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Supplementary Information for:

Cascade oxime formation, cyclization to a nitrone, and intermolecular dipolar cycloaddition

Rachel C. Furnival, Rungroj Saruengkhanphasit, Heather E. Holberry, Jonathan R. Shewring, Hélène D. S. Guerrand, Harry Adams, Iain Coldham*

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK
Fax: +44(0)114 222 9346
E-mail: i.coldham@sheffield.ac.uk

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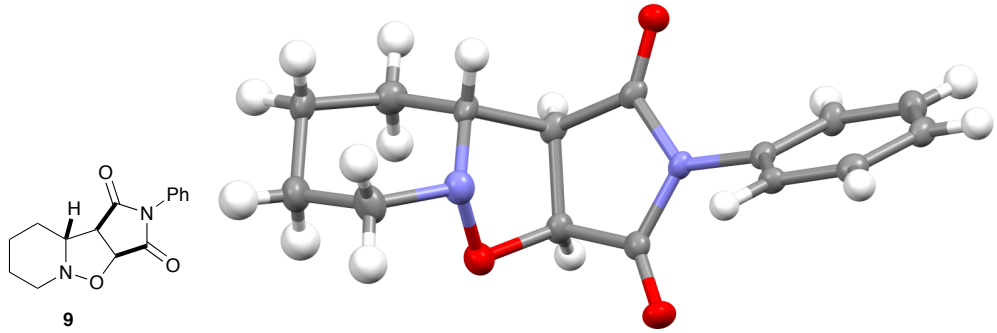
1. Molecular structure data for compounds **9**, **12**, **16a**, **17**, **22**, **24**, **27**, **28**

Data for compound **9**:

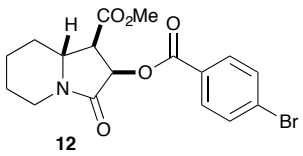


9

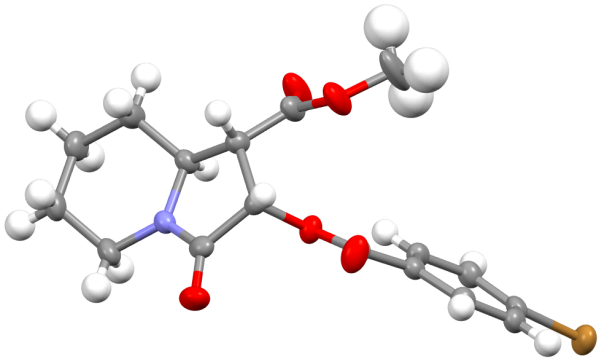
Empirical formula	C15 H16 N2 O3	
Formula weight	272.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.9691(19) Å	a= 90°.
	b = 6.6225(11) Å	b= 104.005(11)°.
	c = 15.583(3) Å	g = 90°.
Volume	1298.6(4) $Å^3$	
Z	4	
Density (calculated)	1.393 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	576	
Crystal size	0.17 x 0.13 x 0.05 mm^3	
Theta range for data collection	3.24 to 27.54°.	
Index ranges	-16<=h<=16, -8<=k<=6, -20<=l<=20	
Reflections collected	11569	
Independent reflections	2984 [R(int) = 0.0846]	
Completeness to theta = 27.54°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9951 and 0.9835	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2984 / 0 / 181	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0715, wR2 = 0.1899	
R indices (all data)	R1 = 0.1214, wR2 = 0.2195	
Largest diff. peak and hole	0.760 and -0.475 $e.Å^{-3}$	

Crystal data deposited at CCDC 1006040

Data for compound **12**:

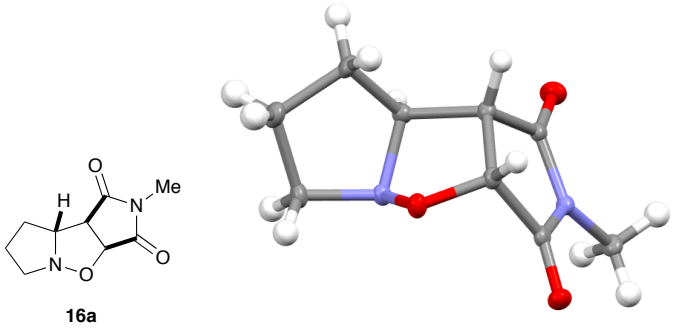


12



Empirical formula	C17 H19 Br N O5.50	
Formula weight	405.24	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.0353(7) Å	a= 90°.
	b = 21.5973(13) Å	b= 101.886(3)°.
	c = 15.0726(9) Å	g = 90°.
Volume	3515.3(4) $Å^3$	
Z	8	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	3.456 mm^{-1}	
F(000)	1656	
Crystal size	0.380 x 0.210 x 0.180 mm^3	
Theta range for data collection	3.629 to 66.827°.	
Index ranges	-13<=h<=13, -25<=k<=25, -17<=l<=17	
Reflections collected	46269	
Independent reflections	6216 [R(int) = 0.0530]	
Completeness to theta = 67.679°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.59 and 0.28	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6216 / 0 / 444	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0794	
R indices (all data)	R1 = 0.0443, wR2 = 0.0835	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.356 and -0.614 $e.Å^{-3}$	
Crystal data deposited at CCDC 1022997		

Data for compound **16a**:

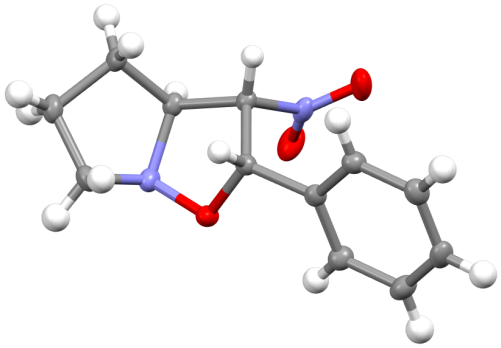


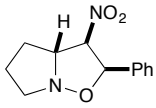
16a

Empirical formula	C9 H12 N2 O3	
Formula weight	196.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 7.9208(3) Å	a= 90°.
	b = 16.5681(9) Å	b= 90°.
	c = 6.7713(3) Å	g = 90°.
Volume	888.62(7) $Å^3$	
Z	4	
Density (calculated)	1.467 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	416	
Crystal size	0.35 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.46 to 27.63°.	
Index ranges	-9<=h<=10, -19<=k<=21, -8<=l<=8	
Reflections collected	4579	
Independent reflections	2018 [R(int) = 0.0210]	
Completeness to theta = 27.63°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9889 and 0.9620	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2018 / 1 / 128	
Goodness-of-fit on F^2	1.279	
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0847	
R indices (all data)	R1 = 0.0363, wR2 = 0.0873	
Largest diff. peak and hole	0.214 and -0.187 $e.Å^{-3}$	

Crystal data deposited at CCDC 1051097

Data for compound **17**:





17

Empirical formula	C12 H14 N2 O3	
Formula weight	234.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.0398(3) Å	a= 90°.
	b = 7.2748(3) Å	b= 98.643(2)°.
	c = 17.0449(6) Å	g = 90°.
Volume	1108.19(7) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	496	
Crystal size	0.45 x 0.32 x 0.18 mm^3	
Theta range for data collection	2.28 to 27.54°.	
Index ranges	-11<=h<=11, -9<=k<=9, -22<=l<=20	
Reflections collected	14308	
Independent reflections	2547 [R(int) = 0.0210]	
Completeness to theta = 27.54°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9818 and 0.9554	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2547 / 0 / 154	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0992	
R indices (all data)	R1 = 0.0395, wR2 = 0.1014	
Largest diff. peak and hole	0.343 and -0.318 $e.Å^{-3}$	
Crystal data deposited at CCDC 1006037		

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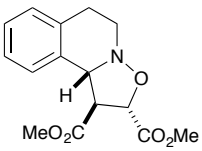
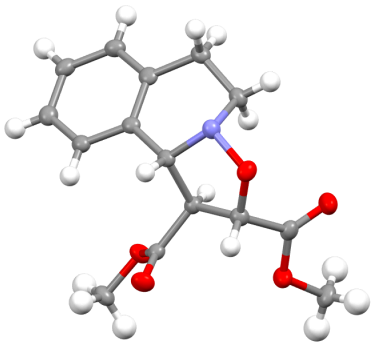


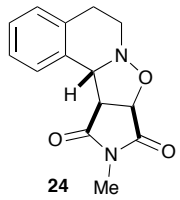
22

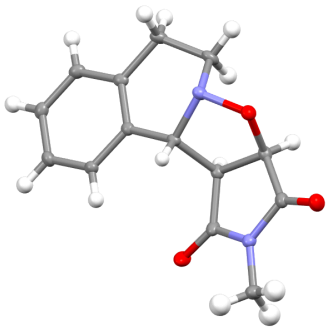


Empirical formula	C15 H17 N O5	
Formula weight	291.30	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.1248(8) Å	a= 90.13°.
	b = 32.242(3) Å	b= 90.000(6)°.
	c = 9.4579(9) Å	g = 90°.
Volume	2782.5(4) $Å^3$	
Z	8	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	1232	
Crystal size	0.32 x 0.11 x 0.11 mm^3	
Theta range for data collection	1.26 to 27.64°.	
Index ranges	-11<=h<=11, -42<=k<=40, -12<=l<=12	
Reflections collected	47642	
Independent reflections	6429 [R(int) = 0.0773]	
Completeness to theta = 27.64°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9885 and 0.9672	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6429 / 0 / 384	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1190	
R indices (all data)	R1 = 0.0681, wR2 = 0.1356	
Largest diff. peak and hole	0.490 and -0.320 $e.Å^{-3}$	

Crystal data deposited at CCDC 1006038

Data for compound **24**:

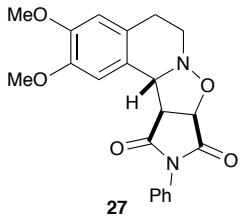




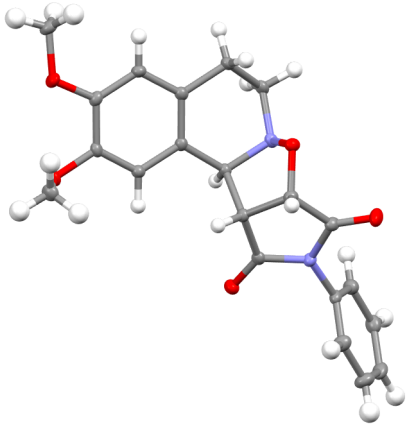
Empirical formula	C14 H14 N2 O3	
Formula weight	258.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.8159(2) Å	a= 90°.
	b = 26.7835(7) Å	b= 114.2140(10)°.
	c = 7.0628(2) Å	g = 90°.
Volume	1175.90(6) Å^3	
Z	4	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	0.104 mm^{-1}	
F(000)	544	
Crystal size	0.34 x 0.12 x 0.04 mm^3	
Theta range for data collection	1.52 to 27.48°.	
Index ranges	-8<=h<=8, -34<=k<=34, -9<=l<=9	
Reflections collected	20165	
Independent reflections	2686 [R(int) = 0.0225]	
Completeness to theta = 27.48°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9958 and 0.9654	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2686 / 0 / 173	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.1041	
R indices (all data)	R1 = 0.0400, wR2 = 0.1157	
Largest diff. peak and hole	0.377 and -0.217 e.Å^{-3}	

Crystal data deposited at CCDC 1006039

Data for compound **27**:



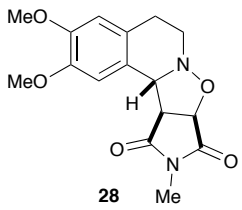
27



Empirical formula	C21 H20 N2 O5	
Formula weight	380.39	
Temperature	97(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.6709(10) Å	a= 90°.
	b = 7.6760(7) Å	b= 97.635(4)°.
	c = 22.1886(18) Å	g = 90°.
Volume	1801.4(3) Å^3	
Z	4	
Density (calculated)	1.403 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	800	
Crystal size	0.43 x 0.38 x 0.35 mm^3	
Theta range for data collection	1.85 to 27.55°.	
Index ranges	-13<=h<=13, -9<=k<=9, -28<=l<=28	
Reflections collected	33725	
Independent reflections	4133 [R(int) = 0.0718]	
Completeness to theta = 27.55°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9654 and 0.9578	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4133 / 0 / 255	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1086	
R indices (all data)	R1 = 0.0488, wR2 = 0.1142	
Largest diff. peak and hole	0.307 and -0.290 e.Å^{-3}	

Crystal data deposited at CCDC 1006041

Data for compound **28**:



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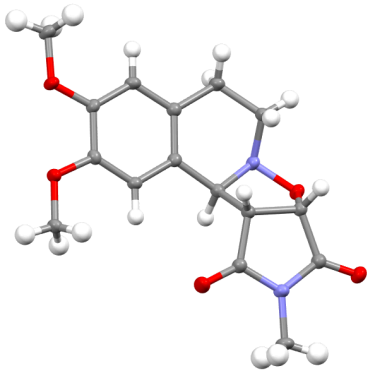
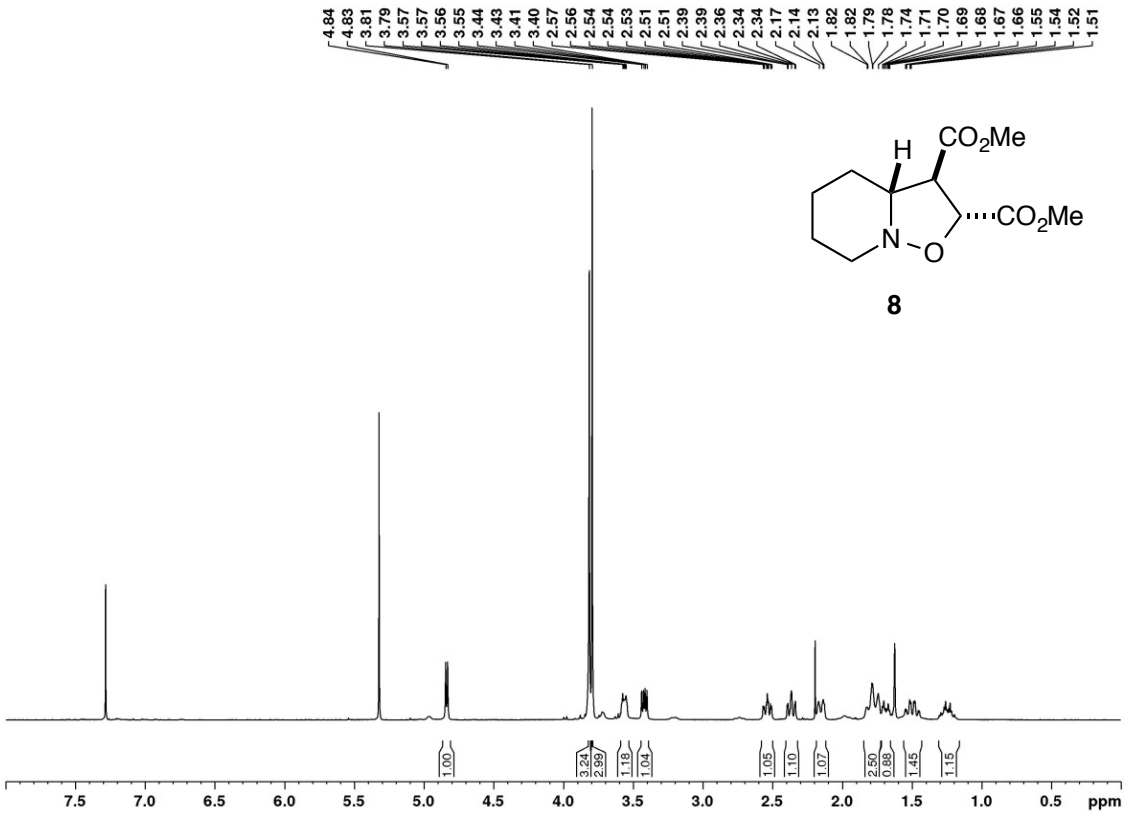
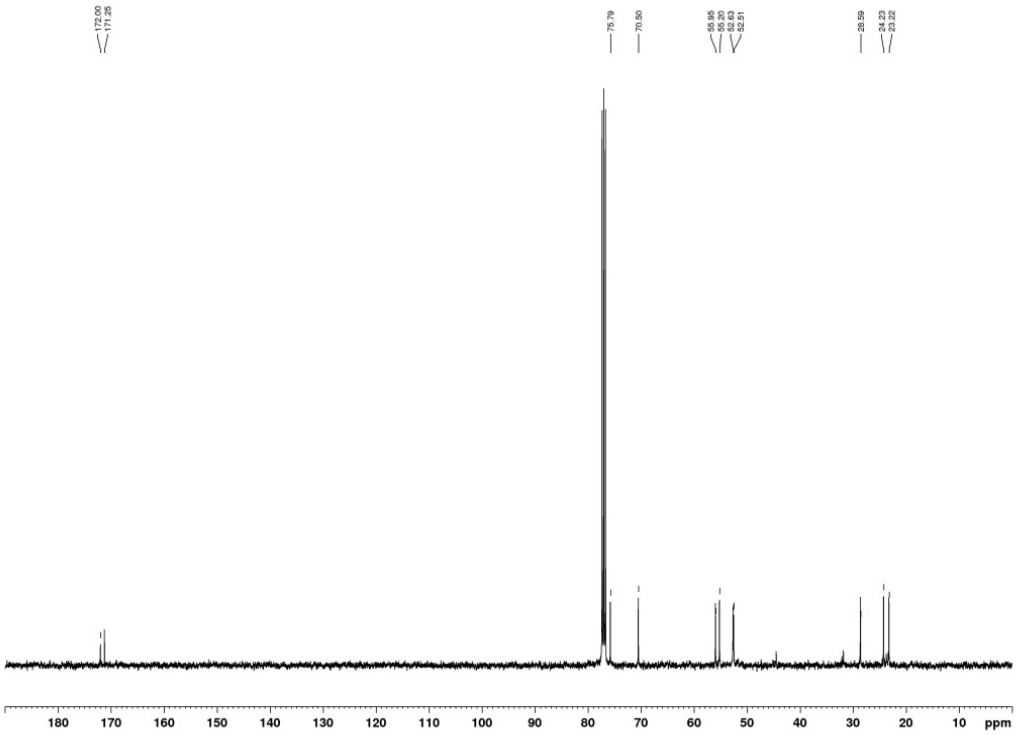
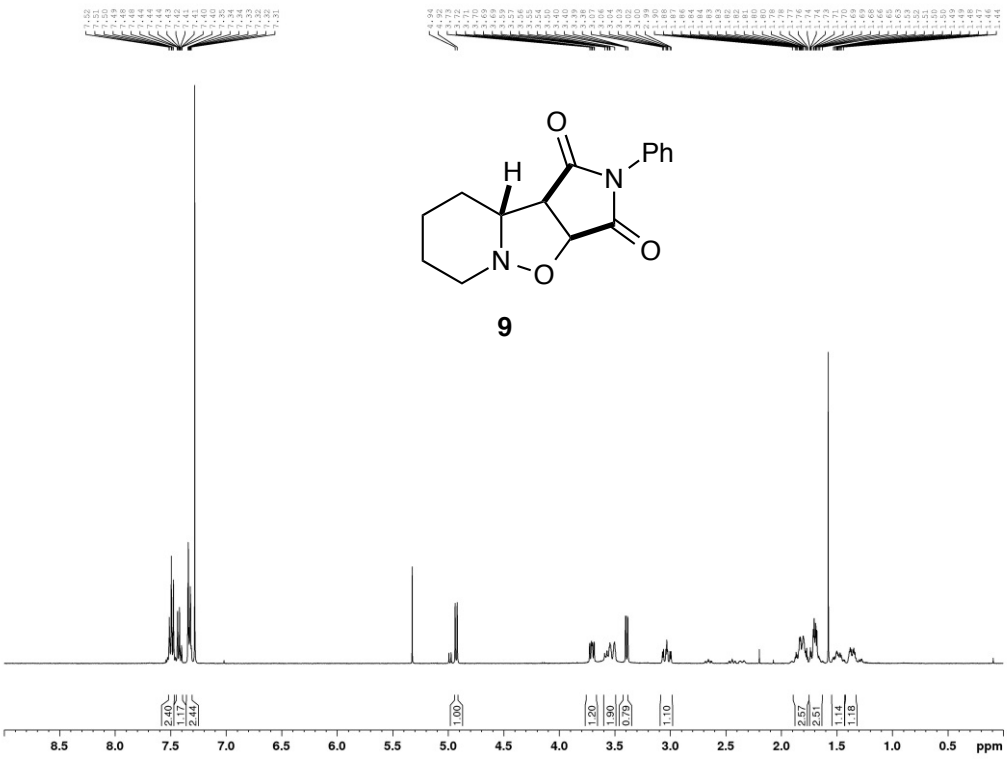


Empirical formula	C16 H18 N2 O5	
Formula weight	318.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.8243(10) Å	a= 90°.
	b = 8.6128(8) Å	b= 104.843(5)°.
	c = 17.8328(18) Å	g = 90°.
Volume	1458.6(2) $Å^3$	
Z	4	
Density (calculated)	1.450 Mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	672	
Crystal size	0.40 x 0.38 x 0.36 mm^3	
Theta range for data collection	2.14 to 27.57°.	
Index ranges	-12<=h<=12, -11<=k<=10, -22<=l<=22	
Reflections collected	13444	
Independent reflections	3284 [R(int) = 0.0681]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9619 and 0.9578	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3284 / 0 / 211	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1267	
R indices (all data)	R1 = 0.0731, wR2 = 0.1399	
Largest diff. peak and hole	0.248 and -0.274 $e.Å^{-3}$	
Crystal data deposited at CCDC 1006042		

2. NMR Spectra for compounds **8**–**12**, **14**–**20**, macronecine, **22**–**24**, and **26–30**







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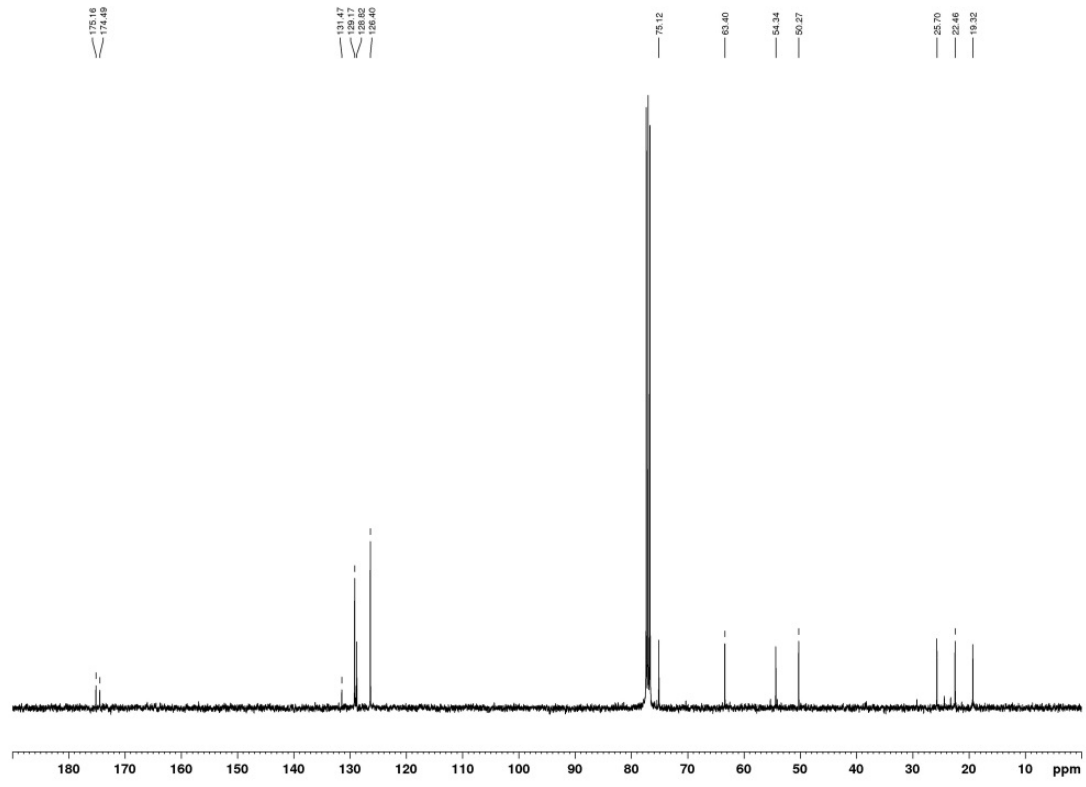

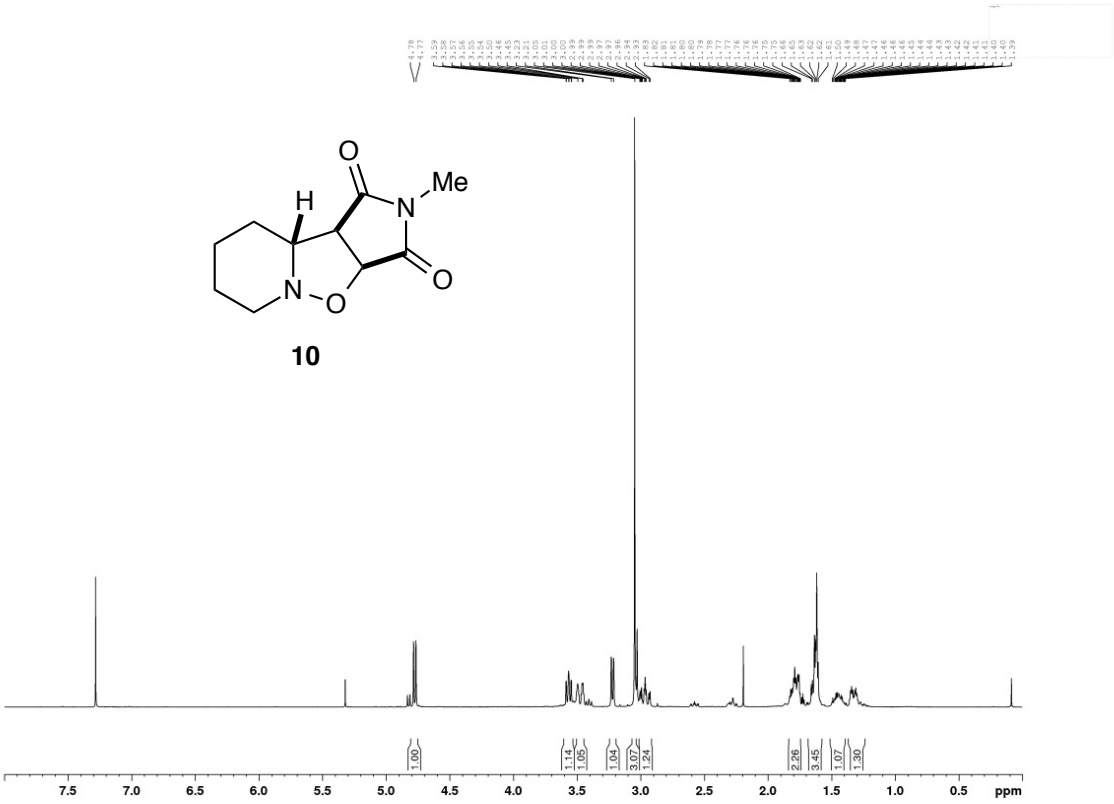
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1.0
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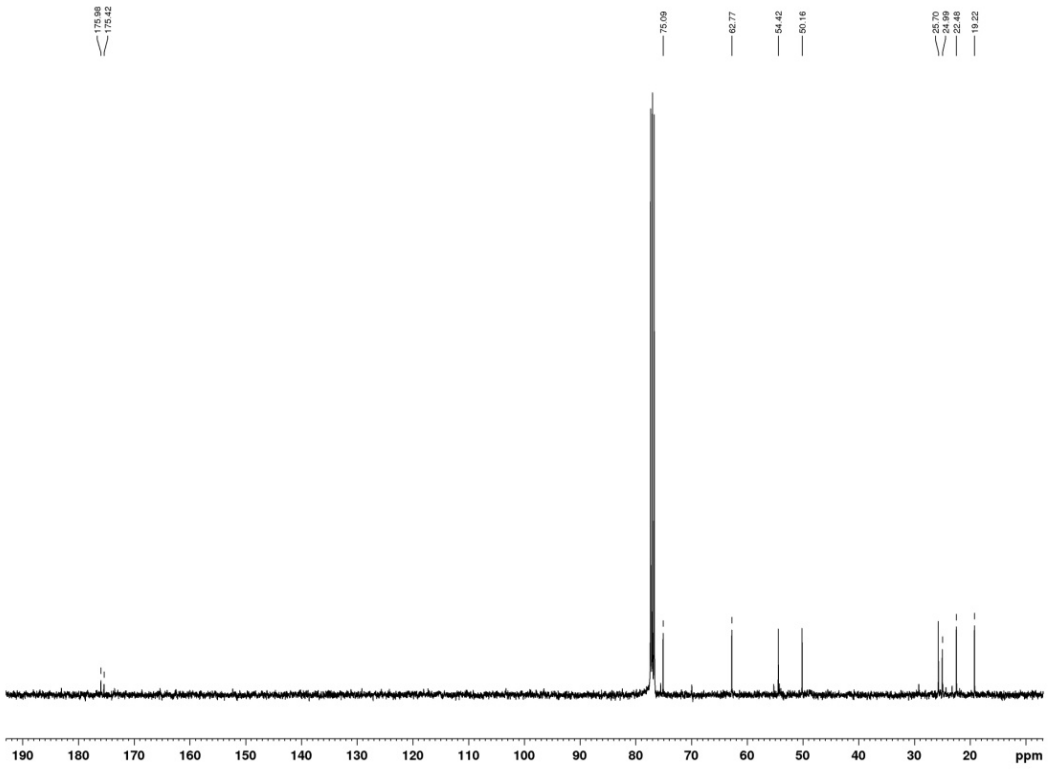
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80
70
60
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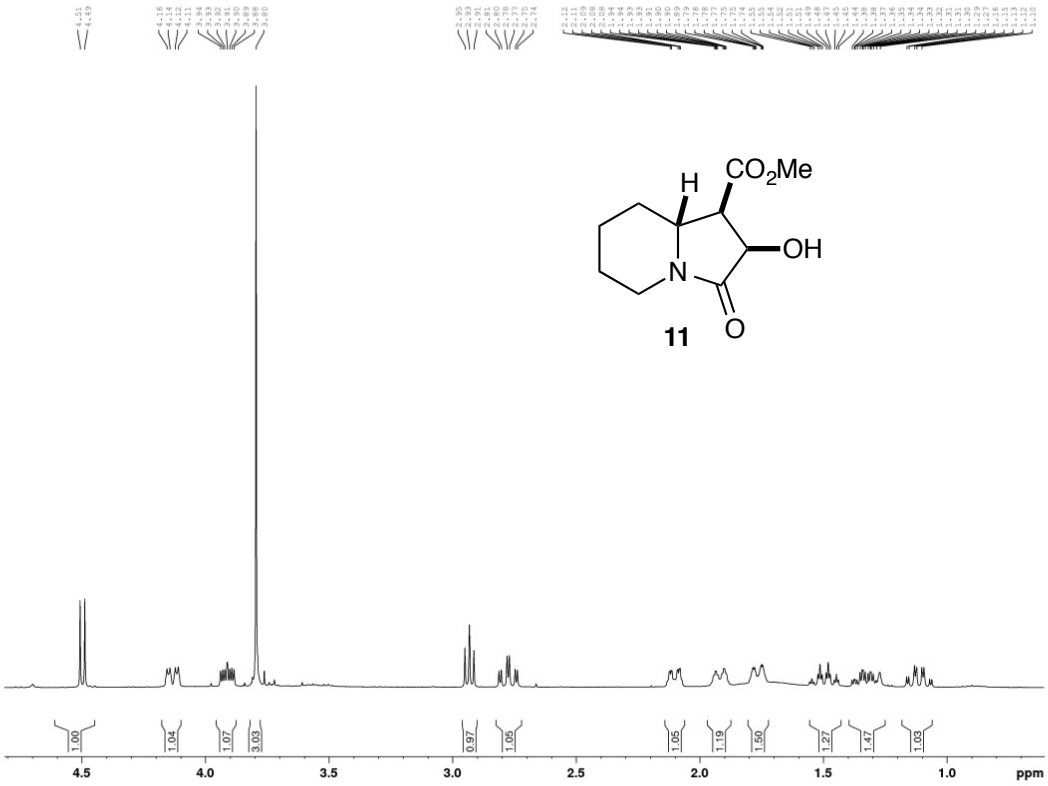
40
30
20
ppm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OH
N
O
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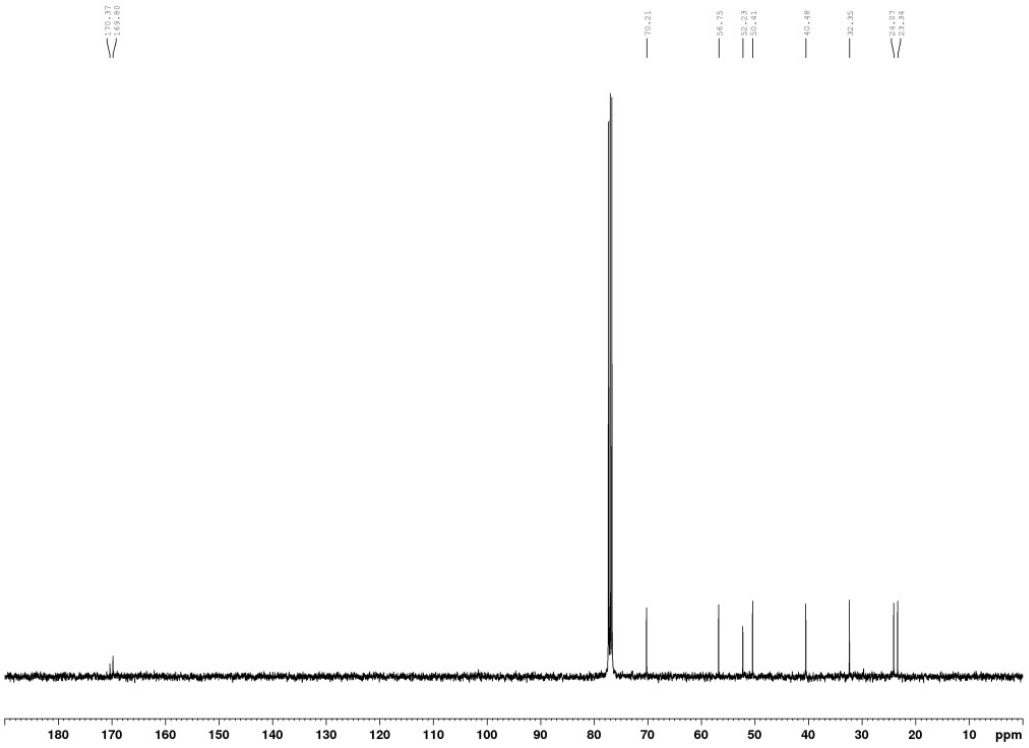
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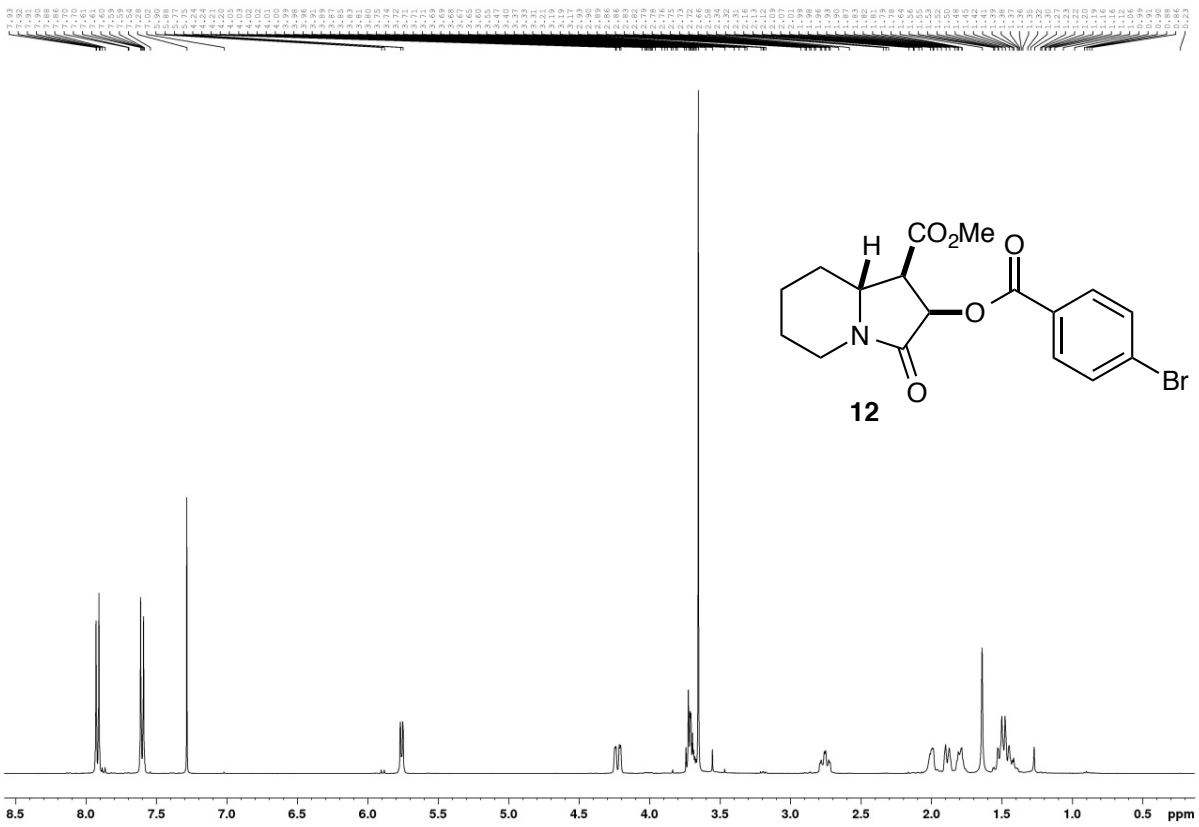
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N
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Br
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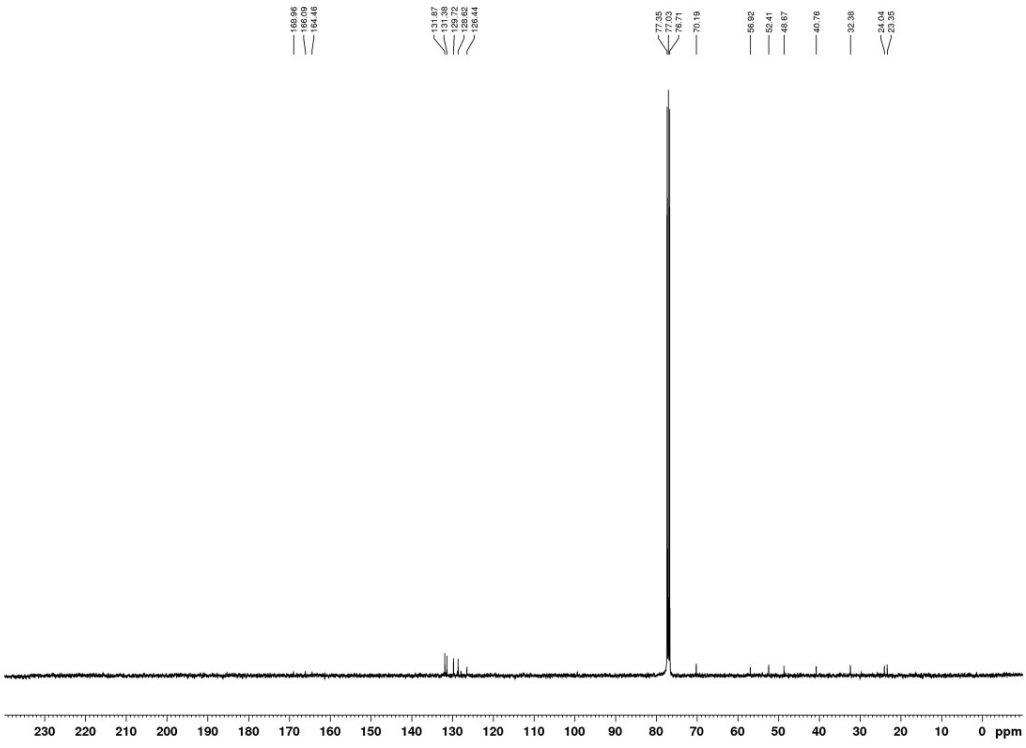
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32.38
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190
180
170
160
150
140
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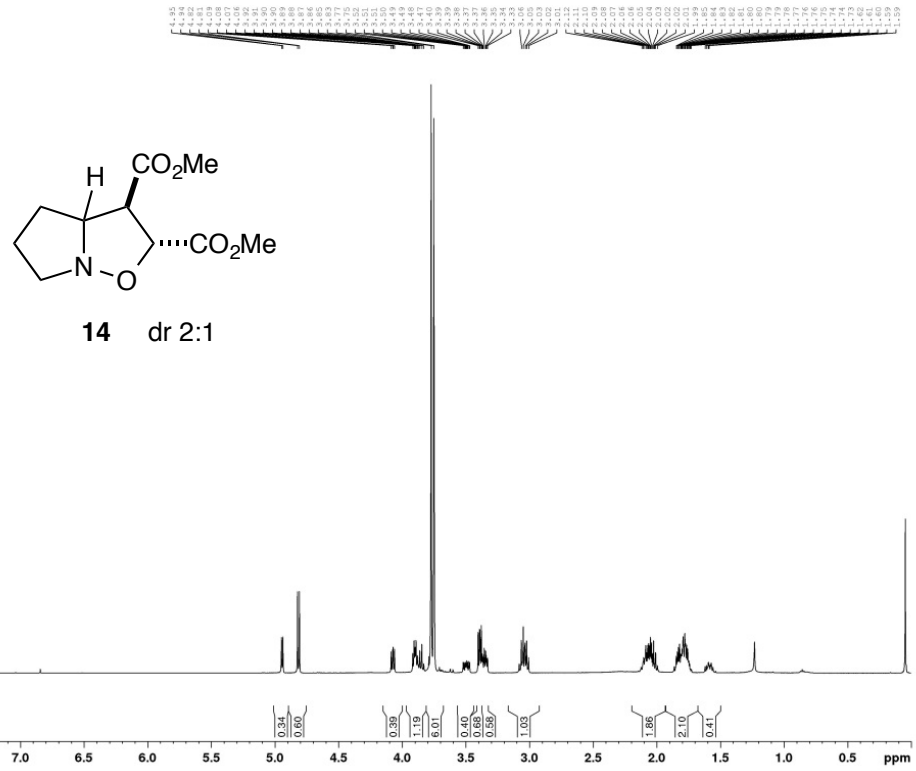
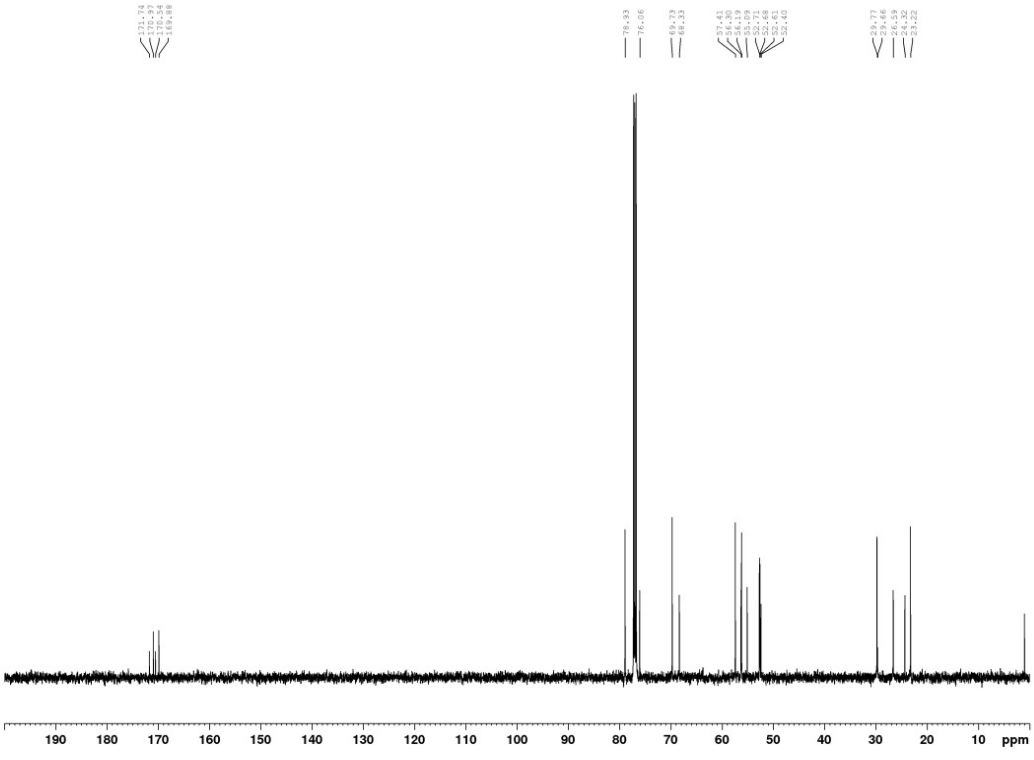
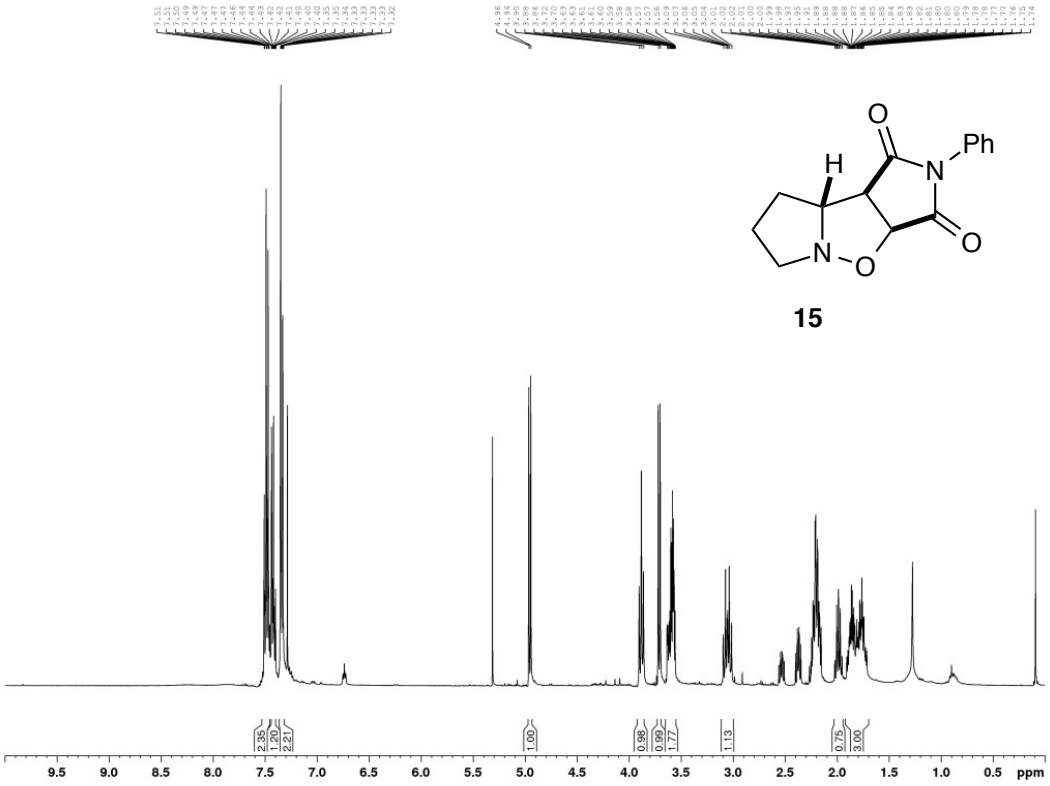
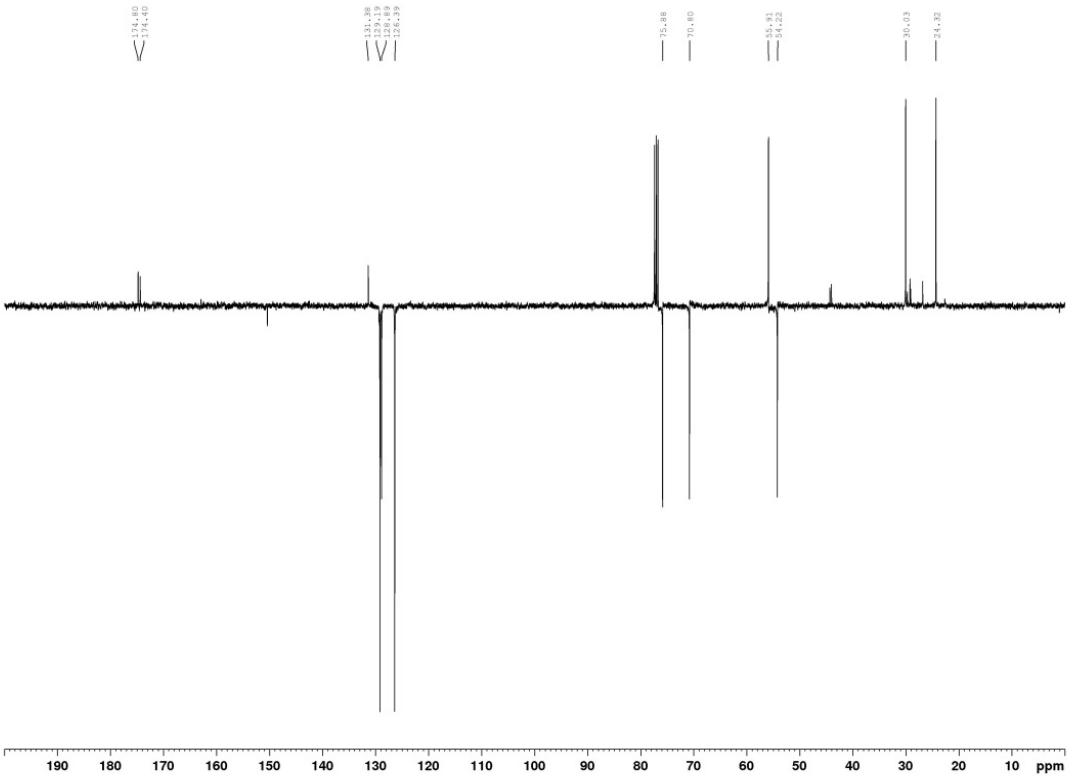
50
40
30
20
10
0
ppm


H
CO2Me
CO2Me
N
O
14 dr 2:1
0.34
0.60
0.39
1.19
6.01
0.40
0.68
0.58
1.03
1.86
2.10
0.41
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

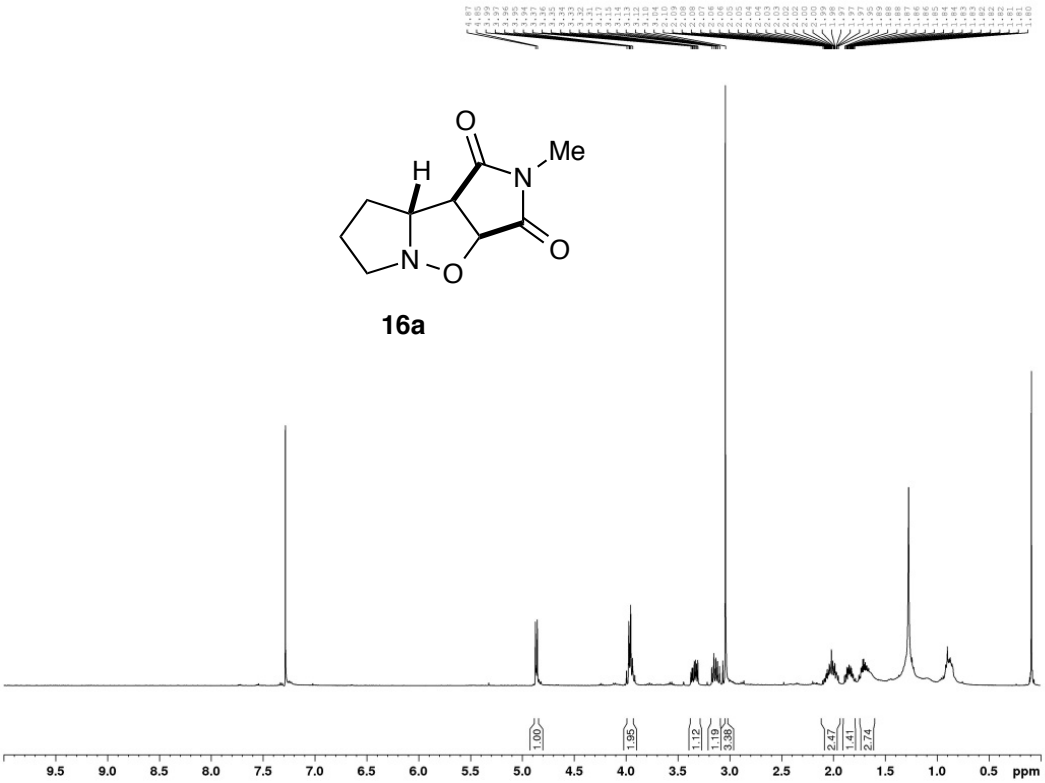

O
Ph
H
N
O
N
O
2.35
1.20
2.21
1.00
0.98
0.99
1.77
1.13
0.75
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

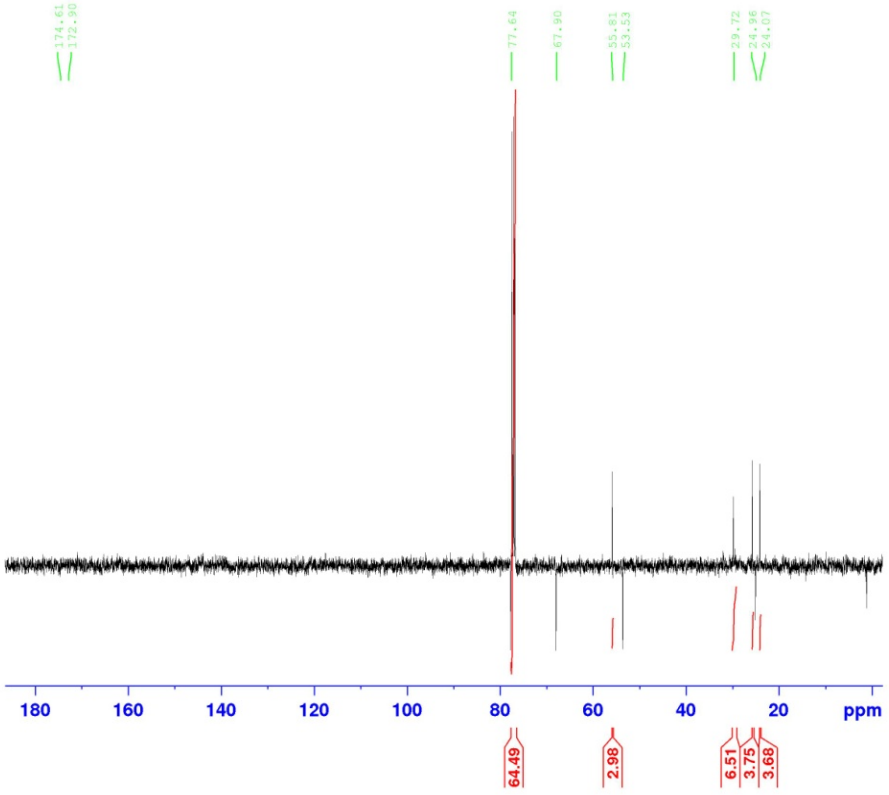
15

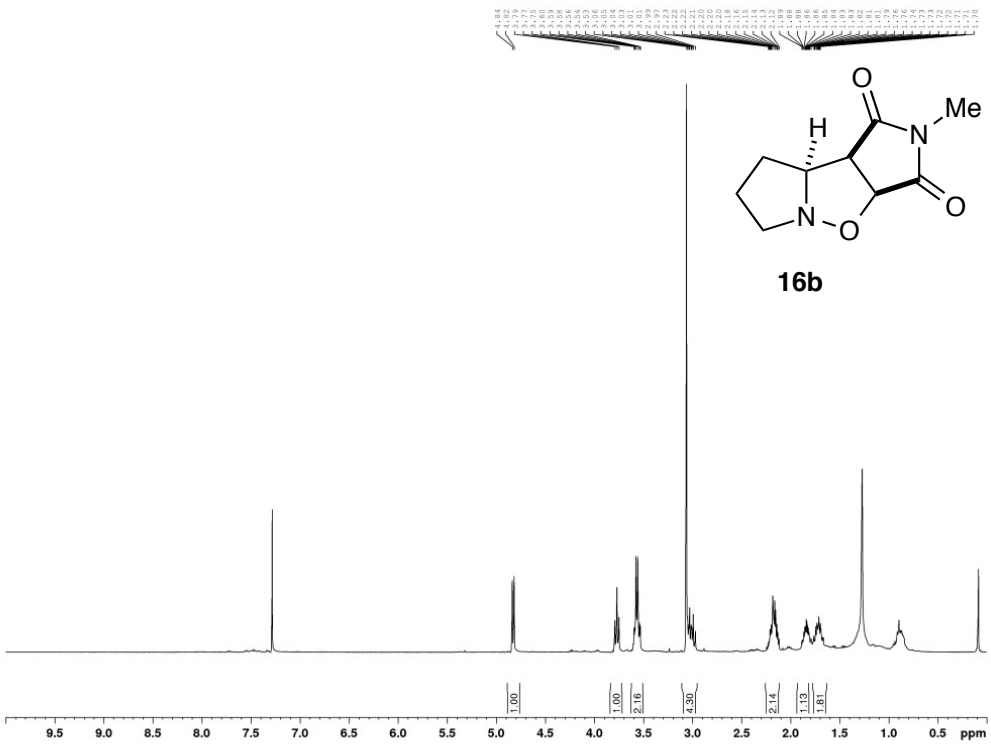

174.80
174.40
131.38
129.19
128.39
75.88
70.80
55.91
54.22
30.03
24.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

O
Me
H
N
O
N
O

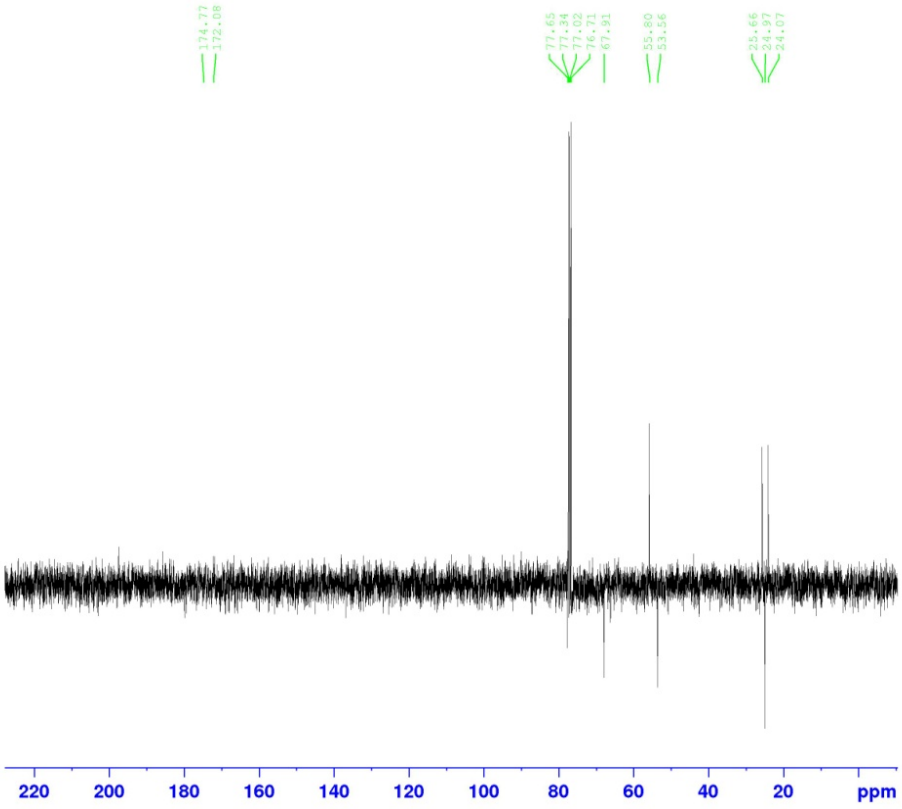
16a

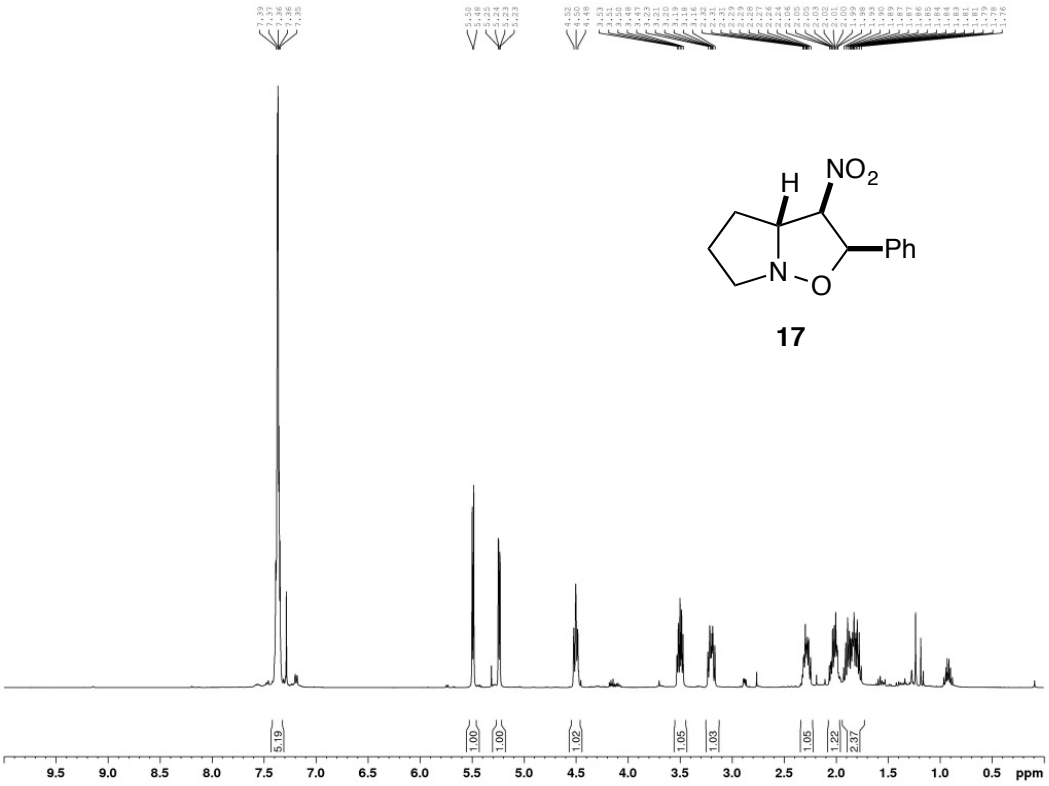

1.00
1.95
1.12
1.19
3.38
2.47
1.41
2.74
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

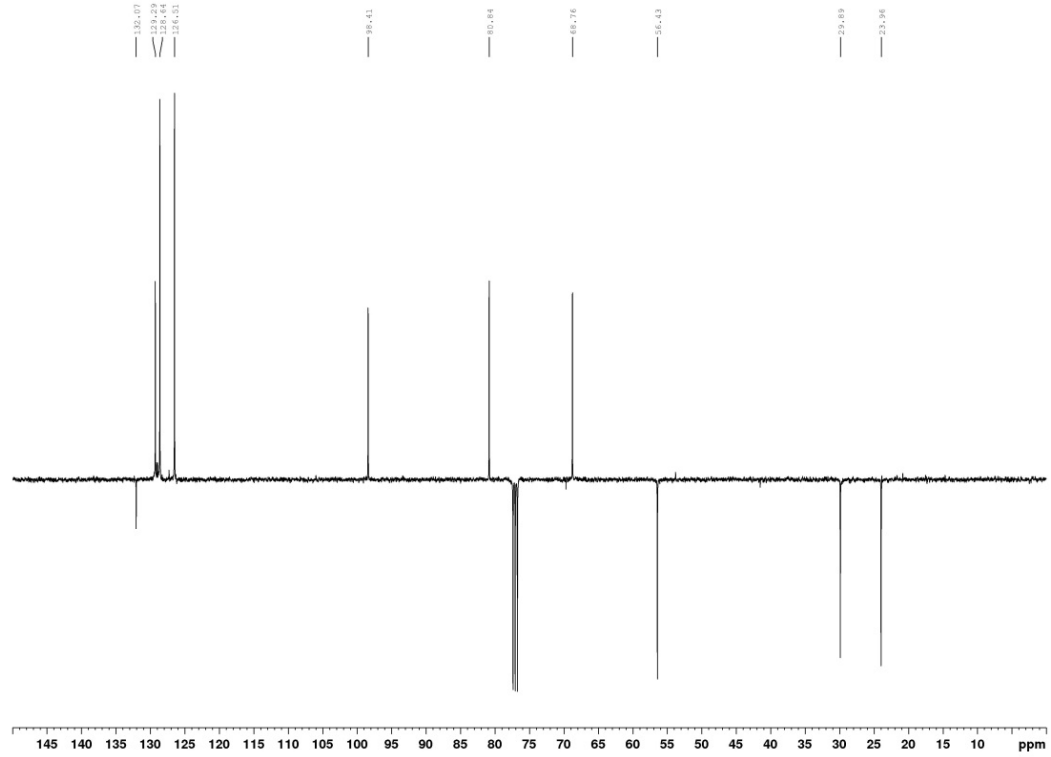

174.61
172.90
77.64
67.90
55.81
53.53
29.72
24.96
24.07
180 160 140 120 100 80 60 40 20 ppm
64.49
2.98
6.51
3.75
3.68

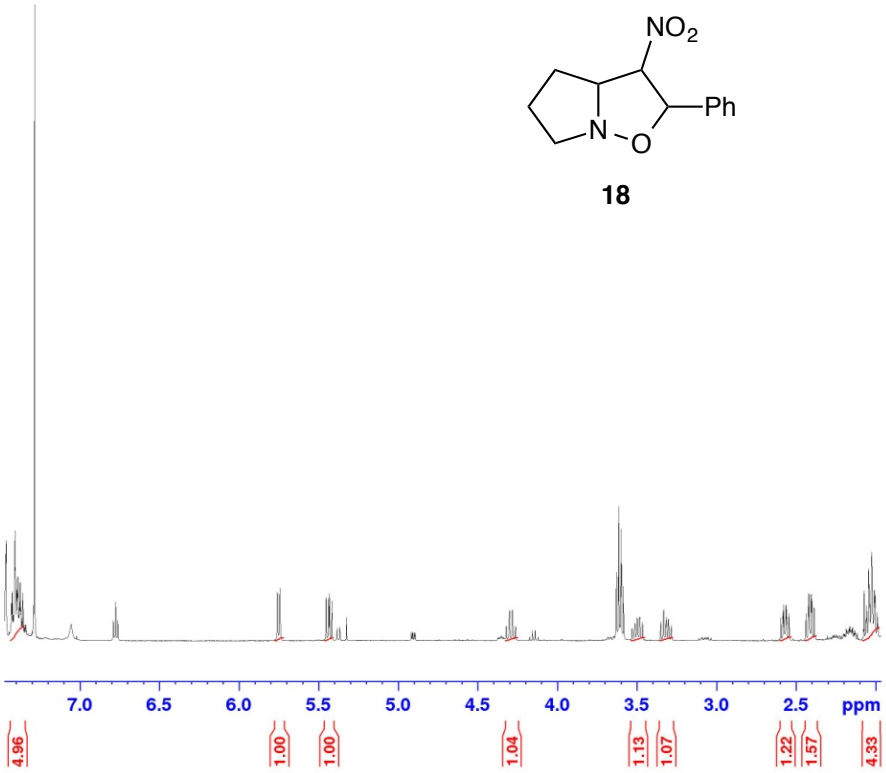

O
Me
H
N
O
N
O
1.00
1.00
2.16
4.30
2.14
1.13
1.61
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

16b

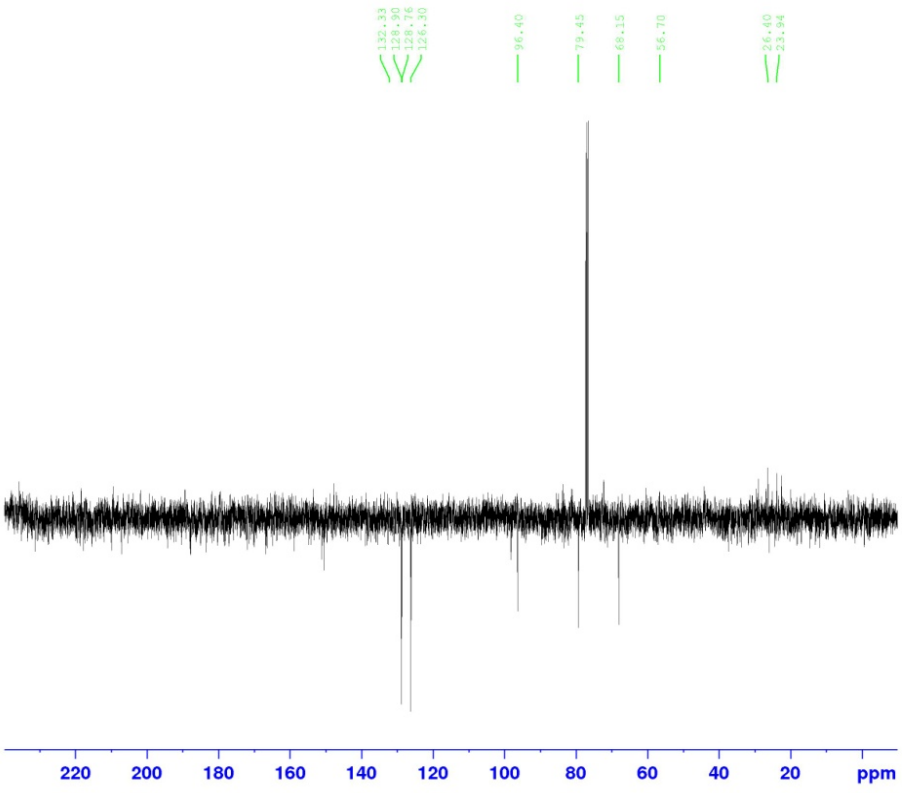

174.77
172.08
77.65
77.34
77.02
76.71
67.91
55.80
53.56
28.66
24.97
24.07
220 200 180 160 140 120 100 80 60 40 20 ppm

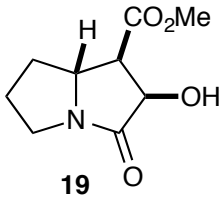

NO2
H
Ph
N
O
17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


132.07
129.29
128.64
126.51
98.41
80.84
68.76
56.43
29.89
23.96
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 ppm

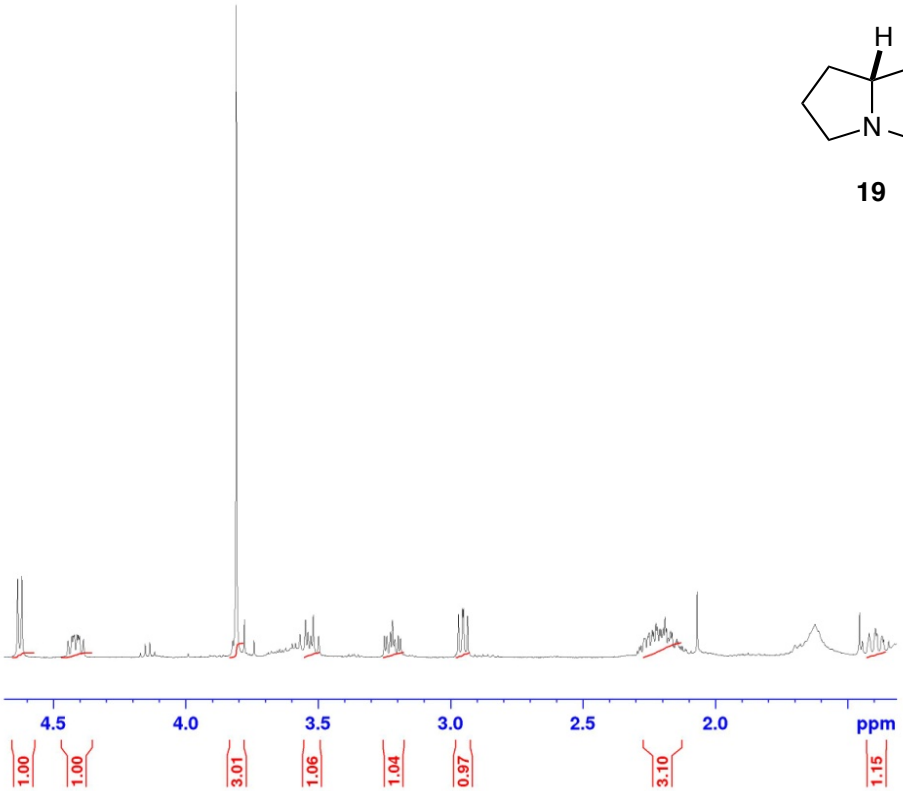


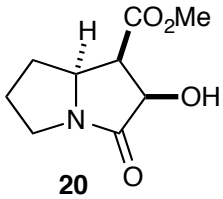
(note: compound **18** is difficult to purify)



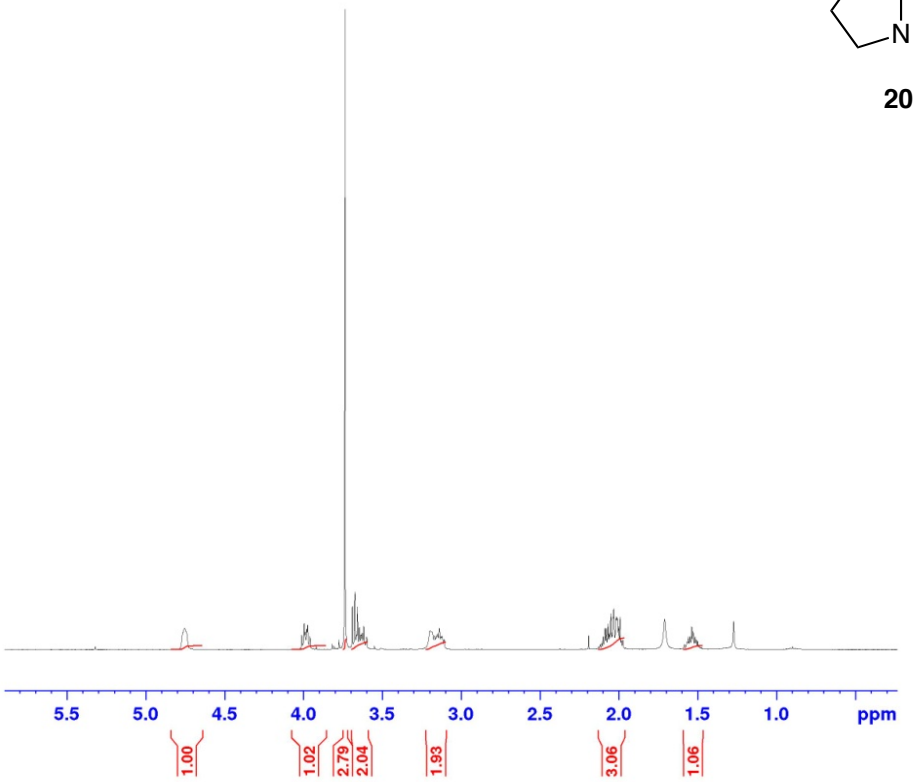

H
CO2Me
OH
N
O

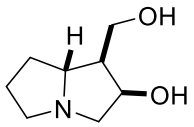
19


4.5
4.0
3.5
3.0
2.5
2.0
ppm
1.00
1.00
3.01
1.06
1.04
0.97
3.10
1.15

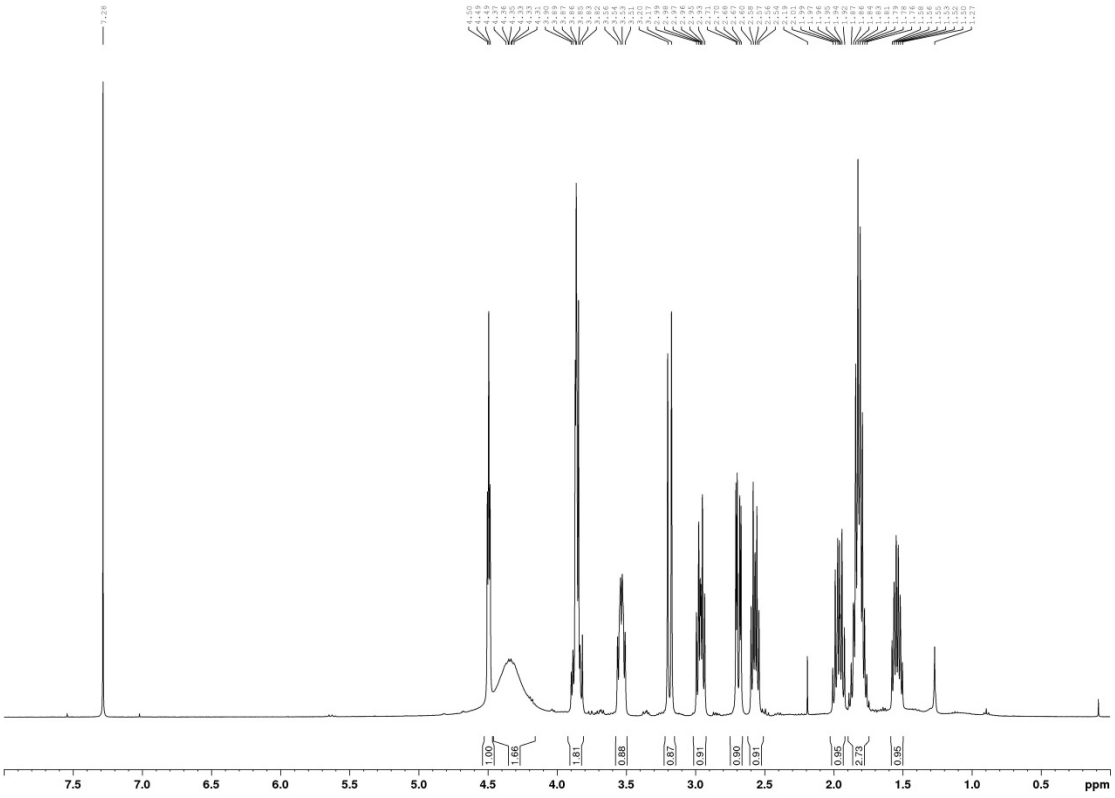

H
CO2Me
OH
N
O

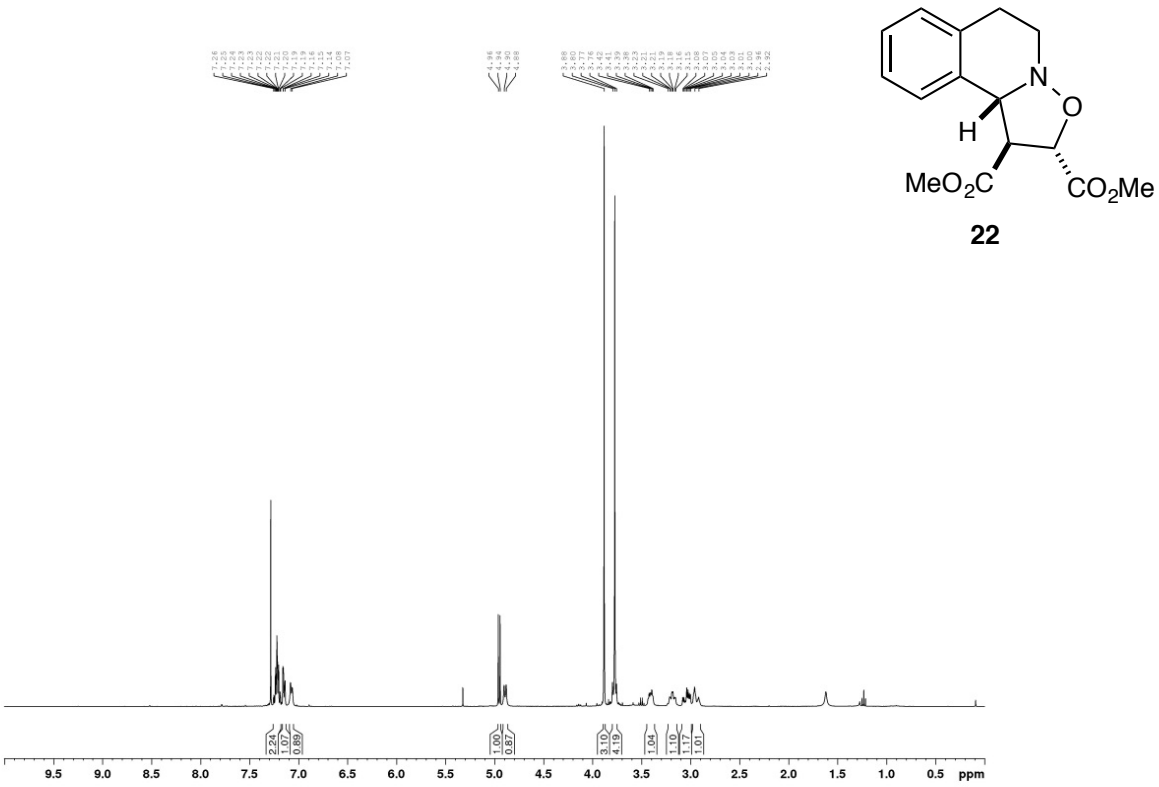
20


5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
2.79
2.04
1.93
3.06
1.06



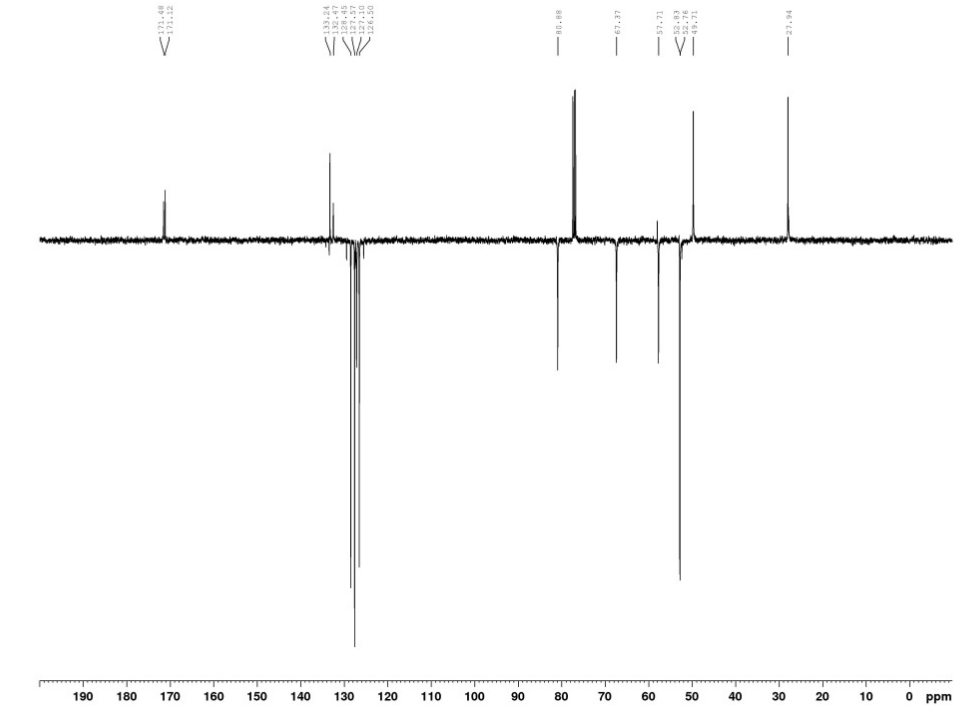
macronecine

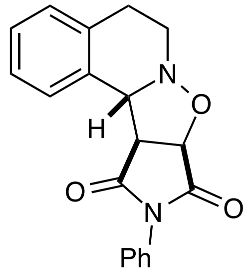



N
O
H
MeO2C
CO2Me

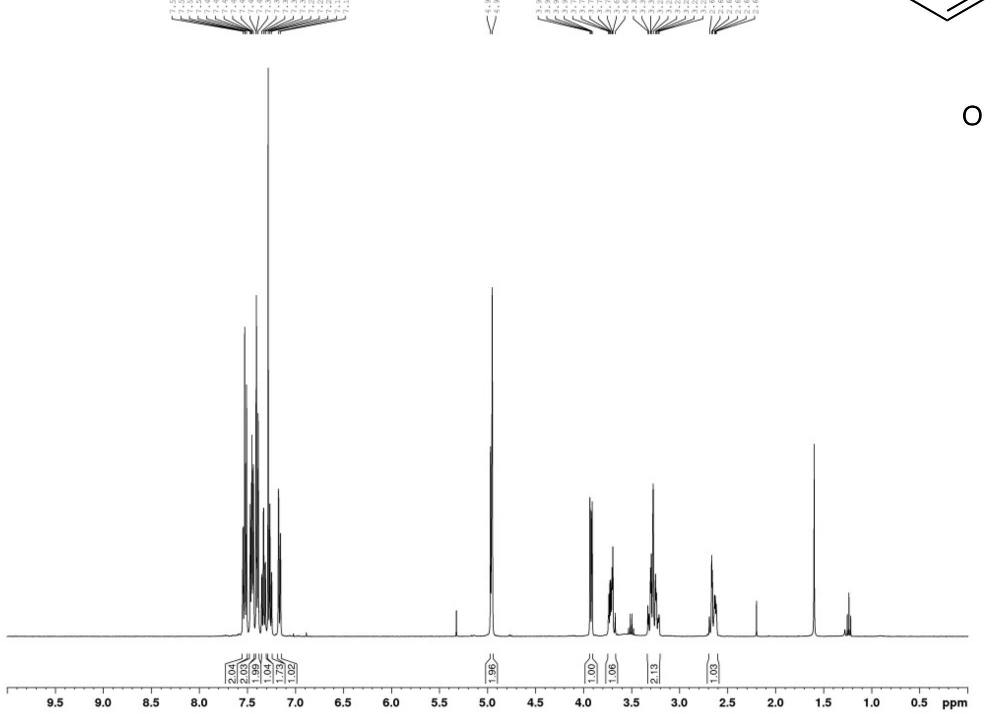
22

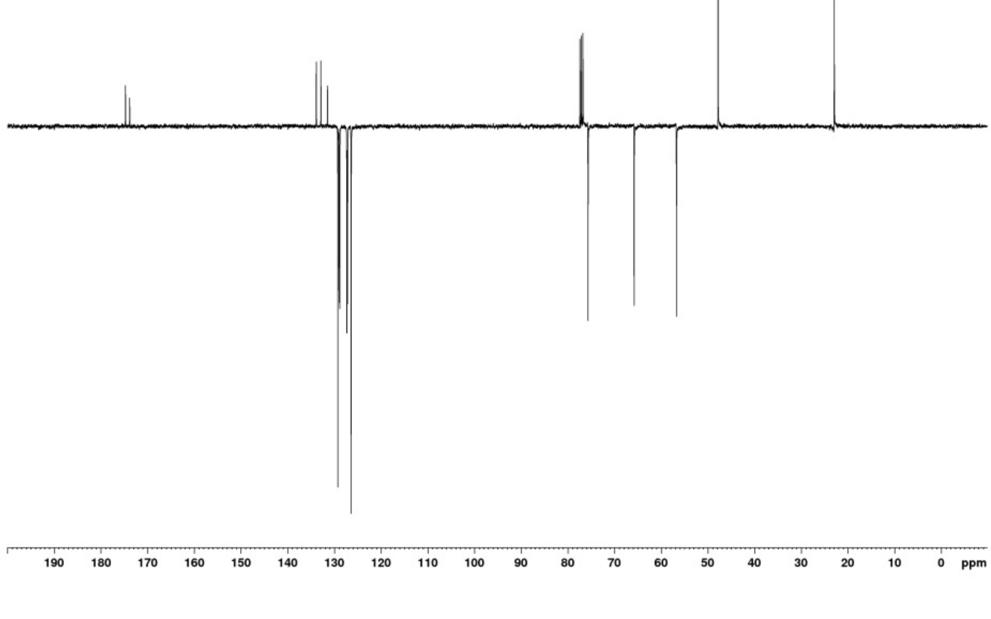
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

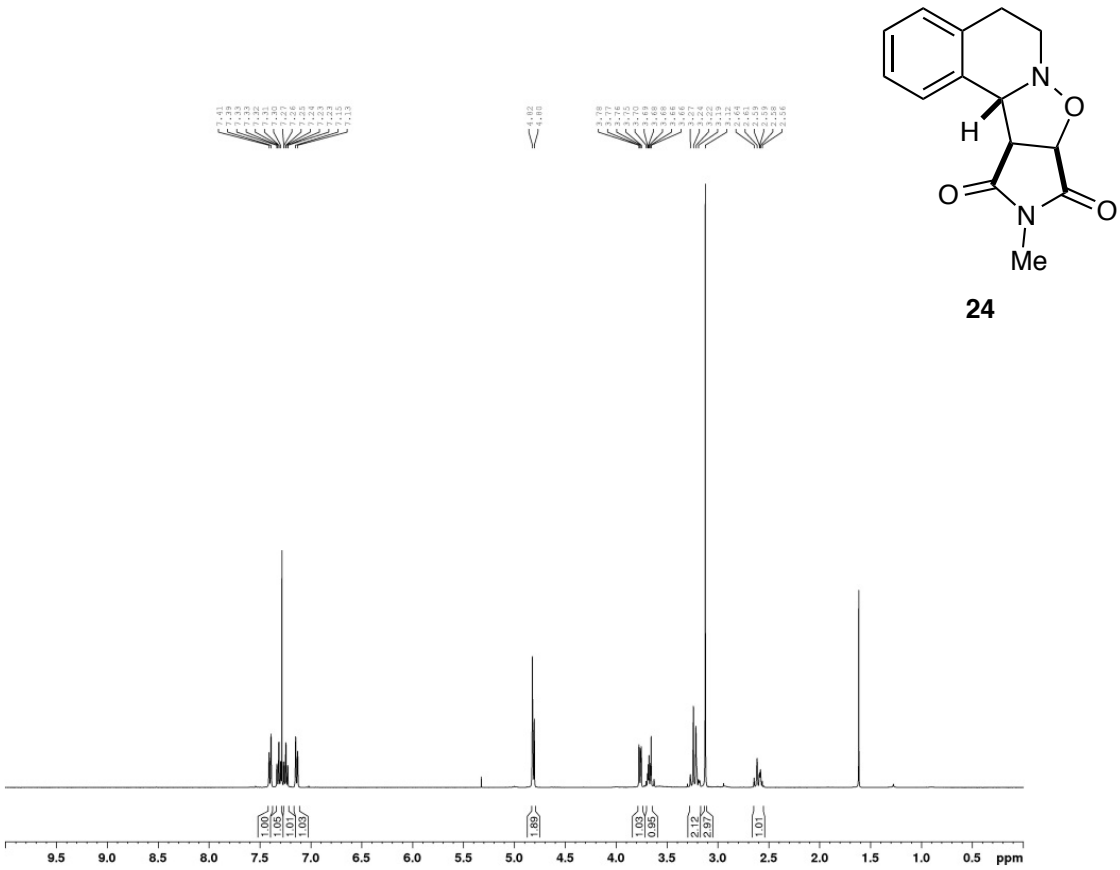

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
O
H
O
N
O
Ph

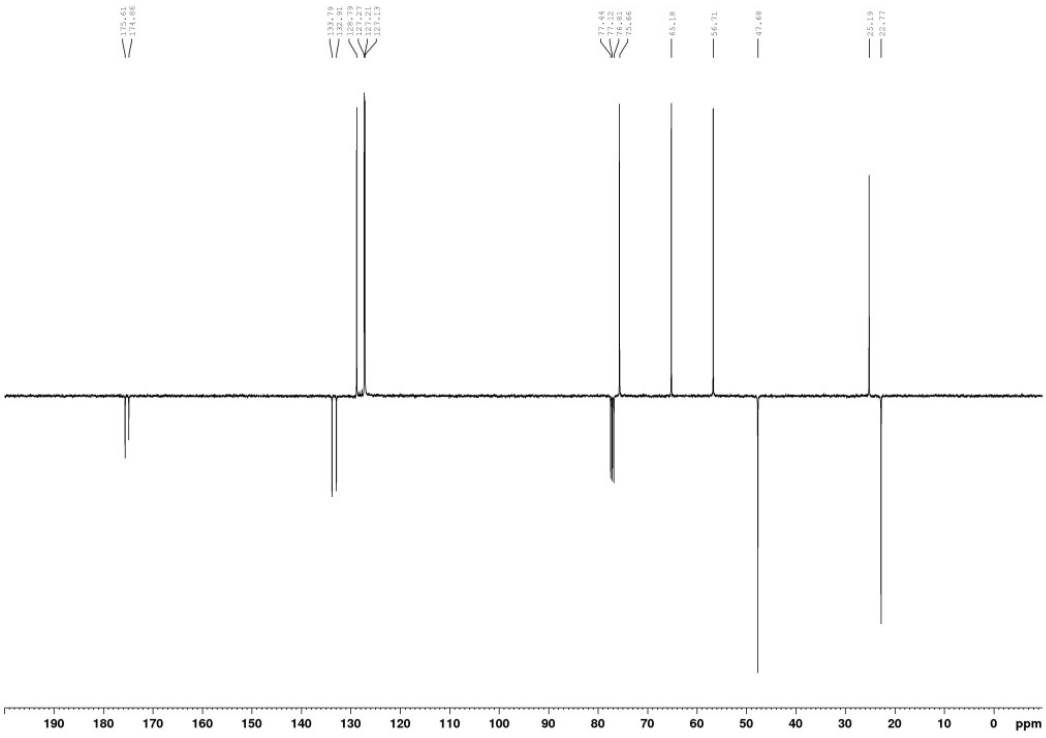
23

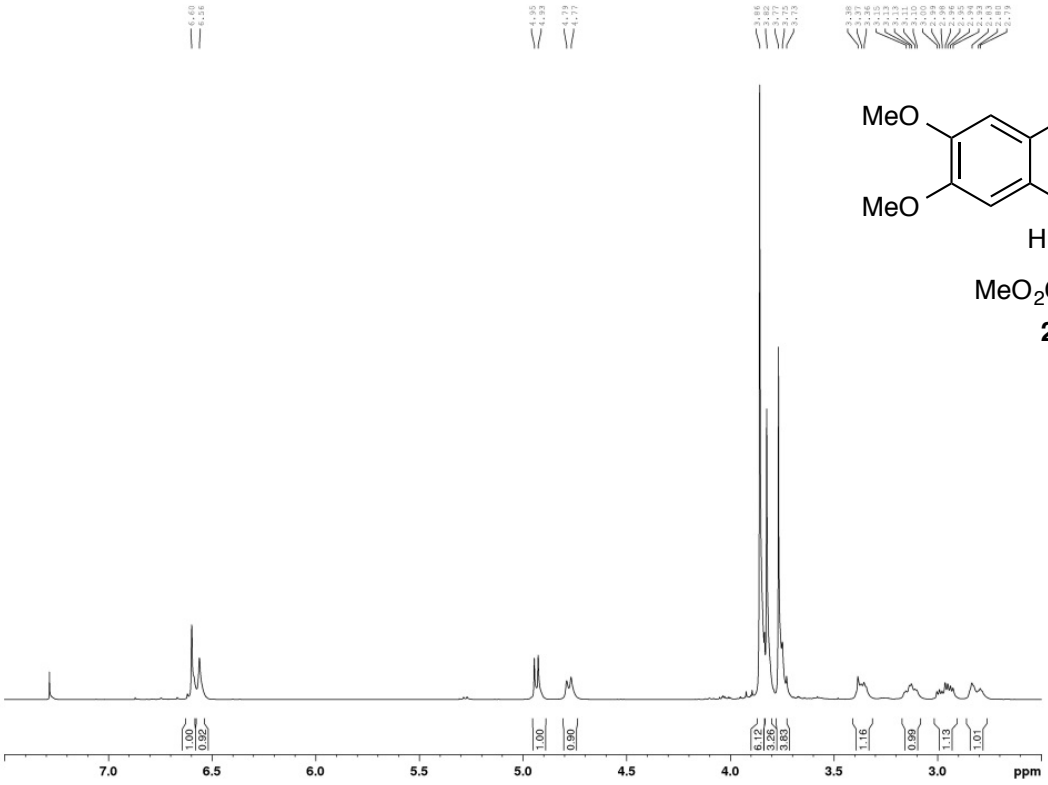

2.04
2.03
1.99
1.04
1.73
1.02
1.96
1.00
1.06
2.13
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

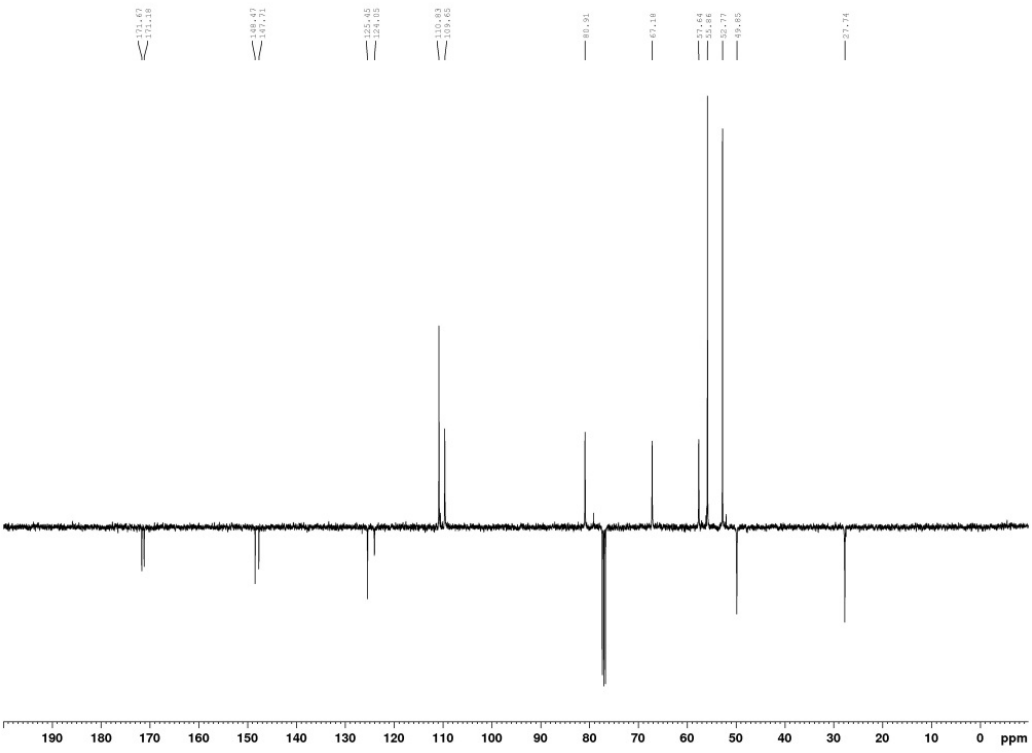

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

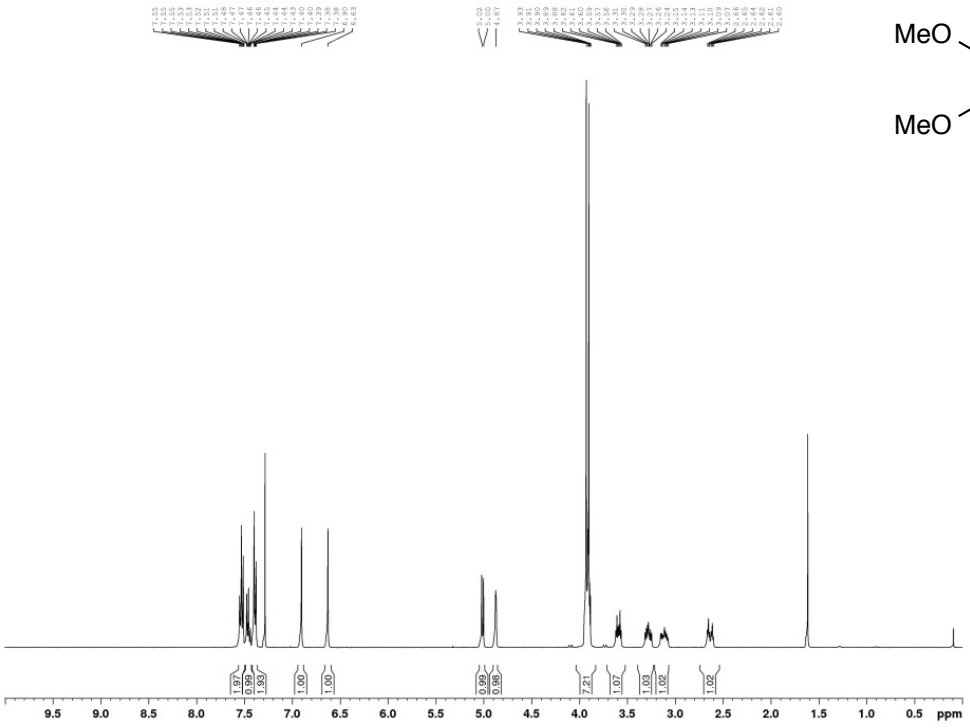


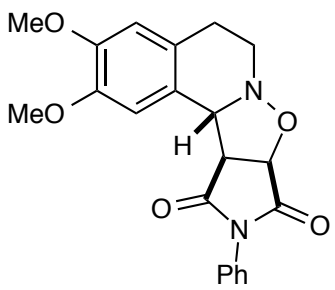
24



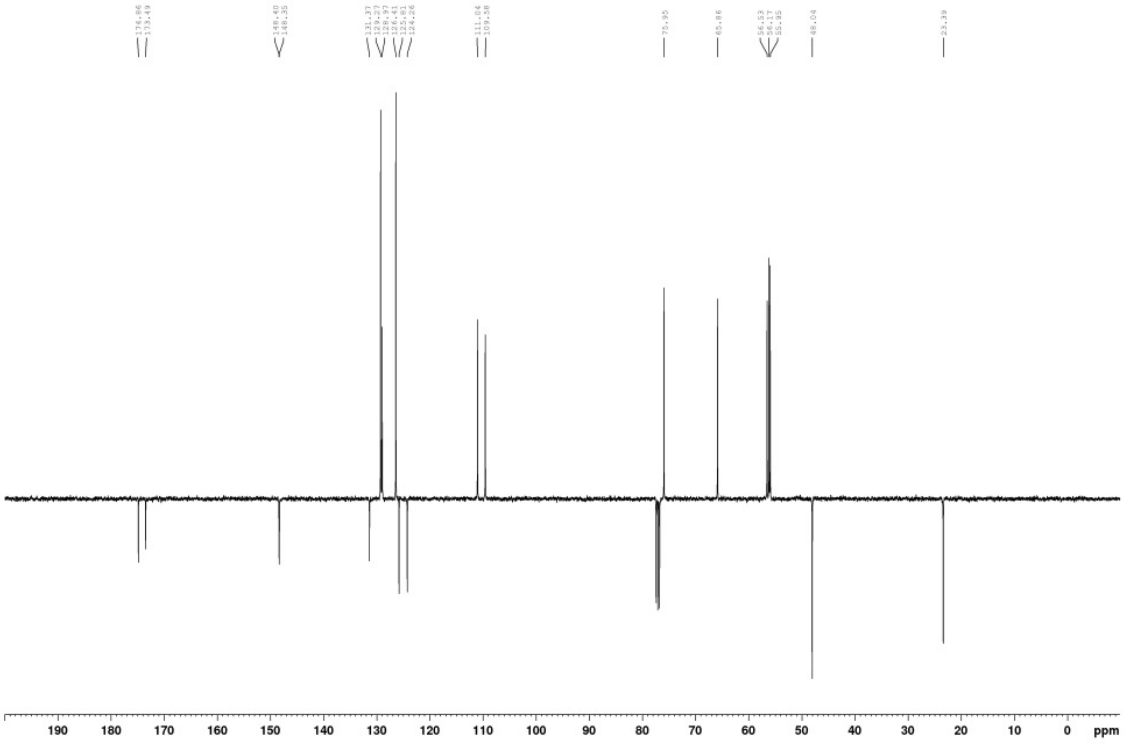

MeO
MeO
N
O
H
MeO2C
CO2Me
26
ppm

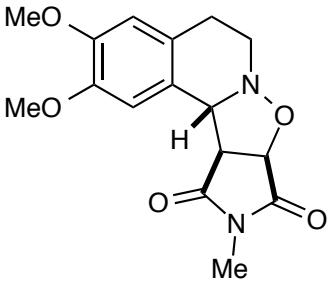

ppm



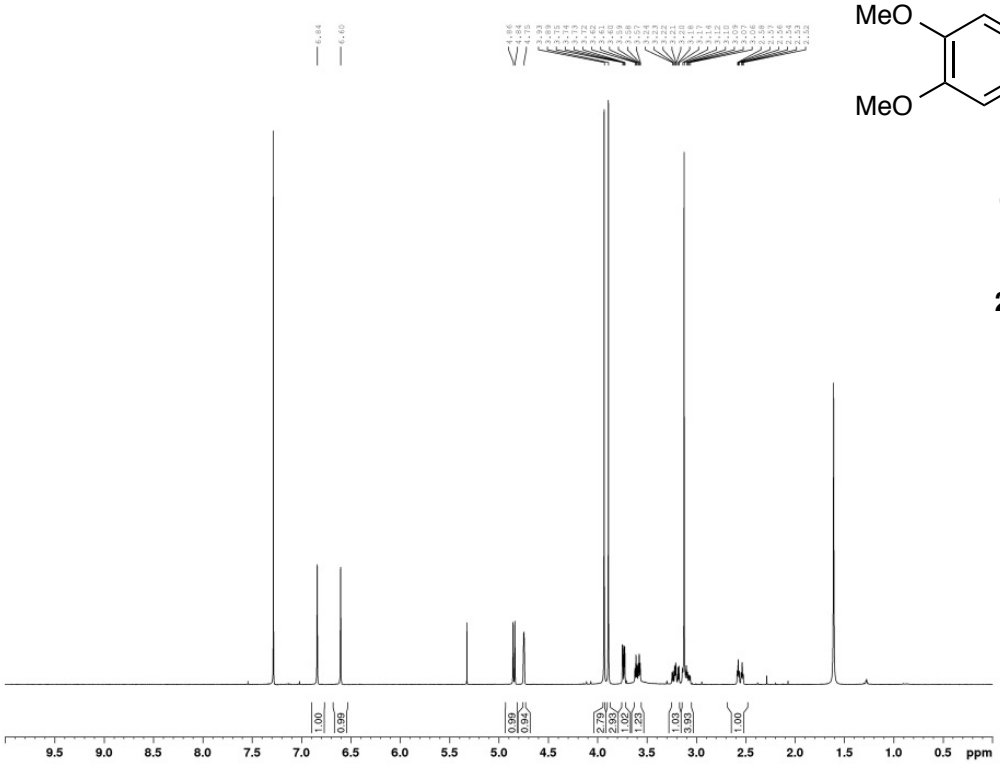


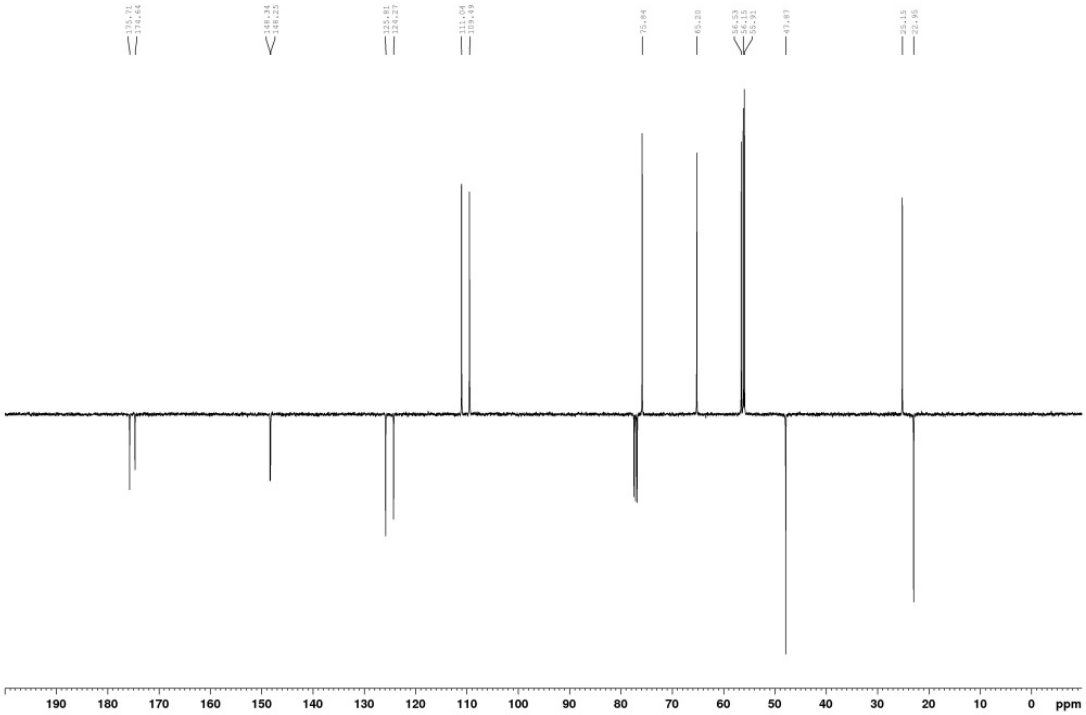
27

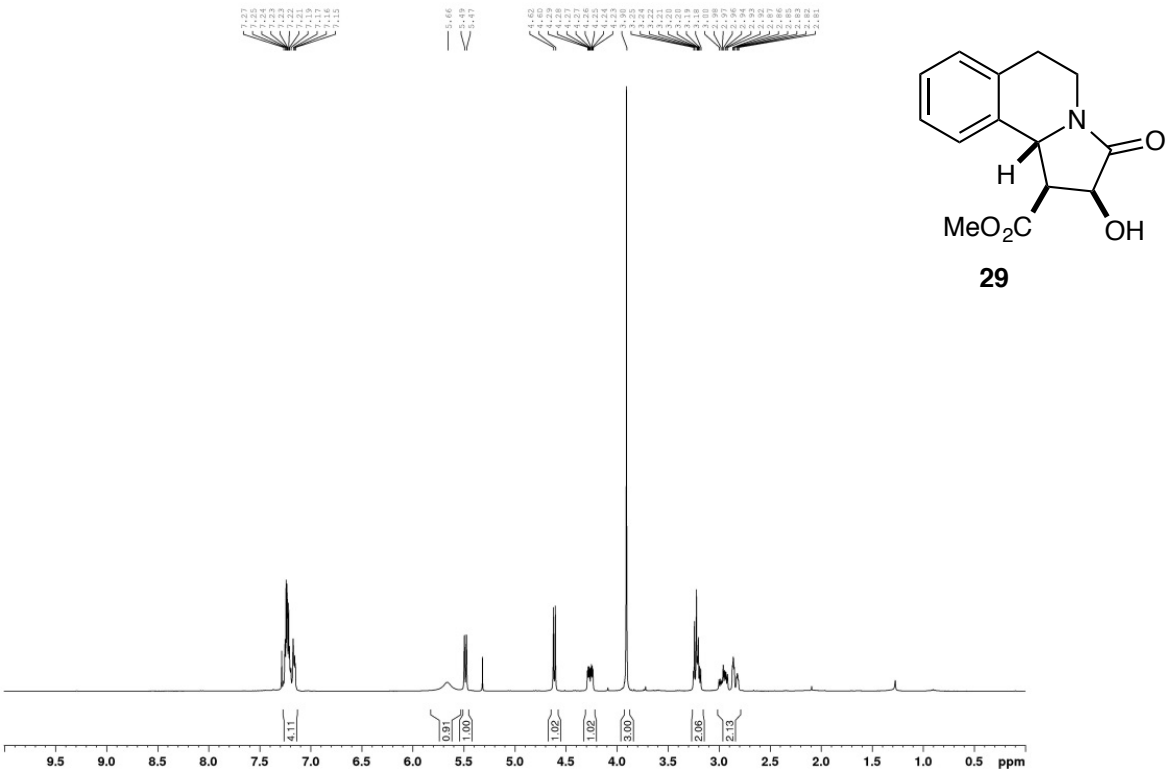



MeO
MeO
N
O
H
O
N
O
Me

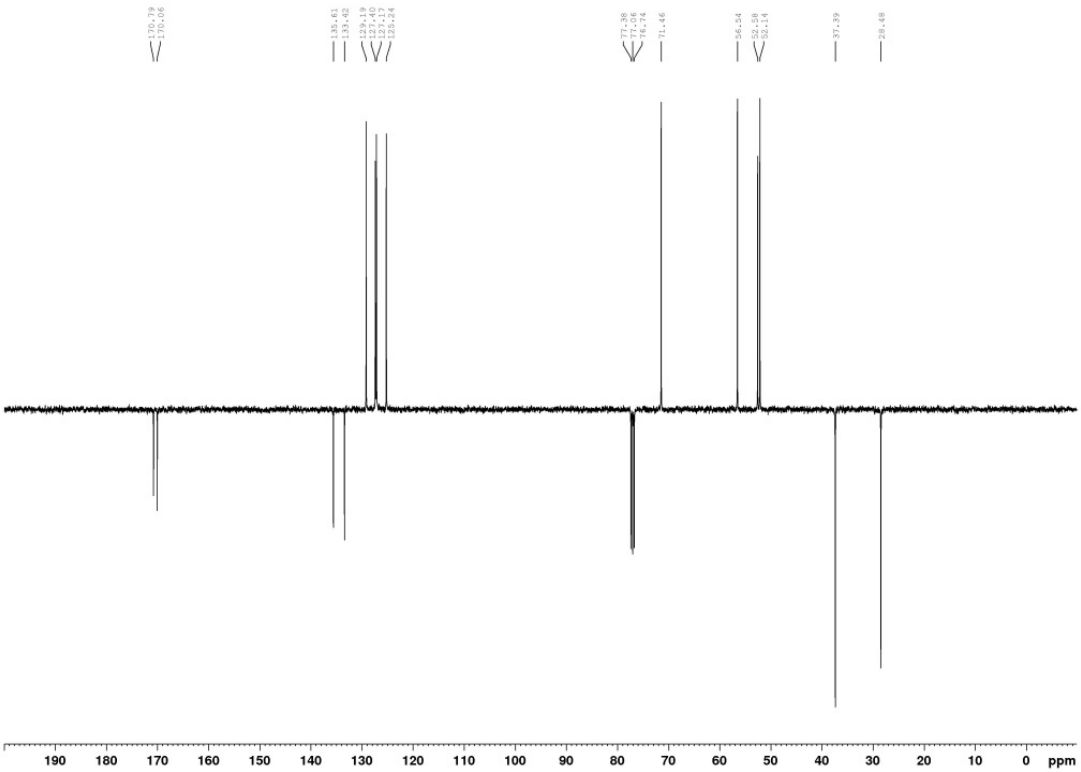
28

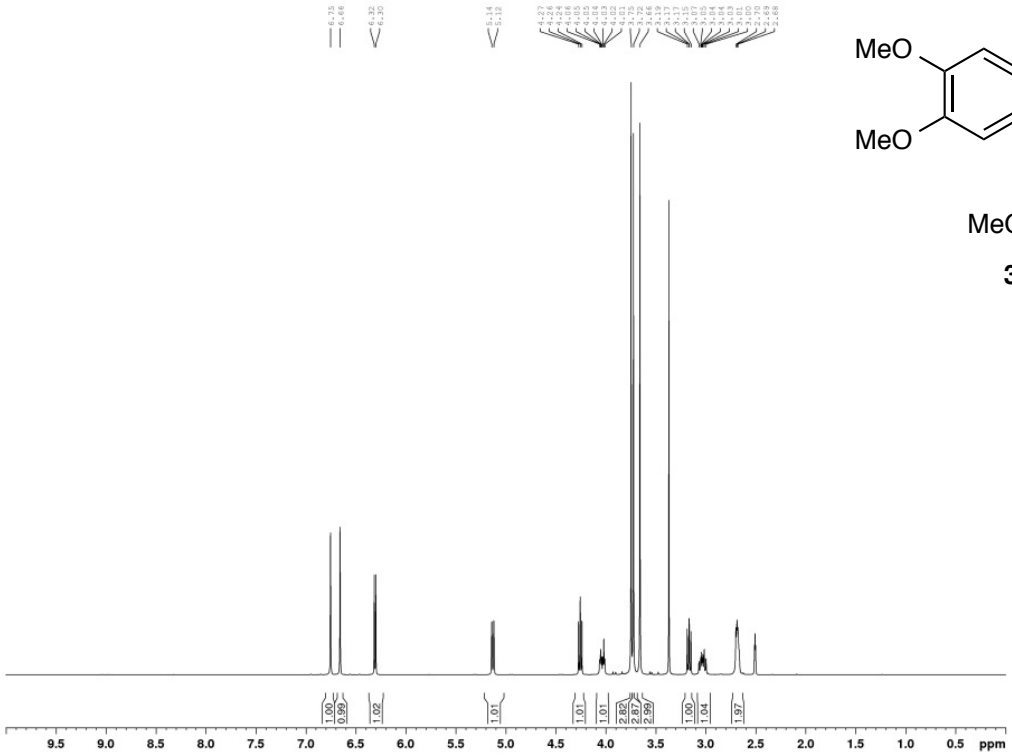

6.84
6.80
1.00
0.99
0.99
0.94
2.79
2.93
1.02
1.23
1.03
3.90
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



29





30