Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

2-Methoxyphenylisocyanate: A chemoselective multitasking reagent for amine protection/deprotection sequence

Anand Babu Velappan,[a] Kogatam Subhashini,[a] Dhrubajyoti Datta,[b] Rakshantha Srithar,[a] Nanjappan Gunasekaran[a] and Joy Debnath[a*]

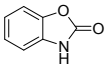
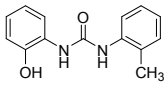
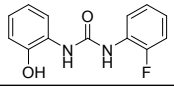
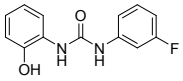
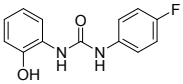
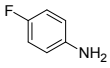
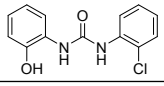
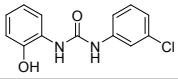
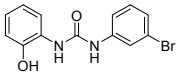
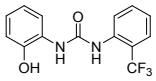
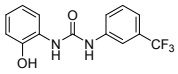
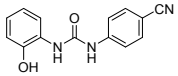
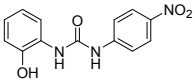
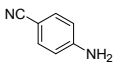
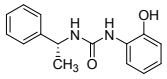
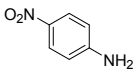
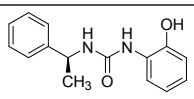
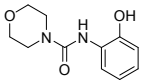
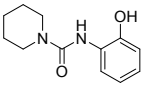
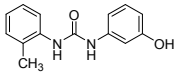
[a]*Department of Chemistry, SCBT, SASTRA Deemed University, Tamilnadu 613401, India.*

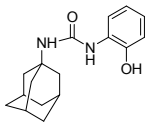
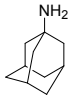
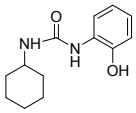
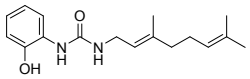
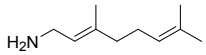
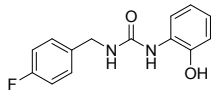
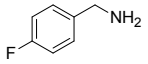
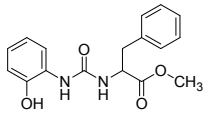
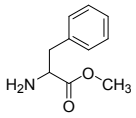
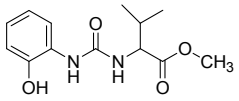
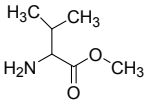
[b]*Department of Chemistry, Indian Institute of Science Education and Research , Pune, Maharashtra, 411008, India.*

Supporting Information III

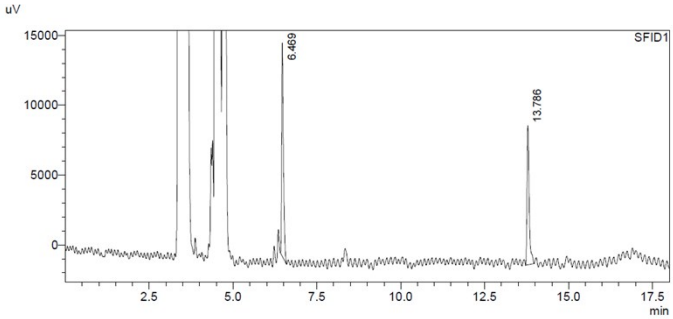
Table of content:

1. Table for the retention time of the standards in GC and HPLC:

Compounds	Retention time (min)		Compounds	Retention time (min)	
	For GC	For HPLC		For GC	For HPLC
EtOAc (solvent)	3.493	-			
Xylene (solvent)	4.573	-			
	13.809	14.224		8.324	23.764
	6.473	15.225		8.325	-
	5.182	-		8.329	-
	5.664	-		8.334	-
	5.588	-		7.419	-
	7.287	-		7.153	-
	8.397	-		8.591	-
	9.324	-		7.878	-
	10.000	-		8.332	-
	5.295	-		9.548	-
	3.459	-		15.650	-
	12.487	-		7.542	-
	15.621	-		7.542	-
	6.169	3.610		6.477	-
	6.168	4.736		8.315	-
	4.106	-		-	18.798

	3.993	-		-	-
	9.136	-		9.249	-
	4.471	-		-	-
	8.521	-		8.537	-
	5.861	-		-	-
	11.957	-		-	-
	11.969	-			

2. GC Spectrum for regeneration of amine **1a**:

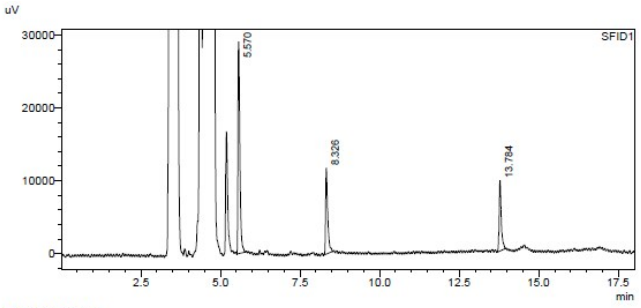


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.469	54931	15252	55.395	55.395
2	13.786	44231	9959	44.605	44.605
Total		99162	25212		100.000

3. GC Spectrum for regeneration of amine **1b**:

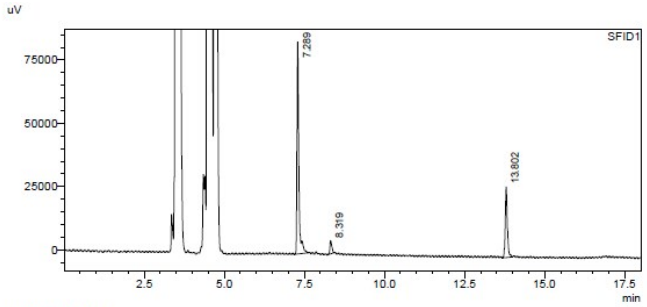


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.570	117662	29119	54.029	54.029
2	8.326	54972	11807	25.242	25.242
3	13.784	45141	9671	20.728	20.728
Total		217775	50597		100.000

4. GC Spectrum for regeneration of amine **1c**:

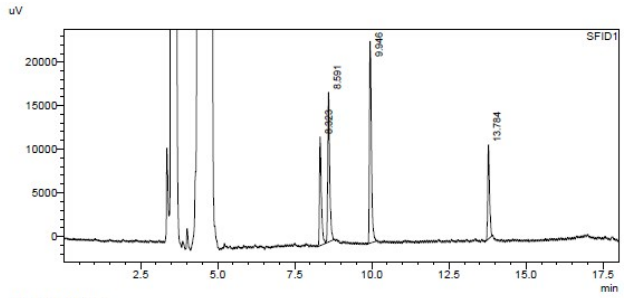


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.289	337317	83684	68.945	68.945
2	8.319	22785	5233	4.657	4.657
3	13.802	129156	27896	26.398	26.398
Total		489258	116814		100.000

5. GC Spectrum for regeneration of amine **1d**:

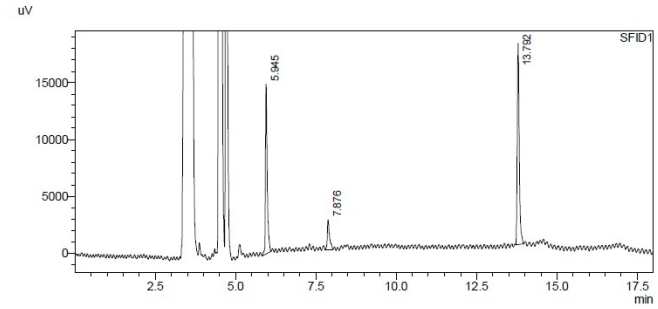


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.323	54593	12443	19.747	19.747
2	8.591	76622	17227	27.715	27.715
3	9.946	100708	23127	36.428	36.428
4	13.784	44538	10815	16.110	16.110
Total		276460	63611		100.000

6. GC Spectrum for regeneration of amine **1e**:

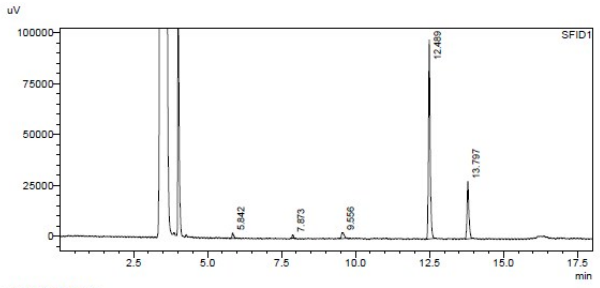


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.945	57584	14962	39.269	39.269
2	7.876	12905	2653	8.800	8.800
3	13.792	76153	17706	51.931	51.931
Total		146642	35321		100.000

7. GC Spectrum for regeneration of amine **1f**:

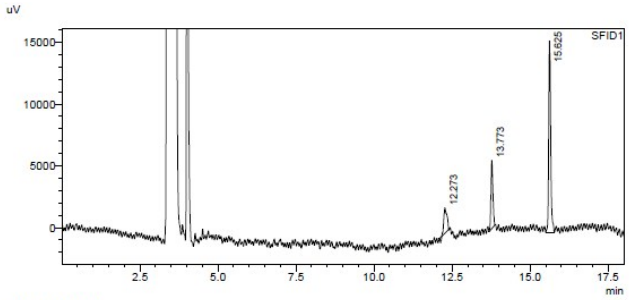


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.842	11306	2762	2.018	2.018
2	7.873	5663	1818	1.011	1.011
3	9.556	18350	2874	3.275	3.275
4	12.489	400212	98042	71.435	71.435
5	13.797	124713	28494	22.260	22.260
Total		560244	133990		100.000

8. GC Spectrum for regeneration of amine **1g**:

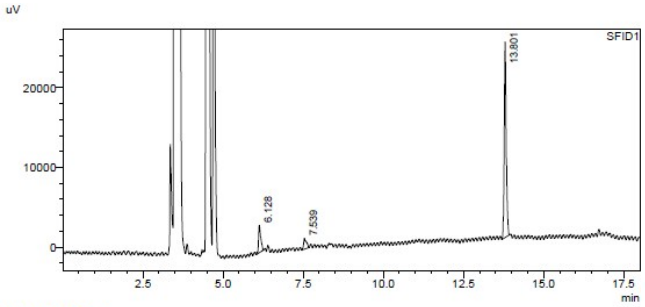


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	12.273	12844	2045	12.224	12.224
2	13.773	23992	5519	22.834	22.834
3	15.625	68234	15536	64.941	64.941
Total		105070	23100		100.000

9. GC Spectrum for regeneration of amine **1h**:

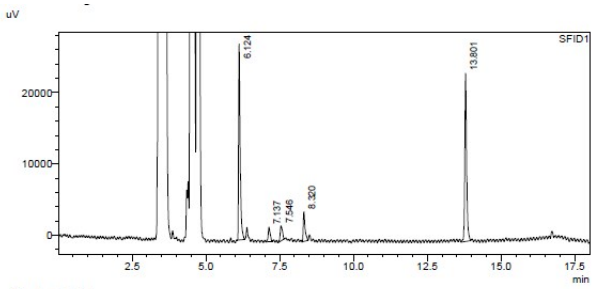


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.128	17097	3457	12.834	12.834
2	7.539	8283	1349	6.218	6.218
3	13.801	107836	24618	80.948	80.948
Total		133217	29424		100.000

10. GC Spectrum for regeneration of amine **1i**:

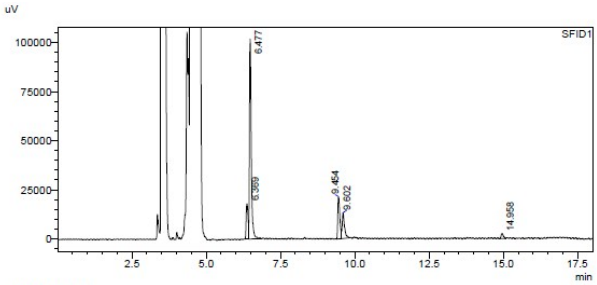


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.124	105896	27523	42.658	42.658
2	7.137	9858	2047	3.971	3.971
3	7.546	10867	2073	4.377	4.377
4	8.320	18312	4177	7.377	7.377
5	13.801	103310	23626	41.616	41.616
Total		248242	59446		100.000

11. GC Spectrum for regeneration of amine **1j**:

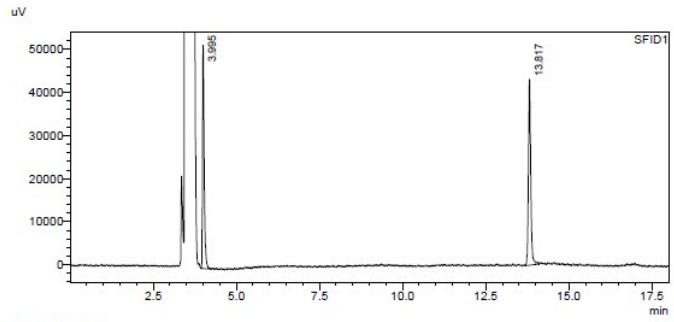


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.369	76218	17888	11.139	11.139
2	6.477	423053	101809	61.830	61.830
3	9.454	98169	21465	14.348	14.348
4	9.602	72933	13134	10.659	10.659
5	14.958	13848	2658	2.024	2.024
Total		684222	156953		100.000

12. GC Spectrum for regeneration of amine **1k**:

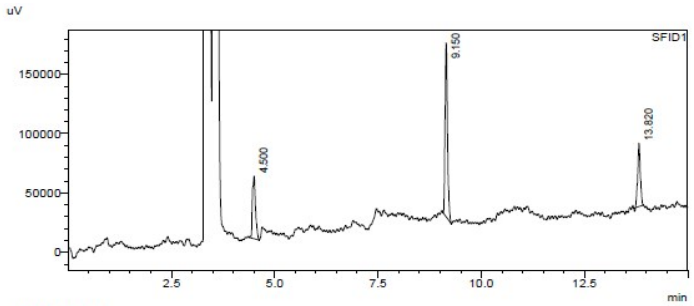


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	3.995	183416	51951	46.947	46.947
2	13.817	207274	43249	53.053	53.053
Total		390690	95201		100.000

13. GC Spectrum for regeneration of amine **1l**:

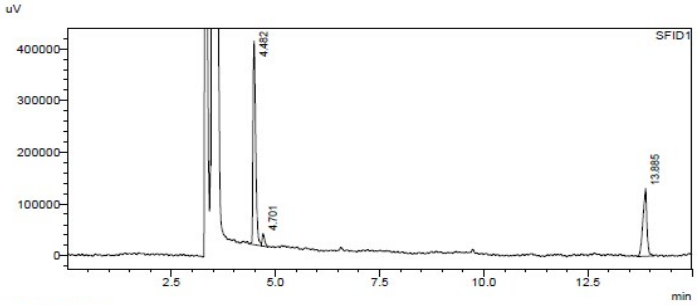


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.500	273729	53047	24.642	24.642
2	9.150	596117	147055	53.665	53.665
3	13.820	240959	53409	21.692	21.692
Total		1110804	253510		100.000

14. GC Spectrum for regeneration of amine **1m**:

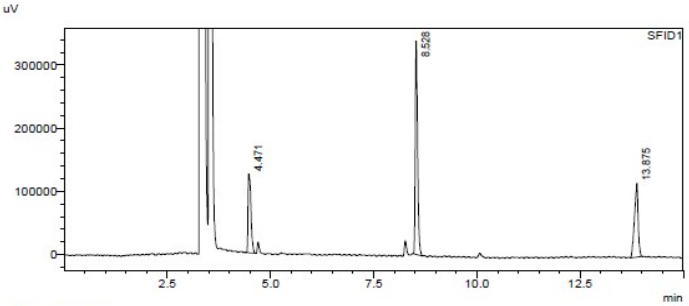


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.482	1725399	394470	64.133	64.133
2	4.701	100144	24547	3.722	3.722
3	13.885	864820	131266	32.145	32.145
Total		2690363	550282		100.000

15. GC Spectrum for regeneration of amine **1n**:

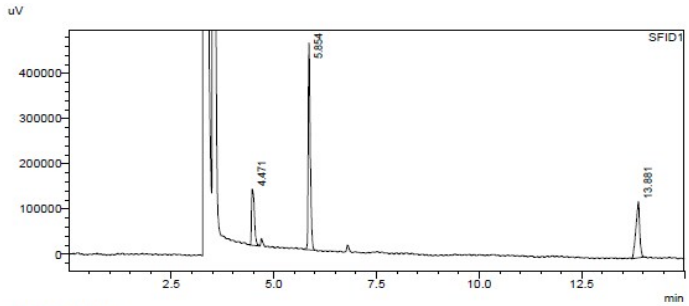


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.471	611579	125773	23.244	23.244
2	8.528	1300622	338554	49.431	49.431
3	13.875	718964	117458	27.325	27.325
Total		2631166	581784		100.000

16. GC Spectrum for regeneration of amine **1o**:

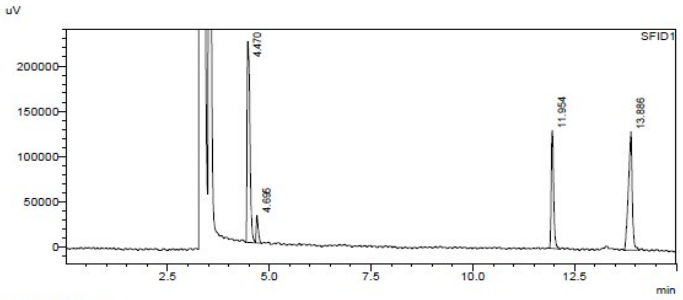


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.471	599379	124221	19.853	19.853
2	5.854	1630246	457937	53.999	53.999
3	13.881	789424	125207	26.148	26.148
Total		3019049	707365		100.000

17. GC Spectrum for regeneration of amine **1p**:

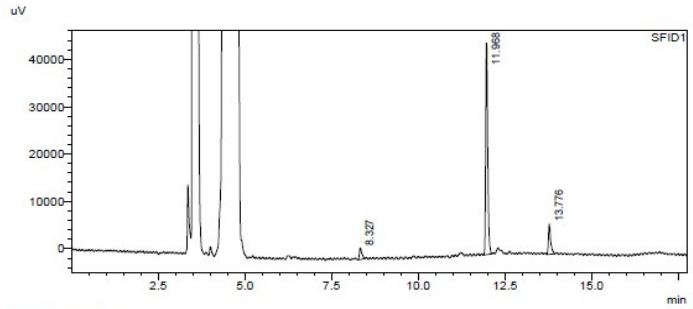


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	4.470	1076520	222030	41.983	41.983
2	4.695	105382	30677	4.110	4.110
3	11.954	526901	130278	20.548	20.548
4	13.886	855400	131146	33.359	33.359
Total		2564202	514132		100.000

18. GC Spectrum for regeneration of amine **1q**:

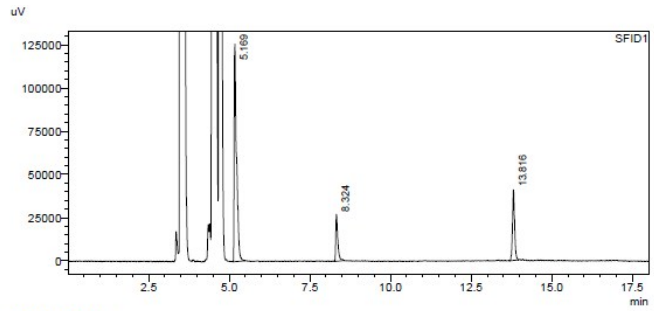


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.327	11957	2425	5.488	5.488
2	11.968	176561	44688	81.041	81.041
3	13.776	29349	6423	13.471	13.471
Total		217867	53536		100.000

19. GC Spectrum for regeneration of amine **1r**:

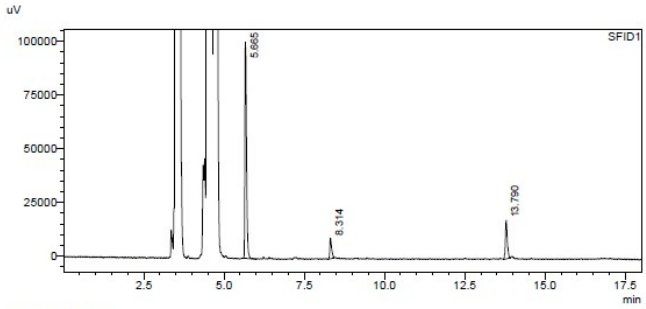


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.169	623212	126143	66.845	66.845
2	8.324	120423	27189	12.916	12.916
3	13.816	188688	40933	20.239	20.239
Total		932324	194266		100.000

20. GC Spectrum for regeneration of amine **1s**:

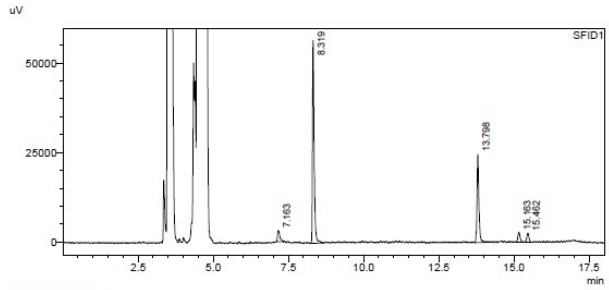


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.665	343229	100717	74.964	74.964
2	8.314	39145	9658	8.550	8.550
3	13.790	75482	17956	16.486	16.486
Total		457856	128331		100.000

21. GC Spectrum for regeneration of amine **1t**:

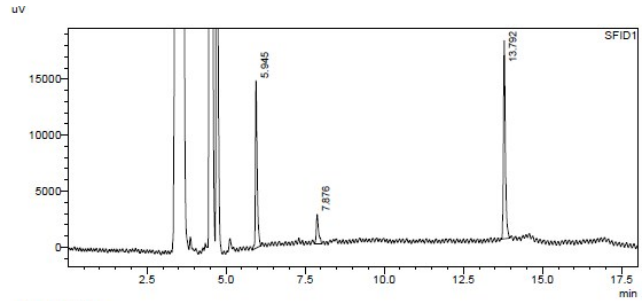


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.163	16965	3142	4.513	4.513
2	8.319	223394	56703	59.430	59.430
3	13.798	109177	24712	29.045	29.045
4	15.163	13444	2813	3.577	3.577
5	15.462	12914	2581	3.436	3.436
Total		375894	89951		100.000

22. GC Spectrum for regeneration of amine **1u**:

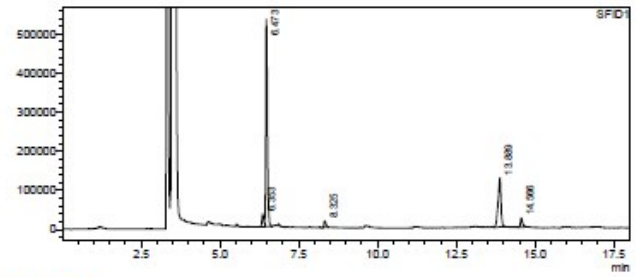


<Peak Table>

SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.945	57584	14962	39.269	39.269
2	7.876	12905	2653	8.800	8.800
3	13.792	76153	17706	51.931	51.931
Total		146642	35321		100.000

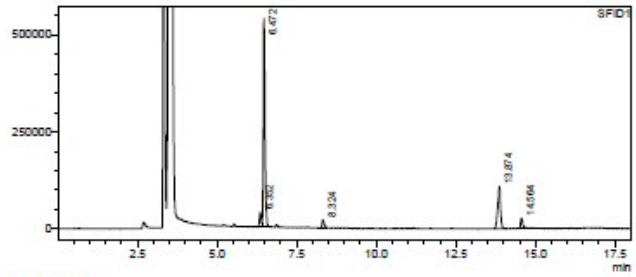
23. GC Spectrum for p-TSA mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.353	120206	32842	4.021	4.021
2	6.473	1878338	531200	62.831	62.831
3	8.325	79678	17621	2.665	2.665
4	13.889	796071	127120	26.629	26.629
5	14.566	115192	24315	3.853	3.853
Total		2989486	733096		100.000

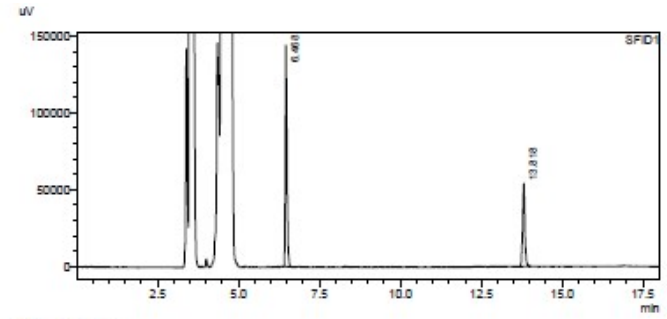
24. GC Spectrum for $ZnCl_2$ mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.352	146169	39285	4.961	4.961
2	6.472	1920691	537651	65.195	65.195
3	8.324	93897	21247	3.187	3.187
4	13.874	659033	109563	22.368	22.368
5	14.564	126365	26744	4.289	4.289
Total		2946356	734590		100.000

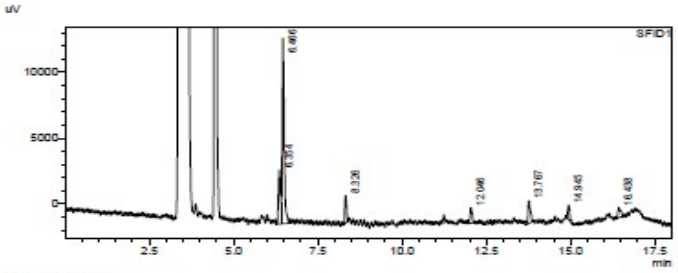
25. GC Spectrum for $Zn(OAc)_2$ mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.468	502376	144546	65.675	65.675
2	13.818	262562	54431	34.325	34.325
Total		764938	199077		100.000

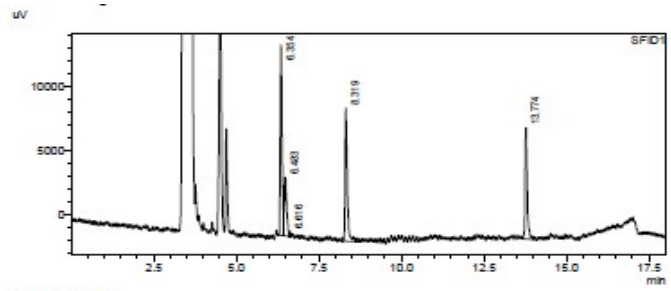
26. GC Spectrum for H_2O mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.354	17459	4121	16.716	16.716
2	6.466	56730	14116	54.313	54.313
3	8.326	7673	2130	7.347	7.347
4	12.046	5438	1189	5.207	5.207
5	13.767	8412	1737	8.054	8.054
6	14.945	4616	1092	4.419	4.419
7	16.438	4120	772	3.945	3.945
Total		104450	25158		100.000

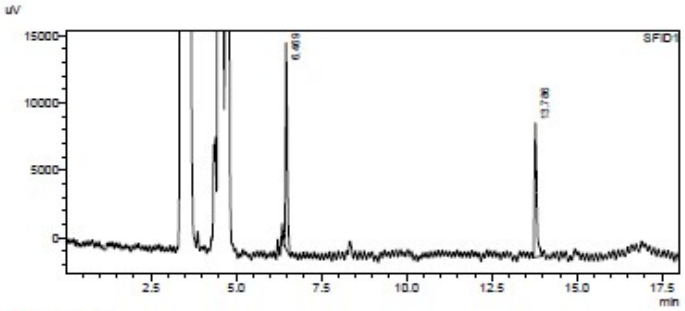
27. GC Spectrum for meat deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.354	58639	14813	35.038	35.038
2	6.483	22418	4581	13.418	13.418
3	6.616	1151	427	0.689	0.689
4	8.319	46457	10402	27.807	27.807
5	13.774	38505	8672	23.047	23.047
Total		167070	38896		100.000

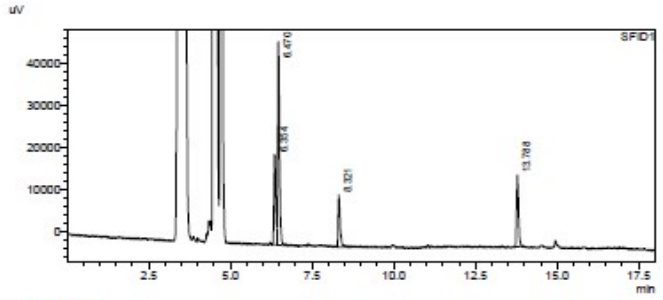
28. GC Spectrum for KO^{t}Bu mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.469	54931	15252	55.395	55.395
2	13.786	44231	9959	44.605	44.605
Total		99162	25212		100.000

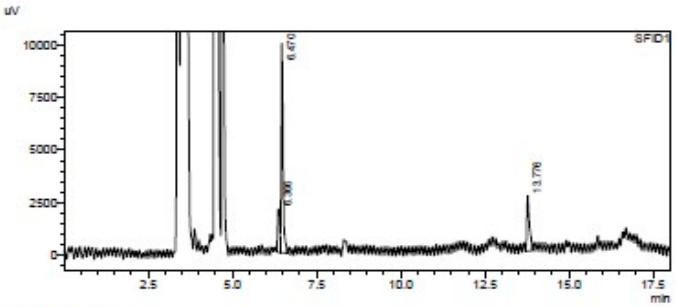
29. GC Spectrum for NaH mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.354	78541	21448	20.283	20.283
2	6.470	184081	48491	47.539	47.539
3	8.321	52965	12380	13.678	13.678
4	13.788	71632	17115	18.499	18.499
Total		387219	99434		100.000

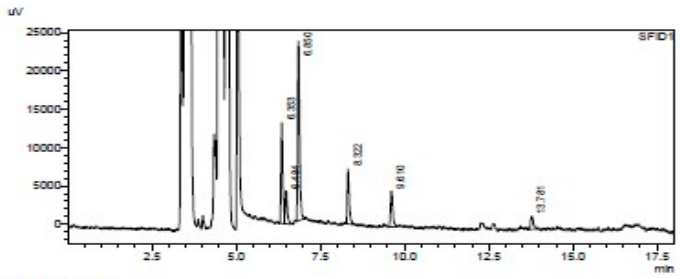
30. GC Spectrum for DBU mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.366	8441	2060	14.103	14.103
2	6.470	37805	9940	63.167	63.167
3	13.776	13604	2651	22.730	22.730
Total		59850	14651		100.000

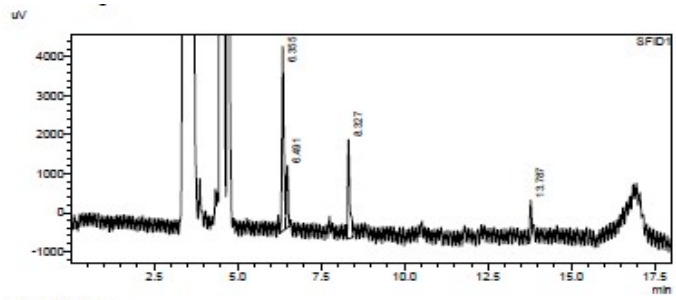
31. GC Spectrum for CaH_2 mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.353	50725	13215	22.617	22.617
2	6.484	19068	4323	8.065	8.065
3	6.650	94292	23440	42.041	42.041
4	8.322	29032	7150	12.944	12.944
5	9.510	22031	4713	9.823	9.823
6	13.781	10116	1729	4.510	4.510
Total		224265	54579		100.000

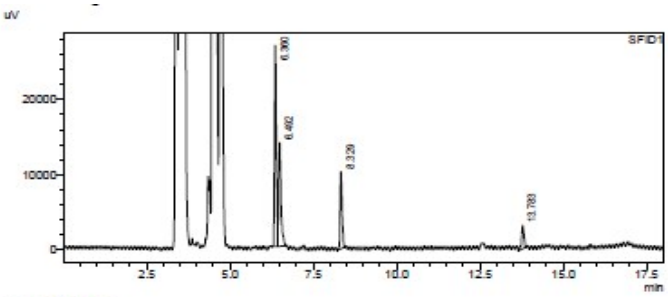
32. GC Spectrum for Oxone mediated deprotection:



<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.355	19895	4758	49.668	49.668
2	6.491	5688	1602	14.201	14.201
3	8.327	11324	2558	28.271	28.271
4	13.787	3148	951	7.860	7.860
Total		40056	9868		100.000

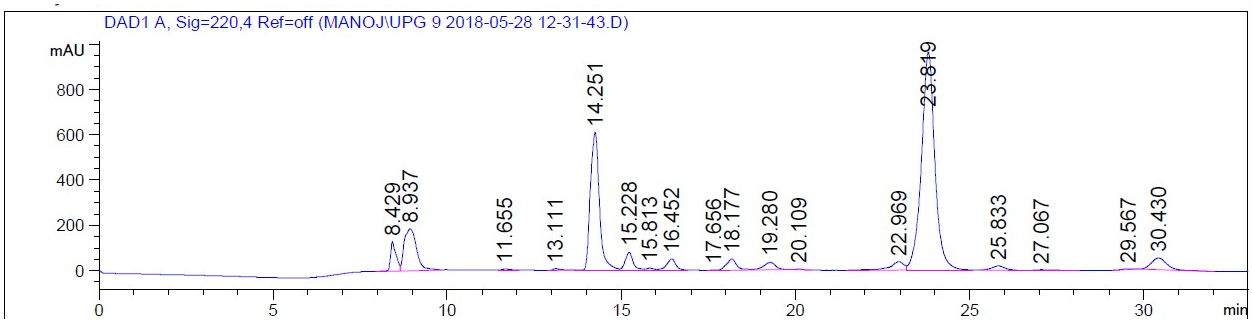
33. GC Spectrum for CAN mediated deprotection:



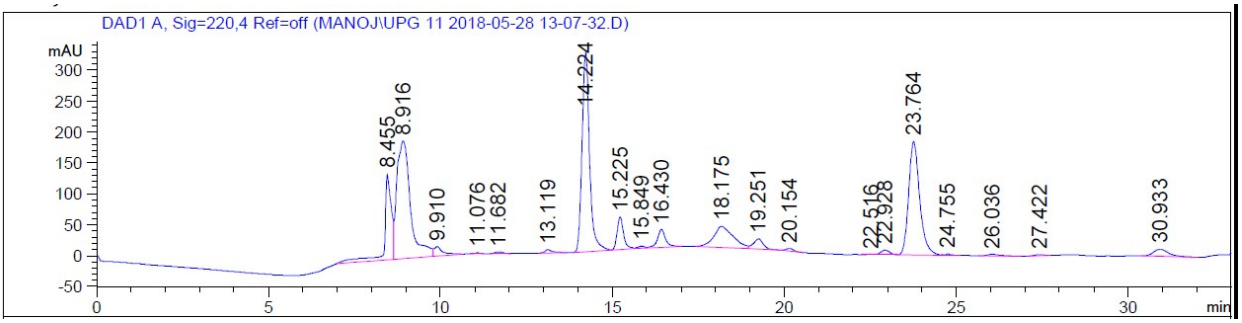
<Peak Table>
SFID1

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.360	105042	26824	46.196	46.196
2	6.492	64377	13817	28.259	28.259
3	8.329	42809	10321	18.791	18.791
4	13.783	15387	3106	6.754	6.754
Total		227615	54067		100.000

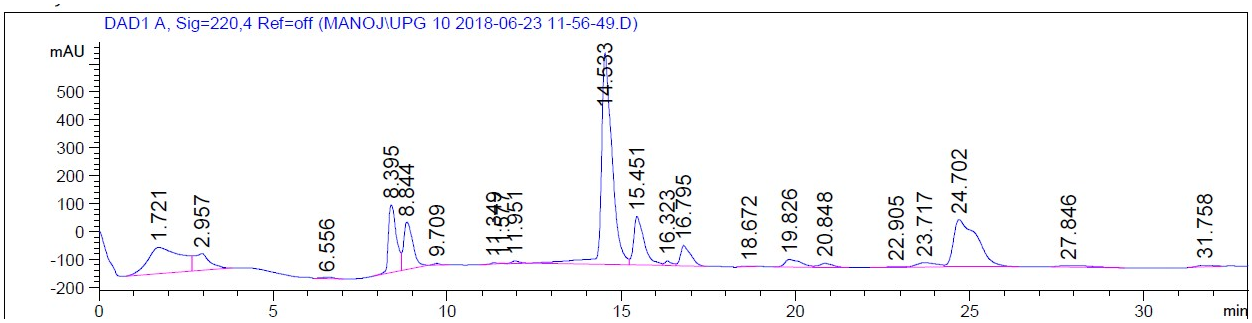
34. HPLC Profile for reaction mixture at 30 min.



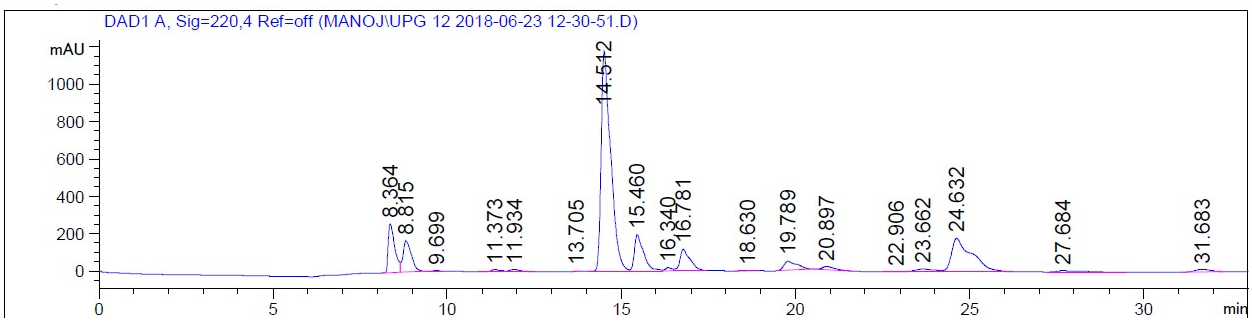
35. HPLC Profile for reaction mixture at 60 min.



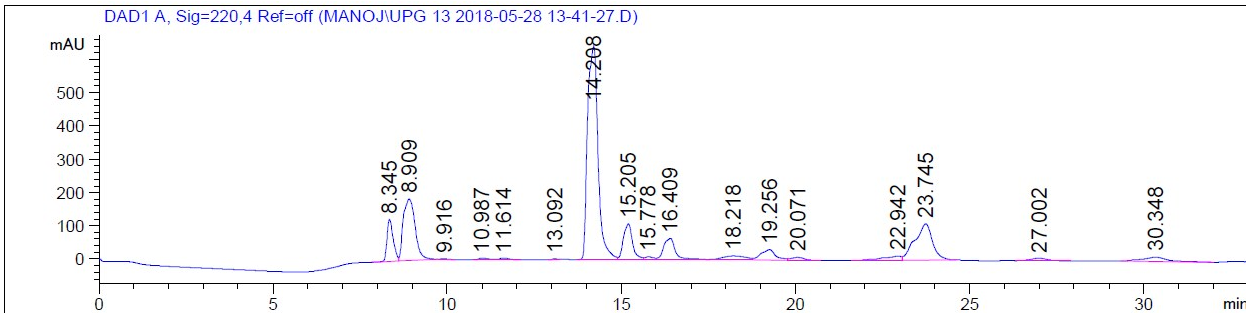
36. HPLC Profile for reaction mixture at 90 min.



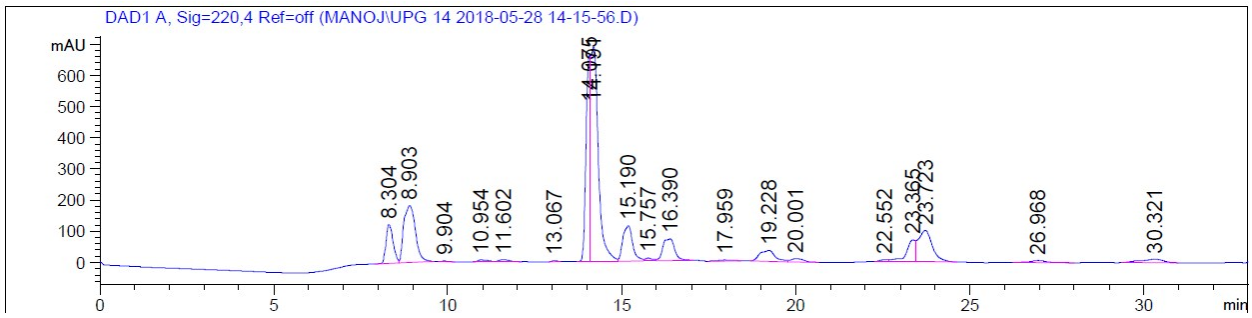
37. HPLC Profile for reaction mixture at 120 min.



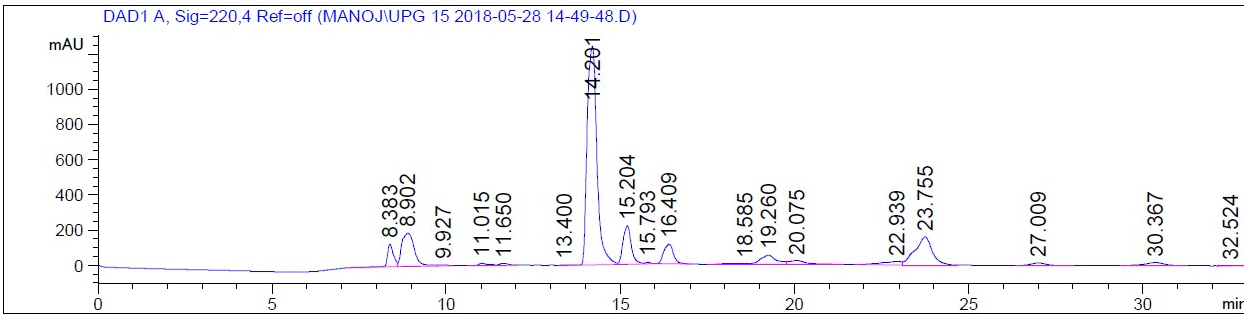
38. HPLC Profile for reaction mixture at 150 min.



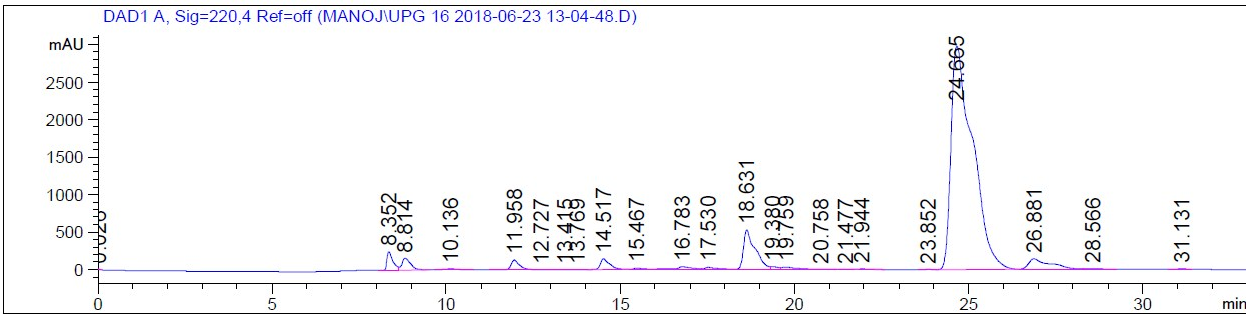
39. HPLC Profile for reaction mixture at 180 min.



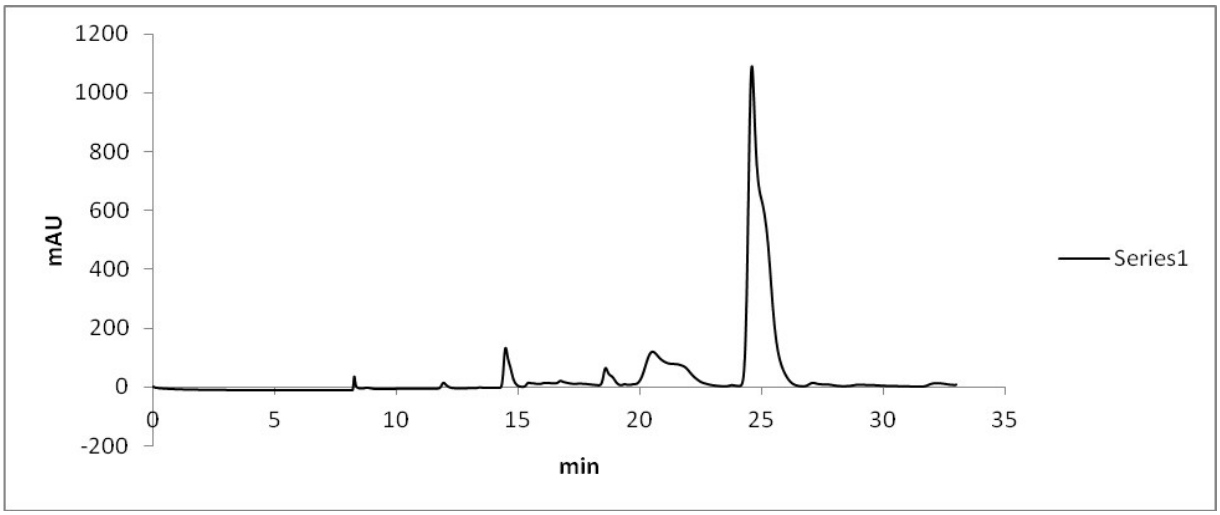
40. HPLC Profile for reaction mixture at 240 min.



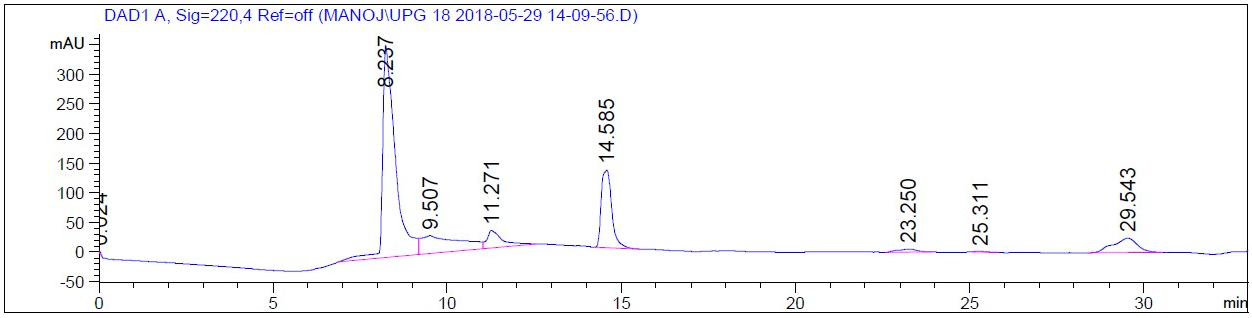
41. HPLC Profile for reaction mixture at 50 °C.



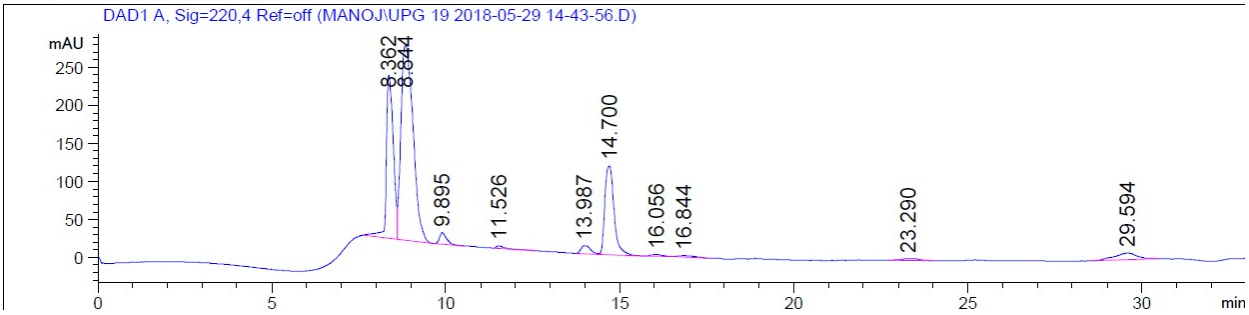
42. HPLC Profile for reaction mixture at 70 °C.



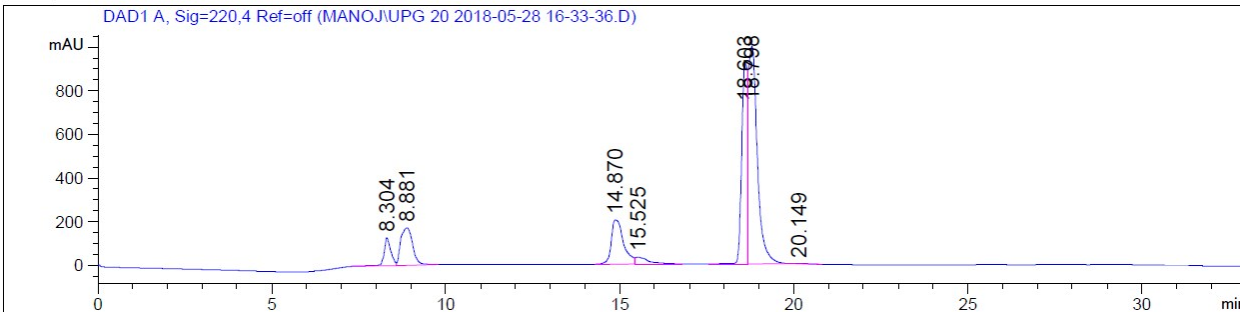
43. HPLC Profile for reaction mixture at 90 °C.



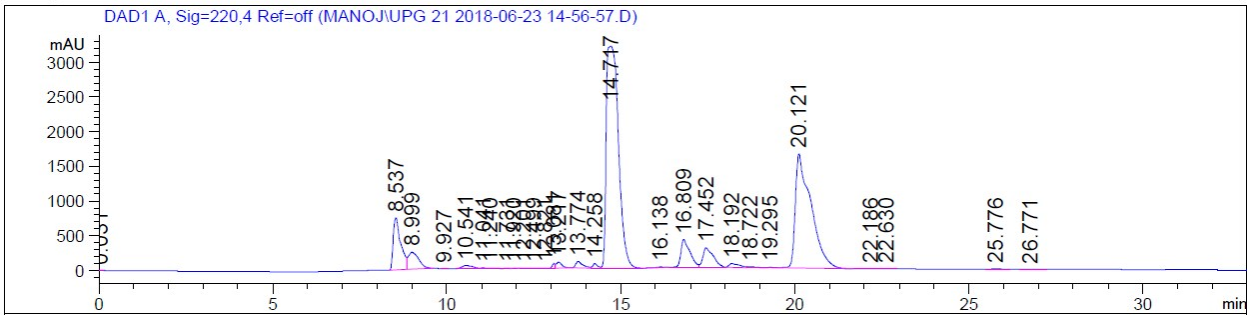
44. HPLC Profile for reaction mixture at 120 °C.



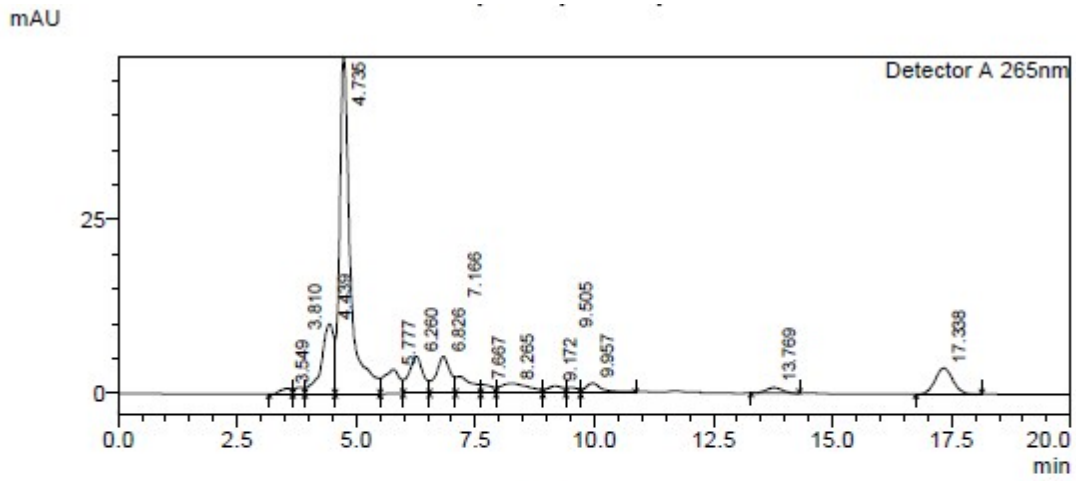
45. HPLC Profile for pure 1-(3-Hydroxy-phenyl)-3-o-tolyl-urea



46. HPLC Profile for reaction mixture of 1-(3-Hydroxy-phenyl)-3-o-tolyl-urea



47. HPLC Profile (S)-Phenylmethylamine recovered after deprotection:

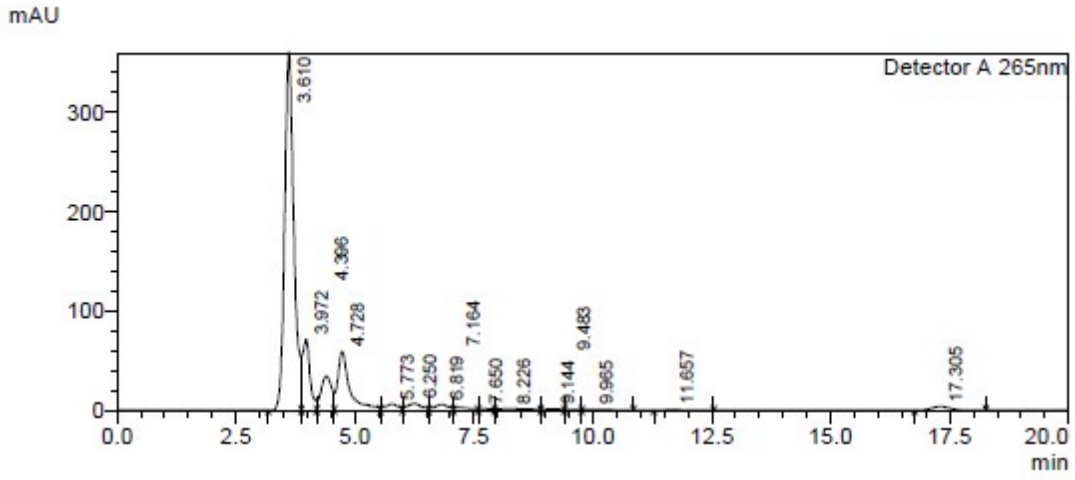


Peak Table

Detector A 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.549	12503	804	0.000			
2	3.810	12783	968	0.000		V	
3	4.439	182497	10005	0.000		V	
4	4.735	755315	48274	0.000		V	
5	5.777	79000	3462	-0.103	mM	V	Acid
6	6.260	111290	5339	0.000		V	
7	6.826	111654	5294	0.000		V	
8	7.166	57313	2455	0.000		V	
9	7.667	20414	1246	0.000		V	
10	8.265	61274	1457	-0.032	mM	V	methyl
11	9.172	24236	1007	0.000		V	
12	9.505	14317	856	0.000		V	
13	9.957	390555	1445	0.000		V	
14	13.769	17950	791	0.000			
15	17.338	95249	3716	0.000			
Total		1594849	87119				

48. HPLC Profile (R)-Phenylmethylamine recovered after deprotection:



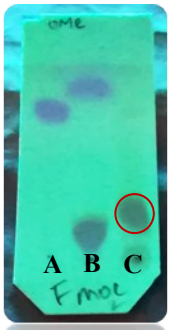
Peak Table

Detector A 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.610	4843042	358885	0.000			
2	3.972	801095	71227	0.000		V	
3	4.396	535200	34235	0.000		V	
4	4.728	1030672	59310	0.000		V	
5	5.773	127616	6179	-0.103	mM	V	Acid
6	6.250	148573	6651	0.000		V	
7	6.819	125375	5851	0.000		V	
8	7.164	73761	3143	0.000		V	
9	7.650	30806	1668	0.000		V	
10	8.226	72929	1702	-0.032	mM	V	methyl
11	9.144	27345	1033	0.000		V	
12	9.483	15375	838	0.000		V	
13	9.965	25490	637	0.000		V	
14	11.657	12426	366	0.000		V	
15	17.305	105065	4008	0.000		V	
Total		7974770	555752				

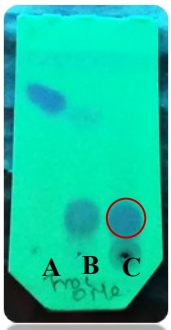
49. TLC profile:

TLC profile for entry **10**:



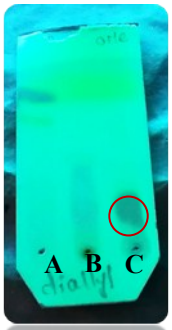
A: Reactant
B: Rex mix
C: H/CH_3

TLC profile for entry **12**:



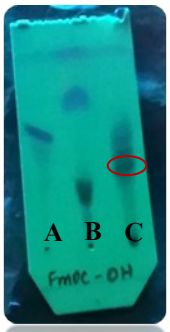
A: Reactant
B: Rex mix
C: H/ CH_3

TLC profile for entry **13**:



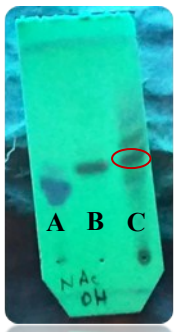
A: Reactant
B: Rex mix
C: H/ CH_3

TLC profile for entry **15**:



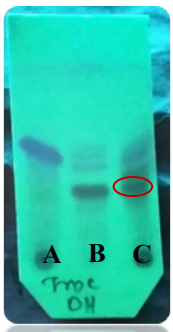
A: Reactant
B: Rex mix
C: H/H

TLC profile for entry **16**:



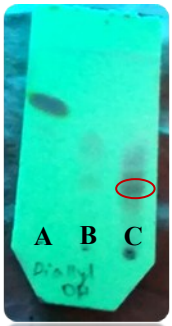
A: Reactant
B: Rex mix
C: H/H

TLC profile for entry **17**:

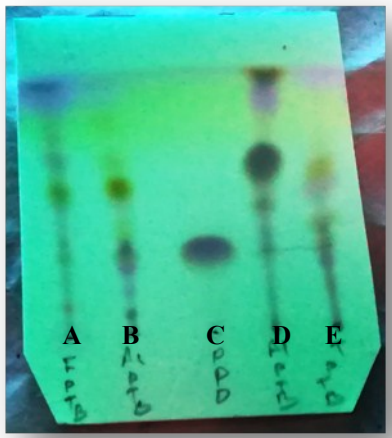


A: Reactant
B: Rex mix
C: H/H

TLC profile for entry **18**:

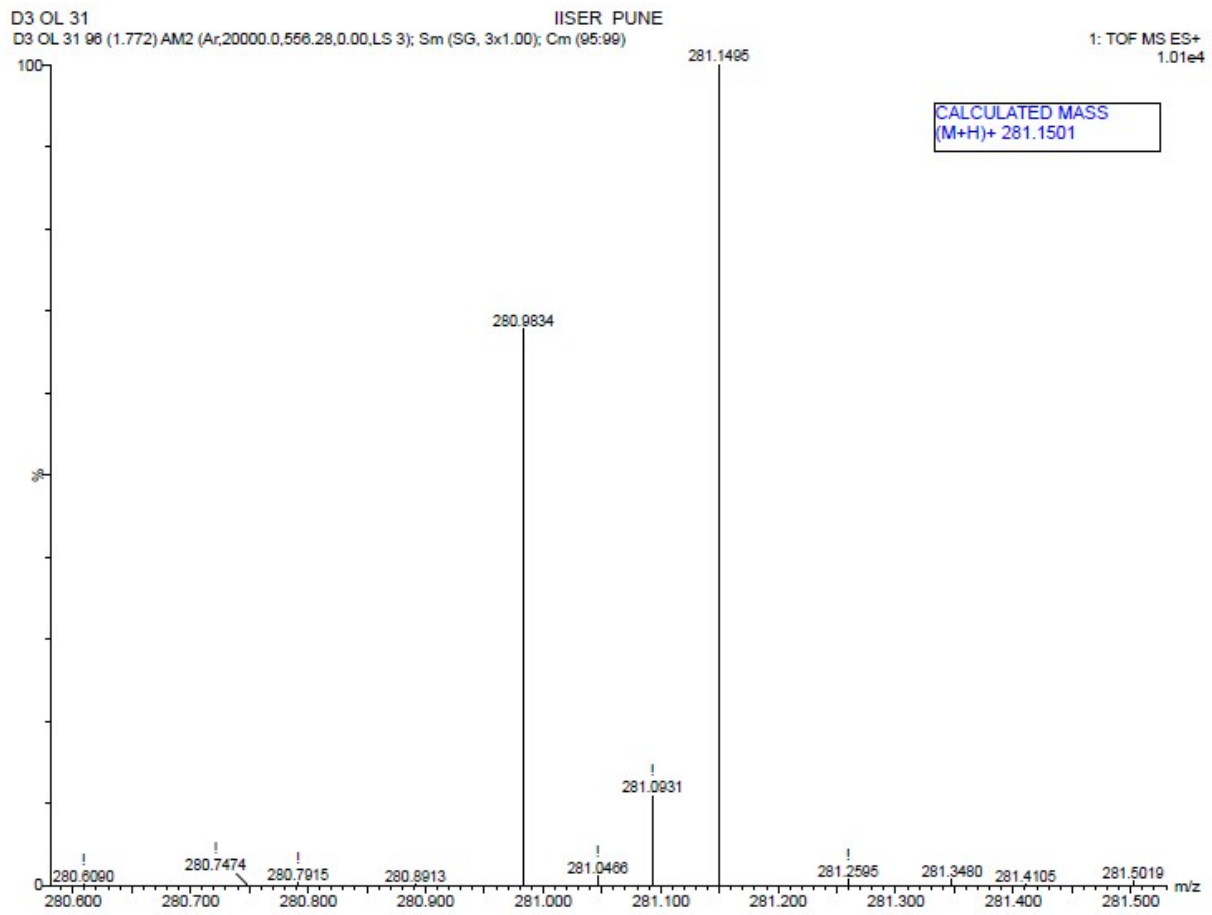


A: Reactant
B: Rex mix
C: H/H

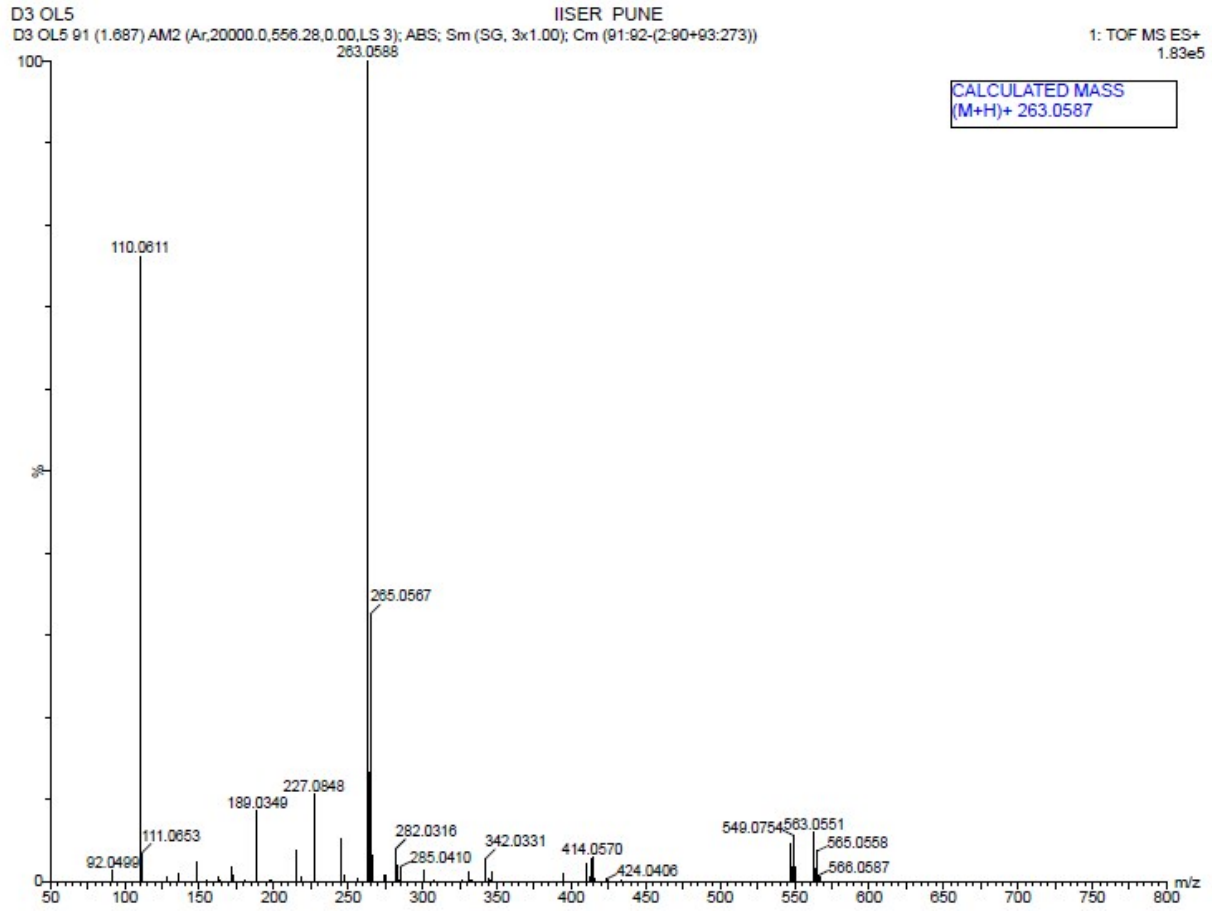


A = 15 rex mix; B = 16 rex mix;C = *p*-phenylenediamine;
D = 18 rex mix; E = 17 rex mix;

50. HRMS of **2q**

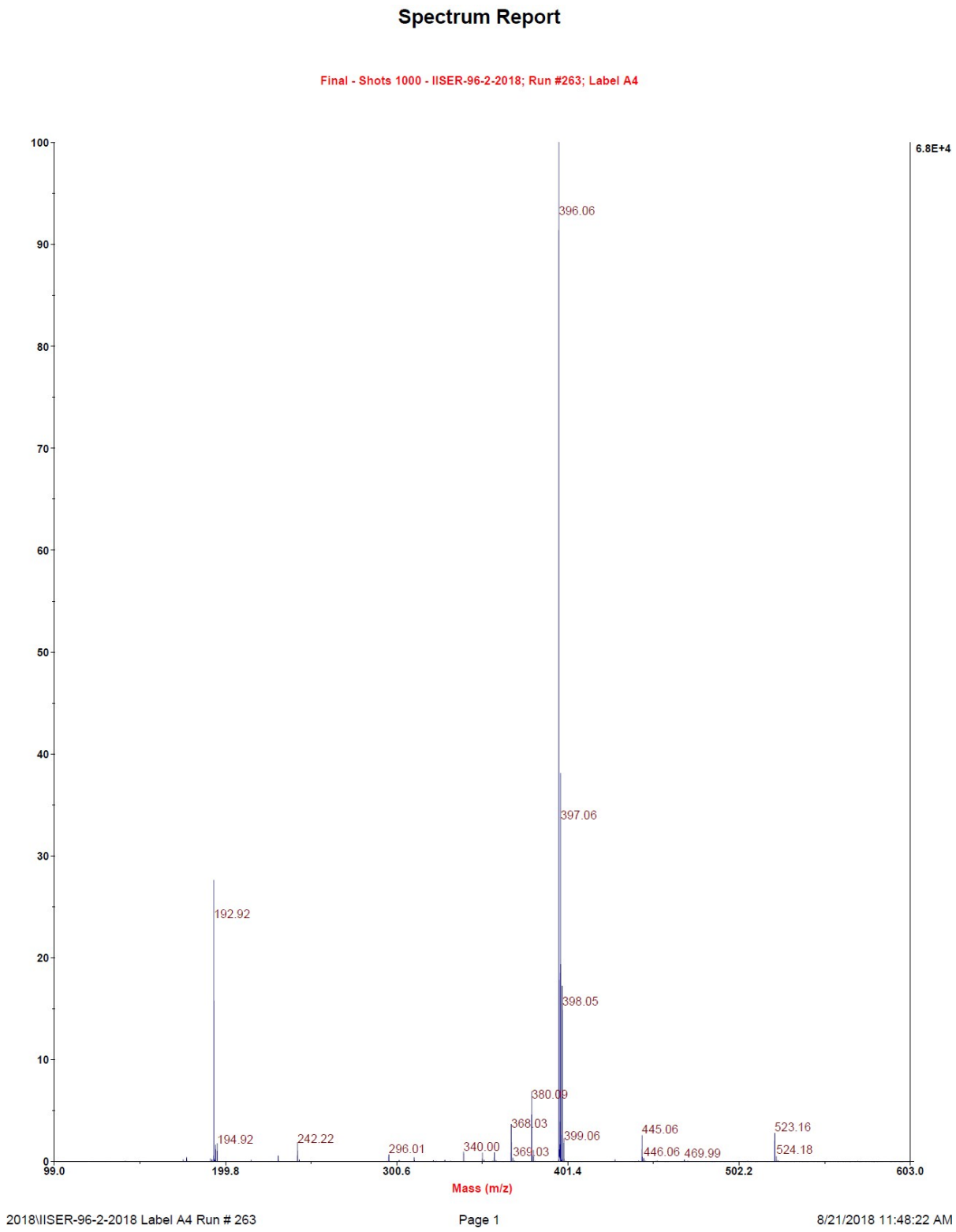

D3 OL 31
IISER PUNE
D3 OL 31 96 (1.772) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00); Cm (95:99)
1: TOF MS ES+
1.01e4
CALCULATED MASS
(M+H)+ 281.1501
281.1496
280.9834
281.0931
280.6090
280.7474
280.7915
280.8913
281.0466
281.2595
281.3480
281.4105
281.5019
%
m/z

51. HRMS of **3c**

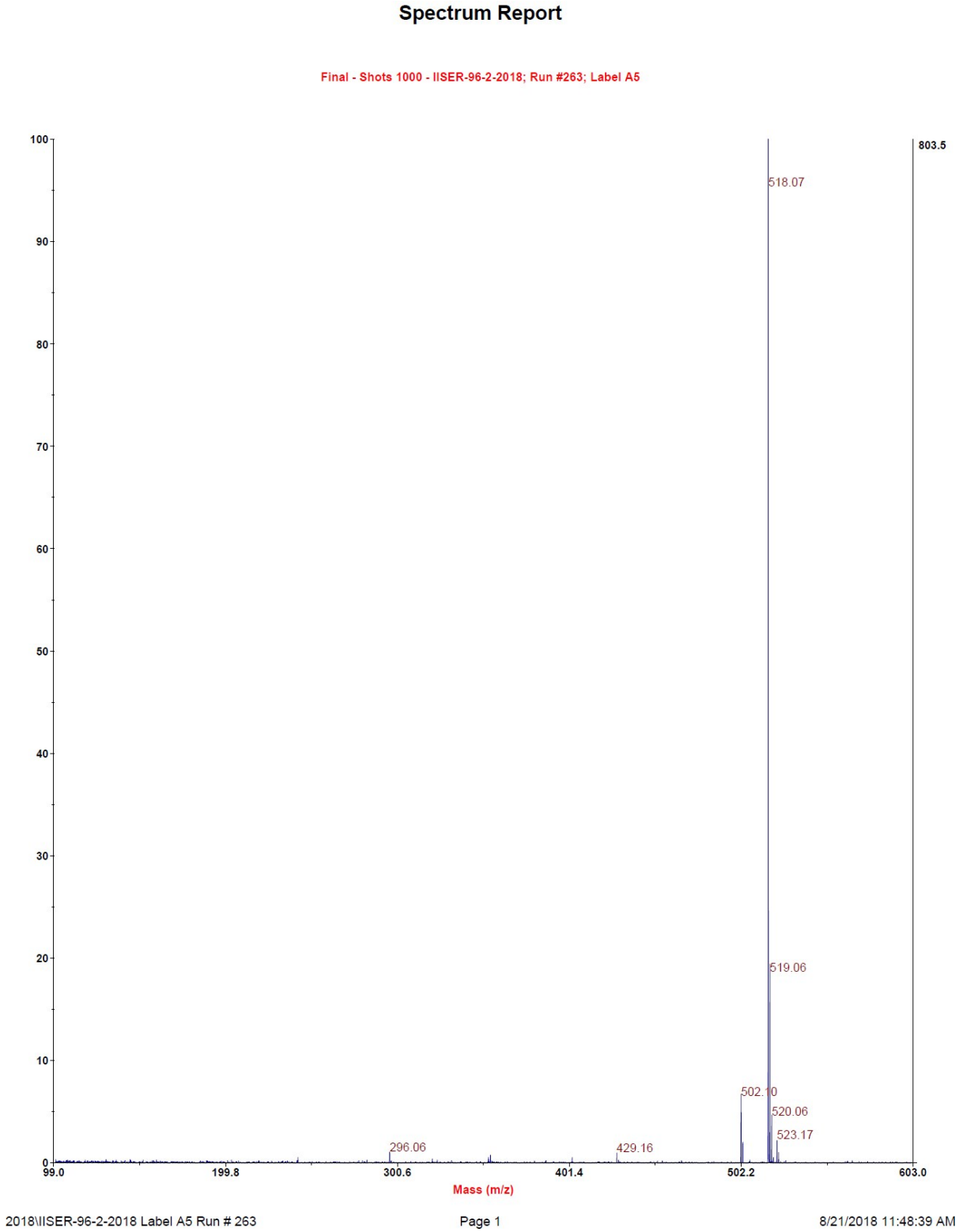

D3 OL5
IISER PUNE
D3 OL5 91 (1.687) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 3x1.00); Cm (91:92-(2:90+93:273))
1: TOF MS ES+
1.83e5
CALCULATED MASS
(M+H)+ 263.0587
263.0588
110.0611
265.0567
227.0848
189.0349
111.0653
92.0499
282.0316
285.0410
342.0331
414.0570
424.0406
549.0754
563.0551
565.0558
566.0587
%
m/z

52. HRMS of **3f**

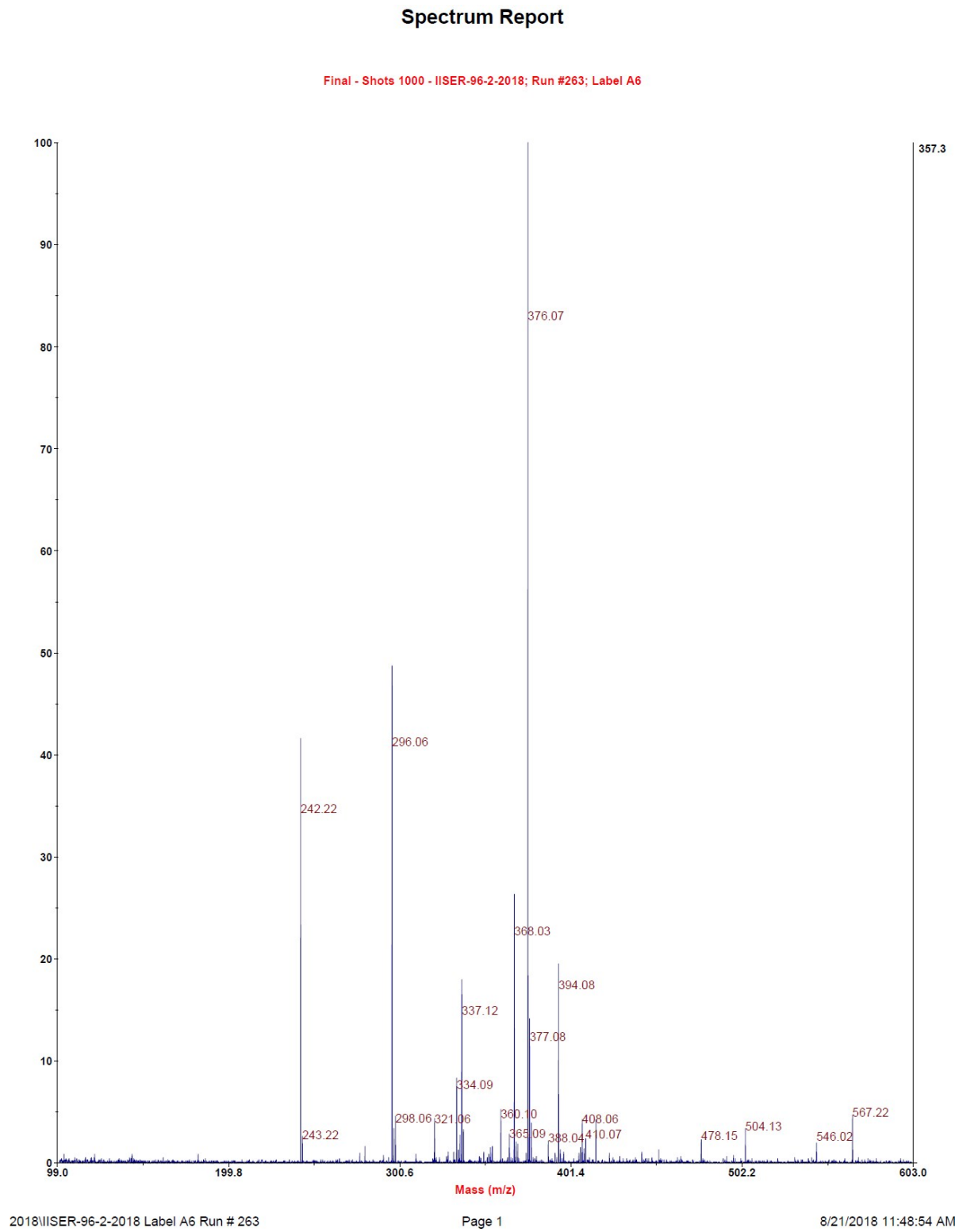
53. LRMS of **9**


Spectrum Report
Final - Shots 1000 - IISER-96-2-2018; Run #263; Label A4
6.8E+4
396.06
397.06
192.92
398.05
380.09
368.03
399.06
445.06
523.16
194.92
242.22
296.01
340.00
369.03
446.06
469.99
524.18
100
90
80
70
60
50
40
30
20
10
0
99.0
199.8
300.6
401.4
502.2
603.0
Mass (m/z)
2018\IISER-96-2-2018 Label A4 Run # 263
Page 1
8/21/2018 11:48:22 AM

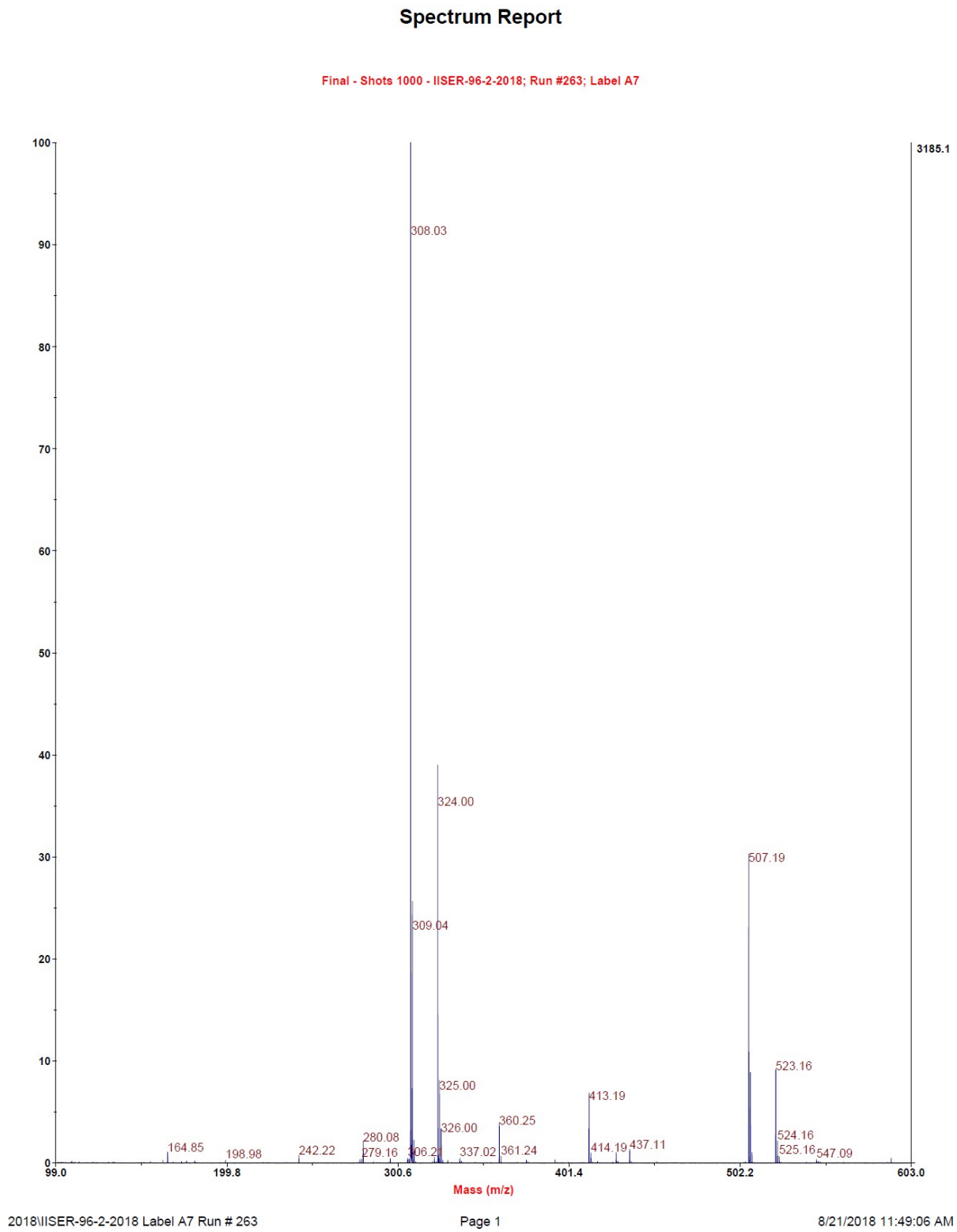
54. LRMS of **10**


Spectrum Report
Final - Shots 1000 - IISER-96-2-2018; Run #263; Label A5
100
90
80
70
60
50
40
30
20
10
0
803.5
518.07
519.06
502.10
520.06
523.17
296.06
429.16
99.0
199.8
300.6
401.4
502.2
603.0
Mass (m/z)
2018\IISER-96-2-2018 Label A5 Run # 263
Page 1
8/21/2018 11:48:39 AM

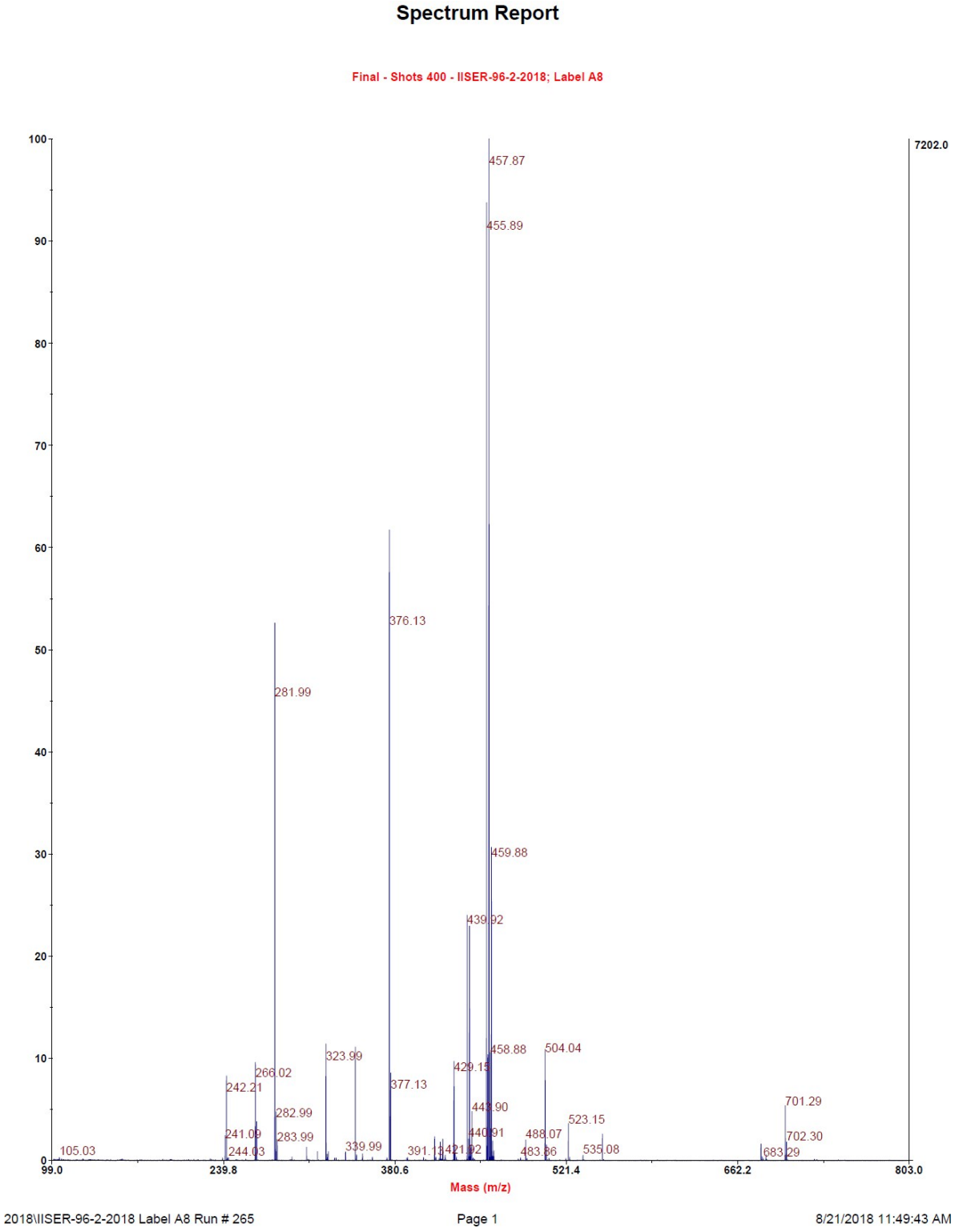
55. LRMS of **13**


Spectrum Report
Final - Shots 1000 - IISER-96-2-2018; Run #263; Label A6
357.3
376.07
296.06
242.22
368.03
394.08
337.12
377.08
334.09
298.06
321.06
360.10
365.09
388.04
408.06
410.07
243.22
478.15
504.13
546.02
567.22
100
90
80
70
60
50
40
30
20
10
0
99.0
199.8
300.6
401.4
502.2
603.0
Mass (m/z)
2018\IISER-96-2-2018 Label A6 Run # 263
Page 1
8/21/2018 11:48:54 AM

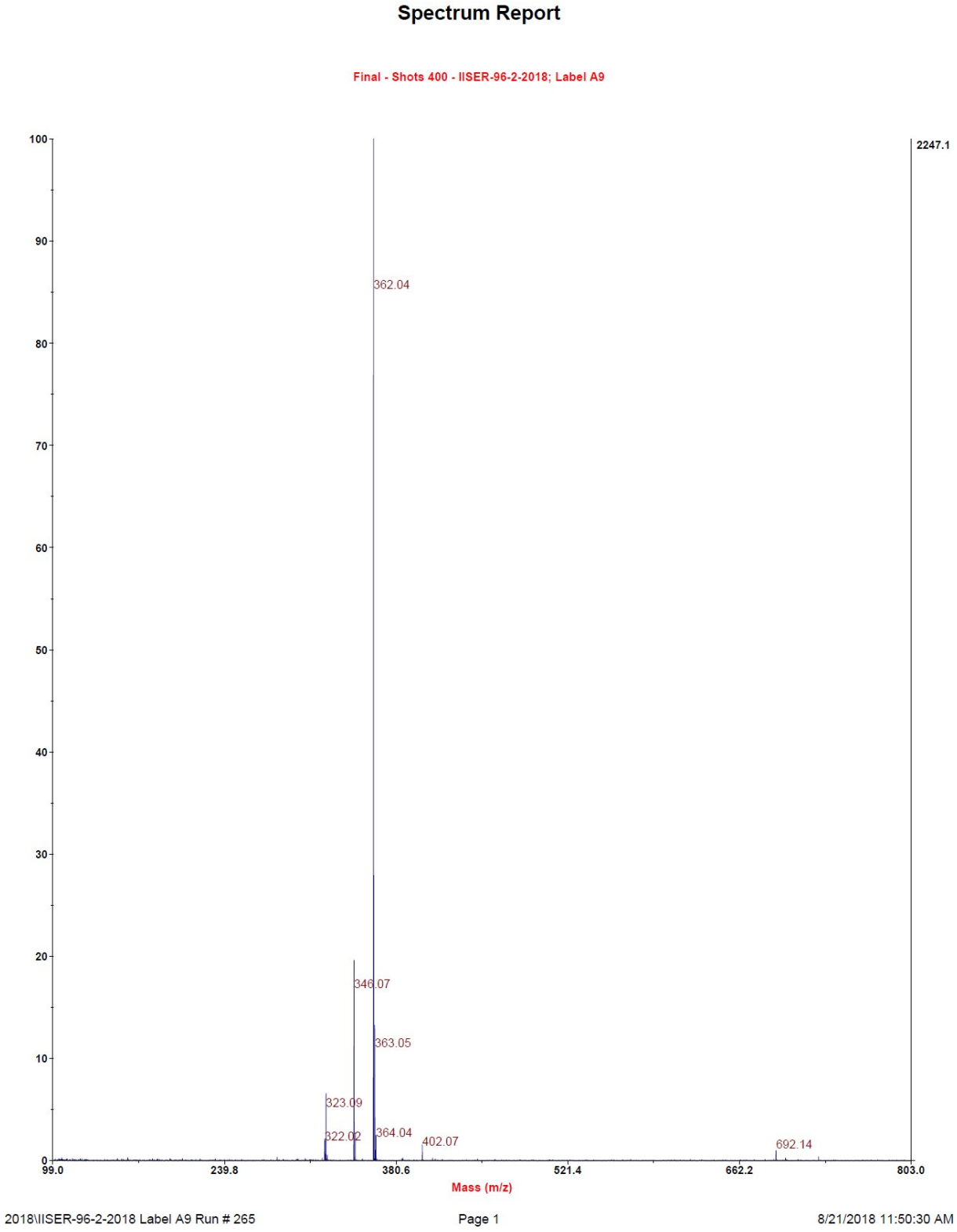
56. LRMS of **16**


Spectrum Report
Final - Shots 1000 - IISER-96-2-2018; Run #263; Label A7
3185.1
308.03
324.00
309.04
507.19
523.16
325.00
413.19
326.00
360.25
524.16
164.85
198.98
242.22
280.08
279.16
306.21
337.02
361.24
414.19
437.11
525.16
547.09
Mass (m/z)
2018\IISER-96-2-2018 Label A7 Run # 263
Page 1
8/21/2018 11:49:06 AM

57. LRMS of **17**


Spectrum Report
Final - Shots 400 - IISER-96-2-2018; Label A8
7202.0
457.87
455.89
376.13
281.99
459.88
439.92
458.88
504.04
323.99
266.02
242.21
429.15
377.13
282.99
701.29
523.15
241.09
283.99
339.99
702.30
105.03
244.03
535.08
683.29
Mass (m/z)
2018\IISER-96-2-2018 Label A8 Run # 265
Page 1
8/21/2018 11:49:43 AM

58. LRMS of **18**


Spectrum Report
Final - Shots 400 - IISER-96-2-2018; Label A9
2247.1
362.04
346.07
363.05
323.09
322.02
364.04
402.07
692.14
100
90
80
70
60
50
40
30
20
10
0
99.0
239.8
380.6
521.4
662.2
803.0
Mass (m/z)
2018\IISER-96-2-2018 Label A9 Run # 265
Page 1
8/21/2018 11:50:30 AM