Supporting Information

Synthesis of the spiroimine fragment of portimines A and B

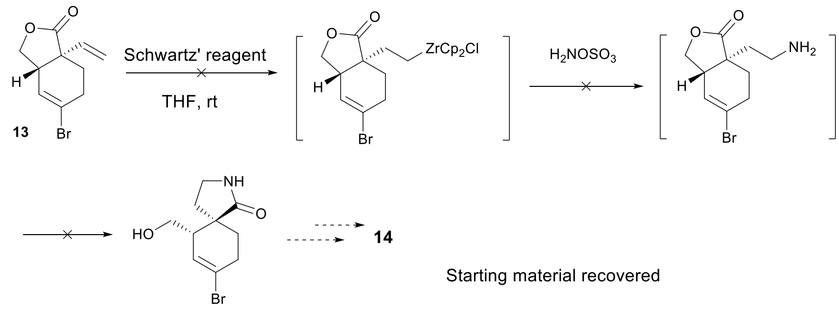
Xiao-Bo Ding,[a,b] Alexander Wung,[a] Daniel P. Furkert,[a,b] Margaret A. Brimble*[a,b]

[a] School of Chemical Sciences, The University of Auckland, 23 Symonds Street, Auckland, 1010, New Zealand
[b] The Maurice Wilkins Centre for Molecular Biodiscovery, The University of Auckland, 3 Symonds Street, Auckland, 1010, New Zealand

1. Attempted functionalization of terminal alkene **13** S2
2. Reduction of the olefin of nitroalkene **15** S3
3. Optimisation of conditions for enzymatic resolution of alcohol **11** S4
4. HPLC spectra S4
5. X-ray crystallographic data for (+)-**11** S6
6. NMR spectra S8

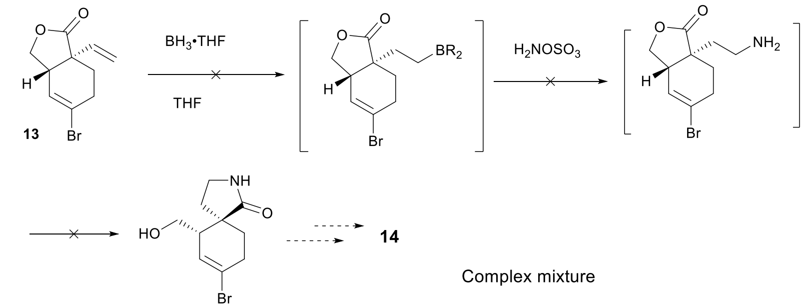
1. Failed trials on functionalization of terminal alkene **13**.

A. Hydrozirconation/amination [1]



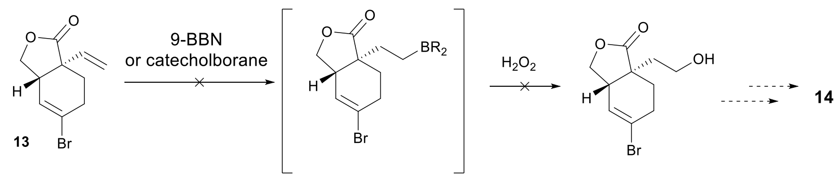
Starting material recovered

B. Brown's hydroboration/amination [2]



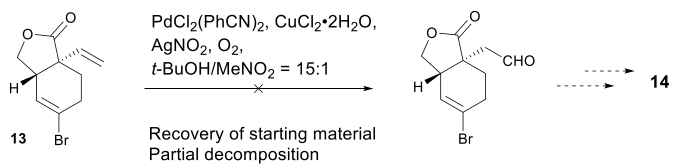
Complex mixture

C. Hydroboration/oxidation

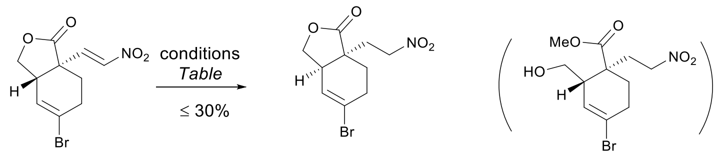


Recovery of starting material
Partial decomposition

D. Wacker-type oxidation [3]



2. Reduction of the double bone of nitroalkene **15**.



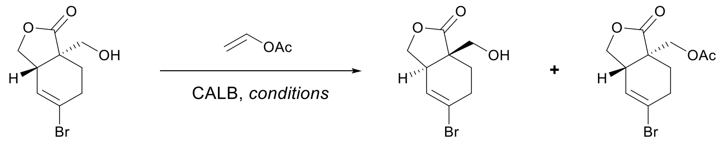
15 **16** **S1**

Entry	Conditions	Results
1	$NaBH_4$, MeOH, 0 °C to rt	15% **16** + 15% **S1** + decomposition
2	$NaBH_4$, MeOH/THF, 0 °C to rt	15% **16** + **S1** + decomposition
3	$NaBH_4$, ^{i}PrOH/DCM, 0 °C to rt	20% **16** + decomposition
4	Bu_3SnH, MeOH/DCM [4]	decomposition
5	Hantzsch ester, toluene, silica, reflux [5]	No reaction
6	$NaBH_3CN$, MeOH, 0 °C	25% **16** + decomposition
7	$NaBH_3CN$, THF, 0 °C	30% **16** + decomposition
8	$NaBH(OAc)_3$, THF, 0 °C to reflux	No reaction
9	$NaBH(OAc)_3$, MeOH, 0 °C to reflux	Slow decomposition

Note: By-product **S1** was isolated and characterised.

By-product **S1**. IR (neat) ν_{max} 3340, 2952, 1723, 1553, 1383, 1434, 1248, 1204, 1097, 1078, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.93-5.88 (m, 1H), 4.69-4.61 (m, 1H), 4.41-4.31 (m, 1H), 3.72 (s, 3H), 3.66 (d, 2H, J = 5.9 Hz), 3.08-3.01 (m, 1H), 2.59-2.35 (m, 3H), 2.28-2.08 (m, 2H), 1.92-1.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.4, 127.3, 122.5, 72.1, 62.2,52.6, 45.5, 44.8, 32.2, 29.9, 28.9; HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{12}BrNNaO_4$ 322.1550; Found 322.1557.

3. Optimisation of conditions for enzymatic resolution of alcohol (±)-**11**.



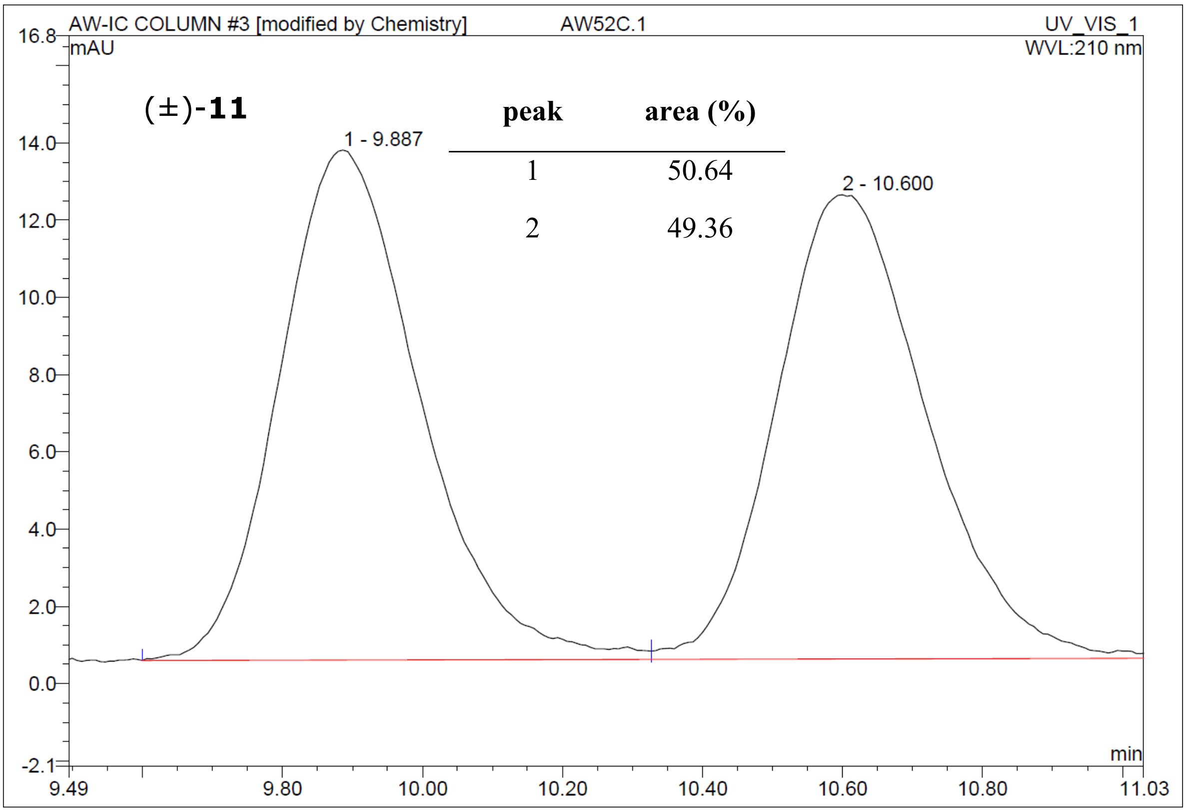
(±)-**11** (–)-**11** (+)-**25**

Entry	Solvent [a]	Temperature (°C)	Time (h)	Conversion (%) [b]
1	MeCN	25	6	trace
2	MeCN	45	48	19
3	DME	25	6	trace
4	DME	45	48	48
5	EtOAc	25	6	22
6	EtOAc	45	6	45
7	**EtOAc**	**45**	**48**	**50**
8	Acetone	25	6	11
9	Acetone	45	48	30

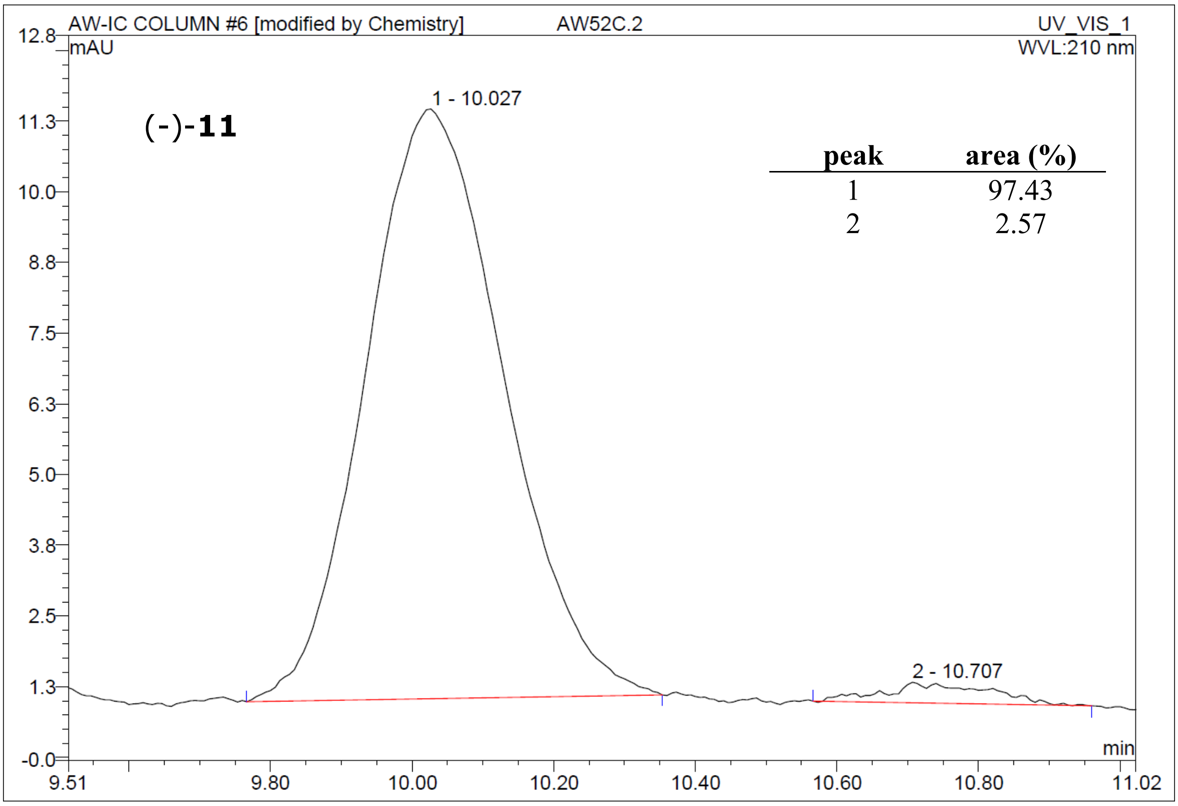
a. concentration 1 M; *b*. Conversion was determined by crude ^{1}H NMR integrations.

4. HPLC traces

Daicel 83325 CHIRALPAK® IC normal phase chiral column, mobile phase CH_2Cl_2-*i*PrOH = 99:1, flow rate 1.0 mL/min, λ = 210 nm, retention times tR(major) = 9.9 min, tR(minor) = 10.6 min; 94.0%ee.



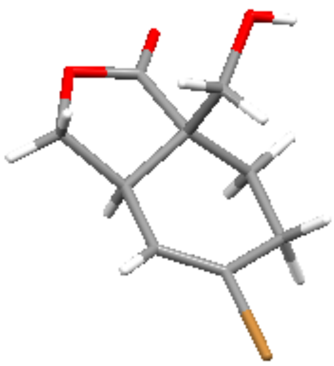
peak	area (%)
1	50.64
2	49.36



peak	area (%)
1	97.43
2	2.57

5. Crystal data and structure refinement for (-)-**11**.

The crystals suitable for X-ray analysis were prepared *via* slow evaporation of a EtOAc/petroleum ether (1:2) solution of the sample at room temperature.



Identification code	shelx	
Empirical formula	C9 H10 Br O3	
Formula weight	246.08	
Temperature	373(2) K	
Wavelength	1.54184 A	
Crystal system, space group	Monoclinic, P 21	
Unit cell dimensions	a = 7.6869(2) A	alpha = 90 deg.
	b = 5.97800(10) A	beta = 95.575(2) deg.
	c = 10.0410(2) A	gamma = 90 deg.
Volume	459.224(17) A^3	
Z, Calculated density	2, 1.780 Mg/m^3	
Absorption coefficient	5.892 mm^-1	
F(000)	246	
Crystal size	0.200 x 0.160 x 0.100 mm	
Theta range for data collection	5.783 to 68.153 deg.	
Limiting indices	-8<=h<=9, -7<=k<=7, -11<=l<=12	
Reflections collected / unique	4287 / 1634 [R(int) = 0.0168]	
Completeness to theta = 67.684	97.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1634 / 1 / 120	

Goodness-of-fit on F^2 0.977

Final R indices [I>2sigma(I)] R1 = 0.0167, wR2 = 0.0447

R indices (all data) R1 = 0.0168, wR2 = 0.0447

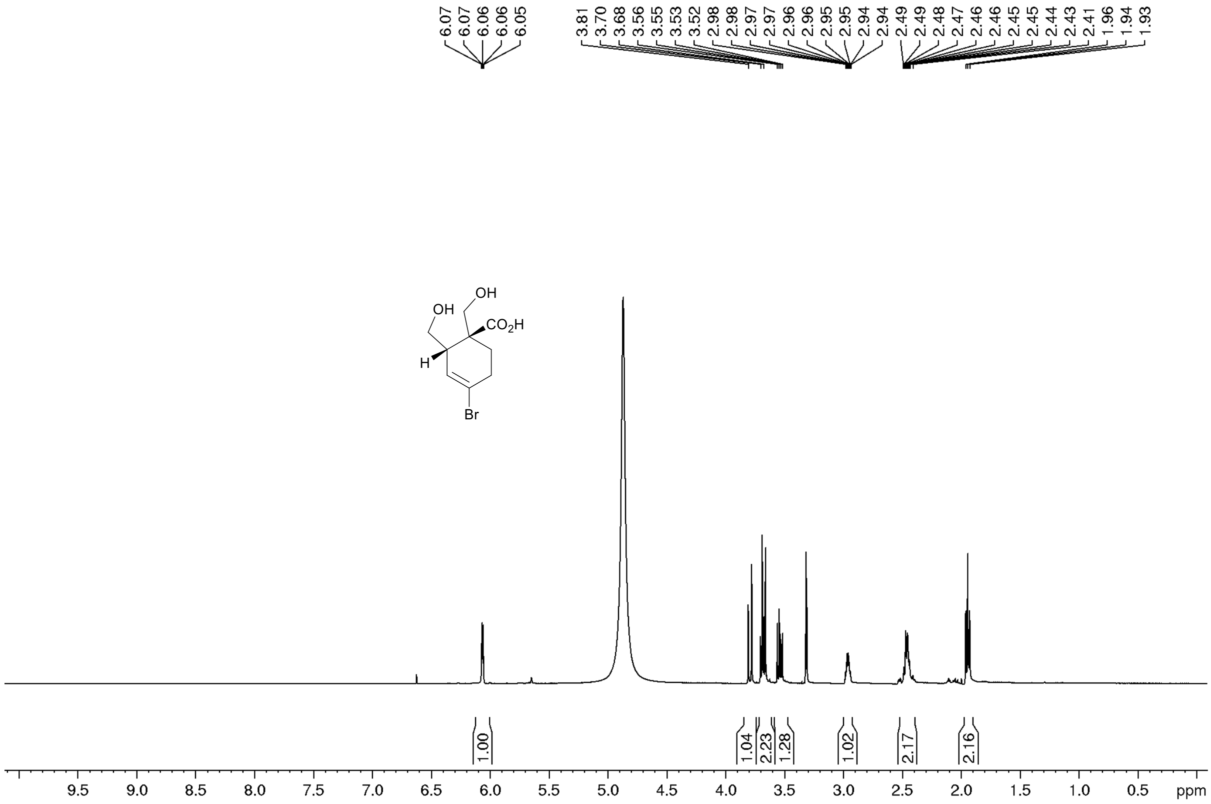
Absolute structure parameter -0.027(15)

Extinction coefficient 0.0029(4)

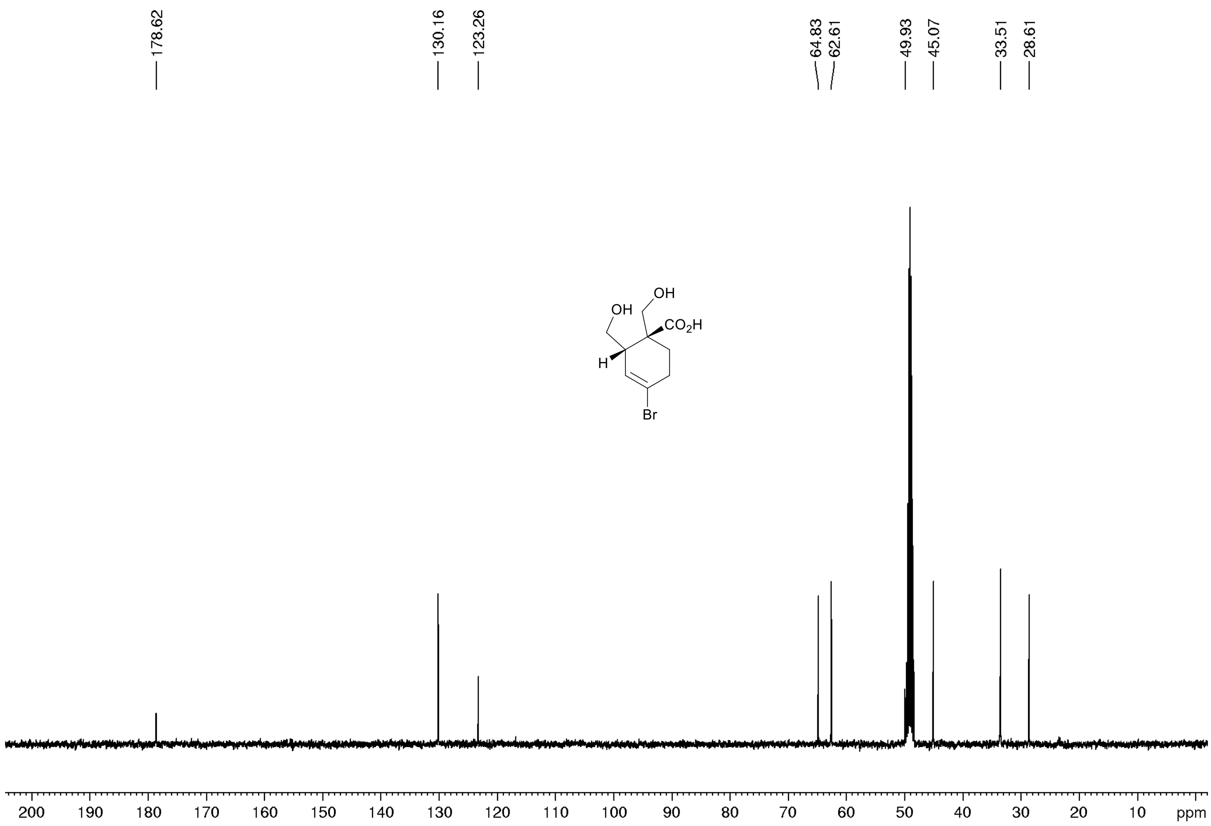
Largest diff. peak and hole 0.274 and -0.244 e.A^-3

6. NMR Spectra

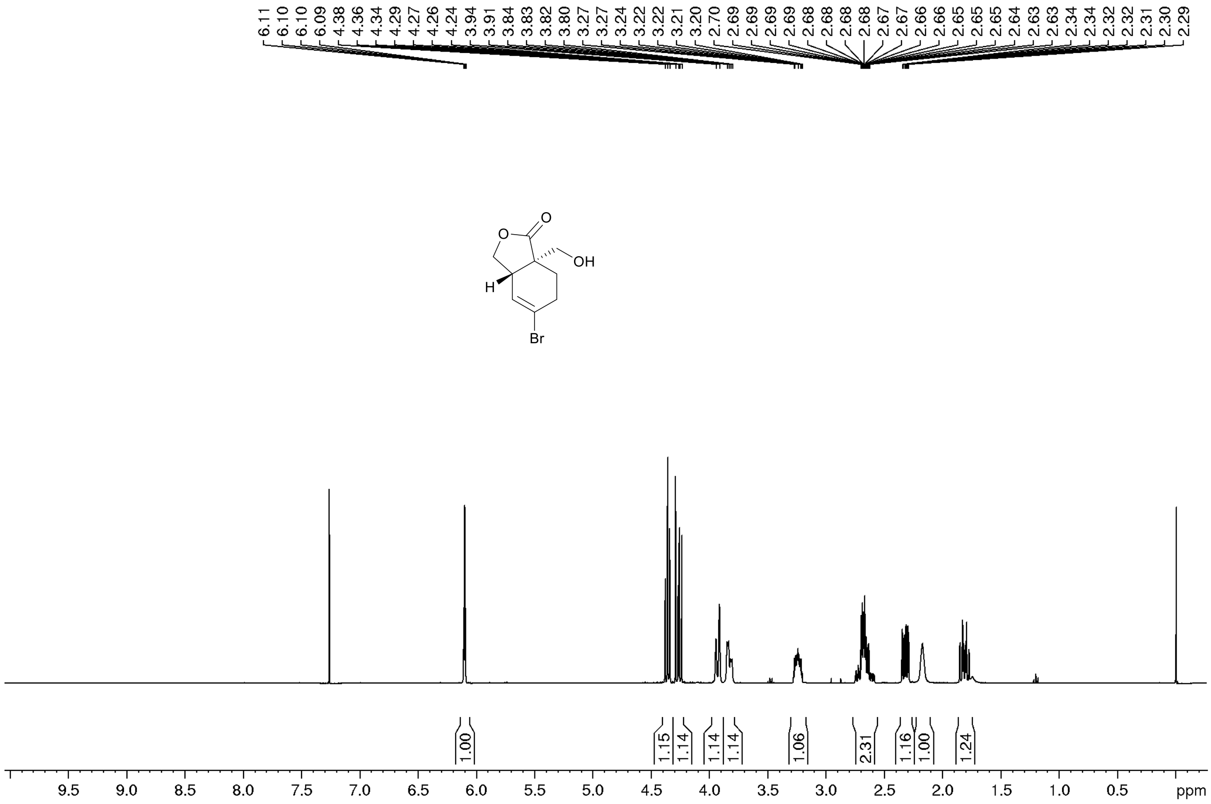
10, ^{1}H NMR (CD_3OD, 400 MHz)



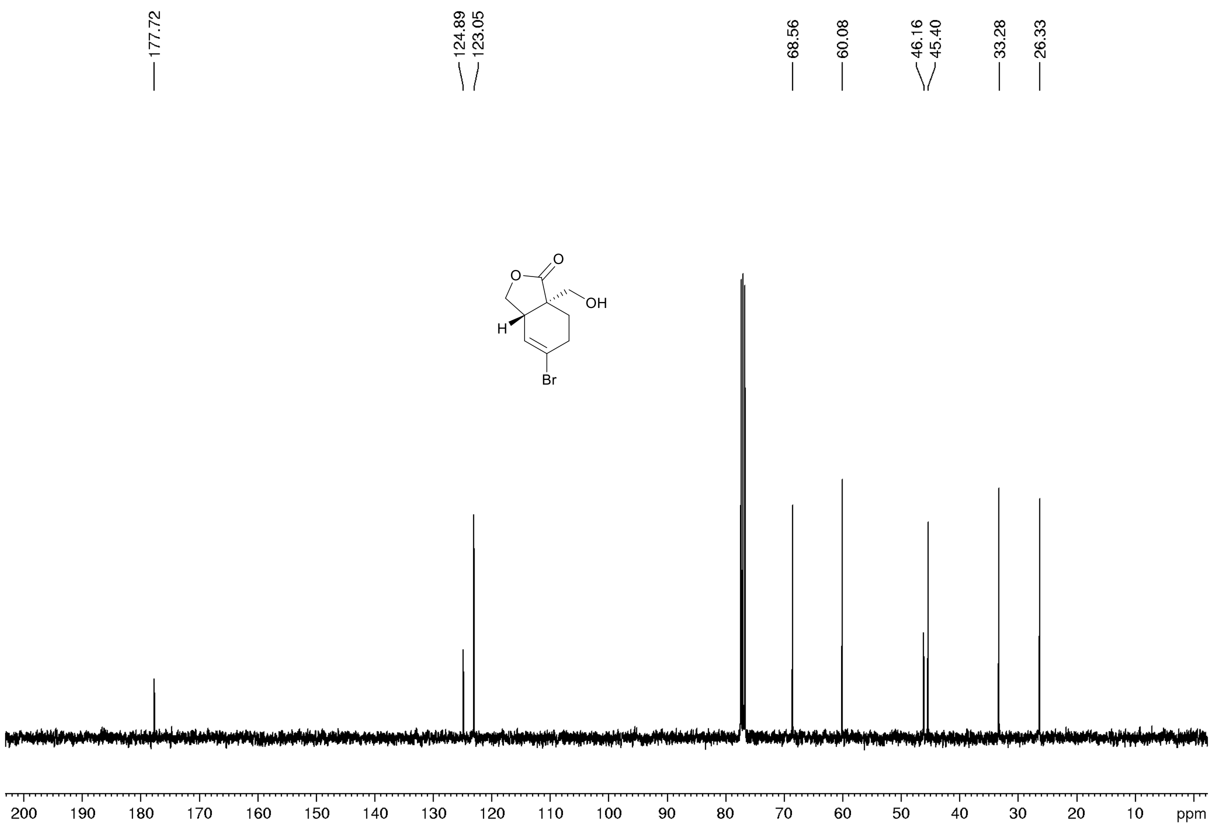
10, ^{13}C {^{1}H} NMR (CD_3OD, 100 MHz)



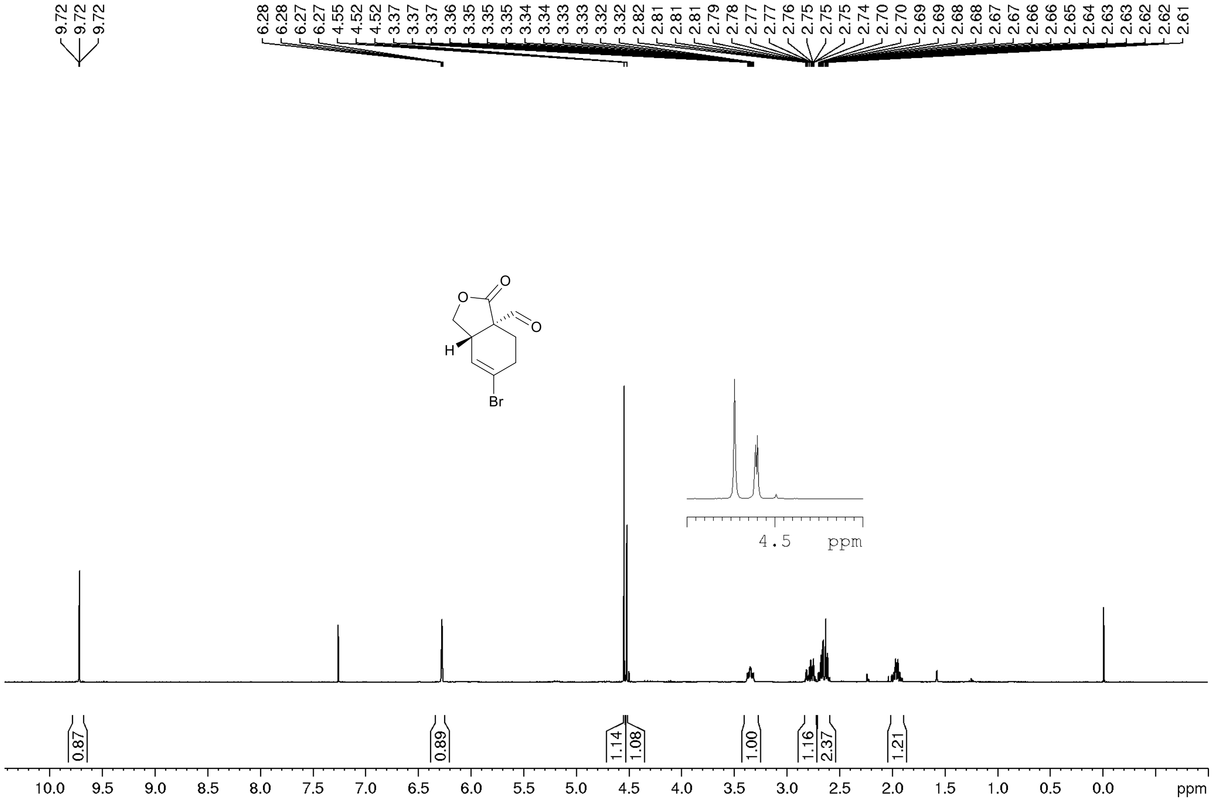
11, ^{1}H NMR ($CDCl_3$, 400 MHz)



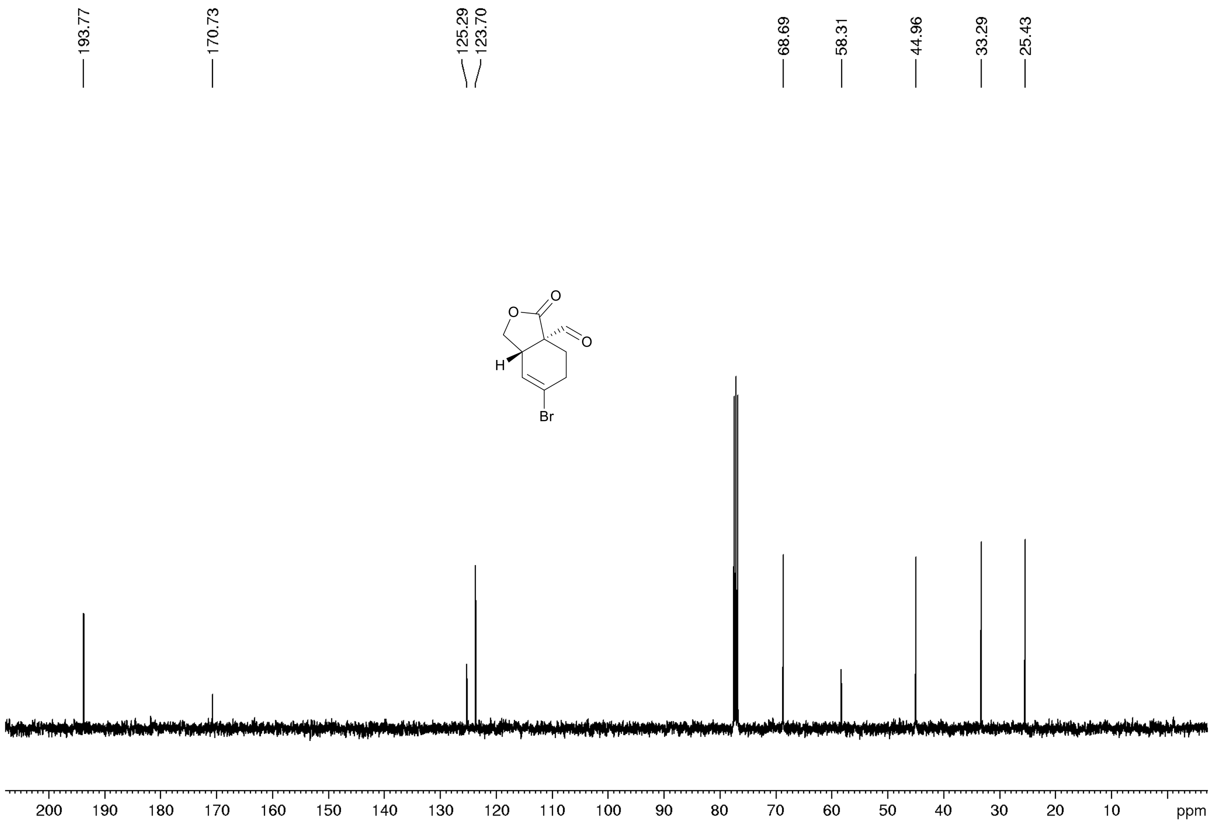
11, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



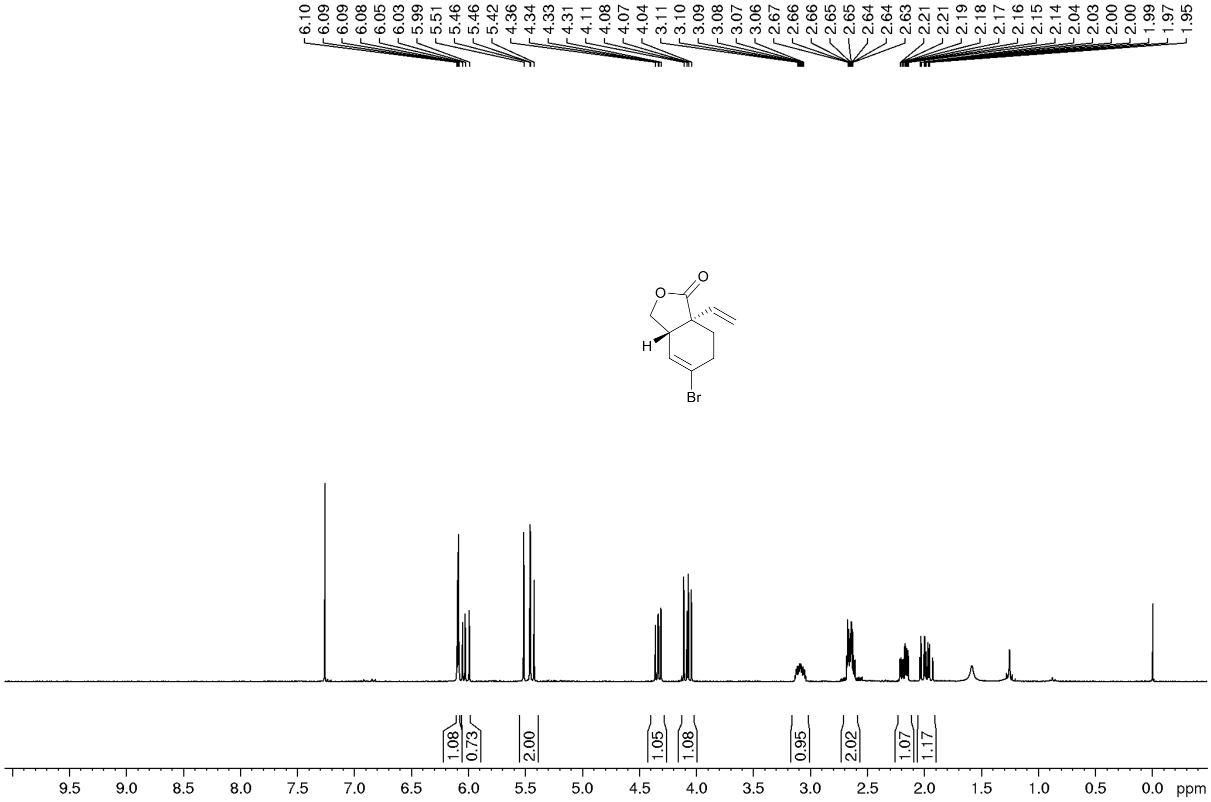
12, ^{1}H NMR ($CDCl_3$, 400 MHz)



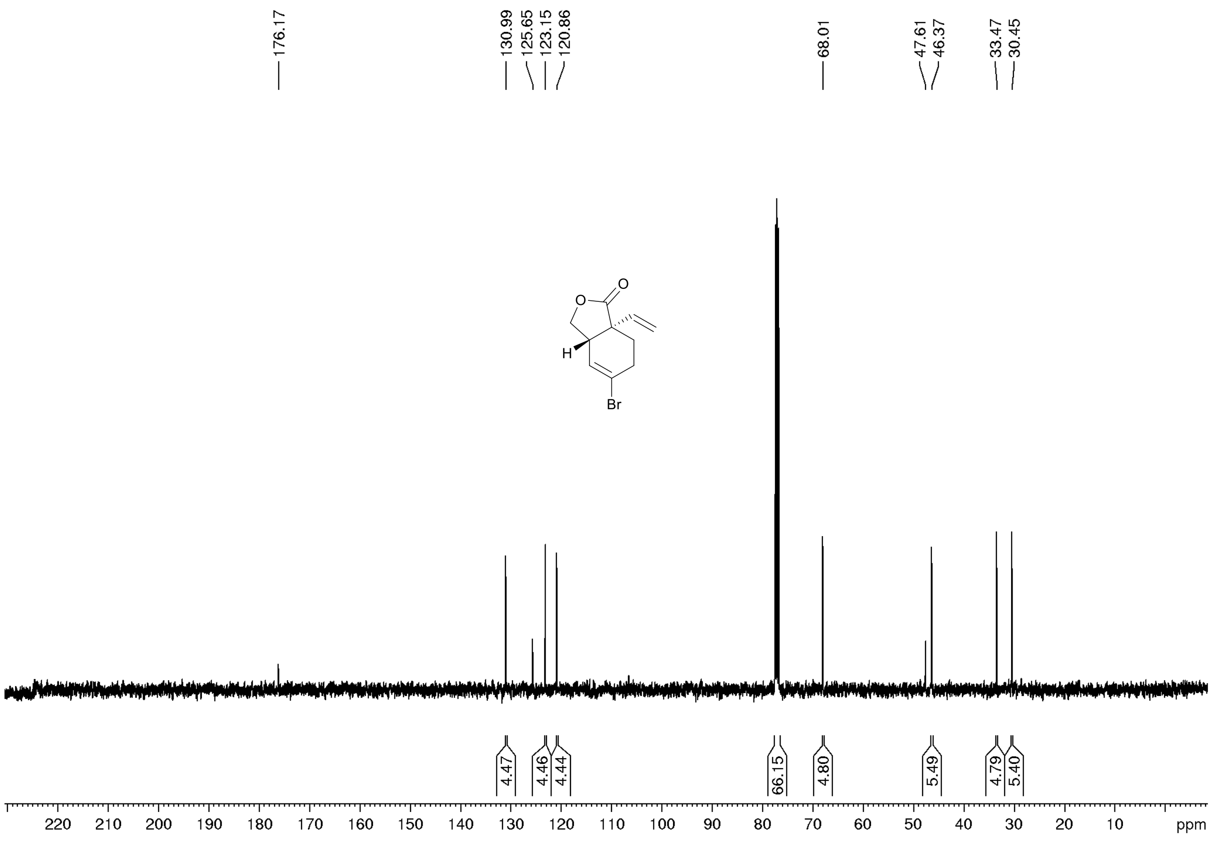
12, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



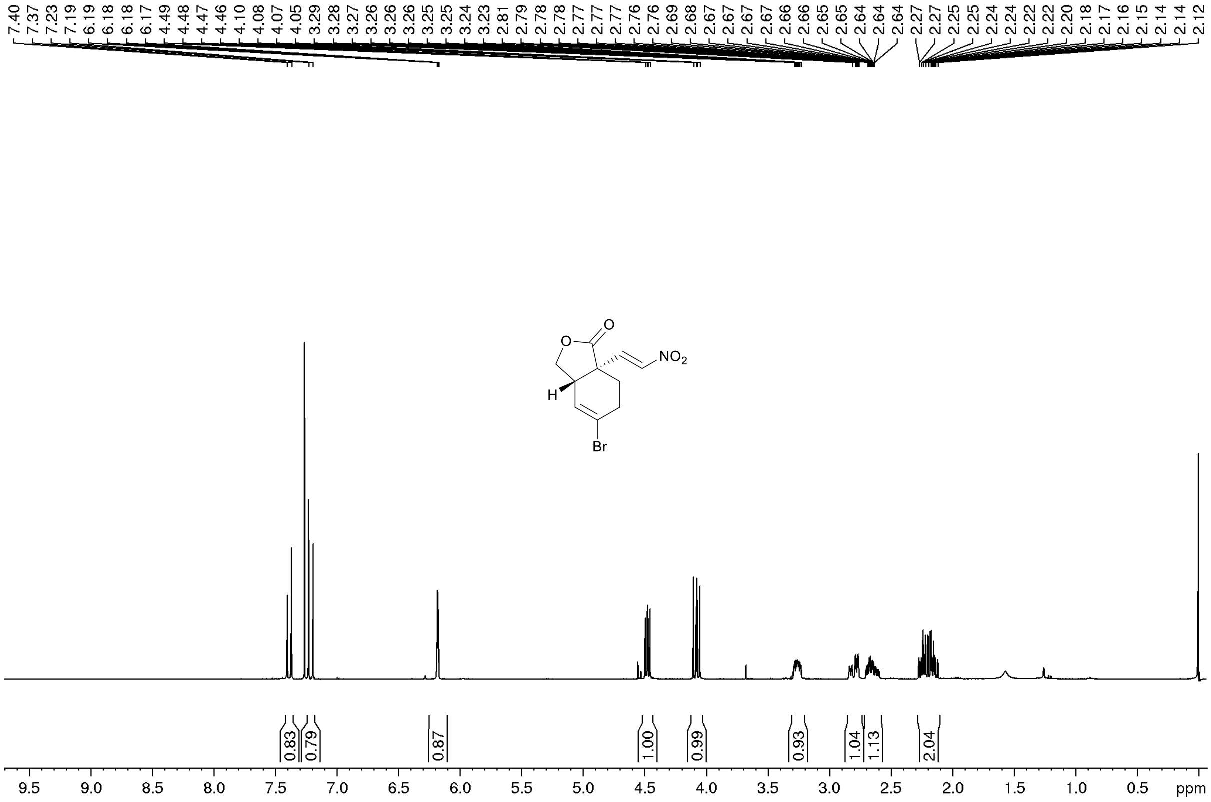
13, ^{1}H NMR ($CDCl_3$, 400 MHz)



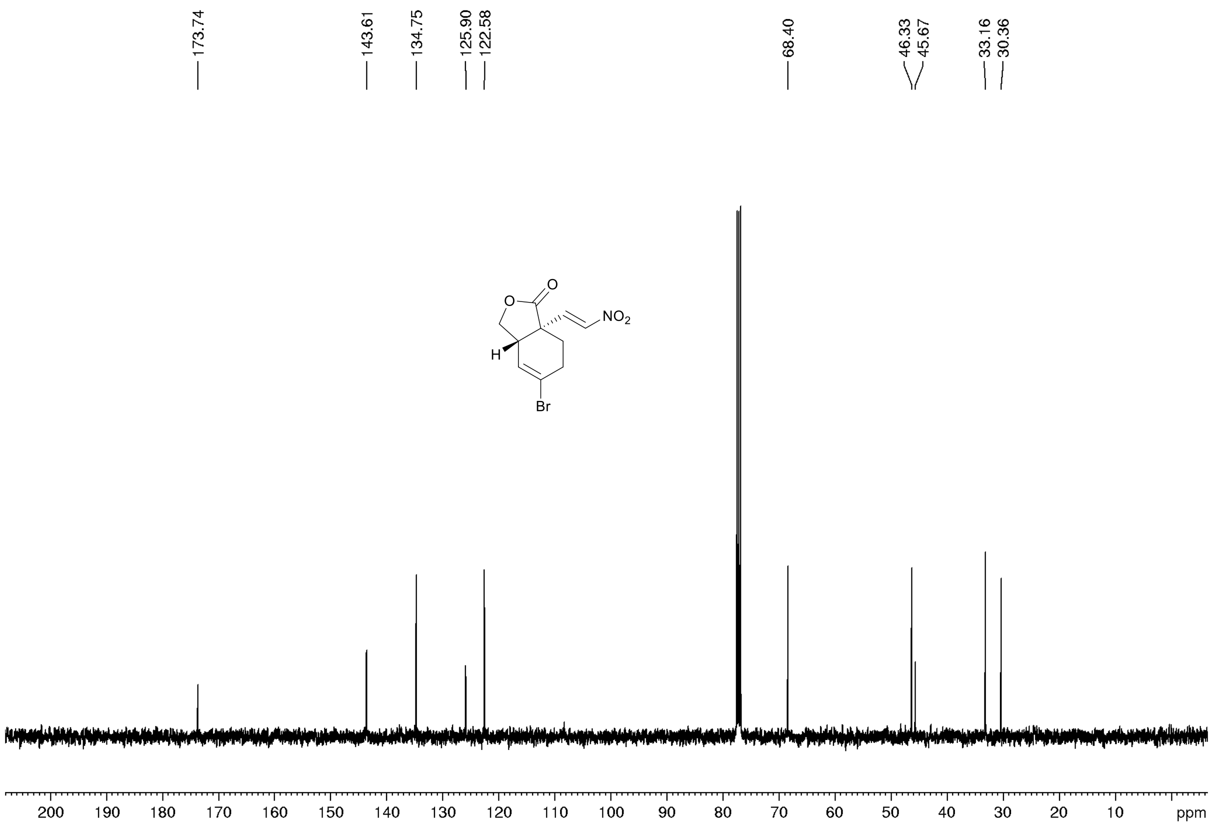
13, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



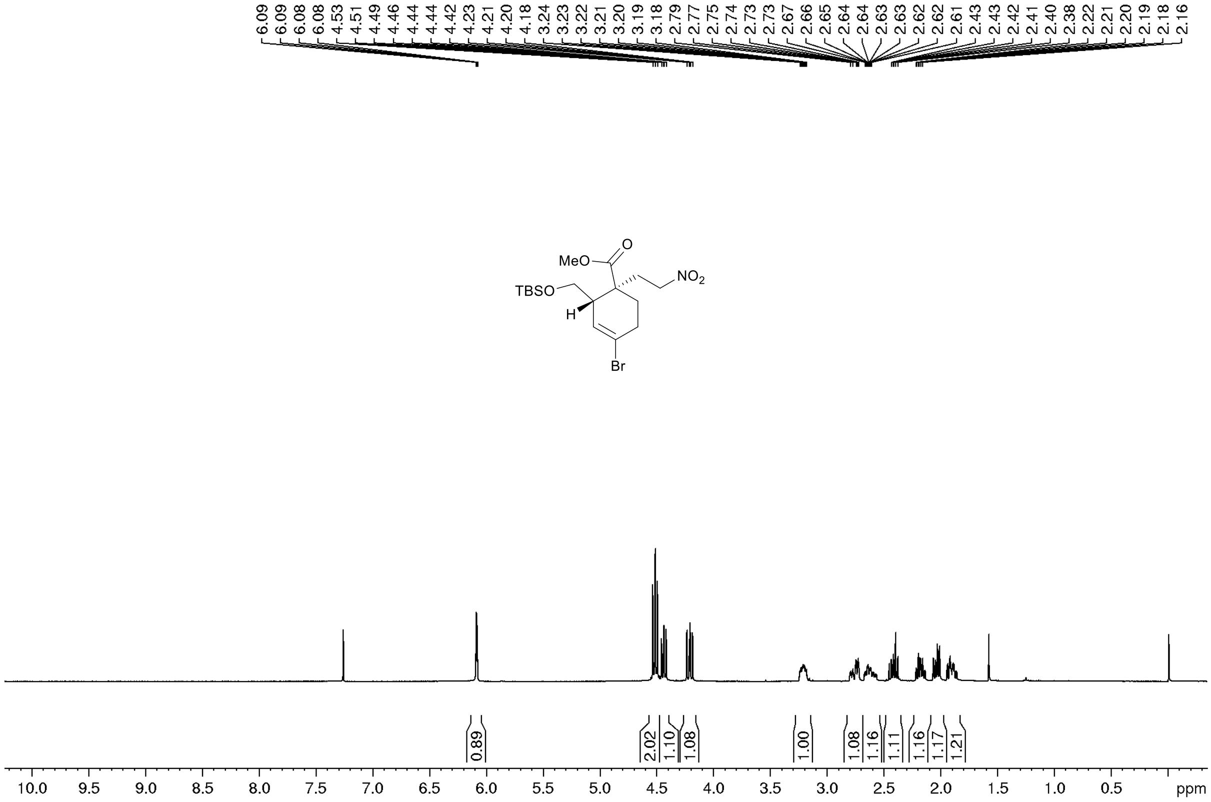
15, ^{1}H NMR ($CDCl_3$, 400 MHz)



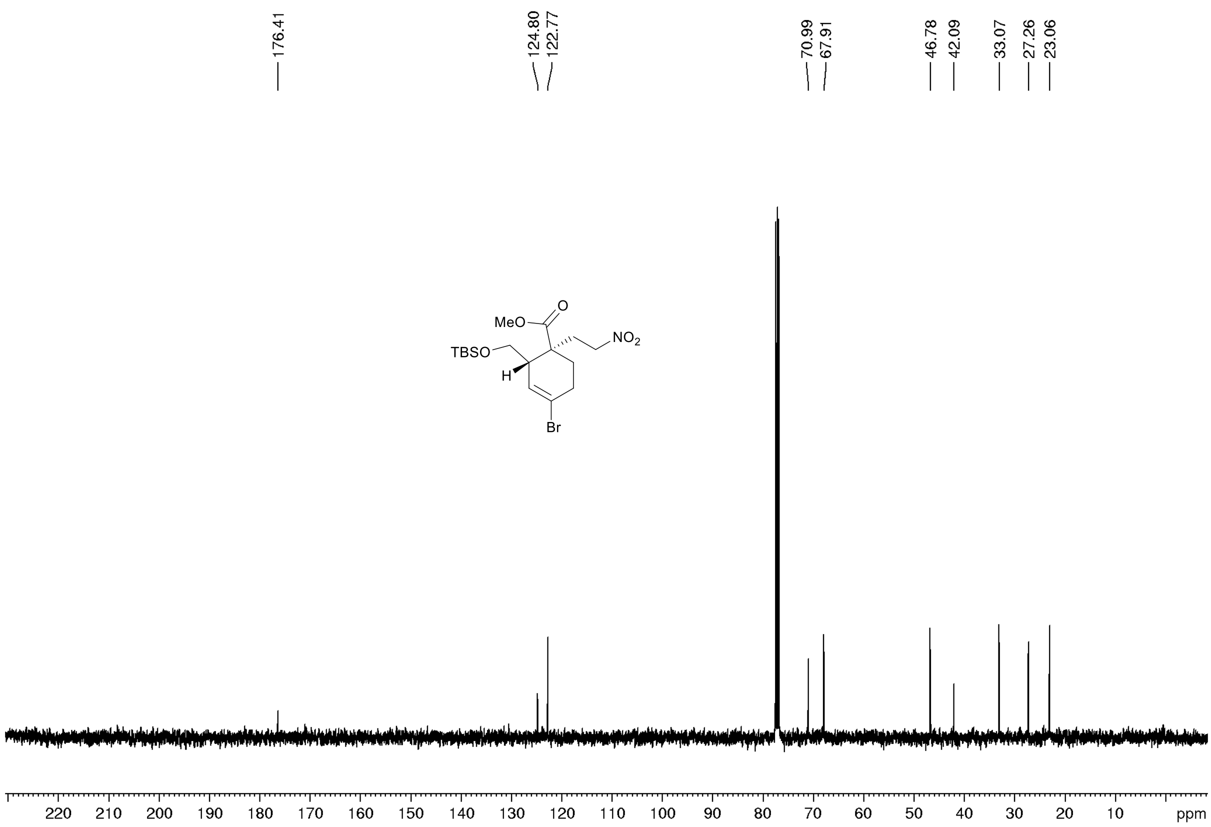
15, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



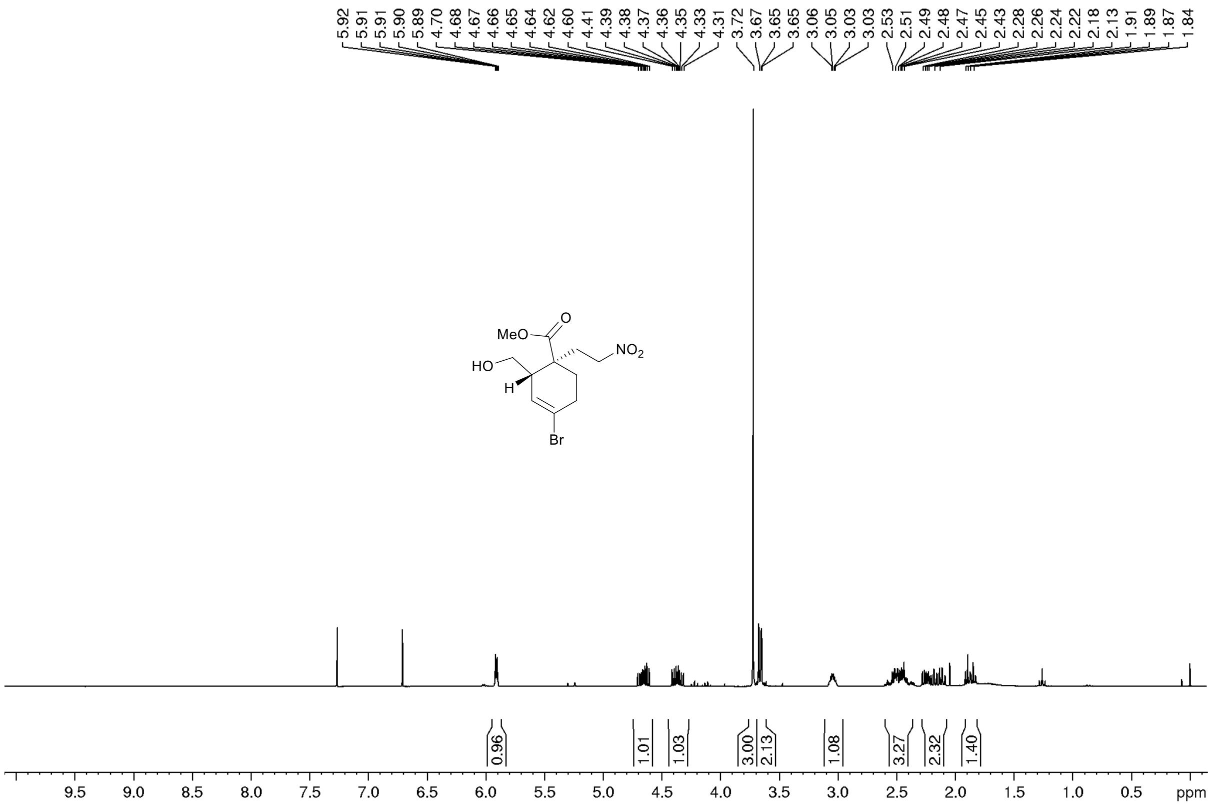
16, ^{1}H NMR ($CDCl_3$, 400 MHz)



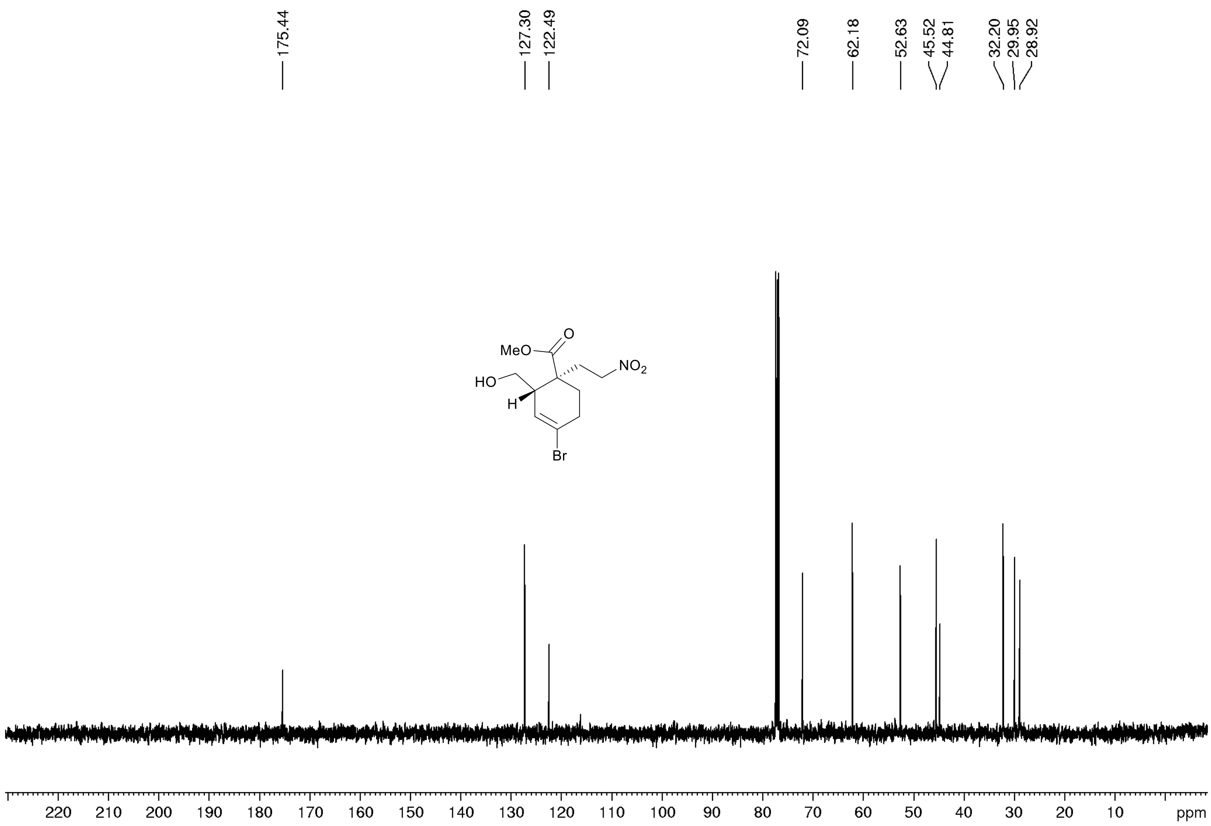
16, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



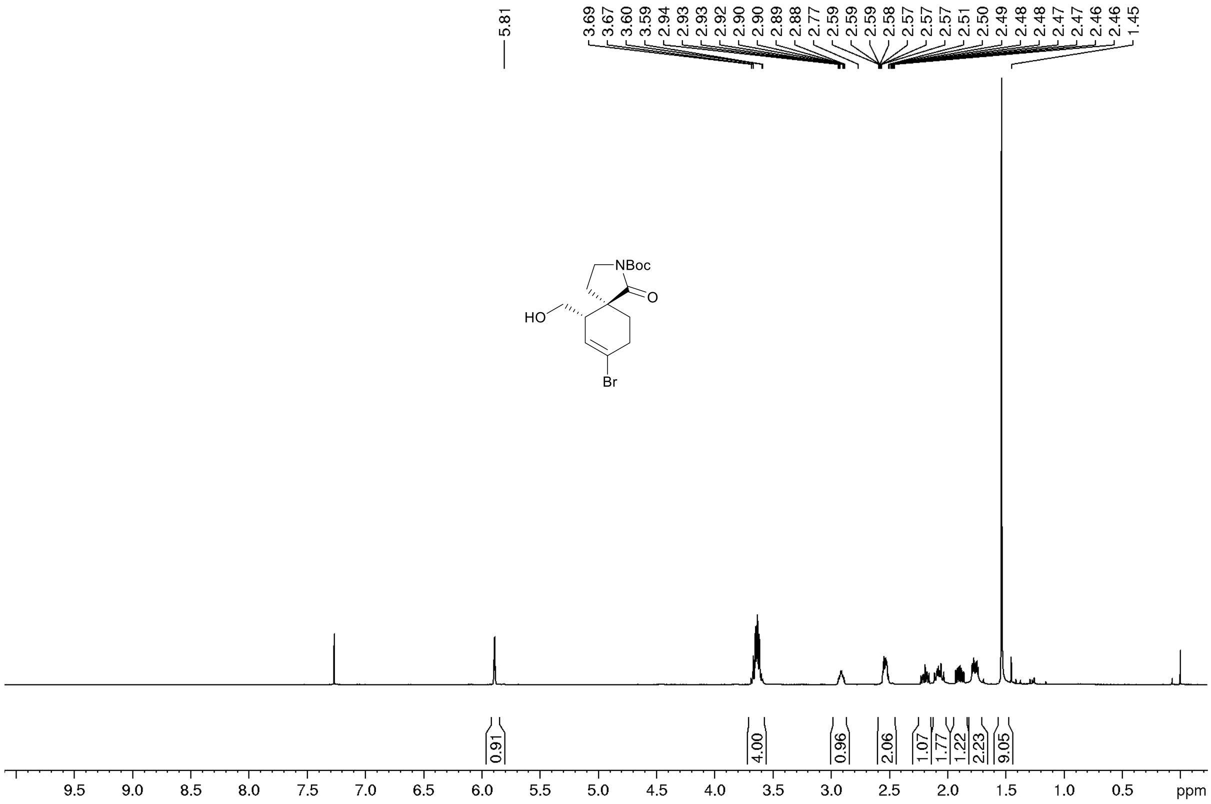
S1, ^{1}H NMR ($CDCl_3$, 400 MHz)



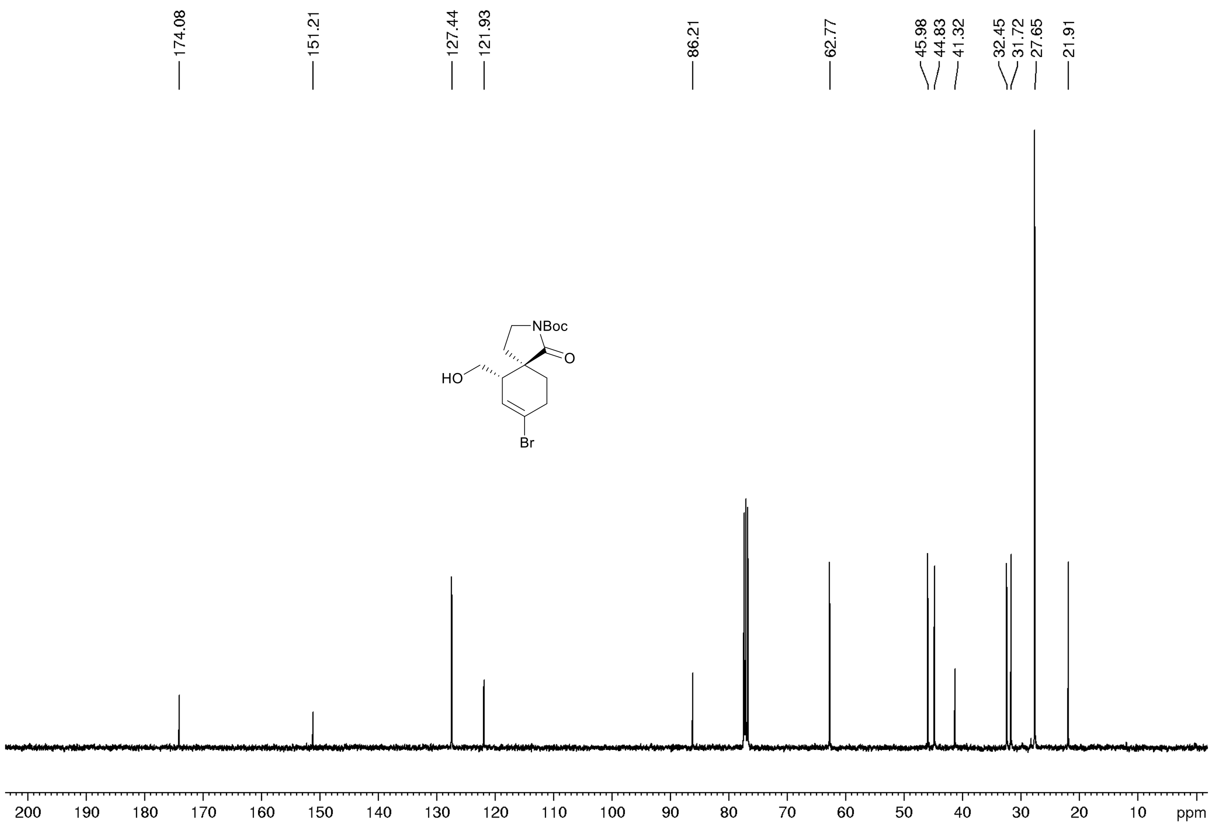
S1, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



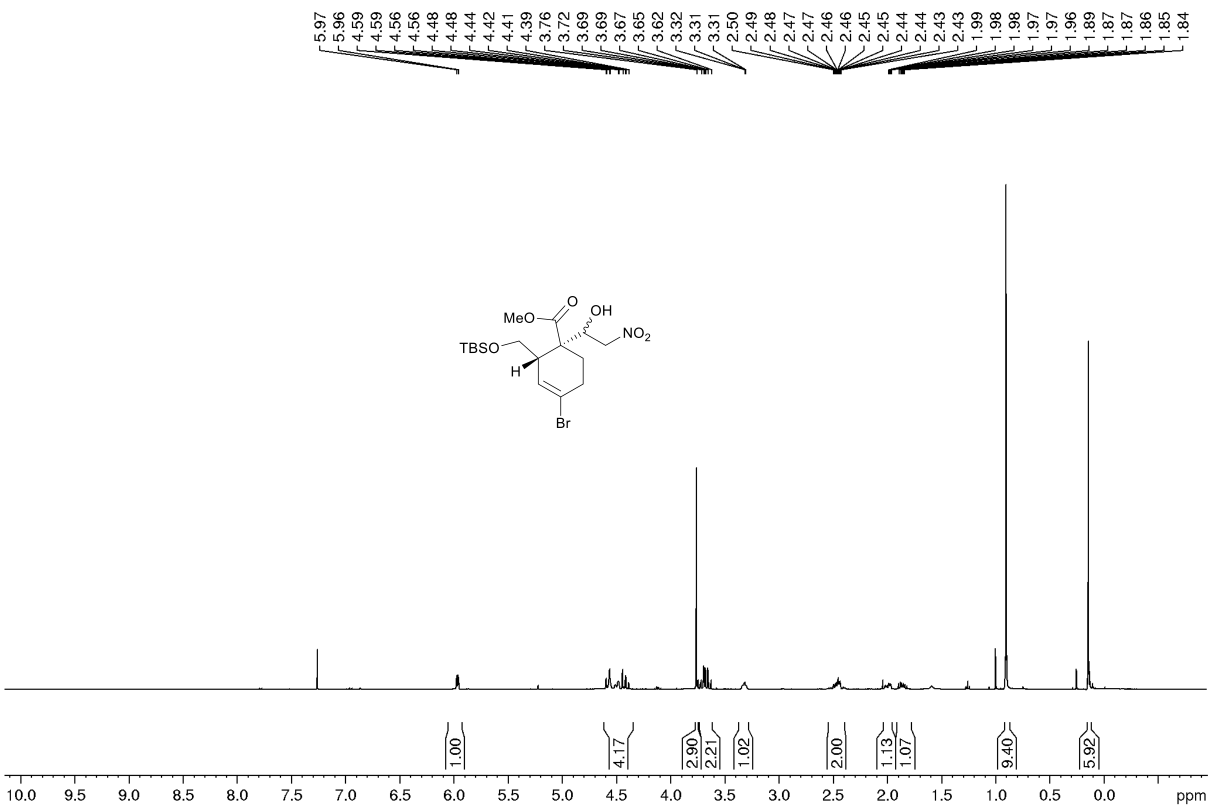
17, ^{1}H NMR ($CDCl_3$, 400 MHz)



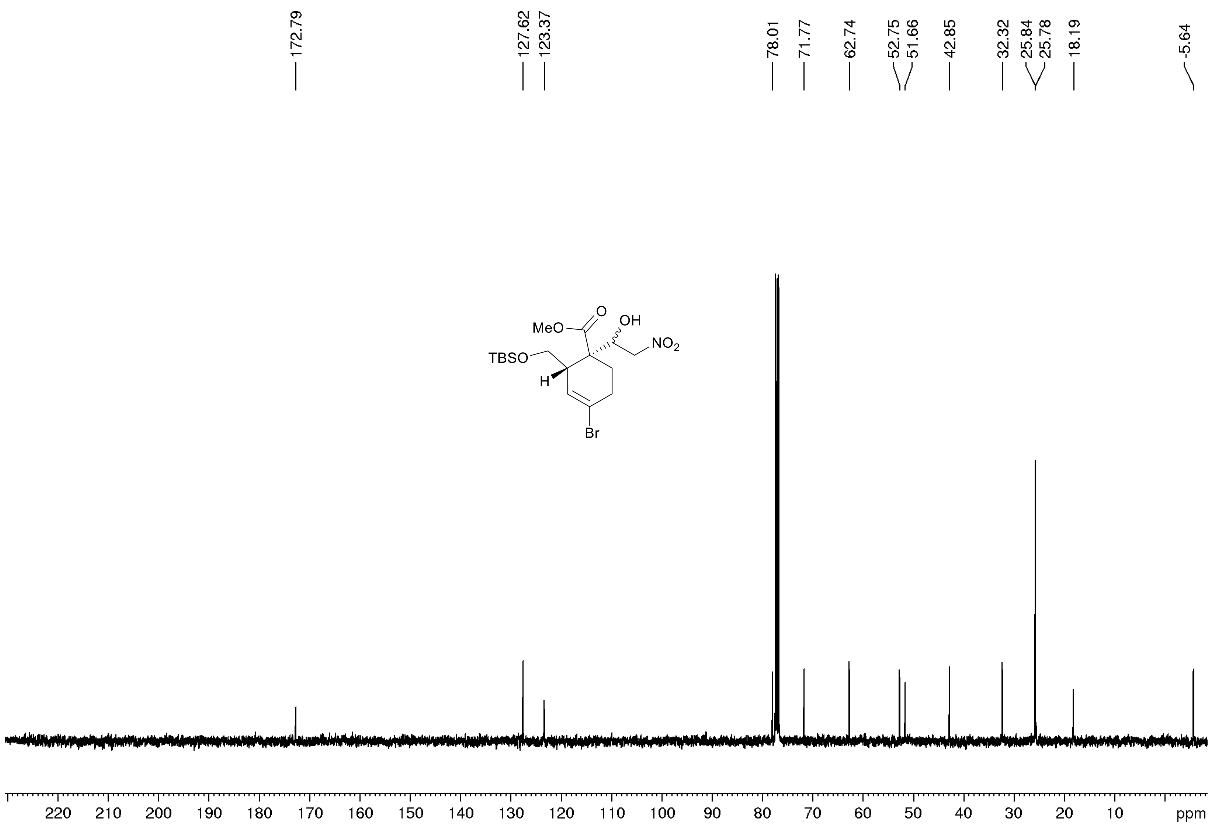
17, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



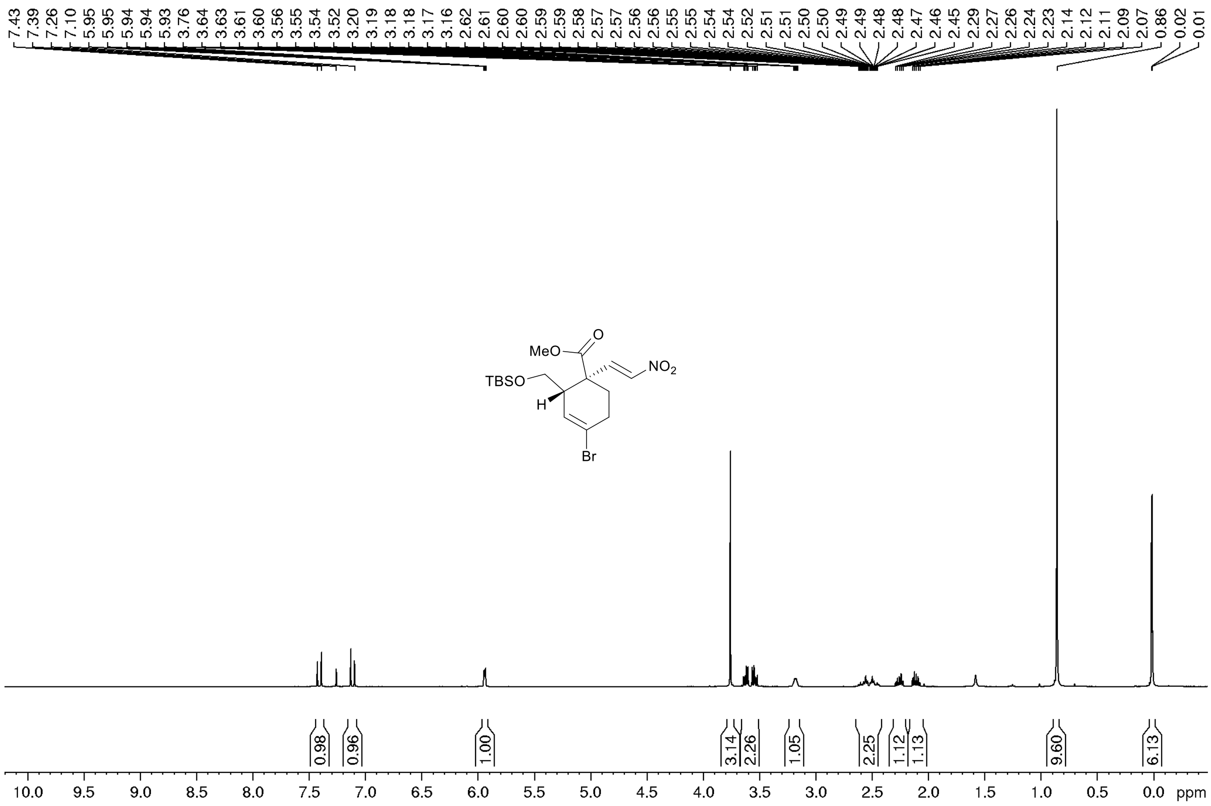
20, ^{1}H NMR ($CDCl_3$, 400 MHz)



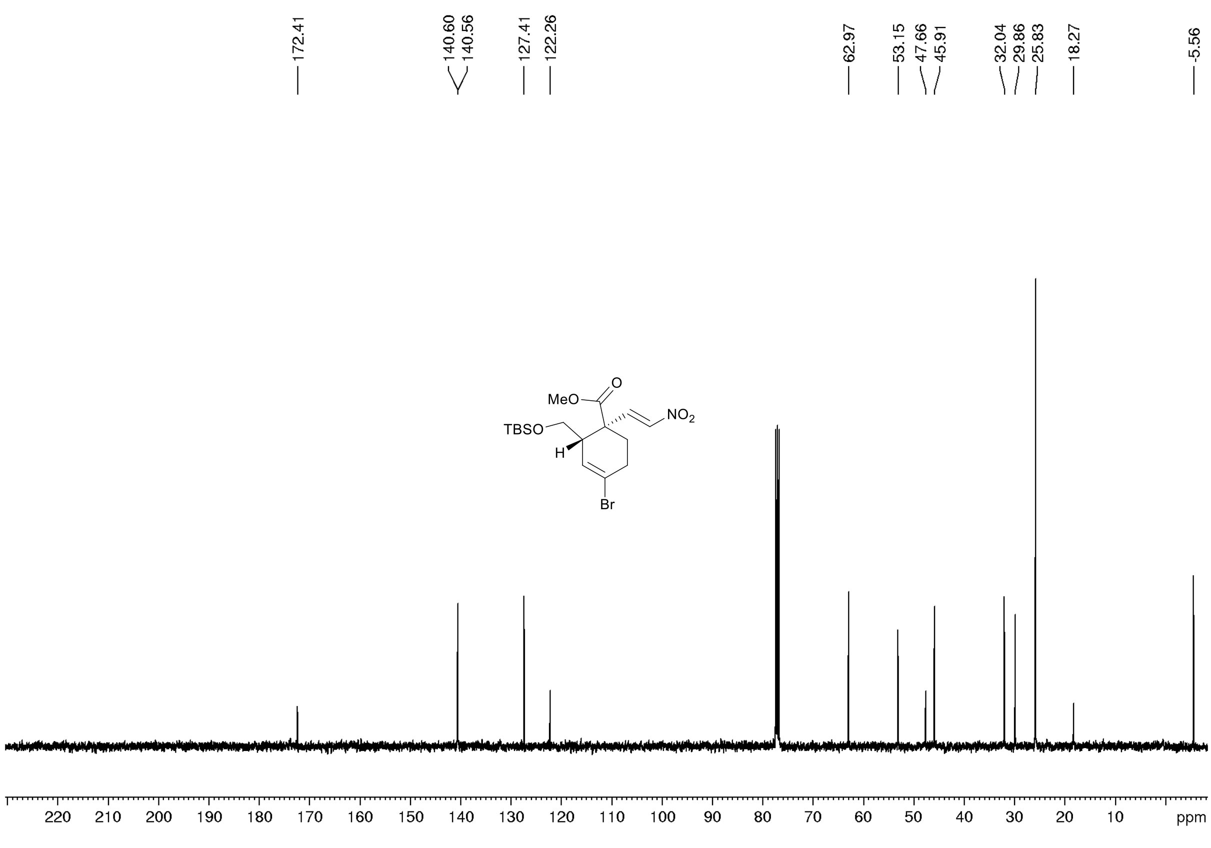
20, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



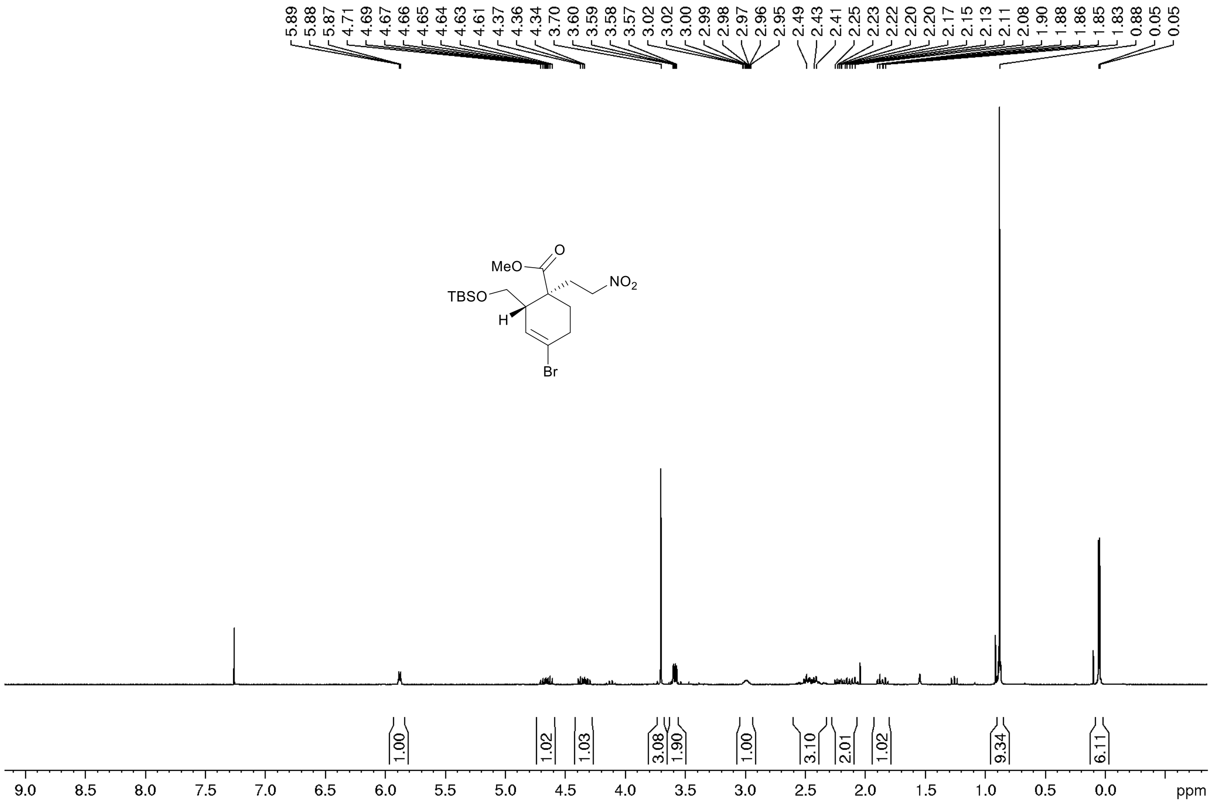
21, ^{1}H NMR ($CDCl_3$, 400 MHz)



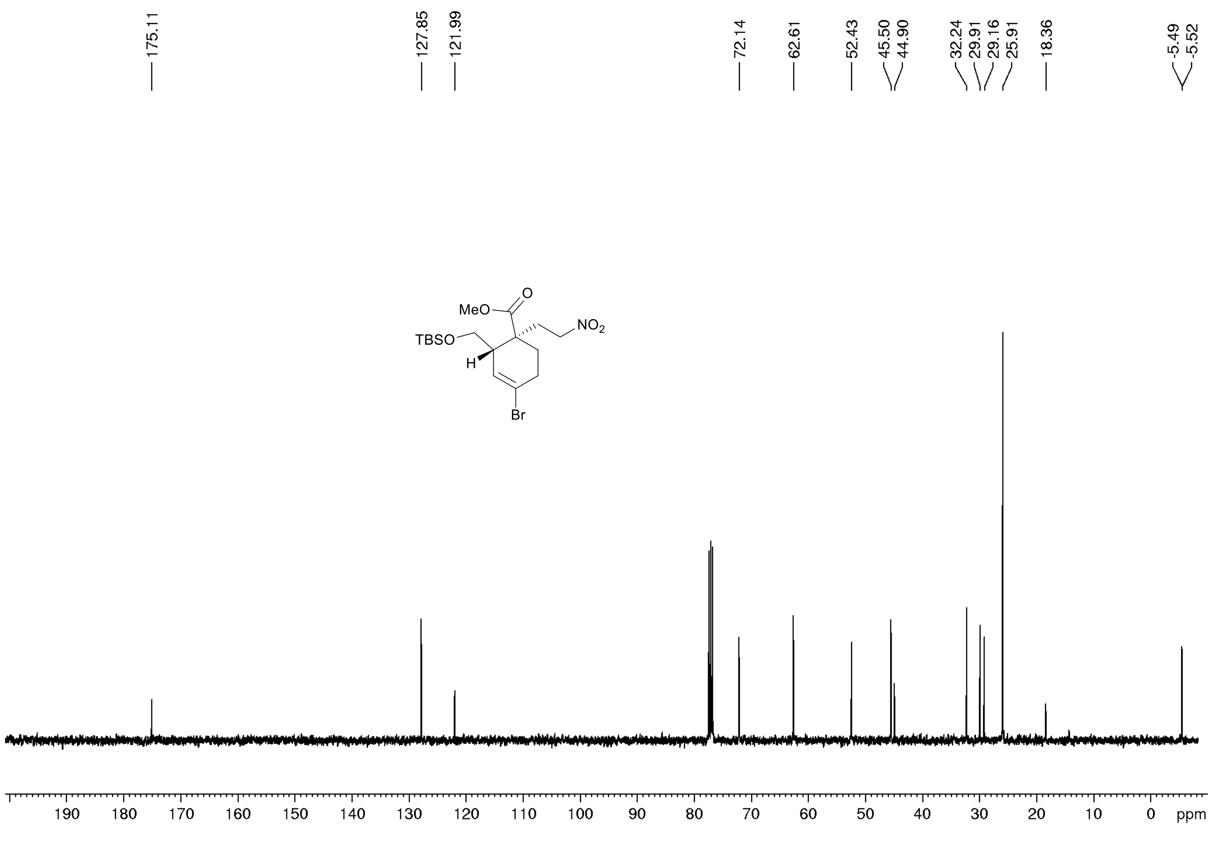
21, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



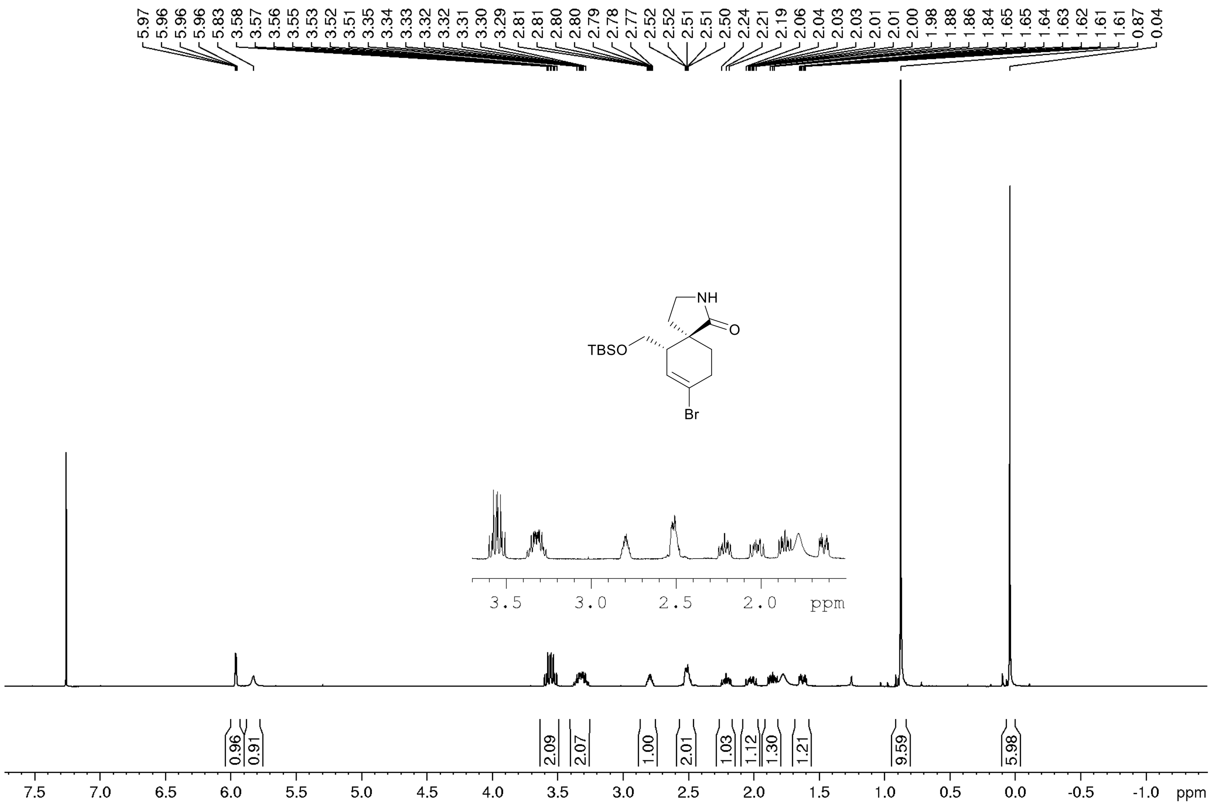
22, ^{1}H NMR ($CDCl_3$, 400 MHz)



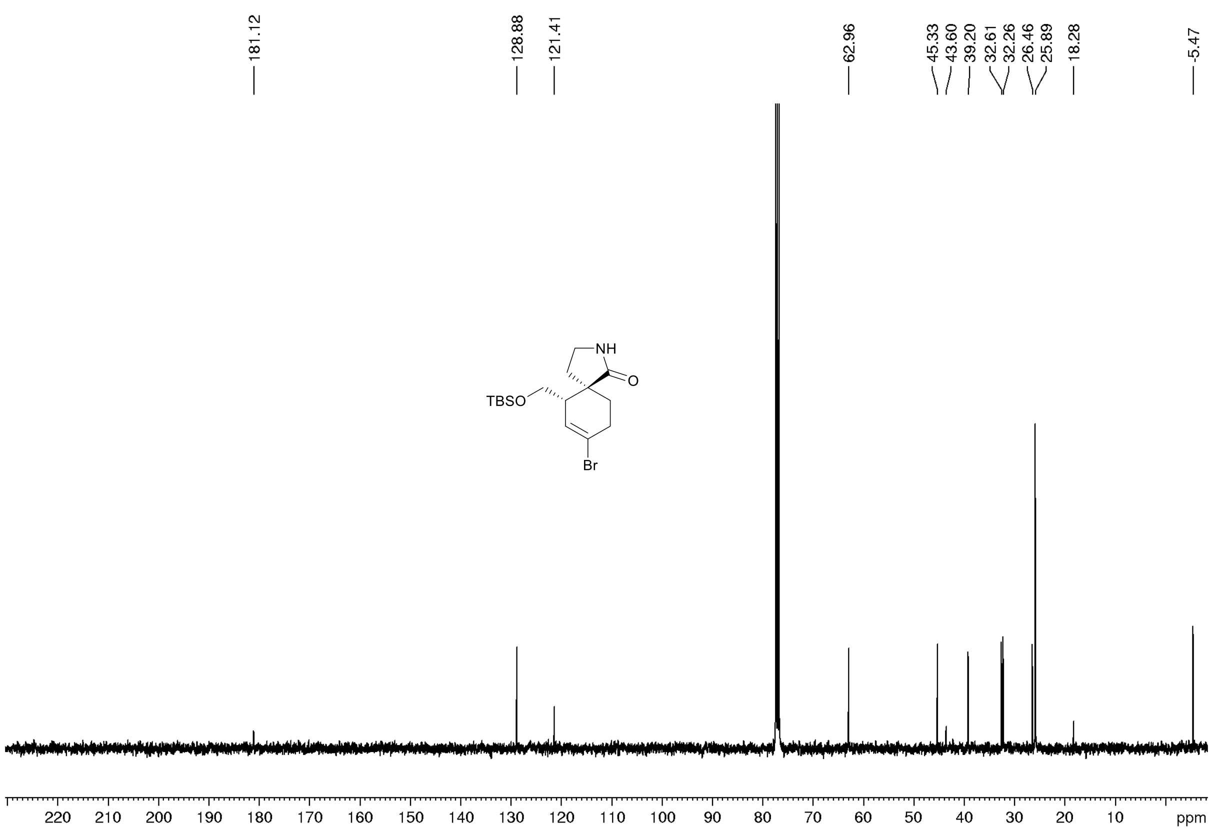
22, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



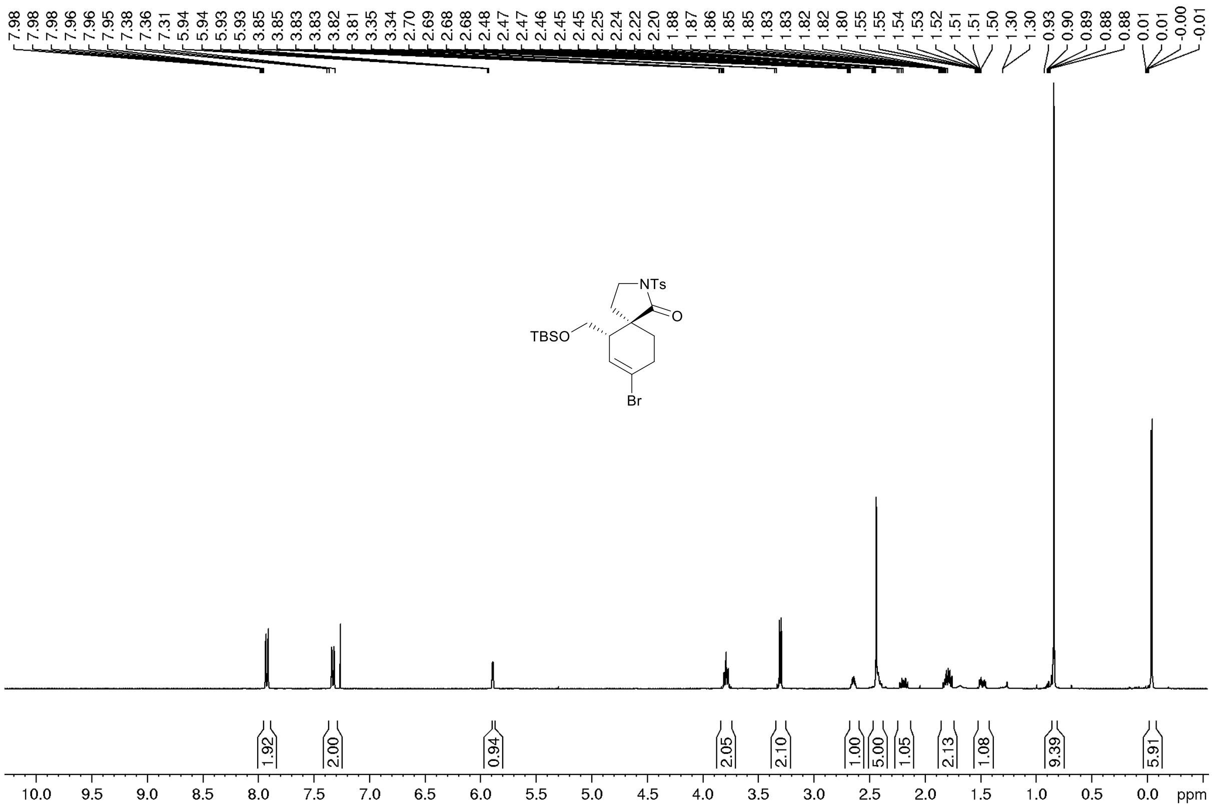
23, ^{1}H NMR ($CDCl_3$, 400 MHz)



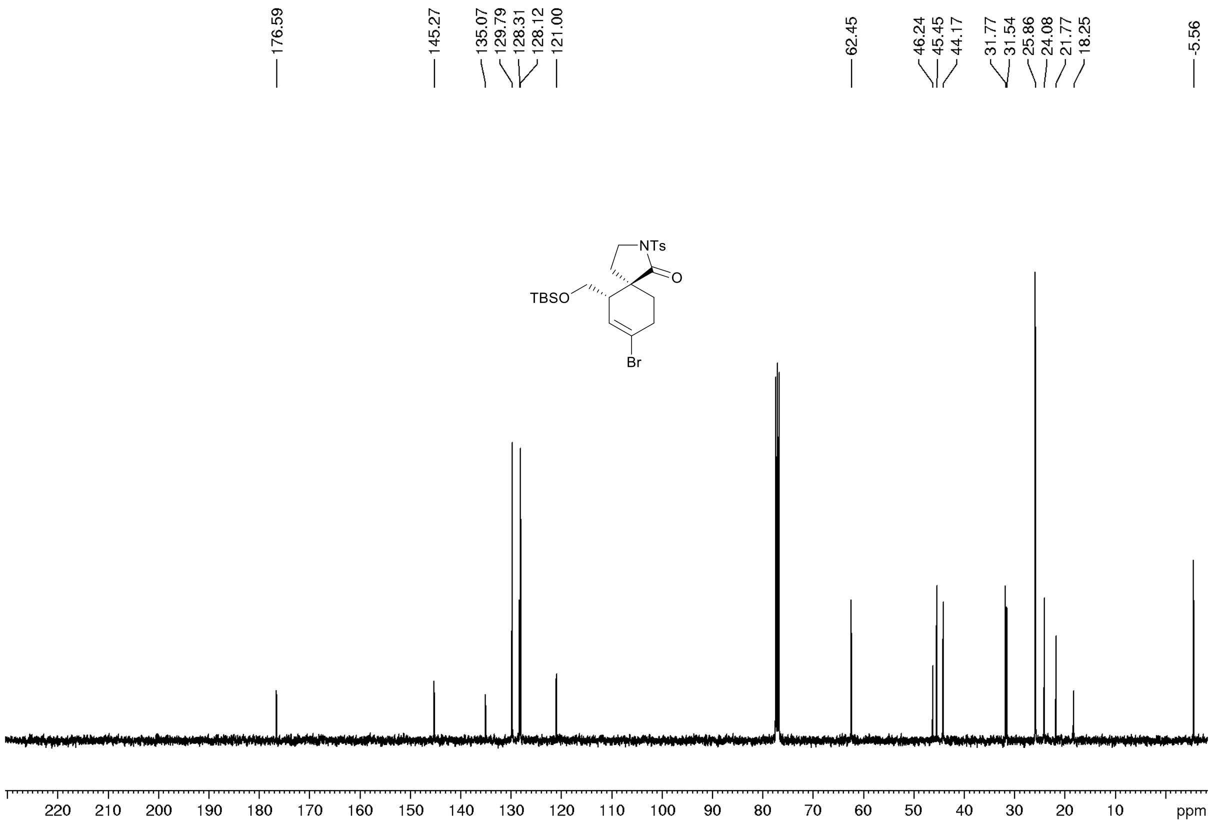
23, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



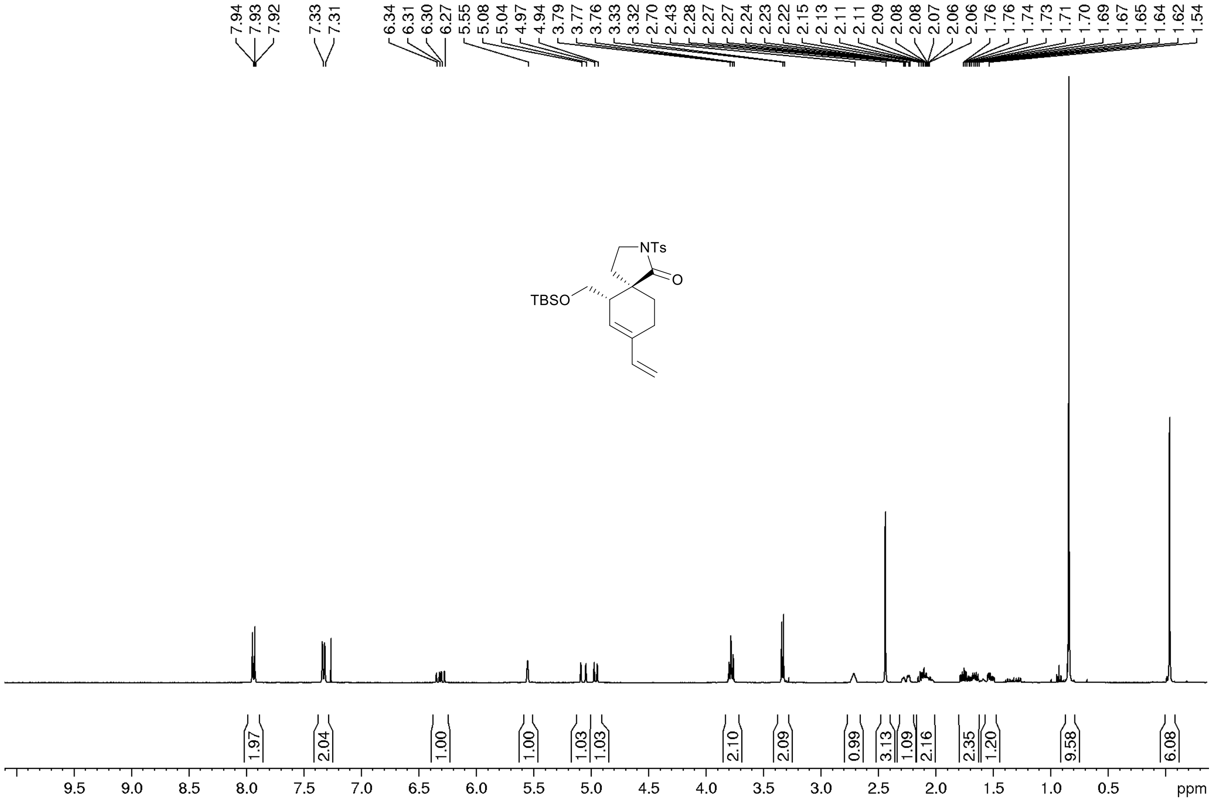
24a, [1]H NMR ($CDCl_3$, 400 MHz)



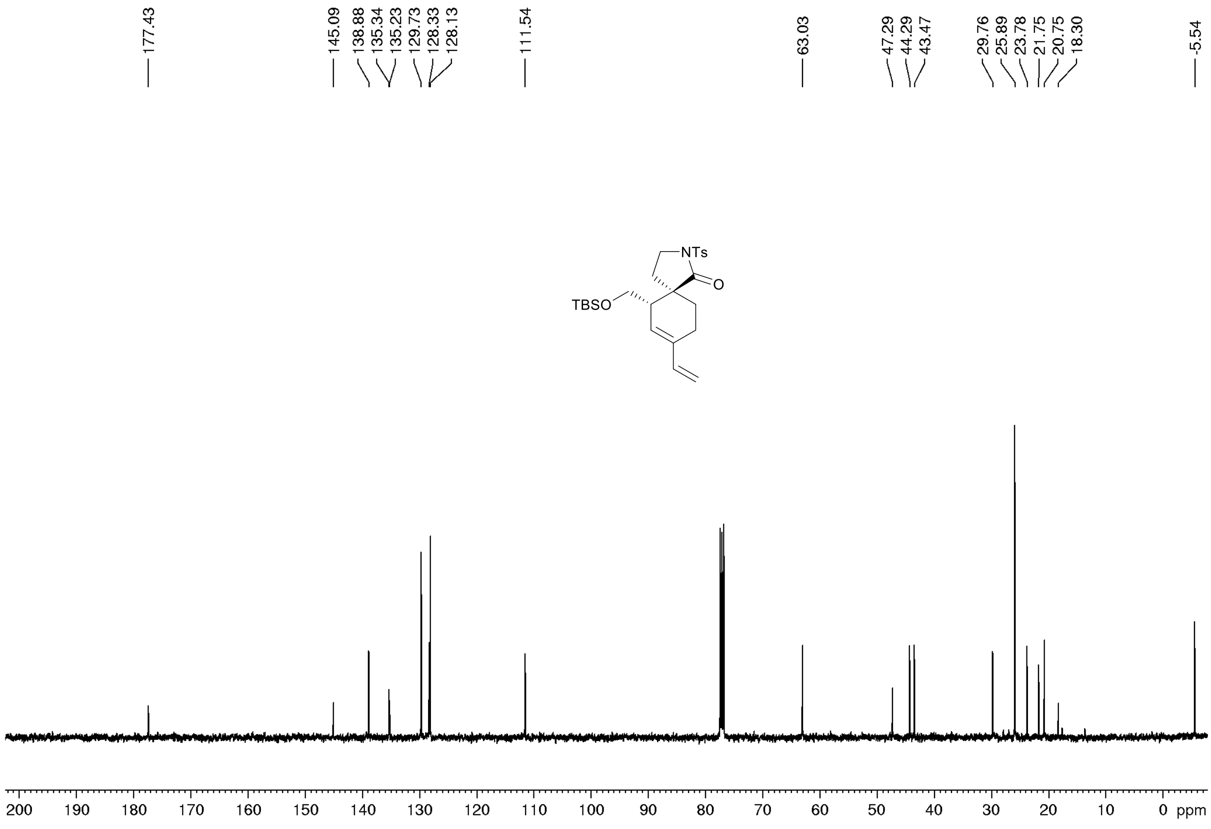
24a, [13]C {[1]H} NMR ($CDCl_3$, 100 MHz)



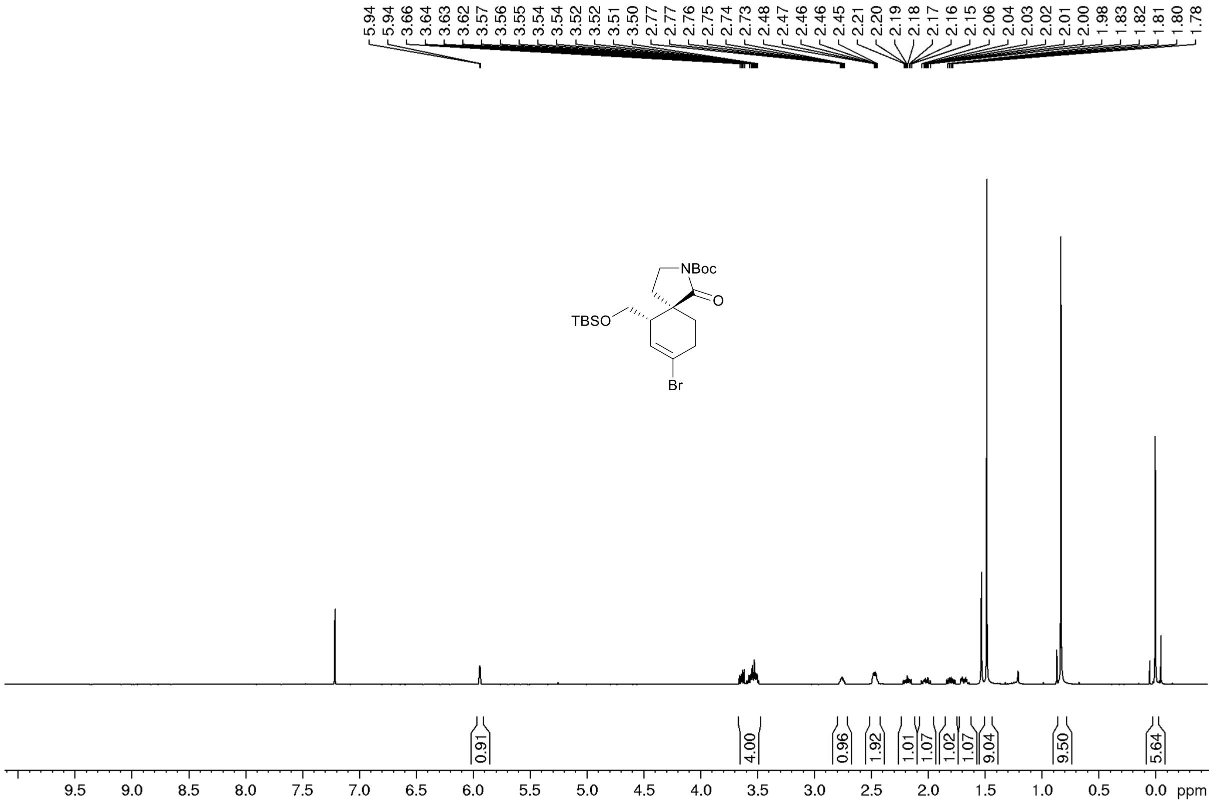
5a, ^{1}H NMR ($CDCl_3$, 400 MHz)



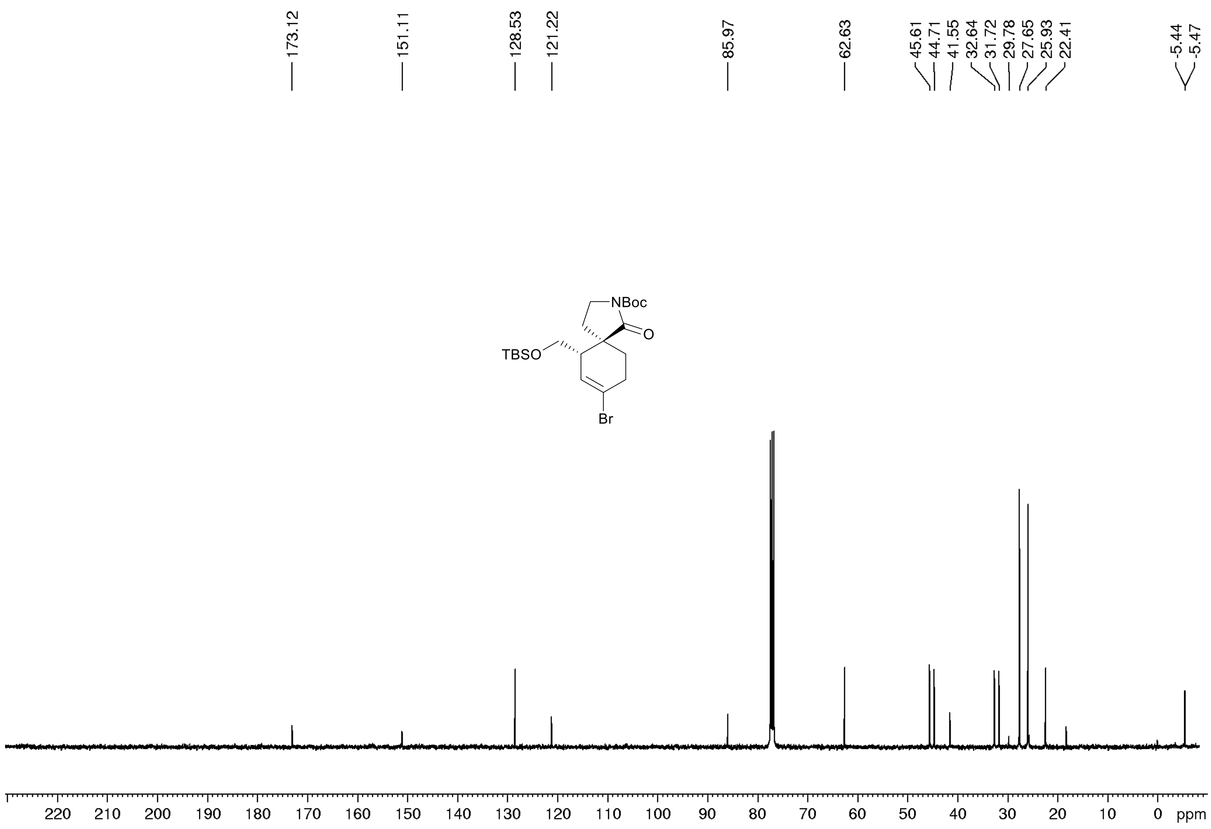
5a, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



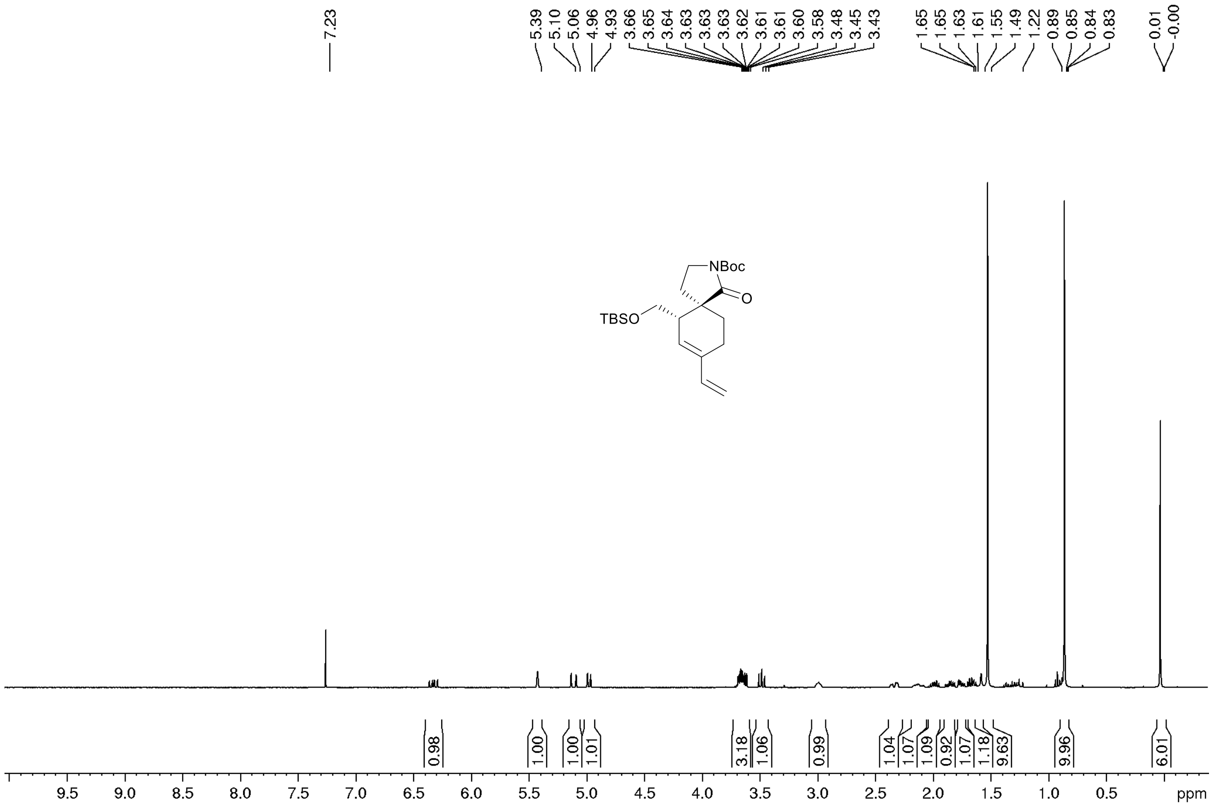
24b, ^{1}H NMR ($CDCl_3$, 400 MHz)



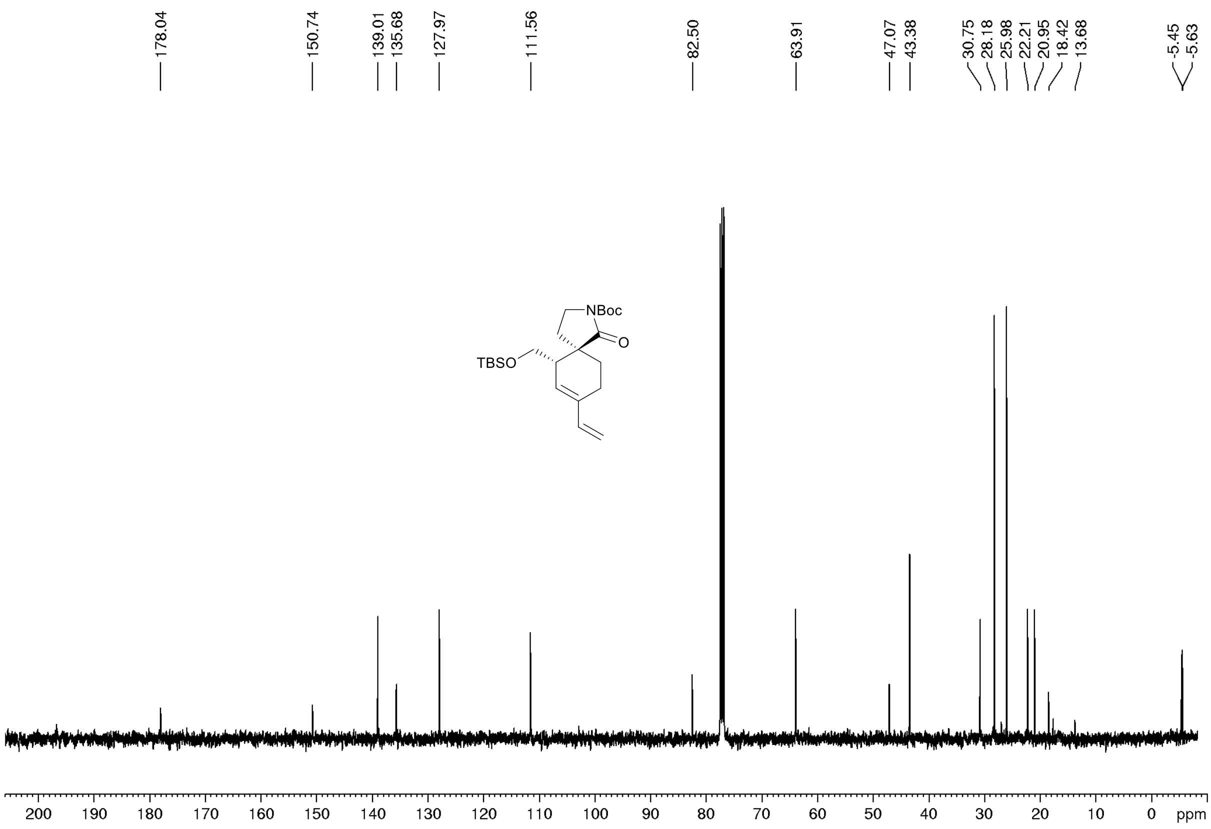
24b, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



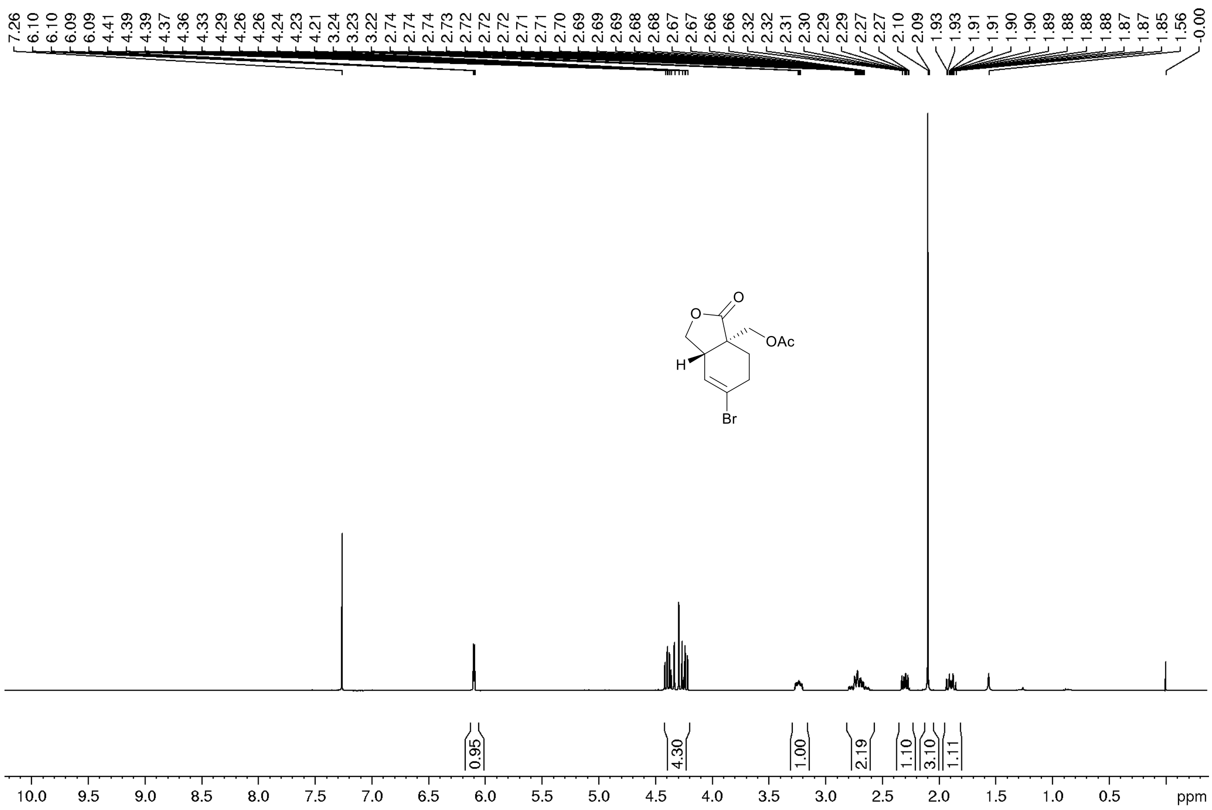
5b, ^{1}H NMR ($CDCl_3$, 400 MHz)



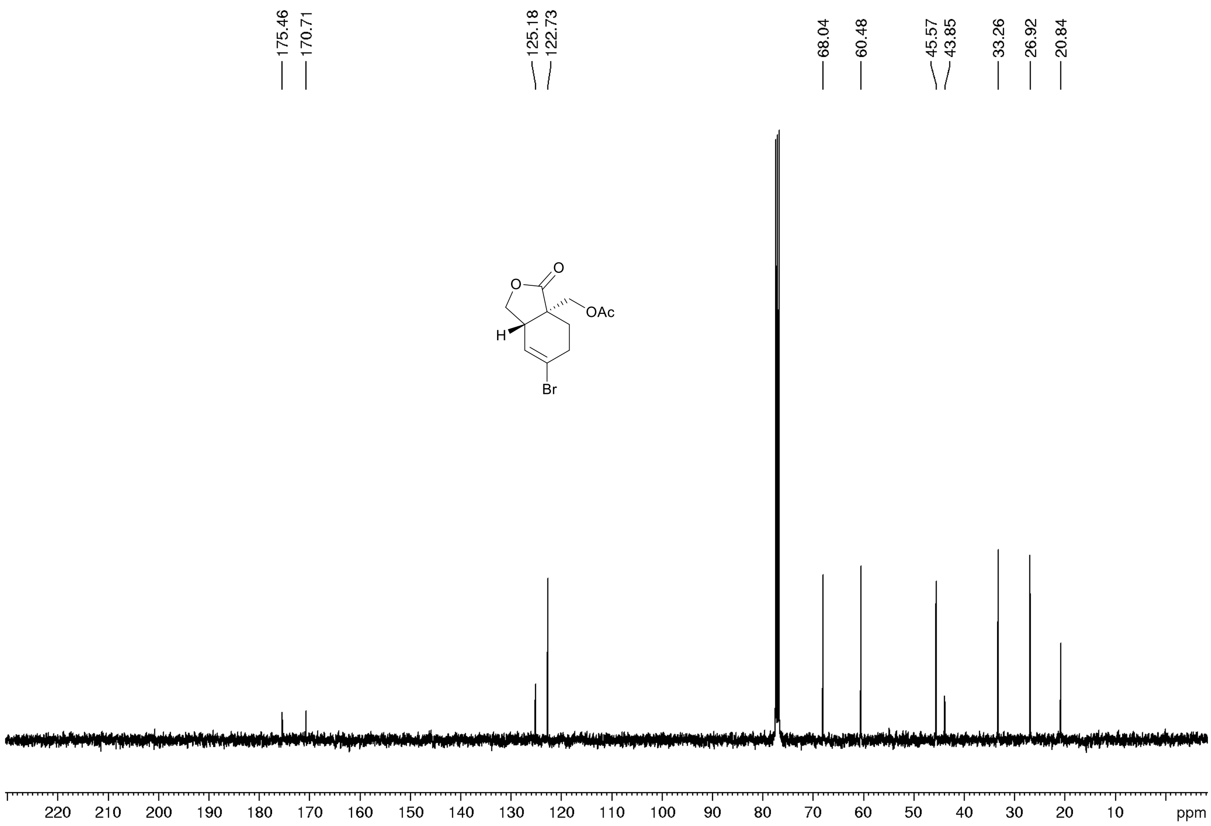
5b, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



25, ^{1}H NMR ($CDCl_3$, 400 MHz)



25, ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz)



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4. C. Palomo, J. M. Aizpurua, F. P.Cossio, J. M. Garcia, M. C. Lopez and M. Oiarbide, *J. Org. Chem.* **1990**, *55*, 2070–2078.

5. M. Node, H. Nagasawa, Y. Naniwa and K. Fuji, *Synthesis* **1987**, 729-32.