

Supporting Information

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1. UV-Vis spectra of PM 546, PM 597 and Coumarin 6

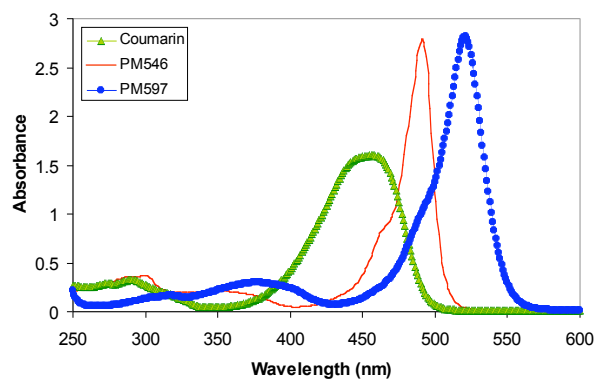


Figure 1. UV-Vis spectra of **4**, **5**, and **6** in dry acetonitrile

2. LFP data.

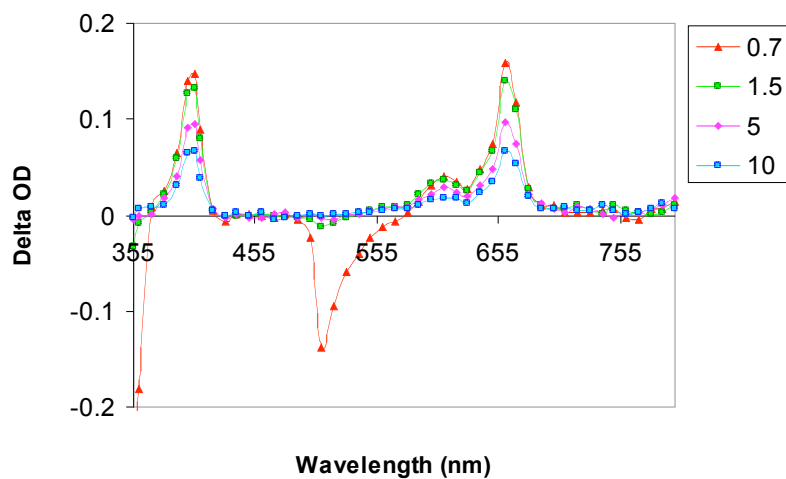


Figure 2. Transient absorption spectra for PM 546 with pyromellitic dianhydride (PMDA)

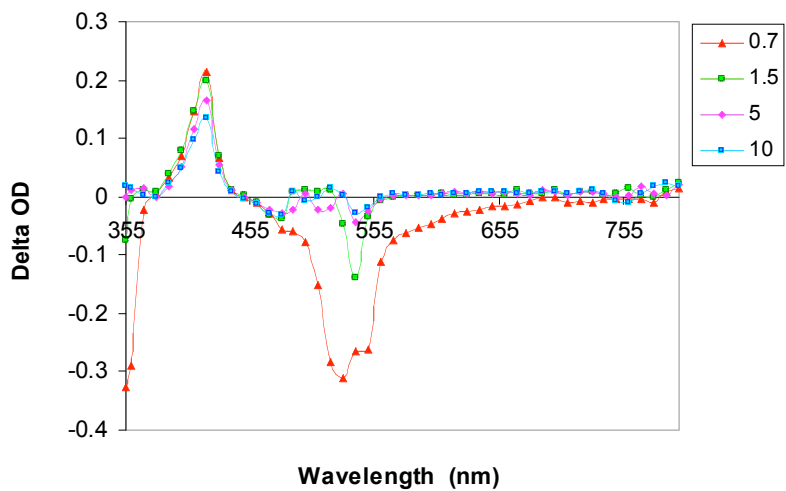


Figure 3. Transient absorption spectra of PM597 with picolinium ester **1a**

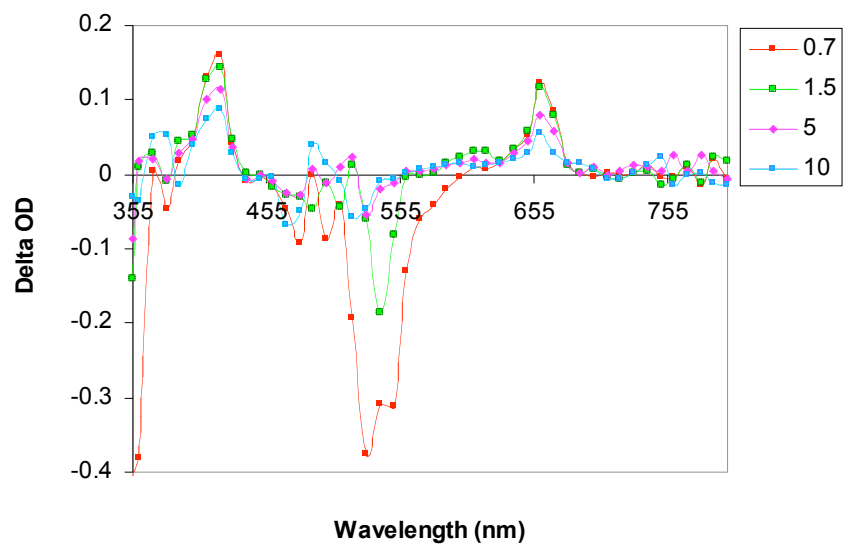


Figure 4. Transient absorption spectra for PM 597 with PMDA

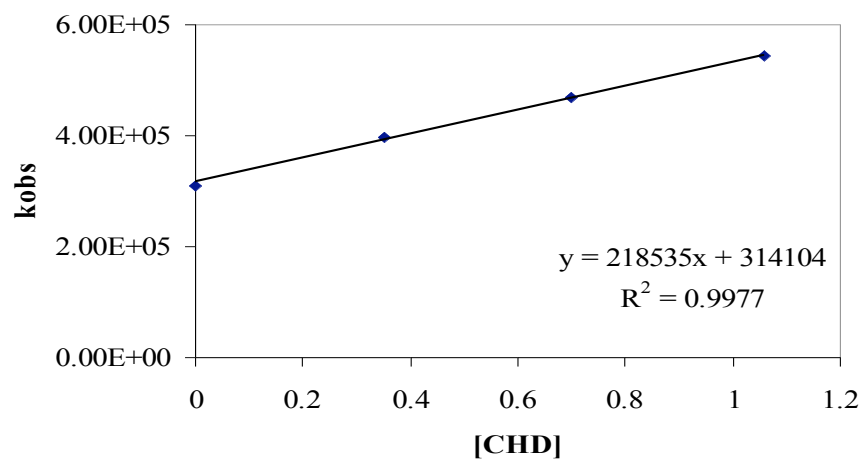


Figure 5. Quenching of PM 546 cation radical by CHD with ester **1a**

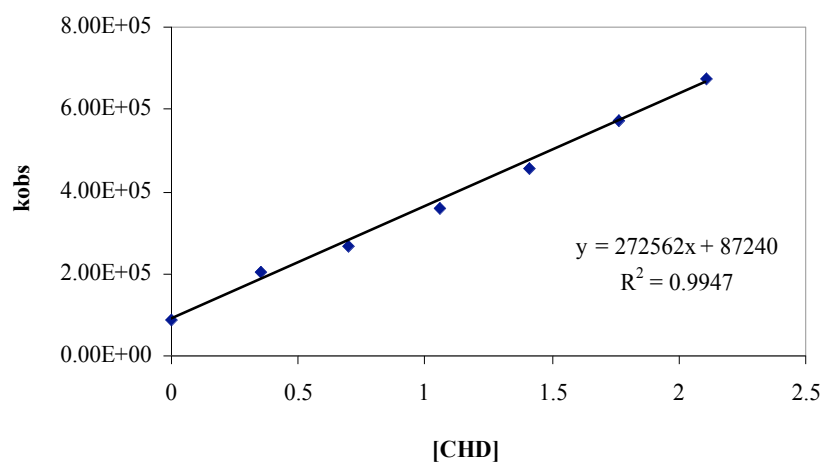


Figure 6. Quenching of PM546 cation radical by CHD with PMDA

3. Fluorescence data.

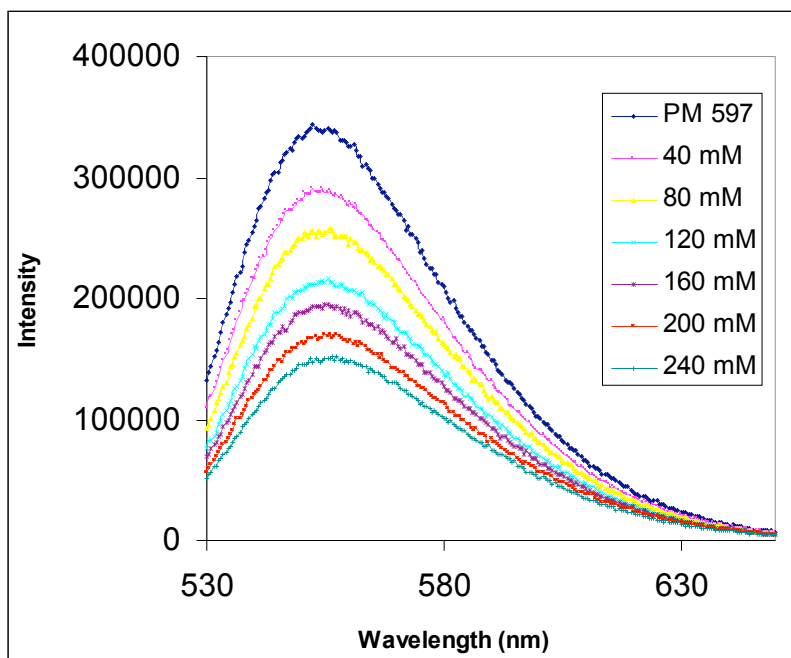


Figure 7. Fluorescence quenching data for PM 597 with ester **1a**

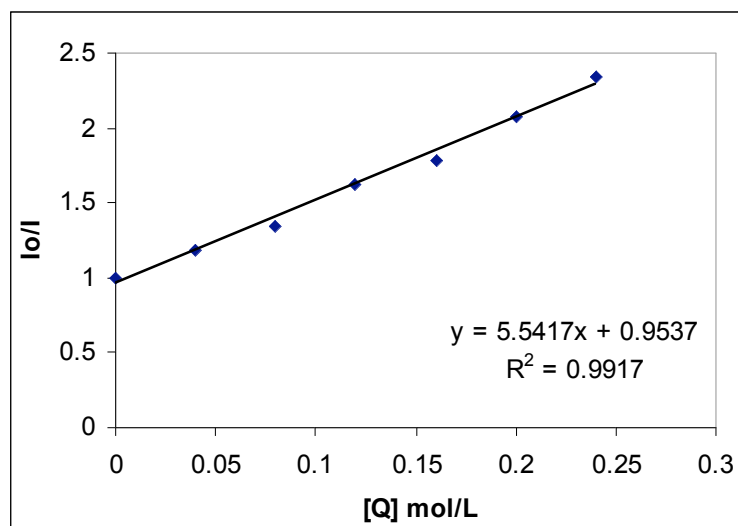


Figure 8. Stern-Volmer plot for fluorescence quenching of PM 597 by ester **1a**

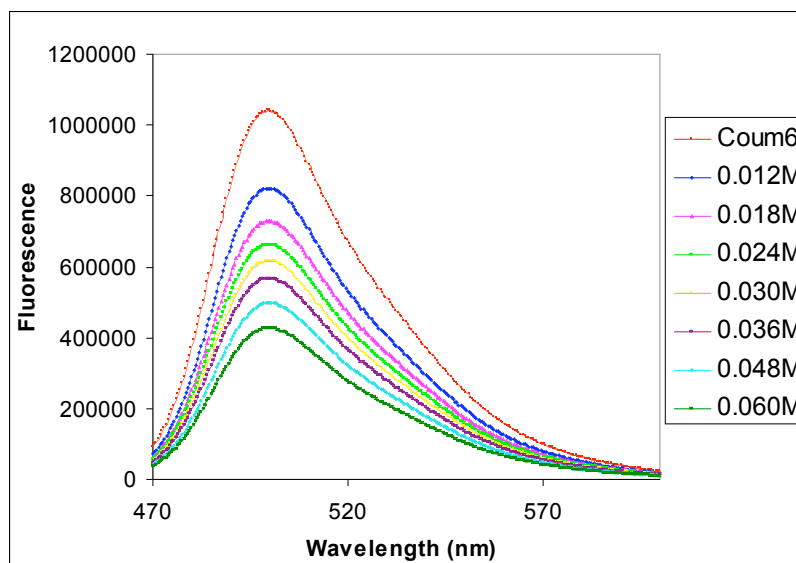


Figure 9. Fluorescence quenching data for Coumarin 6 with ester **1a**

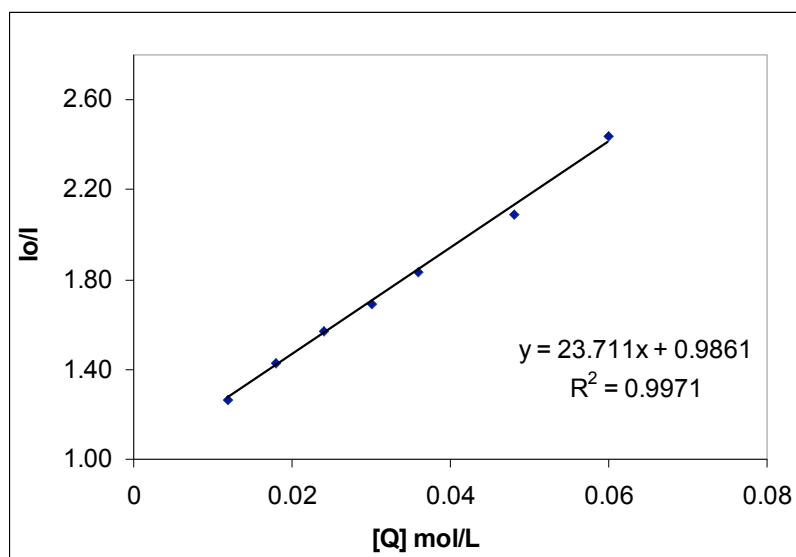


Figure 10. Stern-Volmer plot for fluorescence quenching of Coumarin 6 by ester **1a**

General Procedures.

All ^1H and ^{13}C NMR were obtained using a 400 MHz spectrometer. Deuterated CD_3CN or CD_3OD were used for all NMR experiments. Acetonitrile was distilled from calcium hydride under nitrogen atmosphere. Ultraviolet-visible spectra were recorded on a spectrophotometer.

Fluorescence Quenching Experiments.

Fluorescence quenching experiments were performed on a luminescence spectrometer. Samples in dry CH_3CN solvent were placed in 1 cm quartz cuvettes, sealed with rubber septums and purged with N_2 for 10-15 min. Sample concentrations were prepared such that the optical densities at the excitation wavelength were about 0.1- 0.3.

Quantum Yield Determination.

The solutions were photolyzed by the output of a 1000 W Hg-Xe lamp after passing through a spectral energy monochromator set to absorption maximum of the dye ± 20 nm. Solutions of ester and sensitizer (3.5 mM, OD at λ_{max} about 0.1-0.3) were placed in a 1 cm quartz cuvette and purged with N_2 for 15 min. The samples were irradiated and the amount of ester converted was determined by ^1H NMR integration. Light intensities were measured by a radiometer calibrated by ferrioxalate actinometry.

Deprotection Photolysis.

A solution of 4-10 mg of the picolinium ester and an equal amount or slight excess of sensitizer was prepared in 5 mL of CH_3CN and 1mL CHD (3.5 mM of ester and

sensitizer, 1.7 M CHD). Half of the solution was used as dark control and the remaining half was N₂ purged and photolyzed using a 300 W tungsten lamp with continuous stirring. The dark control and irradiated solutions were then evaporated and redissolved in CD₃OD with hexamethyldisiloxane as the internal standard and ¹H NMR spectra were obtained. The percent yields were determined by ¹H NMR integration of the carboxylic acid peaks relative to the internal standard.

Control experiments were also carried out to ensure that deprotection was effected by the visible light alone and not by any UV component that might be emanating from the tungsten light source. In several cases, the esters were photolyzed under identical conditions with and without a 400 nm filter and the same yields were obtained in both cases within experimental error ($\pm 5\%$).

Preparative Photolysis.

The preparative photolysis mixture was scaled up by a factor of 4, from the deprotection photolysis, and the irradiation time was scaled up by a factor of 6 to ensure complete conversion of the ester. A 1 mL aliquot was used as dark control and the remaining solution was N₂ purged and photolyzed using a 300 W tungsten lamp with continuous stirring. A 1 mL aliquot was then removed for determining ester conversion by ¹H NMR as described above. The remaining solution was evaporated, and the residue dissolved in CH₂Cl₂ (20 mL). The free acid was extracted into aqueous layer by addition of NaHCO₃ (4 x 10 mL). The aqueous layer was acidified and extracted with CH₂Cl₂ (4 x 10 mL). The organic layer was dried over MgSO₄, and concentrated in vacuo. The product was weighed and analyzed by ¹H NMR and compared against the standard.

Laser Flash Photolysis.

Laser flash photolysis experiments were performed using a Nd:YAG laser as the pump beam source. The laser used was capable of 355 nm pulses between 4-6 ns duration. A 350 MHz digital oscilloscope was used to observe the waveforms. The samples were prepared such that the absorbances were between 1.5 and 2.0 at the excitation wavelength of 355 nm. The samples were placed in 1 cm quartz cuvettes and N₂ purged for 15 min, and stirred continuously during the photolysis.

4. Synthesis and characterization of picolinium esters 1a-e.

The esters were prepared in three steps.

Step 1. Preparation of picolyl esters.

Picolyl ester a : was prepared using the procedure of Abele et al.¹ To a solution of 4-pyridyl carbinol (3.45 g, 31.6 mmol) in 40 mL of benzene, triethylamine (7.97 ml, 56.8 mmol) was added. A solution of phenylacetyl chloride (50.5 mmol) in 15 mL of benzene was added dropwise. The reaction mixture was stirred at room temperature for 16 h. 30 ml of H₂O was added and the organic layer was separated, dried over MgSO₄, and concentrated in vacuo. Characterization data for picolyl ester **a** has been reported previously.²

Picolyl ester b: was prepared using the procedure of Camble et al.³ *N*, *N'*-Dicyclohexylcarbodiimide (DCC) (3.40 g, 16.4 mmol) was added to a solution of diphenylacetic acid (16.4 mmol) and 4- pyridyl carbinol (1.62 g, 14.8 mmol) in 50 mL of dichloromethane. The reaction mixture was stirred at room temperature for about 24 h, and checked by t.l.c for disappearance of starting material. The urea precipitate was filtered off and the filtrate was washed with NaHCO₃ (2 x 25 mL) and H₂O (2 x 10 mL). The organic layers were collected and dried over MgSO₄ and the solvent was evaporated. Characterization data for picolyl ester **b** has been reported previously.²

Picolyl esters **c** and **d** : were prepared using the procedure of Camble et al.³ A solution of *N*-benzoylcarbonyl-L-glycine or *N*-benzoylcarbonyl-L-serine (10 mmoles), 4-picolyl chloride hydrochloride (1.6 g, 10 mmoles), and triethylamine (2.1 g, 20 mmoles) in dimethylformamide was heated at 90° C for 3 h, till t.l.c showed absence of 4-picolyl chloride. The solvent was distilled off, and 30 mL of ethyl acetate was added to the residue. The solution was washed with sat. NaHCO₃ (3 x 10 mL), water (2 x 10 mL) and brine (10 mL) and then dried over MgSO₄. After evaporation of the solvent, the dark brown solid was recrystallized twice to give the ester.

Picolyl ester c. (Picolyl Glycinate) was prepared using *N*-benzyloxycarbonyl glycine. The product is a pale pink solid after recrystallizing twice from ether (1.6 g, 53%). Mp 70-72 °C (lit³ 71.5-73.5); ¹H NMR (CD₃CN): δ 3.93 (d, *J*=6.2, 2H), 5.08 (s, 2H), 5.16 (s, 2H), 7.36-7.28 (m, 7H), 8.54 (d, *J*=6.2, 2H); ¹³C NMR (CD₃CN): 43.2, 65.3, 67.1, 122.7, 128.4, 128.8, 129.8, 149.7, 150.4, 157.5, 170.9; LRMS (FAB) 301 ((M+H)⁺, 100), 119 (50); HRMS (FAB) calcd for C₁₆H₁₆N₂O₄ 301.1188 (M+H)⁺, found 301.1176.

Picolyl ester d. (Picolyl Serinate) was prepared using *N*-benzyloxycarbonyl serine. The product is a pale peach solid after recrystallizing twice from ether (0.95 g, 29%). Mp 130-132 °C; ¹H NMR (CD₃CN): δ 3.80 (dd, *J*=4.2, 6.4, 1H), 3.90 (dd, *J*=4.2, 6.4, 1H), 4.39-4.37 (m, 1H), 5.09 (s, 2H), 5.19 (d, *J*=5.4, 2H), 7.36-7.28 (m, 7H), 8.53 (d, *J*=5.4, 2H); ¹³C NMR (CD₃CN): 57.3, 62.6, 65.5, 67.1, 122.4, 128.6, 128.8, 129.3, 137.9, 145.9, 150.7, 157.1, 171.4; LRMS (DEI) 330 (M⁺, 20), 223 (7), 181 (6); HRMS (FAB) calcd for C₁₇H₁₈N₂O₅ 330.1216, found 330.1214.

Picolyl ester e : was prepared using a modified procedure of Givens et al.⁴ To a solution of 4-pyridyl methanol (2.2 g, 20.2 mmol) in 8 mL of pyridine maintained at -2° C, diethyl phosphoryl chloride (6.4 mL, 41.6 mmol) was added dropwise. The solution was stirred at -2° C for 2 hrs and then stirred at room temperature for 12-16 hrs. About 50 mL of water was added to the reaction mixture and the pH of the solution was raised to 8.5 by adding base. The mixture was extracted with dichloromethane (3 x 30 mL). The organic layers were collected and washed with water (2 x 30 mL), and then dried over MgSO₄. The solvent was evaporated and the product dried under reduced pressure.

Picolyl ester e (Picolyl Diethylphosphate) is a dark brown thick liquid (2.8 g, 64%). The product was not purified further, as it appeared pure by ¹H NMR. ¹H NMR (CD₃CN): δ 1.29-1.25 (m, 6H), 4.09-4.05 (m, 4H), 5.04 (d, *J*=8.0, 2H), 7.33 (d, *J*=5.8, 2H), 8.56 (d, *J*=5.8, 2H); ¹³C NMR (CD₃CN): 16.2, 62.7, 64.8, 67.5, 122.4, 150.7; LRMS (FAB) 217 (M⁺, 100), 108 (55); HRMS (FAB) calcd for C₈H₁₂NPO₄ 217.0504, found 217.0508.

Step 2. Methylation of picolyl esters

About 0.02 mol of the corresponding picolyl ester was dissolved in 15-20 ml of CH₃OH, and methyl iodide (4.26 g, 0.03 mol) was added slowly. The reaction mixture was refluxed at 70 °C for 8 h. The solvent was removed under reduced pressure and the residue was recrystallized from hot methanol or ethanol. The picolinium iodides were checked for purity by ¹H NMR and taken directly to step 3.

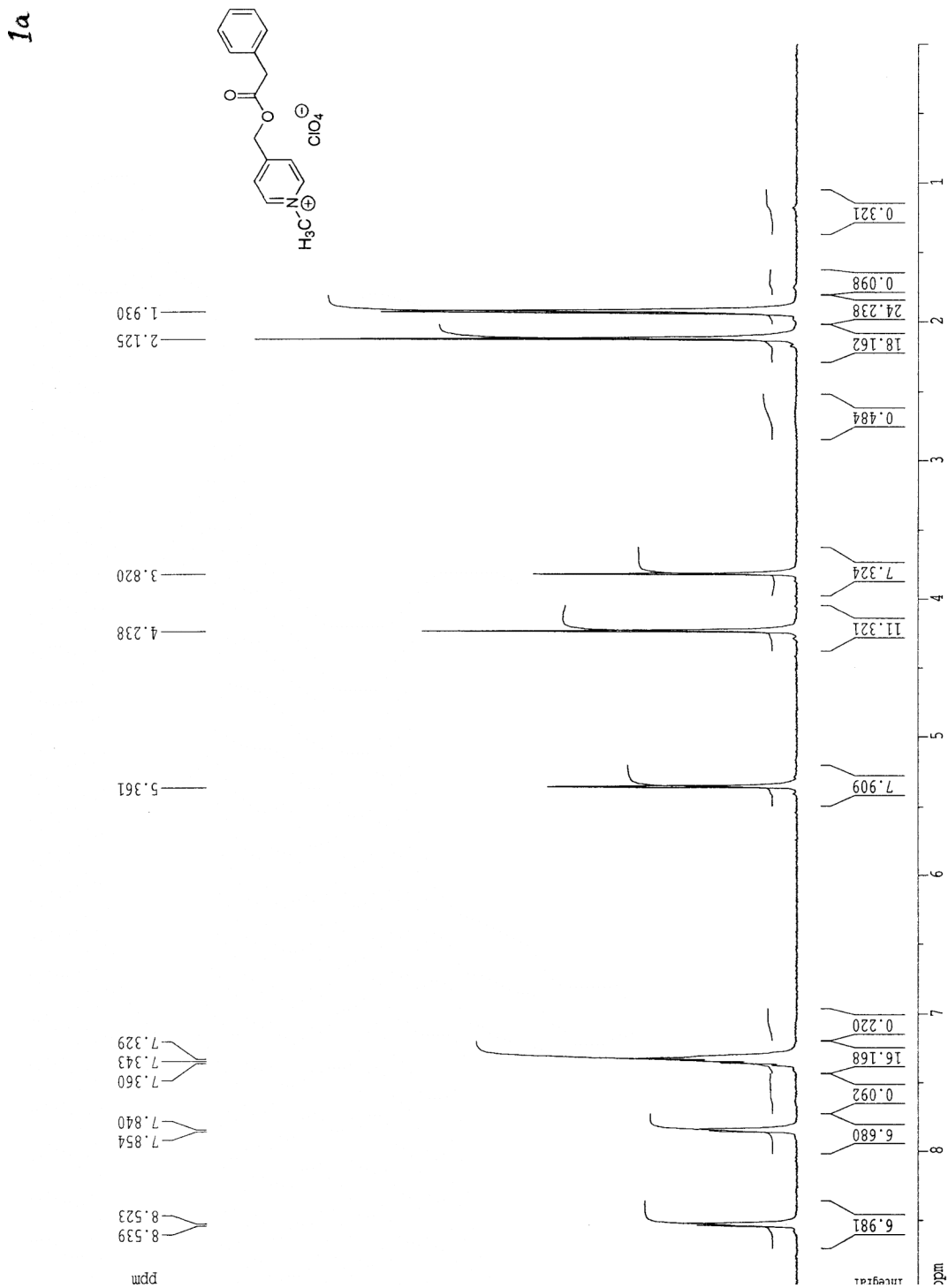
Step 3. Counter-ion exchange to give perchlorate salts 1a-e

The picolyl methiodide (5 mmol) is dissolved in the minimum amount of acetonitrile. A solution of silver perchlorate (1.04 g, 5 mmol) in acetonitrile was added and the reaction mixture was stirred overnight at room temperature. The yellow AgI precipitate was filtered off and the filtrate was concentrated in vacuo and recrystallized from hot ethanol.

5. Characterization data for picolinium esters 1a-e

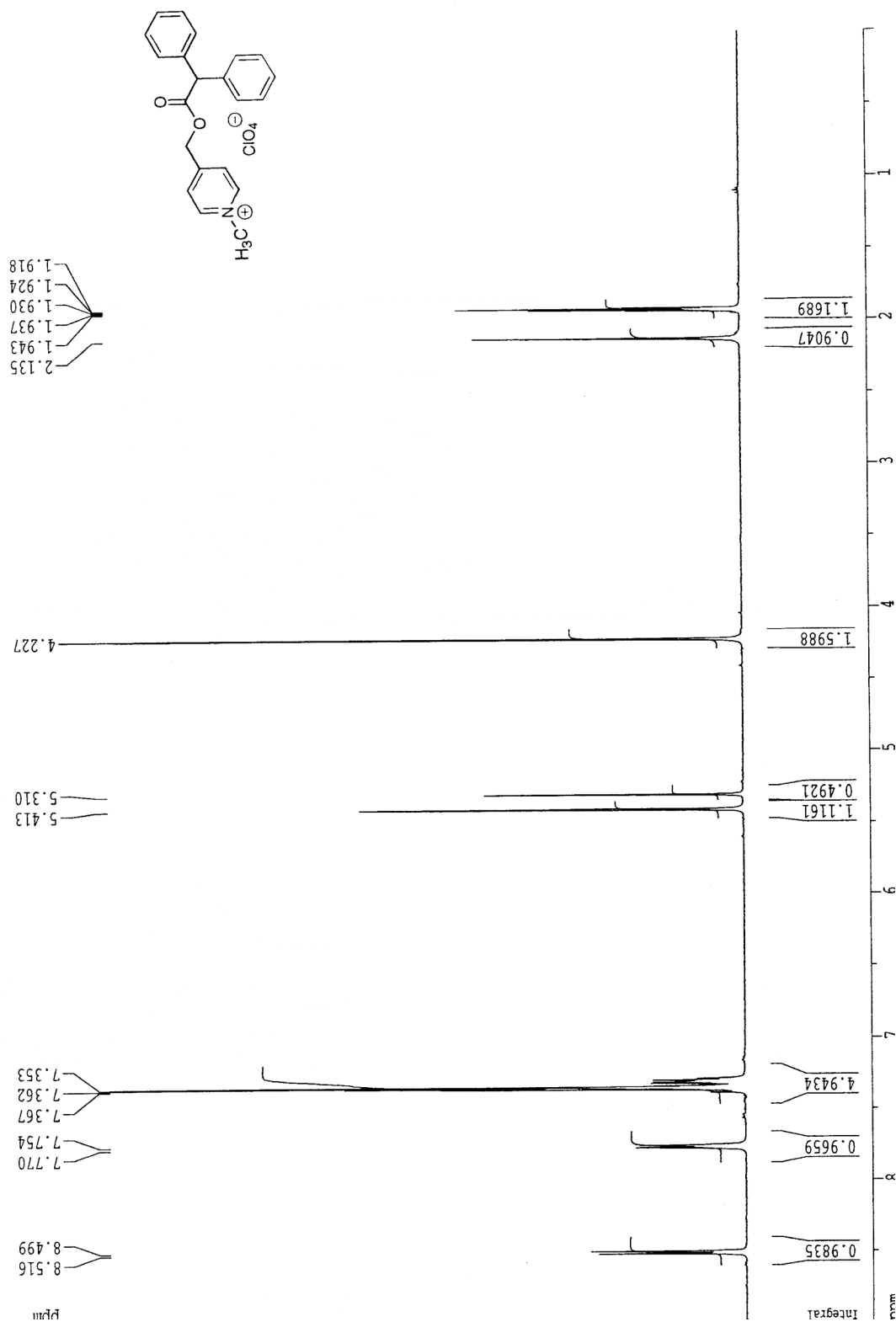
The ^1H NMRs and MS data for picolinium perchlorates **1a-e** are given below.

Ester 1a. Has already been reported (Sundararajan, C.; Falvey, D. E. *J. Org. Chem.* **2004**, *69*, 5547-5554)

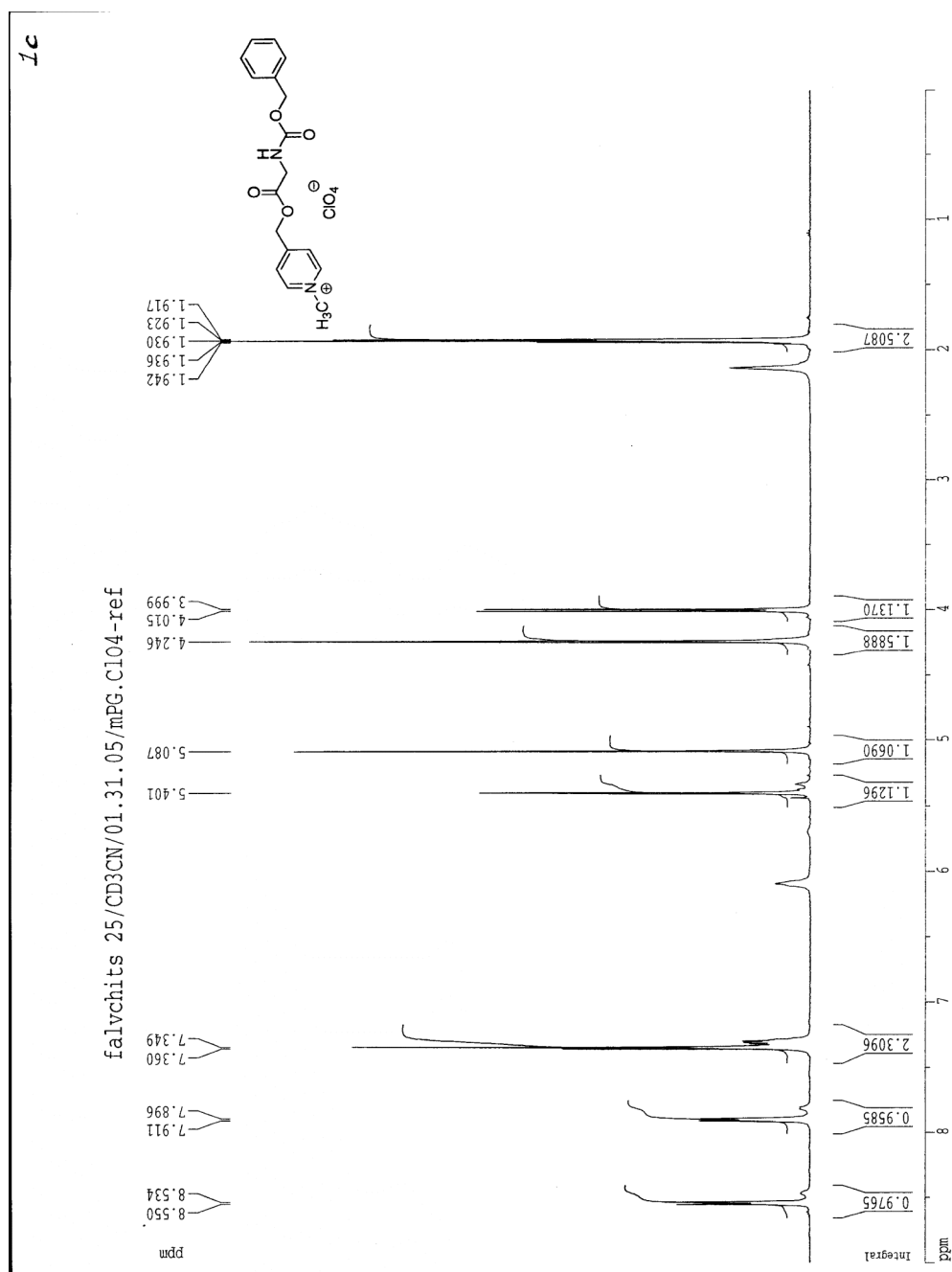


Ester 1b. Has already been reported (Sundararajan, C.; Falvey, D. E. *J. Org. Chem.* **2004**, 69, 5547-5554)

1b

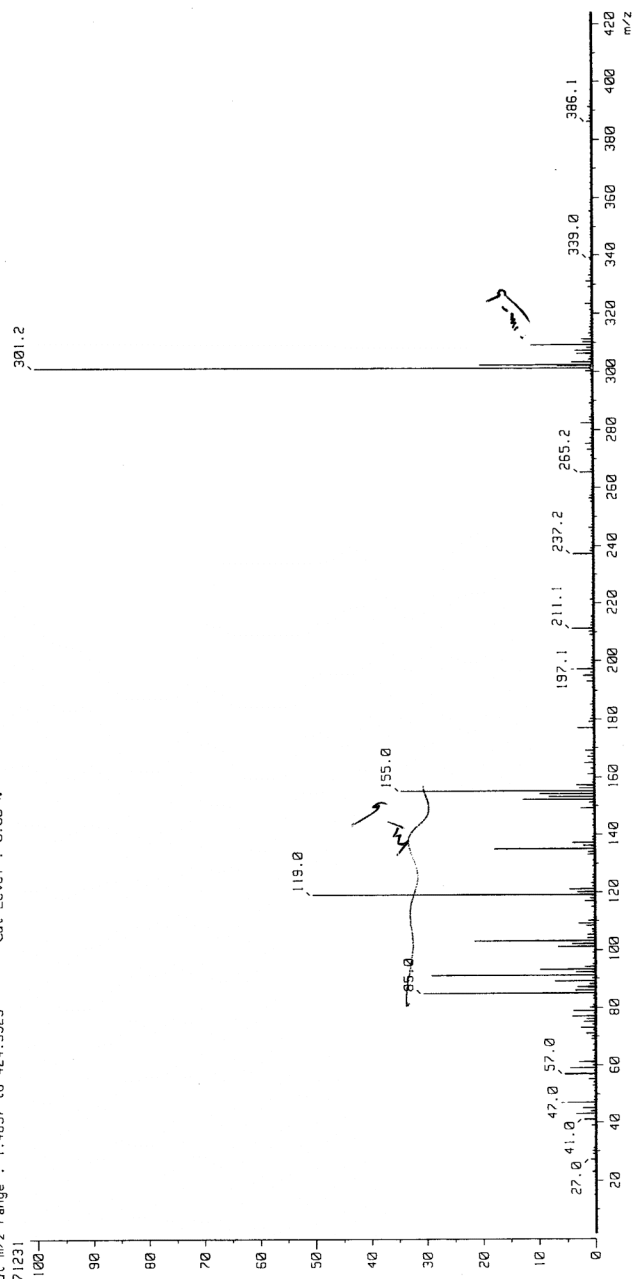


Ester 1c. Compound **1c** was a pale peach colored solid (1.85 g, 90%). Mp 62-64 °C; ^{13}C NMR (CD_3CN) δ 43.1, 48.9, 64.5, 67.8, 125.7, 128.3, 128.7, 129.2, 137.7, 145.3, 156.6, 157.4, 170.7; LRMS (FAB) 315 ($(\text{M})^+$, 100), 119 (20), 85 (20); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_4$ 315.1345, found 315.1356.



Ester 1c

[Mass Spectrum]
 Date : 02-Oct-2002 11:45
 Sample: Sunderarajan, CSK3 pg. 300, m-b
 Note : -
 Inlet : Direct Ion Mode : FAB+
 Spectrum Type : Normal Ion (MF-Linear)
 Scan# : (2,3)
 RT : 0.20 min
 BP : m/z 301.1908 Int. : 59.74
 Output m/z range : 1.4837 to 424.3323
 Cut Level : 0.00 %
 1271231



1c

[Elemental Composition]

Page: 1

Data : UMSX102a1779

Date : 02-Oct-2002 12:14

Sample: Sundararajan, CSM3 PG, 300, m-b/peg

Note : -

Inlet : Direct

Ion Mode : FAB+

RT : 0.35 min

Scan#: (3,6)

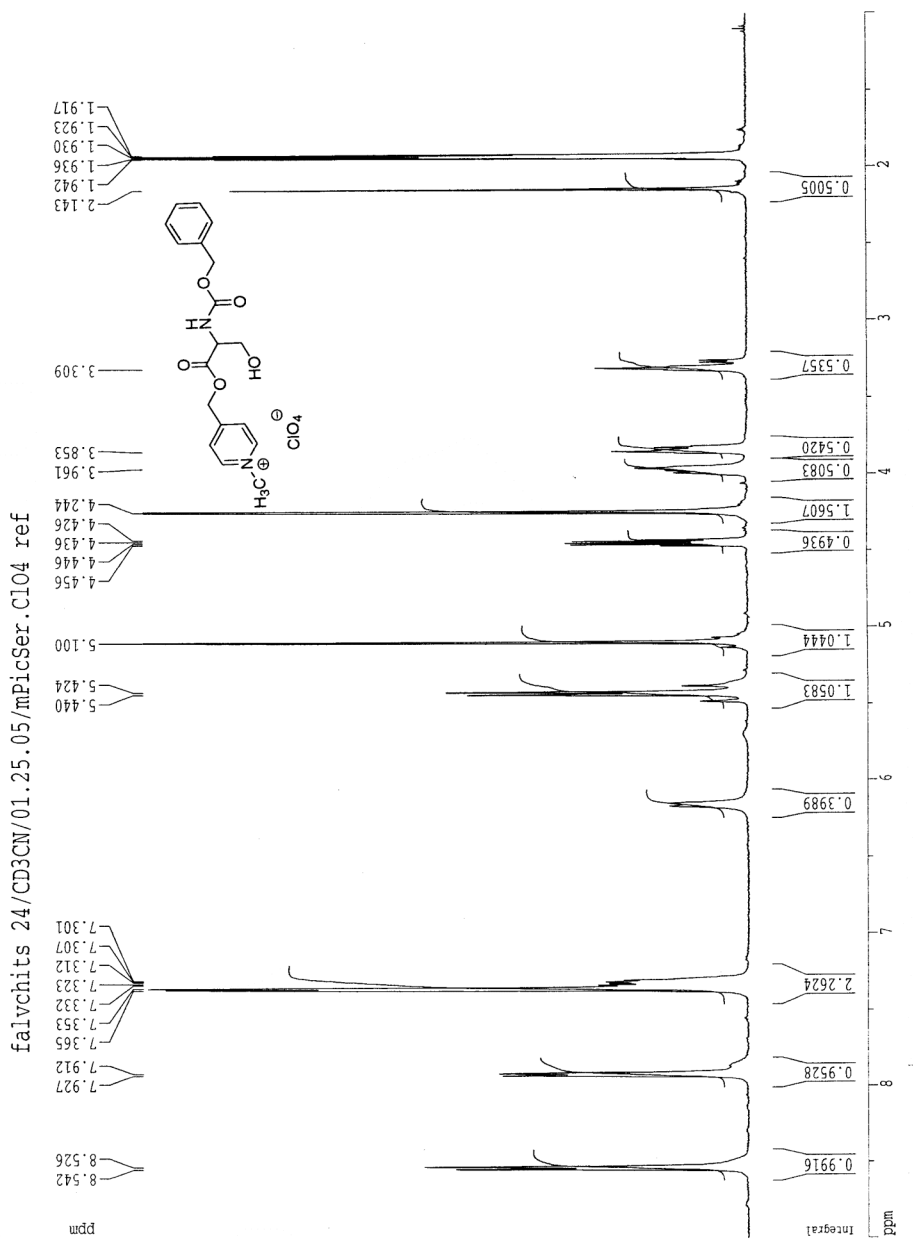
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Mass Tolerance : 1000ppm, 25mmu if m/z > 25

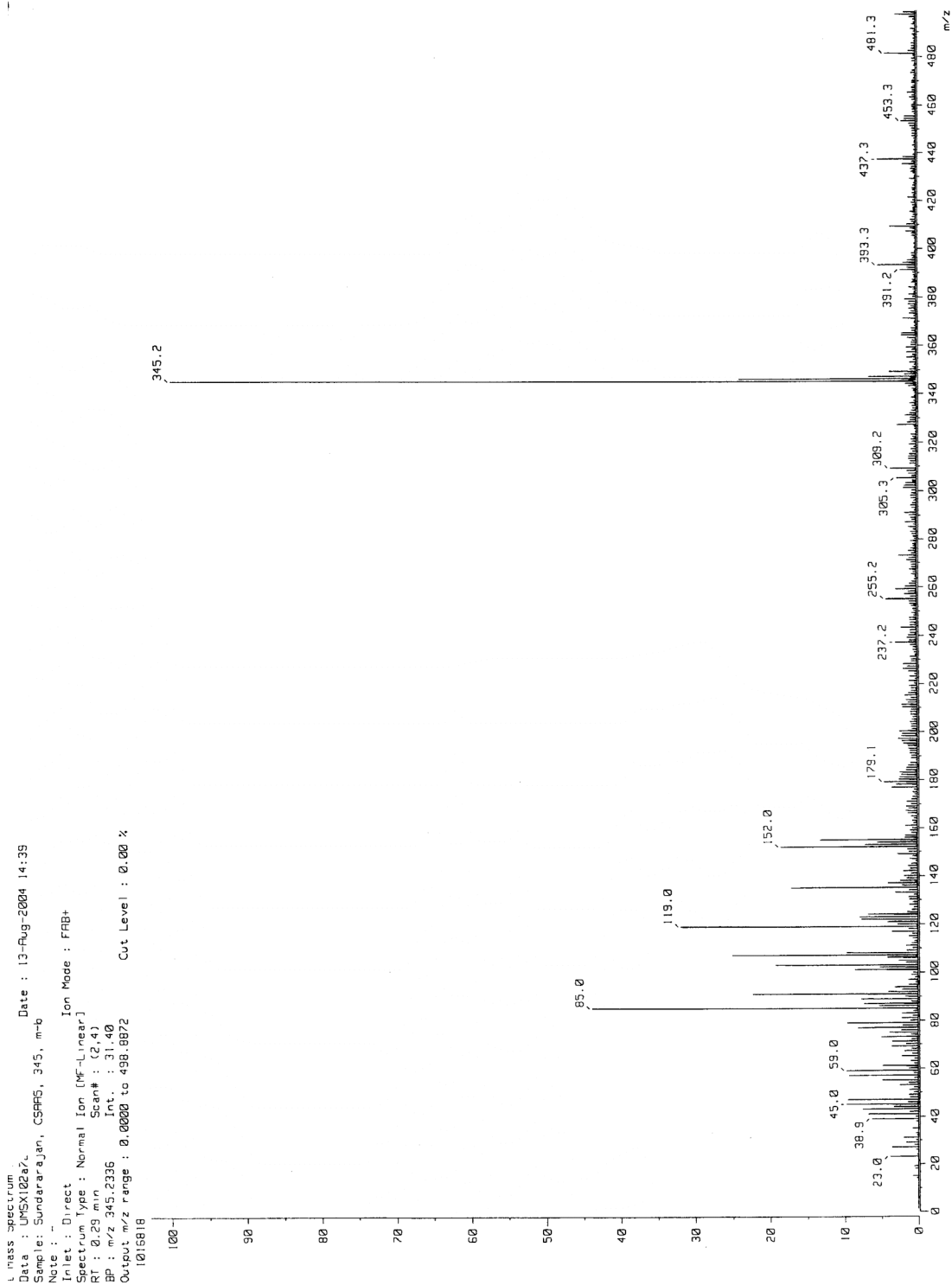
Unsaturation (U.S.) : -5.0 - 35.0

Observed m/z	Int%					
301.1176	100.0					
Estimated m/z	Error[ppm]	U.S.	12C	H	O	N
301.1017	+52.6	18.5	24	13	-	-
301.1229	-17.6	13.5	21	17	2	-
301.1103	+24.2	14.0	20	15	2	1
301.1314	-46.0	9.0	17	19	4	1
301.1341	-54.9	13.5	20	17	1	2
301.0977	+65.9	14.5	19	13	2	2
301.1188	-4.2	9.5	16	17	4	2
301.1215	-13.1	14.0	19	15	1	3
301.1063	+37.5	10.0	15	15	4	3

Ester 1d. Compound **1d** was a pale orange solid (0.99 g, 71%). Mp 108-110 °C; ^{13}C NMR (CD_3CN): 48.7, 57.2, 62.6, 64.5, 67.2, 125.7, 128.5, 128.8, 129.3, 137.8, 145.9, 156.9, 157.1, 171.1; LRMS (FAB) 345 (M^+ , 100), 152 (20), 85 (45); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_5$ 345.1450, found 345.1465.



Ester 1d



Ester 1d

8

[Elemental Composition]

Page: 1

Data : UMSX102a7300

Date : 13-Aug-2004 14:46

Sample: Sundararajan, CSAA5, 345, m-b/peg

Note : -

let : Direct

Ion Mode : FAB+

RT : 0.64 min

Scan#: (5,7)

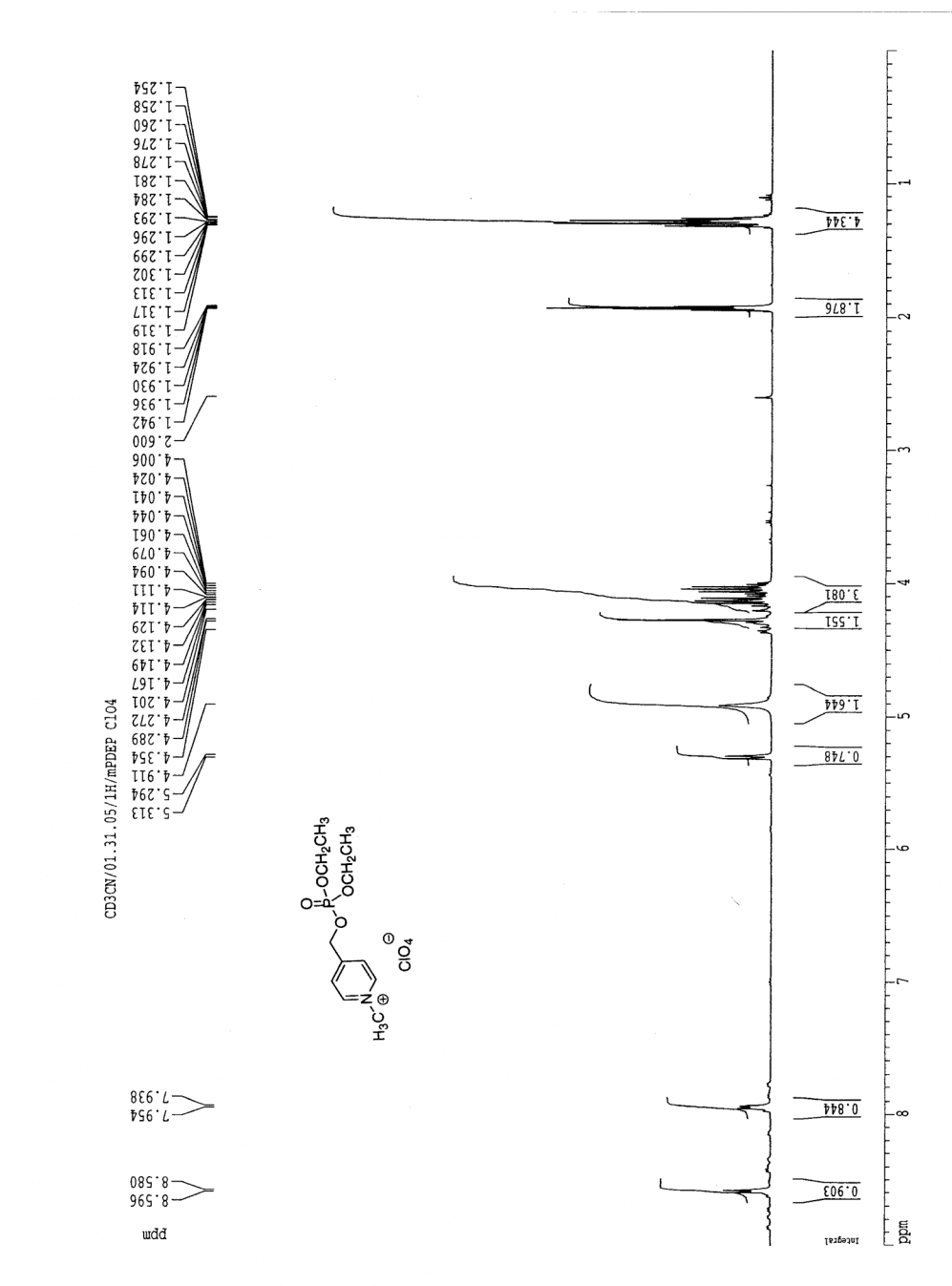
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Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 30mmu if m/z > 30

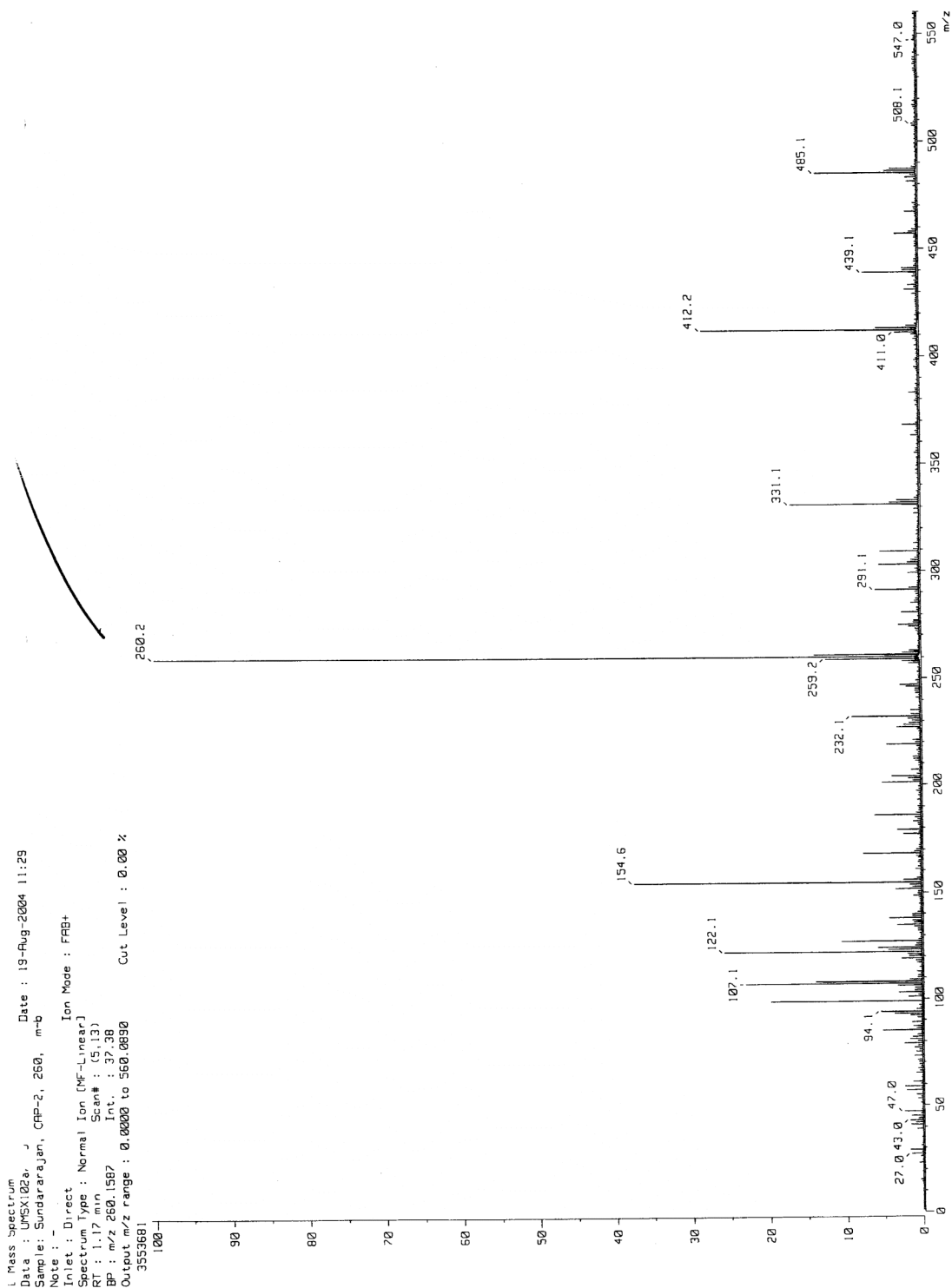
Unsaturation (U.S.) : -5.0 - 50.0

Observed m/z	Int%					
345.1465	100.0					
Estimated m/z	Error [ppm]	U.S.	12C	1H	O	N
345.1702	-68.6	8.5	20	25	5	-
345.1338	+36.8	9.5	19	21	6	-
345.1576	-32.2	9.0	19	23	5	1
345.1212	+73.2	10.0	18	19	6	1
345.1450	+4.3	9.5	18	21	5	2

Ester 1e. Compound **1e** is a thick pale yellow liquid (1.21 g, 65%). ^{13}C NMR (CD_3CN) δ 16.3, 48.9, 64.5, 65.4, 73.2, 125.6, 146.0; LRMS (FAB) 260 (M^+ , 100), 154 (38), 122 (27), 107 (25); HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{19}\text{NPO}_4$ 260.1052, found 260.1040.

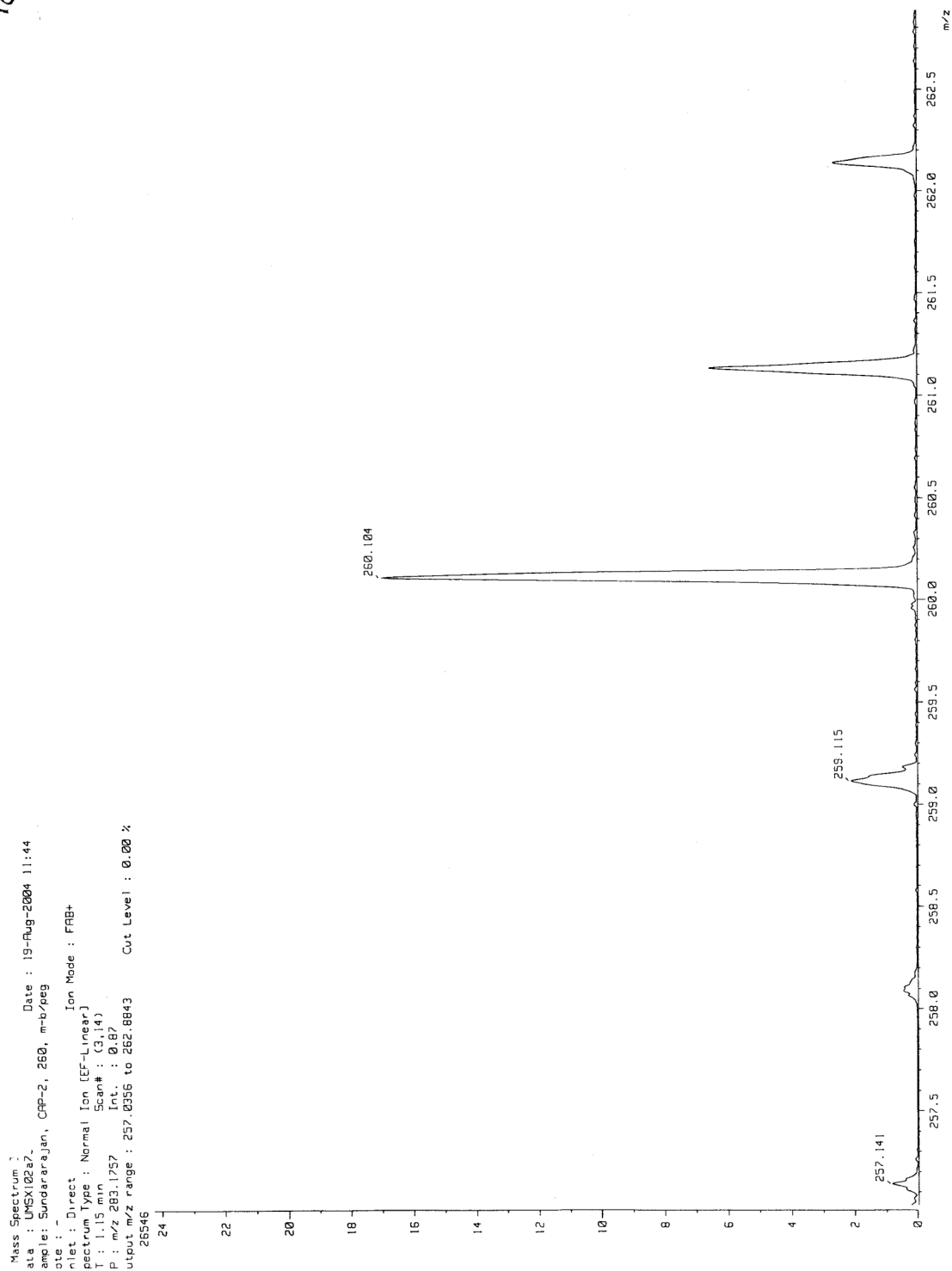


Ester 1e



Ester 1e

1e



Ester 1e

1e

[Elemental Composition]

Page: 1

Data : UMSX102a7370

Date : 19-Aug-2004 11:44

Sample: Sundararajan, CAP-2, 260, m-b/peg

Note : -

let : Direct

Ion Mode : FAB+

RT : 1.15 min

Scan#: (3,14)

Elements : 12C 100/0, 1H 150/0, O 5/2, N 1/0, P 1/0

Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 30mmu if m/z > 30

Unsaturation (U.S.) : -5.0 - 50.0

Observed m/z	Int%						
260.1040	51.9						
Estimated m/z	Error[ppm]	U.S.	12C	1H	O	N	P
260.0837	+77.9	13.0	18	12	2	-	-
260.1049	-3.3	8.0	15	16	4	-	-
260.1287	-94.8	7.5	15	18	3	1	-
260.0923	+45.1	8.5	14	14	4	1	-
260.0966	+28.4	9.0	15	17	2	-	1
260.1177	-52.8	4.0	12	21	4	-	1
260.0814	+87.0	5.0	11	17	5	-	1
260.0840	+76.7	9.5	14	15	2	1	1
260.1052	-4.5	4.5	11	19	4	1	1

References:

- (1) Abele, E.; Abele, R.; Gaukhman, A.; Lukevics, E. *Synthesis of Alkyl Heteryl Ethers from Acetates under Interphase Catalysis Conditions in a Liquid/Solid System*; Wiley-Interscience: New York, 1998; Vol. 34.
- (2) Sundararajan, C.; Falvey, D. E. *J. Org. Chem.* **2004**, *69*, 5547-5554.
- (3) Camble, R.; Garner, R.; Young, G. T. *J. Chem. Soc. (C)* **1969**, 1911-1916.
- (4) Givens, R. S.; Athey, P. S.; Matuszewski, B.; L. William Kueper, I.; Xue, J.-y.; Fister, T. *J. Am. Chem. Soc.* **1993**, *115*, 6001-6012.