Electronic Supplementary Material (ESI) for Dalton Transactions

Molecular and Merrifield supported chiral diamines for enantioselective addition of ZnR_2 (R = Me, Et) to ketones

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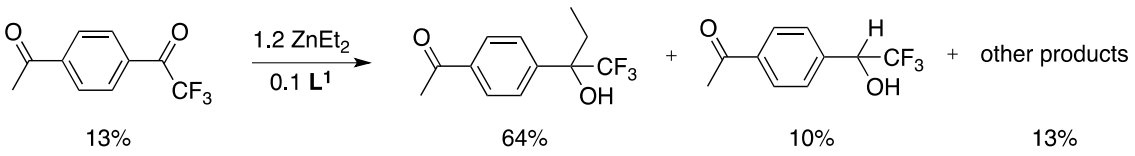
Supporting Information

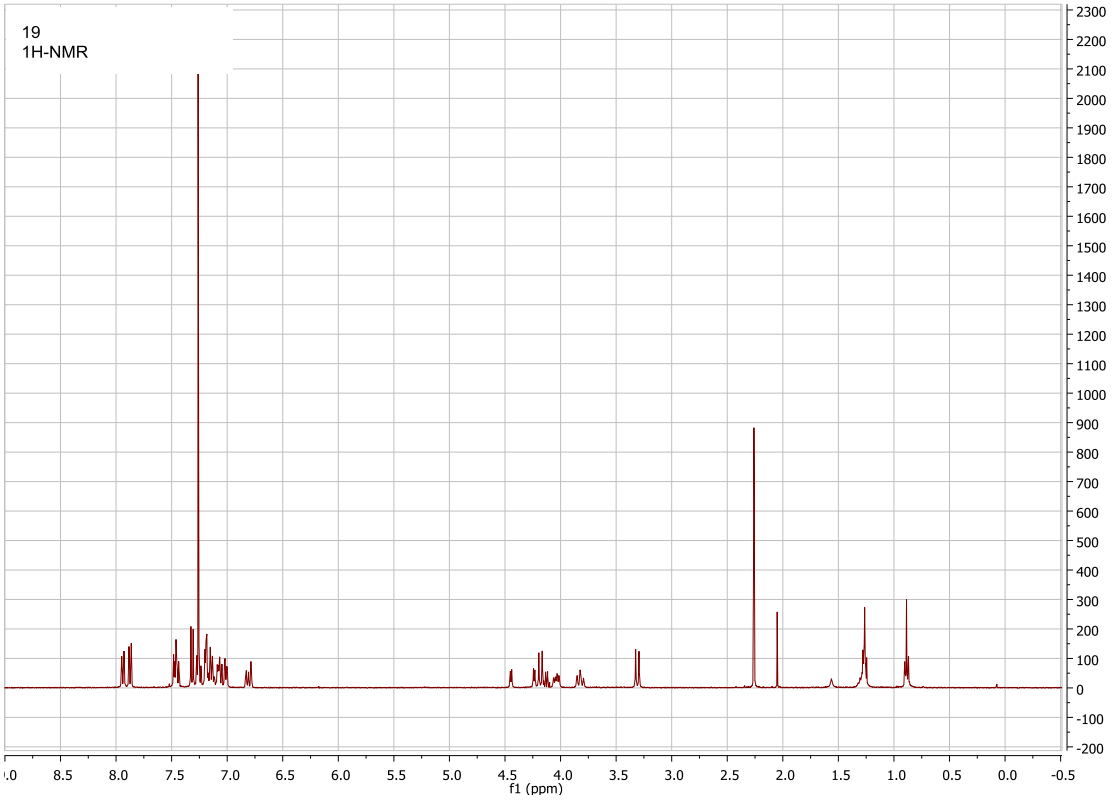
1. Chemo- and enantioselective addition to 1-(4-acetylphenyl)-2,2,2-trifluoroethanone.

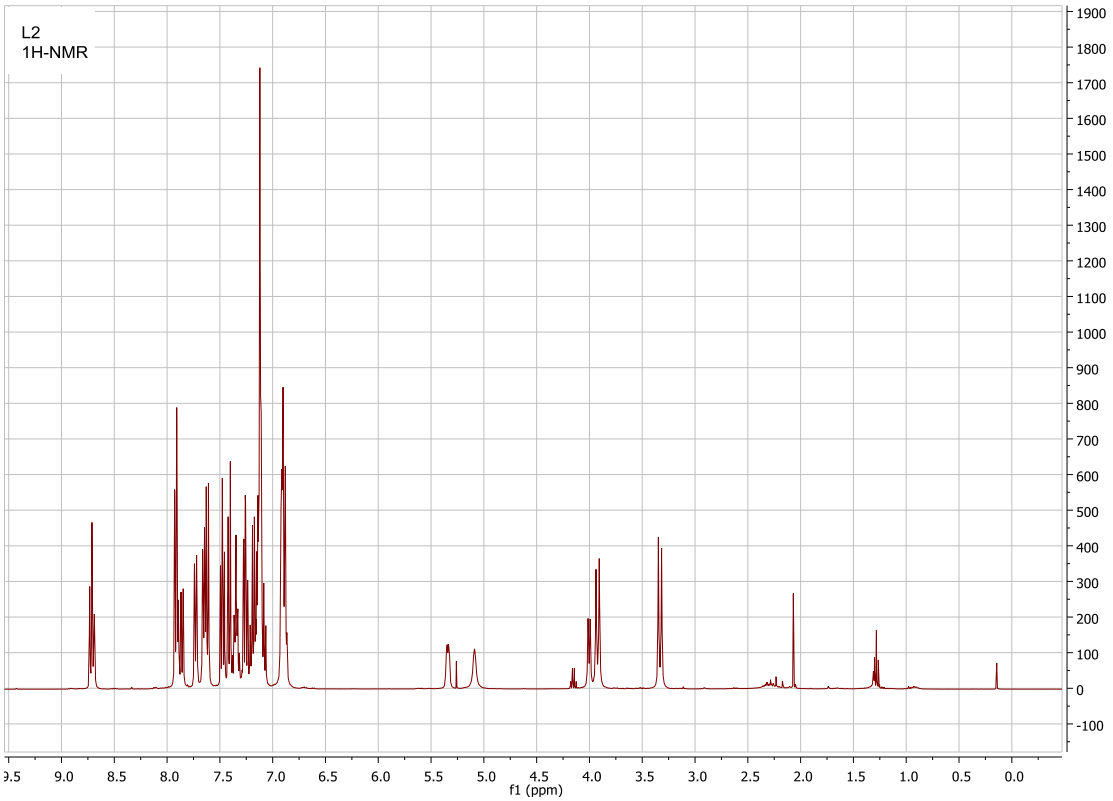


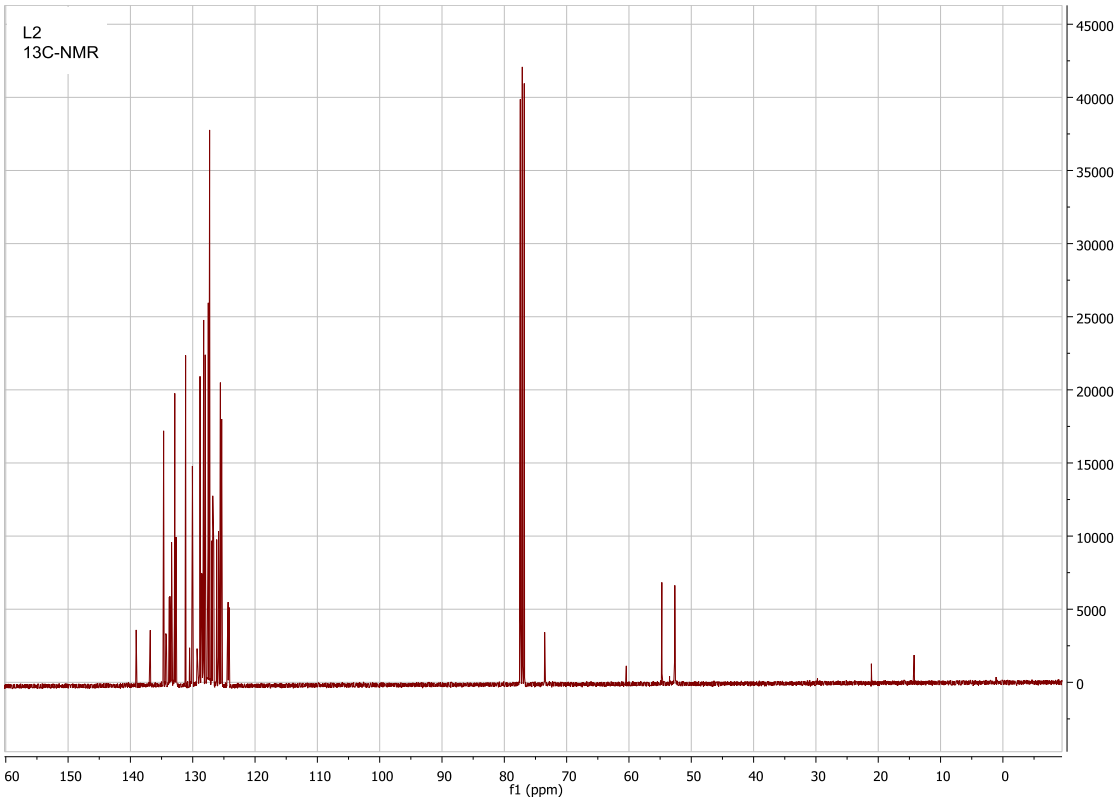
Diethylzinc (1.0 M in toluene, 0.28 mL, 0.28 mmol) was added to a solution of diamine L^1 (35 mg, 0.046 mmol, 10 mol %) in anhydrous toluene (1 mL) under argon at -20 °C. The solution was stirred for 30 minutes and *1-(4-acetylphenyl)-2,2,2-trifluoroethanone* (50 mg, 0.23 mmol) was added at -40 °C and this temperature is retained. After the reaction was complete, it was quenched with saturated ammonium chloride solution, extracted with ether, and filtered over silica gel. The solvents were removed under reduced pressure. The ee was determined by HPLC on Chiralpak IA using n-hexane/IPA 90:10 as the mobile phase, t_1 = 6.86 min, t_2 = 7.53 min. 47% ee. Chemical yields were determined by ^{19}F NMR.

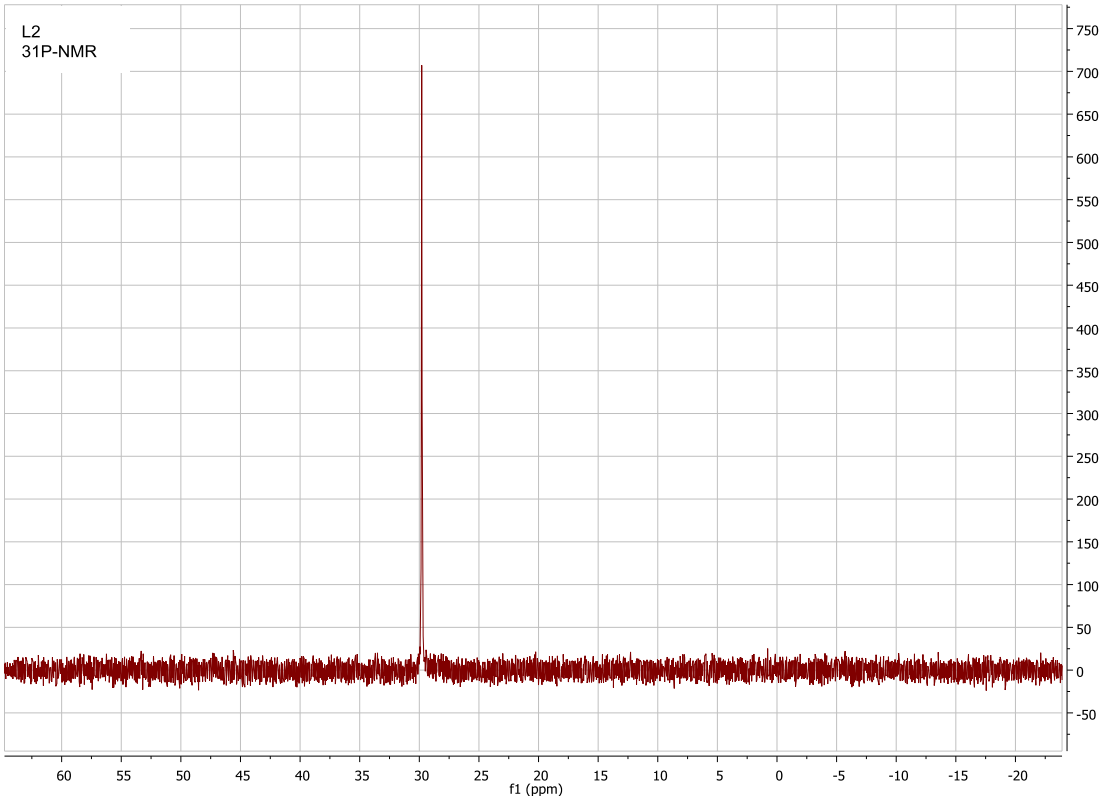
1-(4-(1,1,1-trifluoro-2-hydroxybutan-2-yl)phenyl)ethanone. ^{19}F NMR (376.50 MHz, CD_3OD) δ = -81.57. ^1H NMR (400.13 MHz, CD_3OD) δ = 0.73 (t, J = 7.2 Hz, 3H), 2.10 (m, J = 7.19 Hz, 1H), 2.25 (m, J = 7.19 Hz, 1H), 4.88 (s, 3H), 7.72 (d, J = 7.5 Hz, 2H), 8.02 (d, J = 7.5 Hz, 2H). MS: Calculated mass: 246.09; Measured mass: 246.08.

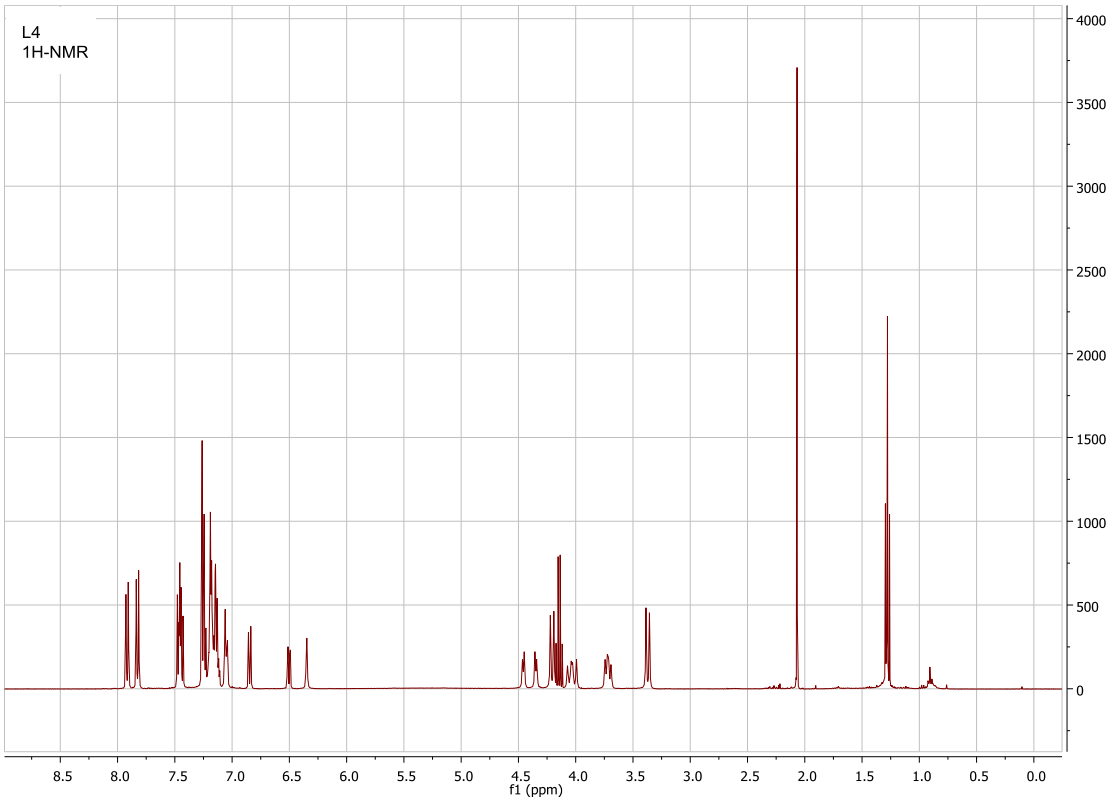
2. NMR spectra:

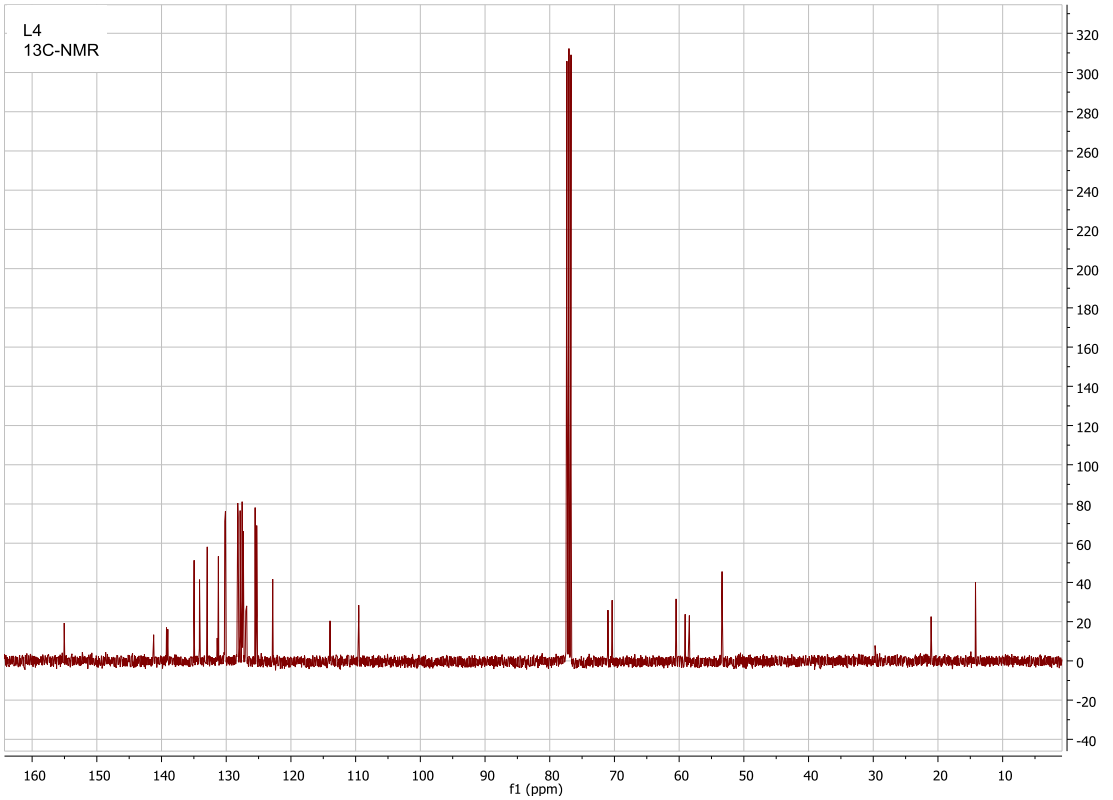


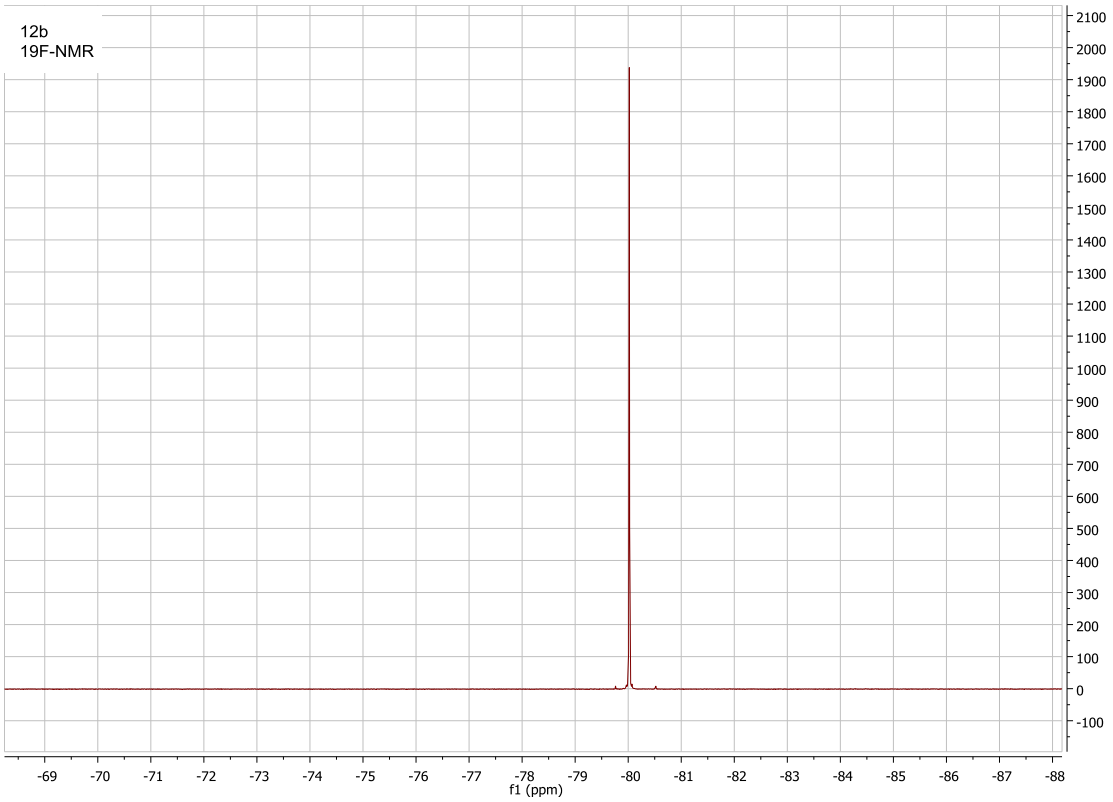


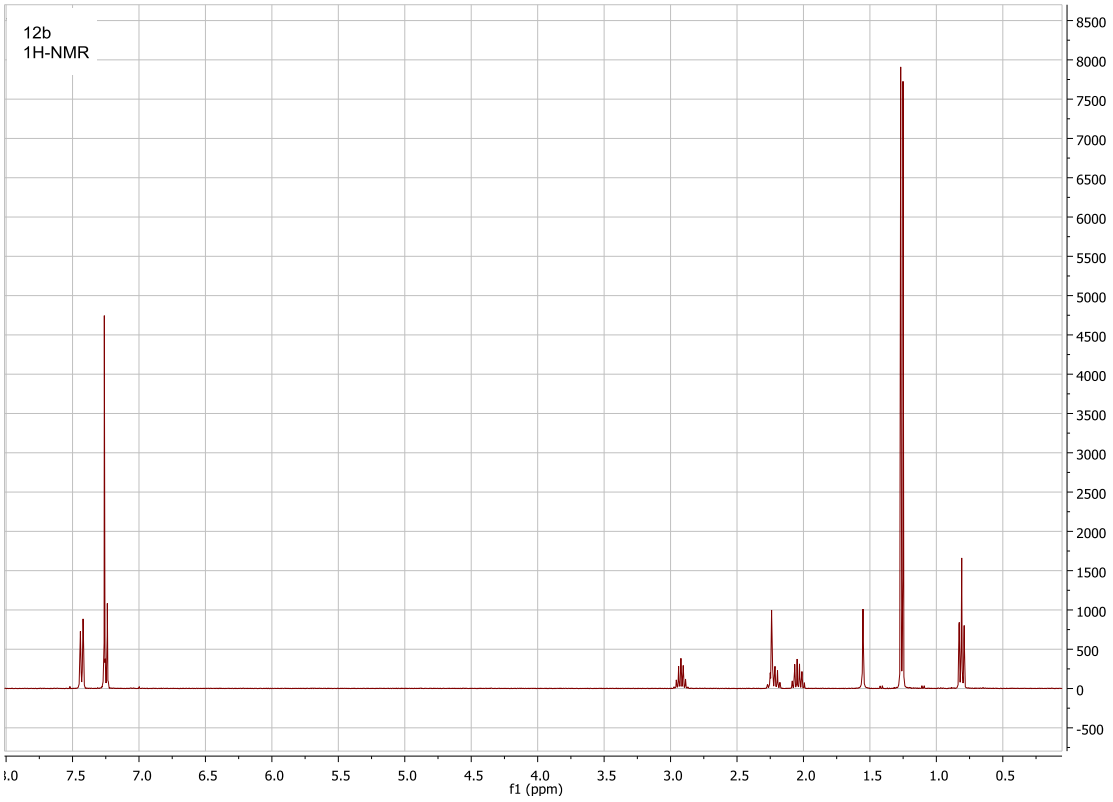


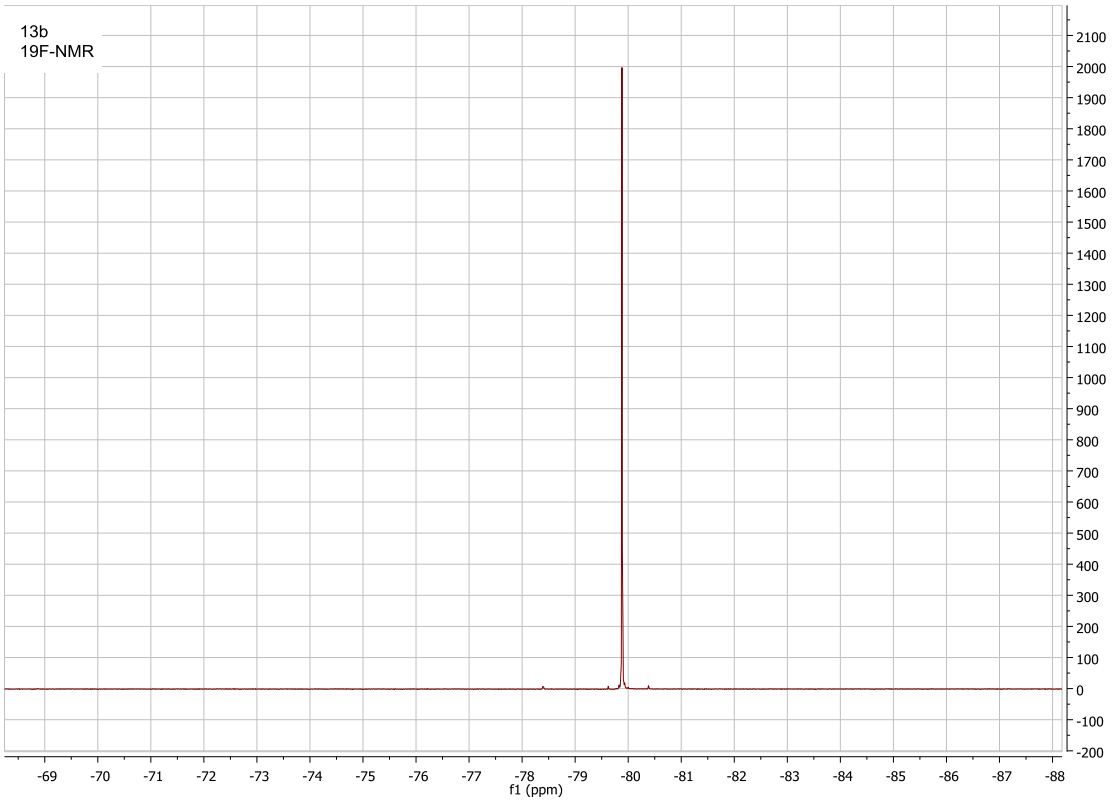


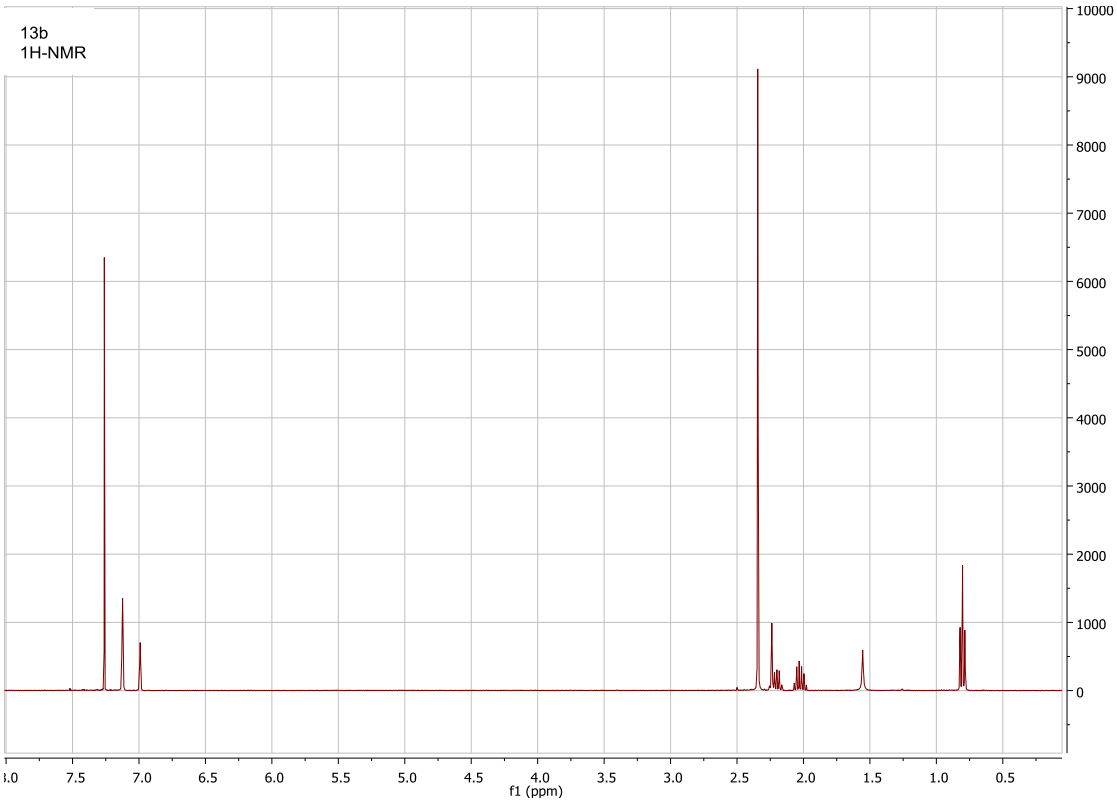


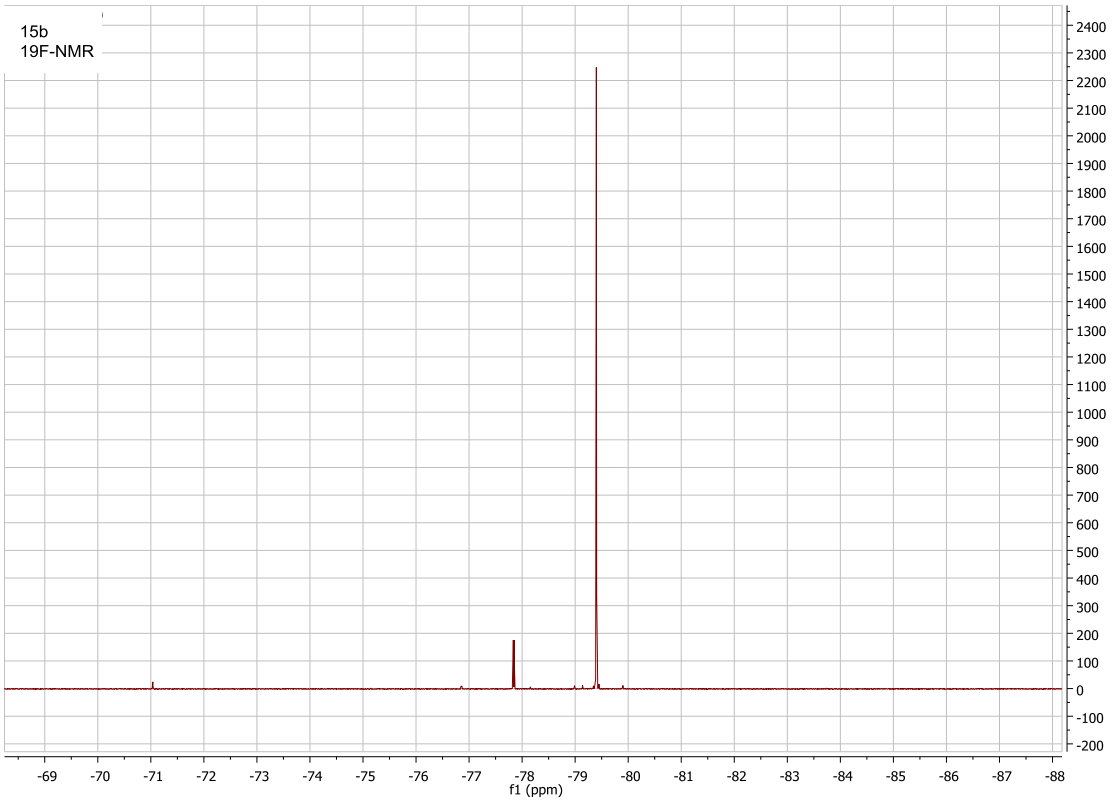


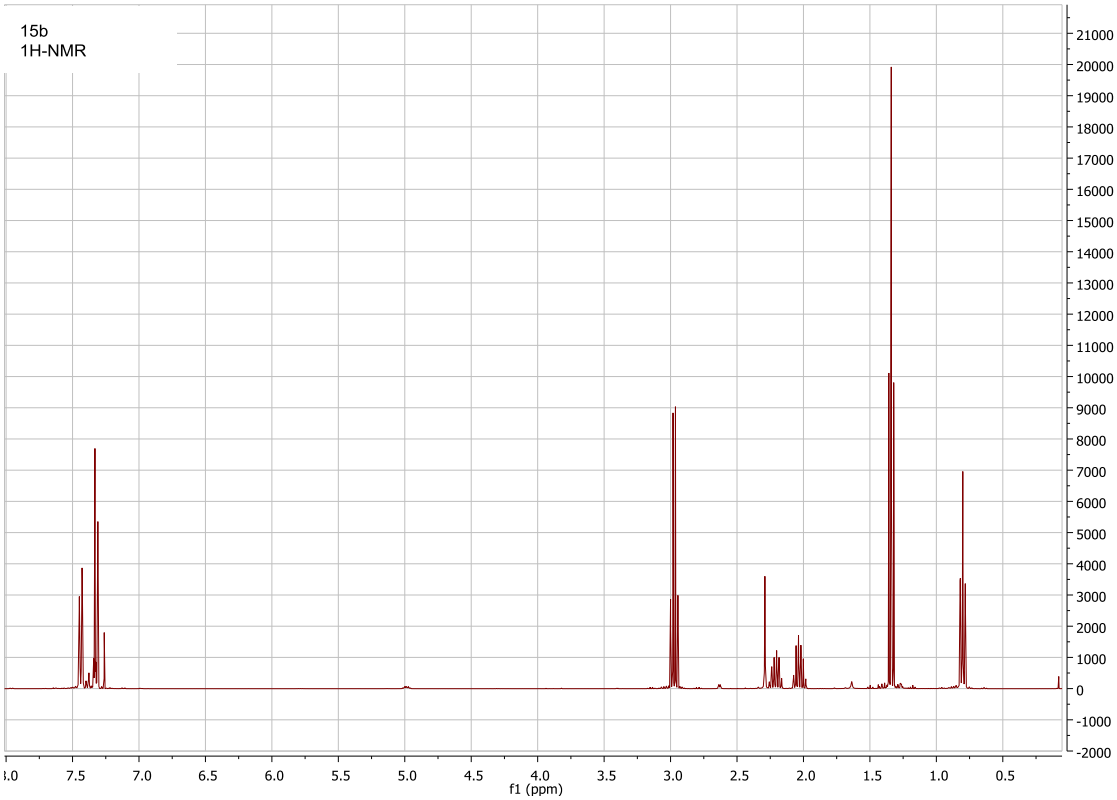


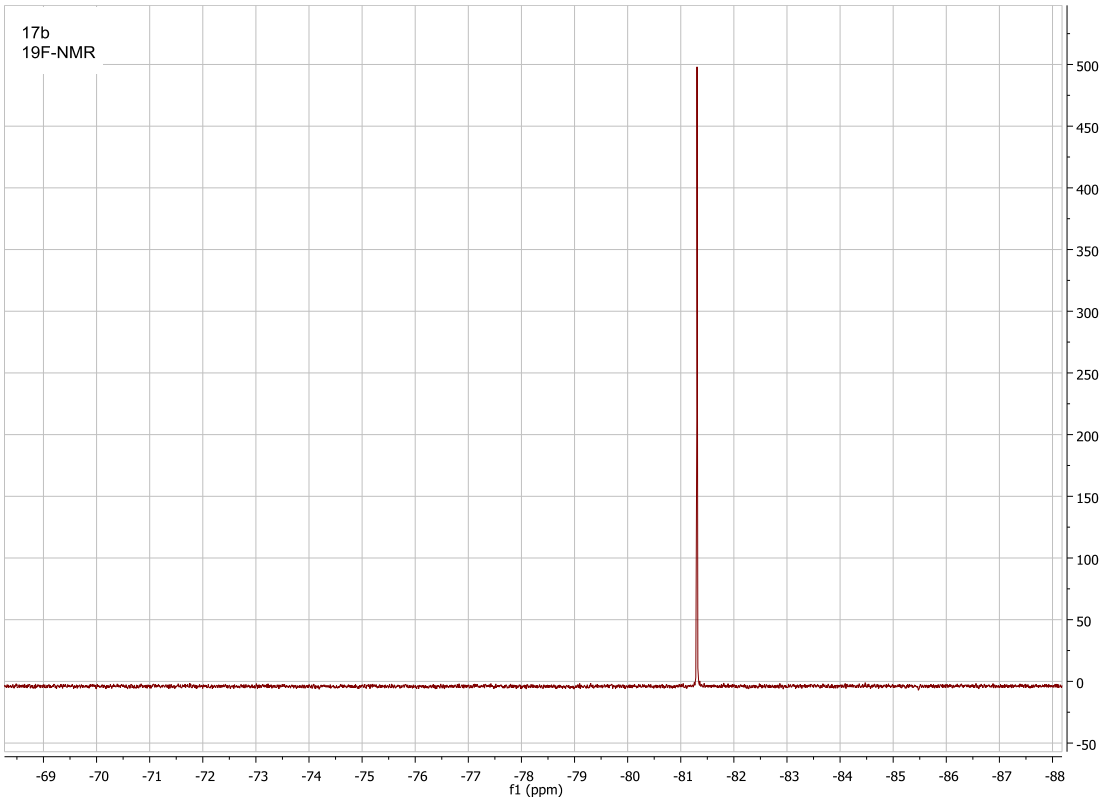


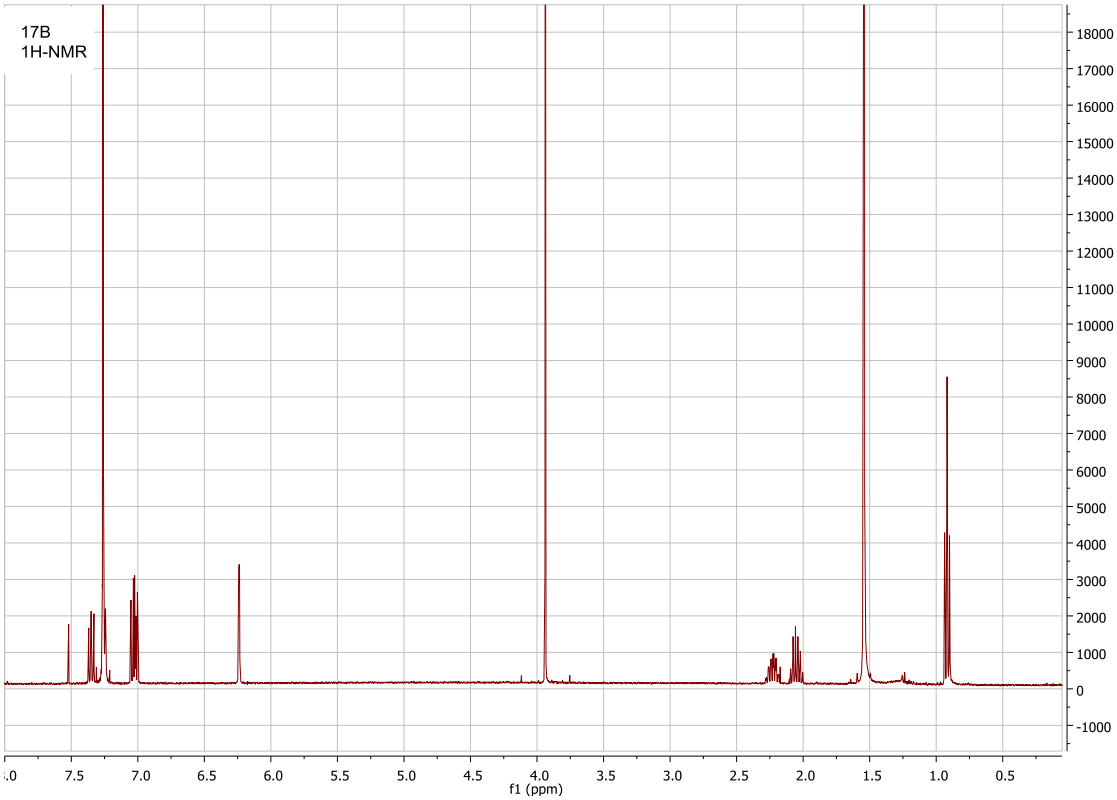


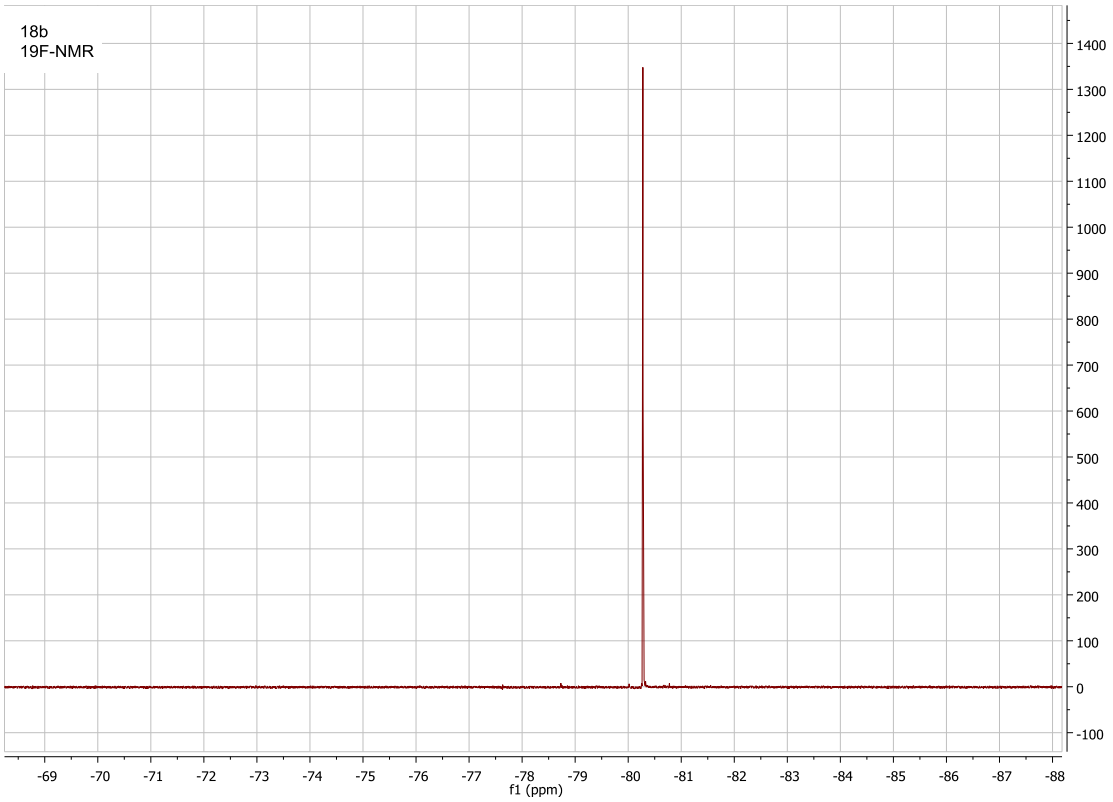


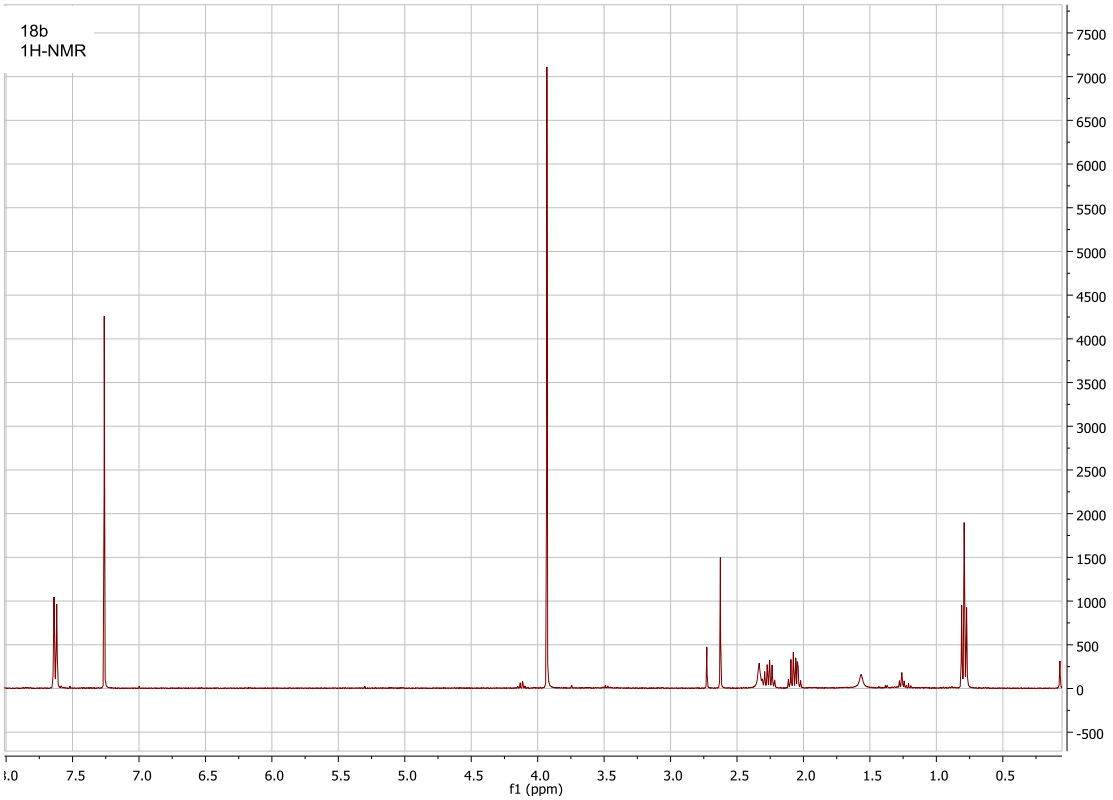


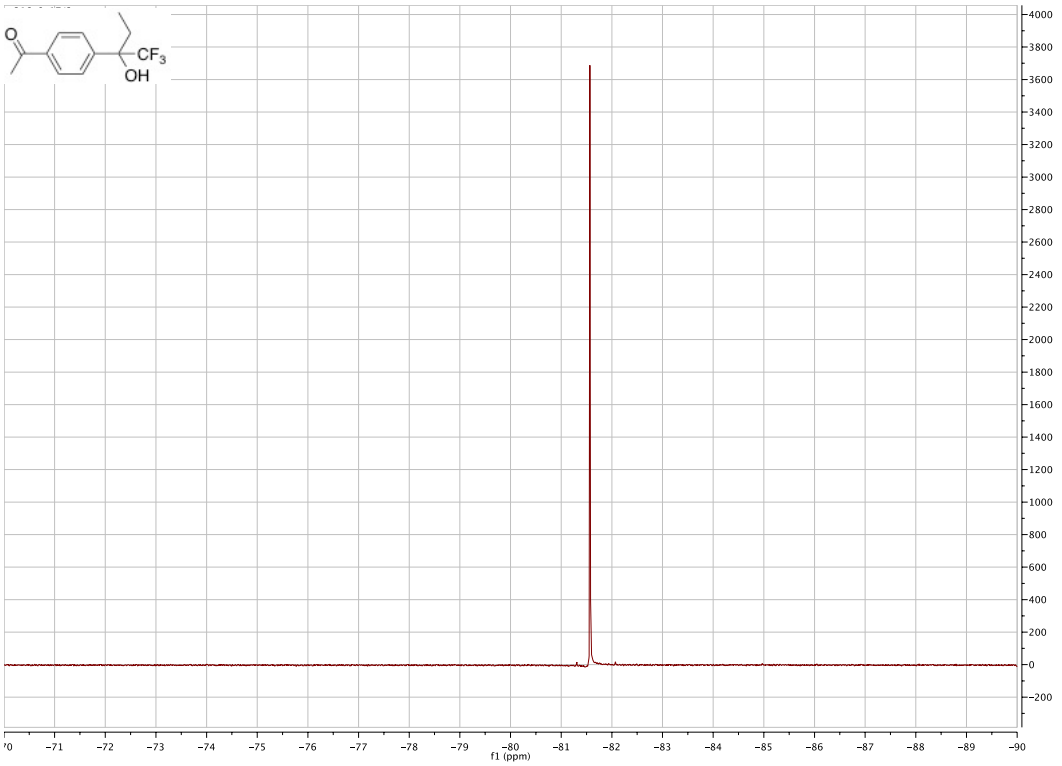


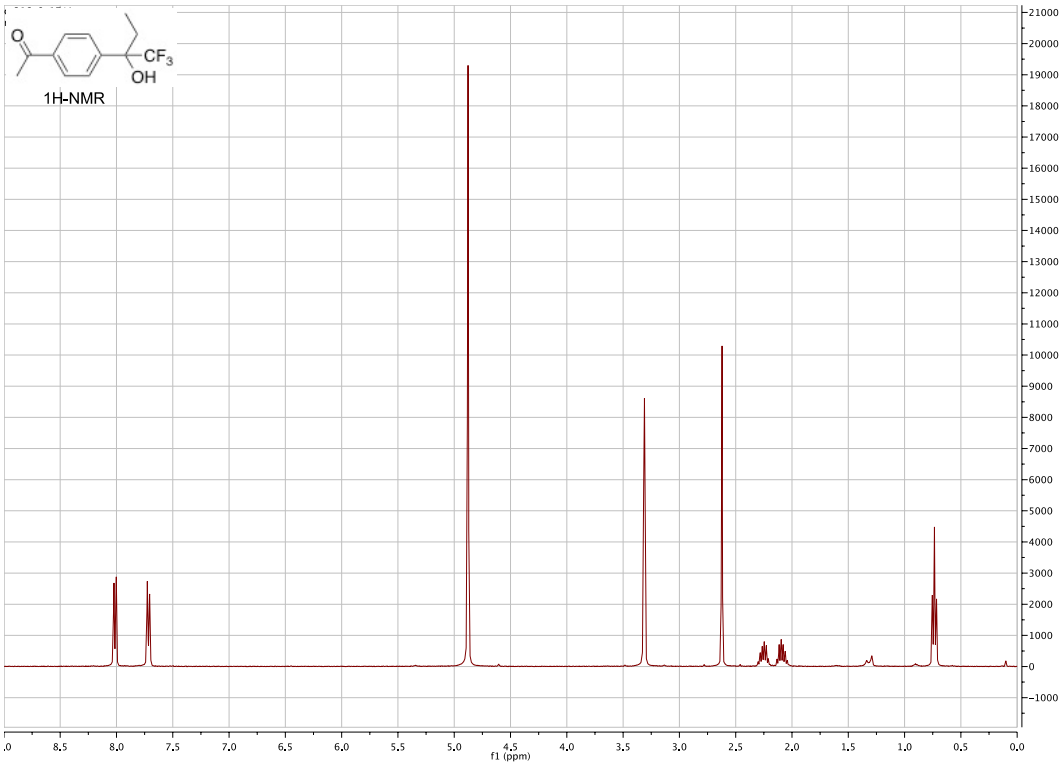






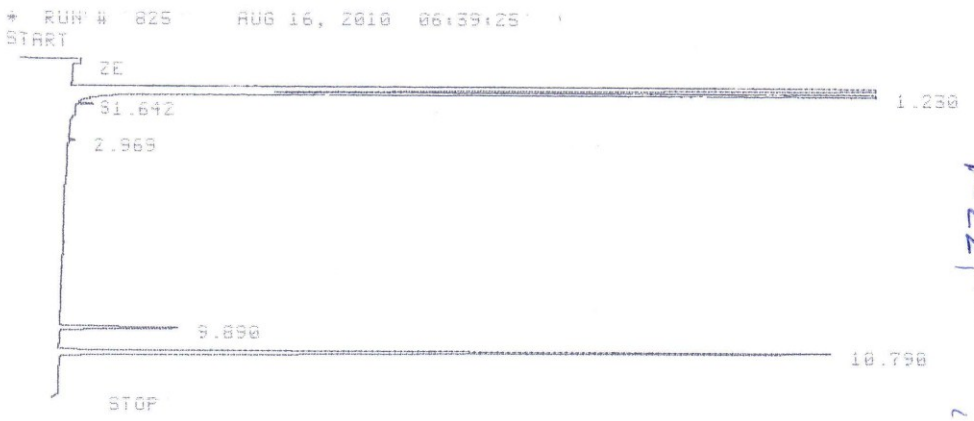






3. CG and HPLC Chromatograms

7a



RUN# 825 AUG 16, 2010 06:39:25

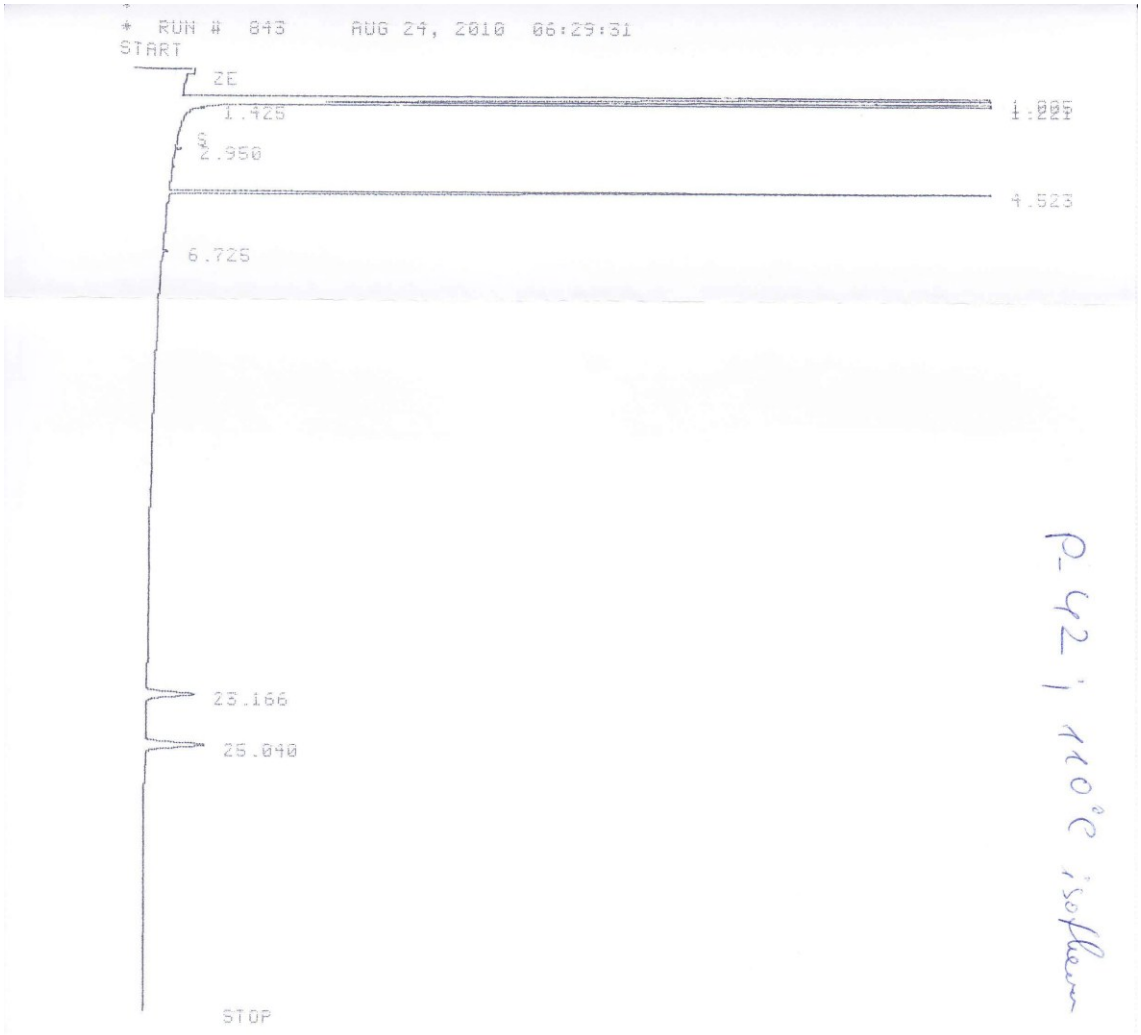
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.230	25153440	VSPB	.045	96.53338
1.642	4261	BB	.025	.01777
2.969	3470	BV	.046	.01447
9.890	103074	PV	.090	.42975
10.790	720664	BB	.097	3.00466

P-22; 110 °C isotherm
Lipodex E

- 75% ee

12a



RUN# 843 AUG 24, 2010 06:29:31

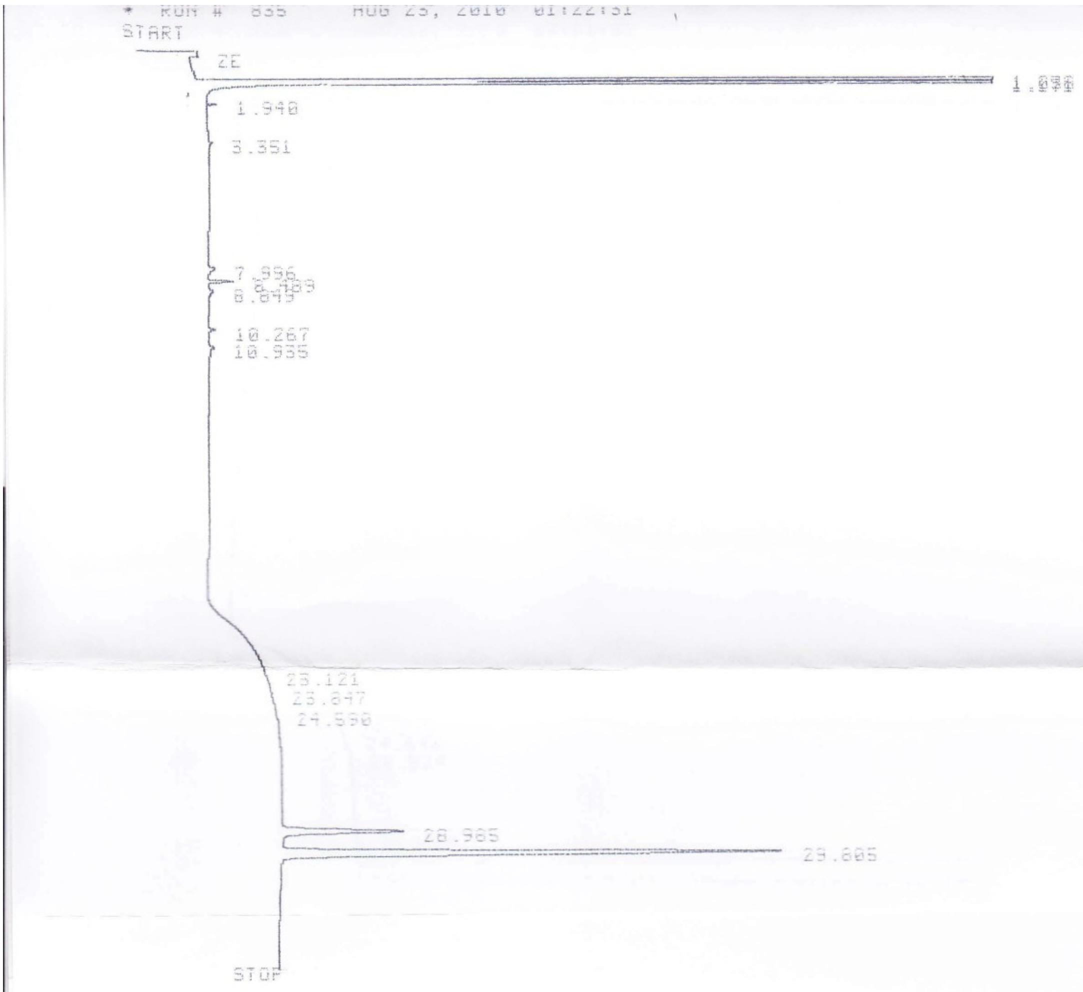
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.005	43577952	>SBB	.085	60.67709
1.221	27474640	>TBB	.054	38.25514
1.425	1376	TBB	.018	.00192
2.950	2725	BB	.039	.00379
4.523	543646	BB	.044	.75696
6.725	5151	VP	.084	.00717
23.166	95379	PP	.205	.13280
25.040	118633	BP	.213	.16518

TOTAL AREA=7.1819E+07
MUL FACTOR=1.0000E+00

Electronic Supplementary Material (ESI) for Dalton Transactions

14a



RUN# 835 AUG 23, 2010 01:22:31

AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.038	40704544	>SHH	.079	57.42483
1.171	28308624	>SHB	.055	39.93702
1.940	4453	TBV	.057	.00628
3.351	14891	TVV	.203	.02101
7.996	16880	TVV	.204	.02381
8.489	21077	TVV	.081	.02973
8.849	13600	TVV	.207	.01919
10.267	10292	TVV	.131	.01452
10.935	12033	TVV	.170	.01698
23.121	432162	PV	1.577	.60968
23.847	148877	VV	.766	.21003
24.590	124753	VV	.870	.17600
28.985	210398	VV	.179	.29682
29.805	860647	VB	.180	1.21418

– 61% ee

TOTAL AREA=7.0883E+07
MUL FACTOR=1.0000E+00

R-27; 130°C 20 min; then 140°C Lipodex E

15a

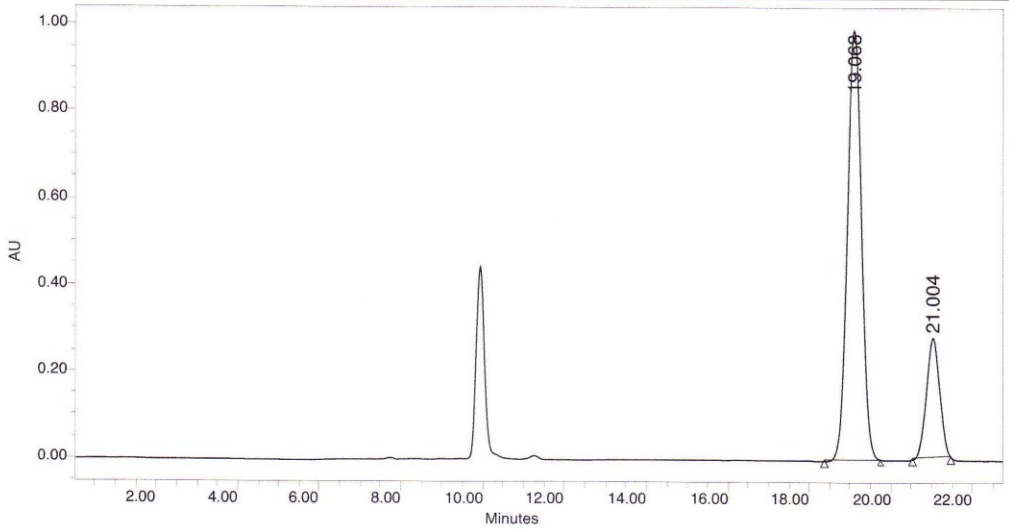
UVA

Project Name: Miroslav
Reported by User: System

'Breeze

SAMPLE INFORMATION

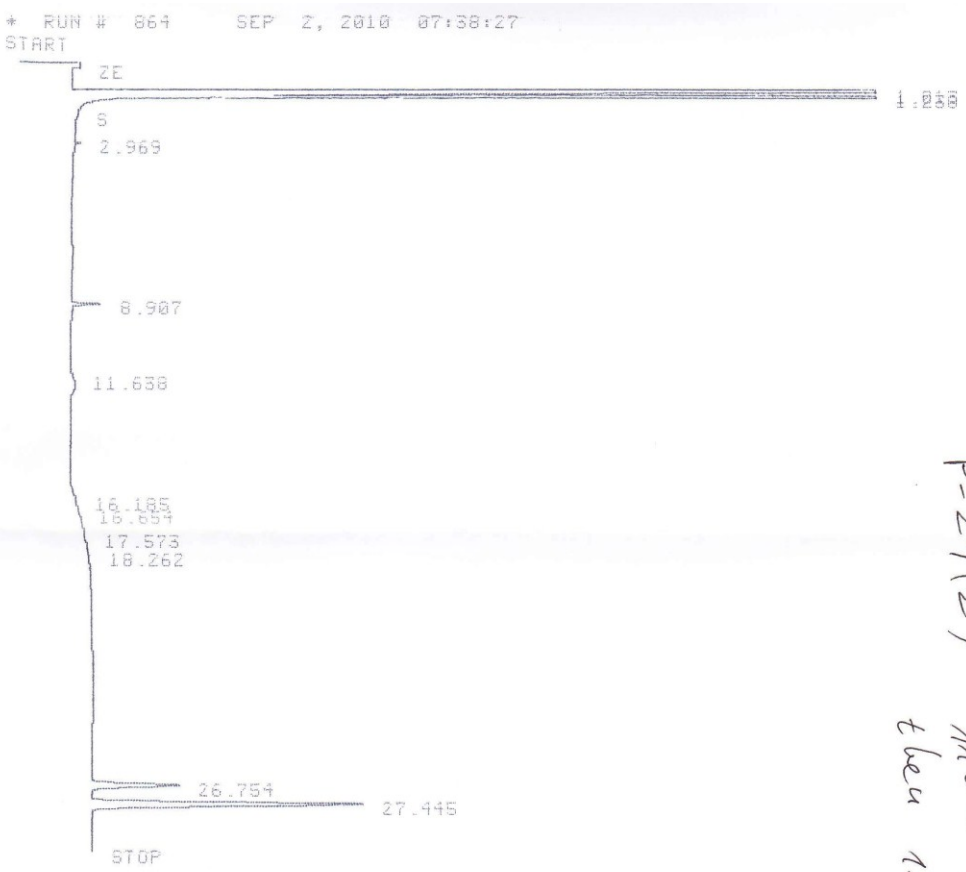
Sample Name:	P-48_AD_column	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17/9/10 10.18.19
Vial:	1	Acq. Method:	miro_95_5
Injection #:	2	Date Processed:	17/9/10 10.42.11
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	80.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19.068	24051596	79.19	992010	78.06
2	21.004	6320496	20.81	278804	21.94

Report Method: Sin t tulo Printed 10.42.20 17/9/10 Page: 1 of 1

16a



P-24(2) 110°C 15 min then 120°C

RUN# 864 SEP 2, 2010 07:38:27

AREA%

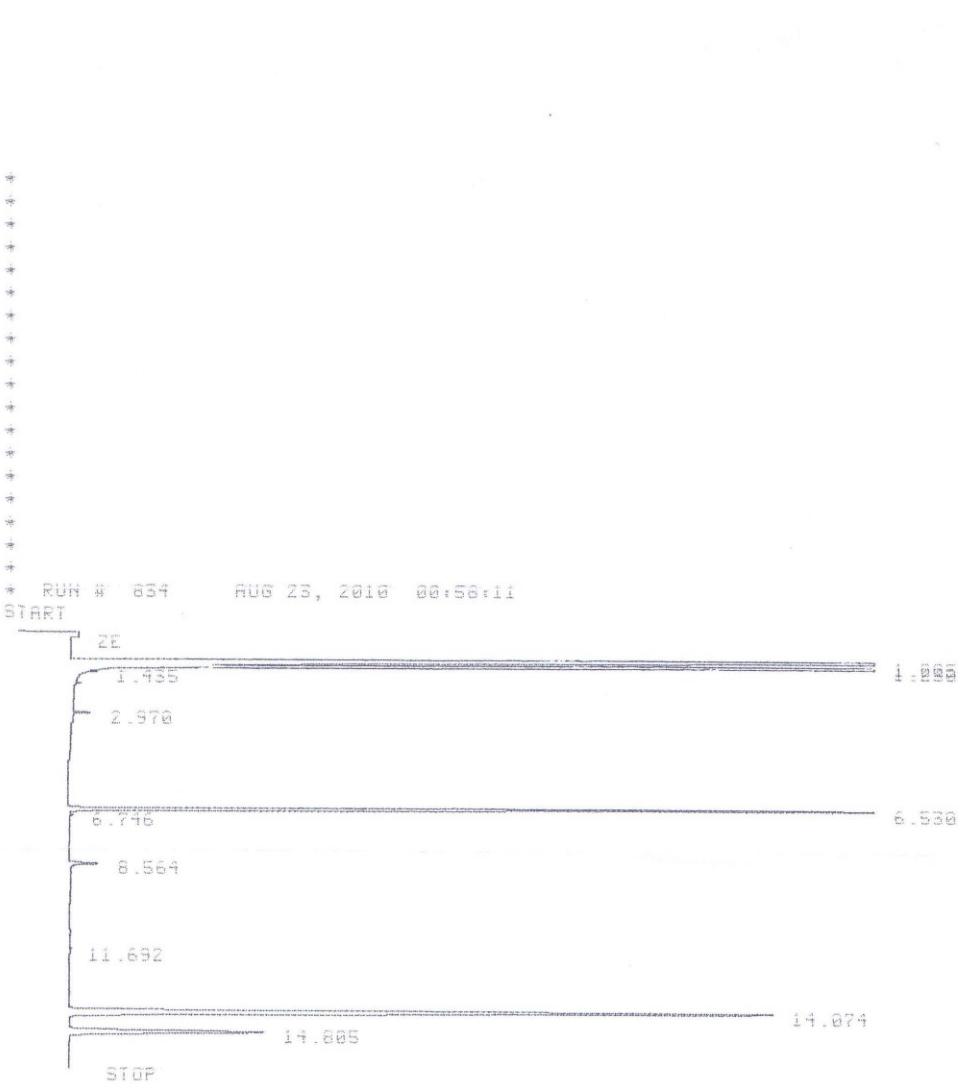
RT	AREA	TYPE	WIDTH	AREA%
1.013	47429184	>SBH	.092	69.30483
1.238	20278896	>SHB	.039	29.63208
2.969	2962	BP	.044	.00433
8.907	23837	PU	.084	.03483
11.638	15016	PU	.348	.02194
16.185	5579	PU	.274	.00815
16.654	12164	VU	.354	.01777
17.573	37594	VU	.812	.05493
18.262	35361	VU	.615	.05167
26.754	144424	BV	.169	.21104
27.445	450644	PU	.173	.65849

= 52 % ee

TOTAL AREA=6.8436E+07
MUL FACTOR=1.0000E+00

*
*

17a



RUN# 834 AUG 23, 2010 00:58:11

AREA%

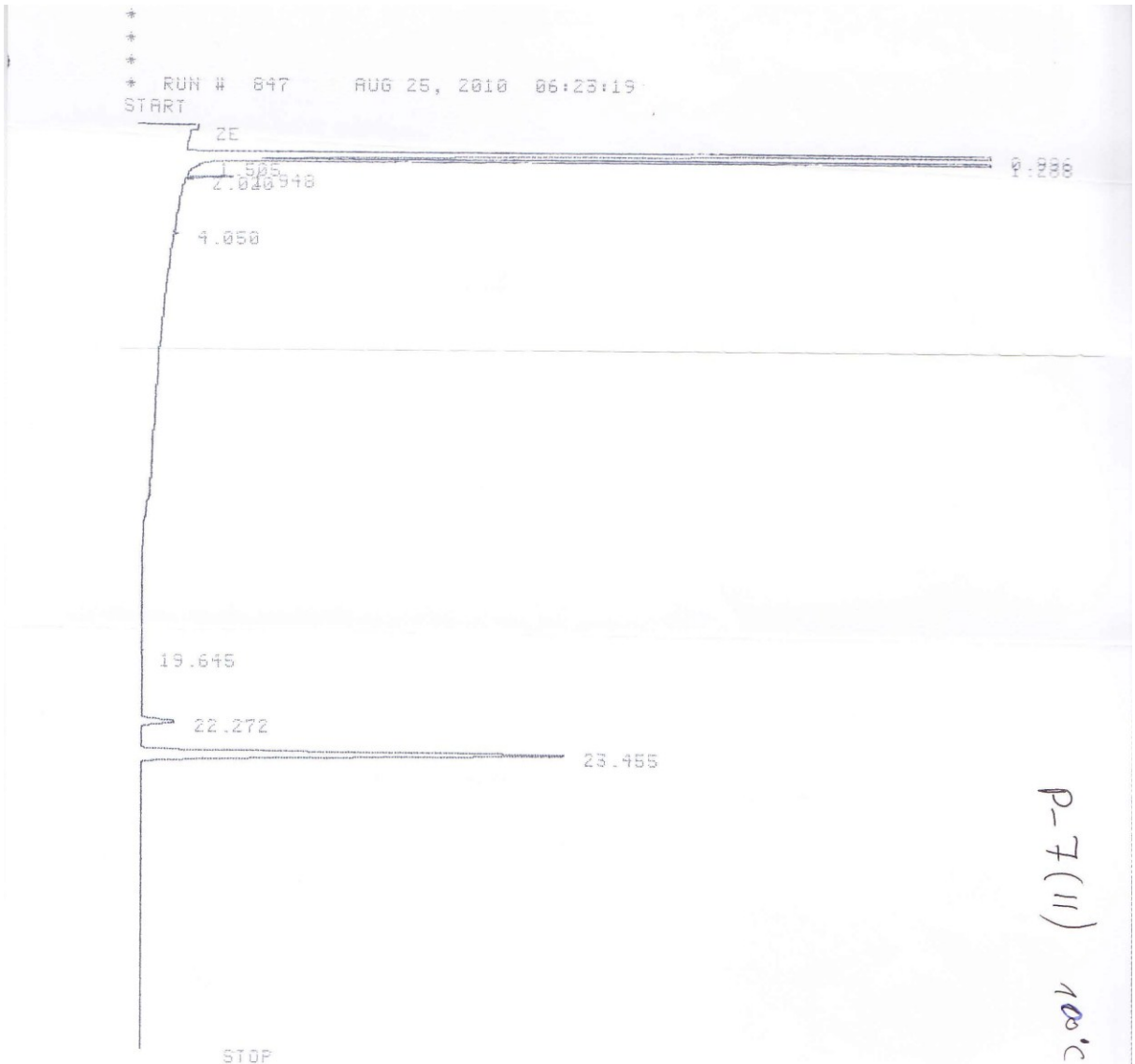
RT	AREA	TYPE	WIDTH	AREA%
1.005	50454912	>SFM	.058	63.62677
1.230	27086196	>SMB	.053	34.15776
1.435	3946	TBB	.036	.00498
2.970	7745	BP	.041	.00977
6.530	630123	PB	.062	.79471
6.746	2454	BP	.059	.00309
8.564	23684	PV	.085	.02987
11.692	997	VB	.024	.00126
14.074	834223	PV	.123	1.05201
14.805	245717	PP	.130	.30986

TOTAL AREA=7.9298E+07
MUL FACTOR=1.0000E+00

~ 55% ee

P-26
110°C isothermic
Lipodex E

7b



RUN# 847 AUG 25, 2010 06:23:19

AREA%

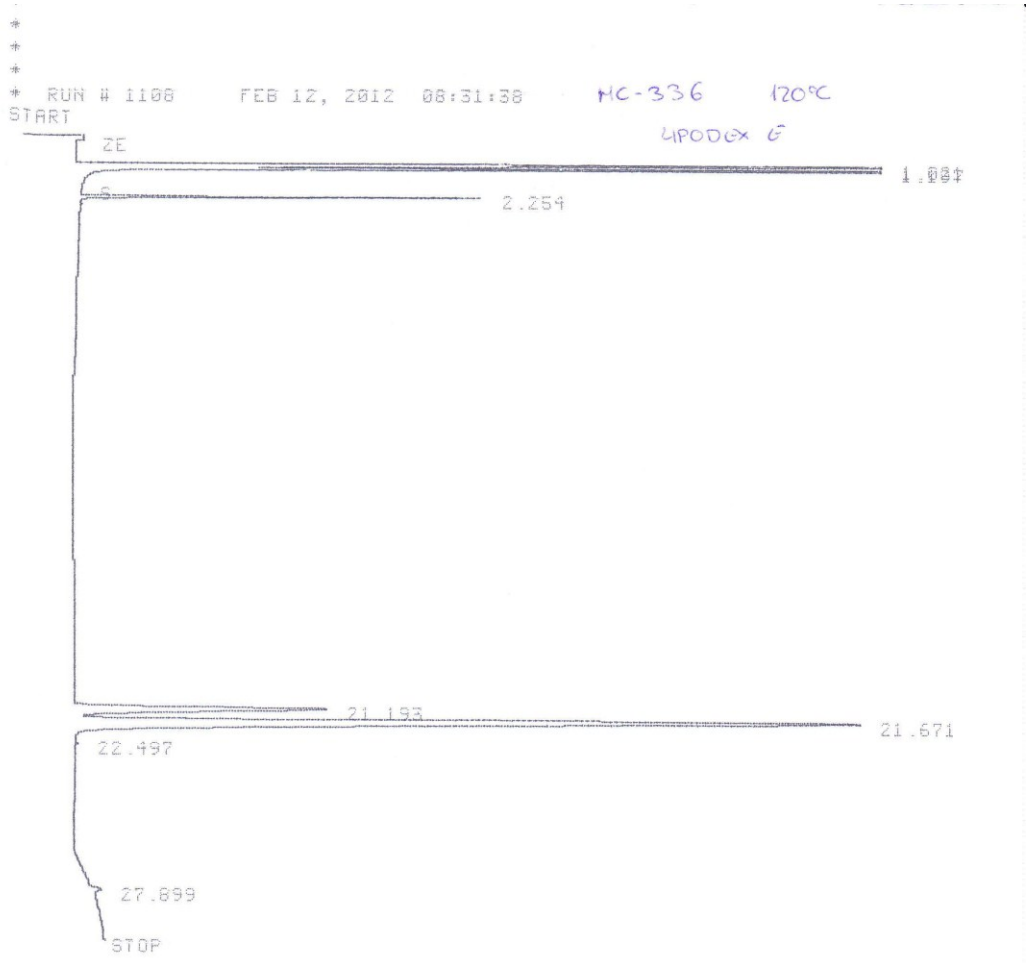
RT	AREA	TYPE	WIDTH	AREA%
.996	47809216	>SBH	.093	66.84678
1.288	22744448	>SHB	.044	31.80126
1.505	2400	TBB	.059	.00336
1.948	15647	PU	.033	.02188
2.020	2704	VP	.033	.00378
4.050	2037	BP	.043	.00285
19.645	1045	I PB	.026	.00146
22.272	67429	BV	.201	.09428
23.455	875724	PU	.214	1.22444

TOTAL AREA=7.1521E+07
MUL FACTOR=1.0000E+00

P-7(11) 100°C isothermic Lipolex E

= 86% ee

8b



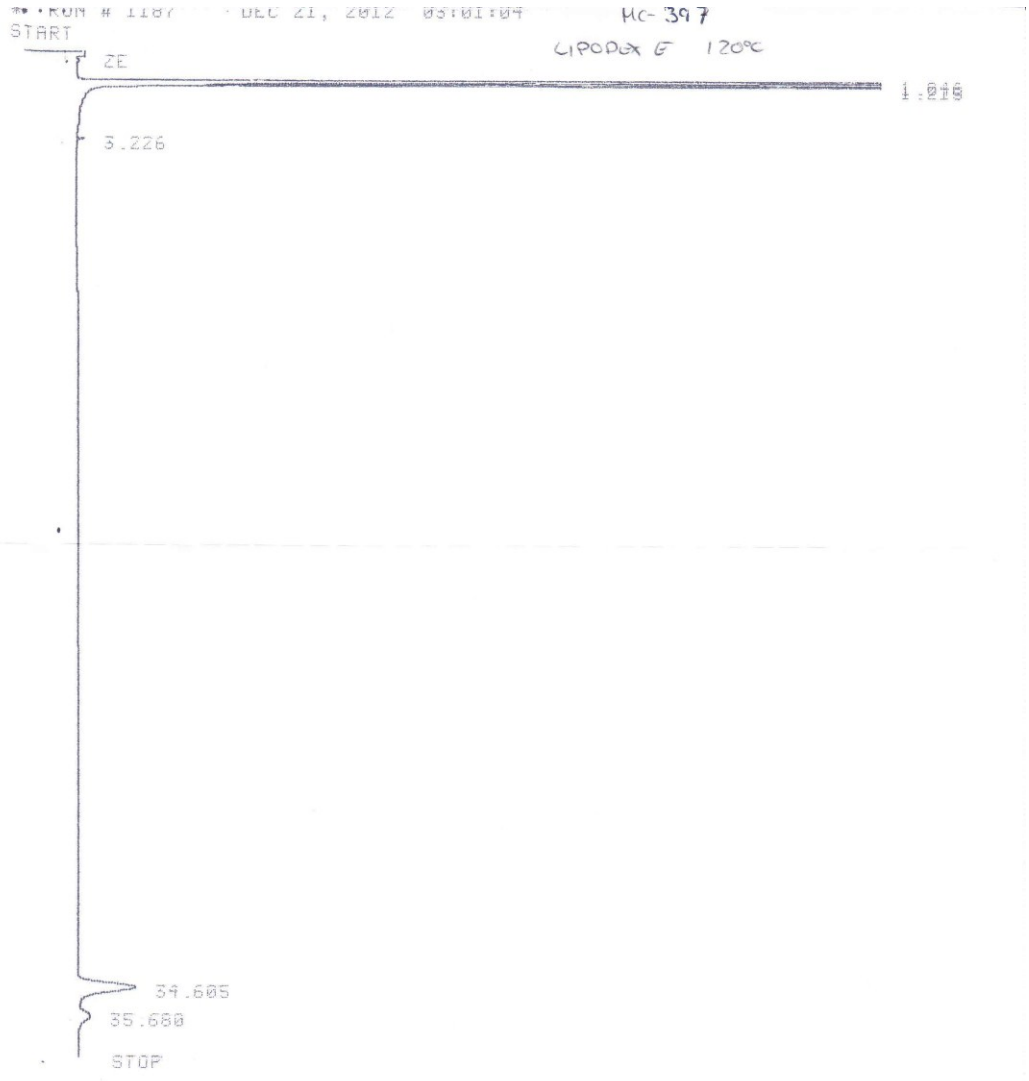
RUN# 1108 FEB 12, 2012 08:31:38

AREA%

RT	AREA	TYPE	WIDTH	AREA%	
1.021	36975040	>SPH	.072	83.53539	
1.197	4872234	SHB	.027	11.00753	
2.254	132909	PB	.035	.30027	
21.193	470489	BV	.195	1.06295	56%ee
21.671	1627586	VV	.217	3.67710	
22.497	1753	VB	.034	.00396	
27.899	182734	VV	.668	.41284	

TOTAL AREA=4.4263E+07
MUL FACTOR=1.0000E+00

9b



RUN# 1187 DEC 21, 2012 03:01:04

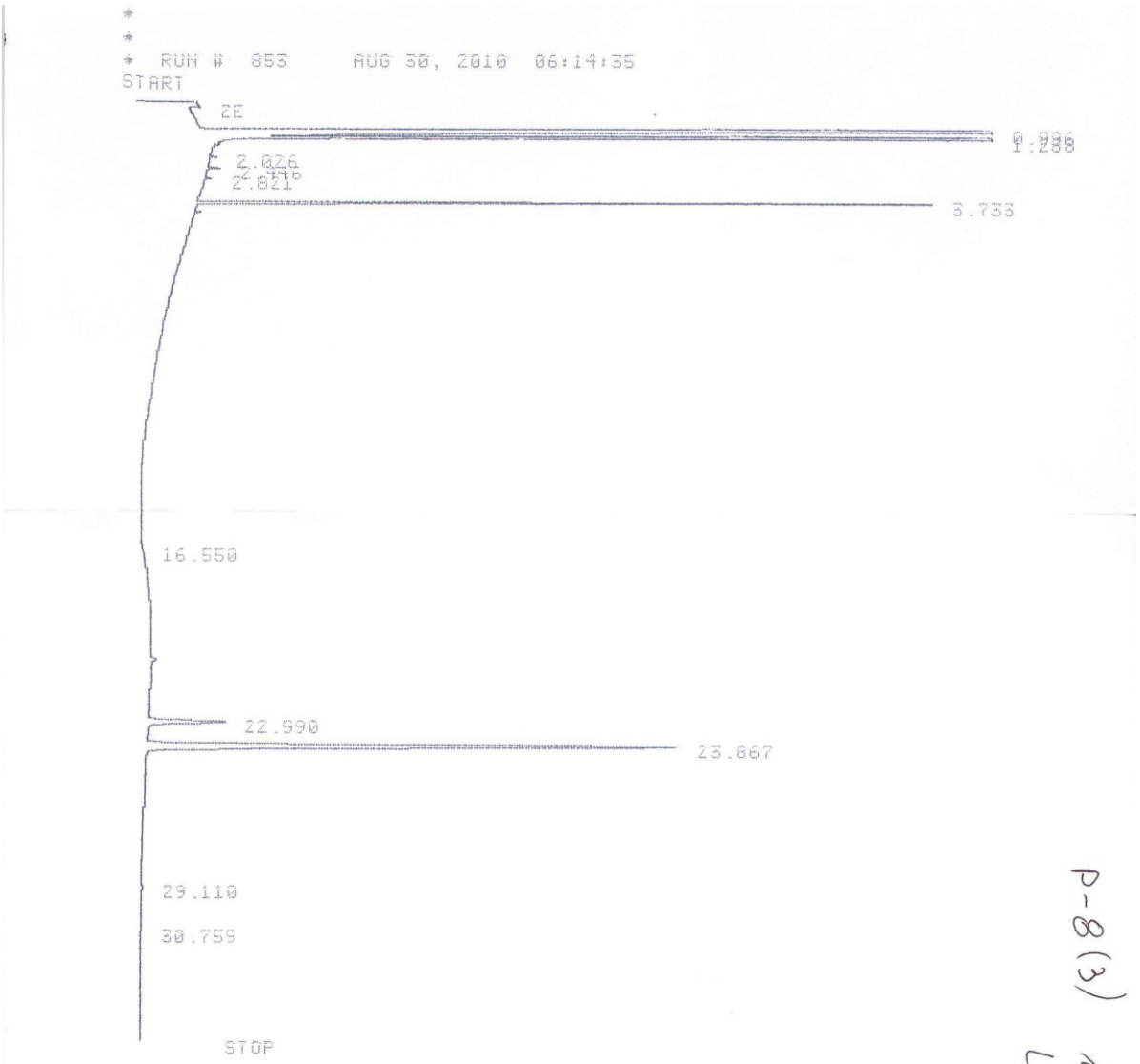
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.046	27946864	>SBB	.054	85.26320
1.215	4557578	TBB	.017	13.90473
3.226	4270	PB	.053	.01303
34.605	220417	PV	.399	.67247
35.680	48036	VP	.398	.14655

64 bee

TOTAL AREA=3.2777E+07
MUL FACTOR=1.0000E+00

10b (T = -40 ºC)



RUN# 853 AUG 30, 2010 06:14:35

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.996	51562016	>SBB	.101	66.80237
1.288	24438720	>TBB	.048	31.66215
2.026	2506	BP	.032	.00325
2.446	6010	VV	.042	.00779
2.821	3965	VB	.048	.00514
3.733	309944	BB	.043	.40156
16.550	13889	BV	.430	.01799
22.990	100506	BP	.136	.13021
23.867	733703	PB	.144	.95057
29.110	6513	BP	.172	.00844
30.759	8215	PP	.206	.01064

TOTAL AREA=7.7186E+07
MUL FACTOR=1.0000E+00

= 76% ee

P-8(3) 100°C 10 min, then 110°C
Lipodex E

11b

P-10 (1) 110°C isotherme

RUN# 848 AUG 25, 2010 07:00:52

AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.005	42649280	>SPH	.083	65.41696
1.230	21402272	>SHB	.042	32.82757
1.429	1987	TBB	.031	.00305
1.743	1924	TBB	.031	.00295
2.328	2276	BP	.050	.00349
2.868	3812	BP	.034	.00585
2.960	3374	PV	.043	.00518
3.818	408935	BB	.040	.62724
17.931	7622	VV	.174	.01169
23.571	100940	PP	.205	.15483 — 72% ee
24.458	613668	PV	.217	.94127 —

TOTAL AREA=6.5196E+07
MUL FACTOR=1.0000E+00

12b

P-342

RUN# 842 AUG 24, 2010 01:16:08

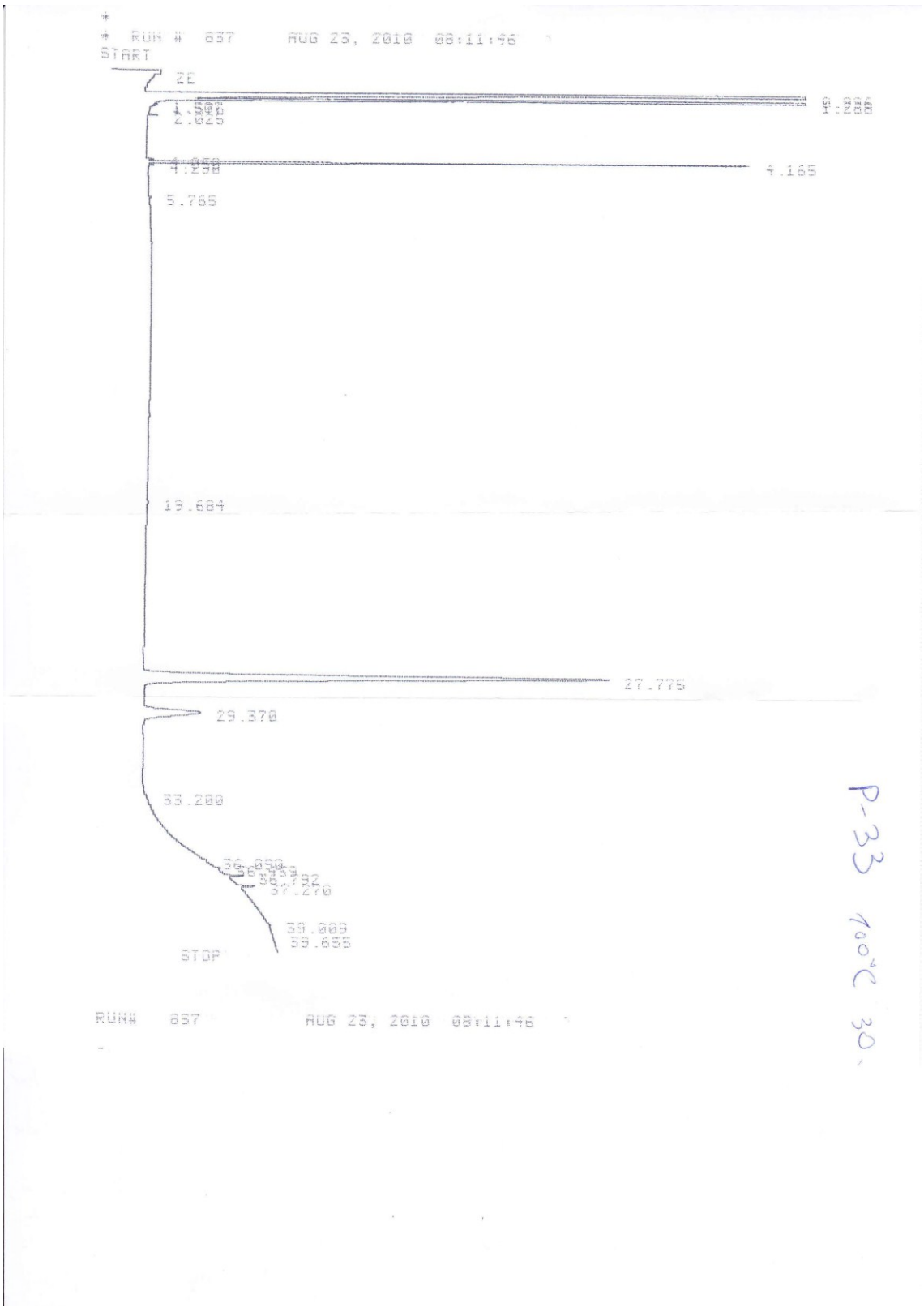
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.005	37822336	>SBB	.074	60.14960
1.221	24152400	>TBB	.047	38.41003
1.431	2242	TBB	.040	.00357
1.750	3894	BP	.034	.00619
2.963	3742	PU	.046	.00595
4.534	794915	PB	.045	1.26417
27.080	31145	PP	.240	.04953
27.694	69797	PP	.247	.11100

38%

TOTAL AREA=6.2880E+07
MUL FACTOR=1.0000E+00

13b


RUN # 837 AUG 23, 2010 08:11:46
START
2E
1.286
4.165
5.765
19.684
27.775
29.370
33.200
37.270
39.655
STOP
RUN# 837 AUG 23, 2010 08:11:46
P-33 100°C 30

RUN# 837 AUG 23, 2010 08:11:46

AREA%

RT	AREA	TYPE	WIDTH	AREA%
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1.288	24143008	>SHB	.047	32.43765
1.507	1788	TBP	.037	.00240
1.576	3466	TPB	.045	.00466
2.025	4515	VP	.035	.00606
4.050	4692	PV	.047	.00630
4.165	311559	VV	.044	.41860
4.290	6281	VV	.067	.00844
5.765	2025	VV	.066	.00272
19.684	6134	PV	.199	.00824
27.775	1366615	BP	.250	1.83613
29.370	183765	PP	.269	.24690
33.200	12105	VV	.224	.01626
36.090	922457	VV	1.202	1.23938
36.439	306106	VV	.325	.41127
36.792	348463	VV	.252	.46818
37.270	541716	VV	.406	.72783
39.009	2367597	VV	1.559	3.18101
39.655	836787	VV	.576	1.12458

TOTAL AREA=7.4429E+07
MUL FACTOR=1.0000E+00

30 min, then 140°C

~ 77% ee

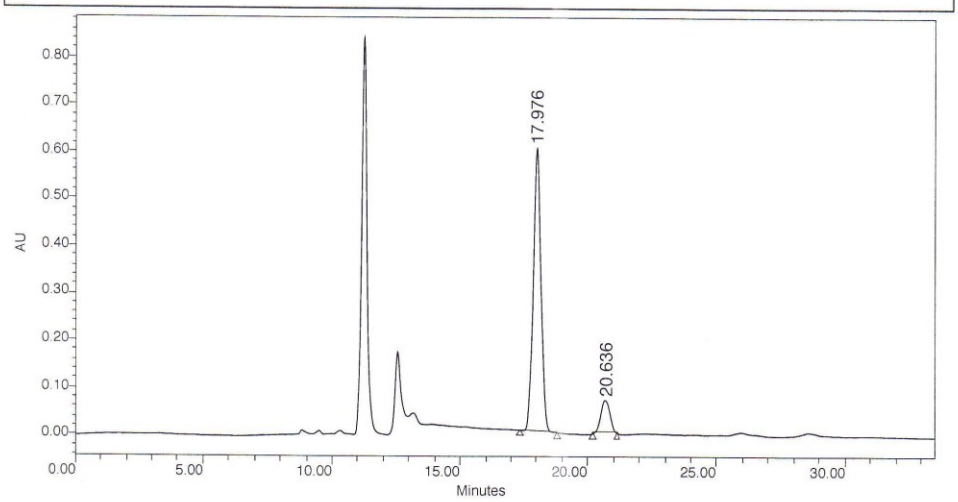
14b

UVA
Project Name: Miroslav
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	P-12	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/9/10 16.58.58
Vial:	1	Acq. Method:	miro_95_5
Injection #:	1	Date Processed:	1/9/10 17.36.53
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	80.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	17.976	12572860	87.79	600793	89.56
2	20.636	1747991	12.21	70028	10.44

Report Method: Sin t tulo Printed 17.39.11 1/9/10 Page: 1 of 1

15b

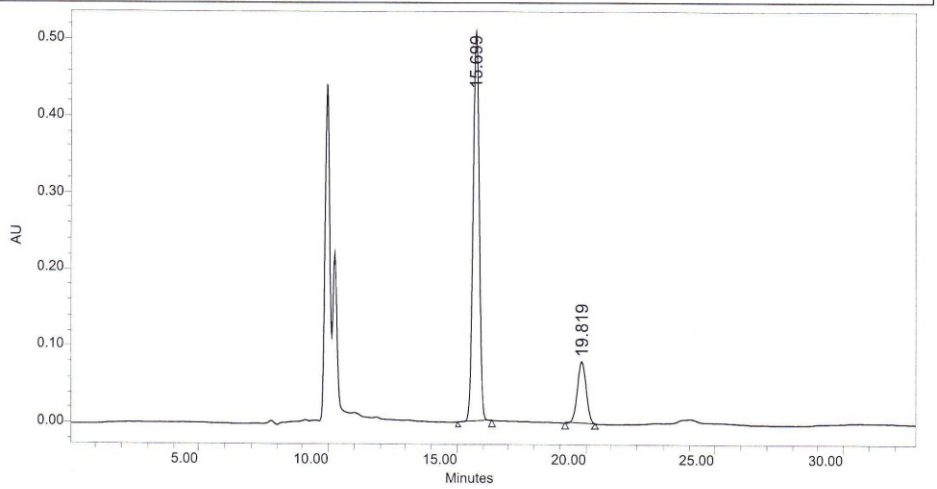
UVA

Project Name: Miroslav
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	P-46_AD_column	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17/9/10 18.01.05
Vial:	1	Acq. Method:	miro_95_5
Injection #:	3	Date Processed:	17/9/10 18.34.17
Injection Volume:	10.00 ul	Channel Name:	2487Channel 1
Run Time:	80.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	15.699	8557827	81.79	506294	86.29
2	19.819	1904858	18.21	80435	13.71

16b

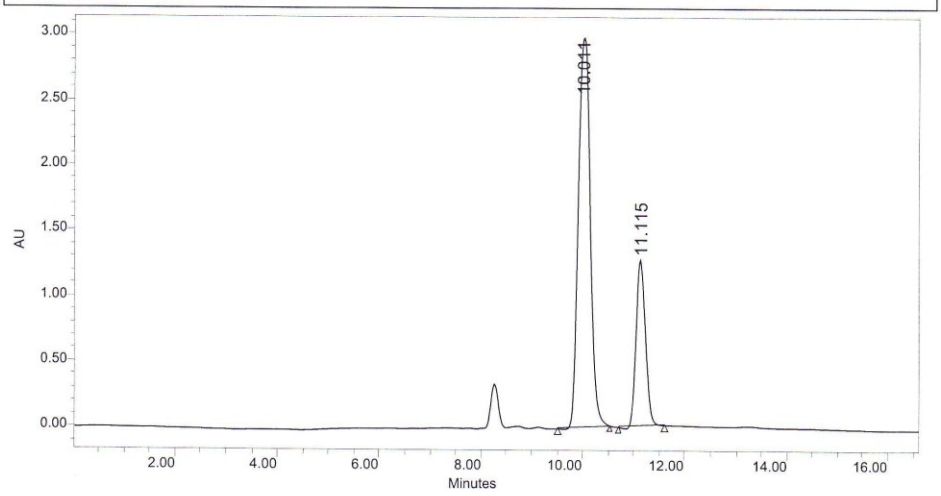
UVA

Project Name: Miroslav
Reported by User: System

Breeze

SAMPLE INFORMATION

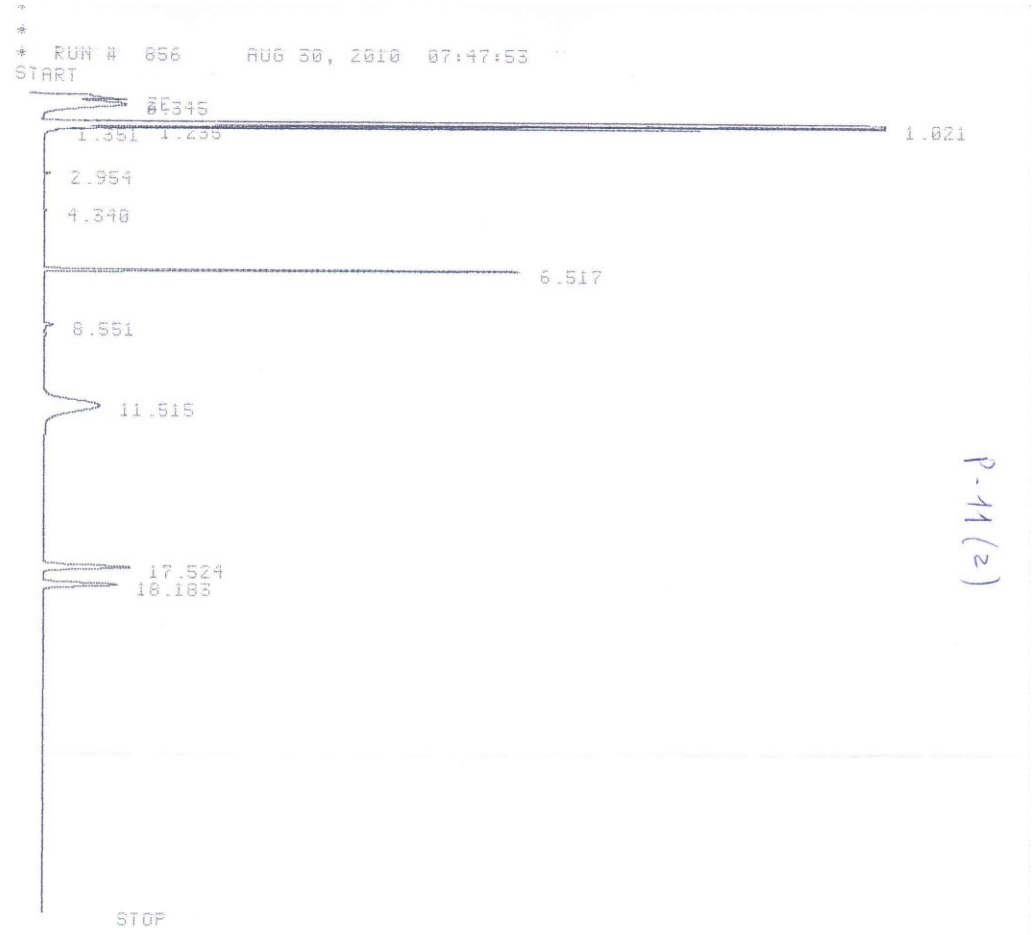
Sample Name:	P-9(2)_AD_column	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	16/9/10 9.40.56
Vial:	1	Acq. Method:	miro_95_5
Injection #:	1	Date Processed:	16/9/10 9.58.16
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	80.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.011	48245071	74.66	2982946	70.14
2	11.115	16372052	25.34	1269840	29.86

Report Method: Sin t tulo Printed 10.29.30 20/9/10 Page: 1 of 1

17b



P-11(2)

RUN# 856 AUG 30, 2010 07:47:53

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.345	251483	BP	.315	.62293
1.021	39206912	>SPB	.076	97.11712
1.235	110905	TBB	.019	.27472
2.954	2500	PB	.032	.00619
4.340	1300	BV	.037	.00322
6.517	273017	PB	.059	.67627
8.551	8299	PP	.087	.02056
11.515	271934	BP	.509	.67359
17.524	129809	PP	.154	.32154
18.183	114617	PP	.160	.28391

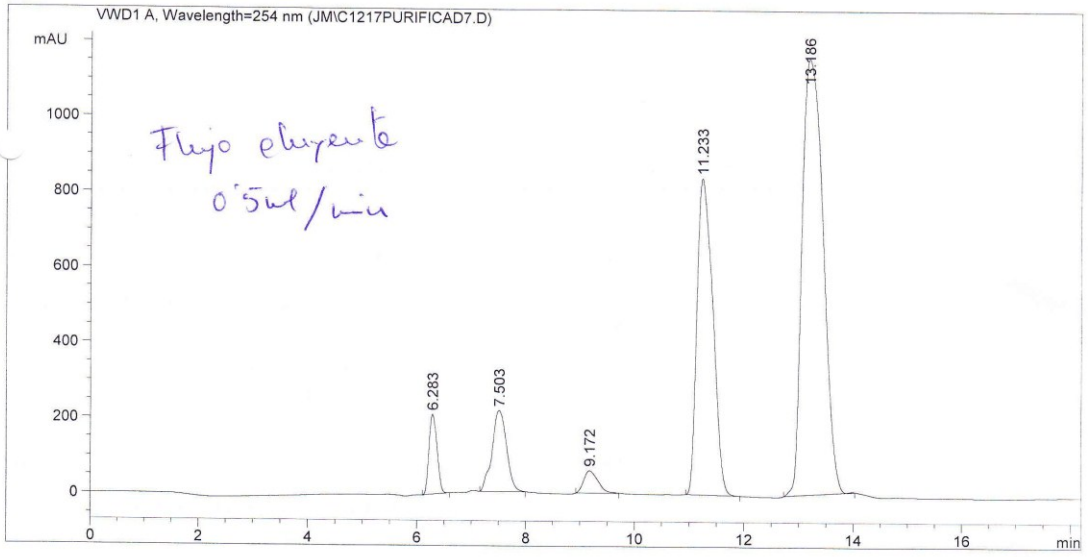
TOTAL AREA=4.0371E+07
MUL FACTOR=1.0000E+00

18b

Data File C:\CHEM32\1\DATA\JM\C1217PURIFICAD7.D
Sample Name: C1217purificado

HC-363 después de columna

```
=====================================================================
Acq. Operator    : Marta
Acq. Instrument  : HPLC 1200 Analitico          Location : Vial 1
Injection Date   : 6/5/2012 11:48:30 AM
                                                Inj Volume : 5 µl
Acq. Method      : C:\CHEM32\1\METHODS\MIROSLAV.M
Last changed     : 6/5/2012 11:47:35 AM by Marta
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\MIROSLAV.M
Last changed     : 6/5/2012 12:43:10 PM by Marta
                   (modified after loading)
Sample Info      : muestra pasada por columna para purificarla disulelto e
                   n nhexano:IPA(95:5) 5microlitros de inyección 0,5ml/min
```

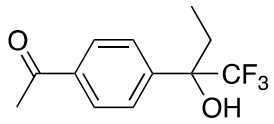


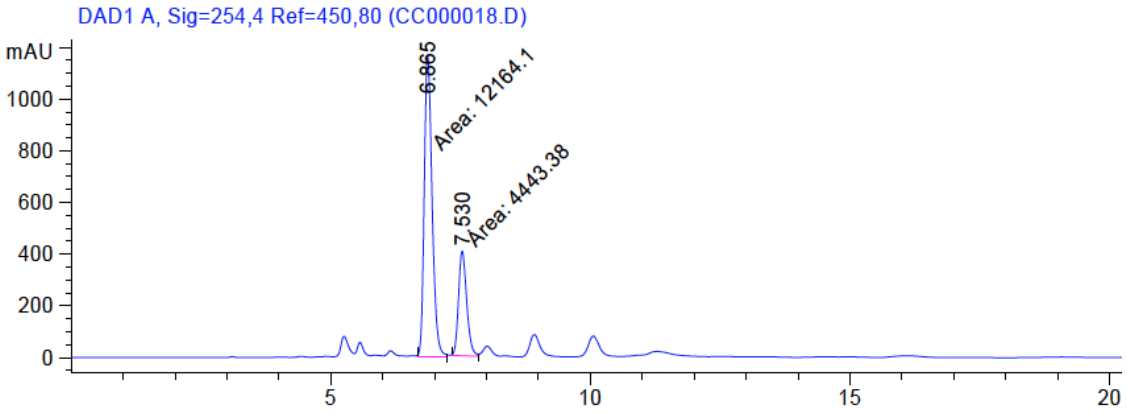

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.283 BB    0.1672 2161.36841  211.55856   3.9194
   2   7.503 BB    0.2876 3980.05493  214.72899   7.2173
   3   9.172 BB    0.2918 1063.90503   59.04171   1.9293
   4  11.233 BB    0.3377 1.68525e4   839.04865  30.5598
   5  13.186 BB    0.4403 3.10882e4  1156.62903  56.3743
```






```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=450,80

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.865 MM    0.1736 1.21641e4  1167.76672  73.2447
   2   7.530 MM    0.1825 4443.38037  405.85910  26.7553

Totals :                  1.66075e4  1573.62582


Signal 2: DAD1 B, Sig=220,4 Ref=450,80


Signal 3: DAD1 C, Sig=254,4 Ref=off

=====================================================================
                         *** End of Report ***
```