1	-0.9247942	0.0412608	3.6474043
9	H	H2	-3.3762678	-0.9932181	3.5490748
10	H	H3	-5.0028543	1.0776846	2.8174793
11	P	P1	1.1653849	0.5644892	1.2572336
12	O	O3	1.0481923	1.5267759	2.3902879
13	O	O4	-0.0557872	0.1652794	0.5244097
14	O	O2	-1.0209691	2.7769149	2.8176380

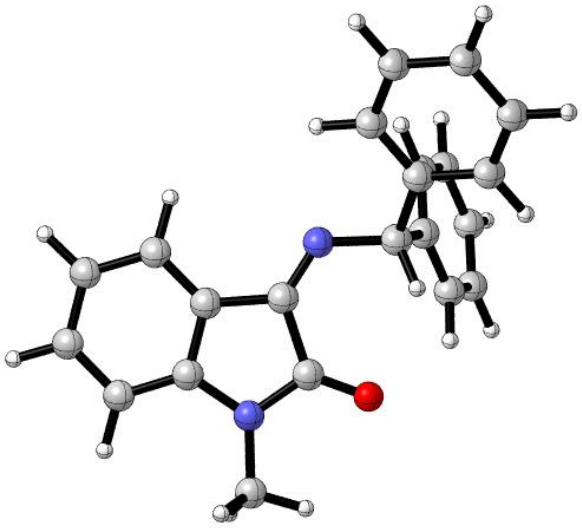
15	H	H10	-0.0543471	2.3808481	2.6744477
16	H	H8	-1.6392658	0.4485824	0.4120849
17	O	O5	2.1559651	1.0815160	0.0812300
18	O	O6	1.7725550	-0.8528104	1.7815924
19	C	C6	3.5052279	0.8339957	0.1577242
20	C	C7	3.9548515	-0.5055907	0.0728706
21	C	C8	5.7647633	1.6155109	0.3907823
22	C	C9	5.3508021	-0.7802845	0.2519530
23	C	C10	4.3961484	1.9110548	0.2845513
24	C	C11	6.2491015	0.3024482	0.3948483
25	C	C12	5.9083204	-2.0836700	0.3185207
26	H	H12	8.3138009	0.9079355	0.6613622
27	H	H13	6.4665712	2.4417146	0.5082417
28	C	C13	7.2787145	-2.3019905	0.4816780
29	H	H14	5.2699128	-2.9624452	0.2529983
30	H	H15	7.6635757	-3.3172270	0.5245900
31	C	C14	8.1399228	-1.2219849	0.5941511
32	H	H16	9.2060924	-1.3822398	0.7242735
33	C	C15	7.6262694	0.0714134	0.5546445
34	C	C16	2.0029883	-1.8433961	0.8562587
35	C	C17	2.9730682	-1.6092102	-0.1382022
36	C	C18	1.3368247	-3.8904976	-0.1737906
37	C	C19	3.0068942	-2.4773582	-1.2652314
38	C	C20	1.2244467	-3.0085886	0.9106107
39	C	C21	2.1780545	-3.6267056	-1.2684147
40	C	C22	3.8260535	-2.2588879	-2.3989903
41	H	H18	1.5808436	-5.4000930	-2.3638897
42	H	H19	0.7457737	-4.8053254	-0.1698036
43	C	C23	3.8405364	-3.1438948	-3.4786407
44	H	H20	4.4617621	-1.3770155	-2.4569583
45	H	H21	4.4811766	-2.9442376	-4.3334453

46	C	C24	3.0343357	-4.2730201	-3.4568446
47	H	H22	3.0423482	-4.9651514	-4.2941719
48	C	C25	2.2093275	-4.5119005	-2.3592617
49	C	C26	-3.9554460	-1.0951757	0.4647039
50	N	N2	-5.2726541	-1.3167882	0.1320569
51	C	C27	-5.0581384	0.9726035	0.1615522
52	C	C28	-7.6769467	1.4620962	-0.5034437
53	C	C29	-5.9341122	-0.0956854	-0.0580975
54	C	C30	-5.4625353	2.2894628	0.0942178
55	C	C31	-6.7932794	2.5304005	-0.2513840
56	C	C32	-7.2517074	0.1314728	-0.4040304
57	H	H23	-4.7757538	3.0994681	0.3109781
58	H	H24	-7.1554222	3.5546926	-0.3205444
59	H	H25	-7.9465173	-0.6803663	-0.5870773
60	H	H26	-8.7106135	1.6775670	-0.7692370
61	O	O7	-3.0383217	-1.8594368	0.6820144
62	C	C33	-2.5465997	1.4014538	-1.2382851
63	H	H6	-3.3914595	2.0801103	-1.3801152
64	C	C34	-5.8557292	-2.6085413	-0.0822110
65	H	H7	-6.7289254	-2.7267365	0.5657948
66	H	H9	-5.1320477	-3.3957821	0.1483066
67	C	C35	-1.3374045	2.2917439	-1.4852625
68	C	C36	0.7979793	4.0757093	-1.9131419
69	C	C37	-0.5752104	2.2399722	-2.6649563
70	C	C38	-1.0169653	3.2756931	-0.5390440
71	C	C39	0.0469580	4.1527624	-0.7453190
72	C	C40	0.4889059	3.1194133	-2.8731859
73	H	H5	-0.7915493	1.5132247	-3.4441947
74	H	H28	-1.5921154	3.3662504	0.3776829
75	H	H29	0.2956506	4.8865852	0.0162528
76	H	H30	1.0785518	3.0525966	-3.7829416

77	H	H31	1.6301844	4.7546192	-2.0677791
78	C	C41	-2.7097933	0.2243014	-2.1964701
79	C	C42	-3.0551201	-1.9368431	-3.9607375
80	C	C43	-3.7540715	0.2243827	-3.1361971
81	C	C44	-1.8369065	-0.8749139	-2.1655935
82	C	C45	-2.0098952	-1.9479670	-3.0407276
83	C	C46	-3.9260063	-0.8507024	-4.0099418
84	H	H4	-4.4408071	1.0661504	-3.1966557
85	H	H32	-1.0072583	-0.9062871	-1.4617487
86	H	H33	-1.3195234	-2.7871577	-3.0026874
87	H	H34	-4.7351277	-0.8362984	-4.7351903
88	H	H35	-3.1827563	-2.7705332	-4.6456134
89	C	C53	0.3413219	-3.3268793	2.0543528
90	C	C54	-1.3269933	-3.9687685	4.2469851
91	C	C55	-0.9707114	-3.7854790	1.8623412
92	C	C56	0.7958420	-3.2072334	3.3802477
93	C	C57	-0.0284937	-3.5201747	4.4654894
94	C	C58	-1.7985018	-4.1015191	2.9448885
95	H	H17	-1.3754422	-3.8723088	0.8556641
96	H	H40	1.8109468	-2.8670207	3.5789536
97	H	H41	0.3502568	-3.4135073	5.4783419
98	H	H42	-2.8139107	-4.4405156	2.7613126
99	H	H43	-1.9681041	-4.2137298	5.0888033
100	C	C59	3.9876352	3.3247582	0.3322064
101	C	C60	3.3727319	6.0723418	0.4897933
102	C	C61	3.2678330	3.8411178	1.4183567
103	C	C62	4.3920132	4.2178555	-0.6758765
104	C	C63	4.0901607	5.5803930	-0.5974566
105	C	C64	2.9588491	5.2021542	1.4955212
106	H	H11	2.9464232	3.1869287	2.2263952
107	H	H44	4.9515726	3.8489941	-1.5327911

108	H	H45	4.4118857	6.2527549	-1.3876119
109	H	H46	2.3896867	5.5725763	2.3443678
110	H	H47	3.1305403	7.1293995	0.5524281
111	H	H50	-6.1553349	-2.7001581	-1.1304224

Imine 1c, Z isomer



Energy = -1033.91076 au

G^0 (233K) = -1033.59296 au

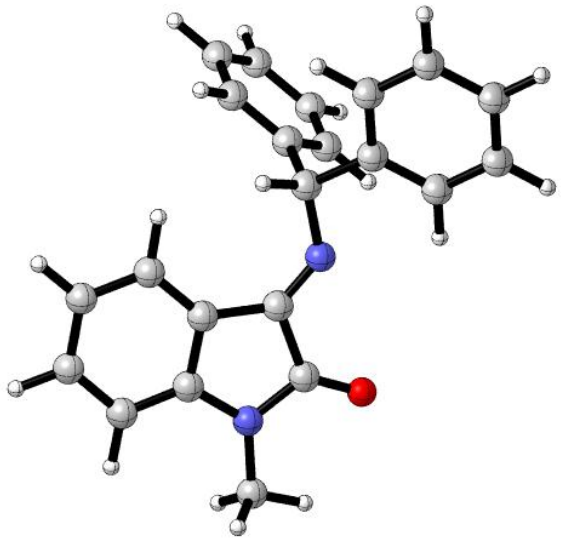
ZPE = 219.420 kcal/mol

Cartesian Coordinates (Angstroms)

1	H	H1	1.6983367	1.8316152	2.2006059
2	C	C1	2.5515245	1.4738133	1.6607855
3	C	C4	4.7557267	0.5062955	0.2150722
4	C	C2	2.3787644	0.6995054	0.5435566
5	C	C6	3.8475770	1.7738529	2.0682618
6	C	C5	4.9285281	1.2939355	1.3503516
7	C	C3	3.4705957	0.2184794	-0.1733757
8	H	H6	4.0096063	2.3763205	2.9387380
9	H	H5	5.9235748	1.5302617	1.6713336
10	H	H4	5.6011506	0.1412545	-0.3300329
11	C	C7	1.1563919	0.2280654	-0.1237422
12	C	C8	1.6587577	-0.6037522	-1.3043136
13	N	N1	3.0254848	-0.5445725	-1.2615363
14	O	O1	1.0071120	-1.2089380	-2.1341064

15	N	N2	-0.0195004	0.4820961	0.2174238
16	C	C9	3.8815880	-1.2137354	-2.2298033
17	H	H7	3.2390923	-1.7200823	-2.9332875
18	H	H8	4.5193108	-1.9377982	-1.7377216
19	C	C16	-1.2215889	-0.0212158	-0.4930921
20	H	H13	-0.9797050	-0.2880716	-1.5090883
21	C	C17	-1.6751876	-1.2784388	0.2488284
22	C	C18	-2.4309806	-3.5837736	1.6021163
23	C	C19	-2.3546711	-1.1904259	1.4543107
24	C	C20	-1.3656805	-2.5266955	-0.2687944
25	C	C21	-1.7481392	-3.6758499	0.4037320
26	C	C22	-2.7301203	-2.3372531	2.1279015
27	H	H2	-2.5983297	-0.2272853	1.8530682
28	H	H15	-0.8131272	-2.5921630	-1.1840427
29	H	H16	-1.5108048	-4.6367275	-0.0084910
30	H	H17	-3.2578019	-2.2598616	3.0579388
31	H	H18	-2.7283599	-4.4724440	2.1229605
32	C	C23	-2.2930154	1.0584755	-0.4921995
33	C	C24	-4.3158376	2.9684540	-0.5493699
34	C	C25	-2.2177149	2.1800762	0.3148770
35	C	C26	-3.3872470	0.9024546	-1.3335583
36	C	C27	-4.3923900	1.8488770	-1.3629900
37	C	C28	-3.2282057	3.1293544	0.2869165
38	H	H14	-1.3701724	2.3059354	0.9535324
39	H	H19	-3.4535977	0.0331857	-1.9594110
40	H	H20	-5.2313089	1.7158826	-2.0171414
41	H	H21	-3.1594779	3.9941758	0.9172622
42	H	H22	-5.0946917	3.7047103	-0.5715961
43	H	H25	4.4954673	-0.4930656	-2.7558146

Imine 1c, E isomer



Energy = -1033.90317 au

G^0 (233K) = -1033.58595 au

ZPE = 219.044 kcal/mol

Cartesian Coordinates (Angstroms)

1	H	H1	0.9611839	-1.5586879	1.7477127
2	C	C1	1.9341083	-1.1933145	1.4999900
3	C	C4	4.5037915	-0.3137979	0.8279681
4	C	C2	2.1002495	-0.1813843	0.5818385
5	C	C6	3.0508912	-1.7637549	2.0994494
6	C	C5	4.3168103	-1.3213868	1.7663239
7	C	C3	3.3919982	0.2422850	0.2421461
8	H	H6	2.9278085	-2.5505306	2.8152899
9	H	H5	5.1739810	-1.7658883	2.2318689
10	H	H4	5.4885283	0.0138259	0.5679582
11	C	C7	1.1595762	0.6226722	-0.2260439
12	C	C8	2.0462061	1.5221839	-1.0881296
13	N	N1	3.3451360	1.2381282	-0.7278832
14	O	O1	1.7039656	2.3354220	-1.9094074
15	N	N2	-0.0800122	0.7276462	-0.3289577

16	C	C9	4.4968494	1.9014926	-1.3173590
17	H	H7	4.1221539	2.6124458	-2.0375538
18	H	H8	5.1379526	1.1860862	-1.8185149
19	C	C16	-1.0959684	-0.0041782	0.4394728
20	H	H13	-0.7281455	-0.2870992	1.4180033
21	C	C17	-2.3154662	0.8988450	0.6205604
22	C	C18	-4.5710522	2.4836512	0.9857749
23	C	C19	-2.4711324	2.0669103	-0.1056959
24	C	C20	-3.2919332	0.5336645	1.5368466
25	C	C21	-4.4136435	1.3186500	1.7192940
26	C	C22	-3.5984947	2.8528022	0.0766479
27	H	H2	-1.7095186	2.3566224	-0.7975142
28	H	H15	-3.1815597	-0.3716168	2.1027106
29	H	H16	-5.1610615	1.0244901	2.4294805
30	H	H17	-3.7098544	3.7551309	-0.4917111
31	H	H18	-5.4406587	3.0947256	1.1257498
32	C	C23	-1.4846872	-1.2608406	-0.3354891
33	C	C24	-2.2344740	-3.5355110	-1.7465085
34	C	C25	-1.7259616	-1.1898848	-1.7009871
35	C	C26	-1.6184247	-2.4758394	0.3127308
36	C	C27	-1.9955481	-3.6110606	-0.3887852
37	C	C28	-2.0971245	-2.3203145	-2.4006322
38	H	H14	-1.6186011	-0.2512994	-2.2042625
39	H	H19	-1.4343849	-2.5449044	1.3682056
40	H	H20	-2.0975385	-4.5458555	0.1260563
41	H	H21	-2.2807240	-2.2559669	-3.4547493
42	H	H22	-2.5238660	-4.4111038	-2.2927981
43	H	H25	5.0672942	2.4244938	-0.5592633