Supporting Information

Formal Synthesis of (±)-Pentalenolactone A Methyl Ester.

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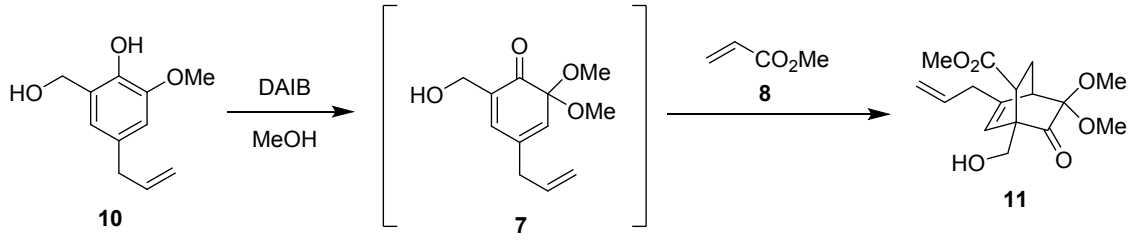
Experimental Data

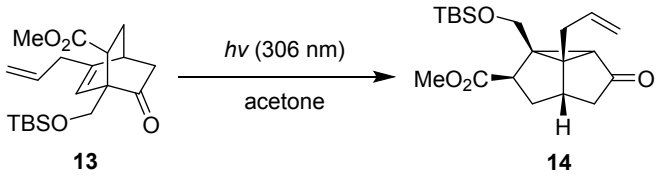
Optimization of Reactions

Table S1. Studies for Diel-Alder Reaction of MOB 7 with methyl acrylate 8



Entry	Conditions	Yield of **11**
1	methyl acrylate (5 equiv.), MeOH/CH_2Cl_2	63%
2	methyl acrylate (20 equiv.), MeOH/CH_2Cl_2	70%
3	methyl acrylate (20 equiv.), MeOH	80%
4	methyl acrylate (20 equiv.), MeOH, BHT (10 wt%)	88%

Table S2. Studies for ODPM Rearrangement of 13

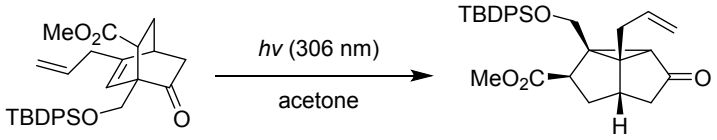


Entry	Lamps[a]	Material[b]	Concetration	Time	Yield[c]
1	16	quartz	80 mg/80 mL	240 min	59%
2	16	quartz	80 mg/80 mL	180 min	50%
3	16	quartz	80 mg/80 mL	60 min	53%
4	16	quartz	160 mg/160 mL	300 min	25%
5	16	quartz	40 mg/80 mL	60 min	35%
6	16	quartz	97 mg/10 mL	315 min	21%
7[d]	16	quartz	97 mg/10 mL	315 min	S.M. recovered

8	8	quartz	80 mg/80 mL	60 min	48% (57% brsm)
9	8	Pyrex	80 mg/80 mL	60 min	35% (51% brsm)
10	4	quartz	80 mg/80 mL	150 min	35% (53% brsm)
11[e]	8	quartz	80 mg/80 mL	75 min	43% (62% brsm)
12	8	quartz	80 mg/80 mL	50 min	39% (73% brsm)
13[f]	8	quartz	80 mg/80 mL	75 min	30% (42% brsm)

[a]The number of lamps in the photoreactor. [b]The material of the photoreaction tube. [c]Isolated yield. [d]The addition of 10 equiv. acetophenone as a sensitizor. [e]Two tubes a time during the irradiation. [f]Three tubes a time during the irradiation.

Table S3. Studies for ODPM Rearrangement of 16



16 **17**

Entry	Lamps[a]	Concentration	Pump speed	Yield[b]
1	16	0.002 M	1 mL/min	41%
2	16	0.002 M	2 mL/min	43%
3	16	0.002 M	4 mL/min	52%
4	16	0.002 M	6 mL/min	45%
5	16	0.001 M	1 mL/min	19%
6[c]	16	0.002 M	4 mL/min	44%
7	16	0.004 M	4 mL/min	47%
8[d]	8	0.004 M	4 mL/min	26%
9[e]	8	0.004 M	4 mL/min	41%
10[f]	16	0.004 M	4 mL/min	54%
11	16	0.004 M	5 mL/min	51%

[a]The number of lamps in the photoreactor. [b]Isolated yield. [c]Gram-scale. [d]New lamps was installed on the photoreactor. [e]Old lamps was used for the photoreaction. [f]The photoreaction was carried out after the pump and tubing were washed with solvents.

Continuous-Flow Conditions:

Pump: HPLC pump (JASCO PU-2080 PLUS)

Tubing: PTFE (ID: 1.34 mm, OD: 1.64 mm, 54 mL)

Figure S1. Continuous-Flow Photoreaction

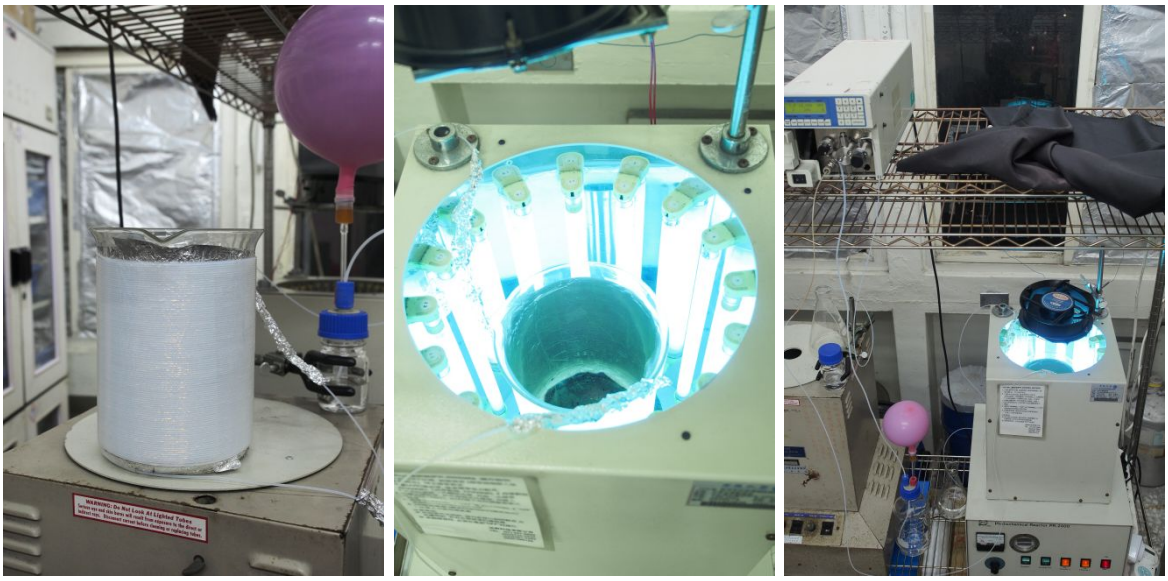
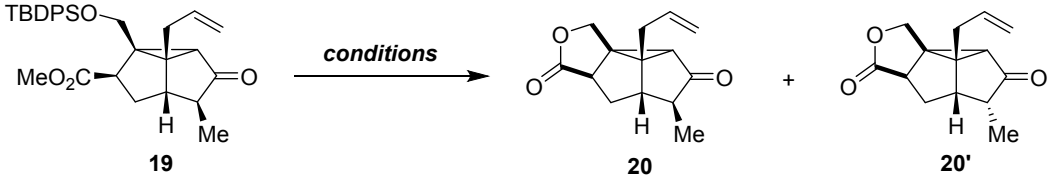


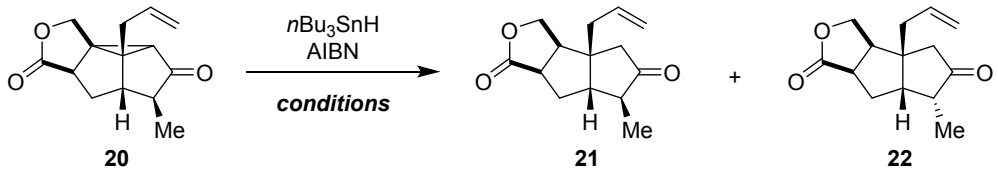
Table S4. Studies for Desilylation/Lactonization of 19



Entry	Conditions	Yield[a] (Ratio **20** : **20'**)[b]
1	TBAF (1 M/THF), rt, 15 h	90% (5 : 1)
2	TBAF (1 M/THF), rt, 25 h	76% (1 : 1)
3	TFA, CH_2Cl_2, rt, 48 h	quant. (1 : 0)
4	TFA, DCE, reflux, 5 h	79% (5 : 1)

[a]Isolated yield. [b]The ratio of **20** and **20'** were determined by ^{1}H NMR from the isolated products.

Table S5. Studies for *n*Bu$_3$SnH Reduction of 20

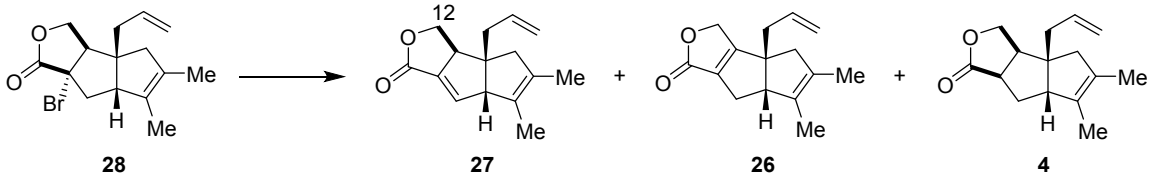


20 **21** **22**

Entry	Conditions	Yield[a]
1	Benzene (0.1 M), reflux, 8 h	**21**, 49% (70% brsm)+**22**, 8%
2	Benzene (0.1 M), reflux, 30 h	**21**, 36% (67% brsm)+**22**, 24%
3	Benzene (0.1 M), 160^{o}C(μw), 30 min	**21**, 65% (71% brsm)
4[b]	Benzene (0.1 M), 160^{o}C(μw), 1 h	**21**, 60% (70% brsm)
5	toluene (0.2 M), 160^{o}C(μw), 30 min	**21**, 74% (87% brsm)
6	toluene (0.2 M), 140^{o}C(μw), 30 min	**21**, 59% (69% brsm)
7	toluene (0.4 M), 160^{o}C(μw), 30 min	**21**, 78% (88% brsm)

[a]Isolated yield. [b](TMS)$_3$SiH was used as the hydride source with AIBN as the radical initiator.

Table S6. Studies for dehydrobromination of 28

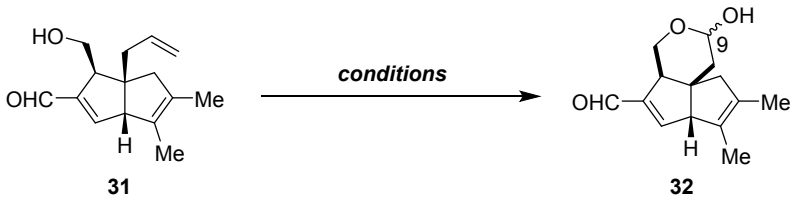


28 **27** **26** **4**

Entry	Conditions	Yield[a] (**27**/**26**/**4**)
1	DBU(2 equiv.), 0.2 M, reflux, 22 h	38%(54% brsm)/10%/9%
2[b]	DBU(2 equiv.), 0.2 M, reflux, 22 h	13%(28% brsm)/3%/19%
3	DBU(2 equiv.), 0.2 M, reflux, 14 h	23%(43% brsm)/5%/trace
4	DBU(2 equiv.), 0.2 M, reflux, 36 h	29%(38% brsm)/10%/trace
5	DBU(4 equiv.), 0.2 M, reflux, 22 h	27%(30% brsm)/14%/10%
6	DBU(2 equiv.), 0.3 M, reflux, 22 h	38%(50% brsm)/16%/trace
7	DBU(2 equiv.), 0.5 M, reflux, 22 h	0%/10%/trace
8	DBU(2 equiv.), 0.5 M, reflux, 4 h	36%(54% brsm)/11%/trace
9	DBU(2 equiv.), 0.5 M, reflux, 2 h	16%(54% brsm)/7%/trace
10	DBU(2 equiv.), 0.5 M, reflux, 1 h	18%(66% brsm)/8%/trace
11	DBU(2 equiv.), 0.5 M, 50 ^{o}C, 22 h	7%(19% brsm)/0%/0%
12	DBU(2 equiv.), 0.5 M, 70 ^{o}C, 22 h	17%(77% brsm)/0%/0%
13	DBU(2 equiv.), 0.5 M, 90 ^{o}C, 22 h	21%(28% brsm)/13%/0%
14	DBU(4 equiv.), 0.5 M, reflux, 1 h	31%(72% brsm)/trace/trace
15	DBU(6 equiv.), 0.5 M, reflux, 1 h	32%(55% brsm)/10%/trace

[a]Isolated yield. [b]BHT as the additive.

Table S7. Studies for Oxidative Cleavage of 31



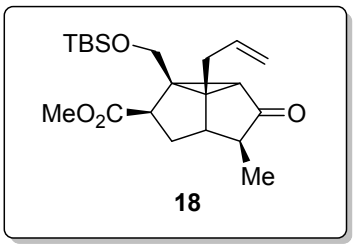
31 **32**

Entry	Conditions	Yield[a] of **32**
1	OsO_4 (0.02 equiv.), $NaIO_4$ (4 equiv.), 2,6-lutidine (2 equiv.), dioxane/H_2O (3:1), rt, 20 h	20% yield (57% brsm)
2	$K_2OsO_4 \bullet 2H_2O$ (0.02 equiv.), $NaIO_4$ (4 equiv.), 2,6-lutidine (2 equiv.), THF/H_2O (1:1), rt, 20 h	26% yield (86% brsm)
3	$K_2OsO_4 \bullet 2H_2O$ (0.22 equiv.), $NaIO_4$ (3 equiv.), 2,6-lutidine (4 equiv.), THF/H_2O (1:1), rt, 8 h	13% yield (14% brsm)

[a]Isolated yield.

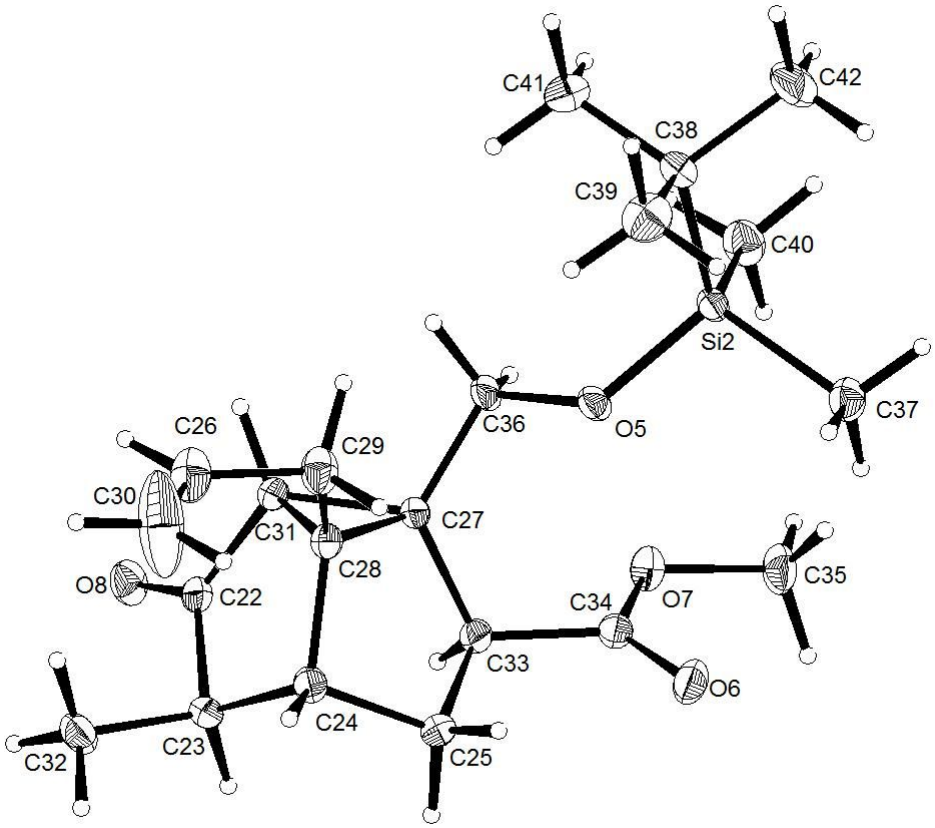
X-ray Crystallographic Analysis

X-ray crystallographic analysis of 18.



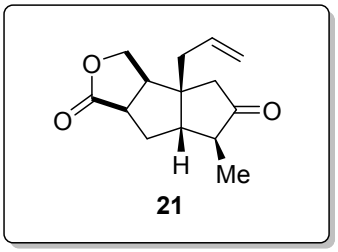
Crystal data and structure refinement		
Empirical formula	C21 H34 O4 Si	
Formula weight	378.57	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8826(2) Å	a= 67.8036(8)°.
	b = 14.0278(2) Å	b= 70.5153(8)°.
	c = 14.7882(3) Å	g = 77.3415(10)°.
Volume	2139.34(7) $Å^3$	
Z	4	
Density (calculated)	1.175 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	824	
Crystal size	0.2 x 0.2 x 0.15 mm^3	
Theta range for data collection	1.548 to 28.323°.	
Index ranges	-15<=h<=15, -18<=k<=18, -19<=l<=18	
Reflections collected	40282	
Independent reflections	10616 [R(int) = 0.0491]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7115	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10616 / 0 / 469	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1125	
R indices (all data)	R1 = 0.0683, wR2 = 0.1246	

Extinction coefficient	n/a
Largest diff. peak and hole	0.391 and -0.467 e.Å^{-3}



X-ray thermal ellipsoid plot of **18** (50% probability)

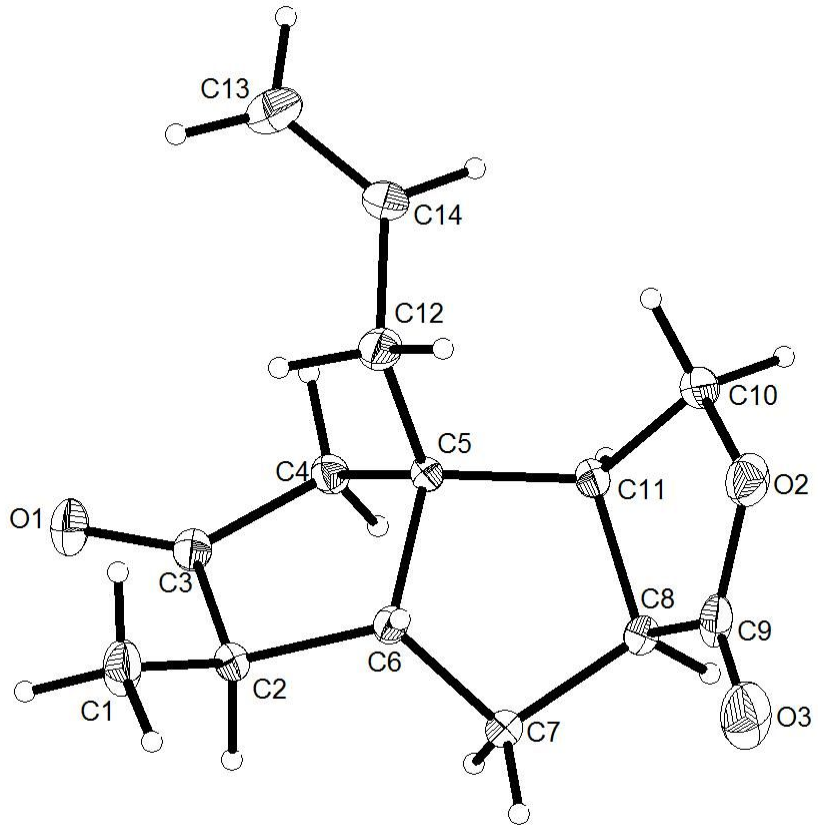
X-ray crystallographic analysis of 21.



21

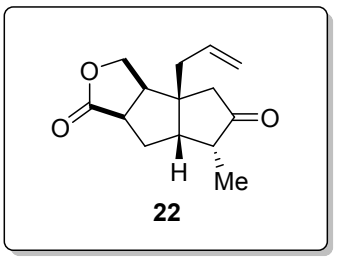
Crystal data and structure refinement

Empirical formula	C14 H18 O3	
Formula weight	234.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 6.4887(4) Å	a= 90°.
	b = 7.1740(4) Å	b= 93.117(4)°.
	c = 25.6544(15) Å	g = 90°.
Volume	1192.44(12) $Å^3$	
Z	4	
Density (calculated)	1.305 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	504	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.95 to 28.31°.	
Index ranges	-8<=h<=8, -9<=k<=9, -30<=l<=34	
Reflections collected	11785	
Independent reflections	2955 [R(int) = 0.0322]	
Completeness to theta = 28.31°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7116	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2955 / 0 / 154	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0977	
R indices (all data)	R1 = 0.0558, wR2 = 0.1067	
Largest diff. peak and hole	0.380 and -0.207 $e.Å^{-3}$	



X-ray thermal ellipsoid plot of **21** (50% probability)

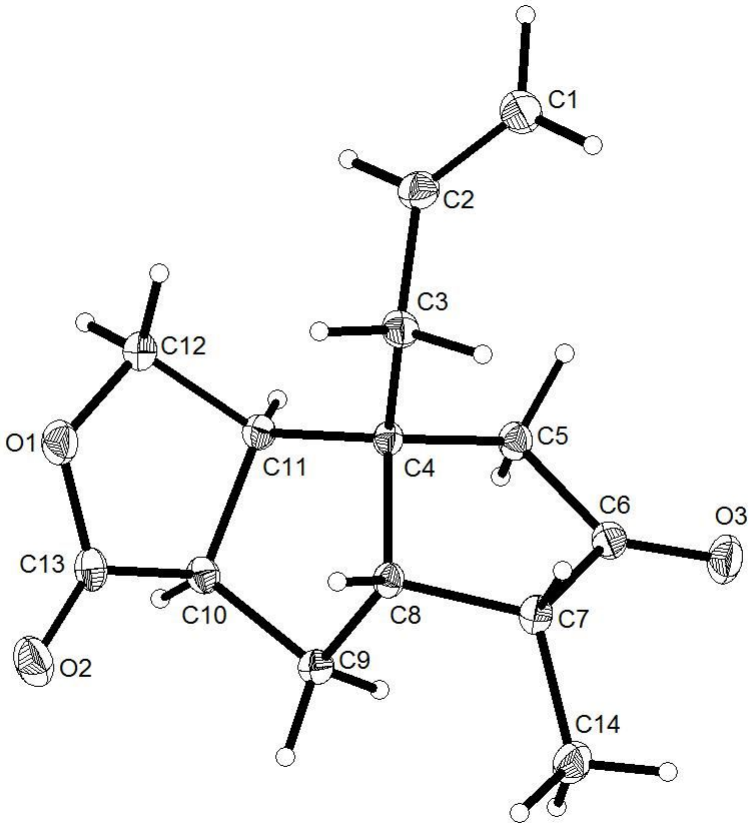
X-ray crystallographic analysis of 22.



22

Crystal data and structure refinement

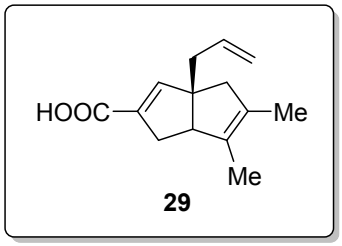
Empirical formula	C14 H18 O3	
Formula weight	234.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.57590(10) Å	a= 90.6670(10)°.
	b = 7.08190(10) Å	b= 99.8020(10)°.
	c = 13.0369(3) Å	g = 100.1960(10)°.
Volume	588.269(18) $Å^3$	
Z	2	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	252	
Crystal size	0.2 x 0.15 x 0.1 mm^3	
Theta range for data collection	1.59 to 28.28°.	
Index ranges	-8<=h<=8, -9<=k<=8, -17<=l<=17	
Reflections collected	10548	
Independent reflections	2909 [R(int) = 0.0149]	
Completeness to theta = 28.28°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7182	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2909 / 0 / 154	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0980	
R indices (all data)	R1 = 0.0412, wR2 = 0.1017	
Largest diff. peak and hole	0.386 and -0.199 $e.Å^{-3}$	



X-ray thermal ellipsoid plot of **22** (50% probability)

X-ray crystallographic analysis of 29.

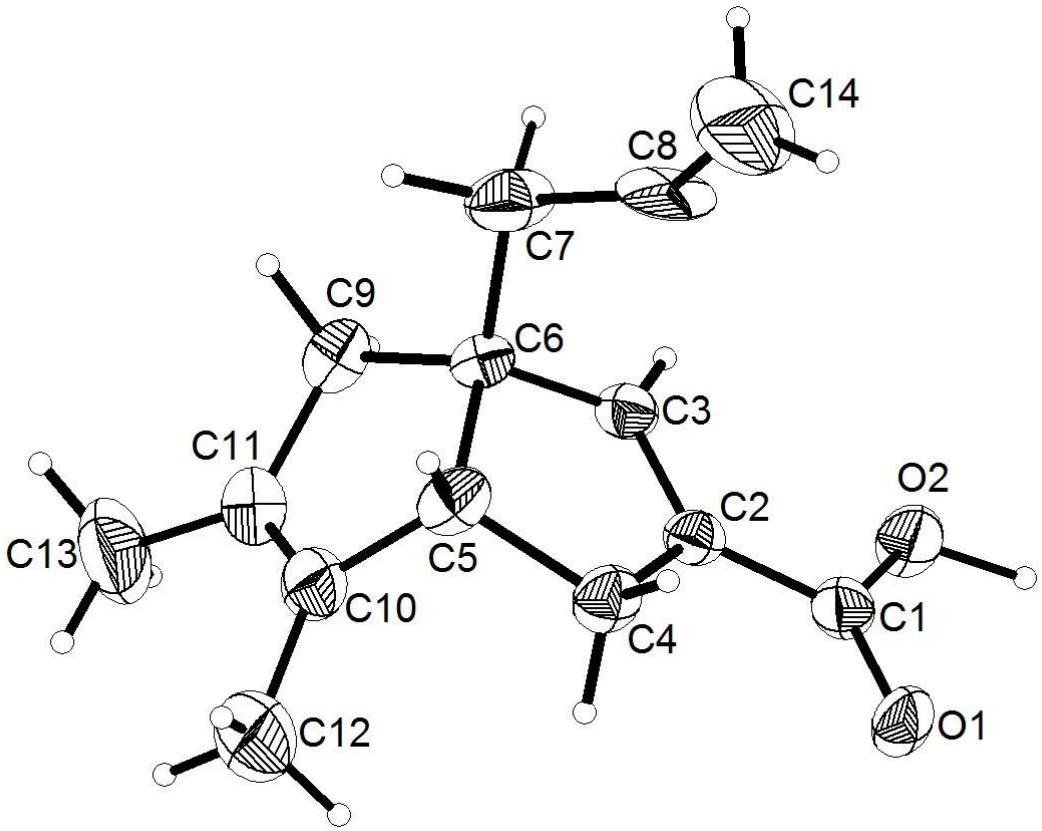
Crystal data and structure refinement



29

Empirical formula	C14 H17 O2	
Formula weight	217.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.6989(2) Å	α= 90°.
	b = 14.1778(3) Å	β= 105.433(2)°.
	c = 12.0083(3) Å	γ = 90°.
Volume	1263.48(5) $Å^3$	
Z	4	
Density (calculated)	1.142 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	468	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
Theta range for data collection	2.271 to 28.282°.	
Index ranges	-10<=h<=10, -18<=k<=18, -15<=l<=12	
Reflections collected	11168	
Independent reflections	3092 [R(int) = 0.0577]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6954	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3092 / 6 / 166	
Goodness-of-fit on F^2	1.126	
Final R indices [I>2sigma(I)]	R1 = 0.1031, wR2 = 0.2106	
R indices (all data)	R1 = 0.1600, wR2 = 0.2306	
Extinction coefficient	n/a	

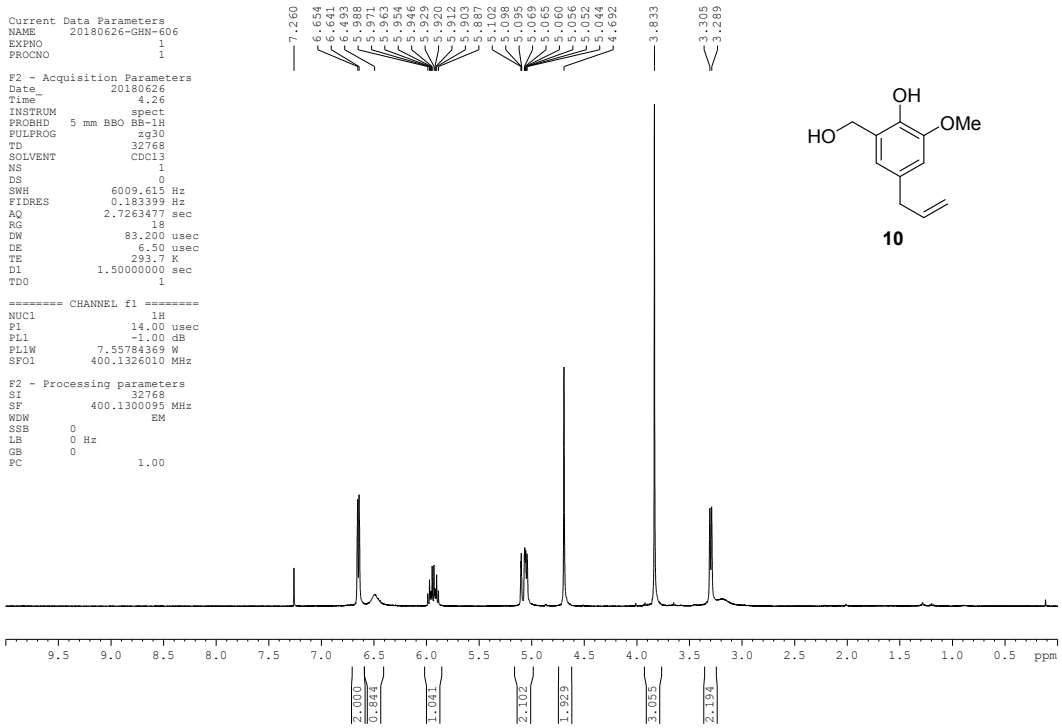
Largest diff. peak and hole	0.325 and -0.294 e.Å^{-3}



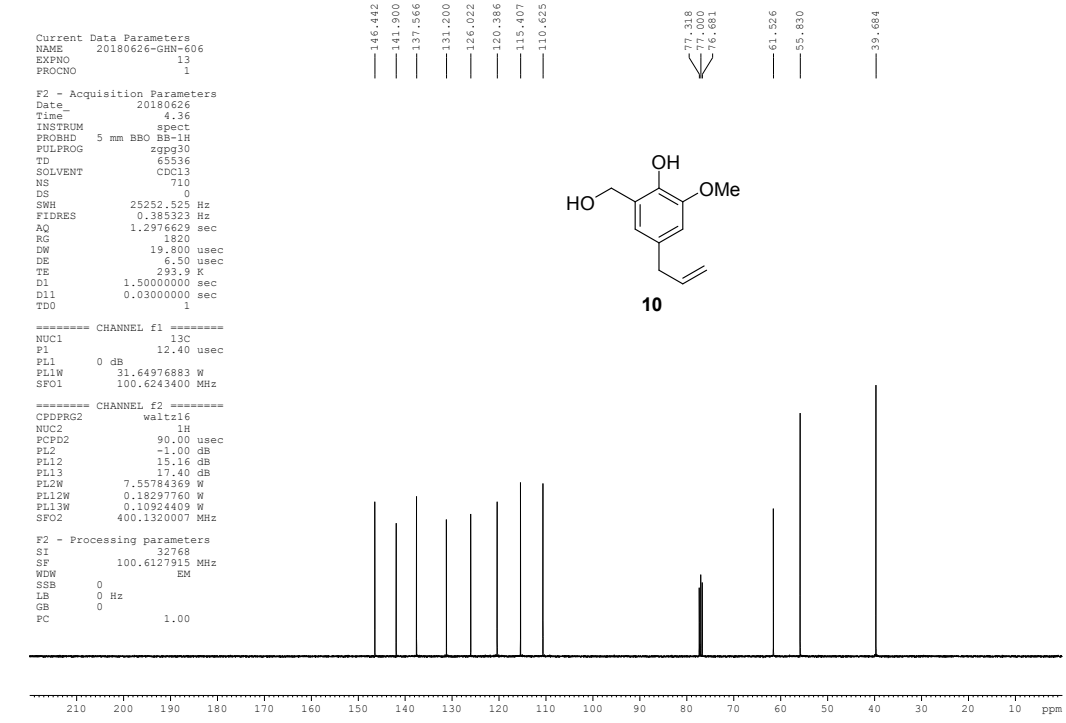
X-ray thermal ellipsoid plot of **29** (50% probability)

Spectroscopic Data

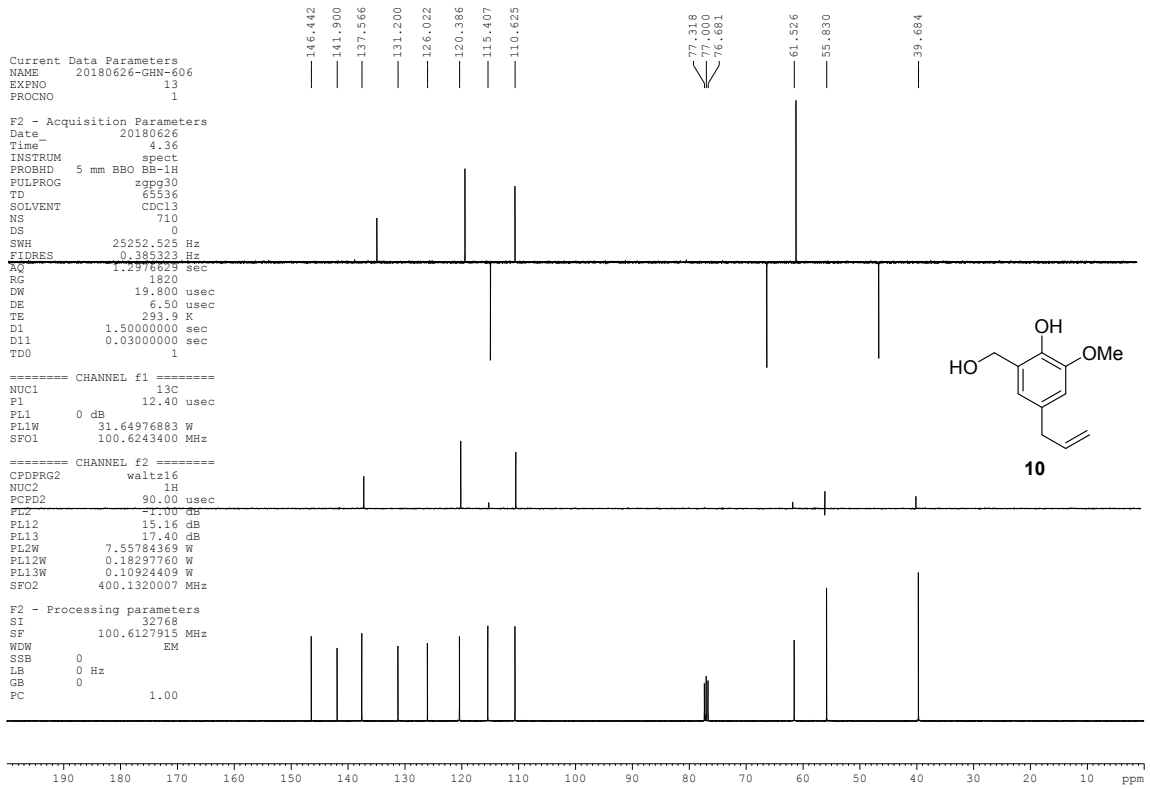
^{1}H NMR of 10, $CDCl_3$, 400 MHz, 24 ^{o}C



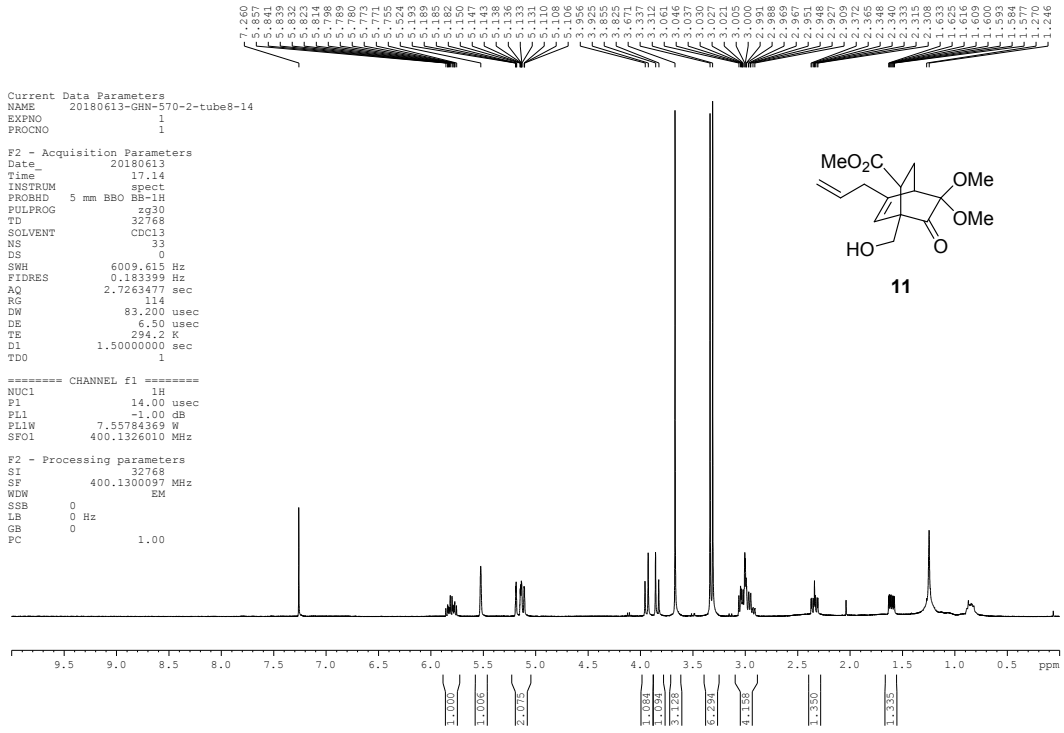
^{13}C NMR of 10, $CDCl_3$, 100 MHz, 24 ^{o}C



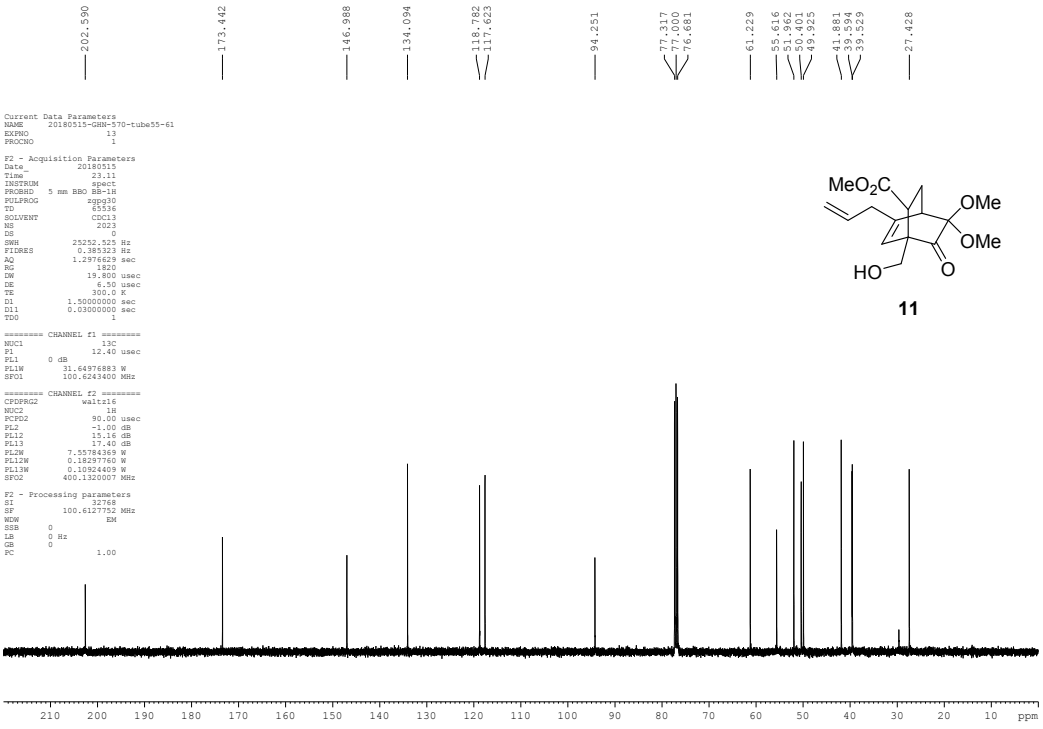
DEPT 135, DEPT 90 and ^{13}C NMR of 10, $CDCl_3$, 100 MHz, 24 ^{o}C



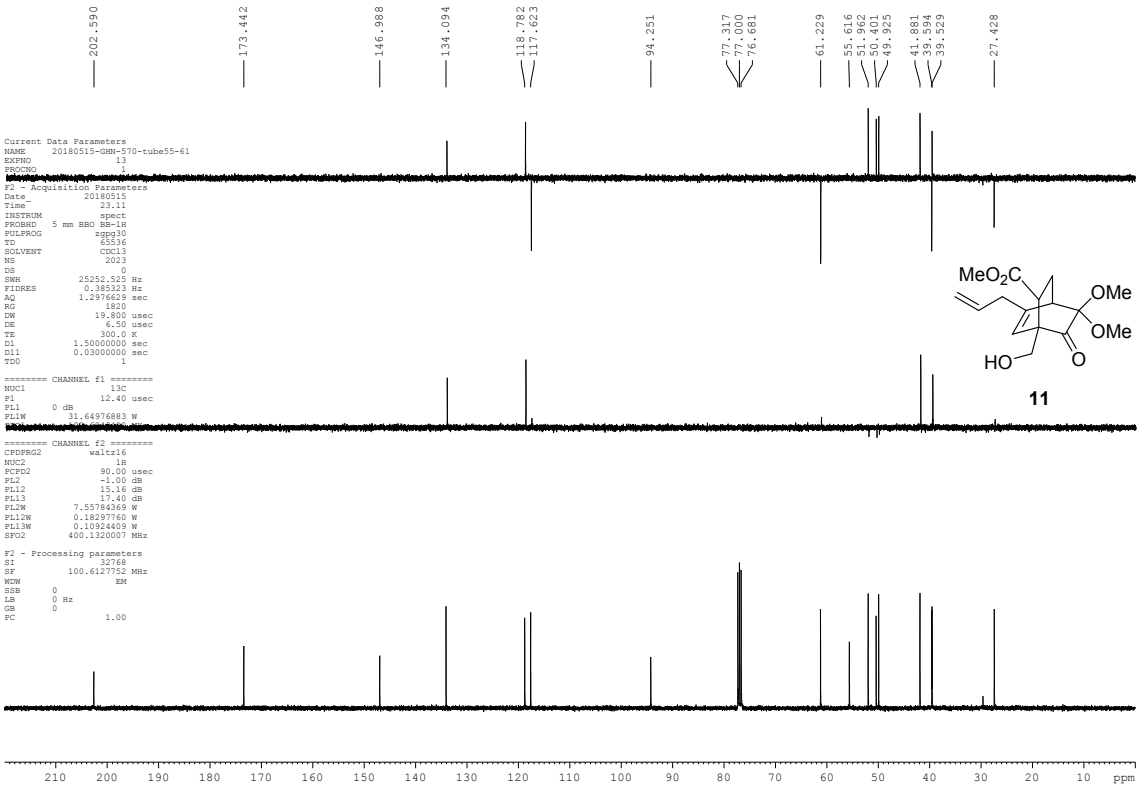
^{1}H NMR of 11, $CDCl_3$, 400 MHz, 24 ^{o}C



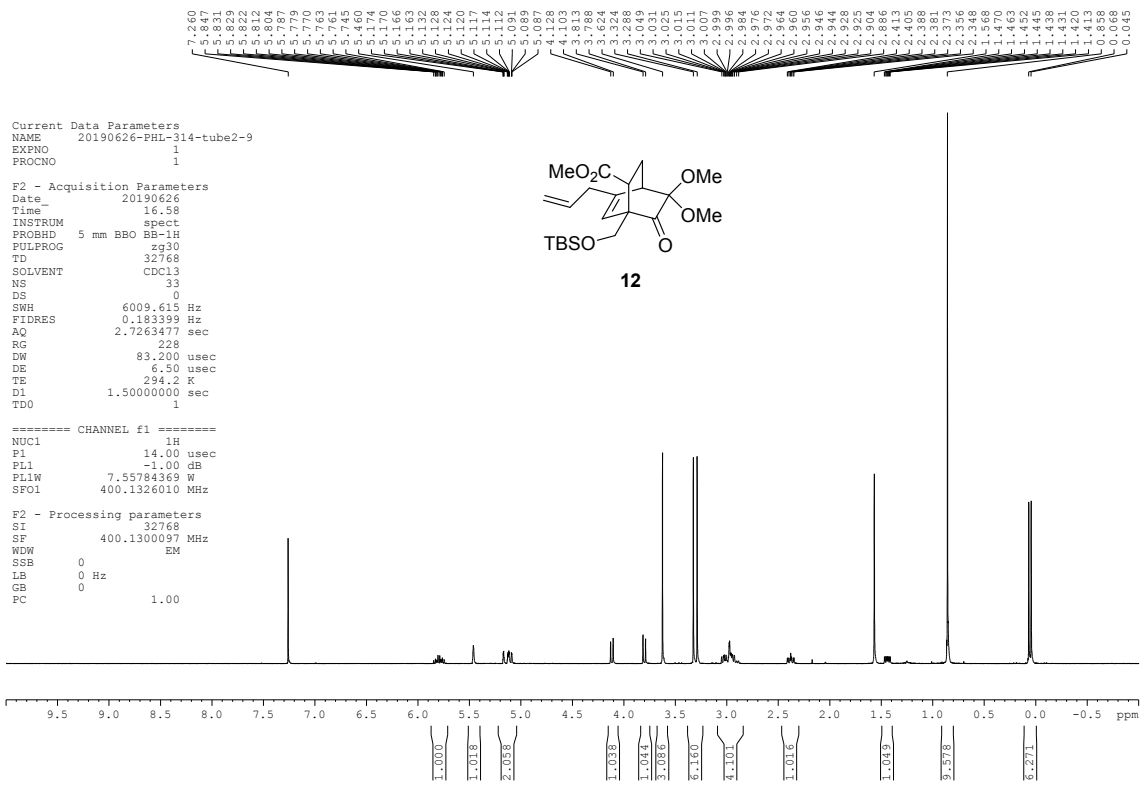
^{13}C NMR of 11, $CDCl_3$, 100 MHz, 24 °C



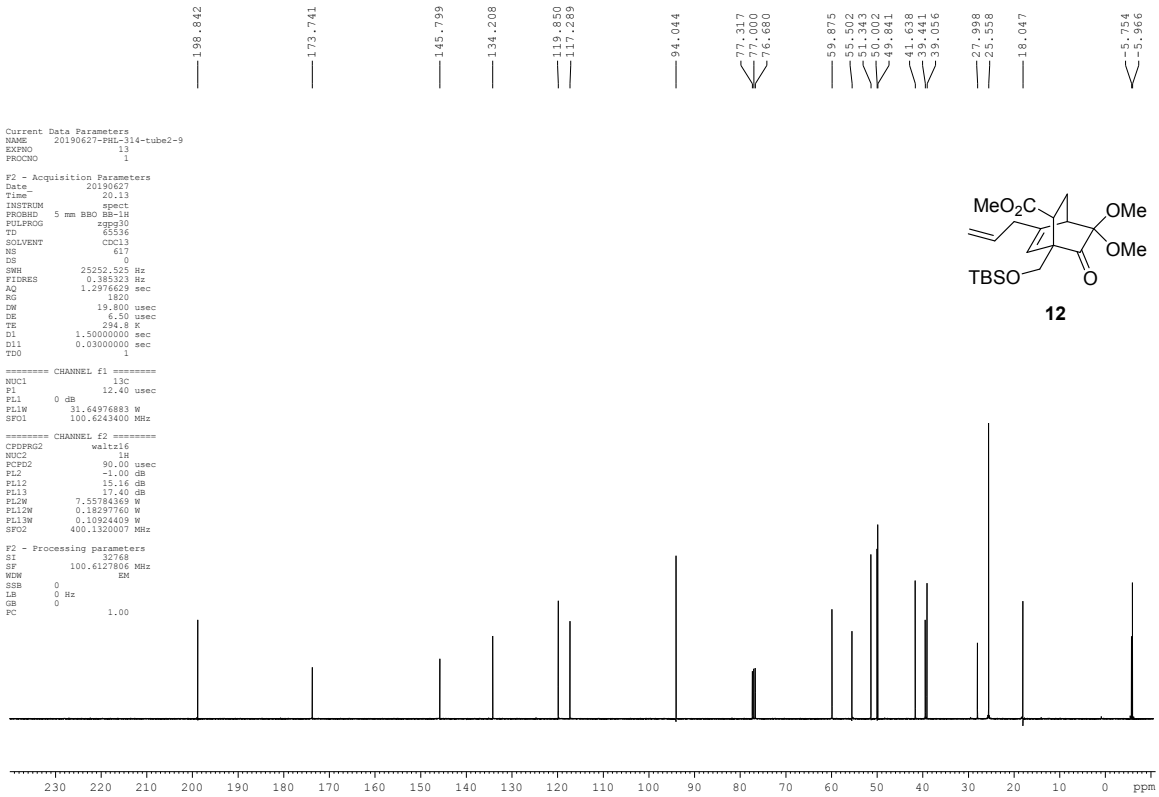
DEPT 135, DEPT 90 and ^{13}C NMR of 11, $CDCl_3$, 100 MHz, 24 °C



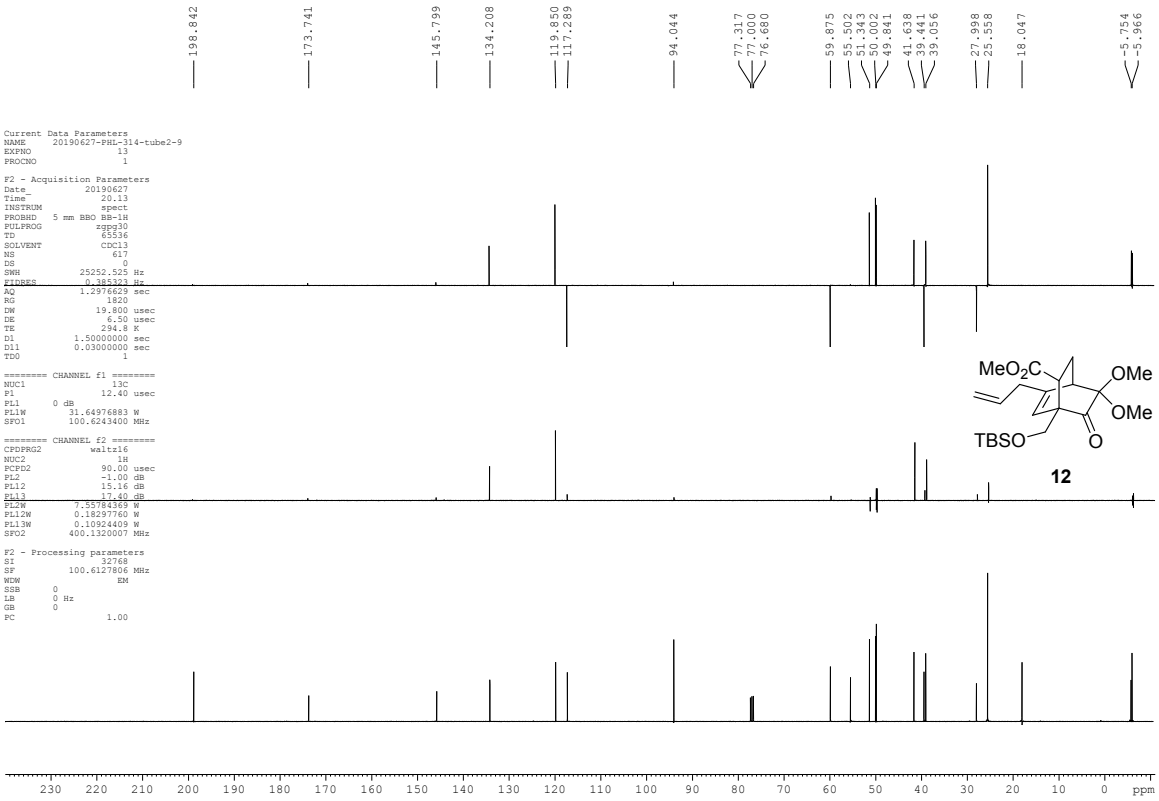
^{1}H NMR of 12, $CDCl_3$, 400 MHz, 24 ^{o}C



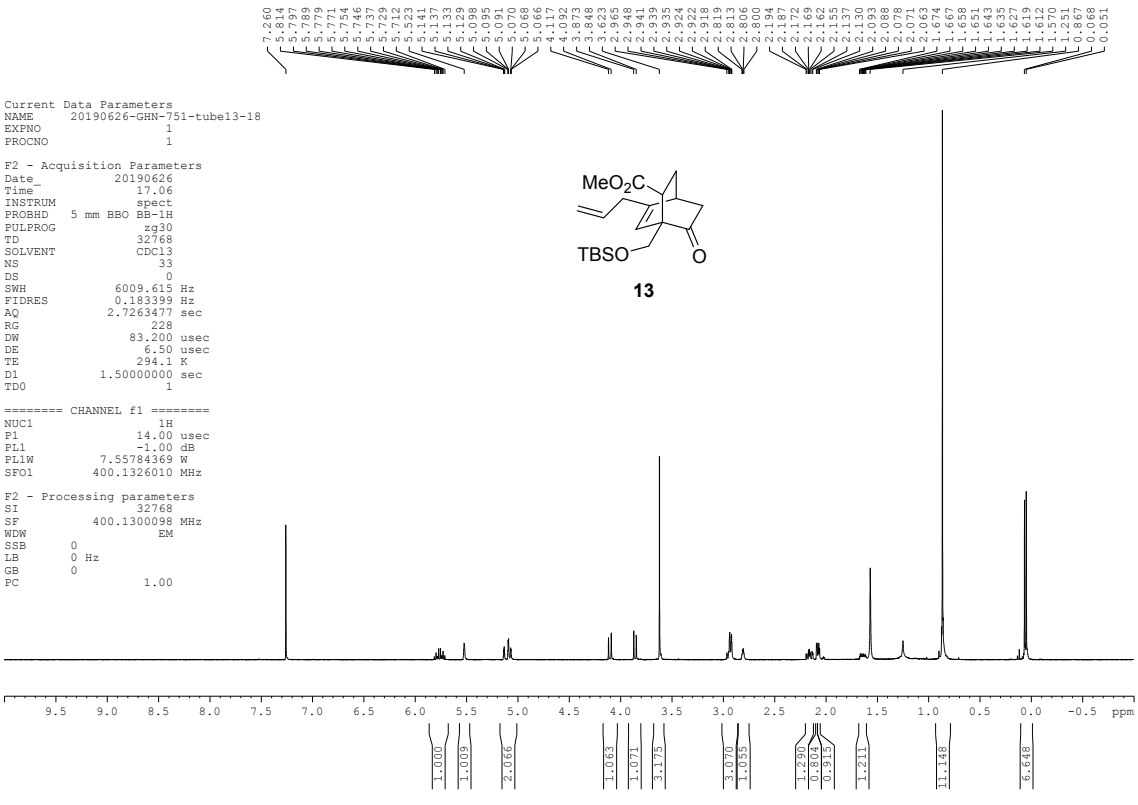
^{13}C NMR of 12, $CDCl_3$, 100 MHz, 24 ^{o}C



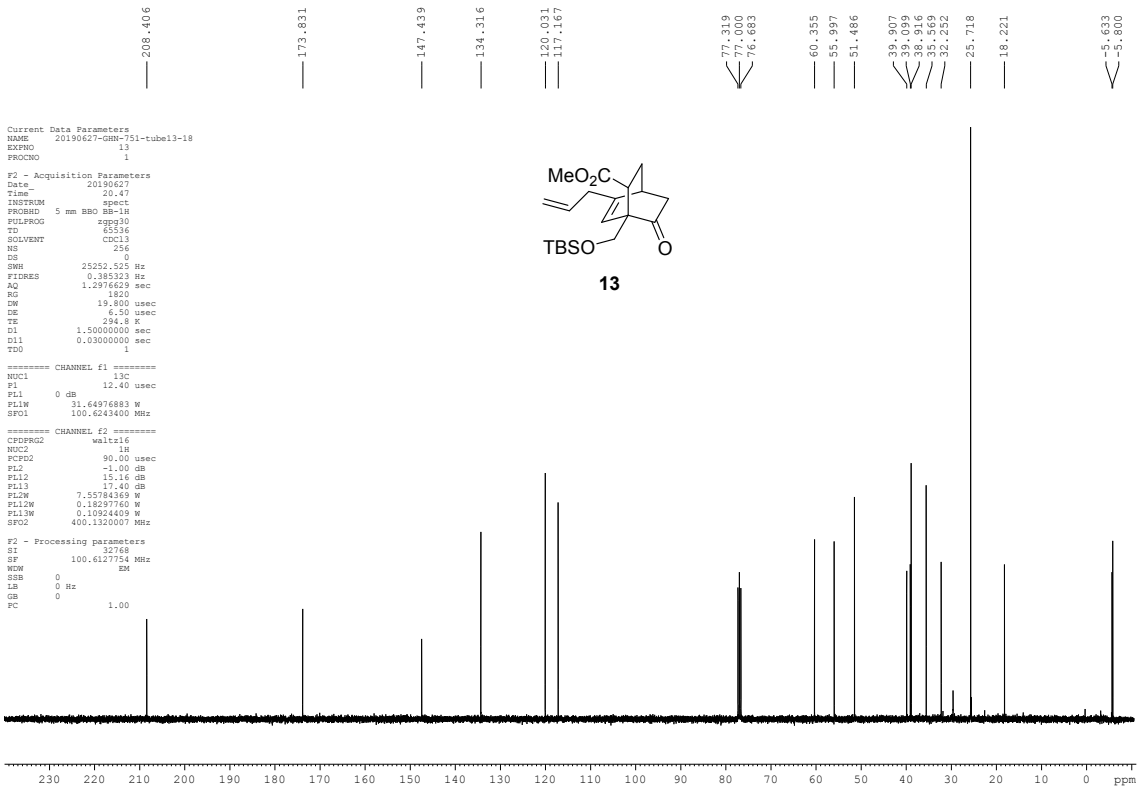
DEPT 135, DEPT 90 and ^{13}C NMR of 12, $CDCl_3$, 100 MHz, 24 °C



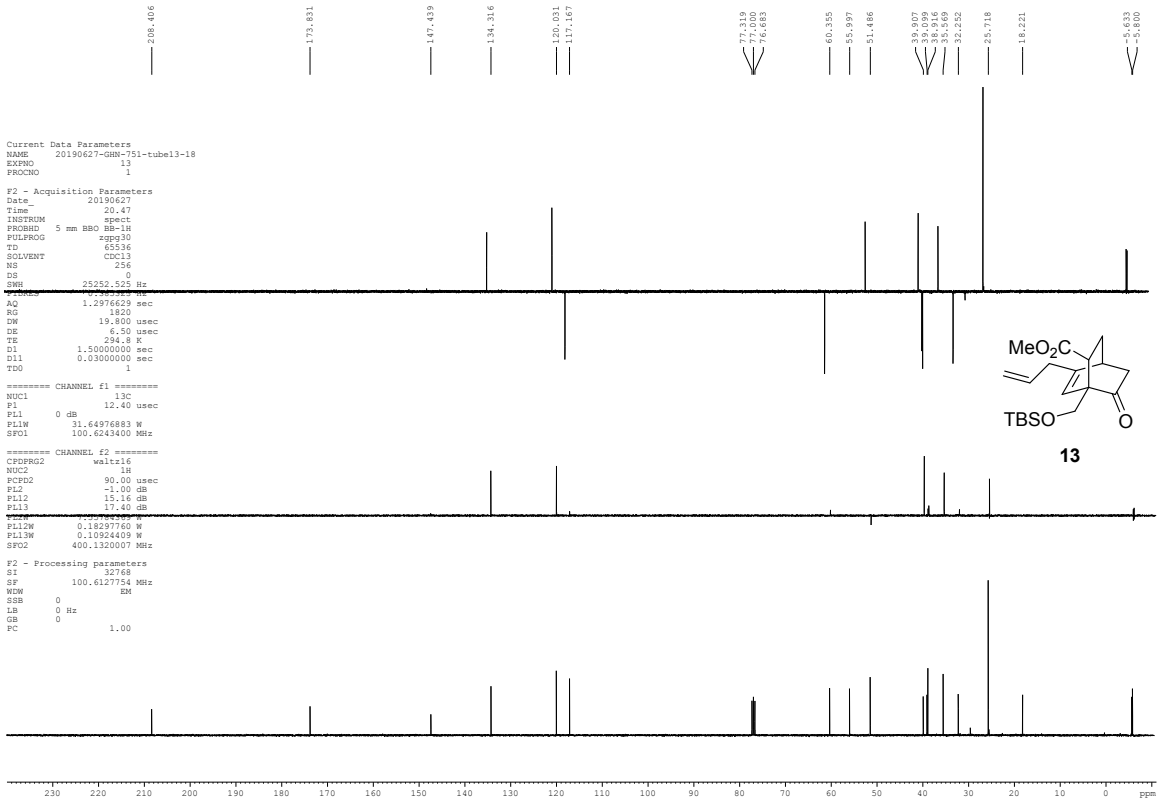
^{1}H NMR of 13, $CDCl_3$, 400 MHz, 24 °C



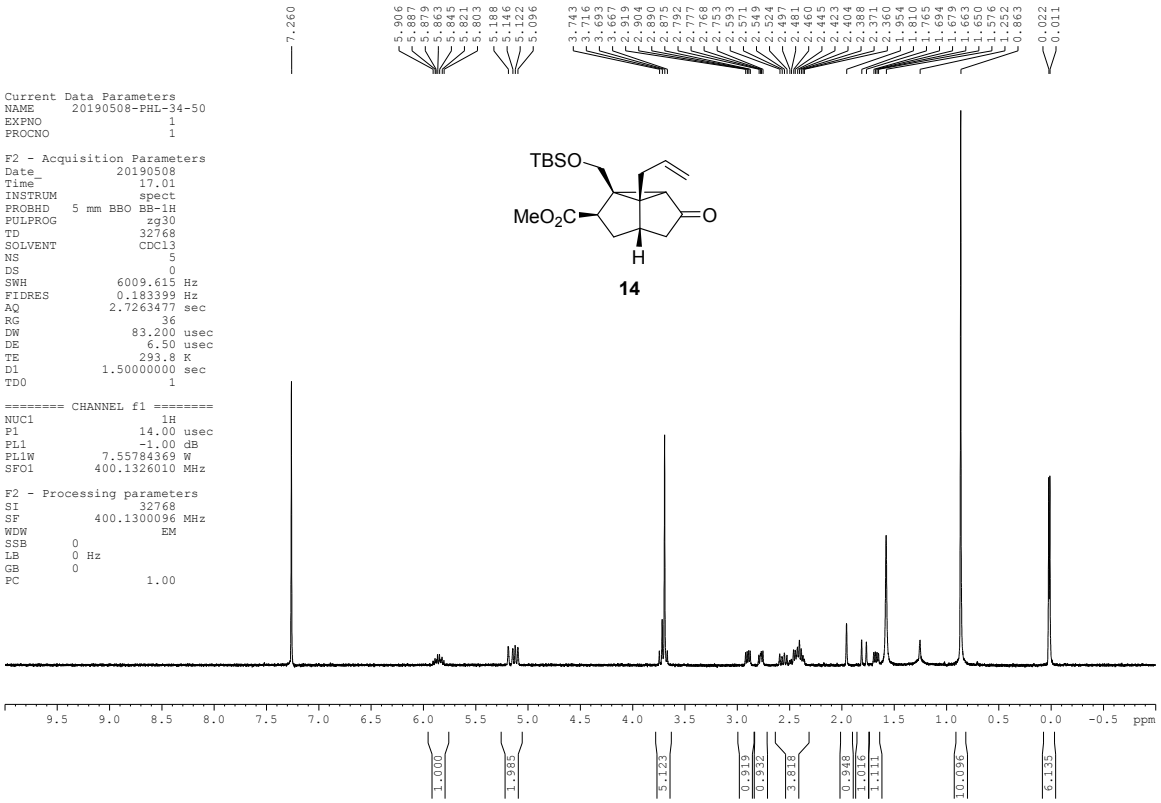
^{13}C NMR of 13, $CDCl_3$, 100 MHz, 24 °C



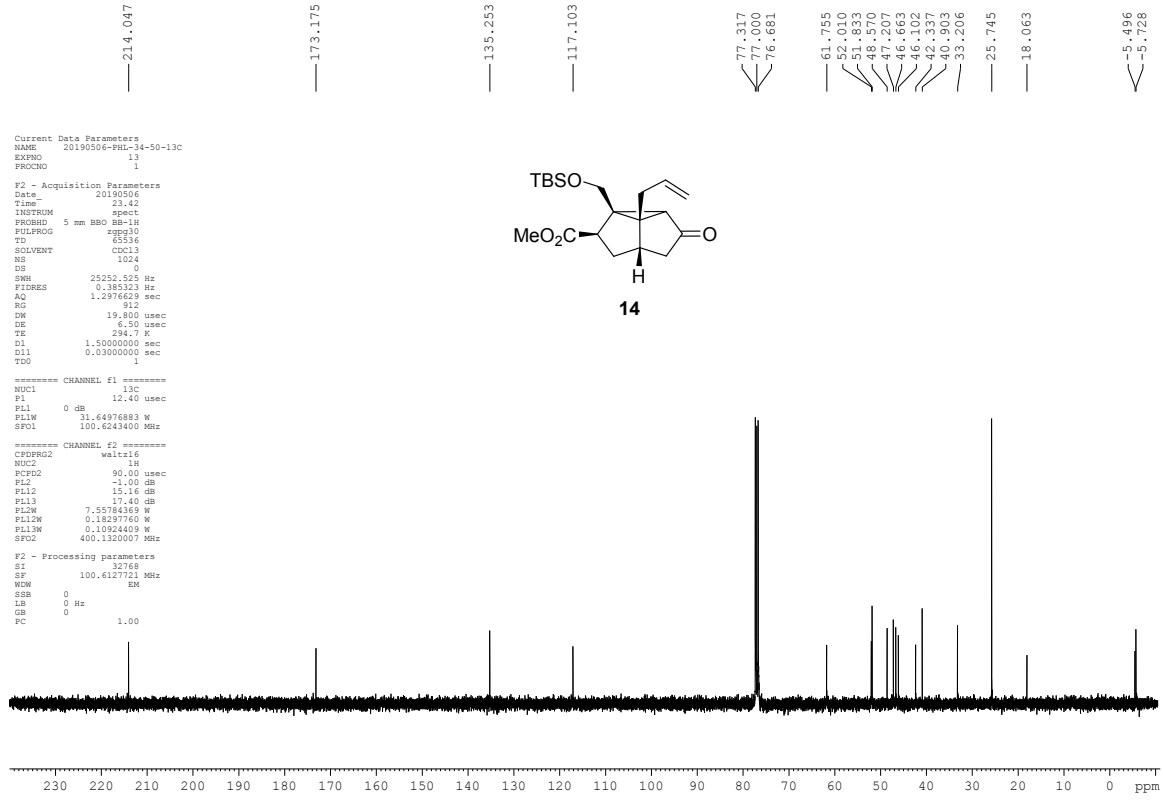
DEPT 135, DEPT 90 and ^{13}C NMR of 13, $CDCl_3$, 100 MHz, 24 °C



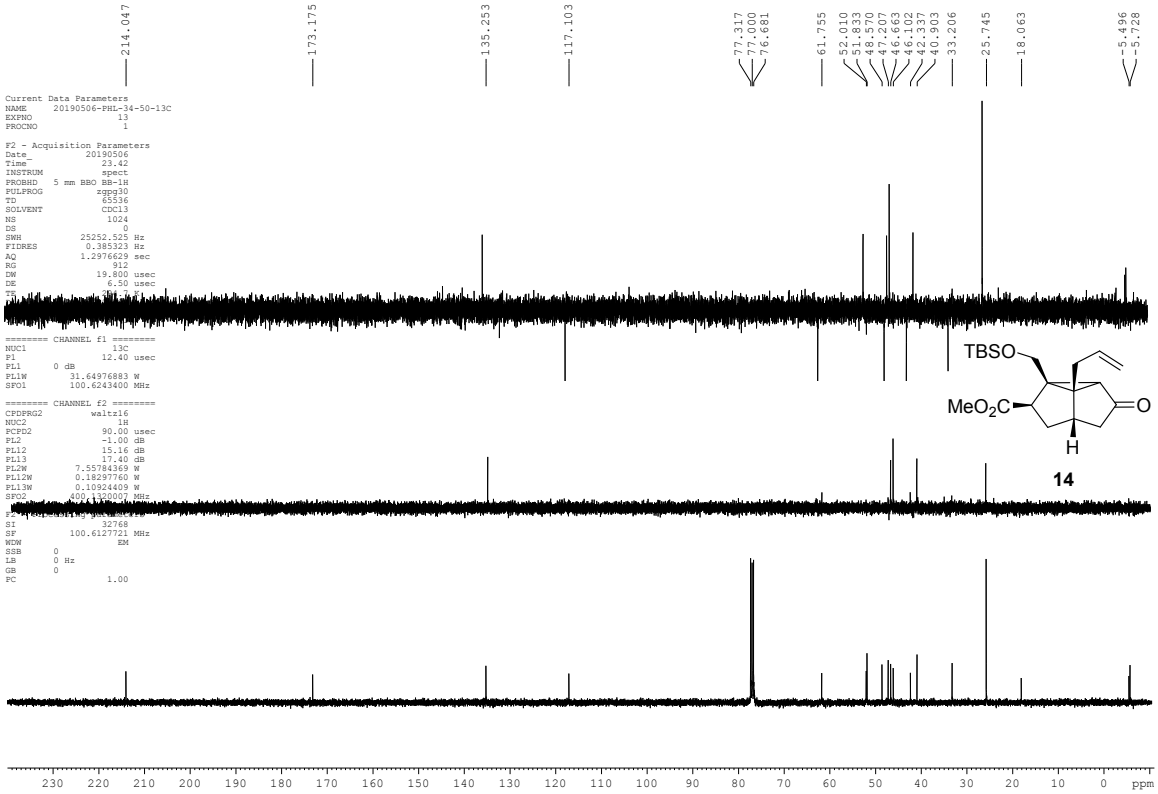
^{1}H NMR of 14, $CDCl_3$, 400 MHz, 24 ^{o}C



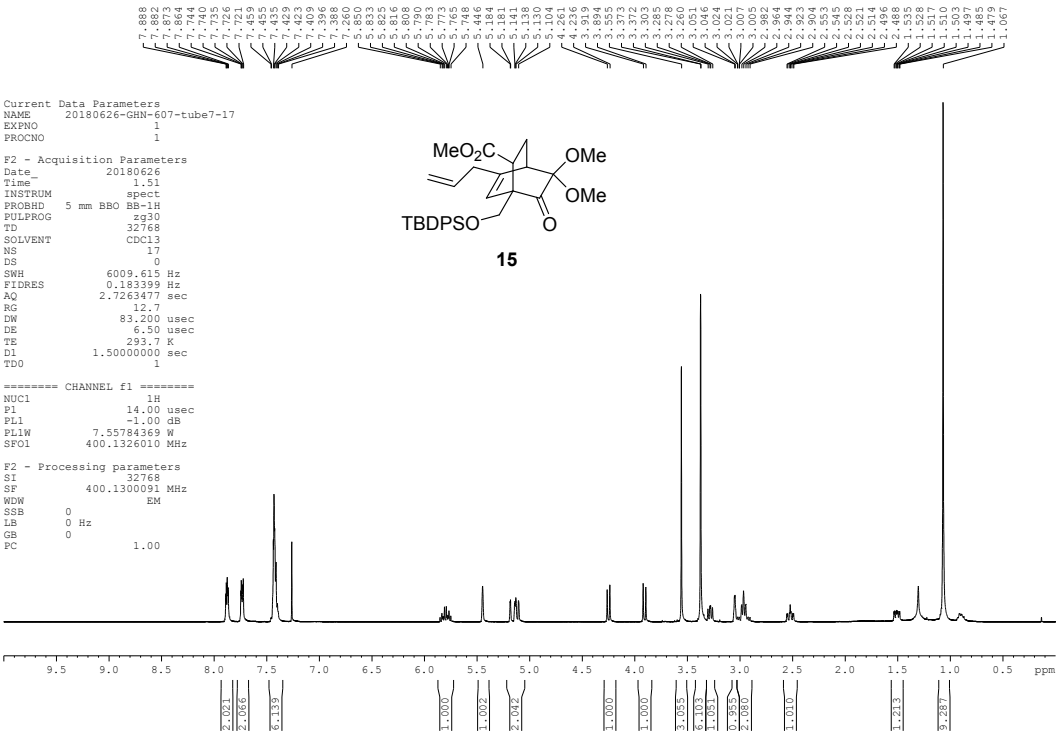
^{13}C NMR of 14, $CDCl_3$, 100 MHz, 24 ^{o}C



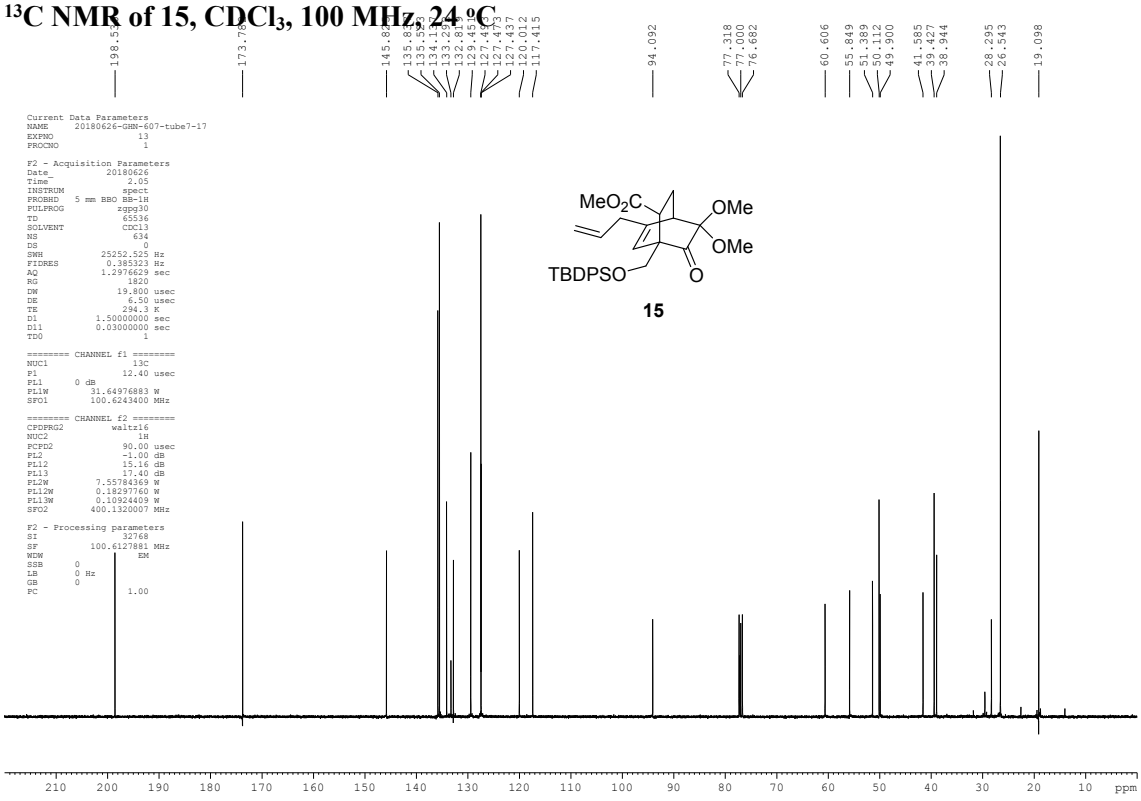
DEPT 135, DEPT 90 and ^{13}C NMR of 14, $CDCl_3$, 100 MHz, 24 °C



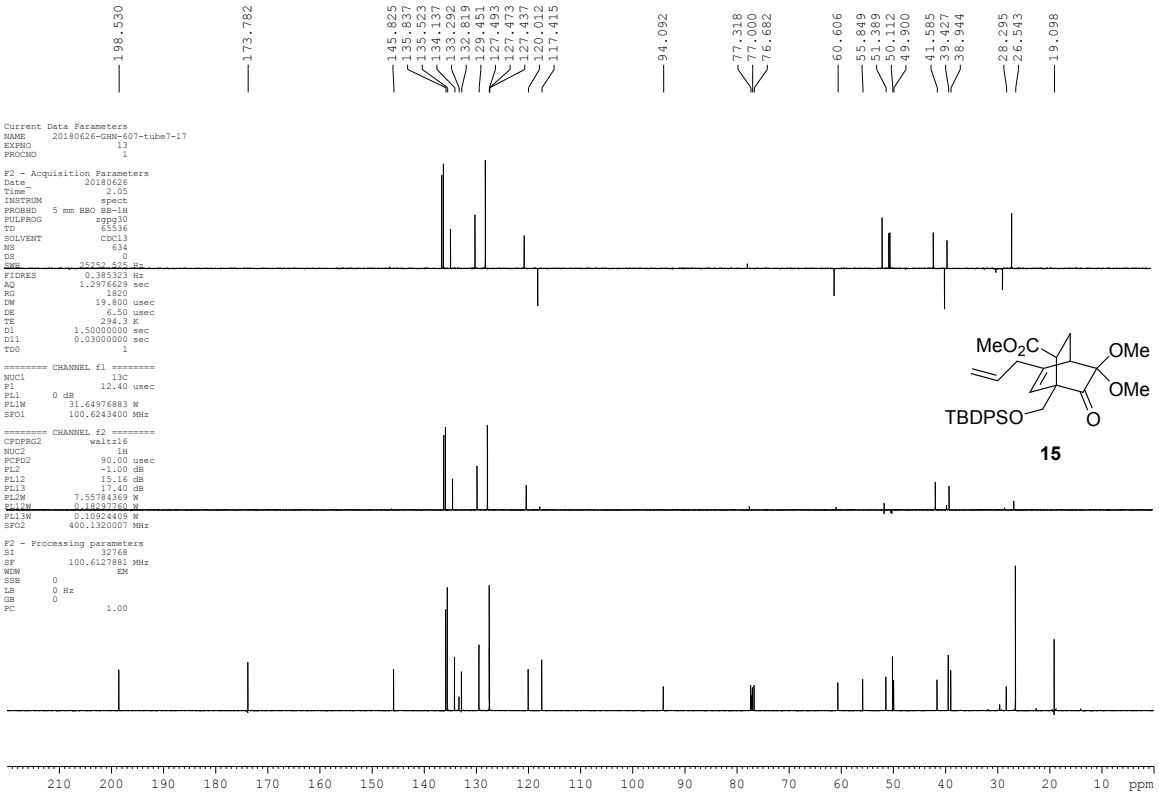
^{1}H NMR of 15, $CDCl_3$, 400 MHz, 24 °C



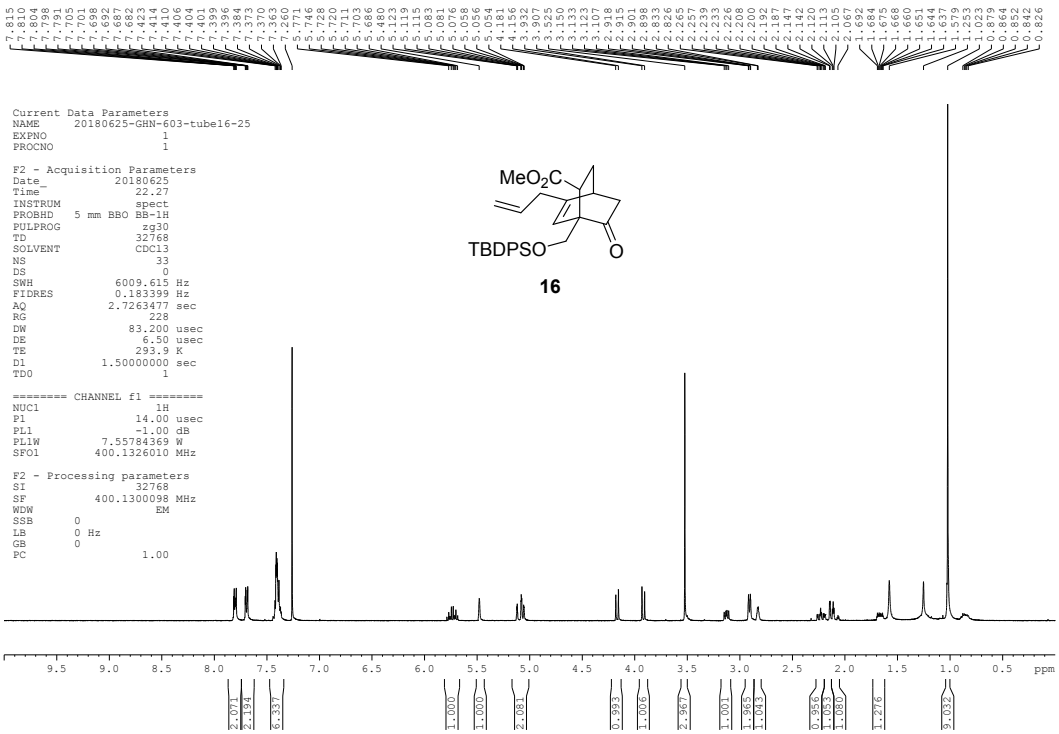
^{13}C NMR of 15, $CDCl_3$, 100 MHz, 24 °C



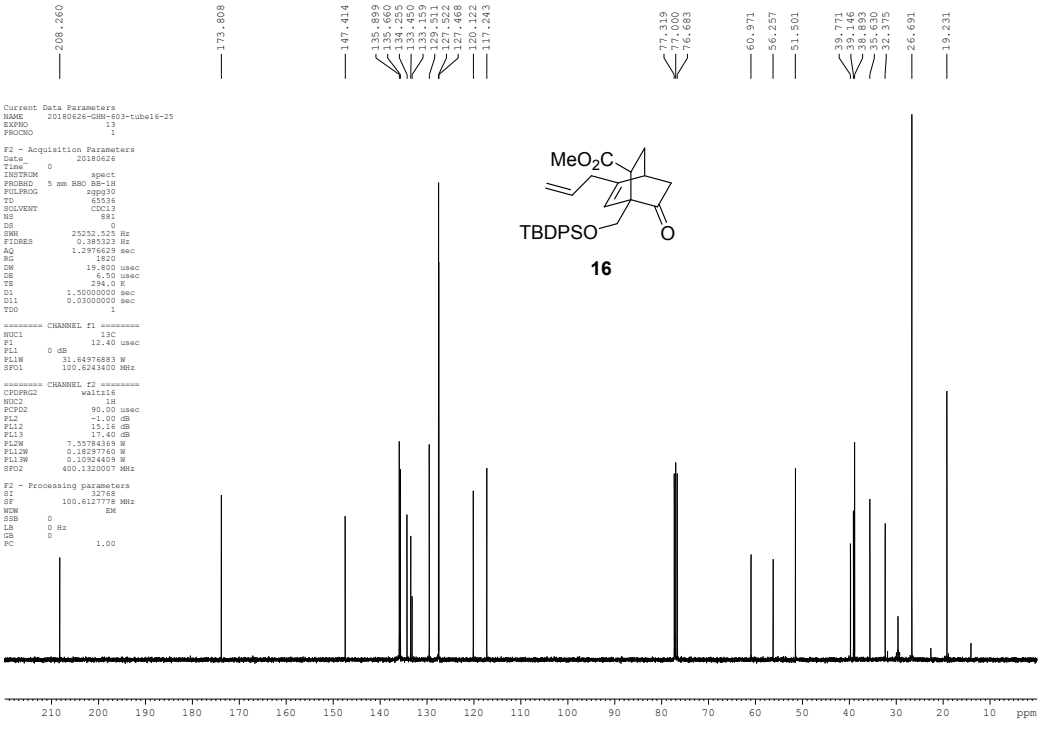
DEPT 135, DEPT 90 and ^{13}C NMR of 15, $CDCl_3$, 100 MHz, 24 °C



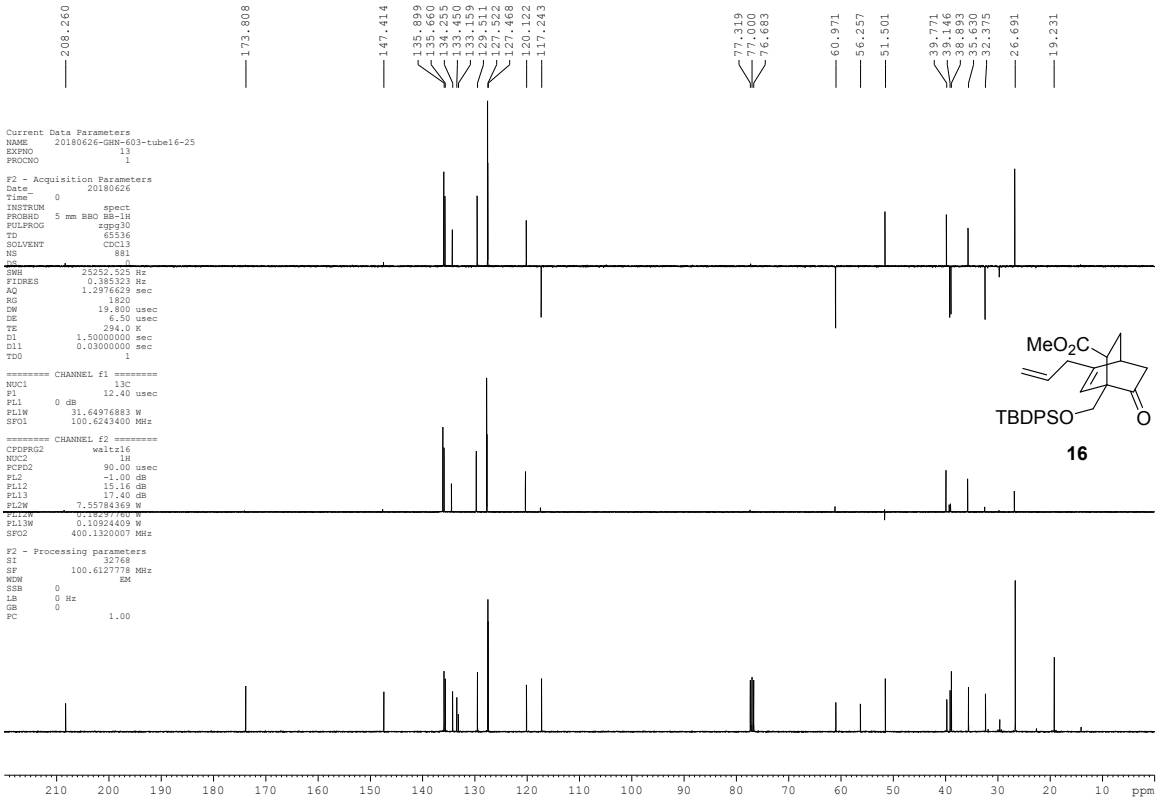
^{1}H NMR of 16, $CDCl_3$, 400 MHz, 24 ^{o}C



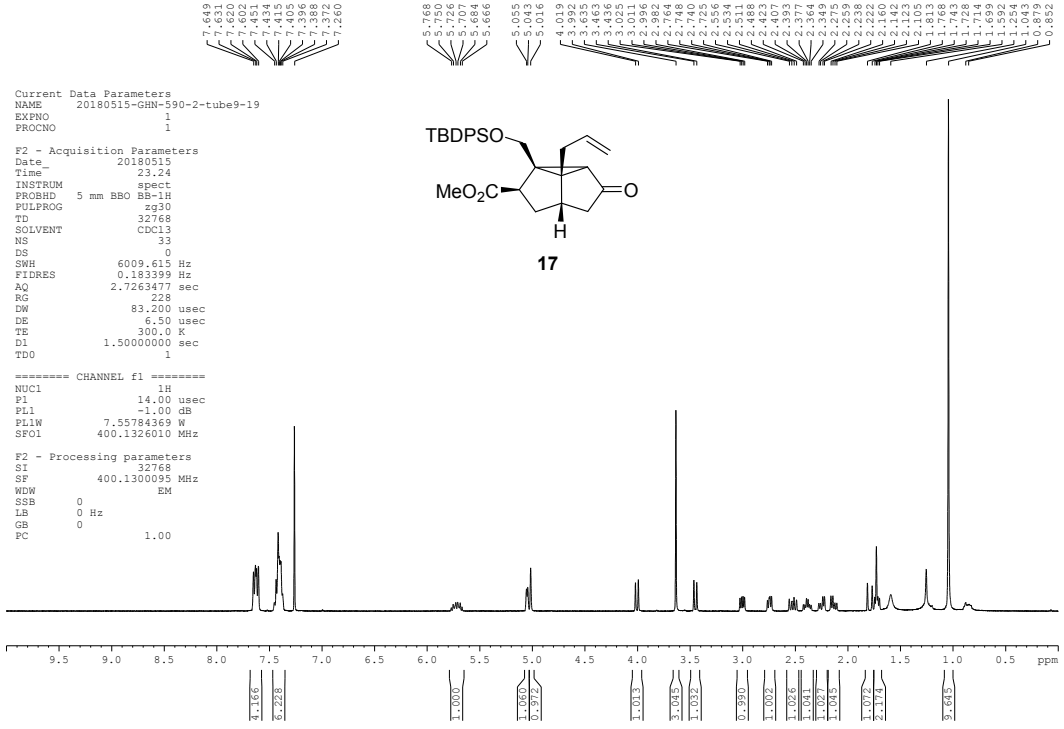
^{13}C NMR of 16, $CDCl_3$, 100 MHz, 24 ^{o}C



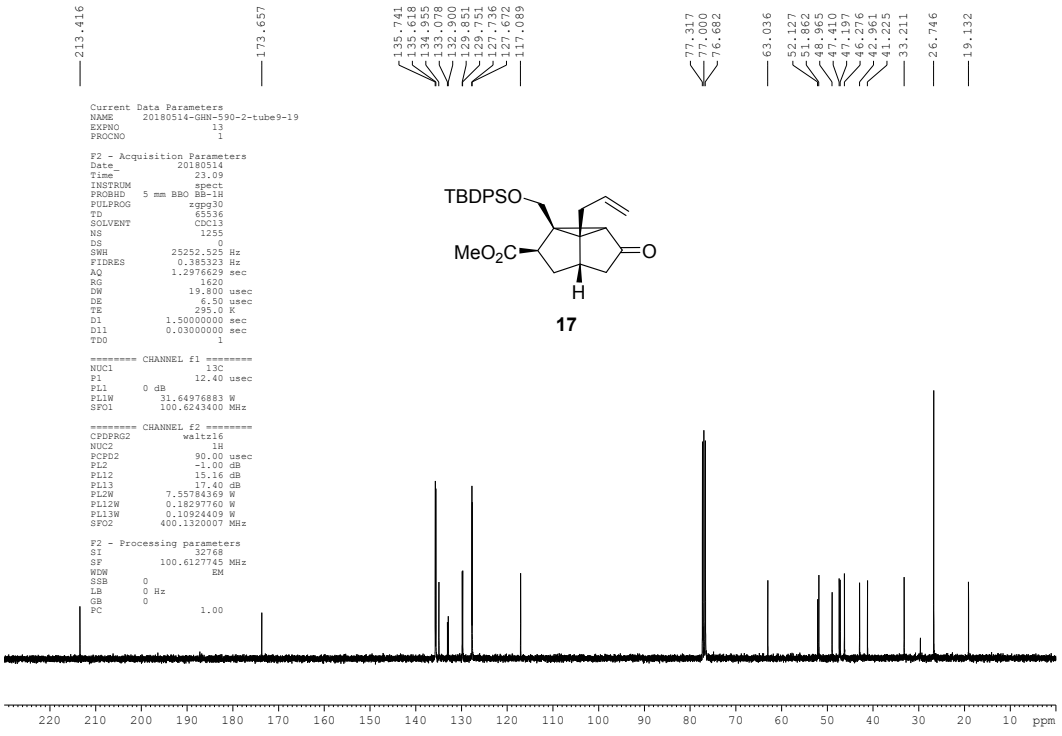
DEPT 135, DEPT 90 and ^{13}C NMR of 16, $CDCl_3$, 100 MHz, 24 °C



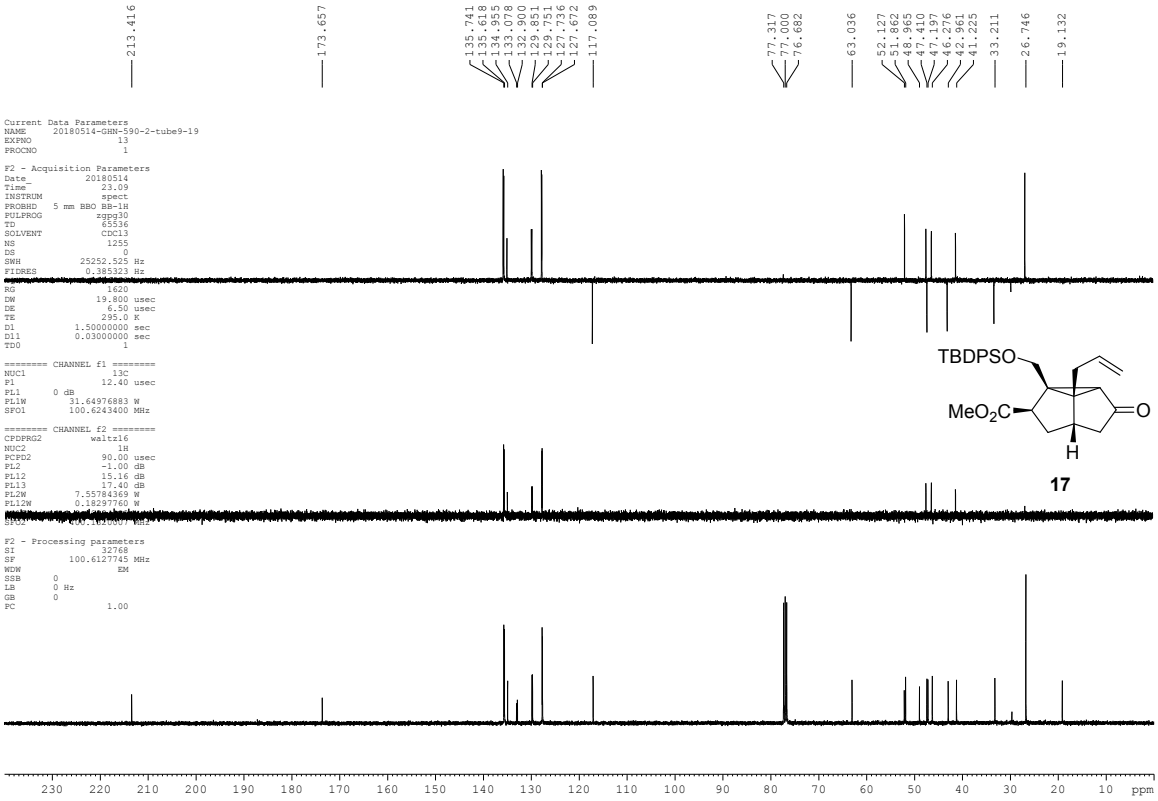
^{1}H NMR of 17, $CDCl_3$, 400 MHz, 24 °C



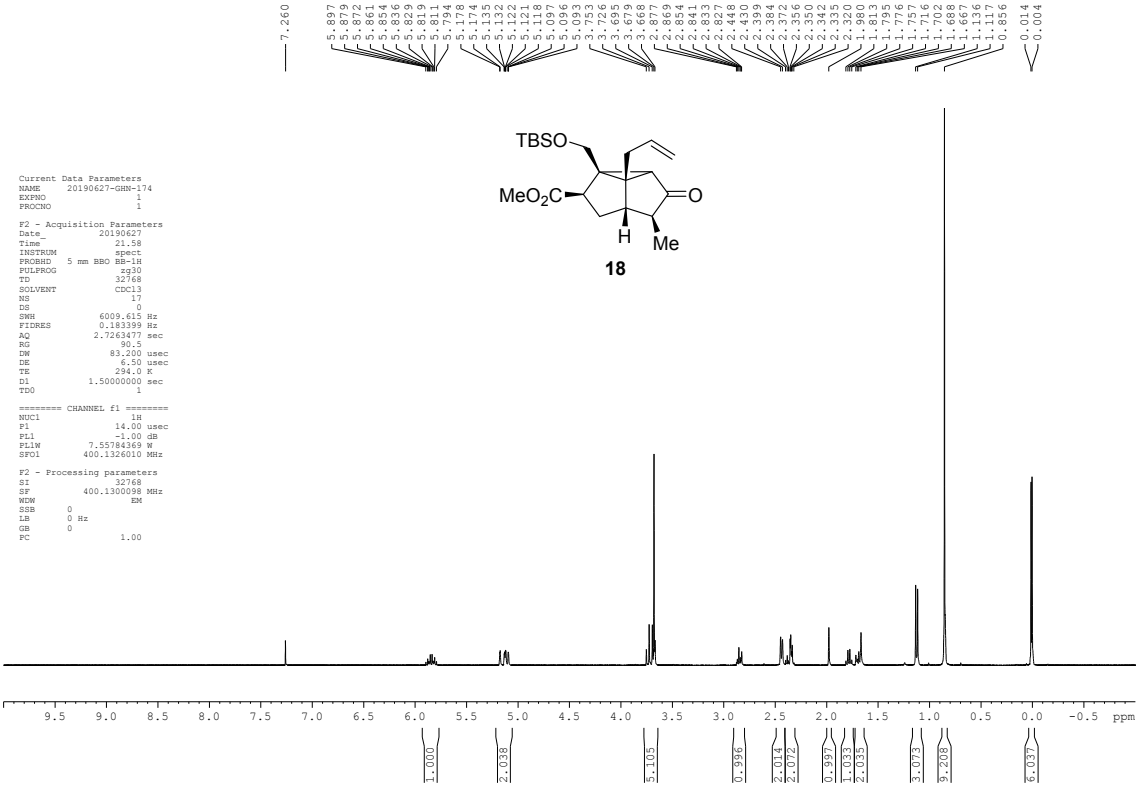
^{13}C NMR of 17, $CDCl_3$, 100 MHz, 24 ^oC



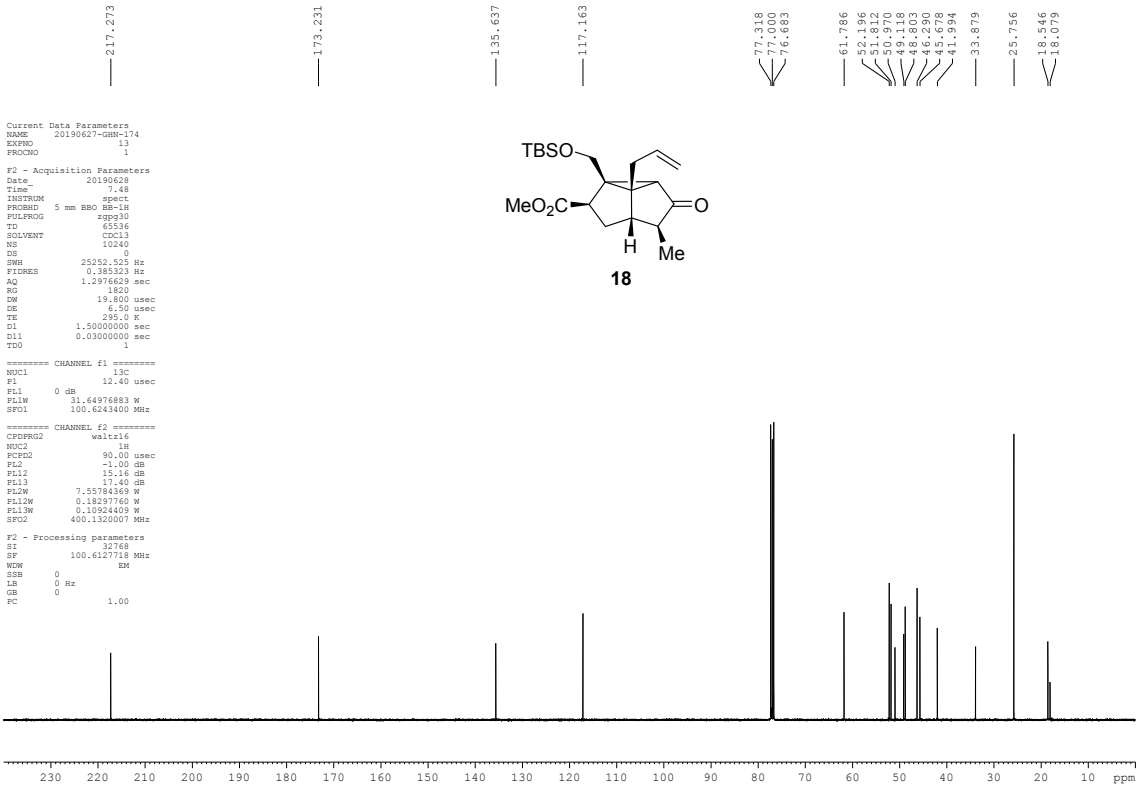
DEPT 135, DEPT 90 and ^{13}C NMR of 17, $CDCl_3$, 100 MHz, 24 ^oC



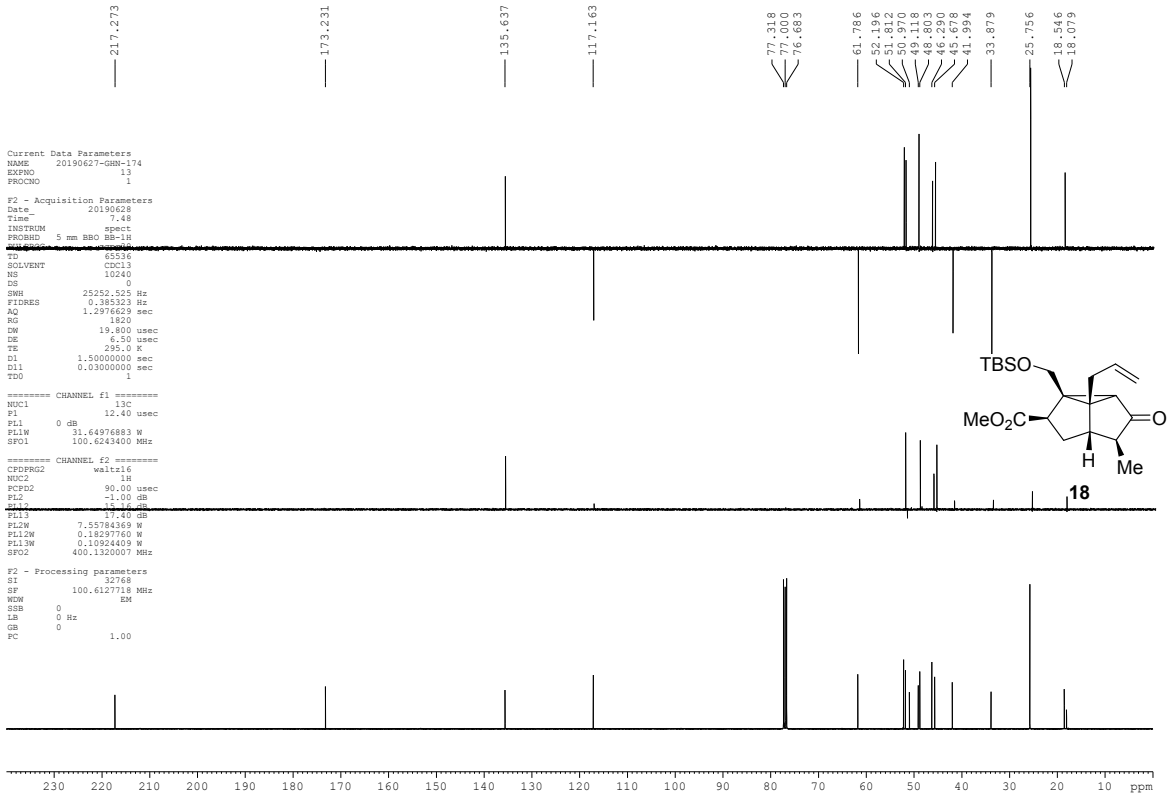
^{1}H NMR of 18, $CDCl_3$, 400 MHz, 24 ^{o}C



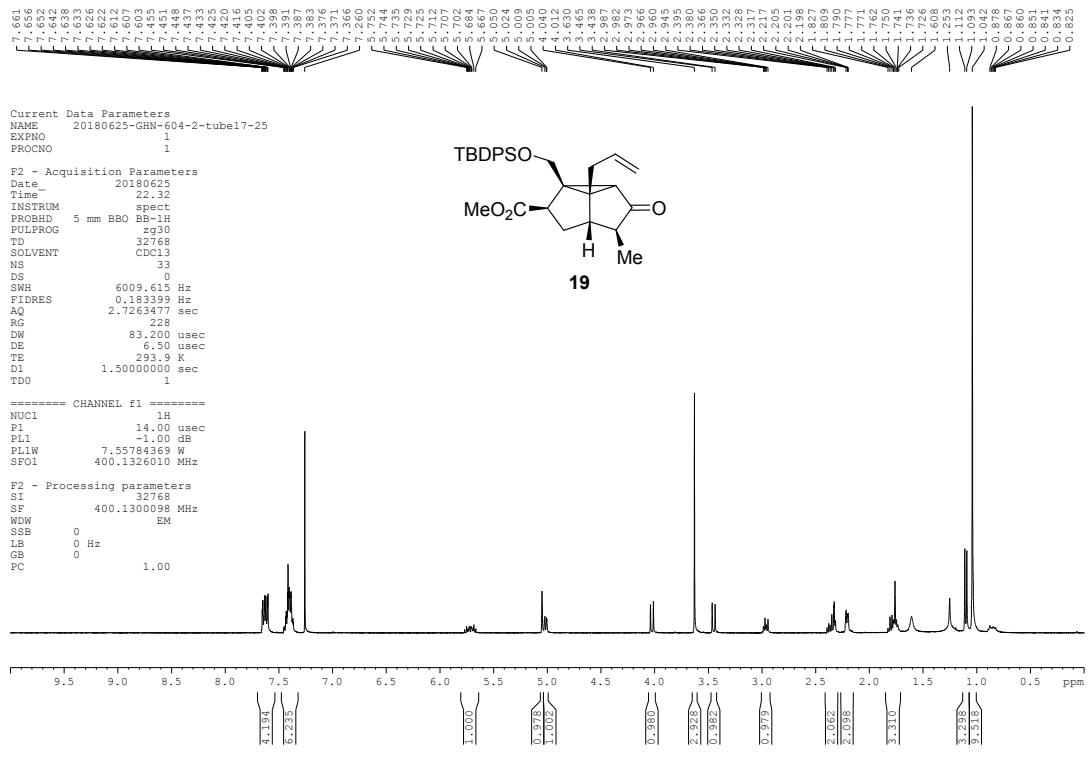
^{13}C NMR of 18, $CDCl_3$, 100 MHz, 24 ^{o}C



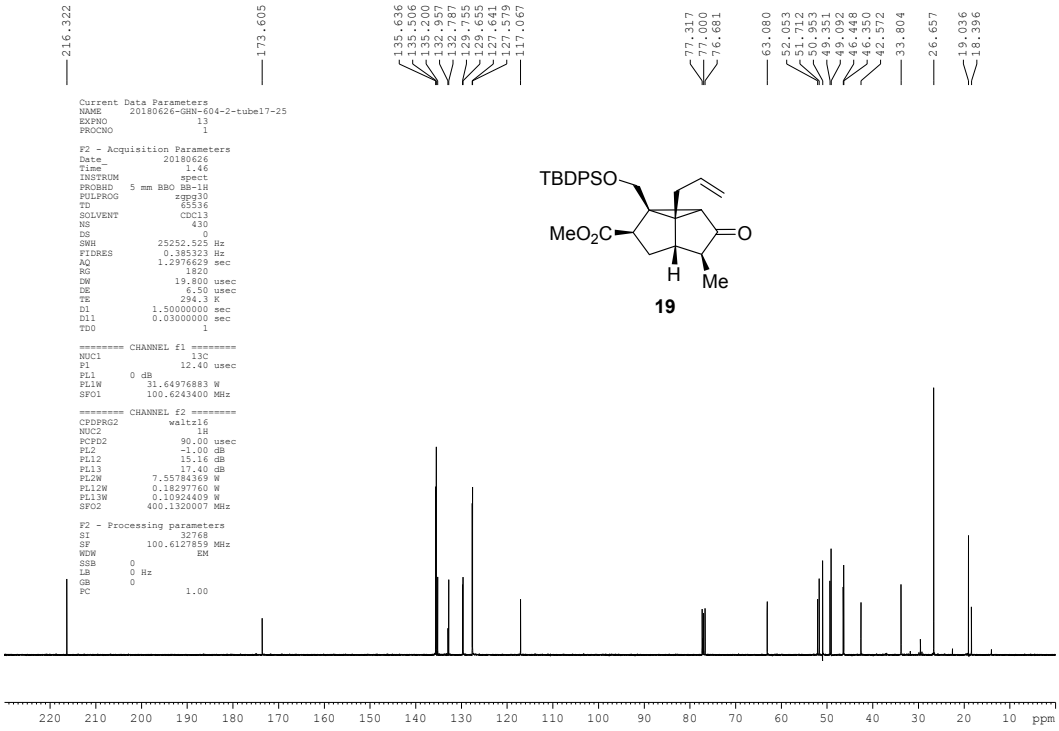
DEPT 135, DEPT 90 and ^{13}C NMR of 18, $CDCl_3$, 100 MHz, 24 °C



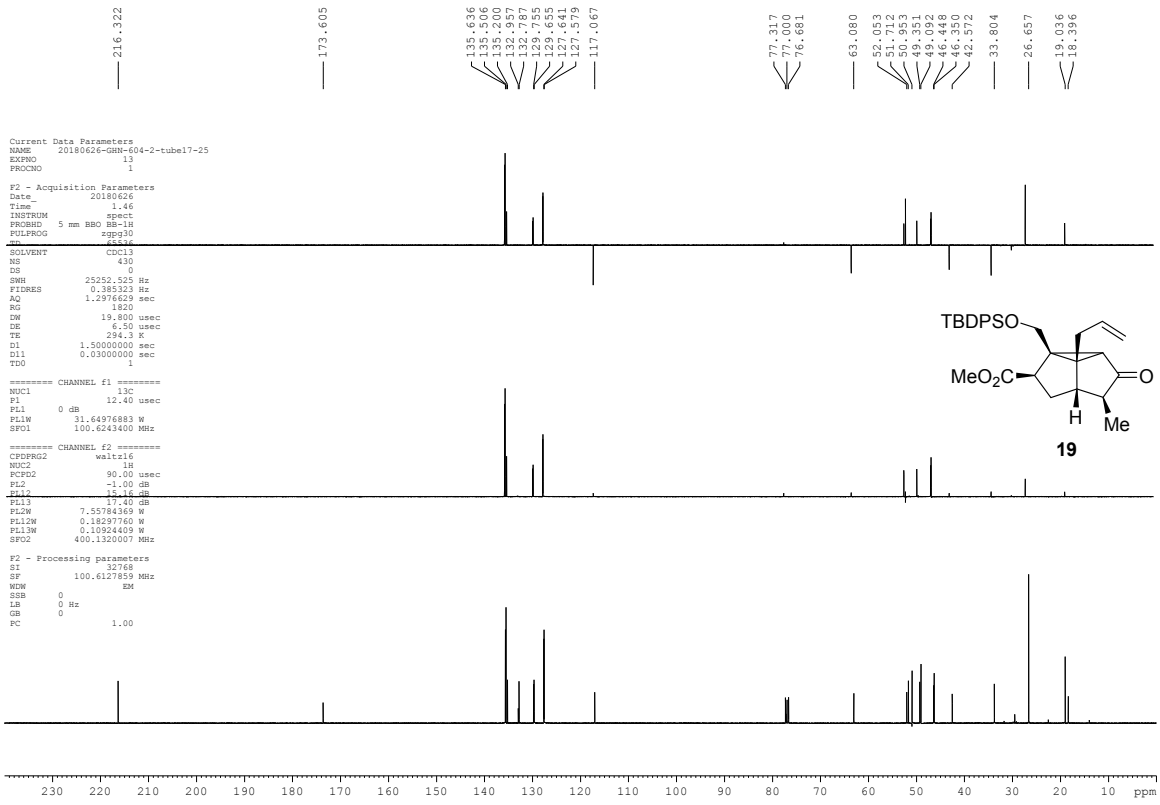
^{1}H NMR of 19, $CDCl_3$, 400 MHz, 24 °C



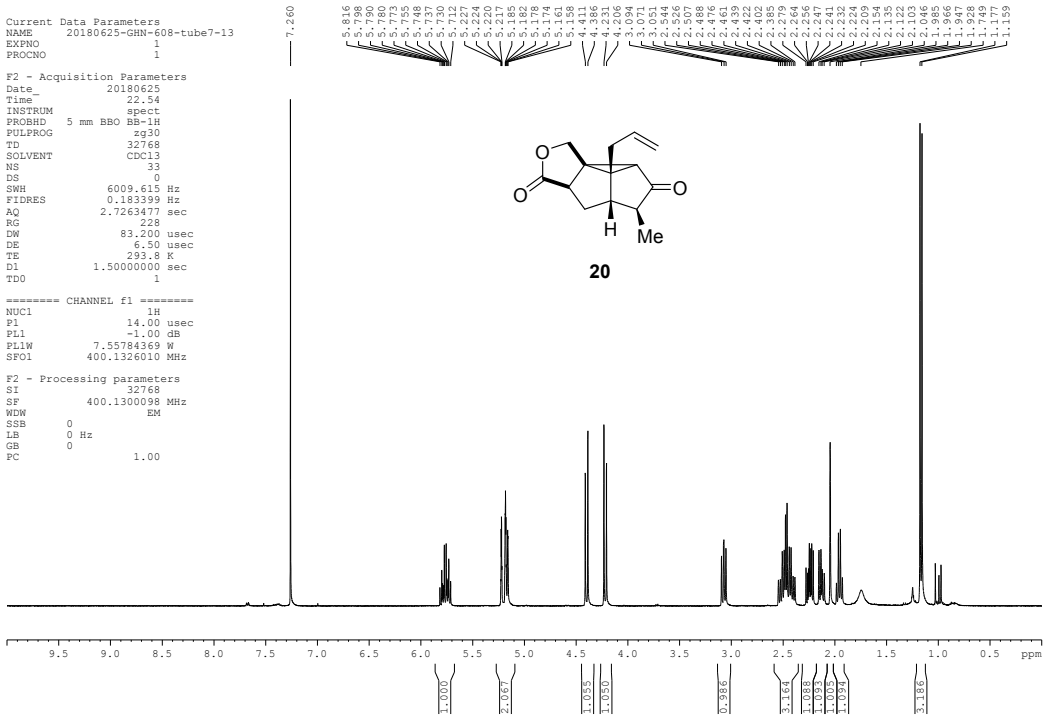
^{13}C NMR of 19, $CDCl_3$, 100 MHz, 24 °C



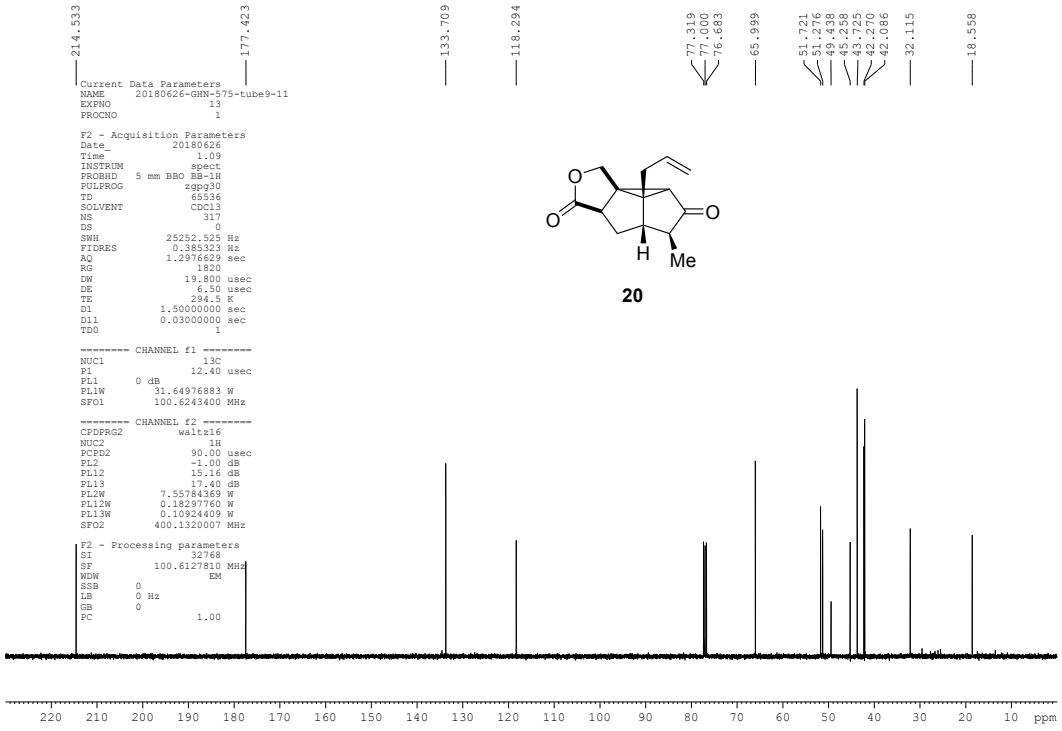
DEPT 135, DEPT 90 and ^{13}C NMR of 19, $CDCl_3$, 100 MHz, 24 °C



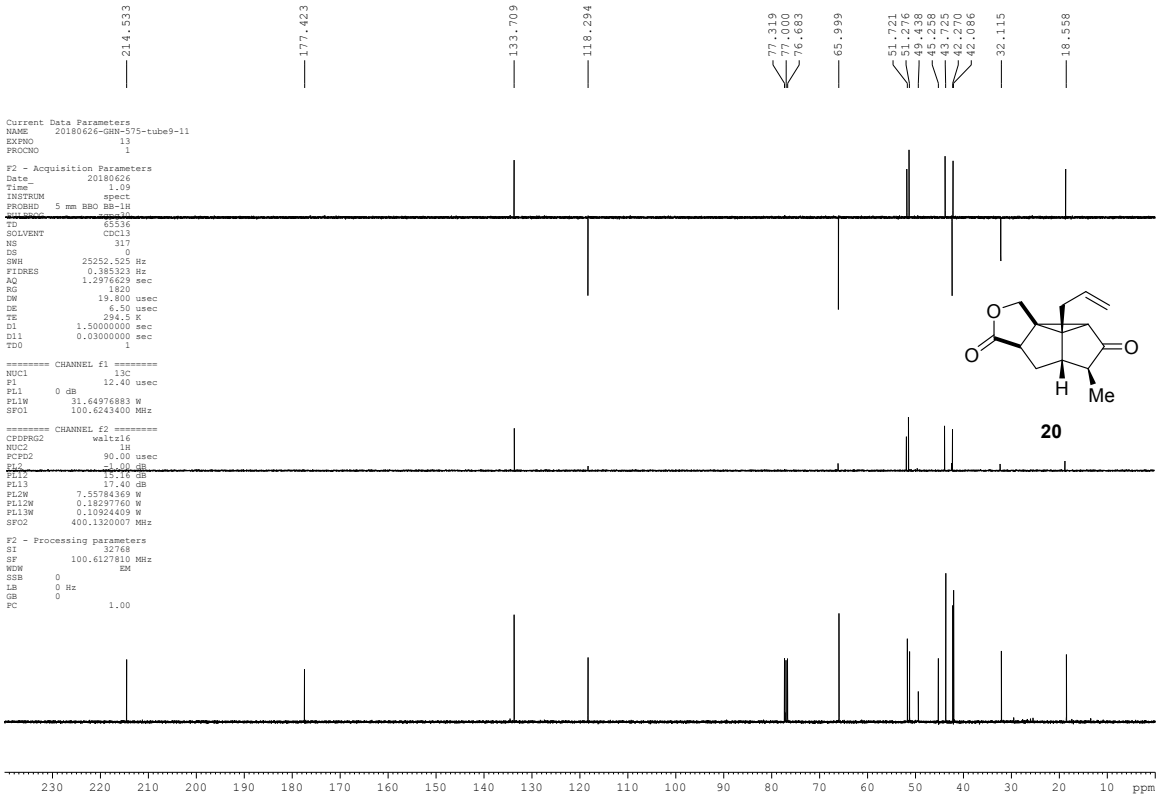
^{1}H NMR of 20, $CDCl_3$, 400 MHz, 24 ^{o}C



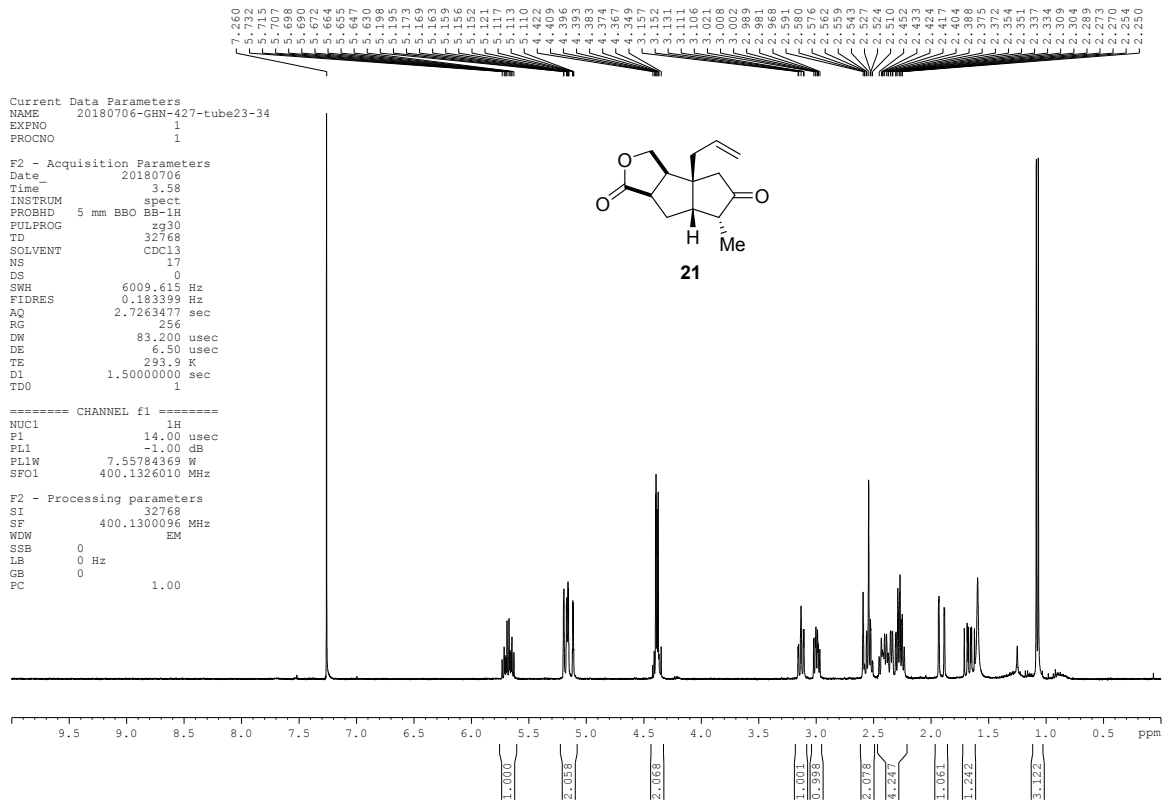
^{13}C NMR of 20, $CDCl_3$, 100 MHz, 24 ^{o}C



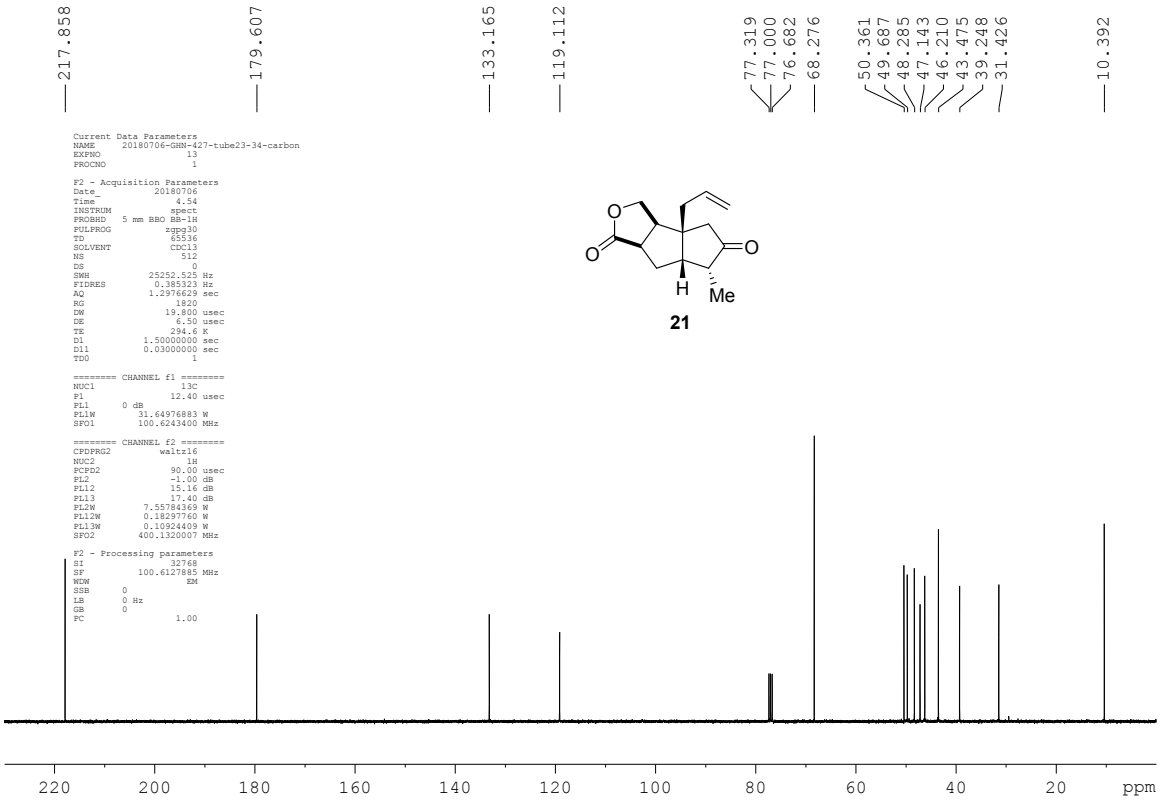
DEPT 135, DEPT 90 and ^{13}C NMR of 20, $CDCl_3$, 100 MHz, 24 ^{o}C



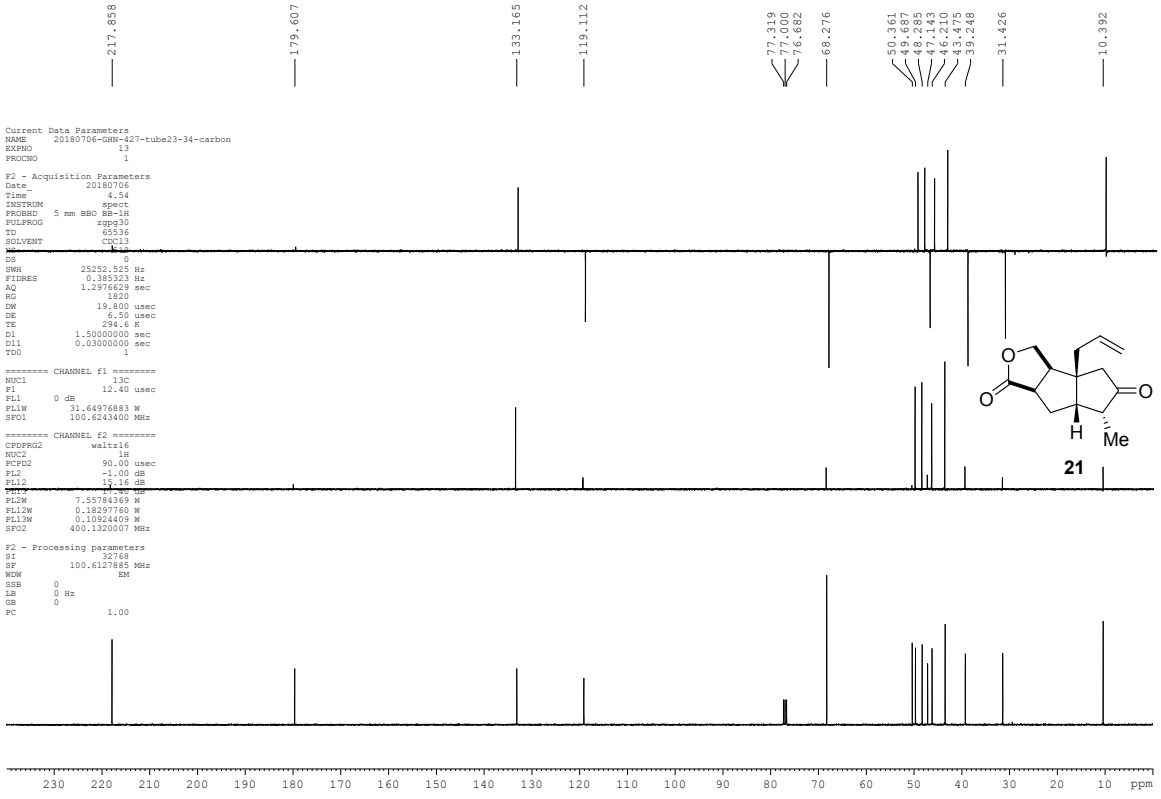
^{1}H NMR of 21, $CDCl_3$, 400 MHz, 24 ^{o}C



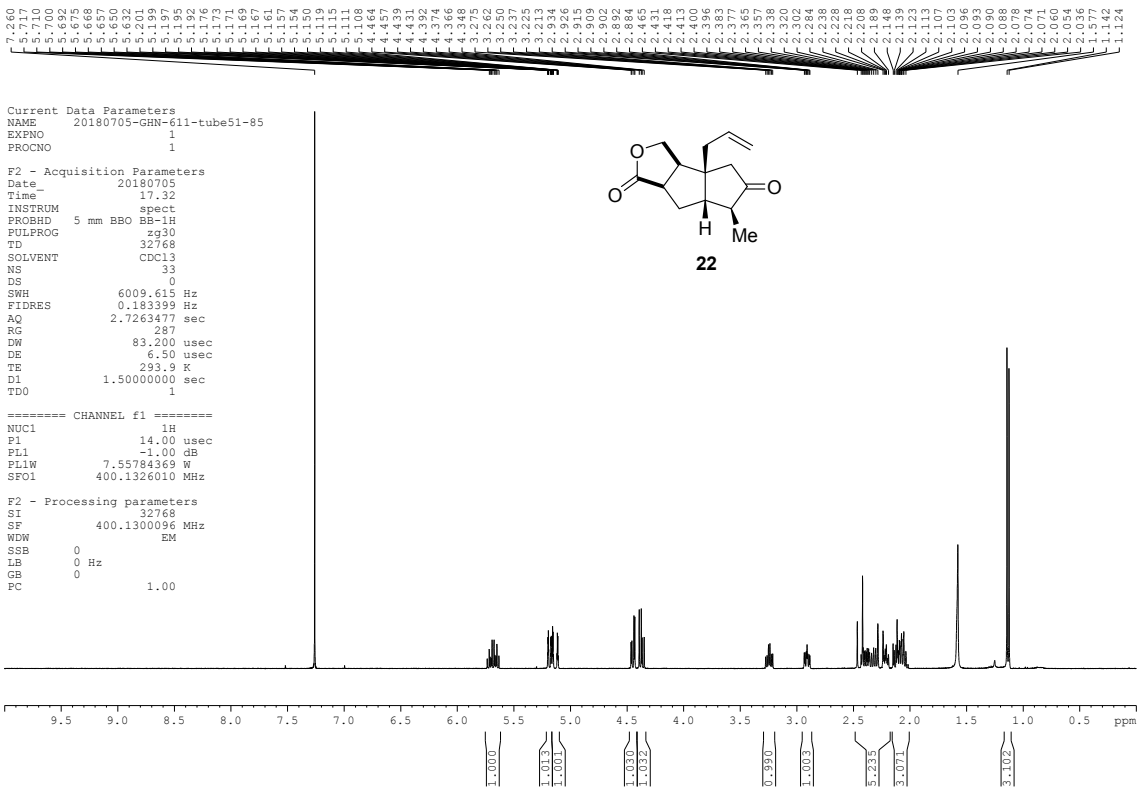
^{13}C NMR of 21, $CDCl_3$, 100 MHz, 24 °C



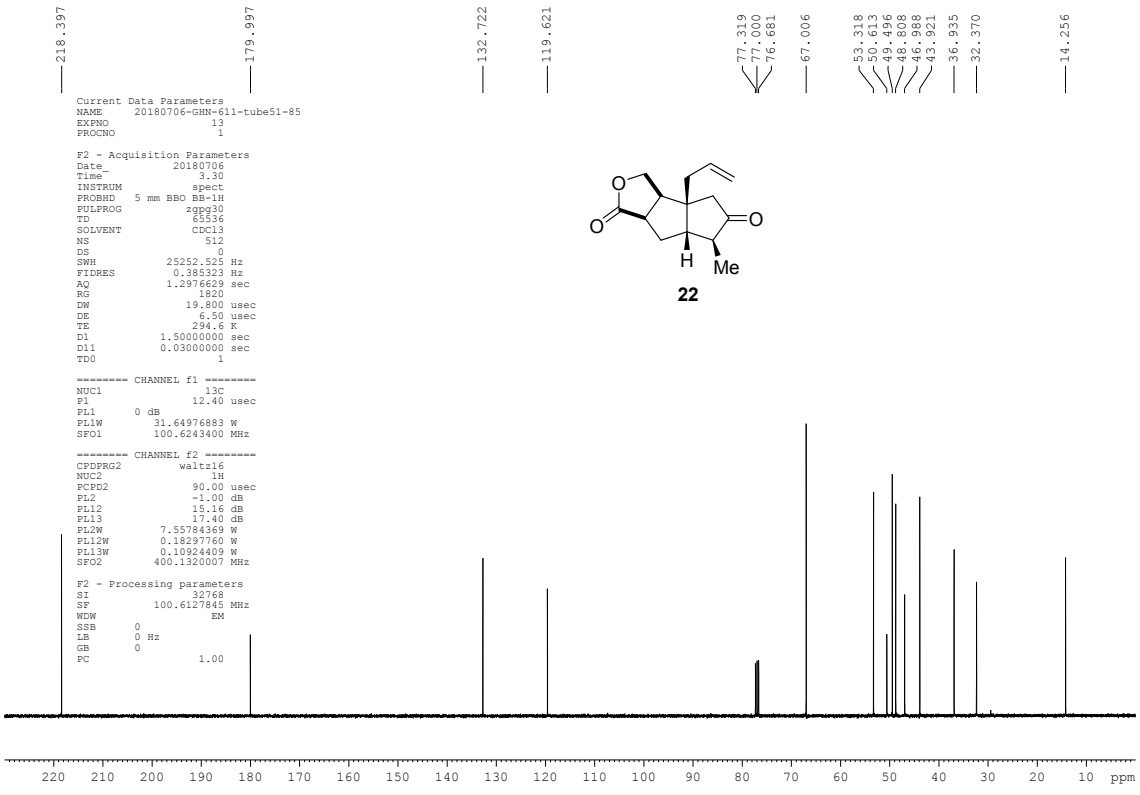
DEPT 135, DEPT 90 and ^{13}C NMR of 21, $CDCl_3$, 100 MHz, 24 °C



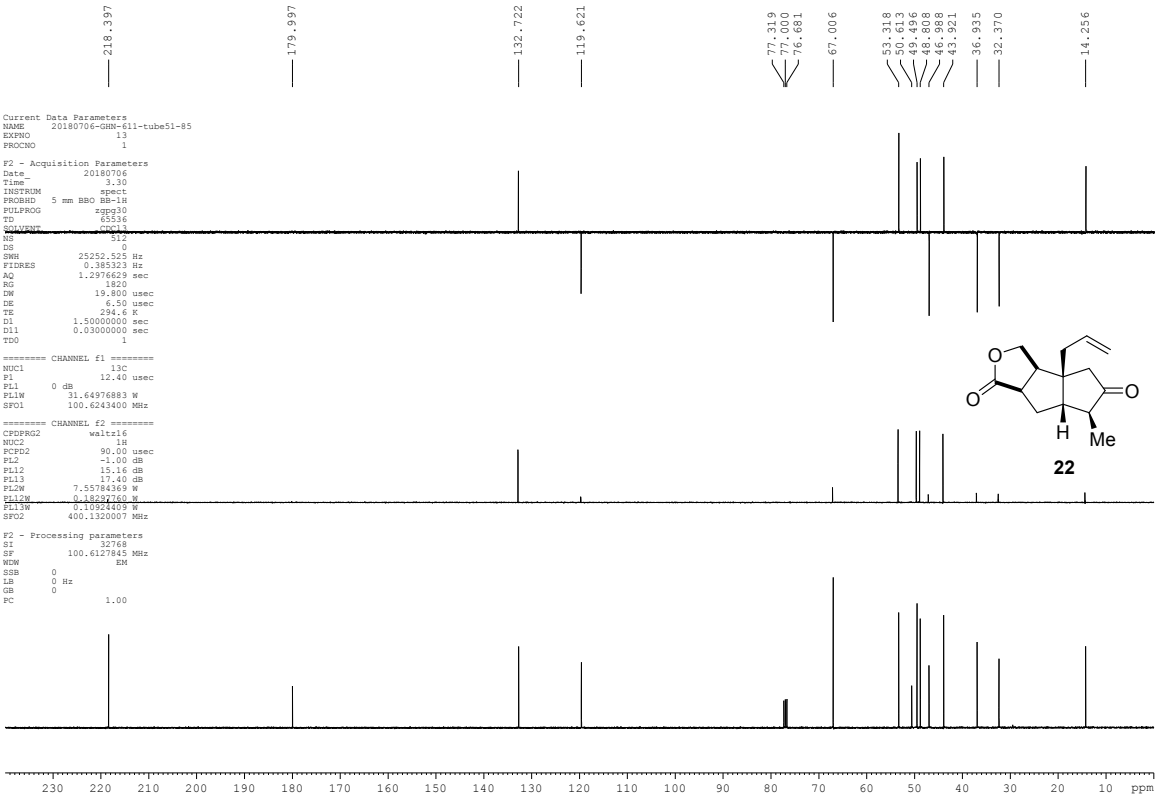
^{1}H NMR of 22, $CDCl_3$, 400 MHz, 24 ^{o}C



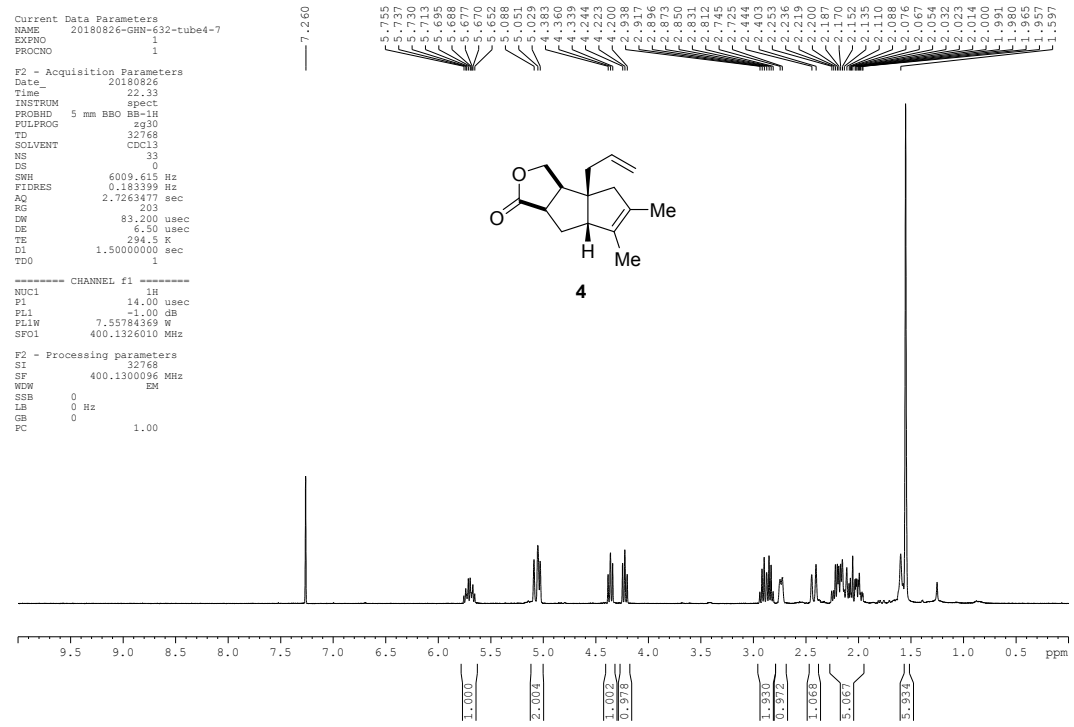
^{13}C NMR of 22, $CDCl_3$, 100 MHz, 24 ^{o}C



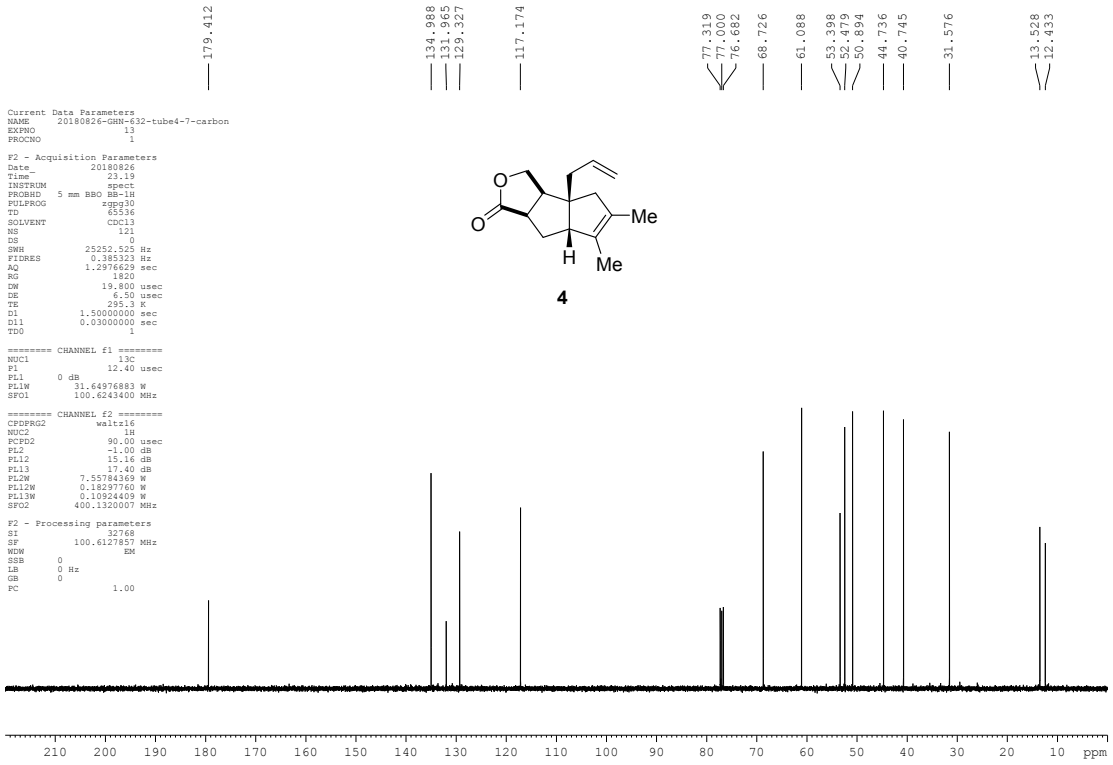
DEPT 135, DEPT 90 and ^{13}C NMR of 22, $CDCl_3$, 100 MHz, 24 ^{o}C



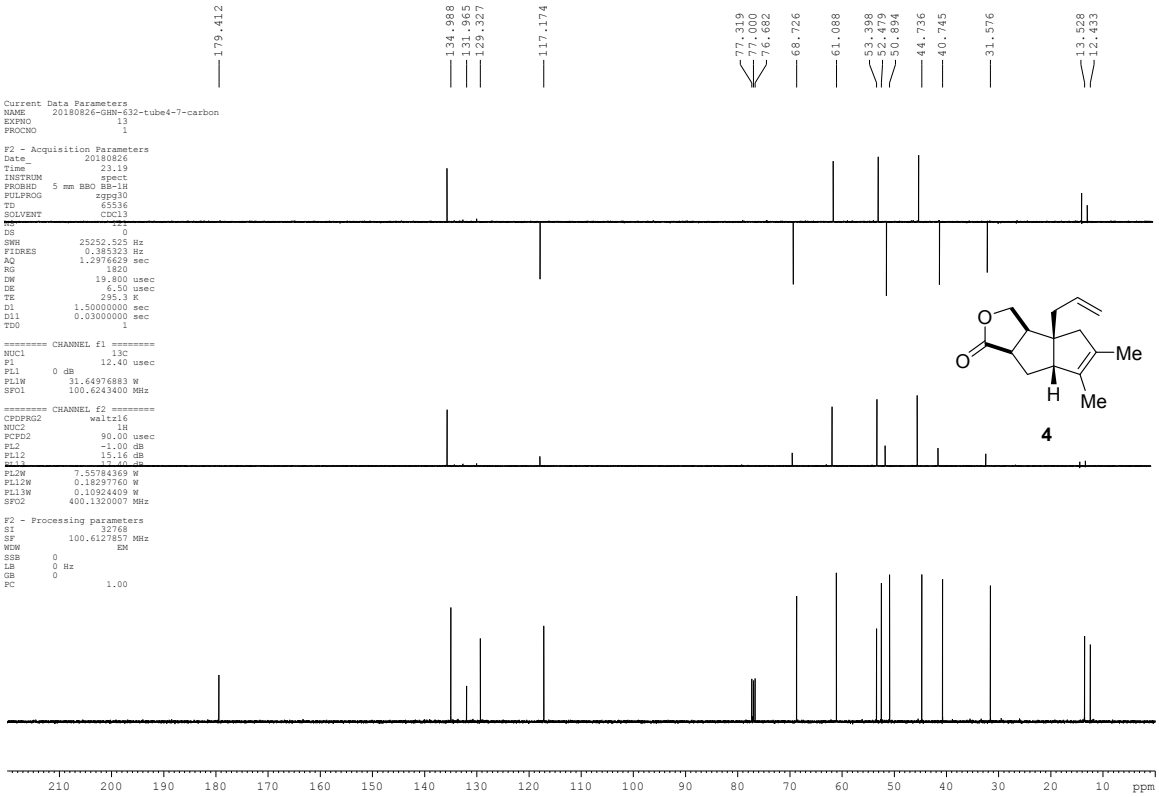
^{1}H NMR of 4, $CDCl_3$, 400 MHz, 24 ^{o}C



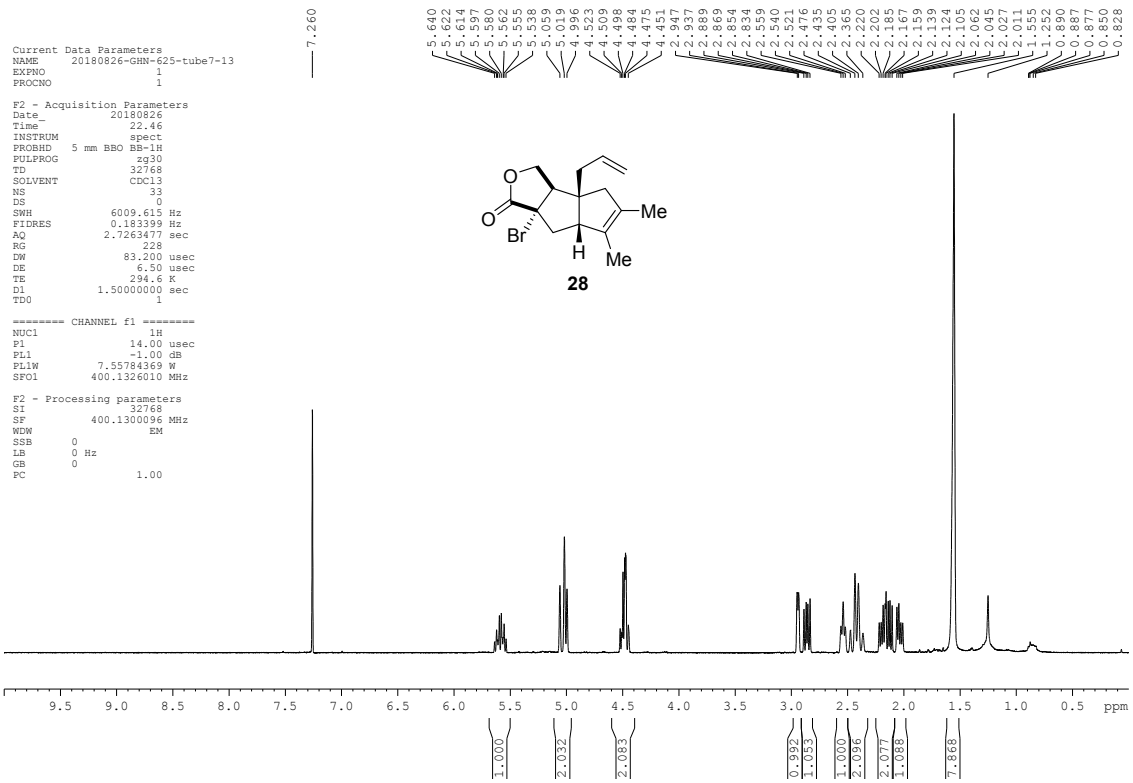
^{13}C NMR of 4, $CDCl_3$, 100 MHz, 24 ^{o}C



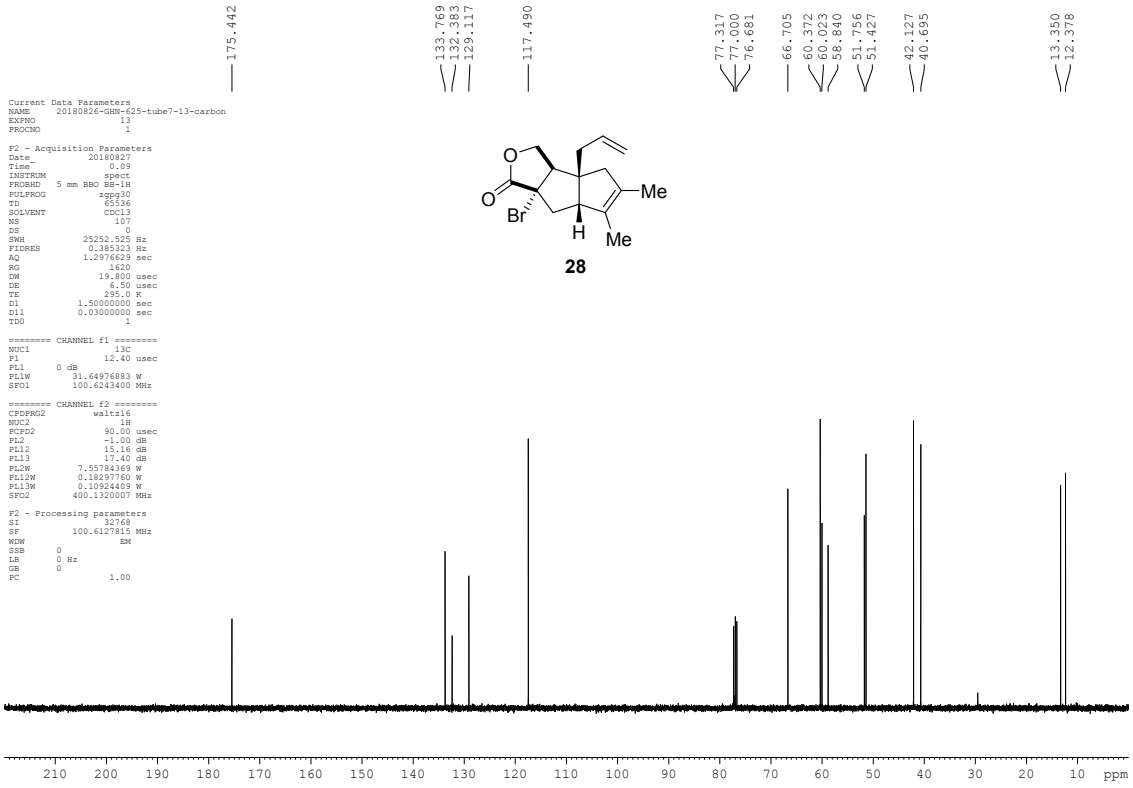
DEPT 135, DEPT 90 and ^{13}C NMR of 4, $CDCl_3$, 100 MHz, 24 ^{o}C



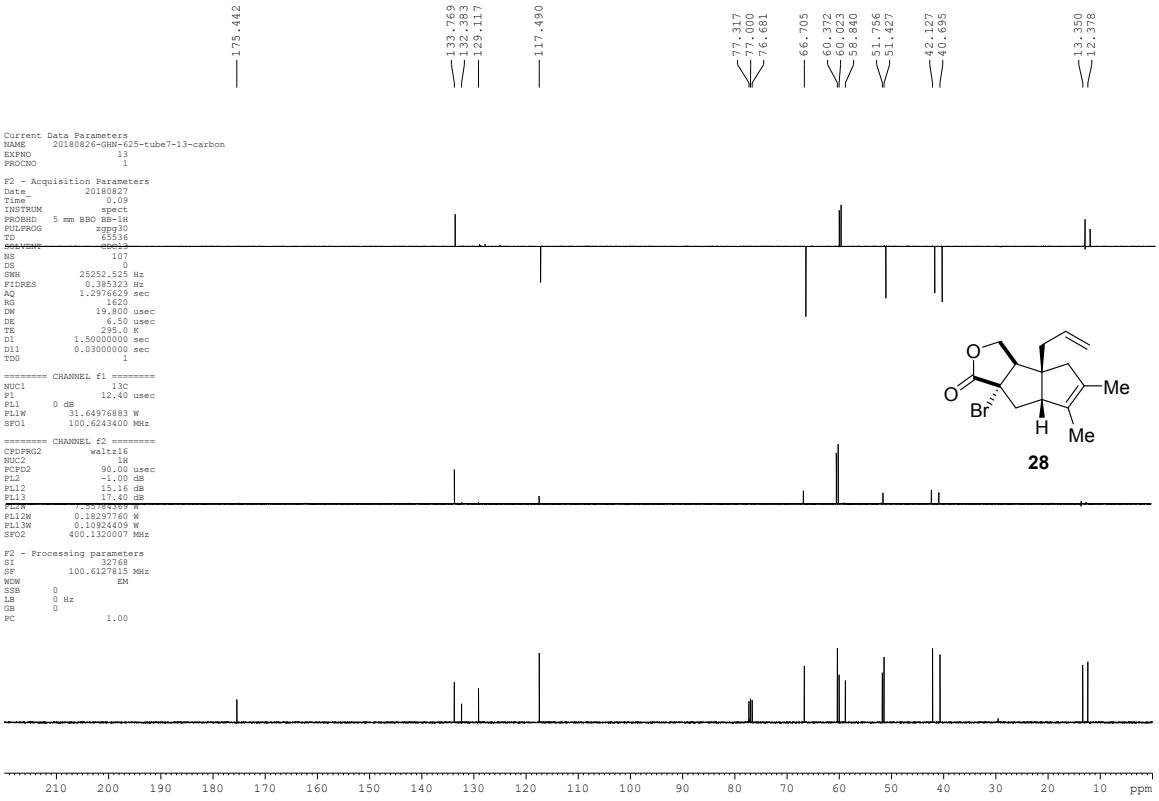
^{1}H NMR of 28, $CDCl_3$, 400 MHz, 24 ^{o}C



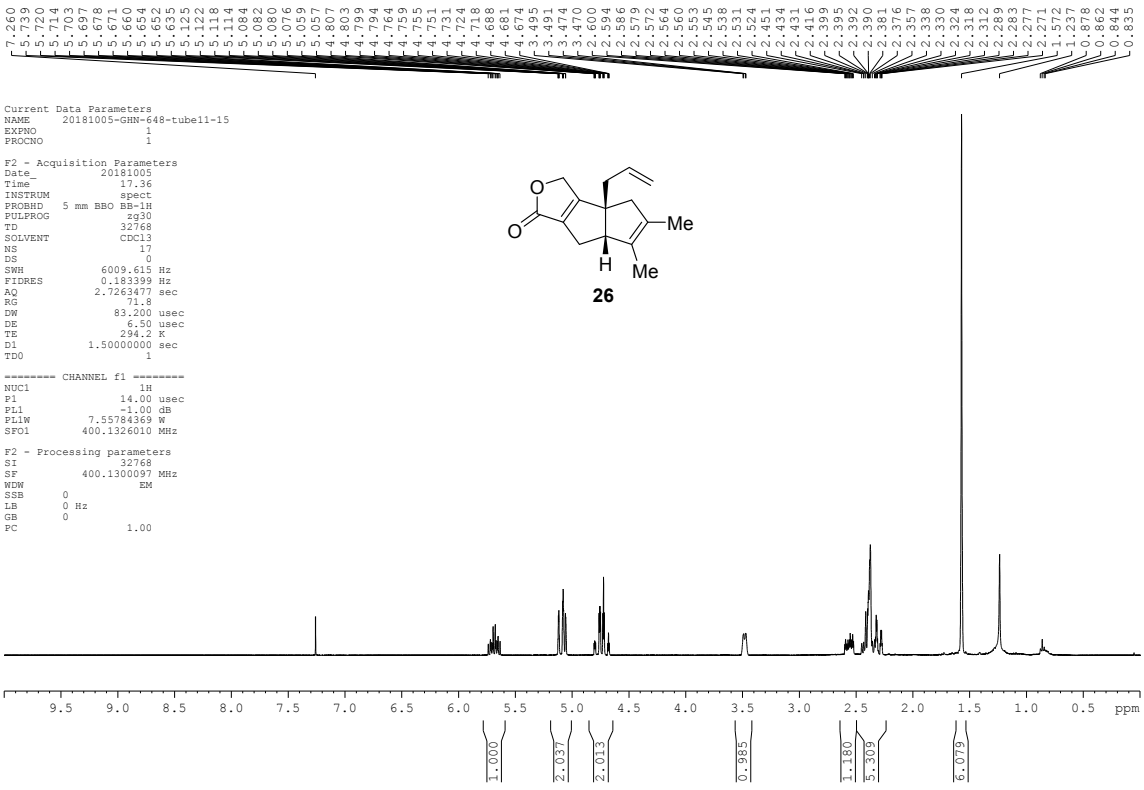
^{13}C NMR of 28, $CDCl_3$, 100 MHz, 24 ^{o}C



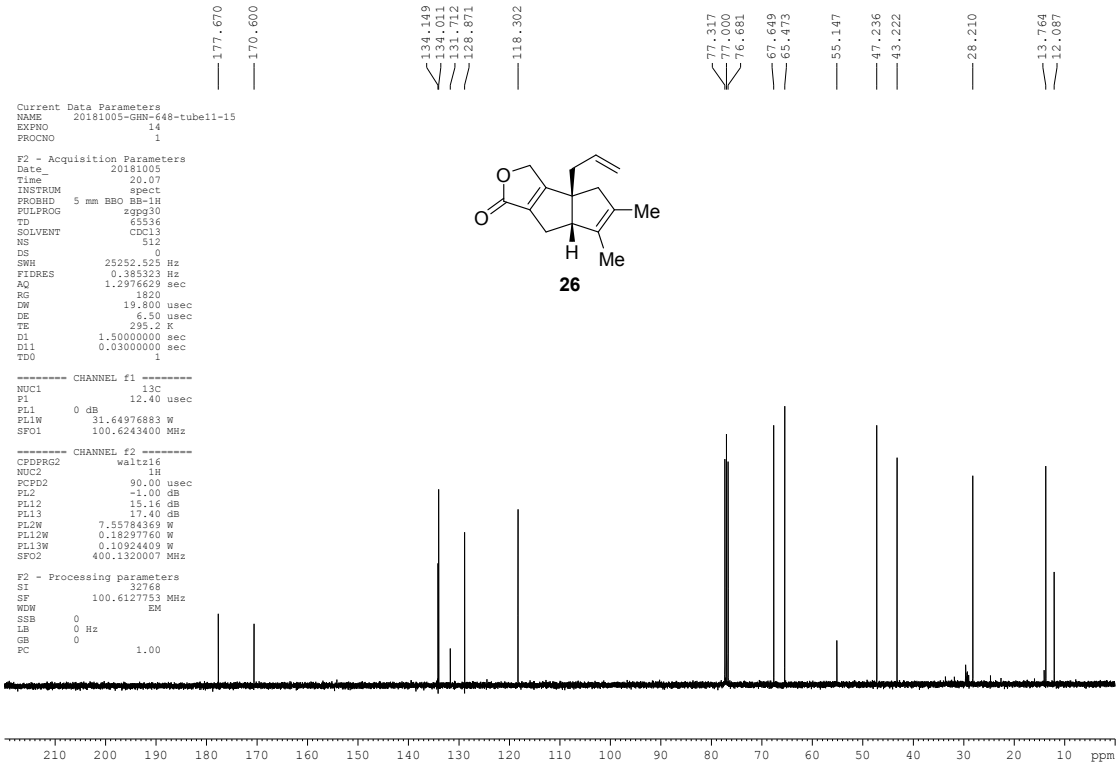
DEPT 135, DEPT 90 and ^{13}C NMR of 28, $CDCl_3$, 100 MHz, 24 ^{o}C



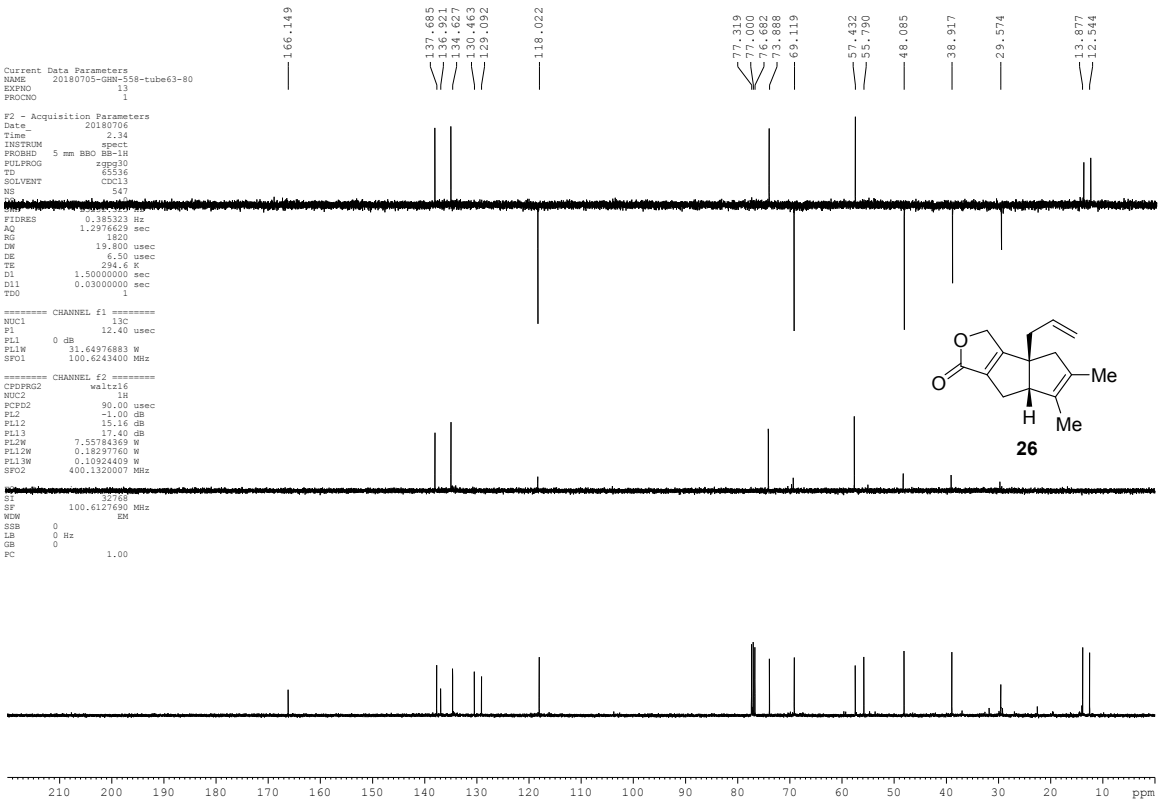
^{1}H NMR of 26, $CDCl_3$, 400 MHz, 24 ^{o}C



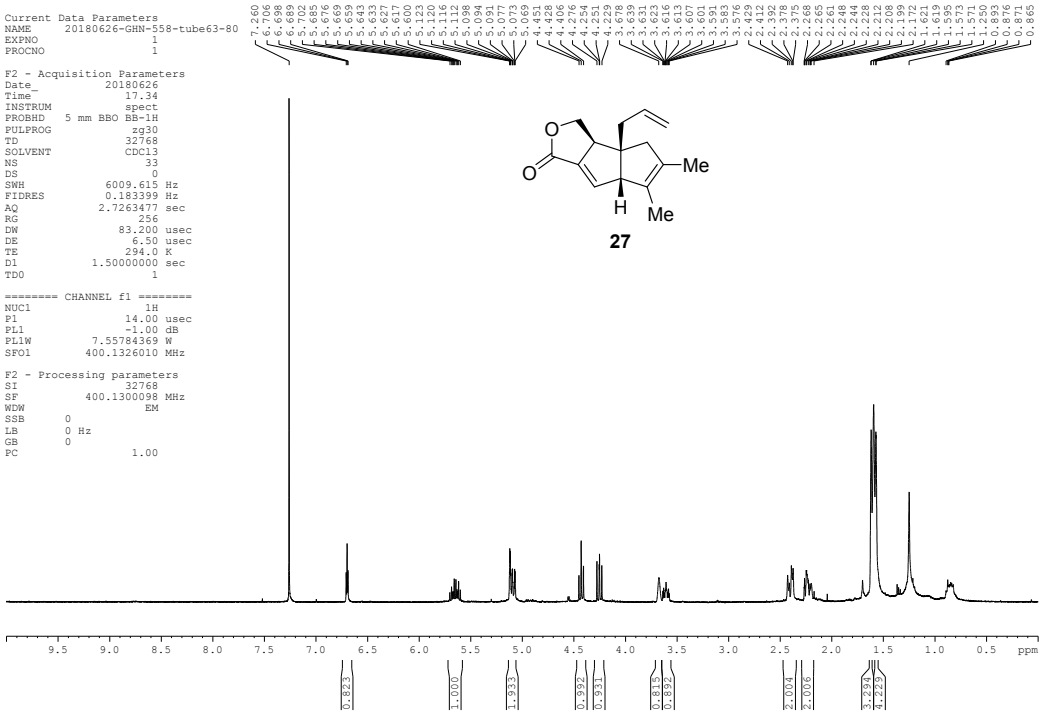
^{13}C NMR of 26, $CDCl_3$, 100 MHz, 24 °C



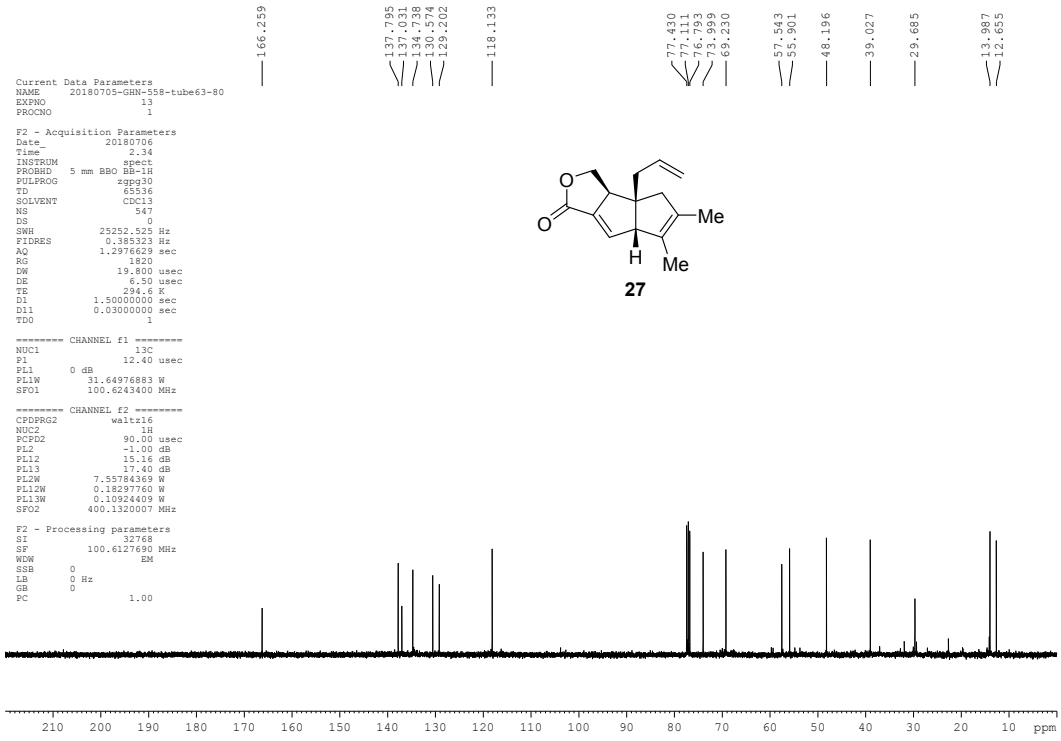
DEPT 135, DEPT 90 and ^{13}C NMR of 26, $CDCl_3$, 100 MHz, 24 °C



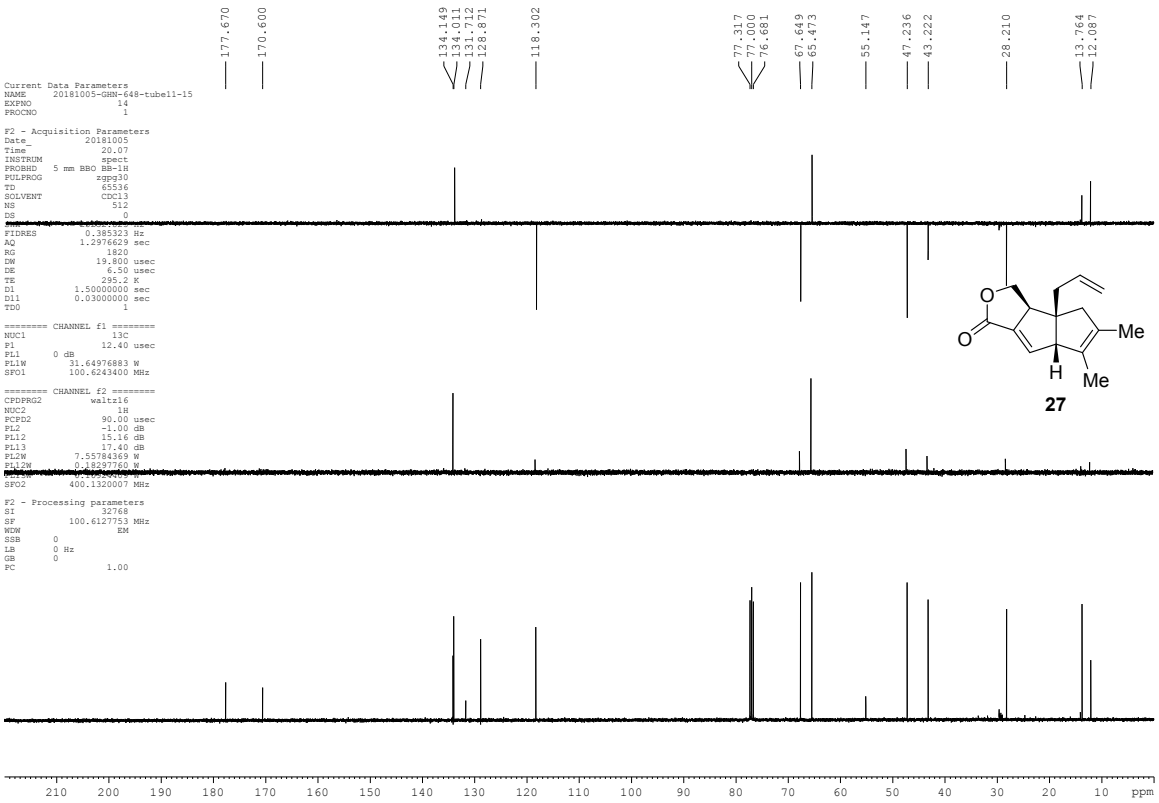
^{1}H NMR of 27, $CDCl_3$, 400 MHz, 24 ^{o}C



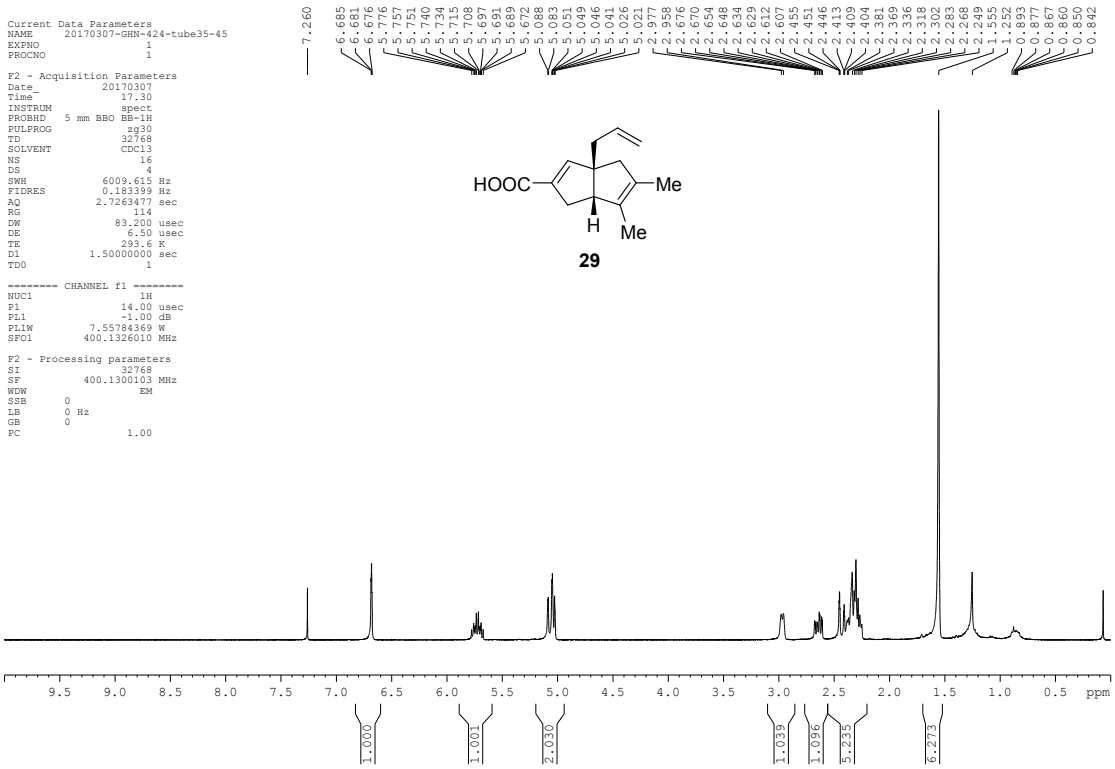
^{13}C NMR of 27, $CDCl_3$, 100 MHz, 24 ^{o}C



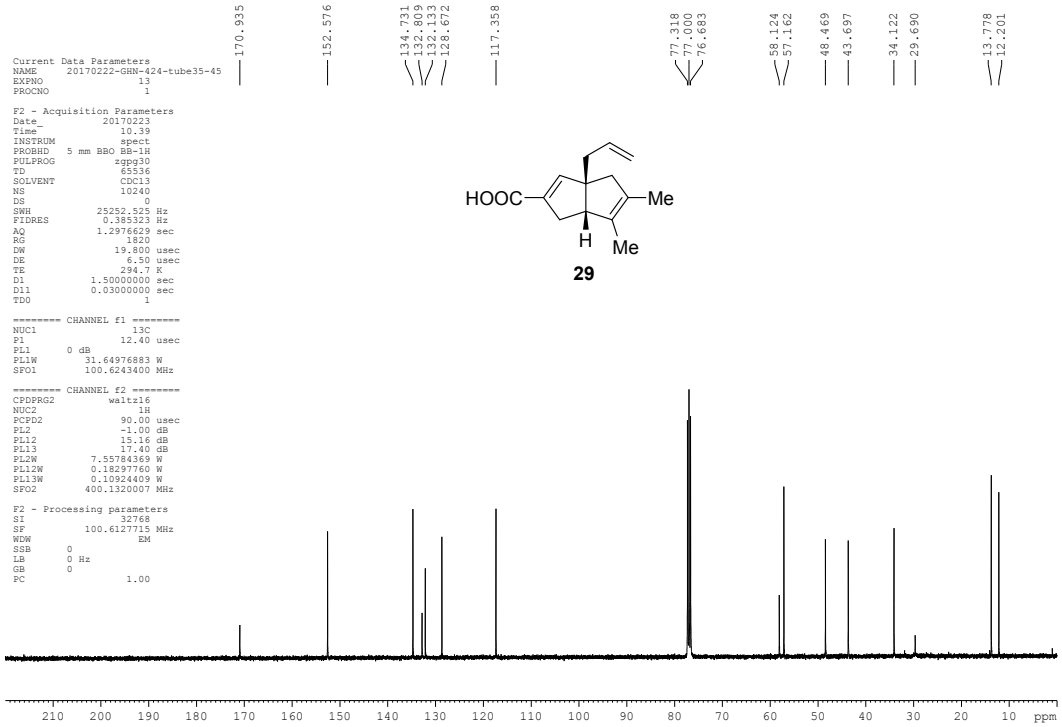
DEPT 135, DEPT 90 and ^{13}C NMR of 27, $CDCl_3$, 100 MHz, 24 ^{o}C



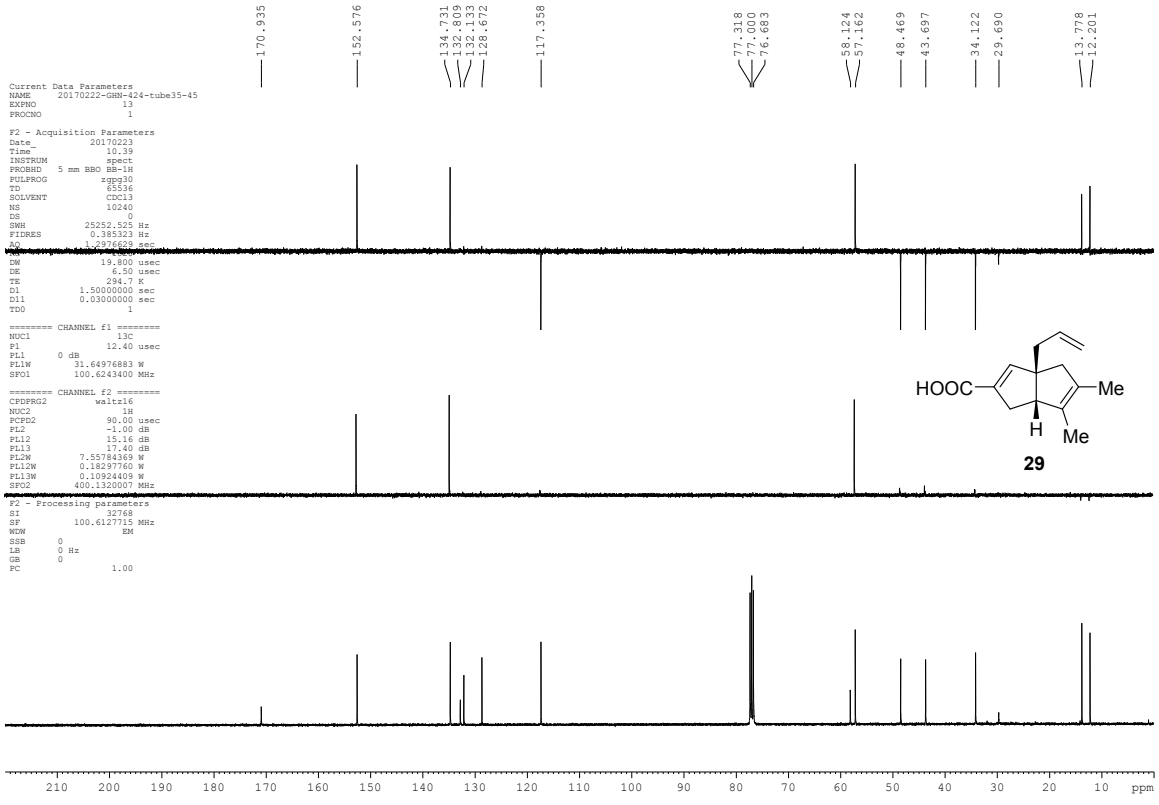
^{1}H NMR of 29, $CDCl_3$, 400 MHz, 24 ^{o}C



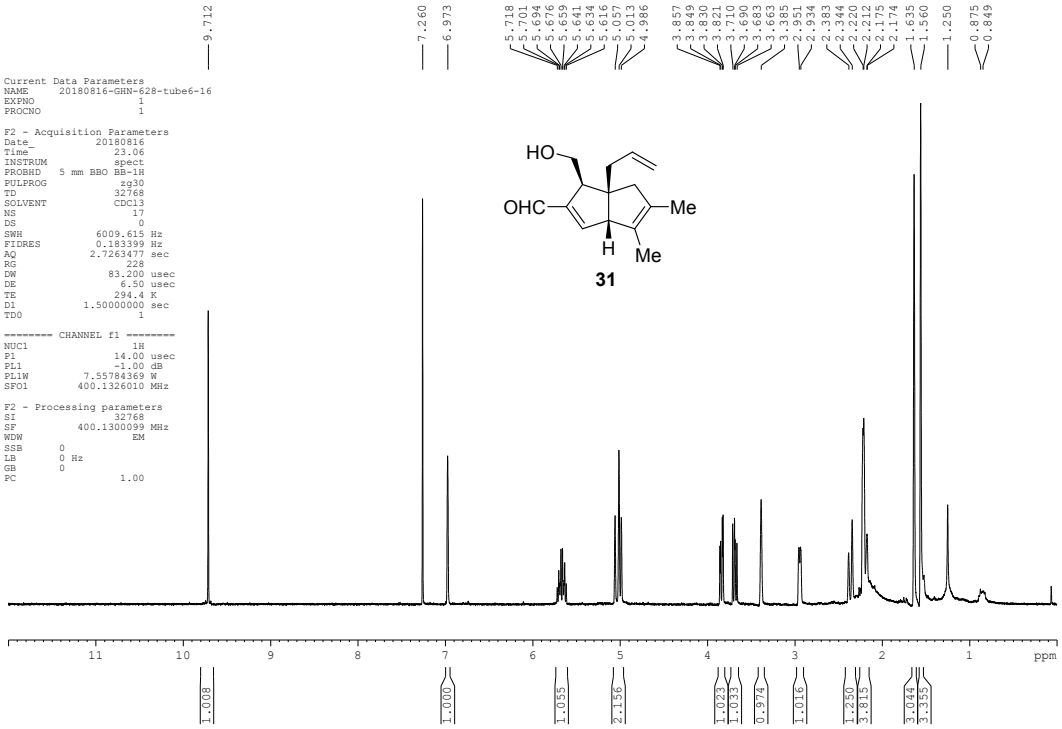
^{13}C NMR of 29, $CDCl_3$, 100 MHz, 24 ^{o}C



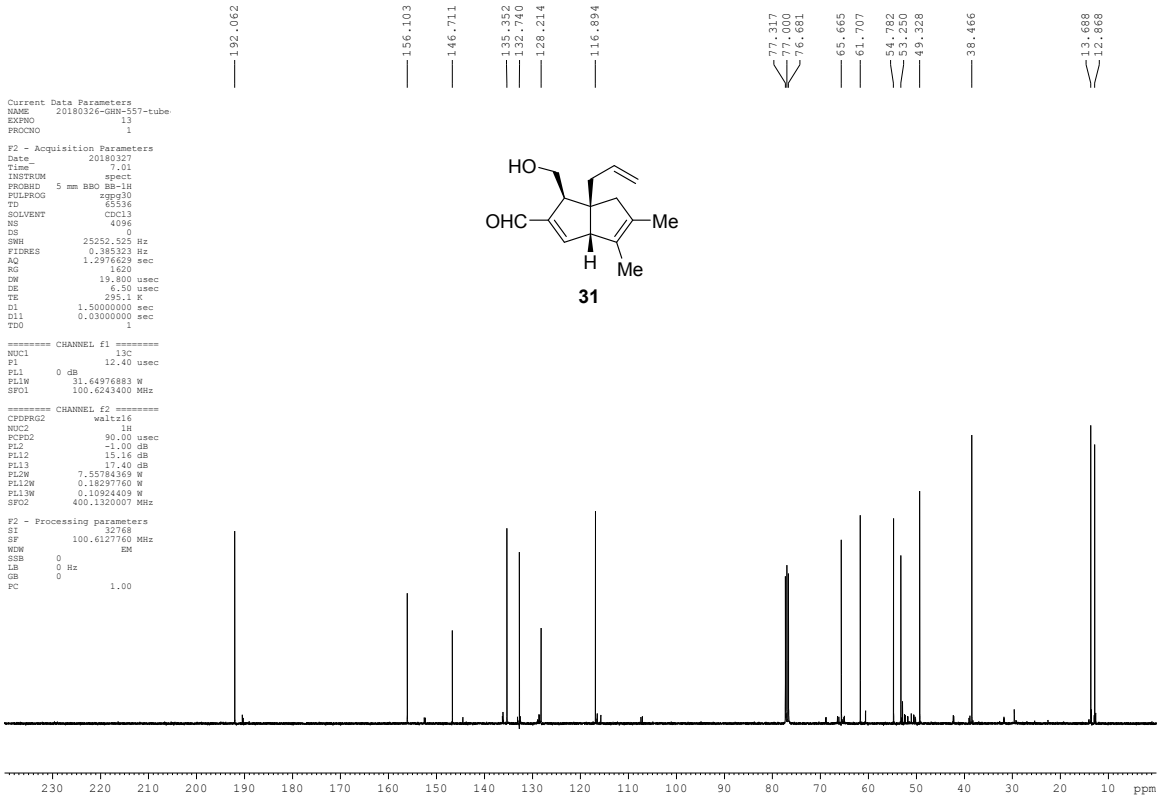
DEPT 135, DEPT 90 and ^{13}C NMR of 29, $CDCl_3$, 100 MHz, 24 ^{o}C



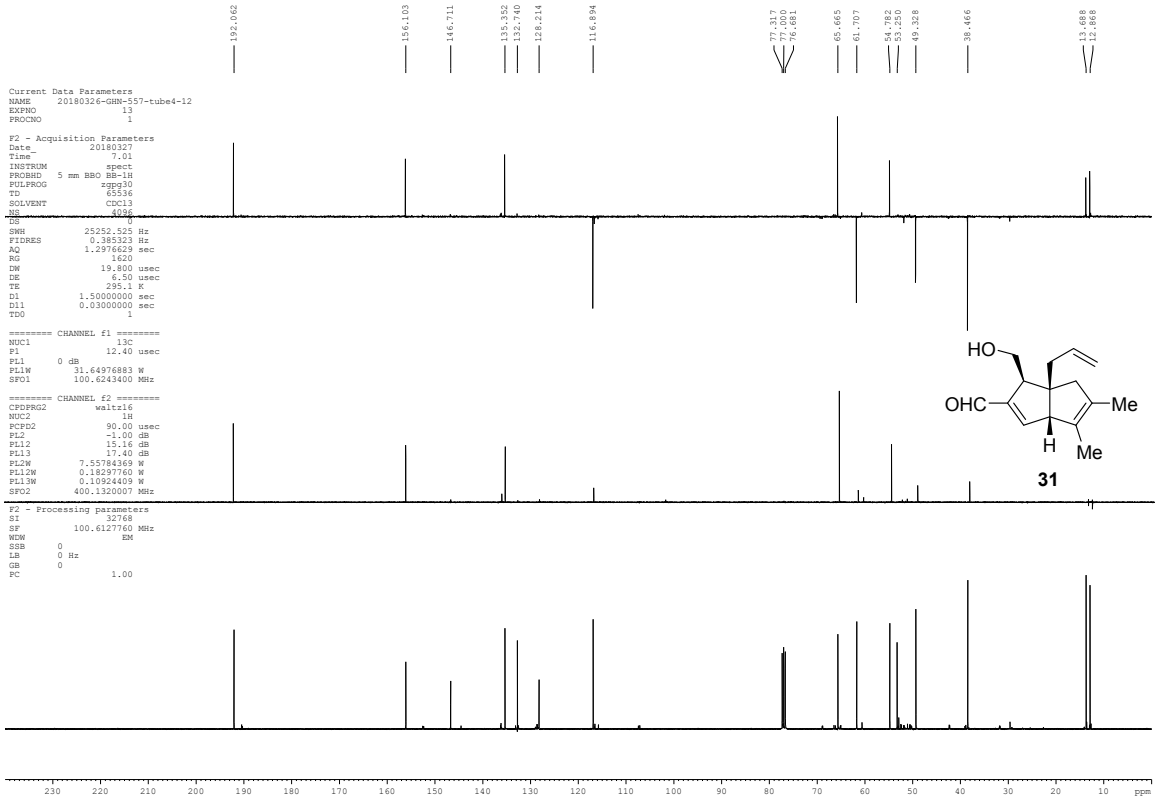
^{1}H NMR of 31, $CDCl_3$, 400 MHz, 24 ^{o}C



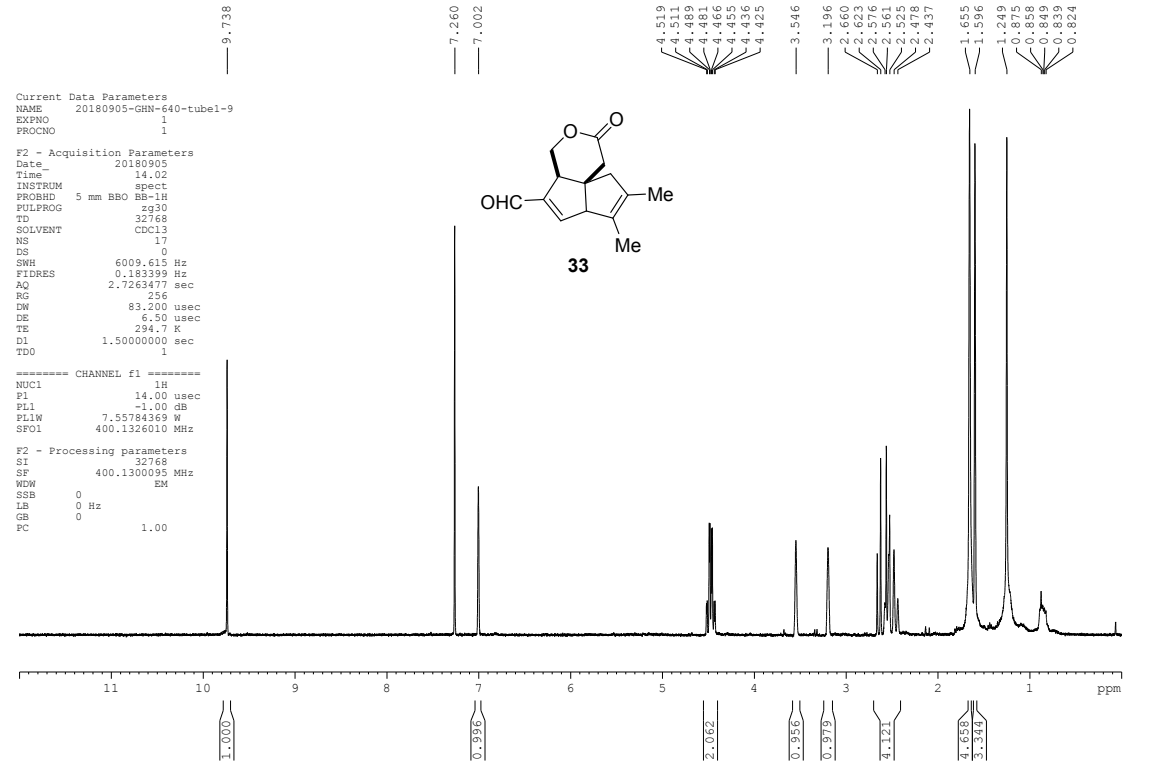
^{13}C NMR of 31, $CDCl_3$, 100 MHz, 24 ^{o}C



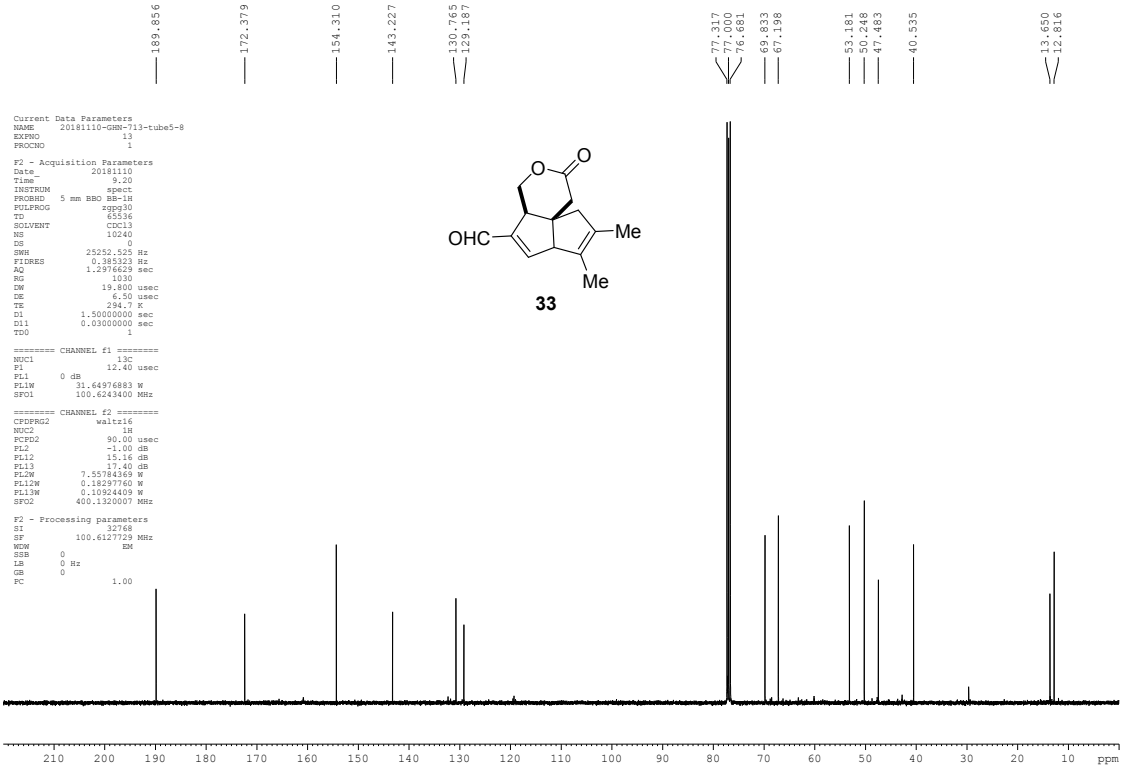
DEPT 135, DEPT 90 and ^{13}C NMR of 31, $CDCl_3$, 100 MHz, 24 ^{o}C



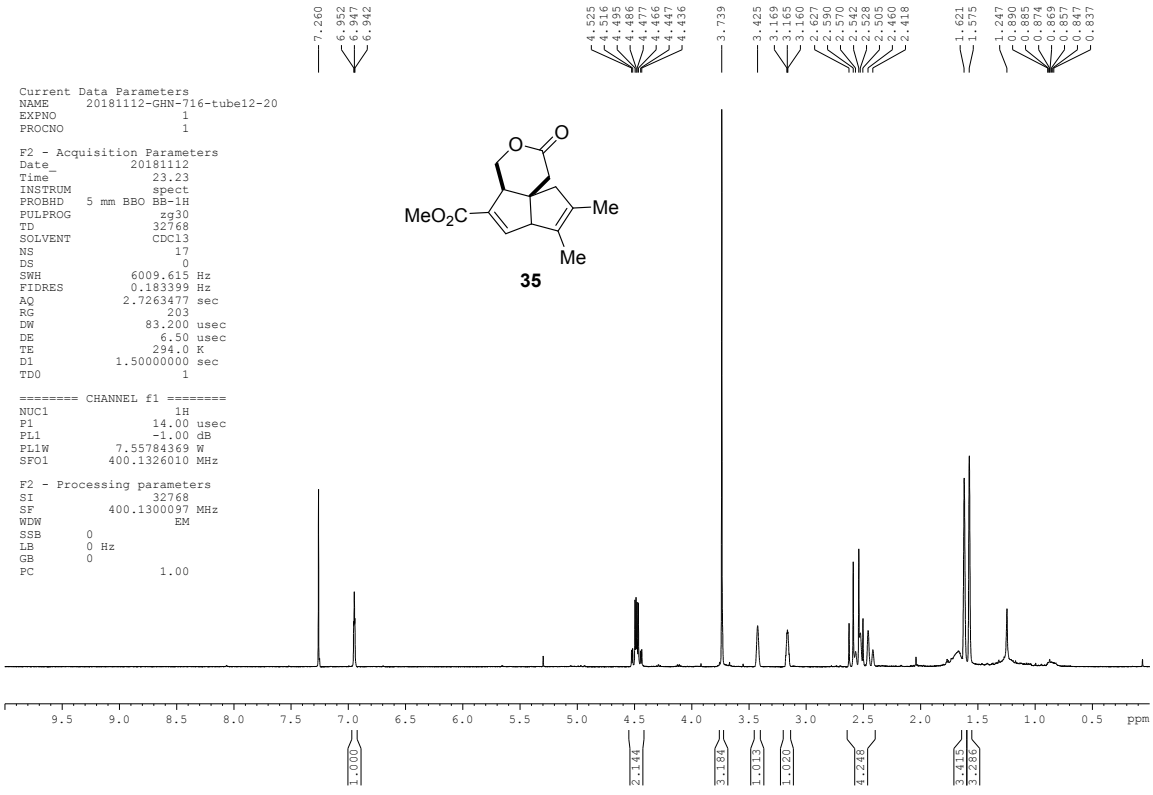
^{1}H NMR of 33, $CDCl_3$, 400 MHz, 24 ^{o}C



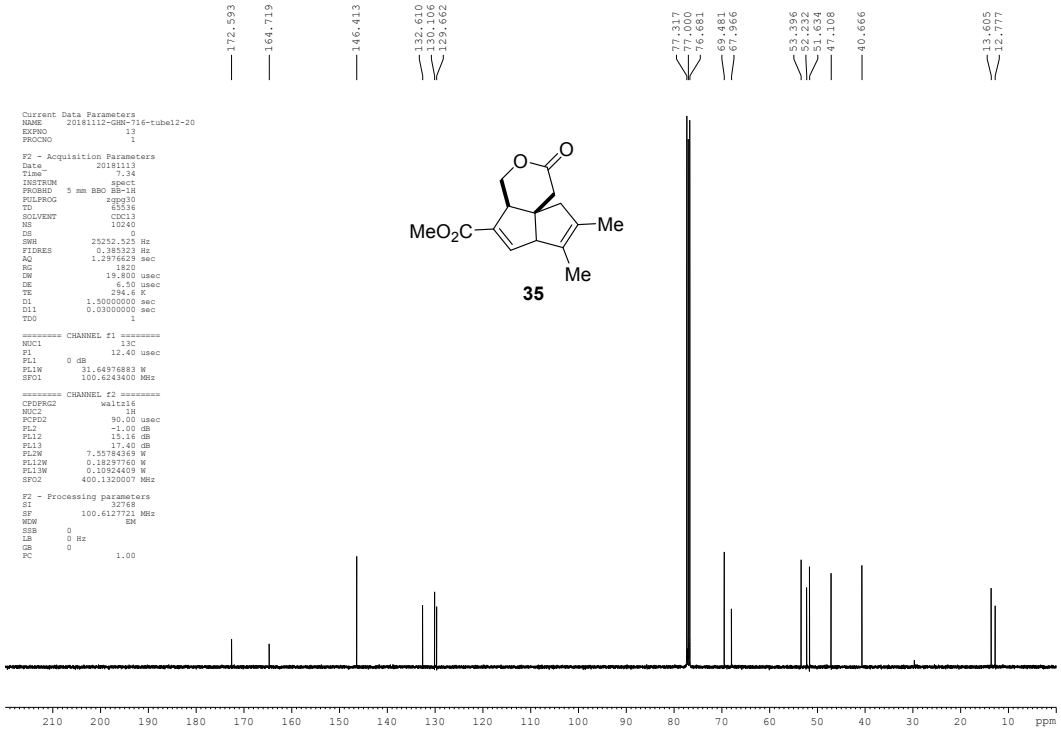
^{13}C NMR of 33, $CDCl_3$, 100 MHz, 24 ^{o}C



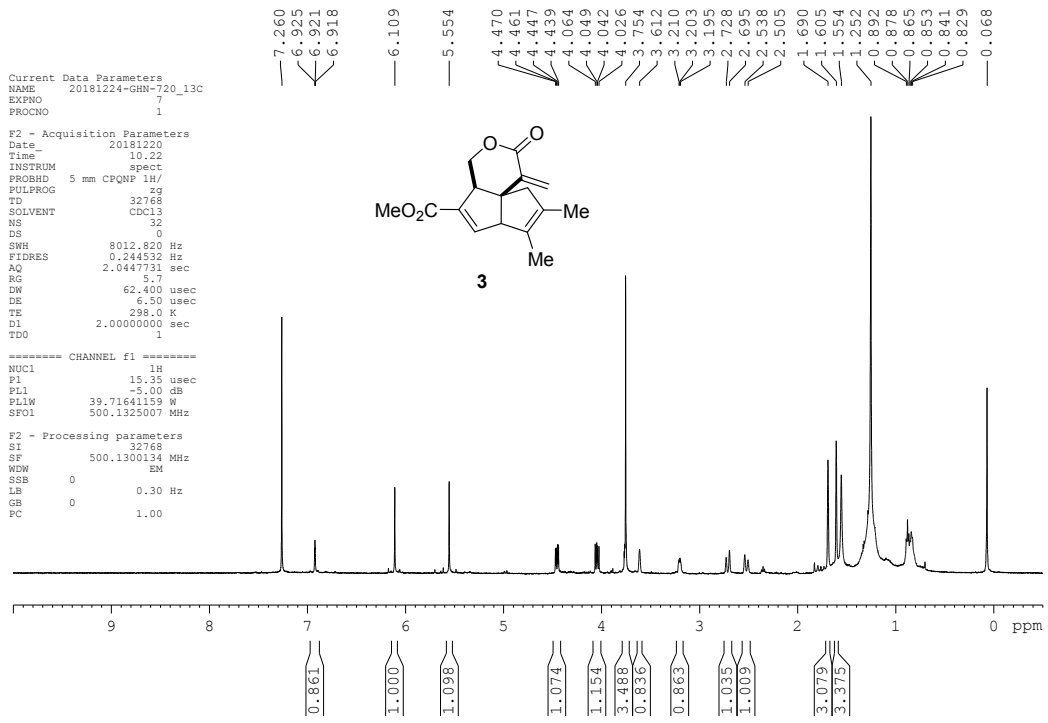
^{1}H NMR of 35, $CDCl_3$, 400 MHz, 24 ^{o}C



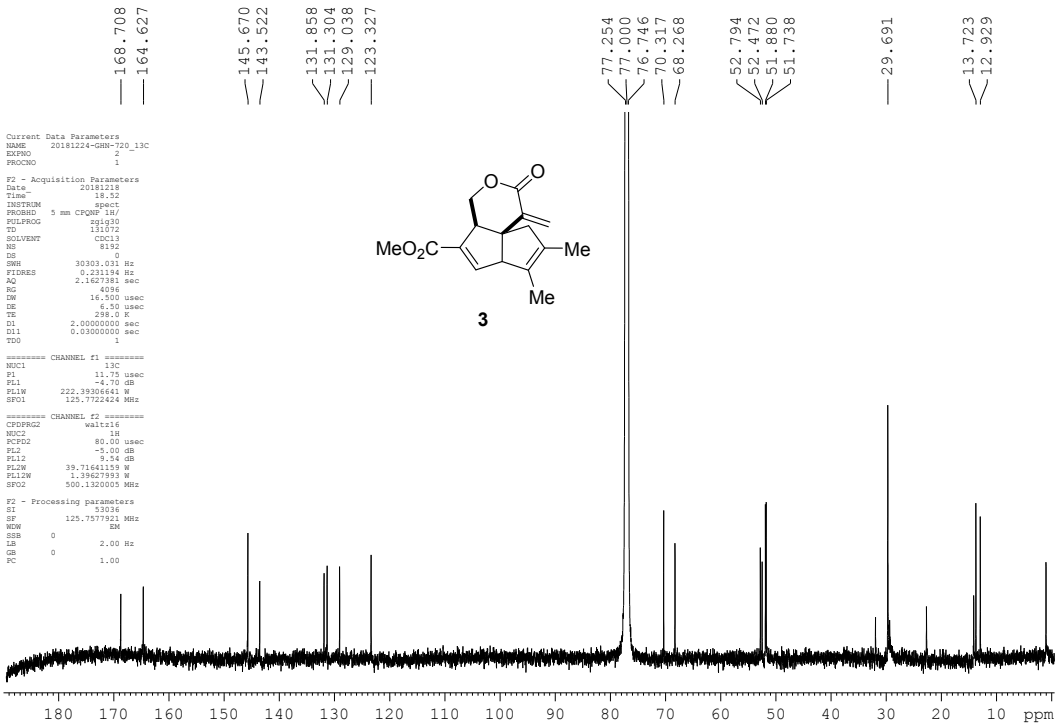
^{13}C NMR of 35, $CDCl_3$, 100 MHz, 24 °C



^{1}H NMR of 3, $CDCl_3$, 500 MHz, 24 °C



^{13}C NMR of 3, $CDCl_3$, 125 MHz, 24 ^{o}C



DEPT 135, DEPT 90 and ^{13}C NMR of 3, $CDCl_3$, 100 MHz, 24 ^{o}C