Electronic Supplementary Information

Chiral Hybrid Materials Based on Pyrrolidine Builder Units to Perform Asymmetric Michael Additions with High Stereocontrol

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Index

Table S1. Effect of the solvent over the enantioselective catalytic performance of HybPyr catalyst.

Entry	t(days)	cat. Mol%	Solvent	TºC	Yield (%)[a]	ee (%)[b]
1	5.5	20%	95/5	rt	84	40
2	3	20%	Brine	rt	62	22
3	3	20%	H_2O	rt	37	20
4	3	20%	ACN	rt	28	13
5	3	20%	AcOEt	rt	21	6
6	2	10%	Toluene	rt	14	-
7	3	20%	$CHCl_3$	rt	34	15
8	2	20%	CPME	rt	39	18
9	3	20%	DCM	rt	35	38
10	3	20%	DMF	rt	8	Racemic
11	3	20%	DMSO	rt	9	Racemic
12	3	20%	Et_2O	rt	56	23
13	3	20%	THF	rt	23	5
14	2	10%	Hexane	rt	18	11[e]
15	6	20%	MeOH	rt	96	51
16	13	20%	MeOH	0	30	46
17	2	20%	MeOH	60	54	22
18	2	10%	MeOH	rt	36	52
19	7.5	20%	EtOH	rt	67	24
20	2	20%	t-BuOH	rt	30	10
21	7.5	20%	iPrOH	rt	64	8
22	3	20%	BuOH	rt	38	22

Reaction conditions: β-nitrostyrene (0.2 mmol), isobutyraldehyde (2 mmol), additive (0.05 mmol), catalyst (10 or 20 mol %), solvent (1 mL), T= 25 ºC. In all cases, the selectivity towards Michael adducts was > 99 %. (a) Yield and conversion were determinate by GC. (b) Determined by HPLC on the purified reaction mixture, using a chiral stationary phase (Chiralpak IC column).

Table S2. Effect of the additive addition over the enantioselective catalytic performance of HybPyr catalyst.

Entry	t(days)	Solvent	TºC	Additive	pKa (water)	Yield (%)[a]	ee(%)[b]
1	5.5	95/5	rt	$PhCO_2H$	4.2	83	38
2	7.5	EtOH	rt	$PhCO_2H$	4.2	60	30
3	7.5	iPrOH	rt	$PhCO_2H$	4.2	64	13
4	2	iPrOH	rt	TFA	-15	5	-
5	6	MeOH	rt	AcOH	4.75	87	55
6	17	MeOH	0	AcOH	4.75	33	55
7	17	MeOH	0	$PhCO_2H$	4.2	36	55
8	5.75	MeOH	rt	$PhCO_2H$	4.2	90	53
9	17	MeOH	rt	TFA	-15	-	-
10	10	MeOH	rt	HCO_2H	3.75	63	38
11	3.75	MeOH	rt	HBA	4.36	66	53
12	3	Toluene	4	TFA	-15	-	-

Reaction conditions: β-nitrostyrene (0.2 mmol), isobutyraldehyde (2 mmol), additive (0.05 mmol, 25 mol %), catalyst (10 mol %), solvent (1 mL), T= 25 ºC. In all cases, the selectivity towards Michael adducts was > 99 %. (a) Yield and conversion were determinate by GC. (b) Determined by HPLC on the purified reaction mixture, using a chiral stationary phase (Chiralpak IC column).TFA: triflic acid, HBA: 4-heptyl-benzoic acid

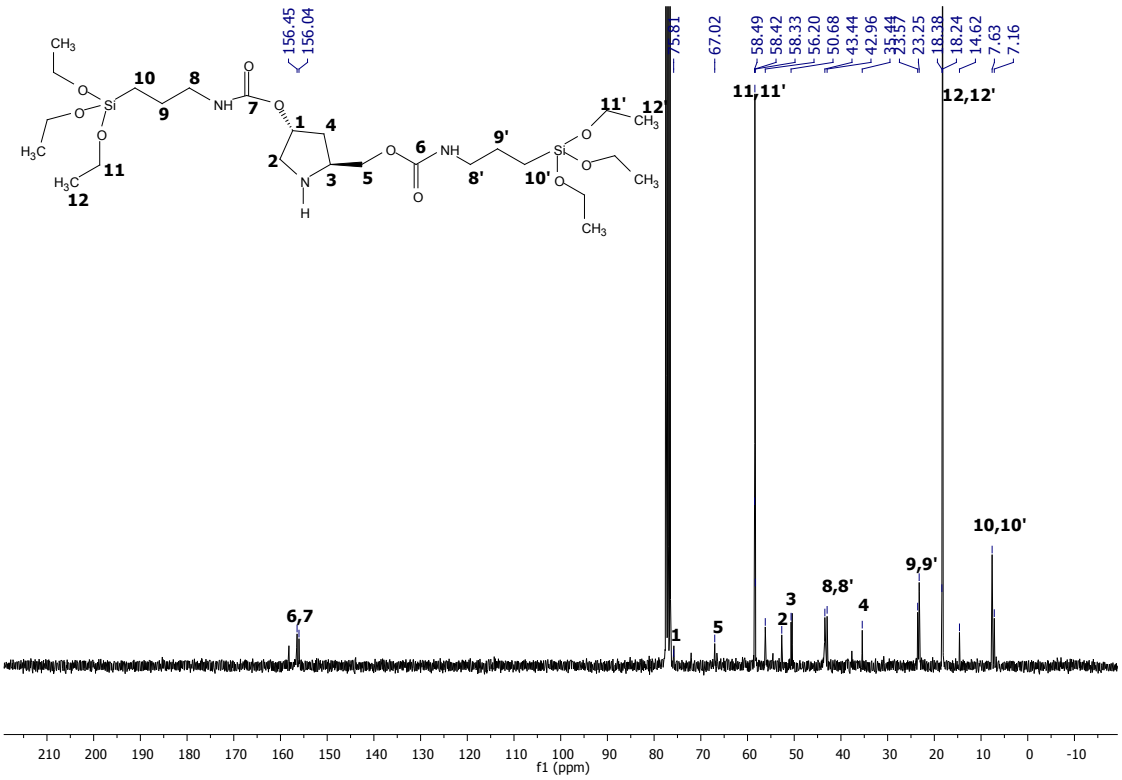


Figure S1. ^{13}C NMR spectrum of pure bis-silylated precursor, PyrSil.

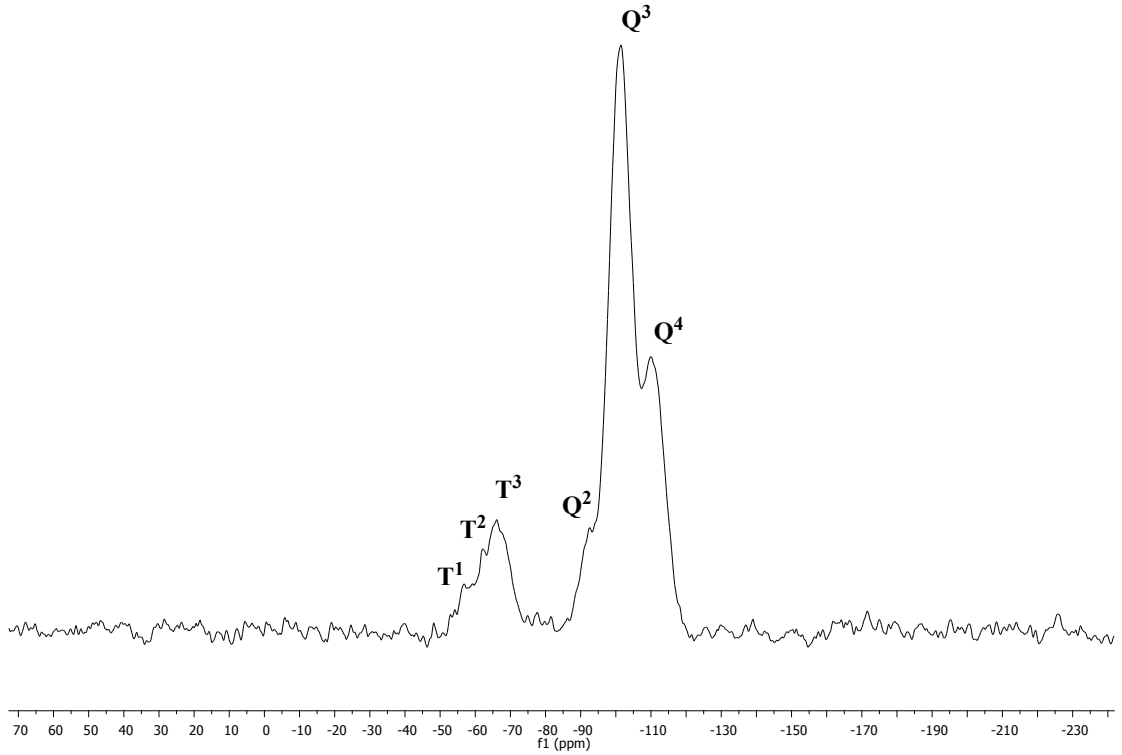


Figure S2. ^{29}Si CP/MAS NMR spectrum of HybPyr after four uses.

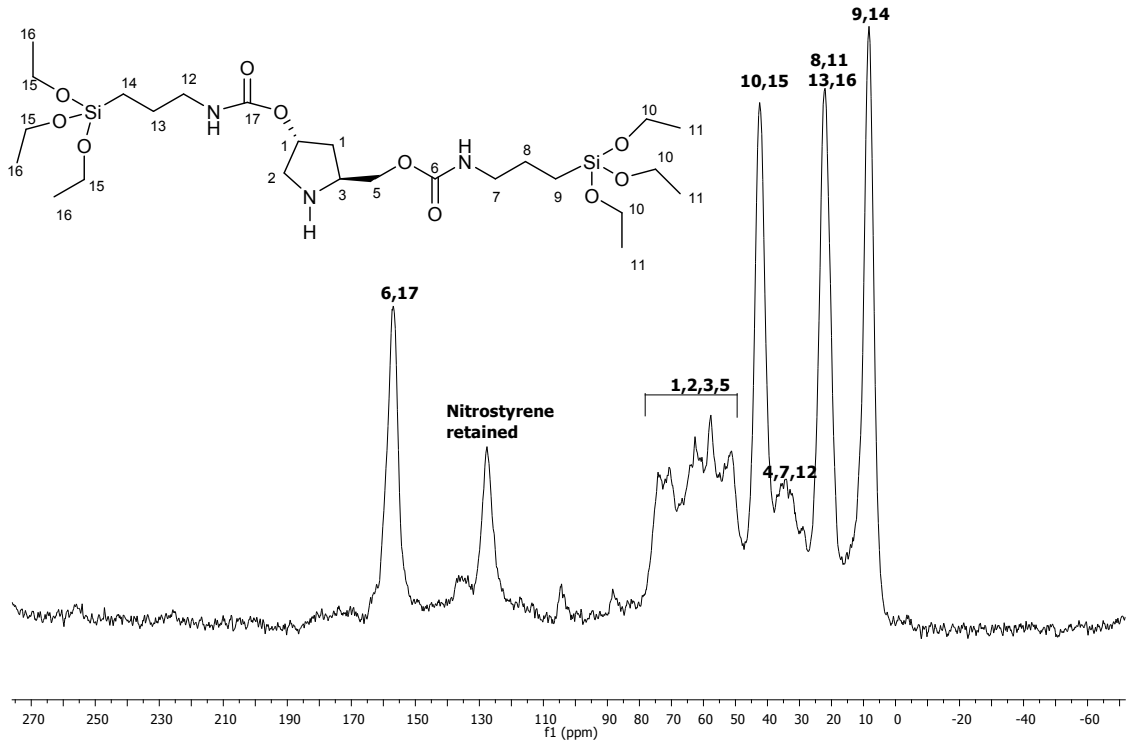
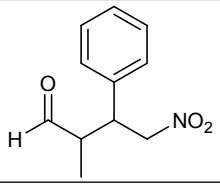
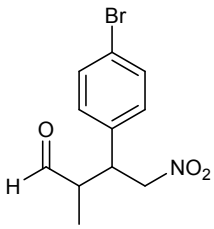
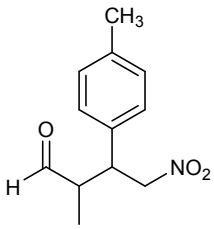
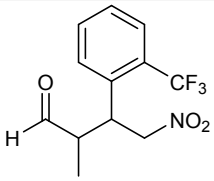
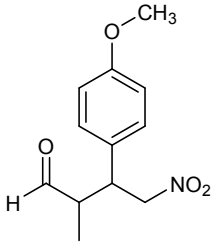
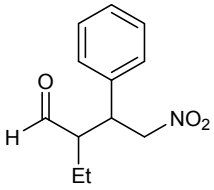


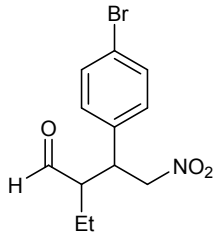
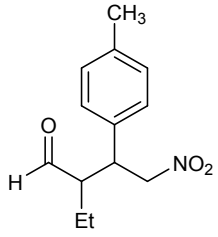
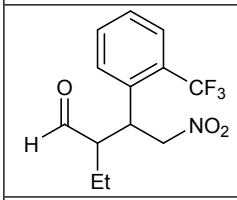
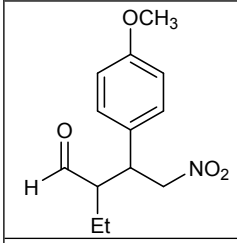
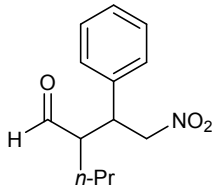
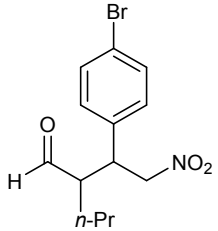
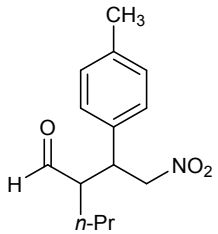
Figure S3. ^{13}C NMR spectrum of HybPyr after four uses.

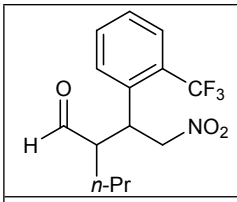
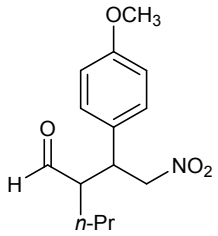
HPLC data

High performance liquid chromatography (HPLC) was performed on an Agilent Technologies chromatograph (1220 Series), using Daicel Chiralpak IC column (4.6 x 250 mm).

Table S3. HPLC data

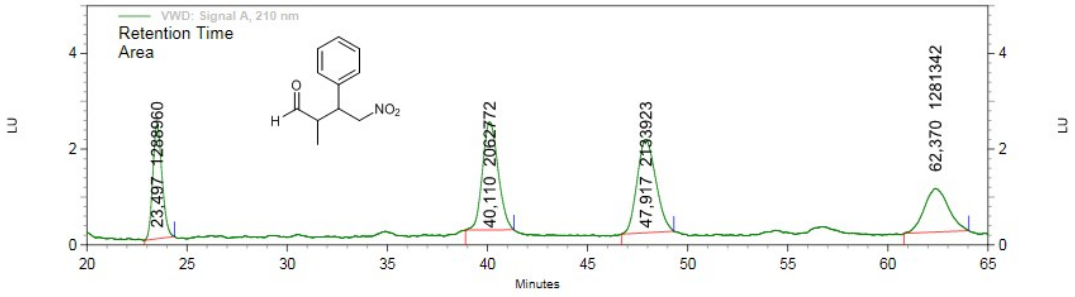
Product	n-Hexane/*i*-PrOH	Flow rate [mL/min]	λ[nm]	t_R[min]
	90:10	1.0	210	*anti*: 23.4, 62.3 *syn*: 40.1,47.9
	90:10	1.0	210	*syn*: 41.9, 45.0
	80:20	1.0	210	*anti*:20.3,47.8 *syn*: 34.4, 40.6
	90:10	1.0	210	*syn*: 20.3, 21.9
	80:20	1.0	210	*anti*:18.3,36.1 *syn*: 27.8,31.5
	90:10	1.0	210	*anti*:18.3,27.0 *syn*: 31.2,35.0

	90:10	0.6	210	*anti*: 31.9, 47.9 *syn*: 55.1, 57.2
	90:10	1.0	210	*anti*: 16.8,23.9 *syn*: 28.8,32.5
	90:10	1.0	210	*syn*: 17.6, 18.7
	80:20	1.0	210	*anti*: 18.3, 24.4 *syn*: 29.1, 31.3
	90:10	1.0	210	*anti*: 16.3, 24.6 *syn*: 26.2, 29.7
	90:10	1.0	210	*anti*: 17.0, 25.6 *syn*: 27.4, 29.5
	80:20	1.0	210	*anti*: 10.7, 15.1 *syn*: 16.5, 18.9

	95:5	0.8	254	*syn*: 24.2,27,4
	80:20	1.0	210	*anti*: 15.4, 20.1 *syn*: 22.4,25.0

Racemic and chiral HPLC chromatograms for Michael adducts

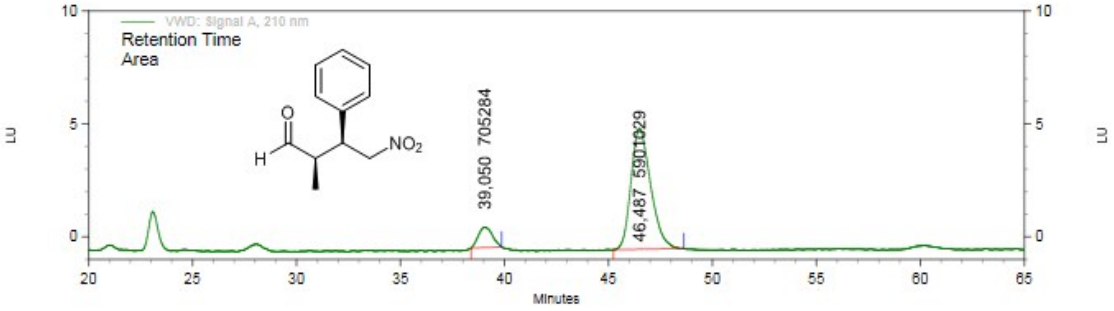
(2R, 3R)-2-methyl-4-nitro-3-phenylbutanal (6a)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	39974	23,497	1288960	**19,048**
2	37887	40,110	2062772	**30,483**
3	32793	47,917	2133923	**31,534**
4	15261	62,370	1281342	**18,935**

Totals	125915		6766997	**100,000**

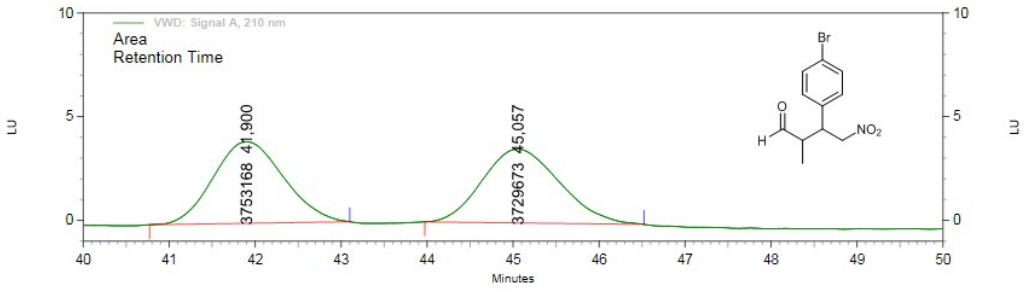


VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	15109	39,050	705284	**10,676**
2	89904	46,487	5901029	**89,324**

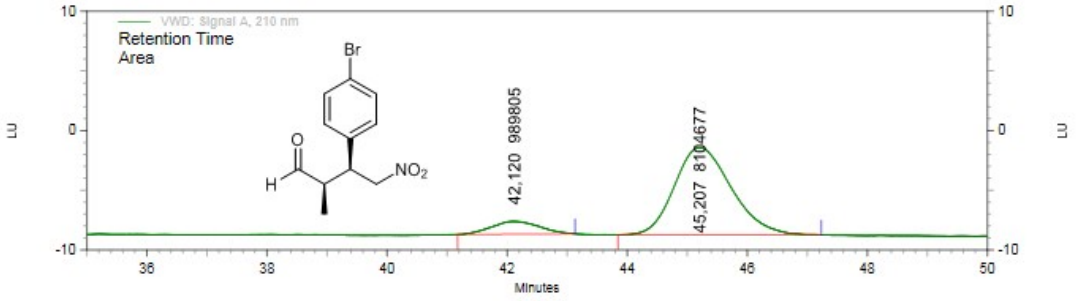
Totals	105013		6606313	**100,000**

(2R, 3R)-3-(4-bromophenyl)-2-methyl-4-nitrobutanal (6b)



VWD: Signal A, 210 nm Results

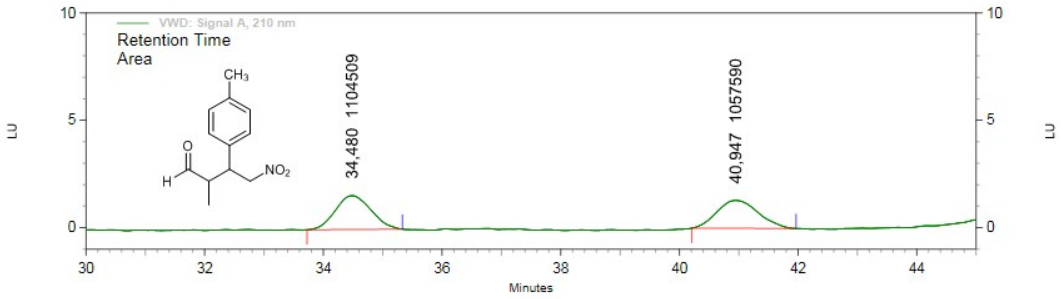
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	65983	41,900	3753168	**50,157**
2	59769	45,057	3729673	**49,843**
Totals	125752		7482841	**100,000**



VWD: Signal A, 210 nm Results

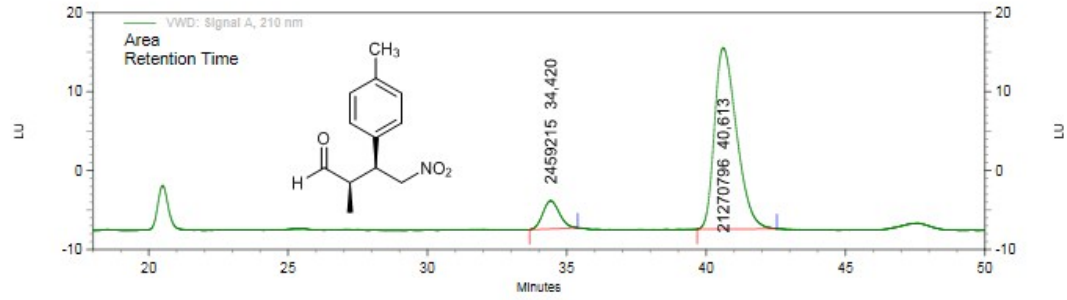
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	17897	42,120	989805	**10,884**
2	122729	45,207	8104677	**89,116**
Totals	140626		9094482	**100,000**

(2R, 3R)-2-methyl-4-nitro-3-(p-tolyl)butanal (6c)



VWD: Signal A, 210 nm Results

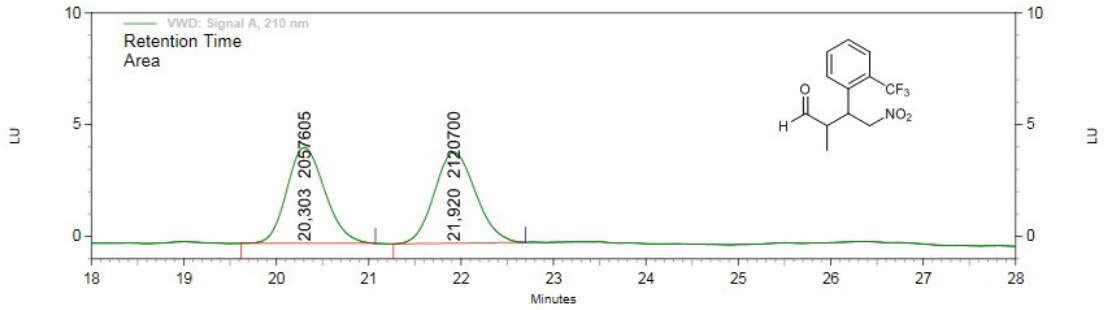
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	26473	34,480	1104509	**51,085**
2	21779	40,947	1057590	**48,915**
Totals	48252		2162099	**100,000**



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	59647	34,420	2459215	**10,363**
2	385448	40,613	21270796	**89,637**
Totals	445095		23730011	**100,000**

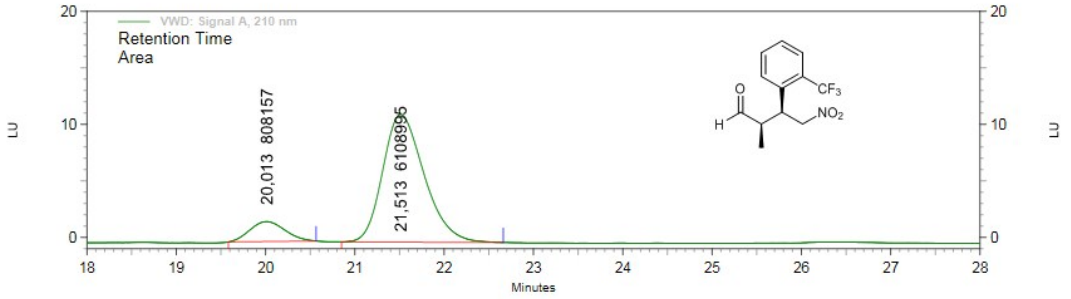
(2R, 3S)-2-methyl-4-nitro-3-(2-(trifluoromethyl)phenyl)butanal (6d)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	71903	20,303	2057605	**49,245**
2	68204	21,920	2120700	**50,755**

Totals	140107		4178305	**100,000**

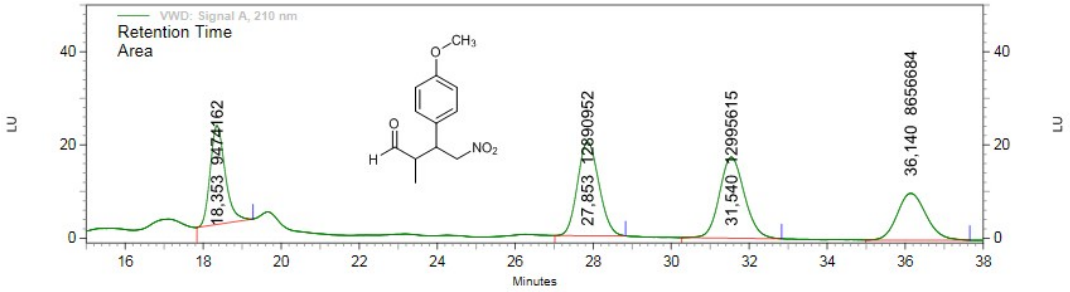


VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	29545	20,013	808157	**11,683**
2	189526	21,513	6108995	**88,317**

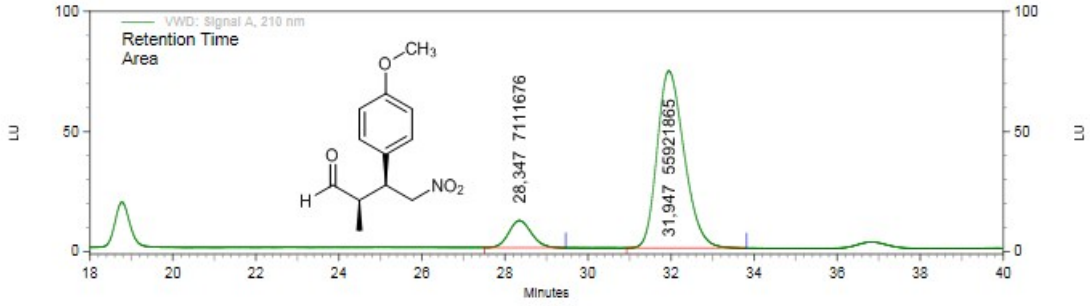
Totals	219071		6917152	**100,000**

(2R, 3R)-3-(4-methoxyphenyl)-2-methyl-4-nitrobutanal (6e)



VWD: Signal A, 210 nm Results

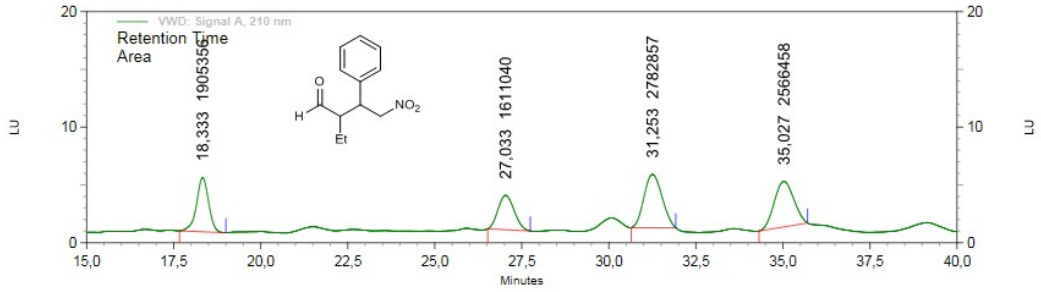
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	355506	18,353	9474162	**21,524**
2	337219	27,853	12890952	**29,286**
3	291811	31,540	12995615	**29,524**
4	168084	36,140	8656684	**19,666**
Totals	1152620		44017413	**100,000**



VWD: Signal A, 210 nm Results

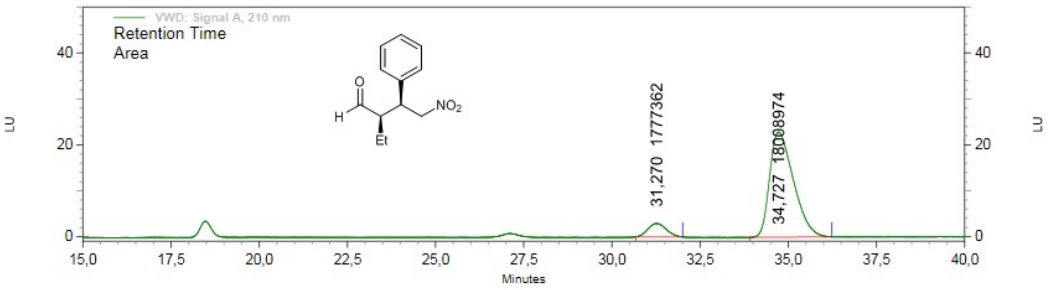
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	188560	28,347	7111676	**11,282**
2	1236103	31,947	55921865	**88,718**
Totals	1424663		63033541	**100,000**

(2R, 3S)-2-ethyl-4-nitro-3-phenylbutanal (7a)



VWD: Signal A, 210 nm Results

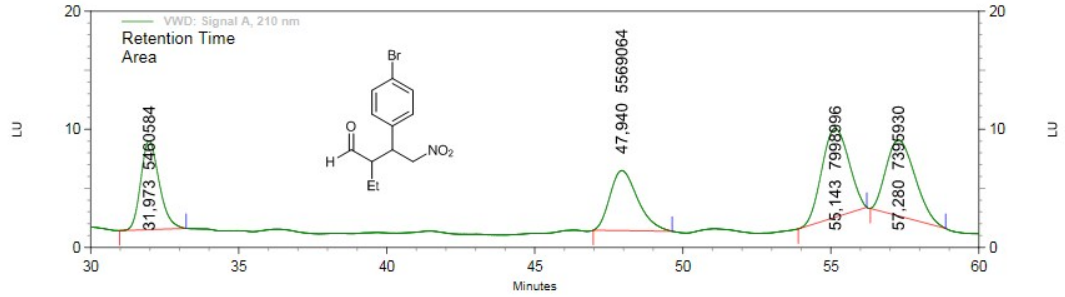
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	78781	18,333	1905356	**21,491**
2	49896	27,033	1611040	**18,172**
3	77354	31,253	2782857	**31,389**
4	65996	35,027	2566458	**28,948**
Totals	272027		8865711	**100,000**



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	49086	31,270	1777362	**8,983**
2	384239	34,727	18008974	**91,017**
Totals	433325		19786336	**100,000**

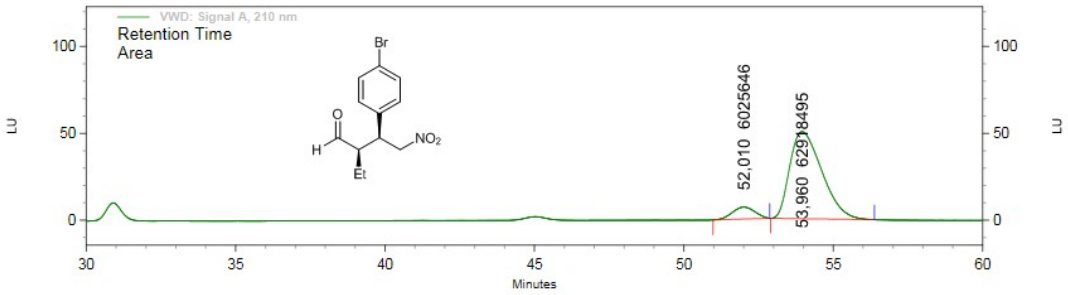
(2R, 3S)-3-(4-bromophenyl)-2-ethyl-4-nitrobutanal (7b)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	126047	31,973	5460584	**20,665**
2	85272	47,940	5569064	**21,075**
3	126327	55,143	7998996	**30,271**
4	107744	57,280	7395930	**27,989**

Totals	445390		26424574	**100,000**

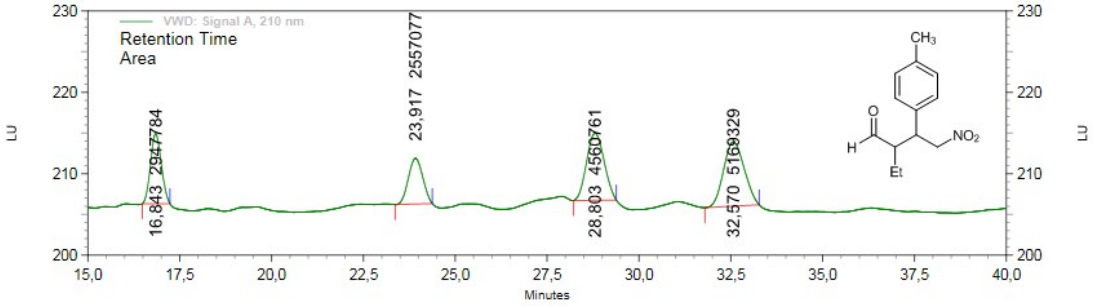


VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	115128	52,010	6025646	**8,740**
2	841328	53,960	62918495	**91,260**

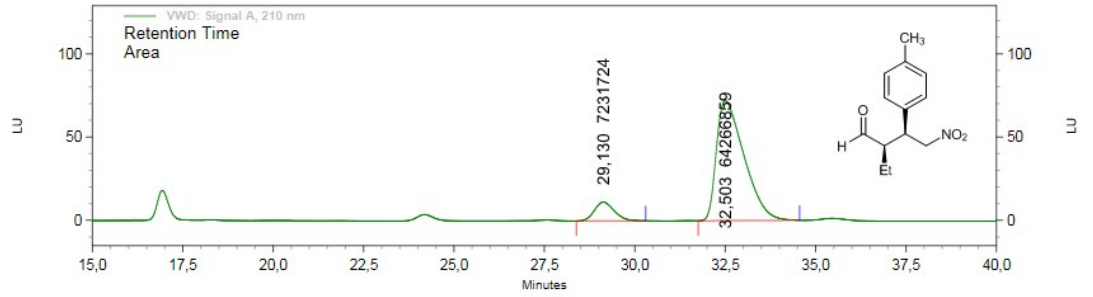
Totals	956456		68944141	**100,000**

(2R, 3S)-2-ethyl-4-nitro-3-(p-tolyl)butanal (7c)



VWD: Signal A, 210 nm Results

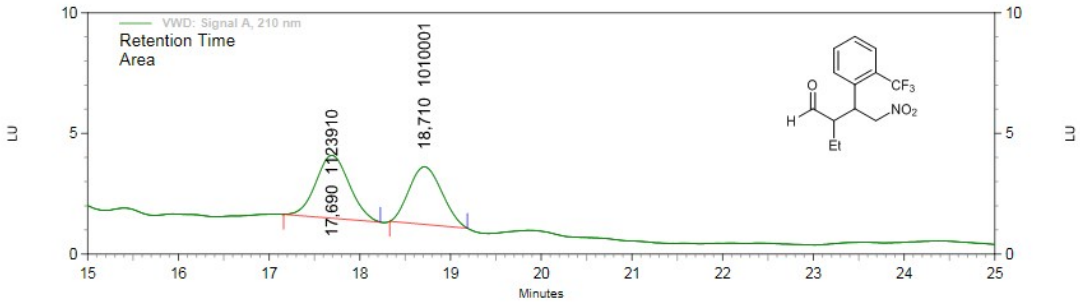
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	143794	16,843	2947784	**19,349**
2	94207	23,917	2557077	**16,784**
3	138174	28,803	4560761	**29,936**
4	132499	32,570	5169329	**33,931**
Totals	508674		15234951	**100,000**



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	188981	29,130	7231724	**10,115**
2	1208818	32,503	64266859	**89,885**
Totals	1397799		71498583	**100,000**

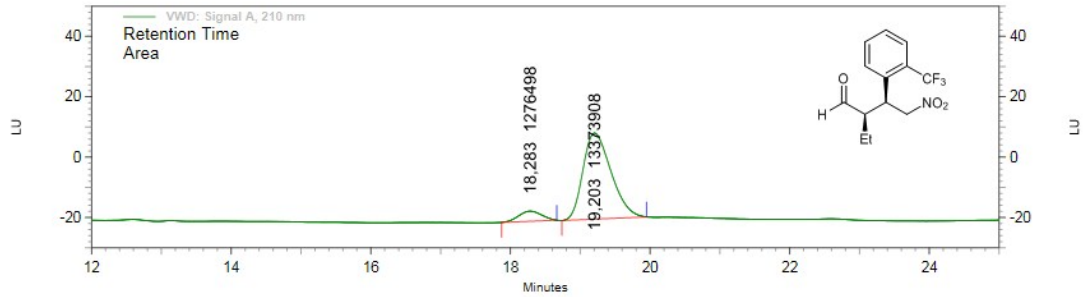
(2R, 3S)-2-ethyl-4-nitro-3-(2-(trifluoromethyl)phenyl)butanal (7d)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	43734	17,690	1123910	**52,669**
2	40080	18,710	1010001	**47,331**

Totals	83814		2133911	**100,000**

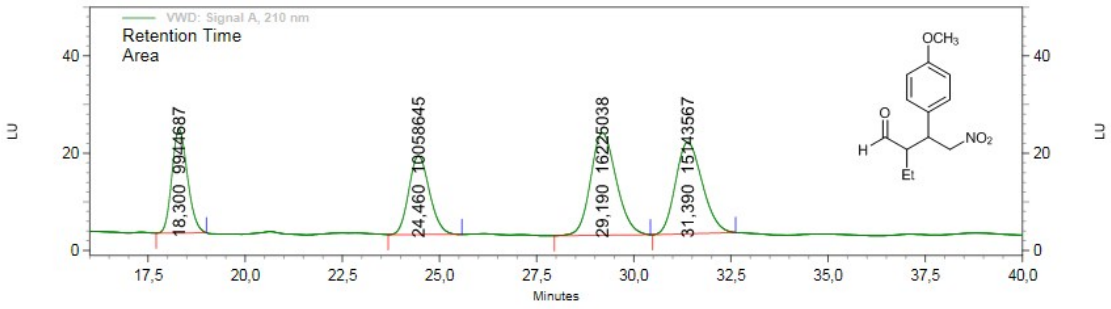


VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	56120	18,283	1276498	**8,713**
2	478306	19,203	13373908	**91,287**

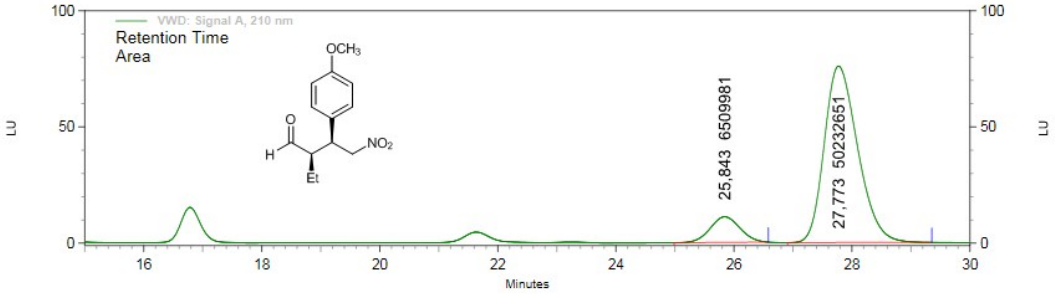
Totals	534426		14650406	**100,000**

(2R, 3S)-2-ethyl-3-(4-methoxyphenyl)-4-nitrobutanal (7e)



VWD: Signal A, 210 nm Results

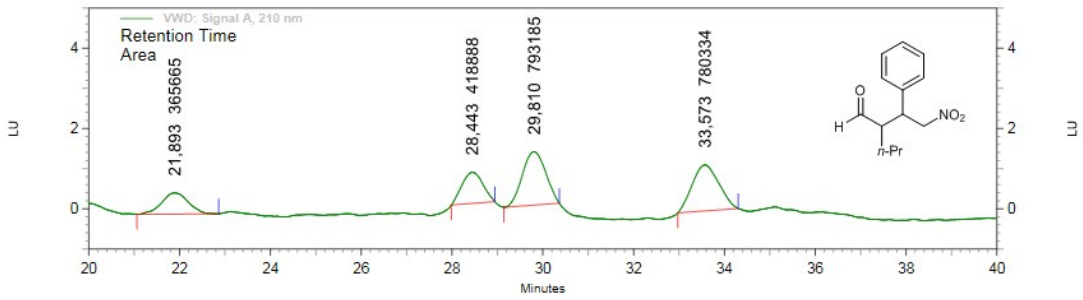
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	357907	18,300	9944687	**19,358**
2	271045	24,460	10058645	**19,580**
3	353738	29,190	16225038	**31,583**
4	315357	31,390	15143567	**29,478**
Totals	1298047		51371937	**100,000**



VWD: Signal A, 210 nm Results

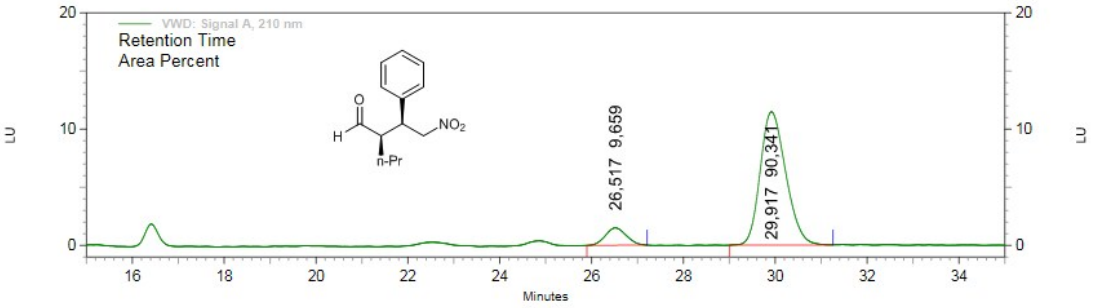
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	185203	25,843	6509981	**11,473**
2	1273766	27,773	50232651	**88,527**
Totals	1458969		56742632	**100,000**

(R)-2-((S)-2-nitro-1-phenylethyl)pentanal (8a)



VWD: Signal A, 210 nm Results

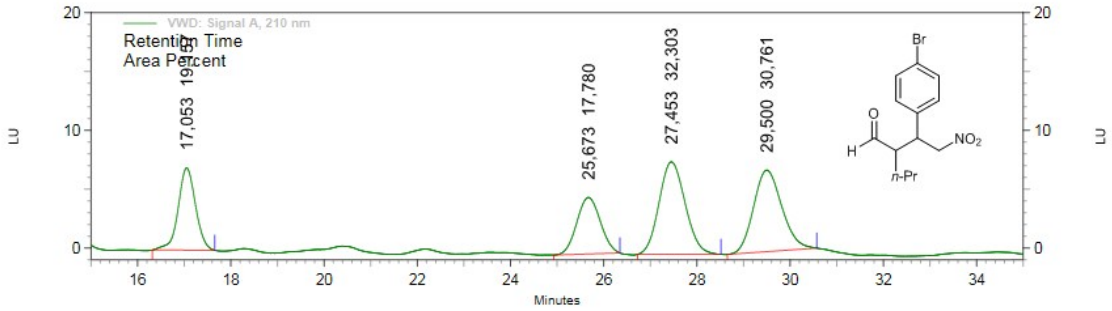
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	8845	21,893	365665	**15,507**
2	13007	28,443	418888	**17,764**
3	22213	29,810	793185	**33,637**
4	19205	33,573	780334	**33,092**
Totals	63270		2358072	**100,000**



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	25090	26,517	794616	**9,659**
2	192335	29,917	7432411	**90,341**
Totals	217425		8227027	**100,000**

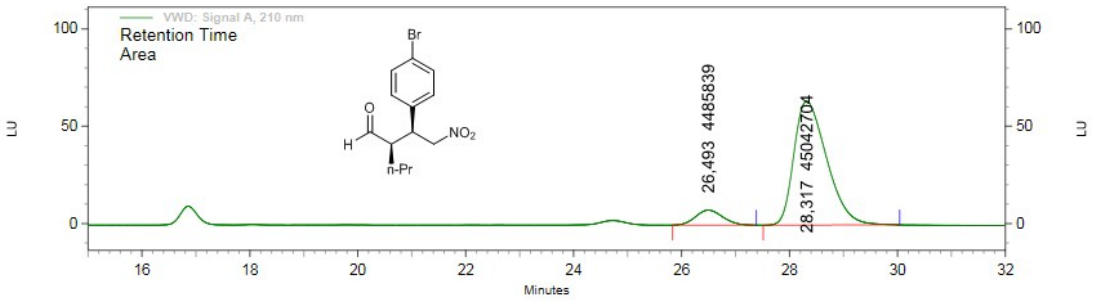
(R)-2-((S)-1-(4-bromophenyl)-2-nitroethyl)pentanal (8b)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
2	117176	17,053	3043669	**19,157**
3	80453	25,673	2824952	**17,780**
4	131788	27,453	5132322	**32,303**
5	116134	29,500	4887346	**30,761**

Totals	445551		15888289	**100,000**

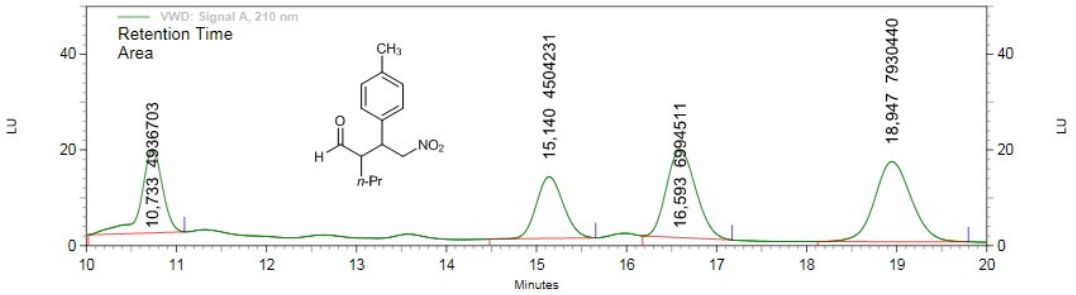


VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	128662	26,493	4485839	**9,057**
2	1066470	28,317	45042704	**90,943**

Totals	1195132		49528543	**100,000**

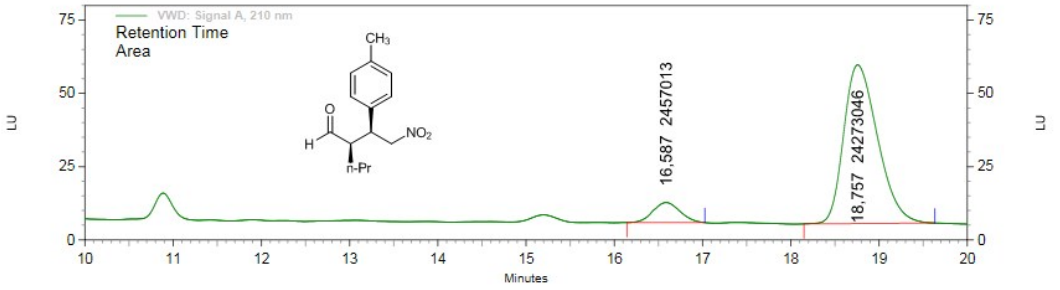
(R)-2-((S)-2-nitro-1-(p-tolyl)ethyl)pentanal (8c)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	294047	10,733	4936703	**20,261**
2	216065	15,140	4504231	**18,486**
3	308165	16,593	6994511	**28,706**
4	281073	18,947	7930440	**32,547**

Totals	1099350		24365885	**100,000**

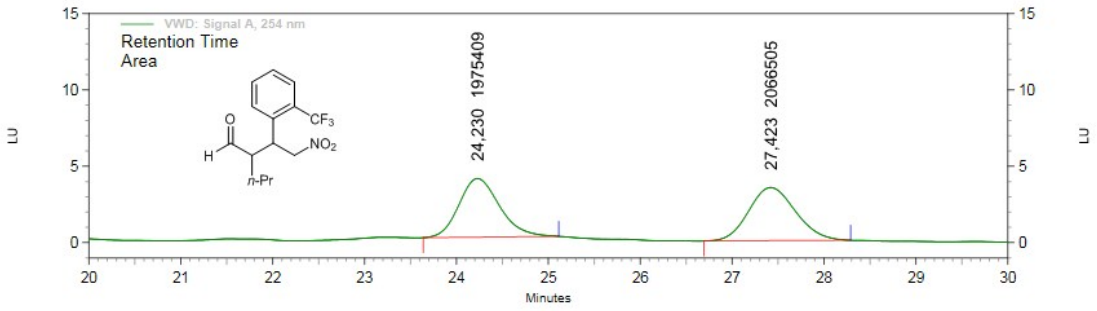


VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	114756	16,587	2457013	**9,192**
2	908223	18,757	24273046	**90,808**

Totals	1022979		26730059	**100,000**

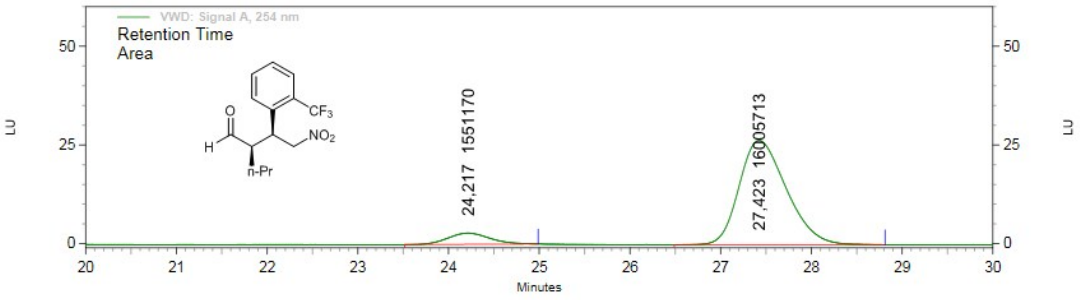
(R)-2-((S)-2-nitro-1-(2-(trifluoromethyl)phenyl)ethyl)pentanal (8d)



VWD: Signal A, 254 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	64364	24,230	1975409	**48,873**
2	58341	27,423	2066505	**51,127**

Totals	122705		4041914	**100,000**

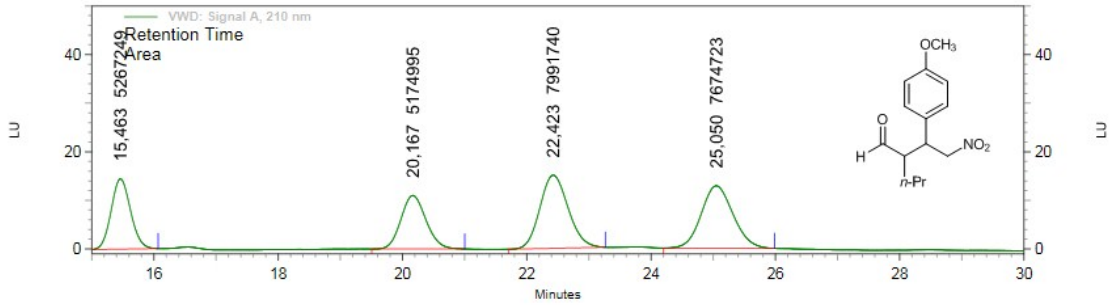


VWD: Signal A, 254 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	47732	24,217	1551170	**8,835**
2	442817	27,423	16005713	**91,165**

Totals	490549		17556883	**100,000**

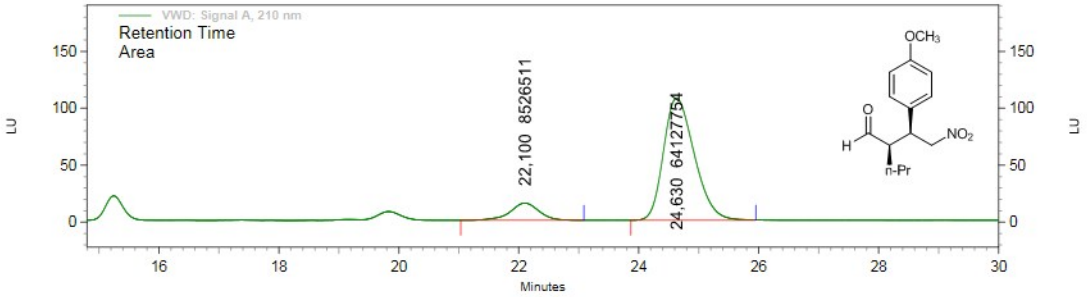
(R)-2-((S)-1-(4-methoxyphenyl)-2-nitroethyl)pentanal (8e)



VWD: Signal A, 210 nm Results

Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	242478	15,463	5267249	**20,174**
2	184660	20,167	5174995	**19,821**
3	252548	22,423	7991740	**30,609**
4	215562	25,050	7674723	**29,395**

Totals	895248		26108707	**100,000**

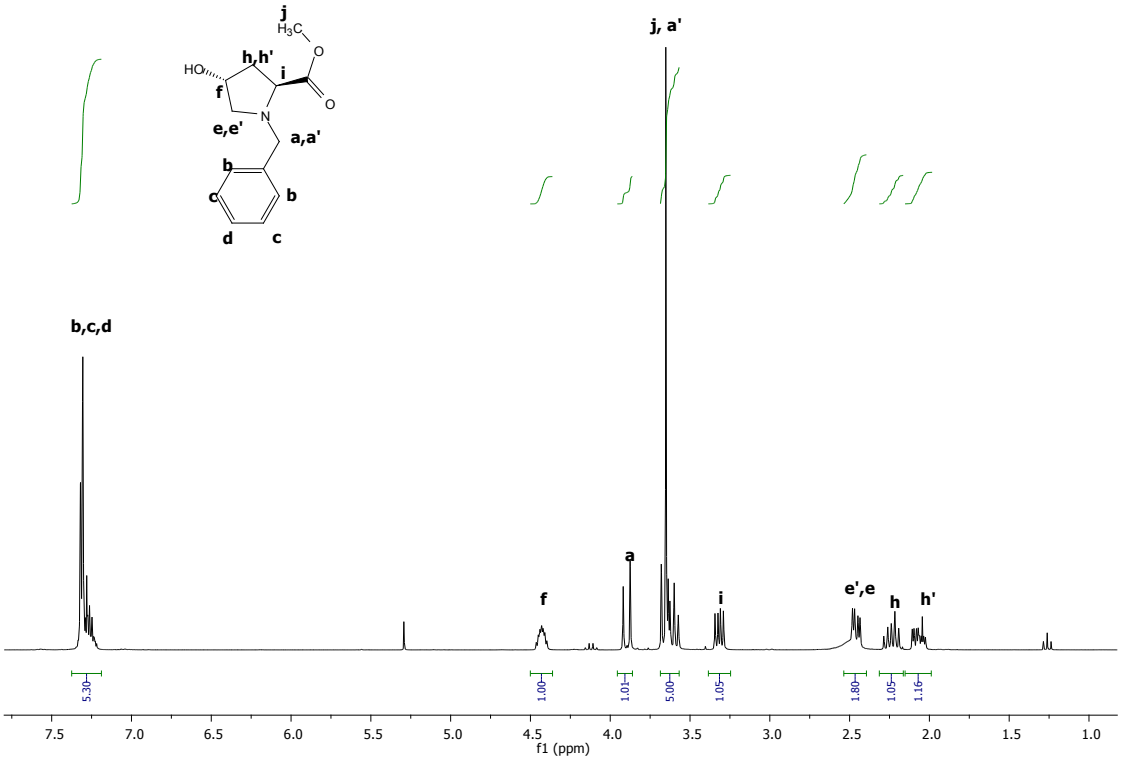


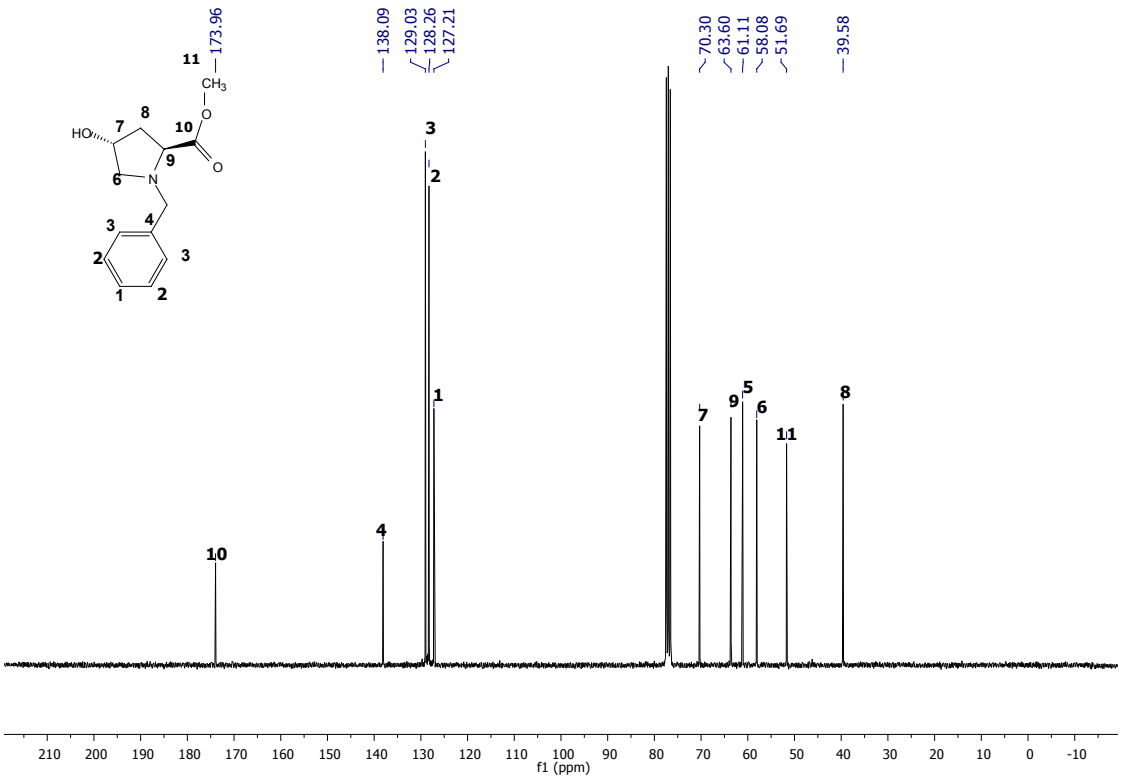
VWD: Signal A, 210 nm Results

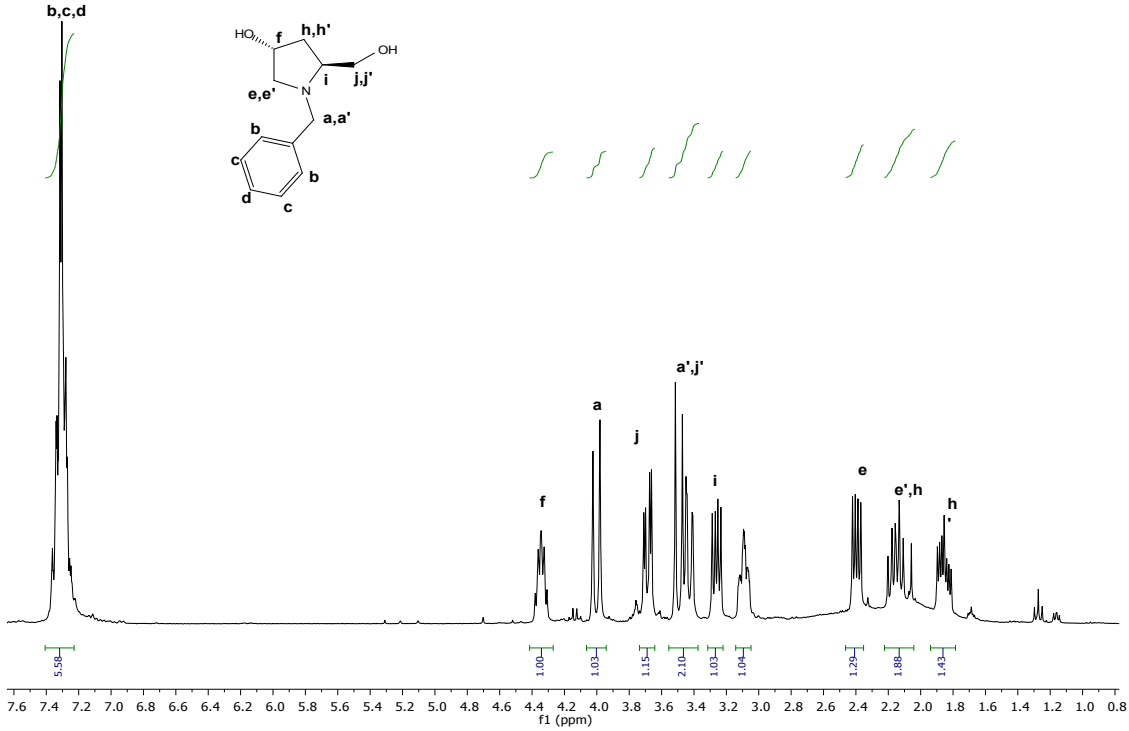
Pk #	*Height*	*Retention Time*	*Area*	*Area Percent*
1	253952	22,100	8526511	**11,736**
2	1797649	24,630	64127754	**88,264**

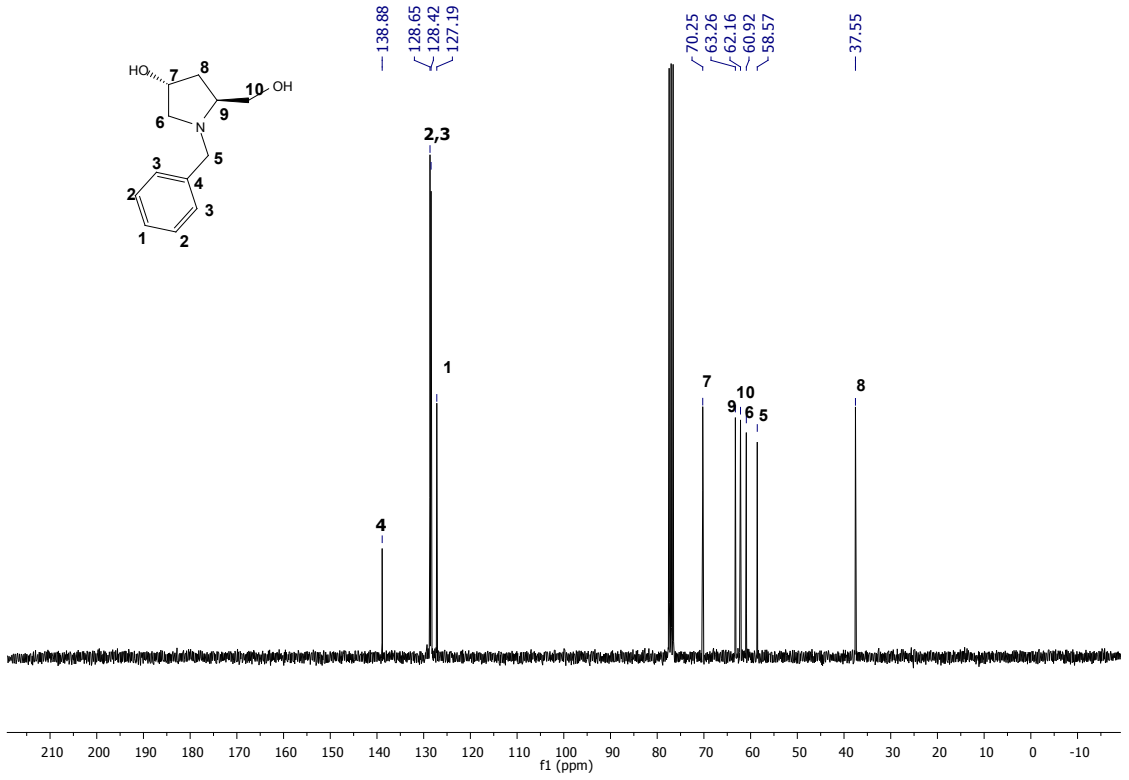
Totals	2051601		72654265	**100,000**

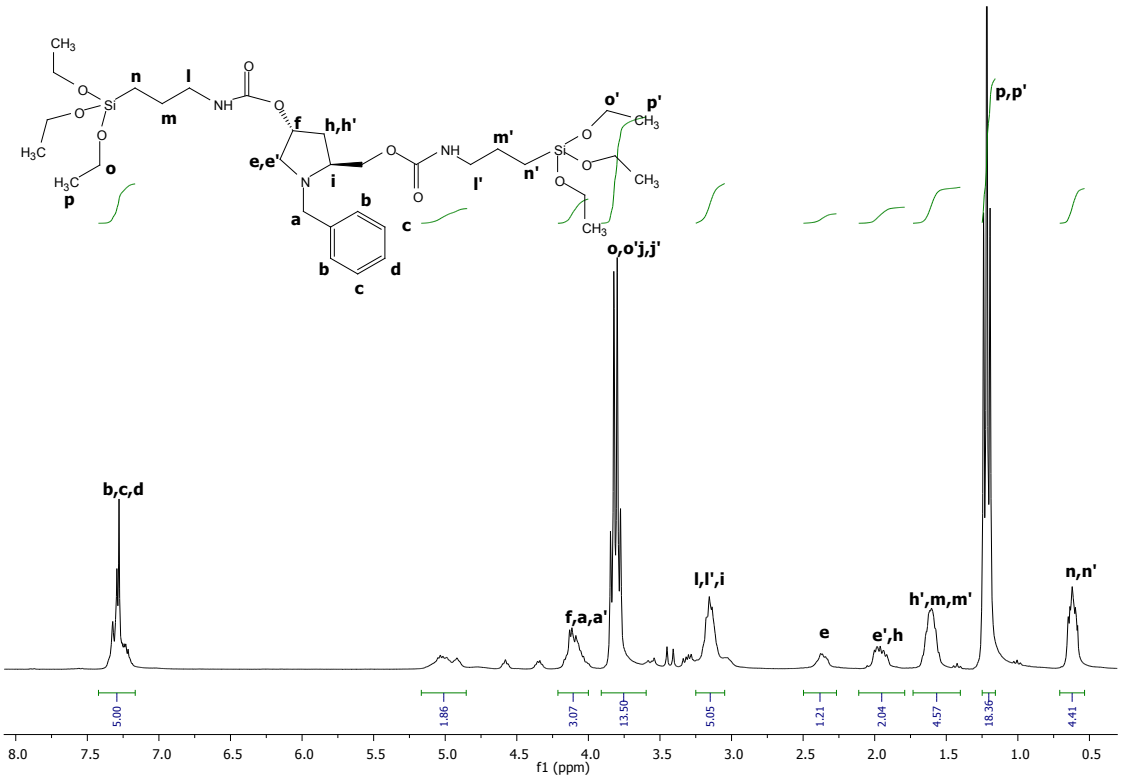
NMR spectra of intermediates for the preparation of HybPyr catalyst

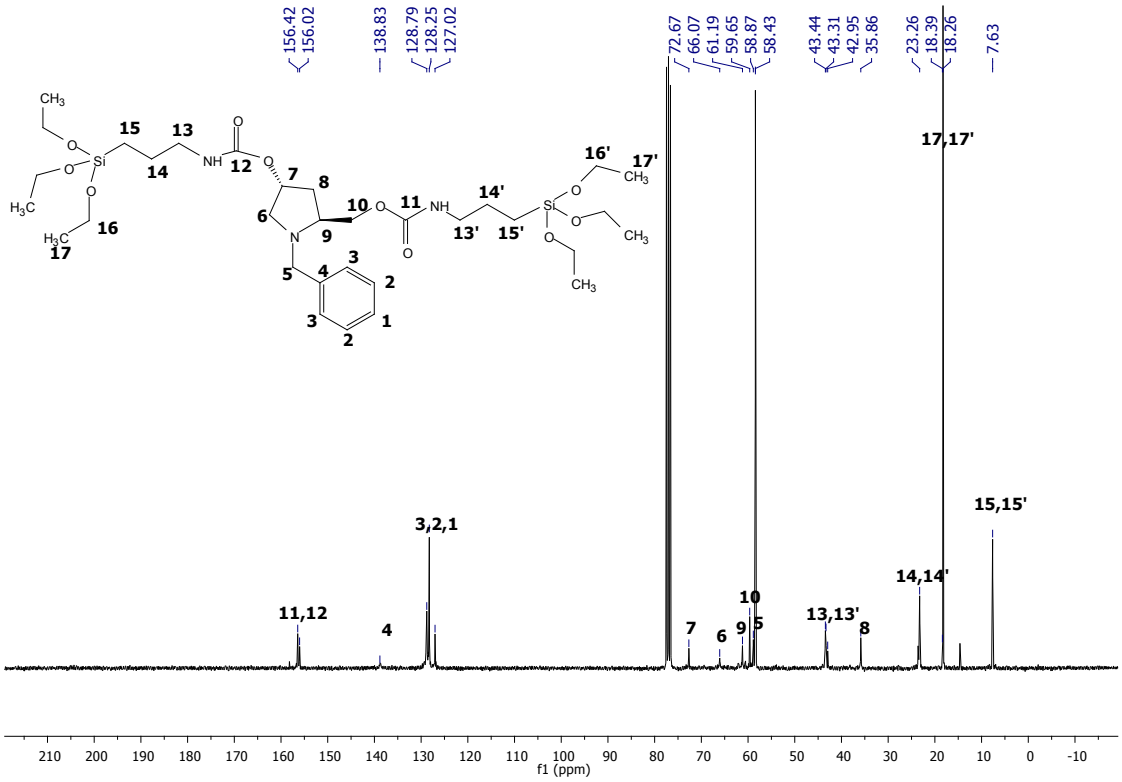


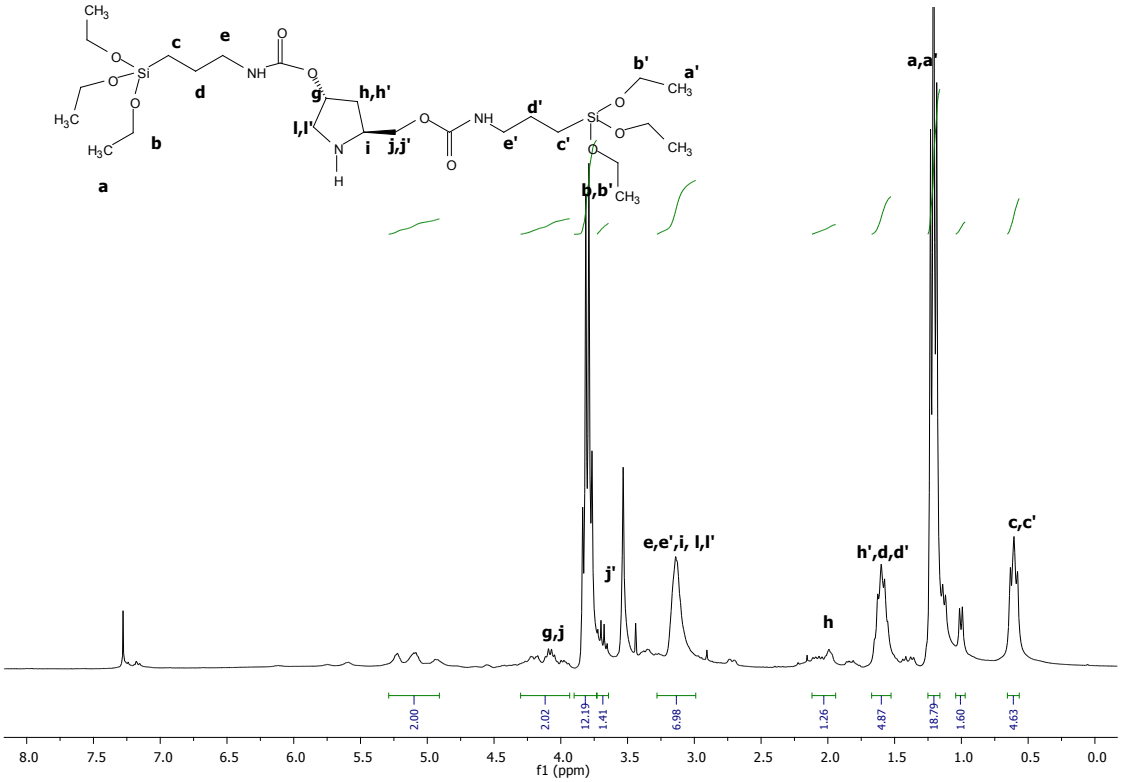


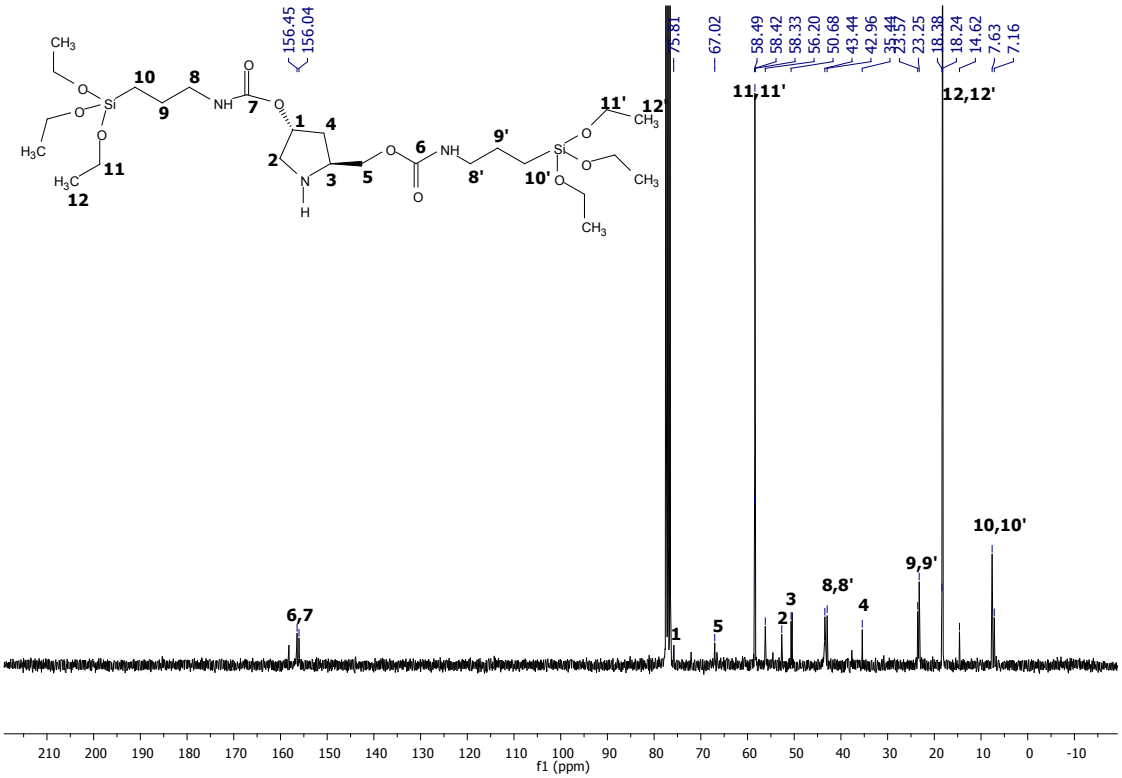

b,c,d
HO
f
h,h'
OH
i
j,j'
e,e'
N
a,a'
b
c
b
d
c
a',j'
a
j
i
f
e
e',h
h'
5.58
1.00
1.03
1.15
2.10
1.03
1.04
1.29
1.88
1.43
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)


138.88
128.65
128.42
127.19
70.25
63.26
62.16
60.92
58.57
37.55
HO
7
8
10
OH
6
9
N
5
3
4
2
3
2
1
2,3
1
4
7
9
10
6
5
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


p,p'
o,o'j,j'
b,c,d
l,l',i
f,a,a'
n,n'
h',m,m'
e
e',h
f1 (ppm)


17,17'
15,15'
3,2,1
14,14'
11,12
13,13'
f1 (ppm)


a
b
c
d
e
g
h,h'
i
j,j'
l,l'
e'
d'
c'
b'
a'
b,b'
a,a'
g,j
j'
e,e',i, l,l'
h
h',d,d'
c,c'
2.00
2.02
12.19
1.41
6.98
1.26
4.87
18.79
1.60
4.63
f1 (ppm)


156.45
156.04
75.81
67.02
58.49
58.42
58.33
56.20
50.68
43.44
42.96
33.44
33.37
23.25
18.38
18.24
14.62
7.63
7.16
11,11'
12,12'
10,10'
9,9'
8,8'
6,7
f1 (ppm)