N-Heterocyclic Carbene-Catalyzed Hydroacylation of Unactivated Double Bonds

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Supporting Information

CONTENTS:

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1 General information

All reactions were carried out in flame-dried reaction vessels with Teflon screw caps under argon. All new compounds were fully characterized. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane. Coupling constants (J) are quoted in Hz.

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with Agilent 5975C VL MSD or 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, only three methods were used (table 1.1). The method used starts with the injection temperature T_0, after holding this temperature for 3 min, the column is heated to the temperature T_1 (ramp) and holds the final temperature for the indicated time.

Table 1.1: GC-MS methods.

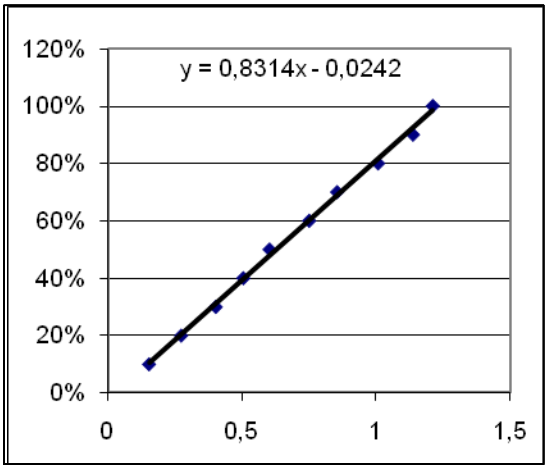
method	T_0 [°C]	ramp/$K \cdot min^{-1}$	T_1[°C] /holding time[min]
A	**50**	**40**	**290 / 3**
B	**50**	**20**	**280 / 3**
C	**50**	**20**	**320 / 8**

2 Optimization Study

2.1 Calibration Data

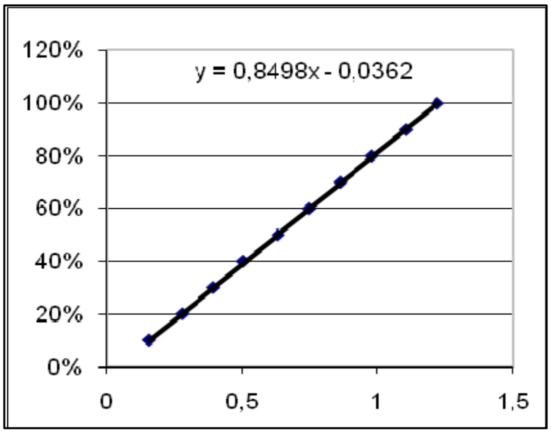
calibration 1

	P	S	P/S	average P/S
10%	25,4	162,7	0,1561156	0,15406311
	28,2	178,3	0,1581604	
	28	189,3	0,1479134	
20%	32,4	119,2	0,2718121	0,2739138
	38,9	140,7	0,2764748	
	37,6	137,5	0,2734545	
30%	47,7	122,6	0,3890701	0,40278617
	55,4	139,6	0,3968481	
	68,9	163,1	0,4224402	
40%	69,8	134	0,5208955	0,50570244
	59,8	119,4	0,5008375	
	58,9	118,9	0,4953743	
50%	33,6	60,3	0,5572139	0,60350799
	64,4	101,7	0,633235	
	66,1	106,6	0,620075	
60%	69	90,1	0,7658158	0,75128313
	66,8	88,3	0,7565119	
	67,3	92	0,7315217	
70%	84,1	96,5	0,8715026	0,85539972
	81,5	95,7	0,8516196	
	82,2	97,5	0,8430769	
80%	96,6	96,1	1,0052029	1,00841158
	107,9	106,3	1,0150517	
	100,9	100,4	1,0049801	
90%	102,9	91,6	1,1233624	1,13863541
	113,6	97,2	1,1687243	
	107,1	95,3	1,1238195	
100%	103,4	84,8	1,2193396	1,21242812
	111,8	91	1,2285714	
	87,3	73,4	1,1893733	

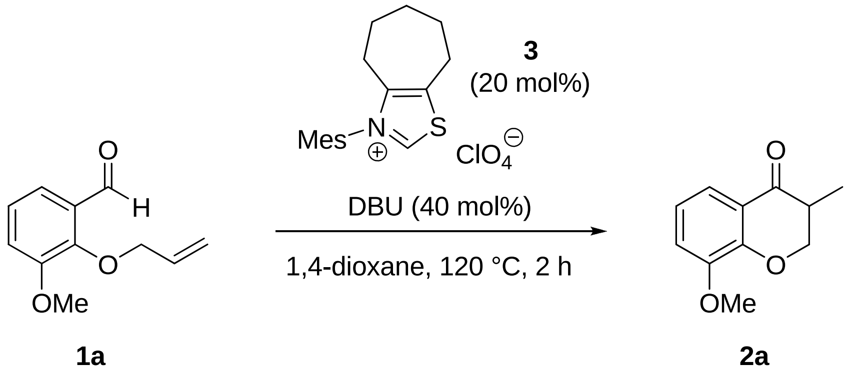


calibration 2

	P	S	P/S	average P/S
10%	18,7	118	0,158474576	0,16027066
	20,9	127,5	0,163921569	
	19,2	121,2	0,158415842	
20%	31,7	113,7	0,27880387	0,28126751
	31	111,3	0,278526505	
	32,4	113,1	0,286472149	
30%	42,8	107,9	0,396663577	0,39703953
	40,6	101,2	0,401185771	
	40,9	104	0,393269231	
40%	51	102,8	0,496108949	0,50547499
	49,3	99,6	0,49497992	
	50,8	96,7	0,525336091	
50%	56,3	93	0,605376344	0,63531521
	55,7	85,7	0,649941657	
	62,2	95,6	0,650627615	
60%	66,6	90	0,74	0,74906028
	64,8	85,2	0,76056338	
	60,7	81,3	0,746617466	
70%	70,1	79,6	0,880653266	0,86322228
	64,6	75,8	0,852242744	
	65,8	76,8	0,856770833	
80%	67,7	70,9	0,954866008	0,97999905
	73,1	73,6	0,993206522	
	73,7	74,3	0,99192463	
90%	79,1	70	1,13	1,10507102
	72,9	66	1,104545455	
	77,7	71,9	1,080667594	
100%	83,4	68,5	1,217518248	1,22078543
	87,1	71	1,226760563	
	84,9	69,7	1,218077475	

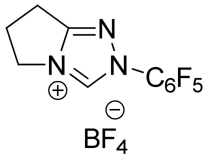
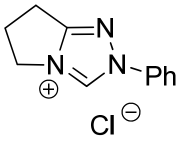
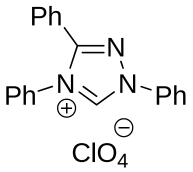
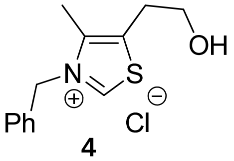
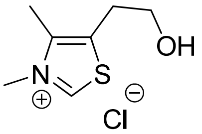


2.2 General Reaction Scheme



All optimization reactions were run with standard substrate **1a**. Deviations from the standard conditions are given in the tables below.

2.3 NHCs[1]

pie-pd-046	A						 **6**
time	Run	P	standard	P/S	average P/S	yield	
60min	1	5,1	85,6	0,0595794	0,0578943	2.4%	
	2	5	86,3	0,0579374			
	3	4,6	81,9	0,0561661			
	B						 **5**
time	Run	P	standard	P/S	average P/S	yield	
60min	1	23	84,2	0,2731591	0,2789927	20.8%	
	2	24	86,4	0,2777778			
	3	25	87,4	0,2860412			
	C						
time	Run	P	standard	P/S	average P/S	yield	
60min	1	6,7	75,6	0,0886243	0,0856473	4.7%	
	2	6,8	82,7	0,0822249			
	3	6,5	75,5	0,0860927			
	D						 **4**
time	Run	P	standard	P/S	average P/S	yield	
60min	1	3,1	98,9	0,0313448	0,0315281	2%	
	2	2,9	93,5	0,031016			
	3	3	93,1	0,0322234			
	E						
time	Run	P	standard	P/S	average P/S	yield	
60min	1	12,6	77,5	0,1625806	0,163992	11.2%	
	2	14,3	86,8	0,1647465			
	3	13,6	82,6	0,1646489			

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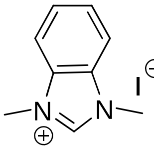
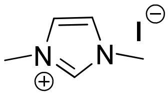
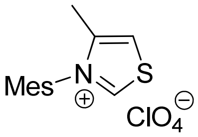
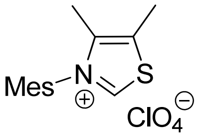
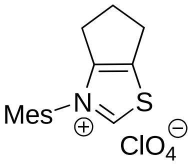
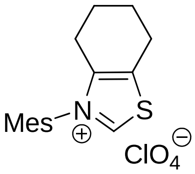
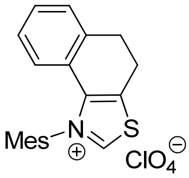
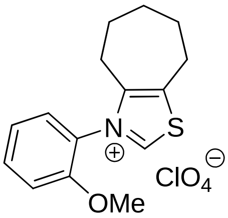
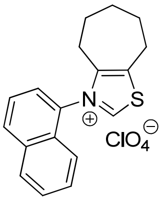
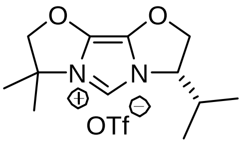
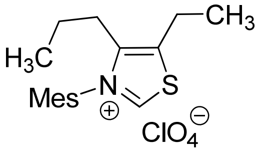
[1] Calibration curve 1 used.

	F						
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	 7
60min	1	33,1	100,3	0,33001	0,3260639	11.2%	
	2	31,1	95,2	0,3266807			
	3	31,7	98,6	0,321501			
	G						
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	2,1	158,9	0,0132159	0,0131223	0%	
	2	1,8	143,2	0,0125698			
	3	1,9	139,9	0,0135811			
khr-km-071							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	34,5	69,9	0,4935622	0,4895306	38.3%	
	2	39,9	80,1	0,4981273			
	3	35,1	73,6	0,4769022			
khr-km-072							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	48,7	63,6	0,7657233	0,7680889	61.4%	
	2	47	61,4	0,7654723			
	3	51,1	66,1	0,7730711			
khr-km-073							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	0	74,9	0	0	0%	
	2	0	70,7	0			
	3	0	71,1	0			
khr-km-074							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	53	69,7	0,7604017	0,7552349	60.4%	
	2	51,4	67,8	0,7581121			
	3	53,2	71,2	0,747191			
khr-km-075							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	5,9	81,2	0,0726601	0,0756803	3.9%	
	2	5,4	71,1	0,0759494			
	3	5,2	66,3	0,0784314			
khr-km-076							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	13	71	0,1830986	0,1842984	12.9%	
	2	14,1	75,5	0,186755			
	3	13,6	74,3	0,1830417			
khr-km-077							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	7,5	65,2	0,1150307	0,1145038	7.1%	
	2	8,1	70,8	0,1144068			
	3	7,7	67,5	0,1140741			

khr-km-078							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	1,5	74,5	0,0201342	0,0180004	0%	
	2	1,3	76,2	0,0170604			
	3	1,2	71,4	0,0168067			
khr-km-079							
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**Yield**	
60min	1	41,3	64	0,6453125	0,6360126	50.5%	
	2	38,7	61,1	0,6333879			
	3	39,9	63,4	0,6293375			
pie-pd-057	**KCN**						KCN
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	0	85,3	0	0	0%	
	2	0	80	0			
	3	0	86,5	0			
pie-pd-058	**PPh_3**						PPh_3
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**	
60min	1	0	92,5	0	0	0%	
	2	0	90,7	0			
	3	0	91,5	0			

2.4 Molecular Sieves, Temperature, Time[2]

pie-pd-044 (without MS 4A)						
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	16,6	49,3	0,336714	0,285061819	21.3%
	2	9,2	36,7	0,2506812		
	3	14,3	53,4	0,2677903		
120min	1	40,1	121	0,331405	0,334392093	25.4%
	2	43,5	126,9	0,3427896		
	3	37,8	114,9	0,3289817		
pie-pd-045 (with MS 4A)						
	Run	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	18,9	106,3	0,1777987	0,176700177	12.3%
	2	18,2	103,7	0,1755063		
	3	19,2	108,6	0,1767956		
120min	1	17,1	90,1	0,1897891	0,192550608	13.6%
	2	18,2	93,2	0,195279		
	3	16,1	83,6	0,1925837		
pie-pd-047 (different T)						
	Run	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	30,2	95,3	0,316894	0,313023229	23.6%
100°C	2	30,7	96,4	0,3184647		
	3	31,1	102,4	0,3037109		

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[2] Calibration curve 1 used.

60min	1	45,1	104,1	0,4332373	0,436879014	33.9%
120°C	2	45,7	103,2	0,4428295		
	3	44,5	102,4	0,4345703		
pie-pd-050 (different reaction times)						
	Run	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	70,2	76,1	0,9224704	0,863880263	69.4%
	2	61,9	74,5	0,8308725		
	3	59,1	70,5	0,8382979		
120min	1	79,3	77,9	1,0179718	1,003096171	81%
	2	81,4	81,3	1,00123		
	3	79,9	80,7	0,9900867		
pie-pd-063 (longer reaction time)			**09.06.2009**	**(Calibration 2 used)**		
	Run	**P**	**standard**	**P/S**	**average P/S**	**yield**
120min	1	64,5	70	0,9214286	0,92073248	70.1%
	2	59,9	66,1	0,9062027		
	3	65,7	70,3	0,9345661		
180min	1	77,4	77,3	1,0012937	0,996903533	76.5%
	2	78,9	77,8	1,0141388		
	3	78,9	80,9	0,9752781		
240min	1	94	100	0,94	0,950169444	72.6%
	2	90,6	95,3	0,9506821		
	3	88,4	92,1	0,9598263		
19h	1	36,3	50	0,726	0,693464236	50.9%
	2	37,5	55,2	0,6793478		
	3	37,6	55,7	0,6750449		

2.5 Solvents[3]

pie-pd-053	**A**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	80,6	95,9	0,8404588	0,8241114	66.4%
toluene	2	76,1	93,7	0,8121665		
	3	73,2	89,3	0,8197088		
PhCl	**B**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	61,8	98,3	0,6286877	0,6349351	50.3%
	2	56,9	89,2	0,6378924		
	3	56,1	87,9	0,6382253		
DMF	**C**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	64,9	80,1	0,8102372	0,8041917	64.7%
	2	64,7	80,9	0,7997528		
	3	68,3	85,1	0,8025852		
t-Amyl-OH	**D**					

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[3] Calibration curve 2 used.

time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	57	79,4	0,7178841	0,7128928	57%
	2	53,4	76,1	0,7017083		
	3	53,5	74,4	0,719086		
1,2-DME	**E**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	56,9	81	0,7024691	0,6996072	55.8%
	2	51,2	72,4	0,7071823		
	3	49	71,1	0,6891702		
1,2-DCE	**F**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	18,2	93	0,1956989	0,1974014	13.2%
	2	18,8	93,7	0,2006403		
	3	18	91,9	0,1958651		
propionitrile	**G**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	53,8	77,4	0,6950904	0,7001559	55.9%
	2	54,1	79,3	0,6822194		
	3	68,7	95	0,7231579		

2.6 Bases[4]

pie-pd-054	**A**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	6,5	85,4	0,0761124	0,0771114	2.9%
Et$_3$N	2	6,1	77,8	0,0784062		
	3	5,5	71,6	0,0768156		
DIPEA	**B**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	4,9	66,9	0,0732436	0,0738131	2.7%
	2	5,3	72,3	0,0733057		
	3	5,1	68,1	0,0748899		
K$_2$CO$_3$	**C**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	32,2	76,2	0,4225722	0,4230986	32.3%
	2	33,8	78,8	0,428934		
	3	31	74,2	0,4177898		
NaH	**D**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	42,7	81,4	0,52457	0,5251673	41.0%
	2	39,5	75,6	0,5224868		
	3	41,8	79,1	0,528445		
KO*t*Bu	**E**					

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[4] Calibration curve 2 used.

time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	80,7	90,7	0,8897464	0,8588919	69.4%
	2	75,8	88,7	0,854566		
	3	71,5	85,9	0,8323632		
Cs_2CO_3	**F**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	22,5	64,2	0,3504673	0,3453841	25.7%
	2	23	66,5	0,3458647		
	3	22,7	66,8	0,3398204		
DBU/DIPEA 1:1	**G**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	35,7	60,1	0,59401	0,5951024	47.0%
	2	39,6	66,5	0,5954887		
	3	39,8	66,8	0,5958084		

2.7 Concentration[5]

1.0M	**pie-pd-059**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	51,8	59,4	0,8720539	0,8794564	71.1%
	2	47,2	54,7	0,8628885		
	3	58	64,2	0,9034268		
0.1M	**pie-pd-060**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	42,1	69,4	0,6066282	0,5997537	47.3%
	2	41,9	70,9	0,5909732		
	3	43,5	72,3	0,6016598		
not degassed	**pie-pd-061**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	70,8	74,7	0,9477912	0,8907874	72.1%
	2	60,2	69,7	0,8637016		
	3	59,4	69	0,8608696		
AcOH	**pie-pd-062**					
time	**Run**	**P**	**standard**	**P/S**	**average P/S**	**yield**
60min	1	20,5	83,2	0,2463942	0,2433845	17.1%
	2	20,5	84,2	0,2434679		
	3	19,8	82,4	0,2402913		

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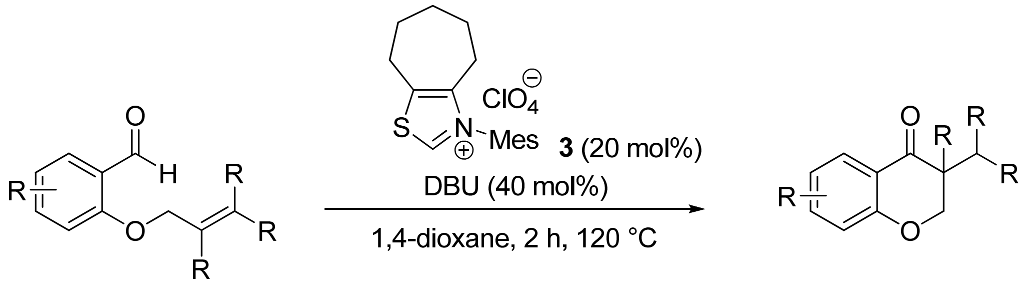
[5] Calibration curve 2 used.

3 Typical Procedure for the N-Heterocyclic Carbene Catalyzed Hydroacylation of Unactivated Double Bonds

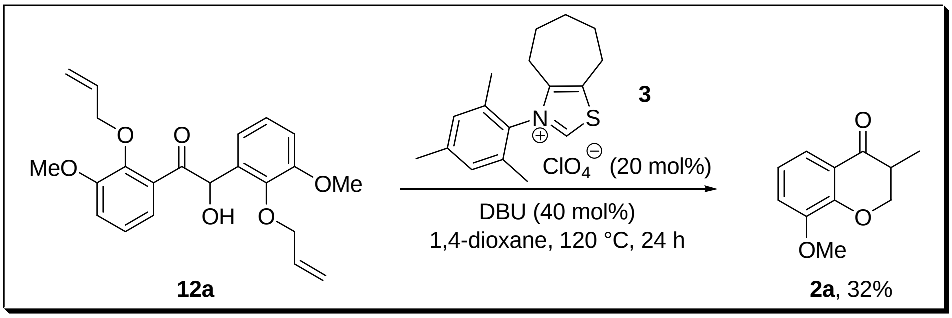


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the aldehyde (1.0 mmol, 1 eq.), thiazolium salt **3** (74.4 mg, 0.2 mmol, 0.2 eq.) and 1,4-dioxane (2.0 mL). The mixture was then degassed by 3 freeze-pump-thaw cycles. DBU (61 mg, 60 µL, 0.4 eq.) was added and the resulting mixture was then stirred in a pre-heated oil bath at 120 °C for the indicated time. After the reaction was complete, the reaction was cooled to ambient temperature, pre-adsorbed on silica gel and purified by column chromatography on silica gel.

4 Mechanistic Investigations

4.1 Employing a Preformed Benzoin as Starting Material

Benzoin **12a** was subjected to the standard reaction conditions in order to check the reversibility of benzoin formation. Remarkably, **12a** was converted to chromanone **2a** in 32% yield, although this reaction was rather slow. Still, most of the starting material **12a** remained as such. This result indicates that the benzoin formation is reversible, and, thus, this side reaction would not necessarily inhibit chromanone formation.[6]



In short: this experiment shows the reversibility of the benzoin formation under the standard reaction conditions.

Following the general procedure, 120 mg 1,2-bis-(2-allyloxy-3-methoxy-phenyl)-2-hydroxy-ethanone (0.31 mmol, 0.5 eq.) were dissolved in 1,4-dioxane (1.2 mL) and 46 mg thiazolium salt **3** (0.124 mmol, 0.2 eq.) were added. After the addition of 38 µL DBU (0.25 mmol, 0.4 eq.) the reaction mixture was stirred at 120 °C for 24 hours. The crude reaction mixture was preadsorbed on silica and purified by flash column chromatography (2 x 10 cm silica, PE/EE = 10/1) to afford 38 mg (0.198 mmol, 32%) of the pure product.

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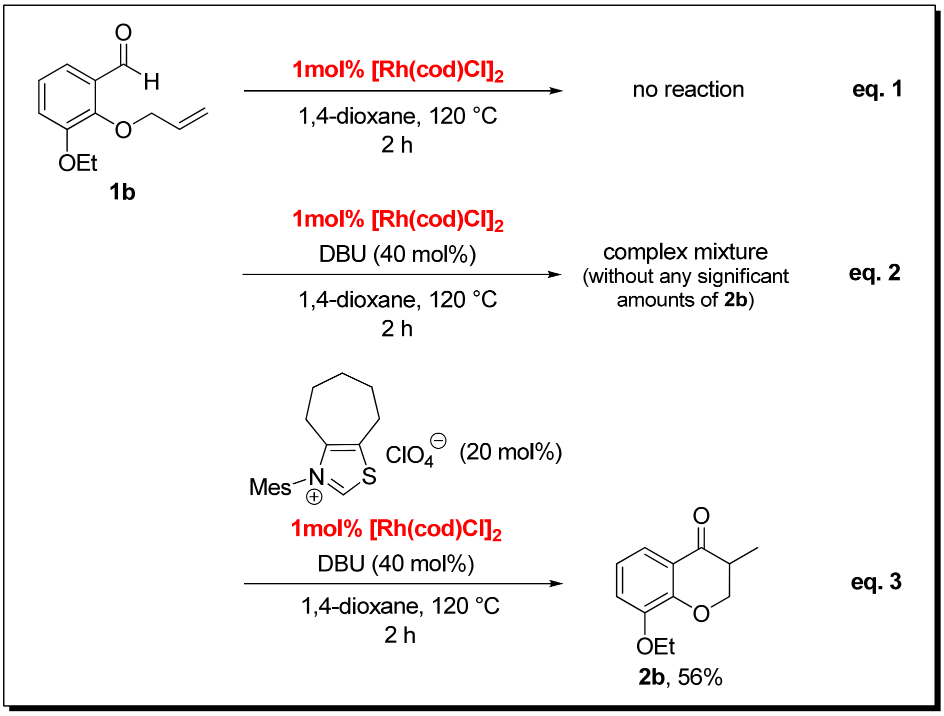
[6] Han, J.; Henseler, A.; Enders, D. *Chem. Commun.* **2008**, 3989.

4.2 Control Experiments with [Rh(cod)Cl]$_2$



In short: experiments 1 and 2 show that [Rh(cod)Cl]$_2$ is no competent catalyst for the given hydroacylation reaction.

Following the general procedure, three control experiments were run in a 1 mmolar scale with the addition of 1 mol% [Rh(cod)Cl]$_2$ each. The standard conditions using additional [Rh(cod)Cl]$_2$ afforded 115 mg of the pure product (0.556 mmol, 56%), compared to 68% without the Rh species (eq. 1), whereas DBU and [Rh] lead to a complex mixture (analyzed by GC-MS) and only the [Rh] species did not yield any product at all (eq. 2+3). Therefore we can exclude the possibility of a Rh-catalyzed hydroacylation.

4.3 ICP-OES Analyses for Metal Contamination

A Spectro CIROS^{CCD} ICP-OES (Spectro Analytical Instruments, Kleve, Germany) instrument with axial plasma viewing was used for element determination. Gas flows were controlled by internal mass flow controllers. The inner diameter of the load coil was 25 mm. The free-running generator was operated at 27.12 MHz with a maximum output of 2 kW. In the Fassel mode (ca. 14 L/min argon consumption), a standard Fassel type torch (No. 75160526, Spectro Analytical Instruments) was employed. For sample introduction, the system's peristaltic pump with a cross flow nebulizer and a double-pass spray chamber (Scott type) was used. Element emission was detected at two individual emission lines simultaneously for each element at least. Operating conditions for ICP-OES measurements are shown in table 1.

Table 1 Instrument parameters (Spectro CIROS^{CCD} ICP-OES, axial plasma viewing).

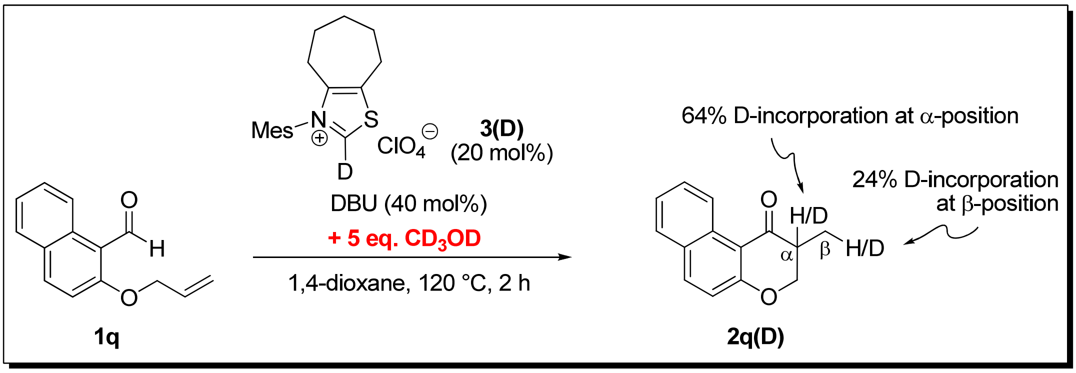
ICP-OES system	Conv. ICP-OES
Rf power (W)	1400
Total argon flow (L/min)	14.05
Sample carrier gas (L/min)	1.05
Auxiliary plasma gas (L/min)	1.00
Outer plasma gas (L/min)	12.0
Torch geometry	Fassel type
Torch injector tube i.d. (mm)	2.5
Nebulizer	CrossFlow
Sample uptake rate (mL/min)	2.00

To ensure that no metal contaminants are present in our reaction mixture, *o*-vanillin derived substrate **1a**, thiazolium salt **3**, DBU and 1,4-dioxane were analyzed separately for virtually all transition metals, as well as the reaction mixture, by ICP-OES measurements. In none of these measurements any significant amount of transition metal (< 500 ng/L; detection limit) was found. Thus, we conclude that a metal-catalyzed process is very unlikely (or would be extremely efficient).

In short: ICP-OES analyses did not show any transition metal to be present in amounts above the detection limit.

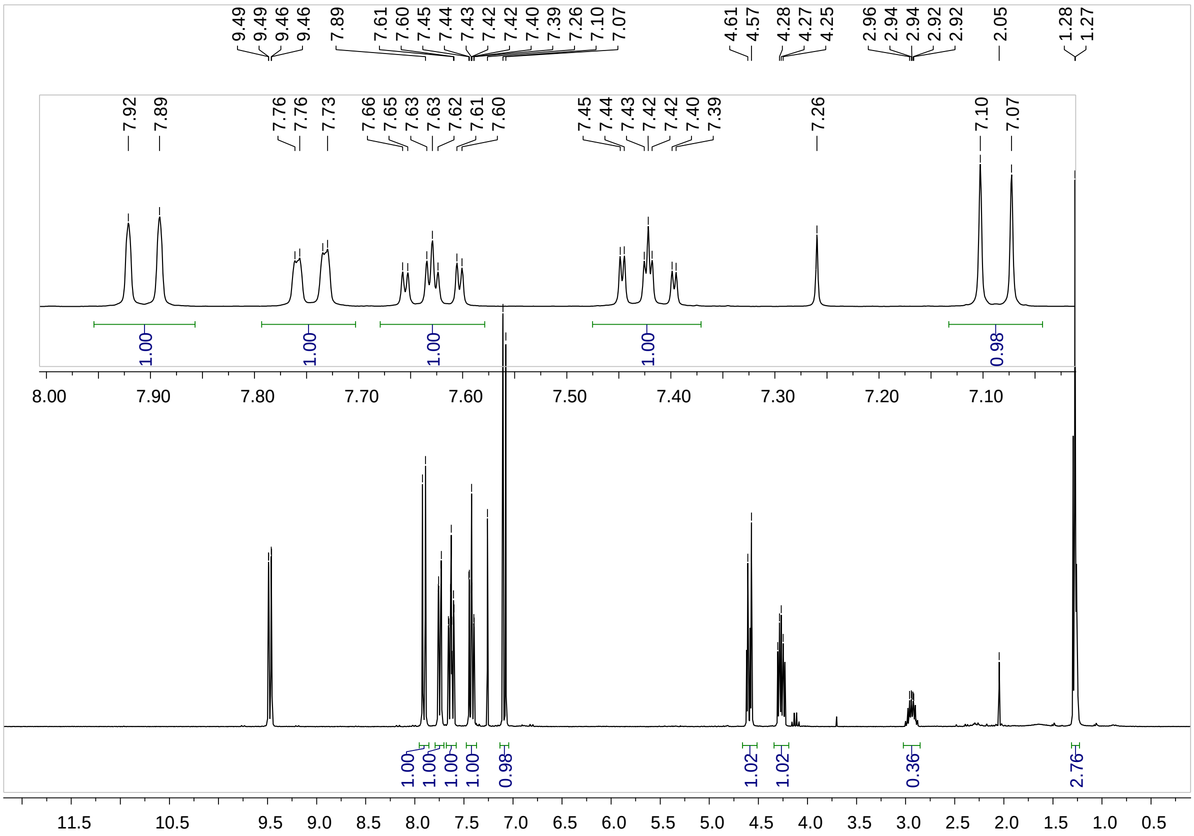
4.4 Experiments with Deuterium-Labelled Substrates

4.4.1 Experiment with External Deuterium Source

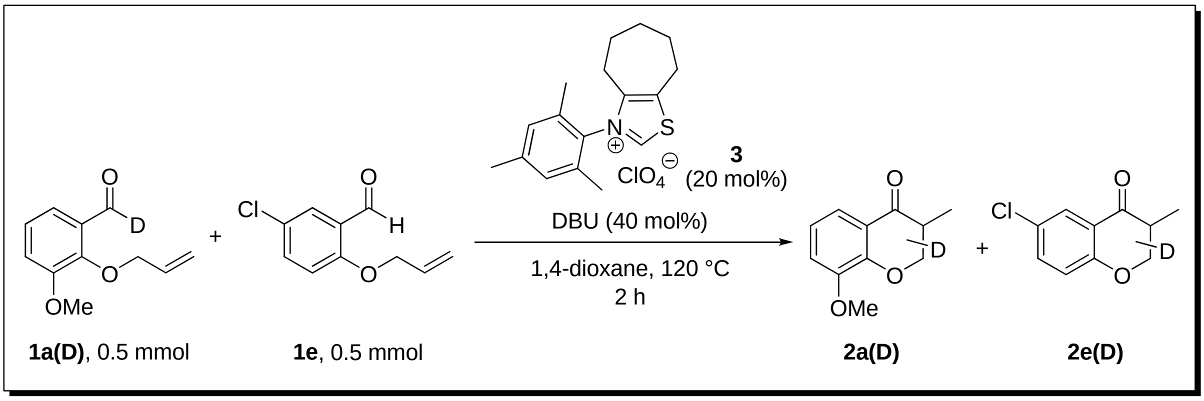


Following the general procedure, 212 mg 2-allyloxy-1-naphthaldehyde (1.0 mmol, 1.0 eq.) and 75 mg deuterated thiazolium salt **d-3** (0.2 mmol, 0.2 eq.) were dissolved in 2 mL 1,4-dioxane. After the addition of 60 µL DBU (0.4 mmol, 0.4 eq.) 203 µL of CD_3OD (5.0 mmol, 5.0 eq.) were added and the reaction mixture was stirred at 120 °C for 2 hours. After cooling to ambient temperature and preadsorbing the reaction mixture on silica gel, flash column chromatography yielded 158 mg (0.744 mmol, 74%) of the pure product as yellow oil.

In short: the reversibility of the formation of the Breslow intermediate is a possible explanation for the β-deuteration. keto-enol-tautomerism would is a likely reason for the α-deuteration.

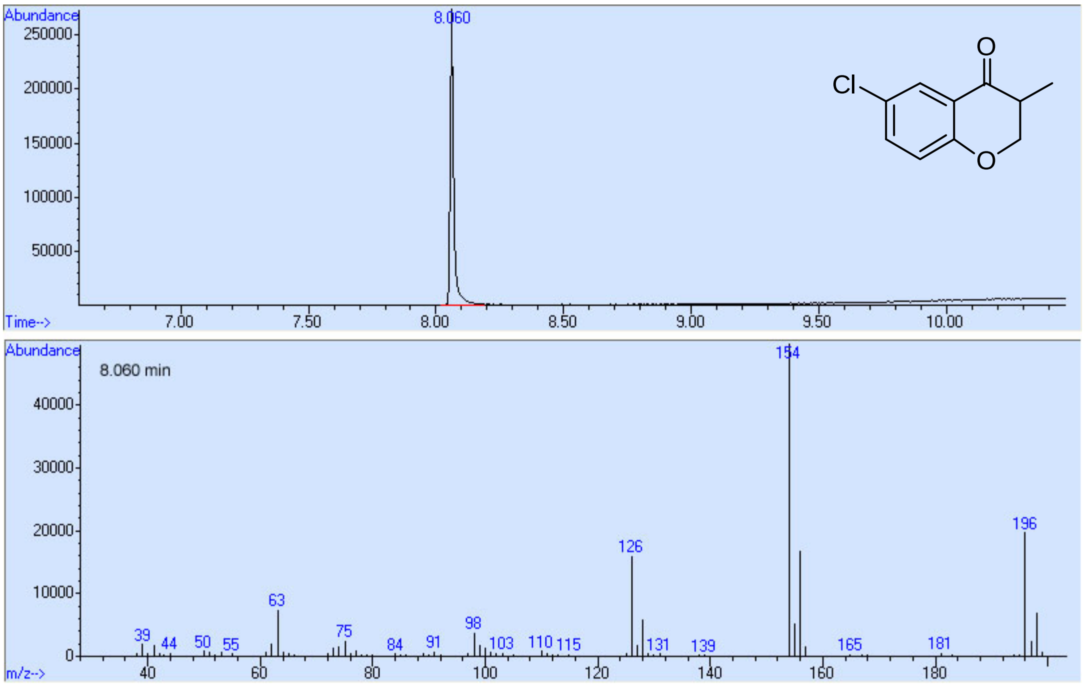


4.4.2 Cross-over Experiment

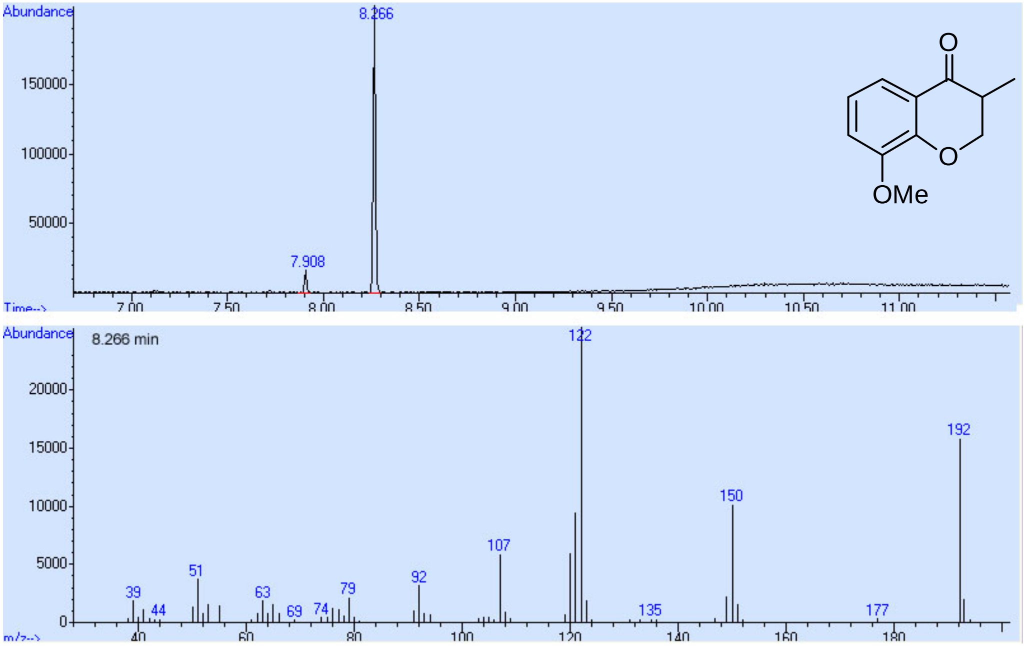


Following the general procedure, 97 mg 2-allyloxy-3-methoxy-benzaldehyde-d$_1$ (0.5 mmol, 0.5 eq.) and 98 mg 2-allyloxy-5-chloro-benzaldehyde (0.5 mmol, 0.5 eq.) were dissolved in 2 mL 1,4-dioxane and 74 mg thiazolium salt **3** (0.2 mmol, 0.2 eq.) were added. After the addition of 60 µL DBU (0.4 mmol, 0.4 eq.) the reaction mixture was stirred at 120 °C for 2 hours. The reaction was analyzed by GC-MS (see GC-MS chromatograms and spectra below). These results show scrambling of deuterium. Comparison of the mass spectra of the non-deuterated and deuterated products does allow the qualitative determination of the deuterium incorporation and shows the incorporation of the deuterium in both products.

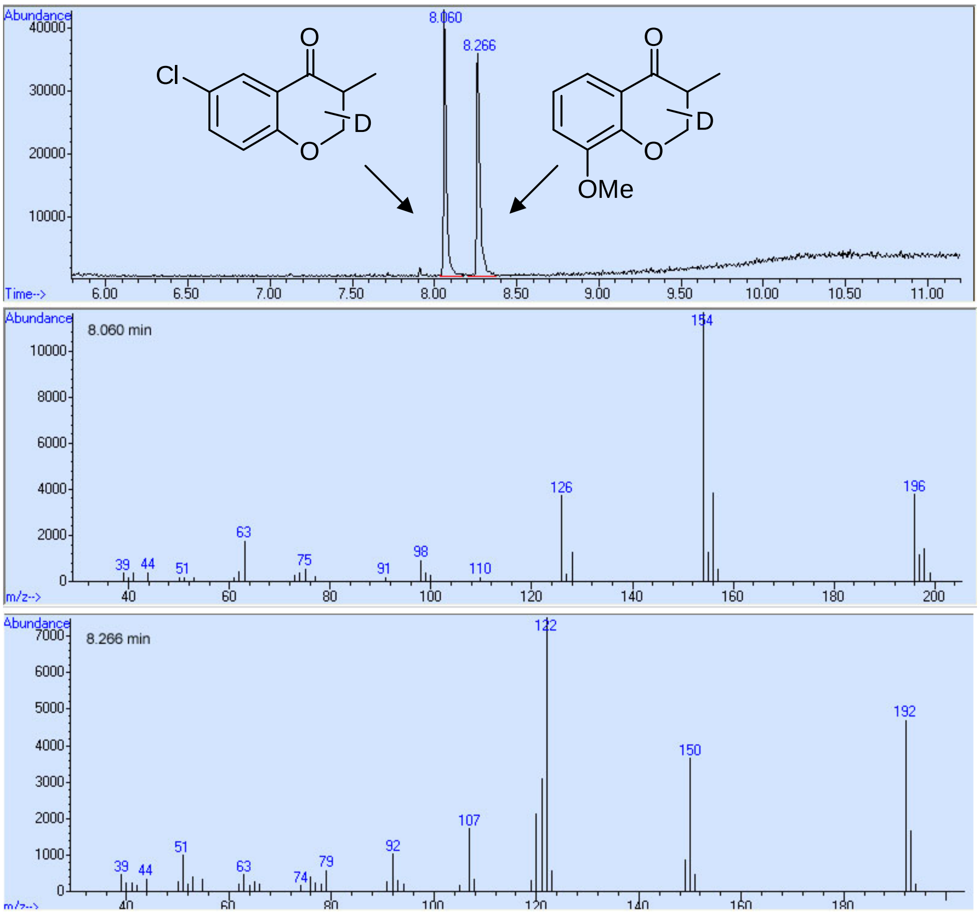
GC-MS chromatogram and EI mass spectra of chromanone 2f:



GC-MS chromatogram and EI mass spectra of chromanone 2a:

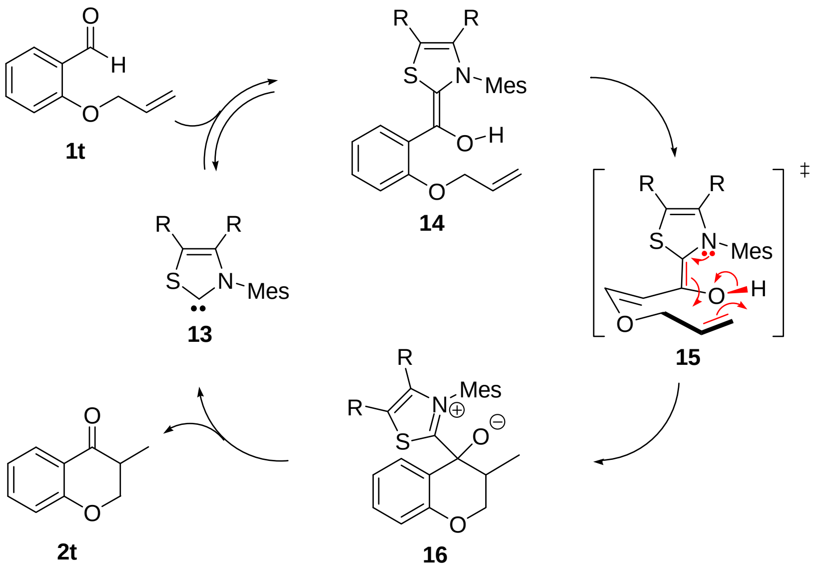


GC-MS chromatogram and EI mass spectra of crossover experiment:



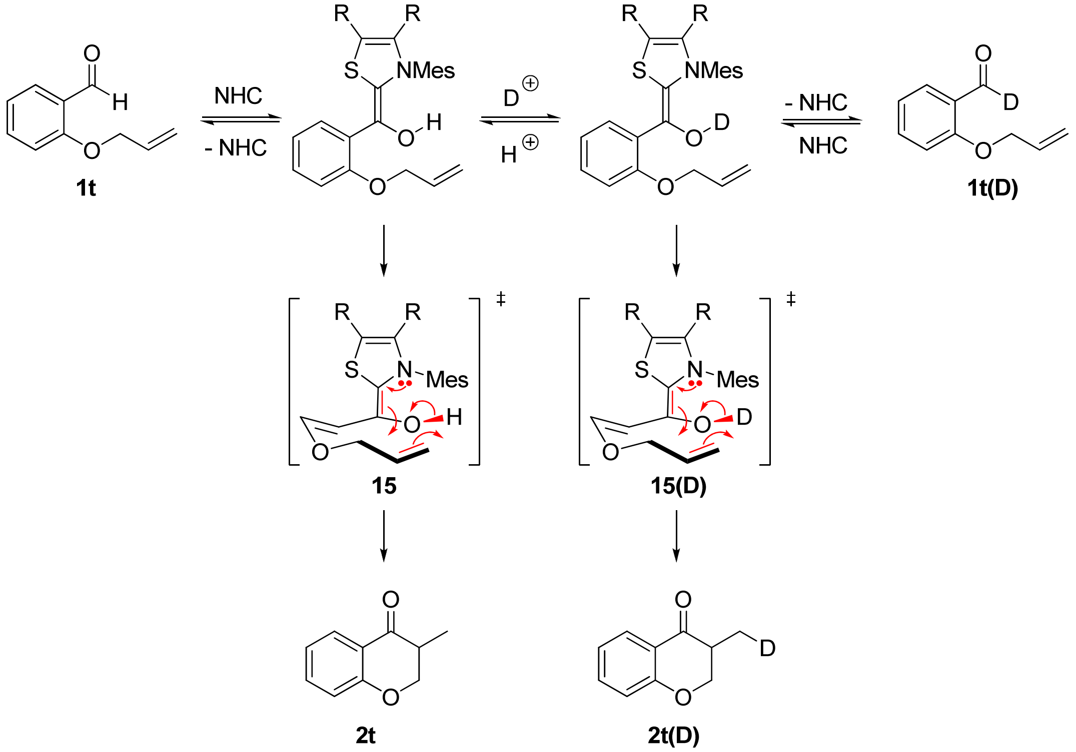
In short: the reversibility of the formation of the Breslow intermediate is a possible explanation for the cross-over.

4.5 Plausible Catalytic Cycle



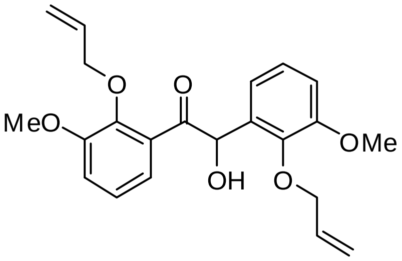
A likely mechanism starts with the addition of the thiazolylidene **13** (derived from thiazolium salt **3**) to the carbonyl group of *o*-allyloxybenzaldehyde (**1t**) to form the Breslow intermediate **14**. As shown by the mechanistic experiments, this should be a reversible process. In a concerted transition state **15**, this could add as a nucleophile to the olefin of the allyl moiety and at the same time the negative charge building up on the other end of the olefin is stabilized by deprotonation of the hydroxyl group. This would be in agreement with the low reactivity of substrates **8a**,**c**, in which the negative charge on the allyl termini would be significantly destabilized. The resulting zwitterionic tetrahedral intermediate **16** liberates the desired product and the catalyst. However, it should be noted that the special reactivity of NHC **13** is not yet fully understood, requiring further investigation.

4.5.1 Plausible Mechanism for the Deuteration Studies



4.6 Synthesis of Substrates for Mechansitic Investigations

1,2-Bis-(2-allyloxy-3-methoxy-phenyl)-2-hydroxy-ethanone (12a)



Following a modified procedure by Miyashita et al.,[7] 2-allyloxy-3-methoxy-benzaldehyde (480.5 mg2.5 mmol, 1.0 eq.) and 68.5 mg *N,N*-dimethylbenzimidazolium iodide (0.25 mmol, 0.1 eq.) were dissolved in 4 mL THF. After the addition of 37 µL DBU (0.25 mmol, 0.1 eq.) the reaction mixture was stirred at 90 °C over night. After the addition of water (5 mL), the mixture was extracted with EtOAc (2 x 30 mL) and the combined organic layers were dried over Na_2SO_4. After removal of residual solvents the crude product was purified by flash column chromatography (2.5 x 10 cm silica, PE/EE = 30/1 → 10/1) to yield 224 mg of the pure product (0.582 mmol, 23%) as a colorless oil.

R*f* (pentane/EtOAc = 5/1): 0.16; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.06-6.76 (m, 6H, H_{ar}), 6.18-5.98 (m, 3H), 5.40-5.21 (m, 4H), 4.62-4.39 (m, 5H), 3.77 (d, *J* = 6.4 Hz, 6H, OMe); **^{13}C NMR (75 MHz, $CDCl_3$):** 201.9 (C=O), 152.8, 152.6, 146.0, 145.9, 134.2, 133.7, 132.5, 131.6, 124.3, 124.1, 121.6, 121.2, 118.4, 117.5, 115.6, 112.6, 75.3, 74.9, 74.4, 55.9, 55.7; **ESI-MS:** calculated $[C_{22}H_{24}O_6Na]^+$: 407.1465, found: 407.1465; calculated $[(C_{22}H_{24}O_6)_2Na]^+$: 791.3038, found: 791.3038; **ATR-FTIR (cm^{-1}):** 3080, 3009, 2940, 2839, 1691, 1580, 1474, 1440, 1421, 1309, 1266, 1216, 1183, 1105, 1085, 1057, 996, 930, 839, 785, 746, 632, 538, 504.

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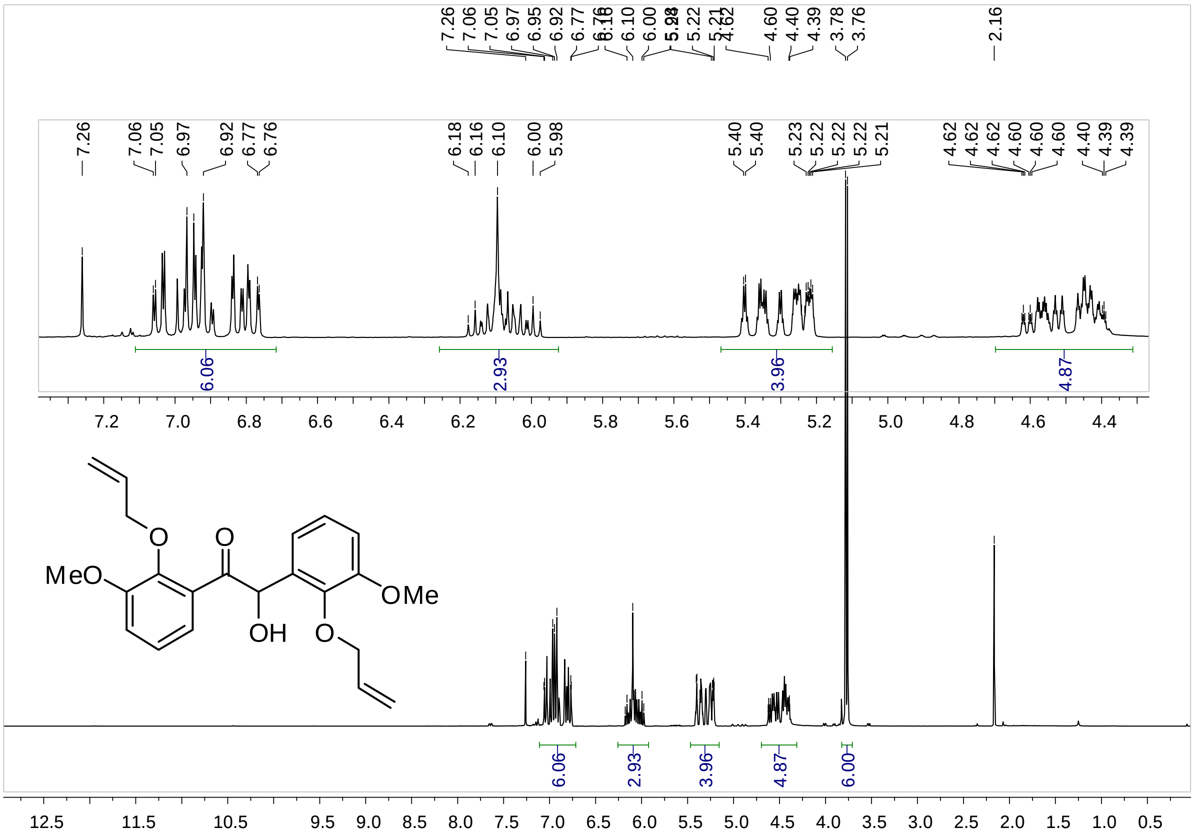
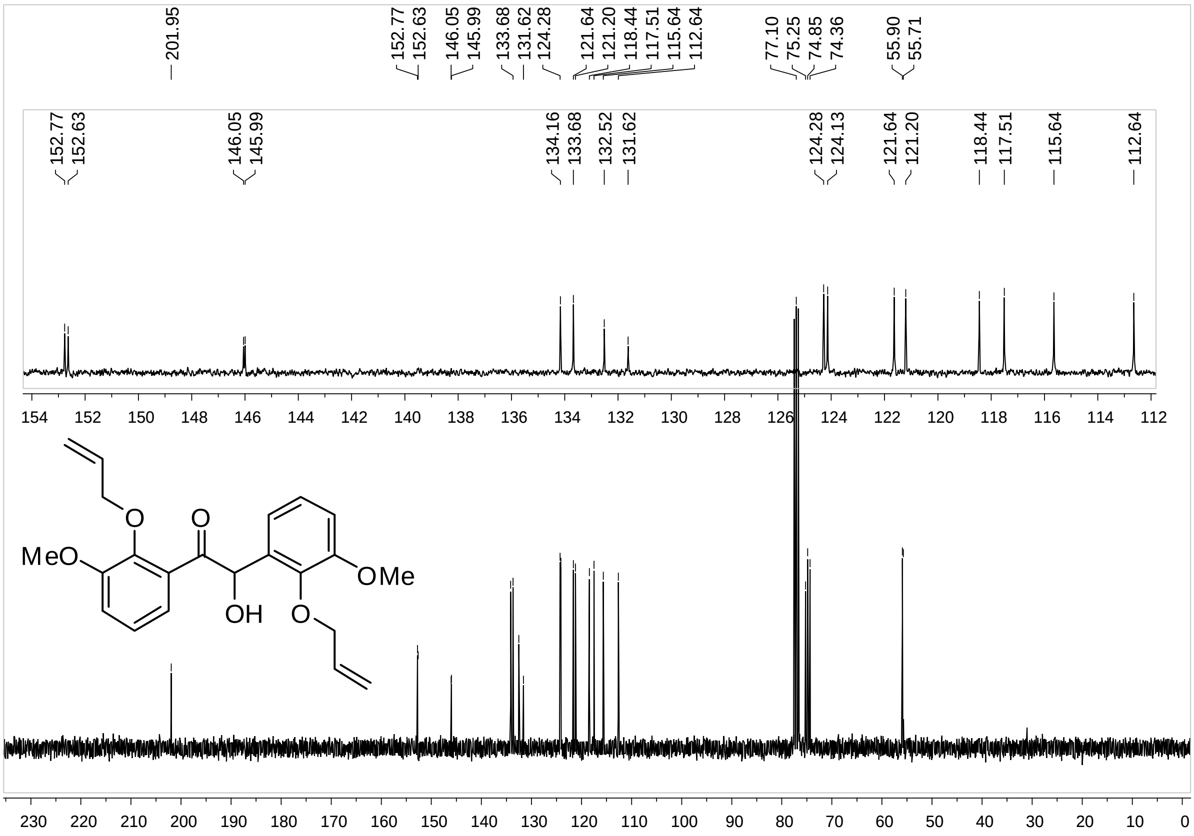
[7] Miyashita, A.; Suzuki, Y.; Iwamoto, K.; Higashino, T. *Chem. Phram. Bull.* **1994**, *42*, 2633.


7.26
7.06
7.05
6.97
6.95
6.92
6.77
6.76
6.10
6.00
5.22
5.21
4.62
4.60
4.40
4.39
3.78
3.76
2.16
7.26
7.06
7.05
6.97
6.92
6.77
6.76
6.18
6.16
6.10
6.00
5.98
5.40
5.40
5.23
5.22
5.22
5.22
5.21
4.62
4.62
4.62
4.60
4.60
4.60
4.40
4.39
4.39
6.06
2.93
3.96
4.87
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
O
O
MeO
OH
O
OMe
6.06
2.93
3.96
4.87
6.00
12.5
11.5
10.5
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


201.95
152.77
152.63
146.05
145.99
133.68
131.62
124.28
121.64
121.20
118.44
117.51
115.64
112.64
77.10
75.25
74.85
74.36
55.90
55.71
152.77
152.63
146.05
145.99
134.16
133.68
132.52
131.62
124.28
124.13
121.64
121.20
118.44
117.51
115.64
112.64
154
152
150
148
146
144
142
140
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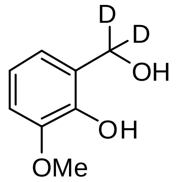
136
134
132
130
128
126
124
122
120
118
116
114
112
O
O
MeO
OH
O
OMe
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2-Hydroxymethyl-6-methoxy-phenol-d$_2$



Following a modified procedure by Dong[8] a suspension of lithium aluminum deuteride (1.26 g, 41.98 mmol, 2.0 eq.) in 60 mL THF was cooled to 0 °C and a solution of 2-hydroxy-3-methoxy-benzoic acid methyl ester (2.73 g, 15.0 mmol, 1.0 eq.) in 15 mL THF was added dropwise. The reaction was warmed to rt, stirred for 1 h and then quenched with EtOAc. 1 M HCl (30 mL) was added and the resulting mixture was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated. Purification by flash column chromatography (silica, 3.5 x 8 cm, PE/EtOAc = 1/1) afforded 2.09 g (13.41 mmol, 89%) 2-hydroxymethyl-6-methoxy-phenol-d$_2$ as a white solid.

R_f (pentane/EtOAc = 1/1): 0.51; **^{1}H NMR (300 MHz, CDCl$_3$):** 6.88-6.83 (m, 3H, H$_{ar}$), 6.10 (s, 1H, OH), 3.89 (s, 3H, OCH_3), 2.33 (s, 1H, CH_2OH); **^{13}C NMR (75 MHz, CDCl$_3$):** 56.2, 110.6, 119.9, 121.0, 126.6, 144.0, 146.7; **ESI-MS:** calculated $[C_8H_8D_2O_3Na]^+$: 179.0651, found: 179.0648; calculated $[C_8H_7D_2O_3Na_2]^+$: 201.0467, found: 201.0487; **ATR-FTIR (cm^{-1}):** 3406, 3338, 3034, 2980, 2941, 2895, 2843, 1621, 1593, 1477, 1436, 1373, 1355, 1303, 1260, 1244, 1220, 1190, 1112, 1088, 1074, 1040, 965, 889, 872, 838, 820, 758, 728, 702, 663, 556, 538.

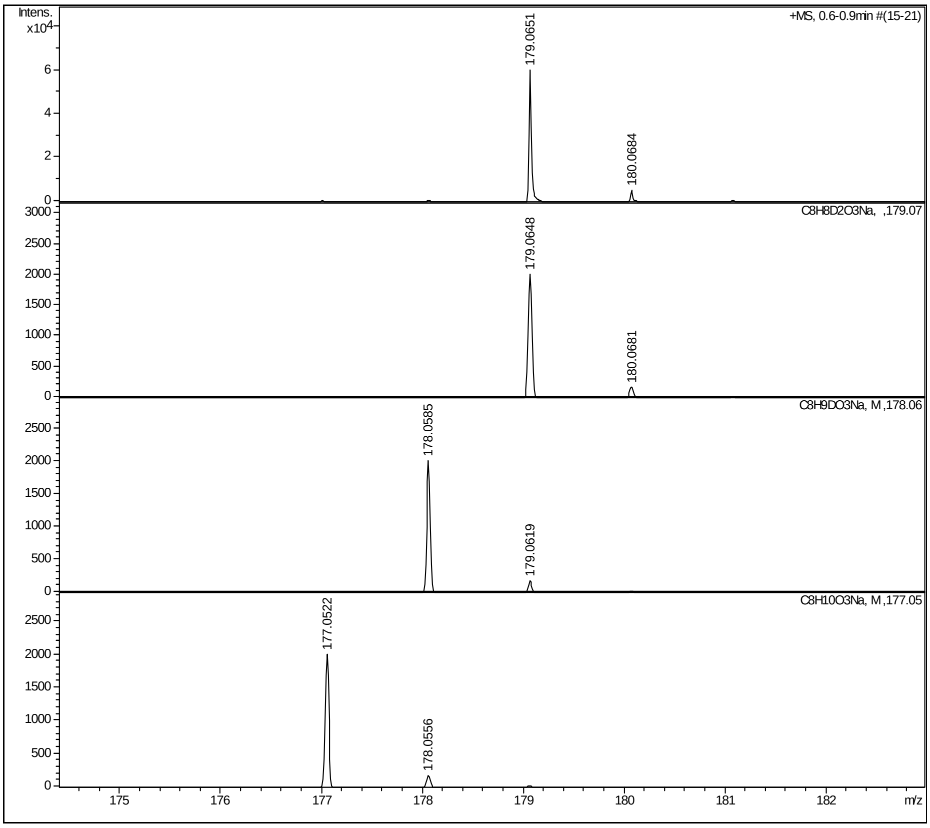
ESI-MS spectra of 2-hydroxymethyl-6-methoxy-phenol-d$_2$

Experiment:

Simulation of $C_8H_8D_2O_3Na$:

Simulation of $C_8H_9DO_3Na$:

Simulation of $C_8H_{10}O_3Na$:



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[8] Shen, Z.; Dornan, P. K.; Khan, H. A.; Woo, T. K.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 1077.

Measured:

#	m/z	Res.	S/N	I	FWHM
1	178.0590	6740	168.7	666	0.0264
2	179.0651	6545	15108.5	59691	0.0274
3	180.0684	7096	1392.1	5501	0.0254
4	181.0694	6874	171.1	676	0.0263

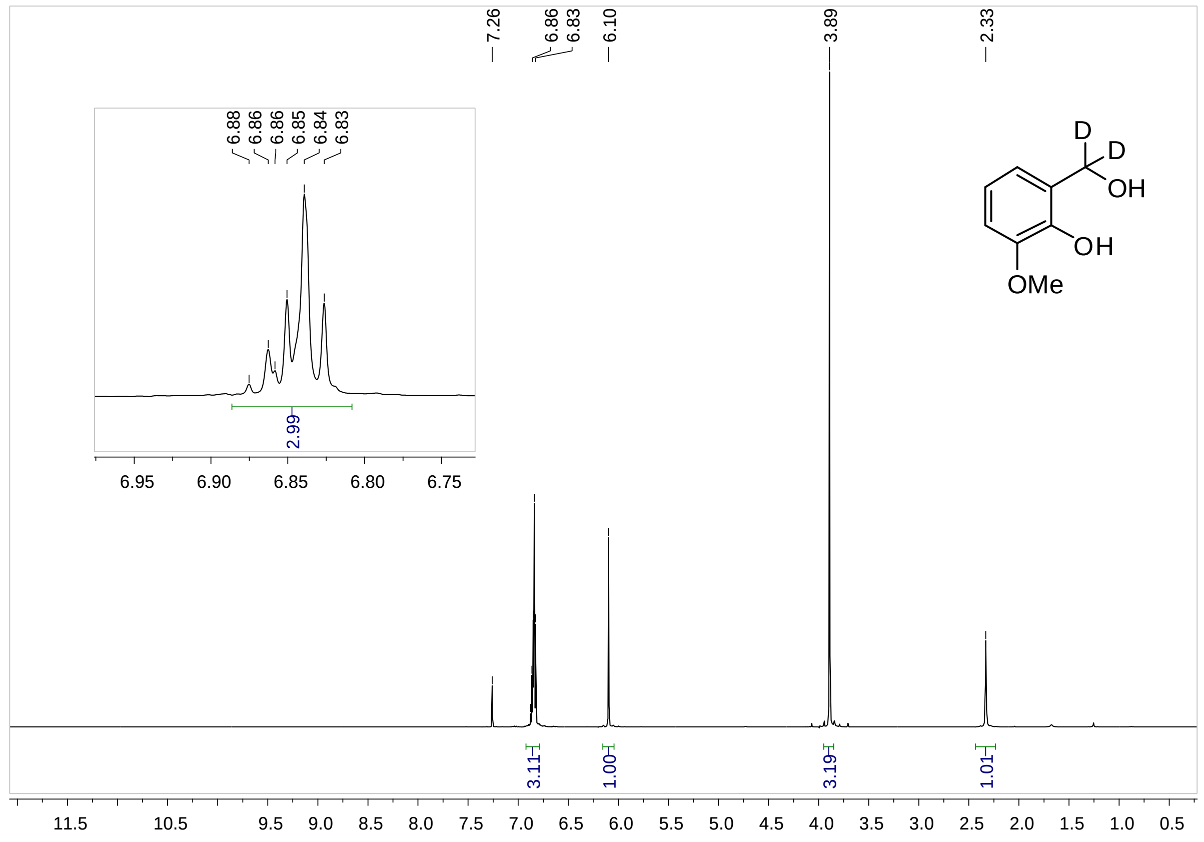
Determination of Deuteration Grade by ESI-MS:

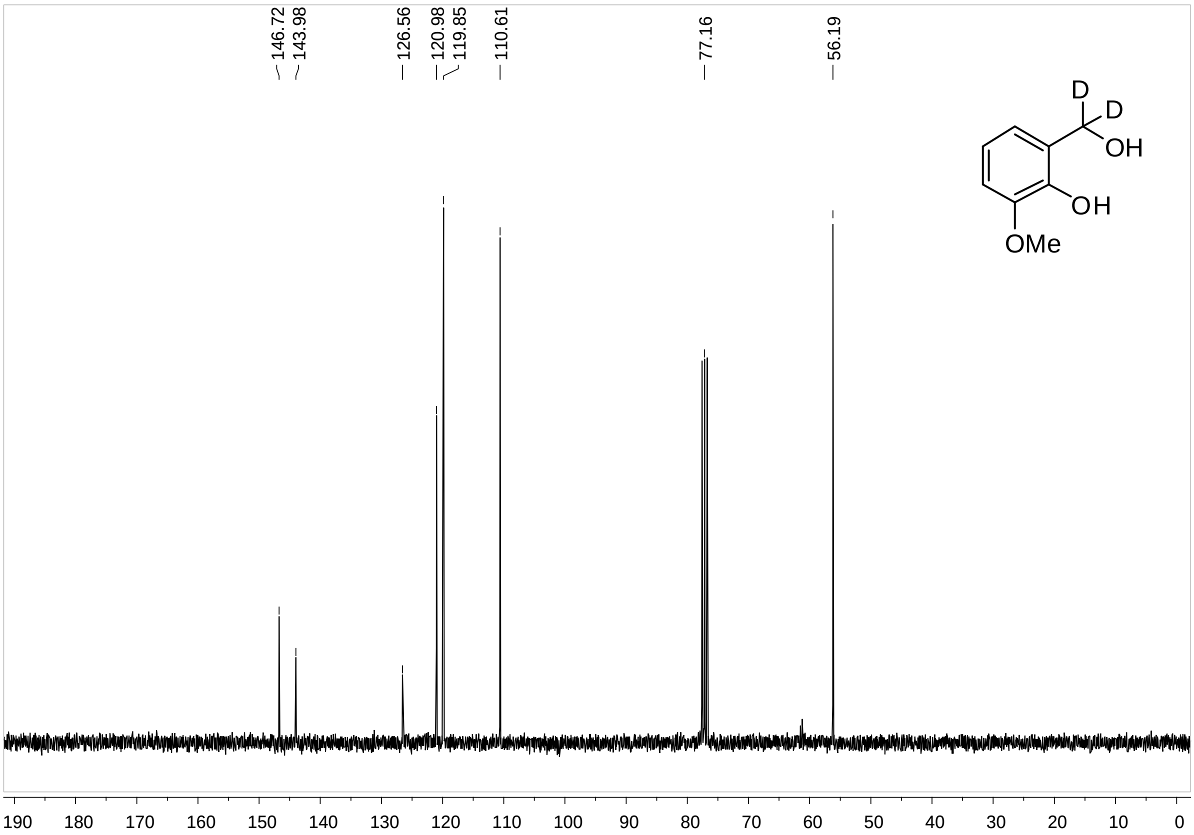
Mono-deuterated product: calculated for $[C_8H_9DO_3Na]^+$: 178.0585, found: 178.0590 (intensity: 666).

Deuterated product: calculated for $[C_8H_8D_2O_3Na]^+$: 179.0648, found: 179.0651 (intensity: 59691, corrected intensity (reduced by carbon-isotope signal of $C_8H_{10}O_3$):

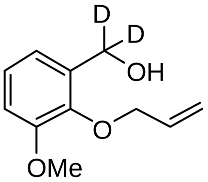
59691 – 666 * 8.7% = 59025.087).

Deuteration grade: 59025.087 / (59025.087 + 666) * 100 = 98.9%





(2-Allyloxy-3-methoxy-phenyl)-methanol-d$_2$



Following a modified procedure by Dong et al.,[9] 2-hydroxymethyl-6-methoxy-phenol-d$_2$ (2.09 g, 13.4 mmol, 1.0 eq.) and K_2CO_3 (2.04 g, 14.74 mmol, 1.1 eq.) were suspended in 25 mL DMF at room temperature. Allyl bromide (1.28 mL, 14.74 mmol, 1.1 eq.) were then added dropwise and the reaction mixture was stirred overnight. The reaction was stopped by the addition of water and the mixture was extracted with EtOAc (3 x 40 mL) and washed with brine (1 x 50 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated to afford the crude product as a light yellow liquid, which was directly used in the next step without further purification.

R*f* (pentane/EtOAc = 2/1): 0.37; **ESI-MS:** calculated $[C_8H_8D_2O_3Na]^+$: 179.0651, found: 179.0648; calculated $[C_8H_7D_2O_3Na_2]^+$: 201.0467, found: 201.0487; **GC-MS, Rt (method A):** 8.0 min, **(EI) m/z (%):** 196.1 (31), 164.1 (24), 155.0 (19), 139.0 (11), 138.0 (66), 137.0 (18), 127.1 (17), 112.1 (38), 109.0 (11), 108.1 (11), 107.0 (10), 96.0 (10), 95.0 (100), 84.1 (16), 79.1 (13), 67.1 (52), 66.1 (10), 41.1 (19), 39.1 (19).

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[9] Coulter, M. M.; Dornan, P. K.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 6932.

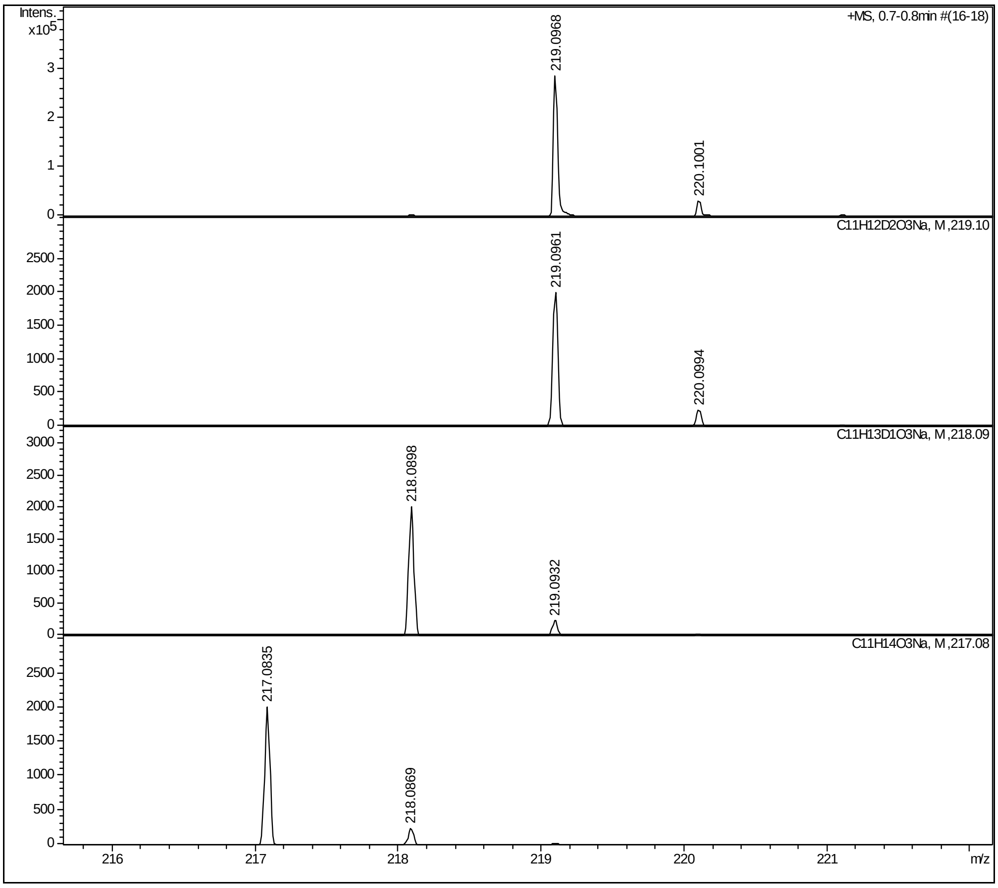
ESI-MS spectra of (2-allyloxy-3-methoxy-phenyl)-methanol-d_2

Experiment:

Simulation of $C_{11}H_{12}D_2O_3Na$:

Simulation of $C_{11}H_{13}DO_3Na$:

Simulation of $C_{11}H_{14}O_3Na$:



Measured:

#	m/z	Res.	S/N	I	FWHM
1	218.0908	7536	338.3	3013	0.0289
2	219.0968	7233	31999.4	285979	0.0303
3	220.1001	7557	3471.2	31146	0.0291
4	221.1016	7686	376.8	3396	0.0288

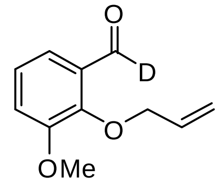
Determination of Deuteration Grade by ESI-MS:

Mono-deuterated product: calculated for $[C_{11}H_{13}DO_3Na]^+$: 218.0898, found: 218.0908 (intensity: 3013).

Deuterated product: calculated for $[C_{11}H_{12}D_2O_3Na]^+$: 219.0961, found: 219.0968 (intensity: 285979, corrected intensity (reduced by carbon-isotope signal of $C_8H_{10}O_3$):
285979 –3013 * 11.9% = 285620.453).

Deuteration grade: 285620.453 / (285620.453 + 3013) * 100 = 99.0%

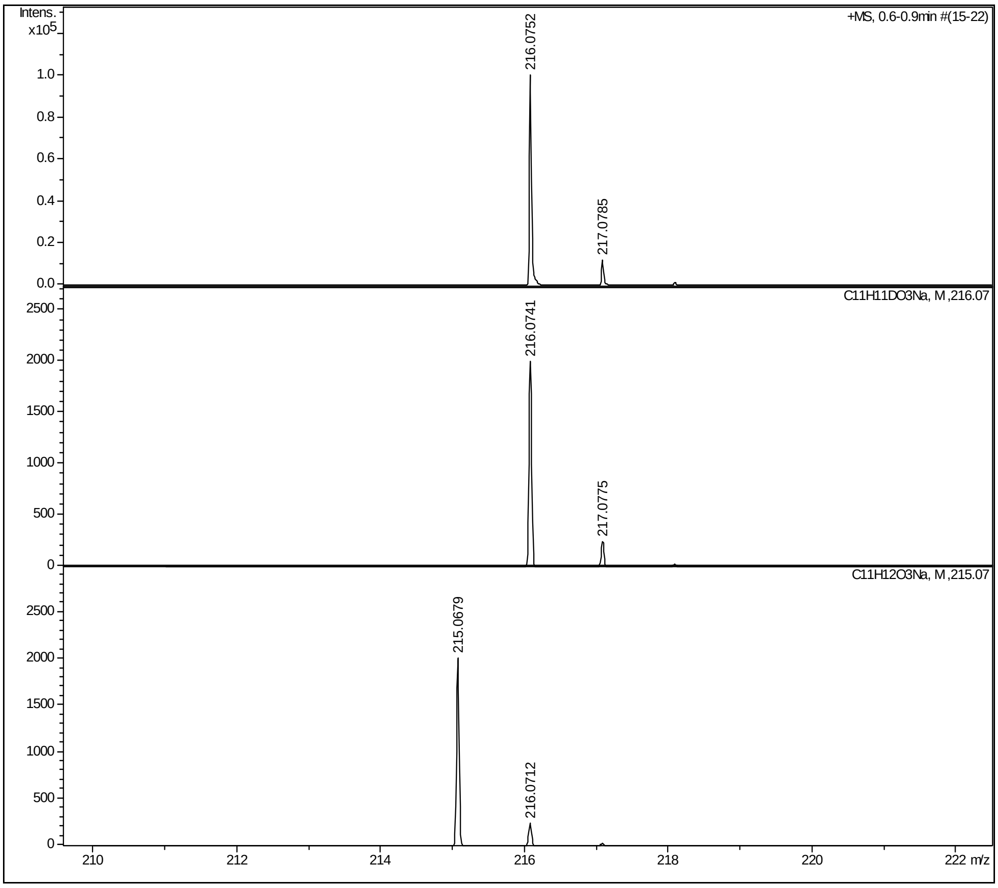
2-Allyloxy-3-methoxy-benzaldehyde-d$_1$ (d-1a)



Following a modified procedure by Dong et al.,[8] DMSO (3.24 mL, 45.56 mmol, 3.4 eq.) was added dropwise to a solution of oxalyl chloride (2.17 mL, 22.78 mmol, 1.7 eq.) in 80 mL CH_2Cl_2 at −78°C over a period of 15 min. The reaction mixture was stirred at −78°C for 1 h and a solution of (2-allyloxy-3-methoxy-phenyl)-methanol-d$_2$ (2.63 g, 13.4 mmol, 1.0 eq.) in 50 mL CH_2Cl_2 was added dropwise. The mixture was again stirred for 2 h at −78°C before Et_3N (9.31 mL, 67.0 mmol, 5.0 eq.) was added slowly over 10 min and the reaction was allowed to warm up to room temperature over night. After the addition of 1 M HCl (50 mL) the crude mixture was extracted with CH_2Cl_2 (3 x 50 mL) and washed with brine (2 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography (3 x 10 cm silica, PE/EtOAc = 30/1 → 10/1) afforded 1.965 g (10.17 mmol, 76%) of the pure product as a colorless liquid.

R$_f$ (pentane/EtOAc = 10/1): 0.32; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.42-7.39 (m, 1H, H$_{ar}$), 7.13-7.11 (m, 2H, H$_{ar}$), 6.12-5.99 (m, 1H, C*H*=CH$_2$), 5.38-5.36 (m, 1H, CH=C*H*$_2$), 5.27-5.23 (m, 1H, CH=C*H*$_2$), 4.65 (dt, *J* = 6.1 Hz, *J* = 1.3 Hz, 2H, CH$_2$), 3.89 (s, 3H, OCH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 56.1, 75.3, 118.0, 119.1, 124.3, 130.1, 133.2, 151.3, 153.1, 190.2; **^{2}H NMR (76.8 MHz, dioxane):** 10.32; **ESI-MS:** calculated $[C_{11}H_{11}DO_3Na]^+$: 216.0741, found: 216.0752; calculated $[C_{11}H_{11}DO_3NaCH_3OH]^+$: 248.1004, found: 248.1010; **GC-MS, Rt (method A):** 7.9 min, **(EI) m/z (%):** 193.1 (42), 176.1 (12), 163.1 (52), 152.0 (38), 150.0 (38), 137.0 (32), 131.0 (21), 122.0 (51), 109.0 (63), 107.0 (32), 94.0 (61), 81.0 (24), 77.0 (32), 68.1 (27), 66.0 (44), 53.0 (49), 42.1 (12), 41.1 (52); **ATR-FTIR (cm^{-1}):** 2943, 2841, 1673, 1586, 1481, 1456, 1314, 1265, 1219, 1188, 1091, 1032, 981, 889, 778, 632, 540, 508.

ESI-MS spectra of 2-allyloxy-3-methoxy-benzaldehyde-d$_1$



Experiment:

Simulation of $C_{11}H_{11}DO_3Na$:

Simulation of $C_{11}H_{12}O_3Na$:

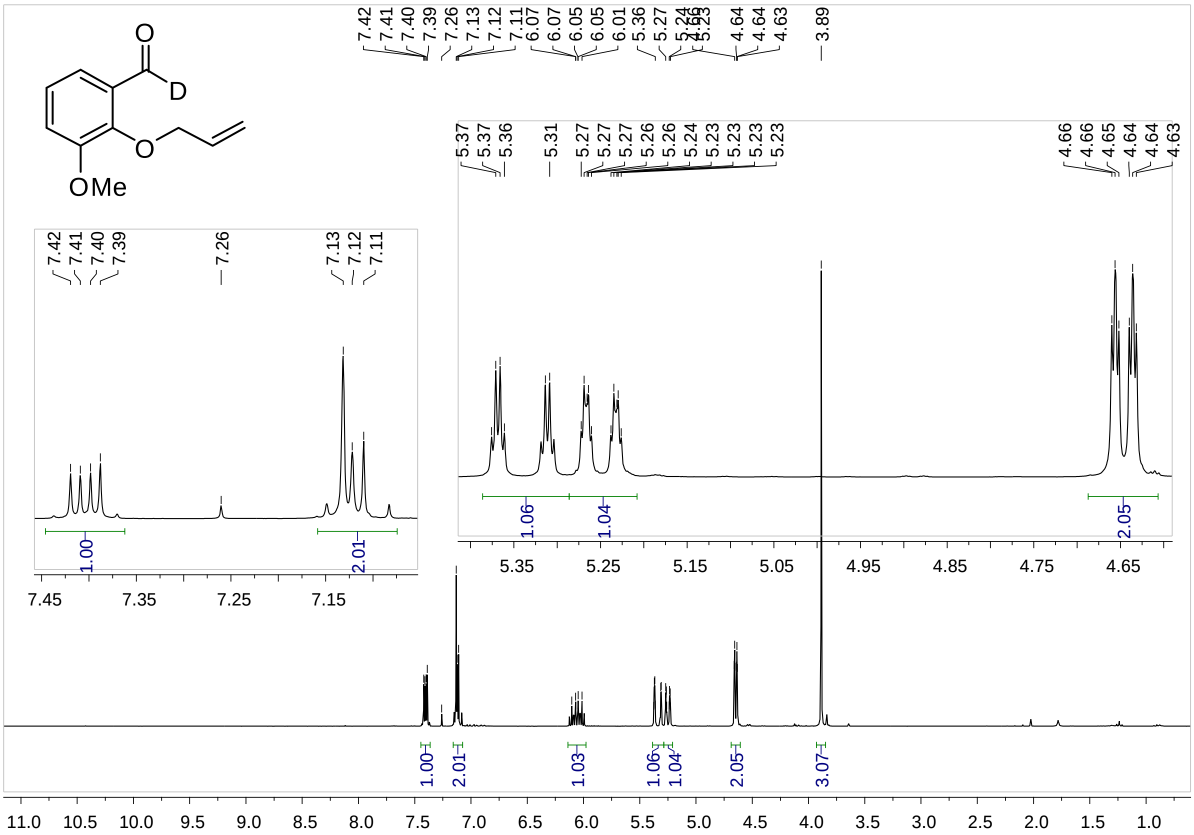
Measured:

#	m/z	Res.	S/N	I	FWHM
1	216.0752	7033	13770.4	100110	0.0307
2	217.0785	7168	1683.4	12328	0.0303

Determination of Deuteration Grade by ESI-MS:

Deuterated product: calculated for $[C_{11}H_{11}DO_3Na]^+$: 216.0741, found: 216.0752.

Deuteration grade: > 99% (non-deuterated species not observed in chromatogram)



O
D
O
OMe
7.42
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7.40
7.39
7.26
7.13
7.12
7.11
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6.05
6.05
6.01
5.36
5.27
5.24
5.23
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3.89
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5.37
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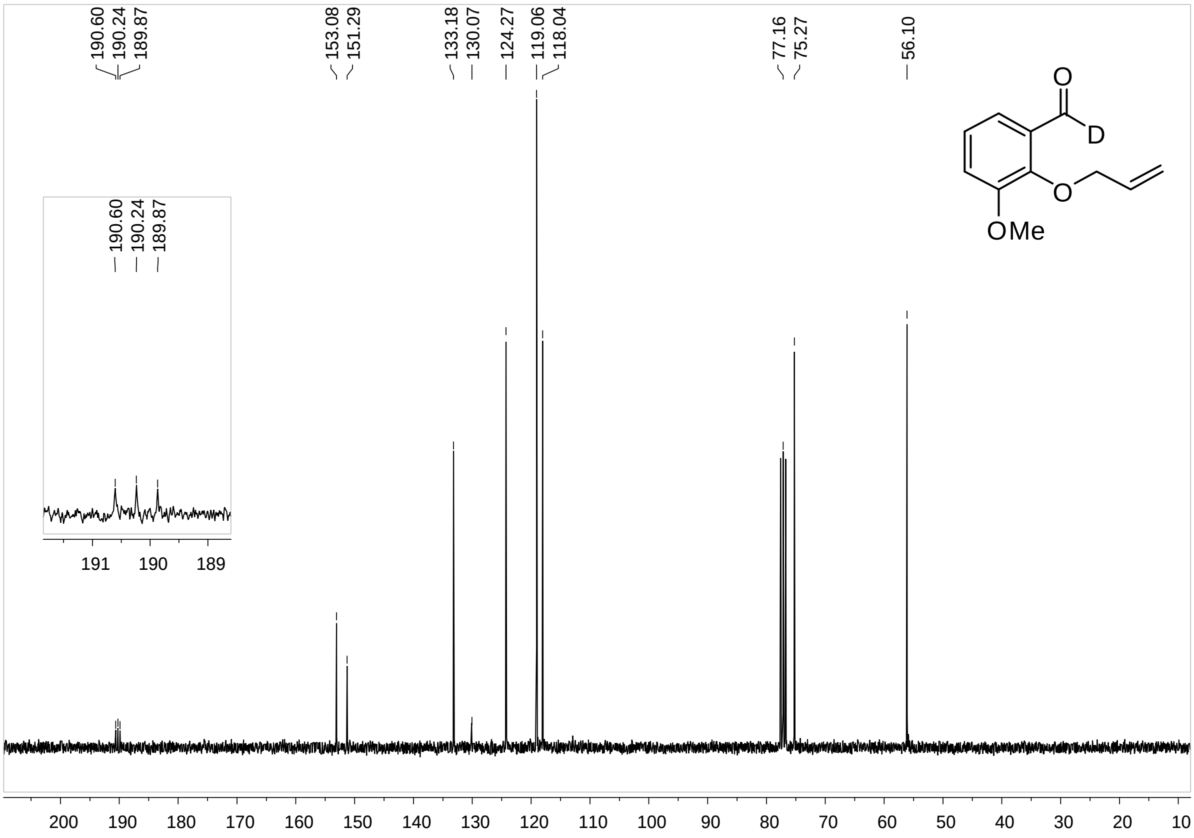

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190.24
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119.06
118.04
77.16
75.27
56.10
O
D
O
OMe
191
190
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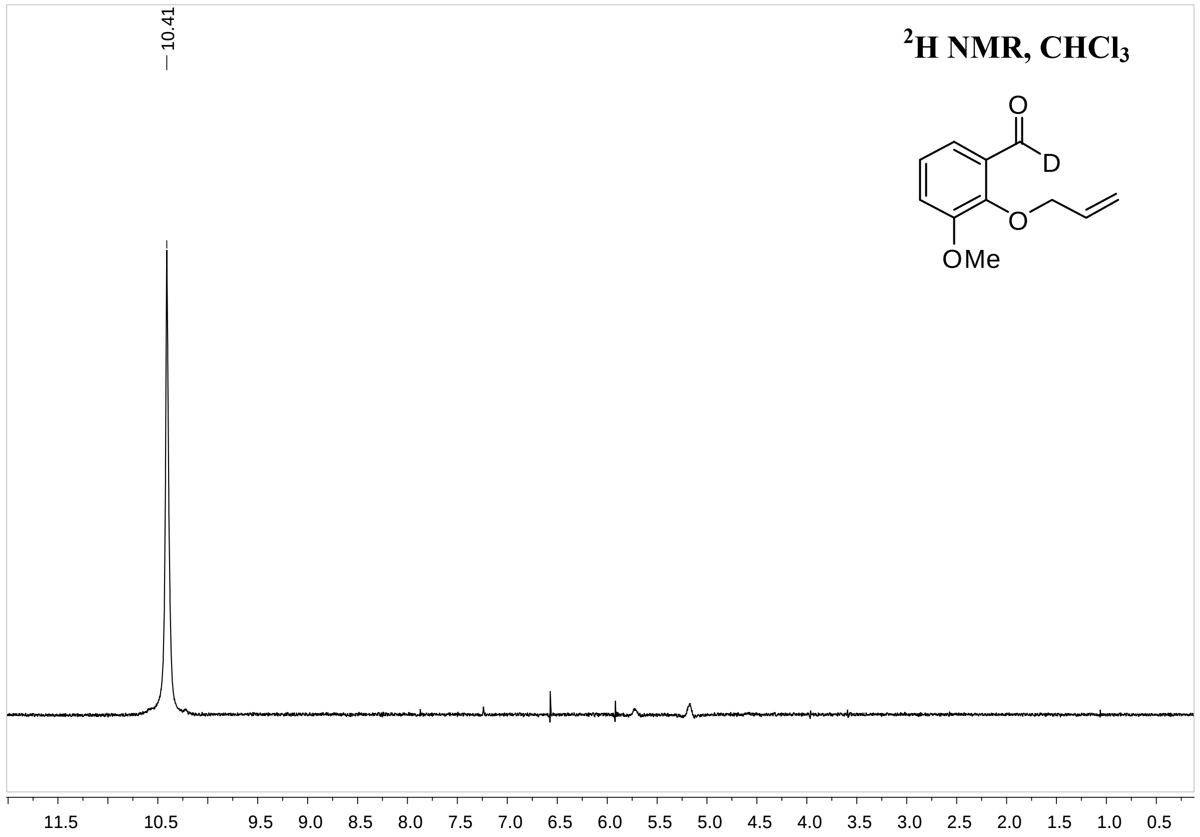
10.41
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D
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OMe
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10.5
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
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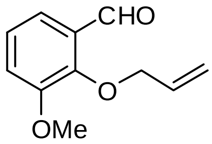
0.5

5 Substrates: Synthesis of Aldehydes

General Procedure for the Synthesis of 2-allyloxy Benzaldehyde Derivatives

Following a known procedure,[10] salicylaldehyde derivative (26.3 mmol, 1.0 eq.) was dissolved in DMF (15 mL) and kept stirring at room temperature. To this stirring solution was added potassium carbonate (28.92 mmol, 1.1 eq.) followed by the dropwise addition of allyl bromide (28.92 mmol, 1.1 eq.). The reaction mixture was then stirred for 15 h at room temperature. Water (50 mL) was then added and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to afford the 2-allyloxy benzaldehyde derivatives.

2-Allyloxy-3-methoxy benzaldehyde (1a)



Following the general procedure, treatment of 3-methoxy salicylaldehyde (4.0 g, 26.3 mmol, 1.0 eq.) with allyl bromide (2.43 mL, 28.92 mmol, 1.1 eq.) and potassium carbonate (3.99 g, 28.92 mmol, 1.1 eq.) in DMF (15 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-3-methoxy benzaldehyde as a colorless liquid (4.61 g, 91%).

R_f (pentane/EtOAc = 90/10): 0.32; **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 10.43 (s, 1H, CHO), 7.41 (dd, J = 6.1 Hz, 3.3 Hz, 1H, H_{ar}), 7.15-7.10 (m, 2H, H_{ar}), 6.14-5.99 (m, 1H, C*H*=CH_2), 5.35 (ddd, J = 17.2 Hz, 2.8 Hz, 1.3 Hz, 1H, CH=CH_2), 5.29-5.22 (m, 1H, CH=CH_2), 4.67-4.63 (m, 2H, OCH_2), 3.89 (s, 3H, OCH_3); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 190.59, 153.12, 151.31, 133.21, 130.24, 124.30, 119.10, 118.05, 75.31, 56.13; **ESI-MS**: calculated $[M+Na]^+$ for $C_{11}H_{12}O_3Na$: 215.0679, found: 215.0670; **ATR-FTIR (cm^{-1})**: 3083, 2942, 1692, 1584, 1482, 1443, 1390, 1311, 1266, 1251, 1216, 1185, 1067, 982.

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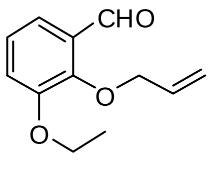
[10] (a) Claisen, L.; Eisleb, O. *Liebigs Ann.* **1913**, *401*, 21. (b) Black, M.; Cadogan, J. I. G.; McNab, H.; MacPherson, A. D.; Roddam, V. P.; Smith, C.; Swenson. H. R. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2483. (b) Bashiardes, G.; Safir, I.; Mohamed, A. S.; Barbot, F.; Laduranty, J. *Org. Lett.* **2003**, *5*, 4915.

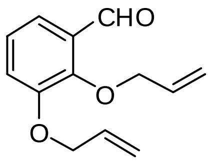
2-Allyloxy-3-ethoxy benzaldehyde (1b)



Following the general procedure, treatment of 3-ethoxy salicylaldehyde (2.0 g, 12.03 mmol, 1.0 eq.) with allyl bromide (1.12 mL, 13.24 mmol, 1.1 eq.) and potassium carbonate (1.83 g, 13.24 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-3-ethyl benzaldehyde as a colorless liquid (2.37 g, 95%).

R*f* (pentane/EtOAc = 95/5): 0.21; **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 10.42 (s, 1H, CHO), 7.37 (dd, *J* = 7.2 Hz, 2.3 Hz, 1H, H_{ar}), 7.13-7.03 (m, 2H, H_{ar}), 5.99-6.12 (m, 1H, C*H*=CH$_2$), 5.39-5.28 (m, 1H, CH=C*H*$_2$), 5.27-5.20 (m, 1H, CH=C*H*$_2$), 4.68-4.64 (m, 2H, OCH_{2allyl}), 4.07 (q, *J* = 7.0 Hz, 2H, OCH_{2ethyl}), 1.45 (t, *J* = 7.0 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 190.56, 152.32, 151.47, 133.32, 130.17, 124.12, 119.22, 118.73, 75.08, 64.61, 14.89. **ESI-MS**: calculated [M+Na]$^+$ for $C_{12}H_{14}O_3Na$: 229.0835, found: 229.0812; **ATR-FTIR (cm^{-1})**: 2981, 2870, 1686, 1583, 1472, 1391, 1310, 1248, 1210, 1084, 1059, 982, 933.

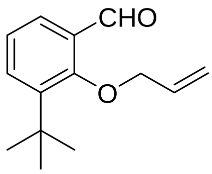
2,3-Diallyloxy benzaldehyde (1c)



Following the general procedure, treatment of 2,3-dihydroxy benzaldehyde (1.0 g, 7.24 mmol, 1.0 eq.) with allyl bromide (1.53 mL, 18.10 mmol, 2.5 eq.) and potassium carbonate (2.51 g, 18.10 mmol, 2.5 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2,3-diallyloxy benzaldehyde as a colorless liquid (1.16 g, 74%).

R*f* (pentane/EtOAc = 95/5): 0.21; **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 10.41 (s, 1H, CHO), 7.38 (dd, *J* = 7.5 Hz, 1.9 Hz, 1H, H_{ar}), 7.14-7.02 (m, 2H, H_{ar}), 6.13-5.96 (m, 2H, C*H*=CH2), 5.46-5.20 (m, 4H, CH=C*H*$_2$), 4.70-4.63 (m, 2H, OCH$_2$), 4.57 (dt, *J* = 5.2 Hz, 1.5 Hz, 2H, OCH$_2$); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 190.35, 151.93, 151.49, 133.18, 132.65, 130.24, 124.06, 119.67, 119.30, 118.89, 117.92, 75.10, 69.75; **ESI-MS**: calculated [M+Na]$^+$ for $C_{13}H_{14}O_3Na$: 241.0835, found: 241.0827; **ATR-FTIR (cm^{-1})**: 3080, 2867, 1685, 1583, 1480, 1248, 1210, 983, 931, 785.

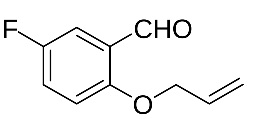
2-Allyloxy-3-*tert*-butyl benzaldehyde (1d)



Following the general procedure, treatment of 3-*tert*-butyl salicylaldehyde (1.0 g, 5.61 mmol, 1.0 eq.) with allyl bromide (0.52 mL, 6.17 mmol, 1.1 eq.) and potassium carbonate (0.653 g, 6.17 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-3-*tert*-butyl benzaldehyde as a colorless liquid (1.05 g, 86%).

R*f* (pentane/EtOAc = 95/5): 0.44; **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 10.29 (s, 1H, CHO), 7.71 (dd, *J* = 7.6 Hz, 1.8 Hz, 1H, H$_{ar}$), 7.59 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H, H$_{ar}$), 7.15 (td, *J* = 7.8 Hz, 0.6 Hz, 1H, H$_{ar}$), 6.18-6.02 (m, 1H, C*H*=CH$_2$), 5.53 (dq, *J* = 17.2 Hz, 1.7 Hz, 1H, CH=C*H*$_2$), 5.34 (dq, *J* = 10.6 Hz, 1.4 Hz, 1H, CH=C*H*$_2$), 4.50 (dt, *J* = 4.9 Hz, 1.6 Hz, 2H, OCH$_2$), 1.42 (s, 9H, C(CH$_3$)$_3$); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 190.59, 161.93, 143.95, 133.58, 132.73, 130.18, 127.66, 124.08, 117.65, 79.47, 35.25, 30.85; **ESI-MS**: calculated [M+Na]$^+$ for $C_{14}H_{18}O_2Na$: 241.1199, found: 241.1192; **ATR-FTIR (cm^{-1})**: 3081, 2961, 2871, 1686, 1650, 1583, 1471, 1432, 1371, 1287, 1252, 1216, 1181, 1139, 984.

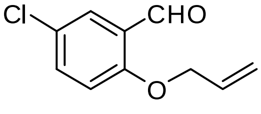
2-Allyloxy-5-fluoro benzaldehyde (1e)



Following the general procedure, treatment of 5-fluoro salicylaldehyde (1.0 g, 7.14 mmol, 1.0 eq.) with allyl bromide (0.67 mL, 7.85 mmol, 1.1 eq.) and potassium carbonate (1.10 g, 7.85 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-5-fluoro benzaldehyde as a colorless liquid (1.18 g, 92%).

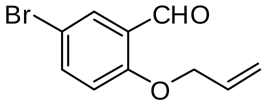
R*f* (pentane/EtOAc = 95/5): 0.24; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 10.43 (s, 1H, CHO), 7.50-7.40 (m, 1H, H$_{ar}$), 7.19 (dddd, *J* = 9.2 Hz, 7.6 Hz, 3.3 Hz, 1.7 Hz, 1H, H$_{ar}$), 6.92 (dd, *J* = 9.1 Hz, 3.9 Hz, 1H, H$_{ar}$), 6.13-5.92 (m, 1H, C*H*=CH2), 5.41 (ddd, *J* = 17.3 Hz, 2.8 Hz, 1.5 Hz, 1H, CH=C*H*$_2$), 5.31 (ddd, *J* = 10.5 Hz, 2.8 Hz, 1.4 Hz, 1H, CH=C*H*$_2$), 4.63-4.59 (m, 2H, OCH$_2$); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 188.65, 158.56, 157.27, 155.37, 132.23, 125.79, 122.63, 122.31, 118.34, 114.65, 114.06, 113.75, 69.86; **ESI-MS**: calculated [M+Na]$^+$ for $C_{10}H_9O_2FNa$: 203.0479, found: 203.0476; **ATR-FTIR (cm^{-1})**: 2870, 1683, 1612, 1487, 1457, 1428, 1396, 1262, 1232, 1200, 1147, 1089, 995, 966, 933.

2-Allyloxy-5-chloro benzaldehyde (1f)



Following the general procedure, treatment of 5-chloro salicylaldehyde (4 g, 25.55 mmol, 1.0 eq.) with allyl bromide (2.38 mL, 28.10 mmol, 1.1 eq.) and potassium carbonate (3.88 g, 28.10 mmol, 1.1 equiv) in DMF (15 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-5-chloro benzaldehyde as white solid (4.34 g, 86%). **R*f*** (pentane/EtOAc = 95/5): 0.30; **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 10.43 (s, 1H, CHO), 7.75 (d, *J* = 2.4 Hz, 1H, H$_{ar}$), 7.48-7.40 (m, 1H, H$_{ar}$), 6.92 (d, *J* = 8.9 Hz, 1H, H$_{ar}$), 6.12-5.96 (m, 1H, C*H*=CH$_2$), 5.43 (dd, *J* = 17.3 Hz, 1.2 Hz, 1H, CH=C*H*$_2$), 5.34 (dd, *J* = 10.5 Hz, 1.2, 1H, CH=C*H*$_2$), 4.63 (dd, *J* = 3.6 Hz, 1.5 Hz, 2H, OCH$_2$); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 188.49, 159.43, 135.41, 132.04, 127.98, 126.57, 125.96, 118.58, 114.63, 69.65; **ESI-MS:** calculated [M+Na]$^+$ for $C_{10}H_9ClO_2Na$: 219.0183, found: 219.0167; **ATR-FTIR (cm^{-1})**: 3081, 2932, 2872, 1683, 1596, 1479, 1414, 1394, 1272, 1236, 1182, 1130, 1102, 1062, 994, 936.

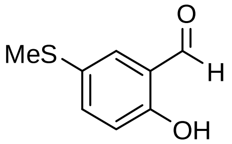
2-Allyloxy-5-bromo benzaldehyde (1g)



Following the general procedure, treatment of 5-bromo salicylaldehyde (4 g, 19.90 mmol, 1.0 eq.) with allyl bromide (1.85 mL, 21.89 mmol, 1.1 eq.) and potassium carbonate (3.03 g, 21.89 mmol, 1.1 eq.) in DMF (15 mL), followed by processing of the reaction mixture and flash column chromatography afforded the 2-allyloxy-5-bromo benzaldehyde as white solid (4.11 g, 86%).

R*f* (pentane/EtOAc = 95/5): 0.23; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.41 (s, 1H, CHO), 7.89 (d, *J* = 2.6 Hz, 1H, H$_{ar}$), 7.58 (dd, *J* = 8.9 Hz, 2.6 Hz, 1H, H$_{ar}$), 6.86 (d, *J* = 8.9 Hz, 1H, H$_{ar}$), 6.11-5.96 (m, 1H, C*H*=CH$_2$), 5.43 (ddd, *J* = 17.3 Hz, 3.0 Hz, 1.6 Hz, 1H, CH=C*H*$_2$), 5.34 (dq, *J* = 10.6 Hz, 1.4 Hz, 1H, CH=C*H*$_2$), 4.63 (dt, *J* = 5.2 Hz, 1.5 Hz, 2H, OCH$_2$); **^{13}C NMR (75 MHz, CDCl$_3$):** 188.36, 159.87, 138.27, 131.99, 131.01, 126.35, 118.61, 115.02, 113.70, 69.59. **ESI-MS**: calculated [M+Na]$^+$ for $C_{10}H_9BrO_2Na$: 262.9678, found: 262.9657. **ATR-FTIR (cm^{-1})**: 3079, 2871, 1682, 1591, 1476, 1392, 1272, 1239, 1181, 1125, 995, 932.

2-Hydroxy-5-methylsulfanyl-benzaldehyde[11]



Following a modified procedure by Skattebøl et al.,[12] 4-(methylthio)-phenol (2.80 g, 20 mmol, 1.0 eq.), anhydrous magnesium chloride (2.86 g, 30 mmol, 1.5 eq.), triethylamine (7.59 g, 10.42 mL, 75 mmol, 3.75 eq.) and paraformaldehyde (4.05 g, 135 mmol, 6.75 eq.) were suspended in 100 mL propionitrile. The reaction mixture was stirred at 100 °C for 5 h and the cooled to rt. The mixture was acidified with 1N aq. HCl until clear two phases were formed. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of volatiles the crude product was purified by column chromatography (5 x 14 cm silica, pentane/EtOAc = 19/1). The desired product was obtained in 71% yield (2.39 g, 14.21 mmol) as a yellow solid.

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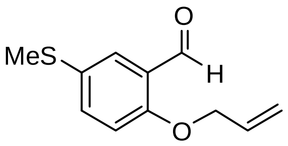
[11] For physical data, see: Ando, M.; Emoto, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2435.

[12] Hofsløkken, N. U.; Skattebøl, L. *Acta Chem. Scand.* **1999**, *53*, 258.

R*f* (pentan/EtOAc = 19/1): 0.28; **^{1}H NMR (400 MHz, CDCl$_3$):** 10.90 (s, 1H, OH), 9.86 (s, 1H, CHO), 7.53-7.46 (m, 2H, H$_{ar}$), 6.98-6.92 (m, 1H, H$_{ar}$), 2.47 (s, 3H, SCH$_3$); **^{13}C NMR (100 MHz, CDCl$_3$):** 196.1, 160.0, 137.8, 133.4, 128.6, 120.9, 118.5, 17.9; **ESI-MS:** calculated [$C_8H_8NaO_2S$]$^+$: 191.0137, found: 191.0130; **GC-MS, Rt (method B):** 7.47 min, **(EI) m/z (%):** 168 (100), 153 (45), 151 (2), 139 (4), 124 (2), 122 (5), 121 (2), 105 (1), 92 (2), 77 (2), 47 (1); **ATR-FTIR (cm^{-1}):** 2964, 2920, 2854, 1681, 1656, 1610, 1577, 1472, 1276, 1183, 1017, 906, 796, 632, 539.

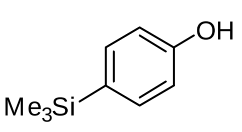
2-Allyloxy-5-methylsulfanyl-benzaldehyde (1h)



2-Hydroxy-5-methylsulfanyl-benzaldehyde (0.99 g, 5.87 mmol, 1.0 eq.) and K_2CO_3 (0.89 g, 6.46 mmol, 1.1 eq.) were suspended in 15 mL DMF and allyl bromide (0.78 mg, 562 µL, 6.46 mmol, 1.1 eq.) was added dropwise. The reaction mixture was stirred at rt for 4 h and then diluted with H_2O (20 mL) and MTBE (20 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 30 mL). The combined organic phases were washed with H_2O (3 x 30 mL) and brine, then dried over $MgSO_4$. After removal of volatiles the crude residue was purified by column chromatography (4 x 17 cm silica, pentane/ CH_2Cl_2 9:1). The desired product was obtained in 75% yield (922 mg, 4.43 mmol) as a yellow liquid.

R*f* (pentane/EtOAc = 9/1): 0.32; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.49 (s, 1H, CHO), 7.74 (d, *J* = 2.6 Hz, 1H, H$_{ar}$), 7.46 (dd, *J* = 8.7, 2.6 Hz, 1H, H$_{ar}$), 6.93 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 6.06 (ddt, *J* = 17.3, 10.5, 5.1 Hz, 1H, CH$_2$C*H*=CH$_2$), 5.44 (ddt, *J* = 17.3, 1.6, 1.4 Hz, 1H, CH$_2$CH=C*H*H), 5.34 (ddt, *J* = 10.5, 1.4, 1.4 Hz, 1H, CH$_2$CH=CH*H*), 4.64 (ddd, *J* = 10.5, 1.6, 1.4 Hz, 2H, C*H*$_2$CH=CH$_2$), 2.47 (s, 3 H, SCH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 189.1, 159.2, 135.4, 132.2, 130.3, 127.0, 125.4, 118.2, 113.8, 69.4, 17.0; **ESI-MS:** calculated [$C_{11}H_{12}NaO_2S$]$^+$: 231.0450, found: 231.0449; **GC-MS, Rt (method B):** 8.76 min, **(EI) m/z (%):** 208 (72), 193 (6), 181 (3), 179 (6), 167 (100), 151 (4), 138 (3), 132 (6), 122 (2), 107 (2), 91 (5), 77 (24); **ATR-FTIR (cm^{-1}):** 2984, 2921, 2865, 2759, 1682, 1593, 1571, 1482, 1392, 1276, 1239, 1186, 1135, 995, 907, 813, 679, 644, 635, 556, 538.

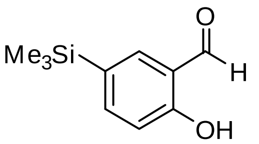
4-Trimethylsilanyl-phenol[13]



Following the procedure by Node et al.,[14] 4-bromophenol (3.46 g, 20 mmol, 1 eq.) was dissolved in 70 mL THF and the solution was cooled to –78 ˚C. *n*-BuLi (1.6 M in *n*-hexane, 28 mL, 44.8 mmol, 2.24 eq.) was slowly added to the solution over 15 min and the resulting mixture was stirred at the same temperature for 1.5 h. Trimethylsilylchloride (5.63 g, 6.62 mL, 51.8 mmol, 2.59 eq.) was then added slowly. The stirring was continued at –78 ˚C for 2 h and at ambient temperature for additional 12 h. The reaction was quenched with 1 N aq. HCl (30 mL) and stirred at rt for 1 h. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. After the volatiles were removed under reduced pressure, the crude product was purified by column chromatography (5 x 12 cm, silica, pentane/EtOAc = 19/1). The desired product was obtained in 90% yield (2.98 g, 17.9 mmol) as a white solid.

R_f (pentane/EtOAc = 19/1): 0.14; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.45-7.40 (m, 2H, H_{ar}), 6.88-6.83 (m, 2H, H_{ar}), 5.02 (s, 1H, OH), 0.26 (s, 9H, $Si(CH_3)_3$); **^{13}C NMR (100 MHz, $CDCl_3$):** 156.1, 135.0, 131.7, 114.9, −0.97; **ESI-MS:** calculated $[C_9H_{13}OSi]^-$: 165.0730, found: 165.0755; **GC-MS, Rt (method B):** 6.93 min, **(EI) m/z (%):** 166 (13), 151 (100), 121 (3), 77 (4), 73 (1); **ATR-FTIR (cm^{-1}):** 3144, 2956, 1599, 1584, 1502, 1421, 1361, 1284, 1251, 1235, 1181, 1107, 839, 813, 754, 711, 694, 651, 600, 516.

2-Hydroxy-5-trimethylsilanyl-benzaldehyde



Following the modified procedure by Skattebøl et al.,[12] 4-trimethylsilanyl-phenol (2.50 g, 15 mmol, 1 eq.) was dissolved in 75 mL propionitrile and anhydrous Magnesium chloride (2.14 g, 22.5 mmol, 1.5 eq.), triethylamine (5.70 g, 7.30 mL, 56.3 mmol, 3.75 eq.) and paraformaldehyd (2.97 g, 98.9 mmol, 6.59 eq.) were added. The resulting reaction mixture was stirred at 100 ˚C for 5 h. After cooling to ambient temperature the suspension was diluted with MTBE (100 mL) and acidified with 1 N aq. HCl, till clear two phases were formed. The phases were separated and the aqueous phase was extracted with MTBE (3 x 100 mL) and the combined organic phases were washed with brine and dried over $MgSO_4$. After removal of volatiles the residue was purified by column chromatography (4 x 15 cm silica, pentane/EtOAc = 19/1). The desired product was obtained in 85% yield (2.47 g, 12.7 mmol) as a yellowish liquid.

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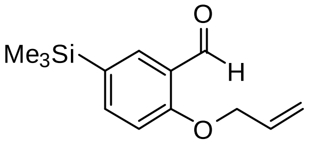
[13] For physical data, see: McNeill, E.; Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2007**, 9, 3785.

[14] Nishide, K.; Ohsugi, S.; Miyamoto, T.; Kumar, K.; Node, M. *Monatshefte Chemie* **2004**, *135*, 189.

R*f* (pentane/EtOAc = 19/1): 0.43; **^{1}H NMR (300 MHz, $CDCl_3$):** 11.06 (s, 1H, OH), 9.92 (d, *J* = 0.5 Hz, 1H, CHO), 7.69-7.63 (m, 2H, H_{ar}), 7.02-6.96 (m, 1H, H_{ar}), 0.28 (s, 9H, $Si(CH_3)_3$); **^{13}C NMR (75 MHz, $CDCl_3$):** 197.0, 162.2, 141.7, 139.2, 131.1, 120.5, 117.1, –1.1; **ESI-MS:** calculated $[C_{10}H_{14}NaO_2Si]^+$: 217.0655, found: 217.0657; **GC-MS, Rt (method B):** 7.39 min, **(EI) m/z (%):** 194 (17), 180 (20), 179 (100), 177 (5), 165 (1), 164 (2), 150 (1), 149 (5), 135 (3), 121 (1), 105 (2), 91 (4), 77 (4), 73 (2); **ATR-FTIR (cm^{-1}):** 2956, 2896, 2843, 1686, 1655, 1609, 1579, 1479, 1411, 1367, 1285, 1250, 1234, 1188, 1099, 913, 831, 759, 717, 632, 543, 507.

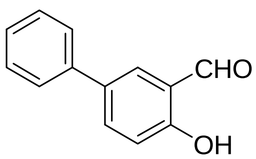
2-Allyloxy-5-trimethylsilanyl-benzaldehyde (1i)



2-Hydroxy-5-trimethylsilanyl-benzaldehyde (1.94 g, 10 mmol, 1.0 eq.) and K_2CO_3 (1.52 g, 11 mmol, 1.1 eq.) were suspended in 20 mL DMF and allyl bromide (1.33 g, 957 µL, 11 mmol, 1.1 eq.) was added dropwise. The resulting reaction mixture was stirred at rt for 13 h and then diluted with H_2O (30 mL) und MTBE (30 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 50 mL). The combined organic phases were washed with H_2O (3 x 50 mL) and brine, and dried over $MgSO_4$. After removal of volatiles under reduced pressure, the crude product was purified by column chromatography (4.5 x 32 cm silica, pentane/EtOAc = 200/1 → 100:1). The desired product was obtained in 92% yield (2.16 g, 9.22 mmol) as a colorless liquid.

R*f* (pentan/EtOAc = 19/1): 0.36; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.55 (s, 1H, CHO), 7.98 (d, *J* = 1.8 Hz, 1H, H_{ar}), 7.67 (dd, *J* = 8.3, 1.8 Hz, 1H, H_{ar}), 6.97 (d, *J* = 8.3 Hz, 1H, H_{ar}), 6.08 (ddt, *J* = 17.3, 10.5, 5.1 Hz, 1H, $CH_2CH{=}CH_2$), 5.50-5.41 (m, 1H, $CH_2CH{=}CHH$), 5.37-5.30 (m, 1H, $CH_2CH{=}CHH$), 4.70-4.64 (m, 2H, $CH_2CH{=}CH_2$), 0.26 (s, 9H, $Si(CH_3)_3$); **^{13}C NMR (75 MHz, $CDCl_3$):** 190.1, 161.5, 140.9, 133.6, 132.4, 132.0, 124.4, 118.1, 112.3, 69.0, −1.1; **ESI-MS:** calculated $[C_{13}H_{18}NaO_2Si]^+$: 257.0968, found: 257.0969; **GC-MS, Rt (method B):** 8.42 min, **(EI) m/z (%):** 234 (12), 220 (19), 219 (100), 205 (1), 204 (1), 193 (8), 190 (1), 189 (1), 177 (19), 164 (1), 161 (2), 148 (1), 147 (2), 135 (11), 120 (1), 105 (3), 91 (6), 73 (12), 41 (9); **ATR-FTIR (cm^{-1}):** 3016, 2955, 2899, 2861, 2361, 2339, 1683, 1591, 1567, 1489, 1457, 1400, 1387, 1291, 1264, 1249, 1194, 1144, 1093, 1014, 995, 912, 839, 633, 550, 544, 535.

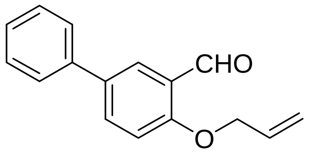
5-Phenyl salicylaldehyde



Following a modified literature procedure,[15] a mixture of 5-bromo salicylaldehyde (1.0 g, 4.97 mmol), phenyl boronic acid (0.607 g, 4.97 mmol), sodium carbonate (0.567 g, 4.97 mmol), $PdCl_2$ (9.0 mg, 0.249 mmol) and dppf (137.7 mg, 0.249 mmol) were stirred in DME : H_2O (3:1 v:v, 10 mL, degassed with Ar) and stirred at 100 °C for 4 h. After cooling to rt, the reaction contents were poured into H_2O (50 mL). The aqueous mixture was extracted with CH_2Cl_2 (3 × 25 mL) and the combined extracts were dried over Na_2SO_4 before being concentrated under reduced pressure. The crude aldehyde was purified by flash chromatography on silica gel to afford a yellow solid (0.637 g, 65%).

R*f* (pentane/EtOAc = 95/5): 0.39; **^{1}H NMR (300 MHz, $CDCl_3$):** 11.02 (s, 1H, CHO), 9.98 (s, 1H, ArOH), 7.80-7.75 (m, 2H, H_{ar}), 7.59-7.53 (m, 2H, H_{ar}), 7.50-7.42 (m, 2H, H_{ar}), 7.38 (dt, *J* = 9.5 Hz, 4.3 Hz, 1H, H_{ar}), 7.09 (d, *J* = 9.2 Hz, 1H, H_{ar}); **^{13}C NMR (75 MHz, $CDCl_3$):** 196.82, 161.10, 139.46, 135.89, 133.45, 132.01, 129.13, 127.54, 126.73, 120.84, 118.27; **ESI-MS:** calculated $[M+Na]^+$ for $C_{13}H_{10}O_2Na$: 221.0573, found: 221.0573; **ATR-FTIR (cm^{-1}):** 3041, 2853, 1680, 1650, 1623, 1587, 1511, 1472, 1375, 1298, 1259, 1234, 1177, 1155, 1135, 1079, 1042, 1000.

2-Allyloxy-5-phenyl benzaldehyde (1j)



Following the general procedure, treatment of 5-phenyl salicylaldehyde (0.50 g, 2.52 mmol, 1.0 eq.) with allyl bromide (0.24 mL, 2.78 mmol, 1.1 eq.) and potassium carbonate (0.384 g, 2.78 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-5-phenyl benzaldehyde as white solid (0.458 g, 76%).

R*f* (pentane/EtOAc = 95/5): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.59 (s, 1H, CHO), 8.09 (d, *J* = 2.5 Hz, 1H, H_{ar}), 7.78 (dd, *J* = 8.7 Hz, 2.5 Hz, 1H, H_{ar}), 7.58 (dd, *J* = 5.2 Hz, 3.3 Hz, 2H, H_{ar}), 7.48-7.40 (m, 2H, H_{ar}), 7.35 (dt, *J* = 9.5 Hz, 4.3 Hz, 1H, H_{ar}), 7.06 (d, *J* = 8.7 Hz, 1H, H_{ar}), 6.11 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.1 Hz, 1H, C*H*=CH2), 5.48 (dd, *J* = 17.3 Hz, 1.4 Hz, 1H, CH=C*H*$_2$), 5.37 (dd, *J* = 10.6 Hz, 1.3 Hz, 1H, CH=C*H*$_2$), 4.76-4.67 (m, 2H, OCH_2); **^{13}C NMR (75 MHz, $CDCl_3$):** 189.85, 160.48, 139.58, 134.36, 134.08, 132.46, 129.00, 127.45, 126.82, 125.26, 118.36, 113.48, 69.49; **ESI-MS:** calculated $[M+Na]^+$ for $C_{16}H_{14}O_2Na$:

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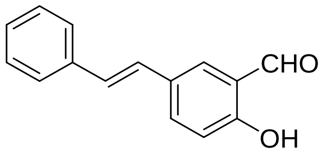
[15] Morris, G. A.; Nguyen, S. T. *Tetrahedron Lett.* **2001**, *42*, 2093.

261.0886, found: 261.0877; **ATR-FTIR (cm^{-1}):** 3035, 2863, 1681, 1606, 1510, 1480, 1450, 1426, 1391, 1371, 1309, 1266, 1237, 1183, 1121, 1049, 992, 923.

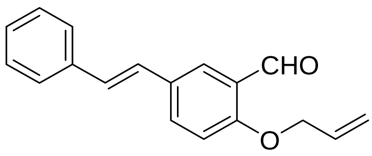
2-Hydroxy-5-(2-phenylvinyl) benzaldehyde



Following a modified procedure,[16] a mixture of 5-bromosalicylaldehyde (1.0 g, 4.97 mmol), styrene (1.14 mL, 9.95 mmol), palladium acetate (0.112 g, 0.497 mmol), tri-*o*-tolylphosphine (0.306 g, 0.994 mmol) and triethylamine (3 mL) in acetonitrile (50 ml) was heated to reflux for 6 h. The reaction mixture was concentrated under reduced pressure and then purified by flash column chromatography to afford 2-hydroxy-5-(2-phenylvinyl) benzaldehyde as a yellow solid (0.592 g, 53%).

R*f* (pentane/EtOAc = 95/5): 0.30; **^{1}H NMR (300 MHz, CDCl$_3$):** 11.03 (s, 1H, CHO), 9.94 (s, 1H, ArOH), 7.75-7.64 (m, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32-7.26 (m, 1H), 7.08-6.98 (m, 3H); **^{13}C NMR (75 MHz, CDCl$_3$):** 196.73, 161.19, 137.08, 134.76, 131.67, 129.82, 128.89, 128.21, 127.89, 126.60, 120.69, 118.23; **ESI-MS:** calculated $[M+Na]^+$ for $C_{15}H_{12}O_2Na$: 247.0730, found: 247.0723; **ATR-FTIR (cm^{-1}):** 3023, 2853, 1654, 1615, 1586, 1481, 1449, 1411, 1376, 1341, 1310, 1285, 1270, 1234, 1208, 1193, 1149, 1074, 1029, 964, 893.

2-Allyloxy -5-(2-phenylvinyl) benzaldehyde (2k)



Following the general procedure, treatment of 2-hydroxy-5-(2-phenylvinyl) benzaldehyde (0.460 g, 2.05 mmol, 1.0 eq.) with allyl bromide (0.19 mL, 2.26 mmol, 1.1 eq.) and potassium carbonate (0.312 g, 2.78 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-5-(2-phenylvinyl)benzaldehyde as a white solid (0.451 g, 83%).

R*f* (pentane/EtOAc = 95/5): 0.21; **^{1}H NMR (400 MHz, CDCl$_3$):** 10.56 (s, 1H, CHO), 8.01 (d, *J* = 2.4 Hz, 1H, H$_{ar}$), 7.66 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H, H$_{ar}$), 7.52-7.49 (m, 2H, H$_{ar}$), 7.38 (dd, *J* = 10.3 Hz, 4.8 Hz, 2H, H$_{ar}$), 7.30-7.24 (m, 1H, H$_{ar}$), 7.06 (s, 2H, CH=CH), 6.98 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 6.10 (ddt, *J* = 17.2 Hz, 10.5 Hz, 5.1 Hz, 1H, C*H*=CH$_2$), 5.48 (dd, *J* = 17.3 Hz, 1.4 Hz, 1H, CH=C*H*$_2$), 5.37 (dd, *J* = 10.6 Hz, 1.3 Hz, 1H, CH=C*H*$_2$), 4.68 (d, *J* = 5.1 Hz, 2H,

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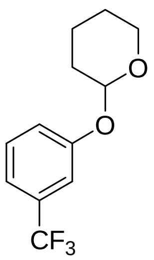
[16] Lee, S. H.; Cho, Y. J.; Bae, J. W.; Yoon, C. M. *Synth. Commun.* **2000**, *30*, 1003-1008.

OCH_2); **^{13}C NMR (100 MHz, $CDCl_3$):** 189.75, 160.41, 137.17, 133.83, 132.38, 130.49, 128.81, 128.45, 127.76, 126.92, 126.52, 126.04, 125.11, 118.30, 113.29, 69.42; **ESI-MS:** calculated $[M+Na]^+$ for $C_{18}H_{16}O_2Na$: 287.1043, found: 287.1051; **ATR-FTIR (cm^{-1}):** 2865, 1678, 1595, 1572, 1497, 1448, 1420, 1384, 1294, 1256, 1204, 1171, 1112, 1009, 991, 967, 929, 857.

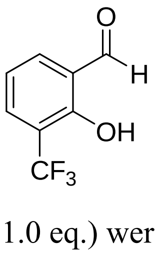
2-[(4-Trifluoromethyl)phenoxy]tetrahydro-*2H*-pyrane



Following a procedure by Schäfer and Geneste,[17] 10 g 3-trifluoromethylphenol (61.69 mmol, 1.0 eq.) were added dropwise to a solution of 14.1 mL dihydropyrane (154.23 mmol, 2.5 eq.) and 1 mL of HCl in 1,4-dioxane (4 M) in 30 mL DCM at room temperature. After stirring overnight the reaction mixture was extracted with saturated aq. $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and the residual solvent was evaporated under reduced pressure to afford 14.295 g (58.06 mmol, 94%) of the crude product as a light yellow liquid, which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.21 (m, 4H, H_{ar}), 5.46 (t, J = 3.1 Hz, 1H, THP), 3.92-3.84 (m, 1H, THP), 3.66-3.60 (m, 1H, THP), 2.08-1.57 (m, 6H, THP); **^{13}C NMR (100 MHz, $CDCl_3$):** 157.3 ($C_{ar}O$), 131.8 (q, $J_{(C,F)}$ = 32.3 Hz, $C_{ar}CF_3$), 129.9 (CH_{ar}), 124.1 (q, $J_{(C,F)}$ = 271.7 Hz, CF_3), 119.8 (CH_{ar}), 118.3 (q, $J_{(C,F)}$ = 3.9 Hz, CH_{ar}), 113.6 (q, $J_{(C,F)}$ = 3.9 Hz, CH_{ar}), 96.6 (THP), 62.1 (THP), 30.3 (THP), 25.2 (THP), 18.7 (THP); **GC-MS, Rt (method A):** 7.5 min, **(EI) m/z (%):** 162.0 (34), 143.0 (22), 85.1 (100), 67.1 (21), 57.1 (21), 55.1 (21), 43.1 (14), 41.1 (19).

2-Hydroxy-5-(trifluoromethyl)-benzaldehyde



Again following a procedure by Schäfer[17] 13.7 mL TMEDA (91 mmol, 1.4 eq.) were dissolved in 300 mL THF and cooled to −10 °C. 56.9 mL *n*-BuLi in *n*-hexane (1.6 M, 91 mmol, 1.4 eq.) were added dropwise over a period of 30 min at −10 °C. 16 g 2-[(4-trifluoromethyl)phenoxy]tetrahydro-*2H*-pyrane (65 mmol, 1.0 eq.) were added dropwise at −10 °C and the reaction mixture was stirred at −10 °C for 2 h. 7.03 mL DMF (91 mmol, 1.4 eq.) were added dropwise and the mixture was again stirred for 15 min. The crude mixture was added to a solution of half-concentrated aq. HCl at max. 45 °C and stirred overnight. After extraction with CH_2Cl_2 (5 x 40 mL), the combined organic layers

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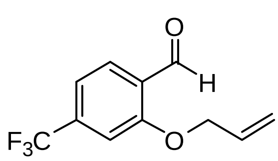
[17] Geneste, H.; Schäfer, B. *Synthesis* **2001**, 2259.

were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by flash column chromatography on silica (5 x 22 cm silica, PE/EE = 100/1 → 100/5) afforded 6.907 g of the pure product as a light yellow liquid (36.33 mmol, 56%).

R*f* (pentane/EtOAc = 100/1): 0.26; **^{1}H NMR (400 MHz, $CDCl_3$):** 10.96 (s, 1H), 9.87 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.16-7.12 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** 196.3 (CHO), 161.5 (C_{ar}-OH), 137.8 (q, $J_{(C,F)}$ = 32.8 Hz, C_{ar}-CF_3), 134.4 (CH_{ar}), 123.1 (q, $J_{(C,F)}$ = 272.4 Hz, CF_3), 116.3 (q, $J_{(C,F)}$ = 3.7 Hz, CH_{ar}), 115.3 (q, $J_{(C,F)}$ = 3.7 Hz, CH_{ar}); **ESI-MS:** calculated $[C_8H_4F_3O_2]^-$: 189.0169, found : 189.0174; **GC-MS, Rt (method A):** 5.9 min, **(EI) m/z (%):** 190.0 (98), 189.0 (100), 172.0 (24), 171.0 (13), 161.0 (31), 144.0 (27), 113.0 (13), 63.1 (13).

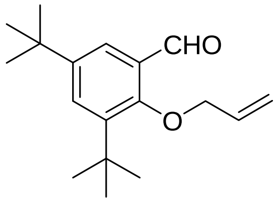
2-Allyloxy-4-trifluoromethyl-benzaldehyde (1l)



Following the general procedure, 1.90 g 4-trifluoromethyl salicylaldehyde (10.0 mmol, 1.0 eq.) were dissolved in DMF (20 mL) and kept stirring at rt. To the stirred solution was added 1.52 g potassium carbonate (11.0 mmol, 1.1 eq.) followed by the dropwise addition of 0.96 mL allyl bromide (11.0 mmol, 1.1 eq.). The reaction mixture was then stirred for 15 h. Water (50 mL) was then added and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography on silica (3 x 10 cm silica, PE/EE = 100/2) to afford the the pure product as a white solid (1.933 g, 8.40 mmol, 84%).

R*f* (pentane/EtOAc = 20/1): 0.48; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.59 (s, 1H, CHO), 7.87 (d, *J* = 8.1 Hz, 1H, H_{ar}), 7.33 (d, *J* = 8.3 Hz, 1H, H_{ar}), 6.19-6.07 (m, $1H_{ar}$), 5.56-5.49 (m, 1H, CH=C*H*$_2$), 5.45-5.41 (m, 1H, CH=C*H*$_2$), 4.77 (dt, *J* = 5.3 Hz, *J* = 1.4 Hz, 2H, OCH_2); **^{13}C NMR (75 MHz, $CDCl_3$):** 188.9 (CHO), 160.8 (C_{ar}), 136.8 (q, $J_{(C,F)}$ = 32.4 Hz, $C_{ar}CF_3$), 131.7 (CH_{ar}), 129.3 (CH_{ar}), 127.3 (C_{ar}), 123.4 (d, $J_{(C,F)}$ = 260.8 Hz, CF_3), 119.0 (CH=C*H*$_2$), 117.7 (q, $J_{(C,F)}$ = 3.9 Hz, CH_{ar}), 110.1 (q, $J_{(C,F)}$ = 3.9 Hz, CH_{ar}), 69.7 (OCH_2); **^{19}F NMR (282.2 MHz, $CDCl_3$):** 63.46; **ESI-MS:** calculated $[C_{11}H_9F_3O_2Na]^+$: 253.0447, found: 253.0434; calculated $[C_{11}H_9F_3O_2CH_3OHNa]^+$: 285.0709, found: 285.0699; **GC-MS (method A), Rt:** 7.1 min, **(EI) m/z (%):** 230.1 (11), 202.0 (12), 201.1 (21), 189.0 (69), 188.0 (69), 161.0 (21), 160.0 (19), 113.0 (15), 63.1 (14), 41.1 (100), 39.1 (28); **ATR-FTIR (cm^{-1}):** 3106, 3083, 3062, 3031, 3005, 2922, 2871, 1685, 1619, 1587, 1501, 1433, 1390, 1325, 1242, 1916, 1166, 1120, 1075, 999, 938, 909, 880, 826, 748, 726, 664, 628, 556.

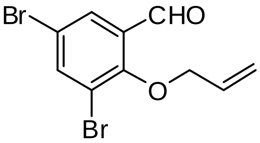
2-Allyloxy-3,5-di-*tert*-butyl benzaldehyde (1m)



Following the general procedure, treatment of 3,5-di-*tert*-butyl salicylaldehyde (1.0 g, 4.27 mmol, 1.0 eq.) with allyl bromide (0.40 mL, 4.7 mmol, 1.1 eq.) and potassium carbonate (0.650 g, 4.7 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-3-*tert*-butyl benzaldehyde as a white solid (0.963 g, 82%).

R*f* (pentane/EtOAc = 95/5): 0.61; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.29 (s, 1H, CHO), 7.71 (d, *J* = 2.6 Hz, 1H, H$_{ar}$), 7.63 (d, *J* = 2.6 Hz, 1H, H$_{ar}$), 6.20-6.00 (m, 1H, C*H*=CH$_2$), 5.54 (dt, *J* = 15.5 Hz, 1.7 Hz, 1H, CH=C*H*$_2$), 5.38-5.29 (m, 1H, CH=C*H*$_2$), 4.48 (dt, *J* = 4.9 Hz, 1.6 Hz, 2H, OCH$_2$), 1.43 (s, 9H, C(CH$_3$)$_3$), 1.32 (s, 9H, C(CH$_3$)$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 191.04, 159.89, 146.59, 143.13, 132.92, 130.98, 129.41, 123.95, 117.55, 79.44, 35.45, 34.83, 31.44, 30.96; **ESI-MS:** calculated [M+Na]$^+$ for $C_{18}H_{26}O_2Na$: 297.1825, found: 297.1835; **ATR-FTIR (cm^{-1}):** 2964, 2868, 1679, 1648, 1594, 1444, 1391, 1363, 1265, 1239, 1220, 1204, 1165, 1116, 1098, 982, 925.

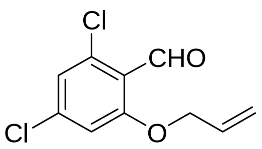
2-Allyloxy-3,5-dibromo benzaldehyde (1n)



Following the general procedure, treatment of 3,5-dibromo salicylaldehyde (2.0 g, 7.15 mmol, 1.0 eq.) with allyl bromide (0.67 mL, 7.86 mmol, 1.1 eq.) and potassium carbonate (1.09 g, 7.86 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-3,5-dibromo benzaldehyde as a white solid (2.01 g, 88%).

R*f* (pentane/EtOAc = 95/5): 0.38; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.24 (s, 1H, CHO), 7.93 (d, *J* = 2.4 Hz, 1H, H$_{ar}$), 7.89 (d, *J* = 2.3 Hz, 1H, H$_{ar}$), 6.16-6.01 (m, 1H, C*H*=CH$_2$), 5.37 (ddd, *J* = 13.7 Hz, 11.2 Hz, 1.1 Hz, 2H, CH=C*H*$_2$), 4.59 (d, *J* = 6.1 Hz, 2H, OCH$_2$); **^{13}C NMR (75 MHz, CDCl$_3$):** 188.05, 157.90, 141.44, 132.11, 131.75, 130.51, 120.50, 119.60, 118.30, 76.74; **ESI-MS:** calculated [M+Na]$^+$ for $C_{10}H_8Br_2O_2Na$: 342.8763, found: 342.8772; **ATR-FTIR (cm^{-1}):** 3070, 2947, 1686, 1572, 1446, 1439, 1421, 1396, 1360, 1227, 1216, 1145, 1088, 981, 955.

2-Allyloxy-4,6-dichloro benzaldehyde (1o)



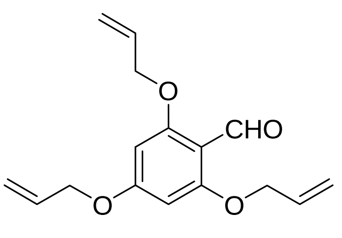
Following the general procedure, treatment of 4,6-dichloro salicylaldehyde (1.0 g, 5.24 mmol, 1.0 eq.) with allyl bromide (0.049 mL, 5.76 mmol, 1.1 eq.) and potassium carbonate (0.796 g, 5.76 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-4,6-dichloro benzaldehyde as a white solid (1.065 g, 88%).

R$_f$ (pentane/EtOAc = 95/5): 0.32; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.45 (s, 1H, CHO), 7.04 (d, *J* = 1.7 Hz, 1H, H$_{ar}$), 6.88 (d, *J* = 1.8 Hz, 1H, H$_{ar}$), 6.01 (ddd, *J* = 20.7 Hz, 10.5 Hz, 5.2 Hz, 1H, C*H*=CH$_2$), 5.47 (ddd, *J* = 17.3 Hz, 2.9 Hz, 1.6 Hz, 1H, CH=C*H*$_2$), 5.35 (ddd, *J* = 10.6 Hz, 2.7 Hz, 1.4 Hz, 1H, CH=C*H*$_2$), 4.62 (dt, *J* = 5.0 Hz, 1.5 Hz, 2H, OCH$_2$); **^{13}C NMR (75 MHz, CDCl$_3$):** 187.99, 161.46, 140.34, 137.16, 131.37, 123.44, 121.12, 118.93, 112.45, 70.17; **ESI-MS**: calculated [M+Na]$^+$ for $C_{10}H_8Cl_2O_2Na$: 252.9795, found: 252.9795; **ATR-FTIR (cm^{-1}):** 3086, 3027, 2993, 2890, 2797, 1686, 1578, 1557, 1458, 1409, 1385, 1365, 1286, 1251, 1206, 1176, 1157, 1094, 1013, 994, 976, 930, 915, 871, 961, 840, 747, 712, 671, 641, 619, 589, 551.

2,4,6-Triallyloxy benzaldehyde (1p) and 3-allyl-2,4,6-triallyloxy benzaldehyde (1s)

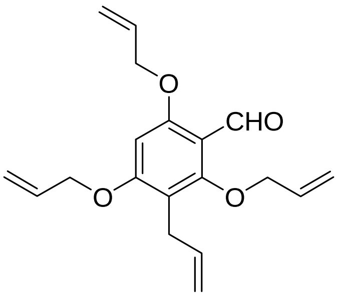
Following the general procedure, treatment of 2,4,6-trihydroxy benzaldehyde (1.0 g, 6.58 mmol, 1.0 eq.) with allyl bromide (1.95 mL, 21.69 mmol, 3.3 eq.) and potassium carbonate (3.0 g, 21.69 mmol, 1.1 eq.) in DMF (10 mL), followed by workup of the reaction mixture and flash column chromatography afforded 2,4,6-triallyloxy benzaldehyde **1p** and 3-allyl-2,4,6-triallyloxy benzaldehyde **1s**.

2,4,6-Triallyloxy benzaldehyde (1p)



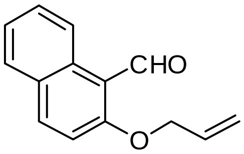
White solid (1.13 g, 63%). **R$_f$** (pentane/EtOAc = 80/20): 0.23; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.42 (s, 1H, CHO), 6.10-5.95 (m, 5H, H$_{ar}$, C*H*=CH$_2$), 5.52 (dd, *J* = 3.2 Hz, 1.7 Hz, 1H, CH=C*H*$_2$), 5.44 (ddd, *J* = 18.7 Hz, 10.2 Hz, 1.5 Hz, 2H, CH=C*H*$_2$), 5.31 (ddt, *J* = 7.7 Hz, 4.4 Hz, 1.4 Hz, 3H, CH=C*H*$_2$), 4.57 (ddt, *J* = 9.8 Hz, 5.4 Hz, 1.5 Hz, 6H, OCH$_2$). **^{13}C NMR (75 MHz, CDCl$_3$):** 187.60, 164.96, 163.02, 132.35, 118.60, 117.96, 109.54, 92.46, 69.56, 69.14. **ESI-MS:** calculated [M+Na]$^+$ for $C_{16}H_{18}O_4Na$: 275.1278, found: 275.1271. **ATR-FTIR (cm^{-1}):** 3022, 2875, 1669, 1600, 1569, 1443, 1415, 1389, 1365, 1330, 1304, 1287, 1229, 1200, 1174, 1125, 1090, 1047, 1020, 955, 928, 808.

3-Allyl-2,4,6-triallyloxy benzaldehyde (1s)



White solid (0.338 g, 16%). **R_f** (pentane/EtOAc = 80/20): 0.20; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.36 (s, 1H, CHO), 6.26 (s, 1H, H$_{ar}$), 6.20-5.81 (m, 4H, C*H*=CH$_2$), 5.53-5.23 (m, 6H, CH=C*H*$_2$), 5.04-4.91 (m, 2H, CH=C*H*$_2$), 4.66-4.54 (m, 4H, OCH$_2$), 4.41 (dt, *J* = 5.7 Hz, 1.3 Hz, 2H, OCH$_2$), 3.37 (dt, *J* = 6.1 Hz, 1.5 Hz, 2H, CH$_2$). **^{13}C NMR (75 MHz, CDCl$_3$):** 188.00, 162.90, 161.73, 160.45, 136.73, 133.63, 132.46, 118.28, 117.80, 115.69, 114.84, 113.16, 93.60, 76.62, 69.83, 69.17, 27.59. **ESI-MS:** calculated [M+Na]$^+$ for $C_{19}H_{22}O_4Na$: 337.1410, found: 337.1410. **ATR-FTIR (cm^{-1}):** 3080, 2869, 1676, 1639, 1590, 1570, 1454, 1413, 1357, 1322, 1286, 1217, 1125, 1084, 992, 955, 920.

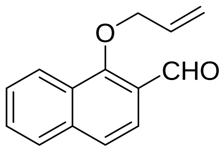
2-Allyloxy-1-naphthaldehyde (1q)



Following the general procedure, treatment of 2-hydroxy 1-naphthaldehyde (4.0 g, 23.23 mmol, 1.0 eq.) with allyl bromide (2.16 mL, 25.54 mmol, 1.1 eq.) and potassium carbonate (3.53 g, 25.54 mmol, 1.1 eq.) in DMF (15 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-1-naphthaldehyde as a white solid (3.66 g, 75%).

R_f (pentane/EtOAc = 95/5): 0.21; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.94 (s, 1H, CHO), 9.29 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 7.99 (d, *J* = 9.1 Hz, 1H, H$_{ar}$), 7.75 (d, *J* = 8.1 Hz, 1H, H$_{ar}$), 7.61 (dd, *J* = 11.5 Hz, 4.0 Hz, 1H, H$_{ar}$), 7.41 (t, *J* = 7.5 Hz, 1H, H$_{ar}$), 7.21 (dd, *J* = 9.1 Hz, 2.6 Hz, 1H, H$_{ar}$), 6.02-6.15 (m, 1H, C*H*=CH$_2$), 5.46 (d, *J* = 17.3 Hz, 1H, CH=C*H*$_2$), 5.35 (dd, *J* = 10.6 Hz, 0.8 Hz, 1H, CH=C*H*$_2$), 4.79-4.72 (m, 2H, OCH$_2$). **^{13}C NMR (75 MHz, CDCl$_3$):** 191.95, 163.02, 137.35, 132.23, 131.43, 129.75, 128.14, 124.75, 118.24, 116.89, 113.69, 70.01. **ESI-MS:** calculated [M+Na]$^+$ for $C_{14}H_{12}O_2Na$: 235.0730, found: 235.0726. **ATR-FTIR (cm^{-1}):** 3024, 2801, 1658, 1617, 1591, 1564, 1511, 1468, 1456, 1434, 1370, 1338, 1267, 1242, 1176, 1149, 1052, 1023, 1006, 955.

1-Allyloxy-2-naphthaldehyde (1r)

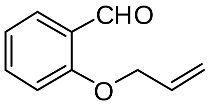


Following the general procedure, treatment of 1-hydroxy 2-naphthaldehyde (1.0 g, 6.4 mmol, 1.0 eq.) with allyl bromide (0.54 mL, 6.4 mmol, 1.1 eq.) and potassium carbonate (0.885 g, 6.4 mmol, 1.1 eq.) in

DMF (10 mL), followed by processing of the reaction mixture and flash column chromatography afforded the 1-allyloxy-2-naphthaldehyde as a colorless liquid (1.084 g, 88%).

R*f* (pentane/EtOAc = 95/5): 0.34; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.58 (s, 1H, CHO), 8.24 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.86 (d, *J* = 8.6 Hz, 2H, H_{ar}), 7.67-7.55 (m, 3H, H_{ar}), 6.27-6.12 (m, 1H, $CH=CH_2$), 5.55-5.43 (m, 1H, $CH=CH_2$), 5.37 (dd, *J* = 10.4 Hz, 1.1 Hz, 1H, $CH=CH_2$), 4.72 (d, *J* = 5.7 Hz, 2H, OCH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** 190.01, 161.21, 138.17, 132.63, 129.46, 128.50, 128.17, 126.93, 125.43, 124.84, 123.47, 122.66, 119.25, 78.88. **ESI-MS:** calculated $[M+Na]^+$ for $C_{14}H_{12}O_2Na$: 235.0730, found: 235.0727. **ATR-FTIR (cm^{-1}):** 3062, 2927, 1674, 1624, 1597, 1574, 1541, 1507, 1458, 1433, 1388, 1264, 1229, 1184, 1148, 1081, 1026, 974, 936.

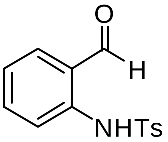
2-Allyloxy-benzaldehyde (1t)



Following the general procedure, treatment of salicylaldehyde (4.0 g, 32.75 mmol, 1.0 eq.) with allyl bromide (3.05 mL, 36.03 mmol, 1.1 eq.) and potassium carbonate (4.98 g, 36.03 mmol, 1.1 eq.) in DMF (15 mL), followed by workup of the reaction mixture and flash column chromatography afforded the 2-allyloxy-benzaldehyde as a colorless liquid (4.67 g, 88%).

R*f* (pentane/EtOAc = 95/5): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$):** 10.49 (s, 1H, CHO), 7.79 (dd, *J* = 7.7 Hz, 1.8 Hz, 1H, H_{ar}), 7.51-7.45 (m, 1H, H_{ar}), 7.00-6.92 (m, 2H, H_{ar}), 6.03 (ddt, *J* = 17.2 Hz, 10.4 Hz, 5.1 Hz, 1H, $CH=CH_2$), 5.41 (ddd, *J* = 17.3 Hz, 2.9 Hz, 1.4 Hz, 1H, $CH=CH_2$), 5.29 (dd, *J* = 10.6 Hz, 1.3 Hz, 1H, $CH=CH_2$), 4.61 (dt, *J* = 5.1 Hz, 1.3 Hz, 2H, OCH_2); **^{13}C NMR (100 MHz, $CDCl_3$):** 189.64, 160.90, 135.86, 132.37, 128.30, 125.00, 120.79, 117.98, 112.85, 69.09; **ESI-MS:** calculated $[M+Na]^+$ for $C_{10}H_{10}O_2Na$: 185.0573, found: 185.0572; **ATR-FTIR (cm^{-1}):** 2923, 2863, 1683, 1613, 1582, 1494, 1457, 1417, 1397, 1285, 1246, 1222, 1162, 1118, 996.

N-(2-Formyl-phenyl)-4-methyl-benzenesulfonamide[18]



Following the modified procedure by König et al.,[19] 2-aminobenzyl alcohol (2.39 g, 19.4 mmol, 1.0 eq.) and pyridine (1.88 g, 1.92 mL, 23.7 mmol, 1.22 eq.) were dissolved in 72 mL $CHCl_3$ and *para*-toluenesulfonyl chloride (4.12 g, 21.6 mmol, 1.11 eq.) dissolved in 72 mL $CHCl_3$ was added slowly to the solution.

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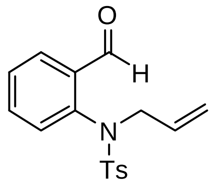
[18] For physical data, see: Goujon, J.-Y.; Zammattio, F.; Chrétien, J.-M.; Beaudet, I. *Tetrahedron* **2004**, *60*, 4037.

[19] Fonseca, M. H.; Eibler, E.; Zabel, M.; König, B. *Tetrahedron Asym.* **2003**, *14*, 1989.

The resulting mixture was stirred at rt for 16 h and then the volatiles were removed under reduced pressure. The obtained brown solid, crude *N*-(2-hydroxymethyl-phenyl)-4-methyl-benzenesulfonamide, was dissolved in 53 mL $CHCl_3$ without further purification and treated with activated MnO_4 (8.43 g, 97 mmol, 5 eq.). The suspension was stirred at 60 °C for 6 h and cooled to rt. The unsoluble materials were removed by filtration through a short pad of Celite© and the filtrate was concentrated under reduced pressure to afford a solid. The solid was purified by trituration in cold MTBE and the product was obtained in 71% yield (3.78 g, 13.7 mmol, over 2 steps) as an off-white solid.

R*f* (pentane/EtOAc = 3/1): 0.31; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.79 (br s, 1H, NH), 9.81 (d, *J* = 0.6 Hz, 1H, CHO), 7.76 (d, *J* = 8.4 Hz, 2H, H_{ar}), 7.67 (br d, *J* = 8.3 Hz, 1H, H_{ar}), 7.59 (dd, *J* = 7.6, 1.6 Hz, 1H, H_{ar}), 7.54-7.56 (m, 1H, H_{ar}), 7.23 (d, *J* = 8.3 Hz, 2H, H_{ar}), 7.18 (dt, *J* = 7.5, 1.0 Hz, 1H, H_{ar}), 2.35 (s, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 195.0, 144.2, 139.8, 136.2, 136.1, 135.8, 129.7, 127.2, 122.9, 121.7, 117.6, 21.5.; **ESI-MS:** calculated $[C_{14}H_{13}NNaO_3S]^+$: 298.0508, found: 298.0501; **GC-MS, Rt (method B):** 10.10 min, **(EI) m/z (%):** 275 (14), 168 (1), 155 (6), 139 (4), 120 (100), 91 (57), 77 (2), 65 (26); **ATR-FTIR (cm^{-1}):** 3137, 2855, 2771, 1674, 1602, 1585, 1495, 1463, 1411, 1340, 1285, 1206, 1154, 1118, 1089, 1045, 927, 844, 810, 762, 673, 661, 616, 562, 549.

N-Allyl-*N*-(2-formyl-phenyl)-4-methyl-benzenesulfonamide (1u)[20]



N-(2-Formyl-phenyl)-4-methyl-benzenesulfonamide (1.50 g, 5.45 mmol, 1 eq.) and K_2CO_3 (829 mg, 6.0 mmol, 1.1 eq.) were suspended in 10 mL DMF and allyl bromide (725 mg, 522 µL, 6.0 mmol, 1.1 eq.) was added dropwise. The resulting mixture was stirred at rt for 18 h and diluted with H_2O (30 mL) and MTBE (15 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 60 mL). The combined organic phases were washed with H_2O (3 x 60 mL) and dried over $MgSO_4$. After removal of volatiles under reduced pressure the crude product was purified by recrystallization from a mixture of CH_2Cl_2 and MTBE. The product was obtained in 73% yield (1.25 g, 3.95 mmol) as a white solid.

R*f* (pentane/EtOAc = 3/1): 0.35; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.41 (d, *J* = 0.6 Hz, 1H, CHO), 8.02-7.94 (m, 1H, H_{ar}), 7.51-7.39 (m, 4H, H_{ar}), 7.32-7.25 (m, 2H, H_{ar}), 6.74-6.66 (m, 1H, H_{ar}), 5.82-5.65 (m, 1H, $NCH_2CH{=}CH_2$), 5.09-4.96 (m, 2H, $NCH_2CH{=}CH_2$), 4.57 (br s, 1H, $NCHHCH{=}CH_2$), 3.85 (brs, 1H, $NCHHCH{=}CH_2$), 2.44 (s, 3H, CH_3); **^{13}C NMR (75**

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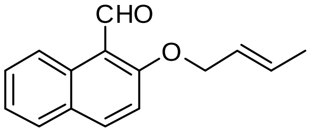
[20] For physical data, see: Fürstner, A.; Schlecker, A.; Lehmann, C. W. *Chem. Commun.* **2007**, 4277.

MHz, $CDCl_3$): 190.1, 144.2, 141.2, 135.9, 134.2, 134.0, 131.5, 129.7, 128.5, 128.3, 127.9, 127.8, 120.5, 54.3, 21.6; **ESI-MS:** calculated $[C_{17}H_{17}NNaO_3S]^+$: 338.0821, found: 338.0814; **GC-MS, Rt (method B):** 10.41 min, **(EI) m/z (%):** 160 (100), 155 (2), 139 (1), 133 (5), 131 (6), 119 (2), 105 (5), 91 (30), 77 (16), 64 (3); **ATR-FTIR (cm^{-1}):** 3092, 2864, 1695, 1654, 1596, 1483, 1451, 1391, 1343, 1281, 1266, 1215, 1166, 1090, 1057, 988, 936, 886, 870, 824, 815, 786, 746, 728, 705, 661, 623, 575, 550, 540, 509.

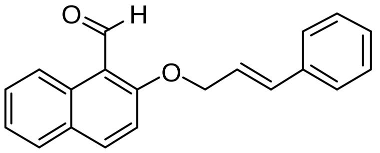
2-[((*E*)-But-2-enyl)oxy]-naphthalene-1-carbaldehyde (8a)



2-Hydroxy-naphthalene-1-carbaldehyde (1.12 g, 7.0 mmol, 1.0 eq.) and K_2CO_3 (1.06 g, 7.7 mmol, 1.1 eq.) were mixted in 14 mL DMF and *trans*-crotyl bromide (85% purity, contaminated by 3-bromo-1-butene, 1.22 g, 934 µL, 9.04 mmol, 1.29 eq.) was added dropwise. The resulting mixture was stirred at rt fot 16 h and diluted with H_2O (50 mL) and MTBE (30 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 30 mL). The combined organic phases were washed with H_2O (3 x 50 mL) and dried over $MgSO_4$. After removal of volatiles, the crude product was purified by column chromatography (5 x 15 cm silica, pentane/EtOAc = 30/1 → 20:1). The desired product was obtained in 83% yield (1.32 g, 5.83 mmol) as a slightly sticky off-white solid.

R_f (pentane/EtOAc = 19/1): 0.29; **^{1}H NMR (400 MHz, $CDCl_3$):** 10.90 (s, 1H, CHO), 9.28 (d, *J* = 8.6 Hz, 1H, H_{ar}), 7.98 (d, *J* = 9.2 Hz, 1H, H_{ar}), 7.74 (br d, *J* = 8.1 Hz, 1H, H_{ar}), 7.60 (ddd, *J* = 8.7, 6.9, 1.3 Hz, 1H, H_{ar}), 7.40 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H, H_{ar}), 7.22 (d, *J* = 9.2 Hz, 1H, H_{ar}), 5.96-5.68 (m, 2H, $OCH_2CH{=}CHCH_3$), 4.70-4.65 (m, 2H, $OCH_2CH{=}CHCH_3$), 1.79-1.73 (m, 3H, $OCH_2CH{=}CHCH_3$); **^{13}C NMR (100 MHz, $CDCl_3$):** 192.1, 163.3, 137.3, 131.5, 131.2, 129.7, 128.5, 128.1, 125.1, 124.9, 124.7, 117.0, 114.0, 70.2, 17.8; **ESI-MS:** calculated $[C_{15}H_{14}NaO_2]^+$: 249.0886, found: 249.0878; **ATR-FTIR (cm^{-1}):** 3021, 2942, 2879, 2802, 1665, 1622, 1591, 1566, 1511, 1459, 1437, 1416, 1375, 1341, 1267, 1243, 1222, 1179, 1155, 1069, 1049, 1020, 967, 943, 911, 862, 808, 775, 764, 712, 654, 575.

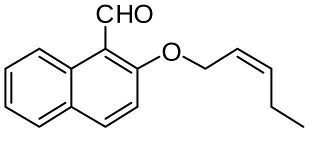
2-((*E*)-3-Phenyl-allyloxy)-naphthalene-1-carbaldehyde (8b)



2-Hydroxy-naphthalene-1-carbaldehyde (3.44 g, 20 mmol, 1.0 eq.) and K_2CO_3 (3.04 g, 22 mmol, 1.1 eq.) were suspended in 40 mL DMF and *trans*-cinnamyl chloride (3.36 g, 22 mmol, 1.1 eq.) was added. The resulting mixture was stirred at 80 °C for 3.5 h and then allowed to cool to rt. The reaction was diluted with H_2O (100 mL) and the aqueous phase was continueously extracted with CH_2Cl_2 till no solid was observed in the aqueous phase. The combined organic phases were washed with H_2O (3 x) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the crude residue was pre-absorbed on silica gel, then purified by column chromatography (6 x 13 cm silica, pentane/EtOAc 30:1 → 20:1 → 10:1 → 5:1 → 1:1 → CH_2Cl_2). The pure fractions contained 420 mg pure product and the slightly contaminated fractions were concentrated under reduced pressure to yield a solid. The solid was washed with cold MTBE to afford an additional 3.88 g pure product. The product was obtained in 75% yield (4.30 g, 14.93 mmol) as an off-white solid.

R_f (pentane/EtOAc = 9/1): 0.25; **^{1}H NMR (300 MHz, DMSO-d$_6$):** 10.87 (s, 1H, CHO), 9.13 (br d, $J = 8.6$ Hz, 1H, H_{ar}), 8.28 (d, $J = 9.2$ Hz, 1H, H_{ar}), 7.94 (br d, $J = 8.0$ Hz, 1H, H_{ar}), 7.68-7.60 (m, 2H, H_{ar}), 7.54-7.43 (m, 3H, H_{ar}), 7.39-7.23 (m, 3H, H_{ar}), 6.85 (d, $J = 16.1$ Hz, 1H, $OCH_2CH{=}C\mathit{H}Ph$), 6.60 (dt, $J = 16.1, 5.8$ Hz, 1H, $OCH_2C\mathit{H}{=}CHPh$), 5.07 (dd, $J = 5.7, 1.0$ Hz, 2H, $OC\mathit{H}_2CH{=}CHPh$); **^{13}C NMR (75 MHz, DMSO-d$_6$):** 192.4, 164.2, 138.8, 136.9, 134.0, 131.7, 130.7, 129.6, 129.6, 129.2, 129.0, 127.5, 125.7, 125.2, 124.9, 117.0, 116.1, 70.9; **ESI-MS:** calculated $[C_{20}H_{16}NaO_2]^+$: 311.1043, found: 311.1033; **ATR-FTIR (cm^{-1}):** 3084, 3061, 3031, 3010, 2942, 2875, 2806, 1656, 1620, 1590, 1579, 1567, 1513, 1497, 1467, 1448, 1439, 1418, 1393, 1374, 1343, 1284, 1269, 1240, 1224, 1181, 1160, 1152, 1117, 1076, 1069, 1053, 1026, 1002, 990, 971, 947, 919, 866, 840, 827, 808, 776, 757, 731, 713, 693, 659; **Elemental analysis:** calculated (%) for $C_{20}H_{16}O_2$ (288.34): C 83.31, H 5.59, found: 83.09, H 5.39.

2-[((*Z*)-Pent-2-enyl)oxy]-naphthalene-1-carbaldehyde (8c)



(*Z*)-1-bromo-pent-2-ene (1.48 g, 9.9 mmol, 1.1 eq.) prepared from *cis*-2-penten-1-ol under the condition of the bromination by Kuehne[21] was added slowly to the suspension of 2-hydroxy-naphthalene-1-carbaldehyde (1.55 g, 9 mmol, 1 eq.) and K_2CO_3 (1.37 g, 9.9 mmol, 1.1 eq.) in 18 mL DMF. The resulting mixture was stirred at rt for 8.5 h and the diluted with H_2O (50 mL) und MTBE (30 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 30 mL). The combined organic phases were washed with H_2O (3 x 50 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the crude product was purified by column chromatography (5 x 12 cm silica, pentane/EtOAc = 30/1). The product was obtained in 88% yield (1.91 g, 7.95 mmol) as a yellowish solid.

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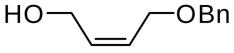
[21] Kuehne, M. E.; Wang, T.; Seraphin, D. *J. Org. Chem.* **1996**, *61*, 7873.

R$_f$ (pentane/EtOAc = 19/1): 0.33; **^{1}H NMR (400 MHz, CDCl$_3$):** 10.80 (s, 1H, CHO), 9.19 (br d, J = 8.7 Hz, 1H, H$_{ar}$), 7.90 (d, J = 9.2 Hz, 1H, H$_{ar}$), 7.65 (d, J = 8.1 Hz, 1H, H$_{ar}$), 7.55-7.46 (m, 1H, H$_{ar}$), 7.35-7.26 (m, 1H, H$_{ar}$), 7.14 (d, J = 9.2 Hz, 1H, H$_{ar}$), 5.68-5.52 (m, 2H, OCH$_2$C*H*=C*H*Et), 4.71 (d, J = 5.6 Hz, 2H, OC*H*$_2$CH=CHCH$_2$CH$_3$), 2.14-2.01 (m, 2H, OCH$_2$CH=CHC*H*$_2$CH$_3$), 0.94 (t, J = 7.5 Hz, 3H, OCH$_2$CH=CHCH$_2$C*H*$_3$); **^{13}C NMR (100 MHz, CDCl$_3$):** 192.2, 163.4, 137.4, 137.1, 131.6, 129.8, 128.6, 128.2, 125.0, 124.8, 123.1, 117.2, 114.0, 65.5, 21.3, 14.0; **ESI-MS:** calculated [$C_{16}H_{16}NaO_2$]$^+$: 263.1043, found: 263.1036; **ATR-FTIR (cm^{-1}):** 3054, 3017, 2969, 2934, 2874, 2810, 1665, 1623, 1591, 1567, 1511, 1475, 1459, 1436, 1418, 1373, 1342, 1310, 1265, 1242, 1232, 1215, 1177, 1150, 1056, 1022, 966, 947, 863, 810, 748, 711, 650, 564, 540; **Elemental analysis:** calculated (%) for $C_{16}H_{16}O_2$ (240.30): C 79.97, H 6.71, found: C 79.87, H 6.72.

(*Z*)-4-Benzyloxy-but-2-en-1-ol



In analogy to the procedure by Hirsemann and Körner,[22] NaH (60% in mineral oil, 8.0 g, 199.5 mmol, 1.05 eq.) was added very carefully to a solution of *cis*-2-butene-1,4-diol (50.0 g, 567 mmol, 2.98 eq.) in 200 mL THF at 0 ˚C (caution!: violent evolution of H_2 gas). The resulting mixture was stirred at rt for 1.5 h and then benzyl bromide (32.5 g, 22.4 mL, 190 mmol, 1.0 eq.) was added. The reaction mixture was stirred at 90 ˚C for 1 h and then cooled to ambient temperature. The reaction was acidified with 1 N aq. HCl carefully and the resulting two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic phases were dried over $MgSO_4$. After removal of volatiles under reduced pressure the residue was purified by column chromatography (5.5 x 26 cm silica, pentane/EtOAc 10:1 → 5:1 → 1:1). The product was obtained in 88% yield (29.86 g, 167.5 mmol) as a yellow oil.

R$_f$ (pentane/EtOAc = 1/1): 0.28; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.39-7.26 (m, 5H, C$_6$H$_5$), 5.87-5.68 (m, 2H, CH=CH), 4.52 (s, 2H, C*H*$_2$Ph), 4.19-4.13 (m, 2H, C*H*$_2$OH), 4.12 (m, 2H, C*H*$_2$OBn), 2.03 (br s, 1H, OH); **^{13}C NMR (75 MHz, CDCl$_3$):** 137.8, 132.3, 128.4, 128.2, 127.8, 127.8, 72.5, 65.6, 58.7; **ESI-MS:** calculated [$C_{11}H_{14}NaO_2$]$^+$: 201.0897, found: 201.0886; **GC-MS, Rt (method B):** 7.95 min, **(EI) m/z (%):**107 (13), 91 (100), 87 (1), 77 (10), 57 (1), 54 (11), 44 (1); **ATR-FTIR (cm^{-1}):** 3065, 3031, 2941, 2876, 1720, 1452, 1277, 1202, 1173, 1105, 1072, 897, 632, 542, 505.

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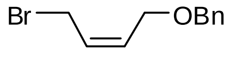
[22] Körner, M.; Hiersemann, M. *Org. Lett.* **2007**, 9 , 4979.

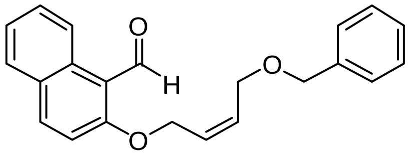
((*Z*)-4-Bromo-but-2-enyloxymethyl)-benzene[23]



Following the modified procedure by Kuehne et al.,[24] (*Z*)-4-benzyloxy-but-2-ene-1-ol (8.91 g, 50 mmol, 1.0 eq.) was dissolved in 100 mL ether and the solution was cooled to 0 °C. Phosphorous tribromide (5.41 g, 1.88 mL, 20 mmol, 0.40 eq.) was added dropwise and the the mixture was allowed to warm to rt. The mixture was stirred at rt for 11 h and then diluted with 100 mL ether. After neutralization with satd. aq. $NaHCO_3$ the organic phase was separated and dried over $MgSO_4$. After removal of volatiles yellowish liquid was obtained in 98% (11.87 g, 49.23 mmol) and this crude product was used without further purification.

R*f* (pentane/EtOAc = 9/1): 0.71; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.40-7.25 (m, 5H, C_6H_5), 5.97-5.83 (m, 1H, C*H*CH_2Br), 5.81-5.70 (m, 1H, C*H*CH_2OBn), 4.53 (s, 2H, OC*H*$_2$Ph), 4.15 (dd, *J* = 6.3, 1.5 Hz, 2H, CH_2OBn), 4.00 (d, *J* = 8.2 Hz, 2H, C*H*$_2$Br); **^{13}C NMR (75 MHz, $CDCl_3$):** 137.8, 131.1, 128.4, 128.4, 127.8, 127.8, 72.5, 64.9, 26.5; **ESI-MS:** calculated $[C_{11}H_{13}BrNaO]^+$: 263.0042, found: 263.0043; **GC-MS, Rt (method B):** 8.21 min, **(EI) m/z (%):** 161 (3), 107 (3), 91 (100), 79 (6), 77 (8), 70 (1), 54 (5), 40 (1).

2-((*Z*)-4-Benzyloxybut-2-enyloxy)-naphthalene-1-carbaldehyde (8d)



2-Hydroxy-naphthalene-1-carbaldehyde (2.89 g, 16.8 mmol, 1.0 eq.) and K_2CO_3 (2.56 g, 18.5 mmol, 1.1 eq.) were suspended in 34 mL DMF and ((*Z*)-4-bromo-but-2-enyloxymethyl)-benzene (4.46 g, 18.5 mmol, 1.1 eq.) was added dropwise. The resulting suspension was stirred at rt for 12 h and diluted with H_2O (30 mL) and MTBE (30 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 30 mL). The combined organic phases were washed with H_2O (3 x 30 mL) and brine, then dried over $MgSO_4$. After removal of volatiles the crude mixture was purified by column chromatography (5 x 13 cm silica, pentane/EtOAc 20/1 → 10/1). The product was obtained in 86% yield (4.80 g, 14.43 mmol) as a yellowish solid.

R*f* (pentane/EtOAc = 9/1): 0.15; **^{1}H NMR (400 MHz, $CDCl_3$):** 10.91 (s, 1H, CHO), 9.29 (br d, *J* = 8.7 Hz, 1H, H_{ar}), 8.00 (d, *J* = 9.1 Hz, 1H, H_{ar}), 7.77 (br d, *J* = 8.1 Hz, 1H, H_{ar}), 7.63 (ddd, *J* = 8.7, 6.9, 1.2 Hz, 1H, H_{ar}), 7.46-7.40 (m, 1H, H_{ar}), 7.39-7.27 (m, 5H, C_6H_5), 7.20 (d, *J* = 9.1 Hz, 1H, H_{ar}), 5.97-5.87 (m, 2H, OCH_2C*H*=C*H*CH_2OBn), 4.89-4.82 (m, 2H, OC*H*$_2$CH=CHCH_2OBn), 4.56 (s, 2H, OCH_2CH=CHCH_2OC*H*$_2$Ph), 4.23-4.13 (m, 2H,

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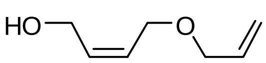
[23] For physical data, see: Chattopadhyay, A.; Dhotare, B.; Hassarajani, S. *J. Org. Chem.* **1999**, *64*, 6874.

[24] Kuehne, M. E.; Wang, T.; Seraphin, D. *J. Org. Chem.* **1996**, *61*, 7873.

$OCH_2CH{=}CHCH_2OBn$); **^{13}C NMR (100 MHz, $CDCl_3$):** 192.0, 163.0, 137.8, 137.3, 131.5, 130.4, 129.8, 128.6, 128.4, 128.2, 127.8, 127.8, 127.3, 124.9, 124.8, 117.0, 113.7, 72.5, 65.9, 65.6; **ESI-MS:** calculated $[C_{22}H_{20}NaO_3]^+$: 355.1305, found: 355.1304; **ATR-FTIR (cm^{-1}):** 3028, 2886, 2804, 1665, 1620, 1590, 1511, 1458, 1435, 1399, 1375, 1330, 1267, 1242, 1176, 1151, 1102, 1053, 1018, 988, 941, 862, 814, 751, 736, 707, 695, 511, 490.

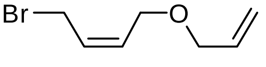
(*Z*)-4-Allyloxy-but-2-en-1-ol[25]



In analogy to the procedure by Hirsemann and Körner,[22] NaH (60% in mineral oil, 1.6 g, 39.9 mmol, 1.05 eq.) was added very carefully to a solution of *cis*-2-butene-1,4-diol (9.99 g, 113.4 mmol, 2.98 eq.) in 40 mL THF at 0 ˚C (caution!: violent evolution of H_2 gas). The resulting mixture was stirred at rt for 1 h and then allyl bromide (4.60 g, 3.31 mL, 38.0 mmol, 1.0 eq.) was added slowly. The reaction mixture was stirred at rt for 30 min and then at 75 ˚C for 1 h. After cooling to ambient temperature the mixture was acidified with 1 N aq. HCl carefully and CH_2Cl_2 (100 mL) was added. The resulting two phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried over $MgSO_4$. After removal of volatiles under reduced pressure the residue was purified by column chromatography (5 x 10 cm silica, pentane/EtOAc = 5:1 → 1:1). The product was obtained in 77% yield (3.74 g, 29.18 mmol) as a yellowish liquid.

R_f (pentane/EtOAc = 1/1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$):** 5.89 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H, $OCH_2CH{=}CH_2$), 5.83-5.62 (m, 2H, $OCH_2CH{=}CHCH_2OH$)), 5.31-5.22 (m, 1H, $OCH_2CH{=}CHH$), 5.21-5.14 (m, 1H, $OCH_2CH{=}CHH$), 4.17 (d, *J* = 6.3 Hz, 2H, $CHCH_2OH$), 4.04 (d, *J* = 6.0 Hz, 2H, $CH_2OAllyl$), 4.00-3.94 (m, 2H, $OCH_2CH{=}CH_2$), 2.46 (br s, 1H, OH); **^{13}C NMR (75 MHz, $CDCl_3$):** 134.3, 132.3, 128.0, 117.4, 71.3, 65.5, 58.5; **ESI-MS:** calculated $[C_7H_{12}NaO_2]^+$: 151.0730, found: 151.0734; **GC-MS, Rt (method B):** 6.05 min, **(EI) m/z (%):** 110 (9), 97 (14), 87 (1), 71 (8), 70 (34), 57 (25), 54 (11), 41 (100); **ATR-FTIR (cm^{-1}):** 893, 632, 545, 537, 520, 506, 499, 484.

(*Z*)-1-Allyloxy-4-bromo-but-2-ene



Following the modified procedure by Kuehne et al.,[21] (*Z*)-4-allyloxy-but-2-ene-1-ol (1.41 g, 11 mmol, 1 eq.) was dissolved in 22 mL ether and the solution was cooled to 0 °C. Phosphorous tribromide (1.19 g, 414 µL, 4.4 mmol, 0.4

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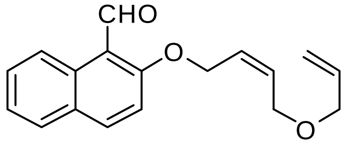
[25] For physical data, see: Hansen, E. C.; Lee, D. *Org. Lett.* **2004**, *6*, 2035.

eq.) was added dropwise and the the mixture was allowed to warm to rt. The mixture was stirred at rt for 2.5 h and then diluted with 20 mL ether. After neutralization with satd. aq. $NaHCO_3$ the organic phase was separated and washed with brine, then dried over $MgSO_4$. After removal of volatiles colorless liquid was obtained in 93% yield (1.95 g, 10.2 mmol) and this crude product was used without further purification.

R*f* (pentane/EtOAc = 9/1): 0.56; **^{1}H NMR (300 MHz, $CDCl_3$:** 6.00 (m, 2H, C*H*CH_2Br, OCH_2C*H*=CH_2), 5.77-5.66 (m, 1H, C*H*CH_2OAllyl), 5.35-5.26 (m, 1H, OCH_2CH=C*H*H), 5.25-5.18 (m, 1H OCH_2CH=CH*H*), 4.19 (dd, *J* = 6.3, 1.5 Hz, 2H, OCH_2), 4.04-3.97 (m, 4H, OCH_2, CH_2Br); **^{13}C NMR (75 MHz, $CDCl_3$):** 134.4, 131.1, 128.2, 117.5, 71.4, 64.9, 26.5; **ESI-MS:** calculated $[C_7H_{11}BrNaO]^+$: 212.9885, found: 212.9878; **GC-MS, Rt (method B):** 6.41 min, **(EI) m/z (%):** 149 (1), 133 (18), 119 (1), 111 (10), 93 (17), 79 (3), 70 (2), 57 (4), 54 (29), 41 (100).

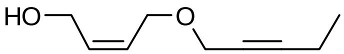
2-((*Z*)-4-Allyloxy-but-2-enyloxy)-naphthalene-1-carbaldehyde (8e)



2-Hydroxy-naphthalene-1-carbaldehyde (1.12 g, 7 mmol, 1.0 eq.) and K_2CO_3 (1.06 g, 7.7 mmol, 1.1 eq.) were suspended in 14 mL DMF and (*Z*)-1-allyloxy-4-bromo-but-2-ene (1.47 g, 7.7 mmol, 1.1 eq.) was added slowly. The resulting mixture was stirred at rt for 8 h and then diluted with H_2O (30 mL) and MTBE (15 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 30 mL) and the combined organic phases were washed with H_2O (3 x 50 mL), then dried over $MgSO_4$. After removal of volatiles under reduced pressure the residue was purified by column chromatography (4 x 11 cm, pentane/EtOAc = 9/1). The product was obtained in 86% yield (1.71 g, 6.05 mmol) yield as a yellowish solid.

R$_F$ (pentane/EtOAc = 9/1): 0.14; **^{1}H NMR (400 MHz, $CDCl_3$):** 10.89 (s, 1H, CHO), 9.30-9.24 (m, 1H, H_{ar}), 8.01 (d, *J* = 9.1 Hz, 1H, H_{ar}), 7.75 (br d, *J* = 8.1 Hz, 1H, H_{ar}), 7.61 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H, H_{ar}), 7.41 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H, H_{ar}), 7.24 (d, *J* = 9.1 Hz, 1H, H_{ar}), 5.98-5.82 (m, 3H, CH_2C*H*=C*H*CH_2, OCH_2C*H*=CH_2), 5.30 (ddt, *J* = 17.2, 1.7, 1.6 Hz, 1H, OCH_2CH=C*H*H), 5.21 (ddt, *J* = 10.4, 1.7, 1.3 Hz, 1H, OCH_2CH=CH*H*), 4.90-4.86 (m, 2H, ArOCH_2), 4.16-4.12 (m, 2H, OC*H*$_2$CH=CH_2), 4.03-3.99 (m, 2H, CH_2OAllyl); **^{13}C NMR (100 MHz, $CDCl_3$):** 192.0, 163.0, 137.4, 134.4, 131.5, 130.5, 129.8, 128.6, 128.2, 127.0, 124.9, 124.8, 117.4, 117.0, 113.7, 71.4, 65.9, 65.6; **ESI-MS:** calculated $[C_{18}H_{18}NaO_3]^+$: 305.1148, found: 305.1145; **ATR-FTIR (cm^{-1}):** 3078, 3039, 2878, 2839, 2805, 1665, 1620, 1590, 1566, 1512, 1470, 1458, 1436, 1415, 1391, 1373, 1344, 1324, 1268, 1244, 1176, 1150, 1107, 1055, 1025, 1014, 1000, 965, 943, 921, 862, 815, 775, 755, 700, 648, 611, 569, 523.

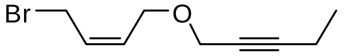
(*Z*)-4-Pent-2-ynyloxy-but-2-en-1-ol



In analogy to the procedure by Hirsemann and Körner,[22] NaH (60% in mineral oil, 1.6 g, 39.9 mmol, 1.05 eq.) was added very carefully to a solution of *cis*-2-butene-1,4-diol (9.99 g, 113.4 mmol, 2.98 eq.) in 40 mL THF at 0 ˚C (caution!: violent evolution of H_2 gas). The resulting mixture was stirred at rt for 1 h and then 1-bromo-2-pentyne (5.59 g, 4.01 mL, 38.0 mmol, 1.0 eq.) was added. The reaction mixture was stirred at rt for 30 min, then at 90 ˚C for 1 h. After cooling to ambient temperature the reaction was acidified with 1 N aq. HCl carefully and the resulting two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried over $MgSO_4$. After removal of volatiles under reduced pressure the residue was purified by column chromatography (5 x 14 cm silica, pentane/EtOAc = 5:1 → 2:1). The product was obtained in 70% yield (4.13 g, 26.78 mmol) as a yellow liquid.

R*f* (pentane/EtOAc = 2/1): 0.29; **^{1}H NMR (400 MHz, $CDCl_3$):** 5.88-5.76 (m, 1H, $CH_2CH{=}CHCH_2$), 5.72-5.62 (m, 1H, $CH_2CH{=}CHCH_2$), 4.23-4.18 (m, 2H, $OCH_2C{\equiv}CCH_2CH_3$), 4.14-4.08 (m, 4H, $CH_2CHC{=}HCH_2$), 2.28-2.18 (m, 2H, CH_2CH_3), 2.15 (br s, 1H, OH), 1.13 (dt, *J* = 7.5, 0.9 Hz, 3H, CH_2CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 132.8, 127.6, 88.7, 74.8, 64.6, 58.5, 57.8, 13.7, 12.4; **ESI-MS:** calculated $[C_9H_{14}NaO_2]^+$: 177.0886, found: 177.0884; **GC-MS, Rt (method B):** 7.14 min, **(EI) m/z (%):** 125 (2), 123 (6), 94 (4), 87 (1), 83 (14), 81 (12), 71 (7), 68 (12), 67 (83), 57 (29), 54 (18), 53 (24), 44 (3), 41 (100), 38 (5); **ATR-FTIR (cm^{-1}):** 2978, 2940, 2881, 1719, 1455, 1359, 1320, 1256, 1137, 1075, 1034, 894, 632, 535, 543, 500.

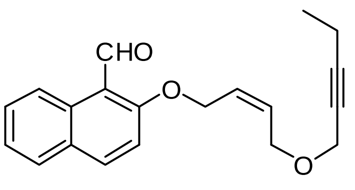
1-((*Z*)-4-Bromo-but-2-enyloxy)-pent-2-yne



Following the modified procedure by Kuehne et al.,[21] (*Z*)-4-pent-2-ynyloxy-but-2-ene-1-ol (11 mmol, 1.70 g, 1.0 eq.) was dissolved in 22 mL CH_2Cl_2 and the solution was cooled to 0 °C. Phosphorous tribromide (1.19 g, 414 μL, 4.4 mmol, 0.4 eq.) was added dropwiese and the the mixture was allowed to warm to rt. The mixture was stirred at rt for 1 h and then quenched with 20 mL H_2O. The phases were separated and the organic phase was washed with sat. aq. $NaHCO_3$ and washed with brine, then dried over $MgSO_4$. After removal of volatiles brown liquid was obtained in 90% yield (2.15 g, 9.90 mmol) and this crude product was used without further purification.

R*f* (pentane/EtOAc = 9/1): 0.68; **^{1}H NMR (300 MHz, $CDCl_3$)**: 5.98-5.83 (m, 1H, $CHCH_2Br$), 5.77-5.65 (m, 1H, OCH_2CH), 4.19 (dd, *J* = 6.5, 1.4 Hz, 2H, OCH_2CH), 4.14 (t, *J* = 2.2 Hz, 2H, $OCH_2C{\equiv}CCH_2CH_3$), 4.03 (d, *J* = 8.3 Hz, 2H, $CHCH_2Br$), 2.25 (tq, *J* = 7.5, 2.2 Hz, 2H, CH_2CH$_3$), 1.16 (t, *J* = 7.5 Hz, 3H, CH$_2$CH_3); **^{13}C NMR (75 MHz, CDCl$_3$):** 130.5, 129.0, 88.8, 74.8, 63.9, 58.0, 26.3, 13.8, 12.4; **ESI-MS:** calculated $[C_9H_{13}BrNaO]^+$: 239.0042, found: 239.0034; **GC-MS, Rt (method B):** 7.42 min, **(EI) m/z (%):** 187 (1), 149 (2), 137 (2), 133 (4), 108 (4), 97 (1), 93 (14), 83 (3), 79 (22), 70 (4), 68 (11), 67 (100), 54 (24), 53 (36), 41 (64), 40 (9).

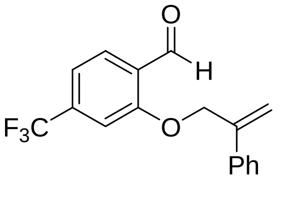
2-((*Z*)-4-Pent-2-ynyloxy-but-2-enyloxy)-naphthalene-1-carbaldehyde (8f)



2-Hydroxy-naphthalene-1-carbaldehyde (1.38 g, 8 mmol, 1 eq.) and K_2CO_3 (1.22 g, 8.8 mmol, 1.1 eq.) were suspended in 16 mL DMF and 1-((*Z*)-4-bromo-but-2-enyloxy)-pent-2-yne (1.91 g, 8.8 mmol, 1.1 eq.) was added. The resulting suspension was stirred at rt for 11 h, then diluted with H_2O (30 mL) and MTBE (20 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 30 mL). The combined organic phases were washed with H_2O (3 x 50 mL) and then dried over $MgSO_4$. The volatiles were removed under reduced pressure and the residue was purified by column chromatography (4 x 11.5 cm silica, pentane/EtOAc = 19/1 → 9/1). The product was obtained in 71% yield (1.75 g, 5.68 mmol) as a yellow oil.

R_f (pentane/EtOAc = 9/1): 0.18; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.90 (s, 1H, CHO), 9.28 (br d, *J* = 8.8 Hz, 1H, H$_{ar}$), 8.02 (d, *J* = 9.2 Hz, 1H, H$_{ar}$), 7.76 (br d, *J* = 8.1 Hz, 1H, H$_{ar}$), 7.61 (ddd, *J* = 8.8, 6.9, 1.4 Hz, 1H, H$_{ar}$), 7.42 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H, H$_{ar}$), 7.28 (d, *J* = 9.2 Hz, 1H, H$_{ar}$), 5.99-5.80 (m, 2H, CH$_2$C*H*=C*H*CH$_2$), 4.95-4.89 (m, 2H, ArOCH$_2$), 4.24-4.19 (m, 2H, CH_2OCH$_2$C≡CCH$_2$CH$_3$), 4.17 (t, *J* = 2.2 Hz, 2H, OCH_2C≡CCH$_2$CH$_3$), 2.21 (tq, *J* = 7.5, 2.2 Hz, 2H, CH_2CH$_3$), 1.12 (t, *J* = 7.5 Hz, 3H, CH$_2$CH_3); **^{13}C NMR (100 MHz, CDCl$_3$):** 192.0, 163.0, 137.4, 131.5, 130.0, 129.8, 128.6, 128.2, 127.8, 124.9, 124.8, 117.0, 113.7, 88.8, 74.8, 65.5, 64.9, 58.0, 13.7, 12.4; **ESI-MS:** calculated $[C_{20}H_{20}NaO_3]^+$: 331.1305, found: 331.1306; **ATR-FTIR (cm^{-1}):** 2975, 2937, 2879, 1672, 1620, 1591, 1567, 1512, 1461, 1437, 1368, 1268, 1243, 1214, 1155, 1072, 1056, 1024, 892, 813, 755, 712, 632, 545, 539, 533, 504.

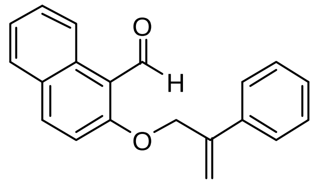
2-(2-Phenyl-allyloxy)-4-trifluoromethyl-benzaldehyde (10b)



Following the general procedure, 1.90 g 4-trifluoromethyl salicylaldehyde (10.0 mmol, 1.0 eq.) were dissolved in DMF (20 mL) and kept stirring at rt. To the stirred solution was added 1.52 g potassium carbonate (11.0 mmol, 1.1 eq.) followed by the dropwise addition of 3.18g (1-Bromomethyl-vinyl)-benzene (13.0 mmol, 1.3 eq.). The reaction mixture was then stirred for 15 h. Water (50 mL) was then added and the mixture was extracted with diethyl ether (4 x 40 mL). The combined organic extracts were washed with brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by flash column chromatography on silica (3 x 15 cm silica, PE/EE = 100/5 → 10/1) to afford the the pure product as a white solid (2.711 g, 8.85 mmol, 89%).

R*f* (pentane/EtOAc = 20/1): 0.43; **^{1}H NMR (300 MHz, CDCl$_3$):** 10.27 (s, 1H, CHO), 7.83 (dd, J = 8.4 Hz, J = 0.8 Hz, 1H, H_{ar}), 7.37-7.19 (m, 7H, H_{ar}), 5.57 (s, 1H, $OCH_2{=}CH_2$), 5.41 (s, 1H, $OCH_2{=}CH_2$), 4.99 (s, 2H, OCH_2); **^{13}C NMR (75 MHz, CDCl$_3$):** 188.8 (CHO), 160.7 (C_{ar}), 142.2 (C_{ar}), 137.7 (C_{ar}), 136.9 (q, $J_{(C,F)}$ = 32.5 Hz, $C_{ar}CF_3$), 129.3 (CH_{ar}), 128.8 (CH_{ar}), 128.6 (CH_{ar}), 127.5 (C_{ar}), 126.2 (CH_{ar}), 123.3 (d, $^1J_{(C,F)}$ = 272.8 Hz, CF_3), 117.9 (q, $J_{(C,F)}$ = 3.8 Hz, CH_{ar}), 116.1 (=CH_2), 110.5 (q, $J_{(C,F)}$ = 3.8 Hz, CH_{ar}), 71.0 (OCH_2); **^{19}F NMR (282.2 MHz, CDCl$_3$):** –63.36 ; **ESI-MS:** calculated $[C_{17}H_{13}F_3O_2Na]^+$: 329.0760, found: 329.0757; calculated $[C_{17}H_{13}F_3O_2CH_3OHNa]^+$: 361.1022, found: 361.1019; **ATR-FTIR (cm^{-1}):** 3083, 3062, 2870, 1687, 1618, 1586, 1498, 1428, 1393, 1325, 1238, 1179, 1124, 1074, 1025, 917, 902, 884, 868, 825, 776, 742, 711, 673, 663, 625.

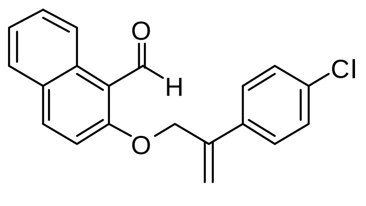
2-(2-Phenyl-allyloxy)-naphthalene-1-carbaldehyde (10c)



Following the modified procedure by Kuehne et al.,[21] 2-Phenyl-prop-2-en-1-ol (2.68 g, 20 mmol, 1.0 eq.) was dissolved in 40 mL ether und and the solution was cooled to 0 ˚C. Phosphorous tribromide (2.17 g, 753 µL, 8 mmol, 0.4 eq.) was added dropwise and the resulting mixture was allowed to warm to rt. After 12 h the reaction was diluted with MTBE (80 mL) and washed with satd. aq. $NaHCO_3$ (2 x 30 mL) and brine, then dried over Na_2SO_4. The volatiles were removed under reduced pressure and the crude, (1-bromomethyl-vinyl)-benzene was obtained in 86% yield (3.38 g, 17.2 mmol) as brown oil and used for the following reaction without further purification. (1-Bromomethyl-vinyl)-benzene (3.25 g, 16.5 mmol, 1.1 eq.) was added to a suspension of 2-hydroxy-naphthalene-1-carbaldehyde (2.58 g, 15 mmol, 1 eq.) and K_2CO_3 (2.28 g, 16.5 mmol, 1.1 eq.) in 28 mL DMF. The resulting mixture was stirred at rt for 15 h and then diluted with MTBE (100 mL), CH_2Cl_2 (20 mL) and H_2O (100 mL). The phases were separated and the aqueous phase was extracted with MTBE (3 x 100 mL). The combined organic phases were washed with H_2O (3 x 100 mL) and brine, then dried over $MgSO_4$. The volatiles were removed under reduced pressure to yield an orange solid as a crude product, which was purified by recrystallization from MTBE. The product was obtained in 81% yield (3.51 g, 12.17 mmol) as a light yellow solid.

R_f (pentane/EtOAc = 3/1): 0.61; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.79 (s, 1H, CHO), 9.32-9.25 (m, 1H, H_{ar}), 8.04 (d, *J* = 9.1 Hz, 1H, H_{ar}), 7.81-7.75 (m, 1H, H_{ar}), 7.62 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1H, H_{ar}), 7.52-7.29 (m, 7H, H_{ar}), 5.69-5.63 (m, 1H, $CH_2C(Ph)=C\mathit{H}H$), 5.53-5.48 (m, 1H, $CH_2C(Ph)=CH\mathit{H}$), 5.19-5.13 (m, 2H, $C\mathit{H}_2C(Ph)=CH_2$); **^{13}C NMR (75 MHz, $CDCl_3$):** 192.0, 162.9, 142.5, 137.7, 137.4, 131.5, 129.8, 128.6, 128.6, 128.3, 128.2, 126.0, 124.9, 124.9, 117.2, 115.4, 113.9, 71.2; **ESI-MS:** calculated $[C_{20}H_{16}NaO_2]^+$: 311.1043, found: 311.1035; **ATR-FTIR (cm^{-1}):** 3060, 3037, 2883, 2800, 1668, 1620, 1591, 1566, 1514, 1466, 1446, 1435, 1413, 1374, 1343, 1267, 1240, 1216, 1182, 1148, 1057, 1025, 954, 913, 904, 864, 819, 774, 750, 740, 708, 677, 654, 575, 544; **Elemental analysis:** calculated (%) for $C_{20}H_{16}O_2$ (288,34): C 83.31, H 5.59, found: C 83.02, H 5.32.

2-[2-(4-Chloro-phenyl)-allyloxy]-naphthalene-1-carbaldehyde (10d)



2-Hydroxy-naphthalene-1-carbaldehyde (1.72 g, 10 mmol, 1.0 eq.) and K_2CO_3 (1.52 g, 11 mmol, 1.1 eq.) were suspended in 20 mL DMF and 1-(1-bromomethyl-vinyl)-4-chloro-benzene (81% purity, contaminated by 1-((*E*)-2-bromo-1-methyl-vinyl)-4-chloro-benzene; 3.14 g, 13.6 mmol, 1.36 eq.) prepared following the procedure by Debaert[26] was added. The resulting suspension was stirred at rt for 16 h and then H_2O (100 mL) was added slowly to afford light yellow precipitate. The precipitate was collected by filtration using a glasfritt and washed with H_2O (50 mL) and cold ether (5 mL). The solid was dried in the air and purified by recrystallization from a mixture of CH_2Cl_2 und MTBE. The product was obtained in 63% yield (2.02 g, 6.25 mmol) as a light yellow solid.

R_f (pentane/EtOAc = 9/1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** 10.76 (s, 1H, CHO), 9.25 (br d, *J* = 8.6 Hz, 1H, H_{ar}), 8.06 (d, *J* = 9.1 Hz, 1H, H_{ar}), 7.78 (br d, *J* = 8.1 Hz, 1H, H_{ar}), 7.62 (ddd, *J* = 8.7, 6.9, 1.4 Hz, 1H, H_{ar}), 7.48-7.38 (m, 3H, H_{ar}), 7.38-7.30 (m, 3H, H_{ar}), 5.65 (s, 1H, $OCH_2C(Ar)=C\mathit{H}H$), 5.52 (s, 1H, $OCH_2C(Ar)=CH\mathit{H}$), 5.14 (s, 2H, $OC\mathit{H}_2C(Ar)=CH_2$); **^{13}C NMR (75 MHz, $CDCl_3$):** 191.8, 162.7, 141.5, 137.4, 136.1, 134.2, 131.4, 129.9, 128.8, 128.7, 128.2, 127.3, 124.9, 124.9, 117.2, 116.2, 113.7, 71.0; **ESI-MS:** calculated $[C_{20}H_{15}ClNaO_2]^+$: 345.0653, found: 345.0657; **ATR-FTIR (cm^{-1}):** 3089, 2870, 2794, 1660, 1622, 1593, 1569, 1516, 1494, 1471, 1437, 1417, 1391, 1377, 1346, 1304, 1268, 1242, 1191, 1158, 1087, 1059, 1032, 1010, 959, 891, 867, 833, 818, 796, 773, 748, 731, 711, 673, 632,

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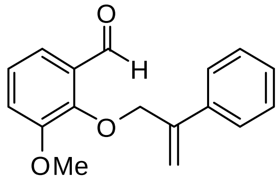
[26] Vaccher, C.; Berthelot, P.; Flouquet, N.; Vaccher, M.-P.; Debaert, M. *Synth. Commun.* **1993**, *23*, 671.

578, 503, 486; **Elemental analysis:** calculated (%) für $C_{20}H_{15}ClO_2$ (322.78): C 74.42, H 4.68, found: C 74.48, H 4.60.

3-Methoxy-2-(2-phenyl-allyloxy)-benzaldehyde (10a)

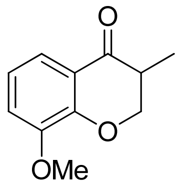


o-Vanillin (1.61 g, 10.6 mmol, 1.0 eq.) and K_2CO_3 (1.62 g, 11.7 mmol, 1.1 eq.) were suspended in 20 mL DMF and (1-bromomethyl-vinyl)-benzene (2.30 g, 11.7 mmol, 1.1 eq.) was added. The reaction mixture was stirred at rt for 15 h and then diluted with MTBE (30 mL) and H_2O (30 mL). The phases were separated and the organic phase was extracted with MTBE (3 x 30 mL). The combined organic phases were washed with H_2O (3 x 30 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the residue was purified by column chromatography (4 x 12 cm silica, pentane/EtOAc = 20/1). The product was obtained in 88% yield (2.51 g, 9.35 mmol) as a yellowish oil, which solidified in a refrigerator.

R*f* (pentane/EtOAc = 9/1): 0.29; **^{1}H NMR (300 MHz, $CDCl_3$):** 9.94 (s, 1H, CHO), 7.44-7.35 (m, 2H, H_{ar}), 7.31-7.15 (m, 4H, H_{ar}), 7.06-6.94 (m, 2H, H_{ar}), 5.45 (d, *J* = 1.0 Hz, 1H, $OCH_2C(Ph)=C\mathit{H}H$), 5.30-5.23 (m, 1H, $OCH_2C(Ph)=CH\mathit{H}$), 4.99 (d, *J* = 0.8 Hz, 2H, $O\mathit{CH_2}C(Ph)=CH_2$), 3.78 (s, 3H, OCH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 190.1, 152.8, 150.8, 143.4, 138.0, 130.0, 128.4, 128.0, 126.0, 124.0, 118.8, 117.7, 116.3, 75.5, 55.9; **ESI-MS:** calculated $[C_{17}H_{16}NaO_3]^+$: 291.0992, found: 291.0979; **ATR-FTIR (cm^{-1}):** 3063, 3009, 2941, 2885, 2842, 1859, 1694, 1596, 1583, 1480, 1457, 1439, 1392, 1372, 1315, 1261, 1247, 1231, 1213, 1186, 1065, 1034, 966, 955, 926, 911, 847, 778, 757, 736, 708, 678, 668, 632, 588, 534, 521, 514, 506.

6 Characterization of Chroman-4-ones

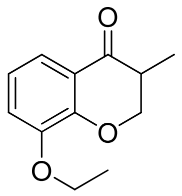
8-Methoxy-3-methyl-chroman-4-one (2a)



Following the general procedure, treatment of 2-allyloxy-3-methoxy benzaldehyde **1a** (0.19 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 8-Methoxy-3-methyl-chroman-4-one **2a** as a white solid (0.162 g, 85%); **R*f*** (pentane/EtOAc = 80/20): 0.21; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.48 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H, H_{ar}), 7.03 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H, H_{ar}), 6.94 (t,

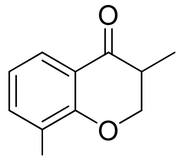
J = 7.9 Hz, 1H, H_{ar}), 4.59 (dd, J = 11.3 Hz, 5.0 Hz, 1H, OCH_2), 4.21 (t, J = 11.1 Hz, 1H, OCH_2), 3.89 (s, 3H, OCH_3), 2.93-2.79 (m, 1H, CH), 1.21 (d, J = 7.0 Hz, 3H, CH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** 194.80, 153.69, 148.78, 121.20, 120.91, 118.58, 116.41, 72.82, 56.29, 40.68, 10.81; **ESI-MS:** calculated $[M+Na]^+$ for $C_{11}H_{12}O_3Na$: 215.0679, found: 215.0686; **GC-MS, Rt (method A):** 8.08 min, **(EI) m/z (%):** 192 (76), 150 (46), 122 (100), 121 (38), 120 (25), 107 (21), 92 (12), 79 (7), 63 (6), 51 (12); **ATR-FTIR (cm^{-1}):** 2963, 2839, 1682, 1605, 1584, 1490, 1451, 1436, 1391, 1335, 1300, 1263, 1240, 1213, 1182, 1131, 1084, 1061, 1020, 981, 946.

8-Ethoxy-3-methyl-chroman-4-one (2b)



Following the general procedure, treatment of 2-allyloxy-3-ethoxy benzaldehyde **1b** (0.206 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 8-ethoxy-3-methyl-chroman-4-one **2b** as a white solid (0.139 g, 68%). **R_f** (pentane/EtOAc = 80/20): 0.32; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.44 (dd, J = 7.9 Hz, 1.2 Hz, 1H, H_{ar}), 7.00 (d, J = 6.9 Hz, 1H, H_{ar}), 6.89 (t, J = 7.9 Hz, 1H, H_{ar}), 4.57 (dd, J = 11.3 Hz, 5.0 Hz, 1H, OCH_2), 4.18 (t, J = 11.1 Hz, 1H, OCH_2), 4.07 (q, J = 7.0 Hz, 2H, OCH_2), 2.92-2.74 (m, 1H, CH), 1.45 (t, J = 7.0 Hz, 3H, CH_3), 1.18 (d, J = 7.0 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 194.84, 151.85, 148.04, 121.21, 120.78, 118.42, 117.62, 72.65, 64.67, 40.55, 14.76, 10.74; **ESI-MS:** calculated $[M+Na]^+$ for $C_{12}H_{14}O_3Na$: 229.0835, found: 229.0835; **GC-MS, Rt (method A):** 8.40 min, **(EI) m/z (%):** 206 (42), 178 (5), 164 (4), 149 (18), 136 (100), 120 (6), 108 (10), 80 (6), 52 (6); **ATR-FTIR (cm^{-1}):** 2981, 2876, 1680, 1603, 1580, 1492, 1473, 1446, 1400, 1389, 1342, 1295, 1262, 1238, 1205, 1173, 1145, 1112, 1086, 1062, 1023, 999, 937.

8-Allyloxy-3-methyl-chroman-4-one (2c)

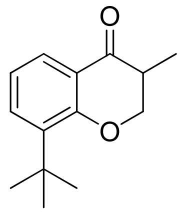


Following the general procedure, treatment of 2,3-diallyloxy benzaldehyde **1c** (0.218 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 8-allyloxy-3-methyl-chroman-4-one **2c** as a white solid (0.170 g, 78%).

R_f (pentane/EtOAc = 90/10): 0.18; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.46 (dd, J = 7.9 Hz, 1.6 Hz, 1H, H_{ar}), 7.01 (dd, J = 8.0 Hz, 1.5 Hz, 1H, H_{ar}), 6.88 (t, J = 7.9 Hz, 1H, H_{ar}), 6.05 (ddt, J

= 17.2 Hz, 10.8 Hz, 5.5 Hz, 1H, C*H*=CH2), 5.39 (dq, *J* = 17.3 Hz, 1.5 Hz, 1H, CH=CH_2), 5.28 (dq, *J* = 10.5 Hz, 1.3 Hz, 1H, CH=CH_2), 4.57 (m, 3H, OCH_{2allyl}, OCH_{2ring}), 4.17 (t, *J* = 11.2 Hz, 1H, OCH_2), 2.92-2.75 (m, 1H, CH), 1.18 (d, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, CDCl$_3$):** 194.73, 151.99, 147.63, 132.74, 121.30, 120.68, 118.83, 118.57, 118.38, 72.63, 70.10, 40.55, 10.71; **ESI-MS**: calculated $[M+Na]^+$ for $C_{13}H_{14}O_3Na$: 241.0835, found: 241.0831. **GC-MS, Rt (method A):** 8.64 min, **(EI) m/z (%):** 218 (69), 177 (72), 149 (13), 135 (47), 121 (8), 107 (100), 91 (8), 79 (13), 69 (14), 51 (18); **ATR-FTIR (cm^{-1}):** 2982, 2872, 1684, 1602, 1577, 1485, 1454, 1426, 1389, 1343, 1296, 1260, 1235, 1206, 1172, 1082, 1053, 1006, 983, 939.

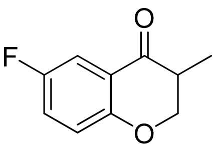
8-*Tert*-butyl-3-methyl-chroman-4-one (2d)



Following the general procedure, treatment of 2-allyloxy-3-*tert*-butyl benzaldehyde **1d** (0.218 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 8-*tert*-butyl-3-methyl-chroman-4-one **2d** as a white solid (0.208 g, 95%).

R$_f$ (pentane/EtOAc = 95/5): 0.33; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.81 (dd, *J* = 7.8 Hz, 1.7 Hz, 1H, H$_{ar}$), 7.45 (dd, *J* = 7.6 Hz, 1.7 Hz, 1H, H$_{ar}$), 6.94 (t, *J* = 7.7 Hz, 1H, H$_{ar}$), 4.54 (dd, *J* = 11.2 Hz, 5.0 Hz, 1H, OCH_2), 4.13 (t, *J* = 11.1 Hz, 1H, OCH_2), 2.85 (ddd, *J* = 10.9 Hz, 7.0 Hz, 5.0 Hz, 1H, CH), 1.38 (s, 9H, $C(CH_3)_3$), 1.22 (d, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, CDCl$_3$):** 195.61, 161.00, 138.89, 132.72, 125.56, 121.40, 120.90, 71.78, 40.64, 34.99, 29.70, 10.86; **ESI-MS**: calculated $[M+Na]^+$ for $C_{14}H_{18}O_2Na$: 241.1199, found: 241.1196; **GC-MS, Rt (method A):** 8.31 min, **(EI) m/z (%):** 218 (34), 203 (100), 175 (3), 161 (79), 148 (3), 133 (12), 115 (7), 103 (7), 77 (11), 65 (4); **ATR-FTIR (cm^{-1})**: 2952, 2874, 1676, 1592, 1479, 1464, 1430, 1387, 1356, 1336, 1292, 1268, 1250, 1215, 1189, 1143, 1085, 1023, 984, 949, 931.

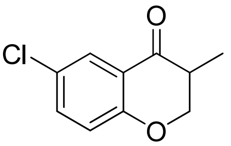
6-Fluoro-3-methyl-chroman-4-one (2e)



Following the general procedure, treatment of 2-allyloxy-5-fluoro benzaldehyde **1e** (0.180 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 6-fluoro-3-methyl-chroman-4-one **2e** as a white solid (0.103 g, 57%).

R$_f$ (pentane/EtOAc = 95/5): 0.22; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.52 (dd, *J* = 8.3 Hz, 3.2 Hz, 1H, H$_{ar}$), 7.17 (ddd, *J* = 9.1 Hz, 7.7 Hz, 3.2 Hz, 1H, H$_{ar}$), 6.93 (dd, *J* = 9.1 Hz, 4.2 Hz, 1H, H$_{ar}$), 4.48 (dd, *J* = 11.4 Hz, 5.1 Hz, 1H, OCH$_2$), 4.12 (t, *J* = 11.2 Hz, 1H, OCH$_2$), 2.92-2.74 (m, 1H, CH), 1.21 (d, *J* = 7.0 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 194.19, 158.94, 158.08, 155.74, 123.35, 119.50, 112.35, 72.47, 40.68, 10.70; **ESI-MS:** calculated [M+Na]$^+$ for $C_{10}H_9O_2FNa$: 203.0479, found: 203.0479; **GC-MS, Rt (method A):** 7.36min, **(EI) m/z (%):** 180 (43), 139 (11), 138 (100), 110 (46), 94 (4), 82 (16), 63 (4), 57 (3), 41 (4); **ATR-FTIR (cm^{-1})**: 2954, 1682, 1619, 1484, 1433, 1293, 1261, 1203, 1160, 1122, 1022, 955, 901, 875, 821.

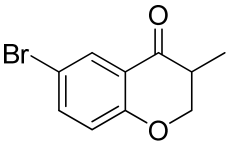
6-Chloro-3-methyl-chroman-4-one (2f)



Following the general procedure, treatment of 2-allyloxy-5-chloro benzaldehyde **1f** (0.197 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 μL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 6-chloro-3-methyl-chroman-4-one **2f** as a white solid (0.121 g, 62%).

R$_f$ (pentane/EtOAc = 90/10): 0.33; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.83 (d, *J* = 2.7 Hz, 1H, H$_{ar}$), 7.39 (dd, *J* = 8.8 Hz, 2.7 Hz, 1H, H$_{ar}$), 6.92 (d, *J* = 8.8 Hz, 1H, H$_{ar}$), 4.50 (dd, *J* = 11.4 Hz, 5.1 Hz, 1H, OCH$_2$), 4.14 (t, *J* = 11.2 Hz, 1H, OCH$_2$), 2.93-2.77 (m, 1H, CH), 1.21 (d, *J* = 7.0 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 193.82, 160.28, 135.66, 126.98, 126.76, 121.41, 119.62, 72.41, 40.64, 10.70; **ESI-MS:** calculated [M+Na]$^+$ for $C_{10}H_9O_2ClNa$: 219.0183, found: 219.0189; **GC-MS, Rt (method A):** 8.06 min, **(EI) m/z (%):** 196 (43), 156 (33), 154 (100), 128 (11), 126 (39), 98 (8), 75 (6), 63 (18); **ATR-FTIR (cm^{-1}):** 2995, 2882, 1686, 1603, 1476, 1457, 1420, 1317, 1291, 1262, 1222, 1181, 1136, 1104, 1020, 987, 950.

6-Bromo-3-methyl-chroman-4-one (2g)

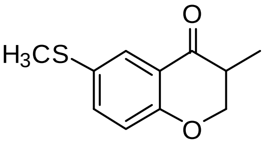


Following the general procedure, treatment of 2-allyloxy-5-bromo benzaldehyde **1g** (0.241 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 μL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 6-bromo-3-methyl-chroman-4-one **2g** as a white solid (0.134 g, 56%).

R$_f$ (pentane/EtOAc = 90/10): 0.33; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.98 (d, *J* = 2.5 Hz, 1H, H$_{ar}$), 7.52 (dd, *J* = 8.8 Hz, 2.6 Hz, 1H, H$_{ar}$), 6.86 (d, *J* = 8.8 Hz, 1H, H$_{ar}$), 4.50 (dd, *J* = 11.4

Hz, 5.1 Hz, 1H, OCH_2), 4.13 (t, *J* = 11.2 Hz, 1H, OCH_2), 2.93-2.77 (m, 1H, CH), 1.21 (d, *J* = 7.0 Hz, 3H, CH_3); **13C NMR (75 MHz, $CDCl_3$):** 193.67, 160.72, 138.43, 129.88, 121.90, 119.98, 114.12, 72.37, 40.59, 10.70; **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_9O_2BrNa$: 262.9678, found: 262.9686; **GC-MS, Rt (method A):** 8.38 min, **(EI) m/z (%):** 242 (43), 240 (44), 200 (98), 199 (10), 198 (100), 172 (33), 170 (33), 144 (6), 91 (5), 63 (36), 62(10); **ATR-FTIR (cm^{-1})**: 2994, 2879, 1688, 1600, 1568, 1473, 1455, 1415, 1315, 1291, 1260, 1222, 1183, 1136, 1099, 1018, 950.

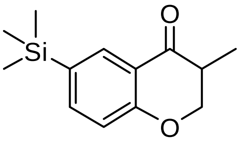
3-Methyl-6-methylsulfanyl-chroman-4-one (2h)



Following our general procedure, 2-allyloxy-5-methylsulfanyl-benzaldehyde (**1h**) (208.3 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 24 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 36 cm silica, pentane/EtOAc 19/1) the product was obtained in 51% yield (106 mg, 0.51 mmol) as a yellow liquid.

R_f (pentane/EtOAc = 19/1): 0.18; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.78 (d, *J* = 2.5 Hz, 1H, H_{ar}), 7.41 (dd, *J* = 8.7, 2.5 Hz, 1H, H_{ar}), 6.91 (d, *J* = 8.7 Hz, 1H, H_{ar}), 4.49 (dd, *J* = 11.3, 5.0 Hz, 1H, OC*H*H), 4.14 (t, *J* = 10.1 Hz, 1H, OCH*H*), 2.85 (ddq, *J* = 10.9, 7.0, 5.0 Hz, 1H, C(=O)C*H*), 2.48 (s, 3H, SCH_3), 1.22 (d, *J* = 7.0 Hz, 3H, CHCH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** 194.3, 159.9, 135.6, 130.8, 125.4, 120.8, 118.5, 72.2, 40.6, 17.0, 10.7; **ESI-MS:** calculated $[C_{11}H_{12}NaO_2S]^+$: 231.0450, found: 231.0453; **GC-MS, Rt (method B):** 8.81 min, **(EI) m/z (%):**208 (81), 193 (3), 166 (100), 163 (1), 161 (1), 151 (11), 150 (1), 138 (7), 123 (13), 122 (1), 107 (1), 103 (1), 91 (2), 70 (2), 58 (1); **ATR-FTIR (cm^{-1}):** 2975, 2921, 2873, 1694, 1601, 1479, 1413, 1290, 1190, 1020, 895, 632, 548, 533, 502.

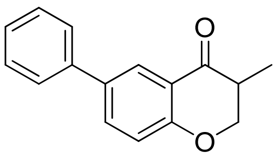
3-Methyl-6-trimethylsilanyl-chroman-4-one (2i)



Following our general procedure, 2-allyloxy-5-trimethylsilanyl-benzaldehyde (**1i**) (234.4 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 24 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 32 cm silica, pentane/EtOAc = 100/1) the product was obtained in 39% yield (91.8 mg, 0.39 mmol) as a yellow liquid.

R*f* (pentane/EtOAc = 50/1): 0.15; **^{1}H NMR (400 MHz, CDCl$_3$):** 8.05 (br d, *J* = 1.7 Hz, 1H, H$_{ar}$), 7.60 (dd, *J* = 8.2, 1.7 Hz, 1H, H$_{ar}$), 6.95 (d, *J* = 8.2 Hz, 1H, H$_{ar}$), 4.50 (dd, *J* = 11.3, 5.0 Hz, 1H, OC*H*H), 4.15 (t, *J* = 11.0 Hz, 1H, OCH*H*), 2.93-2.79 (m, 1H, C(=O)CH), 1.22 (d, *J* = 7.0 Hz, 3H, CHC*H*$_3$), 0.26 (s, 9H, Si(CH$_3$)$_3$).; **^{13}C NMR (100 MHz, CDCl$_3$):** 195.1, 162.3, 140.6, 132.7, 132.6, 119.9, 117.2, 72.2, 40.8, 10.8, −1.1; **ESI-MS:** calculated [$C_{13}H_{18}NaO_2Si$]$^+$: 257.0968, found: 257.0966; **GC-MS, Rt (method B):** 8.42 min, **(EI) m/z (%):** 234 (15), 219 (100), 192 (2), 189 (1), 178 (4), 145 (1), 119 (2), 103 (1), 91 (2), 75 (2), 73 (2); **ATR-FTIR (cm^{-1}):** 2956, 2877, 1693, 1597, 1566, 1488, 1458, 1400, 1331, 1294, 1280, 1249, 1225, 1192, 1145, 1113, 1102, 1084, 1022, 988, 965, 949, 861, 830, 757, 724, 694, 632, 604, 538.

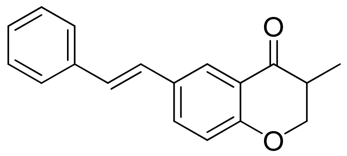
3-Methyl-6-phenyl chroman-4-one (2j)



Following the general procedure, treatment of 2-allyloxy-5-phenyl benzaldehyde **1j** (0.238 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 μL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 3-methyl-6-phenyl-chroman-4-one **2j** as a white solid (0.155 g, 65%).

R*f* (pentane/EtOAc = 90/10): 0.28; **^{1}H NMR (400 MHz, CDCl$_3$):** 8.14 (d, *J* = 2.4 Hz, 1H, Har), 7.73 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H, H$_{ar}$), 7.58 (dd, *J* = 8.3 Hz, 1.3 Hz, 2H, H$_{ar}$), 7.48-7.40 (m, 2H, H$_{ar}$), 7.37-7.30 (m, 1H, H$_{ar}$), 7.05 (d, *J* = 8.6 Hz, 1H, H$_{ar}$), 4.54 (dd, *J* = 11.3 Hz, 5.1 Hz, 1H, OCH$_2$), 4.20 (t, *J* = 11.1 Hz, 1H, OCH$_2$), 2.99-2.82 (m, 1H, CH), 1.25 (d, *J* = 7.0 Hz, 3H, CH3); **^{13}C NMR (100 MHz, CDCl$_3$):** 194.98, 161.26, 139.82, 134.56, 128.99, 127.42, 126.87, 125.55, 118.40, 72.44, 40.92, 10.90; **ESI-MS**: calculated [M+Na]$^+$ for $C_{16}H_{14}O_2Na$: 261.0886, found: 261.0878; **GC-MS, Rt (method A):** 9.77min, **(EI) m/z (%):** 238 (62), 197 (16), 196 (100), 168 (21), 140 (21), 139 (52), 115 (4), 102 (4), 63 (4); **ATR-FTIR (cm^{-1})**: 2979, 2882, 1688, 1609, 1511, 1476, 1453, 1410, 1332, 1298, 1269, 1228, 1183, 1144, 1123, 1099, 1040, 1012, 978, 950.

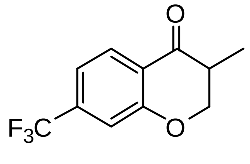
3-Methyl-6-(2-phenylvinyl) chroman-4-one (2k)



Following the general procedure, treatment of 2-allyloxy-5-(2-phenylvinyl) benzaldehyde **1k** (0.106 g, 0.4 mmol) with thiazolium salt **3** (29.8 mg, 0.08 mmol) and DBU (24 μL, 0.16 mmol) in 1,4-dioxane (1 mL) at 120 °C for 2 h followed by column chromatography afforded 3-methyl-6-(2-phenylvinyl) chroman-4-one **2j** as a white solid (0.066 g, 62%).

R*f* (pentane/EtOAc = 90/10): 0.37; **^{1}H NMR (300 MHz, CDCl$_3$):** 8.02 (d, J = 2.3 Hz, 1H, H$_{ar}$), 7.65 (dd, J = 8.6 Hz, 2.3 Hz, 1H, H$_{ar}$), 7.53-7.48 (m, 2H, H$_{ar}$), 7.36 (dd, J = 8.1 Hz, 6.7 Hz, 2H, H$_{ar}$), 7.29-7.22 (m, 3H, H$_{ar}$), 7.06 (s, 2H, CH=CH), 6.97 (d, J = 8.6 Hz, 1H, H$_{ar}$), 4.53 (dd, J = 11.3 Hz, 5.1 Hz, 1H, OCH$_2$), 4.18 (t, J = 11.1 Hz, 1H, OCH$_2$), 2.89 (ddd, J = 10.9 Hz, 7.0 Hz, 5.1 Hz, 1H, CH), 1.24 (d, J = 7.0 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 194.93, 161.30, 137.26, 133.63, 131.10, 128.85, 128.40, 127.78, 127.21, 126.56, 125.18, 120.60, 118.32, 72.42, 40.89, 10.88; **ESI-MS**: calculated [M+Na]$^+$ for $C_{18}H_{16}O_2Na$: 287.1043, found: 287.1045; **GC-MS, Rt (method A):** 11.05 min, **(EI) m/z (%):** 264 (94), 222 (44), 221 (15), 194 (13), 166 (23), 165 (100), 164 (12), 152 (4), 139 (10), 115 (7), 82 (8); **ATR-FTIR (cm^{-1}):** 2978, 2880, 1689, 1654, 1606, 1573, 1491, 1450, 1424, 1388, 1335, 1291, 1260, 1223, 1199, 1167, 1142, 1093, 1075, 1019, 998, 960.

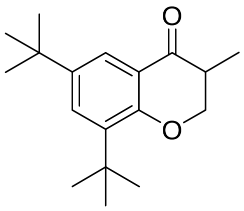
3-Methyl-7-trifluoromethyl-chroman-4-one (2l)



Following our general procedure, 2-allyloxy-4-trifluoromethyl-benzaldehyde (**1l**) (230 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 μL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 ˚C for 2 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2.5 x 8 cm silica, pentane/EtOAc 10/1) the product was obtained in 58% yield (134 mg, 0.584 mmol) as a light yellow solid.

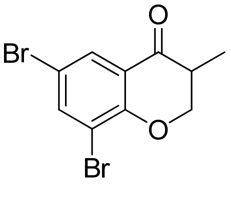
R*f* (pentane/EtOAc = 10/1): 0.48; **^{1}H NMR (300 MHz, CDCl$_3$):** 8.0 (d, J = 8.6 Hz, 1H, H$_{ar}$), 7.24 (s, 2H, H$_{ar}$), 4.59-4.53 (m, 1H, CH$_2$), 4.20 (m, 1H, CH$_2$), 2.94-2.89 (m, 1H, C*H*CH$_3$), 1.24 (t, J = 6.9 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 194.0 (C=O), 161.6 (C$_{ar}$), 136.9 (q, $J_{(C,F)}$ = 33.1 Hz, C$_{ar}$CF$_3$), 128.4 (CH$_{ar}$), 123.3 (d, $J_{(C,F)}$ = 272.9 Hz, CF$_3$), 122.8 (C$_{ar}$), 117.8 (q, $J_{(C,F)}$ = 3.6 Hz, CH$_{ar}$), 115.5 (q, $J_{(C,F)}$ = 3.9 Hz, CH$_{ar}$), 72.5 (CH), 40.8 (CH$_2$), 10.6 (CH$_3$); **^{19}F NMR (282.2 MHz, CDCl$_3$):** 63.66; **ESI-MS:** calculated [$C_{11}H_9F_3O_2Na$]$^+$: 253.0447, found: 253.0440; calculated [$(C_{11}H_9F_3O_2)_2Na]^+$: 483.1001, found: 483.0994; **GC-MS, Rt (method A):** 7.3 min, **(EI) m/z (%):** 230.1 (37), 189.0 (12), 188.0 (100), 160.0 (58), 132.0 (13); **ATR-FTIR (cm^{-1}):** 3059, 2990, 2944, 2890, 1689, 1628, 1580, 1550, 1494, 1469, 1436, 1381, 1333, 1311, 1253, 1208, 1166, 1138, 1120, 1101, 1084, 1065, 1025, 974, 945, 897, 827, 765, 731, 695, 675, 653, 620, 577, 525.

6,8-Di-*tert*-butyl-3-methyl-chroman-4-one (2m)



Following the general procedure, treatment of 2-allyloxy-3,5-di-*tert*-butyl benzaldehyde **1m** (0.274 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 6,8-di-*tert*-butyl-3-methyl-chroman-4-one **2m** as a white solid (0.262 g, 96%). **R*f*** (pentane/EtOAc = 95/5): 0.49; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.81 (d, *J* = 2.6 Hz, 1H, H_{ar}), 7.53 (d, *J* = 2.6 Hz, 1H, H_{ar}), 4.52 (dd, *J* = 11.1 Hz, 5.0 Hz, 1H, OCH_2), 4.12 (t, *J* = 10.9 Hz, 1H, OCH_2), 2.83 (ddq, *J* = 10.8 Hz, 7.0 Hz, 5.0 Hz, 1H, CH), 1.40 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.22 (d, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 196.01, 159.01, 143.29, 138.26, 130.51, 121.44, 120.65, 71.79, 40.73, 35.20, 34.60, 31.47, 29.81, 11.05; **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{26}O_2Na$: 297.1825, found: 297.1820; **ATR-FTIR (cm^{-1})**: 2955, 2872, 1691, 1601, 1478, 1441, 1383, 1363, 1299, 1242, 1218, 1196, 1179, 1136, 1032, 1002, 950, 899, 866.

6,8-Dibromo-3-methyl-chroman-4-one (2n)

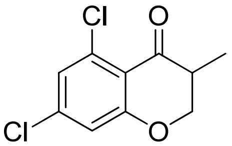


Following the general procedure, treatment of 2-allyloxy-3,5-dibromo benzaldehyde **1n** (0.320 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 6,8-dibromo-3-methyl-chroman-4-one **2n** as a white solid (0.227 g, 71%).

R*f* (pentane/EtOAc = 90/10): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.95 (d, *J* = 2.4 Hz, 1H, H_{ar}), 7.82 (d, *J* = 2.4 Hz, 1H, H_{ar}), 4.63 (dd, *J* = 11.5 Hz, 5.2 Hz, 1H, OCH_2), 4.22 (t, *J* = 11.4 Hz, 1H, OCH_2), 2.94-2.85 (m, 1H, CH), 1.22 (d, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** 192.75, 157.28, 140.90, 129.37, 122.51, 114.02, 112.68, 72.87, 40.25, 10.59; **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_8O_2Br_2Na$: 342.8763, found: 342.8779; **GC-MS, Rt (method A):** 8.96 min, **(EI) m/z (%):** 320 (39), 318 (21), 280 (50), 278 (100), 276 (51), 250

(10), 199 (9), 197 (10), 143 (15), 141 (14), 62 (14); **ATR-FTIR (cm^{-1}):** 2969, 2876, 1689, 1662, 1584, 1556, 1472, 1444, 1429, 1405, 1379, 1288, 1242, 1180, 1083, 1007, 983, 944.

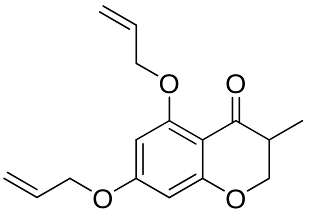
5,7-Dichloro-3-methyl-chroman-4-one (2o)



Following the general procedure, treatment of 2-allyloxy-4,6-dichloro benzaldehyde **1o** (0.231 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 μL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 5,7-dichloro-3-methyl-chroman-4-one **2o** as a white solid (0.132 g, 57%).

R_f (pentane/EtOAc = 90/10): 0.49; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.03 (d, *J* = 2.0 Hz, 1H, H_{ar}), 6.90 (d, *J* = 2.0 Hz, 1H, H_{ar}), 4.49 (dd, *J* = 11.3 Hz, 5.2 Hz, 1H, OCH_2), 4.14 (t, *J* = 11.3 Hz, 1H, OCH_2), 2.87 (ddd, *J* = 11.2 Hz, 6.9 Hz, 5.2 Hz, 1H, CH), 1.19 (d, *J* = 6.9 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 192.05, 163.23, 140.13, 135.57, 124.86, 117.11, 116.49, 72.03, 41.26, 10.62; **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_8O_2Cl_2Na$: 252.9794, found: 252.9791. **GC-MS, Rt (method A):** 8.64 min, **(EI) m/z (%):** 230 (43), 192 (11), 190 (66), 189 (10), 188 (100), 162 (23), 160 (38), 97 (11); **ATR-FTIR (cm^{-1}):** 2983, 2900, 1688, 1590, 1552, 1498, 1472, 1459, 1419, 1378, 1367, 1314, 1236, 1201, 1173, 1115, 1088, 1035, 972.

5,7-Diallyloxy-3-methyl-chroman-4-one (2p)

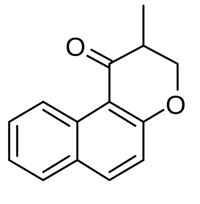


Following the general procedure, treatment of 2-allyloxy-4,6-dichloro benzaldehyde **1p** (0.274 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 μL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 3 h followed by column chromatography afforded 5,7-diallyloxy-3-methyl-chroman-4-one **2p** as a white solid (0.180 g, 66%).

R_f (pentane/EtOAc = 80/20): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** 6.12-5.93 (m, 4H, H_{ar}, C*H*=CH_2), 5.64 (dq, *J* = 17.2 Hz, 1.7 Hz, 1H, CH=CH_2), 5.39 (dq, *J* = 17.3 Hz, 1.5 Hz, 1H, CH=CH_2), 5.34-5.26 (m, 2H, CH=CH_2), 4.57-4.47 (m, 4H, OCH_{2allyl}), 4.38 (dd, *J* = 11.0 Hz, 5.0 Hz, 1H, OCH_{2ring}), 4.05 (t, *J* = 10.8 Hz, 1H, OCH_{2ring}), 2.72 (ddd, *J* = 10.5 Hz, 7.0 Hz, 5.0 Hz, 1H, CH), 1.15 (d, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 192.05, 164.96, 164.37, 161.23, 132.27, 118.44, 117.68, 105.74, 94.39, 94.08, 72.00, 69.35, 69.00, 41.22, 11.11; **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{18}O_4Na$: 297.1097, found: 297.1097; **ATR-**

FTIR (cm^{-1}): 2991, 2872, 1677, 1602, 1572, 1508, 1469, 1443, 1402, 1362, 1331, 1288, 1250, 1227, 1200, 1168, 1135, 1114, 1051, 1023, 998, 954, 942.

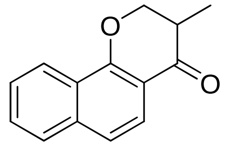
2-Methyl-2,3-dihydro-benzo[*f*]chromen-1-one (2q)



Following the general procedure, treatment of 2-allyloxy-1-naphthaldehyde **1q** (0.212 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 2-Methyl-2,3-dihydro-benzo[*f*]chromen-1-one **2q** as a white solid (0.202 g, 95%).

R*f* (pentane/EtOAc = 90/10): 0.33; **^{1}H NMR (300 MHz, CDCl$_3$):** 9.49 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 7.89 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 7.73 (d, *J* = 8.0 Hz, 1H, H$_{ar}$), 7.63 (ddd, *J* = 8.6 Hz, 6.9 Hz, 1.5 Hz, 1H, H$_{ar}$), 7.42 (ddd, *J* = 8.0 Hz, 7.0 Hz, 1.1 Hz, 1H, H$_{ar}$), 7.07 (d, *J* = 9.0 Har, 1H, H$_{ar}$), 4.58 (dd, *J* = 11.2 Hz, 5.1 Hz, 1H, OCH$_2$), 4.25 (t, *J* = 10.9 Hz, 1H, OCH$_2$), 2.93 (dqd, *J* = 10.8 Hz, 7.0 Hz, 5.1 Hz, 1H, CH), 1.27 (d, *J* = 7.0 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 196.15, 163.62, 137.25, 131.80, 129.59, 129.27, 128.45, 125.89, 124.80, 118.75, 111.98, 72.16, 41.32, 11.38; **ESI-MS:** calculated [M+Na]$^+$ for C$_{14}$H$_{12}$O$_2$Na : 235.0730, found: 235.0728; **GC-MS, Rt (method A):** 9.17 min, **(EI) m/z (%):** 212 (43), 171 (13), 170 (100), 142 (27), 114 (40), 113 (11), 63 (4); **ATR-FTIR (cm^{-1}):** 2971, 2874, 1667, 1618, 1597, 1568, 1511, 1471, 1434, 1381, 1345, 1291, 1233, 1207, 1178, 1129, 1109, 1051, 1029, 990, 957.

3-Methyl-2,3-dihydro-benzo[*h*]chromen-4-one (2r)

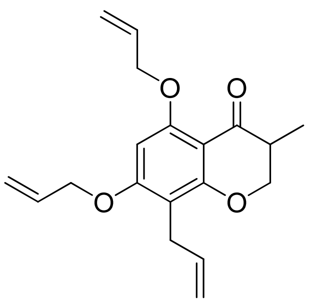


Following the general procedure, treatment of 1-allyloxy-2-naphthaldehyde **1r** (0.212 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 2 h followed by column chromatography afforded 3-methyl-2,3-dihydro-benzo[*h*]chromen-4-one **2r** as a white solid (0.171 g, 81%).

R*f* (pentane/EtOAc = 90/10): 0.30; **^{1}H NMR (300 MHz, CDCl$_3$):** 8.32-8.25 (m, 1H, H$_{ar}$), 7.88 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 7.78 (d, *J* = 8.1 Hz, 1H, H$_{ar}$), 7.60 (ddd, *J* = 8.2 Hz, 6.9 Hz, 1.4 Hz, 1H, H$_{ar}$), 7.52 (ddd, *J* = 8.2 Hz, 6.9 Hz, 1.3 Hz, 1H, H$_{ar}$), 7.39 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 4.73 (dd, *J* = 11.2 Hz, 5.1 Hz, 1H, OCH$_2$), 4.34 (t, *J* = 11.1 Hz, 1H, OCH$_2$), 3.01-2.86 (m, 1H, CH), 1.28 (d, *J* = 7.0 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 194.60, 159.94, 137.39, 132.34, 129.57, 128.60, 127.90, 126.24, 124.85, 123.43, 122.21, 121.06, 114.99, 73.04, 40.14, 11.05; **ESI-MS:** calculated [M+Na]$^+$ for C$_{14}$H$_{12}$O$_2$Na : 235.0730, found: 235.0729. **GC-MS,**

Rt (method A): 9.22 min, **(EI) m/z (%):** 212 (41), 171 (13), 170 (100), 142 (4), 115 (9), 114 (46), 113 (11), 88 (6), 63 (4). **ATR-FTIR (cm^{-1}):** 2984, 2873, 1677, 1623, 1596, 1573, 1509, 1456, 1435, 1366, 1322, 1294, 1269, 1244, 1230, 1195, 1151, 1132, 1090, 1075, 1016, 973.

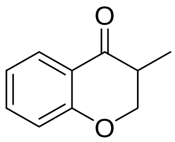
8-Allyl-5,7-diallyloxy-3-methyl-chroman-4-one (2s)



Following the general procedure, treatment of 3-allyl-2,4,6-triallyloxy benzaldehyde **1s** (0.100 g, 0.32 mmol) with thiazolium salt **3** (23.7 mg, 0.064 mmol) and DBU (19 µL, 0.123 mmol) in 1,4-dioxane (1 mL) at 120 °C for 2 h followed by column chromatography afforded 8-allyl-5,7-diallyloxy-3-methyl-chroman-4-one **2s** as a yellow solid (0.77 g, 77%).

R*f* (pentane/EtOAc = 80/20): 0.27; **^{1}H NMR (300 MHz, $CDCl_3$):** 6.13-5.81 (m, 4H, H_{ar}, C*H*=CH_2), 5.61 (dq, *J* = 17.2 Hz, 1.7 Hz, 1H, CH=CH_2), 5.42-5.24 (m, 3H, CH=CH_2), 4.92 (ddq, *J* = 9.2 Hz, 7.5 Hz, 1.6 Hz, 2H, CH=CH_2), 4.55 (ddd, *J* = 6.5 Hz, 3.8 Hz, 1.4 Hz, 4H, OCH_{2allyl}), 4.41 (dd, *J* = 11.0 Hz, 4.9 Hz, 1H, OCH_{2ring}), 4.03 (t, *J* = 10.7 Hz, 1H, OCH_{2ring}), 3.31 (dt, *J* = 6.1 Hz, 1.5 Hz, 2H, CH_2), 2.71 (ddd, *J* = 10.4 Hz, 7.0 Hz, 4.9 Hz, 1H, CH), 1.15 (d, *J* = 7.0 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 192.74, 161.62, 159.78, 136.42, 132.59, 117.58, 114.15, 108.39, 105.82, 91.23, 71.85, 69.57, 68.90, 41.28, 26.73, 11.09. **ESI-MS:** calculated $[M+Na]^+$ for $C_{19}H_{22}O_4Na$: 337.1410, found: 337.1410. **ATR-FTIR (cm^{-1}):** 2980, 2899, 1675, 1635, 1595, 1579, 1490, 1450, 1422, 1133, 1317, 1285, 1234, 1218, 1155, 1128, 1074, 1028, 993, 954.

3-Methyl-chroman-4-one (2t)

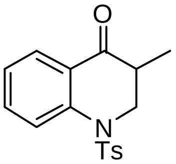


Following the general procedure, treatment of 2-allyloxy-benzaldehyde **1t** (0.162 g, 1 mmol) with thiazolium salt **3** (74.4 mg, 0.2 mmol) and DBU (60 µL, 0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C for 6 h followed by column chromatography afforded 3-methyl-chroman-4-one **2t** as a colorless liquid (0.98 g, 60%).

R*f* (pentane/EtOAc = 95/5): 0.22; **^{1}H NMR (300 MHz, $CDCl_3$):** 7.89 (dd, *J* = 7.9 Hz, 1.7 Hz, 1H, H_{ar}), 7.50-7.42 (m, 1H, H_{ar}), 7.04-6.92 (m, 2H, H_{ar}), 4.50 (dd, *J* = 11.3 Hz, 5.1 Hz, 1H, OCH_2), 4.15 (t, *J* = 11.1 Hz, 1H, OCH_2), 2.86 (ddd, *J* = 11.0 Hz, 7.0 Hz, 5.1 Hz, 1H, CH), 1.22 (d, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 194.96, 161.84, 135.82, 127.47, 121.46, 120.66, 117.85, 72.33, 40.84, 10.81; **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_{10}O_2Na$:

185.0573, found: 185.0576; **GC-MS, Rt (method A):** 7.43 min, **(EI) m/z (%):** 162 (46), 121 (8), 120 (100), 92 (51), 65 (4), 64 (10), 63 (10); **ATR-FTIR (cm^{-1}):** 2974, 2934, 2877, 1688, 1606, 1580, 1478, 1456, 1387, 1325, 1296, 1248, 1212, 1148, 1129, 1104, 1038, 1014, 941.

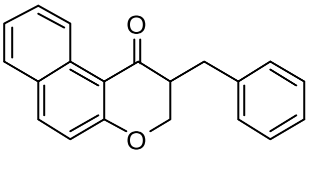
3-Methyl-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-quinolin-4-one (2u)



Following our general procedure, *N*-allyl-*N*-(2-formyl-phenyl)-4-methyl-benzenesulfonamide (**1u**) (217.0 mg, 0.69 mmol, 1.0 eq.) and catalyst **3** (51.2 mg, 0.14 mmol, 0.2 eq.) were mixed in 1.4 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (41.9 mg, 41 μL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 132 h. The crude mixture was carefully pre-absorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 26 cm silica, pentane/EtOAc = 10/1) the product was obtained in 71% yield (154.8 mg, 0.49 mmol) as an off-white solid.

R$_f$ (pentane/EtOAc = 9/1): 0.16; **^{1}H NMR (300 MHz, CDCl$_3$):** 7.96 (ddd, *J* = 7.8, 1.8, 0.3 Hz, 1H, H$_{ar}$), 7.84 (ddd, *J* = 8.5, 1.0, 0.3 Hz, 1H, H$_{ar}$), 7.65-7.58 (m, 2H, H$_{ar}$), 7.53 (ddd, *J* = 8.5, 7.3, 1.8 Hz, 1H, H$_{ar}$), 7.29-7.18 (m, 3H, H$_{ar}$), 4.48 (dd, *J* = 14.0, 5.1 Hz, 1H, NC*H*H), 3.64 (dd, *J* = 14.0, 12.7 Hz, 1H, NCH*H*), 2.46 (ddq, *J* = 12.7, 6.8, 5.1 Hz, 1H, CH$_3$CH), 2.39 (s, 3H, SO$_2$C$_6$H$_4$C*H*$_3$), 1.13 (d, *J* = 6.8 Hz, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 195.5, 144.5, 142.4, 136.8, 134.4, 130.0, 128.1, 126.8, 125.0, 124.6, 123.0, 52.3, 40.2, 21.5, 12.3; **ESI-MS:** calculated [C$_{17}$H$_{17}$NNaO$_3$S]$^+$: 338.0821, found: 338.0813; **GC-MS, Rt (method B):** 11.24 min, **(EI) m/z (%):** 315 (55), 273 (10), 160 (85), 155 (29), 145 (2), 132 (34), 117 (25), 104 (6), 91 (100), 77 (31), 64 (9); **ATR-FTIR (cm^{-1}):** 3036, 2983, 2941, 2881, 1687, 1597, 1474, 1453, 1378, 1347, 1295, 1222, 1185, 1160, 1086, 1067, 1037, 976, 961, 900, 873, 808, 782, 758, 736, 674, 660, 620, 572, 547, 534.

2-Benzyl-2,3-dihydro-benzo[*f*]chromen-1-one (9b)

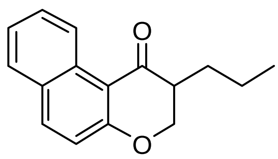


Following our general procedure, 2-((*E*)-3-phenyl-allyloxy)-naphthalene-1-carbaldehyde (**8b**) (288.3 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 μL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 2 h. The crude mixture was carefully pre-absorbed on silica on the rotary evaporator. After purification by column chromatography (2 x

12.5 cm silica, pentane/EtOAc 100/1) and by preparative TLC (pentane/MTBE = 9/1) the product was obtained in 25% yield (71.1 mg, 0.25 mmol) as a light yellow oil.

R*f* (pentane/EtOAc = 9/1): 0.60; **^{1}H NMR (400 MHz, $CDCl_3$):** 9.51 (br d, *J* = 8.7 Hz, 1H, H_{ar}), 7.93 (d, *J* = 9.0 Hz, 1H, H_{ar}), 7.80-7.75 (m, 1H, H_{ar}), 7.66 (ddd, *J* = 8.7, 7.0, 1.4 Hz, 1H, H_{ar}), 7.45 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, H_{ar}), 7.38-7.31 (m, 2H, H_{ar}), 7.31-7.23 (m, 3H, H_{ar}), 7.11 (d, *J* = 9.0 Hz, 1H, H_{ar}), 4.46 (dd, *J* = 11.4, 4.4 Hz, 1H, OC*H*H), 4.29 (dd, *J* = 11.4, 7.8 Hz, 1H, OCH*H*), 3.35 (dd, *J* = 13.8, 4.4 Hz, 1H, C*H*HPh), 3.04-2.94 (m, 1H, C(=O)CH), 2.78 (dd, *J* = 13.8, 10.6 Hz, 1H, CH*H*Ph); **^{13}C NMR (100 MHz, $CDCl_3$):** 194.9, 163.4, 138.4, 137.4, 131.7, 129.6, 129.2, 129.1, 128.7, 128.4, 126.6, 125.8, 124.8, 118.6, 112.0, 69.2, 48.4, 33.0; **ESI-MS:** calculated $[C_{20}H_{16}NaO_2]^+$: 311.1043, found: 311.1032; **GC-MS, Rt (method B):** 11.89 min, **(EI) m/z (%):** 288 (49), 197 (6), 170 (100), 142 (16), 91 (25); **ATR-FTIR (cm^{-1}):** 3105, 3086, 3060, 3027, 2925, 2875, 1736, 1668, 1617, 1598, 1568, 1513, 1471, 1454, 1435, 1403, 1376, 1365, 1345, 1280, 1238, 1208, 1170, 1155, 1143, 1127, 1052, 1030, 1003, 991, 895, 824, 755, 702, 632, 550, 535, 508, 500.

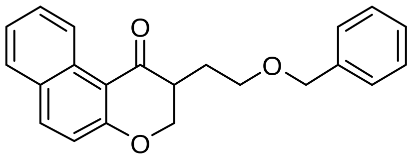
2-Propyl-2,3-dihydro-benzo[*f*]chromen-1-one (9c)



Following our general procedure, 2-[((*Z*)-pent-2-enyl)oxy]-naphthalene-1-carbaldehyde (**8c**) (240.3 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 2 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 28 cm silica, pentane/EtOAc 30/1) the product was obtained in 2% yield (5.4 mg, 0.02 mmol) as a greenish oil.

R*f* (pentane/EtOAc = 9/1): 0.64; **^{1}H NMR (400 MHz, $CDCl_3$):** 9.49-9.44 (m, 1H, H_{ar}), 7.91 (d, *J* = 9.0 Hz, 1H, H_{ar}), 7.77-7.72 (m, 1H, H_{ar}), 7.63 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1H, H_{ar}), 7.42 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, H_{ar}), 7.08 (d, *J* = 9.0 Hz, 1H, H_{ar}), 4.62 (dd, *J* = 11.3, 4.3 Hz, 1H, OC*H*H), 4.40 (dd, *J* = 11.3, 7.6 Hz, 1H, OCH*H*), 2.76-2.68 (m, 1H, C(=O)CH), 1.97-1.84 (m, 1H, C*H*HCH_2CH_3), 1.62-1.38 (m, 3H, CH*H*CH_2CH_3, CH_2C*H*$_2CH_3$), 0.97 (t, *J* = 7.2 Hz, 3H, CH_2CH_2C*H*$_3$); **^{13}C NMR (100 MHz, $CDCl_3$):** 196.0, 163.2, 137.1, 131.8, 129.5, 129.2, 128.4, 125.8, 124.7, 118.6, 112.0, 70.3, 46.5, 29.1, 20.3, 14.0; **ESI-MS:** calculated $[C_{16}H_{16}NaO_2]^+$: 263.1043, found: 263.1034; **GC-MS, Rt (method B):** 9.70 min, **(EI) m/z (%):** 240 (23), 197 (15), 170 (100), 142 (26), 114 (50); **ATR-FTIR (cm^{-1}):** 2961, 2930, 2872, 1671, 1618, 1598, 1569, 1513, 1471, 1435, 1376, 1277, 1261, 1237, 1207, 890, 823, 795, 754, 632, 537.

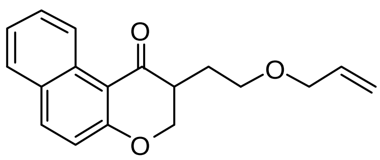
2-(2-Benzyloxy-ethyl)-2,3-dihydro-benzo[*f*]chromen-1-one (9d)



Following our general procedure, 2-((*Z*)-4-Benzyloxybut-2-enyloxy)-naphthalene-1-carbaldehyde (**8d**) (332.4 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 ˚C for 24 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 28 cm silica, pentane/EtOAc 40/1) the product was obtained in 93% yield (310.3 mg, 0.93 mmol) as a light yellow oil.

R*f* (pentane/EtOAc = 9/1): 0.56; **^{1}H NMR (300 MHz, CDCl$_3$):** 9.45 (br d, *J* = 8.7 Hz, 1H, H$_{ar}$), 7.91 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 7.79-7.71 (m, 1H, H$_{ar}$), 7.63 (ddd, *J* = 8.7, 7.0, 1.5 Hz, 1H, H$_{ar}$), 7.42 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, H$_{ar}$), 7.37-7.24 (m, 5H, C_6H_5), 7.09 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 4.69 (dd, *J* = 11.3, 4.7 Hz, 1H, OC*H*H), 4.59-4.48 (m, 2H, OCH_2Ph), 4.39 (dd, *J* = 11.3, 9.4 Hz, 1H, OCH*H*), 3.76-3.60 (m, 2H, CH_2OBn), 3.06-2.93 (m, 1H, C(=O)CH), 2.38-2.21 (m, 1H, C*H*HCH$_2$OBn), 1.91-1.75 (m, 1H, CH*H*CH$_2$OBn); **^{13}C NMR (75 MHz, CDCl$_3$):** 195.4, 163.4, 138.2, 137.2, 131.5, 129.3, 129.0, 128.2, 128.2, 127.4, 127.4, 125.6, 124.5, 118.6, 112.0, 73.0, 70.7, 68.1, 44.2, 26.8; **ESI-MS:** calculated $[C_{22}H_{20}NaO_3]^+$: 355.1305, found: 355.1309; **GC-MS, Rt (method C):** 17.83 min, **(EI) m/z (%):** 332 (13), 241 (11), 225 (5), 211 (6), 197 (24), 178 (1), 170 (50), 142 (15), 126 (2), 115 (13), 107 (3), 91 (60), 87 (1), 77 (16), 55 (6), 41 (4); **ATR-FTIR (cm^{-1}):** 3061, 3031, 2922, 2865, 1670, 1618, 1598, 1569, 1513, 1471, 1454, 1436, 1377, 1345, 1278, 1238, 1207, 1100, 1029, 993, 889, 825, 754, 698, 632, 538, 498; **Elemental analysis:** calculated (%) for $C_{22}H_{20}O_3$ (332.39): C 79.50, H 6.06, found: C 79.49, H 6.14.

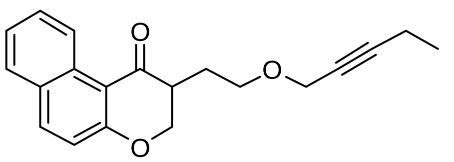
2-(2-Allyloxy-ethyl)-2,3-dihydro-benzo[*f*]chromen-1-one (9e)



Following our general procedure, 2-((Z)-4-allyloxy-but-2-enyloxy)-naphthalene-1-carbaldehyde (**8e**) (282.3 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 24 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 28 cm silica, pentane/EtOAc 40/1) the product was obtained in 89% yield (250.2 mg, 0.89 mmol) as a light yellow oil.

R*f* (pentane/EtOAc = 9/1): 0.31; **^{1}H NMR (300 MHz, CDCl$_3$):** 9.45 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 7.90 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 7.74 (br d, *J* = 8.1 Hz, 1H, H$_{ar}$), 7.67-7.58 (m, 1H, H$_{ar}$), 7.48-7.37 (m, 1H, H$_{ar}$), 7.08 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 6.00-5.83 (m, OCH$_2$C*H*=CH$_2$), 5.33-5.22 (m, 1H, OCH$_2$CH=C*H*H), 5.22-5.12 (m, 1H, OCH$_2$CH=CH*H*), 4.70 (dd, *J* = 11.3, 4.7 Hz, 1H, ArOC*H*H), 4.40 (dd, *J* = 11.3, 9.5 Hz, 1H, ArOCH*H*), 4.06-3.93 (m, 2H, OC*H*$_2$CH=CH$_2$), 3.71-3.54 (m, 2H, CH$_2$Oallyl), 3.04-2.90 (m, 1H, C(=O)CH), 2.35-2.18 (m, 1H, C*H*HCH$_2$Oallyl), 1.89-1.72 (m, 1H, CH*H*CH$_2$Oallyl); **^{13}C NMR (75 MHz, CDCl$_3$):** 195.5, 163.4, 137.2, 134.8, 131.8, 129.5, 129.2, 128.4, 125.8, 124.7, 118.7, 116.9, 112.1, 71.9, 70.8, 68.1, 44.3, 26.8; **ESI-MS:** calculated [C$_{18}$H$_{18}$NaO$_3$]$^+$: 305.1148, found: 305.1145; **GC-MS, Rt (method C):** 15.43 min, **(EI) m/z (%):** 282 (2), 241 (4), 225 (22), 211 (2), 197 (22), 170 (56), 142 (19), 128 (2), 126 (4), 114 (35), 87 (2), 57 (3), 41 (14); **ATR-FTIR (cm^{-1}):** 2963, 1671, 1513, 1261, 1093, 1018, 797, 551, 538, 505, 499, 489.

2-(2-Pent-2-ynyloxy-ethyl)-2,3-dihydro-benzo[*f*]chromen-1-one (9f)

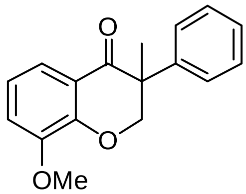


Following our general procedure, 2-((*Z*)-4-pent-2-ynyloxy-but-2-enyloxy)-naphthalene-1-carbaldehyde (**8f**) (308.4 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane, then the mixture was degassed by freeze-pump-thaw cycling. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 24 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 30 cm silica, pentane/EtOAc 40/1) the product was obtained in 83% yield (254.8 mg, 0.83 mmol) as a yellow oil.

R*f* (pentane/EtOAc = 9/1): 0.32; **^{1}H NMR (400 MHz, CDCl$_3$):** 9.48-9.42 (m, 1H, H$_{ar}$), 7.90 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 7.77-7.72 (m, 1H, H$_{ar}$), 7.62 (ddd, *J* = 8.7, 6.9, 1.4 Hz, 1H, H$_{ar}$), 7.42 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H, H$_{ar}$), 7.08 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 4.70 (dd, *J* = 11.3, 4.8 Hz, 1H, ArOC*H*H), 4.41 (dd, *J* = 11.3, 9.6 Hz, 1H, ArOCH*H*), 4.19-4.08 (m, 2H, OC*H*$_2$C≡CEt), 3.76-3.62 (m, 2H, C*H*$_2$OCH$_2$C≡CEt), 3.03-2.93 (m, 1H, C(=O)CH), 2.32-2.22 (m, 1H, C*H*HCH$_2$OCH$_2$C≡CEt), 2.22 (tq, *J* = 7.5, 2.2 Hz, 2H, OCH$_2$CC≡C*H*$_2$CH$_3$), 1.86-1.75 (m, 1H, CH*H*CH$_2$OCH$_2$C≡CEt), 1.13 (t, *J* = 7.5 Hz, 3H, OCH$_2$C≡CCH$_2$C*H*$_3$); **^{13}C NMR (100 MHz,**

$CDCl_3$): 195.4, 163.4, 137.2, 131.7, 129.5, 129.2, 128.4, 125.7, 124.7, 118.6, 112.0, 88.4, 75.2, 70.7, 67.5, 58.7, 44.2, 26.6, 13.8, 12.4; **ESI-MS:** calculated $[C_{20}H_{20}NaO_3]^+$: 331.1305, found: 331.1294; **GC-MS, Rt (method C):** 16.56 min, **(EI) m/z (%):**241 (9), 225 (9), 211 (3), 197 (20), 170 (57), 142 (17), 126 (3), 113 (7), 83 (2), 67 (6), 55 (11), 53 (5), 41 (14); **ATR-FTIR (cm^{-1}):** 2976, 2921, 2876, 1670, 1617, 1598, 1569, 1513, 1472, 1435, 1377, 1365, 1345, 1320, 1278, 1238, 1207, 1174, 1138, 1093, 899, 825, 757, 732, 632, 535, 498.

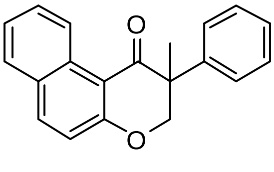
8-Methoxy-3-methyl-3-phenyl-chroman-4-one (11a)



Following our general procedure, 3-methoxy-2-(2-phenyl-allyloxy)-benzaldehyde (268.3 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 ˚C for 1 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 26 cm silica, pentane/EtOAc = 10/1) the product was obtained in 87% yield (232.6 mg, 0.87 mmol) as an off-white solid.

R_f (pentane/EtOAc = 10/1): 0.13; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.55 (dd, *J* = 7.9, 1.7 Hz, 1H, H_{ar}), 7.46-7.40 (m, 2H, H_{ar}), 7.35-7.28 (m, 2H, H_{ar}), 7.26-7.21 (m, 1H, H_{ar}), 6.99 (dd, *J* = 7.9, 1.7 Hz, 1H, H_{ar}), 6.94 (t, *J* = 7.9 Hz, 1H, H_{ar}), 5.02 (d, *J* = 12.1 Hz, 1H, OC*H*H), 4.42 (d, *J* = 12.1 Hz, 1H, OCH*H*), 3.87 (s, 3H, OCH_3), 1.49 (s, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** 194.8, 150.8, 148.5, 138.8, 128.7, 127.4, 126.5, 120.9, 120.8, 118.9, 116.2, 74.9, 56.1, 49.3, 21.4; **ESI-MS:** calculated $[C_{17}H_{16}NaO_3]^+$: 291.0992, found: 291.0989; **GC-MS, Rt (method A):** 9.80 min, **(EI) m/z (%):** 268 (25), 253 (7), 150 (94), 122 (100), 118 (8), 107 (16), 104 (2), 91 (13), 77 (13); **ATR-FTIR (cm^{-1}):** 3065, 2975, 2941, 2841, 1679, 1605, 1582, 1491, 1473, 1443, 1385, 1352, 1290, 1265, 1234, 1195, 1080, 1026, 1012, 959, 928, 882, 856, 807, 764, 741, 700, 639, 628, 546, 504.

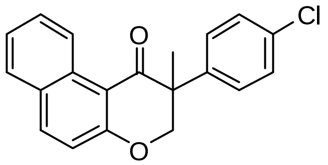
2-Methyl-2-phenyl-2,3-dihydro-benzo[*f*]chromen-1-one (11c)



Following our general procedure, 2-(2-phenyl-allyloxy)-naphthalene-1-carbaldehyde (**10c**) (288.3 mg, 1.0 mmol, 1.0 eq.) and catalyst 3 (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 ˚C for 1 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 30 cm silica, pentane/EtOAc = 100/1) the product was obtained in 94% yield (271.5 mg, 0.94 mmol) as an off-white solid.

R*f* (pentane/EtOAc = 19/1): 0.47; **^{1}H NMR (300 MHz, CDCl$_3$):** 9.52 (br d, *J* = 8.7 Hz, 1H, H$_{ar}$), 7.85 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 7.72 (br s, *J* = 7.9 Hz, 1H, H$_{ar}$), 7.64 (ddd, *J* = 8.7, 7.0, 1.3 Hz, 1H, H$_{ar}$), 7.47-7.37 (m, 3H, H$_{ar}$), 7.33-7.16 (m, 3H, Ar-H, H$_{ar}$), 7.00 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 5.01 (d, *J* = 12.0 Hz, 1H, OC*H*H), 4.51 (d, *J* = 12.0 Hz, 1H, OCH*H*), 1.53 (s, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 196.1, 162.7, 139.9, 137.2, 131.9, 129.5, 129.3, 128.7, 128.4, 127.3, 126.2, 125.8, 124.7, 118.5, 111.9, 74.3, 49.5, 21.7; **ESI-MS:** calculated [C$_{20}$H$_{16}$NaO$_2$]$^+$: 311.1043, found: 311.1063; **GC-MS, Rt (method A):** 11.05 min, **(EI) m/z (%):** 288 (19), 273 (10), 211 (1), 170 (100), 142 (14), 126 (2), 118 (16), 104 (1), 77 (5); **ATR-FTIR (cm^{-1}):** 2993, 2965, 2924, 2866, 1664, 1617, 1596, 1568, 1513, 1496, 1475, 1433, 1376, 1365, 1339, 1282, 1273, 1237, 1207, 1180, 1155, 1138, 1089, 1070, 1053, 1031, 1008, 992, 941, 891, 826, 801, 764, 749, 723, 700, 652, 598, 555; **Elemental analysis:** calculated (%) for C$_{20}$H$_{16}$O$_2$ (288.34): C 83.31, H 5.59, found: C 83.13, H 5.41.

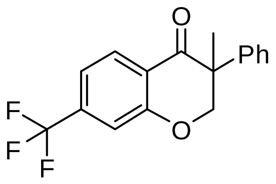
2-(4-Chloro-phenyl)-2-methyl-2,3-dihydro-benzo[*f*]chromen-1-one (11d)



Following our general procedure, 2-[2-(4-Chloro-phenyl)-allyloxy]-naphthalene-1-carbaldehyde (**10d**) (322.8 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane. DBU (60.9 mg, 60 µL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 °C for 1 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 28 cm silica, pentane/EtOAc = 50/1) the product was obtained in 94% yield (303.4 mg, 0.94 mmol) as a yellowish solid.

R*f* (pentane/EtOAc = 20/1): 0.38; **^{1}H NMR (300 MHz, CDCl$_3$):** 9.53-9.46 (m, 1H, H$_{ar}$), 7.84 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 7.73-7.67 (m, 1H, H$_{ar}$), 7.63 (ddd, *J* = 8.7, 7.0, 1.5 Hz, 1H, H$_{ar}$), 7.40 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, H$_{ar}$), 7.38-7.33 (m, 2H, H$_{ar}$), 7.27-7.20 (m, 2H, H$_{ar}$), 6.99 (d, *J* = 9.0 Hz, 1H, H$_{ar}$), 4.93 (d, *J* = 12.1 Hz, 1H, OC*H*H), 4.47 (d, *J* = 12.1 Hz, 1H, OCH*H*), 1.49 (s, 3H, CH$_3$); **^{13}C NMR (100 MHz, CDCl$_3$):** 195.5, 162.7, 138.3, 137.4, 133.2, 131.8, 129.6, 129.3, 128.8, 128.5, 127.6, 125.6, 124.8, 118.4, 111.6, 74.0, 49.1, 21.6; **ESI-MS:** calculated [C$_{20}$H$_{15}$ClNaO$_2$]$^+$: 345.0653, found: 345.0648; **GC-MS, Rt (method A):** 12.19 min, **(EI) m/z (%):**322 (9), 307 (3), 170 (100), 152 (13), 142 (13), 126 (2), 112 (2), 89 (2); **ATR-FTIR (cm^{-1}):** 2929, 1670, 1616, 1595, 1567, 1510, 1490, 1472, 1432, 1399, 1379, 1365, 1342, 1276, 1236, 1207, 1182, 1155, 1138, 1095, 1083, 1058, 1032, 1013, 1003, 988, 941, 887, 828, 799, 764, 749, 719, 698, 652, 618, 550, 531, 517, 507.

3-Methyl-3-phenyl-7-trifluoromethyl-chroman-4-one (11b)



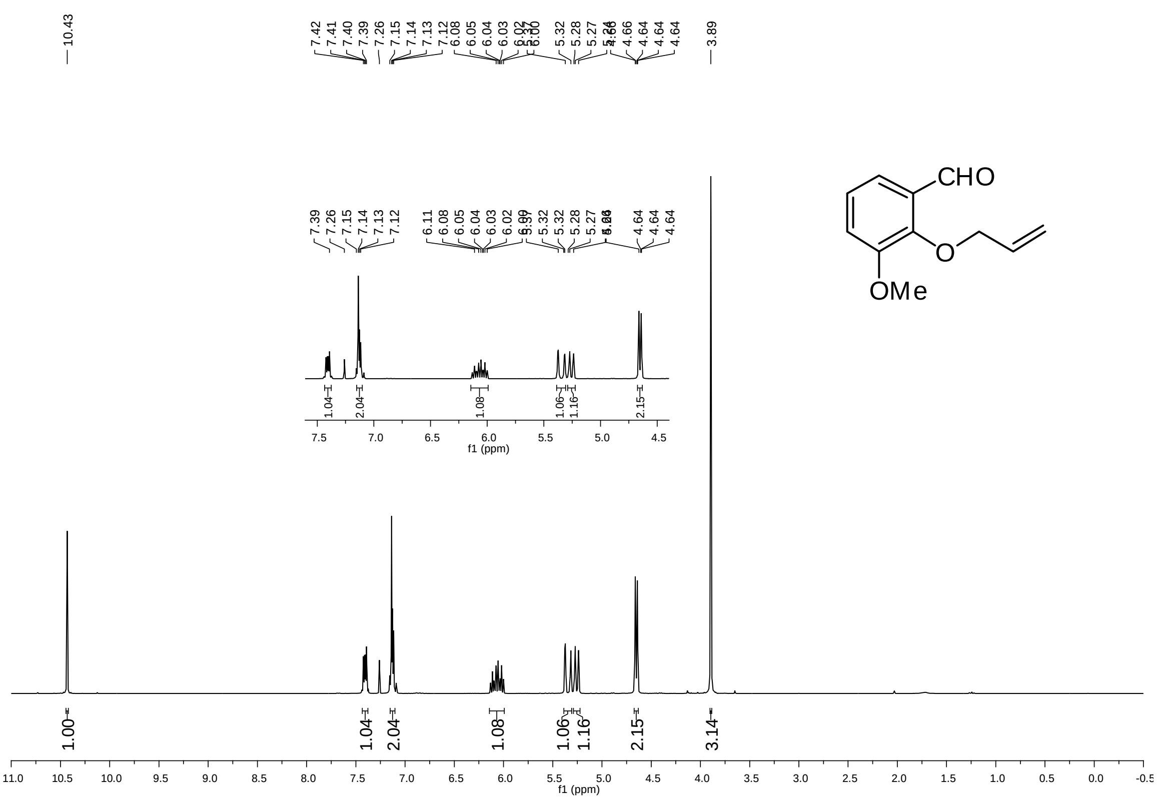
Following our general procedure, 2-(2-phenyl-allyloxy)-4-trifluoromethyl-benzaldehyde (**10b**) (340.7 mg, 1.0 mmol, 1.0 eq.) and catalyst **3** (74.4 mg, 0.20 mmol, 0.2 eq.) were mixed in 2 mL 1,4-dioxane. DBU (60.9 mg, 60 μL, 0.40 mmol, 0.4 eq.) was added at rt and the mixture was stirred in a pre-heated oil bath at 120 ˚C for 1 h. The crude mixture was carefully pre-adsorbed on silica on the rotary evaporator. After purification by column chromatography (2 x 28 cm silica, pentane/EtOAc = 100/1) the product was obtained in 87% yield (233.5 mg, 0.76 mmol) as a yellowish solid.

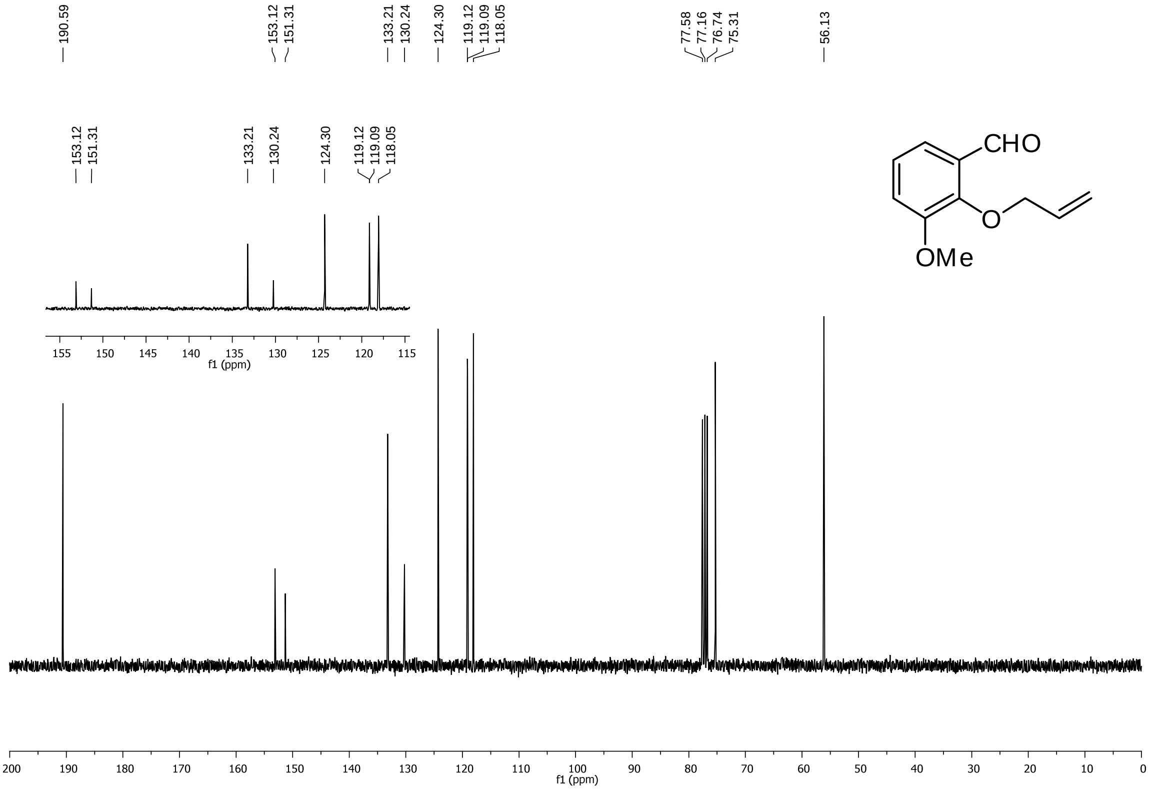
R*f* (pentane/EtOAc = 19/1): 0.44; **^{1}H NMR (300 MHz, CDCl$_3$):** 8.04 (br d, *J* = 8.2 Hz, 1H, H$_{ar}$), 7.42-7.36 (m, 2H, H$_{ar}$), 7.36-7.29 (m, 2H, H$_{ar}$), 7.29-7.24 (m, 1H, H$_{ar}$), 7.24-7.19 (m, 1H, H$_{ar}$), 7.19-7.15 (m, 1H, H$_{ar}$), 4.97 (d, *J* = 12.3 Hz, 1H, OC*H*H), 4.41 (d, *J* = 12.3 Hz, 1H, OCH*H*), 1.50 (s, 3H, CH$_3$); **^{13}C NMR (75 MHz, CDCl$_3$):** 194.0, 160.6, 138.2, 136.7 (q, *J* = 33 Hz), 128.9, 128.8, 127.8, 126.3, 123.1 (q, *J* = 273 Hz), 122.3 (q, *J* = 1 Hz), 117.8 (q, *J* = 4 Hz), 115.3 (q, *J* = 4 Hz), 74.4, 49.5, 21.3; **^{19}F NMR (282 MHz, CDCl$_3$):** −63.7; **ESI-MS:** calculated [$C_{17}H_{13}F_3NaO_2$]$^+$: 329.0760, found: 329.0767; **GC-MS, Rt (method A):** 8.89 min, **(EI) m/z (%):** 306 (11), 291 (4), 188 (3), 132 (3), 118 (100), 91 (8), 77 (8); **ATR-FTIR (cm^{-1}):** 3062, 2977, 2932, 2875, 1697 1627, 1580, 1495, 1468, 1435, 1388, 1334, 1314, 1270, 1203, 1169, 1131, 1064, 1035, 949, 885, 838, 699, 632, 548, 534, 498.

7 Scans

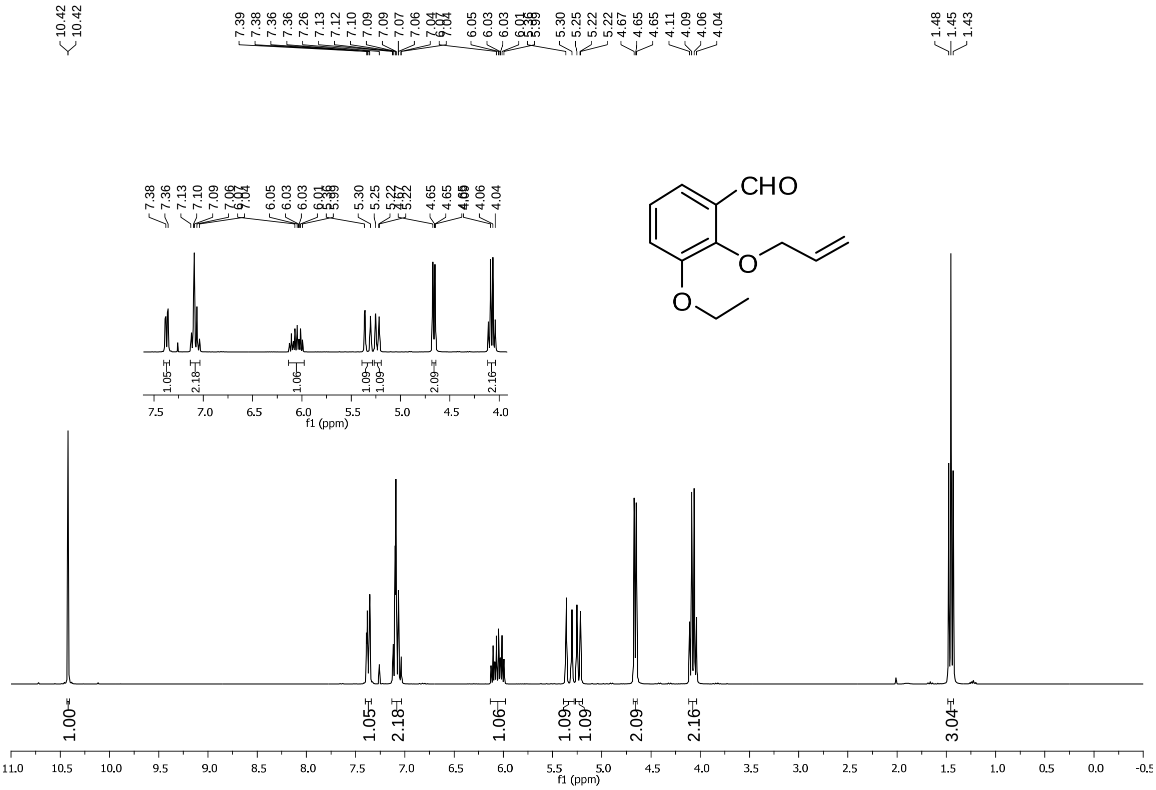
7.1 Substrates

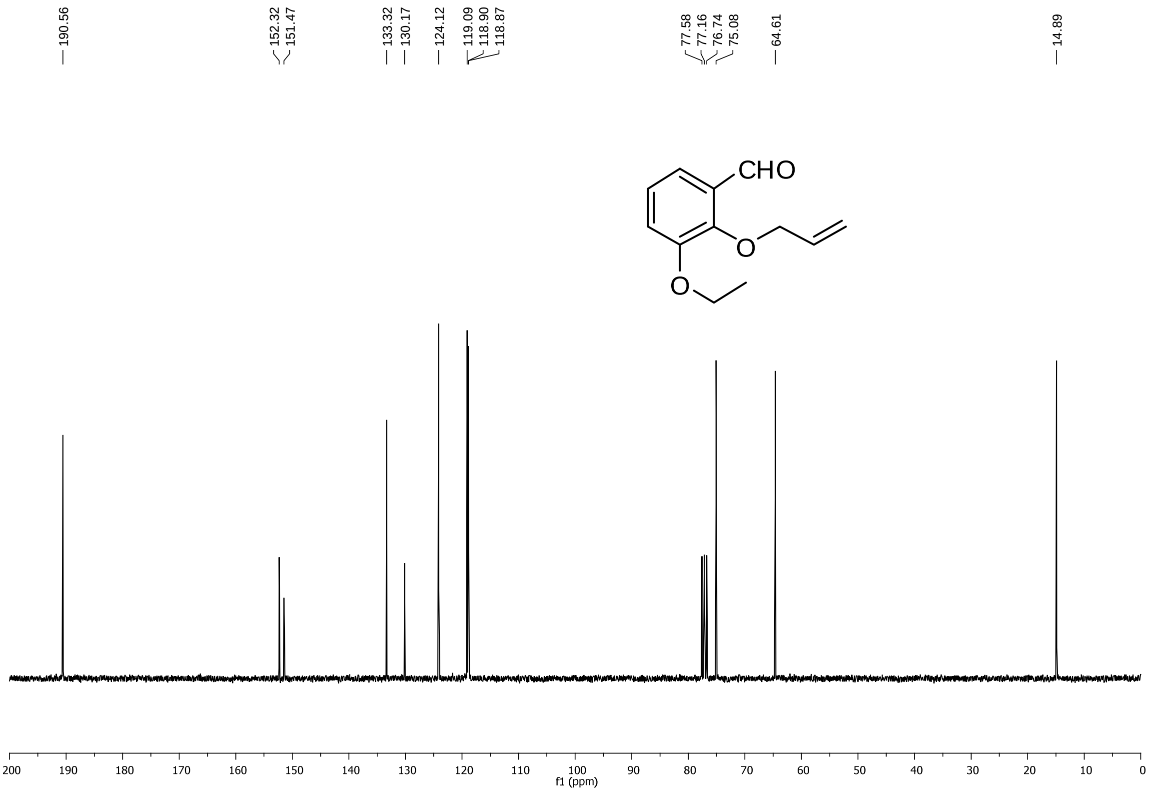
2-Allyloxy-3-methoxy benzaldehyde (1a)



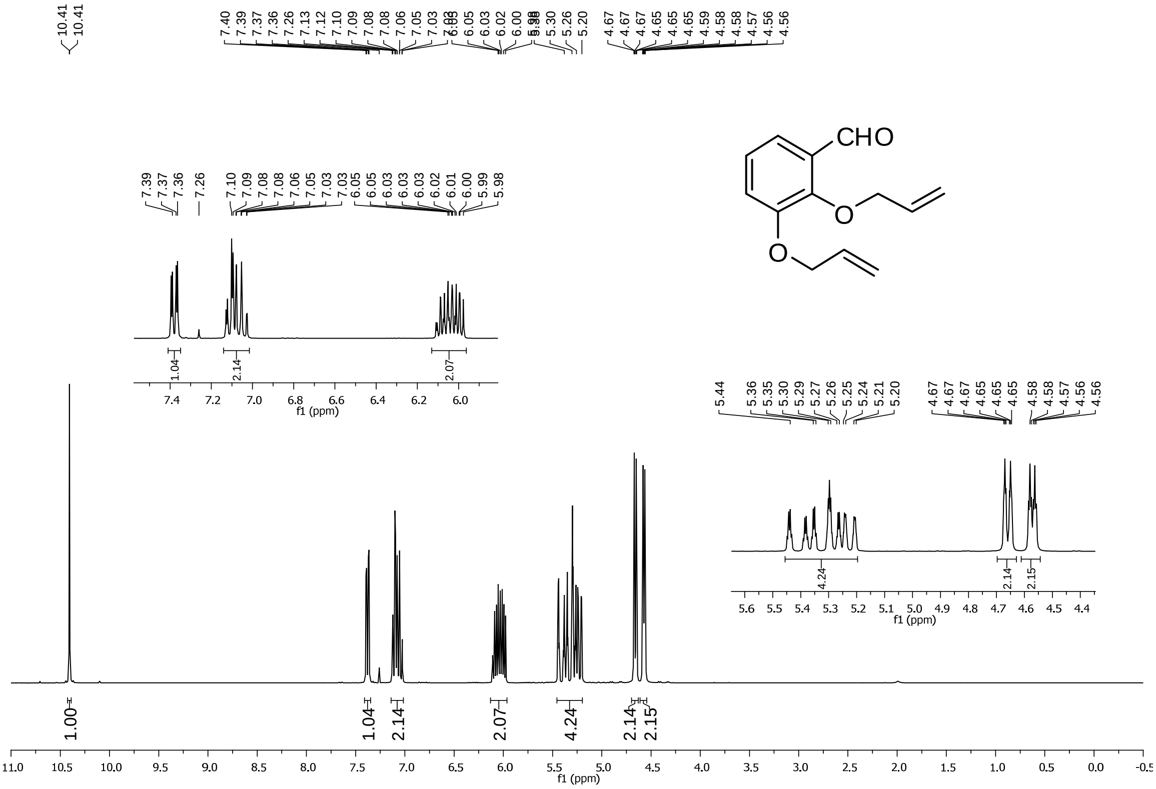


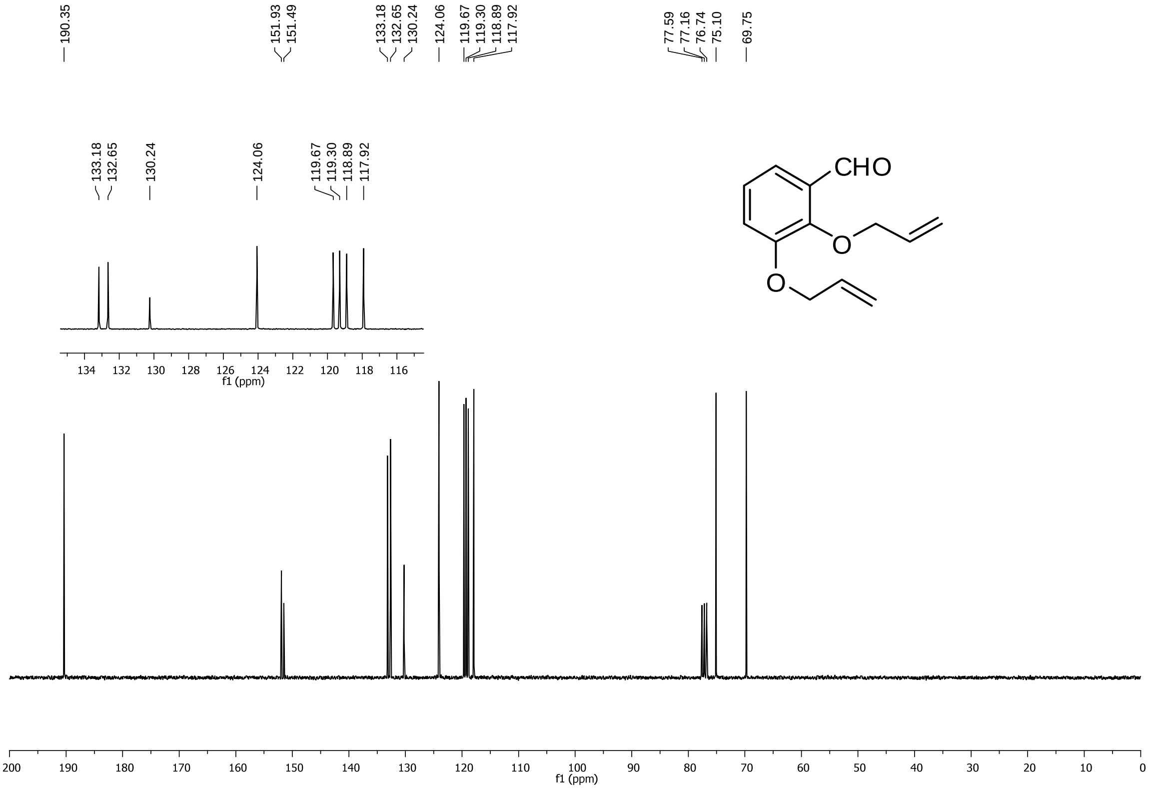
2-Allyloxy-3-ethoxy benzaldehyde (1b)



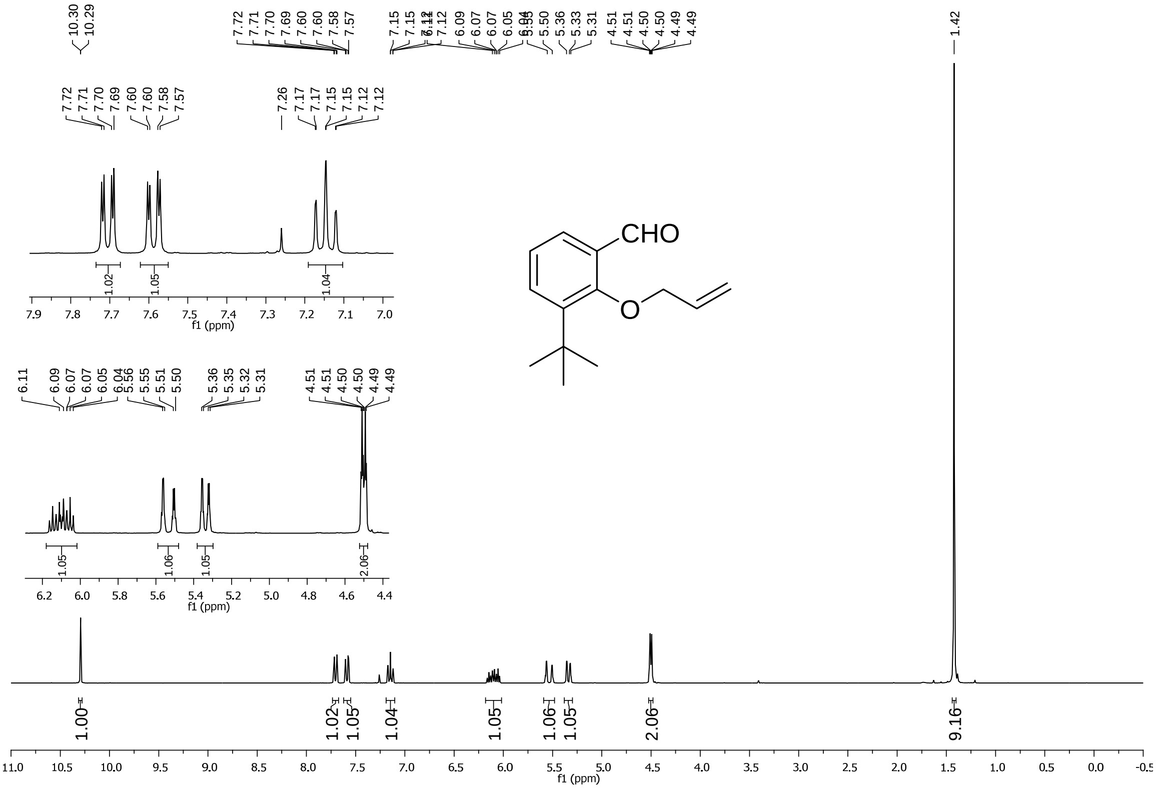


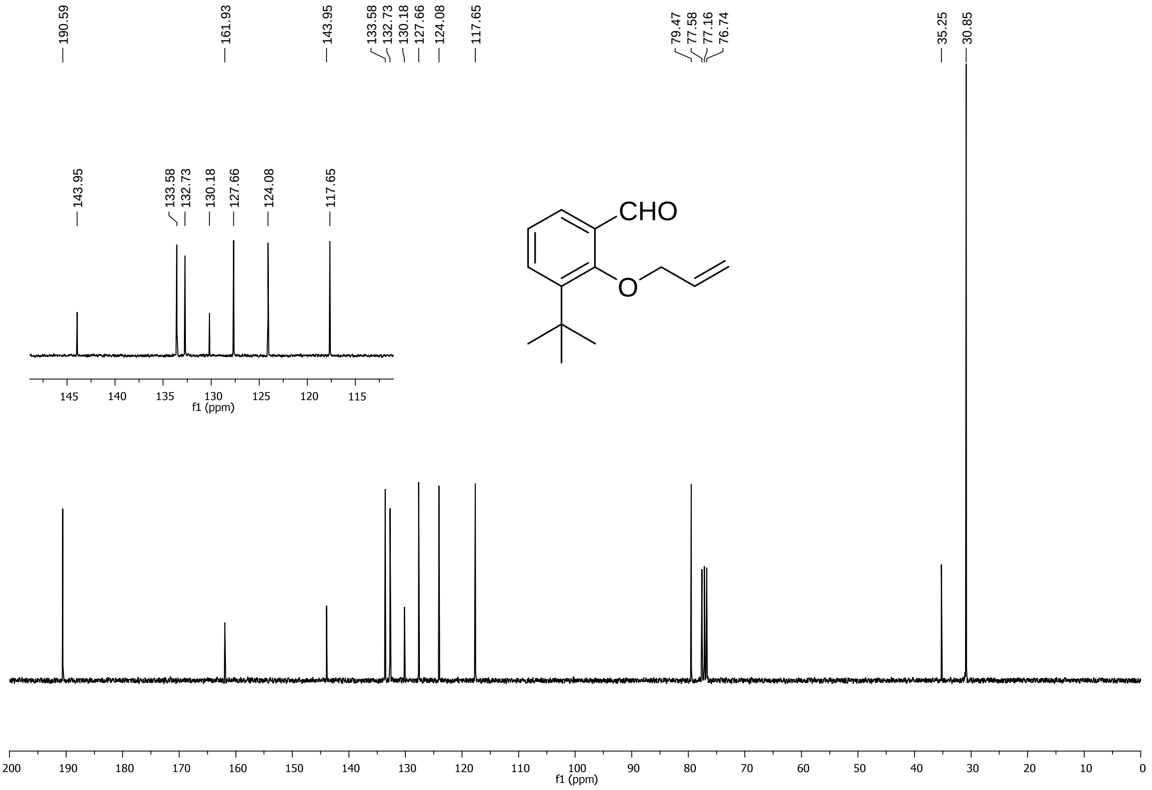
2,3-Diallyloxy benzaldehyde (1c)



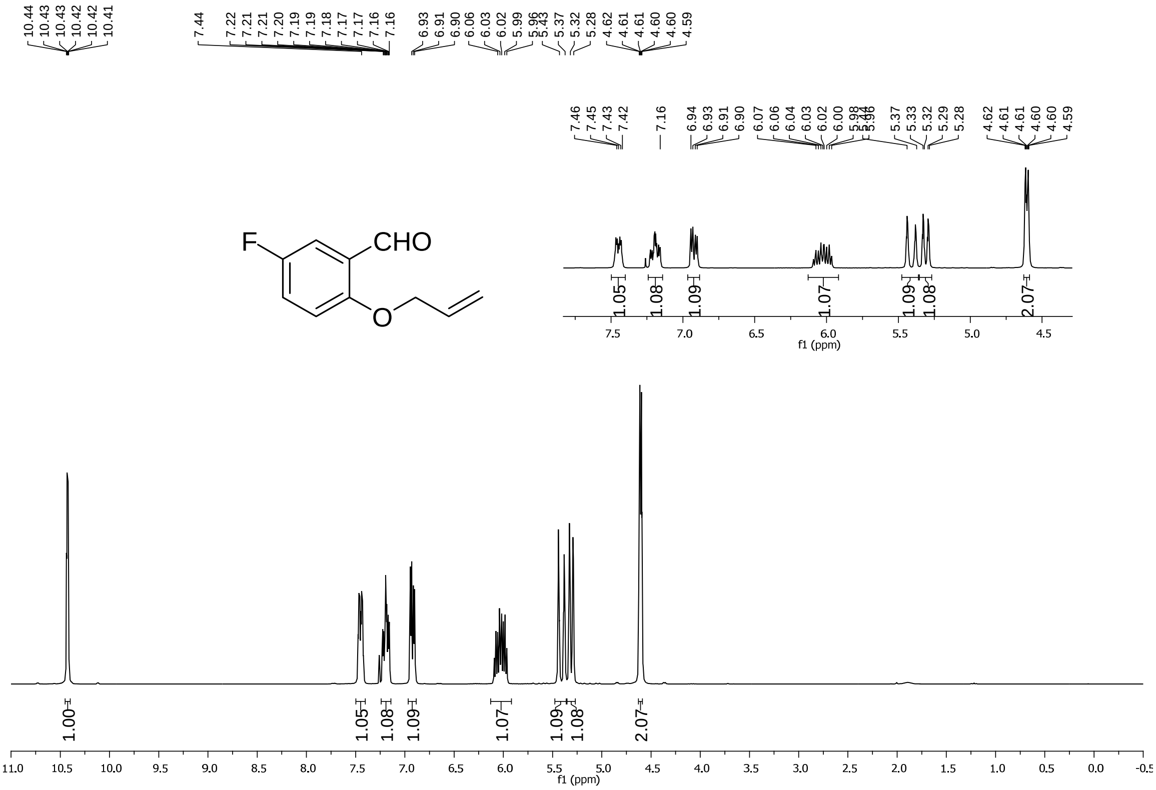


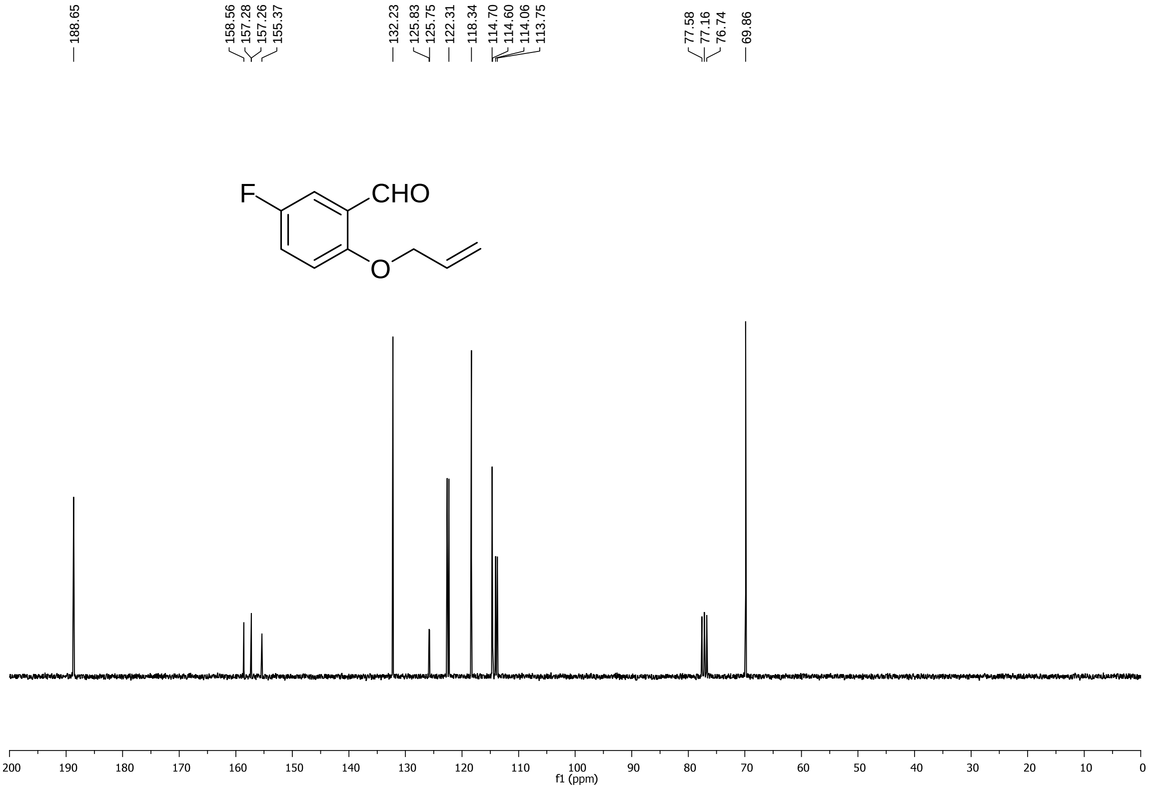
2-Allyloxy-3-*tert*-butyl benzaldehyde (1d)



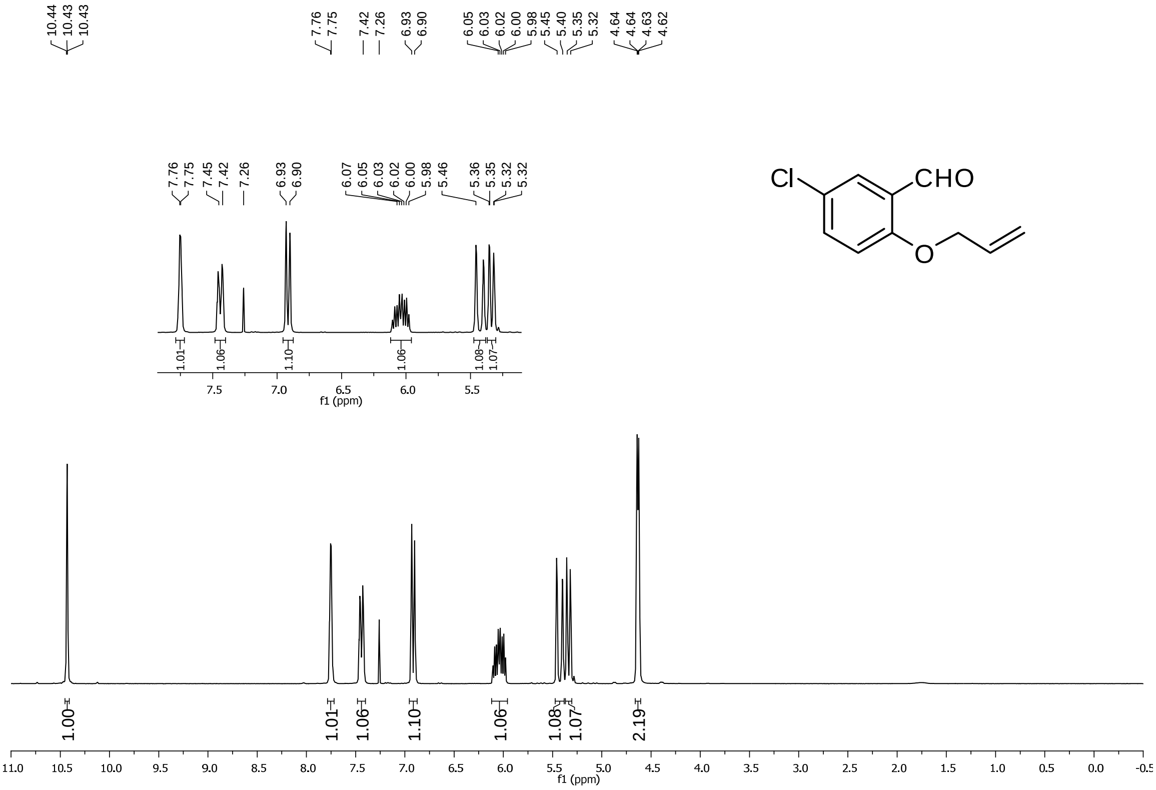


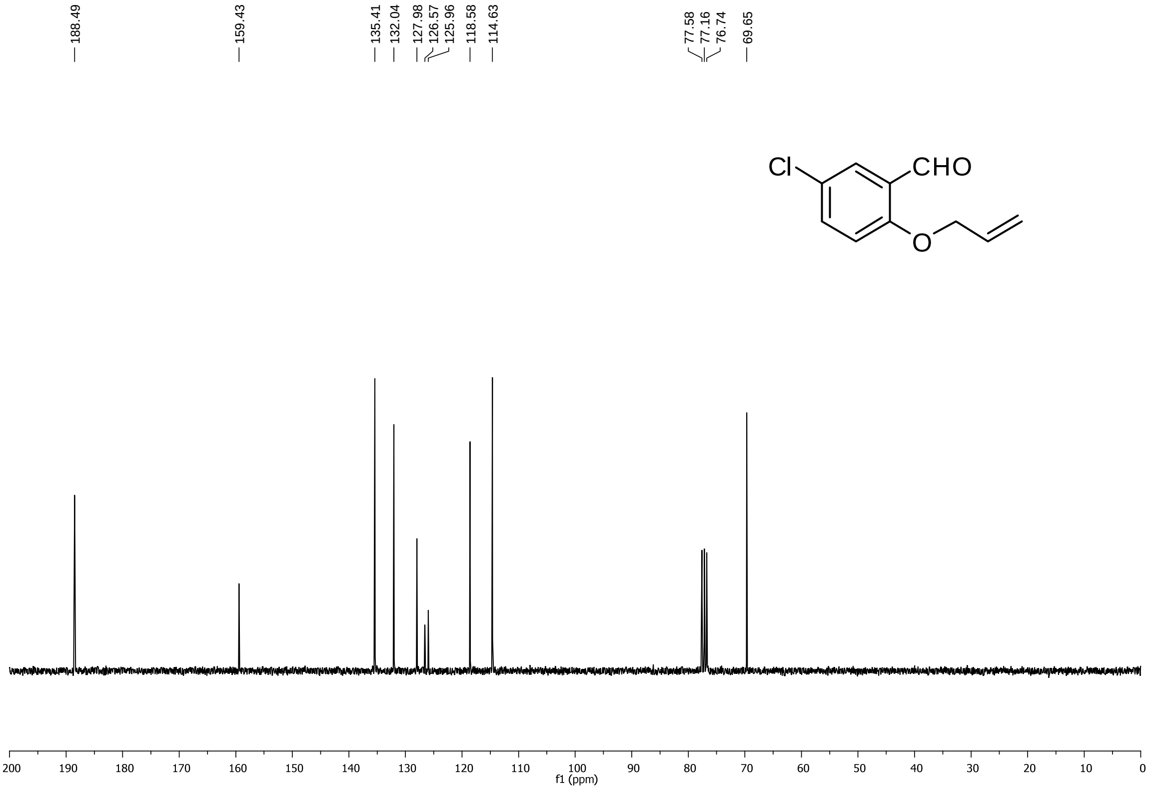
2-Allyloxy-5-fluoro benzaldehyde (1e)



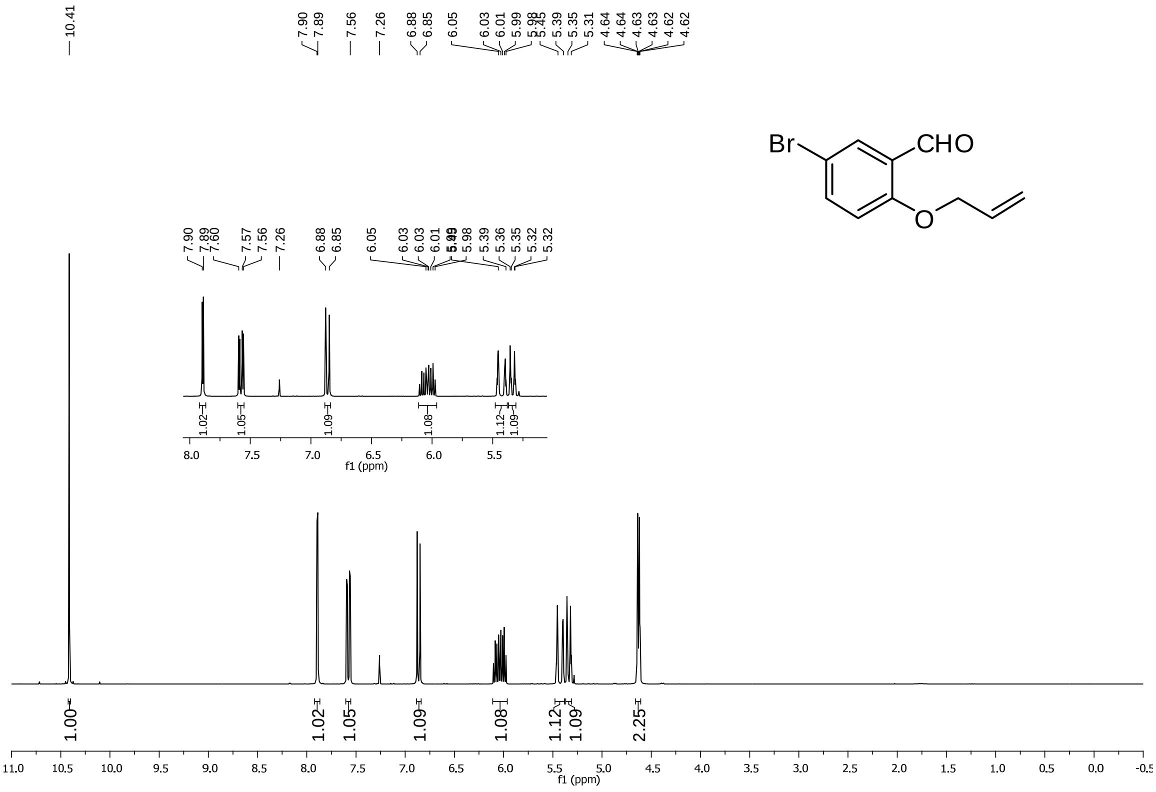


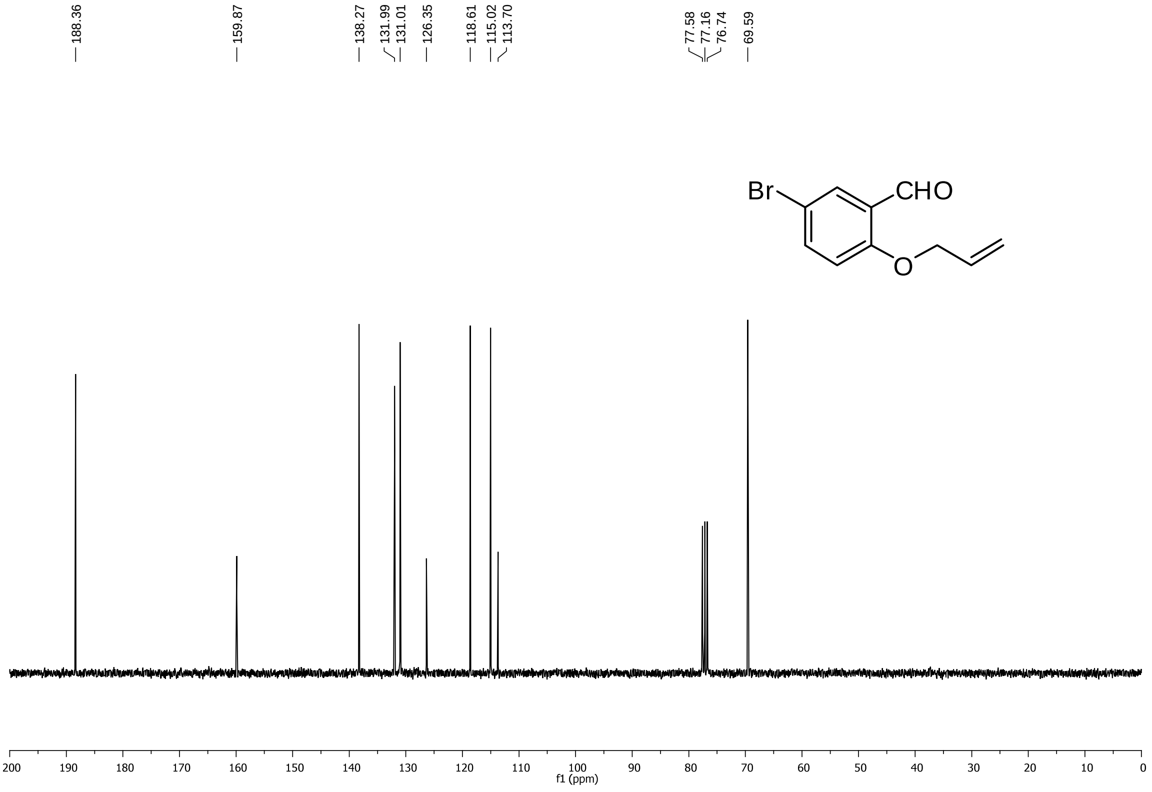
2-Allyloxy-5-chloro benzaldehyde (1f)



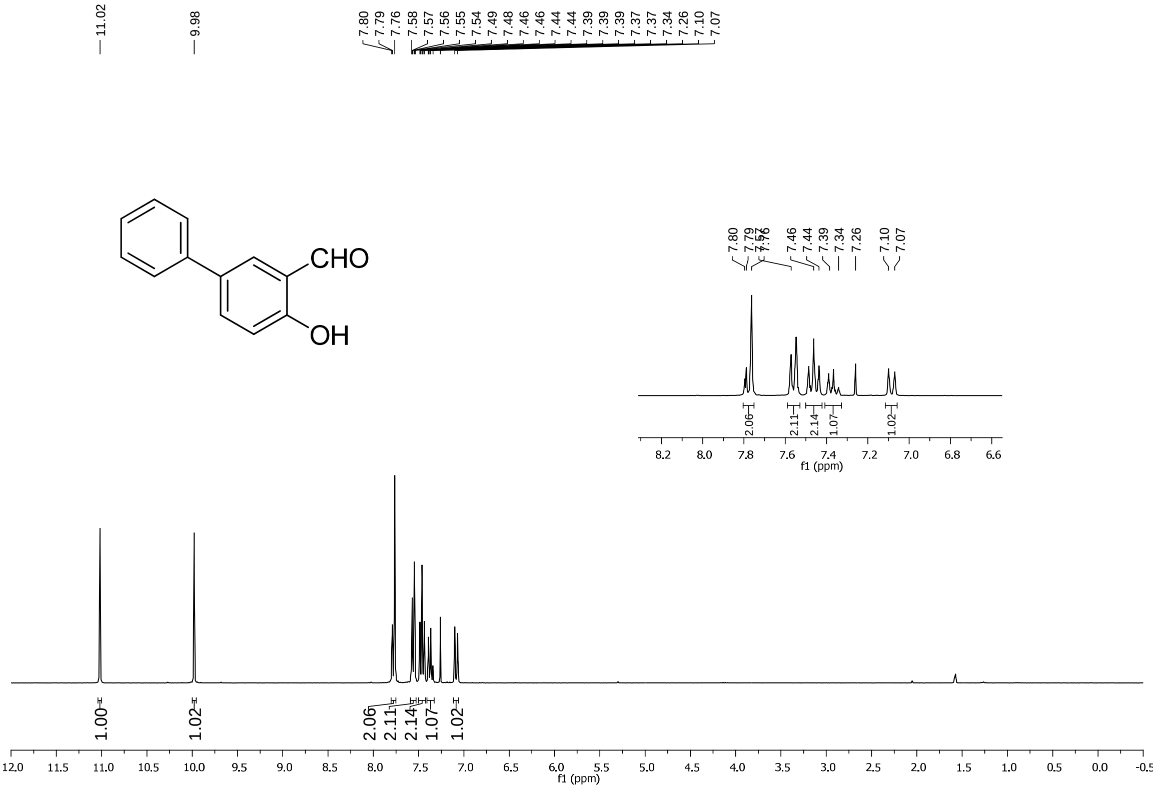


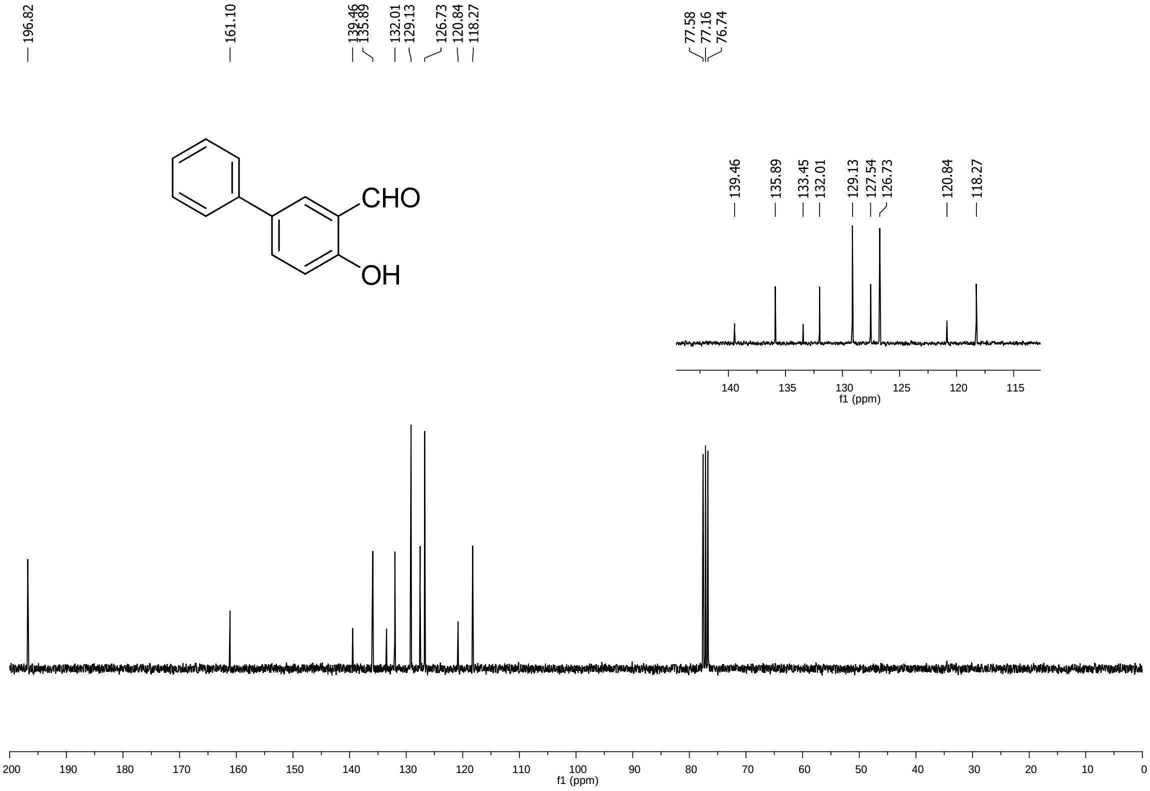
2-Allyloxy-5-bromo benzaldehyde (1g)



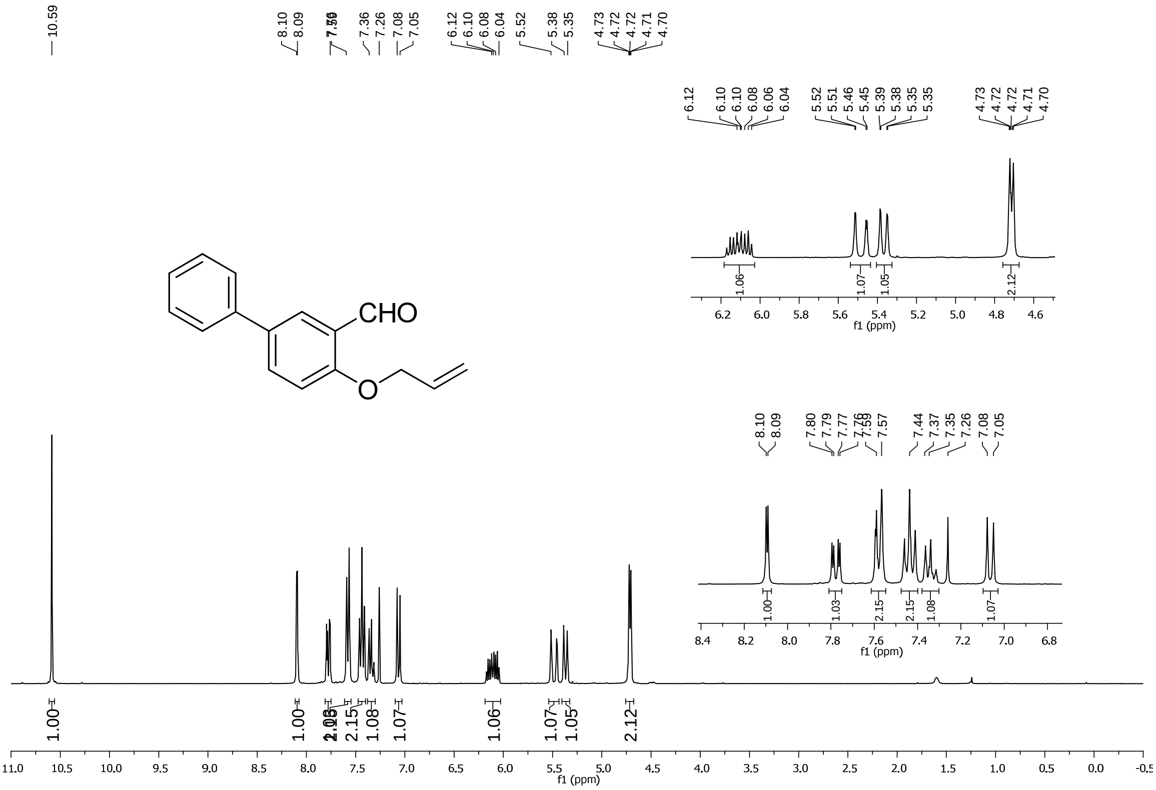


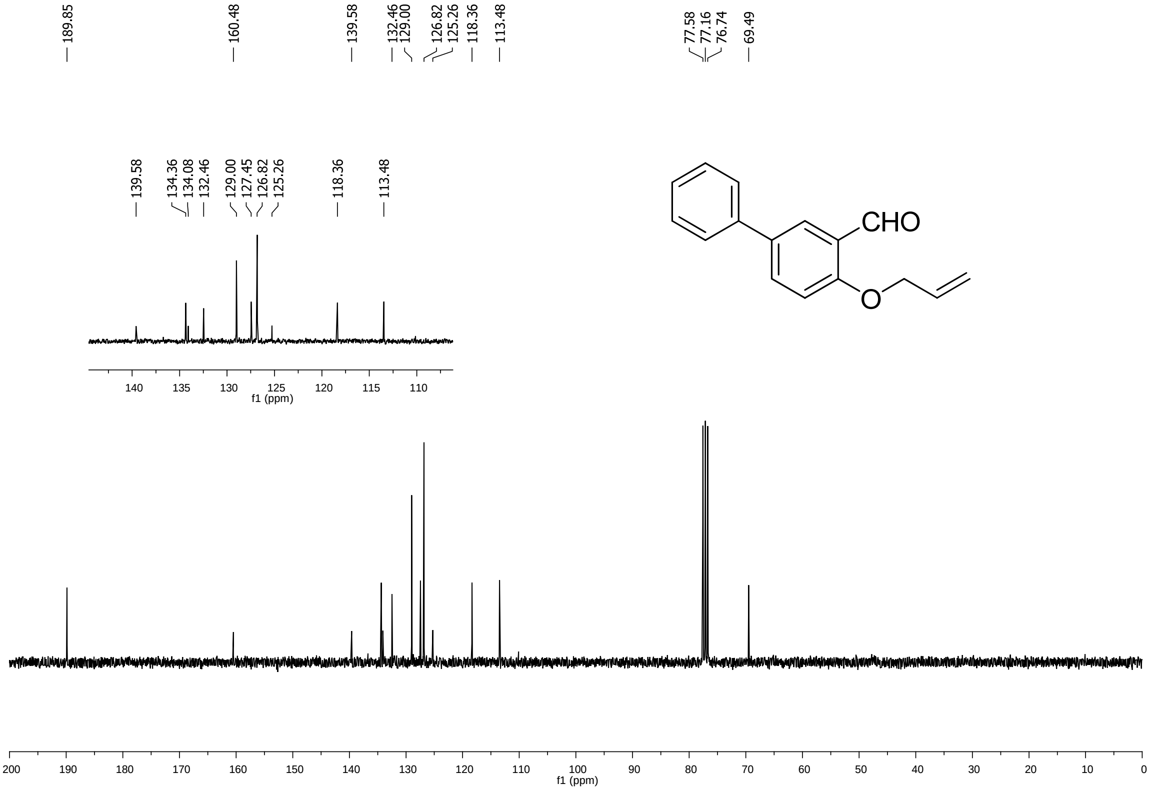
5-Phenyl salicylaldehyde



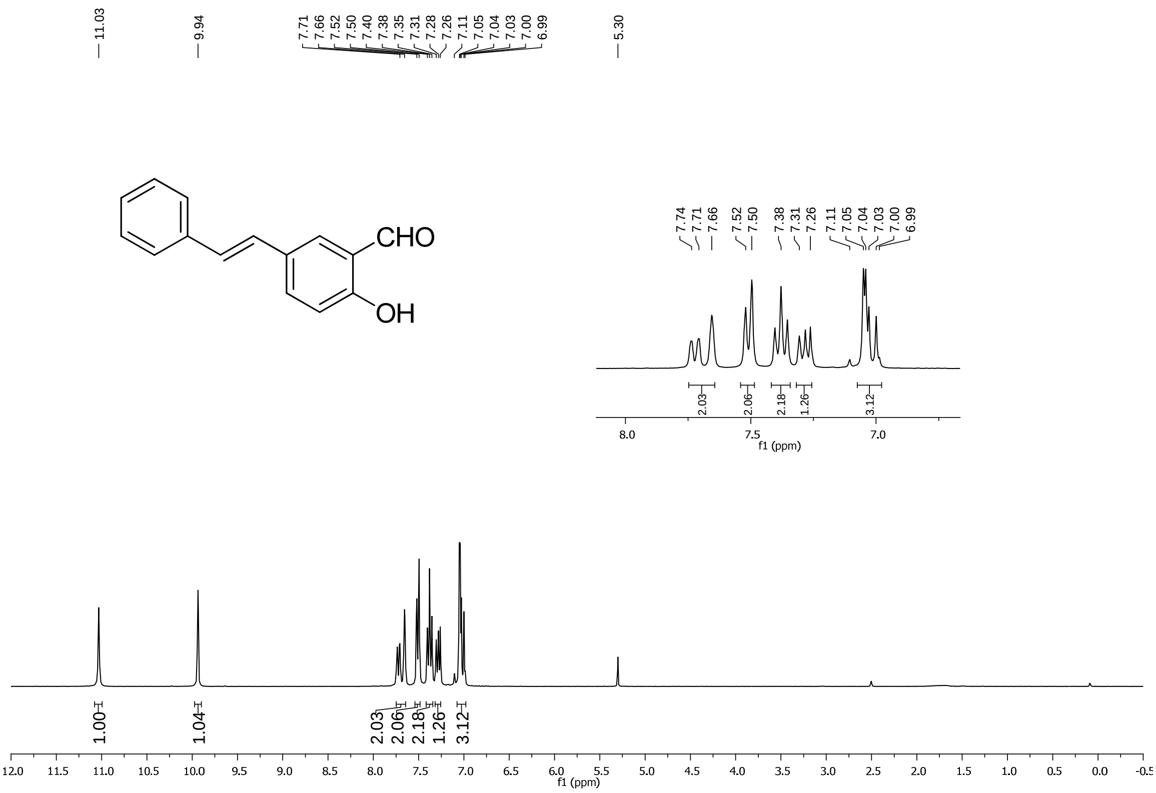


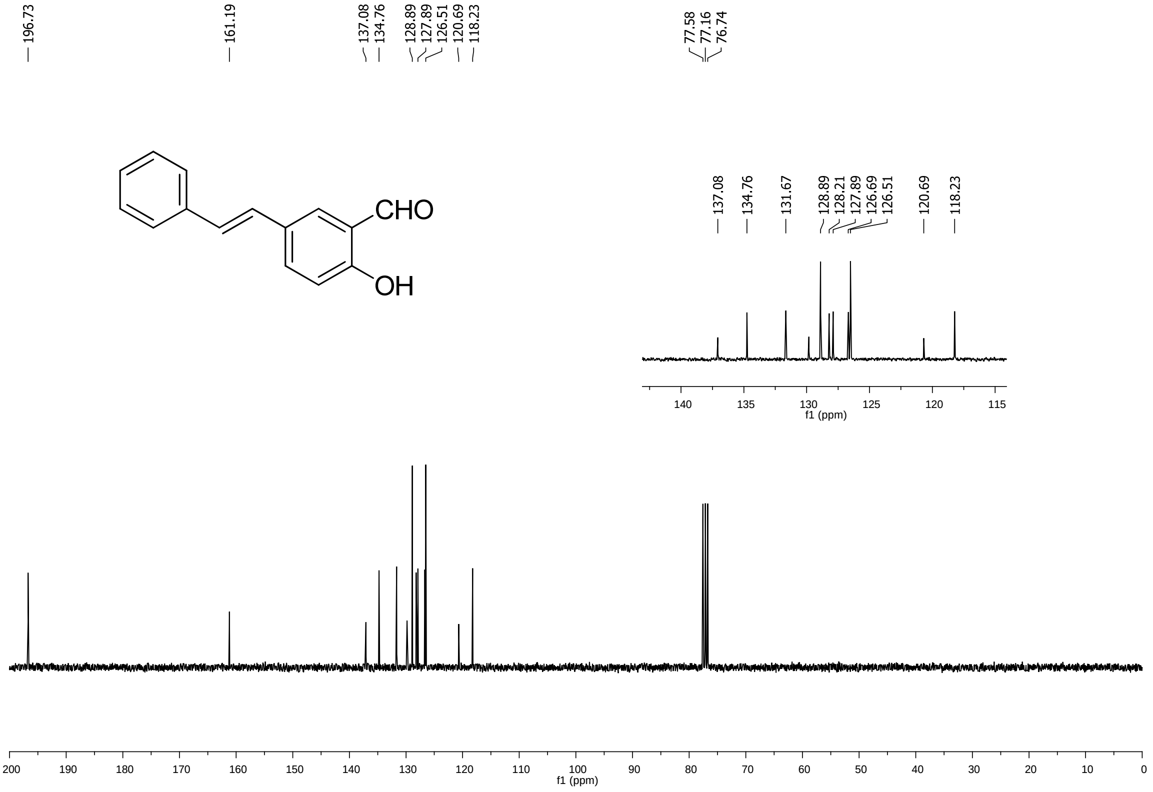
2-Allyloxy-5-phenyl benzaldehyde (1j)



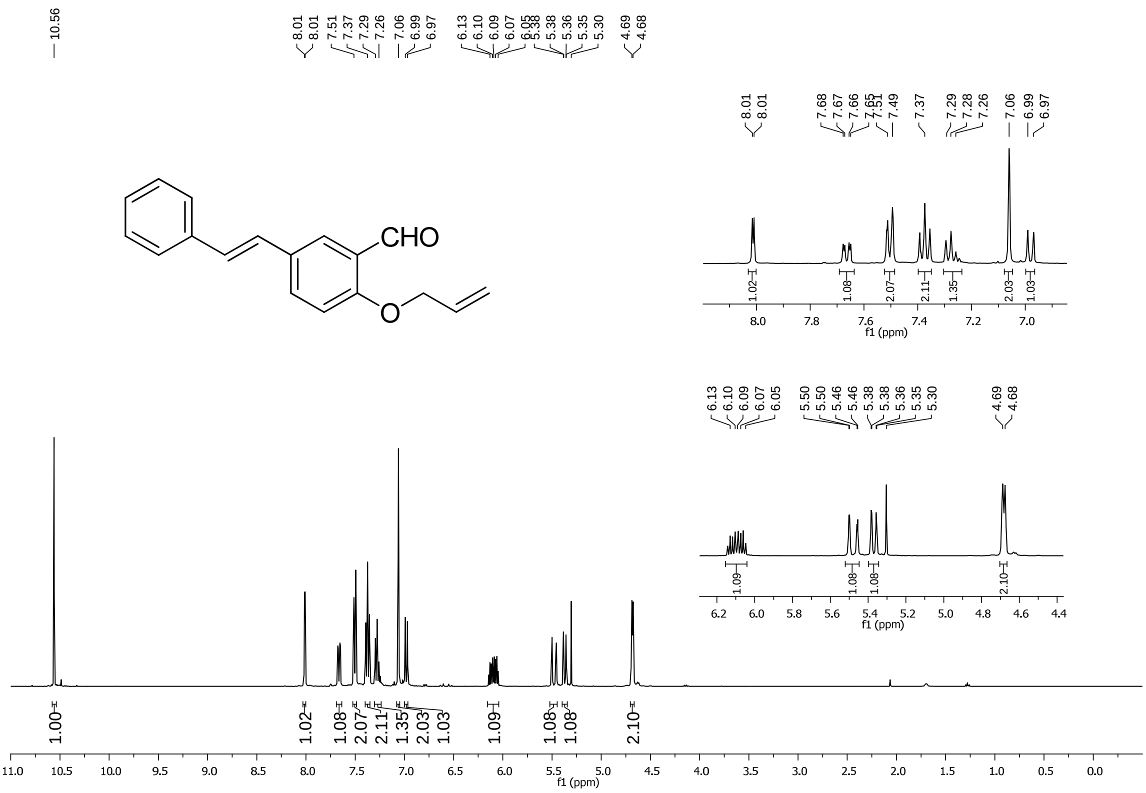


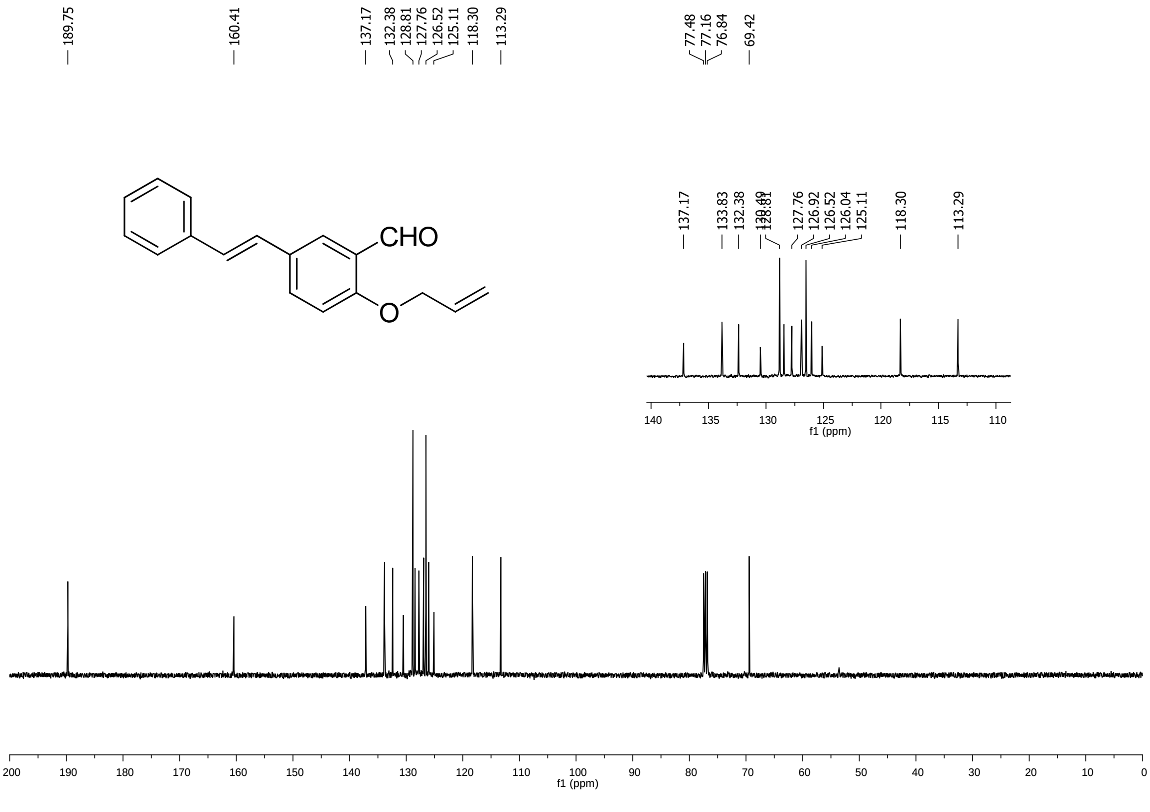
2-Hydroxy-5-(2-phenylvinyl) benzaldehyde



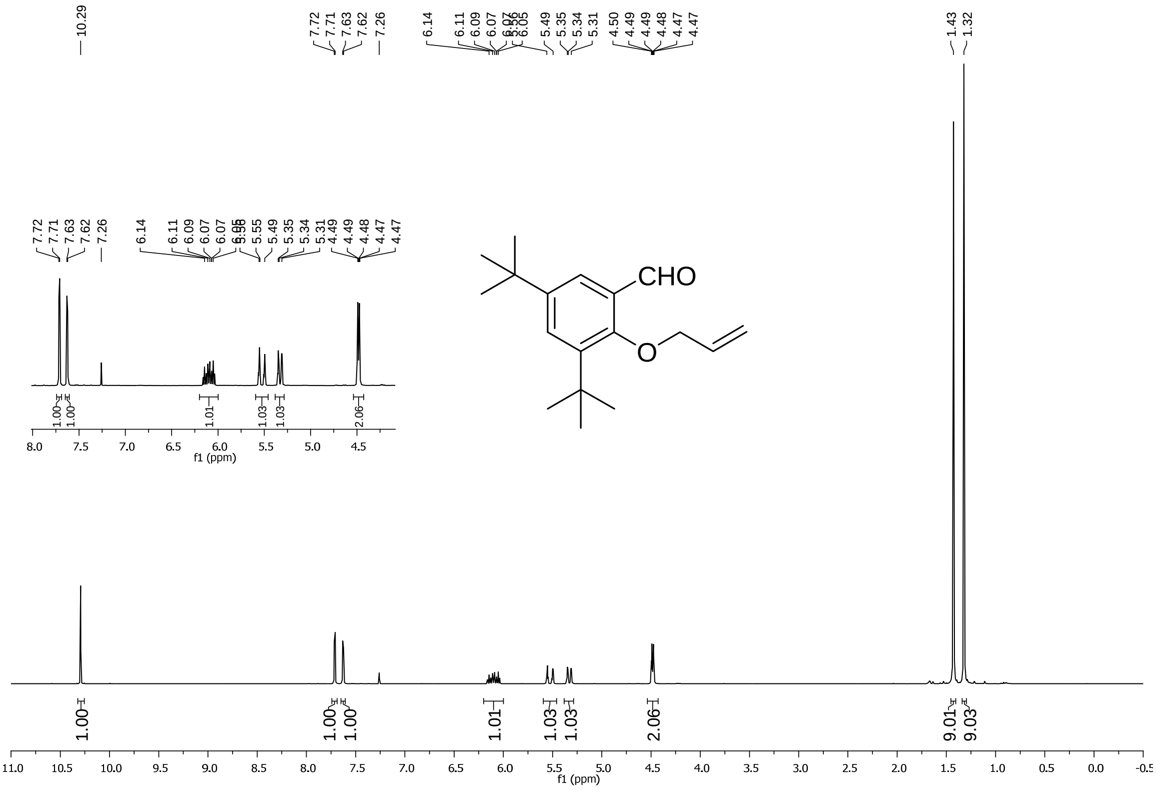


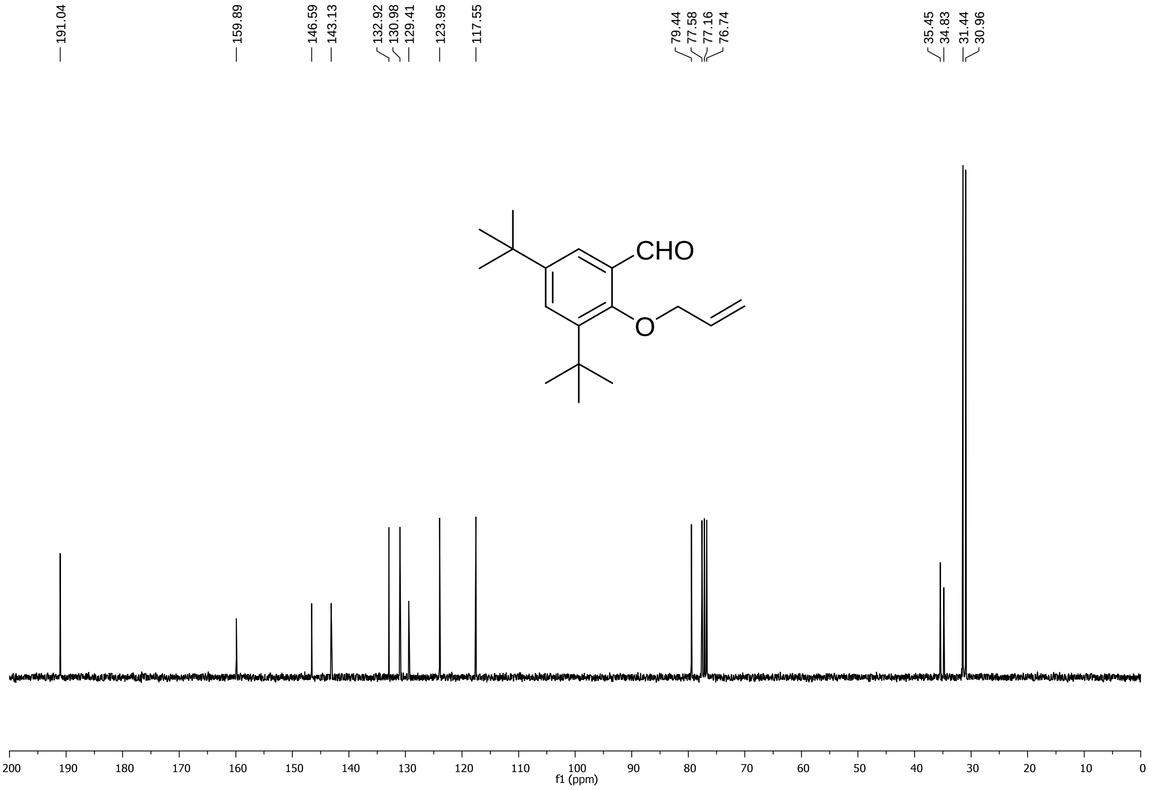
2-Allyloxy -5-(2-phenylvinyl) benzaldehyde (2k)



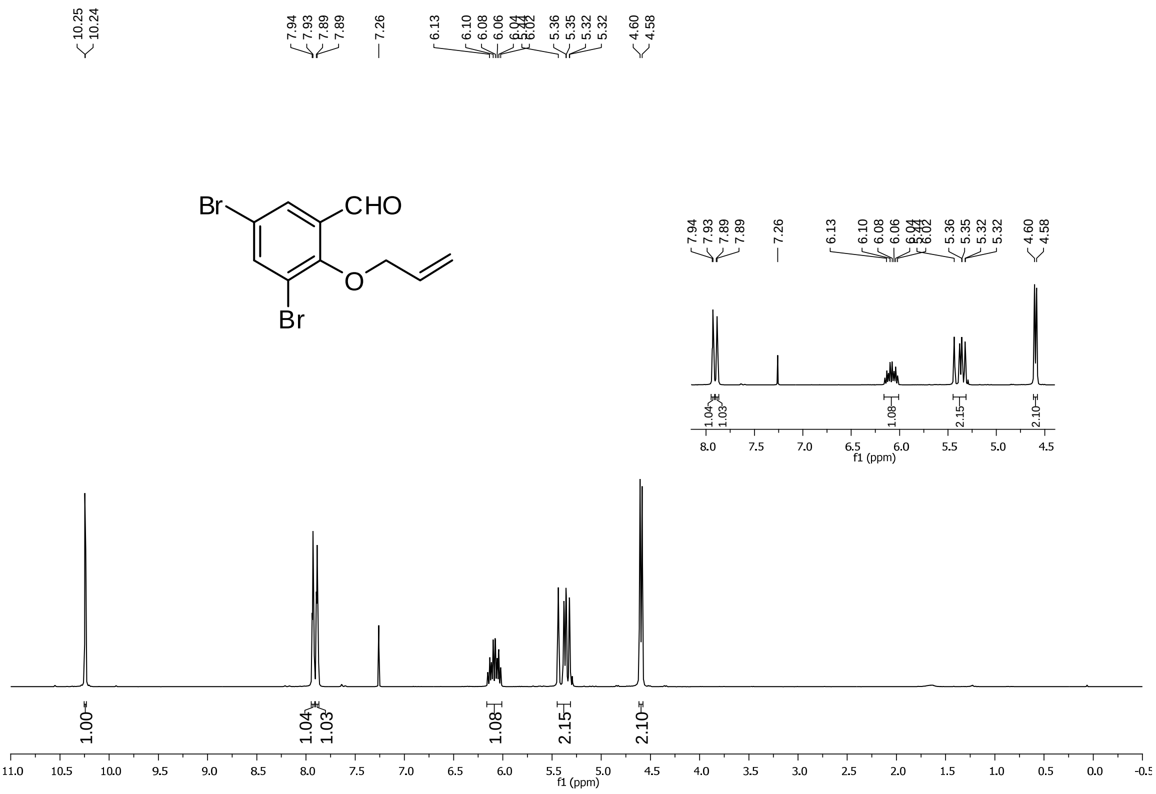


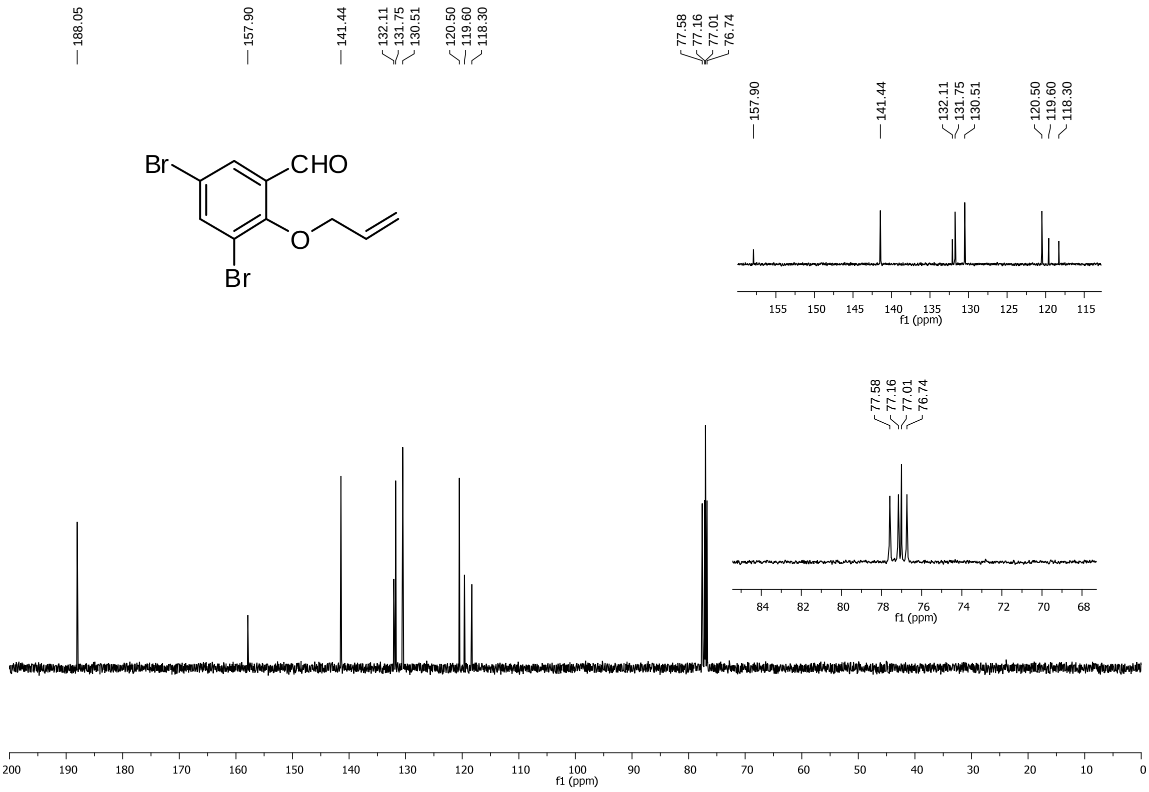
2-Allyloxy-3,5-di-*tert*-butyl benzaldehyde (1m)



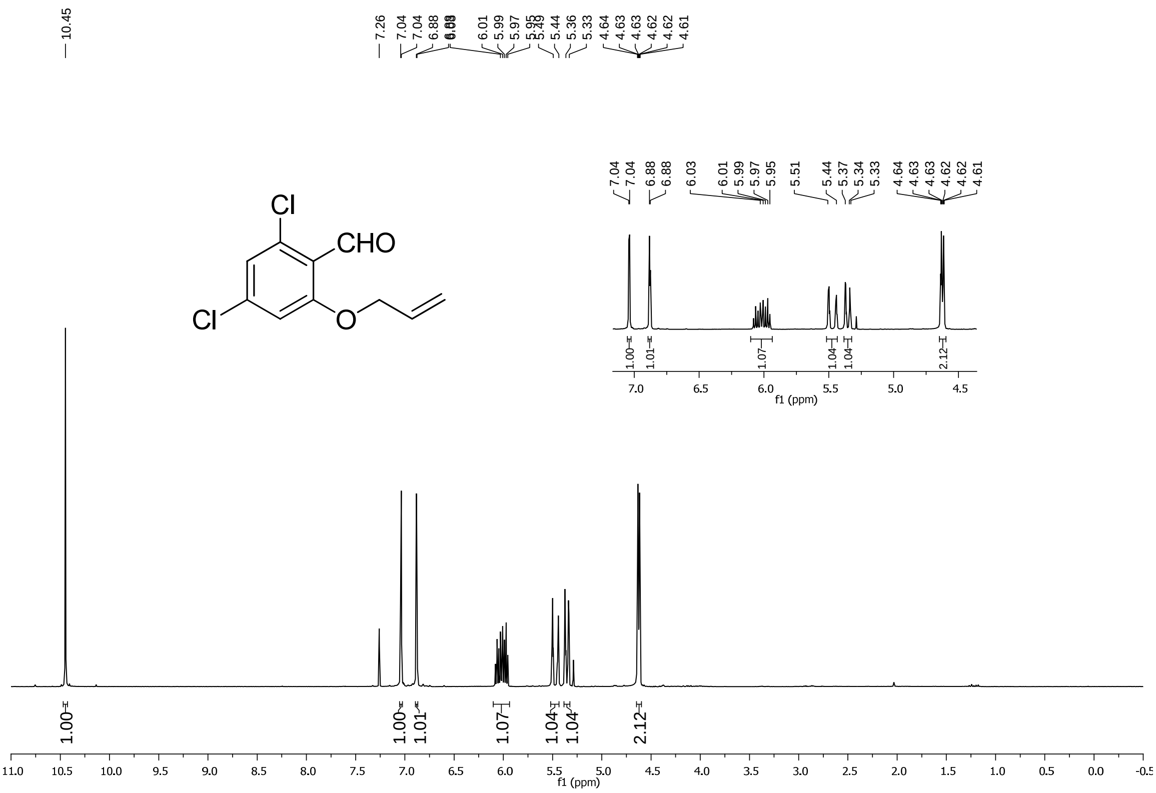


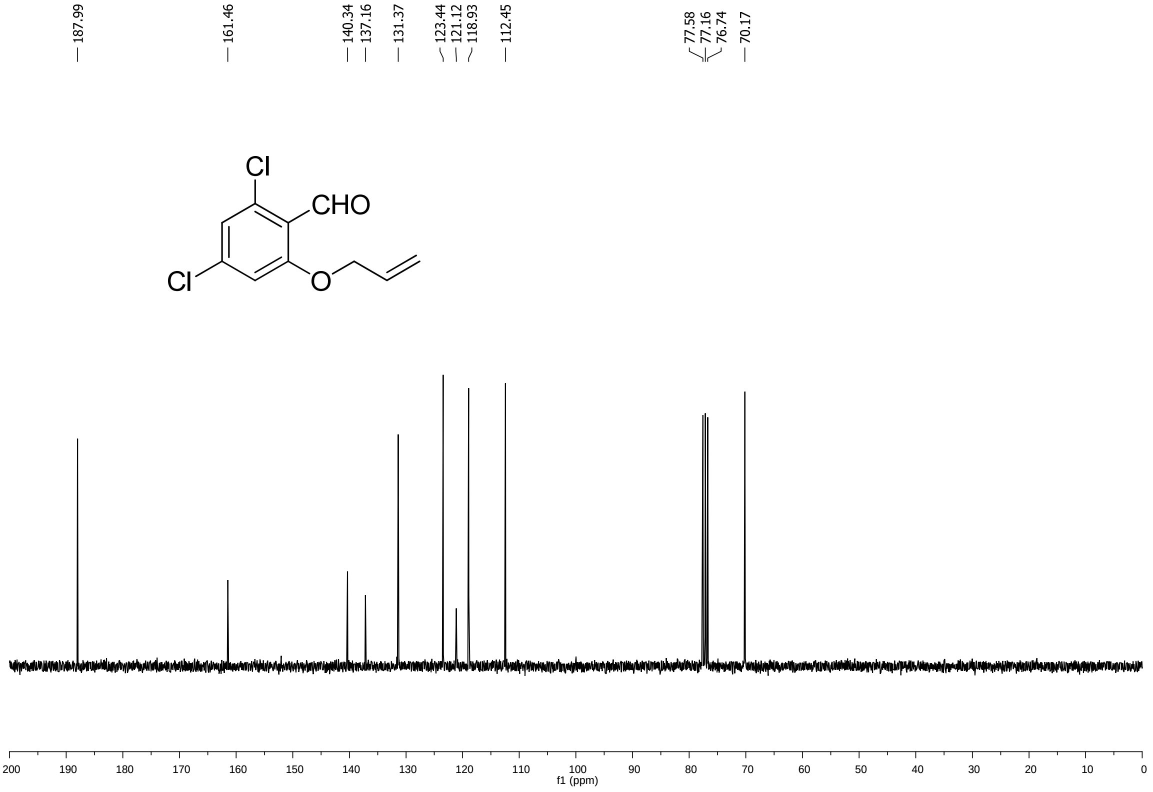
2-Allyloxy-3,5-dibromo benzaldehyde (1n)



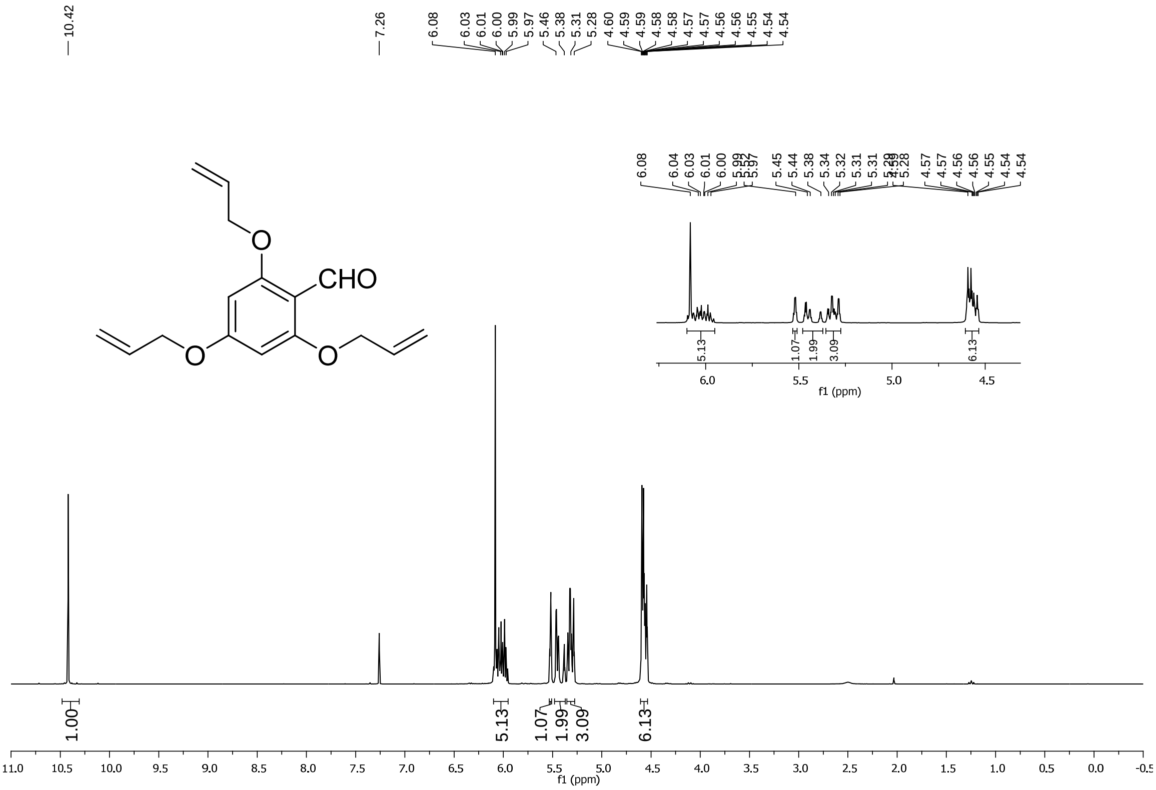


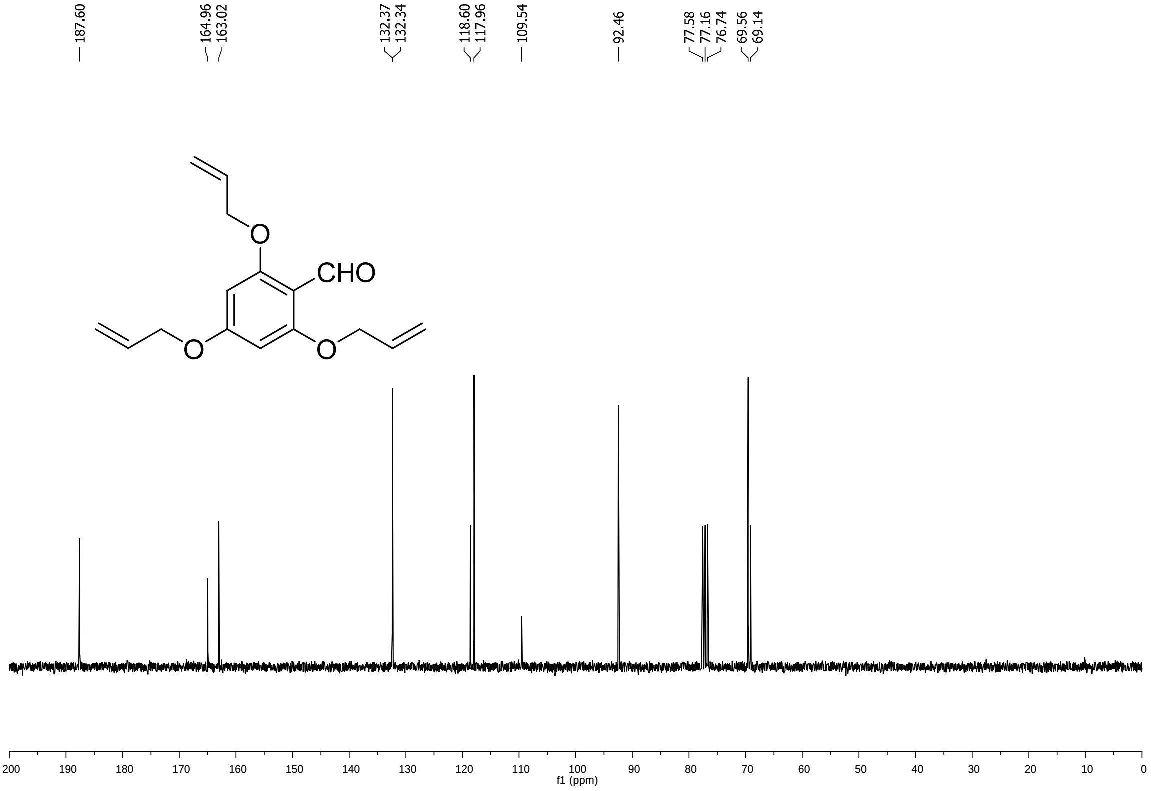
2-Allyloxy-4,6-dichloro benzaldehyde (1o)



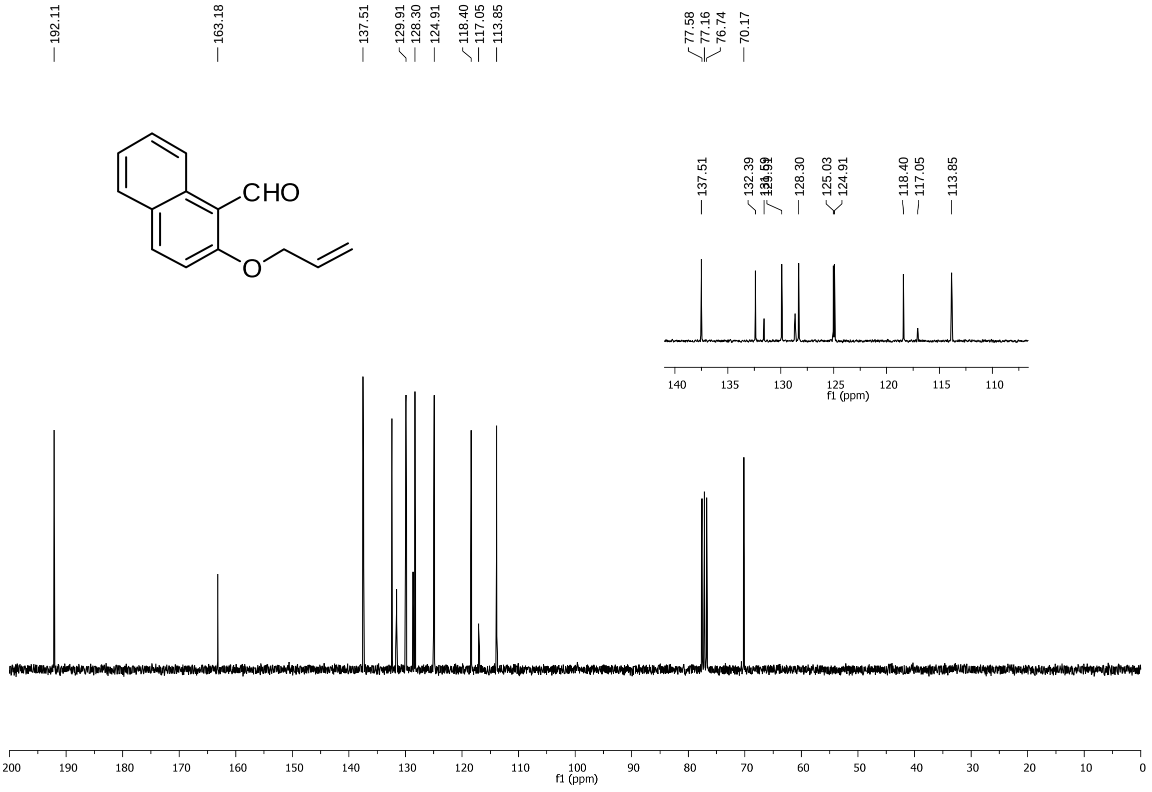


2,4,6-Triallyloxy benzaldehyde (1p)

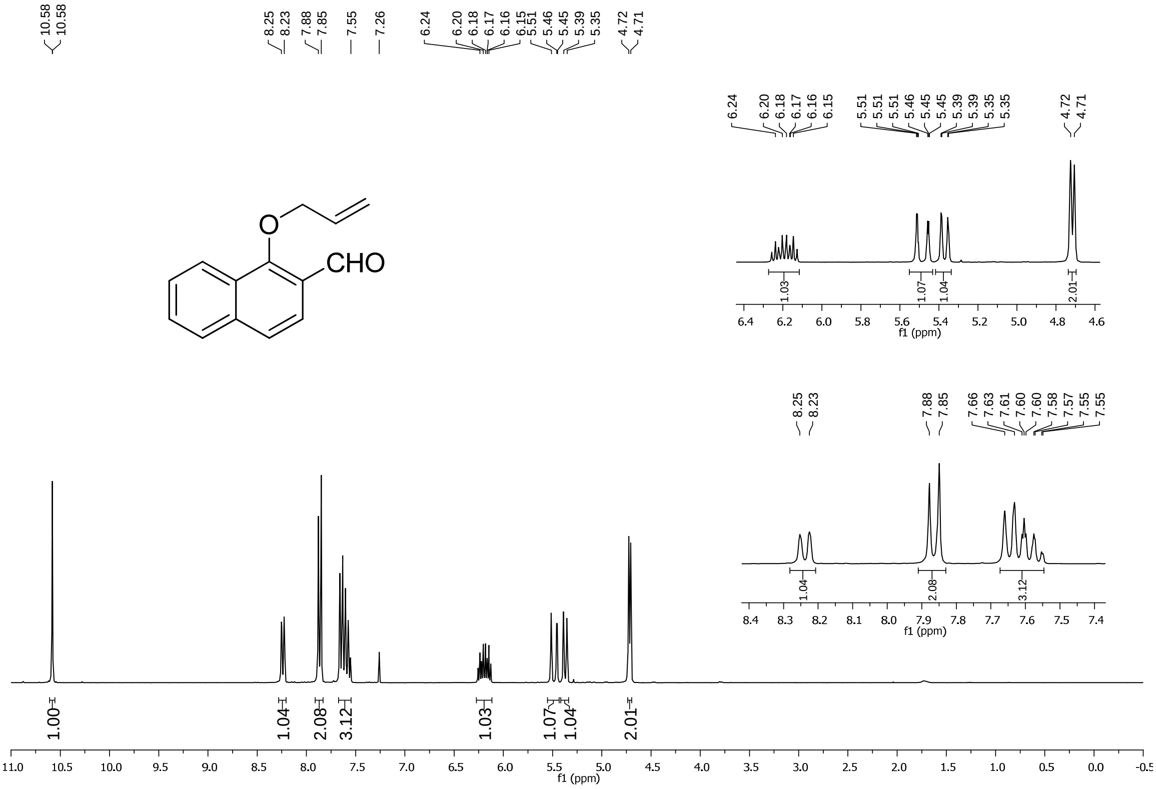


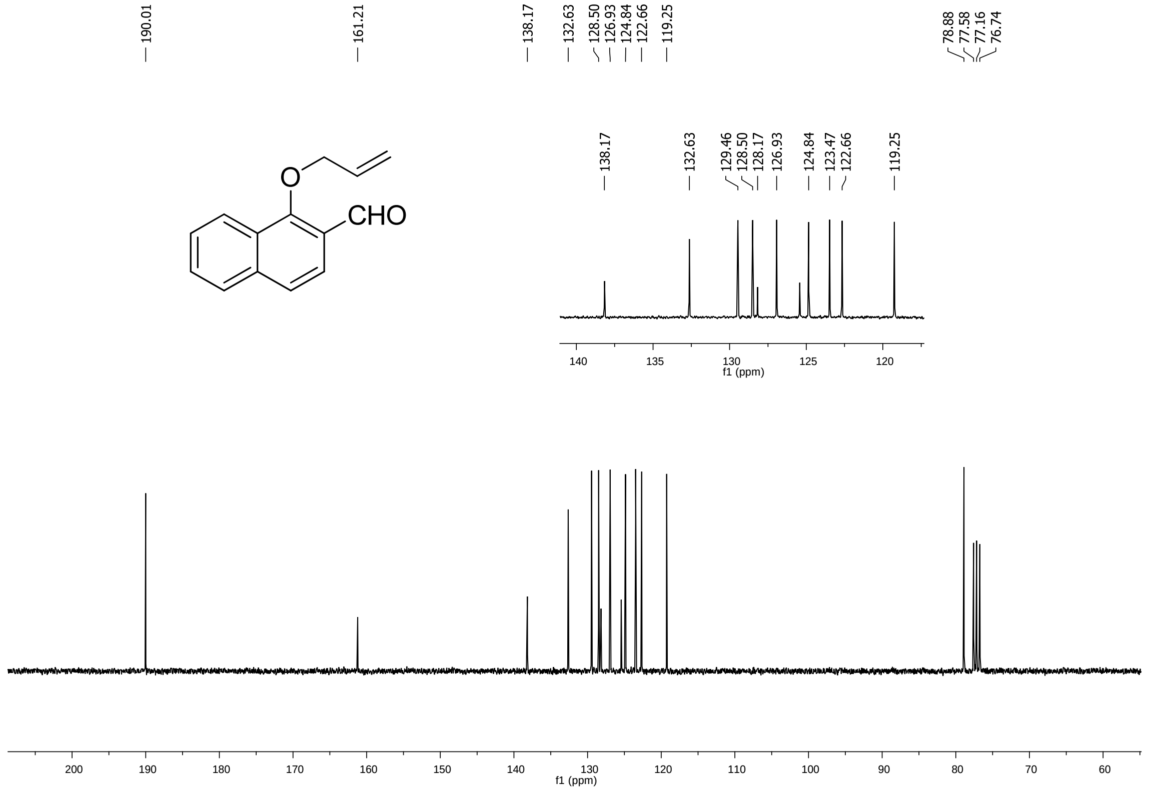


2-Allyloxy-1-Naphthaldehyde (1q)

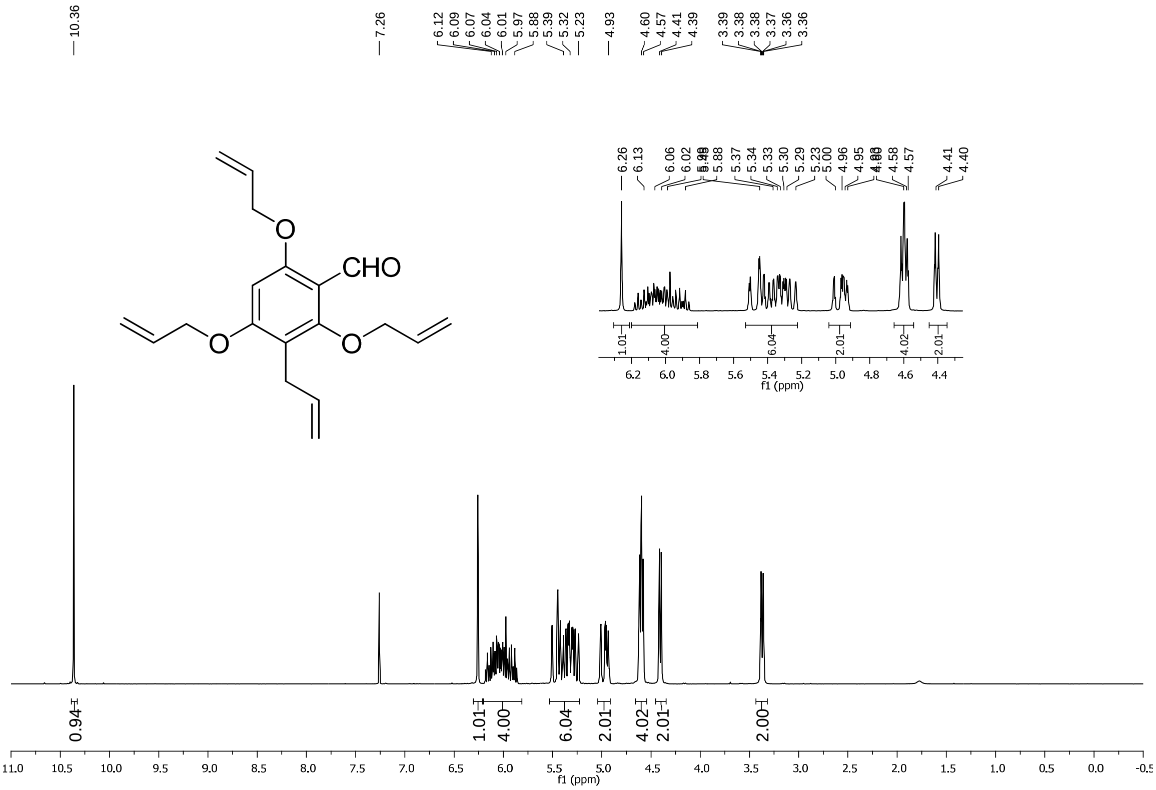


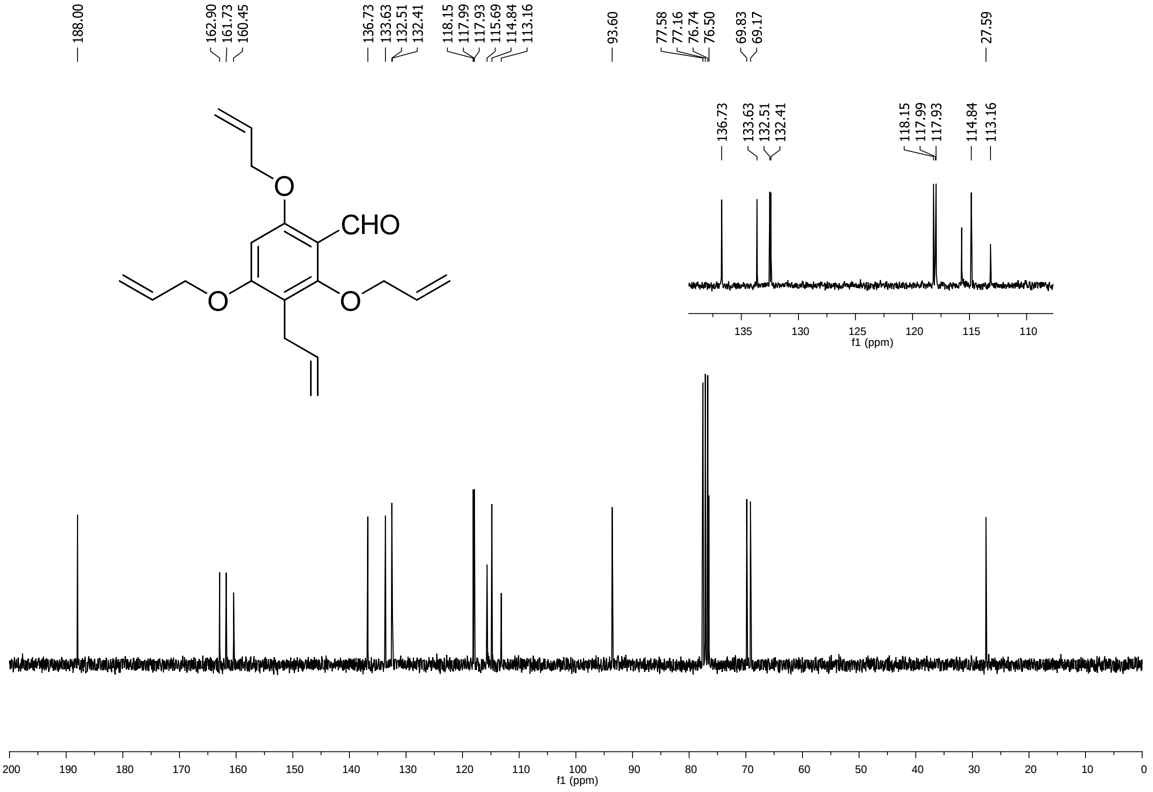
1-Allyloxy-2-Naphthaldehyde (1r)



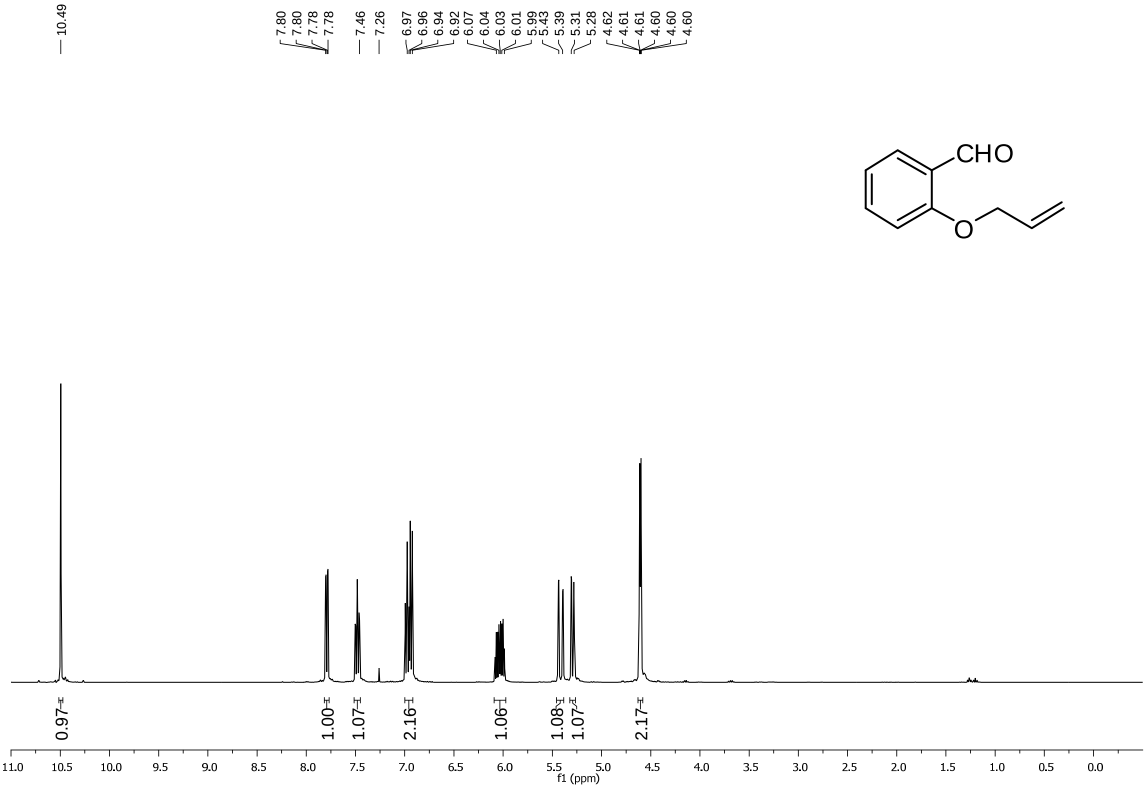


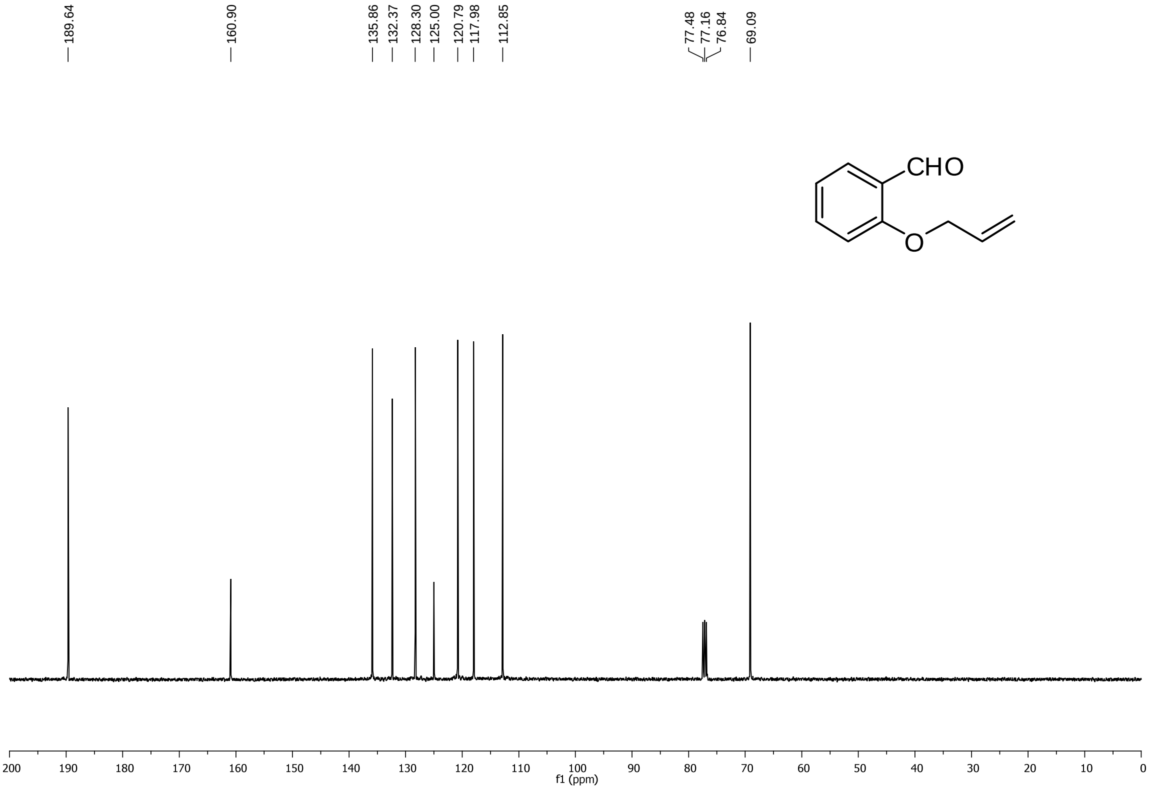
3-Allyl-2,4,6-triallyloxy benzaldehyde (1s)



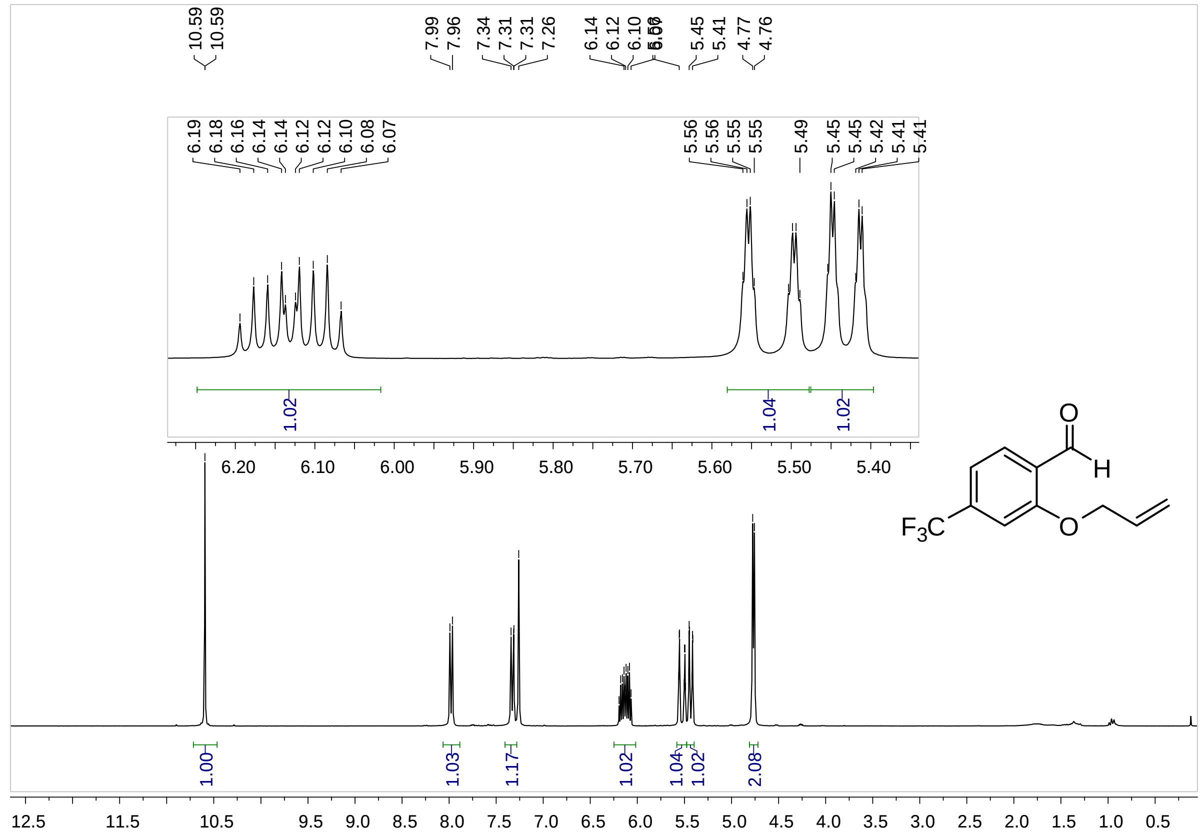


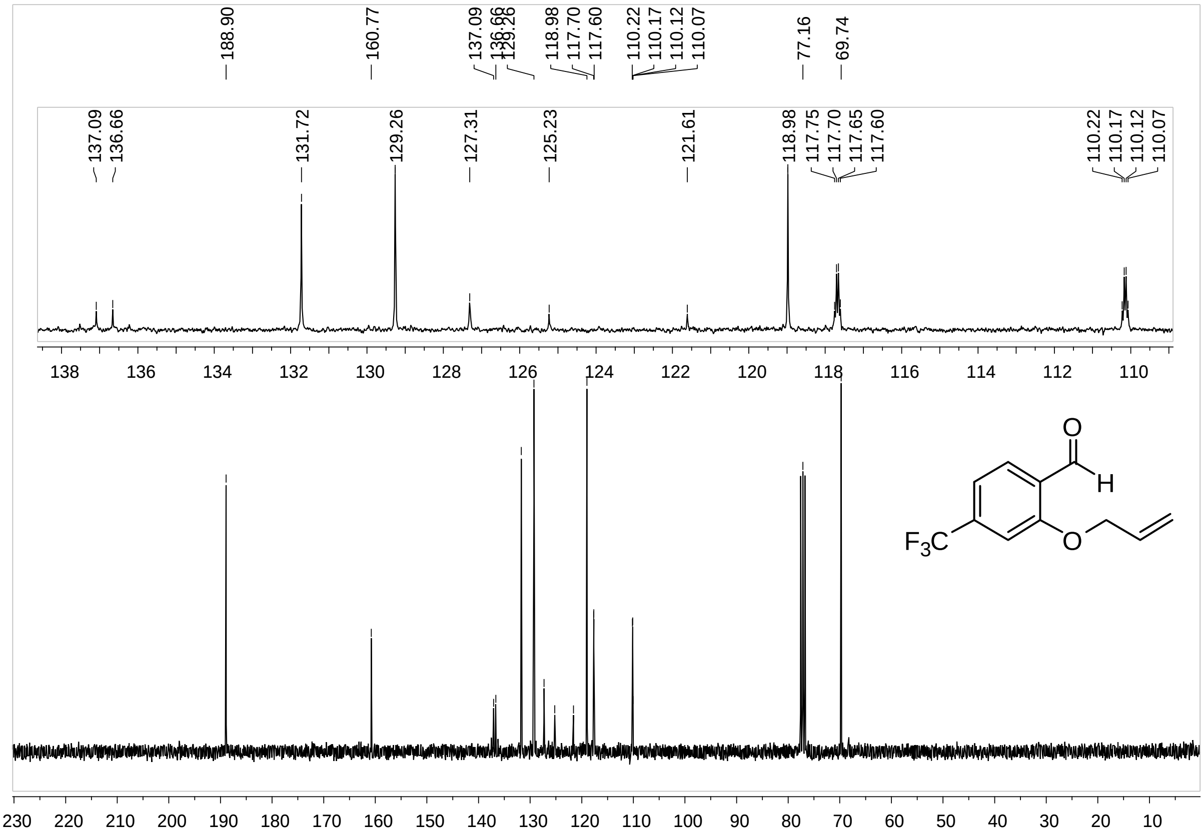
2-Allyloxy-benzaldehyde (1t)

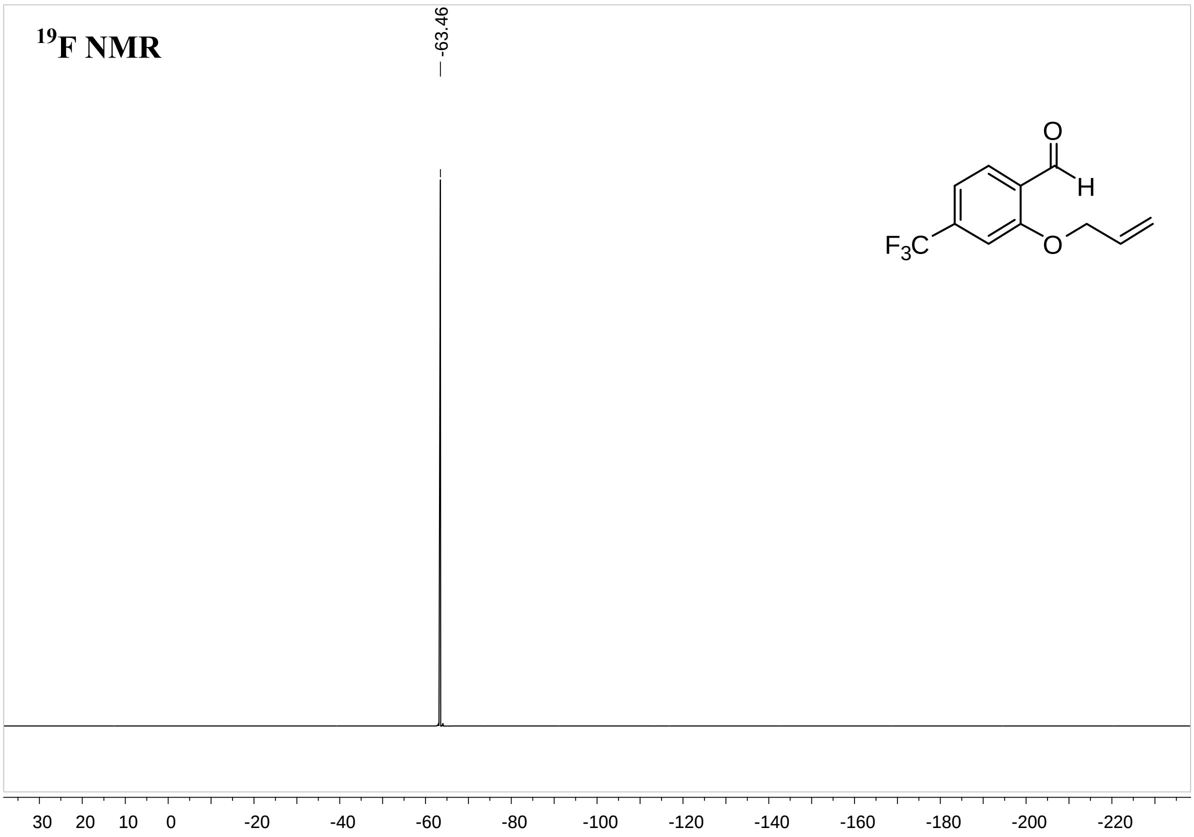




2-Allyloxy-4-trifluoromethyl-benzaldehyde (1l)



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O
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20
10
0
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-200
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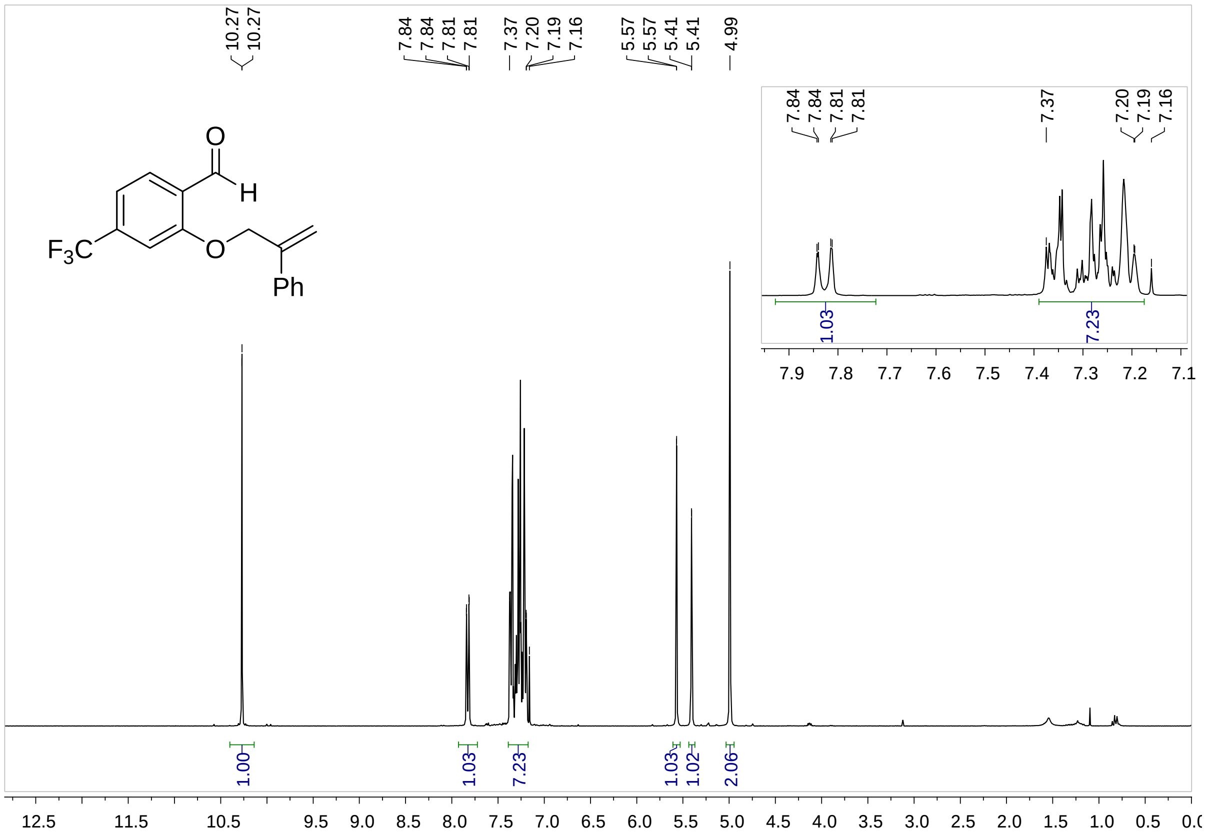
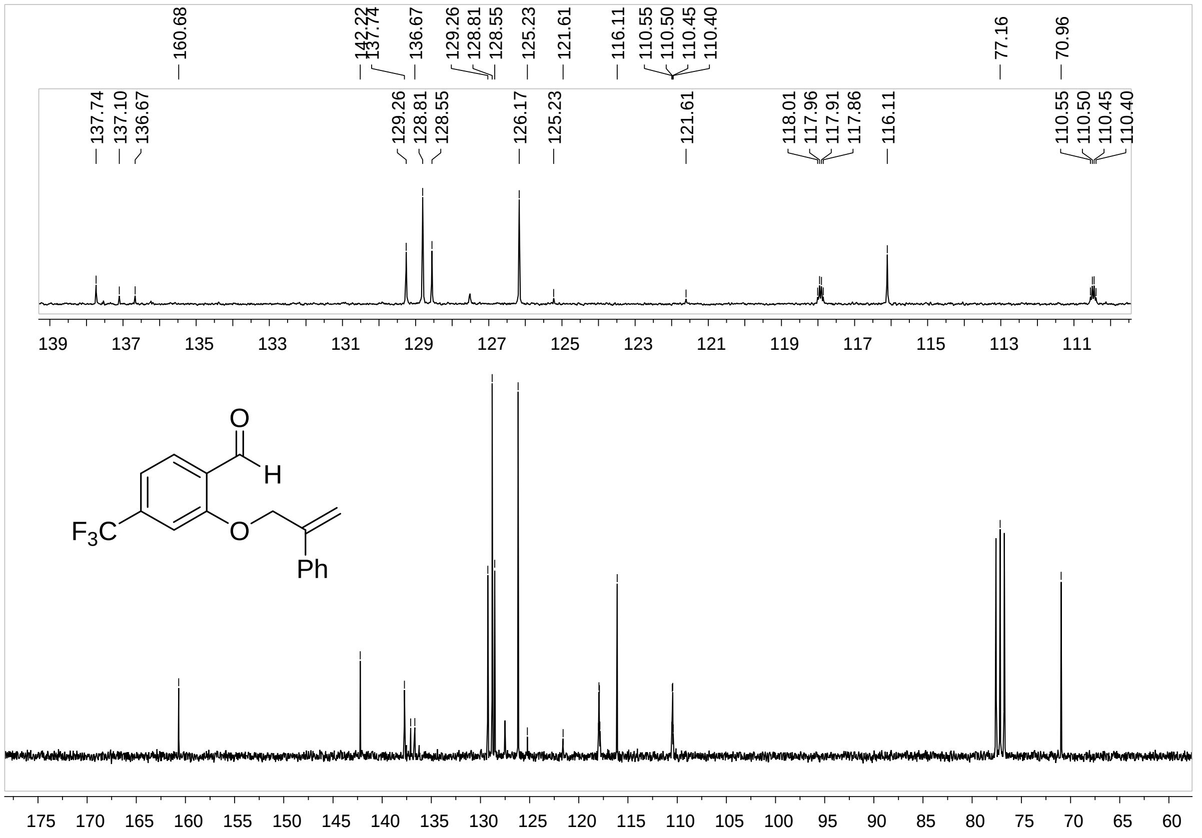
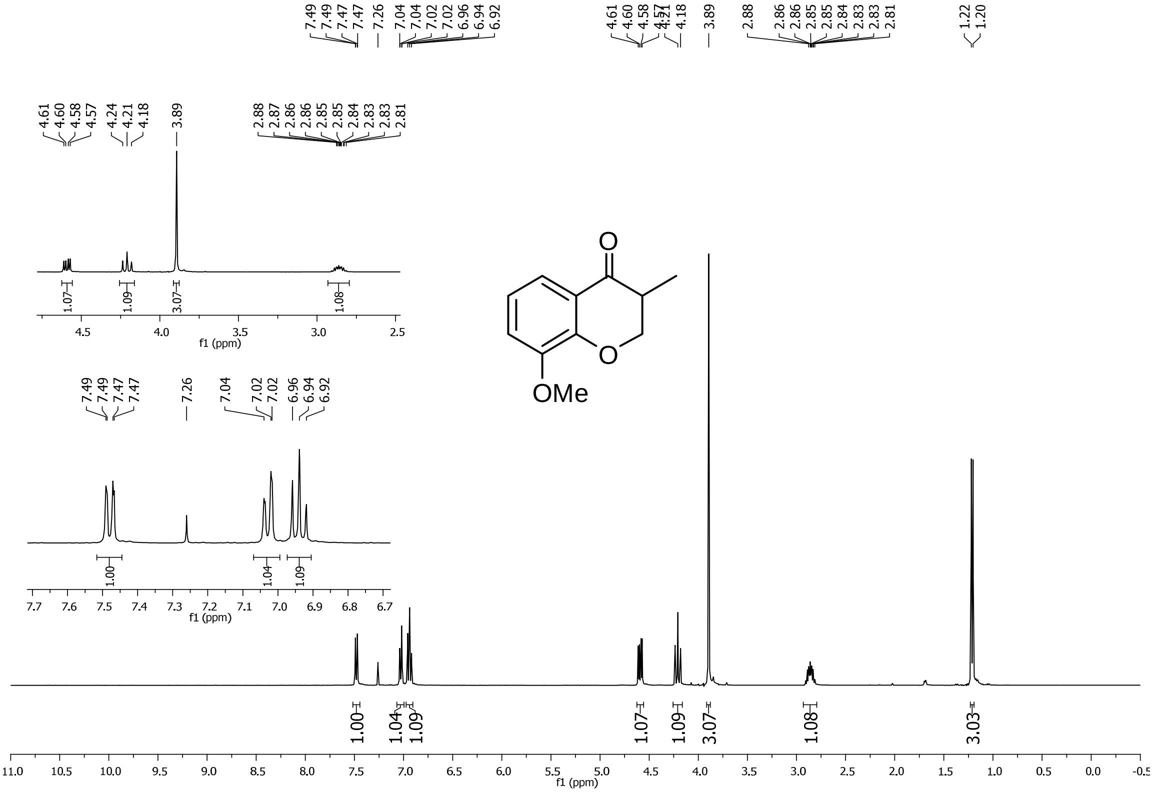
2-(2-Phenyl-allyloxy)-4-trifluoromethyl-benzaldehyde (10b)

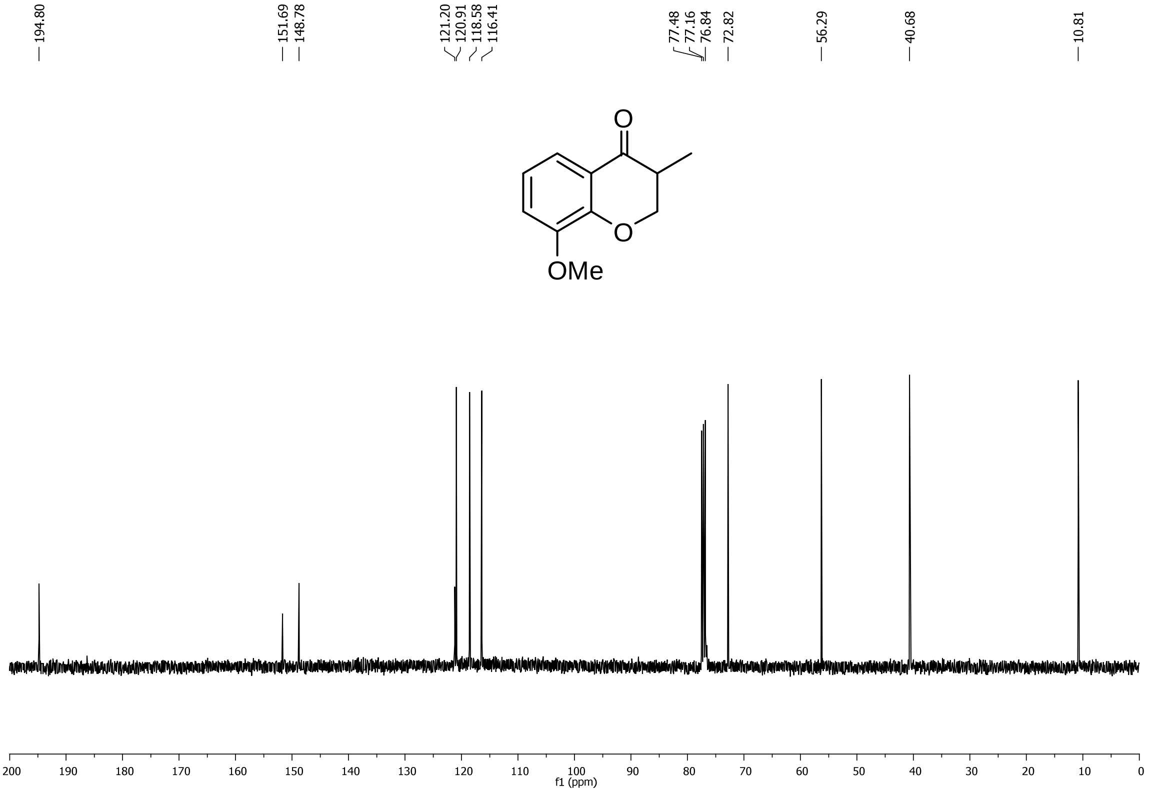




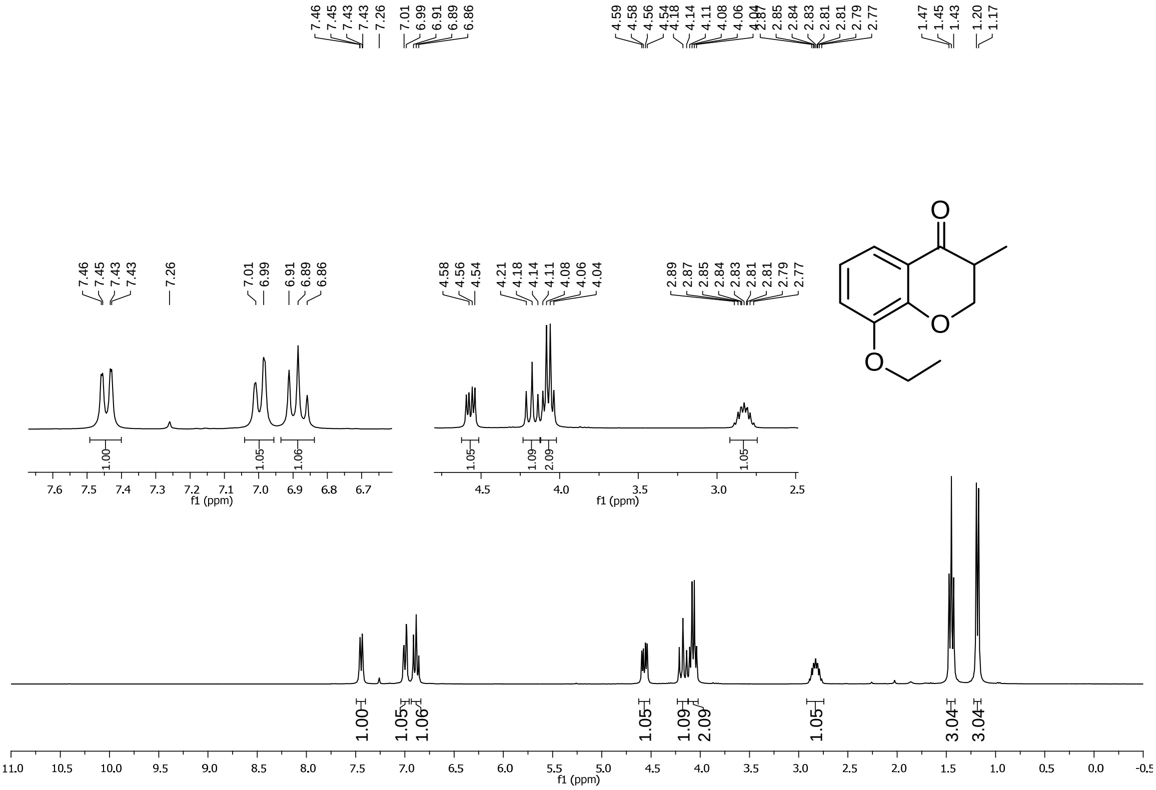
7.2 Products

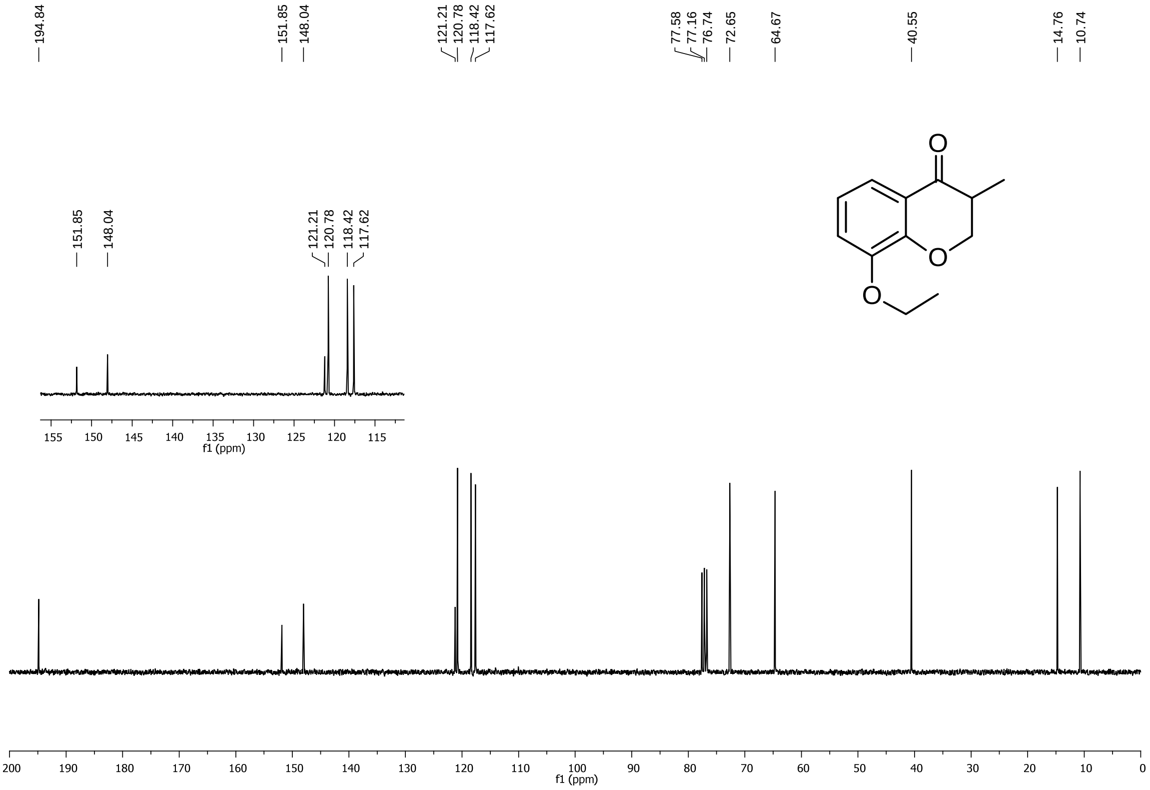
8-Methoxy-3-methyl-chroman-4-one (2a)



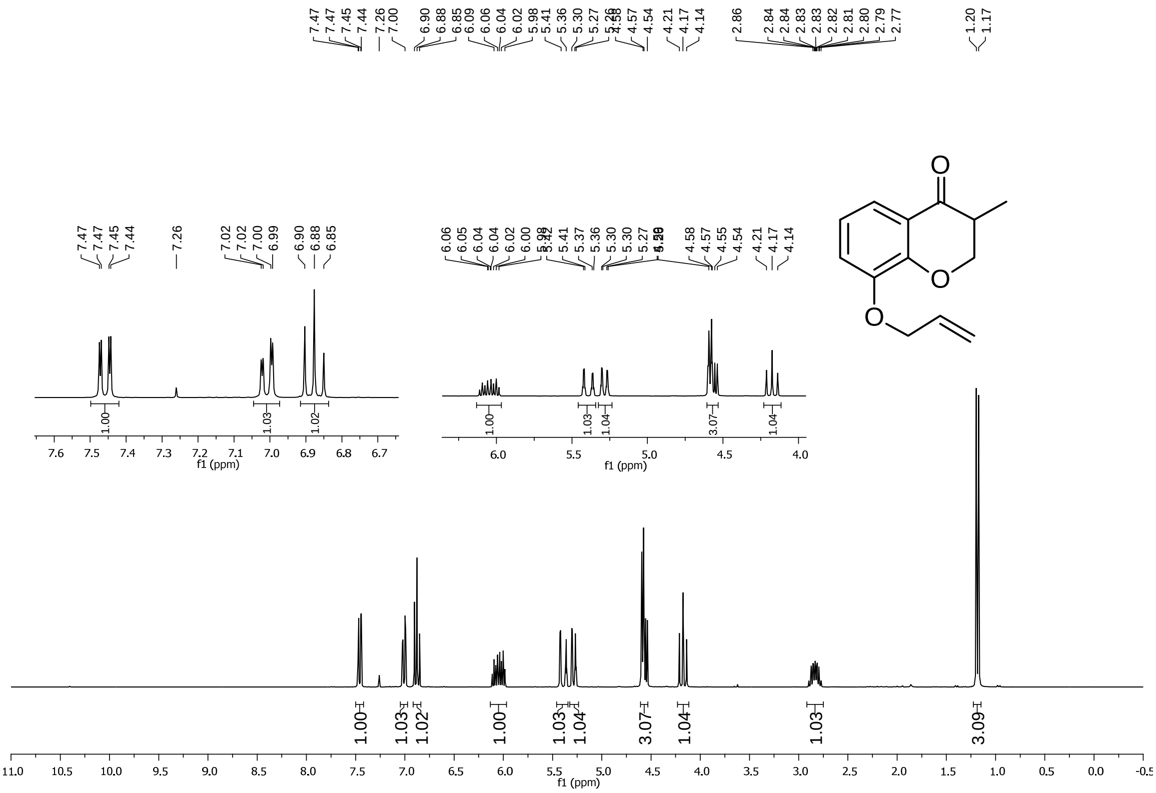


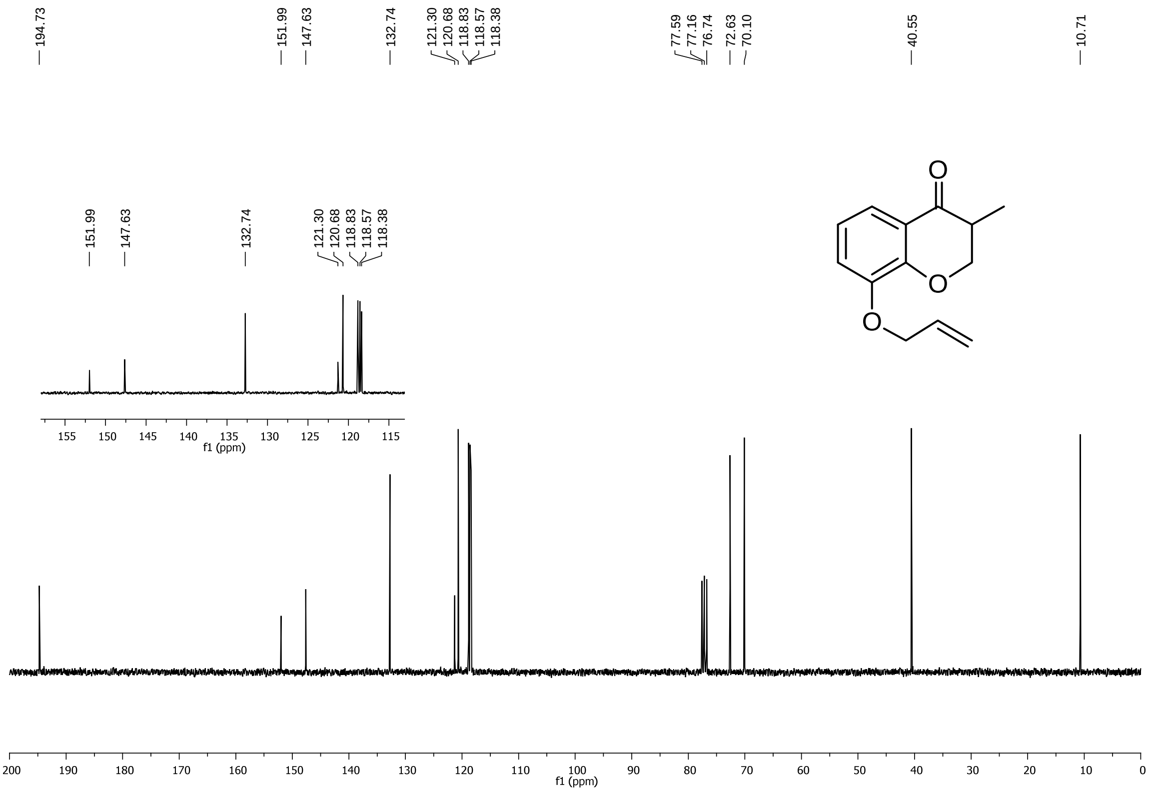
8-Ethoxy-3-methyl-chroman-4-one (2b)



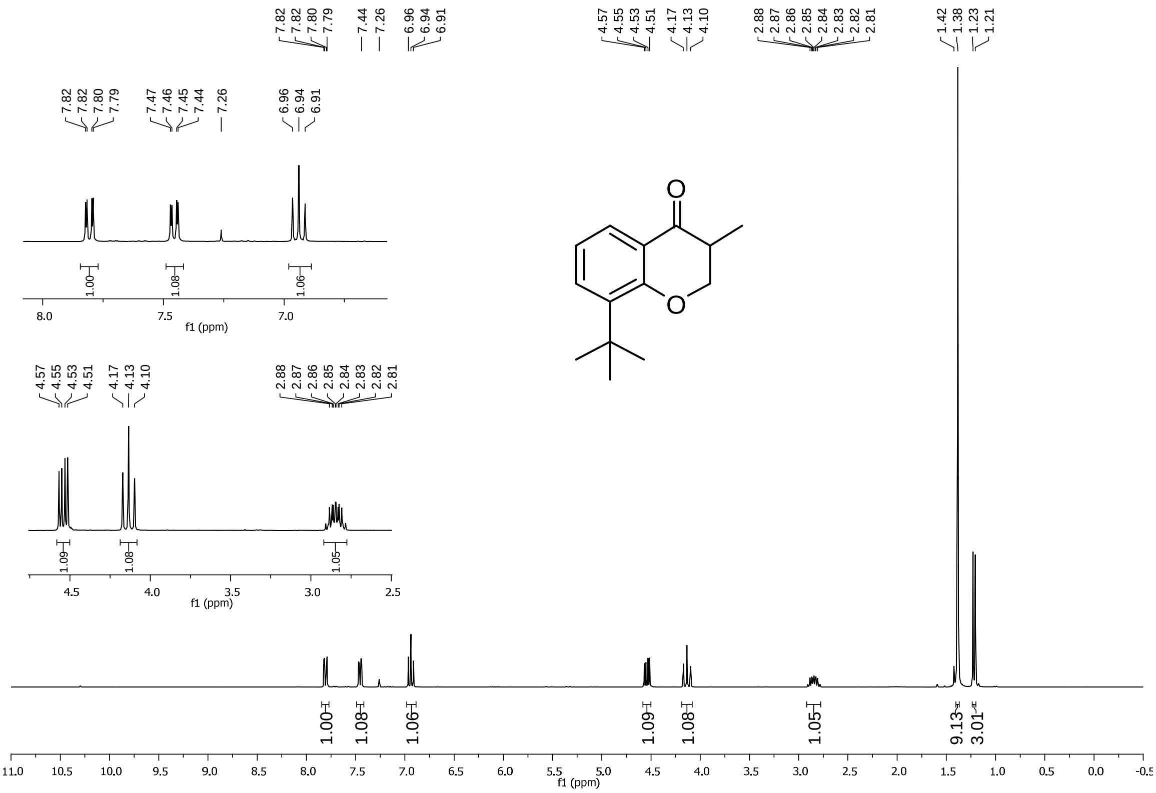


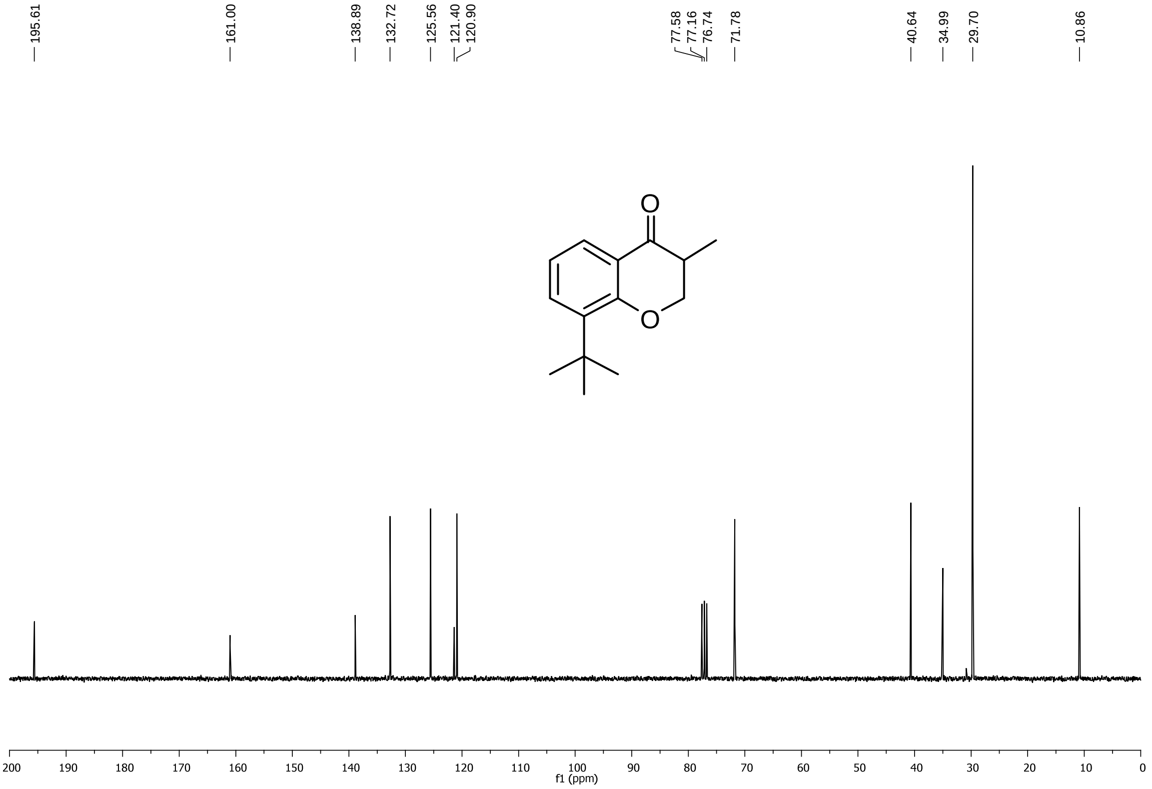
8-Allyloxy-3-methyl-chroman-4-one (2c)



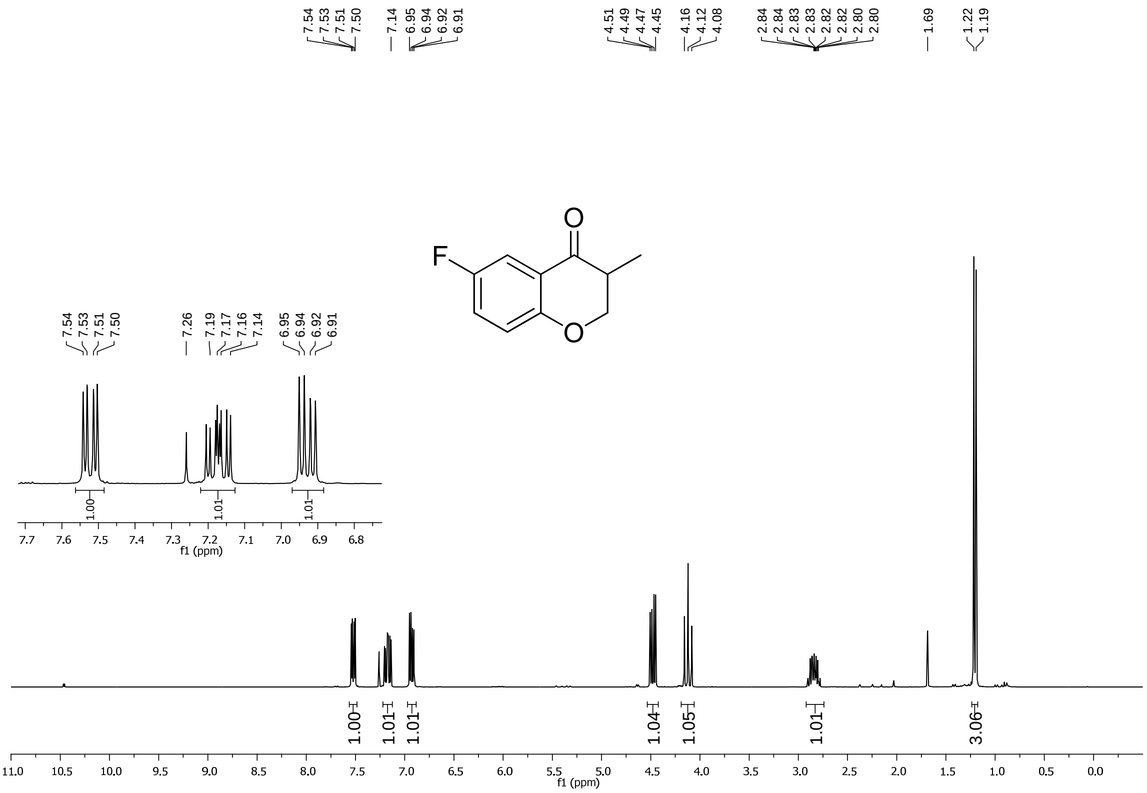


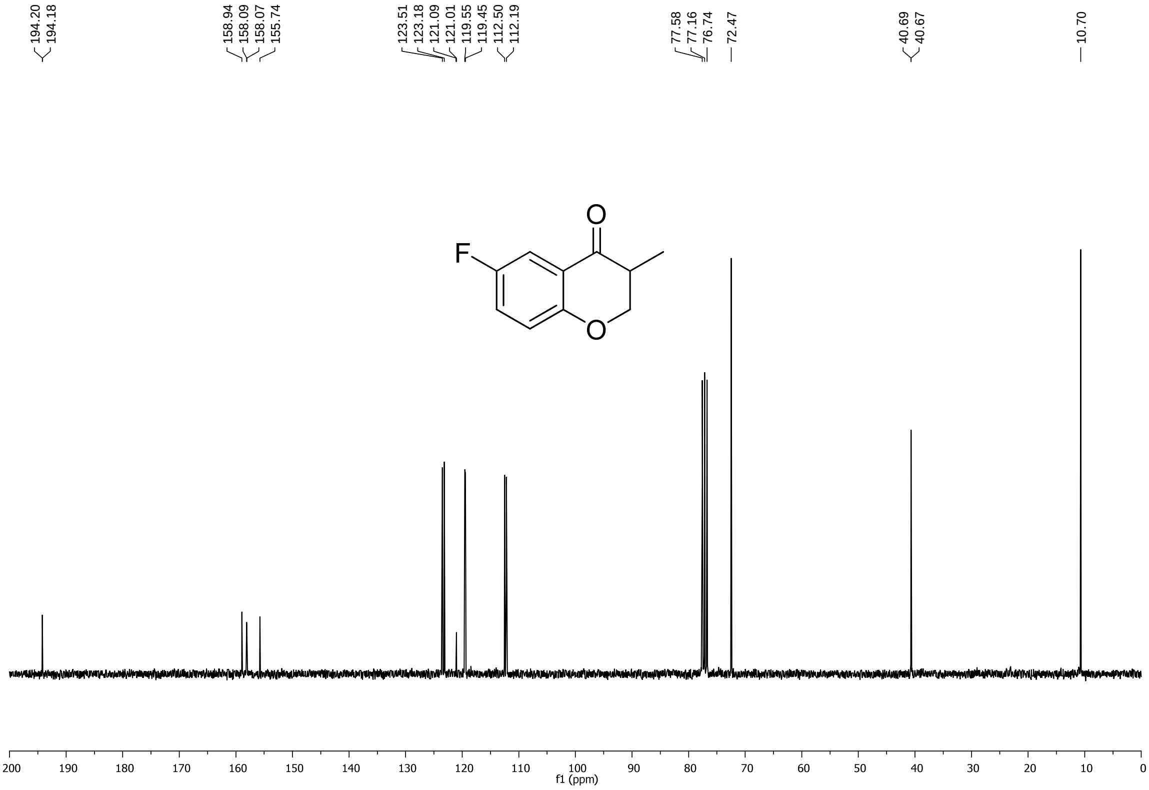
8-*Tert*-butyl-3-methyl-chroman-4-one (2d)



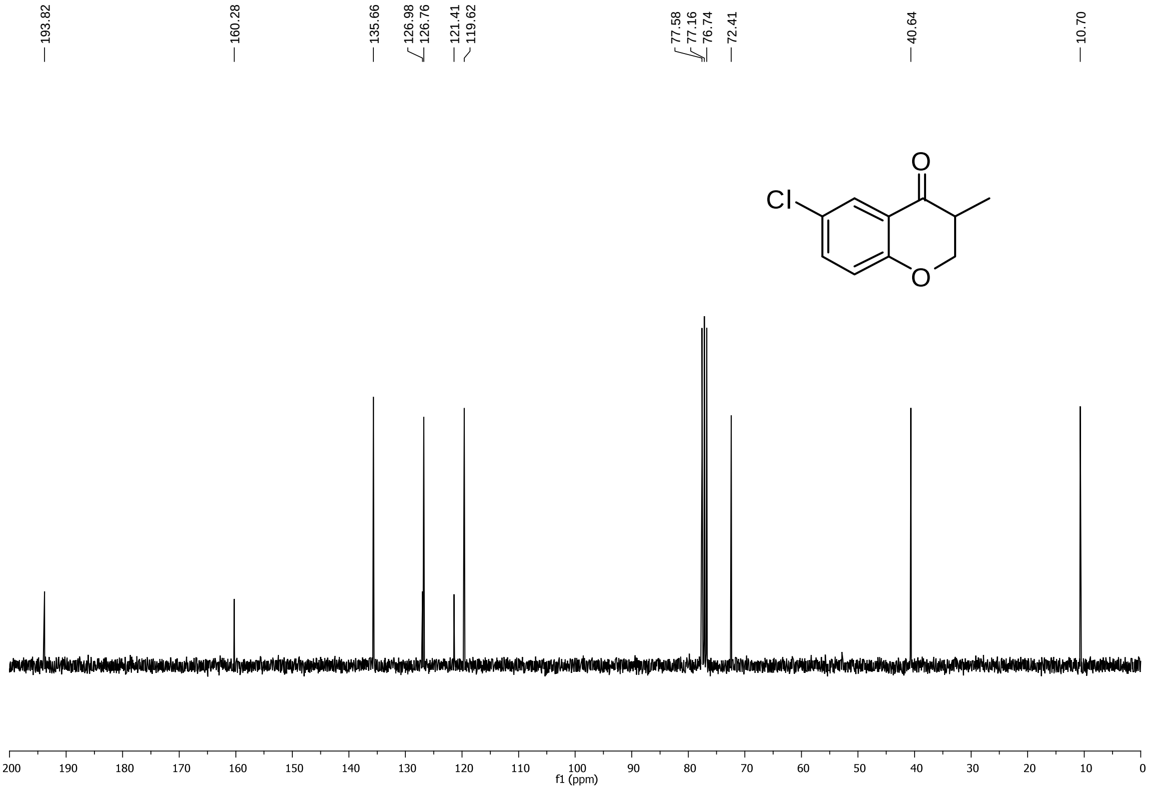


6-Fluoro-3-methyl-chroman-4-one (2e)

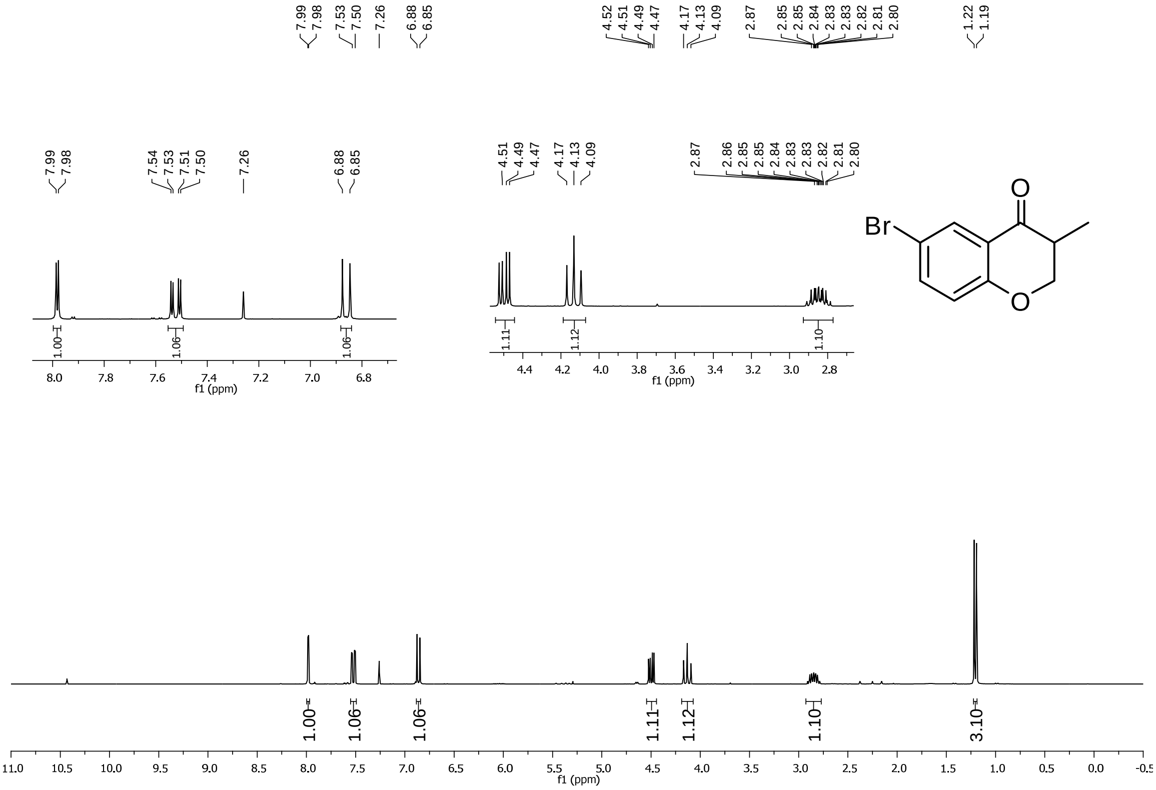


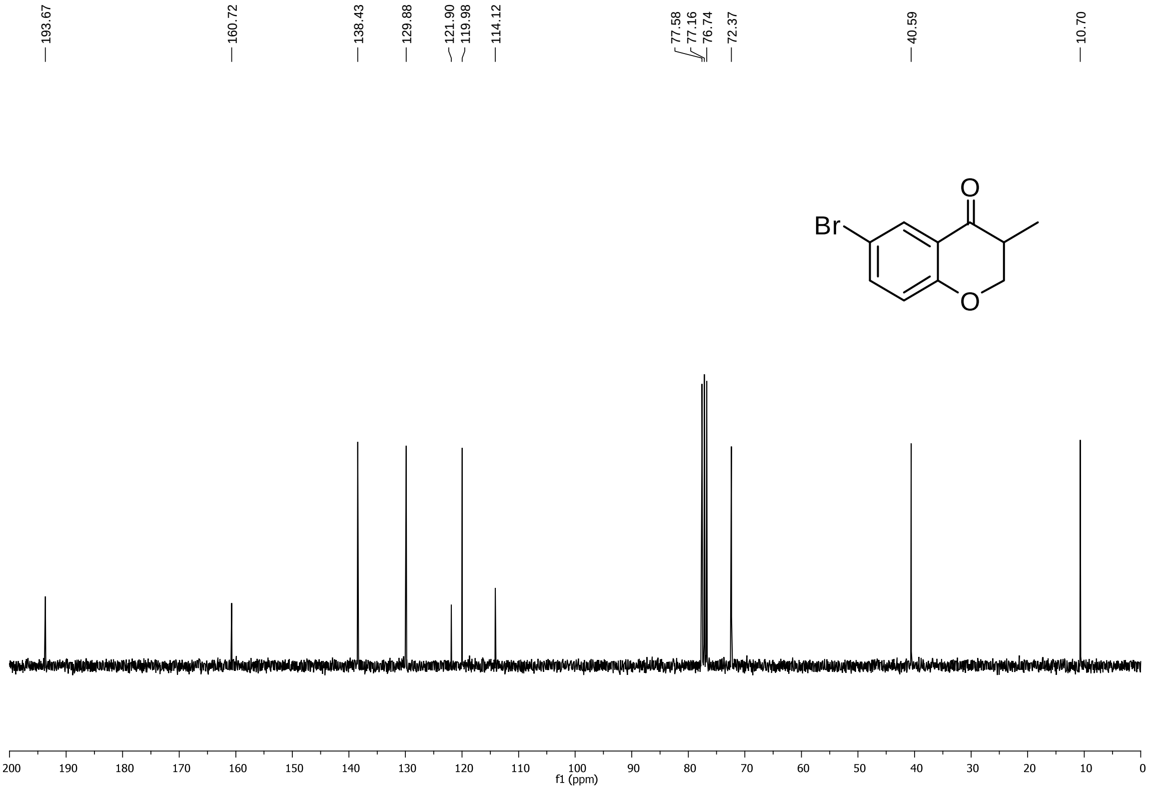


6-Chloro-3-methyl-chroman-4-one (2f)

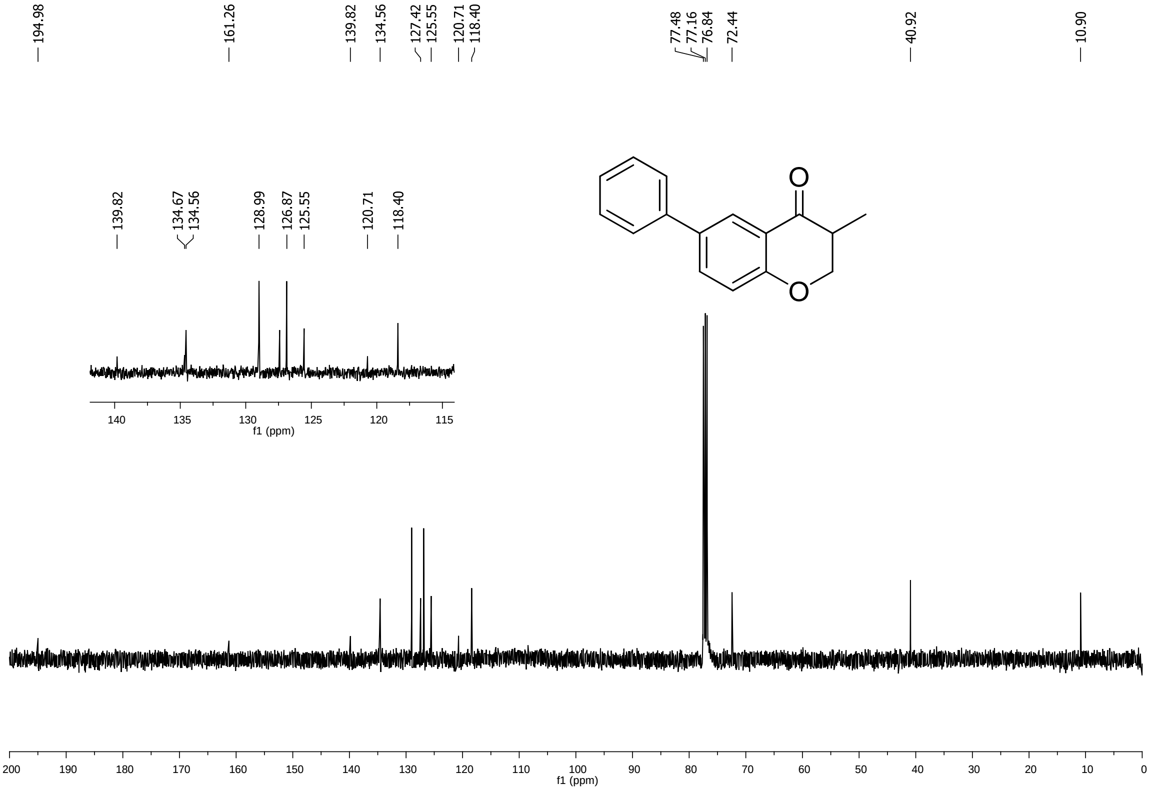


6-Bromo-3-methyl-chroman-4-one (2g)

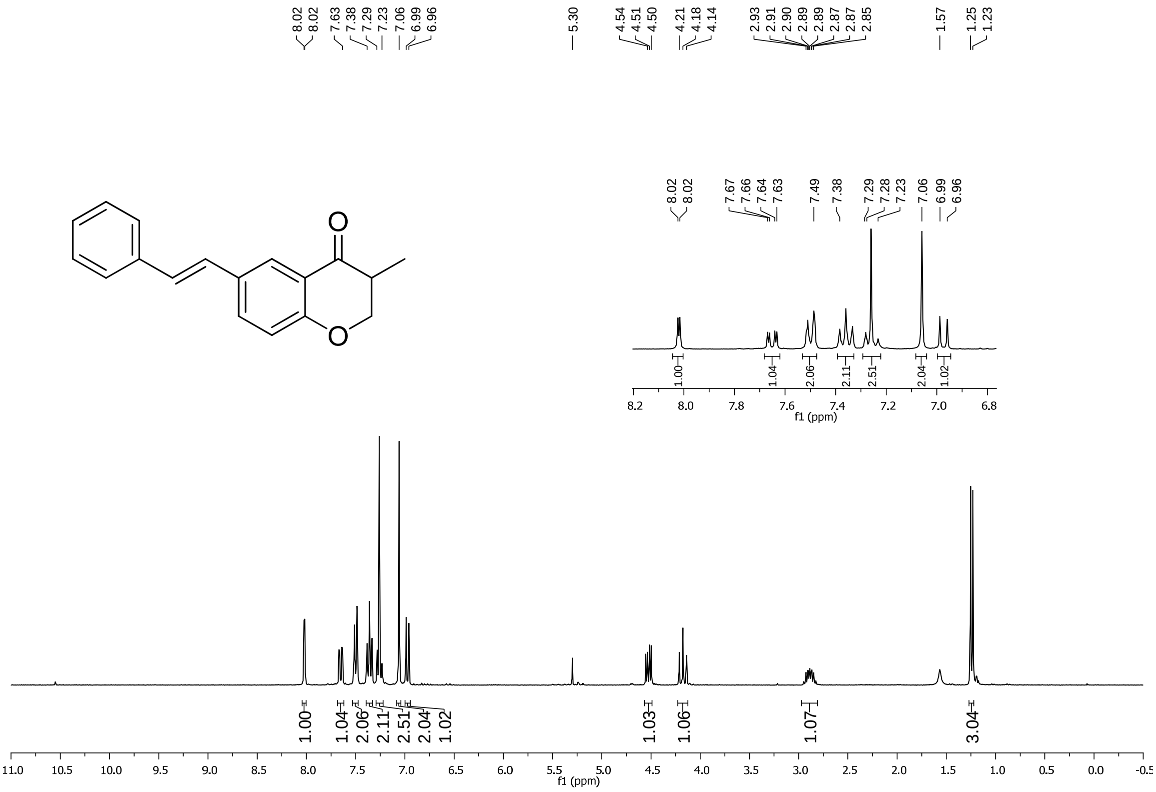


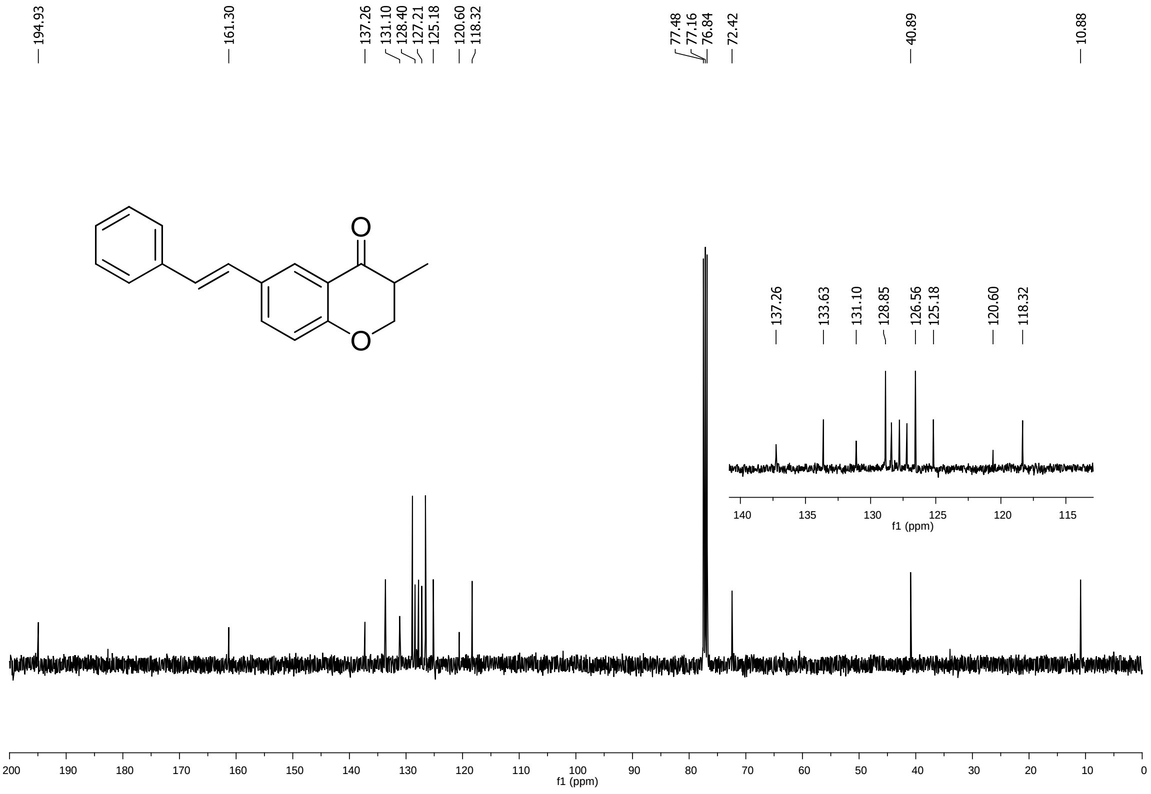


3-Methyl-6-phenyl chroman-4-one (2j)

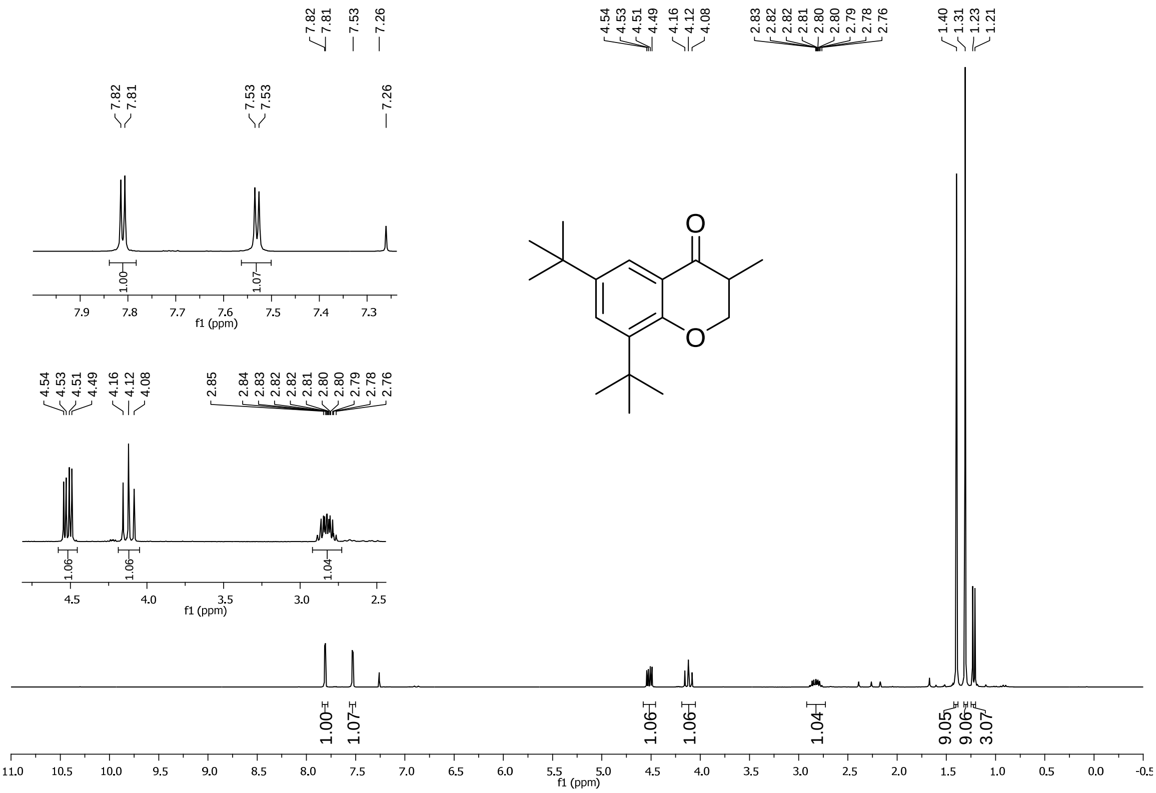


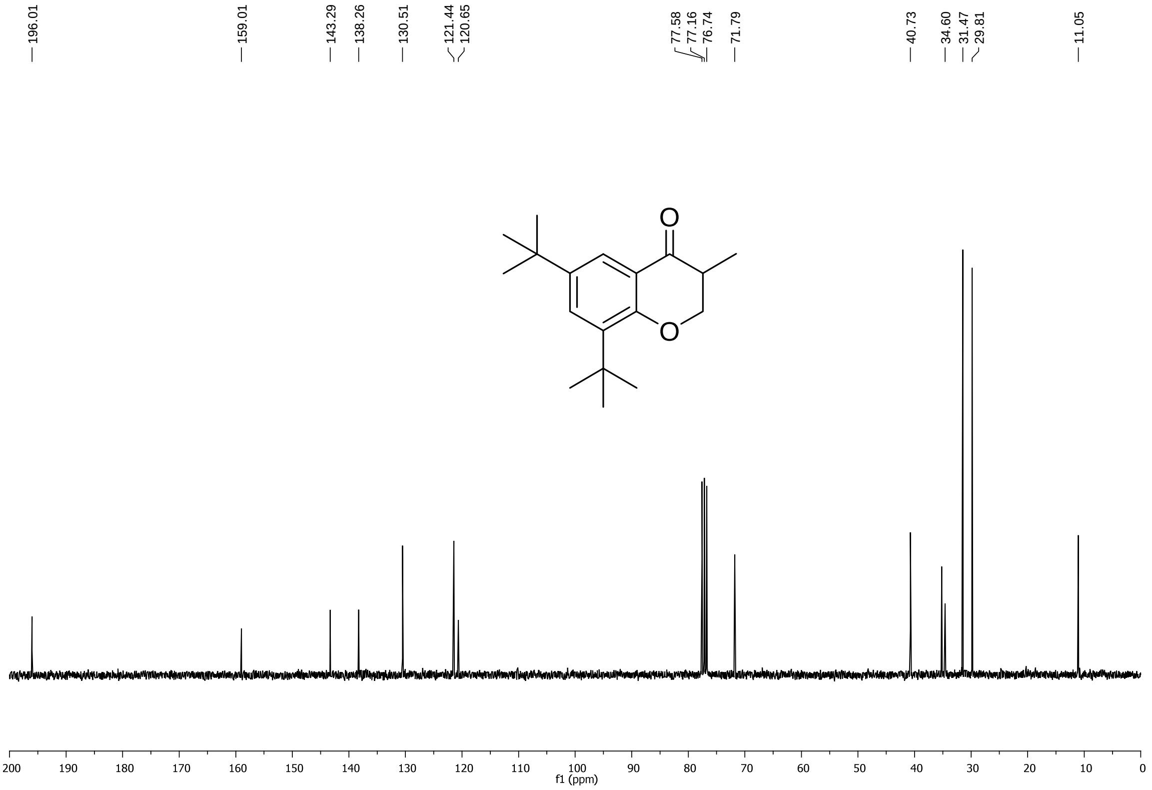
3-Methyl-6-(2-phenylvinyl) chroman-4-one (2k)



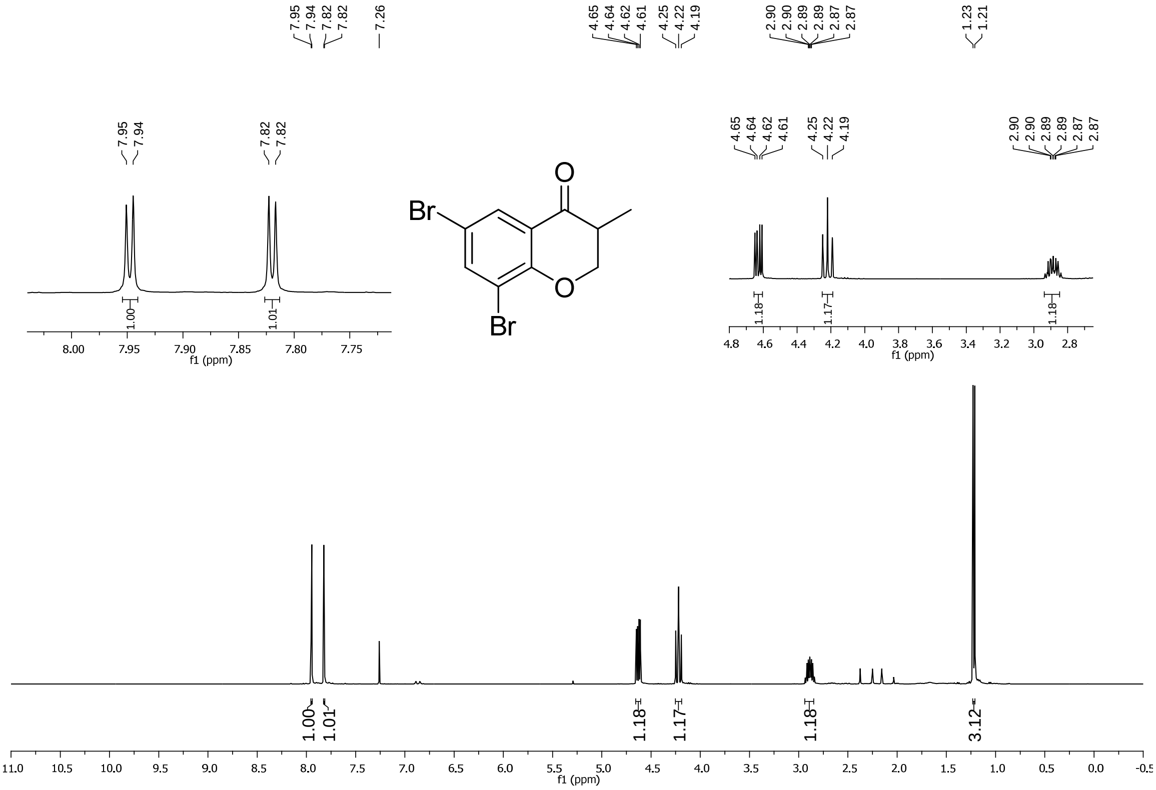


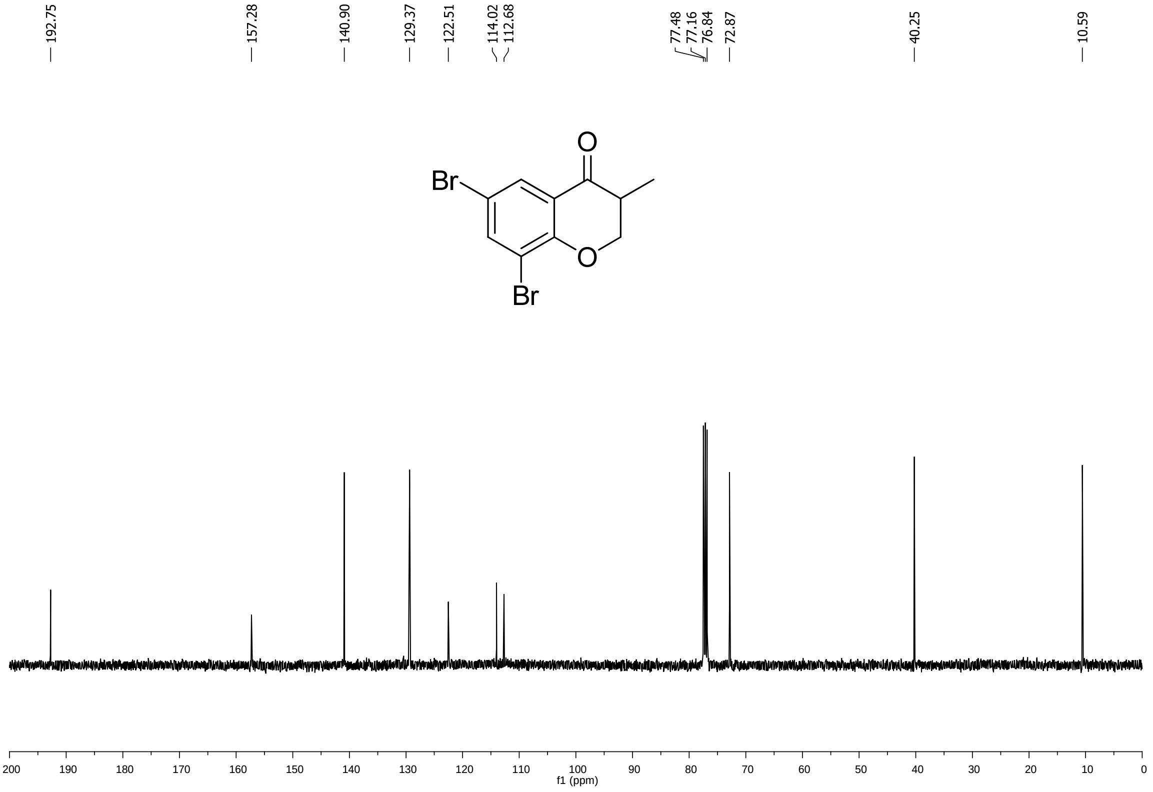
6,8-Di-*tert*-butyl-3-methyl-chroman-4-one (2m)



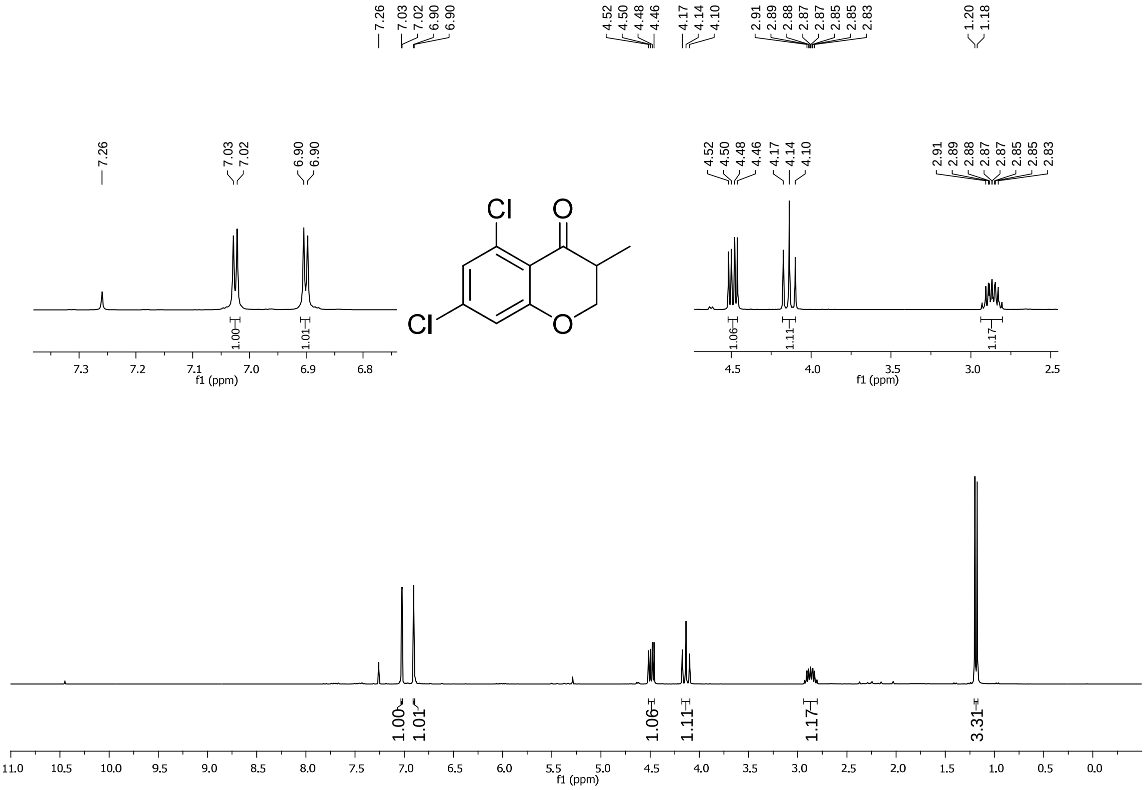


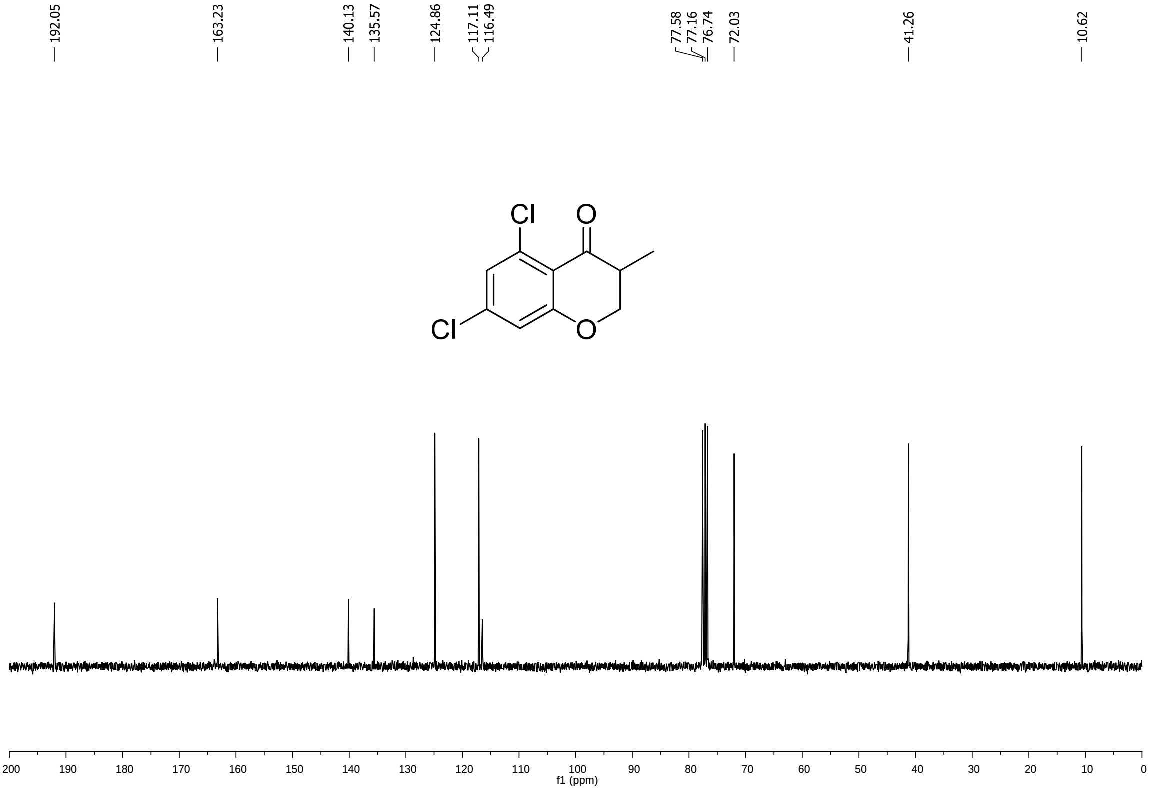
6,8-Dibromo-3-methyl-chroman-4-one (2n)



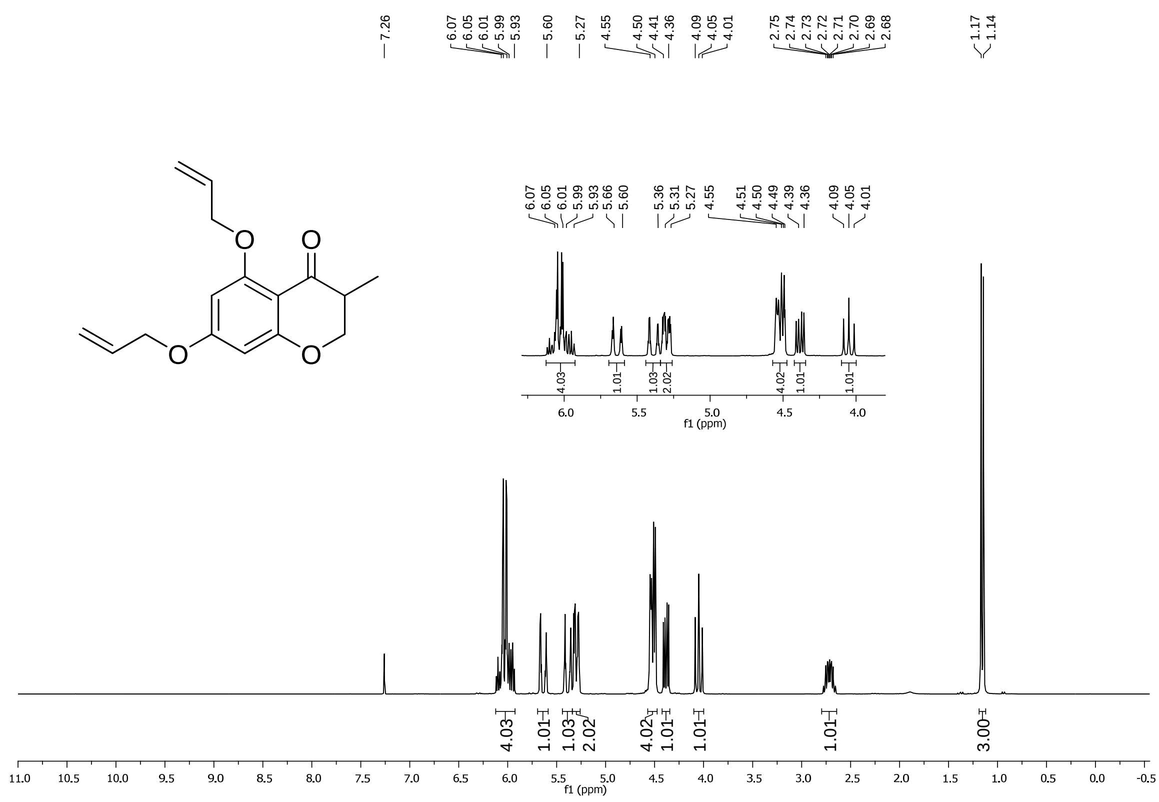


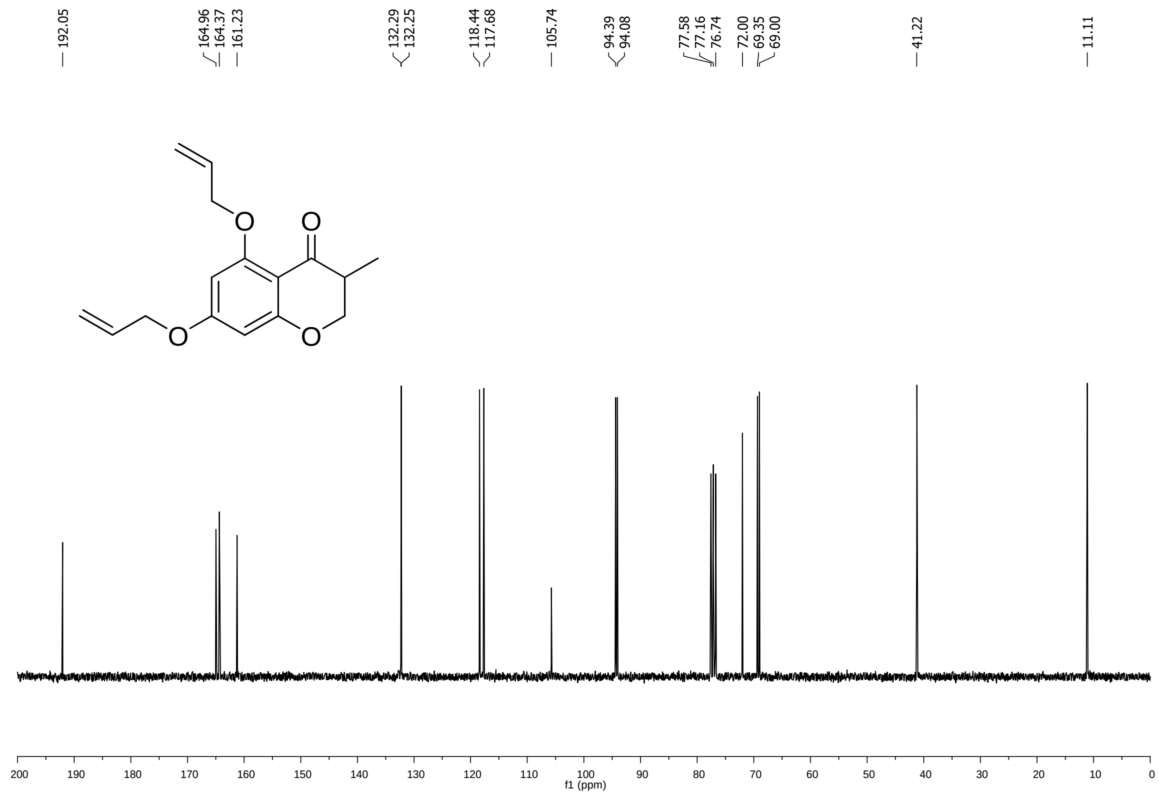
5,7-Dichloro-3-methyl-chroman-4-one (2o)



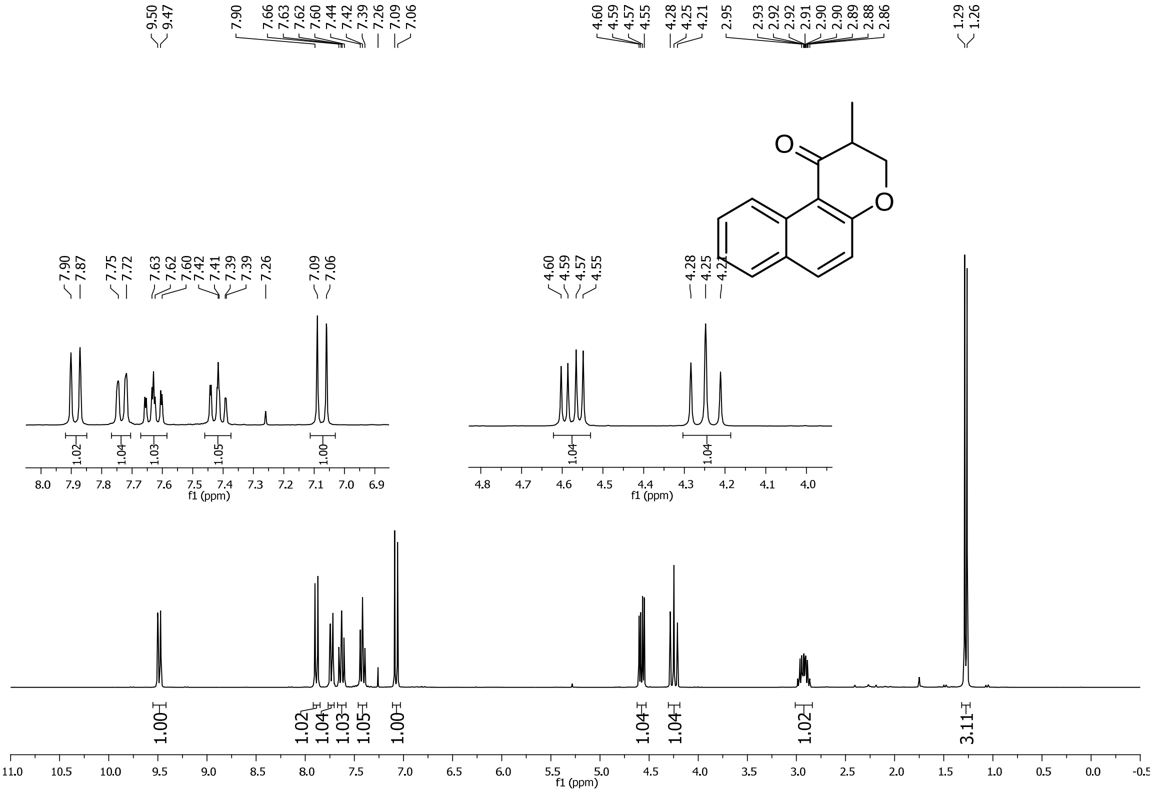


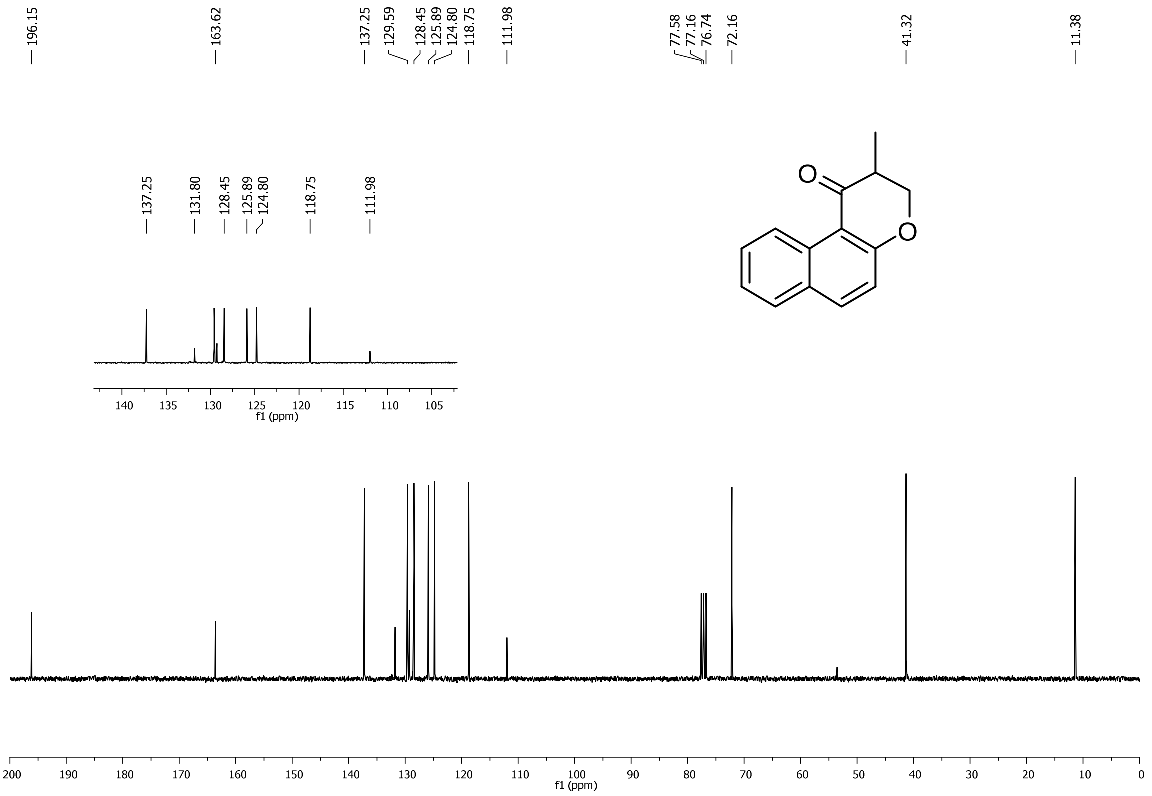
5,7-Diallyloxy-3-methyl-chroman-4-one (2p)



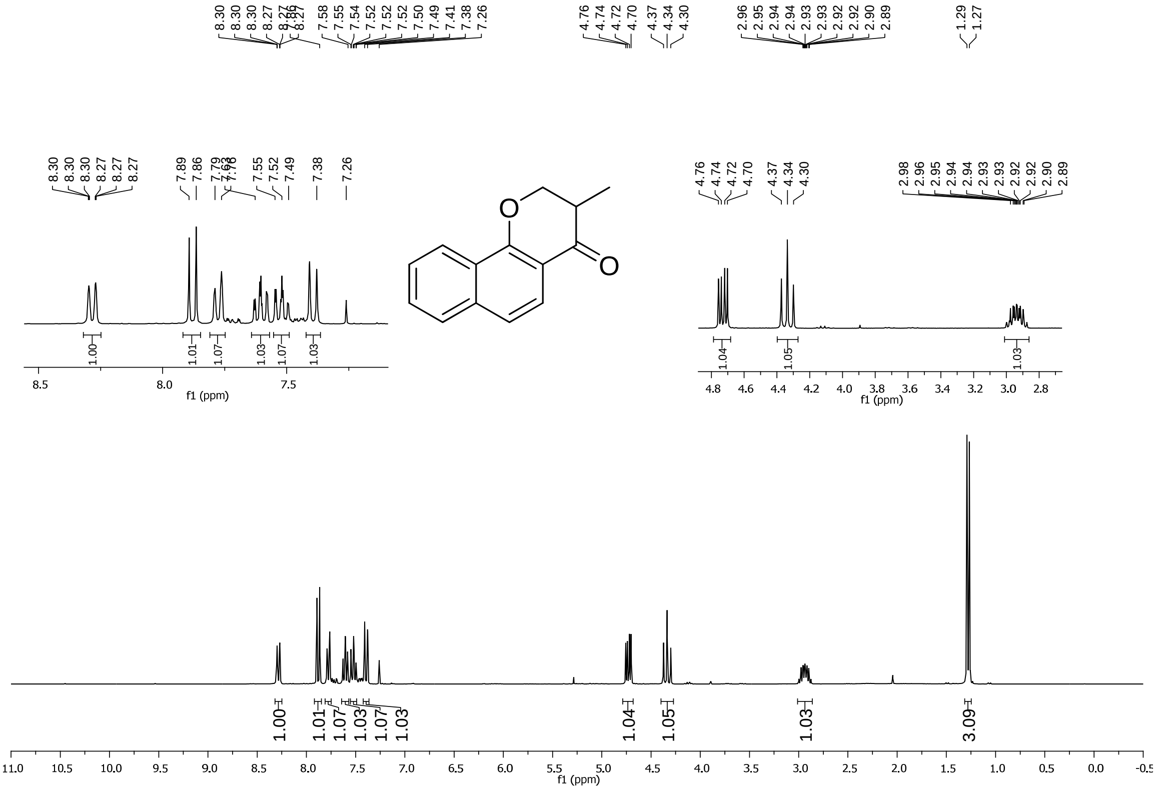


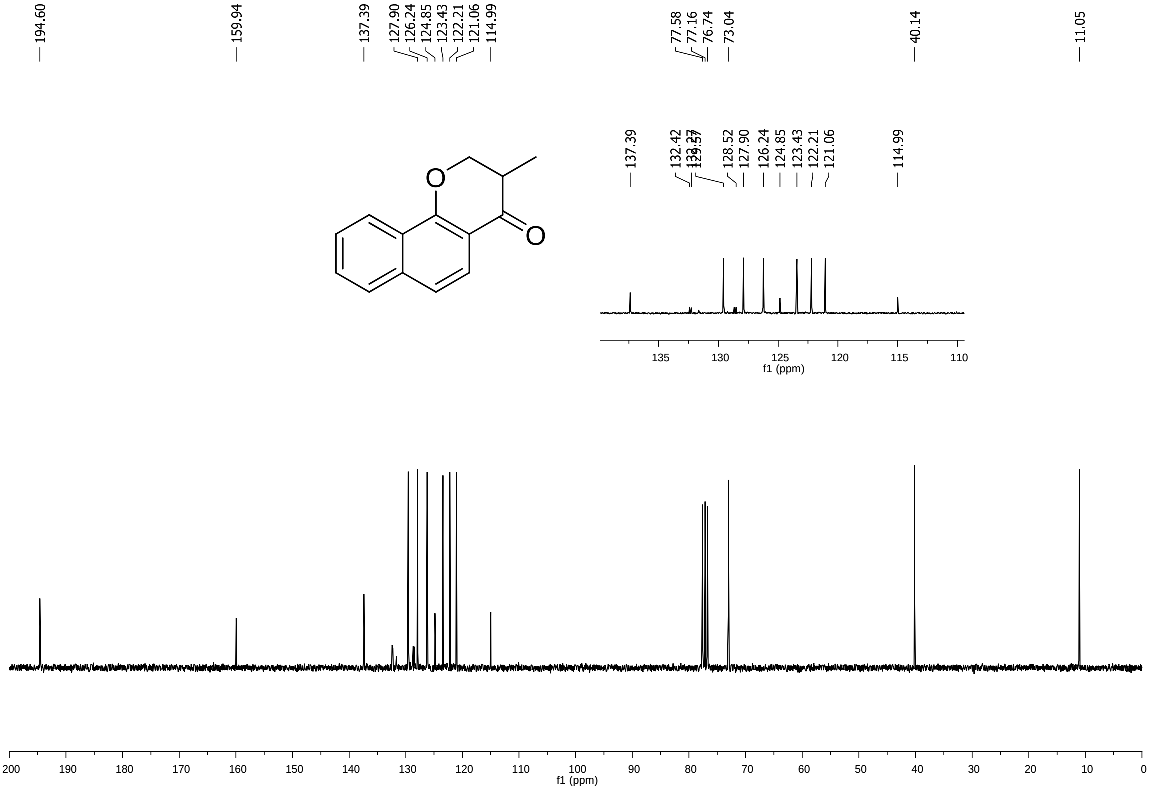
2-Methyl-2,3-dihydro-benzo[*f*]chromen-1-one (2q)



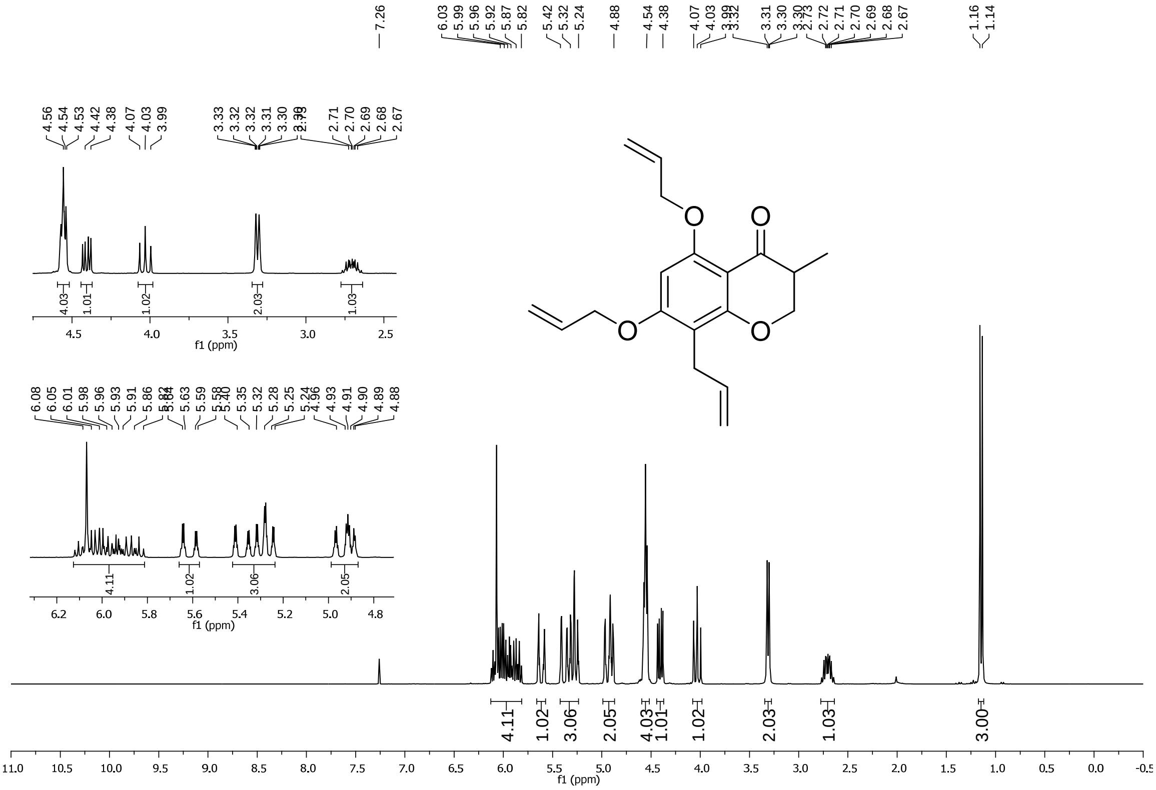


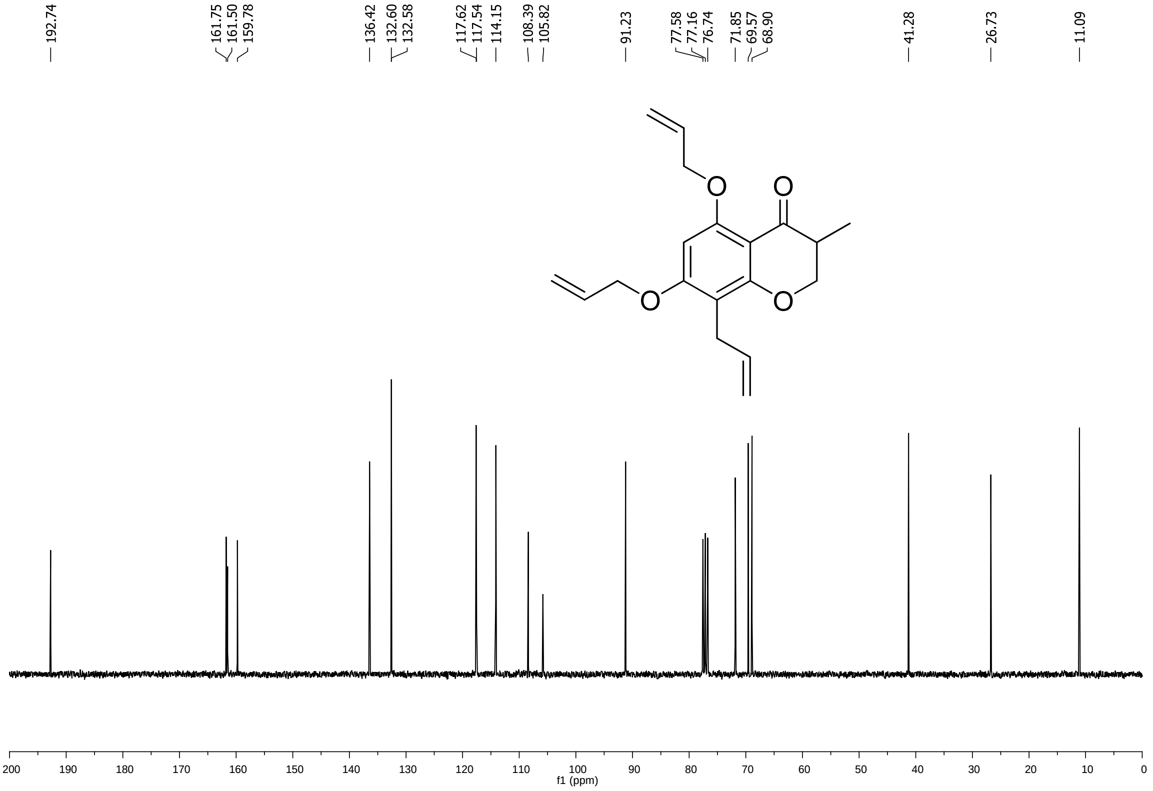
3-Methyl-2,3-dihydro-benzo[*h*]chromen-4-one (2r)



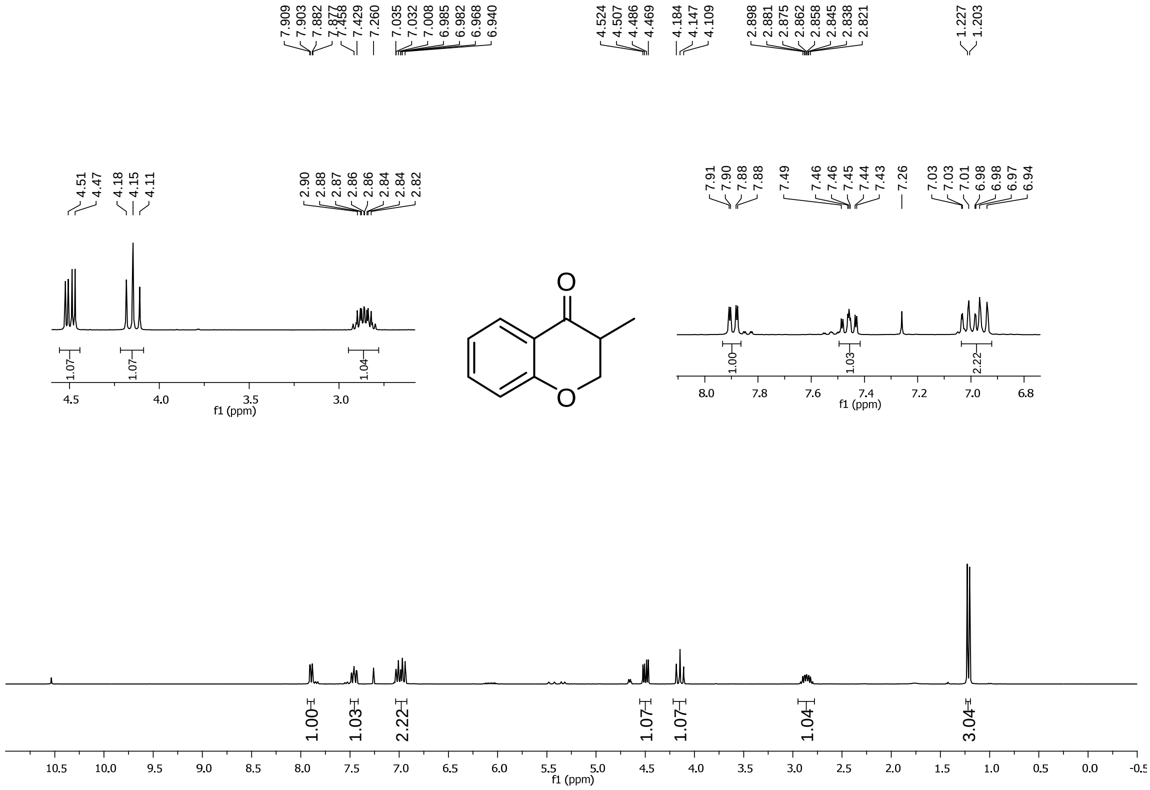


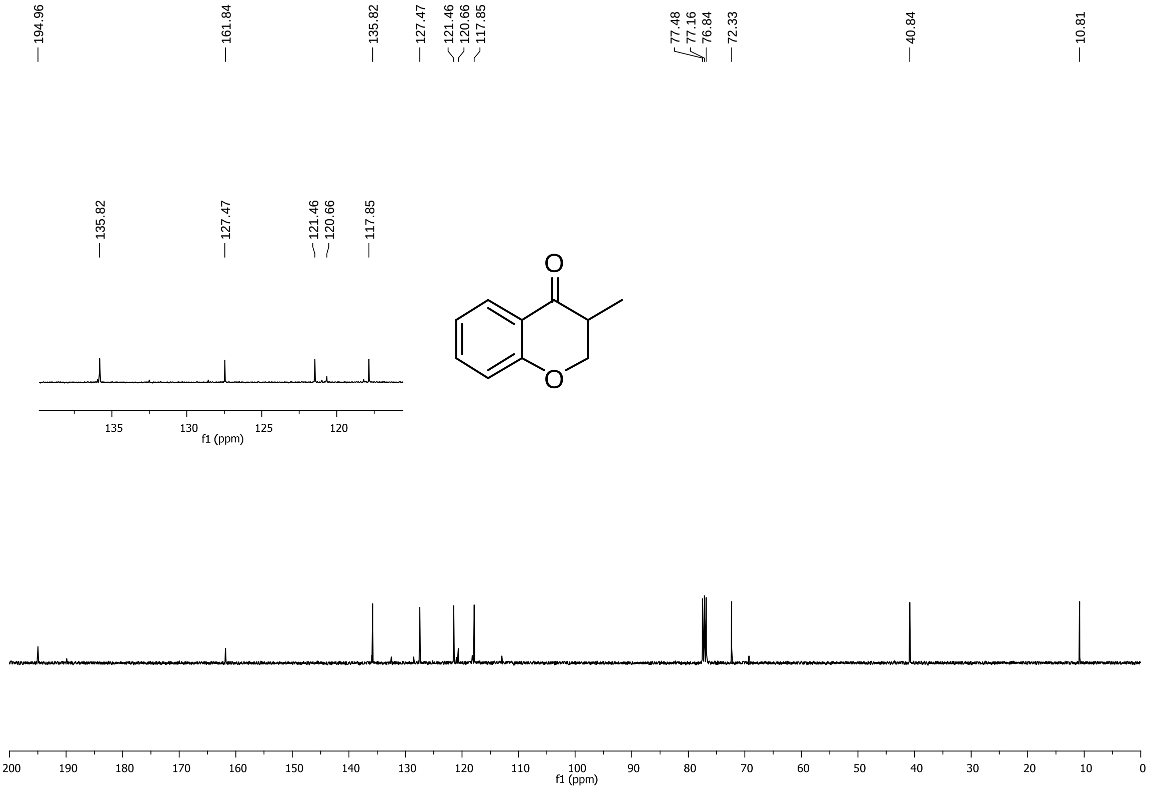
8-Allyl-5,7-diallyloxy-3-methyl-chroman-4-one (2s)



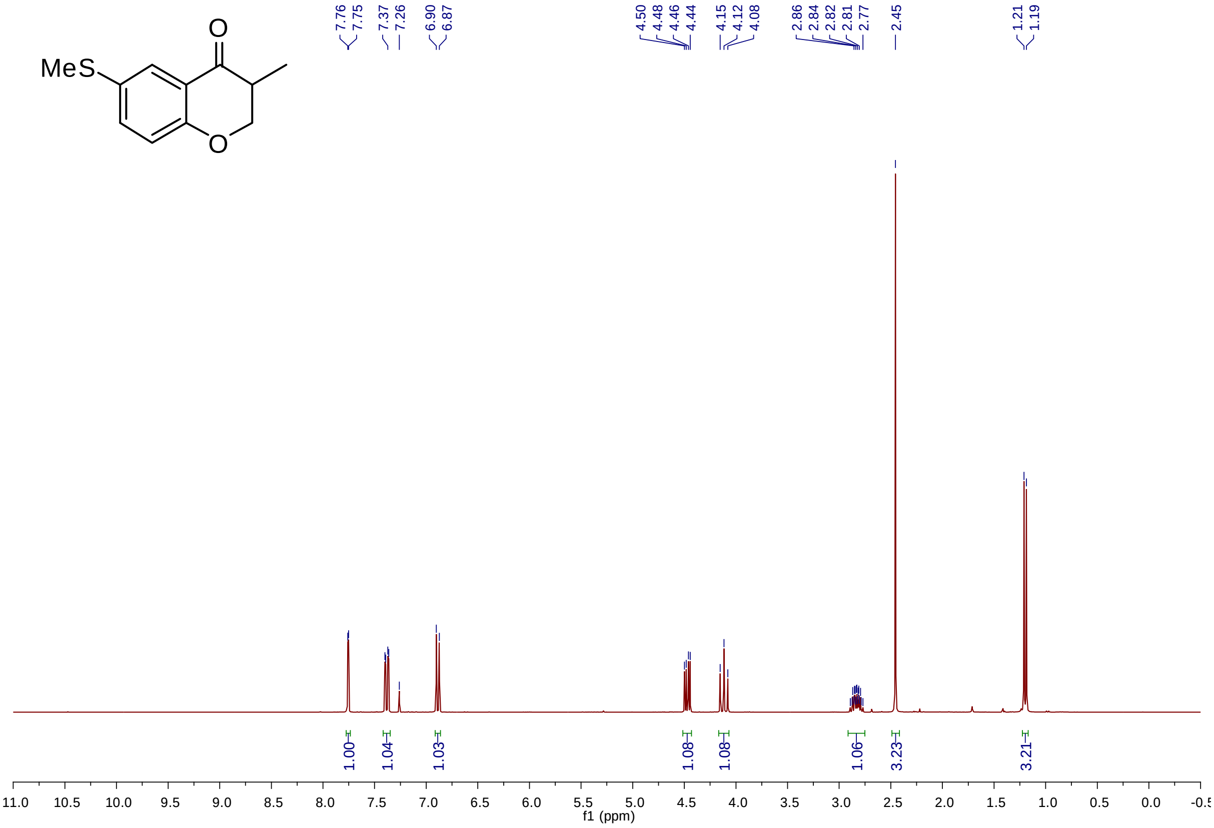


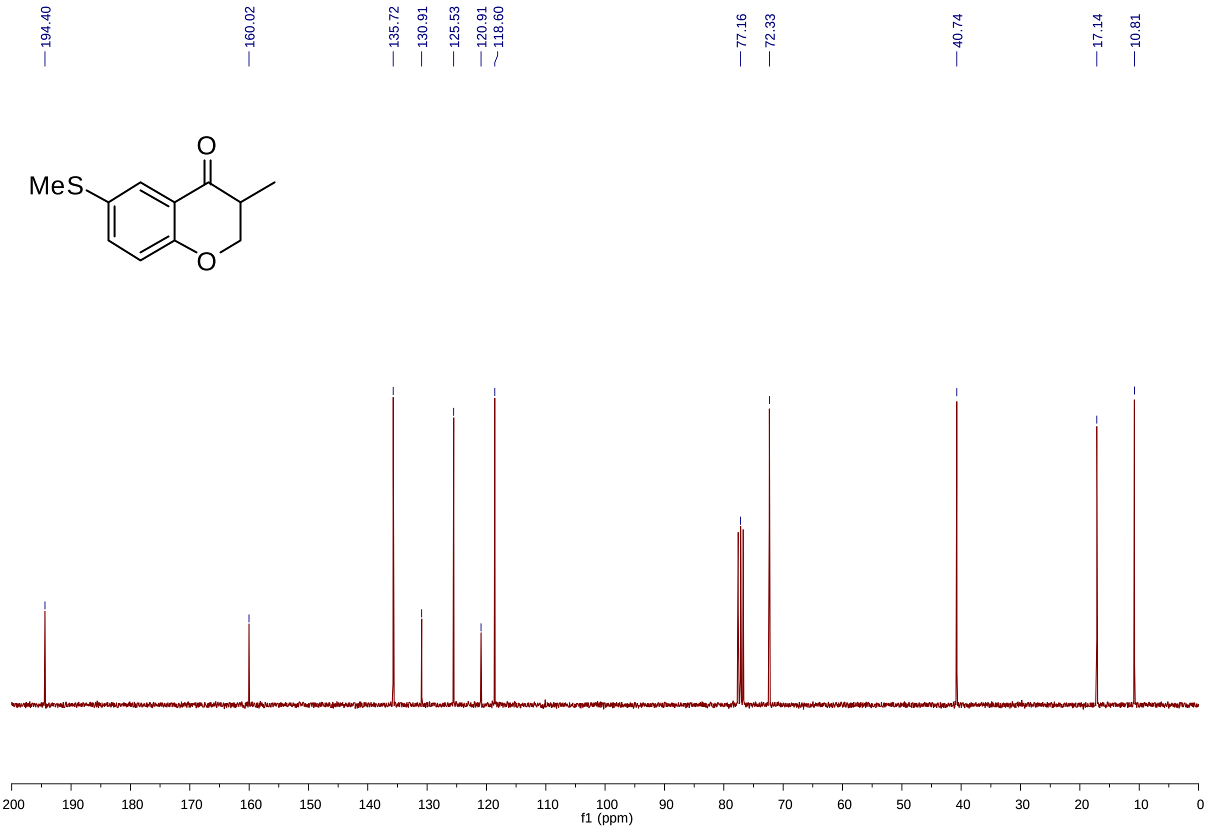
3-Methyl-chroman-4-one (2t)



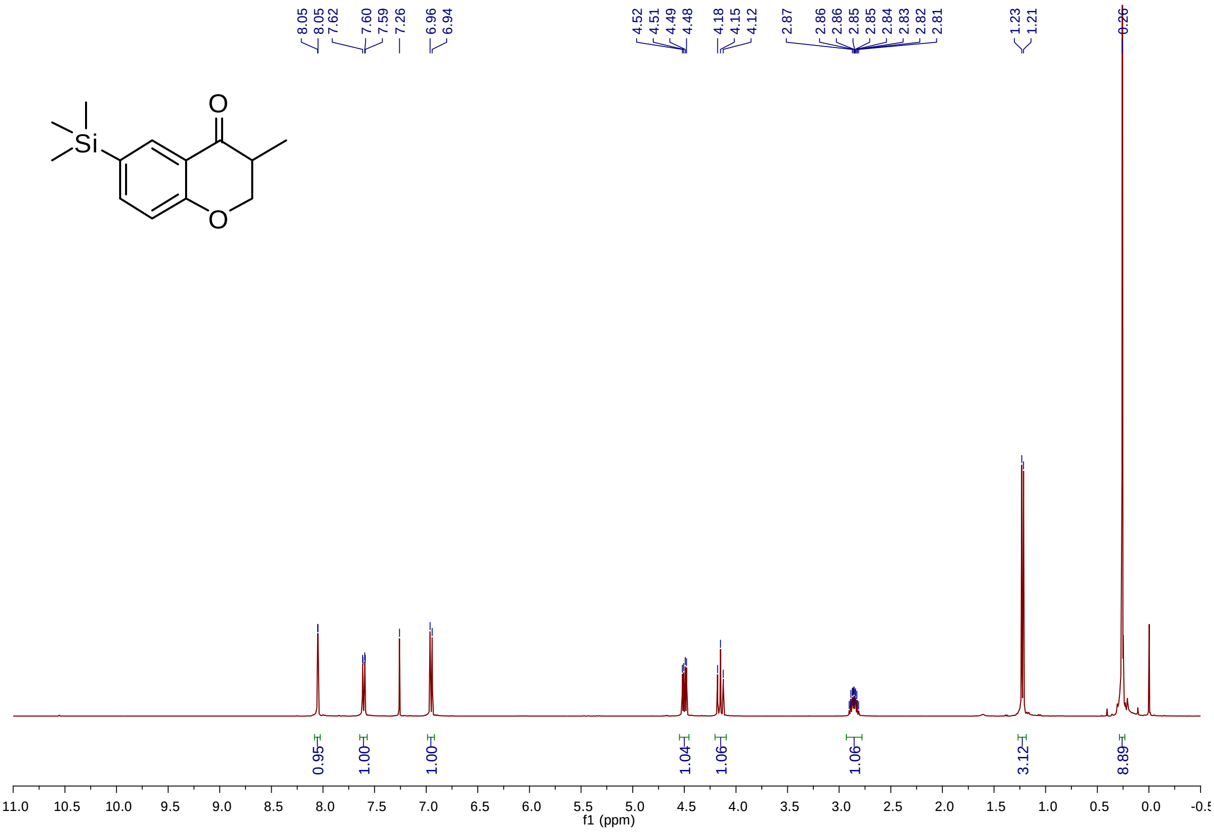


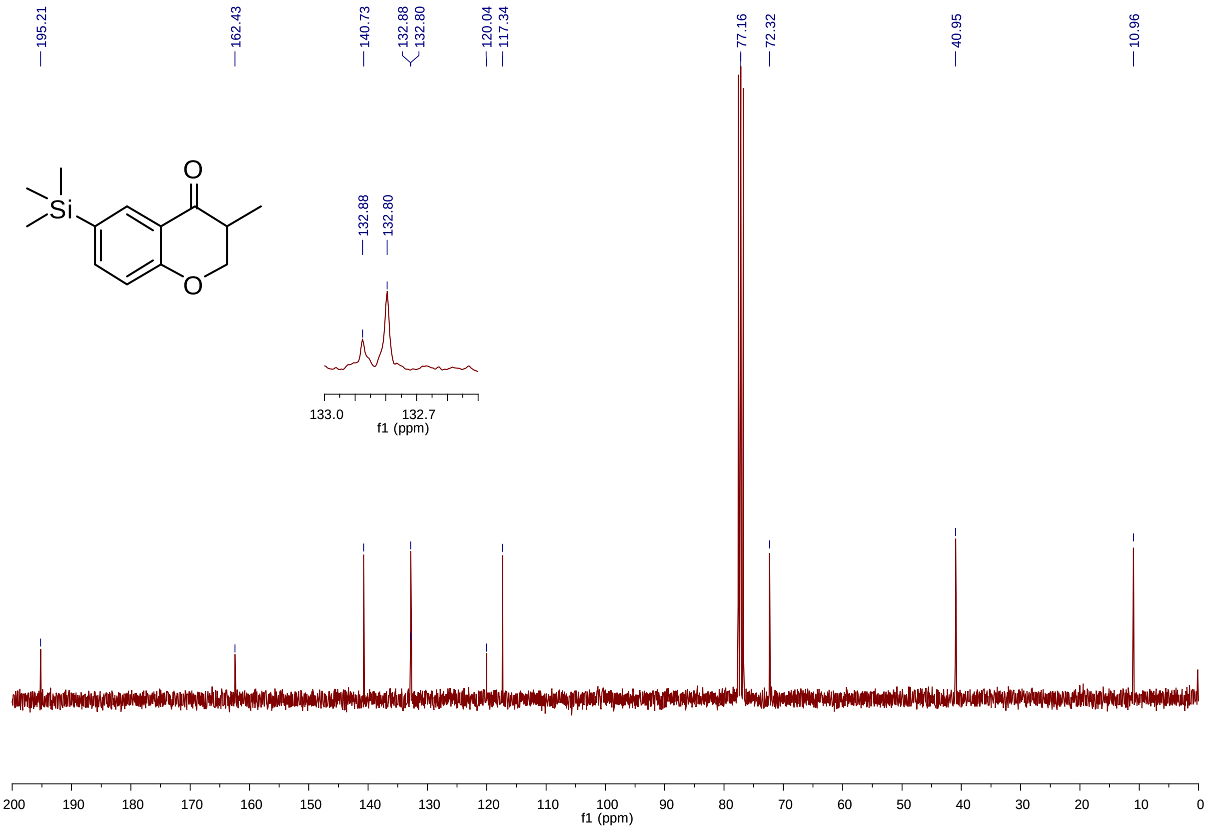
3-Methyl-6-methylsulfanyl-chroman-4-one (2h)



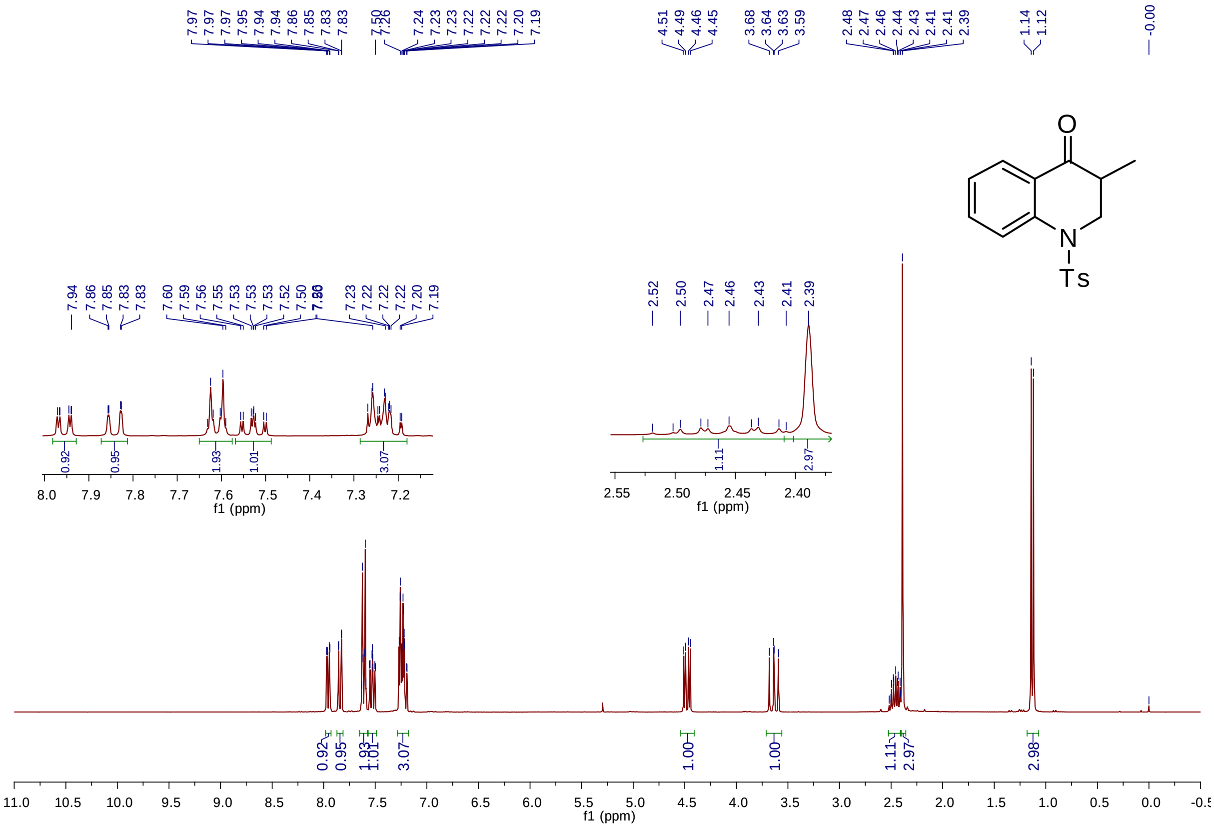


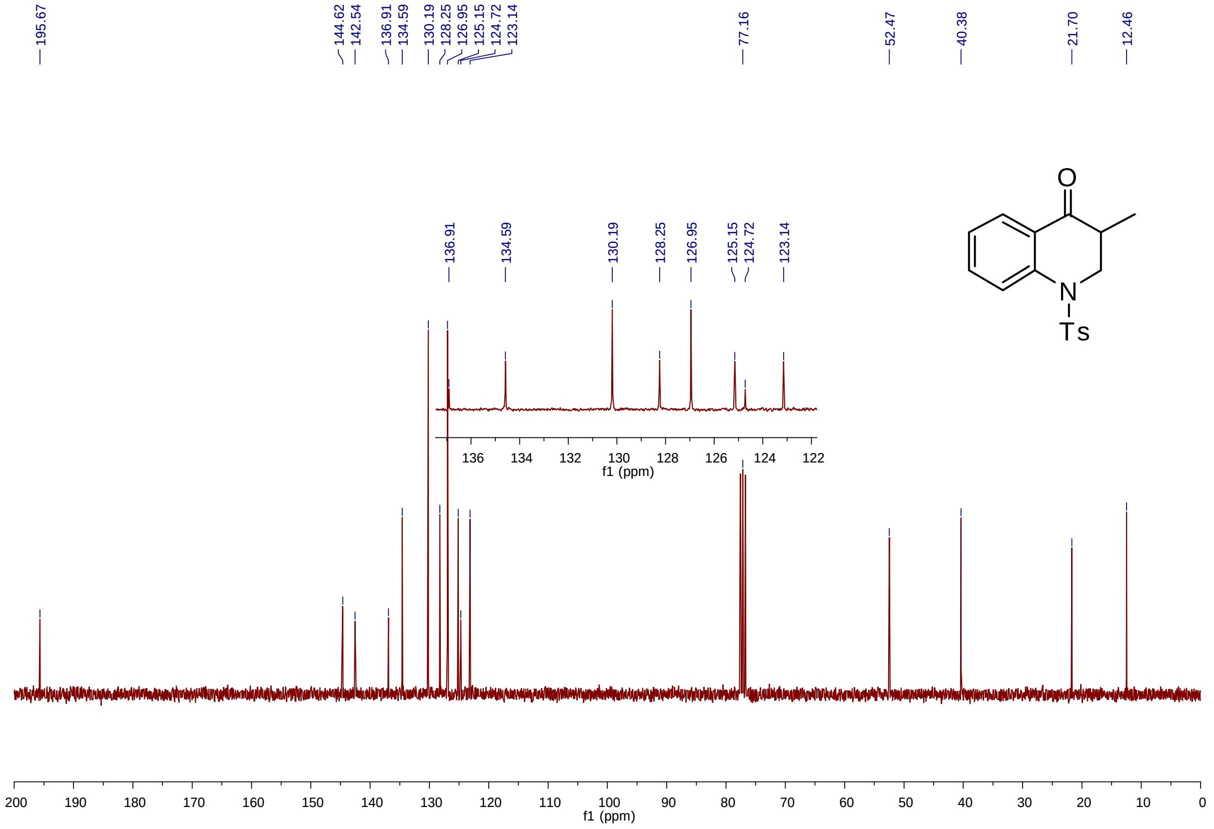
3-Methyl-6-trimethylsilanyl-chroman-4-one (2i)



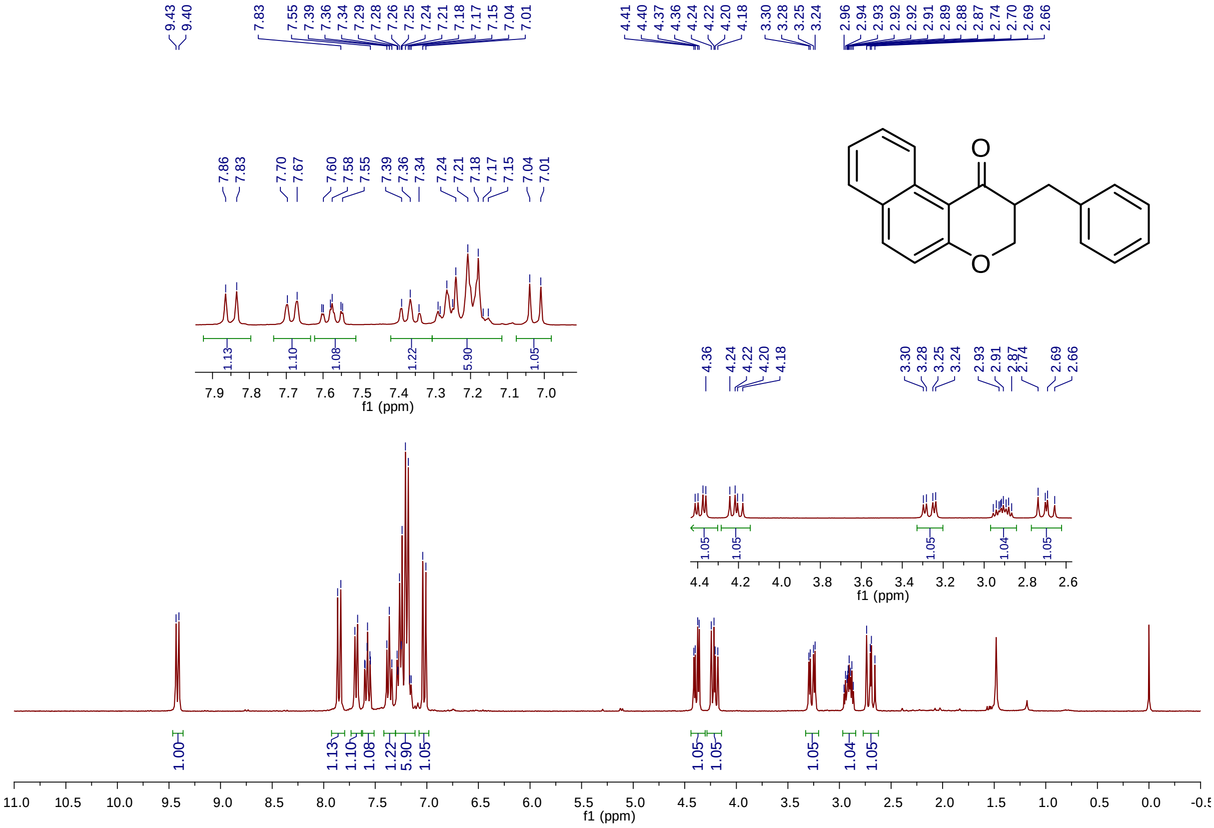


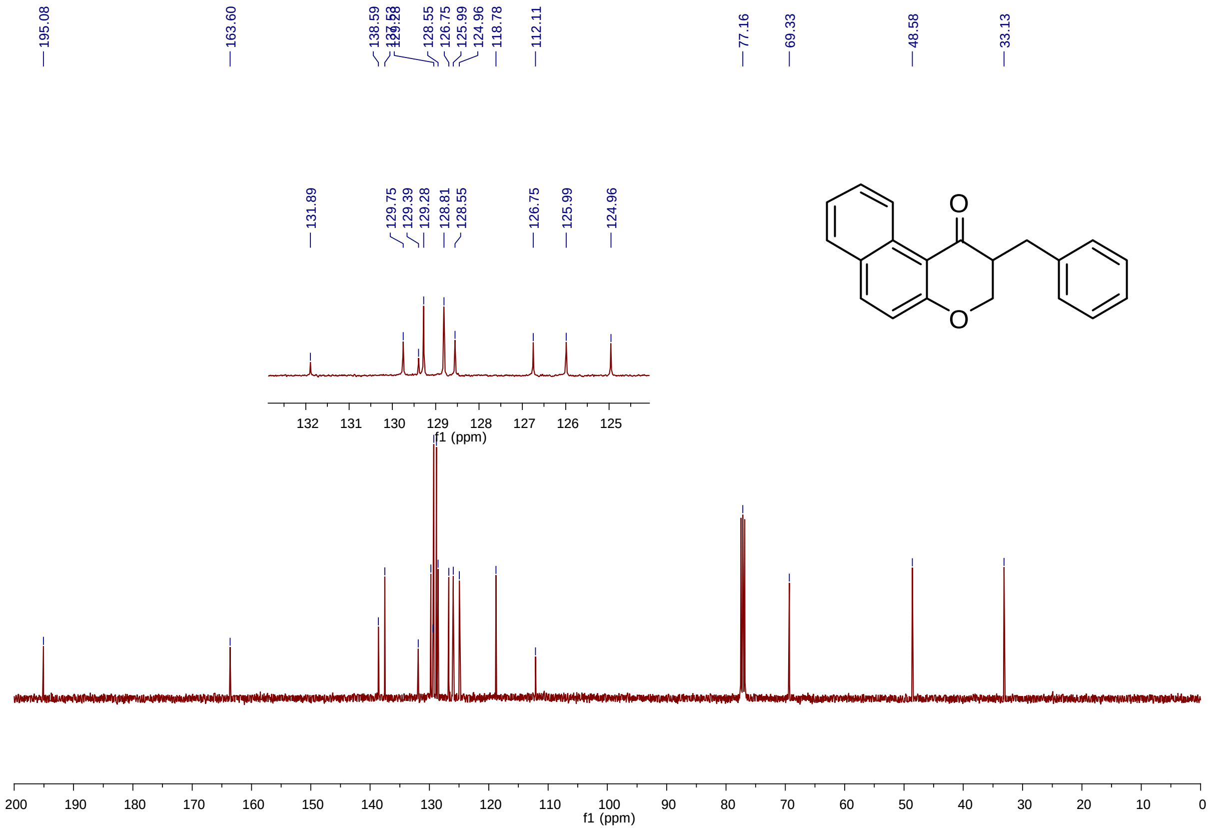
3-Methyl-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-quinolin-4-one (4u)



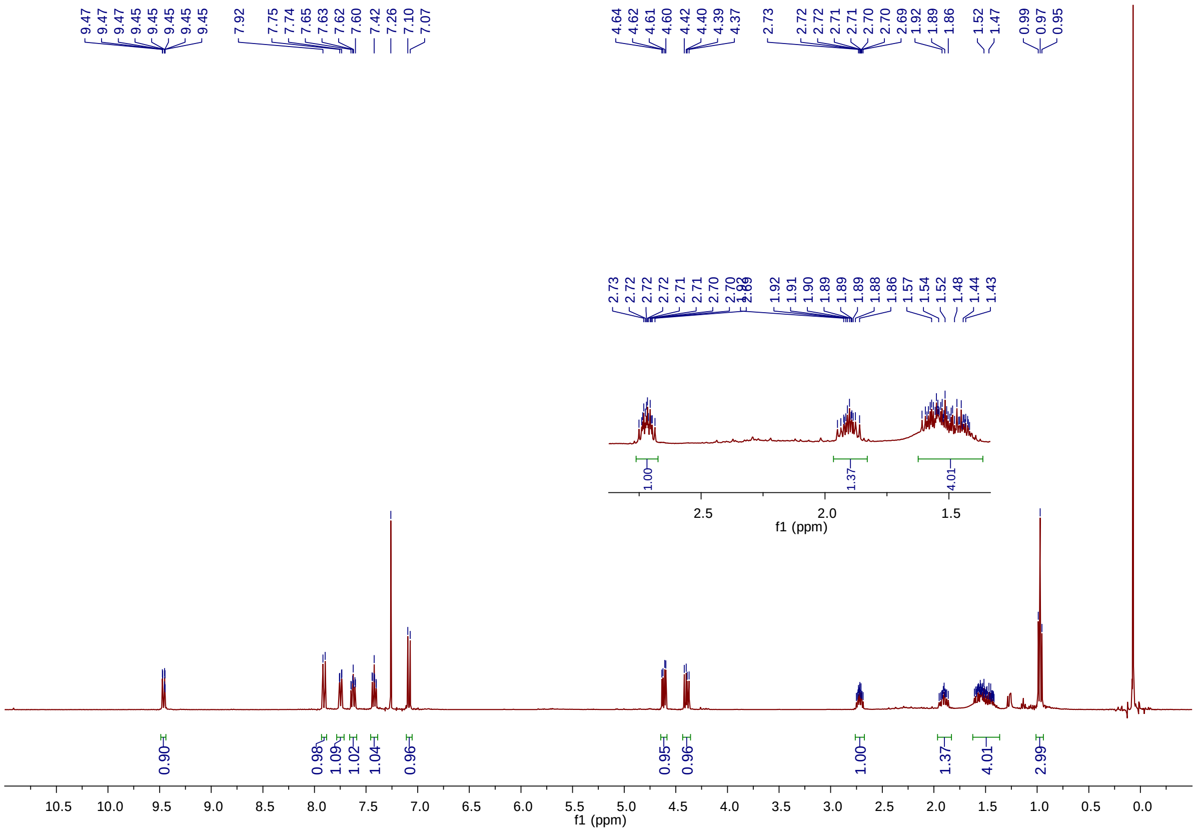


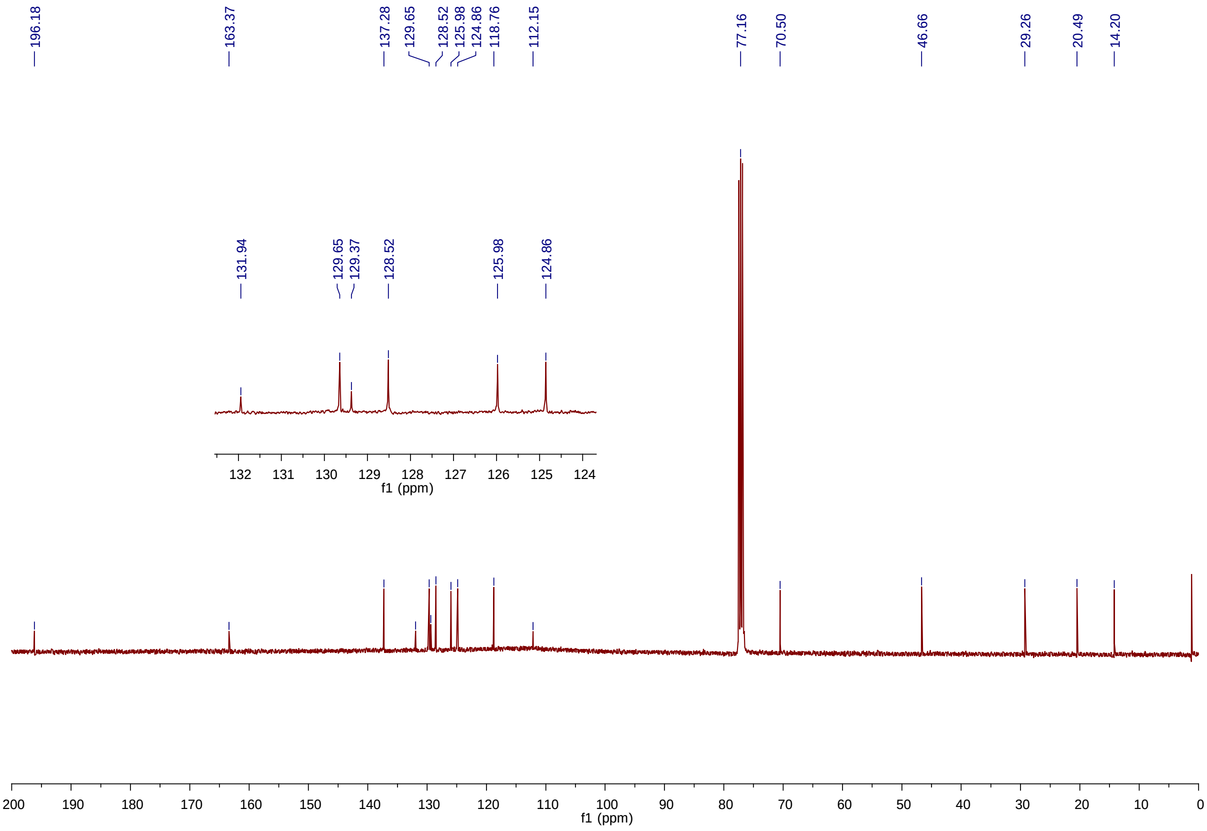
2-Benzyl-2,3-dihydro-benzo[*f*]chromen-1-one (9b)



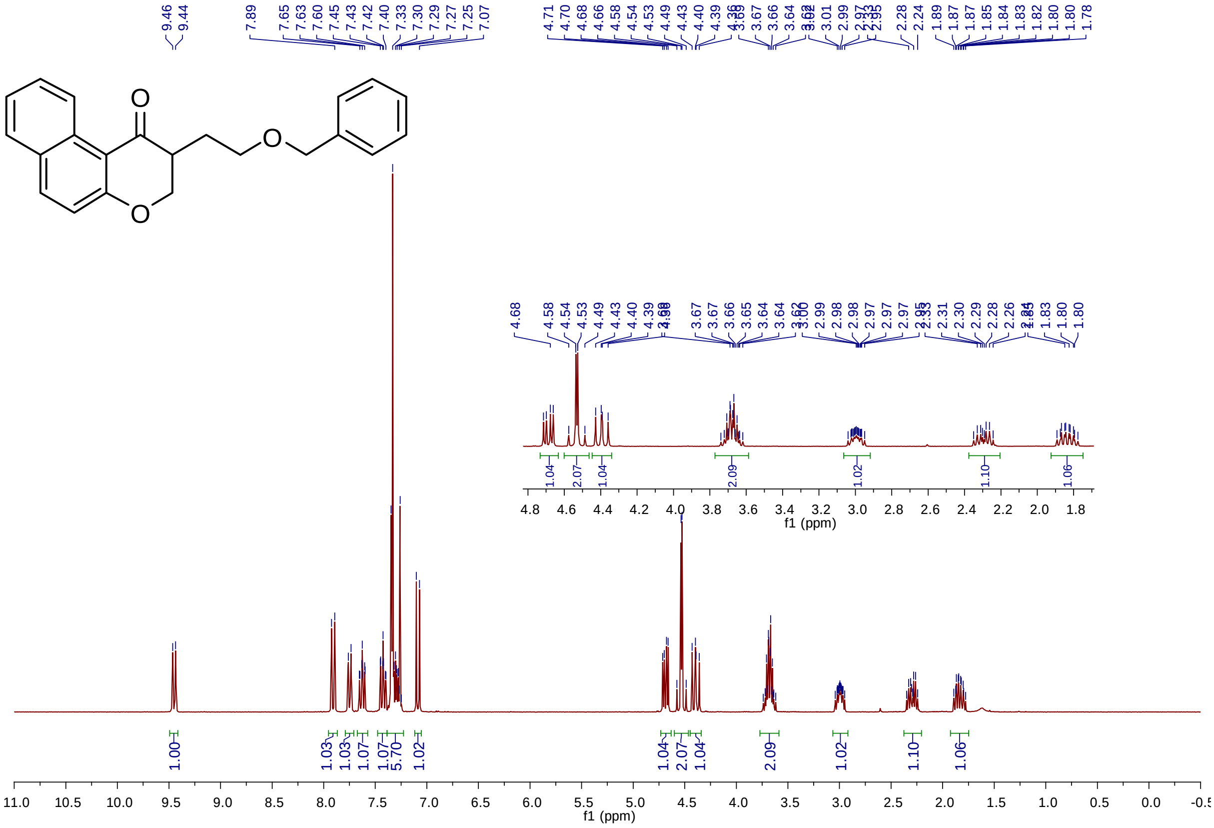


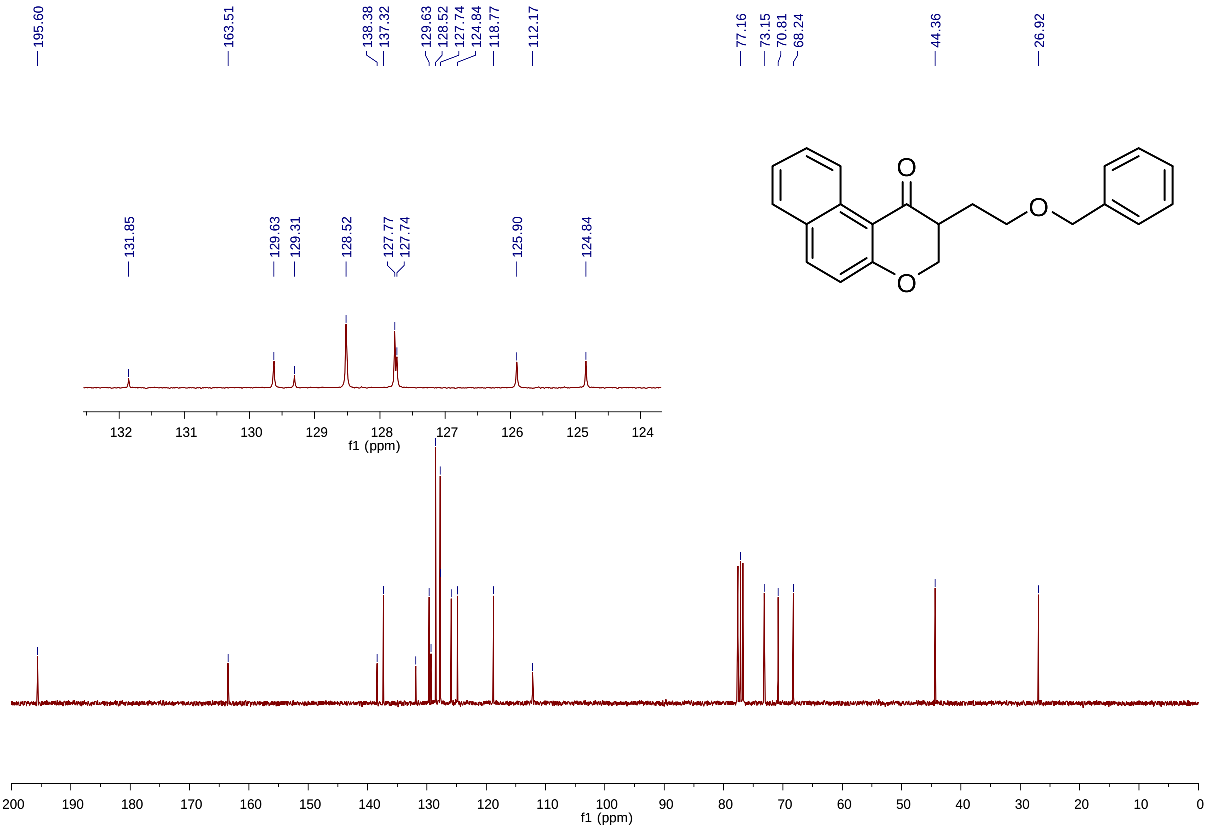
2-Propyl-2,3-dihydro-benzo[*f*]chromen-1-one (9c)



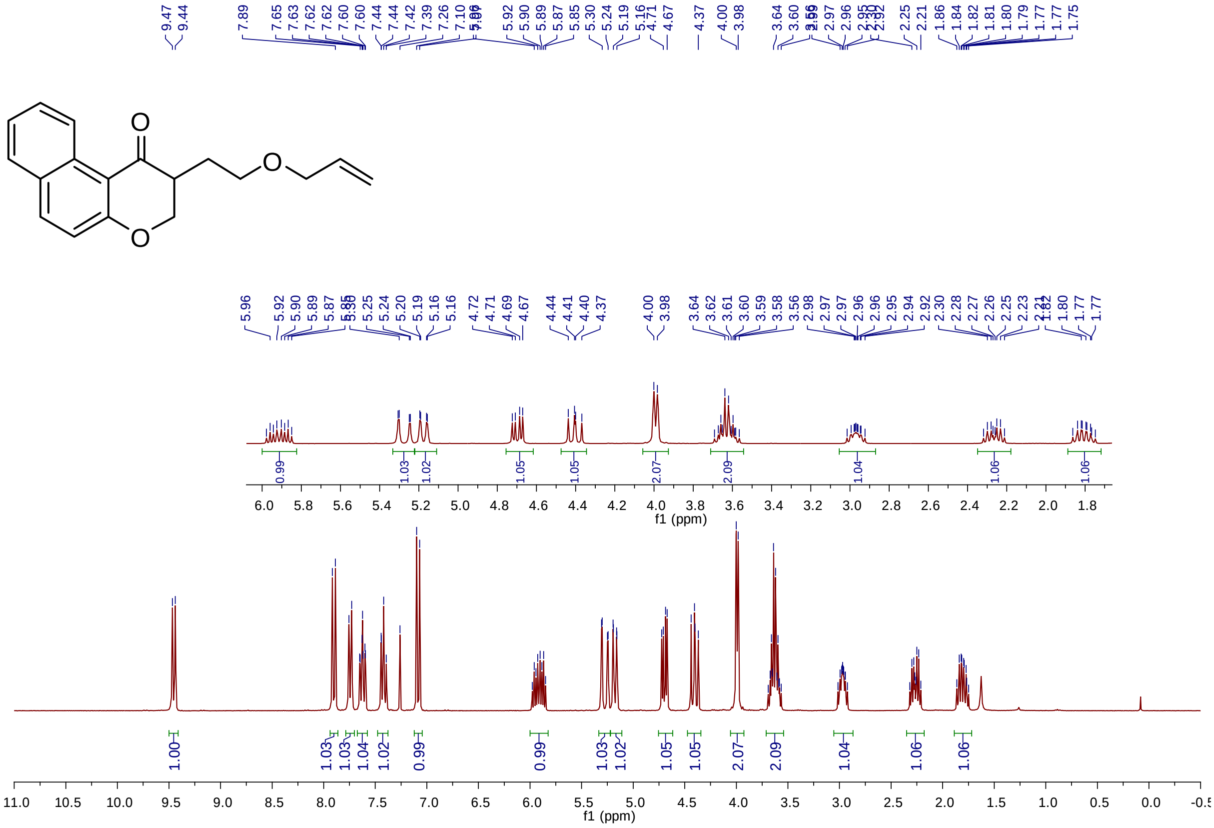


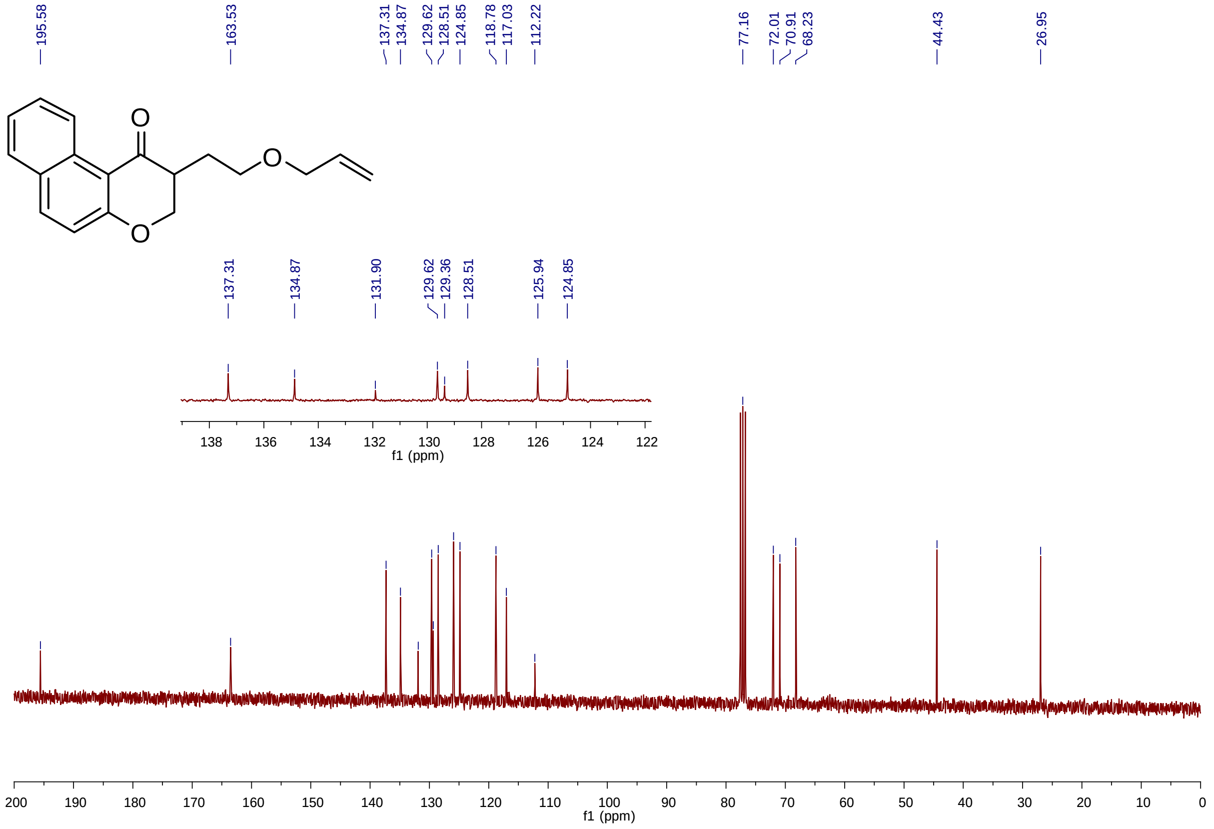
2-(2-Benzyloxy-ethyl)-2,3-dihydro-benzo[*f*]chromen-1-one (9d)



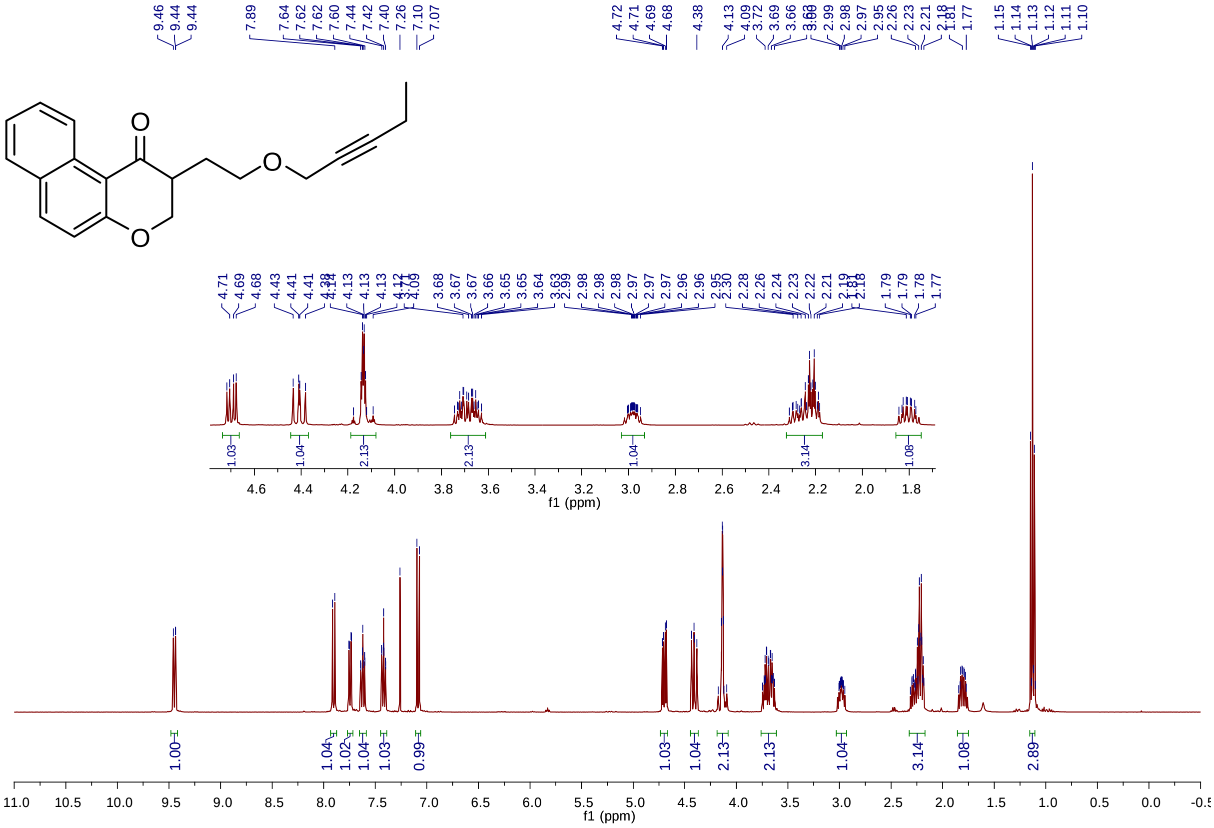


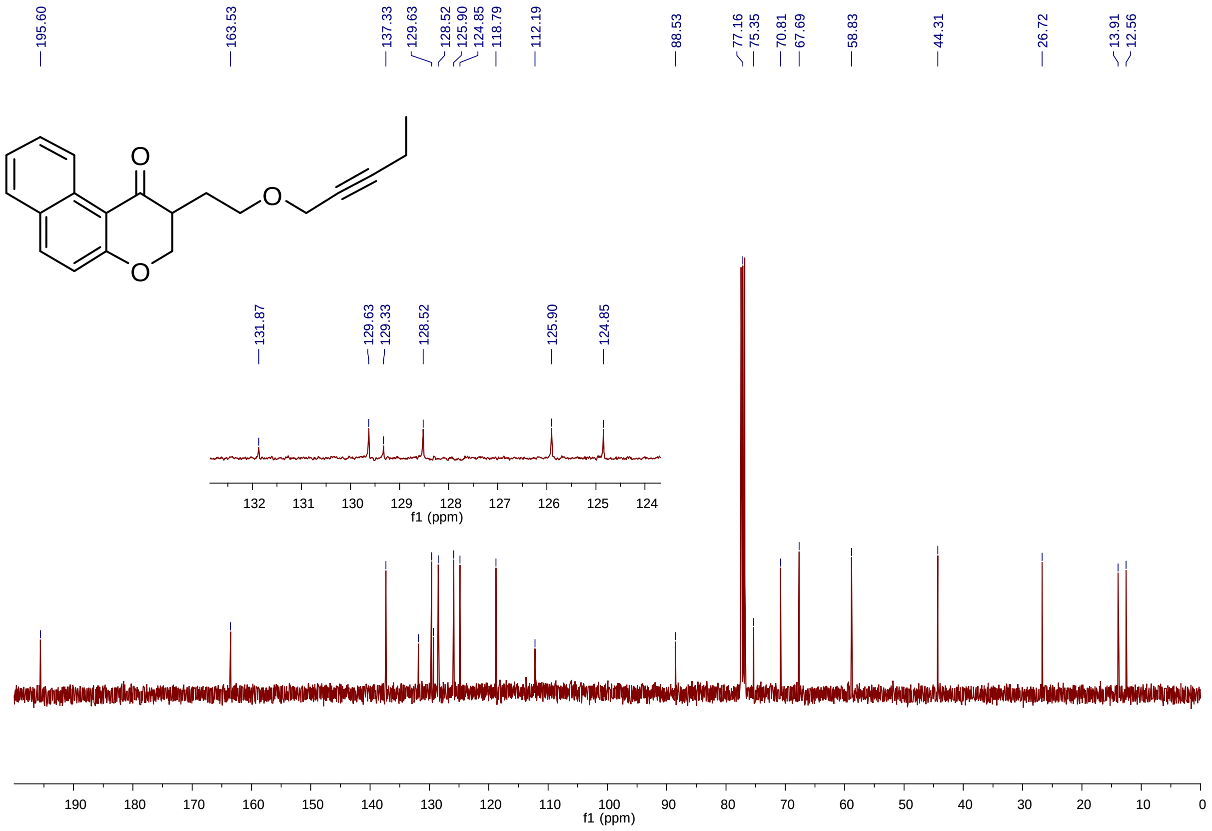
2-(2-Allyloxy-ethyl)-2,3-dihydro-benzo[*f*]chromen-1-one (9e)



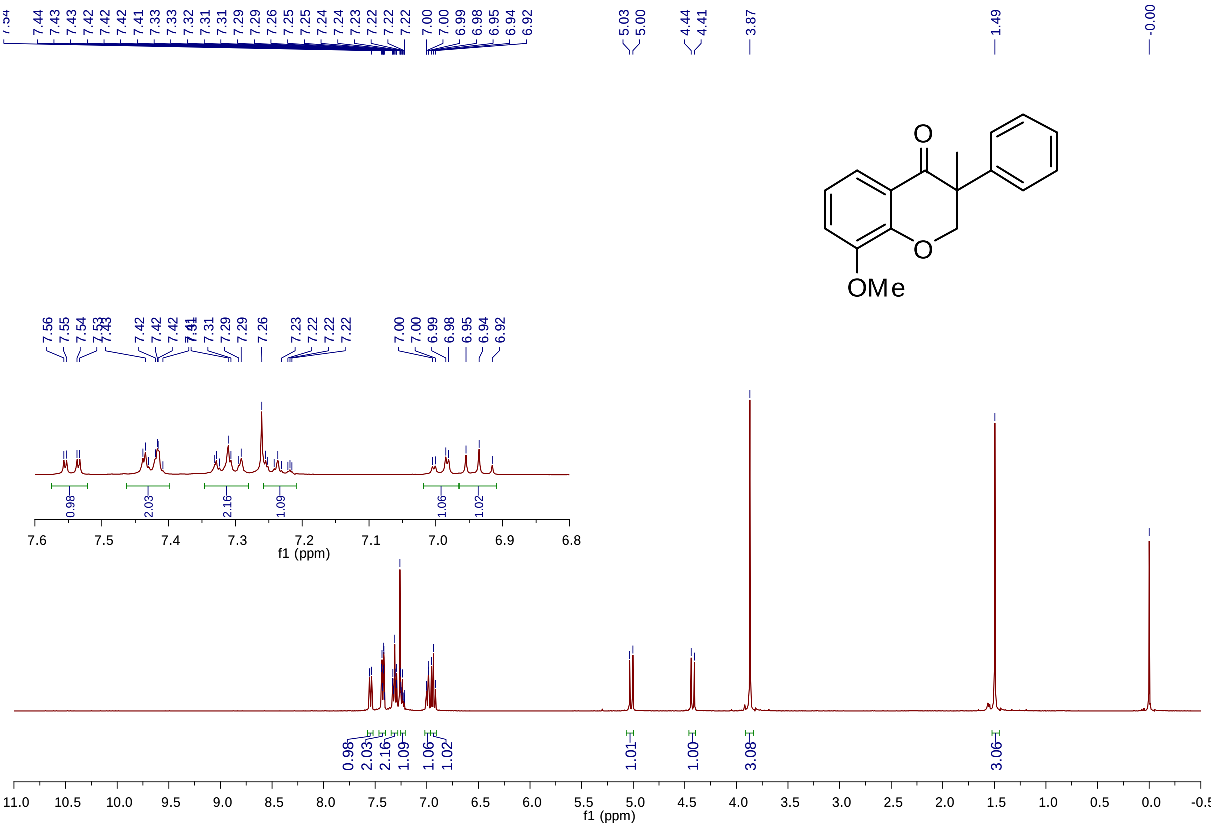


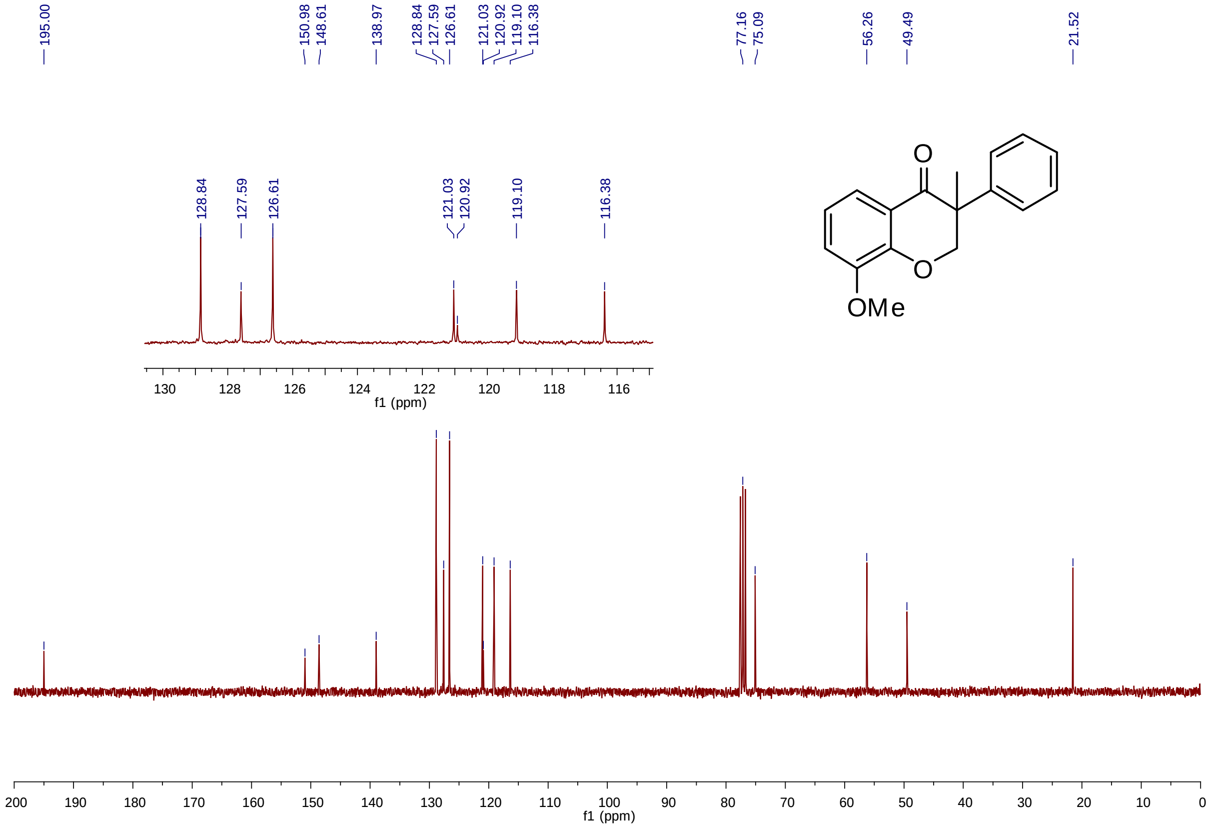
2-(2-Pent-2-ynyloxy-ethyl)-2,3-dihydro-benzo[*f*]chromen-1-one (9f)



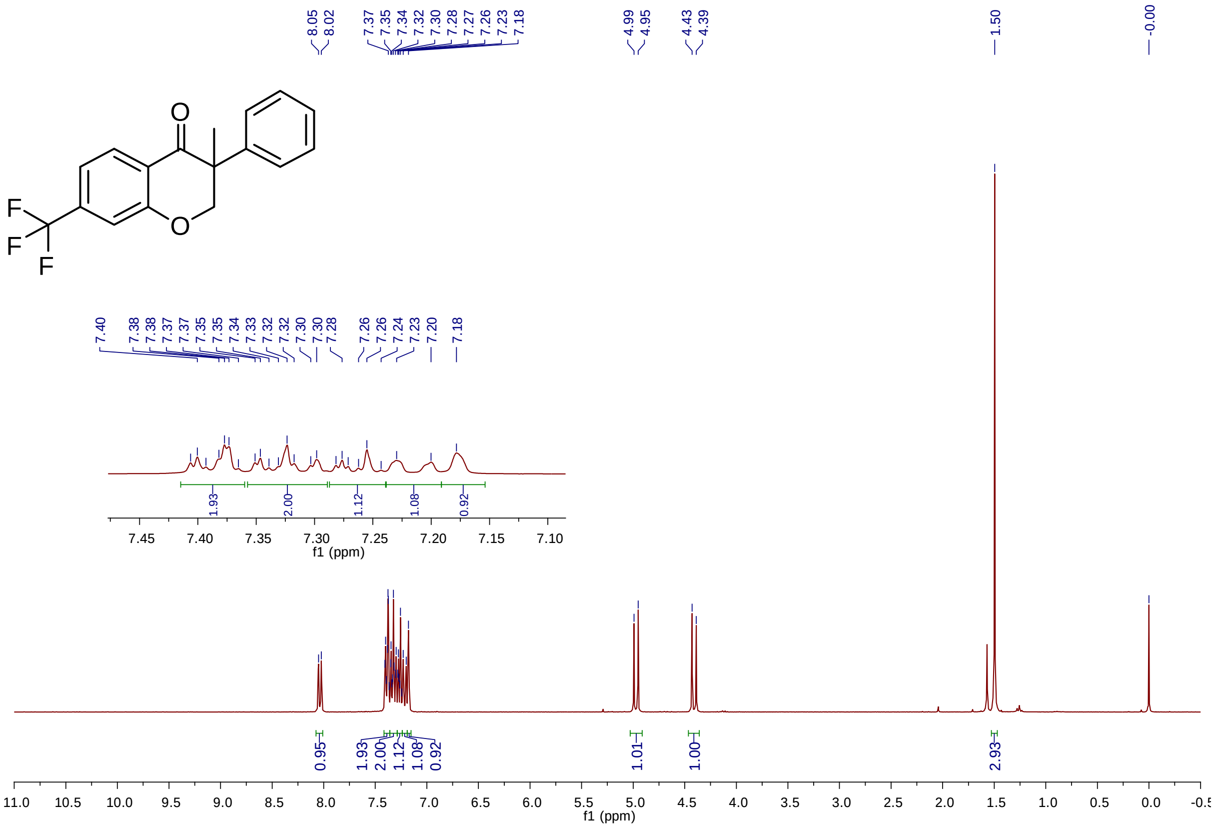


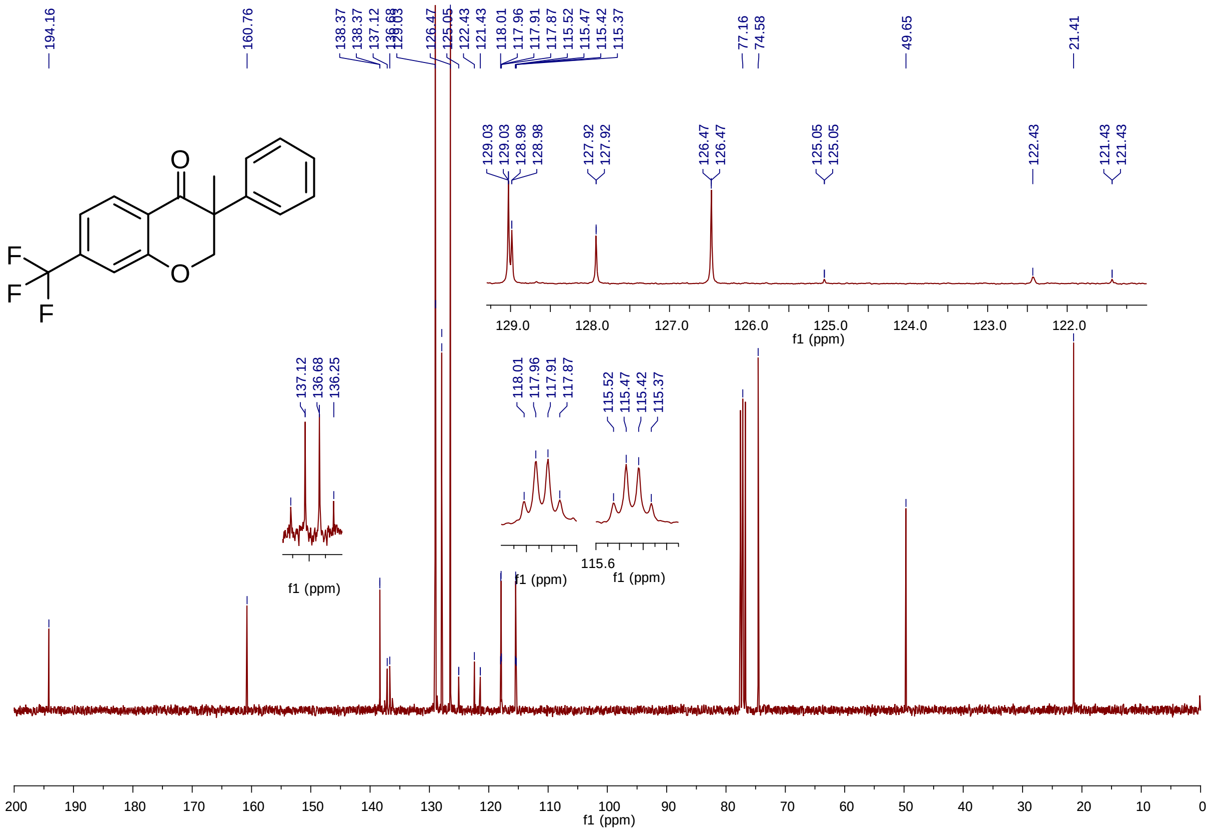
8-Methoxy-3-methyl-3-phenyl-chroman-4-one (11a)

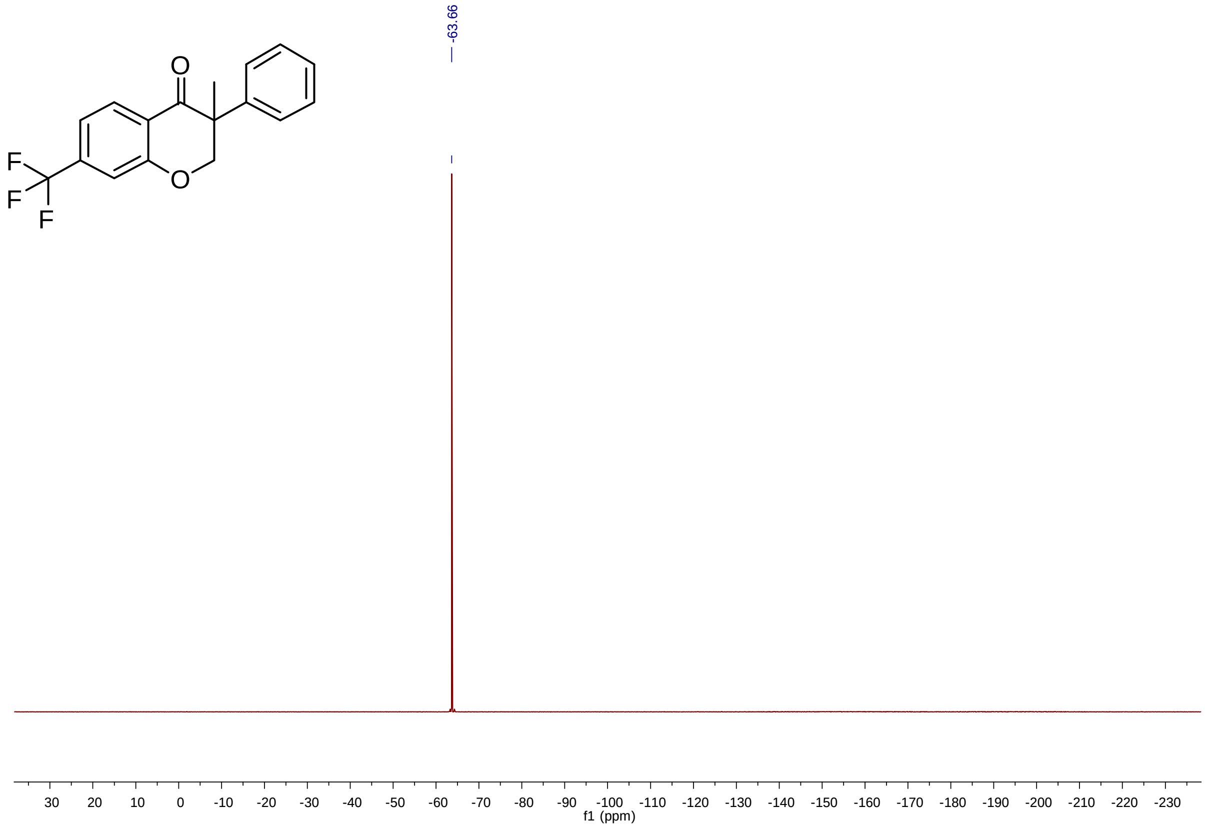




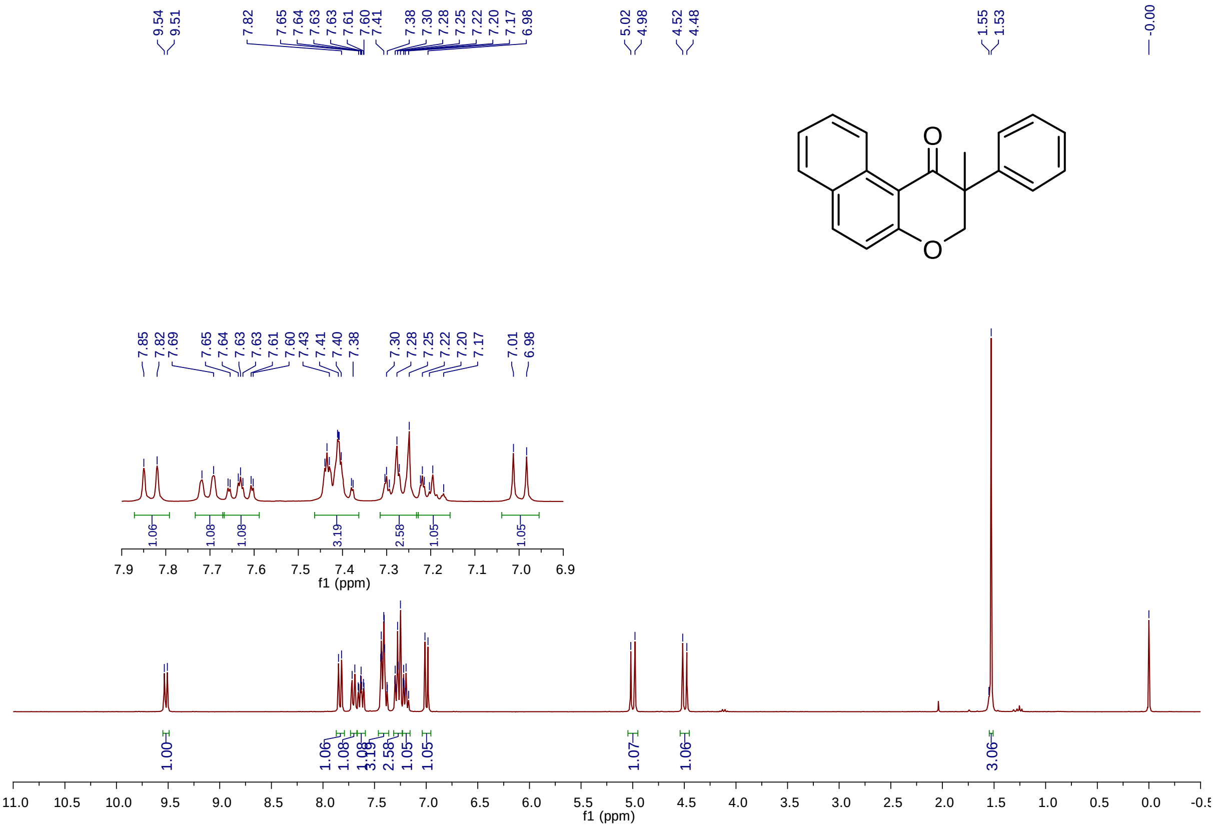
3-Methyl-3-phenyl-7-trifluoromethyl-chroman-4-one (11b)

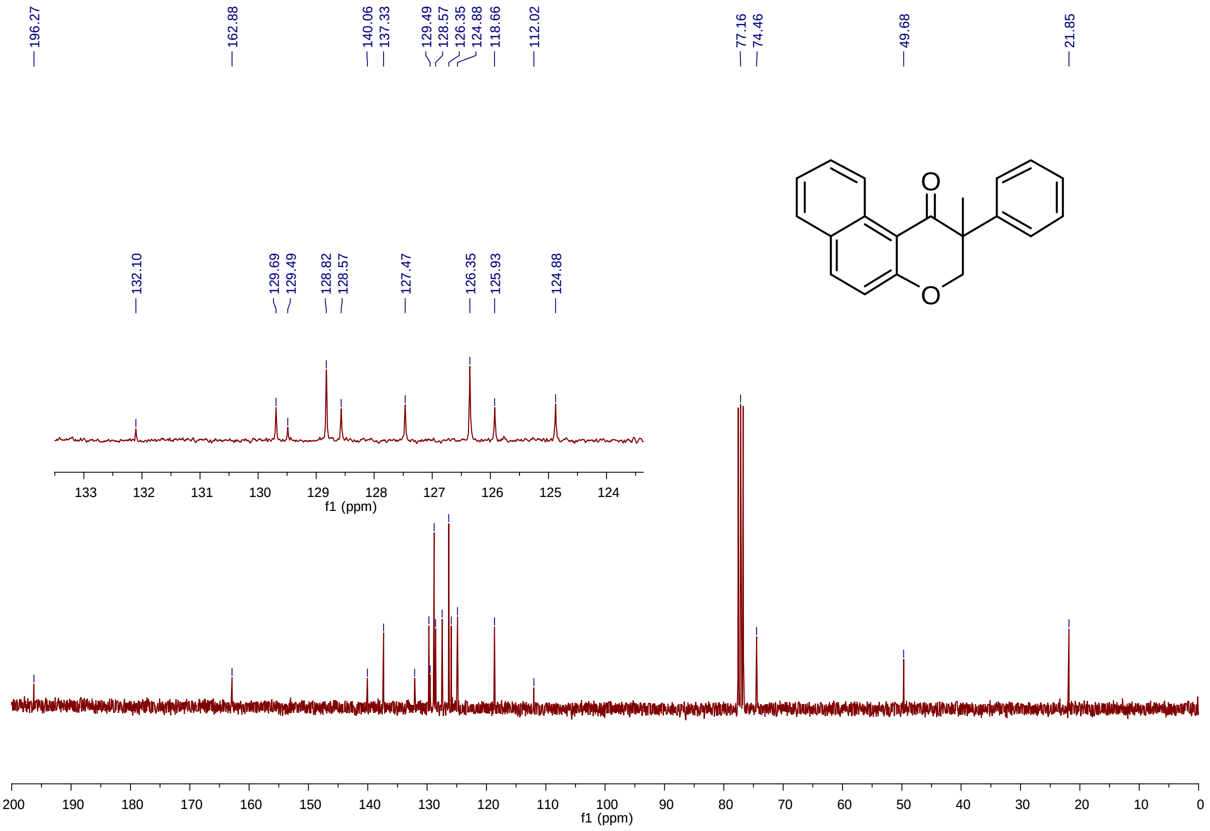





-63.66
O
O
F
F
F
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

2-Methyl-2-phenyl-2,3-dihydro-benzo[*f*]chromen-1-one (11c)





2-(4-Chloro-phenyl)-methyl-2,3-dihydro-benzo[*f*]chromen-1-one (11d)