

Supporting Information

Enantioselective Mukaiyama-Michael with 2-Enoyl Pyridine *N*-Oxides Catalyzed by PYBOX-DIPH-Zn(II)-Complexes at Ambient Temperature

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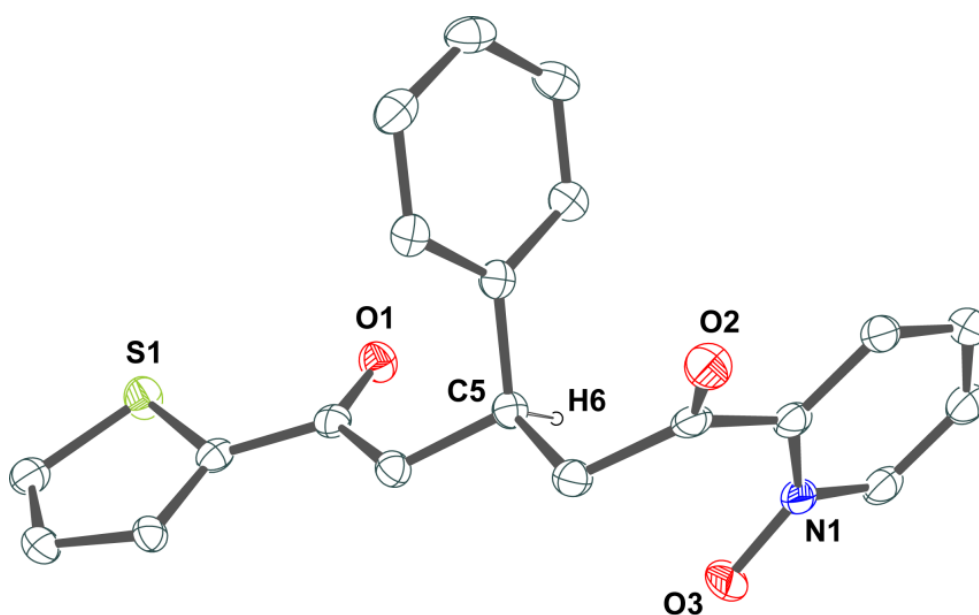
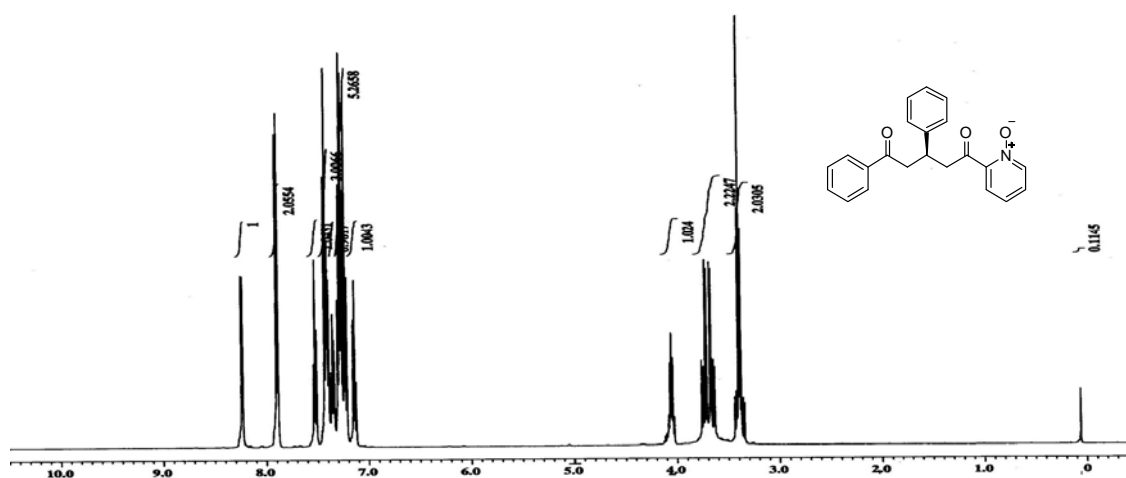


Figure 3. ORTEP diagrams of **4n** with thermal ellipsoids at the 50% probability limit (other H-atoms are deleted for clarity).

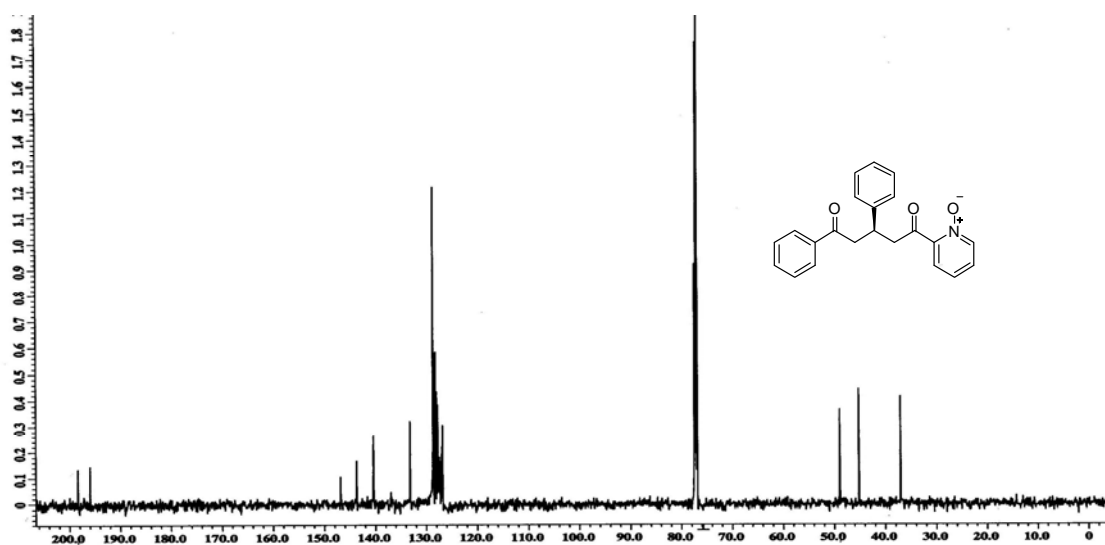
Table 1. Crystal data and structure refinement parameters of compound **4n**.

Parameters	Compound 4n
Empirical formula	C ₂₀ H ₁₇ N O ₃ S
Formula weight	351.41
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Unit cell dimensions	$a = 11.7359(8)$ Å $b = 5.5595(4)$ Å $c = 12.5993(9)$ Å $\alpha = 90.000^\circ$ $\beta = 90.641(2)^\circ$ $\gamma = 90.000^\circ$

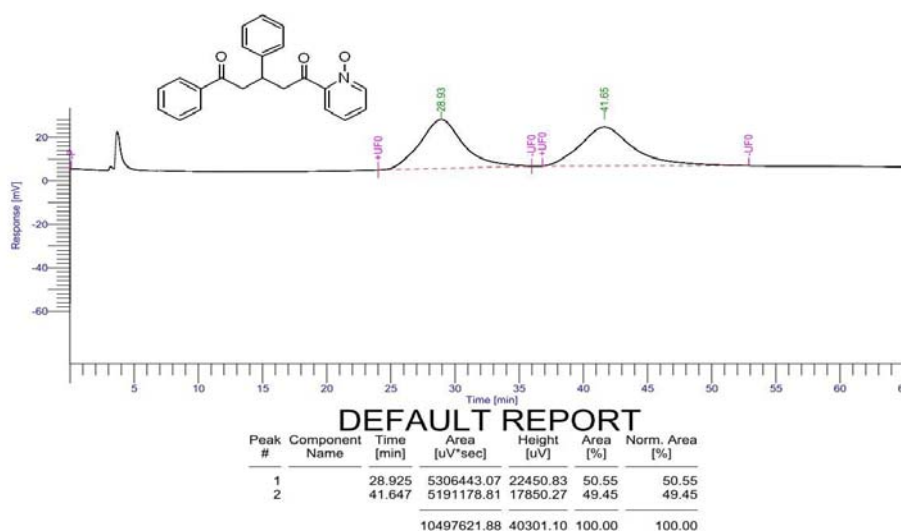
Volume	822.00(10) Å ³
Z, Calculated density	2, 1.420 Mg/m ³
Absorption coefficient	0.216 mm ⁻¹
F(000)	368
Colour, Shape	Colourless, Block
Crystal size	0.22 x 0.18 x 0.16 mm ³
θ range for data collection	2.36 to 25.50°
Limiting indices	-13 ≤ h ≤ 14, -6 ≤ k ≤ 6, -15 ≤ l ≤ 14
Reflections collected / unique	5875 / 3009 [R(int) = 0.0193]
Reflections used	4834
Completeness to theta	99.9 %
Data / restraints / parameters	3009 / 1 / 226
Goodness-of-fit on F ²	1.075
Final R indices [I > 2σ(I)]	R ₁ = 0.0296, wR ₂ = 0.0708
R indices (all data)	R ₁ = 0.0323, wR ₂ = 0.0726
Flack parameter	-0.05(7)
Largest diff. peak and hole	0.207 and -0.167 e.Å ⁻³



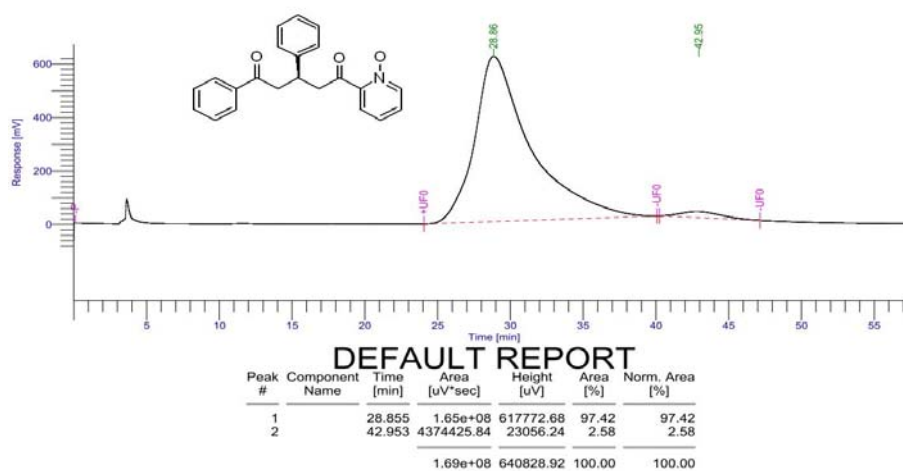
500 MHz ^1H NMR spectra of compound **4a** in CDCl_3



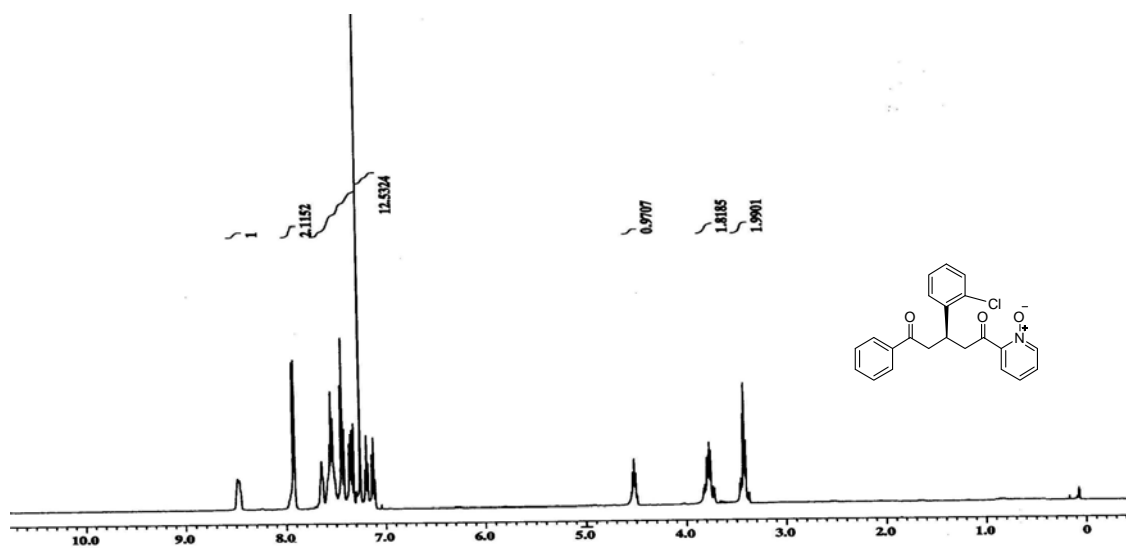
125 MHz ^{13}C NMR spectra of compound **4a** in CDCl_3



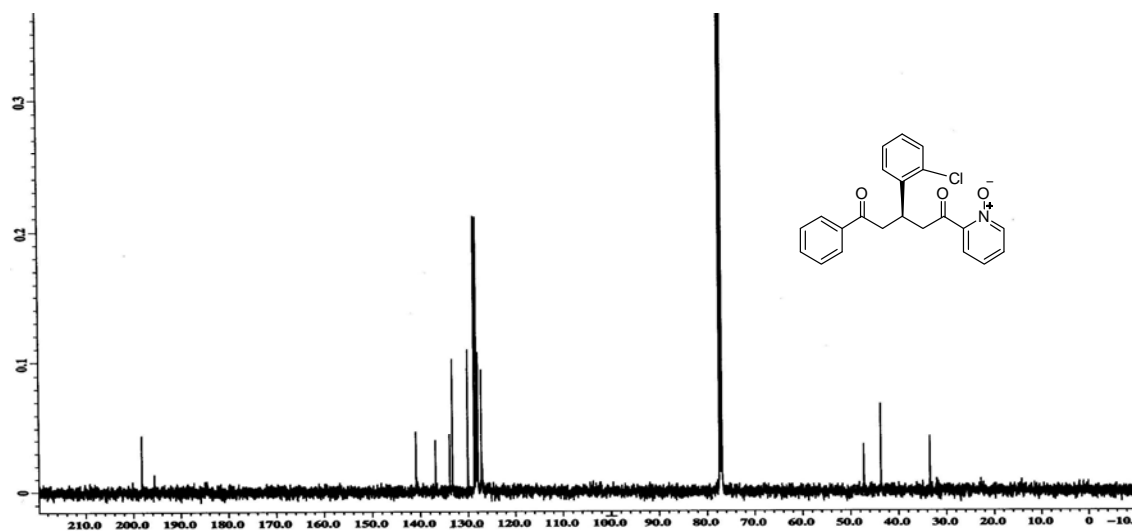
HPLC chromatogram of compound **4a** (racemic)



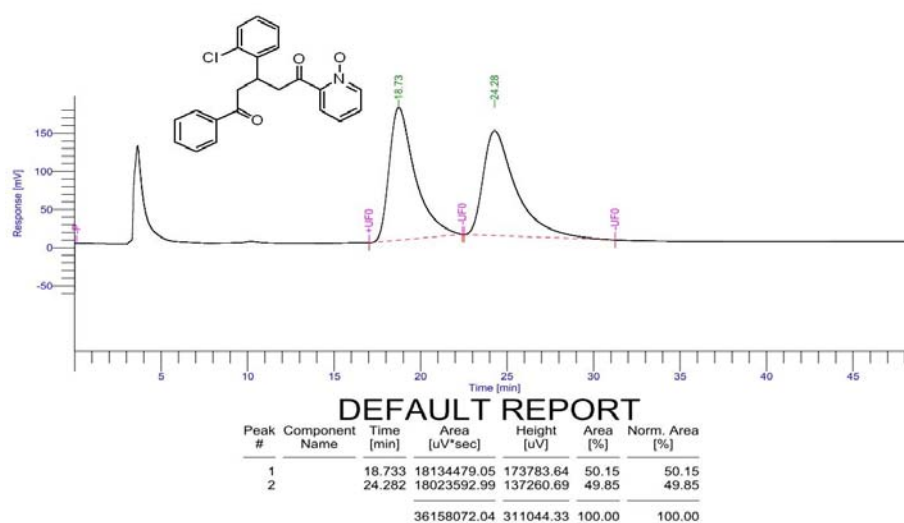
HPLC chromatogram of compound **4a** (Chiral)



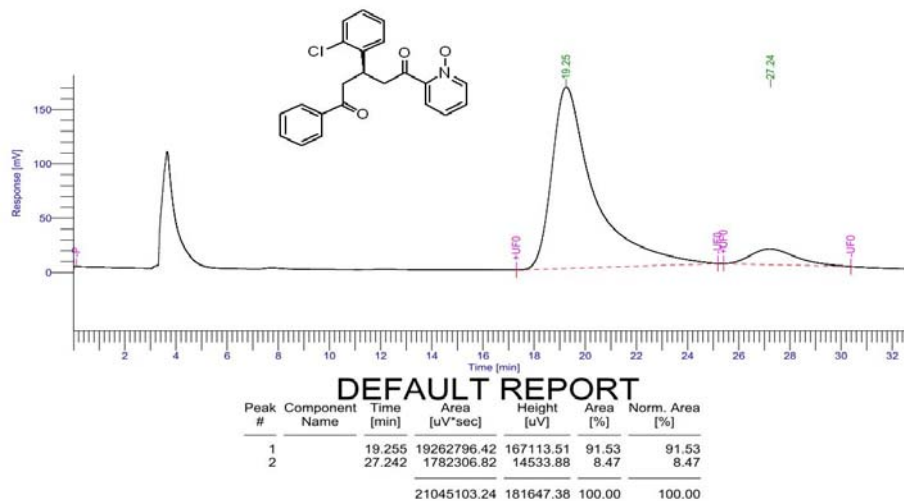
500 MHz ^1H NMR spectra of compound **4b** in CDCl_3



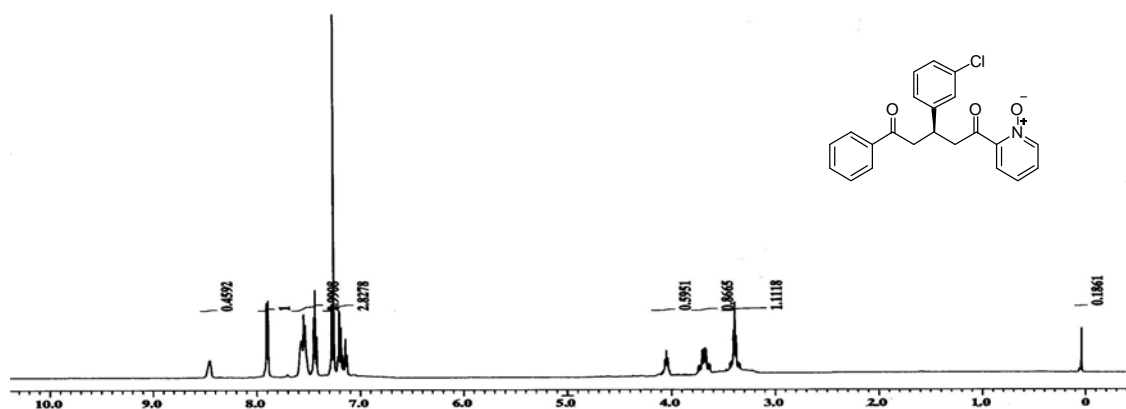
125 MHz ^{13}C NMR spectra of compound **4b** in CDCl_3



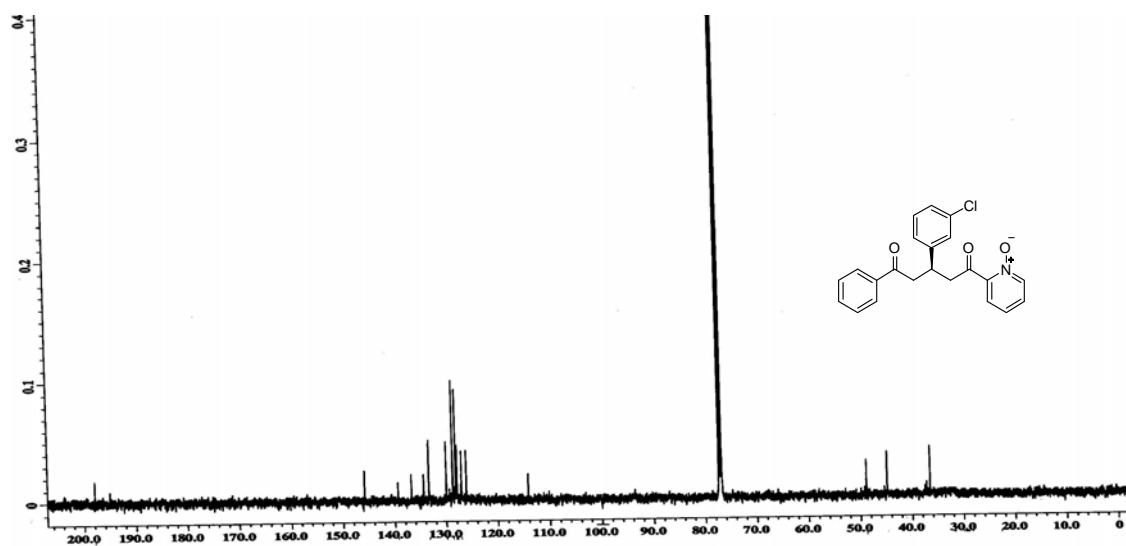
HPLC chromatogram of compound **4b** (racemic)



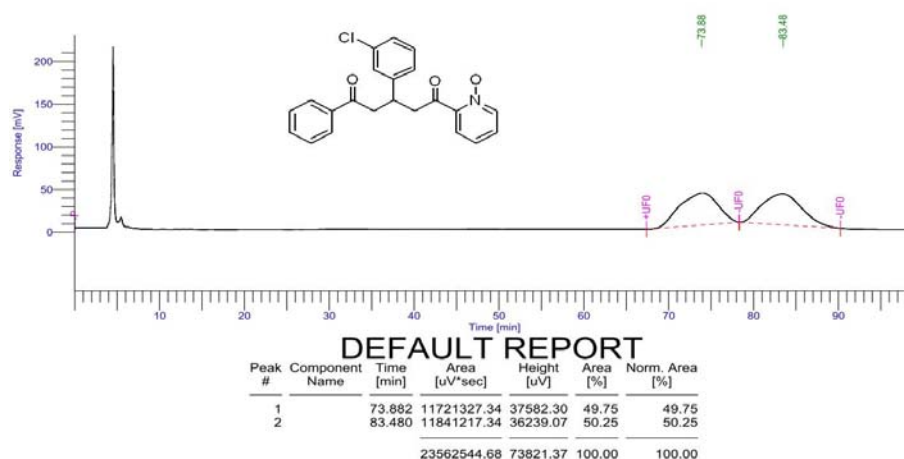
HPLC chromatogram of compound **4b** (chiral)



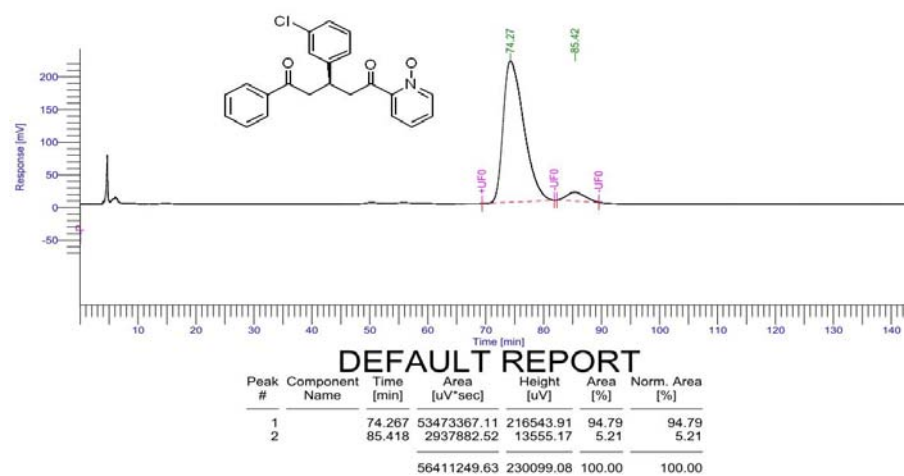
500 MHz ^1H NMR spectra of compound **4c** in CDCl_3



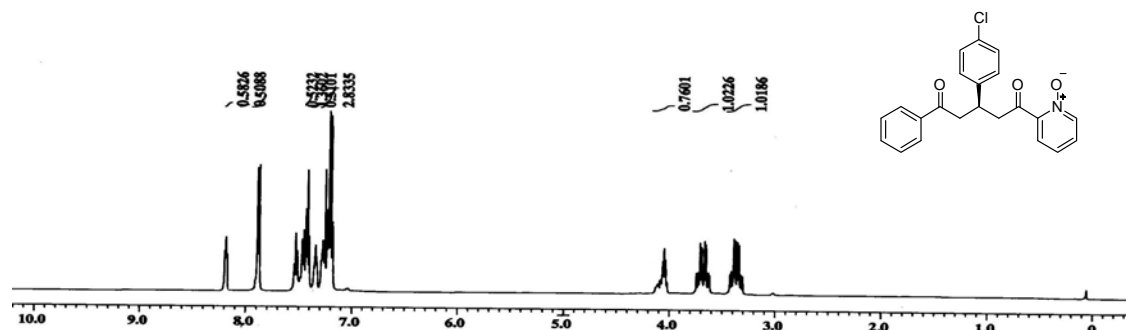
125 MHz ^{13}C NMR spectra of compound **4c** in CDCl_3



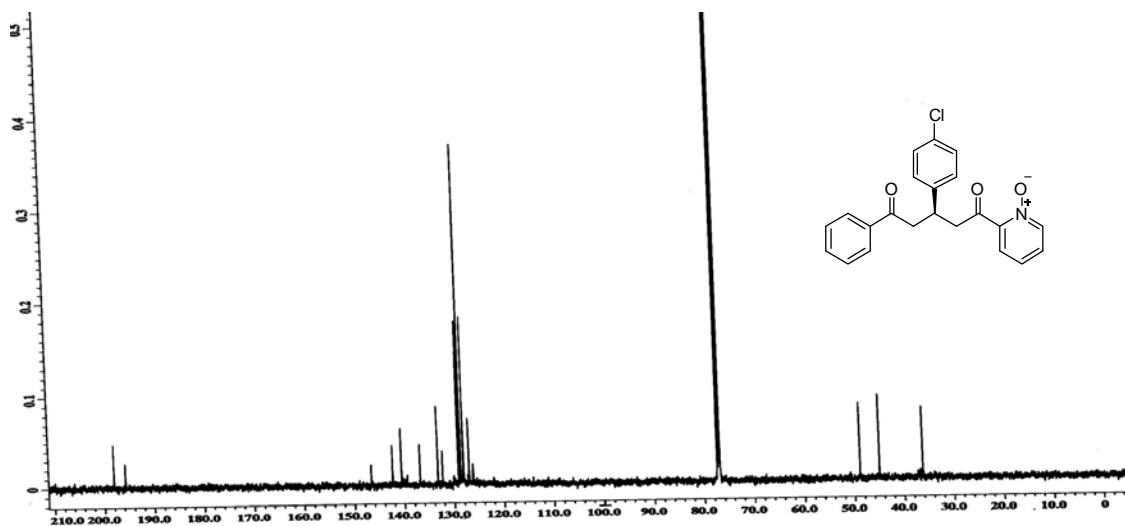
HPLC chromatogram of compound **4c** (racemic)



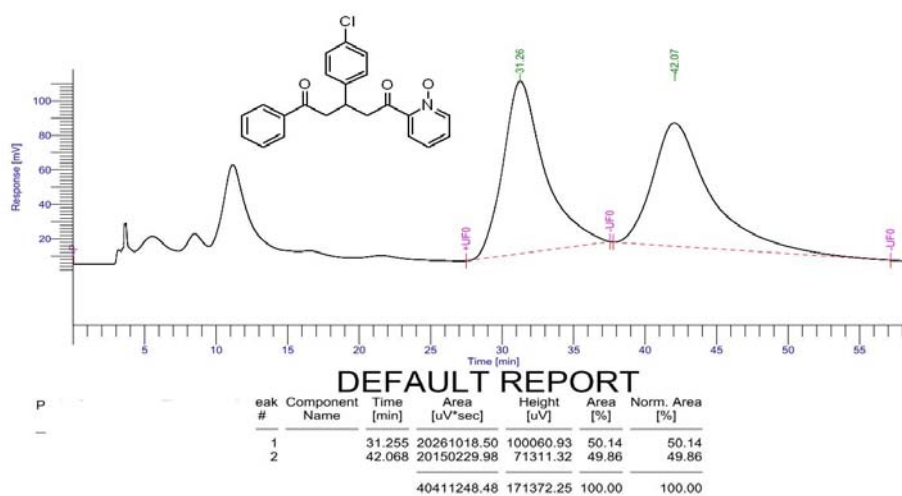
HPLC chromatogram of compound **4c** (Chiral)



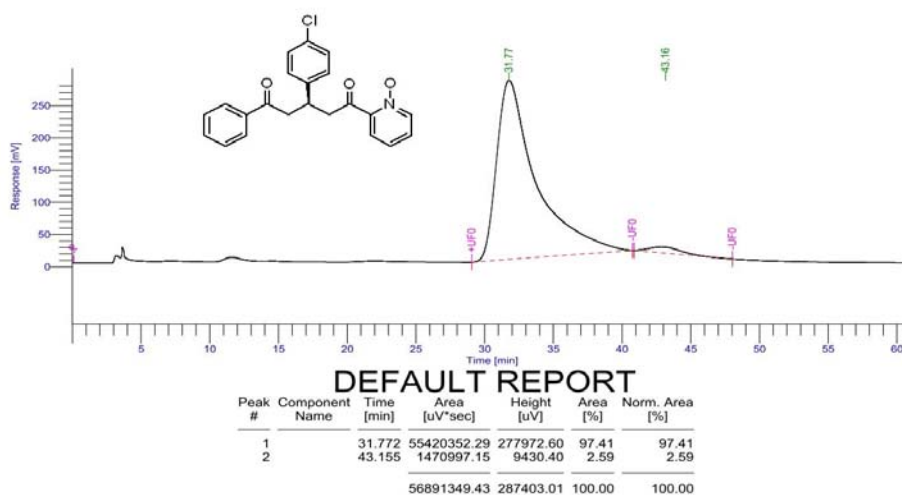
500 MHz ^1H NMR spectra of compound **4d** in CDCl_3



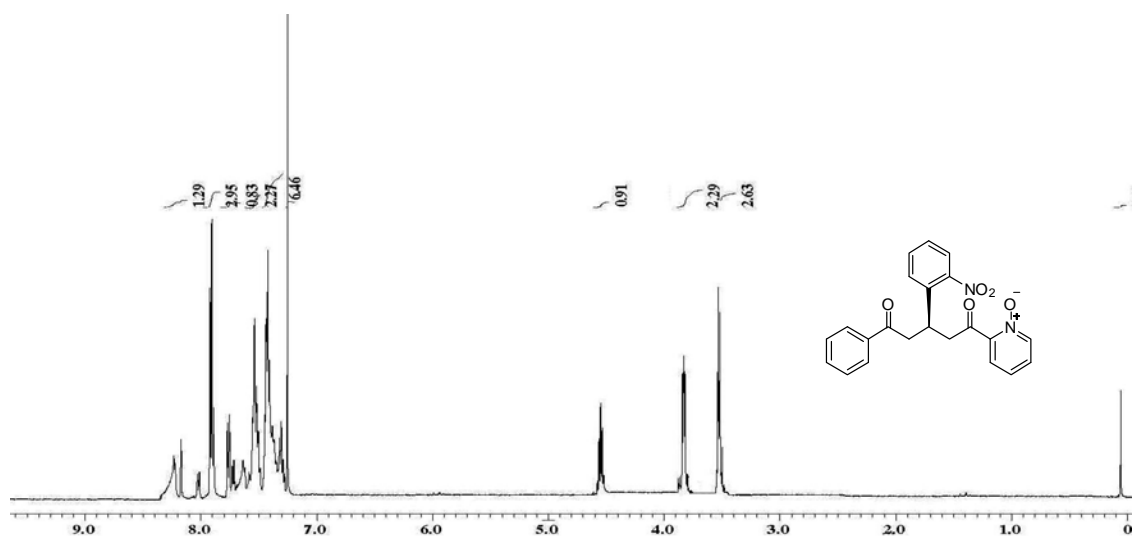
125 MHz ^{13}C NMR spectra of compound **4d** in CDCl_3



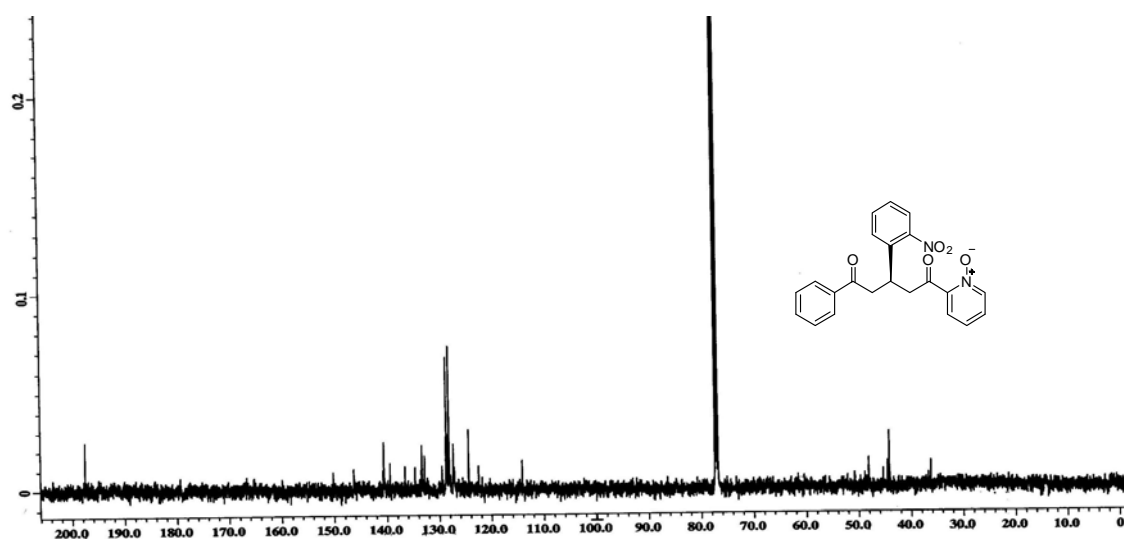
HPLC chromatogram of compound **4d** (racemic)



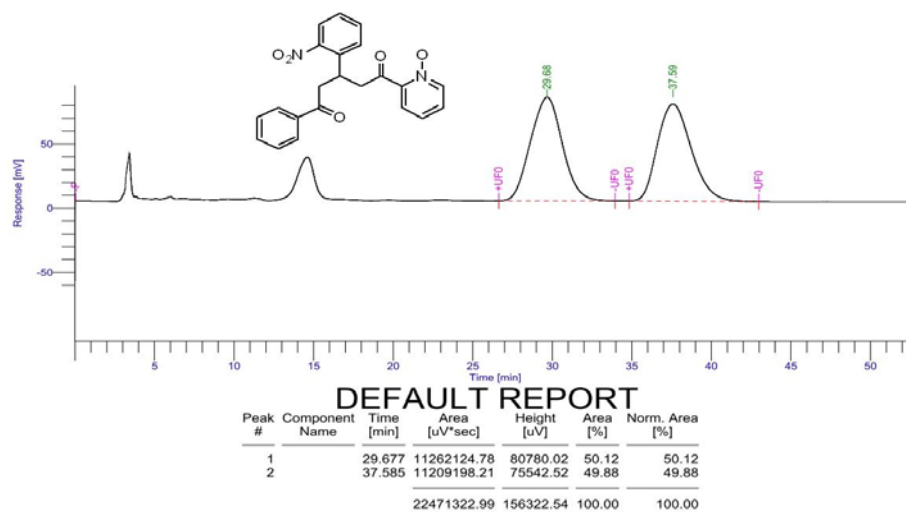
HPLC chromatogram of compound **4d** (chiral)



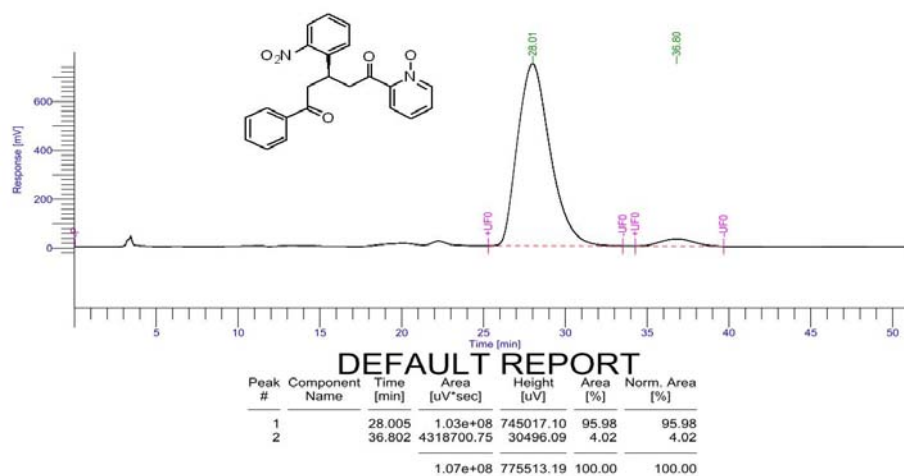
500 MHz ^1H NMR spectra of compound **4e** in CDCl_3



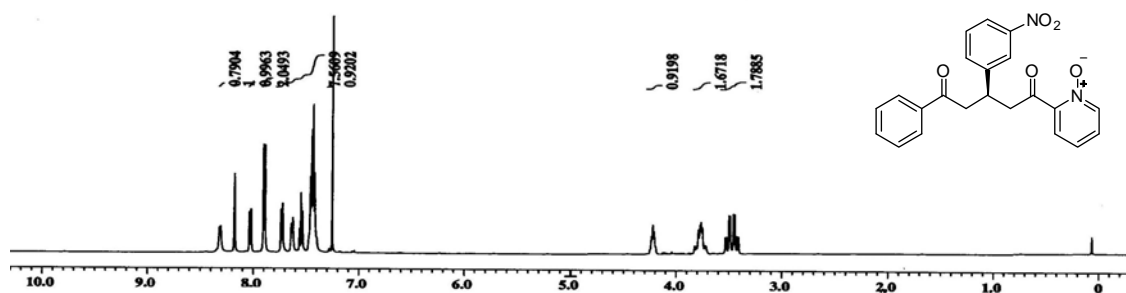
125 MHz ^{13}C NMR spectra of compound **4e** in CDCl_3



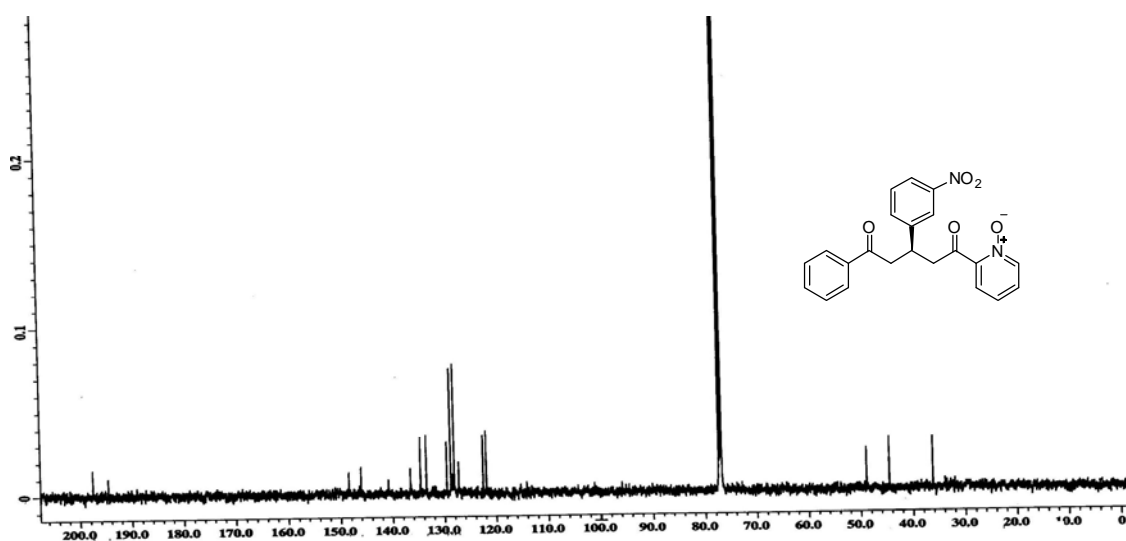
HPLC chromatogram of compound **4e** (racemic)



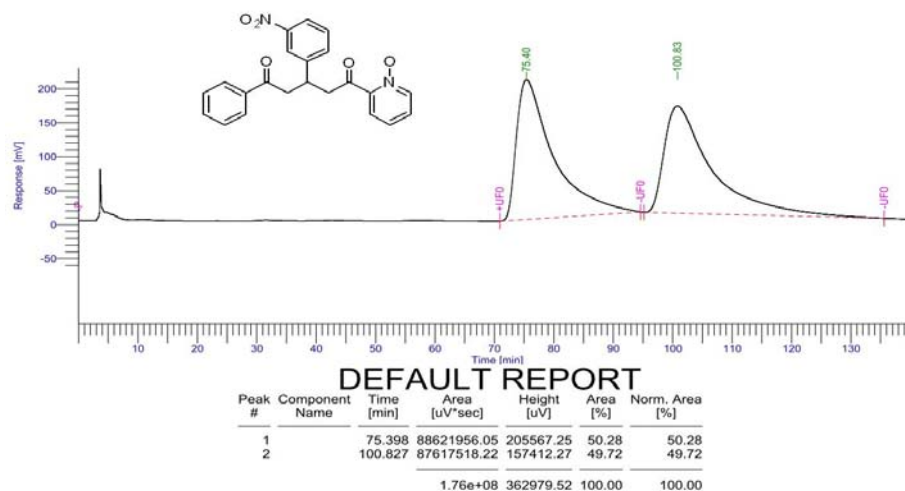
HPLC chromatogram of compound **4e** (chiral)



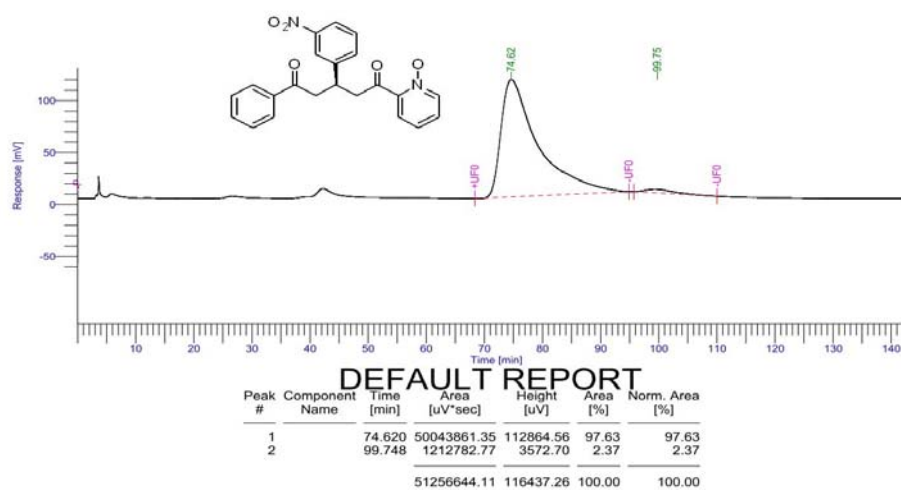
500 MHz ^1H NMR spectra of compound **4f** in CDCl_3



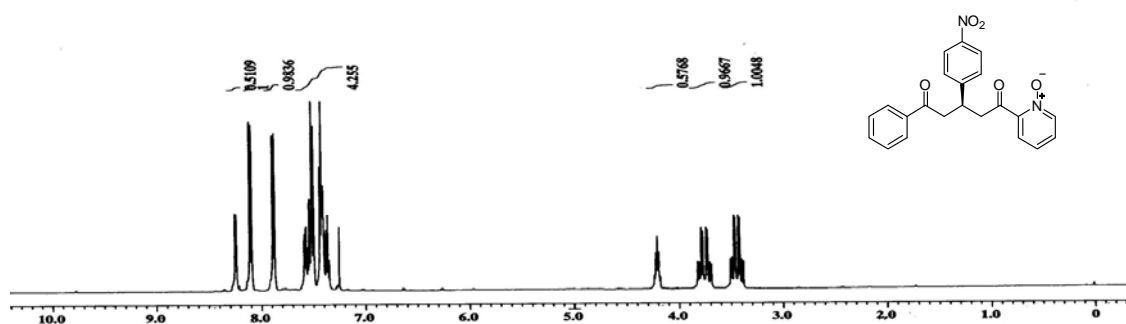
125 MHz ^{13}C NMR spectra of compound **4f** in CDCl_3



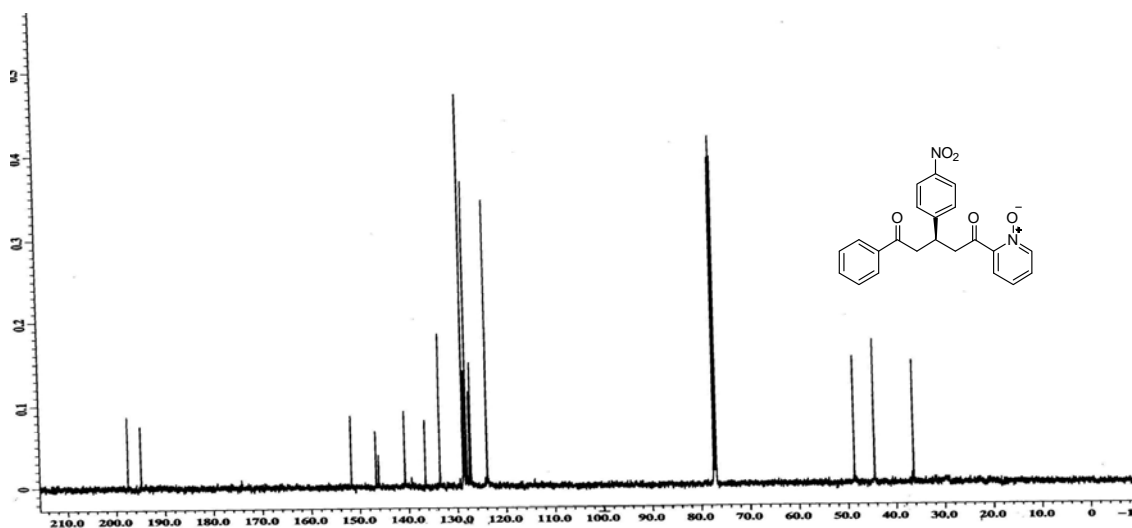
HPLC chromatogram of compound **4f** (racemic)



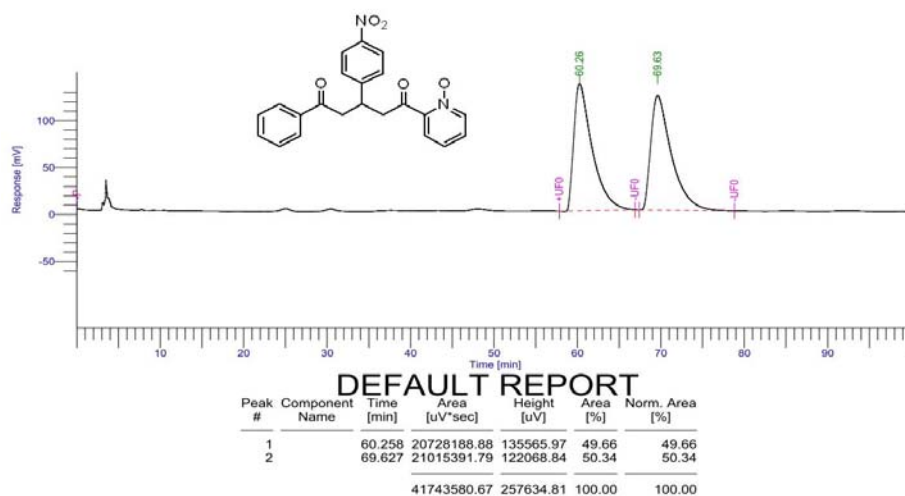
HPLC chromatogram of compound **4f** (chiral)



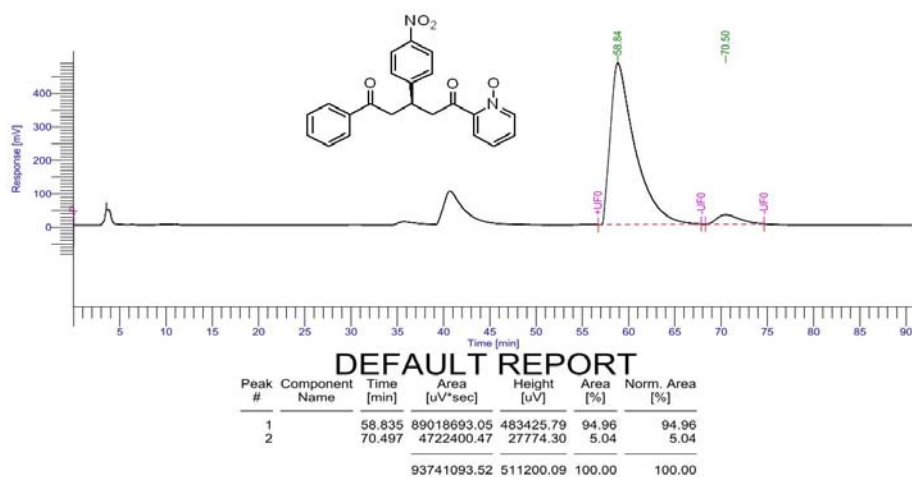
500 MHz ^1H NMR spectra of compound **4g** in CDCl_3



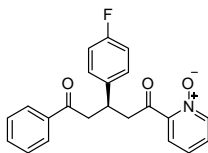
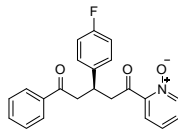
125 MHz ^{13}C NMR spectra of compound **4g** in CDCl_3



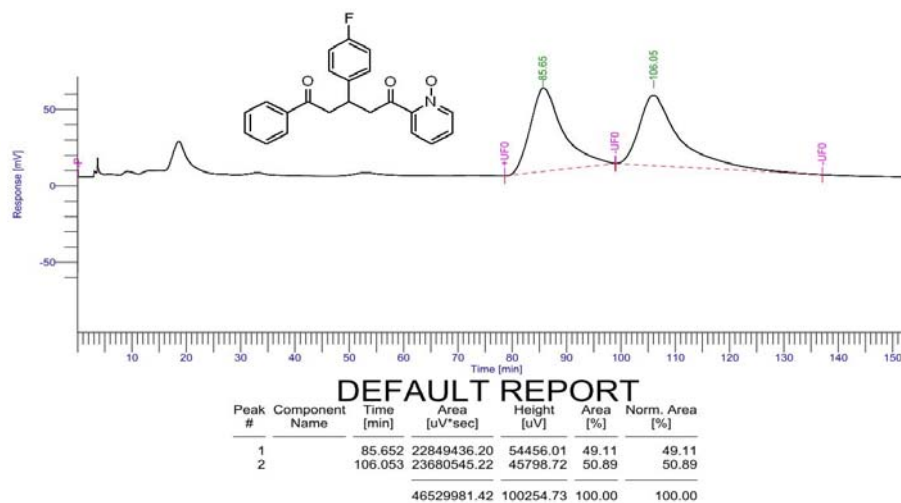
HPLC chromatogram of compound **4g** (racemic)



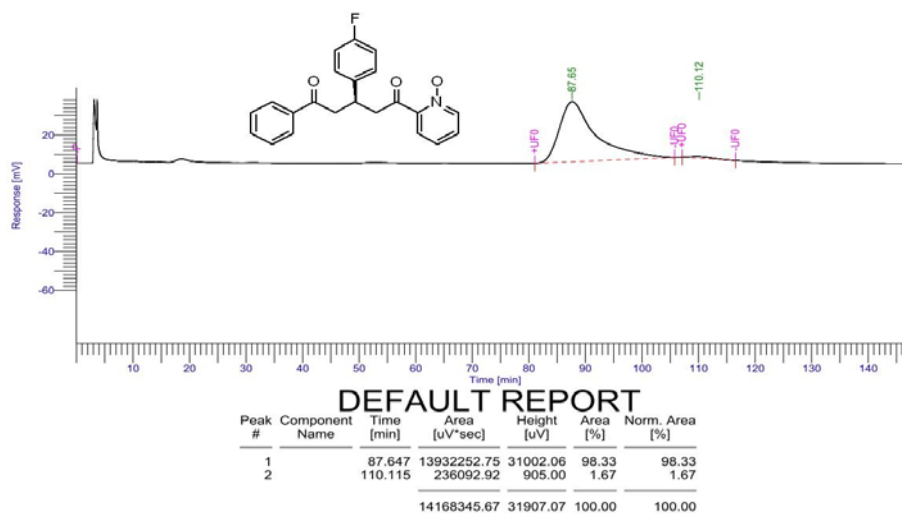
HPLC chromatogram of compound **4g** (chiral)

500 MHz ¹H NMR spectra of compound **4h** in CDCl₃

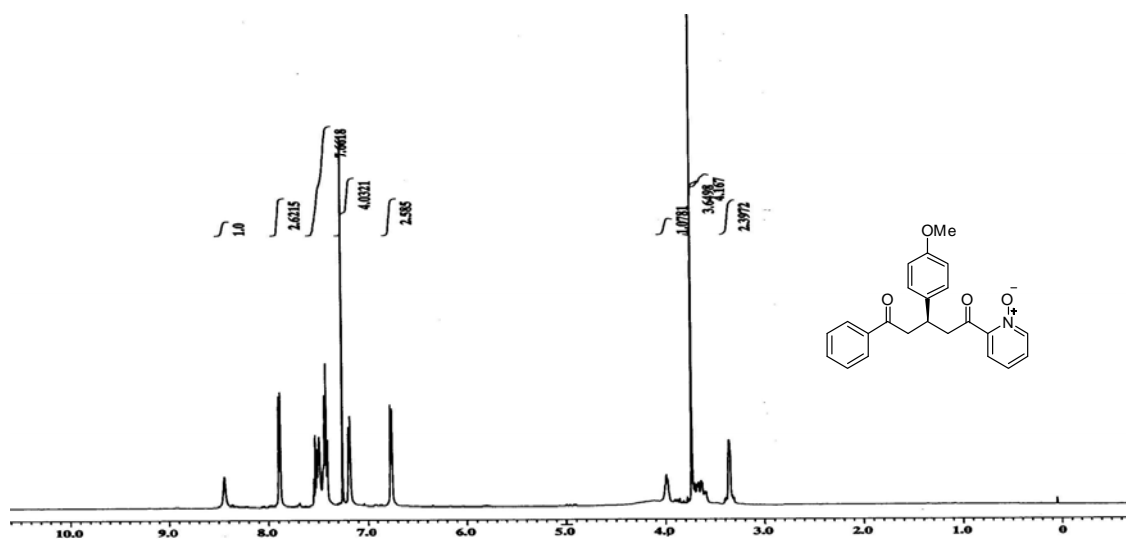
125 MHz ^{13}C NMR spectra of compound **4h** in CDCl_3



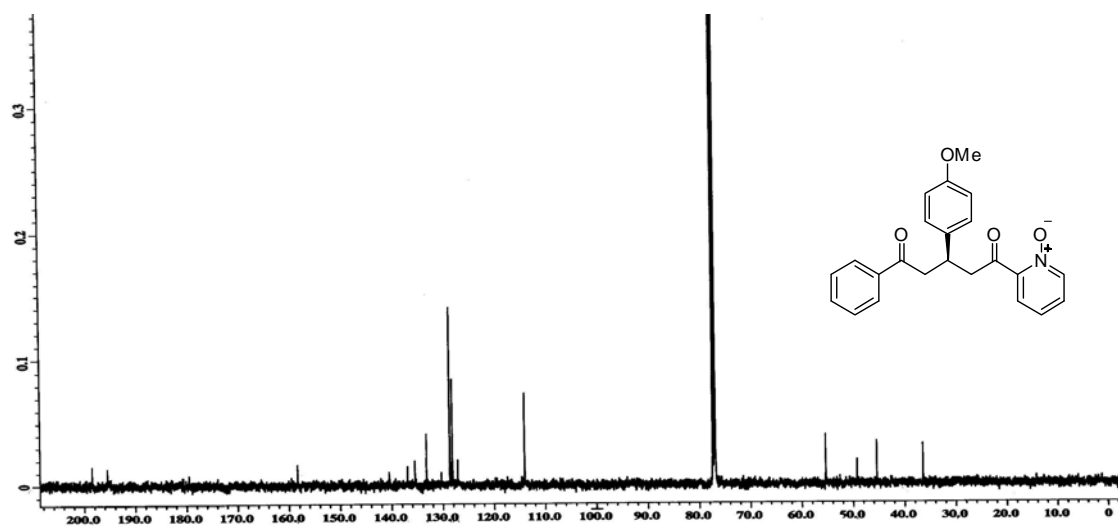
HPLC chromatogram of compound **4h** (racemic)



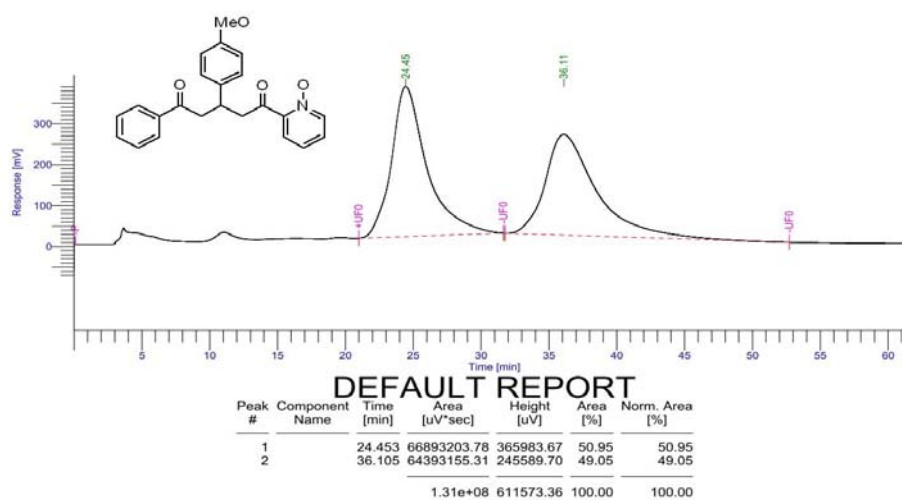
HPLC chromatogram of compound **4h** (chiral)



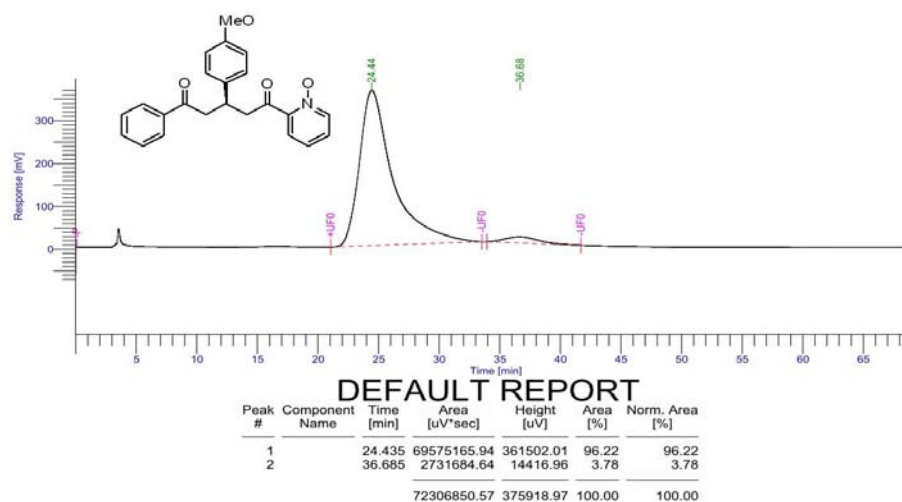
500 MHz ^1H NMR spectra of compound **4i** in CDCl_3



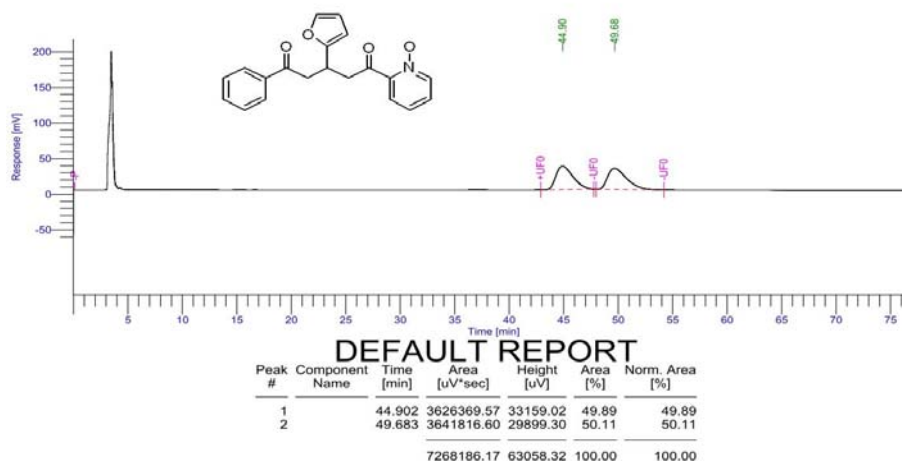
125 MHz ^{13}C NMR spectra of compound **4i** in CDCl_3



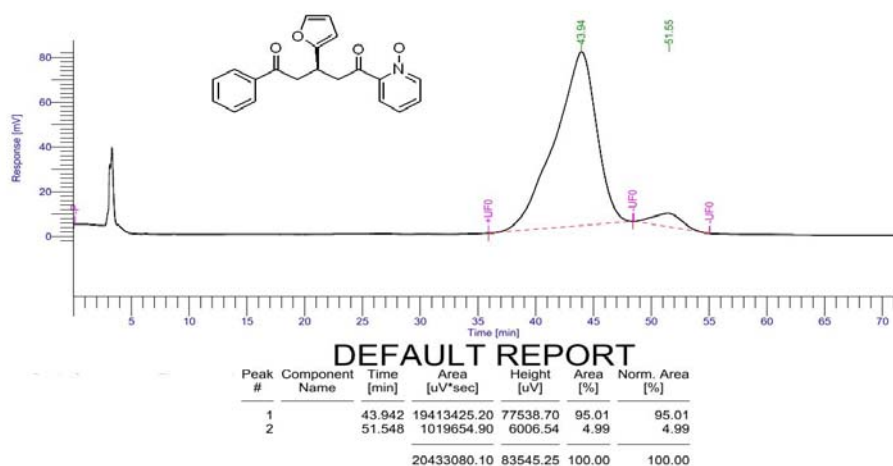
HPLC chromatogram of compound **4i** (racemic)



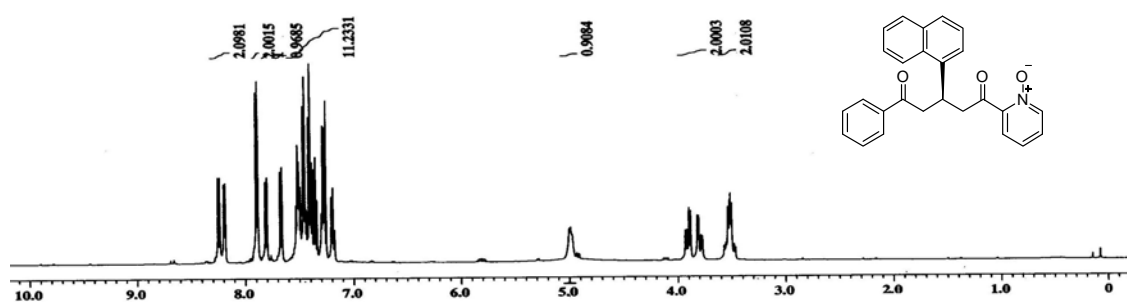
HPLC chromatogram of compound **4i** (chiral)



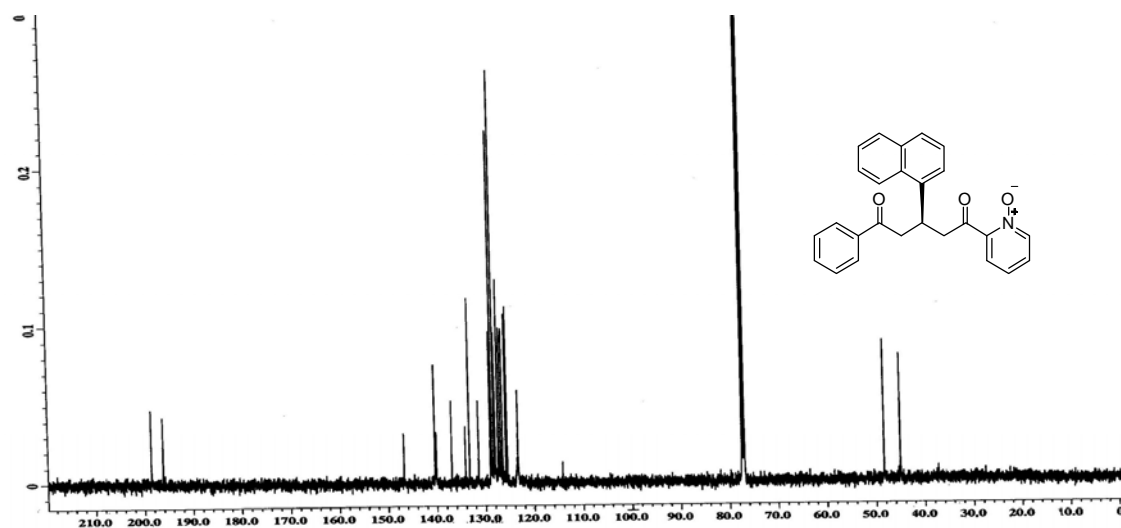
HPLC chromatogram of compound **4j** (racemic)



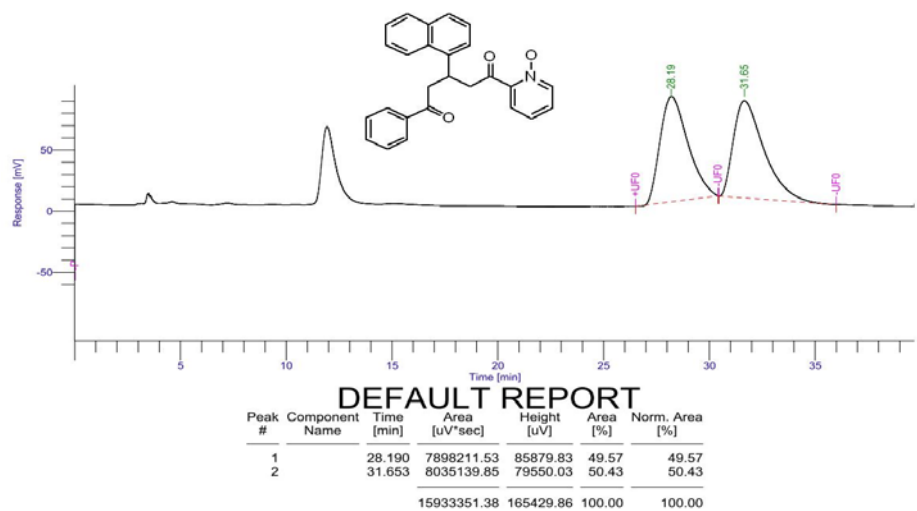
HPLC chromatogram of compound **4j** (chiral)



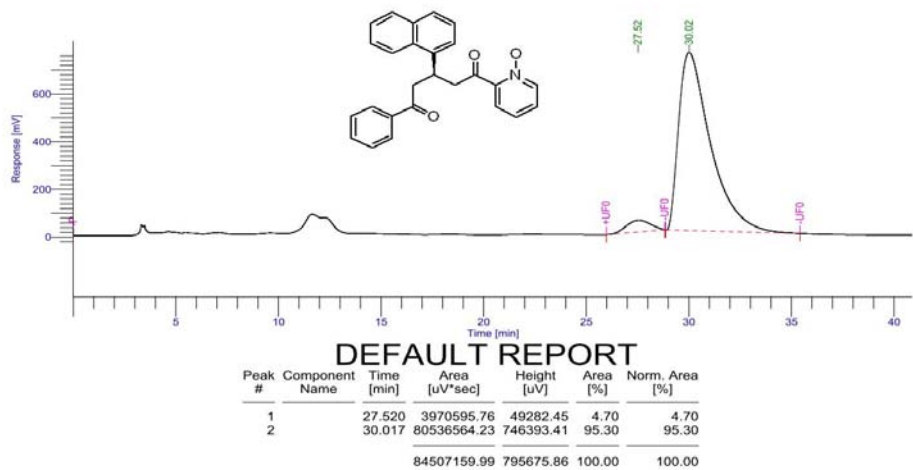
500 MHz ^1H NMR spectra of compound **4k** in CDCl_3



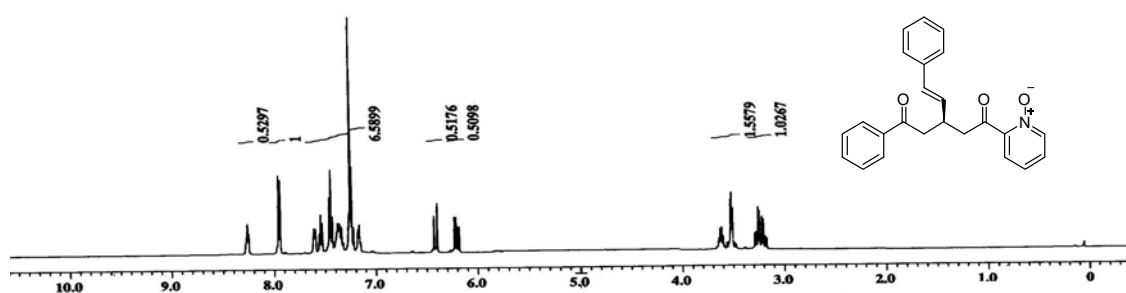
125 MHz ^{13}C NMR spectra of compound **4k** in CDCl_3



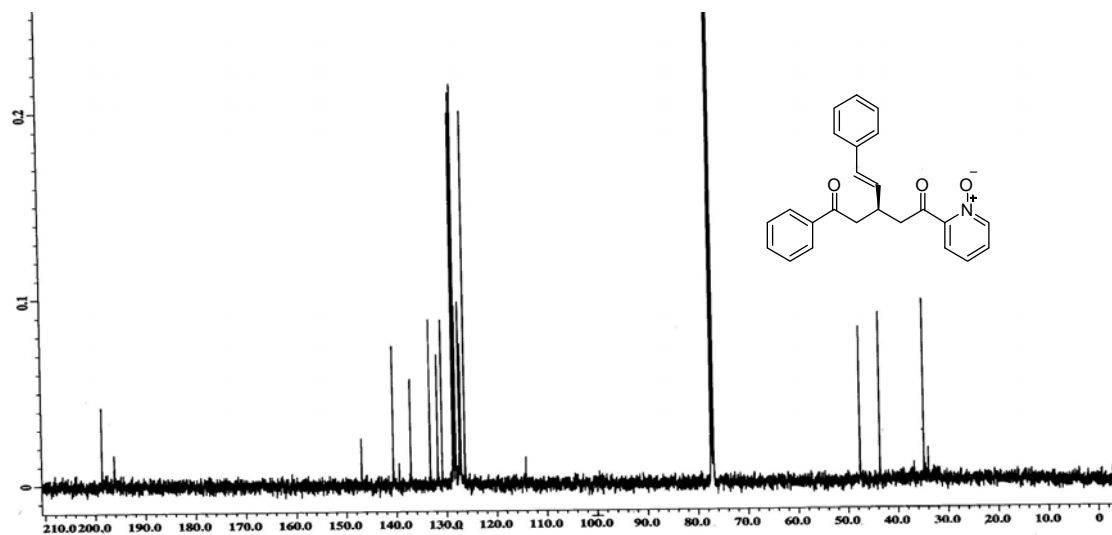
HPLC chromatogram of compound **4k** (racemic)



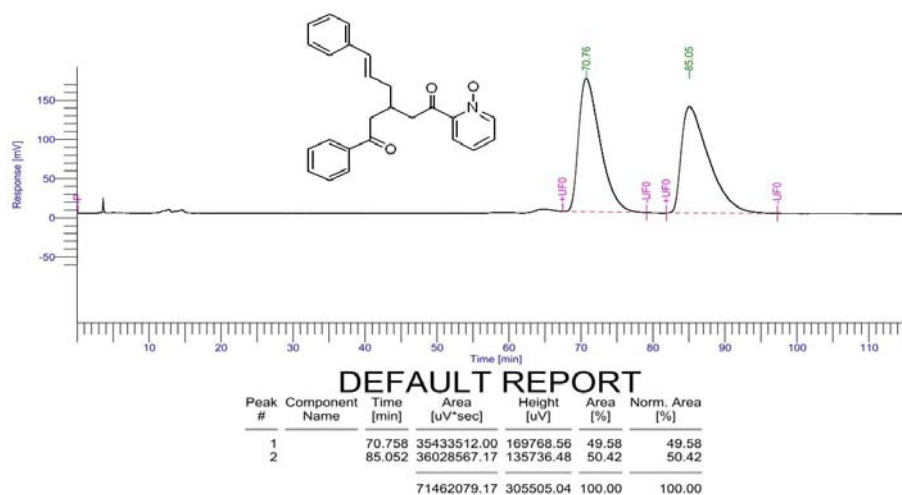
HPLC chromatogram of compound **4k** (chiral)



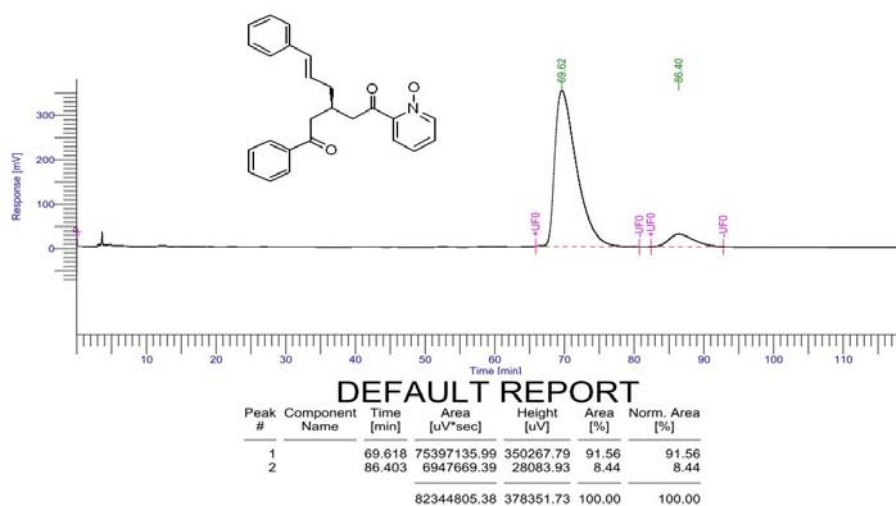
500 MHz ¹H NMR spectra of compound **4l** in CDCl₃



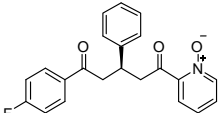
125 MHz ¹³C NMR spectra of compound **4l** in CDCl₃



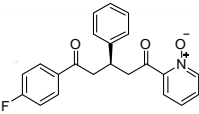
HPLC chromatogram of compound **4I** (racemic)



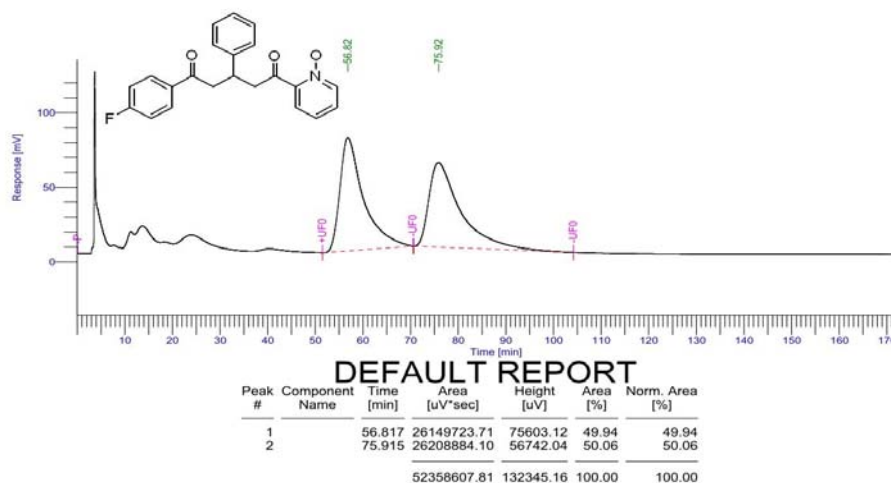
HPLC chromatogram of compound **4I** (chiral)



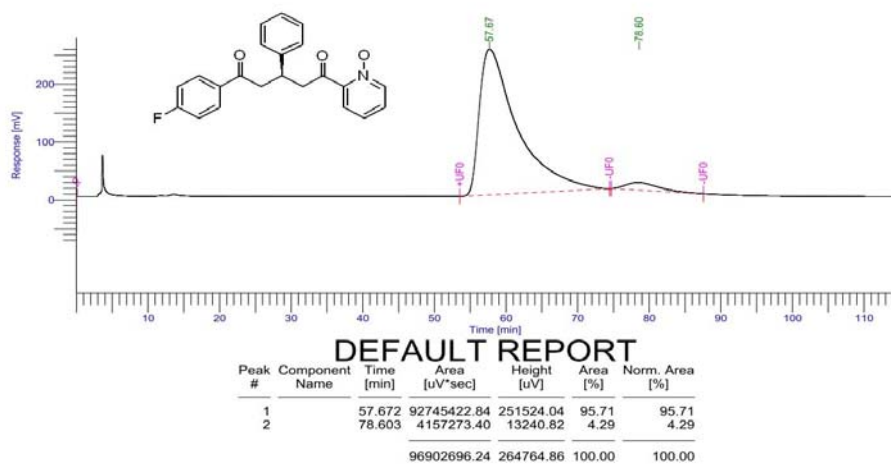
500 MHz ^1H NMR spectra of compound **4m** in CDCl_3



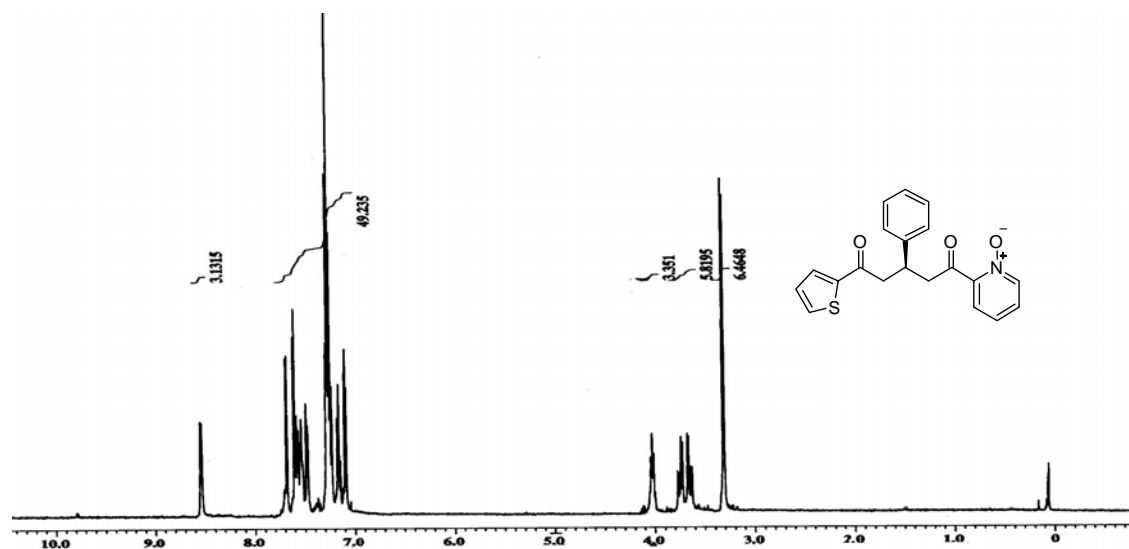
125 MHz ^{13}C NMR spectra of compound **4m** in CDCl_3



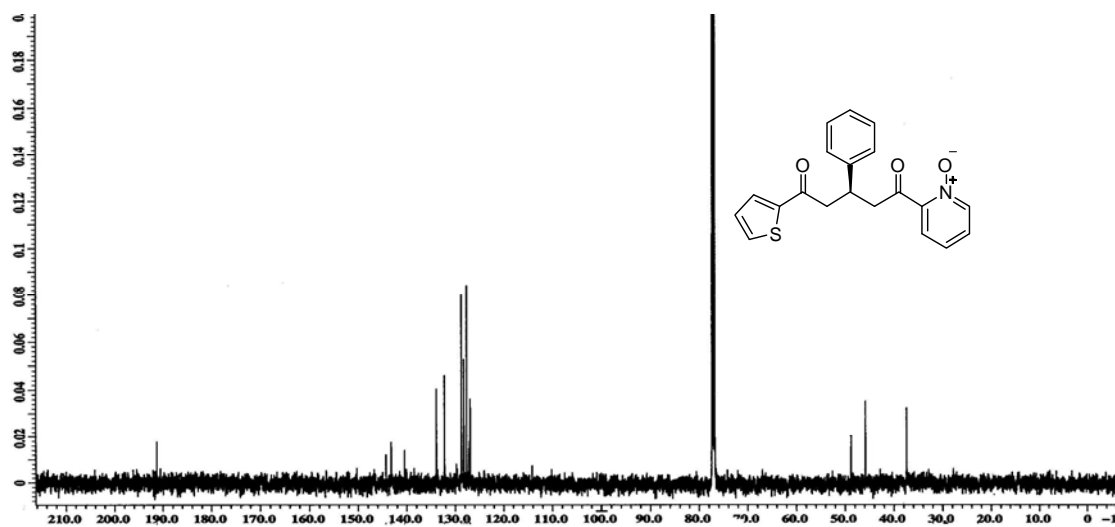
HPLC chromatogram of compound **4m** (racemic)



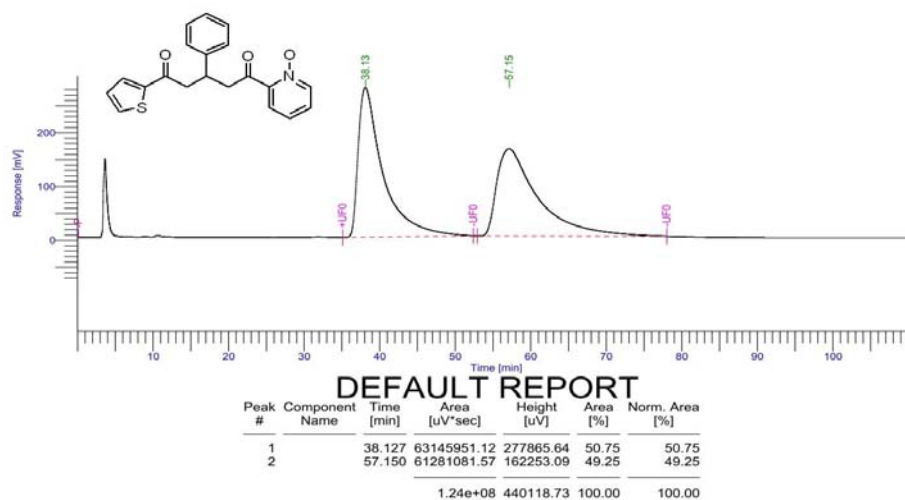
HPLC chromatogram of compound **4m** (chiral)



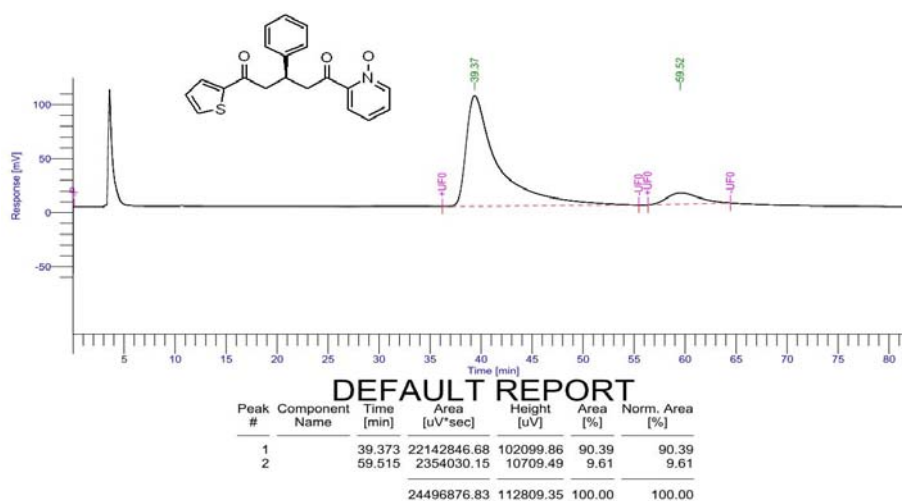
500 MHz ^1H NMR spectra of compound **4n** in CDCl_3



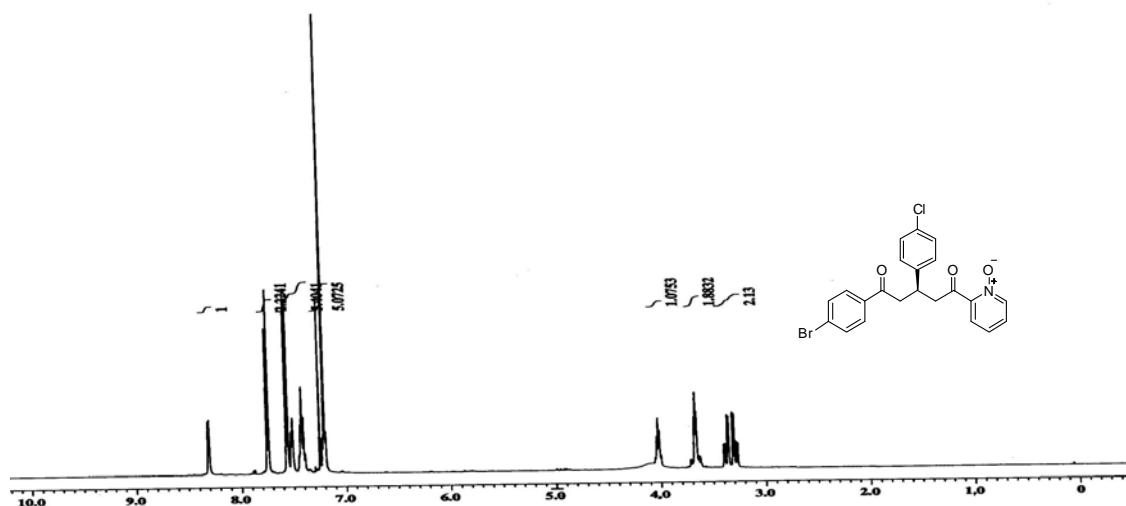
125 MHz ^{13}C NMR spectra of compound **4n** in CDCl_3



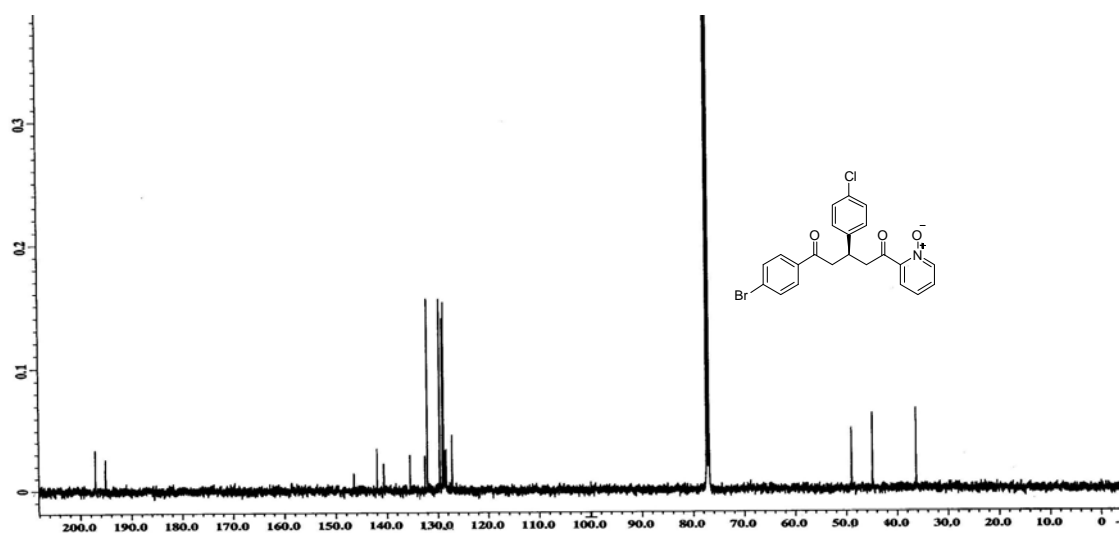
HPLC chromatogram of compound **4n** (racemic)



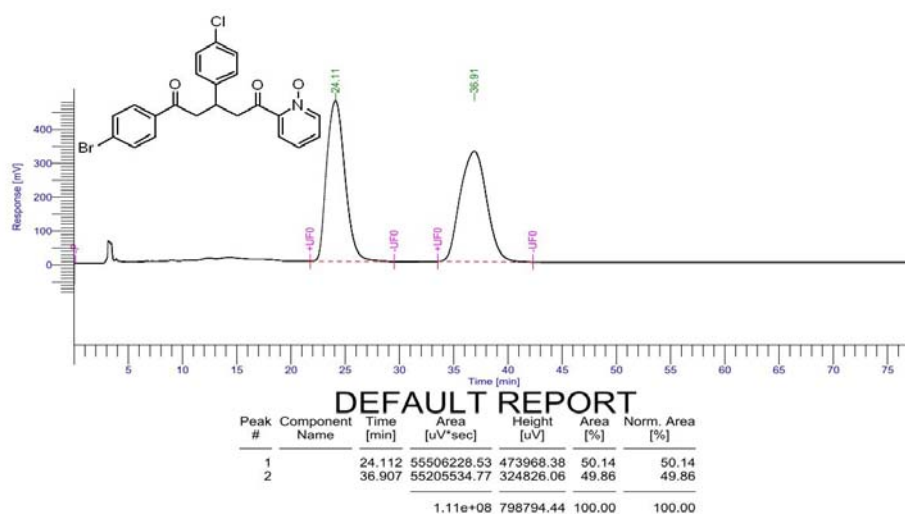
HPLC chromatogram of compound **4n** (chiral)



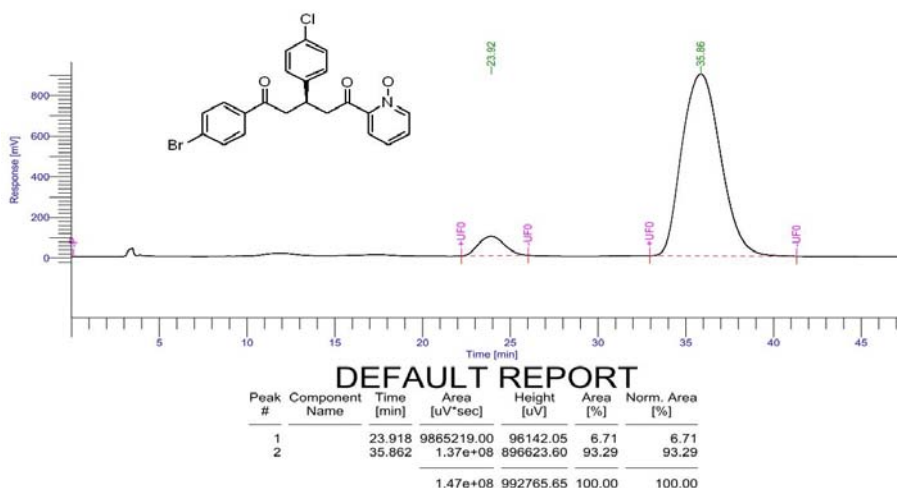
500 MHz ^1H NMR spectra of compound **4o** in CDCl_3



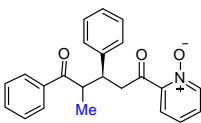
125 MHz ^{13}C NMR spectra of compound **4o** in CDCl_3



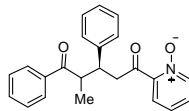
HPLC chromatogram of compound **4o** (racemic)



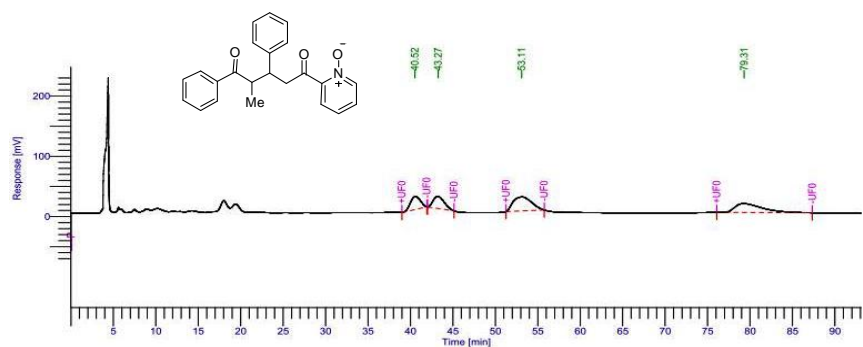
HPLC chromatogram of compound **4o** (chiral)



500 MHz ^1H NMR spectra of compound **6a** in CDCl_3



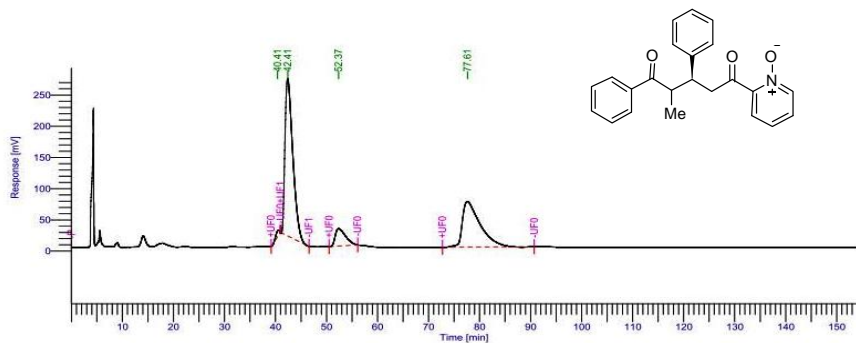
125 MHz ¹³C NMR spectra of compound **6a** in CDCl₃



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		40.523	1758573.52	21465.68	16.88	16.88
2		43.265	1856646.01	20246.87	17.82	17.82
3		53.105	3500593.93	23323.53	33.60	33.60
4		79.310	3302529.97	14839.45	31.70	31.70
			10418343.43	79875.53	100.00	100.00

HPLC chromatogram of compound **6a** (racemic)

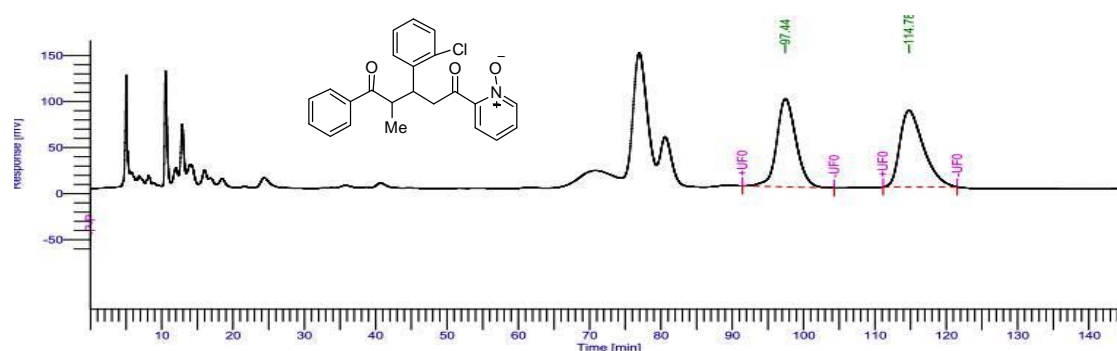


DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		40.407	416885.97	9327.13	0.85	0.85
2		42.410	26901925.97	251944.73	55.06	55.06
3		52.367	3836037.89	28071.65	8.06	8.06
4		77.607	17600318.97	73193.34	36.03	36.03
			48855168.80	362536.85	100.00	100.00

The ¹³C NMR spectrum shows peaks in the aromatic region (120-145 ppm) and aliphatic region (20-35 ppm). The chemical structure of compound 10 is shown as an inset: Cc1ccccc1C(=O)[C@H](c2ccccc2Cl)CC(=O)c3cc[n+](O-)[c+]3. The structure features a central chiral carbon bonded to a phenyl ring, a benzoyl group, a 2-chlorophenyl group, and a 4-pyridylmethyl group.

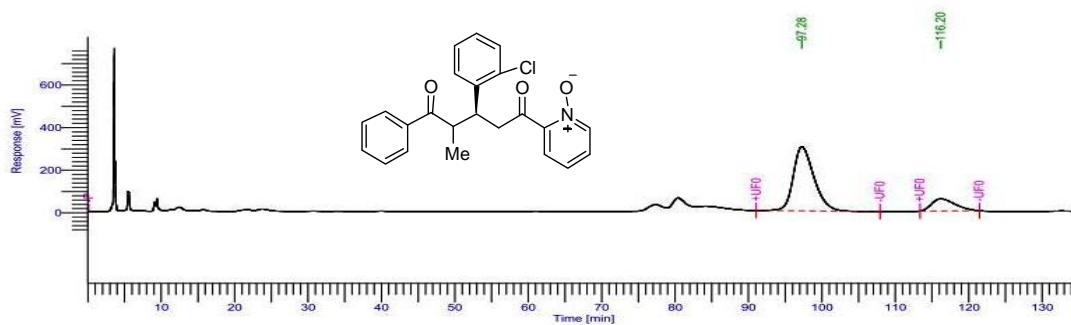
125 MHz ^{13}C NMR spectra of compound **6b** in CDCl_3



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		97.440	17903400.37	95489.91	48.41	48.41
2		114.783	19078413.84	82948.09	51.59	51.59
			36981814.21	178438.00	100.00	100.00

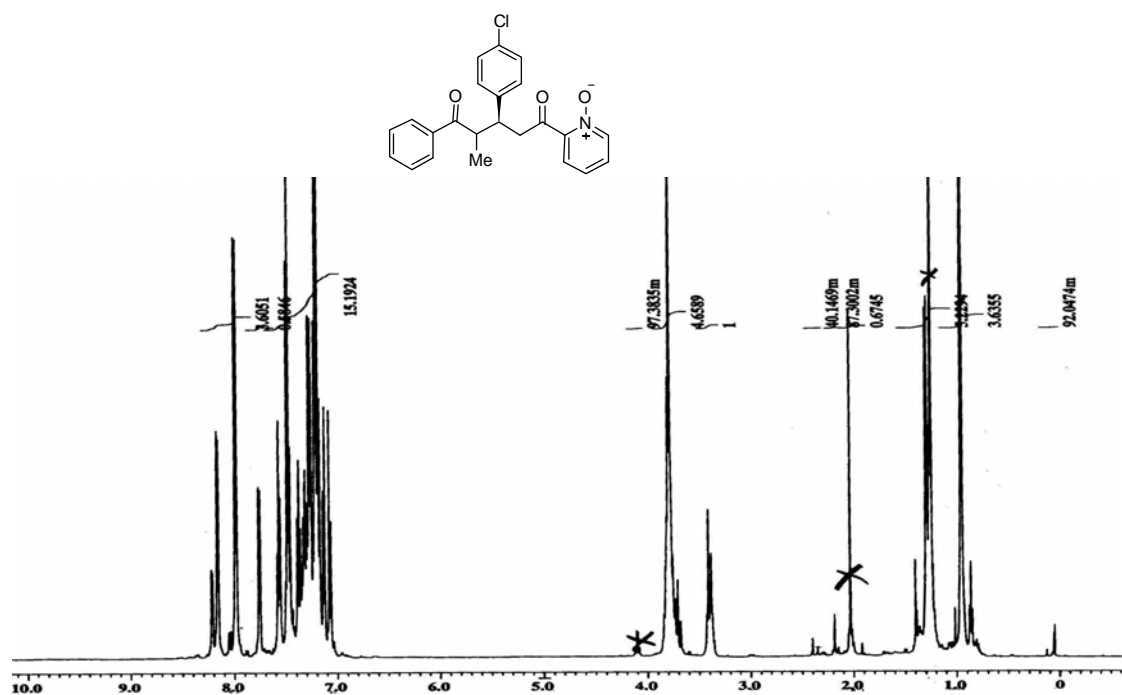
HPLC chromatogram of compound **6b** (racemic)



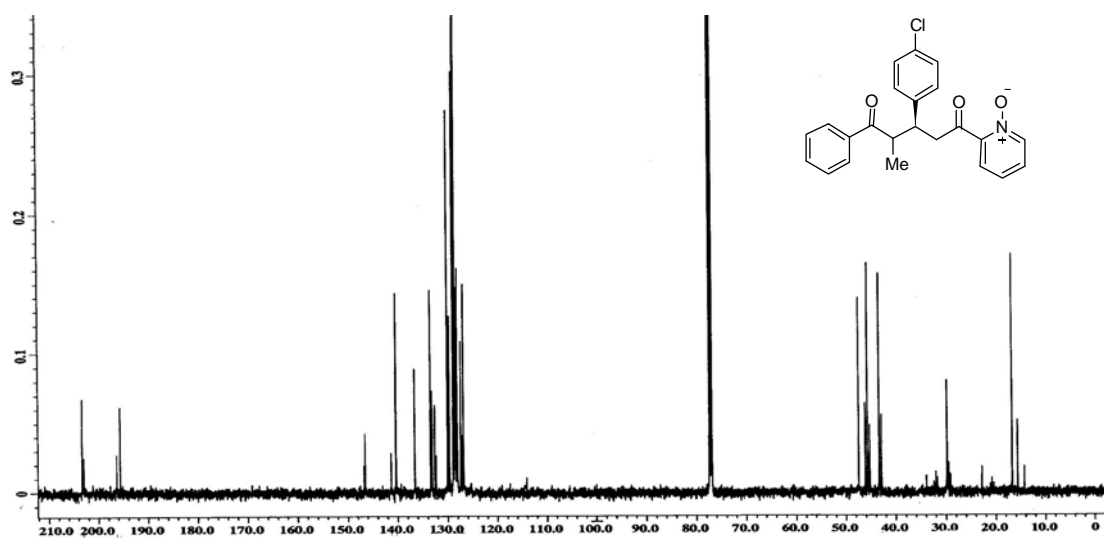
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		97.277	58976431.19	300994.55	82.54	82.54
2		116.197	12476025.96	56492.45	17.46	17.46
			71452457.15	357487.00	100.00	100.00

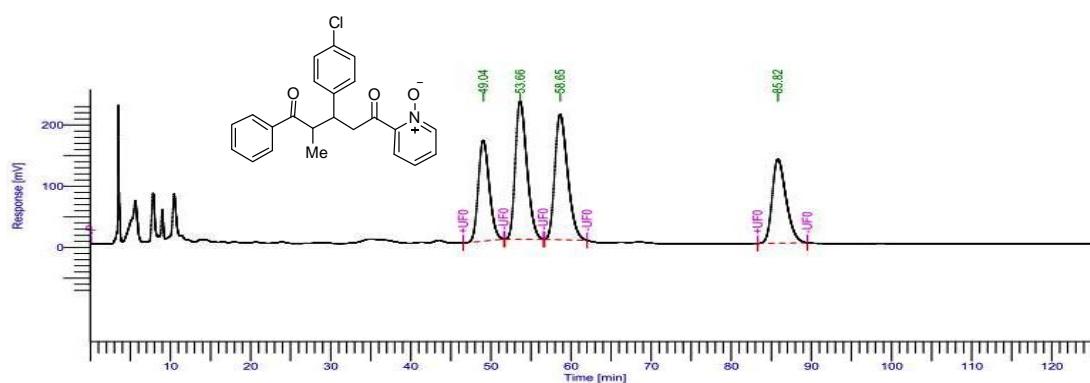
HPLC chromatogram of compound **6b** (Chiral)



500 MHz ^1H NMR spectra of compound **6c** in CDCl_3



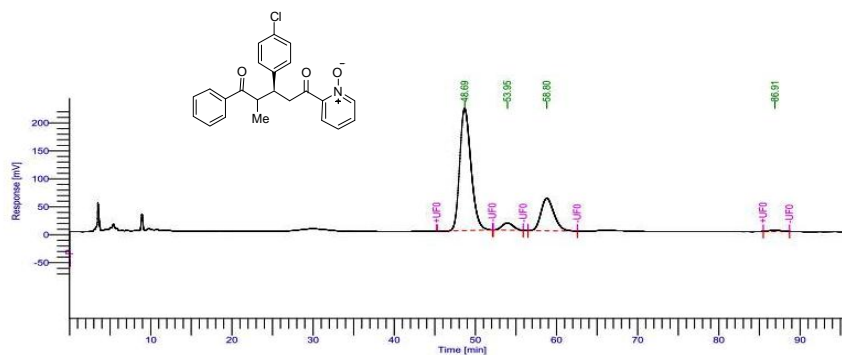
125 MHz ^{13}C NMR spectra of compound **6c** in CDCl_3



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		49.043	15702597.14	164674.63	20.20	20.20
2		53.665	22700604.33	225703.42	29.20	29.20
3		58.645	22768215.17	205090.92	29.29	29.29
4		85.823	16557328.80	137817.15	21.30	21.30
			77728745.44	733286.12	100.00	100.00

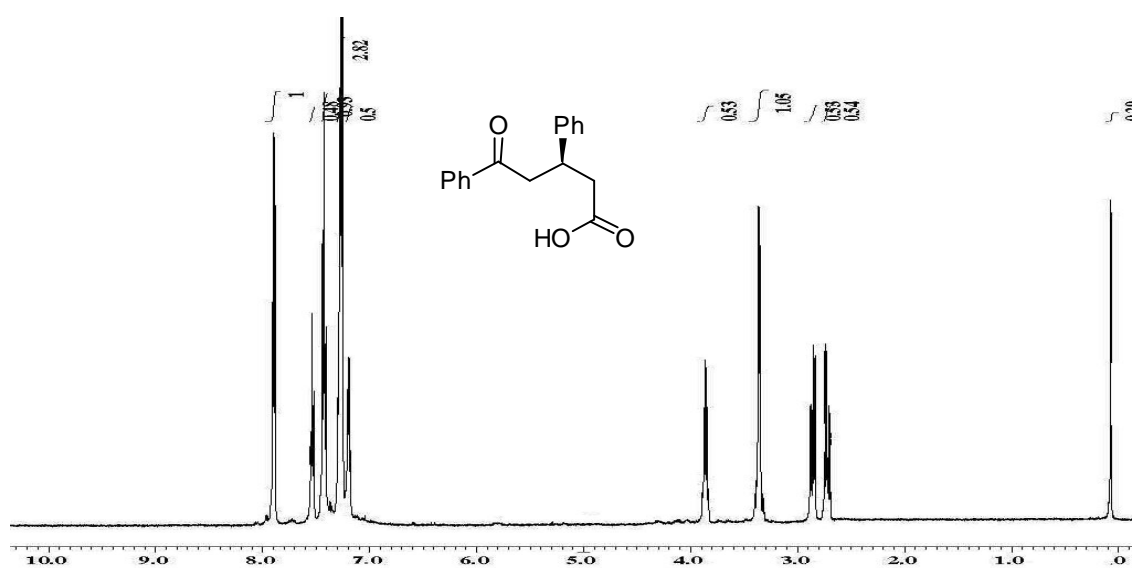
HPLC chromatogram of compound **6c** (racemic)



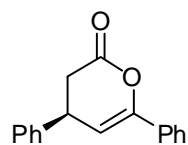
DEFAULT REPORT

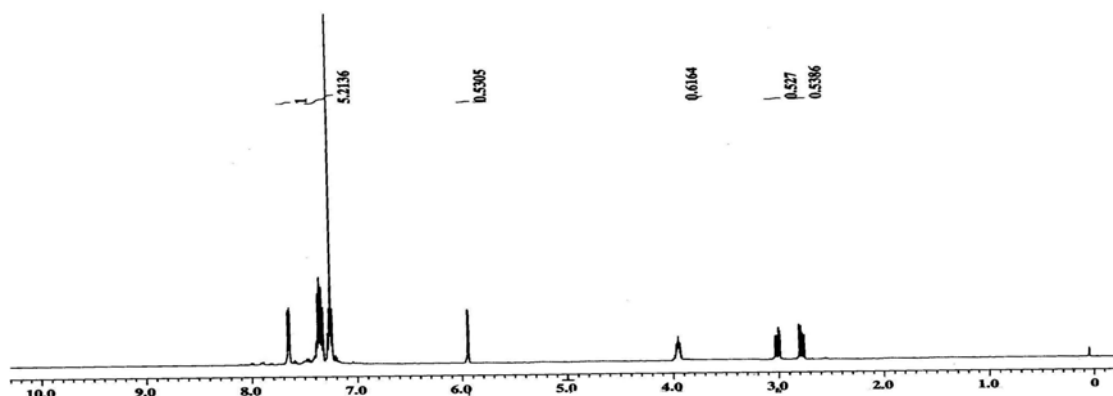
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		48.688	21105204.70	218810.65	72.56	72.56
2		53.952	1240515.53	13078.90	4.27	4.27
3		58.798	6521909.26	58187.31	22.42	22.42
4		86.905	217246.20	2116.38	0.75	0.75
			29084875.69	292193.24	100.00	100.00

HPLC chromatogram of compound **6c** (Chiral)

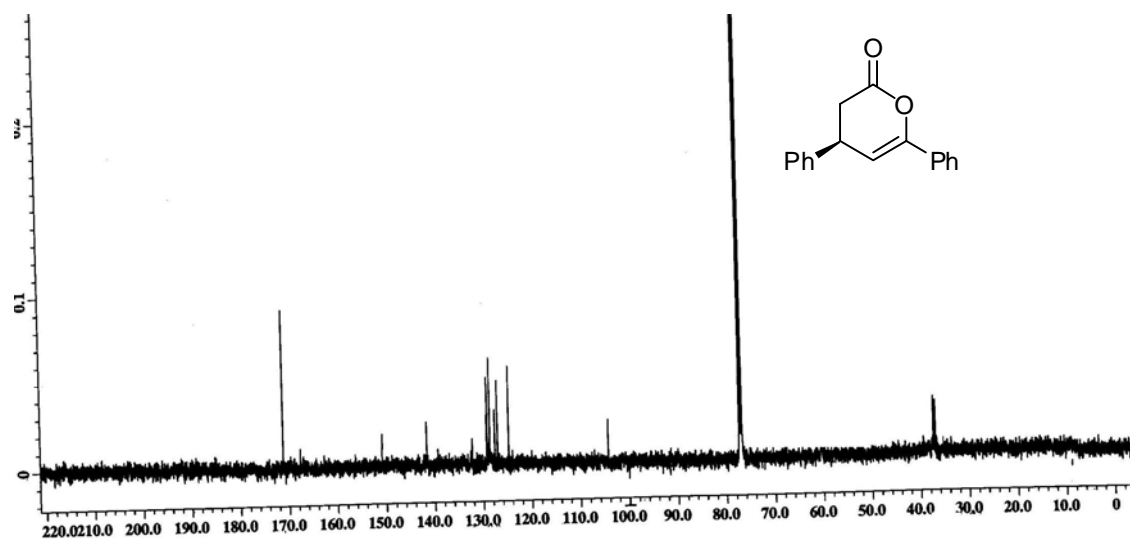


500 MHz ^1H NMR spectra of compound **7** in CDCl_3

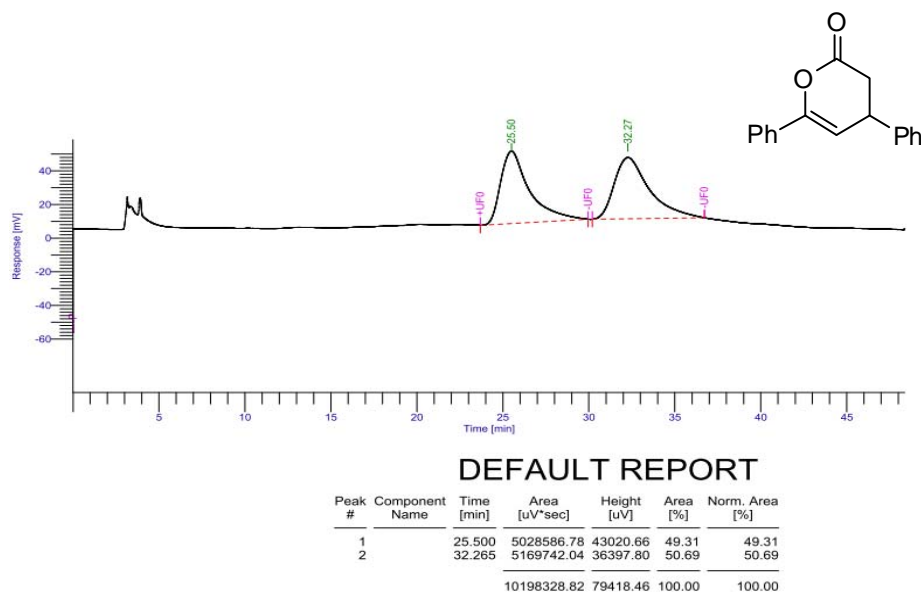




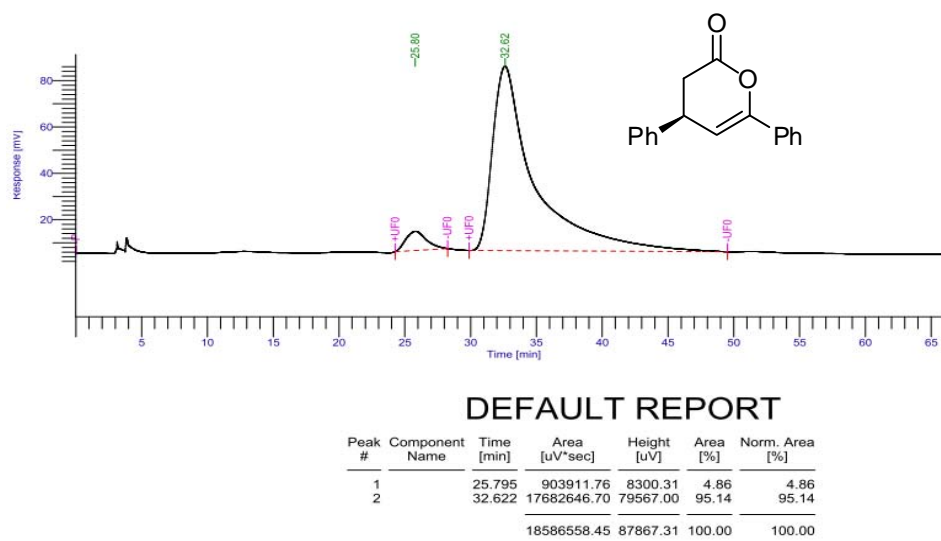
500 MHz ^1H NMR spectra of compound **8** in CDCl_3



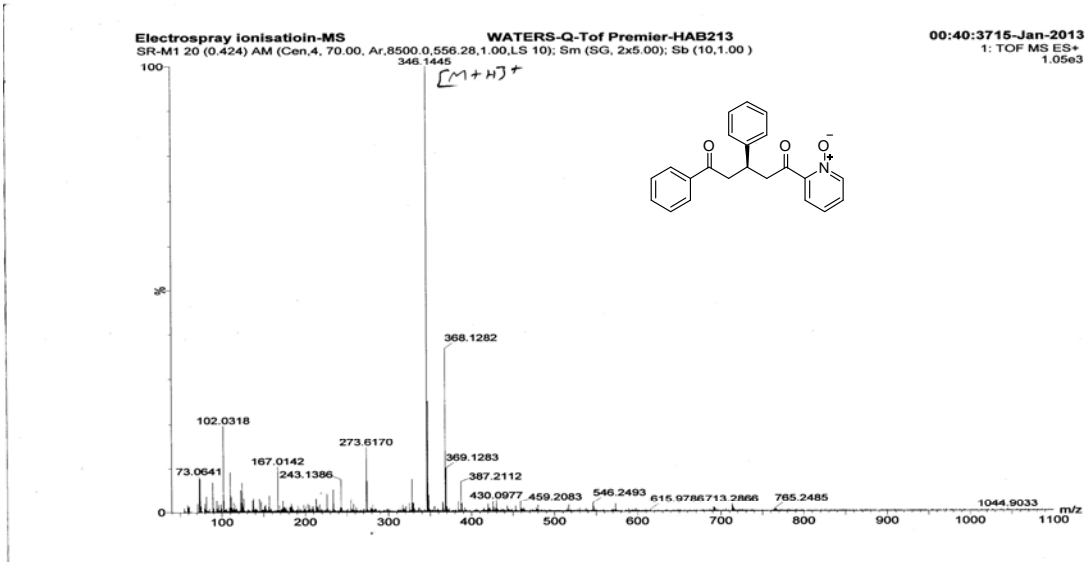
125 MHz ^{13}C NMR spectra of compound **8** in CDCl_3



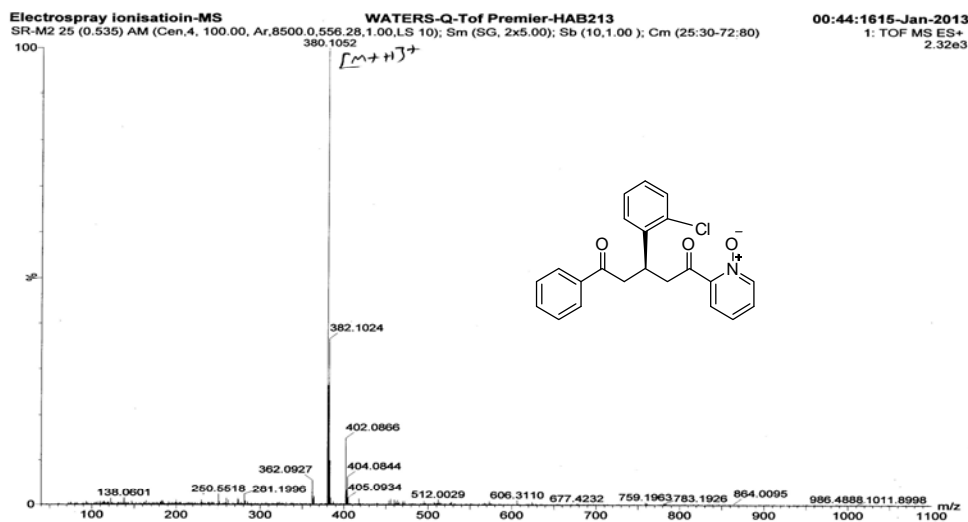
HPLC chromatogram of compound **8** (racemic)



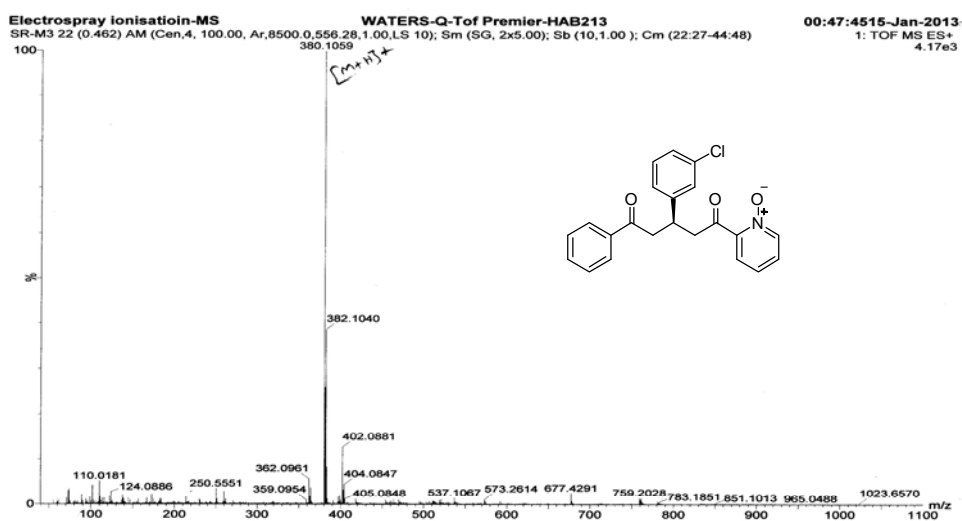
HPLC chromatogram of compound **8** (Chiral)



Mass spectrum of compound 4a

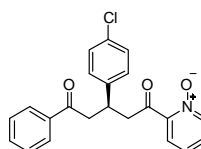


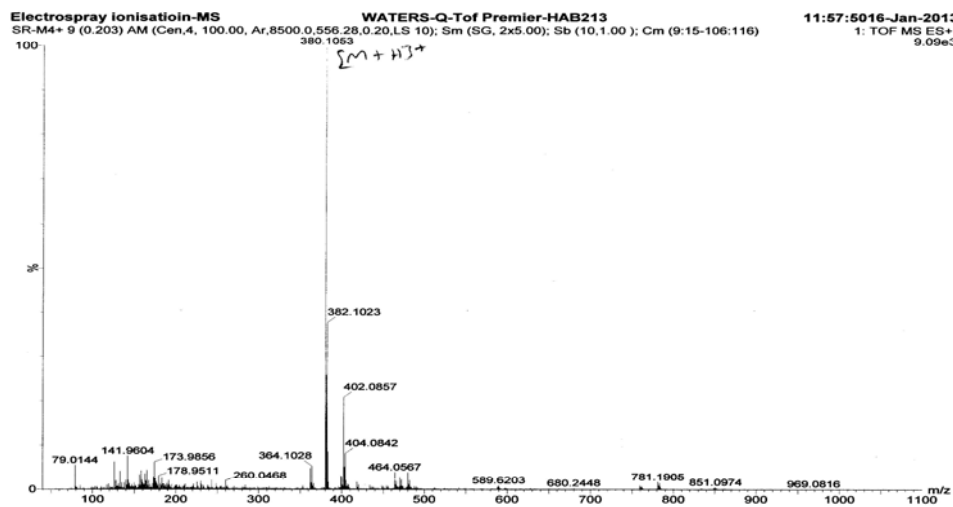
Mass spectrum of compound 4b



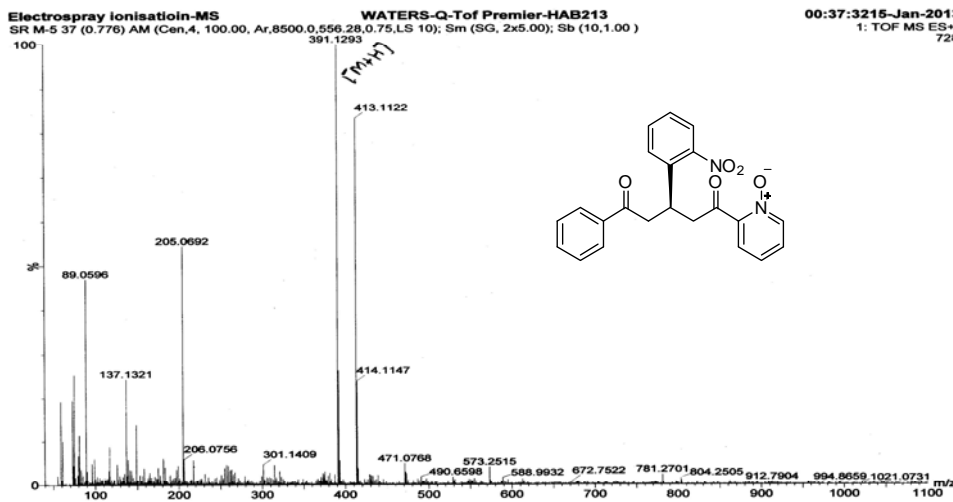
Mass spectrum of compound 4c

S44

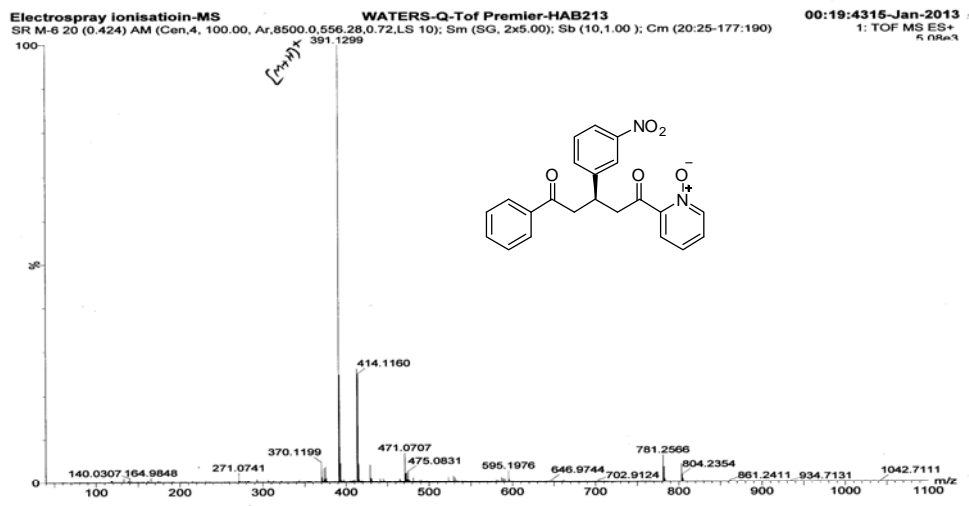




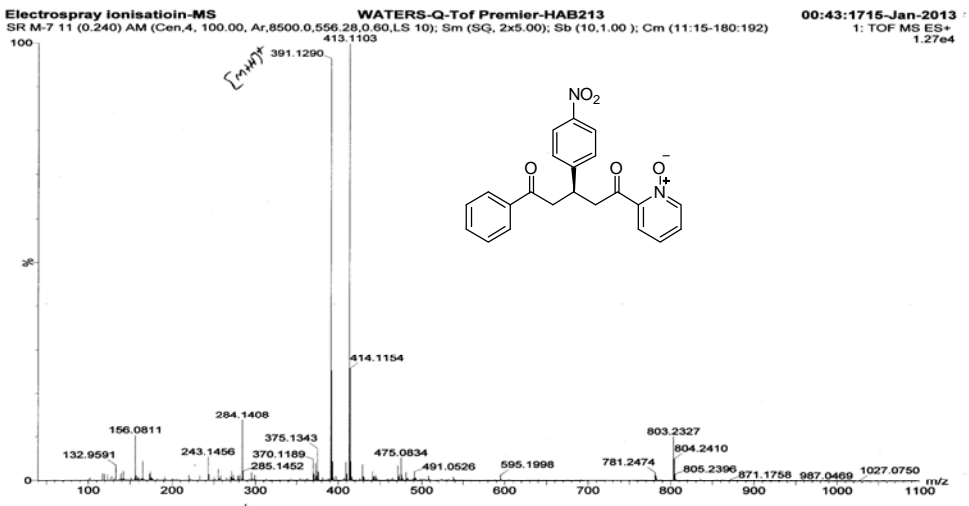
Mass spectrum of compound 4d



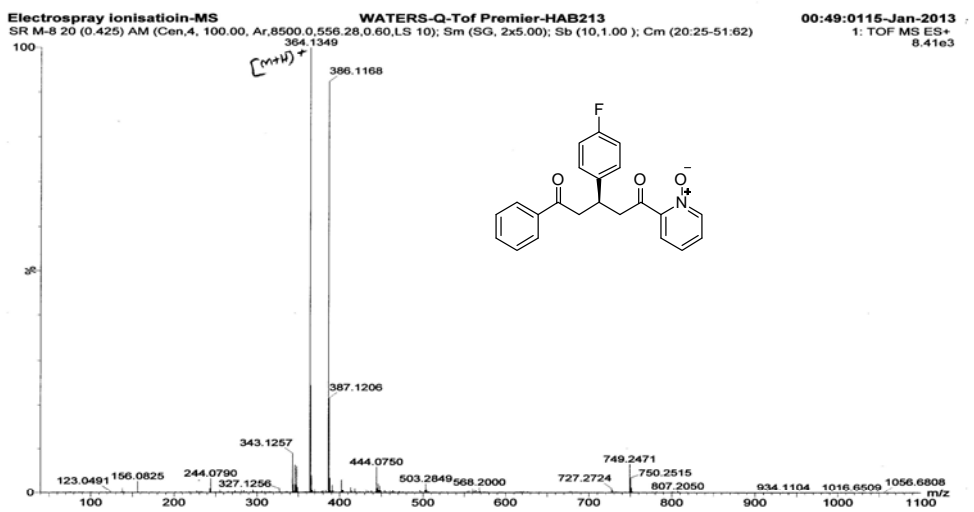
Mass spectrum of compound 4e



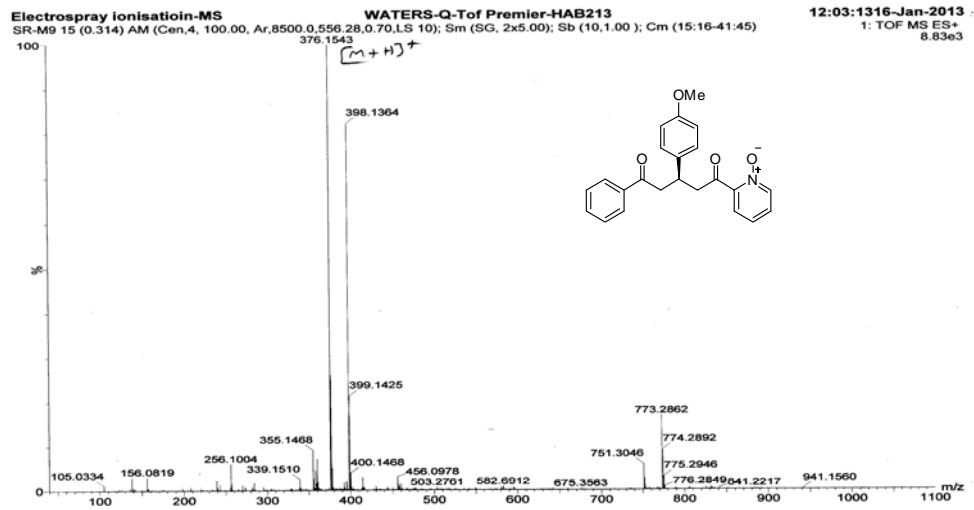
Mass spectrum of compound 4f



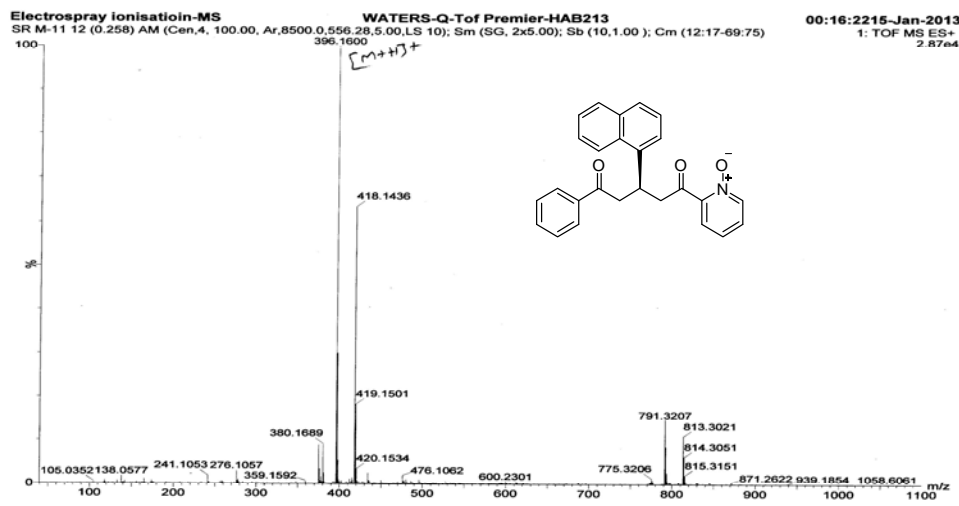
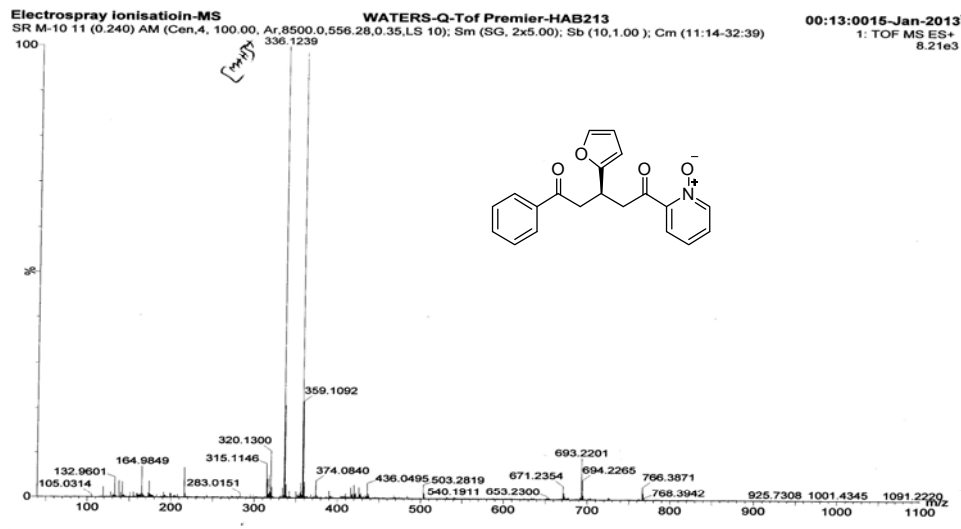
Mass spectrum of compound 4g

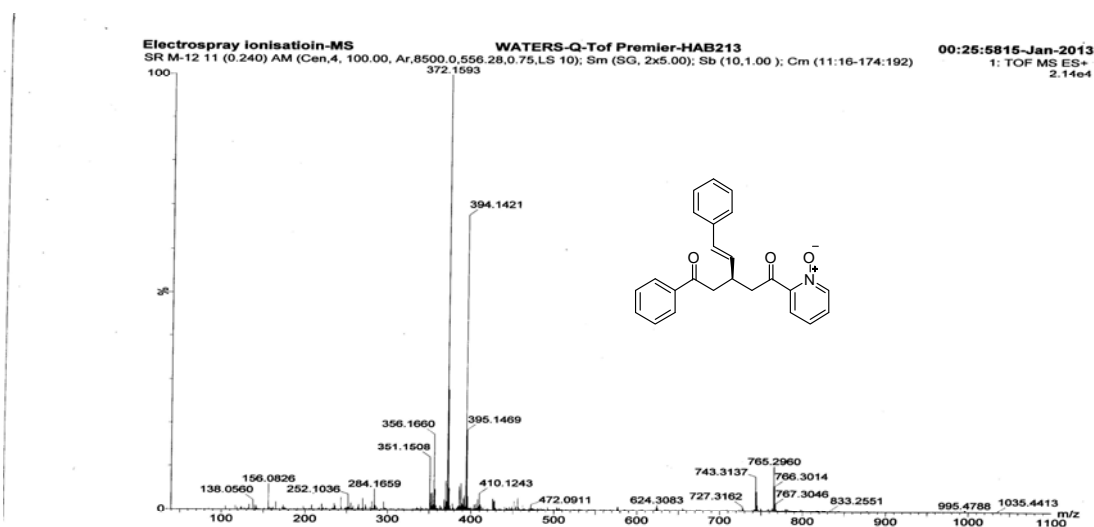


Mass spectrum of compound 4h

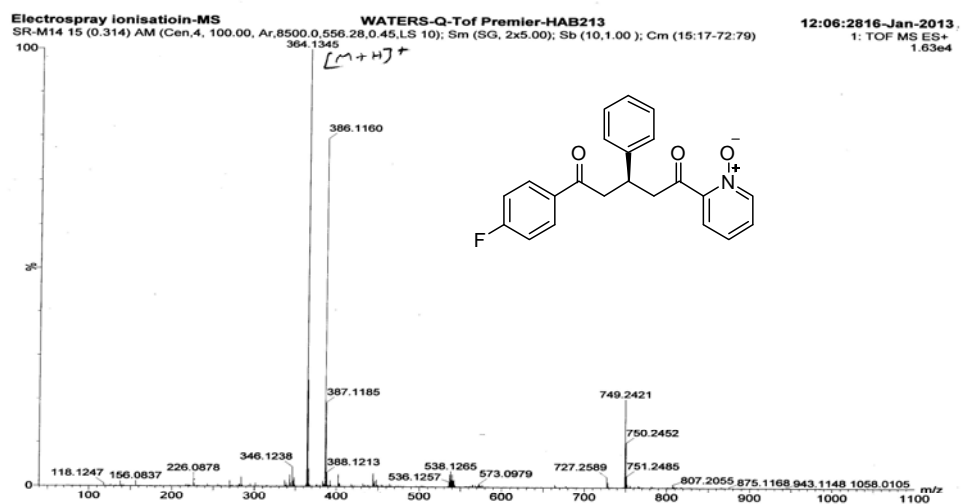


Mass spectrum of compound 4i

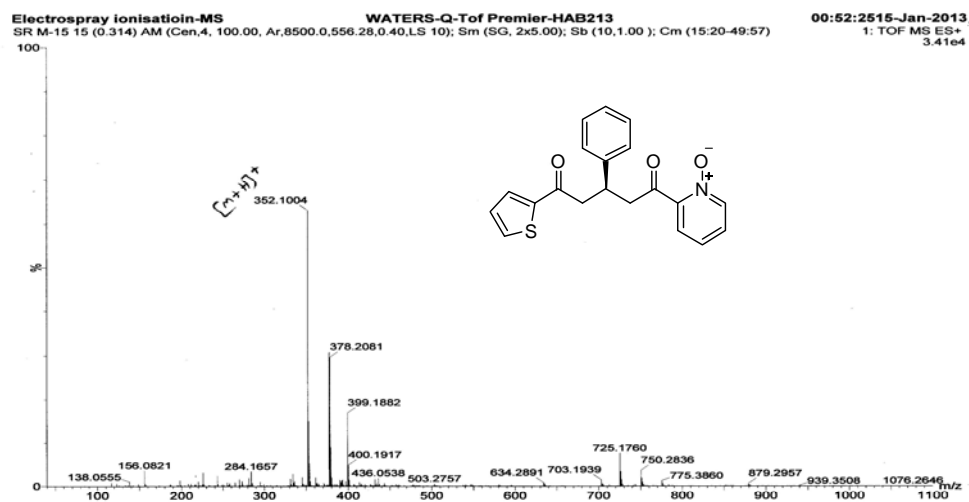




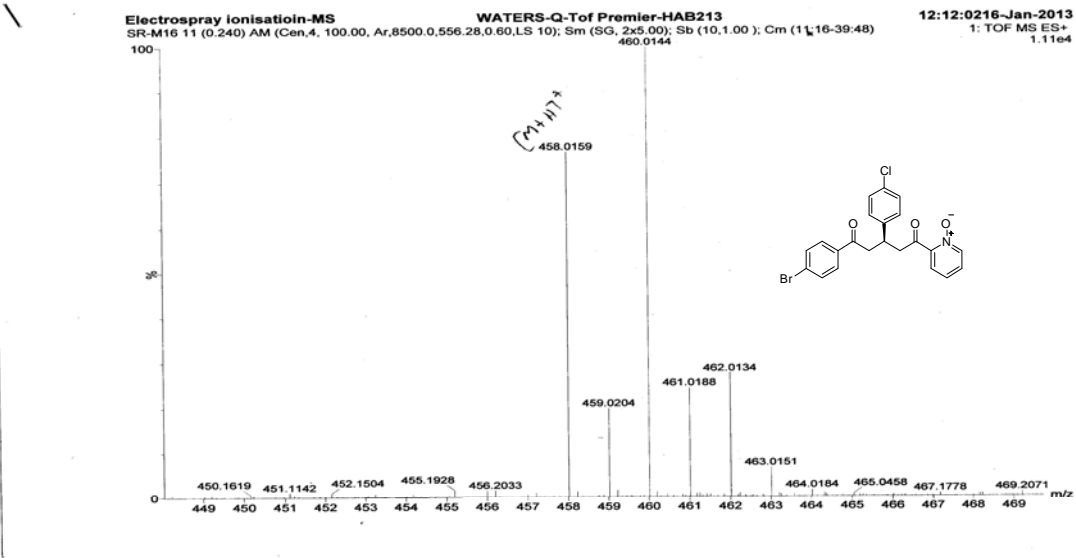
Mass spectrum of compound **4l**



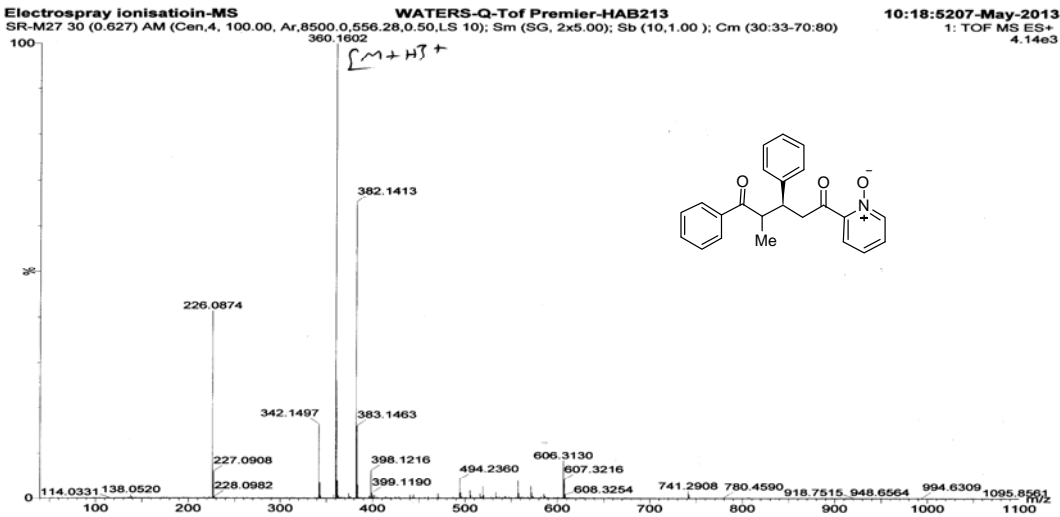
Mass spectrum of compound **4m**



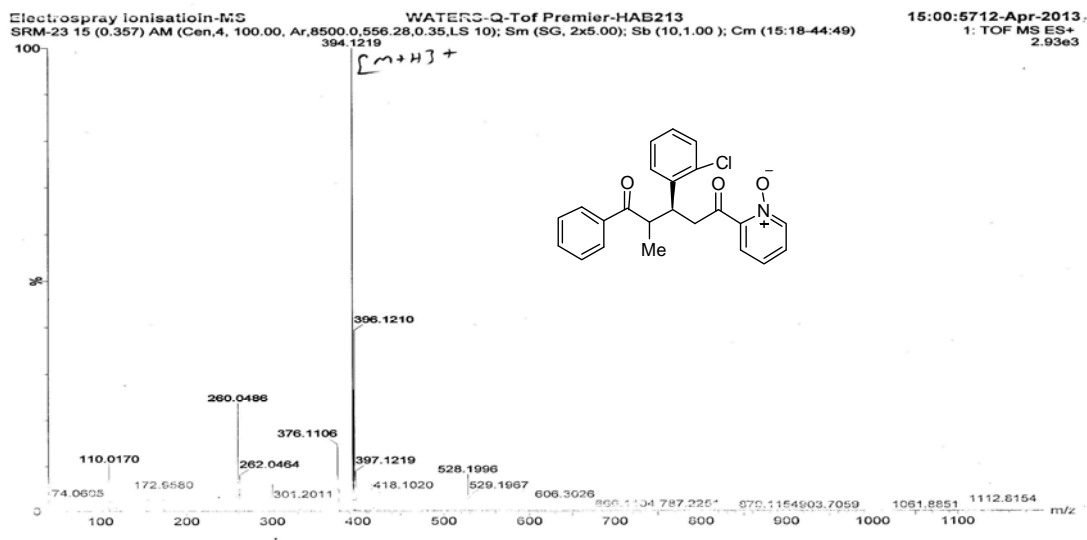
Mass spectrum of compound **4n**



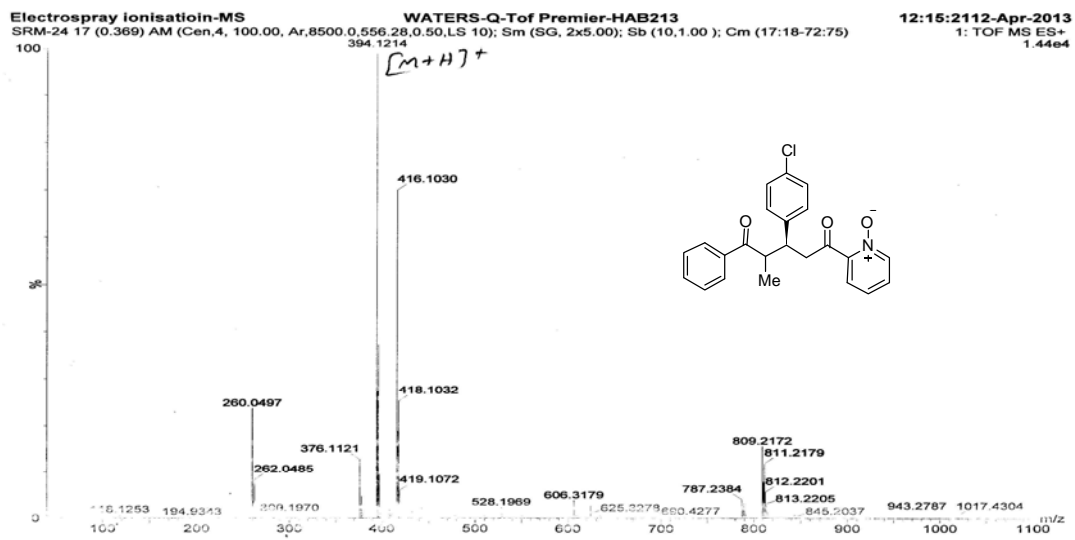
Mass spectrum of compound **4o**



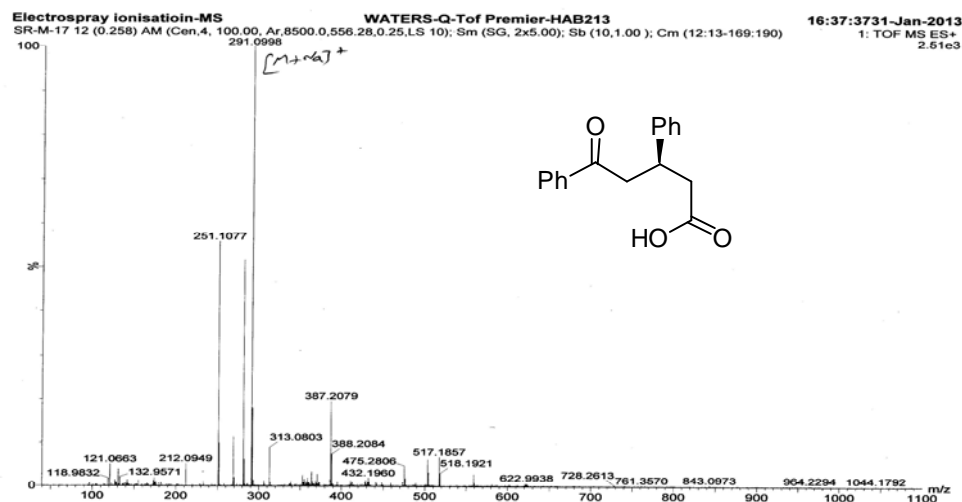
Mass spectrum of compound **6a**



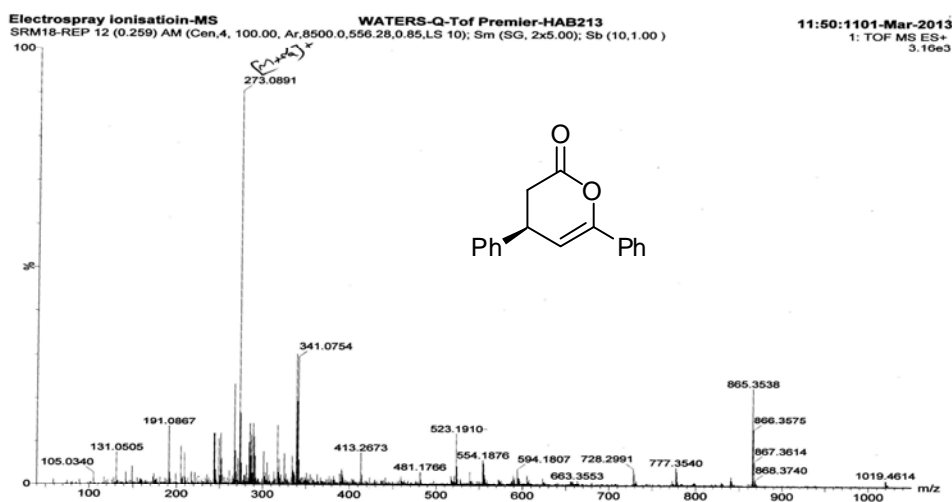
Mass spectrum of compound **6b**



Mass spectrum of compound **6c**



Mass spectrum of compound 7



Mass spectrum of compound 8