Supplementary Material (ESI) for Organic & Biomolecular Chemistry

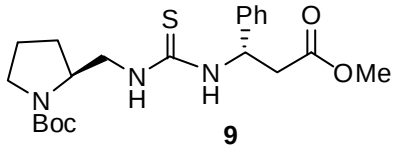
Novel pyrrolidine-thiohydantoins/thioxotetrahydeopyrimidinones as highly effective catalysts for the asymmetric Michael addition

*Christoforos G. Kokotos, Dimitris Limnios, Despoina Triggidou, Maria Trifonidou and George Kokotos**

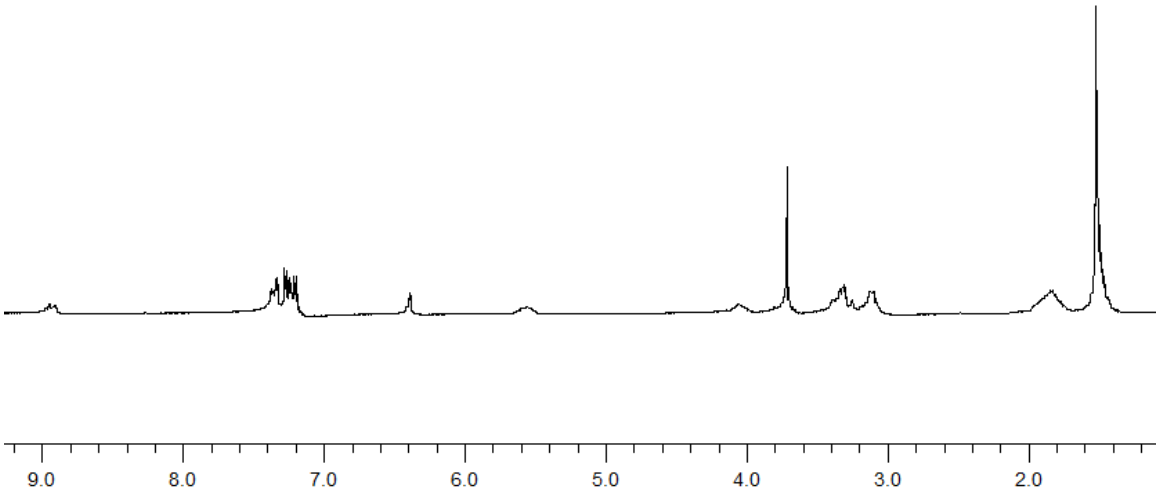
Laboratory of Organic Chemistry, Department of Chemistry, University of Athens, Athens 15771, Greece

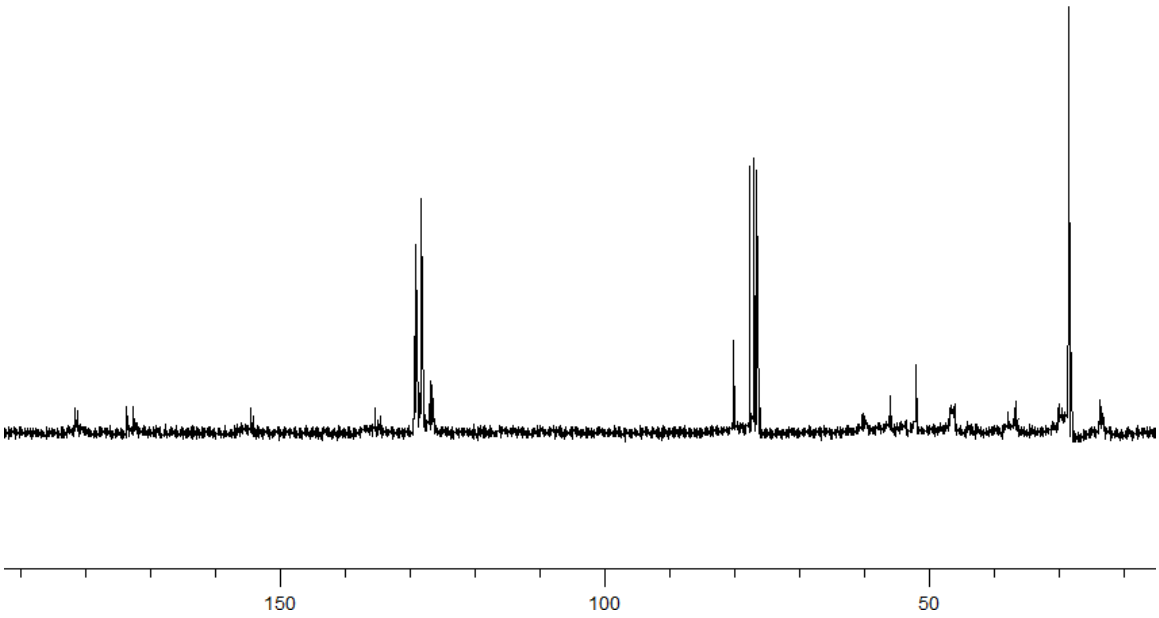
Supporting Information

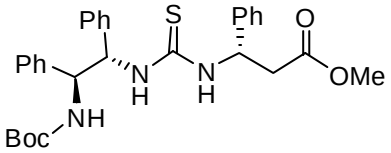
Table of Contents	**Page**
^{1}H and ^{13}C NMR spectra	**S2**
HPLC data	**S25**
Structures of enamine intermediates	**S35**



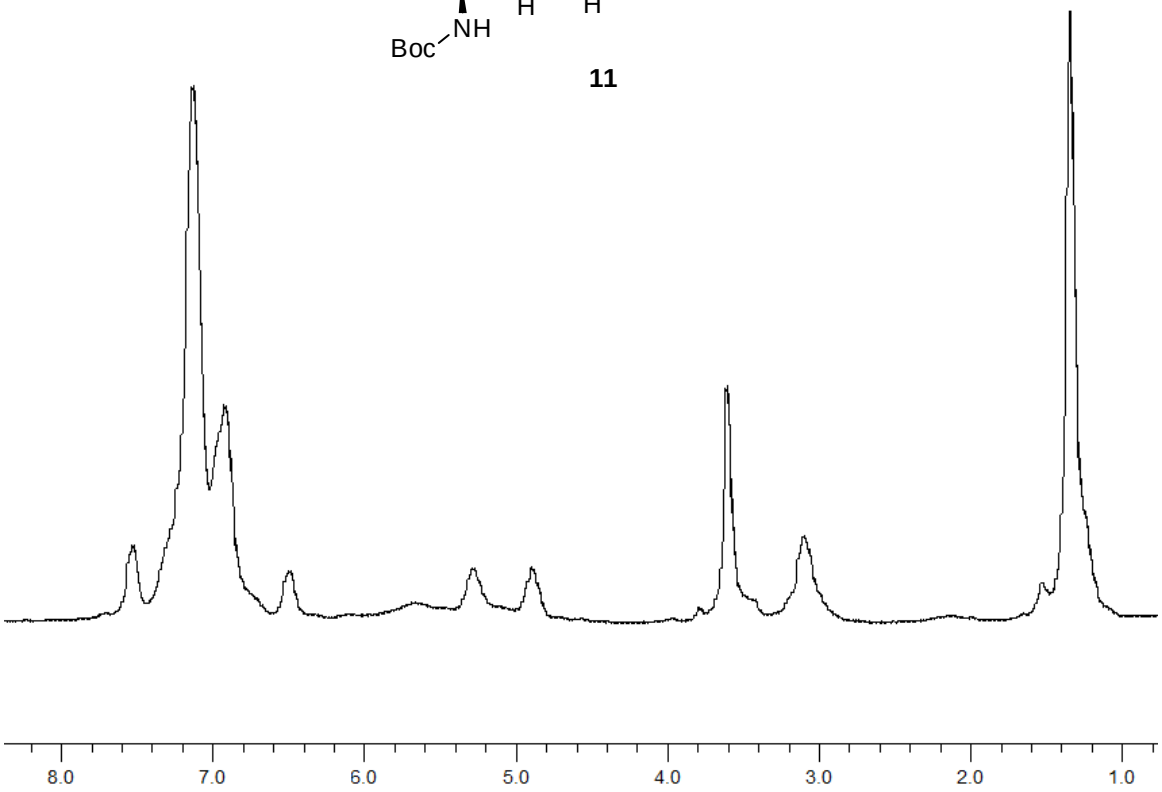
9

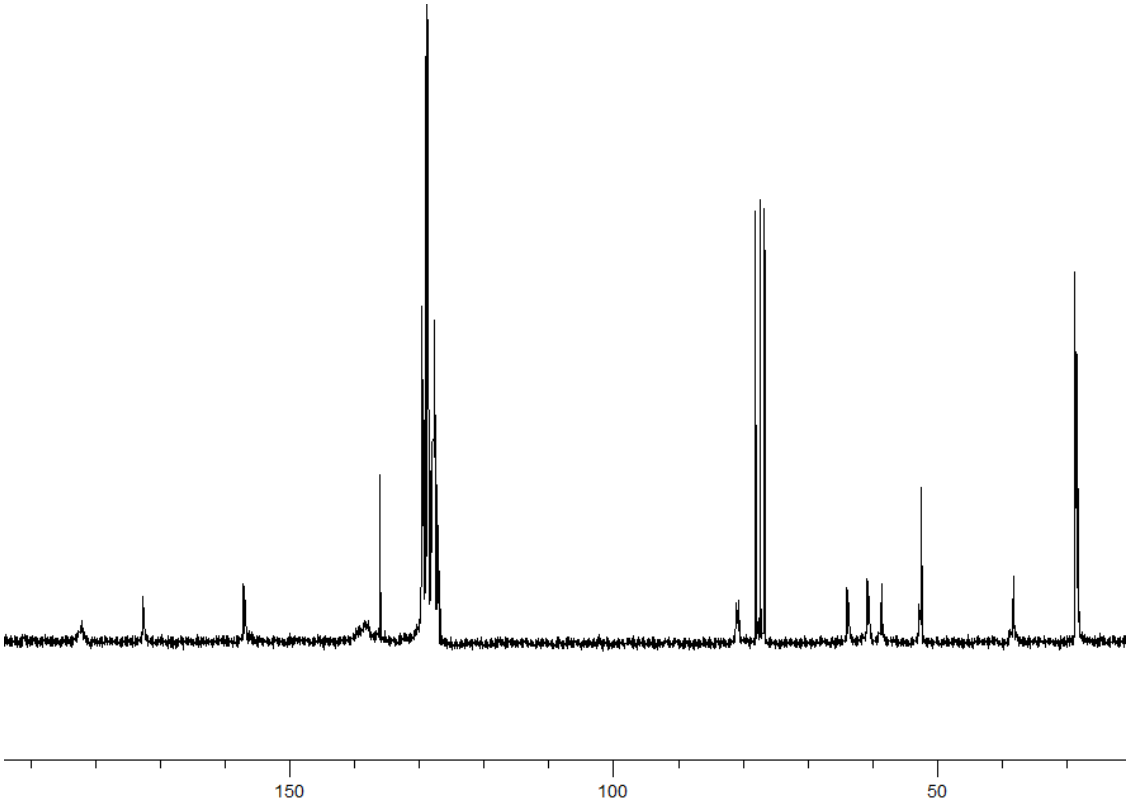


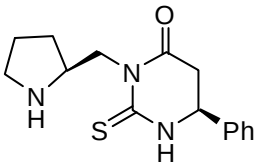




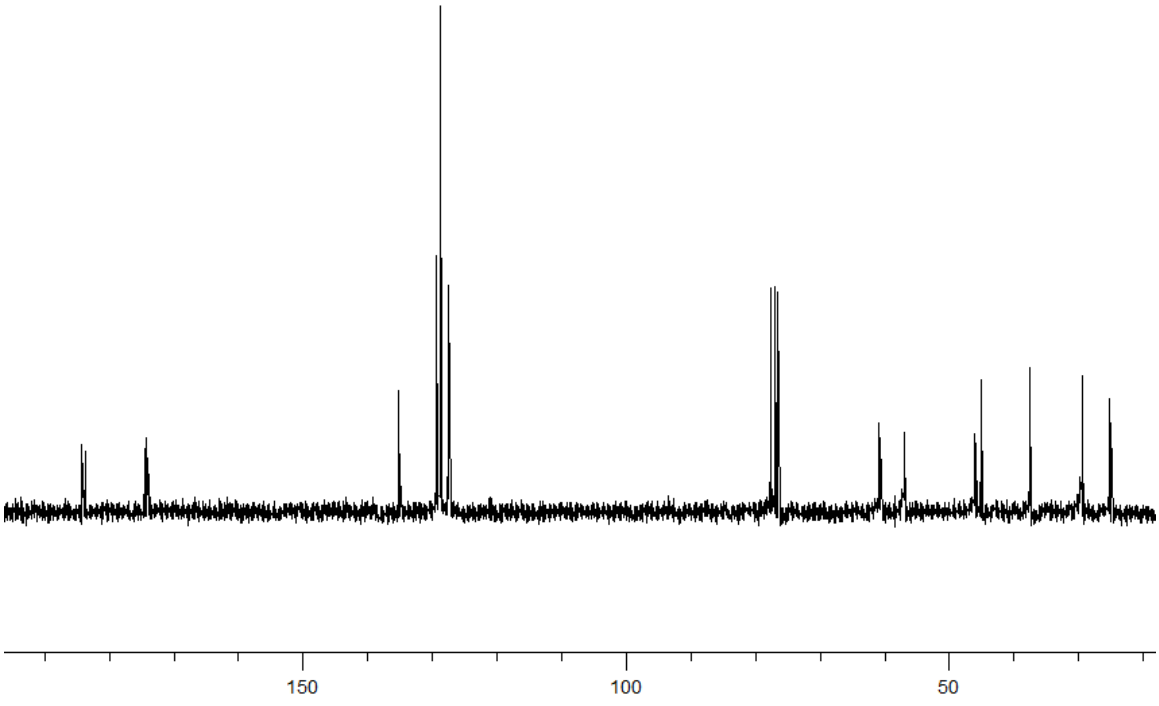
11

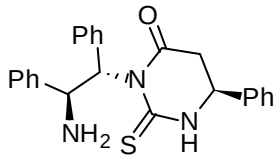




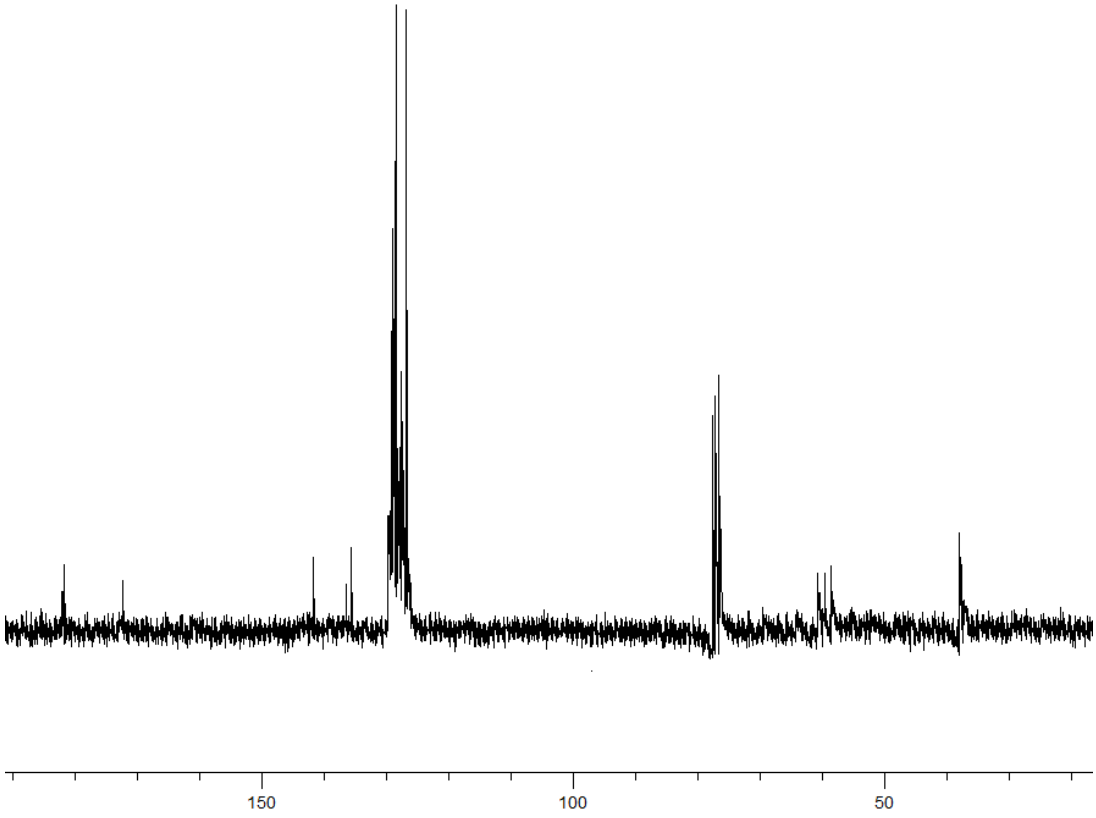


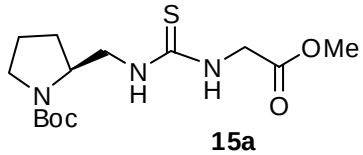
12



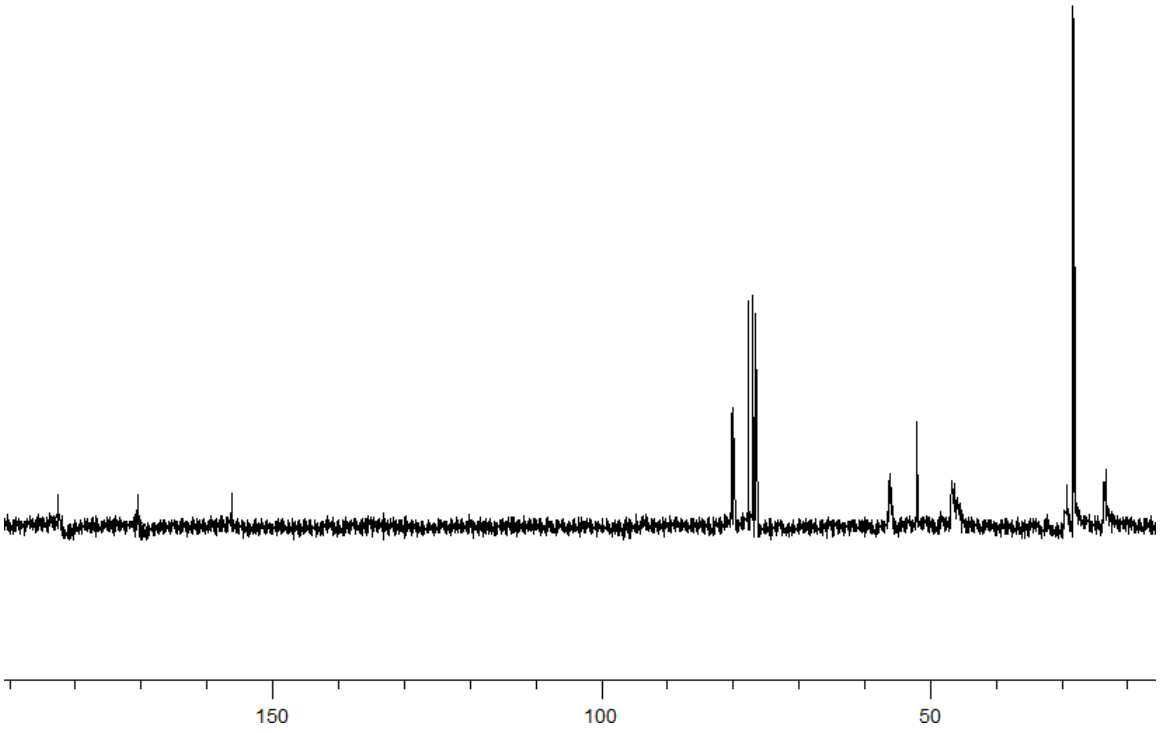


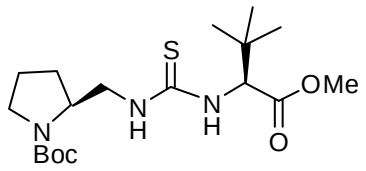
13



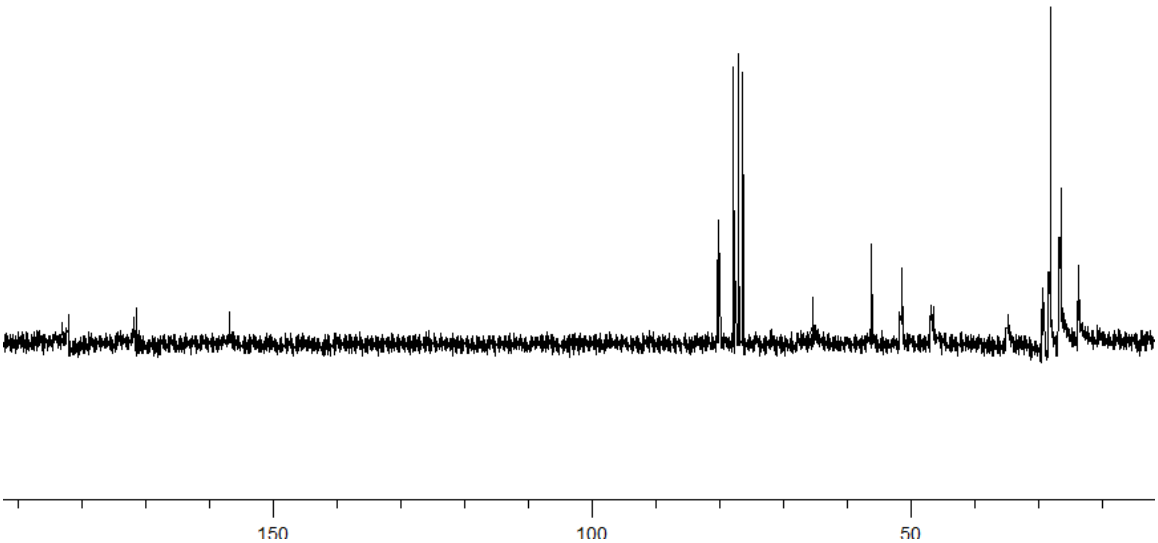


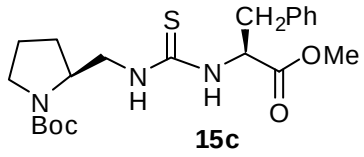
15a



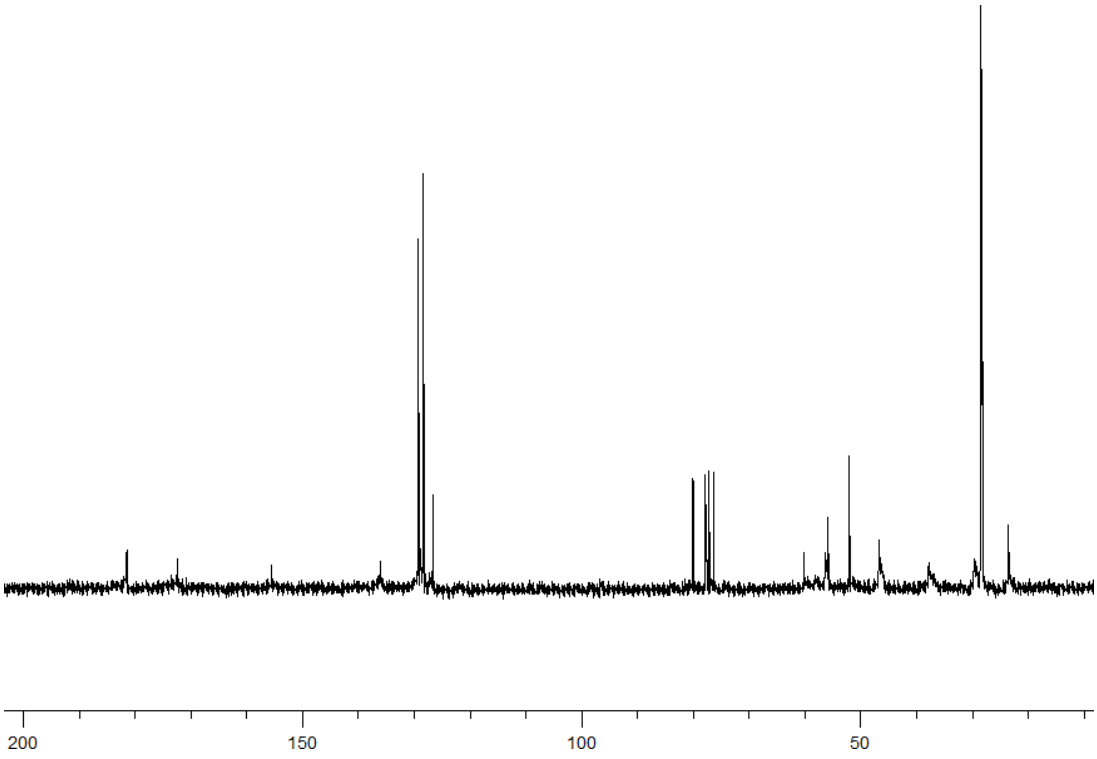


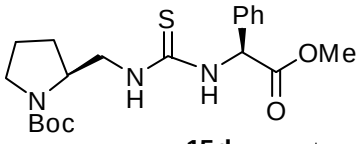
15b



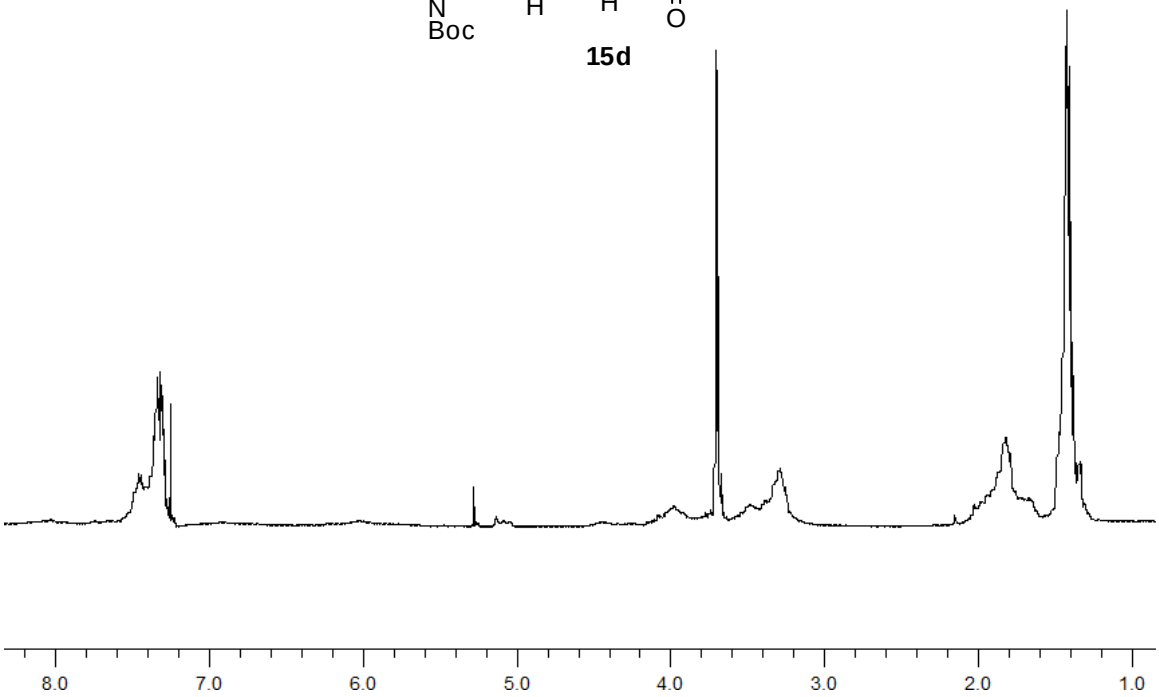


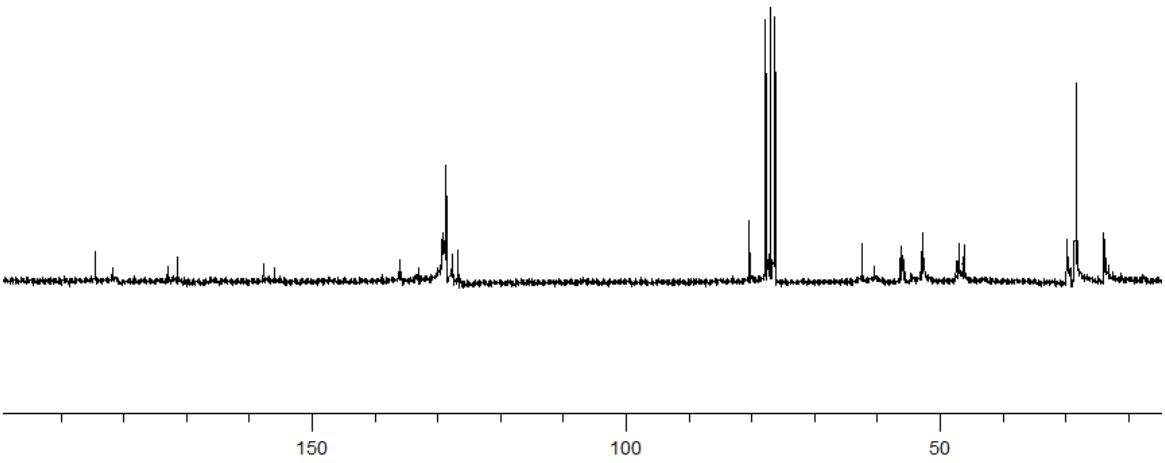
15c

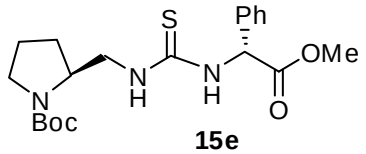




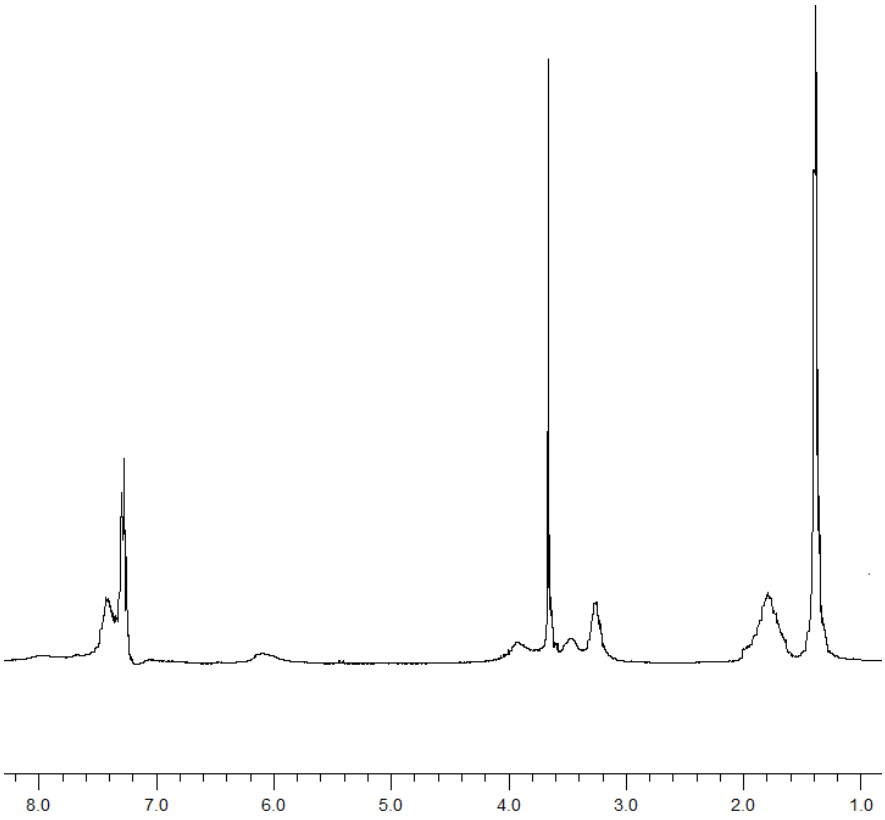
15d

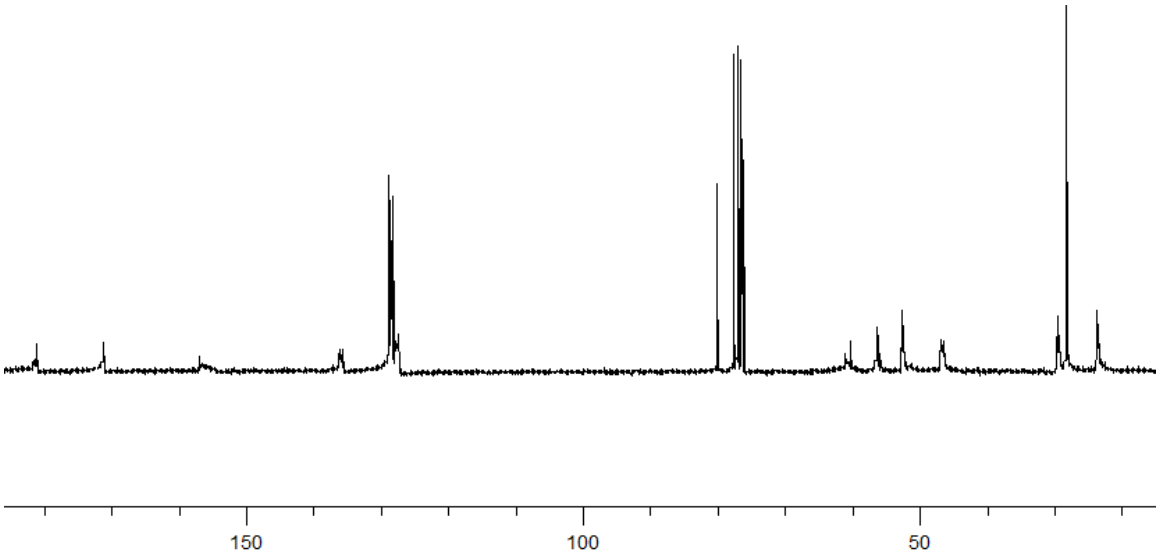


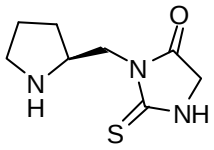




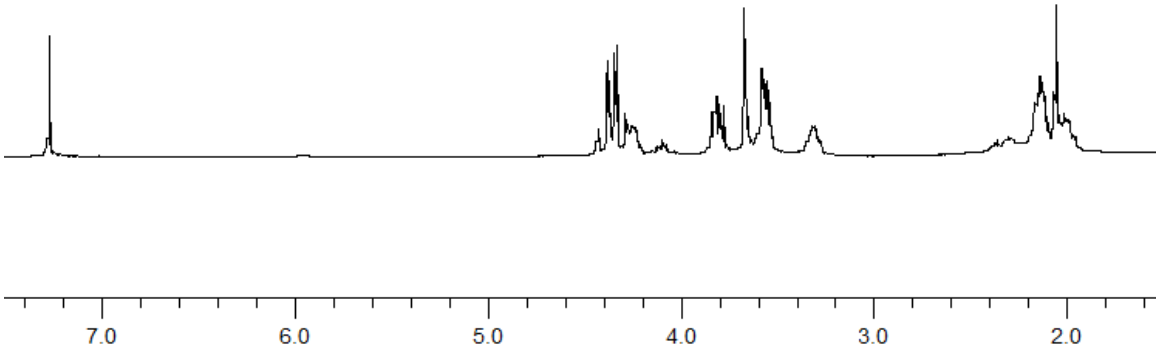
15e

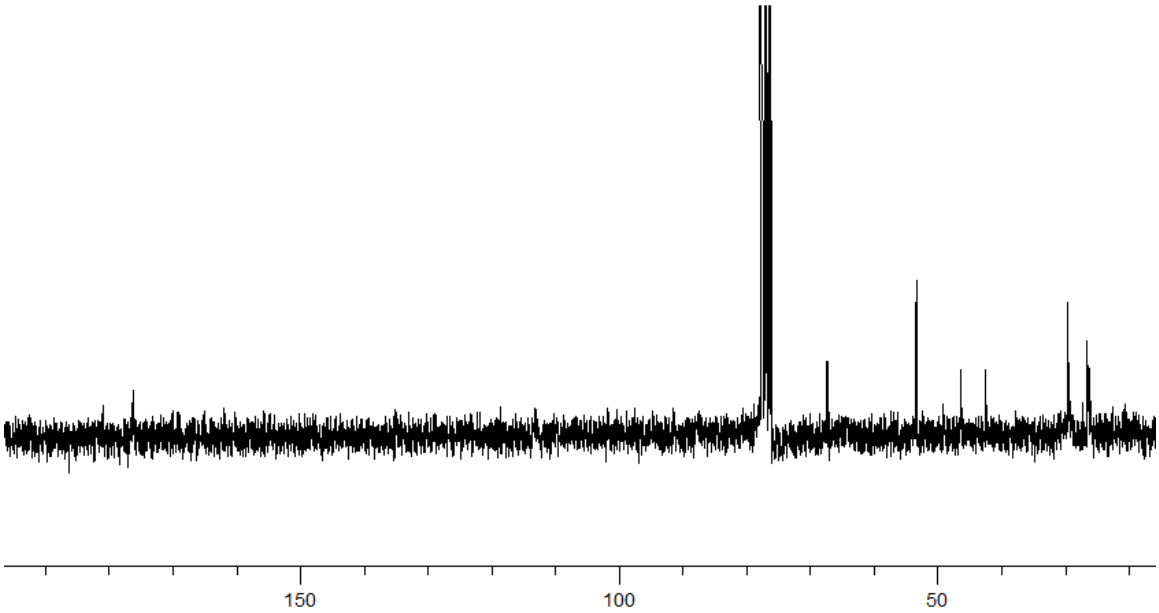


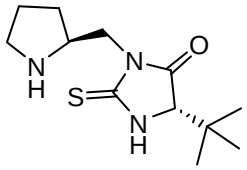




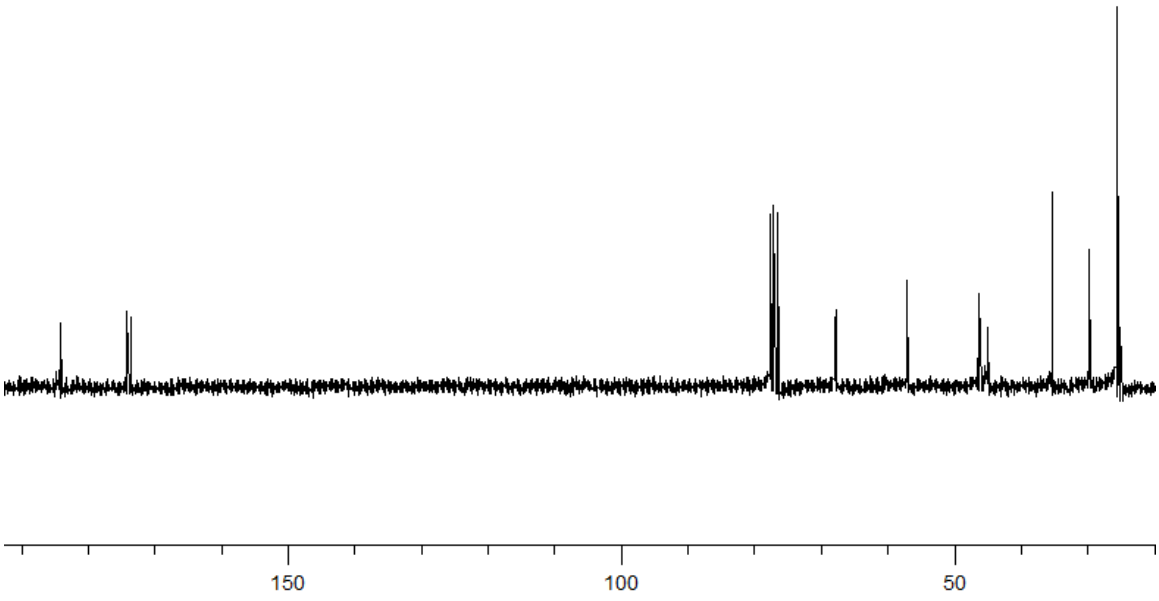
16a

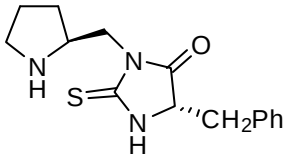




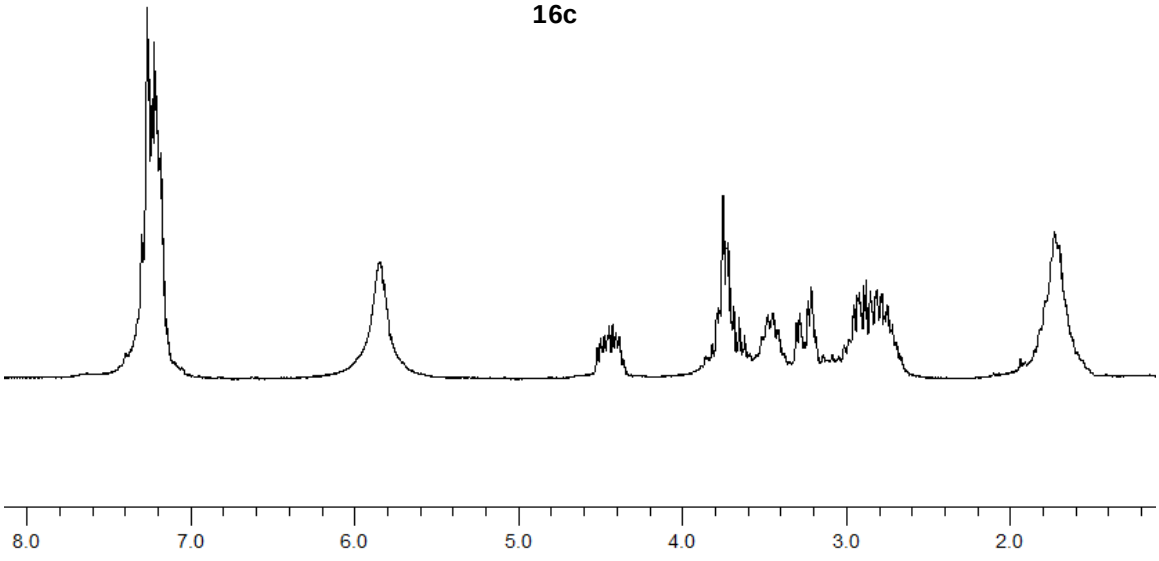


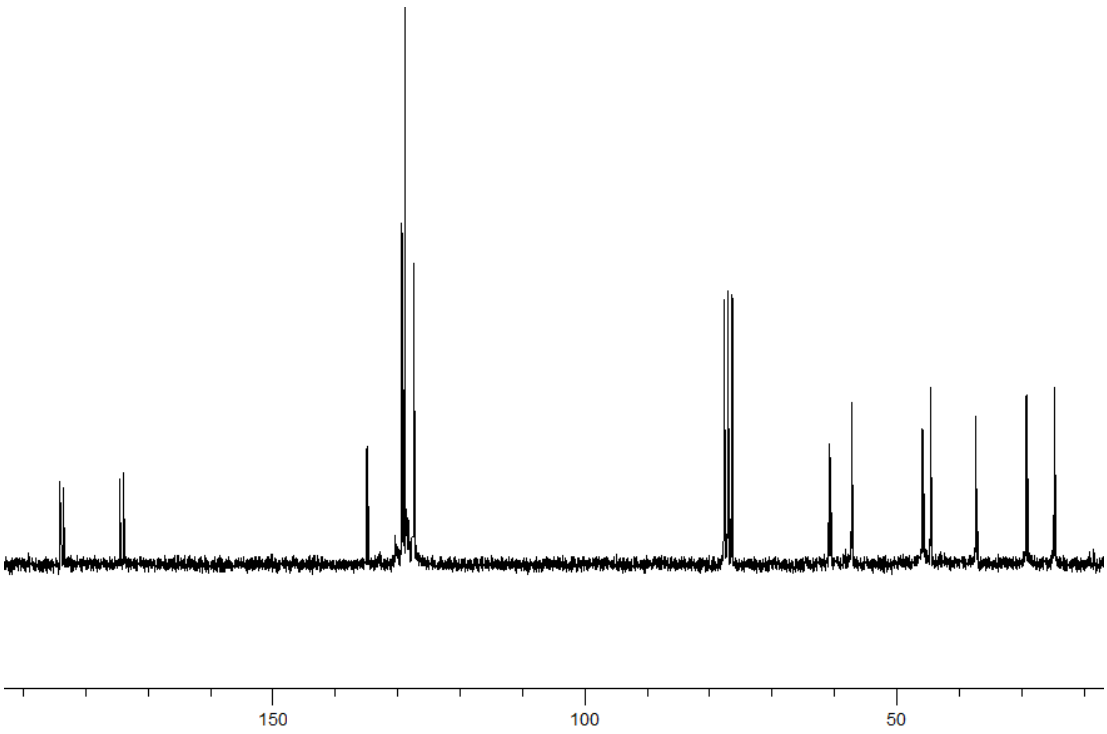
16b

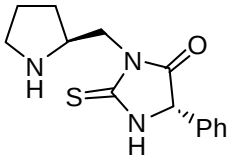




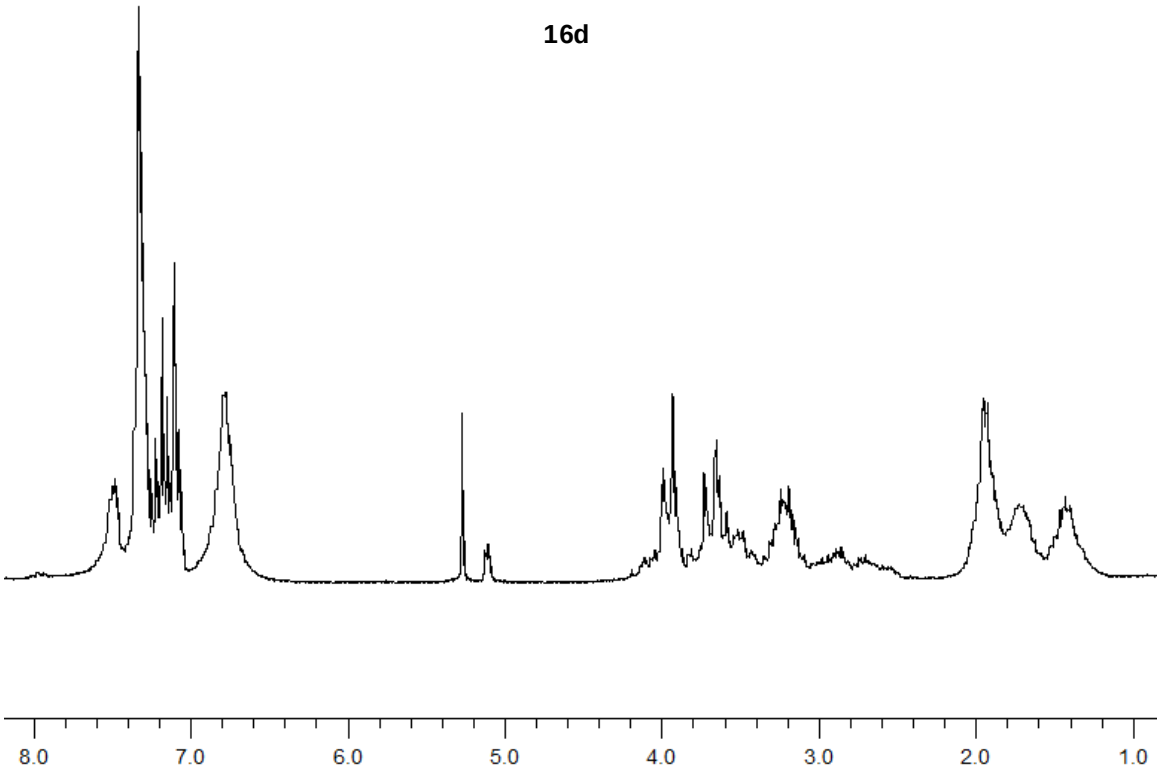
16c

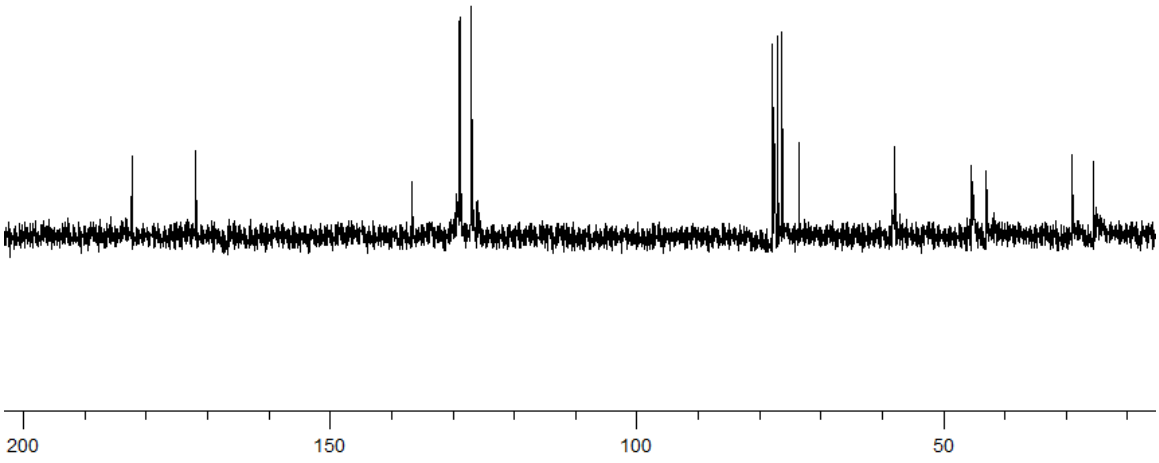


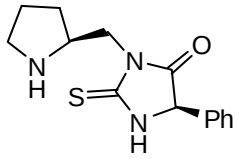




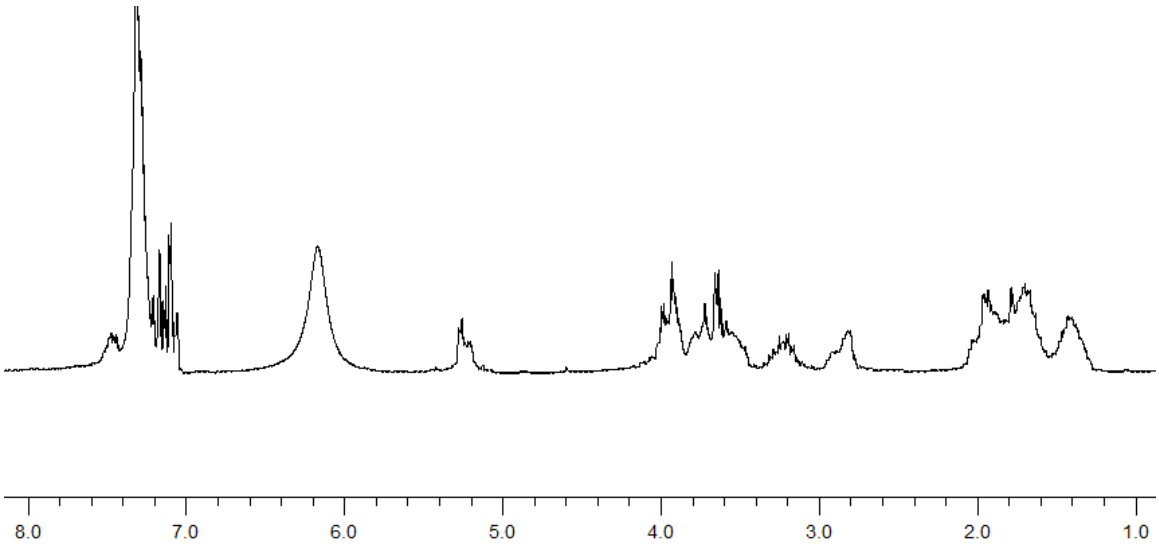
16d

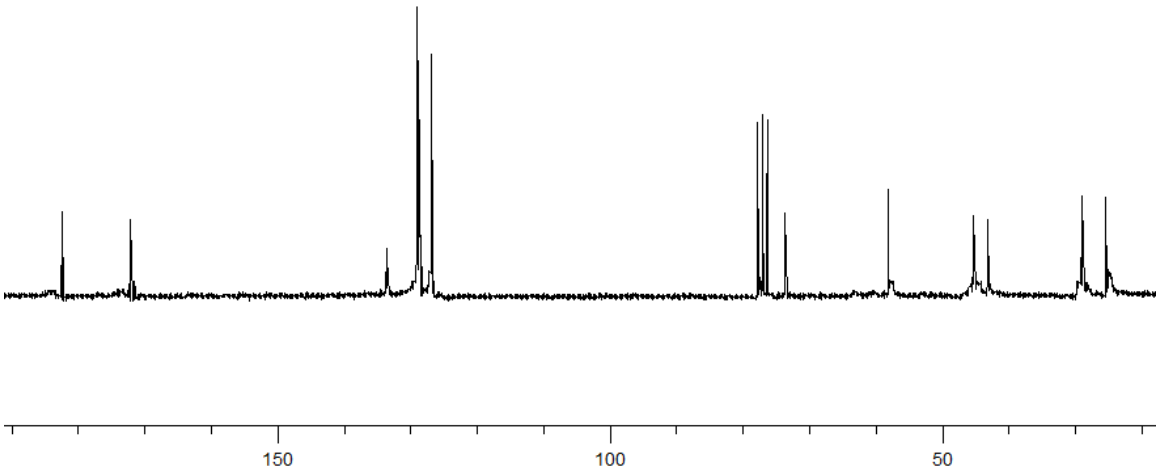


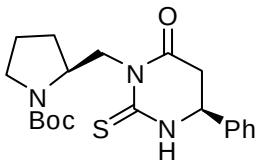




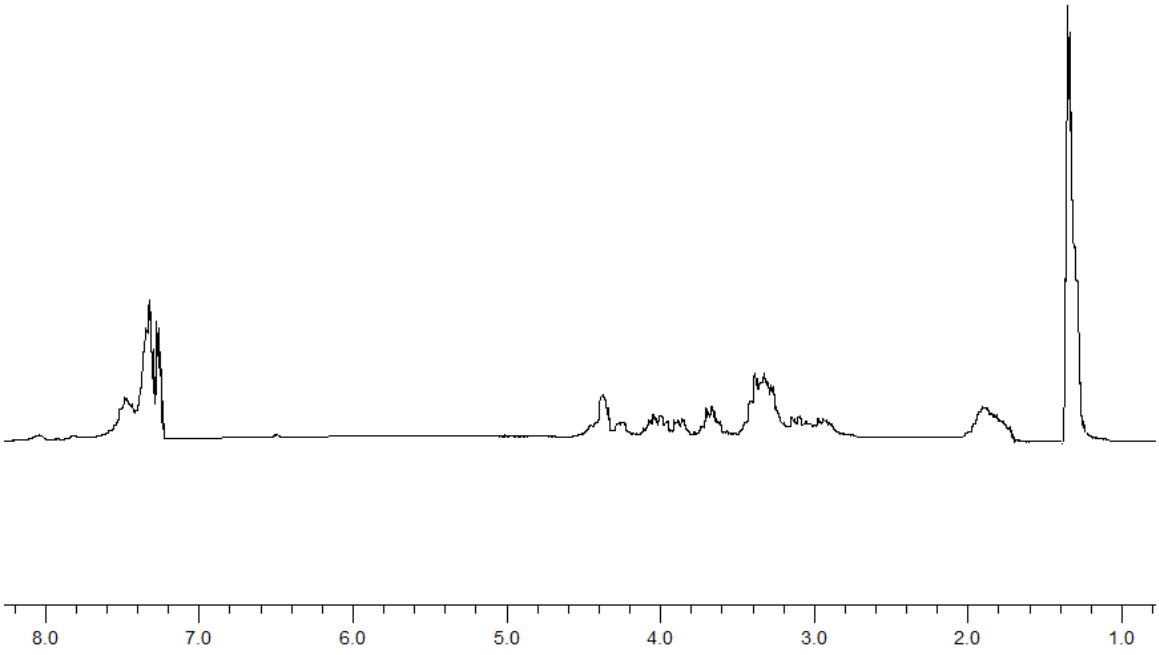
16e

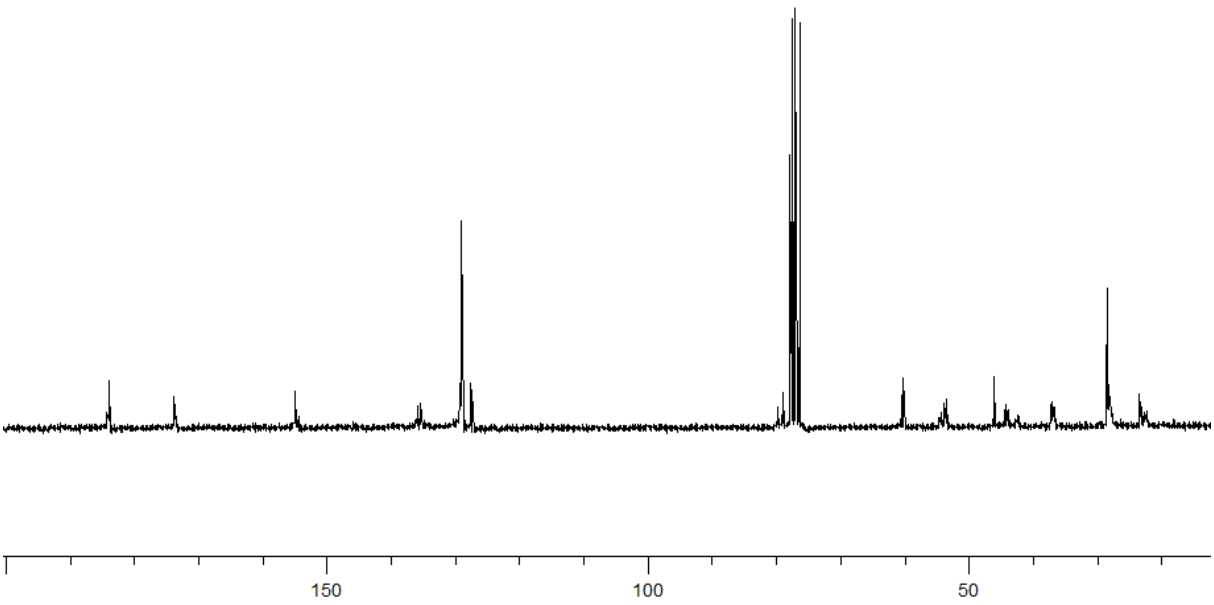


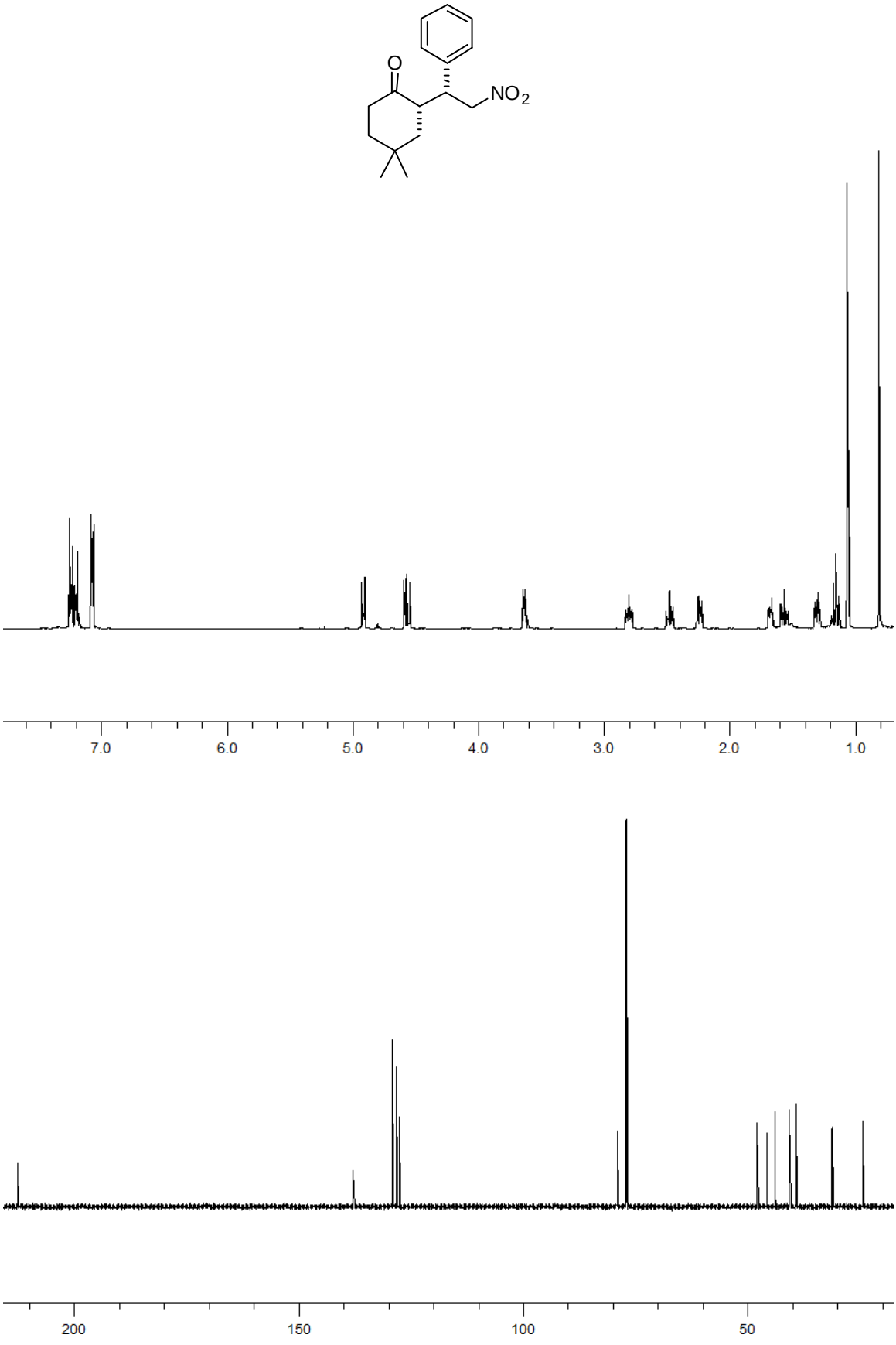


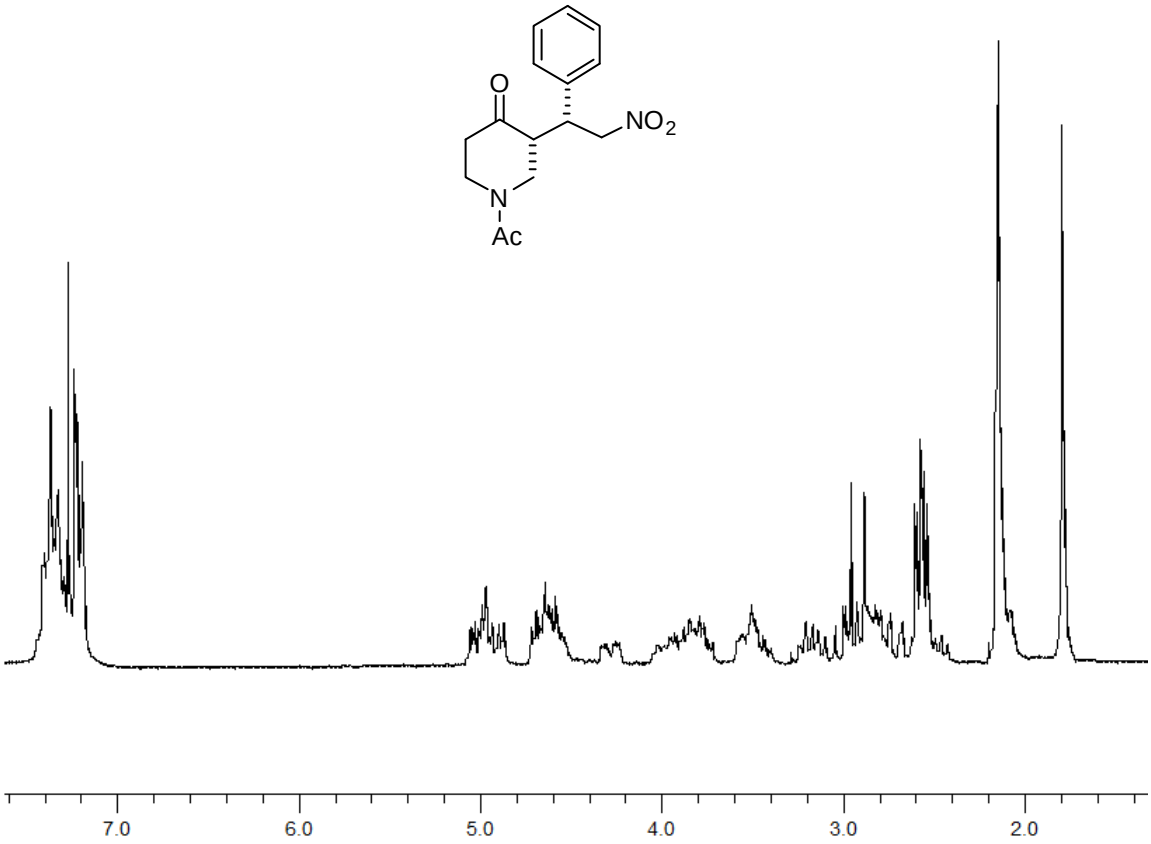


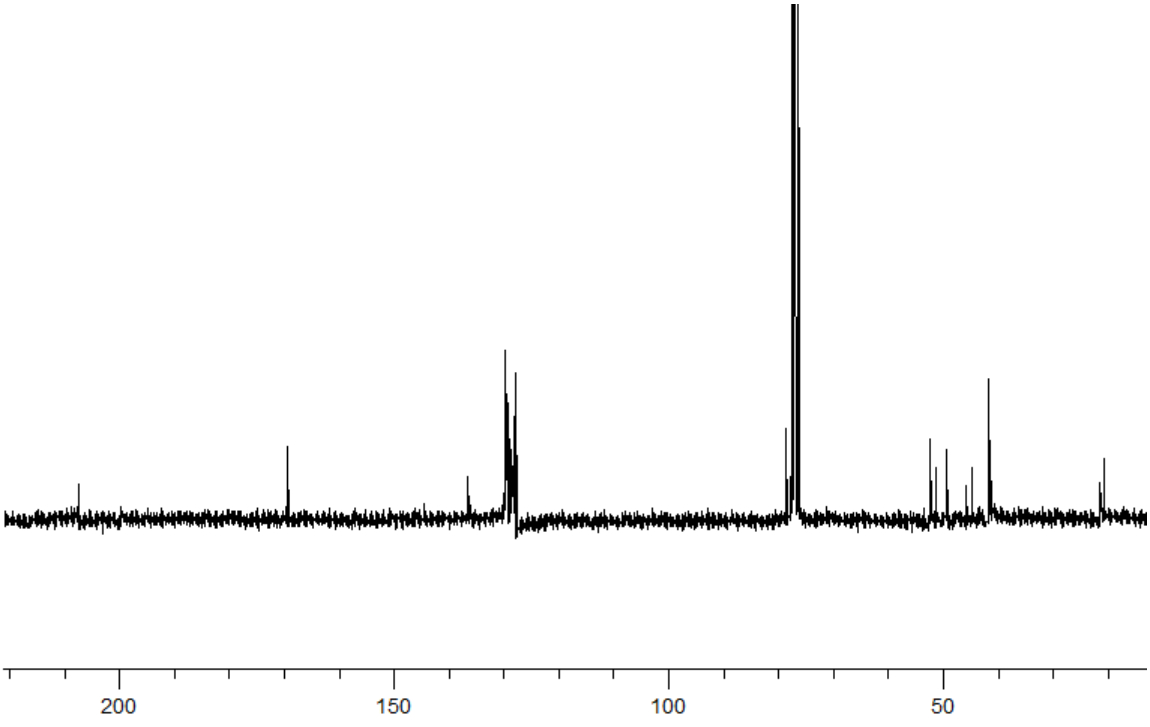
17

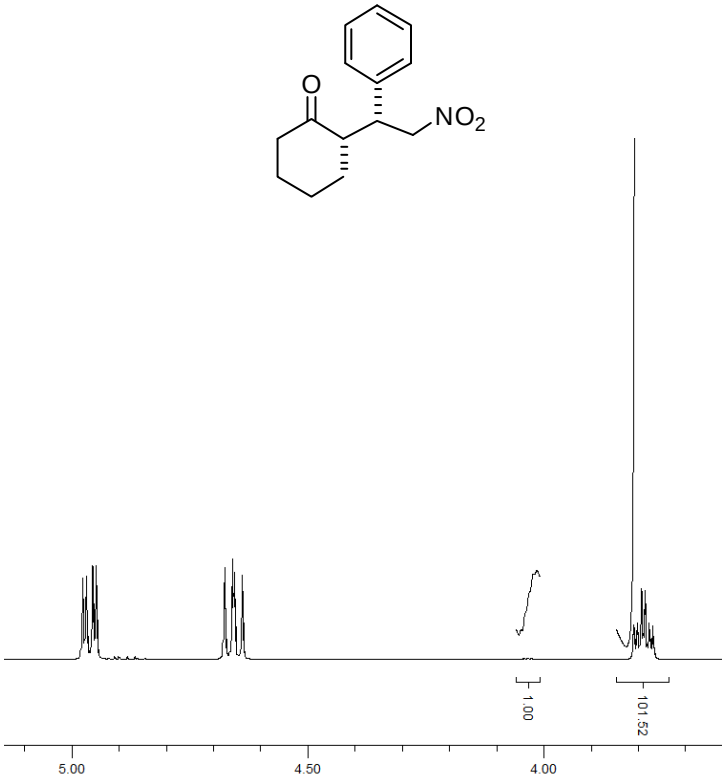


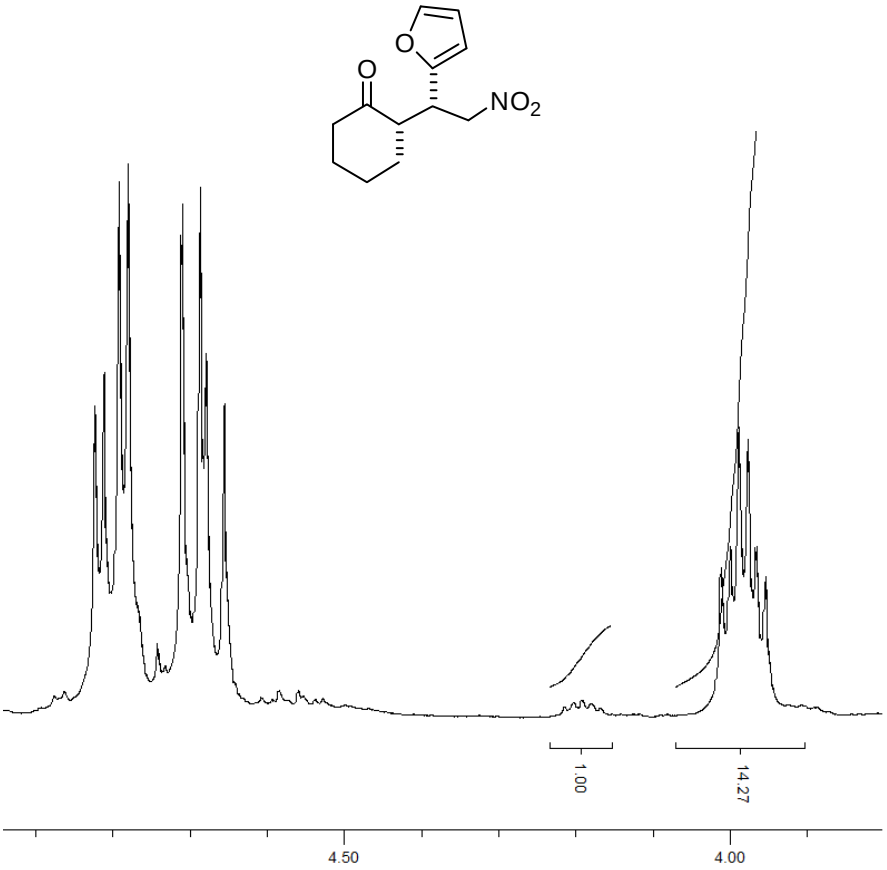


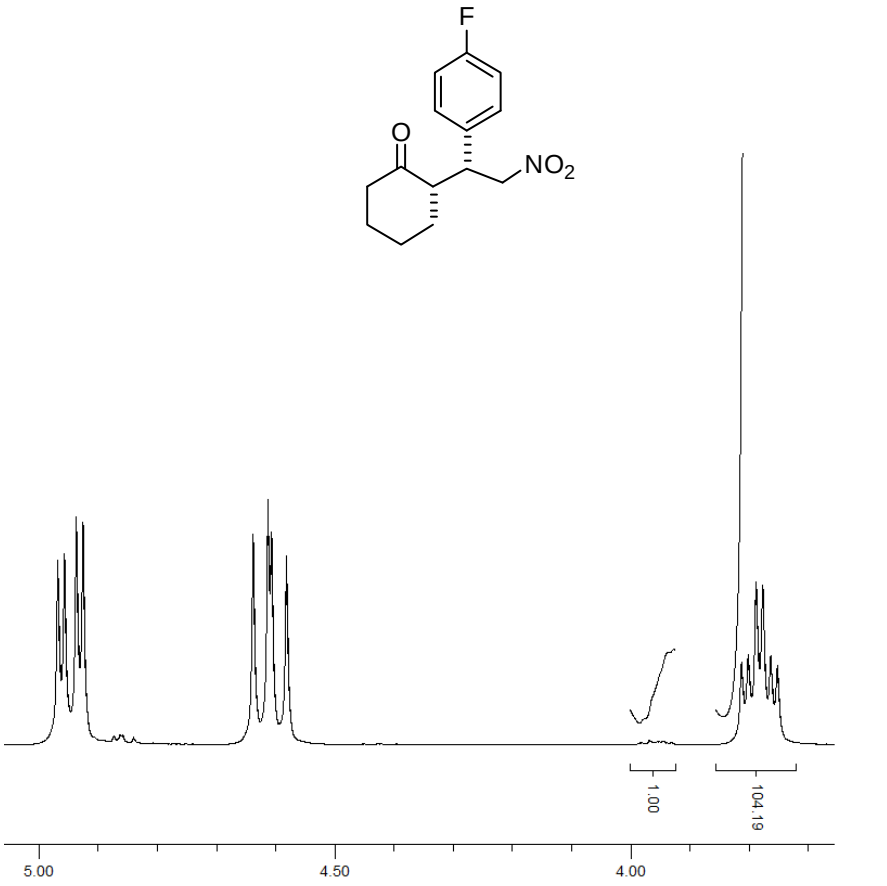

O
NO2
7.0
6.0
5.0
4.0
3.0
2.0
1.0
200
150
100
50

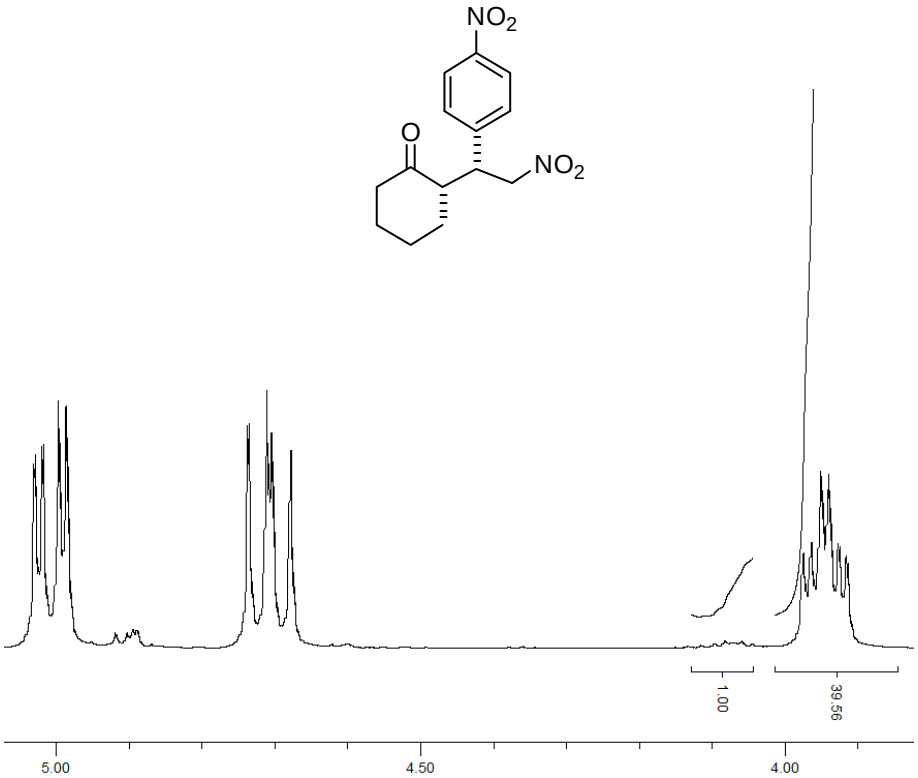

O
NO2
N
Ac
7.0
6.0
5.0
4.0
3.0
2.0

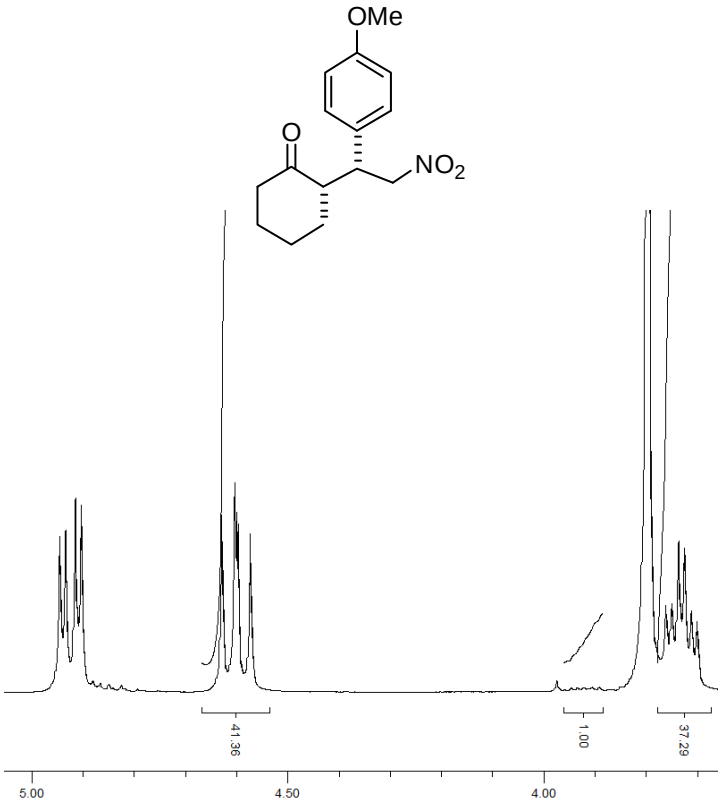

200
150
100
50

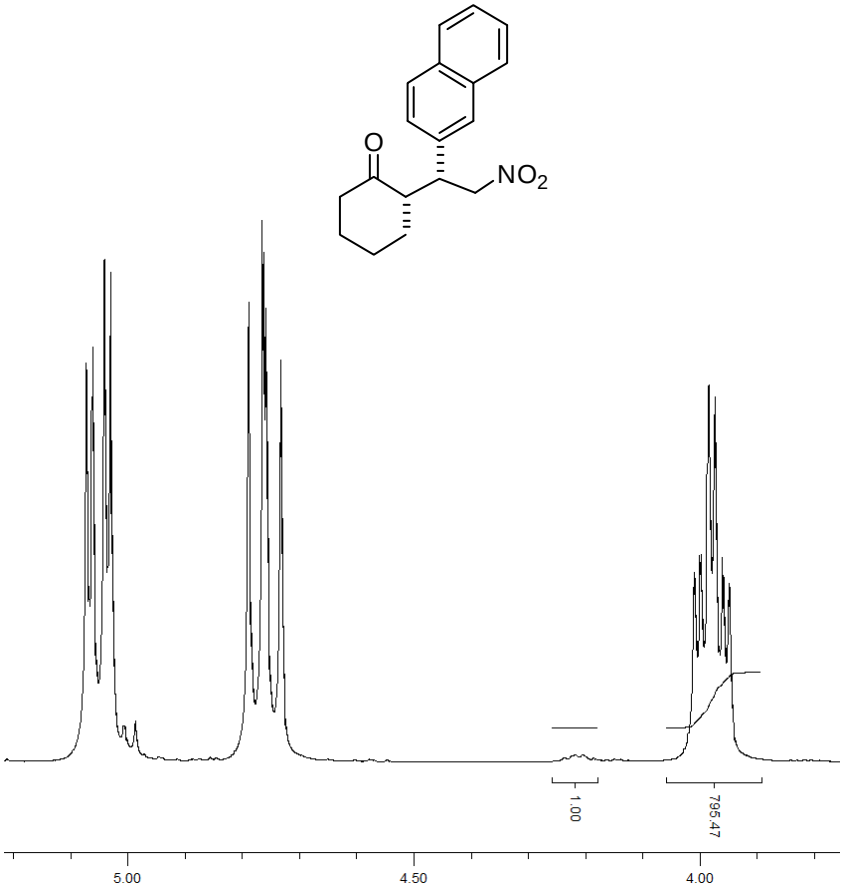

O
NO2
1.00
101.52
5.00
4.50
4.00

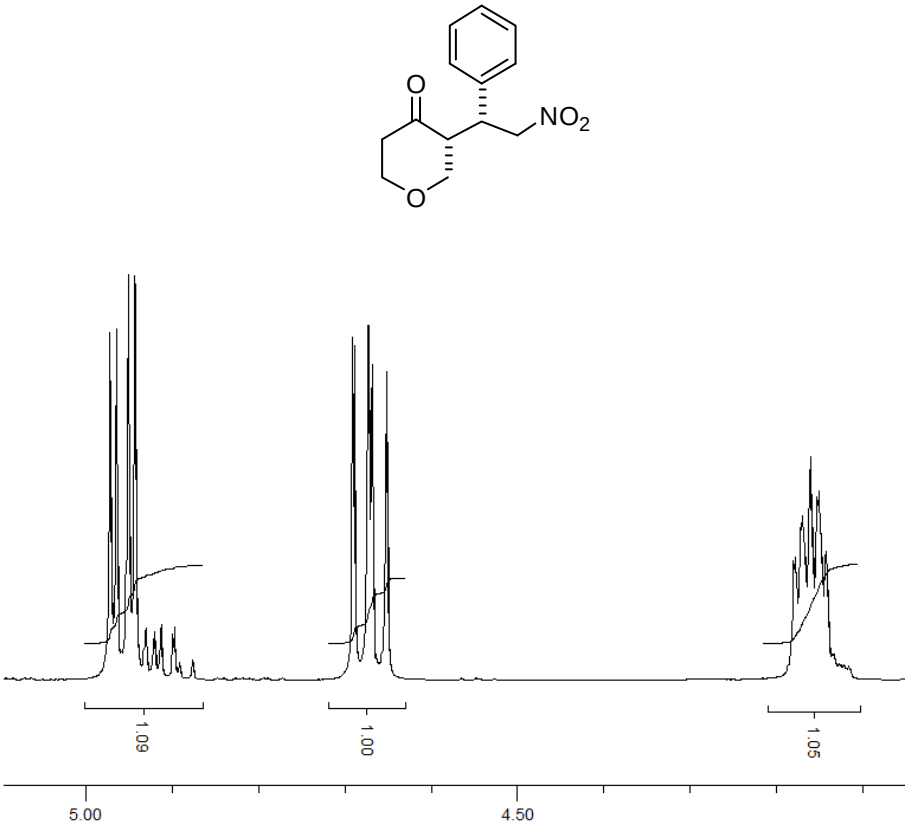

O
O
NO2
1.00
14.27
4.50
4.00

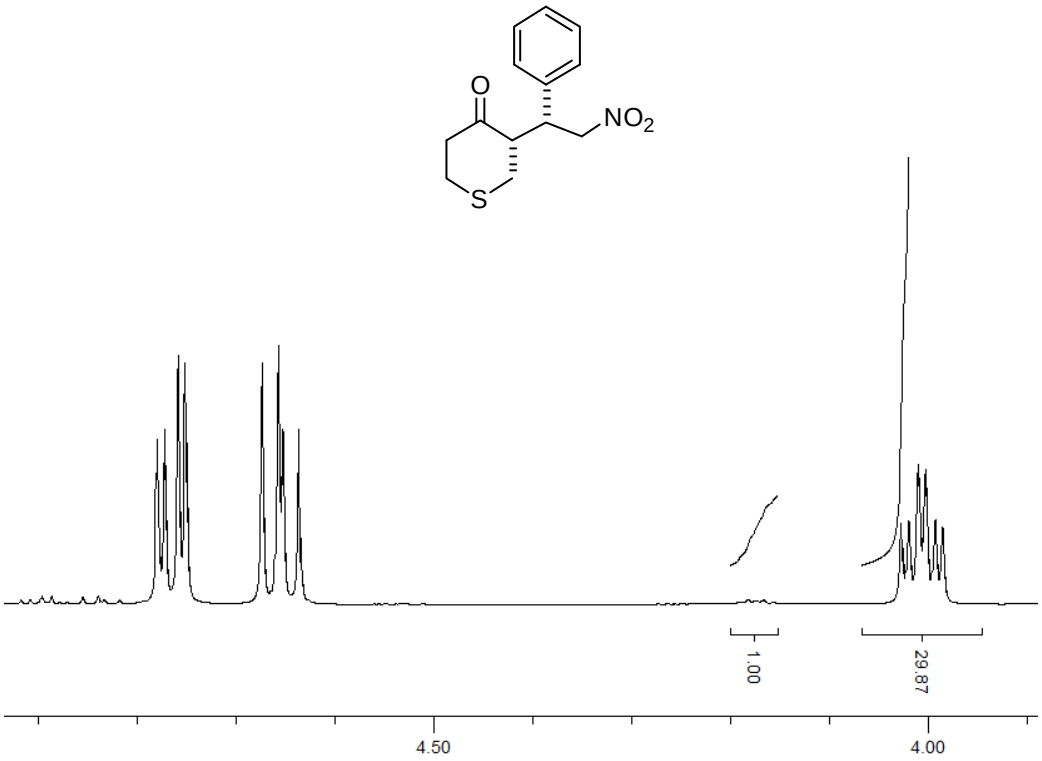

F
O
NO2
1.00
104.19
5.00
4.50
4.00

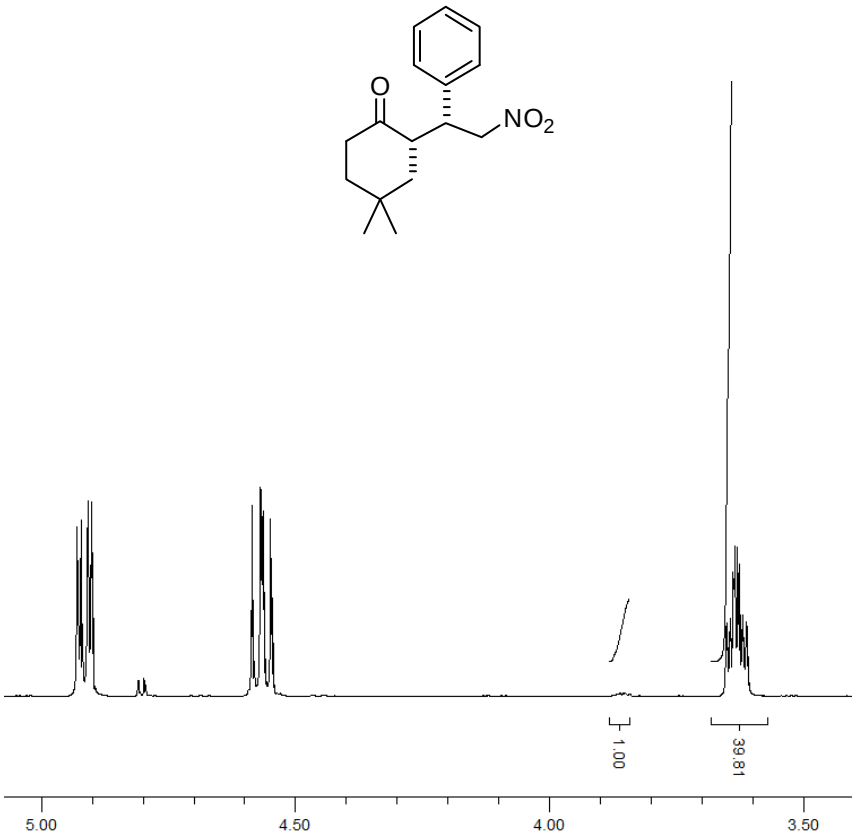

NO2
O
NO2
1.00
39.56
5.00
4.50
4.00

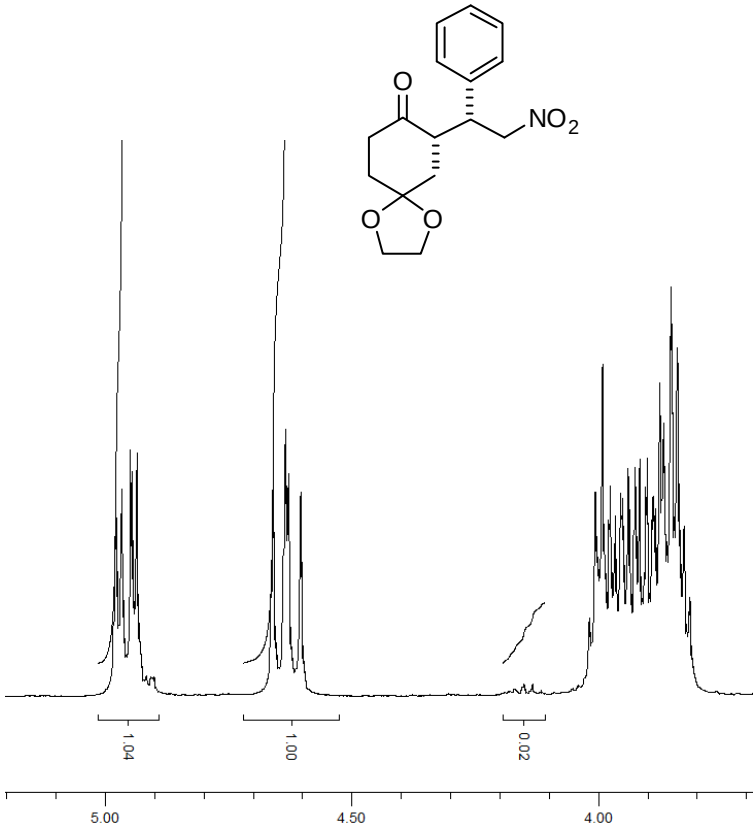

OMe
O
NO2
41.36
1.00
37.29
5.00
4.50
4.00

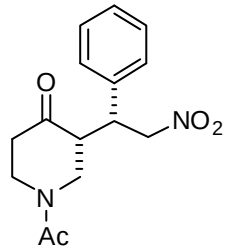

O
NO2
1.00
795.47
5.00
4.50
4.00


O
NO2
O
1.09
1.00
1.05
5.00
4.50

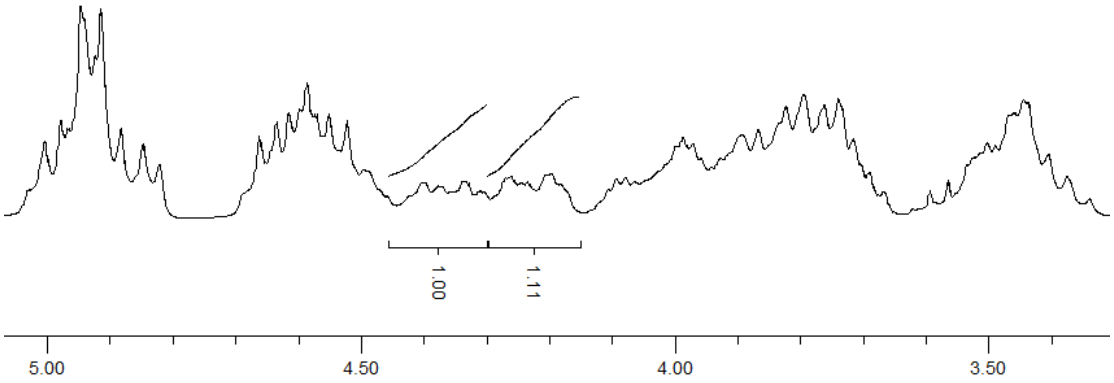

O
NO2
S
1.00
29.87
4.50
4.00


O
NO2
1.00
39.81
5.00
4.50
4.00
3.50

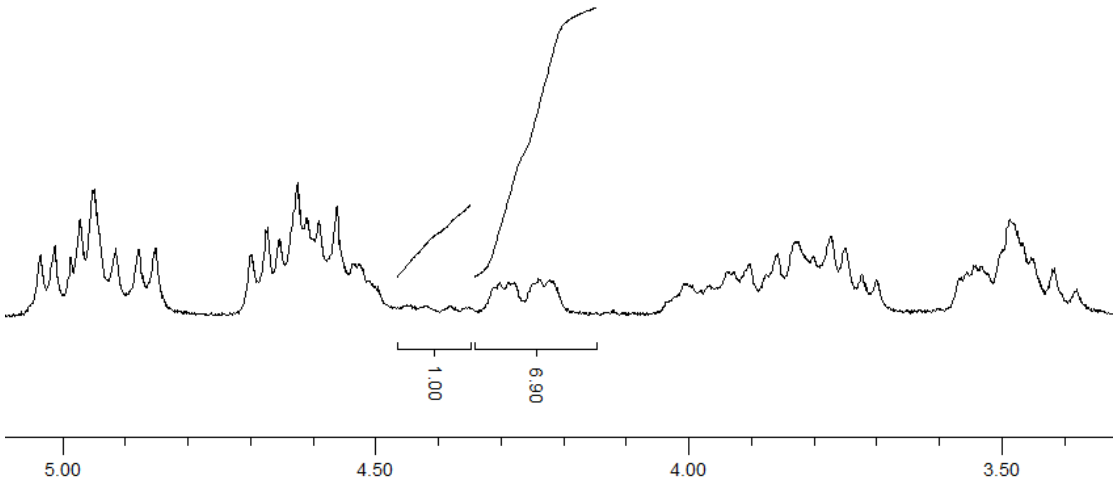

O
NO2
O
O
1.04
1.00
0.02
5.00
4.50
4.00

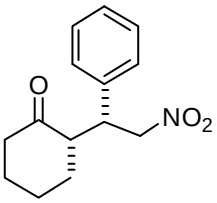


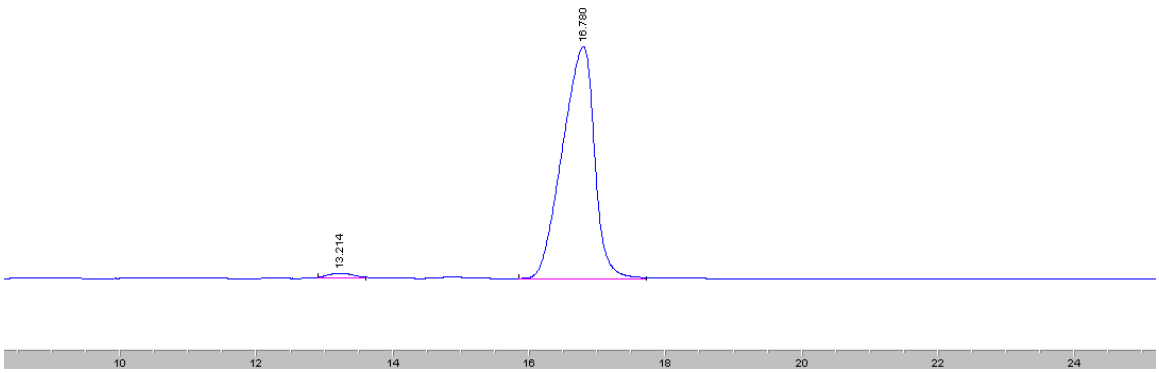
syn:anti 53:47



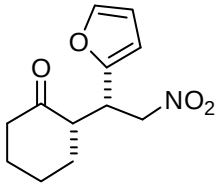
Reaction with organocatalyst **7a**

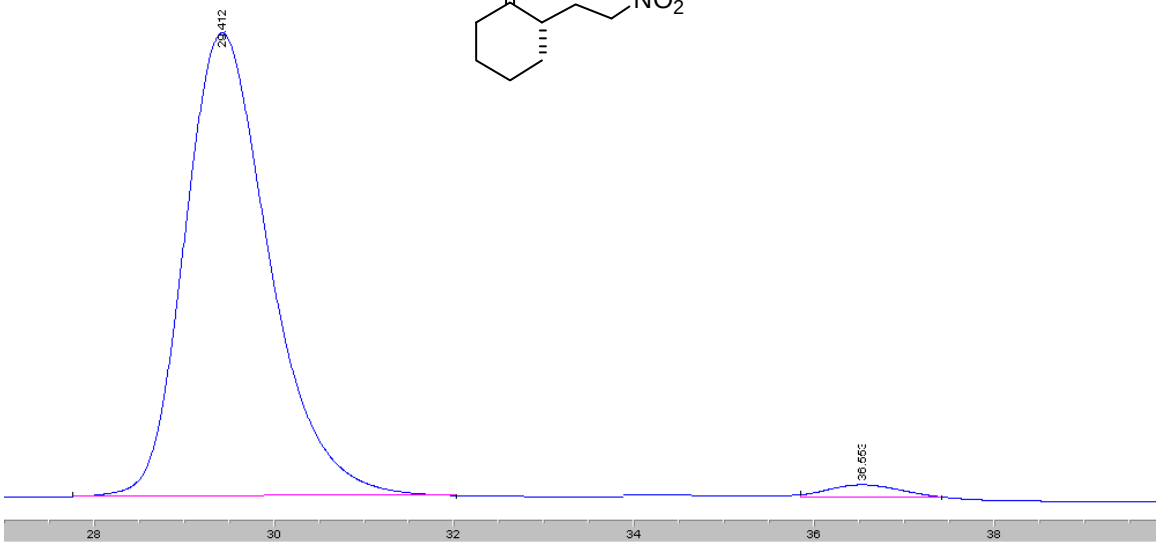




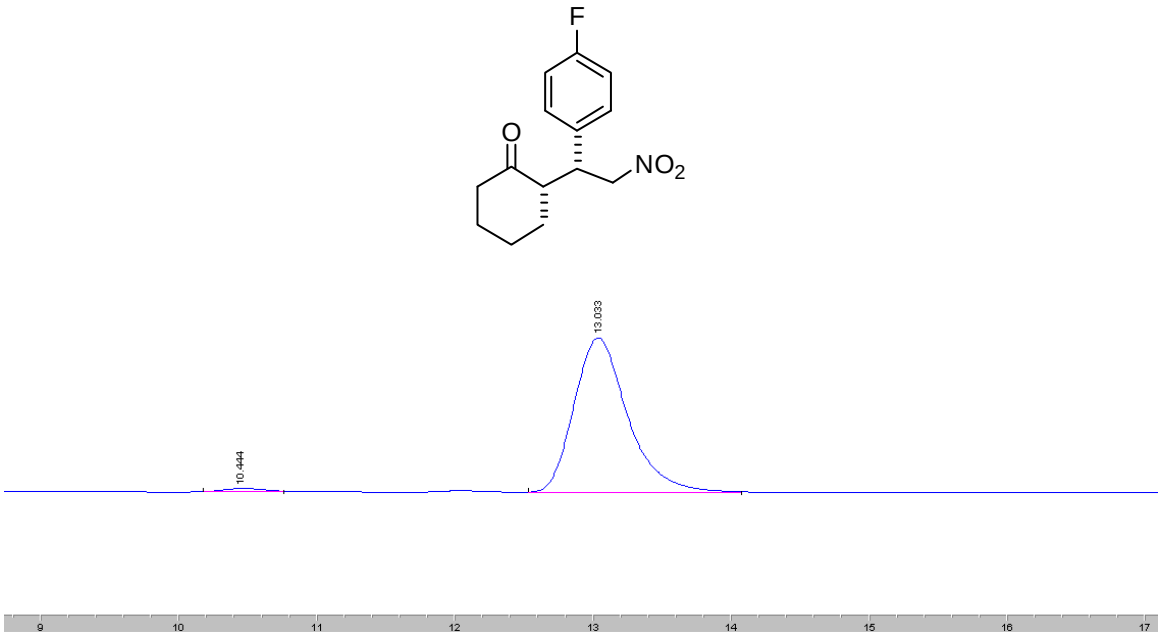


#	Time	Area	Height	Width	Area%	Symmetry
1	13.214	91.2	3.5	0.4283	1.544	0.893
2	16.78	5813	177.3	0.5466	98.456	1.711

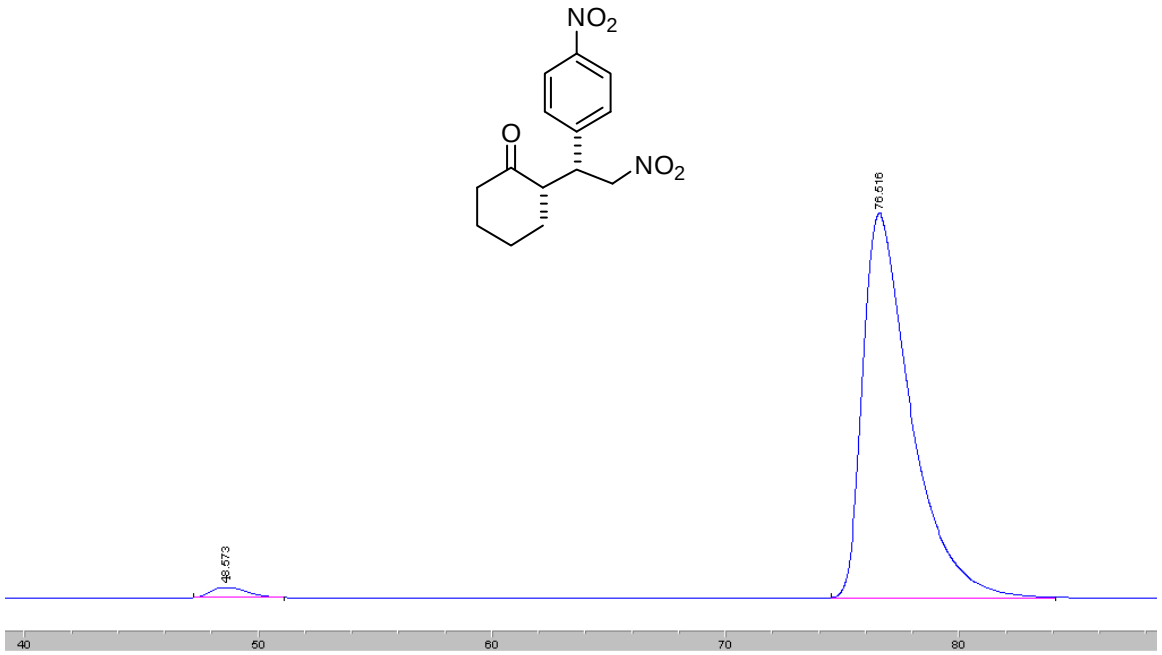




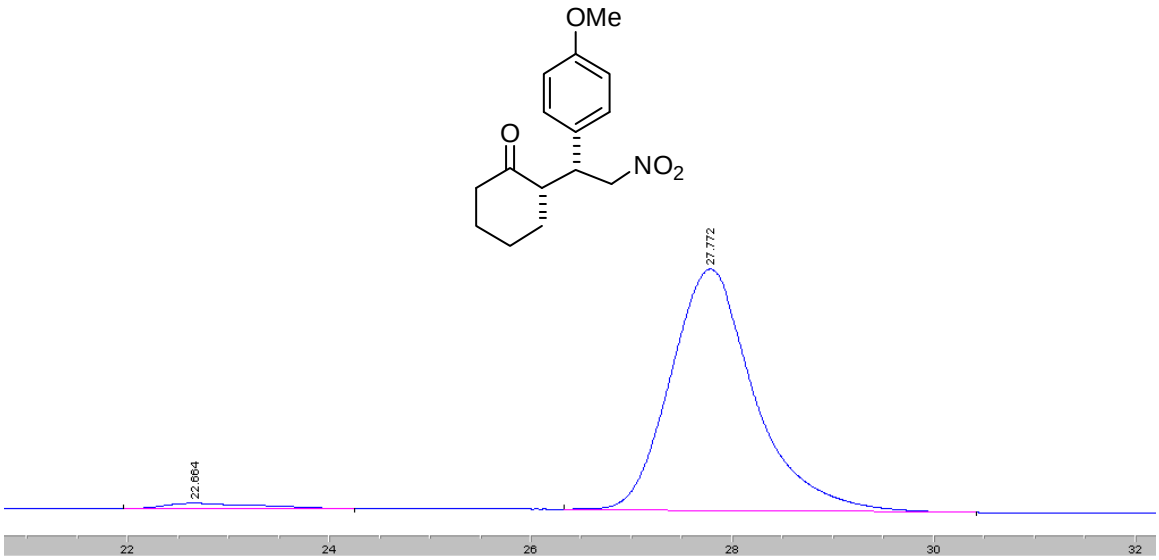
#	Time	Area	Height	Width	Area%	Symmetry
1	29.412	51413.8	784.9	1.0022	98.088	0.744
2	36.553	1002.3	19.3	0.8643	1.912	0.98



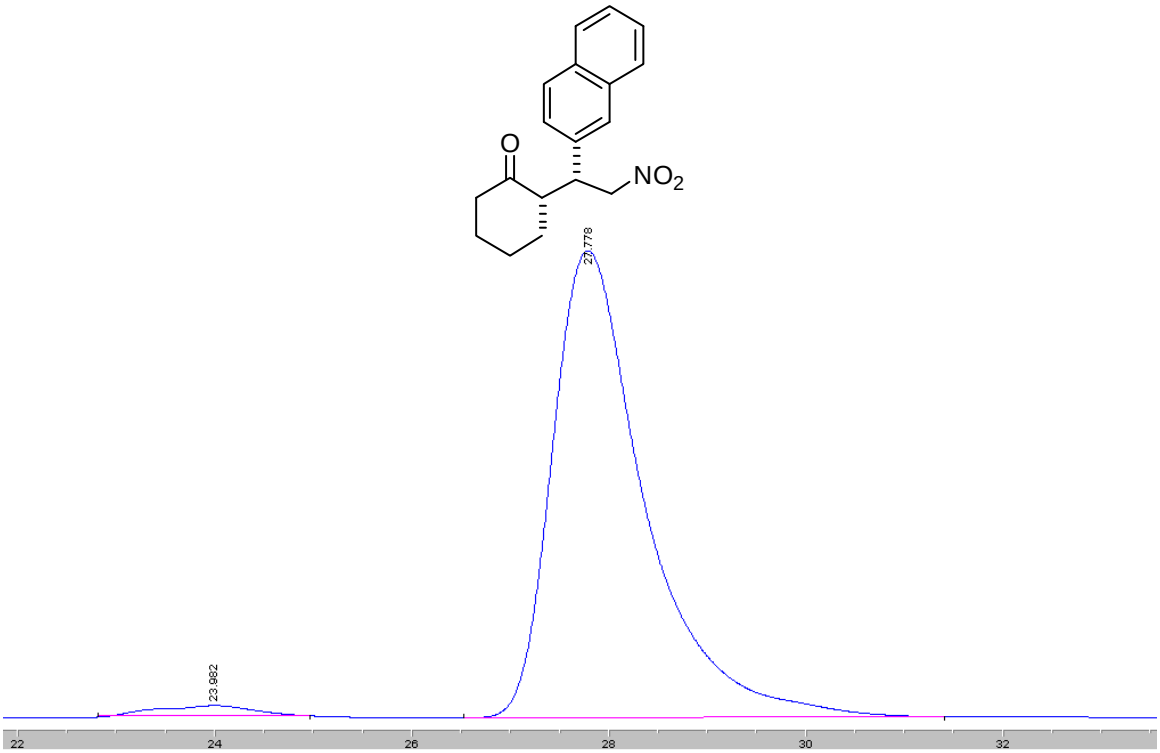
#	Time	Area	Height	Width	Area%	Symmetry
1	10.444	35.1	1.8	0.2449	1.495	0.79
2	13.033	2312.8	86.2	0.415	98.505	0.782



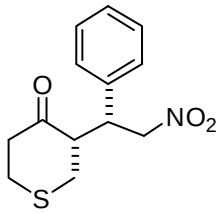
#	Time	Area	Height	Width	Area%	Symmetry
1	48.573	2024.9	19.5	1.735	1.633	0.797
2	76.516	121977.6	828.9	2.4527	98.367	0.488



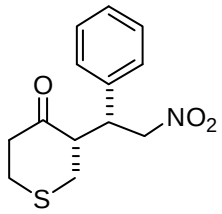
#	Time	Area	Height	Width	Area%	Symmetry
1	22.664	150.7	4.2	0.6038	0.751	0.649
2	27.772	19908.3	345.3	0.8386	99.249	0.852

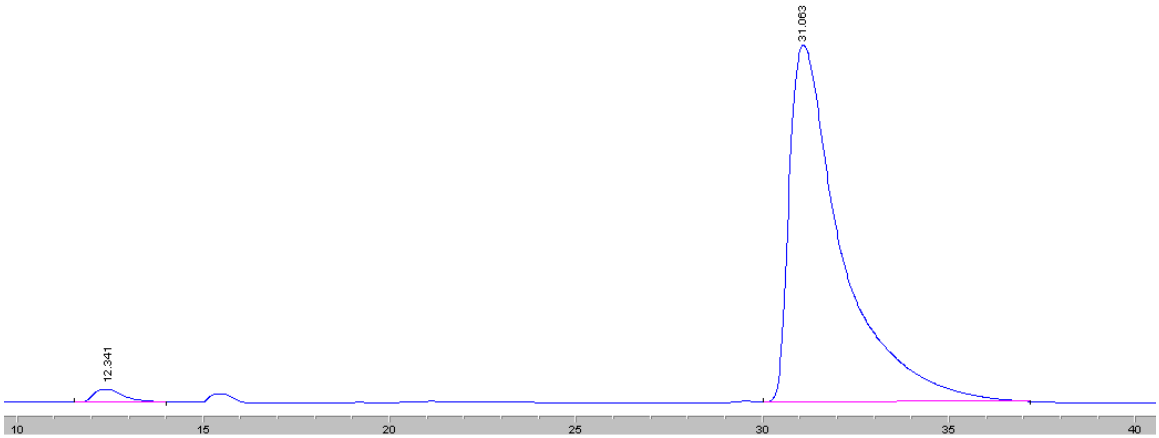


#	Time	Area	Height	Width	Area%	Symmetry
1	23.982	1983.3	31.6	1.0448	1.906	1.466
2	27.778	102058.1	1557.8	0.9704	98.094	0.577

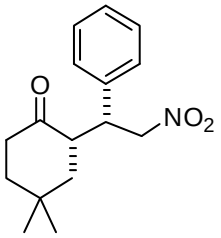


racemic

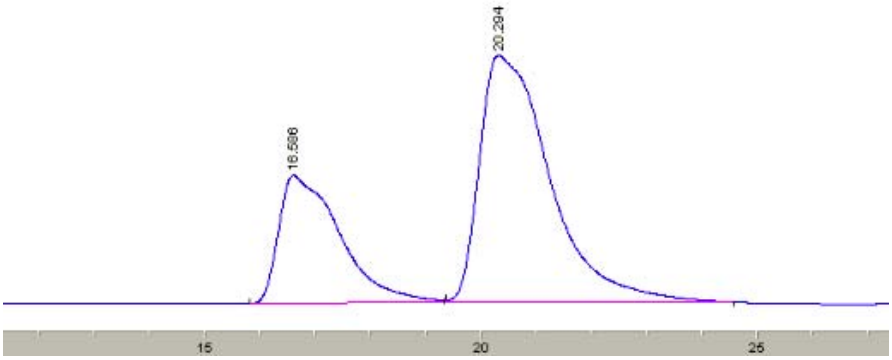


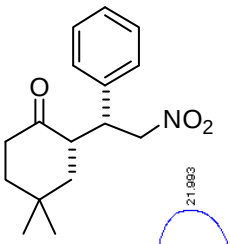


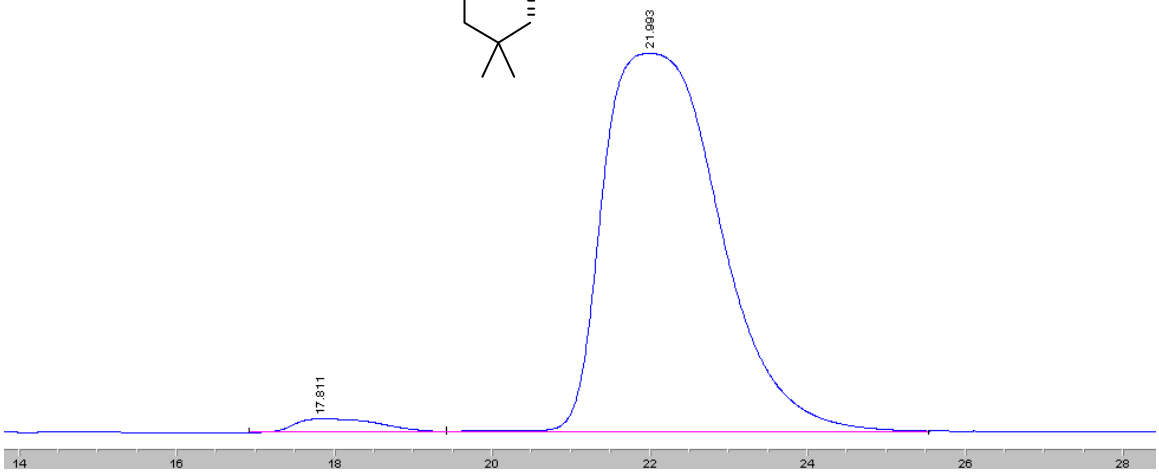
#	Time	Area	Height	Width	Area%	Symmetry
1	12.341	2213.7	53.2	0.6939	1.951	0.804
2	31.063	111253.3	1131.6	1.361	98.049	0.326



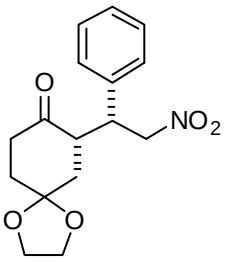
racemic



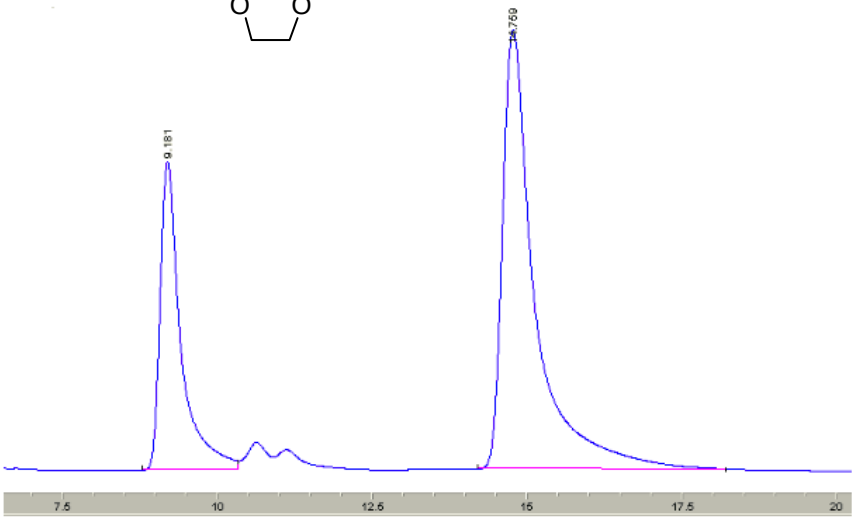


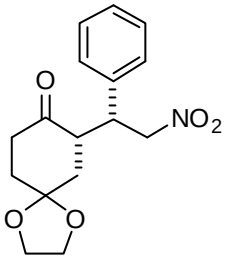


#	Time	Area	Height	Width	Area%	Symmetry
1	17.811	2530.9	37.7	1.1198	1.921	0.418
2	21.993	129217.3	1259.1	1.2093	98.079	0.657

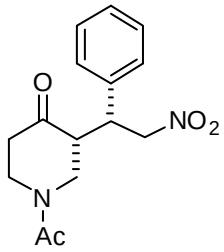


racemic

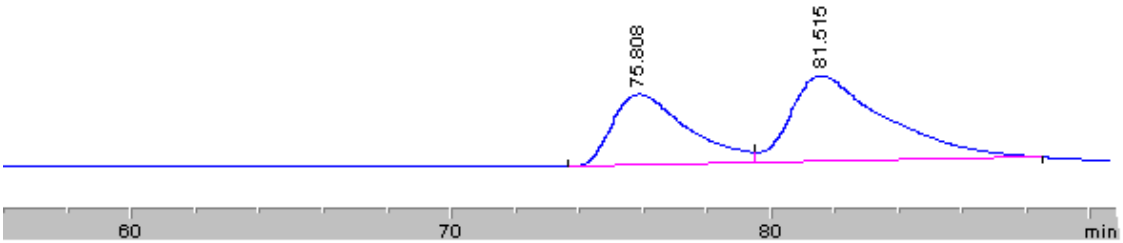


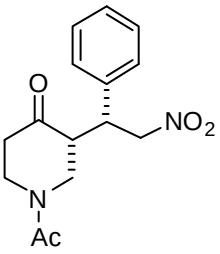


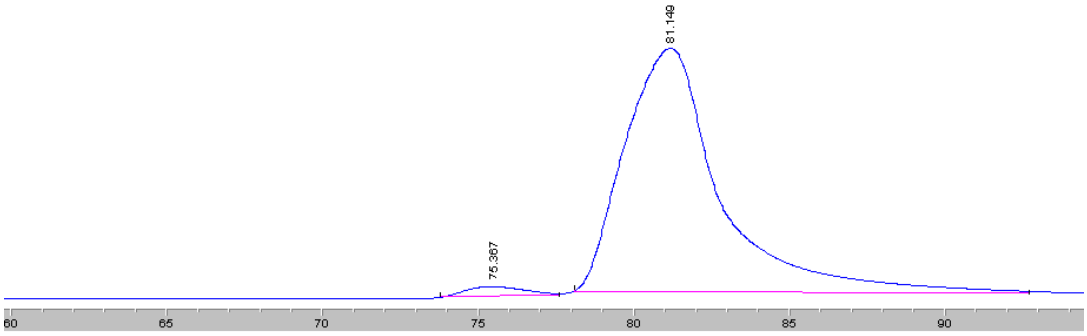
#	Time	Area	Height	Width	Area%	Symmetry
1	9.026	1177.2	70.3	0.2793	1.828	0.78
2	14.369	63216.1	1501.4	0.6172	98.172	0.421



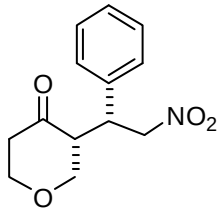
racemic

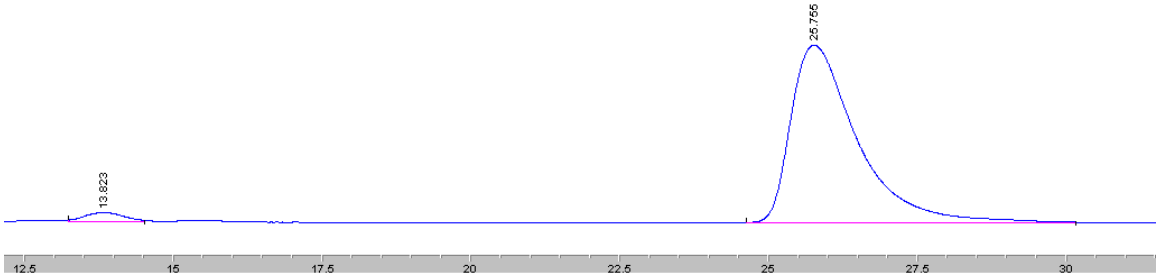




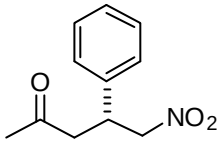


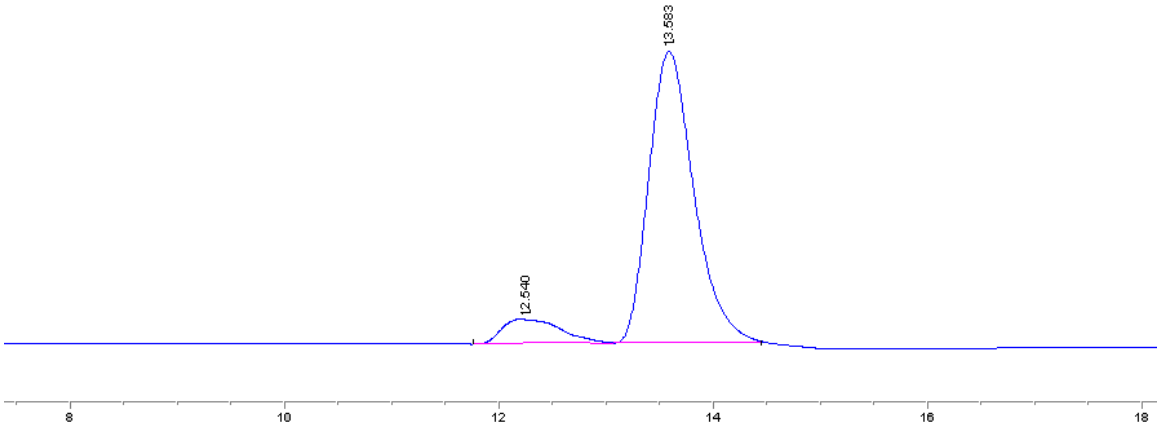
#	Time	Area	Height	Width	Area%	Symmetry
1	75.367	3342.2	27.8	1.412	1.941	0.866
2	81.149	168871	787.8	2.8848	98.059	0.866



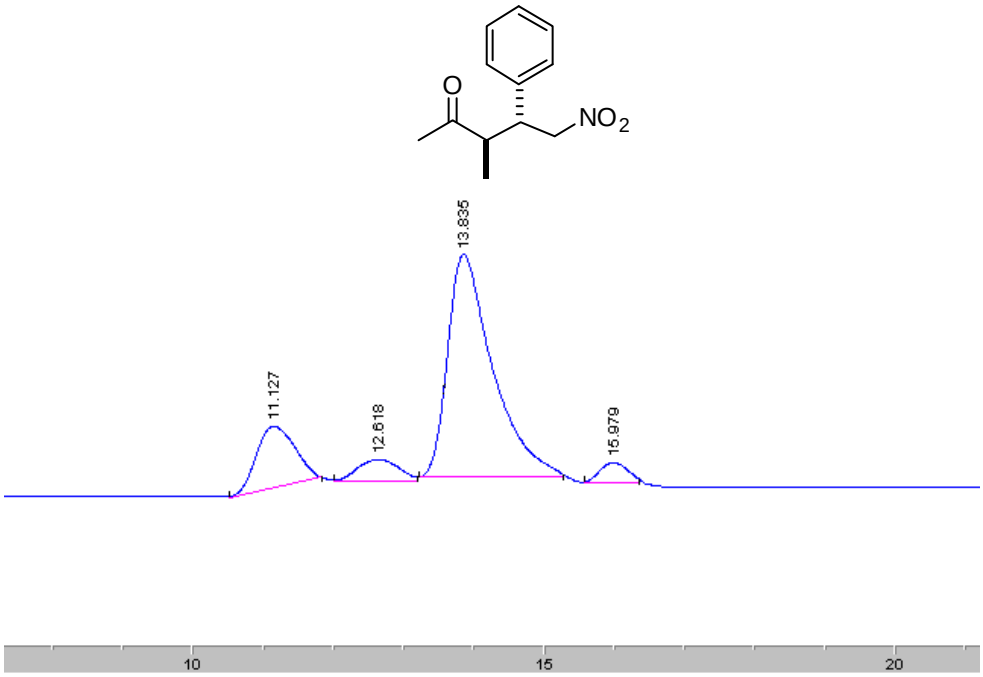


#	Time	Area	Height	Width	Area%	Symmetry
1	13.823	325.1	9	0.599	1.715	1.014
2	25.755	18634.2	252	1.1008	98.285	0.536

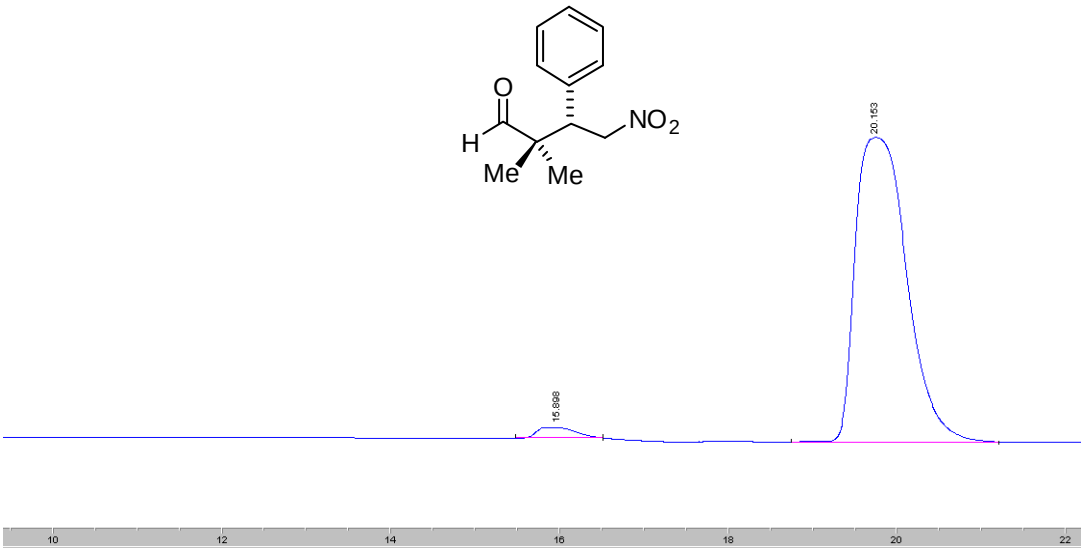




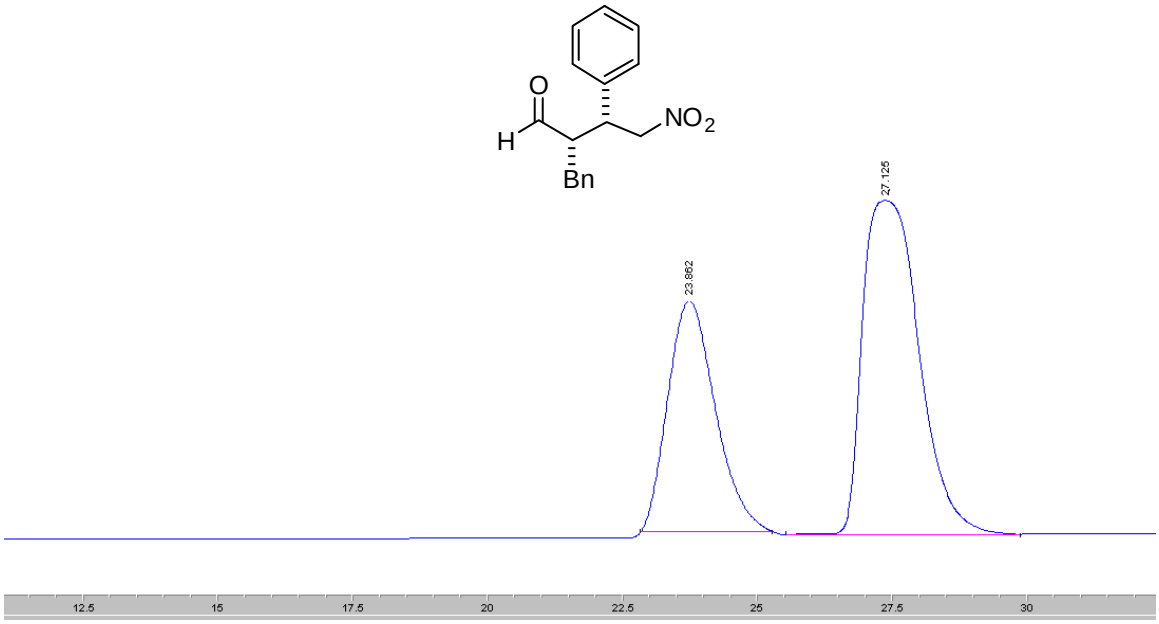
#	Time	Area	Height	Width	Area%	Symmetry
1	12.54	948.5	49.2	0.3211	8.875	0.889
2	13.583	9739.2	331.4	0.4898	91.125	0.778



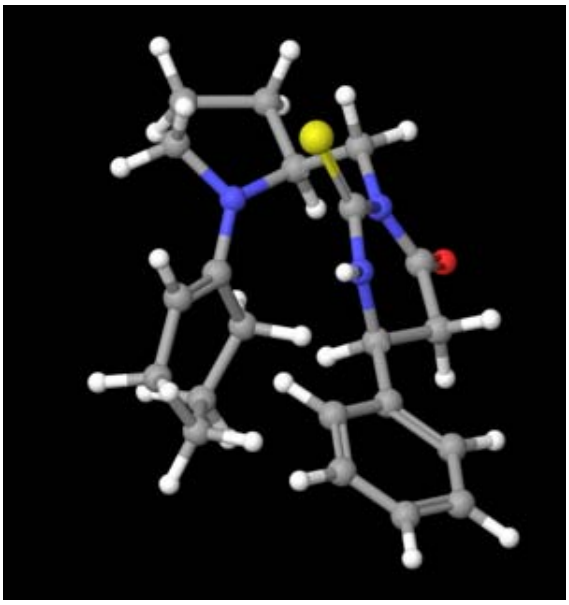
#	Time	Area	Height	Width	Area%	Symmetry
1	11.127	1340.3	34.6	0.6451	17.240	0.83
2	12.618	503.8	12.1	0.6913	6.480	0.965
3	13.835	5607.6	124.5	0.7508	72.130	0.533
4	15.979	322.6	11.3	0.4745	4.150	1.013



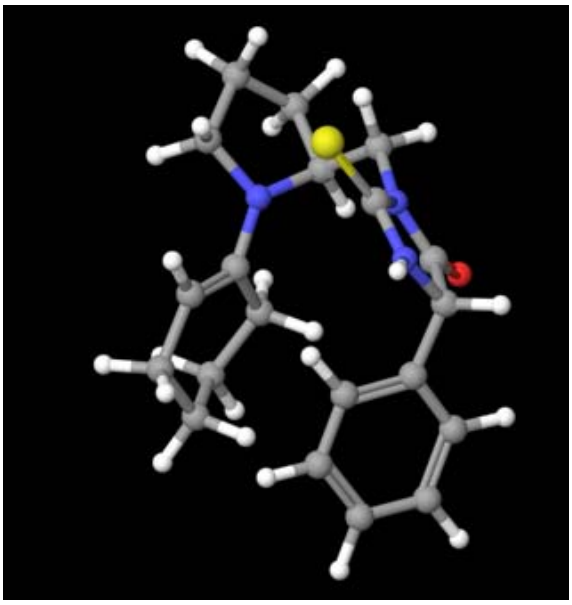
#	Time	Area	Height	Width	Area%	Symmetry
1	15.898	108.6	4.6	0.3923	5.846	1.151
2	20.153	1748.9	29.4	0.7142	94.154	1.52



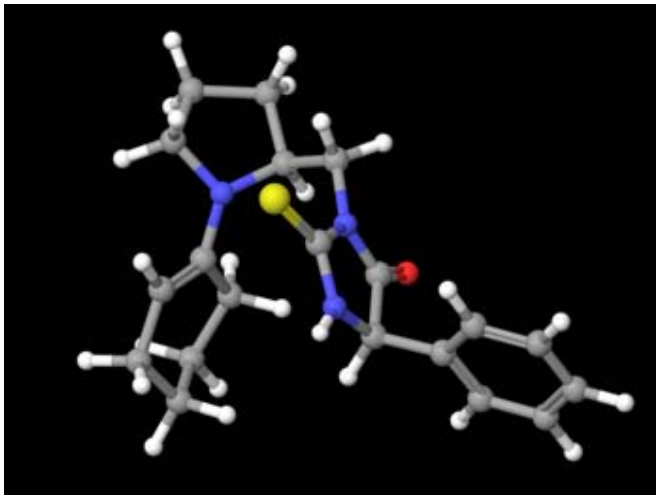
#	Time	Area	Height	Width	Area%	Symmetry
1	23.862	2164.2	25.1	1.4375	33.111	0.577
2	27.125	4372.1	37.6	1.9383	66.889	0.556



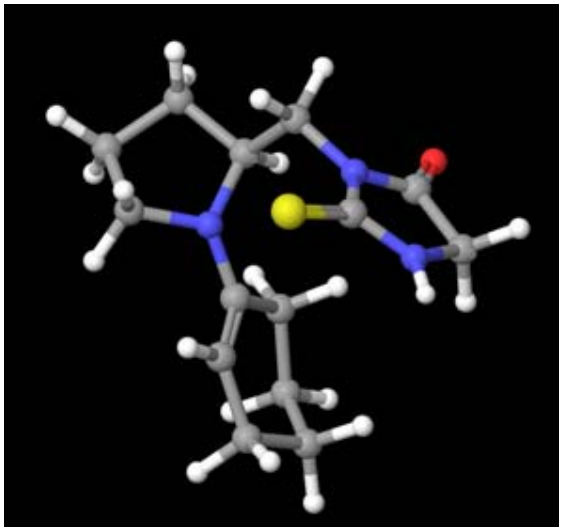
enamine of catalyst **12**



enamine of catalyst **16e**



enamine of catalyst **16d**



enamine of catalyst **16a**

Maestro 9.1 Macromodel

Force field: OPLS_2005

Solvent: $CHCl_3$

Electrostatic treatment: Constant dielectric

Dielectric constant: 1.0

Charges from: Force field

Cutoff: Extended

Method: PRCG

Max. iterations: 5000

Converge on: Gradient

Convergethreshold: 0.01