

Supporting Information
for
Synthesis of new pyrrolidine-based organocatalysts
and study of their use in the asymmetric Michael
addition of aldehydes to nitroolefins

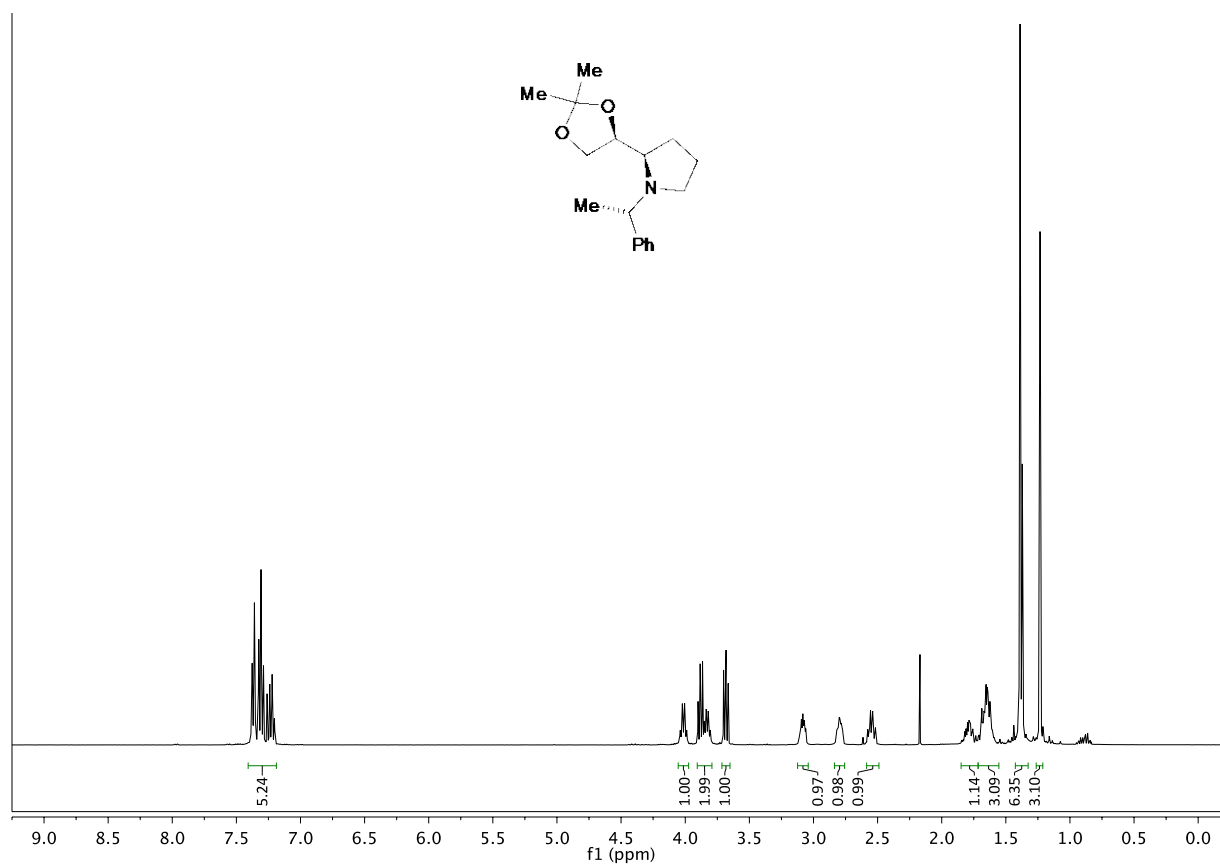
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Universidad de Zaragoza, Departamento de Química Orgánica, Pedro Cerbuna 12,
E-50009 Zaragoza, Spain

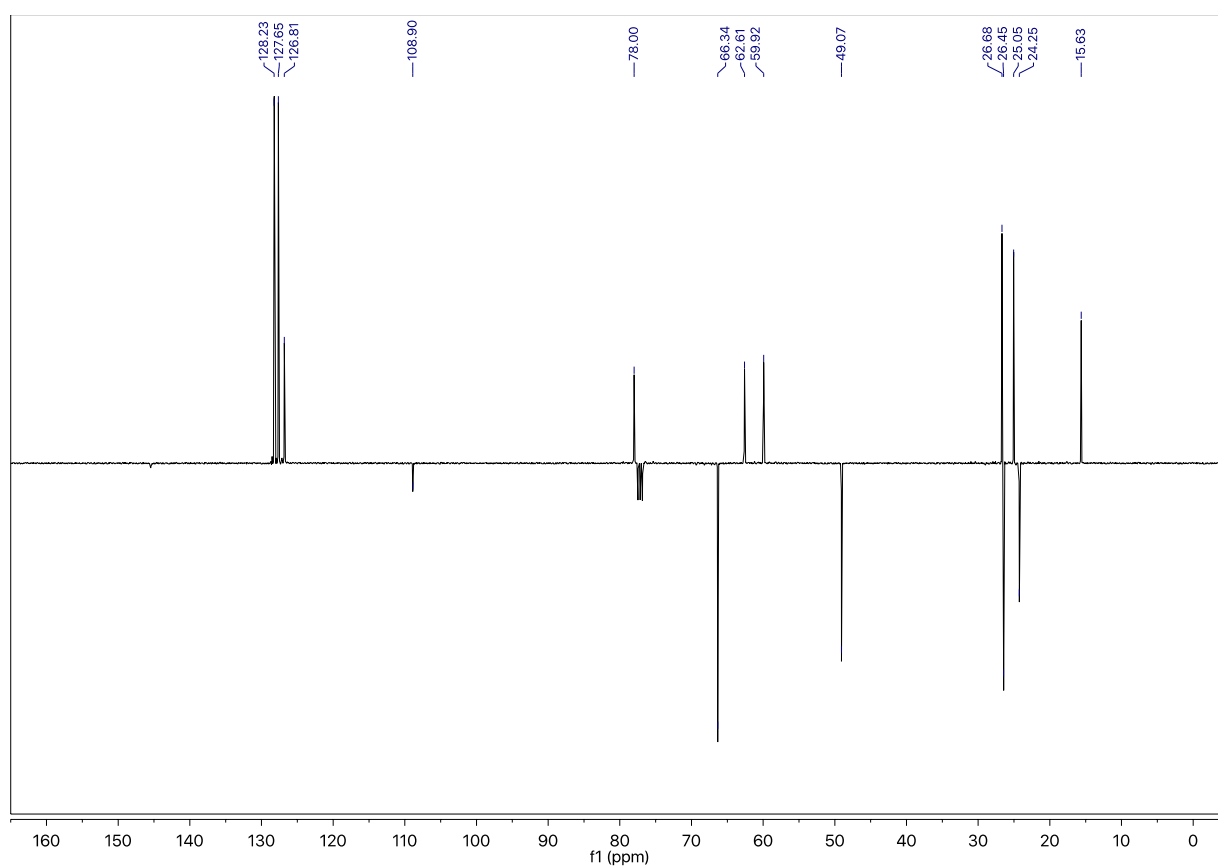
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*Corresponding author

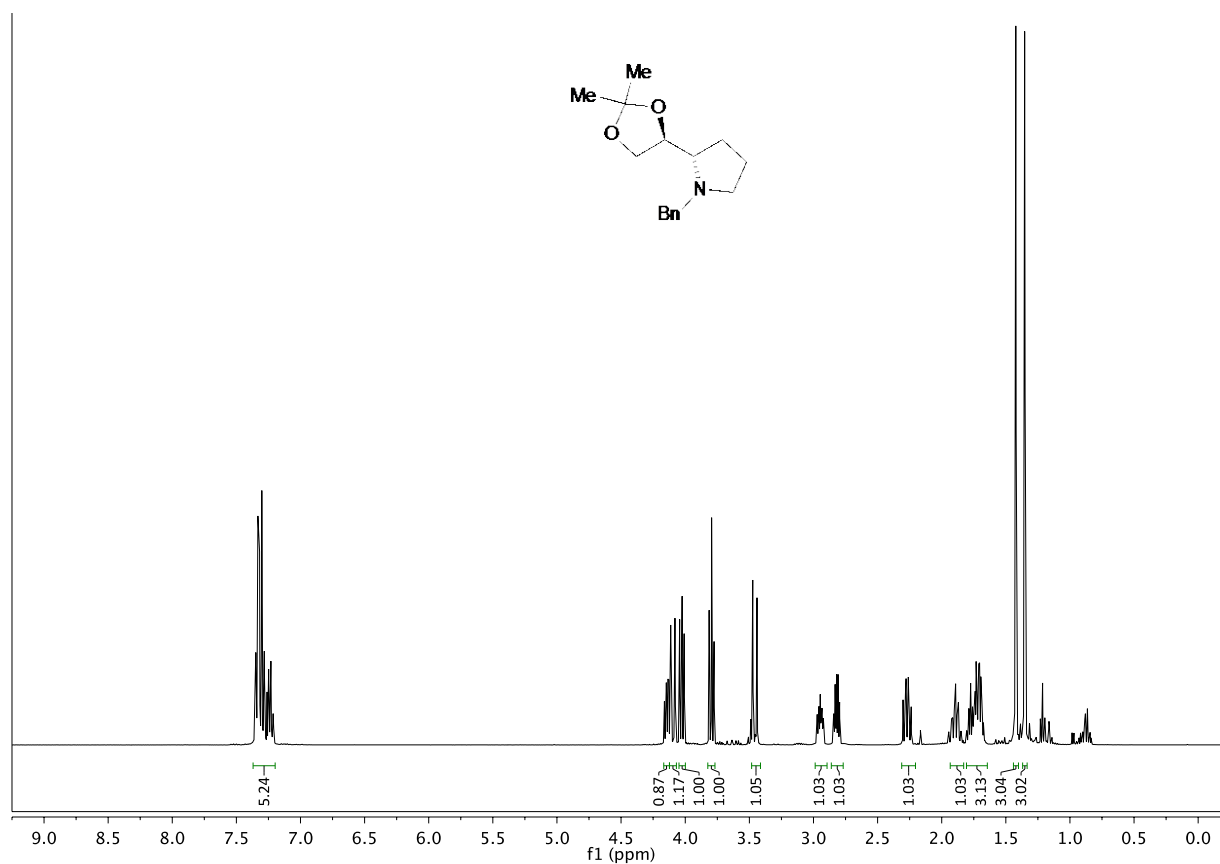
NMR spectra and HPLC chromatograms



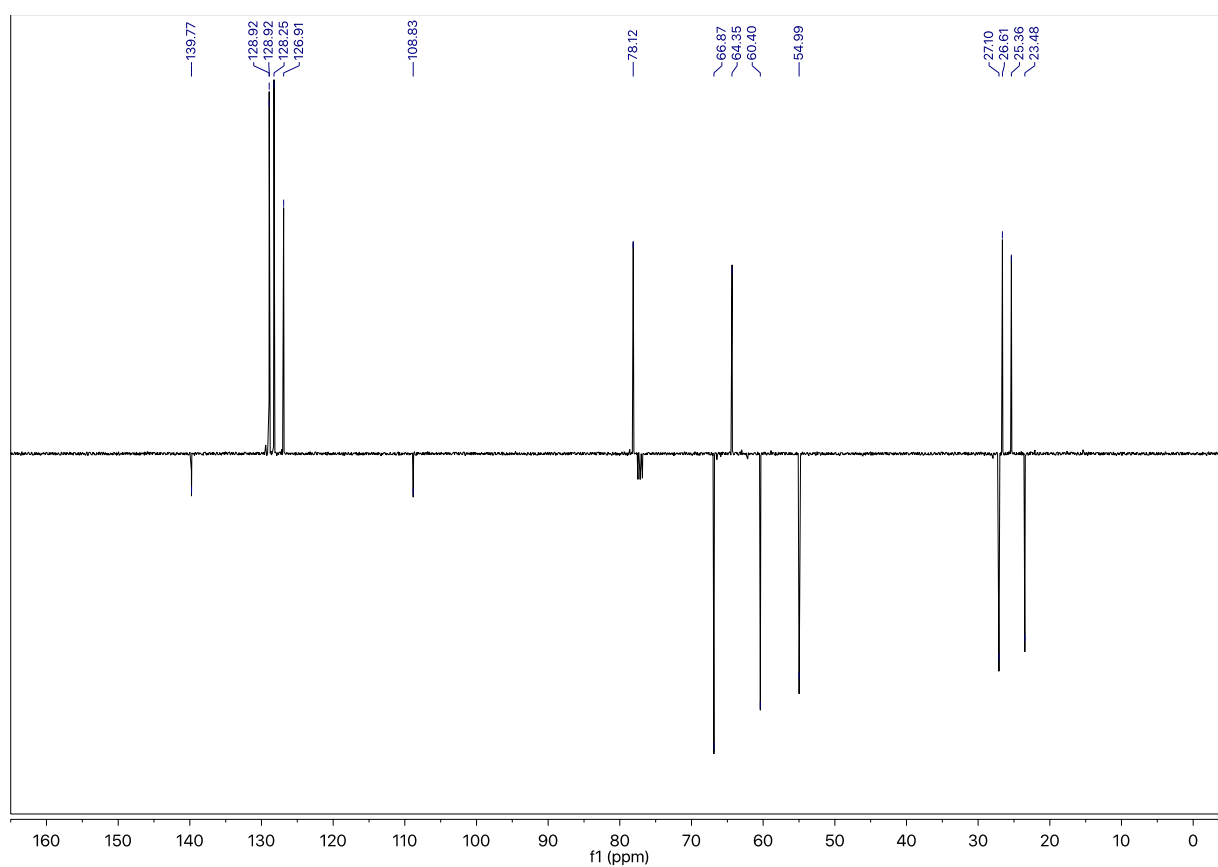
^1H NMR of **2**



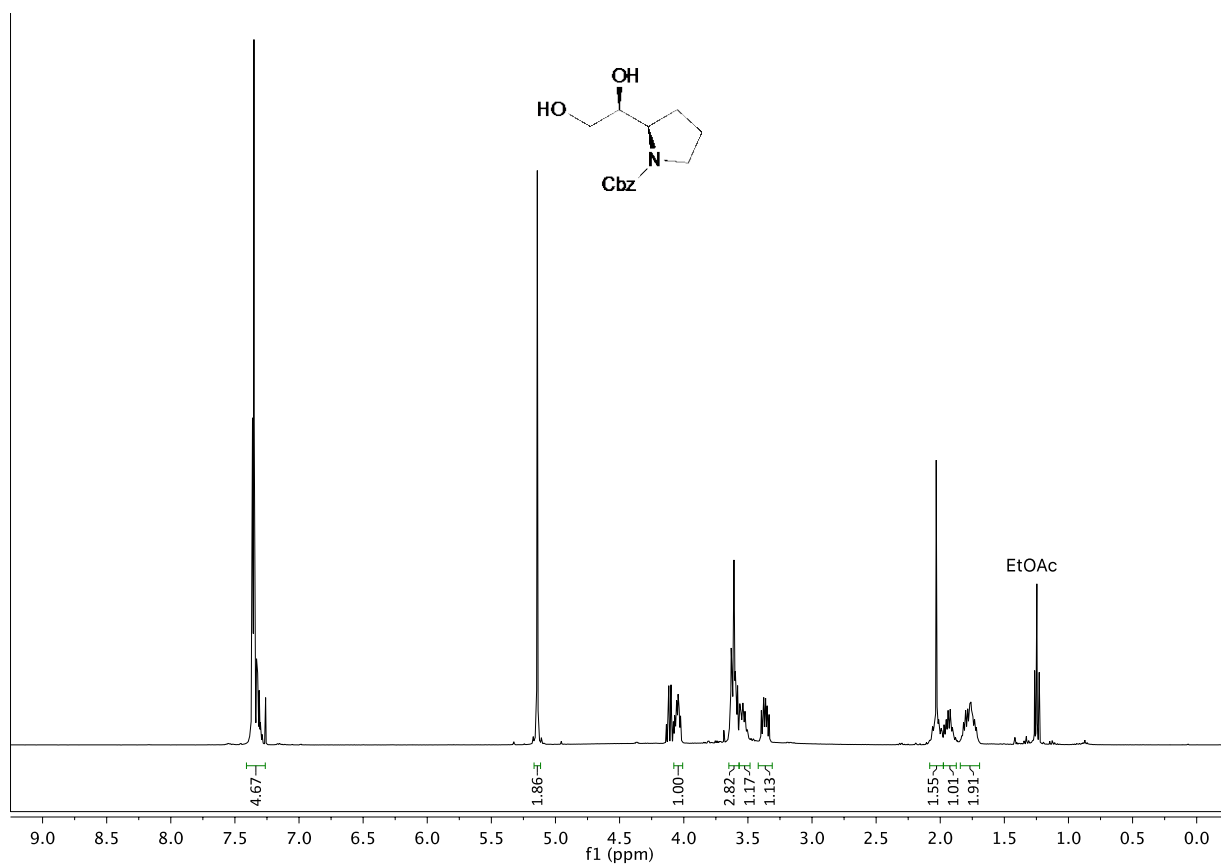
^{13}C NMR of **2**



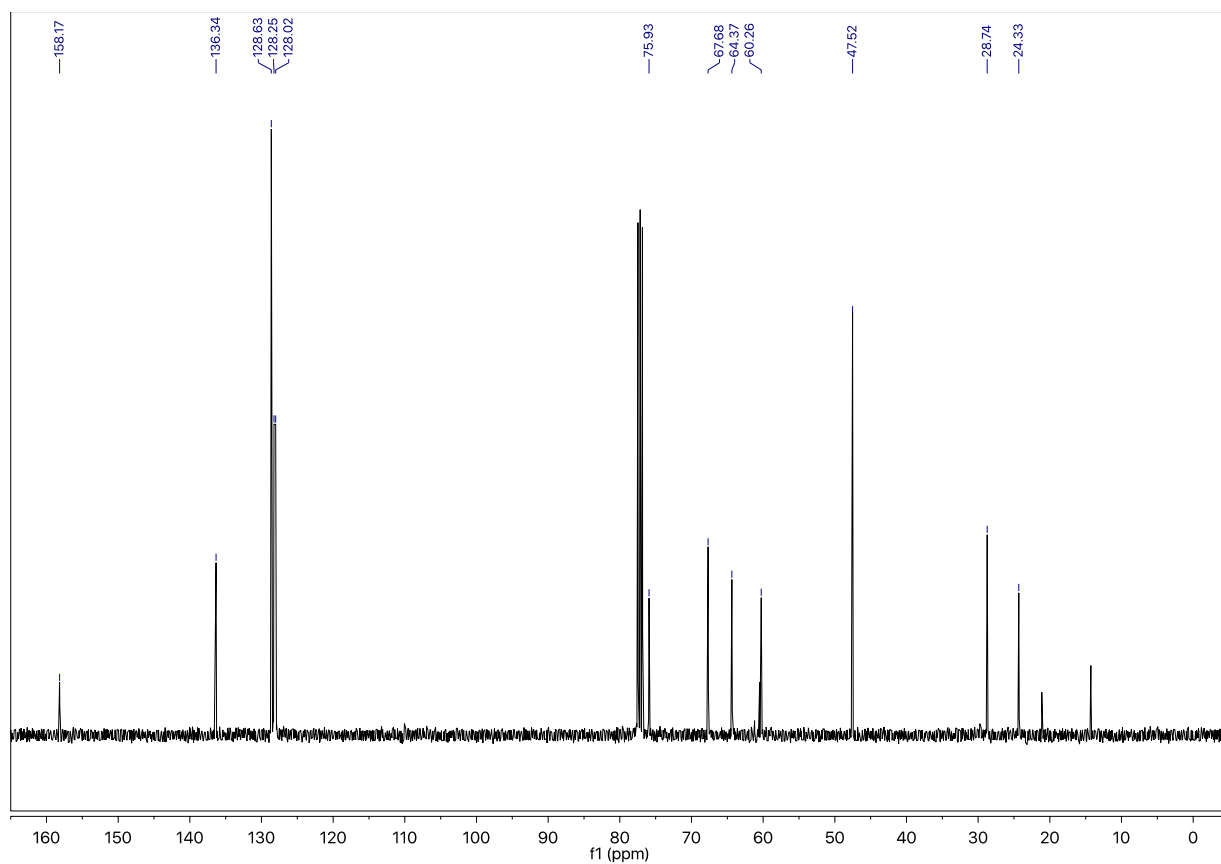
^1H NMR of **4**



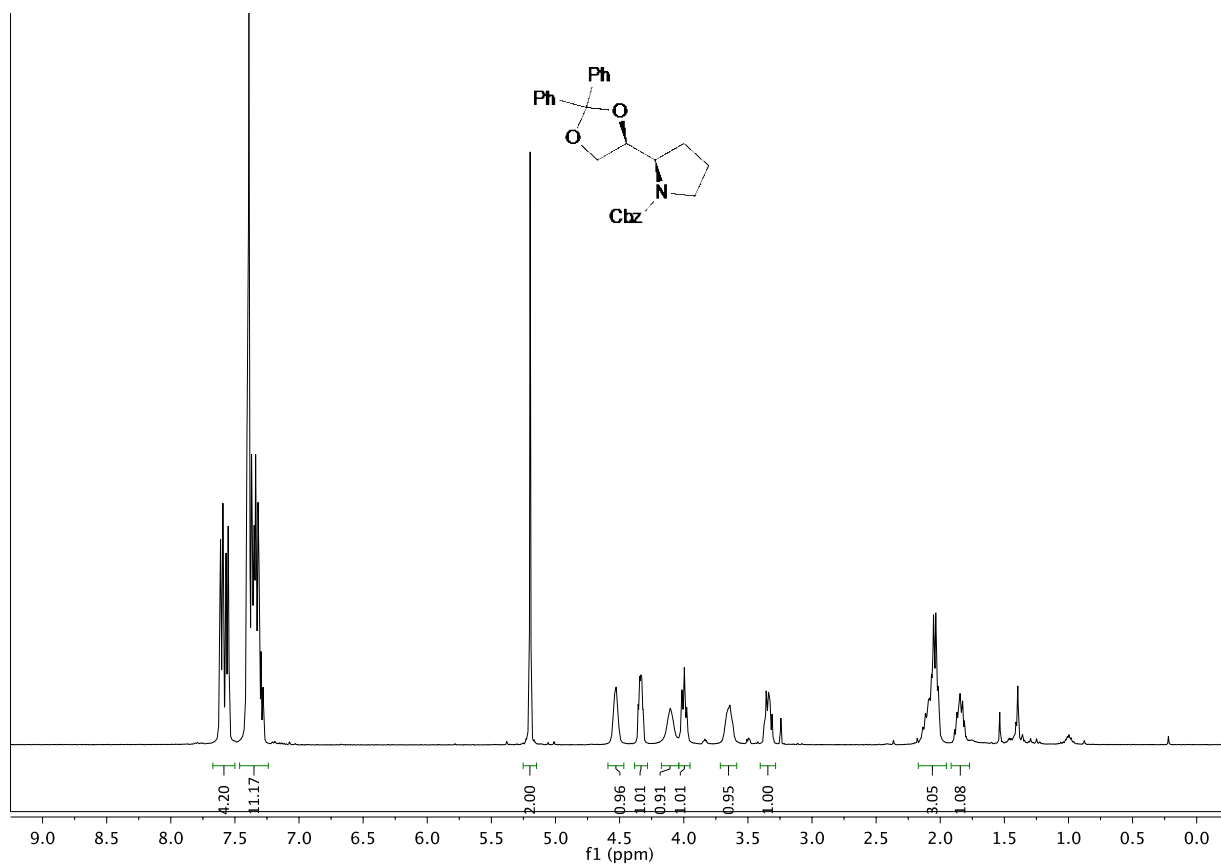
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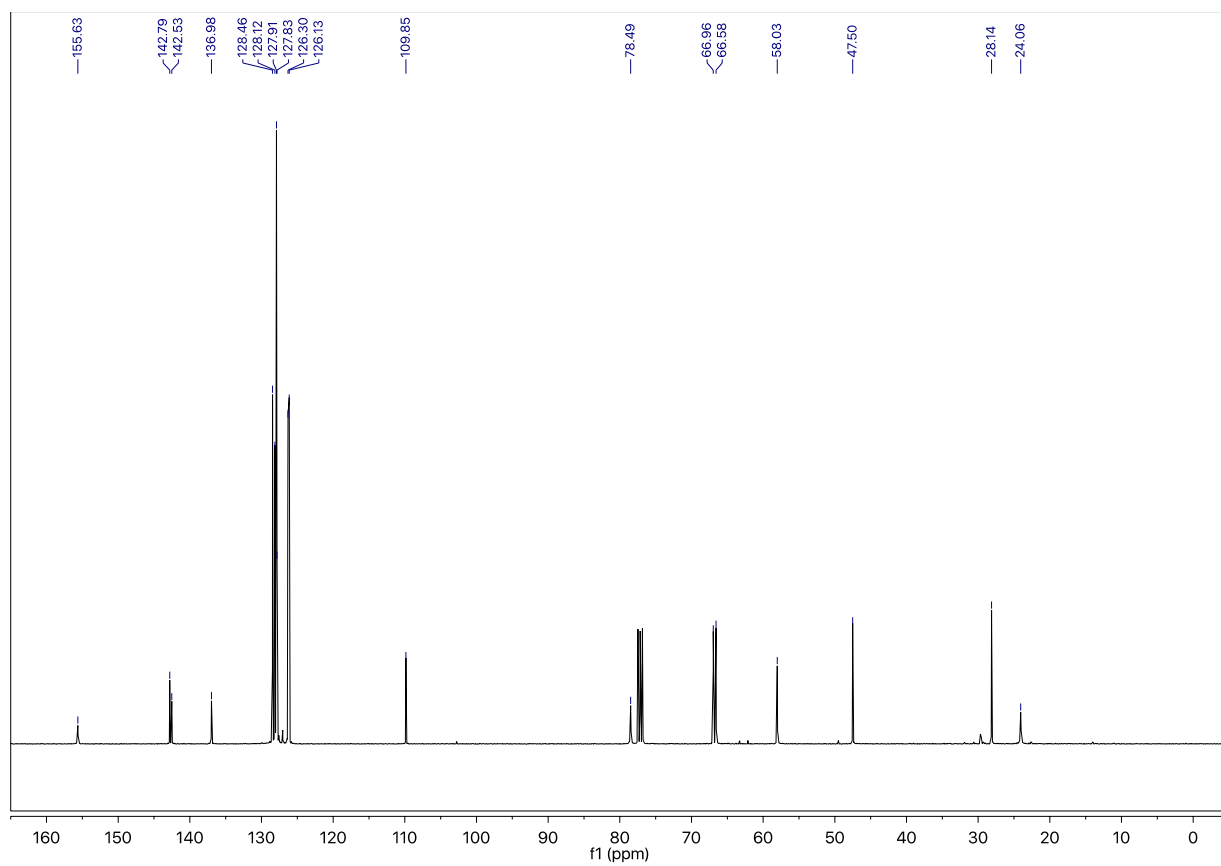
¹H NMR of 5



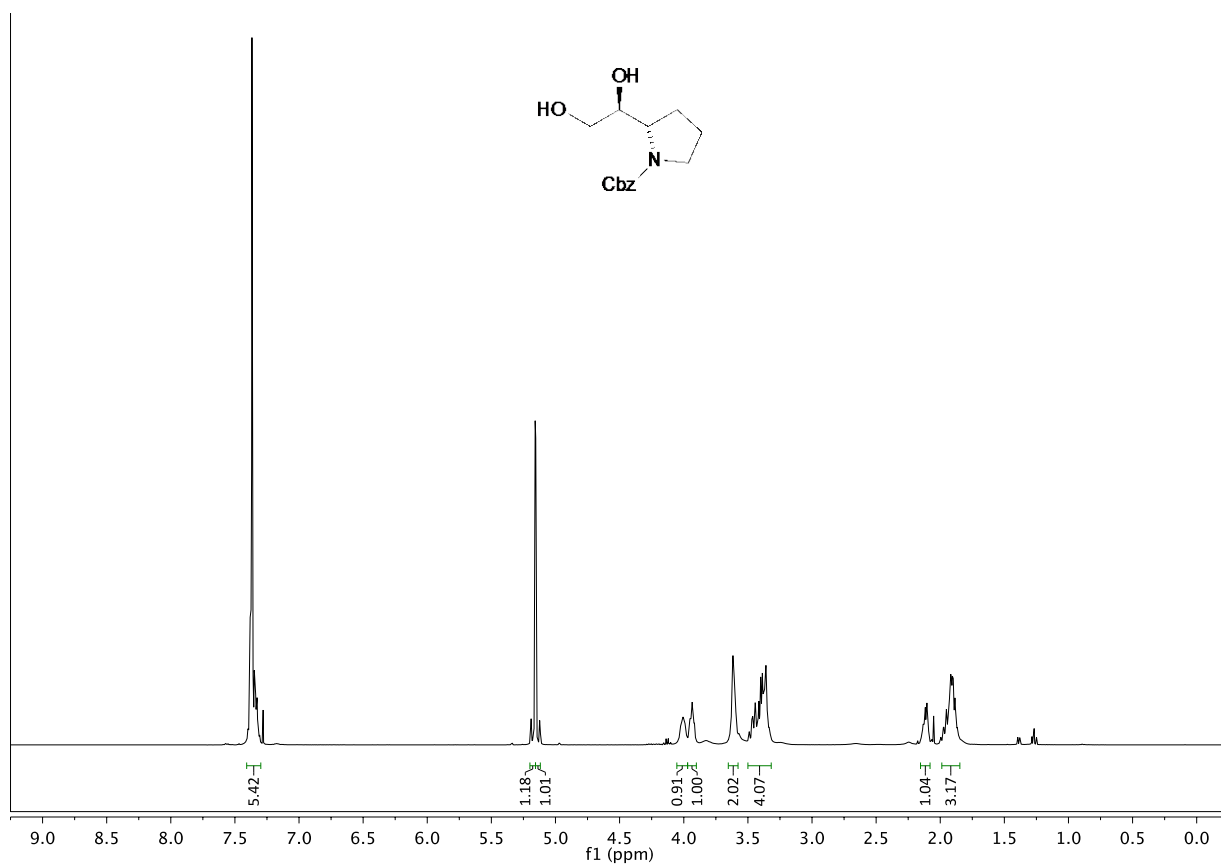
¹³C NMR of 5



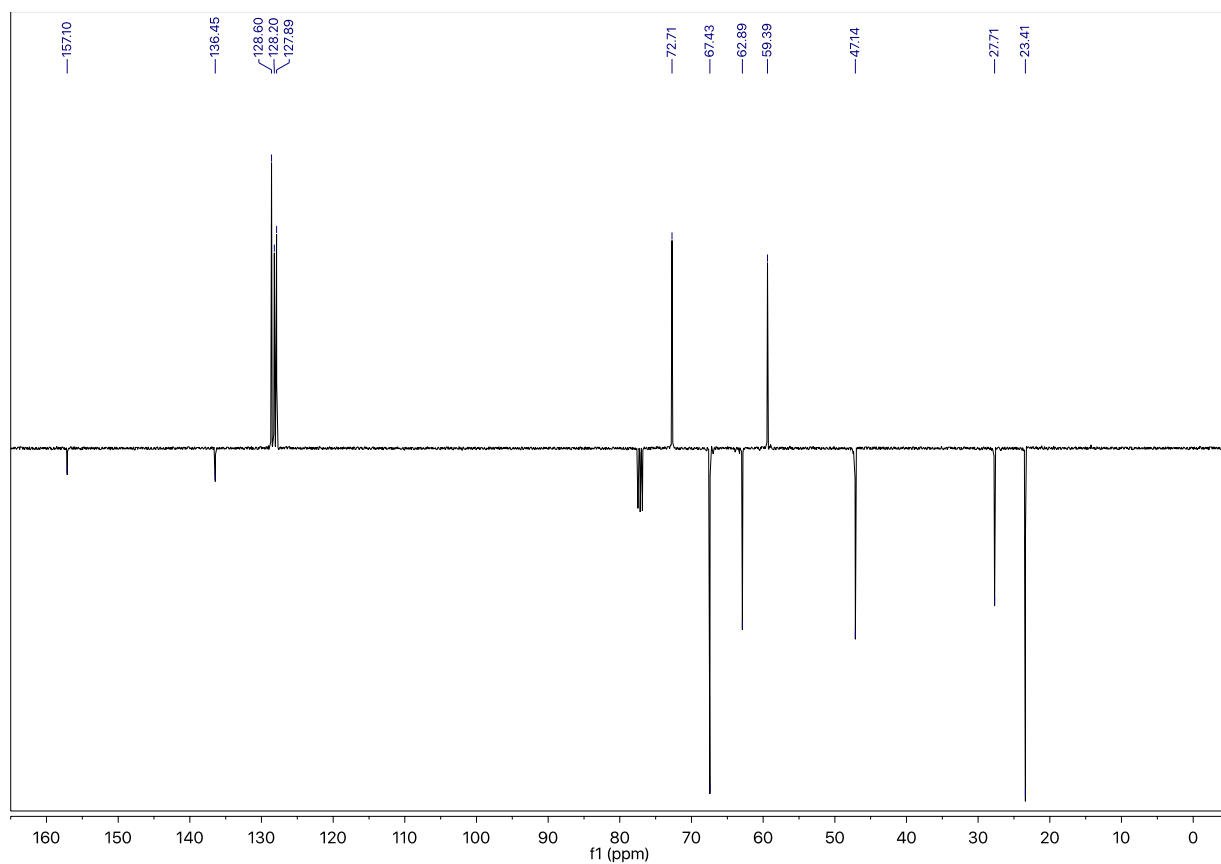
¹H NMR of 6



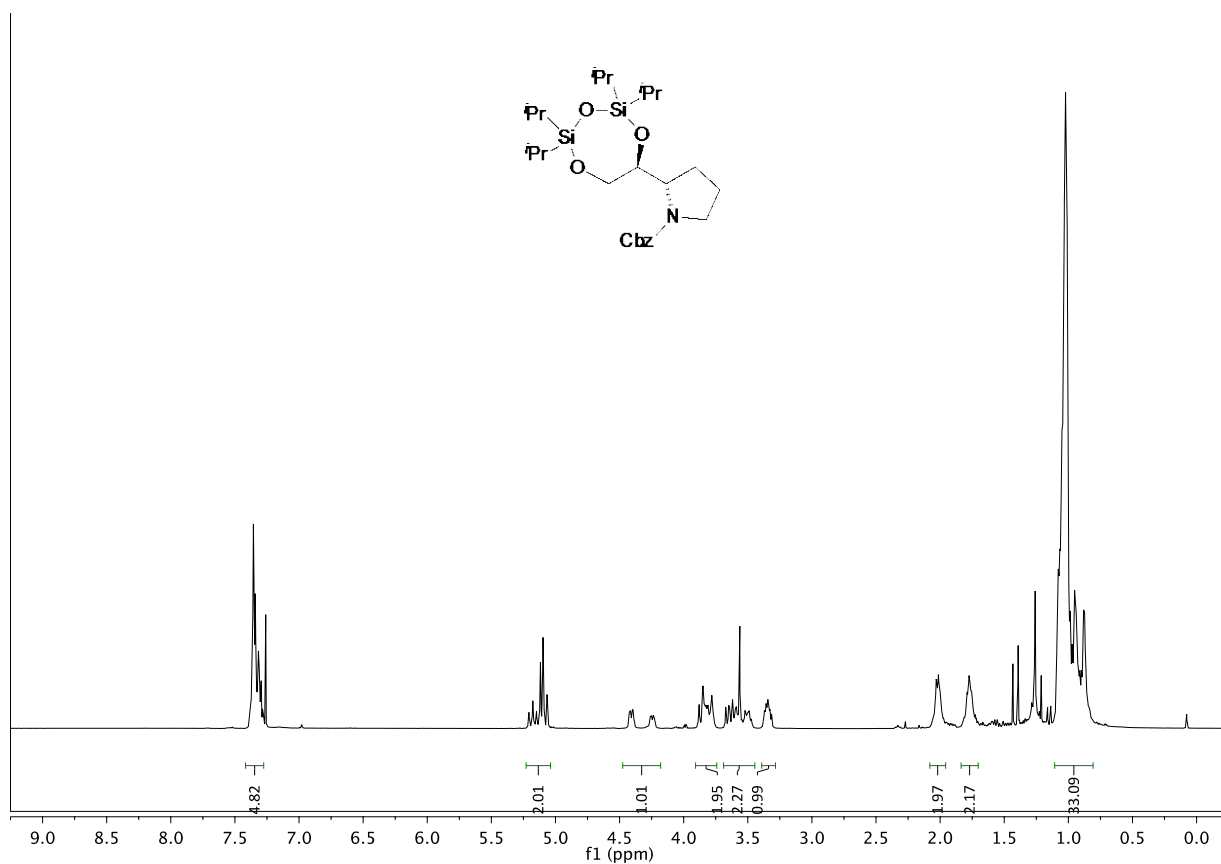
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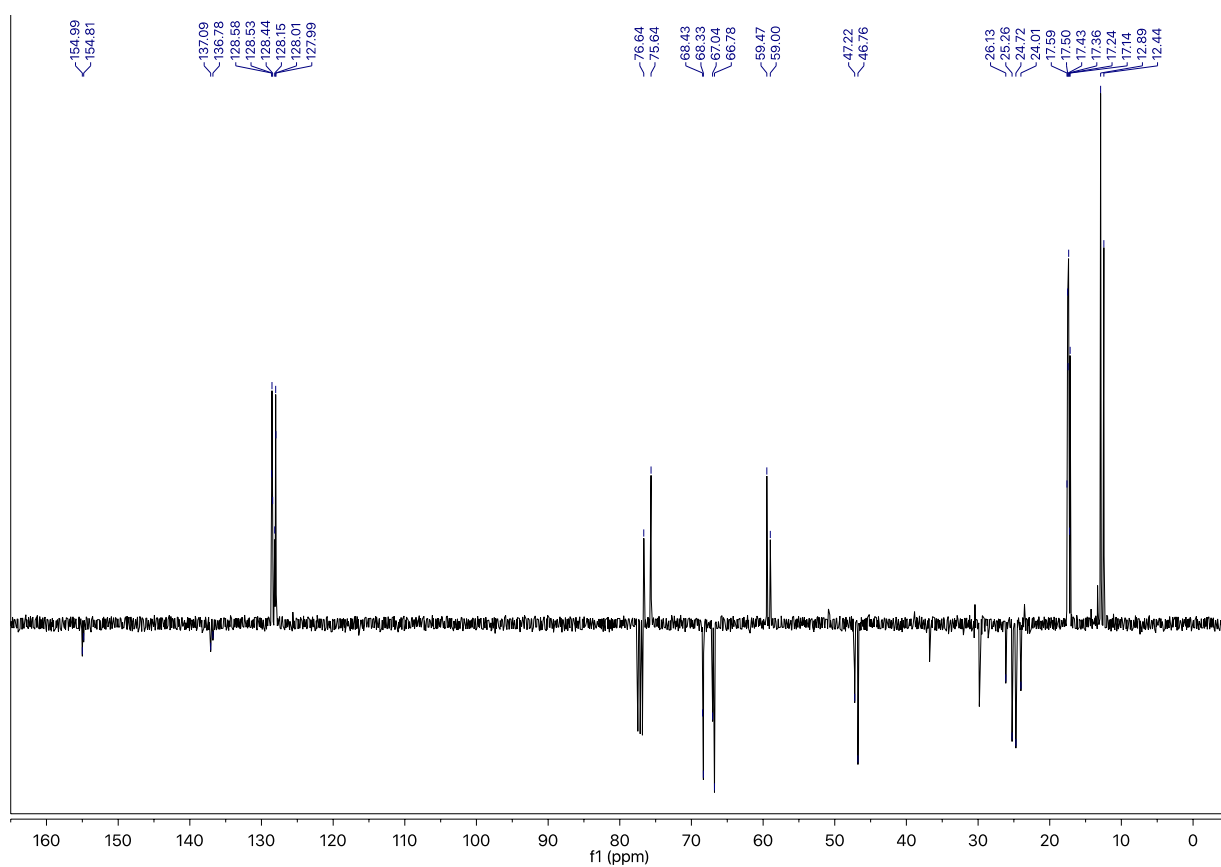
^1H NMR of 7



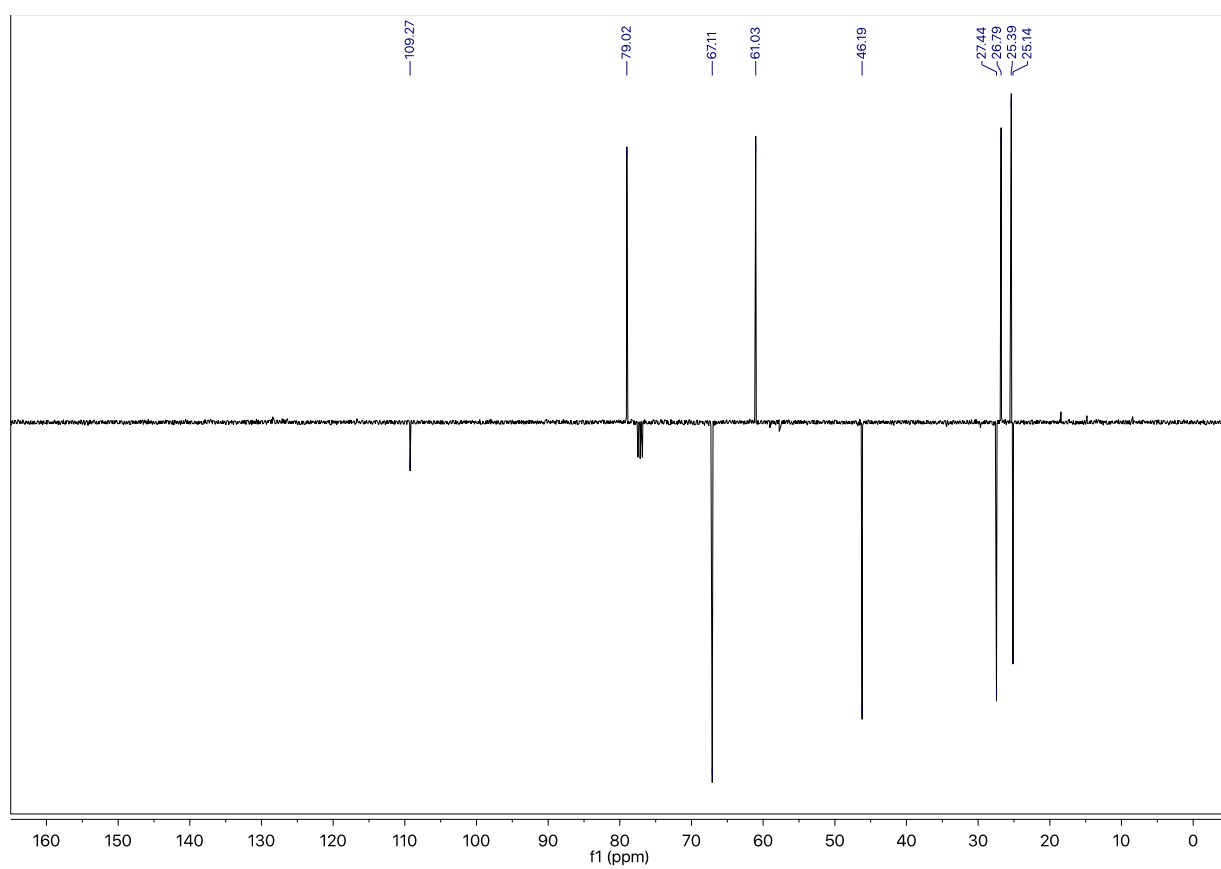
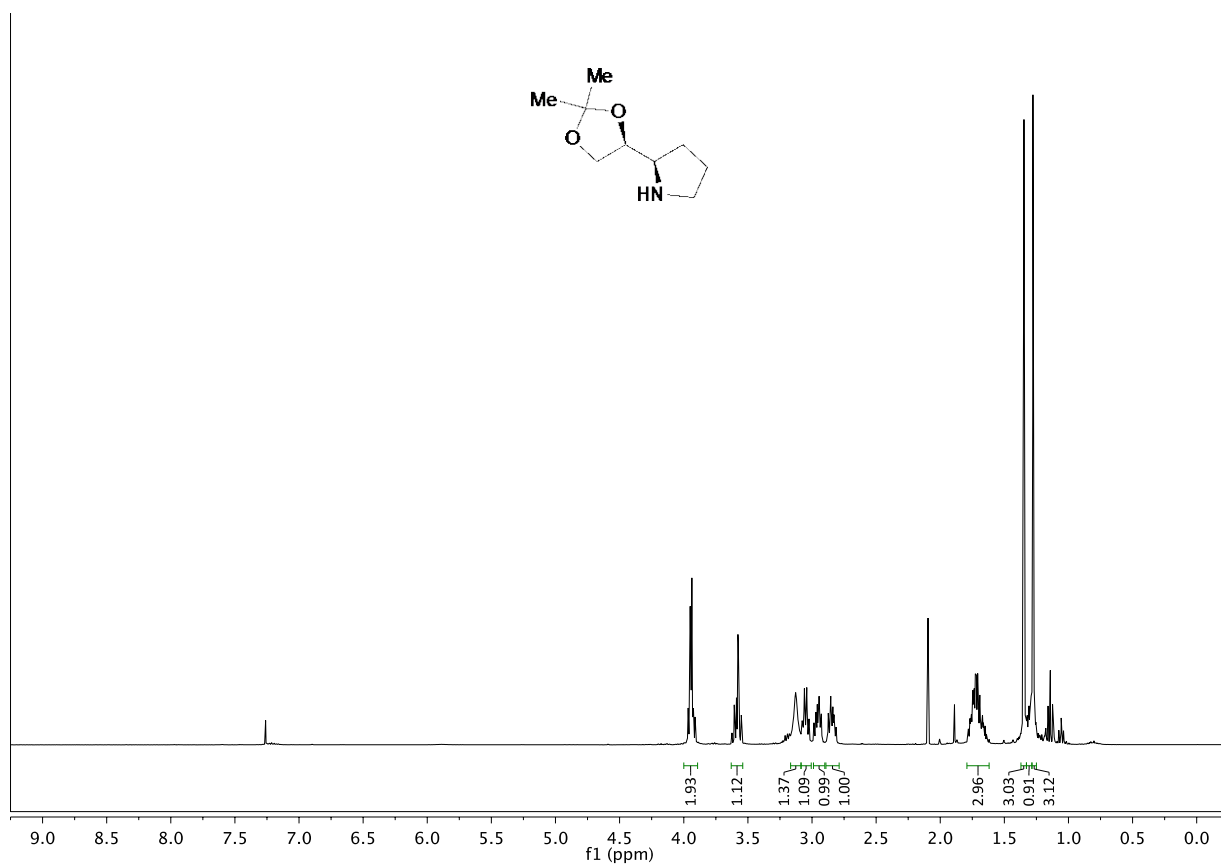
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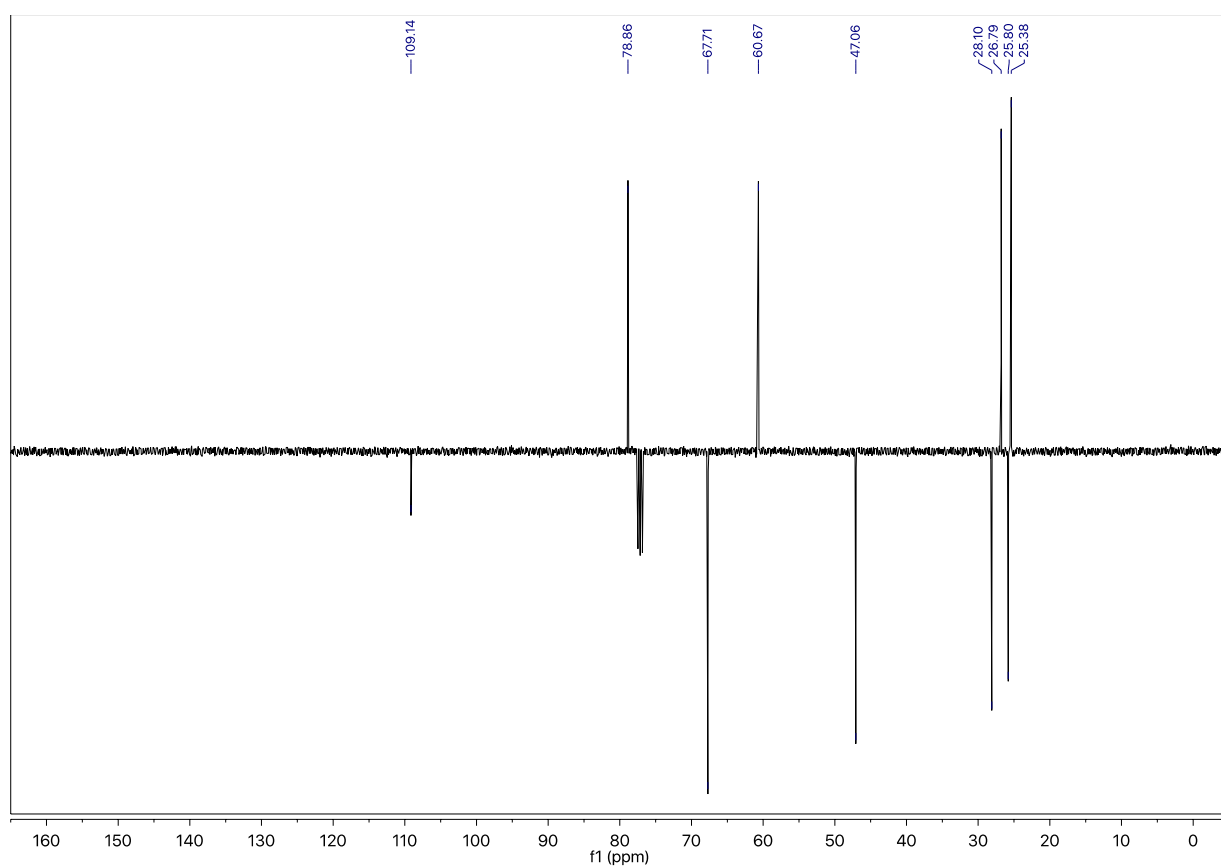
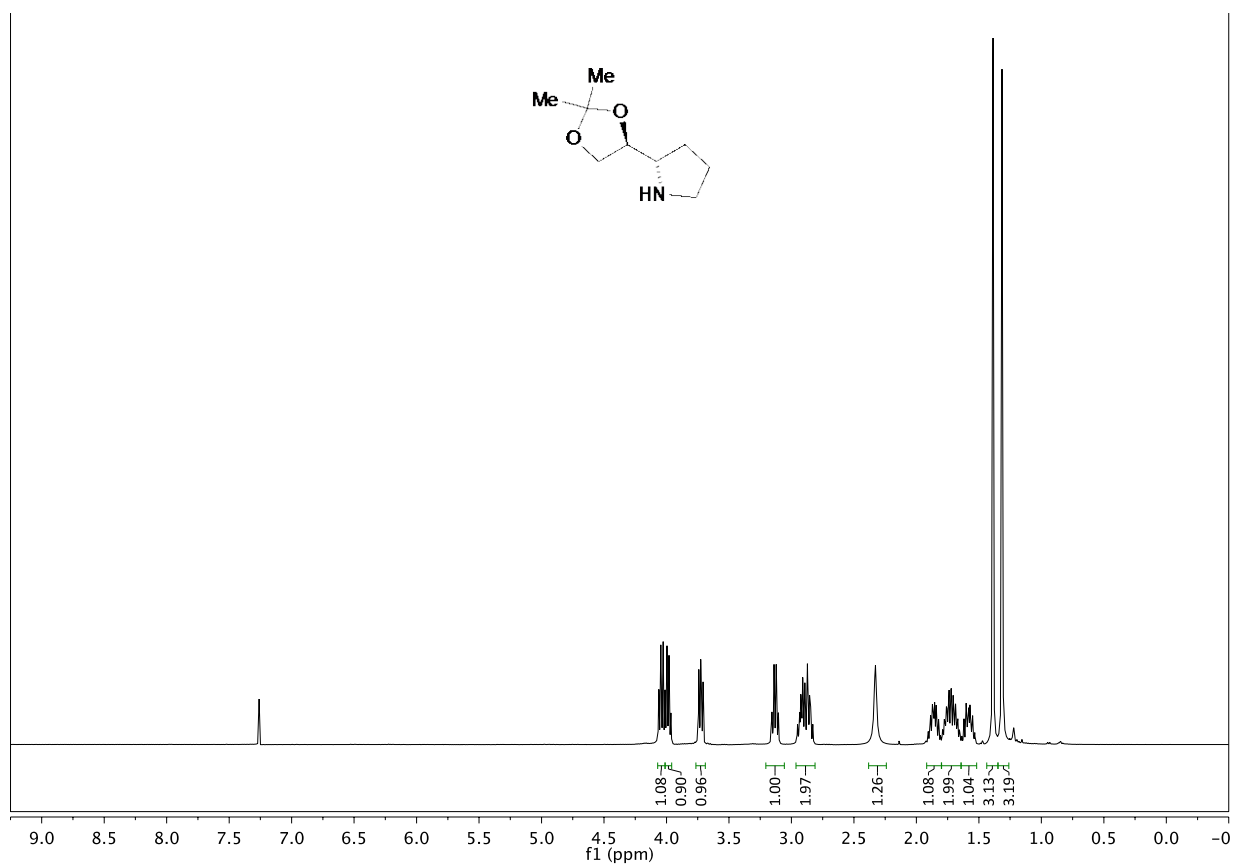


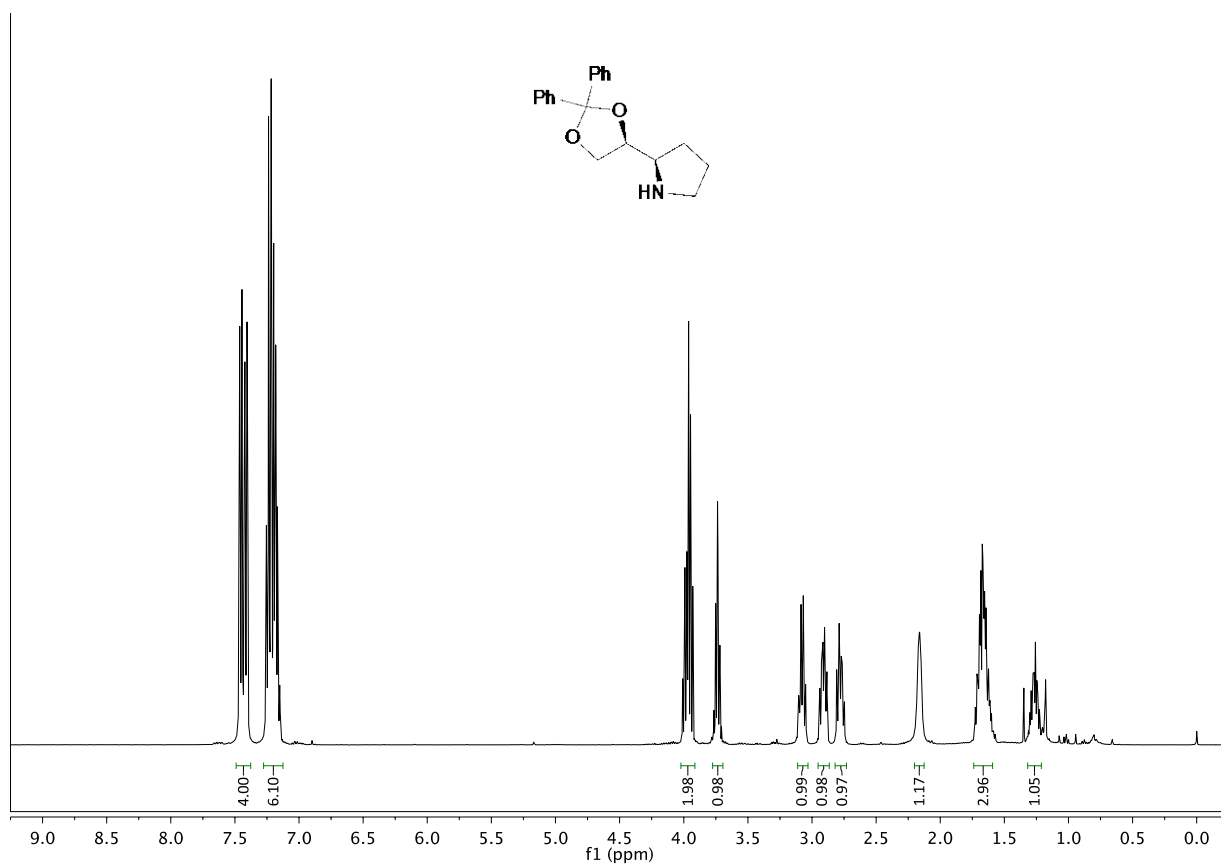
¹H NMR of **8**



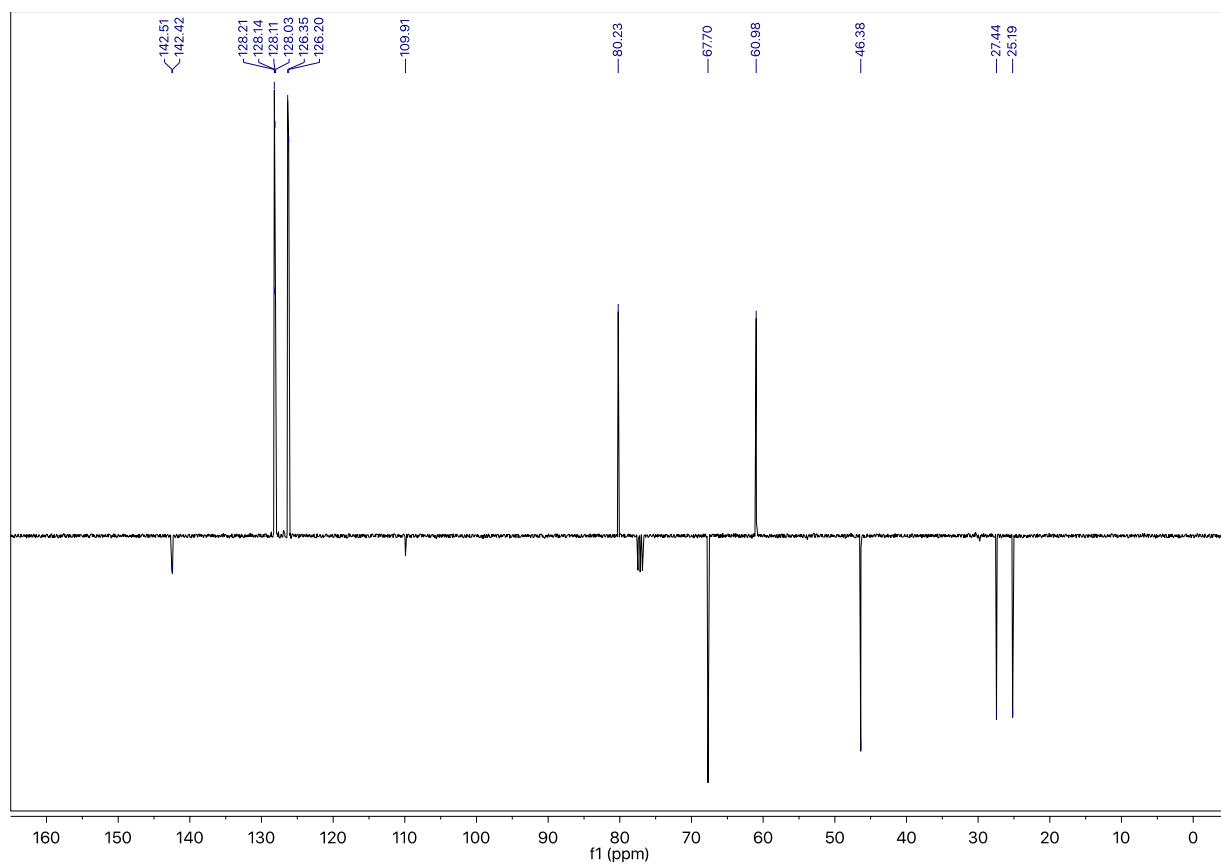
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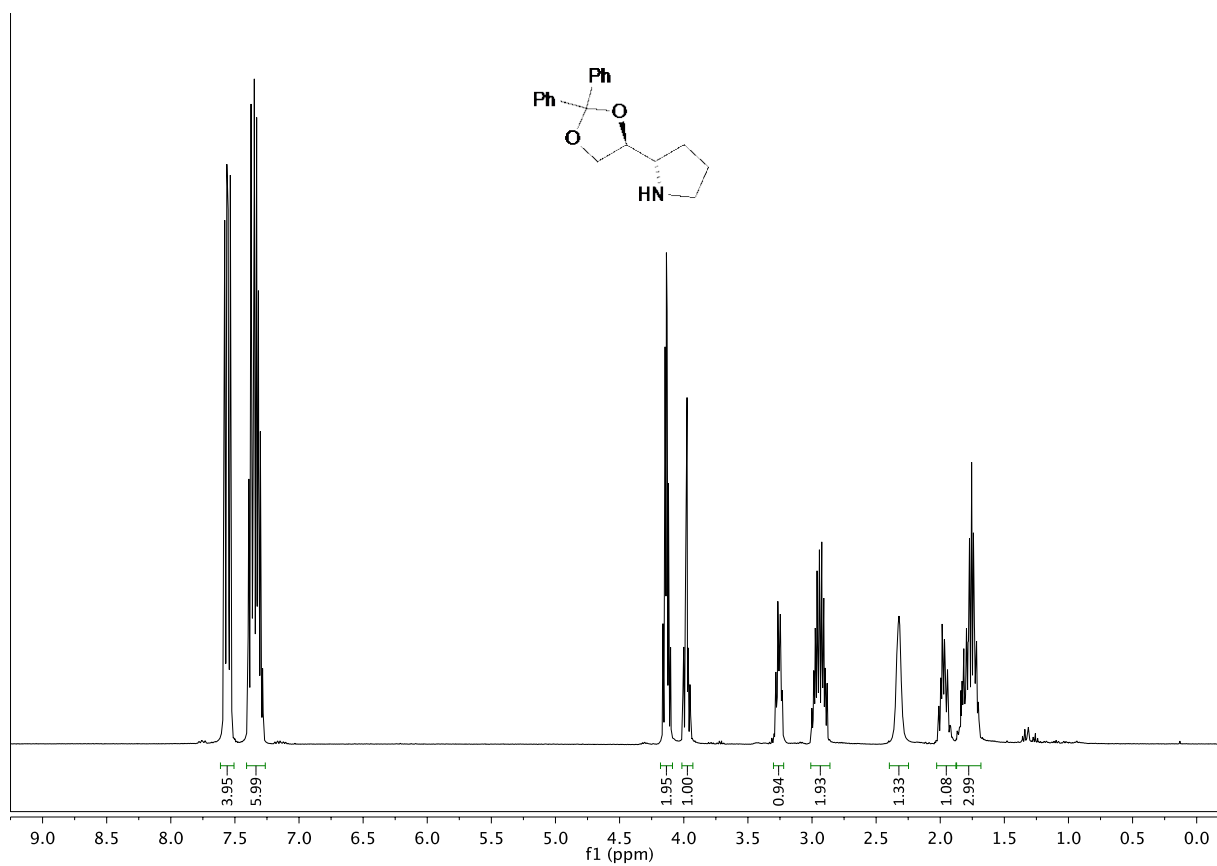




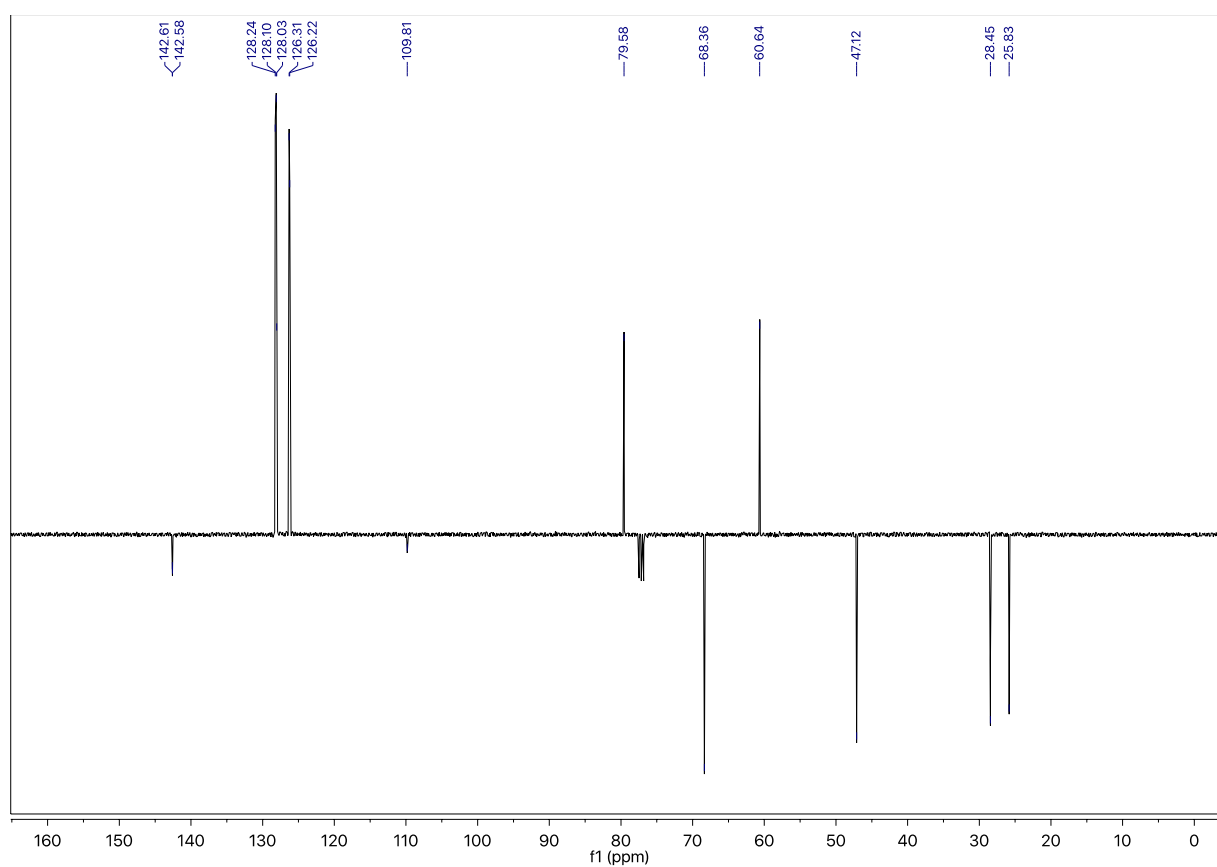
¹H NMR of OC3



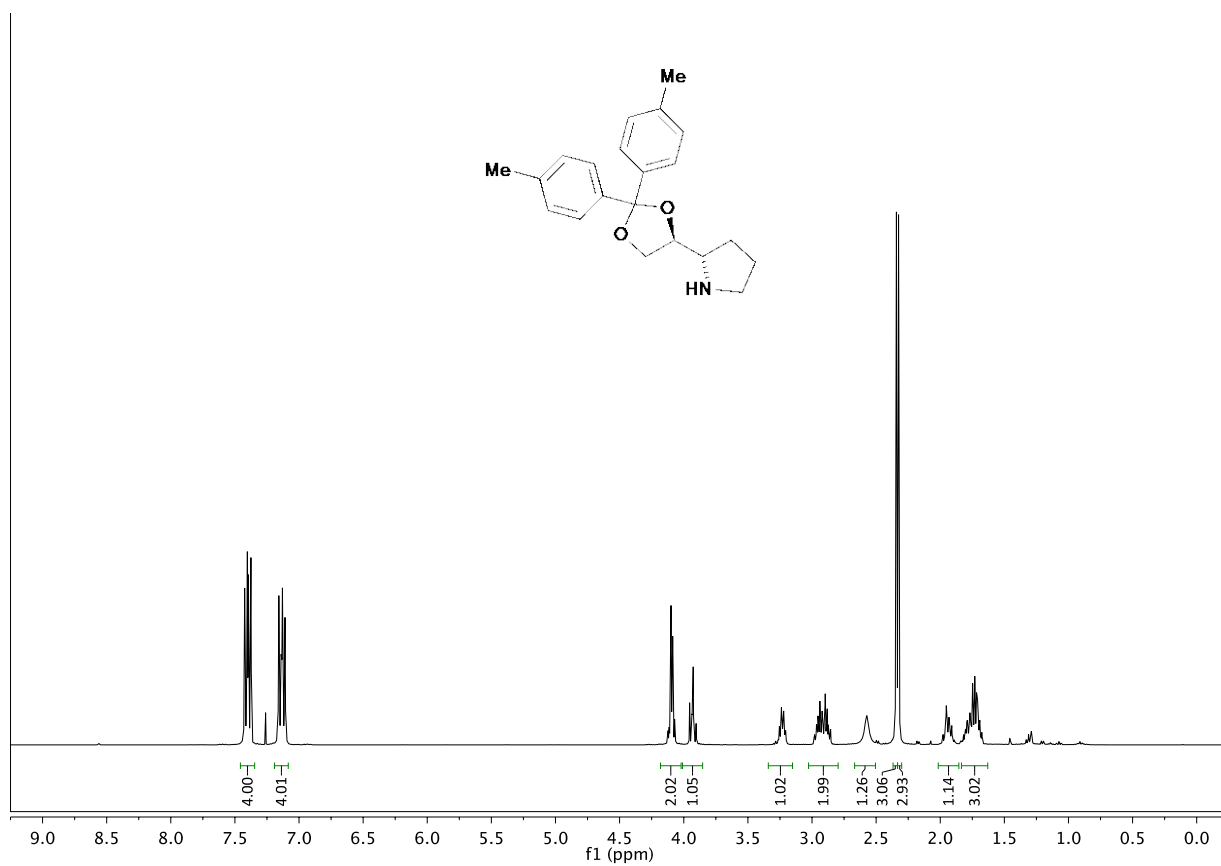
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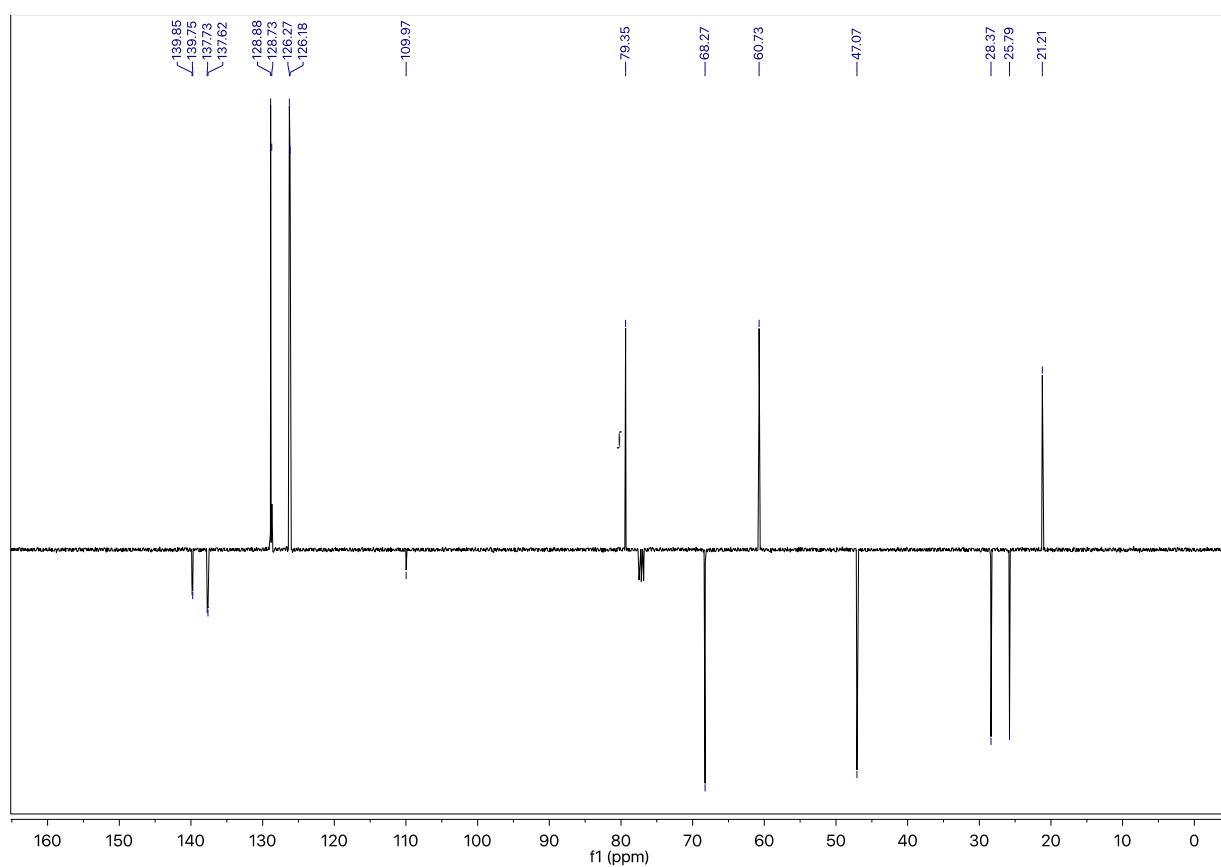
¹H NMR of OC4



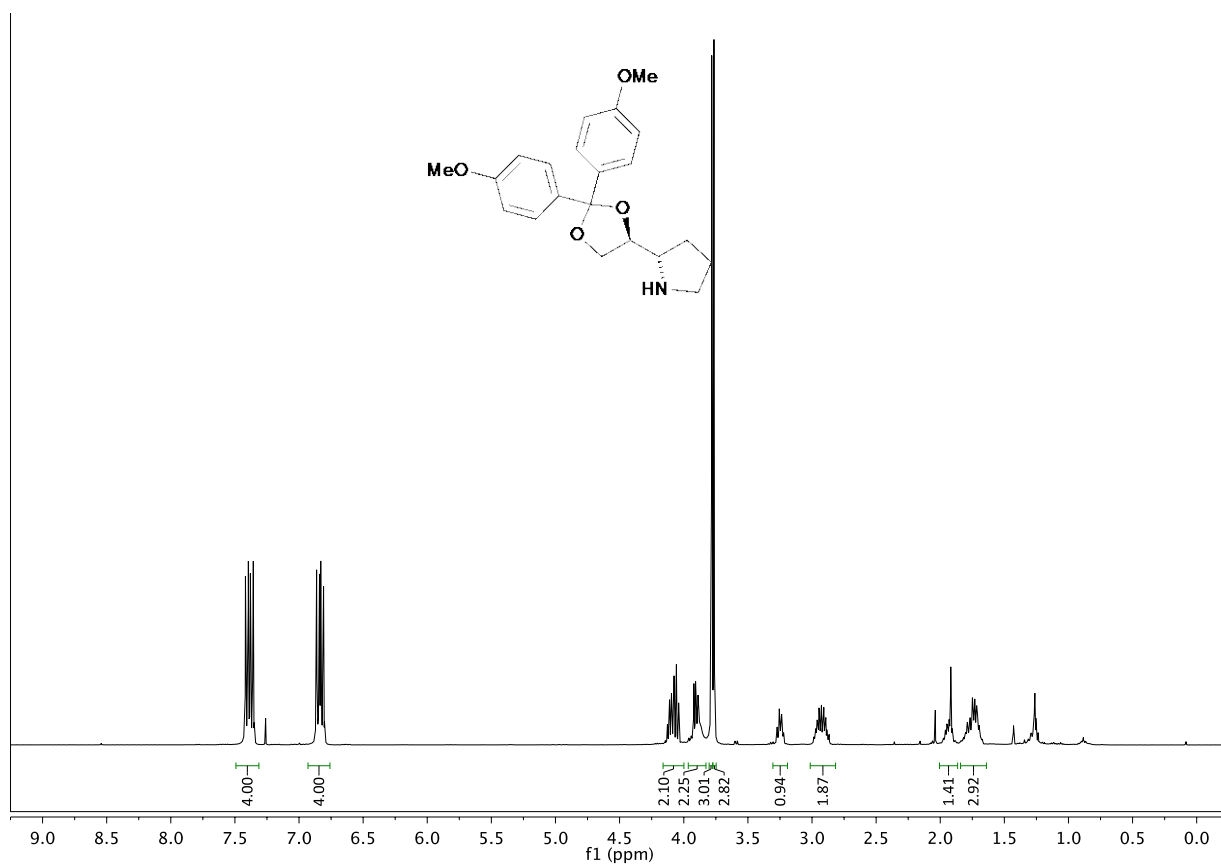
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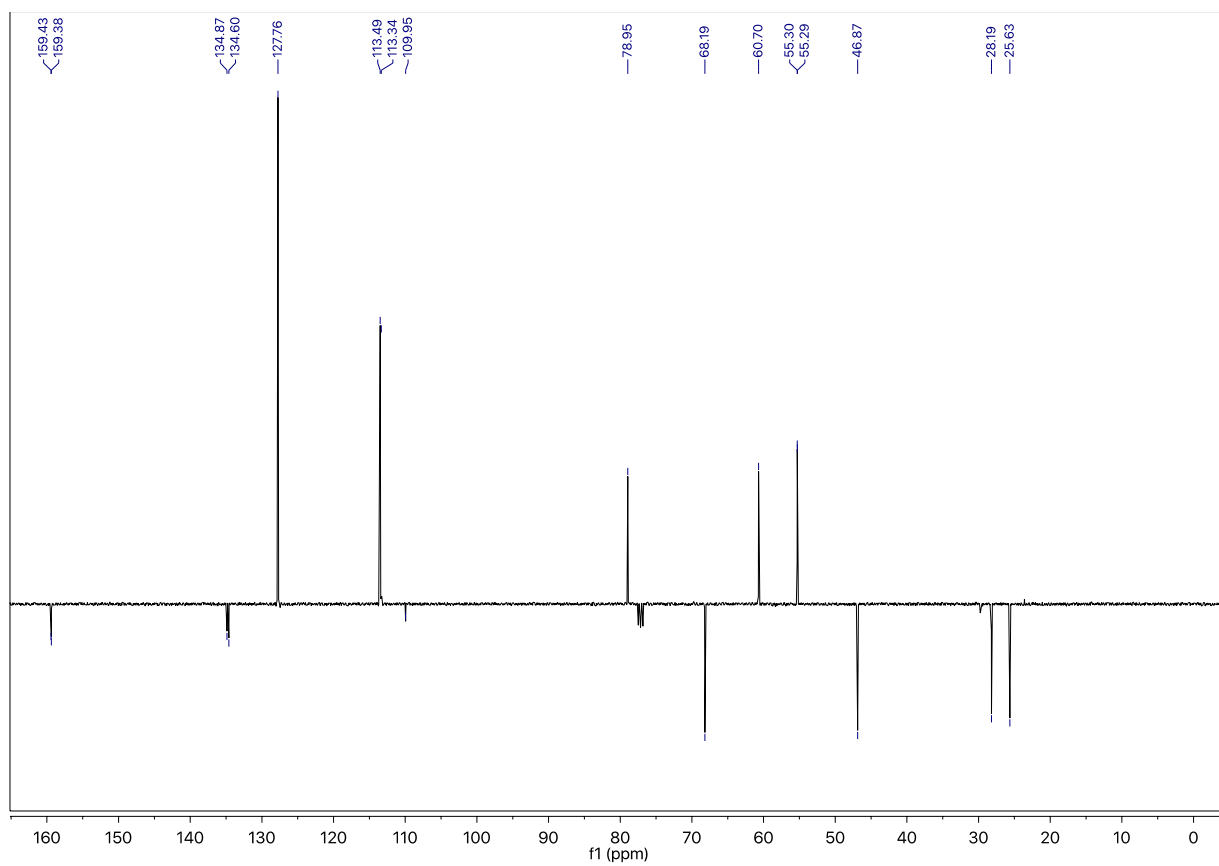
¹H NMR of OC5



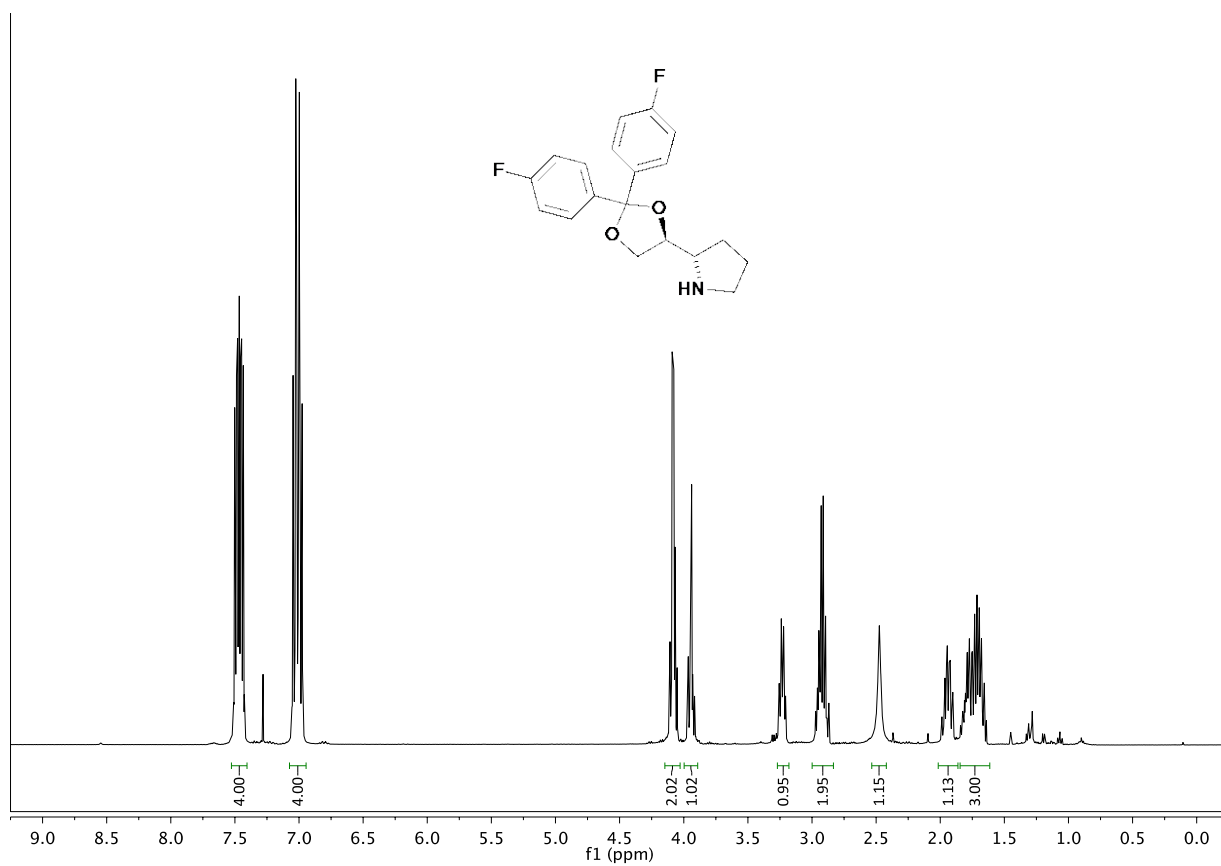
¹³C NMR of OC5



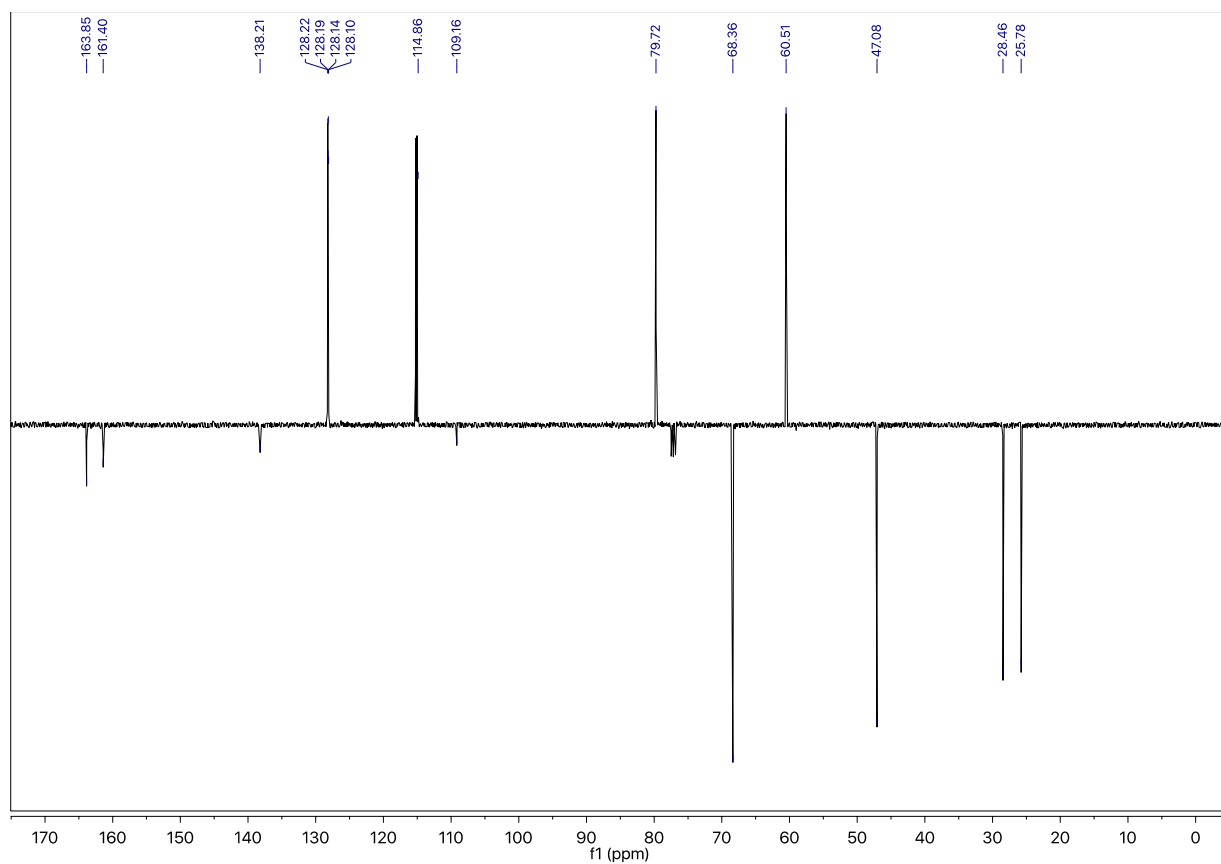
¹H NMR of OC6



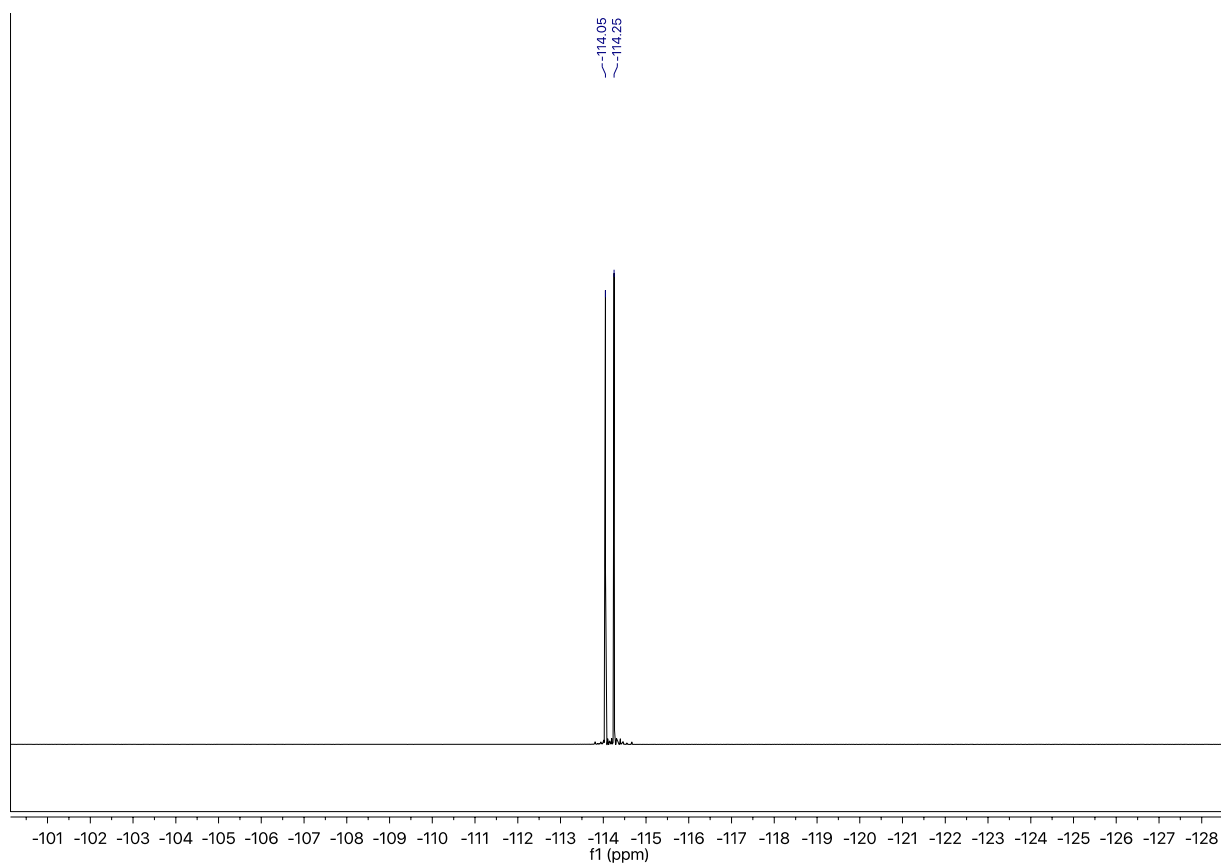
¹³C NMR of OC6



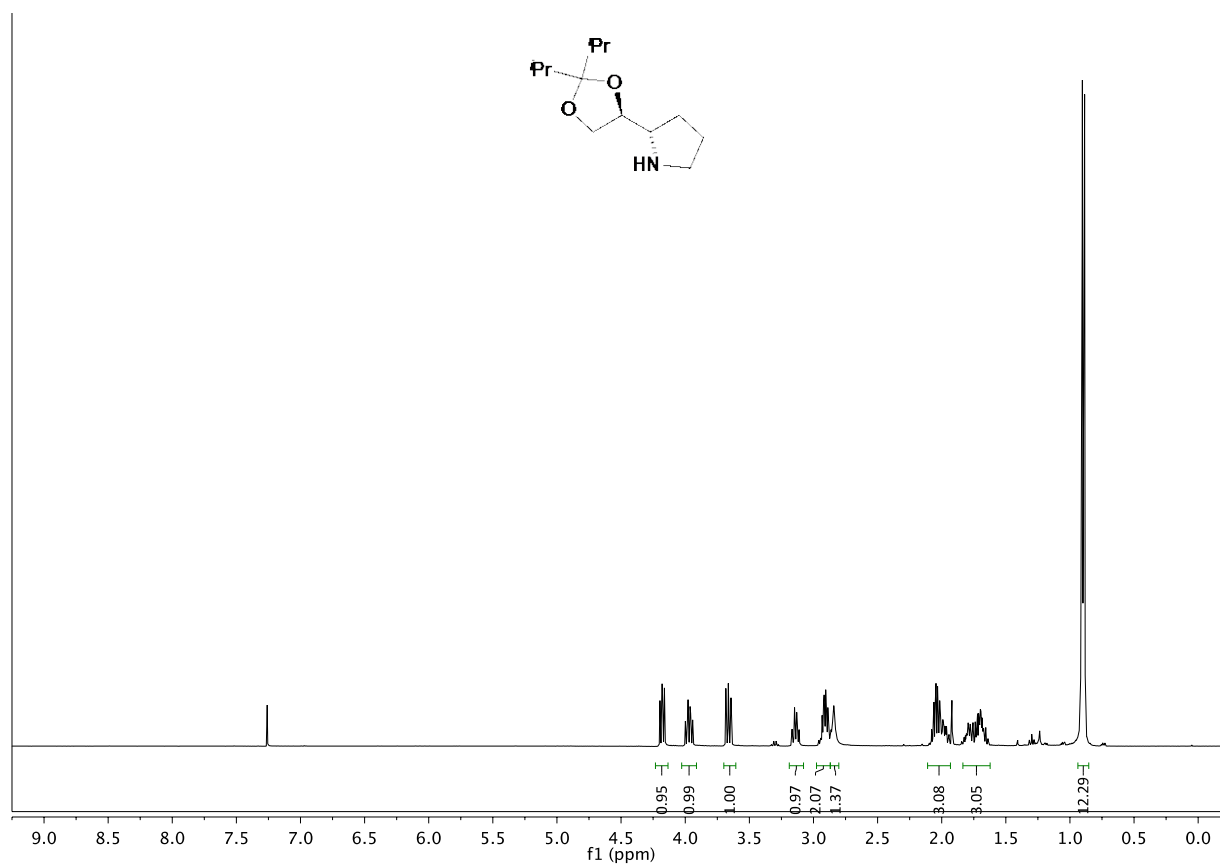
¹H NMR of OC7



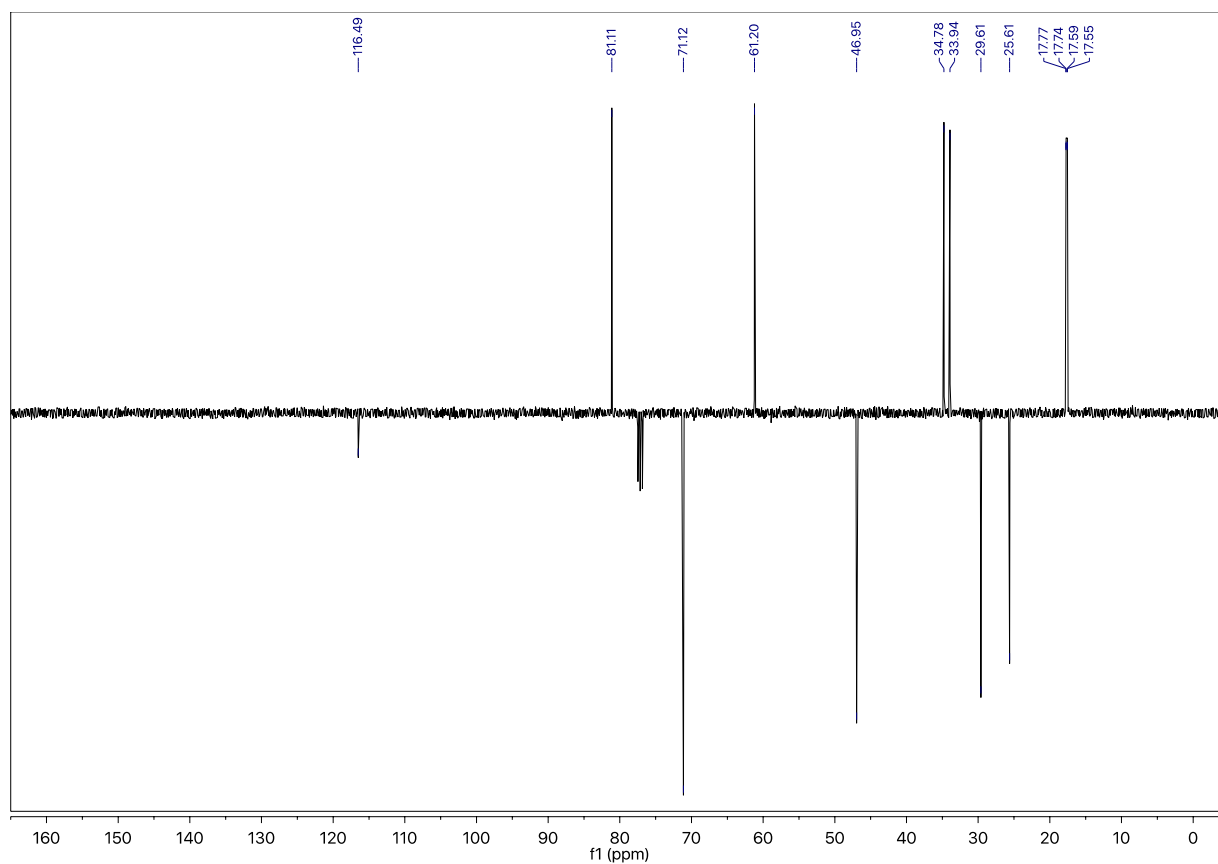
¹³C NMR of OC7



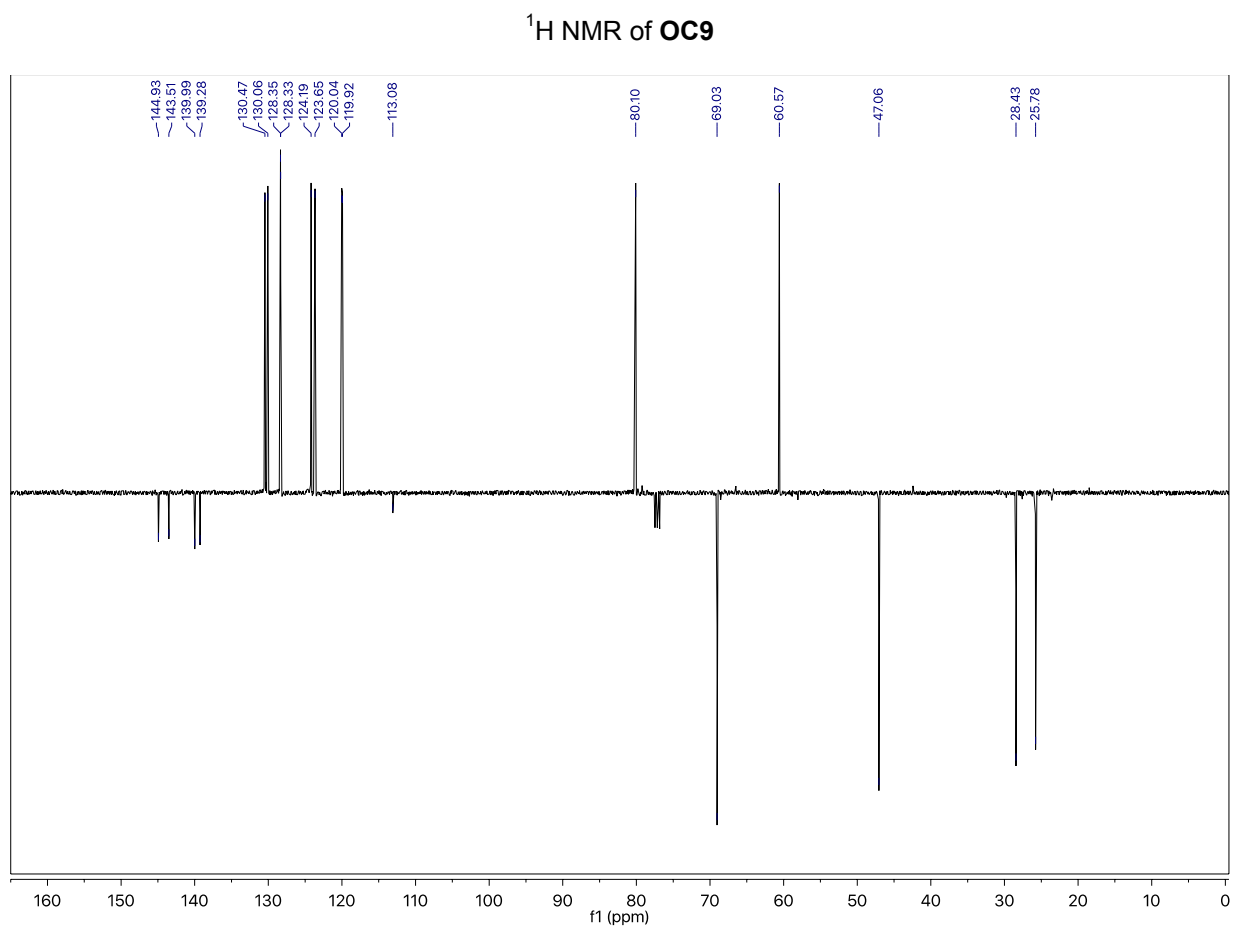
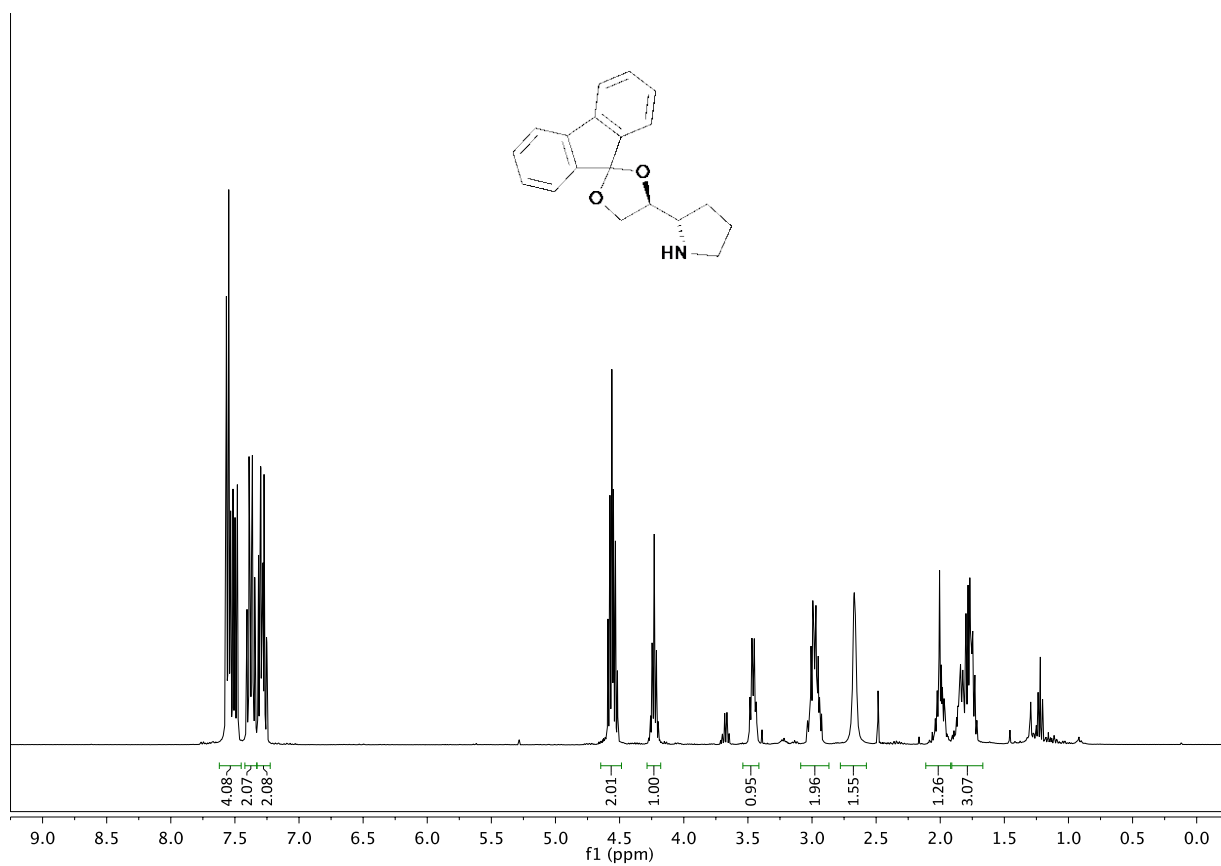
^{19}F NMR of **OC7**

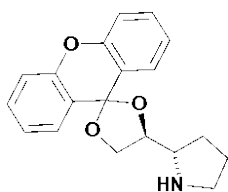


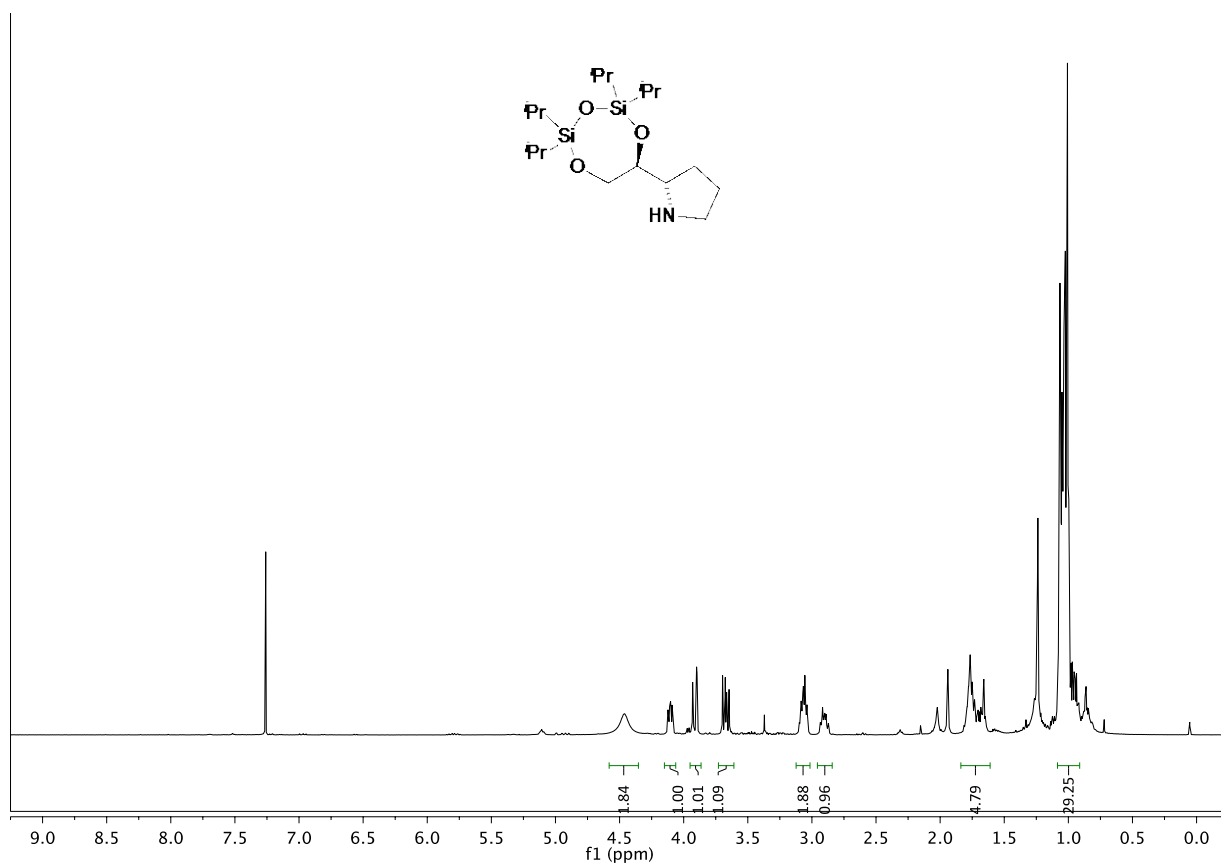
¹H NMR of OC8



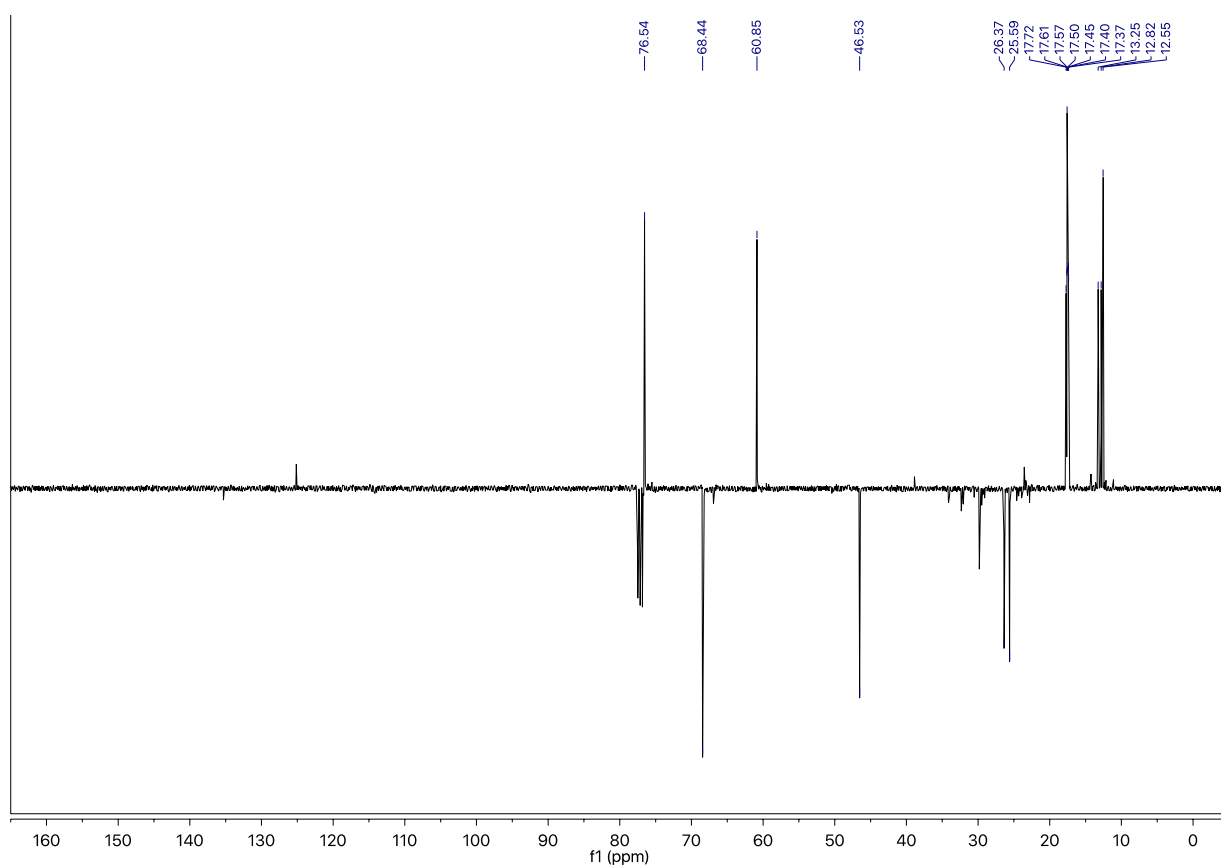
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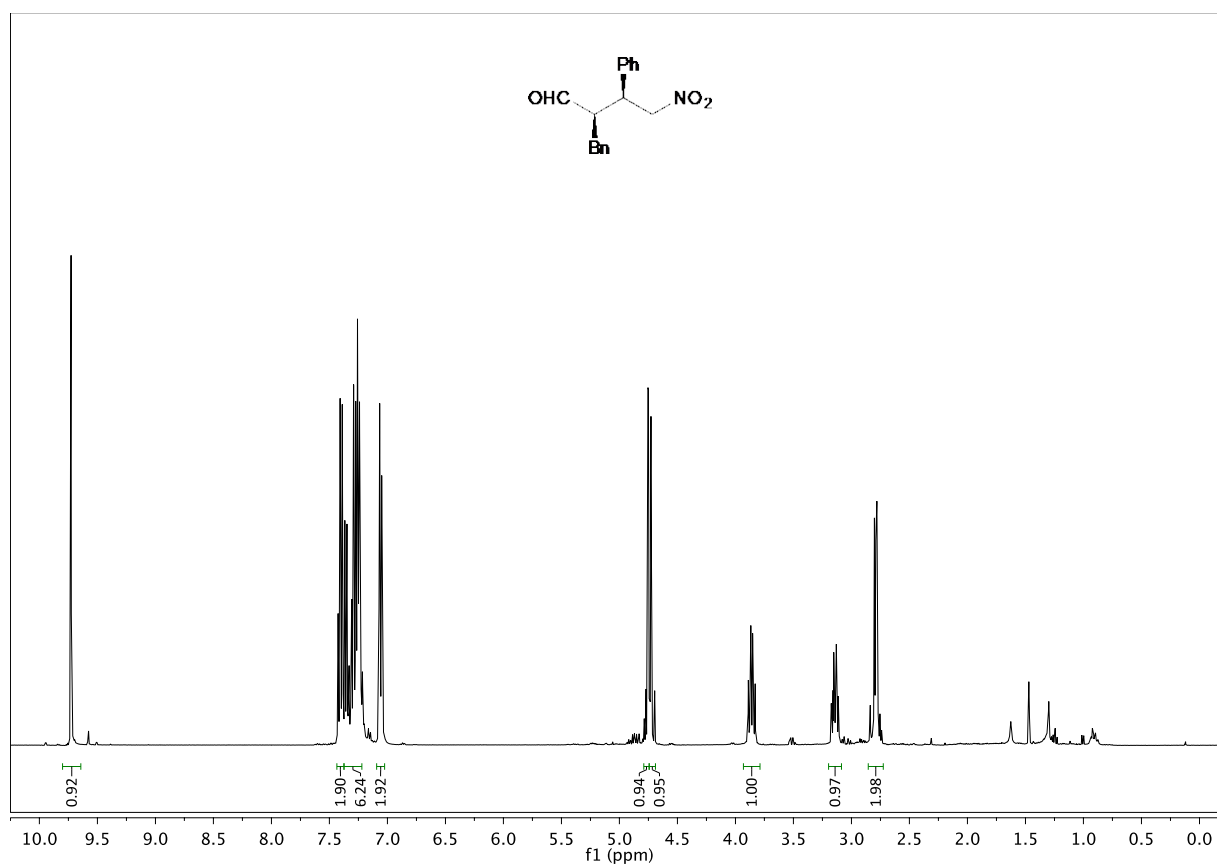




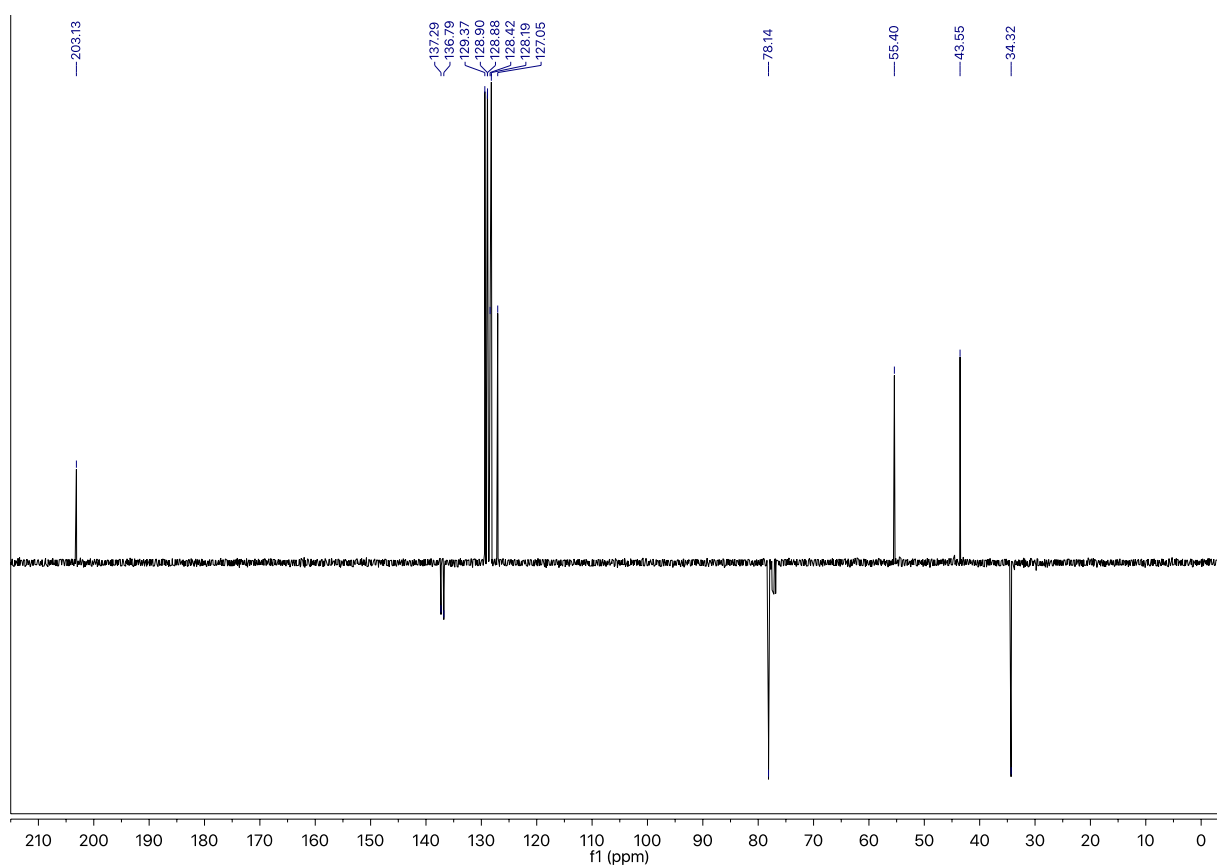
¹H NMR of OC11



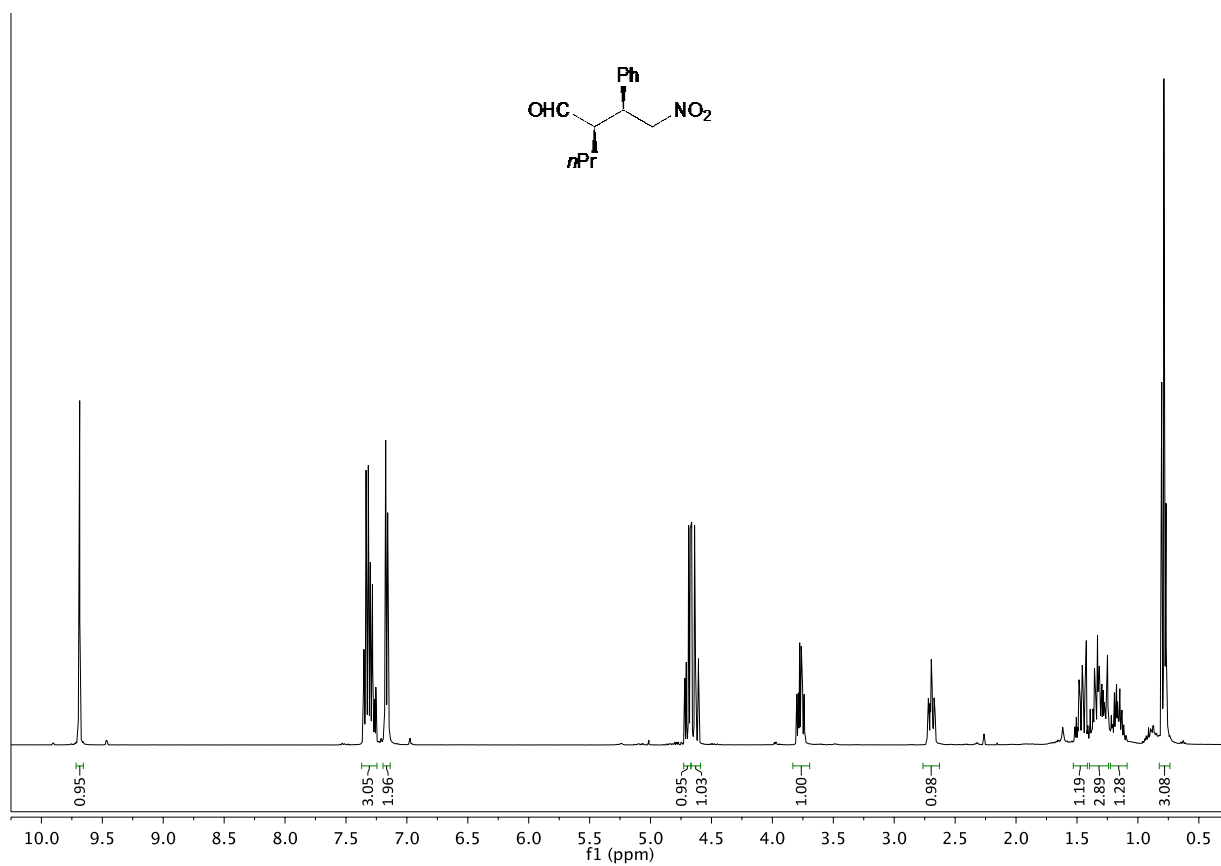
¹³C NMR of OC11



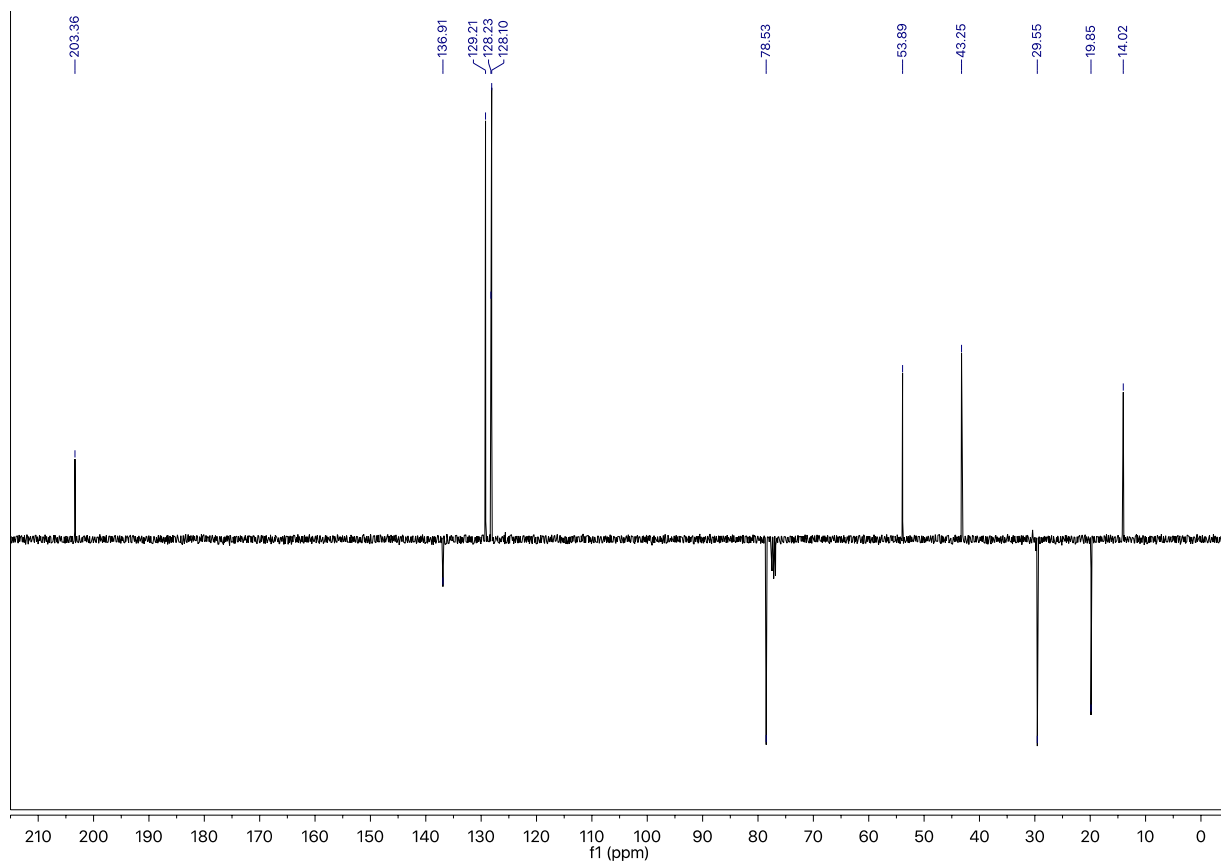
¹H NMR of (2R,3S)-2-benzyl-4-nitro-3-phenylbutanal **9a**



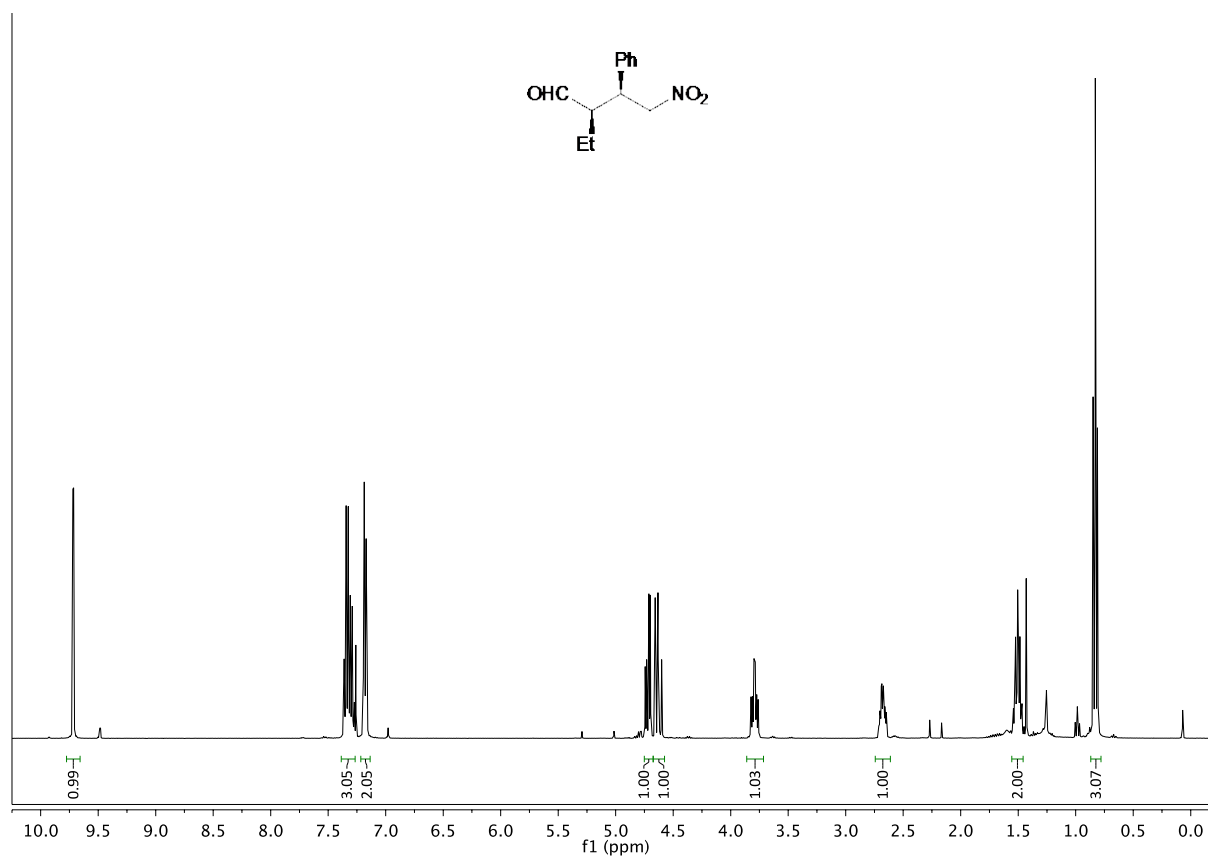
¹³C NMR of (2R,3S)-2-benzyl-4-nitro-3-phenylbutanal **9a**



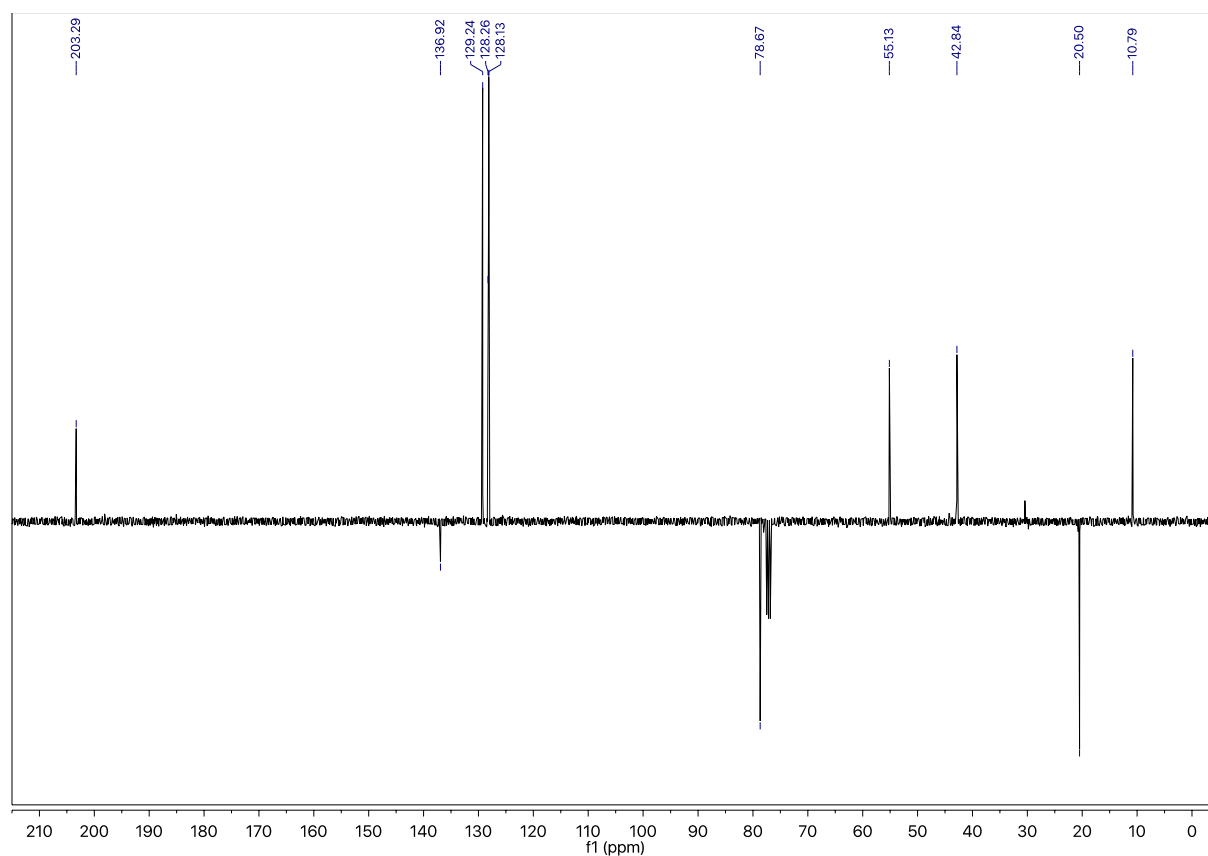
¹H NMR of (*R*)-2-[(*S*)-2-nitro-1-phenylethyl]pentanal **9b**



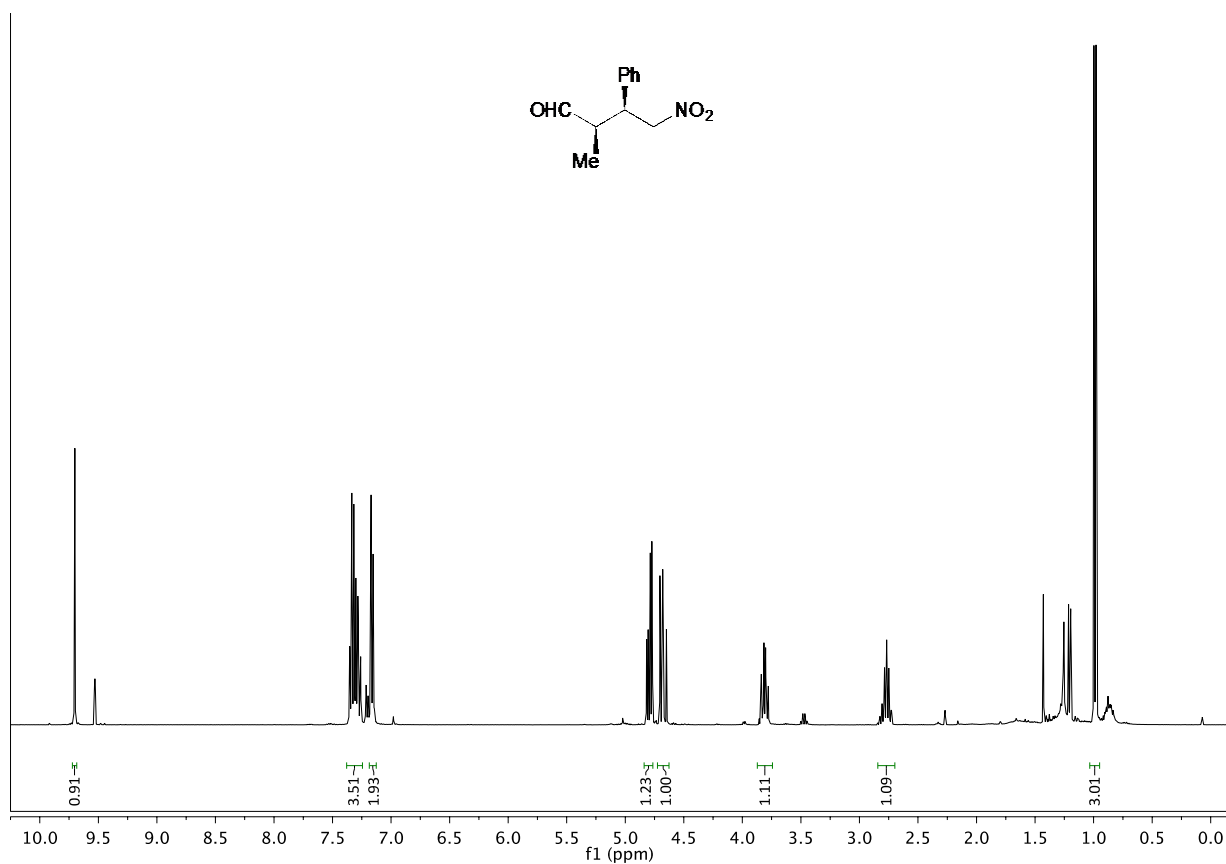
¹³C NMR of (*R*)-2-[(*S*)-2-nitro-1-phenylethyl]pentanal **9b**



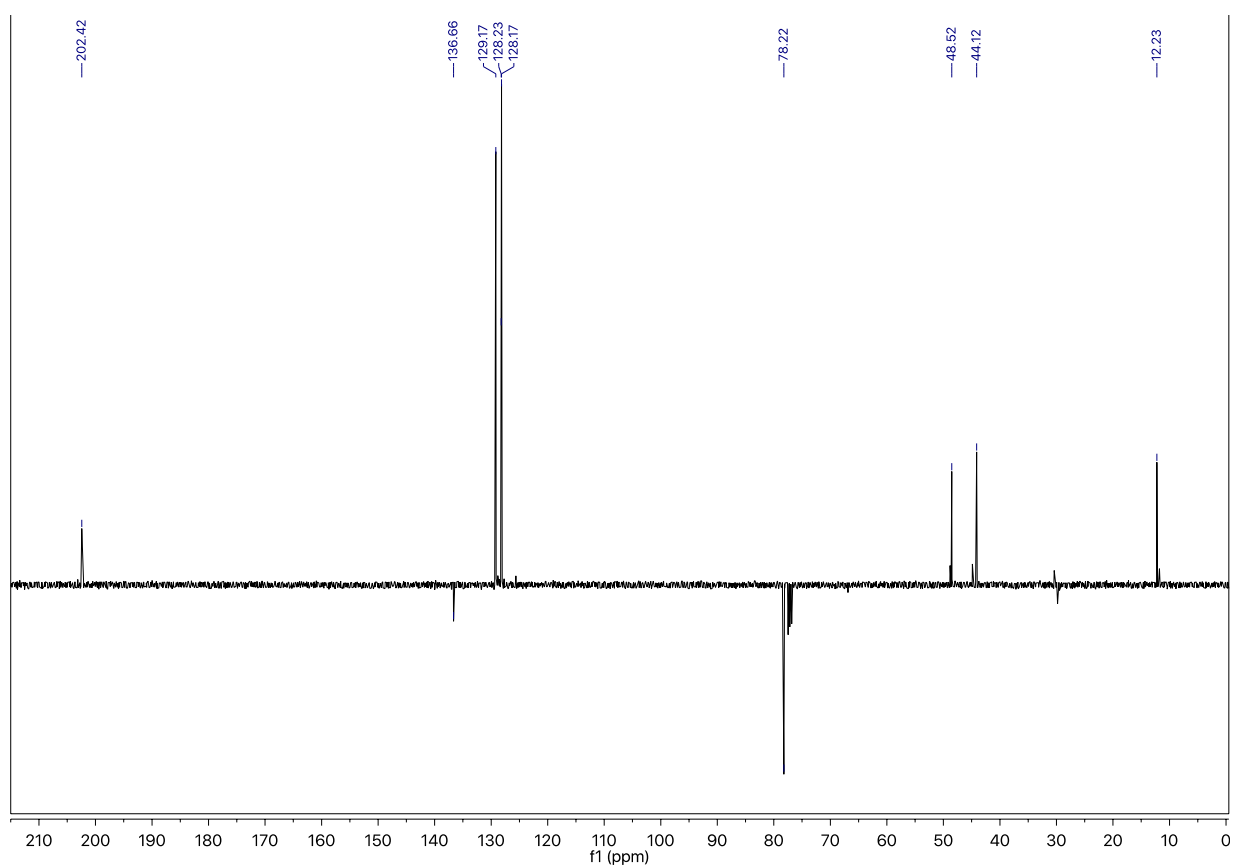
¹H NMR of (2R,3S)-2-ethyl-4-nitro-3-phenylbutanal **9c**



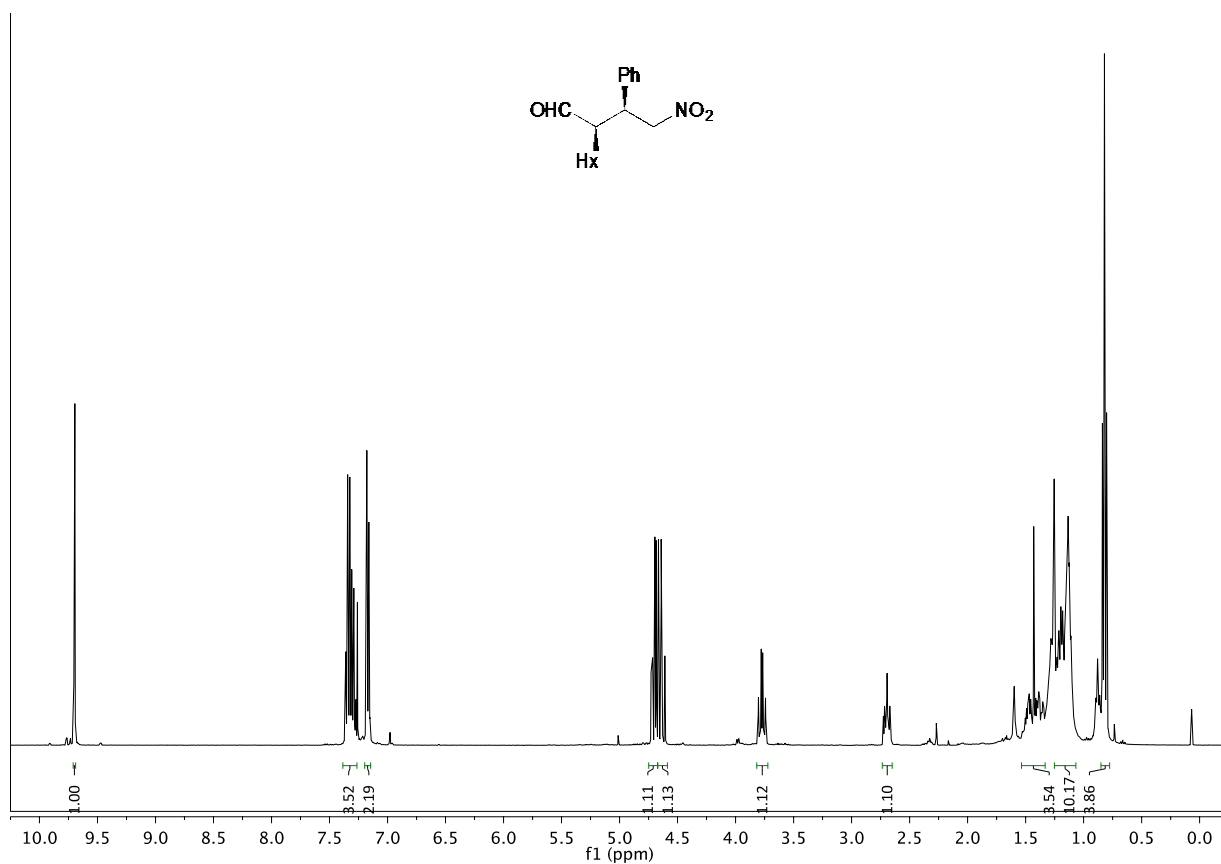
¹³C NMR of (2R,3S)-2-ethyl-4-nitro-3-phenylbutanal **9c**



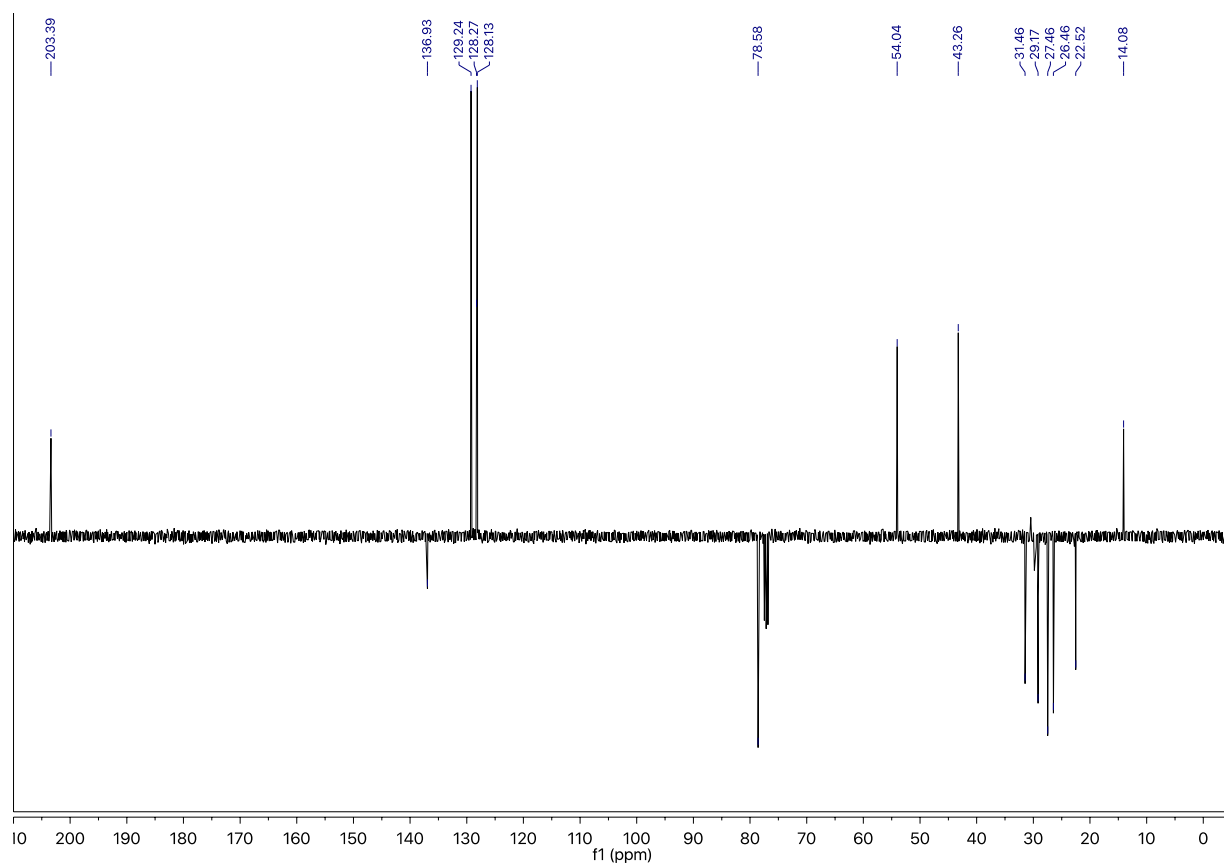
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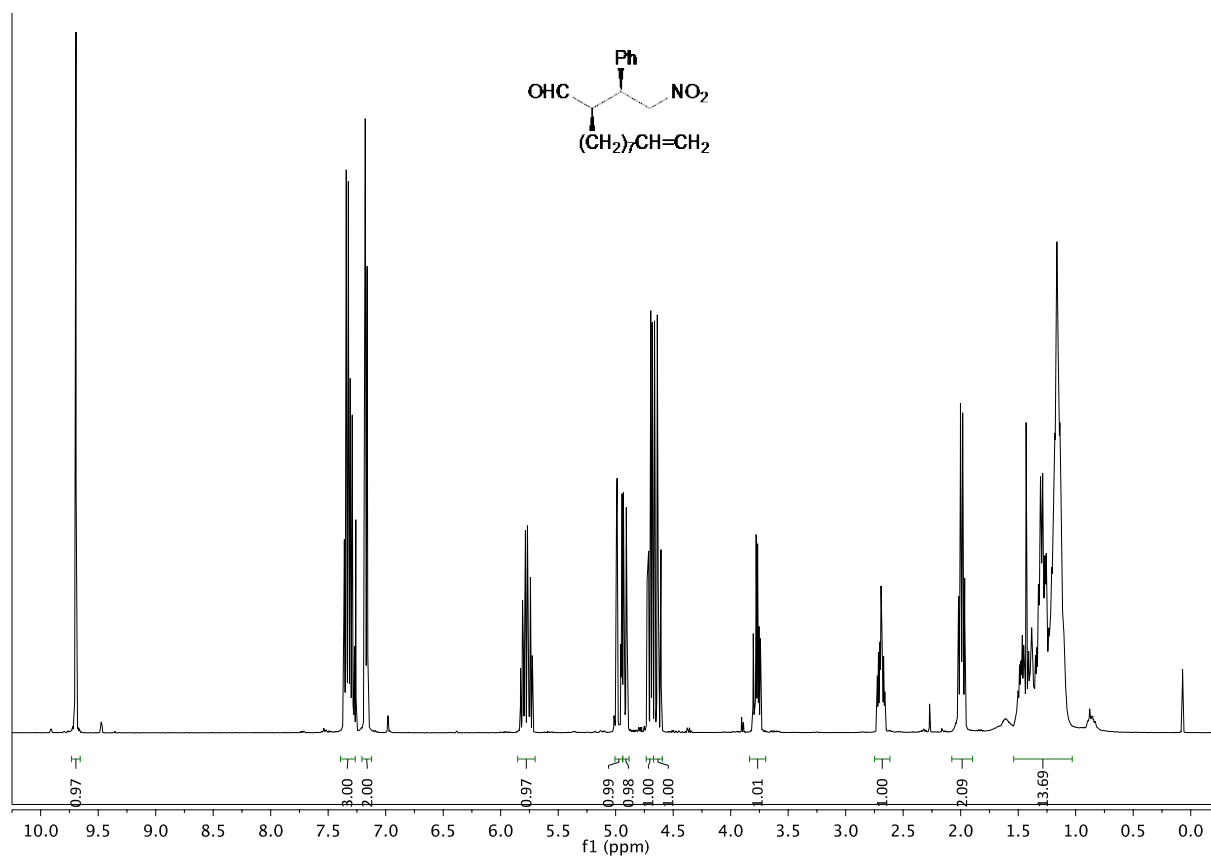
¹³C NMR of (2R,3S)-2-methyl-4-nitro-3-phenylbutanal **9d**



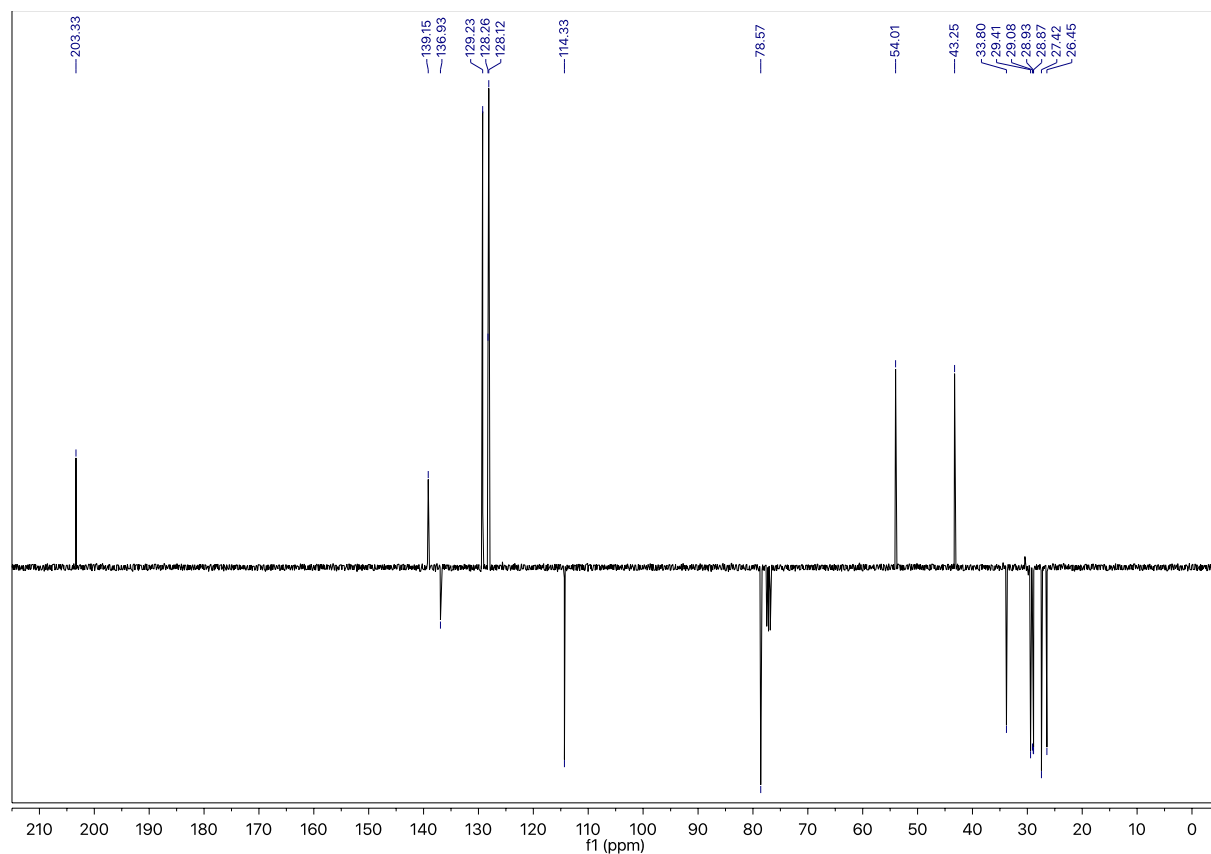
¹H NMR of (R)-2-[(S)-2-nitro-1-phenylethyl]octanal **9e**



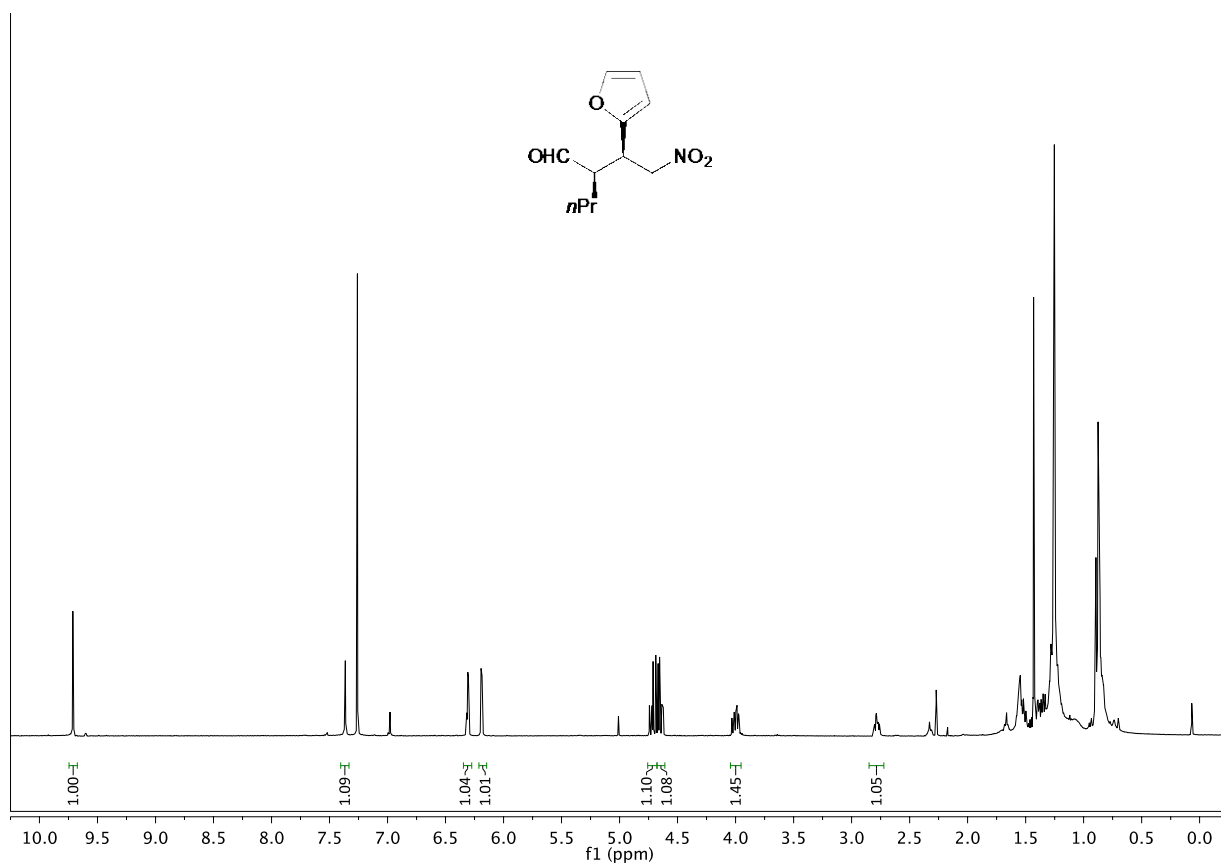
¹³C NMR of (R)-2-[(S)-2-nitro-1-phenylethyl]octanal **9e**



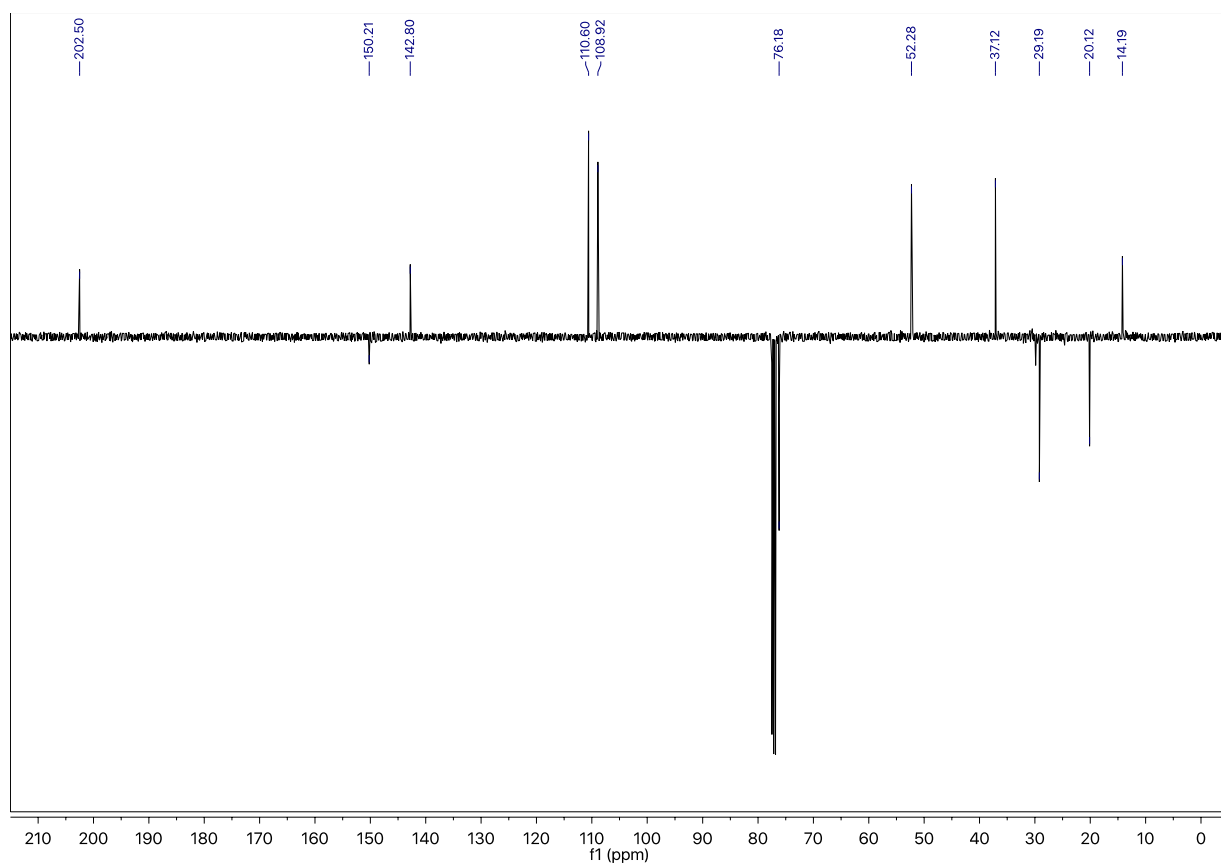
¹H NMR of (*R*)-2-[(*S*)-2-nitro-1-phenylethyl]undec-10-enal **9f**



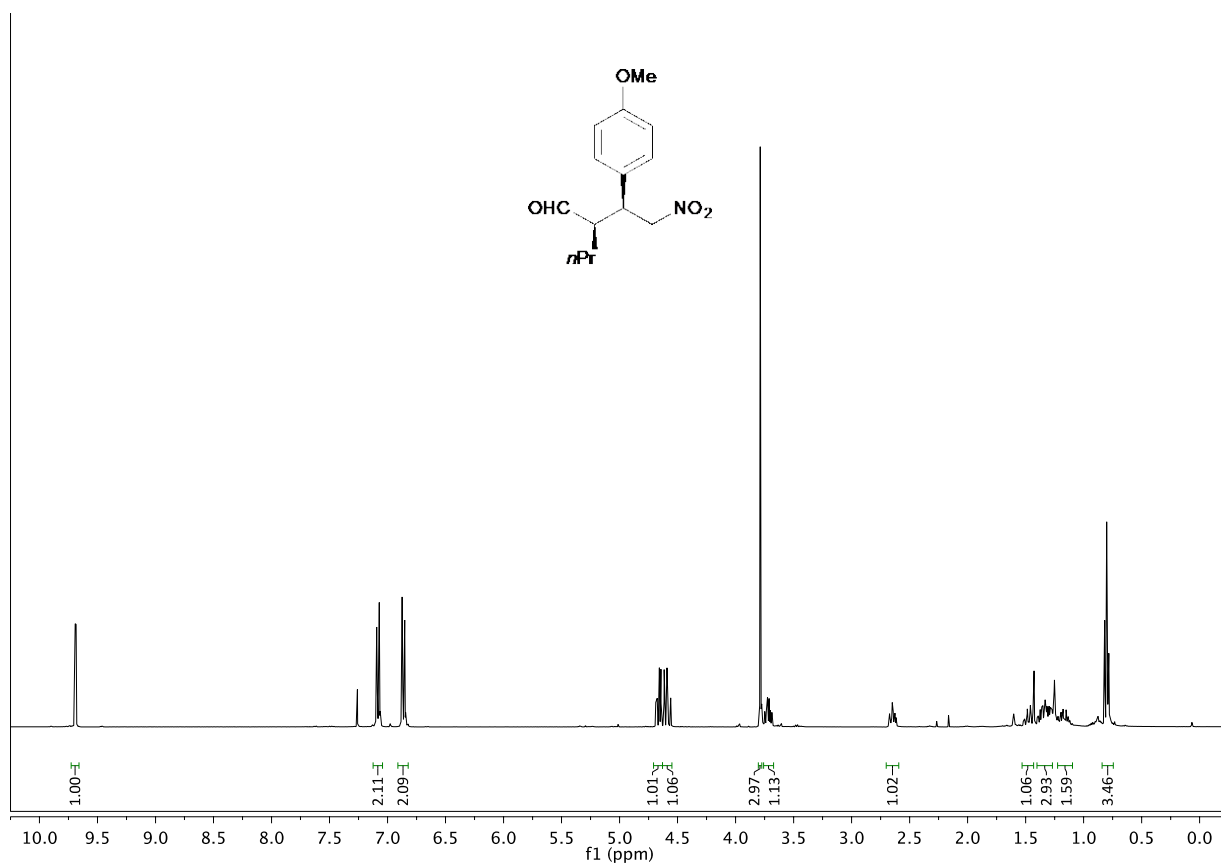
¹³C NMR of (*R*)-2-[(*S*)-2-nitro-1-phenylethyl]undec-10-enal **9f**



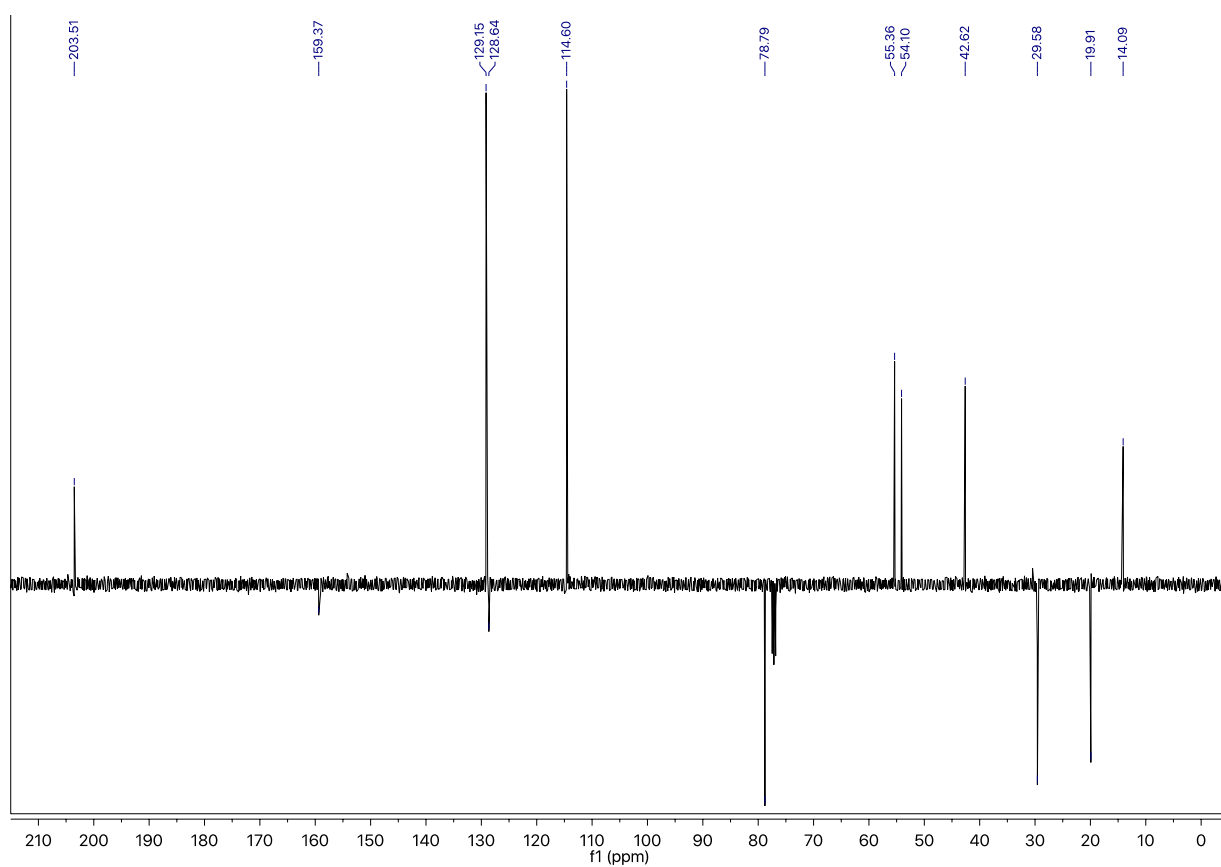
¹H NMR of (*R*)-2-[(*R*)-1-(furan-2-yl)-2-nitroethyl]pentanal **9g**



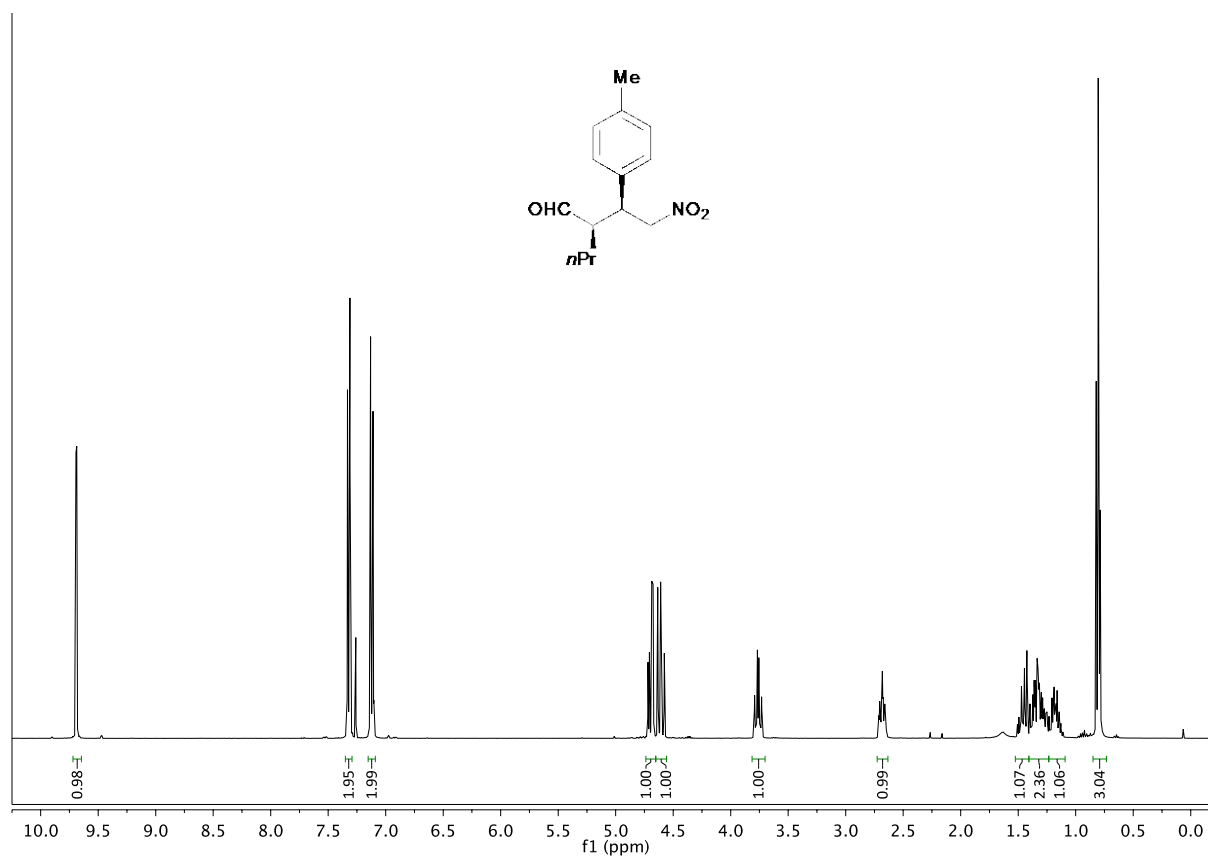
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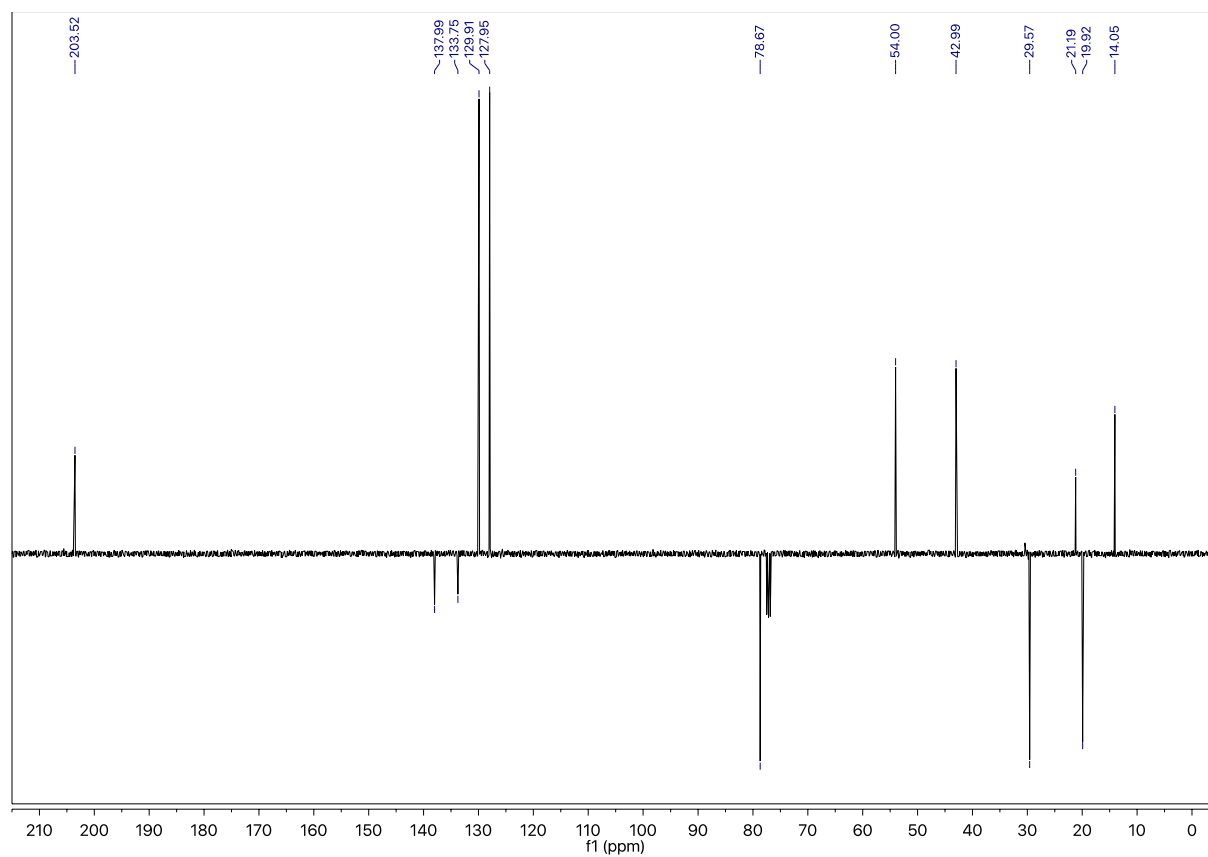
¹H NMR of (R)-2-[(S)-1-(4-methoxyphenyl)-2-nitroethyl]pentanal **9h**



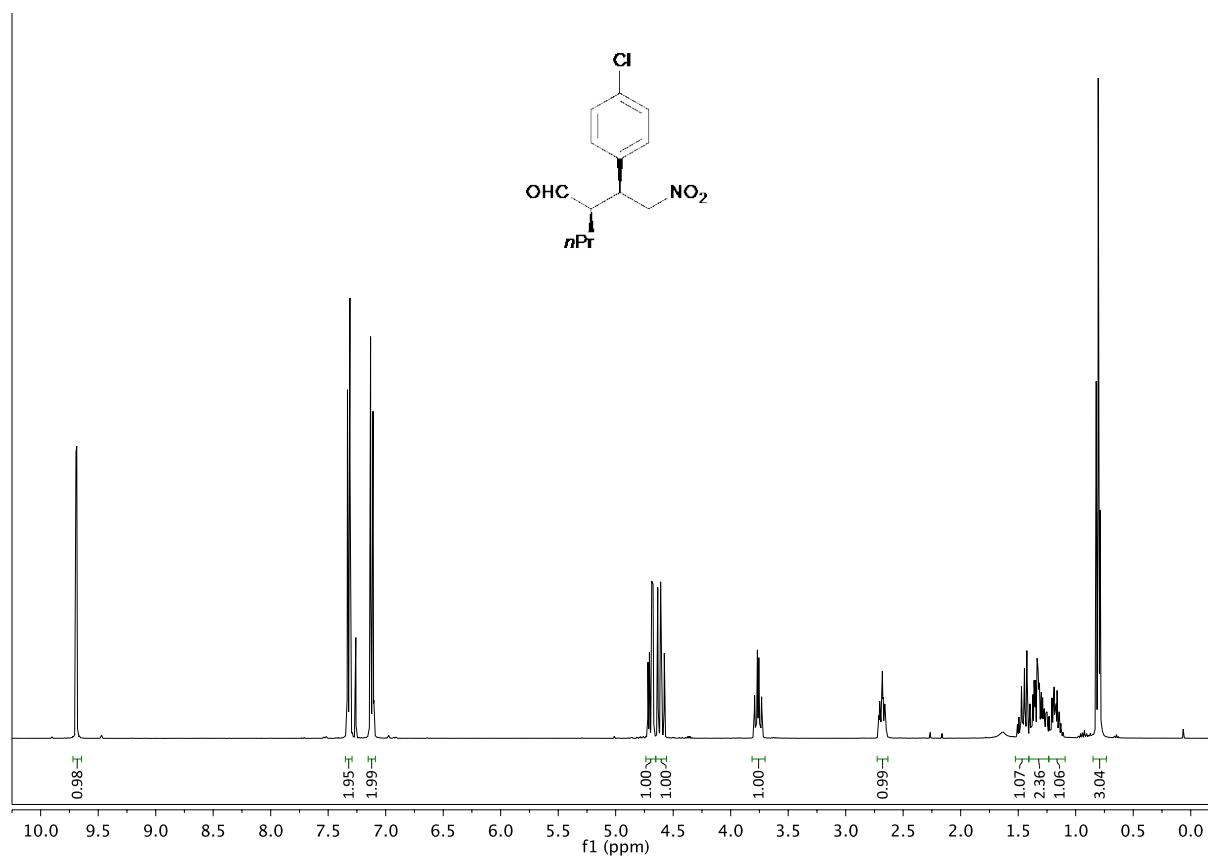
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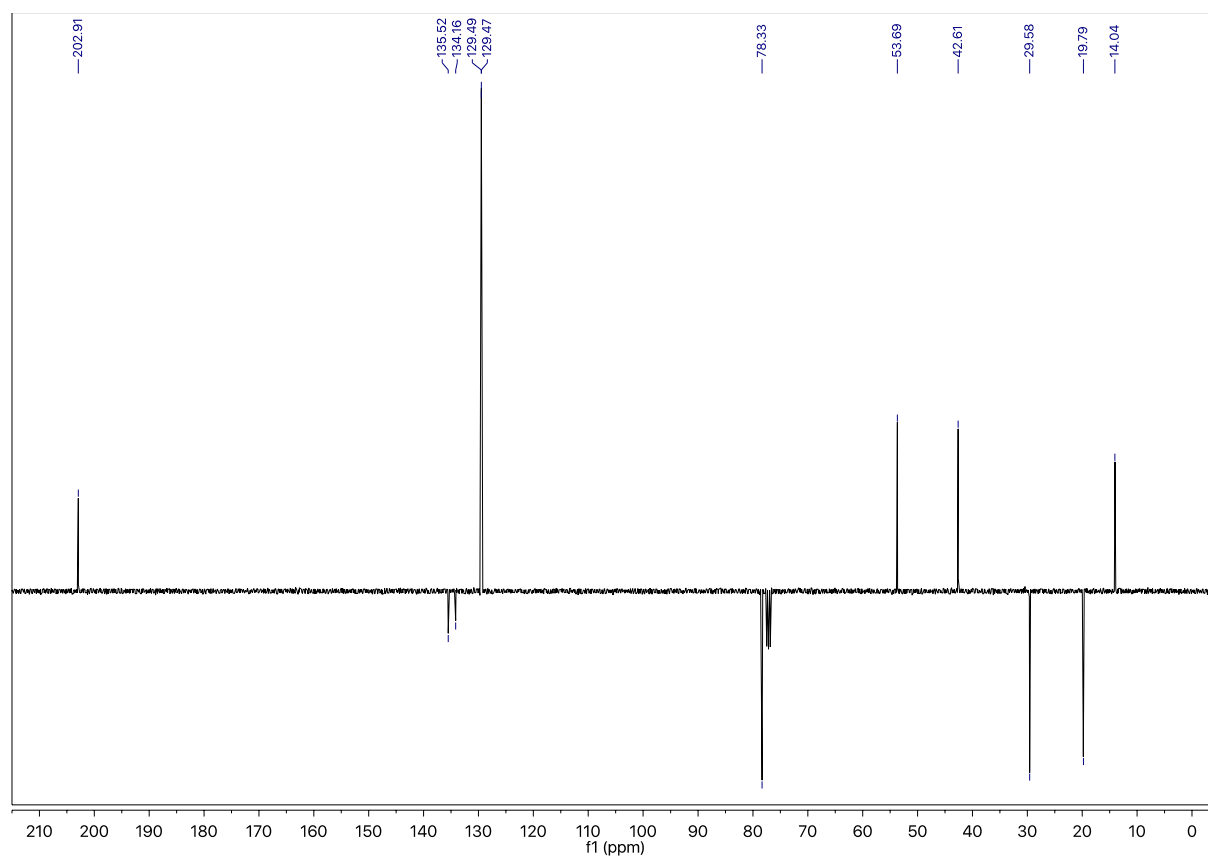
¹H NMR of (*R*)-2-[(*S*)-1-(4-methylphenyl)-2-nitroethyl]pentanal **9i**



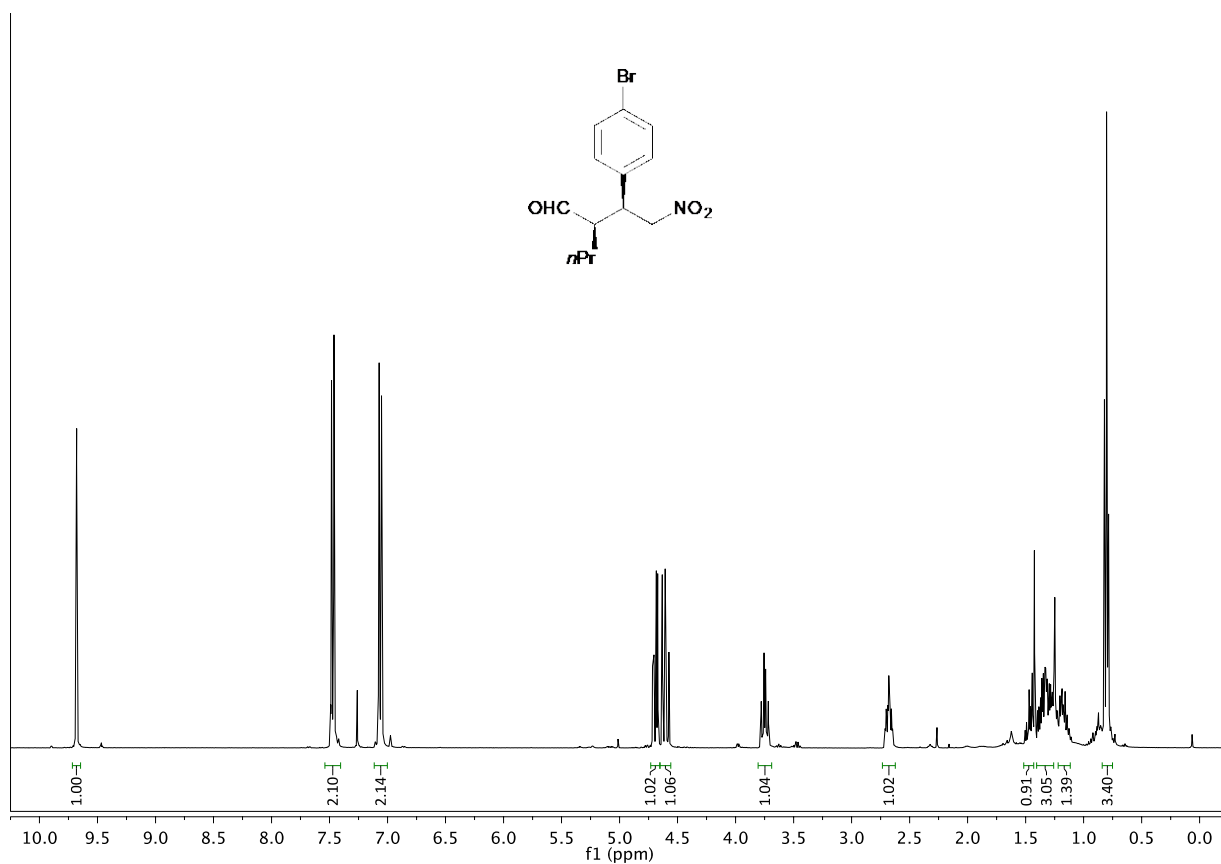
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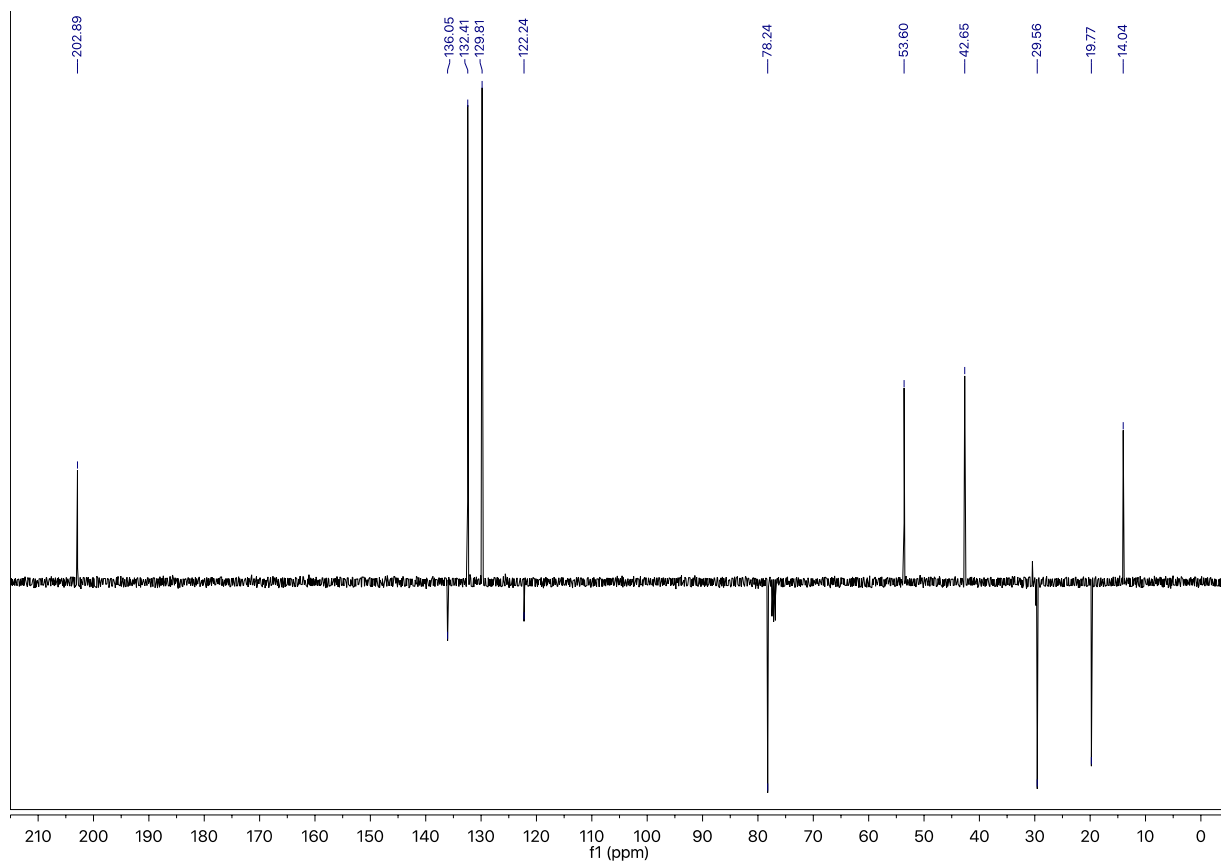
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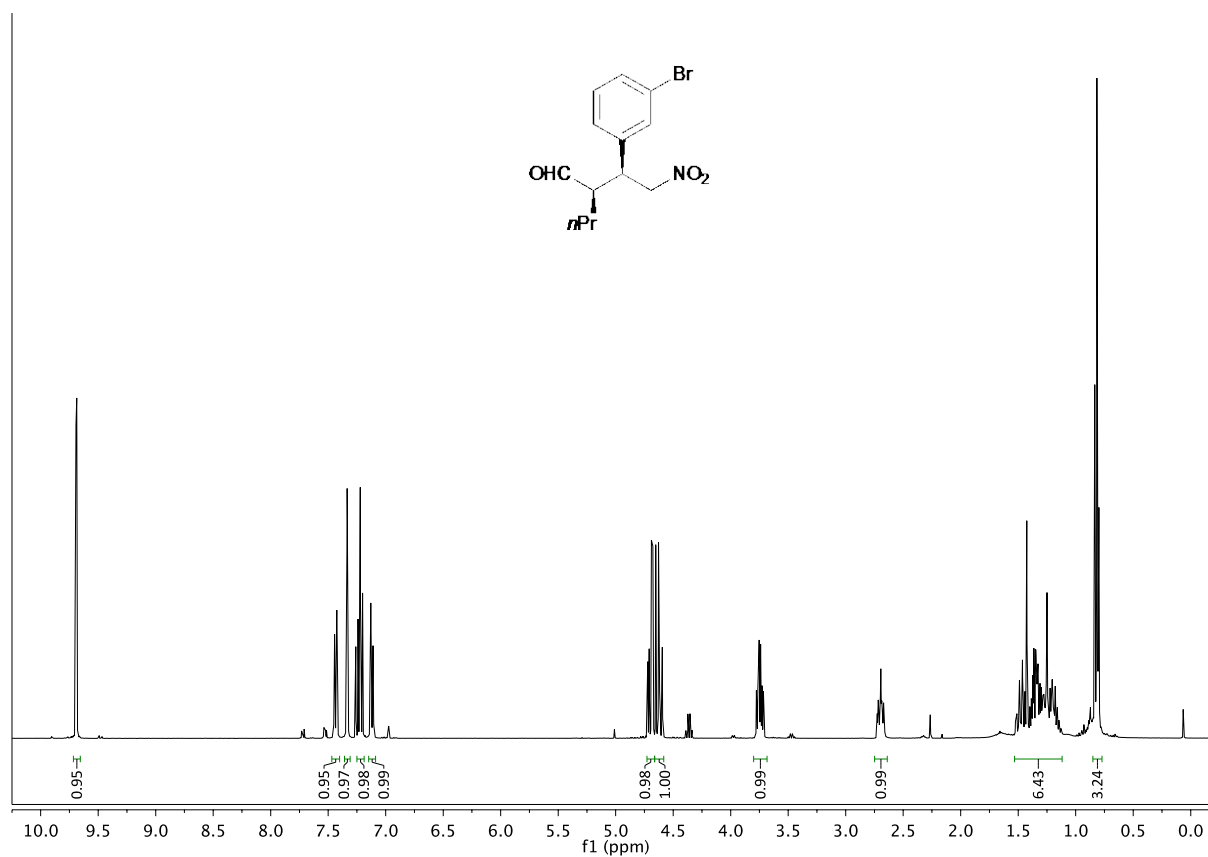
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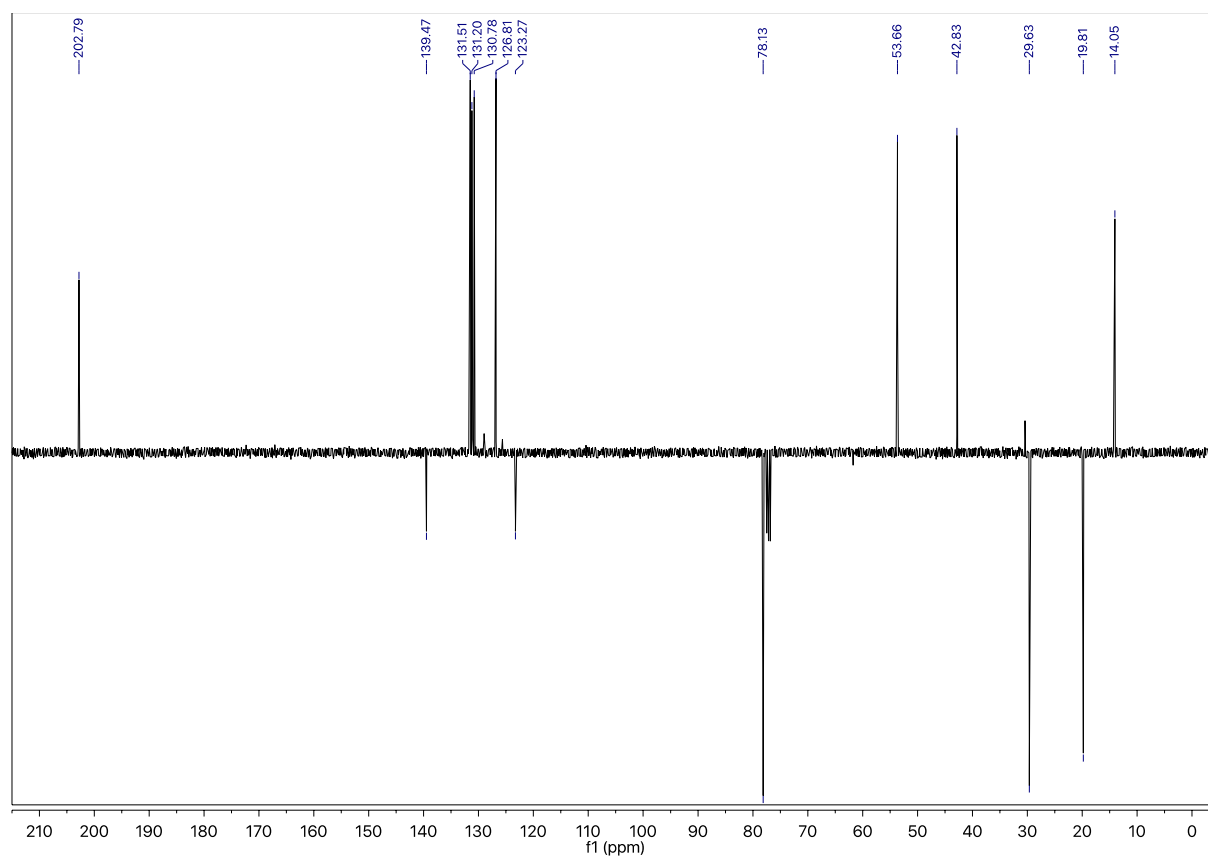
¹H NMR of (*R*)-2-[(*S*)-1-(4-bromophenyl)-2-nitroethyl]pentanal **9k**



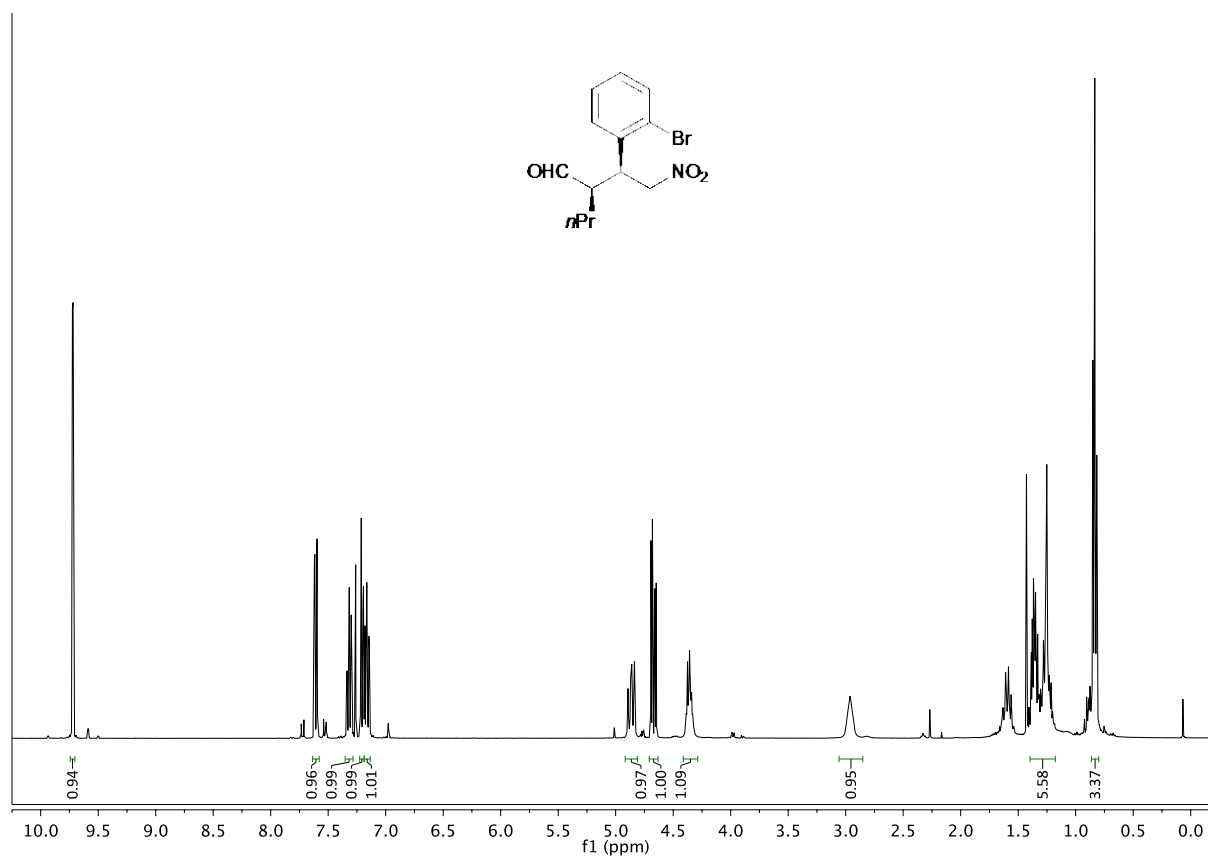
¹³C NMR of (*R*)-2-[(*S*)-1-(4-bromophenyl)-2-nitroethyl]pentanal **9k**



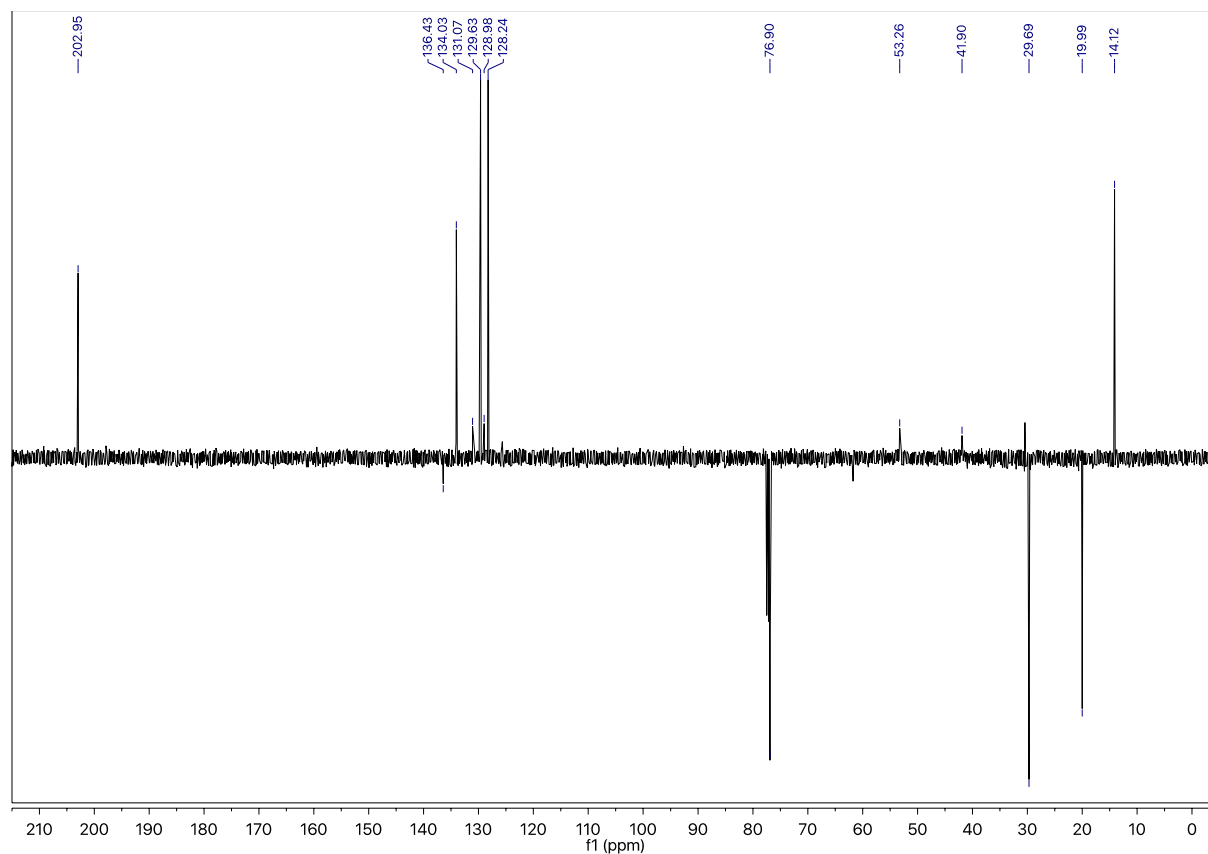
¹H NMR of (R)-2-[(S)-1-(3-bromophenyl)-2-nitroethyl]pentanal **9I**



¹³C NMR of (R)-2-[(S)-1-(3-bromophenyl)-2-nitroethyl]pentanal **9I**

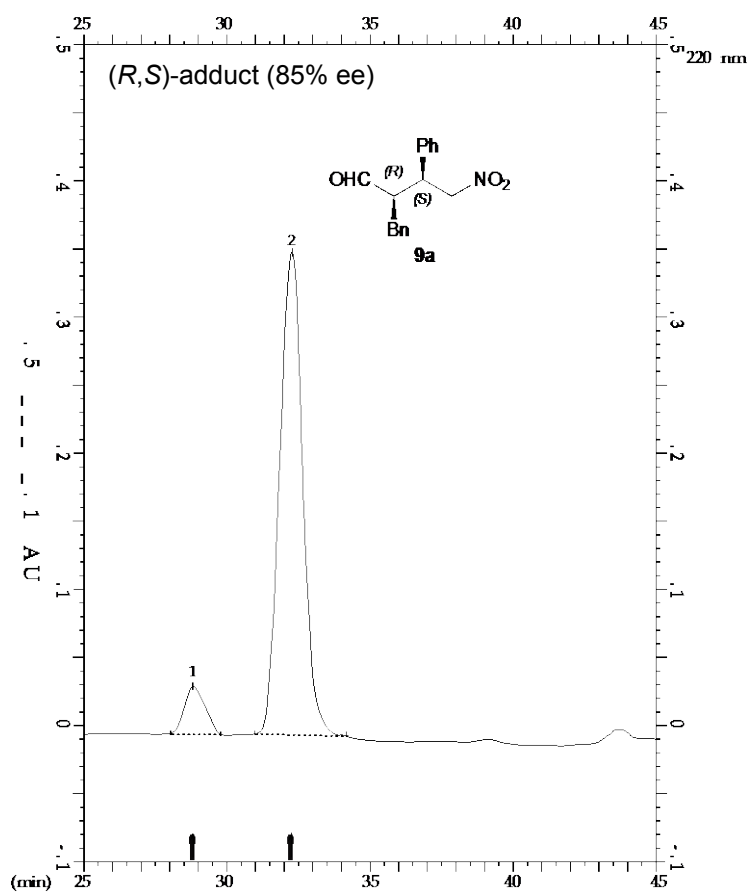
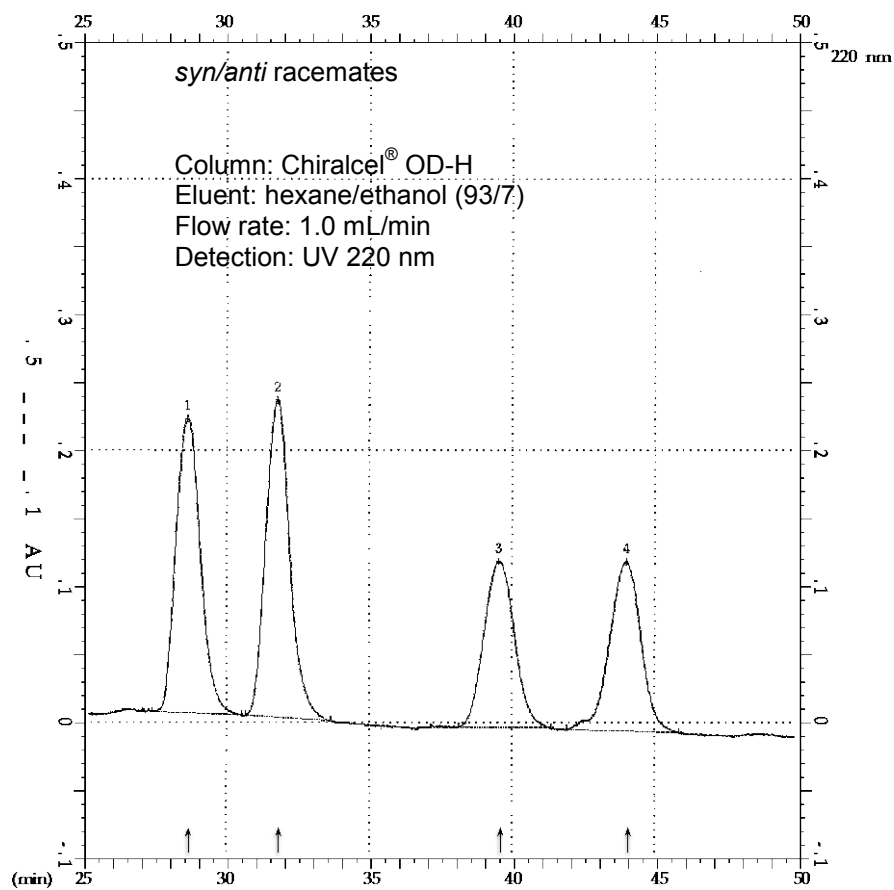


¹H NMR of (*R*)-2-[(*S*)-1-(2-bromophenyl)-2-nitroethyl]pentanal **9m**

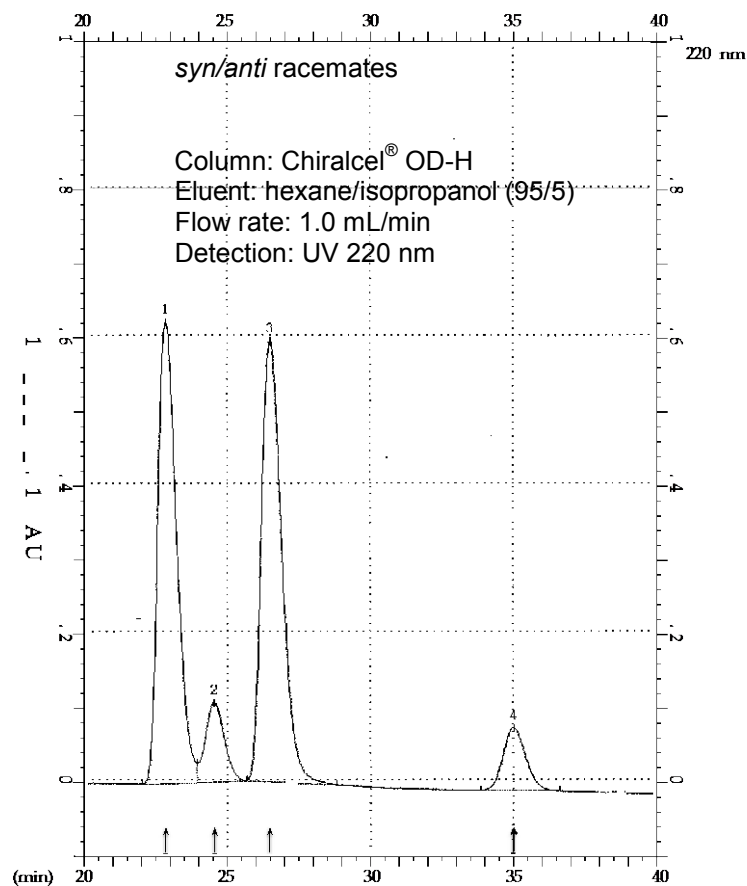


¹³C NMR of (*R*)-2-[(*S*)-1-(2-bromophenyl)-2-nitroethyl]pentanal **9m**

2-Benzyl-4-nitro-3-phenylbutanal

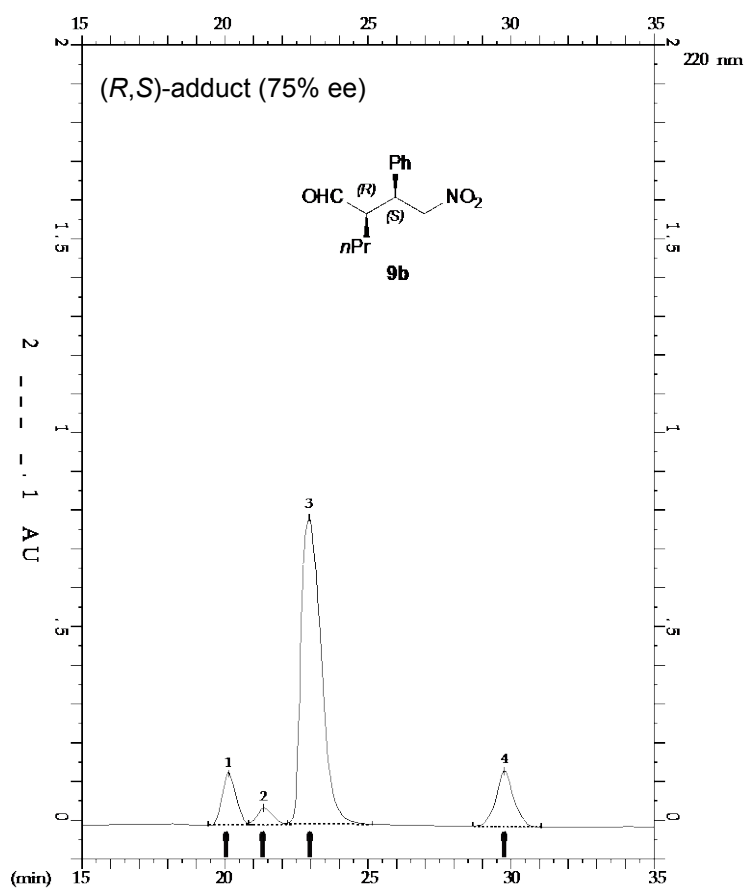


2-(2-Nitro-1-phenylethyl)pentanal



Report File PUL23001.DT3

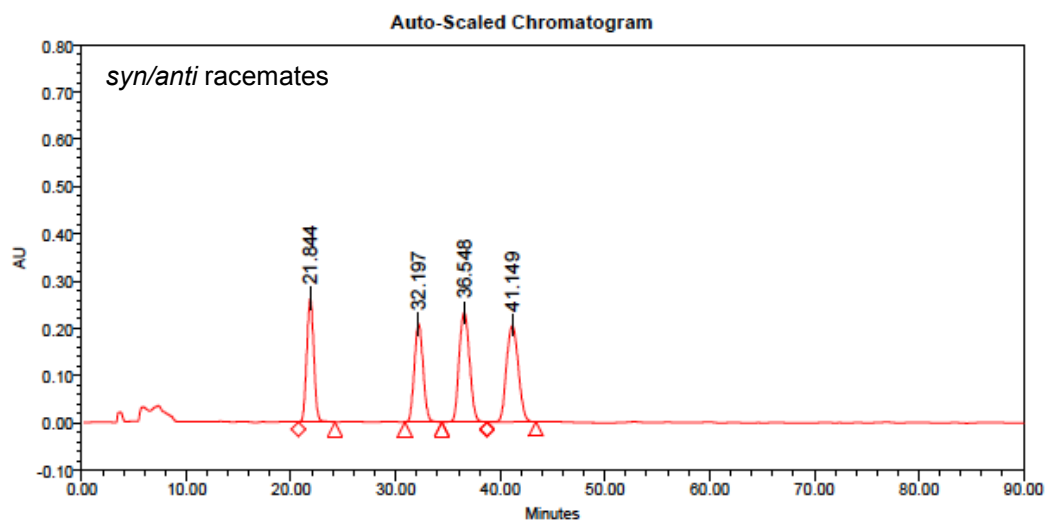
No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	22.85	0.6223	22.00	23.00	0.477169	42.197	Y
2	24.54	0.1089	23.94	25.67	0.082345	7.282	I
3	26.50	0.5952	25.64	28.83	0.492885	43.586	I
4	35.01	0.0847	33.88	36.64	0.078422	6.935	I



Report File YBAN2001.DT3

No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	20.12	0.1265	19.48	20.86	0.086142	10.609	Y
2	21.40	0.0402	20.86	22.27	0.028260	3.480	I
3	23.00	0.7790	22.23	25.19	0.607107	74.771	I
4	29.74	0.1286	28.71	31.10	0.090446	11.139	I

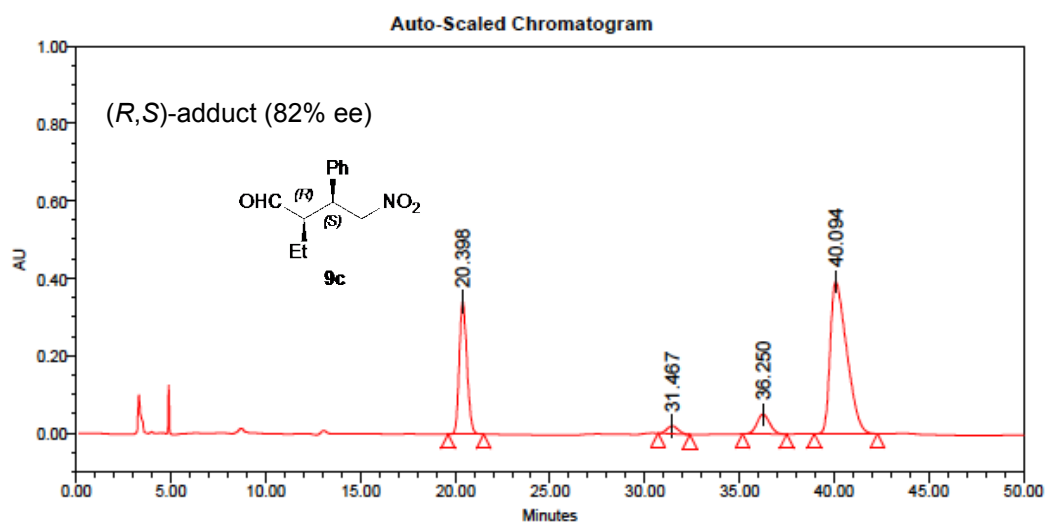
(2*R*,3*S*)-2-Ethyl-4-nitro-3-phenylbutanal



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1	21.844	12369715	21.76	261765
2	Peak2	32.197	12309531	21.65	207955
3	Peak3	36.548	16133522	28.38	231364
4	Peak4	41.149	16043287	28.22	203876

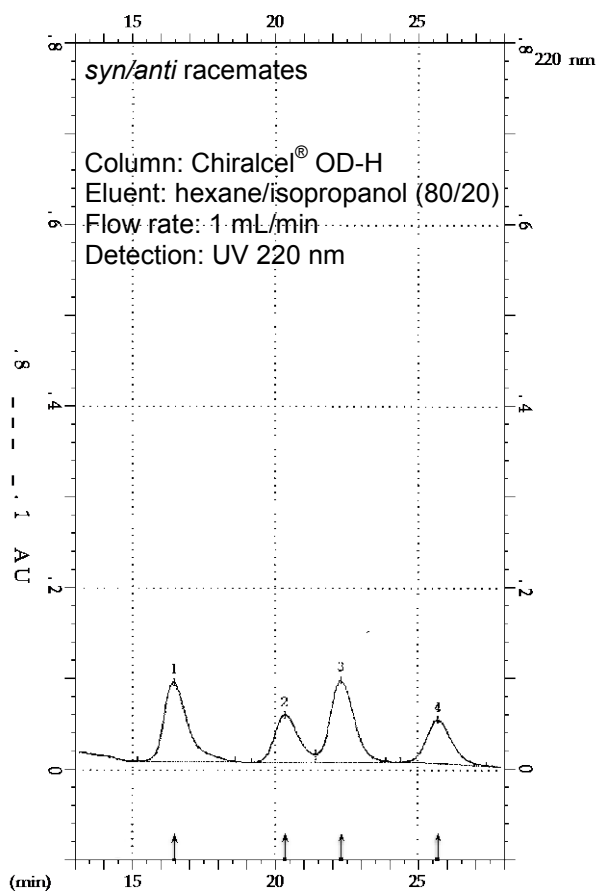
Column: Chiralpak® IC
 Eluent: hexane/isopropanol (90/10)
 Flow rate: 1 mL/min
 Detection: UV 220 nm



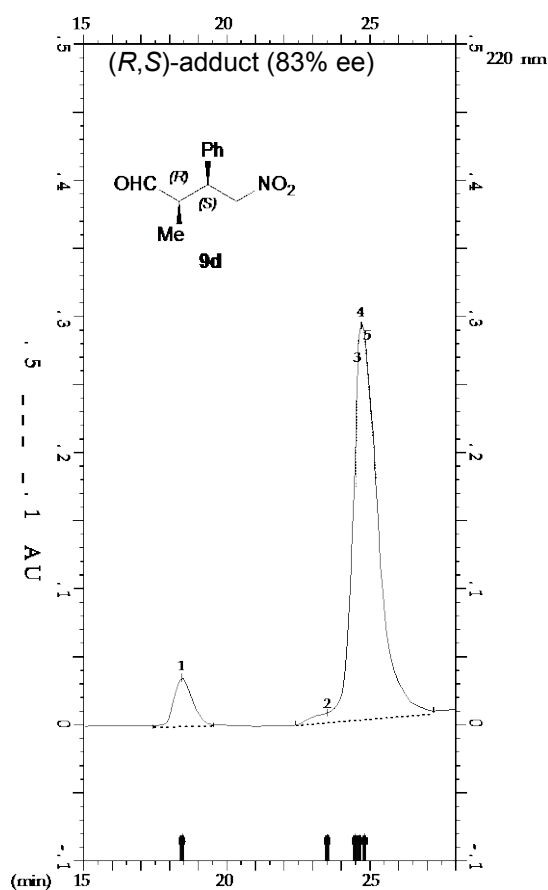
Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1	20.398	9707481	26.40	341729
2	Peak2	31.467	830263	2.26	20123
3	Peak3	36.250	2382084	6.48	51033
4	Peak4	40.094	23850533	64.86	392498

(2*R*,3*S*)-2-Methyl-4-nitro-3-phenylbutanal

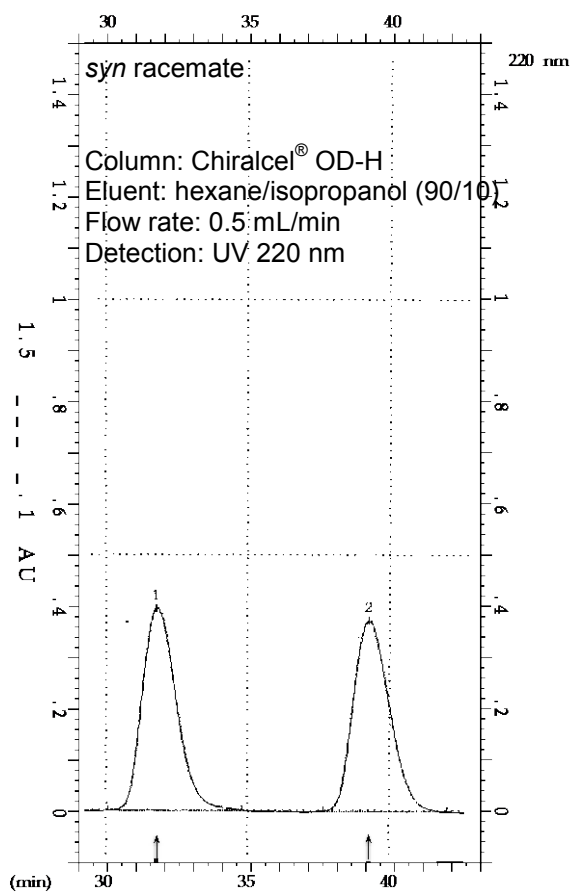


220 nm		Report		File PUL23001.DT3			
No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	16.48	0.0871	15.18	18.60	0.065382	31.081	I
2	20.33	0.0523	19.17	21.43	0.052145	18.982	I
3	22.31	0.0901	21.43	23.88	0.066726	31.570	V
4	25.71	0.0479	24.40	27.39	0.050458	18.368	I

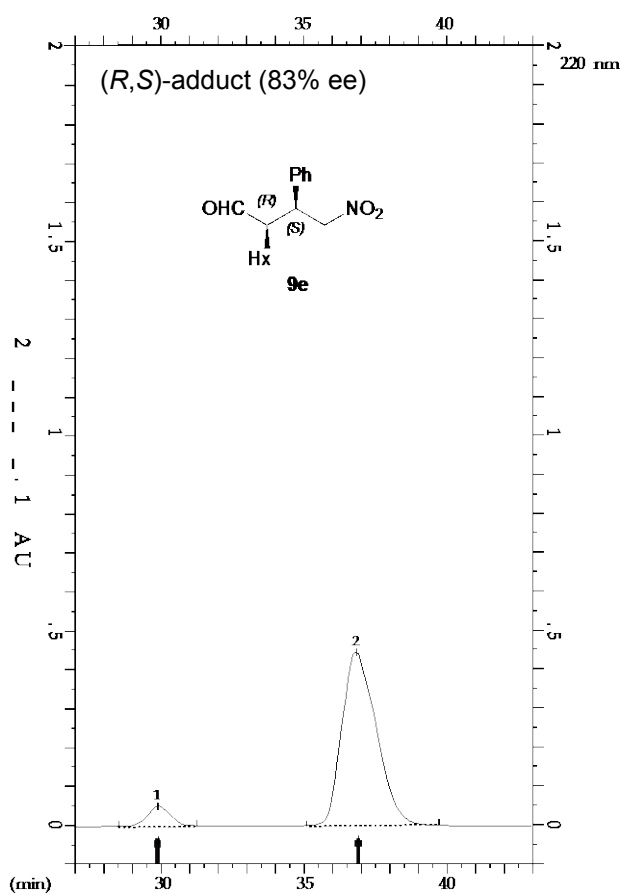


220 nm		Report	File yban4001.DT3				
No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	18.43	0.0384	17.17	19.54	0.029683	8.398	I
2	23.50	0.0074	22.43	23.74	0.005164	1.461	TB
3	24.45	0.0322	24.18	24.65	0.008288	2.345	V
4	24.68	0.2971	23.37	27.20	0.302806	85.672	TA
5	24.90	0.0233	24.71	25.31	0.007507	2.124	TA

2-(2-Nitro-1-phenylethyl)octanal

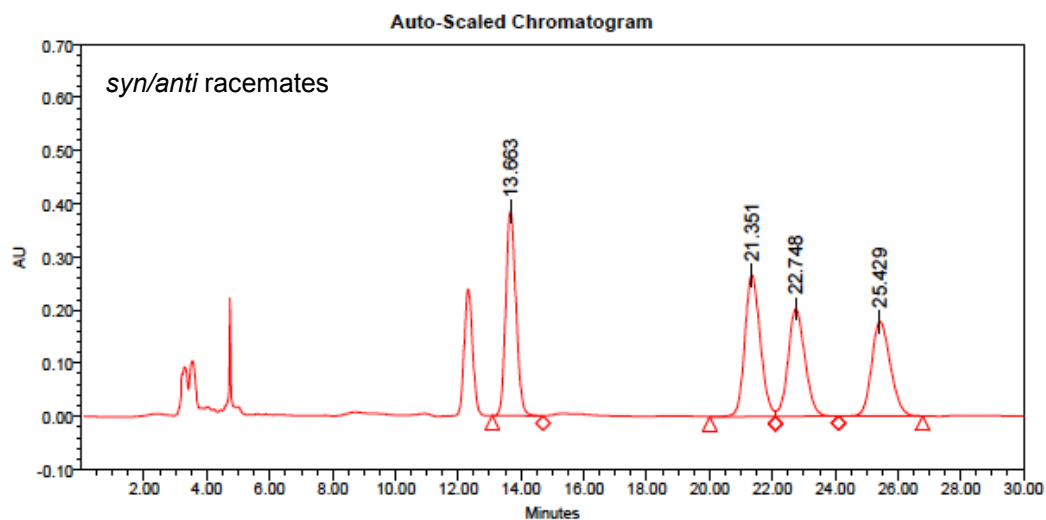


Report		File yban3001.DT3		220 nm	
No.	Retention time	Height [AU]	Left time	Right time	Mark
1	31.79	0.3962	30.06	34.82	I
2	39.26	0.3750	37.66	42.06	I



Report		File YBAN3001.DT3		220 nm	
No.	Retention time	Height [AU]	Left time	Right time	Mark
1	29.95	0.0498	28.56	31.39	I
2	36.98	0.4443	35.07	39.82	I

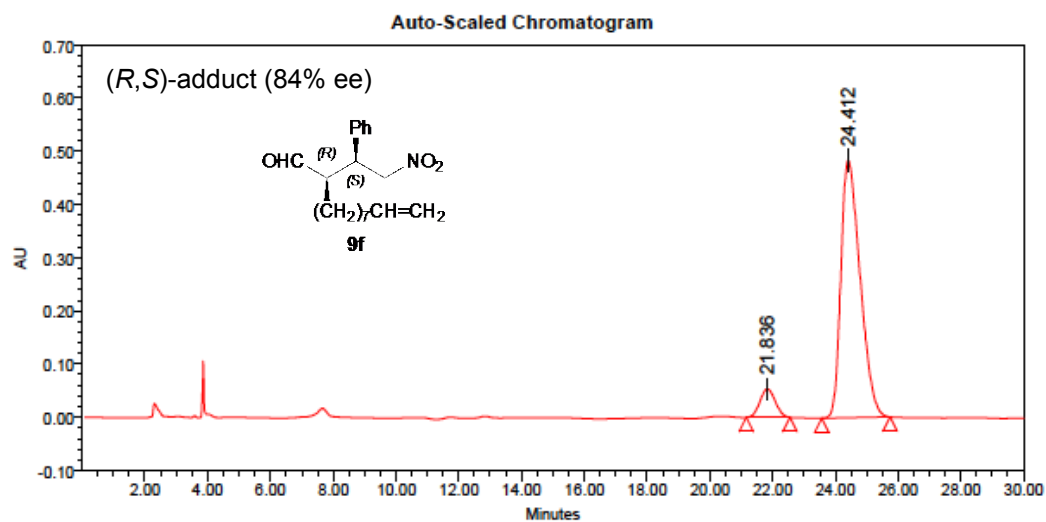
2-(2-Nitro-1-phenylethyl)undec-10-enal



Processed Channel:

Peak Name	Retention Time (min)	Area	% Area	Height
1 Peak1	13.663	8729994	26.67	384646
2 Peak2	21.351	9098892	27.80	266172
3 Peak3	22.748	7543260	23.04	202115
4 Peak4	25.429	7362156	22.49	177689

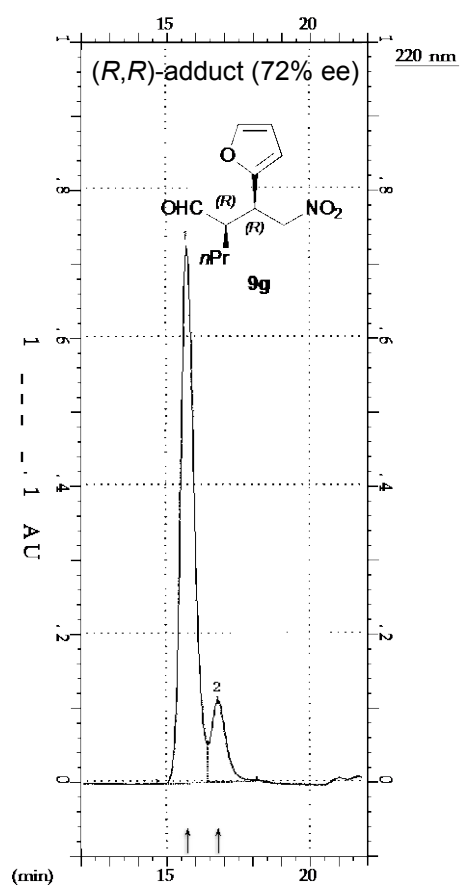
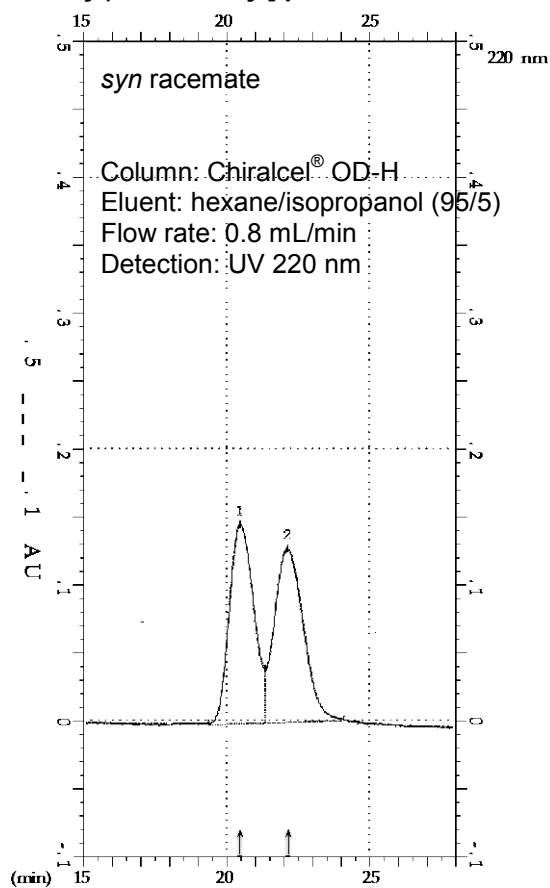
Column: Chiralpak[®] IC
 Eluent: hexane/isopropanol (90/10)
 Flow rate: 1 mL/min
 Detection: UV 220 nm



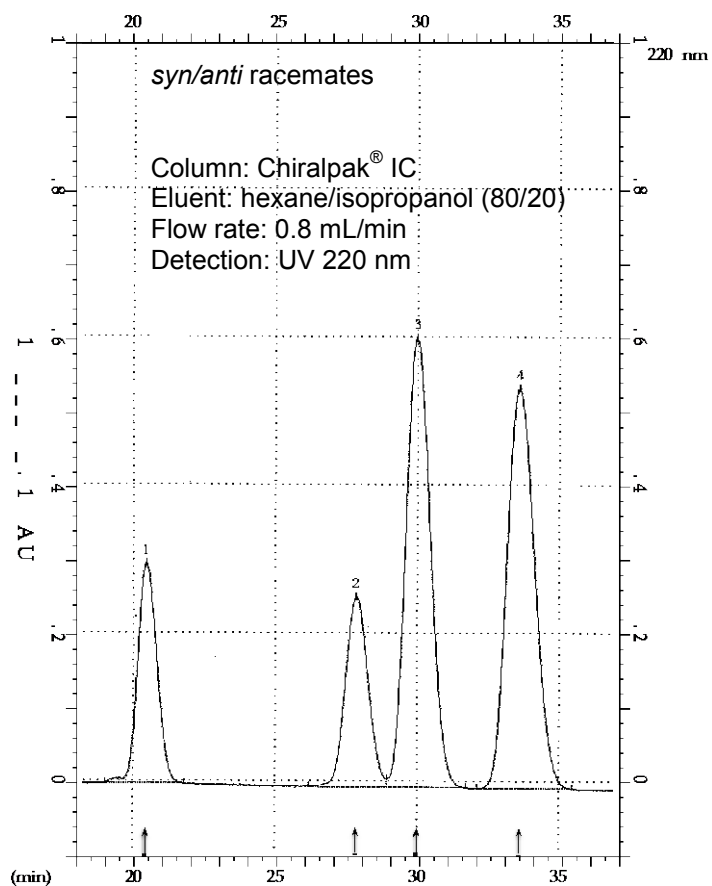
Processed Channel:

Peak Name	Retention Time (min)	Area	% Area	Height
1 Peak1	21.836	1821301	8.14	53429
2 Peak2	24.412	20557355	91.86	484042

2-[1-(Furan-2-yl)-2-nitroethyl]pentanal

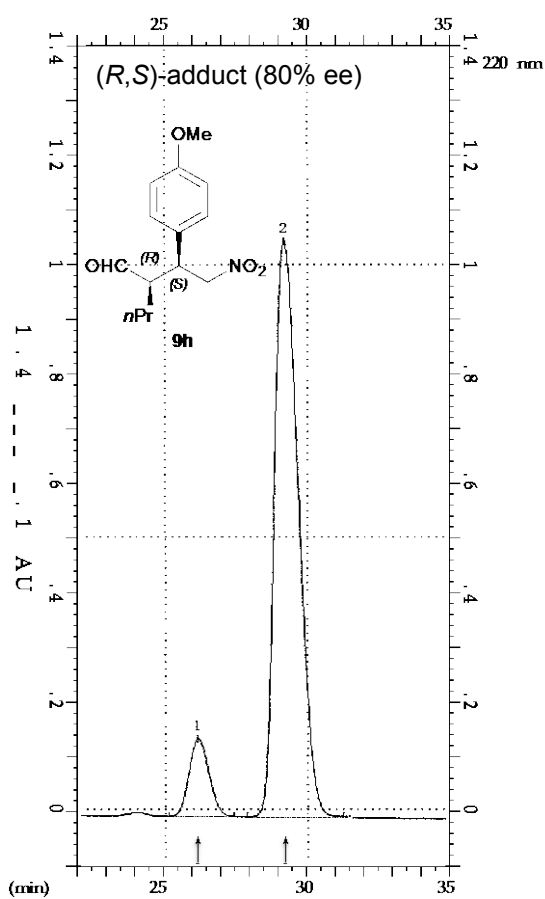


2-[1-(4-Methoxyphenyl)-2-nitroethyl]pentanal



Report File YBAN2001.DT3

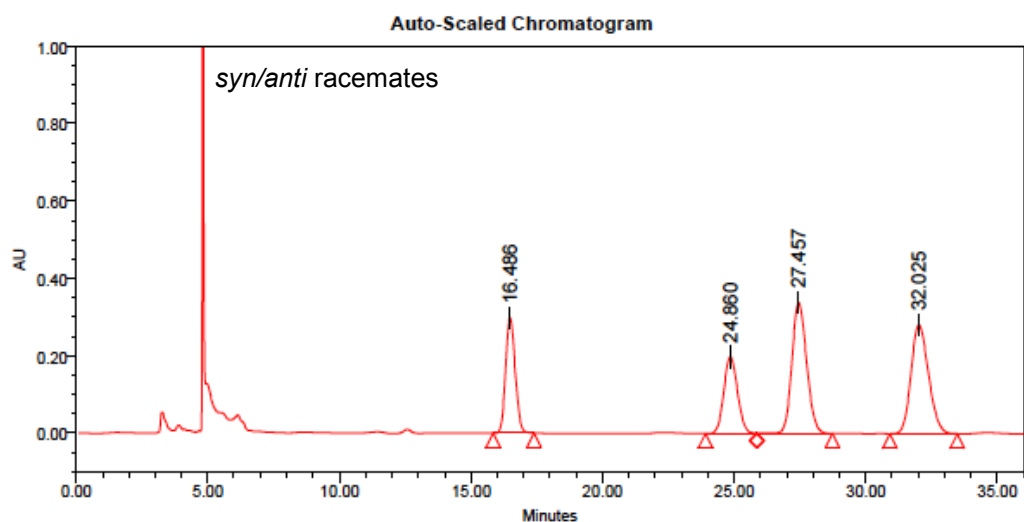
No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	20.46	0.2972	19.00	21.82	0.237271	14.014	I
2	27.83	0.2570	26.19	28.93	0.237125	14.005	V
3	29.99	0.6070	28.93	31.70	0.609378	35.992	I
4	33.60	0.5403	32.12	35.47	0.609339	35.989	I



Report File YBAN1001.DT3

No.	Retention time	Height [AU]	Left time	Right time	Area [AU*min]	Area [%]	Mark
1	26.13	0.1432	25.13	27.42	0.116853	10.237	I
2	29.17	1.0575	27.87	31.26	0.024589	89.763	I

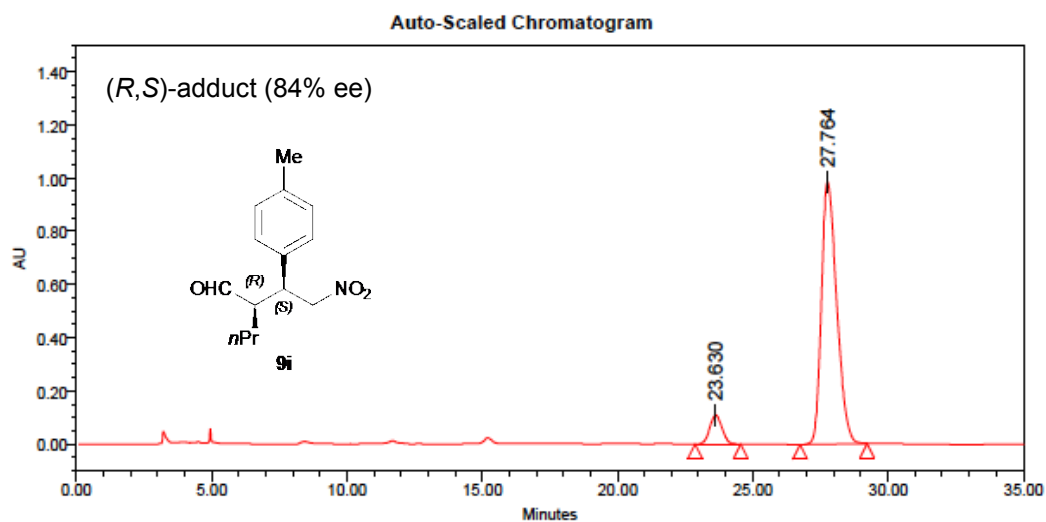
2-[1-(4-Methylphenyl)-2-nitroethyl]pentanal



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1	16.486	7563572	18.43	298126
2	Peak2	24.860	7197350	17.53	199174
3	Peak3	27.457	13238987	32.25	338499
4	Peak4	32.025	13049130	31.79	281732

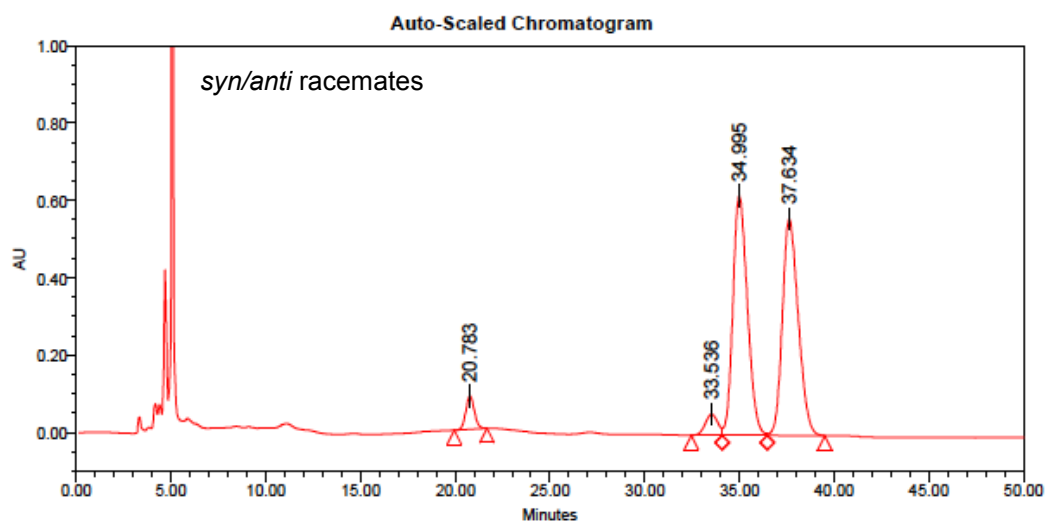
Column: Chiralpak[®] IC
 Eluent: hexane/isopropanol (90/10)
 Flow rate: 1 mL/min
 Detection: UV 220 nm



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1	23.630	3452856	8.20	109017
2	Peak2	27.764	38677823	91.80	985229

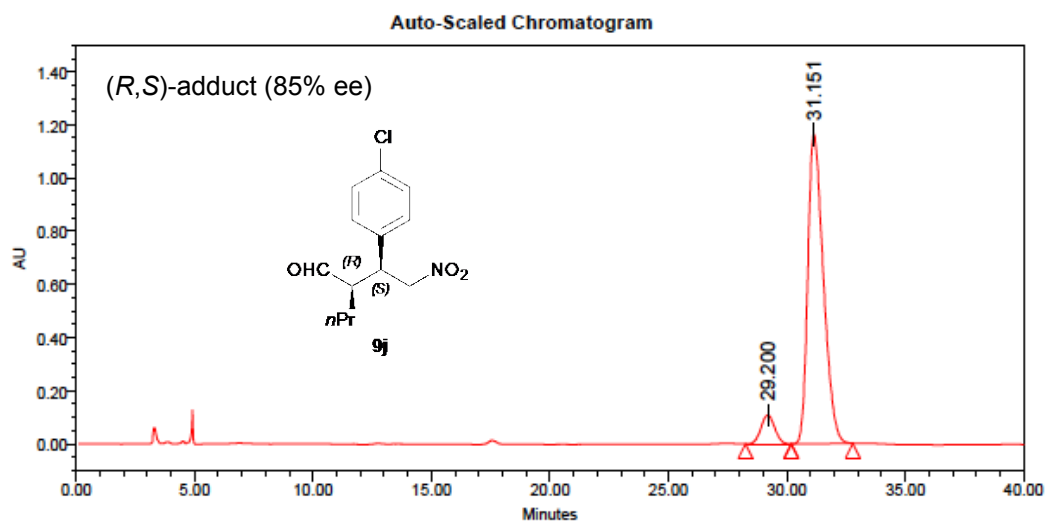
2-[1-(4-Chlorophenyl)-2-nitroethyl]pentanal



Processed Channel:

Peak Name	Retention Time (min)	Area	% Area	Height
1 Peak1	20.783	2697137	3.80	85793
2 Peak2	33.536	2521514	3.55	54810
3 Peak3	34.995	33026303	46.55	619620
4 Peak4	37.634	32704407	46.10	560072

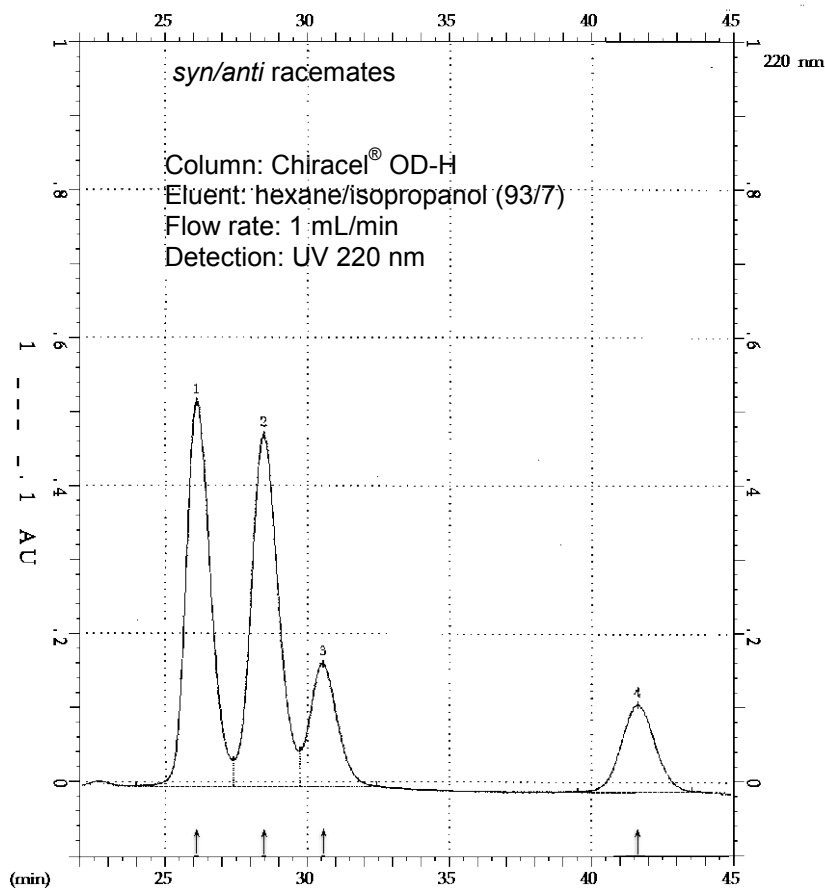
Column: Chiralpak® IC
 Eluent: hexane/isopropanol (90/10)
 Flow rate: 1 mL/min
 Detection: UV 220 nm



Processed Channel:

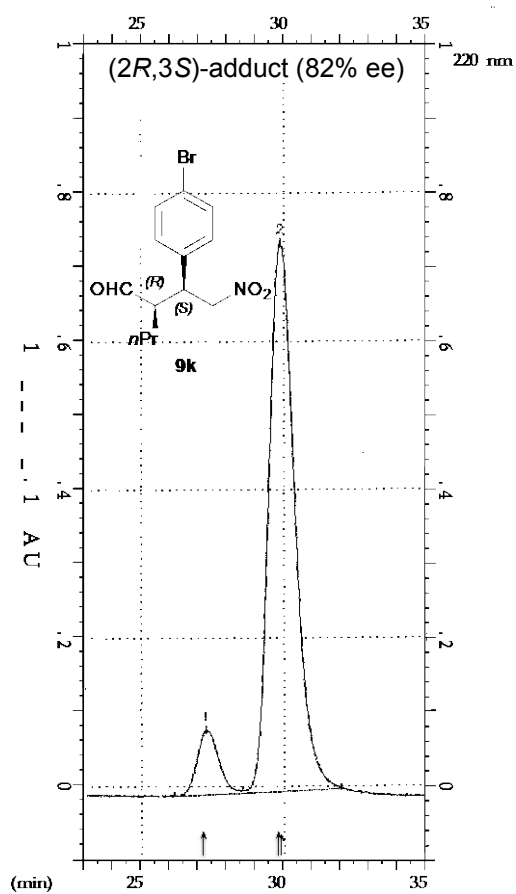
Peak Name	Retention Time (min)	Area	% Area	Height
1 Peak1	29.200	4415849	7.67	108885
2 Peak2	31.151	53137878	92.33	1163159

2-[1-(4-Bromophenyl)-2-nitroethyl]pentanal



Report File PUL12001.DT3

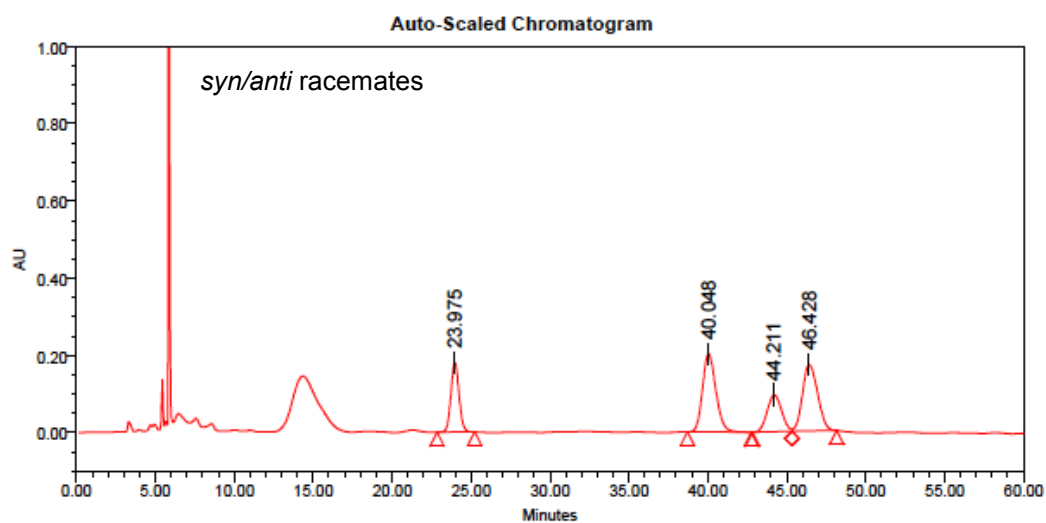
220 nm



Report File YBAN4001.DT3

220 nm

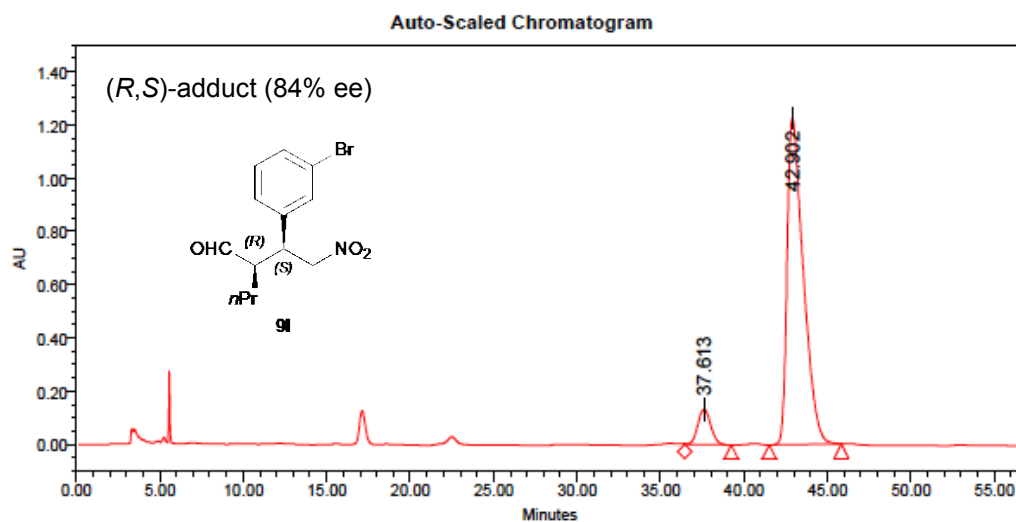
2-[1-(3-Bromophenyl)-2-nitroethyl]pentanal



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1 2487Channel 1	23.975	6443861	17.93	179574
2	Peak2 2487Channel 1	40.048	11977582	33.33	202334
3	Peak3 2487Channel 1	44.211	6085578	16.88	95254
4	Peak4 2487Channel 1	46.428	11453171	31.87	171632

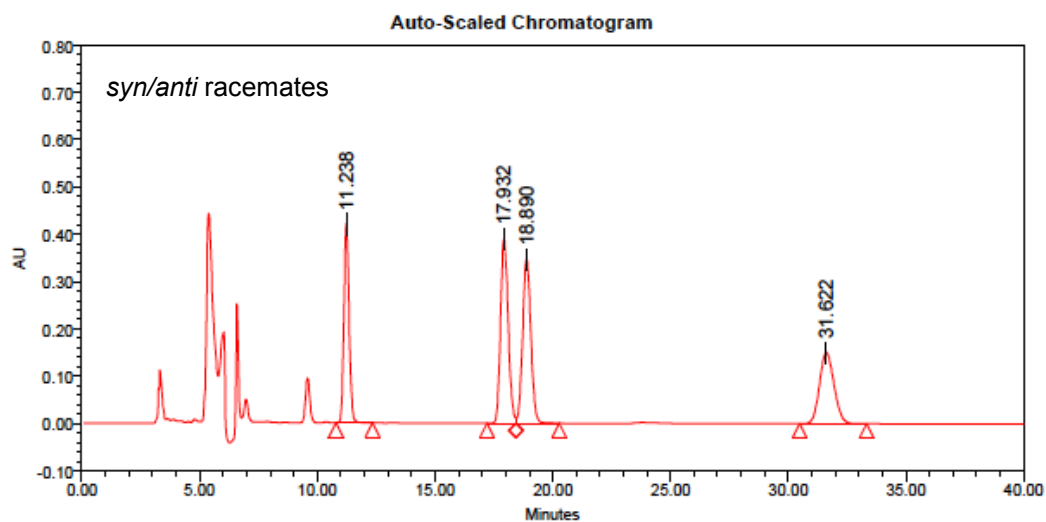
Column: Chiralpak® IC
 Eluent: hexane/isopropanol (95/5)
 Flow rate: 1 mL/min
 Detection: UV 220 nm



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1	37.613	7221985	8.07	133117
2	Peak2	42.902	82305323	91.93	1225475

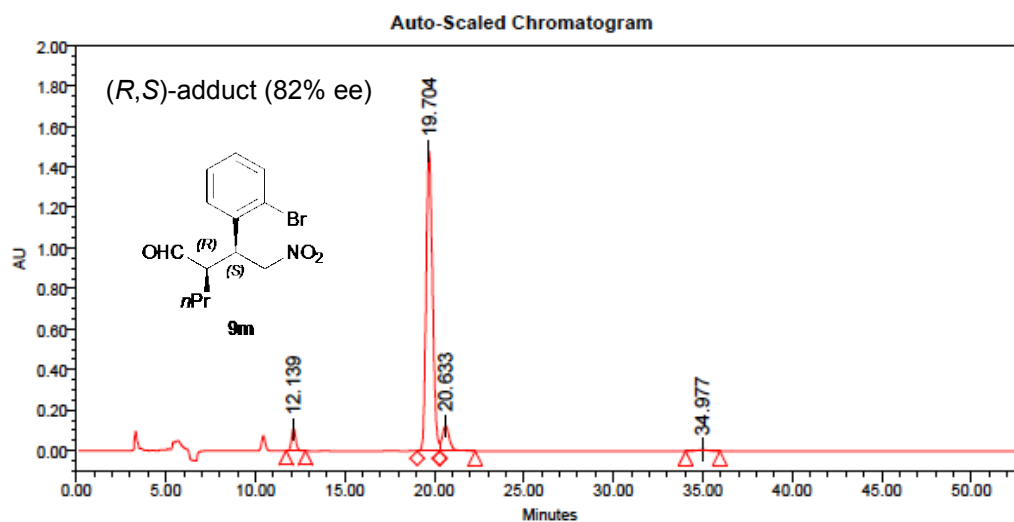
2-[1-(2-Bromophenyl)-2-nitroethyl]pentanal



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1	11.238	6453038	21.39	421259
2	Peak2	17.932	8813518	29.21	389924
3	Peak3	18.890	8444232	27.99	346020
4	Peak4	31.622	6461770	21.42	151025

Column: Chiralpak[®] IC
 Eluent: hexane/isopropanol/acetone (95/4/1)
 Flow rate: 1 mL/min
 Detection: UV 220 nm



Processed Channel:

	Peak Name	Retention Time (min)	Area	% Area	Height
1	Peak1 2487Channel 1	12.139	1798995	4.23	108907
2	Peak2 2487Channel 1	19.704	36874281	86.61	1480248
3	Peak3 2487Channel 1	20.633	3555275	8.35	124551
4	Peak4 2487Channel 1	34.977	345501	0.81	7540