APPENDICES

Appendix 1

DEVELOPMENT OF A SCANNER TO ESTIMATE TOTAL VISUAL SET OFF

Procedures

The following procedures show the sequence of events required to setup the instrument, calibrate the instrument and perform a test.

Setup

1. Adjust the height of the camera to achieve the required scan area and resolution.
2. Ensure the lights give an even coverage over the observed sample area.
3. Focus the lens and set the scale of the image.
4. Calibrate the instrument using palettes created from the substrate and ink residues to be examined for. Palettes should be prepared using the method described in FSA project A03010/11/12 [ref 1 page 89].

Camera optimisation

1. Exposure time should be adjusted to clearly show the set off palette on the calibration plaque.
2. Set the focus to clearly show the palette.
3. Adjust the offset to bring peak colour levels below 255.
4. Identify the dominant background colour and reduce the gain and offset to give the greatest contrast between palette and background.
5. Determine the dominant colour of the set off palette and adjust the gain and offsets to increase the intensity.
6. Ensure that a good range of pixel intensities are present (20 – 230).
7. Capture the image.

Image optimisation

8. Apply softening/smoothing to minimise any texture in the image background.
9. Adjust image brightness settings to highlight the set off against the background.
10. Apply the colour filters to achieve a maximum contrast between the set off and background – apply the colour filter to any colours not present.
11. Adjust the threshold levels to span the intensities of the set off.
12. Set the abundance of set off in ug/cm2 for the peak threshold level.
13. Save the setup.

Test scan

1. Enter the distance between the cameras home position and the of the start web.
2. Enter the width of the web.
3. Select appropriate scan parameters (speed and acceleration).
4. Enter the failure criteria in mg/100cm^2.
5. Start the test.

Calibration test

Figure 18 - Coated paper with IRGACURE 379 contamination under UV illumination

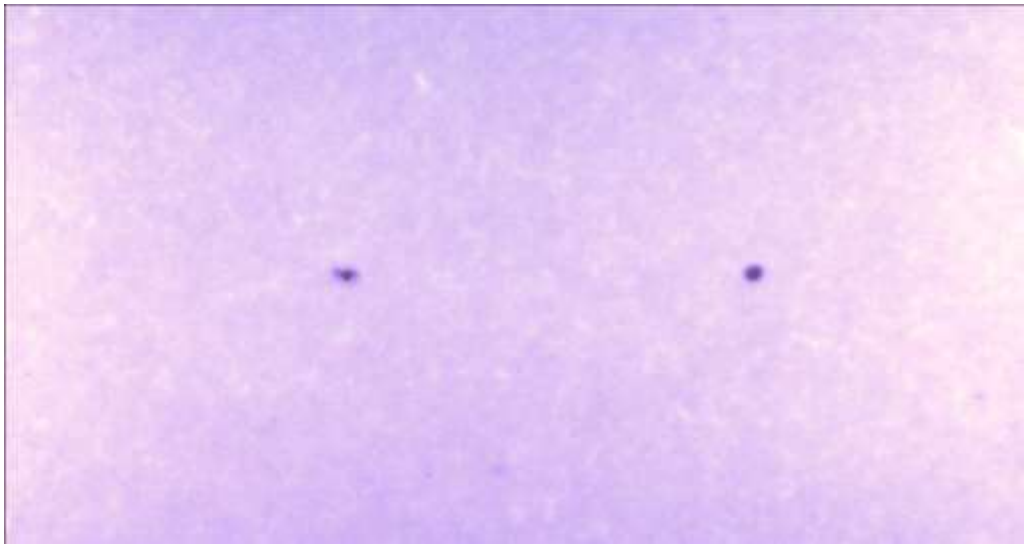


Figure 19 - Processed image of coated paper with IRGACURE 379 contamination under UV illumination

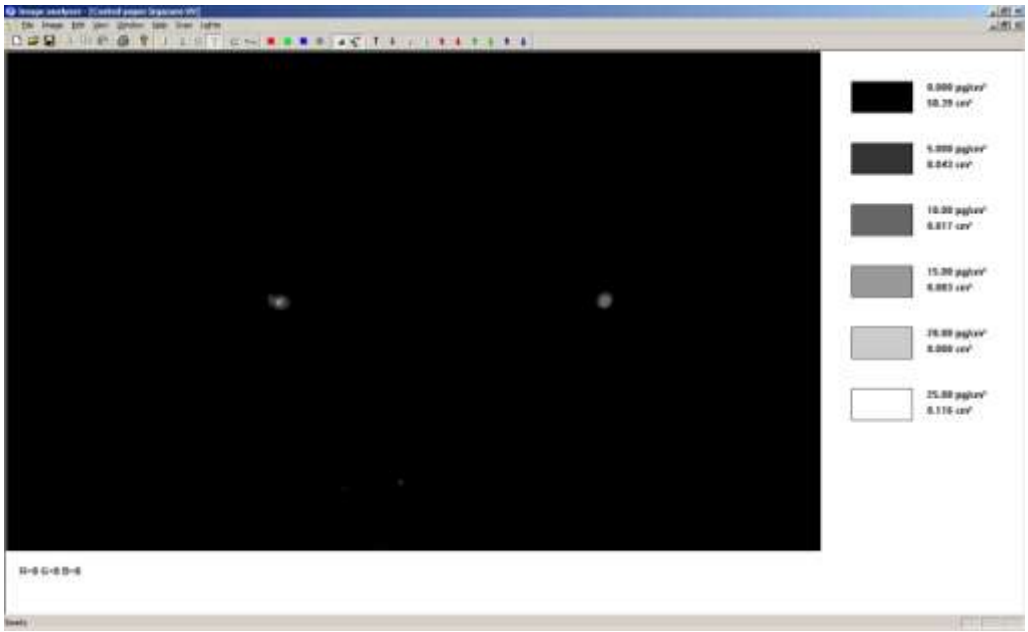


Figure 20 - Red film with IRGACURE 379 contamination under UV illumination

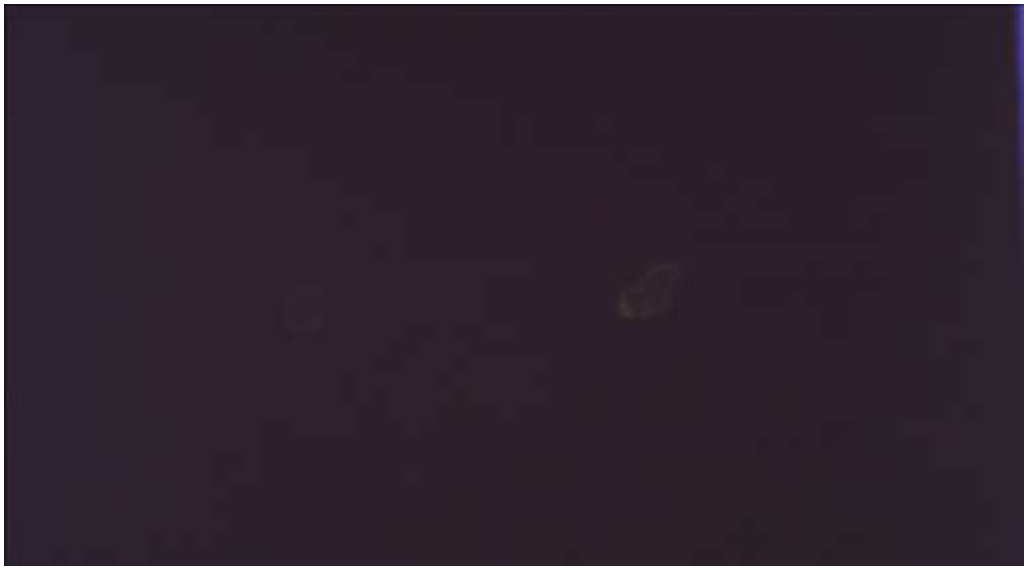


Figure 21 - Processed image of Red film with IRGACURE 379 contamination under UV illumination

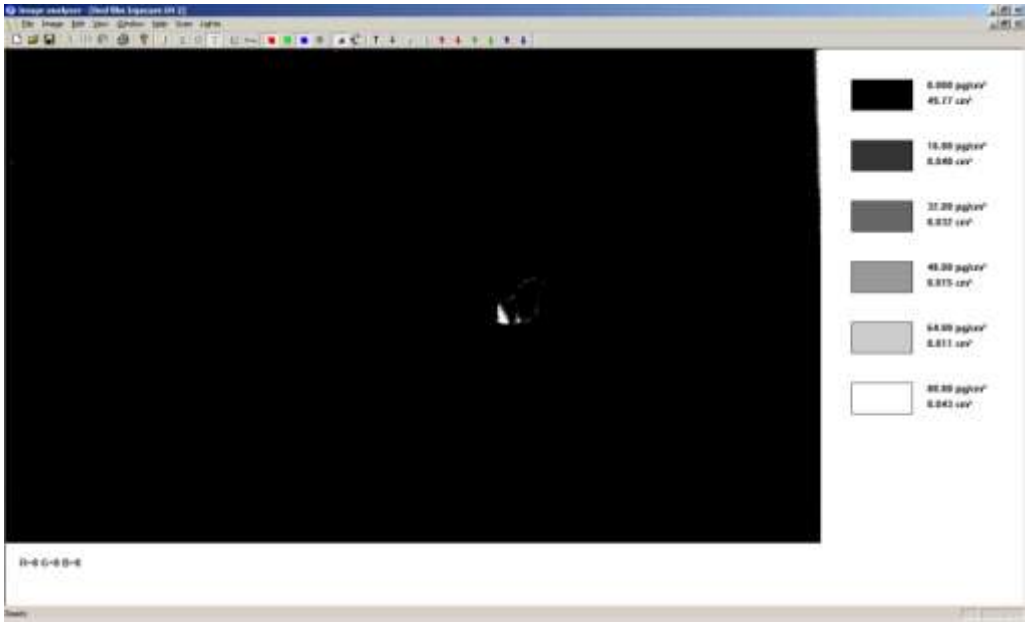


Figure 22 - Uncoated paper with IRGACURE 379 contamination under UV illumination

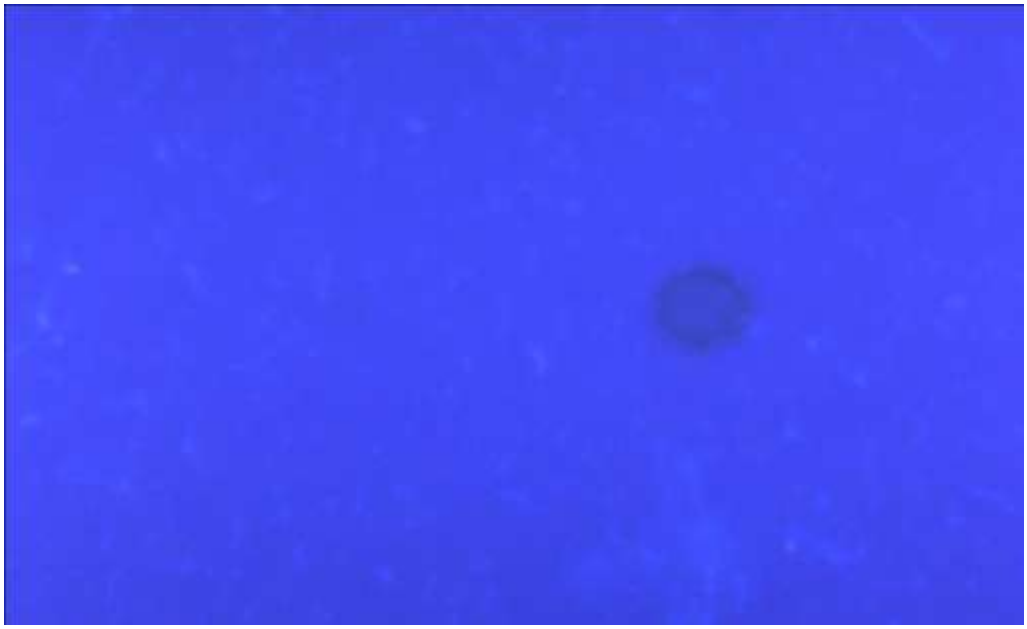


Figure 23 - Processed image of uncoated paper with IRGACURE 379 contamination under UV illumination

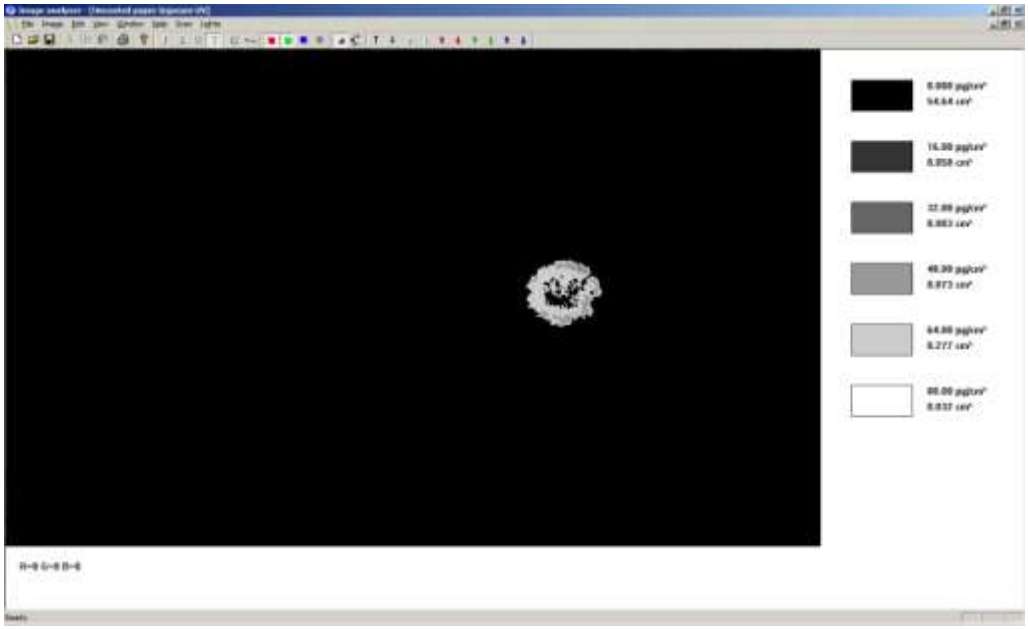


Figure 24 - White film (with print show-through) with IRGACURE 379 contamination under UV illumination

Figure 25 - Processed image of White film (with print show-through) with IRGACURE 379 contamination under UV illumination

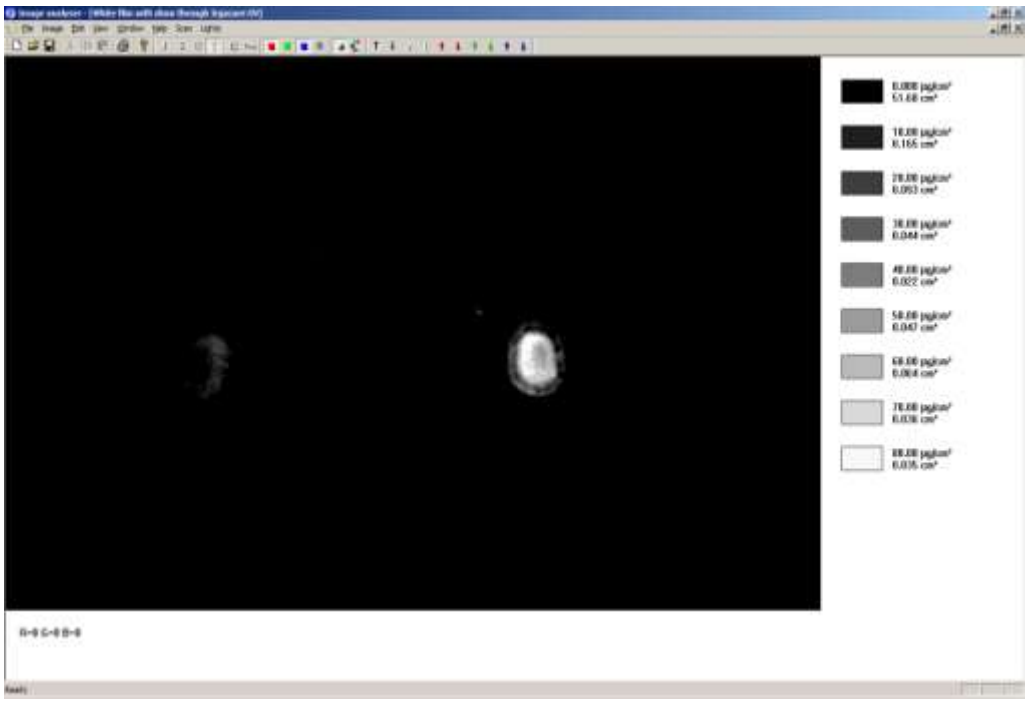
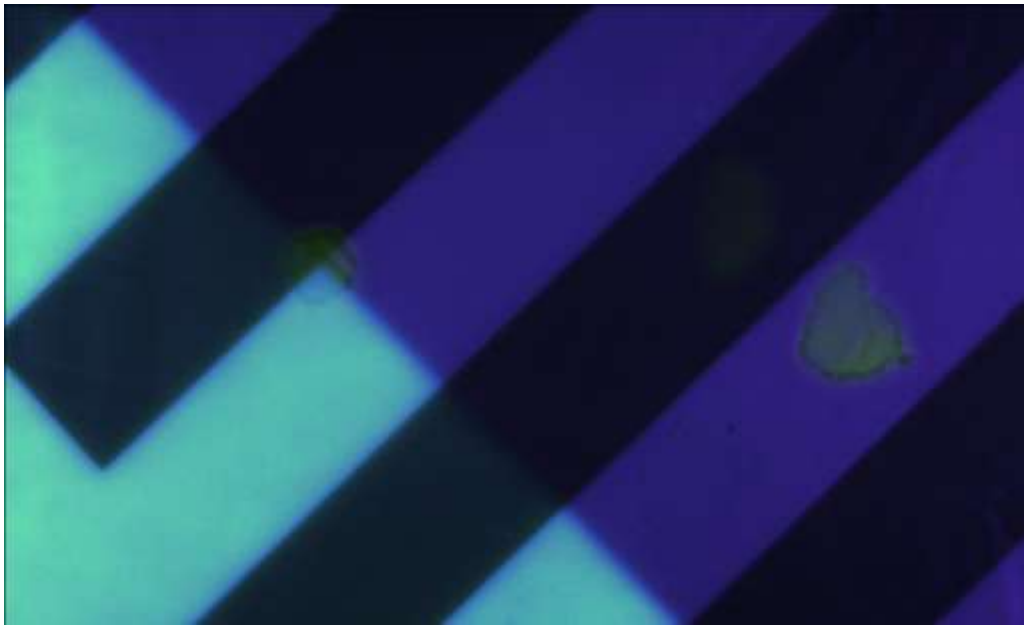


Figure 26 - Thin white film (with print show-through) contaminated with IRGACURE 379 under UV illumination



Example palette calibration settings for test films contaminated with IRGACURE 379

Parameters		Coated paper	Red film	Uncoated paper	White film with show through	Thin white film with show through	Aluminium foil
Camera settings	image height (pixels)	700	700	700	700	Could not be calibrated with current scanner setup	Could not be calibrated with current scanner setup
	image width (pixels)	1150	1150	1150	1150		
	exposure time (ms)	50	1000	100	500		
	colour offset (intensity 0-255)	-10	0	-20	-130		
	red gain (factor)	3	0.9	1.5	1		
	green gain (factor)	1.5	1	1.3	1.1		
	blue gain (factor)	1	0.6	1.1	0.5		
Softening	Radius (pixels)	0	0	1	1		
Colour optimisation	max red (intensity 0-255)	255	255	255	255		
	red band-pass filter	FALSE	FALSE	FALSE	FALSE		
	min red (intensity 0-255)	0	60	35	0		
	red cut-off amplifier	FALSE	FALSE	FALSE	FALSE		
	max green (intensity 0-255)	255	50	255	35		
	green band-pass filter	FALSE	FALSE	FALSE	FALSE		
	min green (intensity 0-255)	0	38	35	5		
	green cut-off amplifier	FALSE	FALSE	FALSE	FALSE		
	max blue (intensity 0-255)	255	255	210	255		
	blue band-pass filter	FALSE	FALSE	TRUE	FALSE		
	min blue (intensity 0-255)	0	60	150	0		
	blue cut-off amplifier	FALSE	FALSE	FALSE	FALSE		
Threshold settings	Number of levels	5	5	5	8		
	upper limit (intensity 0-255)	255	255	255	255		
	lower limit (intensity 0-255)	0	0	0	0		
	red filter	FALSE	TRUE	TRUE	TRUE		
	green filter	FALSE	FALSE	TRUE	FALSE		
	blue filter	FALSE	TRUE	FALSE	TRUE		
	Invert colours	TRUE	FALSE	FALSE	FALSE		

Appendix 2

Set off data from test films

All the data in this appendix are expressed to one decimal place without regard to the number of significant figures, to allow a better statistical comparison using the ANOVA calculations in Appendix 3. RSD values were not calculated where set off values were low.

Table A2-1 Film 2 Set off solvent extraction 5 hours at 60 °C

Ink component	*Iso-octane µg/dm²*			*Dioxane µg/dm²*			*95 % ethanol µg/dm²*		
	Reel Start 0 psi	Position Start 1.2 psi	End 1.2 psi	Reel Start 0 psi	Position Start 1.2 psi	End 1.2 psi	Reel Start 0 psi	Position Start 1.2 psi	End 1.2 psi
CAS 0071868-10-5									
Replicate 1	0.2	0.5	0.3	0.1	0.3	0.5	0.3	0.4	0.7
Replicate 2	<0.1	0.5	0.5	0.1	0.4	0.8	0.4	0.5	0.8
Replicate 3	0.1	0.3	0.3	0.1	0.4	0.2	0.5	0.1	0.7
Mean	0.1	0.4	0.4	0.1	0.4	0.5	0.4	0.3	0.7
4-phenyl benzophenone									
Replicate 1	6.8	8.8	9.5	5.7	6.1	10.4	7.1	4.4	22.0
Replicate 2	2.9	8.9	8.1	8.8	8.4	13.0	7.8	5.7	9.0
Replicate 3	6.3	7.0	9.5	3.8	7.1	11.0	9.1	11.9	13.0
Mean	5.3	8.2	9.0	6.1	7.2	12.5	8.0	7.3	14.7
RSD %	40	13	9	41	16	12	13	55	45
Ethyl-4-dimethylamino benzoate									
Replicate 1	3.6	4.4	3.7	2.6	3.1	4.1	3.6	4.3	9.1
Replicate 2	1.7	2.0	3.8	4.7	5.7	5.6	4.3	5.1	6.8
Replicate 3	3.7	4.4	2.9	2.1	2.5	3.0	5.1	6.0	5.8
Mean	3.0	3.6	3.5	3.1	3.8	4.2	4.3	5.1	7.2
RSD %	38	38	14	44	45	31	17	17	23
Pentaerythritol triacrylate									
Replicate 1	1.0	2.1	3.1	1.1	0.7	1.2	1.5	0.9	5.5
Replicate 2	0.3	2.5	2.7	1.9	0.7	2.1	2.9	1.2	3.1
Replicate 3	1.9	1.3	3.2	0.6	0.7	2.6	2.3	2.6	4.1
Mean	1.1	2.0	3.0	1.2	0.7	2.0	2.2	1.6	4.2
RSD%	73	31	9	55	-	35	32	57	29

Table A2-2 Film 3 Set off solvent extraction 5 hours at 60 °C

Compound	*Iso-octane µg/dm²*	*Dioxane µg/dm²*	*95 % ethanol µg/dm²*
CAS 0071868-10-5			
Replicate 1	10.1	15.6	19.3
Replicate 2	14.8	11.8	20.2
Replicate 3	13.3	23.8	15.1
Mean	12.7	17.1	18.2
RSD %	19	36	15
4-phenyl benzophenone			
Replicate 1	61.3	61.6	39.2
Replicate 2	41.5	37.8	41.5
Replicate 3	37.4	101.7	27.9
Mean	46.7	67.0	36.2
RSD %	27	48	20
Ethyl-4-dimethylamino benzoate			
Replicate 1	35.8	35.0	26.0
Replicate 2	34.4	27.9	27.4
Replicate 3	30.3	56.5	18.6
Mean	33.5	39.8	24.0
RSD %	34	40	24

Table A2-3 Film 4 Set off solvent extraction 5 hours at 60 °C

Compound	*Iso-octane µg/dm²*			*Dioxane µg/dm²*				*95 % ethanol µg/dm²*			
	Start 0 psi	*Mid 1.2 psi*	*End 1.2 psi*	*Start 0 psi*	*Start 1.2 psi*	*Mid 1.2 psi*	*End 1.2 psi*	*Start*	*Start 1.2 psi*	*Mid 1.2 psi*	*End 1.2 psi*
CAS 0071868-10-5	< 0.1	0.9	4.5	0.1	< 0.1	3.3	0.9	0.2	0.2	0.7	1.2
Replicate 1											
Replicate 2	< 0.1	1.4	14.3	< 0.1	< 0.1	0.9	0.6	0.2	0.3	0.6	1.8
Replicate 3	< 0.1	1.0	4.3	< 0.1	< 0.1	0.9	1.0	0.2	0.3	1.1	1.6
Mean	< 0.1	1.1	7.7	< 0.1	< 0.1	1.7	0.8	0.2	0.3	0.8	1.5
4-phenyl benzophenone											
Replicate 1	19.1	3.1	4.5	8.8	14.2	11.0	3.3	9.5	13.8	2.7	3.2
Replicate 2	14.3	4.2	14.3	8.3	10.6	3.0	3.3	8.1	14.2	3.6	4.2
Replicate 3	13.9	3.4	4.3	9.1	17.9	3.0	3.6	11.1	13.0	3.1	3.8
Mean	15.8	3.6	7.7	8.7	14.2	5.7	3.4	9.6	13.7	3.1	3.7
RSD %	18	16	74	5	26	82	5	16	4	14	13
CAS 0000947-19-3	4.6	2.4	2.8	3.6	4.3	8.7	2.4	2.9	5.6	2.2	2.4
Replicate 1											
Replicate 2	3.7	3.0	3.5	2.9	4.0	2.4	2.2	3.1	6.9	2.9	3.1
Replicate 3	2.3	2.5	2.7	3.5	4.3	2.3	2.5	2.2	6.2	2.6	2.9
Mean	3.5	2.6	3.0	3.3	4.2	4.5	2.4	2.7	6.2	2.6	2.8
RSD %	33	12	15	11	4	82	6	17	10	14	13
Irgacure 369 Replicate 1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Replicate 2	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Replicate 3	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Mean	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Irgacure 379 Replicate 1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Replicate 2	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Replicate 3	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
Mean	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m	< 0.1	< 0.1	n m	n m
LUCIRIN TPO Replicate 1	< 0.1	n m	n m	0.1	< 0.1	1.7	2.6	< 0.1	< 0.1	1.1	n m
Replicate 2	< 0.1	n m	n m	< 0.1	< 0.1	2.7	1.2	< 0.1	< 0.1	1.6	n m
Replicate 3	< 0.1	n m	n m	< 0.1	< 0.1	1.2	2.2	< 0.1	< 0.1	< 0.1	n m
Mean	< 0.1	n m	n m	< 0.1	< 0.1	1.9	2.0	< 0.1	< 0.1	0.9	n m
Irgacure 2959 Replicate 1	< 0.1	n m	n m	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Replicate 2	< 0.1	n m	n m	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Replicate 3	< 0.1	n m	n m	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Mean	< 0.1	n m	n m	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

n m = not measured

Set off measurements were obtained for three representative acrylates included in the ink formulation for film 4.

Table A2-4 Film 4 set off solvent extraction 5 hours at 60 °C

Compound	*Iso-octane µg/dm²*				*Dioxane µg/dm²*				*95 % ethanol µg/dm²*			
	Start 0 psi	*Start 1.2 psi*	*Mid 1.2 psi*	*End 1.2 psi*	*Start 0 psi*	*Start 1.2 psi*	*Mid 1.2 psi*	*End 1.2 psi*	*Start 0 psi*	*Start 1.2 psi*	*Mid 1.2 psi*	*End 1.2 psi*
Di-(trimethylolpropane tetra acrylate												
Replicate 1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1	0.1	< 0.1
Replicate 2	< 0.1	0.1	< 0.1	0.3	< 0.1	0.1	< 0.1	0.1	< 0.1	< 0.1	0.1	0.1
Replicate 3	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Mean	< 0.1	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
GPTA												
Replicate 1	n m	n m	0.8	2.1	n m	n m	2.1	1.8	n m	n m	1.3	1.3
Replicate 2	n m	n m	0.9	6.2	n m	n m	2.0	1.6	n m	n m	2.0	1.7
Replicate 3	n m	n m	2.0	2.1	n m	n m	1.5	1.9	n m	n m	1.4	1.7
Mean	n m	n m	1.2	3.5	n m	n m	1.9	1.8	n m	n m	1.6	1.6
Dipropylene glycol diacrylate												
Replicate 1	1.7	1.4	< 0.1	< 0.1	0.3	1.0	< 0.1	< 0.1	0.1	0.5	< 0.1	< 0.1
Replicate 2	1.9	0.4	< 0.1	< 0.1	0.4	0.8	< 0.1	0.1	0.2	0.7	< 0.1	< 0.1
Replicate 3	1.3	0.1	< 0.1	< 0.1	0.4	0.8	< 0.1	< 0.1	0.1	0.7	< 0.1	< 0.1
Mean	1.6	0.6	< 0.1	< 0.1	0.4	0.9	< 0.1	< 0.1	0.1	0.6	< 0.1	< 0.1

Set off measurements were obtained for three representative acrylates included in the ink formulation for film 4 at two test pressure, 0 and 1.2 psi.

Table A2-5 Film 4 set off iso-octane extraction 5 hours at 60 °C

Compound	*Start 0 psi µg/dm²*	*Start 1.2 psi µg/dm²*	*Middle 1.2 psi µg/dm²*	End 1.2 psi *µg/dm²*
Di-(trimethylolpropane tetra acrylate				
Replicate 1	< 0.1	< 0.1	< 0.1	0.1
Replicate 2	< 0.1	0.1	< 0.1	0.3
Replicate 3	< 0.1	< 0.1	< 0.1	0.1
Mean	< 0.1	< 0.1	< 0.1	0.2
GPTA				
Replicate 1	n m	n m	0.8	2.1
Replicate 2	n m	n m	0.9	6.2
Replicate 3	n m	n m	2.0	2.1
Mean	n m	n m n m	1.2	3.5
Dipropylene glycol diacrylate				
Replicate 1	1.7	1.4	< 0.1	< 0.1
Replicate 2	1.9	0.4	< 0.1	< 0.1
Replicate 3	1.3	0.1	< 0.1	< 0.1
Mean	1.6	0.6	< 0.1	< 0.1

Table A2-6 Film 4 set off dioxane extraction 5 hours at 60 °C

Compound	*Start 0 psi µg/dm²*	*Start 1.2 psi µg/dm²*	*Middle 1.2 psi µg/dm²*	End 1.2 psi *µg/dm²*
Di-(trimethylolpropane tetra acrylate				
Replicate 1	< 0.1	< 0.1	0.2	< 0.1
Replicate 2	< 0.1	0.1	< 0.1	0.1
Replicate 3	< 0.1	< 0.1	< 0.1	< 0.1
Mean	< 0.1	< 0.1	< 0.1	< 0.1
GPTA				
Replicate 1	n m	n m	2.1	1.8
Replicate 2	n m	n m	2.0	1.6
Replicate 3	n m	n m	1.5	1.9
Mean	n m	n m	1.9	1.8
Dipropylene glycol diacrylate				
Replicate 1	0.3	1.0	< 0.1	< 0.1
Replicate 2	0.4	0.8	< 0.1	0.1
Replicate 3	0.4	0.8	< 0.1	< 0.1
Mean	0.4	0.9	< 0.1	< 0.1

Table A2-7 Film 4 Ethanol (95 %) extraction solvent 5 hours at 60 °C

Compound	*Start 0 psi µg/dm²*	*Start 1.2 psi µg/dm²*	*Middle 1.2 psi µg/dm²*	End 1.2 psi µg/dm²
Di-(trimethylolpropane tetra acrylate				
Replicate 1	< 0.1	< 0.1	0.1	< 0.1
Replicate 2	< 0.1	< 0.1	0.1	0.1
Replicate 3	< 0.1	< 0.1	< 0.1	< 0.1
Mean	< 0.1	< 0.1	< 0.1	< 0.1
GPTA				
Replicate 1	n m	n m	1.3	1.3
Replicate 2	n m	n m	2.0	1.7
Replicate 3	n m	n m	1.4	1.7
Mean	n m	n m	1.6	1.6
Dipropylene glycol diacrylate				
Replicate 1	0.1	0.5	< 0.1	< 0.1
Replicate 2	0.2	0.7	< 0.1	< 0.1
Replicate 3	0.1	0.7	< 0.1	< 0.1
Mean	0.1	0.6	< 0.1	< 0.1

Table A2-8 Film 5A Set off solvent extraction 5 hours at 60 °C

Compound	*Iso-octane* $\mu g/dm^2$			Dioxane $\mu g/dm^2$			95 % ethanol $\mu g/dm^2$		
	Start 0 psi	Start 1.2 psi	End 1.2 psi	Start 0 psi	Start 1.2 psi	End 1.2 psi	Start 0 psi	Start 1.2 psi	End 1.2 psi
4-phenyl benzophenone									
Replicate 1	0.1	1.2	1.1	1.1	2.3	0.9	1.0	3.4	1.3
Replicate 2	< 0.1	1.3	1.1	1.7	2.9	1.7	0.9	1.4	1.3
Replicate 3	< 0.1	1.3	0.7	1.0	0.5	1.1	1.9	1.9	1.1
Mean	< 0.1	1.3	1.0	1.3	1.9	1.2	1.3	2.2	1.2
Benzoic acid-2-benzoyl methyl ester									
Replicate 1	< 0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.5	0.1
Replicate 2	< 0.1	0.2	0.1	0.1	0.3	0.1	0.1	0.3	0.1
Replicate 3	< 0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.3	0.1
Mean	< 0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.4	0.1

Table A2-9 Film 5B Set off solvent extraction 5 hours at 60 °C

Compound	*Iso-octane* $\mu g/dm^2$			Dioxane $\mu g/dm^2$			95 % ethanol $\mu g/dm^2$		
	Start 0 psi	Start 1.2 psi	End 1.2 psi	Start 0 psi	Start 1.2 psi	End 1.2 psi	Start 0 psi	Start 1.2 psi	End 1.2 psi
4-phenyl benzophenone									
Replicate 1	0.7	1.6	1.1	0.5	1.1	4.5	0.7	3.8	0.8
Replicate 2	0.6	1.3	1.2	0.4	1.0	4.2	1.0	5.4	1.2
Replicate 3	0.6	1.4	1.1	0.5	0.6	1.1	0.7	4.8	1.3
Mean	0.6	1.4	1.1	0.5	0.9	3.3	0.8	4.7	1.1
Benzoic acid-2-benzoyl methyl ester									
Replicate 1	0.1	0.5	0.1	0.1	0.3	0.5	0.1	1.2	0.1
Replicate 2	0.1	0.3	0.1	0.1	0.3	0.6	0.1	1.8	0.2
Replicate 3	0.1	0.3	0.1	0.1	0.2	0.2	0.1	1.8	0.2
Mean	0.1	0.4	0.1	0.1	0.3	0.4	0.1	1.6	0.2

Table A2-10 Film 6 set off solvent extraction 5 hours at 60 °C

Compound	*Iso-octane*			*Dioxane*			*95 % ethanol*		
	Start 0 psi	**Start 1.2 psi**	**End 1.2 psi**	**Start 0 psi**	**Start 1.2 psi**	**End 1.2 psi**	**Start 0 psi**	**Start 1.2 psi**	**End 1.2 psi**
	µg/dm²	***µg/dm²***	***µg/dm²***	***µg/dm²***	***µg/dm²***	***µg/dm²***	***µg/dm²***	***µg/dm²***	***µg/dm²***
Di-(trimethylolpropane tetra acrylate									
Replicate 1	1.4	0.4	0.4	1.2	0.4	0.7	0.5	0.9	1.6
Replicate 2	0.8	0.4	0.4	0.9	0.1	1.4	0.3	0.8	0.4
Replicate 3	1.6	0.3	0.5	0.6	0.1	1.7	0.3	0.7	1.1
Mean	1.3	0.4	0.4	0.9	0.2	1.3	0.4	0.8	1.0
4-phenyl benzophenone									
Replicate 1	0.5	0.1	< 0.1	0.4	0.4	0.2	0.1	0.2	1.7
Replicate 2	0.6	0.1	< 0.1	0.4	0.1	0.4	0.1	0.2	0.3
Replicate 3	0.6	0.1	< 0.1	0.1	0.1	0.4	0.1	0.3	0.5
Mean	0.6	0.1	< 0.1	0.3	0.2	0.3	0.1	0.2	0.8
Trimethylolpropane ethoxylate									
Replicate 1	2.1	1.7	not	4.8	2.1	0.7	2.0	3.0	10.0
Replicate 2	2.1	1.6	measured	3.4	0.5	1.2	1.8	2.6	2.4
Replicate 3	1.8	1.4		1.6	0.5	1.2	2.3	3.8	3.7
Mean	2.0	1.5		3.3	1.4	1.0	2.0	3.1	5.4

Table A2-11 Repeat Film 3 set off 5 hours at 60 °C

Ink component	*Iso-octane* $\mu g/dm^2$			*Dioxane* $\mu g/dm^2$			95 % ethanol $\mu g/dm^2$		
	Reel position								
	Start	Middle	End	Start	Middle	End	Start	Middle	End
Benzophenone									
Replicate 1	264.9	308.9	239.9	258.0	392.4	649.2	275.9	474.7	363.0
Replicate 2	251.9	320.7	278.4	289.3	397.2	581.8	323.7	348.9	325.9
Replicate 3	274.5	287.7	280.1	345.0	469.2	656.0	347.8	316.8	417.7
Replicate 4	276.7	290.3	-	339.3	486.8	534.9	263.2	312.3	488.2
Mean	**267.0**	**301.9**	**266.1**	**307.9**	**436.4**	**605.5**	**302.7**	**363.2**	**398.7**
RSD %	4	5	9	14	11	10	13	21	18
Ethyl-4-dimethylamino benzoate									
Replicate 1	50.0	59.8	41.2	52.4	76.4	115.0	56.2	98.9	64.8
Replicate 2	45.2	68.6	53.6	49.1	80.2	98.3	68.8	71.4	65.2
Replicate 3	52.2	57.5	44.8	63.8	81.2	121.7	69.6	62.8	86.6
Replicate 4	47.2	56.0	-	61.9	91.3	93.0	54.2	69.8	88.4
Mean	**48.7**	**60.5**	**46.5**	**56.8**	**82.3**	**107.0**	**62.2**	**75.7**	**76.3**
RSD %	6	9	14	13	8	13	13	21	17
CAS 0071868-10-5									
Replicate 1	14.0	34.7	24.9	21.6	30.4	37.0	27.4	41.3	30.7
Replicate 2	12.0	43.0	31.1	14.4	33.2	29.0	33.2	33.1	32.5
Replicate 3	13.0	32.3	26.9	19.5	28.1	33.8	34.5	28.5	41.0
Replicate 4	10.3	36.3	-	20.6	36.6	29.5	27.1	34.7	43.1
Mean	**12.3**	**36.6**	**27.6**	**19.0**	**32.1**	**32.3**	**30.6**	**34.4**	**36.8**
RSD %	13	13	11	17	11	12	13	15	17
4-phenyl benzophenone									
Replicate 1	21.2	56.5	42.2	47.1	55.1	79.8	51.0	55.5	41.5
Replicate 2	19.6	67.4	51.9	39.4	53.9	66.5	63.0	43.6	44.1
Replicate 3	18.1	54.4	49.0	39.6	53.4	77.8	65.3	36.3	52.6
Replicate 4	16.8	59.4	-	49.4	60.1	62.3	51.6	44.2	60.7
Mean	**18.9**	**59.4**	**47.7**	**43.9**	**55.6**	**71.6**	**57.7**	**44.9**	**49.7**
RSD %	**10**	**10**	**10**	**12**	**6**	**12**	**13**	**18**	**18**

Table A2-12 Repeat Film 3 Ethanol (95 %) extraction solvent 5 hours at 60 °C

Ink component	*Reel position* *Start Rep1* µg/dm²	*Start rep 2* µg/dm²	*End Rep 1* µg/dm²	*End rep 2* µg/dm²	*End Rep 3* µg/dm²	End Rep 4 µg/dm²
Benzophenone						
Replicate 1	337.4	280.1	225.3	226.4	238.9	227.3
Replicate 2	393.3	267.6	226.8	204.0	353.0	264.3
Replicate 3	319.1	656.2	237.2	242.2	238.8	265.7
Replicate 4	362.4	559.9	233.2	254.8	245.2	360.9
Mean	**353.1**	**441.0**	**230.6**	**231.9**	**269.0**	**279.6**
RSD %	9	45	2	9	21	20
Ethyl-4-dimethylamino benzoate						
Replicate 1	63.0	53.3	39.2	48.8	49.8	42.8
Replicate 2	73.7	49.9	39.6	49.9	66.5	48.8
Replicate 3	57.1	125.8	37.3	53.4	46.1	51.1
Replicate 4	67.2	106.7	39.1	58.6	50.3	67.7
Mean	**65.3**	**83.9**	**38.8**	**52.7**	**53.2**	**52.6**
RSD %	11	45	3	8	17	20
CAS 0071868-10-5						
Replicate 1	21.6	18.1	13.2	20.6	23.2	15.7
Replicate 2	24.1	16.5	12.6	24.5	33.6	18.4
Replicate 3	18.6	43.2	13.1	24.1	22.1	19.6
Replicate 4	22.0	36.3	12.6	25.4	24.3	24.9
Mean	**21.6**	**28.5**	**12.9**	**23.7**	**25.8**	**19.7**
RSD %	10	47	2	9	20	20
4-phenyl benzophenone						
Replicate 1	54.0	46.2	50.7	28.5	22.6	35.7
Replicate 2	60.0	41.1	52.4	32.2	32.1	42.1
Replicate 3	48.1	102.6	50.4	30.8	22.9	41.9
Replicate 4	55.6	87.4	48.7	32.4	21.7	54.9
Mean	**54.4**	**69.3**	**50.6**	**31.0**	**24.8**	**43.7**
RSD %	**9**	**44**	**3**	**6**	**20**	**18**

Table A2-13 Repeat Film 3 Iso-octane extraction solvent 5 hours at 60 °C

Ink component	*Reel position* *Start Rep1* µg/dm^2	*Start rep 2* µg/dm^2	*End Rep 1* µg/dm^2	End rep 2 µg/dm^2
Benzophenone				
Replicate 1	393.1	303.7	226.8	224.7
Replicate 2	508.7	239.4	230.0	388.3
Replicate 3	362.9	280.9	226.6	374.0
Replicate 4	333.2	284.5	229.5	352.9
Mean	**399.5**	**277.1**	**228.2**	**335.0**
RSD %	19	10	1	22
Ethyl-4-dimethylamino benzoate				
Replicate 1	82.0	82.8	33.6	38.4
Replicate 2	59.5	52.1	34.6	66.4
Replicate 3	59.5	40.2	35.3	65.4
Replicate 4	53.2	48.8	35.8	59.4
Mean	**63.6**	**56.0**	**34.8**	**57.4**
RSD %	20	33	3	23
CAS 0071868-10-5				
Replicate 1	8.5	16.9	11.8	11.3
Replicate 2	16.8	13.5	9.9	19.1
Replicate 3	11.9	15.2	7.5	23.5
Replicate 4	10.0	17.6	14.6	18.2
Mean	**11.8**	**15.8**	**11.0**	**18.0**
RSD %	31	12	27	28
4-phenyl benzophenone				
Replicate 1	75.1	64.2	56.4	50.2
Replicate 2	106.2	52.3	57.5	87.9
Replicate 3	78.3	60.3	59.6	84.1
Replicate 4	71.4	61.1	65.5	76.1
Mean	**82.8**	**59.5**	**59.8**	**74.6**
RSD %	**19**	**9**	**7**	**23**

The data presented below are the means of tables A2-11, A2-12 and A2-13 above.

Table A2-14 Mean Set off repeat production reel 3 extraction for 5 hours at 60 °C

Ink component	Reel position								
	start(1) *µg/dm²*	start(2) *µg/dm²*	start(3) *µg/dm²*	Middle *µg/dm²*	end(1) *µg/dm²*	end(2 *µg/dm²*	end(3 *µg/dm²*	end(4 *µg/dm²*	end(5) *µg/dm²*
95 % ethanol									
benzophenone	303	353	274	363	399	231	232	269	280
ethy-4-(dimethylamino)benzoate	62	65	52	76	76	39	53	53	53
CAS 0071868-10-5	31	22	17	34	37	13	24	26	20
4-phenyl benzophenone	58	54	69	45	50	51	31	25	44
Iso-octane									
benzophenone	267	400	277	302	266	228	335	-	-
ethy-4-(dimethylamino)benzoate	49	64	56	61	47	35	57	-	-
CAS 0071868-10-5	12	12	16	37	28	11	18	-	-
4-phenyl benzophenone	19	83	60	59	48	60	75	-	-

Table A2-15 Repeat Film 3 migration into EU alternative fat test simulants

Simulant	Benzophenone *µg/dm²*	Ethyl-4-dimethylamino benzoate *µg/dm²*	CAS 0071868-10-5 *µg/dm²*	4-phenyl benzophenone *µg/dm²*
10 days 40 °C in 95 % ethanol	263.0	47.6	25.0	24.5
10 days 40 °C in 95 % ethanol	223.9	37.0	20.0	16.8
10 days 40 °C in 95 % ethanol	242.5	39.4	21.7	21.7
10 days 40 °C in 95 % ethanol	324.2	70.7	34.1	36.8
10 days 40 °C in 95 % ethanol	249.6	38.6	23.2	23.8
Mean	**260.6**	**46.6**	**24.8**	**24.7**
RSD %	15	30	22	30
2 days at 20 °C in Iso-octane	202.1	30.0	7.5	9.6
2 days at 20 °C in Iso-octane	209.8	31.9	8.8	7.9
2 days at 20 °C in Iso-octane	231.5	34.8	10.7	10.7
2 days at 20 °C in Iso-octane	211.0	26.0	4.1	7.1
2 days at 20 °C in Iso-octane	231.9	23.3	9.0	7.6
Mean	**217.3**	**29.2**	**8.0**	**8.6**
RSD %	6	16	31	18
2 days at 20 °C in Iso-octane	214.8	34.3	9.0	15.2
2 days at 20 °C in Iso-octane	203.7	29.9	8.2	13.3
2 days at 20 °C in Iso-octane	209.1	27.5	6.0	13.7
2 days at 20 °C in Iso-octane	199.7	31.0	9.3	15.8
Mean	**206.8**	**30.7**	**8.1**	**14.5**
RSD %	3	9	18	8

Table A2-16 Film 7 Ink series X under cured 40/20 set off solvent extraction at 60 °C

Compound		*Iso-octane*			*Dioxane*			95 % ethanol		
		½ hour µg/dm²	1 hour µg/dm²	5 hours µg/dm²	½ hour µg/dm²	1 hour µg/dm²	5 hours µg/dm²	½ hour µg/dm²	1 hour µg/dm²	5 hours µg/dm²
1, 6-Hexanediol diacrylate	**Replicate 1**	5.7	6.4	<1	6.2	4.7	<1	2.8	8.3	<1
	Replicate 2	6.2	6.6	1.3	6.1	6.5	<1	2.7	8.1	1.2
	Replicate 3	5.7	6.4	1.9	6.0	6.5	1.1	3.1	7.8	1.1
	Replicate 4	5.1	6.7	1.7	5.4	7.2	<1	3.1	7.3	1.0
	Mean	**5.7**	**6.5**	**1.2**	**5.9**	**6.2**	**<1**	**2.9**	**7.9**	**<1**
	RSD %	8	2	25	6	17	-	7	6	-
CAS 0000947-19-3	**Replicate 1**	62.1	83.7	312.0	55.9	58.9	304.1	18.0	60.7	243.1
	Replicate 2	63.0	64.0	333.8	50.5	64.6	333.1	19.5	60.2	327.7
	Replicate 3	61.8	61.7	287.0	53.7	58.4	392.3	20.7	59.5	323.5
	Replicate 4	52.5	64.2	328.6	54.7	69.1	328.2	20.0	54.9	351.6
	Mean	**59.9**	**68.4**	**315.4**	**53.7**	**62.8**	**339.4**	**19.6**	**58.8**	**311.5**
	RSD %	**8**	15	7	**4**	8	11	**6**	5	15
CAS 0071868-10-5	**Replicate 1**	51.7	54.9	15.9	22.1	28.9	8.8	5.4	24.0	8.2
	Replicate 2	34.6	33.4	14.8	17.4	27.1	10.3	5.4	22.9	11.8
	Replicate 3	38.0	33.4	11.7	17.6	23.5	12.7	5.9	22.6	10.8
	Replicate 4	33.4	32.5	14.5	21.9	32.8	9.5	6.2	21.0	13.1
	Mean	**39.4**	**38.6**	**14.2**	**19.8**	**28.1**	**10.3**	**5.7**	**22.6**	**11.0**
	RSD %	21	28	13	13	14	16	7	5	19
4-Phenyl benzophenone	**Replicate 1**	46.3	47.2	62.2	55.5	63.6	42.3	13.0	44.0	30.3
	Replicate 2	38.3	61.8	65.7	51.5	62.4	52.1	12.6	45.1	43.6
	Replicate 3	44.6	66.7	55.5	53.6	58.1	62.6	12.4	42.7	40.2
	Replicate 4	35.2	68.2	63.3	56.4	65.9	51.8	12.3	38.0	49.3
	Mean	**41.0**	**61.0**	**61.7**	**54.3**	**62.5**	**52.2**	**12.6**	**42.5**	**40.9**
	RSD %	**13**	**15**	**7**	**4**	**5**	**15**	**2**	**7**	**18**
Di(trimethylolpropane) tetraacylate	**Replicate 1**	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Replicate 2	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Replicate 3	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Replicate 4	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Mean	**<1**	**<1**	**<1**	**<1**	**<1**	**<1**	**<1**	**<1**	**<1**
Lucirin TPO	**Replicate 1**	8.5	5.7	9.6	1.7	1.9	8.8	<1	1.4	6.3
	Replicate 2	8.4	5.5	9.2	1.5	2.6	8.4	<1	1.1	7.6
	Replicate 3	7.7	6.0	8.7	1.4	2.8	11.0	<1	1.2	7.5
	Replicate 4	8.4	6.0	7.1	1.5	2.2	6.9	<1	1.2	6.5
	Mean	**8.3**	**5.8**	**8.7**	**1.5**	**2.4**	**8.8**	**<1**	**1.2**	**7.0**
	RSD %	**4**	**4**	**13**	**8**	**17**	**19**	**-**	**10**	**10**

Table A2-17 Film 7 fully cured 80/40 set off solvent extraction 5 hours at 60 °C

Compound	*95 % ethanol µg/dm²*	*Iso-octane µg/dm²*	*Dioxane µg/dm²*
1, 6-Hexanediol diacrylate			
Replicate 1	<1	<1	<1
Replicate 2	<1	<1	<1
Replicate 3	<1	<1	<1
Replicate 4	<1	<1	<1
Mean	**<1**	**<1**	**<1**
CAS 0000947-19-3			
Replicate 1	39.5	36.0	31.9
Replicate 2	32.9	37.7	31.5
Replicate 3	34.3	11.0	33.3
Replicate 4	38.0	34.4	36.8
Mean	**36.2**	**29.8**	**33.4**
RSD %	**9**	**42**	**7**
CAS 0071868-10-5			
Replicate 1	16.0	11.1	2.9
Replicate 2	10.9	11.0	2.5
Replicate 3	11.6	3.5	2.4
Replicate 4	16.9	7.5	8
Mean	**13.9**	**8.3**	**4.0**
RSD %	**22**	**43**	**69**
4-Phenyl benzophenone			
Replicate 1	46.4	58.3	44.8
Replicate 2	36.4	61.8	41.5
Replicate 3	37.5	47.1	50.2
Replicate 4	50.5	48.3	52.1
Mean	**42.7**	**53.9**	**47.2**
RSD %	**16**	**14**	**10**
Trimethylolpropane tetraacylate			
Replicate 1	<1	<1	<1
Replicate 2	<1	<1	<1
Replicate 3	<1	<1	<1
Replicate 4	<1	<1	<1
Mean	**<1**	**<1**	**<1**

Table A2-18 Test film 8 Ink series Y fully-cured 40/20 set off 5 hours at 60 °C

Compound	*95 % ethanol µg/dm²*	*Iso-octane µg/dm²*	*Dioxane µg/dm²*
Irgacure 2959			
Replicate 1	<1	1.1	1.8
Replicate 2	<1	2.0	2.2
Replicate 3	<1	2.5	2.1
Replicate 4	<1	3.1	1.9
Mean	**<1**	**2.2**	**2.0**
Ethyl-4-dimethylamino benzoate			
Replicate 1	61.8	43.6	60.1
Replicate 2	63.3	46.5	59.4
Replicate 3	62.8	52.2	60.0
Replicate 4	58.6	60.1	50.4
Mean	**61.6**	**50.6**	**57.5**
RSD %	**3**	**14**	**8**
Irgacure 369			
Replicate 1	4.3	-	1.7
Replicate 2	4.9	-	1.6
Replicate 3	5.0	-	1.4
Replicate 4	4.9	-	1.2
Mean	**4.8**	-	**1.5**
Irgacure 379			
Replicate 1	1.8	-	<1
Replicate 2	1.9	-	<1
Replicate 3	2.0	-	<1
Replicate 4	2.2	-	**<1**
Mean	**2.0**	-	<1

Table A2-19 Test film 8 Ink series Y under cured 80/40 set off dioxane 5 hours 60 °C

Compound	*µg/dm²*
Irgacure 2959	
Replicate 1	1.0
Replicate 2	<1
Replicate 3	1.0
Replicate 4	1.2
Mean	**<1**
Ethyl-4-dimethylamino benzoate	
Replicate 1	21.2
Replicate 2	16.4
Replicate 3	19.1
Replicate 4	22.7
Mean	**19.9**
RSD %	14
Irgacure 369	
Replicate 1	4.0
Replicate 2	3.1
Replicate 3	3.8
Replicate 4	4.9
Mean	**4.0**
RSD %	19
Irgacure 379	
Replicate 1	3.7
Replicate 2	3.7
Replicate 3	4.1
Replicate 4	6.6
Mean	**4.5**
RSD %	31

Appendix 3

Statistical calculations

Analysis of Variance (ANOVA) was carried out where appropriate using an Excel spreadsheet. The set off data in Appendix 2 was used to determine the significance of controlled factors such as test pressure, on extraction solvent and position on the reel. Worked examples from Miller J and Miller J "Statistics for analytical chemistry" Chichester 1986, were calculated to ensure the correct use of the spreadsheet functions, and the correct selection of the appropriate F test critical values for the variances.

Film 2 Set off 5 hours at 60 °C

The effect of pressure on set off was investigated by comparing results obtained at the beginning of the reel as given in Table A2-1 Appendix 2 page 99.

Benzophenone

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
start 0 psi	3	16	5.333333	4.503333
start 1.2 psi	3	24.7	8.233333	1.143333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12.615	1	12.615	4.468123	0.102053	7.708647
Within Groups	11.29333	4	2.823333			
Total	23.90833	5				

Ethyl-4-dimethylamino benzoate

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
start 0 psi	3	9	3	1.27
start 1.2 psi	3	10.8	3.6	1.92

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.54	1	0.54	0.338558	0.591879	7.708647
Within Groups	6.38	4	1.595			
Total	6.92	5				

No significant difference observed between test pressures.

Film 3 Set off 5 hours at 60 °C

The data in Table A2-2 page 99 was tested for a significant difference between extraction solvents.

CAS 0071868-10-5

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Iso-octane	3	38.2	12.73333	5.763333
Dioxane	3	51.2	17.06667	37.61333
95 % ethanol	3	54.6	18.2	7.41

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	49.94667	2	24.97333	1.47519	0.3013	5.143253
Within Groups	101.5733	6	16.92889			
Total	151.52	8				

4-phenyl benzophenone

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Iso-octane	3	140.2	46.7333333	163.3433333
Dioxane	3	201.1	67.0333333	1042.943333
95 % ethanol	3	108.6	36.2	52.99

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1473.73556	2	736.867778	1.755454851	0.251066	5.143253
Within Groups	2518.55333	6	419.758889			
Total	3992.28889	8				

Ethyl-4-dimethylamino benzoate

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Iso-octane	3	100.5	33.5	8.17
Dioxane	3	119.4	39.8	221.77
95 % ethanol	3	72	24	22.36

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	379.58	2	189.79	2.256718	0.185874	5.143253
Within Groups	504.6	6	84.1			
Total	884.18	8				

There was no significant difference between extraction solvents.

Film 4 Set off 5 hours at 60 °C

The mean set off in Table A2-3 Appendix 2 page 100 from the mid and end positions on the reel were compared against extraction solvent.

4-phenyl benzophenone

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
iso-octane	2	11.3	5.65	8.405
dioxane	2	9.1	4.55	2.645
95 % ethanol	2	6.8	3.4	0.18
mid	3	12.4	4.133333	1.903333
end	3	14.8	4.933333	5.763333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	5.063333	2	2.531667	0.493022	0.669783	19
Columns	0.96	1	0.96	0.186952	0.707621	18.51282
Error	10.27	2	5.135			
Total	16.29333	5				

There was no significant difference at the 95 % confidence interval between extraction solvents or reel positions.

CAS 0000947-19-3

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
iso-octane	2	5.6	2.8	0.08
dioxane	2	6.9	3.45	2.205
95 % ethanol	2	5.4	2.7	0.02
mid	3	9.7	3.233333	1.203333
end	3	8.2	2.733333	0.093333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.663333	2	0.331667	0.343696	0.744216	19
Columns	0.375	1	0.375	0.388601	0.596652	18.51282
Error	1.93	2	0.965			
Total	2.968333	5				

There was no significant difference at the 95 % confidence level between set off results obtained in the reel positions or solvents.

Film 5 Set off 5 hours at 60 °C

No useful data

Film 6 Set off 5 hours at 60 °C

The set off data in Table A2-10 Appendix 2 page 105 was used to examine the effect of test pressure and choice of extraction solvents. A two way ANOVA was carried out on the mean set off results.

Trimethylolpropane ethoxylate

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
0 psi	3	7.3	2.433333	0.521111
1.2 psi	3	5.733333	1.911111	1.191481
iso-octane	2	3.566667	1.783333	0.093889
dioxane	2	4.3	2.15	2.493889
95 % ethanol	2	5.166667	2.583333	0.605

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.409074	1	0.409074	0.293906	0.642055	18.51282
Columns	0.641481	2	0.320741	0.230442	0.812716	19
Error	2.783704	2	1.391852			
Total	3.834259	5				

There was no significant difference at the 95 % confidence interval between extraction solvents or test pressure.

Repeat test film 3 set off 5 hours at 60 °C

The mean set off data A2-11 Appendix 2 page 106 was used to investigate the effect of extraction solvent and reel position on set off value.

benzophenone

	solvent		
reel position	iso-octane	dioxane	95 % ethanol
start	267.0	307.9	302.7
middle	301.9	436.4	363.2
end	266.1	605.5	398.7

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
start	3	877.55	292.5166667	495.215833
middle	3	1101.475	367.1583333	4534.46271
end	3	1270.30833	423.4361111	29247.0981
iso-octane	3	835.033333	278.3444444	416.335926
dioxane	3	1349.775	449.925	22274.9144
95 % ethanol	3	1064.525	354.8416667	2358.48396

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	25878.46761	2	12939.2338	2.13686195	0.233731871	6.94427191
Columns	44332.55233	2	22166.27617	3.66067055	0.124831512	6.94427191
Error	24221.00091	4	6055.250228			
Total	94432.02085	8				

Ethyl-4-dimethyl aminobenzoate

reel position	iso-octane	dioxane	95 % ethanol
start	48.7	56.8	62.2
middle	60.5	82.3	75.7
end	46.5	107.0	76.3

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
start	3	167.65	55.88333	46.53083
middle	3	218.475	72.825	125.1175
end	3	229.7833	76.59444	914.1434
iso-octane	3	155.6583	51.88611	56.44683
dioxane	3	246.075	82.025	630.0569
95 % ethanol	3	214.175	71.39167	63.43396

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	730.1789043	2	365.0895	1.897317	0.263347	6.944272
Columns	1401.887099	2	700.9435	3.642701	0.125628	6.944272
Error	769.6964198	4	192.4241			
Total	2901.762423	8				

CAS number 0071868-10-5

reel position	iso-octane	dioxane	95 % ethanol
start	12.3	19.0	30.6
middle	36.6	32.1	34.4
end	27.6	32.3	36.8

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
start	3	61.9	20.63333	85.72333
middle	3	103.1	34.36667	5.063333
end	3	96.7	32.23333	21.16333
iso-octane	3	76.5	25.5	150.93
dioxane	3	83.4	27.8	58.09
95 % ethanol	3	101.8	33.93333	9.773333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	327.7156	2	163.8578	5.965454	0.063043	6.944272
Columns	114.0289	2	57.01444	2.075685	0.240801	6.944272
Error	109.8711	4	27.46778			
Total	551.6156	8				

4-phenyl benzophenone

reel position	iso-octane	dioxane	95 % ethanol
start	18.9	43.9	57.7
middle	59.4	**55.6**	44.9
end	47.7	71.6	49.7

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
start	3	120.525	40.175	386.6275
middle	3	159.95	53.31667	56.74021
end	3	169.025	56.34167	175.6377
iso-octane	3	126.05	42.01667	434.2877
dioxane	3	171.1	57.03333	193.6565
95 % ethanol	3	152.35	50.78333	41.96021

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	443.2151	2	221.6076	0.988665	0.447822	6.944272
Columns	341.4172	2	170.7086	0.761587	0.524496	6.944272
Error	896.5936	4	224.1484			
Total	1681.226	8				

There was no significant effect on the mean set off value from the choice of extraction solvents or reel position.

Repeat Film 3 with 95 % ethanol extraction solvent 5 hours at 60 °C

The set off data from Table A2-12 page 107 was examined for the effect of sampling position on the reel on set off.

Benzophenone

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	1412.2	353.05	1035.003333
position 2	4	1763.8	440.95	38801.53667
position 3	4	922.5	230.625	30.94916667
position 3	4	927.4	231.85	479.7166667
position 4	4	1075.9	268.975	3146.829167
position 5	4	1118.2	279.55	3257.423333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	134060.4	5	26812.08	3.441015697	0.023426053	2.77285315
Within Groups	140254.4	18	7791.91			
Total	274314.8	23				

Ethyl-4-dimethylamino benzoate

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	261	65.25	48.8966667
position 2	4	335.7	83.925	1455.93583
position 3	4	155.2	38.8	1.04666667
position 3	4	210.7	52.675	19.4491667
position 4	4	212.7	53.175	82.4225
position 5	4	210.4	52.6	113.58

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4694.76375	5	938.9527	3.27288421	0.028219395	2.772853
Within Groups	5163.9925	18	286.8885			
Total	9858.75625	23				

CAS 0071868-10-5

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	86.3	21.575	5.135833
position 2	4	114.1	28.525	176.3625
position 3	4	51.5	12.875	0.1025
position 3	4	94.6	23.65	4.43
position 4	4	103.2	25.8	27.84667
position 5	4	78.6	19.65	14.91

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	594.8238	5	118.9648	3.119875	0.033519	2.772853
Within Groups	686.3625	18	38.13125			
Total	1281.186	23				

4-phenyl benzophenone

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	217.7	54.425	24.21583
position 2	4	277.3	69.325	921.7825
position 3	4	202.2	50.55	2.296667
position 3	4	123.9	30.975	3.229167
position 4	4	99.3	24.825	23.7825
position 5	4	174.6	43.65	65.07667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5258.195	5	1051.639	6.064913	0.001847	2.772853
Within Groups	3121.15	18	173.3972			
Total	8379.345	23				

There was a significant difference in results obtained at different positions on the reel for all ink components**.**

Repeat Film 3 Iso-octane extraction solvent 5 hours at 60 °C

The set off data from Table A2-13 page 108 was examined for the effect of sampling position on the reel on set off.

Anova: Single Factor benzophenone

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	5	1997.375	399.475	4425.21188
position 2	5	1385.625	277.125	549.511875
position 3	5	1141.125	228.225	2.361875
position 4	5	1674.875	334.975	4212.09687

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	81987.1625	3	27329.1	11.8961852	0.000239541	3.238871522
Within Groups	36756.73	16	2297.3			
Total	118743.8925	19				

Ethyl-4-dimethylamino benzoate

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	254.2	63.55	160.11
position 2	4	223.9	55.975	344.9758
position 3	4	139.3	34.825	0.909167
position 4	4	229.6	57.4	170

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1879.3125	3	626.4375	3.706758	0.04264758	3.490294821
Within Groups	2027.985	12	168.99875			
Total	3907.2975	15				

CAS 0071868-10-5

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	47.2	11.8	13.04667
position 2	4	63.2	15.8	3.366667
position 3	4	43.8	10.95	9.016667
position 4	4	72.1	18.025	25.4625

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	134.001875	3	44.66729	3.510717	0.049247	3.490295
Within Groups	152.6775	12	12.72313			
Total	286.679375	15				

4-phenyl benzophenone

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
position 1	4	331	82.75	252.35
position 2	4	237.9	59.475	25.70917
position 3	4	239	59.75	16.45667
position 4	4	298.3	74.575	288.2492

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1585.4225	3	528.4742	3.627357	0.045189	3.490295
Within Groups	1748.295	12	145.6913			
Total	3333.7175	15				

There was a significant difference in results obtained at different positions on the for all ink components**.**

Film 7 Ink series X under cured 40/20 solvent extraction at 60 °C

The mean set of values from Table A2-16 Appendix 2 page 111 were used to examine the effect of extraction time and choice of solvent on the set off value.

CAS 0000947-19-3

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
iso-octane	3	443.6	147.8666667	21056.28
dioxane	3	455.875	151.9583333	26378.29
95 % 95 % ethanol	3	389.85	129.95	25099.13
1/2 hour	3	133.1	44.36666667	471.3558
1 hour	3	189.975	63.325	23.16813
5 hours	3	966.25	322.0833333	229.304

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*		
Rows	822.1154	2	411.0577083	2.628497	*P-value*	*F crit*
Columns	144441.8	2	72220.92021	461.8146	0.186715	6.944272
Error	625.5404	4	156.3851042		1.86E-05	6.944272
Total	145889.5	8				

CAS 0071868-10-5

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
iso-octane	3	92.2	30.73333	204.5852
dioxane	3	58.15	19.38333	78.86646
95 % 95 % ethanol	3	39.325	13.10833	74.81583
1/2 hour	3	64.9	21.63333	286.5827
1 hour	3	89.25	29.75	65.50562
5 hours	3	35.525	11.84167	4.365833

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	478.8388	2	239.4194	4.091422	0.107801	6.944272
Columns	482.4654	2	241.2327	4.12241	0.106712	6.944272
Error	234.0696	4	58.5174			
Total	1195.374	8				

4-phenylbenzophenone

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
iso-octane	3	166.4333	55.47778	198.8104
dioxane	3	171.4667	57.15556	19.27815
95 % ethanol	3	98.73333	32.91111	315.9848
1/2 hour	3	105.6333	35.21111	441.4415
1 hour	3	169.6333	56.54444	163.0604
5 hours	3	161.3667	53.78889	75.5837

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1099.862	2	549.9312	8.450449	0.036626	6.944272
Columns	807.838	2	403.919	6.206771	0.05939	6.944272
Error	260.3086	4	65.07716			
Total	2168.009	8				

Lucirin TPO

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
iso-octane	3	22.7	7.566667	2.380833
dioxane	3	12.675	4.225	15.7075
95 % ethanol	3	8.2	2.733333	13.86896
1/2 hour	3	9.775	3.258333	19.26896
1 hour	3	9.4	3.133333	5.663958
5 hours	3	24.4	8.133333	1.010208

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	36.75292	2	18.37646	4.857214	0.085068	6.944272
Columns	48.78125	2	24.39063	6.446861	0.056062	6.944272
Error	15.13333	4	3.783333			
Total	100.6675	8				

There was a significant difference in set off with time for CAS 0000947-19-3 and a significant difference with solvent for 4-phenyl benzophenone only.

Film 7 Fully Cured 80/40 solvent extraction 5 hours at 60 °C

The mean set off in Table A2-17 Appendix 2 page 112 was used to examine the effect of choice of solvent on set off value obtained.

CAS 0000947-19-3

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
95 % ethanol	4	144.7	36.175	9.5425
Iso-octane	4	119.1	29.775	158.4825
Dioxane	4	133.5	33.375	5.809167

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	82.34667	2	41.17333	0.710562	0.517	4.256495
Within Groups	521.5025	9	57.94472			
Total	603.8492	11				

CAS 0071868-10-5

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
95 % ethanol	4	55.4	13.85	9.23
Iso-octane	4	33.1	8.275	12.93583333
dioxane	4	15.8	3.95	7.336666667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	197.061667	2	98.5308333	10.01923566	0.005137	4.256495
Within Groups	88.5075	9	9.83416667			
Total	285.569167	11				

4-phenyl benzophenone

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
95 % ethanol	4	170.8	42.7	47.08667
Iso-octane	4	215.5	53.875	53.1225
Dioxane	4	188.6	47.15	23.75

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	253.2117	2	126.6058	3.064053	0.096619	4.256495
Within Groups	371.8775	9	41.31972			
Total	625.0892	11				

The results for CAS 0071868-10-5 were found to be significantly different between solvents with results obtained in 95 % ethanol lower than the other two solvents. The choice of solvent did not show a significant difference in results obtained for the other two ink components.

Set off measurements for Film 8 Ink series Y

The data was taken from Table A2-18 Appendix 2 page 113.

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
95 % ethanol	4	246.5	61.625	4.4558
Iso-octane	4	202.4	50.6	52.873
Dioxane	4	229.9	57.475	22.342

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	248.0516667	2	124.0258	4.6701	0.040622	4.256494729
Within Groups	239.015	9	26.55722			
Total	487.0666667	11				

The choice of solvent is just significant (at a confidence level of 0.04 it was not significant).

Appendix 4

Analytical methods

Analytical methods for measuring migration of photoinitiators in foods

Technique selection table for Compounds Analysed

Compound Name	GC-MS	LC-MS	HPLC -UV	HPLC-CAD
CAS 0071868-10-5 *	√	*	NA	NA
Ethyl-4-dimethylamino benzoate	√	NA	NA	NA
4-Phenyl benzophenone	√	NA	NA	NA
Pentaerithritol triacrylate	√	NA	NA	NA
Irgacure 369	X	√	NA	NA
Irgacure 379	X	√	NA	NA
Lucirin TPO	X	√	NA	NA
Irgacure 2959	√	NA	NA	NA
Di-(trimethylolpropane) tetraacrylate	√	NA	NA	NA
1-Phenyl-2-butanone	√	NA	NA	NA
Benzoic acid-2-benzoyl Methyl ester	√	NA	NA	NA
Speedcure 7005	X	X	√	NA
Speedcure 7010	X	X	√	NA
Dipropylene glycol diacrylate	√	NA	NA	NA
Trimethylpropane triacrylate	√	NA	NA	NA
CAS 0000947-19-3	√	NA	NA	NA
1,6-Hexanediol diacrylate	√	NA	NA	NA
Irgacure 2959	√	NA	NA	NA
Esacure 1	√	√	√	√
Omnipol ASA	X	√	√	√
Omnipol TX	X	√	√	√
Esacure 1001 M	X	√	√	√
Genopol TX1	X	√	√	√
Esacure KIP 75 LT	X	√	√	√
3-dimethylaminopropyl acrylate	NA	NA	NA	√
Tri(propyleneglycol)diacrylate	NA	NA	NA	√
Trimethylolpropane triacrylate	NA	NA	NA	√
Trimethylolpropane ethoxylate triacrylate	NA	NA	NA	√
Glycerol propoxylate (1PO/OH) triacrylate	NA	NA	NA	√
Hexamethylene diacrylate	NA	NA	NA	√
Phosphoric acid 2-hydroxyethyl methylacrylate	NA	NA	NA	√

* CAS 0071868-10-5 was run by MSD but was also used on the LC-MS as the Internal standard for Irgacure 369 and 379.

Those compounds that are amenable to GC-MS can be assumed to be amenable to GC-FID.

√ Does work by that technique.
X Does not work by that technique.
NA Not applicable/not tried

Analytical methods for soup and orange juice

Under-cured films 7 (40-20 Ink series X) and film 8 (40-20 Ink series Y) series were used for the migration tests into food. The food contact side of each test replicate of the film was measured so that a 0.7dm^2 cell was placed over the part of the food contact surface that had been in contact with the same region of the print design on the non food contact side.

1) Cells were prepared as described above.
2) The relevant food was decanted into the cells from beakers and weighed by difference.
3) Orange juice containing "Bits" and Cream of Tomato Soup were chosen.
4) Foods were spiked in duplicate in Schott bottles and stored over the test conditions the same as the samples.
5) The cells were stored for 10 days at 40^{o}C and after this time the exposed food samples were decanted into Schott bottles and stored in the fridge until ready for analysis.
6) Samples portions (10g) were accurately weighed into 40ml vials.
7) Spikes were prepared in duplicate with the addition of a mixed spike solution (200µl of approximately 100µg/ml solution prepared from an accurately weighed stock solution). A blank was also prepared with no spike solution added.
8) Deuterated benzophenone (100µl of approximately 1000µg/ml) was added to the samples then 4 ml of acetonitrile.
9) Sodium sulphate (4g) was weighed into the vials and the vials were mixed on a food blender to disperse the sodium sulphate.
10) The vials were shaken on a mechanical shaker for 1 hour then centrifuged for 5 minutes at 3000 rpm.
11) Aliquots of the top acetonitrile layer were filtered through syringe filters and run on the MSD and/or LCMS.

This was the procedure used for the Ink series X; for the Ink series Y, the masses taken were scaled up to 20g but the ratio to acetonitrile and sodium sulphate remained the same.

CAS 0071868-10-5 (50µl of approximately 100µg/ml) was used as the internal standard for Irgacure 369 and 379 in the Ink series Y.

Calibration Standards

Calibration standards were prepared in the blank food using the same mass of food for each of the standards that was used as in the analysis. Aliquots of the mixed stock solution were added to the standard vials at the same time as adding the internal standard.

MSD Instrument Conditions

Gas Chromatograph	Agilent 7890 A *msd1 NC*
Injection mode	Splitless (3:1)
Inlet purge on time	0.5 minutes
Injector temperature	280°C
Column head pressure	Constant flow 1.0 ml/min
Column	Phenomenex HP 5MS 30m x 0.25mm x 0.25μm
Temperature program	75°C hold 2 minutes ramped at 20°C/minute to 250°C then 10 °C/min to 300 °C (17 minutes)
Mass spectrometer	Agilent 5975 C
Detector mode	SIM (See ions below) m/z
Tune compound	PFTBA
Tune ions	69, 219, 502m/z

LCMS Instrument Conditions (LCMS Method: 369.M)

Column	Kinetex 2.6μ XB-C18 100F 100x4.6mm			
Mobile phase	Time/min	% acetonitrile	%Water	%IPA
	0	10	85	5
	1	10	85	5
	4	45	50	5
	4.5	45	0	55
	15	45	0	55
	15.5	10	85	5
	25	10	85	5
Flow rate	0.5ml/min			
Injection volume	30μL			

GCMS Ions

D10 Benzophenone (INT STD)	82, 110, 192
4-Phenyl benzophenone	152, 181, 258
CAS 0000947-19-3	77, 81, 99, 105
Benzoic acid-2-benzoyl methyl ester	77, 105, 163, 240
Ethyl-4-dimethylamino benzoate	148, 164, 193
1,6-Hexanediol diacrylate	55, 67, 82
CAS 0071868-10-5	128, 84
Irgacure 2959	121, 165, 166
Di-(trimethylolpropane) tetraacrylate	55, 225

LCMS Ions

Irgacure 369	367.2, 368.2
Irgacure 379	381.2, 382.2
CAS 0071868-10-5 (Internal standard)	280.2, 281.2

Cereal Analysis

The test cereal was blended in a food processor. The method used was based upon that described in "Survey of Benzophenone and 4-Hydroxybenzophenone migration from food packaging into foodstuffs" Number 18/06 November 2006 [Ref 13].

1) Blended food sample was weighed out (50g ± 0.1g) into a 250ml Schott bottle.
2) Deuterated benzophenone internal standard (100µl of approx 800pm D_{10} benzophenone in dichloromethane, chloroform or acetonitrile) was added to each sample. The samples were shaken gently to disperse the internal standard. *Irgacure 369 and 379 required a different internal standard – see notes.*
3) Relevant spike solution was added to recoveries in duplicate (0.2ml of 100µg/ml stock) plus one sample was spiked at the LOD (5µl of 100µg/ml stock). The samples were shaken gently to disperse the internal standard and spike solution.
4) Dichloromethane/acetonitrile (100ml, 50/50) was added to each sample with a measuring cylinder, followed by two small spatulas of sodium sulphate. *The mass was not critical to the experiment as this was intended just to dry the solvent in preparation for the next step.*
5) Samples were blended on the Ultra-Turrax sample blender for at least one minute so that all potential migrants were extracted from the food into the solvent.
6) The Ultra-Turrax was washed with warm tap water, rinsed with acetone and the blade was dried between samples.
7) After all samples had been blended approximately 35ml of the extract was decanted into a 40ml vial. The amount was not critical as internal standard has been added (i.e. not all of the extract was used for further analysis).
8) Each sample was centrifuged then approximately 20ml was decanted into a fresh 40ml vial
9) Each sample was evaporated down on a hot plate under a stream of nitrogen until half the 20ml taken had been evaporated.
10) Hexane (10ml) was added to each sample and shaken on a mechanical shaker for at least 10 minutes. Each sample aliquot was centrfrifuged then the bottom acetonitrile layer was carefully transferred to a new 40ml vial using a Pasteur pipette.
11) Acetonitrile (4ml) was added to the hexane layer and the shaking was repeated for a further 10 minutes and then centrifuged at 5000 rpm for 5 minutes.
12) The acetonitrile layers were combined and dried down on a hot plate under a stream of nitrogen to approximately 2-3mls. A couple of drops of dioxane were then added.
13) The extract were cooled for several hours at 5 °C filtered through a syringe filter
14) Standards were made up in acetonitrile and run with the samples on the GC-MS.

Calibration standards

A mixed stock standard was prepared containing the appropriate compounds. The stock was initially dissolved in chloroform and the working standards then diluted with acetonitrile.

For calibration standards the same volume of D_{10} benzophenone was added into 10ml volumetric flasks and aliquots of the stock solution were added (10, 50, 100, 250, 350, 500, 750µl). They were made to the mark with acetonitrile.

GC-MS Instrument Conditions

Gas Chromatograph	HP 6890N (MSD1) *NC*
Injection mode	Splitless (3:1)
Inlet purge on time	0.5 minutes
Injector temperature	280°C
Column head pressure	Constant flow 1.0 ml/min
Column	Phenomenex HP 5MS 30m x 0.25mm x 0.25µm
Temperature program	75°C hold 2 minutes ramped at 20°C/minute to 250°C then 10 °C/min to 300 °C (17 minutes)
Mass spectrometer	HP 5975 C
Detector mode	SIM (See ions below) m/z
Tune compound	PFTBA
Tune ions	69, 219, 502m/z

LCMS Instrument Conditions (LCMS Method: 369.M)

Column	Kinetex 2.6µ XB-C18 100F 100x4.6mm			
Mobile phase	Time/min	% acetonitrile	%Water	%IPA
	0	10	85	5
	1	10	85	5
	4	45	50	5
	4.5	45	0	55
	15	45	0	55
	15.5	10	85	5
	25	10	85	5
Flow rate	0.5ml/min			
Injection volume	30µL			

GCMS monitoring mass ion selections

Benzophenone	77, 105, 182
D10 Benzophenone (INT STD)	82, 110, 192
4-Methyl benzophenone	119, 196
4-Phenyl benzophenone	152, 181, 258

CAS 0000947-19-3	77, 81, 99, 105
Benzoic acid-2-benzoyl methyl ester	77, 105, 163, 240
2-Ethylhexyl-4-dimethylamino benzoate	148, 165, 277
Ethyl-4-dimethylamino benzoate	148, 164, 193
2,2-Dimethoxy-2-phenyl acetophenone	91, 105, 151
1-Phenyl-2-butanone	57, 91, 148
CAS 0071868-10-5	128, 84
Quanticure BMS	184, 227, 304
Di(propylene glycol) dibenzoate	77, 105, 163
Di(ethylene glycol) dibenzoate	77, 105, 149
Methyl-4hydroxybenzoate	91, 121, 152
Irgacure 2959	121, 165, 166

LCMS monitoring mass ion selections

Irgacure 369	367.2, 368.2
Irgacure 379	381.2, 382.2
CAS 0071868-10-5 (internal standard)	280.2, 281.2

Notes

It is not essential to make calibration standards in 10ml volumetric flasks, glass vials may be used.

It is important to evaporate off the dichloromethane as much as possible otherwise excessive fat may remain in the acetonitrile extract. Cooling of the extract is designed to filter off excess fat.

Irgacure 369 and Irgacure 379 are quantified by LC-MS so CAS 0071868-10-5 or Irgacure 369 or Irgacure 379 (if only one is present) are suitable choices as internal standards.

The two morpholino photoinitiators Irgacure 369 and Irgacure 379 could not be quantified by GC-MS in split or splitless mode using the capillary columns available (non polar and intermediate polar) and no spectra were found in the Wiley library 7n. It was not possible to separate them by HPLC. The two compounds tailed using a C18 column reverse phase column. Although triethylamine may be added to the mobile phase to improve the chromatography, this would result in unacceptable levels of contamination to the LC-MS and is not recommended for LC-MS analysis.

The chromatography of Irgacure 369, 379 and the internal standard CAS 0071868-10-5 can be improved by adding propan-2-ol (5%) to the mobile phase and the acetonitrile proportion therefore reduced and this resulted in much sharper peaks coming out at the same retention time.

General procedure for measuring set off

1) If the ink composition is not known, extract ½ dm^2 of the print surface by immersion overnight in chloroform. Filter and inject for GC-MS or LC-MS to identify photoinitiators, synergists and acrylates.
2) Ensure that a representative sample of the reel or stack has been obtained.
3) Discard the first few metres of the packaging.
4) Step off the repeat print image in contact with the food contact surface by marking on the food contact surface.
5) Cut out sub-samples as in step 4 in triplicate at the start, mid and end of the reel or stack.
6) Place the sub-samples food contact side up in test cells (minimum area 0.7 dm^2).
7) Select the most appropriate extraction solvent based upon knowledge of solubility and stability in either dioxane, iso-octane or 95 % ethanol. Iso-octane is not suitable for direct injection for LC-MS analysis of the extracts.
8) Add the extraction solvent (minimum of 30 ml for ink components that are freely soluble in the extraction solvent for a 0.7 dm^2 test surface area). For Tenax, 4.0 g of the powder was found convenient for 0.7 dm^2 test surfaces. The procedure given in EN 14338, “Paper and board intended to come into contact with foodstuffs-Conditions for determination of migration from paper and board using modified polyphenylene oxide (MPPO) as a simulant” was followed.
9) Seal the cell and place in an oven maintained at 60 °C for 5 hours.
10) Fortify blank extraction solvent in duplicate with known amounts of the ink components in the concentration range 10 – 20 µg/dm^2 equivalent. Store in glass vials in the oven at 60 °C alongside the test extracts.
11) After 5 hours exposure, add an internal standard into the cells. Decant the extracts from the cells into separate 40 ml glass vials. For Tenax, extract with two 20 ml portions of diethyl ether, combine and add 5 ml acetonitrile.
12) Concentrate the extracts by evaporation to approximately 2 ml under a stream of nitrogen on hotplate, filter through a syringe filter into 2 ml vials and inject for GC-MS and or LC-MS analysis using the equipment and operating conditions on page 130.
13) Repeat step 12 for the stability/recovery mixtures prepared in step 10.
14) Calibrate using external calibration solutions of the ink components prepared in pure extraction solvent.
15) If necessary, correct the set off values in µg/dm^2 for the analytical recovery measured in step 13.
16) Report results in units of µg/dm^2 .
17) To compare the set off values obtained against a migration limit assuming that 100 % of the set off will transfer to the food, proceed as follows. Calculate the means from each triplicate measurement taken from the reel or stack position. This will provide triplicate means from which an overall mean may be calculated. The overall mean may be multiplied by 6 to give the theoretical maximum migration in µg/kg.

Appendix 5

Stabilities of ink components under test conditions

Table A5-1 Recovery 10 days at 40 °C in 95 % ethanol

Ink component	*Replicates (%)*						Mean %
	1	**2**	**3**	**4**	**5**	**6**	
benzophenone	101	101	98	107	98	111	**103**
Ethyl-4-dimethylamino benzoate	111	114	111	120	111	116	**114**
CAS 0071868-10-5	79	77	69	79	74	73	**75**
4-phenyl benzophenone	69	65	60	64	58	58	**62**
Trimethyl propane ethoxylate	64	61	55	55	54	44	**56**
Pentaerythritol triacrylate	20	20	20	22	19	19	**20**

The data in table A5-1 were obtained by adding the ink components (in the range 16 to 20 µg for all except the acrylates which were added at 100 µg) into glass vials containing 40 ml of the set off extraction solvents and subjecting these mixtures to the analytical procedure (from step 11) given in Appendix 4 page 134, at the end of the exposure time period.

Table A5-2 Recoveries 5 hours at 60 °C

	Dioxane Replicates (%)		*Mean %*	*95 % ethanol Replicates (%)*		*Mean %*	*Iso-octane Replicates (%)*		Mean %
Irgacure 379	105	106	**106**	110	116	**113**	102	96	**99**
4-phenyl benzophenone	82	86	**84**	101	100	**101**	78	84	**81**
Irgacure 2959	89	91	**90**	102	112	**107**	92	107	**100**
CAS 0071868-10-5	95	99	**97**	121	116	**119**	100	103	**102**

The data in table A5-2 were obtained by adding the ink components (in the range 1 to 2 µg) into glass vials containing 40 ml of the set off extraction solvents and subjecting these mixtures to the analytical procedure (from step 11) given in Appendix 4 page 134, at the end of the exposure time period.

Table A5-3 Recoveries after 5 hours at 60 °C

Ink component	*Dioxane %*	*95 % ethanol %*	Iso-octane %
GPTA			
Replicate 1	< 1	< 1	< 1
Replicate 2	< 1	< 1	< 1
Replicate 3	< 1	< 1	< 1
Replicate 4	< 1	< 1	< 1
Mean	**< 1**	**< 1**	**< 1**
Ethyl-4-dimethylamino benzoate			
Replicate 1	95	95	83
Replicate 2	91	93	82
Replicate 3	83	92	70
Replicate 4	92	76	77
Mean	**90**	**89**	**78**
CAS 0000947-19-3			
Replicate 1	91	86	65
Replicate 2	91	100	61
Replicate 3	104	91	53
Replicate 4	98	93	60
Mean	**96**	**93**	**60**
Benzoic acid-2-benzoyl methyl ester (Speed cure MBB)			
Replicate 1	76	66	81
Replicate 2	77	66	78
Replicate 3	79	59	68
Replicate 4	76	63	76
Mean	**77**	**64**	**76**
1-phenyl-2-butanone			
Replicate 1	108	111	93
Replicate 2	106	108	90
Replicate 3	111	100	79
Replicate 4	105	103	87
Mean	**108**	**106**	**87**

Test cells containing 40 ml of solvent were fortified in the range 4 to 10 µg.

Table A5-4 Ink series Z Recoveries in Solvent 5hrs at 60°C

Compound	*Speedcure 7005 (%)*	*Speedcure 7010 (%)*
Dioxane		
Replicate 1	104	136
Replicate 2	98	124
Mean	**101**	**130**
95%EtOH		
Replicate 1	93	61
Replicate 2	92	46
Mean	**93**	**54**
Iso-octane		
Replicate 1	92	13
Replicate 2	87	17
Mean	**90**	**15**

Glass vials containing 25 ml of solvent were fortified with Speedcure 7005 (1,145 µg) and Speedcure 7010 (562 µg).

Tables A5-5 to A5-7 show analytical recoveries obtained by adding the ink components in the range 1 to 10 µg to test cells containing 40 ml of the solvents and subjecting these mixtures immediately to the analytical procedure (from step 11) given in Appendix 4 page 134.

Table A5-5 Recoveries from 95 % ethanol

Ink component	Benzophenone	Ethyl-4-dimethyl amino benzoate	CAS number 0000947-19-3	4-phenyl benzophenone	CAS number 0071868-10-5
Day 1	100	94	92	-	72
	100	93	86	-	-
	99	93	92	-	-
	99	95	87	-	-
	98	92	81	-	-
	100	90	-	-	-
Day 2	78	82	-	72	87
	94	106	-	-	-
Day 3	92	82	85	-	-

Table A5-6 Recoveries from Iso-octane

Ink component	Benzophenone	Ethyl-4-dimethylamino benzoate	4-phenyl benzophenone	CAS 0071868-10-5
Day 1	80	70	117	-
Day 2	139	124	148	109

Table A5-7 Recoveries from chloroform

Replicate	*Benzophenone*	*Ethyl-4-dimethylamino benzoate*	*4-phenyl benzophenone*	CAS 0071868-10-5
1	105	122	124	104
2	99	101	108	101
Mean	**102**	**112**	**116**	**103**

Appendix 6

Stabilities and recoveries of photoinitiators from foods

Table A6-1 Stabilities in Food. 10days at 40°C

Compound	*Orange juice (%)*	*Cereal (%)*	*Soup (%)*	*3% Acetic acid (%)*
1, 6-Hexanediol diacrylate				
Replicate 1	77	95	-	100
Replicate 2	77	104	-	103
Mean	**77**	**100**	**-**	**102**
CAS 0000947-19-3				
Replicate 1	135	98	102	97
Replicate 2	135	95	102	98
Mean	**135**	**97**	**102**	**98**
CAS 0071868-10-5				
Replicate 1	107	103	90	32
Replicate 2	105	114	91	32
Mean	**106**	**109**	**91**	**32**
4-Phenyl benzophenone				
Replicate 1	109	153	131	88
Replicate 2	109	156	112	123
Mean	**109**	**155**	**126**	**106**
Di(trimethylolpropane)tetraacylate				
Replicate 1	30	-	94	120
Replicate 2	28	-	100	109
Mean	**29**	**-**	**97**	**115**
Ethyl-4-dimethylamino benzoate				
Replicate 1	90	49	88	-
Replicate 2	92	60	80	-
Mean	**91**	**55**	**84**	**-**
Irgacure 2959				
Replicate 1	89	53	118	-
Replicate 2	82	47	87	-
Mean	**86**	**50**	**103**	**-**
Irgacure 369				
Replicate 1	107	84	100	-
Replicate 2	121	64	87	-
Mean	**114**	**74**	**94**	**-**
Irgacure 379				
Replicate 1	105	89	96	-
Replicate 2	120	71	86	-
Mean	**113**	**80**	**91**	**-**

Table A6-1 shows analytical recoveries obtained by adding the ink components in the range 40 to 100 µg to 80 to 110g of food and subjecting these mixtures at the end of the exposure time to the analytical procedure given in Appendix 4 pages 129 to 133.

Recoveries in Food

A6-2 Analytical recoveries from food

Compound	*Orange juice (%)*	*Cereal (%)*	*Soup (%)*	*3% Acetic acid (%)*
1, 6-Hexanediol diacrylate				
Replicate 1	77	98	84	63
Replicate 2	78	-	89	89
Mean	**78**	**-**	**87**	**76**
CAS 0000947-19-3				
Replicate 1	129	105	104	70
Replicate 2	119	-	94	100
Mean	**124**	**-**	**99**	**-**
CAS 0071868-10-5				
Replicate 1	120	144	98	19
Replicate 2	111	-	-	-
Mean	**116**	**-**	**-**	**-**
4-Phenyl benzophenone				
Replicate 1	118	109	95	141
Replicate 2	112	-	-	-
Mean	**115**	**-**	**-**	**-**
Di(trimethylolpropane) tetraacylate				
Replicate 1	81	-	66	164
Replicate 2	84	-	71	-
Mean	**83**	**-**	**69**	**-**
Ethyl-4-dimethylamino benzoate				
Replicate 1	93	88	95	-
Replicate 2	95	115	96	-
Mean	**94**	**102**	**96**	**-**
Irgacure 2959				
Replicate 1	82	103	114	-
Replicate 2	83	109	76	-
Mean	**83**	**106**	**95**	**-**
Irgacure 369				
Replicate 1	115	97	94	-
Replicate 2	112	108	88	-
Mean	**114**	**103**	**91**	**-**
Irgacure 379				
Replicate 1	116	84	92	-
Replicate 2	114	64	88	-
Mean	**115**	**74**	**90**	**-**

Table A6-2 shows analytical recoveries obtained by adding the ink components in the range 10 to 40 µg to 80 to 110g of food and immediately subjecting these mixtures to the analytical procedure given in Appendix 4 pages 129 to 133.

The analytical recoveries tabulated in Table A6-3 below were obtained by adding the ink components in the range 10 to 20 µg in 80 to 100g of food and 10 to 20 µg in 4g of Tenax. The foods were immediately subjected to the analytical procedure given in Appendix pages 129 to 133. The Tenax was immediately extracted with two 20 ml portions of diethyl ether. The extracts were evaporated to 1 ml after the addition of 5 ml of acetonitrile. The extracts were injected for analysis by GC-MS as described in Appendix 4 page 130.

A6-3 Analytical recoveries obtained from migration test media

Ink component	***Orange juice***	***Soup***	**Tenax**
Ethyl-4-dimethylamino benzoate	105	75	113
	105	76	99
Benzophenone	102	80	114
	102	92	98
CAS 0071868-10-5	56	130	78
	57	140	59
4-phenyl benzophenone	130	125	130
	132	114	-

Appendix 7

Analysis of Test Films 8 and 9 by DART

The following is a summary of a scoping piece of work.

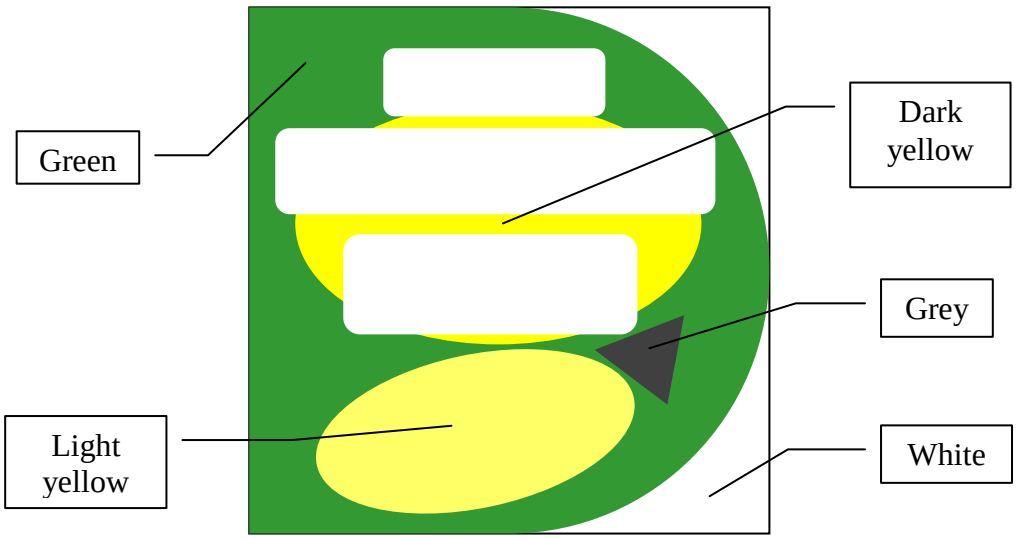
REPORT PIRA SAMPLES

Karim Bentayeb, Luke Ackerman, Tim Begley

OBJECTIVE

The goal of this work is to detect photoinitiators on the inner food contact surface (set off contamination) of food packaging samples provided by PIRA. The films were stapled to maintain the relative position of the image in contact with the food contact surface. Different sub-samples were cut representing the major colours of the packaging (Figure 1). Sub-samples of the inner surface were classified according to the colour they had been in contact with.

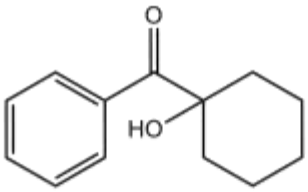
Figure 1. Packaging image



The image has been edited to protect commercial anonymity.
Two different samples were provided according to the kind of photoinitiators used:
a) “Ink series X” containing the following photoinitiators (Figure 2): CAS 0000947-19-3, Irgacure 369, Irgacure 379, CAS 0071868-10-5, LUCIRIN TPO (2,4,6-trimethyl benzoyldiphenyl phosphine oxide) and phenyl benzophenone.

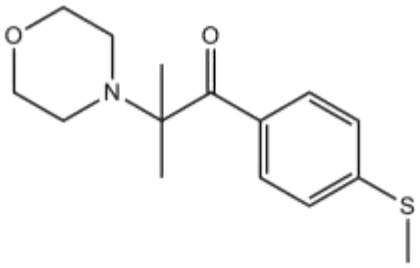
b) “Ink series Z” containing the following photoinitiators (Figure 3): Omnipol 910, Speedcure 7005 and Speedcure 7010.

947-19-3



Chemical Formula: $C_{13}H_{16}O_2$
Exact Mass: 204.115

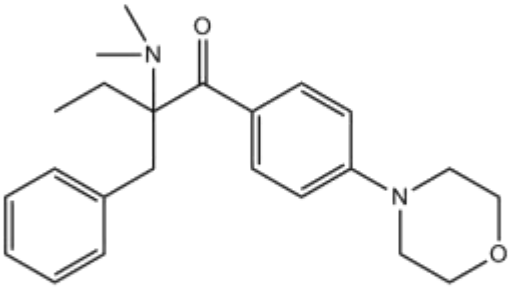
71868-10-5



Chemical Formula: $C_{15}H_{21}NO_2S$
Exact Mass: 279.129

Irgacure 369

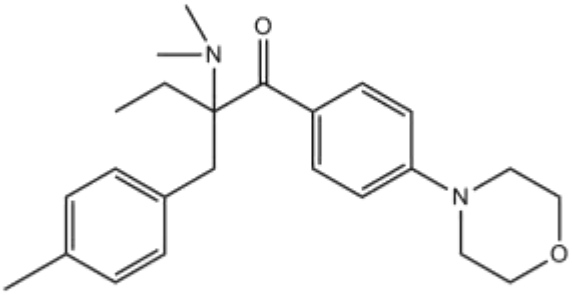
119313-12-1



Chemical Formula: $C_{23}H_{30}N_2O_2$
Exact Mass: 366.231

Irgacure 379

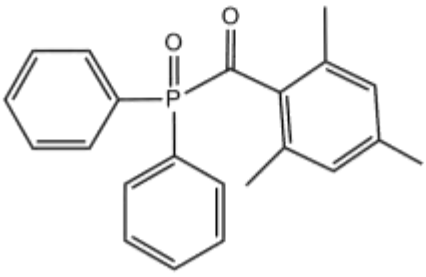
119344-86-4



Chemical Formula: $C_{24}H_{32}N_2O_2$
Exact Mass: 380.246

2,4,6-Trimethyl benzoyldiphenyl phosphine oxide (TPO)

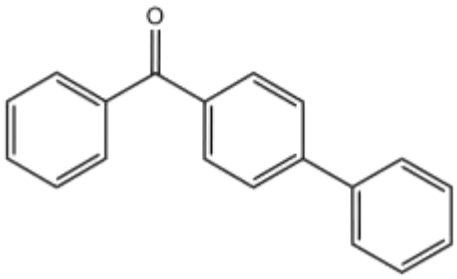
75980-60-8



Chemical Formula: $C_{22}H_{21}O_2P$
Exact Mass: 348.128

4-phenyl benzophenone

2128-93-0



Chemical Formula: $C_{19}H_{14}O$
Exact Mass: 258.104

Figure 2. Photoinitiators (Ink series X)

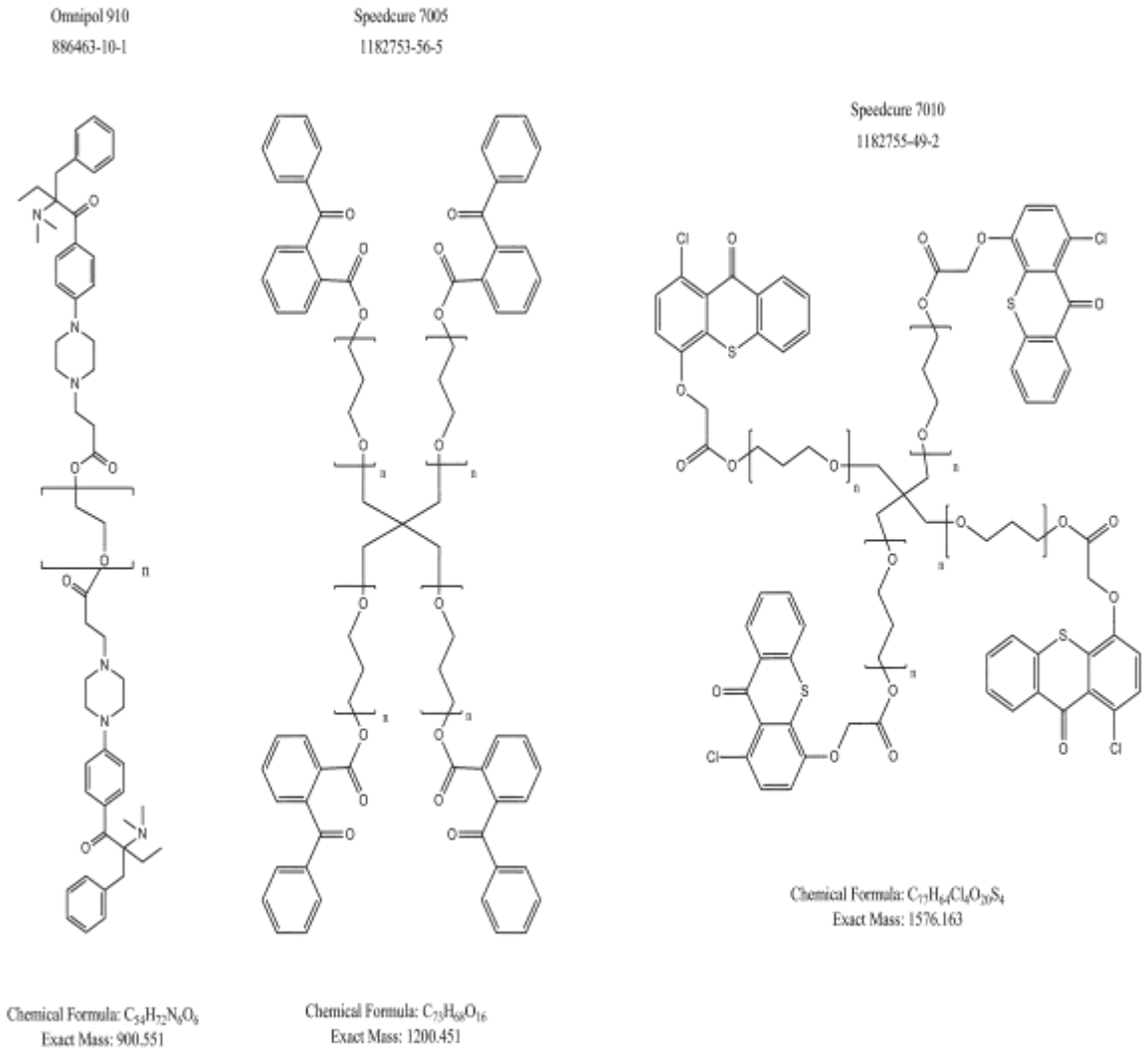


Figure 3. Photoinitiators (Ink series Z)

The structures of Omnipol 910, Speedcure 7005 and Speedcure 7010 were obtained by a search on the internet and have not been verified.

EXPERIMENTAL

Standards of the photoinitiators were also provided by PIRA. Standard solutions of the photoinitiators were prepared in methanol with concentrations of 100-700 µg g^{-1}. All but Speedcure 7010 were completely disolved after sonication in an ultrasound bath. However, the solubility of Speedcure in methanol was enough to acquire the corresponding spectra at different voltages with good sensitivity.

DART experiments were performed using an AccuTOF-DART™ (IonSense, Saugus, MA, USA). The distance between the DART exit and the mass spectrometer entrance was 1.0 cm and the DART sample distance was 2-3 mm. The helium flow rate was 1.0 ml/min and the DART exit grid voltage was set up at 530 V. Experiments were performed in positive mode. DART helium temperature was 500 °C. Four different *orifice 1 voltages* were applied in order to fragment the compounds: 5, 15, 40 and 70 V. Peak voltage was set at 600 V and 2000 V for Ink series X and Ink series Z, respectively. The rest of parameters were set up according to the seller specifications and previous knowledge of the device: ring lens voltage 5 V, orifice 2 voltage 5 V, orifice 1 temperature 105 °C, bias voltage 30 V, pusher bias voltage -0.20 V, focus voltage -120 V, focus lens voltage 10.0 V, quadrupole lens voltage 20.0 V, right/left -1.0 V, top/bottom 6.5 V, reflectron voltage 800.0 V and detector voltage 2300 V.

Sample spectra were acquired by cutting a small packaging area, holding it in such a way that only the surface under study was in contact to the helium stream. Using tweezers the sample was oriented slightly off-centered about 2-3 mm after the DART exit. In this way, sample spectra were acquired preceded by the acquisition of PEG in order to perform a mass calibration in every file. Acquisitions were performed from 25 to 800 Da and from 25 to 2000 Da for Ink series X and Ink series Z, respectively. The acquired spectra were calibrated using PEG 600 and PEG 1000 for Ink series X and Ink series Z, respectively.

RESULTS

From the acquisition of the standard solutions at different voltages, the most abundant ion was registered at every single voltage. All photoinitiators provided unique ions and were detectable in solutions. Using these unique ions the photoinitiators were looked for within the spectra of the sub-samples both on the inner and the outer surface. The following table contains the relative abundance of the ions in the spectra of the sub-samples, both inner and outer film surface.

Table 1. Relative abundance of the ions of the photoinitiators in the spectra of the subsamples in percentage. Red color means “consistent results”, yellow color means there is some evidence.

		ink series X											
		CAS 0000947-19-3				Irgacure 369				Irgacure 379			
		5V	15V	40V	70V	5V	15V	40V	70V	5V	15V	40V	70V
	Ions	187.122	187.122	187.122	105.034	367.238	367.238	367.238	176.144	381.254	381.254	381.254	190.160
Outer	White												
	Green	6.6	4.1	9.9	100.0	4.8	1.8	15.7					
	Letters	3.5		4.9	97.2								
	Rice	1.5	1.3	6.6	54.7								
	Fork	12.5	7.8	9.9	40.9	6.3	11.3	12.0					
Inner	White			15.3									
	Green	2.0	3.0	15.3	100.0								
	Letters			5.4	100.0								
	Rice	2.6	4.3	3.3	100.0								
	Fork	5.2	9.8	16.7	100.0								
		CAS 0071868-10-5				LUCIRIN TPO				4-phenyl benzophenone			
		5V	15V	40V	70V	5V	15V	40V	70V	5V	15V	40V	70V
	Ions	280.137	280.137	280.137	165.073	147.081	147.081	147.081	119.086	259.112	259.112	259.112	105.034
Outer	White												
	Green	48.7	10.9	100.0	66.7			9.1	7.5	14.5	6.8	25.7	100.0
	Letters	19.9	2.6	31.8	74.1			6.9	18.5	12.1	2.1	14.4	97.2
	Rice	5.2	12.8	51.1	100.0			6.1	8.6	3.3	4.2	12.5	54.7
	Fork	87.8	69.4	100.0	100.0		1.2	6.0	3.8	30.3	15.1	16.7	40.9
Inner	White												
	Green	2.4	7.0	25.7	18.6			3.5	1.4	8.1	13.6	58.5	100.0
	Letters		1.4	5.7	38.0				7.5		4.9	20.2	100.0
	Rice	22.7	10.0	1.4	35.6				5.3	24.9	13.9	3.0	100.0
	Fork	19.8	14.1	73.7	33.8			2.6	1.5	27.6	24.0	100.0	100.0

		Ink series Z											
		Onmipol 910				Speedcure 7005				Speedcure 7010			
		5V	15V	40V	70V	5V	15V	40V	70V	5V	15V	40V	70V
	Ions	366.254	366.254	452.291	452.291	209.060	209.060	209.060	253.086	349.030	320.998	320.998	320.998
Outer	White												
	Green						2.0	5.2					
	Letters							4.4					
	Rice						1.9	3.7					
	Fork	15.4	14.3				2.6	2.1					
Inner	White												
	Green												
	Letters												
	Rice						1.3	2.0					
	Fork						4.1	13.1					

Note: tabulated data are abundance data which can not be related to concentration (ppb).

CONCLUSIONS

CAS 0000947-19-3, CAS 0071868-10-5, LUCIRIN TPO, 4-phenyl benzophenone and Speedcure 7005 were detected both on the outer and on the inner food contact surface of the packaging material.

Irgacure 369 and Onmipol 910 were detected only on the outer surface of the packaging.

Irgacure 379 and Speedcure 7010 were not detected on the samples.

Photoinitiators were not detected on the white part of the image (with the exception of one sub-sample).

In Ink series X, photoinitiators (when found) where not related to a single subsample but where found in all sub samples (except white), indicating that the photoinitiators detected belong to the yellow color which was applied on all the subsamples.
In Ink series Z, much less set off evidence was detected.

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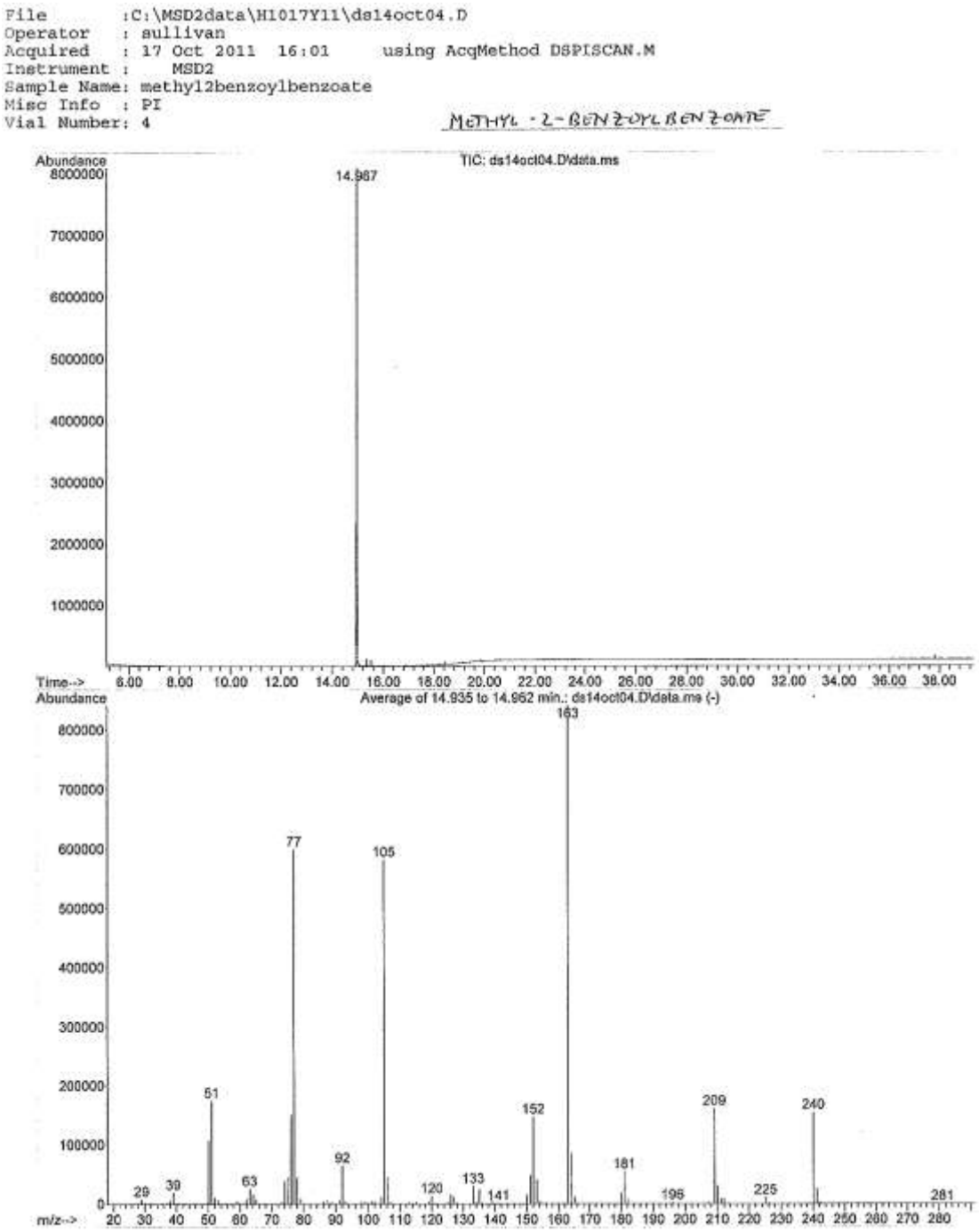
Office of Regulatory Science
Center for Food Safety and Applied Nutrition
Food and Drug Administration
5100 Paint Branch Parkway
College Park, Maryland 20740
301-436-1893

Appendix 8

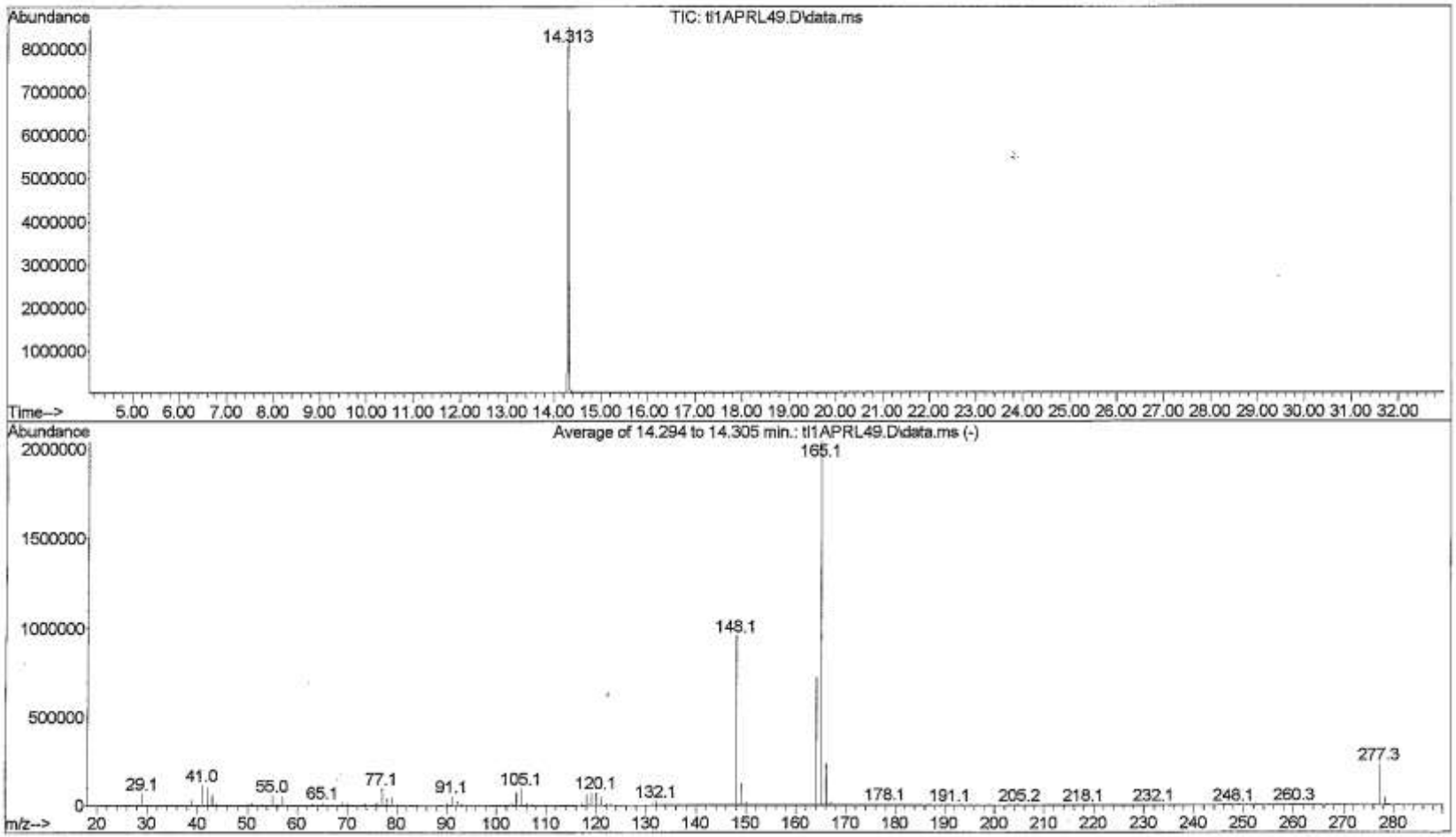
GC-MS Chromatograms and mass spectra of ink components

The best computer match to a library mass spectrum is shown in some cases and this should not be considered a reliable match.

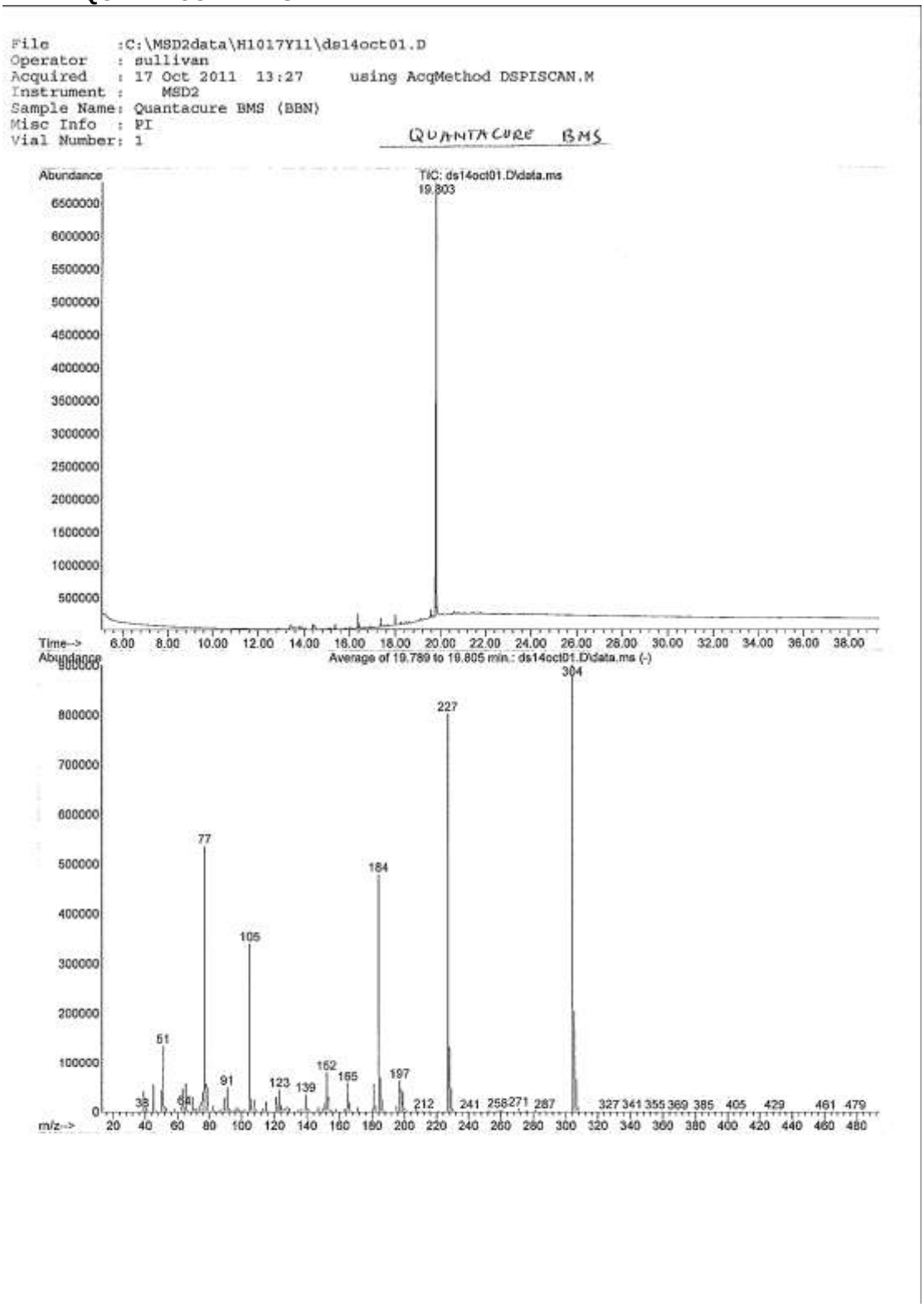


Instrument : MSD1
Sample Name: AV
Misc Info :
Vial Number: 34

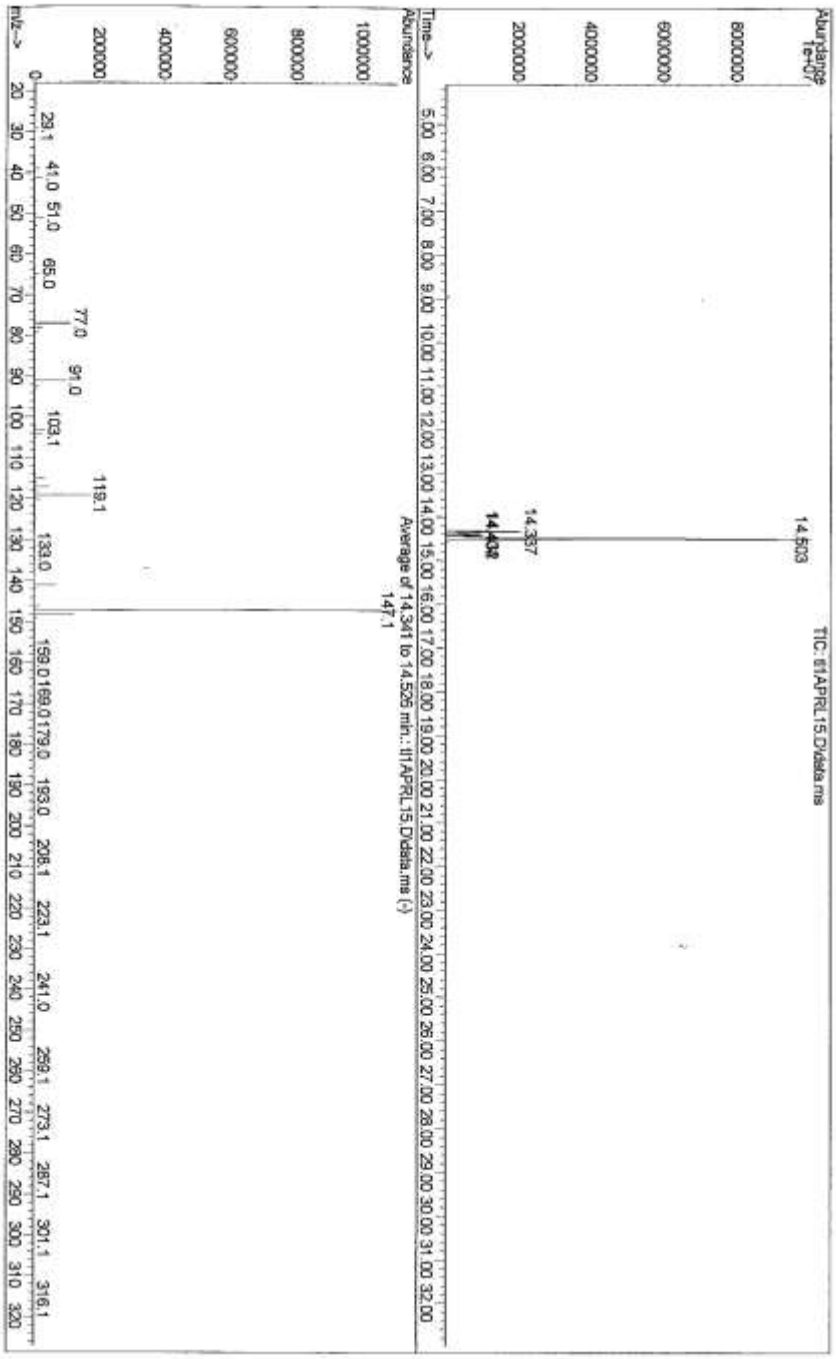
2-ethylhexyl-4-(dimethylamino)benzoate.



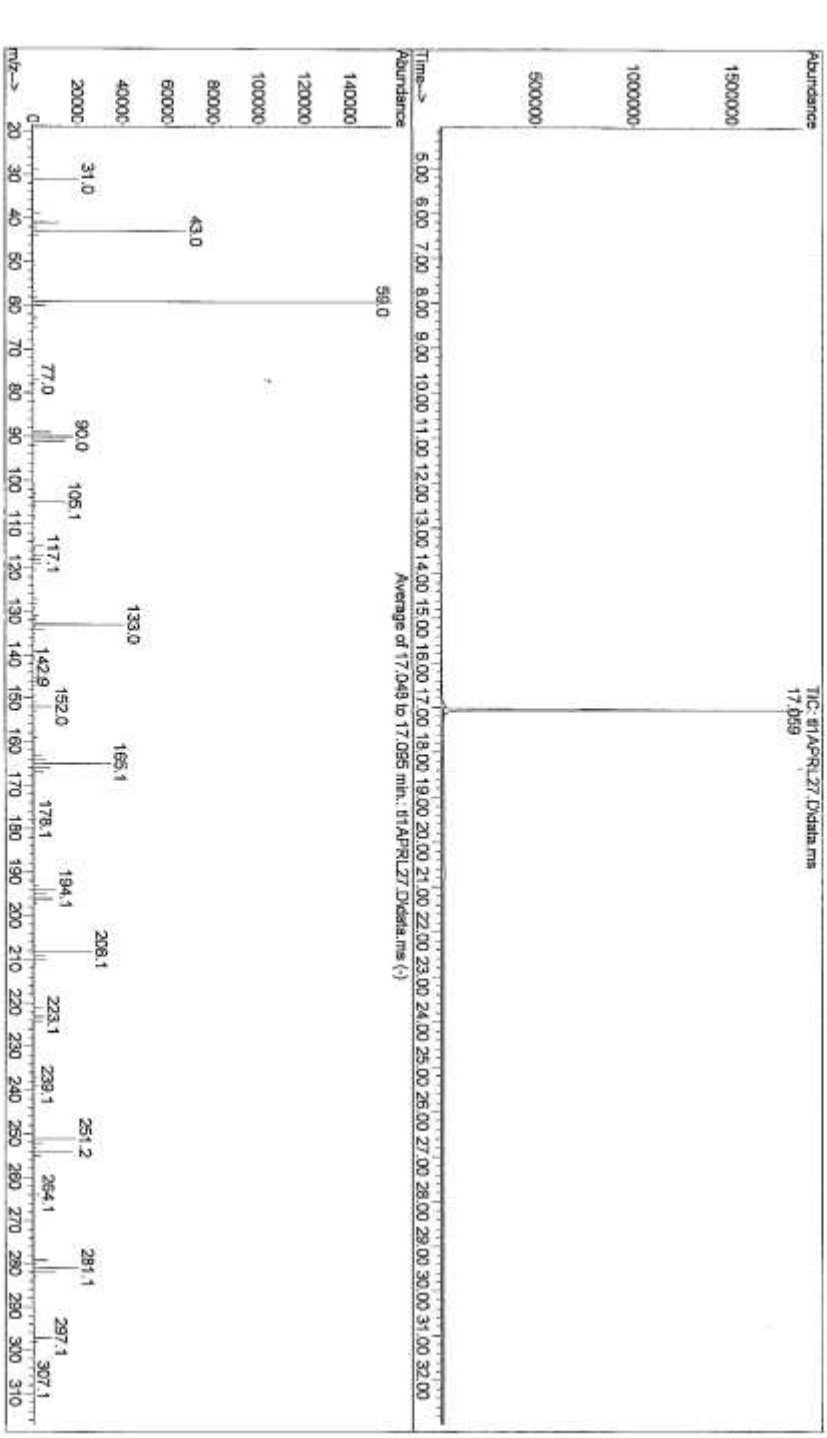
QUANTACURE BMS



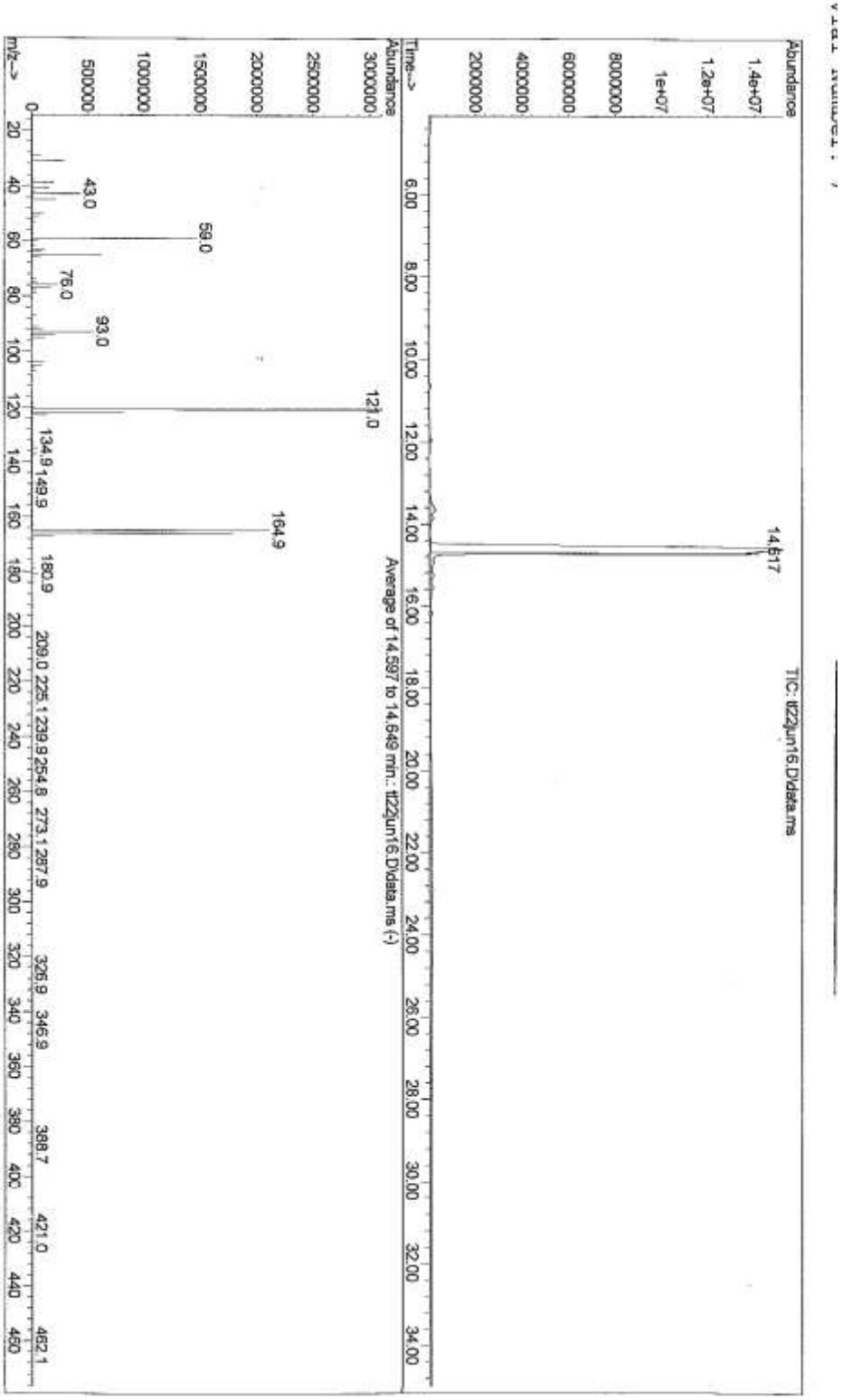
BLEND CAS 84434-11-7 & 162881-26-7



IRGACURE 127

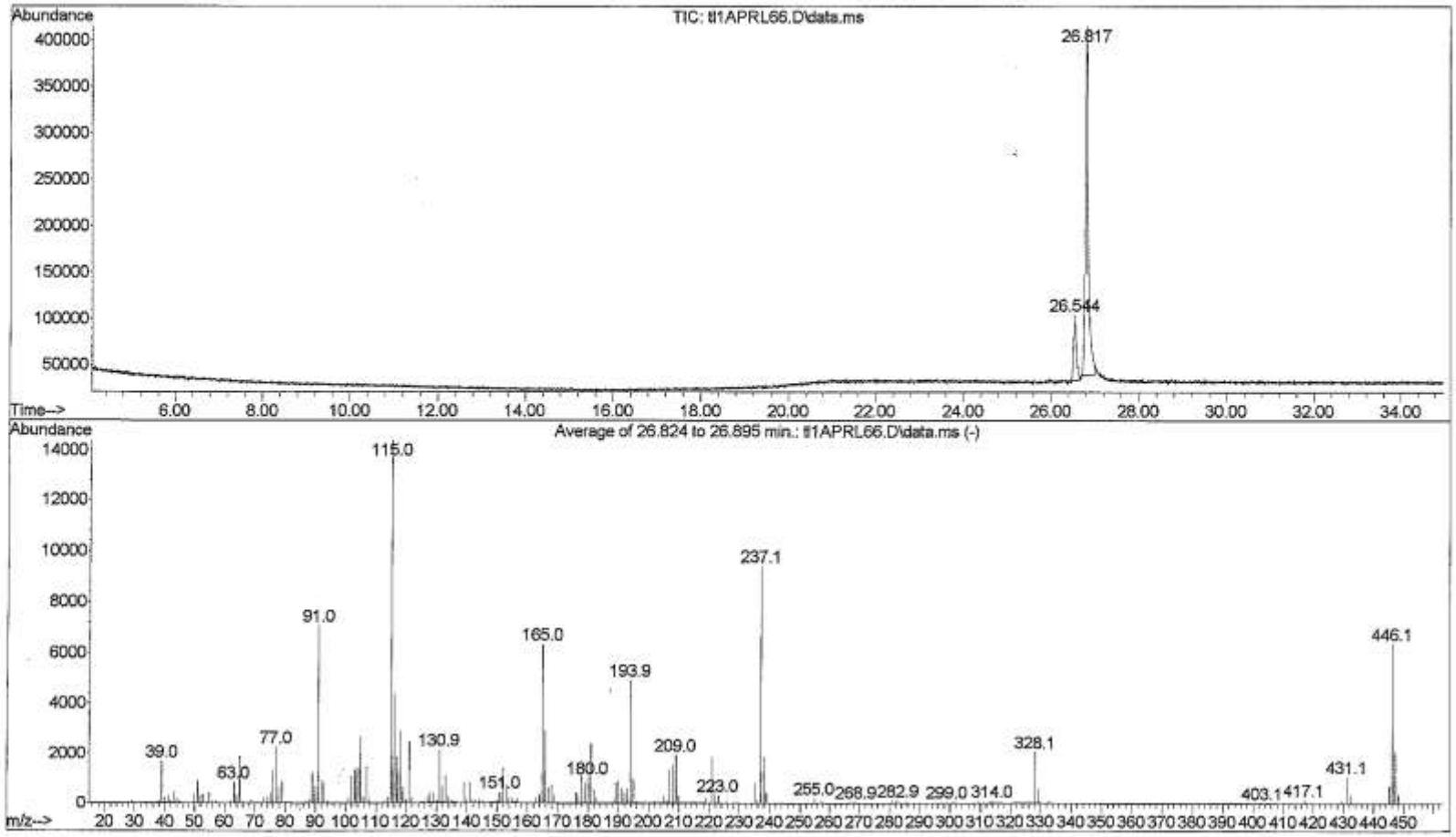


Irgacure 2959 (Batch 1)

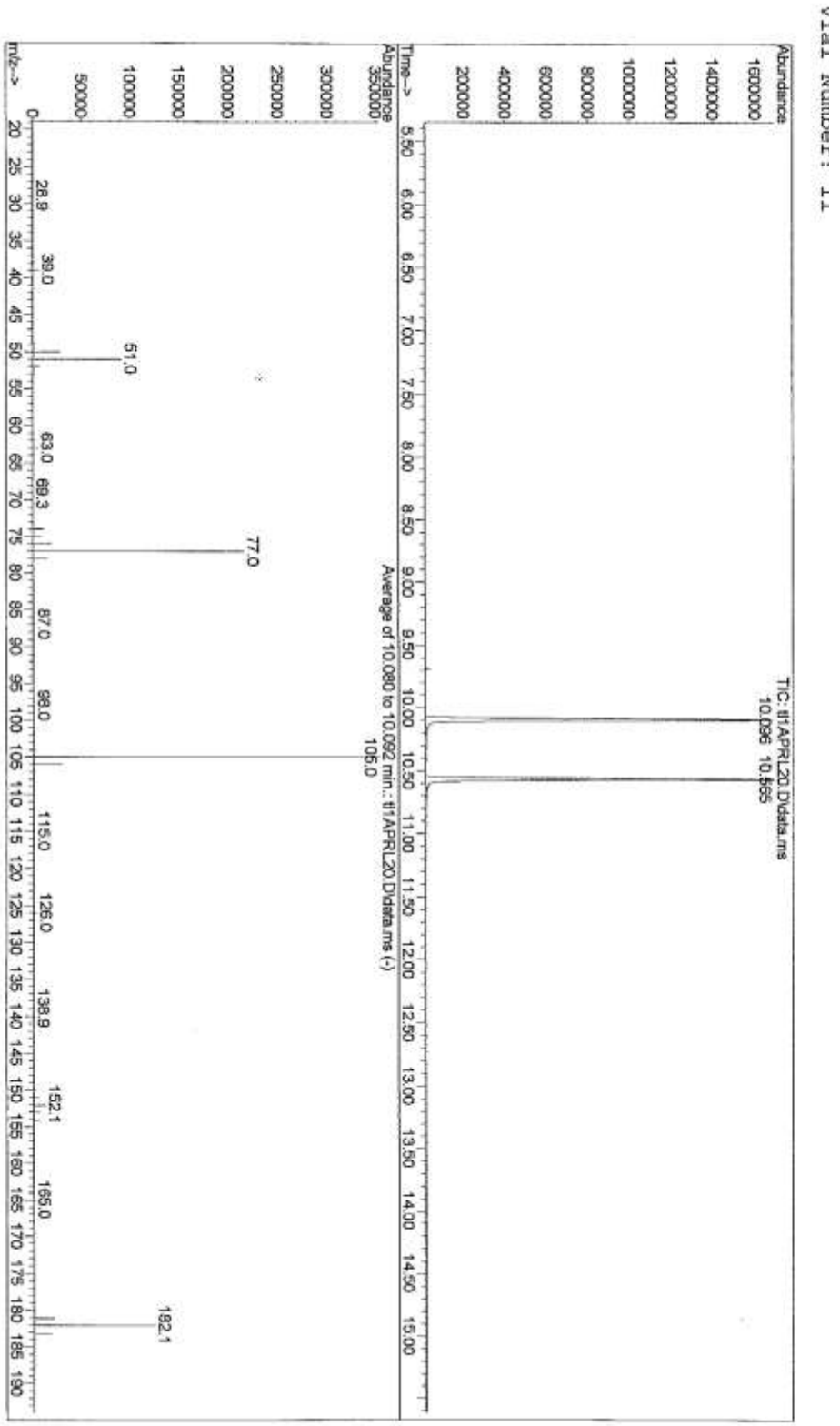


Instrument : MSD1
Sample Name: AF
Misc Info :
Vial Number: 51

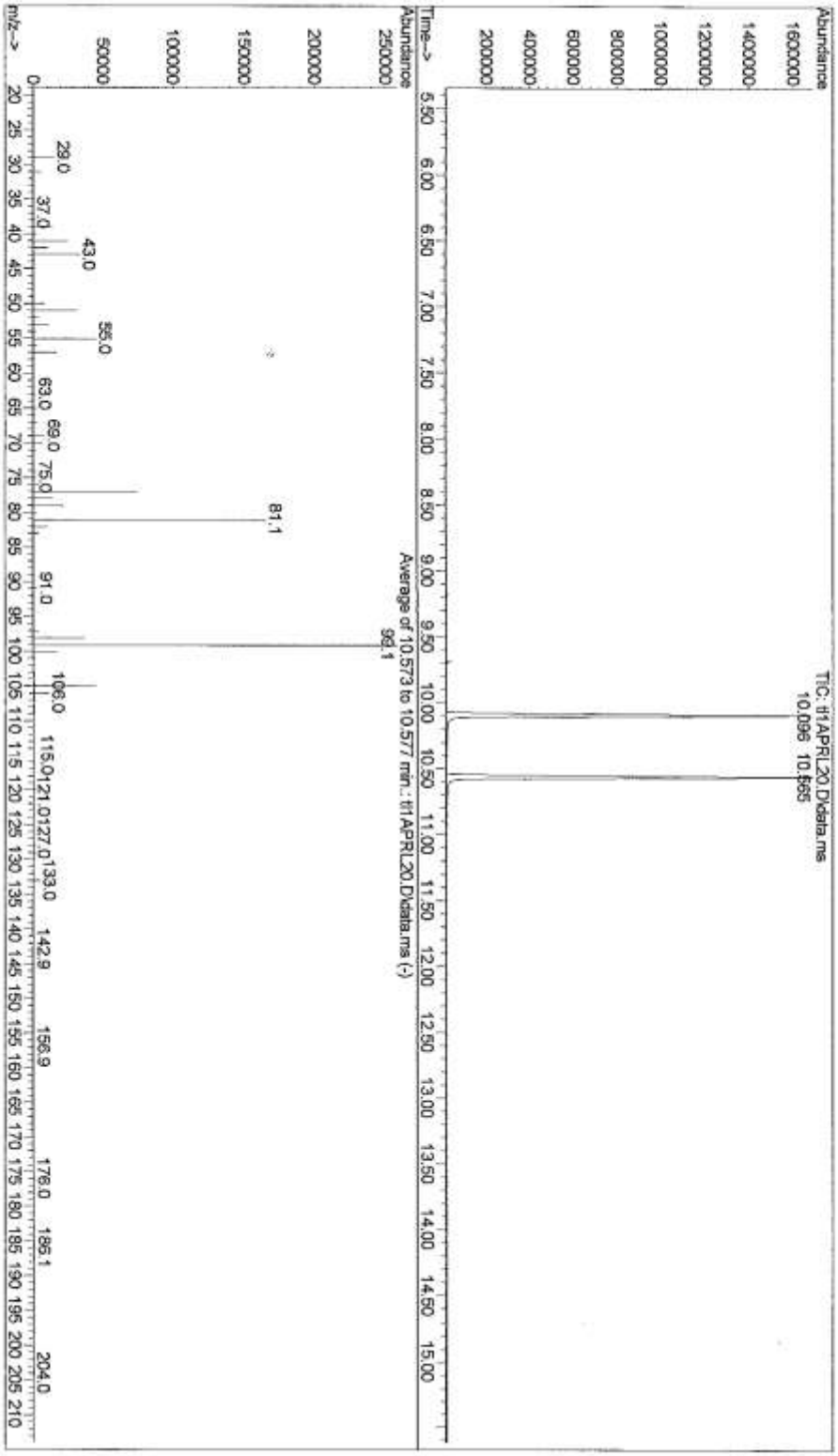
4-4-Bis(2-(1-propenyl)phenoxy)benzophenone



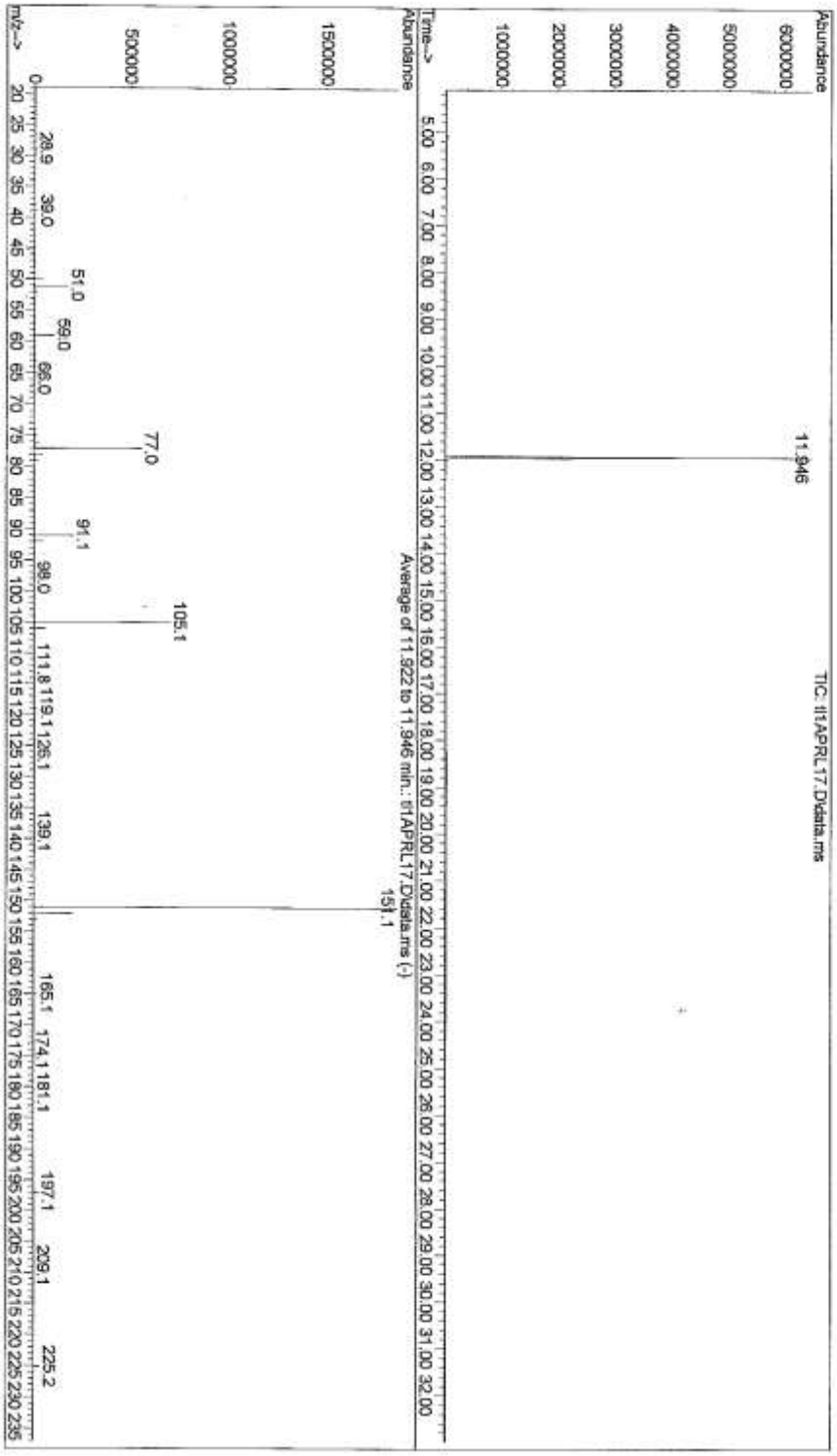
50 % BLEND CAS 0000947-19-3 & BENZOPHENONE



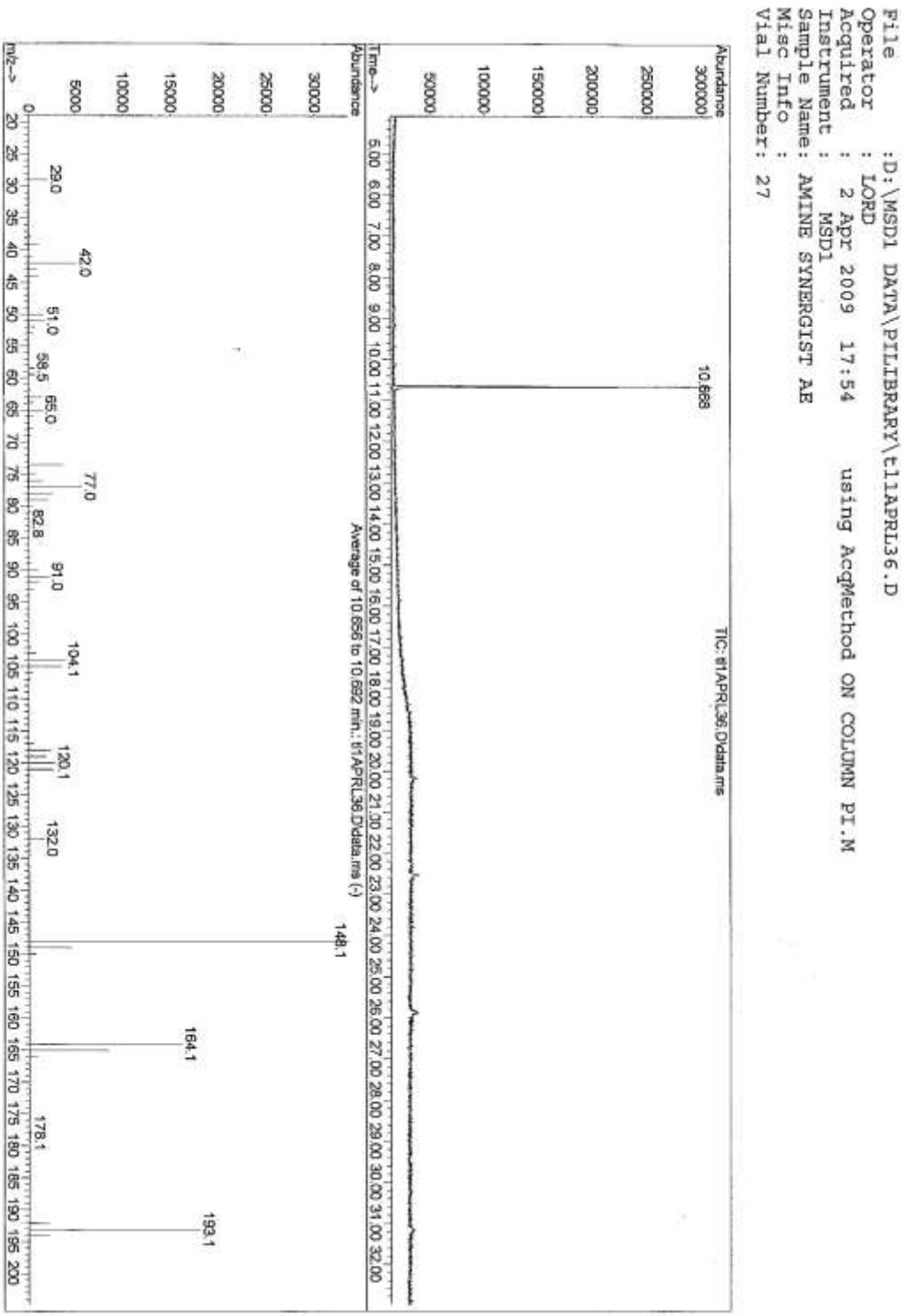
50 % BLEND CAS 0000947-19-3 & BENZOPHENONE



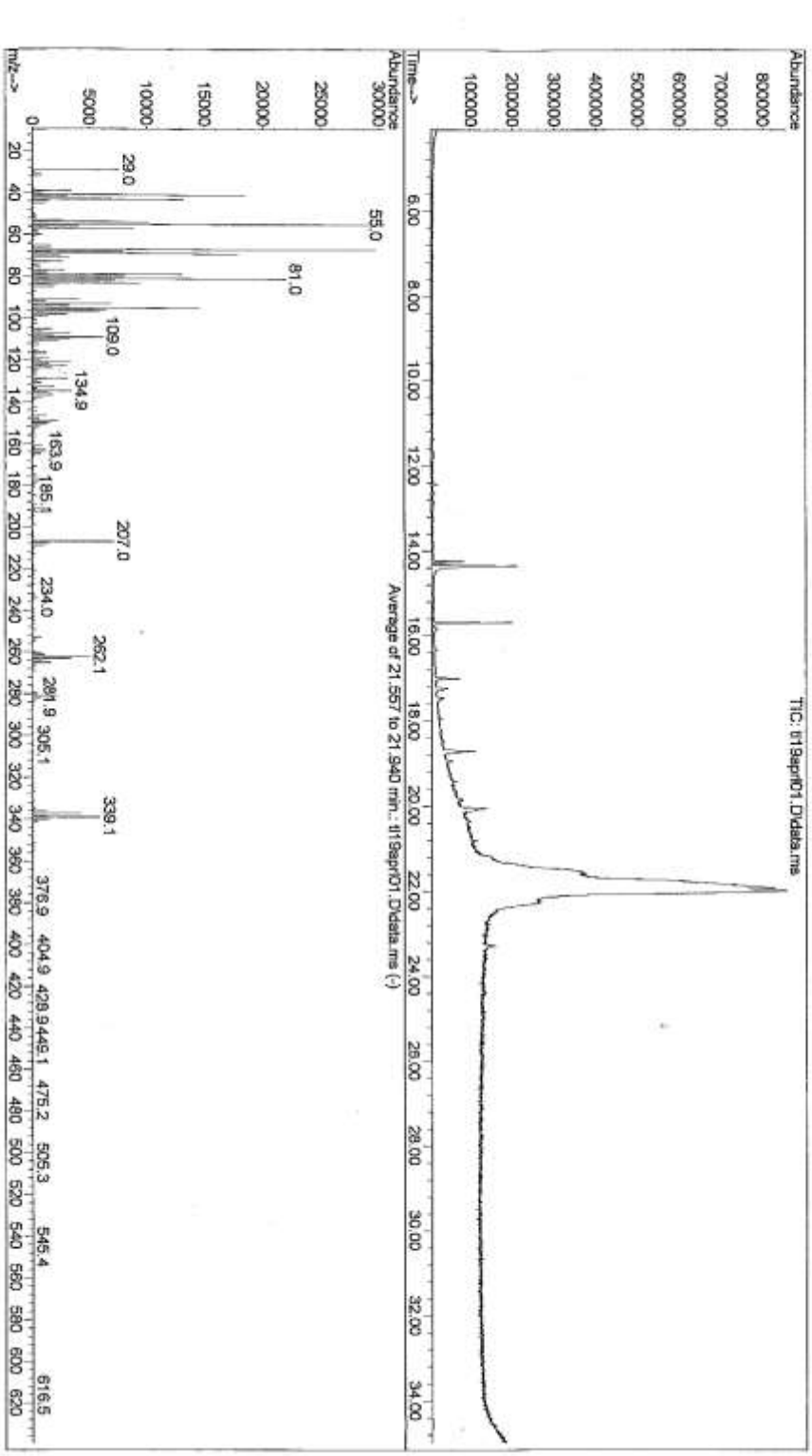
Pira code 659



AMINE SYNERGIST



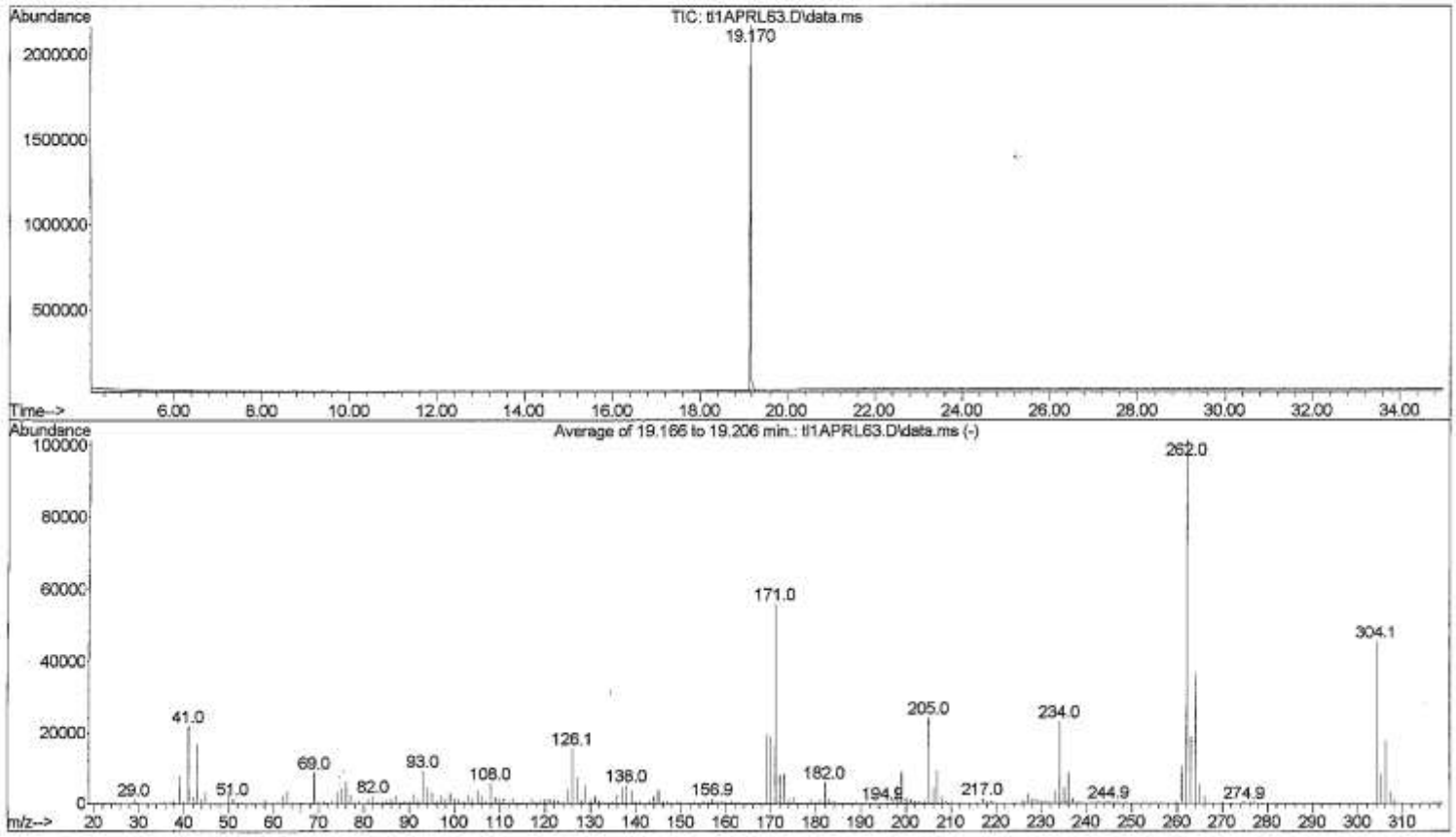
EPECRYL P39


File :D:\MSD1 DATA\PILIBRARY\tl19apr101.D
Operator : LORD
Acquired : 19 Jun 2009 15:44 using AcqMethod ON COLUMN PI.M
Instrument : MSD1
Sample Name: epecryl p39
Misc Info :
Vial Number: 1
Abundance
TIC: tl19apr01.D\data.ms
Time-->
Abundance
Average of 21.557 to 21.940 min.: tl19apr01.D\data.ms (-)
m/z-->

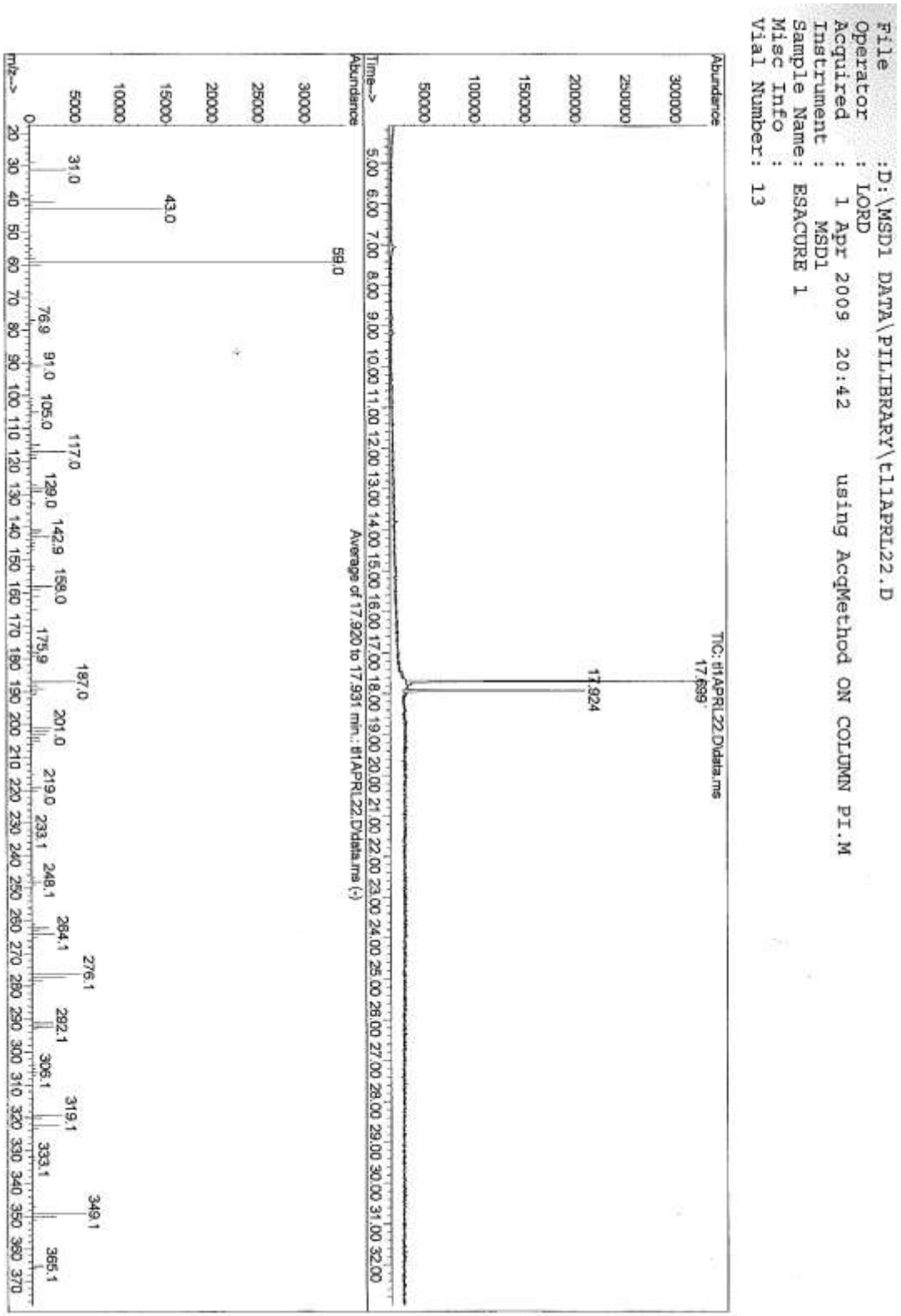
Irgacure 2959 (batch 2)

File :D:\MSD1 DATA\PILIBRARY\t11APRL63.D
Operator : LORD
Acquired : 3 Apr 2009 16:36 using AcqMethod ON COLUMN PI.M
Instrument : MSD1
Sample Name: AJ
Misc Info :
Vial Number: 48

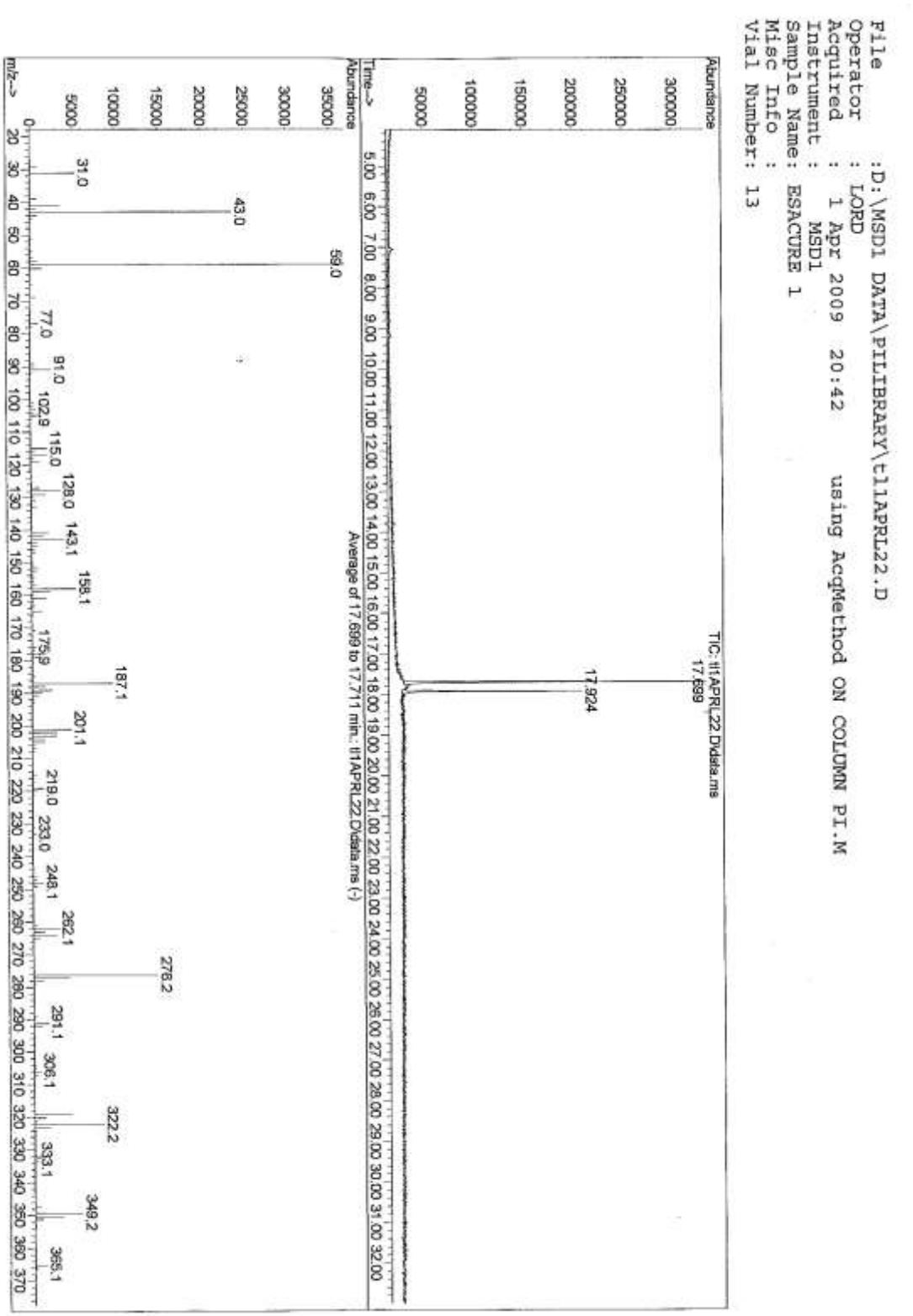
1-Chloro-4-propoxy-9H-thioxanthen-9-one.



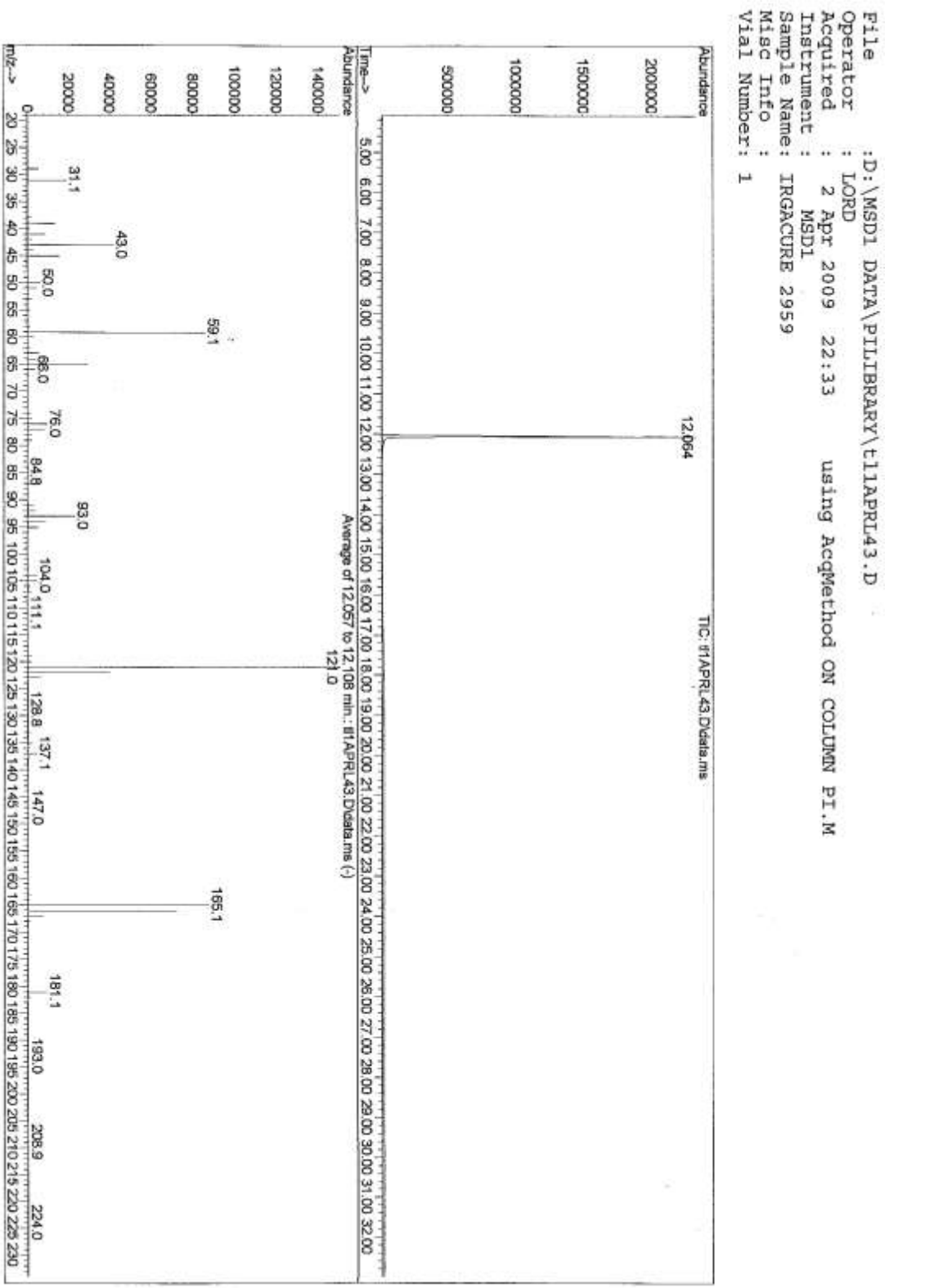
ESACURE 1


File :D:\MSD1 DATA\PILIBRARY\t11APRL22.D
Operator : LORD
Acquired : 1 Apr 2009 20:42 using AcqMethod ON COLUMN PI.M
Instrument : MSD1
Sample Name: ESACURE 1
Misc Info :
Vial Number: 13
Abundance
TIC: t11APRL22.D\data.ms
17.699
17.924
Time-->
Abundance
Average of 17.920 to 17.931 min.: t11APRL22.D\data.ms (-)
59.0
43.0
31.0
117.0
187.0
276.1
349.1
m/z-->

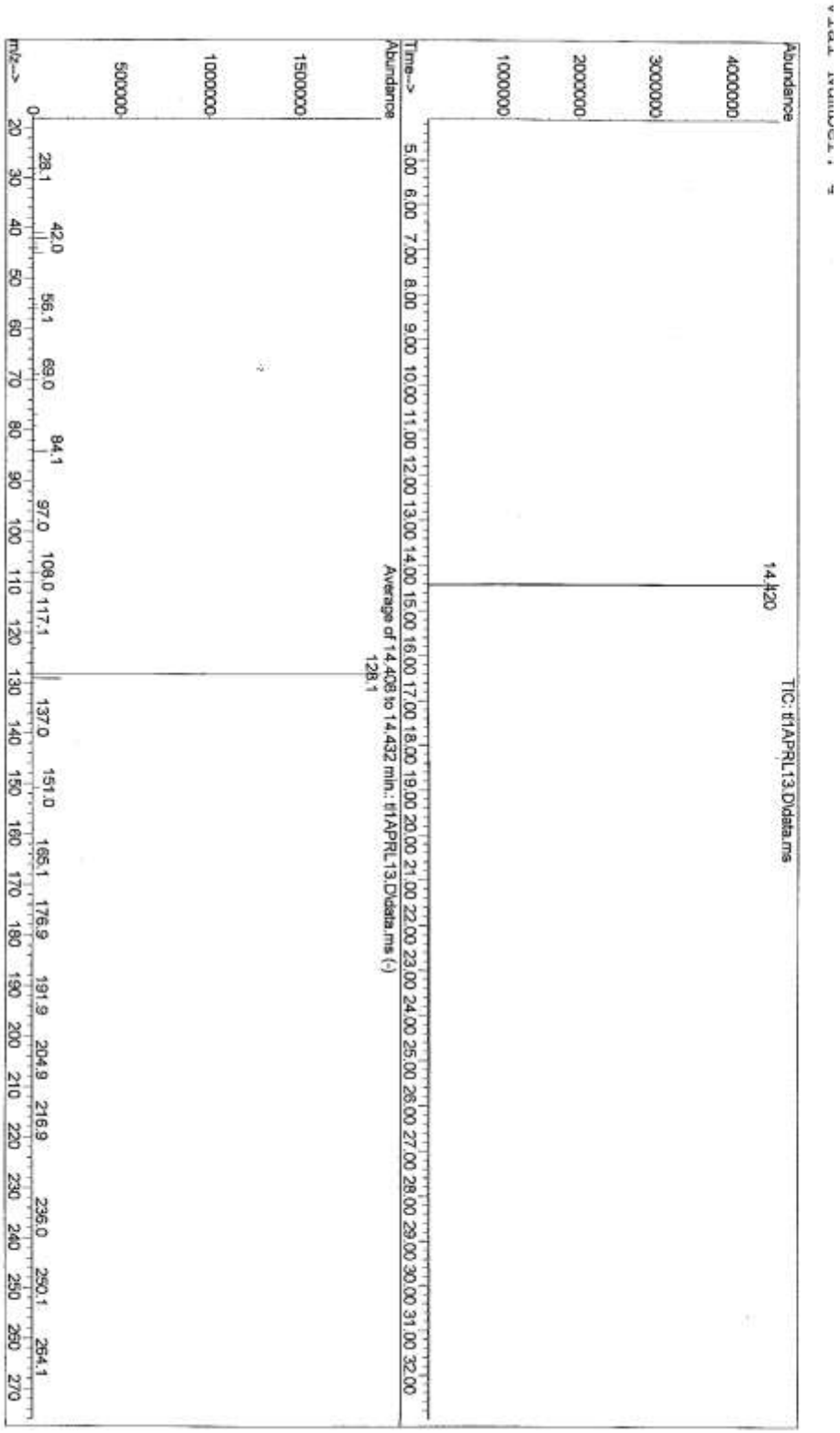
ESACURE 1


File :D:\MSD1 DATA\PILIBRARY\t11APRL22.D
Operator : LORD
Acquired : 1 Apr 2009 20:42 using AcqMethod ON COLUMN PI.M
Instrument : MSD1
Sample Name: ESACURE 1
Misc Info :
Vial Number: 13
Abundance
TIC: t11APRL22.D\data.ms
17.699
17.924
Time-->
Abundance
Average of 17.699 to 17.711 min.: t11APRL22.D\data.ms (-)
59.0
43.0
31.0
77.0
91.0
102.9
115.0
128.0
143.1
158.1
175.9
187.1
201.1
219.0
233.0
248.1
262.1
276.2
291.1
306.1
322.2
333.1
349.2
365.1
m/z-->

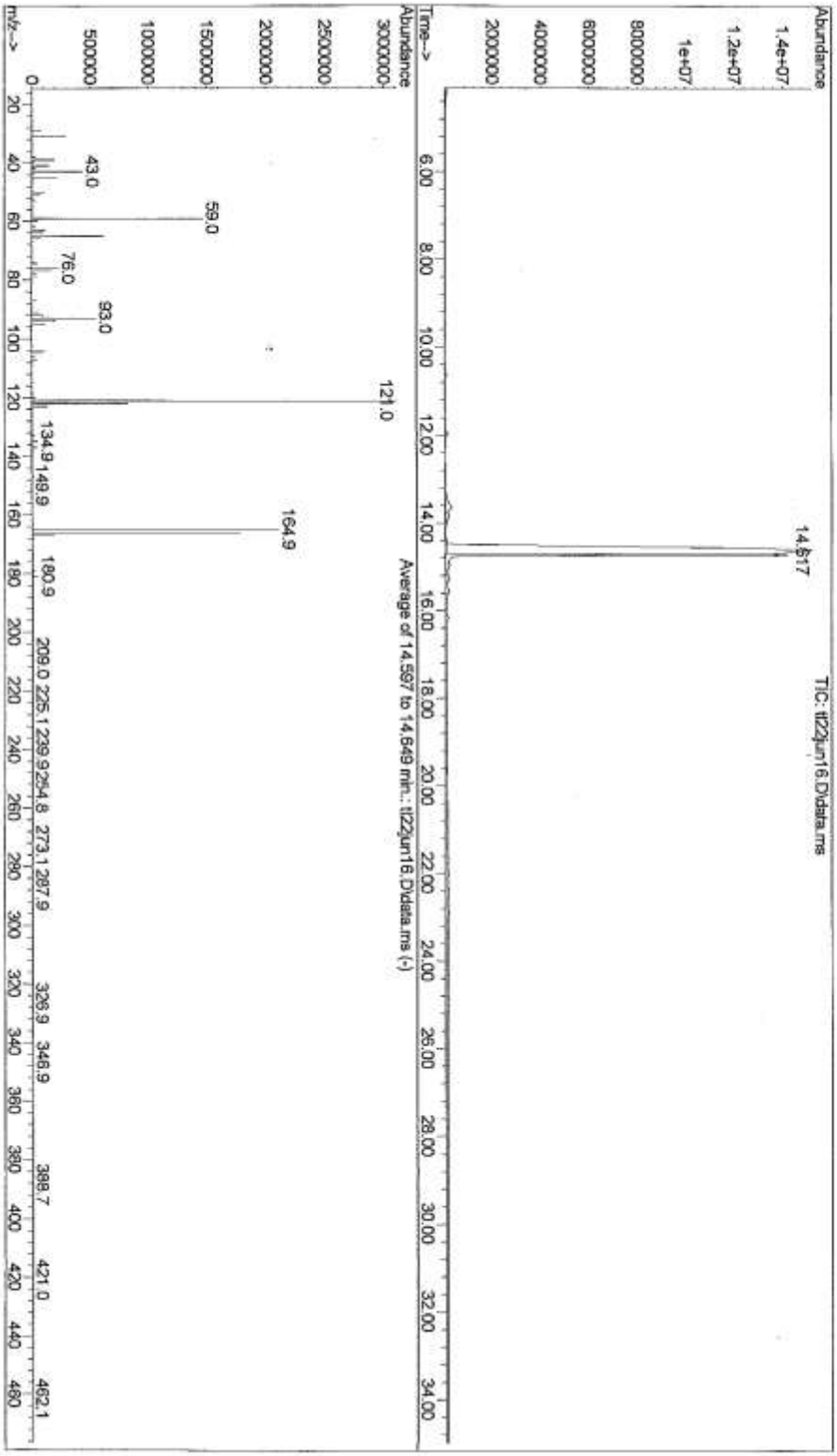
IRGACURE 2959 (batch 3)



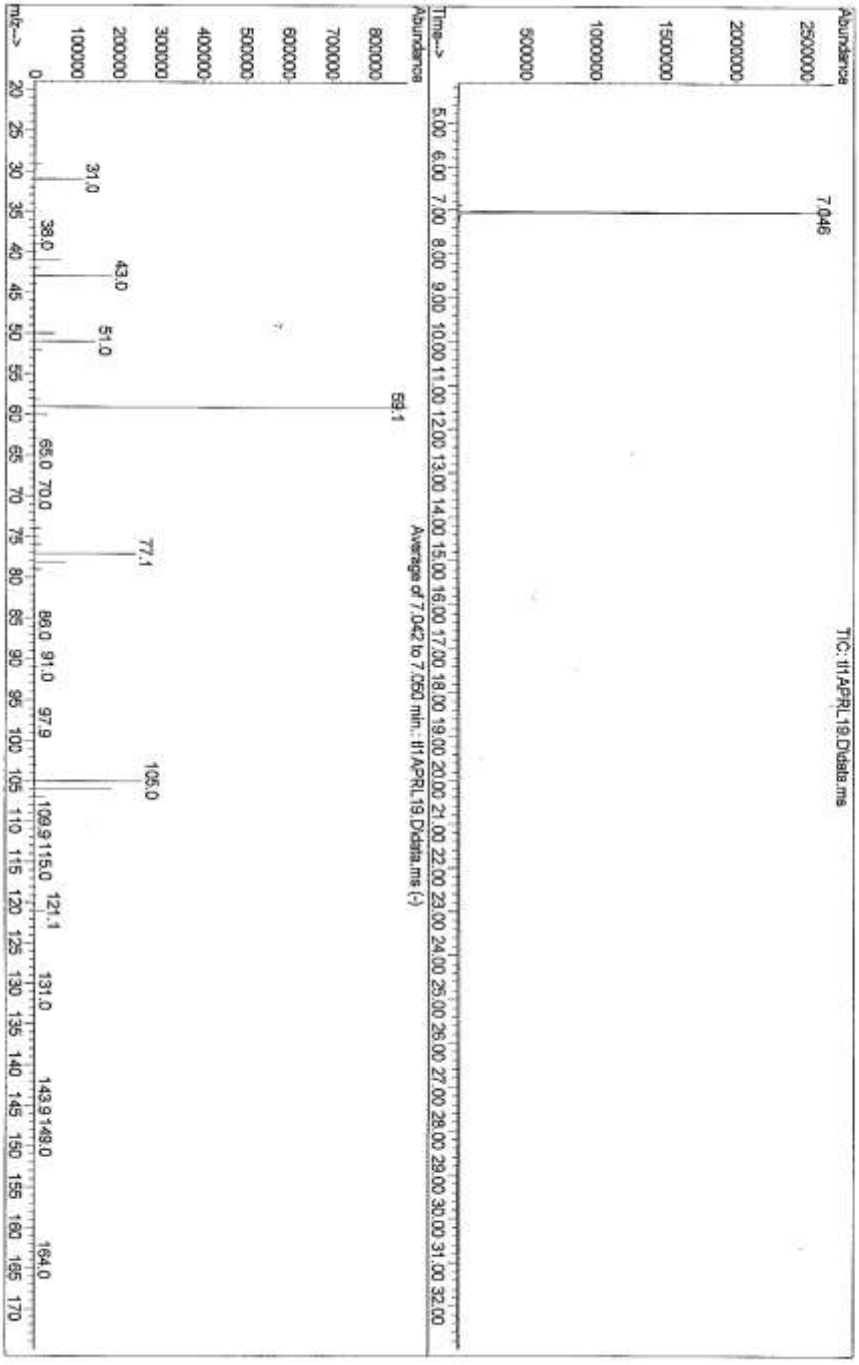
CAS 0071868-10-5



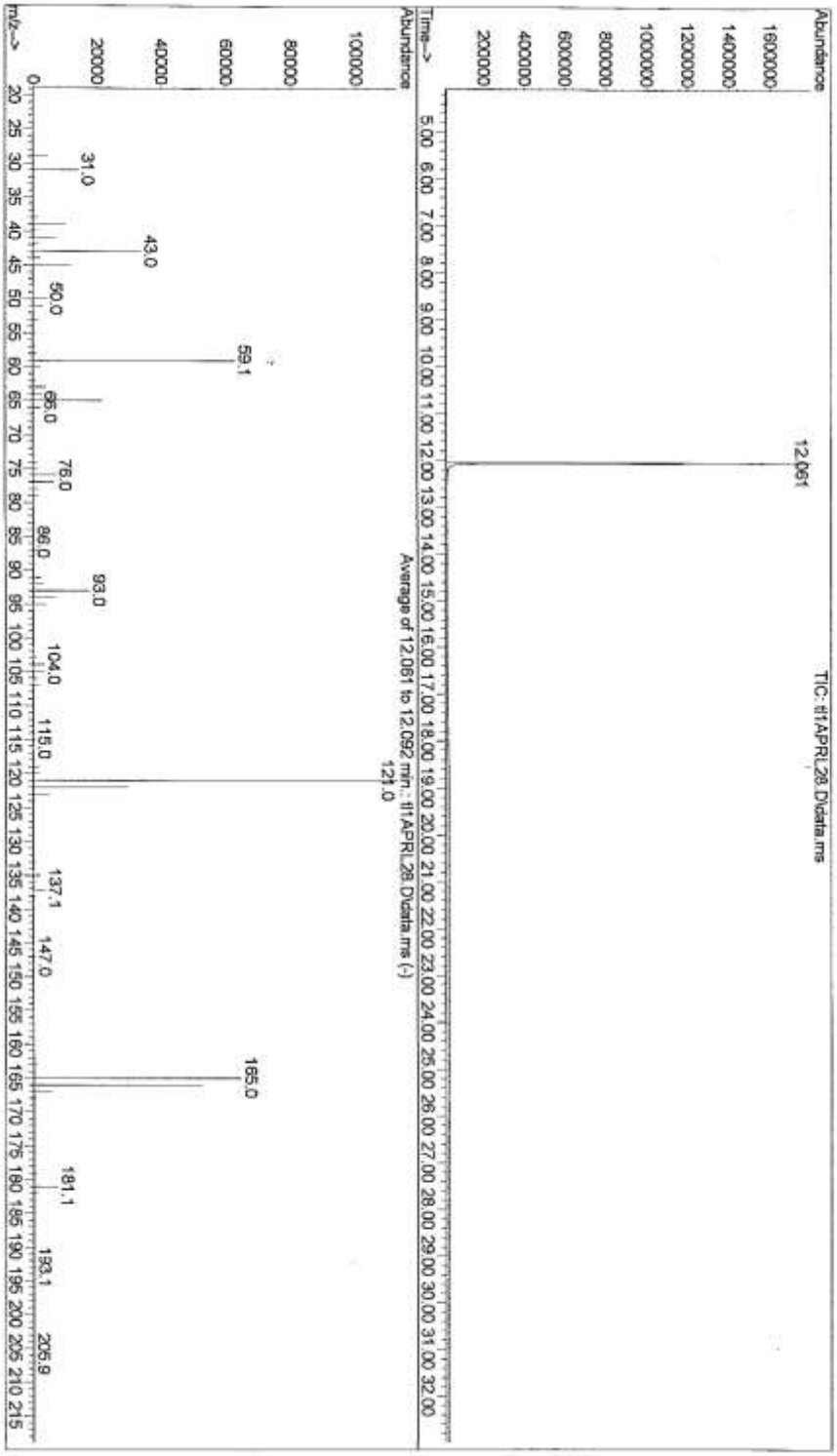
IRGACURE 2959 (mass spectrum not altered by UV exposure)



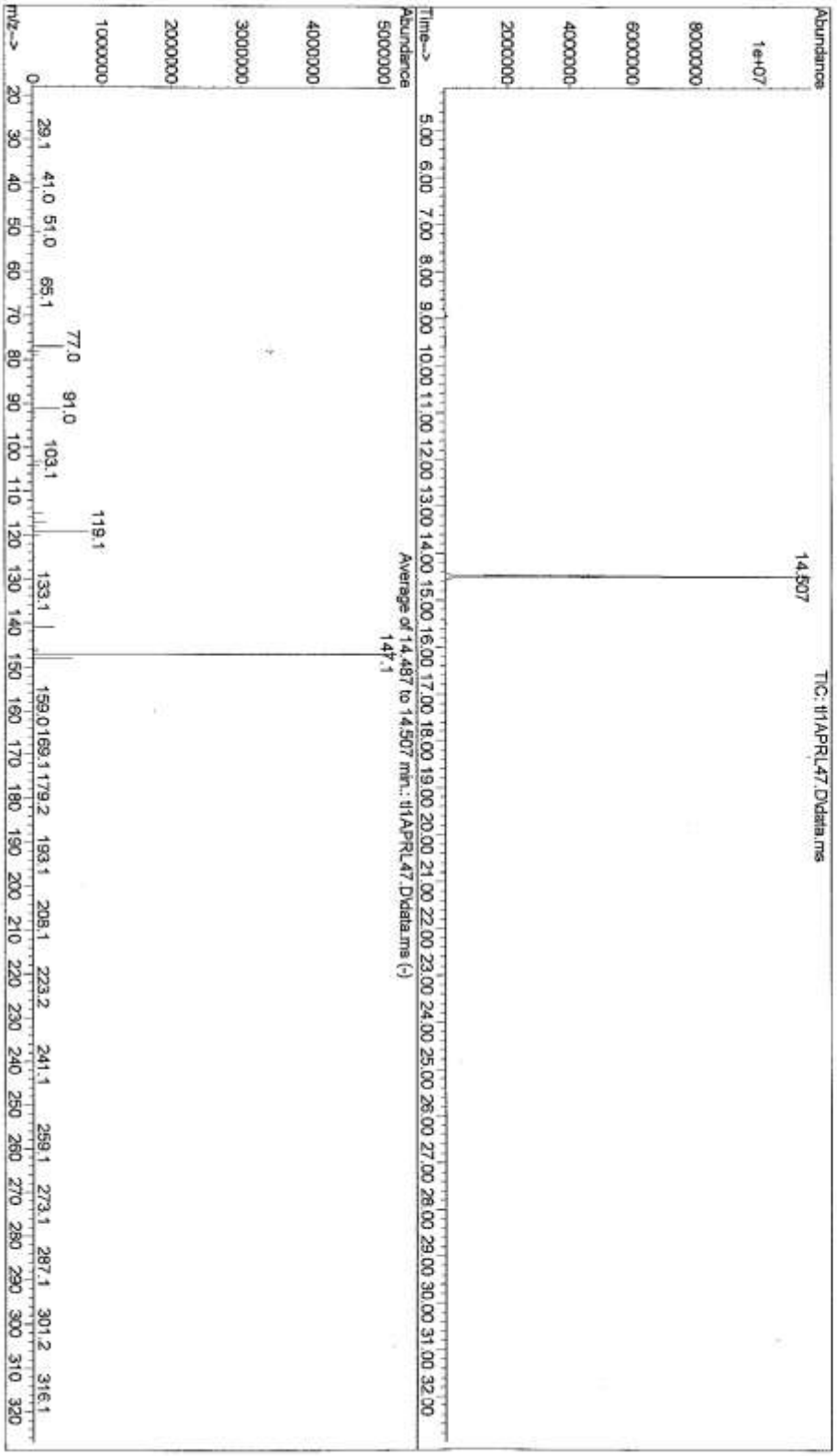
CAS 0007473-98-5



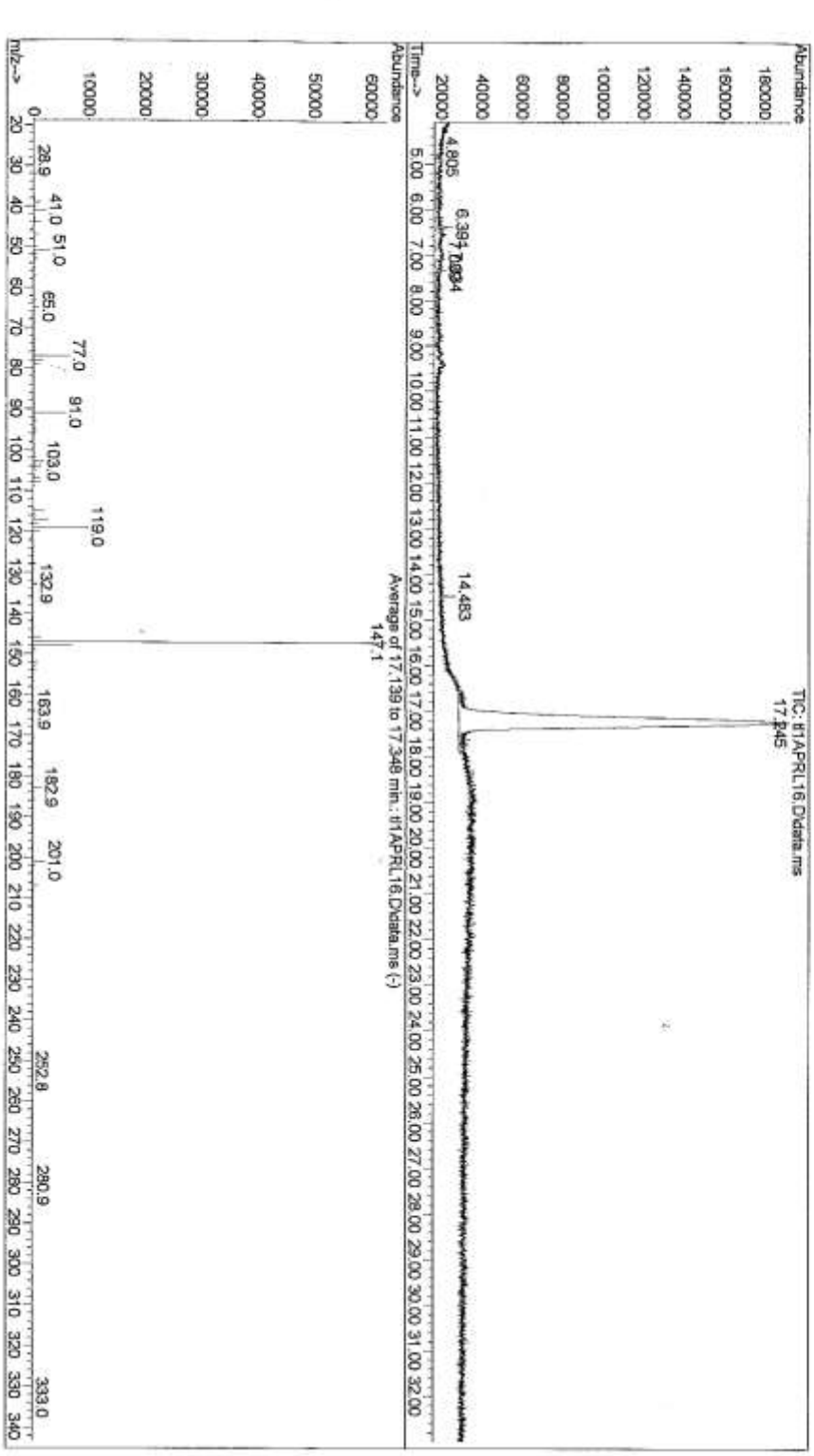
IRGACURE 2959 (batch 4)



BLEND CAS 84434-11-7 & 162881-26-7

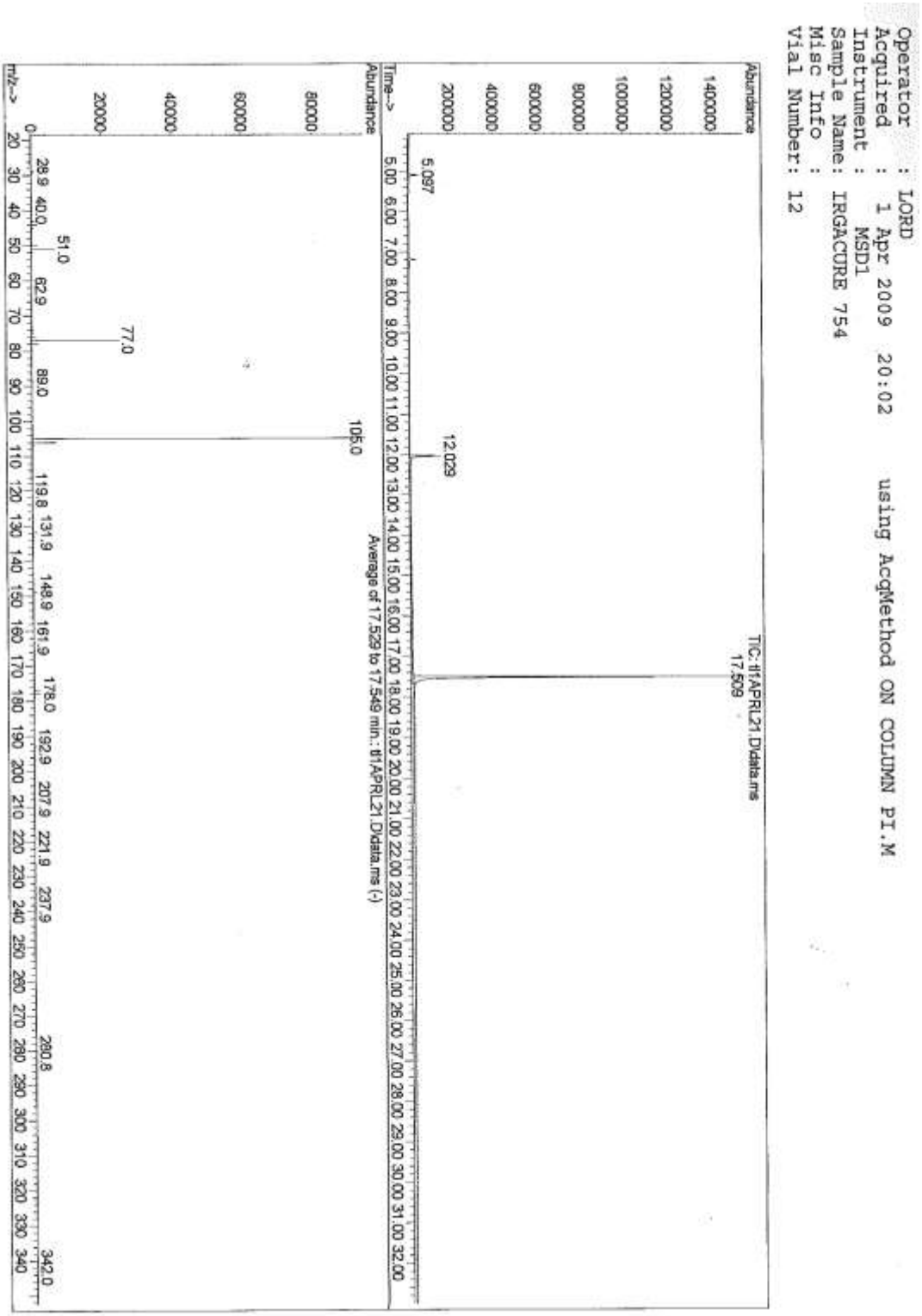


LUCIRIN TPO

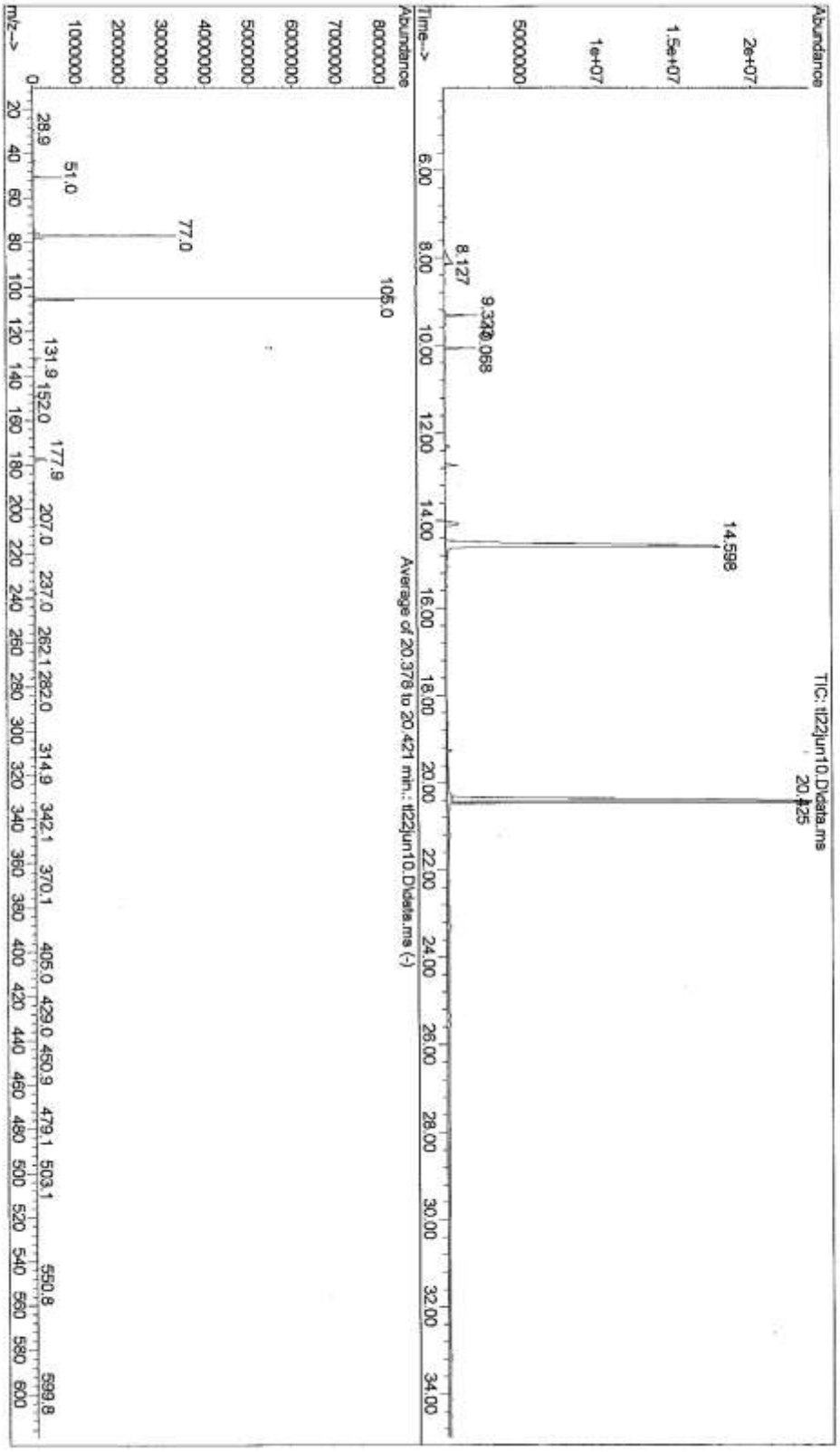

Vial Number: 7
Abundance
TIC: f1APRL16.D\data.ms
17.845
14.483
4.805
6.391
7.084
Time-->
Abundance
Average of 17.139 to 17.348 min.: f1APRL16.D\data.ms (-)
147.1
119.0
77.0
91.0
103.0
132.9
163.9
182.9
201.0
252.8
280.9
333.0
41.0
51.0
65.0
28.9
m/z-->

The following ink components were found to produce fragmentation under UV light

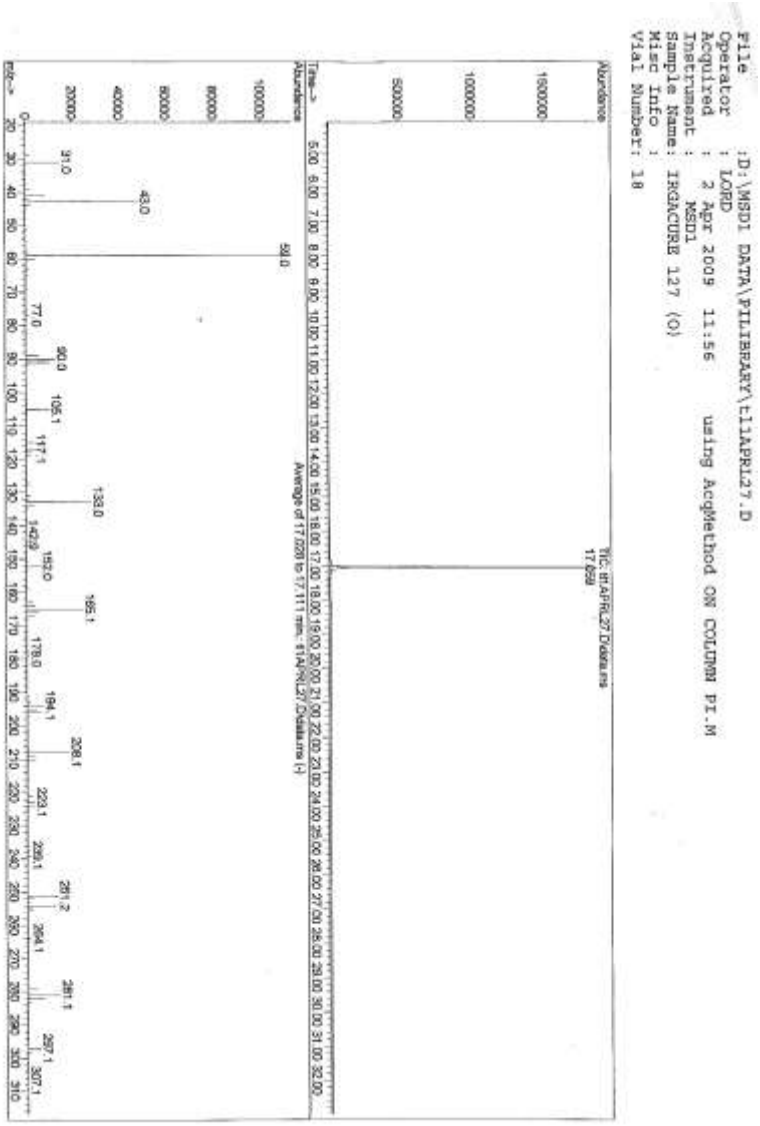
BLEND CAS 0211510-16-6 & 0442536-99-4



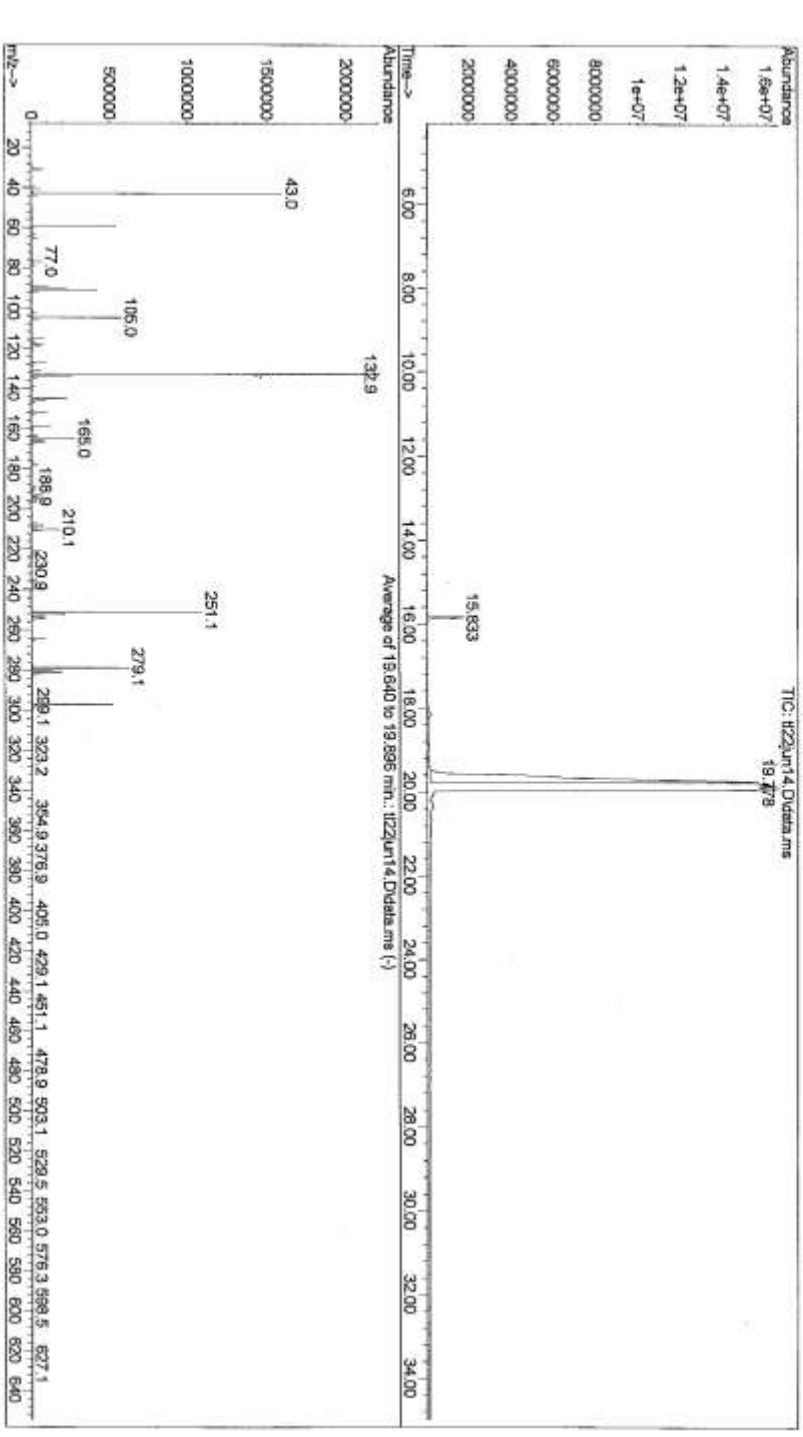
UV EXPOSED BLEND CAS 0211510-16-6 & 0442536-99-4



IRGACURE 127

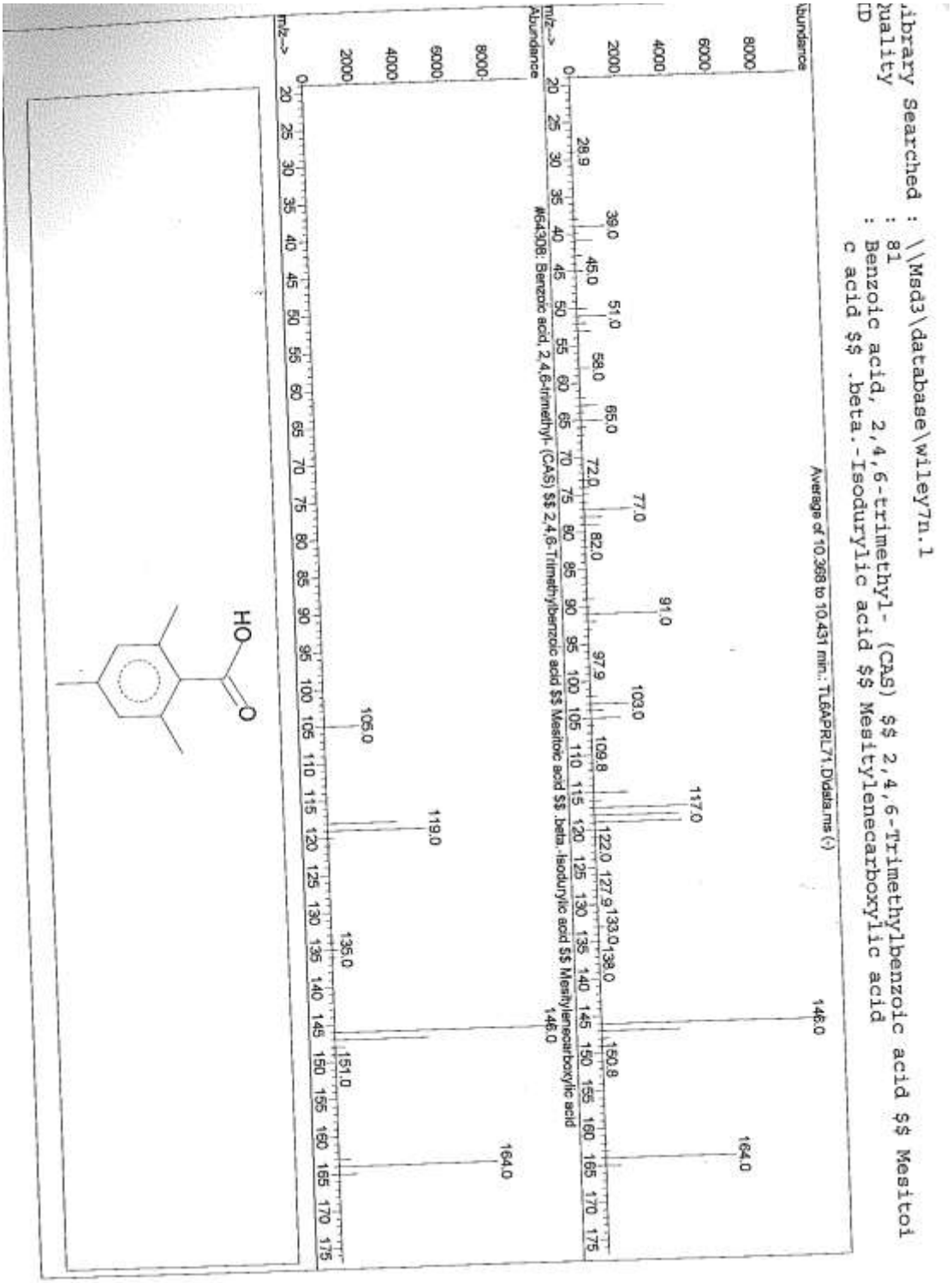


UV EXPOSED IRGACURE 127

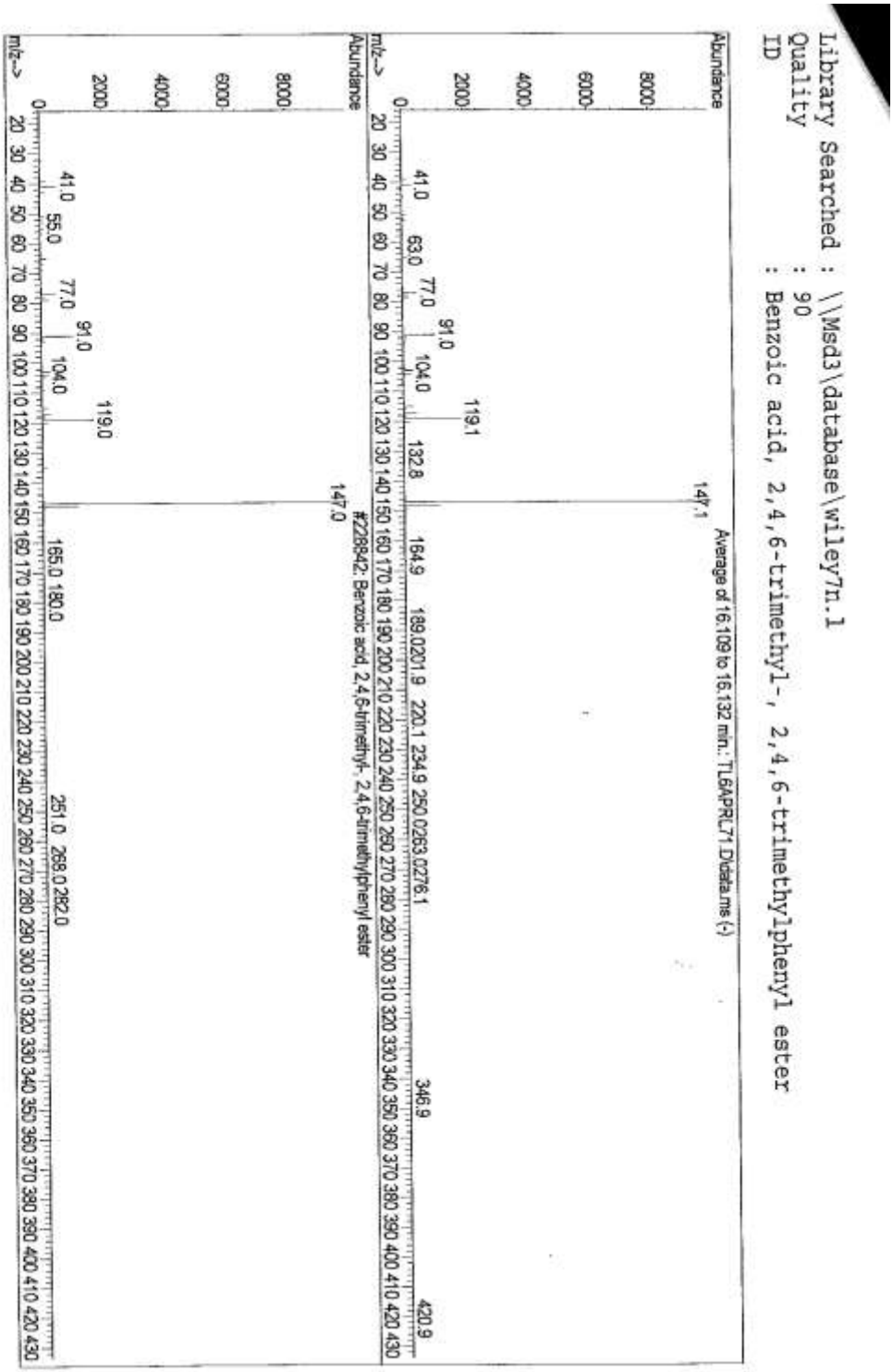


UV EXPOSED IRGACURE 819

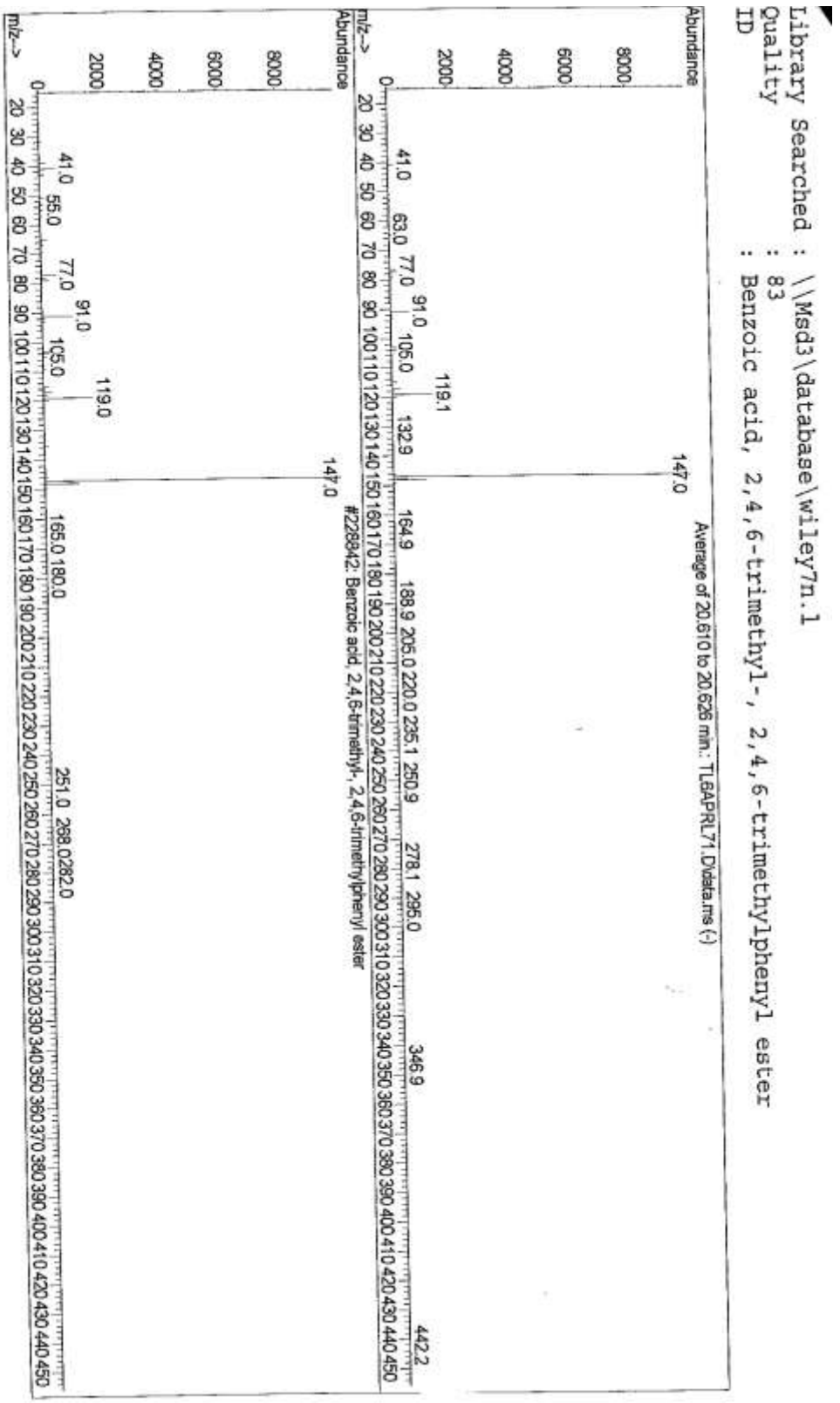
MASS SPECTRUM OF PEAK AT 10.4 MINUTES ON PAGE 174



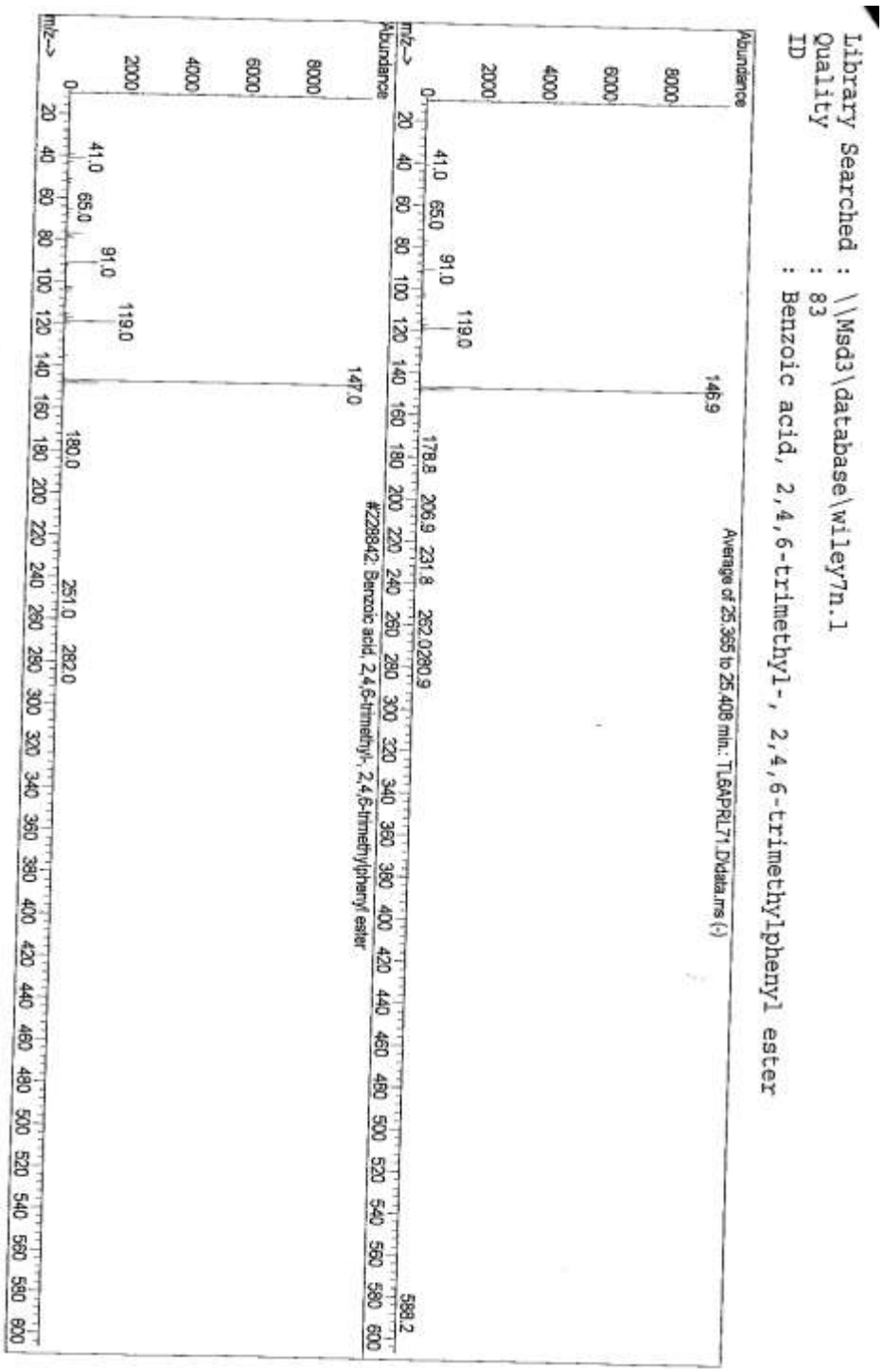
MASS SPECTRUM OF PEAK AT 16.1 MINUTES ON PAGE 174



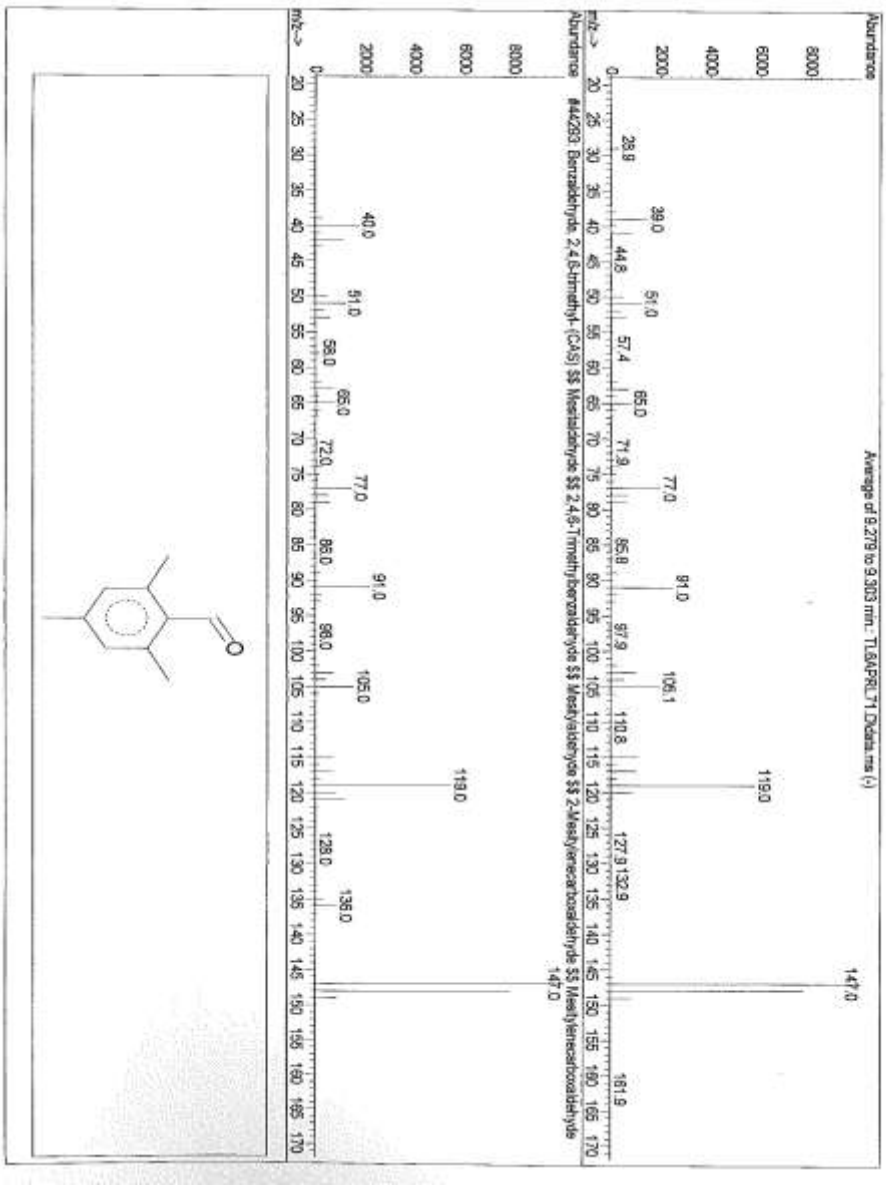
MASS SPECTRUM OF PEAK AT 20.6 MINUTES ON PAGE 174



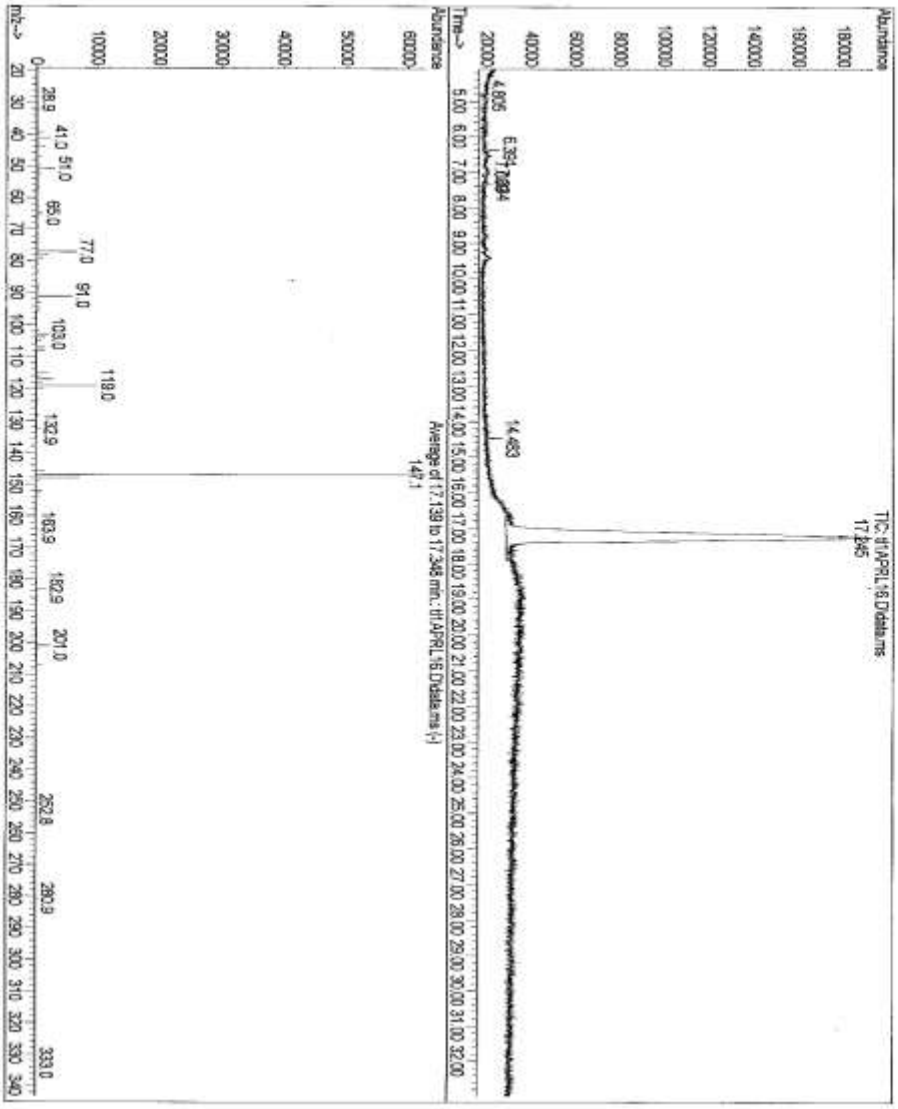
MASS SPECTRUM OF PEAK AT 25.4 MINUTES ON PAGE 174



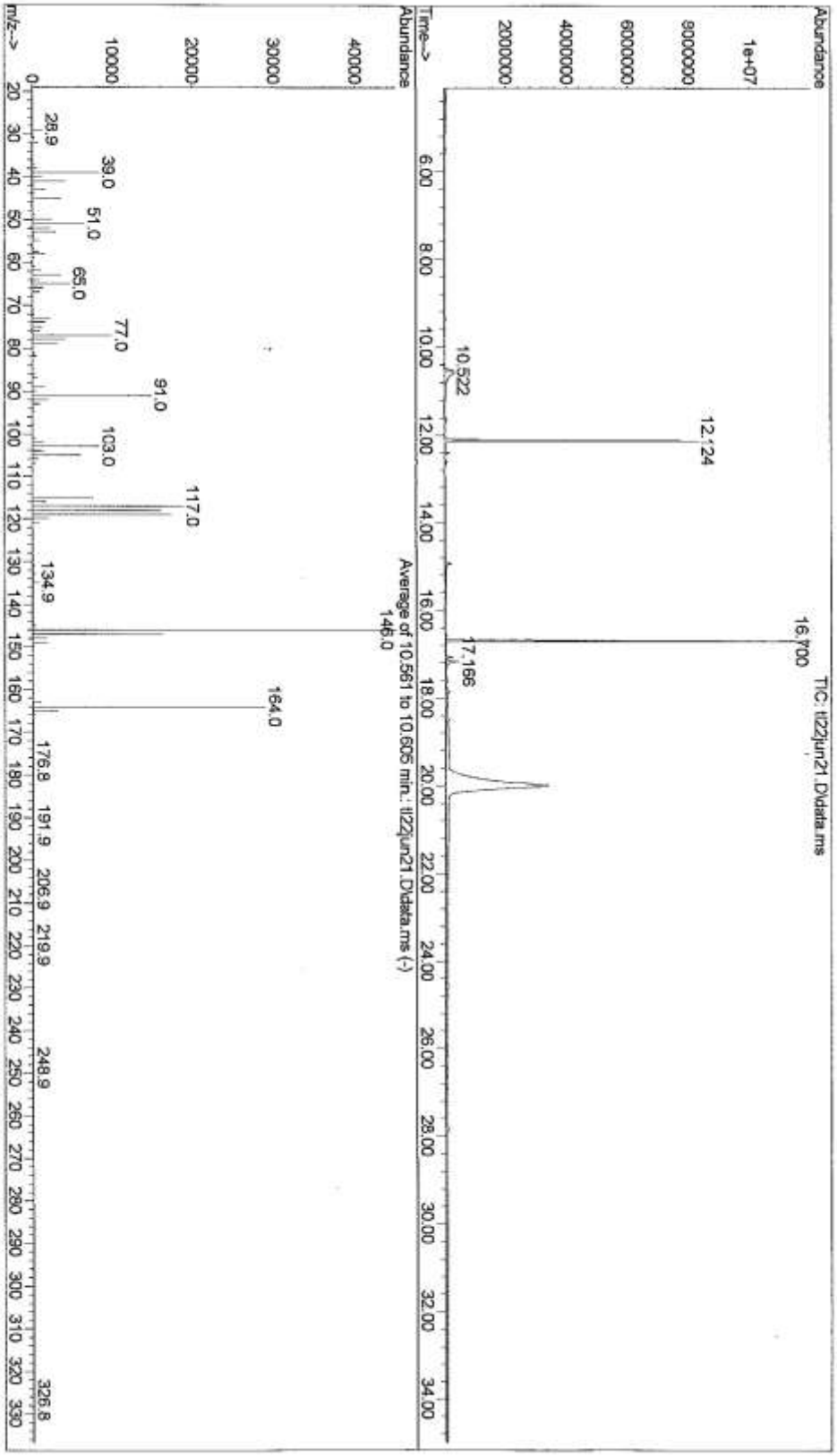
MASS SPECTRUM OF PEAK AT 9.3 MINUTES ON PAGE 174



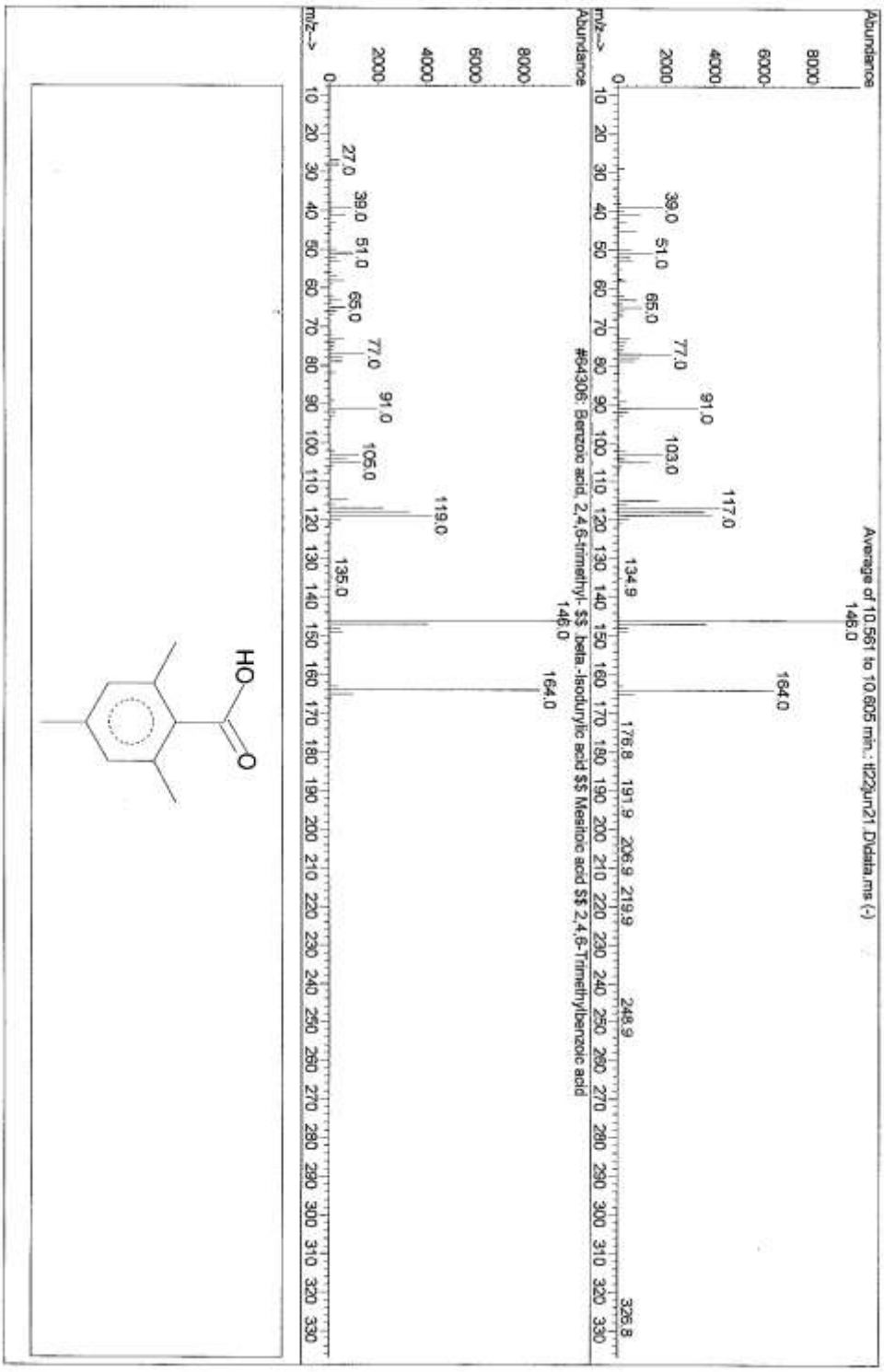
LUCIRIN TPO


Abundance
TIC: tf1APRIL16.D\data.ms
17.345
14.493
Time-->
Abundance
Average of 17.139 to 17.348 min.: tf1APRIL16.D\data.ms (-)
147.1
m/z-->
28.9
41.0
51.0
65.0
77.0
91.0
103.0
118.0
132.9
163.9
182.9
201.0
252.8
280.9
333.0

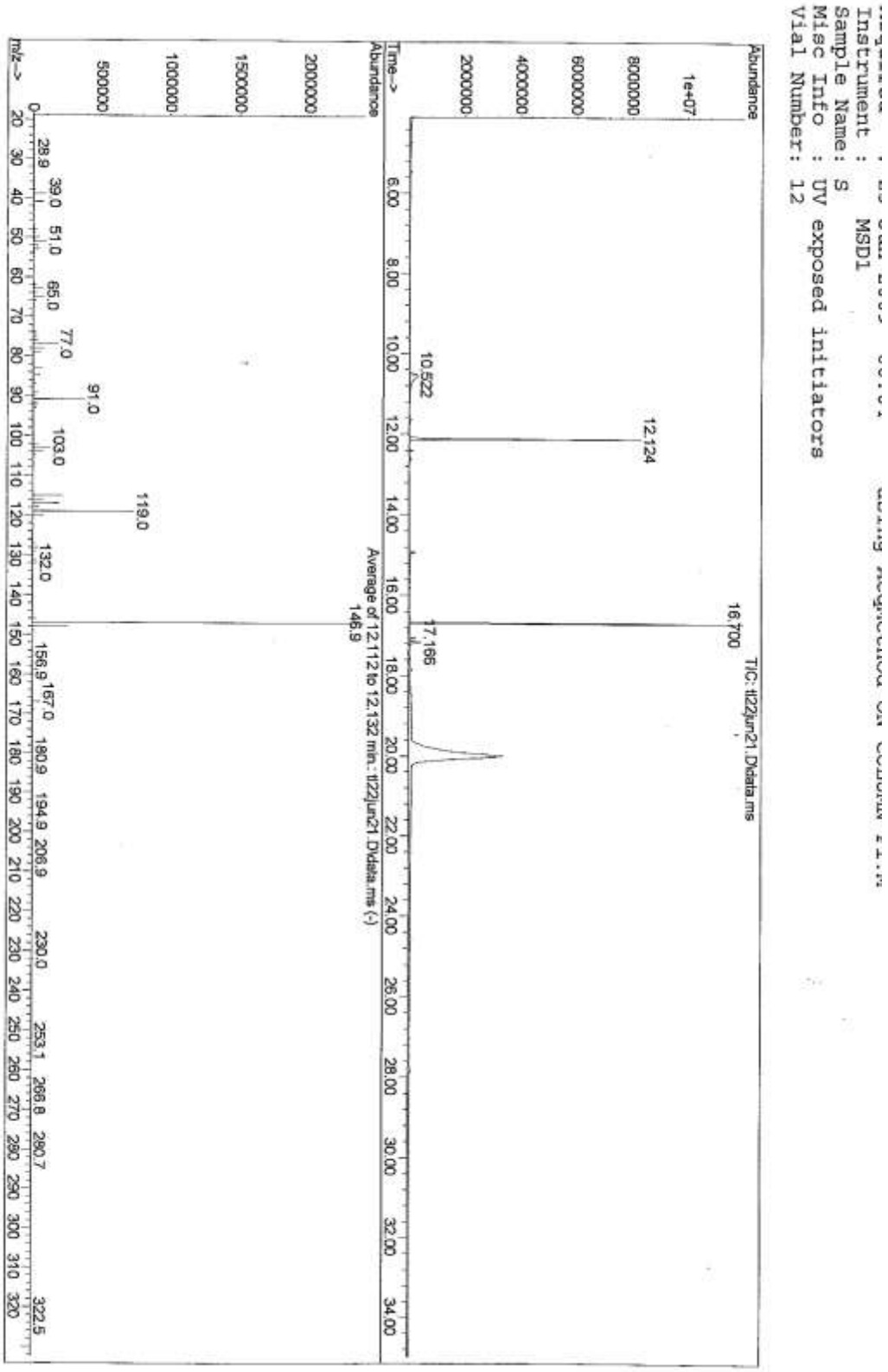
UV EXPOSED LUCIRIN TPO



MASS SPECTRUM OF PEAK AT 10.5 MINUTES ON PAGE 181

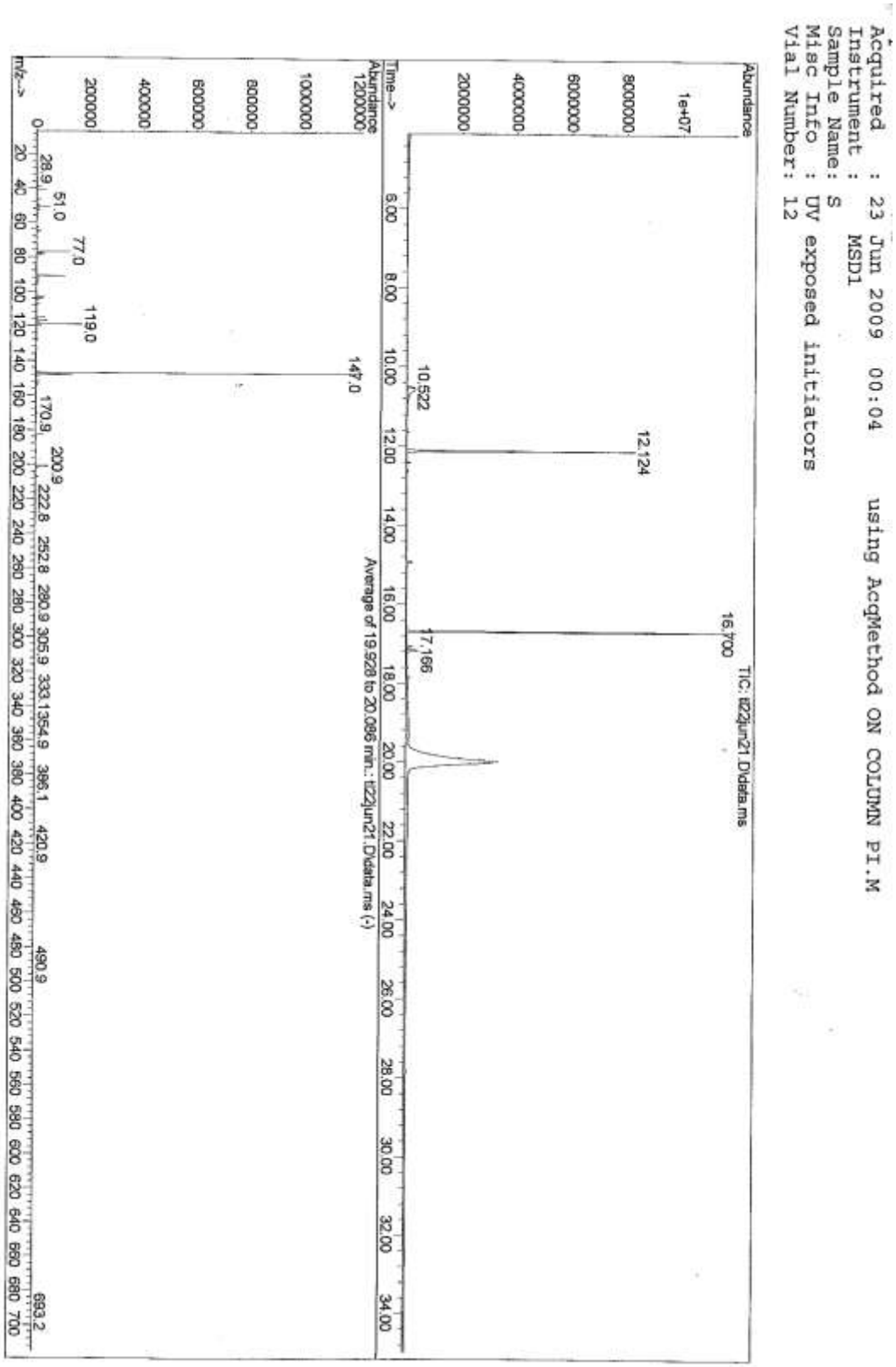


UV EXPOSED LUCIRIN TPO



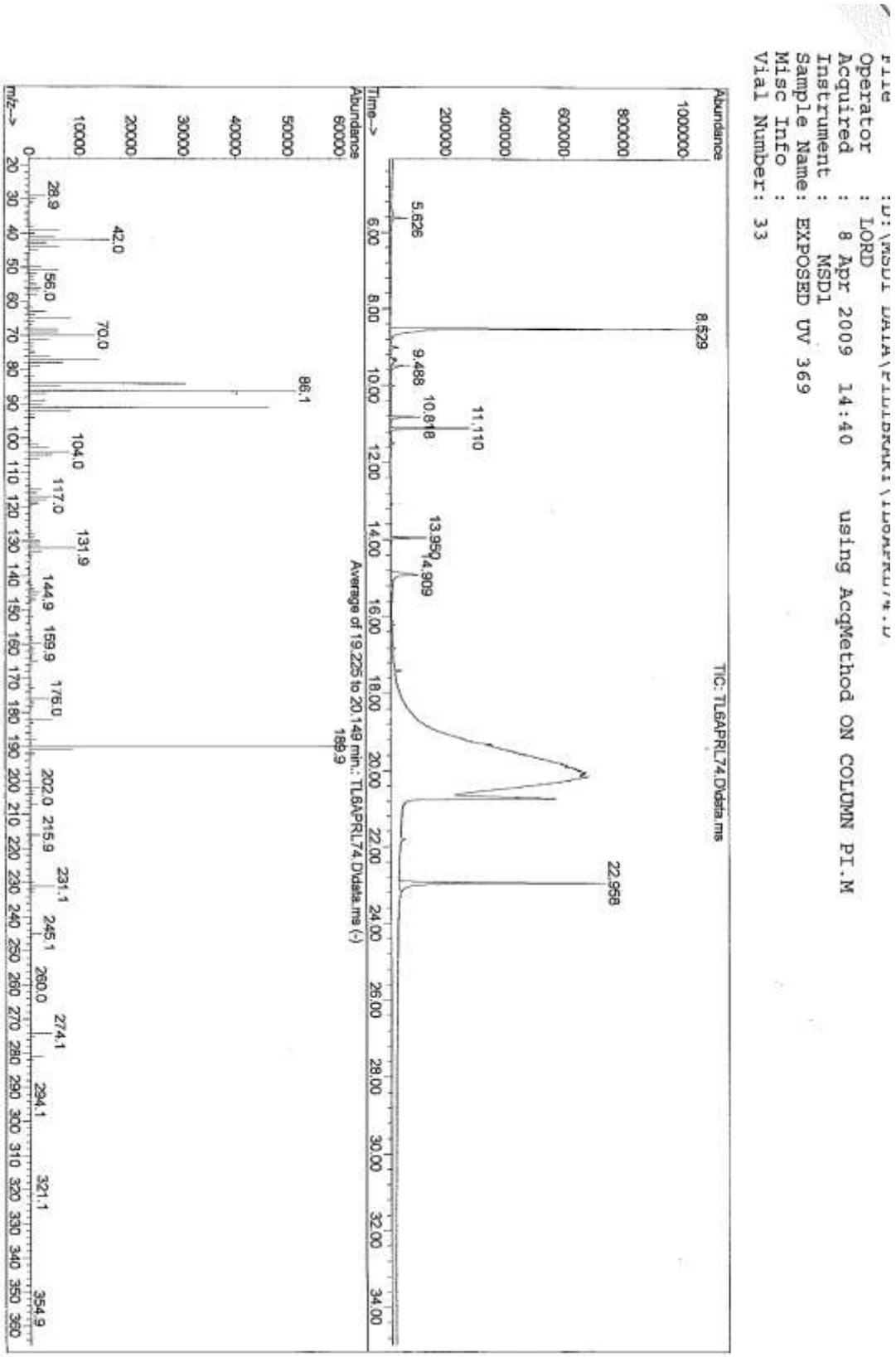
MASS SPECTRUM OF PEAK AT 16.7 MINUTES ON PAGE 183

LUCIRIN TPO

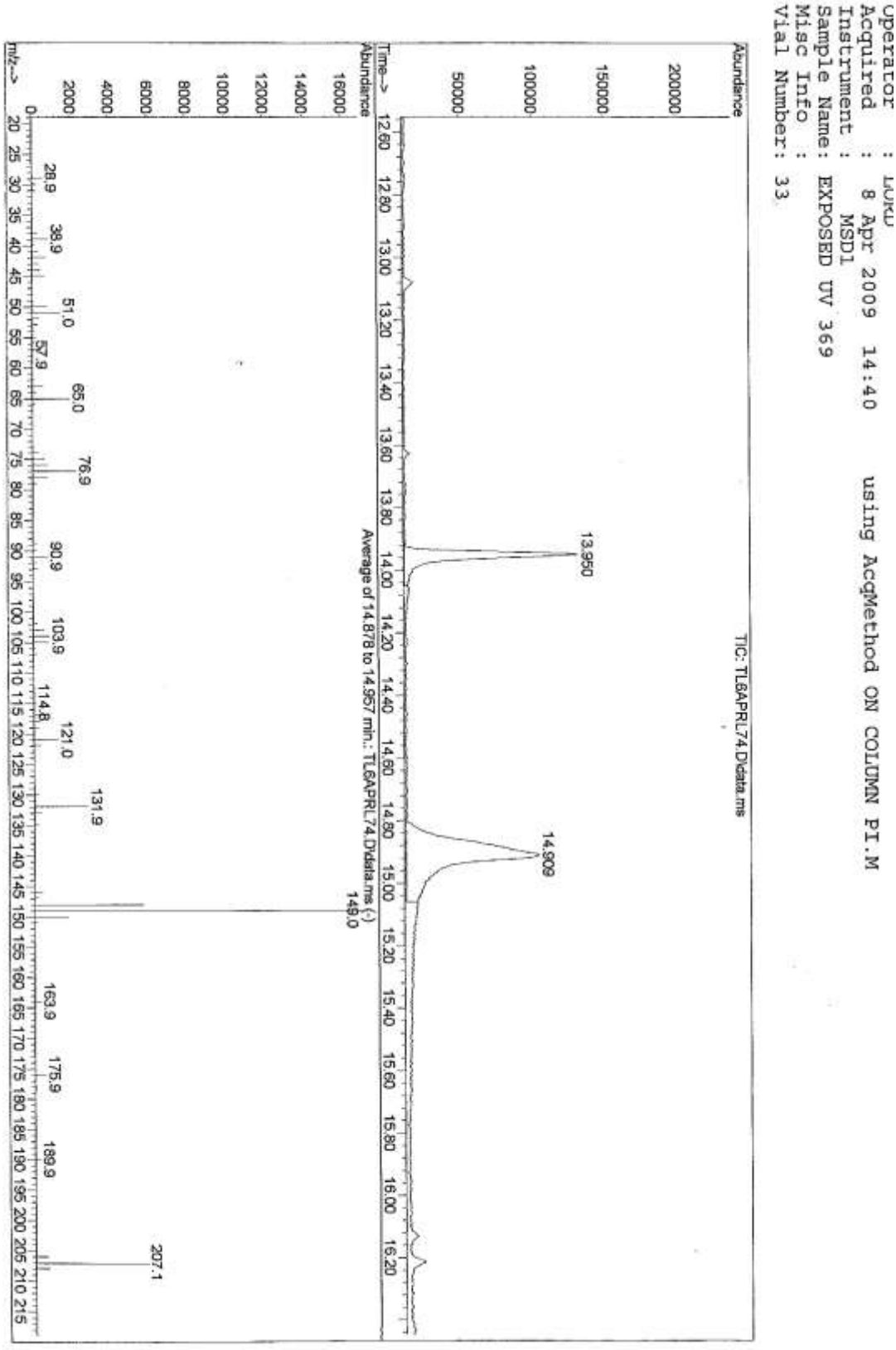

Acquired : 23 Jun 2009 00:04 using AcqMethod ON COLUMN PI.M
Instrument : MSD1
Sample Name: S
Misc Info : UV exposed initiators
Vial Number: 12
Abundance
TIC: tt22jun21.Dldata.ms
16.700
12.124
10.522
17.166
Time-->
Abundance
Average of 19.928 to 20.096 min.: tt22jun21.Dldata.ms (-)
147.0
m/z-->

IRGACURE 369

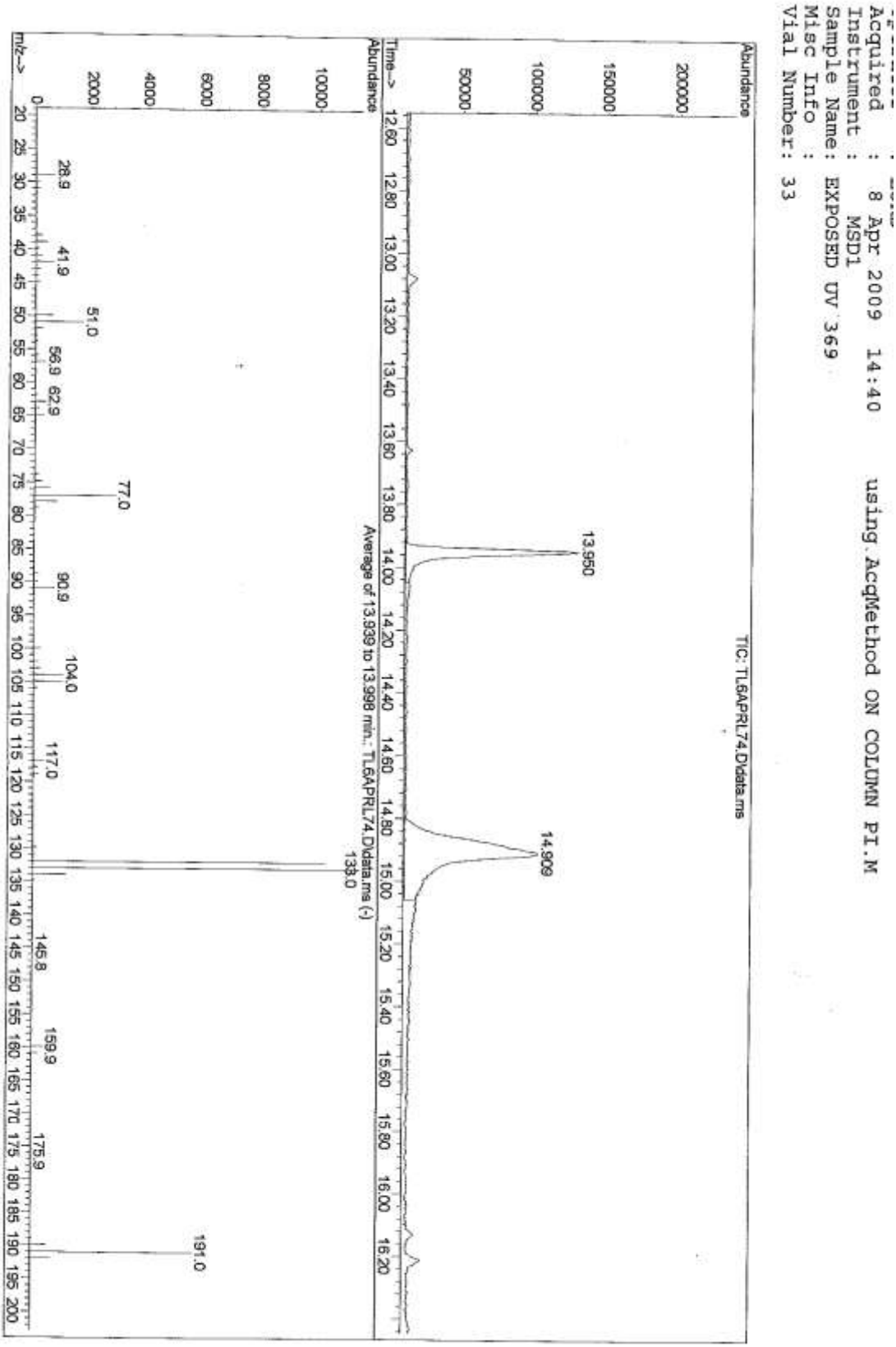
UV EXPOSED IRGACURE 369



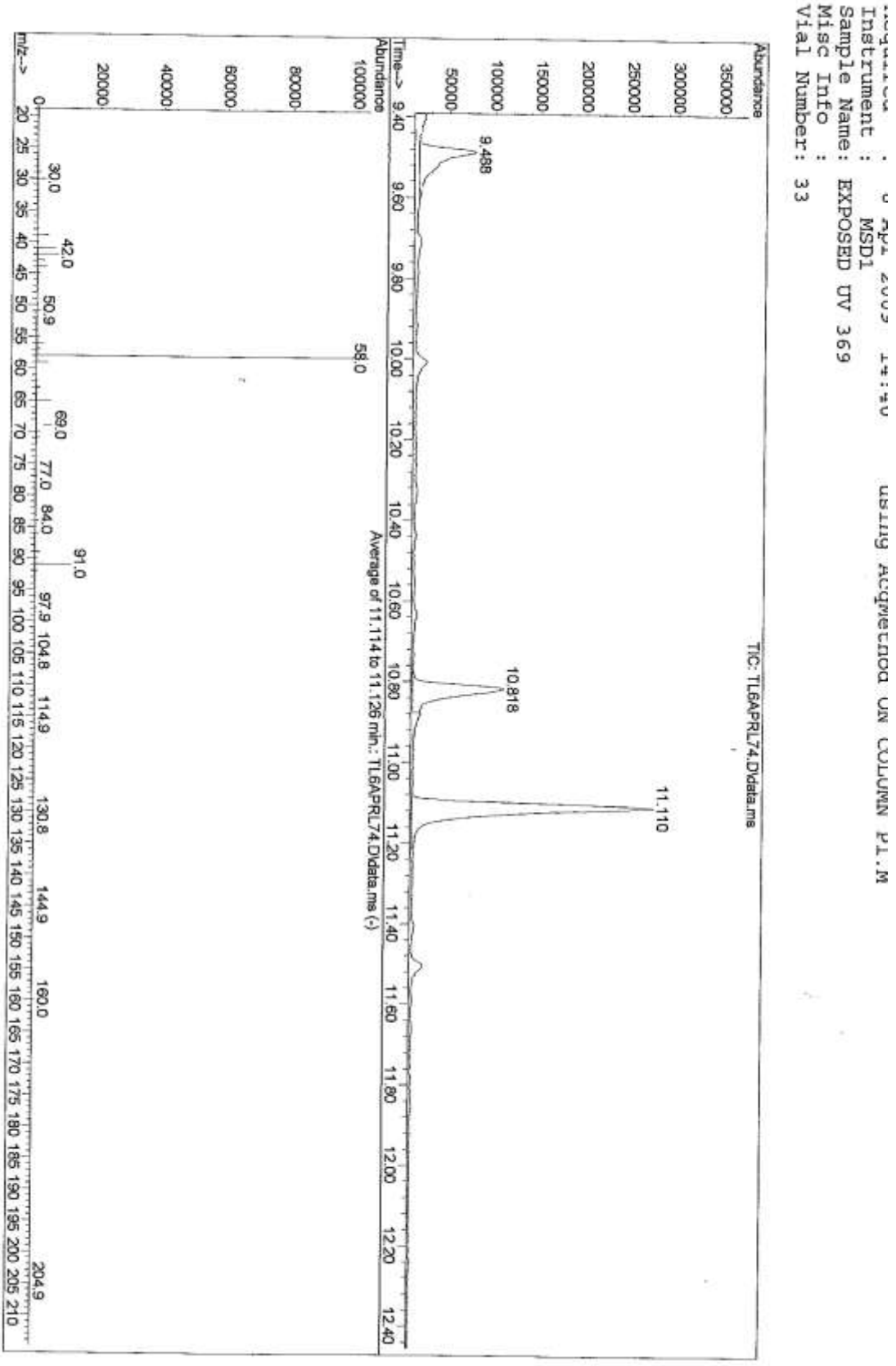
MASS SPECTRUM AT 14.9 MINUTES ON PAGE 187



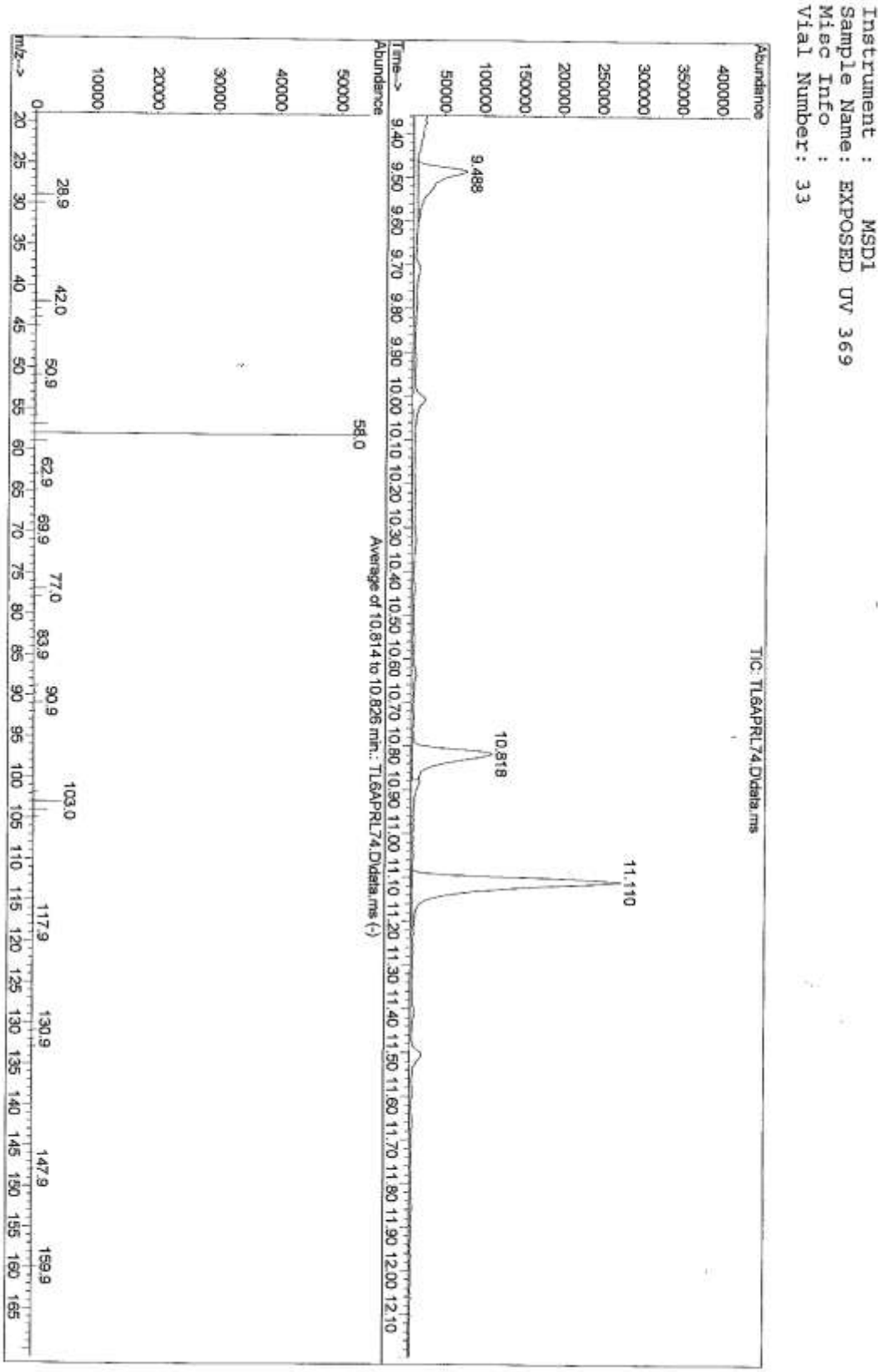
MASS SPECTRUM AT 13.9 MINUTES ON PAGE 187



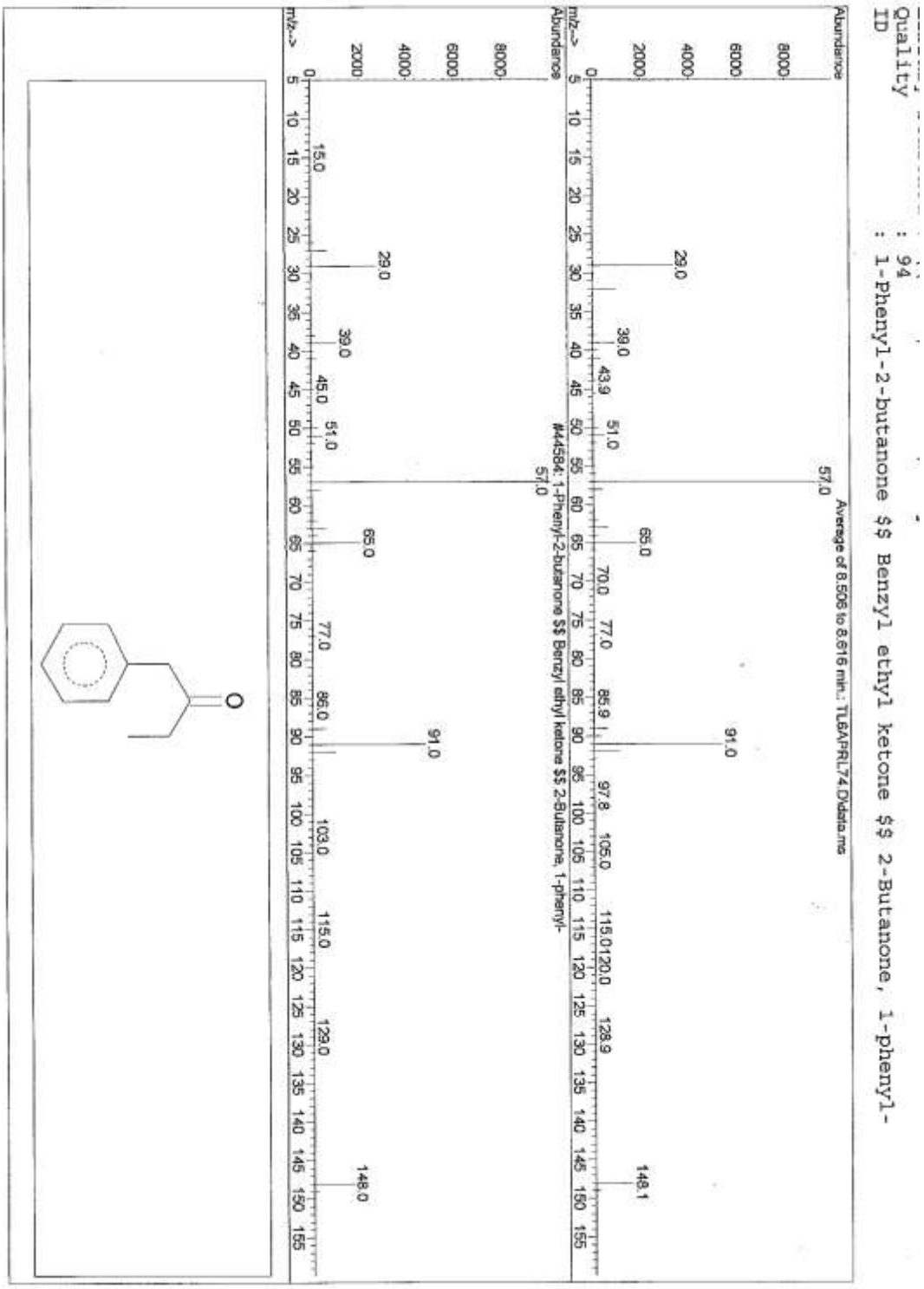
MASS SPECTRUM AT 11.1 MINUTES ON PAGE 187



MASS SPECTRUM AT 10.8 MINUTES ON PAGE 187



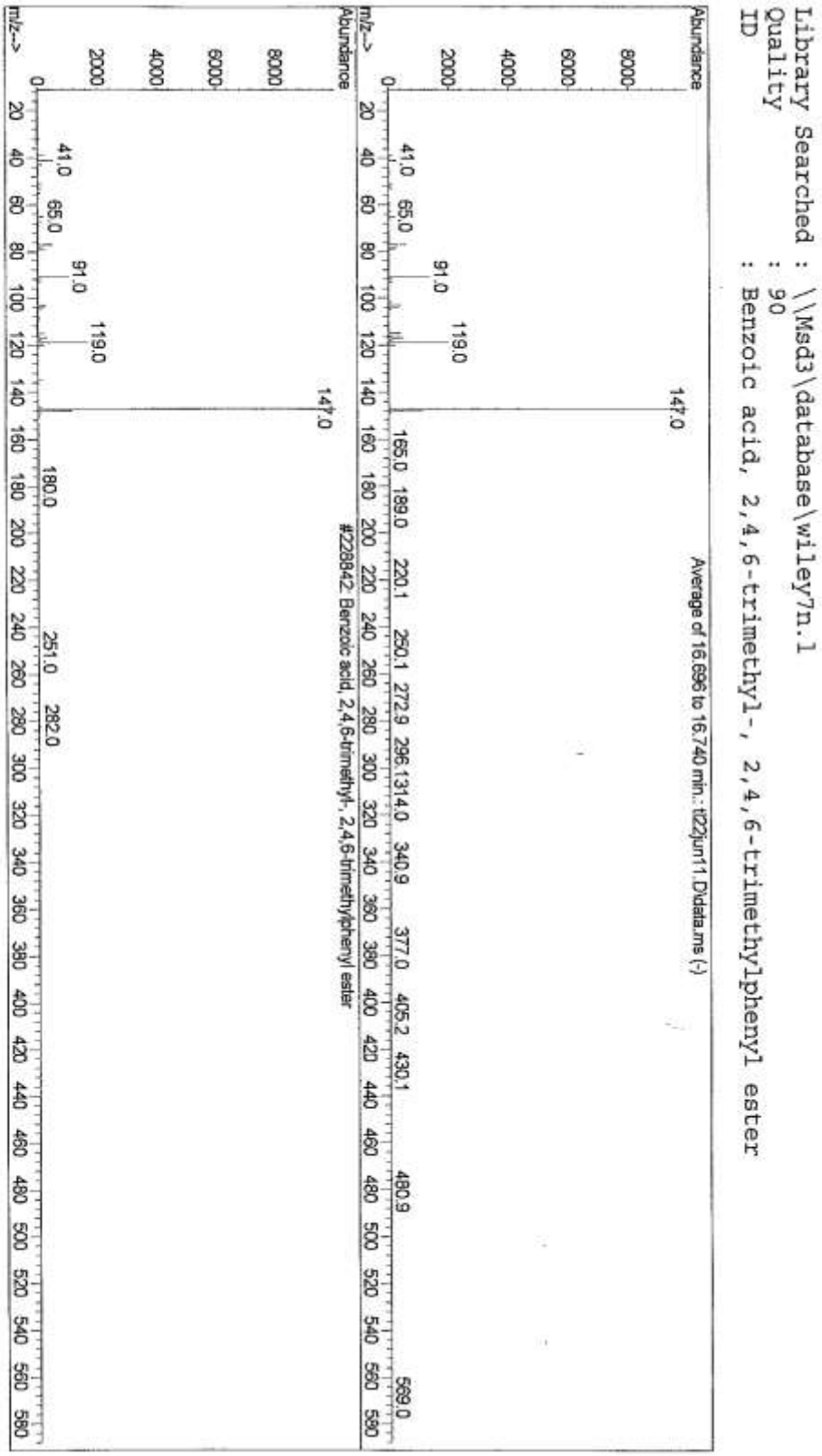
MASS SPECTRUM AT 8.5 MINUTES ON PAGE 187



IRGACURE 819 DW

UV EXPOSED IRGACURE 819 DW

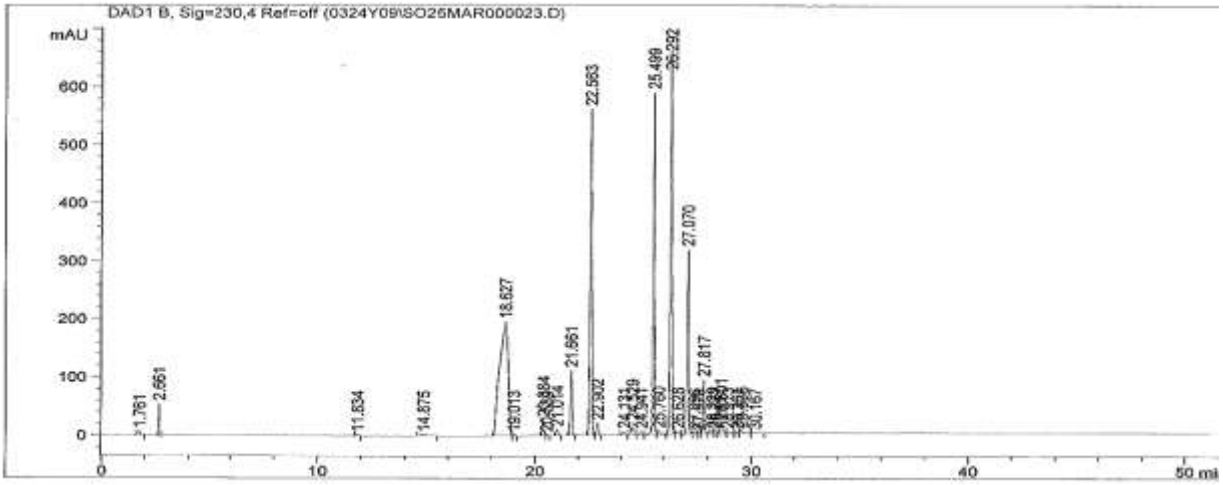
MASS SPECTRUM AT 16.7 MINUTES ON PAGE 194



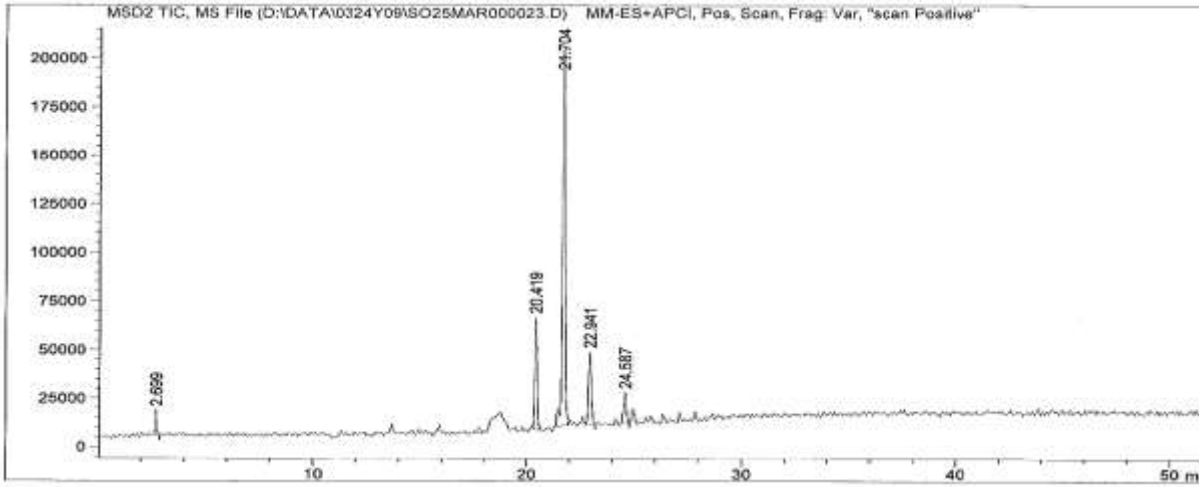
Appendix 9

LC-MS chromatograms and UV and mass spectra

LC-UV Chromatogram for Omnipol BP polymeric photoinitiator 230 nm

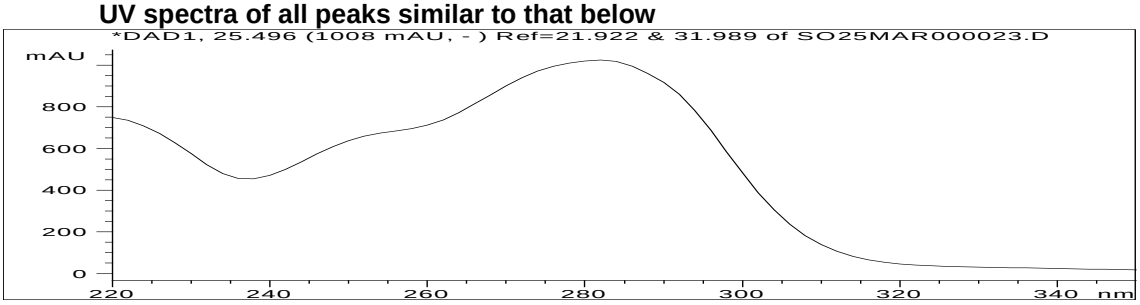


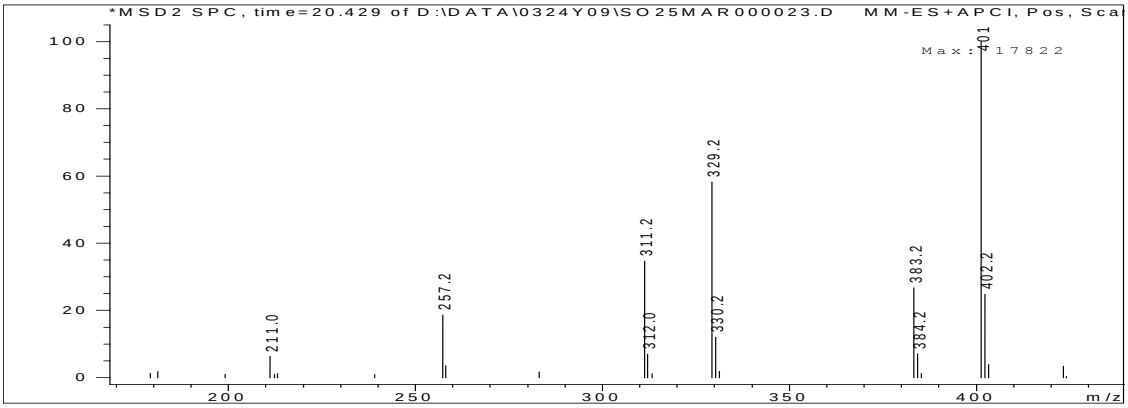
LC-MS Chromatogram for Omnipol BP polymeric photoinitiator

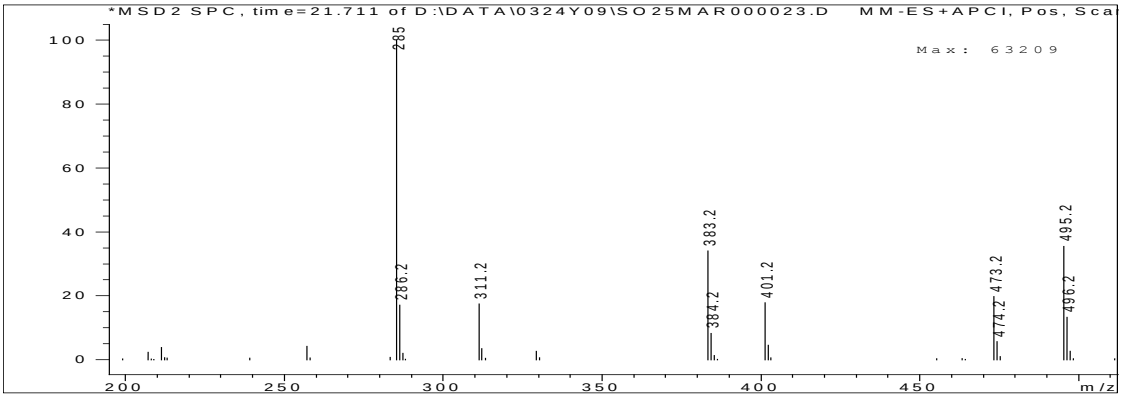


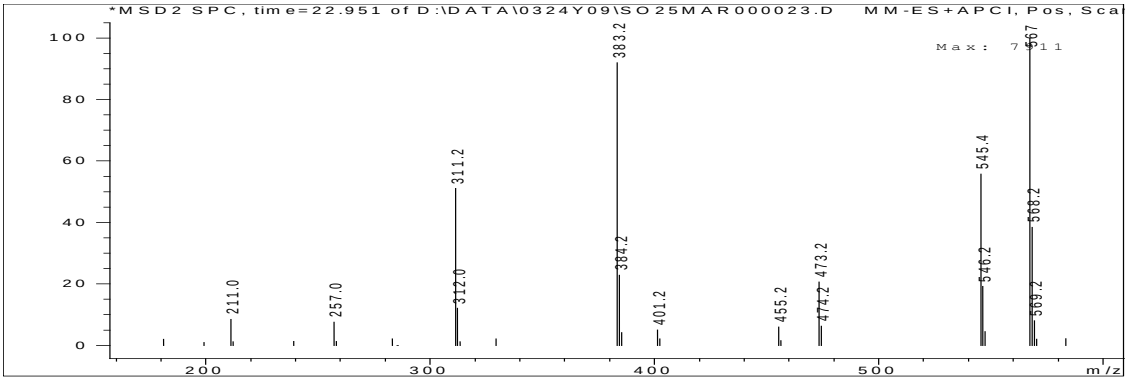
OMNIPOL BP

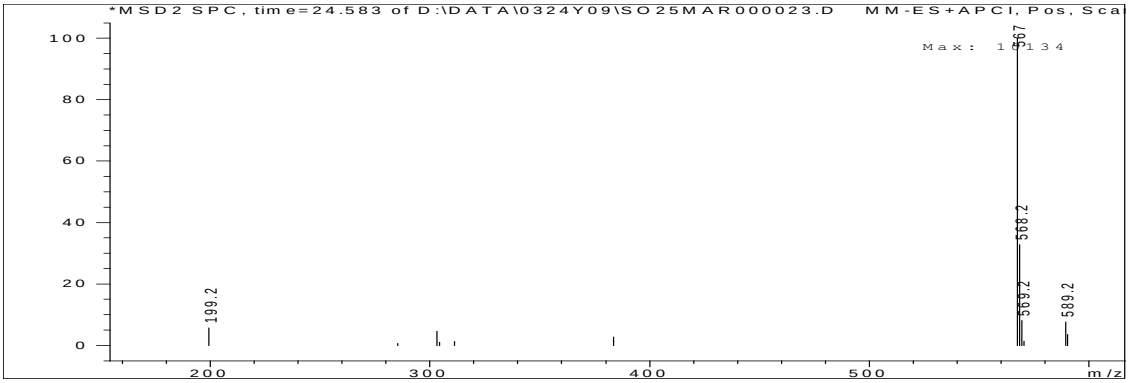
UV spectra of all peaks similar to that below



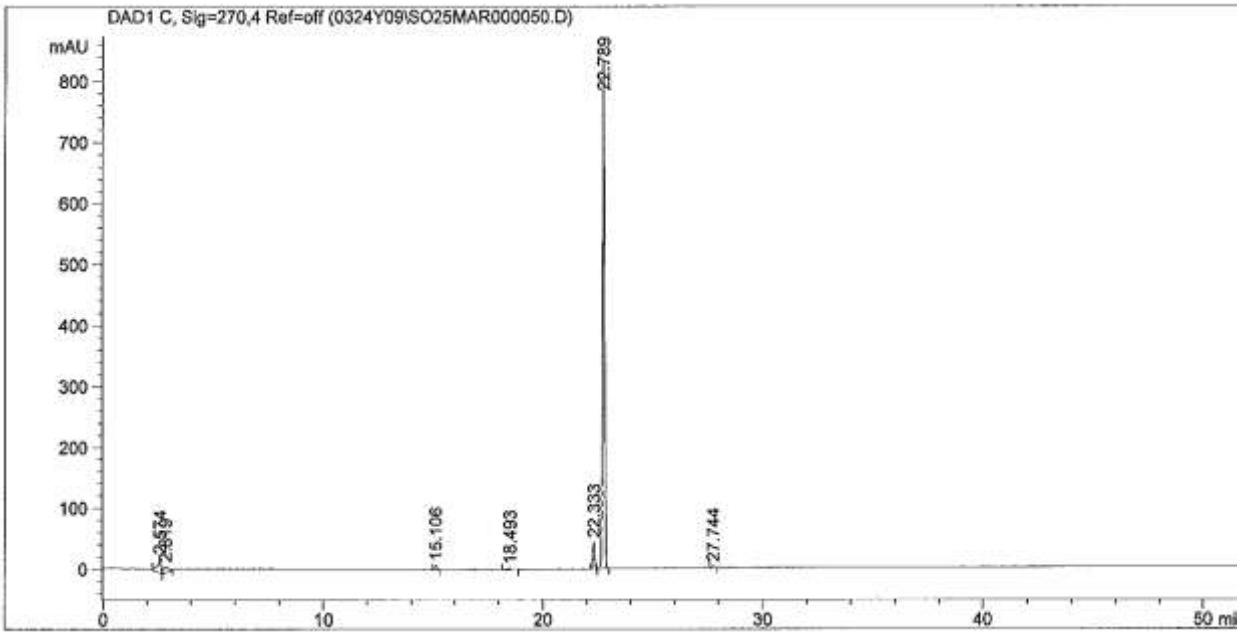




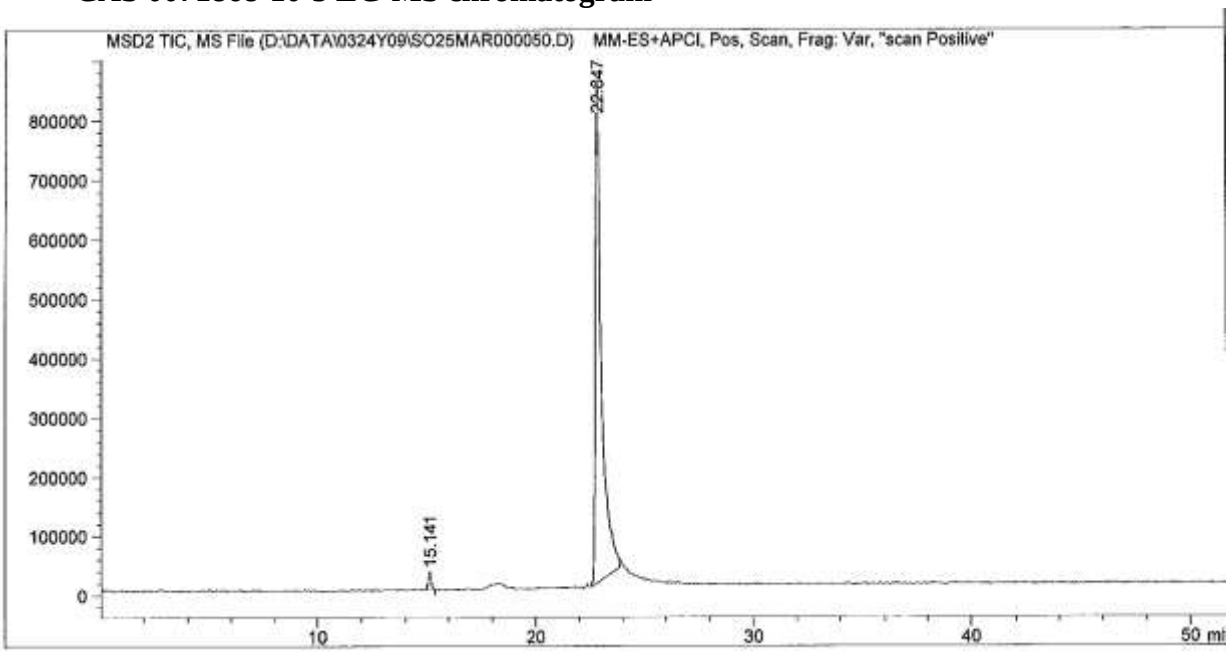


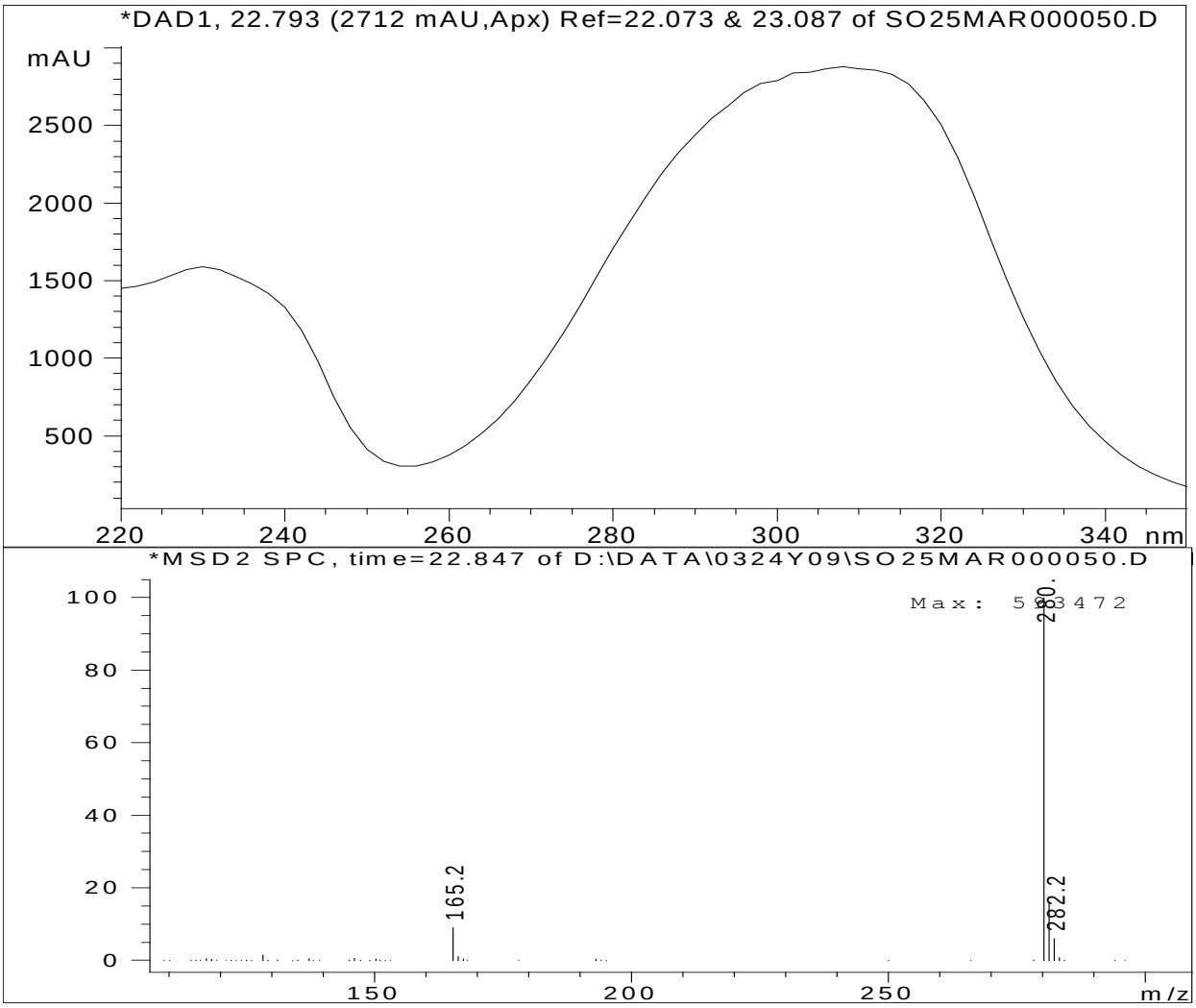

*MSD2 SPC, time=24.583 of D:\DATA\0324Y09\SO25MAR000023.D MM-ES+APCI, Pos, Sca
Max: 1
100
80
60
40
20
0
199.2
567
568.2
569.2
589.2
200
300
400
500
m/z

CAS 0071868-10-5 LC-UV chromatogram 270 nm

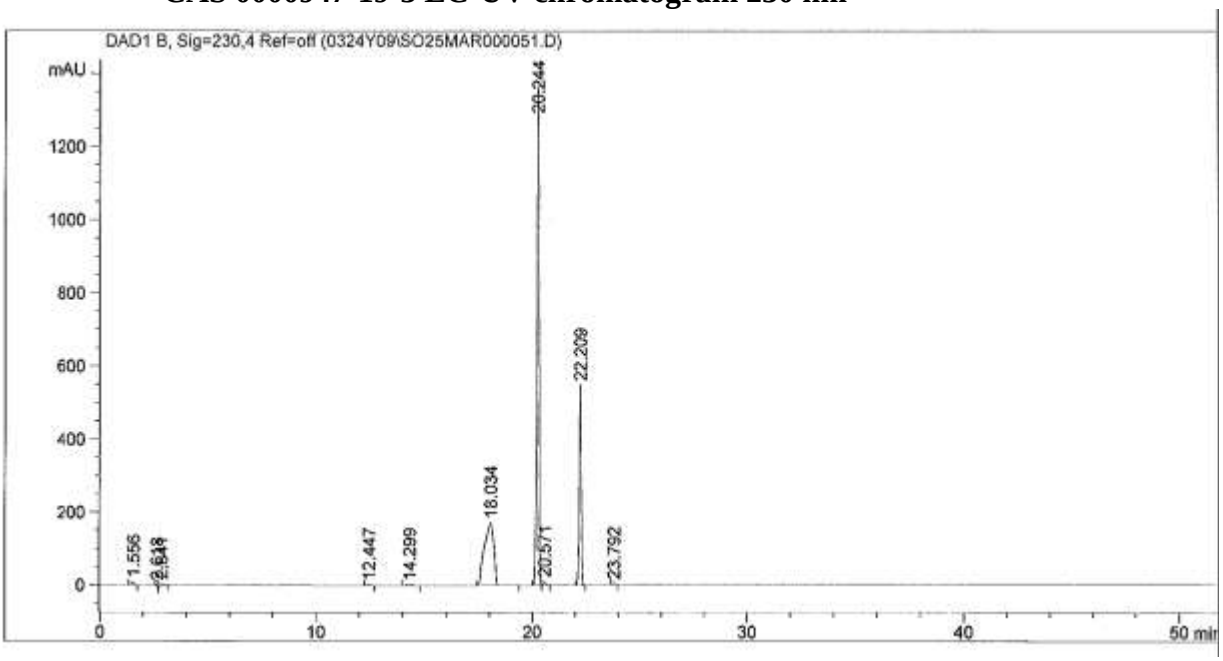


CAS 0071868-10-5 LC-MS chromatogram

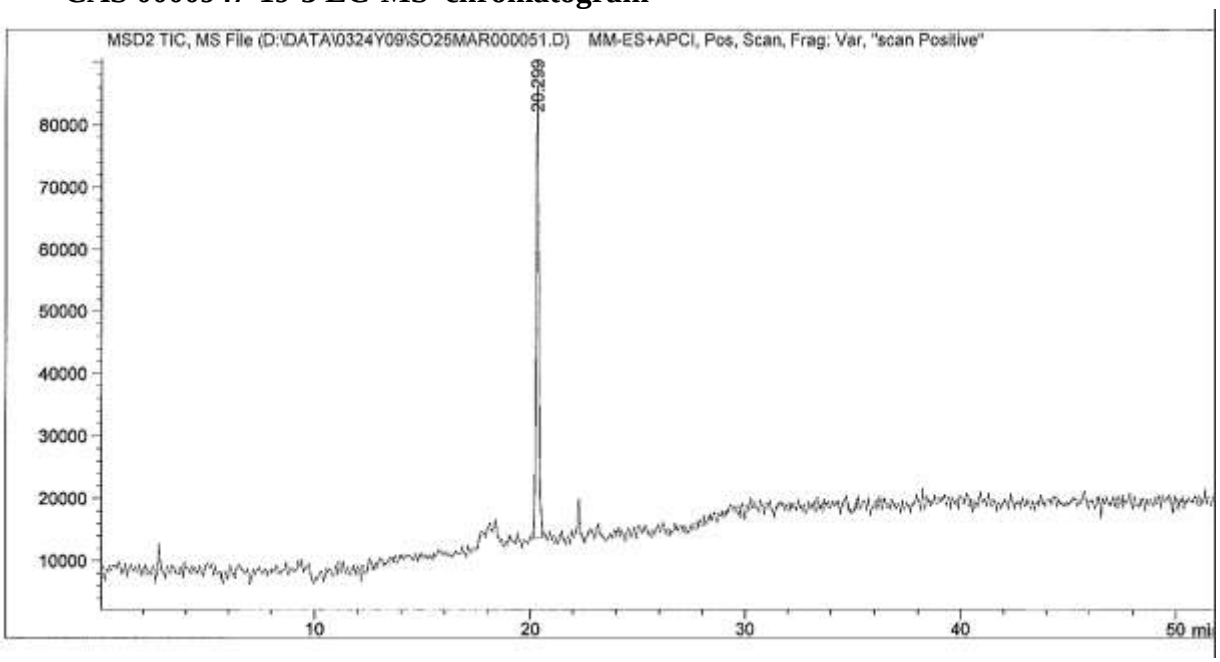


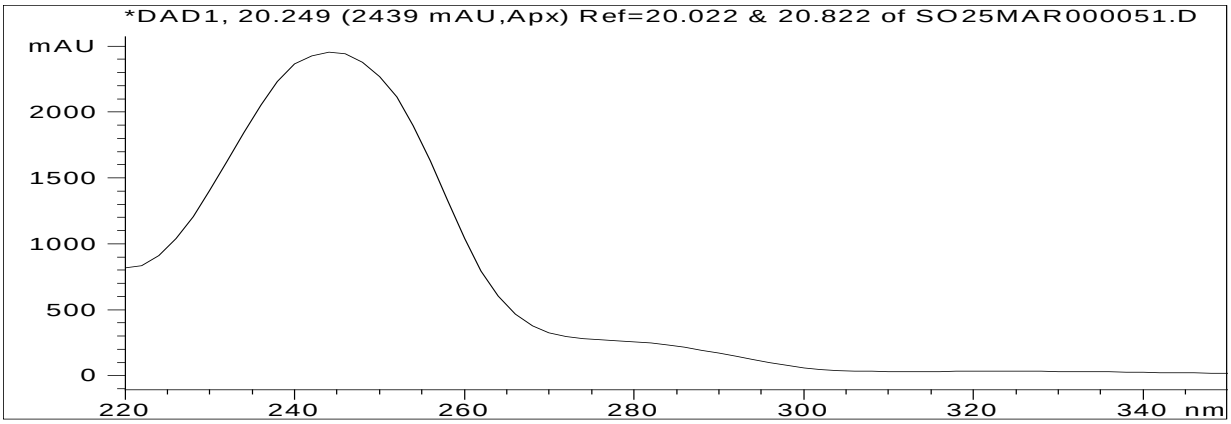

*DAD1, 22.793 (2712 mAU,Apx) Ref=22.073 & 23.087 of SO25MAR000050.D
mAU
2500
2000
1500
1000
500
220
240
260
280
300
320
340 nm
*MSD2 SPC, time=22.847 of D:\DATA\0324Y09\SO25MAR000050.D
100
80
60
40
20
0
Max: 583472
280.
165.2
282.2
150
200
250
m/z

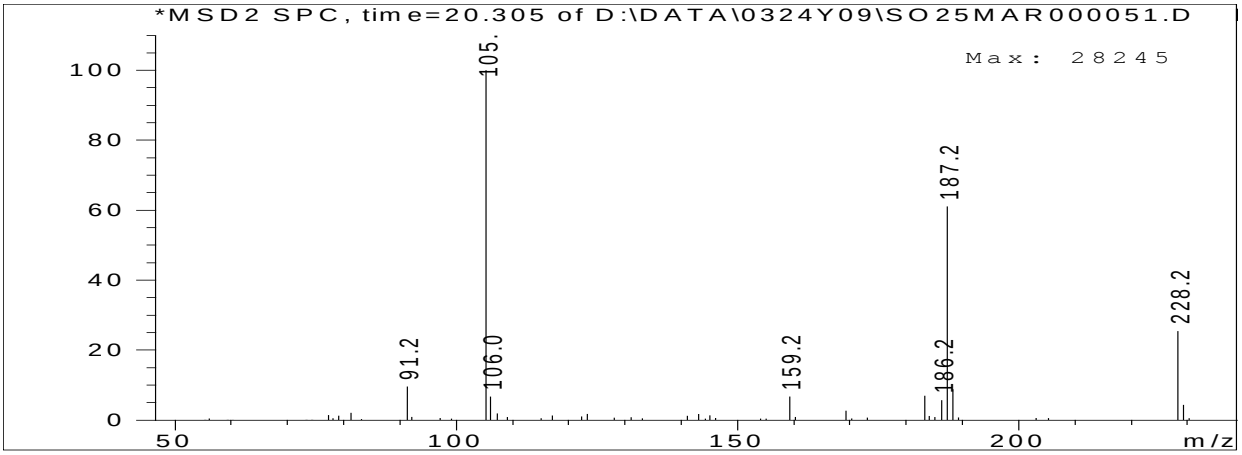
CAS 0000947-19-3 LC-UV chromatogram 230 nm



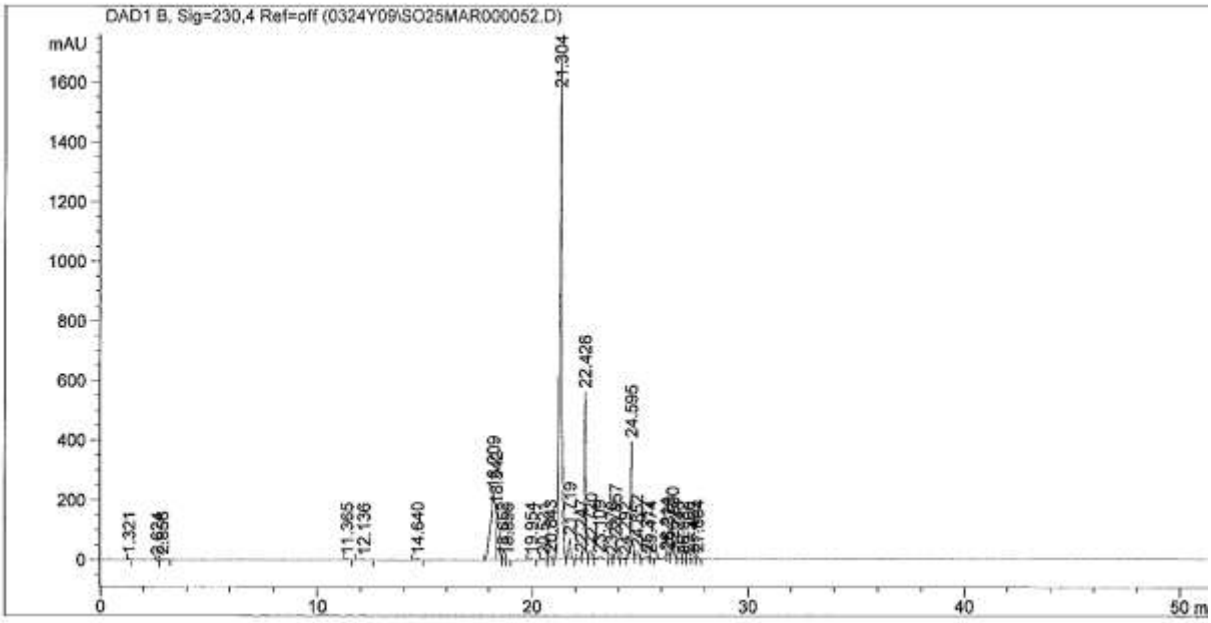
CAS 0000947-19-3 LC-MS chromatogram



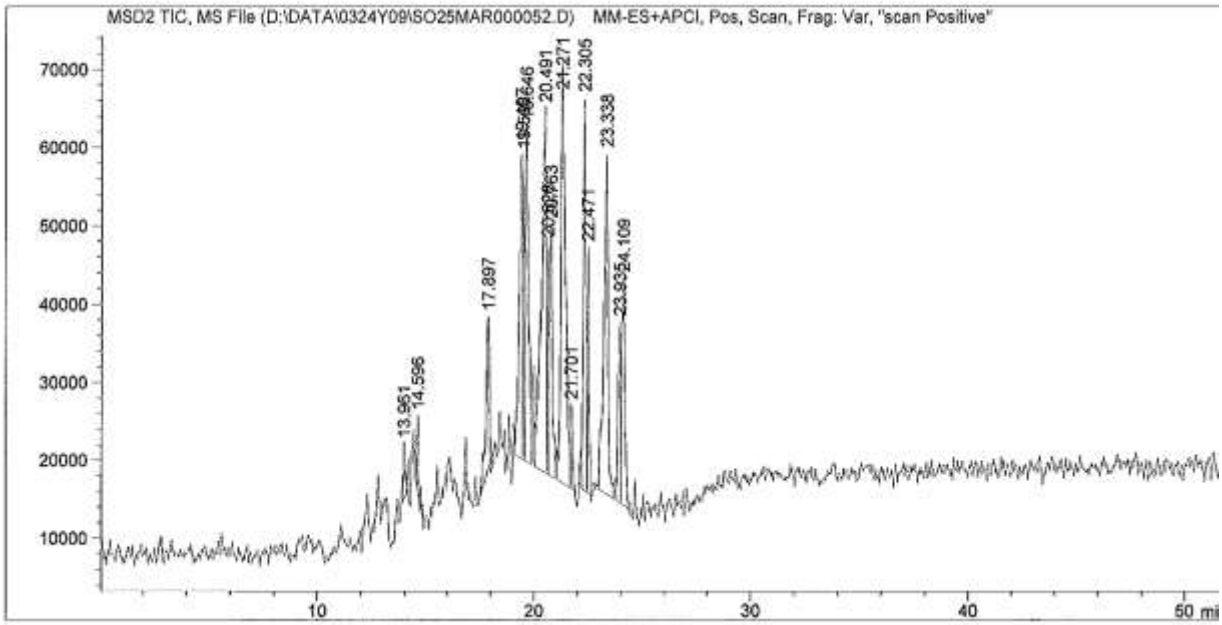



*MSD2 SPC, time=20.305 of D:\DATA\0324Y09\SO25MAR000051.D
Max: 28245
105.
187.2
228.2
91.2
106.0
159.2
186.2
100
80
60
40
20
0
50
100
150
200
m/z

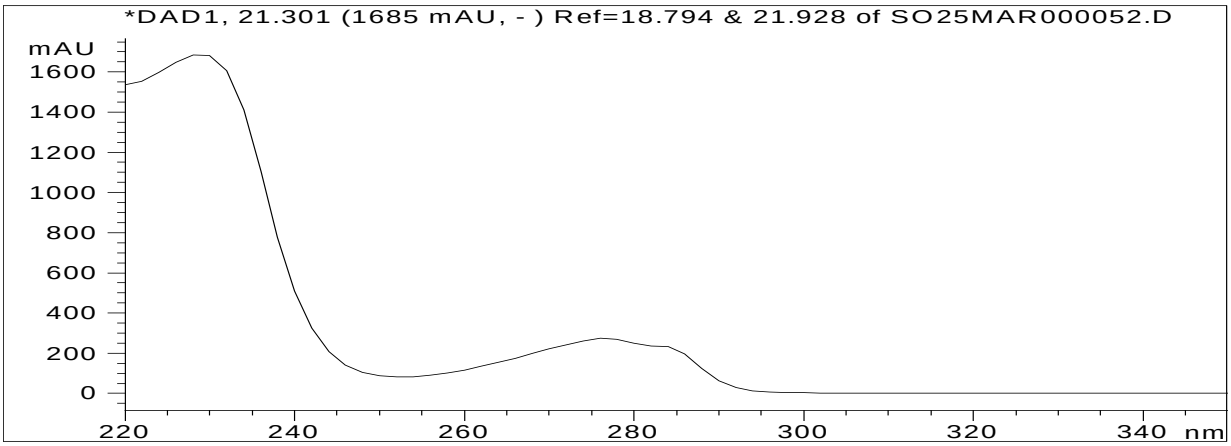
Epoxy acrylate monomer LC-UV chromatogram 230 nm

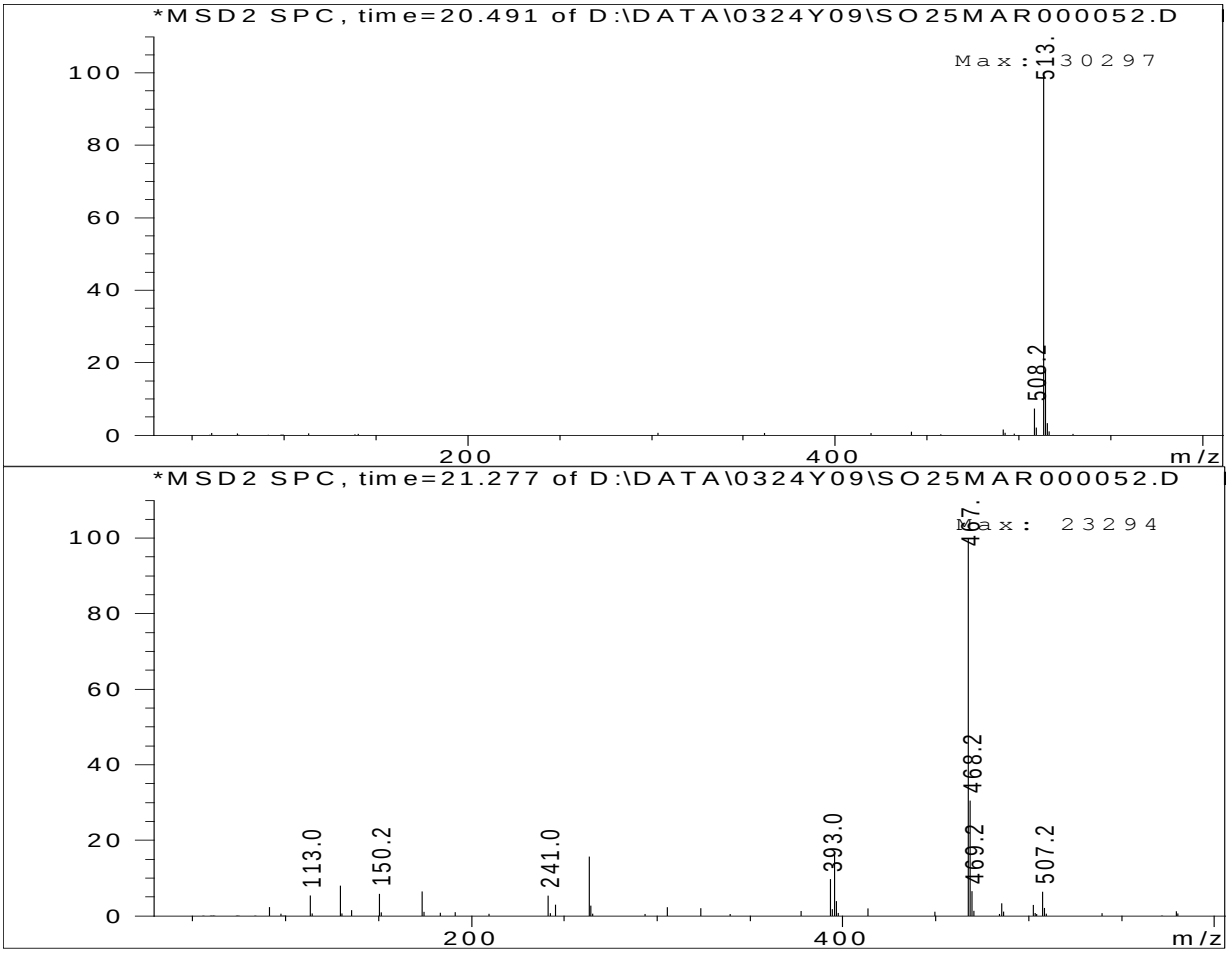


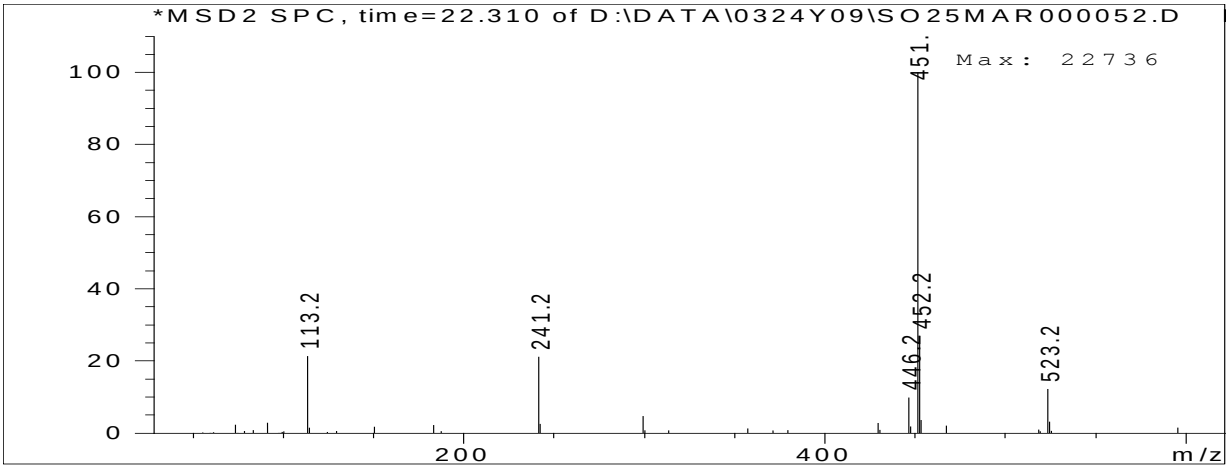
Epoxy acrylate monomer LC-MS chromatogram

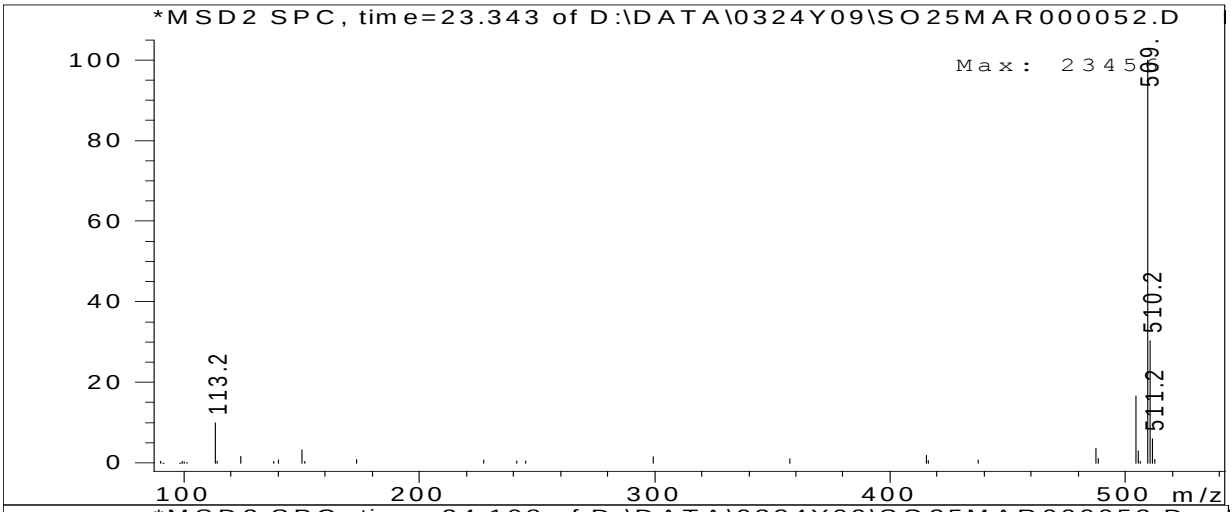


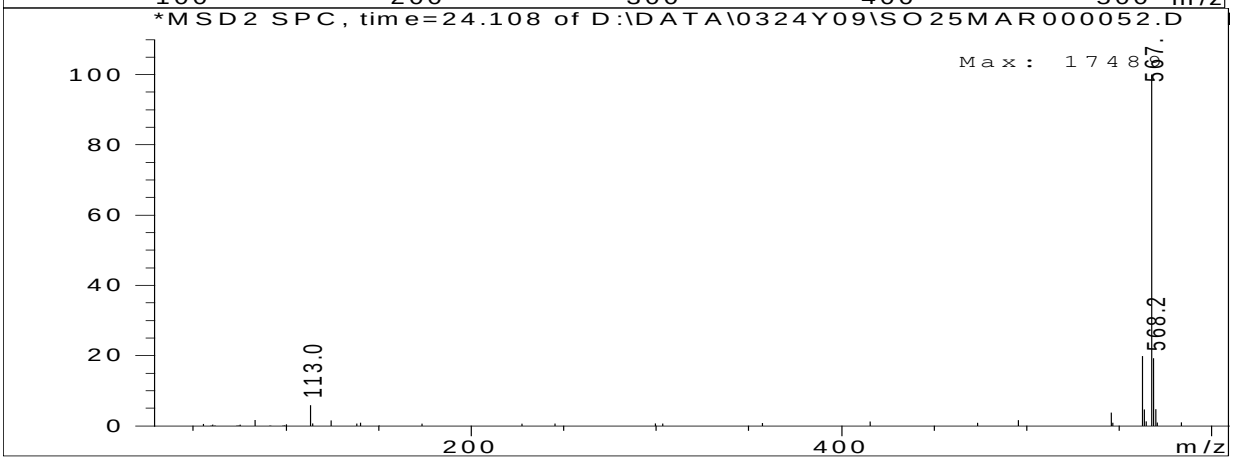
EPOXY ACRYLATE



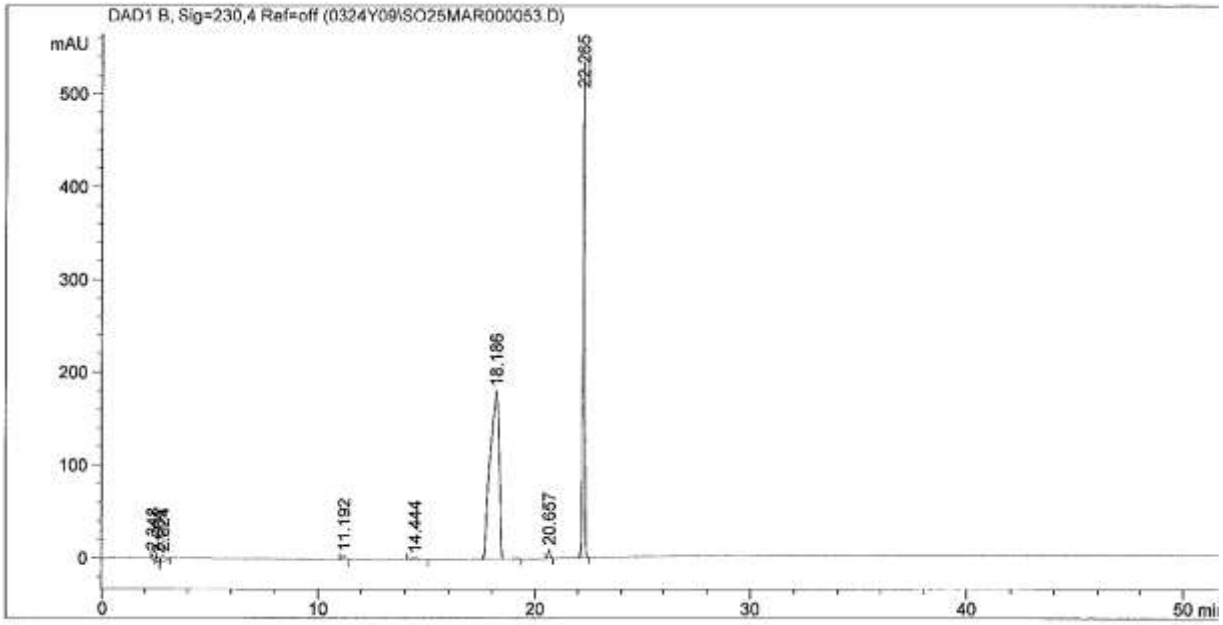



*MSD2 SPC, time=22.310 of D:\DATA\0324Y09\SO25MAR000052.D
Max: 22736
451.
113.2
241.2
452.2
446.2
523.2
m/z

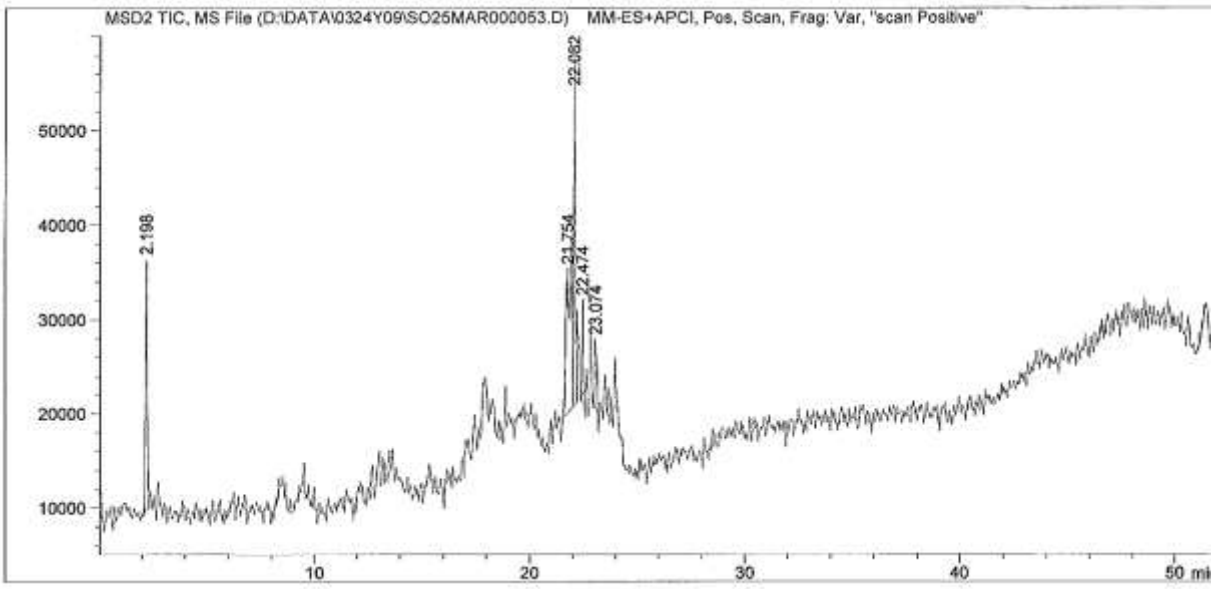

*MSD2 SPC, time=23.343 of D:\DATA\0324Y09\SO25MAR000052.D
Max: 23450
509.
510.2
511.2
113.2
m/z

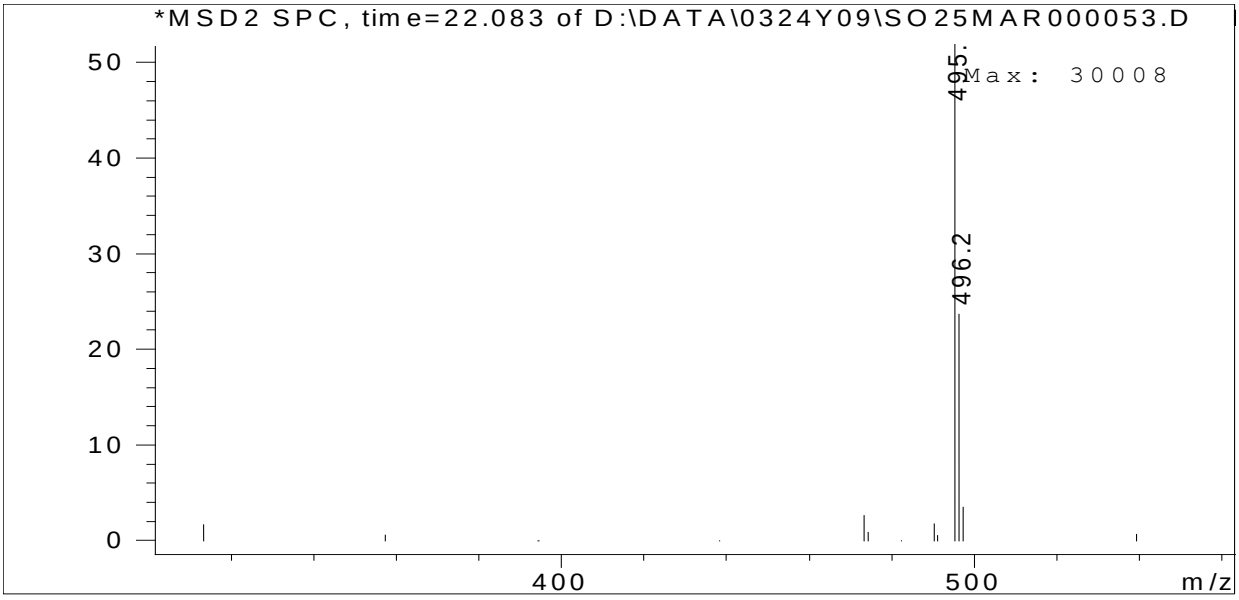

*MSD2 SPC, time=24.108 of D:\DATA\0324Y09\SO25MAR000052.D
Max: 17487
567.
568.2
113.0
m/z

Acrylated amine synergist LC –UV Chromatogram

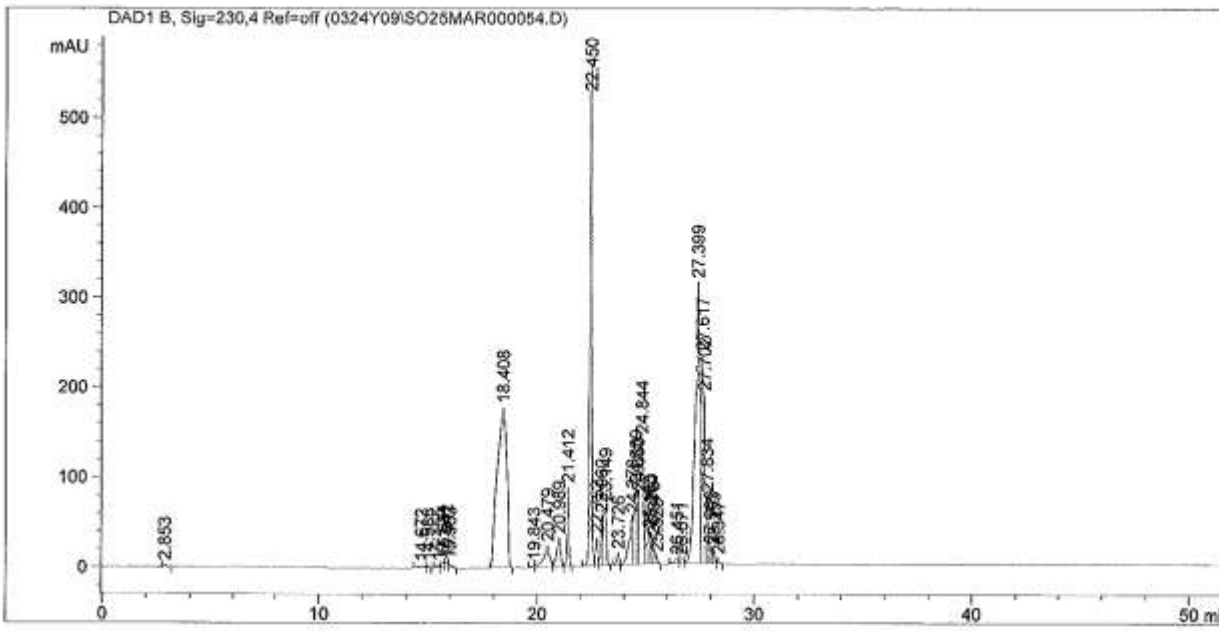


Acrylated amine synergist LC-MS Chromatogram

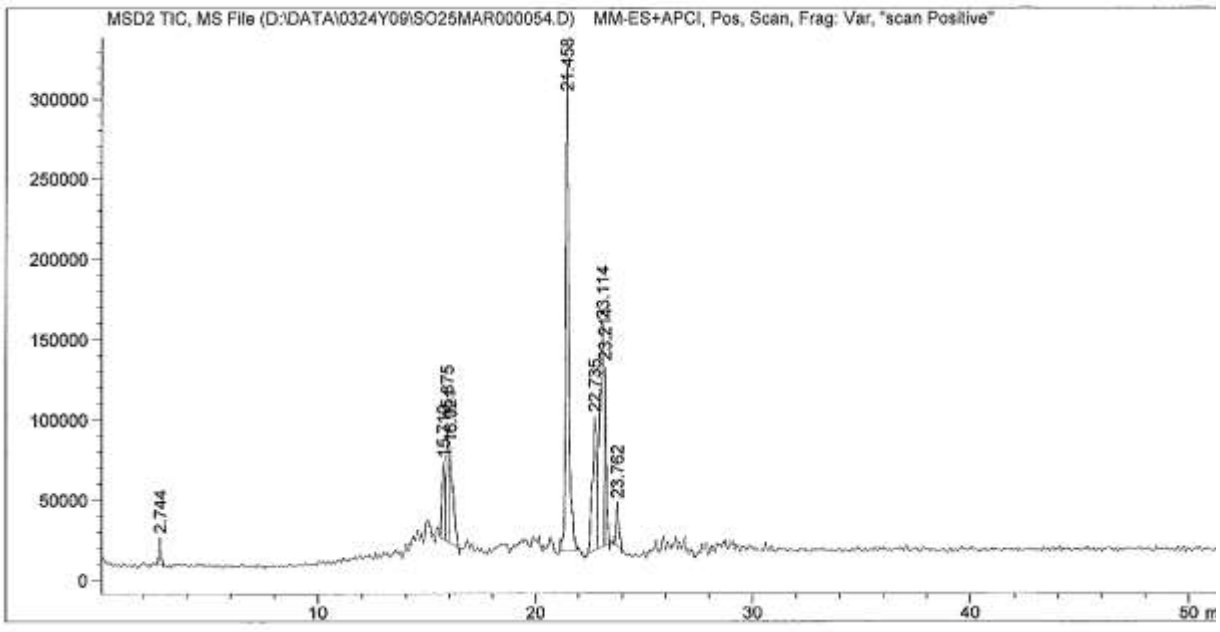



*MSD2 SPC, time=22.083 of D:\DATA\0324Y09\SO25MAR000053.D
Max: 30008
495.
496.2
50
40
30
20
10
0
400
500
m/z

Amine synergist LC-UV chromatogram

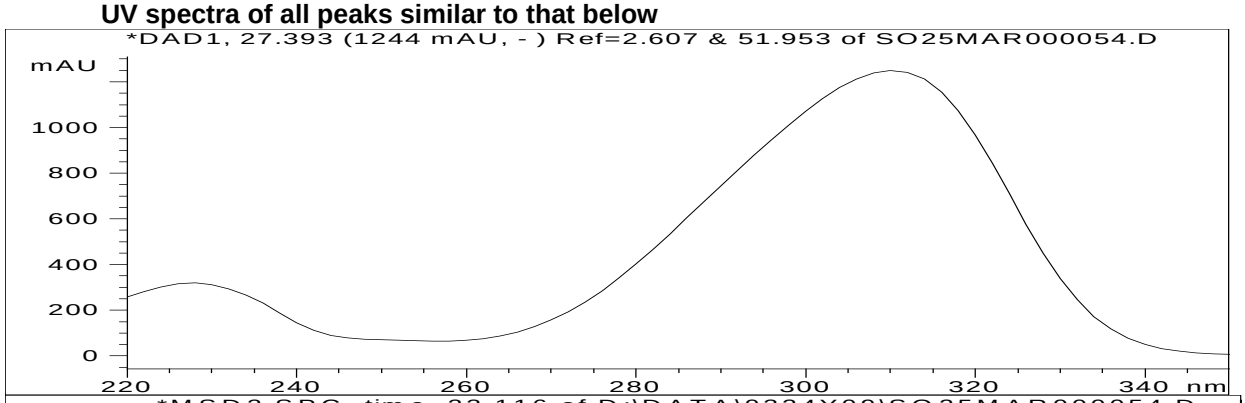


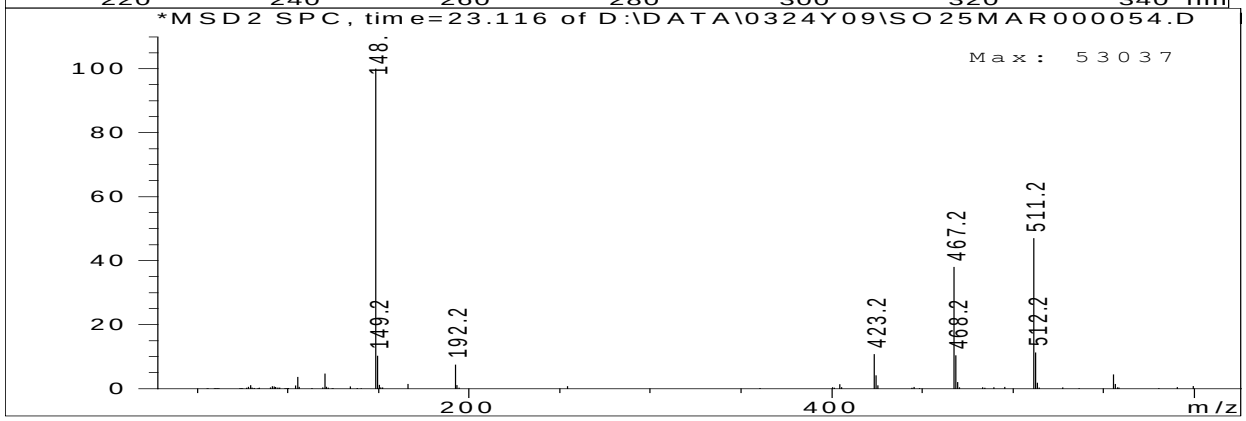
Amine synergist LC-MS Chromatogram

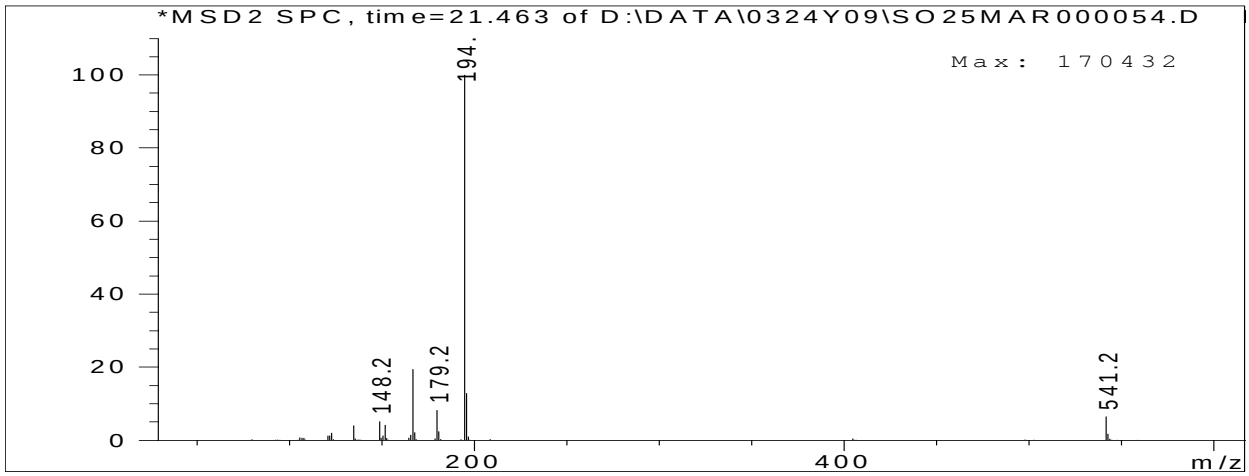


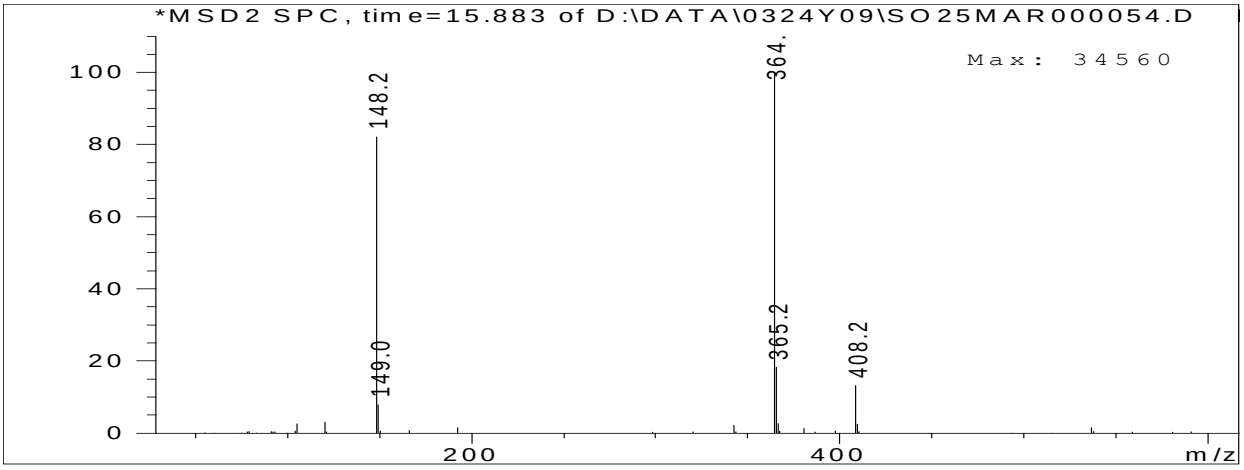
AMINE SYNERGIST

UV spectra of all peaks similar to that below

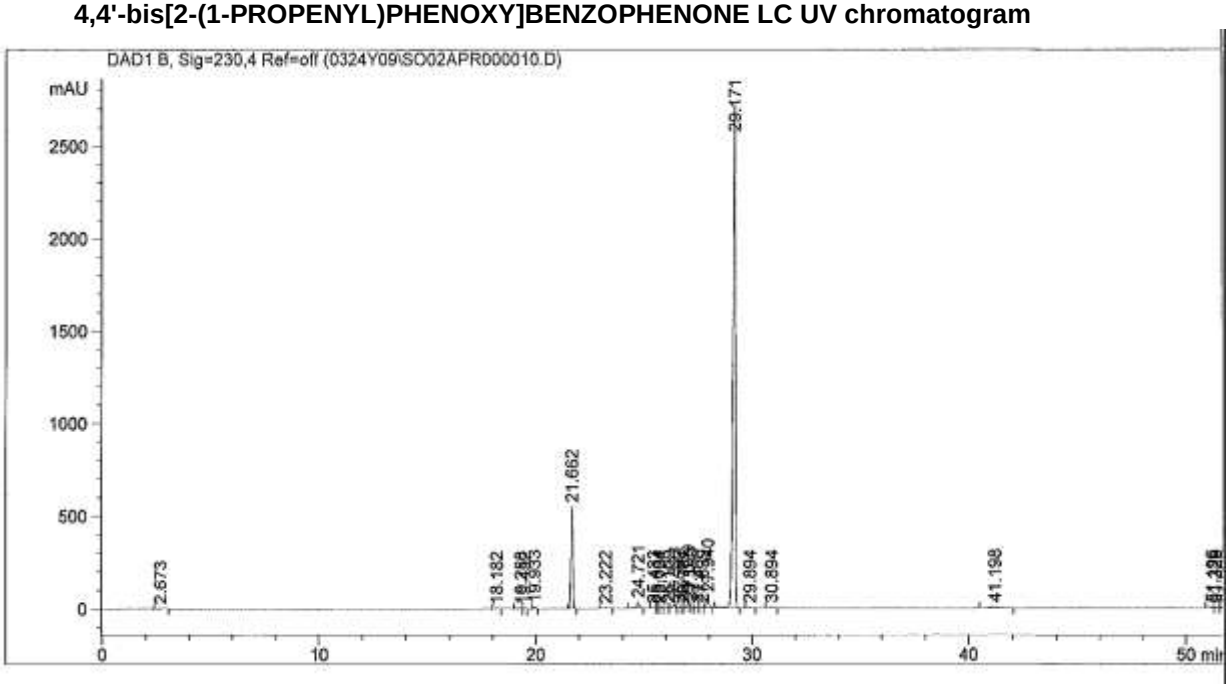




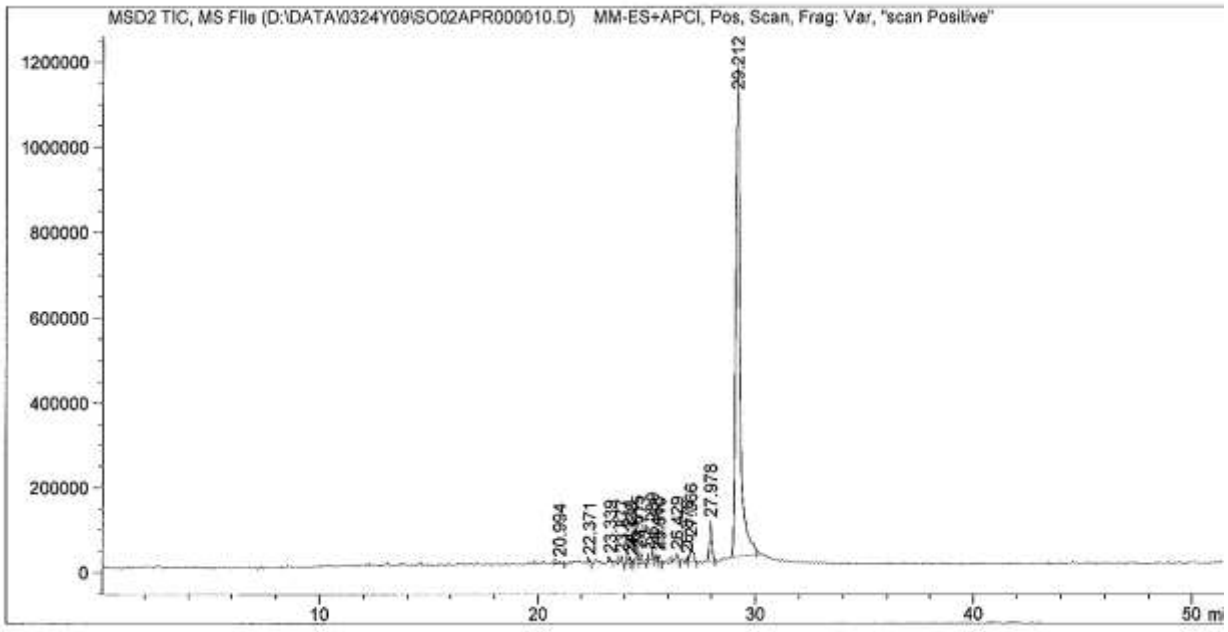



*MSD2 SPC, time=15.883 of D:\DATA\0324Y09\SO25MAR000054.D
Max: 34560
100
80
60
40
20
0
148.2
149.0
364.
365.2
408.2
200
400
m/z

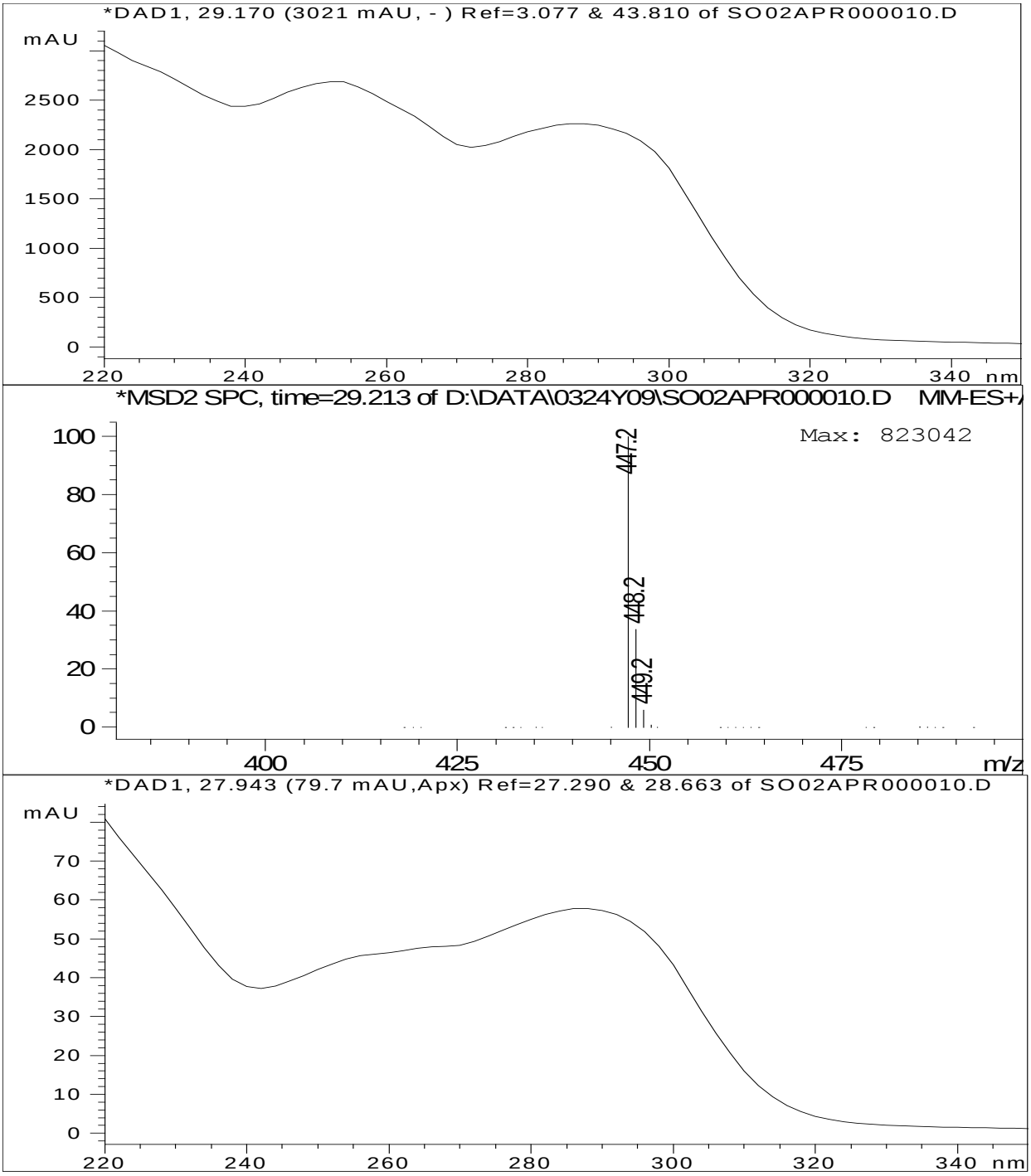
4,4'-bis[2-(1-PROPENYL)PHENOXY]BENZOPHENONE LC UV chromatogram

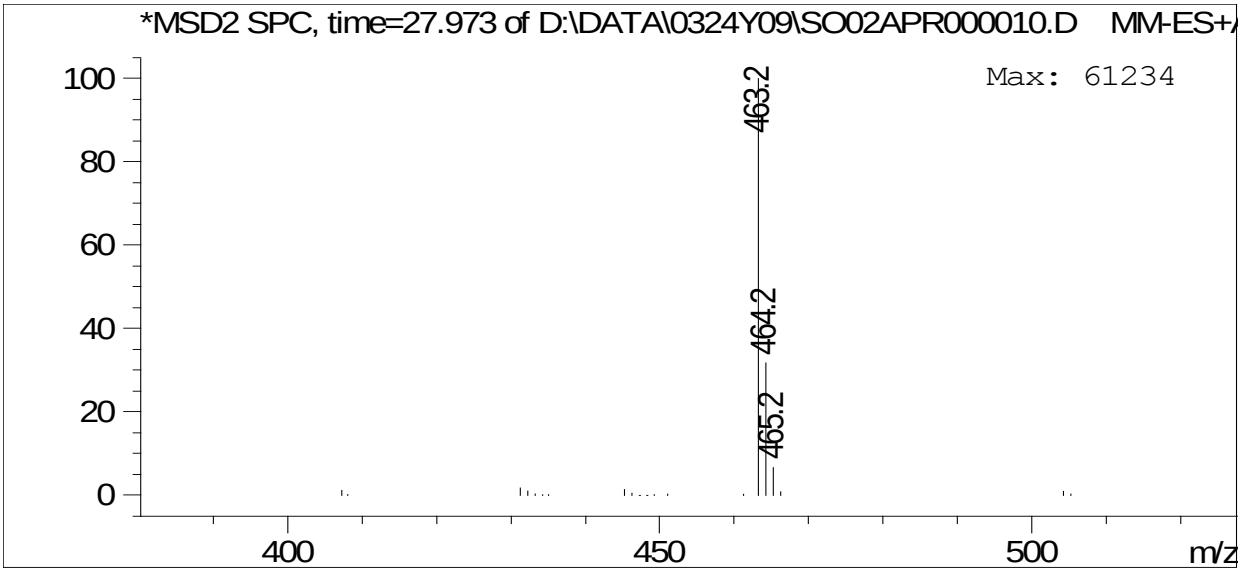


4,4'-bis[2-(1-PROPENYL)PHENOXY]BENZOPHENONE LC MS chromatogram

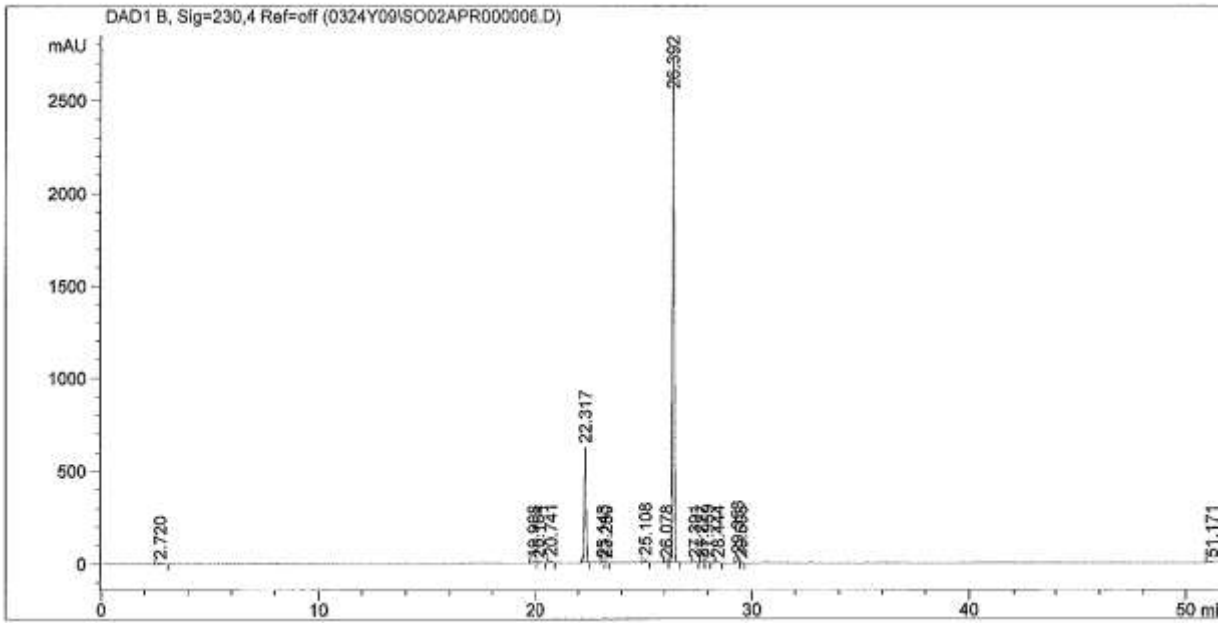


4,4'-bis[2-(1-PROPENYL)PHENOXY]BENZOPHENONE

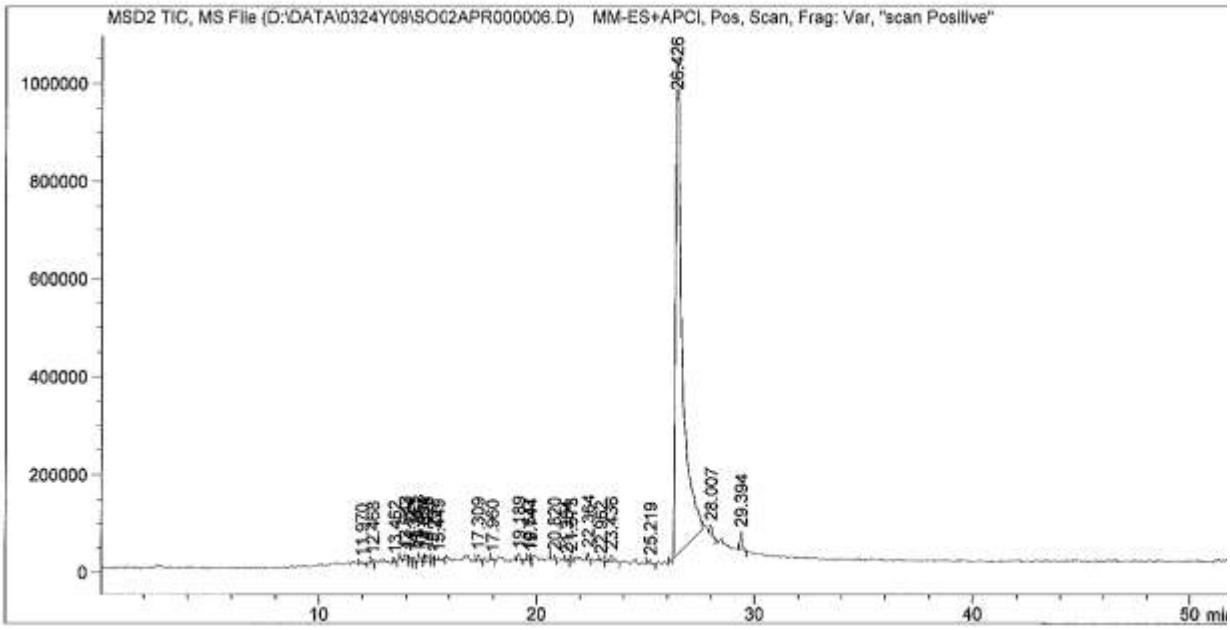



*MSD2 SPC, time=27.973 of D:\DATA\0324Y09\SO02APR000010.D MM-ES+A
Max: 61234
463.2
464.2
465.2
100
80
60
40
20
0
400
450
500
m/z

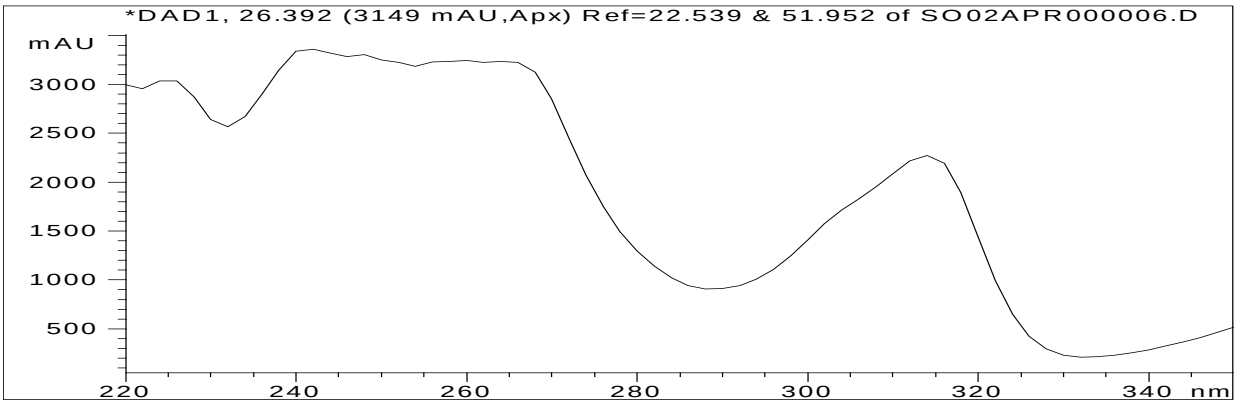
1-CHLORO-4-PROPOXY-9H-THIOXANTHEN-9-ONE LC-UV chromatogram

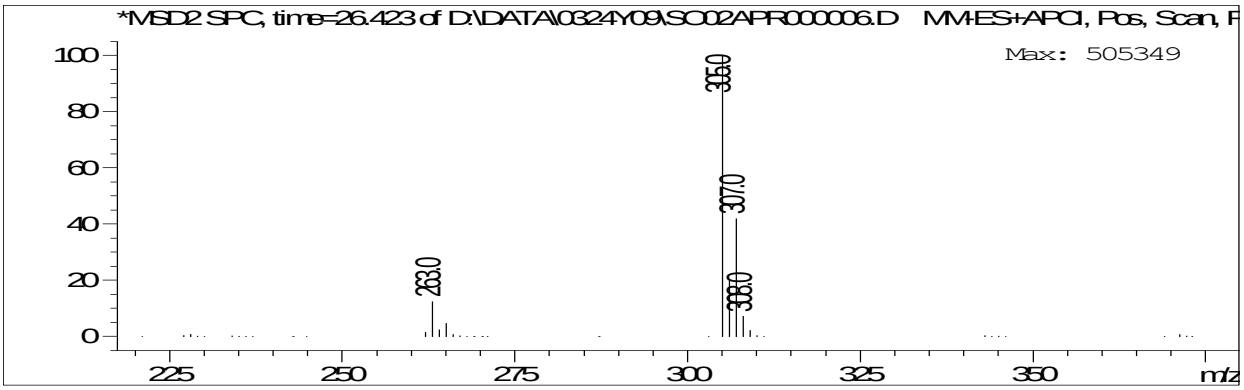


1-CHLORO-4-PROPOXY-9H-THIOXANTHEN-9-ONE LC-MS chromatogram

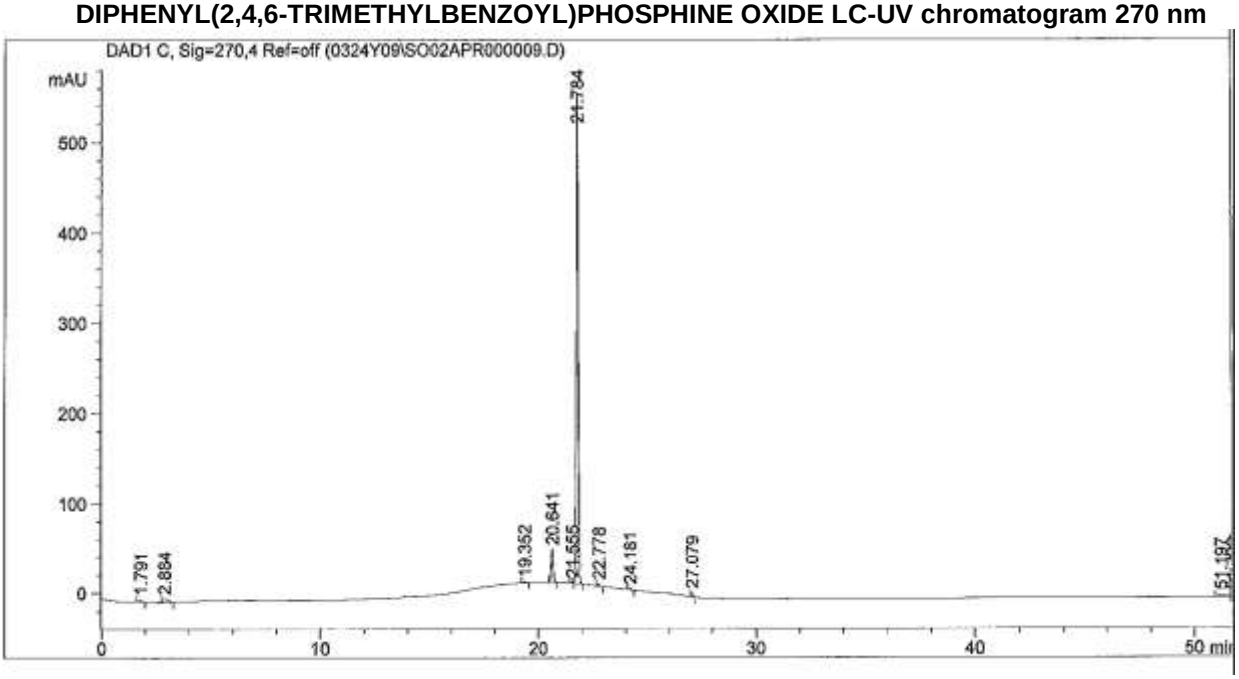


1-CHLORO-4-PROPOXY-9H-THIOXANTHEN-9-ONE

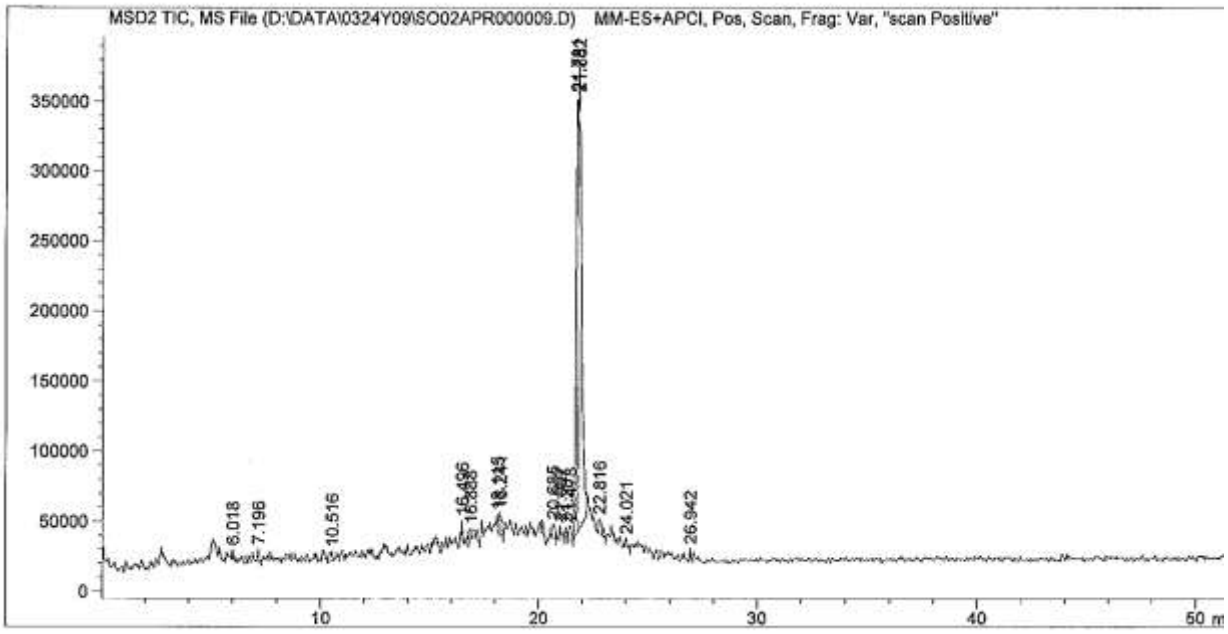




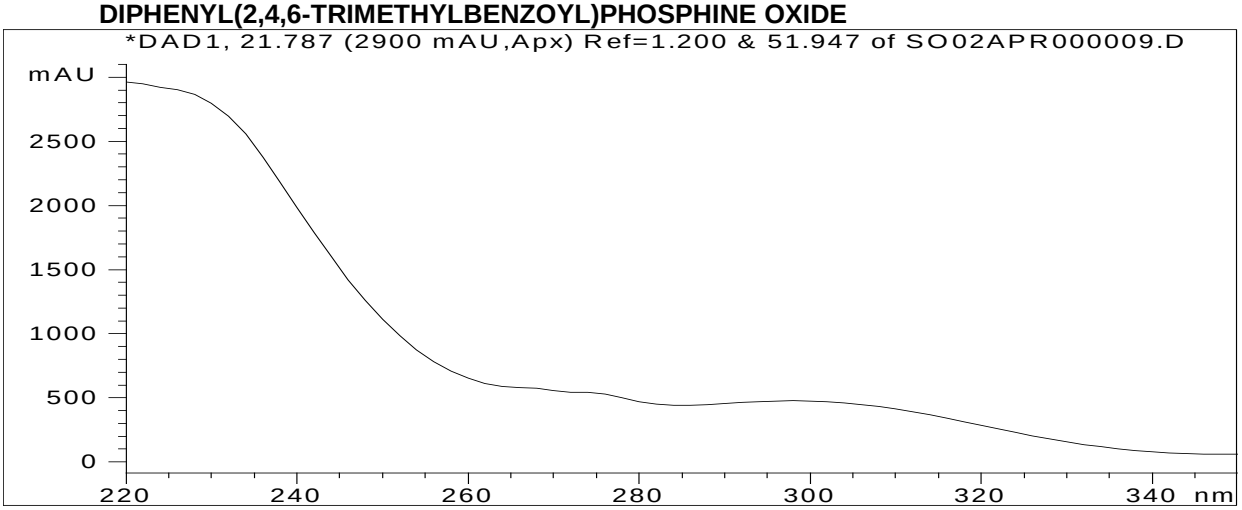
DIPHENYL(2,4,6-TRIMETHYLBENZOYL)PHOSPHINE OXIDE LC-UV chromatogram 270 nm

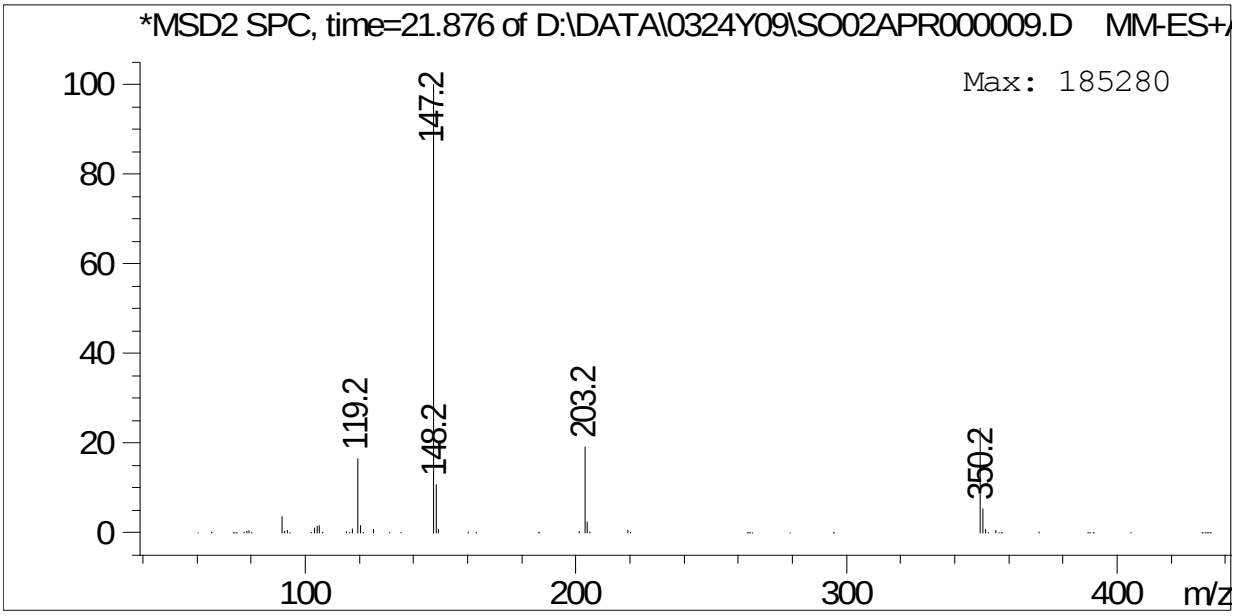


DIPHENYL(2,4,6-TRIMETHYLBENZOYL)PHOSPHINE OXIDE LC-MS chromatogram

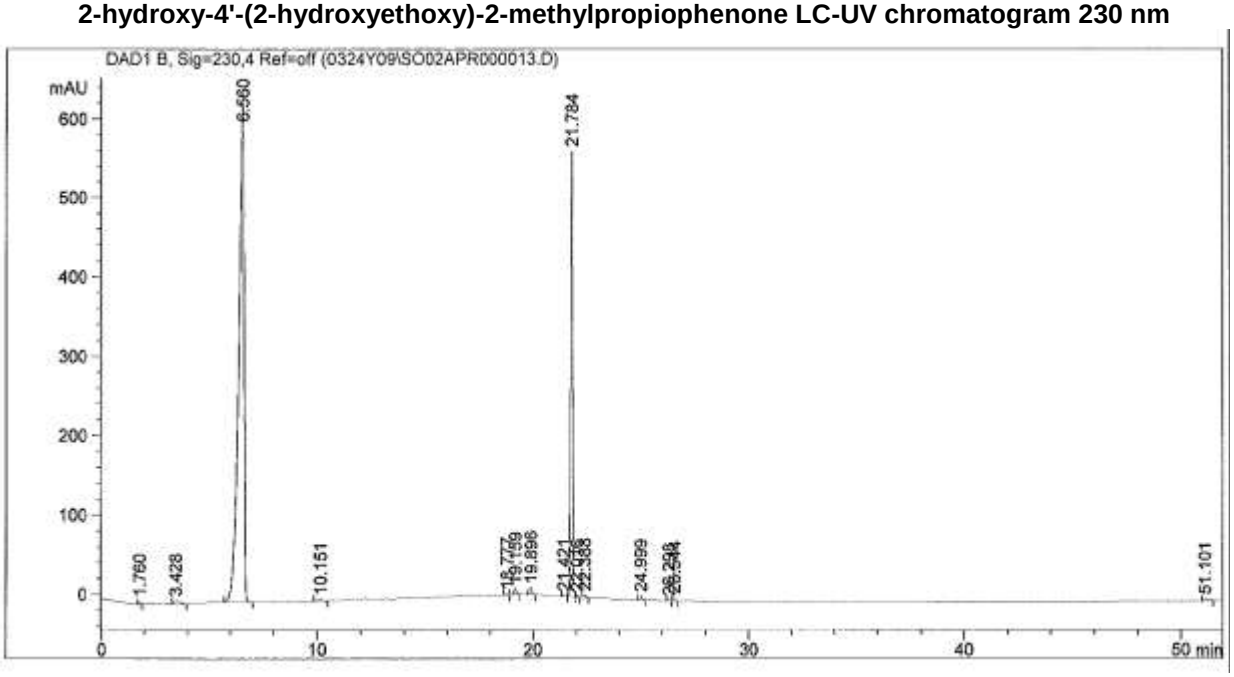


DIPHENYL(2,4,6-TRIMETHYLBENZOYL)PHOSPHINE OXIDE

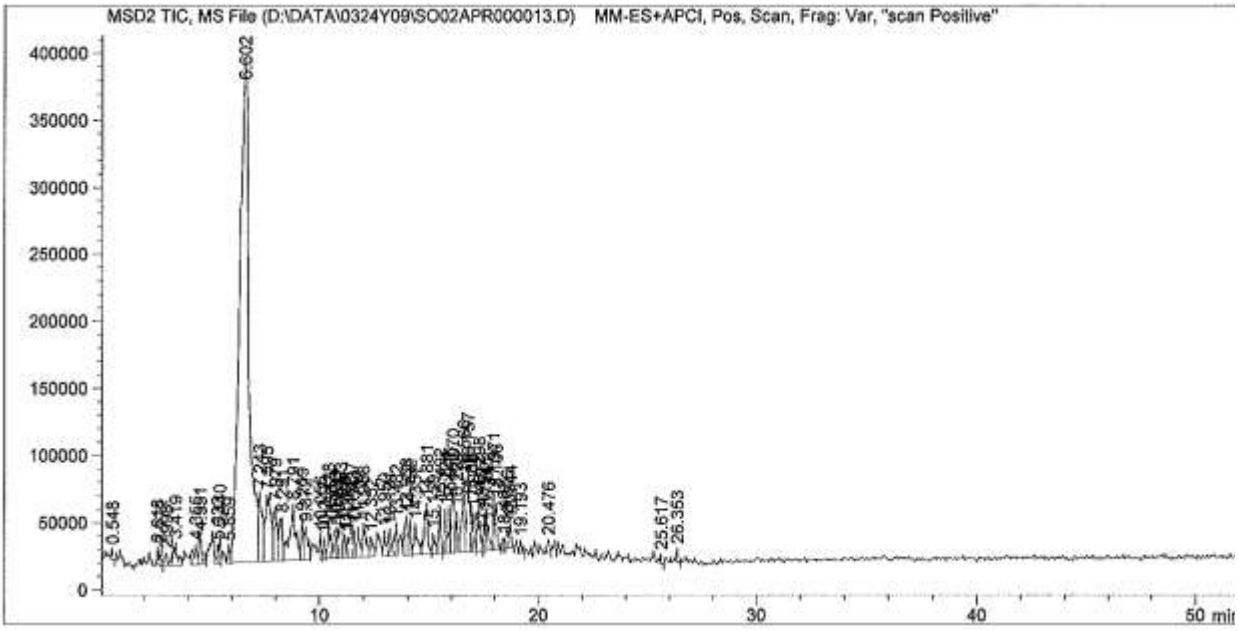




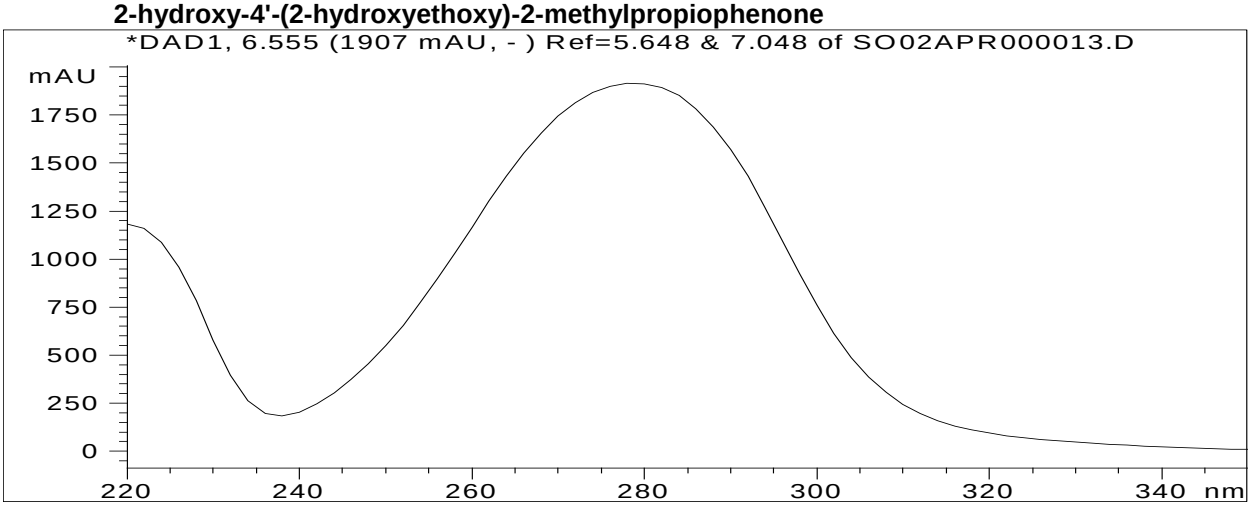
2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone LC-UV chromatogram 230 nm

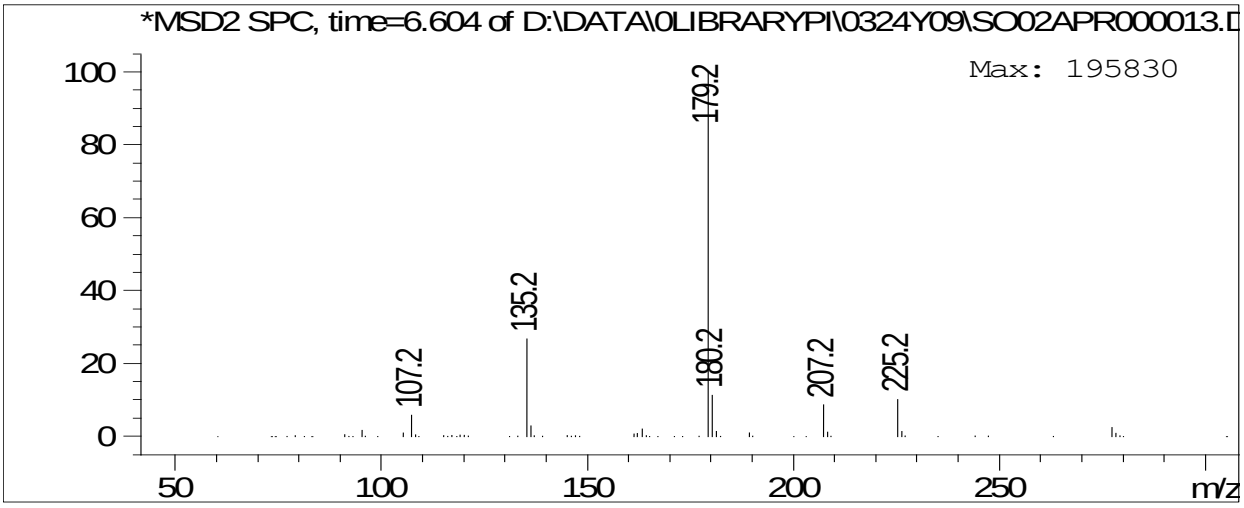


2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone LC-MS chromatogram

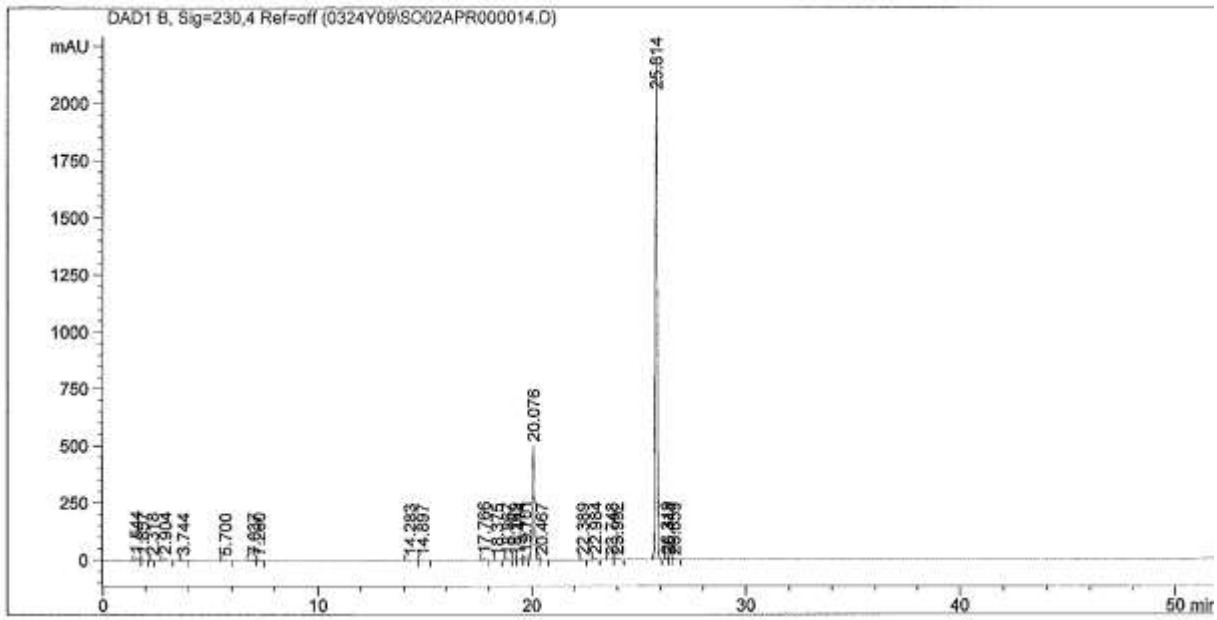


2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone

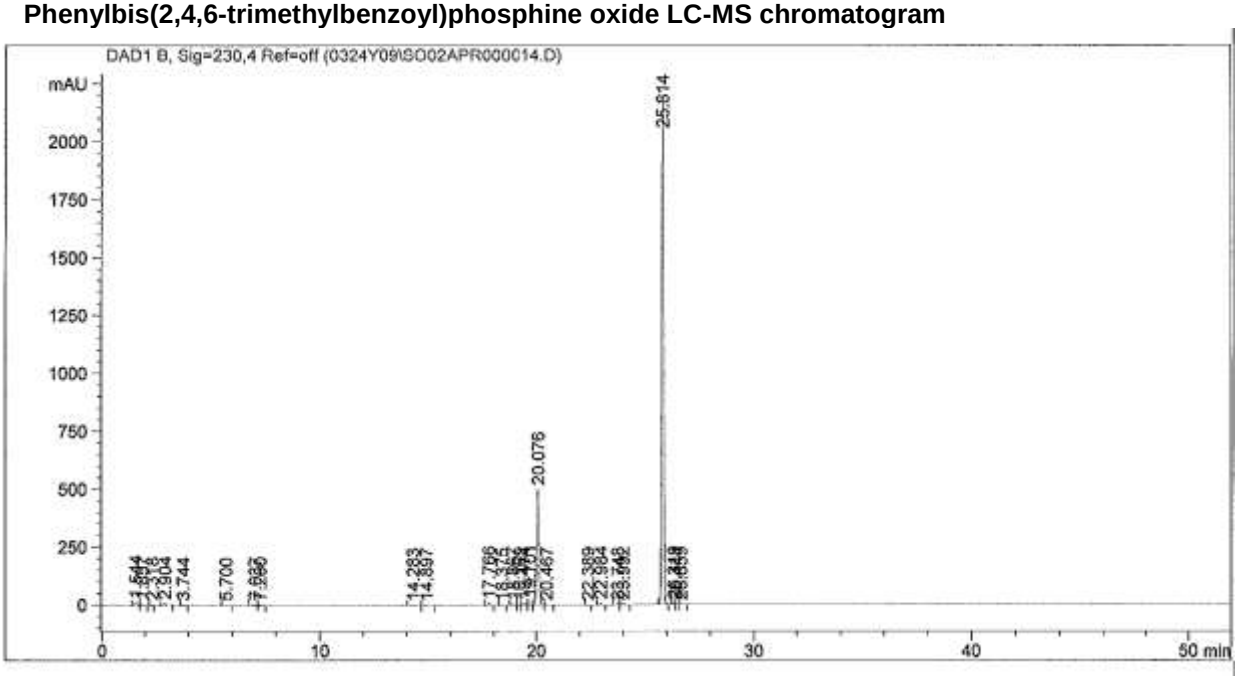




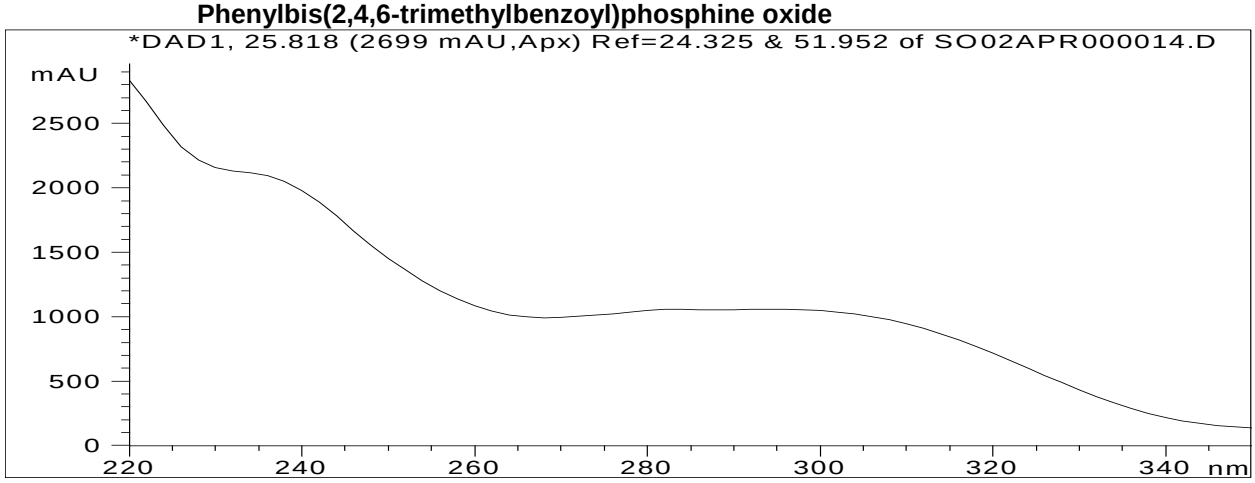
Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide LC-UV chromatogram 230 nm

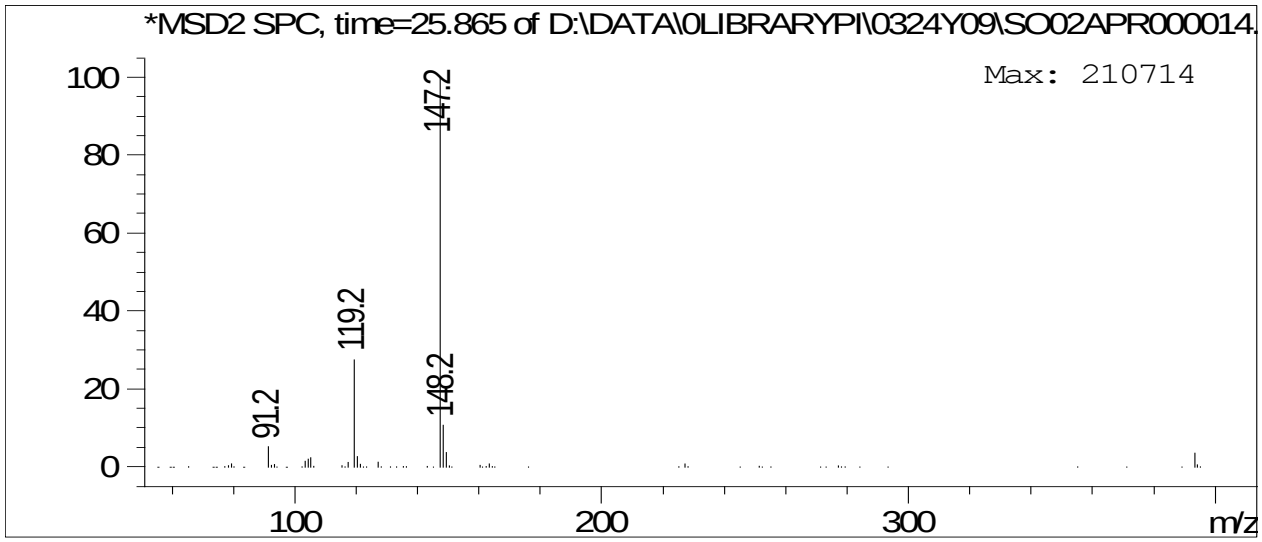


Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide LC-MS chromatogram

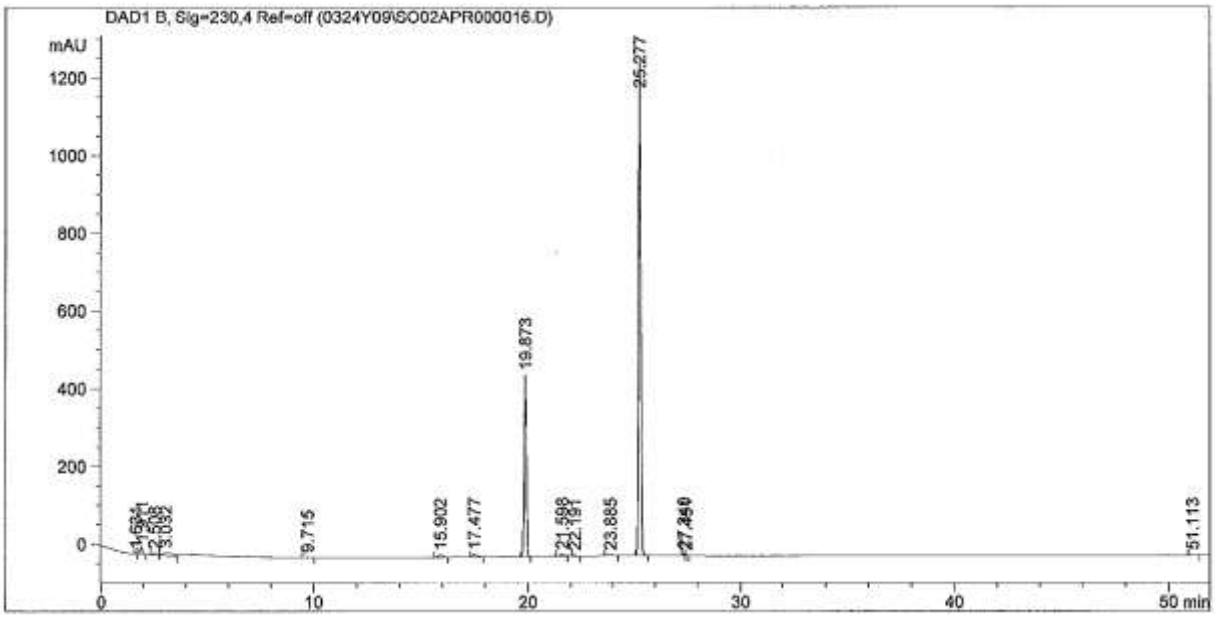


Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide

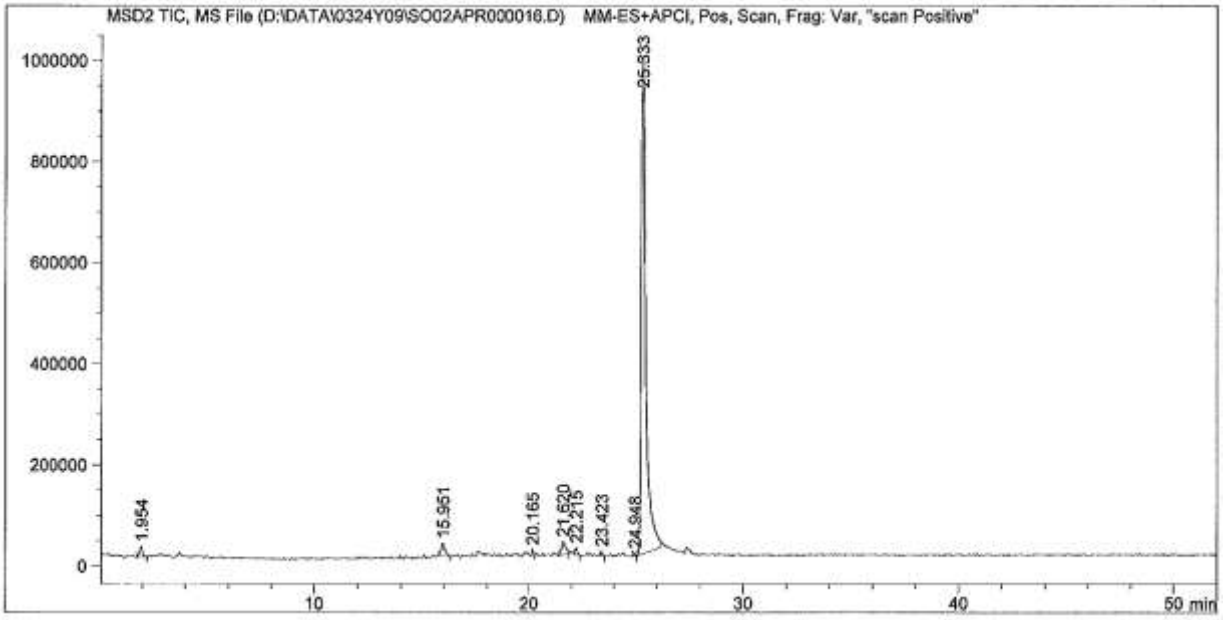




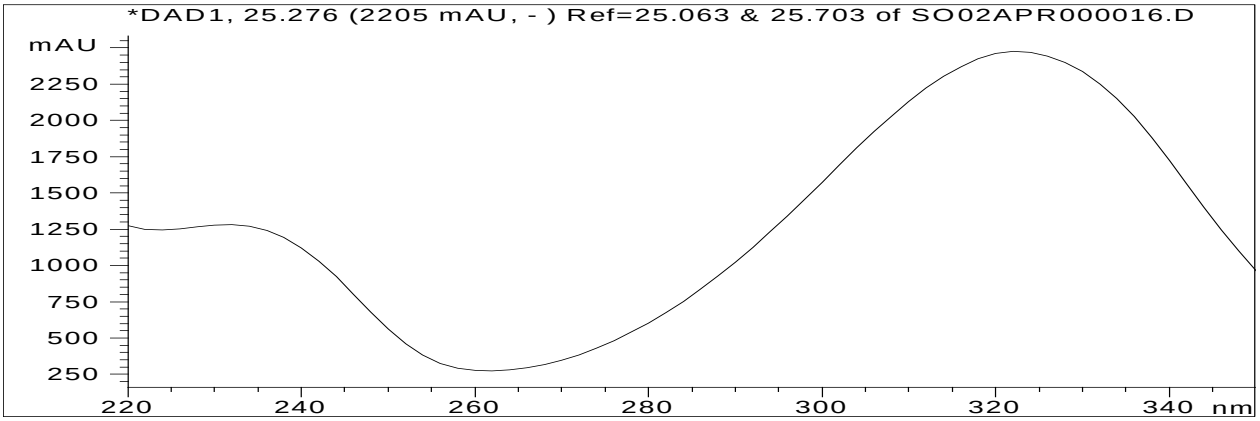
2-Benzyl-2-(dimethylamino)-4'morpholinobutyrophenone LC-UV Chromatogram 230 nm

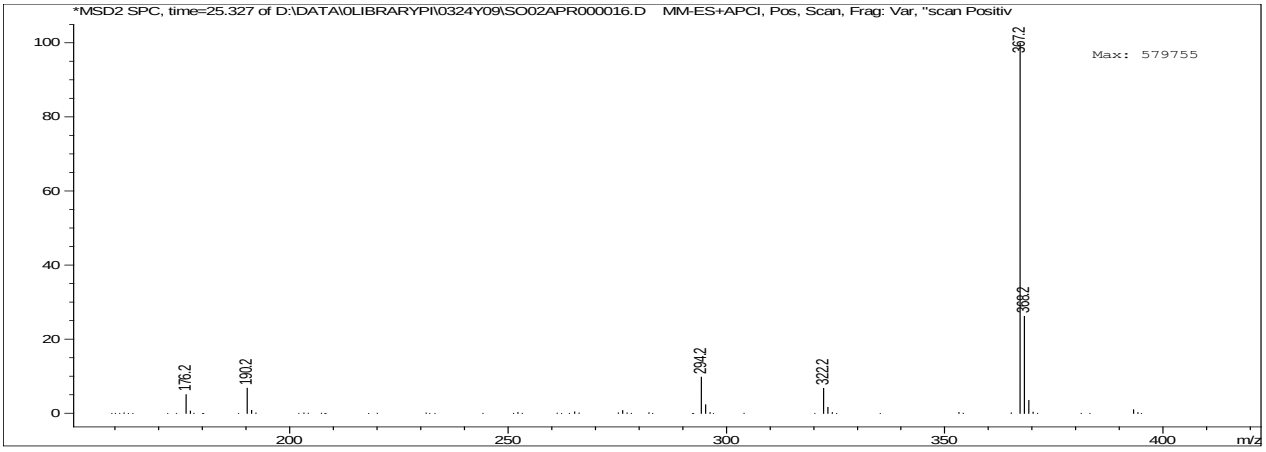


2-Benzyl-2-(dimethylamino)-4'morpholinobutyrophenone LC-MS Chromatogram

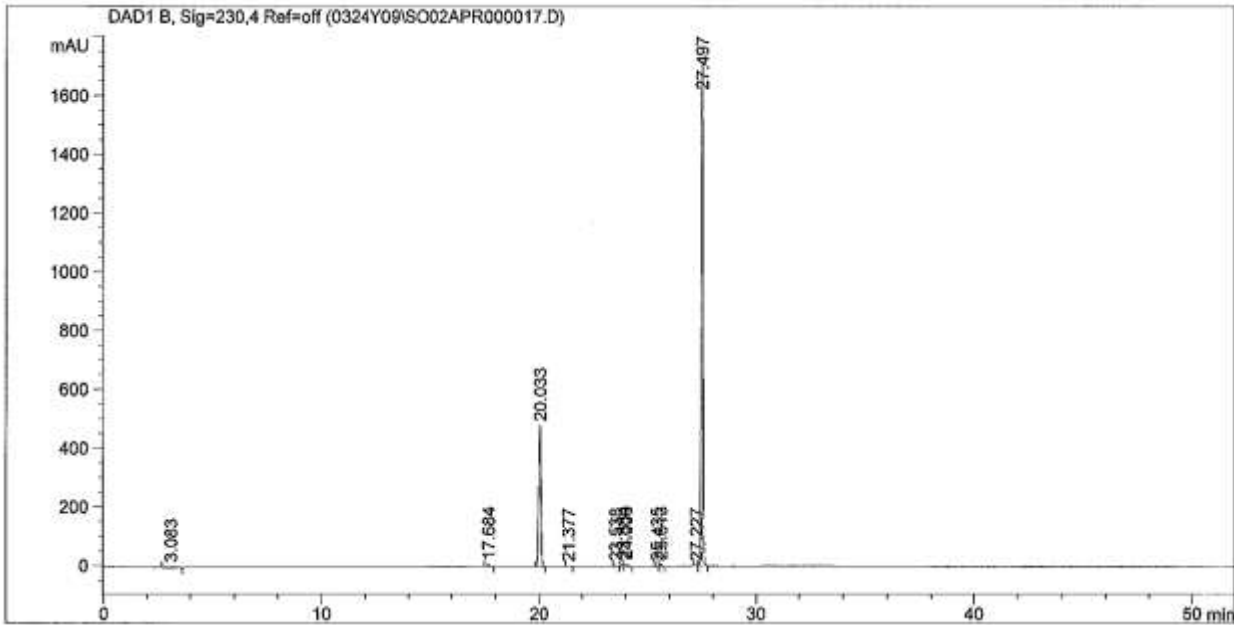


-Benzyl-2-(dimethylamino)-4'morpholinobutyrophenone

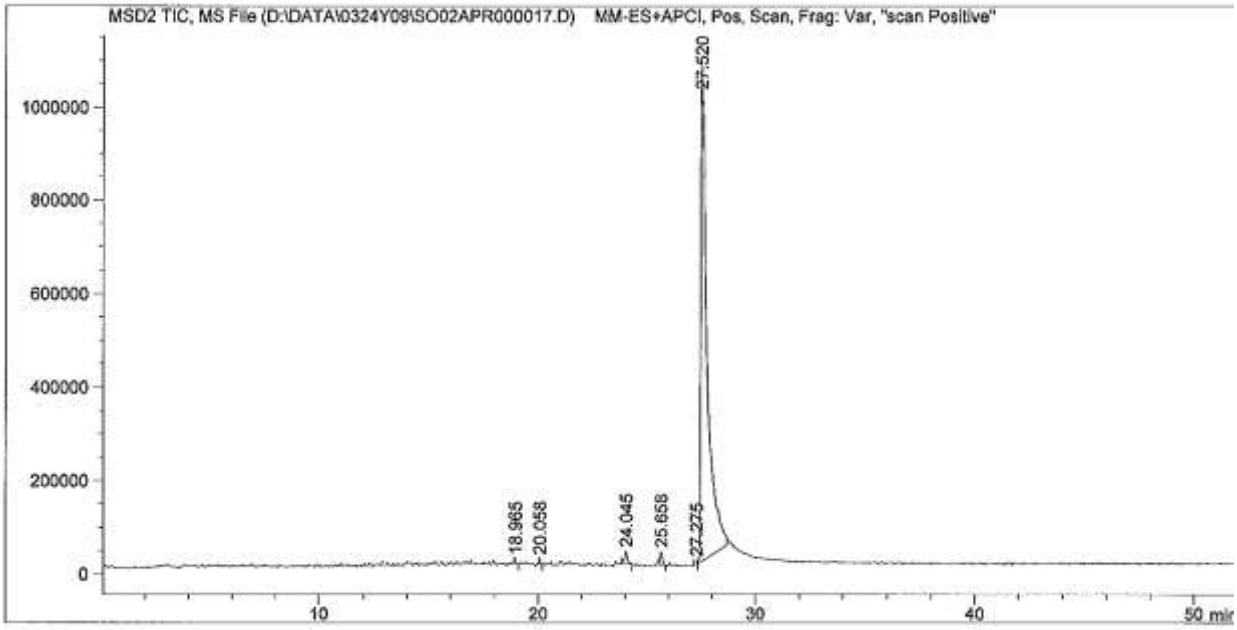




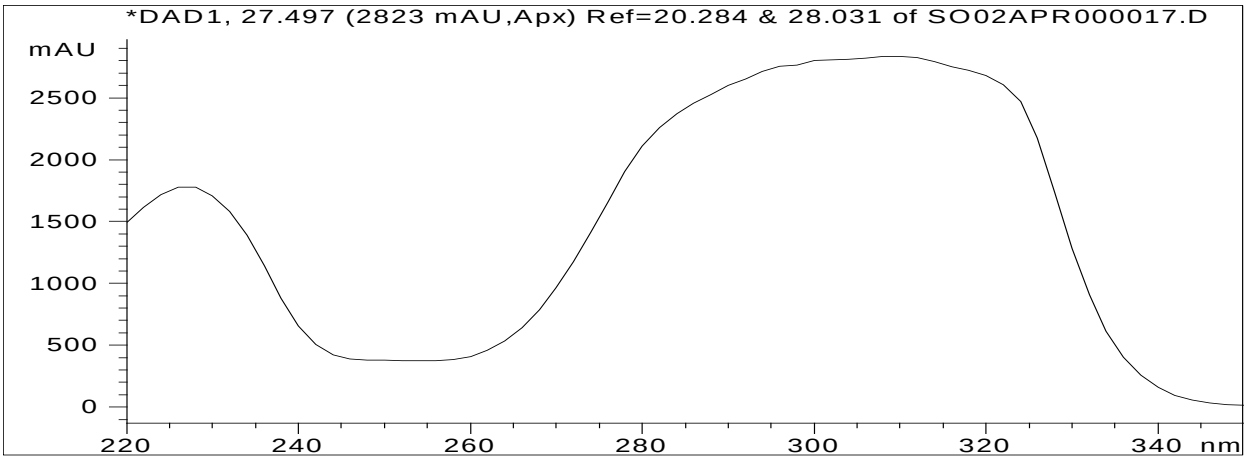
2-ethylhexyl-4-(dimethylamino)benzoate LC-UV Chromatogram 230 nm

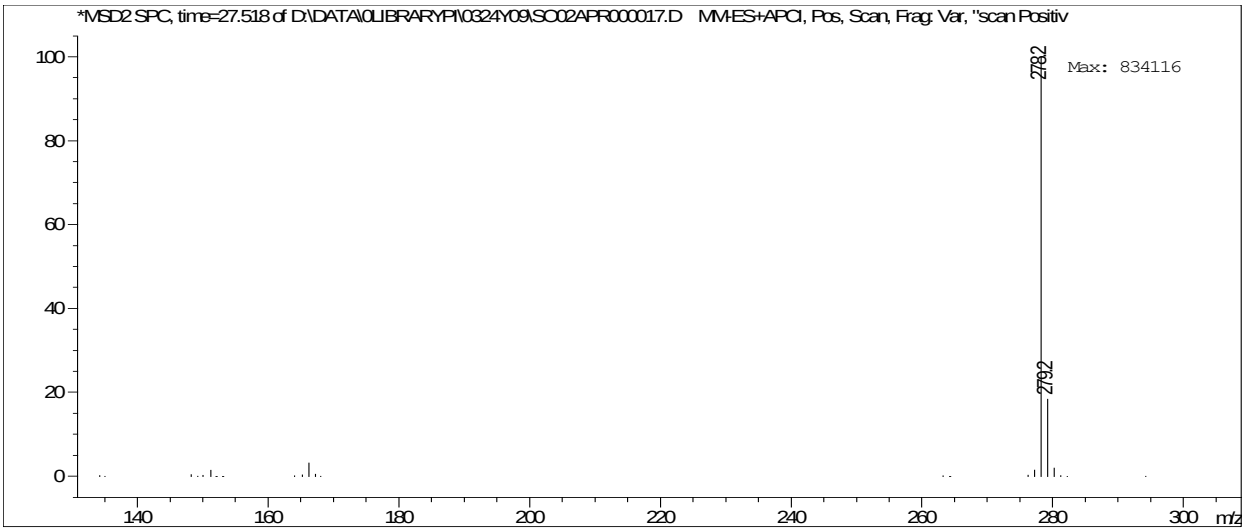


2-ethylhexyl-4-(dimethylamino)benzoate LC-MS Chromatogram

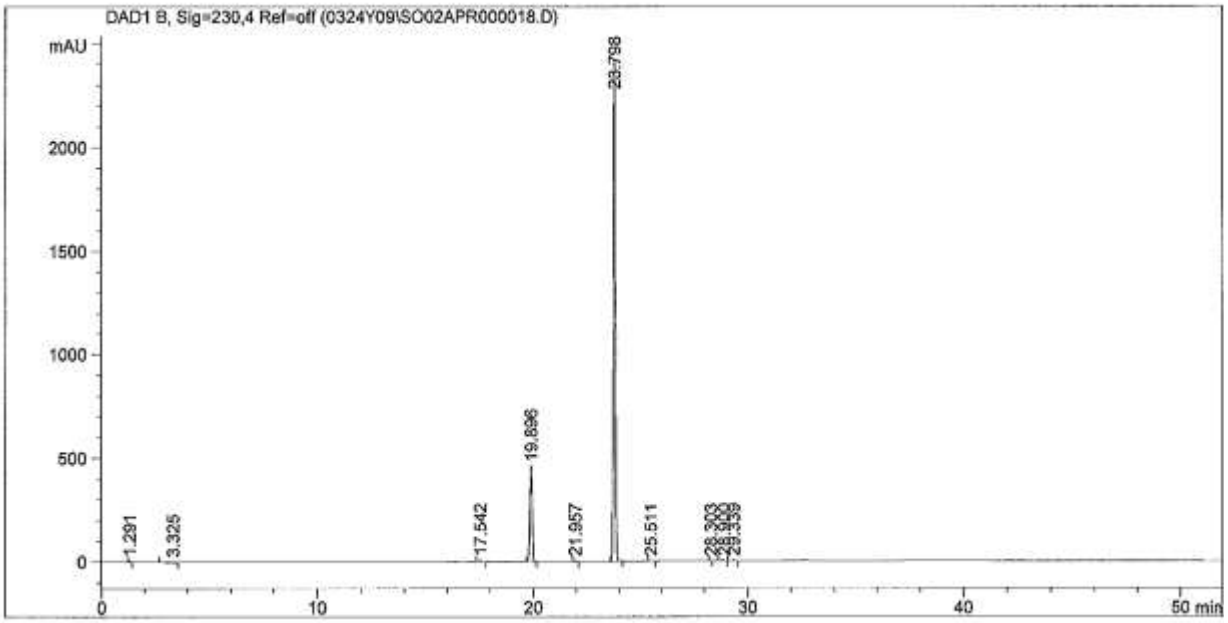


2-ethylhexyl-4-(dimethylamino)benzoate

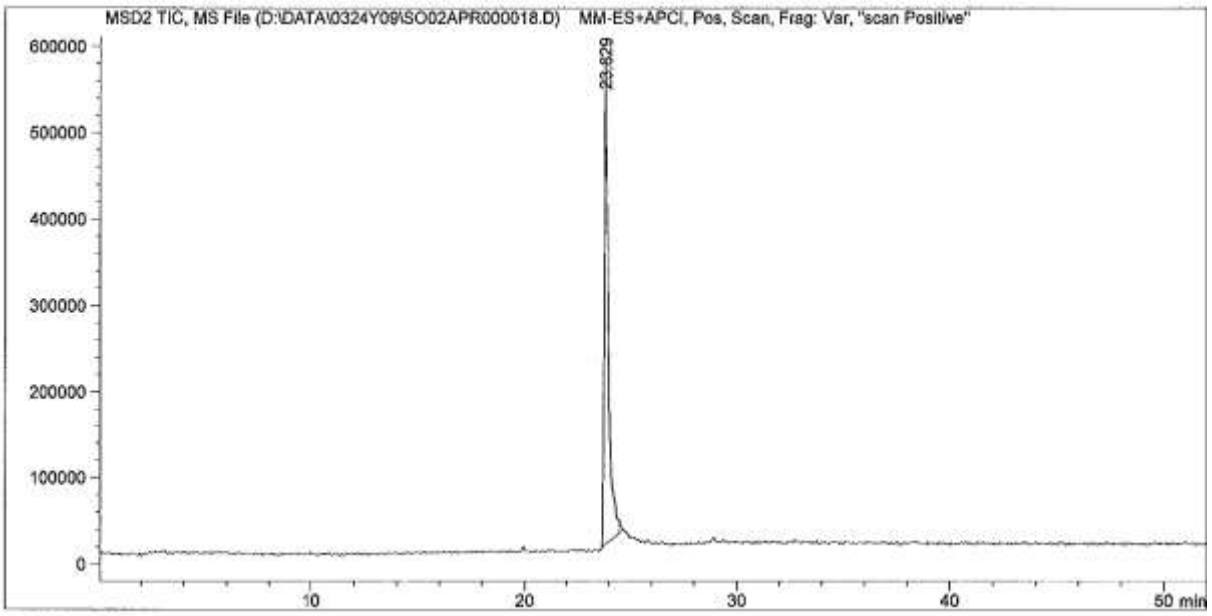




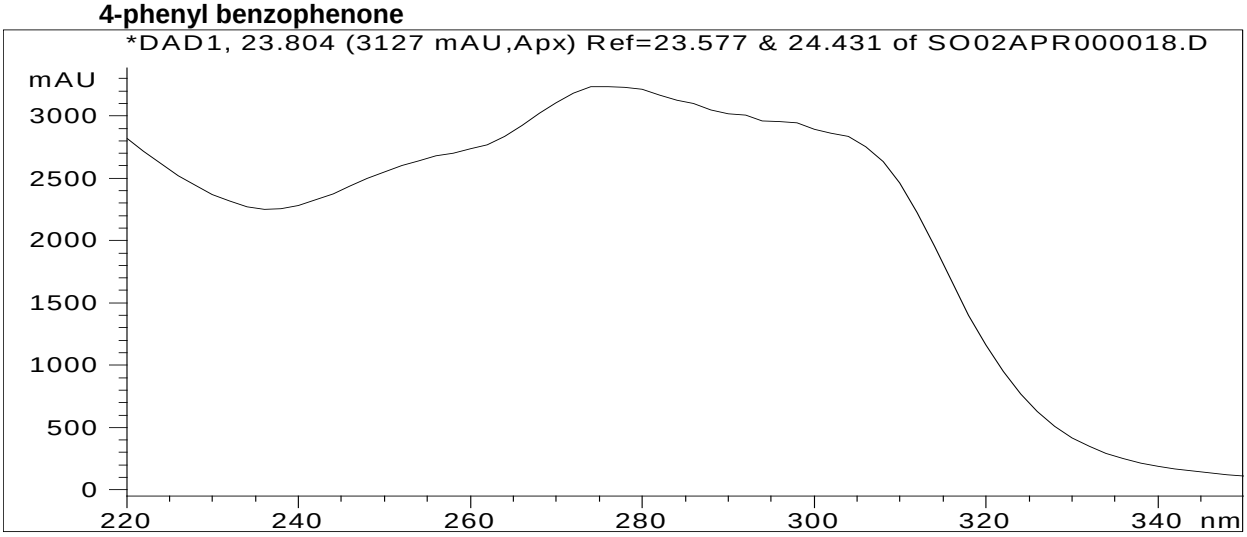
4-phenyl benzophenone LC-UV Chromatogram 230 nm

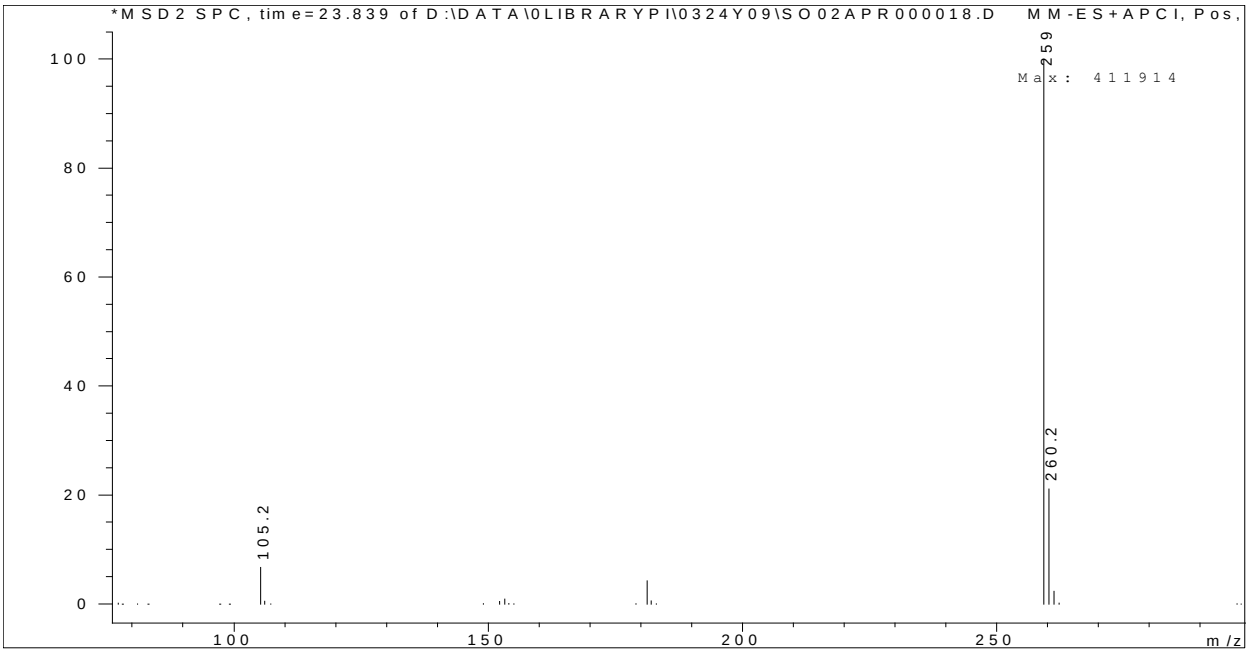


4-phenyl benzophenone LC-MS Chromatogram

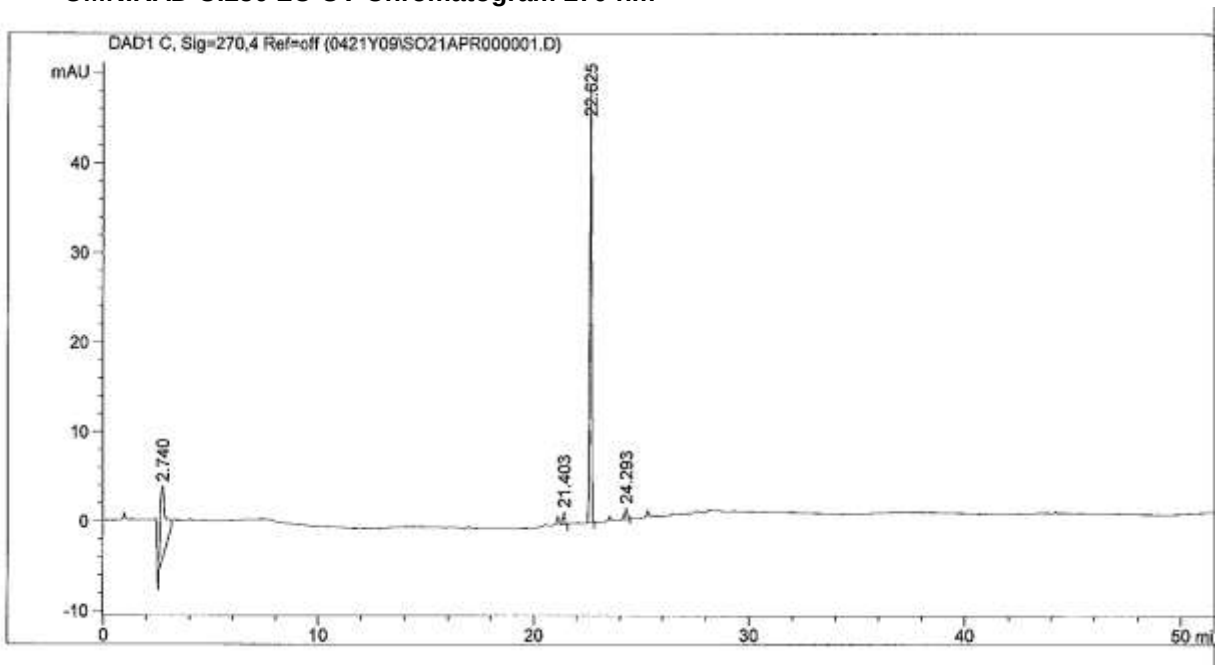


4-phenyl benzophenone

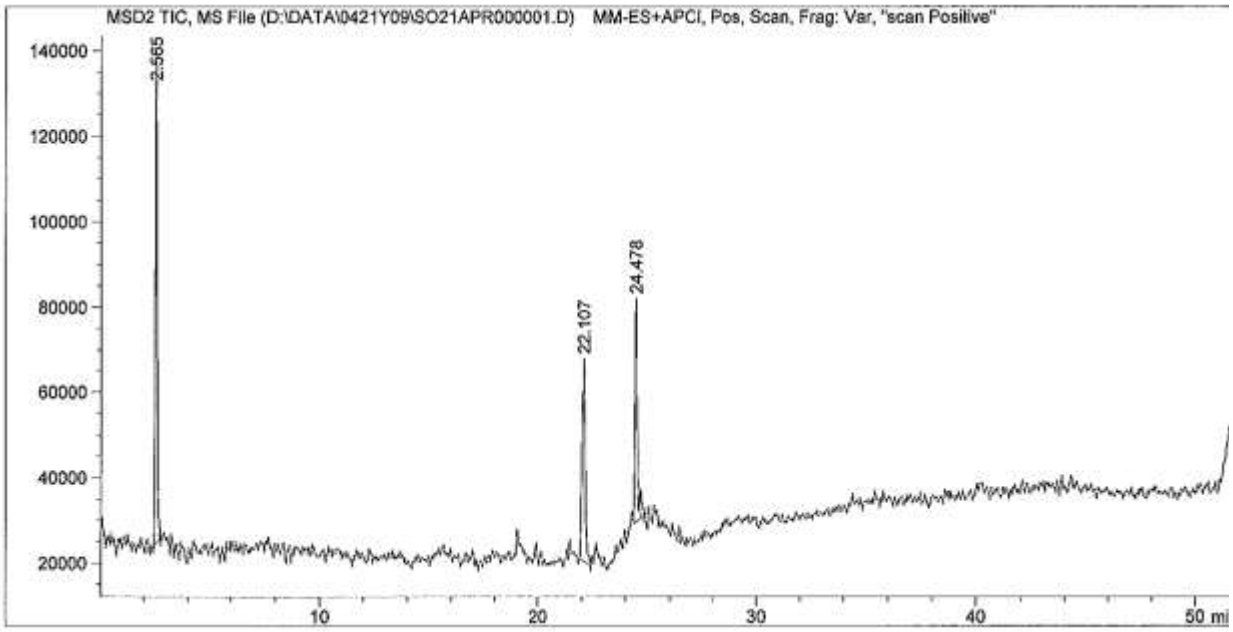




OMNIRAD CI250 LC-UV Chromatogram 270 nm

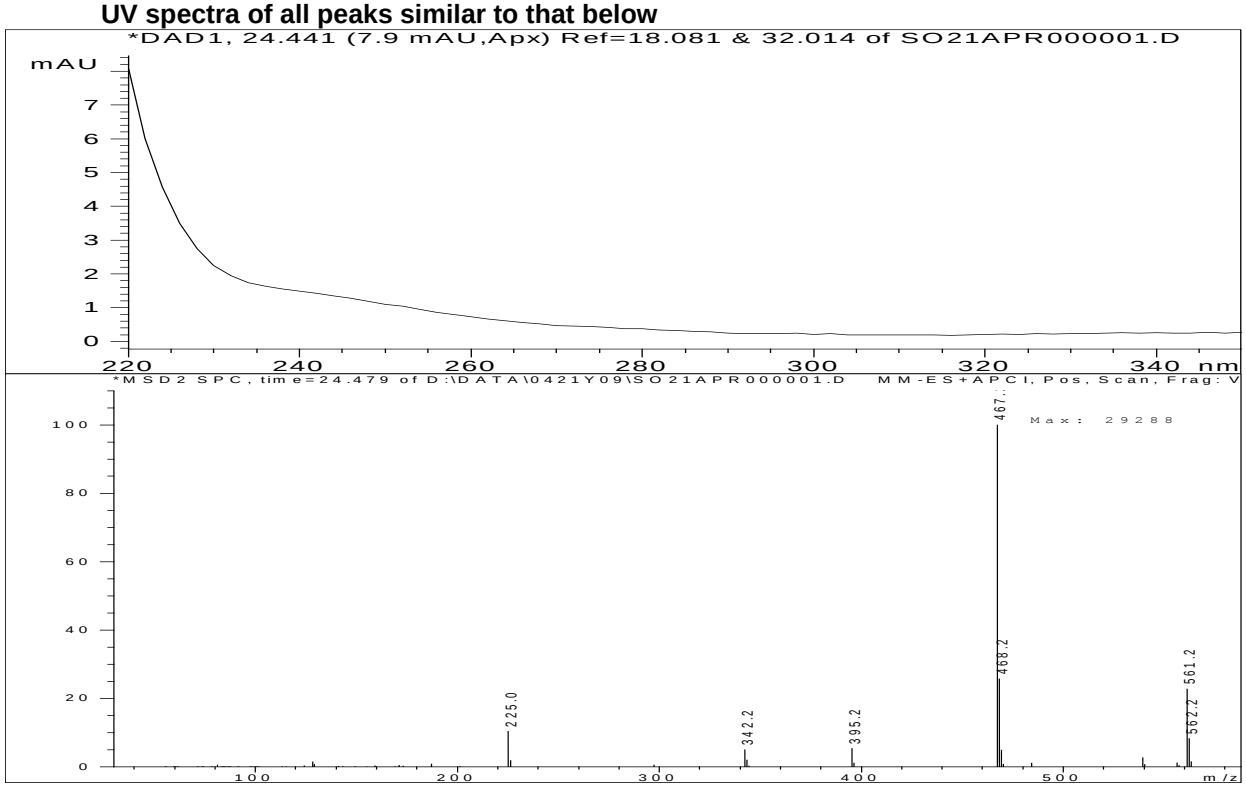


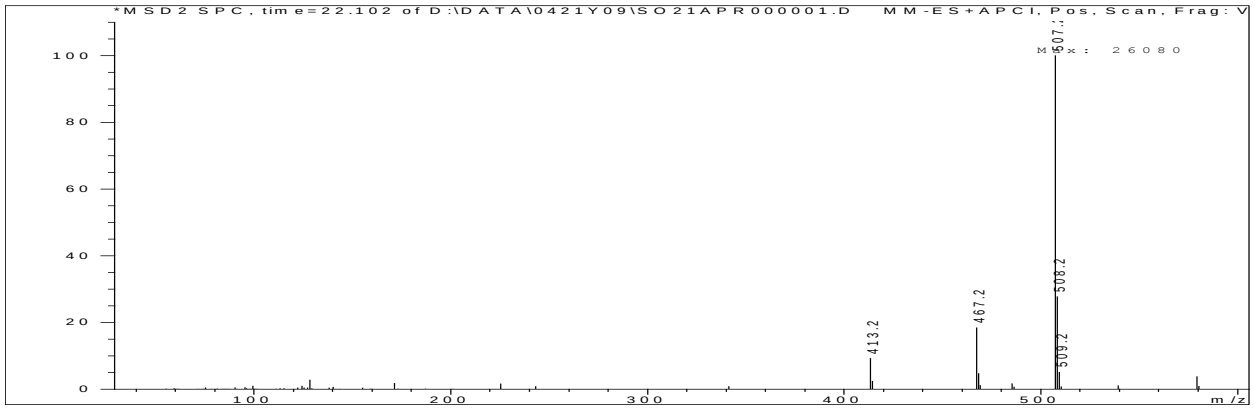
OMNIRAD CI250 LC-MS Chromatogram



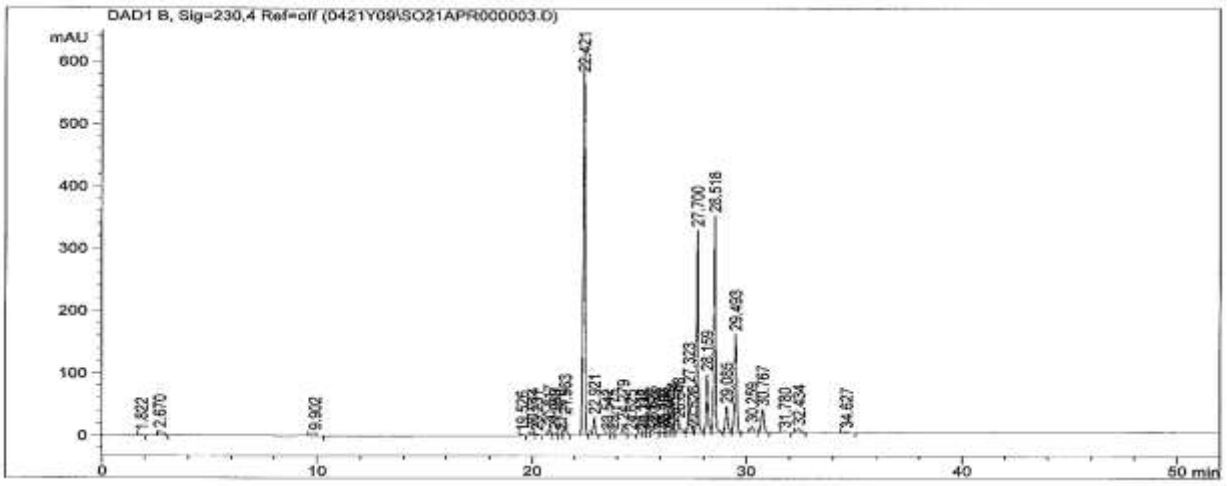
OMNIRAD CI250

UV spectra of all peaks similar to that below

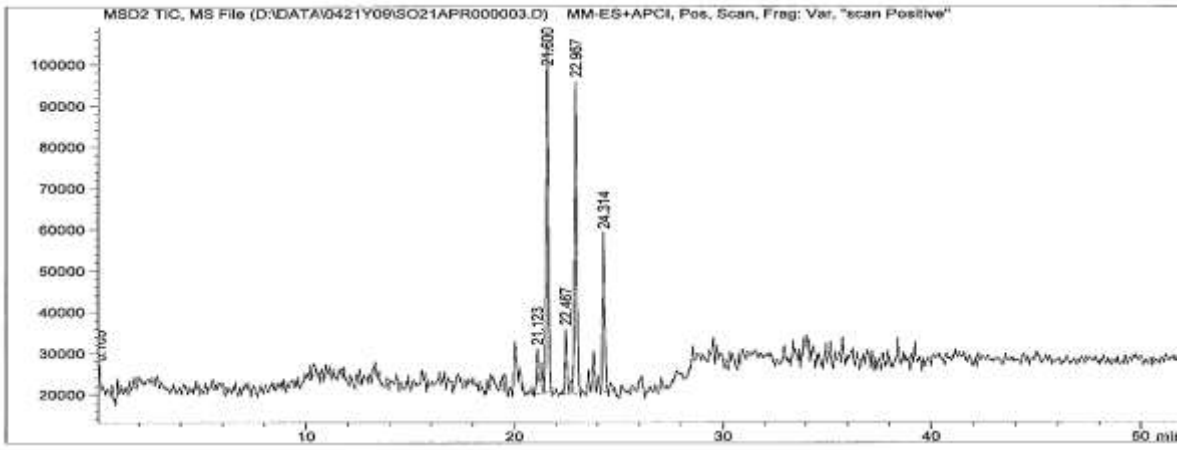




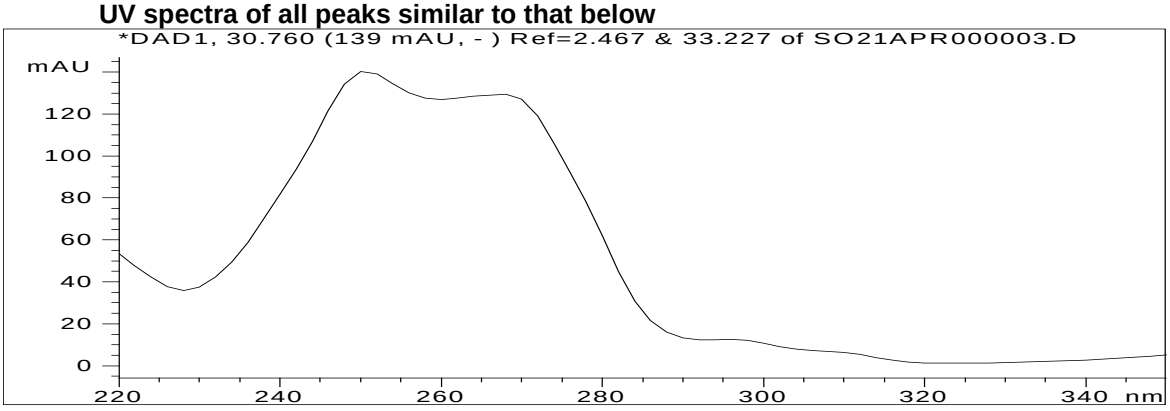
OMNIPOL TX LC-UV chromatogram 230 nm

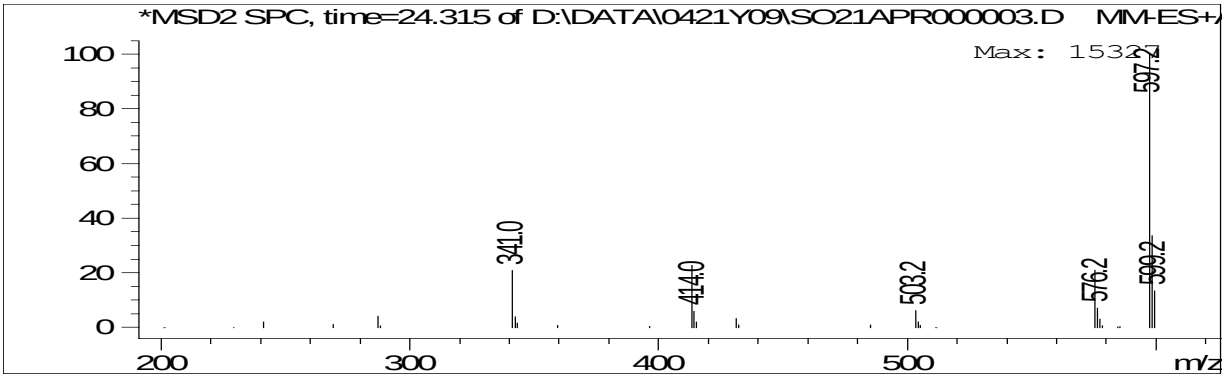


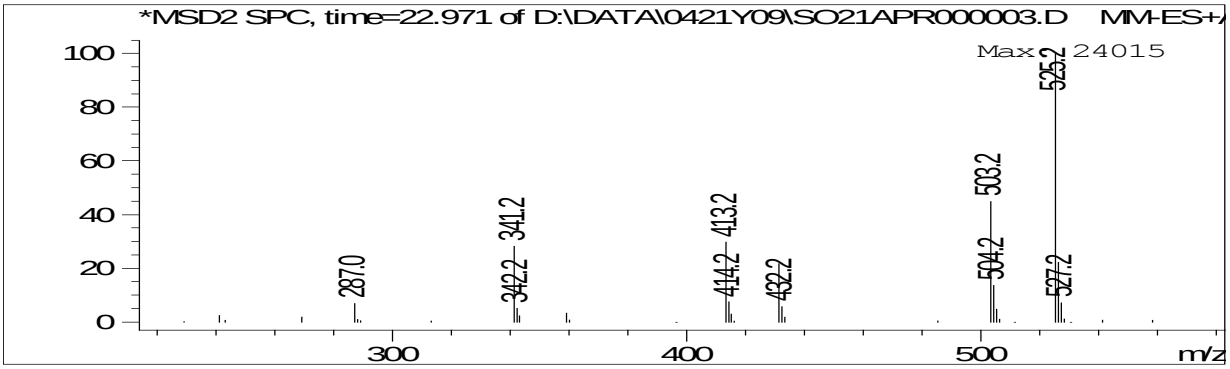
OMNIPOL TX LC-MS chromatogram

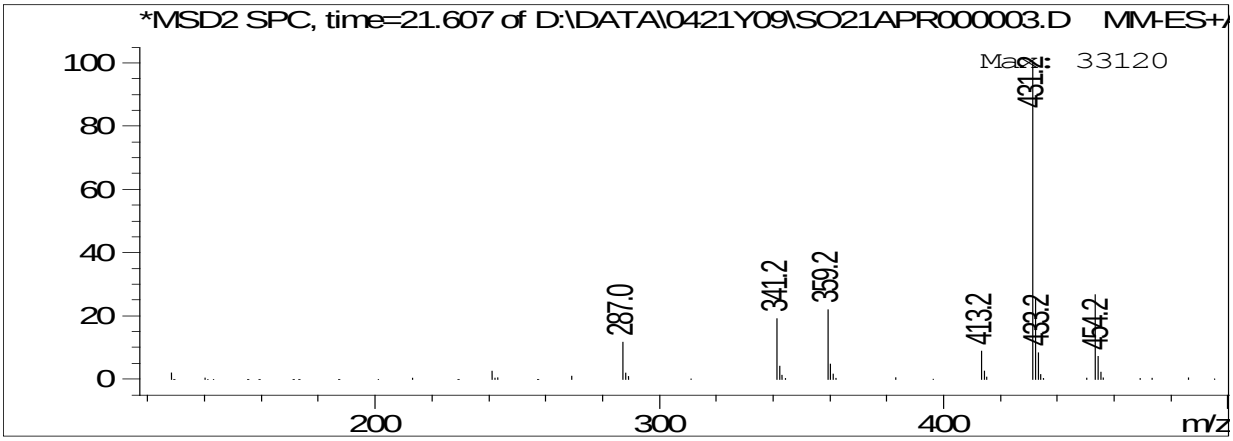


OMNIPOL TX
UV spectra of all peaks similar to that below

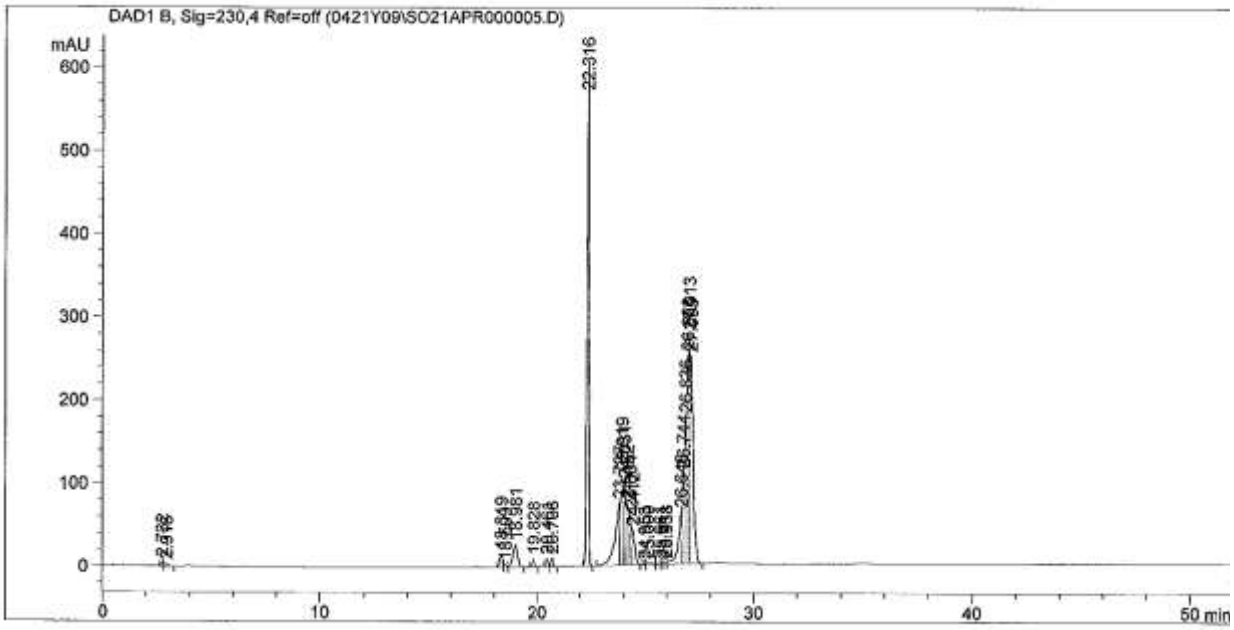



*MSD2 SPC, time=24.315 of D:\DATA\0421Y09\SO21APR000003.D MM-ES+A
Max: 1532
597.2
341.0
414.0
503.2
576.2
599.2
100
80
60
40
20
0
200
300
400
500
m/z

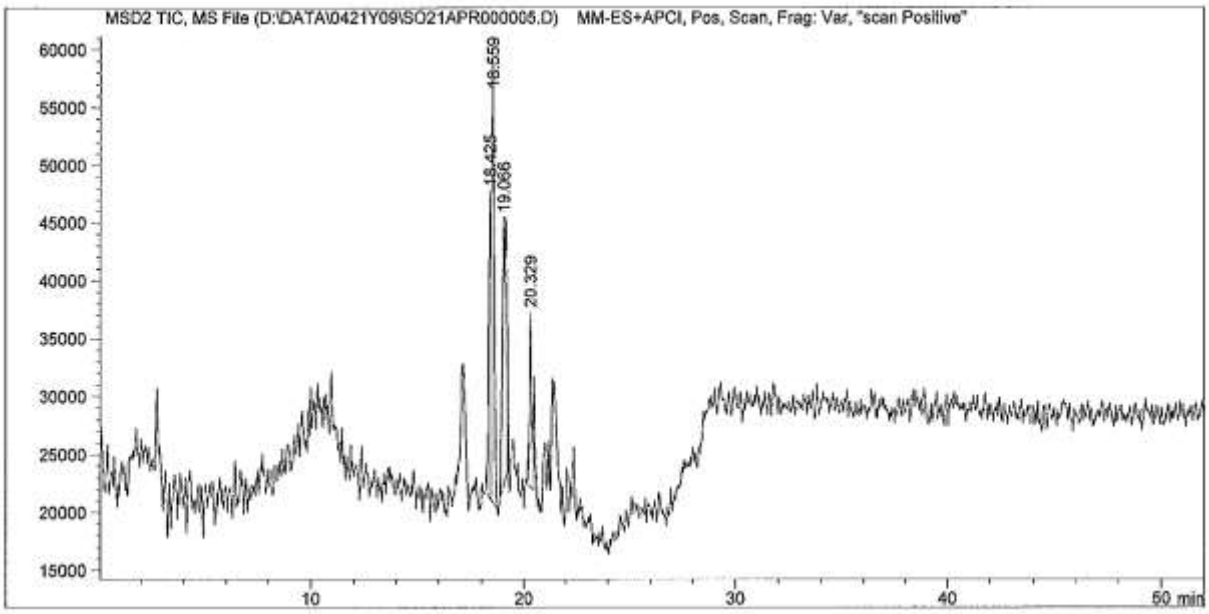

*MSD2 SPC, time=22.971 of D:\DATA\0421Y09\SO21APR000003.D MM-ES+A
Max: 24015
525.2
503.2
341.2
413.2
287.0
342.2
414.2
432.2
504.2
527.2
100
80
60
40
20
0
300
400
500
m/z


*MSD2 SPC, time=21.607 of D:\DATA\0421Y09\SO21APR000003.D MM-ES+A
Max: 33120
431.2
341.2
359.2
287.0
413.2
433.2
454.2
100
80
60
40
20
0
200
300
400
m/z

Genopol BP1 LC-UV chromatogram 230 nm

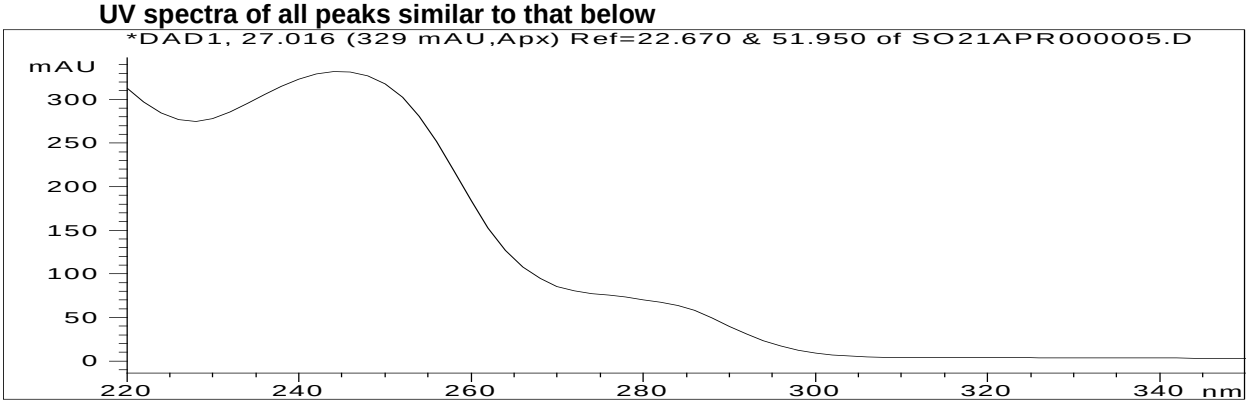


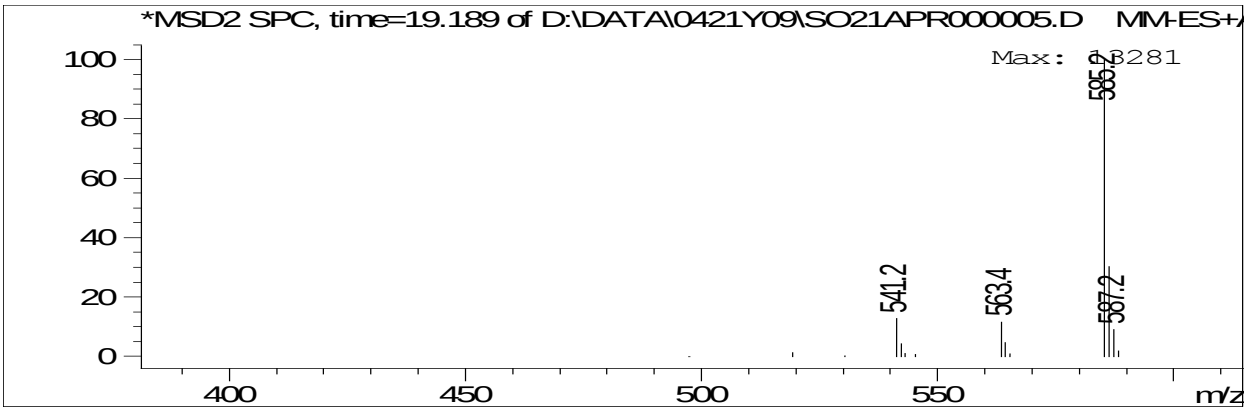
Genopol BP1 LC-MS chromatogram

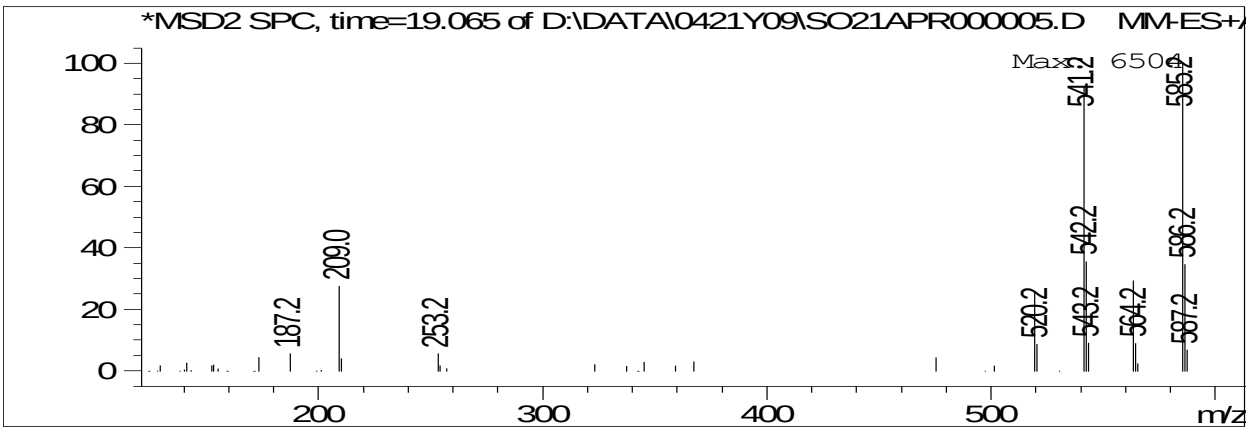


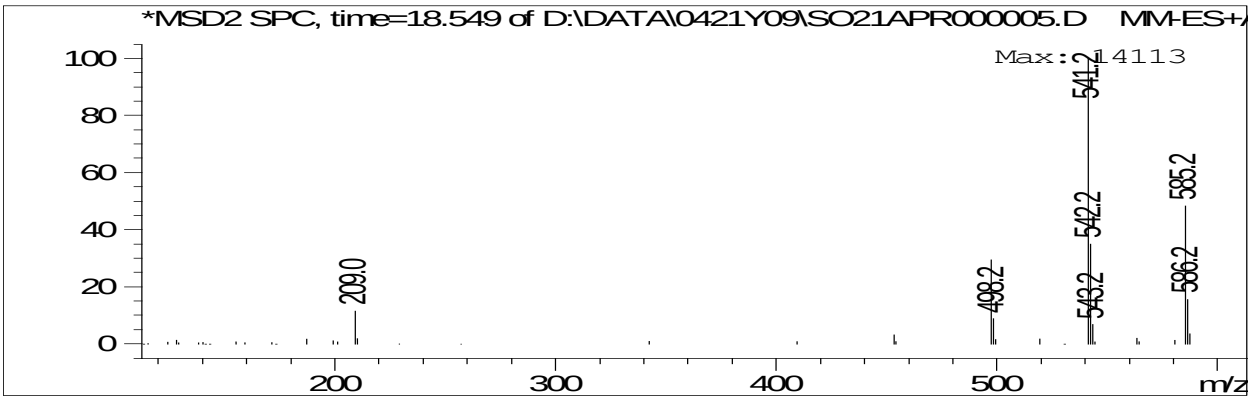
GENOPOL BP1

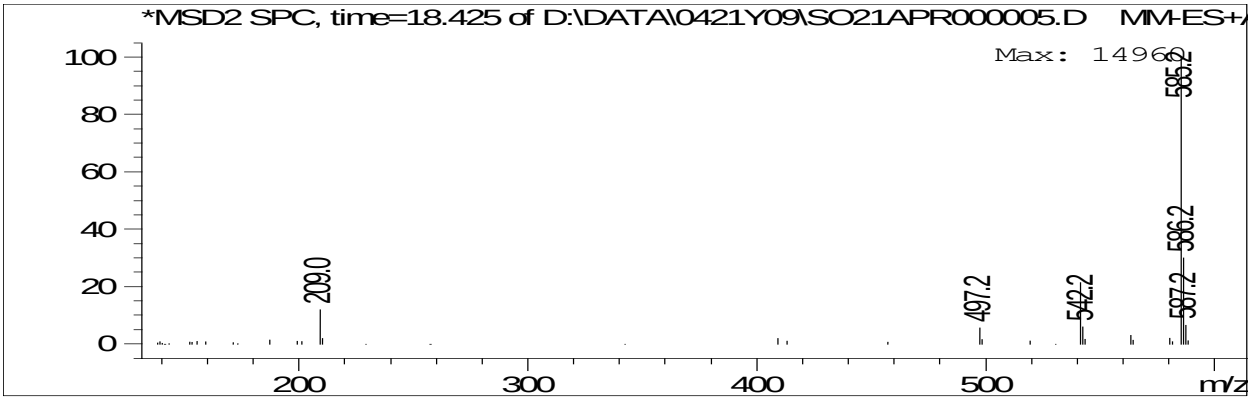
UV spectra of all peaks similar to that below

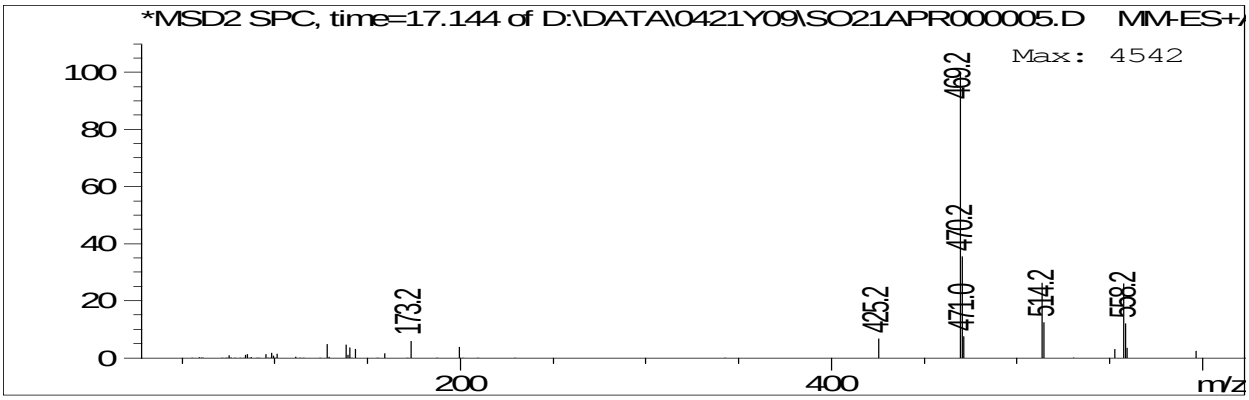




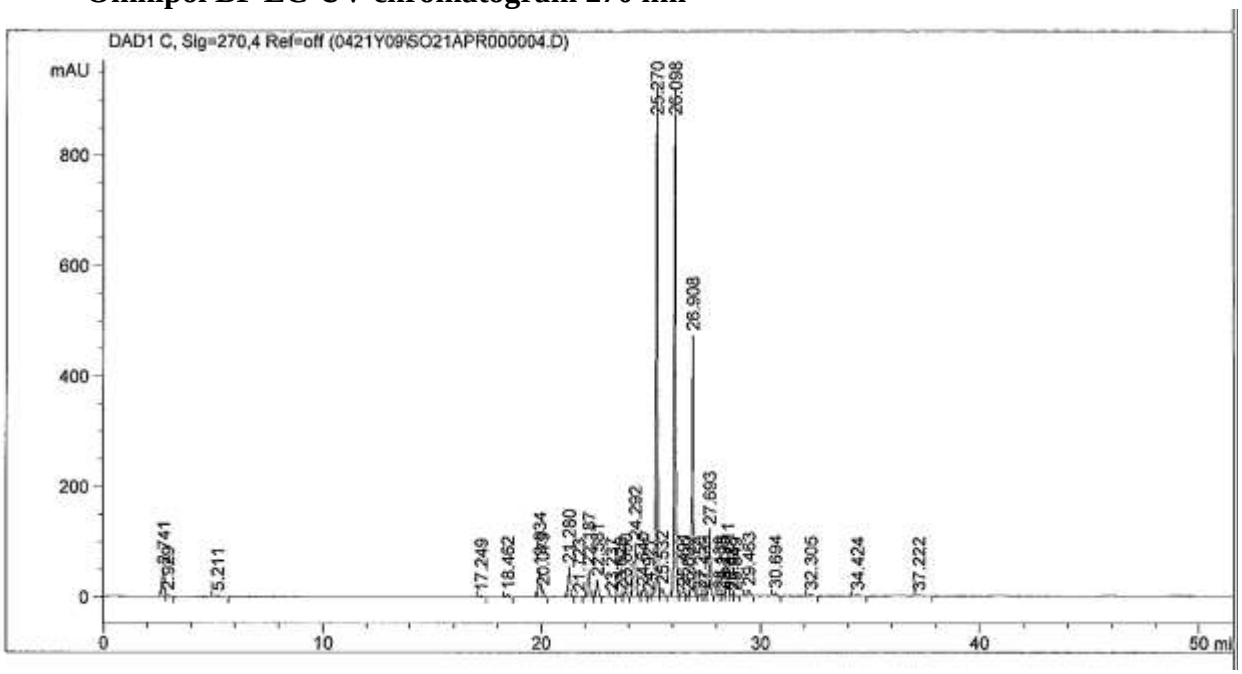




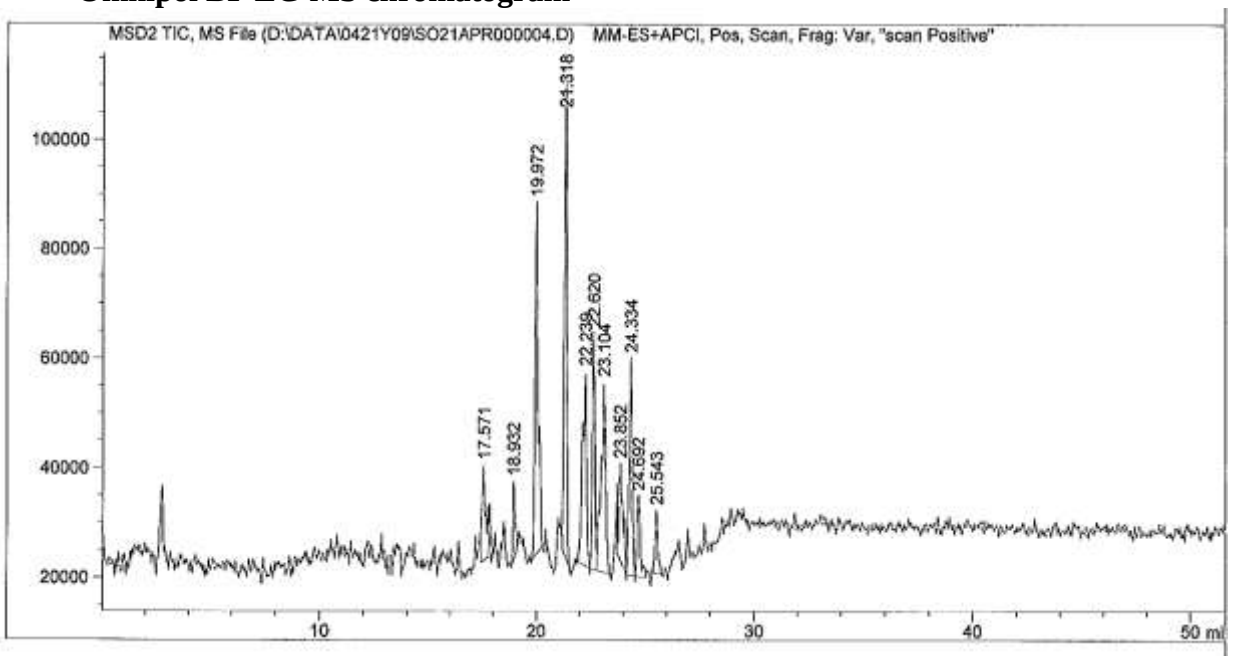

*MSD2 SPC, time=18.425 of D:\DATA\0421Y09\SO21APR000005.D MM-ES+A
Max: 14966
100
80
60
40
20
0
209.0
497.2
542.2
585.2
586.2
587.2
200
300
400
500
m/z


*MSD2 SPC, time=17.144 of D:\DATA\0421Y09\SO21APR000005.D MM-ES+A
Max: 4542
100
80
60
40
20
0
173.2
425.2
469.2
470.2
471.0
514.2
558.2
200
400
m/z

Omnipol BP LC-UV chromatogram 270 nm

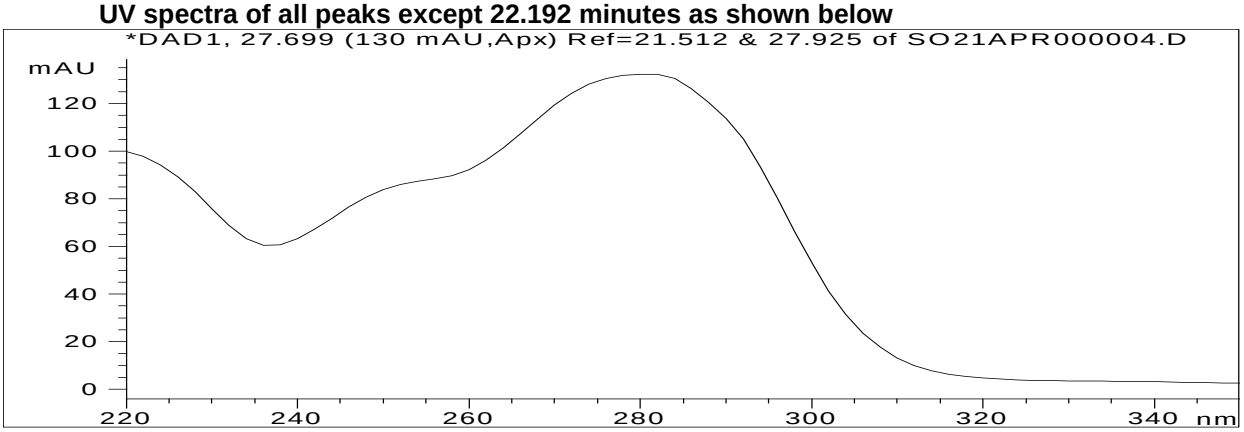


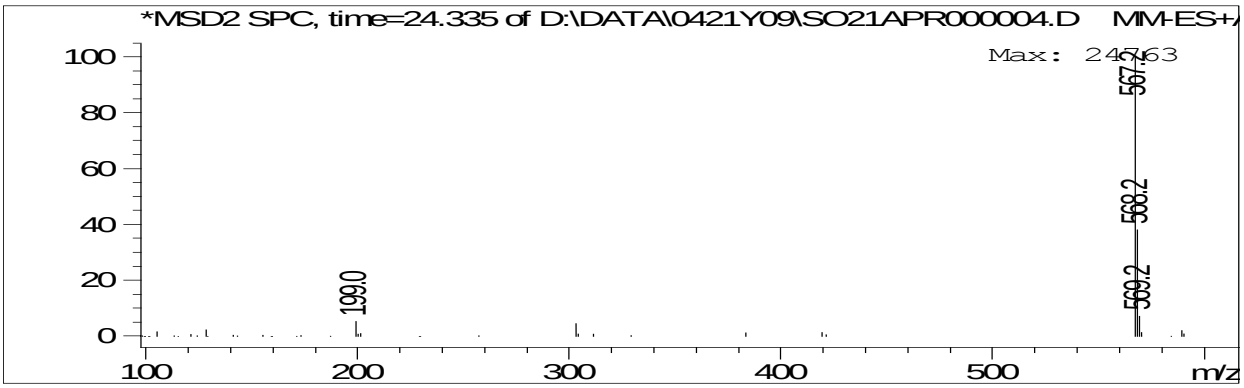
Omnipol BP LC-MS chromatogram

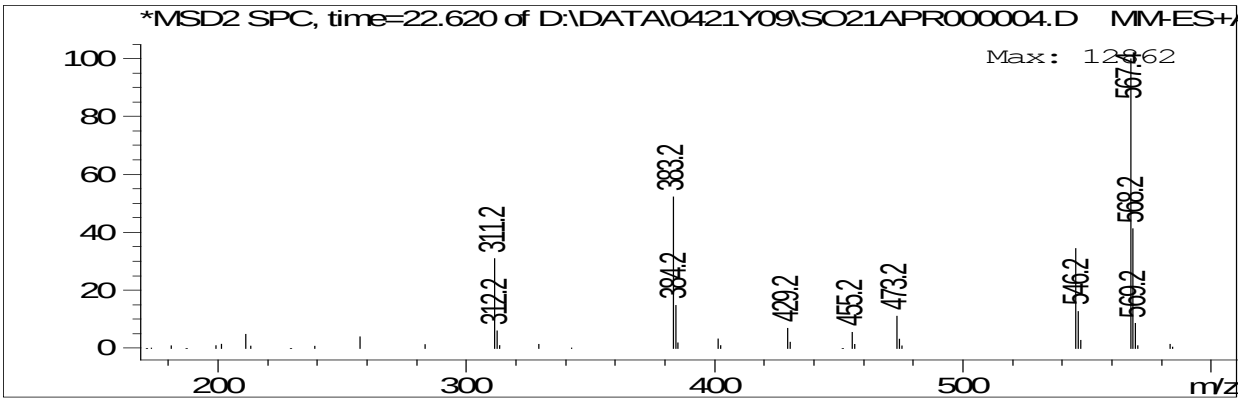


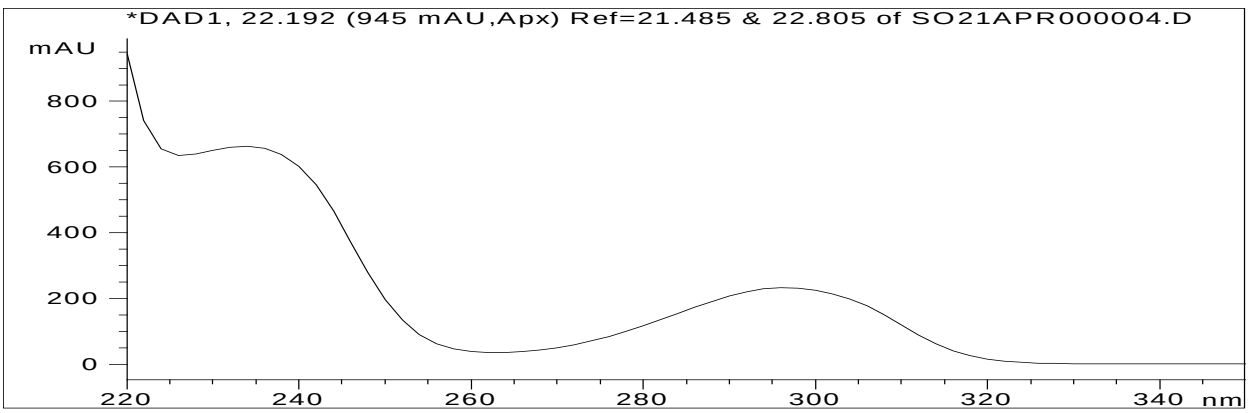
OMNIPOL BP

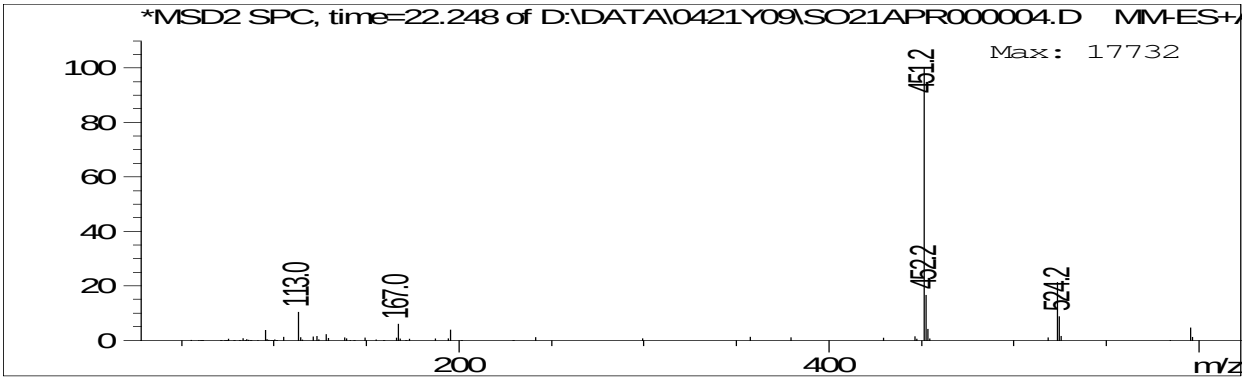
UV spectra of all peaks except 22.192 minutes as shown below

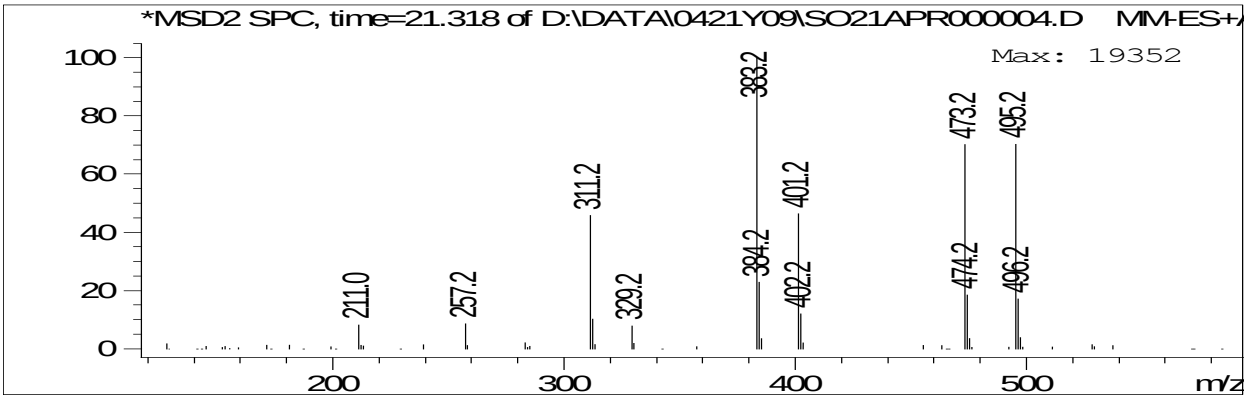


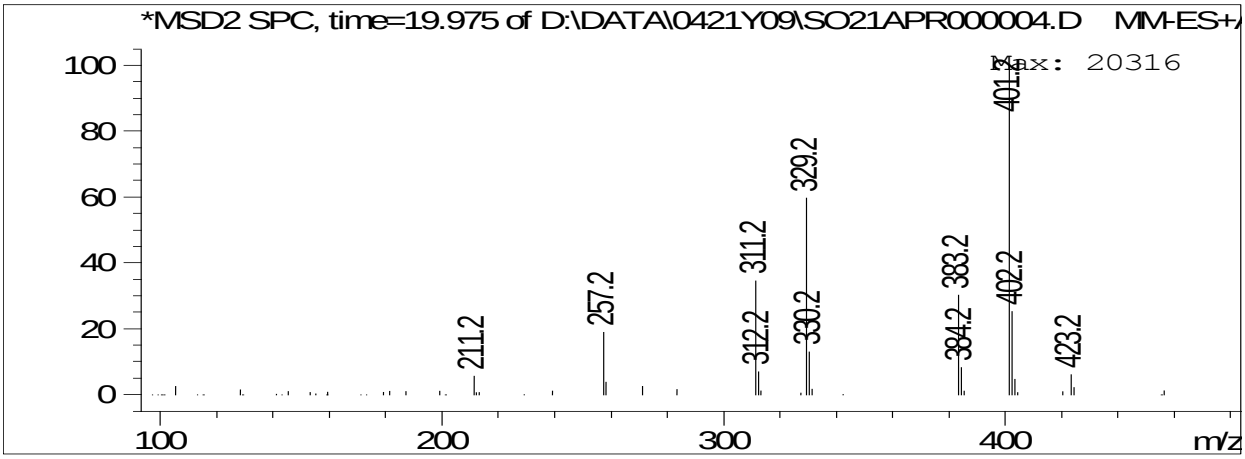




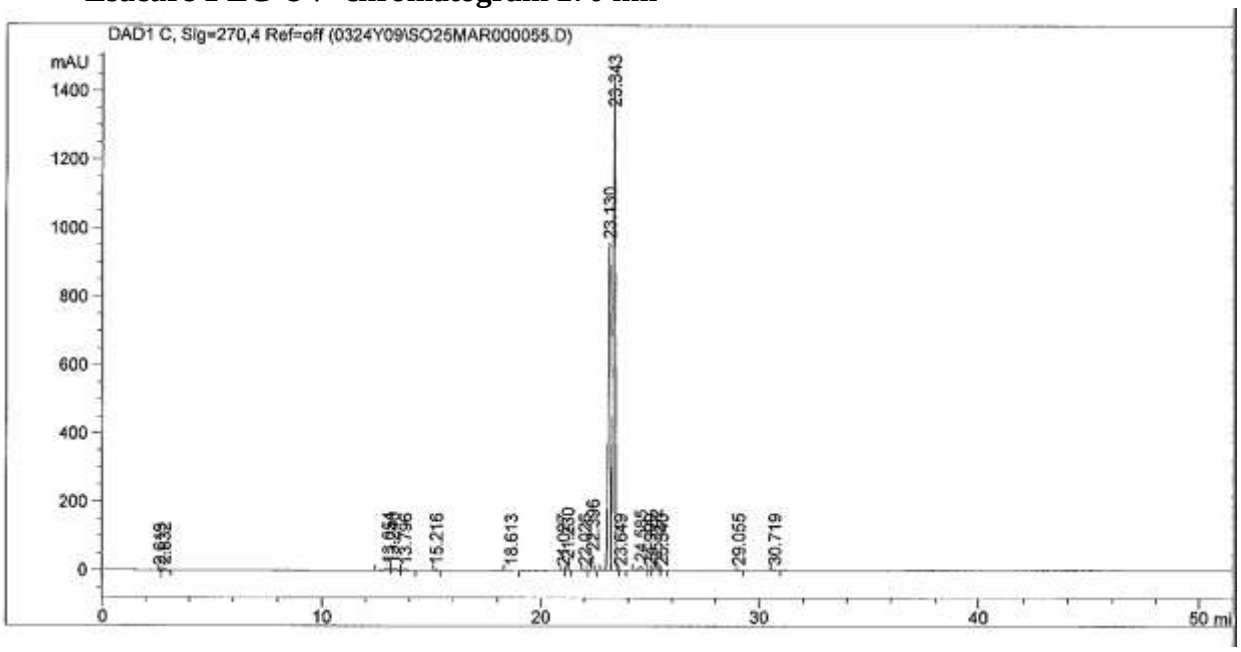



*MSD2 SPC, time=22.248 of D:\DATA\0421Y09\SO21APR000004.D MM-ES+A
Max: 17732
451.2
452.2
113.0
167.0
524.2
m/z

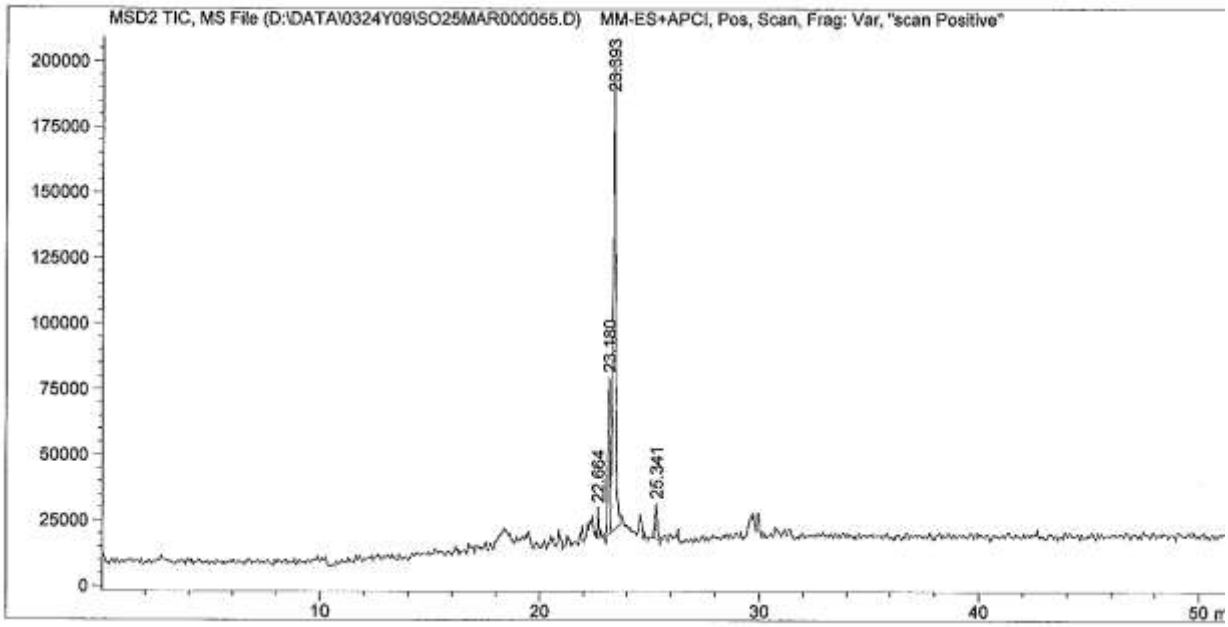

*MSD2 SPC, time=21.318 of D:\DATA\0421Y09\SO21APR000004.D MM-ES+A
Max: 19352
383.2
473.2
495.2
311.2
401.2
384.2
474.2
496.2
211.0
257.2
329.2
402.2
m/z


*MSD2 SPC, time=19.975 of D:\DATA\0421Y09\SO21APR000004.D MM-ES+A
Max: 20316
401.2
329.2
311.2
383.2
257.2
402.2
211.2
312.2
330.2
384.2
423.2
m/z

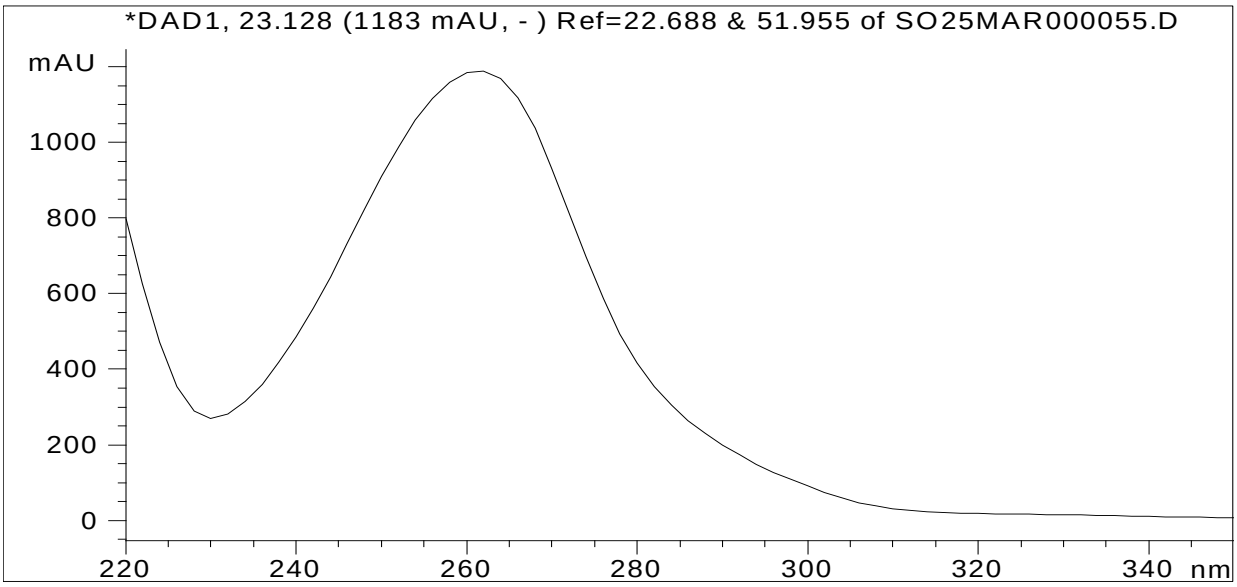
Esacure 1 LC-UV chromatogram 270 nm

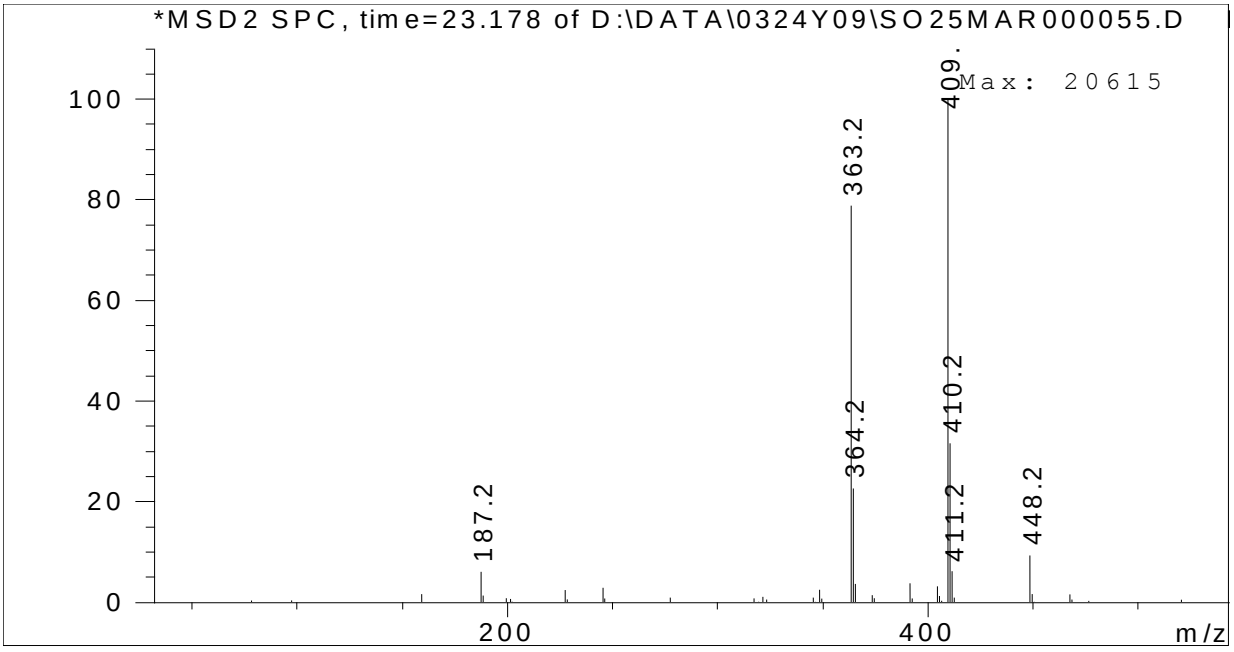


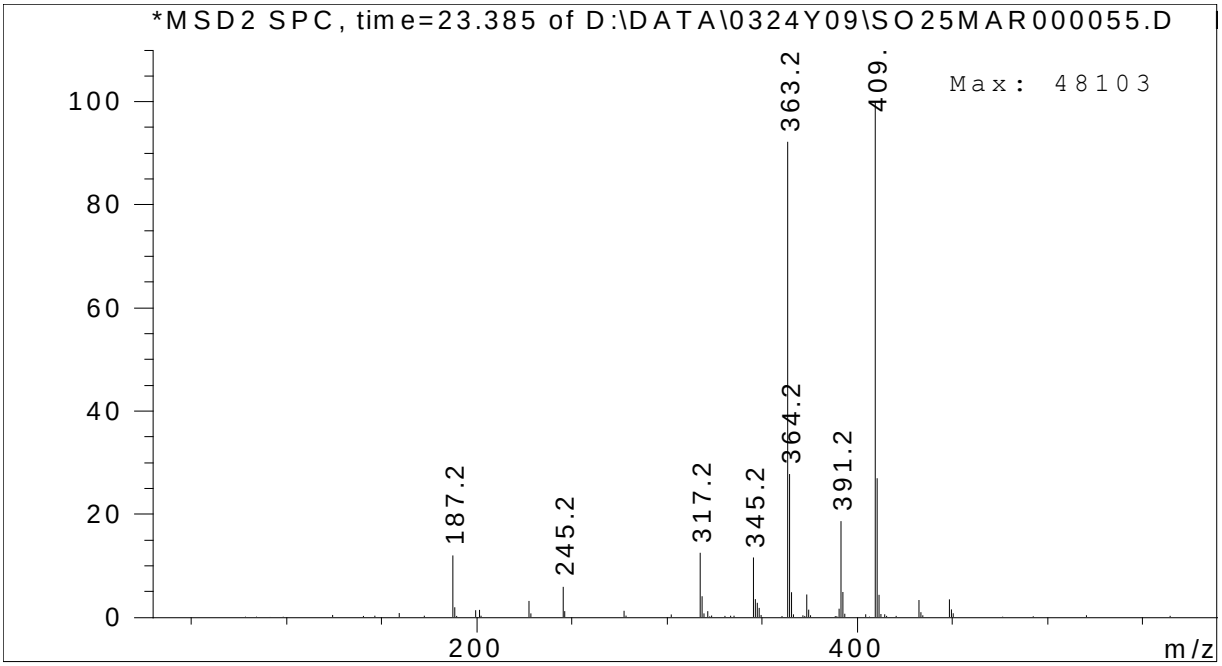
Esacure 1 LC-MS chromatogram



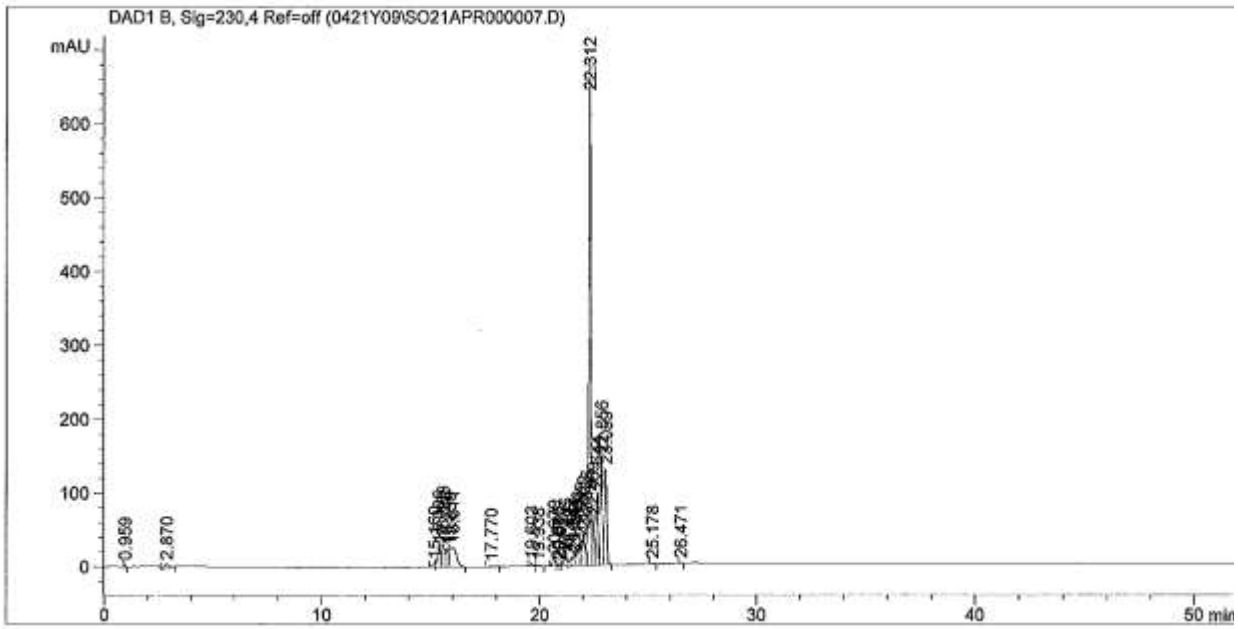
UV spectra of all peaks as shown below


*DAD1, 23.128 (1183 mAU, -) Ref=22.688 & 51.955 of SO25MAR000055.D
mAU
1000
800
600
400
200
0
220
240
260
280
300
320
340
nm

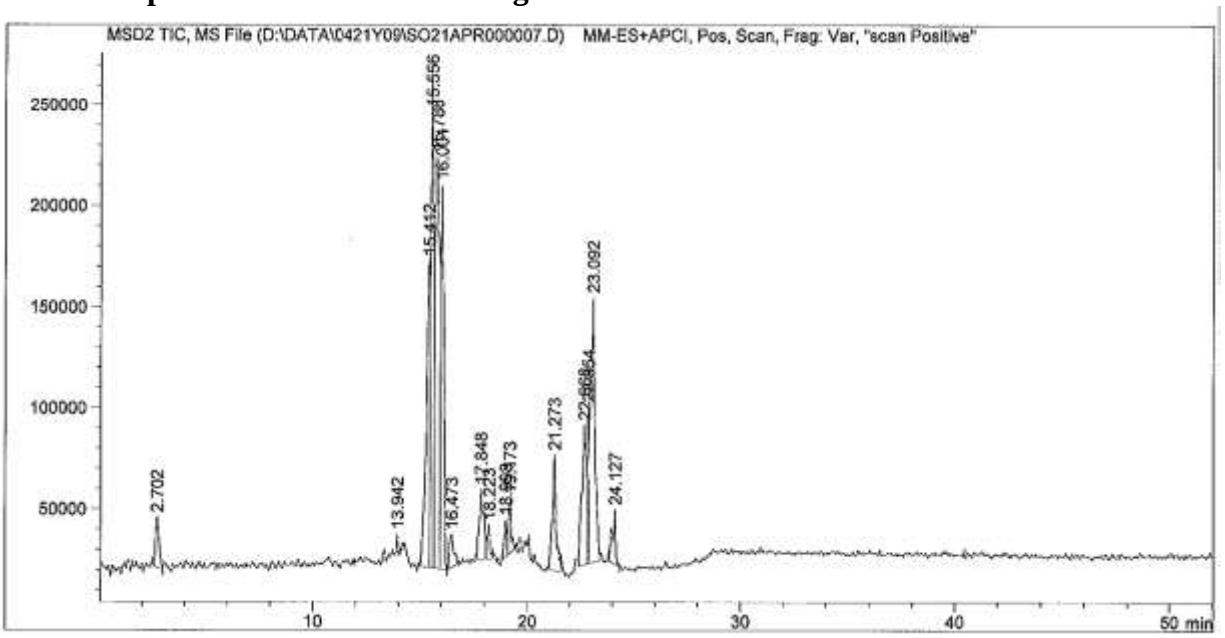

*MSD2 SPC, time=23.178 of D:\DATA\0324Y09\SO25MAR000055.D
Max: 20615
409.
363.2
410.2
364.2
411.2
448.2
187.2
100
80
60
40
20
0
200
400
m/z


*MSD2 SPC, time=23.385 of D:\DATA\0324Y09\SO25MAR000055.D
Max: 48103
100
80
60
40
20
0
200
400
m/z
187.2
245.2
317.2
345.2
363.2
364.2
391.2
409.

Omnipol ASA LC-UV chromatogram 230 nm

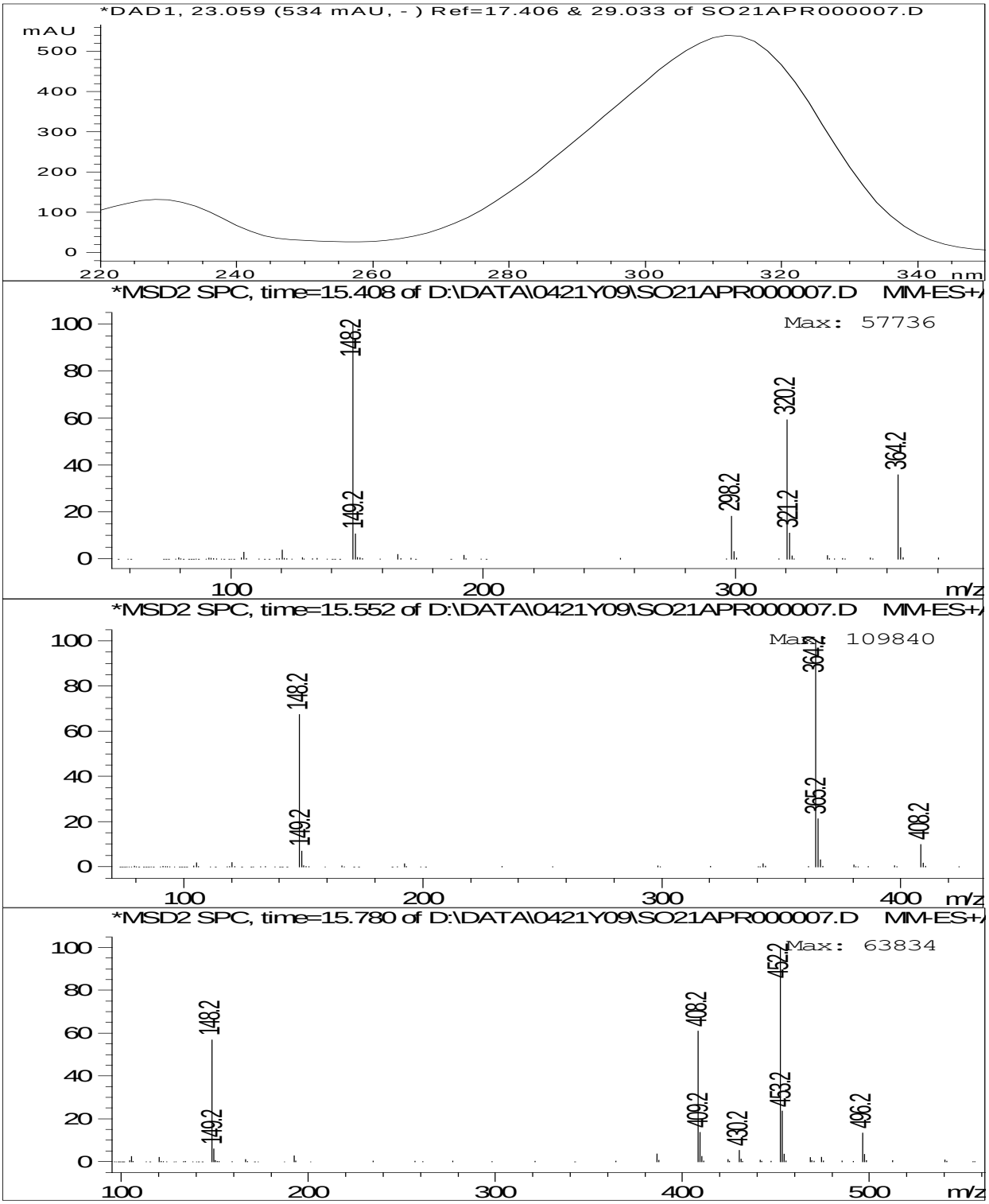


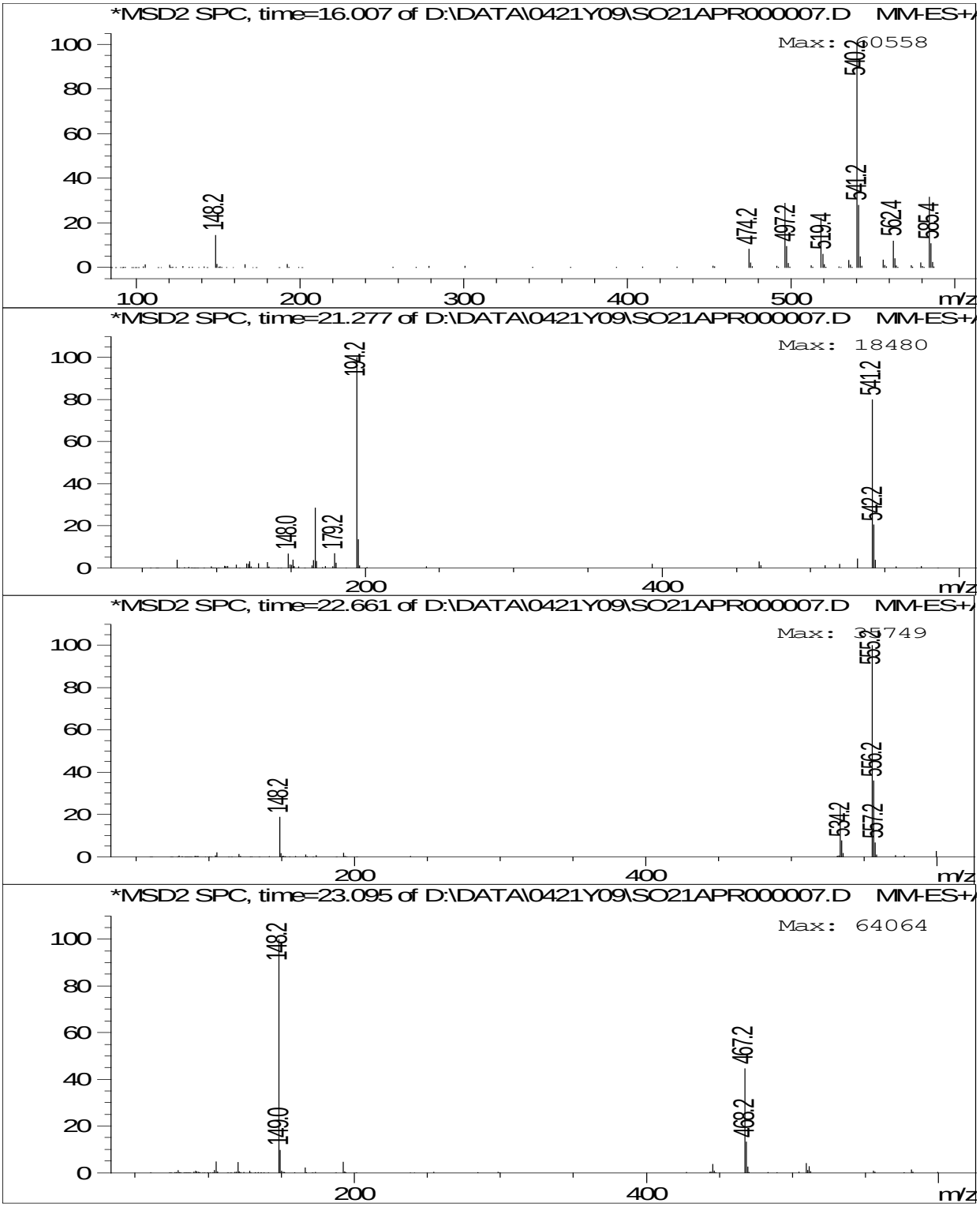
Omnipol ASA LC-MS chromatogram



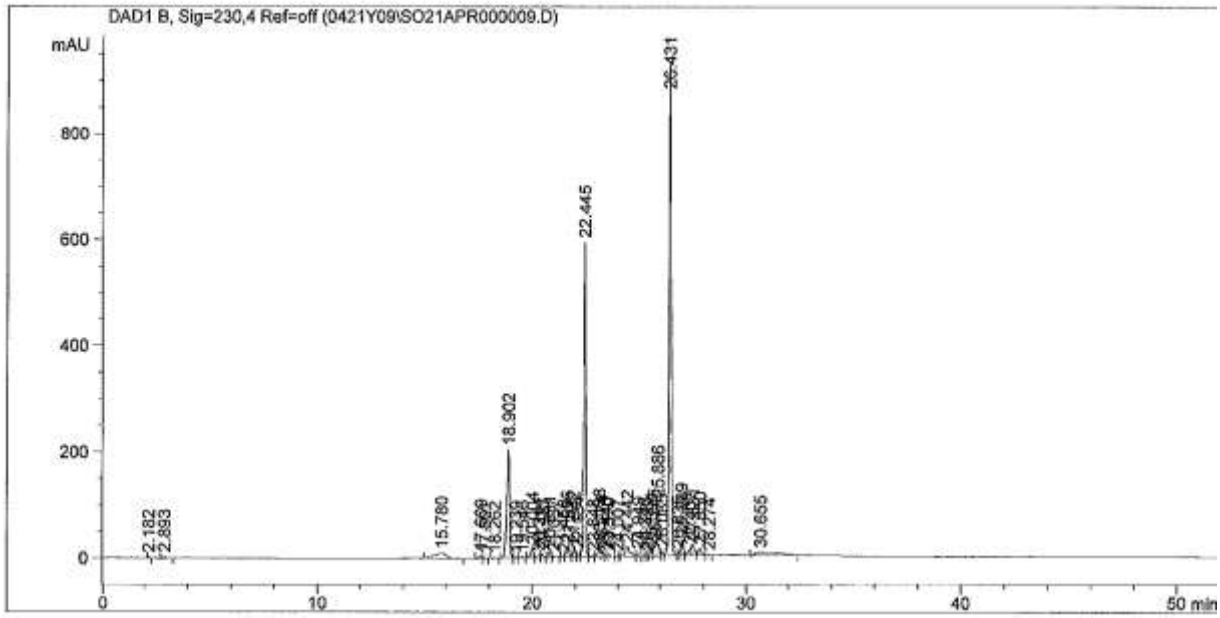
OMNIPOL ASA

ALL PEAKS HAVE SIMILAR UV SPECTRUM AS BELOW

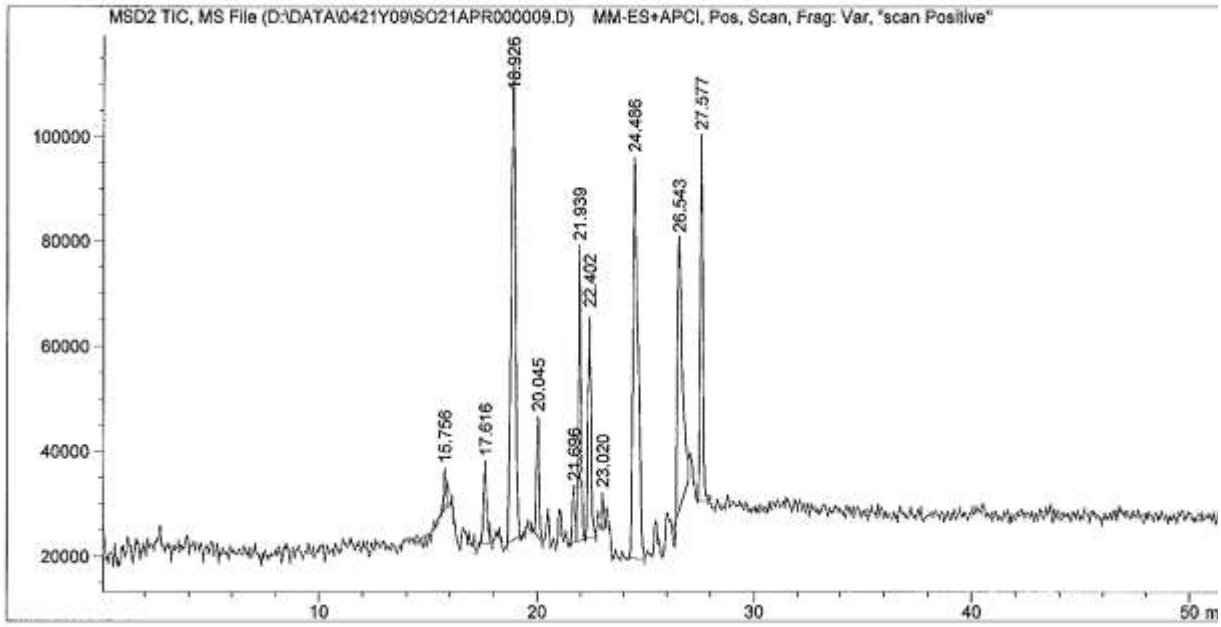



*MSD2 SPC, time=16.007 of D:\DATA\0421Y09\SO21APR000007.D MM-ES+A
Max: 60558
148.2
474.2
497.2
519.4
540.2
541.2
562.4
585.4
m/z
*MSD2 SPC, time=21.277 of D:\DATA\0421Y09\SO21APR000007.D MM-ES+A
Max: 18480
148.0
179.2
194.2
541.2
542.2
m/z
*MSD2 SPC, time=22.661 of D:\DATA\0421Y09\SO21APR000007.D MM-ES+A
Max: 35749
148.2
534.2
555.2
556.2
557.2
m/z
*MSD2 SPC, time=23.095 of D:\DATA\0421Y09\SO21APR000007.D MM-ES+A
Max: 64064
148.2
149.0
467.2
468.2
m/z

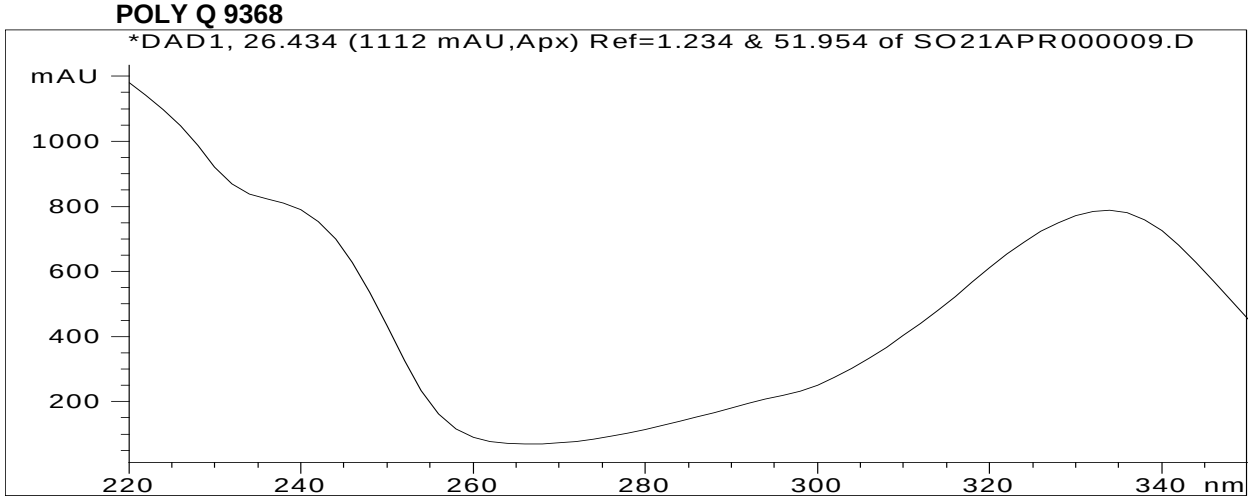
LC-UV 230 nm chromatogram PolyQ 9368

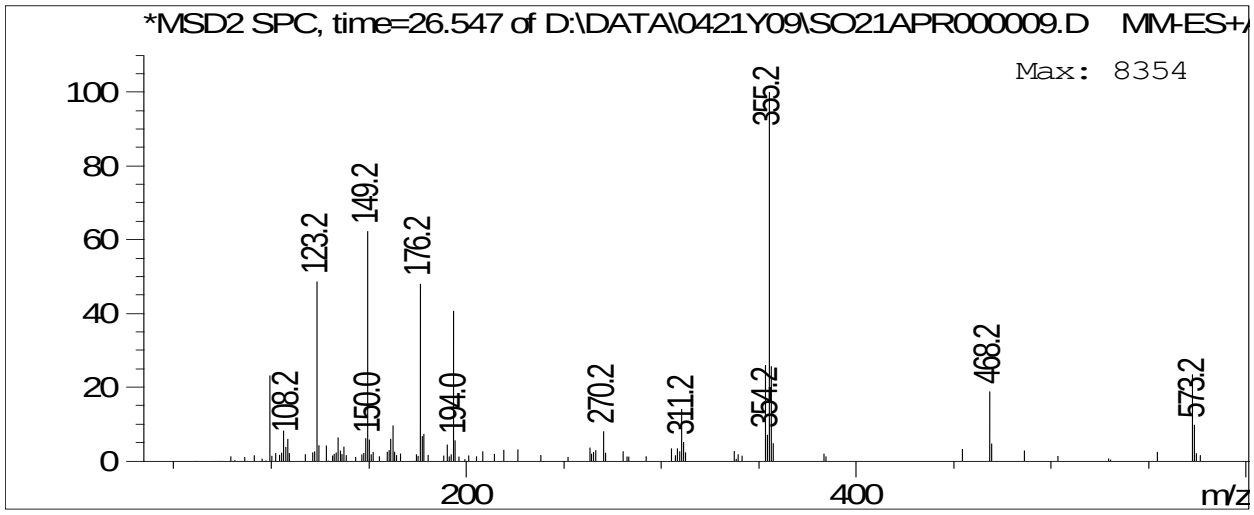


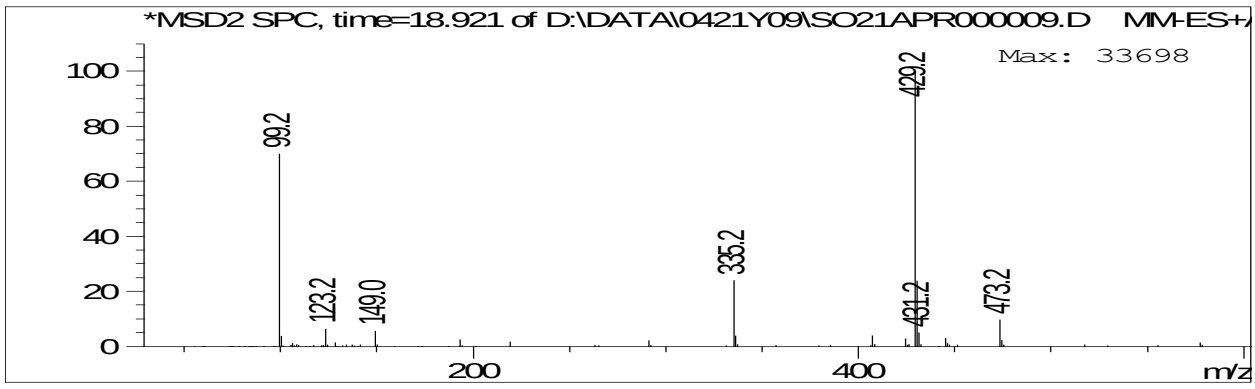
LC-MS chromatogram PolyQ 9368

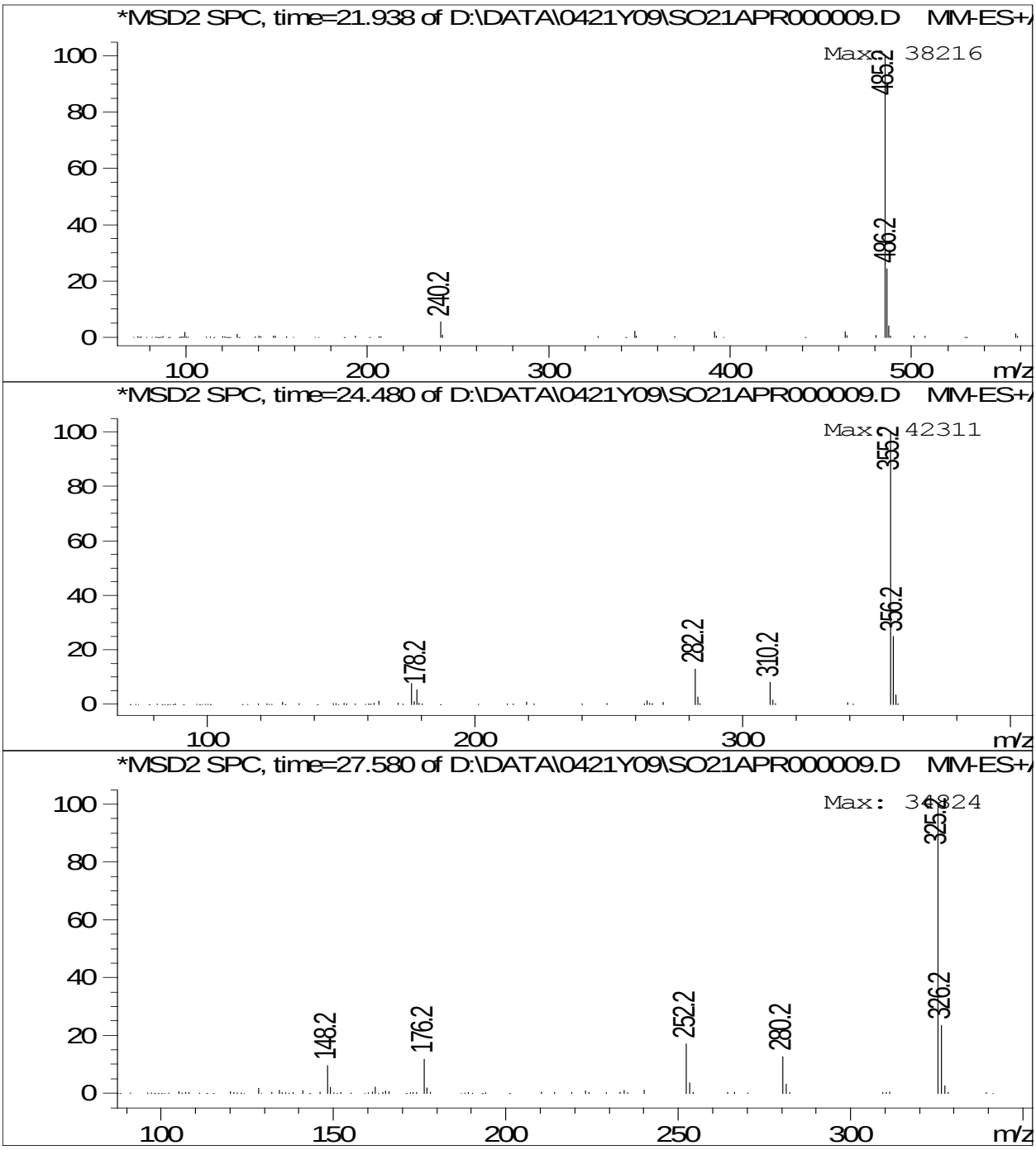


POLY Q 9368

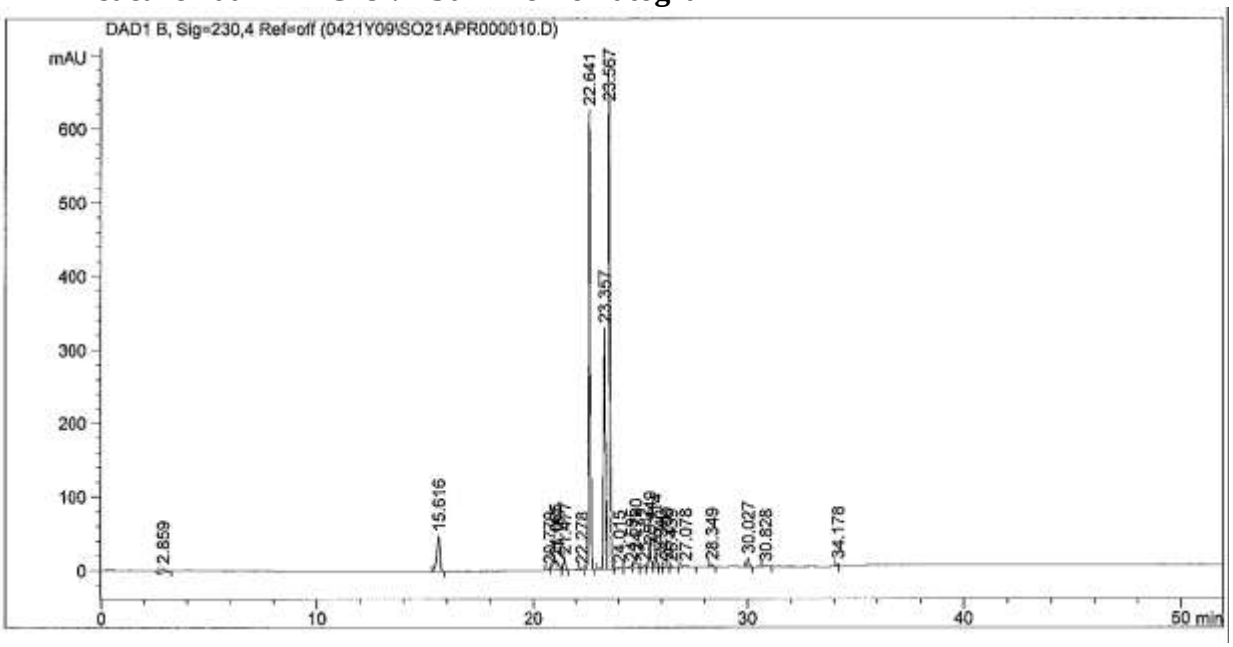

*DAD1, 26.434 (1112 mAU,Apx) Ref=1.234 & 51.954 of SO21APR000009.D
mAU
1000
800
600
400
200
220
240
260
280
300
320
340 nm


*MSD2 SPC, time=26.547 of D:\DATA\0421Y09\SO21APR000009.D MM-ES+
Max: 8354
355.2
149.2
123.2
176.2
108.2
150.0
194.0
270.2
311.2
354.2
468.2
573.2
100
80
60
40
20
0
200
400
m/z

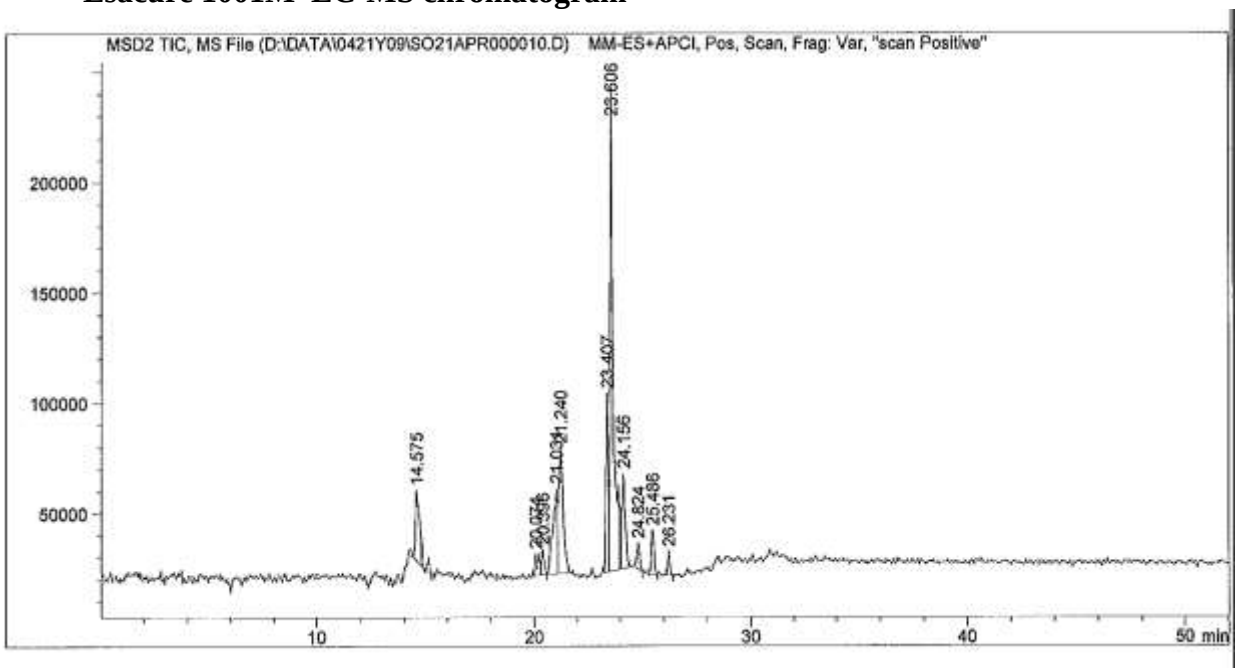

*MSD2 SPC, time=18.921 of D:\DATA\0421Y09\SO21APR000009.D MM-ES+
Max: 33698
429.2
99.2
335.2
123.2
149.0
431.2
473.2
100
80
60
40
20
0
200
400
m/z


*MSD2 SPC, time=21.938 of D:\DATA\0421Y09\SO21APR000009.D MM-ES+A
Max: 38216
485.2
486.2
240.2
*MSD2 SPC, time=24.480 of D:\DATA\0421Y09\SO21APR000009.D MM-ES+A
Max: 42311
355.2
356.2
178.2
282.2
310.2
*MSD2 SPC, time=27.580 of D:\DATA\0421Y09\SO21APR000009.D MM-ES+A
Max: 34824
325.2
326.2
148.2
176.2
252.2
280.2
m/z

Esacure 1001M LC-UV 230 nm chromatogram

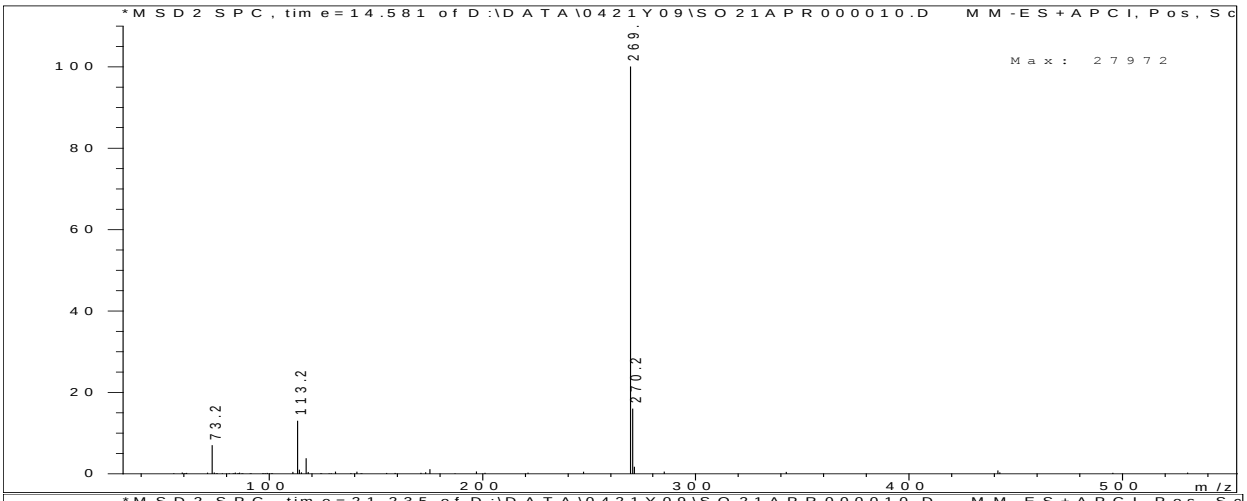


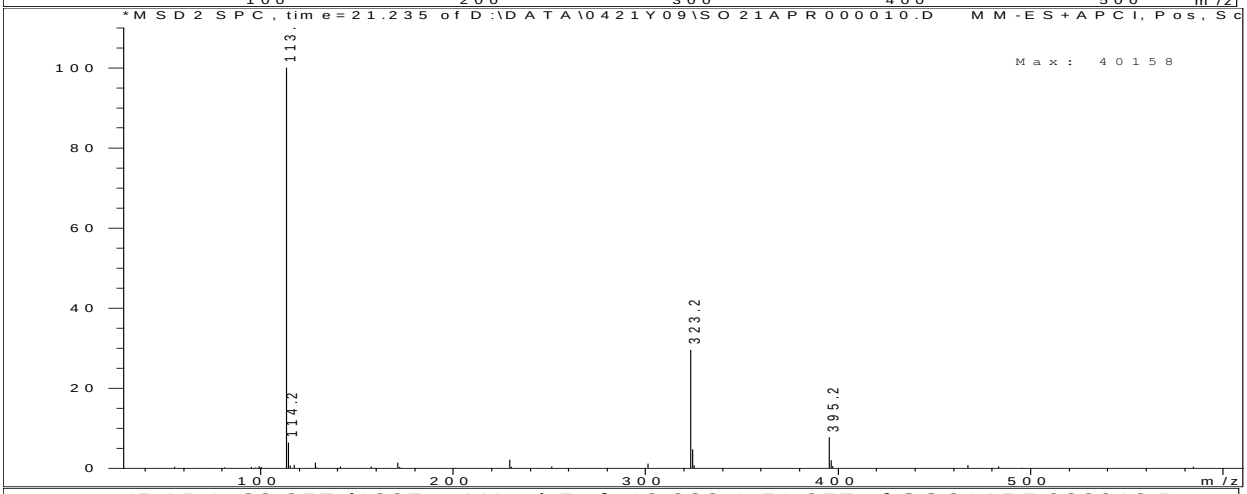
Esacure 1001M LC-MS chromatogram

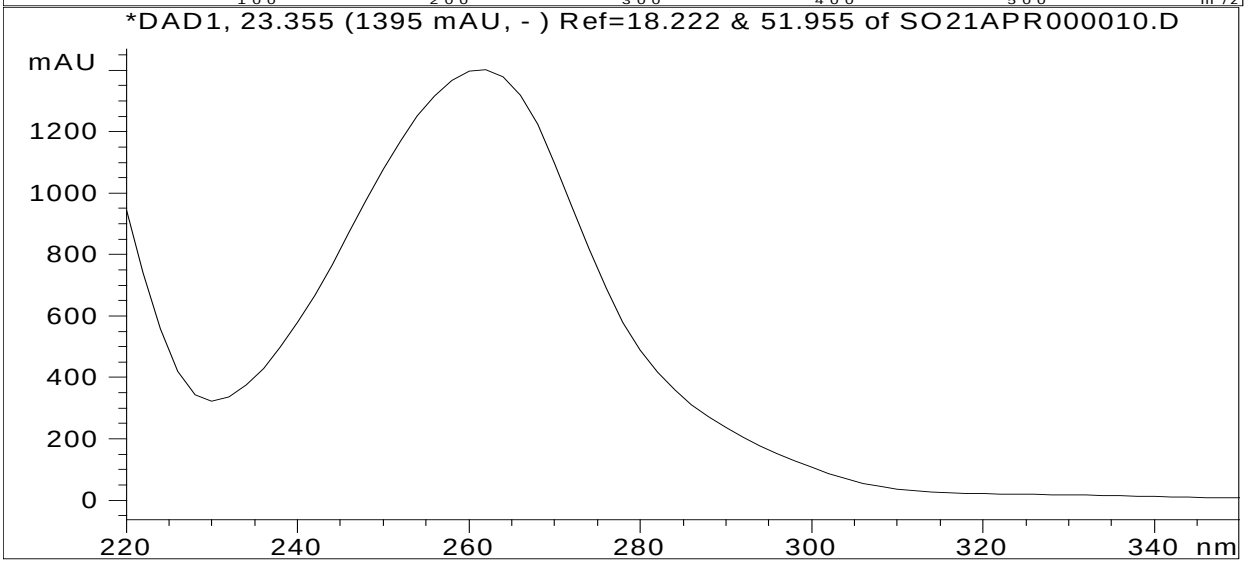


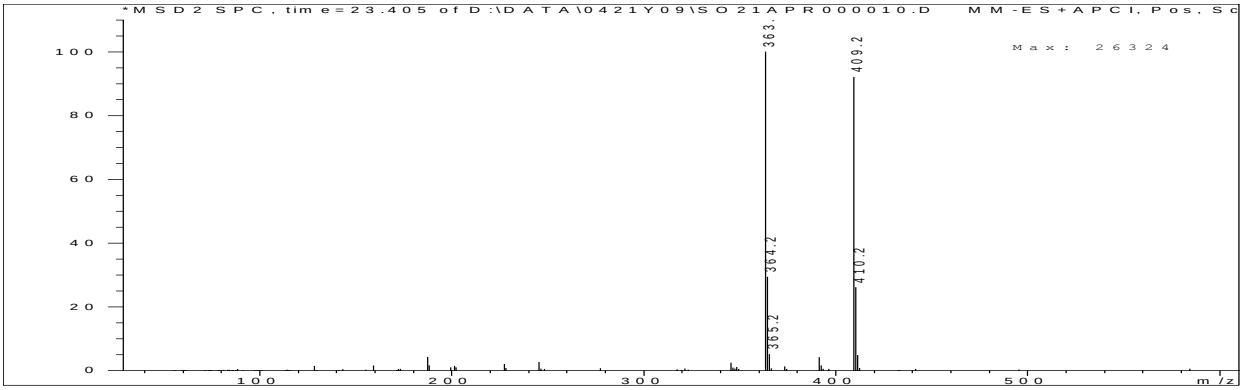
UV spectra the same for all peaks unless indicated otherwise

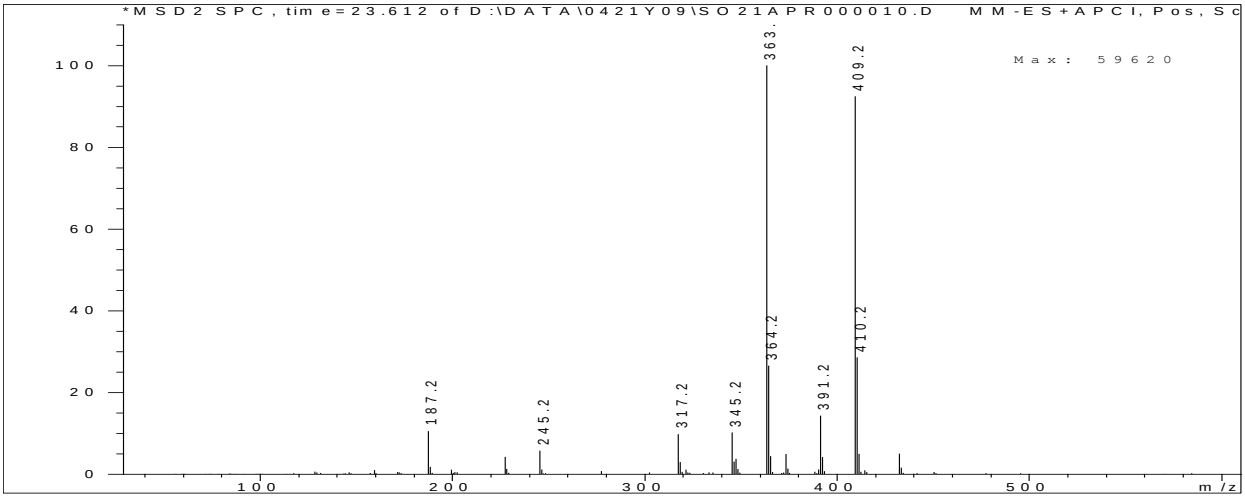
ESACURE 1001M

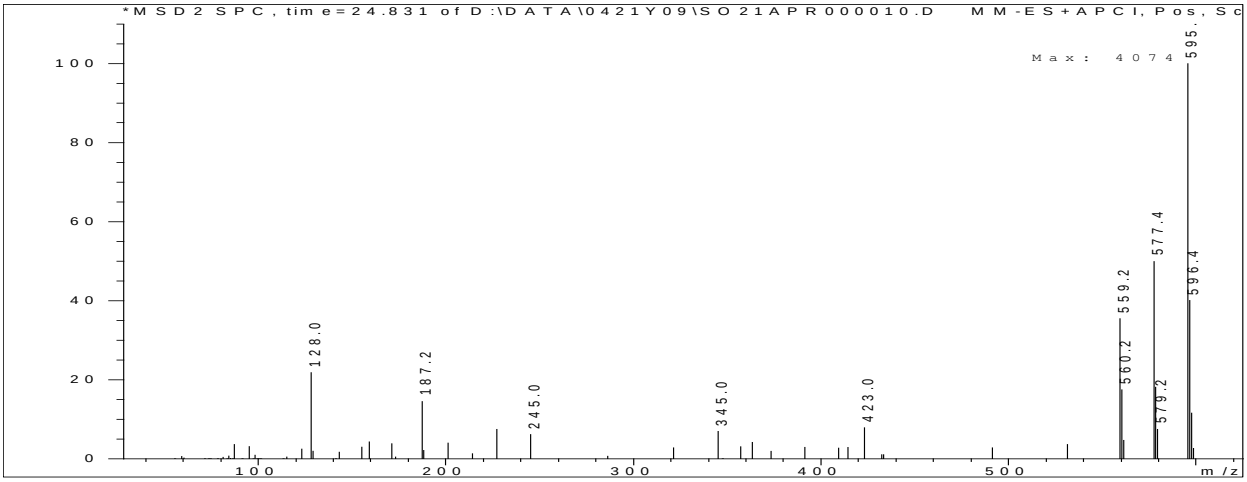


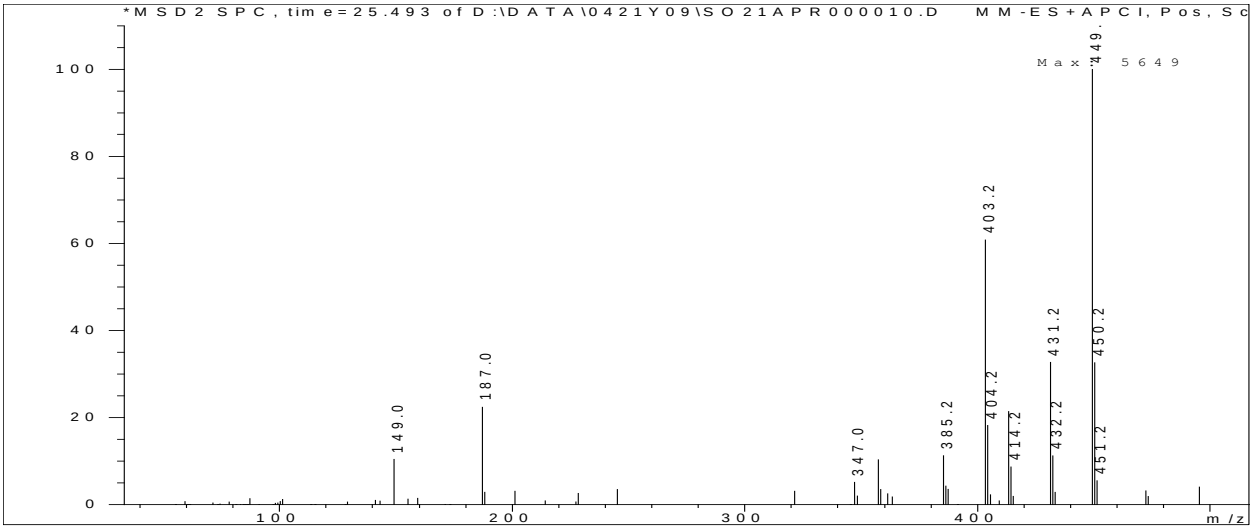




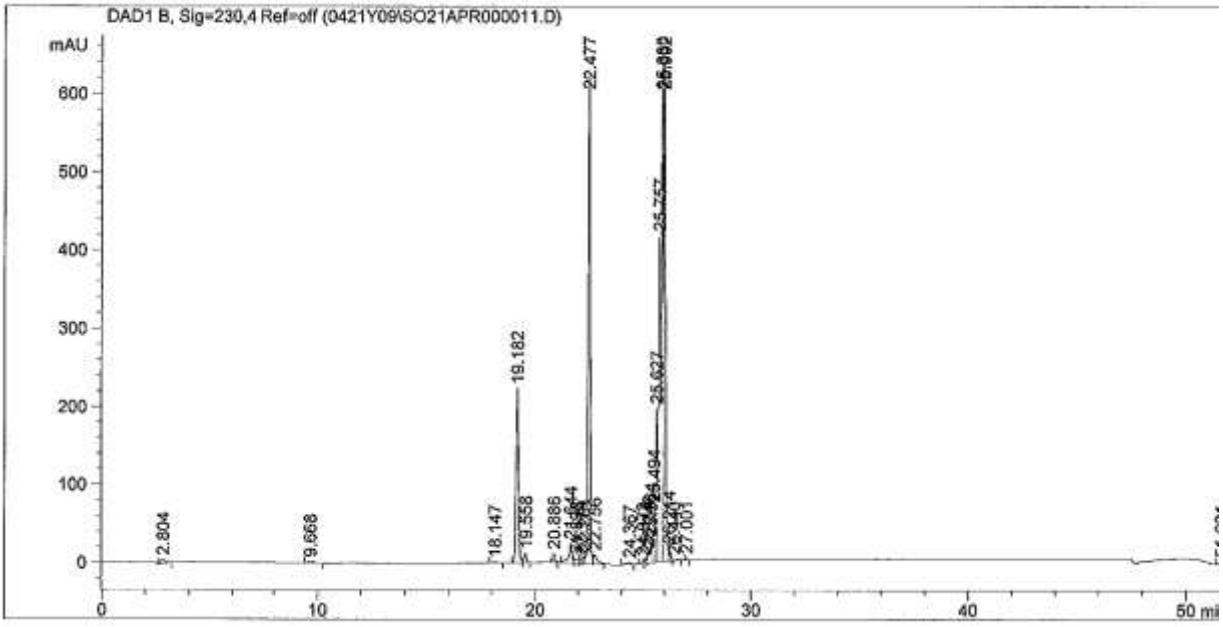

*MSD2 SPC, time=23.405 of D:\DATA\0421Y09\SO21APR000010.D MM-ES+APCI, Pos, Sc
Max: 26324
363.2
409.2
364.2
410.2
365.2
100
80
60
40
20
0
100
200
300
400
500
m/z


*MSD2 SPC, time=23.612 of D:\DATA\0421Y09\SO21APR000010.D MM-ES+APCI, Pos, Sc
Max: 59620
363.2
409.2
364.2
410.2
187.2
245.2
317.2
345.2
391.2
100
80
60
40
20
0
100
200
300
400
500
m/z

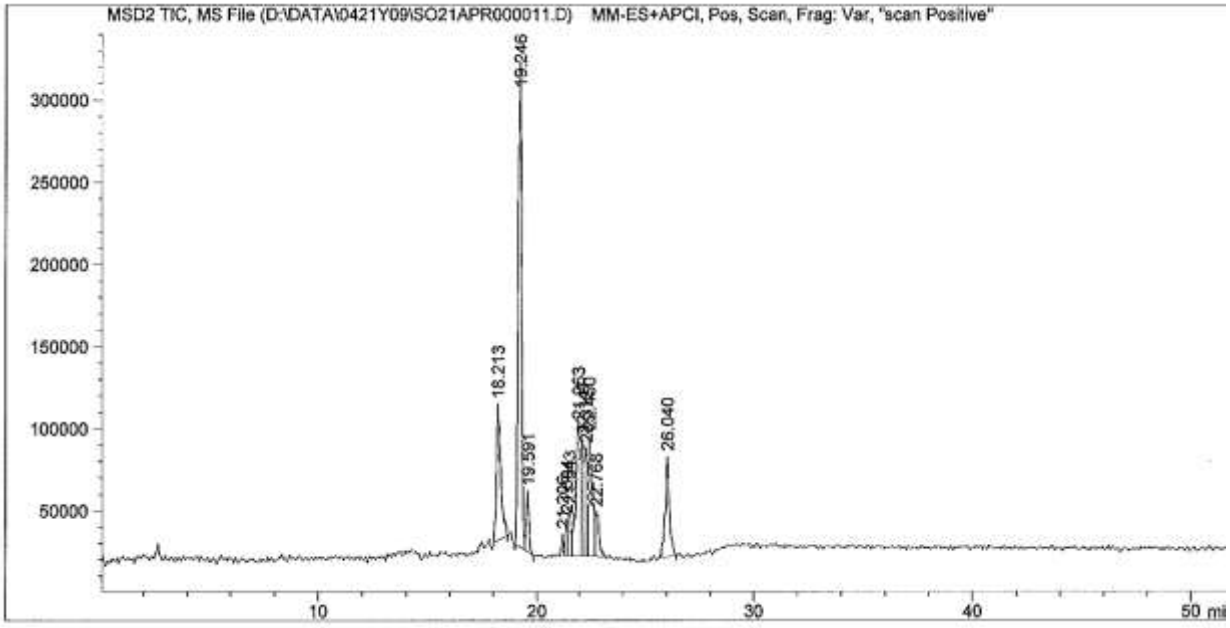

*MSD2 SPC, time=24.831 of D:\DATA\0421Y09\SO21APR000010.D MM-ES+APCI, Pos, Sc
Max: 4074
595.4
577.4
596.4
559.2
560.2
579.2
128.0
187.2
245.0
345.0
423.0
100
80
60
40
20
0
100
200
300
400
500
m/z


*MSD2 SPC, time=25.493 of D:\DATA\0421Y09\SO21APR000010.D MM-ES+APCI, Pos, Sc
Max 5649
449.
403.2
450.2
431.2
404.2
187.0
149.0
385.2
414.2
432.2
347.0
451.2
100
80
60
40
20
0
100
200
300
400
m/z

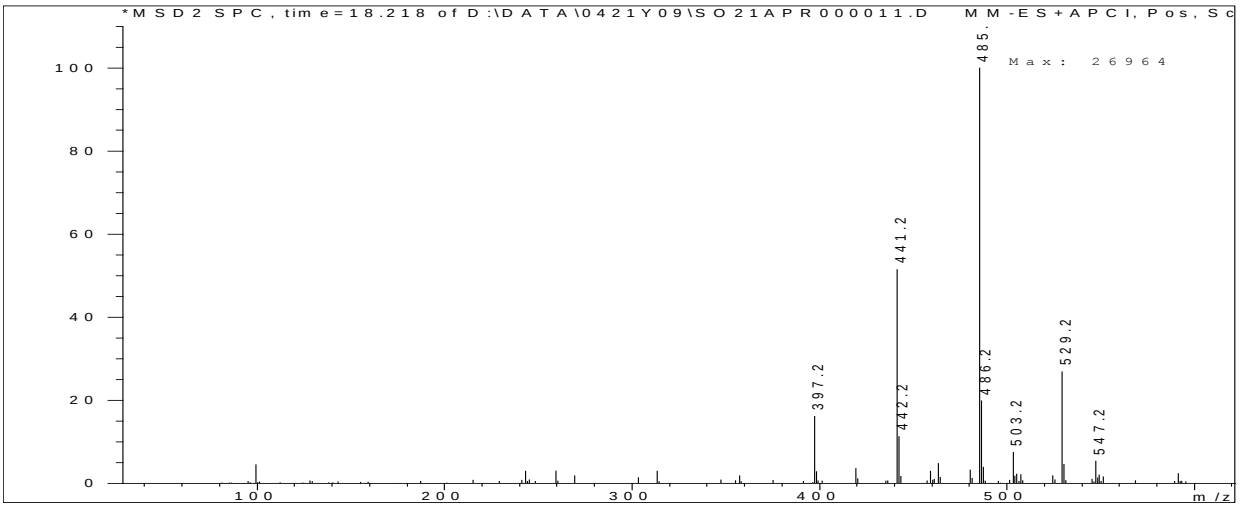
Ebercryl P39 LC-UV chromatogram 230 nm

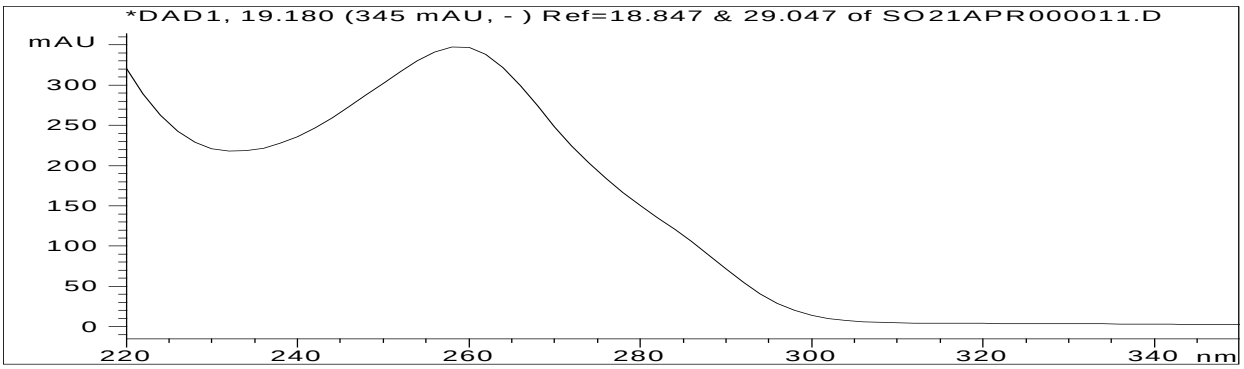


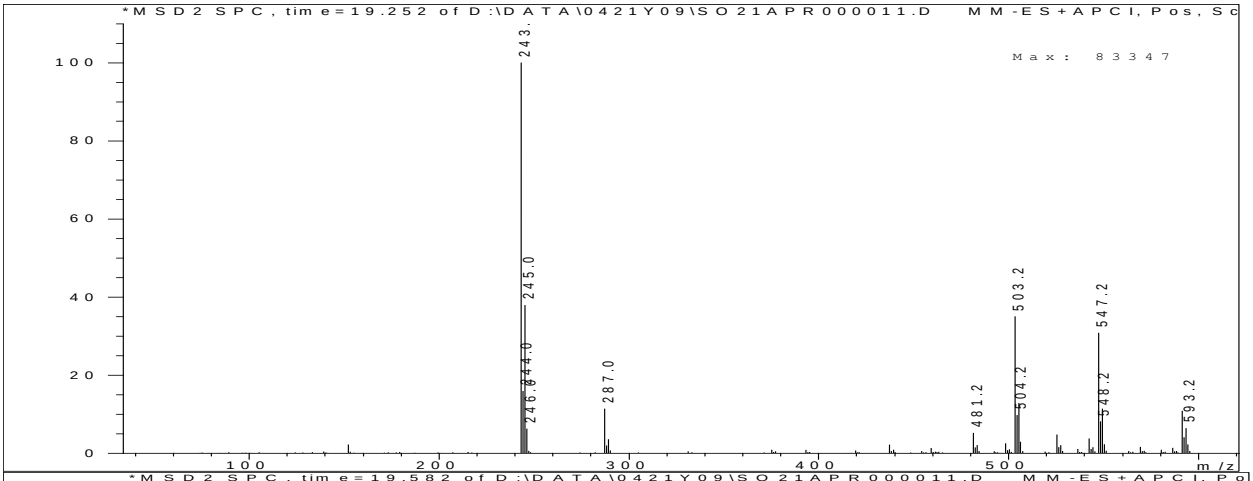
Ebercryl P39 LC-MS chromatogram

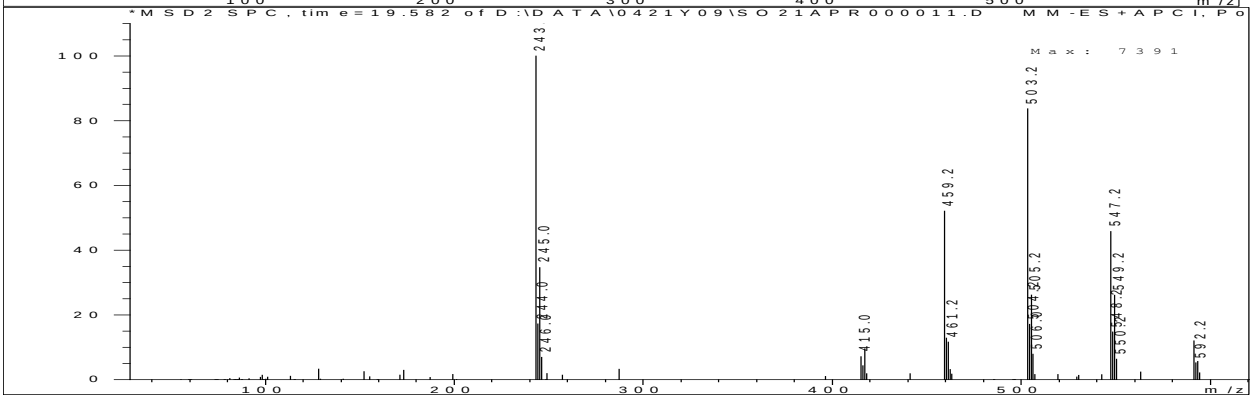


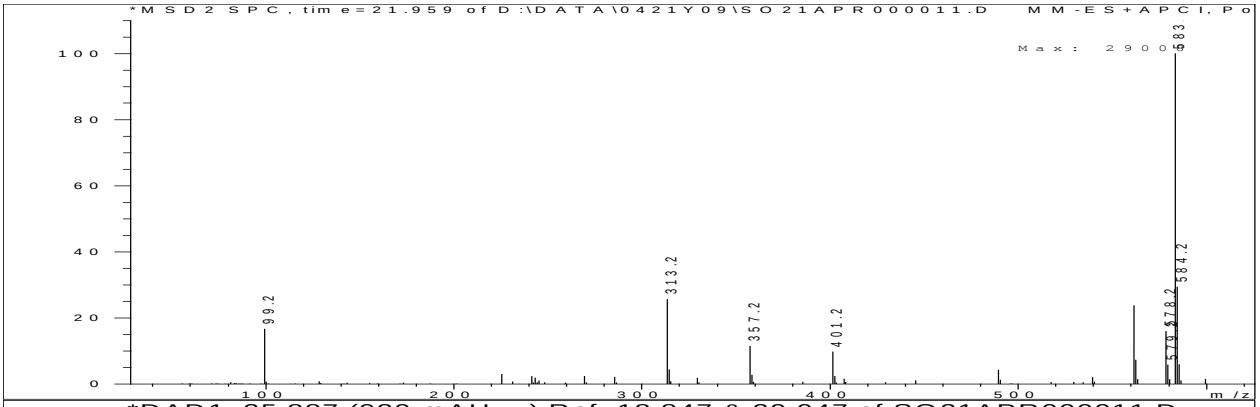
EBECRYL P39

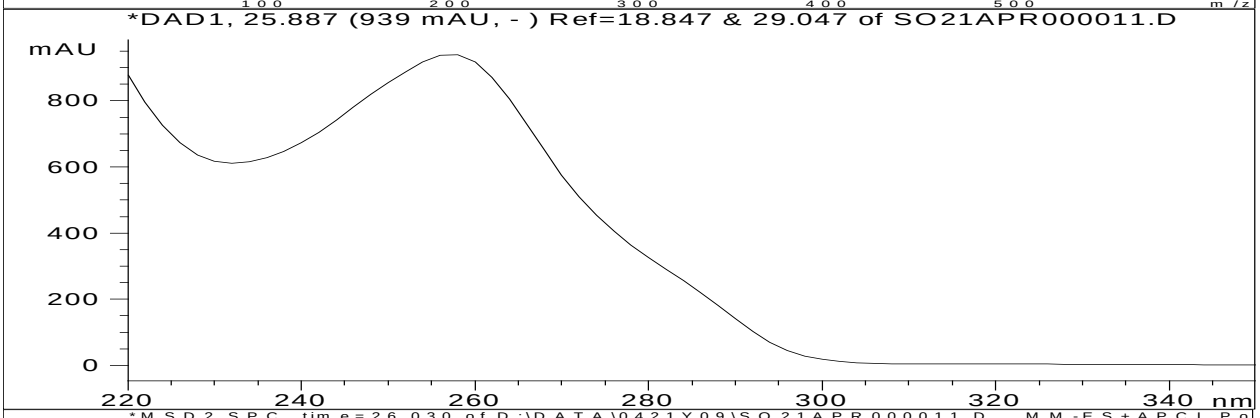

*MSD2 SPC, time=18.218 of D:\DATA\0421Y09\SO21APR000011.D MM-ES+APCI, Pos, Sc
Max: 26964
485.
441.2
397.2
442.2
486.2
503.2
529.2
547.2
m/z

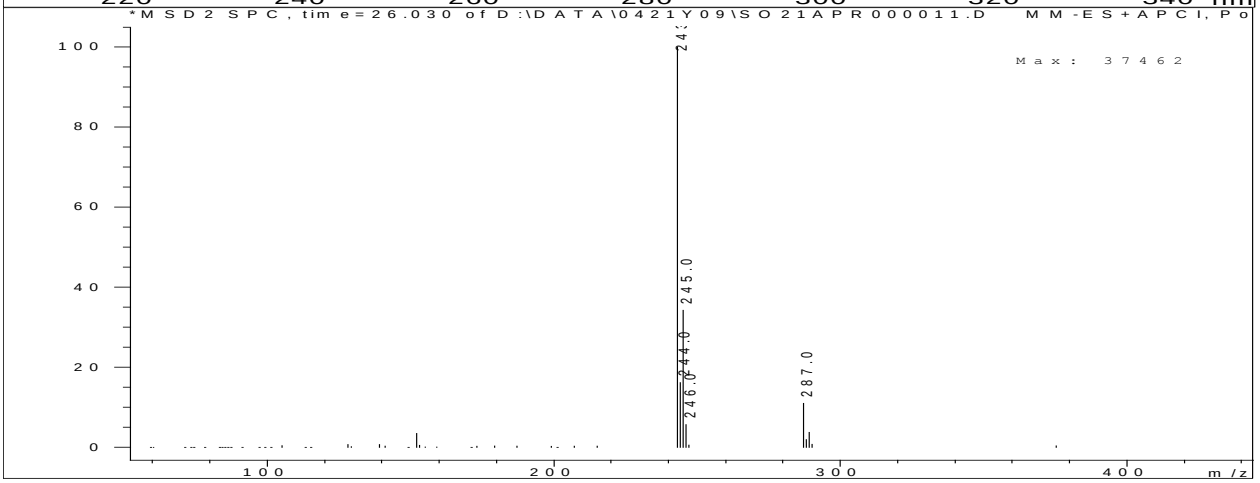

*DAD1, 19.180 (345 mAU, -) Ref=18.847 & 29.047 of SO21APR000011.D
mAU
nm


*MSD2 SPC, time=19.252 of D:\DATA\0421Y09\SO21APR000011.D MM-ES+APCI, Pos, Sc
Max: 83347
243.
245.0
503.2
547.2
287.0
481.2
504.2
548.2
593.2
m/z

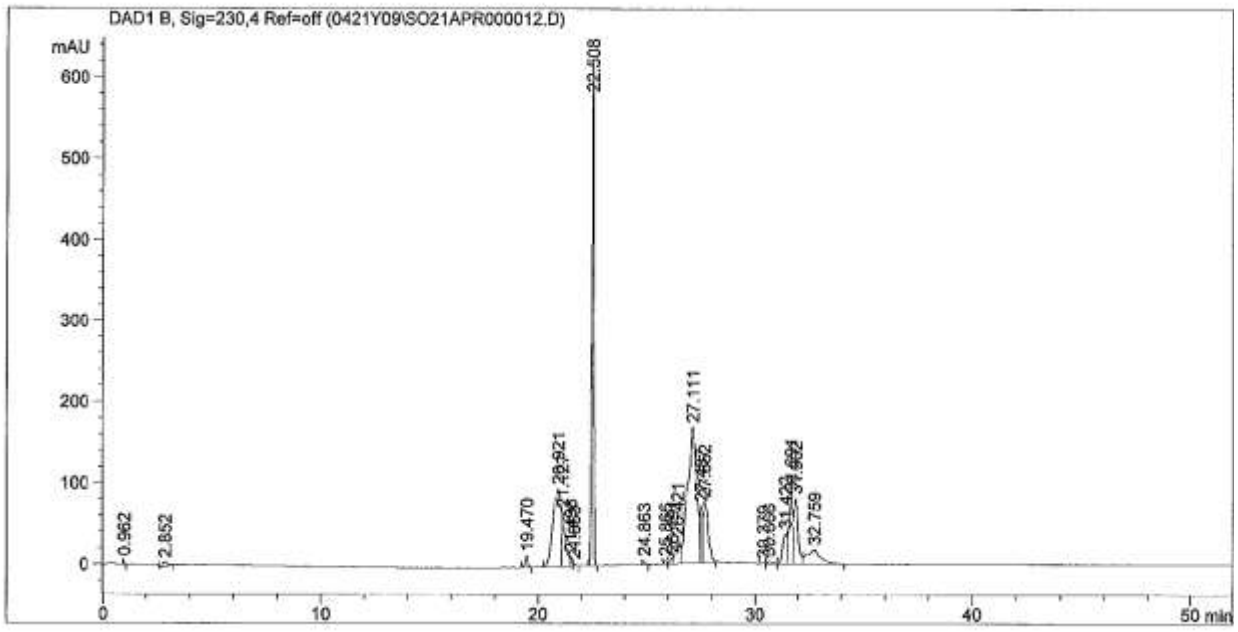

*MSD2 SPC, time=19.582 of D:\DATA\0421Y09\SO21APR000011.D MM-ES+APCI, Po
Max: 7391
243
503.2
459.2
245.0
547.2
415.0
461.2
592.2
m/z


*M S D 2 S P C , tim e = 2 1 . 9 5 9 of D :\D A T A \0 4 2 1 Y 0 9 \S O 2 1 A P R 0 0 0 0 1 1 . D M M - E S + A P C I , Po
Max: 2900
583
584.2
313.2
357.2
401.2
99.2
m/z

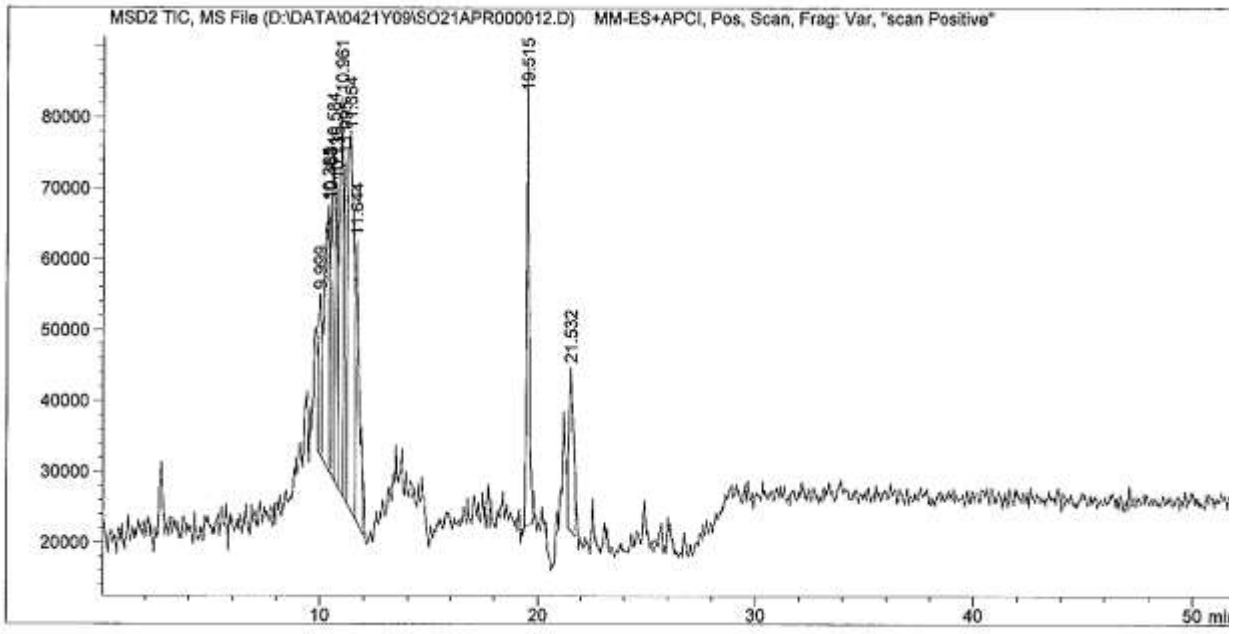

*DAD1, 25.887 (939 mAU, -) Ref=18.847 & 29.047 of SO21APR000011.D
mAU
nm


*M S D 2 S P C , tim e = 2 6 . 0 3 0 of D :\D A T A \0 4 2 1 Y 0 9 \S O 2 1 A P R 0 0 0 0 1 1 . D M M - E S + A P C I , Po
Max: 37462
245.0
244.0
246.0
287.0
m/z

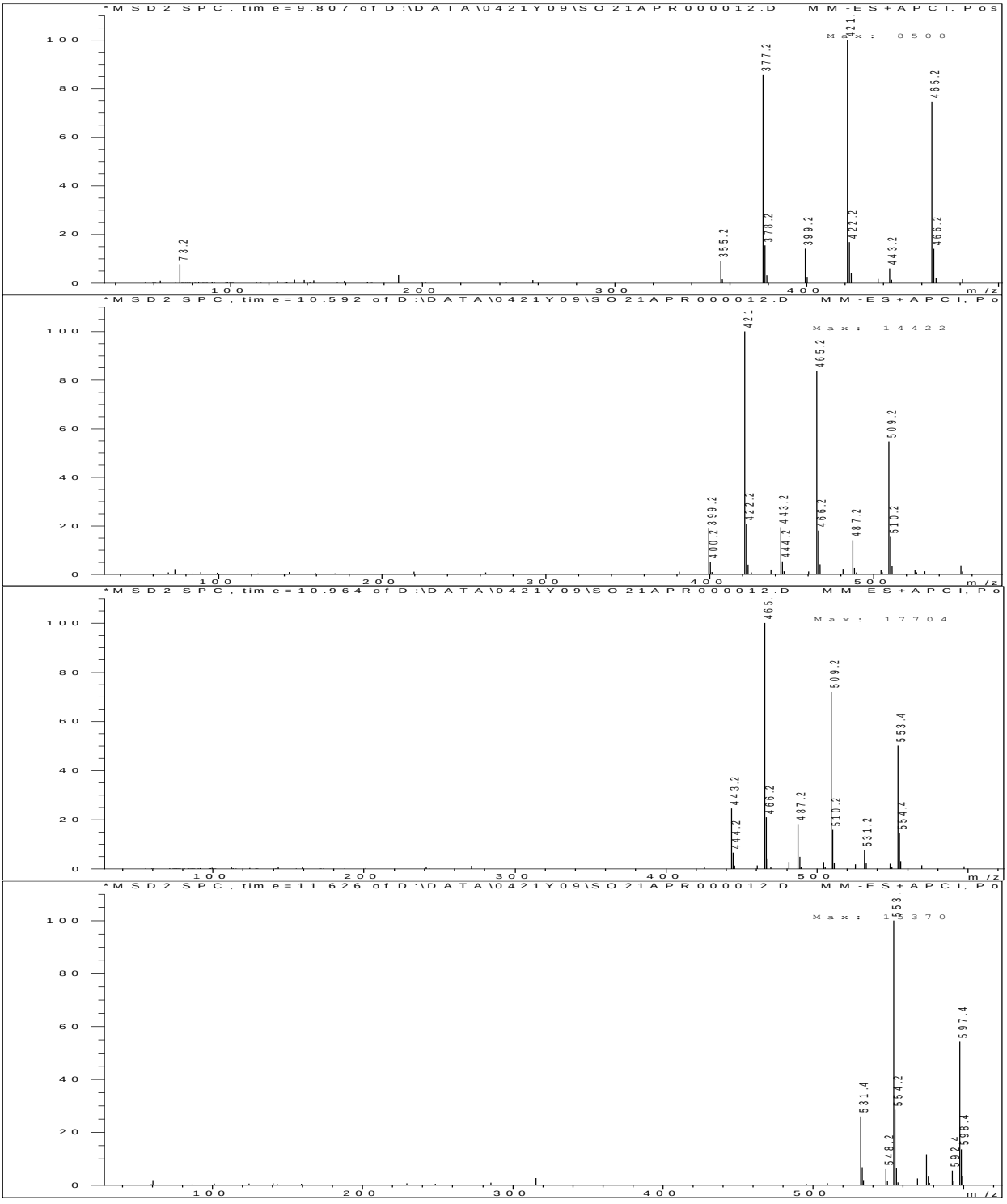
Genopol TX 1 LC-UV chromatogram 230 nm

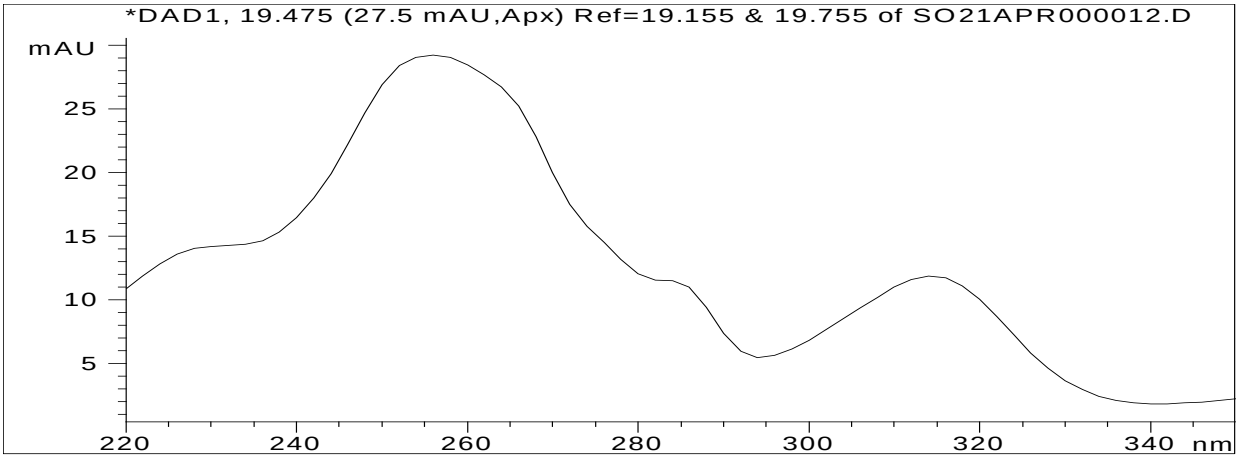


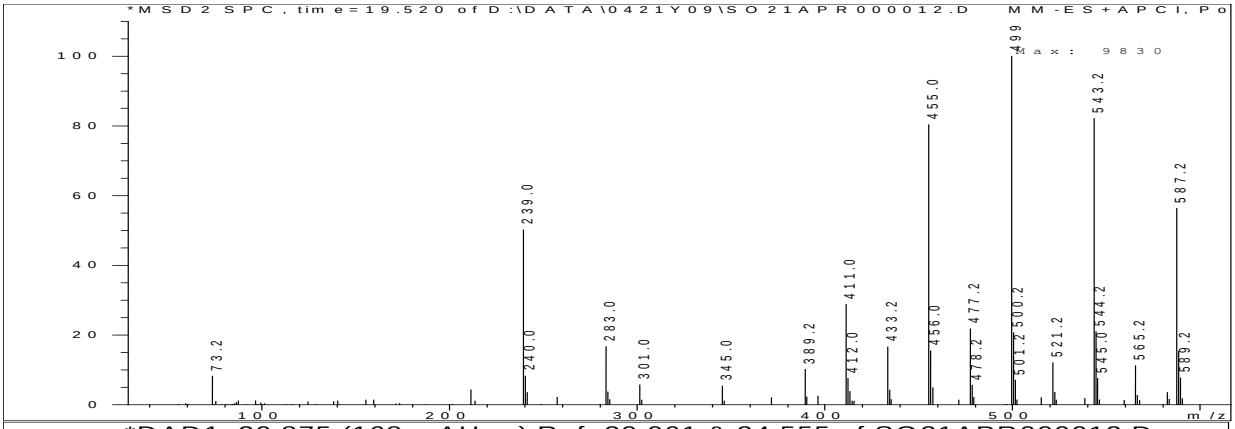
Genopol TX 1 LC-MS chromatogram

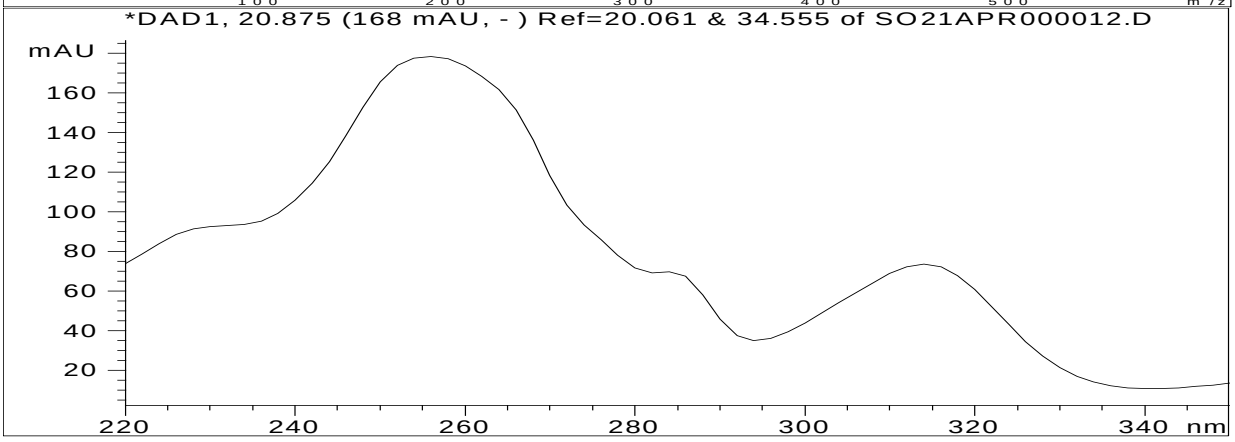


Multi component peaks had numerous different mass spectra, selections below

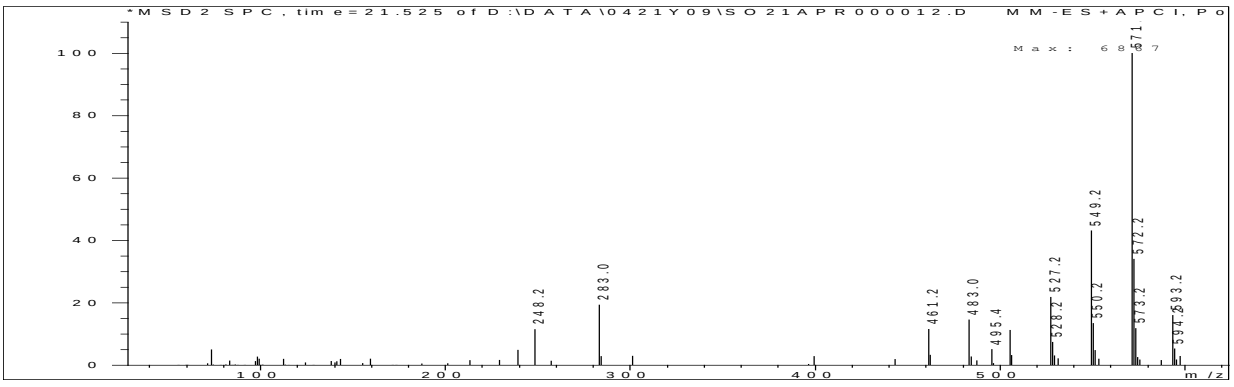


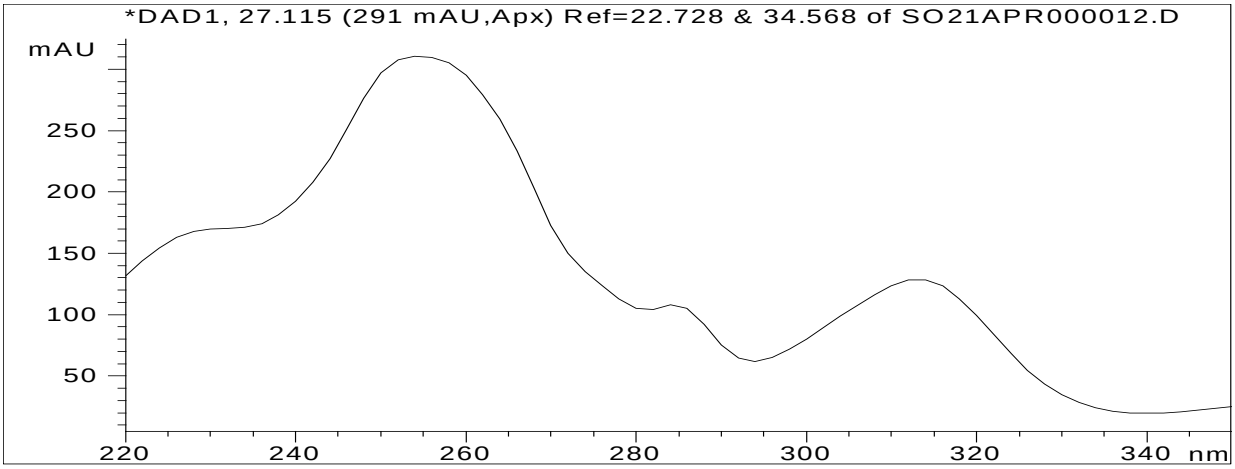


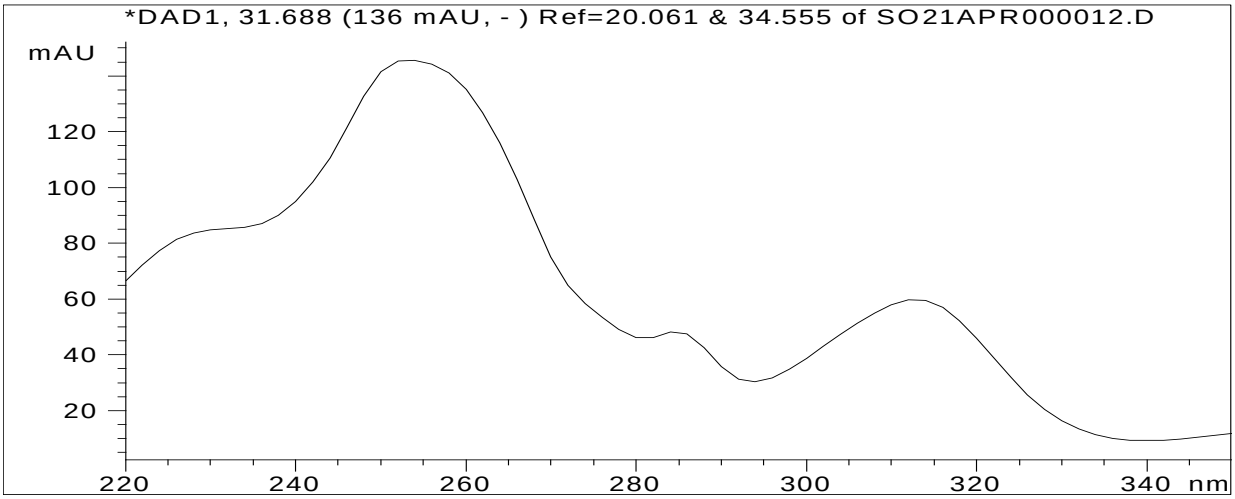




BH GENOPOL TX1

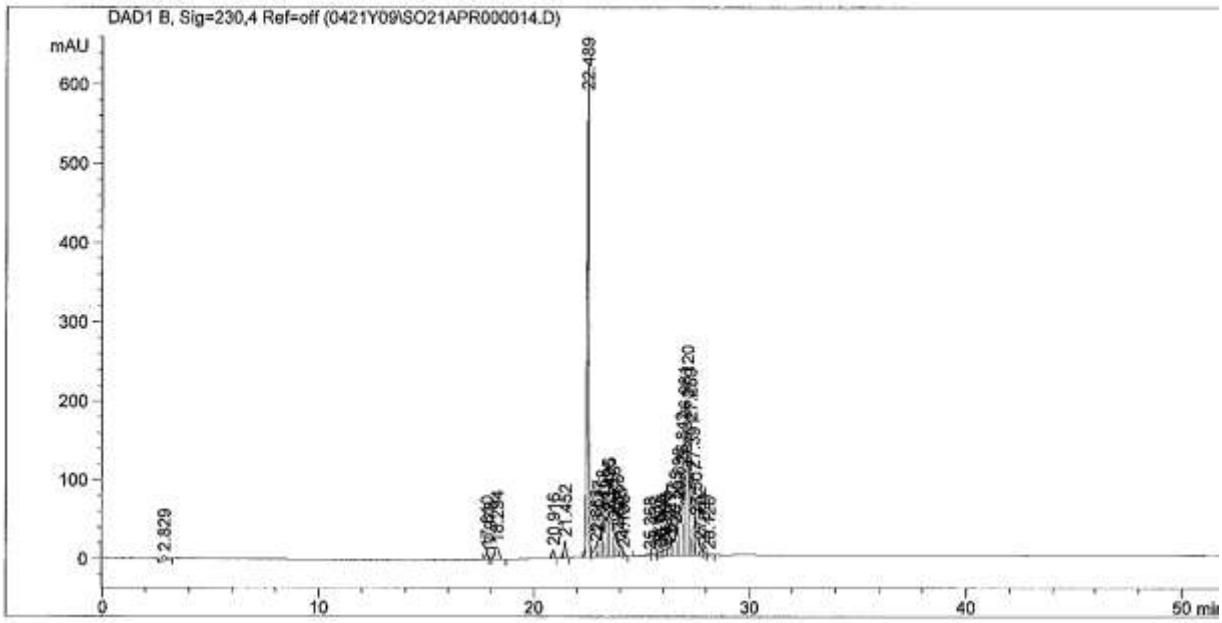




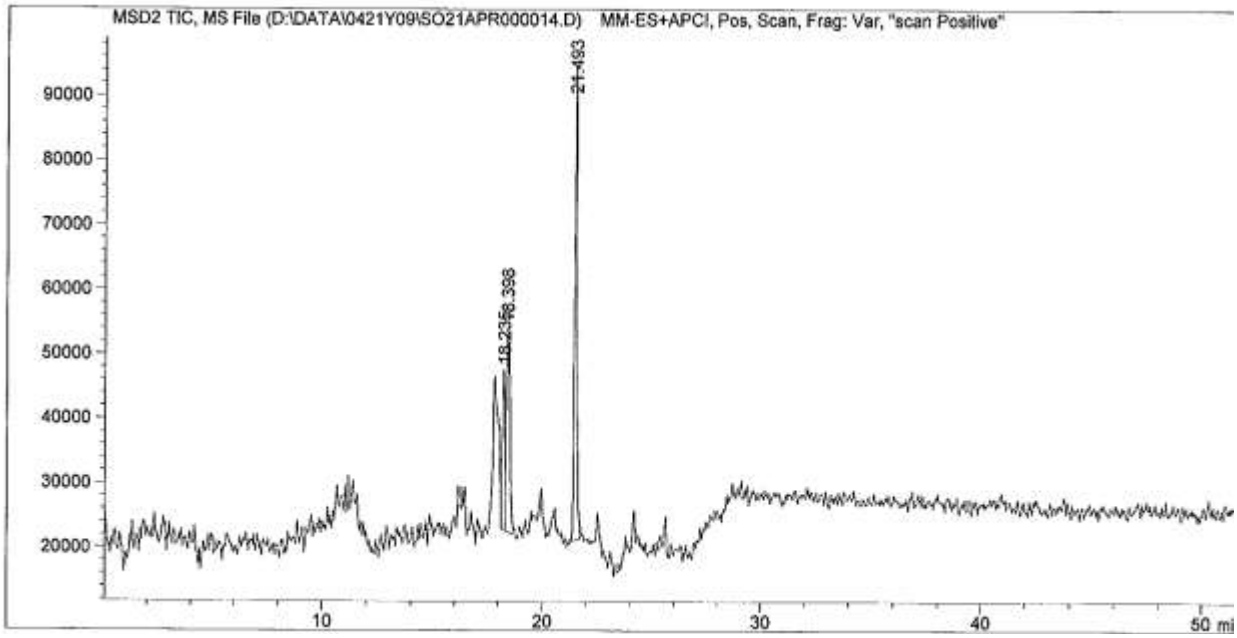


BH GENOPOL TX1

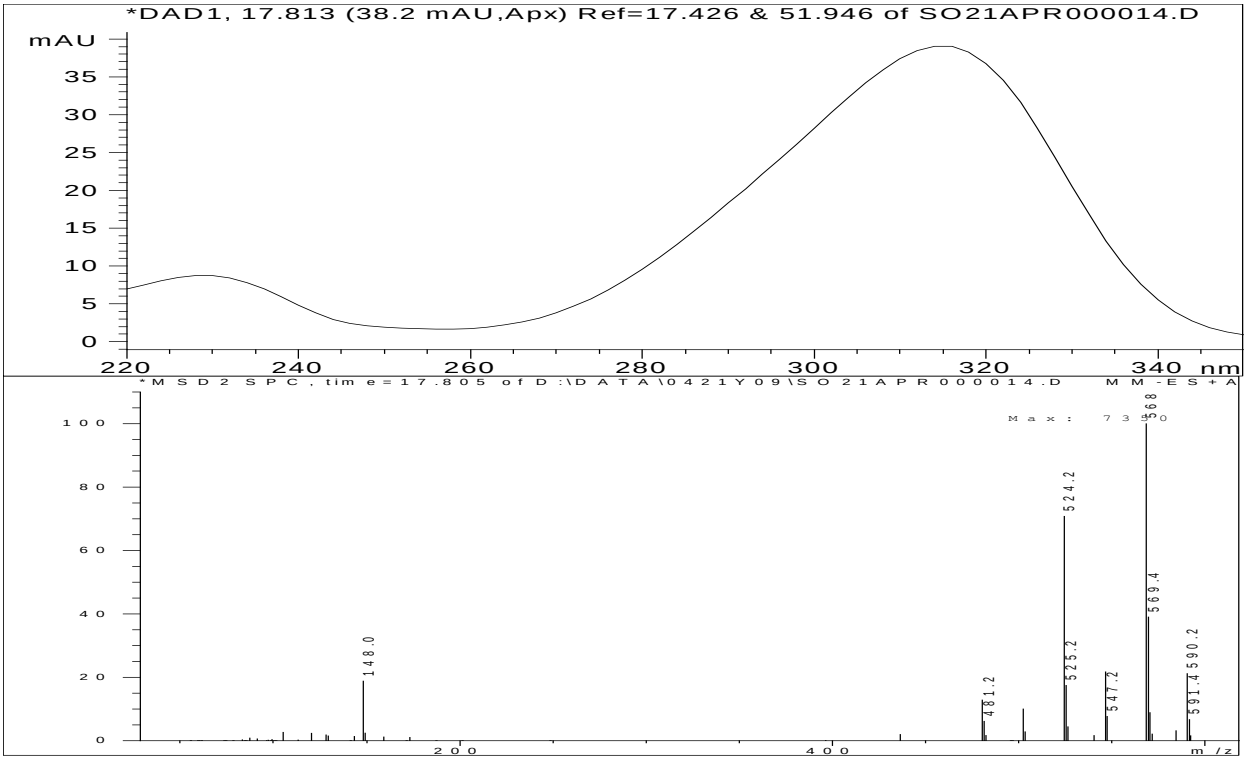
Genopol AB1 LC-UV chromatogram 230 nm



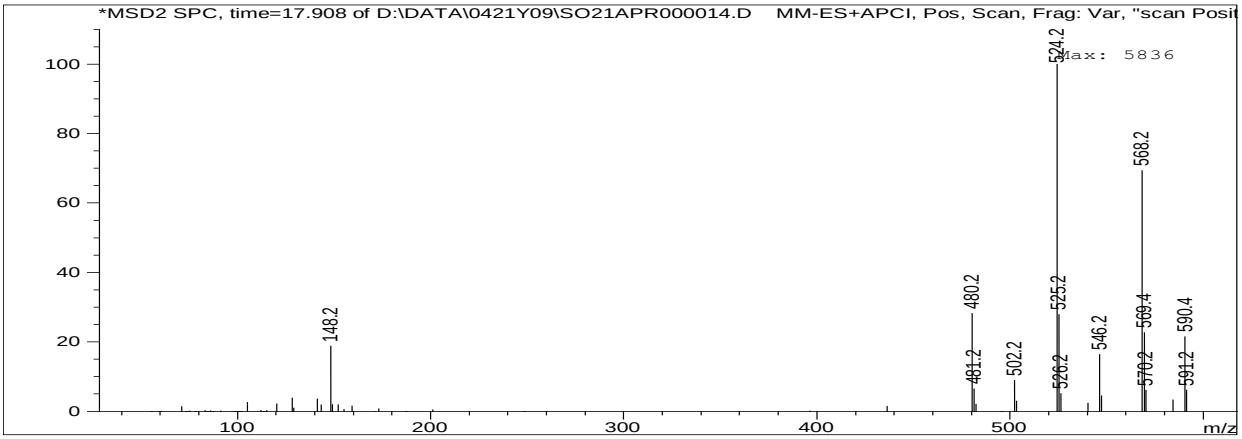
Genopol AB1 LC-MS chromatogram

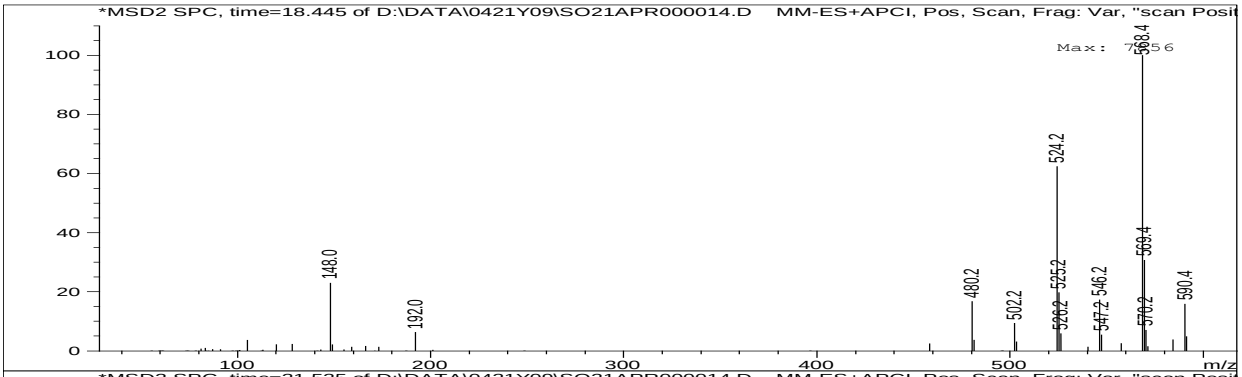


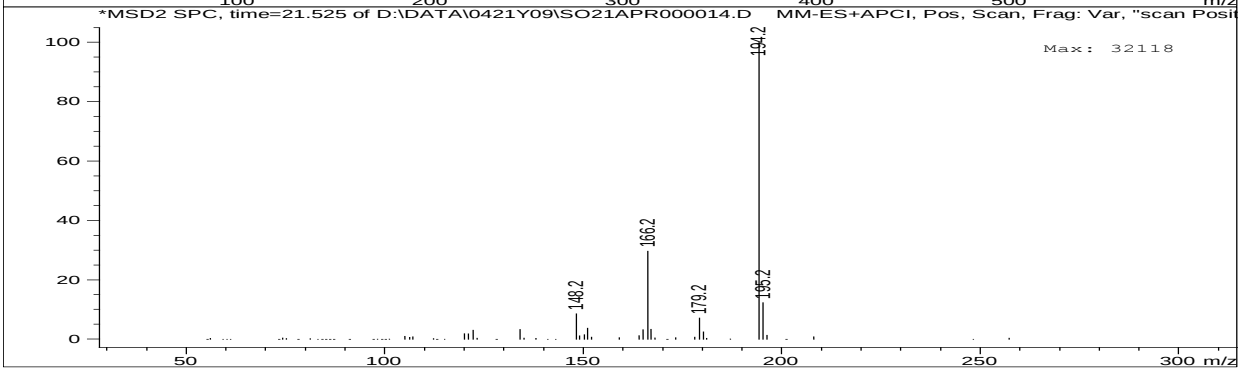
UV spectra of all peaks as shown below


*DAD1, 17.813 (38.2 mAU,Apx) Ref=17.426 & 51.946 of SO21APR000014.D
mAU
nm
*MSD2 SPC, time=17.805 of D:\DATA\0421Y09\SO21APR0000014.D MM-ES+A
Max: 73150
568
524.2
569.4
148.0
481.2
525.2
547.2
590.2
591.4
m/z
*MSD2 SPC, time=18.404 of D:\DATA\0421Y09\SO21APR0000014.D MM-ES+A
Max: 140999
568
148.2
502.2
524.2
525.2
569.2
590.4
591.2
m/z
*MSD2 SPC, time=21.483 of D:\DATA\0421Y09\SO21APR0000014.D MM-ES+A
Max: 39070
148.2
166.2
179.2
195.2
m/z

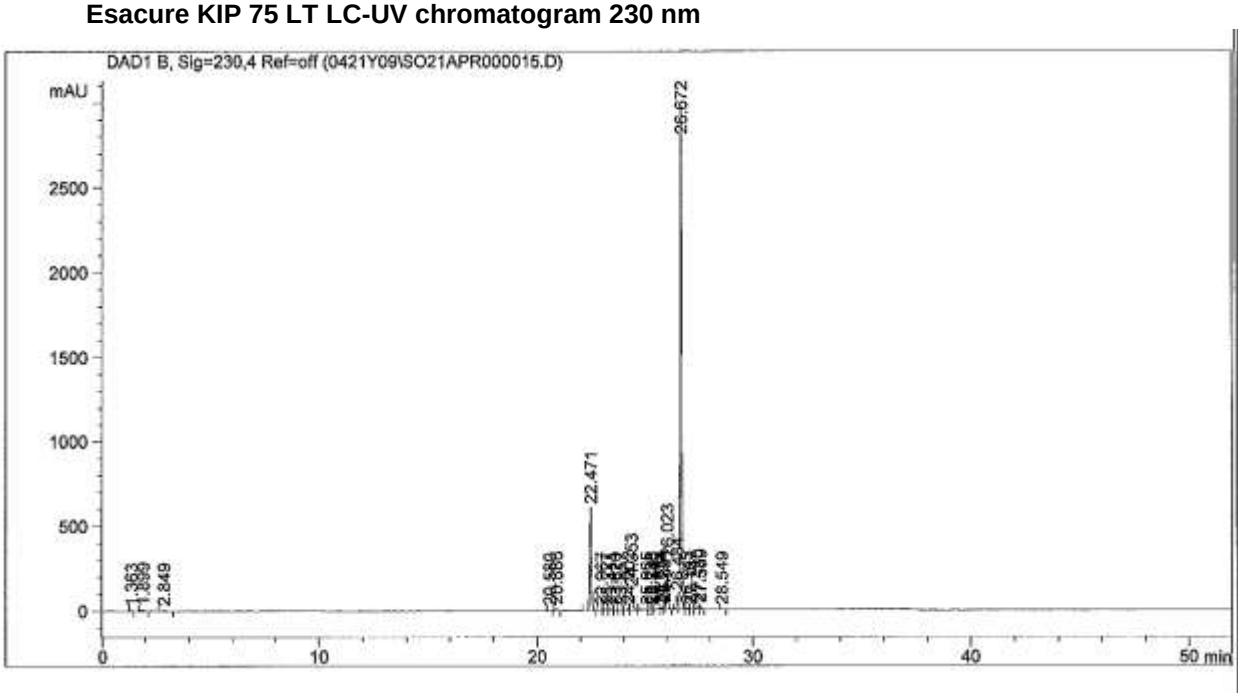
GENOPOL AB1


*MSD2 SPC, time=17.908 of D:\DATA\0421Y09\SO21APR000014.D MM-ES+APCI, Pos, Scan, Frag: Var, "scan Posit
Max: 5836
524.2
568.2
480.2
525.2
148.2
546.2
569.4
590.4
481.2
502.2
526.2
570.2
591.2
m/z

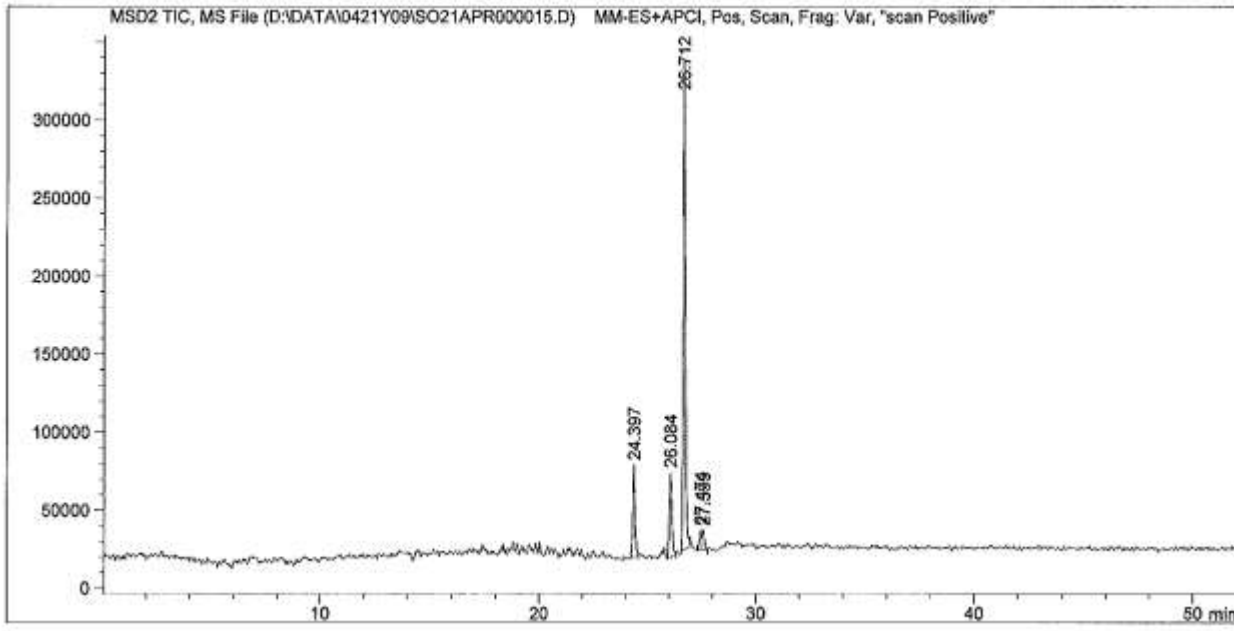

*MSD2 SPC, time=18.445 of D:\DATA\0421Y09\SO21APR000014.D MM-ES+APCI, Pos, Scan, Frag: Var, "scan Posit
Max: 7556
568.4
524.2
148.0
569.4
480.2
525.2
546.2
192.0
502.2
590.4
m/z


*MSD2 SPC, time=21.525 of D:\DATA\0421Y09\SO21APR000014.D MM-ES+APCI, Pos, Scan, Frag: Var, "scan Posit
Max: 32118
194.2
166.2
148.2
195.2
179.2
m/z

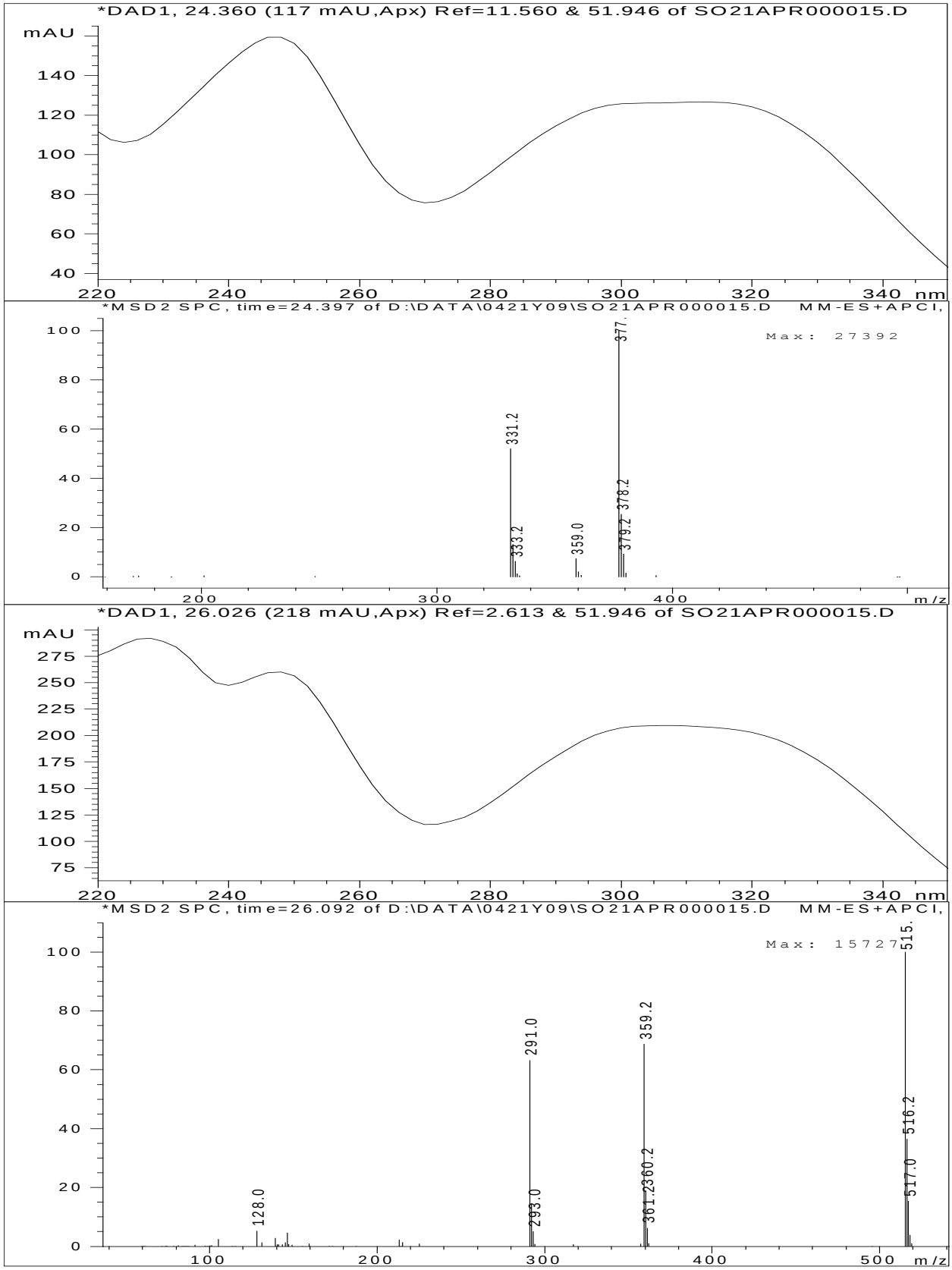
Esacure KIP 75 LT LC-UV chromatogram 230 nm

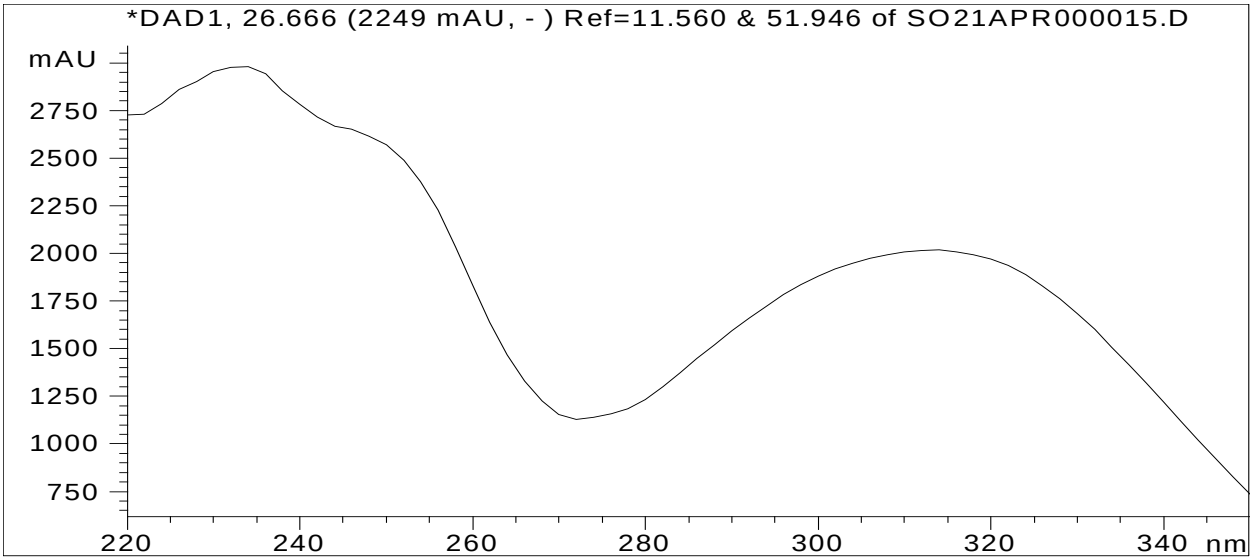


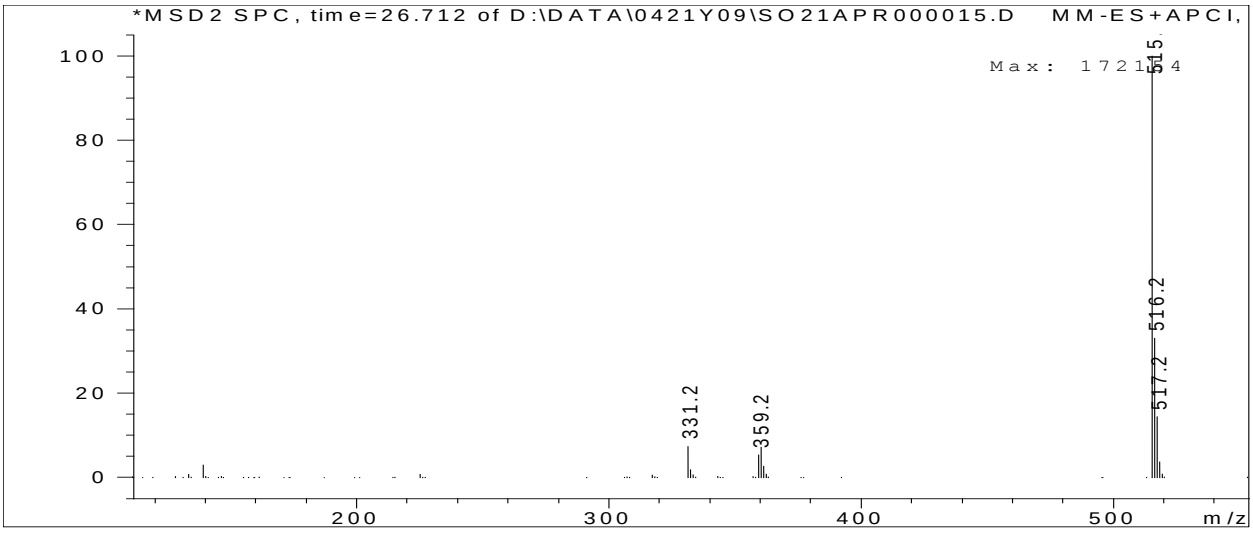
Esacure KIP 75 LT LC-MS chromatogram



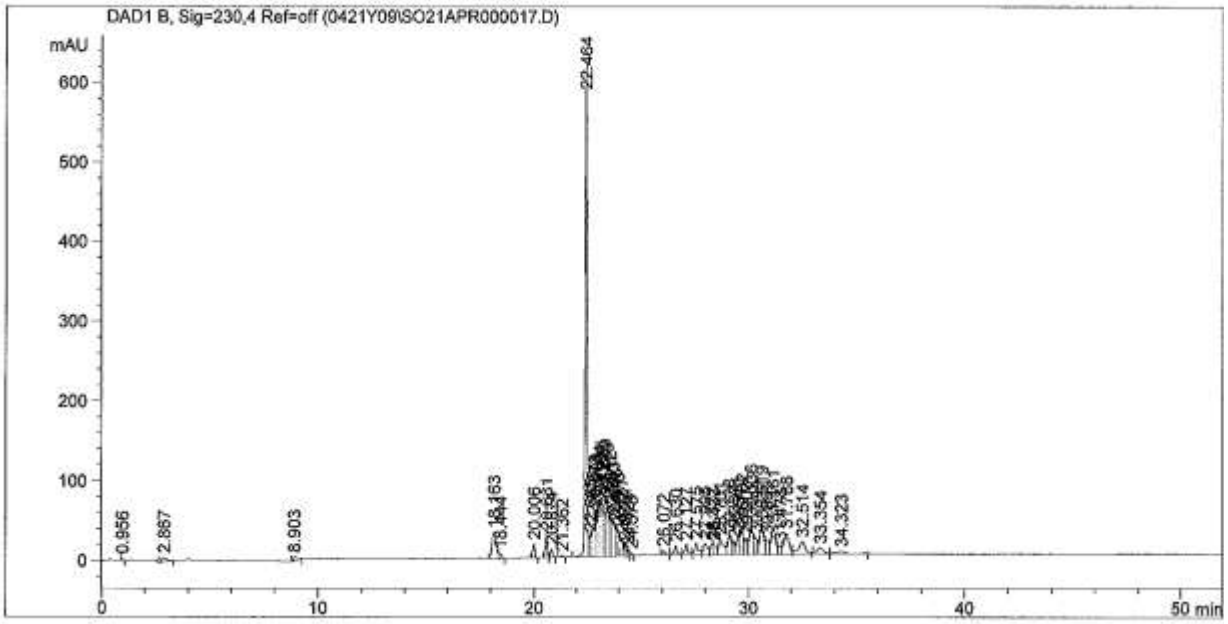
ESACURE KIP 75 LT



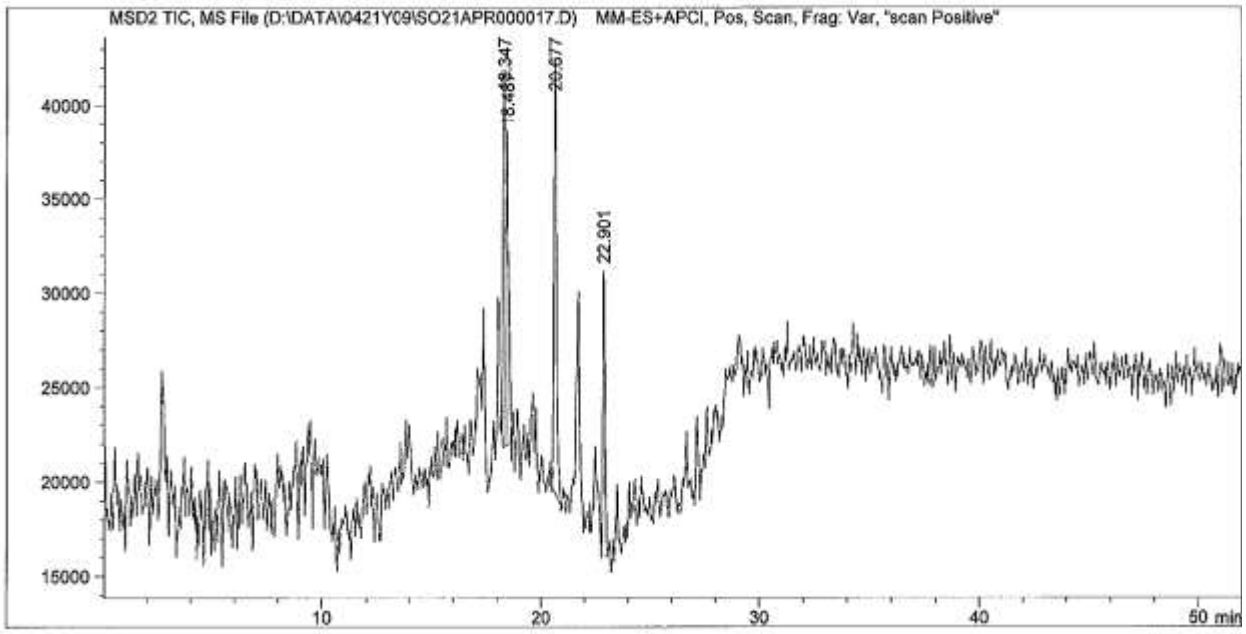

*DAD1, 26.666 (2249 mAU, -) Ref=11.560 & 51.946 of SO21APR000015.D
mAU
2750
2500
2250
2000
1750
1500
1250
1000
750
220
240
260
280
300
320
340
nm


*MSD2 SPC, time=26.712 of D:\DATA\0421Y09\SO21APR000015.D MM-ES+APCI,
Max: 172154
100
80
60
40
20
0
331.2
359.2
515
516.2
517.2
200
300
400
500
m/z

Speedcure 7005 LC-UV chromatogram 230 nm

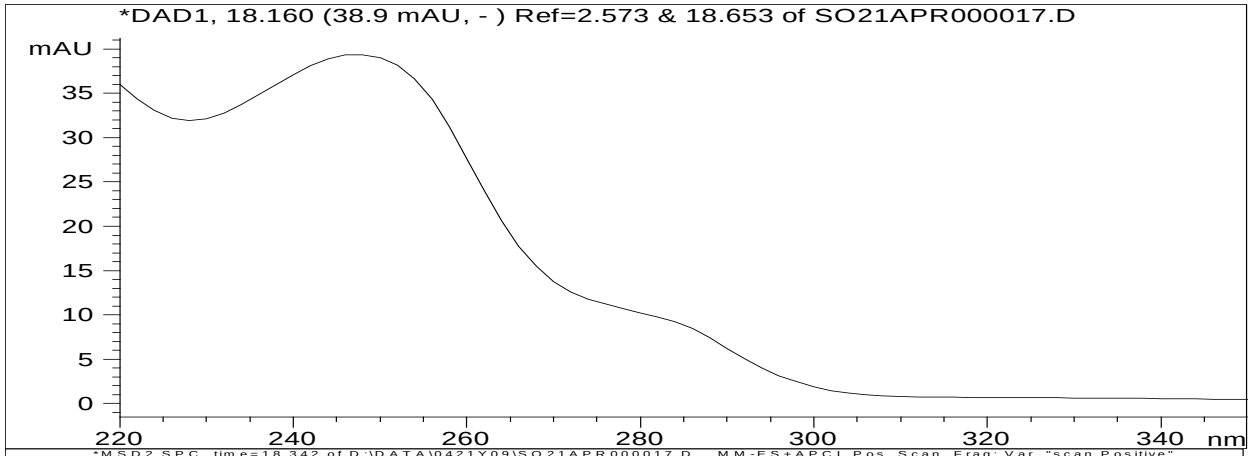


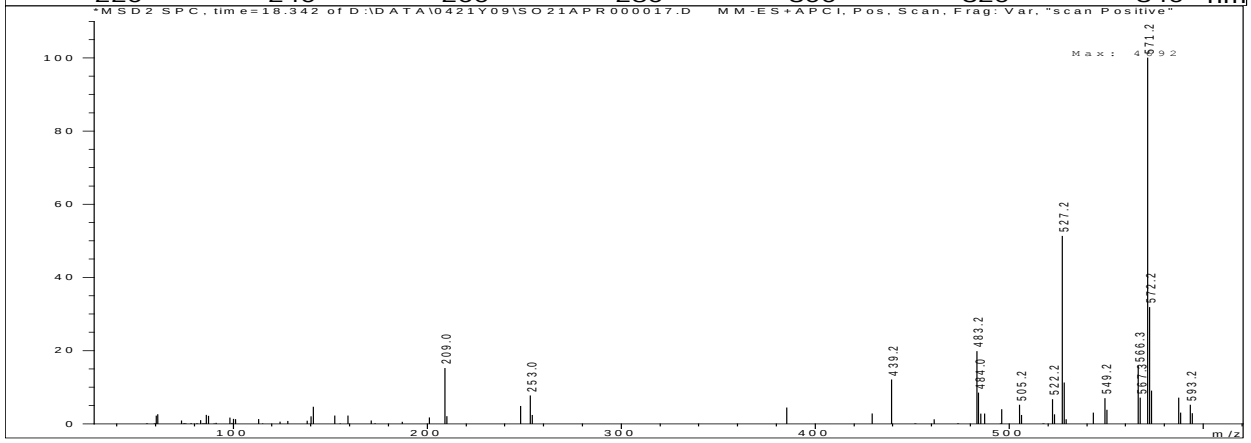
Speedcure 7005 LC-MSchromatogram

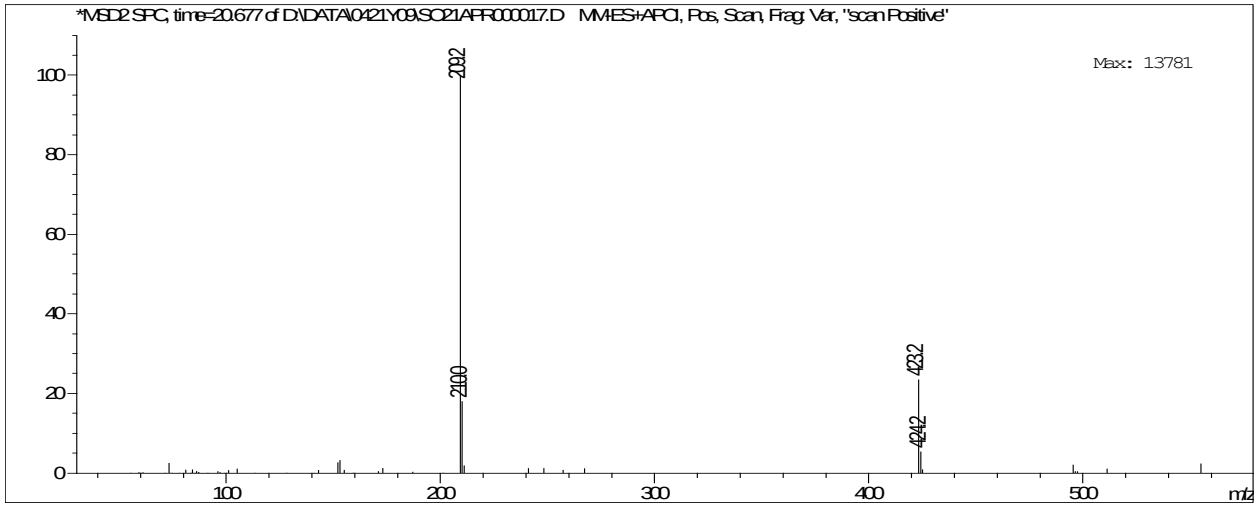


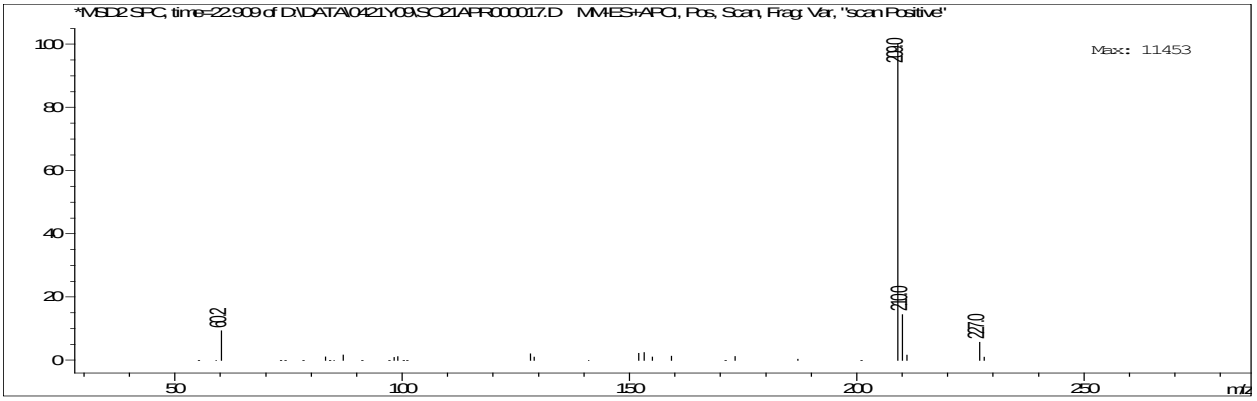
UV spectra of all peaks as shown below

SPEEDCURE 7005



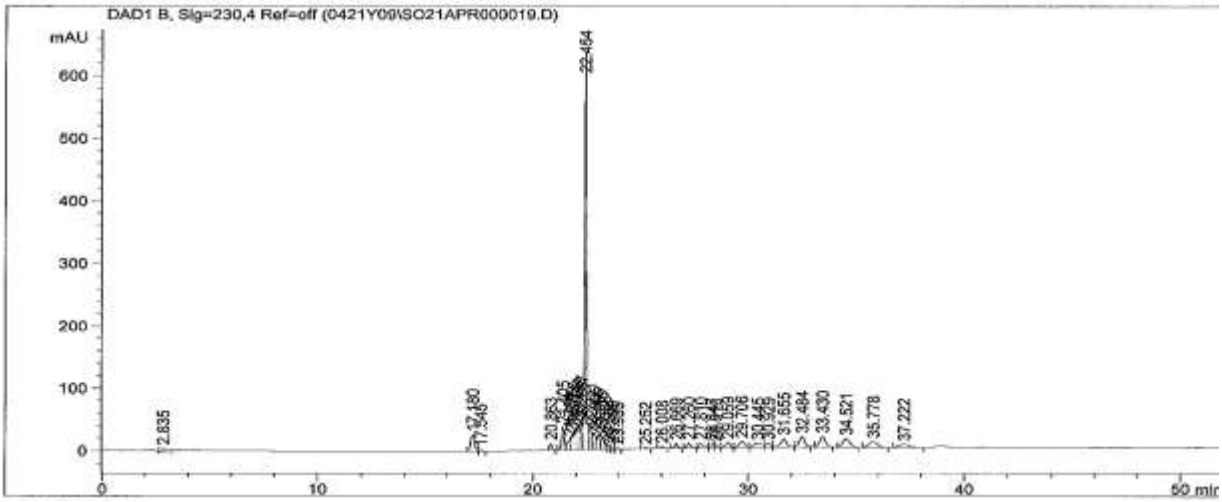




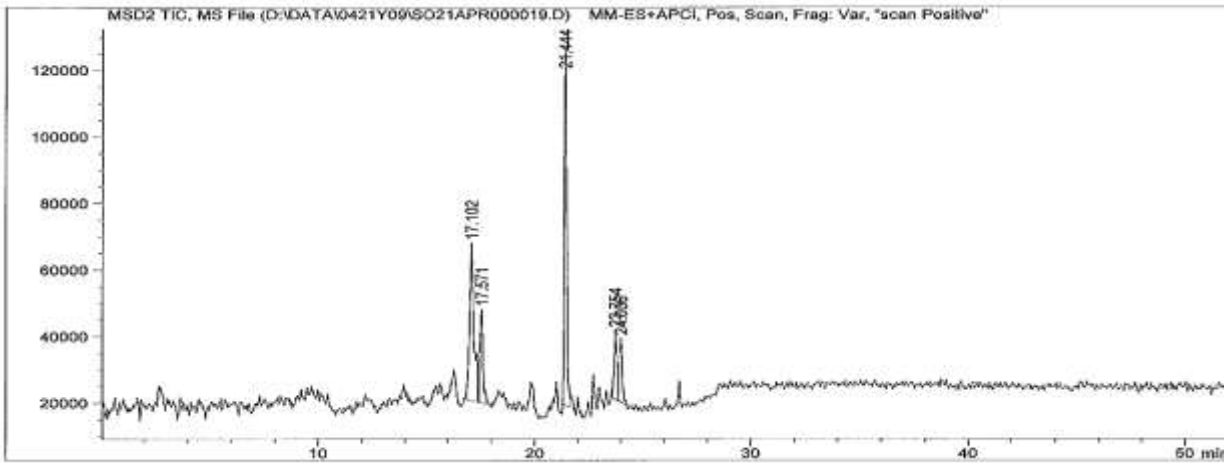


SPEEDCURE 7005

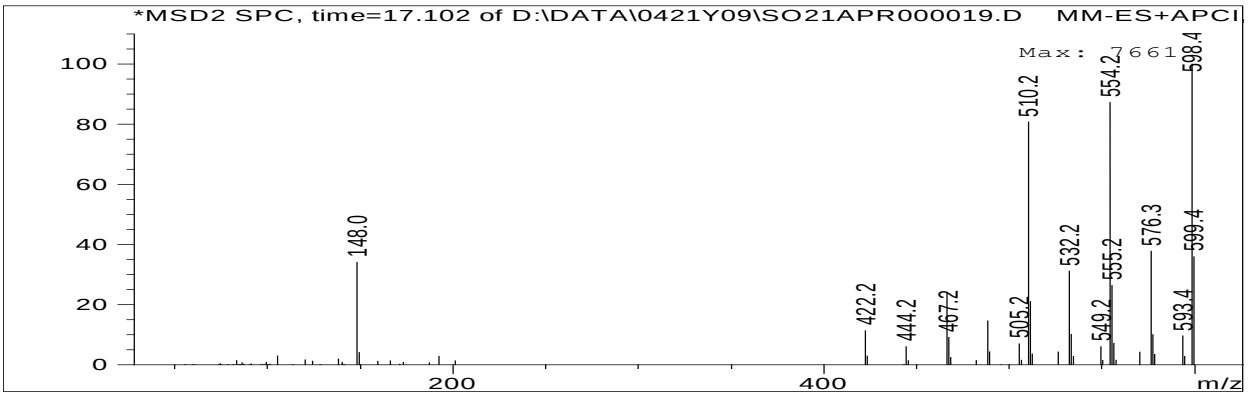
LC-UV chromatogram Speedcure 7040 at 230 nm

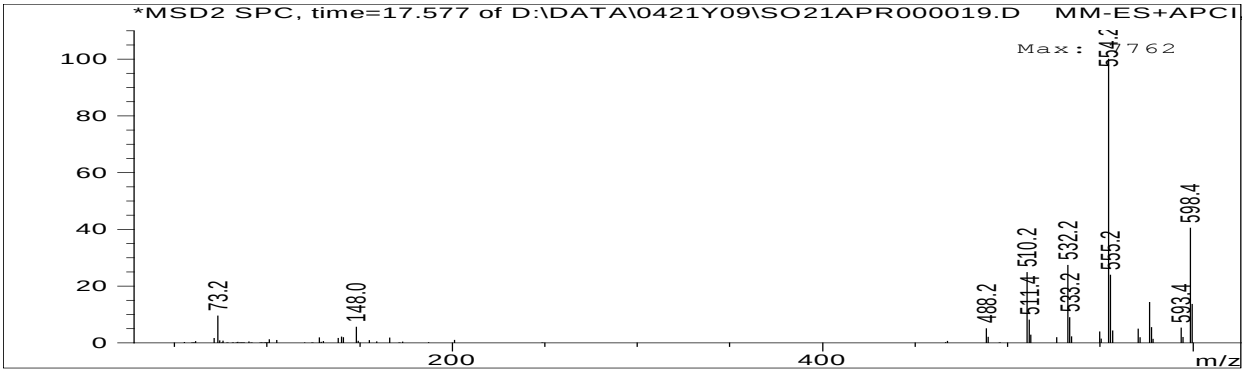


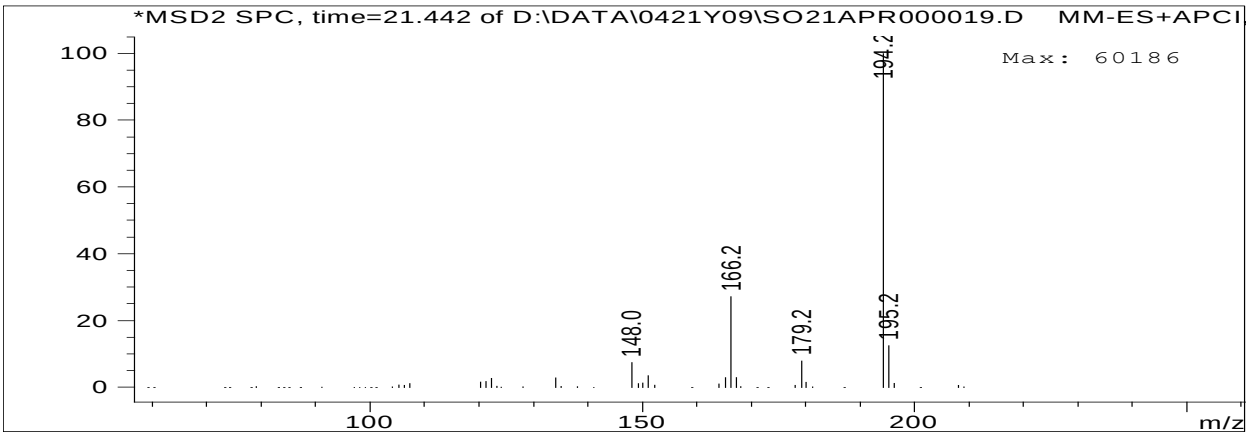
LC-MS chromatogram Speedcure 7040

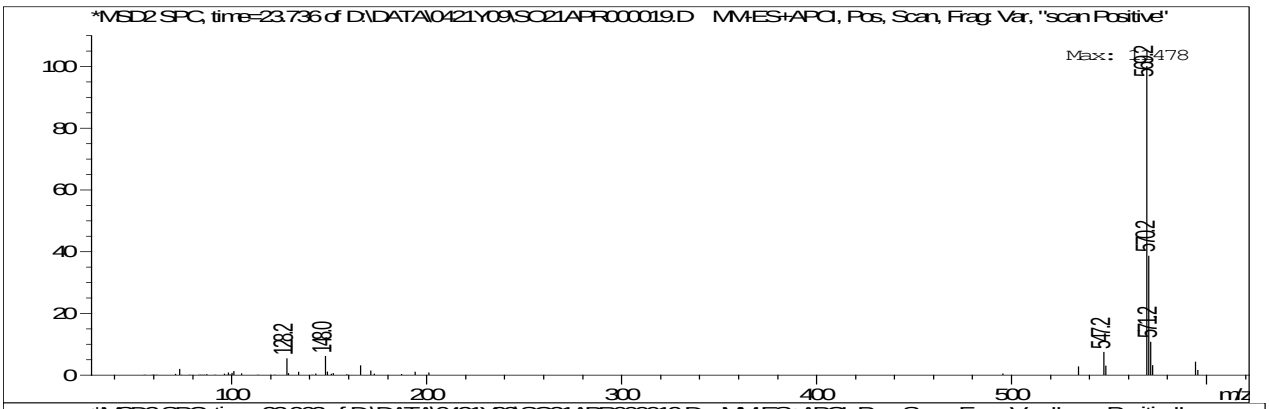


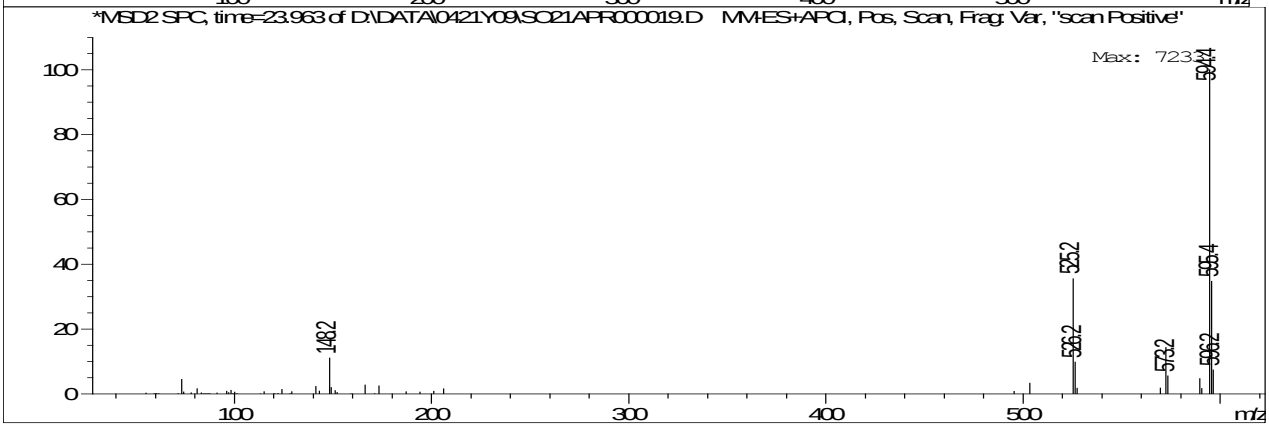
UV spectra of all peaks as shown below



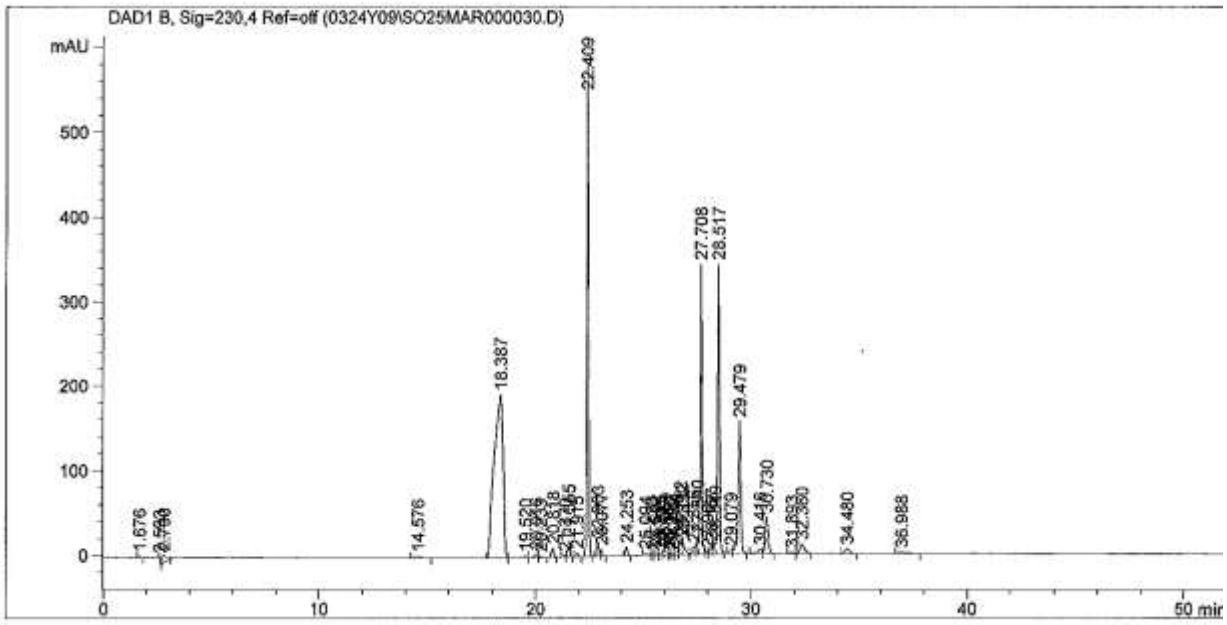

*MSD2 SPC, time=17.577 of D:\DATA\0421Y09\SO21APR000019.D MM-ES+APCI
Max: 7762
73.2
148.0
488.2
510.2
532.2
555.2
598.4
m/z


*MSD2 SPC, time=21.442 of D:\DATA\0421Y09\SO21APR000019.D MM-ES+APCI
Max: 60186
148.0
166.2
179.2
195.2
m/z

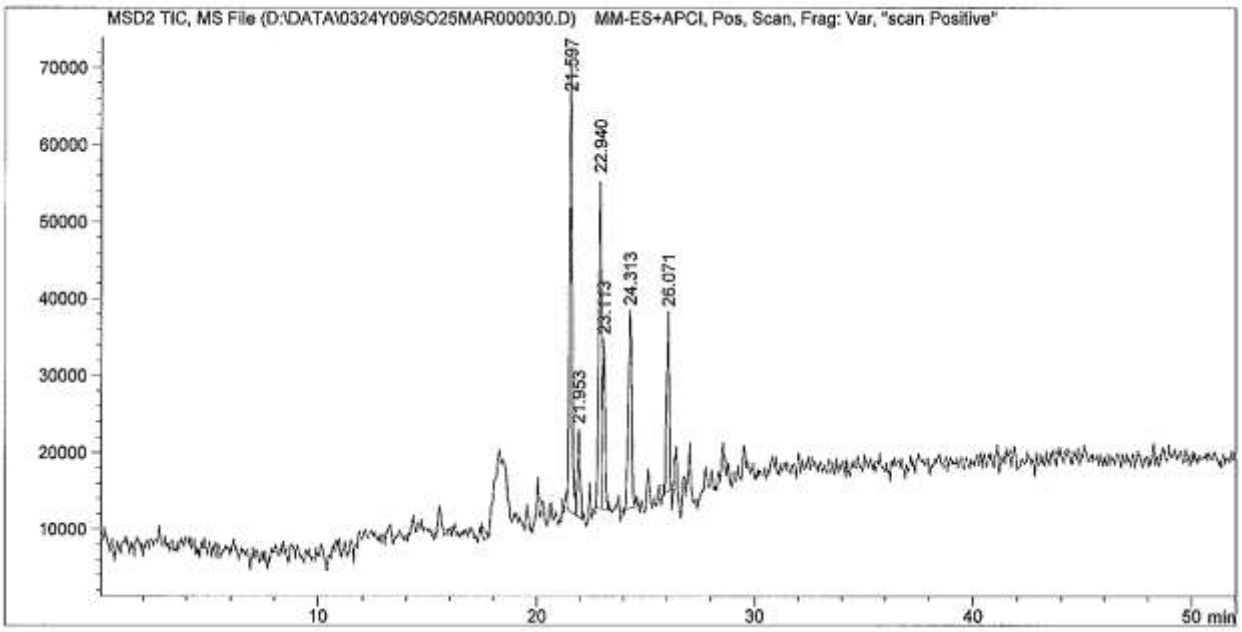

*MSD2 SPC, time=23.736 of D:\DATA\0421Y09\SO21APR000019.D MM-ES+APCI, Pos, Scan, Frag: Var, "scan Positive"
Max: 2478
128.2
148.0
547.2
570.2
m/z


*MSD2 SPC, time=23.963 of D:\DATA\0421Y09\SO21APR000019.D MM-ES+APCI, Pos, Scan, Frag: Var, "scan Positive"
Max: 7231
148.2
525.2
526.2
573.2
m/z

Omnipol TX LC-UV chromatogram 270

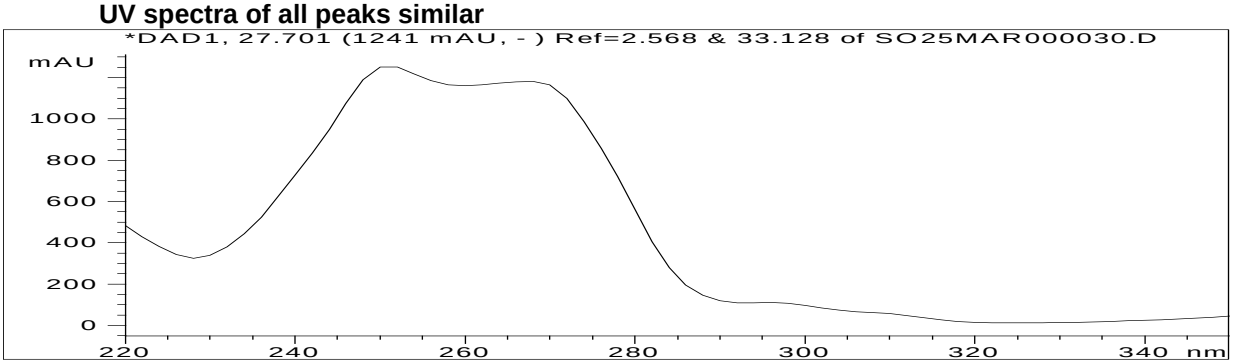


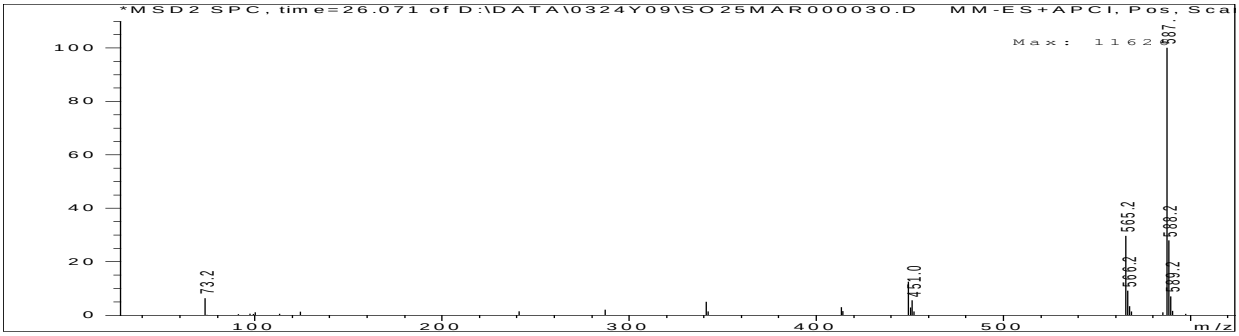
Omnipol TX LC-MS chromatogram

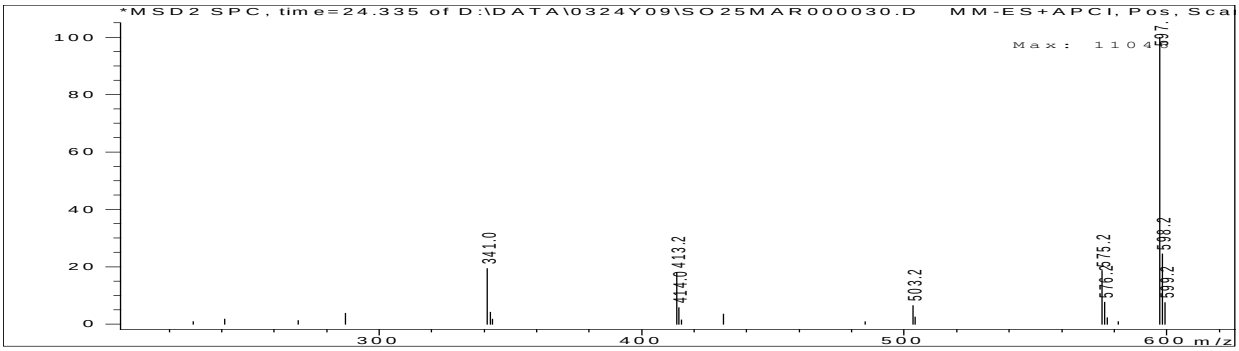


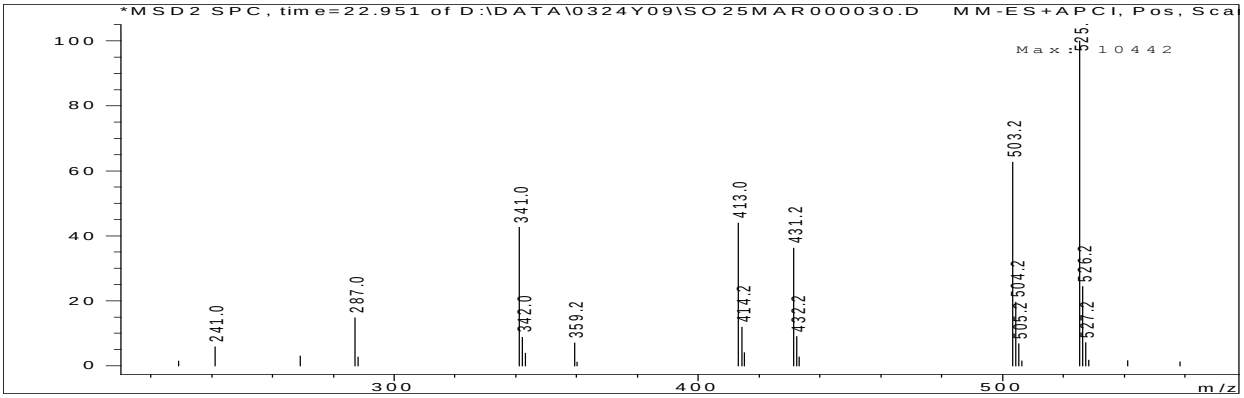
OMNIPOL TX

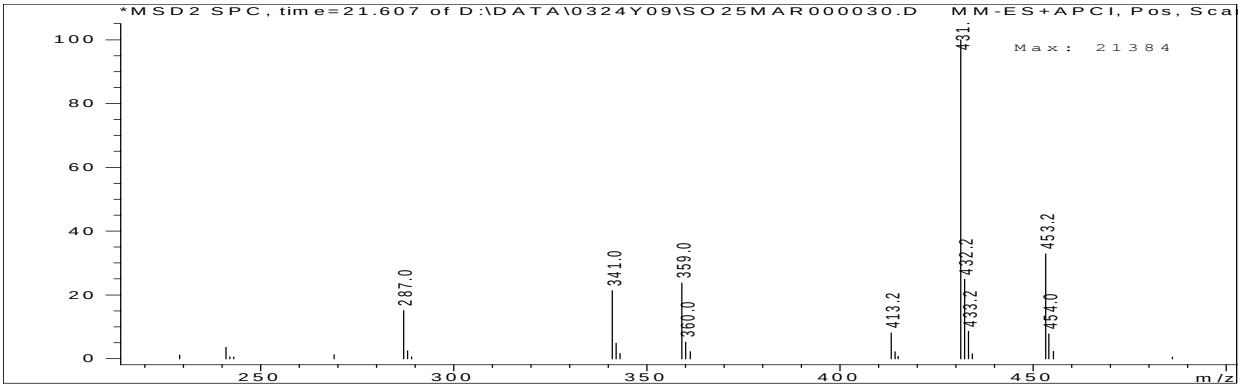
UV spectra of all peaks similar



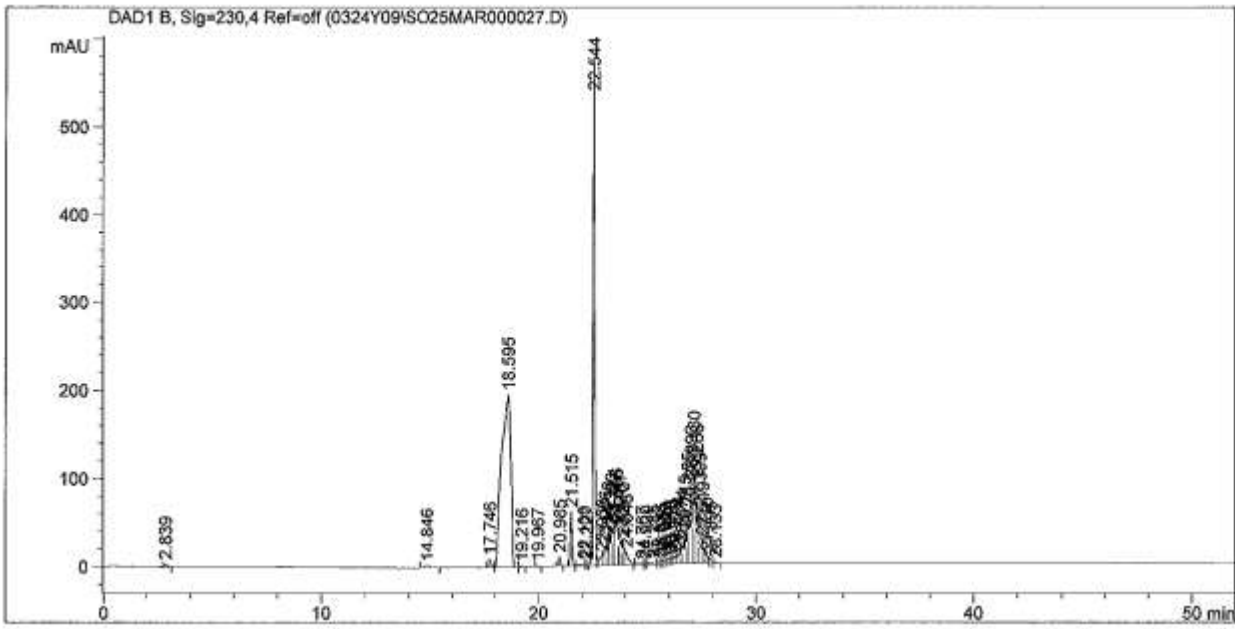




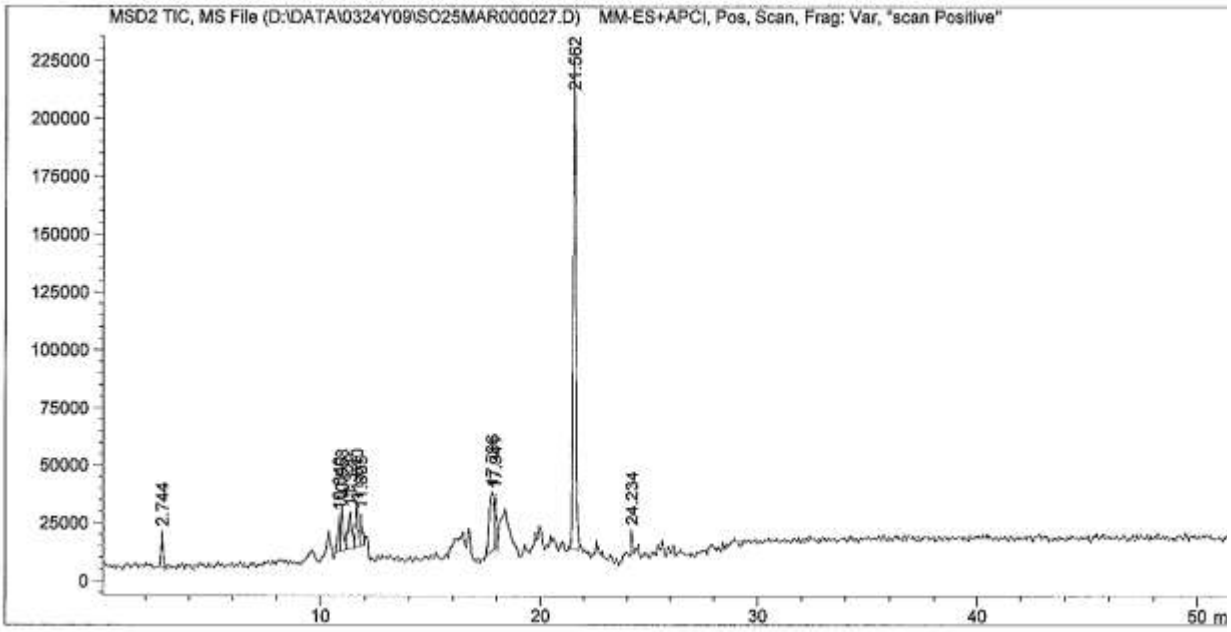



*MSD2 SPC, time=21.607 of D:\DATA\0324Y09\SO25MAR000030.D MM-ES+APCI, Pos, Sca
Max: 21384
100
80
60
40
20
0
250
300
350
400
450
m/z
287.0
341.0
359.0
360.0
413.2
431.
432.2
433.2
453.2
454.0

Genopol AB1 LC-UV chromatogram 230 nm

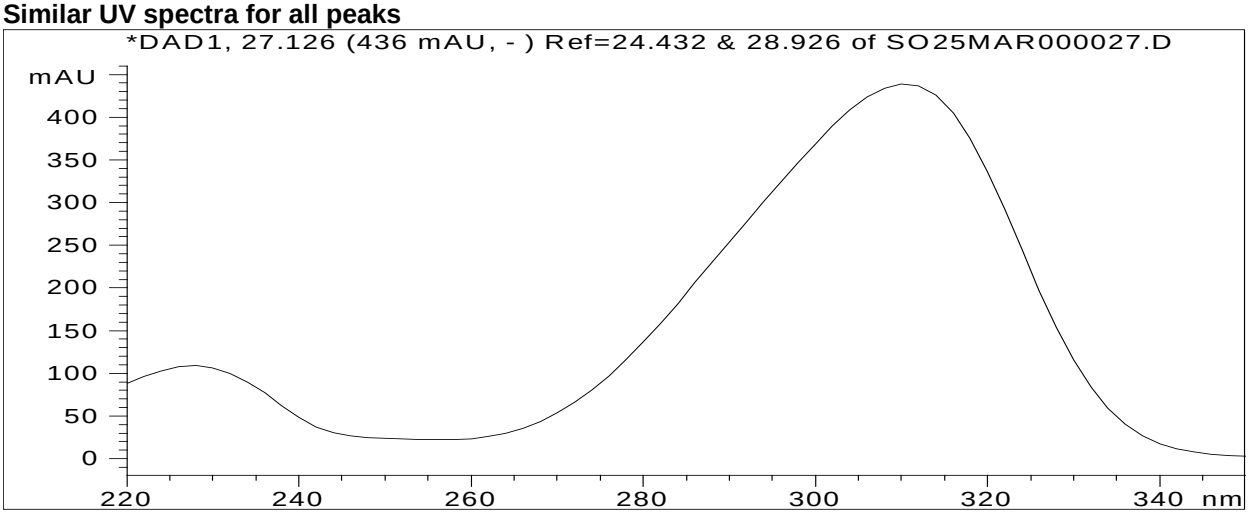


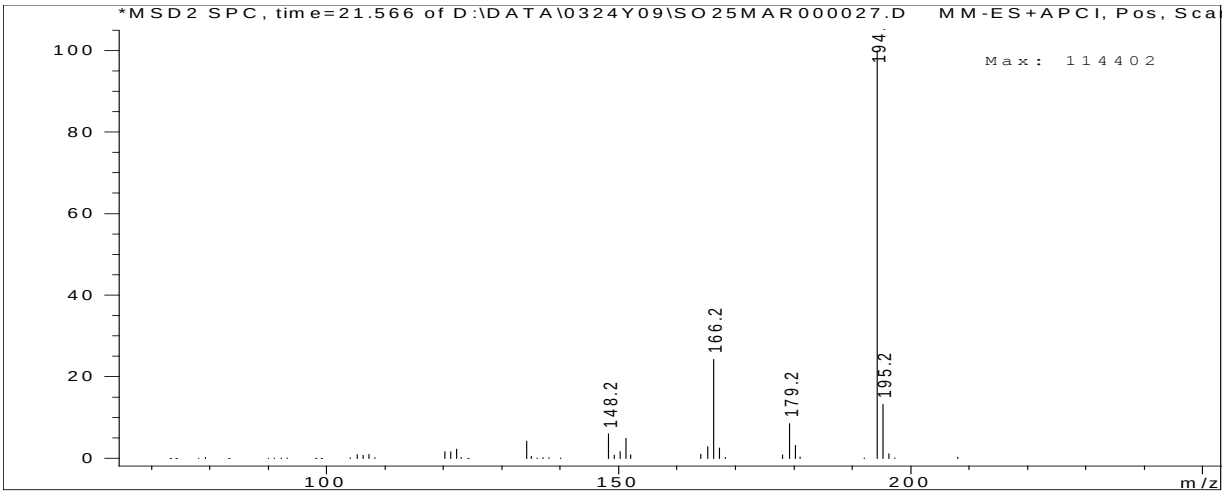
Genopol AB1 LC-MS chromatogram

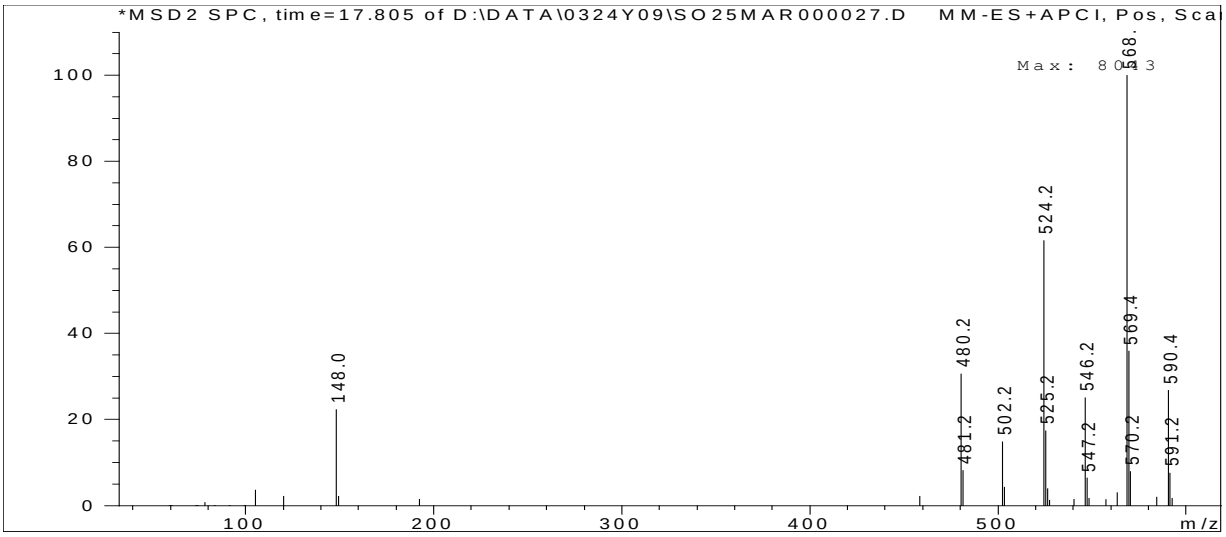


GENOPOL AB1

Similar UV spectra for all peaks

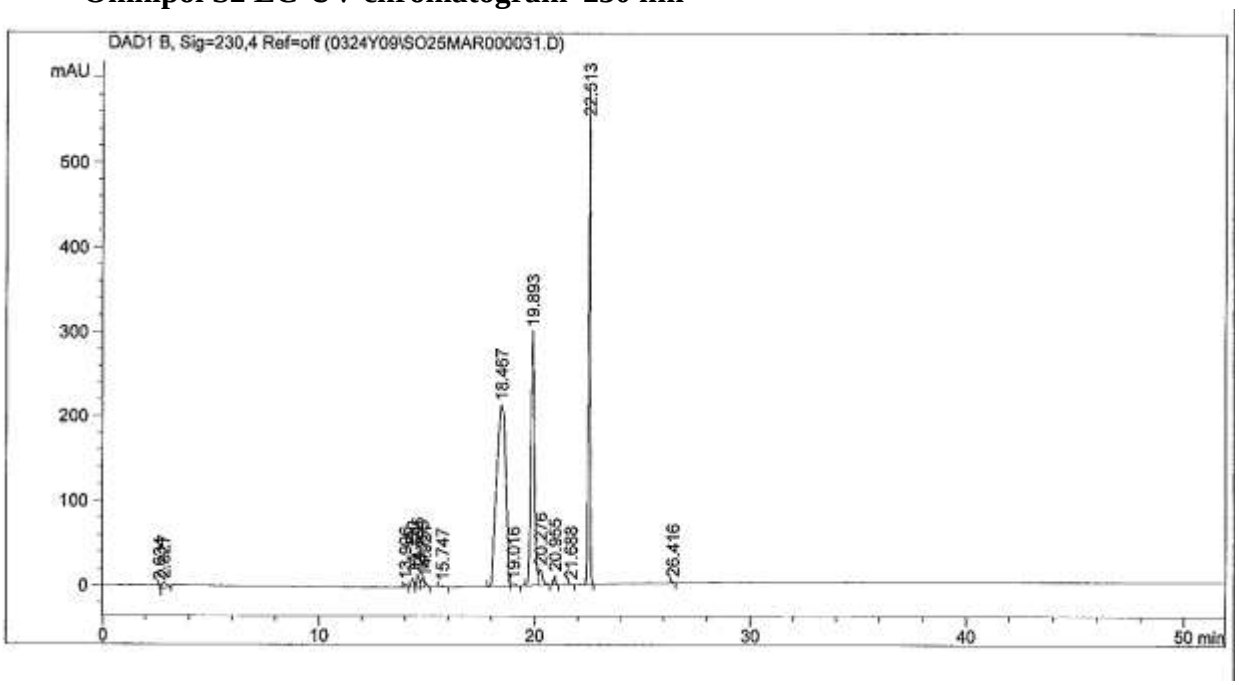




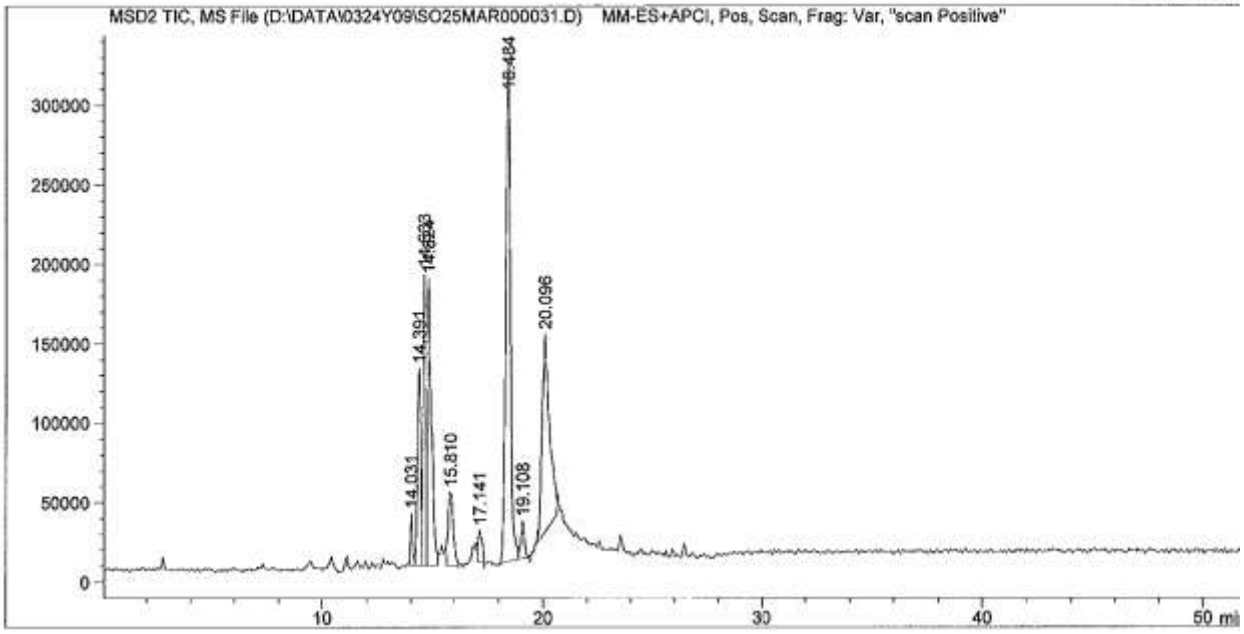


GENOPOL AB1

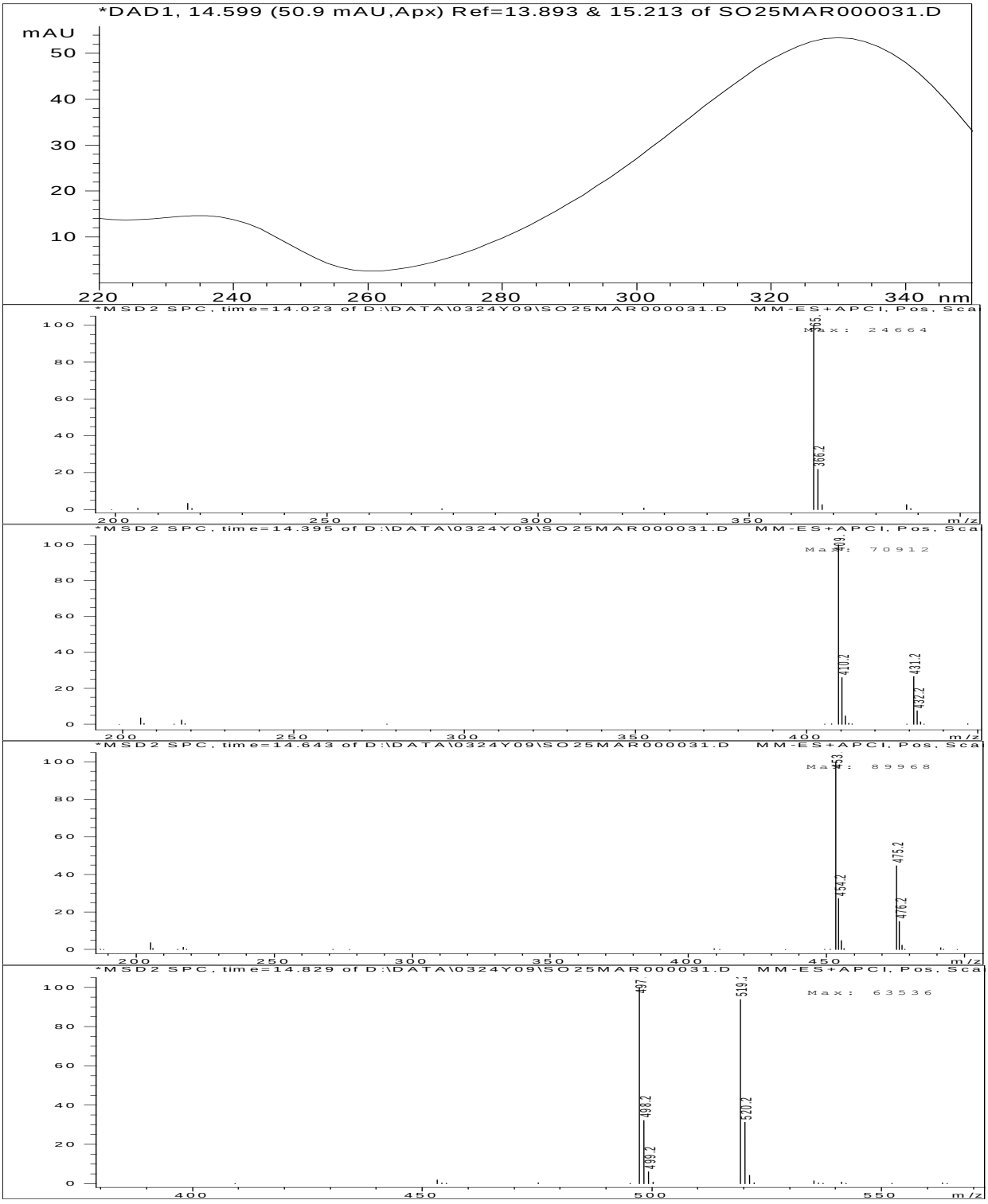
Omnipol S2 LC-UV chromatogram 230 nm

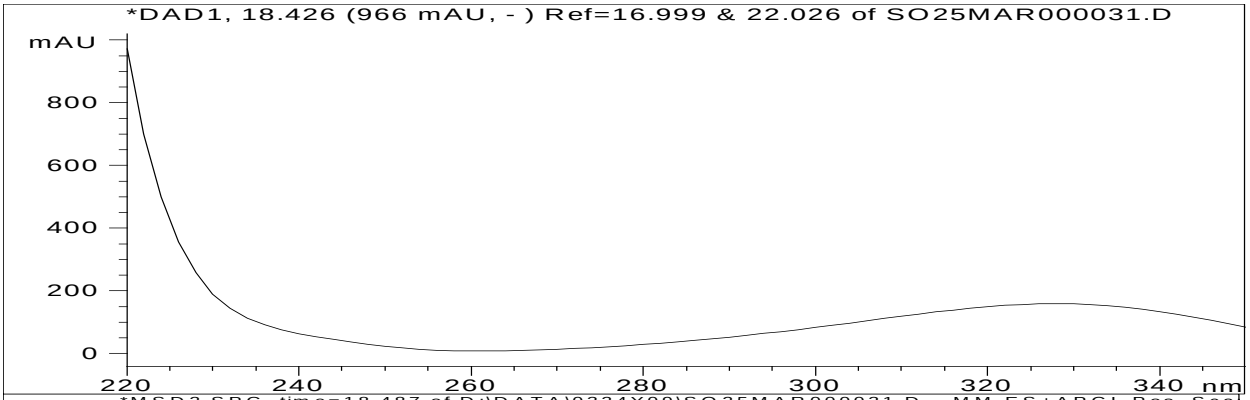


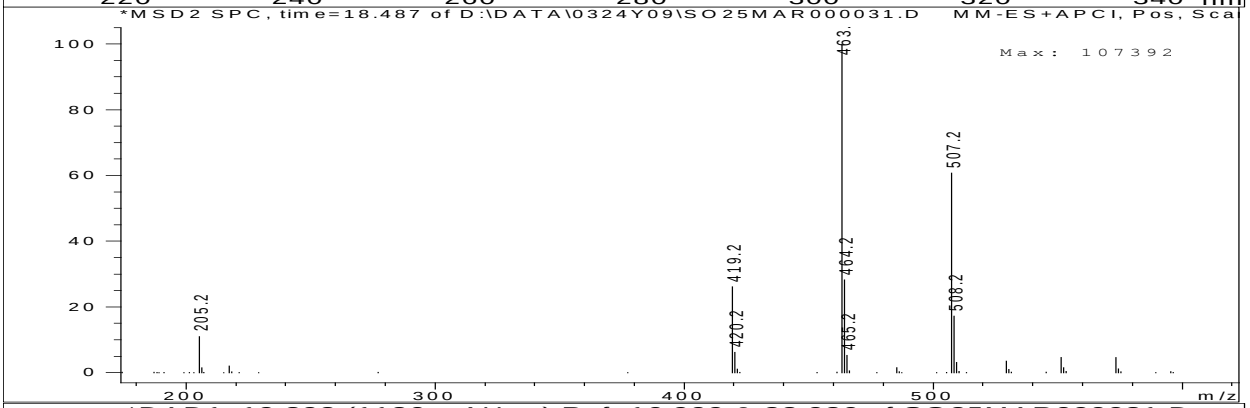
Omnipol S2 LC-MS chromatogram

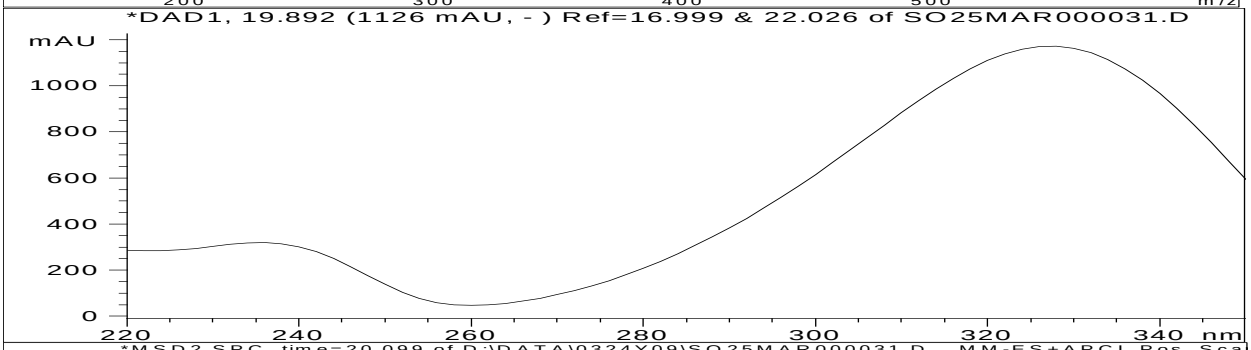


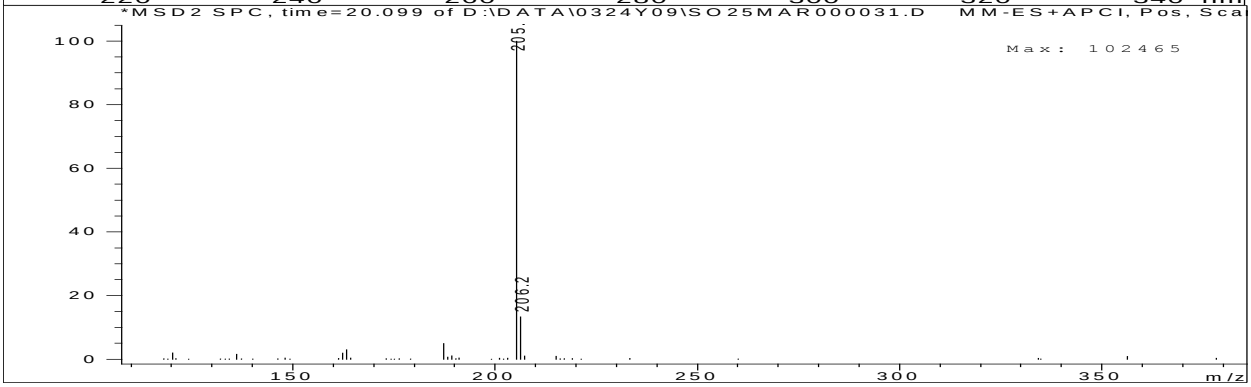
OMNIPOL S2


*DAD1, 14.599 (50.9 mAU,Apx) Ref=13.893 & 15.213 of SO25MAR000031.D
mAU
nm
*MSD2 SPC, time=14.023 of D:\DATA\0324Y09\SO25MAR000031.D MM-ES+APCI, Pos, Sca
Max: 24664
365.2
366.2
*MSD2 SPC, time=14.395 of D:\DATA\0324Y09\SO25MAR000031.D MM-ES+APCI, Pos, Sca
Max: 70912
410.2
431.2
432.2
*MSD2 SPC, time=14.643 of D:\DATA\0324Y09\SO25MAR000031.D MM-ES+APCI, Pos, Sca
Max: 89968
453
454.2
475.2
476.2
*MSD2 SPC, time=14.829 of D:\DATA\0324Y09\SO25MAR000031.D MM-ES+APCI, Pos, Sca
Max: 63536
497
498.2
499.2
519.2
520.2
m/z


*DAD1, 18.426 (966 mAU, -) Ref=16.999 & 22.026 of SO25MAR000031.D
mAU
nm

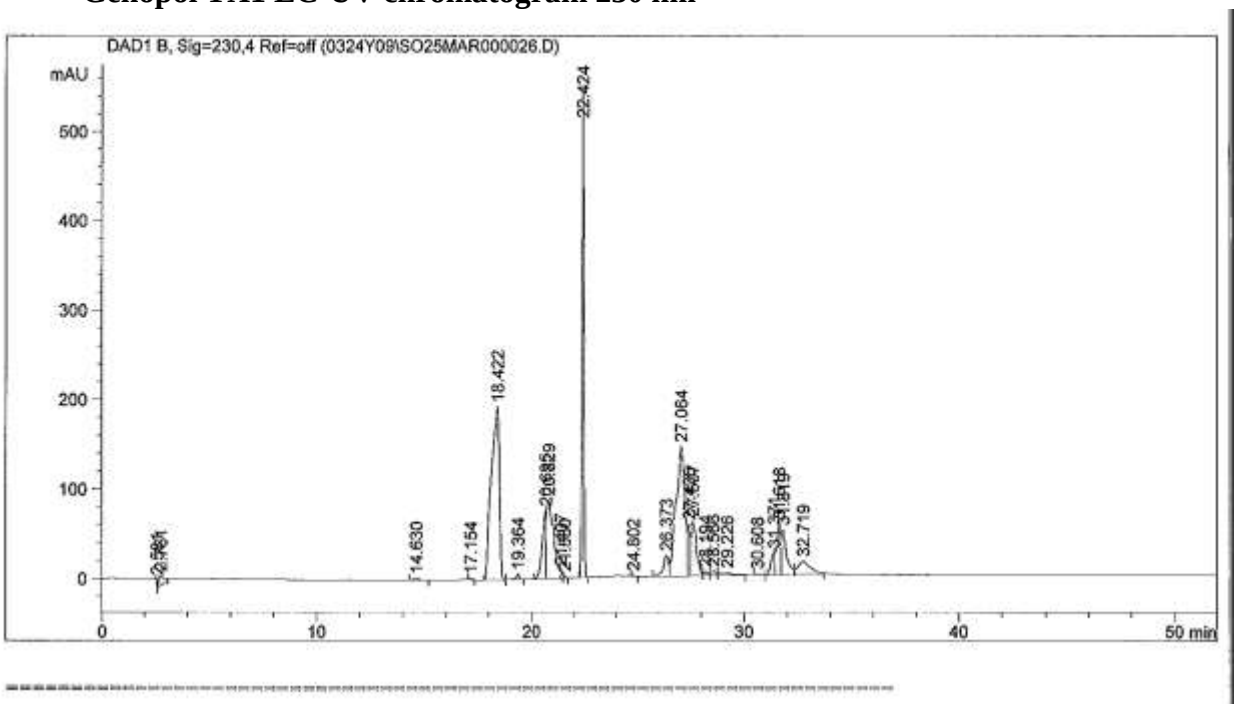

*MSD2 SPC, time=18.487 of D:\DATA\0324Y09\SO25MAR000031.D MM-ES+APCI, Pos, Scal
Max: 107392
463.
507.2
419.2
464.2
205.2
508.2
420.2
465.2
m/z


*DAD1, 19.892 (1126 mAU, -) Ref=16.999 & 22.026 of SO25MAR000031.D
mAU
nm

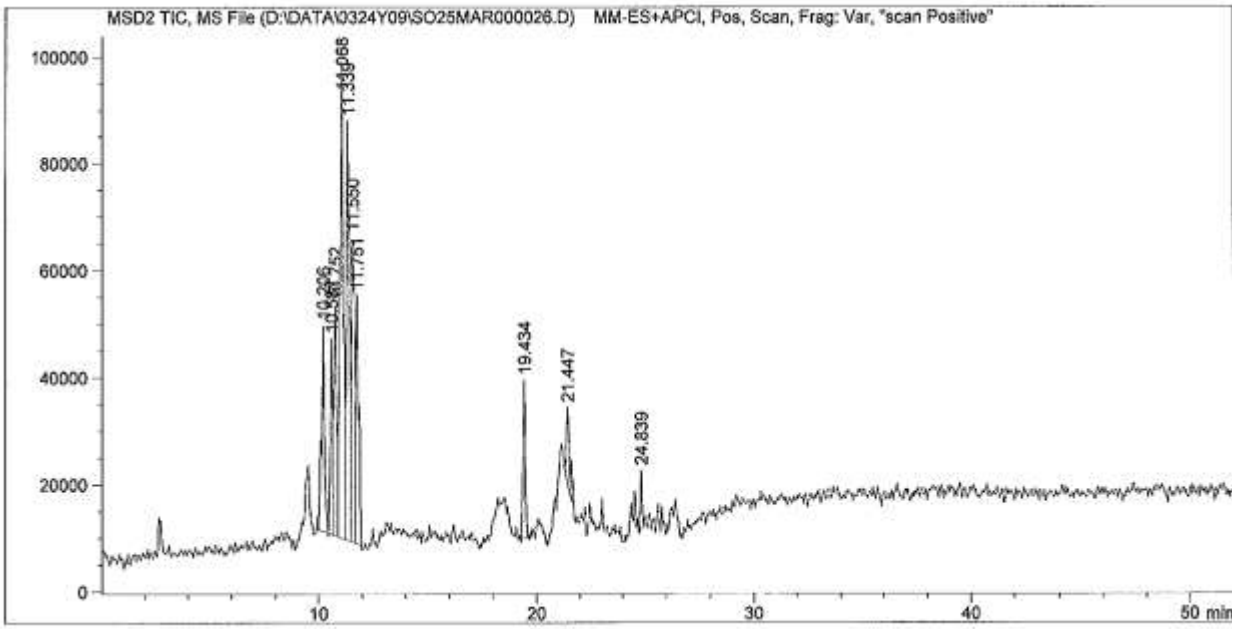

*MSD2 SPC, time=20.099 of D:\DATA\0324Y09\SO25MAR000031.D MM-ES+APCI, Pos, Scal
Max: 102465
205.
206.2
m/z

OMNIPOL S2

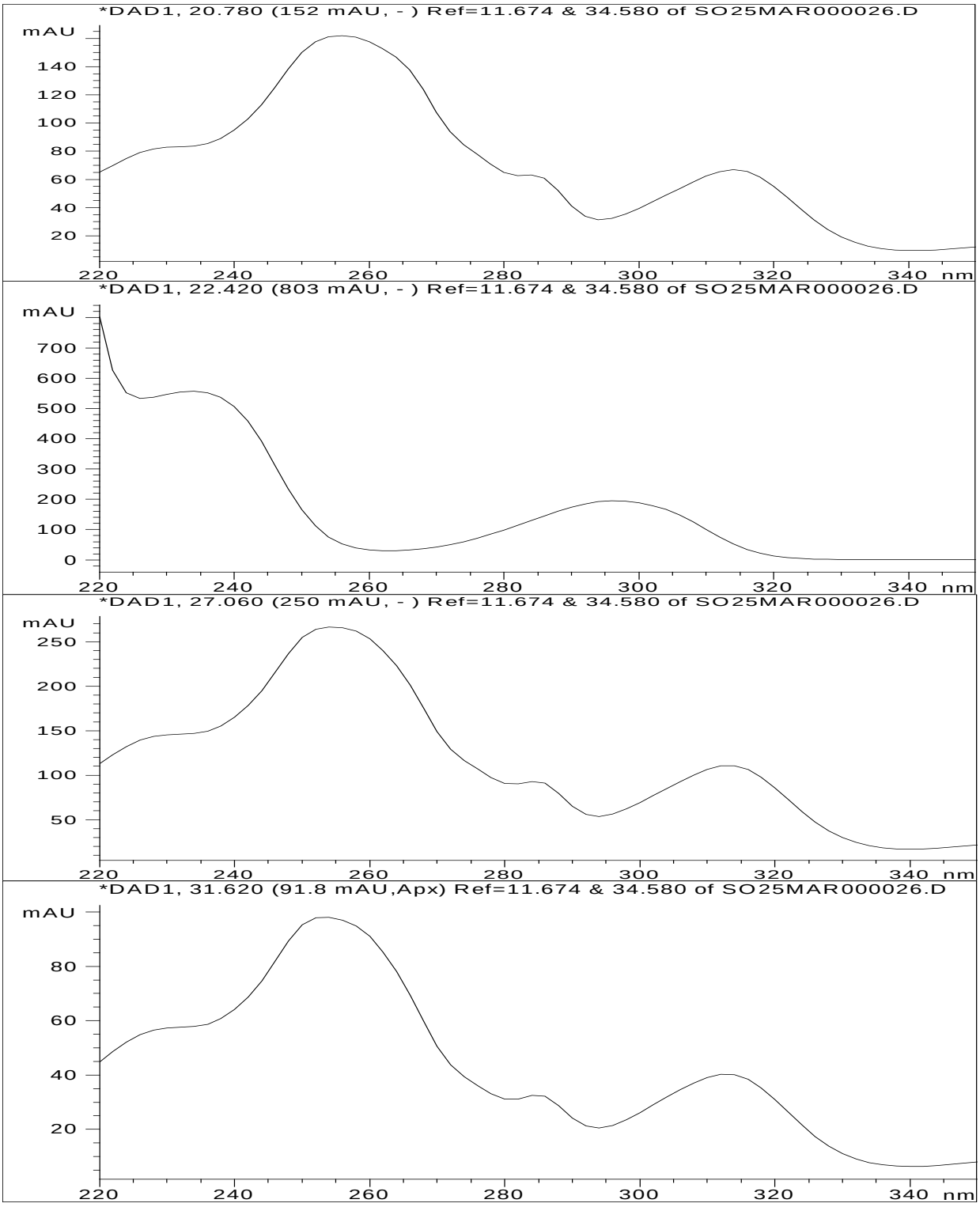
Genopol TX1 LC-UV chromatogram 230 nm

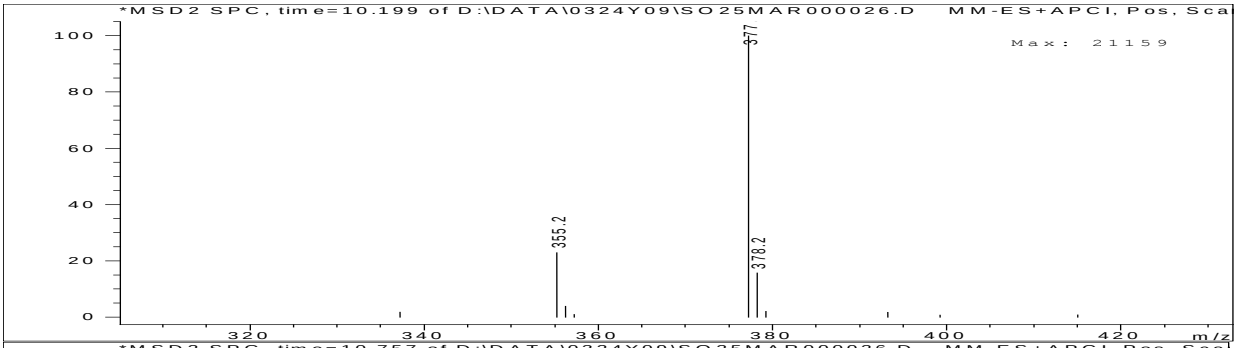


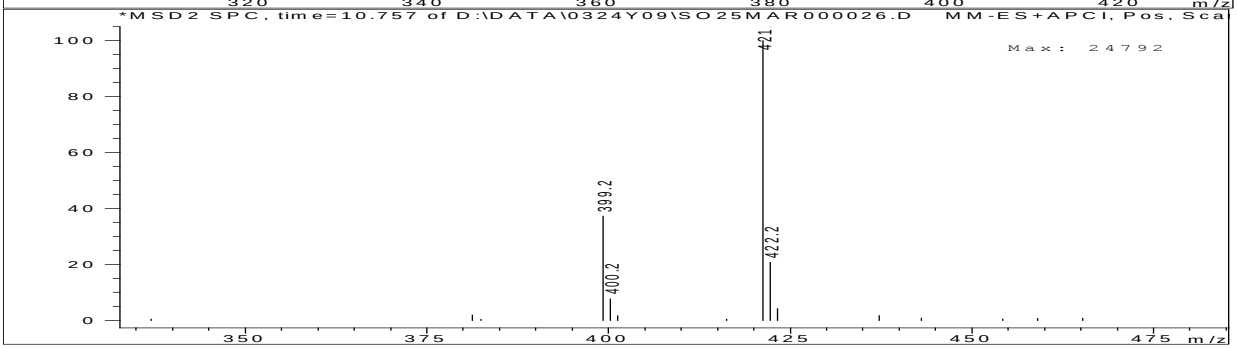
Genopol TX1 LC-MS chromatogram

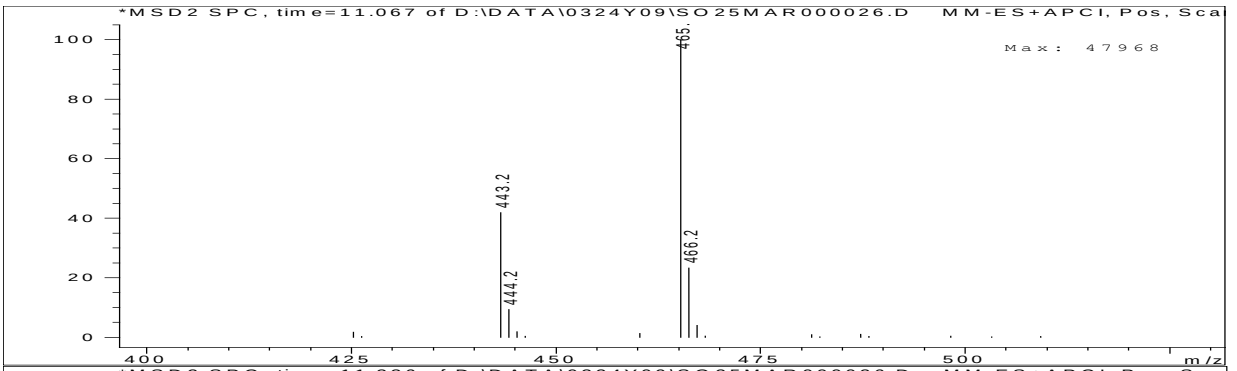


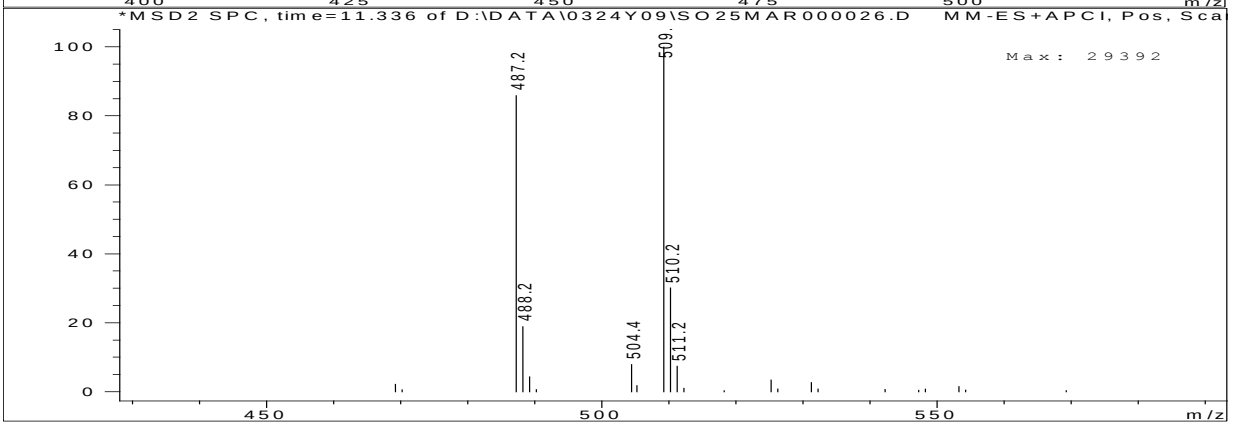
GENOPOL TX1

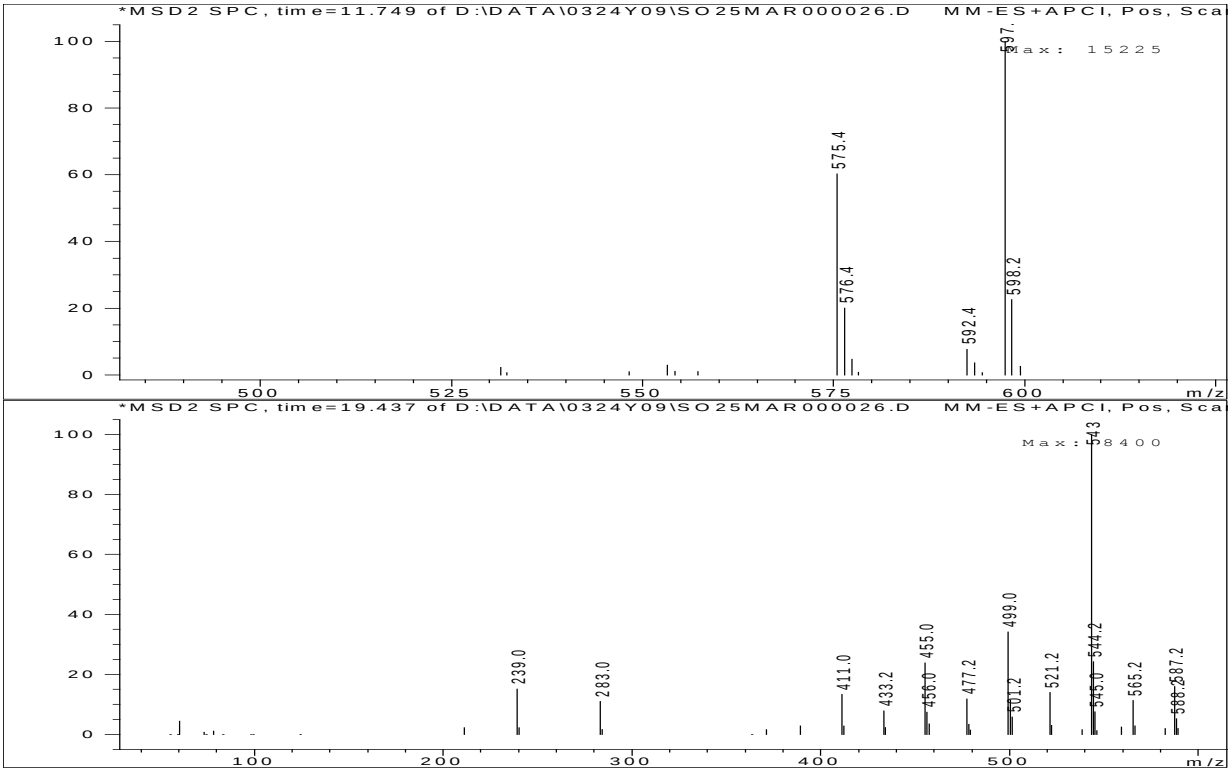

*DAD1, 20.780 (152 mAU, -) Ref=11.674 & 34.580 of SO25MAR000026.D
mAU
140
120
100
80
60
40
20
220
240
260
280
300
320
340 nm
*DAD1, 22.420 (803 mAU, -) Ref=11.674 & 34.580 of SO25MAR000026.D
mAU
700
600
500
400
300
200
100
0
220
240
260
280
300
320
340 nm
*DAD1, 27.060 (250 mAU, -) Ref=11.674 & 34.580 of SO25MAR000026.D
mAU
250
200
150
100
50
220
240
260
280
300
320
340 nm
*DAD1, 31.620 (91.8 mAU,Apx) Ref=11.674 & 34.580 of SO25MAR000026.D
mAU
80
60
40
20
220
240
260
280
300
320
340 nm


*MSD2 SPC, time=10.199 of D:\DATA\0324Y09\SO25MAR000026.D MM-ES+APCI, Pos, Scal
Max: 21159
377
355.2
378.2
m/z

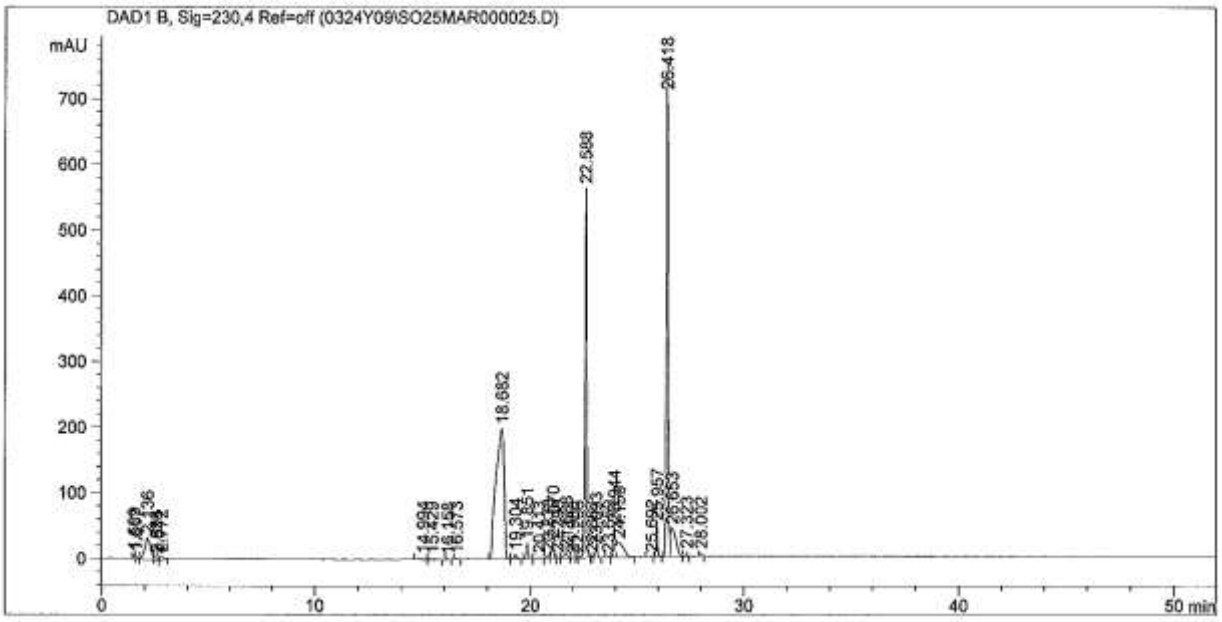

*MSD2 SPC, time=10.757 of D:\DATA\0324Y09\SO25MAR000026.D MM-ES+APCI, Pos, Scal
Max: 24792
421
399.2
400.2
422.2
m/z


*MSD2 SPC, time=11.067 of D:\DATA\0324Y09\SO25MAR000026.D MM-ES+APCI, Pos, Scal
Max: 47968
465.
443.2
444.2
466.2
m/z

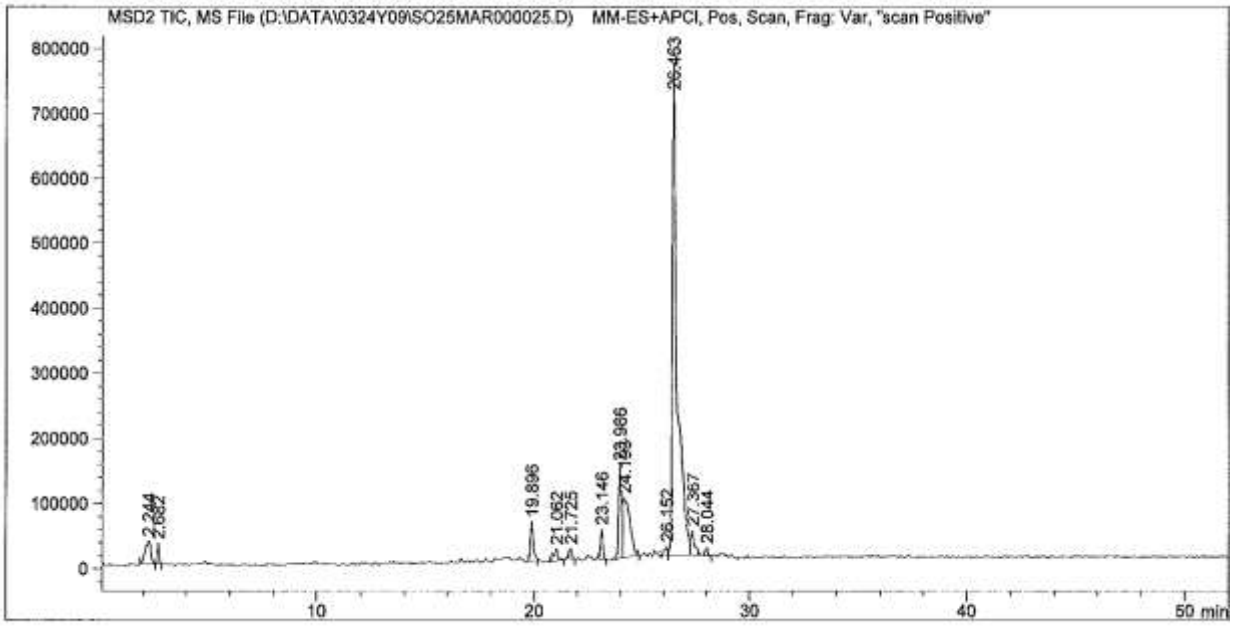

*MSD2 SPC, time=11.336 of D:\DATA\0324Y09\SO25MAR000026.D MM-ES+APCI, Pos, Scal
Max: 29392
509.
487.2
488.2
504.4
510.2
511.2
m/z


*MSD2 SPC, time=11.749 of D:\DATA\0324Y09\SO25MAR000026.D MM-ES+APCI, Pos, Scan
Max: 15225
575.4
576.4
592.4
597.
598.2
m/z
*MSD2 SPC, time=19.437 of D:\DATA\0324Y09\SO25MAR000026.D MM-ES+APCI, Pos, Scan
Max: 58400
239.0
283.0
411.0
433.2
455.0
456.0
477.2
499.0
501.2
521.2
543
544.2
545.0
565.2
587.2
588.2
m/z

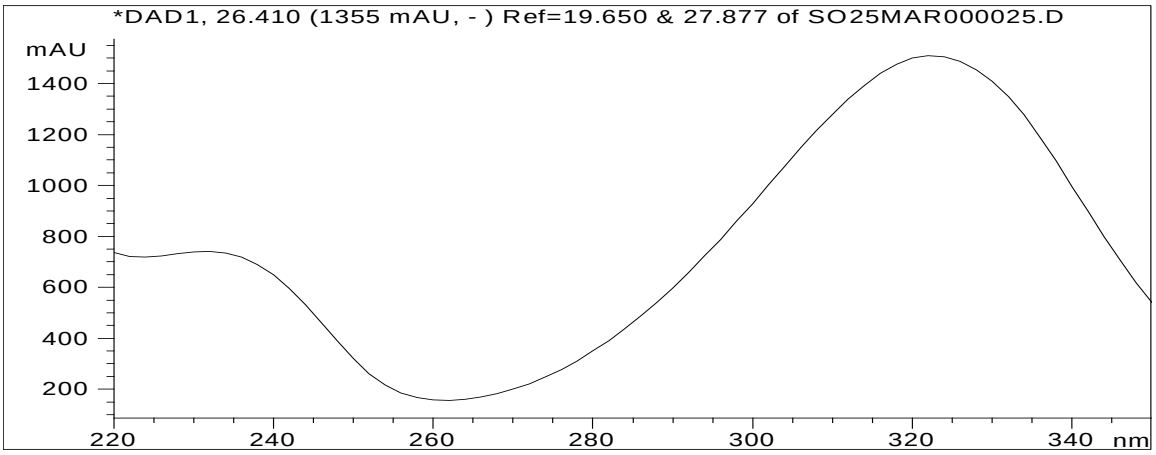
Irgacure 369 LC-UV chromatogram 230 nm

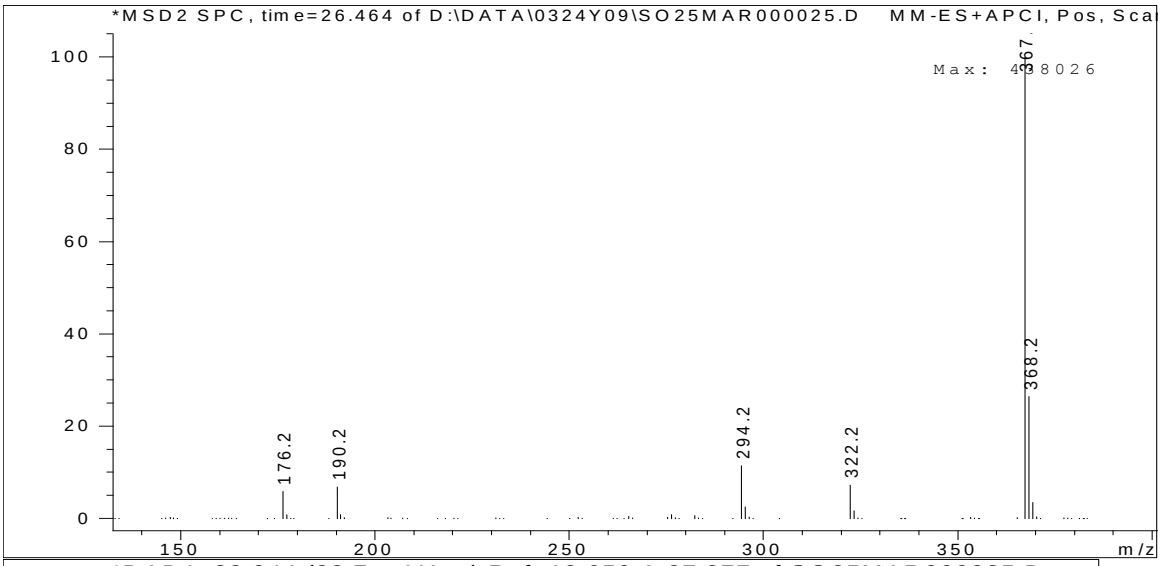


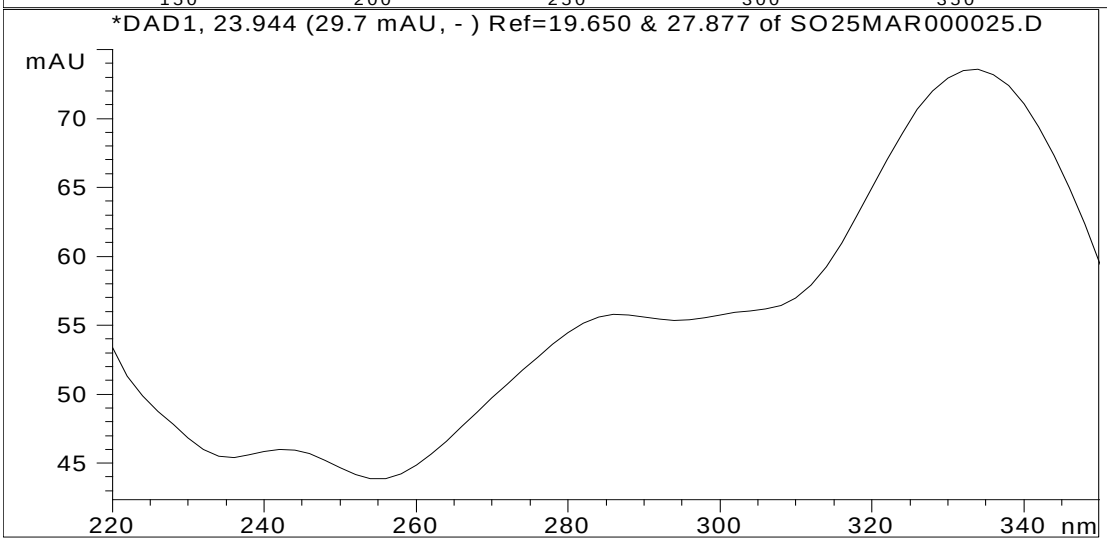
Irgacure 369 LC-MS chromatogram

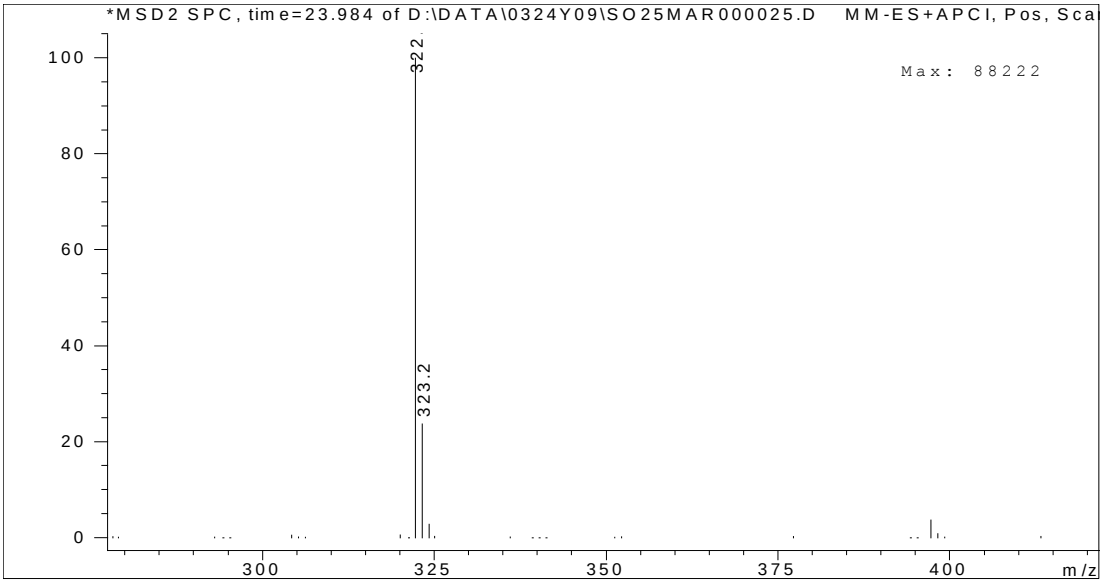


IRGACURE 369

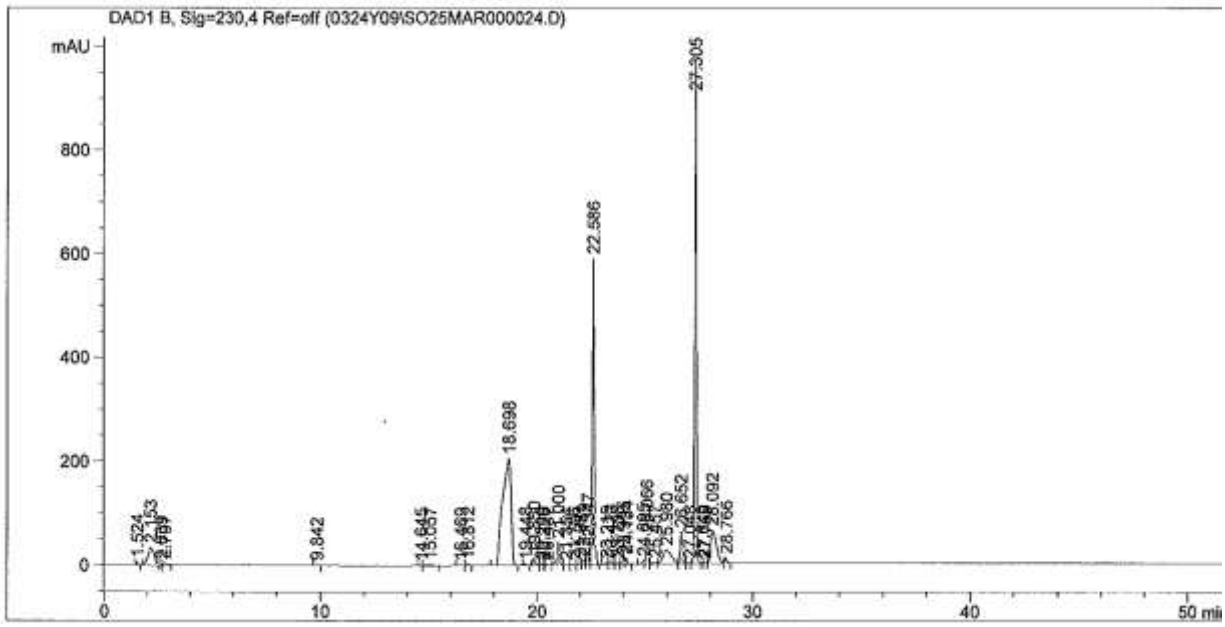




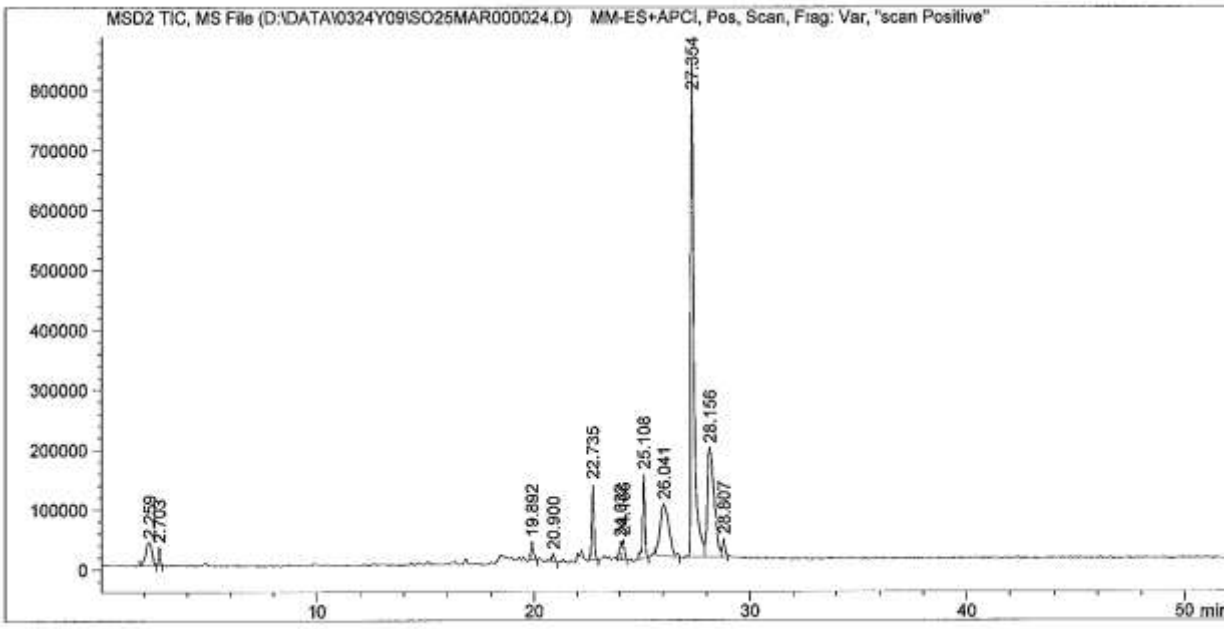


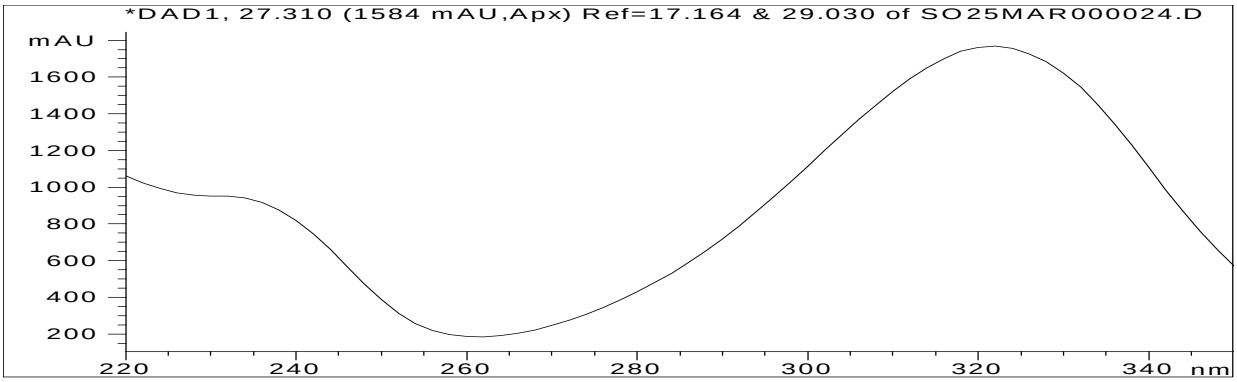

*MSD2 SPC, time=23.984 of D:\DATA\0324Y09\SO25MAR000025.D MM-ES+APCI, Pos, Scal
Max: 88222
322.
323.2
100
80
60
40
20
0
300
325
350
375
400
m/z

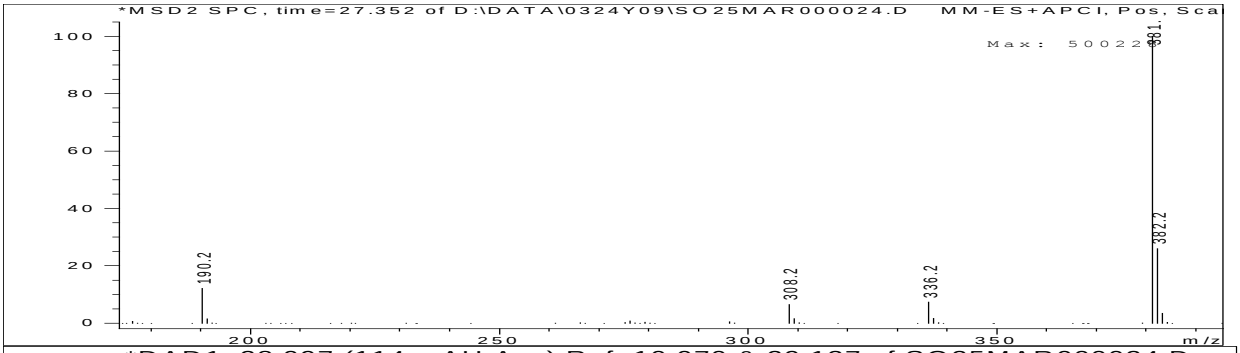
Irgacure 379 LC-UV chromatogram 230 nm

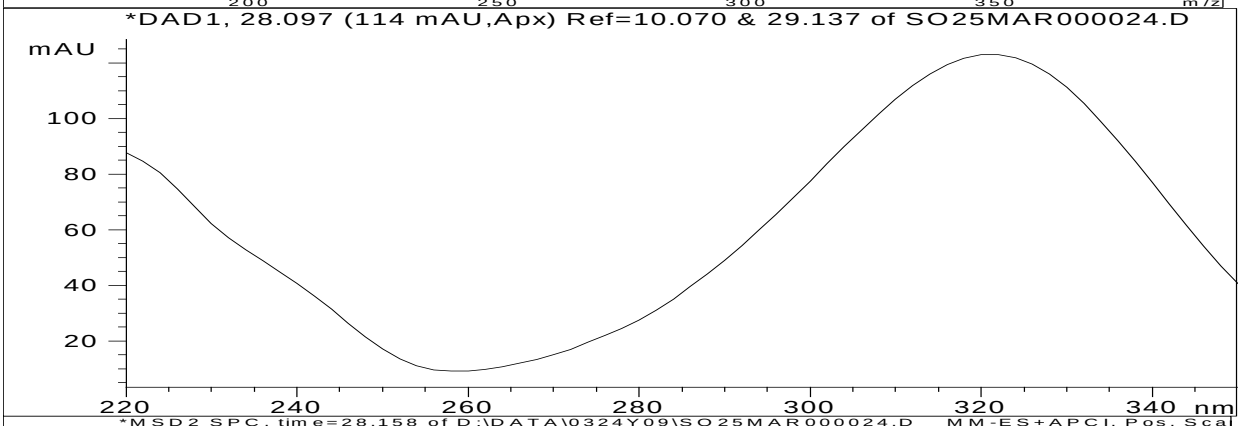


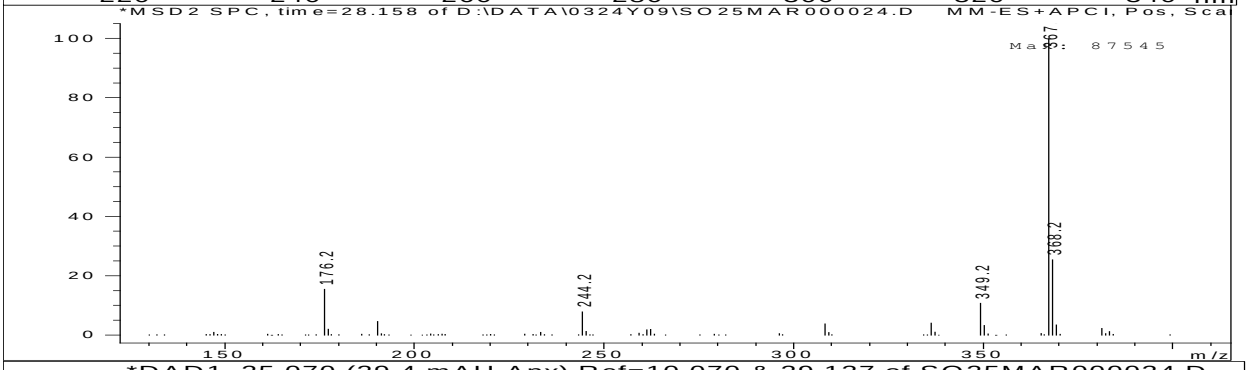
Irgacure 379 LC-MS chromatogram

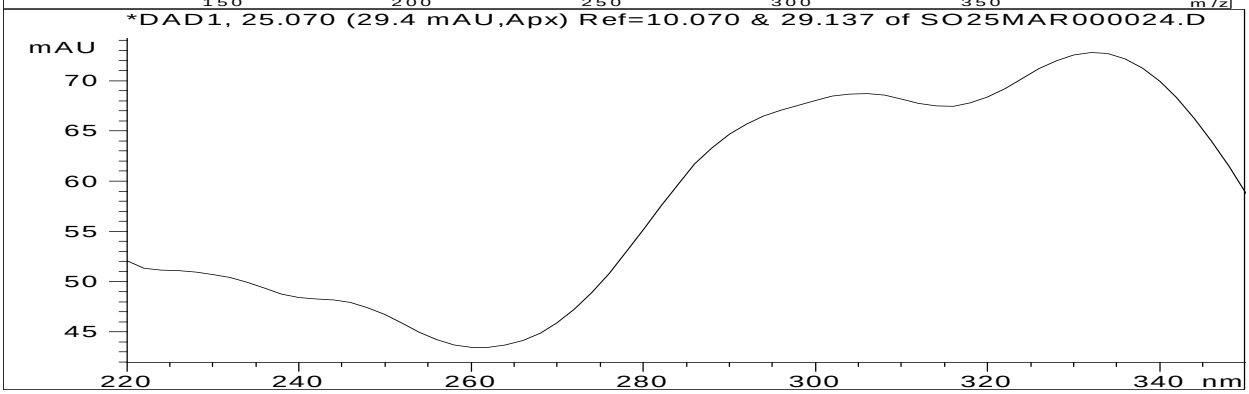


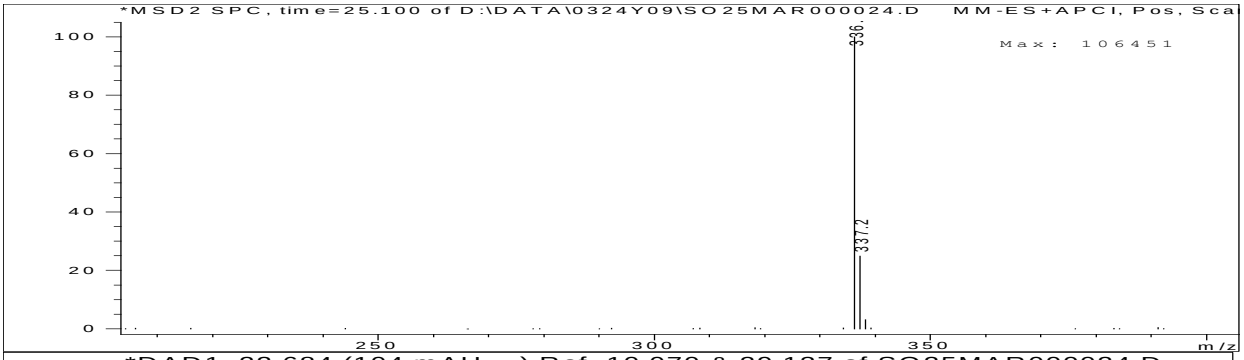


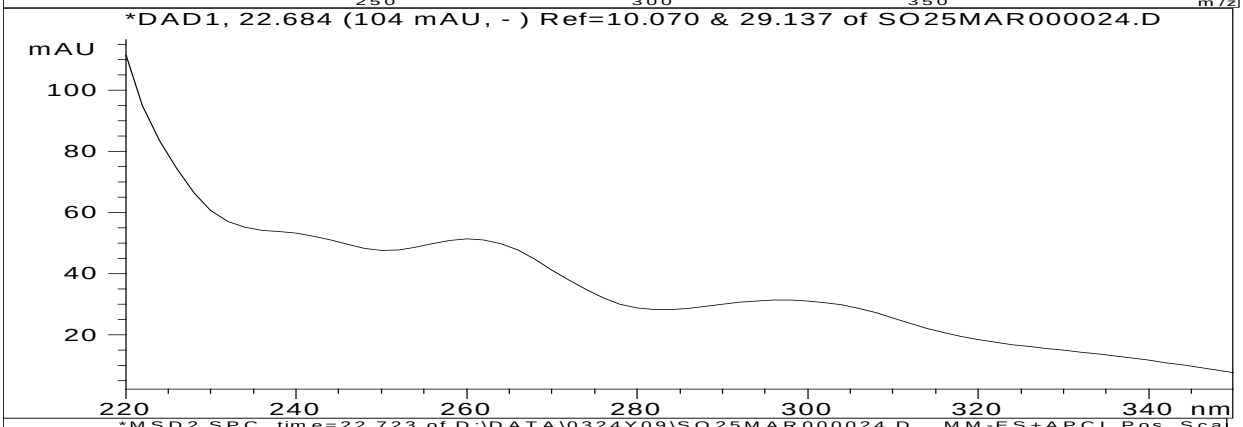

*MSD2 SPC, time=27.352 of D:\DATA\0324Y09\SO25MAR000024.D MM-ES+APCI, Pos, Scan
Max: 50022
381.2
382.2
190.2
308.2
336.2
m/z

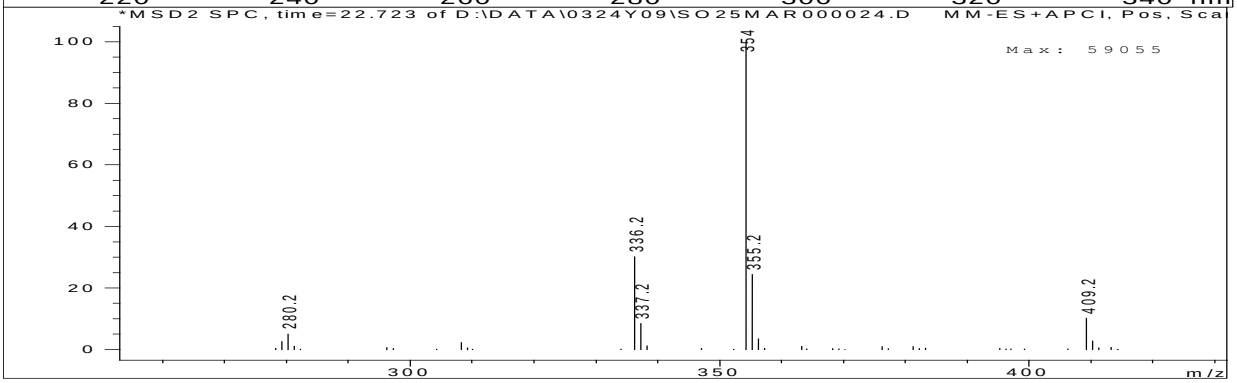

*DAD1, 28.097 (114 mAU,Apx) Ref=10.070 & 29.137 of SO25MAR000024.D
mAU
nm


*MSD2 SPC, time=28.158 of D:\DATA\0324Y09\SO25MAR000024.D MM-ES+APCI, Pos, Scan
Max: 87545
367.2
368.2
176.2
244.2
349.2
m/z

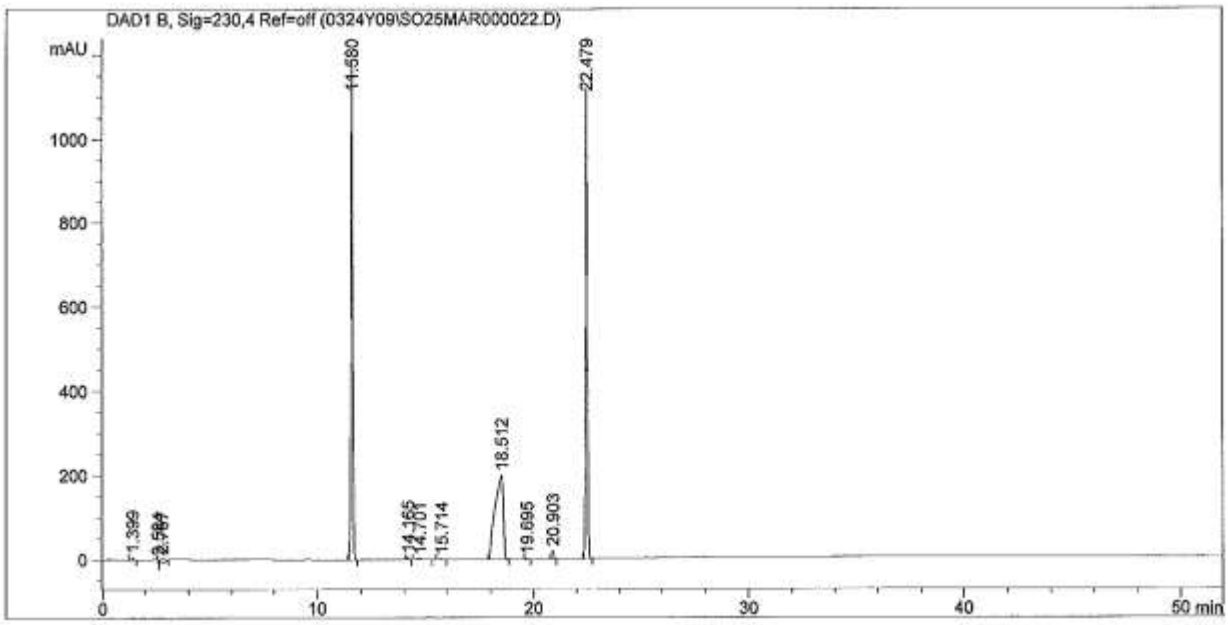

*DAD1, 25.070 (29.4 mAU,Apx) Ref=10.070 & 29.137 of SO25MAR000024.D
mAU
nm


*MSD2 SPC, time=25.100 of D:\DATA\0324Y09\SO25MAR000024.D MM-ES+APCI, Pos, Scal
Max: 106451
336.
337.2
m/z

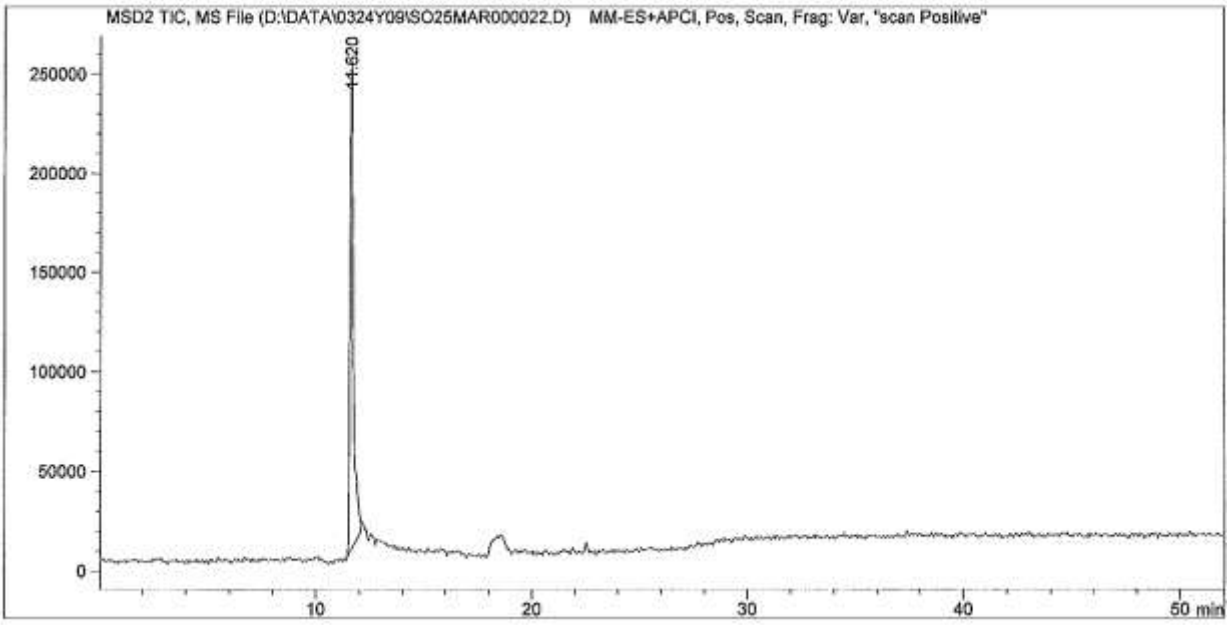

*DAD1, 22.684 (104 mAU, -) Ref=10.070 & 29.137 of SO25MAR000024.D
mAU
nm


*MSD2 SPC, time=22.723 of D:\DATA\0324Y09\SO25MAR000024.D MM-ES+APCI, Pos, Scal
Max: 59055
354
336.2
355.2
337.2
280.2
409.2
m/z

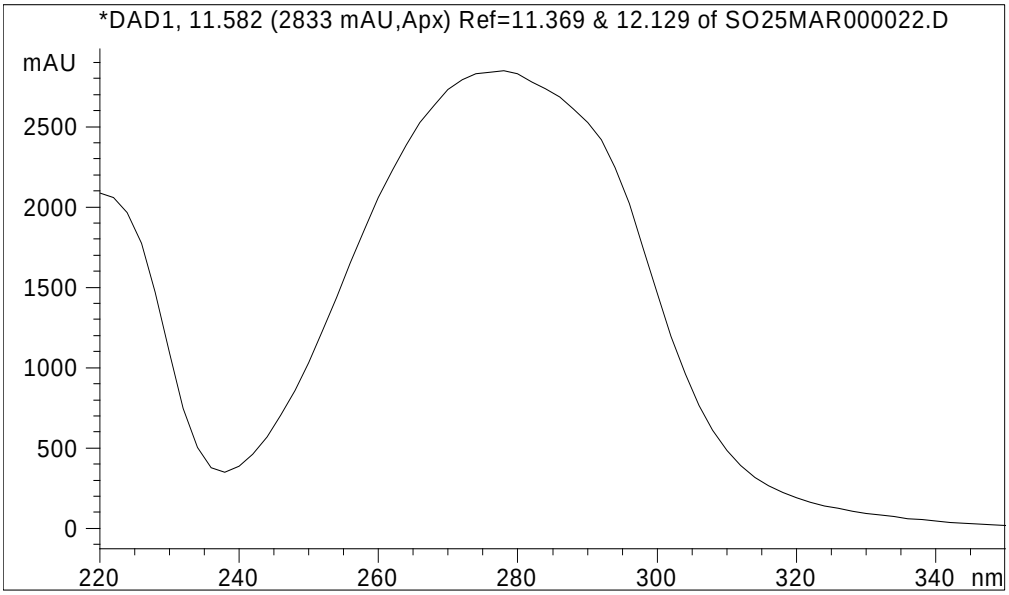
LC-UV chromatogram Irgacure 2959 at 230 nm

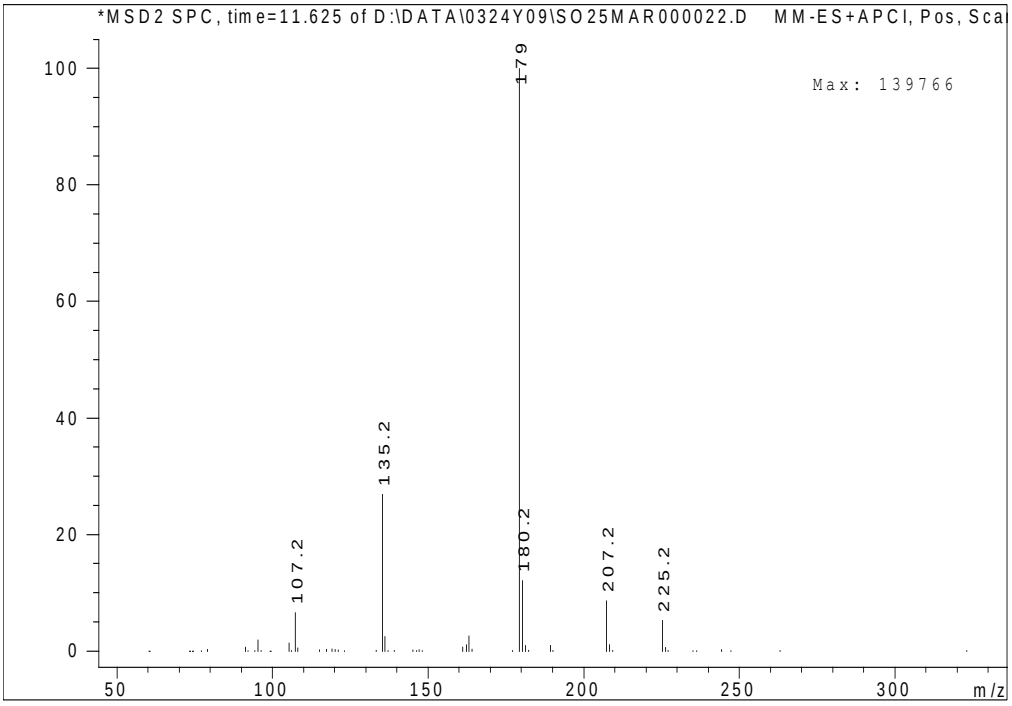


LC-MS chromatogram Irgacure 2659

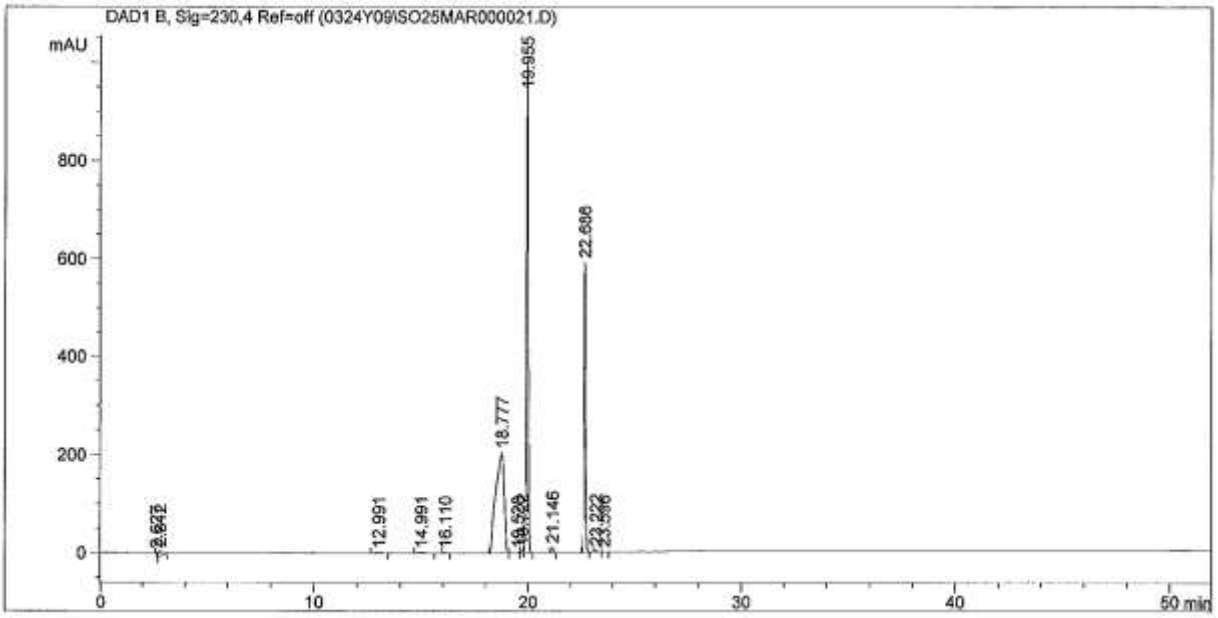


IRGACURE 2659

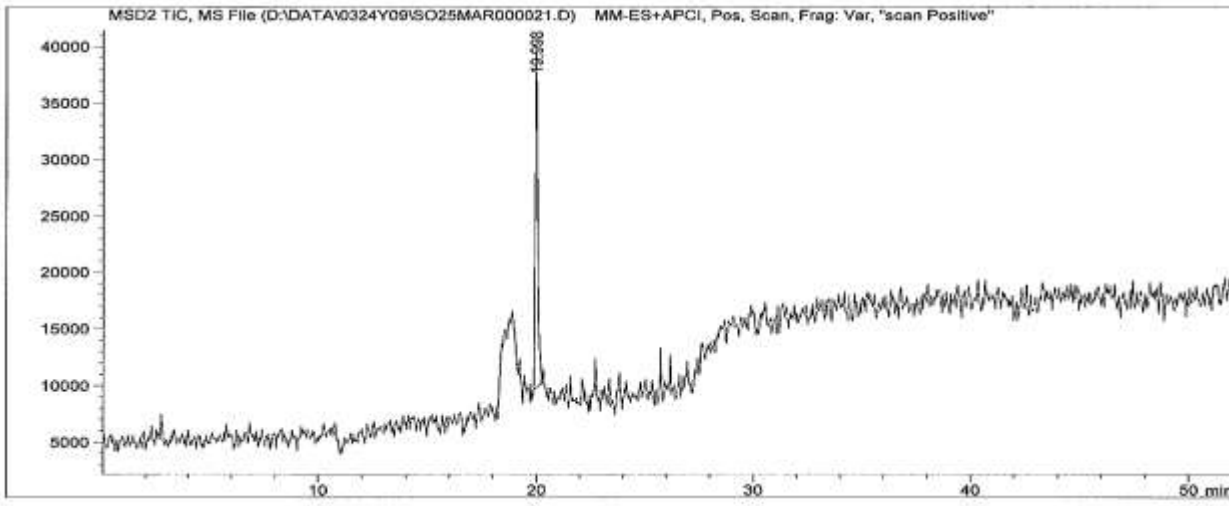




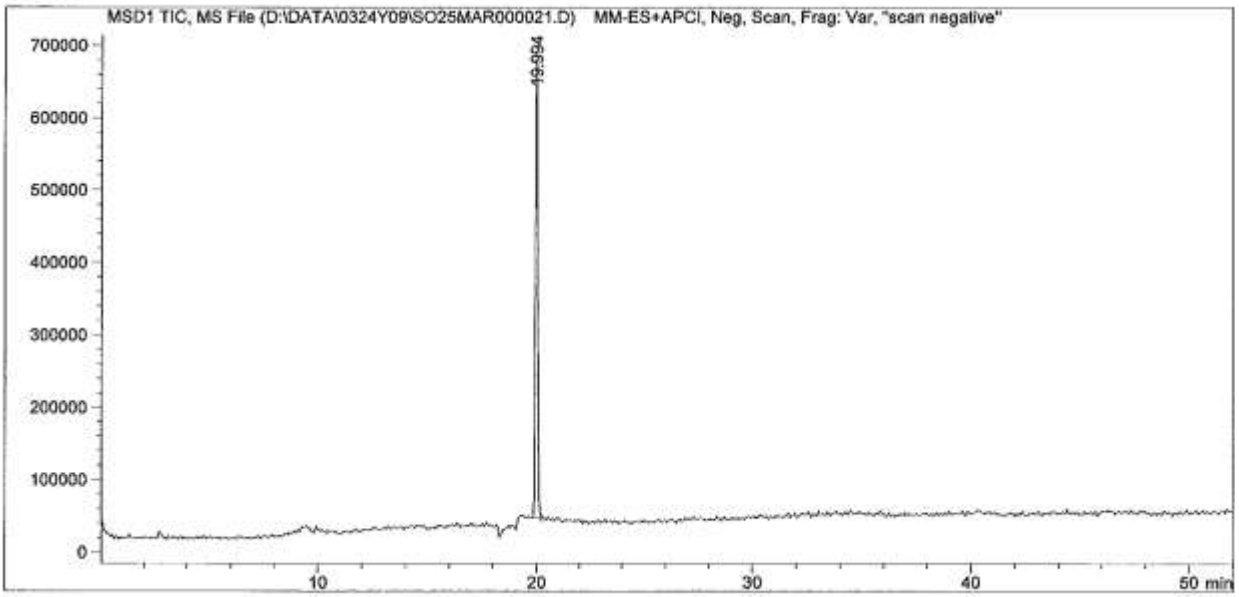
Irgacure 127 LC-UV chromatogram



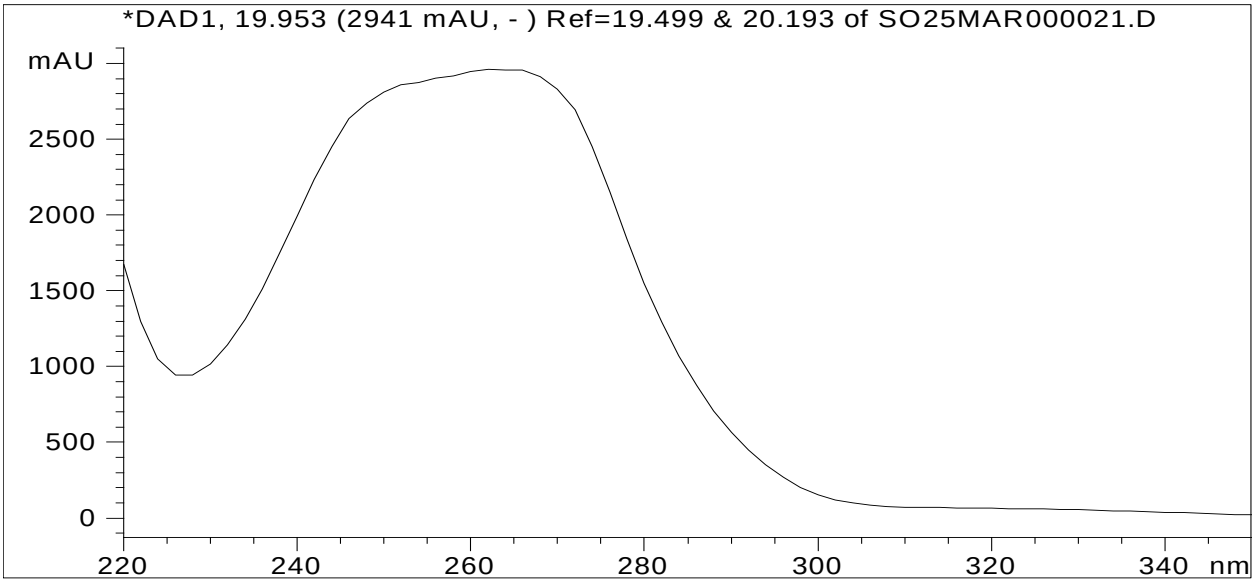
Irgacure 127 LC-MS chromatogram

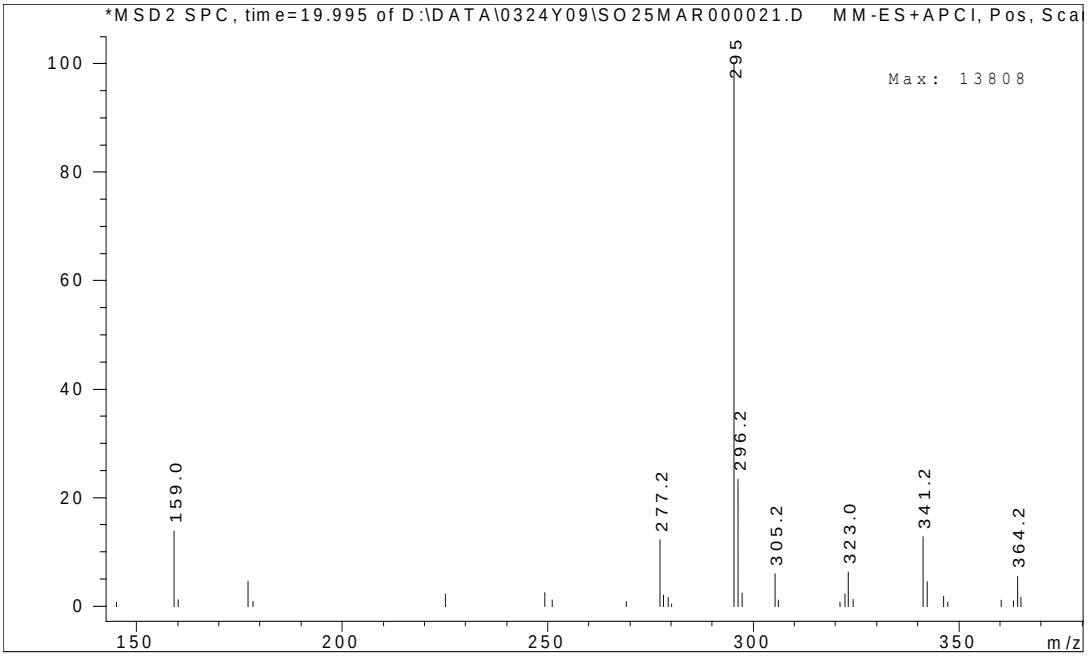


Irgacure 127 LC-MS chromatogram obtained in the negative scan mode

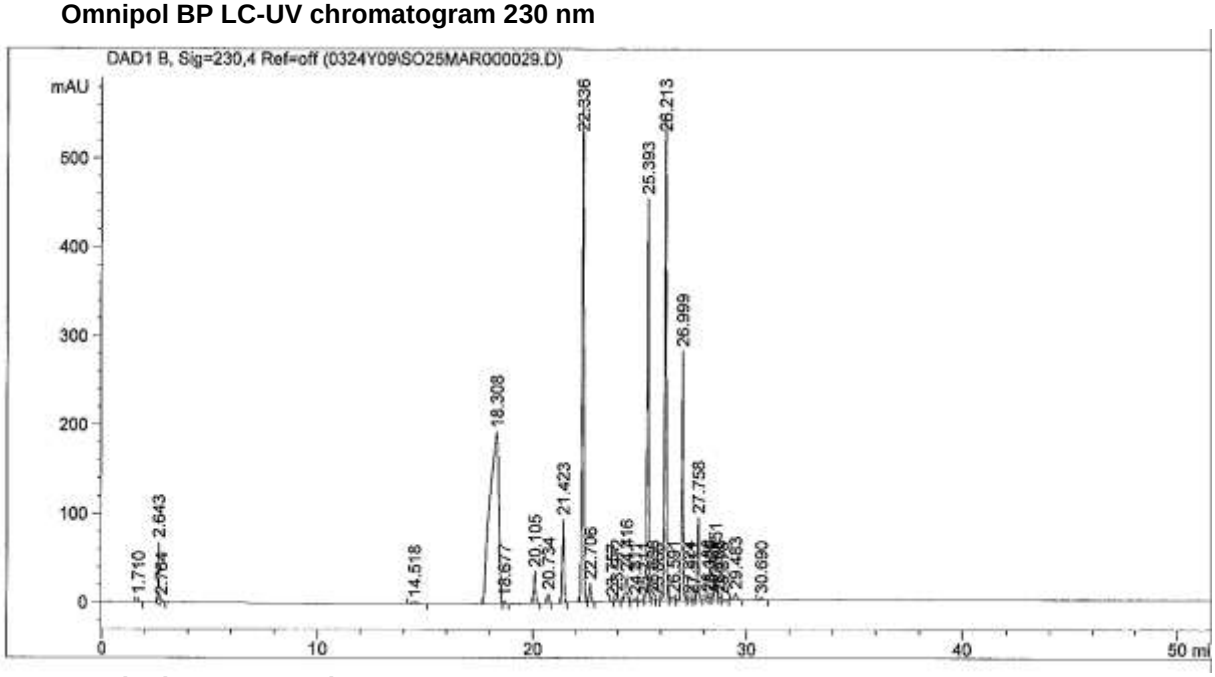


IRGACURE127

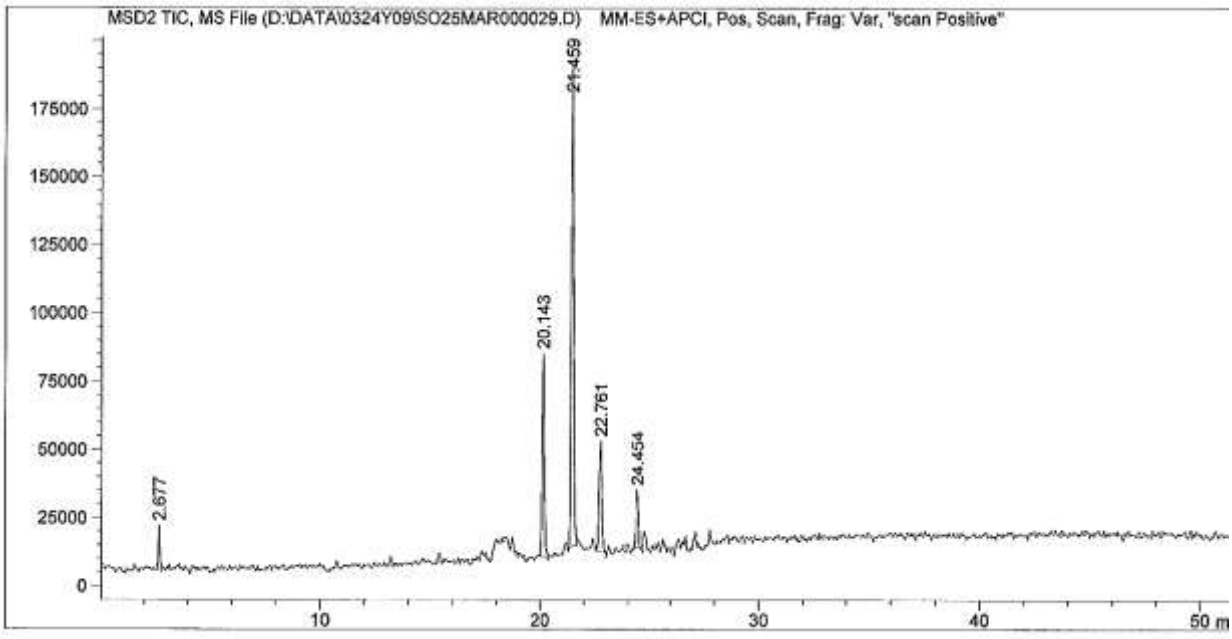



*MSD2 SPC, time=19.995 of D:\DATA\0324Y09\SO25MAR000021.D MM-ES+APCI, Pos, Sca
Max: 13808
100
80
60
40
20
0
150
200
250
300
350
m/z
159.0
277.2
295
296.2
305.2
323.0
341.2
364.2

Omnipol BP LC-UV chromatogram 230 nm

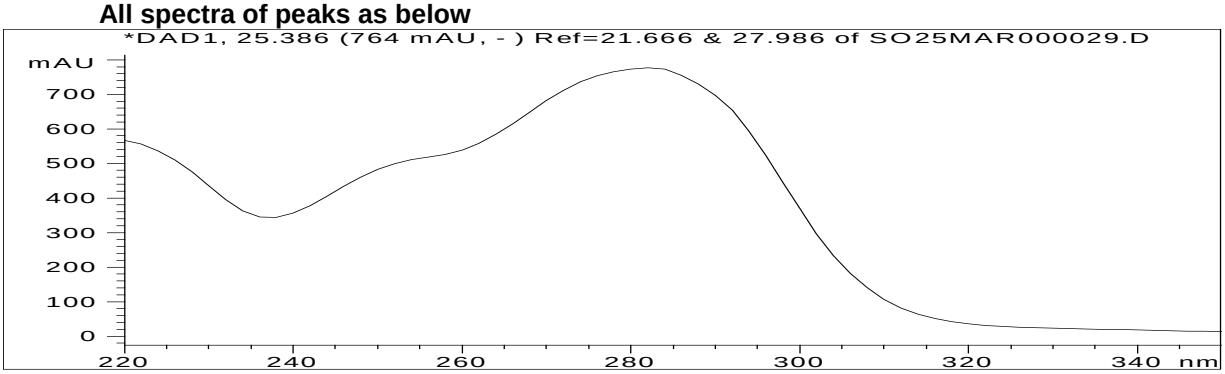


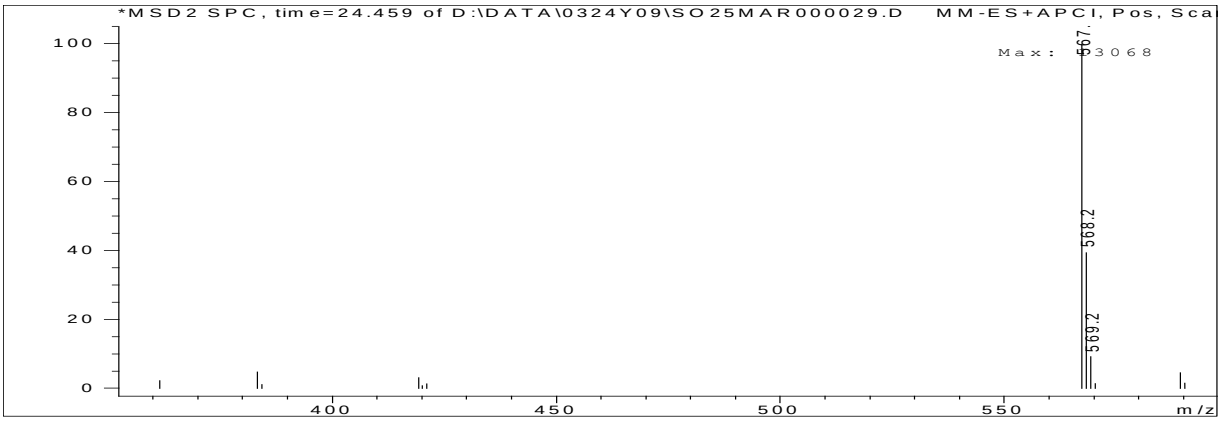
Omnipol BP LC-MS chromatogram

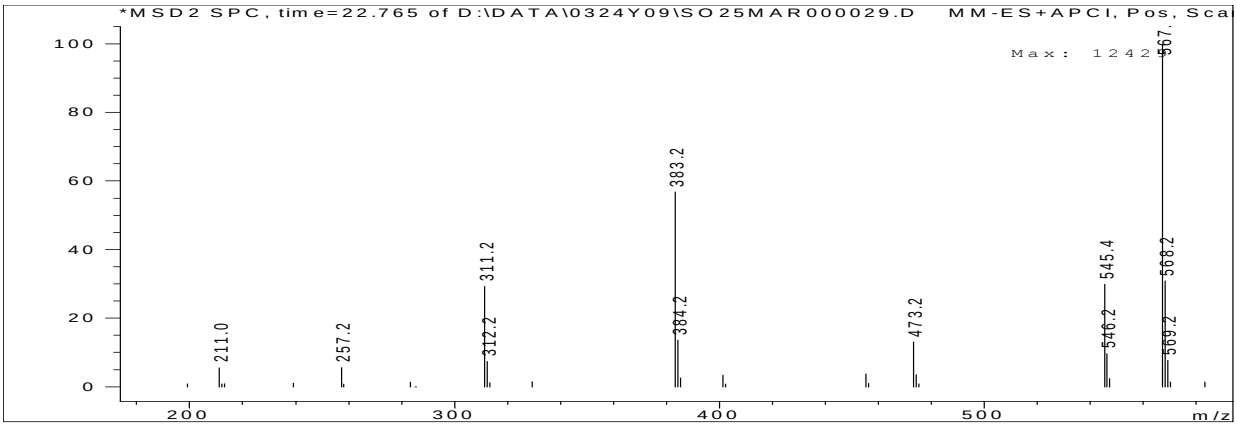


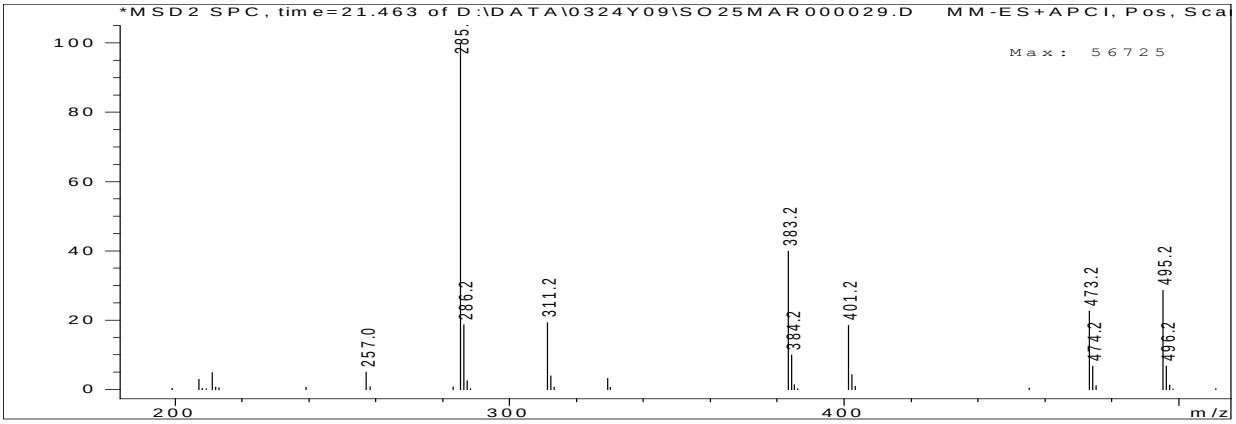
OMNIPOL BP

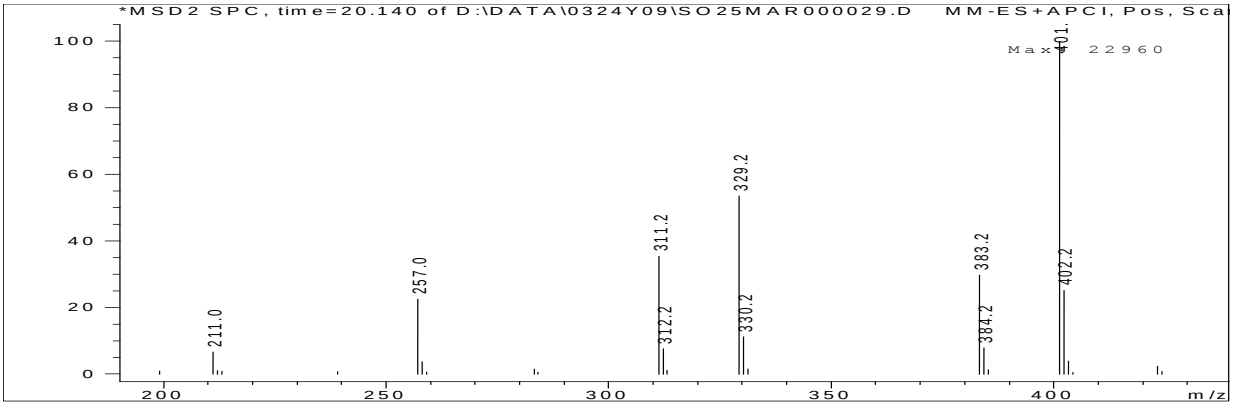
All spectra of peaks as below



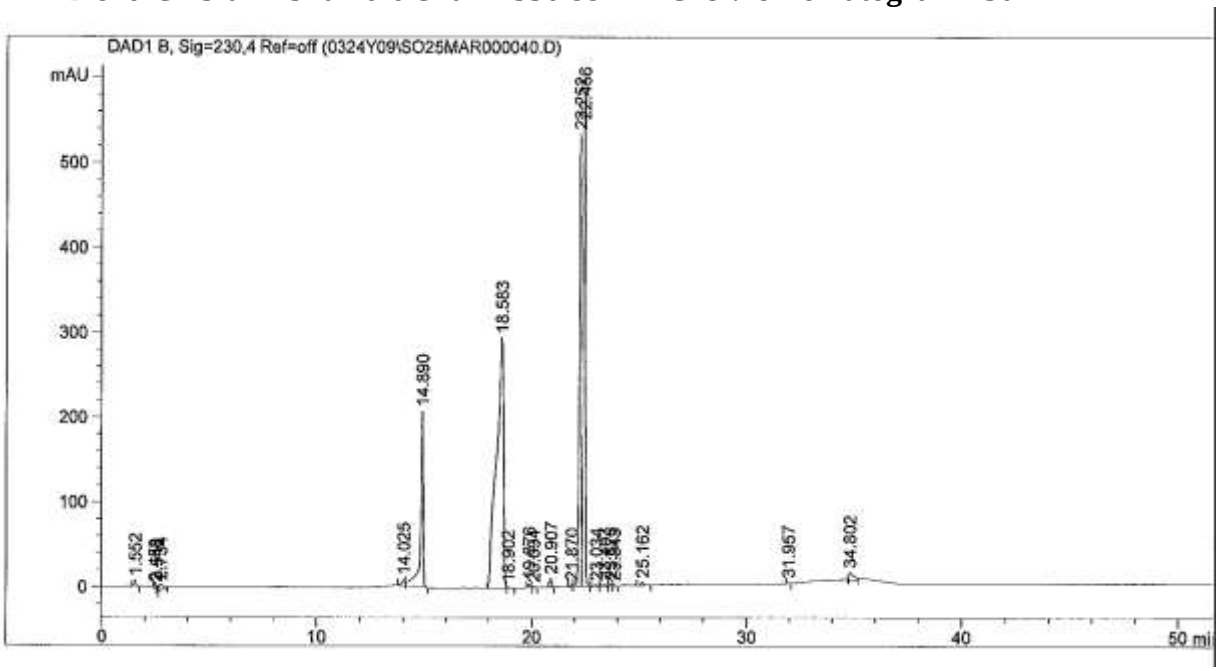




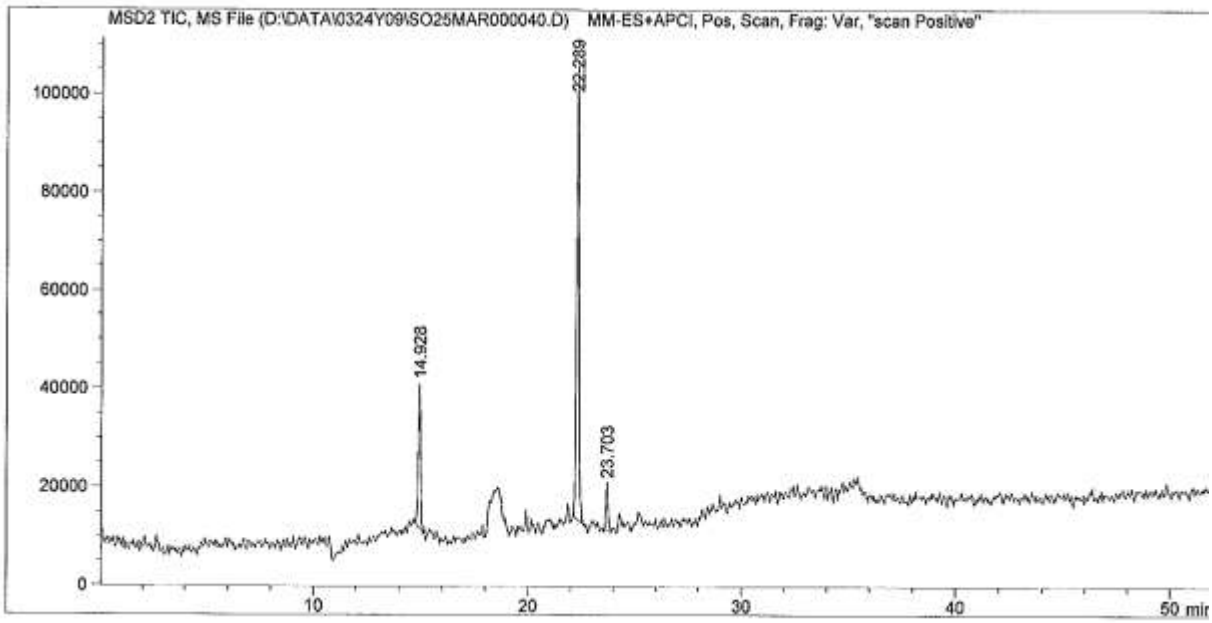

*MSD2 SPC, time=21.463 of D:\DATA\0324Y09\SO25MAR000029.D MM-ES+APCI, Pos, Scal
Max: 56725
285.
383.2
311.2
401.2
286.2
257.0
384.2
473.2
495.2
474.2
496.2
100
80
60
40
20
0
200
300
400
m/z


*MSD2 SPC, time=20.140 of D:\DATA\0324Y09\SO25MAR000029.D MM-ES+APCI, Pos, Scal
Max 401. 22960
329.2
311.2
257.0
383.2
402.2
211.0
312.2
330.2
384.2
100
80
60
40
20
0
200
250
300
350
400
m/z

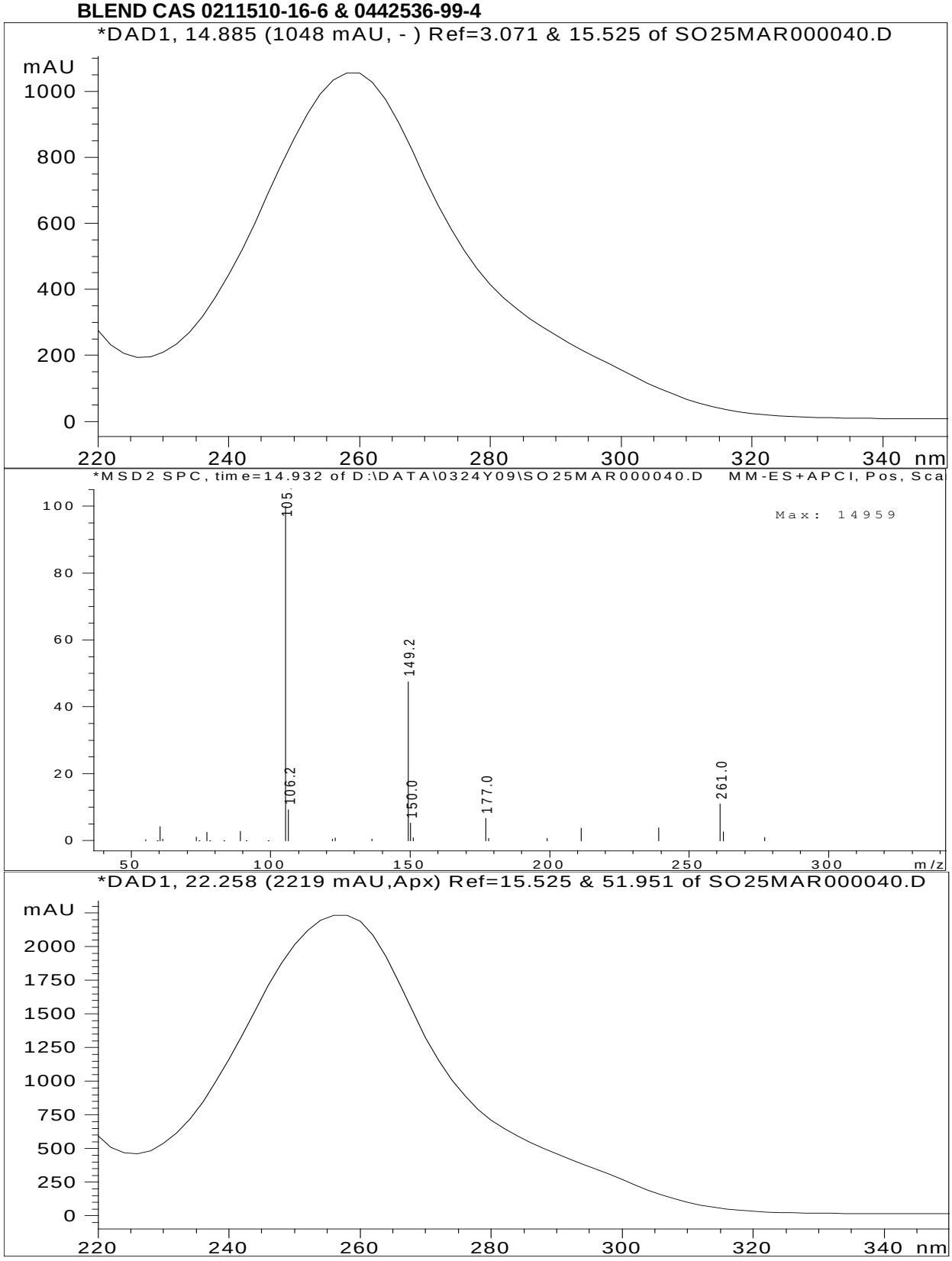
Blend CAS 0211510-16-6 & 0442536-99-4 LC-UV chromatogram 230 nm

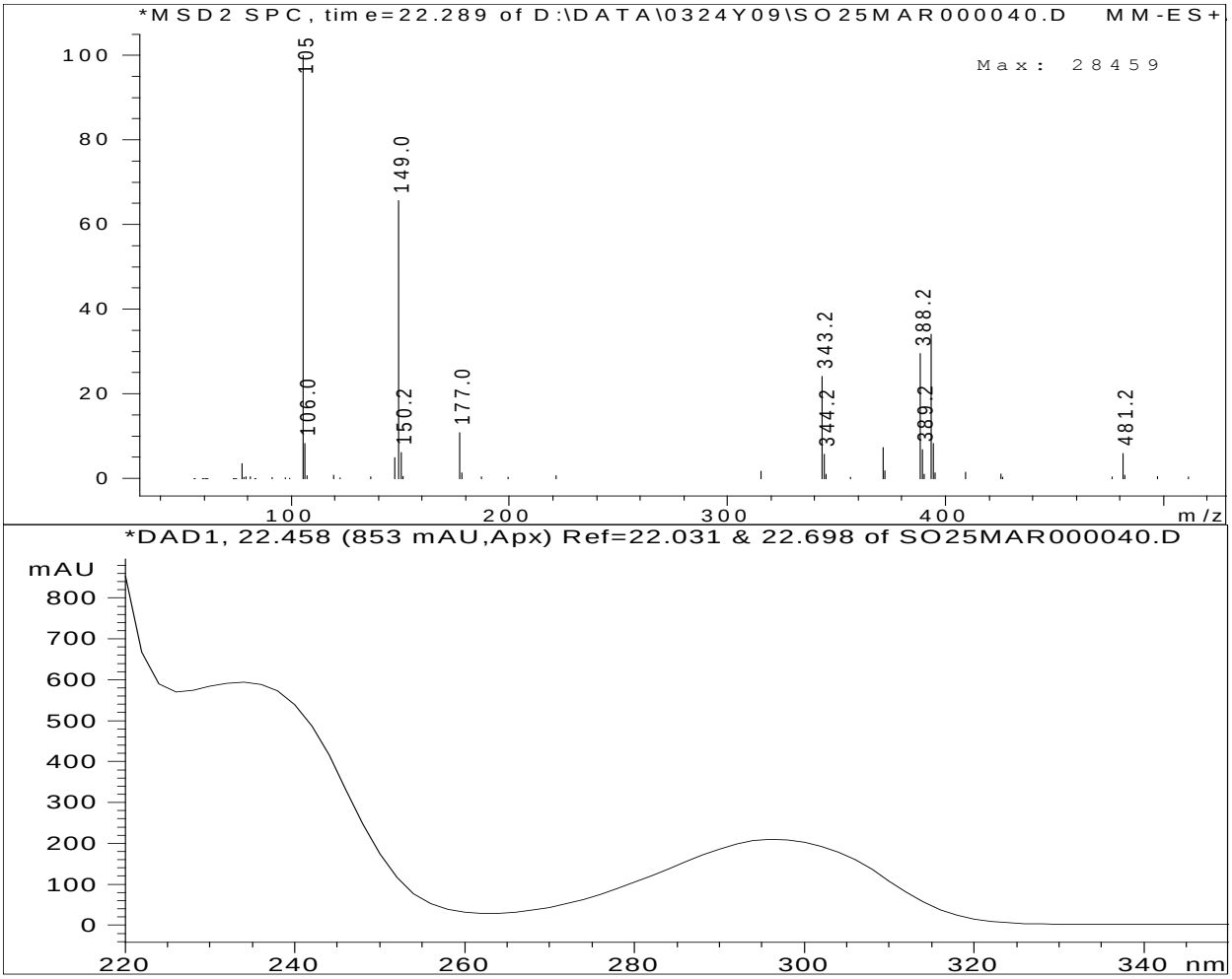


Blend CAS 0211510-16-6 & 0442536-99-4 LC-MS chromatogram

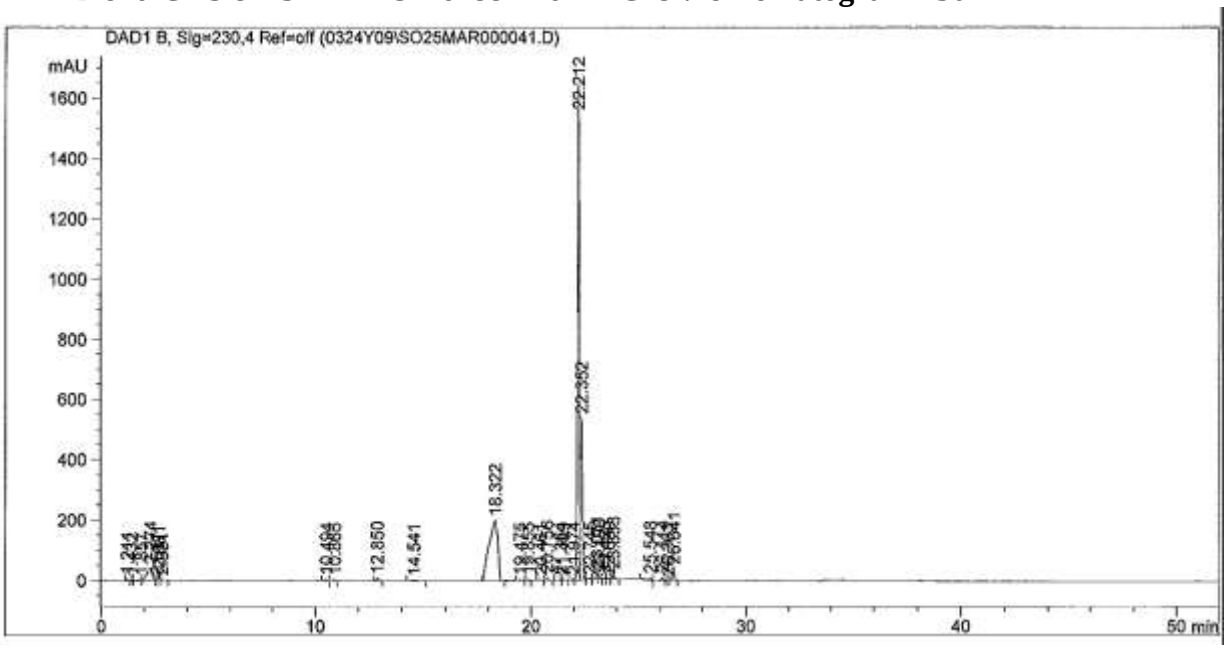


BLEND CAS 0211510-16-6 & 0442536-99-4

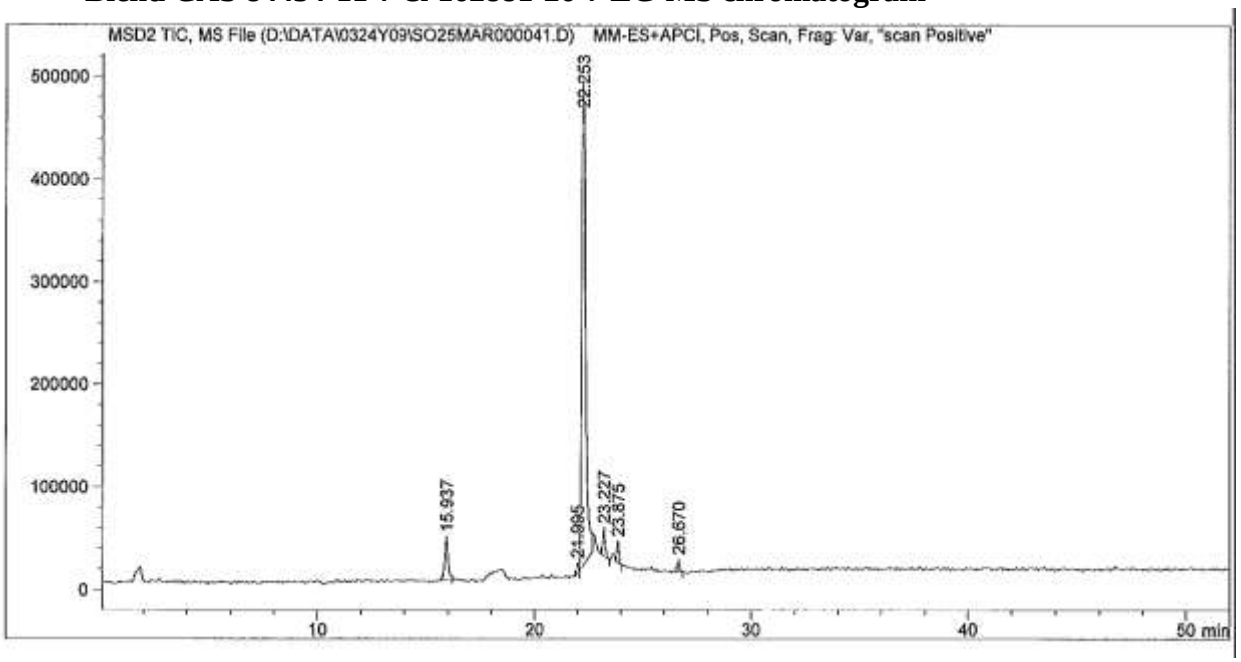



*MSD2 SPC, time=22.289 of D:\DATA\0324Y09\SO25MAR000040.D MM-ES+
Max: 28459
105
149.0
106.0
150.2
177.0
343.2
344.2
388.2
389.2
481.2
m/z
*DAD1, 22.458 (853 mAU,Apx) Ref=22.031 & 22.698 of SO25MAR000040.D
mAU
nm

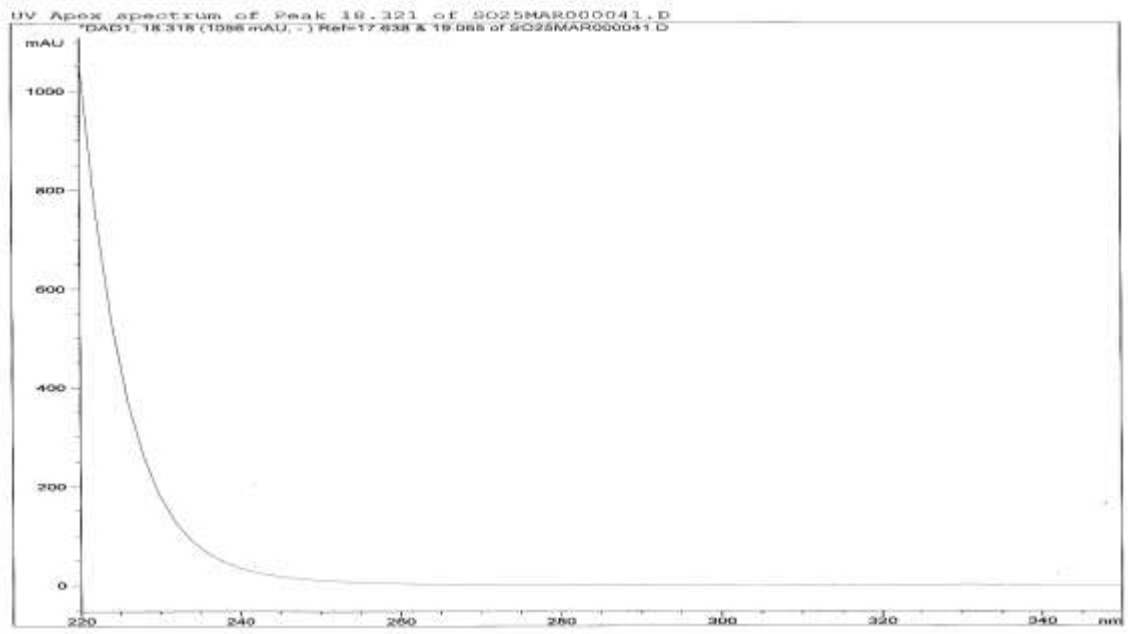
Blend CAS 84434-11-7 & 162881-26-7 LC-UV chromatogram 230 nm

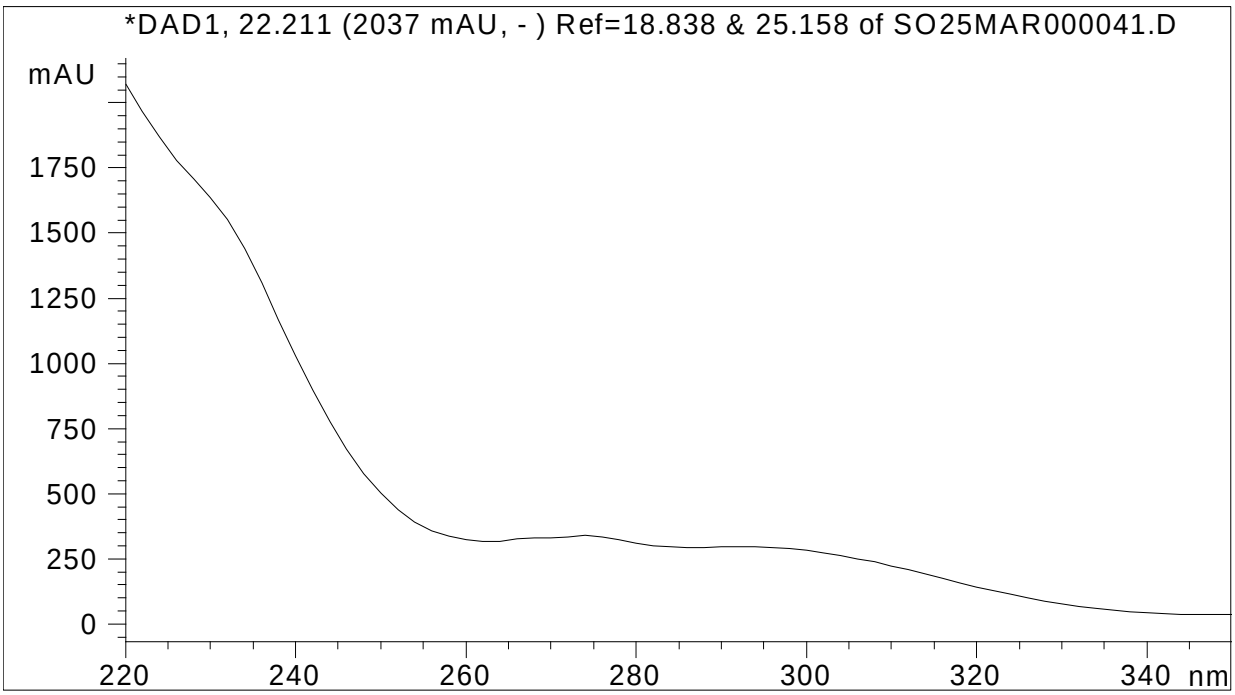


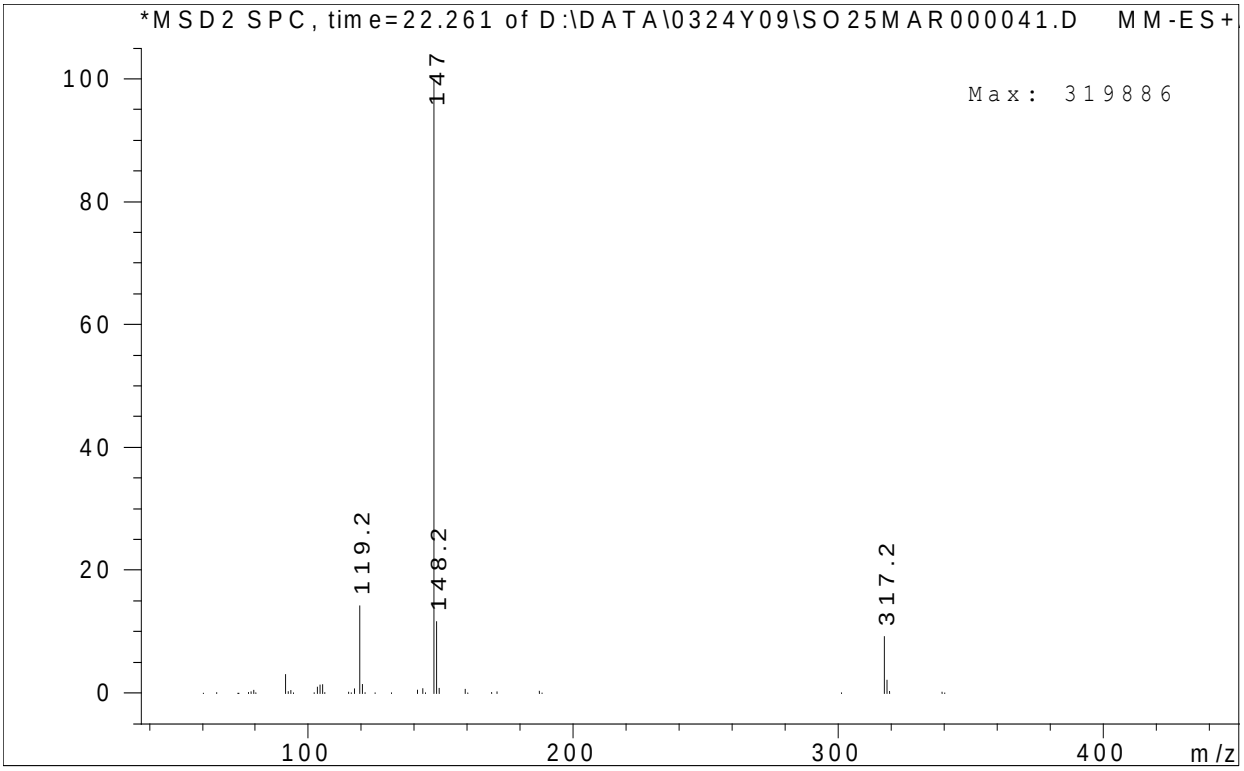
Blend CAS 84434-11-7 & 162881-26-7 LC-MS chromatogram



BLEND CAS 84434-11-7 & 162881-26-7

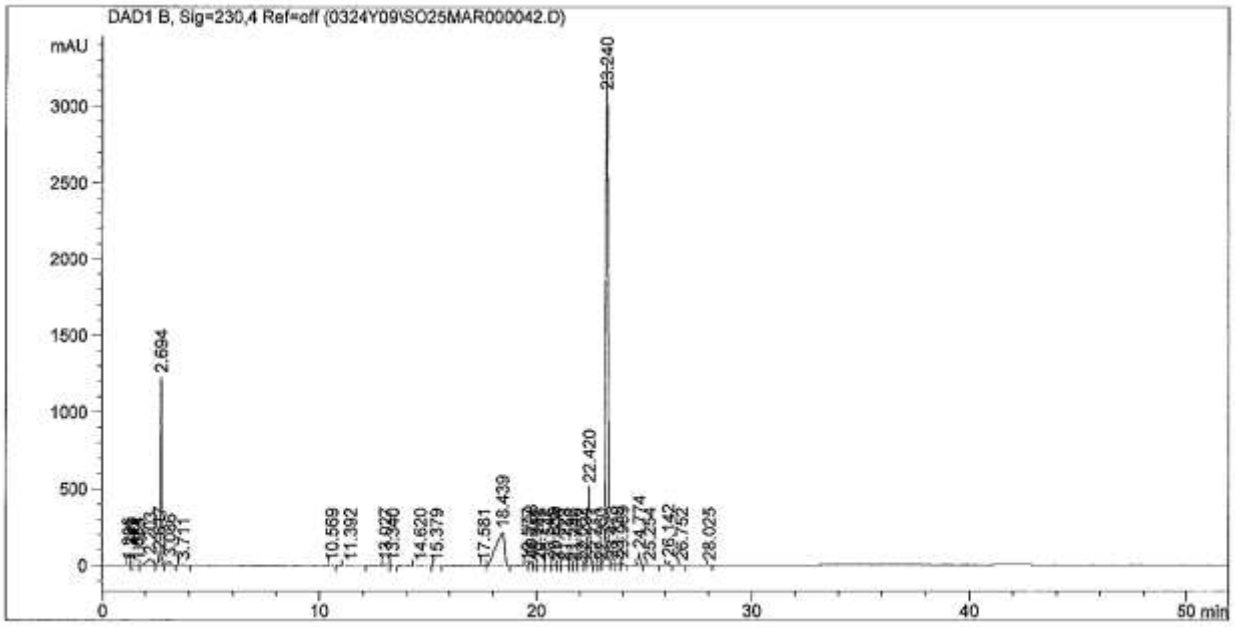




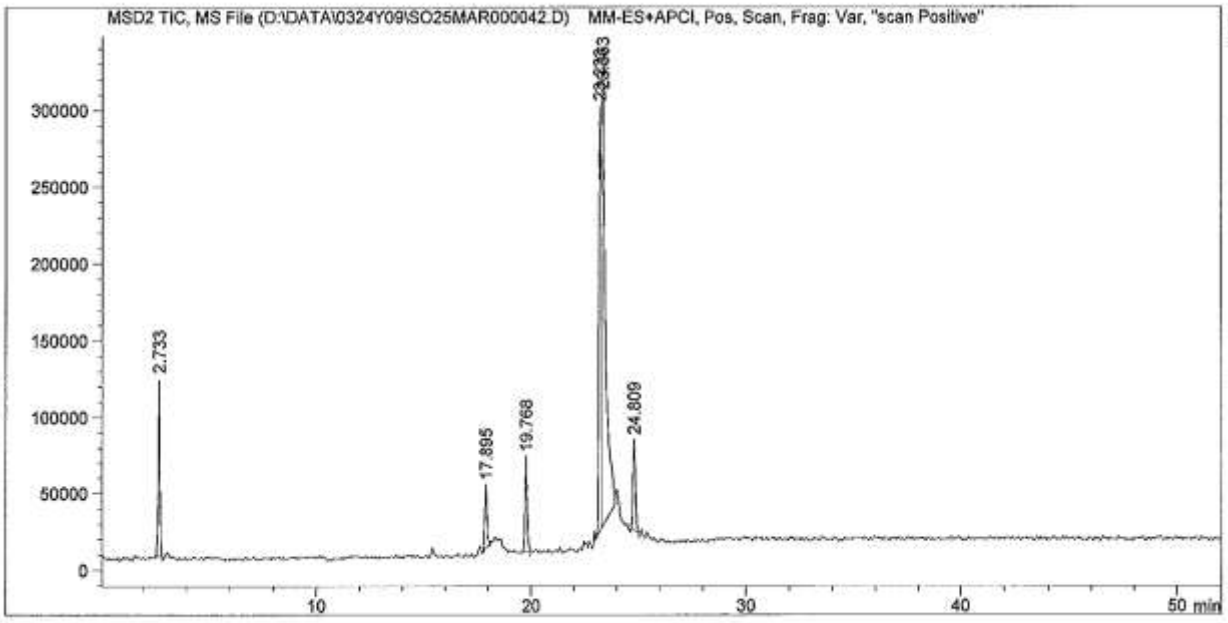


BLEND CAS 84434-11-7 & 162881-26-7

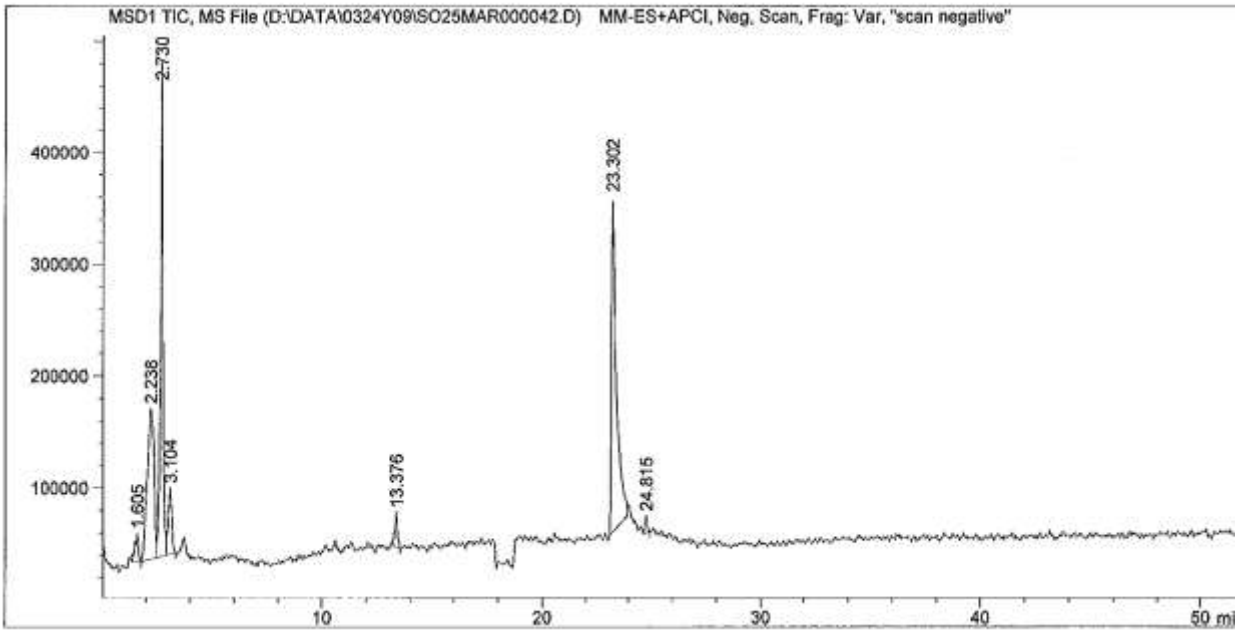
Lucirin TPO LC-UV chromatogram 230 nm



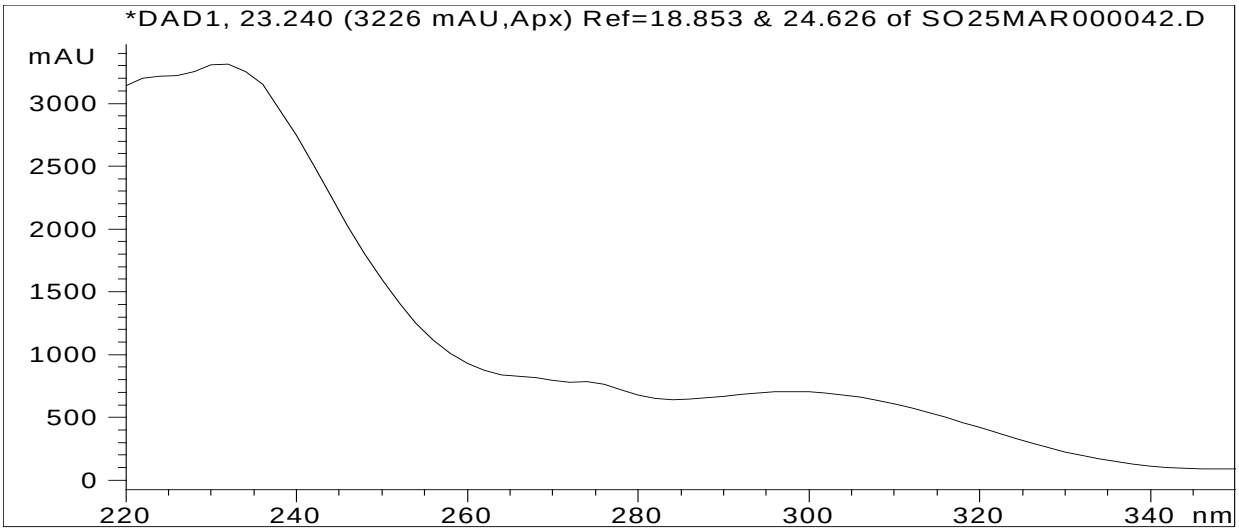
Lucirin TPO LC-MS chromatogram

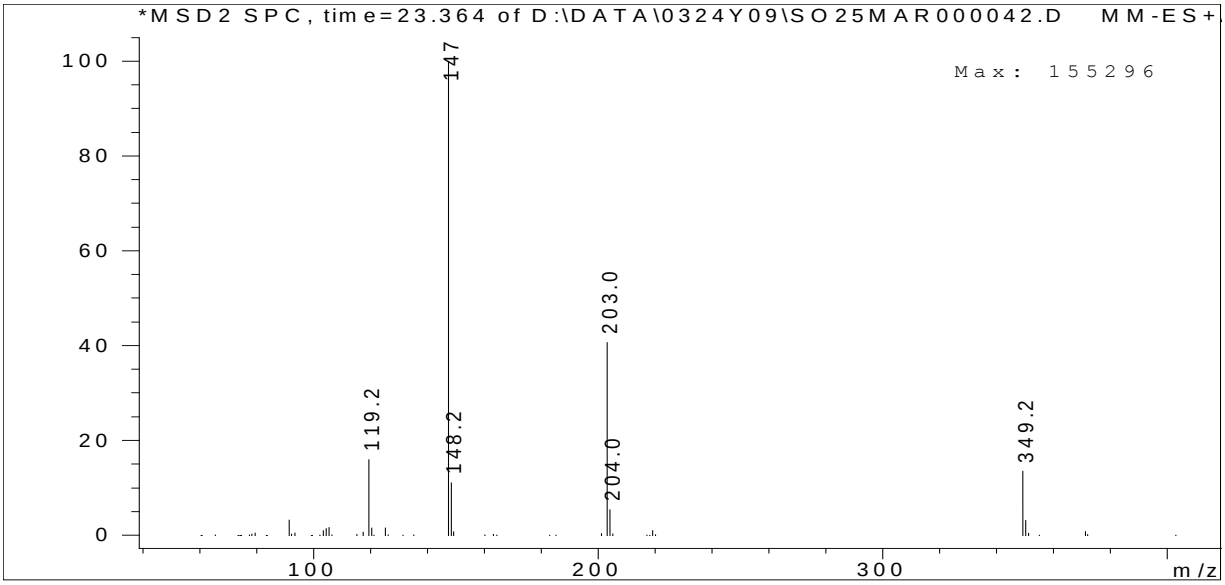


Lucirin TPO LC-MS chromatogram obtained in the negative scan mode

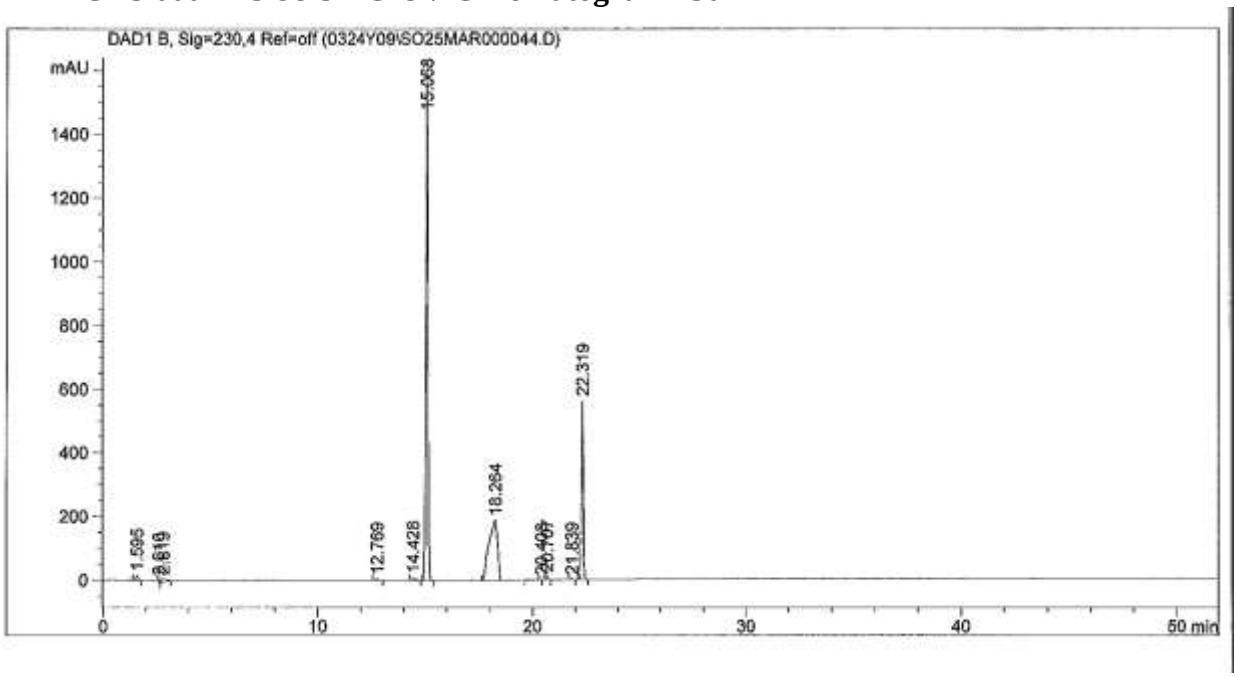


LUCIRIN TPO

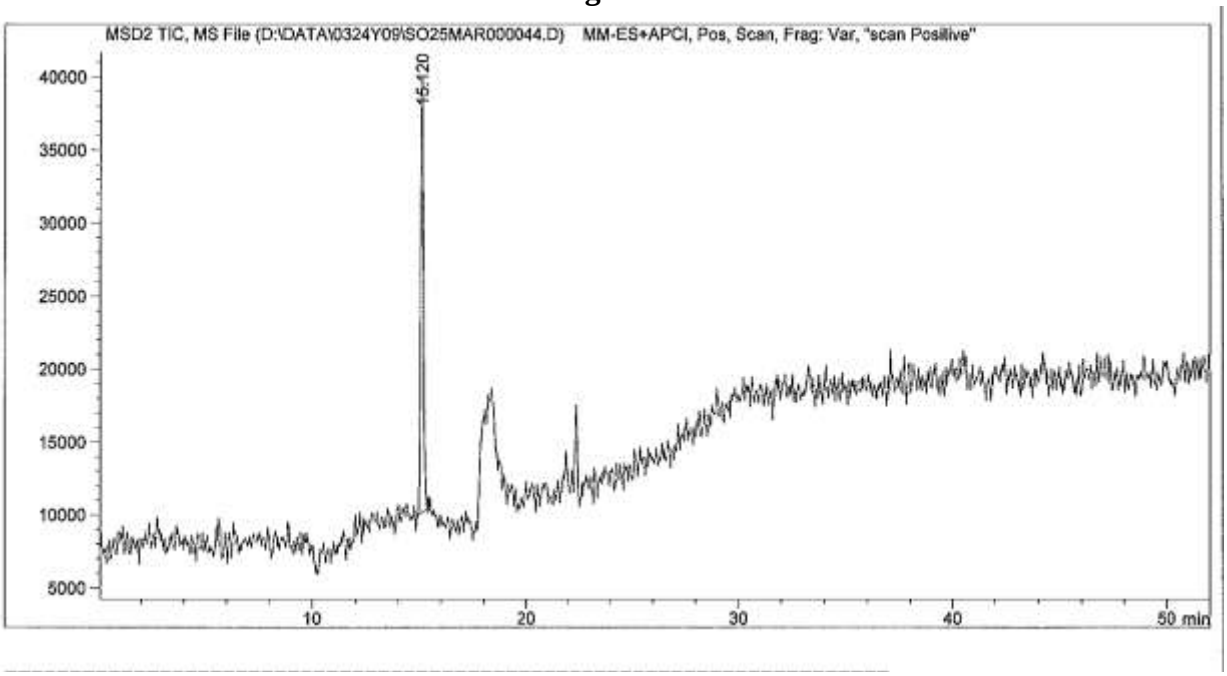



*MSD2 SPC, time=23.364 of D:\DATA\0324Y09\SO25MAR000042.D MM-ES+
Max: 155296
100
80
60
40
20
0
147
203.0
119.2
148.2
204.0
349.2
100
200
300
m/z

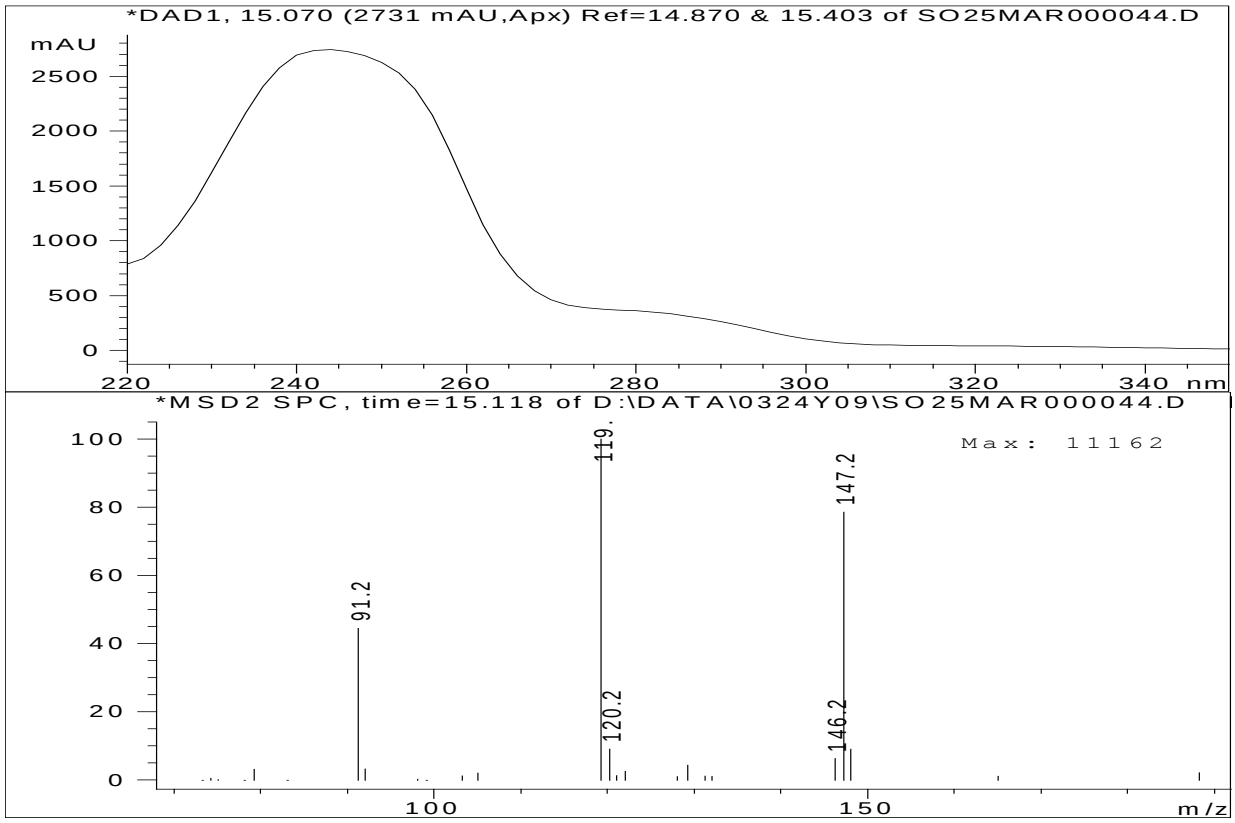
CAS 0007473-98-5 LC-UV Chromatogram 230 nm



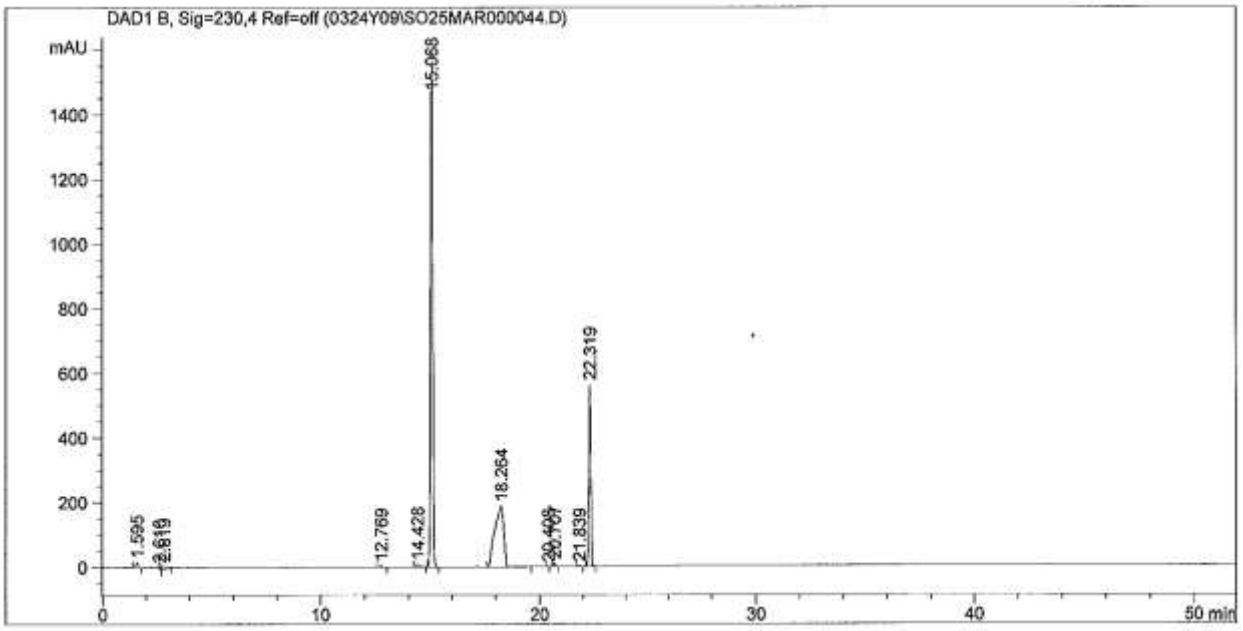
CAS 0007473-98-5 LC-MS Chromatogram



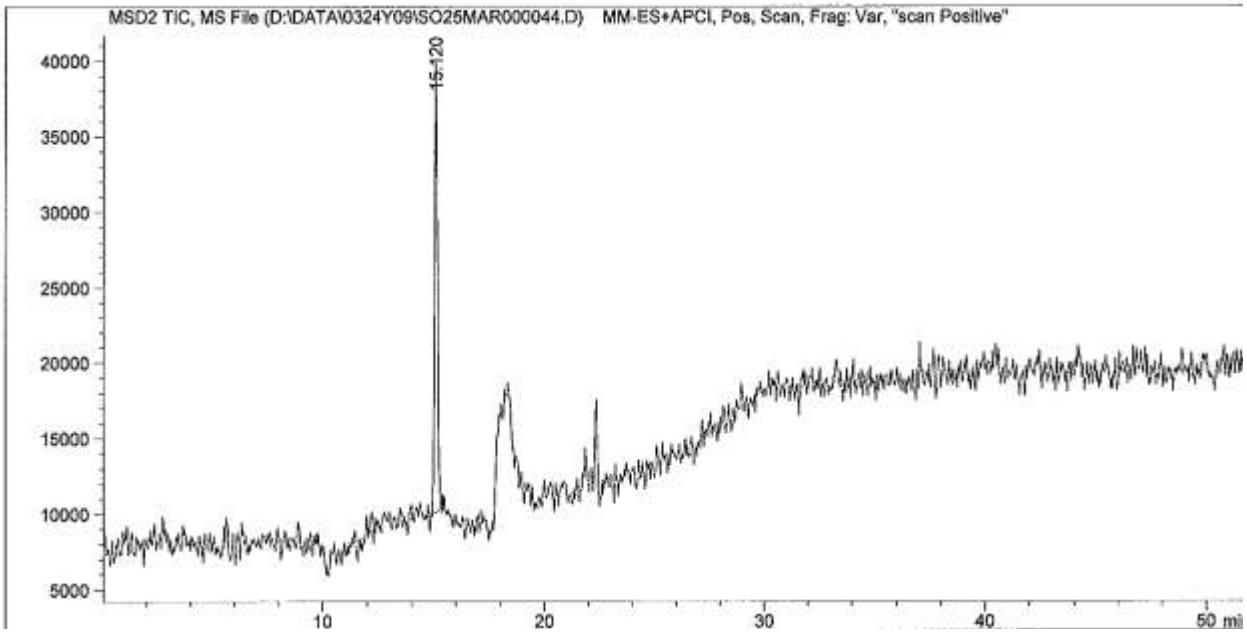
CAS 0007473-98-5



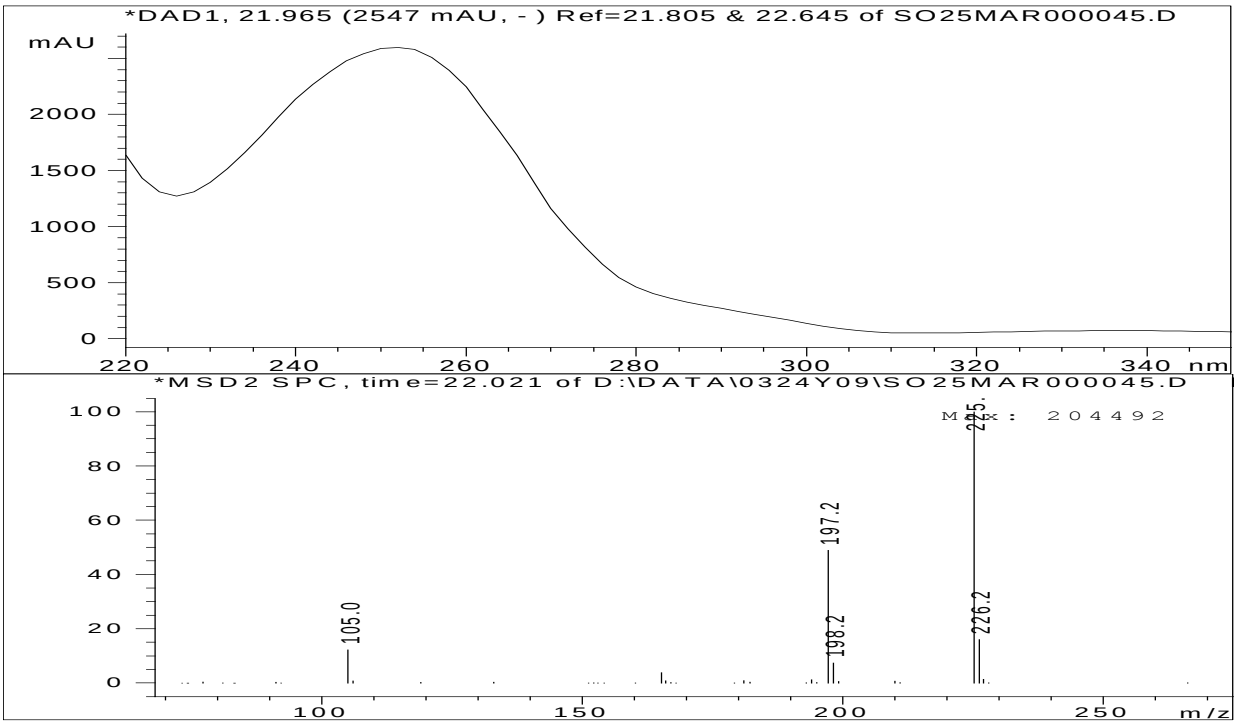
CAS 0024650-42-8 LC-UV chromatograms 230 nm

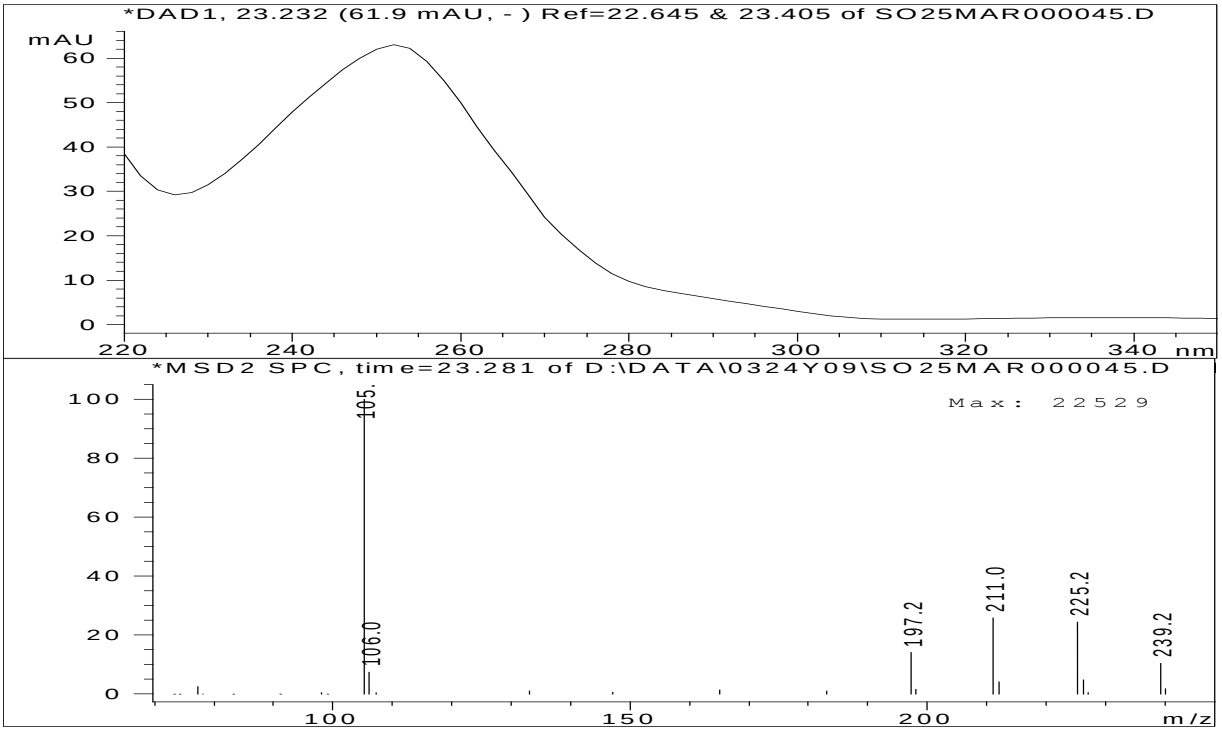


CAS 0024650-42-8 LC-MS chromatograms

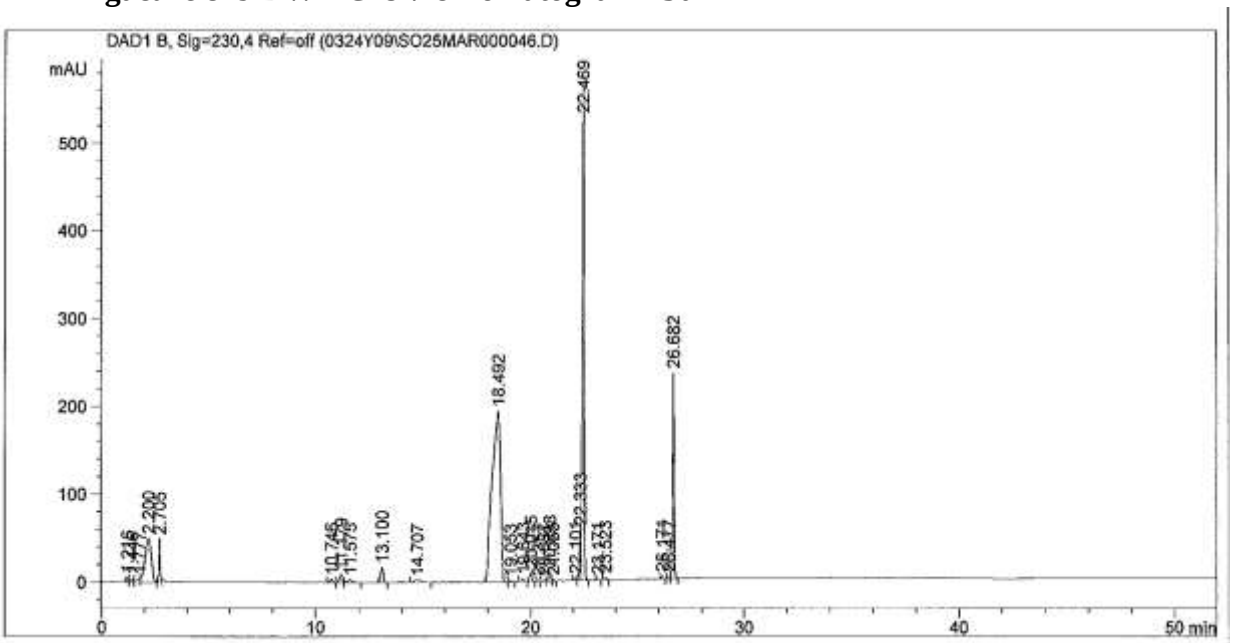


CAS 0024650-42-8

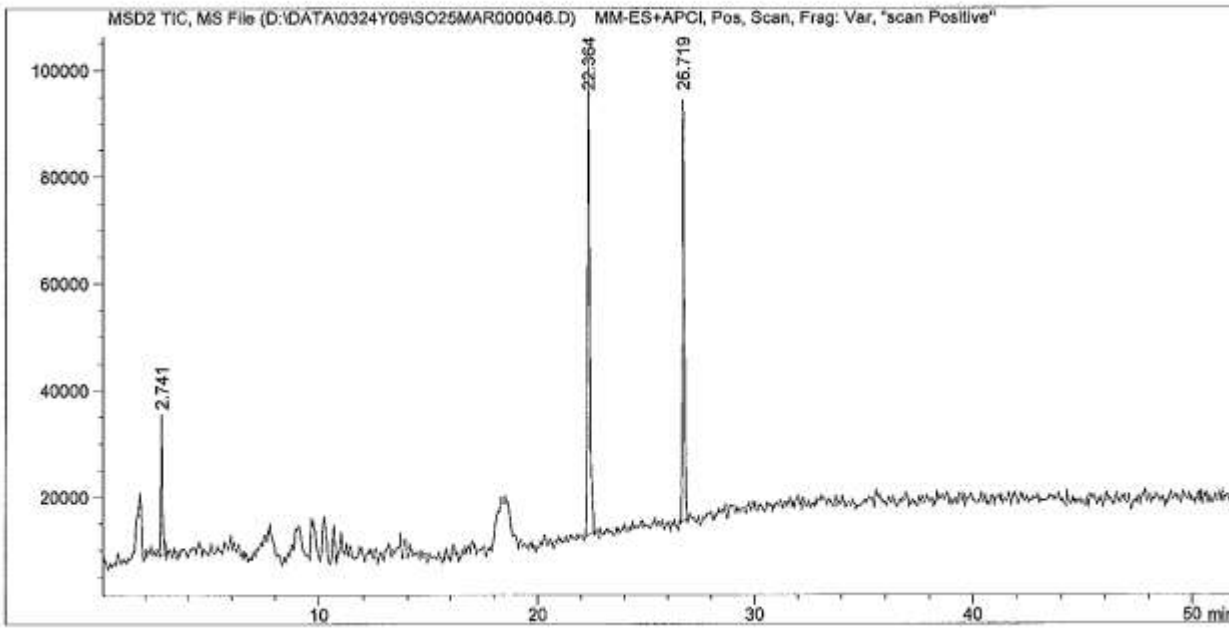




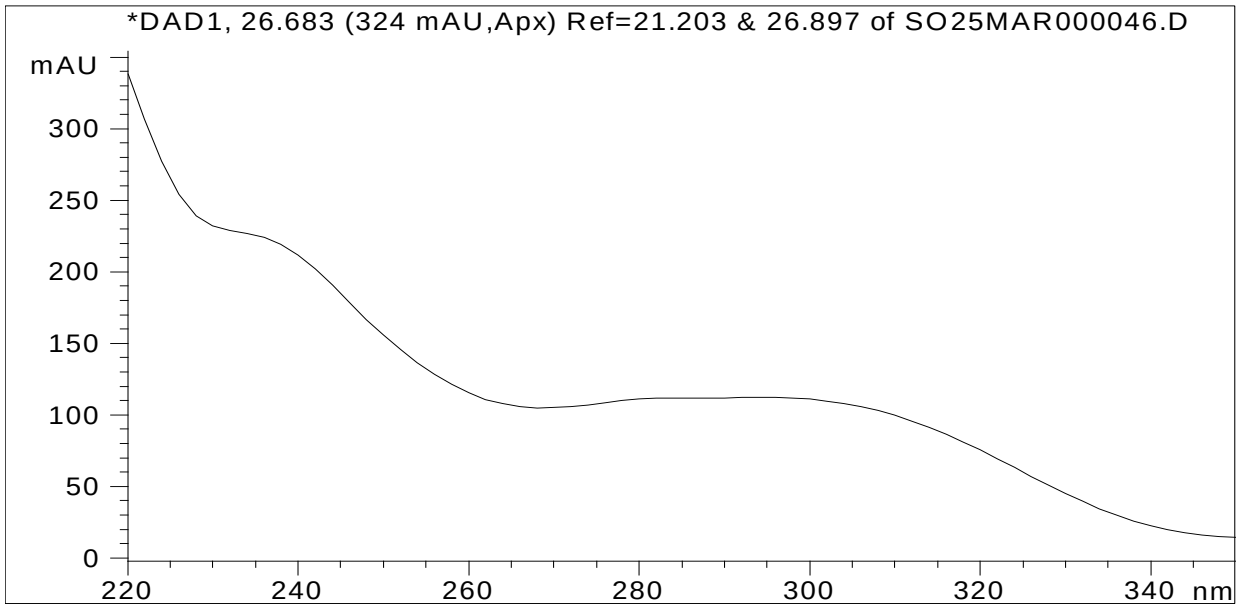
Irgacure 819 DW LC-UV chromatogram 230 nm

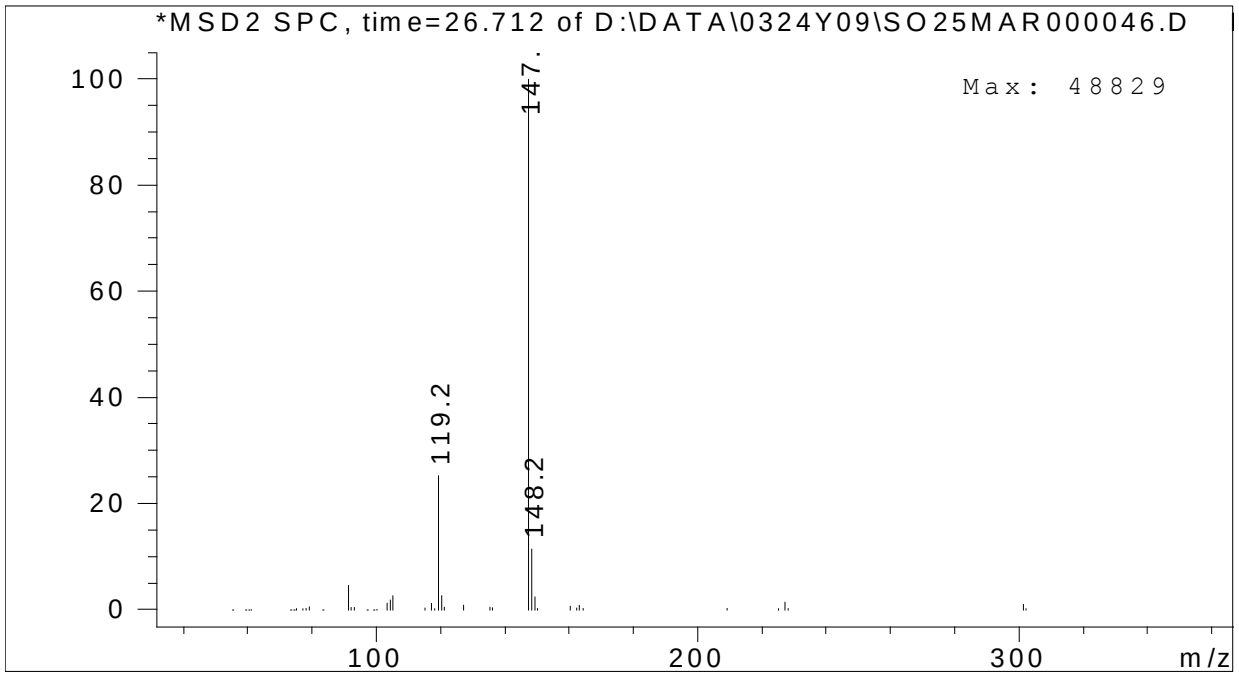


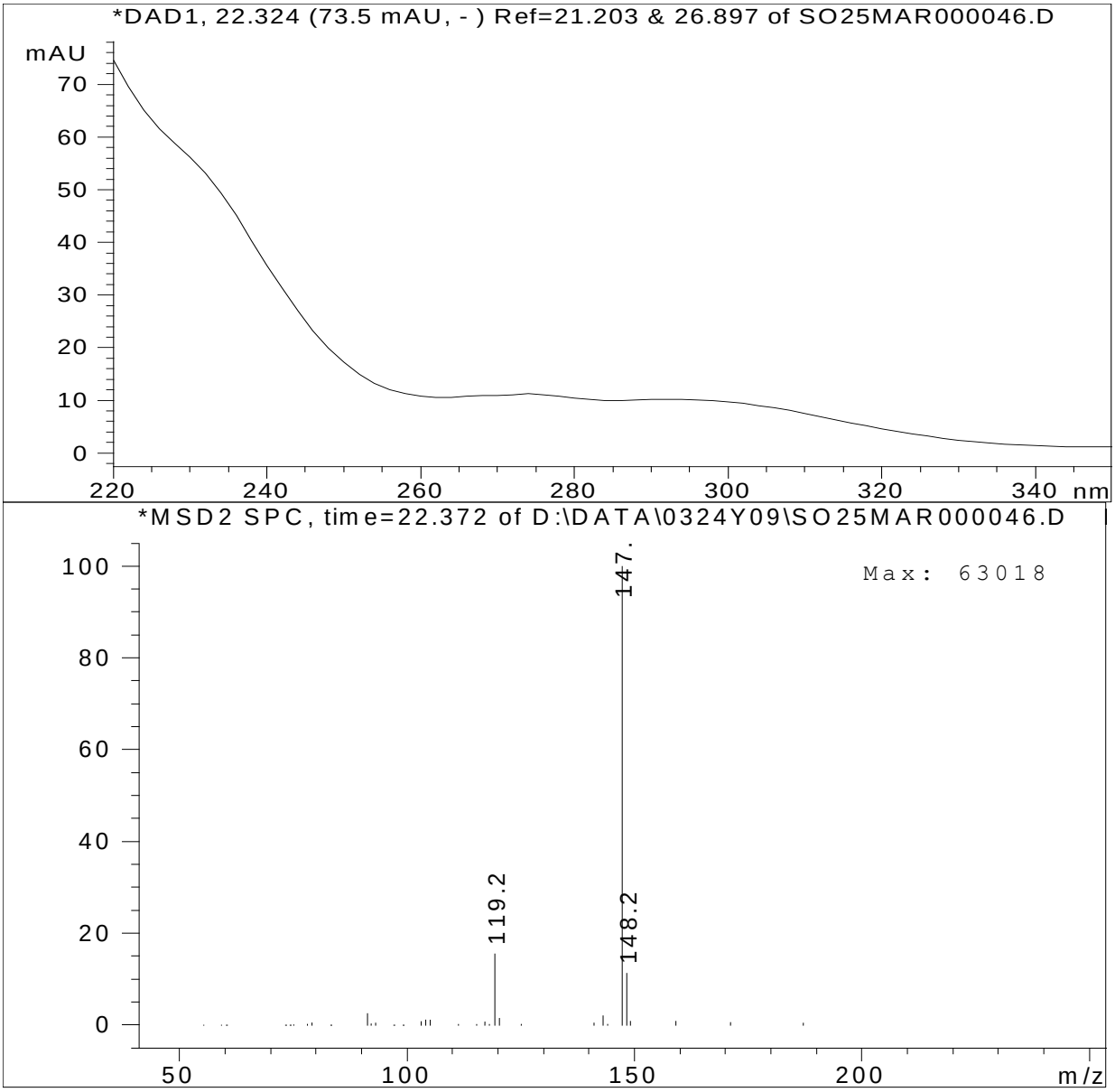
Irgacure 819 DW LC-MS chromatogram



IRGACURE 819 DW

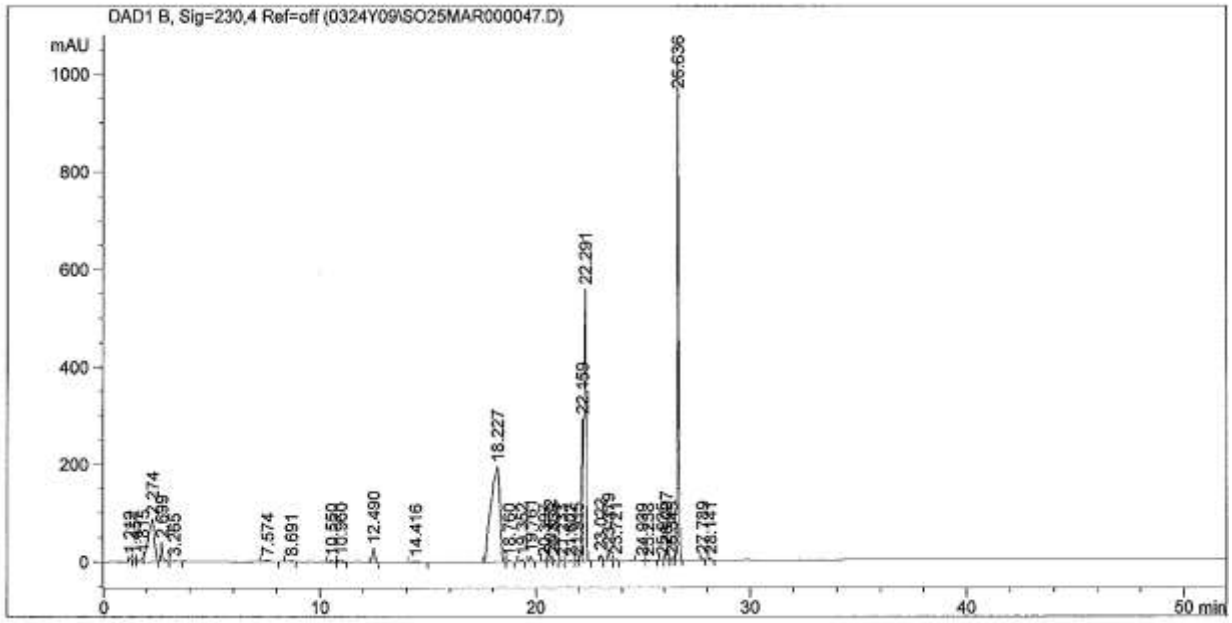




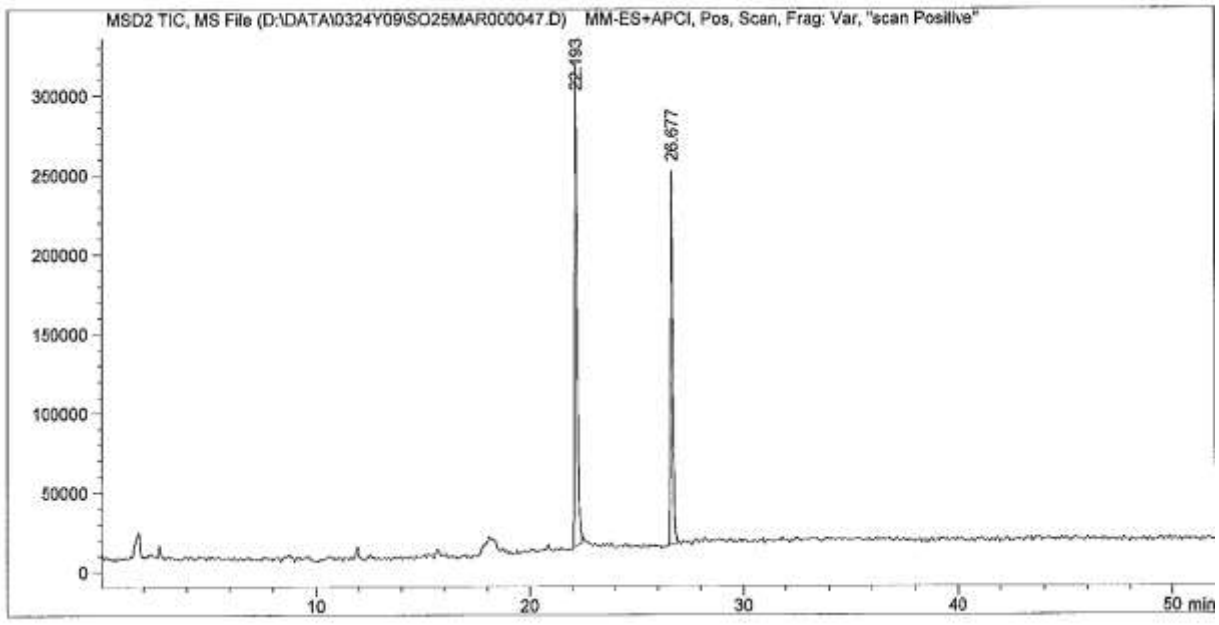


IRGACURE 819DW

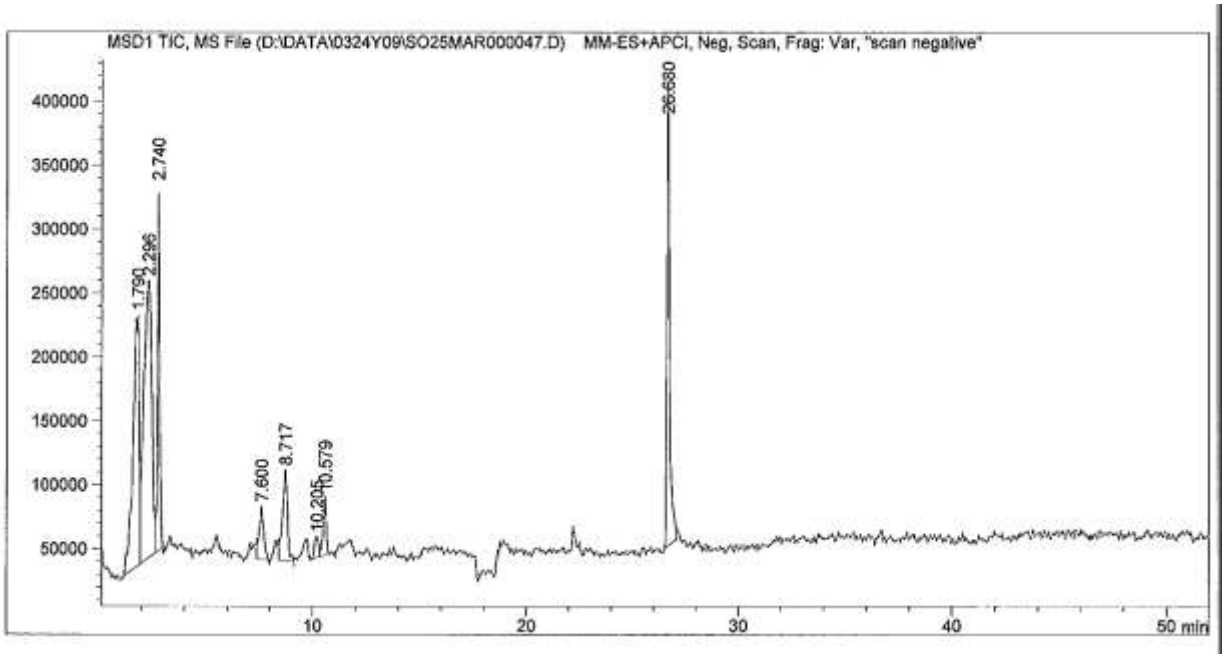
Irgacure 819 LC-UV Chromatogram 230 nm



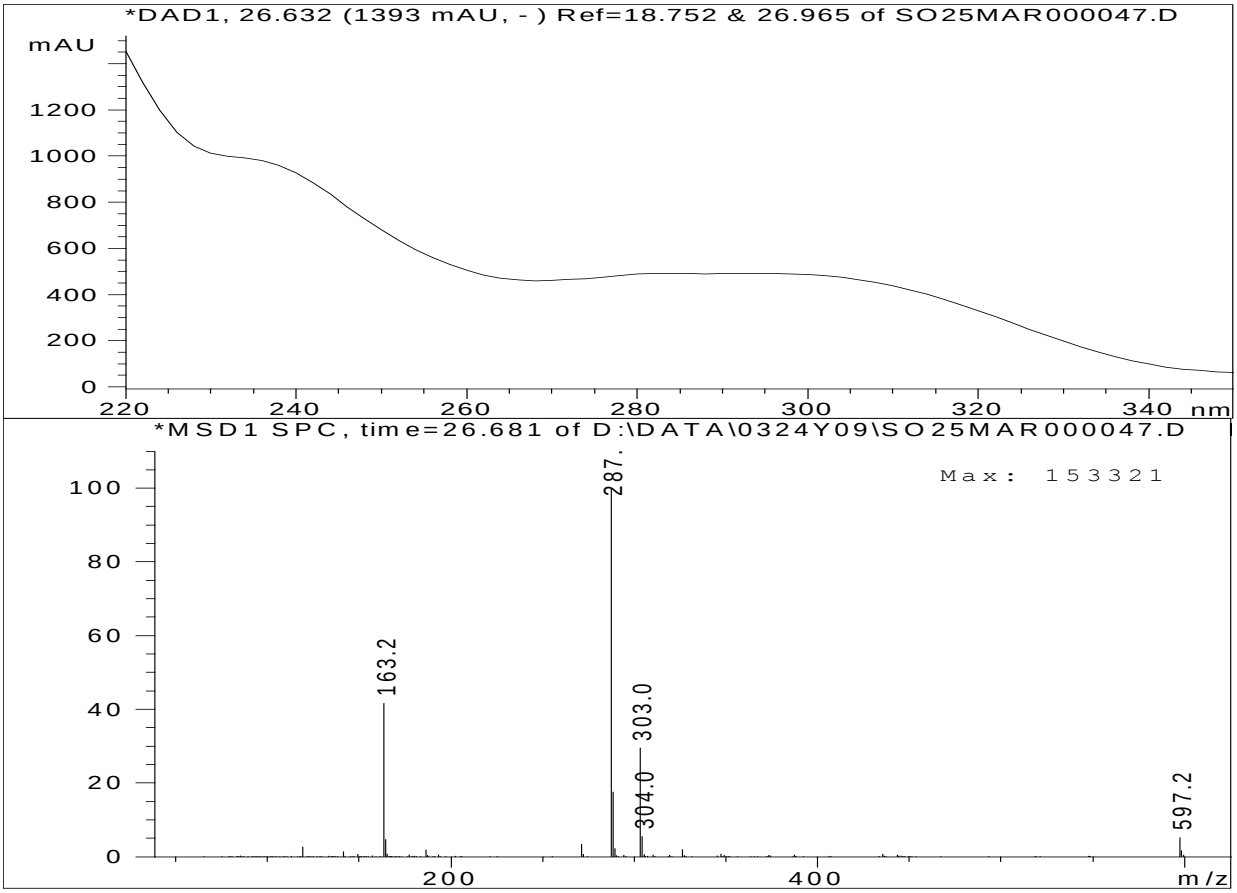
Irgacure 819 LC-MS Chromatogram

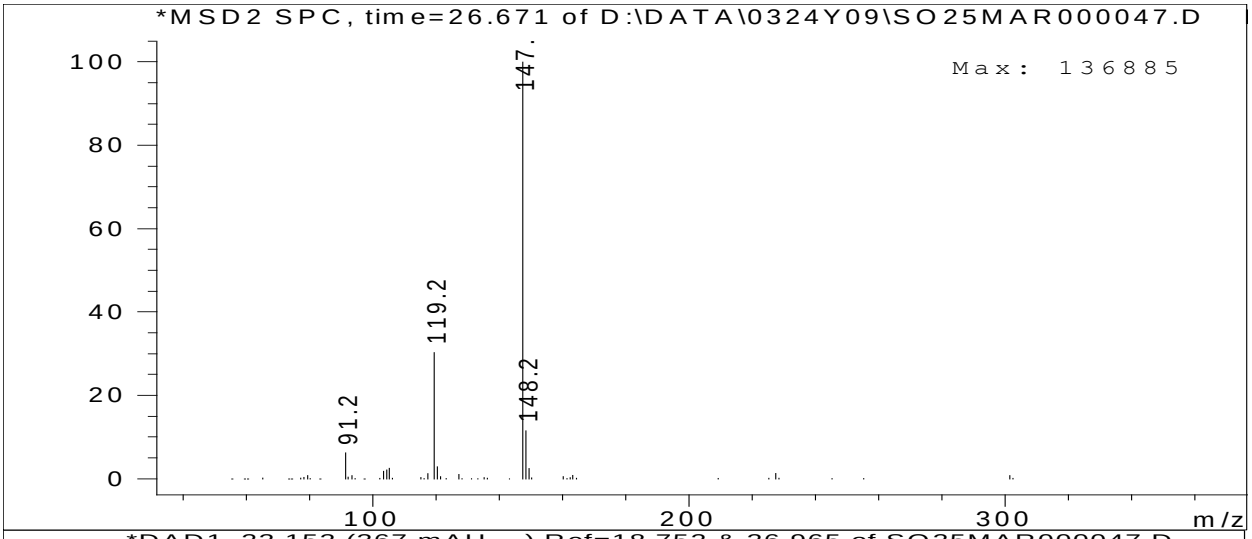


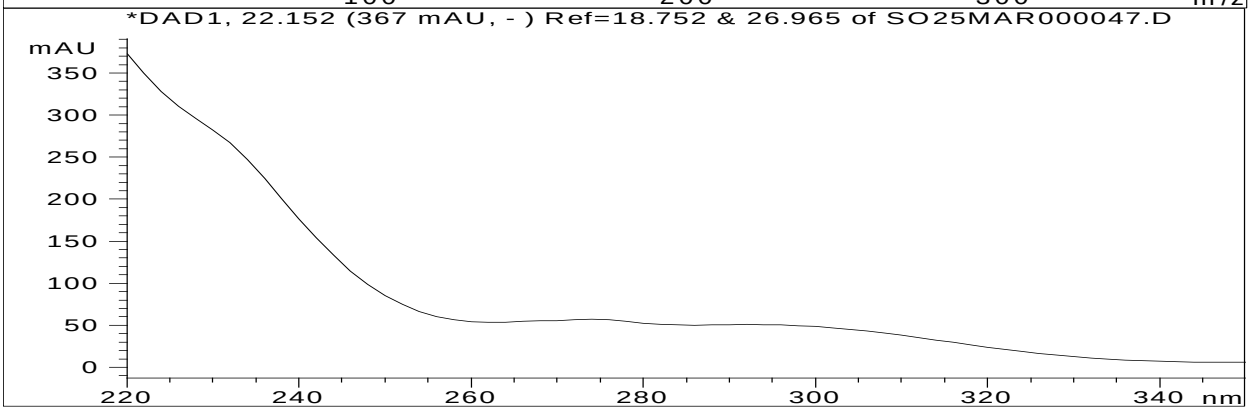
Irgacure 819 LC-MS Chromatogram obtained in the negative scan mode

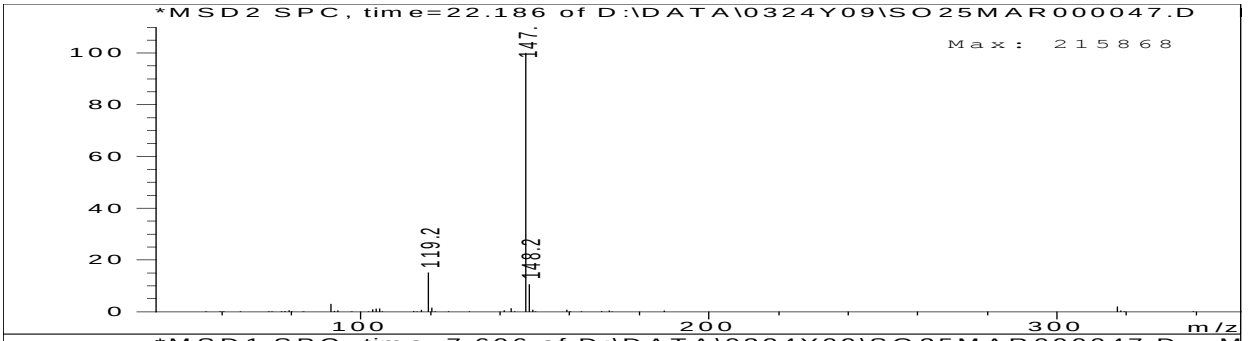


IRGACURE 819




*MSD2 SPC, time=26.671 of D:\DATA\0324Y09\SO25MAR000047.D
Max: 136885
147.
119.2
148.2
91.2
m/z


*DAD1, 22.152 (367 mAU, -) Ref=18.752 & 26.965 of SO25MAR000047.D
mAU
nm


*MSD2 SPC, time=22.186 of D:\DATA\0324Y09\SO25MAR000047.D
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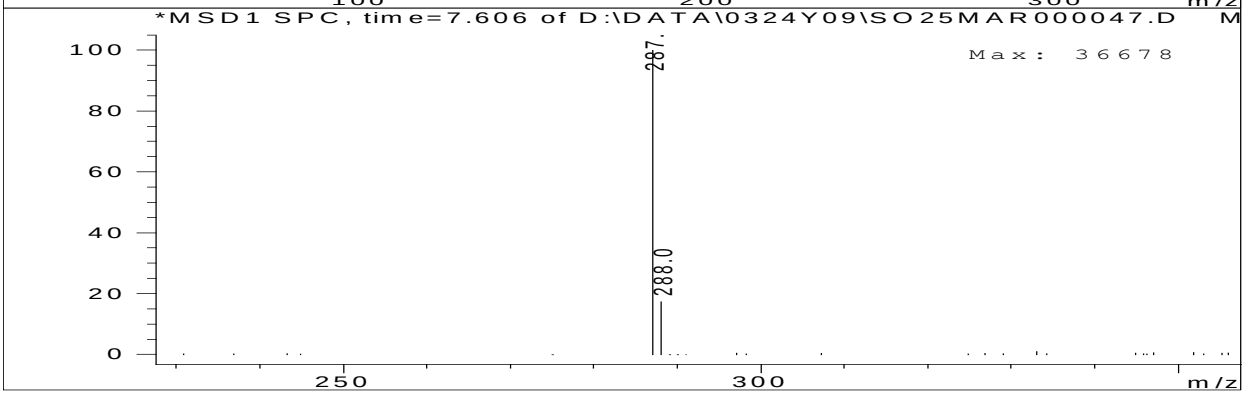
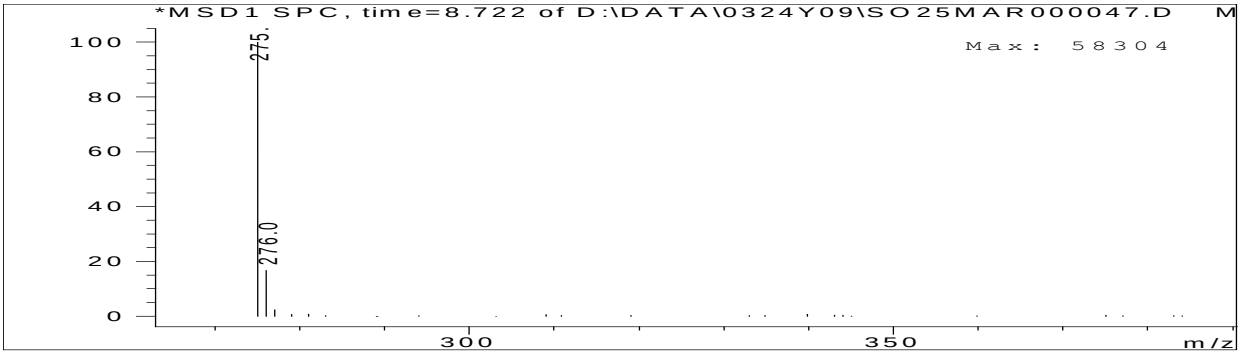
147.
119.2
148.2
m/z

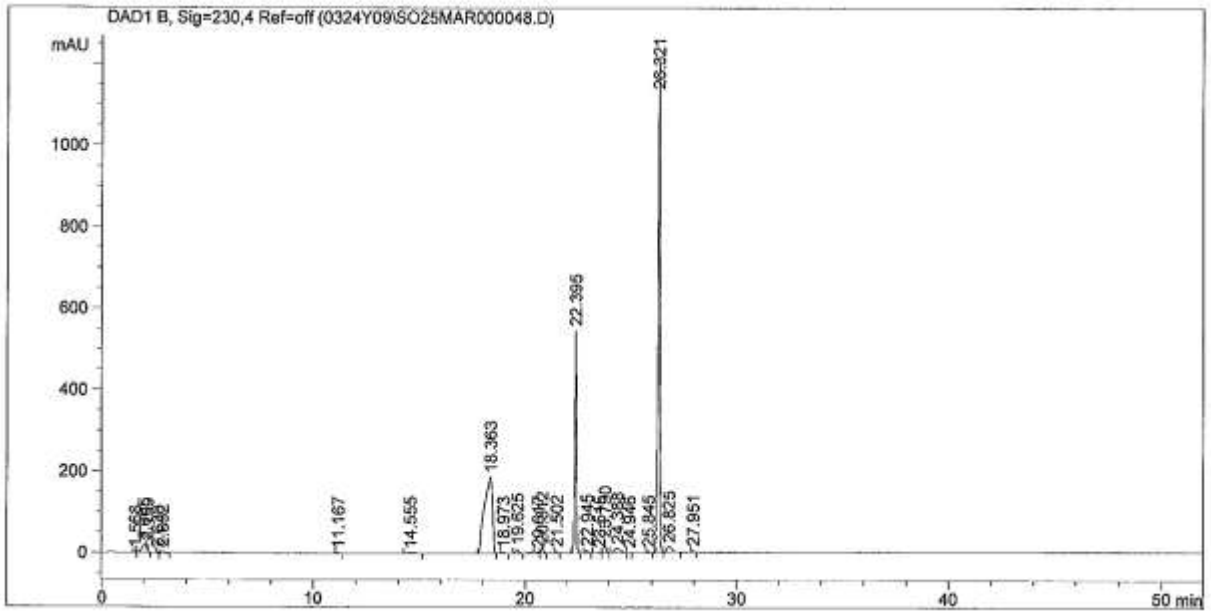

*MSD1 SPC, time=7.606 of D:\DATA\0324Y09\SO25MAR000047.D
Max: 36678
287.
288.0
m/z



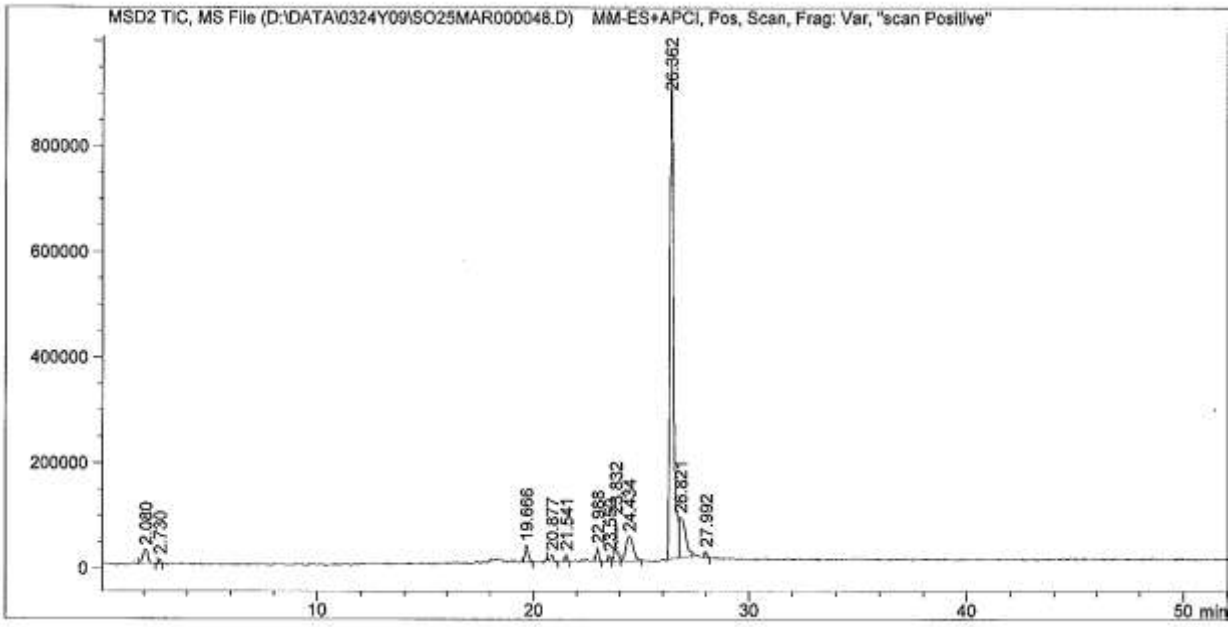
IRGACURE 819

Note: Chromatogram and mass spectra with the title "MSD1" are negative scan
Chromatogram and mass spectra with the title "MSD2" are positive scan

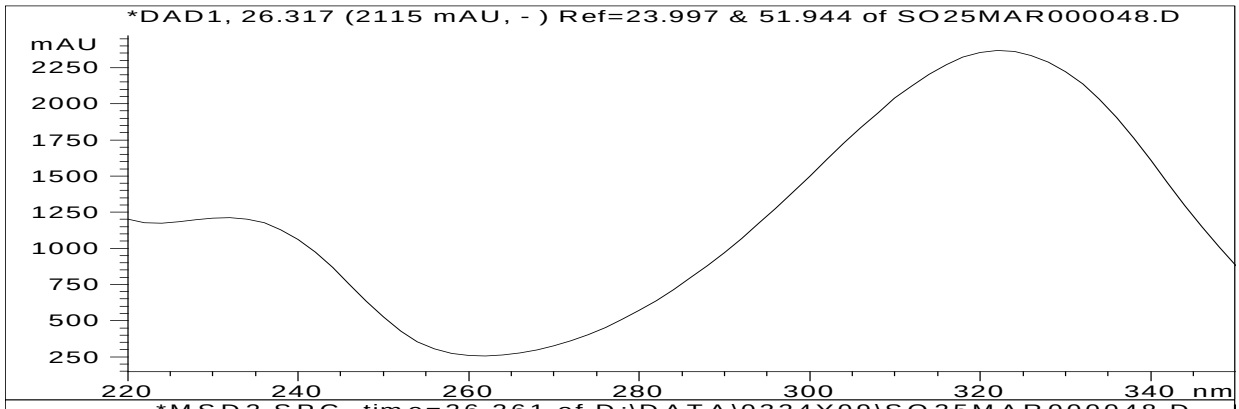
Irgacure 369 LC-UV chromatogram 230 nm

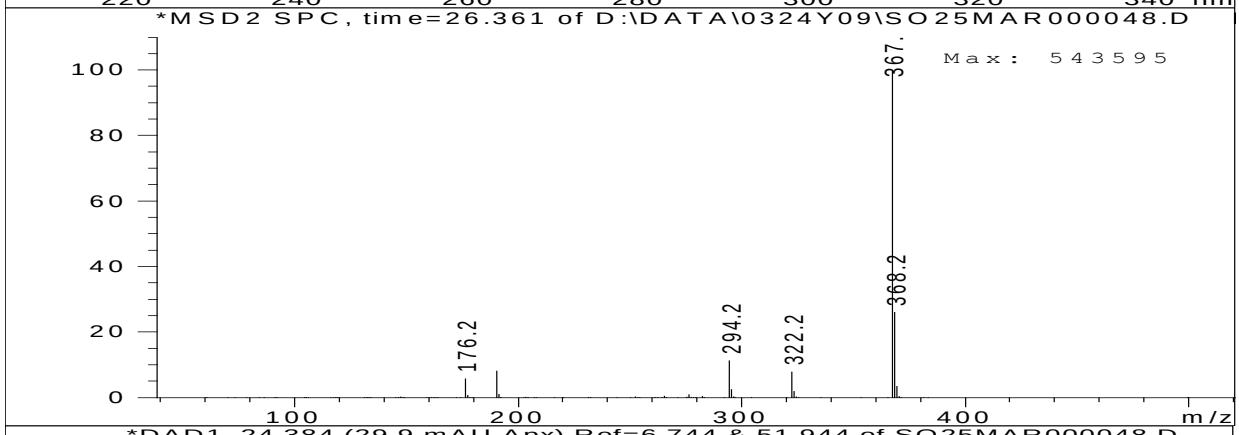


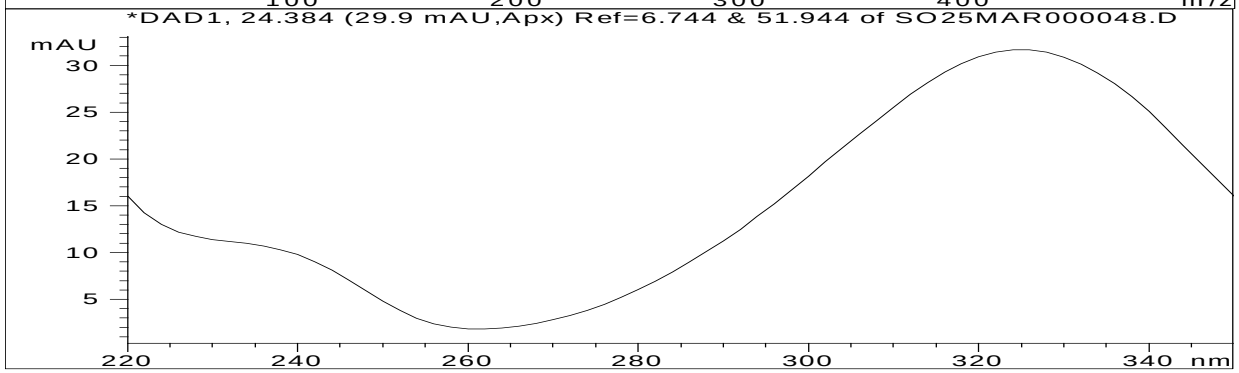
Irgacure 369 LC-MS chromatogram

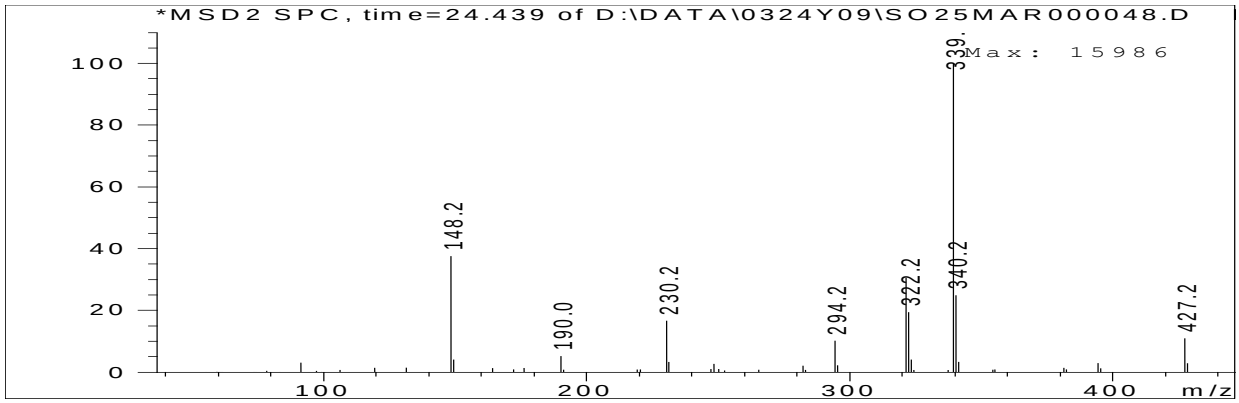


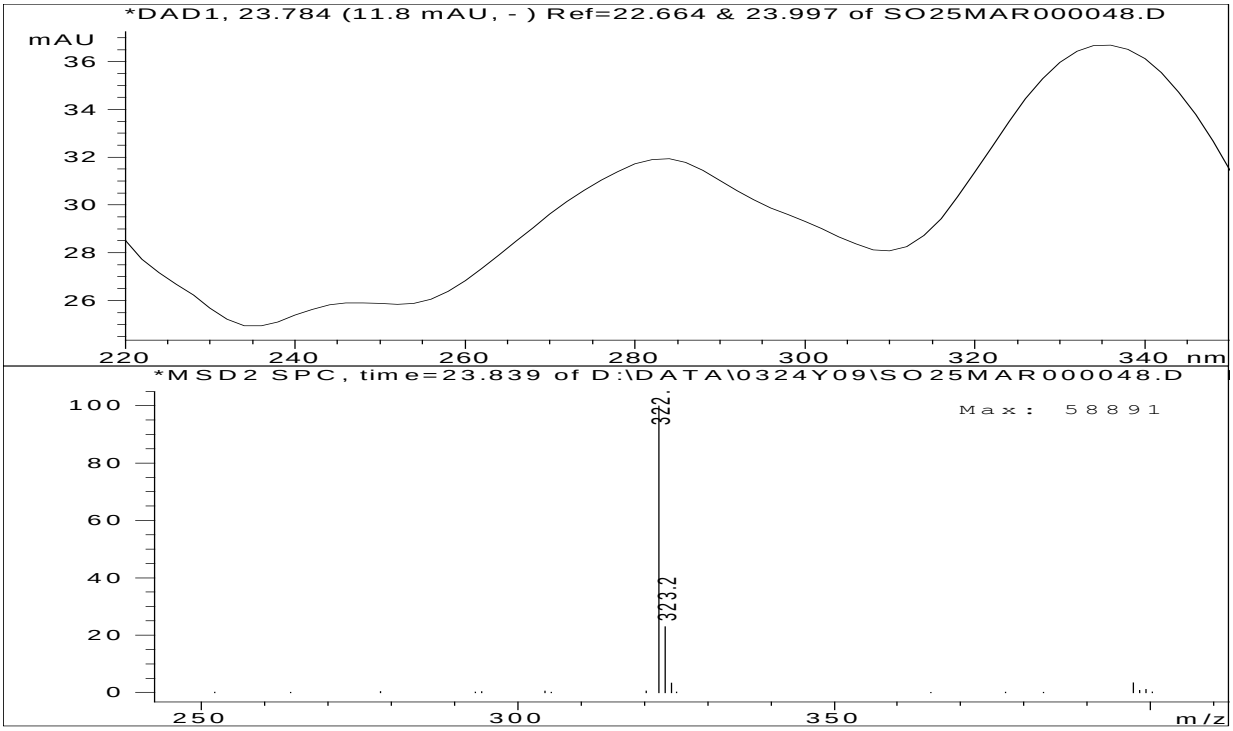
IRGACURE 369





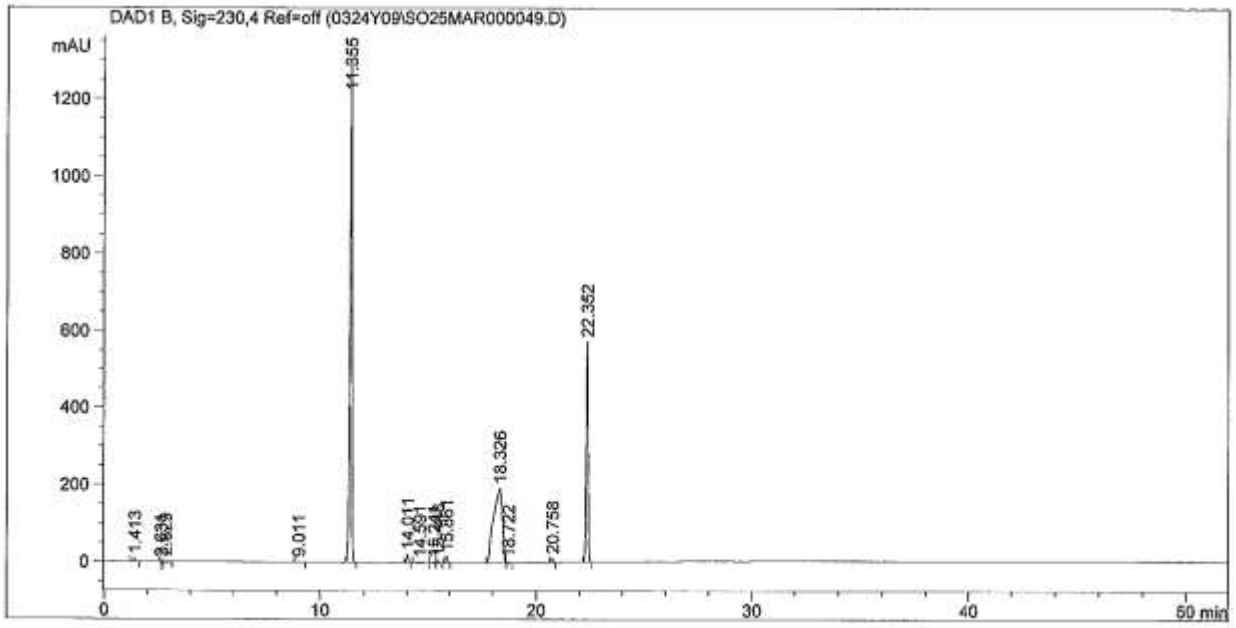




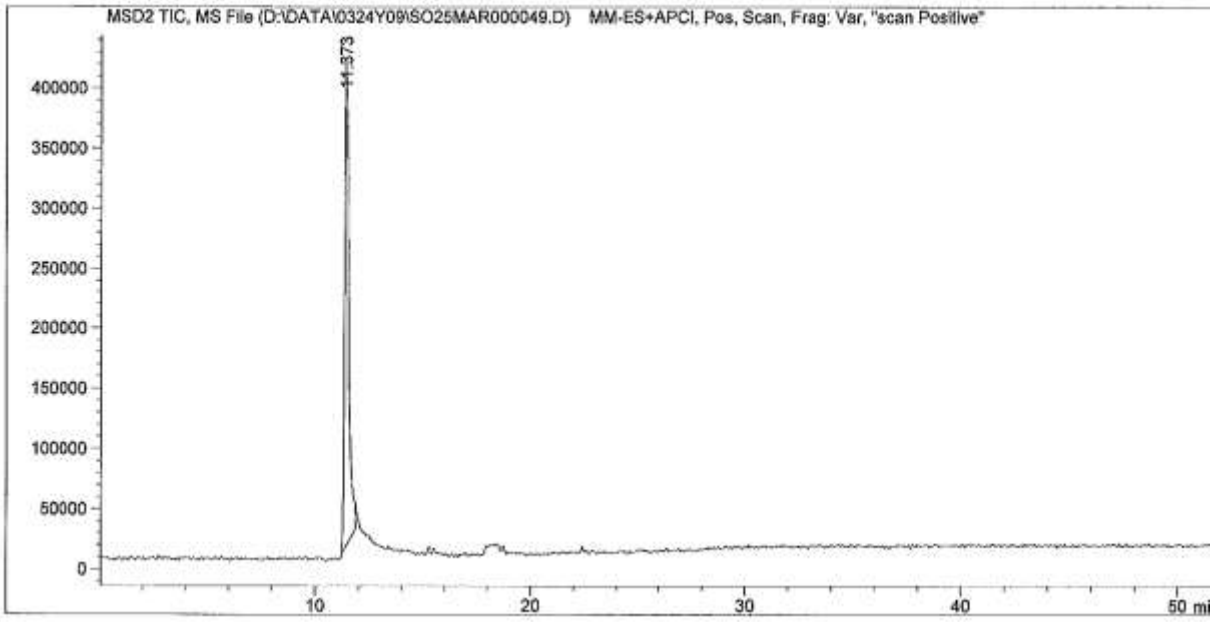


IRGACURE 369

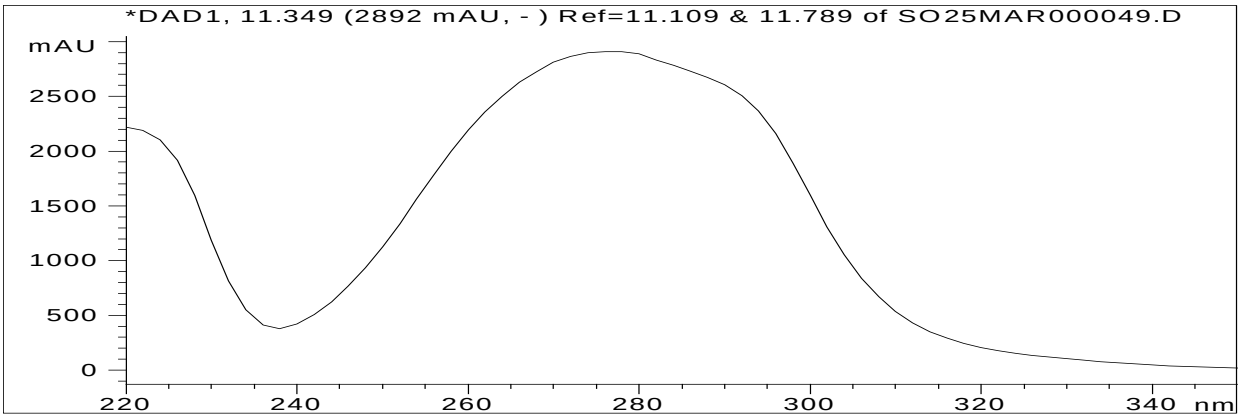
Irgacure 2959 LC-UV chromatogram 230 nm

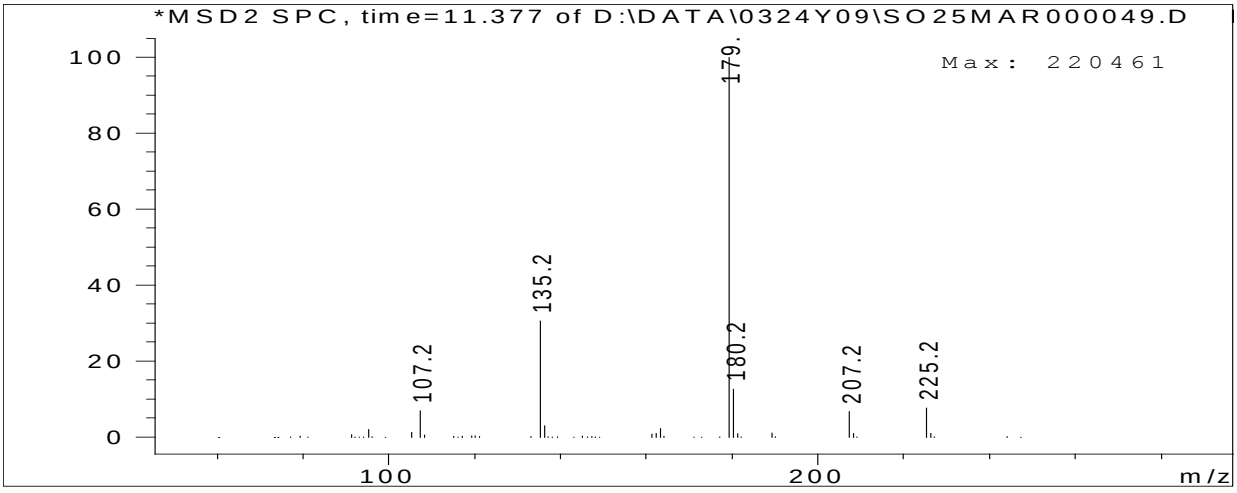


Irgacure 2959 LC-MS chromatogram



IRGACURE 2959





Appendix 10

Equipment and operating parameters used for the reference library and method development work.

The extracts obtained in section 3.3.3 on page 28 were analysed by GC-MS using the following instrumental parameters.

Gas Chromatograph	Agilent 6890N *msd3*
Injection mode	Splitless
Inlet purge on time	0.70 minute
Injector temperature	280°C
Constant Flow	1.0ml/ minute
Column	Phenomenex ZB50 30m x 0.25mm x 0.5μm 50%phenyl/50%dimethyl polysiloxane
Temperature program	40°C (2 minutes) 10°/minute to 100°C 20°/minute to 310°C 310°C (15minutes)
Mass spectrometer	HP 5972
Transfer temperature	280°C
Detector mode	Scan mode 28-800 m/z
Tune compound	PFTBA
Tune ions	69, 219, 502m/z

The concentrated extracts obtained for film A on page 28 were then analysed by GC-MS in the SIM mode looking specifically for 4-phenyl benzophenone and 2-ethylhexyl-4-(dimethylamino)benzoate. The instrumental conditions were as follows;

Gas Chromatograph	HP 6890N *msd1 PIlibrary2*
Injection mode	Split
Injector temperature	280°C
Constant Flow	1.0ml/ minute
Column	Agilent - HP5MS 30m x 0.25mm x 0.25μm film
Temperature program	40°C (2 minutes) 15°/minute to 320°C 320°C (15minutes)
Mass spectrometer	HP 5973 msd
Transfer temperature	280°C
Detector mode	SIM 77, 105, 110, 148, 152, 265, 181, 182, 192, 258, 277 m/z
Tune compound	PFTBA
Tune ions	69, 219, 502m/z

The equipment and operating parameters listed below were used to obtain chromatograms and spectra for the reference inventory of compounds described on page 35 and also the results described in 4.2 on page 37. Solutions of the ink components of approximate concentration 250 ppm were prepared in acetonitrile.

LC-MS-UV Equipment and operating parameters (FSASETOFF1)

Chromatograph Agilent 1100 Quaternary Pump

Mobile phase

Time/ minutes	**Water%**	**Acetonitrile %**
0	90	10
4	90	10
15	50	50
25	0	100
50	0	100
52	10	90

Stationary phase SGE 250 mm x 4 mm GL WAKOSIL C18RS (glass lined) 5 µm part number 207026

Flow rate 1.0 ml/min

Injection volume 20 µl

Detection Diode Array 270 nm

Agilent quadrapole MS model 6100

Ionisation mode MM-ES+APCI Negative

Scan 50 – 600 m/z

Fragmentor voltage 110V

MM – ES +APCI Positive

Scan 50 – 600 m/z

Fragmentor voltage 140V

Gas temperature	300 °C
Vaporizer	200 °C
Drying Gas	12 l/min
Nebuliser pressure	35 psig
Voltage capillary (positive)	2000 V
Voltage capillary negative	2000 V
Corona (Negative)	5.0 µA
Voltage Charge (positive)	2000 V
Voltage charge (negative)	2000 V

The equipment and operating parameters listed below were used to obtain the results described in 5.1 on page 47.

LC-CAD Equipment and operating parameters (PICORONA1)

Chromatograph Agilent 1100 Quaternary Pump

Mobile phase

Time/ minutes	Water%	Acetonitrile %
0	60	40
7.5	60	40
8.0	15	85
50	15	85
52	60	40

Stationary phase	SGE 250 mm x 4 mm GL WAKOSIL C18RS (glass lined) 5 µm part number 207026
Flow rate	1.0 ml/min
Injection volume	20 µl
Detection	ESA Corona plus CAD
Detector pressure	35 psi
Range	100 pA
Filter	None

GC-MS Analysis of reference inventory compounds

The solutions of the reference inventory compounds prepared on page 35 were analysed by GC-MS using the following instrumental parameters.

Gas Chromatograph	Agilent 7890 A *msd1*
Injection mode	splitless
Inlet temperature	280 °C
Inlet purge open	0.7 minutes
Pressure	Constant flow 1.0ml/ minute
Column	Phenomenex HP 5MS 30m x 0.25mm x 0.25µm
Temperature program	40 °C (2 minutes) 15/minute to 320°C 320°C (15minutes)
Mass spectrometer	Agilent 5975 C
Transfer temperature	280°C
Detector mode	Scan mode 28-1000 m/z
Tune compound	PFTBA
Tune ions	69, 219, 502m/z

The solutions obtained after UV exposure in 4.1 on page 36 and solutions of the reference inventory compounds prepared on page 35 that were not amenable to splitless injection were analysed by GC-MS using the following instrumental parameters.

Gas Chromatograph	Agilent 7890 A *msd1*
Injection mode	On column
Injector temperature	50 °C then tracked oven
Pressure	Constant flow 1.0ml/ minute
Column	Phenomenex HP 5MS 30m x 0.25mm x 0.25μm
Temperature program	50 °C (2 minutes) 15/minute to 320°C 320°C (15minutes)
Mass spectrometer	Agilent 5975 C
Transfer temperature	280°C
Detector mode	Scan mode 28-700 m/z
Tune compound	PFTBA
Tune ions	69, 219, 502m/z

Suggestions for calibration of GC-FID

In the ideal case, calibration of the GC-FID would be carried out using each ink component for which set off is being measured. To reduce the cost of the analysis, a reduced number of calibrations could, in principle, be carried out by calibrating using one ink component for each set of structurally similar ink components to be measured. To reduce the calibration error discussed on page 54, it suggested that Table 8-1 below could be used to select calibrants. For each class of photoinitiators appearing in the columns, one may be selected to calibrate all the others in the column.

Table 8-1 Selected Ink components amenable to GC-FID with structural similarity

Benzilketals	Hydroxyl-alkylphenones	Aminoalkyl Phenone derivatives	Benzophenone derivatives	Thioxanthones	Amine coinitiators
BDK	CAS number 0000947-19-3	CAS number 0071868-10-5 *	Benzophenone	Kayacure CTX	ethanolamines
Uvatone 8302	CAS number 0007473-98-5	Irgacure 379	4-phenyl benzophenone	Quantacure ITX	Speedcure EDB
Genocure DEAP	Irgacure 2959	Irgacure 369	Methyl benzophenones	Quantacure CPTX	Speedcure BEDB
Uvatone 8301	Irgacure 127		Speedcure MBB	Speedcure DETX	Kayacure DMBI
	Esacure 1			Kayacure RTX	Quantacure DMB
	Genocure DMHA				Quantacure EHA
	Omnirad 102				PPA

* structural similarity borderline with other members