Supplementary Material (ESI) for Chemical Communications

Enantioselective Hydroxylation of Nitroalkenes: An Organocatalytic Approach

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Supporting Information

Contents

General Methods. NMR spectra were acquired on a Varian AS 400 spectrometer, running at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). ^{13}C NMR spectra were acquired on a broad band decoupled mode. Mass spectra were recorded on a Micromass LCT spectrometer using electrospray (ES^+) ionization techniques. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or $KMnO_4$ dip. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC (Daicel Chiralpak AD or Daicel Chiralcel OD/OJ columns).

Materials. Analytical grade solvents and commercially available reagents were used as received. For flash chromatography (FC) Iatrobeads (Iatrobeads 6RS-8060) or silica gel (Silica gel 60, 230-400 mesh) was used.

Racemic samples were prepared using Et_3N or a mixture of the catalysts **4a** and **4b**. Procedure for preparation of racemic samples using Et_3N: To a sample vial equipped with a magnetic stirring bar and nitroalkene **1** (1 equiv, 0.25 M) in toluene was added oxime **2** (2 equiv.) and Et_3N (1 equiv.). After full conversion as monitored by ^{1}H NMR the reaction mixture was loaded onto Iatrobeads and the product **5** was obtained by FC.

General Procedure for the Oxime Addition to Nitroalkenes: To a sample vial equipped with a magnetic stirring bar was added the catalyst **4d** (5 mol%, 0.0125 mmol), nitroalkene **1** (0.25 mmol) and toluene (1.0 mL). The mixture was stirred for 15 min at -24° C and oxime **2** (0.50 mmol) was added. After 16 h (or the time indicated – monitored by ^{1}H NMR), the reaction was completed and the reaction mixture was loaded onto Iatrobeads and the product **5** was obtained by FC.

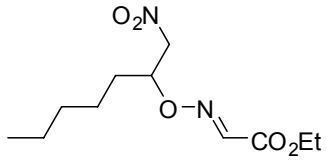
General Procedure for the Reduction of 5 to Nitro Alcohols 6: Compound **5** (0.4 mmol) was dissolved in THF (1.0 mL). $ZrCl_4$ (120 mg, 1.3 equiv.) and $NaBH_4$ (61 mg, 4 eq) were mixed in THF (1.0 mL) and this was added to the stirred solution of the oxime ether **5** at 0 ^{o}C. After full conversion of **5**, $HCL_{(aq)}$ (1M, 1.0 mL) was added dropwise. $NaOH_{(aq)}$ (1M) was then added until basic pH was achieved. The aqueous phase was extracted with EtOAc (5 x 1 mL), dried ($MgSO_4$) and evaporated. FC afforded the pure product.

General Procedure for the Hydrogenation of 5 to Amino Alcohol 7: Compound **5** (0.5 mmol) was dissolved in EtOAc (7.5 mL). 10% Pd/C (81 mg) was added and the stirred suspension was hydrogenated

at 15 bar. After 3.5 h the suspension was filtered through Celite. The EtOAc was evaporated and the crude amino alcohol dissolved in DMF (5 mL). To the stirred solution was added $(Boc)_2O$ and Et_3N. After 3 h Et_2O (5 mL) was added and the organic layer was extracted thoroughly with water. The organic layer was dried ($MgSO_4$) and evaporated. FC afforded the pure product **7**.

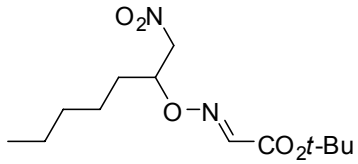
Notice about HPLC-traces. As stated in the manuscript (ref. 10), the products **5** are unstable. It was therefore not possible for some of the products to obtain a steady baseline in HPLC, as the products decomposed by the contact with *i*-PrOH and the various column materials.

(*E*)-Ethyl 2-(1-nitroheptan-2-yloxyimino)acetate (5a):



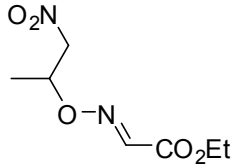
The title compound was obtained according to the general procedure as colourless oil (79% yield) after 16 h reaction. ^{1}H NMR ($CDCl_3$) δ 7.48 (s, 1H), 4.91-4.85 (m, 1H), 4.63 (dd, *J* = 7.6, 12.8 Hz, 1H), 4.50 (dd, *J* = 4.0, 12.9 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.81-1.72 (m, 1H), 1.65-1.57 (m, 1H), 1.43-1.21 (m, 9H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.4, 142.3, 81.0, 77.3, 61.7, 31.3, 30.9, 24.5, 22.3, 14.0, 13.8, HRMS calc.: $C_{11}H_{20}N_2NaO_5^+$ 283.1264; found: 283,1257. The ee was determined by chiral HPLC using a Chiralcel OD column; τ_{major} = 11.1 min, τ_{minor} = 10.2 min (91% ee). $[\alpha]_D^{23}$ +10.5 (c 1.05, $CHCl_3$).

(*E*)-*tert*-Butyl 2-(1-nitroheptan-2-yloxyimino)acetate (5b):



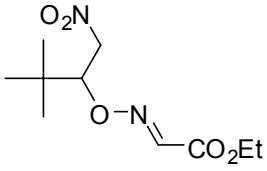
The title compound was obtained according to the general procedure as colourless oil (83% yield) after 16 h. ^{1}H NMR ($CDCl_3$) δ 7.42 (s, 1H), 4.98-4.78 (m, 1H), 4.66 (dd, *J* = 7.5, 12.8 Hz, 1H), 4.52 (dd, *J* = 4.1, 12.8 Hz, 1H), 1.86-1.73 (m, 1H), 1.70-1.57 (m, 1H), 1.51 (s, 9H), 1.46-1.20 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 160.4, 143.5, 82.9, 80.7, 77.3, 31.3, 30.8, 27.9 (3C), 24.6, 22.3, 13.9. HRMS calc.: $C_{13}H_{24}N_2NaO_5^+$ 311.1577; found: 311.1576. The ee was determined by chiral HPLC using a Chiralcel OD column; τ_{major} = 9.5 min, τ_{minor} = 8.9 min (90% ee). $[\alpha]_D^{23}$ +12.5 (c 1.01, CH_2Cl_2).

(*E*)-Ethyl 2-(1-cyclohexyl-2-nitroethoxyimino)acetate (5c):



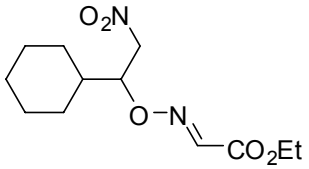
The title compound was obtained according to the general procedure as colourless oil (63% yield) after 16 h reaction. ^{1}H NMR ($CDCl_3$) δ 7.49 (s, 1H), 5.17-4.99 (m, 1H), 4.66 (dd, *J* = 7.7, 13.0 Hz, 1H), 4.51 (dd, *J* = 4.1, 12.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.42 (d, *J* = 6.6 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.4, 142.4, 78.1, 77.1, 61.8, 16.9, 14.1. HRMS calc.: $C_7H_{12}N_2NaO_5^+$ 227.0638; found: 227.0635. The ee was determined by chiral HPLC using a Chiralcel OJ column; τ_{major} = 21.3 min, τ_{minor} = 18.8 min (90% ee). $[\alpha]_D^{23}$ +1.8 (c 1.04, CH_2Cl_2).

(*E*)-Ethyl 2-(3,3-dimethyl-1-nitrobutan-2-yloxyimino)acetate (5d):



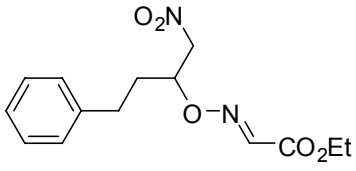
The title compound was obtained according to the general procedure as colourless oil (69% yield). ^{1}H NMR ($CDCl_3$) δ 7.49 (s, 1H), 4.86 (ddd, *J* = 6.1, 12.2, 18.4 Hz, 1H), 4.58 (d, *J* = 6.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 1.32 (t, *J* = 6.0 Hz, 3H), 1.0 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 161.5, 141.4, 89.3, 75.8, 61.7, 34.7, 26.0 (3C), 14.1. HRMS calc.: $C_{10}H_{18}N_2NaO_5^+$ 269.1108; found: 269.1114. The ee was determined by chiral HPLC using a Chiralcel OD column; τ_{major} = 12.2 min, τ_{minor} = 11.2 min (90% ee). $[\alpha]_D^{23}$ -1.7 [c 0.57, CH_2Cl_2].

(*E*)-Ethyl 2-(1-cyclohexyl-2-nitroethoxyimino)acetate (5e):



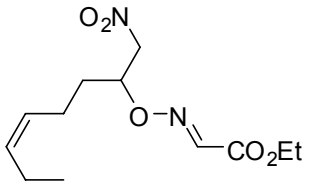
The title compound was obtained according to the general procedure as colourless oil (82% yield). ^{1}H NMR ($CDCl_3$) δ 7.45 (s, 1H), 4.79-4.75 (m, 1H), 4.61 (dd, *J* = 12.9, 8.4 Hz, 1H), 4.51 (dd, *J* = 12.9, 3.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.86-1.47 (m, 6H), 1.27 (t, 3H), 1.23-0.89 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 161.4, 142.1, 85.4, 75.6, 61.7, 39.2, 28.3, 28.2, 26.0, 25.7, 25.6, 14.0. HRMS calc.: $C_{12}H_{20}N_2NaO_5^+$ 295.1264; found: 295.1264. The ee was determined by chiral HPLC using a Chiralcel OD column; τ_{major} = 18.3 min, τ_{minor} = 14.9 min (90% ee). $[\alpha]_D^{23}$ +7.8 (c 1.06, CH_3Cl_2).

(*E*)-Ethyl 2-(1-nitro-4-phenylbutan-2-yloxyimino)acetate (5f):



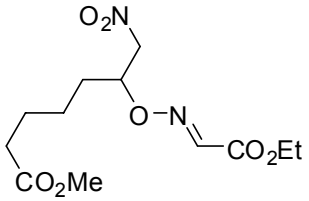
The title compound was obtained according to the general procedure as colourless oil (68% yield). ^{1}H NMR ($CDCl_3$) δ 7.51 (s, 1H), 7.09-7.32 (m, 5H), 4,89-4,83 (m, 1H), 4.66 (dd, *J* = 7.4, 12.9 Hz, 1H), 4.50 (dd, *J* = 4.0, 12.9 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.89-2.58 (m, 2H), 2.22-2.06 (m, 1H), 2.01-1.89 (m, 1H) 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.3, 142.6, 140.1, 128.6 (2C), 128.3 (2C), 126.3, 80.1, 77.2, 61.8, 32.5, 31.0, 14.0. HRMS calc.: $C_{14}H_{18}N_2NaO_5^+$ 317.1108; found: 317.1107. The ee was determined by chiral HPLC using a Chiralcel OJ column; τ_{major} = 43.3 min, τ_{minor} = 34.5 min (89% ee). $[\alpha]_D^{23}$ +37.3 (c 0.86, $CHCl_3$).

(*E*)-Ethyl 2-((E)-1-nitrohex-4-en-2-yloxyimino)acetate (5g):



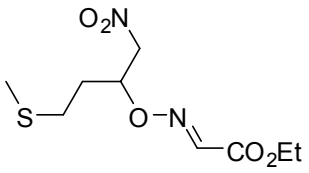
The title compound was obtained according to the general procedure as colourless oil (79% yield). ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 1H), 5.41-5.31 (m, 1H), 5.25-5.19 (m, 1H), 4.90-4.83 (m, 1H), 4.63 (dd, *J* = 7.4, 12.8 Hz, 1H), 4.50 (dd, *J* = 4.0, 12.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.13-2.08 (m, 2H), 1.99-1.92 (m, 2H), 1.89-1.80 (m, 1H), 1.68-1.60 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.4, 142.4, 133.6, 126.5, 80.3, 77.3, 61.8, 30.8, 22.5, 20.5, 14.1 (2C). HRMS calc.: $C_{12}H_{20}N_2NaO_5^+$ 295.1264; found: 295.1276. The ee was determined by HPLC using a Chiralcel OD colum; τ_{major} = 19.6 min, τ_{minor} = 18.0 min (93% ee). $[\alpha]_D^{23}$ +33.2 (c 0.56, CH_2Cl_2).

(*E*)-Methyl 6-(2-ethoxy-2-oxoethylideneaminooxy)-7-nitroheptanoate (5h):



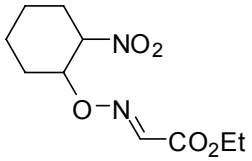
The title compound was obtained according to the general procedure as colourless oil (68% yield) after 5d reaction. ^{1}H NMR ($CDCl_3$) δ 7.50 (s, 1H), 4.95-4.89 (m, 1H), 4.67 (dd, *J* = 7.5, 12.9 Hz, 1H), 4.54 (dd, *J* = 4.0, 12.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.89-1.78 (m, 1H), 1.75-1.58 (m, 2H), 1.54-1.36 (m, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 173.5, 161.2, 142.4, 80.6, 76.5, 61.7, 51.4, 33.4, 30.4, 24.2 (2C), 13.9. HRMS calc.: $C_{12}H_{20}N_2NaO_7^+$ 327.1163; found: 327.1162. The ee was determined by chiral HPLC using a Chiralcel OD column; τ_{major} = 13.0 min, τ_{minor} = 11.5 min (90% ee). $[\alpha]_D^{23}$ +12.6 (c 1.1, CH_2Cl_2).

(*E*)-Ethyl 2-(4-(methylthio)-1-nitrobutan-2-yloxyimino)acetate (5i):



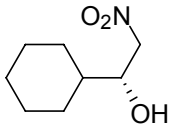
The title compound was obtained according to the general procedure as yellow oil (82% yield). ^{1}H NMR ($CDCl_3$) δ 7.52 (s, 1H), 5.11-5.05 (m, 1H), 4.73 (dd, *J* = 7.2, 12.9 Hz, 1H), 4.61 (dd, *J* = 4.2, 12.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.66-2.53 (m, 2H), 2.18-2.10 (m, 1H), 2.10 (s, 3H), 1.99-1.91 (m, 1H), 1.33 (t, *J* = 7.14 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.2, 142.8, 79.4, 77.0, 61.9, 30.3, 29.4, 15.5, 14.0. HRMS calc.: $C_9H_{16}N_2NaO_5S^+$ 287.0672; found: 287.0677. The ee was determined by chiral HPLC using a Chiralpak AD column; τ_{major} = 16.9 min, τ_{minor} = 15.6 min (89% ee). $[\alpha]_D^{23}$ +32.4 (c 1.01, CH_2Cl_2).

(*E*)-Ethyl 2-(2-nitrocyclohexyloxyimino)acetate (5j):



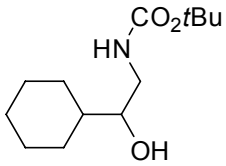
The title compound was obtained according to the general procedure as colourless oil (73% yield, dr = 20:1). ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 1H), 5.11-5.08 (m, 1H), 4.52 (dt, *J* = 4.0, 10.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.31 (ddd, *J* = 4.0, 6.9, 8.7 Hz, 1H), 2.21-2.04 (m, 2H), 1.91 (ddd, *J* = 4.2, 8.6, 13.0 Hz 1H), 1.63-1.54 (m, 1H), 1.52-1.45 (m, 2H), 1.38-1.32 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.5, 142.2, 84.0, 80.2, 61.8, 28.6, 24.6, 22.8, 19.3, 14.1. HRMS calc.: $C_{10}H_{16}N_2NaO_5^+$ 267.0951; found: 267.0953. The ee was determined by chiral HPLC using a Chiralcel OJ column; *major diastereomer*: τ_{major} = 17.6 min, τ_{minor} = 13.2 min (48% ee), *minor diastereomer*: τ_{major} = 11.5 min, τ_{minor} = 10.7 min (42% ee). $[\alpha]_D^{23}$ -21.7 (c 0.90, $CHCl_3$).

(*R*)-1-Cyclohexyl-2-nitroethanol (6e):



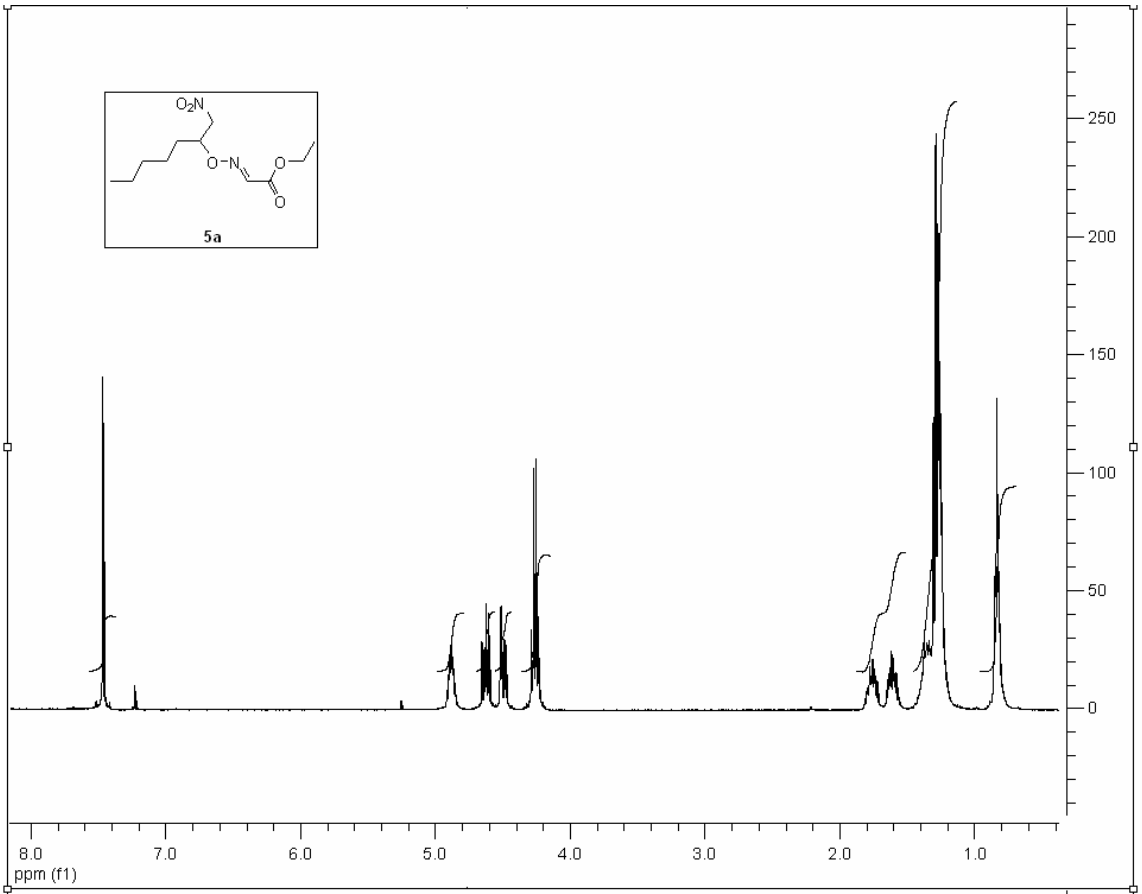
The title compound was obtained according to the general procedure. Spectroscopic data were identical to those reported in literature.[1] $[\alpha]_D^{23}$ -11.6 (c 1.40, $CHCl_3$). [Lit[1]: -20.3 (c = 1.2, $CHCl_3$)].

***tert*-Butyl 2-cyclohexyl-2-hydroxyethylcarbamate (7e):**



The title compound was obtained according to the general procedure as colourless crystals at 4 °C. ^{1}H NMR ($CDCl_3$) δ 5.02 (bs, 1H), 3.44-3.26 (m, 2H), 3.10-2.93 (m, 1H), 2.61 (bs, 1H), 1.89-1.56 (m, 5H), 1.42 (s, 9H), 1.36-1.29 (m, 1H), 1.28-0.93 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 156.8, 79.4, 75.7, 44.4, 41.8, 28.9, 28.3 (3C), 28.2, 26.3, 26.1, 25.9. HRMS calc.: $C_{13}H_{25}NNaO_3^+$ 266.1727; found: 266.1721.

[1] C. Palomo, M. Oiarbide, A. Laso *Angew. Chem. Int. Ed.* 2005, **44**, 3881.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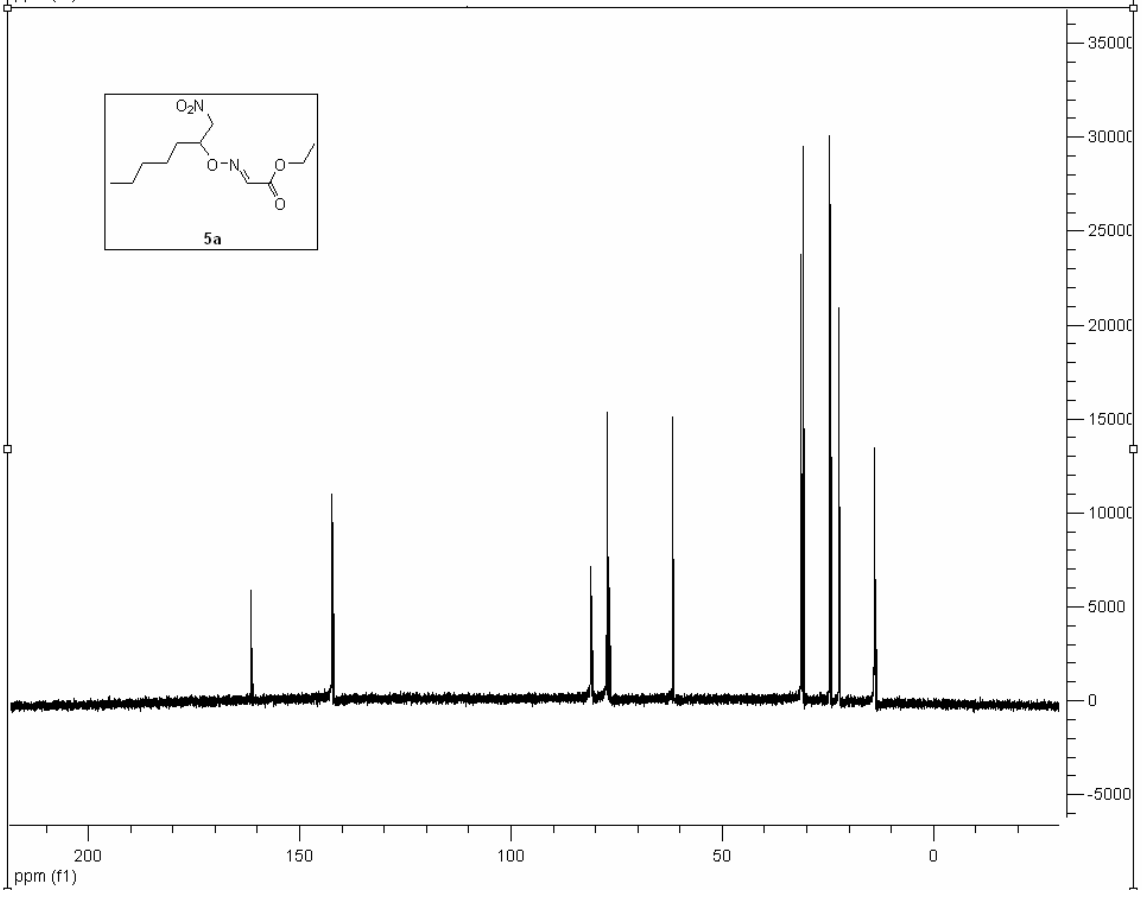
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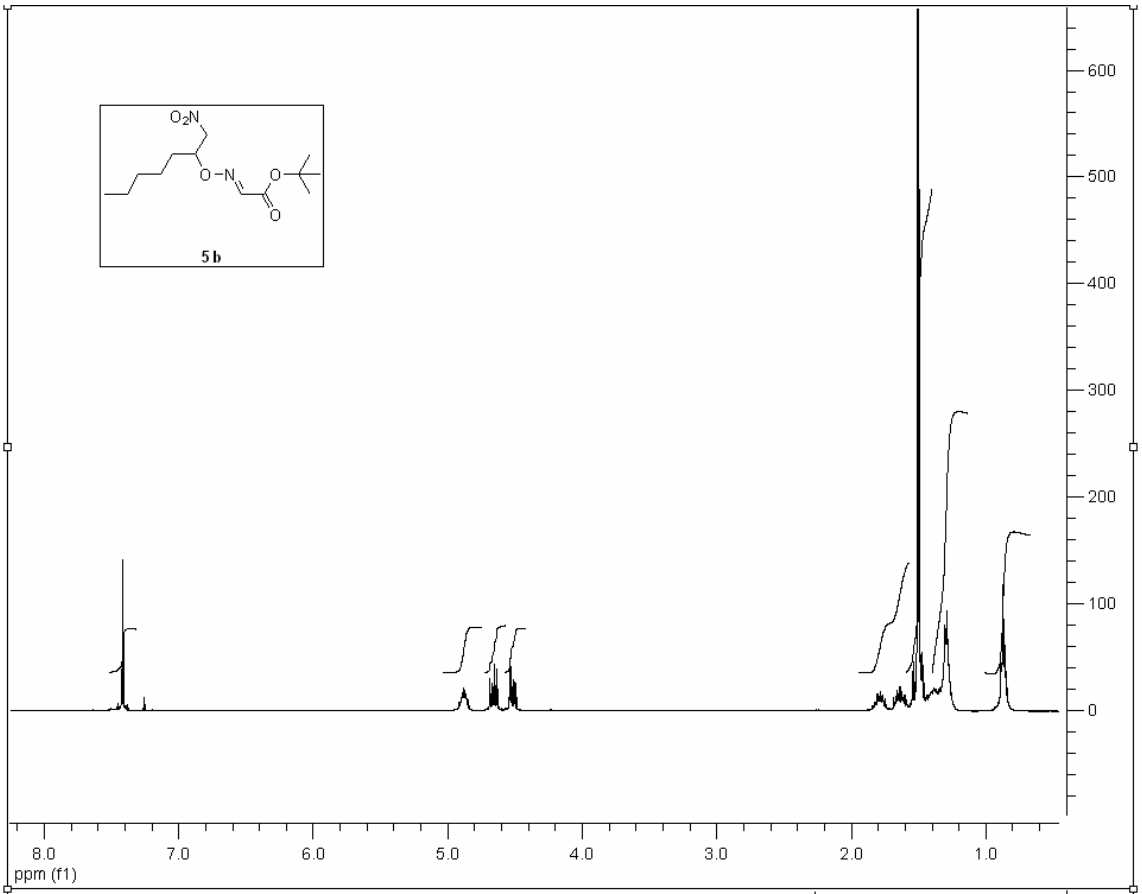
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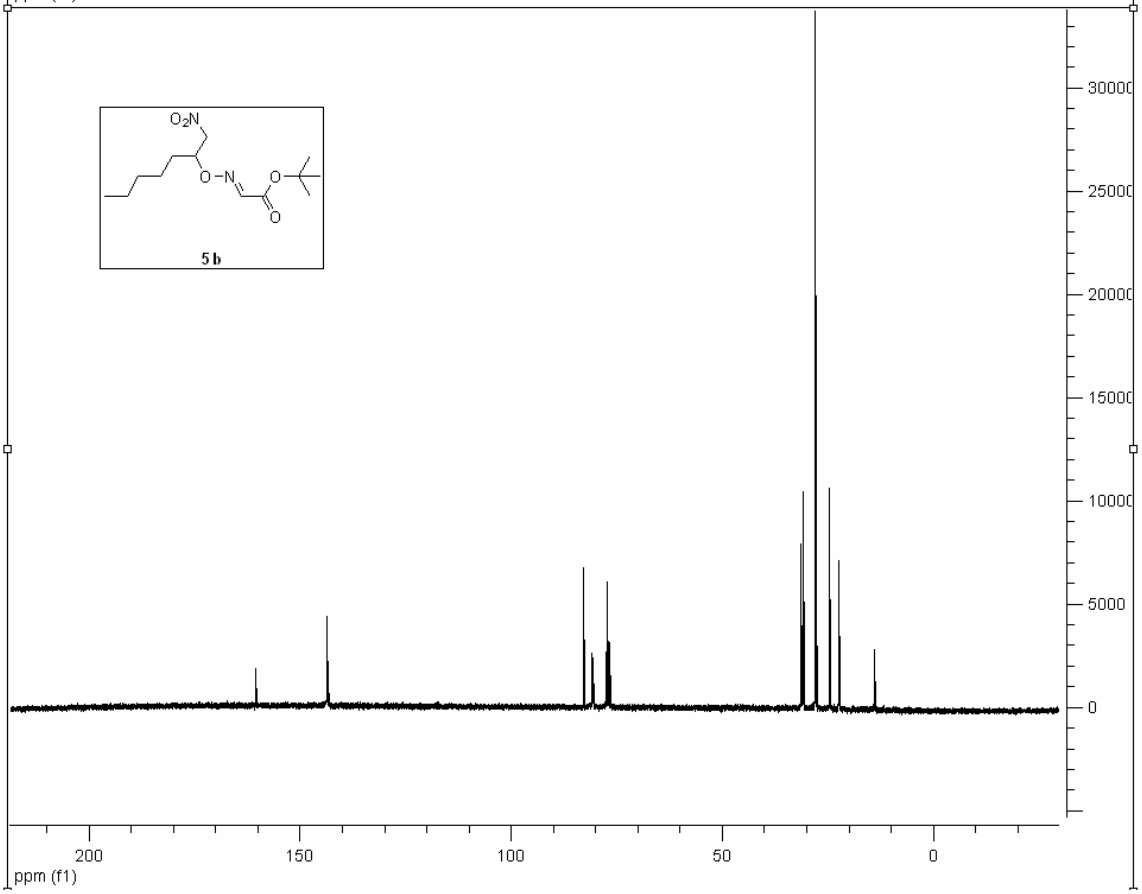
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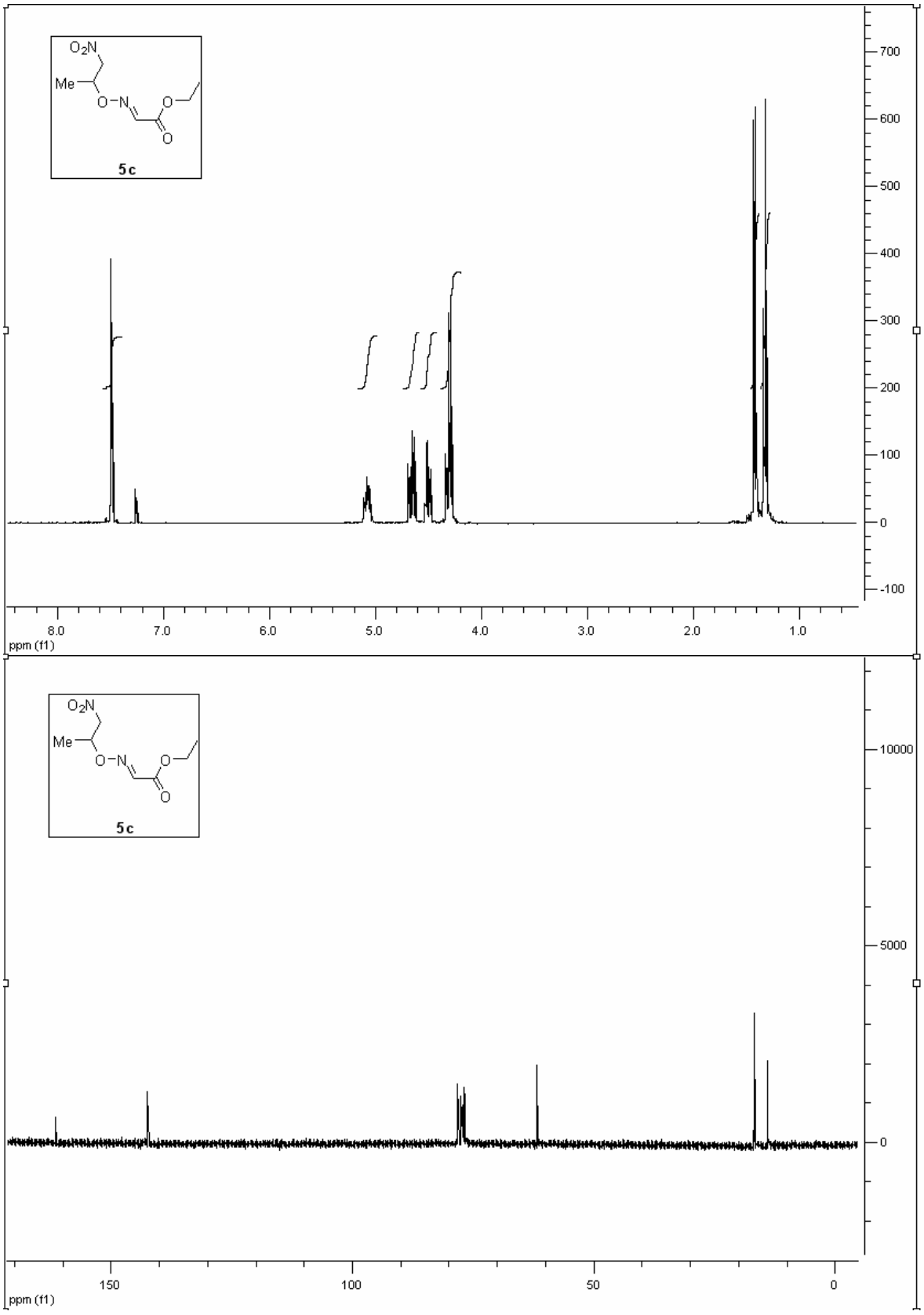
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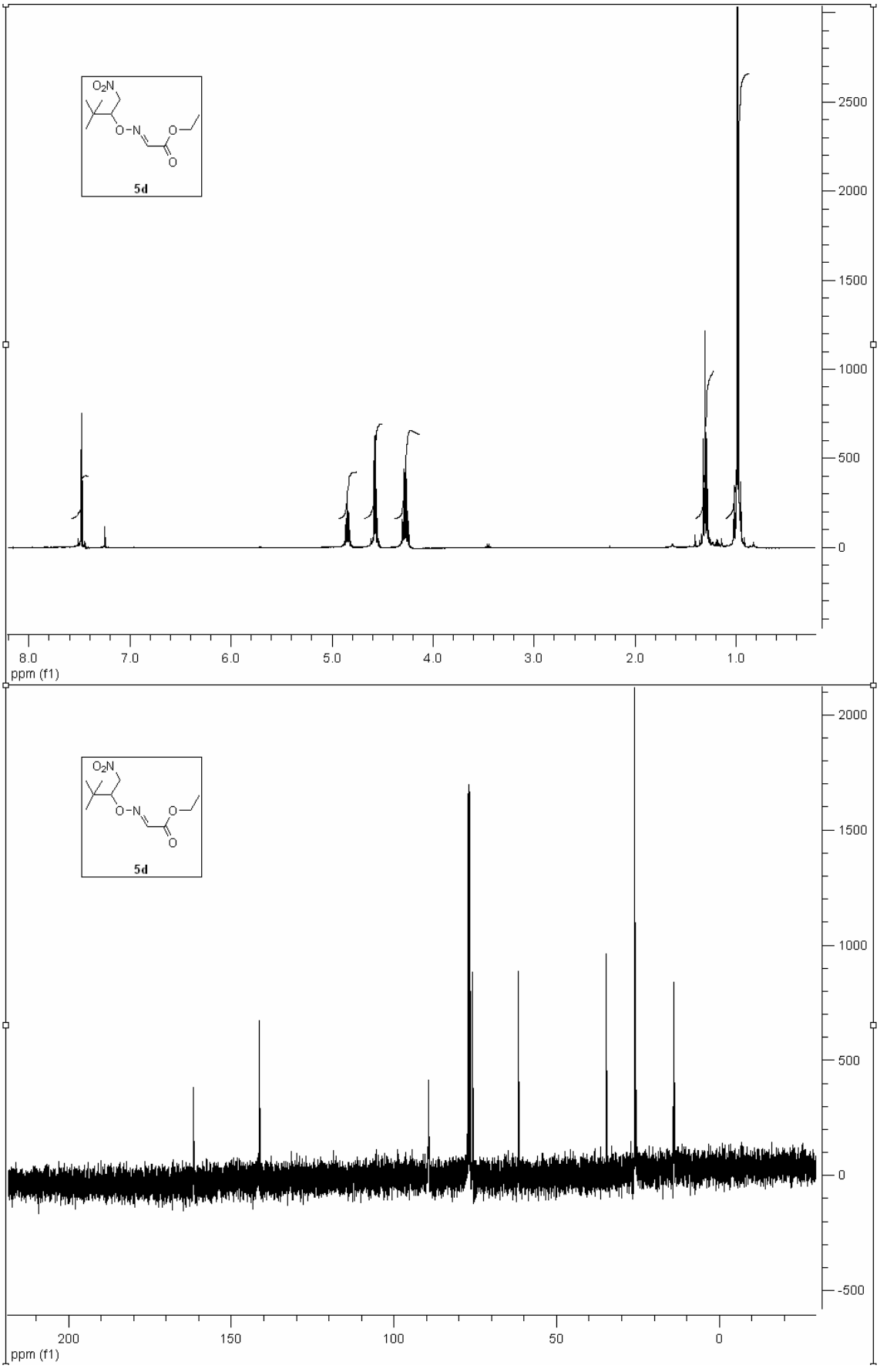
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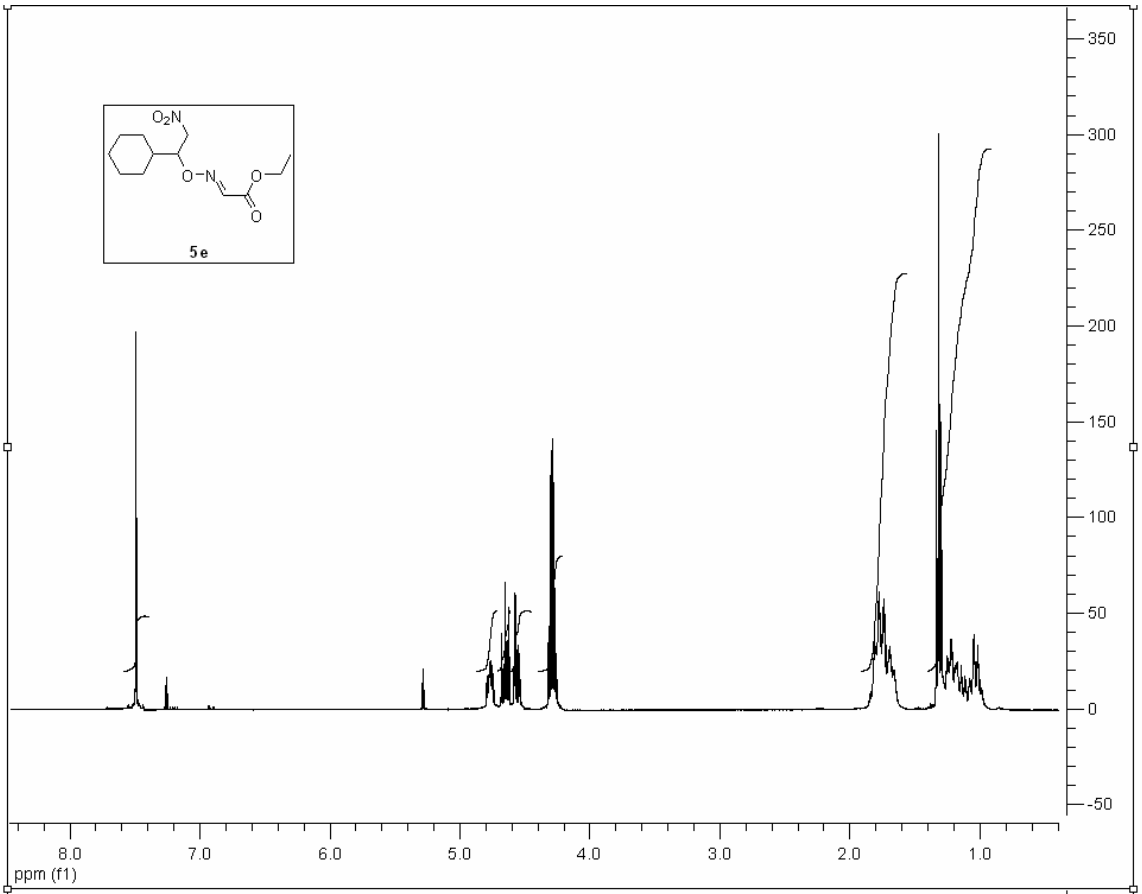
ppm (f1)


O2N
O
N
O
O
5e
350
300
250
200
150
100
50
0
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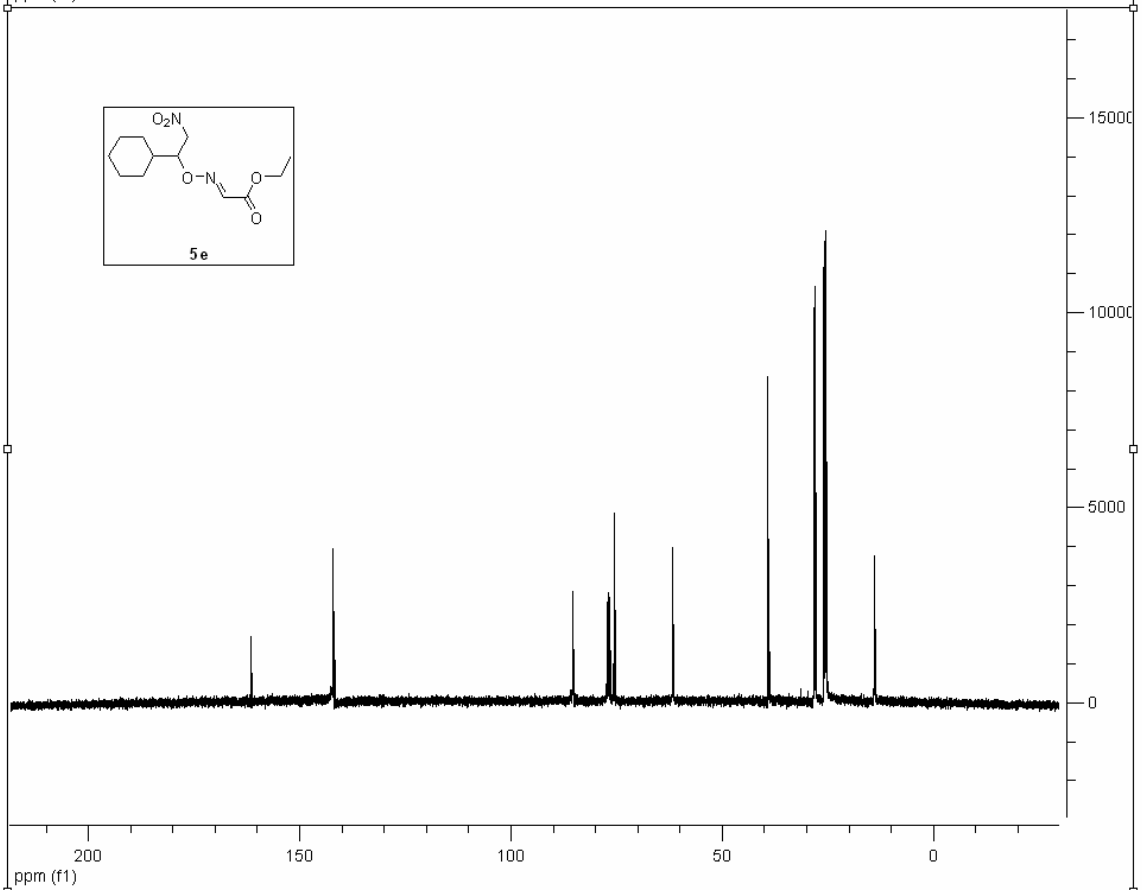
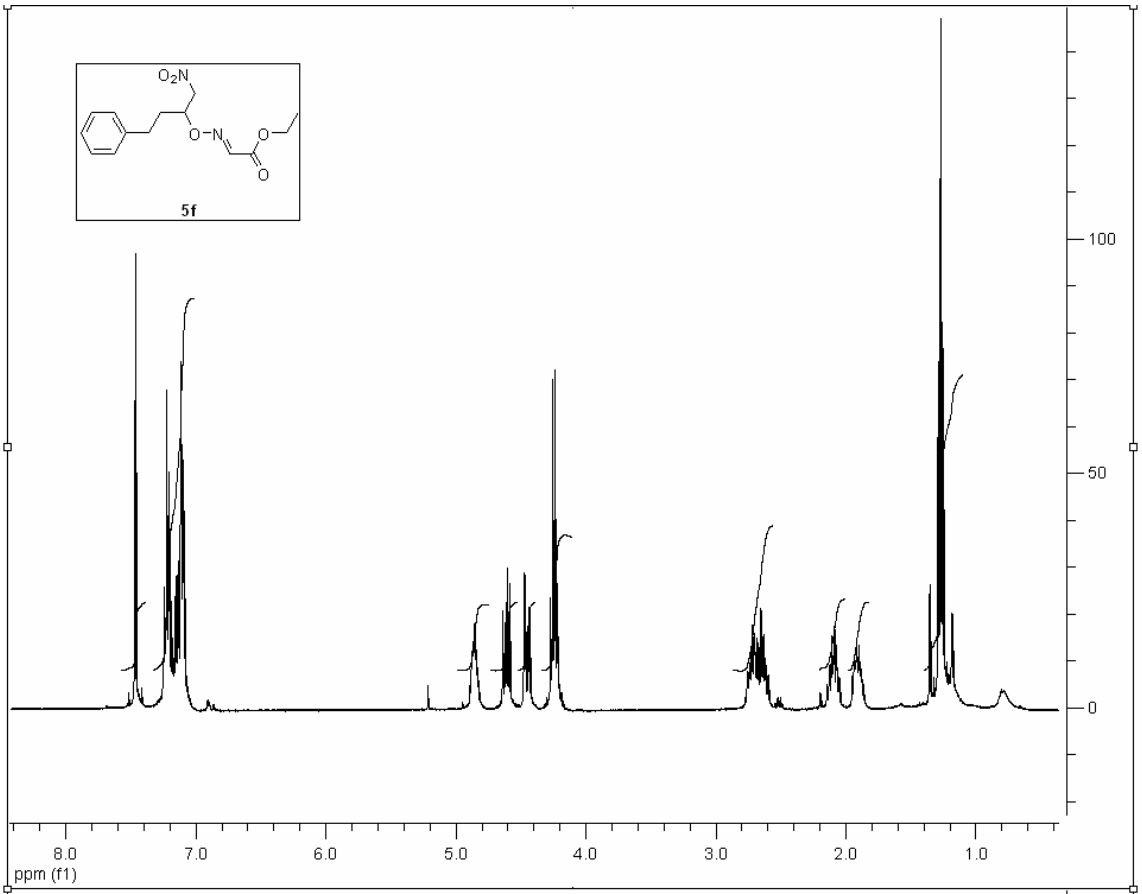
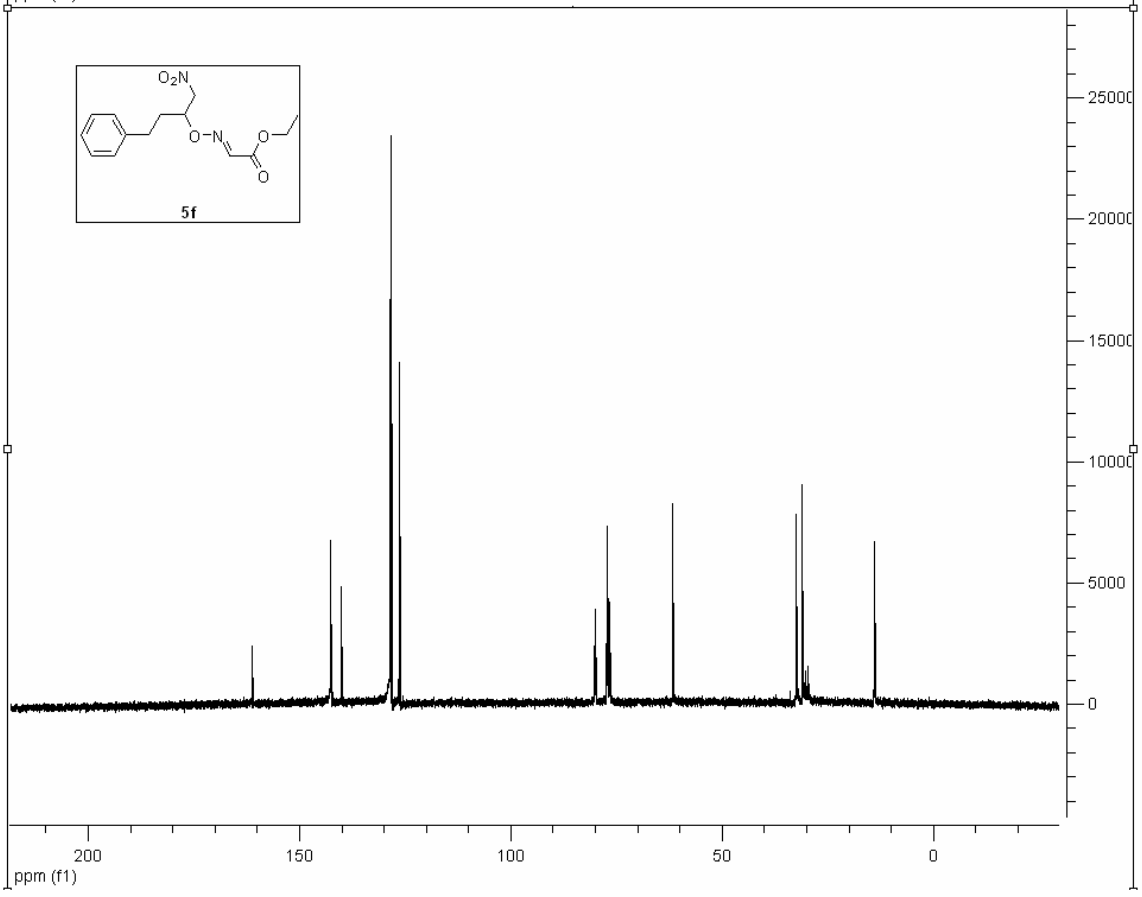
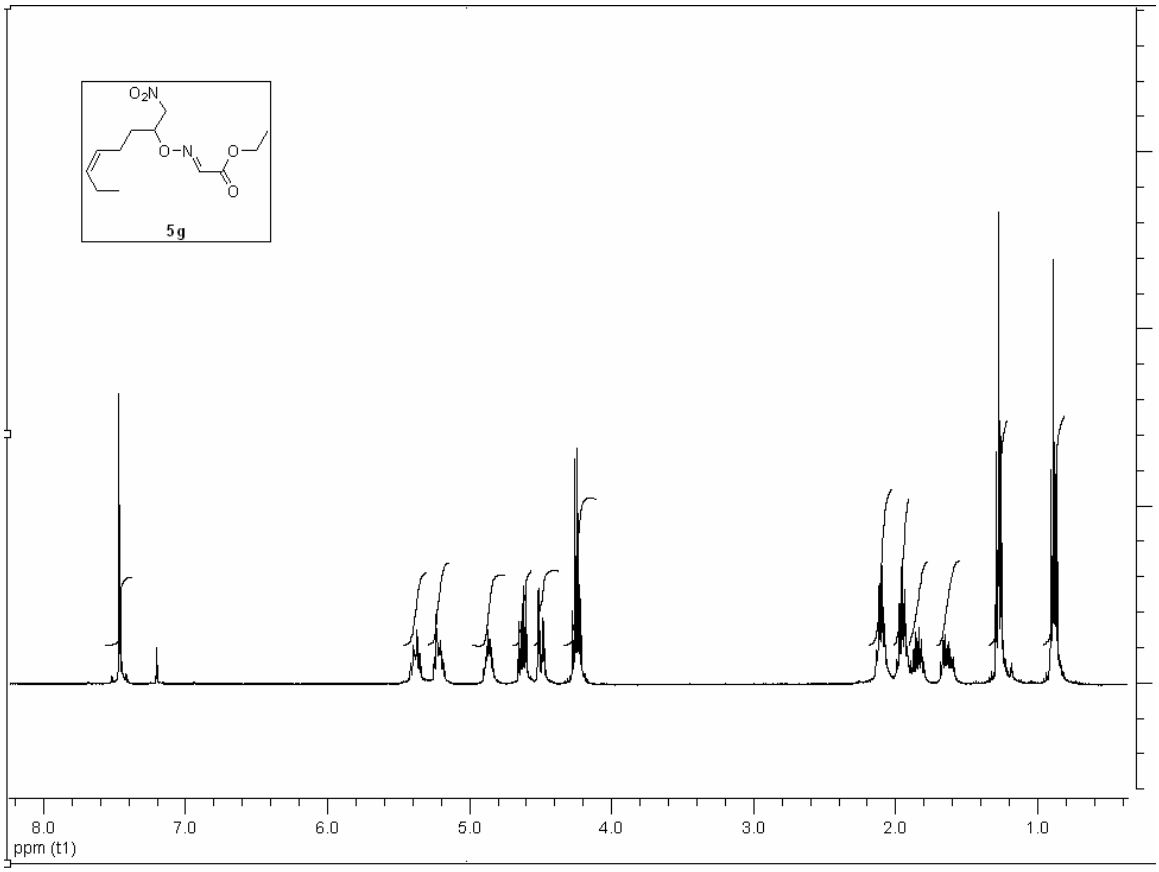
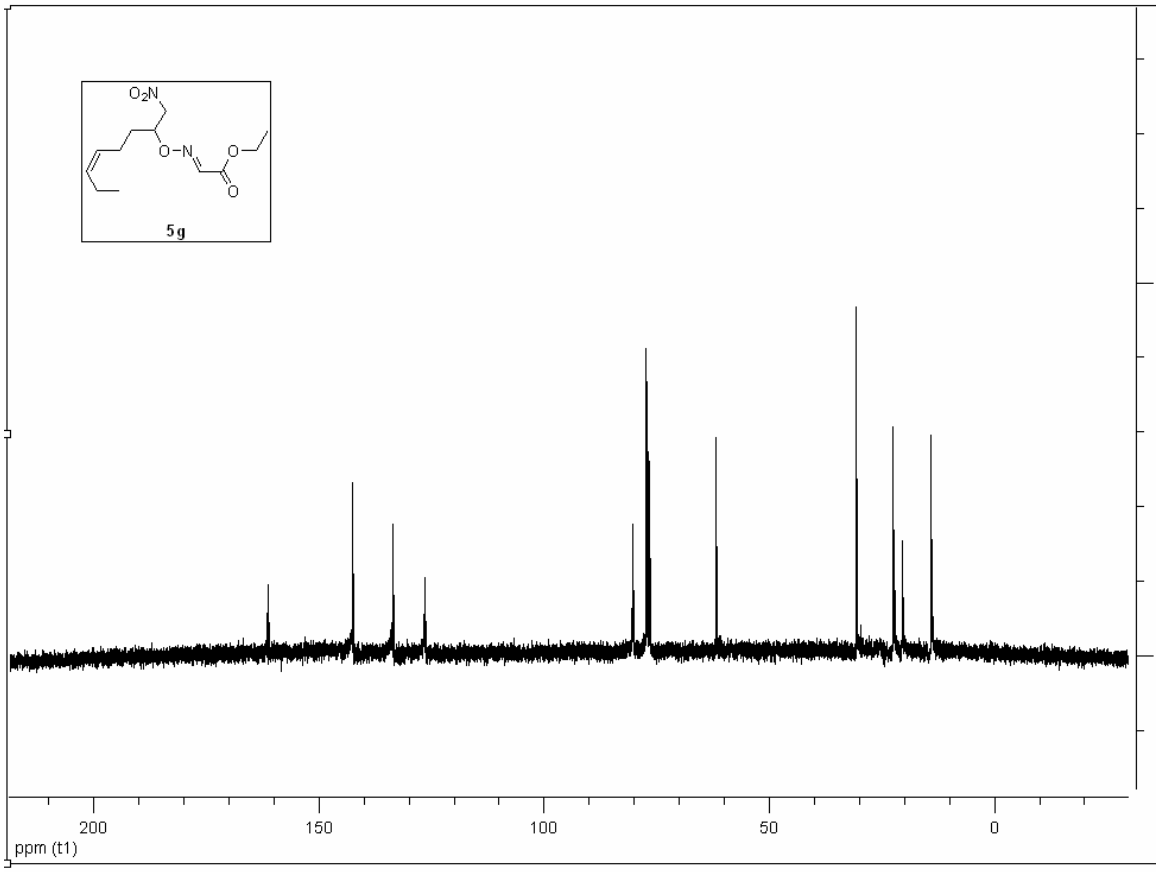
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

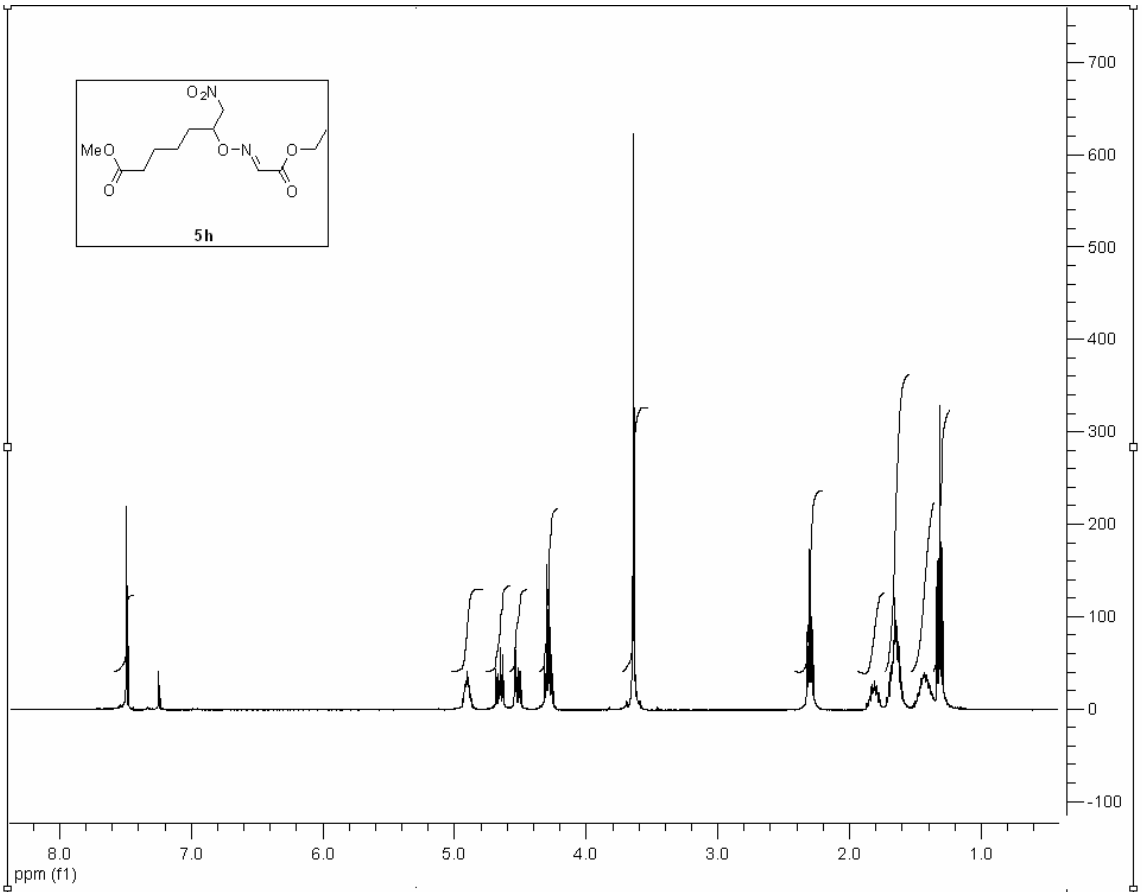

O2N
O
N
O
O
5e
15000
10000
5000
0
200
150
100
50
0
ppm (f1)


O2N
O-N
O
O
5f
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


O2N
O-N
O
O
5f
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (f1)


O2N
O-N
O
O
5g
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


O2N
O-N
O
O
5g
200
150
100
50
0
ppm (t1)


O2N
MeO
O-N
O
O
O
O
5h
700
600
500
400
300
200
100
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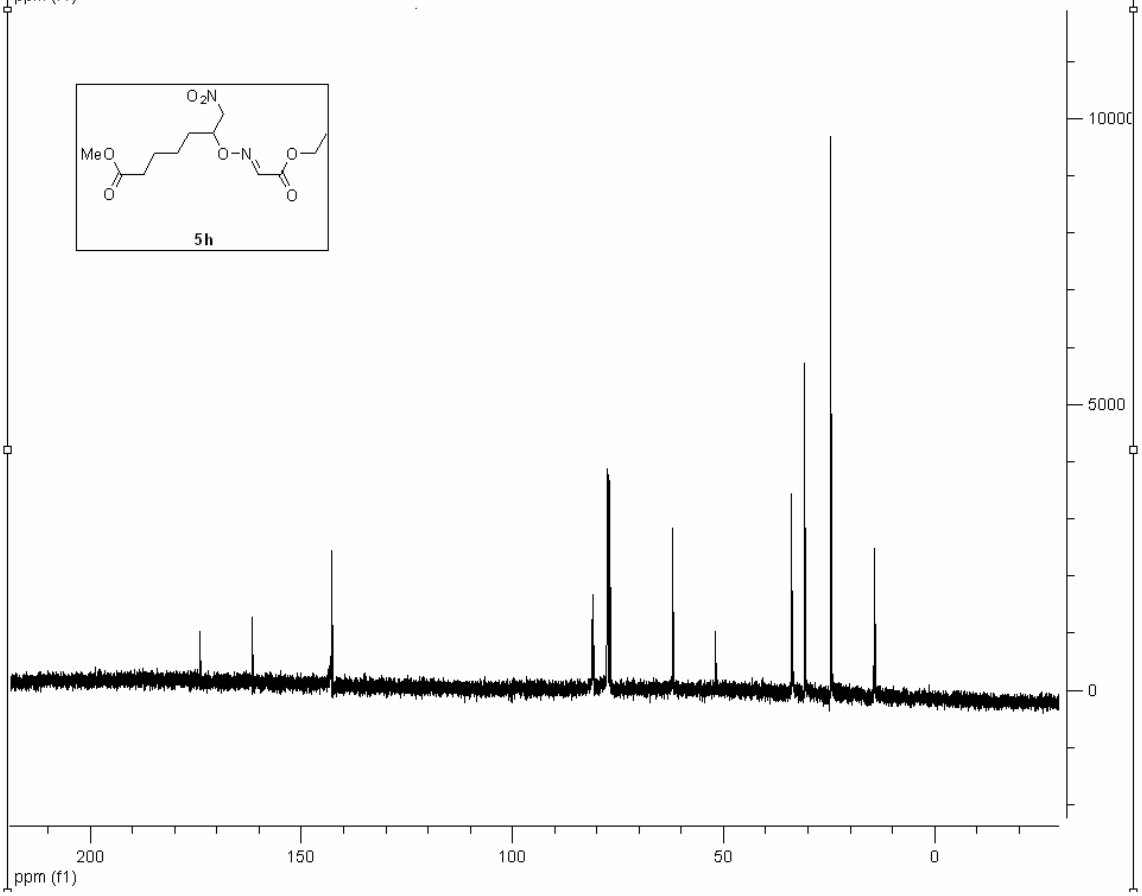
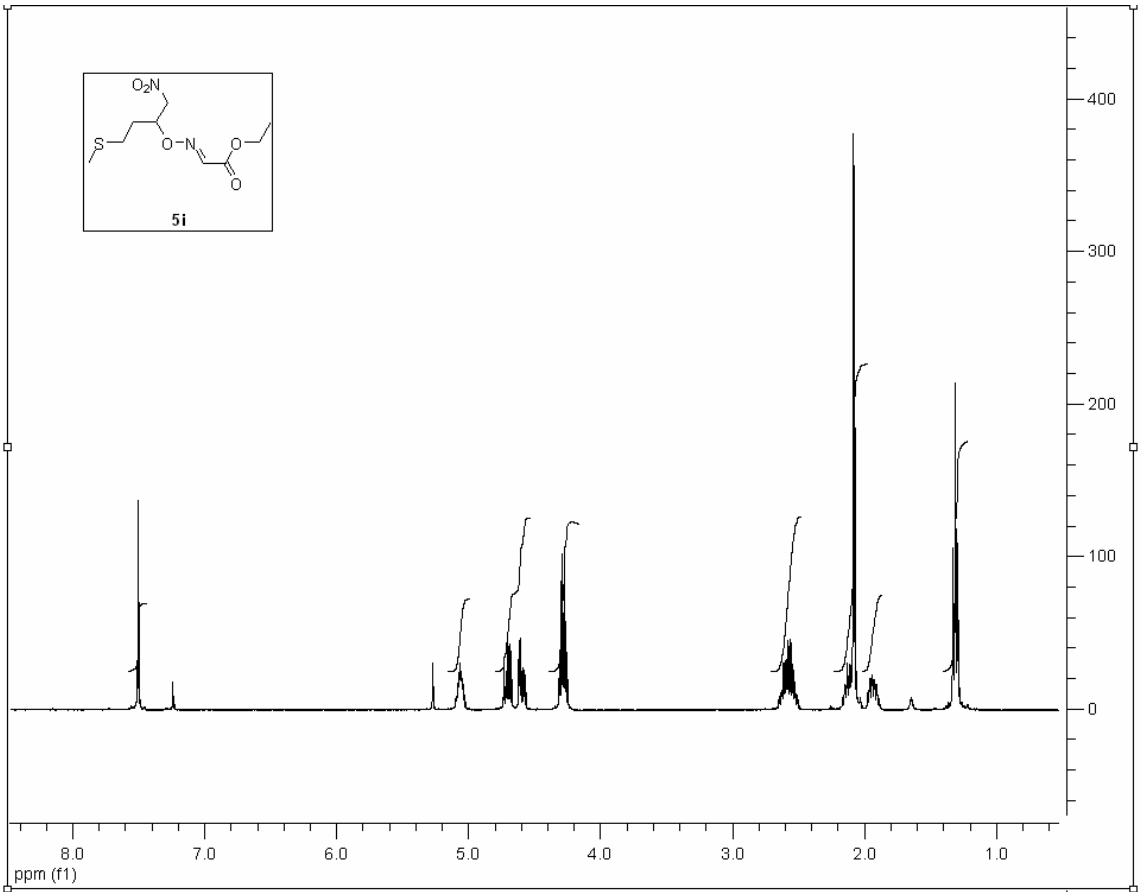
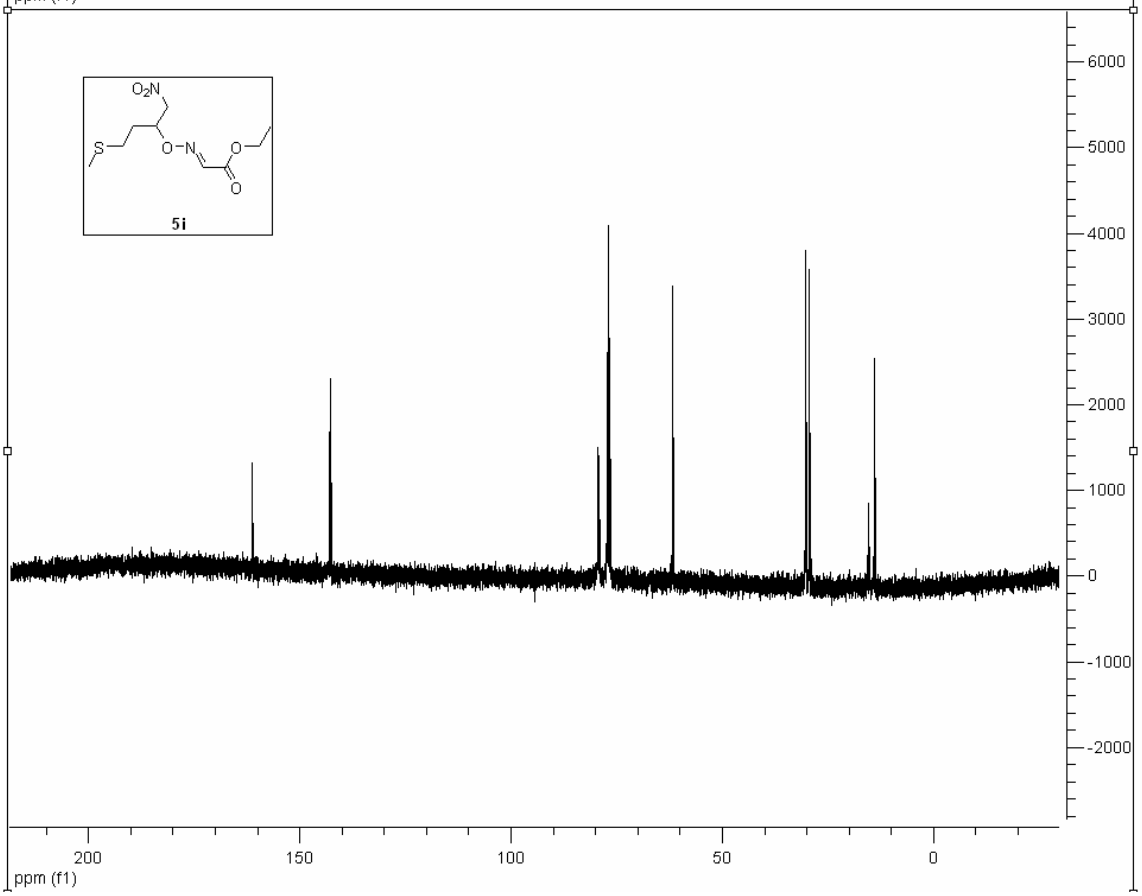
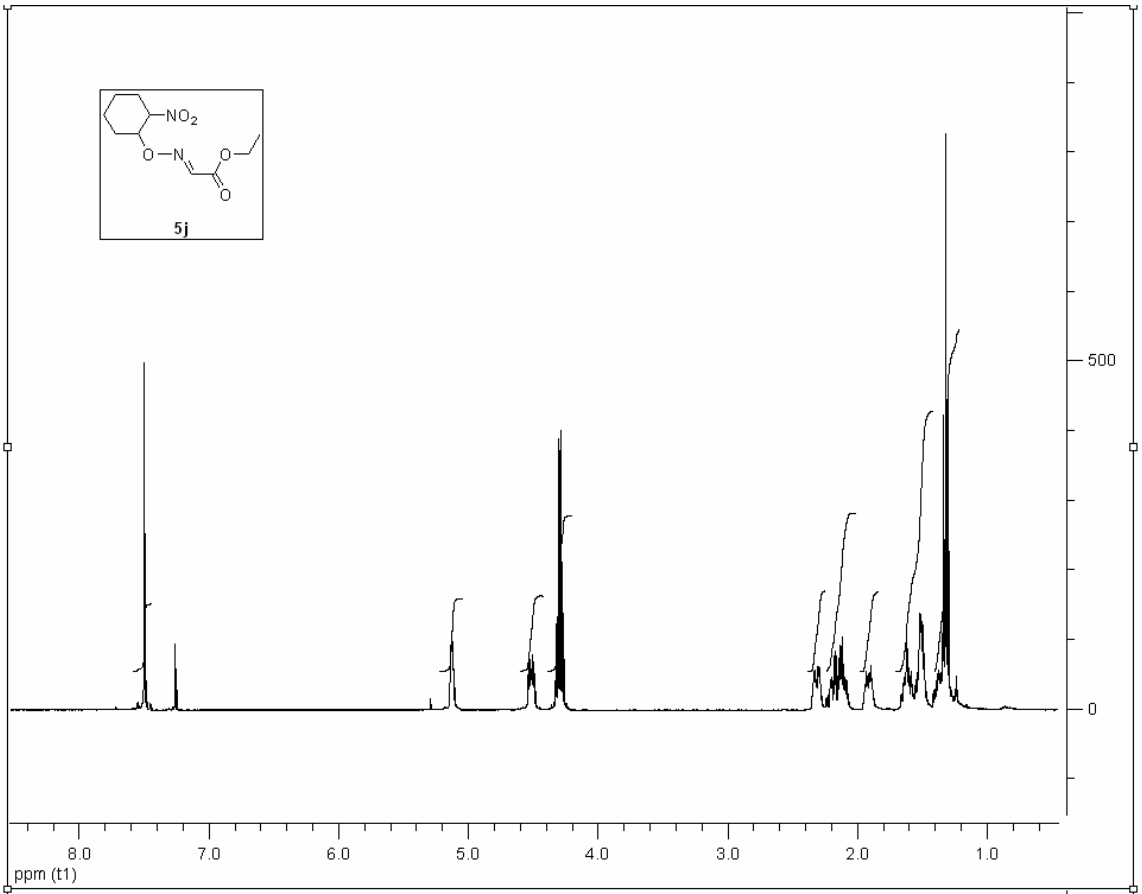
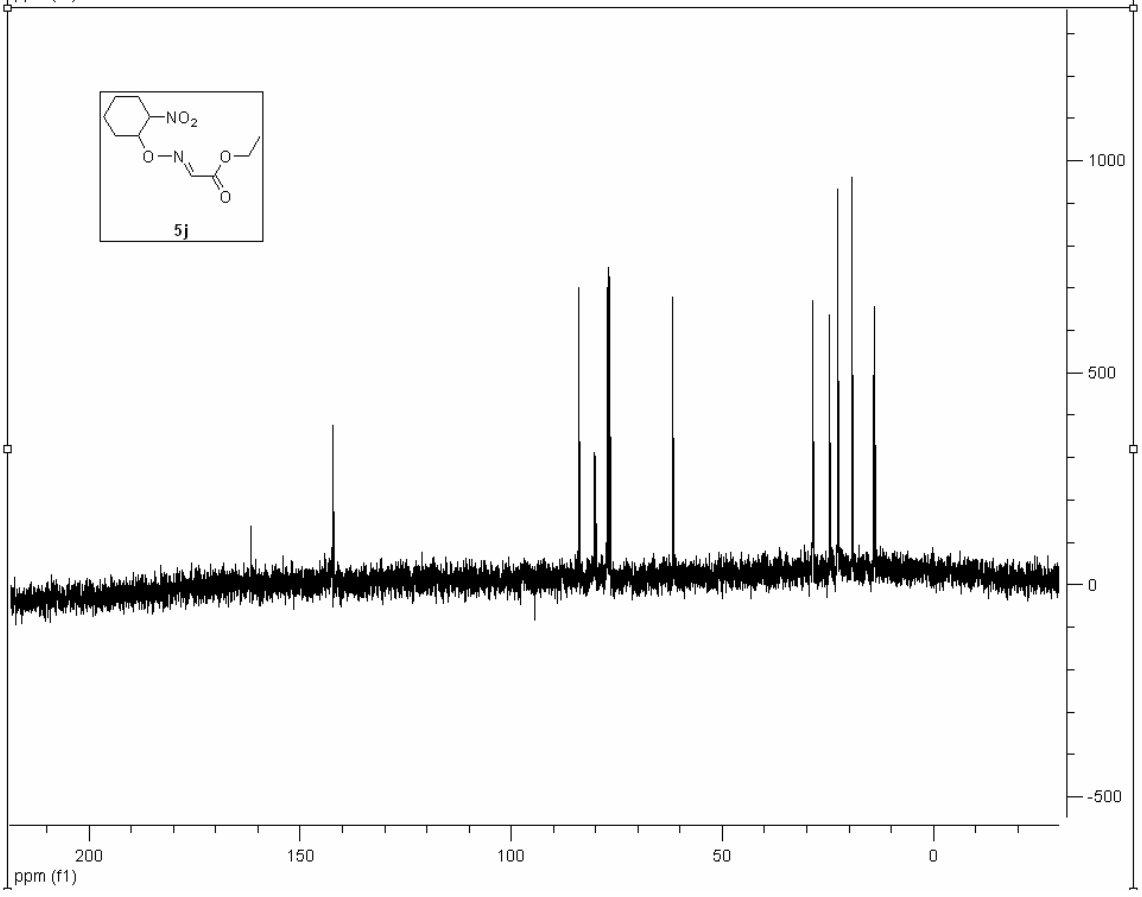
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

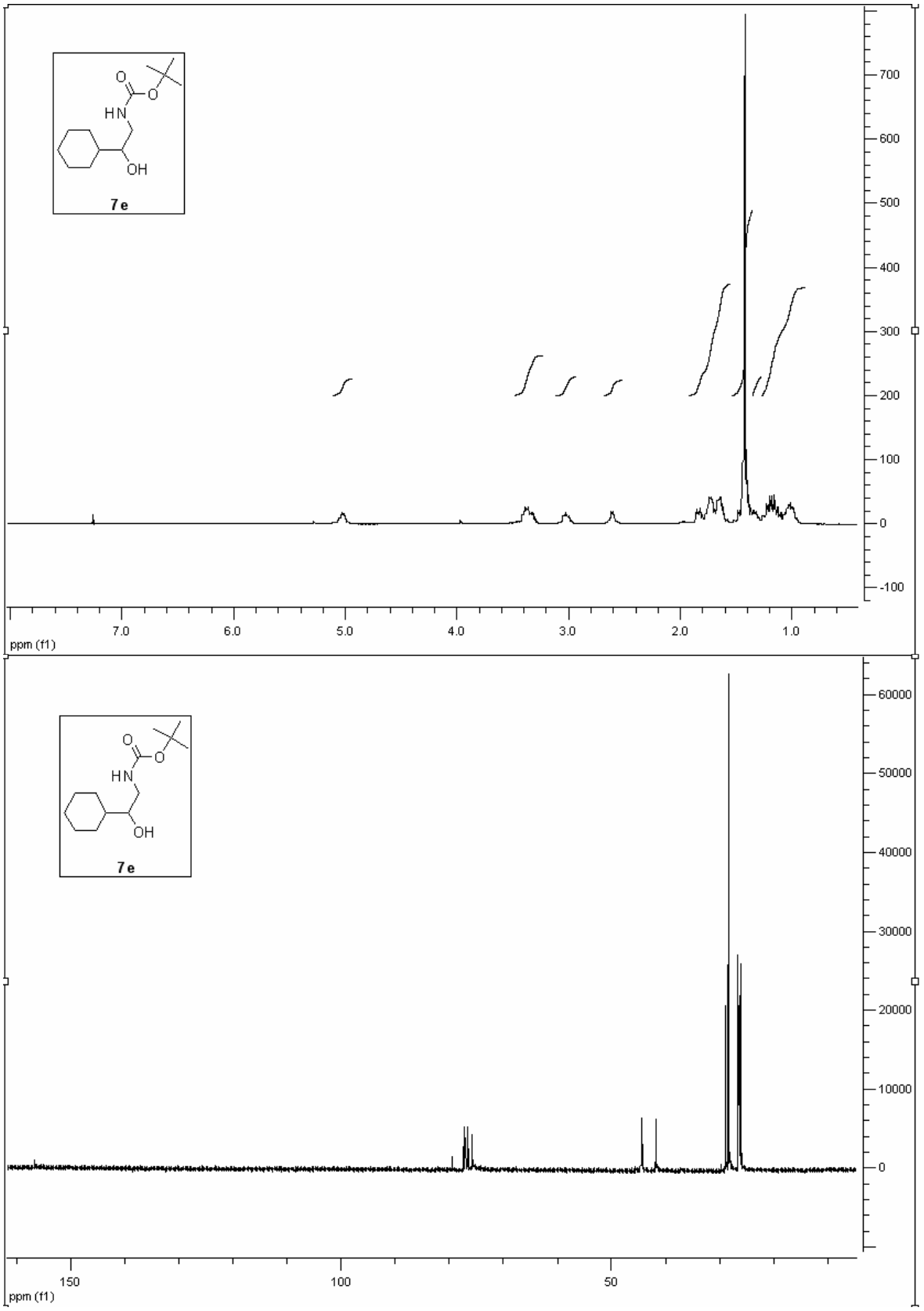

O2N
MeO
O-N
O
O
O
O
5h
10000
5000
0
200
150
100
50
0
ppm (f1)

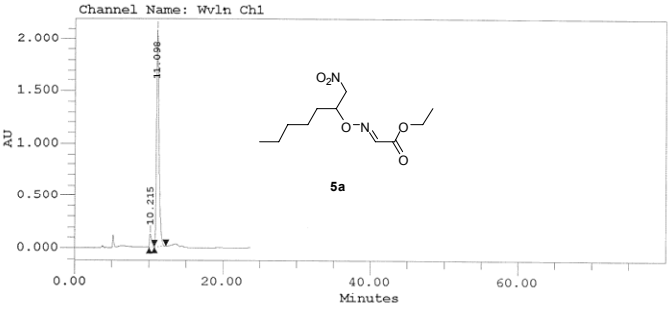

O2N
S
O-N
O
O
5i
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


O2N
S
O-N
O
O
5i
6000
5000
4000
3000
2000
1000
0
-1000
-2000
200
150
100
50
0
ppm (f1)

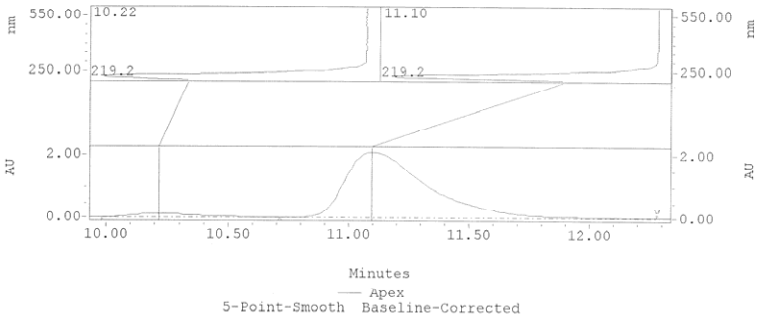

NO2
O
N
O
O
5j
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


NO2
O
N
O
O
5j
1000
500
0
-500
200
150
100
50
0
ppm (f1)


O
O
HN
OH
7e
700
600
500
400
300
200
100
0
-100
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
O
O
HN
OH
7e
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (f1)



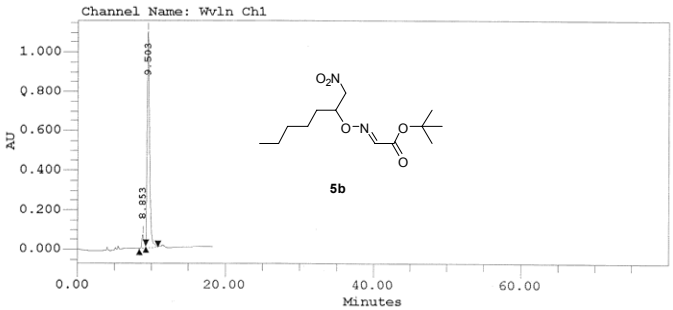
Spectrum Index Plot Peaks 1 to 2



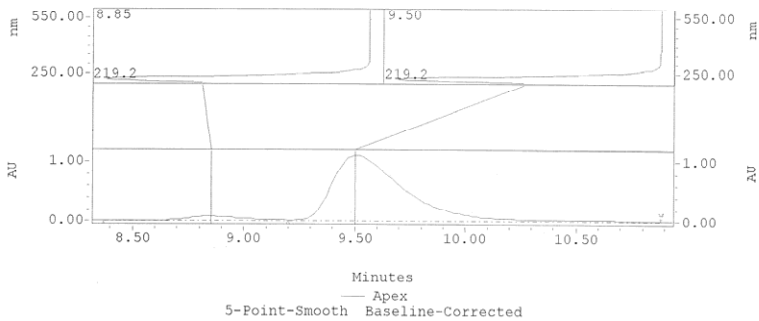
Apex
5-Point-Smooth Baseline-Corrected

Integrationstabel

#	Ret Time (min)	Area (uV*sec)	Int Type	Start Time (min)	End Time (min)	% Area
1	10.215	2233798	MV	9.982	10.715	4.36
2	11.098	48947455	VM	10.715	12.282	95.64



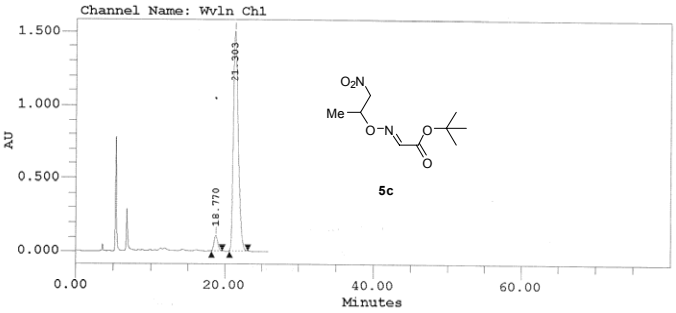
Spectrum Index Plot Peaks 1 to 2



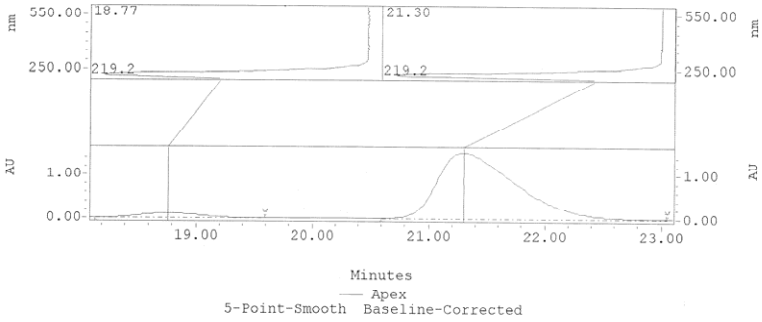
Apex
5-Point-Smooth Baseline-Corrected

Integrationstabel

#	Ret Time (min)	Area (uV*sec)	Int Type	Start Time (min)	End Time (min)	% Area
1	8.853	1307000	MV	8.370	9.203	5.03
2	9.503	24668188	VM	9.203	10.887	94.97

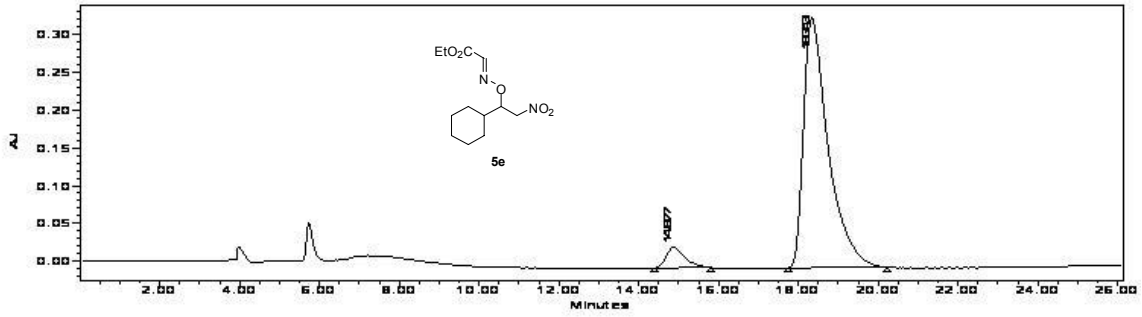


Spectrum Index Plot Peaks 1 to 2

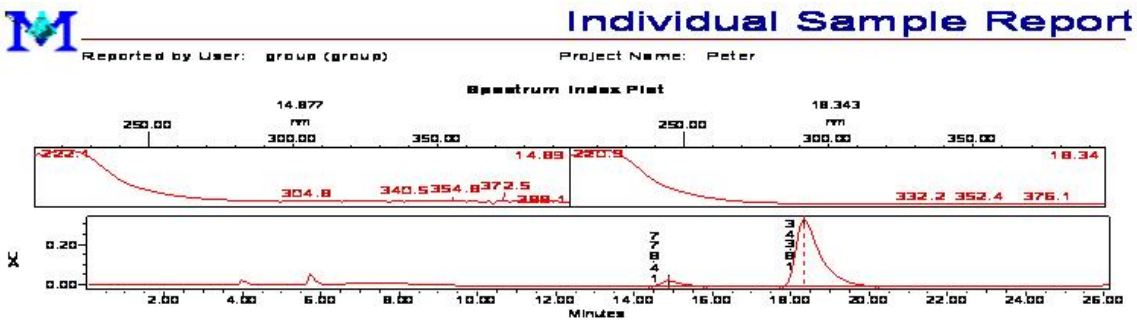


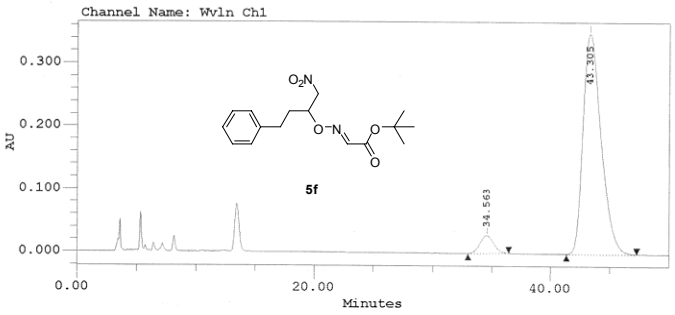
Integrationstabel

#	Ret Time (min)	Area (uV*sec)	Int Type	Start Time (min)	End Time (min)	% Area
1	18.770	3767273	MM	18.153	19.603	5.10
2	21.303	70103880	MM	20.603	23.053	94.90

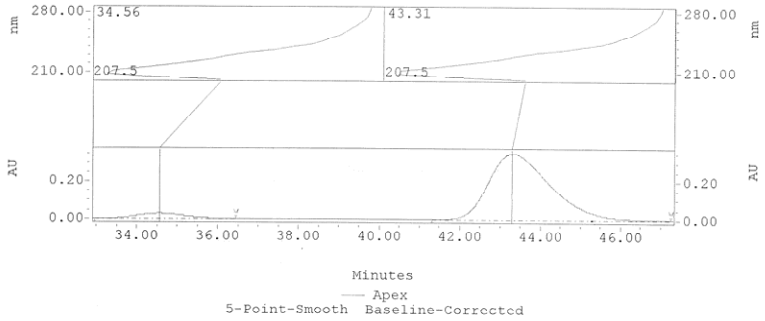


	RT	Area	% Area	Height
1	14.877	858589	5.70	26827
2	18.343	14214954	94.30	330434



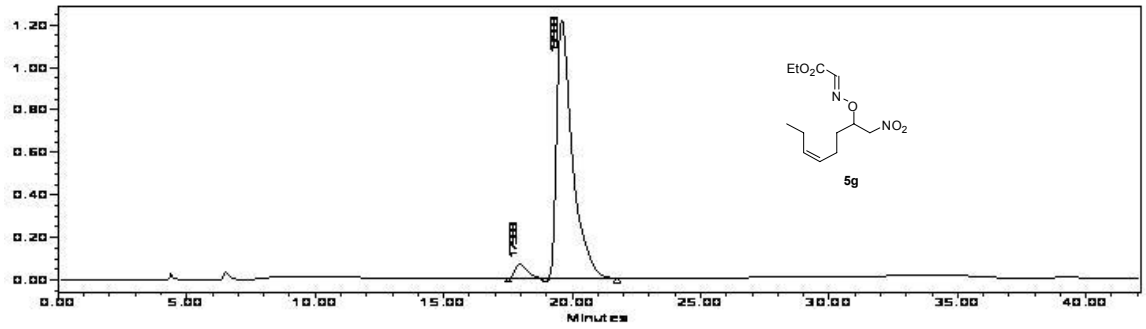


Spectrum Index Plot Peaks 1 to 2

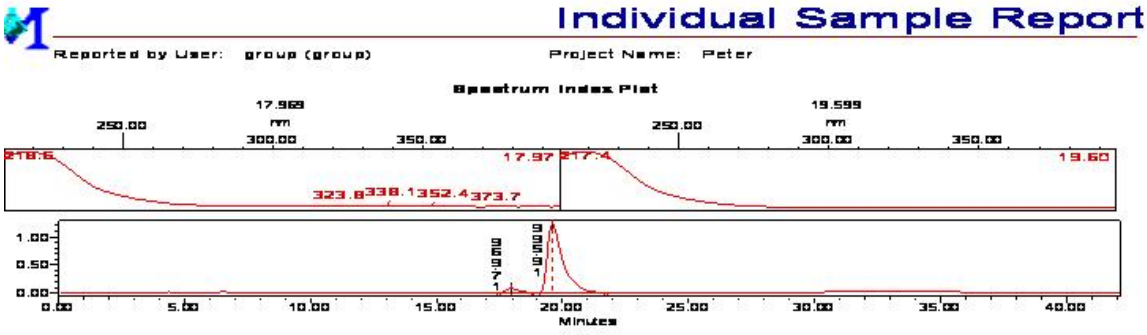


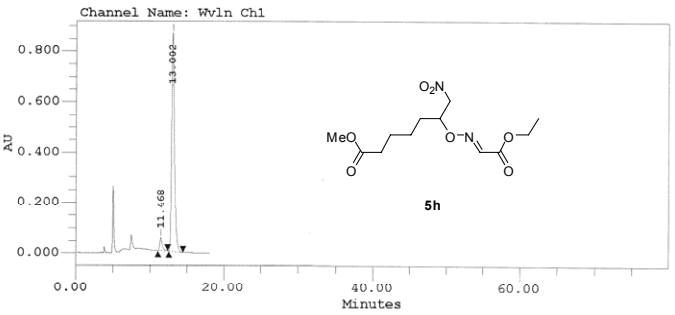
Integrationstabel

#	Ret Time (min)	Area (uV*sec)	Int Type	Start Time (min)	End Time (min)	% Area
1	34.563	2241529	MM	32.963	36.438	5.69
2	43.305	37136662	MM	41.322	47.263	94.31

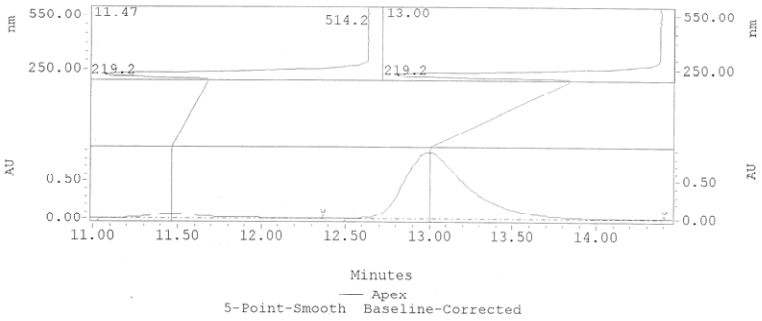


	RT	Area	% Area	Height
1	17.969	2243746	4.15	69051
2	19.599	51855764	95.85	1215589



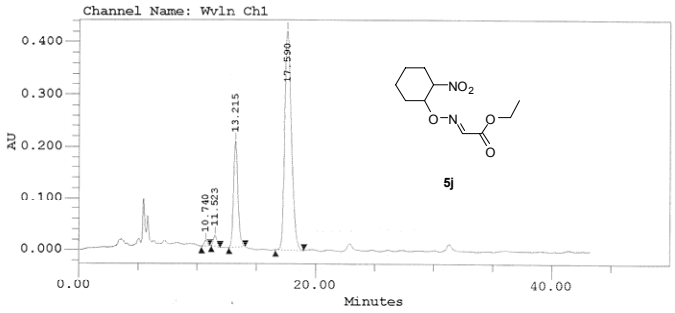


Spectrum Index Plot Peaks 1 to 2

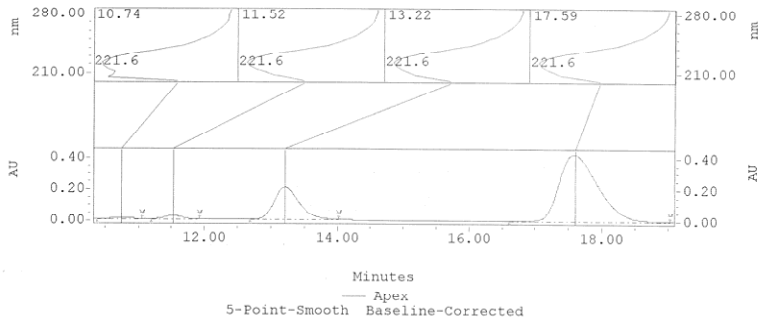


Integrationstabel

#	Ret Time (min)	Area (uV*sec)	Int Type	Start Time (min)	End Time (min)	% Area
1	11.468	1231108	MM	11.035	12.368	5.04
2	13.002	23189672	MM	12.502	14.402	94.96



Spectrum Index Plot Peaks 1 to 4



Integrationstabel

#	Ret Time (min)	Area (uV*sec)	Int Type	Start Time (min)	End Time (min)	% Area
1	10.740	180479	MM	10.382	11.065	0.78
2	11.523	443394	MM	11.207	11.932	1.92
3	13.215	5396809	MM	12.690	14.032	23.33
4	17.590	17109679	MM	16.607	19.040	73.97