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Total Syntheses of the Regenerative Natural Products Vinaxanthone, Xanthofulvin, and Eupalinilide E

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Total Syntheses of the Regenerative Natural Products Vinaxanthone, Xanthofulvin, and Eupalinilide E

by

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Dedication

For Mom and Dad

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Total Syntheses of the Regenerative Natural Products Vinaxanthone, Xanthofulvin, and Eupalinilide E

Matthew Ryan Chin, Ph. D.

The University of Texas at Austin, 2015

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The fungal metabolites vinaxanthone and xanthofulvin possess the remarkable ability to restore motor function in animal models of complete spinal cord transection making them the most promising small molecules for the development of spinal cord injury (SCI) therapeutics. A concise nine-step total synthesis of vinaxanthone was accomplished utilizing a biomimetic dimerization of the putative precursor 5,6-dehydropolivione and the first reported synthesis of xanthofulvin was achieved in 15-steps highlighted by an unprecedented enaminone O-to-C carboxyl transfer to forge key carbon-carbon bonds. Both natural products were also identified as positive allosteric modulators of the G-protein coupled receptor (GPCR), GPR91, thus elucidating their modes of action accounting for their regenerative capabilities. Furthermore, a unique ynone coupling reaction was developed in order to access various vinaxanthone analogs for structure activity relationship (SAR) studies. This resulted in the preparation of a small molecule library of 25 vinaxanthone analogs that demonstrated pronounced neuronal regeneration within laser axotomy assays performed *in vivo* on *C. elegans*.

The plant derived natural product eupalinilide E has been found to promote the *ex vivo* expansion of hematopoietic stem and progenitor cells (HSPCs) which have the potential to improve the success of medical procedures such as bone marrow transplants. In light of its promising applications, unknown mechanism of action, and scarcity in nature the total synthesis of eupalinilide E was undertaken. Efforts culminated in the first enantioselective total synthesis of the natural product in 20-steps, which showcases a Favorskii rearrangement, borylative enyne cyclization, aldehyde-ene ring closure, and a dual allylic oxidation.

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List of Abbreviations

1D-NMR	one dimensional nuclear magnetic resonance
2D-NMR	two dimensional nuclear magnetic resonance
7TMR	seven transmembrane receptor
Å	angstrom
Ac	acetate
AcCl	acetyl chloride
Ac_2O	acetic anhydride
AcOH	acetic acid
$AgNO_3$	silver nitrate
AhR	aryl hydrocarbon receptor
AIBN	azobisisobutyronitrile
$AlCl_3$	aluminum trichloride
aq.	aqueous
ATP	adenosine triphosphate
$Ba(OH)_2$	barium hydroxide
BBr_3	boron tribromide
BCl_3	boron trichloride
$BF_3 \bullet Et_2O$	boron trifluoride diethyl etherate
BINOL	1,1'-bi-2-naphthol
BHT	butylated hydroxytoluene
Boc_2O	di-*tert*-butyl carbonate
B_2pin_2	bis(pinacolato)diboron
Br_2	bromine

Bu_4NHSO_4	tetrabutylammonium bisulfate
Bu_3SnH	tributyltin hydride
°C	degrees Celsius
calc.	calculated
CAM	ceric ammonium molybdenate
cAMP	cyclic adenosine monophosphate
CD	circular dichroism
CD4	cluster of differentiation 4
C_6D_6	deuterated benzene
CD_2Cl_2	deuterated methylene chloride
$CDCl_3$	deuterated chloroform
$(CD_3)_2SO$	deuterated dimethyl sulfoxide
C. elegans	*Caenohabditis elegans*
$CeCl_3•7H_2O$	cerium(III) chloride heptahydrate
CH_2Cl_2	methylene chloride
$CHCl_3$	chloroform
CH_2N_2	diazomethane
$CH(OMe)_3$	trimethylorthoformate
cis	*L.* on the same side
Cl_3CCOCl	trichloroacetyl chloride
$ClCO_2Me$	methyl chloroformate
cm^{-1}	wavenumber
^{13}C-NMR	carbon nuclear magnetic resonance
CNS	central nervous system
CoA	coenzyme A

$(CO)_2Cl_2$	oxalyl chloride
CrO_3	chromium trioxide
(+)-CSA	camphor sulfonic acid
CSPG	chondroitin sulphate proteoglycans
Cu^{2+}	copper(II) ion
CuI	copper(I) iodide
$Cu(OAc)_2 \bullet H_2O$	copper(II) acetate monohydrate
$CuSO_4$	copper(II) sulfate
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	N,N'-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
Δ	*G.* delta, heat
δ	*G.* delta, chemical shift
DHP	2,3-dihydropyran
DIBAL	diisobutylaluminum hydride
DMAP	dimethylaminopyridine
DMAPP	γ,γ-dimethylallyl pyrophosphate
DMDO	dimethyl dioxirane
DME	dimethoxyethane
DMF	N,N-dimethylformamide
DMM	dimethoxymethane
DMP	Dess-Martin periodinane
3,5-DMP	3,5-dimethylpyrazole
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid

3,5-DNBC	3,5-dinitrobenzoyl chloride
E	*Ger.* entgegen
EC-CI	electron capture chemical ionization
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide
EPO	erythropoietin
ESI	electronspray ionization
Et	ethyl
Et_2AlCl	diethylaluminum chloride
Et_3N	triethylamine
Et_2O	diethyl ether
EtOAc	ethyl acetate
EtOH	ethanol
equiv.	equivalent
EVE	ethyl vinyl ether
FabI	enoyl reductase
FLIPR	fluorescent imaging plate reader
FPP	farnesyl pyrophosphate
FTIR	fourir transform infrared spectroscopy
g	gram
GCSF	granulocyte colony stimulating factor
GFP	green fluorescent protein
GMCSF	granulocyte-marcophage colony stimulating factor
GPCR	G-protein coupled receptor

GPP	geranyl pyrophosphate
HBr	hydrogen bromide
HBTU	N,N,N',N'-tetramethyl-O-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate
$H_2C=CHMgBr$	vinyl magnesium bromide
$(H_2C=CH)_4Sn$	tetravinyl tin
HCl	hydrochloric acid
HCO_2H	formic acid
HDAC	histone deacetylase
HF	hydrogen fluoride
HMG-CoA	β-hydroxy-β-methylglutaryl coenzyme A
HMPA	hexamethylphosphoramide
^{1}H-NMR	proton nuclear magnetic resonance
H_2O	water
H_2O_2	hydrogen peroxide
HRMS	high resolution mass spectroscopy
HSC	hematopoietic stem cell
HSCoA	coenzyme A
H_2SO_4	sulfuric acid
HSPC	hematopoietic stem and progenitor cell
hν	light
Hz	hertz
I_2	iodine
IC_{50}	half maximal inhibitory concentration
IL3	interleukin-3

in situ	*L.* on site
in vacuo	*L.* vacuum
in vitro	*L.* in glass
in vivo	*L.* within the living
IPP	isopentenyl pyrophosphate
i-Pr_2NEt	N,N-diisopropylethylamine
i-$PrNH_2$	isopropylamine
i-Pr_2NH	diisopropylamine
i-PrOH	isopropanol
$(i\text{-PrO})_2TiCl_2$	dichlorotitanium diisopropoxide
IR	infrared spectroscopy
J	coupling constant
KBr	potassium bromide
K_2CO_3	potassium carbonate
kcal	kilocalorie
kD	kilodalton
KH_2PO_4	monopotassium phosphate
$KMnO_4$	potassium permanganate
KOH	potassium hydroxide
L	liter
$LiAlH_4$	lithium aluminum hydride
LiCl	lithium chloride
$LiClO_4$	lithium perchlorate
LT	long-term
M9 buffer	3.0 g KH_2PO_4, 6.0 g Na_2HPO_4, 0.5 g NaCl,

	1.0 g, NH_4Cl, 1 L, H_2O
MAG	myelin-associated glycoprotein
m-CPBA	*meta*-chloroperoxybenzoic acid
M	molar
Me	methyl
MeCN	acetonitrile
Me_2CO	acetone
MeLi	methyllithium
$MeNO_2$	nitromethane
MeOAc	methyl acetate
MeOD	deuterated methanol
MeOH	methanol
NaOMe	sodium methoxide
MEM	2-methoxyethoxymethyl
MEMCl	2-methoxyethoxymethyl chloride
$Me_2NCH(OMe)_2$	dimethylformamide dimethyl acetal
$MeNH_2$	methylamine
Me_2SO_4	dimethyl sulfate
mg	milligram
$MgSO_4$	magnesium sulfate
MHz	megahertz
mL	milliliter
mmol	millimole
$Mn(OAc)_3•2H_2O$	manganese(III) acetate dihydrate
mol	mole

MOM	methoxymethyl
MOMCl	methoxymethyl chloride
MVA	mevolonic acid
MVK	methyl vinyl ketone
n	normal
N_2	nitrogen
$NaBH_4$	sodium borohydride
$NaBH_3CN$	sodium cyanoborohydride
NaCl	sodium chloride
NADPH	nicotinamide adenine dinucleotide phosphate
NaH	sodium hydride
$NaHCO_3$	sodium bicarbonate
Na_2HPO_4	sodium phosphate dibasic
$NaIO_4$	sodium periodate
NaOH	sodium hydroxide
Na_2SO_4	sodium sulfate
$Na_2S_2O_4$	sodium thiosulfate
n-BuLi	normal butyllithium
NF-κB	nuclear factor kappa-light-chain-enhancer of activated B cells
NH_4Cl	ammonium chloride
nM	nanomolar
NMR	nuclear magnetic resonance
Nogo	neurite outgrowth inhibitor

NP-1	neuropilin-1
[o]	oxidation
O_2	oxygen
O_3	ozone
obs.	observed
OMgp	oligodendrocyte-myelin glycoprotein
p	*para*
$Pb(OAc)_4$	lead(IV) acetate
PDC	pyridinium dichromate
$Pd(OAc)_2$	palladium(II) acetate
$Pd(PPh_3)_2Cl_2$	bis(triphenylphosphine)palladium(II) dichloride
Ph	phenyl
PhMe	toluene
$Ph_3P{=}CH_2$	methylene triphenylphosphine
pin	pinacolate
Piv	pivaloyl
PivCl	pivaloyl chloride
pKa	acid dissociation constant
PKC	protein kinase C
PKS	polyketide synthase
PLM	posterior lateral microtubule
PMB	*para*-methoxybenzyl
$PMBO(C{=}NH)CCl_3$	*para*-methoxybenzyl 2,2,2 trichloroacetamide

PP	pyrophosphate
ppm	parts per million
PPTS	pyridinium para-toluenesulfonic acid
PyBOP	(benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate
pyr•HCl	pyridinium hydrochloride
RCM	ring closing metathesis
R_f	retention factor
RNAi	ribonucleic acid interferance
SAR	structure activity relationship
sat.	saturated
Sema3A	semaphorin 3A
SCI	spinal cord injury
sp.	species
SR1	stremregenin1
SUCNR1	succinate receptor 1
TBAF	tetrabutylammonium fluoride
TBDPS	*tert*-butyldiphenyl
TBSCl	tert-butyldimethylsilyl chloride
TBS	*tert*-butyldimethylsilyl
TBSOTf	*tert*-butyldimethylsilyl triflate
t-Bu	*tert*-butyl
2,4,6-TCBC	2,4,6-trichlorobenzoyl chloride
TEPA	tetra-ethylene-pentamine

TES	triethylsilyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
THP	tetrahydropyran
TLC	thin-layer chromatography
TMS	trimethylsilyl
TMSCl	trimethylsilyl chloride
trans	*L.* across
TsOH	*para*-toluenesulfonic aicd
μg	microgram
μM	micromolar
μm	micrometer
μmol	micromole
UV	ultraviolet
VEGF	vascular endothelial growth factor
Z	*Ger.* zusammen

Chapter 1: Total Syntheses and Biological Evaluation of Vinaxanthone, Xanthofulvin, and Analogs Thereof

Spinal cord injury (SCI) is a debilitation that nearly a quarter of a million people around the world suffer each year. Such injuries are persistent and lack practical means of treatment due to the limited inherent ability of vital axons in the central nervous system (CNS) to regenerate after sustaining trauma.[1,2] Previous studies have proposed that the minimal capacity for neuronal regeneration is influenced by both the accumulation of extrinsic inhibitory components as well as the insufficient performance of intrinsic growth factors.[3-6] Myelin-associated proteins (Nogo, MAG, OMgp)[7-15] and extracellular matrix molecules such as chondroitin sulphate proteoglycans (CSPGs)[6,16-18] and semaphorin 3A (Sema3A)[19-22] are among some of the noteworthy inhibitors of axonal growth investigated thus far. Research has also suggested that the suppression of these inhibiting growth factors may lead to the ability of axons to regenerate.[16,20-34]

Popular approaches to promote CNS regeneration involve gene therapy, growth factors, and stem cells, whereas the use of low-molecular-weight compounds has received considerably less attention.[35] However, the use of small molecules in the context of SCI holds significant potential for the rapid advancement of new therapeutics. The delivery of drugs through direct spinal injection may benefit from the minimal metabolizing enzymes and neutral environment associated with the forgiving pharmacokinetics of cerebrospinal fluid. In addition, recent progress in hydrogel and polymer technology for continuous drug delivery specifically designed for spinal cord therapy would provide a unique and promising platform for therapeutic development when coupled with a validated small molecule.[36-39]

The natural products vinaxanthone (**1**, also named SM-345431) and xanthofulvin (**2**, also named SM-216289) represent two of the most promising small molecule leads for

the future development of SCI treatment (Figure 1.1). Both small molecules exhibit remarkable regenerative effects in animal models of complete spinal cord transection highlighted by the enhanced recovery of motor function.[30,31] Additionally, vinaxanthone (**1**) has been observed to promote nerve growth following corneal transplant.[40] The natural products were co-isolated from fungal extracts of *Penicillium* sp. SPF-3059 and were discovered through an extensive screen to identify inhibitors of Sema3A-mediated growth cone collapse. Vinaxanthone (**1**) and xanthofulvin (**2**) displayed potent *in vitro* inhibitory activity toward Sema3A with IC_{50} values of 0.1 and 0.09 μg/mL, respectively. Furthermore, cytotoxicity and alterations in the cellular morphology were not observed at concentrations >1,000 times the effective dose providing a sizable window of opportunity for preclinical assessments.[32-34]

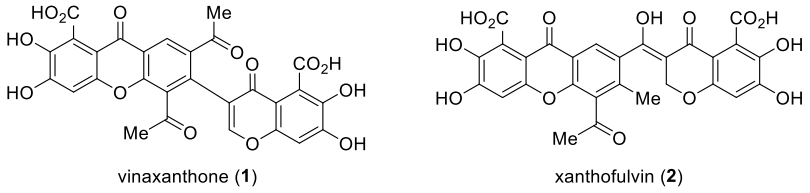


Figure 1.1. Structures of vinaxanthone (**1**) and xanthofulvin (**2**).

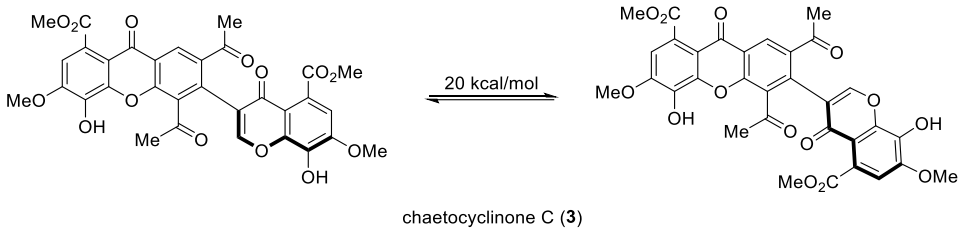
Nikolov and co-workers structurally elucidated Sema3A as a soluble 65 kDa extracellular matrix protein that accumulates in the resultant scar tissue surrounding the site of SCI.[19-22,41] Sema3A-mediated growth cone collapse operates through the modulation of the actin cytoskeleton and microtubules resulting in the failure of injured neurons to regenerate.[19-22,42-47] Typically, Sema3A binds with the transmembrane glycoprotein neuropilin-1 (NP-1) before interacting with its plexin receptor to signal downstream biological cues for neurite growth cone collapse. Vinaxanthone (**1**) and xanthofulvin (**2**) unhinge the binding between Sema3A and NP-1 by altering the steric

environment associated with the two proteins resulting in a disruption of the normal plexin interaction responsible for inhibition of neuronal outgrowth.[31,48,49]

While the regenerative effects of vinaxanthone (**1**) and xanthofulvin (**2**) have been attributed to their ability to strongly inhibit Sema3A following traumatic SCI, it is interesting that the same regenerative profile was not observed in an independent study that genetically eliminated Sema3A function altogether.[50] This result suggests that the inhibitory effects of the compounds against Sema3A are not solely responsible for the pronounced regeneration and that a more complex mode of action likely exists. Nevertheless, sustained administration of either natural product through continual infusion or the use of a solid matrix drug delivery system in adult rats following complete spinal cord transection generated regenerative responses. These small molecule treatments profoundly increased the regeneration and survival of injured neurons, led to robust myelination, reduction of the number of apoptotic cells, and significantly enhanced angiogenesis all contributing to a notable recovery.[30,31] In addition, treatment with vinaxanthone (**1**) in combination with treadmill training to promote proper axonal rewiring resulted in an even greater restoration of hindlimb motor function.[30]

The fermentation of *Penicillium vinacaeum*, the strain from which vinaxanthone (**1**) was originally isolated in 1991 by Yokose and Seto in a screen for phospholipase C inhibitors provided 30 mg/L of the natural product.[51] Vinaxanthone (**1**) had also been isolated from other strains of *penicillium* and had been identified as an effective CD4-binder and FabI inhibitor as well.[52,53] The fermentation of *Penicillium* sp. SPF-3059 most notably yielded 11 mg/L of vinaxanthone (**1**) and 21 mg/L of xanthofulvin (**2**) as co-isolates.[33] Thus far, no significant advances toward an efficient fermentation process have been realized.

Structural elucidation of vinaxanthone (**1**) and xanthofulvin (**2**) was accomplished using mass spectroscopy and ^{1}H-, ^{13}C-, and 2D-NMR experiments. Both natural products possess a xanthone and chromone core as well as a characteristic pattern of polyacidic functionality.[33,51-53] Despite containing a biaryl linkage, computational chiroptical calculations performed by Řezanka and co-workers on the structurally similar compound chaetocyclinone C (**3**) revealed that vinaxanthone (**1**) does not exhibit axial chirality (Figure 1.2). Chaetocyclinone C (**3**) was calculated to possess a barrier of rotation of 20 kcal/mol about the aryl-chromone bond under ambient conditions.[54,55] This conclusion is in accord with the lack of optical rotation and inconclusive CD spectrum associated with chaetocyclinone C (**3**).[56]



chaetocyclinone C (**3**)

Figure 1.2. Barrier of rotation for chaetocyclinone C (**3**).

Xanthofulvin (**2**) on the other hand does not contain a biaryl linkage but does possess an enol that exists as a 4:1 ratio with its keto form **4** in d_6-DMSO (Figure 1.3). Interestingly, the hemiketal natural product 411J (**5**) also exists as a 4:1 ratio with its keto tautomer **6**.[52] Careful analysis revealed that xanthofulvin (**2**) and 411J (**5**) possessed identical spectral properties. Since both xanthofulvin (**2**) and 411J (**5**) were reported as co-isolated products with vinaxanthone (**1**) it is likely that they are the same. Total synthesis of xanthofulvin (**2**), the more likely structure would easily resolve this inconsistency.

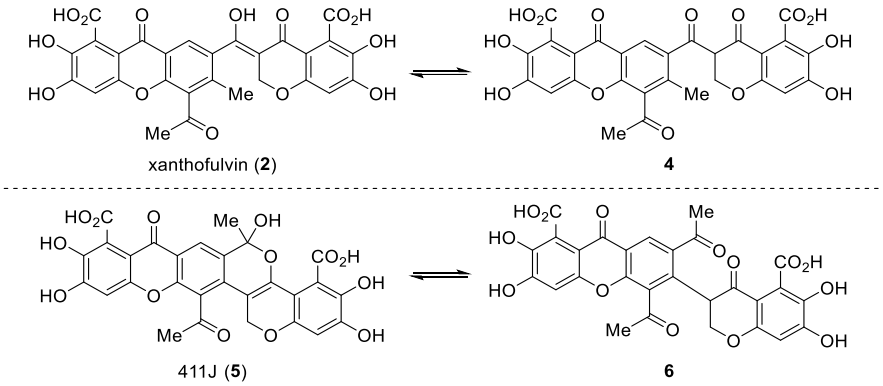


Figure 1.3. Equilibria of xanthofulvin (**2**) and **4** and 411J (**5**) and **6**.

Biosynthetic studies regarding vinaxanthone (**1**) and xanthofulvin (**2**) have yet to be reported, however research into the biosynthesis of the structurally similar polyketide metabolite, chaetocyclinone C (**3**) was performed by Zeeck (Figure 1.4).[56] Chaetocyclinone A (**7**), B (**8**), and C (**3**) were produced by the fermentation of *Chaetomium* sp. (strain Gö 100/2), which was isolated from marine algae.

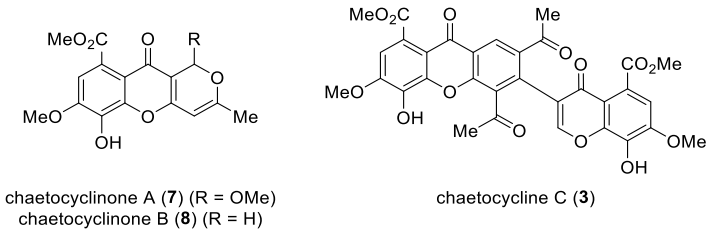
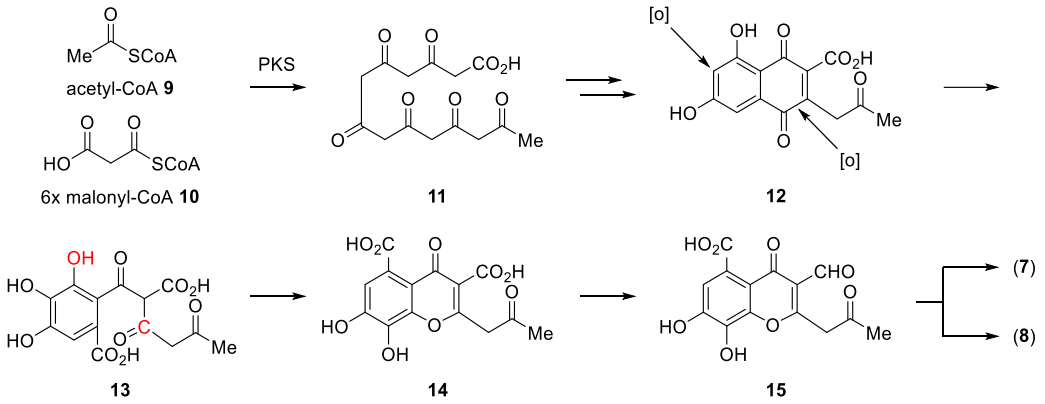


Figure 1.4. Structures of chaetocyclinone A (**7**), B (**8**), and C (**3**).

Through a series of ^{13}C-labelled acetate feeding experiments Zeeck suggested that a single chain heptaketide undergoes a typical fungal polyketide-folding event to establish the core of the C_{14} polyketides (Scheme 1.1). The biosynthetic pathway involves an initial condensation of the single chain heptaketide **11** and oxygenation to form hydroxynaphthoquinone **12**. Hydroxylation and oxidative ring cleavage follows to give benzoic acid derivative **13**. Condensation then affords chromone intermediate **14** whose terminal polyketide carboxyl group is subsequently reduced to aldehyde **15**. At this point

aldehyde **15** may cyclize and undergo methylation to provide chaetocyclinone A (**7**) or experience further reduction prior to methylation to generate chaetocyclinone B (**8**).



Scheme 1.1. Putative biosynthetic pathway for chaetocyclinone A (**7**) and B (**8**).

Zeeck's conclusions are consistent with previous biosynthetic studies performed on related fulvate-type natural products **16-19** (Figure 1.5).[57,58] It is important to note the structural similarity between these compounds and that of the chaetocyclinones, moreover their oxidation patterns also resemble that of vinaxanthone (**1**) and xanthofulvin (**2**).

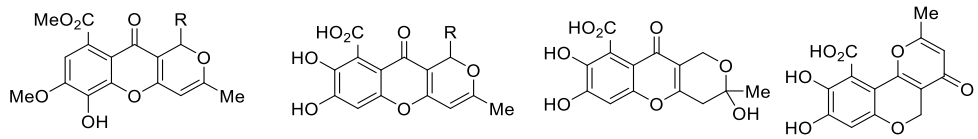
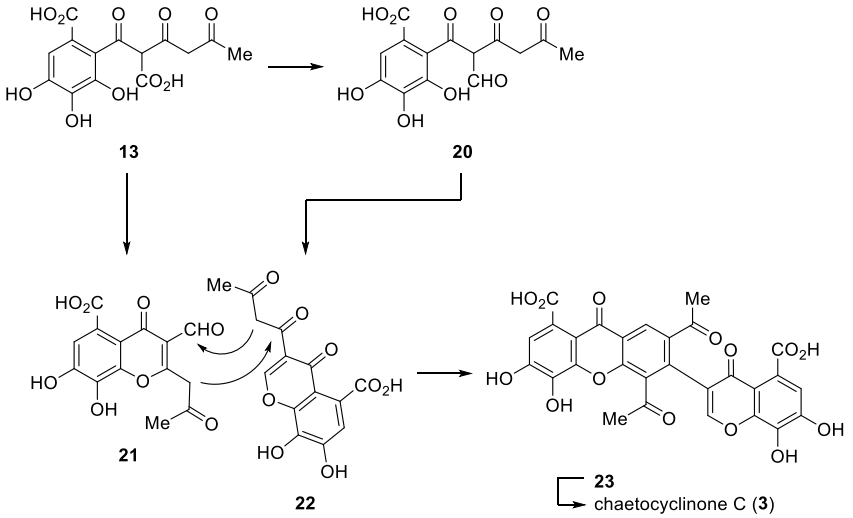


Figure 1.5. Structures of fulvate-type natural products.

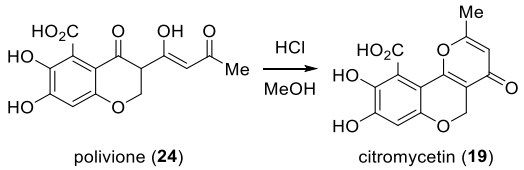
Zeeck also developed a biosynthetic proposal for the dimer species chaetocyclinone C (**3**) (Scheme 1.2). Originating from common intermediate **13** involved in the biosynthesis of chaetocyclinone A (**7**) and B (**8**), reactive precursors **21** and **22** could be obtained. A dual aldol condensation would consequently forge the xanthone core of chaetocyclinone C (**3**). Similar feeding experiments were conducted and

significant enrichment at the carbon atoms of the central rings was present, however diminishing and inconsistent yields of enriched chaetocyclinone C (**3**) failed to provide a complete labeling assignment. Although Zeeck had inconclusive data he asserts that chaetocyclinone C (**3**) arises from the dimerization of two highly reactive C_{14} polyketides, a hypothesis also put forth by Wrigley in his initial isolation work on vinaxanthone (**1**).[52]



Scheme 1.2. Putative biosynthetic pathway for chaetocyclinone C (**3**).

It is noteworthy to mention that Staunton's experiments with the metabolite polivione (**24**) which has the same oxygenation pattern as vinaxanthone (**1**) and xanthofulvin (**2**) revealed that polivione (**24**) could easily be transformed into citromycetin (**19**) (Scheme 1.3).[59-62] This highlights the correlation between previously proposed intermediate structures and known natural products.



Scheme 1.3. Transformation of polivione (**24**) into citromycetin (**19**).

Interestingly, an unsaturated version of the polivione scaffold with an aromatic oxygenation pattern consistent with the chaetocyclinones, lapidosin (**25**) is also a known isolated natural product (Figure 1.6).[59-62] Although it seems likely that vinaxanthone (**1**), xanthofulvin (**2**), and chaetocyclinone C (**3**) arise from non-enzymatic processes further studies are warranted to support such claims.

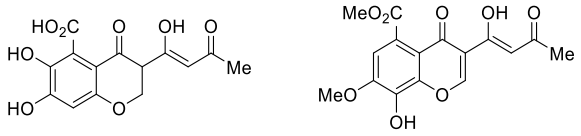
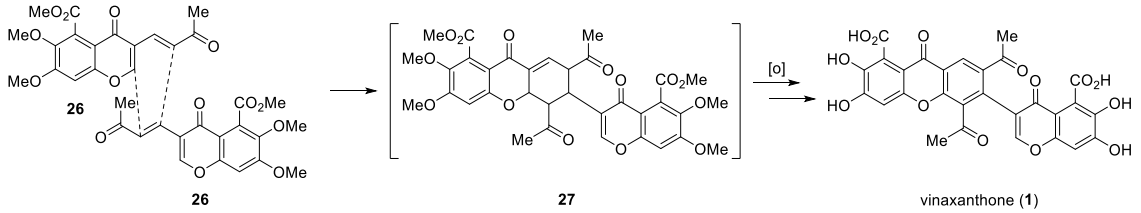


Figure 1.6. Structures of polivione (**24**) and lapidosin (**25**).

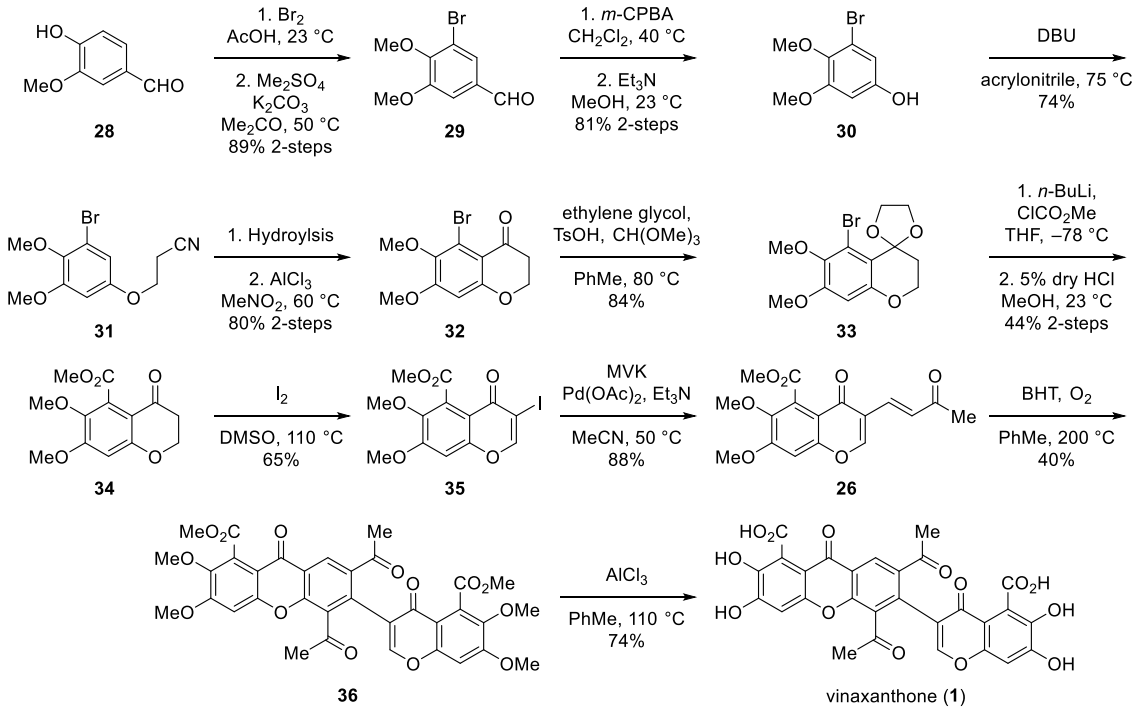
In 2007, Tatsuta disclosed the first total synthesis of vinaxanthone (**1**).[63] Interested in the biogenesis of the natural product an intermolecular Diels-Alder cycloaddition between two molecules of unsaturated ketone **26** was hypothesized to afford the vinaxanthone core following oxidative aromatization (Scheme 1.4).



Scheme 1.4. Tatsuta's Diels-Alder cycloaddition.

Tatsuta's total synthesis of vinaxanthone (**1**) began with the regioselective bromination and O-methylation of readily available vanillin **28** to afford 3-bromobenzaldehyde **29** (Scheme 1.5).[64] Dakin reaction proceeded to convert benzaldehyde **29** directly to phenol **30**.[65] Michael addition of phenol **30** into acrylonitrile gave nitrile **31** that was subsequently hydrolyzed and cyclized via an intramolecular Friedel-Crafts type reaction with aluminum trichloride to produce chromanone **32**.[66] Protection of the resultant ketone **32** as its ethylene ketal **33** was necessary to avoid

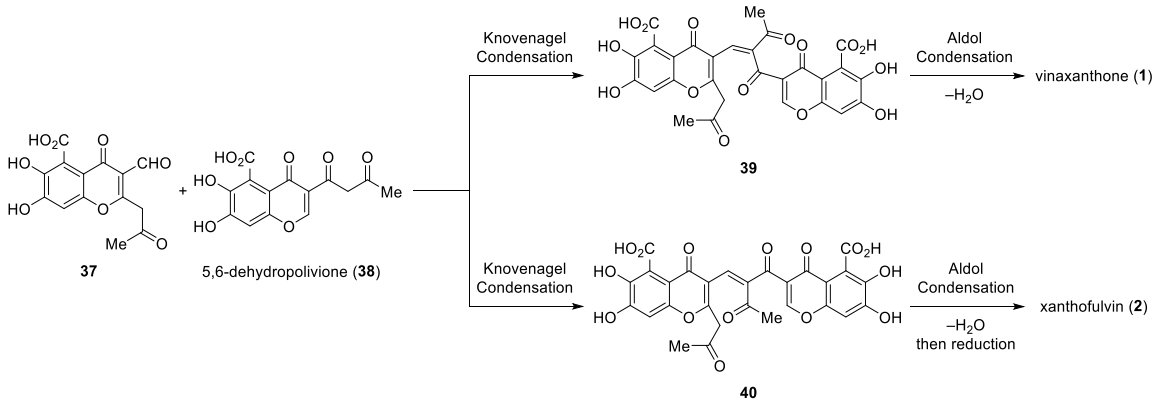
complications in downstream chemistry. Lithium-halogen exchange followed by trapping of the metallated species with methyl chloroformate furnished, after hydrolysis of the ketal, elaborated chromanone **34**. Vinyl iodide **35** was obtained by treating chromanone **34** with molecular iodine at elevated temperature in dimethyl sulfoxide. Palladium (II) acetate mediated Heck cross-coupling between vinyl iodide **35** and methyl vinyl ketone gave key dimerization precursor **26**.[67] Dimerization of vinyl ketone **26** via a Diels-Alder cycloaddition/oxidative aromatization process proceeded in toluene in a sealed tube at 200 °C in the presence of air to afford permethylated vinaxanthone **36**. Tatsuta believed that such a dimerization accounts for the biosynthetic pathway that leads to vinaxanthone (**1**) in nature. A final deprotection of all oxygen bond methyl groups was realized with aluminum trichloride in refluxing toluene to afford vinaxanthone (**1**).[68]



Scheme 1.5. Tatsuta's synthesis of vinaxanthone (**1**).

Although Tatsuta's synthesis is concise and utilizes a unique dimerization strategy, it lacks the scalability needed to produce large quantities of vinaxanthone (**1**) or structurally similar pharmaceutical agents for subsequent analyses for potential SCI therapeutics. The likelihood of a biomimetic Diels-Alder cycloaddition being the operative pathway in nature is also unlikely.[69-71]

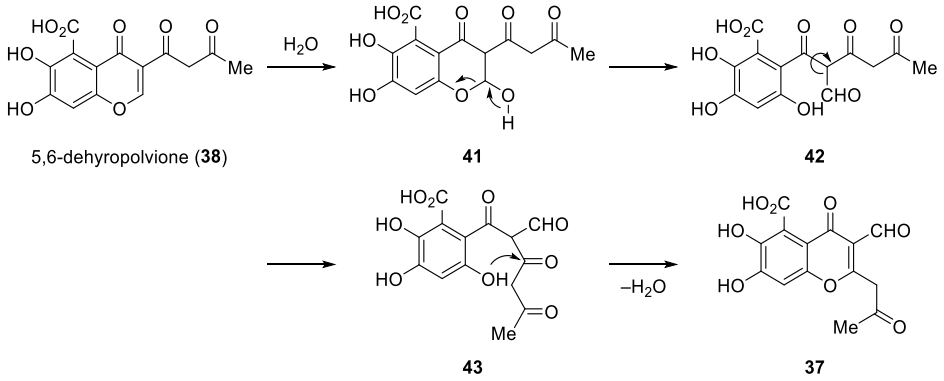
In light of their ability to promote axonal regeneration and scarcity in nature vinaxanthone (**1**) and xanthofulvin (**2**) are attractive targets for total synthesis. Wrigley hypothesized that a homodimerization of a C_{14} polyketide related to polivione (**24**) would afford vinaxanthone (**1**) and 411J (**5**) in nature.[52] In concert with this notion Zeeck proposed that a structurally similar intermediate to polivione (**24**) might undergo a heterodimerization with another reactive C_{14} polyketide to produce chaetocyclinone C (**3**), a molecule that exhibits the same carbon framework as vinaxanthone (**1**) (Scheme 1.6). Zeeck also noted that the formation of xanthofulvin (**2**) may arise from the difference in regiochemistry between Knovenagel intermediates **39** and **40** precluding aldol condensation.[56]



Scheme 1.6. Zeeck's insight into vinaxanthone (**1**) and xanthofulvin (**2**) formation.

The putative natural product 5,6-dehydropolivione (**38**) seemed like a viable C_{14} polyketide precursor that could generate both vinaxanthone and xanthofulvin scaffolds

(Scheme 1.7). Further analysis revealed that the other reactive C_{14} polyketide intermediate set forth by Zeeck is simply the addition of water into 5,6-dehydropolivione (**38**). Presumably water can add in a conjugate fashion resulting in the expulsion of a free phenol. Unhindered bond rotation then allows for rearrangement prior to condensation to afford reactive keto-aldehyde **37**.[72]



Scheme 1.7. Relationship between 5,6-dehydropolivione (**38**) and keto-aldehyde **37**.

Interestingly, 5,6-dehydropolivione (**38**) possesses dual reactivity as both a Michael donor and Michael acceptor (Figure 1.7). Therefore the rearrangement to another reactive coupling partner is not necessary for dimerization to occur and it may be possible that 5,6-dehydropolivione (**38**) is the only precursor needed to furnish vinaxanthone (**1**) and xanthofulvin (**2**) directly by way of a non-enzymatic pathway.

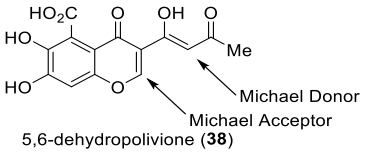
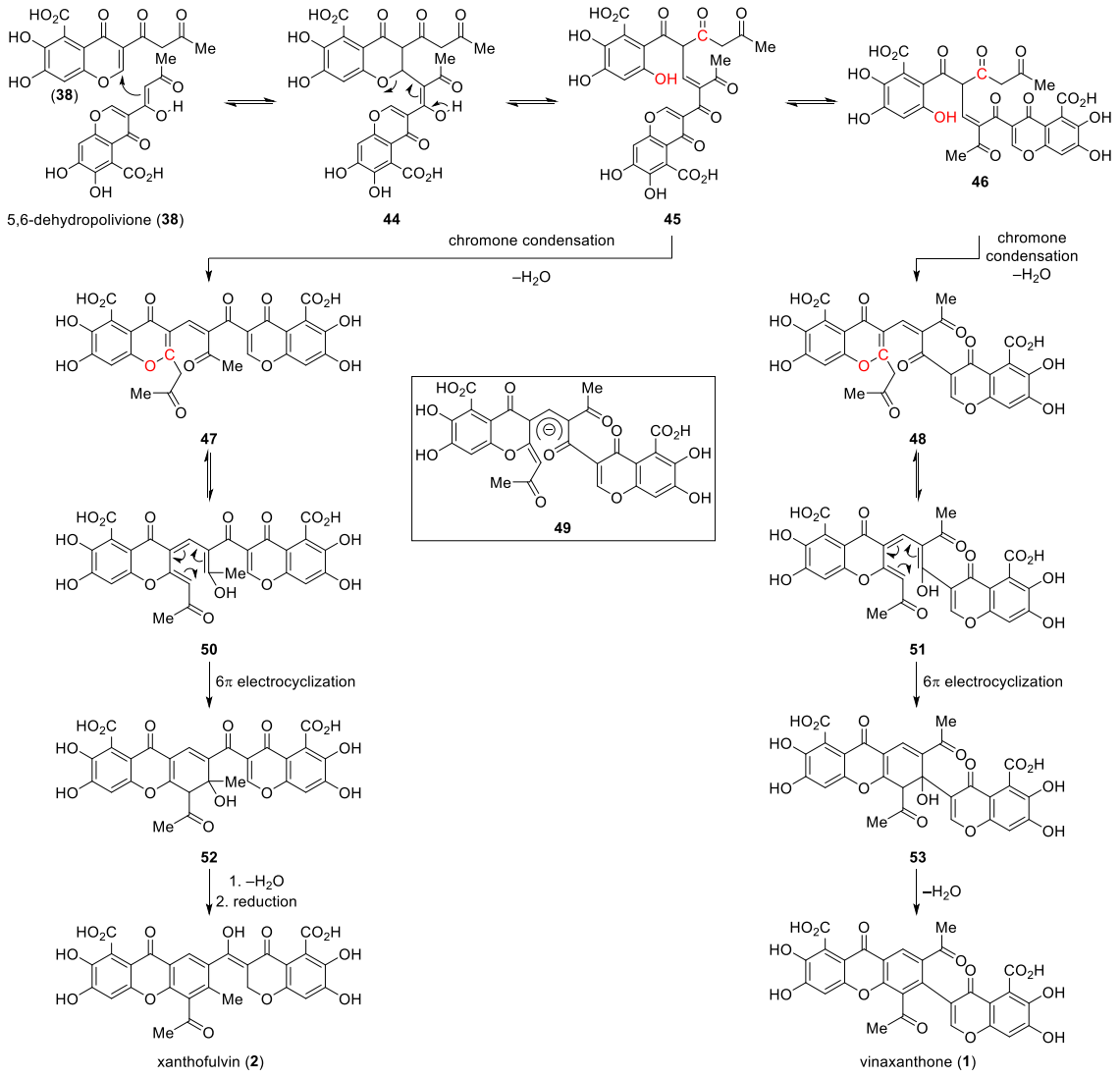


Figure 1.7. Dual reactivity of 5,6-dehydropolivione (**38**).

Michael addition of 5,6-dehydropolivione (**38**) into the chromone of a second molecule of 5,6-dehydropolivione **(38**) provides adduct **44** (Scheme 1.8). β-elimination leads to the formation of enediones **45** and **46** that are in equilibrium due to the

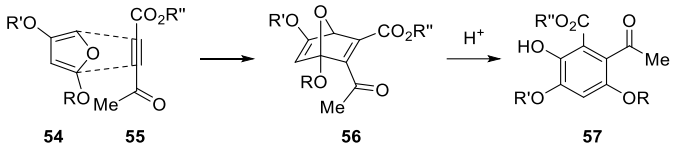
delocalized carbonyl system.[73] Chromone condensation of **45** and **46** results in the formation of chromones **47** and **48**.[74] These intermediates are also in equilibrium due to the highly delocalized tetracarbonyl system **49**. At this point previous hypotheses would suggest that an aldol condensation would take place. However, it appears strange that an anion would attack a carbonyl that is responsible for its delocalized nature and stability. Since the pKa's of **47** and **48** are probably quite low it is likely that they exist in their trienol forms **50** and **51** at biological pH. In this orientation a 6π electrocyclization may be responsible for the formation of the final ring closure to give **52** and **53**.[75,76] Elimination of water from **53** would furnish vinaxanthone (**1**) directly whereas **52** would require the elimination of water followed by reduction to afford xanthofulvin (**2**).



Scheme 1.8. Proposed non-enzymatic formation of vinaxanthone (**1**) and xanthofulvin (**2**).

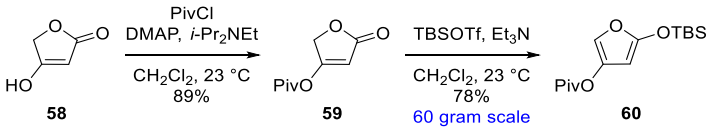
In order to examine the validity of our non-enzymatic hypothesis for the formation of vinaxanthone (**1**) and xanthofulvin (**2**) in nature, a concise synthesis of the putative precursor, 5,6-dehydropolivione (**38**) was developed. One of the retrosynthetic challenges in deconstructing this substrate included the ability to generate the polyoxygenated arene ring. A Diels-Alder cycloaddition between an appropriately functionalized furan **54** and an alkynyl ester **55** was envisioned to provide bicycle **56**

(Scheme 1.9). Upon acid-mediated ring opening/aromatization the desired arene **57** was believed to be accessible.[77]



Scheme 1.9. Diels-Alder cycloaddition strategy.

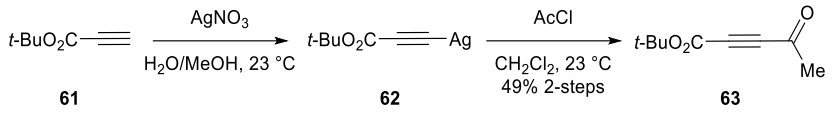
Initial studies regarding functionalized 2-siloxyfurans revealed that furans possessing strong electron donating groups at their 4-position lead to rapid decomposition and poor results in experiments probing Diels-Alder reactivity. A pivaloyl group was utilized to help attenuate the electronics of the furan and eliminate such weaknesses. A reliable two-step sequence allowed the preparation of furan **60** in large quantities without the need for purification (Scheme 1.10). Acylation of tetronic acid **58** with pivaloyl chloride in the presence of catalytic 4-dimethylaminopyridine afforded pivaloyl tetronate **59** which was subsequently treated with triethylamine and freshly prepared *tert*-butyldimethylsilyl triflate[78] to furnish furan **60** as a viscous amber oil.[79]



Scheme 1.10. Synthesis of furan **60**.

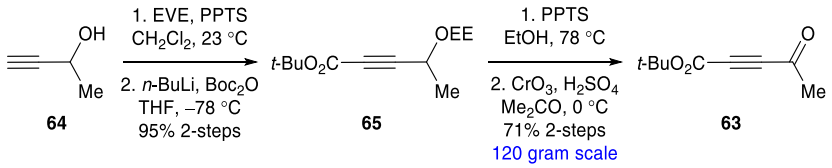
Keto-ester **63** was also synthesized in as few as two steps (Scheme 1.11). The silver acetylide of *tert*-butyl propiolate **61** was discretely generated before being trapped with acetyl chloride.[80,81] Despite delivering moderate yields this reaction sequence was far from ideal. Attempts to perform this sequence on a larger scale were unsuccessful due to diminishing yields. Significant quenching of silver acetylide **62** resulted in the presence of starting material that needed to be removed via column chromatography. The work-up

of silver acetylide **62** also required carbon tetrachloride to extract product from the aqueous layer, which became costly on scale. The use of chloroform or methylene chloride as substitutes or co-solvents was far less effective.



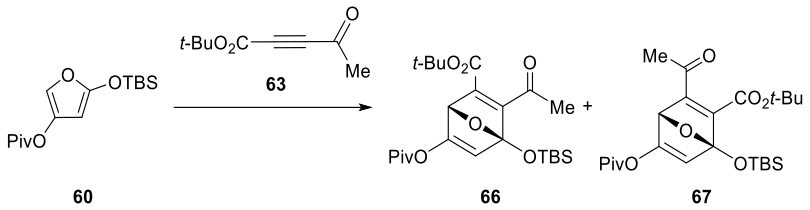
Scheme 1.11. Synthesis of keto-ester **63**.

To circumvent these drawbacks an alternative synthesis of keto-ester **63** was adopted (Scheme 1.12). Commercially available 3-butyn-2-ol **64** was treated with ethyl vinyl ether in the presence of catalytic pyridinium *p*-toluenesulfonate prior to deprotonation with *n*-butyllithium and trapping with di-*tert*-butyl dicarbonate to afford ester **65**. Removal of the ethoxyethyl ether group in refluxing ethanol followed by Jones oxidation once again furnish keto-ester **63**.[82] Although this sequence required an additional two steps, each transformation can be performed on >100 gram scale, does not require purification, and provides excellent yields.



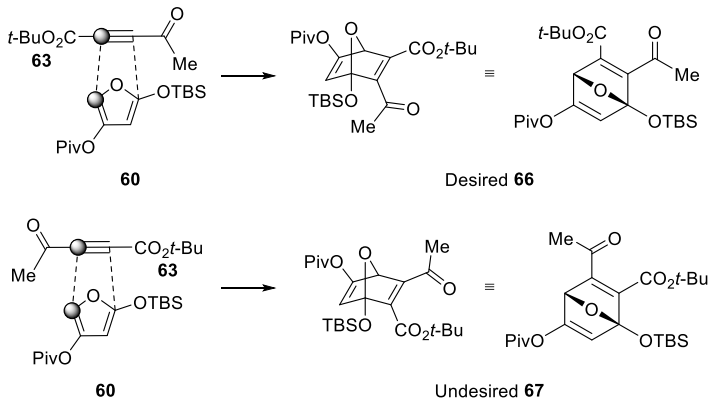
Scheme 1.12. Alternative synthesis of keto-ester **63**.

With a suitable diene and dienophile in hand the Diels-Alder cycloaddition between furan **60** and keto-ester **63** was investigated (Scheme 1.13). The Diels-Alder between a siloxy furan and symmetrical alkynoates such as dimethyl acetylenedicaboxylate are well documented in the literature,[77,83] however the use of unsymmetrical alkynoates has garnered much less attention.[84,85] In this scenario the cycloaddition may generate two possible regioisomeric bicyclic adducts.



Scheme 1.13. Diels-Alder regioisomers **66** and **67**.

The desired cycloadduct **66** arises from the engagement of the most nucleophilic carbon of the furan at the β-position in respect to the ketone functionality of the keto-ester **63** (Scheme 1.14). This outcome was anticipated to be the most favorable because a ketone typically possesses more of an electron withdrawing effect than does an ester and would therefore impart a greater directing ability on the system. The undesired cycloadduct **67** would consequently arise from the influence of the ester functionality in directing the reaction.

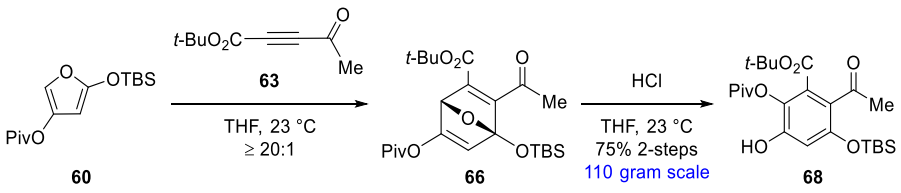


Scheme 1.14. Diels-Alder regioselectivity.

It seemed reasonable that the stronger electron withdrawing character of the ketone compared to that of the ester would work in concert with the polarization of the furan to influence the regioselective outcome in our favor. Despite being aided by an intramolecular tether similar transformations have been reported in the literature.[86] However, the use of an unsymmetrical aldehyde-ester alkyne has also been reported to

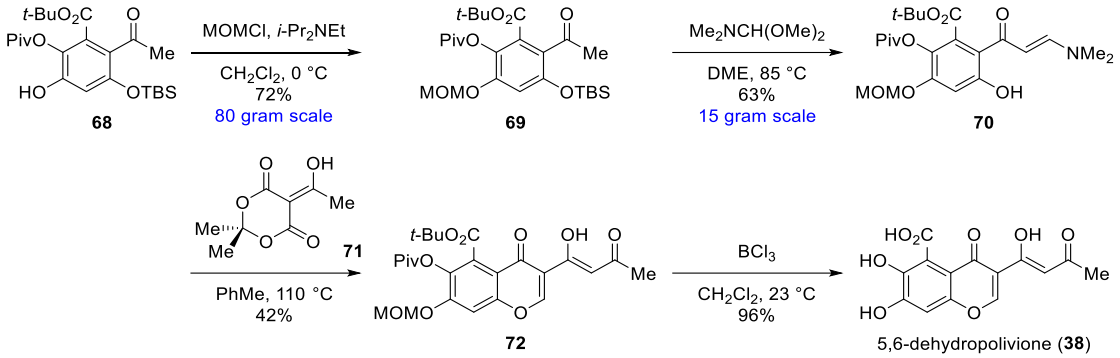
primarily afford the regioisomer governed by the ester and not the aldehyde.[87] Therefore the regioselective outcome of our intended furan, keto-ester Diels-Alder reaction appeared less predictable than first assumed.

A solution of furan **60** and keto-ester **63** in tetrahydrofuran at 23 °C resulted in a viscous amber oil that upon concentration gave a single regioisomeric product by ^{1}H- and ^{13}C-NMR analysis (Scheme 1.15). Both spectra revealed the presence of an enol ether and bridgehead methine, characteristic of the desired product **66**. Bicycle **66** was then treated under acidic conditions to initiate ring opening/aromatization to afford phenol **68**. Initially, 0.1 N hydrochloric acid was used for this transformation. However, it became evident that the use of dry hydrochloric acid eliminated the need for an aqueous work-up resulting in superior yields. Comparison of spectral data for phenol **68** to an earlier variant of the substrate, which contained a methyl carbonate instead of the pivaloyl ester and its structure unambiguously assigned by x-ray crystallography revealed the desired regioselectivity as well as concomitant migration of the pivaloyl group.



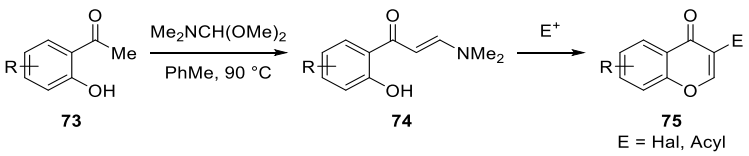
Scheme 1.15. Synthesis of phenol **68**.

With ample quantities of phenol **68** at our disposal the next synthetic challenge was to obtain the acetoacetylated chromone scaffold of 5,6-dehydropolivione (**38**) (Scheme 1.16). Protection of the free phenol as its methoxymethyl ether **69** was necessary to avoid complications arising from the incompatibility of the phenol with subsequent chemistry.[88]



Scheme 1.16. Synthesis of 5,6-dehydropolivione (**38**).

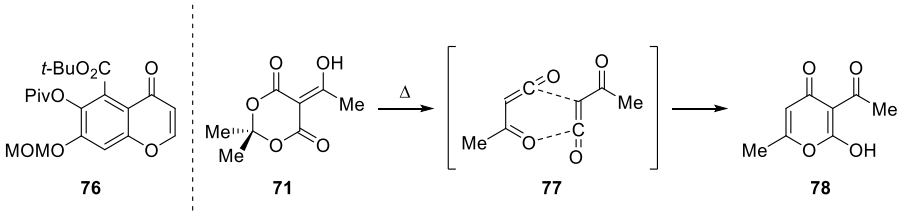
At this point the implementation of a vinylogous amide arose as a viable option for providing a synthetic handle for chromone formation (Scheme 1.17). In 1979, Gammill disclosed the homologation of 2'-hydroxyacetophenones **73** to enaminones **74** followed by cyclization and concomitant trapping of an electrophile to form 3-substituted chromones **75**.[89] In the context of this report halogens and acylating species were used as the electrophiles. Gratifyingly, when heated in toluene with excess N,N-dimethylformamide dimethyl acetal acetophenone **69** furnished enaminone **70** in a moderate 42% yield. More importantly was the simultaneous cleavage of the *tert*-butyl dimethylsilyl protecting group to set the stage for chromone formation. Despite being the most utilized solvent for such transformations, toluene often gave inconsistent results. It seemed reasonable that a more polar solvent would have the ability to stabilize the ionization of N,N-dimethylformamide dimethyl acetal and lower the energy of the reactive intermediates. Consequently, by switching the solvent to dimethoxyethane a more consistent and higher yielding reaction was obtained.



Scheme 1.17. Gammill's 3-substituted chromone synthesis.

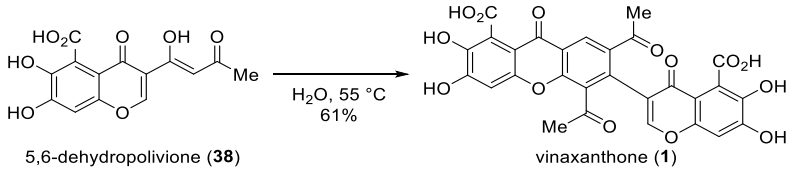
Although Gammill produced acylated chromones our objective was to invoke acetoacetylation (Scheme 1.16). Various reagents including diketene were used to generate acyl ketene before identifying acyl-Meldrum's acid **71** as the best option for acetoacetylation.[90] Upon heating acyl-Meldrum's acid **71** to reflux in toluene a retrocyclization provided acyl ketene **77**, which engaged enaminone **70** in the desired fashion to afford protected 5,6-dehydropolivione **72**. Subsequent global deprotection with boron trichloride was uneventful providing a near quantitative yield of 5,6-dehydropolivione (**38**).[91]

Unfortunately, extensive attempts to optimize the acetoacetylation failed to exceed 42% yield. Problems arise within the reaction itself as well as in the purification of the product (Scheme 1.18). At high temperatures, enaminone **70** has the potential to cyclize in the absence of an electrophile to produce unsubstituted chromone **76**. Another transformation taking place in the reaction vessel is the cycloaddition between two molecules of acyl ketene **77** to give dehydroacetic acid **78**. Silica gel column chromatography was minimally successful in purification. However, analysis of the original isolation paper of polivione (**24**) revealed that the use of phosphoric acid impregnated silica gel for purification was beneficial.[59,60] Implementing this strategy made a significant improvement in our purification efforts. Despite trying a multitude of solvent systems, separation of the desired product from unwanted chromone **76** and dehydroacetic acid **78** was difficult due to similar R_f values and moderate solubility in the eluent of choice.



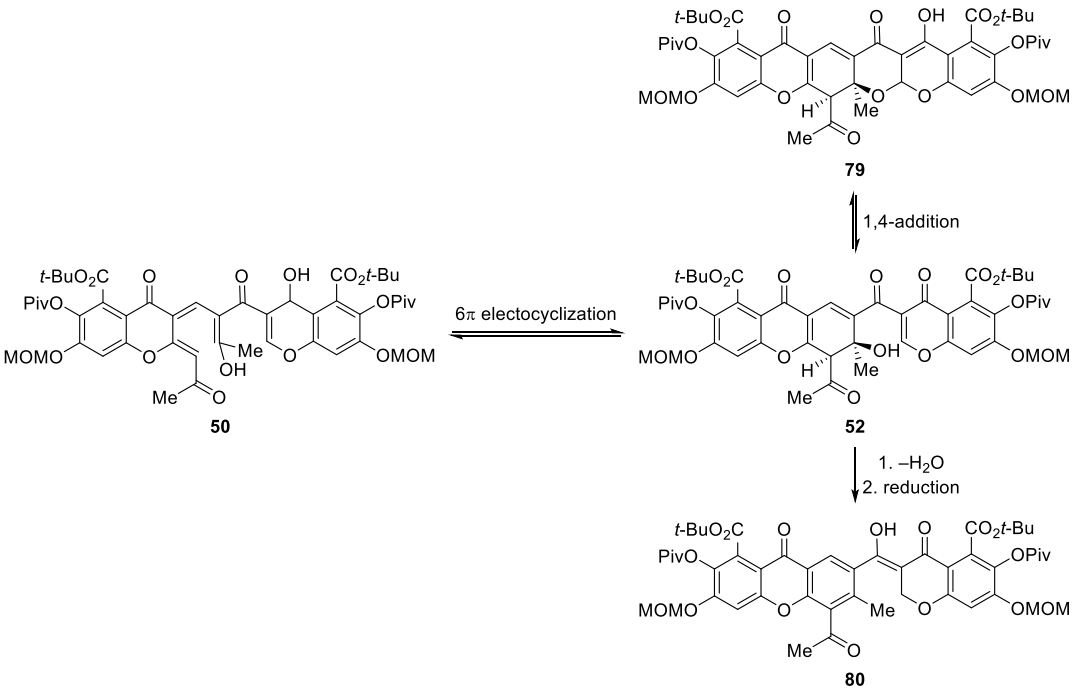
Scheme 1.18. Byproduct formation from acetoacetylation.

Finally, the penultimate biomimetic dimerization of the putative 5,6-dehydropolivione (**38**) precursor could now be investigated (Scheme 1.19). To our delight, simply warming an aqueous solution of 5,6-dehydropolivione (**38**) to 55 °C furnished vinaxanthone (**1**) in a respectable 61% yield.[92] Interestingly, neither xanthofulvin (**2**) nor any other species was detected from the reaction. This result lends credence to the hypothesized non-enzymatic formation of vinaxanthone (**1**) in nature.



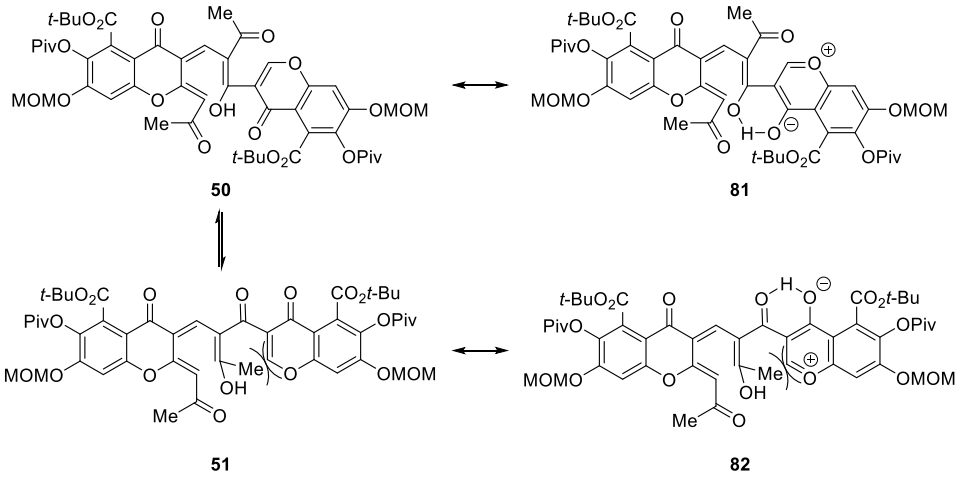
Scheme 1.19. Putative biomimetic dimerization of 5,6-dehydropolivione (**38**) to vinaxanthone (**1**).

Further examination of our mechanistic proposal suggests a couple of reasons for the exclusive formation of vinaxanthone (**1**) (Scheme 1.20). Following the 6π electrocyclization of trienol **50** to give intermediate **52** it is possible for a reversible intramolecular conjugate addition to occur giving species **79**. Such a pathway may suppress the dehydration needed to form the xanthofulvin core.



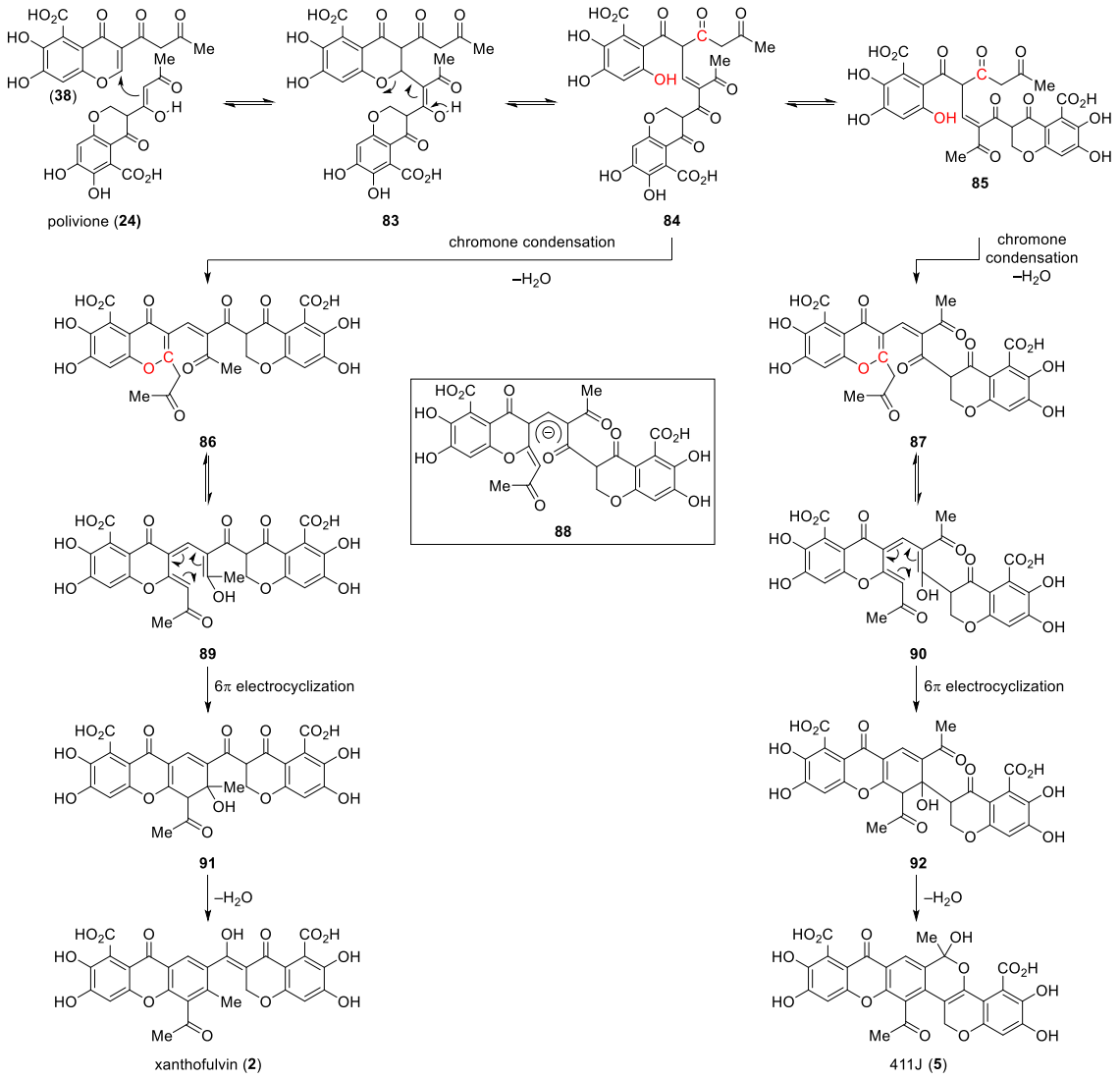
Scheme 1.20. Possible intramolecular conjugate addition.

A second possible account for the exclusive formation of vinaxanthone (**1**) over xanthofulvin (**2**) may be the steric encumbrance associated with the aromaticity-assisted hydrogen bonding found in intermediates **50** and **51** (Scheme 1.21).[93-95] By way of resonance the chromone moiety has the ability to aromatize and stabilize the transition state for the 6π electrocyclization leading toward vinaxanthone (**1**). However, the orientation leading toward xanthofulvin (**2**) possesses a significant amount of steric hindrance thus making this pathway unfavorable.



Scheme 1.21. Aromaticity-assisted hydrogen bonding.

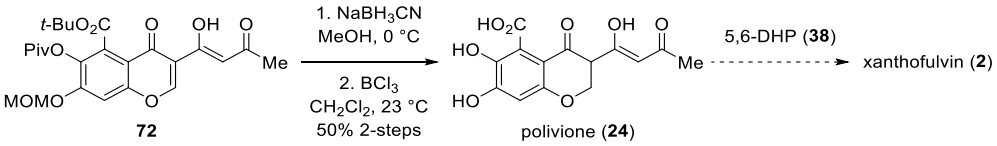
Following the completion of our concise 9-step synthesis of vinaxanthone (**1**) efforts were concentrated on the amendment of our biomimetic strategy to access xanthofulvin (**2**) (Scheme 1.22). It was hypothesized that a heterodimerization between polivione (**24**) and 5,6-dehydropolivione (**38**) would mechanistically be devoid of the reversible intramolecular Michael addition and aromaticity-assisted hydrogen bonding thought to negatively impact our previous proposal for xanthofulvin (**2**) formation. With polivione (**24**) functioning as a discrete Michael donor, conjugate addition into 5,6-dehydropolivione (**38**) followed by β-elimination would provide phenols **84** and **85**. Subsequent chromone condensation and tautomerization to trienols **89** and **90** once again sets the stage for 6π electrocyclization. Due to the inherent saturation in polivione (**24**) loss of water would directly afford xanthofulvin (**2**) and 411J (**5**) without the need for terminal reduction steps following the cascade of bond forming events.



Scheme 1.22. Proposed heterodimerization between polivione (**24**) and 5,6-dehydropolivione (**38**).

Polivione (**24**) was accessed from protected 5,6-dehydropolivione **72** following a conjugate reduction with sodium cyanoborohydride and global deprotection (Scheme 1.23).[91,96,97] Unfortunately, despite several efforts the desired heterodimerization was never obtained. Reactions either yielded exclusive vinaxanthone (**1**) in poor yields or provided reaction mixtures that were inseparable and too difficult to analyze. It should be

noted that although our crude synthetic polivione (**24**) matched known spectral data, conditions for its explicit purification were never realized.[59,60]



Scheme 1.23. Synthesis of polivione (**24**).

In order to overcome the inability to access xanthofulvin (**2**) through a similar biomimetic approach to that utilized for vinaxanthone (**1**) an ynone surrogate **93** was envisioned to attenuate the reactivity associated with the acetoacetyl moiety of protected 5,6-dehydropolivione **72** (Figure 1.8). An ynone precursor was postulated to function solely as a Michael acceptor and would also benefit from possessing the proper oxidation state thus eliminating the need for further manipulation.

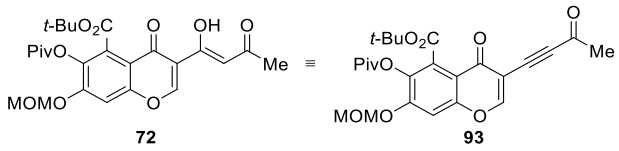
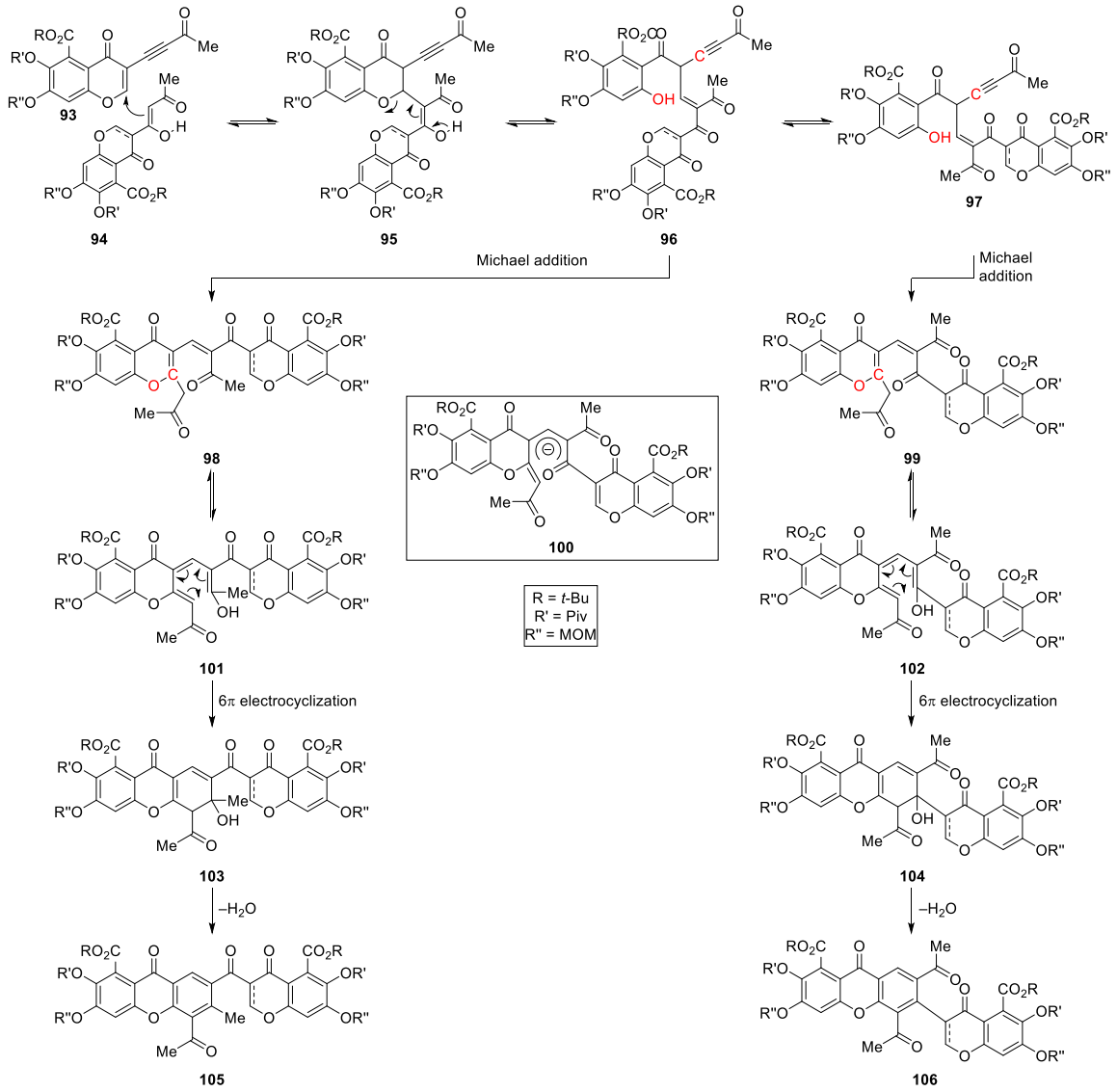


Figure 1.8. Ynone **93** as a surrogate for protected 5,6-dehydropolivione **72**.

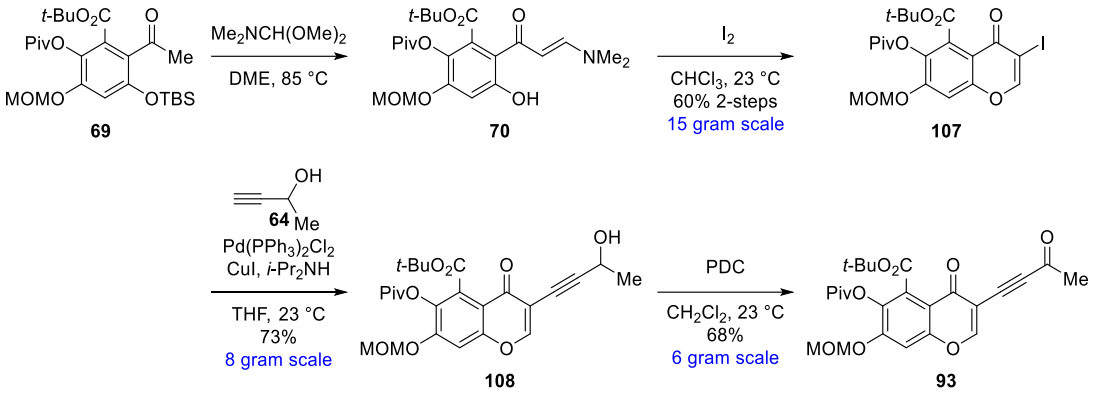
Analogous to our biomimetic proposal, the mechanistic pathway may begin with the addition of protected polivione or protected 5,6-dehydropolivione (represented as **94**) in a Michael fashion to the chromone of ynone **93** (Scheme 1.24). β-elimination would liberate free phenols **96** or **97** that could then participate in intramolecular Michael additions with the requisite alkynone functionalities. At this point the mechanism mirrors our original proposal where isomerism leads to trienols **101** or **102**, the intermediates geared toward 6π electrocyclization. Final elimination of water would generate the core structures of both vinaxanthone (**1**) and xanthofulvin (**2**).



Scheme 1.24. Proposed coupling between ynone **93** and protected polivione/5,6-dehydropolivione **94**.

The synthesis of ynone **93** was easily realized through Gammill's chemistry to provide iodochromone **107** as an excellent handle for cross-coupling transformations (Scheme 1.25).[89] Upon concentration of a dimethoxyethane solution of acetophenone **69** and N'N'-dimethylformamide dimethyl acetal the resultant enaminone **70** was directly taken up in chloroform and treated with molecular iodine at 23 °C to afford

iodochromone **107**. Sonogashira cross-coupling mediated by bis(triphenylphosphine) palladium(II) dichloride of 3-butyn-2-ol **64** (the same starting material used for keto-ester **63**) to vinyl iodide **107** provided propargyl alcohol **108**.[98] It was extremely important to vigorously deoxygenate the tetrahydrofuran used in the Sonogashira reaction by way of iterative freeze-pump thawing. Failure to do so resulted in severely diminished yields. Subsequent pyridinium dichromate oxidation furnished gram quantities of the desired ynone **93** as a white solid.[99]

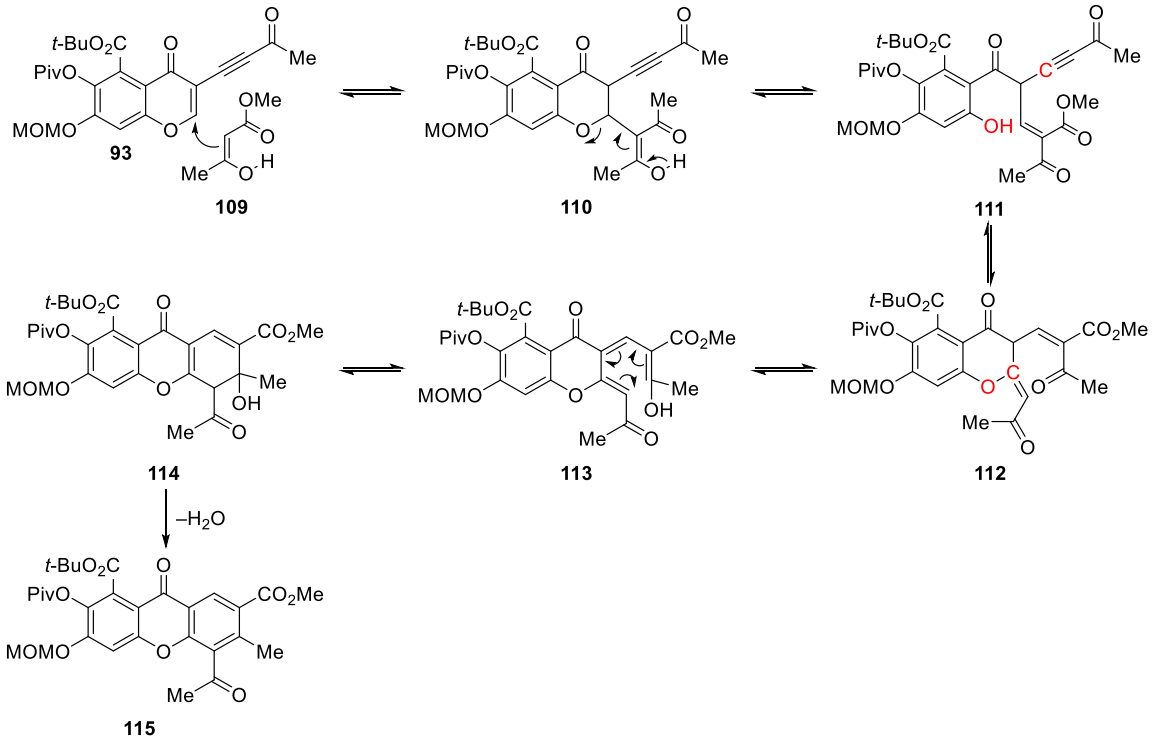


Scheme 1.25. Synthesis of ynone **93**.

It is worthy to note that direct coupling of 3-butyn-2-one was unsuccessful and lead to complete decomposition. This result was not surprising having reviewed Neigishi's work that stated such a transformation is difficult and remains a synthetic challenge.[100,101] Attempts to optimize the oxidation step via Swern, Dess-Martin periodinane, tetrapropylammonium perruthenate, manganese dioxide, and other chromium based oxidant conditions all failed to produce a superior yield. The propargyl alcohol/ynone moiety simply could not withstand the aforementioned reaction conditions.

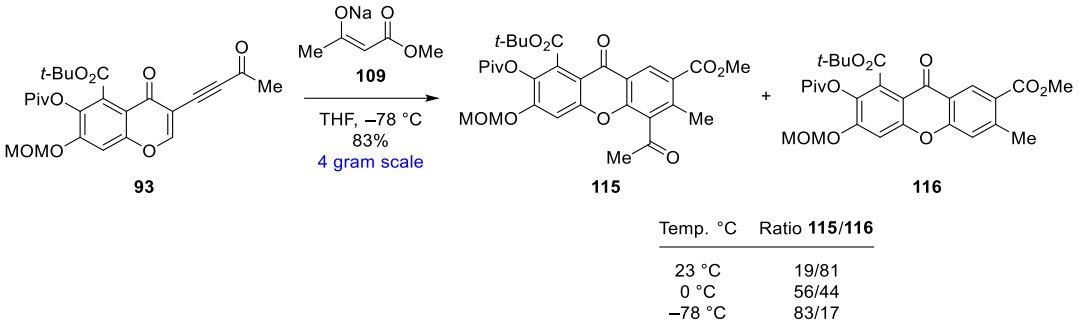
To our disappointment extensive efforts to acquire the xanthofulvin core once again only gave exclusive formation of the vinaxanthone connectivity or an indeterminate

reaction mixture. At this juncture it was decided to focus on a stepwise approach in which a more simplistic xanthone would be synthesized en route toward xanthofulvin (**2**) (Scheme 1.26). Based on our previous mechanistic proposals we believed that the addition of methyl acetoacetate **109** to ynone **93** would provide the correct regioselectivity inherent to xanthofulvin (**2**). Furthermore, the resultant ester could function as a key synthetic handle to append the chromone core. Several reports by Hu and co-workers describing similar outcomes from the addition of 1,3-dicarbonyl species to 3-alkynyl chromones was encouraging.[102-104] Exploitation of 3-alkynyl chromone reactivity is a useful extension of known reactivity displayed by 3-formyl and 3-ketonic chromones.[74,105] Despite having an arene where an acetyl group was desired, Hu's substrates demonstrated the ability to forge the correct connectivity present in the xanthone core of xanthofulvin (**2**).



Scheme 1.26. Coupling of ynone **93** and methyl acetoacetate **109**.

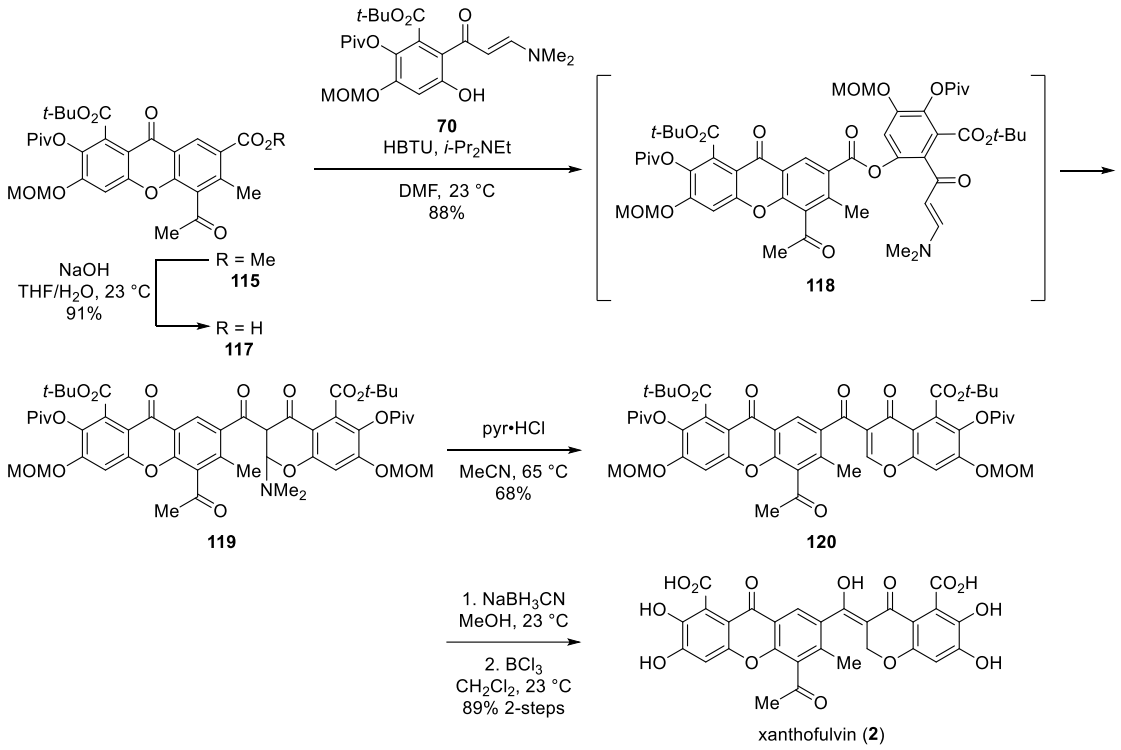
The *in situ* generation of the sodium anion of methyl acetoacetate with sodium hydride at 23 °C led to a poor yielding mixture of the desired xanthone **115** and its deacetylated variant **116** (Scheme 1.27). The use of freshly prepared sodium enolate of methyl acetoacetate **109** rather than *in situ* generation was favorable. Furthermore, by running this reaction at colder temperatures the ratio of desired xanthone **115** to its deacetylated byproduct **116** could be amplified. By performing this reaction at −78 °C in tetrahydrofuran a 5:1 ratio could be obtained with a respectable 83% isolated yield of xanthone **115**.



Scheme 1.27. Synthesis of xanthone **115**.

Selective saponification of methyl ester **115** was achieved with sodium hydroxide in a 3:1 tetrahydrofuran/water solution to yield carboxylic acid **117** (Scheme 1.28). Despite being extremely sluggish (3-4 days) this reaction was clean, high yielding, and didn't require purification. The next challenge was to couple carboxylic acid **117** to enaminone **70** in order to promote an O-to-C carboxyl transfer to forge the xanthofulvin core. Previous methods for coupling ortho-hydroxy aryl enaminones with carboxylic acids to initiate O-to-C carboxyl transfers utilized anhydrides and other activated carboxylic acid derivatives.[106-108] The formation of the corresponding acid chloride prior to coupling with enaminone **70** in the presence of triethylamine was indeed successful, however it was low yielding. Direct coupling using standard peptide coupling reagents such as N'N'-dicyclohexylcarbodiimide (DCC), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), and (benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate (PyBOP) provided better yields but were plagued by difficulties in purification. N,N,N',N'-tetramethyl-O-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) on the other hand smoothly promoted the coupling of carboxylic acid **117** to enaminone **70** in the presence of Hunig's base to generate aminal **119** in a gratifying 88% yield. The use of coupling reagents was more direct and tolerant of sensitive functionality.[109] Unfortunately, dimethylamine would not eliminate under

various O-to-C transfer conditions and required an independent step for removal. The dimethylamine was eliminated by heating an acetonitrile solution of aminal **119** in the presence of pyridinium hydrochloride. It was important to conduct this reaction under anhydrous conditions, as cleavage of the xanthone followed by chromone formation was a competing pathway. Finally, conjugate reduction with sodium cyanoborohydride was straightforward and as before the six oxygen-bound protecting groups were removed simultaneously with boron trichloride in methylene chloride at 23 °C to provide material that was in accord with the spectral values reported for xanthofulvin (**2**) and 411J (**5**) [91,96,97] Therefore, we were able to appropriately reassign the hemiketal structure of 411J (**5**) to that of xanthofulvin (**2**).[33,52,92] With adequate quantities of synthetic vinaxanthone (**1**) and xanthofulvin (**2**) in hand we were poised to study their biological profiles in the context of neuronal regeneration.



Scheme 1.28. Synthesis of xanthofulvin (**2**).

The neuroregenerative effects of vinaxanthone (**1**) and xanthofulvin (**2**) have previously been attributed to their abilities to prevent Sema3A-mediated growth cone collapse.[48] However, genetic removal of Sema3A function does not lead to the same regeneration following injury.[50] This result suggests that the inhibitory action of the compounds against Sema3A is not solely responsible for the pronounced regeneration and that other growth promoting pathways also exist. The potential polypharmacology of these natural products to block regrowth inhibition and actively promote growth provide a pharmacological solution that has thus far eluded SCI treatment.[110] In light of these observations mode of action studies were pursued using synthetic vinaxanthone (**1**) and xanthofulvin (**2**) regarding G-protein-coupled receptors.

G-protein-coupled receptors (GPCRs) also referred to as seven transmembrane receptors (7TMRs), constitute over 800 of the most versatile and ubiquitous chemical

sensors found in nature. They are responsible for the regulation of nearly all known physiological processes in the human body including the senses of sight, smell, and taste. It is noteworthy that greater than half of all prescription drug sales worldwide can be attributed to pharmaceuticals targeting GPCRs. Furthermore, the 2012 Nobel Prize in chemistry awarded to Robert Lefkowtiz and Brian Kobilka highlights the importance of GPCRs in modern medicine and science.[111]

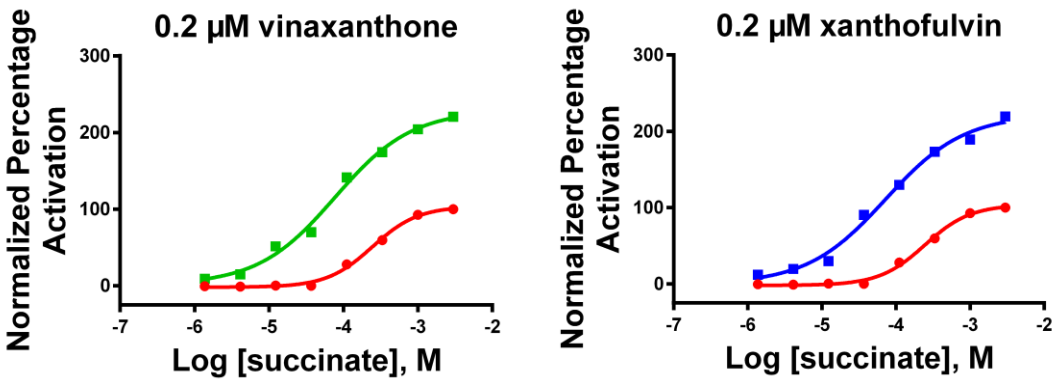
Cells throughout the body communicate with each other using chemical messengers such as hormones and neurotransmitters. GPCRs facilitate these communications by allowing cells to process information encoded in various chemical messengers such as photons, protons, small organic molecules, peptides, and glycoproteins among other chemical entities.[112] Therefore the optimization of the ligand efficacy of GPCRs may lead to biological responses that can be fine-tuned to elicit desired therapeutic outcomes.

Vinaxanthone (**1**) and xanthofulvin (**2**) were subjected to EMD Millipore's Full GPCRProfiler® Panel, a screen of various GPCRs with the objective of identifying agonist and antagonist activity. Fluorescent imaging plate reader (FLIPR) assays were conducted to measure the receptor-induced mobilization of intracellular calcium. By monitoring the [Ca^{2+}] flux generated by the addition of test compounds, fluorescent data can be interpreted as biological activity.[113] Neither natural product displayed agonist nor antagonist activity however both were identified as strong positive allosteric modulators of succinate receptor 1 (SUCNR1), also referred to as GPR91.

Succinate, an intermediate in the energy producing Krebs cycle is the endogenous ligand of SUCNR1 and has a half-maximal response concentration (EC_{50}) of 28-56 μM. Interestingly, other intermediates of the Krebs cycle, 800 pharmacologically active compounds and known GPCR ligands, and 200 carboxylic acids/succinate looking

molecules failed to increase agonist activity at the orthosteric site beyond that of the native succinate.[114] Vinaxanthone (**1**) and xanthofulvin (**2**) on the other hand presumably bind to a topographically distinct allosteric site and in this case potentiate the signaling of the endogenous succinate ligand.

Both natural products markedly enhanced the affinity and efficacy of GPR91 towards succinate (Figure 1.9). At 0.2 μM concentrations, identical concentrations to those used in the original Sema3A-mediated growth cone collapse assays, vinaxanthone (**1**) and xanthofulvin (**2**) displayed dose ratios of 0.33 and 0.32 with efficacy values of 230% and 222%, respectively, when compared to the reference agonist sodium succinate alone.[33]



Agonist(s)	Predicted EC_{50} Potency (μM)	Predicted Dose Ratio	Efficacy
Sodium succinate	230	1	100%
Sodium succinate + 0.2 μM vinaxanthone (**1**)	76	0.33	230%
Sodium succinate + 0.2 μM xanthofulvin (**2**)	73	0.32	222%

Figure 1.9. Efficacy of vinaxanthone (**1**) and xanthofulvin (**2**) compared to the lone reference agonist, sodium succinate in activating GPR91.

Therefore in the presence of these positive allosteric modulators only about 1/3 of the concentration of succinate is required to elicit the same response in their absence. Furthermore, the modulators also increase the efficacy of succinate more than two-fold. Concentration dependent data with respect to vinaxanthone (**1**) also demonstrates the ability of the compound to continually and effectively act as a positive allosteric modulator at concentrations as low as 1 nM (Figure 1.10).

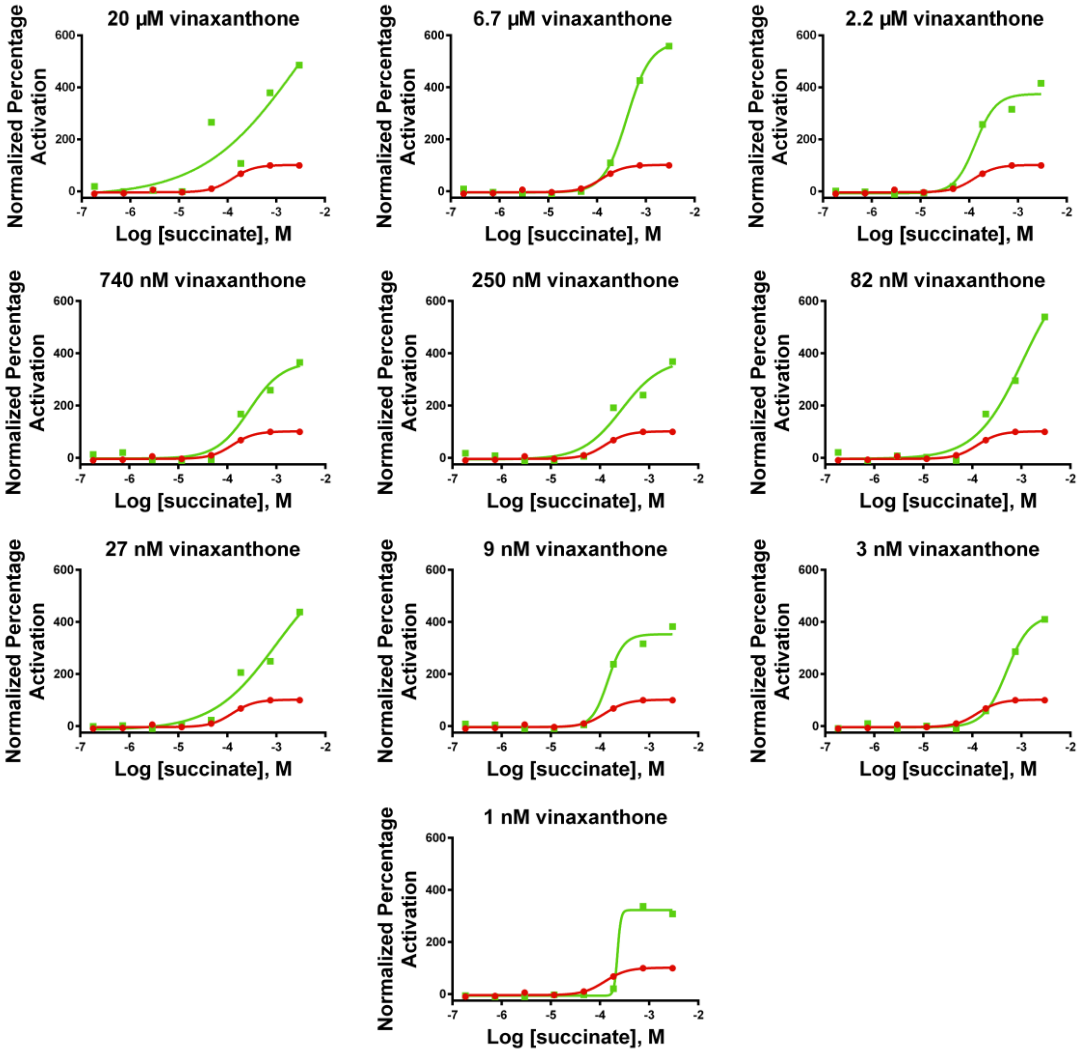


Figure 1.10. Concentration dependent efficacy of vinaxanthone (**1**) (green) versus the lone reference agonist, sodium succinate (red) in activating GPR91.

Succinate accumulates under hypoxic conditions and functions through GPR91 to promote vessel growth. Following increased succinate levels, GPR91 leads to the production of numerous angiogenic factors, notably vascular endothelial growth factor (VEGF).[115,116] GPR91 indirectly opposes the action of Sema3A by stimulating increased vascular proliferation and angiogenesis.[117,118] By identifying vinaxanthone (**1**) and xanthofulvin (**2**) as positive allosteric modulators of GPR91 a mode of action has been discovered that accounts for the observed regenerative effects in the absence of Sema3A. The fact that allosteric ligands have already advanced to market, with many others in clinical trials and late preclinical development lends credence to the sound and tractable advantage of targeting allosteric modulators.[113]

Having identified a viable mode of action for the regenerative properties of vinaxanthone (**1**) and xanthofulvin (**2**), efforts were concentrated on the further elucidation of their biological profiles. Initial *in vivo* neuronal outgrowth assays in *C. elegans* revealed that vinaxanthone (**1**) and xanthofulvin (**2**) enhanced neuronal outgrowth by 31% and 32% at 2 μM, respectively (Figure 1.11).[92] Comparable activity was demonstrated for the known neurotrophic compound dibutyryl cAMP, which promoted branching in 36% of animals at 2 μM.[119] Encouraged by these results, plans were devised to study neuronal regeneration upon transected neurons in *C. elegans*. The synthesis of analogs for structure activity relationship (SAR) studies and the eventual biological optimization was also a priority.

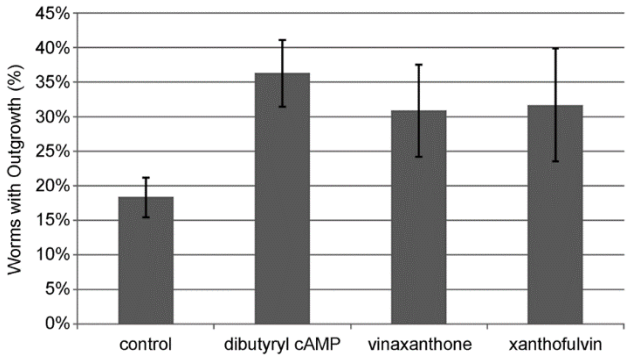


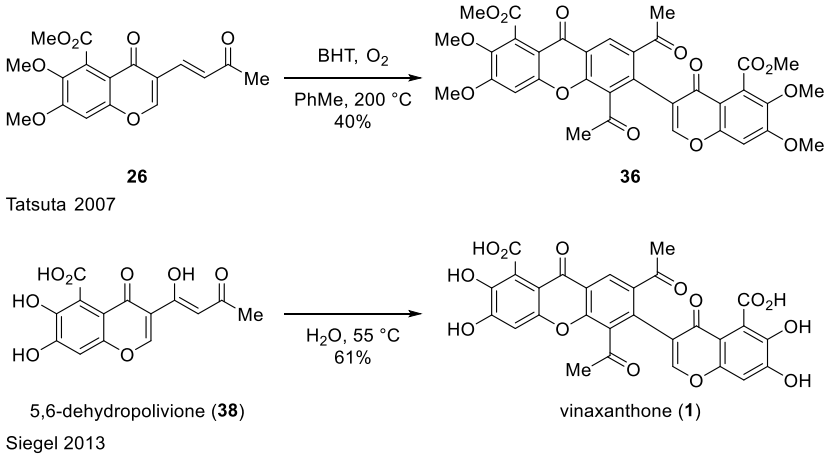
Figure 1.11. Outgrowth of GFP-labelled cholinergic neurons *in vivo* in *C. elegans* after treatment with dibutyryl cAMP, vinaxanthone (**1**), and xanthofulvin (**2**). Control: 0.2% DMSO in M9 buffer.

While performing neuronal outgrowth assays it became evident that there was a disparity between vinaxanthone (**1**) and xanthofulvin (**2**) in respect to their stability. As evidenced by ^{1}H-NMR analysis xanthofulvin (**2**) showed significant decomposition when exposed to air as a solution in d_6-DMSO. Vinaxanthone (**1**) on the other hand revealed no discernable decomposition following a six month period under similar conditions. Furthermore, vinaxanthone (**1**) exhibited the same stability when subjected to 60 °C heat in d_6-DMSO for two weeks. Vinaxanthone (**1**) appeared to be the superior molecule to proceed with biological testing due to its thermal and oxidative stability.

At this point the polypharmacology of vinaxanthone (**1**) was investigated for the purpose of SAR studies and biological optimization. The goal was to synthesize analogs of vinaxanthone that differed from the parent natural product by the omission of various carboxyl and hydroxyl functionality. In the previous two syntheses of vinaxanthone (**1**) a homodimerization of some sort was utilized to forge the vinaxanthone core.[63,92] These methods would be applicable in the synthesis of vinaxanthone analogs that contained symmetrical functionality on both the xanthone and chromone cores of the molecule. However, if two different monomers were combined under either condition a statistical

mixture of products would be expected. These dimerizations lack electronic or steric information that could differentiate the two fragments and select for their positioning.

In Tatsuta's case, the unsaturated ketone monomer **26** possesses dual reactivity as either a diene or dienophile and in our initial report the putative 5,6-dehydropolivione (**38**) precursor may function as both a Michael acceptor and Michael donor (Scheme 1.29).[63,92] The inability to efficiently produce edited analogs with distinct xanthone and chromone cores would significantly hinder the procurement of 56 of the 64 possible serially deleted analogs (Figure 1.12).



Scheme 1.29. Previous approaches to the vinaxanthone core.

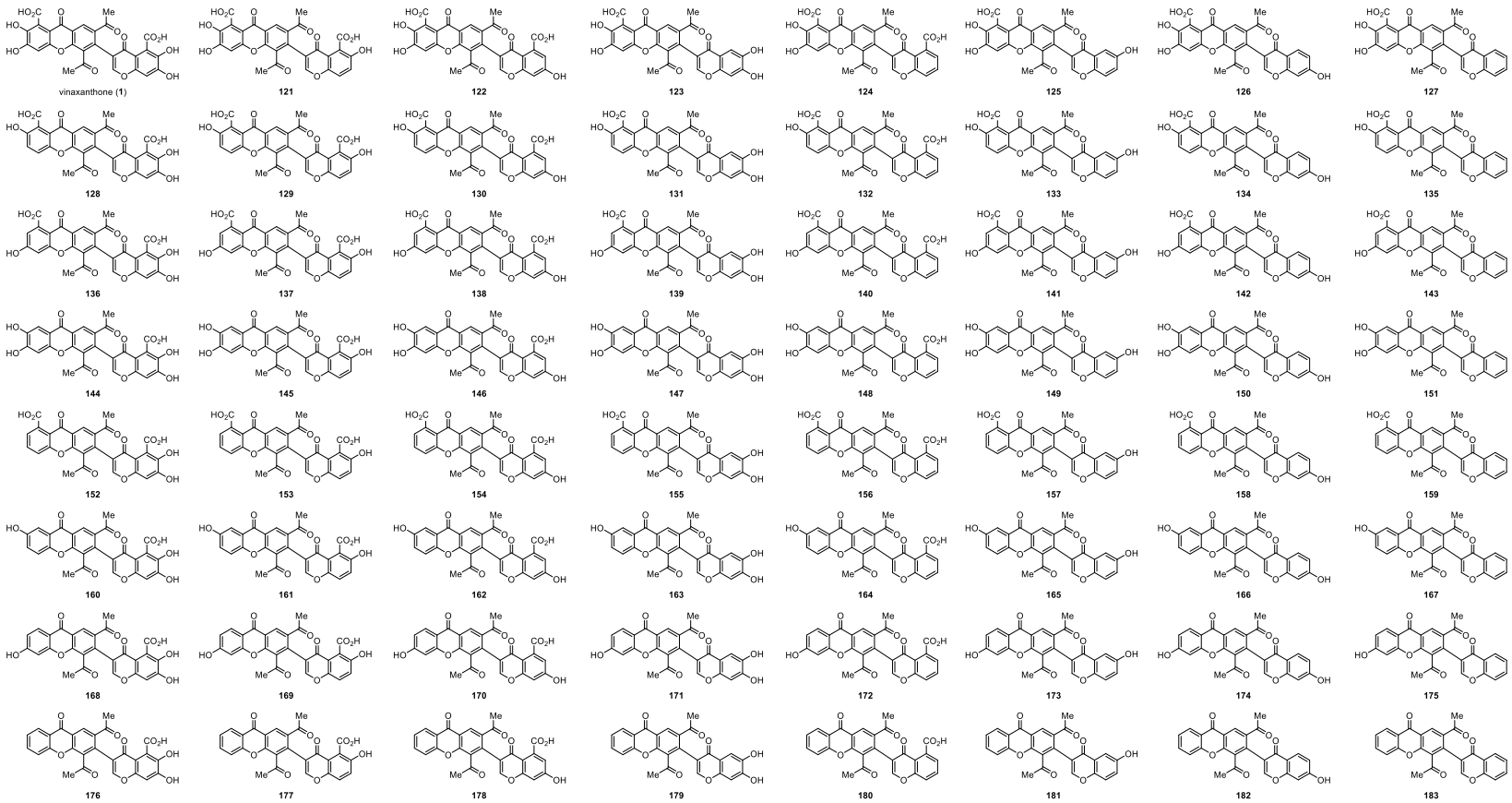
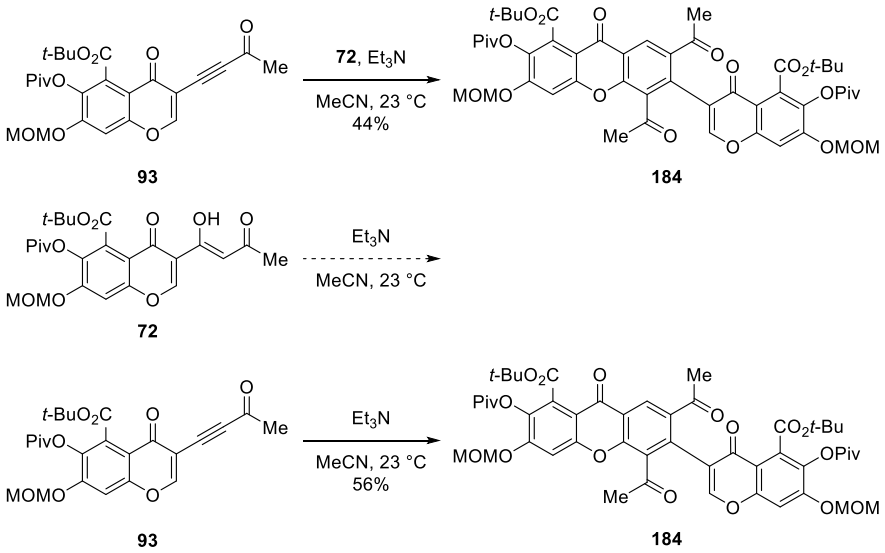


Figure 1.12. 64 vinaxanthone derivatives containing serially deleted carboxyl and hydroxyl functionality.

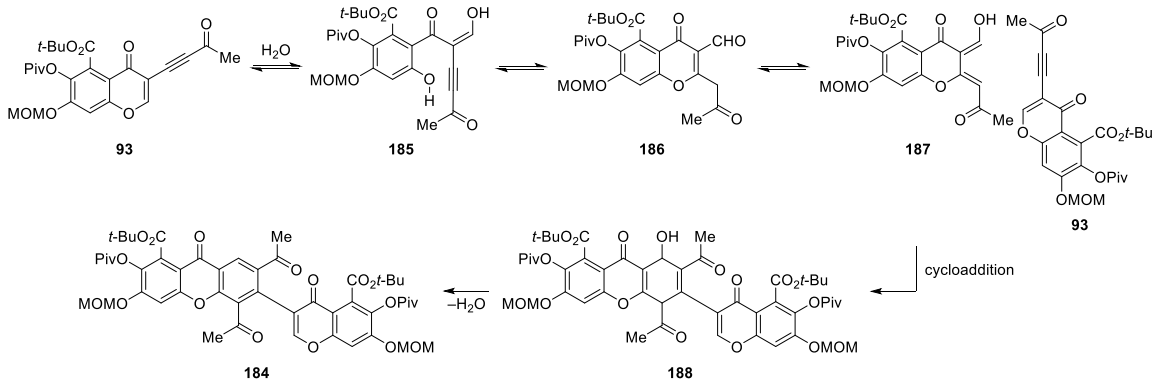
Serendipitously a solution to this challenge presented itself upon analysis of earlier investigations into the use of ynone **93** as a surrogate for protected 5,6-dehydropolivione **72** (Scheme 1.30). When combined in a one-to-one ratio in acetonitrile with triethylamine at ambient temperature ynone **93** and protected 5,6-dehydropolivione **72** furnished protected vinaxanthone **184**. Previous experiments revealed that under these reaction conditions protected 5,6-dehydropolivione **72** could not produce the desired compound on its own. Therefore the control experiment in which ynone **93** was treated with triethylamine in acetonitrile by itself was conducted. Surprisingly, protected vinaxanthone **184** was generated and it was discovered that ynone **93** could generate the xanthone core of the natural product on its own. Further control experiments revealed that triethylamine was necessary and that when ran under scrupulously anhydrous conditions neither product nor conversion of starting material in any fashion was observed.



Scheme 1.30. Synthesis of protected vinaxanthone **184**.

With the knowledge that both water and base were required for this transformation and the fact that a small impurity in the ^{1}H-NMR of the crude reaction

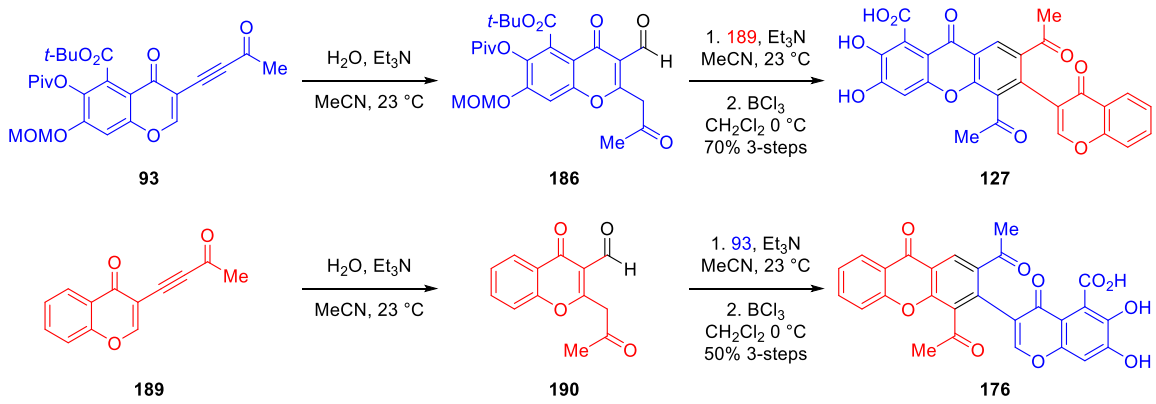
mixture of the ynone dimerization revealed an aldehydic species the following mechanism was proposed (Scheme 1.31). Water can add in a conjugate fashion to the chromone of ynone **93** resulting in the expulsion of free phenol **185**. Michael addition of the free phenol into the alkynone would generate 3-formyl chromone **186**. Upon tautomerization diene **187** would be geared for a cycloaddition with the alkyne of another molecule of ynone **93** to afford the core of the natural product **188**. Finally, elimination of water would forge the central aromatic ring of protected vinaxanthone **184**.



Scheme 1.31. Proposed ynone dimerization mechanism.

In hopes of discerning more information about the ynone dimerization ynone **93** was treated with a large excess of water in the presence of triethylamine (Scheme 1.32). Gratifyingly, aldehyde **186** was isolated in near quantitative yield further supporting our proposed mechanism. More importantly was the realization that starting from a single ynone precursor a simple transformation was available in which we could potentially control which starting ynone would reside as the xanthone and chromone portions of the vinaxanthone scaffold in a coupling reaction. To this end ynone **93** was transformed into aldehyde **186** prior to the addition of ynone **189** (prepared in 4-steps). Consequently, our hypothesis held true and upon deprotection vinaxanthone analog **127** was synthesized in a

terrific 70% overall yield starting from ynone **93**. To our delight transforming ynone **189** into aldehyde **190** prior to the addition of ynone **93** had the analogous affect providing vinaxanthone analog **176** in 50% overall yield.



Scheme 1.32. Synthesis of non-symmetric vinaxanthone analogs.

With this new strategy for the facile synthesis of vinaxanthone derivatives in which *n* ynones allows access to n^2 derivatives we sought to begin our preparation of a small chemical library. We envisioned that the serial deletion of the carboxyl and hydroxyl functional groups of vinaxanthone (**1**) would provide key information regarding the natural product's active pharmacophore. Consequently, 64 possible vinaxanthone analogs exist of which can be accessed through the synthesis of only eight ynone precursors (Figure 1.13).

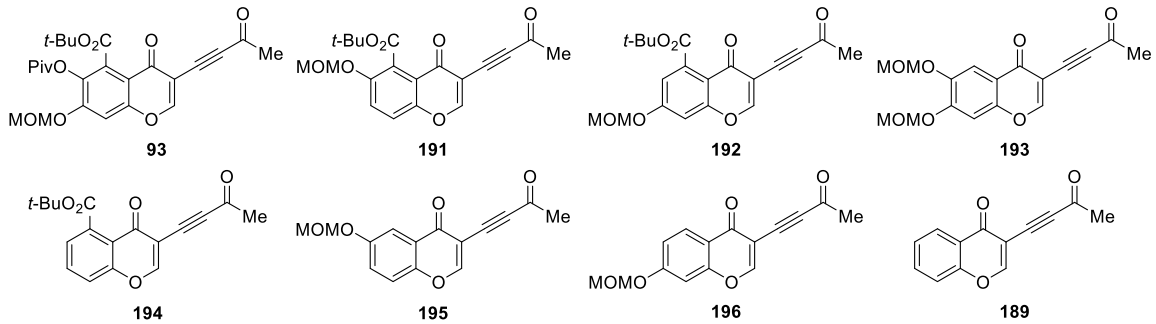
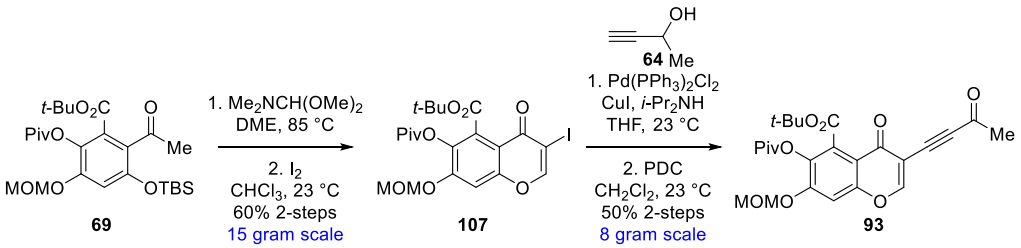


Figure 1.13. Ynone precursors.

Thus far five ynone precursors were synthesized in order to provide a 25 vinaxanthone analog library for biological evaluation. Ynone **93** from the parent natural product synthesis was accompanied by four others exhibiting deletion of various acidic functionalities. The carboxylic acid moiety was removed from ynone **193**. Similarly the carboxyl and a single hydroxyl group were deleted to afford ynones **195** and **196**. Lastly, ynone **189** was constructed without acidic functionality to provide the most basic precursor scaffold. The syntheses of ynones **193**, **195**, **196**, and **189** were quite straightforward and paralleled that of ynone **93**.

The synthesis of ynone **93** demonstrated that a 2'-hydroxyacetophenone could be transformed into its corresponding 3-ynone chromone via a robust 4-step sequence (Scheme 1.33). Use of Gammill's two-step preparation of iodochromones followed by Sonogashira cross-coupling with 3-butyn-2-ol **64** and subsequent pyridinium dichromate oxidation can furnish the desired ynone.[89,98,99] Therefore if various 2'-hydroxyacetophenones can be accessed the ability to acquire the corresponding ynone precursors should follow.

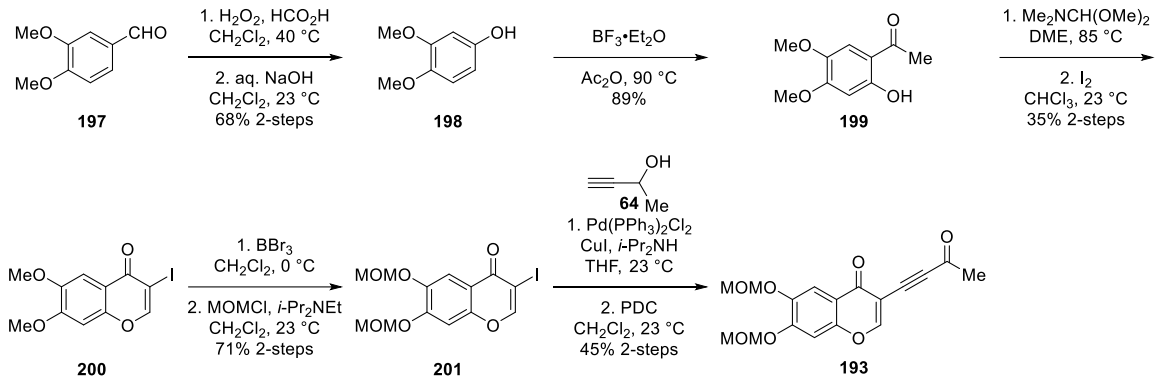


Scheme 1.33. Synthesis of ynone **93**.

Ynone **193** was synthesized starting from readily available 3,4-dimethoxybenzaldehyde **197** (Scheme 1.34). Hydrogen peroxide mediated Baeyer-Villiger oxidation followed by hydrolysis of the resulting formate otherwise known as the Dakin reaction generated the corresponding phenol **198**.[65] Subsequent Fries

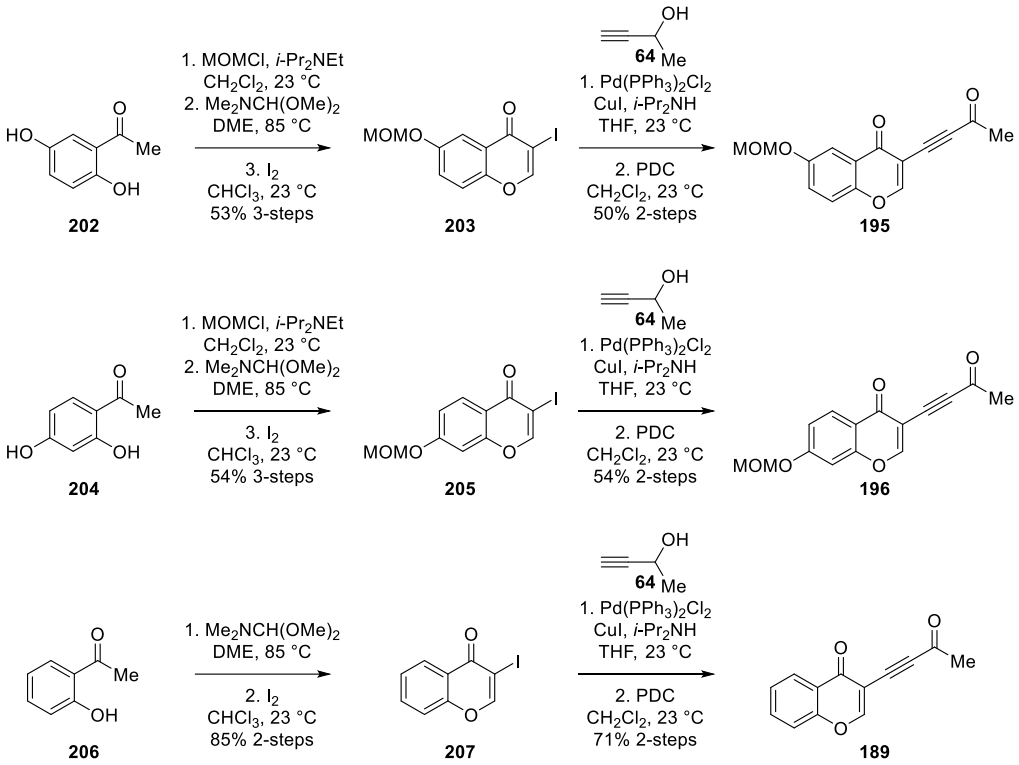
rearrangement promoted by boron trifluoride diethyl etherate at 90 °C in neat acetic anhydride provided pure dimethoxyacetophenone **199** as white needles following recrystallization from hot ethanol.[120] Recrystallization of this intermediate was crucial for the success of iodochromone formation. Although crude dimethoxyacetophenone **199** could undergo enaminone formation, the formation of iodochromone was inoperable. Presumably, lingering boron species coordinate to the molecule and shut down its ability to cyclize. Recrystallized dimethoxyacetophenone **199** was then treated with N'N'-dimethylformamide dimethyl acetal followed by molecular iodine to afford dimethoxyiodochromone 2**00**.[89]

At this point the methoxy groups were transposed with methoxymethyl ether protecting groups. Dimethoxyiodochromone **200** was treated with boron tribromide prior to its protection with Hunig's base and methoxymethyl chloride to provide dimethoxymethyl ether iodochromone **201**.[88,90] It is important to note that the methoxy variant proceeds through the intended sequence to give the appropriate vinaxanthone analogs, however after extensive investigations a clean deprotection procedure to reveal the free phenols was never realized in any appreciable yield or purity. Interestingly, early introduction of the methoxymethyl ethers lead to failure of the Fries rearrangement and attempts to swap out the protecting groups in the presence of a free phenol were fraught with solubility problems. With dimethoxymethyl iodochromone **201** in hand the Sonogashira cross-coupling with 3-butyn-2-ol **64** and subsequent oxidation with pyridinium dichromate generated ynone **193** as a white solid.[97,98] Once again it was imperative to use freshly freeze-pump thawed tetrahydrofuran devoid of oxygen to obtain good yields.



Scheme 1.34. Synthesis of ynone **193**.

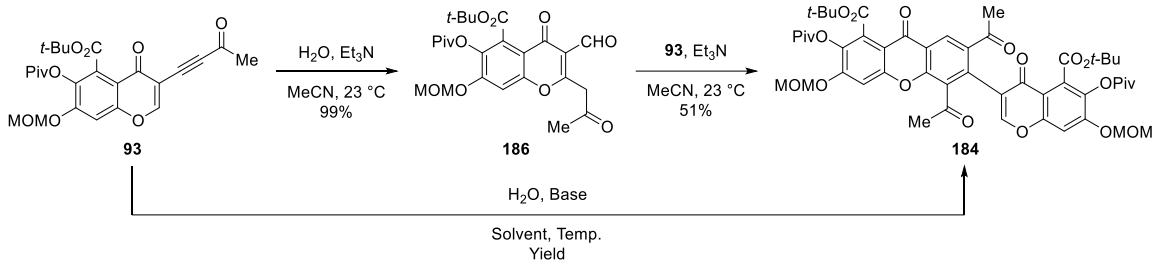
Commercially available 2',5'-dihydroxyacetophenone **202**, 2',4'-dihydroxyacetophenone **204**, and 2'-hydroxyacetophenone **205** provided easy entry into the syntheses of ynones **195**, **196**, and **189** respectively (Scheme 1.35). For both of the dihydroxyacetophenone starting materials the appropriate auxiliary hydroxyl group was initially protected as its methoxymethyl ether.[88] These reactions were straightforward and there was no evidence of methoxymethylation at the undesired hydroxyl sites. It makes sense that the hydroxyl group adjacent to the acetyl group is less reactive because it is involved in a hydrogen bond with the carbonyl, which is evident in the downfield ^{1}H-NMR shift of the hydroxyl hydrogen. Following our reliable 4-step sequence toward ynones, precursors **195**, **196**, and **189** were obtained as white solids in good yields. Interestingly, the Sonogashira reaction for these three substrates did not require thoroughly deoxygenated solvent, as tetrahydrofuran acquired directly from the solvent purifier was sufficient to provide excellent yields.



Scheme 1.35. Syntheses of ynones **195**, **196**, and **189**.

With significant quantities of five unique ynones containing functional group subsets of the parent natural product 25 vinaxanthone analogs were synthesized. Since five of the 25 derivatives contain symmetric functionality on both the xanthone and chromone core the dimerization could be performed in a single operation. Treatment of an acetonitrile solution of the intended ynone with stoichiometric water and triethylamine at 23 °C provided the five symmetric vinaxanthone analogs in protected form. Further investigations pertaining to the number of equivalents of water used in this reaction lead to the optimization of the ynone **93** dimerization to protected vinaxanthone **184** (Figure 1.14). It was discovered that the implementation of 0.5 equivalents of water proceeds to give a satisfying 87% yield. Furthermore, this efficient transformation lead to the preparation of over a gram of vinaxanthone (**1**) in a single synthetic sequence. Presumably, the use of greater amounts of water would promote the formation of

aldehyde **186** at a rate faster than the dimerization could occur thus leading to a mismatch in coupling partners and diminishing yields. On the other hand, even though the reaction proceeds with catalytic amounts of water the reaction may be too slow to reach an optimal yield.



Entry	H_2O	Base	Solvent	Temperature (°C)	Time (hrs)	% Yield
1	Bench Top MeCN	N/A	MeCN	23	16	0%
2	Bench Top MeCN	Et_3N	MeCN	23	16	56%
3	0 eq.	Et_3N	MeCN	23	16	0%
4	0.1 eq.	Et_3N	MeCN	23	16	65%
5	0.5 eq.	Et_3N	MeCN	23	16	87%
6	1.0 eq.	Et_3N	MeCN	23	16	67%
7	2.0 eq.	Et_3N	MeCN	23	16	59%

Figure 1.14. Optimization of ynone **93** dimerization to protected vinaxanthone **184**.

Moving forward the remaining analogs were synthesized utilizing our proposed coupling strategy (Figure 1.15).[121] The ynone intended to represent the xanthone core was treated with triethylamine in the presence of excess water to promote full conversion to the desired 3-formyl chromone. The aldehyde was then subjected to the desired ynone intended to represent the chromone core with additional triethylamine. The 25 protected

vinaxanthone analogs were alas generated in yields spanning 21% to 87% with a majority of reactions providing modest yields in the vicinity of 50%. Despite several low yields practically all reactions retained very good mass balance. In a majority of reactions both of the ynone homodimers were co-isolated (see supporting information for isolated yields). Therefore bonus material was obtained for subsequent deprotections and biological testing. It is noteworthy that the undesired heterodimer was never present within the reaction mixture. Although a general procedure has been developed to efficiently synthesize various vinaxanthone analogs significant optimization would be needed to acquire superior yields for each individual analog. The disparity between reaction yields was hypothesized to be due to the solubility differences amongst the different ynones, intermediates, and vinaxanthone derivatives.

Final liberation of oxygen bearing functionalities of protecting groups was done in one of two ways. Simple treatment of a given protected vinaxanthone analog with boron trichloride in methylene chloride rapidly removed all protecting groups.[91] The only downside to this procedure was the need to remove boron impurities. This was accomplished by trituration with mixtures of methanol and pentane. Alternatively, a protected vinaxanthone analog could be taken up in methanol and treated with dry hydrochloric acid. This solution was heated to 65 °C and upon complete conversion (monitored by aliquot ^{1}H-NMR) the reaction mixture was purged with nitrogen gas to remove gaseous HCl and concentrated to reveal pure vinaxanthone analogs. This method unfortunately was unsuccessful on analogs bearing carboxylic acids because under these conditions transesterification to the methyl ester was prominent. With the preparation of our small library of 25 vinaxanthone analogs we were equipped with adequate material to study their regenerative capabilities within an animal model.

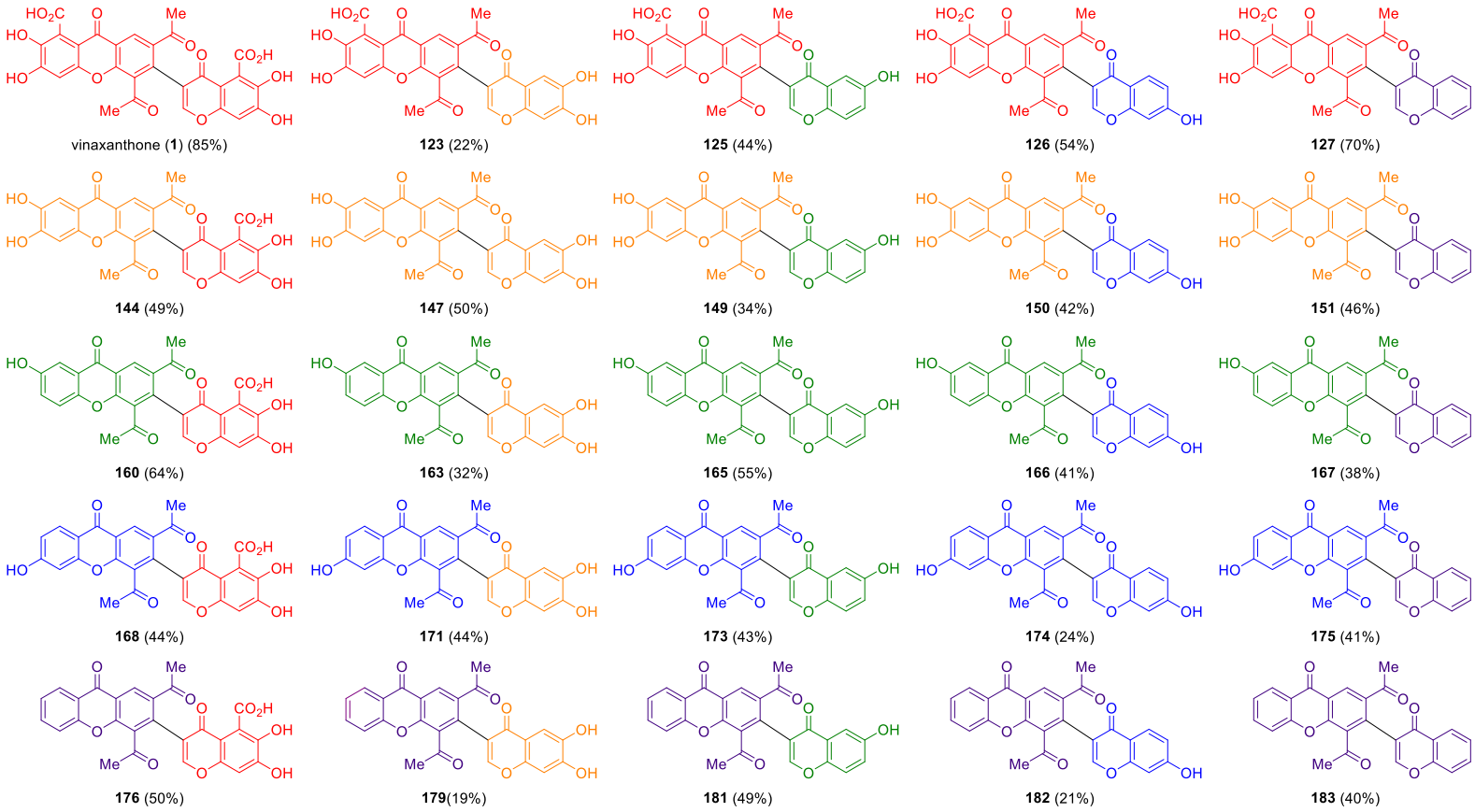


Figure 1.15. Vinaxanthone analogs (Yields represent total transformation from ynone precursors). Colors are provided for SAR comparison

The nematode *Caenorhabditis elegans* (*C. elegans*) has emerged as an ideal animal model for the investigation of regenerative responses in the context of medicinal chemistry. Application of the *C. elegans* axotomy model can generate single compound results within hours and entire library screens within days compared to the substantial time required to produce such results using murine models. It is important to point out that the worm has played significant roles in the discovery of various human health related biological processes including apoptosis[122] and RNAi.[123-125] Its manageable size, well-documented neurobiology, and translucent nature allow monitoring of neurons in living organisms via fluorescent labeling and therefore make the worm very useful for chemical-neurobiological investigations. The striking similarity of numerous genes related to neuronal survival and axonal regeneration between vertebrates and *C. elegans* lends further credence to its use as a biologically relevant model organism.[126] In addition, the utilization of *C. elegans* in high throughput organism-based screens has already proven effective in the identification of small molecules with phenotypic effects.[127,128]

Axonal injury can be induced in *C. elegans* using highly precise laser microsurgery to severe individual green fluorescent protein (GFP) labeled axons in live animals.[128] Following the surgical transection, neuronal survival and growth are monitored. Numerous genetic determinants of neuronal regeneration have been identified in large part due to laser axotomy in *C. elegans*.[130-132] Despite the fact that a majority of axonal regeneration studies in *C. elegans* have primarily focused on native promoters and suppressors, the worm offers a unique opportunity for small molecule development. The development of high throughput screens to identify compounds that can promote regeneration following laser axotomy have already been implemented to this end.[133]

Laser axotomy was utilized to transect the posterior lateral microtubule (PLM) cells of *C. elegans*. The PLM cells consist of two mechanosensory neurons that are responsible for the worm's reaction to light posterior touch. They are located in the tail and extend longitudinally toward the midbody with one along each side of the worm. Moreover, each of these neurons builds an individual synaptic branch with the ventral nerve cord.[134,135] Due to their relatively large

size and distinct axonal morphology the mechanosensory neurons have been used extensively for laser axotomy experiments.[136] Neurodegenerative diseases in humans have also been studied using mechanosensory neurons, establishing a relevant connection to the worm model.[137,138]

The synaptic branch of mechanosensory neurons has been implicated as a juncture in innate regenerative ability where PLM neurons only regrow when severed proximal to the synaptic branch and not when severed distally.[138] Severing the axon beyond the branch point and limiting the intrinsic regrowth following injury established a standard location to initiate our microsurgeries. Furthermore, a model encompassing an inhibitory branching environment may parallel the collateral branches of spinal cord neurons that have been noted to influence growth potential.[139,140]

Laser axotomy was performed to sever a point approximately 15 μm distal to the synaptic branch point on the PLM of late L4-stage *C. elegans* (zdls5) (Figure 1.16A). There was a slight variance between worms in respect to the distance of the synaptic branch point from the cell body. It is noteworthy that regeneration was less likely to occur as the distance between the injury and cell body increased.[138] Nematodes possessing a synaptic branch with a maximum distance of 100 μm between the cell body and the branch point were selected as having the desired PLM morphology. This provided a standardized location of axotomy to conduct experiments employing the vinaxanthone analog library.

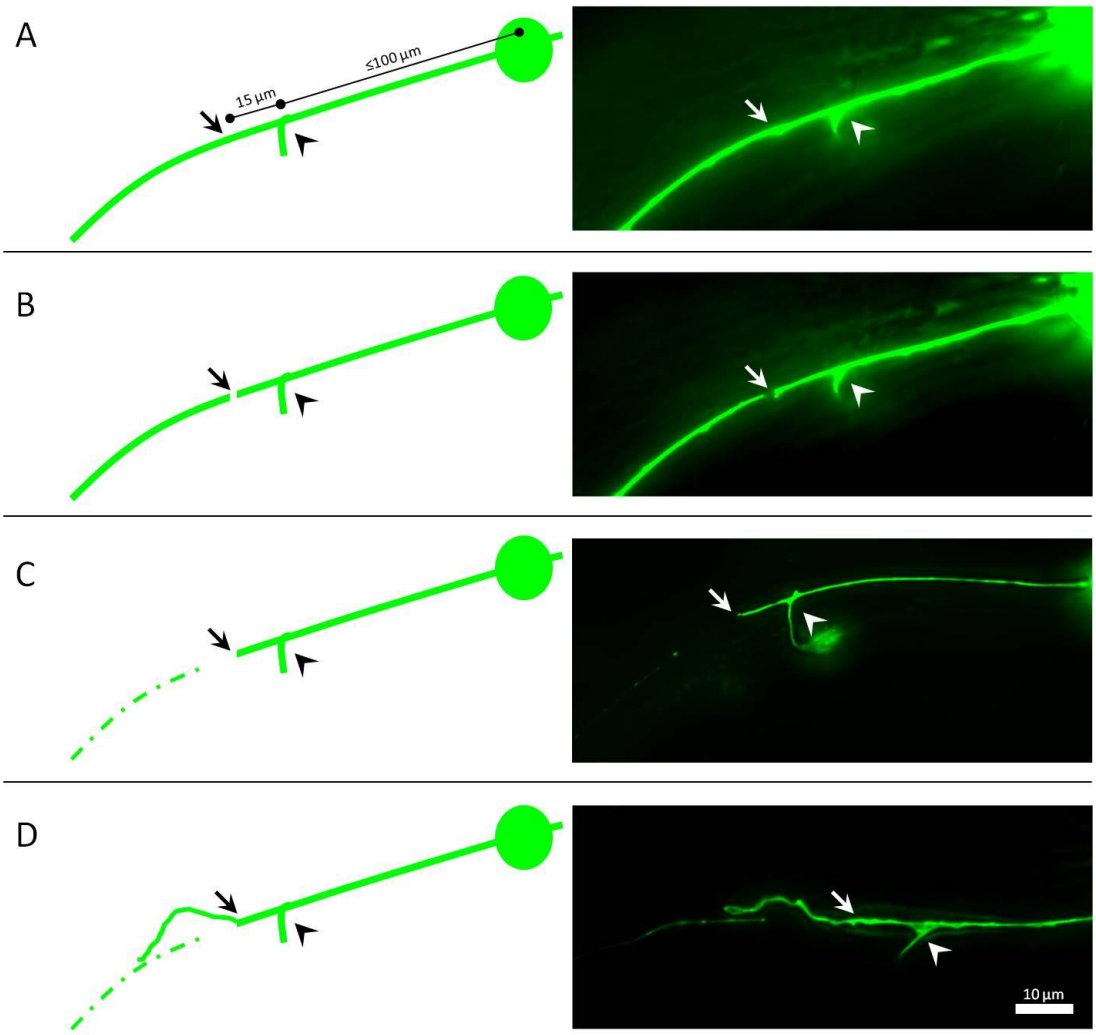


Figure 1.16. Representative images of *in vivo* laser axotomy.
A) Laser axotomy is performed on the PLM about 15 µm distal to the synaptic branch point when the branch is ≤ 100 µm from the cell body. B) The injured neuron immediately following axotomy. C) No regrowth from the severed proximal axon of control worms at 24 hours post-axotomy. The distal fragment has begun to degenerate as seen by the faint, beaded appearance. D) Regrowth of the severed proximal axon at 24 hours post-axotomy. Arrows indicate the site of axotomy and arrowheads indicate the synaptic branch.

Following axotomy a characteristic series of events begins to unfold. As the laser ruptures the neuron plasma formation and the generation of cavitation bubbles at the injury site lead to a small break in the axon (Figure 1.16B).[141] Within a few hours the ends of the severed axon retract, resulting in an increased distance between the fragments. A stump begins to from as the distal fragment begins to degenerate and the proximal axon no longer exhibits regrowth (Figure 1.16C). The beading and disappearance of GFP associated with distal fragment

degeneration is well documented and is comparable to Wallerian degeneration.[142] In the event that a regenerative process is initiated, a growth cone forms on the proximal fragment and the axon will begin to extend as it regrows (Figure 1.16D). The regrowing axon occasionally finds its distal fragment leading to a fusion that consequently prevents distal degeneration.[143]

A small number of control worms (27%) displayed the ability to regrow after their axon was severed distal to the synaptic branch. Interestingly, the potential for regrowth was enhanced in worms treated with vinaxanthone (**1**) (Figure 1.17). Laser surgery was performed and nematodes were exposed to an analog from the vinaxanthone library. Regeneration of the severed proximal axon was quantified by measuring the distance between the start of the new growth at the axonal injury site to the end of the longest regrowing process 24 hours following axotomy. The regrowing processes exhibited a wide variety of morphologies. Some extended in a virtually linear fashion across the injury site while others displayed arching around the axotomy scar. Branching in search of axon distal fragments was also noted with some growths reaching the ventral cord on occasion. A positive regrowth event was characterized by the regrowth and reconnection to the distal portion. However, if growth was not observed from the proximal portion of the cut axon it was labeled as negative for regrowth.

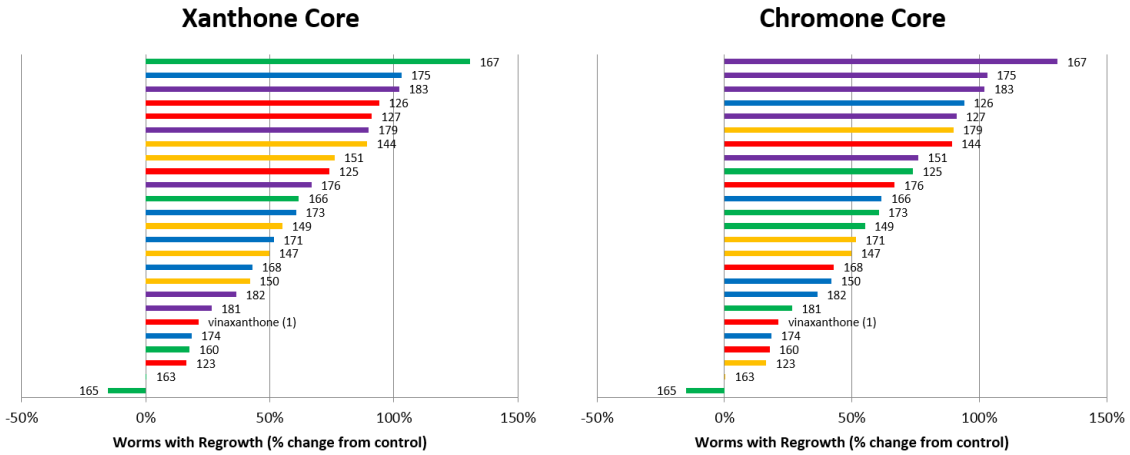


Figure 1.17. Worms exposed to vinaxanthone analogs exhibiting varying levels of neuronal regrowth, represented as a percent change relative to controls. Colors are provided for SAR comparisons.

When exposed to the vinaxanthone analogs worms displayed varying degrees of regeneration in respect to the number of worms exhibiting regrowth relative to controls as well as the lengths of the regrown neurons.[121] Analog **167** which has a monohydroxylated xanthone core and a bare chromone core had the highest rate of regrowth, with a 130% increase from controls in the number of worms displaying regrowth morphologies (Figure 1.18). The parent compound vinaxanthone (**1**) comparatively only showed a 21% increase in regrowth rate. Interestingly, exposure to analog **163** resulted in virtually no change in regrowth potential and analog **165** even showed a 15% decrease in regrowth rate. A cursory examination of the SAR data reveals a striking correlation amongst the analogs (**167**, **175**, **183**, **126**, and **127**) exhibiting high levels of regrowth (over 75% increase). Four of the five compounds possess the same abridged structure for their chromone core.

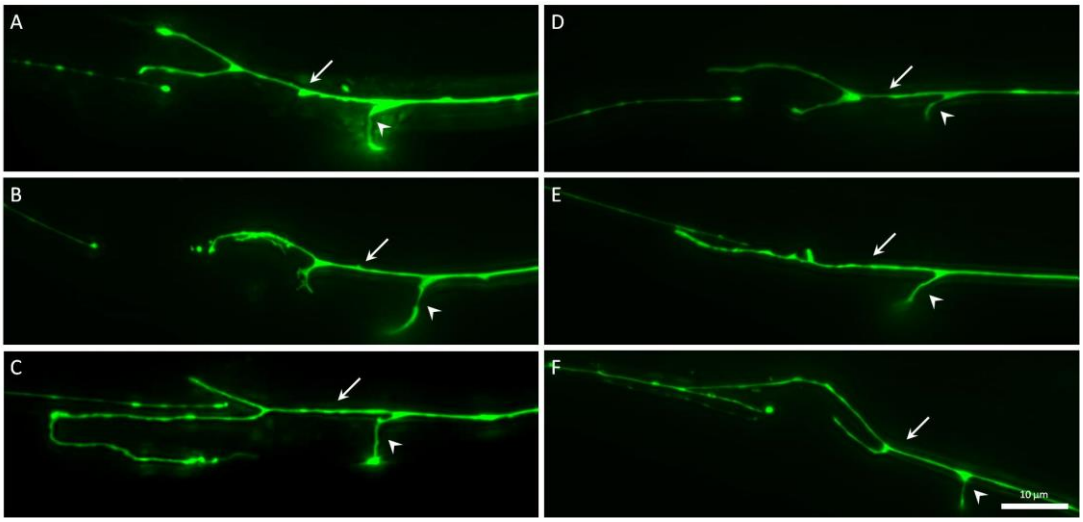


Figure 1.18. Regrowth of PLM neurons 24 hours after laser axotomy.
A) Branching regrowth following treatment with 2 µM vinaxanthone (**1**). B) Arching regrowth following treatment with 2 µM analog **167**. C) Regrowth with branching to the ventral nerve cord. D) Branching regrowth following treatment with 2 µM analog **167**. E) Linear regrowth following treatment with 2 µM analog **167**. F) Regrowth with reconnection to the distal fragment. Arrows indicate the beginning of regrowth and arrowheads indicate the synaptic branch.

In the interest of investigating neuroregenerative natural products the concise total syntheses of vinaxanthone (**1**) and xanthofulvin (**2**) were accomplished.[92] Subsequently, both

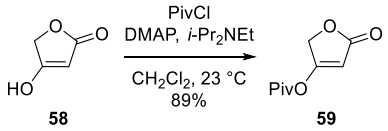
compounds were discovered to act as strong positive allosteric modulators of the G-protein-coupled receptor GPR91. This effectively provided a mode of action for the regenerative abilities observed within animal models associated with these natural products. A new ynone coupling reaction was also developed to provide a rapid method for the exponential syntheses of chemically edited analogs of vinaxanthone (**1**). Utilization of this method resulted in a 25 compound library of vinaxanthone analogs that demonstrated regrowth-inducing potentials in laser axotomy experiments in *C. elegans*.[121] Based on structure activity relationship analysis that followed it was determined that the functional group free chromone core is an important chromophore for *in vivo* regrowth. Future directions of this work will entail the use of the ynone coupling reaction to prepare additional analogs of vinaxanthone (**1**) and subsequent additional optimization using *C. elegans* to transition regenerative compounds into higher organisms.

EXPERIMENTAL SECTION

General Information

All reactions were performed in flame dried round bottom or modified Schlenk (Kjedahl shape) flasks fitted with rubber septa under a positive pressure of argon or nitrogen, unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred via syringe or cannula. Organic solutions were concentrated by rotary evaporation at 20 torr in a water bath heated to 40 °C unless otherwise noted. Diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF) and toluene (PhMe) were purified using a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Acetonitrile (MeCN) was purified using a Vac 103991 Solvent Purification System (Vacuum Atmospheres). Dimethoxyethane (DME) was purchased from Acros (99+%, stabilized with BHT), N,N,-Dimethylformamide (DMF) was purchased from Acros (99.8%, anhydrous), ethanol (EtOH) was purchased from Pharmco-Aaper (200 proof, absolute), and methanol (MeOH) was purchased from Sigma-Aldrich (99.8%, anhydrous). Where necessary, solvents were deoxygenated by iterative freeze-pump thaw using liquid nitrogen three times. The molarity of *n*-butyllithium was determined by titration against diphenylacetic acid. All other reagents were used directly from the supplier without further purification unless otherwise noted. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical) and visualized using a UV lamp and/or aqueous ceric ammonium molybdate (CAM) or aqueous potassium permanganate (KMnO4) stain, or ethanolic vanillin. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film or KBr pellet technique. High-resolution mass spectra (HRMS) were recorded on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, [M] or $[M–H]^–$. Nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) were recorded with a Varian Gemini [(400 MHz, ^{1}H at 400 MHz, ^{13}C at 100 MHz), (500 MHz, ^{1}H at 500 MHz, ^{13}C at 125 MHz), (600 MHz, ^{1}H at 600 MHz, ^{13}C at 150 MHz)]. For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvent; $CHCl_3$ δ H (7.26 ppm) and

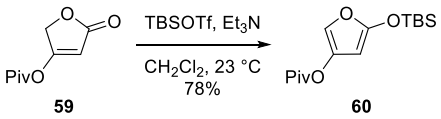
$CDCl_3$ δ D (77.0 ppm). For $(CD_3)_2SO$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $(CD_3)(CHD_2)SO$ δ H (2.50 ppm) or $(CD_3)_2SO$ δ C (39.5 ppm). For $(CD_3)_2CO$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $(CD_3)(CHD_2)CO$ δ H (2.50 ppm) or $(CD_3)_2CO$ δ C (29.8 ppm). For C_6D_6 solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; C_6HD_5 δ H (7.16 ppm) or C_6D_6 δ C (128 ppm). For CD_3OD solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; CHD_2OD δ H (3.31 ppm) or CD_3OD δ C (49.0 ppm). For CD_2Cl_2 solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHDCl_2$ δ H (5.32 ppm) or CD_2Cl_2 δ C (53.5 ppm). Coupling constants are reported in Hertz (Hz). Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q= quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, ddq = doublet of doublet of quartets, bs = broad singlet, bd = broad doublet, m = multiplet, coupling constant (Hz), and integration). Melting points were measured on a MEL-TEMP device without corrections.



5-oxo-2,5-dihydrofuran-3yl pivalate (**59**)

To a stirred solution of tetronic acid **58** (25.0 g, 250 mmol, 1.0 equiv.), 4-dimethylaminopyridine (1.53 g, 12.5 mmol, 0.05 equiv.) and N,N-diisopropylethylamine (45.8 mL, 262 mmol, 1.05 equiv.) in CH_2Cl_2 (500 mL, 0.5 M) at 0 °C was added neat pivaloyl chloride (25.9 mL, 262 mmol, 1.05 equiv.) dropwise over 40 minutes. Upon complete addition the reaction mixture was allowed to warm to 23 °C. After 16 hours, the reaction mixture was concentrated *in vacuo* to give an amber oil. The oil was dissolved in Et_2O (500 mL) and washed with H_2O (500 mL). The aqueous layer was extracted with Et_2O (5 x 500 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to give tetronate **59** (41.0 g, 223 mmol, 89%) as clear amber crystals (m.p. 46-47 °C).

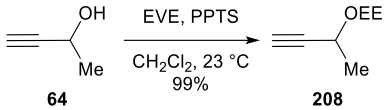
$\mathbf{R}_f$ = 0.60 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.00 (t, J = 1.4 Hz, 1H), 4.91 (d, J = 1.4 Hz, 2H), 1.32 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 173.2, 172.2, 169.1, 100.2, 68.2, 38.3, 26.4; **IR** (film, cm^{-1}): 1779, 1746, 1072.



5-((*tert*-butyldimethylsilyl)oxy)furan-3-yl pivalate (60)

To a stirred solution of tetronate **59** (30.0 g, 163 mmol, 1.0 equiv.) and triethylamine (29.8 mL, 212 mmol, 1.3 equiv.) in CH_2Cl_2 (230 mL, 0.72 M) at 0 °C was added neat *tert*-butyldimethylsilyl triflate (37.8 mL, 165 mmol, 1.01 equiv.) dropwise over 10 minutes. Upon complete addition the reaction mixture was allowed to warm to 23 °C. After 1 hour, the reaction mixture was concentrated *in vacuo* to give an amber oil. The oil was suspended in pentane (200 mL) and stirred for 1 hour at 23 °C. The organic layer was decanted and washed with sat. aq. $NaHCO_3$ (3 x 100 mL), H_2O (100 mL), and brine (100 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give furan **60** (37.9 g, 127 mmol, 78%) as an amber oil.

$\mathbf{R_f}$ = 0.55 (silica gel, 20:1 hexanes:EtOAc); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 7.10 (d, *J* = 1.2 Hz, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 1.29 (s, 9H), 0.96 (s, 9H), 0.24 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.3, 154.3, 139.4, 120.6, 80.1, 39.0, 27.1, 25.4, 18.0, -4.85; **IR** (film, cm^{-1}): 3202, 3141, 1753, 1627; **HRMS** (ESI) calc. for $C_{15}H_{27}O_4Si$ $[M+H]^+$: 299.20000, obs. 299.20000.

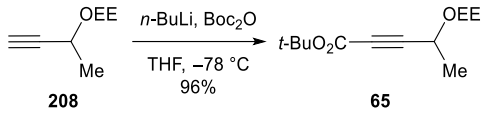


64 208

3-(1-ethoxyethoxy)but-1-yne (208)

To a stirred solution of 3-butyn-2-ol **64** (100 g, 1.43 mol, 1.0 equiv.) and ethyl vinyl ether (151 mL, 1.57 mol, 1.1 equiv.) in CH_2Cl_2 (3 L, 0.48 M) at 23 °C was added solid pyridinium *p*-toluenesulfonate (35.9 g, 143 mmol, 0.1 equiv.). After 1 hour, the reaction mixture was diluted with Et_2O (1 L) and washed with brine (2 L). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a mixture of diastereomeric alkynes **208** (201 g, 1.41 mol, 99%) as a clear amber oil.

$\mathbf{R}_f$ = 0.40 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.96 (q, *J* = 5.5 Hz, 1H), 4.85 (q, *J* = 5.5 Hz, 1H), 4.50 (q, *J* = 6.7 Hz, 1H), 4.35 (q, *J* = 6.7 Hz, 1H), 3.75 (m, 1H), 3.62 (m, 1H), 3.53 (m, 2H), 2.40 (s, 1H), 2.39 (s, 1H), 1.46 (d, *J* = 3.1 Hz, 3H), 1.44 (d, *J* = 3.1 Hz, 3H), 1.35 (d, *J* = 2.7 Hz, 3H), 1.34 (d, *J* = 2.7 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 98.5, 97.5, 84.5, 83.6, 72.4, 72.0, 61.1, 60.5, 60.0, 59.9, 22.3, 21.9, 20.0, 19.9, 15.2, 14.9; **HRMS** (EC-CI) calc. for $C_8H_{13}O_2$ $[M+H]^+$: 141.0916, obs. 141.0918.

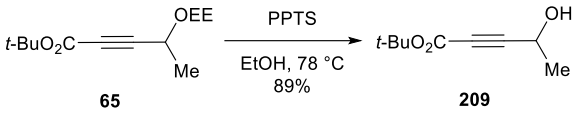


208 65

***tert*-butyl 4-(1-ethoxyethoxy)pent-2-ynoate (65)**

To a stirred solution of diastereomeric alkynes **208** (110 g, 774 mmol, 1.0 equiv.) in THF (4.5 L, 0.17 M) at −78 °C was added a 2.0 M solution of *n*-butyllithium in hexanes (404 mL, 808 mmol, 1.05 equiv.). After 15 minutes, neat di-*tert*-butyl dicarbonate (186 mL, 808 mmol, 1.05 equiv.) was added over 10 minutes. Upon complete addition the reaction mixture was allowed to warm to 23 °C. The reaction mixture was diluted with Et_2O (1.5 L) and washed with H_2O (3 L) and brine (3 L). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to give a mixture of diastereomeric esters **65** (180 g, 743 mmol, 96%) as an amber oil.

R_f = 0.21 (silica gel, 20:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.91 (q, *J* = 5.1 Hz, 1H), 4.82 (q, *J* = 5.1 Hz, 1H), 4.56 (q, *J* = 6.8 Hz, 1H), 4.40 (q, *J* = 6.8 Hz, 1H), 3.73 (m, 1H), 3.62 (m, 1H), 3.56 (m, 1H), 3.50 (m, 1H), 1.49 (s, 18 H), 1.46 (d, *J* = 1.7 Hz, 6H), 1.34 (d, *J* = 1.4 Hz, 6H) 1.12 (t, *J* = 8.5 Hz, 6H); **^{13}C-NMR** (100 MHz, C_6D_6): δ 152.6, 152.5, 99.3, 98.3, 86.1, 85.2, 82.9, 82.7, 78.3, 77.9, 61.0, 60.4, 60.3, 60.2, 27.8 (2 signals), 21.8, 21.5, 20.1, 20.0, 15.5, 15.3; **IR** (film, cm^{-1}): 1710, 1274, 1160; **HRMS** (ESI) calc. for $C_{13}H_{22}NaO_4$ $[M+Na]^+$: 265.14103, obs. 265.14100.

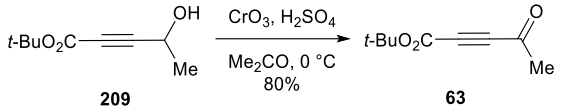


65 209

***tert*-butyl 4-hydroxypent-2-ynoate (209)**

To a stirred solution of diastereomeric esters **65** (117 g, 483 mmol, 1.0 equiv.) in EtOH (4.8 L, 0.1 M) at 23 °C was added solid pyridinium *p*-toluenesulfonate (12.1 g, 48.3 mmol, 0.1 equiv.). The reaction mixture was stirred at 78 °C for 2 hours before being allowed to cool to 23 °C. The reaction mixture was diluted with Et_2O (2.4 L) and washed with brine (4 L). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to give alcohol **209** (73.1 g, 429 mmol, 89%) as an amber oil.

$\mathbf{R}_f$ = 0.30 (silica gel, 3:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.62 (m, 1H), 2.13 (s, 1H), 1.51 (m, 12H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 152.8, 86.8, 82.9, 77.5, 57.8, 27.8, 23.1; **IR** (film, cm^{-1}): 3400, 1709; **HRMS** (EC-CI) calc. for $C_9H_{15}O_3$ $[M+H]^+$: 171.1021, obs. 171.1019.

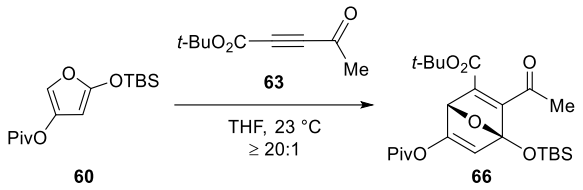


209 **63**

***tert*-butyl 4-oxopent-2-ynoate (63)**

To a stirred solution of alcohol **209** (73.0 g, 429 mmol, 1.0 equiv.) in Me_2CO (1.2 L, 0.43 M) at 0 °C was slowly added ice-cold 1.53 M (67.0 g CrO_3, 58.0 mL conc. H_2SO_4 and 160 mL H_2O) Jones reagent (280 mL, 429 mmol, 1.0 equiv.) over 15 minutes. After 30 minutes, *i*-PrOH (40 mL) was added to neutralize any excess Jones reagent and the reaction mixture was diluted with CH_2Cl_2 (1 L). The organic layer was decanted and washed with H_2O (1 L), sat. aq. $NaHCO_3$ (1 L), and brine (1 L). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give keto-ester **63** (57.5 g, 342 mmol, 80%) as a clear amber oil.

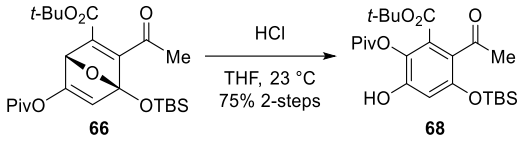
$\mathbf{R}_f$ = 0.40 (silica gel, 10:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 1.52 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 182.8, 151.0, 85.4, 79.2, 79.0, 32.3, 27.9; **IR** (film, cm^{-1}): 1716, 1689; **HRMS** (EC-CI) calc. for $C_9H_{13}O_3$ $[M+H]^+$: 169.0865, obs. 169.0866.



***tert*-butyl 3-acetyl-4-((*tert*-butyldimethlsilyl)oxy)-6-(pivaloyloxy)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (66)**

To a stirred solution of furan **60** (70.4 g, 236 mmol, 1.0 equiv.) in THF (210 mL, 1.1 M) at 0 °C was added keto-ester **63** (39.7 g, 236 mmol, 1.0 equiv.). Upon complete addition the reaction mixture was allowed to warm to 23 °C. After 1 hour, the reaction mixture was concentrated *in vacuo* to give bicycle **66** (110 g, 236 mmol, yield taken after subsequent step) in > 20:1 regioselectivity as a viscous burgundy oil.

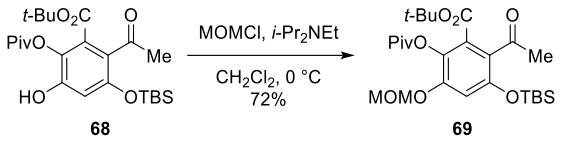
$\mathbf{R_f}$ = 0.35 (silica gel, 10:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.38 (s, 1H), 5.24 (s, 1H), 2.43 (s, 3H), 1.47 (s, 9H), 1.25 (s, 9H), 0.90 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 199.3, 174.3, 167.7, 163.7, 161.2, 146.3, 118.5, 113.9, 82.3, 78.2, 39.2, 30.7, 27.9, 26.8, 25.4, 17.7, -3.5, -3.7; **IR** (film, cm^{-1}): 1769, 1712; **HRMS** (EC-CI) calc. for $C_{24}H_{38}O_7Si$ $[M+Na]^+$: 489.22790, obs. 489.22801.



***tert*-butyl 2-acetyl-3-((*tert*-butyldimethlsilyl)oxy)-5-hydroxy-6-(pivaloyloxy)benzoate (68)**

To a stirred solution of bicycle **66** (110 g, 236 mmol, 1.0 equiv.) in THF (470 mL, 0.5 M) at 0 °C was slowly added a 4.0 M solution of hydrochloric acid in dioxane (47.1 mL, 47.1 mmol, 0.2 equiv.) over 5 minutes. Upon complete addition the reaction mixture was allowed to warm to 23 °C. After 2 hours, the reaction mixture was concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (20:1 hexanes:EtOAc) to give pure phenol **68** (82.9 g, 178 mmol, 75% over 2-steps) as a clear light-yellow oil.

R_f = 0.38 (silica gel, 10:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 10.91 (s, 1H), 6.71 (s, 1H), 2.48 (s, 3H), 1.54 (s, 9H), 1.38 (s, 9H), 0.94 (s, 9H), 0.18 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 202.3, 176.3, 168.4, 148.7, 142.5, 139.7, 131.9, 119.9, 111.0, 85.7, 39.2, 32.5, 27.8, 27.2, 25.5, 18.0, -4.4; **IR** (film, cm^{-1}): 1763, 1716, 1673; **HRMS** (EC-CI) calc. for $C_{24}H_{38}O_7Si$ $[M+Na]^+$: 489.22790, obs. 489.22813.

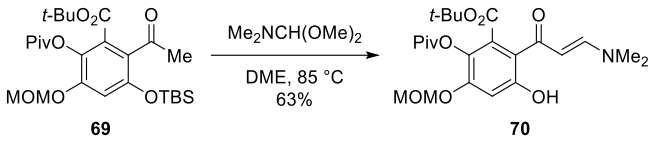


68 69

***tert*-butyl 2-acetyl-3-((*tert*-butyldimethlsilyl)oxy)-5-(methoxymethoxy)-6-(pivaloyloxy)benzoate (69)**

To a stirred solution of phenol **68** (82.9 g, 178 mmol, 1.0 equiv.) in CH_2Cl_2 (1.7 L, 0.1 M) at 0 °C was added neat N,N-diisopropylethylamine (63.4 mL, 355 mmol, 1.5 equiv.). A 2.1 M solution of chloromethyl methyl ether in PhMe/MeOAc (127 mL, 267 mmol, 1.5 equiv.) was then added slowly over 20 minutes. Upon complete addition the solution was allowed to warm to 23 °C. After 1 hour, the reaction mixture was diluted with 0.1 N HCl (500 mL) and extracted with CH_2Cl_2 (3 x 500 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (10:1 hexanes:EtOAc) to give acetophenone **69** (65.0 g, 127 mmol, 72%) as a white solid (m.p. 60-62 °C).

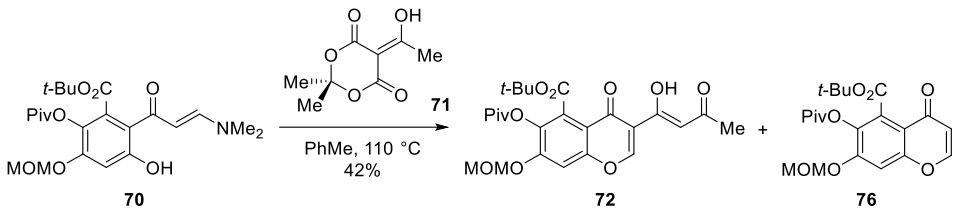
$\mathbf{R_f}$ = 0.61 (silica gel, 3:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.76 (s, 1H), 5.10 (s, 2H), 3.42 (s, 3H), 2.54 (s, 3H), 1.49 (s, 9H), 1.34 (s, 9H), 0.97 (s, 9H), 0.21 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 200.9, 175.7, 163.5, 150.9, 150.4, 132.8, 128.1, 125.7, 108.6, 94.6, 82.5, 55.9, 38.9, 31.7, 27.7, 27.1, 25.6, 18.1, -4.4; **IR** (film, cm^{-1}): 1761, 1733, 1703; **HRMS** (ESI) calc. for $C_{26}H_{42}NaO_8Si$ $[M+Na]^+$: 533.25412, obs. 533.25387.



***tert*-butyl (*E*)-2-(3-(dimethylamino)acryloyl)-3-hydroxy-5-(methoxymethoxy)-6-(pivaloyloxy)benzoate (70)**

To a stirred solution of acetophenone **69** (15.4 g, 30.2 mmol, 1.0 equiv.) in DME (300 mL, 0.1 M) at 85 °C was added N,N-dimethylformamide dimethyl acetal (16.1 mL, 121 mmol, 4.0 equiv.) in one portion. After 3 hours, the reaction mixture was cooled to 23 °C and concentrated *in vacuo* to give a dark amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure enaminone **70** (8.59 g, 19.0 mmol, 63%) as an orange solid (m.p. 118-119 °C).

$\mathbf{R}_f$ = 0.26 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 12.43 (bs, 1H), 7.77 (d, *J* = 12 Hz, 1H), 6.70 (s, 1H), 5.49 (d, *J* = 12 Hz, 1H), 5.13 (s, 2H), 3.41 (s, 3H), 3.15 (s, 3H), 2.84 (s, 3H), 1.47 (s, 9H), 1.34 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 189.4, 175.8, 165.6, 159.3, 154.4, 151.6, 130.1, 128.5, 113.7, 104.0, 95.2, 94.0, 82.4, 56.0, 45.1, 38.7, 37.1, 27.6, 27.0; **IR** (film, cm^{-1}): 1751, 1716, 1632, 1111; **HRMS** (ESI) calc. for $C_{23}H_{33}NNaO_8$ $[M+Na]^+$: 474.20984, obs. 474.21058.



To a stirred solution of enaminone **70** (1.44 g, 3.19 mmol, 1.0 equiv.) in PhMe (32 mL, 0.1 M) was added freshly ground acyl Meldrum's acid **71** (1.78 g, 9.57 mmol, 3.0 equiv.). The reaction mixture was stirred at 110 °C for 45 minutes before being cooled to 23 °C and concentrated *in vacuo* to give a brown solid. The crude material was purified via acidified silica gel* column chromatography (7:1 hexanes:EtOAc) to give pure protected 5,6-dehydropolivione **72** (650 mg, 1.33 mmol, 42%) as a yellow solid (m.p. 181-182 °C).

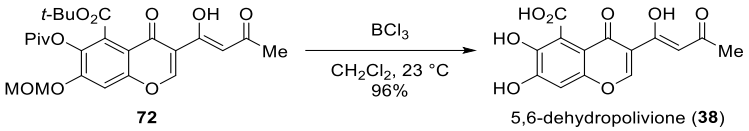
*To a vigorously stirred slurry of silica gel (400 g) and deionized water (2.5) was added 85% phosphoric acid (6.50 mL) to give a pH of 2. After 20 minutes, the silica gel was filtered, washed with EtOAc (500 mL), and dried in an oven at 120 °C overnight.

***tert*-butyl (*Z*)-3-(1-hydroxy-3-oxobut-1-en-1-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (72)**

R_f = 0.24 (silica gel, 3:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 15.87 (s, 1H), 8.66 (s, 1H), 7.23 (s, 1H), 7.05 (s, 1H), 5.24 (s, 2H), 3.45 (s, 3H), 2.22 (s, 3H), 1.65 (s, 9H), 1.38 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$, The highly concentrated ^{13}C sample produced a mixture of keto and enol tautomers): δ 202.5, 197.6, 192.1, 174.3, 172.6, 163.6, 161.7, 159.4, 154.5, 154.2, 153.4, 136.7, 128.6, 120.9, 118.0, 116.3, 115.8, 103.9, 103.8, 101.7, 94.7, 83.1, 57.7, 56.7, 56.6, 39.2, 30.7, 28.2, 27.2, 26.9; **IR** (film, cm^{-1}): 1762, 1734, 1663, 1621; **HRMS** (ESI) calc. for $C_{25}H_{30}NaO_{10}$ $[M+Na]^+$: 513.17312, obs. 513.17341.

***tert*-butyl 7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (76)**

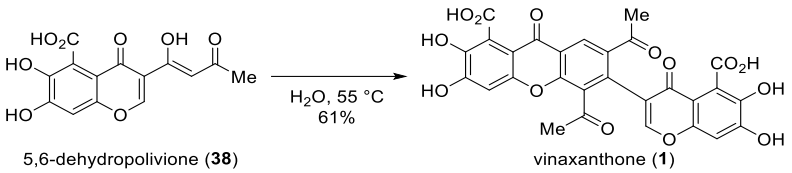
R_f = 0.52 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 5.5 Hz, 1H), 6.25 (d, *J* = 5.5 Hz, 1H), 5.23 (s, 2H), 3.45 (s, 3H), 1.63 (s, 9H), 1.38 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 192.1, 175.3, 163.6, 155.1, 154.5, 153.0, 135.8, 127.8, 115.9, 112.7, 103.7, 82.9, 56.5, 39.1, 28.0, 27.2; **IR** (film, cm^{-1}): 1657, 1460, 1280, 1155, 1095; **HRMS** (ESI) calc. for $C_{21}H_{26}NaO_8$ $[M+Na]^+$: 429.15199, obs. 429.15240; **m.p.** 156-158 °C.



(*Z*)-6,7-dihydroxy-3-(1-hydroxy-3-oxobut-1-en-1-yl)-4-oxo-4*H*-chromene-5-carboxylic acid (38)

To a stirred solution of protected 5,6-dehydropolivione **72** (50.0 mg, 0.102 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL, 0.1 M) at 0 °C was added a 1.0 M solution of boron trichloride in CH_2Cl_2 (1.22 mL, 1.22 mmol, 12 equiv.). Upon complete addition the reaction mixture was allowed to warm to 23 °C. After 1 hour, the reaction mixture was cooled to 0 °C and quenched with 2.0 N HCl (2 mL) and stirred at 0 °C for 5 minutes. The solution was diluted with EtOAc (30 mL) and the pH of the aqueous layer was adjusted to pH 7 using a 0.2 M phosphate pH = 10 buffer (40 mL). The organic layer was then extracted with 0.2 M phosphate pH = 7.0 buffer (3 x 30 mL). The combined aqueous extractions were re-acidified to a pH of 2 using 2.0 N HCl and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield 5,6-dehydropolivione (**38**) (20.1 mg, 0.098 mmol, 96% yield) as a yellow solid (m.p. 231-232 °C).

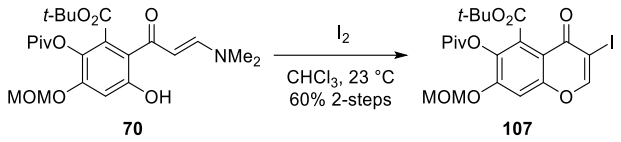
R_f = 0.54 (silica gel, 9:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ [enol] 16.10 (bs, 1H), 12.71 (bs, 1H), 11.55 (bs, 1H), 9.50 (bs, 1H), 8.84 (s, 1H), 6.98 (s, 1H), 6.96 (s, 1H), 2.19 (s, 3H). [keto] 12.71 (bs, 1H), 11.55 (bs, 1H), 9.50 (bs, 1H), 8.73 (s, 1H), 6.96 (s, 1H), 4.09 (s, 2H), 2.20 (s, 3H); **^{13}C-NMR** (100 MHz, $(CD_3)_2SO$): δ [enol] 196.7, 176.0, 172.3, 167.4, 160.2, 152.6, 149.8, 142.0, 120.2, 116.2, 113.2, 102.4, 100.8, 26.3 [keto] 203.0, 192.7, 173.0, 161.7, 152.6, 150.1, 120.4, 120.2, 113.6, 102.5, 57.4, 30.6; **IR** (film, cm^{-1}): 3280, 1617, 1473; **HRMS** (ESI) calc. for $C_{14}H_9O_8$ $[M-H]^-$: 305.03029, obs. 305.03013.



vinaxanthone (1)

A solution of 5,6-dehydropolivione (**38**) (10.0 mg, 0.033 mmol, 1.00 eq) in H_2O (0.33 mL, 0.1 M) was stirred at 55 °C for 4 days. The reaction mixture was quenched with conc. ammonium hydroxide (2 mL). The solution was washed with EtOAc (2 x 20 mL) and then re-acidified to a pH of 1 using conc. HCl at 0 °C. The residue was extracted with EtOAc (3 x 20 mL), washed with aq. 0.2 M pH = 2.0 phosphate buffer (20 mL) and brine (30 mL), and dried over $MgSO_4$ to give a brown solid. The crude material was purified by trituration with MeOH (3 x 1 mL) to give pure vinaxanthone (**1**) (5.7 mg, 0.0099 mmol, 61%) as a yellow solid (m.p. >280 °C).

$\mathbf{R_f}$ = 0.05 (sílica gel, 95:5 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.89 (bs, 1H), 12.72 (bs, 1H), 11.69 (bs, 1H), 11.44 (bs, 1H), 9.42 (bs 2H), 9.42 (bs, 2H), 8.53 (s, 1H), 8.18 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 2.55 (s, 3H), 2.53 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.1, 172.9, 172.6, 167.4, 167.4, 154.1, 152.7, 152.5, 152.1, 150.7, 150.3, 141.7, 141.0, 136.2, 133.4, 132.6, 126.3, 120.8, 120.5, 119.8, 119.6, 112.4, 110.0, 102.4, 102.3, 32.1, 29.1; **IR** (KBr, cm^{-1}): 3236, 1683, 1653, 1472, 1288; **HRMS** (ESI) calc. for $C_{28}H_{15}O_{14}$ $[M–H]^-$: 575.04673, obs. 575.04679.

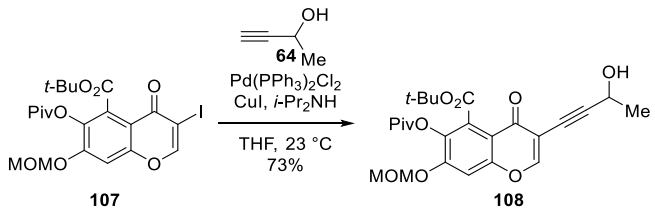


70 107

***tert*-butyl 3-iodo-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (107)**

To a stirred solution of crude enaminone **70** (13.6 g, 30.2 mmol, 1.0 equiv.) in $CHCl_3$ (300 mL, 0.1 M) at 23 °C was added solid iodine (15.3 g, 60.4 mmol, 2.0 equiv.) in one portion. After 40 minutes, the solution was diluted with sat. aq. $Na_2S_2O_3$ (300 mL) and extracted with CH_2Cl_2 (300 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a tan solid. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure iodochromone **107** (9.65 g, 18.1 mmol, 60% over 2-steps) as a white solid (m.p. 189-190 °C).

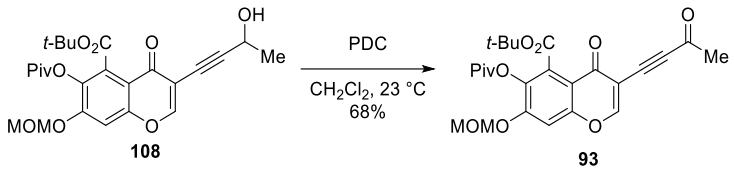
R_f = 0.32 (silica gel, 3:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.17 (s, 1H), 5.23, (s, 2H), 3.25 (s, 3H), 1.64 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.4, 170.9, 163.2, 156.8, 154.9, 153.3, 136.5, 128.3, 112.8, 103.5, 94.7, 86.7, 83.3, 56.6, 39.2, 28.2, 27.2; **IR** (film, cm^{-1}): 1764, 1731, 1650; **HRMS** (ESI) calc. for $C_{21}H_{25}INaO_8$ $[M+Na]^+$: 555.04863, obs. 555.04881.



***tert*-butyl 3-(3-hydroxybut-1-yn-1-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (108)**

To a stirred solution of iodochromone **107** (8.08 g, 15.2 mmol, 1.0 equiv.), bis(triphenylphosphine) palladium (II) dichloride (213 mg, 0.30 mmol, 0.02 equiv.) and copper iodide (289 mg, 1.54 mmol, 0.1 equiv.) in degassed THF (51 mL, 0.3 M) at 23 °C was added 3-butyn-2-ol **64** (4.8 mL, 60.7 mmol, 4.0 equiv.) followed by neat diisopropylamine (6.5 mL, 45.5 mmol, 3.0 equiv.). After 1 hour, the reaction mixture was diluted with aq. 0.2 M pH = 7.0 phosphate buffer (100 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure propargyl alcohol **108** (5.23 g, 11.0 mmol, 73%) as a tan solid (m.p. 132-134 °C).

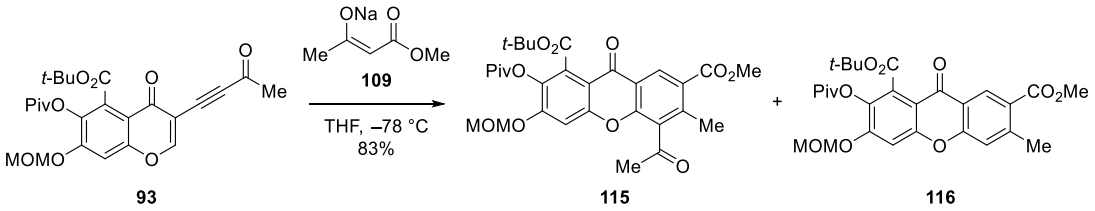
R_f = 0.21 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.14 (s, 1H), 5.21 (s, 2H), 4.75 (m, 1H), 3.43 (s, 3H), 3.20 (bs, 1H), 1.63 (s, 9H), 1.51 (d, *J* = 6.7 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.5, 173.3, 163.3, 157.5, 154.6, 153.2, 136.3, 128.1, 114.5, 110.5, 103.8, 97.5, 94.6, 83.2, 73.8, 58.6, 56.6, 39.2, 28.2, 27.2, 23.8; **IR** (film, cm^{-1}): 3435, 1763, 1735, 1731, 1461; **HRMS** (ESI) calc. for $C_{25}H_{30}NaO_9$ $[M+Na]^+$: 497.1782, obs. 497.1785.



***tert*-butyl 3-(3-hydroxybut-1-yn-1-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (93)**

To a stirred solution of propargyl alcohol **108** (5.23 g, 11.0 mmol, 1.0 equiv.) and activated 4.0 Å molecular sieves (2.6 g, 50% by weight) in CH_2Cl_2 (110 mL, 0.1 M) at 23 °C was added solid pyridinium dichromate (19.9 g, 55.1 mmol, 5.0 equiv.) in one portion. After 2 hours the black solution was filtered through a pad of Celite and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure ynone **93** (3.54 g, 7.50 mmol, 68%) as a white solid (m.p. 178-179 °C).

$\mathbf{R}_f$ = 0.41 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.21 (s, 1H), 5.24 (s, 2H), 3.44 (s, 3H), 2.46 (s, 3H), 1.64 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 184.2, 175.4, 172.1, 163.1, 160.4, 154.6, 153.7, 136.8, 128.3, 114.6, 108.7, 104.0, 94.7, 93.5, 83.5, 81.0, 56.7, 39.2, 32.7, 28.2, 27.2; **IR** (film, cm^{-1}): 1762, 1734, 1672, 1620, 1459, 1264, 1246, 1155, 1091; **HRMS** (ESI) calc. for $C_{25}H_{28}NaO_9$ $[M+Na]^+$: 495.1626, obs. 495.1632.



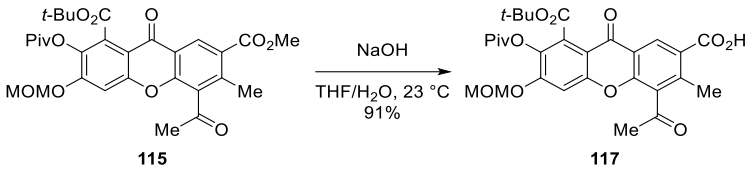
To a stirred suspension of 60% sodium hydride (556 mg, 13.9 mmol, 1.0 equiv.) in THF (55.7 mL, 0.25 M) was added methyl acetoacetate (1.50 mL, 13.9 mmol, 1.0 equiv.) dropwise over 5 minutes to furnish a 0.25 M stock solution of the sodium enolate of methyl acetoacetate **109** (stored in a Schlenk flask under argon). To a stirred solution of ynone **93** (500 mg, 1.06 mmol, 1.0 equiv.) in THF (88 mL, 0.01 M) at -78 °C was added a 0.25 M solution of the sodium enolate of methyl acetoacetate in THF (8.50 mL, 2.12 mmol, 2.0 equiv.) dropwise down the side of the flask over 10 minutes. Upon complete addition the red-amber solution was stirred at -78 °C. After 5 hours, the excess sodium enolate of methyl acetoacetate was quenched with 1.0 N HCl (1.5 mL). The resulting yellow solution was diluted with EtOAc (150 mL), washed with H_2O (3 x 50 mL) and brine (50 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a yellow residue. The crude material was purified via silica gel column chromatography (3:1 hexanes:EtOAc) to give pure methyl ester **115** (502 mg, 0.88 mmol, 83%) as a tan solid (m.p. 199-201 °C) and deacetylated byproduct **116** (95 mg, 0.18 mmol, 17%) as a white solid (m.p. 186-187 °C).

1-(*tert*-butyl) 7-methyl 5-acetyl-3-(methoxymethoxy)-6-methyl-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1,7-dicarboxylate (115)

$\mathbf{R_f}$ = 0.40 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.17 (s, 1H), 5.27 (s, 2H), 3.93 (s, 3H), 3.47 (s, 3H), 2.67 (s, 3H), 2.62 (s, 3H), 1.67 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 202.4, 175.9, 173.6, 166.6, 163.8, 154.8, 154.7, 153.4, 142.8, 135.8, 133.2, 129.9, 129.0, 127.6, 119.3, 112.7, 103.9, 95.1, 83.5, 56.9, 52.6, 39.5, 32.9, 28.3, 27.4, 18.2; **IR** (film, cm^{-1}): 1760, 1735, 1663, 1599; **HRMS** (ESI) calc. for $C_{30}H_{34}NaO_{11}$ $[M+Na]^+$: 593.19933, obs. 593.19976.

1-(*tert*-butyl) 7-methyl 3-(methoxymethoxy)-6-methyl-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1,7-dicarboxylate (116)

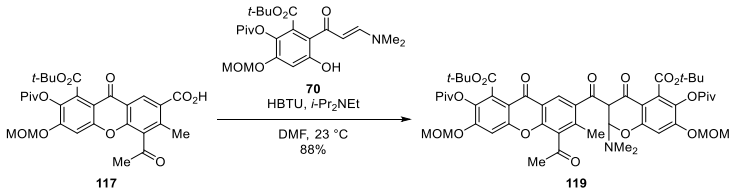
$\mathbf{R_f}$ = 0.54 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.29 (s, 1H), 7.23 (s, 1H), 5.27 (s, 2H), 3.91 (s, 3H), 3.47 (s, 3H), 2.75 (s, 3H), 1.68 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (100 MHz, CD_2Cl_2): δ 176.1, 147.3, 166.8, 164.1, 157.5, 155.2, 154.5, 148.3, 135.5, 130.2, 129.0, 126.6, 120.4, 119.4, 113.0, 104.0, 95.1, 83.4, 56.9, 52.3, 39.5, 28.3, 27.4, 22.4; **IR** (film, cm^{-1}): 1727, 1460, 1095; **HRMS** (ESI) calc. for $C_{28}H_{32}NaO_{10}$ $[M+Na]^+$: 551.18877, obs. 551.18915.



4-acetyl-8-(*tert*-butoxycarbonyl)-6-(methoxymethoxy)-3-methyl-9-oxo-7-(pivaloyloxy)-9*H*-xanthene-2-carboxylic acid (117)

To a stirred solution of methyl ester **115** (920 mg, 1.61 mmol, 1.0 equiv.) in THF (65 mL, 0.025 M) at 0 °C was added 0.1 N NaOH (19.4 mL, 1.94 mmol, 1.2 equiv.) dropwise over 2 minutes. Upon complete addition the gold-orange solution was allowed to warm to 23 °C. After 36 hours, the reaction mixture was diluted with H_2O (100 mL) and washed with Et_2O (3 x 50 mL). The aqueous layer was acidified using 0.1 N HCl (20 mL), extracted with EtOAc (3 x 250 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give pure carboxylic acid **117** (816 mg, 1.43 mmol, 91%) as a white solid (m.p. 203-204 °C).

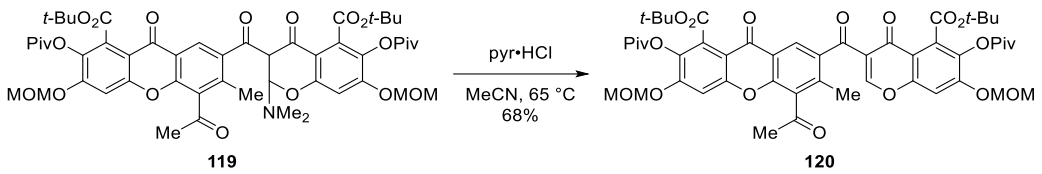
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 1H), 7.17 (s, 1H), 5.27 (s, 2H), 3.47 (s, 3H), 2.69 (s, 3H), 2.65 (s, 3H), 1.67 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 202.3, 175.6, 173.2, 168.9, 163.5, 154.5, 154.4, 153.6, 143.1, 135.8, 133.0, 131.4, 129.0, 125.7, 119.2, 112.8, 103.7, 94.8, 83.4, 56.7, 39.2, 32.8, 28.2, 27.3, 18.3; **IR** (film, cm^{-1}): 1760, 1688, 1666, 1619, 1596; **HRMS** (ESI) calc. for $C_{29}H_{32}NaO_{11}$ $[M+Na]^+$: 579.18368, obs. 579.18373.



***tert*-butyl 5-acetyl-7-(5-(*tert*-butoxycarbonyl)-2-(dimethylamino)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)chromane-3-carbonyl)-3-(methoxymethoxy)-6-methyl-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (119)**

To a stirred solution of carboxylic acid **117** (373 mg, 0.67 mmol, 1.1 equiv.) in DMF (3.0 mL, 0.2 M) at 23 °C was added solid HBTU (254 mg, 0.67 mmol, 1.1 equiv.) in one portion followed by neat N,N-diisopropylethylamine (0.27 mL, 1.52 mmol, 2.5 equiv.). The dark amber solution was stirred for 5 minutes before adding solid enaminone **70** (275 mg, 0.61 mmol, 1.1 equiv.) in one portion. After 6 hours, the reaction mixture was diluted with 1:1 hexanes/EtOAc (100 mL) and washed with sat. aq. LiCl (8 x 30 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a dark yellow solid. The crude material was purified via silica gel column chromatography (1:2 hexanes:EtOAc, 2% Et_3N) to give pure aminal **119** (528 mg, 5.33 mmol, 88%) as a dark yellow solid (m.p. 124-126 °C).

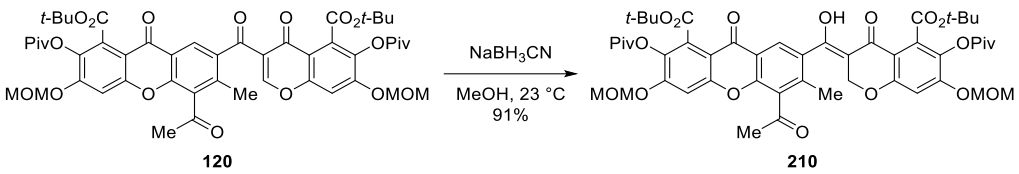
R_f = 0.25 (silica gel, 1:1 hexanes:EtOAc, 2% Et_3N); **^{1}H-NMR** (400 MHz, $(CD_3)_2CO$): δ 8.87 (s, 1H), 7.42 (s, 1H), 7.30 (s, 1H), 5.46 (s, 2H), 5.28 (s, 2H), 5.23 (d, *J* = 13.3 Hz, 1H), 3.47 (s, 3H), 3.44 (s, 3H), 3.07 (s, 3H), 2.86 (d, *J* = 13.3 Hz , 1H), 2.74 (s, 3H), 2.72 (s, 3H), 2.59 (s, 3H), 1.64 (s, 9H), 1.44 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 202.2, 175.5, 175.3, 173.0, 163.9, 163.5, 157.5, 154.8, 154.5, 154.4, 153.4, 149.4, 144.9, 143.2, 136.4, 136.3, 135.7, 132.9, 130.9, 128.9, 128.8, 126.1, 120.1, 119.1, 112.7, 111.6, 103.6, 94.8, 94.7, 83.2, 83.1, 82.5, 56.7, 56.3, 44.9, 39.2, 39.0, 36.9, 32.8, 28.1, 27.7, 27.2, 27.1, 18.1; **IR** (film, cm^{-1}): 1766, 1730, 1660, 1610; **HRMS** (ESI) calc. for $C_{52}H_{63}NNaO_{18}$ $[M+Na]^+$: 1012.39374, obs. 1012.39398.



***tert*-butyl 5-acetyl-7-(5-(*tert*-butoxycarbonyl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-3-carbonyl)-3-(methoxymethoxy)-6-methyl-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (120)**

To a stirred solution of aminal **119** (84 mg, 0.084 mmol, 1.0 equiv.) in MeCN (5.6 mL, 0.015 M) at 23 °C was added solid pyridinium hydrochloride (49 mg, 0.42 mmol, 5.0 equiv.) in one portion. The yellow solution was then stirred to 65 °C. After 18 hours, the reaction mixture was concentrated to give a yellow residue. The crude material was purified via silica gel column chromatography (3:1 to 2:1 hexanes:EtOAc) to give pure enedione **120** (54 mg, 0.057 mmol, 68%) as a clear-yellow solid (m.p. 185-188 °C).

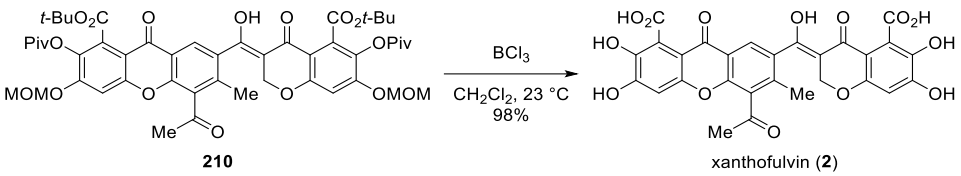
$\mathbf{R}_f$ = 0.21 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.25 (s, 1H), 7.27 (s, 1H), 7.17 (s, 1H), 5.26 (s, 4H), 3.48 (s, 3H), 3.47 (s, 3H), 2.68 (s, 3H), 2.45 (s, 3H), 1.61 (s, 9H), 1.42 (s, 9H), 1.38 (s, 9H), 1.35 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 202.2, 192.1, 175.5, 175.3, 173.2, 172.1, 163.5, 162.9, 160.4, 154.6, 154.4, 154.3, 153.7, 152.6, 140.6, 136.8, 136.4, 135.6, 132.3, 128.9, 128.6, 127.3, 123.8, 118.7, 116.5, 112.7, 104.0, 103.6, 94.8, 94.7, 83.2, 83.1, 56.7, 56.6, 39.2, 39.1, 32.7, 28.2, 27.9, 27.3, 27.2, 17.5; **IR** (film, cm^{-1}): 1760, 1732, 1663, 1607, 1591; **HRMS** (ESI) calc. for $C_{50}H_{56}NaO_{18}$ $[M+Na]^+$: 967.33589, obs. 967.33504.



***tert*-butyl (*Z*)-5-acetyl-7-((5-(*tert*-butoxycarbonyl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)chroman-3-ylidene)(hydroxy)methyl)-3-(methoxymethoxy)-6-methyl-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (210)**

To a stirred solution of endione **120** (30 mg, 0.032 mmol, 1.0 equiv.) in MeOH (0.64 mL, 0.5 M) at 23 °C was added solid $NaBH_3CN$ (4.0 mg, 0.063 mmol, 2.0 equiv.) in one portion. After 20 minutes, the reaction mixture was diluted with aq. 0.2 M pH = 7.0 phosphate buffer (0.25 mL) before being diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (2 x 10 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a yellow residue. The crude material was purified via silica gel column chromatography (2:1 hexanes:EtOAc) to give pure protected xanthofulvin **210** (27 mg, 0.029 mmol, 91 %) as a bright yellow solid (mp: 184-186 °C).

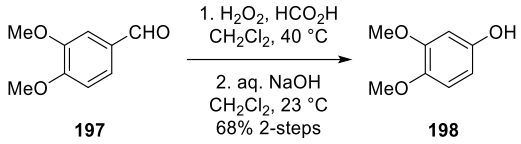
R_f = 0.5 (silica gel, 1:1 hexanes/EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 15.43 (s, 1H), 8.12 (s, 1H), 7.18 (s, 1H), 6.68 (s, 1H), 5.28 (s, 2H), 5.16 (s, 2H), 4.74 (bs, 2H), 3.48 (s, 3H), 3.42 (s, 3H), 2.71 (s, 3H), 2.41 (s, 3H), 1.66 (s, 9H), 1.62 (s, 9H), 1.39 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 201.9, 183.6, 175.7, 173.3, 173.1, 163.9, 163.6, 160.0, 154.9, 154.5, 152.3, 139.6, 135.7, 133.4, 132.4, 130.3, 129.3, 128.9, 126.9, 119.2, 112.7, 111.9, 103.9, 103.8, 103.5, 94.8, 94.4, 93.4. 83.3, 82.9, 66.7, 56.7, 56.5, 39.2, 39.1, 32.7, 29.7, 28.2, 28.1, 27.3, 27.2, 16.9; **IR** (film, cm^{-1}): 1765, 1730, 1666, 1602, 1458; **HRMS** (ESI) calc. for $C_{50}H_{58}NaO_{18}$ $[M+Na]^+$: 969.35154, obs. 969.35120.



xanthofulvin (**2**)

To a stirred solution of protected xanthofulvin **210** (20 mg, 0.02 mmol, 1.0 equiv.) in CH_2Cl_2 (2.1 mL, 0.1 M) at 23 °C was added a 1.0 M solution of boron trichloride in CH_2Cl_2 (0.25 mL, 0.25 mmol, 12 equiv.). After 45 minutes, the reaction mixture was treated with conc. HCl (0.09 mL) and diluted with EtOAc (10 mL). The bright orange solution was stirred vigorously for 15 minutes and then concentrated *in vacuo* to give an organge residue. The orange residue was diluted with MeOH (15 mL) and re-concentrated *in vacuo* give a yellow residue. The crude material was purified by trituration with $CHCl_3$ (10 mL) to give pure xanthofulvin **(2)** (11.8 mg, 0.020 mmol, 98%) as a 3.6:1 ratio of enol:keto tautomers as a bright yellow solid (m.p. 252-253 °C).

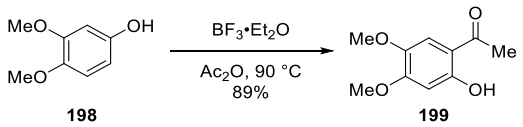
$\mathbf{R}_f$ = 0.14 (silica gel, 20:1 EtOAc/AcOH); **^{1}H-NMR** (500 MHz, $(CD_3)_2SO$): δ [enol] 15.61 (s, 1H), 12.75 (s, 1H), 11.62 (s, 1H), 11.23 (s, 1H), 9.33 (s, 1H), 8.69 (s, 1H), 7.95 (s, 1H), 6.93 (s, 1H), 6.39 (s, 1H), 4.66 (s, 2H), 2.70 (s, 3H), 2.31 (s, 3H) [keto] 11.15 (s, 1H), 8.88 (s, 1H), 8.51 (s, 1H), 6.92 (s, 1H), 6.42 (s, 1H), 5.01 (dd, *J* = 4.7 Hz, 8.1 Hz, 1H), 4.71 (dd, *J* = 4.2 Hz, 11.3 Hz, 1H), 4.60 (m, 1H), 2.67 (s, 3H), 2.29 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ [enol] 202.6, 183.7, 172.7, 172.7, 167.5, 167.5, 156.3, 154.5, 153.9, 152.2, 150.2, 140.8, 137.6, 132.4, 129.4, 128.3, 125.9, 120.7, 120.7, 118.7, 110.1, 104.4, 102.4, 102.4, 65.9, 32.4, 16.6 [keto] 202.9, 199.1, 186.3, 172.7, 167.7, 167.7, 156.3, 154.7, 153.9, 152.2, 150.1, 140.9, 139.2, 137.6, 134.9, 132.4, 127.7, 122.2, 120.8, 118.3, 110.1, 108.8, 102.4, 68.0, 56.3, 32.4, 17.1; **IR** (KBr, cm^{-1}): 3419, 2926, 1607, 1468, 1288, 1021; **HRMS** (ESI) calc. for $C_{28}H_{17}O_{14}$ $[M-H]^-$: 577.06238, obs. 577.06186.



3,4-dimethoxyphenol (**198**)

To a stirred solution of 3,4-dimethoxybenzaldehyde **197** (30.0 g, 181 mmol, 1.0 equiv.) in CH_2Cl_2 (360 mL, 0.5 M) at 23 °C was added 30% aq. H_2O_2 (46.1 mL, 451 mmol, 2.5 equiv.) and formic acid (27.7 mL, 722 mmol, 4.0 equiv.). The reaction mixture was stirred at 40 °C. After 42.5 hours, the reaction mixture was cooled to 23 °C and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to about 360 mL (0.5 M). 5.0 N NaOH (251 mL, 1.26 mol, 10 equiv.) was then slowly added over 20 minutes and the reaction mixture was stirred at 23 °C for an additional 20 minutes. The organic layer was separated and the aqueous layer was washed with CH_2Cl_2 (3 x 100 mL). The aqueous layer was acidified to pH = 1.0 with conc. HCl and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to give pure 3,4-dimethoxyphenol **198** (19.1 g, 124 mmol, 68%) as an amber solid (m.p. 58-60 °C).

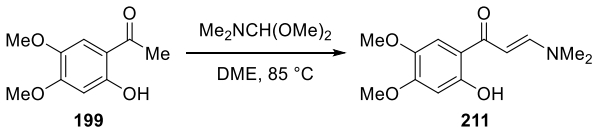
$\mathbf{R_f}$ = 0.43 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.71 (d, *J* = 8.4 Hz, 1H), 6.46 (d, *J* = 2.7 Hz, 1H), 6.35 (dd, *J* = 8.4, 2.7 Hz, 1H), 5.93 (bs, 1H), 3.79 (s, 3H), 3.76 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 150.2, 149.7, 142.8, 112.5, 105.9, 100.6, 56.5, 55.6; **IR** (film, cm^{-1}): 3382, 1513, 1223; **HRMS** (EC-CI) calc. for $C_8H_{11}O_3$ $[M+H]^+$: 155.0708, obs. 155.0700.



1-(2-hydroxy-4,5-dimethoxyphenyl)ethan-1-one (**199**)

To a stirred solution of 3,4-dimethoxyphenol **198** (3.0 g, 19.5 mmol, 1.0 equiv.) in acetic anhydride (9.75 mL, 103 mmol, 5.3 equiv.) at 0 °C was added neat boron trifluoride diethyl etherate (4.80 mL, 38.9 mmol, 2.0 equiv.). The reaction mixture was stirred at 90 °C for 1 hour and then allowed to sit at 23 °C for 16 hours. The precipitate was collected and recrystallized from EtOH to give pure dimethoxy hydroxyacetophenone **199** (3.38 g, 17.7 mmol, 89%) as white needles (m.p. 104-105 °C).

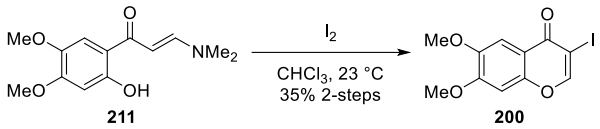
R_f = 0.58 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 12.65 (s, 1H), 7.05 (s, 1H), 6.46 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 2.56 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 202.0, 160.0, 156.7, 141.8, 111.6, 111.5, 100.5, 56.6, 56.1, 26.3; **IR** (film, cm^{-1}): 1632, 1511, 1265, 1160, 1063; **HRMS** (EC-CI) calc. for $C_{10}H_{13}O_4$ $[M+H]^+$: 197.0814, obs. 197.0810.



(*E*)-3-(dimethylamino)-1-(2-hydroxy-4,5-(dimethoxyphenyl)prop-2-en-1-one (**211**)

To a stirred solution of dimethoxy hydroxyacetophenone **199** (15.4 g, 30.2 mmol, 1.0 equiv.) in DME (300 mL, 0.1 M) at 85 °C was added N,N-dimethylformamide dimethyl acetal (16.1 mL, 121 mmol, 4.0 equiv.) in one portion. After 4 hours, the reaction mixture was cooled to 23 °C and concentrated *in vacuo* to give a dark amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give dimethoxy enaminone **211** (8.59 g, 19.0 mmol, yield taken after subsequent step) as a yellow solid (m.p. 157-158 °C).

R_f = 0.18 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 14.25 (bs, 1H), 7.84 (d, *J* = 12 Hz, 1H), 7.10 (s, 1H), 6.44 (s, 1H), 5.60 (d, *J* = 12 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.16 (bs, 3H), 2.96 (bs, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 190.3, 160.1, 155.0, 154.1, 141.2, 111.7, 111.1, 100.8, 89.7, 57.1, 55.9, 45.3, 37.3; **IR** (film, cm^{-1}): 1630, 1543, 1376, 1228, 1113; **HRMS** (ESI) calc. for $C_{13}H_{18}NO_4$ $[M+H]^+$: 252.12303, obs. 252.12258.



3-iodo-6,7-dimethoxy-4*H*-chromen-4-one (**200**)

To a stirred solution of crude dimethoxy enaminone **211** (11.8 g, 60.3 mmol, 1.0 equiv.) in $CHCl_3$ (600 mL, 0.1 M) at 23 °C was added solid iodine (30.7 g, 121 mmol, 2.0 equiv.) in one portion. After 40 minutes, the solution was diluted with sat. aq. $Na_2S_2O_3$ (300 mL) and extracted with CH_2Cl_2 (300 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a tan solid. The crude material was purified via silica gel column chromatography (2:1 hexanes:EtOAc) to give pure dimethoxy iodochromone **200** (7.01 g, 21.1 mmol, 35% over 2-steps) as a white solid (m.p. 170-172 °C).

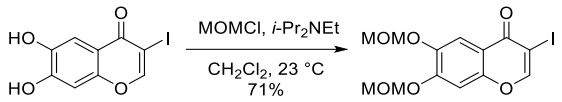
$\mathbf{R}_f$ = 0.32 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.55 (s, 1H), 6.86 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.2, 156.7, 154.5, 152.1, 147.9, 115.0, 104.8, 99.3, 86.4, 56.4, 56.3; **IR** (film, cm^{-1}): 1615, 1505, 1471, 1289, 1226; **HRMS** (ESI) calc. for $C_{11}H_9INaO_4$ $[M+Na]^+$: 354.94377, obs. 354.94418.

200 **212**

6,7-dihydroxy-3-iodo-4*H*-chromen-4-one (212)

To a stirred solution of dimethoxy iodochromone **200** (500 mg, 1.51 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL, 0.1 M) at 0 °C was slowly added neat boron tribromide (0.86 mL, 9.03 mmol, 6.0 equiv.) over 5 minutes. The solution was allowed to warm to 23 °C. After 1.5 hours, the reaction mixture was carefully quenched with 1.25 M methanolic HCl (1.20 mL, 2.08 mmol, 1.0 equiv.) at 0 °C over 5 minutes and stirred for an additional 5 minutes. The reaction mixture was purged with N_2 in order to remove residual gaseous HCl and concentrated *in vacuo* to give pure catechol **212** (458 mg, 1.51 mmol, 99%) as a grey solid (m.p. 215 °C (decomp.)).

R_f = 0.72 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, CD_3OD): δ 8.49 (s, 1H), 7.40 (s, 1H), 6.89 (s, 1H); **^{13}C-NMR** (100 MHz, CD_3OD): δ 174.8, 159.6, 154.5, 153.4, 146.6, 115.6, 108.9, 103.5, 85.4; **IR** (KBr, cm^{-1}): 3218, 1616, 1471, 1308; **HRMS** (EC-CI) calc. for $C_9H_6O_4$ $[M+H]^+$: 304.9311, obs. 304.9308.

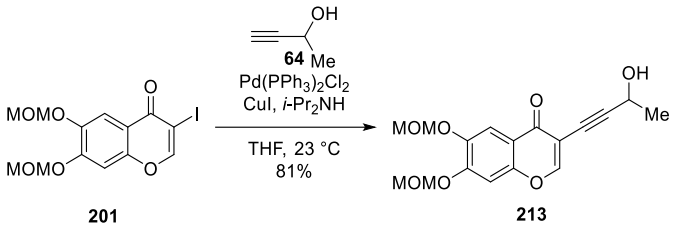


212 201

3-iodo-6,7-bis(methoxymethoxy)-4*H*-chromen-4-one (201)

To a stirred solution of catechol **200** (454 mg, 1.49 mmol, 1.0 equiv.) in CH_2Cl_2 (7.5 mL, 0.2 M) at 0 °C was added neat N,N-diisopropylethylamine (0.78 mL, 4.47 mmol, 3.0 equiv.). A 2.1 M solution of chloromethyl methyl ether in PhMe/MeOAc (2.13 mL, 4.47 mmol, 3.0 equiv.) was then added slowly over 20 minutes. Upon complete addition the solution was allowed to warm to 23 °C. After 1 hour, the reaction mixture was diluted with 0.1 N HCl (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (2:1 hexanes:EtOAc) to give pure dimethoxymethyl ether iodochromone **201** (417 mg, 1.06 mmol, 71%) as a white solid (m.p. 105-106 °C).

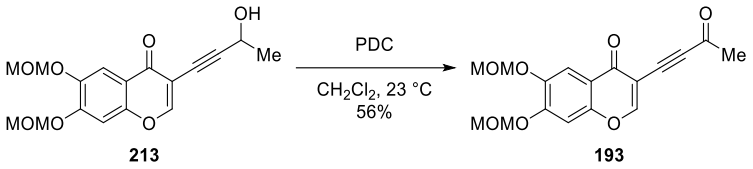
R*f* = 0.29 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.79 (s, 1H), 7.17 (s, 1H), 5.31 (s, 2H), 5.27 (s, 2H), 3.50 (s, 3H), 3.48 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.2, 157.0, 152.7, 152.4, 145.5, 116.0, 110.8, 103.5, 95.4, 95.1, 86.3, 56.5, 56.3; **IR** (film, cm^{-1}): 1617, 1453, 1284, 1152, 1041; **HRMS** (ESI) calc. for $C_{13}H_{13}INaO_6$ $[M+Na]^+$: 414.96490, obs. 414.96555.



3-(3-hydroxybut-1-yn-1-yl)-6,7-bis(methoxymethoxy)-4*H*-chromen-4-one (**213**)

To a stirred solution of dimethoxymethyl ether iodochromone **201** (1.40 g, 3.58 mmol, 1.0 equiv.), bis(triphenylphosphine) palladium (II) dichloride (50 mg, 0.072 mmol, 0.02 equiv.), and copper iodide (68 mg, 0.358 mmol, 0.1 equiv.) in degassed THF (36 mL, 0.1 M) at 23 °C was added 3-butyn-2-ol **64** (1.12 mL, 14.3 mmol, 4.0 equiv.) followed by neat diisopropylamine (1.52 mL, 10.7 mmol, 3.0 equiv.). After 1 hour, the reaction mixture was diluted with aq. 0.2 M pH = 7.0 phosphate buffer (30 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (1:1 to 1:2 hexanes:EtOAc) to give pure dimethoxymethyl ether propargyl alcohol **213** (970 mg, 2.90 mmol, 81%) as an amber oil.

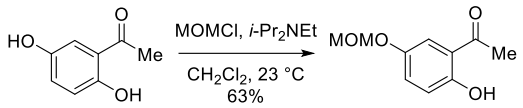
R_f = 0.12 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.82 (s, 1H), 7.20 (s, 1H), 5.33 (s, 2H), 5.30 (s, 2H), 4.79 (q, *J* = 6.7 Hz, 1H), 3.52 (s, 3H), 3.51 (s, 3H), 3.30 (bs, 1H), 1.54 (d, *J* = 6.7 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 174.7, 157.6, 152.7, 152.3, 145.5, 117.8, 110.4, 109.9, 103.9, 97.2, 95.5, 95.1, 74.2, 58.6, 56.6, 56.5, 24.0; **IR** (film, cm^{-1}): 3397, 1621, 1494, 1460, 1266, 1227, 986; **HRMS** (ESI) calc. for $C_{17}H_{18}NaO_7$ $[M+Na]^+$: 357.09447, obs. 357.09487.



6,7-bis(methoxymethoxy)-3-(3-oxbut-1-yn-1-yl)-4*H*-chromen-4-one (**193**)

To a stirred solution of dimethoxymethyl ether propargyl alcohol **213** (973 mg, 2.91 mmol, 1.0 equiv.) and activated 4.0 Å molecular sieves (500 mg, 50% by weight) in CH_2Cl_2 (29 mL, 0.1 M) at 23 °C was added solid pyridinium dichromate (5.47 g, 14.5 mmol, 5.0 equiv.) in one portion. After 5 hours, the black solution was filtered through a pad of Celite and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (5:2:1 CH_2Cl_2:EtOAc:hexanes) to give pure dimethoxymethyl ether ynone **193** (540 mg, 1.63 mmol, 56%) as a white solid (m.p. 119-120 °C).

R*f* = 0.51 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.86 (s, 1H), 7.26 (s, 1H), 5.35 (s, 2H), 5.32 (s, 2H), 3.54 (s, 3H), 3.53 (s, 3H), 2.49 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 184.3, 173.5, 160.7, 153.0, 152.2, 146.0, 117.8, 110.4, 108.1, 104.1, 95.5, 95.2, 93.4, 81.8, 56.7, 56.5, 32.7; **IR** (film, cm^{-1}): 1668, 1640, 1615, 1271, 970; **HRMS** (ESI) calc. for $C_{17}H_{17}O_7$ $[M+H]^+$: 333.09688, obs. 333.09704.

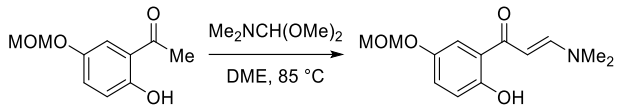


202 214

1-(2-hydroxy-5-(methoxymethoxy)phenyl)ethan-1-one (214)

To a stirred solution of 2',5'-dihydroxyacetophenone **202** (23.9 g, 157 mmol, 1.0 equiv.) in CH_2Cl_2 (780 mL, 0.2 M) at 0 °C was added neat N,N-diisopropylethylamine (41.0 mL, 236 mmol, 1.5 equiv.). A 2.1 M solution of chloromethyl methyl ether in PhMe/MeOAc (112 mL, 236 mmol, 1.5 equiv.) was then added slowly over 20 minutes. Upon complete addition the solution was allowed to warm to 23 °C. After 1 hour, the reaction mixture was diluted with 0.1 N HCl (500 mL) and extracted with CH_2Cl_2 (3 x 500 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (10:1 hexanes:EtOAc) to give pure 5'-methoxymethyl ether **214** (19.4 g, 99.0 mmol, 63%) as a clear yellow oil.

R*f* = 0.40 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 11.92 (s, 1H), 7.40 (d, *J* = 3.1 Hz, 1H), 7.23 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.93 (d, *J* = 9.2 Hz, 1H), 5.13 (s, 2H), 3.50 (s, 3H), 2.62 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 204.1, 157.6, 149.3, 126.5, 119.3, 119.2, 117.1, 95.5, 56.0, 26.8; **IR** (film, cm^{-1}): 1646, 1491, 1150, 994; **HRMS** (ESI) calc. for $C_{10}H_{12}NaO_4$ $[M+Na]^+$: 219.06278, obs. 219.06255.

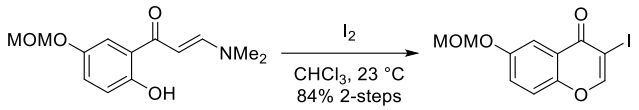


214 **215**

(*E*)-3-(dimethylamino)-1-(2-hydroxy-5-(methoxymethoxy)phenyl)prop-2-en-1-one (**215**)

To a stirred solution of 5'-methoxymethyl ether **214** (17.0 g, 86.4 mmol, 1.0 equiv.) in DME (860 mL, 0.1 M) at 85 °C was added N,N-dimethylformamide dimethyl acetal (45.9 mL, 346 mmol, 4.0 equiv.) in one portion. After 4 hours, the reaction mixture was cooled to 23 °C and concentrated *in vacuo* to give a dark amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give 5'-methoxymethyl ether enaminone **215** (21.7 g, 86.4 mmol, yield taken after subsequent step) as a yellow solid (m.p. 94-95 °C).

$\mathbf{R}_f$ = 0.25 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 12 Hz, 1H), 7.36 (d, *J* = 2.7 Hz, 1H), 7.12 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.87 (d, *J* = 9.2 Hz, 1H), 5.72 (d, *J* = 12 Hz, 1H), 5.12 (s, 2H), 3.50 (s, 3H), 3.20 (bs, 3H), 2.98 (bs, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 191.0, 158.1, 154.9, 148.8, 123.4, 120.2, 118.7, 115.7, 95.7, 90.0, 55.9, 45.4, 37.5; **IR** (film, cm^{-1}): 3420, 1635, 1538, 1269; **HRMS** (ESI) calc. for $C_{13}H_{17}NNaO_4$ $[M+Na]^+$: 274.10498, obs. 274.10491.

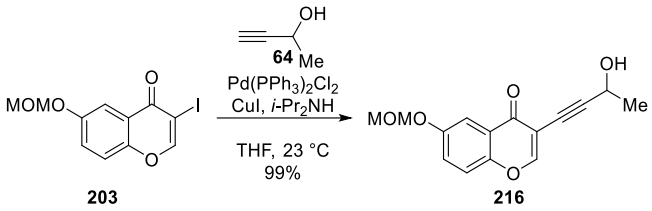


215 **203**

3-iodo-6-(methoxymethoxy)-4*H*-chromen-4-one (**203**)

To a stirred solution of crude 5'-methoxymethyl ether enaminone **215** (21.7 g, 86.4 mmol, 1.0 equiv.) in $CHCl_3$ (860 mL, 0.1 M) at 23 °C was added solid iodine (43.9 g, 173 mmol, 2.0 equiv.) in one portion. After 40 minutes, the solution was diluted with sat. aq. $Na_2S_2O_3$ (500 mL) and extracted with CH_2Cl_2 (500 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a tan solid. The crude material was purified via silica gel column chromatography (3:1 hexanes:EtOAc) to give pure 5'-methoxymethyl ether iodochromone **203** (24.1 g, 72.6 mmol, 84% over 2-steps) as an off-white solid (m.p. 122-123 °C).

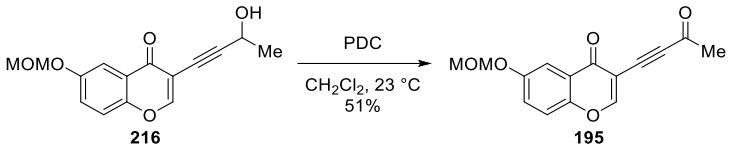
$\mathbf{R}_f$ = 0.19 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.38 (dd, *J* = 9.2, 2.7 Hz, 1H), 5.25 (s, 2H), 3.49 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.6, 161.7, 157.6, 157.3, 128.1, 116.4, 116.2, 102.9, 94.3, 87.0, 56.5; **IR** (film, cm^{-1}): 1641, 1480, 1141; **HRMS** (ESI) calc. for $C_{11}H_9INaO_4$ $[M+Na]^+$: 354.94377, obs. 354.94380.



3-(3-hydroxybut-1-yn-1-yl)-6-(methoxymethoxy)-4*H*-chromen-4-one (216)

To a stirred solution of 5'-methoxymethyl ether iodochromone **203** (1.01 g, 3.04 mmol, 1.0 equiv.), bis(triphenylphosphine) palladium (II) dichloride (43 mg, 0.061 mmol, 0.02 equiv.), and copper iodide (58 mg, 0.304 mmol, 0.1 equiv.) in THF (30 mL, 0.1 M) at 23 °C was added 3-butyn-2-ol **64** (0.95 mL, 12.2 mmol, 4.0 equiv.) followed by neat diisopropylamine (1.29 mL, 9.12 mmol, 3.0 equiv.). After 1 hour, the reaction mixture was diluted with aq. 0.2 M pH = 7.0 phosphate buffer (30 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure 5'-methoxymethyl ether propargyl alcohol **216** (826 mg, 3.01 mmol, 99%) as an amber oil.

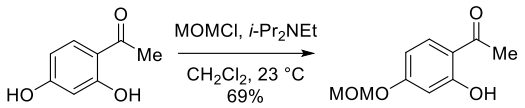
$\mathbf{R_f}$ = 0.30 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.77 (d, *J* = 2.7 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.36 (dd, *J* = 9.0, 2.7 Hz, 1H), 5.24 (s, 2H), 4.79 (q, *J* = 6.7 Hz, 1H), 3.48 (s, 3H), 2.77 (bs, 1H), 1.56 (d, *J* = 6.7 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.5, 157.9, 154.6, 151.2, 124.4, 124.0, 119.5, 109.7, 109.7, 97.6, 94.6, 73.9, 58.4, 56.2, 23.9; **IR** (film, cm^{-1}): 3412, 1646, 1485, 1147; **HRMS** (ESI) calc. for $C_{15}H_{14}NaO_5$ $[M+Na]^+$: 298.07674, obs. 298.07670.



6-(methoxymethoxy)-3-(3-oxbut-1-yn-1-yl)-4*H*-chromen-4-one (195)

To a stirred solution of 5'-methoxymethyl ether propargyl alcohol **216** (650 mg, 2.37 mmol, 1.0 equiv.) and activated 4.0 Å molecular sieves (325 mg, 50% by weight) in CH_2Cl_2 (24 mL, 0.1 M) at 23 °C was added solid pyridinium dichromate (4.46 g, 11.9 mmol, 5.0 equiv.) in one portion. After 5 hours, the black solution was filtered through a pad of Celite and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (3:1 to 2:1 hexanes:EtOAc) to give pure 5'-methoxymethyl ether ynone **195** (330 mg, 1.21 mmol, 51%) as a white solid (m.p. 145-146 °C).

$\mathbf{R}_f$ = 0.65 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.81 (d, *J* = 3.1 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.41 (dd, *J* = 9.2, 3.1 Hz, 1H), 5.26 (s, 2H), 3.49 (s, 3H), 2.50 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 184.2, 174.2, 160.9, 155.1, 151.0, 124.7, 124.2, 119.7, 109.9, 107.8, 94.6, 93.4, 81.5, 56.3, 32.7; **IR** (film, cm^{-1}): 1668, 1485, 1285, 1233; **HRMS** (ESI) calc. for $C_{15}H_{12}NaO_5$ $[M+Na]^+$: 295.05769, obs. 295.05759.

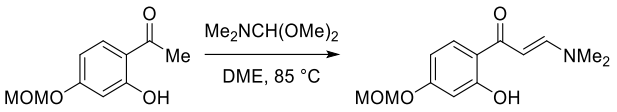


204 **217**

1-(2-hydroxy-4-(methoxymethoxy)phenyl)ethan-1-one (217)

To a stirred solution of 2',4'-dihydroxyacetophenone **204** (9.95 g, 65.4 mmol, 1.0 equiv.) in CH_2Cl_2 (330 mL, 0.2 M) at 0 °C was added neat N,N-diisopropylethylamine (17.1 mL, 98.0 mmol, 1.5 equiv.). A 2.1 M solution of chloromethyl methyl ether in PhMe/MeOAc (46.7 mL, 98.0 mmol, 1.5 equiv.) was then added slowly over 20 minutes. Upon complete addition the solution was allowed to warm to 23 °C. After 1 hour, the reaction mixture was diluted with 0.1 N HCl (300 mL) and extracted with CH_2Cl_2 (3 x 300 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (10:1 hexanes:EtOAc) to give pure 4'-methoxymethyl ether **217** (8.84 g, 45.1 mmol, 69%) as a clear oil.

$\mathbf{R}_f$ = 0.45 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 12.62 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 6.55 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.21 (s, 2H), 3.48 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 202.7, 164.7, 163.5, 132.4, 114.6, 108.1, 103.6, 93.9, 56.3, 26.1; **IR** (film, cm^{-1}): 3406, 1635, 1244, 991; **HRMS** (EC-CI) calc. for $C_{10}H_{13}O_4$ $[M+H]^+$: 197.0814, obs. 197.0814.

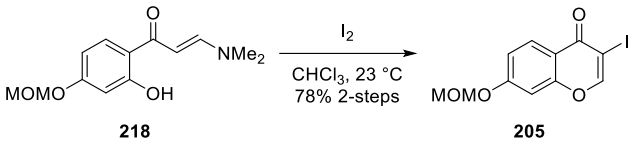


217 **218**

(*E*)-3-(dimethylamino)-1-(2-hydroxy-4-(methoxymethoxy)phenyl)prop-2-en-1-one (**218**)

To a stirred solution of 4'-methoxymethyl ether **217** (8.85 g, 45.1 mmol, 1.0 equiv.) in DME (450 mL, 0.1 M) at 85 °C was added N,N-dimethylformamide dimethyl acetal (24.0 mL, 180 mmol, 4.0 equiv.) in one portion. After 4 hours, the reaction mixture was cooled to 23 °C and concentrated *in vacuo* to give a dark amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give 4'-methoxymethyl ether enaminone **218** (11.3 g, 45.1 mmol, yield taken after subsequent step) as a yellow solid (m.p. 95-96 °C).

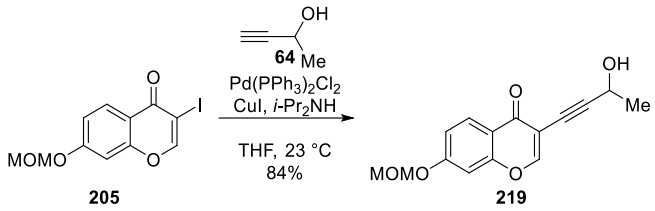
$\mathbf{R}_f$ = 0.25 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 12 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 6.48 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.69 (d, *J* = 12 Hz, 1H), 5.19 (s, 2H), 3.47 (s, 3H), 3.18 (bs, 3H), 2.96 (bs, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 190.4, 165.0, 161.6, 154.1, 129.6, 114.8, 106.9, 103.8, 93.9, 89.6, 56.1, 45.2, 37.2; **IR** (film, cm^{-1}): 1627, 1535, 1235, 1108; **HRMS** (ESI) calc. for $C_{13}H_{17}NNaO_4$ $[M+Na]^+$: 274.10498, obs. 274.10491.



3-iodo-7-(methoxymethoxy)-4*H*-chromen-4-one (**205**)

To a stirred solution of crude 4'-methoxymethyl ether enaminone **218** (11.3 g, 45.1 mmol, 1.0 equiv.) in $CHCl_3$ (450 mL, 0.1 M) at 23 °C was added solid iodine (22.9 g, 90.0 mmol, 2.0 equiv.) in one portion. After 40 minutes, the solution was diluted with sat. aq. $Na_2S_2O_3$ (300 mL) and extracted with CH_2Cl_2 (300 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a tan solid. The crude material was purified via silica gel column chromatography (3:1 hexanes:EtOAc) to give pure 4'-methoxymethyl ether iodochromone **205** (11.69 g, 35.2 mmol, 78% over 2-steps) as a white solid (m.p. 101-102 °C).

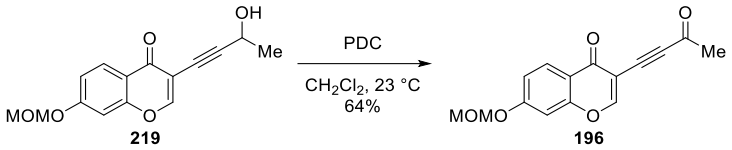
$\mathbf{R}_f$ = 0.28 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.10 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.08 (d, *J* = 2.1 Hz, 1H), 5.27 (s, 2H), 3.50 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.4, 161.6, 157.4, 157.2, 127.8, 116.2, 116.1, 102.8, 94.2, 86.9, 56.4; **IR** (film, cm^{-1}): 1646, 1624, 1149; **HRMS** (ESI) calc. for $C_{11}H_9INaO_4$ $[M+Na]^+$: 354.94377, obs. 354.94436.



3-(3-hydroxybut-1-yn-1-yl)-7-(methoxymethoxy)-4*H*-chromen-4-one (219)

To a stirred solution of 4'-methoxymethyl ether iodochromone **205** (1.00 g, 3.02 mmol, 1.0 equiv.), bis(triphenylphosphine) palladium (II) dichloride (42 mg, 0.060 mmol, 0.02 equiv.), and copper iodide (58 mg, 0.302 mmol, 0.1 equiv.) in THF (30 mL, 0.1 M) at 23 °C was added 3-butyn-2-ol **64** (0.95 mL, 12.1 mmol, 4.0 equiv.) followed by neat diisopropylamine (1.28 mL, 9.06 mmol, 3.0 equiv.). After 1 hour, the reaction mixture was diluted with aq. 0.2 M pH = 7.0 phosphate buffer (30 mL) and extracted with CH_2Cl_2 (30 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure 4'-methoxymethyl ether propargyl alcohol **219** (696 mg, 2.54 mmol, 84%) as an amber oil.

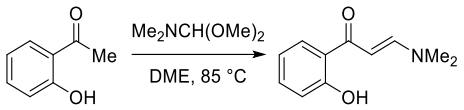
$\mathbf{R_f}$ = 0.28 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.09 (s, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 1.0 Hz, 1H), 5.27 (s, 2H), 4.79 (q, *J* = 6.8 Hz, 1H), 3.50 (s, 3H), 2.43 (bs, 1H), 1.56 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.0, 161.7, 157.8, 157.3, 127.5, 117.8, 115.9, 110.6, 103.1, 97.6, 94.3, 73.9, 58.4, 56.4, 23.9; **IR** (film, cm^{-1}): 3392, 1624, 1249, 1077; **HRMS** (ESI) calc. for $C_{15}H_{14}NaO_5$ $[M+Na]^+$: 297.07334, obs. 297.07349.



7-(methoxymethoxy)-3-(3-oxbut-1-yn-1-yl)-4*H*-chromen-4-one (196)

To a stirred solution of 4'-methoxymethyl ether propargyl alcohol **219** (647 mg, 2.36 mmol, 1.0 equiv.) and activated 4.0 Å molecular sieves (325 mg, 50% by weight) in CH_2Cl_2 (24 mL, 0.1 M) at 23 °C was added solid pyridinium dichromate (4.44 g, 11.8 mmol, 5.0 equiv.) in one portion. After 5 hours, the black solution was filtered through a pad of Celite and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (3:1 to 2:1 hexanes:EtOAc) to give pure 4'-methoxymethyl ether ynone **196** (410 mg, 1.51 mmol, 64%) as a white solid (m.p. 139-141 °C).

R_f = 0.65 (silica gel, 1:1 hexanes:EtOAc**); ^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 5.28 (s, 2H), 3.50 (s, 3H), 2.49 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 183.9, 173.5, 162.0, 160.9, 157.1, 127.3, 117.6, 116.3, 108.3, 103.3, 94.2, 93.2, 81.4, 56.3, 32.5; **IR** (film, cm^{-1}): 1669, 1632, 1255, 1158; **HRMS** (ESI) calc. for $C_{15}H_{12}NaO_5$ $[M+Na]^+$: 295.05769, obs. 295.05778.

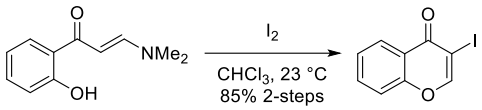


206 **220**

(*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (**220**)

To a stirred solution of 2'-hydroxyacetophenone **206** (2.26 g, 16.6 mmol, 1.0 equiv.) in DME (170 mL, 0.1 M) at 85 °C was added N,N-dimethylformamide dimethyl acetal (8.82 mL, 66.4 mmol, 4.0 equiv.) in one portion. After 4 hours, the reaction mixture was cooled to 23 °C and concentrated *in vacuo* to give a dark amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give 2'-hydroxy enaminone **220** (3.17 g, 16.6 mmol, yield taken after subsequent step) as a yellow solid (m.p. 128-129 °C).

$\mathbf{R_f}$ = 0.24 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 12.0 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.6, 6.8, 1.7 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.82 (ddd, *J* = 8.2, 6.8, 1.0 Hz, 1H), 5.79 (d, J = 12.3 Hz, 1H), 3.20 (s, 3H), 2.98 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 191.3, 162.8, 154.7, 133.8, 128.2, 120.2, 118.0, 117.9, 89.8, 45.3, 37.3; **IR** (film, cm^{-1}): 3425, 1633, 1544, 1489, 1289; **HRMS** (ESI) calc. for $C_{11}H_{14}NO_2$ $[M+H]^+$: 192.10191, obs. 192.10219.

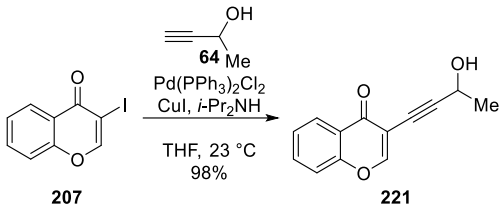


220 **207**

3-iodo-4*H*-chromen-4one (**207**)

To a stirred solution of crude 2'-hydroxy enaminone **220** (3.17 g, 16.6 mmol, 1.0 equiv.) in $CHCl_3$ (170 mL, 0.1 M) at 23 °C was added solid iodine (8.43 g, 33.2 mmol, 2.0 equiv.) in one portion. After 40 minutes, the solution was diluted with sat. aq. $Na_2S_2O_3$ (150 mL) and extracted with CH_2Cl_2 (150 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a tan solid. The crude material was purified via silica gel column chromatography (3:1 hexanes:EtOAc) to give pure unsubstituted iodochromone **207** (3.61 g, 13.3 mmol, 85% over 2-steps) as a white solid (m.p. 89-90 °C).

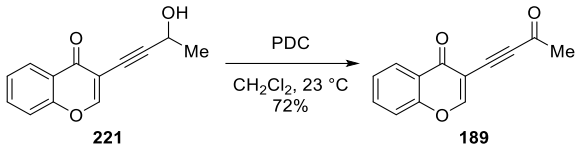
R_f = 0.63 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.25 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 173.2, 157.6, 156.0, 134.0, 126.4, 125.8, 121.6, 117.9, 86.7; **IR** (film, cm^{-1}): 1610, 1462, 1311, 1067, 760; **HRMS** (CI) calc. for $C_9H_6O_2I$ $[M+H]^+$: 272.9413, obs. 272.9411.



3-(3-hydroxybut-1-yn-1-yl)-4*H*-chromen-4-one (**221**)

To a stirred solution of unsubstituted iodochromone **207** (503 mg, 1.85 mmol, 1.0 equiv.), bis(triphenylphosphine) palladium (II) dichloride (26 mg, 0.037 mmol, 0.02 equiv.), and copper iodide (35 mg, 0.185 mmol, 0.1 equiv.) in THF (19 mL, 0.1 M) at 23 °C was added 3-butyn-2-ol **64** (0.58 mL, 7.40 mmol, 4.0 equiv.) followed by neat diisopropylamine (0.78 mL, 5.55 mmol, 3.0 equiv.). After 1 hour, the reaction mixture was diluted with aq. 0.2 M pH = 7.0 phosphate buffer (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (1:1 hexanes:EtOAc) to give pure unsubstituted propargyl alcohol **221** (387 mg, 1.81 mmol, 98%) as an amber solid (m.p. 72-73 °C).

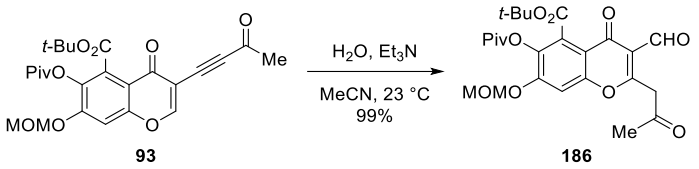
$\mathbf{R}_f$ = 0.20 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.14 (s, 1H), 7.67 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 4.81 (q, *J* = 7.2 Hz, 1H), 3.45 (bs, 1H), 1.56 (d, *J* = 6.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.7, 158.1, 155.9, 134.1, 126.1, 125.8, 123.3, 118.2, 110.6, 97.6, 73.9, 58.6, 24.0; **IR** (film, cm^{-1}): 3393, 1648, 1615, 1466; **HRMS** (ESI) calc. for $C_{13}H_{10}NaO_3$ $[M+Na]^+$: 237.05222, obs. 237.05219.



3-(3-oxobut-1-yn-1-yl)-4*H*-chromen-4-one (198)

To a stirred solution of unsubstituted propargyl alcohol **221** (855 mg, 3.99 mmol, 1.0 equiv.) and activated 4.0 Å molecular sieves (425 mg, 50% by weight) in CH_2Cl_2 (40 mL, 0.1 M) at 23 °C was added solid pyridinium dichromate (7.51 g, 20.0 mmol, 5.0 equiv.) in one portion. After 5 hours, the black solution was filtered through a pad of Celite and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (3:1 to 2:1 hexanes:EtOAc) to give pure unsubstituted ynone **189** (610 mg, 2.87 mmol, 72%) as a white solid (m.p. 122-124 °C).

R_f = 0.43 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.49 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 2.50 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 184.1, 174.4, 161.2, 155.8, 134.6, 126.4, 126.1, 123.4, 118.3, 108.7, 93.5, 81.2, 32.7; **IR** (film, cm^{-1}): 1683, 1651; **HRMS** (ESI) calc. for $C_{13}H_9O_3$ $[M+H]^+$: 213.05462, obs. 213.05462.



***tert*-butyl 3-formyl-7-(methoxymethoxy)-4-oxo-2-(2-oxopropyl)-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (186)**

To a stirred solution of ynone **93** (100 mg, 0.212 mmol, 1.0 equiv.) and H_2O (3.81 mL, 212 mmol, 1000 equiv.) in MeCN (21 mL, 0.01 M) at 23 °C was added triethylamine (0.30 mL, 2.12 mmol, 10 equiv.). After 1 hour, the reaction mixture was diluted with EtOAc (20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give aldehyde **186** (104 mg, 0.212 mmol, 99%) as an amber solid (m.p. 178-179 °C (decomp.)).

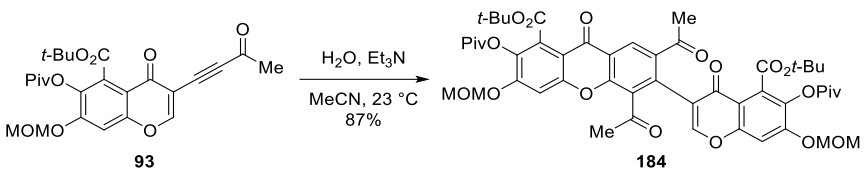
R_f = 0.23 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 10.42 (s, 1H), 7.20 (s, 1H), 5.23 (s, 2H), 4.26 (bs, 2H), 3.45 (s, 3H), 2.38 (s, 3H), 1.64 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 200.0, 190.7, 175.4, 175.0, 168.5, 163.3, 154.5, 153.9, 136.7, 128.2, 117.4, 115.5, 104.1, 94.8, 83.4, 56.6, 47.5, 39.2, 30.4, 28.2, 27.2; **IR** (film, cm^{-1}): 3420, 1762, 1730, 1653, 1595, 1458, 1265, 1157, 1095; **HRMS** (ESI) calc. for $C_{25}H_{30}NaO_{10}$ $[M+Na]^+$: 513.17312, obs. 513.17312.

General Procedure A for Ynone Coupling

To a stirred solution of ynone **XXX** (100 mg, 1.0 equiv.) (Intended xanthone core) and H_2O (1000 equiv.) in MeCN (0.01 M) at 23 °C was added triethylamine (10 equiv.). After 1 hour, the reaction mixture was diluted with EtOAc (20 mL), dried twice over Na_2SO_4, and concentrated *in vacuo* to give crude aldehyde as an amber oil. The crude aldehyde was taken up in MeCN (0.1 M) before adding ynone **XXX** (1.0 equiv.) (Intended chromone core) and triethylamine (2 equiv.) at 23 °C. After 16 hours, the reaction mixture was concentrated *in vacuo* to give a dark amber oil. The crude material was purified via silica gel column chromatography (5:2:1 CH_2Cl_2:EtOAc:hexanes) to give pure protected vinaxanthone analog **XXX**.

General Procedure B for Ynone Coupling

To a stirred solution of ynone **XXX** (100 mg, 1.0 equiv.) in MeCN (0.1 M) at 23 °C was added a 1.0 M solution of H_2O in MeCN (0.5 equiv.) and triethylamine (10 equiv.). After 16 hours, the reaction mixture was concentrated *in vacuo* to give a dark amber residue. The crude material was purified via silica gel column chromatography (5:2:1 CH_2Cl_2:EtOAc:hexanes) to give pure protected vinaxanthone analog **XXX**.

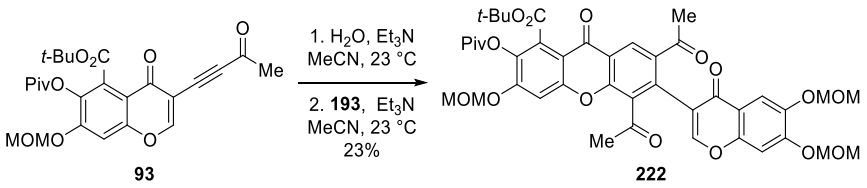


93 184

***tert*-butyl 5,7-diacetyl-6-(5-(*tert*-butoxycarbonyl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromen-3-yl)-3-(methoxymethoxy)-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (184)**

Following general procedure B for ynone coupling, ynone **93** (100 mg, 0.212 mmol, 1.0 equiv.) gave pure protected vinaxanthone **184** (87 mg, 0.092 mmol, 87%) as a white-tan solid (m.p. 224-225 °C).

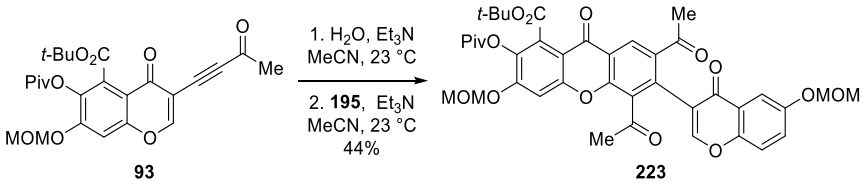
R_f = 0.68 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.62 (bs, 1H), 7.84 (bs, 1H), 7.22 (s, 1H), 7.18 (s, 1H), 5.27 (s, 2H), 5.26 (s, 2H), 3.47 (s, 3H), 3.46 (s, 3H), 2.65 (bs, 3H), 2.41 (bs, 3H), 1.68 (s, 9H), 1.58 (s, 9H), 1.39 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.3, 198.8, 175.4 (2 signals), 173.3 (2 signals), 163.4, 163.3, 155.1, 154.6, 154.5, 154.0, 153.5, 152.6, 136.4 (2 signals), 135.9, 133.9, 132.3, 128.9, 128.2, 126.8, 121.2, 120.7, 115.0, 112.7, 103.9, 103.6, 94.7, 94.6, 83.3, 82.8, 56.7, 56.5, 39.2, 39.1, 32.5, 29.6, 28.1, 28.0, 27.2, 27.1; **IR** (film, cm^{-1}): 1763, 1735 1460, 1264, 1157; **HRMS** (ESI) calc. for $C_{50}H_{56}NaO_{18}$ $[M+Na]^+$: 967.33589, obs. 967.33632.



***tert*-butyl 5,7-diacetyl-6-(6,7-bis(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-3-(methoxymethoxy)-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (222)**

Following general procedure A for ynone coupling, ynone **93** (100 mg, 0.212 mmol, 1.0 equiv.) and ynone **193** (70 mg, 0.212 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **222** (39 mg, 0.049 mmol, 23%) as a yellow solid (m.p. 116-118 °C). Protected vinaxanthone analogs **227** (48 mg, 0.051 mmol, 46%) and **184** (65 mg, 0.097 mmol, 24%) were also isolated.

$\mathbf{R_f}$ = 0.51 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.67 (bs, 1H), 7.98 (s, 1H), 7.84 (bs, 1H), 7.26 (s, 1H), 7.22 (s, 1H), 5.39 (s, 2H), 5.35 (s, 2H), 5.26 (s, 2H), 3.57 (s, 3H), 3.56 (s, 3H), 3.47 (s, 3H), 2.67 (bs, 3H), 2.42 (bs, 3H), 1.58 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.8, 199.0, 175.5, 174.5, 173.5, 163.4, 155.2, 154.2, 153.9, 153.6, 153.1, 152.3, 145.1, 136.4, 134.1, 131.8, 128.2, 126.9, 121.4, 120.6, 115.8, 115.1, 111.4, 110.5, 103.9, 103.8, 95.7, 95.2, 94.7, 82.8, 56.7, 56.6, 56.5, 39.2, 32.5, 28.9, 28.2, 27.3; **IR** (film, cm^{-1}): 1654, 1459, 1268, 1156, 1092; **HRMS** (ESI) calc. for $C_{42}H_{44}NaO_{16}$ $[M+Na]^+$: 827.25220, obs. 827.25320.

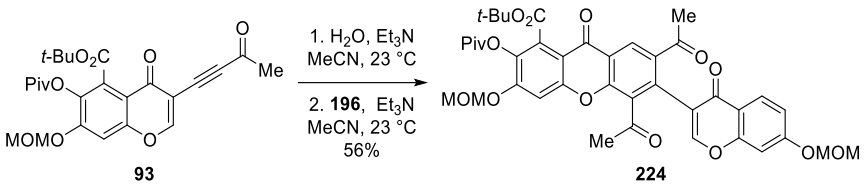


93 223

***tert*-butyl 5,7-diacetyl-3-(methoxymethoxy)-6-(6-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (223)**

Following general procedure A for ynone coupling, ynone **93** (100 mg, 0.212 mmol, 1.0 equiv.) and ynone **195** (58 mg, 0.212 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **223** (93 mg, 0.069 mmol, 44%) as a yellow solid (m.p. 144-145 °C). Protected vinaxanthone analogs **233** (23 mg, 0.042 mmol, 20%) and **184** (24 mg, 0.025 mmol, 12%) were also isolated.

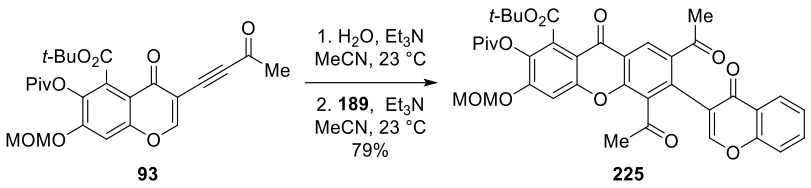
R_f = 0.64 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.68 (bs, 1H), 7.92 (d, *J* = 2.4 Hz, 1H), 7.85 (bs, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.45 (s, 1H), 7.23 (s, 1H), 5.29 (s, 2H), 5.26 (s, 2H), 3.53 (s, 3H), 3.47 (s, 3H), 2.65 (bs, 3H), 2.42 (bs, 3H), 1.58 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 201.7, 198.8, 175.5, 174.8, 173.4, 163.4, 163.2, 157.3, 155.2, 154.0, 153.5, 153.2, 136.4, 136.2, 134.1, 132.1, 128.4, 128.2, 127.0, 121.4, 121.1, 116.2, 115.3, 115.0, 103.9, 103.2, 94.7, 94.4, 82.8, 56.6, 56.5, 39.2, 32.5, 28.8, 28.1, 27.2; **IR** (film, cm^{-1}): 1651,1485, 1455, 1263, 1156, 1094; **HRMS** (ESI) calc. for $C_{40}H_{40}NaO_{14}$ $[M+Na]^+$: 767.23103, obs. 767.23051.



***tert*-butyl 5,7-diacetyl-3-(methoxymethoxy)-6-(7-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (224)**

Following general procedure A for ynone coupling, ynone **93** (100 mg, 0.212 mmol, 1.0 equiv.) and ynone **196** (58 mg, 0.212 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **224** (88 mg, 0.119 mmol, 56%) as a pale off-white solid (m.p. 138-139 °C). Protected vinaxanthone analogs **239** (45 mg, 0.083 mmol, 39%) and **184** (20 mg, 0.021 mmol, 10%) were also isolated.

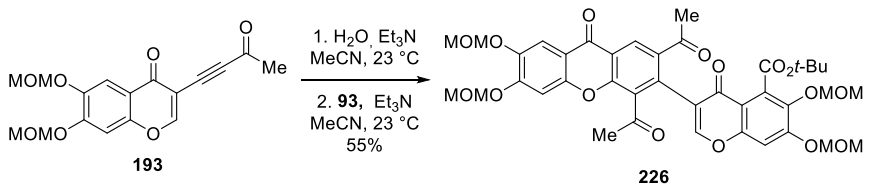
R_f = 0.65 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 8.64 (bs, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.84 (bs, 1H), 7.21 (s, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.06 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.28 (s, 2H), 5.24 (s, 2H), 3.50 (s, 3H), 3.45 (s, 3H), 2.65 (bs, 3H), 2.41 (bs, 3H), 1.56 (s, 9H), 1.36 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.6, 198.8, 175.4, 174.7, 173.4, 163.3, 163.1, 157.3, 155.1, 153.9, 153.5, 153.1, 136.4, 136.0, 134.1, 132.1, 128.4, 128.1, 126.9, 121.3, 121.0, 116.2, 115.3, 115.0, 103.9, 103.1, 94.7, 94.4, 82.7, 56.5 (2 signals), 39.1, 32.4, 28.8, 28.1, 27.2; **IR** (film, cm^{-1}): 1620, 1460, 1262, 1158, 1096; **HRMS** (ESI) calc. for $C_{40}H_{40}NaO_{14}$ $[M+Na]^+$: 767.23103, obs. 767.23148.



***tert*-butyl 5,7-diacetyl-3-(methoxymethoxy)-9-oxo-6-(4-oxo-4*H*-chromen-3-yl)-2-(pivaloyloxy)-9*H*-xanthene-1-carboxylate (225)**

Following general procedure A for ynone coupling, ynone **93** (100 mg, 0.212 mmol, 1.0 equiv.) and ynone **189** (45 mg, 0.212 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **225** (114 mg, 0.167 mmol, 79%) as a pale off-white solid (m.p. 160-162 °C). Protected vinaxanthone analogs **183** (18 mg, 0.042 mmol, 20%) and **184** (6 mg, 6.35 μmol, 3%) were also isolated.

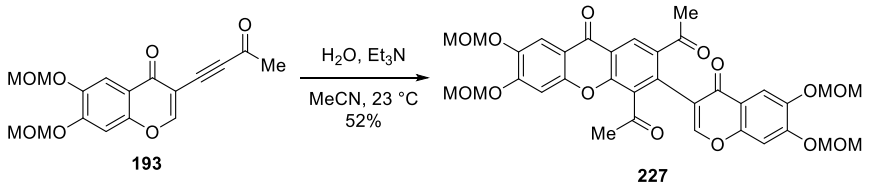
R_f = 0.73 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.69 (bs, 1H), 8.36 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.86 (bs, 1H), 7.79 (ddd, *J* = 8.9, 7.9, 1.7 Hz, 1H), 7.49 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 (ddd, *J* = 8.9, 7.9, 1.7 Hz, 1H), 7.23 (s, 1H), 5.26 (s, 2H), 3.47 (s, 3H), 2.68 (bs, 3H), 2.43 (bs, 3H), 1.58 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.5, 198.8, 175.7, 175.5, 173.4, 163.4, 155.7, 155.2, 154.0, 153.6, 153.2, 136.4, 136.1, 135.6, 134.3, 132.6, 128.2, 127.0, 126.9, 125.1, 121.7, 121.3, 121.0, 118.1, 115.0, 103.9, 94.7, 82.8, 56.6, 39.2, 32.4, 28.9, 28.1, 27.2; **IR** (film, cm^{-1}): 1654, 1460, 1262, 1157, 1093; **HRMS** (ESI) calc. for $C_{38}H_{36}NaO_{12}$ $[M+Na]^+$: 707.20990, obs. 707.20993.



***tert*-butyl 3-(2,4-diacetyl-6,7-bis(methoxymethoxy)-9-oxo-9*H*-xanthen-3-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (226)**

Following general procedure A for ynone coupling, ynone **193** (100 mg, 0.301 mmol, 1.0 equiv.) and ynone **93** (142 mg, 0.301 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **226** (90 mg, 0.166 mmol, 55%) as a yellow solid (m.p. 152-154 °C). Protected vinaxanthone **184** (68 mg, 0.072 mmol, 24%) was also isolated.

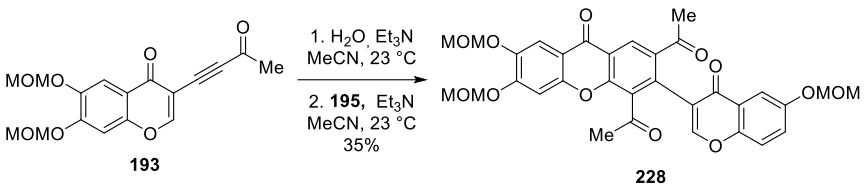
R_f = 0.49 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.26 (s, 1H), 7.19 (s, 1H), 5.37 (s, 2H), 5.32 (d, *J* = 11 Hz, 1H), 5.30 (d, *J* = 11 Hz, 1H), 5.28 (d, *J* = 11 Hz, 1H), 5.26 (d, *J* = 11 Hz, 1H), 3.54 (s, 3H), 3.53 (s, 3H), 3.47 (s, 3H), 2.64 (s, 3H), 2.45 (s, 3H), 1.69 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 201.3, 199.3, 175.5, 174.6, 173.4, 163.5, 154.7, 154.6, 153.9, 152.9, 152.7, 145.6, 136.3, 135.9, 133.9, 133.3, 129.0, 127.4, 122.1, 120.7, 118.1, 112.8, 110.6, 104.1, 103.9, 103.8, 103.7, 95.6, 95.1, 94.8, 83.3, 56.7, 56.5, 39.2, 32.4, 28.9, 28.2, 27.3; **IR** (film, cm^{-1}): 1458, 1155, 1090; **HRMS** (ESI) calc. for $C_{42}H_{44}NaO_{16}$ $[M+Na]^+$: 827.25220, obs. 827.25350.



1,1'-(3-(6,7-bis(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-6,7-bis(methoxymethoxy)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**227**)

Following general procedure B for ynone coupling, ynone **193** (100 mg, 0.301 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **227** (52 mg, 0.078 mmol, 52%) as a yellow solid (m.p. 144-146 °C).

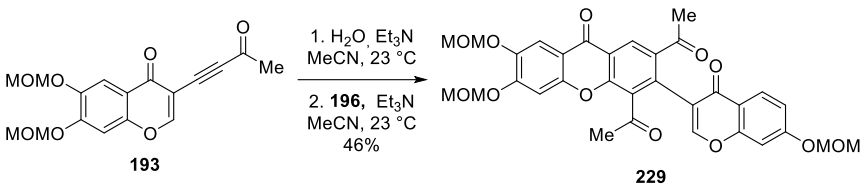
R_f = 0.24 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 7.98 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.26 (s, 1H), 7.23 (s, 1H), 5.38 (s, 2H), 5.37 (s, 2H), 5.35 (s, 2H), 5.32 (d, *J* = 11 Hz, 2H), 5.31 (d, *J* = 11 Hz, 2H), 3.56 (s, 3H), 3.54 (s, 3H), 3.54 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.6, 199.2, 174.7, 174.5, 154.2, 153.8, 153.1, 152.9 (2 signals), 152.3, 145.6, 145.1, 135.8, 134.1, 132.8, 127.4, 121.2, 120.6, 118.1, 115.8, 111.4, 110.6, 104.1, 103.8, 95.7, 95.6, 95.2, 95.1, 56.7, 56.5, (3 signals), 32.4, 28.9; **IR** (film, cm^{-1}): 1618, 1497, 1458, 1269, 1154; **HRMS** (ESI) calc. for $C_{34}H_{32}NaO_{14}$ $[M+Na]^+$: 687.16840, obs. 687.16970.



1,1'-(6,7-bis(methoxymethoxy)-3-(6-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (228)

Following general procedure A for ynone coupling, ynone **193** (100 mg, 0.301 mmol, 1.0 equiv.) and ynone **195** (82 mg, 0.301 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **228** (64 mg, 0.105 mmol, 35%) as a yellow solid (m.p. 134-135 °C). Protected vinaxanthone analog **233** (43 mg, 0.078 mmol, 26%) was also isolated.

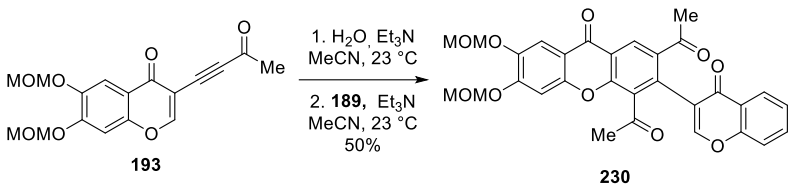
$\mathbf{R}_f$ = 0.39 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.93 (d, *J* = 2.7 Hz, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.45 (d, *J* = 0.7 Hz, 1H), 7.27 (s, 1H), 5.37 (s, 2H), 5.33 (d, *J* = 11 Hz, 1H), 5.31 (d, *J* = 11 Hz, 1H), 5.29 (s, 2H), 3.55 (s, 3H), 3.54 (s, 3H), 3.53 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.5, 199.2, 175.5, 174.6, 154.3, 153.9, 153.2, 152.9 (2 signals), 151.0, 145.6, 135.9, 134.3, 133.4, 127.5, 125.9, 122.3, 121.1, 120.3, 119.5, 118.2, 110.8, 110.6, 104.1, 95.6, 95.2, 94.9, 56.6 (2 signals), 56.3, 32.3, 28.9; **IR** (film, cm^{-1}): 1485, 1456, 1267, 1154; **HRMS** (ESI) calc. for $C_{32}H_{28}NaO_{12}$ $[M+Na]^+$: 627.14730, obs. 627.14810.



1,1'-(6,7-bis(methoxymethoxy)-3-(7-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (229)

Following general procedure A for ynone coupling, ynone **193** (100 mg, 0.301 mmol, 1.0 equiv.) and ynone **196** (82 mg, 0.301 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **229** (84 mg, 0.138 mmol, 46%) as a yellow solid (m.p. 210-212 °C). Protected vinaxanthone analog **239** (44 mg, 0.081 mmol, 27%) was also isolated.

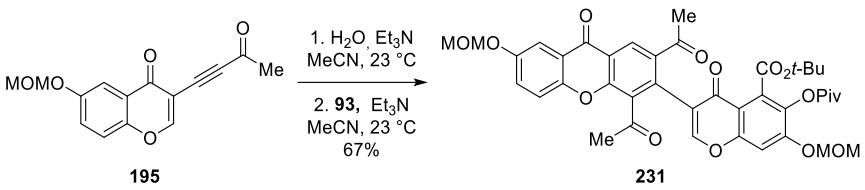
R_f = 0.35 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.28 (d, *J* = 8.9 Hz, 1H), 7.82 (s, 1H), 7.81 (s, 1H), 7.26 (s, 1H), 7.11 (s, 1H), 7.08 (d, *J* = 1.7 Hz, 1H), 5.37 (s, 2H), 5.32 (d, *J* = 11 Hz, 1H), 5.31 (d, *J* = 11 Hz, 1H), 5.30 (s, 2H), 3.54 (s, 3H), 3.53 (s, 3H), 3.52 (s, 3H), 2.65 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.5, 199.2, 174.8, 174.6, 163.2, 157.4, 153.9, 153.3, 152.9 (2 signals), 145.6, 136.0, 134.1, 133.1, 128.5, 127.4, 121.1 (2 signals), 118.2, 116.3, 115.3, 110.6, 104.1, 103.2, 95.6, 95.1, 94.4, 56.5 (3 signals), 32.4, 28.9; **IR** (film, cm^{-1}): 1642, 1621, 1456, 1262, 1155; **HRMS** (ESI) calc. for $C_{32}H_{28}NaO_{12}$ $[M+Na]^+$: 627.14730, obs. 627.14770.



1,1'-(6,7-bis(methoxymethoxy)-9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**230**)

Following general procedure A for ynone coupling, ynone **193** (100 mg, 0.301 mmol, 1.0 equiv.) and ynone **189** (64 mg, 0.301 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **230** (82 mg, 0.150 mmol, 50%) as a yellow solid (m.p. 230-232 °C). Vinaxanthone analog **183** (33 mg, 0.078 mmol, 26%) was also isolated.

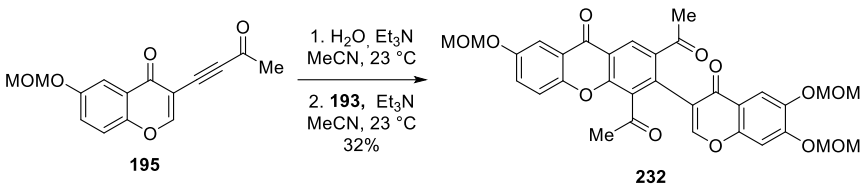
R_f = 0.41 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.37 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.79 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.50 (d, *J* = 6.5 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.27 (s, 1H), 5.37 (s, 2H), 5.33 (d, *J* = 11 Hz, 1H), 5.31 (d, *J* = 11 Hz, 1H), 3.54 (s, 3H), 3.53 (s, 3H), 2.66 (s, 3H), 2.47 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.4, 199.1, 175.7, 174.6, 155.7, 153.9, 153.2, 152.9 (2 signals), 145.6, 136.1, 135.6, 134.3, 133.6, 127.4, 126.9, 125.1, 121.7, 121.1, 121.0, 118.1 (2 signals), 110.6, 104.1, 95.6, 95.1, 56.5 (2 signals), 32.3, 28.9; **IR** (film, cm^{-1}): 1642, 1605, 1461, 1266, 1154; **HRMS** (ESI) calc. for $C_{30}H_{24}NaO_{10}$ $[M+Na]^+$: 567.12620, obs. 567.12720.



***tert*-butyl 3-(2,4-diacetyl-7-(methoxymethoxy)-9-oxo-9*H*-xanthen-3-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (231)**

Following general procedure A for ynone coupling, ynone **195** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **93** (174 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **231** (183 mg, 0.246 mmol, 67%) as a yellow solid (m.p. 120-122 °C). Protected vinaxanthone analogs **184** (42 mg, 0.044 mmol, 12%) and **233** (30 mg, 0.055 mmol, 15%) were also isolated.

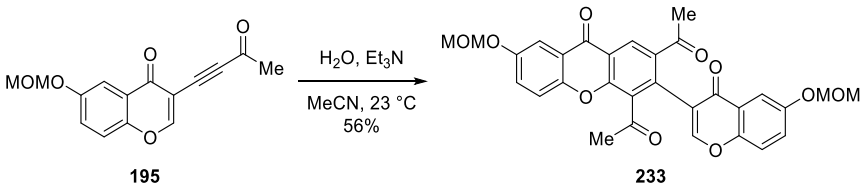
R_f = 0.67 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.87 (s, 1H), 7.77 (d, *J* = 2.7 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.42 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.20 (s, 1H), 5.27 (bs, 2H), 5.26 (d, *J* =12 Hz, 1H), 5.24 (d, *J* = 12 Hz, 1H), 3.50 (s, 3H), 3.47 (s, 3H), 2.65 (s, 3H), 2.45 (s, 3H), 1.69 (s, 9H), 1.40 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 201.3, 199.2, 175.5, 175.3, 173.3, 163.5, 154.7, 154.6, 154.5, 154.3, 152.7, 151.8, 136.1, 135.9, 134.0, 133.1, 128.9, 127.5, 124.8, 124.4, 120.9, 120.7, 119.7, 112.7, 109.9,. 103.7, 94.8, 94.7, 83.4, 56.7, 56.3, 39.2, 32.4, 28.9, 28.2, 27.3; **IR** (film, cm^{-1}): 1483, 1369, 1267, 1155, 1098; **HRMS** (ESI) calc. for $C_{40}H_{40}NaO_{14}$ $[M+Na]^+$: 767.00000, obs. 767.00000.



1,1'-(3-(6,7-bis(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-7-(methoxymethoxy)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (232)

Following general procedure A for ynone coupling, ynone **195** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **193** (122 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **232** (71 mg, 0.118 mmol, 32%) as a yellow solid (m.p. 180-181 °C). Protected vinaxanthone analogs **227** (93 mg, 0.140 mmol, 38%) and **233** (52 mg, 0.095 mmol, 26%) were also isolated.

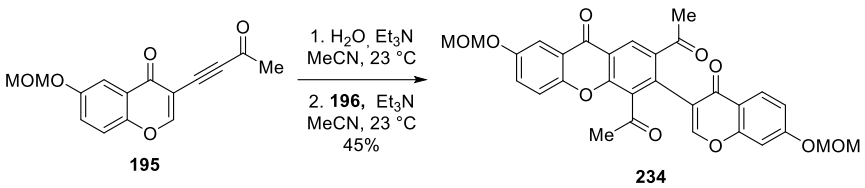
R_f = 0.41 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.99 (s, 1H), 7.87 (s, 1H), 7.77 (d, *J* = 2.7 Hz, 1H), 7.45 (d, *J* = 2.7 Hz, 1H), 7.40 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.23 (s, 1H), 5.39 (s, 2H), 5.36 (s, 2H), 5.26 (d, *J* = 12 Hz, 1H), 5.24 (d, *J* = 13 Hz, 1H), 3.57 (s, 3H), 3.56 (s, 3H), 3.51 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.6, 199.2, 175.4, 174.5, 154.6, 154.2, 153.2, 152.3, 151.8, 145.1, 135.7, 134.2, 132.7, 127.5, 124.7, 124.4, 121.0, 120.6, 119.7, 119.4, 115.9, 111.4, 109.9, 103.8, 95.7, 95.2, 94.7, 56.7, 56.5, 56.3, 32.4, 28.9; **IR** (film, cm^{-1}): 1483, 1461, 1272, 1153; **HRMS** (ESI) calc. for $C_{32}H_{28}NaO_{12}$ $[M+Na]^+$: 627.14730, obs. 627.14630.



1,1'-(7-(methoxymethoxy)-3-(6-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (233)

Following general procedure B for ynone coupling, ynone **195** (100 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **233** (56 mg, 0.103 mmol, 56%) as a pale yellow solid (m.p. 168-169 °C).

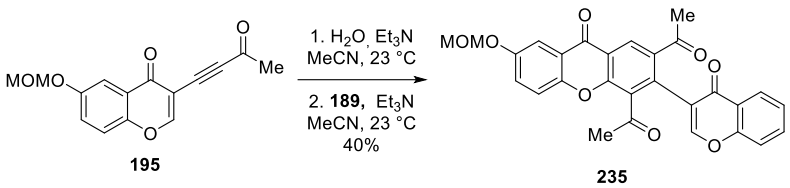
R_f = 0.53 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.88 (s, 1H), 7.77 (d, *J* = 2.7 Hz, 1H), 7.48 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.47 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 2.7 Hz, 1H), 5.29 (s, 2H), 5.26 (d, *J* = 12 Hz, 1H), 5.24 (d, *J* = 12 Hz, 1H), 3.53 (s, 3H), 3.50 (s, 3H), 2.67 (s, 3H), 2.47 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.5, 199.1, 175.5, 175.4, 154.6, 154.2 (2 signals), 153.2, 151.8, 150.9, 135.7, 134.3, 133.2, 127.6, 125.9, 124.8, 124.4, 122.2, 120.9, 120.3, 119.7, 119.5, 110.7, 109.8, 94.8, 94.7, 56.3 (2 signals), 32.3, 28.9; **IR** (film, cm^{-1}): 1652, 1620, 1439, 1254, 1155; **HRMS** (ESI) calc. for $C_{32}H_{28}NaO_{12}$ $[M+Na]^+$: 627.14730, obs. 627.14630.



1,1'-(7-(methoxymethoxy)-3-(7-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (234)

Following general procedure A for ynone coupling, ynone **195** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **196** (100 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **234** (90 mg, 0.165 mmol, 45%) as a yellow solid (m.p. 190-192 °C). Protected vinaxanthone analogs **239** (8 mg, 0.015 mmol, 4%) and **233** (8 mg, 0.015 mmol, 4%) were also isolated.

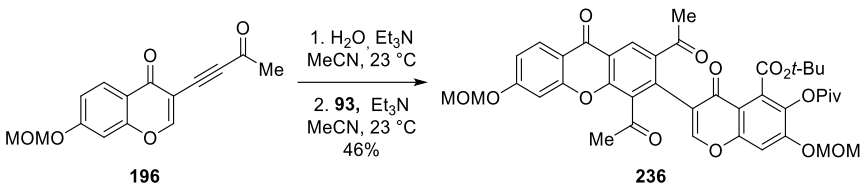
R_f = 0.53 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 7.87 (s, 1H), 7.77 (d, *J* = 2.7 Hz, 1H), 7.45 (s, 1H), 7.40 (d, *J* = 2.7 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 7.09 (s, 1H), 5.30 (s, 2H), 5.26 (d, *J* = 12 Hz, 1H), 5.24 (d, *J* = 13 Hz, 1H), 3.52 (s, 3H), 3.50 (s, 3H), 2.66 (s, 3H), 2.47 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.5, 199.1, 175.4, 174.7, 163.2, 157.3, 154.6, 154.2, 153.3, 151.7, 135.8, 134.2, 133.0, 128.4, 127.5, 124.7, 124.4, 121.1, 120.9, 119.7, 116.2, 115.4, 109.8, 103.2, 94.6, 94.4, 56.5, 56.3, 32.4, 28.9; **IR** (film, cm^{-1}): 16.53, 1643, 1619, 1483, 1153; **HRMS** (ESI) calc. for $C_{30}H_{24}NaO_{10}$ $[M+Na]^+$: 567.12617, obs. 567.12662.



1,1'-(7-(methoxymethoxy)-9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**235**)

Following general procedure A for ynone coupling, ynone **195** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **189** (78 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **235** (71 mg, 0.147 mmol, 40%) as a yellow solid (m.p. 269-270 °C). Protected vinaxanthone analogs **183** (31 mg, 0.073 mmol, 20%) and **233** (36 mg, 0.066 mmol, 18%) were also isolated.

R*f* = 0.54 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.38 (dd, *J* = 9.6, 1.7 Hz, 1H), 7.88 (s, 1H), 7.79 (s, 1H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 5.26 (, *J* = 12 Hz, 1H), 5.24 (d, *J* = 12 Hz, 1H), 3.50 (s, 3H), 2.66 (s, 3H), 2.48 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.4, 199.1, 175.7, 175.4, 155.7, 154.7, 154.3, 153.3, 151.8, 136.0, 135.7, 134.4, 133.5, 127.6, 126.9, 125.2, 124.8, 124.4, 121.7, 121.0, 120.9, 119.7, 118.1, 109.9, 94.7, 56.3, 32.3, 28.9; **IR** (film, cm^{-1}): 1638, 1485, 1465; **HRMS** (ESI) calc. for $C_{28}H_{20}NaO_8$ $[M+Na]^+$: 508.10840, obs. 508.10840.

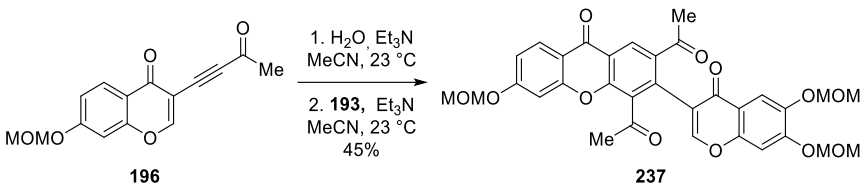


196 236

***tert*-butyl 3-(2,4-diacetyl-6-(methoxymethoxy)-9-oxo-9*H*-xanthen-3-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (236)**

Following general procedure A for ynone coupling, ynone **196** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **93** (174 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **236** (82 mg, 0.169 mmol, 46%) as a pale yellow solid (m.p. 148-149 °C). Protected vinaxanthone analogs **184** (153 mg, 0.162 mmol, 44%) and **239** (50 mg, 0.092 mmol, 25%) were also isolated.

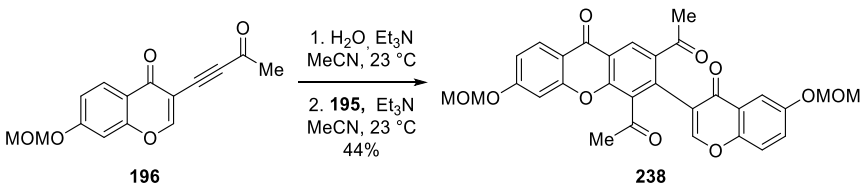
R_f = 0.51 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.82 (s, 1H), 7.19 (s, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.08 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.29 (s, 2H), 5.25 (d, *J* =12 Hz, 1H), 5.26 (d, *J* = 12 Hz, 1H), 3.51 (s, 3H), 3.47 (s, 3H), 2.64 (s, 3H), 2.45 (s, 3H), 1.69 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.2, 199.1, 175.5, 174.9, 173.3, 163.5, 161.9, 157.9, 154.7, 154.6, 154.1, 152.7, 136.3, 135.9, 133.9, 133.1, 129.0, 127.7, 127.4, 121.6, 120.7, 118.3, 115.9, 112.7, 103.7, 103.4, 94.8, 94.3, 83.3, 56.7, 56.4, 39.2, 32.4, 28.9, 28.2, 27.3; **IR** (film, cm^{-1}): 1615, 1463, 1252, 1156, 1091; **HRMS** (ESI) calc. for $C_{40}H_{40}NaO_{14}$ $[M+Na]^+$: 767.23103, obs. 767.23034.



1,1'-(3-(6,7-bis(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-6-(methoxymethoxy)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (237)

Following general procedure A for ynone coupling, ynone **196** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **193** (122 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **237** (80 mg, 0.165 mmol, 45%) as a yellow solid (m.p. 84-85 °C). Protected vinaxanthone analogs **227** (127 mg, 0.191 mmol, 52%) and **239** (6 mg, 0.011 mmol, 3%) were also isolated.

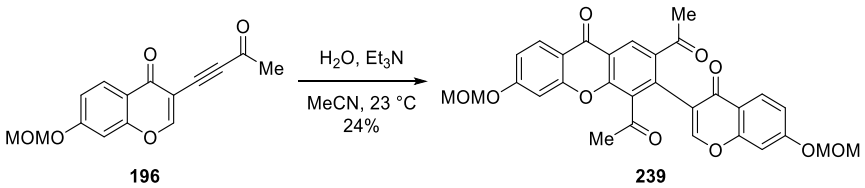
$\mathbf{R}_f$ = 0.33 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 7.99 (s, 1H), 7.81 (s, 1H), 7.23 (s, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.08 (dd, *J* = 8.9, 2.4, 1H), 5.38 (s, 2H), 5.35 (s, 2H), 5.28 (s, 2H), 3.56 (s, 3H), 3.57 (s, 3H), 3.51 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.6, 199.1, 175.1, 174.5, 161.9. 158.0, 154.2, 154.0, 153.2, 152.3, 145.1, 135.8, 134.1, 132.6, 127.8, 127.4, 121.7, 120.6, 118.4, 115.9 (2 signals), 111.4, 103.8, 103.4, 95.7, 95.2, 94.3, 56.7, 56.5, 56.5, 32.4, 28.9; **IR** (film, cm^{-1}): 1619, 1440, 1270, 1254, 1155; **HRMS** (ESI) calc. for $C_{32}H_{28}NaO_{12}$ $[M+Na]^+$: 627.14730, obs. 627.14850.



1,1'-(6-(methoxymethoxy)-3-(6-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (238)

Following general procedure A for ynone coupling, ynone **196** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **195** (100 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **238** (88 mg, 0.162 mmol, 44%) as a yellow solid (m.p. 107-109 °C). Protected vinaxanthone analogs **233** (12 mg, 0.022 mmol, 6%) and **239** (8 mg, 0.015 mmol, 4%) were also isolated.

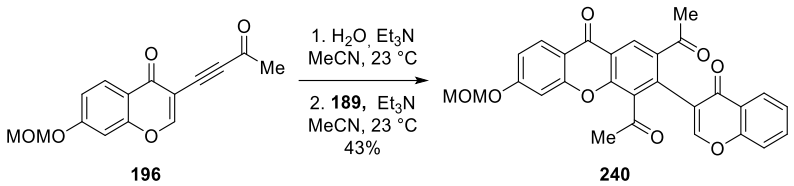
$\mathbf{R}_f$ = 0.42 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 7.93 (d, *J* = 2.1 Hz, 1H), 7.83 (s, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.45 (s, 1H), 7.12 (s, 1H), 7.09 (dd, *J* = 8.9, 2.1 Hz, 1H), 5.29 (s, 2H) (2 signals), 3.53 (s, 3H), 2.46 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.4, 199.1, 175.5, 175.0, 161.9, 157.9, 154.2, 154.0, 153.1, 150.9, 135.8, 134.2, 133.2, 127.7, 127.5, 125.9, 122.2, 121.6, 120.3, 119.4, 118.3, 115.9, 110.7, 103.4, 94.8, 94.3, 56.4, 56.3, 32.3, 28.9; **IR** (film, cm^{-1}): 1647, 1620, 1441, 1254, 1155; **HRMS** (ESI) calc. for $C_{30}H_{24}NaO_{10}$ $[M+Na]^+$: 568.12620, obs. 568.12660.



1,1'-(6-(methoxymethoxy)-3-(7-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (239)

Following general procedure B for ynone coupling, ynone **196** (100 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **239** (24 mg, 0.44 mmol, 24%) as a pale yellow solid (m.p. 215-216 °C).

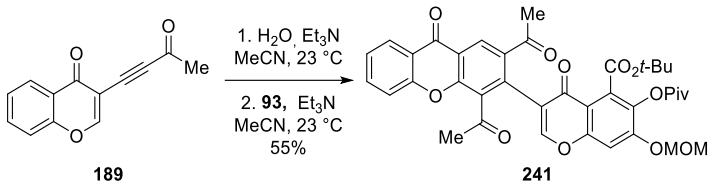
$\mathbf{R}_f$ = 0.50 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.29 (d, *J* = 9.2 Hz, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 7.82 (s, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.31 (s, 2H), 5.29 (s, 2H), 3.52 (s, 3H), 3.51 (s, 3H), 2.66 (s, 3H), 2.47 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 210.5, 199.1, 175.0, 174.7, 163.1, 161.9, 157.9, 157.3, 154.0, 153.2, 135.8, 134.1, 132.9, 128.4, 127.7, 127.4, 121.6, 121.0, 118.3, 116.2, 115.8, 115.3, 103.3, 103.2, 94.4, 94.3, 56.5, 56.4, 32.4, 28.9; **IR** (film, cm^{-1}): 1684, 1636, 1483, 1153; **HRMS** (ESI) calc. for $C_{30}H_{24}NaO_{10}$ $[M+Na]^+$: 567.12617, obs. 567.12611.



1,1'-(6-(methoxymethoxy)-9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**240**)

Following general procedure A for ynone coupling, ynone **196** (100 mg, 0.367 mmol, 1.0 equiv.) and ynone **189** (78 mg, 0.367 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **240** (77 mg, 0.158 mmol, 43%) as a white solid (m.p. 269-270 °C). Protected vinaxanthone analogs **183** (64 mg, 0.151 mmol, 41%) and **239** (44 mg, 0.081 mmol, 22%) were also isolated.

R*f* = 0.50 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.39 (d, *J* = 8.9 Hz, 1H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.83 (s, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.12 (s, 1H), 7.10 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.29 (s, 2H), 3.52 (s, 3H), 2.66 (s, 3H), 2.48 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.5, 199.1, 175.7, 175.4, 155.7, 154.6, 154.3, 153.3, 151.8, 135.9, 135.7, 134.4, 133.5, 127.6, 126.9, 125.2, 124.8, 124.4, 121.7, 121.0, 120.9, 119.7, 118.1, 109.8, 94.7, 56.3, 32.3, 28.9; **IR** (film, cm^{-1}): 1670, 1640, 1484, 1466, 1272, 1152; **HRMS** (ESI) calc. for $C_{28}H_{20}NaO_8$ $[M+Na]^+$: 507.10504, obs. 507.10564.



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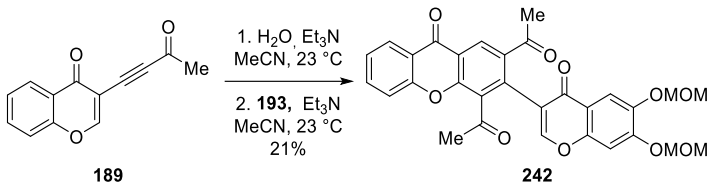
***tert*-butyl 3-(2,4-diacetyl-9-oxo-9*H*-xanthen-3-yl)-7-(methoxymethoxy)-4-oxo-6-(pivaloyloxy)-4*H*-chromene-5-carboxylate (241)**

Following general procedure A for ynone coupling, ynone **189** (100 mg, 0.471 mmol, 1.0 equiv.) and ynone **93** (223 mg, 0.471 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **241** (177 mg, 0.259 mmol, 55%) as a pale yellow solid (m.p. 191-192 °C). Protected vinaxanthone analogs **184** (134 mg, 0.141 mmol, 30%) and **183** (66 mg, 0.156 mmol, 33%) were also isolated.

R_f = 0.64 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.22 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.90 (s, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.45 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.20 (s, 1H), 5.28 (s, 2H), 3.47 (s, 3H), 2.66 (s, 3H), 2.46 (s, 3H), 1.69 (s, 9H), 1.39 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.2, 199.0, 175.6, 175.5, 173.3, 163.5, 156.4, 154.7, 154.6, 154.5, 152.8, 136.1, 135.9, 134.2, 134.0, 133.0, 129.0, 127.5, 126.3, 125.6, 123.7, 121.7, 120.8, 118.3, 112.8, 103.7, 94.8, 83.4, 56.7, 39.2, 32.4, 28.8, 28.2, 27.3; **IR** (film, cm^{-1}): 1652, 1464, 1266, 1157, 1091; **HRMS** (ESI) calc. for $C_{38}H_{36}NaO_{12}$ $[M+Na]^+$: 707.20990, obs. 707.20928.

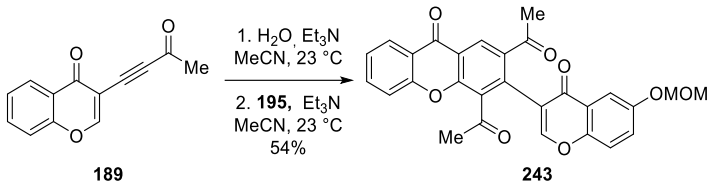


189 242

1,1'-(3-(6,7-bis(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**242**)

Following general procedure A for ynone coupling, ynone **189** (100 mg, 0.471 mmol, 1.0 equiv.) and ynone **193** (157 mg, 0.471 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **242** (54 mg, 0.099 mmol, 21%) as a yellow solid (m.p. 184-185 °C). Protected vinaxanthone analogs **227** (147 mg, 0.221 mmol, 47%) and **183** (88 mg, 0.207 mmol, 44%) were also isolated.

R_f = 0.43 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (500 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.25 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.02 (s, 1H), 7.93 (s, 1H), 7.75 (ddd, *J* = 8.9, 7.9, 1.7 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.47 (ddd, *J* = 8.9, 7.9, 1.7 Hz, 1H), 7.30 (s, 1H), 5.42 (d, *J* = 8.8 Hz, 1H), 5.41 (d, *J* = 9.0 Hz, 1H), 5.39 (s, 2H), 3.60 (s, 3H), 3.59 (s, 3H), 2.70 (s, 3H), 2.50 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.5, 199.0, 175.7, 174.4, 156.4, 154.3, 154.2, 153.2, 152.2, 145.1, 135.6, 134.2, 132.5, 127.5, 126.3, 125.5, 123.7, 121.8, 120.6, 118.3 (2 signals), 115.8, 111.4, 103.8, 95.6, 95.2, 56.7, 56.5, 32.4, 28.8; **IR** (film, cm^{-1}): 1651, 1617, 1462, 1154; **HRMS** (ESI) calc. for $C_{30}H_{24}NaO_{10}$ $[M+Na]^+$: 567.12620, obs. 567.12560.

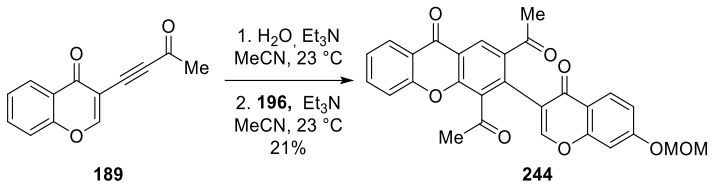


189 243

1,1'-(3-(6-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**243**)

Following general procedure A for ynone coupling, ynone **189** (100 mg, 0.471 mmol, 1.0 equiv.) and ynone **195** (128 mg, 0.471 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **243** (123 mg, 0.254 mmol, 54%) as a pale yellow solid (m.p. 228-229 °C).

$\mathbf{R}_f$ = 0.55 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.90 (s, 1H), 7.73 (ddd, *J* = 8.9, 7.9, 1.7 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 3.1 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.44 (dd, *J* = 3.1, 2.4 Hz, 1H), 5.29 (s, 2H), 3.53 (s, 3H), 2.67 (s, 3H), 2.47 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.5, 199.1, 175.7, 175.5, 156.4, 154.4, 154.3, 153.2, 150.9, 135.6, 134.3, 134.2, 133.1, 127.7, 126.3, 126.0, 125.6, 123.7, 122.2, 121.8, 120.4, 119.4, 118.4, 110.7, 94.8, 56.3, 32.3, 28.9; **IR** (film, cm^{-1}): 1652, 1616, 1483, 1464, 1354, 1270; **HRMS** (ESI) calc. for $C_{28}H_{20}NaO_8$ $[M+Na]^+$: 507.10504, obs. 507.10527.

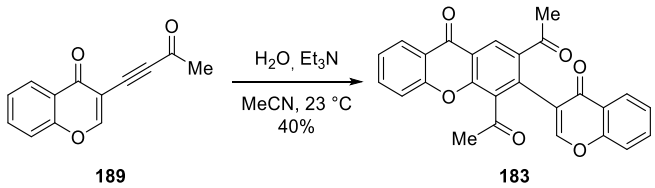


189 244

1,1'-(3-(7-(methoxymethoxy)-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**244**)

Following general procedure A for ynone coupling, ynone **189** (100 mg, 0.471 mmol, 1.0 equiv.) and ynone **196** (123 mg, 0.471 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **244** (48 mg, 0.099 mmol, 21%) as a pale yellow solid (m.p. 198-199 °C).

$\mathbf{R}_f$ = 0.52 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.29 (d, *J* = 8.9 Hz, 1H), 8.23 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.90 (s, 1H), 7.73 (ddd, *J* = 8.9, 7.2, 1.7 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.45 (ddd, *J* = 8.9, 7.2, 1.7 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.31 (s, 2H), 3.53 (s, 3H), 2.67 (s, 3H), 2.48 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.5, 199.0, 175.7, 174.7, 163.2, 157.3, 156.4, 154.3, 153.3, 135.7, 134.2 (2 signals), 132.8, 128.4, 127.6, 126.3, 125.5, 123.6, 121.7, 121.1, 118.3, 116.2, 115.4, 103.1, 94.3, 56.5, 32.4, 28.8; **IR** (film, cm^{-1}): 1653, 1618, 1466, 1253; **HRMS** (ESI) calc. for $C_{28}H_{20}NaO_8$ $[M+Na]^+$: 507.10504, obs. 507.10510.



1,1'-(9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (183)

Following general procedure B for ynone coupling, ynone **189** (100 mg, 0.471 mmol, 1.0 equiv.) gave pure protected vinaxanthone analog **183** (40 mg, 0.094 mmol, 40%) as a white solid (m.p. 264 °C (decomp.)).

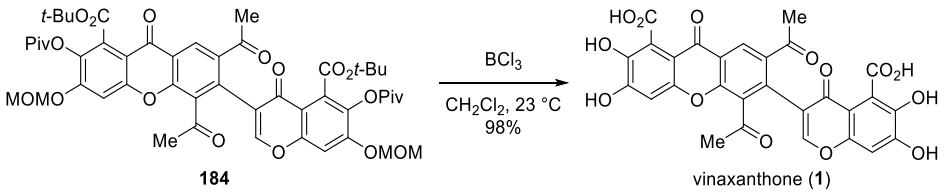
R_f = 0.58 (silica gel, 5:2:1 CH_2Cl_2:EtOAc:hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.37 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.90 (s, 1H), 7.79 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.73 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H), 7.42-7.53 (m, 4H), 2.67 (s, 3H), 2.49 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.4, 199.0, 175.7 (2 signals), 156.4, 155.7, 154.4, 153.3, 135.8, 135.7, 134.4, 134.2, 133.3, 127.6, 126.9, 126.3, 125.6, 125.2, 123.7, 121.7, 121.6, 121.0, 118.3, 118.1, 32.3, 28.9; **IR** (film, cm^{-1}): 1709, 1684, 1639, 1464; **HRMS** (ESI) calc. for $C_{26}H_{16}NaO_6$ $[M+Na]^+$: 447.08391, obs. 447.08391.

General Procedure A for Deprotection

To a stirred solution of protected vinaxanthone analog **XXX** (20 mg, 1.0 equiv.) in CH_2Cl_2 (0.1 M) at 0 °C was added a 1.0 M solution of boron trichloride in CH_2Cl_2 (2.0 equiv. per protecting group). After 1 hour, the reaction mixture was diluted with EtOAc and washed with brine (5x). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give a brown/black solid. The crude material was purified by trituration with pentane:MeOH (ratio varies depending on substrate solubility) to give pure vinaxanthone analog **XXX**.

General Procedure B for Deprotection

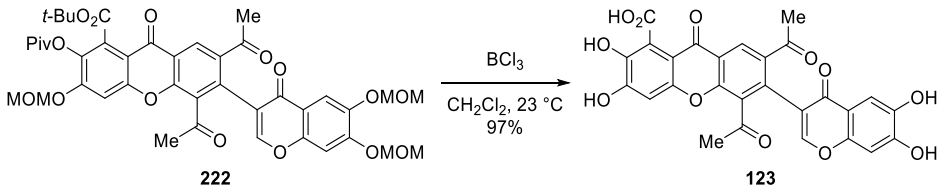
A solution of protected vinaxanthone analog **XXX** (20 mg, 1.0 equiv.) in 1.25 M methanolic HCl (10 equiv. per protected group) was stirred at 65 °C. The reaction was followed by aliquot ^{1}H-NMR. After 8 hours, the reaction mixture was purged with N_2 in order to remove residual gaseous HCl and concentrated *in vacuo* to give a white/magenta solid. The crude material was purified by trituration with pentane:MeOH (ratio varies depending on substrate solubility) to give pure vinaxanthone analog **XXX**.



vinaxanthone (**1**)

Following general procedure A for deprotection, protected vinaxanthone **184** (20 mg, 0.021 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.25 mL, 0.254 mmol, 12 equiv.) to give pure vinaxanthone (**1**) (12 mg, 0.021 mmol, 98%) as a yellow solid (m.p. 280 °C (decomp.)).

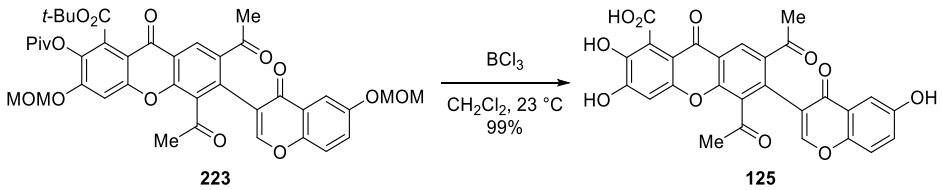
$\mathbf{R}_f$ = 0.05 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.89 (bs, 1H), 12.72 (bs, 1H), 11.69 (bs, 1H), 11.44 (bs, 1H), 9.42 (bs, 2H), 8.53 (s, 1H), 8.18 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 2.55 (s, 3H), 2.53 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.1, 172.9, 172.6, 167.4, 167.4, 154.1, 152.7, 152.5, 152.1, 150.7, 150.3, 141.7, 141.0, 136.2, 133.4, 132.6, 126.3, 120.8, 120.5, 119.8, 119.6, 112.4, 110.0, 102.4, 102.3, 32.1, 29.1; **IR** (KBr, cm^{-1}): 3236, 1683, 1653, 1472, 1288; **HRMS** (ESI) calc. for $C_{28}H_{15}O_{14}$ $[M–H]^–$: 575.04673, obs. 575.04679.



5,7-diacetyl-6-(6,7-dihydroxy-4-oxo-4*H*-chromen-3-yl)-2,3-dihydroxy-9-oxo-9*H*-xanthene-1-carboxylic acid (123)

Following general procedure A for deprotection, protected vinaxanthone analog **222** (20 mg, 0.025 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.25 mL, 0.249 mmol, 10 equiv.) to give pure vinaxanthone analog **123** (13 mg, 0.024 mmol, 97%) as a tan solid (m.p. 248-250 °C (decomp.)).

R_f = 0.14 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.73 (bs, 1H), 11.47 (bs, 1H), 10.87 (bs, 1H), 9.98 (bs, 1H), 9.44 (bs, 1), 8.57 (s, 1H), 8.17 (s, 1H), 7.48 (s, 1H), 6.96 (s, 1H), 6.95 (s, 1H), 2.54 (s, 3H), 2.50 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.2, 199.2, 173.4, 172.9, 167.4, 154.4, 152.7, 152.6, 152.5, 150.8, 150.7, 144.5, 144.7, 136.1, 133.6, 132.4, 126.3, 120.9, 119.8, 119.6, 113.5, 112.5, 108.7, 103.1, 102.3, 32.1, 29.1; **IR** (KBr, cm^{-1}): 3219, 1470, 1196, 803; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{12}$ $[M-H]^-$: 531.05690, obs. 531.05700.

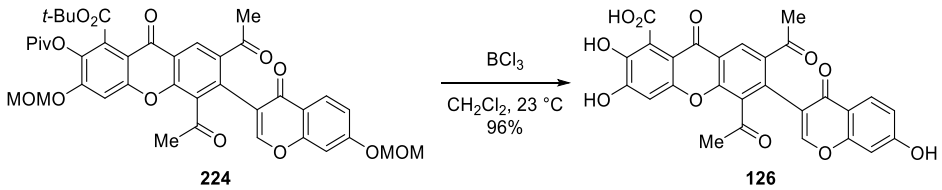


223 125

5,7-diacetyl-2,3-dihydroxy-6-(6-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-1-carboxylic acid (**125**)

Following general procedure A for deprotection, protected vinaxanthone analog **223** (20 mg, 0.027 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.22 mL, 0.215 mmol, 8 equiv.) to give pure vinaxanthone analog **125** (14 mg, 0.027 mmol, 99%) as a light brown solid (m.p. 258-260 °C (decomp.)).

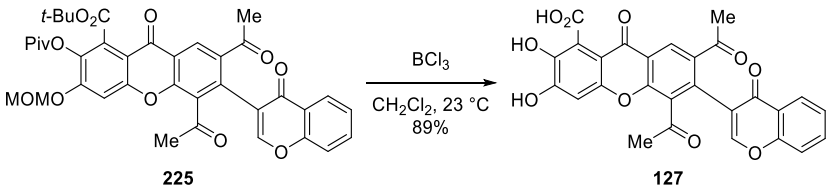
R_f = 0.24 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.69 (bs, 1H), 11.42 (s, 1H), 10.13 (s, 1H), 9.42 (s, 1H), 8.60 (s, 1H), 8.17 (s, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.51 (d, *J* = 3.1 Hz, 1H), 7.36 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.96 (s, 1H), 2.57 (s, 3H), 2.55 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.1, 174.9, 172.8, 167.3, 154.6, 152.8, 152.6, 152.5, 150.7, 148.9, 141.7, 136.3, 133.8, 133.2, 126.4, 124.9, 121.7, 120.8, 119.8, 199.6, 199.5, 112.4, 108.6, 102.3, 32.1, 29.1; **IR** (KBr, cm^{-1}): 3403, 1653, 1464, 1230; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{11}$ $[M-H]^-$: 515.06200, obs. 515.06180.



5,7-diacetyl-2,3-dihydroxy-6-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-1-carboxylic acid (**126**)

Following general procedure A for deprotection, protected vinaxanthone analog **224** (20 mg, 0.027 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.22 mL, 0.215 mmol, 8 equiv.) to give pure vinaxanthone analog **126** (13 mg, 0.026 mmol, 96%) as a tan solid (m.p. 254-255 °C (decomp.)).

R_f = 0.31 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.70 (bs, 1H), 11.42 (bs, 1H), 11.15 (bs, 1H), 9.42 (bs, 1H), 8.57 (s, 1H), 8.17 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.96 (s, 1H), 6.92 (s, 1H), 2.56 (s, 3H), 2.54 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.2, 173.6, 172.8, 167.3, 164.6, 157.2, 152.7, 152.6, 152.5, 150.7, 141.7, 136.5, 133.6, 132.8, 128.1, 126.2, 120.8, 120.3, 119.6, 114.9, 113.8, 112.4, 102.5, 102.3, 32.1, 29.2; **IR** (KBr, cm^{-1}): 3381, 1618, 1466, 1274; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{11}$ $[M-H]^-$: 515.06198, obs. 515.06245.

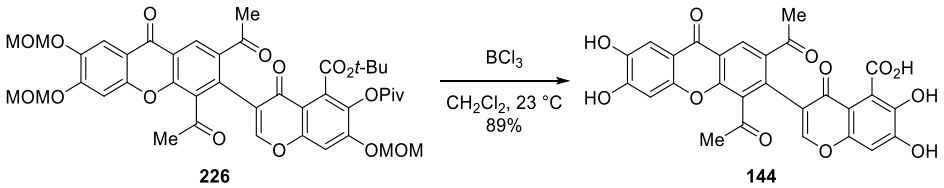


225 127

5,7-diacetyl-2,3-dihydroxy-9-oxo-6-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-1-carboxylic acid (**127**)

Following general procedure A for deprotection, protected vinaxanthone analog **225** (20 mg, 0.029 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.18 mL, 0.175 mmol, 6 equiv.) to give pure vinaxanthone analog **127** (13 mg, 0.026 mmol, 89%) as a tan solid (m.p. 263-265 °C (decomp.)).

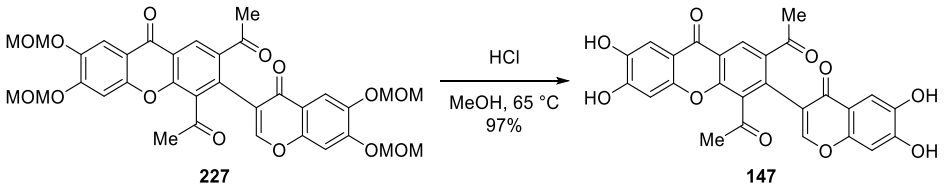
$\mathbf{R}_f$ = 0.45 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 8.61 (s, 1H), 8.24 (d, *J* = 7.2 Hz, 1H), 8.19 (s, 1H), 7.93 (t, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 6.96 (s, 1H), 2.59 (s, 3H), 2.56 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 199.2, 175.1, 172.8, 167.3, 155.3, 152.8, 152.7, 152.6, 150.7, 151.7, 136.7, 136.1, 133.8, 133.5, 126.3, 126.0, 125.3, 121.1, 120.7, 120.2, 119.6, 118.5, 112.4, 102.3, 32.1, 29.2; **IR** (KBr, cm^{-1}): 3395, 1668, 1464, 1279, 1101; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{10}$ $[M–H]^–$: 499.06710, obs. 499.06690.



3-(2,4-diacetyl-6,7-dihydroxy-9-oxo-9*H*-xanthen-3-yl)-6,7-dihydroxy-4-oxo-4*H*-chromene-5-carboxylic acid (144)

Following general procedure A for deprotection, protected vinaxanthone analog **226** (20 mg, 0.025 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.25 mL, 0.249 mmol, 10 equiv.) to give pure vinaxanthone analog **144** (12 mg, 0.022 mmol, 89%) as a tan solid (m.p. 225-226 °C (decomp.)).

R_f = 0.13 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 11.71 (bs, 1H), 10.59 (bs, 1), 9.92 (bs, 1H), 9.44 (bs, 1H), 8.55 (s, 1H), 8.15 (s, 1H), 7.28 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 2.55 (s, 3H), 2.53 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 199.0, 173.5, 172.6, 167.3, 154.0, 152.9, 152.8, 152.1, 151.0, 150.2, 144.9, 140.9, 135.9, 133.2, 132.9, 126.4, 120.6, 120.5, 119.7, 115.7, 110.0, 107.9, 102.9, 102.4, 32.2, 29.1; **IR** (KBr, cm^{-1}): 3393, 1624, 1577, 1466, 1290; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{12}$ $[M-H]^-$: 531.05690, obs. 531.05690.

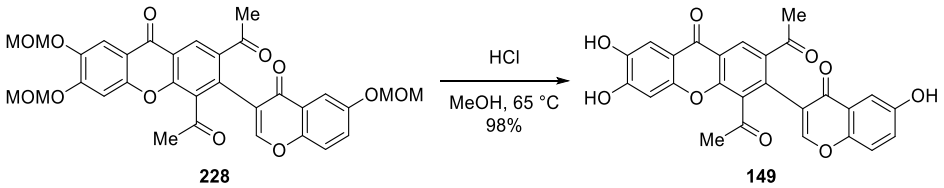


227 147

1,1'-(3-(6,7-dihydroxy-4-oxo-4*H*-chromen-3-yl)-6,7-dihydroxy-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (147)

Following general procedure B for deprotection, protected vinaxanthone analog **227** (20 mg, 0.030 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.96 mL, 1.20 mmol, 40 equiv.) to give pure vinaxanthone analog **147** (14 mg, 0.029 mmol, 97%) as a magenta solid (m.p. 290 °C (decomp.)).

R_f = 0.24 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.83 (bs, 1H), 10.55 (bs, 1H), 9.93 (bs, 2H), 8.58 (s, 1H), 8.12 (s, 1H), 7.49 (s, 1H), 7.28 (s, 1H), 6.94 (s, 1H), 6.93 (s, 1H), 2.55 (s, 3H), 2.53 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.0, 173.6, 173.3, 154.3, 152.8 (2 signals), 152.4, 151.0, 150.6, 144.9, 144.5, 139.8, 135.8, 133.5, 132.7, 162.3, 120.7, 119.7, 115.7, 113.4, 108.6, 107.9, 102.9, 32.2, 29.1; **IR** (KBr, cm^{-1}): 3382, 1617, 1473, 1292; **HRMS** (ESI) calc. for $C_{26}H_{15}O_{10}$ $[M-H]^-$: 487.06707, obs. 487.06709.

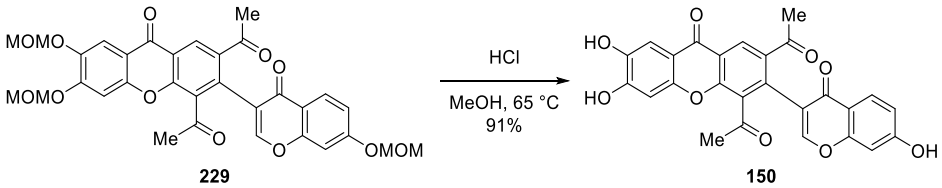


228 149

1,1'-(6,7-dihydroxy-3-(6-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (**149**)

Following general procedure B for deprotection, protected vinaxanthone analog **228** (20 mg, 0.033 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.79 mL, 0.992 mmol, 30 equiv.) to give pure vinaxanthone analog **149** (15 mg, 0.032 mmol, 98%) as a magenta solid (m.p. 208-210 °C (decomp.)).

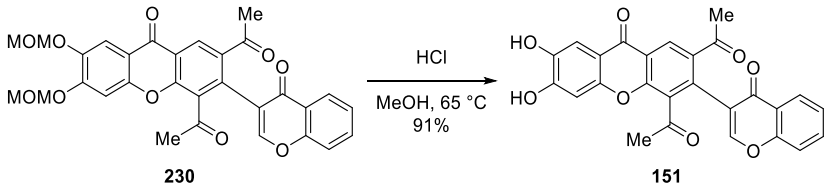
R_f = 0.07 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.56 (bs, 1H), 10.12 (bs, 1H), 9.89 (bs, 1H), 8.61 (s, 1H), 8.14 (s, 1H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 3.1 Hz, 1H), 7.35 (dd, *J* = 9.2, 3.1 Hz, 1H), 7.29 (s, 1H), 6.94 (s, 1H), 2.56 (s, 3H), 2.55 (s, 3H); **^{13}C-NMR** (150 MHz, $(CD_3)_2SO$): δ 201.1, 199.1, 174.9, 173.6, 154.7, 153.0, 152.9, 152.7, 151.2, 148.9, 145.0, 136.0, 133.8, 133.6, 126.6, 124.9, 121.7, 120.7, 119.9, 119.5, 115.8, 108.6, 107.9, 102.9, 32.3, 29.2; **IR** (KBr, cm^{-1}): 3403, 1627, 1567, 1257, 1231; **HRMS** (ESI) calc. for $C_{26}H_{16}NaO_9$ $[M+Na]^+$: 495.06865, obs. 495.06958.



1,1'-(6,7-dihydroxy-3-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (150)

Following general procedure B for deprotection, protected vinaxanthone analog **229** (20 mg, 0.033 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.79 mL, 0.992 mmol, 30 equiv.) to give pure vinaxanthone analog **150** (14 mg, 0.030 mmol, 91%) as a magenta solid (m.p. 218-220 °C (decomp.)).

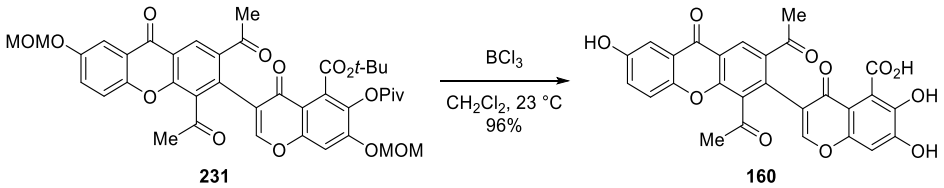
R_f = 0.09 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 11.17 (bs, 1H), 10.59 (bs, 1H), 9.91 (bs, 1H), 8.58 (s, 1H), 8.14 (s, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.29 (s, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 2.55 (s, 3H), 2.54 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 199.0, 173.5, 164.5, 157.2, 152.9, 152.8, 152.6, 151.1, 144.9, 136.2, 133.5, 133.2, 128.0, 126.3, 120.6, 120.3, 115.7, 114.9, 113.8, 107.9, 102.9, 102.5, 100.0, 32.2, 29.1; **IR** (KBr, cm^{-1}): 3406, 1617, 1560, 1466, 1273; **HRMS** (ESI) calc. for $C_{26}H_{15}O_9$ $[M–H]^–$: 471.07216, obs. 471.07279.



1,1'-(6,7-dihydroxy-9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (151)

Following general procedure B for deprotection, protected vinaxanthone analog **230** (20 mg, 0.037 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.59 mL, 0.735 mmol, 20 equiv.) to give pure vinaxanthone analog **151** (15 mg, 0.033 mmol, 91%) as a magenta solid (m.p. 204 °C (decomp.)).

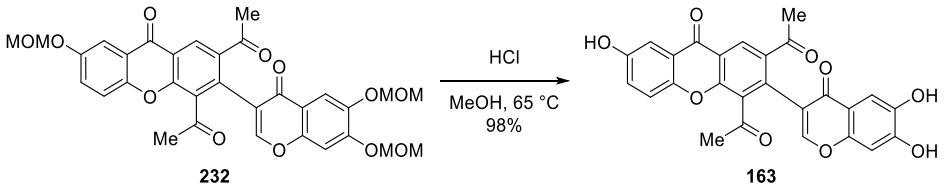
R_f = 0.09 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.58 (bs, 1H), 9.90 (bs, 1H), 8.63 (s, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.16 (s, 1H), 7.93 (t, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.29 (s, 1H), 6.94 (s, 1H), 2.58 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (150 MHz, $(CD_3)_2SO$): δ 201.0, 199.1, 175.1, 173.6, 155.3, 153.0, 152.9, 152.8, 151.1, 145.0, 136.5, 136.1, 133.9, 133.8, 126.4, 126.0, 125.3, 121.1, 120.6, 120.2, 118.5, 115.7, 107.9, 102.9, 32.3, 29.2; **IR** (KBr, cm^{-1}): 3371, 1654, 1617, 1467, 1288, 1221; **HRMS** (ESI) calc. for $C_{26}H_{15}O_8$ $[M-H]^-$: 455.07724, obs. 455.07791.



3-(2,4-diacetyl-7-hydroxy-9-oxo-9*H*-xanthen-3-yl)-6,7-dihydroxy-4-oxo-4*H*-chromene-5-carboxylic acid (**160**)

Following general procedure A for deprotection, protected vinaxanthone analog **231** (20 mg, 0.027 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.22 mL, 0.215 mmol, 8 equiv.) to give pure vinaxanthone analog **160** (13 mg, 0.026 mmol, 96%) as a brick red solid (m.p. 278-280 °C (decomp.)).

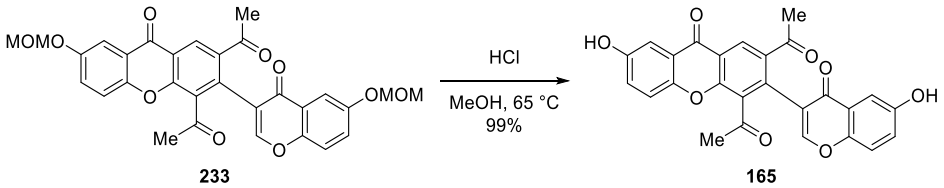
R_f = 0.08 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.85 (bs, 1H), 11.68 (bs, 1H), 10.10 (bs, 1H), 9.42 (bs, 1H), 8.60 (s, 1H), 8.28 (s, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.32 (s, 1H), 7.29 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.95 (s, 1H), 2.57 (s, 3H), 2.55 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.0, 174.6, 172.6, 167.4, 155.1, 154.1, 153.8, 152.3, 150.3, 149.6, 141.0, 135.6, 133.5, 132.7, 126.9, 123.8, 123.7, 120.9, 120.6, 120.0, 119.9, 110.1, 107.8, 102.4, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3221, 1634, 1505, 1471; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{11}$ $[M–H]^-$: 515.06198, obs. 515.06275.



1,1'-(3-(6,7-dihydroxy-4-oxo-4*H*-chromen-3-yl)-7-hydroxy-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (163)

Following general procedure B for deprotection, protected vinaxanthone analog **232** (20 mg, 0.033 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.79 mL, 0.992 mmol, 30 equiv.) to give pure vinaxanthone analog **163** (15 mg, 0.032 mmol, 98%) as a brown solid (m.p. 189-190 °C (decomp.)).

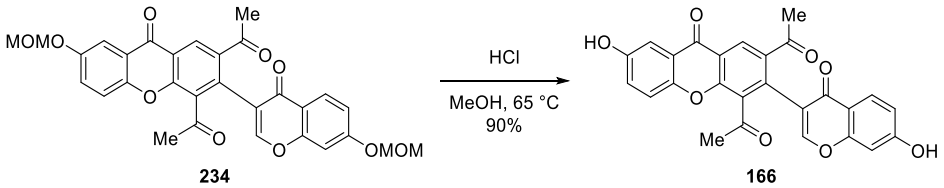
R_f = 0.32 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.88 (bs 1H), 10.14 (bs, 1H), 9.98 (bs, 1H), 8.63 (s, 1H), 8.28 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.49 (s, 1H), 7.31 (s, 1H), 7.30 (d, *J* = 9.2 Hz, 1H), 6.96 (s, 1H), 2.58 (s, 3H), 2.55 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.2, 198.8, 175.6, 173.3, 155.1, 154.4, 153.7, 152.6, 150.7, 149.6, 144.6, 135.5, 133.7, 132.5, 126.8, 125.0, 123.8, 123.6, 120.9, 119.9, 113.5, 108.7, 107.8, 103.1, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3415, 1684, 1618, 1472; **HRMS** (ESI) calc. for $C_{26}H_{15}O_9$ $[M-H]^-$: 471.07216, obs. 471.07236.



1,1'-(7-hydroxy-3-(6-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (165)

Following general procedure B for deprotection, protected vinaxanthone analog **233** (20 mg, 0.037 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.59 mL, 0.735 mmol, 20 equiv.) to give pure vinaxanthone analog **165** (17 mg, 0.036 mmol, 99%) as a yellow solid (m.p. 286 °C (decomp.)).

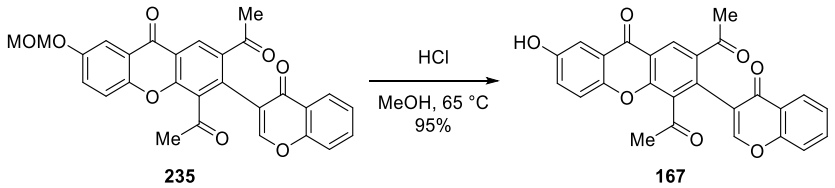
R_f = 0.13 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 11.15 (s, 1H), 10.94 (s, 1H), 8.62 (s, 1H), 8.19 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 6.97 (dt, *J* = 9.6, 2.1 Hz, 2H), 6.91 (t, *J* = 3.1 Hz, 2H), 2.58 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (150 MHz, $(CD_3)_2SO$): δ 201.1, 198.9, 174.9, 174.5, 155.1, 154.6, 153.7, 152.8, 149.5, 148.9, 135.6, 133.9, 133.3, 126.9, 124.9, 123.8, 123.6, 121.7, 120.8, 119.9, 119.8, 119.6, 108.6, 107.8, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3419, 1622, 1267; **HRMS** (ESI) calc. for $C_{26}H_{16}NaO_8$ $[M+Na]^+$: 479.07374, obs. 479.07401.



1,1'-(7-hydroxy-3-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (166)

Following general procedure B for deprotection, protected vinaxanthone analog **234** (20 mg, 0.037 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.59 mL, 0.735 mmol, 20 equiv.) to give pure vinaxanthone analog **166** (15 mg, 0.033 mmol, 90%) as a golden yellow solid (m.p. 262-264 °C (decomp.)).

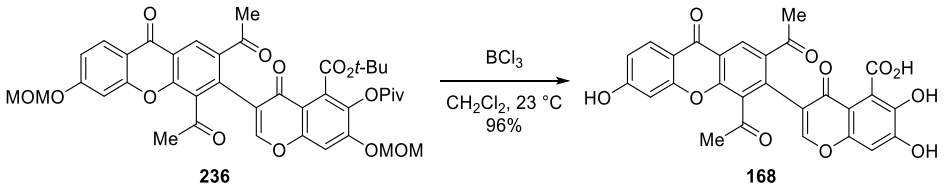
R_f = 0.16 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 11.19 (s, 1H), 10.14 (s, 1H), 8.63 (s, 1H), 8.30 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.32 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.93 (s, 1H), 2.59 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 199.1, 174.6, 173.6, 164.6, 157.3, 155.1, 153.8, 152.8, 149.6, 135.9, 133.7, 133.0, 128.1, 126.8, 123.9, 123.7, 120.9, 120.5, 119.9, 115.0, 113.9, 107.8, 102.6, 32.3, 29.2; **IR** (KBr, cm^{-1}): 3393, 1617, 1469, 1270; **HRMS** (ESI) calc. for $C_{26}H_{15}O_8$ $[M–H]^–$: 455.07720, obs. 455.07670.



1,1'-(7-hydroxy-9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (167)

Following general procedure B for deprotection, protected vinaxanthone analog **235** (20 mg, 0.041 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.33 mL, 0.413 mmol, 10 equiv.) to give pure vinaxanthone analog **167** (17 mg, 0.039 mmol, 95%) as a brick red solid (m.p. 180 °C (decomp.)).

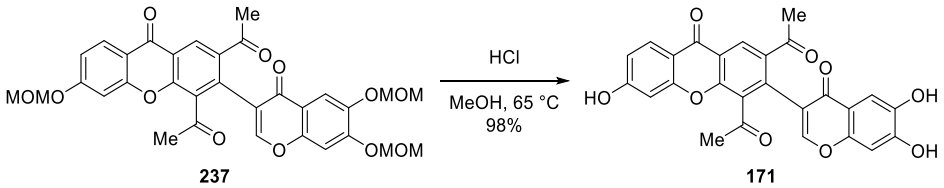
R_f = 0.42 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.11 (s, 1H), 8.68 (s, 1H), 8.31 (s, 1H), 8.26 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.94 (dt, *J* = 8.6, 1.7 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 7.29 (d, *J* = 1.4 Hz, 1H), 2.60 (s, 3H) (2 signals); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 199.0, 175.0, 174.5, 155.3, 155.1, 153.8, 152.9, 149.5, 136.1 (2 signals), 133.9, 133.6, 126.8, 126.0, 125.3, 123.8, 123.7, 121.1, 120.7, 120.4, 119.9, 118.5, 107.8, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3393, 1685, 1654, 1617, 1466; **HRMS** (ESI) calc. for $C_{26}H_{15}O_7$ $[M–H]^–$: 439.08233, obs. 439.08235.



3-(2,4-diacetyl-6-hydroxy-9-oxo-9*H*-xanthen-3-yl)-6,7-dihydroxy-4-oxo-4*H*-chromene-5-carboxylic acid (**168**)

Following general procedure A for deprotection, protected vinaxanthone analog **236** (20 mg, 0.027 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.22 mL, 0.215 mmol, 8 equiv.) to give pure vinaxanthone analog **168** (13 mg, 0.026 mmol, 96%) as a yellow solid (m.p. 208-210 °C (decomp.)).

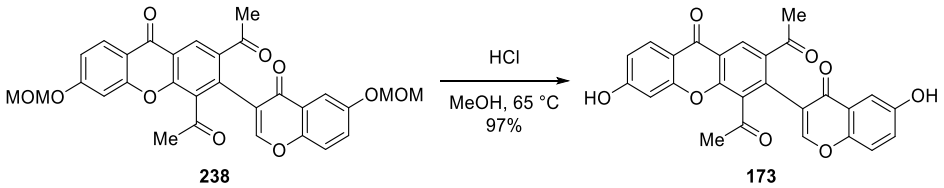
R_f = 0.09 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 11.72 (bs, 1H), 10.96 (bs, 1H), 9.42 (bs, 1H), 8.58 (s, 1H), 8.19 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.93 (s, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 2.57 (s, 3H), 2.55 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 198.9, 173.8, 172.5, 167.3, 163.0, 157.6, 154.0, 153.2, 152.2, 150.2, 140.9, 135.6, 133.3, 132.6, 127.2, 126.6, 121.6, 120.5, 119.8, 115.7, 115.4, 110.0, 102.4, 102.2, 32.2, 29.0; **IR** (KBr, cm^{-1}): 3385, 1624, 1459, 1290, 1101; **HRMS** (ESI) calc. for $C_{27}H_{15}O_{11}$ $[M-H]^-$: 515.061989, obs. 515.06236.



1,1'-(3-(6,7-dihydroxy-4-oxo-4*H*-chromen-3-yl)-6-hydroxy-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (171)

Following general procedure B for deprotection, protected vinaxanthone analog **237** (20 mg, 0.033 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.79 mL, 0.992 mmol, 30 equiv.) to give pure vinaxanthone analog **171** (15 mg, 0.032 mmol, 98%) as a magenta solid (m.p. 208-210 °C (decomp.)).

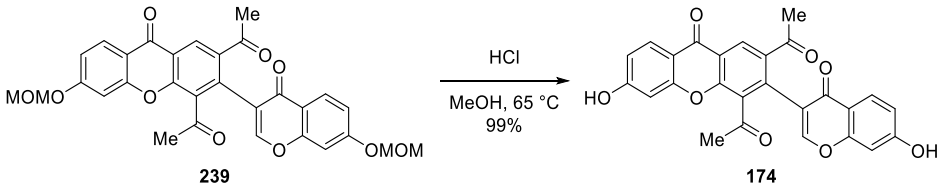
$\mathbf{R}_f$ = 0.06 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.97 bs, 1H), 10.86 (bs, 1H), 9.98 (bs, 1H), 8.62 (s, 1H), 8.19 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.48 (s, 1H), 6.96 (d, *J* = 9.2 Hz, 1H), 6.95 (s, 1H), 6.91 (s, 1H), 2.57 (s, 3H), 2.55 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.2, 199.0, 173.9, 173.3, 163.1, 157.7, 154.4, 153.2, 152.5, 150.7, 144.5, 135.6, 133.6, 132.4, 127.3, 126.6, 121.7, 119.9, 115.8, 115.4, 113.5, 108.7, 103.1, 102.3, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3299, 1624, 1470, 1295; **HRMS** (ESI) calc. for $C_{26}H_{15}O_9$ $[M-H]^-$: 471.07216, obs. 471.07231.



1,1'-(6-hydroxy-3-(6-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (173)

Following general procedure B for deprotection, protected vinaxanthone analog **238** (20 mg, 0.037 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.59 mL, 0.735 mmol, 20 equiv.) to give pure vinaxanthone analog **173** (16 mg, 0.036 mmol, 97%) as a golden yellow solid (m.p. 318-320 °C (decomp.)).

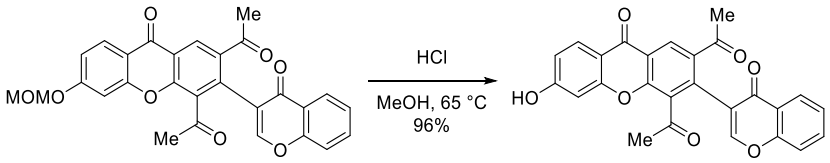
R_f = 0.15 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.98 (bs, 1H), 10.16 (bs, 1H), 8.64 (s, 1H), 8.20 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 3.1 Hz, 1H), 7.35 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.91 (d, *J* = 2.1 Hz, 1H), 2.59 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 198.9, 174.9, 173.9, 163.1, 157.7, 154.7, 153.3, 152.8, 148.9, 135.7, 133.8, 133.2, 127.3, 126.8, 124.9, 121.7, 121.6, 119.8, 119.6, 115.8, 115.5, 108.6, 102.3, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3382, 1630, 1595, 1465, 1266, 1238; **HRMS** (ESI) calc. for $C_{26}H_{15}O_8$ $[M–H]^–$: 455.07724, obs. 455.07768.



1,1'-(6-hydroxy-3-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (174)

Following general procedure B for deprotection, protected vinaxanthone analog **239** (20 mg, 0.037 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.59 mL, 0.735 mmol, 20 equiv.) to give pure vinaxanthone analog **174** (17 mg, 0.036 mmol, 99%) as a tan solid (m.p. 340 °C (decomp.)).

R_f = 0.16 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (500 MHz, $(CD_3)_2SO$): δ 11.14 (s, 1H), 10.93 (s, 1H), 8.61 (s, 1H), 8.19 (s, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 6.91 (s, 1H), 6.91 (s, 1H), 6.98 (ddd, *J* = 11, 7.2, 2.0 Hz, 2H), 2.57 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 199.0, 173.9, 173.6, 164.5, 163.1, 157.7, 157.2, 153.3, 152.8, 136.0, 133.6, 132.9, 128.1, 127.3, 126.6, 121.6, 120.5, 115.8, 115.5, 114.9, 113.8, 102.5, 102.3, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3351, 1619, 1468, 1002; **HRMS** (ESI) calc. for $C_{26}H_{16}NaO_8$ $[M+Na]^+$: 479.07374, obs. 479.07433.

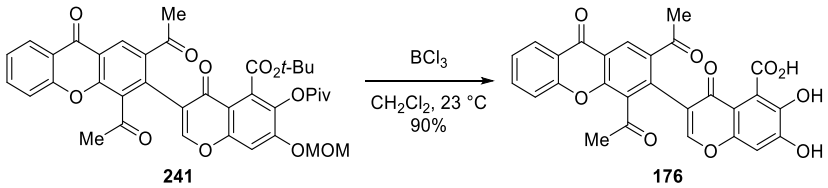


240 175

1,1'-(6-hydroxy-9-oxo-3-(4-oxo-4*H*-chromen-3-yl)-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (175)

Following general procedure B for deprotection, protected vinaxanthone analog **240** (20 mg, 0.041 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.33 mL, 0.413 mmol, 10 equiv.) to give pure vinaxanthone analog **175** (17 mg, 0.040 mmol, 96%) as a golden yellow solid (m.p. 180-182 °C (decomp.)).

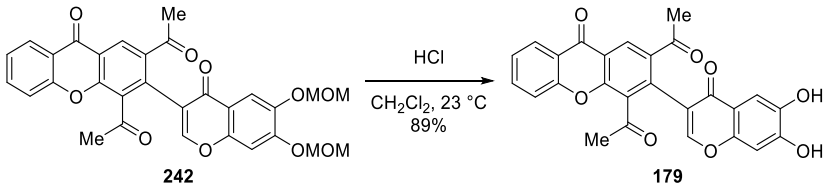
R_f = 0.35 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.97 (bs, 1H), 8.67 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 8.22 (s, 1H), 7.94 (t, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.57 (t, *J* = 8.9 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 2.60 (s, 3H) (2 signals); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.0, 199.0, 175.0, 173.9, 163.1, 157.7, 155.3, 153.4, 152.8, 136.2, 136.1, 133.8, 133.5, 127.3, 126.7, 126.0, 125.3, 121.5, 121.1, 120.4, 118.5, 115.8, 115.5, 102.3, 32.3, 29.2; **IR** (KBr, cm^{-1}): 3438, 1617, 1466, 1097; **HRMS** (ESI) calc. for $C_{26}H_{15}O_7$ $[M-H]^-$: 439.08233, obs. 439.08252.



3-(2,4-diacetyl-9-oxo-9*H*-xanthen-3-yl)-6,7-dihydroxy-4-oxo-4*H*-chromene-5-carboxylic acid (176)

Following general procedure A for deprotection, protected vinaxanthone analog **241** (20 mg, 0.029 mmol, 1.0 equiv.) was treated with 1.0 M boron trichloride (0.18 mL, 0.175 mmol, 6 equiv.) to give pure vinaxanthone analog **176** (13 mg, 0.026 mmol, 90%) as a brick red solid (m.p. 260 °C (decomp.)).

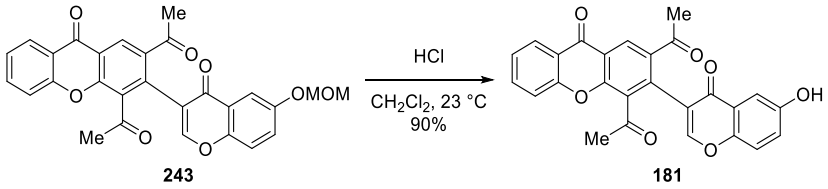
R_f = 0.16 (silica gel, 20:1 EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 12.88 (bs, 1H), 11.69 (bs, 1H), 9.42 (bs, 1H), 8.63 (s, 1H), 8.36 (s, 1H), 8.09 (d, *J* = 6.8 Hz, 1H), 7.89 (t, *J* = 6.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 8.2 Hz, 1H), 6.96 (s, 1H), 2.59 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 198.8, 174.8, 172.6, 167.4, 155.8, 154.1, 153.9, 152.4, 150.2, 141.0, 135.3, 134.7, 133.5, 132.4, 127.1, 125.8, 125.4, 122.9, 122.2, 120.6, 120.1, 118.5, 110.1, 102.4, 32.3, 29.0; **IR** (KBr, cm^{-1}): 3415, 1617, 1577, 1560, 1465, 1290; **HRMS** (ESI) calc. for $C_{27}H_{15}NaO_{10}$ $[M–H]^–$: 499.06707, obs. 499.06808.



1,1'-(3-(6,7-dihydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (179)

Following general procedure B for deprotection, protected vinaxanthone analog **242** (20 mg, 0.037 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.59 mL, 0.735 mmol, 20 equiv.) to give pure vinaxanthone analog **179** (15 mg, 0.033 mmol, 89%) as a magenta solid (m.p. 184-185 °C (decomp.)).

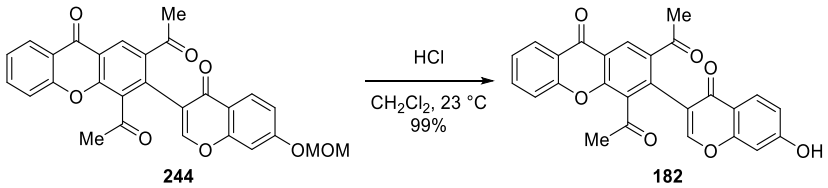
R_f = 0.13 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.85 (bs, 1H), 9.97 (bs, 1H), 8.66 (s, 1H), 8.35 (s, 1H), 8.08 (d, *J* = 7.0 Hz, 1H), 7.89 (t, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49 (s, 1H), 6.96 (s, 1H), 2.60 (s, 3H), 2.57 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.2, 198.9, 174.8, 173.3, 155.8, 154.4, 153.9, 152.7, 150.7, 144.6, 135.2, 134.7, 133.7, 132.2, 127.0, 125.8, 125.4, 122.9, 122.2, 120.0, 118.5, 113.5, 108.7, 103.1, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3159, 1618, 1467, 1294; **HRMS** (ESI) calc. for $C_{26}H_{15}O_8$ $[M–H]^–$: 455.07724, obs. 455.07746.



1,1'-(3-(6-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (181)

Following general procedure B for deprotection, protected vinaxanthone analog **243** (20 mg, 0.041 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.33 mL, 0.413 mmol, 10 equiv.) to give pure vinaxanthone analog **181** (17 mg, 0.037 mmol, 90%) as a tan solid (m.p. 317-318 °C (decomp.)).

R_f = 0.17 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$): δ 10.14 (s, 1H), 8.70 (s, 1H), 8.37 (s, 1H), 8.09 (d, *J* = 6.7 Hz, 1H), 7.89 (t, *J* = 6.7 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.55 (t, *J* = 6.7 Hz, 1H), 7.52 (d, *J* = 3.1 Hz, 1H), 7.37 (dd, *J* = 9.0, 3.1 Hz, 1H), 2.61 (s, 3H), 2.59 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 198.9, 174.9, 174.7, 155.8, 154.7, 153.9, 152.9, 148.9, 135.4, 134.8, 133.9, 133.0, 127.2, 125.9, 125.4, 124.9, 122.9, 122.1, 121.7, 119.9, 119.7, 118.5, 108.6, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3204, 1626, 1599, 1464; **HRMS** (ESI) calc. for $C_{26}H_{16}NaO_7$ $[M+Na]^+$: 463.07882, obs. 463.07889.



1,1'-(3-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)-9-oxo-9*H*-xanthene-2,4-diyl)bis(ethan-1-one) (182)

Following general procedure B for deprotection, protected vinaxanthone analog **244** (20 mg, 0.041 mmol, 1.0 equiv.) was treated with 1.25 M methanolic HCl (0.33 mL, 0.413 mmol, 10 equiv.) to give pure vinaxanthone analog **182** (19 mg, 0.041 mmol, 99%) as a tan solid (m.p. 270 °C (decomp.)).

R_f = 0.38 (silica gel, 10:10:1 hexanes:EtOAc:AcOH); **^{1}H-NMR** (500 MHz, $(CD_3)_2SO$): δ 11.18 (bs, 1H), 8.67 (s, 1H), 8.37 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 1.6 Hz, 1H), 7.89 (t, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.55 (t, *J* = 8.6 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 2.60 (s, 3H), 2.59 (s, 3H); **^{13}C-NMR** (125 MHz, $(CD_3)_2SO$): δ 201.1, 198.9, 174.7, 173.6, 164.6, 157.3, 155.8, 153.9, 152.9, 135.6, 134.8, 133.7, 132.7, 128.1, 127.0, 125.9, 125.4, 122.9, 122.1, 120.6, 118.5, 115.0, 113.8, 102.6, 32.3, 29.1; **IR** (KBr, cm^{-1}): 3391, 1385, 1093; **HRMS** (ESI) calc. for $C_{26}H_{16}NaO_7$ $[M+Na]^+$: 463.07882, obs. 463.07865.

Chapter 2: Total Synthesis of Eupalinilide E

Within the field of regenerative medicine strategies to chemically control stem cell fate and developmental potential have emerged as promising treatments for a variety of human diseases.[144-146] Stem cells are adaptable precursors with the capacity for self-renewal and differentiation toward various cell types in response to instructive cues.[147,148] Pluripotent embryonic stem cells possess the ability to generate any of the more than 200 different cell types responsible for the make-up of an adult organism.[149-151] Tissue-specific stem cells on the other hand are multipotent, giving rise to all cell types limited to a given lineage and are referred to as adult or somatic stem cells. Adult stem cells are also persistent throughout the lifetime of an organism and play a critical role in maintaining homeostasis by providing a physiological mechanism for tissue repair.[147,152-156]

Significant therapeutic research in this area hinges on the development of embryonic stem cell transplantation-based treatments.[157] However, despite the reported efficacies of such therapies, the ability to manipulate embryonic stem cells *ex vivo* is plagued by issues of mutation, immune rejection, and ethical controversy.[158-161] An alternative approach to circumvent such disadvantages is the utilization of small drug-like molecules to directly modulate endogenous adult stem cells *in vivo* or to expand somatic stem cell populations *ex vivo* for transplantation.

Since the success rate of bone marrow transplants is directly correlated to the number of available hematopoietic stem cells (HSCs), the ability to control HSC expansion and differentiation in this manner would be extremely beneficial. Due to a shortage of clinically available HSCs nearly 50% of allogeneic bone marrow transplant candidates fail to find a matched donor.[162,163] HSCs are the only stem cells used routinely in cell-based therapies and are the most well characterized class of somatic stem cells.[157] Residing in the bone marrow HSCs can self-renew and are responsible for the production of all blood lineages.[164,165] Therefore the

ability to manipulate HSC fate has great potential in the development of therapies for various blood-related diseases such as leukemia and autoimmune diseases.

To this end several small molecules possessing the ability to promote HSC self-renewal *in vitro* have been identified (Figure 2.1). The histone deacetylase (HDAC) inhibitors chlamydocin **245** and trichostatin A **246** as well as 5-azacytidine **247**, a DNA methyltransferase inhibitor are capable of expanding HSCs, however their clinical use is limited due to narrow concentration ranges devoid of cytotoxicity.[166,167] A more promising approach using the Cu^{2+} chelator tetra-ethylene-pentamine (TEPA, **248**) is already being tested in a Phase II/III clinical trial involving blood transplantation for hematological malignancies.[168,169] Furthermore, the monoamine neurotransmitter, serotonin **249** has shown the ability to expand HSCs at near physiological concentration (200 nM).[170] Despite their encouraging results, the modes of action by which chelated copper and serotonin **249** operate remain unclear. Schultz and co-workers have also identified the synthetic adenine derivative stremregenin1 (SR1) **250** as a promoter of HSC expansion and discovered that it functions through antagonism of the aryl hydrocarbon receptor (AhR).[171] More recently, the pyrimidoindole derivative UM 171 **251** has shown similar HSC self-renewal capabilities by upregulating the genes associated with human LT-HSC self-renewal.[172]

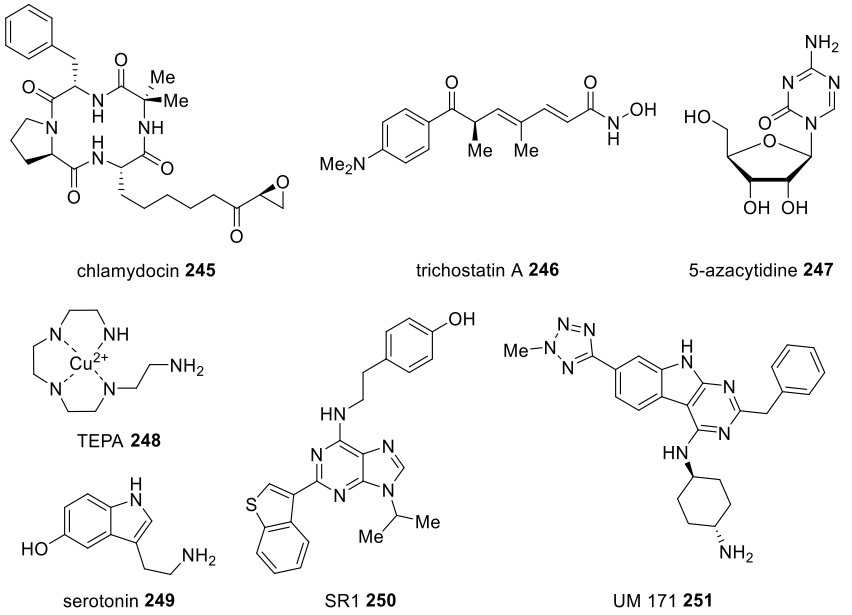


Figure 2.1. Small-molecule modulators of HSC self-renewal.

In regards to HSC differentiation, a class of naphthyridinones **252** have demonstrated the ability to dose-dependently increase megakaryocyte differentiation (Figure 2.2).[173] This may help alleviate some of the problems associated with intensive high-dose chemotherapy by replenishing low platelet counts. The plant-derived natural product euphohelioscopin A (**253**) has also been reported to selectively differentiate $CD34^+$ cells down the granulocyte/monocytic lineage by activating protein kinase C (PKC).[174] These insights may facilitate the application of stem cell therapies aimed at various myeloid dysfunctions. The ability to chemically control stem cell fate with small molecules is still in its infancy but seminal research has set the stage for the advancement of regenerative science and promising therapeutic endeavors.

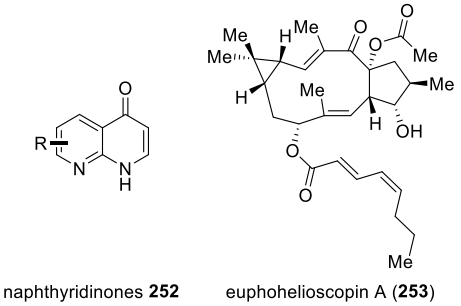


Figure 2.2. Small-molecule modulators of HSC differentiation.

Despite the widespread use of natural products in medicinal research their impact on stem cells has been relatively unexplored (Figure 2.3). The induction of macrophage differentiation by phorbol esters **254**, the aforementioned use of euphohelioscopin A (**253**) to induce granulocyte differentiation, and the recent report describing the *ex vivo* expansion of HSCs with the histone acetyltransferase inhibitor, garcinol (**255**) lend credence to the usefulness of natural products as tools for stem cell biology.[174-176]

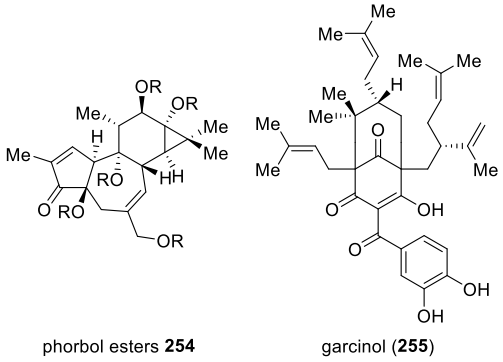


Figure 2.3. Natural product modulators of HSCs.

Although limited success involving secreted factors[177,178] and small drug-like molecules[171,179] have been reported, the *in vitro* expansion of HSCs remains a long standing problem in regenerative medicine. In an attempt to find a solution to this exhaustion phenomenon Schultz and co-workers conducted an unbiased imaged-based screen using primary human $CD34^+$ cells to identify leads that could maintain or selectively differentiate HSCs. After an extensive screen of a Novartis library containing 704 pure natural products from microbial and plant origin the compound eupalinilide E (**256**) was identified as a promising lead (Figure 2.4).[180]

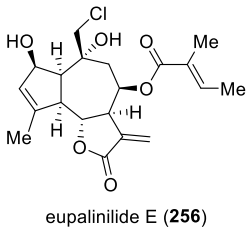


Figure 2.4. Structure of eupalinilide E (**256**).

The plant-derived natural product was discovered to promote the *ex vivo* expansion of hematopoietic stem and progenitor cells (HSPCs) as well as hinder the *in vitro* development of erythrocytes. Furthermore, this activity was additive in the presence of AhR antagonists, which have previously been shown to expand HSCs and are currently in clinical development.[171,181] Therefore the utilization of eupalinilide E (**256**) may be a valid tool for probing the mechanisms of hematopoiesis and improving the *ex vivo* production of progenitors for therapeutic use.

These results were obtained from the flow cytometric analyses of various assays in which the resultant mixture of $CD34^+$ and differentiated cells were quantified in terms of the numbers and percentages of HSCs, HSPCs, and lineage-committed cells based on their immunophenotypes. Long-term cultures incubated with 600 nM eupalinilide E (**256**) (EC_{50} = 210 nM) revealed significant growth and higher maintained percentages of $CD34^+$ cells, especially in cord blood experiments which demonstrated a 45-fold increase over the course of 45 days. In addition, eupalinilide E (**256**) (600 nM) treated cells also showed slower proliferation in the presence of differentiation-inducing medium that contained erythropoietin (EPO), granulocyte-macrophage colony stimulating factor (GMCSF), granulocyte colony stimulating factor (GCSF), and interleukin-3 (IL3). Based on their observations Schultz and co-workers concluded that eupalinilide E (**256**) may promote the expansion of an early hematopoietic progenitor and also inhibits differentiation down the erythrocyte lineage.

Schultz realized that the inhibition of NF-κB signaling by cysteine residue alkylation in the NF-κB DNA-binding domain by several sesquiterpenes was well documented and may explain the beneficial effects caused by eupalinilide E (**256**) (Figure 2.5).[182,183] Unfortunately, the four other sesquiterpene lactones included in the Novartis library, some of which were previously characterized as NF-κB inhibitors did not yield similar results. This suggests that the activity of eupalinilide E (**256**) on HSPC differentiation is mediated by an alternative pathway.

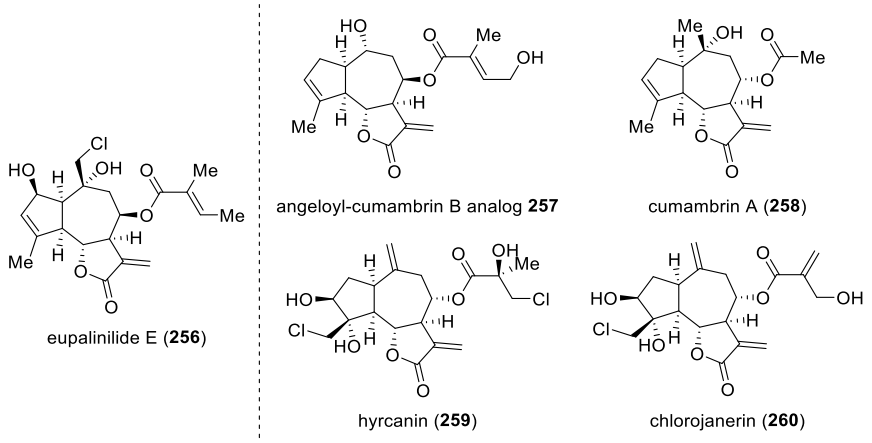


Figure 2.5. Sesquiterpene lactones included in imaged-based screen.

Since AhR antagonism also promotes HSPC expansion, eupalinide E (**256**) was subjected to an AhR antagonism assay but failed to give a positive response.[171,181] Interestingly, the combined treatment of eupalinilide E (**256**) and the AhR antagonist SR1 **250** had an additive effect on $CD34^+$ cell expansion. Thus supporting the notion that eupalinilide E (**256**) affects HSPC differentiation by a new distinct mechanism.[180]

Although the mode of action and biological target of eupalinilide E (**256**) remains unknown, this work highlights the ability of natural products to modulate stem cell biology. Importantly, Schultz comments that, "the lack of synthetic routes to eupalinilide E hinders the generation of affinity probes for target identification." Thus making eupalinilide E (**256**) an attractive target for total synthesis, a new chemical entity that possesses potential in regenerative medicine.

Eupalinilide E (**256**) was isolated from the plant *Eupatorium lindleyanum* DC. and identified as a potent cytotoxic compound against A-549 tumor cell lines.[184] Following conventional NMR analysis, the natural product was characterized as a guaianolide sesquiterpene structurally highlighted by the inclusion of an allylic alcohol on the cyclopentane ring, a chlorohydrin functionality, and a C8 tigloyl ester. Guaianolides encompass a large subset of naturally occurring sesquiterpene lactones that are easily recognized by their 5,7,5-tricyclic framework and γ-butyrolactone moiety. The core structure and etymology of guaianolides is derived from the *cis*-fused 5,7-bicyclic hydroazulene natural product guaiane (**261**) (Figure 2.6).

The hydroazulene core for the most part is always *cis*-fused in the guaianolide skeleton **262**, whereas approximately 85% of all known guaianolides contain a *trans* annulated γ-butyrolactone ring.[185]

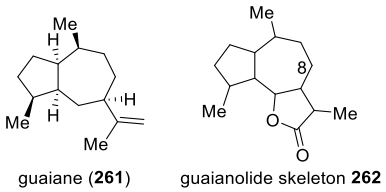
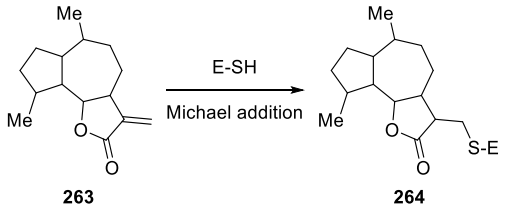


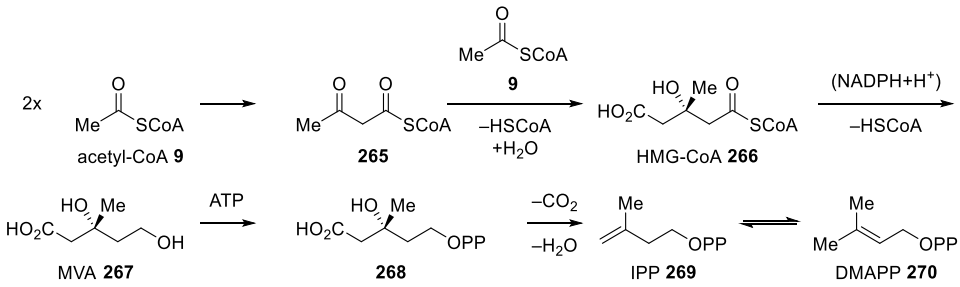
Figure 2.6. Guaianolide framework.

The guaianolide class of natural products displays an array of biological activity, which is often attributed to their interaction with biological nucleophiles such as cysteine or thiol-containing enzymes (Scheme 2.1). This is especially the case in the numerous guaianolides that possess an α-methylene γ-butyrolactone. The auxiliary substitution pattern of the guaianolide is consequently believed to determine the specificity of the resulting biological activity.[186]



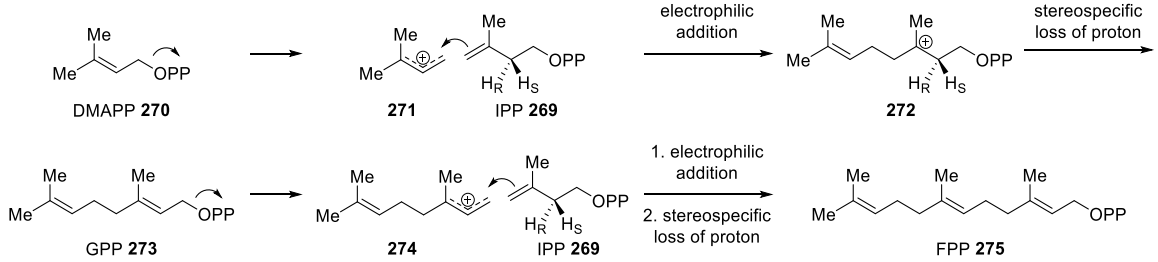
Scheme 2.1. Guaianolide participation in Michael additions.

Guaianolide biosynthesis has been well documented and begins with the common terpene mevalonate (MVA) pathway to generate the quintessential isoprene building blocks isopentenyl pyrophosphate (IPP, **269**) and γ,γ-dimethylallyl pyrophosphate (DMAPP, **270**; Scheme 2.2).[187-190] The assembly of three acetyl-CoA **9** molecules takes place within the cytosol through a Claisen condensation and aldol reaction sequence to provide β-hydroxy-β-methylglutaryl-CoA (HMG-CoA, **266**). Subsequent NADPH+H^+ reduction releases mevalonic acid (MVA, **267**) for ATP activation to afford pyrophosphomevalonic acid **268**. Decarboxylation and elimination leads to IPP **269**, with further olefin isomerization giving rise to DMAPP **270**.



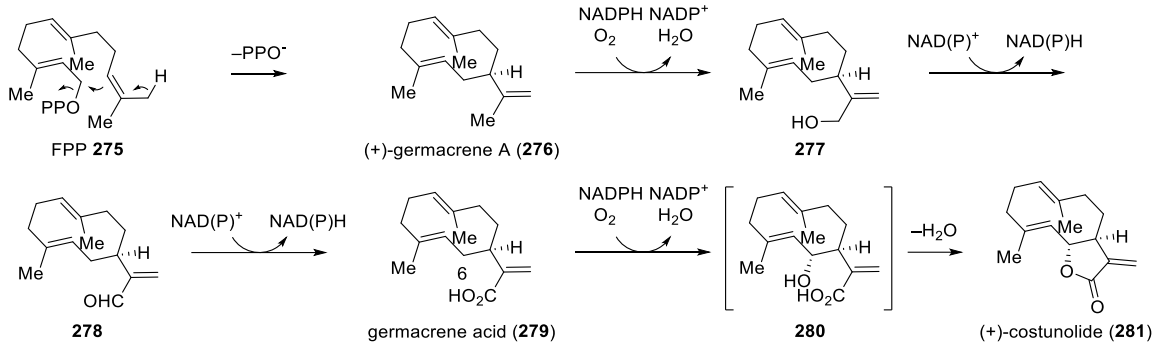
Scheme 2.2. MVA pathway for the biosynthesis of IPP **269** and DMAPP **270**.

Construction of the terpene backbone proceeds upon prenyl transferase mediated head-to-tail connection of IPP **269** and its isomer DMAPP **270** (Scheme 2.3). Initial ionization of DMAPP **270** provides allylic cation **271**, to which regioselective olefin addition of IPP **269** can occur to form tertiary cation **272**. Stereoselective loss of a proton installs a new *trans* olefin to furnish geranyl pyrophosphate (GPP, **273**). A single iteration of the IPP **269** electrophilic addition provides farnesyl pyrophosphate (FPP, **275**), the C_{15} guaianolide precursor.



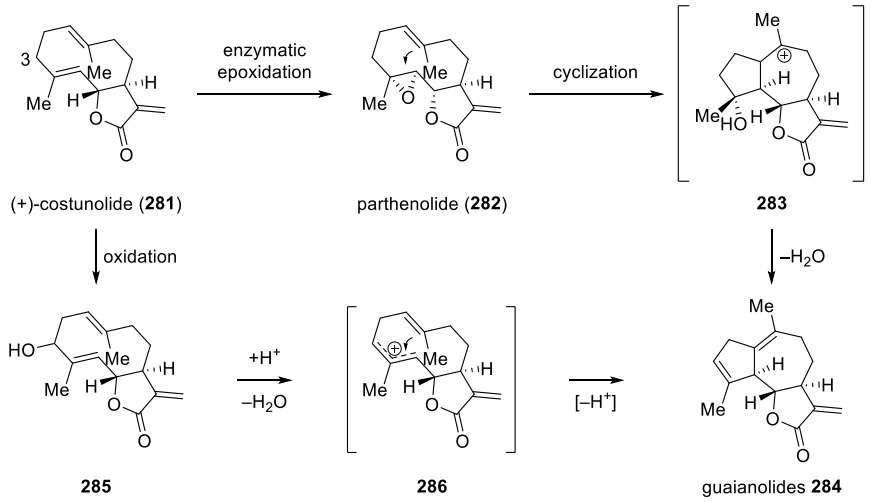
Scheme 2.3. Biosynthesis of FPP **275**.

Cyclization of FPP **275** produces (+)-germacrene A (**276**), a 10-membered ring consisting of two internal (*E*)-alkenes that originate from the olefin configuration inherent to FPP **275** (Scheme 2.4). (+)-Germacrene A-hydroxylase oxidizes the isopropenyl side chain to primary alcohol **277** prior to further oxidation by $NAD(P)^+$-dependent dehydrogenases to give germacrene acid (**279**). Subsequent C6 hydroxylation and lactonization provides (+)-costunolide (**281**).[191-194]



Scheme 2.4. Biosynthesis of (+)-costunolide (**281**).

Enzymatic epoxidation affords parthenolide (**282**), a germacranolide geared by ring strain toward *trans*-annular cyclization to generate the guaianolide framework (Scheme 2.5). Alternatively, the enzymatic C3 hydroxylation of (+)-costunolide (**281**) and subsequent dehydration/cyclization sequence to give the guaianolide core has also been proposed.[195] Additional oxidative manipulation to the 5,7,5-membered ring system ultimately leads to the various functionality patterns observed amongst the diverse guaianolide natural product class.



Scheme 2.5. Biosynthesis of guaianolides **284**.

Despite the existence of several synthetic strategies toward monocyclic γ-butyrolactone natural products there are considerably fewer approaches towards the contruction of bi- and tricyclic γ-butryolactone frameworks such as the guaianolides (Figure 2.7). Therefore it is important to highlight some of the synthetic achievements and strategies in guaianolide natural

product total synthesis. Although eupalinilide E (**256**) has not been previously synthesized it is included for structural comparison.

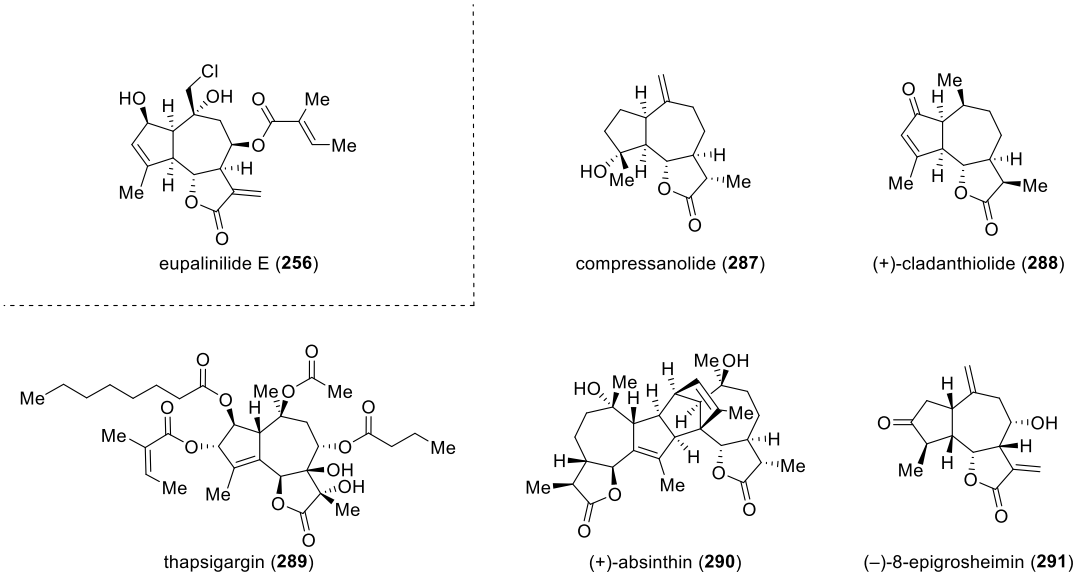
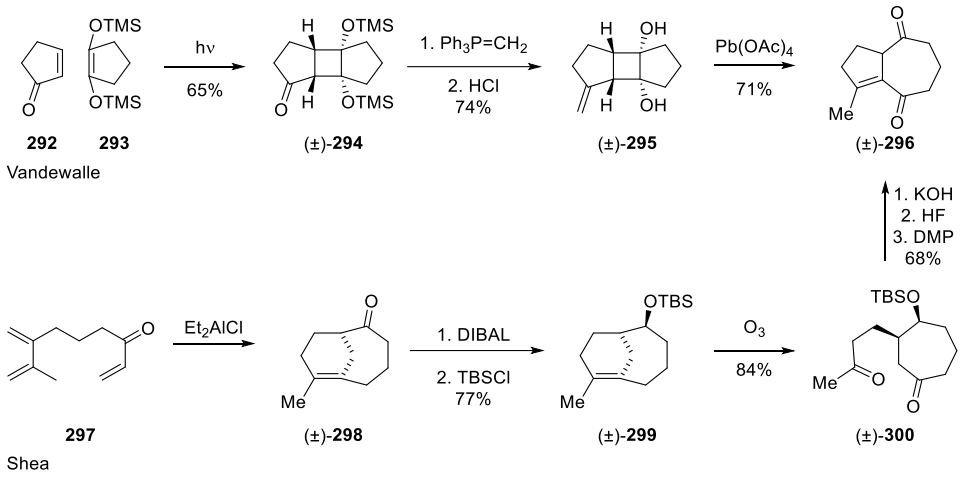


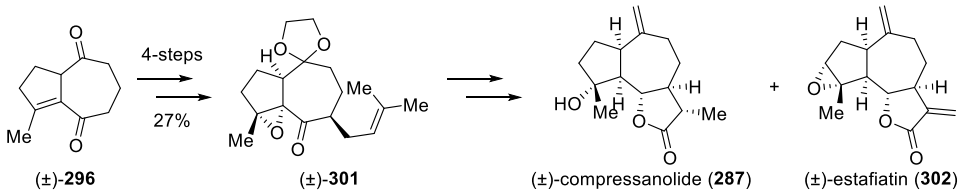
Figure 2.7. Representative guaianolide natural products achieved in total synthesis.

Racemic total syntheses of guaianolide natural products began to surface in the 1980s and were focused on the elaboration of 7-membered rings (Scheme 2.6). En route to (±)-compressanolide (**287**) and (±)-estafiatin (**302**). Vandewalle developed a novel approach toward the 5,7-hydroazulene core through the oxidative diol cleavage of 5,4,5-tricycle (±)-**295**.[196-199] An efficient protocol starting with the photochemical [2+2] cycloaddition between 1,2-bis[trimethylsiloxy]cyclopentene **293** and cyclopentenone **292** generated 5,4,5-tricycle (±)-**294** as a single diastereomer. Subsequent Wittig reaction and TMS removal primed diol (±)-**295** for ring expansion by lead(IV) acetate mediated oxidative cleavage to give key intermediate (±)-**296**. Shea was also capable of synthesizing the important 5,7-hydroazulene intermediate (±)-**296** using a bridged-to-fused-ring-interconversion strategy.[200] An intramolecular Diels-Alder reaction of triene **297** gave rise to bridged ring (±)-**298**. After carbonyl reduction and alcohol protection ozonolysis disconnected the bridgehead to give (±)-**299**, which set the stage for an intramolecular aldol condensation to afford Vandewalle's intermediate (±)-**296** following deprotection and oxidation.



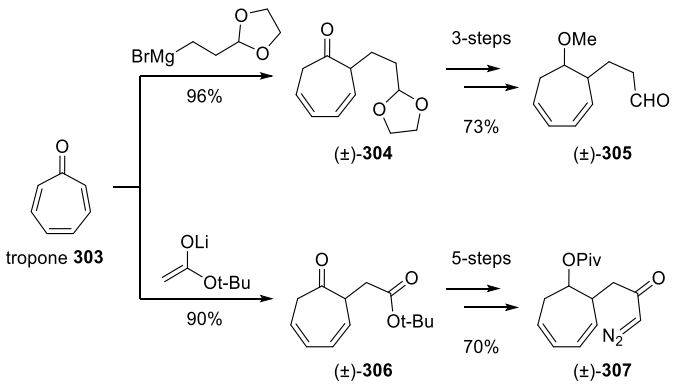
Scheme 2.6. Synthesis of key intermediate (±)-**296**.

The racemic total syntheses of (±)-compressanolide (**287**) and (±)-estafiatin (**302**) were completed upon further functional group manipulation of 5,7-hydroazulene (±)-**296** (Scheme 2.7). It is of interest to note the strategy to use the addition of a prenyl group as a latent surrogate for the lactone by way of ozonolysis, Jones oxidation, and intramolecular esterification.



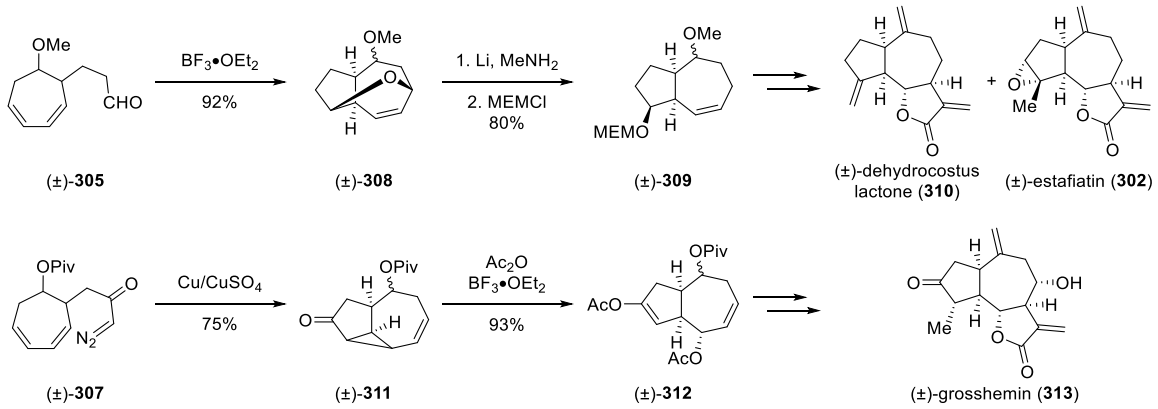
Scheme 2.7. Synthesis of (±)-compressanolide (**287**) and (±)-estafiatin (**302**).

Adopting Vandewalle's approach toward guaianolides through the initial construction of the hydroazulene core Rigby and co-workers took advantage of the 7-membered ring already present in commercially available 2,4,6-cycloheptatrienone (tropone, **303**) (Scheme 2.8).[201,202] Utilizing the appropriate nucleophiles 1,8-addition afforded alkylated species (±)-**304** and (±)-**306**, which were further elaborated to reactive aldehyde (±)-**305** and diazoketone (±)-**307**, respectively.



Scheme 2.8. Functionalization of tropone **303**.

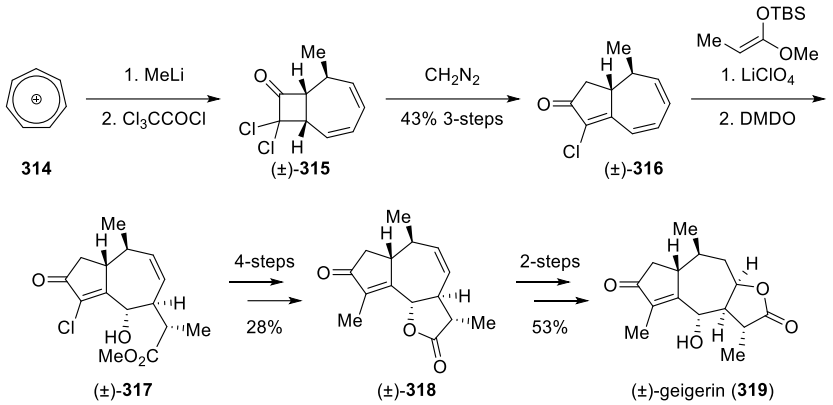
Lewis acid promoted cyclization of (±)-**305** followed by reductive opening of the oxo bridge generated 5,7-hydroazulene precursor (±)-**309** from which (±)-dehydrocostus lactone (**310**) and (±)-estafiatin (**302**) could be accessed (Scheme 2.9). Alternatively, intramolecular cyclopropanation of (±)-**307** generated tricycle (±)-**311**, which was opened by a Lewis acid mediated homoconjugate addition to give intermediate (±)-**312** for the synthesis of (±)-grosshemin (**313**).



Scheme 2.9. Synthesis of (±)-dehydrocostus lactone (**310**), (±)-estafiatin (**302**), and (±)-grosshemin (**313**).

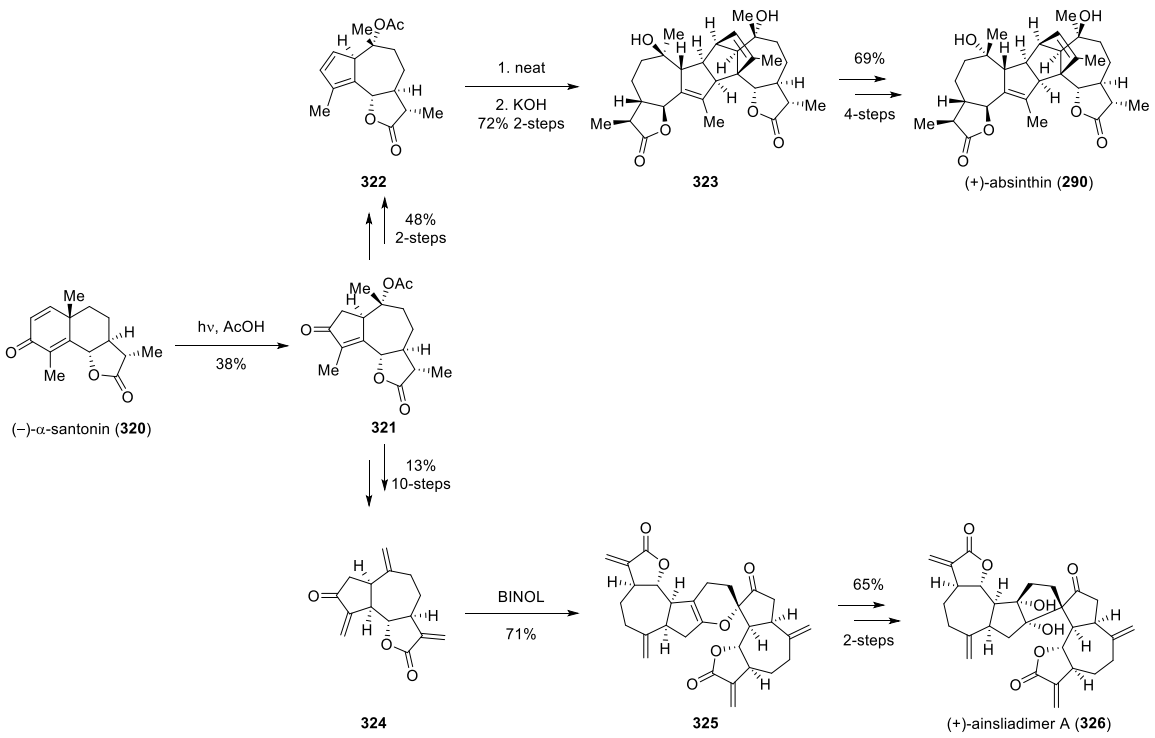
In a similar strategy, Deprés took advantage of the readily available tropylium cation **314** (Scheme 2.10).[203] Methylation and regioselective [2+2] cycloaddition provided dichloro intermediate (±)-**315** which underwent ring expansion to form hydroazulene intermediate (±)-**316**. Subsequent 1,6-conjugate addition of an (*E*)-ketene acetal provided a handle for *trans*

lactone formation. Further manipulation provided guaianolide intermediate (±)-**318** and eventually the 6,12-guaianolide natural product (±)-geigerin (**319**).



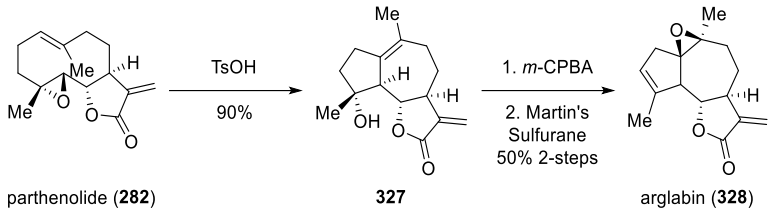
Scheme 2.10. Synthesis of (±)-geigerin (**319**).

Semi-synthetic and biosynthetic efforts have led to a few guaianolide enantioselective total syntheses. It was discovered that photoirradiation of the eudesmanolide (−)-α-santonin (**320**) in acetic acid provided 5,7,5-tricycle **321** (Scheme 2.11).[204,205] With an expedient entry into the guaianolide core estafiatin (**302**) was synthesized once again.[206-208] Zhang and Lei took advantage of this reactivity en route to their biomimetic dimerizations to synthesize (+)-absinthin (**290**) and (+)-ainsliadimer A (**326**), respectively.[209,210] Although analogous photoreactions involving derivatives and (−)-α-santonin like compounds have been reported they are quite limited in scope and utility.[211-213]



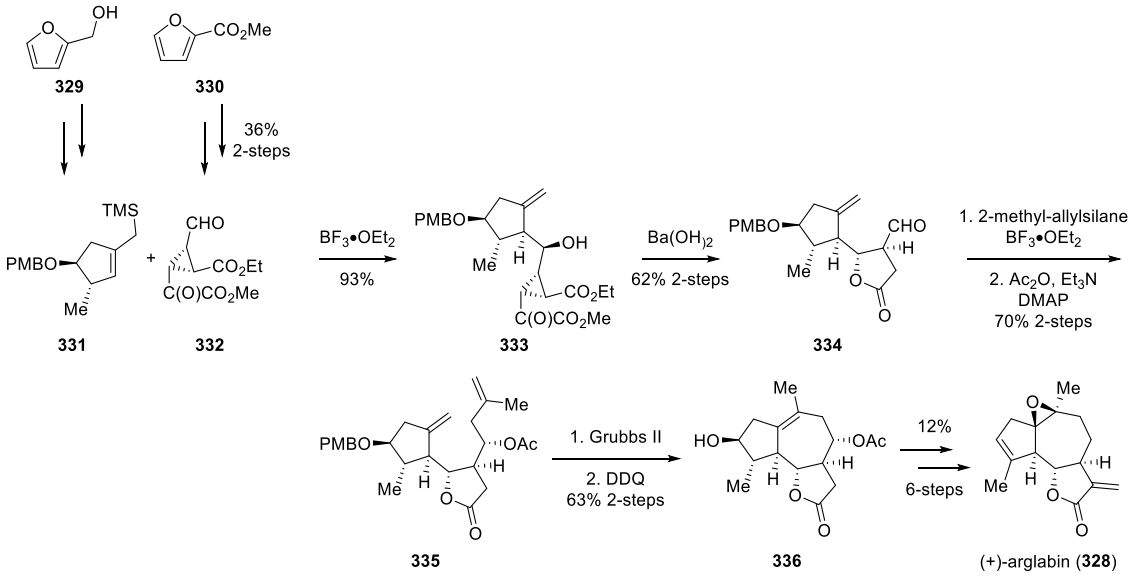
Scheme 2.11. Rearrangement of (−)-α-santonin (**320**) towards (+)-absinthin (**290**) and (+)-ainsliadimer A (**326**).

Biomimetic syntheses of the guaianolide scaffold have also been accomplished from germacranolide natural products such as the proposed biosynthetic precursor parthenolide (**282**) (Scheme 2.12). Zhang and Chen were able to achieve a *p*-toluenesulfonic acid induced rearrangement of parthenolide (**282**) to an advanced intermediate that required only two additional steps to complete the total synthesis of arglabin (**328**).[214] Similar to the eudesmanolide rearrangements modified and germacrolide oriented scaffold rearrangements have been reported but are prone to complex product mixtures and poor yields.[215-226] Despite offering advanced intermediates in as little as one step the use of complex natural product starting materials limit the opportunity for diversity oriented synthesis and renders these strategies useful to only a small subset of guaianolide oxidation patterns.



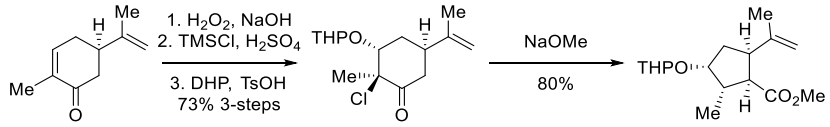
Scheme 2.12. Synthesis of arglabin (**328**) from parthenolide (**282**).

As guaianolides became popular targets for total synthesis innovative strategies arose for their enantioselective syntheses from simple starting materials. Reiser utilized basic furan derivatives to construct two important synthons for the total synthesis of (+)-arglabin (**326**) (Scheme 2.13).[227,228] CuI-catalyzed asymmetric cyclopropanation of methyl-2-furoate **330** followed by ozonolysis provided cyclopropylcarbaldehyde **332**. Furfuryl alcohol **329** on the other hand generated allylsilane **331** prior to enzymatic resolution and straightforward functional group manipulations. These two building blocks were combined with high stereocontrol dictated by the Felkin-Ahn paradigm. Base promoted saponification of the more labile oxalic ester in **333** and subsequent retroaldol-lactonization afforded lactone **334**. Hosomi-Sakurai allylation and acetylation provided ring closing metathesis (RCM) precursor **335**. Grubbs II catalyst efficiently provided the guaianolide core, which was eventually transformed into (+)-arglabin (**328**).



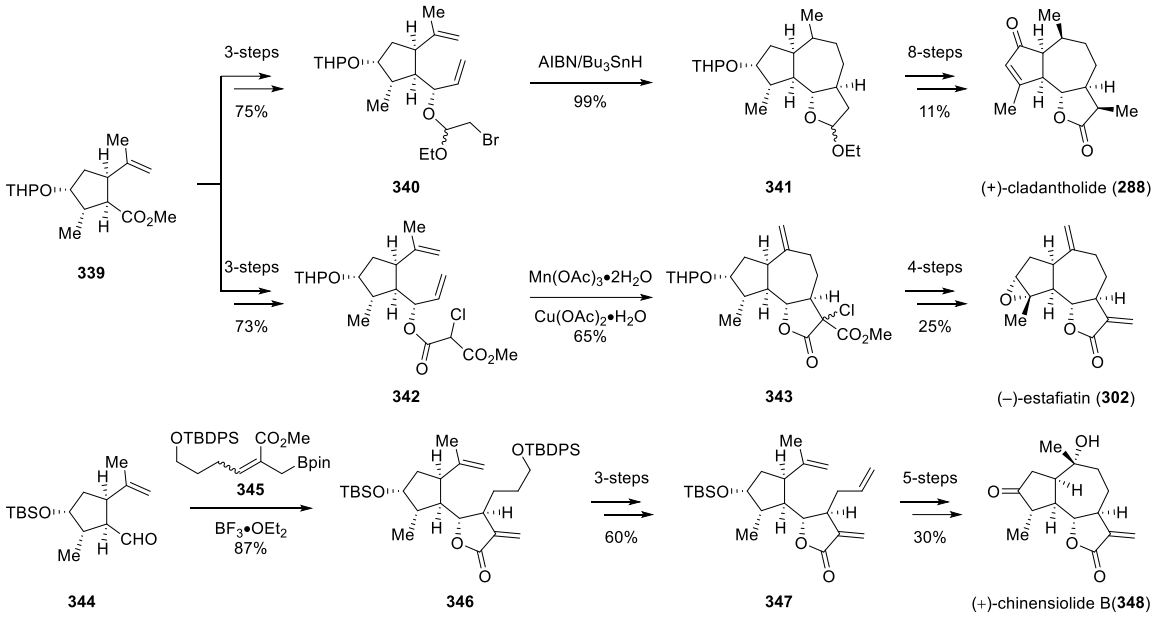
Scheme 2.13. Synthesis of (+)-arglabin (**328**).

Lee and co-workers developed a concise four-step synthesis of key cyclopentane intermediate **339** from (*R*)-carvone **337** (Scheme 2.14).[229] This was an attractive approach because the stereochemical information contained by the carvone precursor could provide substrate control for subsequent stereoselective reactions. Chlorohydrin **328** was synthesized in three steps from (*R*)-carvone **337** setting the stage for a stereoselective Favoskii reaarangement to furnish highly substituted cyclopentanecarboxylate **339**. This approach was adopted by several research groups and led to several guaianolide total syntheses.



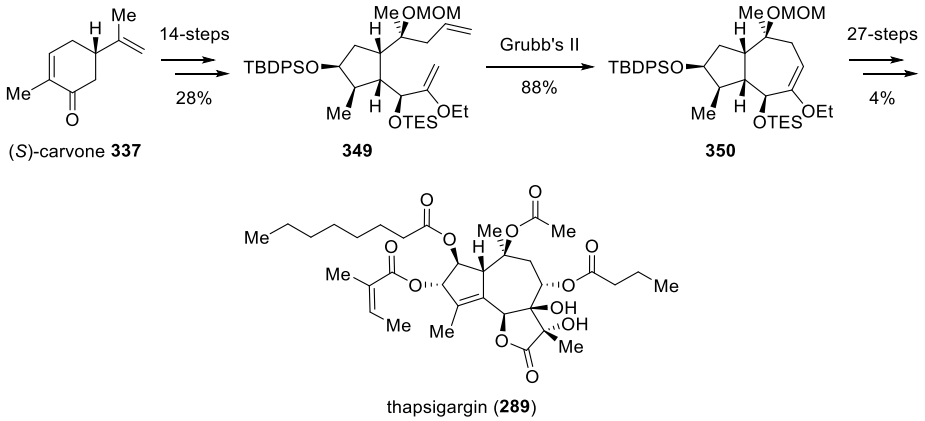
Scheme 2.14. Synthesis of cyclopentanecarboxylate **339**.

Lee successfully elaborated cyclopentane **339** to bromoacetal **340** which underwent a smooth radical cyclization intiated by azobisisobutyronitrile and tributyltin hydride to provide protected lactone **341** in quantitative yield and perfect diastereoselectivity (Scheme 2.15). The synthesis of (+)-clandantholide (**288**) was subsequently obtained.[230] In a parallel manner Lee synthesized (−)-estafiatin (**302**) from α-chloro species **342** using oxidative radical conditions. Hall was able to use Lee's work combined with a unique tandem allyboration/lactonization reaction sequence to give RCM precursor **347** which resulted in the total synthesis of (+)-chinensiolide B (**348**).[231]



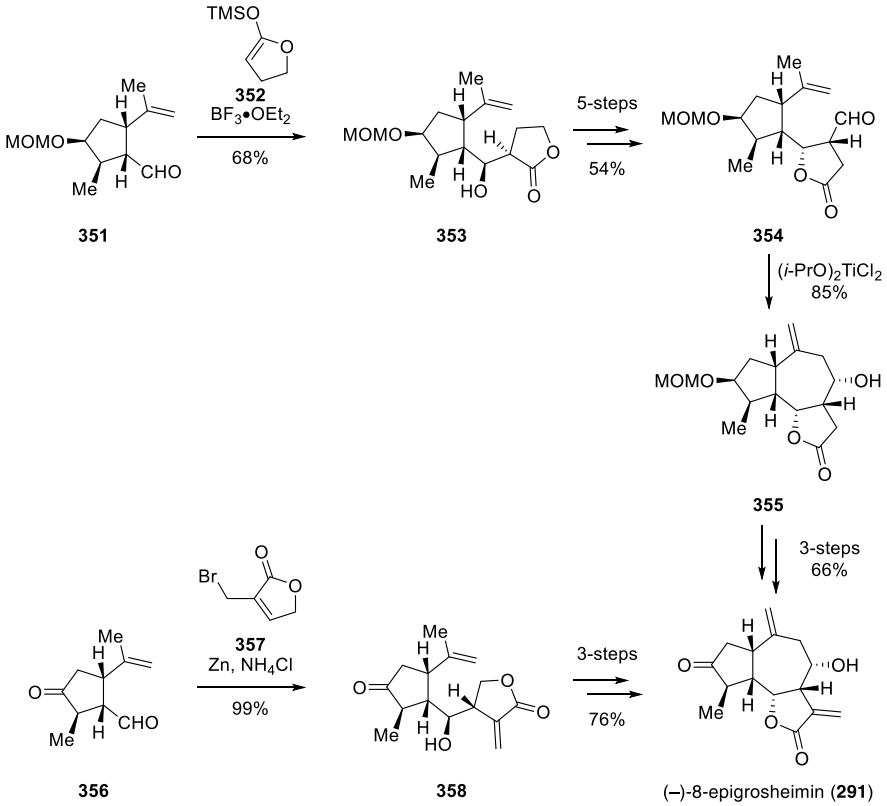
Scheme 2.15. Synthesis of (+)-clandantholide (**288**), (−)-estafiatin (**302**), and (+)-chinensiolide B (**347**).

Utilizing Lee's strategy Ley and co-workers began with (*S*)-carvone **337** in their synthesis of several members of the thapsigargin family (Scheme 2.16). Upon optimization of several stereoselective addition reactions advanced intermediate **349** was obtained and subjected to ring closing metathesis to forge hydroazulene core **350**. Following an array of synthetic manipulations Ley was able to arrive at five stereochemically complex and heavily oxygenated thapsigargin natural products.[232-235]



Scheme 2.16. Synthesis of thapsigargin (**289**).

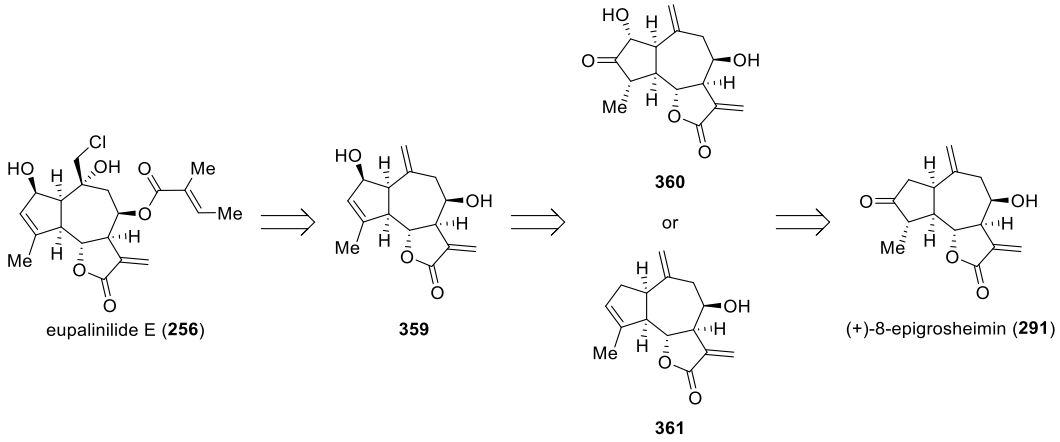
Interestingly, in Xu's synthesis of (−)-8-epigrosheimin (**291**) the closure of the 7-membered ring was a diastereoselective event that not only delivered the exocyclic olefin but also the C8 hydroxylated functionality (Scheme 2.17). The strategy involved the initial construction of the butyrolactone prior to ring closure. In the first synthetic route carvone derived cyclopentane aldehyde **351** was subjected to a Mukaiyama aldol addition to install the latent butyrolactone. An aldehyde-ene reaction promoted by dichlorotitanium diisopropoxide smoothly provided the tricyclic core **355** in excellent yield.[326] In a second-generation synthesis a Barbier reaction was cleverly devised to install the latent butyrolactone in less steps. Subsequent functional group manipulations provided the natural product.[237]



Scheme 2.17. Synthesis of (−)-8-epigrosheimin (**291**).

In an effort to devise a synthetic strategy for the construction of eupalinilide E (**256**) we realized that retrosynthetic analysis could trace the natural product back to previously synthesized (+)-8-epigrosheimin (**291**) (Scheme 2.18).[236,237] Besides chlorohydrin formation from

the requisite exocyclic olefin and tigloyl ester formation at the C8 hydroxyl group the key transformation would entail the conversion of the cyclopentanone to the allylic alcohol present in eupalinilide E (**256**). Fortunately, there was already precedence for such a transformation in the guaianolide natural product literature.

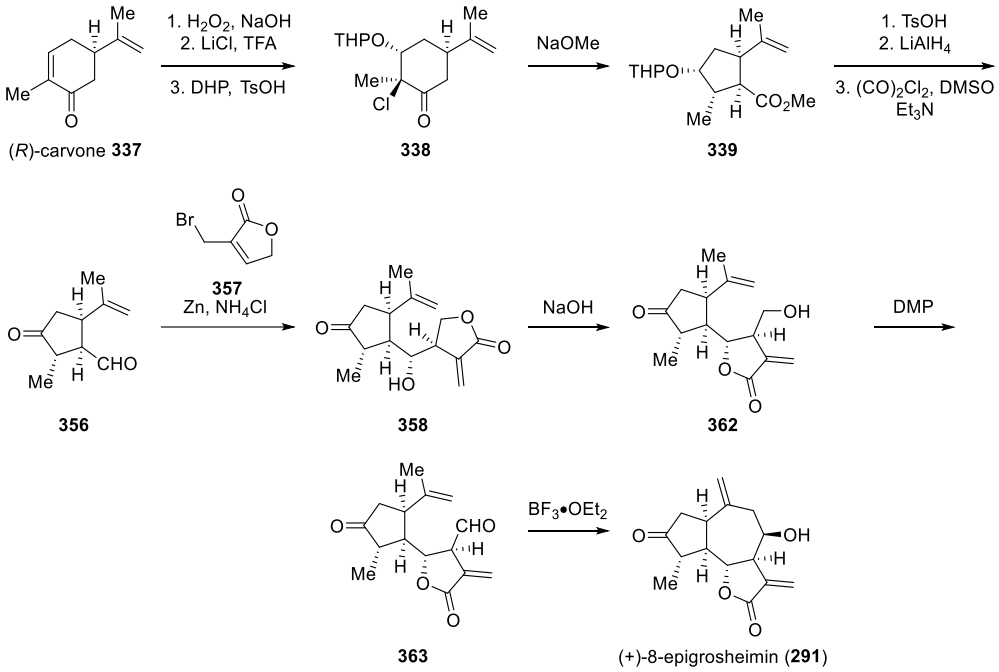


Scheme 2.18. Retrosynthetic analysis of eupalinilide E (**256**).

One method relied on a Rubottom oxidation to install the C4 hydroxyl group followed by a Shapiro reaction to transform the ketone into the desired trisubstituted olefin.[230] According to this report the undesired diastereomer in our case may arise; however, if this event is unavoidable a simple inversion protocol could easily rectify the problem. Alternatively, elimination of the oxygenated functionality at C3 could afford the trisubstituted olefin **361** prior to allylic oxidation setting the stage for a diastereoselective reduction to furnish the allylic alcohol.[206,230]

Although synthetic reports detail the synthesis of biologically active (−)-8-epigrosheimin (**291**) the authors comment that they also synthesized the natural enantiomer from (*R*)-carvone **337** (Scheme 2.19).[237] This is a convenient route that sets the stereocenters associated with the *cis* hydroazulene core, *trans* bicyclic butyrolactone junction, and C8 hydroxyl group of eupalinilide E (**256**). Starting from (*R*)-carvone **337** a hydrogen peroxide mediated epoxidation followed by lithium chloride induced ring opening and tetrahydropyran protection generated precursor **338**. A stereoeselective Favorskii rearrangement would ensue to afford cyclopentane **339** that contains

the stereochemical information necessary for the *cis* hydroazulene assembly. Subsequent protecting group and oxidation state manipulations provided key aldehyde **356** primed for a stereo- and regioselective allylation addition. Zinc promoted Barbier coupling provided α-methylene γ-butyrolactone **358** that underwent a base induced intramolecular translactonization to furnish primary alcohol **362**. Finally, a Dess-Martin oxidation and aldehyde-ene cyclization encouraged by boron trifluoride diethyl etherate provided (+)-8-epigrosheimin (**291**).

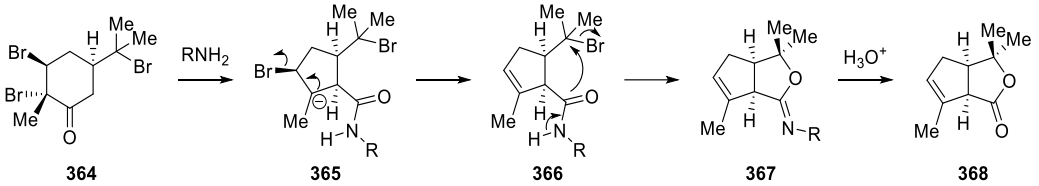


Scheme 2.19. Synthesis of (+)-8-epigrosheimin (**291**).

Initial synthetic studies quickly revealed that the late-stage manipulation of (+)-8-epigrosheimin (**291**) would be difficult and tedious so it was decided that the early construction of the allylic alcohol bearing cyclopentane would be more prudent. Unfortunately, attempts to transform Favorskii product **339** into the desired allylic alcohol were plagued with complications surrounding poor yields and scalability as well as problems associated with epimerization and isomerization.

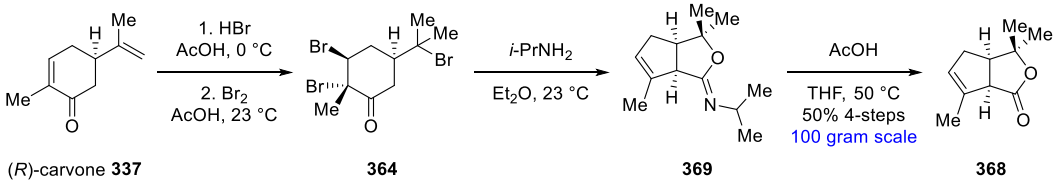
While investigating alternative carvone derived rearrangements a solution presented itself in the form of a cascade sequence capable of transforming tribomide **364** into bicyclic lactone **368** (Scheme 2.20). This underutilized transformation was discovered by Wallach in 1899 and

was briefly studied by Wolinsky some 60 years later.[238-242] The reaction presumably occurs through an initial Favorskii reaction in which the resulting carbanion **365** proceeds to eliminate bromide providing olefin intermediate **366**. Subsequent engagement of the tertiary bromide by the amide gives bicyclic imidate **367** that upon hydrolysis affords bicyclic lactone **368**, an attractive intermediate that retains the stereochemical information required moving forward and possesses the trisubstituted olefin that had previously been a synthetic challenge.



Scheme 2.20. Tribromide **364** Favorskii rearrangement.

Consequently (*R*)-carvone **337** was treated with dry hydrobromic acid to selectively hydrobrominate the terminal olefin prior to its reaction with molecular bromine to furnish tribromide **364** (Scheme 2.21). The Favorskii precursor **364** was then exposed to isopropyl amine and allowed to stir overnight to provide bicyclic imidate **366** that gave bicyclic lactone **368** following acetic acid assisted hydrolysis. Due to the constant shifting between acidic and basic media in highly volatile solvents such as diethyl ether and isopropyl amine these reactions were conducted slowly and with extreme caution in order to avoid violent exothermic reactions. Nonetheless this convenient four-step sequence was routinely run on 100 gram scale to provide pure bicyclic lactone **368** following recrystallization from hexanes as a light-amber crystalline solid in a satisfying 50% overall yield.

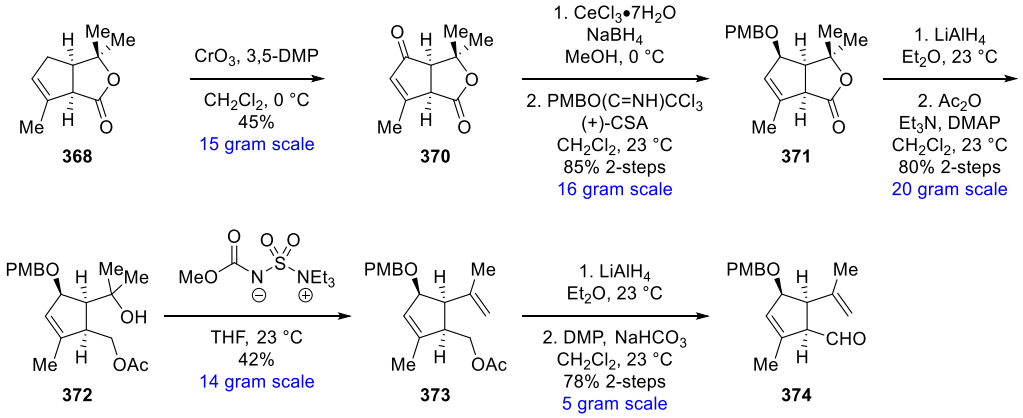


Scheme 2.21. Synthesis of bicyclic lactone **368**.

The rigid and durable structure of bicyclic lactone **368** seemed like a good candidate for allylic oxidation and indeed Mori had already shown the validity of this reaction (Scheme

2.22).[243-245] In the presence of a large excess of chromium trioxide and 3,5-dimethylpyrazole in methylene chloride at ambient temperature bicyclic lactone **368** was converted to enone **370**. Despite the low yield and painstaking effort to purify enone **370** by multiple iterations of column chromatography the product could still be produced as a clear crystalline solid on multigram scale.

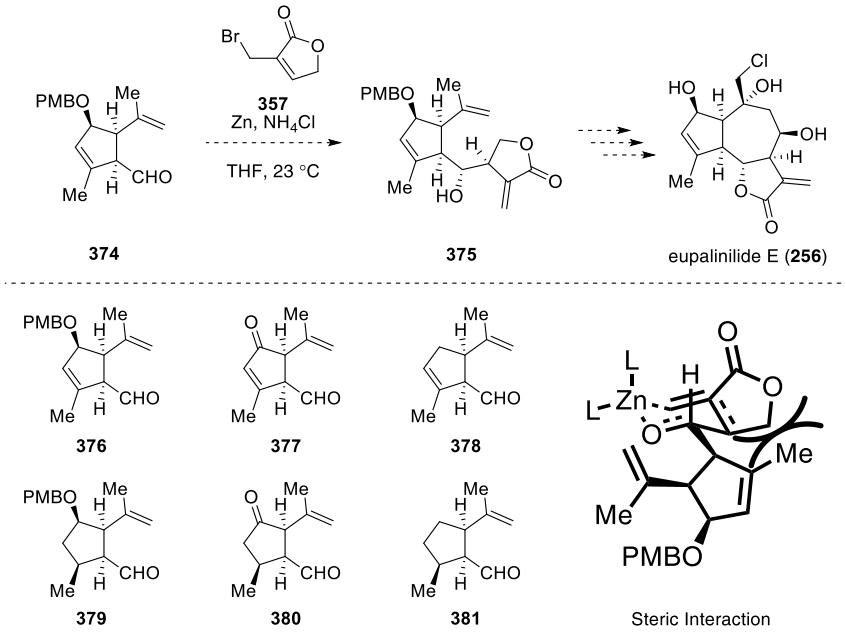
Standard Luche reduction conditions followed by protection using freshly prepared *p*-methoxybenzyl 2,2,2-trichloroacetamide afforded PMB alcohol **371** as a single diastereomer.[246,247] Lithium aluminum hydride was then used to open the bicycle followed by monoacylation to provide tertiary alcohol **372**. Subsequent elimination utilizing the Burgess reagent gave the desired terminal olefin **373** as the only detectable product.[248] Unfortunately, significant decomposition as evidenced by the expulsion of *p*-methoxybenzyl alcohol lead to poor yields. Short reaction times (2 minutes) were critical in avoiding the complete deterioration of material. Nevertheless pushing forward through a deacylation and Dess-Martin oxidation furnished key aldehyde **374** for the intended Barbier coupling.[249]



Scheme 2.22. Synthesis of key aldehyde **374**.

To our dismay the Barbier coupling of key aldehyde **374** with bromolactone **357** did not proceed as it had before (Scheme 2.23). In fact no level of reactivity could be realized even after screening various conditions. Since the Barbier coupling was hypothesized to occur through a six-membered transition state we believed that the steric load of our substrate was the main

culprit. A series of six aldehydes **276-281** were synthesized with varying degrees of unsaturation and oxygenation to see if the Barbier coupling could be achieved. None were successful and it was concluded that an adjacent sp^2 carbon center or a syn methyl relationship prohibits reactivity.



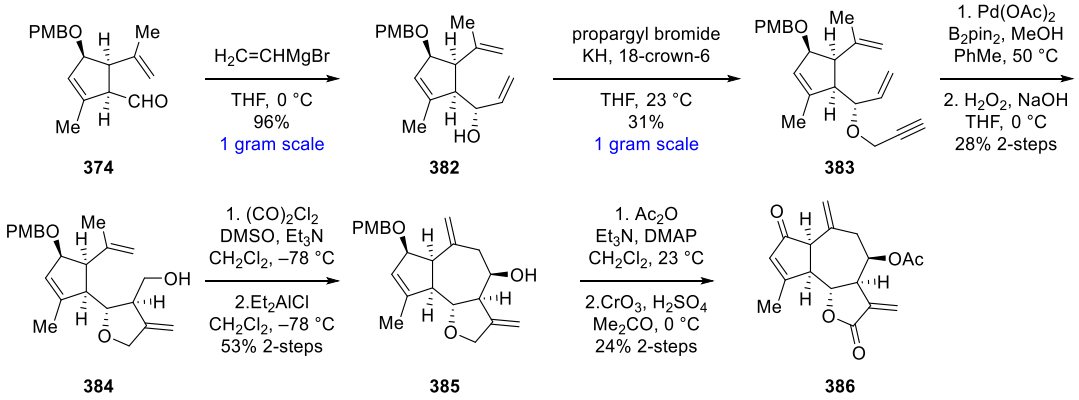
Scheme 2.23. Failed Barbier coupling.

In order to circumvent the difficulties associated with the Barbier reaction we planned to elaborate aldehyde **374** in hopes of employing a radical or transition metal catalyzed transformation to furnish the requisite lactone (Scheme 2.24). To that end allylic alcohol **382** was prepared by treating aldehyde **374** with vinyl magnesium bromide. The goal was to install a propargyl ester that upon enyne cyclization would reveal the α-methylene γ-butyrolactone directly. Unfortunately, allylic alcohol **382** possessed very limited reactivity and despite extensive efforts the only viable reaction that was achieved was its propargylation using potassium hydride with the assistance of 18-crown-6 to furnish enyne **383**. We were confident that once cyclized the activated methylene position would be poised for allylic oxidation and that the lactone could be obtained later on in the synthesis.

With enyne **383** in hand we needed a cyclization capable of installing functionality that could be transformed into the key aldehyde-ene precursor. A suitable transformation was

realized by adapting a borylative enyne cyclization reported by our group that was originally developed for the construction of elaborated cyclopentanes.[250,251] Upon treatment of enyne **383** with palladium(II) acetate in the presence of bis(pinacolato)diboron and an equivalent of methanol in toluene at 50 °C the desired cyclization took place in which a five-membered cyclic ether was constructed as well as a terminal boronate ester which gave alcohol **384** following oxidative work-up.

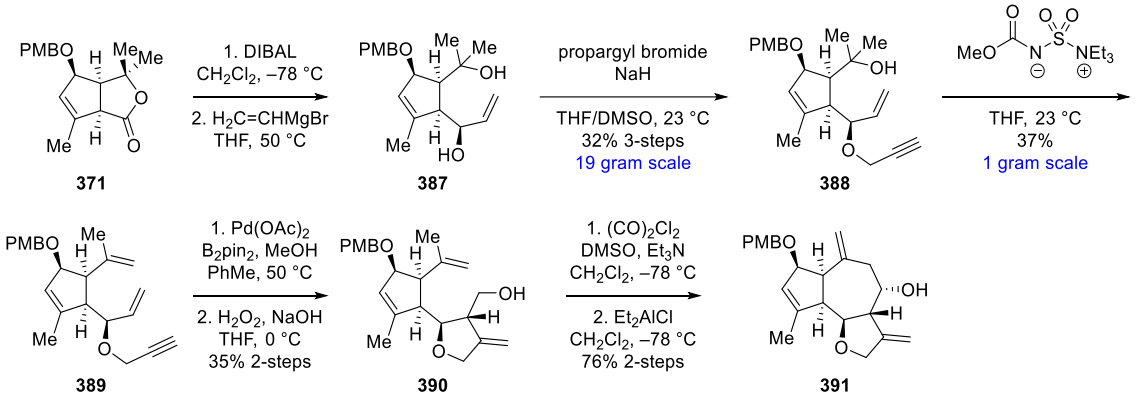
Subsequent Swern oxidation provided the key aldehyde that underwent ring closure when treated with diethylaluminum chloride in methylene chloride at −78 °C to afford 5,7,5-tricycle **385** in 53% overall yield as a single diastereomer.[237,252] In order to test the validity of our hypothesized lactone formation by way of allylic oxidation the primary alcohol **385** was protected as an acetate. At first various attempts to obtain the desired allylic oxidation only lead to decomposition of the starting material. Eventually it was discovered that when oxidized using Jone's conditions the lactone was formed with concomitant deprotection of the *p*-methoxybenzyl group followed by oxidation to the resultant enone to give guaianolide **386**.[253]



Scheme 2.24. Synthesis of guaianolide **386**.

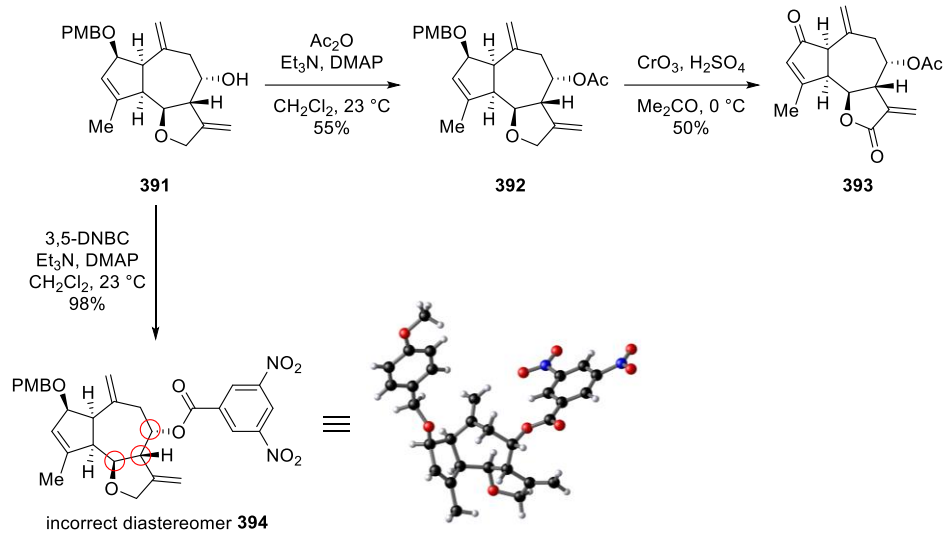
Although it seemed reasonable that the synthesis of eupalinilide E (**256**) could be obtained from guaianolide **386** in due course, the lengthy step count and sequence of poor yielding reactions influenced our attempt to streamline our synthetic route to provide more material for end game chemistry (Scheme 2.25). Instead of vinyl addition on discrete aldehyde **374** we believed that the installation of this group directly from a lactol would be much more

direct. Therefore PMB bicycle **371** was treated with diisobutylaluminum hydride prior to the addition of vinyl magnesium bromide at elevated temperature to give diol **387**. Propargylation of this substrate was more facile than before and could be achieved with sodium hydride. Interestingly, attempts to do the boralytive enyne cyclization on this substrate only returned starting material. The use of Burgess reagent encountered similar problems as before but gave similar yields in providing substrate **389**.[248] Proceeding through the borylative enyne/oxidation sequence and Swern oxidation/aldehyde-ene transformation resulted in 5,7,5-tricycle **391** as a single diastereomer that did not match the spectral data for 5,7,5-tricycle **386**.[237,250-252]



Scheme 2.25. Attempt to streamline synthetic route.

Once again protection of primary alcohol **391** as its acetate prior to Jone's oxidation gave an analogous compound **391** possessing a lactone and enone that was also different from guaianolide **386** procured earlier.[253] Acylation of alcohol **391** with 3,5-dinitrobenzoylchloride provided dinitrobenzoate **394** as a highly crystalline solid. X-ray analysis unambiguously identified the structure as having the desired atomic connectivity with inverted stereochemistry at three of the stereocenters. This result suggests that the vinyl addition to the lactol provided the allylic alcohol resulting from chelation control whereas the addition to discrete aldehyde **374** followed the Felkin-Anh paradigm.[254-257]



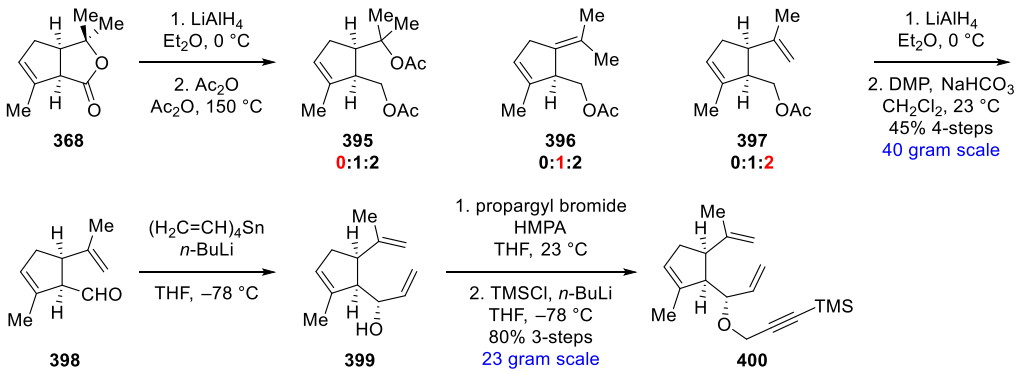
Scheme 2.26. Synthesis of incorrect guaianolide diastereomer **394**.

With experience concerning allylic oxidation on the guaianolide system in hand it was hypothesized that a late-stage dual allylic oxidation would significantly improve our synthetic route. We believed that by combining two inherently poor yielding reactions into a single transformation performed toward the end of the synthesis we could significantly facilitate the ability to acquire late-stage material. Furthermore, complications regarding the decomposition of PMB alcohol substrates would be avoided.

Therefore bicyclic lactone **368** was cleaved with lithium aluminum hydride prior to acetate pyrolysis to give terminal olefin **397** (Scheme 2.27). The acetate pyrolysis reaction was initially unpredictable and gave variable mixtures of terminal and tetrasubstituted olefins ranging from 2:1 to complete conversion to tetrasubstituted olefin **396**. The intermediate diaceate **395** was also isolated on occasssion. However, simply adding activated crushed mol sieves to the reaction lead to a consistent 91% yield with a respectable 2:1 ratio in favor of terminal olefin **397**. Separation of these two compounds was extremely difficult but mitigated when the mixture was deacylated prior to separation. A subsequent Dess-Martin oxidation afforded simplfied aldehyde **398** devoid of the allylic alcohol.[249]

In an attempt to improve the propargylation step we decided to install the vinyl group with vinyl lithium instead of the previously used vinyl magnesium bromide. We thought that we

could take advantage of the *in situ* generated nucleophilic lithium alkoxide and achieve propargylation in a single reaction vessel. The *in situ* generation of vinyl lithium from tetravinyltin and *n*-butyllithium smoothly provided the allylic alkoxide within minutes. At which point the lithium cation was sequestered with freshly distilled hexamethylphosphoramide prior to the introduction of propargyl bromide to afford the desired enyne substrate. Following a quantitative trimethylsilyl protection of the terminal alkyne enyne precursor **400** was obtained in a gratifying 80% yield over three steps.[258] The protected alkyne would immediately pay dividends as it increased the yield of the enyne cyclization and would also serve to protect the reactive α-methylene-γ-butyrolactone moiety.



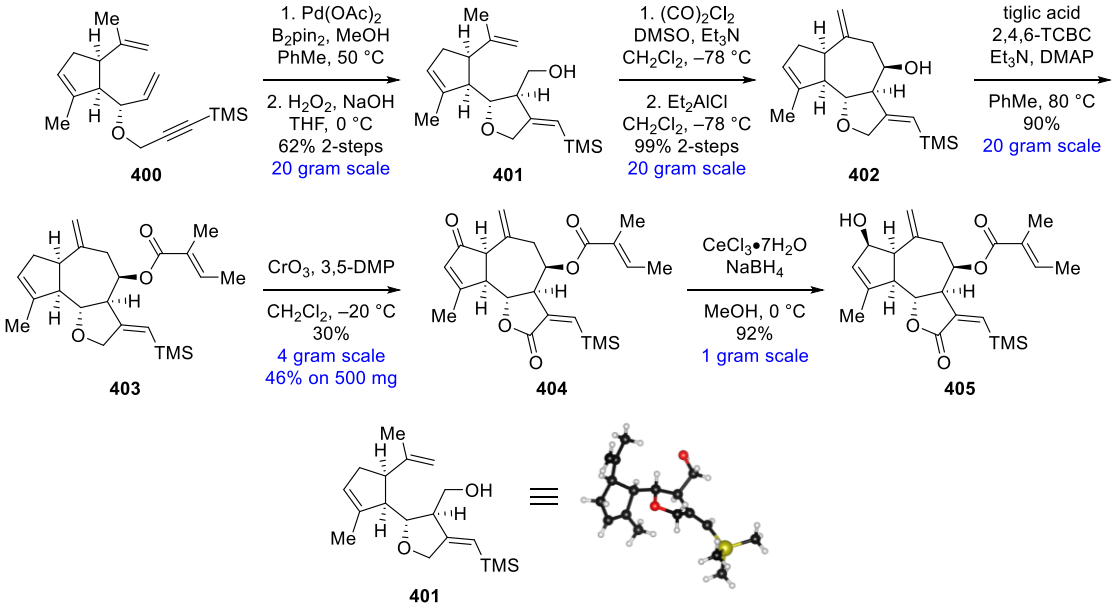
Scheme 2.27. Synthesis of enyne precursor **400**.

With our new enyne precursor **400** in hand the enyne cyclization proceeded in 62% yield which was a two-fold increase over previous substrates (Scheme 2.28).[250,251] Furthermore, the product was highly crystalline and x-ray analysis unambiguously confirmed the Felkin-Anh addition from discrete aldehyde **398** and that the enyne cyclization provided the desired *trans* cyclic ether. Even more impressive was the quantitative yield acquired following the Swern oxidation and diethylaluminum chloride induced aldehyde-ene cyclization to give carbocycle **402**.[237,252]

At this point we were convinced that we could finish the synthesis of eupalinilide E (**256**) and confirm stereochemistry by analysis of the final product. The C8 tigloyl ester was installed using standard Yamaguchi conditions.[259] Exposure of 5,7,5-tricycle **402** to a premixed solution of

tiglic acid and 2,4,6-trichlorobenzyol chloride in the presence of base afforded tiglic ester **403** in good yield.

To our delight treatment of carbocycle **403** with excess chromium trioxide and 3,5-dimethylpyrazole at −20 °C in methylene chloride gave the corresponding enone/butyrolactone product **404** while leaving the tigloyl group untouched. [243-245] However, the unoptimized reaction only gave a 30% isolated yield with nothing else available for recovery. Despite the low yield this reaction could be performed on gram scale to consistently provide hundreds of miligrams of the desired guaianolide **404**. It is important to note that this yield is on par with other cyclopentene allylic oxidations on guaianolide scaffolds and in our case we also achieve allylic oxidation to form the lactone.[206] With guaianolide scaffold **404** possessing the protected α-methylene-γ-butyrolactone moiety in hand a straightforward Luche reduction furnished allylic alcohol **405** as a single diastereomer in 92% yield.[246] In the absence of the trimethylsilyl protecting group the selective reduction of the enone could not be achieved.

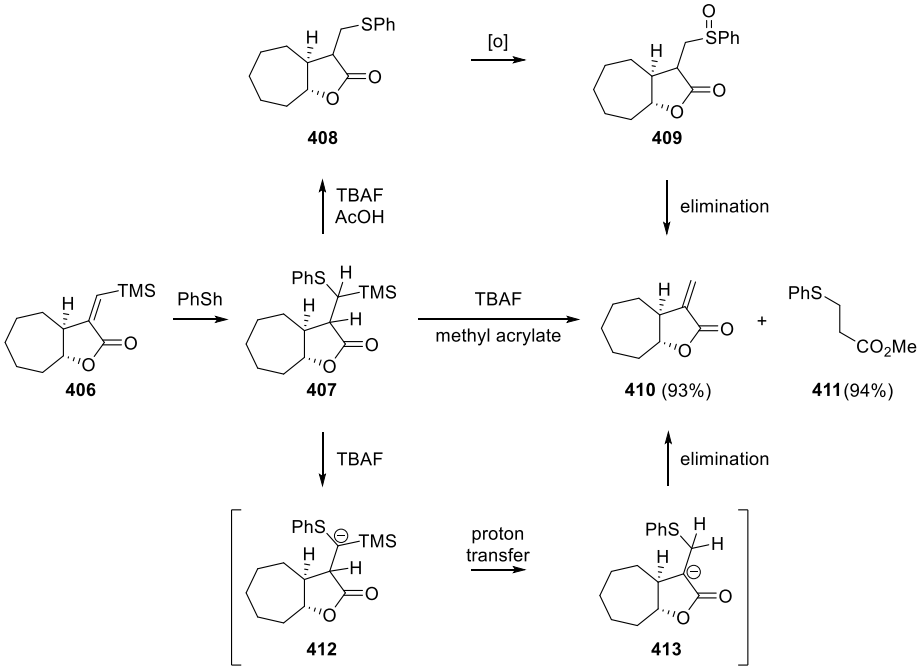


Scheme 2.28. Synthesis of allylic alcohol **405**.

While the fluoride-induced cleavage of Si-C_{sp} bonds in silyl acetylenes is common practice in organic synthesis, the analogous cleavage of Si-C_{sp2} bonds in vinyl silanes is quite

rare.[260] Consequently, the treatment of vinyl silane **405** with tetrabutylammonium fluoride had no effect. An alternative way to remove vinyl silanes involves acid promoted protodesilylation. This reaction proceeds through the initial protonation of the olefin to give a carbocation β to the silicon atom prior to elimination. In the presence of trifluoroacetic acid vinyl silane **405** readily decomposed. This is not surprising given that under the aforementioned pathway the resultant carbocation would also be located α to a carbonyl group, which is highly unfavorable.

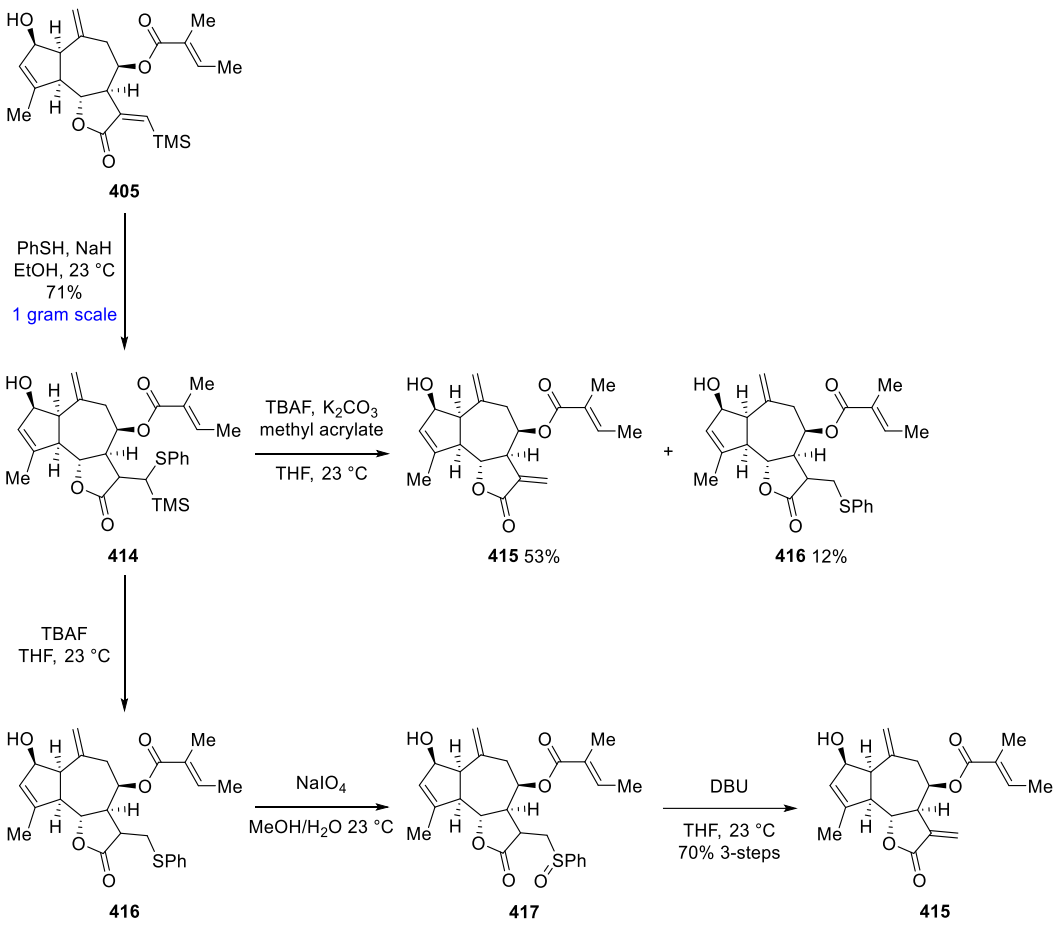
In order to address these shortcomings Bachi disclosed a strategy for the removal of vinyl silanes en route to α-methylene-γ-butyrolactones (Scheme 2.29).[261-263] Initial conjugate addition of thiophenol leads to a Si-C_{sp3} bond that is readily cleaved by a fluoride source to generate a thioadduct **408**. Subsequent oxidation to the sulfoxide **409** facilitates elimination and the desired α,β-unsaturated lactone **410** is obtained. Upon further investigation Bachi discovered that the expulsion of thiophenol occurred in some capacity during the desilylation event. In order to prevent displaced thiophenol from adding back in, an excess of methyl acrylate was added to sequester the nucleophile and allow for the tandem desilylation/sulfide elimination to take place in a single operation.



Scheme 2.29. Bachi's desilylation strategy.

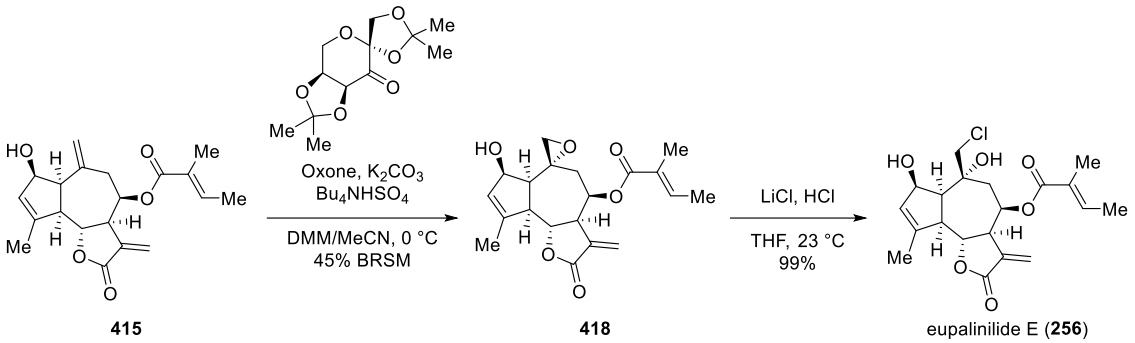
Although Bachi's conditions for the Michael addition of thiophenol did not work on our system, a modified procedure using sodium hydride afforded thio silane **414** in good yield (Scheme 2.30). It is noteworthy that this reaction was sluggish and required at least 48 hours to reach full conversion. Initial attempts to implement the tandem desilylation/sulfide elimination sequence seemed promising, however despite extensive efforts there was always an appreciable quantity of thioadduct **416** in the reaction mixture. A respectable 53% yield of the desired α-methylene-γ-butyrolactone **415** in greater than 90% purity could be obtained but the complete removal of the thioadduct **416** impurity was quite difficult. This was problematic because even trace amounts of thioadduct **416** significantly hindered the success of the following epoxidation reaction.

This minor setback was easily navigated by performing the desired sequence of transformations in a more traditional stepwise fashion. Treatment of thio silane **414** with tetrabutylammonium fluoride in tetrahydrofuran uneventfully furnished thioadduct **416**. Subsequent oxidation to the corresponding sulfoxide was carried out with sodium periodate prior to the 1,8-diazabicycloundec-7-ene induced elimination to afford pure α-methylene-γ-butyrolactone **415** in 70% yield over four-steps as a white solid.



Scheme 2.30. Vinyl TMS deprotection.

All that remained to finish the total synthesis of eupalinilide E (**256**) was the installation of the chlorohydrin. Exposure of guaianolide **415** to *m*-chloroperoxybenzoic acid did not affect the α-methylene-γ-butyrolactone but it was not selective between the exocyclic olefin and allylic alcohol giving rise to a mixture of products. We hypothesized that the use of a bulky epoxidizing agent may provide the selectivity needed to selectively oxidize the exocyclic olefin. This was realized when the Shi catalyst afforded desired epoxide **418**.[264] Subsequent epoxide opening with lithium chloride in the presence of dry hydrochloric acid cleanly revealed the chlorohydrin thus completing the first enantioselective total synthesis of eupalinilide E (**256**). ^{1}H- and ^{13}C-NMR spectral analysis matched that of reported values and 2D-NMR experiments of our own added credence to the assigned structure.



Scheme 2.31. Synthesis of eupalinilide E (**256**).

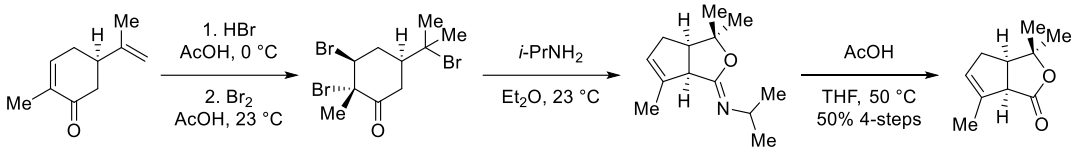
The first enantioselective total synthesis of eupalinilide E (**256**) has been achieved in 20-steps starting from commercially available (*R*)-carvone **337**. Highlighted by a unique Favoskii rearrangement, boralytive enyne cyclization, aldehyde-ene cyclization, and a late-stage dual allylic oxidation a convenient route toward C8 oxygenated guaianolides has been established. Future endeavors will focus on reaction optimization to provide greater quantities of the natural product for subsequent biological testing. Ultimately, we hope to use this knowledge to synthesize affinity probes for mode of action studies to gain insight on how more potent analogs for HSC expansion could be developed.

EXPERIMENTAL SECTION

General Information

All reactions were performed in flame dried round bottom or modified Schlenk (Kjedahl shape) flasks fitted with rubber septa under a positive pressure of argon or nitrogen, unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred via syringe or cannula. Organic solutions were concentrated by rotary evaporation at 20 torr in a water bath heated to 40 °C unless otherwise noted. Diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF) and toluene (PhMe) were purified using a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Acetonitrile (MeCN) was purified using a Vac 103991 Solvent Purification System (Vacuum Atmospheres). Dimethoxyethane (DME) was purchased from Acros (99+%, stabilized with BHT), N,N,-Dimethylformamide (DMF) was purchased from Acros (99.8%, anhydrous), ethanol (EtOH) was purchased from Pharmco-Aaper (200 proof, absolute), and methanol (MeOH) was purchased from Sigma-Aldrich (99.8%, anhydrous). Where necessary, solvents were deoxygenated by iterative freeze-pump thaw using liquid nitrogen three times. The molarity of *n*-butyllithium was determined by titration against diphenylacetic acid. All other reagents were used directly from the supplier without further purification unless otherwise noted. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical) and visualized using a UV lamp and/or aqueous ceric ammonium molybdate (CAM) or aqueous potassium permanganate (KMnO4) stain, or ethanolic vanillin. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film or KBr pellet technique. High-resolution mass spectra (HRMS) were recorded on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, [M] or $[M–H]^–$. Nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) were recorded with a Varian Gemini [(400 MHz, ^{1}H at 400 MHz, ^{13}C at 100 MHz), (500 MHz, ^{1}H at 500 MHz, ^{13}C at 125 MHz), (600 MHz, ^{1}H at 600 MHz, ^{13}C at 150 MHz)]. For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvent; $CHCl_3$ δ H (7.26 ppm) and

$CDCl_3$ δ D (77.0 ppm). For $(CD_3)_2SO$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $(CD_3)(CHD_2)SO$ δ H (2.50 ppm) or $(CD_3)_2SO$ δ C (39.5 ppm). For $(CD_3)_2CO$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $(CD_3)(CHD_2)CO$ δ H (2.50 ppm) or $(CD_3)_2CO$ δ C (29.8 ppm). For C_6D_6 solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; C_6HD_5 δ H (7.16 ppm) or C_6D_6 δ C (128 ppm). For CD_3OD solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; CHD_2OD δ H (3.31 ppm) or CD_3OD δ C (49.0 ppm). For CD_2Cl_2 solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHDCl_2$ δ H (5.32 ppm) or CD_2Cl_2 δ C (53.5 ppm). Coupling constants are reported in Hertz (Hz). Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q= quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, ddq = doublet of doublet of quartets, bs = broad singlet, bd = broad doublet, m = multiplet, coupling constant (Hz), and integration). Melting points were measured on a MEL-TEMP device without corrections.



(*R*)-carvone **337** **364** **369** **368**

(3a*R*,6a*R*)-3,3,6-trimethyl-3,3a,4,6a-tetrahydro-1*H*-cyclopenta[c]furan-1-one (368)[243]

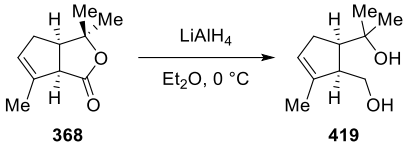
To a stirred solution of 33% hydrobromic acid in acetic acid (219 mL, 1.33 mmol, 2.0 equiv.) at 0 °C was slowly added a solution of *R*-carvone **337** (104 mL, 666 mmol, 1.0 equiv.) in acetic acid (100 mL) dropwise over 15 minutes. After 45 minutes, the reaction mixture was poured over ice H_2O (600 mL) and extracted with EtOAc (3 x 800 mL). The combined organic layers were washed with H_2O (800 mL), half sat. aq. $NaHCO_3$ (800 mL) and brine (800 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude monobromide as an amber oil.

To a stirred solution of crude monobromide (154 g, 666 mmol, 1.0 equiv.) in AcOH (440 mL, 1.5 M) at 23 °C in a water bath was added a solution of bromine (41 mL, 800 mmol, 1.2 equiv.) in AcOH (70 mL) dropwise over 1 hour. After 1.5 hours, the reaction mixture was poured over ice H_2O (600 mL) and extracted with Et_2O (3 x 600 mL). The combined organic layers were washed with H_2O (600 mL), quarter sat. aq. $NaHCO_3$ (5 x 600 mL) and brine (600 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude tribromide **364** as an amber oil.

To a stirred solution of crude tribromide **364** (260 g, 7.32 mol, 1.0 equiv.) in Et_2O (2.66 L, 0.25 M) at 0 °C was slowly added isopropyl amine (630 mL, 7.32 mol, 11 equiv.) over 30 minutes. Upon complete addition, the reaction mixture was allowed to warm to 23 °C. After 12 hours, the reaction mixture was cooled to 0 °C before carefully adding 10% aq. H_2SO_4 (600 mL). The aqueous layer was separated and the organic layer was extracted with 10% aq. H_2SO_4 (3 x 600 mL). The combined aqueous layers were cooled to 0 °C with stirring before being brought to pH = 8.0 with 10 N NaOH (600 mL). The neutralized solution was extracted with EtOAc (4 x 600 mL), washed with brine (600 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude imidate as an amber oil.

A stirred solution of crude imidate (138 g, 666 mol, 1 equiv.) in a 3:1 solution of THF:10% aq. AcOH (1.33 L, 0.5 M) was heated to 50 °C. After 3 hours, the reaction mixture was cooled to 23 °C before pouring over ice and sat. aq. $NaHCO_3$ (1 L). The reaction mixture was extracted with EtOAc (4 x 600 mL), washed with brine (600 mL), dried over Na_2SO_4, and concentrated in vacuo to give an amber oil. The crude material was purified via silica gel column chromatography (5:1 hexanes:EtOAc) followed by recrystallization from hexanes to give pure bicycle **368** (55.3 g, 333 mmol, 50% over 4-steps) as a white solid (m.p. 33-35 °C).

$\mathbf{R}_f$ = 0.41 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.23 (bd, *J* = 2.0 Hz, 1H), 3.39 (d, *J* = 9.0 Hz, 1H), 2.81, (q, *J* = 6.3 Hz, 1H), 2.30 (t, *J* = 2.0 Hz, 2H), 2.28 (t, *J* = 2.0 Hz, 1H), 1.68 (s, 3H), 1.26 (s, 3H), 1.17 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 175.2, 135.5, 126.1, 85.2, 56.1, 47.9, 33.1, 30.2, 23.4, 14.1; **IR** (film, cm^{-1}): 1758, 1270, 1119; **HRMS** (ESI) calc. for $C_{10}H_{14}O_2$ $[M+Na]^+$: 189.08860, obs. 189.08940.

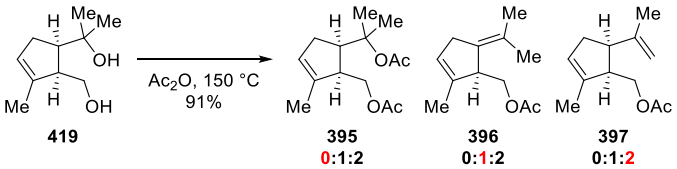


368 **419**

2-((1*R*,2*R*)-2-(hydroxymethyl)-3-methylcyclopent-3-en-1-yl)propan-2-ol (**419**)

To a stirred solution of bicycle **368** (32 g, 193 mmol, 1.0 equiv.) in Et_2O (960 mL, 0.2 M) at 0 °C was slowly added a 4.0 M solution of lithium aluminum hydride in Et_2O (48 mL, 193 mmol, 1.0 equiv.) over 20 minutes. After 40 minutes, the reaction mixture was carefully quenched with H_2O (7.3 mL), 15% aq. NaOH (7.3 mL), and H_2O (21.9 mL) at 0 °C. The reaction mixture was dried over Na_2SO_4 and concentrated *in vacuo* to give pure diol **419** (32.4 g, 191 mmol, 99%) as a white solid (m.p. 73-75 °C).

$\mathbf{R_f}$ = 0.23 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.43 (bs, 1H), 4.57 (bs, 1H), 4.36 (bs, 1H), 3.77 (d, *J* = 12 Hz, 1H), 3.51 (dd, *J* = 11, 5.5 Hz, 1H), 2.5 (bd, *J* = 2.7 Hz, 1H), 2.31-2.23 (m, 2H), 2.09 (bd, *J* = 8.6 Hz, 1H), 1.65 (s, 1H), 1.33 (s, 1H), 1.20 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 139.9, 125.8, 71.1, 60.1, 53.6, 51.4, 32.2, 29.8, 29.4, 15.1; **IR** (film, cm^{-1}): 3282, 1360, 1053, 1004; **HRMS** (ESI): calc. for $C_{10}H_{18}O_2$ $[M+Na]^+$: 193.11930, obs. 193.11990.



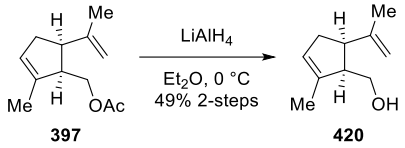
A stirred solution of diol **419** (40 g, 235 mmol, 1 equiv.), activated 4.0 Å molecular sieves (20 g, 50% by weight), and Ac_2O (160 mL, 1.5 M) was heated to 150 °C. After 16 hours, the reaction mixture was cooled to 23 °C and passed through a short silica gel plug (10:1 hexanes:EtOAc) to give an inseparable 2:1 mixture of acetates **397** and **396** (41.5 g, 214 mmol, 91%) as an amber oil.

((1R,5R)-2-methyl-5-(prop-1-en-2-yl)cyclopent-2-en-1-yl)methyl acetate (397)
(*S*)-(2-methyl-5-(propan-2-ylidene)cyclopent-2-en-1-yl)methyl acetate (396)

R_f = 0.46 (silica gel, 10:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [**397**] 5.48 (bs, 1H), 4.86 (s, 1H), 4.80 (s, 1H), 4.07 (dd, *J* = 11, 5.7 Hz, 1H), 3.83 (dd, *J* = 11, 5.7 Hz, 1H), 3.33 (bs, 1H), 2.88 (bs, 1H), 2.43 (td, *J* = 11, 2.0 Hz, 1H), 2.16 (dd, *J* = 15, 7.7 Hz, 1H), 2.00 (s, 3H), 1.79 (s, 3H), 1.75 (s, 3H), [**396**] 5.49 (bs, 1H), 4.25 (dd, *J* = 11, 6.6 Hz, 1H), , 3.97 (dd, *J* = 11, 6.6 Hz, 1H), 2.93 (q, *J* = 8.7 Hz, 1H), 2.88 (bs, 1H), 2.73 (q, *J* = 6.2 Hz, 1H), 2.03 (s, 3H), 1.77 (s, 3H), 1.73 (s, 3H), 1.63 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 171.0, 170.9, 144.5, 140.4, 133.4, 126.2, 125.4, 124.9, 110.9, 110.9, 66.2, 63.6, 63.6, 50.2, 49.6, 48.5, 36.3, 33.8, 23.1, 21.0, 20.9, 20.5, 16.0, 15.9; **IR** (film, cm^{-1}): 1741, 1379, 1252, 1038.

2-((1*R*,2*R*)-2-(acetoxymethyl)-3-methylcyclopent-3-en-1-yl)propan-2-yl acetate (395)

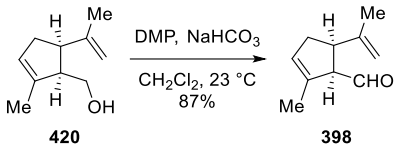
R_f = 0.30 (silica gel, 10:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.47 (bs, 1H), 4.44 (dd, *J* = 11, 5.5 Hz, 1H), 3.94 (dd, *J* = 11, 7.0 Hz, 1H), 2.68 (q, *J* = 7.0 Hz, 1H), 2.40-2.30 (m, 2H), 2.15 (dd, *J* = 11, 5.5 Hz, 1H), 2.01 (s, 3H), 1.95 (s, 3H), 1.76 (s, 3H), 1.65 (s, 3H), 1.50 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 171.0, 170.2, 141.9, 125.8, 125.8, 82.1, 64.6, 55.0, 47.7, 31.2, 25.5, 22.4, 21.1, 16.6; **IR** (film, cm^{-1}): 1732, 1367, 1228, 1023.



((1*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclopent-2-en-1-yl)methanol (420)

To a stirred solution of acetates **396** and **397** (41.5 g, 214 mmol, 1.0 equiv.) in Et_2O (1.1 L, 0.2 M) at 0 °C was slowly added a 4.0 M solution of lithium aluminum hydride in Et_2O (26.7 mL, 107 mmol, 0.5 equiv.) over 20 minutes. After 40 minutes, the reaction mixture was carefully quenched with H_2O (4.1 mL), 15% aq. NaOH (4.1 mL), and H_2O (12.3 mL) at 0 °C. The reaction mixture was dried over Na_2SO_4 and concentrated *in vacuo* to give a clear oil. The crude material was purified via silica gel column chromatography (50:1 to 20:1 hexanes:EtOAc) to give pure alcohol **420** (15.9 g, 105 mmol, 49% over 2-steps) as a clear oil.

R_f = 0.36 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.51 (s, 1H), 4.94 (s, 1H), 4.91 (s, 1H), 3.56 (dd, *J* = 9.4, 4.7, 2H), 2.96 (q, *J* = 8.6 Hz, 1H), 2.63 (bs, 1H), 2.45 (dd, *J* = 12, 6.3 Hz, 1H), 2.17 (dd, *J* = 12, 6.3 Hz, 1H), 1.83 (s, 3H), 1.73 (s, 3H), 1.59 (bs, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 146.4, 139.5, 126.2, 110.8, 61.3, 52.6, 49.3, 34.3, 23.5, 15.5; **IR** (film, cm^{-1}): 3381, 1447, 1037, 888; **HRMS** (EC-CI): calc. for $C_{10}H_{16}O$ [M]: 152.1201, obs. 152.1196.

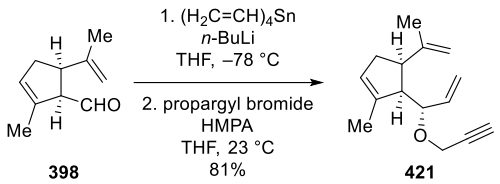


420 398

(1*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclopent-2-ene-1-carbaldehyde (398)

To a stirred solution of alcohol **420** (26.2 g, 172 mmol, 1.0 equiv.) in CH_2Cl_2 (860 mL, 0.2 M) at 23 °C was added solid $NaHCO_3$ (43.4 g, 517 mmol, 3 equiv.), solid Dess-Martin periodinane (110 g, 258 mmol, 1.5 equiv.), and H_2O (1 mL). After 45 minutes, the reaction mixture was diluted with sat. aq. $NaHCO_3$ (500 mL) and sat. $Na_2S_2O_4$ and stirred for 10 minutes. The reaction mixture was extracted with CH_2Cl_2 (3 x 800 mL), washed with brine (800 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (10:1 hexanes:EtOAc) to give pure aldehyde **398** (22.5 g, 150 mmol, 87%) as a clear oil.

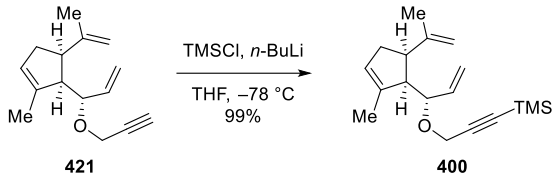
$\mathbf{R}_f$ = 0.56 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 9.35 (d, *J* = 5.5 Hz, 1H), 5.77 (bs, 1H), 4.90 (s, 1H), 4.87 (s, 1H), 3.22 (q, *J* = 9.1 Hz, 1H), 3.17 (t, *J* = 6.3 Hz, 1H), 2.71 (t, *J* = 10 Hz, 1H), 2.43 (dd, *J* = 16, 8.1 Hz, 1H), 1.75 (s, 3H), 1.67 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 201.1, 143.2, 135.5, 130.0, 111.7, 63.4, 49.7, 34.6, 22.9, 15.6; **IR** (film, cm^{-1}): 1720, 1446, 892.



(4*R*,5*R*)-1-methyl-4-(prop-1-en-2-yl)-5-((*S*)-1-(prop-2-yn-1-yloxy)allyl)cyclopent-1-ene (**421**)

To a stirred solution of tetravinyl tin (11 mL, 59.9 mmol, 0.4 equiv.) in THF (600 mL) at −78 °C was added a 2.14 M solution of *n*-butyllithium in hexanes (91 mL, 195 mmol, 1.3 equiv.). The reaction mixture was warmed and stirred at 23 °C for 15 minutes before being cooled back down to −78 °C and adding a solution of aldehyde **398** (22.5 g, 150 mmol, 1 equiv.) in THF (150 mL). After 15 minutes, freshly distilled neat hexamethylphosphoramide (52 mL, 299 mmol, 2 equiv.) was added. After an additional 10 minutes an 80% solution of propargyl bromide in toluene (83 mL, 749 mmol, 5 equiv.) was added. Upon complete addition the reaction mixture was allowed to warm to 23 °C. After 3 hours, the reaction mixture was diluted with sat. aq. NH_4Cl (50 mL), extracted with Et_2O (3 x 50 mL), washed with 3.0 N LiCl (3 x 50 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a yellow oil. The crude material was purified via silica gel column chromatography (straight hexanes to 50:1 to 20:1 hexanes:EtOAc) to give pure enyne **421** (26.2 g, 121 mmol, 81%) as a clear oil.

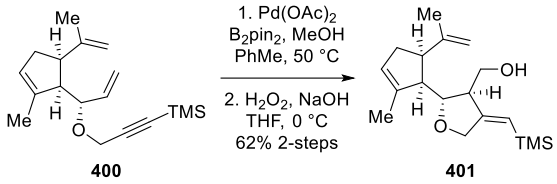
$\mathbf{R}_f$ = 0.50 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.86 (ddd, *J* = 17, 11, 7.4 Hz, 1H), 5.56 (bs, 1H), 5.19 (d, *J* = 10 Hz, 1H), 5.15 (d, *J* = 6.7 Hz, 1H), 4.90 (s, 2H), 4.10 (dd, *J* = 13, 2.4 Hz, 1H), 3.93 (dd, *J* = 13, 2.4 Hz, 1H), 3.88 (dd, *J* = 8.6, 2.7 Hz, 1H), 2.88 (q, *J* = 8.2 Hz, 1H), 2.63 (bd, *J* = 7.8 Hz, 1H), 2.53 (ddq, *J* = 20, 9.4, 2.4 Hz, 1H), 2.32 (t, *J* = 2.7 Hz, 1H), 2.12 (dd, *J* = 11, 7.4 Hz, 1H), 1.80 (s, 3H), 1.79 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 145.3, 139.4, 137.7, 127.4, 116.8, 111.7, 80.7, 80.4, 73.5, 55.7, 54.9, 51.1, 34.8, 23.5, 17.8; **IR** (film, cm^{-1}): 1384, 1074, 404; **HRMS** (EC-CI): calc. for $C_{15}H_{20}O$ [M]: 216.1514, obs. 216.1515.



trimethyl(3-(((*S*)-1-((1*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclopent-2-en-1-yl)allyl)oxy)prop-1-yn-1-yl)silane (**400**)

To a stirred solution of enyne **421** (26.2 g, 121 mmol, 1.0 equiv.) in THF (1.2 L, 0.1 M) at −78 °C was added a 2.14 M solution of *n*-butyllithium in hexanes (68 mL, 145 mmol, 1.2 equiv.). After 20 minutes, freshly distilled neat trimethylsilyl chloride (31 mL, 242 mmol, 2 equiv.) was added. Upon complte addition the reaction mixture was allowed to warm to 23 °C. After 30 minutes, the reaction mixture was quenched with sat. aq. NH_4Cl (400 mL), extracted with Et_2O (3 x 400 mL), washed with brine (400 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give pure TMS enyne **400** (35 g, 121 mmol, 99%) as a clear oil.

$\mathbf{R}_f$ = 0.44 (silica gel, 20:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.85 (ddd, *J* = 17, 11, 7.4 Hz, 1H), 5.55 (bs, 1H), 5.28 (d, *J* = 16 Hz, 1H), 5.14 (d, *J* = 9.0 Hz, 1H), 4.88 (s, 2H), 4.11 (d, *J* = 16 Hz, 1H), 3.95 (d, *J* = 16 Hz, 1H), 3.94 (dd, *J* = 7.8, 2.7 Hz, 1H), 2.87 (q, *J* = 7.8 Hz, 1H), 2.63 (bd, *J* = 6.7 Hz, 1H), 2.50 (ddq, *J* = 20 , 9.4, 2.4 Hz, 1H), 2.13 (dd, *J* = 7.8, 2.7 Hz, 1H), 1.81 (s, 3H), 1.79 (s, 3H), 0.16 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 145.1, 139.6, 137.6, 127.1, 116.8, 111.7, 102.3, 90.3, 80.2, 56.3, 54.8, 50.9, 34.8, 23.3, 17.7, -0.3; **IR** (film, cm^{-1}): 1384, 1251, 1076, 843, 403; **HRMS** (EC-CI): calc. for $C_{18}H_{28}OSi$ [M]: 288.1909, obs. 288.1901.

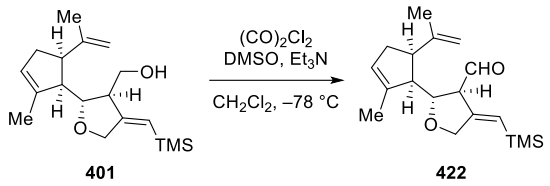


((2*R*,3*R*,*Z*)-2-((1*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclopent-2-en-1-yl)-4-((trimethylsilyl)methylene)tetrahydrofuran-3-yl)methanol (401)

To a stirred solution of TMS enyne **400** (20.8 g, 72.1 mmol, 1.0 equiv.) in PhMe (720 mL, 0.1 M) at 23 °C was added solid bis(pinacolato)diboron (20.1 g, 79 mmol, 1.1 equiv.), palladium(II) acetate (809 mg, 3.60 mmol, 0.05 equiv.), and MeOH (2.92 mL, 72.1 mmol, 1.0 equiv.). The reaction mixture was heated to and stirred at 50 °C. After 15 hours, the reaction mixture was cooled to 23 °C and concentrated *in vacuo* to give the boronate ester as an amber oil.

To a stirred solution of crude boronate ester (30 g, 72.0 mmol, 1.0 equiv.) in THF (1.4 L, 0.05 M) at 0 °C was carefully added 3.33 N NaOH (64.9 mL, 216 mmol, 3 equiv.) and 50% aq. H_2O_2 (130 mL, 2.16 mol, 30 equiv.) over 1 hour. The reaction mixture was diluted with brine (700 mL), extracted with EtOAc (3 x 500 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a yellow oil. The crude material was purified via silica gel column chromatography (5:1 hexanes:EtOAc) to give pure alcohol **401** (13.7 g, 44.7 mmol, 62% over 2-steps) as a white solid (m.p. 62-64 °C).

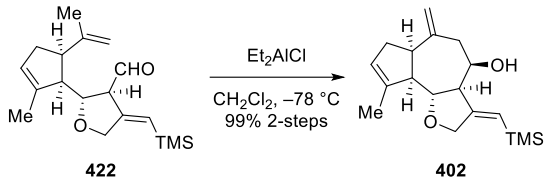
R_f = 0.41 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.54 (bs, 1H), 5.50 (q, *J* = 2.4 Hz, 1H), 4.88 (s, 1H), 4.85 (s, 1H), 4.38 (dd, *J* = 14, 2.4 Hz, 1H), 4.23 (dt, *J* = 14, 2.4 Hz, 1H), 3.91 (t, *J* = 5.1 Hz, 1H), 3.65 (dt, *J* = 11, 6.3 Hz, 1H), 3.60 (dt, *J* = 11, 6.3 Hz, 1H), 2.93 (q, *J* = 7.8 Hz, 1H), 2.70-2.66 (bm, 2H), 2.45 (ddq, *J* = 15, 8.6, 2.4 Hz, 1H), 2.20 (dd, *J* = 14, 7.8 Hz, 1H), 1.81 (s, 3H), 1.76 (s, 3H), 1.63 (t, *J* = 5.9 Hz, 1H), 0.07 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 157.9, 145.9, 140.3, 127.2, 119.9, 111.9, 81.2, 70.2, 64.0, 53.5, 51.8, 51.1, 34.7, 22.8, 17.8, -0.7; **IR** (film, cm^{-1}): 3404, 1384, 401; **HRMS** (ESI): calc. for $C_{18}H_{30}O_2Si$ $[M+Na]^+$: 329.19070, obs. 329.19090.



(2*R*,3*S*,*Z*)-2-((1*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclopent-2-en-1-yl)-4-((trimethylsilyl)methylene)tetrahydrofuran-3-carbaldehyde (422)

To a stirred solution of oxalyl chloride (5.23 mL, 59.8 mmol, 1.5 equiv.) in CH_2Cl_2 (250 mL) at −78 °C was slowly added a solution of dimethyl sulfoxide (14.2 mL, 199 mmol, 5 equiv.) in CH_2Cl_2 (100 mL) over 10 minutes. After 30 minutes, a solution of alcohol **401** (12.2g, 39.9 mmol, 1 equiv.) in CH_2Cl_2 (50 mL) was added. After 2 hours, neat trimethylamine (28.0 mL, 199 mmol, 5 equiv.) was added in a single portion and the reaction mixture was allowed to warm to 23 °C. The reaction mixture was then diluted with 0.1 N HCl (200 mL). The organic layer was separated and washed with 0.1 N HCl (2 x 200 mL) and 3.0 N LiCl (400 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude aldehyde **422** (12.1 g, 39.9 mmol, yield taken after subsequent step) as a clear oil.

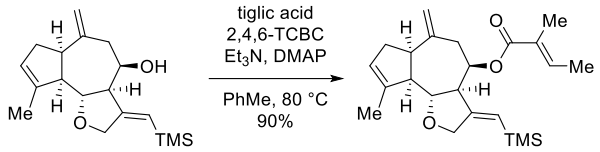
R_f = 0.69 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 9.32 (d, *J* = 3.9 Hz, 1H), 5.55 (s, 1H), 5.53 (bs, 1H), 4.85 (s, 2H), 4.41 (dd, *J* = 14, 2.4 Hz, 1H), 4.33 (t, *J* = 6.3 Hz, 1H), 4.22 (dd, *J* = 14, 2.4 Hz, 1H) 3.40 (bt, *J* = 2.4, 1H), 2.93 (q, *J* = 7.8 Hz, 1H), 2.71 (t, *J* = 6.3 Hz, 1H), 2.46 (dd, *J* = 15, 7.4 Hz, 1H), 2.21 (dd, *J* = 15, 7.4 Hz, 1H), 1.82 (s, 3H), 1.73 (s, 3H), 0.08 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 196.6, 151.9, 144.9, 139.8, 127.4, 124.0, 112.4, 78.7, 70.2, 63.7, 51.7, 50.6, 34.7, 22.9, 17.4, -0.9; **IR** (film, cm^{-1}): 1722, 1249, 840; **HRMS** (ESI): calc. for $C_{18}H_{28}O_2Si$ $[M+Na]^+$: 327.17510, obs. 327.17530.



(3a*R*,4*R*,6a*R*,9a*R*,9b*R*,*Z*)-9-methyl-6-methylene-3-((trimethylsilyl)methylene)-2,3,3a,4,5,6,6a,7,9a,9b-decahydroazuleno[4,5-*b*]furan-4-ol (**402**)

To a stirred solution of crude aldehyde **422** (12.1 g, 39.9 mmol, 1.0 equiv.) in CH_2Cl_2 (400 mL, 0.1 M) at −78 °C was added a 1.0 M solution of diethylaluminum chloride in hexanes (19.9 mL, 19.9 mmol, 0.5 equiv.) in a single portion. After 10 minutes, the reaction mixture was quenched with 10% aq. NaOH (20 mL). The reaction mixture was warmed to 23 °C, further diluted with brine (200 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to give a yellow oil. The crude material was purified via silica gel column chromatography (5:1 hexanes:EtOAc) to give pure 5,7,5-tricycle **402** (12.1 g, 39.9 mmol, 99% over 2-steps) as a white solid (m.p. 64-66 °C).

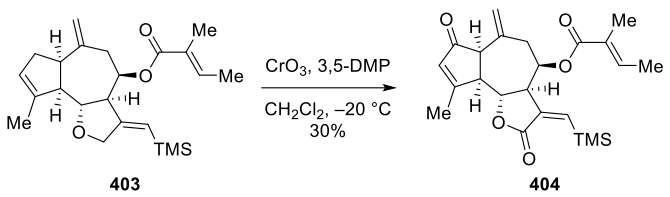
$\mathbf{R}_f$ = 0.60 (silica gel, 5:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.47 (s, 1H), 5.45 (d, *J* = 2.4 Hz, 1H), 4.97 (s, 1H), 4.88 (s, 1H), 4.48 (d, *J* = 14 Hz, 1H), 4.22 (dt, *J* = 8.2, 4.7 Hz, 1H), 4.09 (dt, *J* = 14, 2.4 Hz, 1H), 3.73 (t, *J* = 9.8 Hz, 1H), 3.16 (q, *J* = 8.0 Hz, 1H), 2.63 (t, *J* = 9.0 Hz, 1H), 2.54-2.40 (m, 5H), 1.96 (d, *J* = 4.7 Hz, 1H), 1.84 (s, 3H), 0.10 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 158.6, 145.2, 142.3, 125.1, 117.3, 115.0, 79.3, 71.1, 66.4, 57.0, 56.1, 49.1, 36.8, 17.3, -0.6; **IR** (film, cm^{-1}): 3413, 1065, 838; **HRMS** (ESI): calc. for $C_{18}H_{28}O_2Si$ $[M+Na]^+$: 327.17510, obs. 327.17510.



(3a*R*,4*R*,6a*R*,9a*R*,9b*R*,*Z*)-9-methyl-6-methylene-3-((trimethylsilyl)methylene)-2,3,3a,4,5,6,6a,7,9a,9b-decahydroazuleno[4,5-*b*]furan-4-yl (*E*)-2-methylbut-2-enoate (**403**)

To a stirred solution of tiglic acid (13.8 g, 138 mmol, 2.0 equiv.) in PhMe (345 mL) at 23 °C was added neat trimethylamine (38.4 mL, 276 mmol, 4.0 equiv.) and neat 2,4,6-trichlorobenzoyl chloride (23.7 mL, 152 mmol, 2.2 equiv.). After 1 hour, a solution of 5,7,5-tricycle **402** (21.0 g, 69.0 mmol, 1.0 equiv.) in PhMe (345 mL) and solid dimethylaminopyridine (21.9 g, 179 mmol, 2.6 equiv.) were added. The reaction mixture was then heated to 80 °C. After 45 minutes, the reaction mixture was cooled to 23 °C, diluted with sat. aq. $NaHCO_3$, extracted with EtOAc (3 x 500 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give an amber oil. The crude material was purified via silica gel column chromatography (20:1 hexanes:EtOAc) to give pure tigloyl ester **403** (24.0 g, 62.1 mmol, 90%) as a clear oil.

R_f = 0.18 (silica gel, 20:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.75 (q, *J* = 6.7 Hz, 1H), 5.49 (s, 1H), 5.41 (q, *J* = 5.5 Hz, 1H), 5.31 (s, 1H), 4.91 (s, 1H), 4.77 (s, 1H), 4.47 (d, *J* = 14 Hz, 1H), 4.06 (d, *J* = 14 Hz, 1H), 3.89 (t, *J* = 9.4 Hz, 1H), 3.16 (q, *J* = 7.8 Hz, 1H), 2.69 (d, *J* = 9.0 Hz, 1H), 2.68 (t, *J* = 9.0 Hz, 1H), 2.60 (dd, *J* = 14, 5.5 Hz, 1H), 2.47 (dd, *J* = 14, 5.1 Hz, 1H), 2.43 (d, *J* = 7.0 Hz, 1H), 2.42 (d, *J* = 9.0 Hz, 1H), 1.86 (s, 3H), 1.76 (s, 3H), 1.75 (d, *J* = 6.7 Hz, 3H), 0.0 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 167.5, 156.6, 144.7, 142.1, 136.9, 128.6, 125.3, 117.3, 115.1, 80.5, 71.0, 69.8, 56.3, 55.1, 48.7, 39.4, 37.0, 17.3, 14.3, 12.0, -0.7; **IR** (film, cm^{-1}): 1713, 1250, 1066, 805; **HRMS** (ESI): calc. for $C_{23}H_{34}O_3Si$ $[M+Na]^+$: 409.21710, obs. 409.21690.

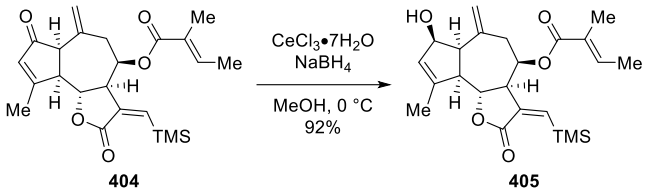


403 404

(3a*R*,4*R*,6a*R*,9a*R*,9b*R*,*Z*)-9-methyl-6-methylene-2,7-dioxo-3-((trimethylsilyl)methylene)-2,3,3a,4,5,6,6a,7,9a,9b-decahydroazuleno[4,5-*b*]furan-4-yl (*E*)-2-methylbut-2-enoate (404)

To a stirred solution of CrO_3 (20.7 g, 207 mmol, 20 equiv.) in CH_2Cl_2 (100 mL, 0.05 M) at 0 °C was added solid 3,5-dimethylpyrazole (19.9 g, 207 mmol, 20 equiv.) in a single portion. A solution of carbocycle **403** (4.0 g, 10.4 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) was then added. After 45 minutes, the reaction mixture was directly purified via florasil column chromatography (2:1 hexanes:EtOAc) to give pure guaianolide **404** (1.29 g, 3.10 mmol, 30%) as a clear oil.

R_f = 0.22 (silica gel, 2:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.70 (q, *J* = 7.0 Hz, 1H), 6.37 (d, *J* = 3.1 Hz, 1H), 6.15 (s, 1H), 5.53 (td, *J* = 4.7, 2.7 Hz, 1H), 5.07 (s, 1H), 4.96 (s, 1H), 4.54 (dd, *J* = 11, 9.0 Hz, 1H), 3.32 (d, *J* = 7.0 Hz, 1H), 3.20 (t, 9.8 Hz, 1H), 3.18 (dt, *J* = 8.6, 2.7 Hz, 1H), 2.55 (bs, 2H), 2.36 (s, 3H), 1.75 (d, *J* = 7.8 Hz, 3H), 1.74 (s, 3H), 0.15 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 206.1, 177.9, 168.6, 166.9, 145.5, 138.9, 138.5, 138.1, 132.3, 127.9, 120.4, 78.1, 67.1, 56.2, 53.4, 51.2, 41.1, 19.9, 14.3, 11.9, -1.0; **IR** (film, cm^{-1}): 1765, 1707, 1249; **HRMS** (ESI): calc. for $C_{23}H_{30}O_5Si$ $[M+Na]^+$: 437.17550, obs. 437.17580.

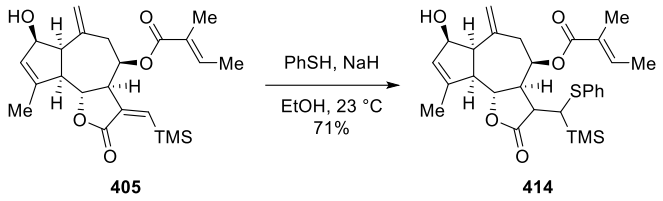


404 405

(3a*R*,4*R*,6a*R*,7*R*,9a*R*,9b*R*,*Z*)-7-hydroxy-9-methyl-6-methylene-2-oxo-3-((trimethylsilyl)methylene)-2,3,3a,4,5,6,6a,7,9a,9b-decahydroazuleno[4,5-*b*]furan-4-yl (*E*)-2-methylbut-2-enoate (**405**)

To a stirred solution of enone **404** (755 mg, 1.82 mmol, 1.0 equiv.) in MeOH (36 mL, 0.05 M) at 0 °C was added solid cerium(III) chloride heptahydrate (1.36 g, 3.64 mmol, 2.0 equiv.). After 20 minutes, solid sodium borohydride (138 mg, 3.64 mmol, 2.0 equiv.) was added in three even portions. After 15 minutes, the reaction mixture was warmed to 23 °C and diluted with 0.2 M aq. pH = 7.0 phosphate buffer. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to give pure allylic alcohol **405** (700 mg, 1.68 mmol, 92%) as a clear oil.

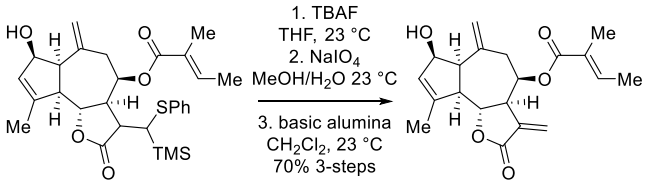
R_f = 0.24 (silica gel, 3:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.69 (q, *J* = 5.5 Hz, 1H), 6.24 (d, *J* = 2.7 Hz, 1H), 5.71 (bs, 1H), 5.43 (td, *J* = 7.8, 3.9 Hz, 1H), 5.09 (s, 2H), 4.71 (bt, *J* = 5.1 Hz, 1H), 4.65 (dd, *J* = 11, 9.0 Hz, 1H), 3.16 (dt, *J* = 6.7, 2.7 Hz, 1H), 3.14 (d, *J* = 3.9 Hz, 1H), 2.88 (dd, *J* = 14, 7.4 Hz, 1H), 2.71 (dd, *J* = 14, 7.4 Hz, 1H), 2.67 (t, *J* = 9.4 Hz, 1H), 1.99 (s, 3H), 1.74 (d, *J* = 5.5 Hz, 3H), 1.73 (s, H), 0.13 (s, 9H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 169.4, 167.2, 147.8, 144.5, 142.0, 139.9, 137.9, 128.9, 128.0, 119.0, 80.8, 79.0, 68.5, 56.2, 52.6, 49.8, 38.7, 17.3, 14.3, 11.9, -1.0; **IR** (film, cm^{-1}): 3485, 1764, 1709, 1259, 1247; **HRMS** (ESI): calc. for $C_{23}H_{32}O_5Si$ $[M+Na]^+$: 439.19110, obs. 439.19110.



(3a*R*,4*R*,6a*R*,7*R*,9a*R*,9b*R*)-7-hydroxy-9-methyl-6-methylene-2-oxo-3-((phenylthio)(trimethylsilyl)methyl)-2,3,3a,4,5,6,6a,7,9a,9b-decahydroazuleno[4,5-*b*]furan-4-yl (*E*)-2-methylbut-2-enoate (414)

To a stirred solution of vinyl silane **405** (267 mg, 0.641 mmol, 1.0 equiv.) in EtOH (6.4 mL, 0.1 M) at 23 °C was added neat thiophenol (2.88 mL, 28.2 mmol, 44 equiv.) and 60% NaH in mineral oil (103 mg, 2.56 mmol, 4.0 equiv.). After 48 hours, the reaction mixture was concentrated *in vacuo* and purified directly via silica gel column chromatography (straight hexanes to 2:1 hexanes:EtOAc) to give pure thio silane **414** (238 mg, 0.452 mmol, 71%) as a white foam.

HRMS (ESI): calc. for $C_{29}H_{38}O_5SSi$ $[M+Na]^+$: 549.21010, obs. 549.21030.



414 415

(3a*R*,4*R*,6a*R*,7*R*,9a*R*,9b*R*)-7-hydroxy-9-methyl-3,6-dimethylene-2-oxo-2,3,3a,4,5,6,6a,7,9a,9b-decahydroazuleno[4,5-*b*]furan-4-yl (*E*)-2-methylbut-2-enoate (415)

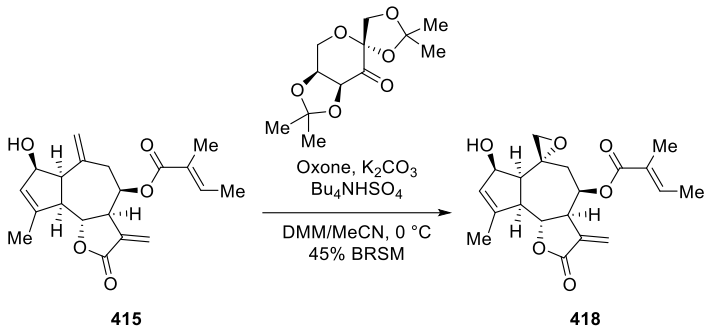
To a stirred solution of thio silane **414** (238 mg, 0.452 mmol, 1.0 equiv.) in THF (4.5 mL, 0.1 M) at 23 °C was added a 1.0 M of tetrabutylammonium fluoride in THF (0.90mL, 1.38 mmol, 1.5 equiv.). After 30 minutes, the reaction mixture was passed through a plug of silica gel (2:1 hexanes:EtOAc) to give crude thio adduct **416** as an amber oil.

To a stirred solution of crude thio adduct **416** (205 mg, 0.452 mmol, 1.0 equiv.) in MeOH (4.5 mL, 0.1 M) at 0 °C was added a solution of sodium periodate (145 mg, 0.678 mmol, 1.5 equiv.) in H_2O (4.5 mL). After 15 hours, the reaction mixture was extracted with EtOAc (3 x 10 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give crude sulfone **417** as a white solid.

A solution of crude sulfone **417** (220 mg, 0.452 mmol, 1.0 equiv.), basic alumina (220 mg, 100% by weight), and CH_2Cl_2 (4.5 mL, 0.1 M) was stirred at 23 °C. After 2 hours, the reaction mixture was passed through a plug of Celite to give a clear oil. The crude material was purified via silica gel column chromatography (2:1 hexanes:EtOAc) to give pure butyrolactone **415** (109 mg, 0.316 mmol, 70%) as a clear oil.

$\mathbf{R}_f$ = 0.54 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.73 (q, *J* = 5.5 Hz, 1H), 6.29 (d, *J* = 3.5 Hz, 1H), 5.73 (bs, 1H), 5.52 (dd, *J* = 11, 3.5 Hz, 1H), 5.51 (d, *J* = 3.5 Hz, 1H), 5.12 (s, 1H), 5.11 (s, 1H), 4.73 (bs, 1H), 4.66 (dd, *J* = 11, 8.6 Hz, 1H), 3.19 (dd, *J* = 12, 2.7 Hz, 1H), 3.17 (d, *J* = 5.9 Hz, 1H), 2.85 (dd, *J* = 14, 6.7 Hz, 1H), 2.73 (dd, *J* = 14, 7.8 Hz, 1H), 2.68 (t, *J* = 9.4 Hz, 1H), 1.99 (s, 3H), 1.76 (d, *J* = 5.9 Hz, 3H), 1.75 (s, 3H), 1.70 (d, *J* = 5.1 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ 169.6, 167.2, 147.3, 141.7, 138.3, 134.2, 129.2, 128.0,

122.4, 119.2, 80.8, 78.8, 67.8, 56.1, 52.6, 47.8, 39.1, 17.3, 14.4, 12.0; **IR** (film, cm^{-1}): 3413, 1384, 1137; **HRMS** (ESI): calc. for $C_{20}H_{24}O_5$ $[M+Na]^+$: 367.15160, obs. 367.15200.

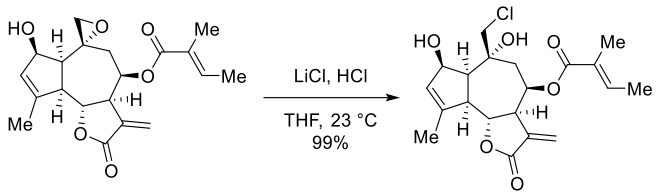


415 418

(3a*R*,4*R*,6*R*,6a*S*,7*R*,9a*R*,9b*R*)-7-hydroxy-9-methyl-3-methylene-2-oxo-3,3a,4,5,6a,7,9a,9b-octahydro-2*H*-spiro[azuleno[4,5-*b*]furan-6,2'-oxiran]-4-yl (*E*)-2-methylbut-2-enoate (418)

To a stirred solution of allylic alcohol **415** (38 mg, 0.110 mmol, 1.0 equiv.) in 2:1 DMM:MeCN (2.2 mL, 0.05 M) at 23 °C was added tetrabutylammonium bisulfate (4 mg, 0.011 mmol, 0.1 equiv.), the Shi catalyst (6 mg, 0.022 mmol, 0.2 equiv.), and pH = 9.3 phosphate buffer. The reaction mixture was cooled to 0 °C before adding a solution of potassium carbonate (0.088 mg, 0.640 mmol, 5.8 equiv.) in H_2O (0.1 mL) and a solution of Oxone (0.075 mg, 0.121 mmol, 1.1 equiv.) in H_2O (0.1 mL) simultaneously over 1 hour. The reaction mixture was diluted with brine (2 mL), extracted with CH_2Cl_2 (3 x 5 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a white solid. The crude material was purified via silica gel column chromatography (2:1 hexanes:EtOAc) to give pure epoxide **418** (18 mg, 0.050 mmol, 45% BRSM) as a clear oil.

R_f = 0.54 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.70 (q, *J* = 6.4 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 5.71 (bs, 1H), 5.57 (td, *J* = 8.6, 4.7 Hz, 1H), 5.55 (d, *J* = 2.8 Hz, 1H), 4.68 (bs, 1H), 4.67 (t, *J* = 8.8 Hz, 1H), 3.56 (dd, *J* = 8.6, 4.7 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 1H), 2.77 (t, *J* = 9.6 Hz, 1H), 2.61 (dd, *J* = 14, 7.6 Hz, 1H), 2.35 (d, *J* = 9.2 Hz, 1H), 2.25 (dd, *J* = 15, 8.4 Hz, 1H), 2.01 (s, 3H), 1.97 (d, *J* = 7.2 Hz, 1H), 1.77 (s, 3H), 1.73 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 169.6, 167.1, 148.9, 138.3, 133.9, 128.9, 128.0, 123.0, 100.0, 81.0, 66.8, 56.3, 55.8, 55.4, 52.4, 47.9, 36.6, 17.5, 14.4, 12.1; **IR** (film, cm^{-1}): 3477, 1768, 1339, 1140, 1037; **HRMS** (ESI): calc. for $C_{20}H_{24}O_6$ $[M+Na]^+$: 383.14650, obs. 383.14680.



418 eupalinilide E (**256**)

eupalinilide E (256)

To a stirred solution of crude epoxide **418** (10 mg, 0.028 mmol, 1.0 equiv.) in THF (1.0 mL, 0.3 M) at 23 °C was added solid lithium chloride (6 mg, 0.139 mmol, 5.0 equiv.) in a single portion followed by a 1.25 M solution of hydrochloric acid in MeOH (0.02 mL, 0.028 mmol, 1.0 equiv.). After 5 minutes, the reaction mixture was diluted with brine (1.0 mL), extracted with CH_2Cl_2 (3 x 2 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a white solid. The crude material was purified via silica gel column chromatography (2:1 hexanes:EtOAc) to give pure eupalinilide E (**256**) (11 mg, 0.028 mmol, 99%) as a white solid (m.p. °C).

$\mathbf{R}_f$ = 0.63 (silica gel, 1:1 hexanes:EtOAc); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.70 (q, *J* = 5.5 Hz, 1H), 6.27 (d, *J* = 3.5 Hz, 1H), 5.75 (bs, 1H), 5.65 (td, *J* = 8.6, 4.7 Hz, 1H), 5.45 (d, *J* = 3.5 Hz, 1H), 4.59 (bs, 1H), 4.58 (t, *J* = 8.6 Hz, 1H), 3.94 (d, *J* = 11 Hz, 1H), 3.93 (bs, 1H), 3.67 (d, *J* = 11 Hz, 1H), 2.77 (dd, *J* = 11, 7.4 Hz, 1H), 2.50-2.44 (m, 4H), 2.04 (s, 3H), 1.74 (d, *J* = 5.3 Hz, 3H), 1.73 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 169.7, 167.2, 150.6, 138.1, 134.4, 128.6, 128.1, 122.1, 82.0, 75.1, 73.6, 66.4, 55.2, 55.0, 52.2, 47.4, 36.4, 18.0, 14.4, 12.0; **IR** (film, cm^{-1}): 3409, 1654, 1384, 1129; **HRMS** (ESI): calc. for $C_{20}H_{25}ClO_6$ $[M+Na]^+$: 419.12320, obs. 419.12290.

Appendix A: Crystallographic Data for 394

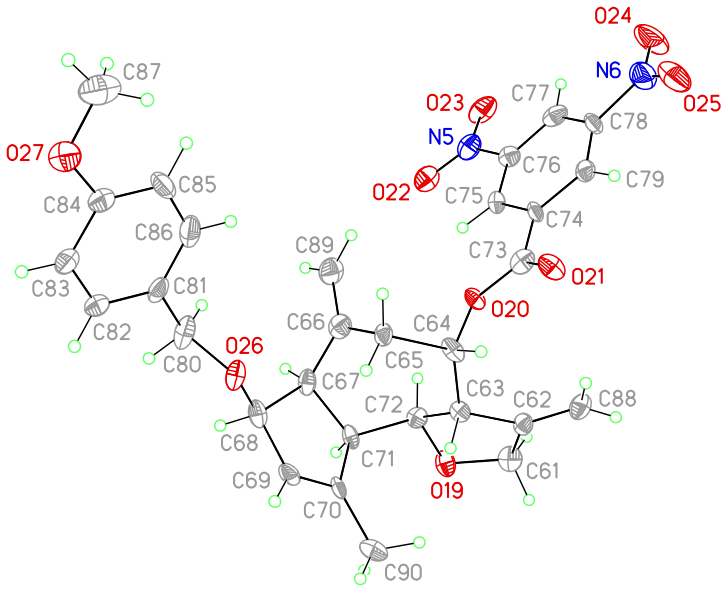


Table 1. Crystal data and structure refinement for 394.

Empirical formula	C30 H30 N2 O9	
Formula weight	562.56	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 25.044(3) Å	α = 90°.
	b = 5.4847(12) Å	β = 97.558(6)°.
	c = 29.751(4) Å	γ = 90°.
Volume	4051.1(11) $Å^3$	
Z	6	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	1776	
Crystal size	0.300 x 0.050 x 0.040 mm	
Theta range for data collection	1.640 to 24.999°.	
Index ranges	-29<=h<=29, -6<=k<=6, -35<=l<=35	
Reflections collected	53001	
Independent reflections	14309 [R(int) = 0.1855]	
Completeness to theta = 25.242°	97.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.854	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14309 / 1 / 1114	
Goodness-of-fit on F^2	0.980	
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.1139	
R indices (all data)	R1 = 0.1907, wR2 = 0.1502	
Absolute structure parameter	-0.6(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.278 and -0.315 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 394. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	-1326(3)	7658(16)	3274(3)	25(2)
C2	-1166(3)	5296(17)	3086(3)	21(2)
C3	-675(3)	4387(15)	3391(2)	16(2)
C4	-271(3)	2970(16)	3167(2)	18(2)
C5	253(3)	2409(15)	3482(2)	16(2)
C6	566(3)	4643(16)	3649(3)	20(2)
C7	455(3)	5860(16)	4078(3)	21(2)
C8	597(3)	4116(17)	4496(3)	24(2)
C9	58(3)	3235(18)	4593(2)	25(2)
C10	-342(3)	4545(16)	4401(3)	19(2)
C11	-151(3)	6487(15)	4098(2)	16(2)
C12	-472(3)	6753(15)	3629(3)	20(2)
C13	-89(3)	3234(19)	2404(3)	21(2)
C14	183(3)	4770(16)	2087(2)	15(2)
C15	475(3)	6817(16)	2247(3)	19(2)
C16	759(3)	8050(16)	1950(3)	20(2)
C17	771(3)	7365(16)	1505(3)	21(2)
C18	481(3)	5271(16)	1365(2)	16(2)
C19	198(3)	3955(17)	1643(2)	21(2)
C20	1505(3)	2930(18)	4481(3)	30(2)
C21	1844(3)	1005(17)	4317(3)	23(2)
C22	1865(3)	692(19)	3853(3)	34(3)
C23	2172(3)	-1109(17)	3691(3)	28(2)
C24	2476(3)	-2622(18)	3982(3)	28(2)
C25	2480(3)	-2298(19)	4446(3)	35(3)
C26	2171(3)	-532(19)	4607(3)	35(3)
C27	2717(3)	-5080(20)	3382(3)	43(3)
C28	-1403(3)	4243(18)	2711(3)	35(3)
C29	942(3)	5548(17)	3419(3)	29(2)
C30	-923(3)	4409(18)	4487(3)	31(2)
C31	4504(3)	3555(18)	86(3)	34(3)

C32	4255(3)	1330(17)	274(3)	21(2)
C33	3797(3)	542(16)	-77(3)	17(2)
C34	3287(3)	-302(16)	88(2)	21(2)
C35	2845(3)	-904(16)	-291(2)	18(2)
C36	2642(3)	1288(16)	-572(3)	18(2)
C37	2898(3)	1955(15)	-990(2)	18(2)
C38	2809(3)	-126(16)	-1351(3)	22(2)
C39	3352(3)	-1248(16)	-1348(2)	22(2)
C40	3743(3)	31(17)	-1115(3)	22(2)
C41	3523(3)	2245(16)	-898(3)	22(2)
C42	3736(3)	2725(17)	-403(2)	23(2)
C43	3016(3)	1034(19)	796(3)	23(2)
C44	2701(3)	3002(17)	999(3)	18(2)
C45	2407(3)	4736(17)	734(3)	26(2)
C46	2103(3)	6420(17)	939(3)	20(2)
C47	2088(3)	6444(18)	1398(3)	26(2)
C48	2371(3)	4653(19)	1651(3)	25(2)
C49	2674(3)	2921(17)	1463(3)	21(2)
C50	1879(3)	-1067(17)	-1433(3)	26(2)
C51	1481(3)	-2766(16)	-1262(3)	20(2)
C52	1261(3)	-4718(17)	-1517(3)	23(2)
C53	928(3)	-6382(17)	-1345(3)	26(2)
C54	814(3)	-6088(17)	-903(3)	22(2)
C55	1007(3)	-4097(16)	-649(3)	20(2)
C56	1337(3)	-2458(17)	-829(3)	26(2)
C57	490(3)	-7994(18)	-269(2)	35(3)
C58	4399(3)	381(18)	678(3)	35(3)
C59	2235(3)	2639(17)	-465(3)	26(2)
C60	4333(3)	-427(19)	-1103(3)	35(3)
C61	7746(3)	12627(16)	3645(3)	27(2)
C62	7581(3)	10201(16)	3812(3)	20(2)
C63	7113(3)	9303(15)	3475(2)	17(2)
C64	6696(3)	7723(16)	3660(2)	19(2)
C65	6198(3)	7229(15)	3320(2)	19(2)
C66	5876(3)	9458(17)	3158(3)	25(2)
C67	6011(3)	10825(16)	2748(2)	21(2)

C68	5921(3)	9217(17)	2304(3)	24(2)
C69	6476(3)	8578(16)	2220(2)	21(2)
C70	6849(3)	9898(16)	2455(3)	18(2)
C71	6612(3)	11576(16)	2773(2)	17(2)
C72	6902(3)	11710(15)	3254(3)	20(2)
C73	6576(3)	7755(18)	4445(3)	23(2)
C74	6348(3)	9158(16)	4800(3)	18(2)
C75	6041(3)	11239(16)	4699(3)	19(2)
C76	5816(3)	12390(17)	5039(3)	23(2)
C77	5850(3)	11479(18)	5471(3)	27(2)
C78	6153(3)	9408(19)	5562(3)	27(2)
C79	6401(3)	8217(17)	5237(3)	22(2)
C80	5021(3)	7825(18)	2222(3)	33(3)
C81	4668(3)	5639(18)	2232(3)	26(2)
C82	4450(3)	4500(19)	1830(3)	30(2)
C83	4096(3)	2596(19)	1836(3)	33(3)
C84	3965(3)	1759(18)	2248(3)	30(3)
C85	4172(3)	2846(19)	2645(3)	33(3)
C86	4526(3)	4767(19)	2633(3)	33(3)
C87	3461(4)	-1130(20)	2623(3)	49(3)
C88	7806(3)	9080(17)	4187(3)	27(2)
C89	5472(3)	10191(17)	3367(3)	31(2)
C90	7436(3)	9986(17)	2389(3)	29(2)
N1	1091(3)	10165(14)	2121(2)	24(2)
N2	515(3)	4361(17)	905(2)	29(2)
N3	1797(3)	8310(16)	660(3)	30(2)
N4	2324(3)	4562(19)	2142(2)	41(2)
N5	5473(3)	14554(15)	4927(3)	30(2)
N6	6164(3)	8291(19)	6016(3)	41(2)
O1	-949(2)	8131(11)	3668(2)	24(2)
O2	-118(2)	4395(10)	2794(2)	18(1)
O3	-251(2)	1186(12)	2308(2)	28(2)
O4	1085(2)	10769(11)	2514(2)	32(2)
O5	1348(2)	11211(12)	1859(2)	30(2)
O6	761(2)	5621(12)	657(2)	36(2)
O7	303(2)	2387(12)	794(2)	30(2)

O8	951(2)	2162(10)	4420(2)	24(2)
O9	2778(2)	-4511(12)	3857(2)	35(2)
O10	4271(2)	3728(11)	-378(2)	28(2)
O11	3088(2)	1622(10)	368(2)	20(1)
O12	3171(2)	-776(12)	998(2)	28(2)
O13	1765(2)	8084(12)	247(2)	36(2)
O14	1600(2)	9974(12)	857(2)	37(2)
O15	2061(3)	6174(14)	2295(2)	46(2)
O16	2564(3)	2921(16)	2358(2)	59(2)
O17	2414(2)	-1907(10)	-1273(2)	20(1)
O18	498(2)	-7897(11)	-752(2)	25(2)
O19	7376(2)	13203(11)	3249(2)	24(2)
O20	6518(2)	8977(10)	4050(2)	19(1)
O21	6778(2)	5764(11)	4508(2)	26(2)
O22	5401(2)	15205(11)	4529(2)	31(2)
O23	5297(2)	15604(12)	5239(2)	37(2)
O24	5981(3)	9452(15)	6307(2)	56(2)
O25	6367(3)	6249(15)	6073(2)	48(2)
O26	5584(2)	7163(10)	2320(2)	25(2)
O27	3607(2)	-186(13)	2208(2)	39(2)

Table 3. Bond lengths [Å] and angles [°] for 394.

C1-O1	1.428(8)	C14-C15	1.389(11)
C1-C2	1.487(11)	C14-C19	1.400(10)
C1-H1A	0.99	C15-C16	1.383(10)
C1-H1B	0.99	C15-H15	0.95
C2-C28	1.325(10)	C16-C17	1.378(10)
C2-C3	1.513(10)	C16-N1	1.478(10)
C3-C4	1.500(10)	C17-C18	1.393(11)
C3-C12	1.532(11)	C17-H17	0.95
C3-H3	1.00	C18-C19	1.366(10)
C4-O2	1.450(8)	C18-N2	1.470(10)
C4-C5	1.539(10)	C19-H19	0.95
C4-H4	1.00	C20-O8	1.439(9)
C5-C6	1.504(11)	C20-C21	1.477(11)
C5-H5A	0.99	C20-H20A	0.99
C5-H5B	0.99	C20-H20B	0.99
C6-C29	1.332(10)	C21-C26	1.393(11)
C6-C7	1.498(11)	C21-C22	1.400(11)
C7-C11	1.565(10)	C22-C23	1.377(12)
C7-C8	1.571(10)	C22-H22	0.95
C7-H7	1.00	C23-C24	1.359(11)
C8-O8	1.427(9)	C23-H23	0.95
C8-C9	1.498(11)	C24-O9	1.362(10)
C8-H8	1.00	C24-C25	1.391(11)
C9-C10	1.302(10)	C25-C26	1.365(12)
C9-H9	0.95	C25-H25	0.95
C10-C30	1.512(10)	C26-H26	0.95
C10-C11	1.512(11)	C27-O9	1.435(9)
C11-C12	1.523(9)	C27-H27A	0.98
C11-H11	1.00	C27-H27B	0.98
C12-O1	1.432(9)	C27-H27C	0.98
C12-H12	1.00	C28-H28A	0.95
C13-O3	1.215(10)	C28-H28B	0.95
C13-O2	1.333(9)	C29-H29A	0.95
C13-C14	1.494(11)	C29-H29B	0.95

C30-H30A	0.98	C43-C44	1.509(12)
C30-H30B	0.98	C44-C45	1.385(11)
C30-H30C	0.98	C44-C49	1.391(10)
C31-O10	1.429(8)	C45-C46	1.389(11)
C31-C32	1.510(11)	C45-H45	0.95
C31-H31A	0.99	C46-C47	1.372(10)
C31-H31B	0.99	C46-N3	1.477(11)
C32-C58	1.314(10)	C47-C48	1.377(11)
C32-C33	1.509(10)	C47-H47	0.95
C33-C34	1.502(10)	C48-C49	1.379(11)
C33-C42	1.537(11)	C48-N4	1.482(10)
C33-H33	1.00	C49-H49	0.95
C34-O11	1.472(9)	C50-O17	1.439(8)
C34-C35	1.510(9)	C50-C51	1.500(11)
C34-H34	1.00	C50-H50A	0.99
C35-C36	1.513(11)	C50-H50B	0.99
C35-H35A	0.99	C51-C52	1.385(11)
C35-H35B	0.99	C51-C56	1.392(11)
C36-C59	1.332(11)	C52-C53	1.379(11)
C36-C37	1.517(10)	C52-H52	0.95
C37-C41	1.561(10)	C53-C54	1.392(10)
C37-C38	1.563(10)	C53-H53	0.95
C37-H37	1.00	C54-C55	1.378(11)
C38-O17	1.429(9)	C54-O18	1.381(10)
C38-C39	1.492(11)	C55-C56	1.376(11)
C38-H38	1.00	C55-H55	0.95
C39-C40	1.324(10)	C56-H56	0.95
C39-H39	0.95	C57-O18	1.438(8)
C40-C60	1.495(10)	C57-H57A	0.98
C40-C41	1.513(11)	C57-H57B	0.98
C41-C42	1.521(10)	C57-H57C	0.98
C41-H41	1.00	C58-H58A	0.95
C42-O10	1.443(9)	C58-H58B	0.95
C42-H42	1.00	C59-H59A	0.95
C43-O12	1.199(10)	C59-H59B	0.95
C43-O11	1.346(9)	C60-H60A	0.98

C60-H60B	0.98	C74-C75	1.387(10)
C60-H60C	0.98	C74-C79	1.389(10)
C61-O19	1.435(8)	C75-C76	1.375(11)
C61-C62	1.497(11)	C75-H75	0.95
C61-H61A	0.99	C76-C77	1.370(11)
C61-H61B	0.99	C76-N5	1.478(11)
C62-C88	1.333(10)	C77-C78	1.372(12)
C62-C63	1.520(10)	C77-H77	0.95
C63-C64	1.516(10)	C78-C79	1.381(11)
C63-C72	1.536(11)	C78-N6	1.479(11)
C63-H63	1.00	C79-H79	0.95
C64-O20	1.466(8)	C80-O26	1.448(9)
C64-C65	1.524(9)	C80-C81	1.492(12)
C64-H64	1.00	C80-H80A	0.99
C65-C66	1.509(11)	C80-H80B	0.99
C65-H65A	0.99	C81-C86	1.376(11)
C65-H65B	0.99	C81-C82	1.395(11)
C66-C89	1.316(10)	C82-C83	1.373(12)
C66-C67	1.510(11)	C82-H82	0.95
C67-C71	1.555(10)	C83-C84	1.388(11)
C67-C68	1.579(10)	C83-H83	0.95
C67-H67	1.00	C84-C85	1.363(11)
C68-O26	1.413(9)	C84-O27	1.388(10)
C68-C69	1.484(10)	C85-C86	1.381(12)
C68-H68	1.00	C85-H85	0.95
C69-C70	1.309(10)	C86-H86	0.95
C69-H69	0.95	C87-O27	1.431(10)
C70-C71	1.496(10)	C87-H87A	0.98
C70-C90	1.510(10)	C87-H87B	0.98
C71-C72	1.520(9)	C87-H87C	0.98
C71-H71	1.00	C88-H88A	0.95
C72-O19	1.444(9)	C88-H88B	0.95
C72-H72	1.00	C89-H89A	0.95
C73-O21	1.207(10)	C89-H89B	0.95
C73-O20	1.345(9)	C90-H90A	0.98
C73-C74	1.480(11)	C90-H90B	0.98

C90-H90C	0.98	N4-O16	1.217(10)
N1-O5	1.217(8)	N4-O15	1.225(10)
N1-O4	1.219(8)	N5-O23	1.225(8)
N2-O6	1.232(9)	N5-O22	1.227(8)
N2-O7	1.233(9)	N6-O24	1.213(9)
N3-O14	1.223(9)	N6-O25	1.232(10)
N3-O13	1.227(8)		

O1-C1-C2	106.6(7)	C29-C6-C5	120.4(8)
O1-C1-H1A	110.4	C7-C6-C5	119.8(7)
C2-C1-H1A	110.4	C6-C7-C11	114.9(6)
O1-C1-H1B	110.4	C6-C7-C8	110.7(7)
C2-C1-H1B	110.4	C11-C7-C8	102.9(6)
H1A-C1-H1B	108.6	C6-C7-H7	109.4
C28-C2-C1	125.6(8)	C11-C7-H7	109.4
C28-C2-C3	126.9(8)	C8-C7-H7	109.4
C1-C2-C3	107.4(7)	O8-C8-C9	112.5(8)
C4-C3-C2	116.5(6)	O8-C8-C7	114.4(7)
C4-C3-C12	116.2(7)	C9-C8-C7	103.4(6)
C2-C3-C12	101.0(7)	O8-C8-H8	108.8
C4-C3-H3	107.5	C9-C8-H8	108.8
C2-C3-H3	107.5	C7-C8-H8	108.8
C12-C3-H3	107.5	C10-C9-C8	113.5(8)
O2-C4-C3	108.8(7)	C10-C9-H9	123.2
O2-C4-C5	106.6(6)	C8-C9-H9	123.2
C3-C4-C5	113.8(6)	C9-C10-C30	126.9(8)
O2-C4-H4	109.2	C9-C10-C11	111.3(8)
C3-C4-H4	109.2	C30-C10-C11	121.5(7)
C5-C4-H4	109.2	C10-C11-C12	116.3(7)
C6-C5-C4	113.8(7)	C10-C11-C7	104.6(6)
C6-C5-H5A	108.8	C12-C11-C7	112.5(6)
C4-C5-H5A	108.8	C10-C11-H11	107.7
C6-C5-H5B	108.8	C12-C11-H11	107.7
C4-C5-H5B	108.8	C7-C11-H11	107.7
H5A-C5-H5B	107.7	O1-C12-C11	108.7(6)
C29-C6-C7	119.8(8)	O1-C12-C3	104.8(6)

C11-C12-C3	116.4(7)	C21-C22-H22	119.1
O1-C12-H12	108.9	C24-C23-C22	120.5(8)
C11-C12-H12	108.9	C24-C23-H23	119.7
C3-C12-H12	108.9	C22-C23-H23	119.7
O3-C13-O2	126.2(8)	C23-C24-O9	125.2(8)
O3-C13-C14	122.6(8)	C23-C24-C25	118.9(9)
O2-C13-C14	111.2(8)	O9-C24-C25	115.9(8)
C15-C14-C19	120.2(8)	C26-C25-C24	120.7(9)
C15-C14-C13	120.2(7)	C26-C25-H25	119.7
C19-C14-C13	119.1(8)	C24-C25-H25	119.7
C16-C15-C14	117.9(7)	C25-C26-C21	121.7(8)
C16-C15-H15	121.0	C25-C26-H26	119.1
C14-C15-H15	121.0	C21-C26-H26	119.1
C17-C16-C15	123.9(8)	O9-C27-H27A	109.5
C17-C16-N1	117.5(8)	O9-C27-H27B	109.5
C15-C16-N1	118.5(7)	H27A-C27-H27B	109.5
C16-C17-C18	115.9(8)	O9-C27-H27C	109.5
C16-C17-H17	122.1	H27A-C27-H27C	109.5
C18-C17-H17	122.1	H27B-C27-H27C	109.5
C19-C18-C17	123.1(8)	C2-C28-H28A	120.0
C19-C18-N2	118.9(8)	C2-C28-H28B	120.0
C17-C18-N2	117.9(8)	H28A-C28-H28B	120.0
C18-C19-C14	118.9(8)	C6-C29-H29A	120.0
C18-C19-H19	120.5	C6-C29-H29B	120.0
C14-C19-H19	120.5	H29A-C29-H29B	120.0
O8-C20-C21	109.6(7)	C10-C30-H30A	109.5
O8-C20-H20A	109.7	C10-C30-H30B	109.5
C21-C20-H20A	109.7	H30A-C30-H30B	109.5
O8-C20-H20B	109.7	C10-C30-H30C	109.5
C21-C20-H20B	109.7	H30A-C30-H30C	109.5
H20A-C20-H20B	108.2	H30B-C30-H30C	109.5
C26-C21-C22	116.2(8)	O10-C31-C32	106.0(7)
C26-C21-C20	123.0(8)	O10-C31-H31A	110.5
C22-C21-C20	120.7(8)	C32-C31-H31A	110.5
C23-C22-C21	121.9(8)	O10-C31-H31B	110.5
C23-C22-H22	119.1	C32-C31-H31B	110.5

H31A-C31-H31B	108.7	C37-C38-H38	108.4
C58-C32-C33	127.6(8)	C40-C39-C38	113.3(8)
C58-C32-C31	125.5(8)	C40-C39-H39	123.4
C33-C32-C31	106.8(7)	C38-C39-H39	123.4
C34-C33-C32	117.6(6)	C39-C40-C60	125.7(8)
C34-C33-C42	115.3(7)	C39-C40-C41	111.3(7)
C32-C33-C42	102.6(7)	C60-C40-C41	122.6(8)
C34-C33-H33	106.9	C40-C41-C42	116.8(7)
C32-C33-H33	106.9	C40-C41-C37	104.8(7)
C42-C33-H33	106.9	C42-C41-C37	113.8(6)
O11-C34-C33	109.3(7)	C40-C41-H41	106.9
O11-C34-C35	108.0(6)	C42-C41-H41	106.9
C33-C34-C35	113.2(6)	C37-C41-H41	106.9
O11-C34-H34	108.7	O10-C42-C41	108.8(6)
C33-C34-H34	108.7	O10-C42-C33	104.3(6)
C35-C34-H34	108.7	C41-C42-C33	118.0(7)
C34-C35-C36	113.5(7)	O10-C42-H42	108.4
C34-C35-H35A	108.9	C41-C42-H42	108.4
C36-C35-H35A	108.9	C33-C42-H42	108.4
C34-C35-H35B	108.9	O12-C43-O11	126.8(9)
C36-C35-H35B	108.9	O12-C43-C44	122.8(8)
H35A-C35-H35B	107.7	O11-C43-C44	110.4(8)
C59-C36-C35	121.5(8)	C45-C44-C49	119.7(8)
C59-C36-C37	118.7(8)	C45-C44-C43	122.0(7)
C35-C36-C37	119.8(7)	C49-C44-C43	118.1(8)
C36-C37-C41	113.7(6)	C44-C45-C46	119.2(8)
C36-C37-C38	110.4(7)	C44-C45-H45	120.4
C41-C37-C38	104.2(6)	C46-C45-H45	120.4
C36-C37-H37	109.5	C47-C46-C45	122.1(8)
C41-C37-H37	109.5	C47-C46-N3	118.2(8)
C38-C37-H37	109.5	C45-C46-N3	119.6(7)
O17-C38-C39	111.5(7)	C46-C47-C48	117.3(8)
O17-C38-C37	115.4(6)	C46-C47-H47	121.3
C39-C38-C37	104.5(6)	C48-C47-H47	121.3
O17-C38-H38	108.4	C47-C48-C49	122.7(8)
C39-C38-H38	108.4	C47-C48-N4	117.5(8)

C49-C48-N4	119.8(8)	H58A-C58-H58B	120.0
C48-C49-C44	118.9(8)	C36-C59-H59A	120.0
C48-C49-H49	120.6	C36-C59-H59B	120.0
C44-C49-H49	120.6	H59A-C59-H59B	120.0
O17-C50-C51	108.7(7)	C40-C60-H60A	109.5
O17-C50-H50A	109.9	C40-C60-H60B	109.5
C51-C50-H50A	109.9	H60A-C60-H60B	109.5
O17-C50-H50B	110.0	C40-C60-H60C	109.5
C51-C50-H50B	110.0	H60A-C60-H60C	109.5
H50A-C50-H50B	108.3	H60B-C60-H60C	109.5
C52-C51-C56	117.9(8)	O19-C61-C62	106.9(7)
C52-C51-C50	121.9(8)	O19-C61-H61A	110.3
C56-C51-C50	120.2(8)	C62-C61-H61A	110.3
C53-C52-C51	121.6(8)	O19-C61-H61B	110.3
C53-C52-H52	119.2	C62-C61-H61B	110.3
C51-C52-H52	119.2	H61A-C61-H61B	108.6
C52-C53-C54	119.0(8)	C88-C62-C61	125.6(8)
C52-C53-H53	120.5	C88-C62-C63	127.4(8)
C54-C53-H53	120.5	C61-C62-C63	107.0(7)
C55-C54-O18	124.4(8)	C64-C63-C62	116.9(6)
C55-C54-C53	120.5(9)	C64-C63-C72	115.6(7)
O18-C54-C53	115.0(8)	C62-C63-C72	101.2(7)
C56-C55-C54	119.3(8)	C64-C63-H63	107.5
C56-C55-H55	120.3	C62-C63-H63	107.5
C54-C55-H55	120.3	C72-C63-H63	107.5
C55-C56-C51	121.5(8)	O20-C64-C63	108.4(6)
C55-C56-H56	119.2	O20-C64-C65	107.5(6)
C51-C56-H56	119.2	C63-C64-C65	113.7(6)
O18-C57-H57A	109.5	O20-C64-H64	109.0
O18-C57-H57B	109.5	C63-C64-H64	109.0
H57A-C57-H57B	109.5	C65-C64-H64	109.0
O18-C57-H57C	109.5	C66-C65-C64	115.1(7)
H57A-C57-H57C	109.5	C66-C65-H65A	108.5
H57B-C57-H57C	109.5	C64-C65-H65A	108.5
C32-C58-H58A	120.0	C66-C65-H65B	108.5
C32-C58-H58B	120.0	C64-C65-H65B	108.5

H65A-C65-H65B	107.5	O20-C73-C74	110.9(8)
C89-C66-C65	120.6(8)	C75-C74-C79	119.4(8)
C89-C66-C67	119.8(9)	C75-C74-C73	121.9(7)
C65-C66-C67	119.5(7)	C79-C74-C73	118.4(8)
C66-C67-C71	114.3(6)	C76-C75-C74	119.1(8)
C66-C67-C68	112.2(7)	C76-C75-H75	120.4
C71-C67-C68	102.6(6)	C74-C75-H75	120.4
C66-C67-H67	109.2	C77-C76-C75	122.8(9)
C71-C67-H67	109.2	C77-C76-N5	117.9(8)
C68-C67-H67	109.2	C75-C76-N5	119.0(8)
O26-C68-C69	113.2(7)	C76-C77-C78	116.9(8)
O26-C68-C67	115.8(7)	C76-C77-H77	121.6
C69-C68-C67	103.9(6)	C78-C77-H77	121.6
O26-C68-H68	107.9	C77-C78-C79	122.7(8)
C69-C68-H68	107.9	C77-C78-N6	117.9(9)
C67-C68-H68	107.9	C79-C78-N6	119.1(9)
C70-C69-C68	113.4(8)	C78-C79-C74	118.9(9)
C70-C69-H69	123.3	C78-C79-H79	120.5
C68-C69-H69	123.3	C74-C79-H79	120.5
C69-C70-C71	111.4(7)	O26-C80-C81	110.9(7)
C69-C70-C90	125.9(8)	O26-C80-H80A	109.4
C71-C70-C90	122.4(7)	C81-C80-H80A	109.5
C70-C71-C72	116.4(7)	O26-C80-H80B	109.4
C70-C71-C67	105.5(6)	C81-C80-H80B	109.4
C72-C71-C67	113.5(6)	H80A-C80-H80B	108.0
C70-C71-H71	107.0	C86-C81-C82	118.2(9)
C72-C71-H71	107.0	C86-C81-C80	121.2(8)
C67-C71-H71	107.0	C82-C81-C80	120.6(9)
O19-C72-C71	108.0(6)	C83-C82-C81	120.6(9)
O19-C72-C63	104.7(6)	C83-C82-H82	119.7
C71-C72-C63	117.1(7)	C81-C82-H82	119.7
O19-C72-H72	108.9	C82-C83-C84	119.5(9)
C71-C72-H72	108.9	C82-C83-H83	120.3
C63-C72-H72	108.9	C84-C83-H83	120.3
O21-C73-O20	125.6(8)	C85-C84-C83	120.9(9)
O21-C73-C74	123.5(8)	C85-C84-O27	125.4(9)

C83-C84-O27	113.7(8)	O6-N2-O7	124.4(8)
C84-C85-C86	119.0(9)	O6-N2-C18	117.4(8)
C84-C85-H85	120.5	O7-N2-C18	118.2(8)
C86-C85-H85	120.5	O14-N3-O13	125.2(8)
C81-C86-C85	121.8(9)	O14-N3-C46	117.9(7)
C81-C86-H86	119.1	O13-N3-C46	116.9(8)
C85-C86-H86	119.1	O16-N4-O15	126.2(8)
O27-C87-H87A	109.5	O16-N4-C48	116.5(8)
O27-C87-H87B	109.5	O15-N4-C48	117.3(9)
H87A-C87-H87B	109.5	O23-N5-O22	125.0(8)
O27-C87-H87C	109.5	O23-N5-C76	117.6(8)
H87A-C87-H87C	109.5	O22-N5-C76	117.4(8)
H87B-C87-H87C	109.5	O24-N6-O25	124.5(9)
C62-C88-H88A	120.0	O24-N6-C78	118.0(9)
C62-C88-H88B	120.0	O25-N6-C78	117.5(9)
H88A-C88-H88B	120.0	C1-O1-C12	107.8(6)
C66-C89-H89A	120.0	C13-O2-C4	117.3(7)
C66-C89-H89B	120.0	C8-O8-C20	111.6(6)
H89A-C89-H89B	120.0	C24-O9-C27	116.2(7)
C70-C90-H90A	109.5	C31-O10-C42	106.5(6)
C70-C90-H90B	109.5	C43-O11-C34	117.4(7)
H90A-C90-H90B	109.5	C38-O17-C50	111.2(6)
C70-C90-H90C	109.5	C54-O18-C57	115.8(6)
H90A-C90-H90C	109.5	C61-O19-C72	108.0(6)
H90B-C90-H90C	109.5	C73-O20-C64	116.6(6)
O5-N1-O4	124.1(8)	C68-O26-C80	111.3(6)
O5-N1-C16	118.0(7)	C84-O27-C87	116.1(7)
O4-N1-C16	117.9(7)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 394. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	17(5)	28(6)	28(5)	1(5)	-9(4)	-1(5)
C2	20(5)	24(6)	20(5)	3(5)	3(4)	-3(5)
C3	19(5)	17(5)	15(5)	2(4)	10(4)	2(4)
C4	35(6)	16(5)	6(4)	3(4)	8(4)	-8(5)
C5	18(5)	18(5)	12(4)	-3(4)	3(4)	0(4)
C6	19(5)	19(6)	22(5)	-1(5)	-2(4)	-4(5)
C7	20(5)	18(6)	23(5)	2(4)	-5(4)	-6(5)
C8	24(5)	22(6)	24(5)	-6(5)	-4(4)	0(5)
C9	32(6)	28(6)	14(5)	-4(5)	-1(4)	-2(5)
C10	22(5)	20(6)	15(5)	-1(4)	-3(4)	2(5)
C11	20(5)	13(5)	15(5)	-8(4)	-6(4)	3(4)
C12	15(5)	16(6)	28(5)	2(4)	3(4)	0(4)
C13	20(5)	28(6)	15(5)	4(5)	-1(4)	8(5)
C14	21(5)	18(5)	7(5)	7(4)	0(4)	3(4)
C15	14(5)	29(6)	14(5)	0(4)	4(4)	0(5)
C16	28(5)	11(5)	19(5)	-3(4)	0(4)	6(5)
C17	19(5)	25(6)	18(5)	5(5)	1(4)	-1(5)
C18	17(5)	23(6)	7(5)	-4(4)	-2(4)	3(4)
C19	19(5)	27(6)	18(5)	3(5)	3(4)	4(5)
C20	25(6)	34(7)	28(5)	-5(5)	-8(4)	-3(5)
C21	9(5)	22(6)	37(6)	-11(5)	-3(4)	0(5)
C22	36(6)	36(7)	28(6)	9(5)	-5(5)	-1(6)
C23	31(6)	27(6)	25(5)	7(5)	4(5)	1(5)
C24	23(6)	34(7)	29(6)	0(5)	5(4)	1(5)
C25	30(6)	45(8)	28(6)	-5(5)	-9(5)	13(6)
C26	26(6)	52(8)	23(5)	-3(6)	-10(5)	1(6)
C27	47(6)	60(8)	24(6)	-8(5)	7(5)	13(6)
C28	37(6)	40(7)	27(6)	-5(5)	-1(5)	7(6)
C29	24(5)	29(6)	33(6)	6(5)	4(4)	-2(5)
C30	29(5)	40(7)	22(5)	6(5)	5(4)	-2(5)
C31	28(6)	44(8)	28(6)	-6(5)	-5(5)	-5(5)

C32	15(5)	30(6)	17(5)	-9(5)	3(4)	-6(5)
C33	9(5)	22(6)	20(5)	1(4)	0(4)	1(4)
C34	23(5)	22(6)	18(5)	-1(4)	-3(4)	-8(5)
C35	12(5)	25(6)	18(5)	3(4)	4(4)	-1(4)
C36	15(5)	19(5)	19(5)	-6(4)	0(4)	-1(4)
C37	15(5)	15(5)	22(5)	-2(4)	-6(4)	-1(4)
C38	22(5)	24(6)	19(5)	8(4)	1(4)	-6(5)
C39	30(6)	18(6)	22(5)	2(4)	11(4)	2(5)
C40	21(5)	30(6)	14(5)	5(4)	3(4)	4(5)
C41	19(5)	19(6)	27(5)	6(5)	5(4)	-1(4)
C42	18(5)	29(6)	19(5)	-2(5)	-5(4)	-6(5)
C43	21(5)	33(7)	15(6)	-12(5)	-1(4)	-15(5)
C44	16(5)	22(6)	15(5)	2(5)	1(4)	-4(5)
C45	31(5)	29(6)	19(5)	-10(5)	9(4)	-17(5)
C46	18(5)	28(6)	15(5)	-1(5)	5(4)	2(5)
C47	10(5)	40(7)	28(6)	-11(5)	1(4)	1(5)
C48	20(5)	39(7)	15(5)	-6(5)	0(4)	1(5)
C49	17(5)	31(6)	15(5)	0(5)	0(4)	2(5)
C50	22(5)	32(6)	20(5)	3(5)	-10(4)	1(5)
C51	17(5)	16(5)	22(5)	3(5)	-10(4)	-6(4)
C52	15(5)	35(7)	18(5)	0(5)	-3(4)	3(5)
C53	23(6)	25(6)	29(6)	-13(5)	-1(4)	-4(5)
C54	20(5)	27(6)	21(5)	1(5)	5(4)	4(5)
C55	19(5)	22(6)	18(5)	4(5)	3(4)	4(5)
C56	21(5)	21(6)	34(6)	-9(5)	2(4)	3(5)
C57	40(6)	45(7)	22(5)	12(5)	13(4)	-7(5)
C58	29(6)	42(7)	32(6)	-2(5)	-2(5)	-10(5)
C59	28(6)	31(6)	18(5)	-2(5)	-1(4)	-7(5)
C60	33(6)	48(7)	25(5)	-5(5)	12(4)	5(6)
C61	31(6)	21(6)	29(5)	-3(5)	2(5)	-1(5)
C62	20(5)	22(6)	18(5)	-6(4)	0(4)	-1(5)
C63	22(5)	12(5)	17(5)	-5(4)	2(4)	-2(4)
C64	35(6)	10(5)	12(5)	-9(4)	4(4)	3(5)
C65	19(5)	20(5)	18(5)	0(4)	-3(4)	-6(4)
C66	24(5)	25(6)	26(5)	-8(5)	1(4)	-2(5)
C67	23(5)	16(5)	22(5)	-4(4)	-6(4)	3(4)

C68	31(6)	22(6)	18(5)	-4(5)	-5(4)	1(5)
C69	29(6)	22(6)	13(5)	-3(4)	4(4)	8(5)
C70	23(5)	21(6)	9(5)	2(4)	-3(4)	-3(5)
C71	27(5)	11(5)	13(5)	-2(4)	-4(4)	-1(4)
C72	21(5)	17(6)	21(5)	-4(4)	2(4)	-9(4)
C73	22(5)	15(6)	31(6)	-7(5)	0(4)	-12(5)
C74	21(5)	20(6)	12(5)	5(4)	-2(4)	-6(5)
C75	20(5)	16(5)	18(5)	0(4)	-2(4)	1(5)
C76	22(5)	21(6)	25(5)	-3(5)	4(4)	-2(5)
C77	19(6)	31(7)	30(6)	-14(5)	6(4)	-5(5)
C78	27(6)	39(7)	14(5)	9(5)	-2(4)	-13(5)
C79	19(5)	27(6)	17(5)	-6(5)	-1(4)	-2(4)
C80	24(6)	31(7)	40(6)	-8(5)	-12(5)	4(5)
C81	13(5)	36(7)	28(6)	-12(5)	-1(4)	5(5)
C82	17(5)	47(7)	27(5)	-2(5)	5(4)	3(5)
C83	18(5)	50(7)	30(6)	-8(5)	2(4)	-6(5)
C84	19(6)	41(7)	30(6)	-2(5)	6(5)	0(5)
C85	34(6)	50(8)	14(5)	3(5)	4(4)	11(6)
C86	25(6)	44(8)	28(6)	-10(5)	-7(5)	10(6)
C87	40(7)	50(8)	62(7)	10(6)	20(6)	1(6)
C88	20(5)	29(6)	31(6)	-1(5)	-2(4)	-4(5)
C89	29(6)	29(6)	35(6)	7(5)	2(5)	7(5)
C90	38(6)	29(6)	21(5)	-4(5)	12(4)	-1(5)
N1	30(5)	22(5)	19(5)	4(4)	3(4)	-3(4)
N2	20(4)	47(6)	20(5)	5(5)	4(4)	12(5)
N3	27(5)	32(6)	29(5)	5(5)	-1(4)	-13(4)
N4	32(5)	66(8)	25(5)	-21(5)	3(4)	2(5)
N5	26(5)	25(5)	37(5)	-7(5)	-1(4)	-6(4)
N6	42(6)	52(7)	27(5)	-1(5)	2(4)	-9(5)
O1	26(3)	23(4)	22(3)	-6(3)	-2(3)	8(3)
O2	23(3)	20(4)	13(3)	2(3)	6(3)	1(3)
O3	36(4)	28(4)	19(3)	-7(3)	4(3)	-5(3)
O4	41(4)	30(4)	27(4)	-8(3)	10(3)	-13(3)
O5	31(4)	28(4)	33(4)	-4(3)	14(3)	-10(3)
O6	44(4)	45(5)	21(4)	-5(3)	13(3)	-14(4)
O7	38(4)	23(4)	29(4)	-8(3)	6(3)	-5(4)

O8	28(4)	23(4)	19(3)	-1(3)	-5(3)	3(3)
O9	39(4)	47(5)	20(4)	-5(3)	4(3)	12(4)
O10	28(4)	35(4)	21(3)	1(3)	-1(3)	-15(3)
O11	28(3)	21(4)	14(3)	-5(3)	9(3)	0(3)
O12	41(4)	26(4)	20(3)	5(3)	10(3)	2(4)
O13	45(4)	45(5)	20(4)	7(4)	12(3)	10(4)
O14	48(4)	24(4)	41(4)	-6(4)	14(3)	0(4)
O15	56(5)	63(6)	21(4)	-5(4)	14(3)	18(5)
O16	64(5)	88(7)	23(4)	6(4)	-4(4)	45(5)
O17	16(3)	21(4)	23(3)	4(3)	-1(3)	3(3)
O18	22(3)	32(4)	22(3)	-1(3)	3(3)	-7(3)
O19	32(4)	18(4)	21(3)	-4(3)	-4(3)	-3(3)
O20	28(3)	13(4)	16(3)	7(3)	3(3)	3(3)
O21	40(4)	18(4)	22(3)	2(3)	8(3)	4(3)
O22	28(4)	23(4)	42(4)	2(3)	3(3)	5(3)
O23	26(4)	34(5)	52(4)	-17(4)	7(3)	6(3)
O24	78(5)	71(6)	25(4)	1(4)	22(4)	9(5)
O25	67(5)	48(5)	30(4)	8(4)	8(4)	-15(5)
O26	23(4)	18(4)	30(3)	-2(3)	-8(3)	1(3)
O27	34(4)	47(5)	37(4)	3(4)	7(3)	0(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 394.

	x	y	z	U(eq)
H1A	-1314	8977	3048	30
H1B	-1696	7555	3355	30
H3	-804	3304	3625	19
H4	-437	1405	3047	22
H5A	163	1474	3747	19
H5B	485	1364	3317	19
H7	675	7380	4126	25
H8	766	5099	4760	29
H9	12	1853	4776	30
H11	-165	8087	4257	20
H12	-249	7659	3429	24
H15	479	7354	2551	23
H17	964	8266	1307	25
H19	14	2509	1537	26
H20A	1624	3256	4806	36
H20B	1542	4456	4310	36
H22	1661	1752	3643	41
H23	2170	-1296	3373	33
H25	2699	-3315	4652	42
H26	2180	-346	4925	42
H27A	2860	-3734	3217	65
H27B	2335	-5311	3271	65
H27C	2915	-6576	3335	65
H28A	-1703	5006	2538	42
H28B	-1273	2726	2616	42
H29A	1138	6961	3526	35
H29B	1014	4781	3147	35
H30A	-979	5521	4735	46
H30B	-1007	2738	4572	46
H30C	-1160	4880	4212	46

H31A	4422	5033	256	41
H31B	4900	3372	109	41
H33	3933	-853	-246	21
H34	3368	-1789	280	26
H35A	2540	-1645	-160	22
H35B	2981	-2130	-492	22
H37	2734	3500	-1123	21
H38	2699	629	-1655	26
H39	3411	-2731	-1499	27
H41	3618	3699	-1074	26
H42	3498	3961	-282	28
H45	2414	4774	415	31
H47	1891	7648	1536	32
H49	2861	1695	1647	26
H50A	1823	-1033	-1768	31
H50B	1828	606	-1321	31
H52	1342	-4917	-1818	27
H53	780	-7708	-1525	31
H55	913	-3858	-353	23
H56	1469	-1084	-655	31
H57A	237	-6772	-182	53
H57B	851	-7654	-113	53
H57C	375	-9620	-185	53
H58A	4205	-961	776	42
H58B	4697	1038	870	42
H59A	2065	2234	-208	31
H59B	2115	4008	-646	31
H60A	4492	870	-1269	52
H60B	4388	-2003	-1245	52
H60C	4505	-447	-788	52
H61A	7731	13887	3882	33
H61B	8119	12550	3569	33
H63	7268	8332	3238	20
H64	6866	6133	3764	23
H65A	6313	6397	3053	23
H65B	5961	6094	3460	23

H67	5780	12316	2702	25
H68	5759	10282	2049	29
H69	6552	7334	2016	25
H71	6619	13253	2642	21
H72	6660	12503	3452	24
H75	5986	11861	4398	22
H77	5673	12245	5696	32
H79	6605	6779	5311	26
H80A	4955	8596	1919	40
H80B	4931	9028	2448	40
H82	4548	5048	1549	36
H83	3941	1857	1561	39
H85	4075	2291	2925	39
H86	4676	5508	2910	40
H87A	3292	157	2783	74
H87B	3785	-1722	2813	74
H87C	3207	-2484	2557	74
H88A	8098	9824	4374	33
H88B	7675	7536	4267	33
H89A	5381	9313	3621	38
H89B	5271	11596	3262	38
H90A	7518	11577	2265	43
H90B	7512	8697	2179	43
H90C	7660	9743	2682	43

Table 6. Torsion angles [°] for 394.

O1-C1-C2-C28	-177.8(8)	C10-C11-C12-O1	79.7(8)
O1-C1-C2-C3	0.2(8)	C7-C11-C12-O1	-159.7(7)
C28-C2-C3-C4	30.9(12)	C10-C11-C12-C3	-38.3(10)
C1-C2-C3-C4	-147.0(7)	C7-C11-C12-C3	82.4(9)
C28-C2-C3-C12	157.9(9)	C4-C3-C12-O1	160.2(6)
C1-C2-C3-C12	-20.0(8)	C2-C3-C12-O1	33.1(7)
C2-C3-C4-O2	53.3(9)	C4-C3-C12-C11	-79.7(9)
C12-C3-C4-O2	-65.7(8)	C2-C3-C12-C11	153.2(7)
C2-C3-C4-C5	172.0(7)	O3-C13-C14-C15	-164.2(8)
C12-C3-C4-C5	53.0(9)	O2-C13-C14-C15	15.0(10)
O2-C4-C5-C6	56.9(8)	O3-C13-C14-C19	7.7(12)
C3-C4-C5-C6	-63.0(9)	O2-C13-C14-C19	-173.1(7)
C4-C5-C6-C29	-90.8(9)	C19-C14-C15-C16	2.4(12)
C4-C5-C6-C7	89.2(8)	C13-C14-C15-C16	174.2(7)
C29-C6-C7-C11	127.9(8)	C14-C15-C16-C17	-0.1(12)
C5-C6-C7-C11	-52.1(10)	C14-C15-C16-N1	-177.3(7)
C29-C6-C7-C8	-116.1(8)	C15-C16-C17-C18	-1.2(12)
C5-C6-C7-C8	64.0(9)	N1-C16-C17-C18	176.0(7)
C6-C7-C8-O8	19.2(9)	C16-C17-C18-C19	0.3(12)
C11-C7-C8-O8	142.5(7)	C16-C17-C18-N2	-175.3(7)
C6-C7-C8-C9	-103.5(8)	C17-C18-C19-C14	1.9(12)
C11-C7-C8-C9	19.8(8)	N2-C18-C19-C14	177.5(7)
O8-C8-C9-C10	-140.1(7)	C15-C14-C19-C18	-3.2(12)
C7-C8-C9-C10	-16.2(9)	C13-C14-C19-C18	-175.1(7)
C8-C9-C10-C30	-169.5(8)	O8-C20-C21-C26	-104.4(9)
C8-C9-C10-C11	4.8(10)	O8-C20-C21-C22	77.8(10)
C9-C10-C11-C12	133.6(8)	C26-C21-C22-C23	3.0(13)
C30-C10-C11-C12	-51.7(10)	C20-C21-C22-C23	-179.1(8)
C9-C10-C11-C7	8.8(9)	C21-C22-C23-C24	-1.4(14)
C30-C10-C11-C7	-176.5(7)	C22-C23-C24-O9	177.5(8)
C6-C7-C11-C10	102.9(8)	C22-C23-C24-C25	-1.0(13)
C8-C7-C11-C10	-17.6(8)	C23-C24-C25-C26	1.7(14)
C6-C7-C11-C12	-24.3(10)	O9-C24-C25-C26	-176.9(8)
C8-C7-C11-C12	-144.7(7)	C24-C25-C26-C21	-0.1(14)

C22-C21-C26-C25	-2.2(13)	C40-C41-C42-O10	76.0(9)
C20-C21-C26-C25	179.9(9)	C37-C41-C42-O10	-161.6(7)
O10-C31-C32-C58	172.9(8)	C40-C41-C42-C33	-42.6(10)
O10-C31-C32-C33	-10.5(9)	C37-C41-C42-C33	79.9(9)
C58-C32-C33-C34	36.8(13)	C34-C33-C42-O10	159.4(6)
C31-C32-C33-C34	-139.7(8)	C32-C33-C42-O10	30.2(8)
C58-C32-C33-C42	164.5(9)	C34-C33-C42-C41	-79.7(9)
C31-C32-C33-C42	-11.9(8)	C32-C33-C42-C41	151.1(7)
C32-C33-C34-O11	56.0(9)	O12-C43-C44-C45	-162.7(8)
C42-C33-C34-O11	-65.3(8)	O11-C43-C44-C45	16.9(11)
C32-C33-C34-C35	176.6(7)	O12-C43-C44-C49	11.9(12)
C42-C33-C34-C35	55.2(10)	O11-C43-C44-C49	-168.5(7)
O11-C34-C35-C36	55.4(8)	C49-C44-C45-C46	2.0(12)
C33-C34-C35-C36	-65.8(10)	C43-C44-C45-C46	176.6(8)
C34-C35-C36-C59	-90.1(9)	C44-C45-C46-C47	0.8(13)
C34-C35-C36-C37	91.1(8)	C44-C45-C46-N3	178.7(7)
C59-C36-C37-C41	127.6(8)	C45-C46-C47-C48	-2.7(13)
C35-C36-C37-C41	-53.6(10)	N3-C46-C47-C48	179.4(7)
C59-C36-C37-C38	-115.8(8)	C46-C47-C48-C49	1.9(13)
C35-C36-C37-C38	63.1(9)	C46-C47-C48-N4	-175.6(7)
C36-C37-C38-O17	13.9(9)	C47-C48-C49-C44	0.9(13)
C41-C37-C38-O17	136.4(7)	N4-C48-C49-C44	178.3(7)
C36-C37-C38-C39	-108.8(7)	C45-C44-C49-C48	-2.9(12)
C41-C37-C38-C39	13.7(8)	C43-C44-C49-C48	-177.6(8)
O17-C38-C39-C40	-135.7(7)	O17-C50-C51-C52	-93.6(9)
C37-C38-C39-C40	-10.5(9)	O17-C50-C51-C56	84.2(9)
C38-C39-C40-C60	-171.0(8)	C56-C51-C52-C53	-2.9(12)
C38-C39-C40-C41	2.3(10)	C50-C51-C52-C53	174.9(7)
C39-C40-C41-C42	133.8(8)	C51-C52-C53-C54	-0.3(12)
C60-C40-C41-C42	-52.6(11)	C52-C53-C54-C55	3.3(12)
C39-C40-C41-C37	6.9(9)	C52-C53-C54-O18	-177.1(7)
C60-C40-C41-C37	-179.6(7)	O18-C54-C55-C56	177.4(7)
C36-C37-C41-C40	107.8(7)	C53-C54-C55-C56	-3.2(12)
C38-C37-C41-C40	-12.5(8)	C54-C55-C56-C51	-0.1(12)
C36-C37-C41-C42	-21.1(10)	C52-C51-C56-C55	3.1(12)
C38-C37-C41-C42	-141.3(7)	C50-C51-C56-C55	-174.8(7)

O19-C61-C62-C88	-176.3(8)	C70-C71-C72-C63	-40.7(10)
O19-C61-C62-C63	3.4(8)	C67-C71-C72-C63	82.1(9)
C88-C62-C63-C64	30.9(12)	C64-C63-C72-O19	161.0(6)
C61-C62-C63-C64	-148.9(7)	C62-C63-C72-O19	33.6(8)
C88-C62-C63-C72	157.4(8)	C64-C63-C72-C71	-79.4(9)
C61-C62-C63-C72	-22.4(8)	C62-C63-C72-C71	153.2(7)
C62-C63-C64-O20	51.4(9)	O21-C73-C74-C75	-169.0(8)
C72-C63-C64-O20	-67.6(8)	O20-C73-C74-C75	9.9(11)
C62-C63-C64-C65	170.9(7)	O21-C73-C74-C79	4.7(12)
C72-C63-C64-C65	51.9(9)	O20-C73-C74-C79	-176.4(7)
O20-C64-C65-C66	57.7(9)	C79-C74-C75-C76	3.0(12)
C63-C64-C65-C66	-62.3(9)	C73-C74-C75-C76	176.6(8)
C64-C65-C66-C89	-92.1(10)	C74-C75-C76-C77	-4.7(13)
C64-C65-C66-C67	89.2(9)	C74-C75-C76-N5	-177.8(7)
C89-C66-C67-C71	128.4(8)	C75-C76-C77-C78	4.1(13)
C65-C66-C67-C71	-52.9(10)	N5-C76-C77-C78	177.3(7)
C89-C66-C67-C68	-115.3(9)	C76-C77-C78-C79	-2.0(13)
C65-C66-C67-C68	63.3(9)	C76-C77-C78-N6	-175.7(7)
C66-C67-C68-O26	19.2(10)	C77-C78-C79-C74	0.6(13)
C71-C67-C68-O26	142.3(7)	N6-C78-C79-C74	174.2(7)
C66-C67-C68-C69	-105.6(8)	C75-C74-C79-C78	-1.0(12)
C71-C67-C68-C69	17.5(8)	C73-C74-C79-C78	-174.9(7)
O26-C68-C69-C70	-140.8(7)	O26-C80-C81-C86	83.4(10)
C67-C68-C69-C70	-14.3(10)	O26-C80-C81-C82	-100.1(9)
C68-C69-C70-C71	4.3(10)	C86-C81-C82-C83	1.3(13)
C68-C69-C70-C90	-169.1(8)	C80-C81-C82-C83	-175.4(8)
C69-C70-C71-C72	134.8(8)	C81-C82-C83-C84	-1.7(13)
C90-C70-C71-C72	-51.6(11)	C82-C83-C84-C85	1.9(14)
C69-C70-C71-C67	7.9(9)	C82-C83-C84-O27	-179.4(8)
C90-C70-C71-C67	-178.5(7)	C83-C84-C85-C86	-1.5(13)
C66-C67-C71-C70	106.2(7)	O27-C84-C85-C86	179.8(8)
C68-C67-C71-C70	-15.5(8)	C82-C81-C86-C85	-1.0(13)
C66-C67-C71-C72	-22.5(10)	C80-C81-C86-C85	175.7(8)
C68-C67-C71-C72	-144.1(7)	C84-C85-C86-C81	1.1(14)
C70-C71-C72-O19	77.1(9)	C17-C16-N1-O5	1.3(11)
C67-C71-C72-O19	-160.0(7)	C15-C16-N1-O5	178.6(7)

C17-C16-N1-O4	-179.5(7)	C9-C8-O8-C20	-160.3(6)
C15-C16-N1-O4	-2.1(11)	C7-C8-O8-C20	82.1(8)
C19-C18-N2-O6	178.1(7)	C21-C20-O8-C8	-169.5(7)
C17-C18-N2-O6	-6.1(11)	C23-C24-O9-C27	-7.1(12)
C19-C18-N2-O7	-2.6(11)	C25-C24-O9-C27	171.4(8)
C17-C18-N2-O7	173.2(7)	C32-C31-O10-C42	30.7(9)
C47-C46-N3-O14	8.6(11)	C41-C42-O10-C31	-165.3(7)
C45-C46-N3-O14	-169.3(8)	C33-C42-O10-C31	-38.5(8)
C47-C46-N3-O13	-171.7(8)	O12-C43-O11-C34	11.9(12)
C45-C46-N3-O13	10.4(11)	C44-C43-O11-C34	-167.7(6)
C47-C48-N4-O16	177.8(8)	C33-C34-O11-C43	-122.9(7)
C49-C48-N4-O16	0.3(12)	C35-C34-O11-C43	113.5(7)
C47-C48-N4-O15	-4.2(12)	C39-C38-O17-C50	-159.2(6)
C49-C48-N4-O15	178.3(8)	C37-C38-O17-C50	81.9(8)
C77-C76-N5-O23	9.5(11)	C51-C50-O17-C38	-168.9(6)
C75-C76-N5-O23	-177.0(8)	C55-C54-O18-C57	-16.1(11)
C77-C76-N5-O22	-172.7(7)	C53-C54-O18-C57	164.4(7)
C75-C76-N5-O22	0.8(11)	C62-C61-O19-C72	18.9(8)
C77-C78-N6-O24	-11.6(12)	C71-C72-O19-C61	-159.0(6)
C79-C78-N6-O24	174.4(8)	C63-C72-O19-C61	-33.5(8)
C77-C78-N6-O25	169.2(8)	O21-C73-O20-C64	2.6(12)
C79-C78-N6-O25	-4.7(12)	C74-C73-O20-C64	-176.2(6)
C2-C1-O1-C12	21.9(8)	C63-C64-O20-C73	-123.0(7)
C11-C12-O1-C1	-160.2(7)	C65-C64-O20-C73	113.7(7)
C3-C12-O1-C1	-35.1(8)	C69-C68-O26-C80	-157.2(6)
O3-C13-O2-C4	11.4(12)	C67-C68-O26-C80	83.0(8)
C14-C13-O2-C4	-167.8(6)	C81-C80-O26-C68	179.0(7)
C3-C4-O2-C13	-135.9(7)	C85-C84-O27-C87	-1.7(12)
C5-C4-O2-C13	101.0(7)	C83-C84-O27-C87	179.6(8)

Appendix B: Crystallographic Data for 401

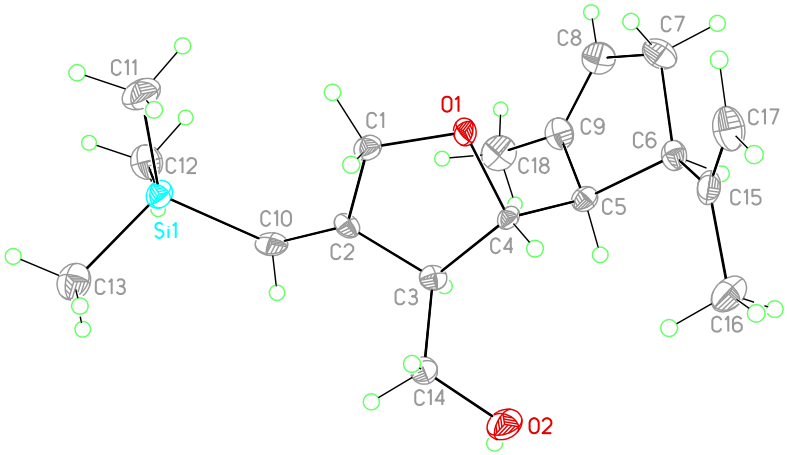


Table 1. Crystal data and structure refinement for 401.

Empirical formula	C18 H30 O2 Si	
Formula weight	306.51	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.9429(18) Å	α = 90°.
	b = 6.4395(12) Å	β = 102.480(6)°.
	c = 13.070(3) Å	γ = 90°.
Volume	899.2(3) $Å^3$	
Z	2	
Density (calculated)	1.132 Mg/m^3	
Absorption coefficient	0.134 mm^{-1}	
F(000)	336	
Crystal size	0.39 x 0.15 x 0.10 mm	
Theta range for data collection	3.544 to 25.464°.	
Index ranges	-13<=h<=9, -7<=k<=7, -15<=l<=15	
Reflections collected	5362	
Independent reflections	3151 [R(int) = 0.0478]	
Completeness to theta = 25.242°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.923	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3151 / 1 / 199	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1078	
R indices (all data)	R1 = 0.0926, wR2 = 0.1184	
Absolute structure parameter	0.02(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.395 and -0.235 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 401. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	5035(5)	6449(7)	2871(4)	16(1)
C2	5046(4)	8692(8)	2499(4)	13(1)
C3	4088(5)	9811(8)	2976(4)	14(1)
C4	3341(4)	8073(7)	3380(4)	12(1)
C5	1921(4)	8183(8)	2992(4)	15(1)
C6	1135(5)	6748(7)	3579(4)	17(1)
C7	917(5)	4763(8)	2903(4)	24(1)
C8	939(5)	5602(9)	1831(5)	24(1)
C9	1482(5)	7454(8)	1866(4)	21(1)
C10	5753(4)	9550(8)	1899(4)	18(1)
C11	7376(6)	5758(8)	1539(5)	35(2)
C12	6430(5)	8968(9)	-189(5)	34(2)
C13	8431(5)	10151(9)	1705(5)	28(2)
C14	4774(5)	11226(8)	3853(4)	18(1)
C15	1615(5)	6523(8)	4739(4)	20(1)
C16	1716(5)	8541(10)	5356(4)	29(1)
C17	1880(5)	4720(9)	5225(5)	28(2)
C18	1693(5)	8661(10)	934(4)	30(1)
O1	3809(3)	6122(5)	3058(3)	20(1)
O2	3913(4)	12361(6)	4328(3)	26(1)
Si1	6991(1)	8566(2)	1248(1)	18(1)

Table 3. Bond lengths [Å] and angles [°] for 401.

C1-O1	1.430(5)	C11-Si1	1.877(6)
C1-C2	1.525(7)	C11-H11A	0.98
C1-H1A	0.99	C11-H11B	0.98
C1-H1B	0.99	C11-H11C	0.98
C2-C10	1.335(6)	C12-Si1	1.864(6)
C2-C3	1.513(7)	C12-H12A	0.98
C3-C14	1.528(7)	C12-H12B	0.98
C3-C4	1.544(6)	C12-H12C	0.98
C3-H3	1.00	C13-Si1	1.864(6)
C4-O1	1.453(6)	C13-H13A	0.98
C4-C5	1.528(6)	C13-H13B	0.98
C4-H4	1.00	C13-H13C	0.98
C5-C9	1.521(7)	C14-O2	1.435(6)
C5-C6	1.571(7)	C14-H14A	0.99
C5-H5	1.00	C14-H14B	0.99
C6-C15	1.500(7)	C15-C17	1.325(7)
C6-C7	1.543(7)	C15-C16	1.521(8)
C6-H6	1.00	C16-H16A	0.98
C7-C8	1.507(8)	C16-H16B	0.98
C7-H7A	0.99	C16-H16C	0.98
C7-H7B	0.99	C17-H17A	0.95
C8-C9	1.329(7)	C17-H17B	0.95
C8-H8	0.95	C18-H18A	0.98
C9-C18	1.505(7)	C18-H18B	0.98
C10-Si1	1.860(5)	C18-H18C	0.98
C10-H10	0.95	O2-H2O	0.83(6)

O1-C1-C2	105.5(4)	C10-C2-C1	128.7(4)
O1-C1-H1A	110.6	C3-C2-C1	105.4(4)
C2-C1-H1A	110.6	C2-C3-C14	108.7(4)
O1-C1-H1B	110.6	C2-C3-C4	105.1(4)
C2-C1-H1B	110.6	C14-C3-C4	112.7(4)
H1A-C1-H1B	108.8	C2-C3-H3	110.0
C10-C2-C3	125.9(5)	C14-C3-H3	110.0

C4-C3-H3	110.0	H11A-C11-H11B	109.5
O1-C4-C5	109.9(4)	Si1-C11-H11C	109.5
O1-C4-C3	106.4(4)	H11A-C11-H11C	109.5
C5-C4-C3	115.4(4)	H11B-C11-H11C	109.5
O1-C4-H4	108.3	Si1-C12-H12A	109.5
C5-C4-H4	108.3	Si1-C12-H12B	109.5
C3-C4-H4	108.3	H12A-C12-H12B	109.5
C9-C5-C4	113.1(4)	Si1-C12-H12C	109.5
C9-C5-C6	101.5(4)	H12A-C12-H12C	109.5
C4-C5-C6	115.8(4)	H12B-C12-H12C	109.5
C9-C5-H5	108.7	Si1-C13-H13A	109.5
C4-C5-H5	108.7	Si1-C13-H13B	109.5
C6-C5-H5	108.7	H13A-C13-H13B	109.5
C15-C6-C7	118.4(4)	Si1-C13-H13C	109.5
C15-C6-C5	116.2(4)	H13A-C13-H13C	109.5
C7-C6-C5	103.9(4)	H13B-C13-H13C	109.5
C15-C6-H6	105.8	O2-C14-C3	111.4(4)
C7-C6-H6	105.8	O2-C14-H14A	109.3
C5-C6-H6	105.8	C3-C14-H14A	109.3
C8-C7-C6	101.8(4)	O2-C14-H14B	109.3
C8-C7-H7A	111.4	C3-C14-H14B	109.3
C6-C7-H7A	111.4	H14A-C14-H14B	108.0
C8-C7-H7B	111.4	C17-C15-C6	124.2(5)
C6-C7-H7B	111.4	C17-C15-C16	120.7(5)
H7A-C7-H7B	109.3	C6-C15-C16	115.0(5)
C9-C8-C7	112.7(5)	C15-C16-H16A	109.5
C9-C8-H8	123.6	C15-C16-H16B	109.5
C7-C8-H8	123.6	H16A-C16-H16B	109.5
C8-C9-C18	125.5(6)	C15-C16-H16C	109.5
C8-C9-C5	110.9(5)	H16A-C16-H16C	109.5
C18-C9-C5	123.5(5)	H16B-C16-H16C	109.5
C2-C10-Si1	134.4(4)	C15-C17-H17A	120.0
C2-C10-H10	112.8	C15-C17-H17B	120.0
Si1-C10-H10	112.8	H17A-C17-H17B	120.0
Si1-C11-H11A	109.5	C9-C18-H18A	109.5
Si1-C11-H11B	109.5	C9-C18-H18B	109.5

H18A-C18-H18B	109.5	C10-Si1-C13	108.4(2)
C9-C18-H18C	109.5	C10-Si1-C12	107.4(3)
H18A-C18-H18C	109.5	C13-Si1-C12	108.6(3)
H18B-C18-H18C	109.5	C10-Si1-C11	112.9(2)
C1-O1-C4	109.0(3)	C13-Si1-C11	109.0(3)
C14-O2-H2O	102(4)	C12-Si1-C11	110.4(3)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 401. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	17(3)	12(3)	18(3)	0(2)	5(2)	3(2)
C2	14(2)	10(3)	15(3)	5(3)	2(2)	-1(3)
C3	18(3)	12(3)	13(3)	3(2)	3(3)	1(2)
C4	14(2)	10(3)	14(3)	1(2)	6(2)	3(2)
C5	16(3)	14(3)	16(3)	1(2)	4(2)	3(2)
C6	12(3)	18(3)	21(4)	3(2)	4(3)	2(2)
C7	22(3)	23(3)	24(4)	-2(3)	0(3)	-6(3)
C8	21(3)	32(4)	17(4)	-6(3)	-3(3)	-4(3)
C9	13(3)	25(3)	21(4)	2(3)	-1(3)	2(2)
C10	21(3)	9(3)	21(4)	2(2)	0(3)	3(2)
C11	44(4)	17(3)	49(5)	-1(3)	24(4)	5(3)
C12	35(3)	32(4)	37(4)	-1(3)	17(3)	-5(3)
C13	27(3)	26(3)	31(4)	5(3)	7(3)	6(3)
C14	17(3)	13(3)	27(4)	1(3)	7(3)	2(2)
C15	17(3)	26(3)	20(4)	-1(3)	10(3)	0(3)
C16	33(3)	30(3)	25(3)	-6(3)	12(3)	3(3)
C17	27(3)	34(4)	24(4)	8(3)	9(3)	-2(3)
C18	30(3)	34(3)	22(3)	2(3)	0(3)	3(3)
O1	13(2)	12(2)	36(3)	2(2)	11(2)	3(2)
O2	37(3)	15(2)	31(3)	0(2)	15(2)	3(2)
Si1	21(1)	16(1)	20(1)	2(1)	9(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 401.

	x	y	z	U(eq)
H1A	5199	5481	2327	19
H1B	5679	6234	3521	19
H3	3519	10652	2429	17
H4	3536	8124	4163	14
H5	1647	9654	3043	18
H6	296	7427	3491	21
H7A	1593	3735	3136	28
H7B	100	4116	2918	28
H8	600	4884	1198	29
H10	5586	10987	1776	21
H11A	8083	5356	1232	52
H11B	6647	4901	1238	52
H11C	7599	5549	2300	52
H12A	6193	10426	-326	50
H12B	5702	8080	-448	50
H12C	7099	8611	-549	50
H13A	8245	11613	1529	41
H13B	9090	9667	1361	41
H13C	8714	10007	2466	41
H14A	5328	10376	4394	22
H14B	5305	12215	3565	22
H16A	2006	8244	6105	43
H16B	893	9211	5237	43
H16C	2313	9469	5125	43
H17A	1767	3463	4835	33
H17B	2182	4684	5963	33
H18A	2587	8660	929	44
H18B	1406	10094	976	44
H18C	1223	8015	289	44
H2O	3720(50)	13360(100)	3920(50)	40(20)

Table 6. Torsion angles [°] for 401.

O1-C1-C2-C10	-154.5(5)	C7-C8-C9-C18	177.5(5)
O1-C1-C2-C3	26.7(5)	C7-C8-C9-C5	-0.2(6)
C10-C2-C3-C14	-71.2(6)	C4-C5-C9-C8	106.6(5)
C1-C2-C3-C14	107.7(5)	C6-C5-C9-C8	-18.2(5)
C10-C2-C3-C4	167.9(5)	C4-C5-C9-C18	-71.1(6)
C1-C2-C3-C4	-13.3(5)	C6-C5-C9-C18	164.1(5)
C2-C3-C4-O1	-4.3(5)	C3-C2-C10-Si1	178.7(4)
C14-C3-C4-O1	-122.6(4)	C1-C2-C10-Si1	0.1(9)
C2-C3-C4-C5	-126.5(4)	C2-C3-C14-O2	179.0(4)
C14-C3-C4-C5	115.2(5)	C4-C3-C14-O2	-64.8(5)
O1-C4-C5-C9	-43.9(5)	C7-C6-C15-C17	0.7(8)
C3-C4-C5-C9	76.4(6)	C5-C6-C15-C17	-124.1(6)
O1-C4-C5-C6	72.7(5)	C7-C6-C15-C16	-175.8(5)
C3-C4-C5-C6	-167.0(4)	C5-C6-C15-C16	59.4(6)
C9-C5-C6-C15	160.4(4)	C2-C1-O1-C4	-30.4(5)
C4-C5-C6-C15	37.5(6)	C5-C4-O1-C1	147.5(4)
C9-C5-C6-C7	28.6(5)	C3-C4-O1-C1	21.9(5)
C4-C5-C6-C7	-94.4(5)	C2-C10-Si1-C13	-123.5(5)
C15-C6-C7-C8	-159.1(4)	C2-C10-Si1-C12	119.3(5)
C5-C6-C7-C8	-28.6(5)	C2-C10-Si1-C11	-2.6(6)
C6-C7-C8-C9	18.8(6)		

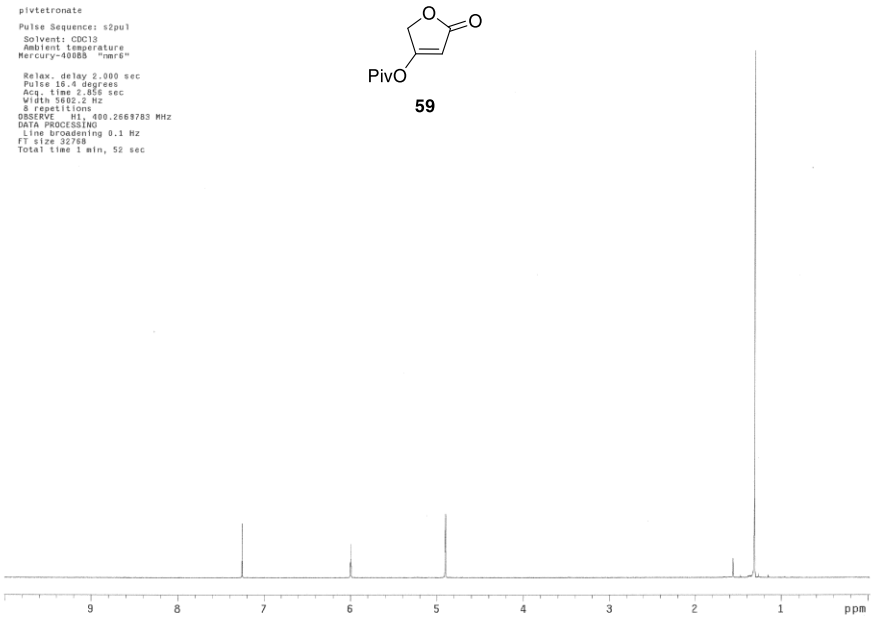
Table 7. Hydrogen bonds for 401 [Å and °].

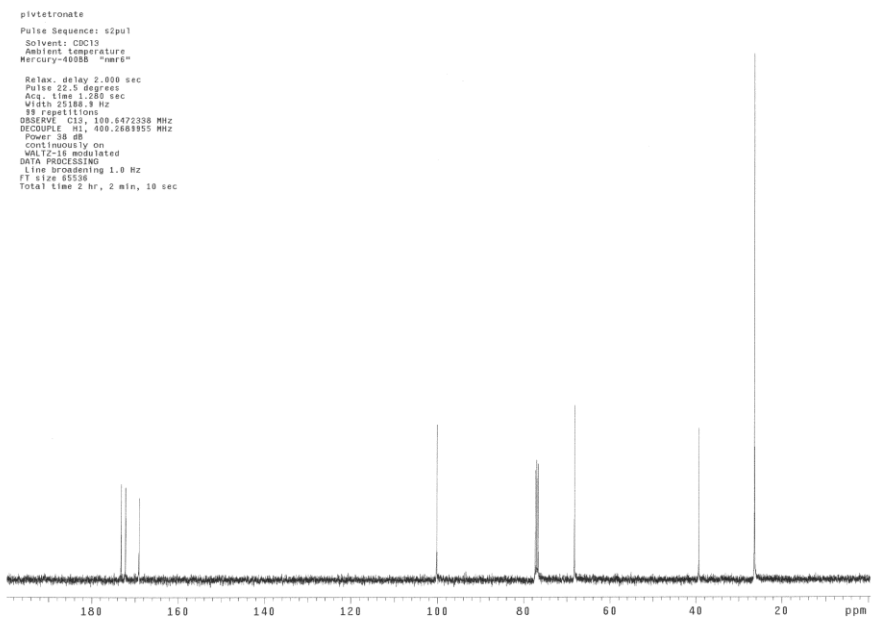
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O2-H2O...O1#1	0.83(6)	2.12(6)	2.924(6)	163(5)

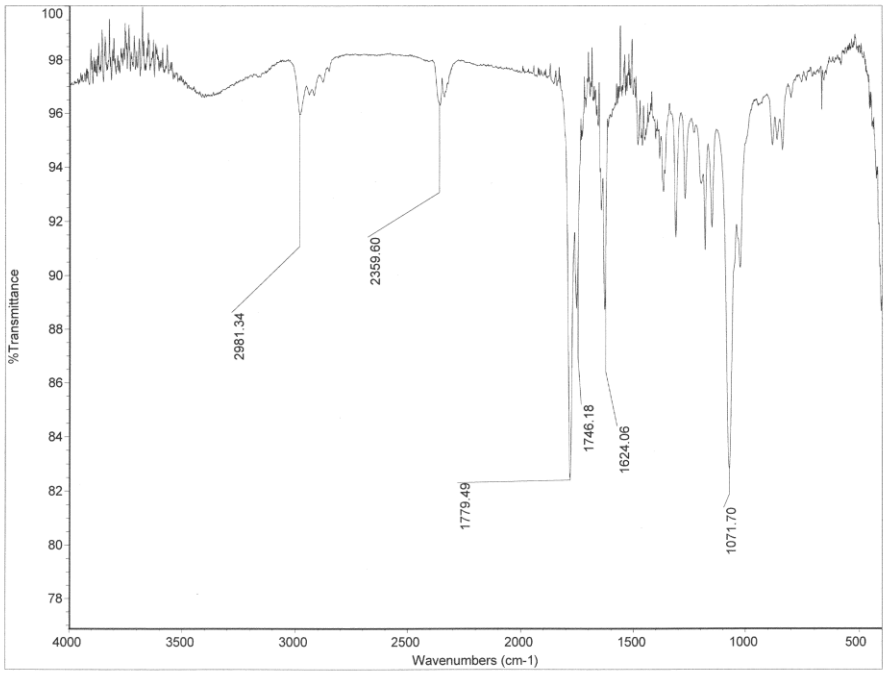
Symmetry transformations used to generate equivalent atoms:

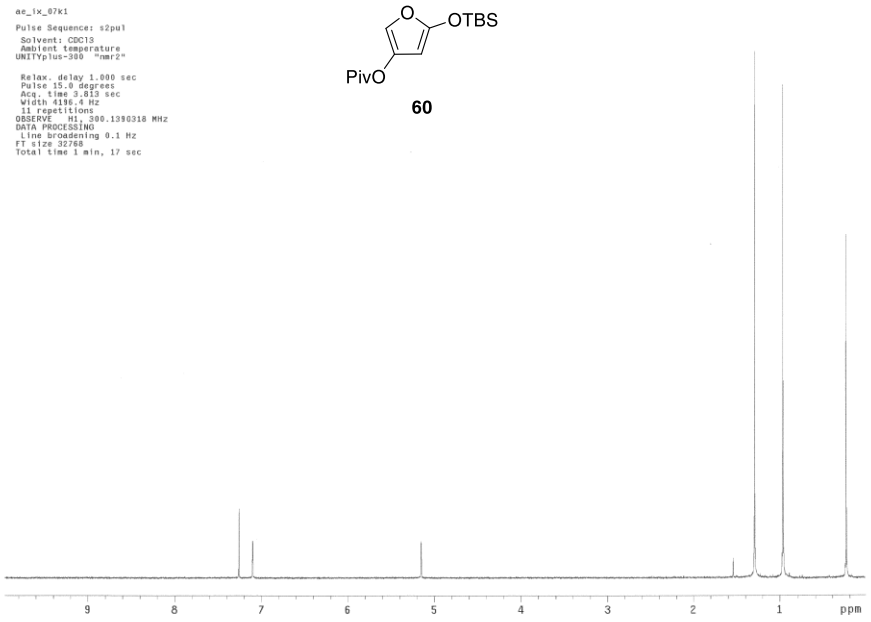
#1 x,y+1,z

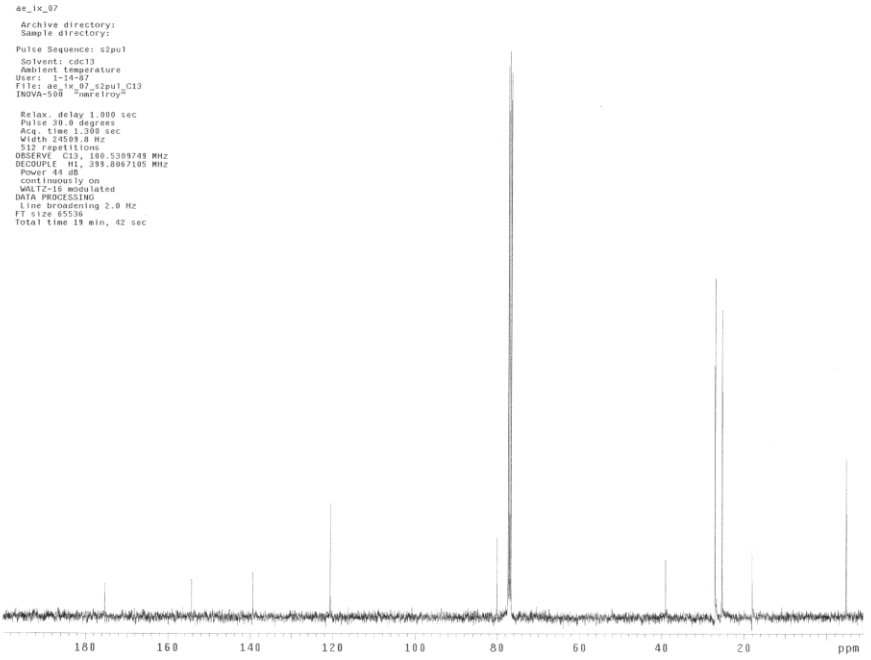
Appendix C: Catalog of Spectra

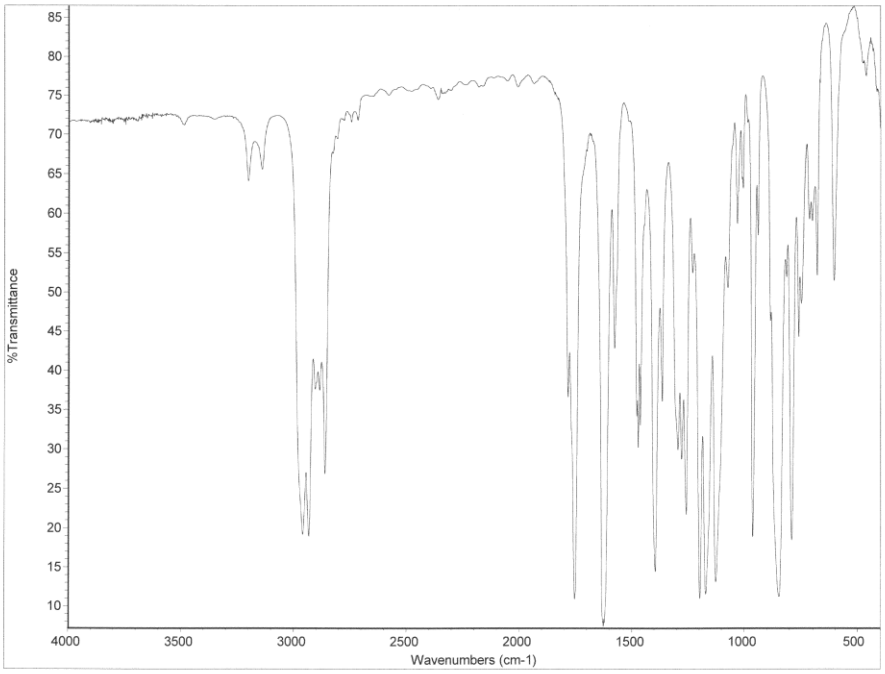





%Transmittance
Wavenumbers (cm-1)
2981.34
2359.60
1779.49
1746.18
1624.06
1071.70


ae_ix_07k1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITYplus-300 "nmr2"
Relax. delay 1.000 sec
Pulse 15.0 degrees
Acq. time 3.013 sec
Width 4196.4 Hz
11 repetitions
OBSERVE H1, 300.1390318 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 17 sec
O
OTBS
PivO
60
9
8
7
6
5
4
3
2
1
ppm


ae_ix_07
Archive directory:
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: ae_ix_07_s2pul_C13
INOVA-500 "nmrelroy"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5309749 MHz
DECOUPLE H1, 399.8067105 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 19 min, 42 sec
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

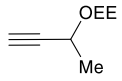
ae_viii_ee

Archive directory: /home/staff31/vnmrsys/data
Sample directory: ae_viii_ee_20120125_01

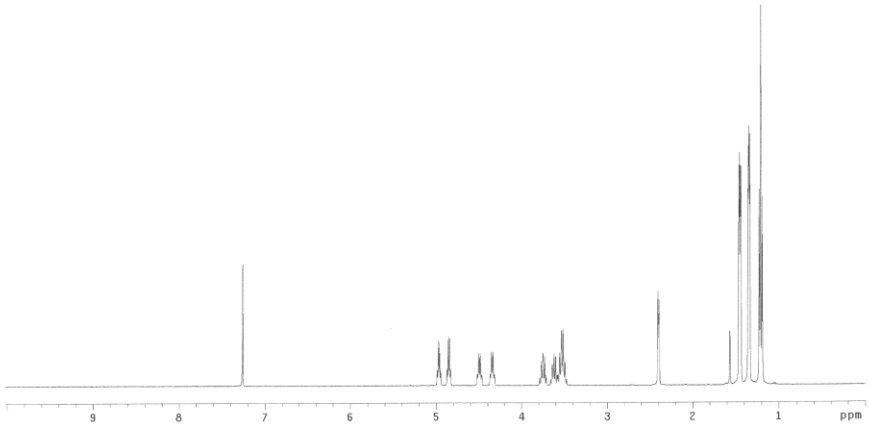
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: PROTON_01
INOVA-500 "nmrfred"

Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
32 repetitions
OBSERVE H1, 399.6763783 MHz
DATA PROCESSING
FT size 32768
Total time 2 min, 26 sec



208

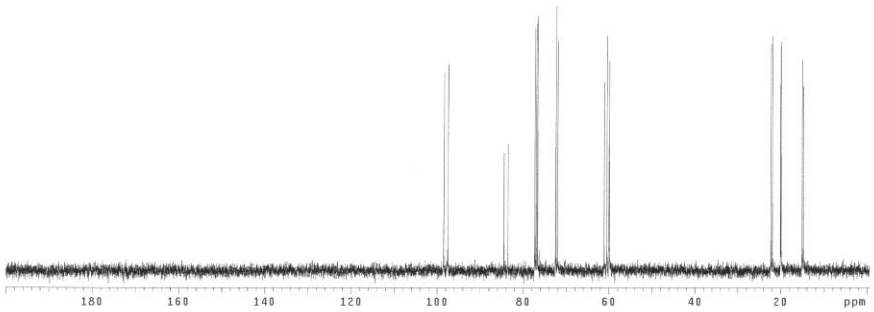


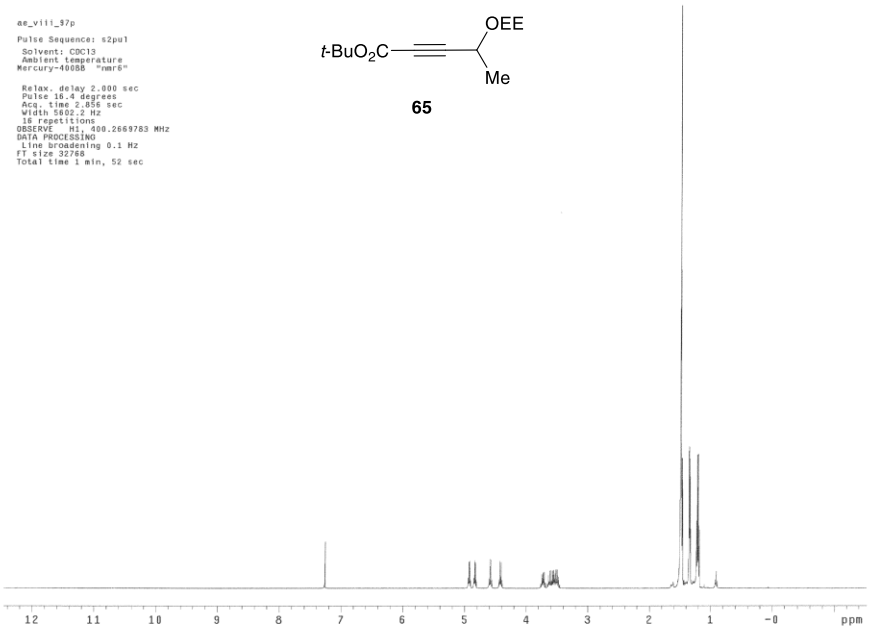
13C OBSERVE

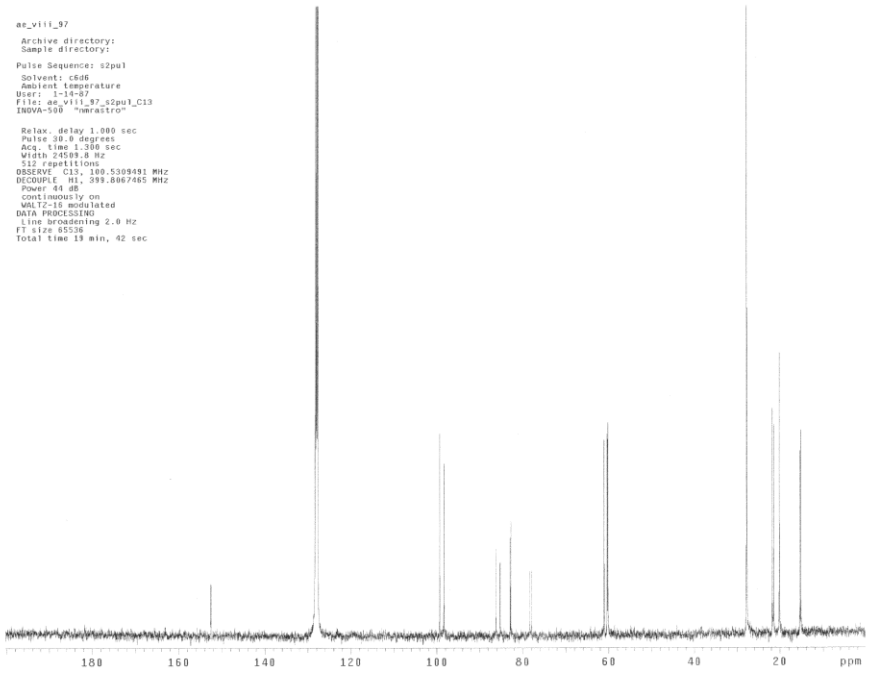
Pulse Sequence: s2pul

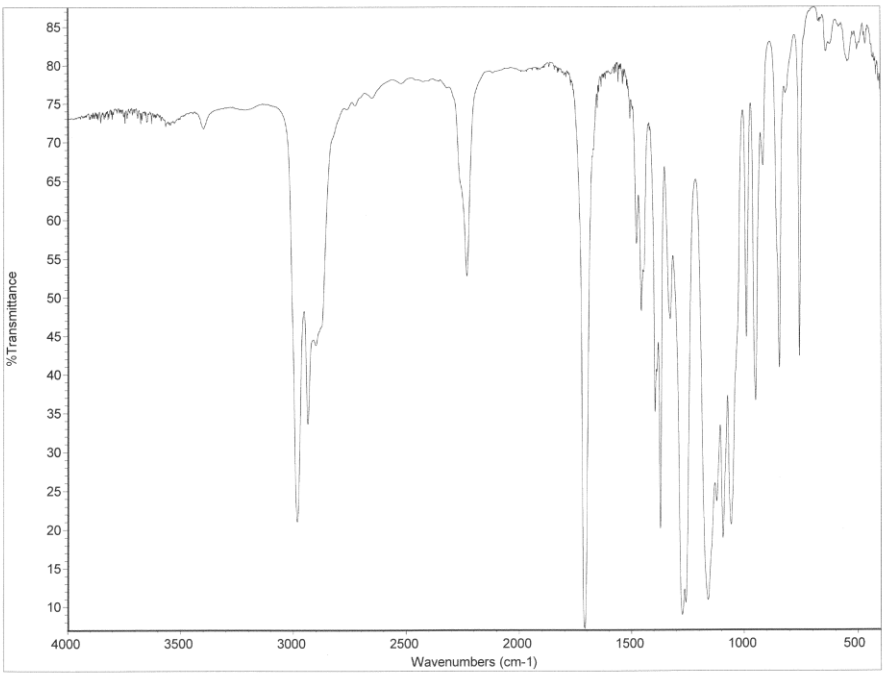
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"

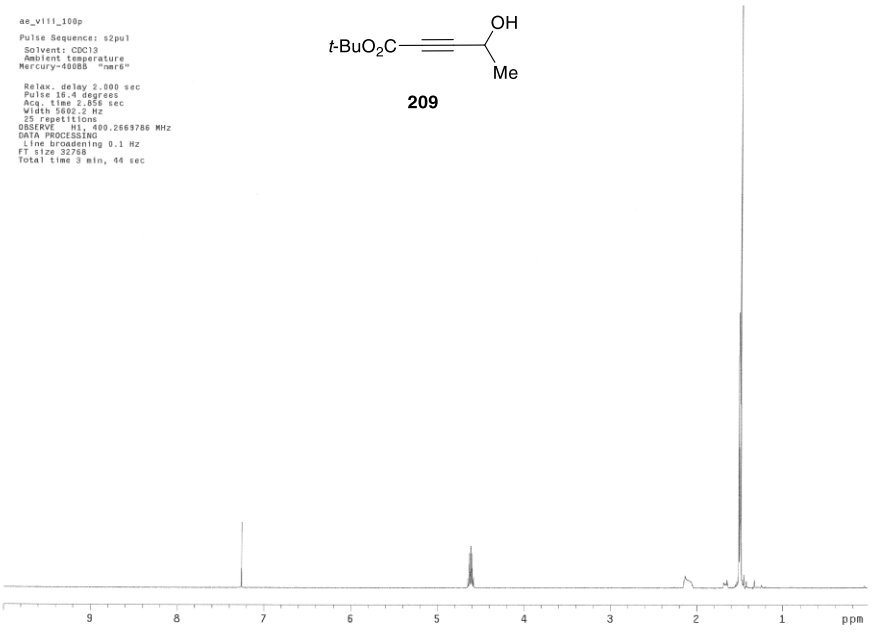
Relax. delay 2.000 sec
Pulse 22.5 degrees
Acq. time 1.280 sec
Width 25188.9 Hz
67 repetitions
OBSERVE C13, 100.6472207 MHz
DECOUPLE H1, 400.2685955 MHz
Power 38 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 15 min, 38 sec

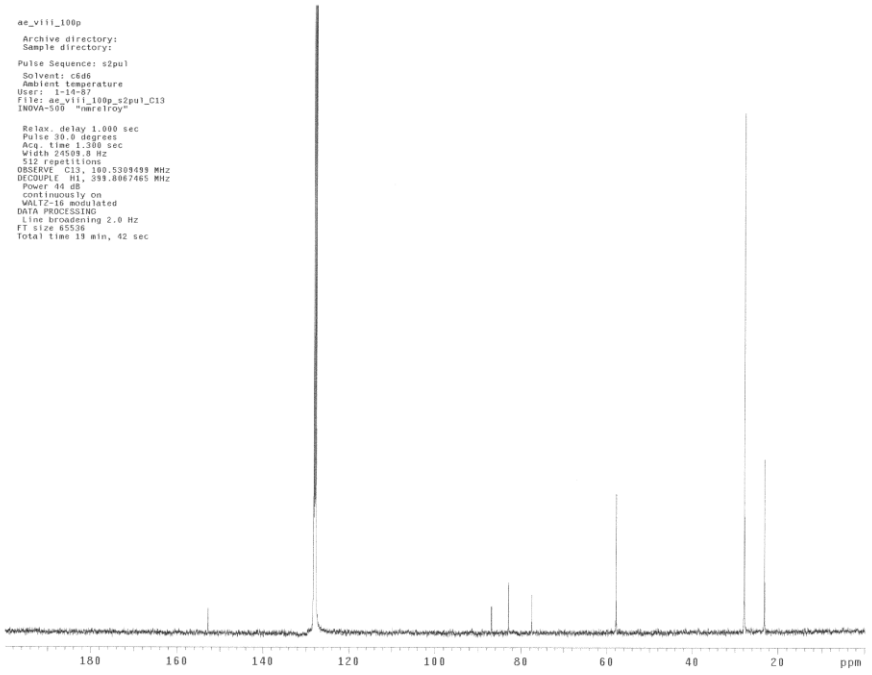


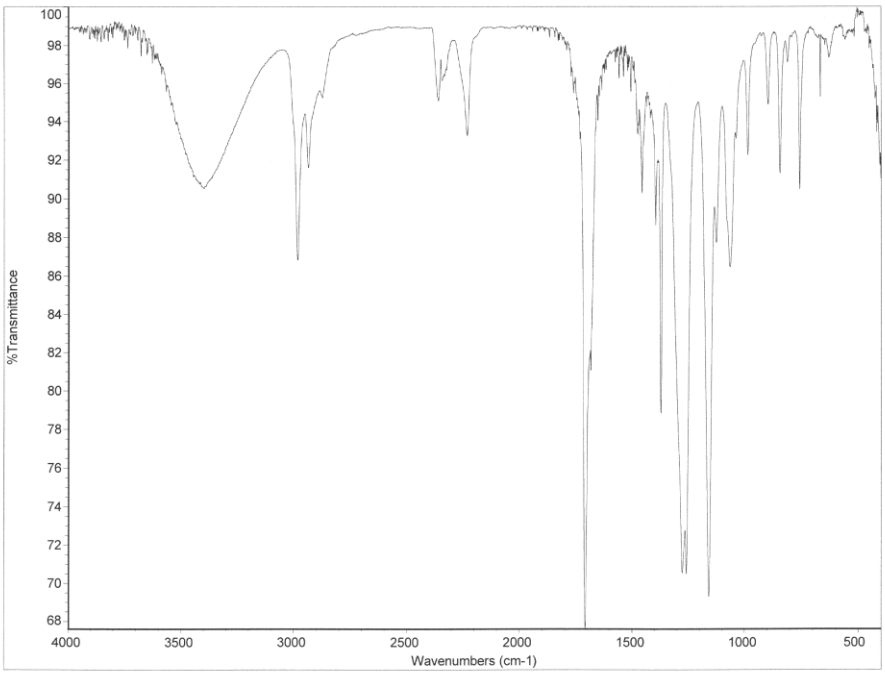

ae_viii_97p
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
16 repetitions
OBSERVE H1, 400.2669783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
t-BuO2C
OEE
Me
65
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


ae_viii_97
Archive directory:
Sample directory:
Pulse Sequence: s2pul
Solvent: c6d6
Ambient temperature
User: 1-14-87
File: ae_viii_97_s2pul_C13
INOVA-500 "nmrastro"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5309491 MHz
DECOUPLE H1, 399.8067465 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 19 min, 42 sec
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


ae_viii_100p
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
25 repetitions
OBSERVE H1, 400.2669786 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 44 sec
t-BuO2C
OH
Me
209
9
8
7
6
5
4
3
2
1
ppm


ae_viii_100p
Archive directory:
Sample directory:
Pulse Sequence: s2pul
Solvent: c6d6
Ambient temperature
User: 1-14-87
File: ae_viii_100p_s2pul_C13
INOVA-500 "nmrelroy"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5309499 MHz
DECOUPLE H1, 399.8067465 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 19 min, 42 sec
180
160
140
120
100
80
60
40
20
ppm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100
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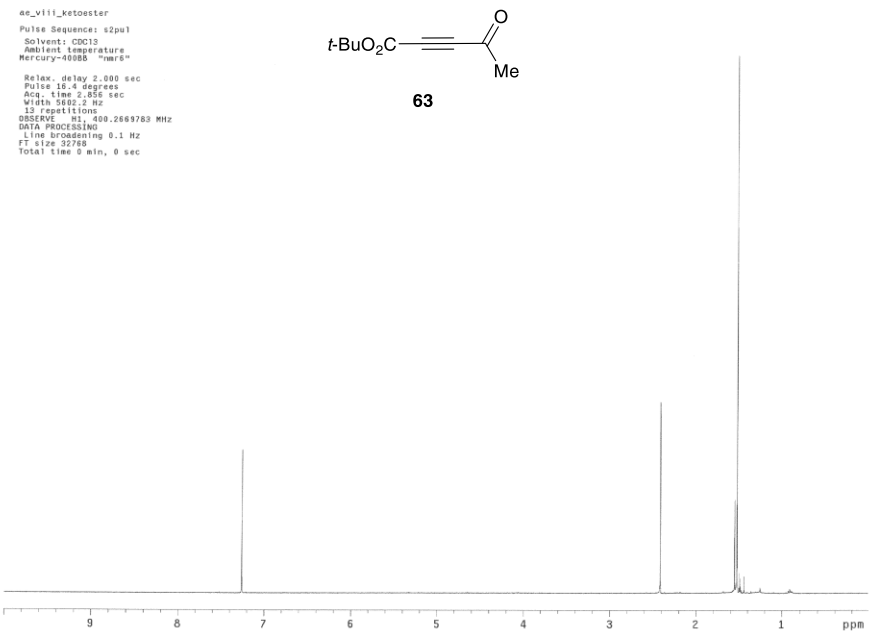
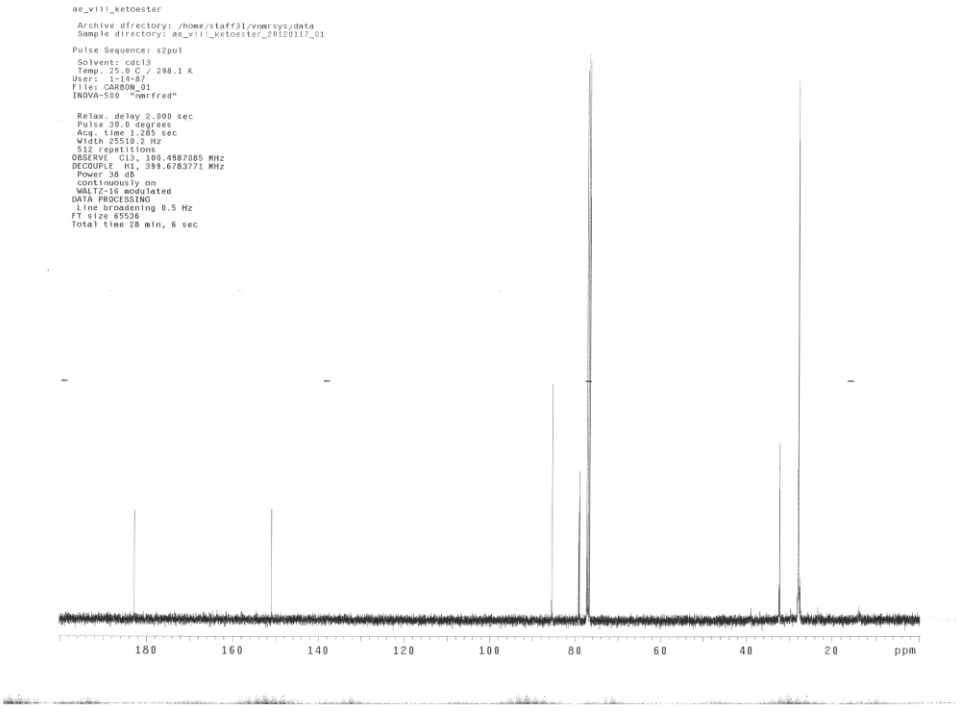
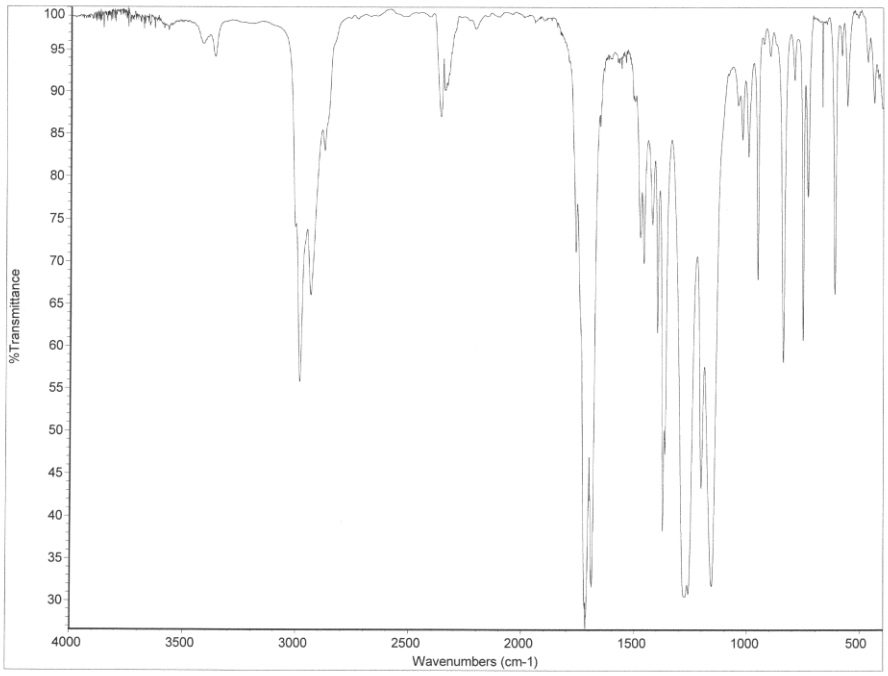
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


ae_viii_ketoester
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
13 repetitions
OBSERVE H1, 400.2669783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
t-BuO2C
O
Me
63
9
8
7
6
5
4
3
2
1
ppm

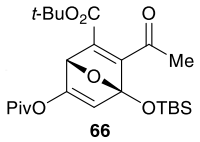

ae_viii_ketoester
Archive directory: /home/staff31/vnmrsys/data
Sample directory: ae_viii_ketoester_20120117_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: l-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.4987085 MHz
DECOUPLE H1, 399.6783771 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 6 sec
180
160
140
120
100
80
60
40
20
ppm


100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

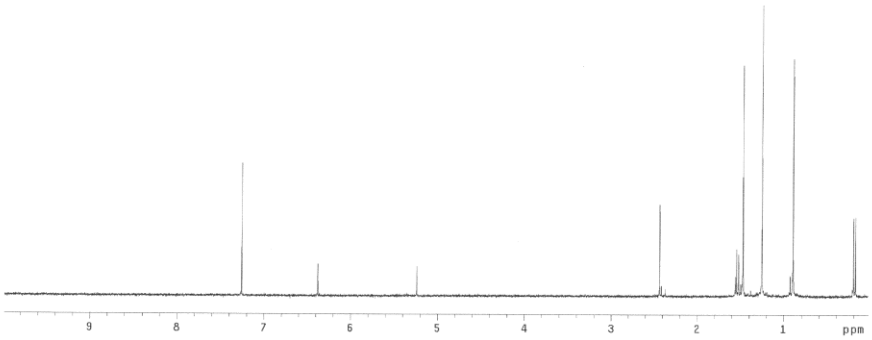
```
ae_ix_11

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
Mercury-400BB  "nmr6"

 Relax. delay 2.000 sec
 Pulse 16.4 degrees
 Acq. time 2.856 sec
 Width 5602.2 Hz
 7 repetitions
OBSERVE  H1, 400.2669786 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
```



66

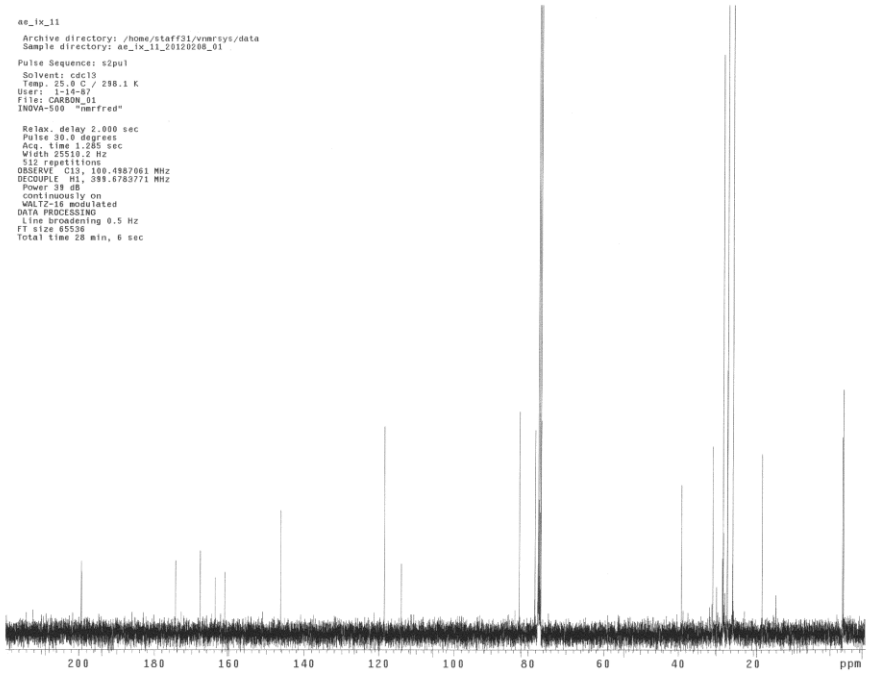


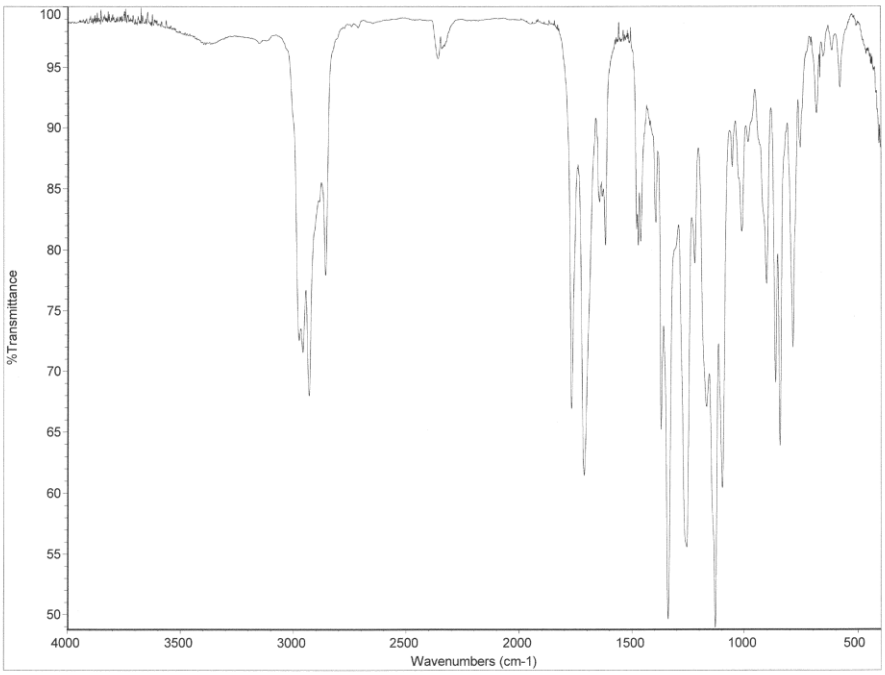

```
ae_ix_11

 Archive directory: /home/staff31/vnmrsys/data
 Sample directory: ae_ix_11_20120208_01

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
User:  l-16-87
File: CARBON_01
INOVA-500  "nmrfred"

 Relax. delay 2.000 sec
 Pulse 30.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
OBSERVE  C13, 100.4987061 MHz
DECOUPLE  H1, 399.6783771 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 6 sec
```

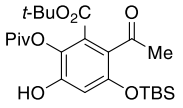



100
95
90
85
80
75
70
65
60
55
50
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

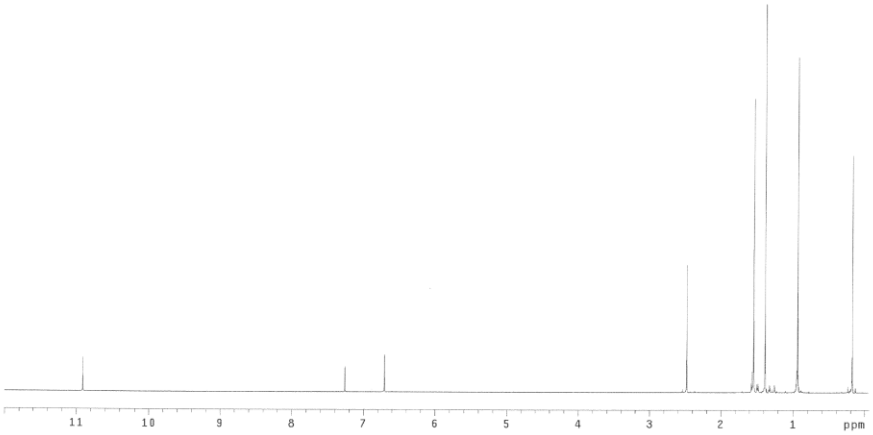
ae_ix_10p2

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"

Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
15 repetitions
OBSERVE H1, 400.2669783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec



68

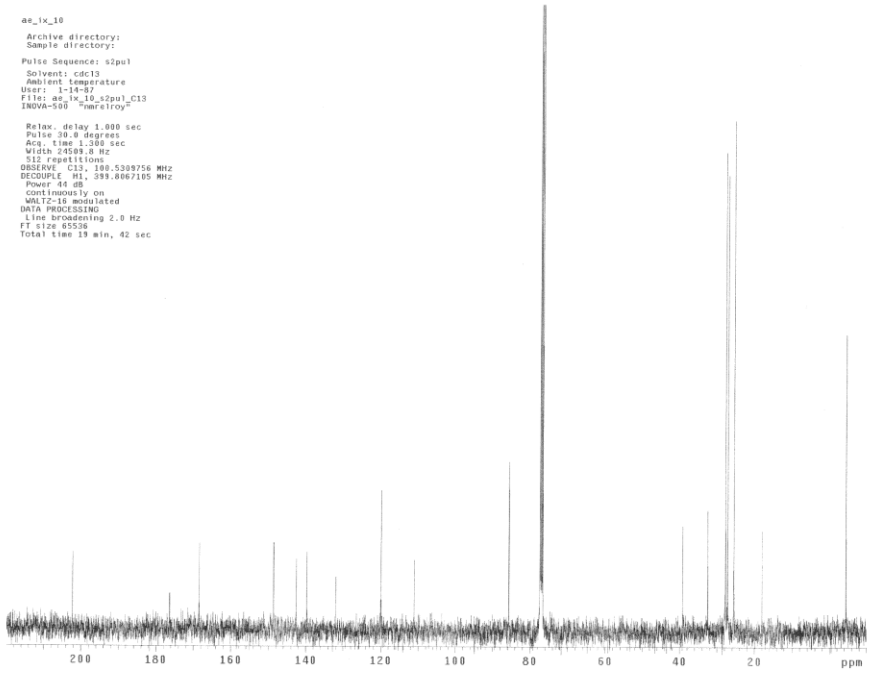


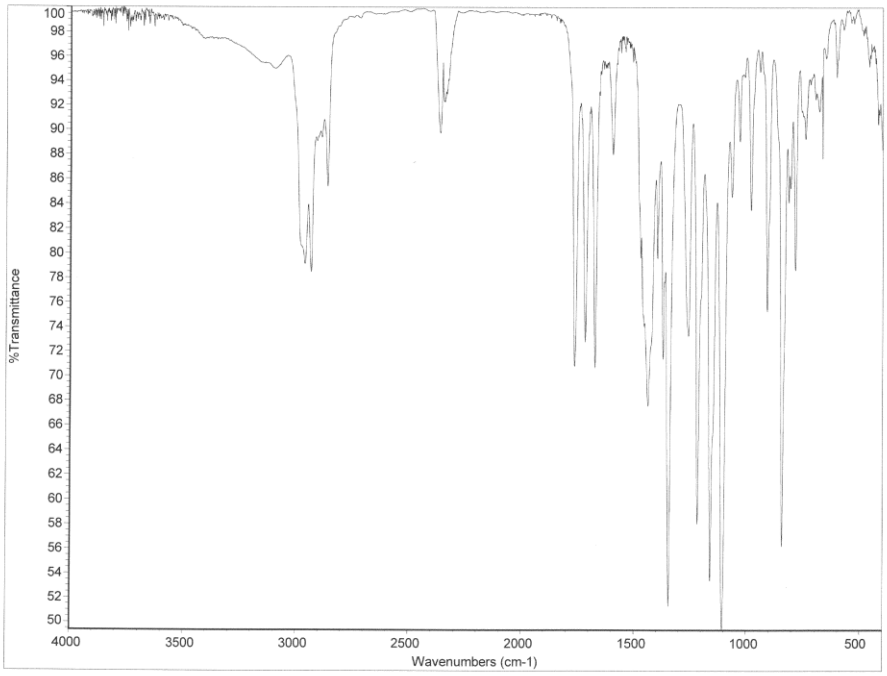
ae_ix_10

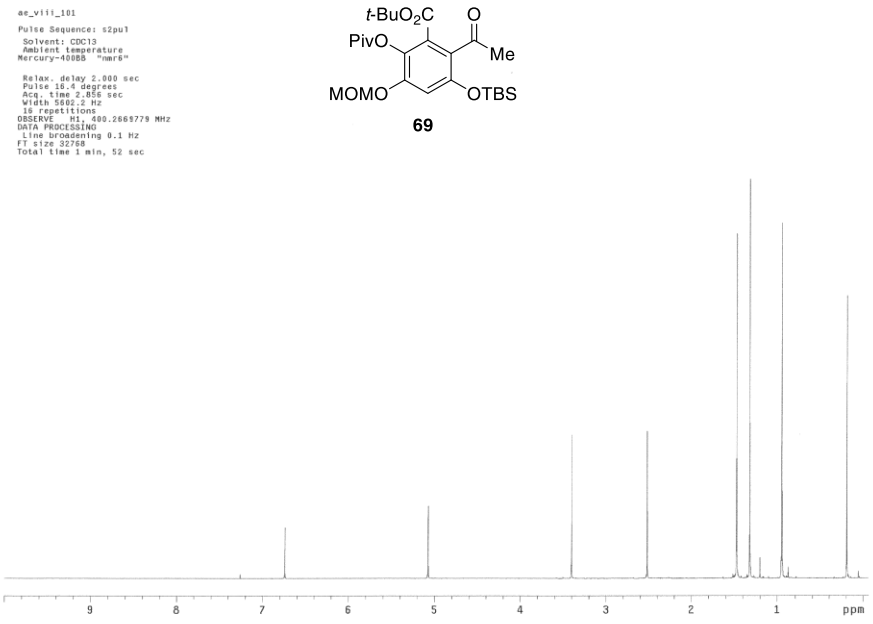
Archive directory:
Sample directory:

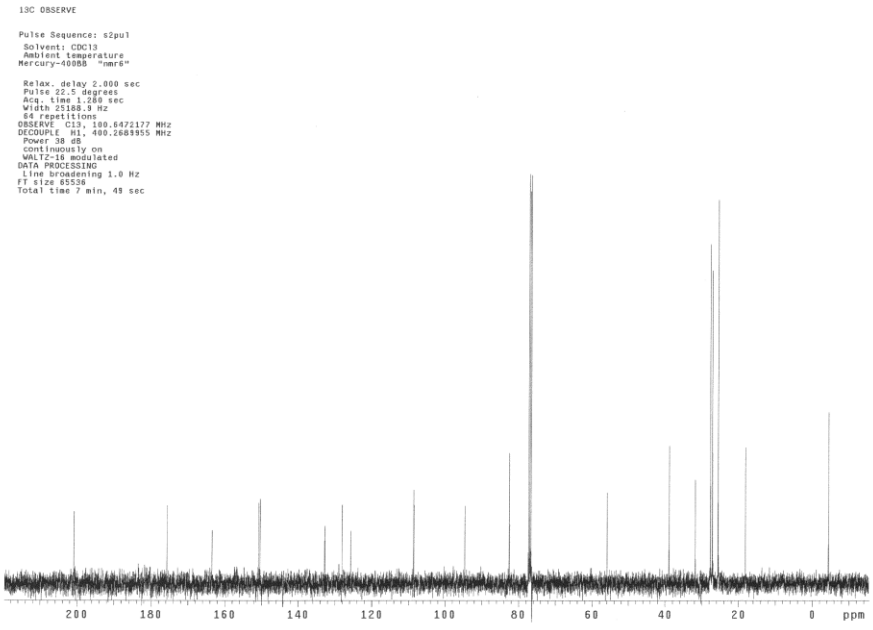
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: ae_ix_10_s2pul_C13
INOVA-500 "nmrelroy"

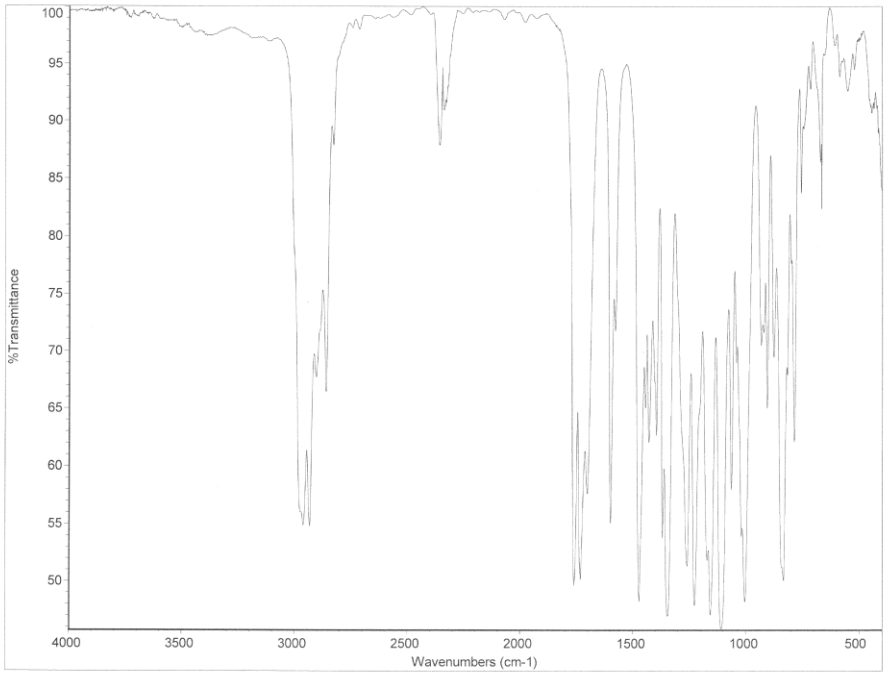
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5309756 MHz
DECOUPLE H1, 399.8067105 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 19 min, 42 sec

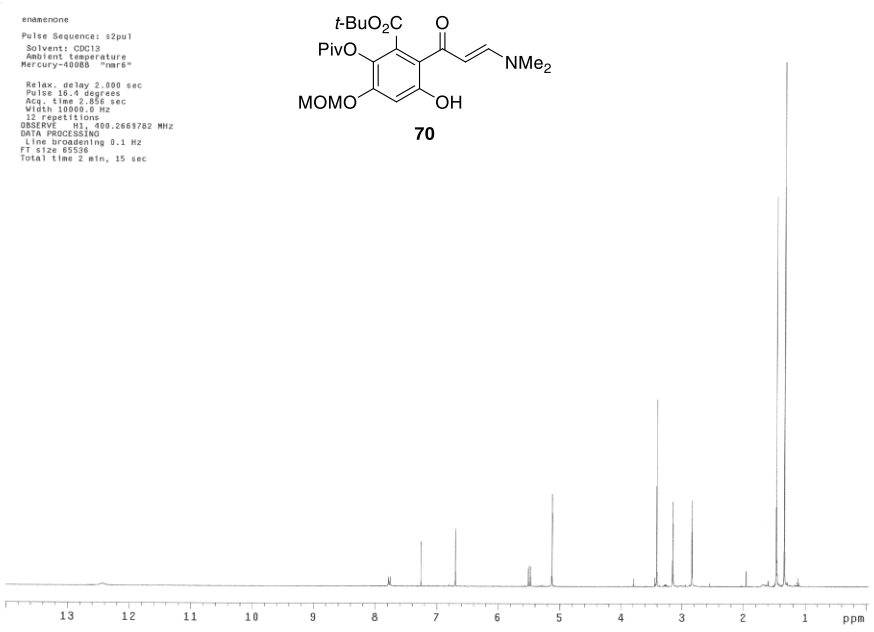


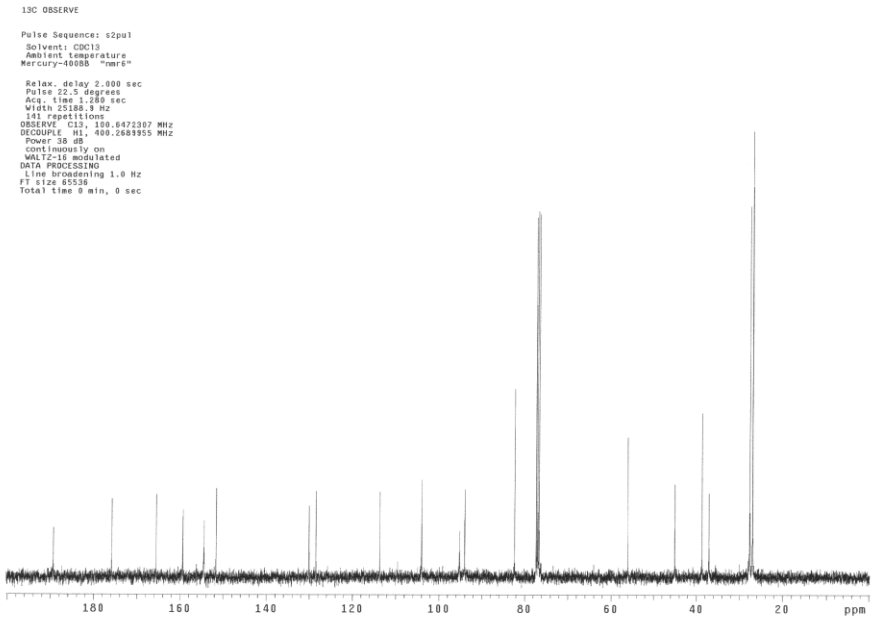

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

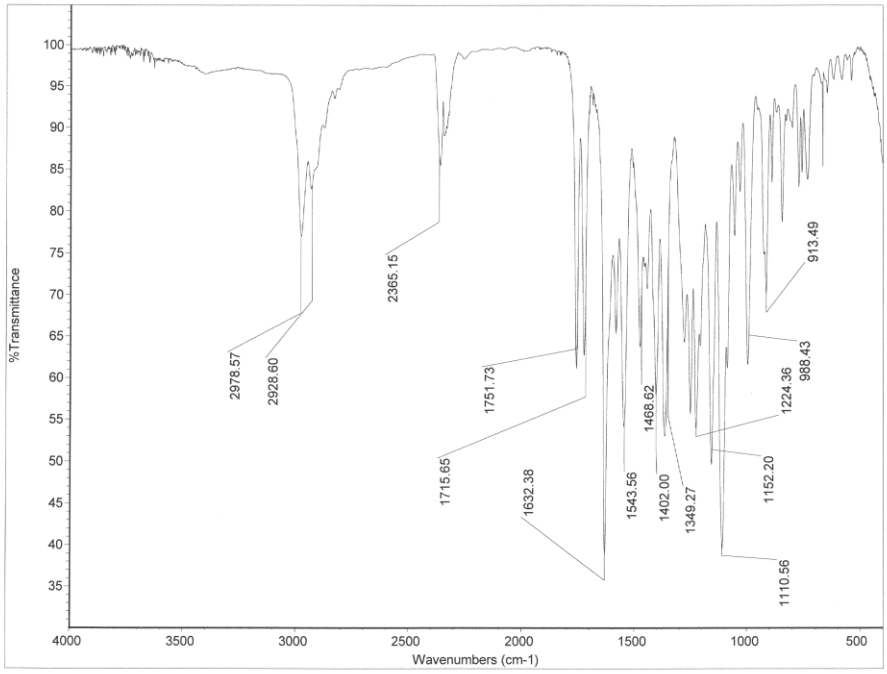

ae_viii_101
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "mmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
16 repetitions
OBSERVE H1, 400.2665779 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
t-BuO2C
O
PivO
Me
MOMO
OTBS
69
9
8
7
6
5
4
3
2
1
ppm

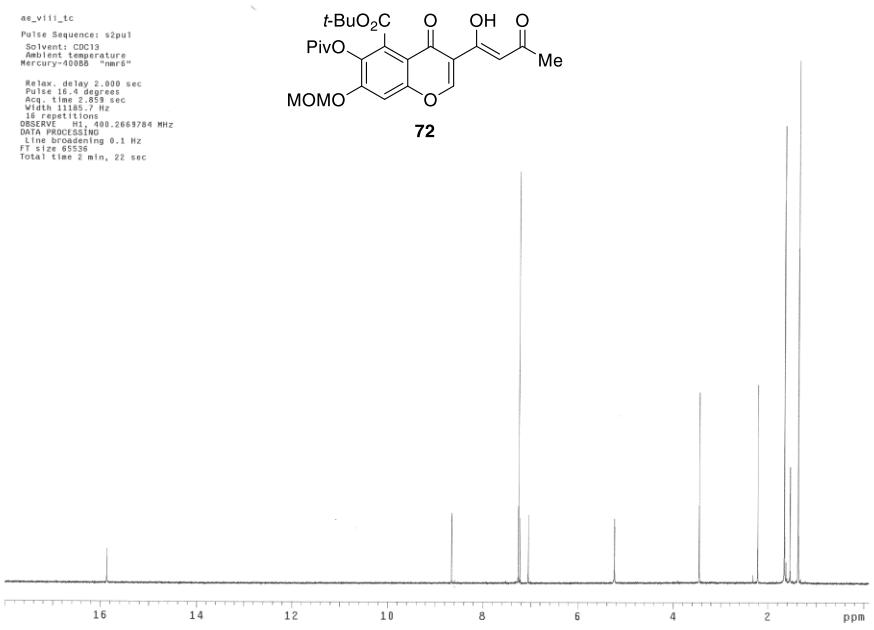

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "mmr6"
Relax. delay 2.000 sec
Pulse 22.5 degrees
Acq. time 1.280 sec
Width 25188.9 Hz
64 repetitions
OBSERVE C13, 100.6472177 MHz
DECOUPLE H1, 400.2683955 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 7 min, 49 sec
200
180
160
140
120
100
80
60
40
20
0
ppm

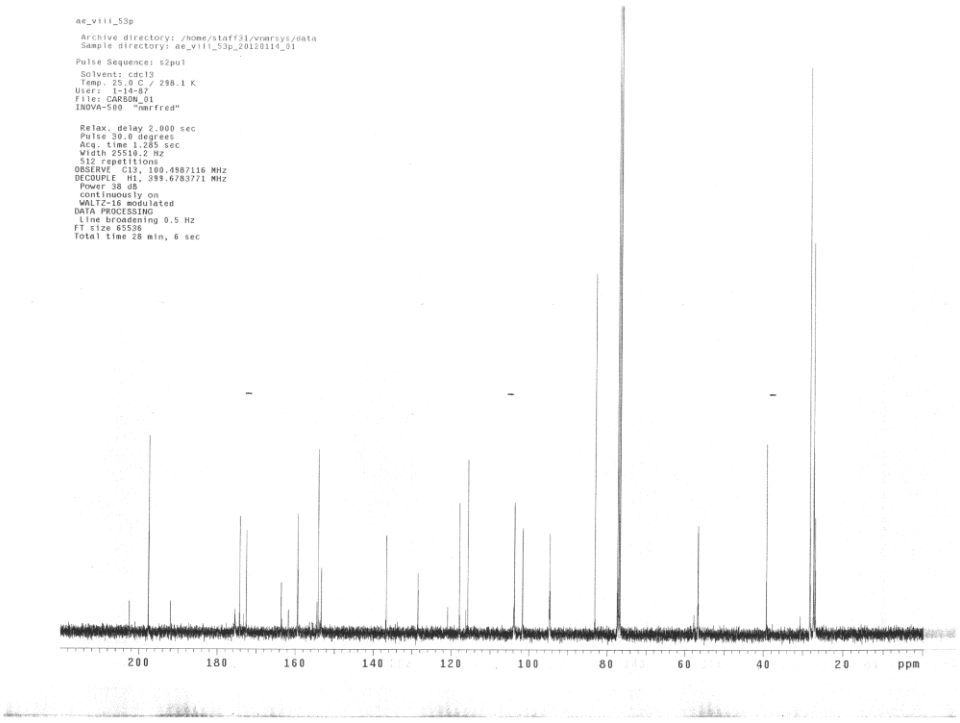

100
95
90
85
80
75
70
65
60
55
50
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

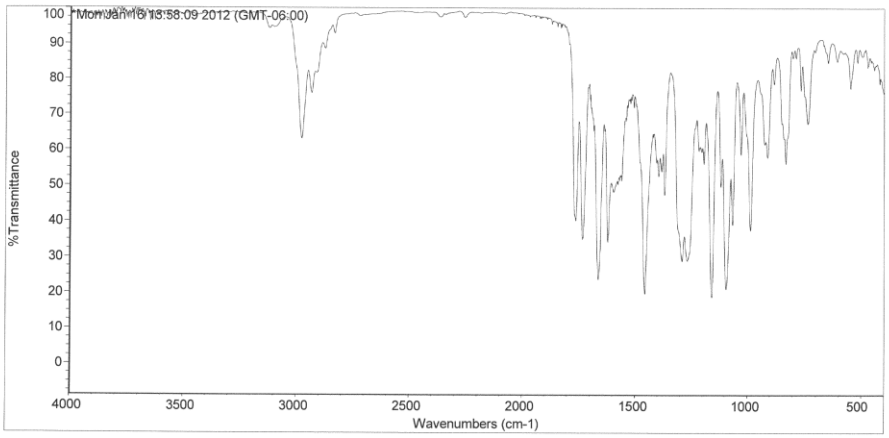

enamenone
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 10000.0 Hz
12 repetitions
OBSERVE H1, 400.2669782 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
Total time 2 min, 15 sec
t-BuO2C
O
PivO
NMe2
MOMO
OH
70
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 22.5 degrees
Acq. time 1.280 sec
Width 25188.9 Hz
141 repetitions
OBSERVE C13, 100.6472307 MHz
DECOUPLE H1, 400.2681955 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 0 min, 0 sec
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
Wavenumbers (cm-1)
2978.57
2928.60
2365.15
1751.73
1715.65
1632.38
1543.56
1468.62
1402.00
1349.27
1224.36
1152.20
1110.56
988.43
913.49


ae_viii_tc
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.859 sec
Width 11185.7 Hz
16 repetitions
OBSERVE H1, 400.2669784 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
Total time 2 min, 22 sec
t-BuO2C
O
OH
O
PivO
Me
MOMO
O
72
16
14
12
10
8
6
4
2
ppm

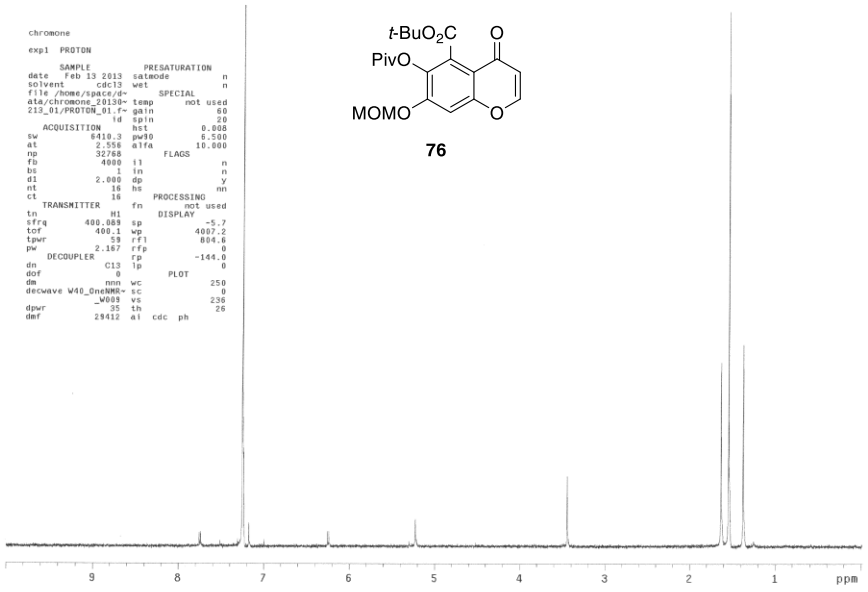

ae_viii_53p
Archive directory: /home/staff31/vnmrsys/data
Sample directory: ae_viii_53p_20120114_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: I-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.4987116 MHz
DECOUPLE H1, 399.6783771 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 6 sec
200
180
160
140
120
100
80
60
40
20
ppm

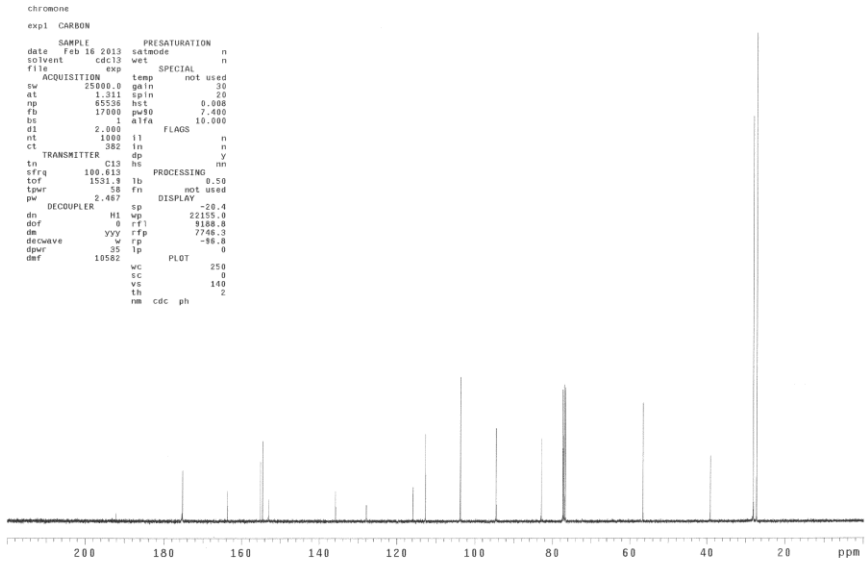


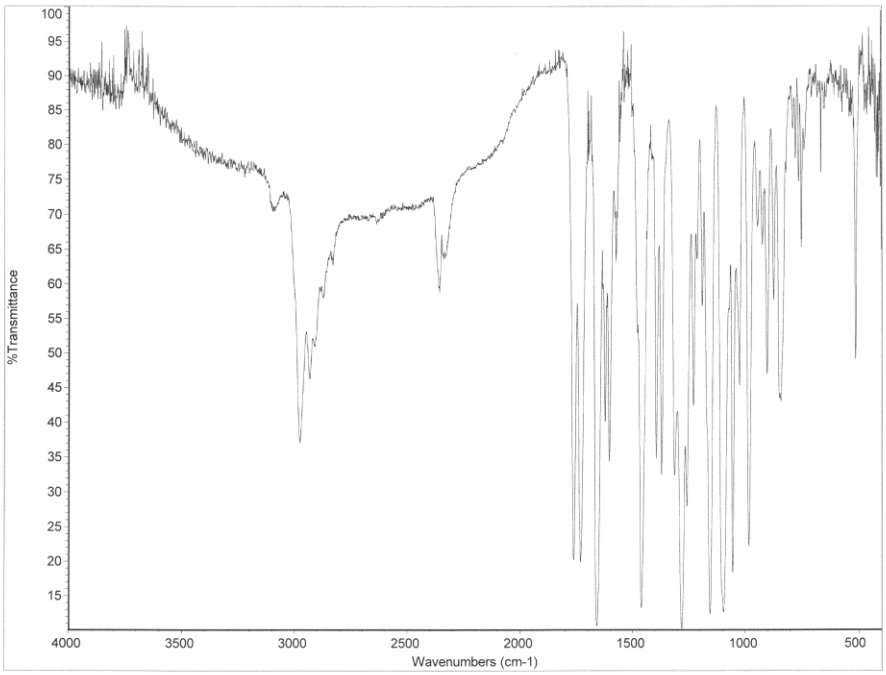
Mon Jan 16 14:02:19 2012 (GMT-06:00)
FIND PEAKS:

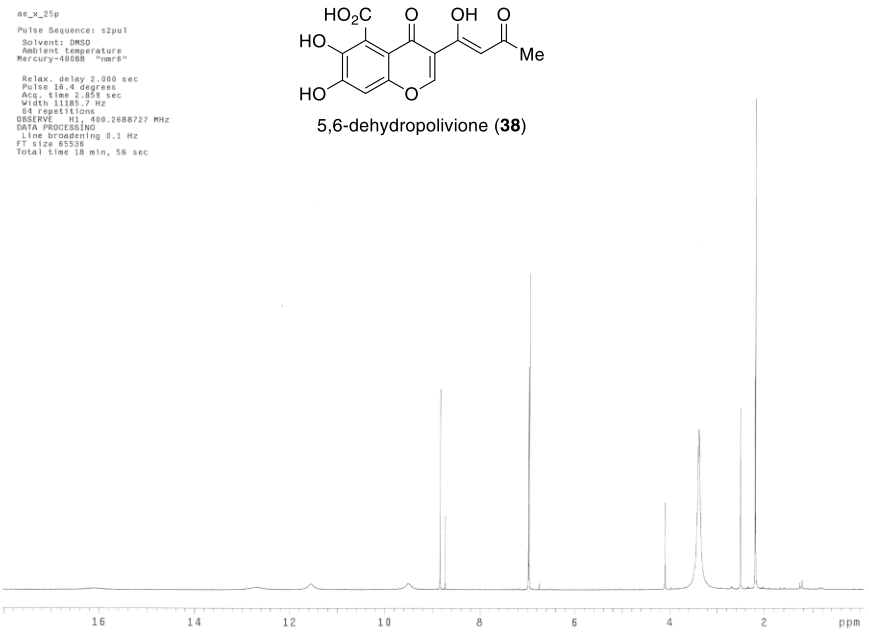
Spectrum:	*Mon Jan 16 13:58:09 2012 (GMT-06:00)	
Region:	4000.00	400.00
Absolute threshold:	15.889	
Sensitivity:	50	
Peak list:		

No peaks were found.

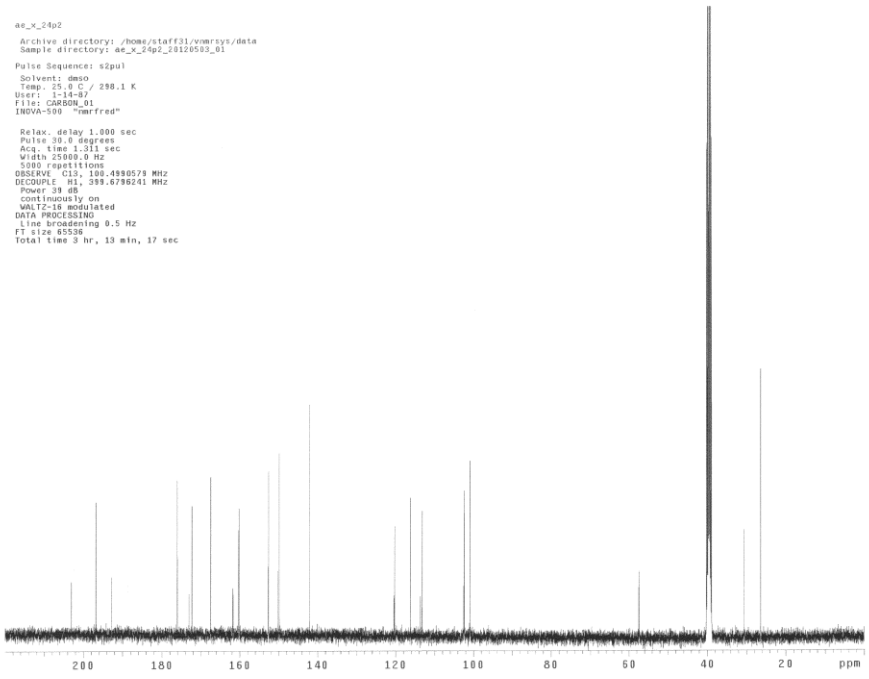

chromone
expl PROTON
SAMPLE
date Feb 13 2013
solvent cdcl3
file /home/space/d~
ata/chromone_20130~
213_01/PROTON_01.f~
id
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_Dec#WM#~
_W009
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 60
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -5.7
wp 4007.2
rf1 804.6
rfp 0
rp -144.0
lp 0
PLOT
wc 250
sc 0
vs 236
th 26
al cdc ph
t-BuO2C
O
PivO
MOMO
O
76
9
8
7
6
5
4
3
2
1
ppm

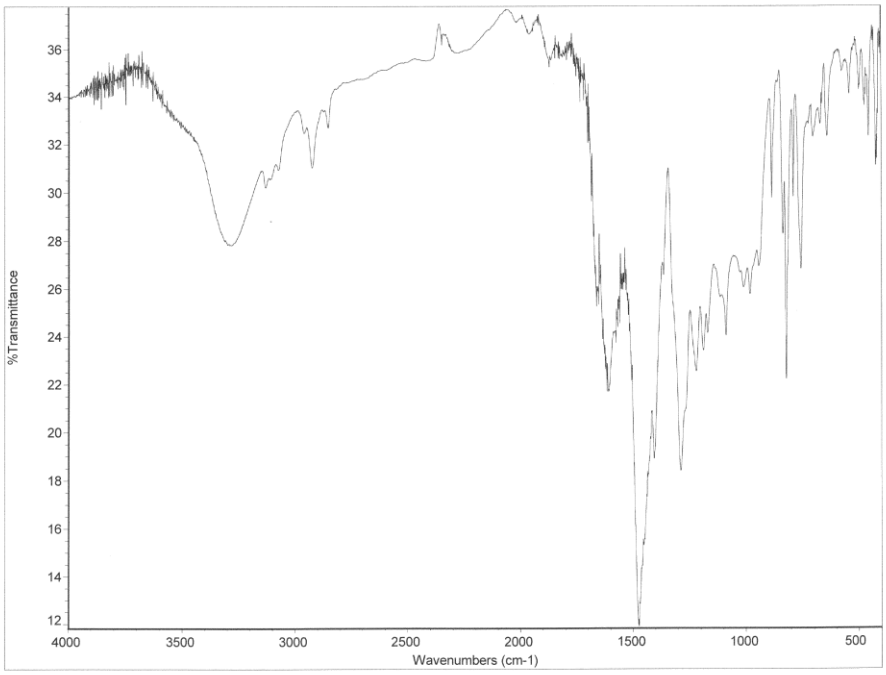

chromone
expl CARBON
SAMPLE
date Feb 16 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 382
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw80 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -20.4
wp 22155.0
rf1 9188.8
rfp 7746.3
rp -96.8
lp 0
PLOT
wc 250
sc 0
vs 140
th 2
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

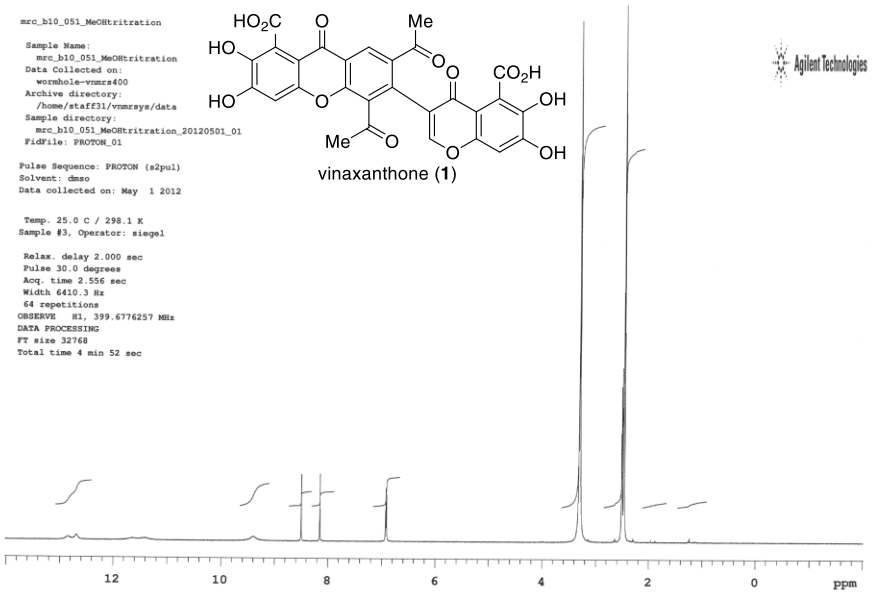

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)



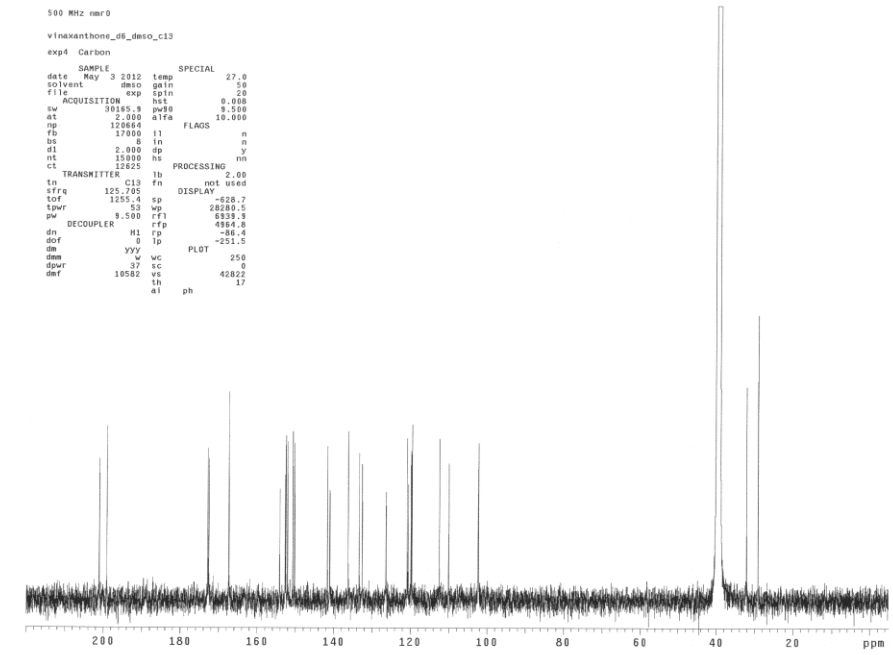
5,6-dehydropolivione (**38**)

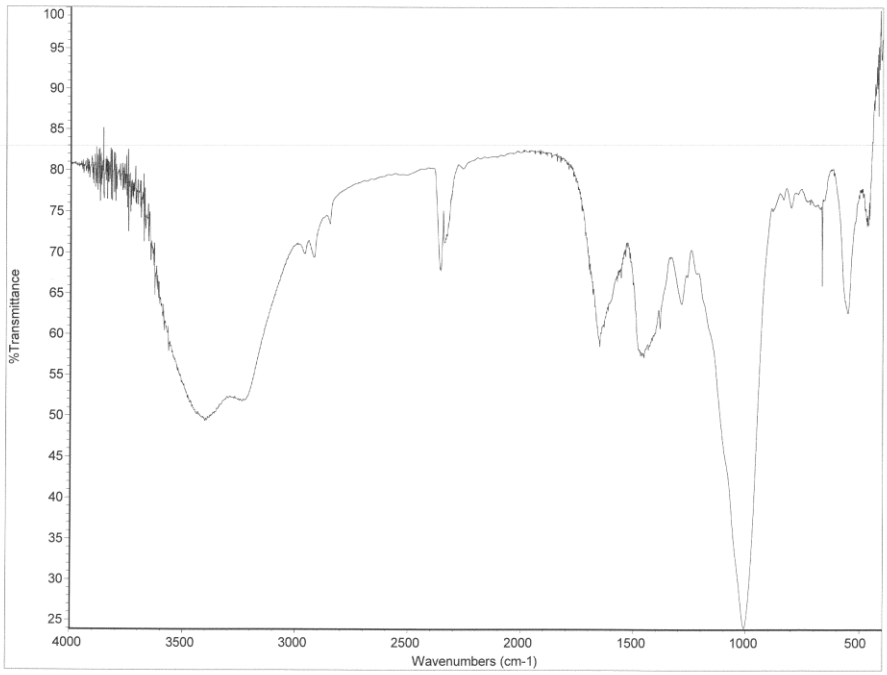


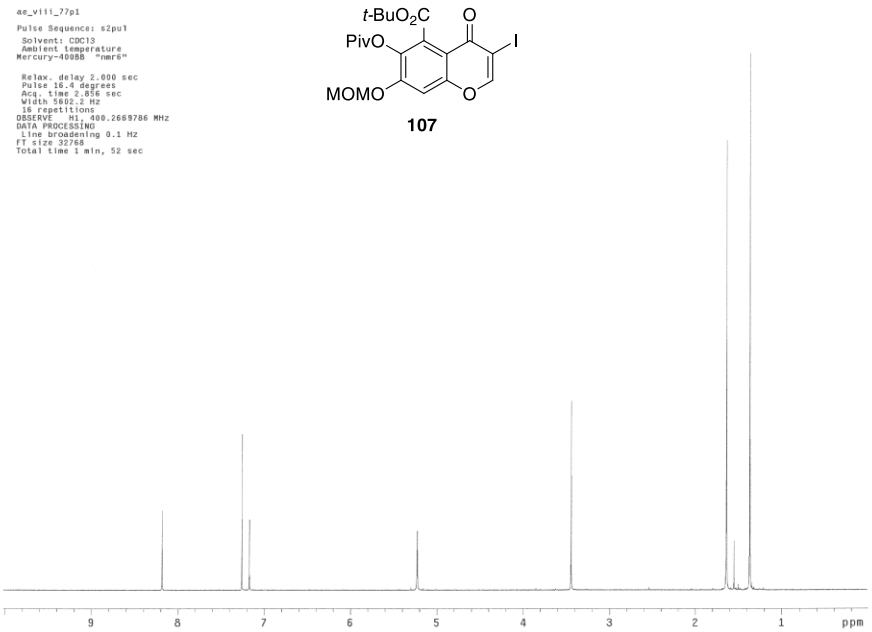

%Transmittance
36
34
32
30
28
26
24
22
20
18
16
14
12
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

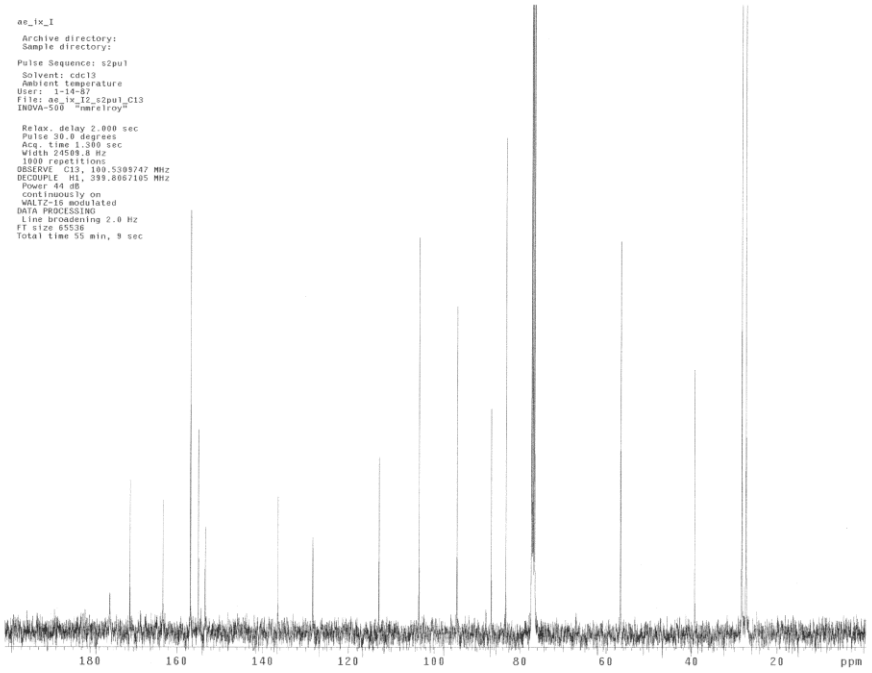


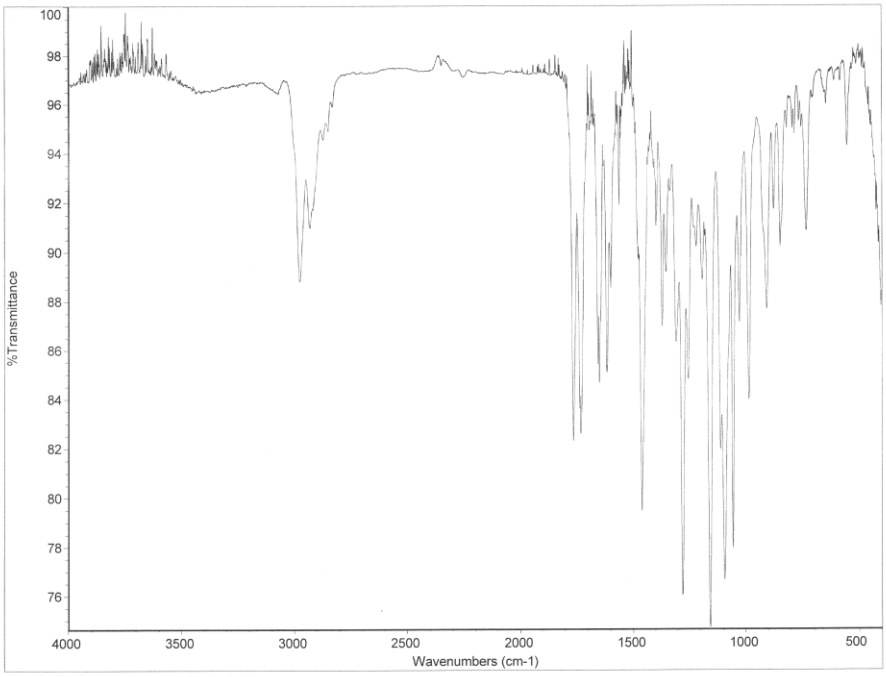
Plotname: PROTON_01_plot01

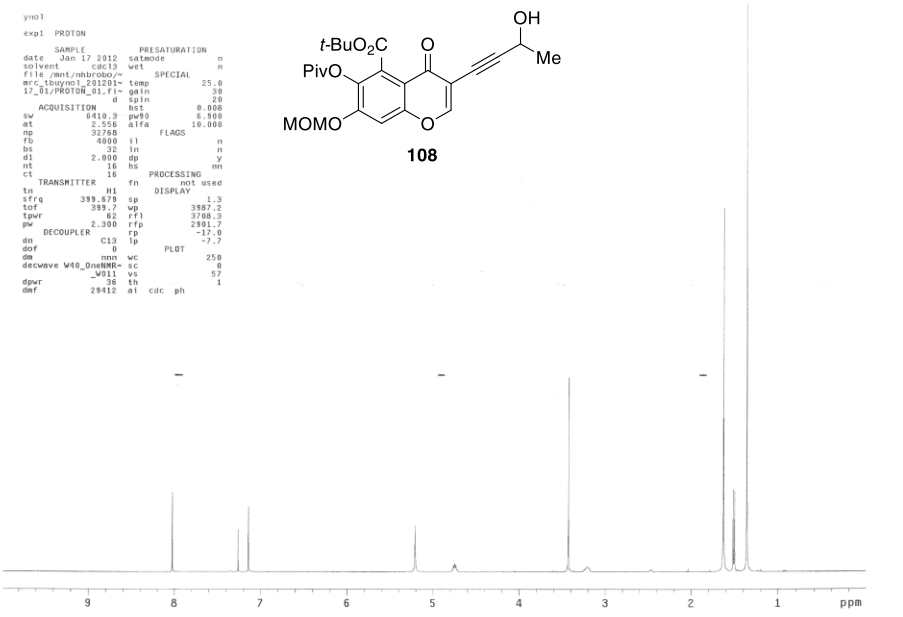


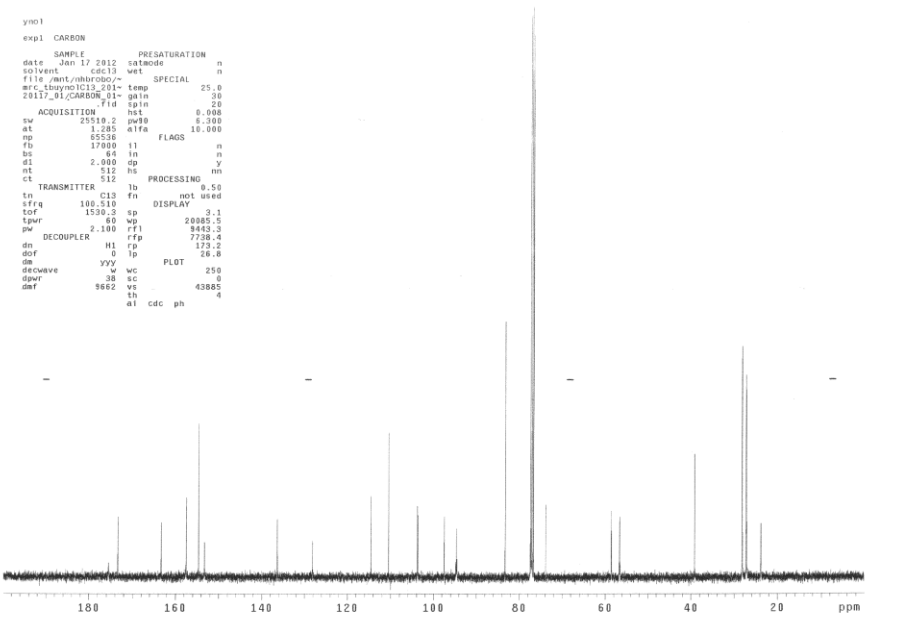

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

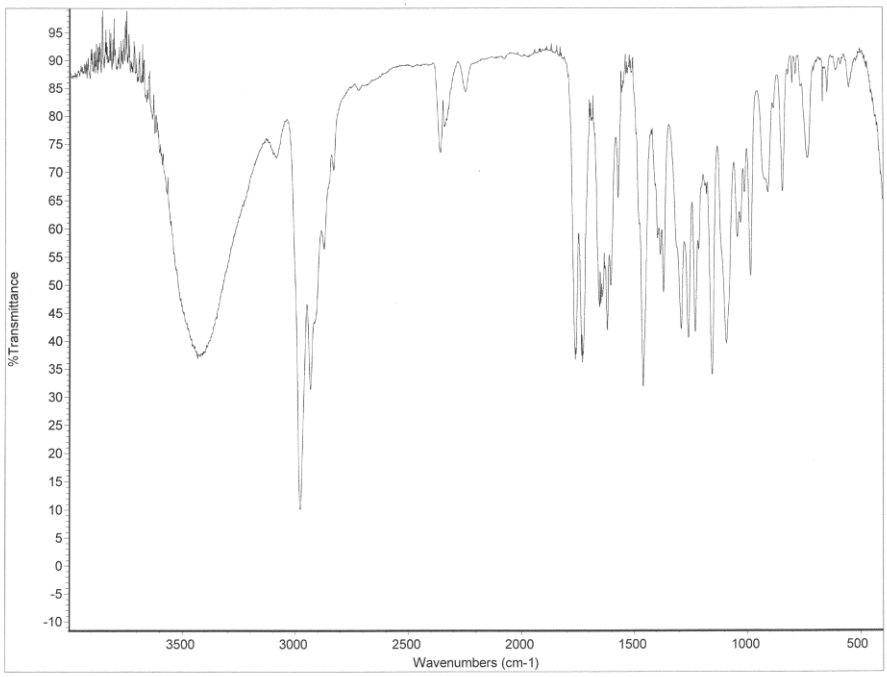

ae_viii_77p1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
16 repetitions
OBSERVE H1, 400.2669786 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
t-BuO2C
O
PivO
I
MOMO
O
107
9
8
7
6
5
4
3
2
1
ppm

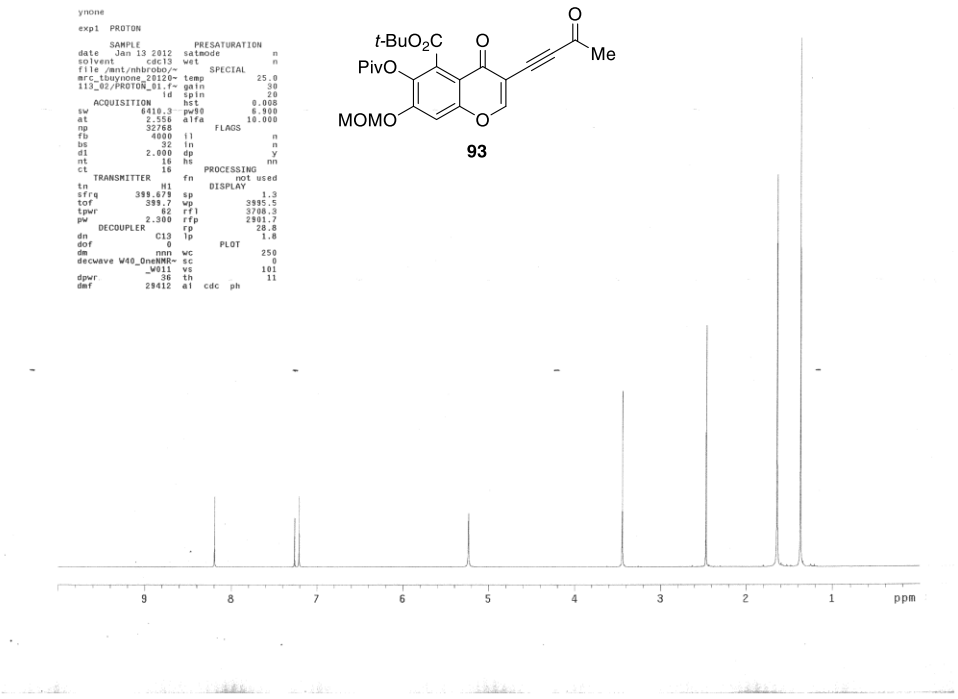

ae_ix_I
Archive directory:
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-97
File: ae_ix_I2_s2pul_C13
INOVA-500 "nmrelroy"
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.380 sec
Width 24509.8 Hz
1000 repetitions
OBSERVE C13, 100.5385747 MHz
DECOUPLE H1, 399.8062105 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 55 min, 9 sec
180
160
140
120
100
80
60
40
20
ppm

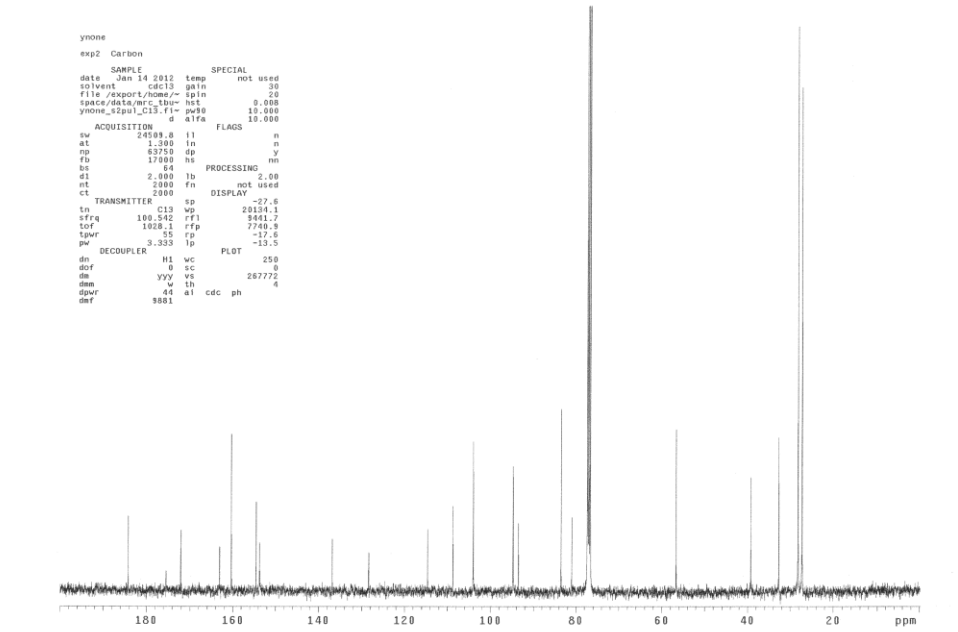

100
98
96
94
92
90
88
86
84
82
80
78
76
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

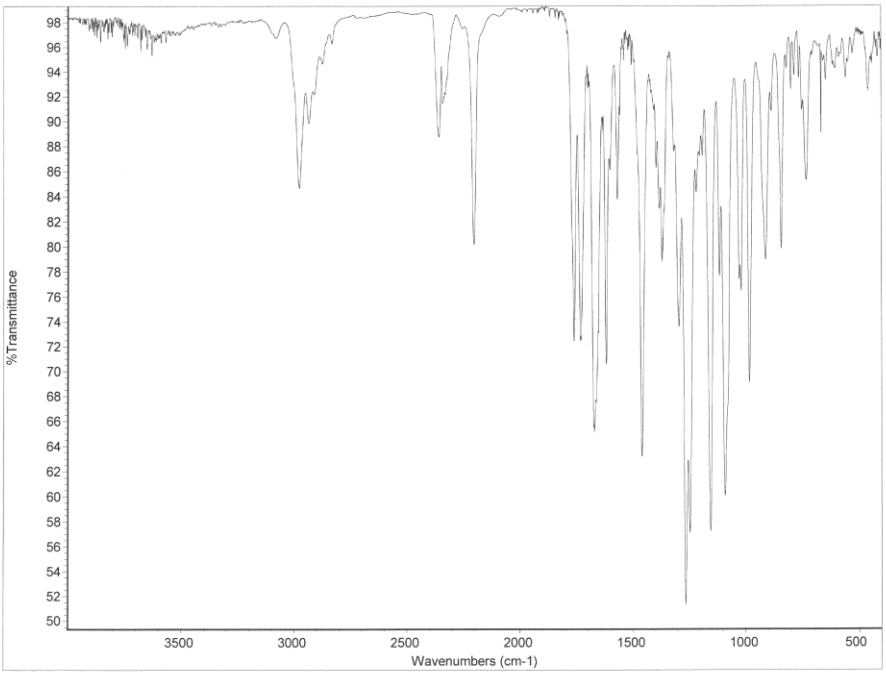

ynol
exp1 PROTON
SAMPLE
date Jan 17 2012
solvent cdcl3
file /mnt/nbbrobo/~
mrc_tbuynol_201201~
17_01/PROTON_01.fi~
d
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 32
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 399.679
tof 399.7
tpwr 62
pw 2.300
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR~
_W911
dpwr 36
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 0.008
pw90 6.900
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 1.3
wp 3987.2
rf1 3788.3
rfp 2901.7
rp -17.0
lp -7.7
PLOT
wc 250
sc 0
vs 57
th 1
al cdc ph
OH
t-BuO2C
O
PivO
Me
MOMO
O
108
9
8
7
6
5
4
3
2
1
ppm

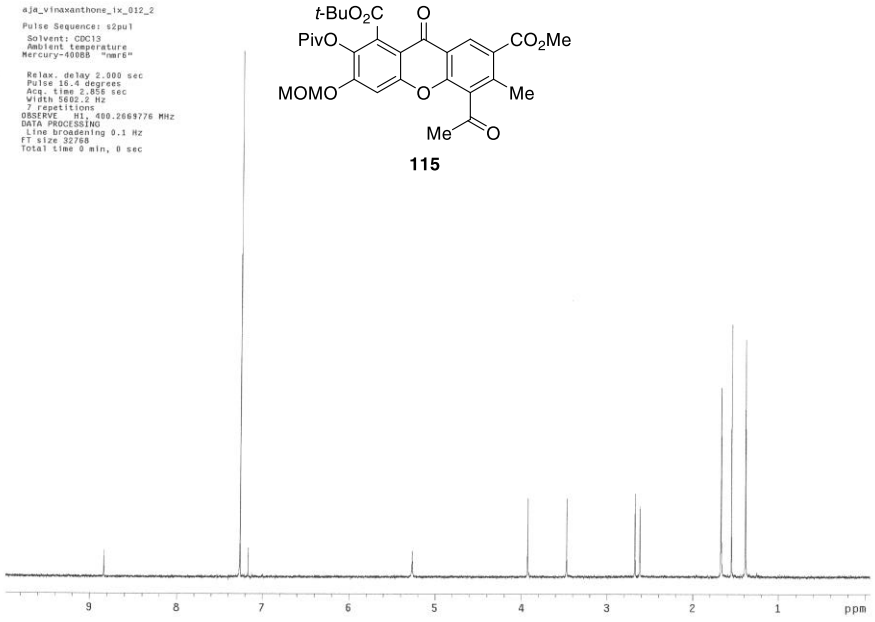

ynol
exp1 CARBON
SAMPLE
date Jan 17 2012
solvent cdcl3
file /mnt/nbbrobo/~
mrc_tbuynolC13_201~
20117_01/CARBON_01~
.fid
ACQUISITION
sw 25519.2
at 1.285
np 65536
fb 17000
bs 64
d1 2.000
nt 512
ct 512
TRANSMITTER
tn C13
sfrq 100.510
tof 1530.3
tpwr 60
pw 2.100
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 38
dmf 9662
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 3.1
wp 20085.5
rf1 9463.3
rfp 7738.4
rp 173.2
lp 26.8
PLOT
wc 250
sc 0
vs 43885
th 4
al cdc ph
180
160
140
120
100
80
60
40
20
ppm

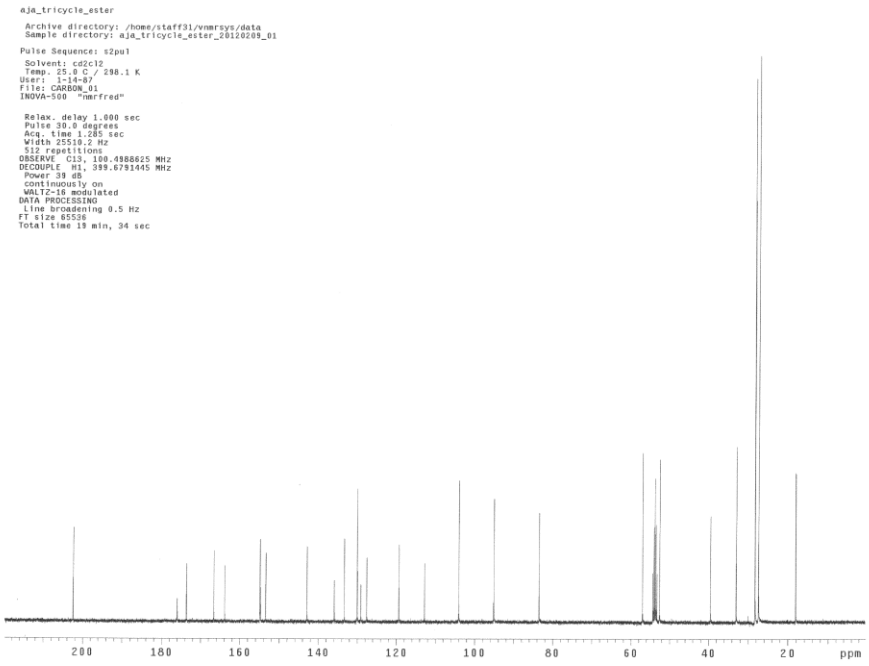

%Transmittance
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

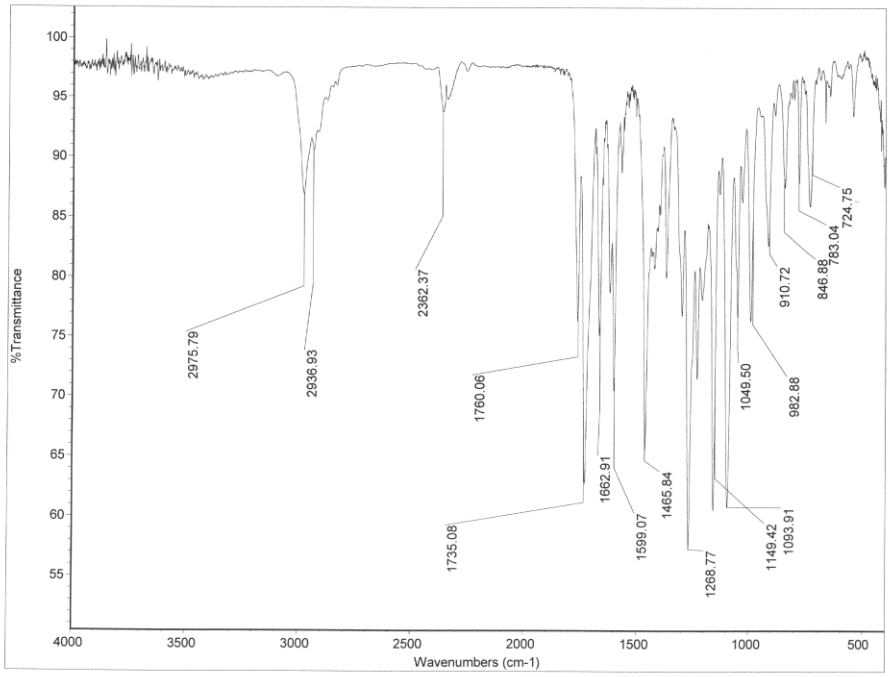

ynone
exp1 PROTON
SAMPLE
date Jan 13 2012
solvent cdcl3
file /mnt/nmrobo/~
mrc_tbuynone_20120~
113_02/PROTON_01.f~
id
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 32
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 399.679
tof 399.7
tpwr 62
pw 2.300
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR~
_W011
dpwr 36
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 8.008
pw90 6.900
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 1.3
wp 3995.5
rfl 3708.3
rfp 2901.7
rp 28.8
lp 1.8
PLOT
wc 250
sc 0
vs 101
th 11
al cdc ph
t-BuO2C
O
PivO
Me
MOMO
O
O
93
9
8
7
6
5
4
3
2
1
ppm

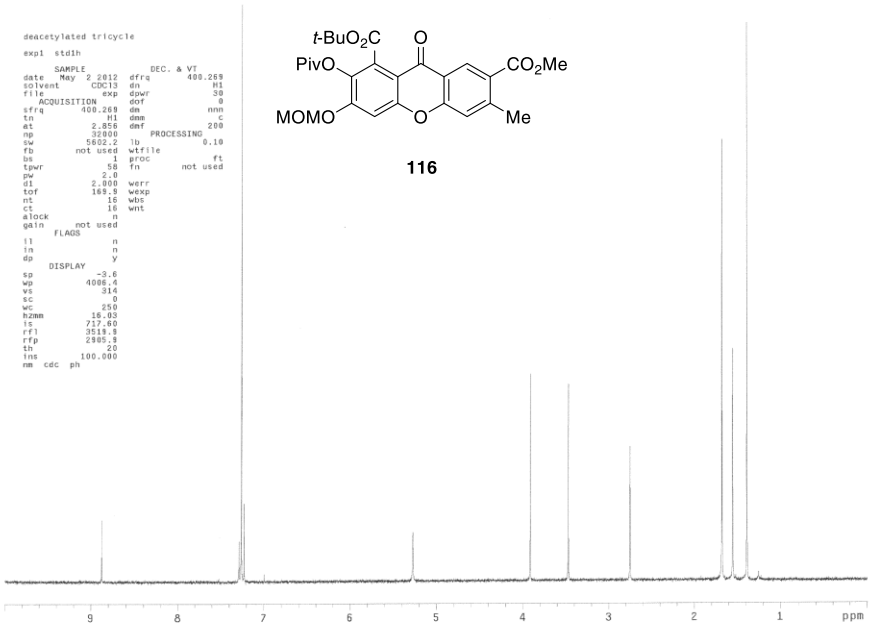

ynone
exp2 Carbon
SAMPLE
date Jan 14 2012
solvent cdcl3
file /export/home/~
space/data/mrc_tbu~
ynone_s2pul_C13.fi~
d
ACQUISITION
sw 24509.8
at 1.300
np 63750
fb 17000
bs 64
d1 2.000
nt 2000
ct 2000
TRANSMITTER
tn C13
sfrq 100.542
tof 1028.1
tpwr 55
pw 3.333
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 44
dmf 9881
SPECIAL
temp not used
gain 30
spin 20
hst 8.008
pw90 10.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 2.00
fn not used
DISPLAY
sp -27.6
wp 20134.1
rfl 9441.7
rfp 7740.9
rp -17.6
lp -13.5
PLOT
wc 250
sc 0
vs 267772
th 4
al cdc ph
180
160
140
120
100
80
60
40
20
ppm

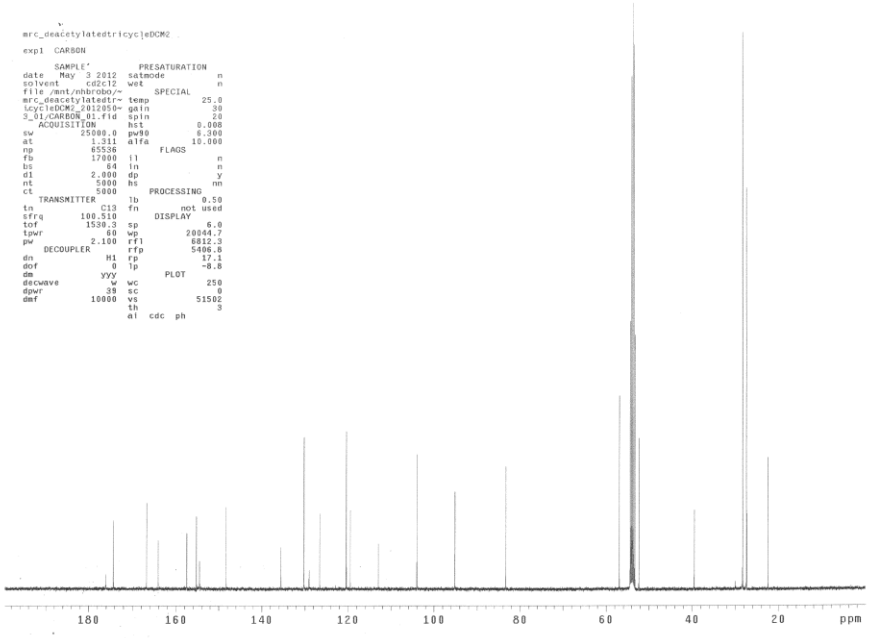

%Transmittance
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

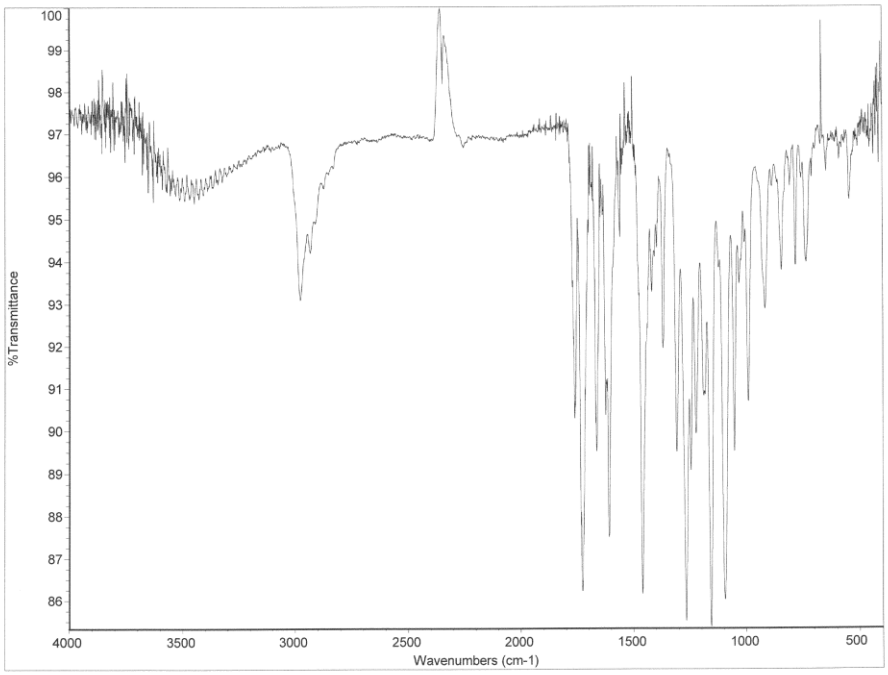

aja_vinaxanthone_1x_012_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.858 sec
Width 5602.2 Hz
7 repetitions
OBSERVE H1, 400.2669776 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
t-BuO2C
O
PivO
CO2Me
MOMO
O
Me
Me
O
115
9
8
7
6
5
4
3
2
1
ppm

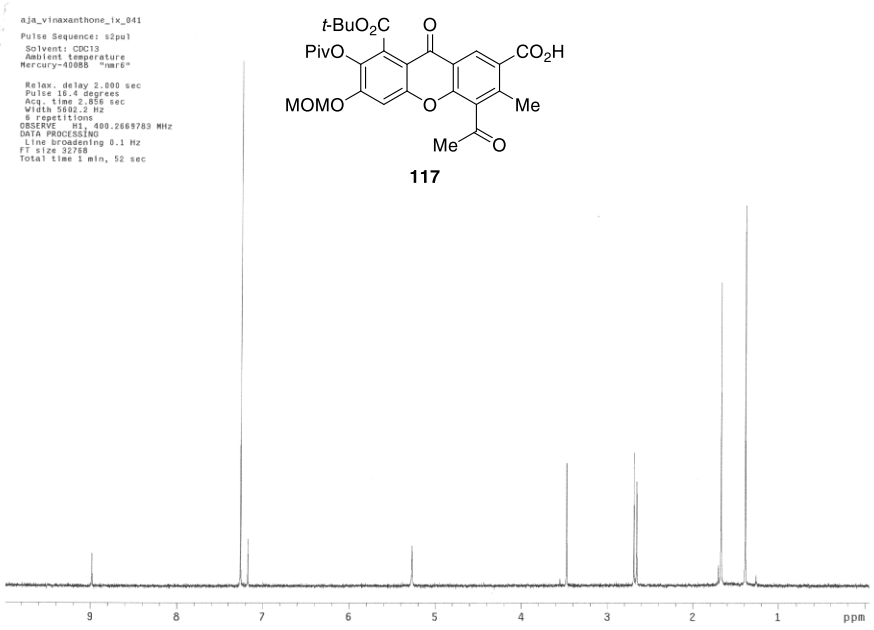

aja_tricycle_ester
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_tricycle_ester_20120209_01
Pulse Sequence: s2pul
Solvent: cd2cl2
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
512 repetitions
OBSERVE C13, 100.4888625 MHz
DECOUPLE H1, 399.6791445 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 34 sec
200
180
160
140
120
100
80
60
40
20
ppm

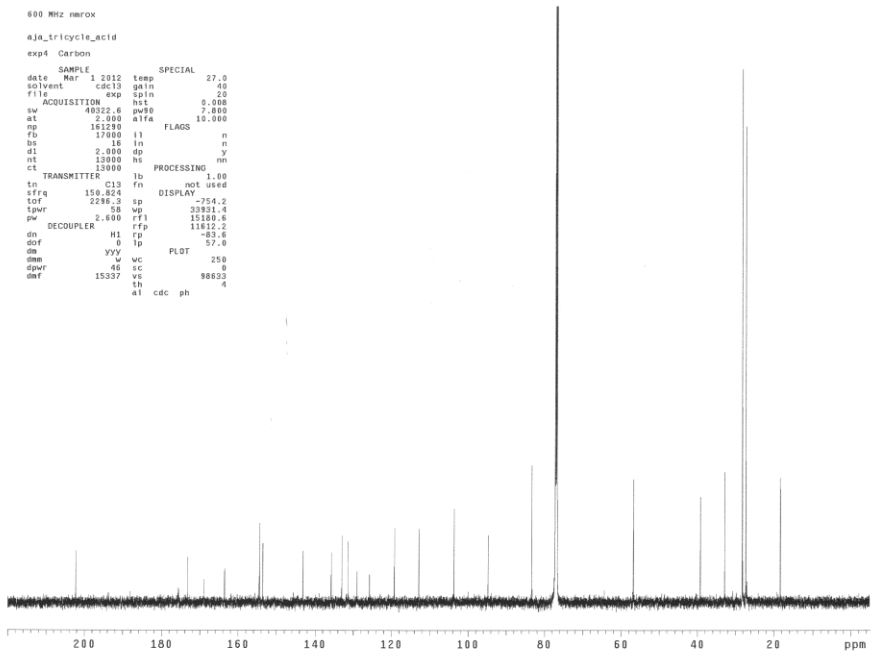

%Transmittance
Wavenumbers (cm-1)
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
2975.79
2936.93
2362.37
1760.06
1735.08
1662.91
1599.07
1465.84
1268.77
1149.42
1093.91
1049.50
982.88
910.72
846.88
783.04
724.75

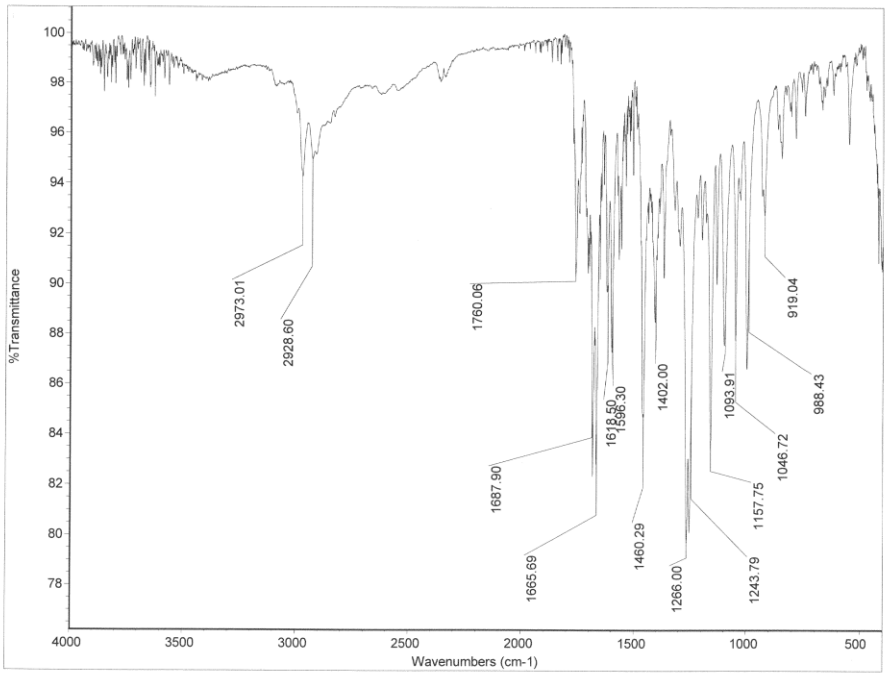

deacetylated tricycle
exp1 stdih
SAMPLE
date May 2 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 314
sc 0
wc 250
hzmm 16.03
is 717.60
rf1 3519.9
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 50
dof 0
dm nnn
dmm C
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
t-BuO2C
O
PivO
CO2Me
MOMO
O
Me
116
9
8
7
6
5
4
3
2
1
ppm

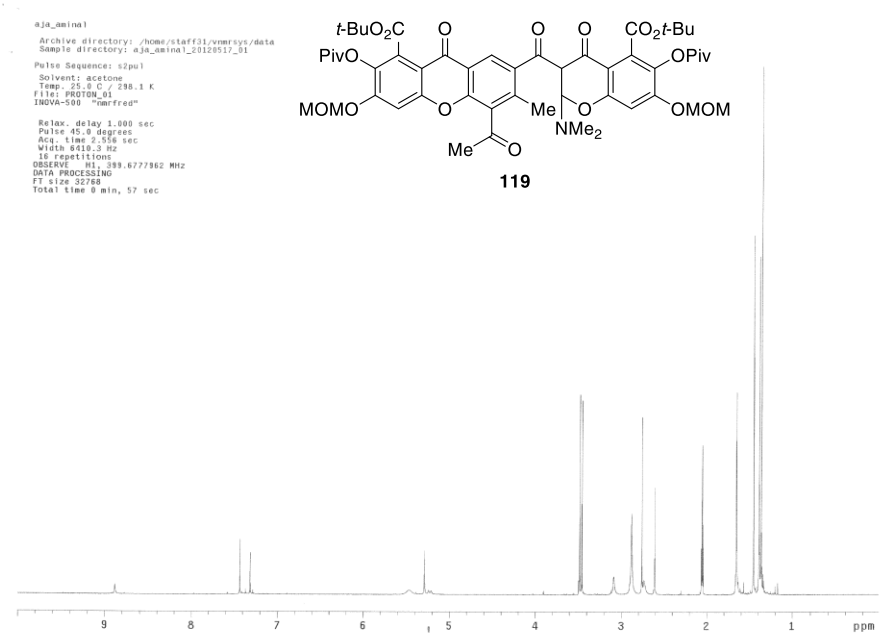

mrc_deacetylatedtricycleDCM2
exp1 CARBON
SAMPLE
date May 3 2012
solvent cd2cl2
file /mnt/nmbrobo/~
mrc_deacetylatedtr~
icycleDCM2_2012050~
3_01/CARBON_01.fid
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 64
d1 2.000
nt 5000
ct 5000
TRANSMITTER
tn C13
sfrq 100.510
tof 1530.3
tpwr 60
pw 2.100
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 10000
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 8.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 6.0
wp 20044.7
rf1 8812.3
rfp 5406.8
rp 17.1
lp -8.8
PLOT
wc 250
sc 0
vs 51502
th 3
al cdc ph
180
160
140
120
100
80
60
40
20
ppm

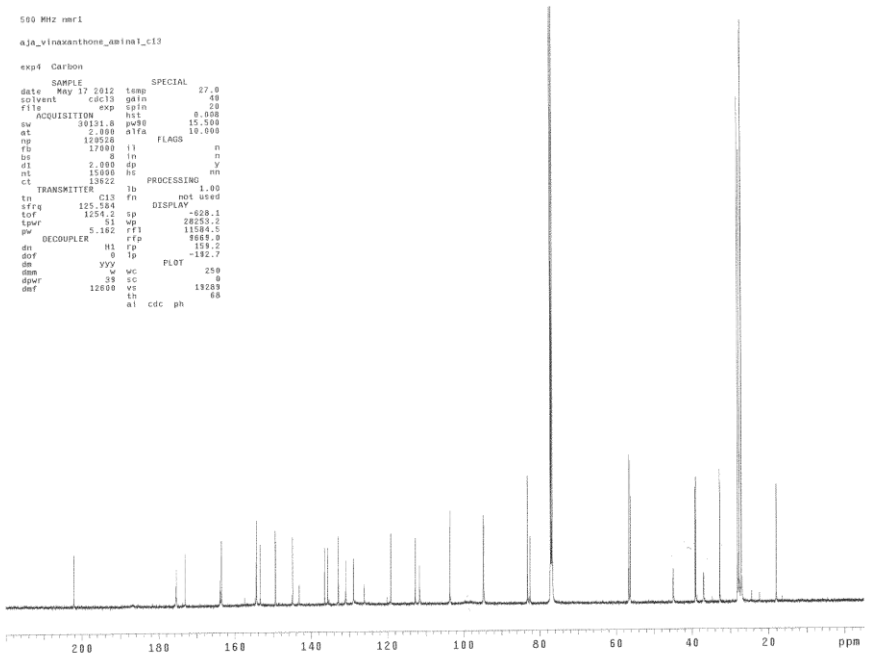

100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

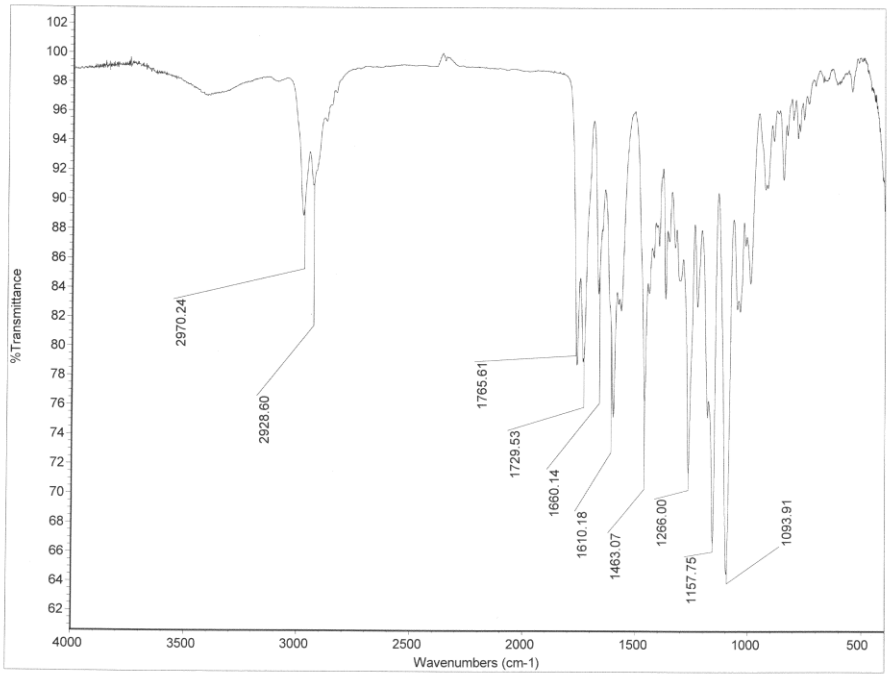

aja_vinaxanthone_ix_041
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
6 repetitions
OBSERVE H1, 400.2669783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
t-BuO2C
O
PivO
CO2H
MOMO
O
Me
Me
O
117
9
8
7
6
5
4
3
2
1
ppm

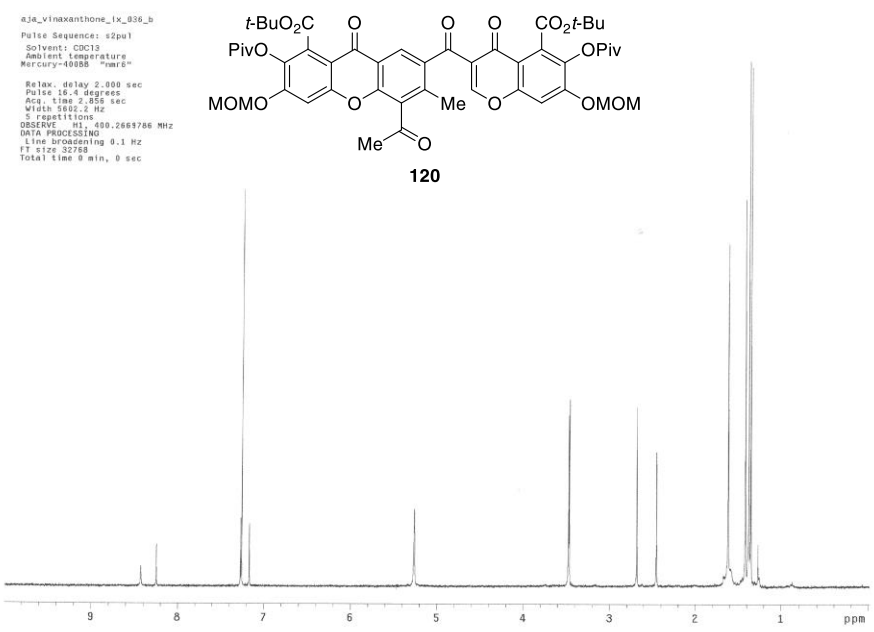

600 MHz nmrox
aja_tricycle_acid
exp4 Carbon
SAMPLE
date Mar 1 2012
solvent cdcl3
file exp
ACQUISITION
sw 40322.6
at 2.000
np 161290
fb 17000
bs 16
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 150.824
tof 2286.3
tpwr 58
pw 2.600
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 46
dmf 15337
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 7.800
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -754.2
wp 33931.4
rf1 15180.6
rfp 11612.2
rp -83.6
lp 57.0
PLOT
wc 250
sc 0
vs 98633
th 4
at cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

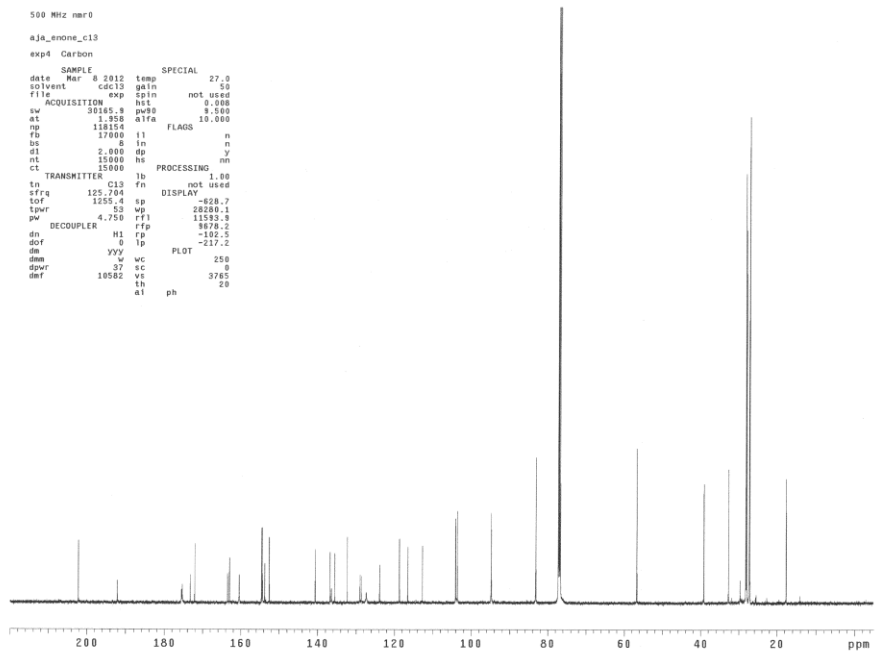

%Transmittance
Wavenumbers (cm-1)
100
98
96
94
92
90
88
86
84
82
80
78
4000
3500
3000
2500
2000
1500
1000
500
2973.01
2928.60
1760.06
1687.90
1665.69
1460.29
1402.00
1266.00
1243.79
1157.75
1093.91
1046.72
988.43
919.04

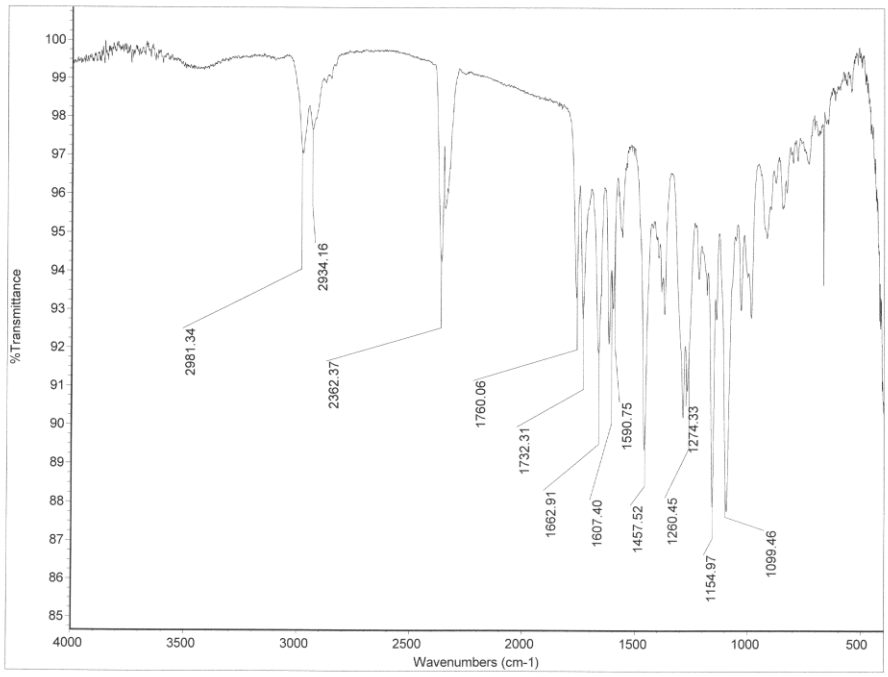

aja_amina1
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_amina1_20120517_01
Pulse Sequence: s2pul
Solvent: acetone
Temp. 25.0 C / 298.1 K
File: PROTON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.6777962 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 57 sec
t-BuO2C
PivO
MOMO
Me
NMe2
CO2t-Bu
OPiv
OMOM
119
9
8
7
6
5
4
3
2
1
ppm

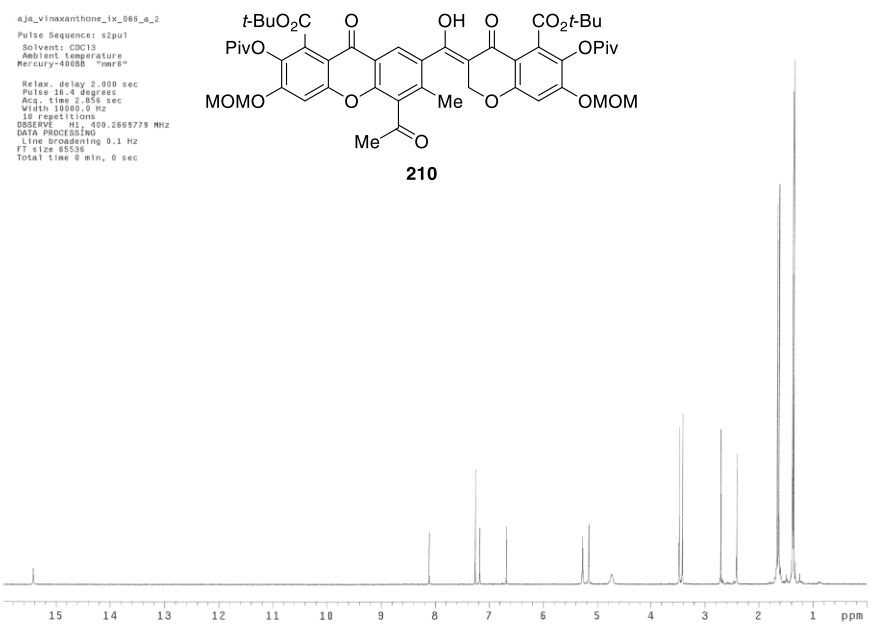

500 MHz nmr1
aja_vinaxanthone_amina1_c13
exp4 Carbon
SAMPLE
date May 17 2012
solvent cdcl3
file exp
ACQUISITION
sw 30131.8
at 2.000
np 120528
fb 17000
bs 8
d1 2.000
nt 15000
ct 13622
TRANSMITTER
tn C13
sfrq 125.584
tof 1254.2
tpwr 51
pw 5.182
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 12600
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 15.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.1
wp 28253.2
rf1 11584.5
rfp 8665.9
rp 159.2
lp -192.7
PLOT
wc 250
sc 9
vs 19289
th 68
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

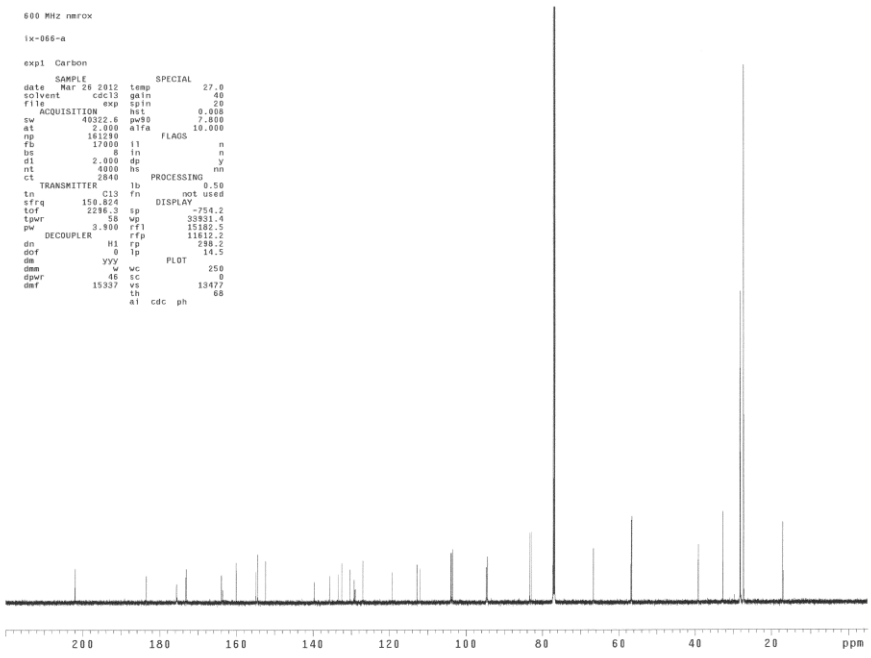

%Transmittance
Wavenumbers (cm-1)
2970.24
2928.60
1765.61
1729.53
1660.14
1610.18
1463.07
1266.00
1157.75
1093.91

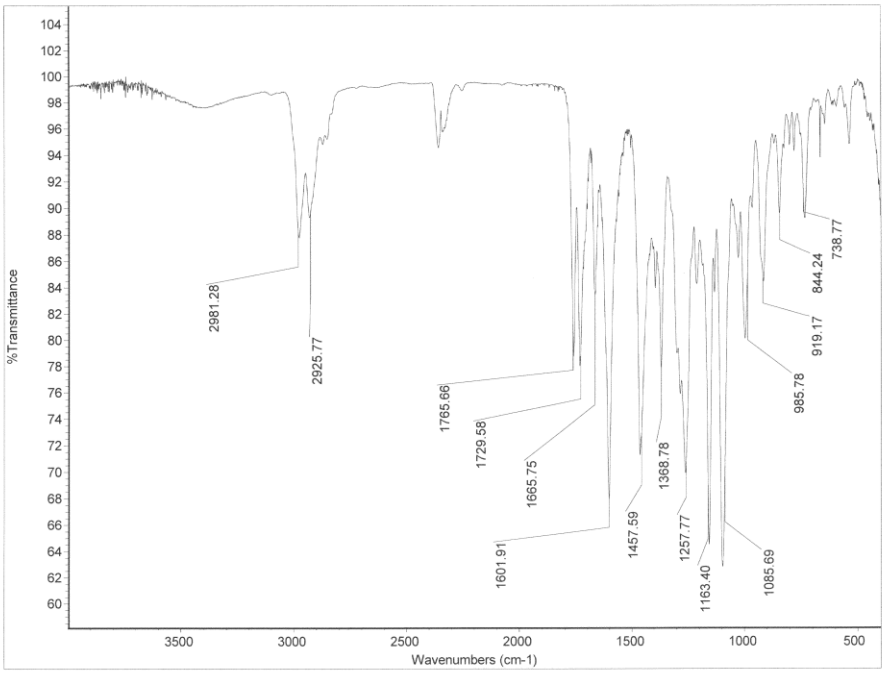

aja_vinaxanthone_1x_036_b
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
5 repetitions
OBSERVE H1, 400.2669786 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
t-BuO2C
PivO
MOMO
O
Me
Me
O
O
O
CO2t-Bu
OPiv
OMOM
O
120
9
8
7
6
5
4
3
2
1
ppm

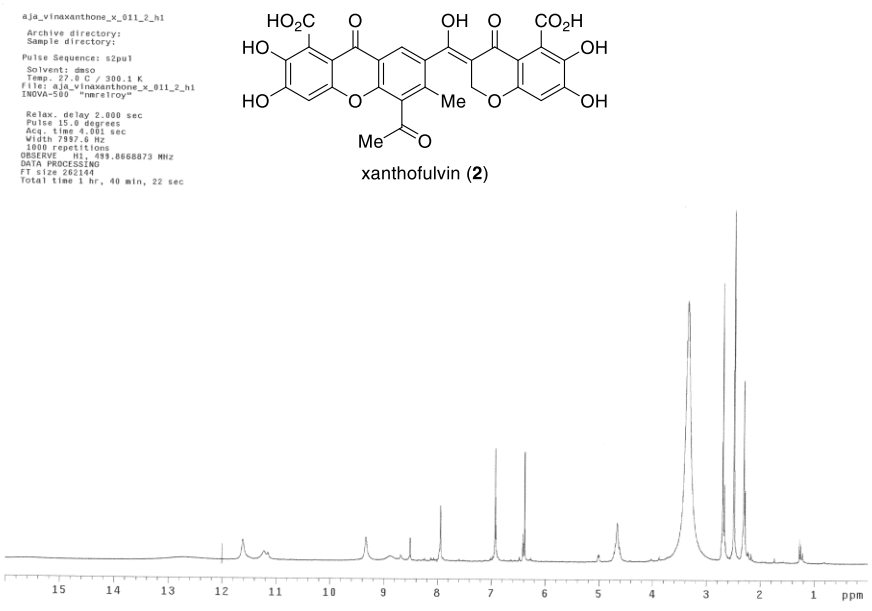

500 MHz nmr0
aja_enone_c13
exp4 Carbon
SAMPLE
date Mar 8 2012
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118154
fb 17000
bs 8
d1 2.000
nt 15000
ct 15000
TRANSMITTER
tn C13
sfrq 125.704
tof 1255.4
tpwr 53
pw 4.750
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 37
dmf 10582
SPECIAL
temp 27.0
gain 50
spin not used
hst 0.008
pw90 9.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -828.7
wp 28280.1
rf1 11593.9
rfp 9878.2
rp -102.5
lp -217.2
PLOT
wc 250
sc 0
vs 3765
th 20
al ph
200
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
Wavenumbers (cm-1)
2981.34
2934.16
2362.37
1760.06
1732.31
1662.91
1607.40
1590.75
1457.52
1274.33
1260.45
1154.97
1099.46

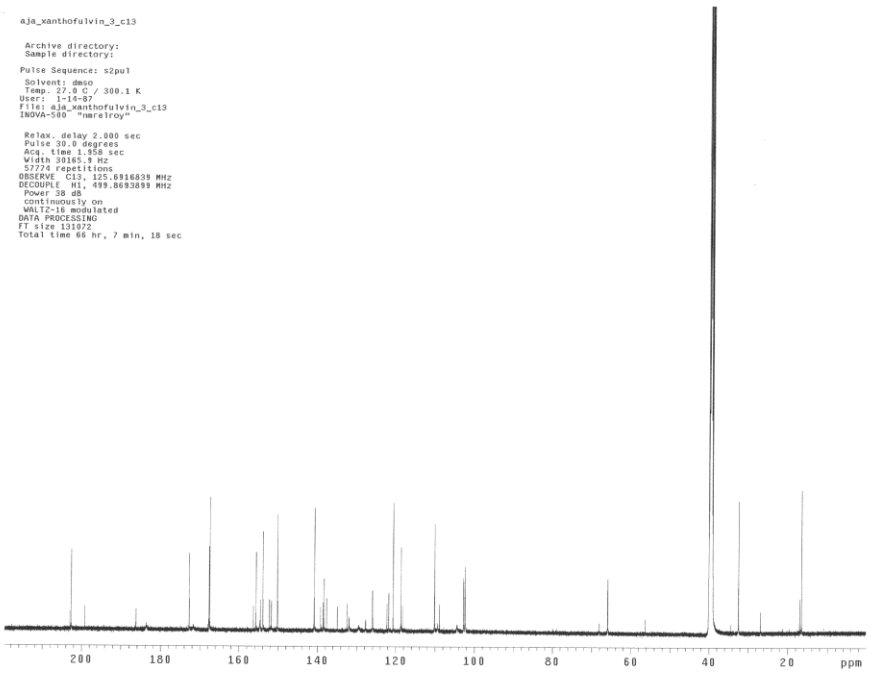

aja_vinaxanthone_ix_066_a_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "mmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 10080.0 Hz
10 repetitions
DSERVE H1, 400.2665779 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
Total time 6 min, 0 sec
t-BuO2C
O
OH
O
CO2t-Bu
PivO
OPiv
MOMO
O
Me
O
OMOM
Me
O
210
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

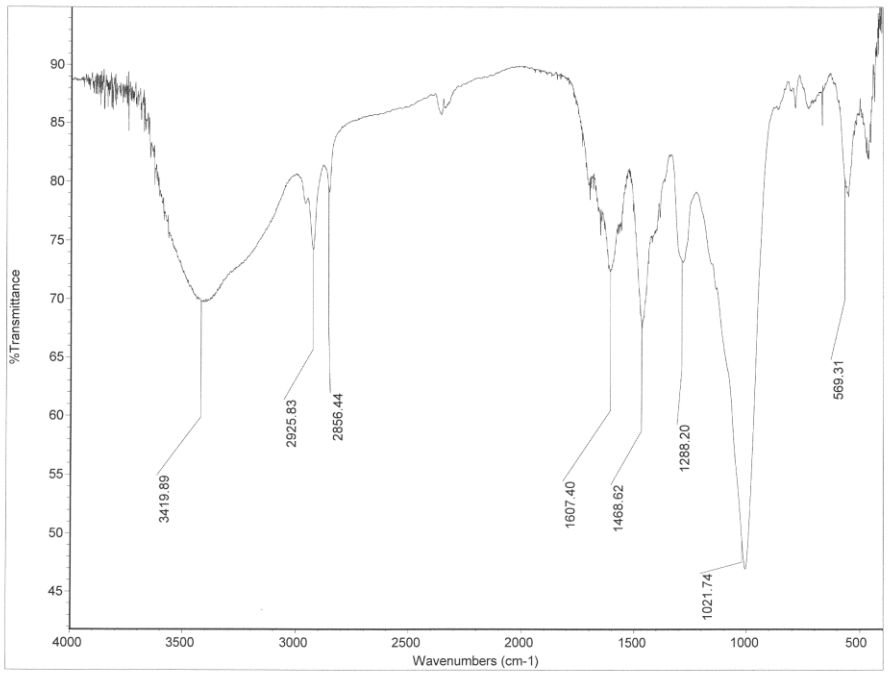

600 MHz nmrox
ix-066-a
exp1 Carbon
SAMPLE
date Mar 26 2012
solvent cdcl3
file exp
ACQUISITION
sw 40322.6
at 2.000
np 161290
fb 17000
bs 8
d1 2.000
nt 4000
ct 2840
TRANSMITTER
tn C13
sfrq 150.824
tof 2296.3
tpwr 58
pw 3.900
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 46
dmf 15337
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 7.800
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -754.2
wp 33931.4
rf1 15182.5
rfp 11612.2
rp 298.2
lp 14.5
PLOT
wc 250
sc 0
vs 13477
th 68
ai cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

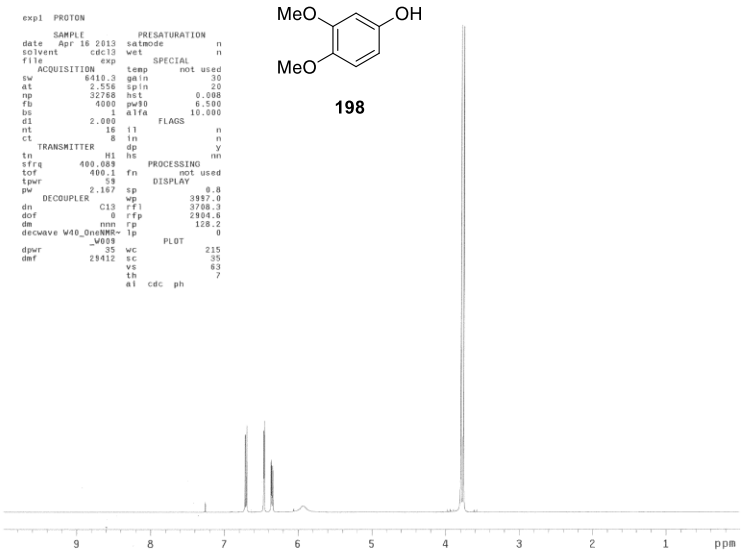

%Transmittance
Wavenumbers (cm-1)
2981.28
2925.77
1765.66
1729.58
1665.75
1601.91
1457.59
1368.78
1257.77
1163.40
1085.69
985.78
919.17
844.24
738.77

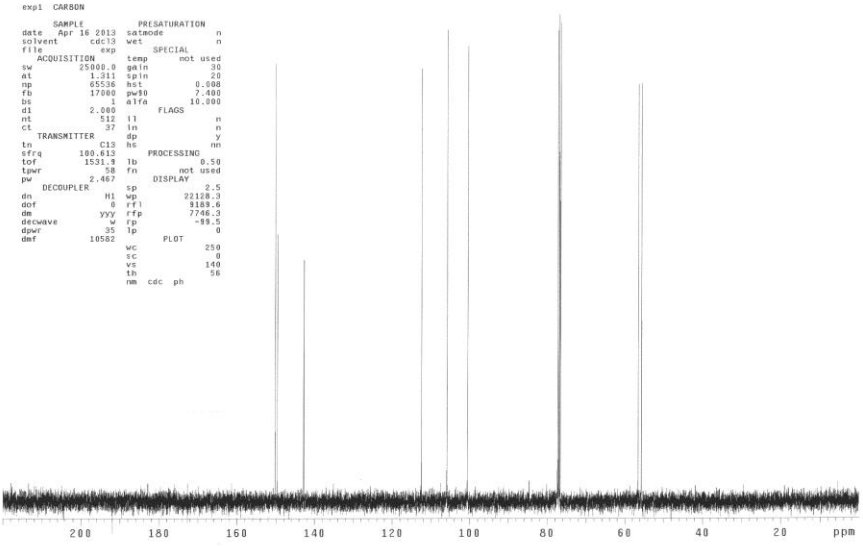


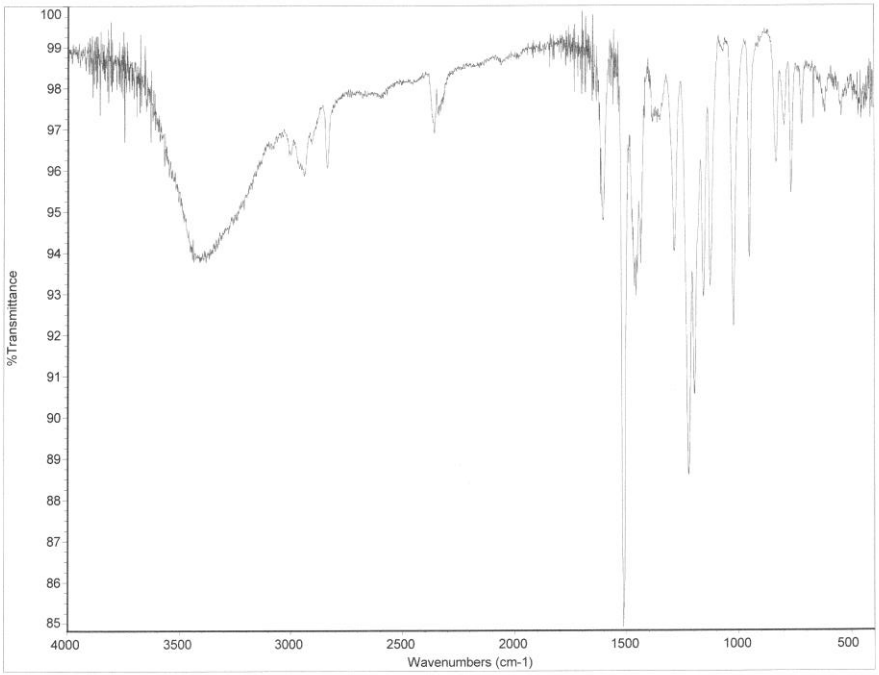
xanthofulvin (**2**)

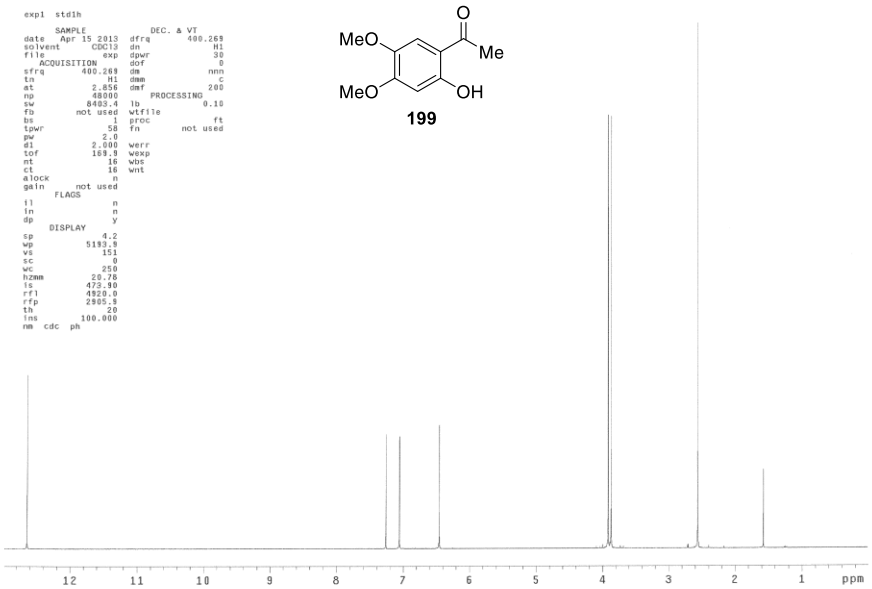


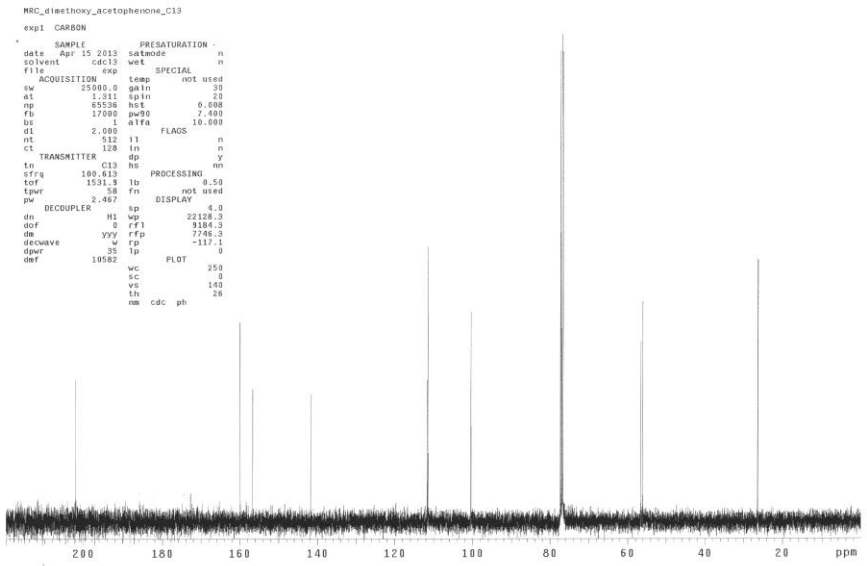

%Transmittance
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3419.89
2925.83
2856.44
1607.40
1468.62
1288.20
1021.74
569.31

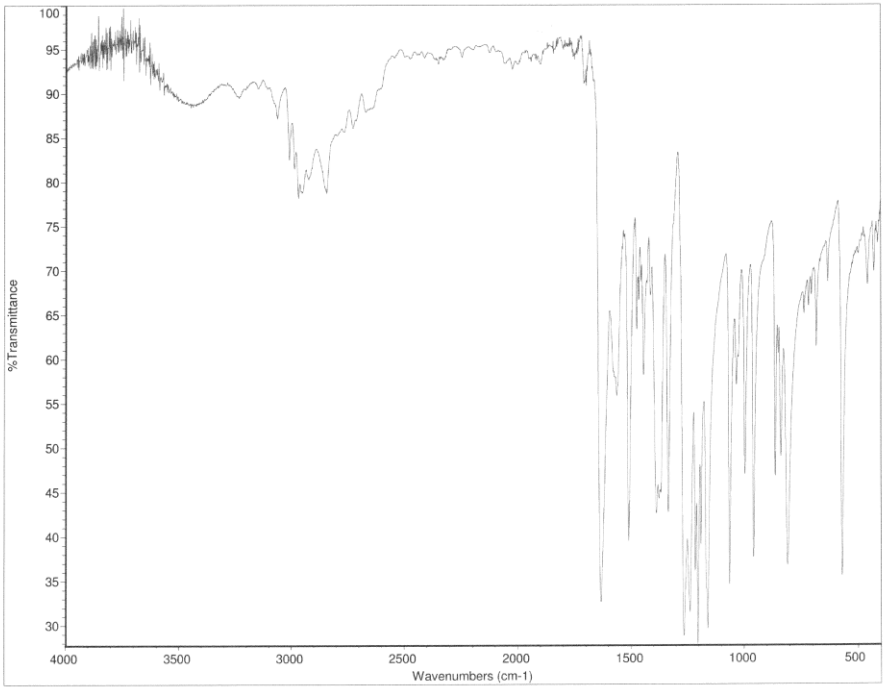

expl PROTON
SAMPLE
date Apr 16 2013
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 8
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR-_W609
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 0.8
wp 3957.0
rfl 3708.3
rfp 2904.6
rp 128.2
lp 0
PLOT
wc 215
sc 35
vs 63
th 7
al cdc ph
MeO
OH
MeO
198
9
8
7
6
5
4
3
2
1
ppm

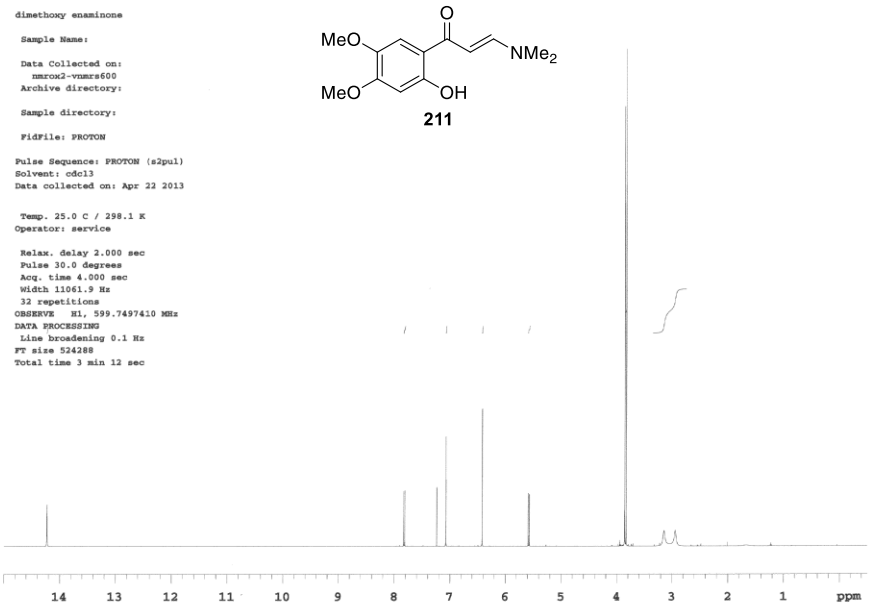

expl CARBON
SAMPLE
date Apr 16 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 512
ct 37
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 2.5
wp 22128.3
rfl 9189.6
rfp 7746.3
rp -59.5
lp 0
PLOT
wc 250
sc 0
vs 140
th 56
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

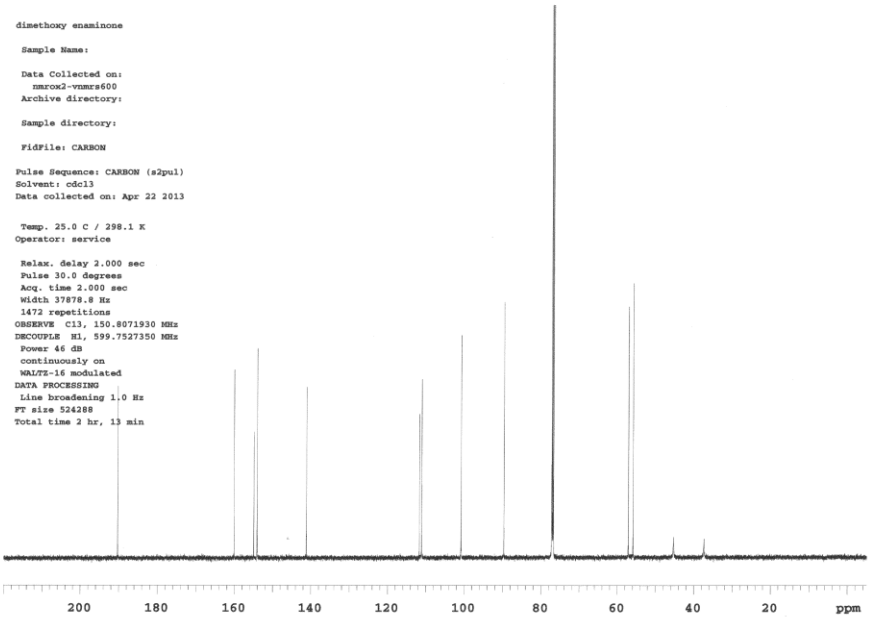

100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

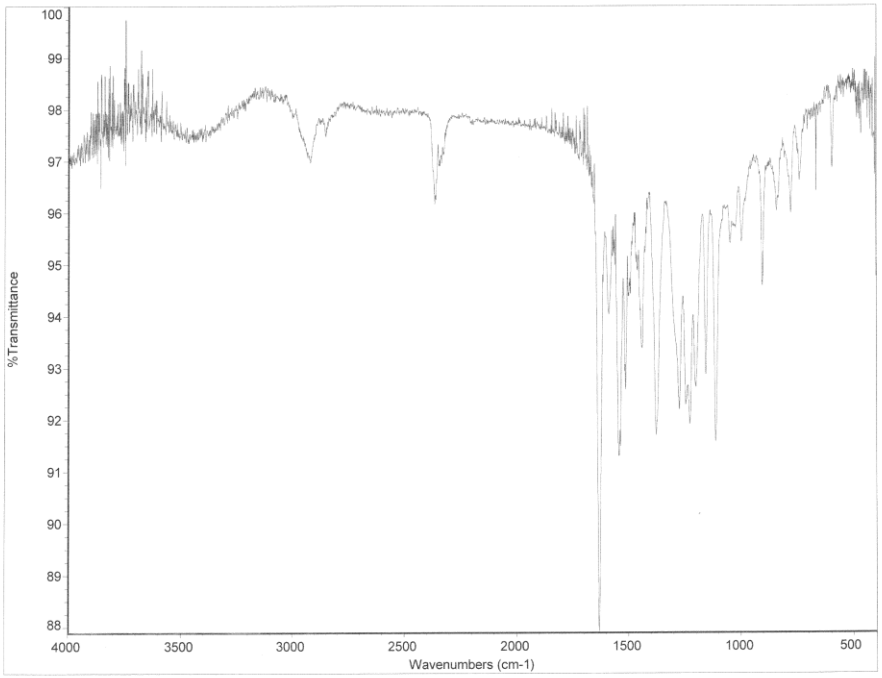

exp1 std1h
SAMPLE
date Apr 15 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.268
tn H1
at 2.856
np 48000
sw 8403.4
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 4.2
wp 5193.9
vs 151
sc 0
wc 250
hzmm 20.78
is 473.90
rfl 4920.0
rfp 2905.8
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.268
dn H1
dpwr 30
dof 0
dm nnn
dmm C
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MeO
MeO
OH
Me
O
199
12
11
10
9
8
7
6
5
4
3
2
1
ppm

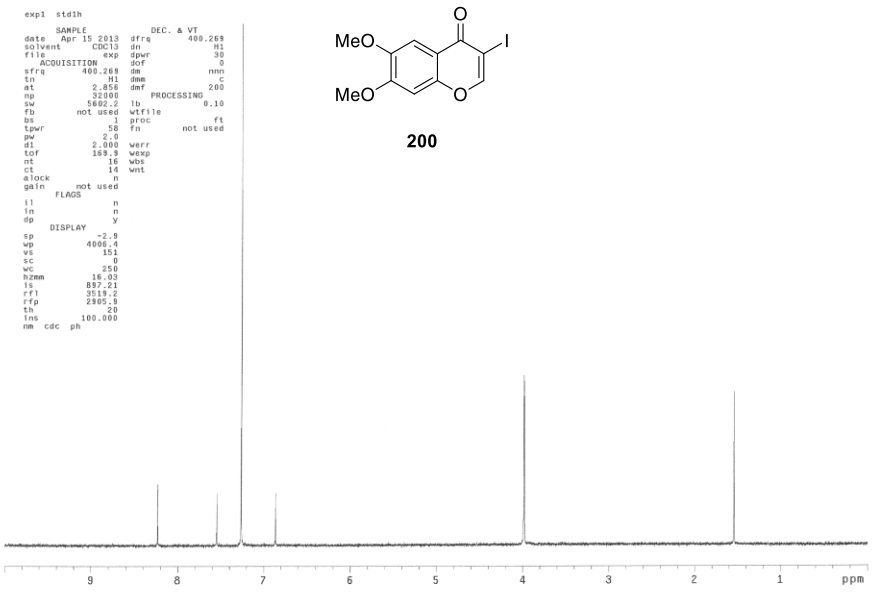

MRC_dimethoxy_acetophenone_C13
exp1 CARBON
SAMPLE
date Apr 15 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 512
ct 128
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.000
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 4.0
wp 22128.3
rf1 9184.3
rfp 7746.3
rp -117.1
lp 0
PLOT
wc 250
sc 0
vs 140
th 26
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

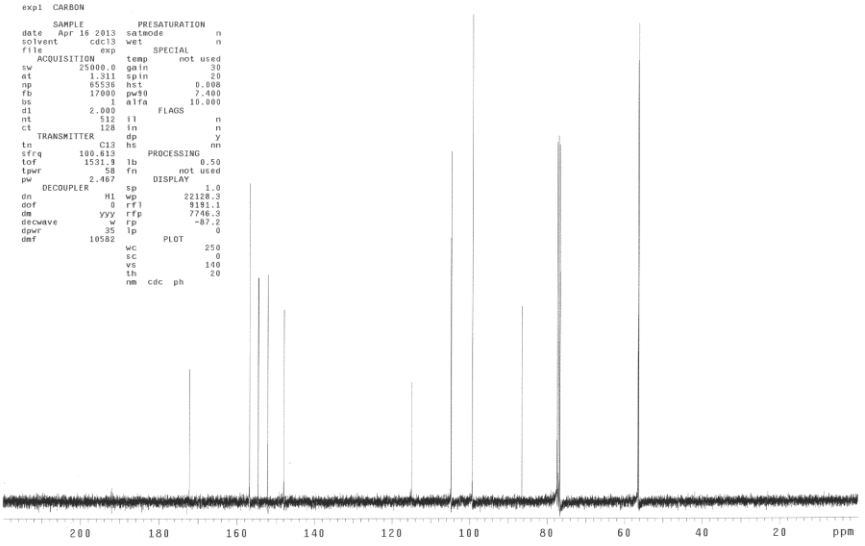

100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

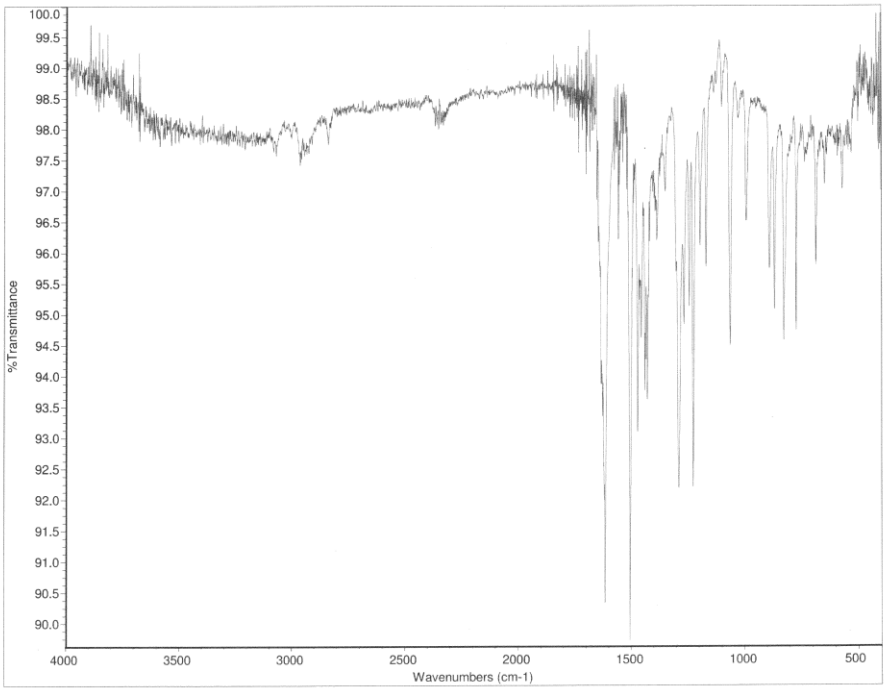

dimethoxy enaminone
Sample Name:
Data Collected on:
nmrox2-vnmrs600
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 22 2013
Temp. 25.0 C / 298.1 K
Operator: service
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 4.000 sec
Width 11061.9 Hz
32 repetitions
OBSERVE H1, 599.7497410 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 524288
Total time 3 min 12 sec
MeO
MeO
OH
O
NMe2
211
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

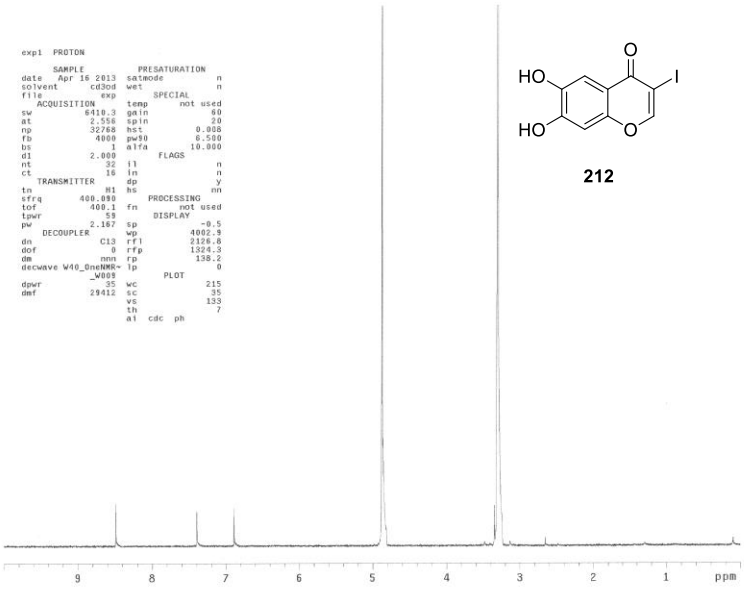

dimethoxy enaminone
Sample Name:
Data Collected on:
nmrox2-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 22 2013
Temp. 25.0 C / 298.1 K
Operator: service
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.000 sec
Width 37878.8 Hz
1472 repetitions
OBSERVE C13, 150.8071930 MHz
DECOUPLE H1, 599.7527350 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 524288
Total time 2 hr, 13 min
200
180
160
140
120
100
80
60
40
20
ppm


100
99
98
97
96
95
94
93
92
91
90
89
88
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


exp1 std1h
SAMPLE
date Apr 15 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 14
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2.9
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 897.21
rfl 3519.2
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MeO
MeO
O
O
I
200
9
8
7
6
5
4
3
2
1
ppm

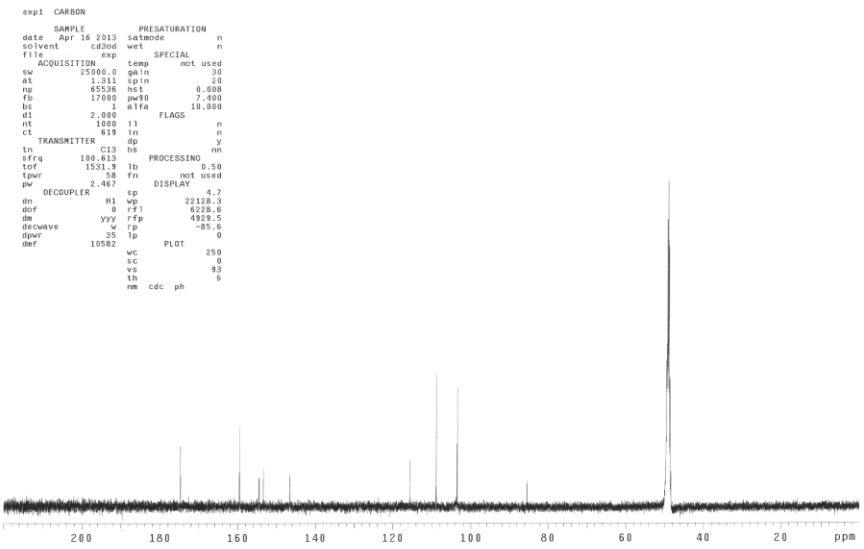

exp1 CARBON
SAMPLE
date Apr 16 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 512
ct 128
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 1.0
wp 22128.3
rfl 9191.1
rfp 7746.3
rp -87.2
lp 0
PLOT
wc 250
sc 0
vs 140
th 20
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

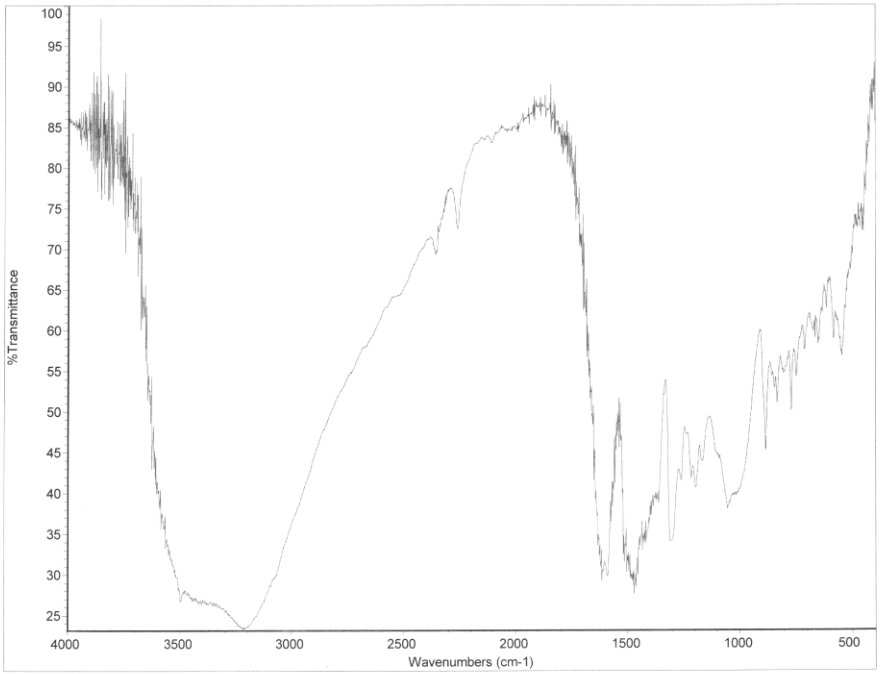

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
90.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

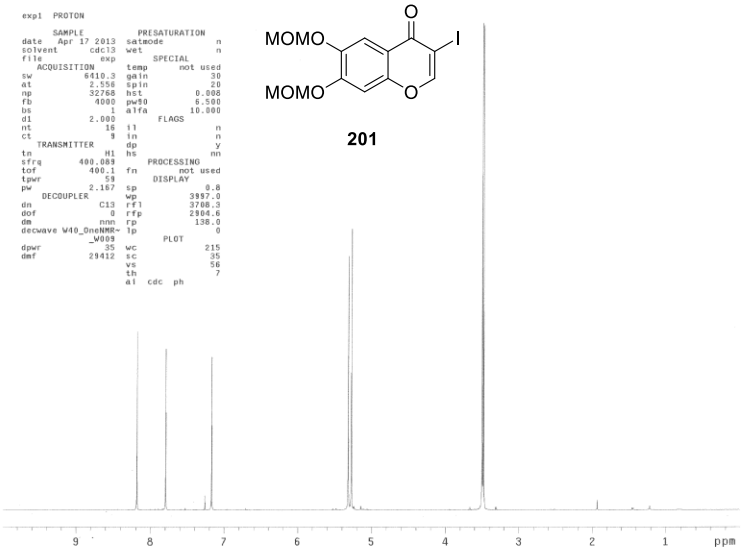

exp1 PROTON
SAMPLE
date Apr 16 2013
solvent cd3od
file exp
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 32
ct 16
TRANSMITTER
tn H1
sfrq 400.090
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR-_W008
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 60
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -0.5
wp 4002.9
rf1 2126.8
rfp 1324.3
rp 138.2
lp 0
PLOT
wc 215
sc 35
vs 133
th 7
al cdc ph
9
8
7
6
5
4
3
2
1
ppm

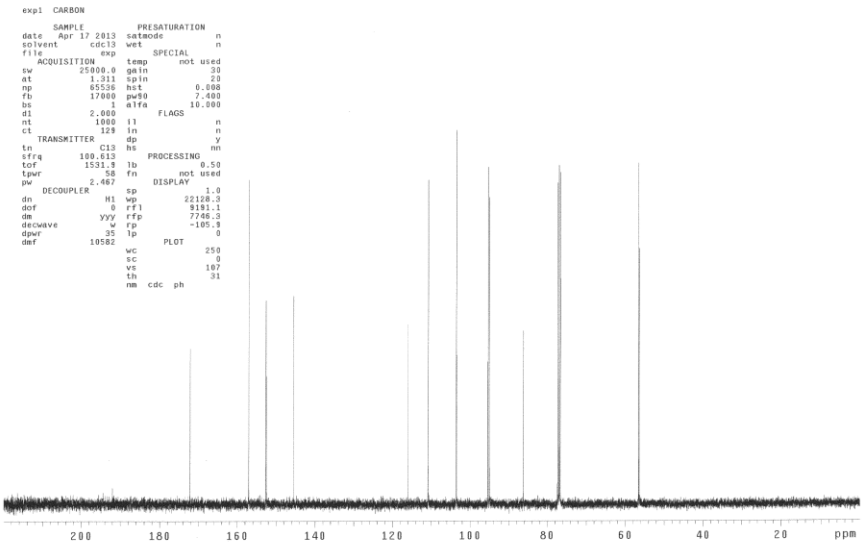
HO
HO
O
O
I

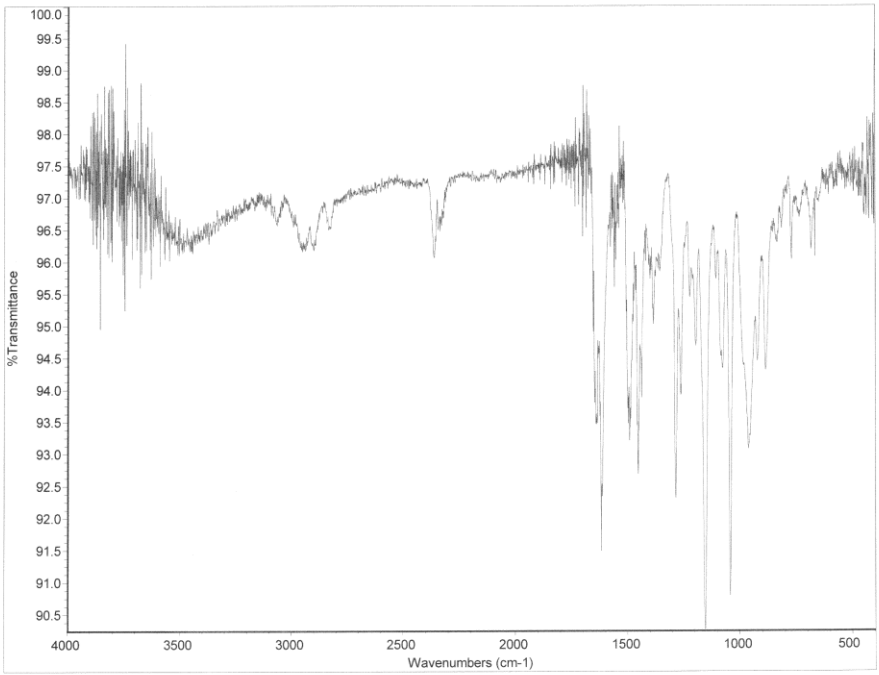
212

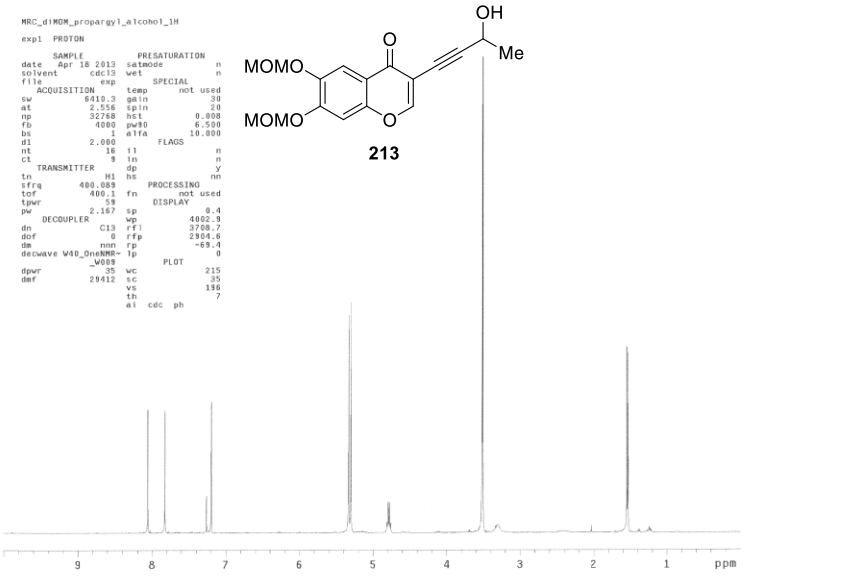

exp1 CARBON
SAMPLE
date Apr 16 2013
solvent cd3od
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 619
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 4.7
wp 22120.3
rf1 6228.6
rfp 4929.5
rp -85.6
lp 0
PLOT
wc 250
sc 0
vs 93
th 6
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

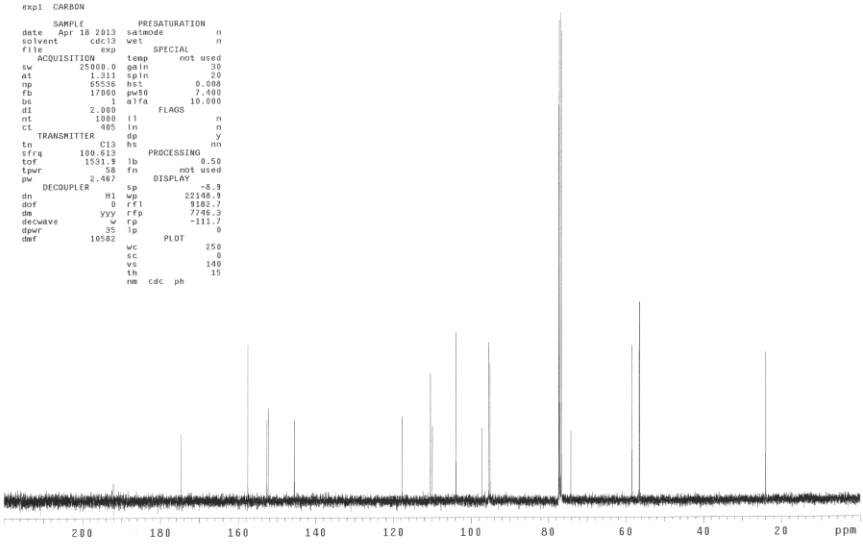

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

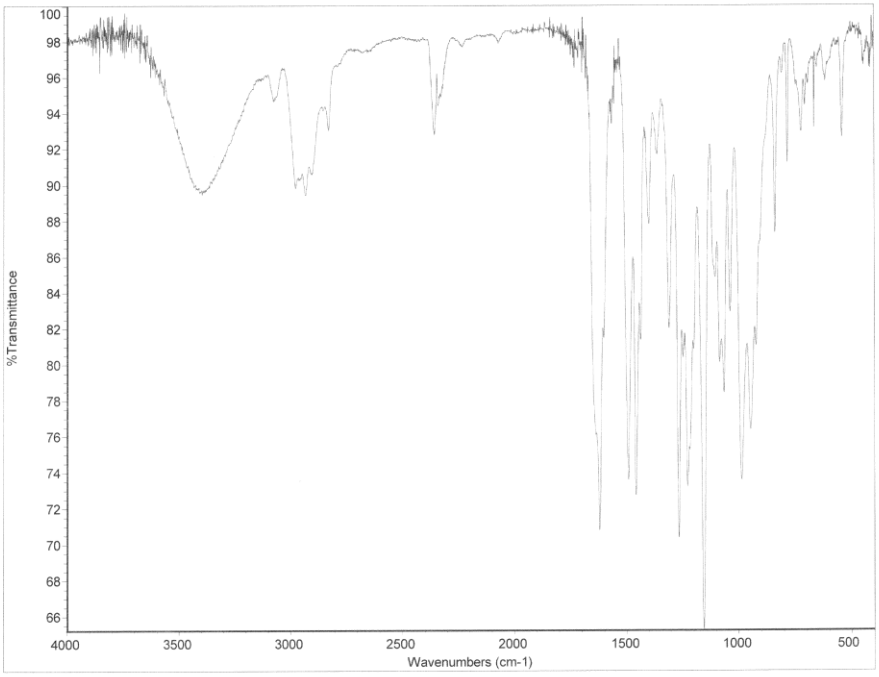

expl PROTON
SAMPLE
date Apr 17 2013
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 9
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR-_W909
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 0.8
wp 3897.0
rf1 3708.3
rfp 2904.6
rp 138.0
lp 0
PLOT
wc 215
sc 35
vs 56
th 7
al cdc ph
MOMO
MOMO
O
O
I
201
9
8
7
6
5
4
3
2
1
ppm

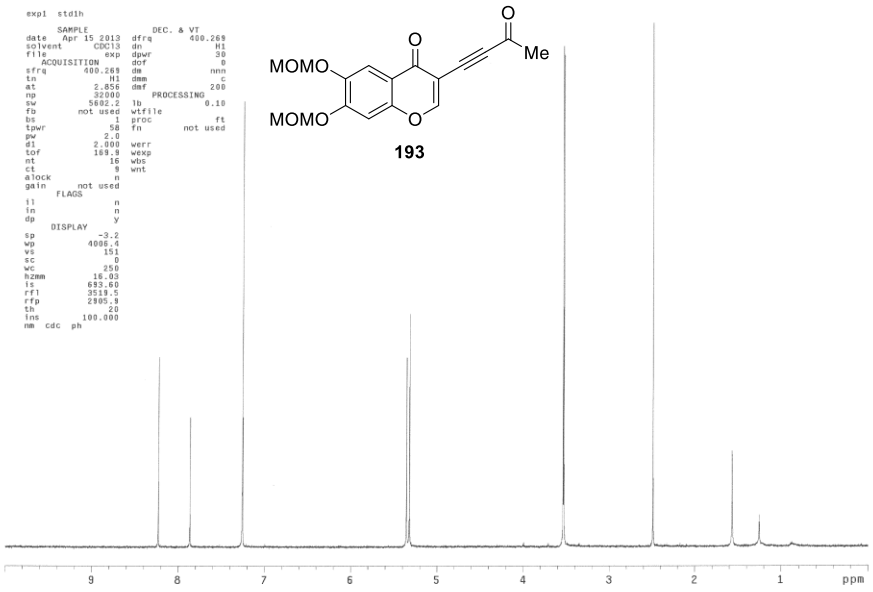

expl CARBON
SAMPLE
date Apr 17 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 128
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 1.0
wp 22120.3
rf1 9191.1
rfp 7746.3
rp -105.9
lp 0
PLOT
wc 250
sc 0
vs 107
th 31
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

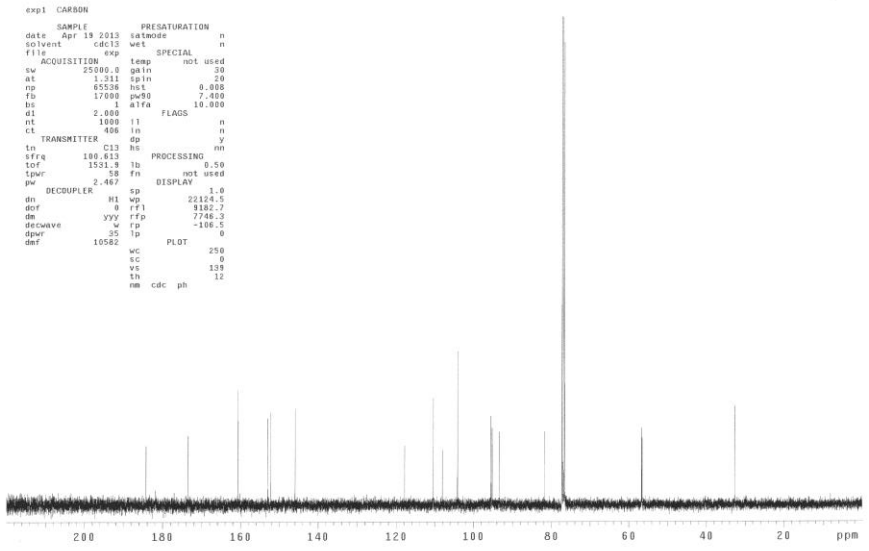

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

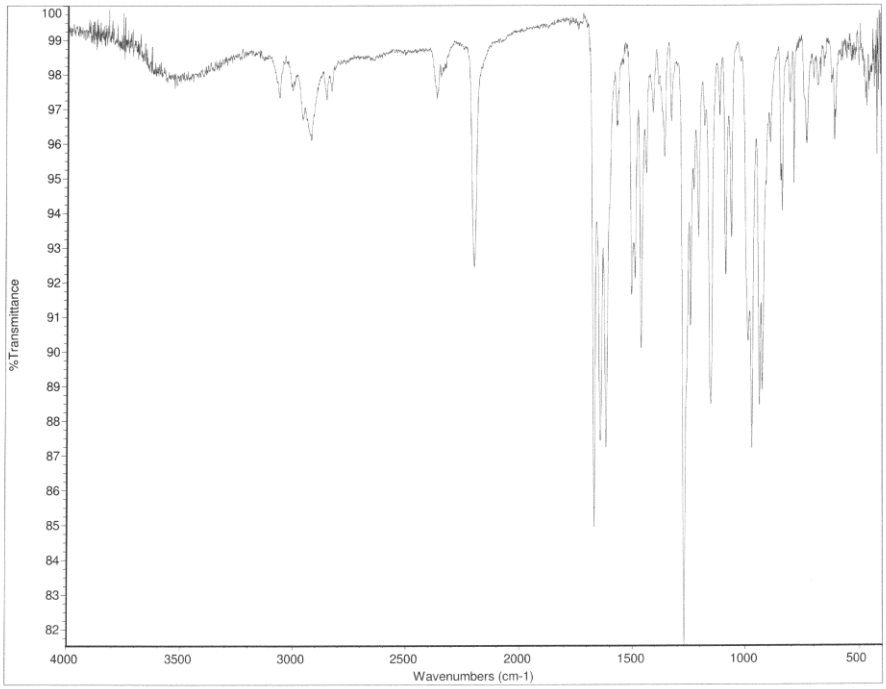

MRC_diMOM_propargyl_alcohol_1H
expl PROTON
SAMPLE
date Apr 18 2013
solvent cdcl3
file exp
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 9
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR-_W009
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 0.4
wp 4002.9
rf1 3708.7
rfp 2904.6
rp -69.4
lp 0
PLOT
wc 215
sc 35
vs 196
th 7
al cdc ph
OH
O
Me
MOMO
MOMO
O
213
9
8
7
6
5
4
3
2
1
ppm

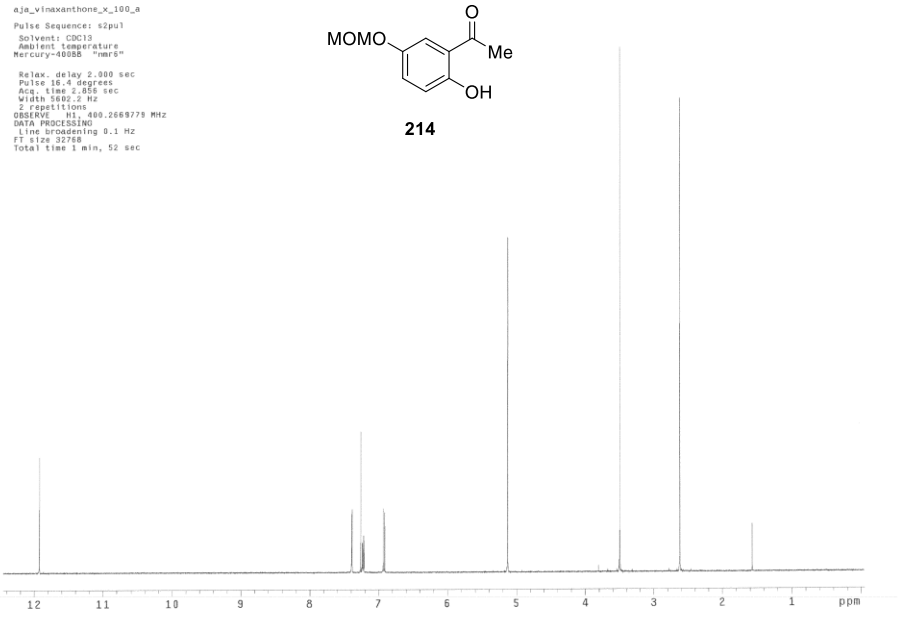

expl CARBON
SAMPLE
date Apr 18 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 405
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -8.9
wp 22148.9
rf1 9182.7
rfp 7746.3
rp -111.7
lp 0
PLOT
wc 250
sc 0
vs 140
th 15
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

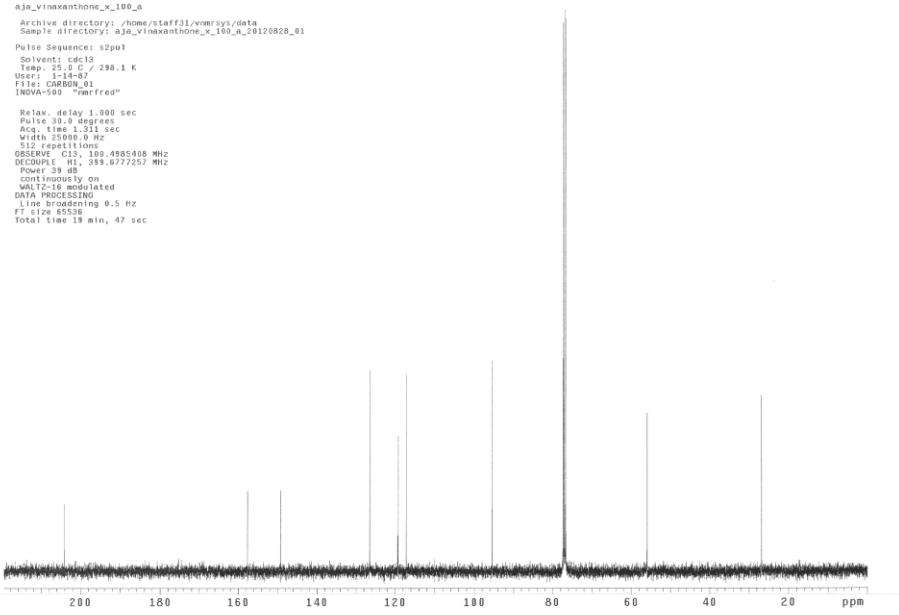

100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

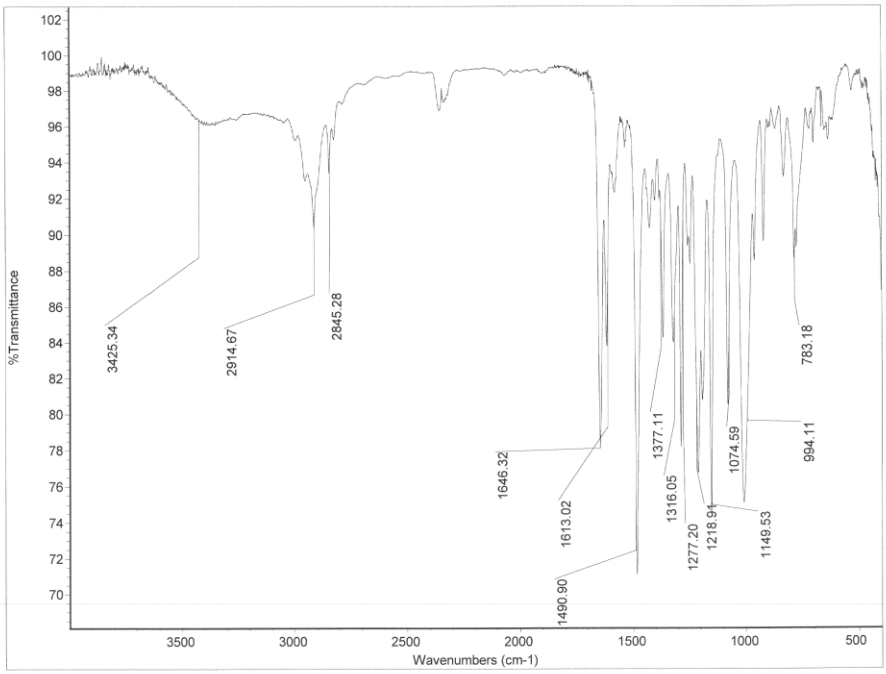

exp1 stdlh
SAMPLE
date Apr 15 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5802.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 9
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
vs 151
sc 0
wc 250
hzmm 16.03
is 693.60
rfl 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
O
O
Me
MOMO
MOMO
O
193
9
8
7
6
5
4
3
2
1
ppm

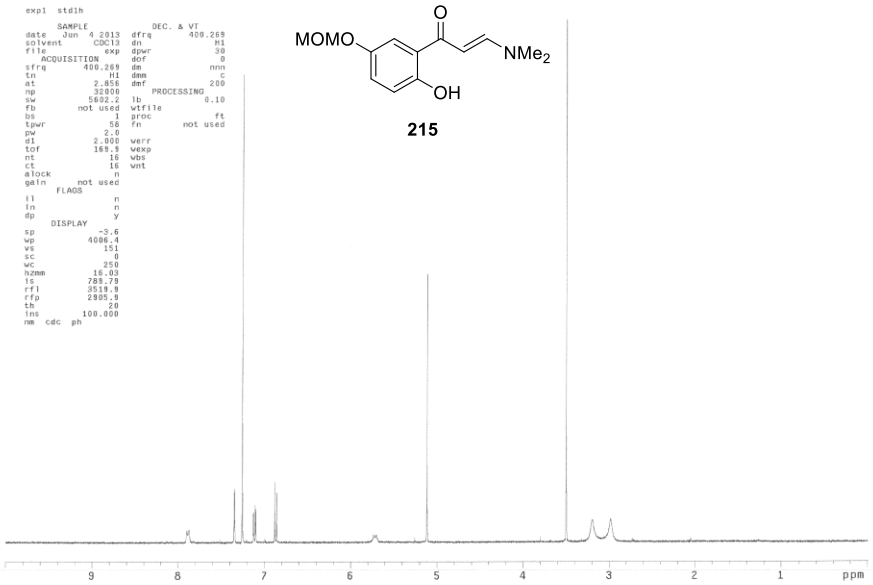

exp1 CARBON
SAMPLE
date Apr 19 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 406
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 1.0
wp 22124.5
rfl 9182.7
rfp 7746.3
rp -106.5
lp 0
PLOT
wc 250
sc 0
vs 139
th 12
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

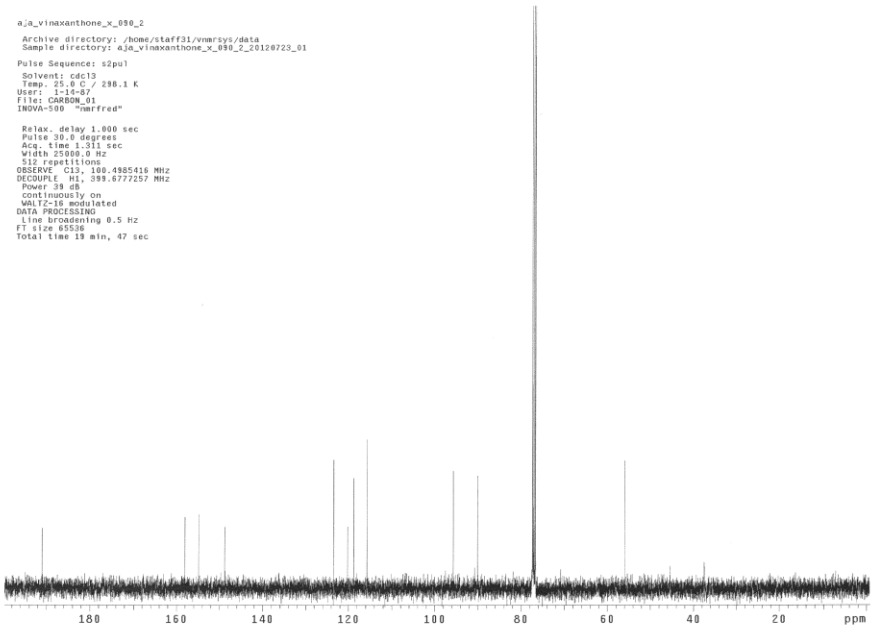

%Transmittance
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
82
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

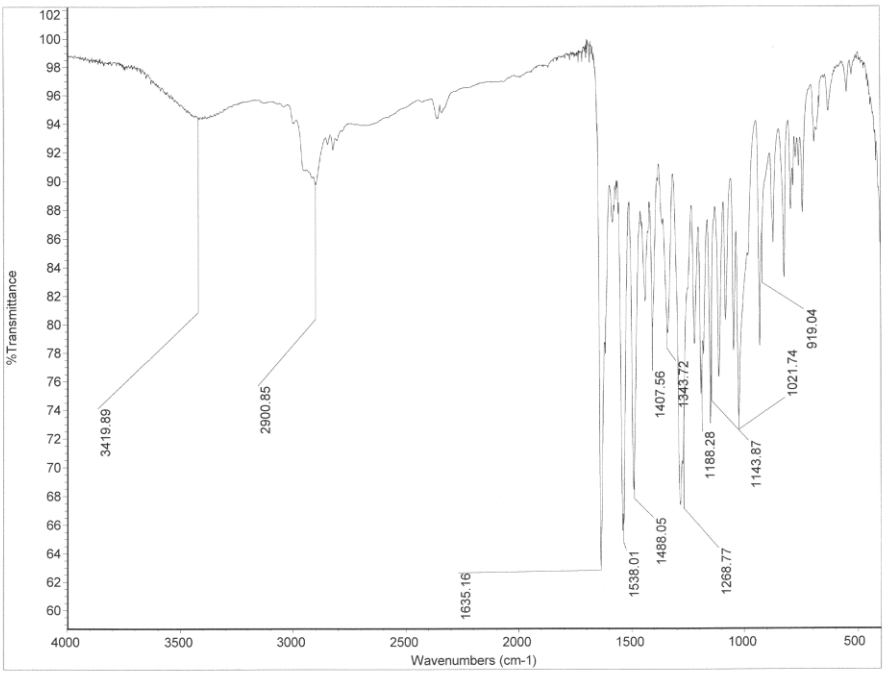

aja_vinaxanthone_x_100_a
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.858 sec
Width 5602.2 Hz
2 repetitions
OBSERVE H1, 400.2669779 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
MOMO
O
Me
OH
214
12
11
10
9
8
7
6
5
4
3
2
1
ppm

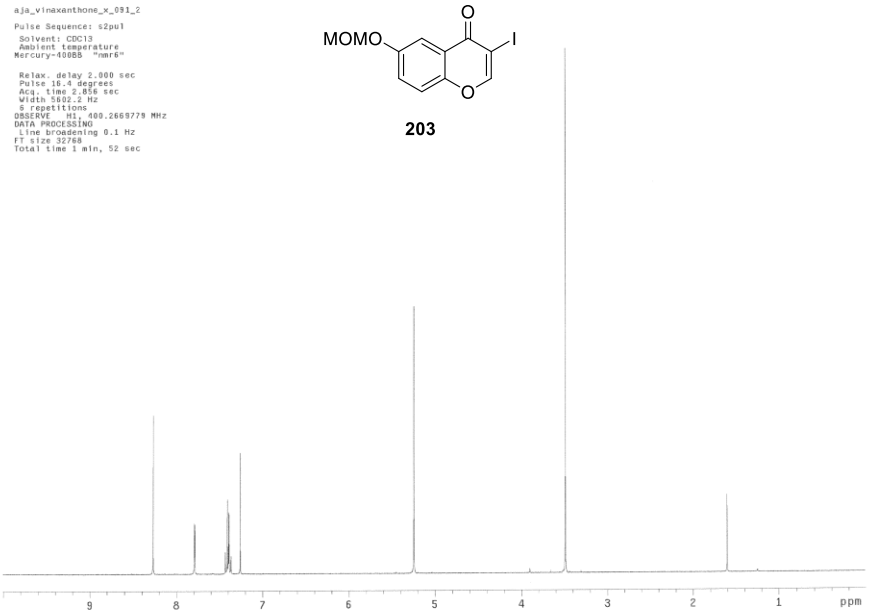

aja_vinaxanthone_x_100_a
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_x_100_a_20120828_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.4985408 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 47 sec
200
180
160
140
120
100
80
60
40
20
ppm

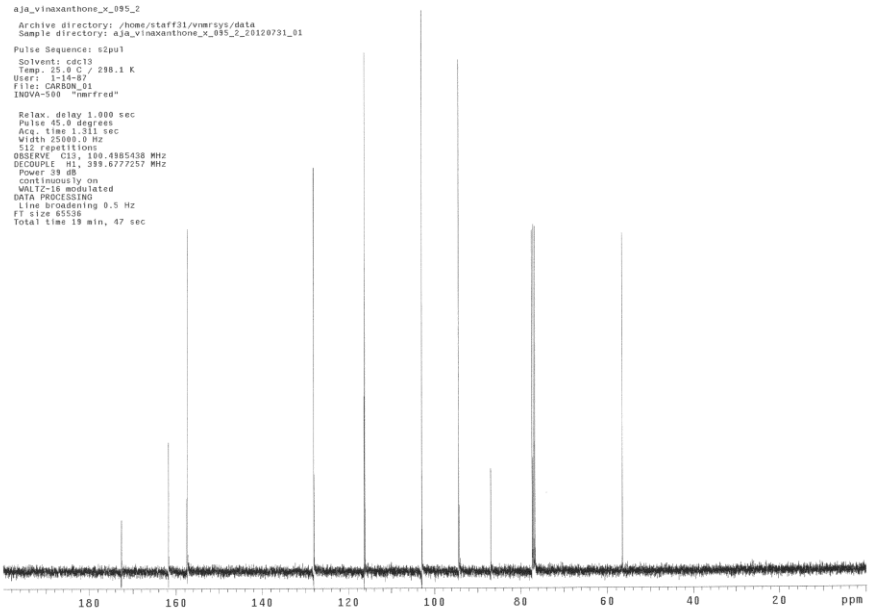

%Transmittance
Wavenumbers (cm-1)
3425.34
2914.67
2845.28
1646.32
1613.02
1490.90
1377.11
1316.05
1277.20
1218.91
1149.53
1074.59
994.11
783.18

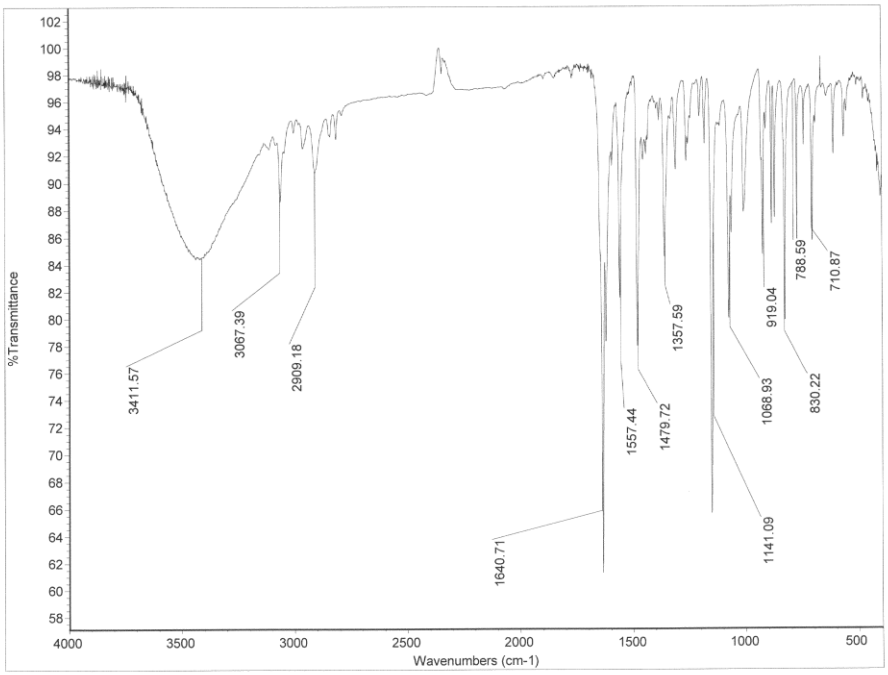

exp1 std1h
SAMPLE
date Jun 4 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.5
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4086.4
vs 151
sc 0
wc 250
hzmm 16.03
is 788.79
rfl 3518.9
rfp 2905.9
th 20
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
O
NMe2
OH
215
9
8
7
6
5
4
3
2
1
ppm

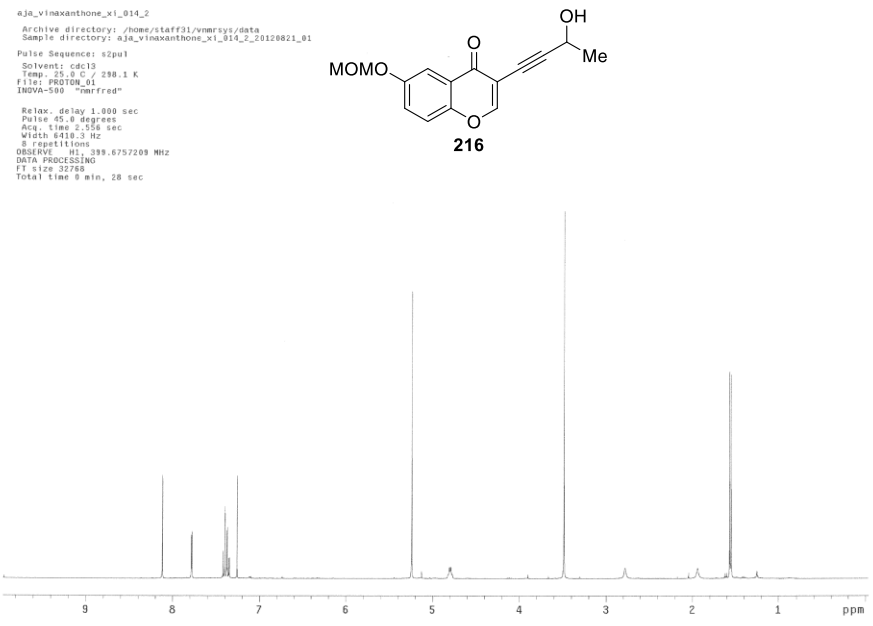

aja_vinaxanthone_x_090_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_x_090_2_20120723_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.4885416 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 47 sec
180
160
140
120
100
80
60
40
20
ppm

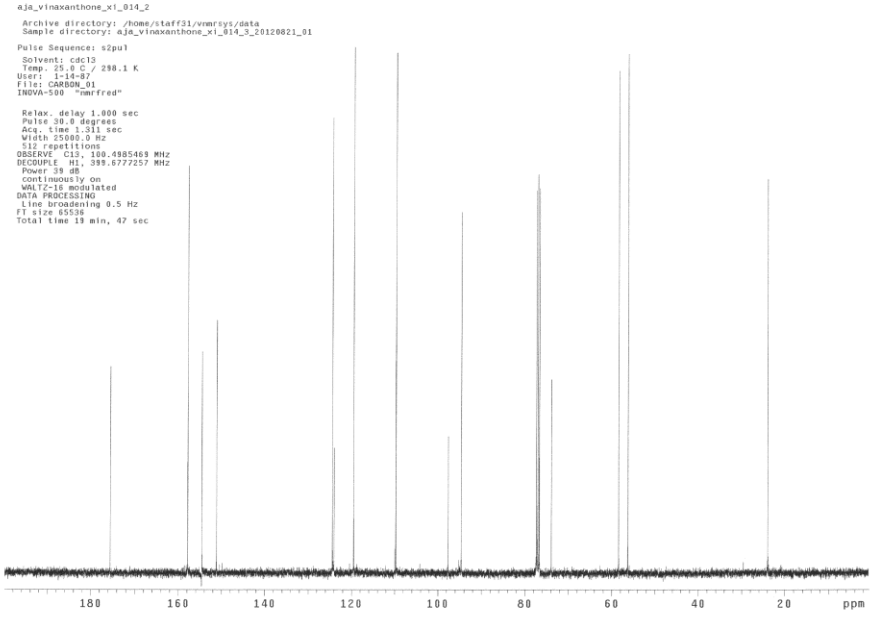

%Transmittance
Wavenumbers (cm-1)
3419.89
2900.85
1635.16
1538.01
1488.05
1407.56
1343.72
1268.77
1188.28
1143.87
1021.74
919.04

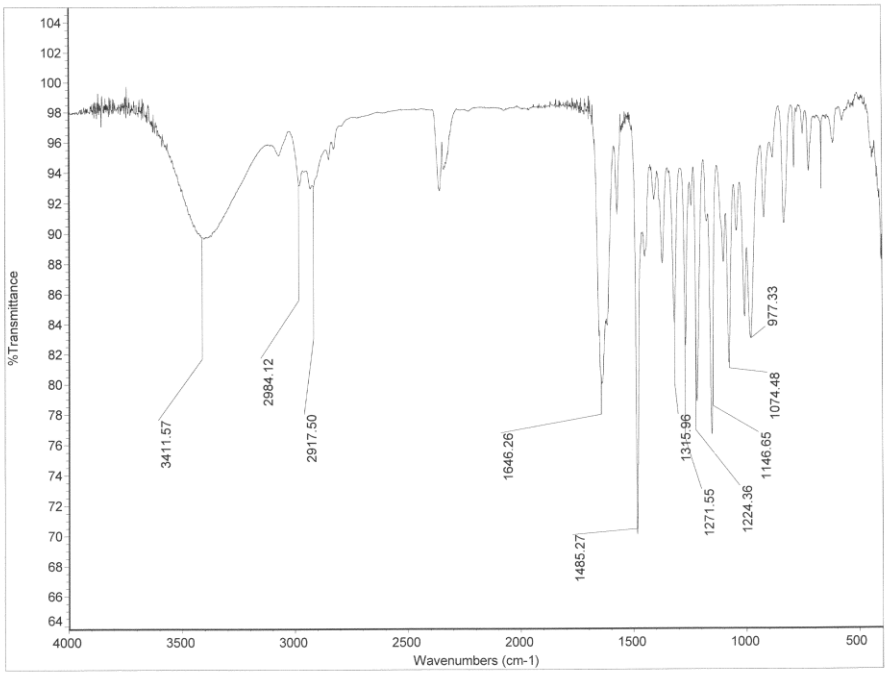

aja_vinaxanthone_x_091_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
8 repetitions
OBSERVE H1, 400.2669779 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
MOMO
O
I
O
203
9
8
7
6
5
4
3
2
1
ppm

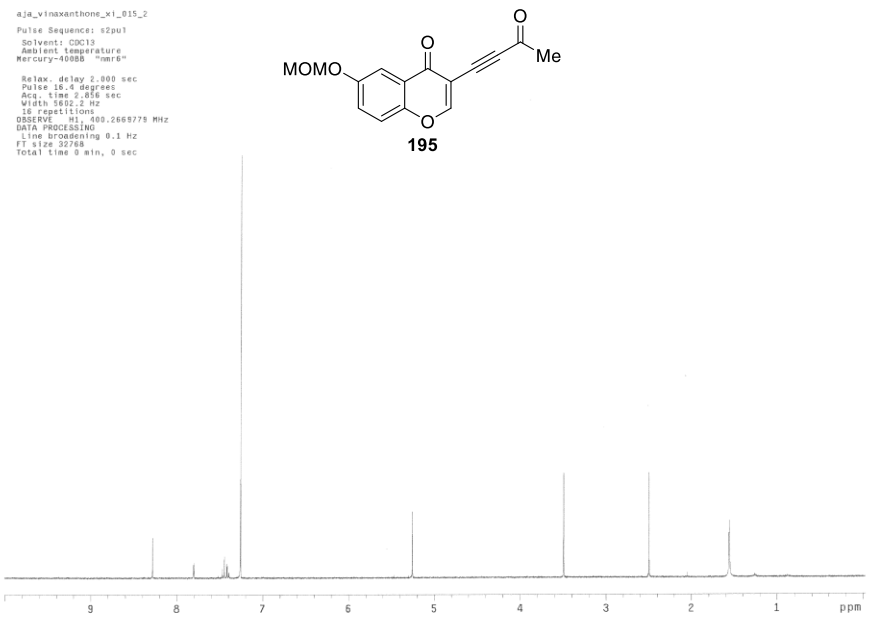

aja_vinaxanthone_x_095_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_x_095_2_20120731_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.4985438 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 47 sec
180
160
140
120
100
80
60
40
20
ppm

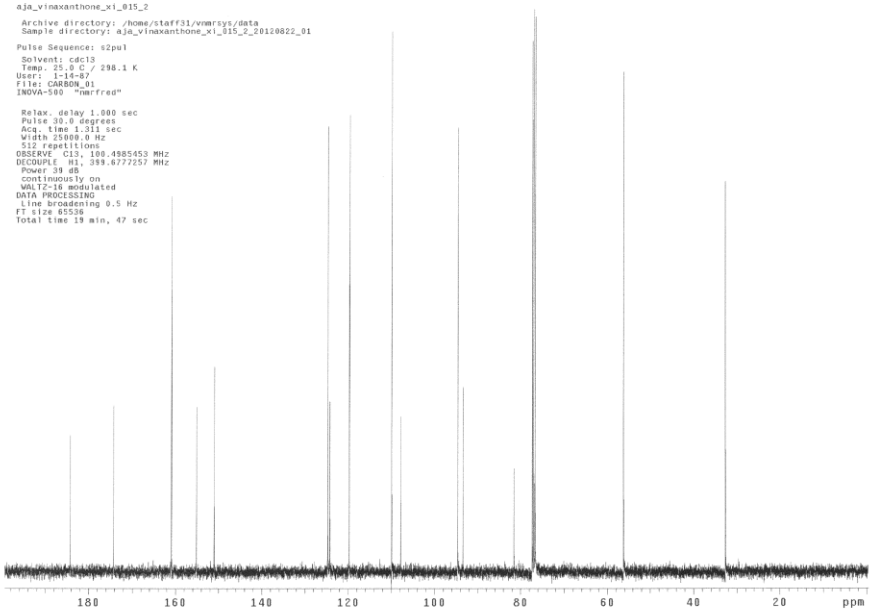

%Transmittance
Wavenumbers (cm-1)
3411.57
3067.39
2909.18
1640.71
1557.44
1479.72
1357.59
1141.09
1068.93
919.04
830.22
788.59
710.87

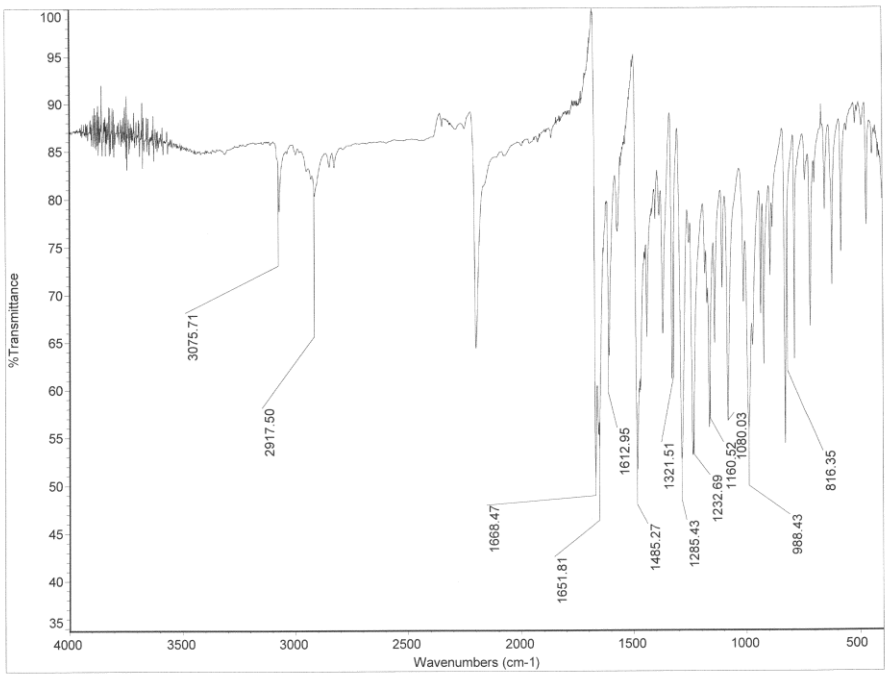

aja_vinaxanthone_xi_014_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_xi_014_2_20120821_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: PROTON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.6757209 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 28 sec
OH
O
Me
MOMO
O
216
9
8
7
6
5
4
3
2
1
ppm

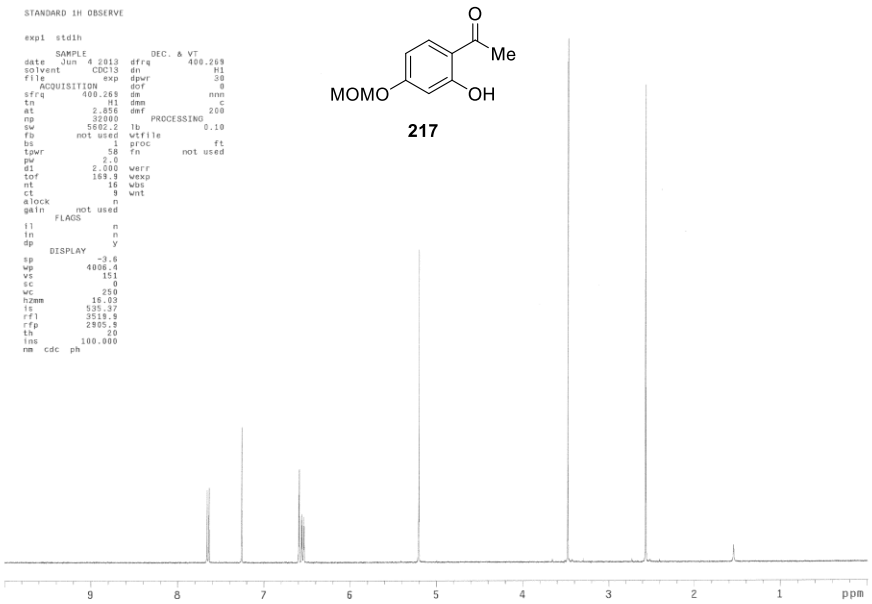

aja_vinaxanthone_xi_014_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_xi_014_3_20120821_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.4985469 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 47 sec
180
160
140
120
100
80
60
40
20
ppm

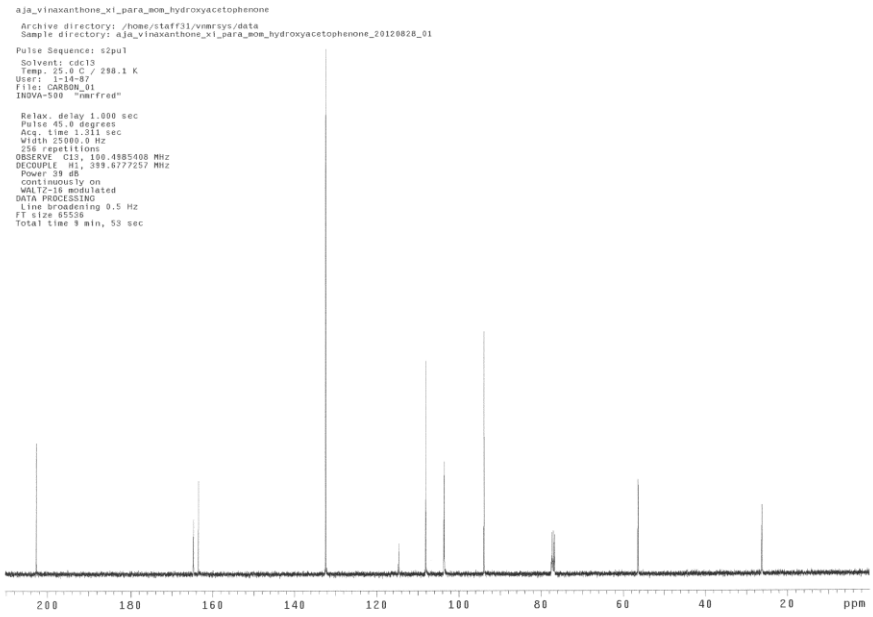

%Transmittance
Wavenumbers (cm-1)
3411.57
2984.12
2917.50
1646.26
1485.27
1315.86
1271.55
1224.36
1146.65
1074.48
977.33

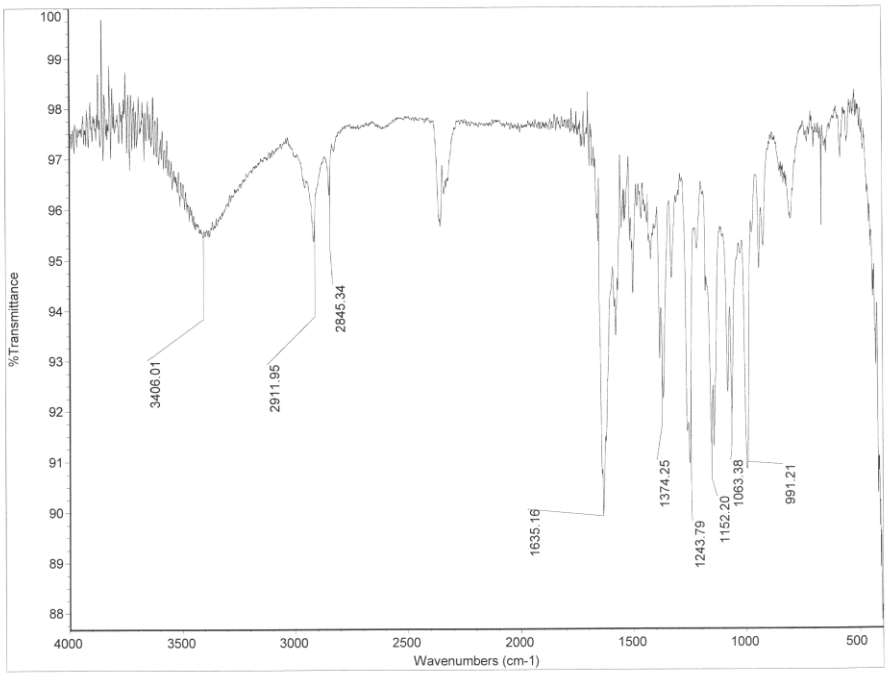

aja_vinaxanthone_xi_015_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.656 sec
Width 5602.2 Hz
16 repetitions
OBSERVE H1, 400.2669779 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
MOMO
O
O
Me
O
195
9
8
7
6
5
4
3
2
1
ppm

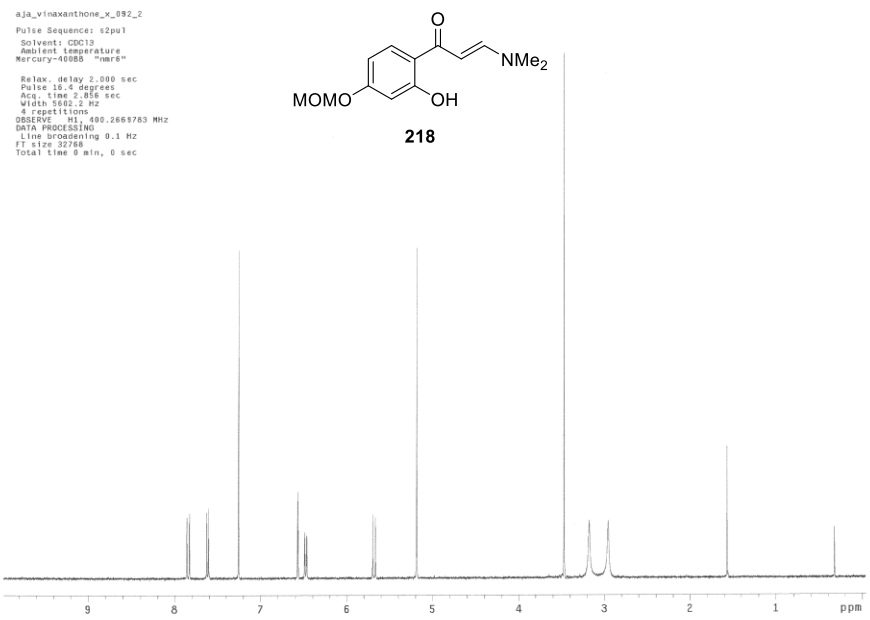

aja_vinaxanthone_xi_015_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_xi_015_2_20120822_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.4885453 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 47 sec
180
160
140
120
100
80
60
40
20
ppm

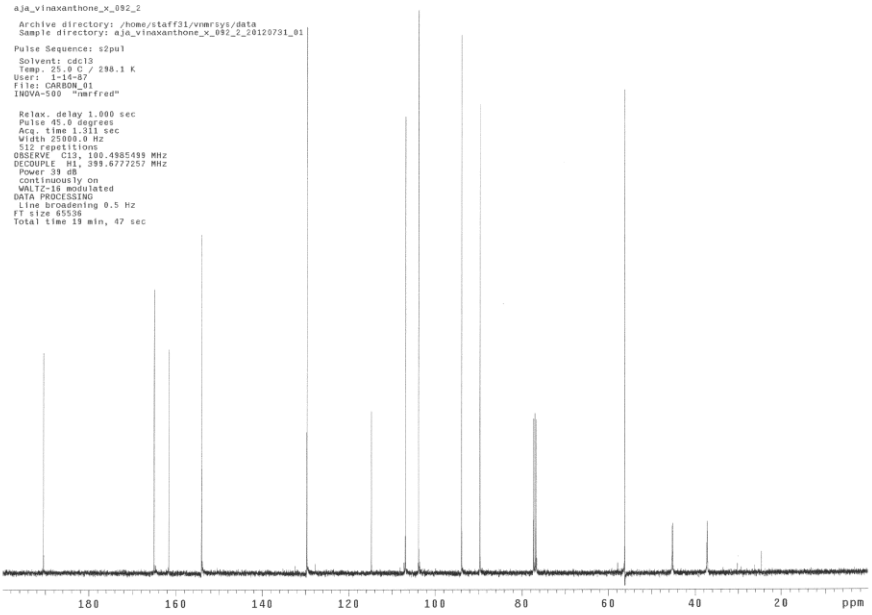

%Transmittance
Wavenumbers (cm-1)
3075.71
2917.50
1668.47
1651.81
1612.95
1485.27
1321.51
1285.43
1232.69
1160.52
1080.03
988.43
816.35

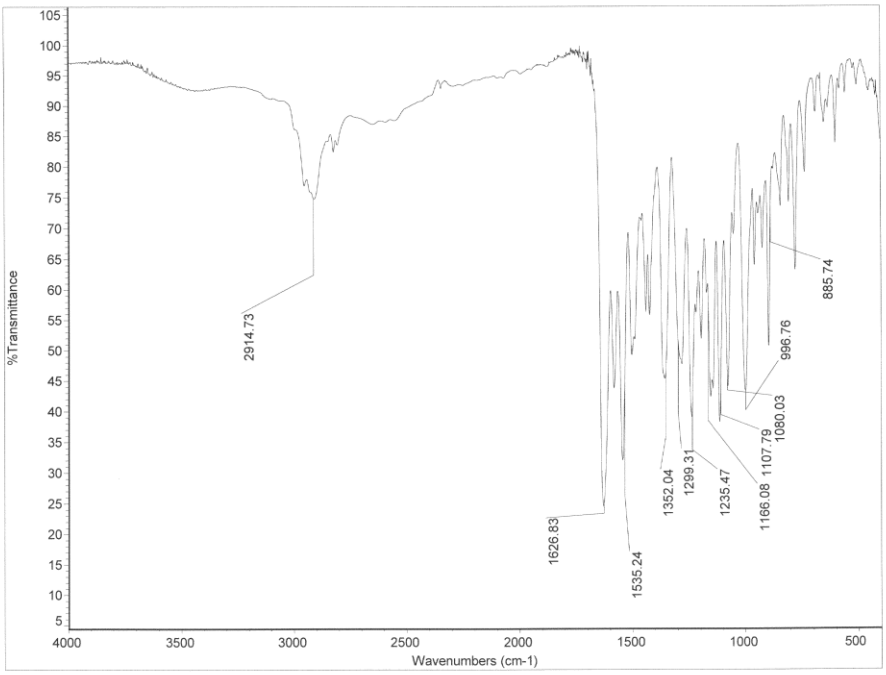

STANDARD 1H OBSERVE
exp1 stdih
SAMPLE
date Jun 4 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.265
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 9
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 535.37
rf1 3518.9
rfp 2905.8
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.265
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
O
Me
MOMO
OH
217
9
8
7
6
5
4
3
2
1
ppm

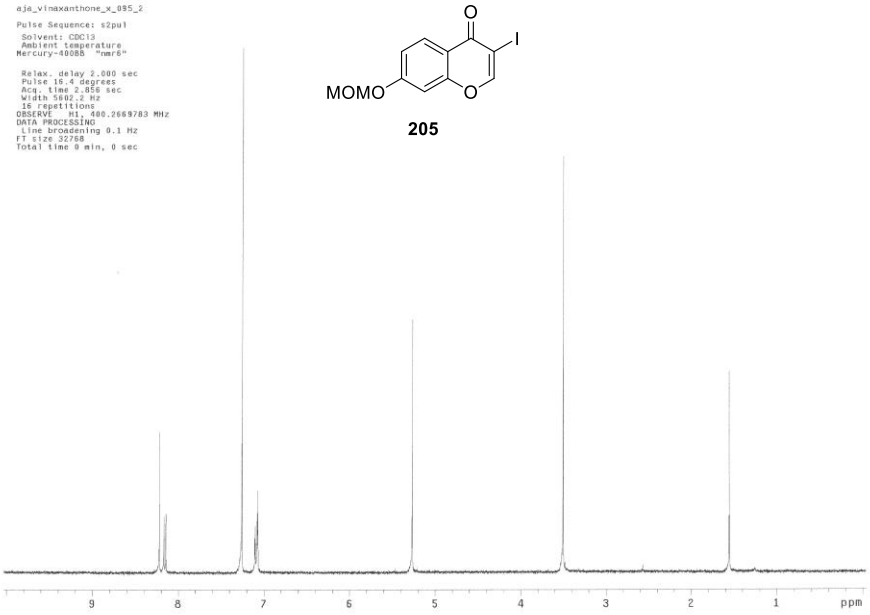

aja_vinaxanthone_xi_para_mom_hydroxyacetophenone
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_xi_para_mom_hydroxyacetophenone_20120828_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: l-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
256 repetitions
OBSERVE C13, 100.4885408 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 53 sec
200
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
Wavenumbers (cm-1)
3406.01
2911.95
2845.34
1635.16
1374.25
1243.79
1152.20
1063.38
991.21

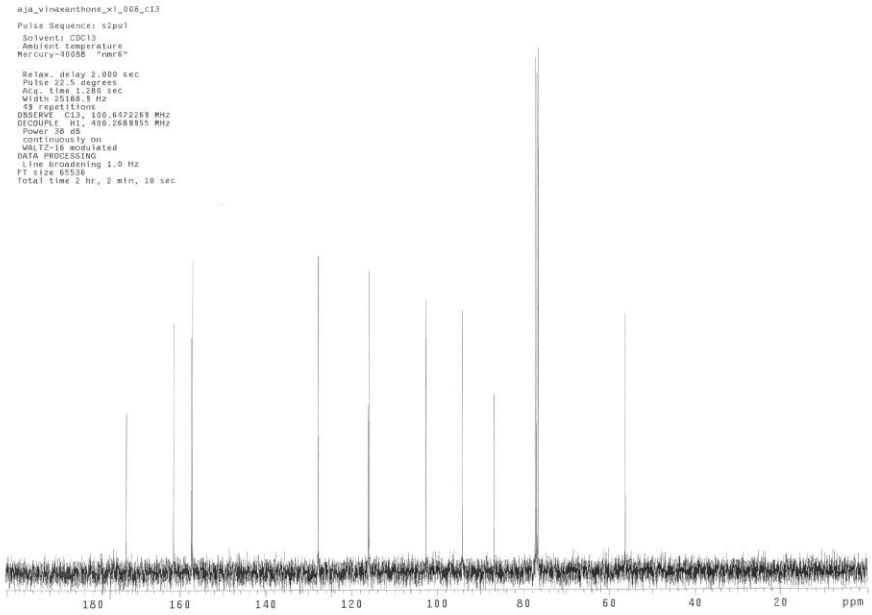

aja_vinaxanthone_x_092_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
4 repetitions
OBSERVE H1, 400.2665783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
O
NMe2
MOMO
OH
218
9
8
7
6
5
4
3
2
1
ppm

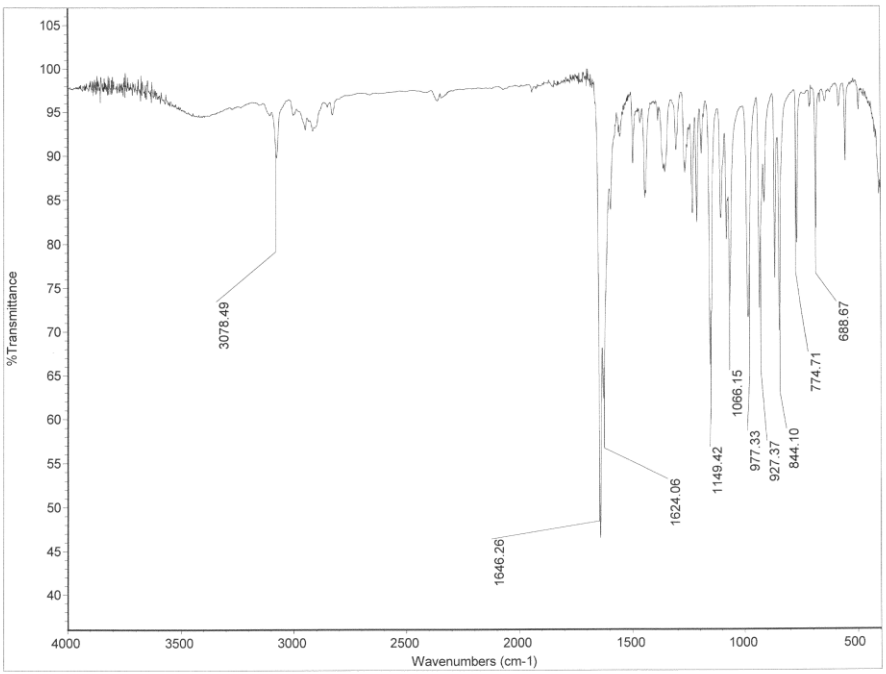

aja_vinaxanthone_x_092_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_x_092_2_20120731_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions
OBSERVE C13, 100.4985499 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 47 sec
180
160
140
120
100
80
60
40
20
ppm

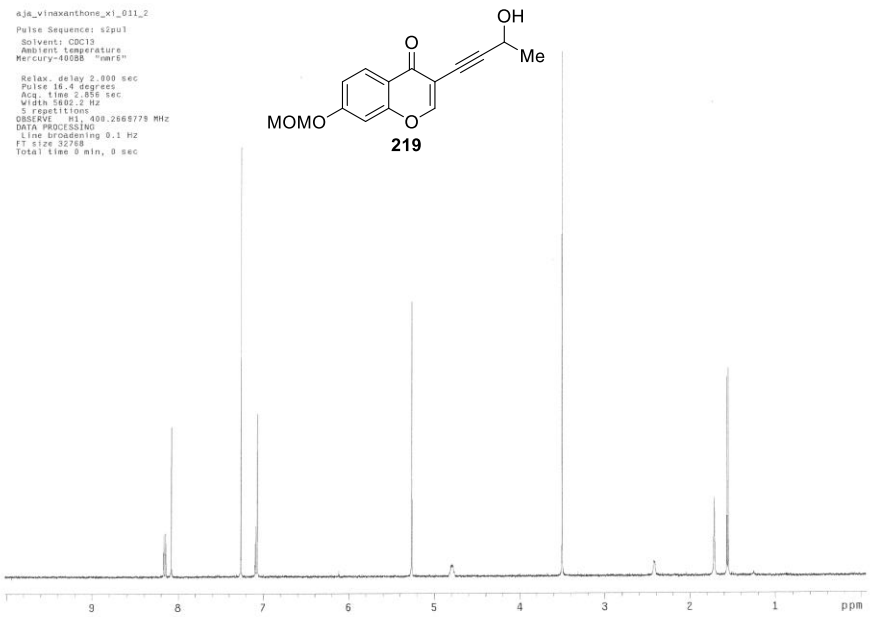

%Transmittance
Wavenumbers (cm-1)
2914.73
1626.83
1535.24
1352.04
1299.31
1235.47
1166.08
1107.79
1080.03
996.76
885.74

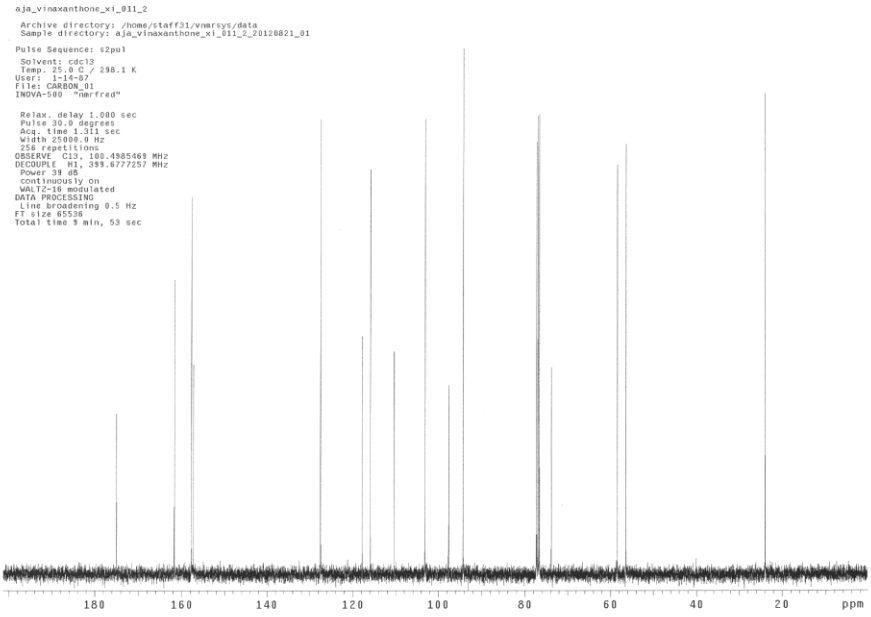

aja_vinaxanthone_x_095_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
16 repetitions
OBSERVE H1, 400.2669783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
O
I
MOMO
O
9
8
7
6
5
4
3
2
1
ppm

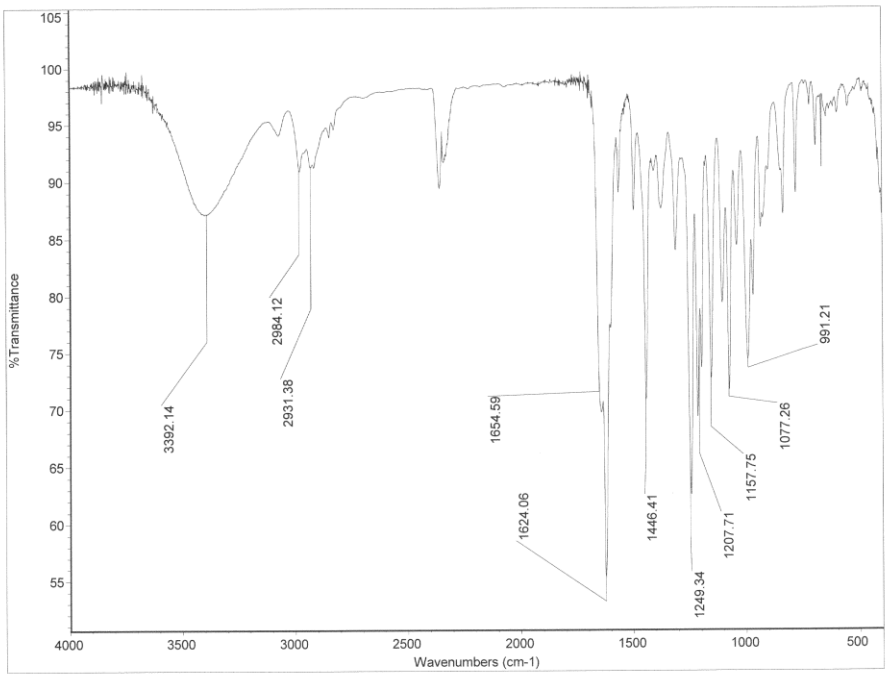
205

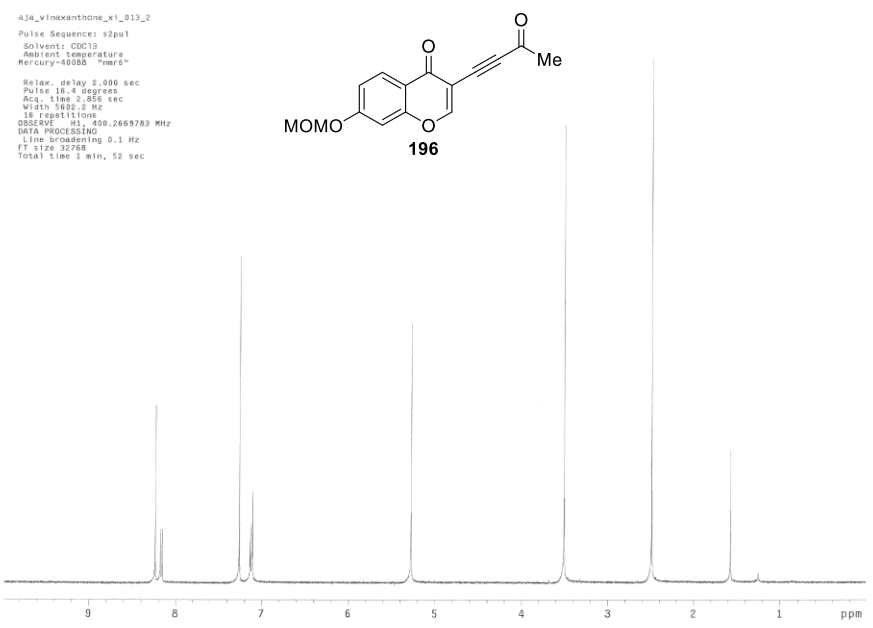

aja_vinaxanthone_xi_008_c13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 22.5 degrees
Acq. time 1.280 sec
Width 25188.9 Hz
49 repetitions
OBSERVE C13, 100.6472269 MHz
DECOUPLE H1, 400.2689955 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 2 min, 10 sec
180
160
140
120
100
80
60
40
20
ppm

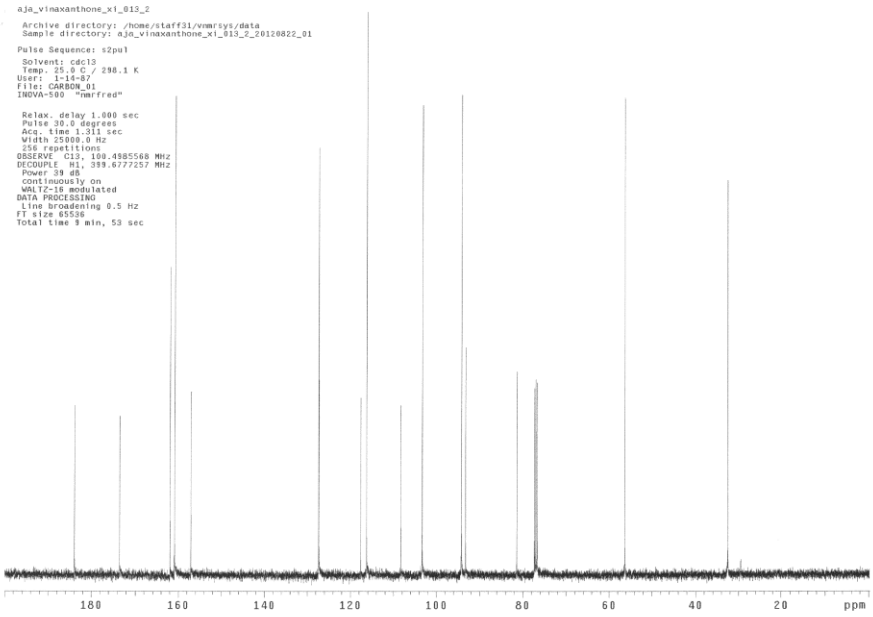

%Transmittance
Wavenumbers (cm-1)
3078.49
1646.26
1624.06
1149.42
1066.15
977.33
927.37
844.10
774.71
688.67

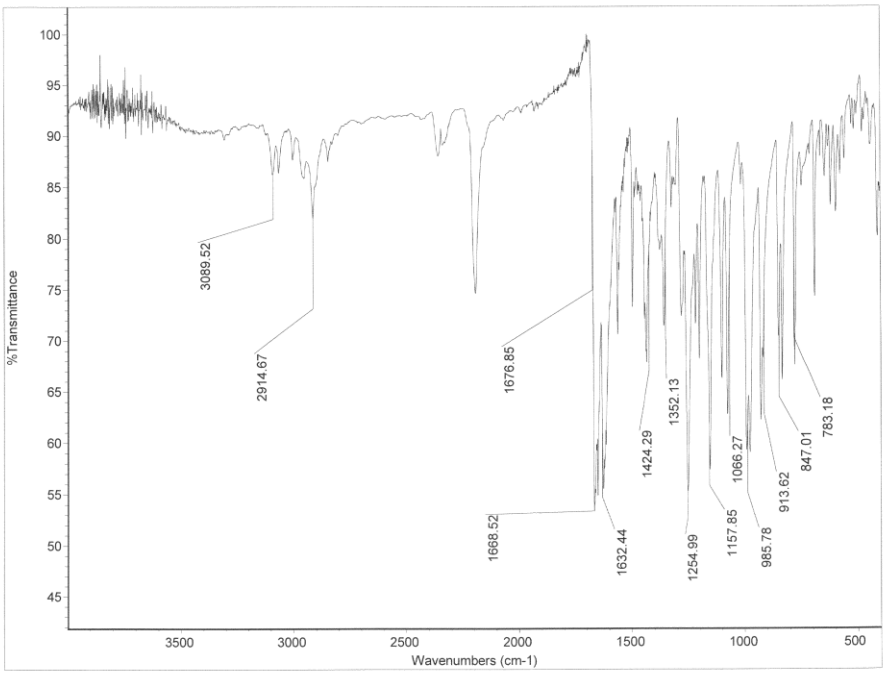

aja_vinaxanthone_xi_011_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
5 repetitions
OBSERVE H1, 400.2666779 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 0 sec
OH
O
Me
MOMO
O
219
9
8
7
6
5
4
3
2
1
ppm


aja_vinaxanthone_xi_011_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_xi_011_2_20120821_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: l-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
256 repetitions
OBSERVE C13, 100.4985469 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 53 sec
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
Wavenumbers (cm-1)
3392.14
2984.12
2931.38
1654.59
1624.06
1446.41
1249.34
1207.71
1157.75
1077.26
991.21


aja_vinaxanthone_xi_013_2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr6"
Relax. delay 2.000 sec
Pulse 16.4 degrees
Acq. time 2.856 sec
Width 5602.2 Hz
16 repetitions
OBSERVE H1, 400.2669783 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec
O
O
Me
MOMO
O
196
9
8
7
6
5
4
3
2
1
ppm

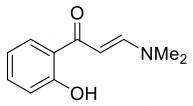

aja_vinaxanthone_xi_013_2
Archive directory: /home/staff31/vnmrsys/data
Sample directory: aja_vinaxanthone_xi_013_2_20120822_01
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: CARBON_01
INOVA-500 "nmrfred"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
256 repetitions
OBSERVE C13, 100.4985568 MHz
DECOUPLE H1, 399.6777257 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 53 sec
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
Wavenumbers (cm-1)
3089.52
2914.67
1676.85
1668.52
1632.44
1424.29
1352.13
1254.99
1157.85
1066.27
985.78
913.62
847.01
783.18

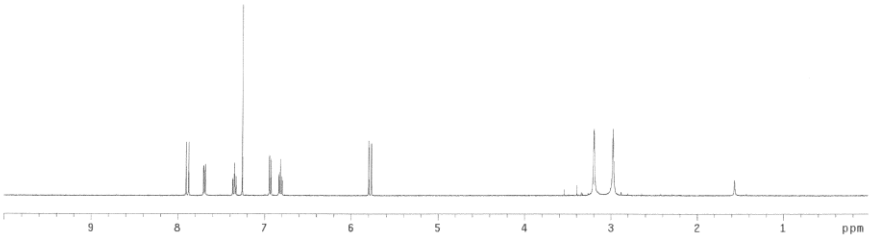
ae_ix_17c

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
Mercury-400BB "nmr6"

 Relax. delay 2.000 sec
 Pulse 16.4 degrees
 Acq. time 2.856 sec
 Width 5602.2 Hz
 16 repetitions
OBSERVE H1, 400.2669779 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 52 sec



220

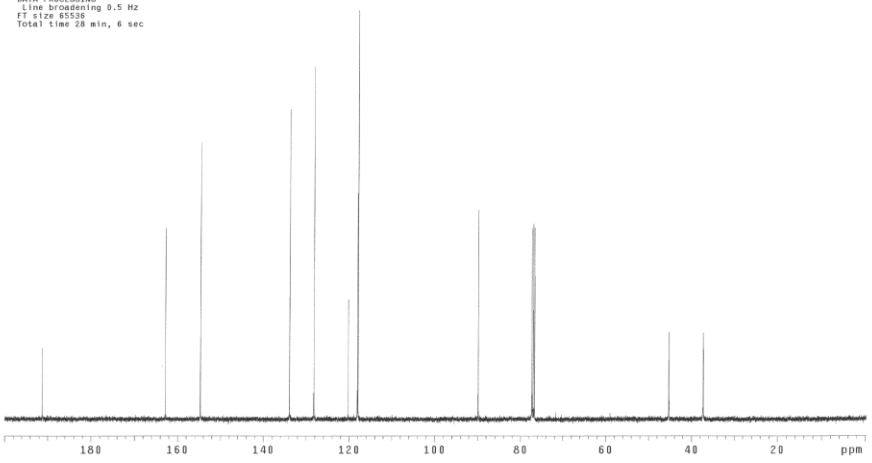


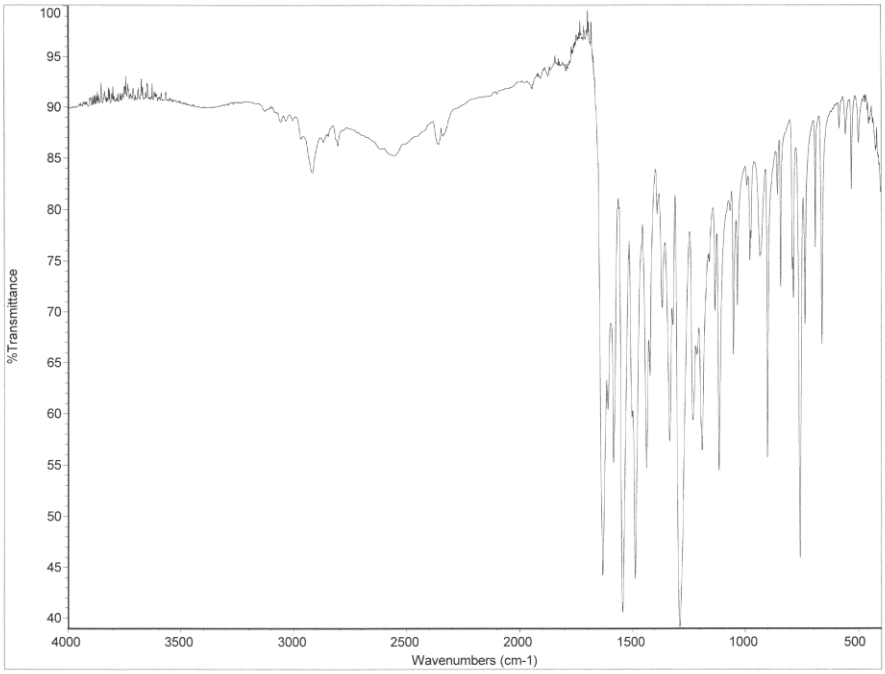
ae-ix-17c

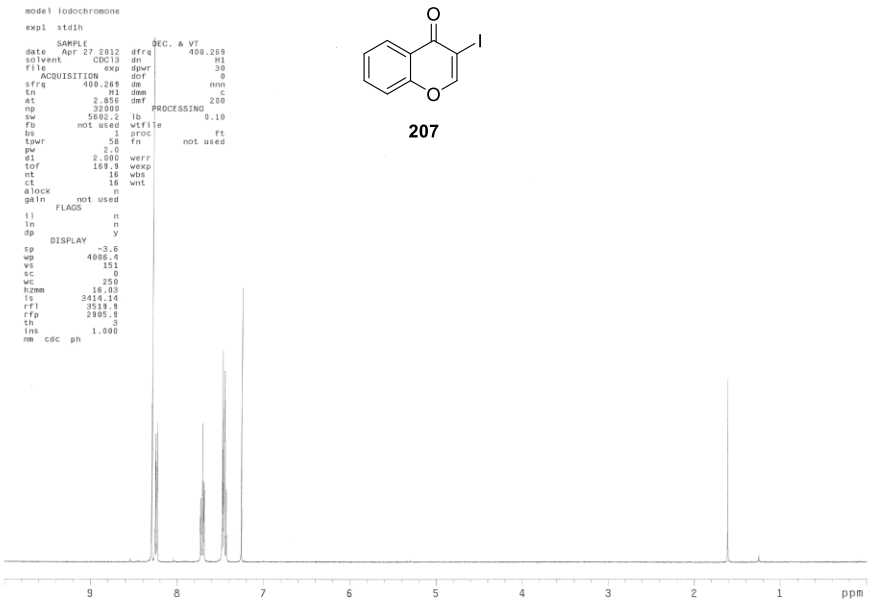
 Archive directory: /home/staff31/vnmrsys/data
 Sample directory: ae_ix_17c_20120211_01

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
User: i-14-87
File: CARBON_01
INOVA-500 "nmrfred"

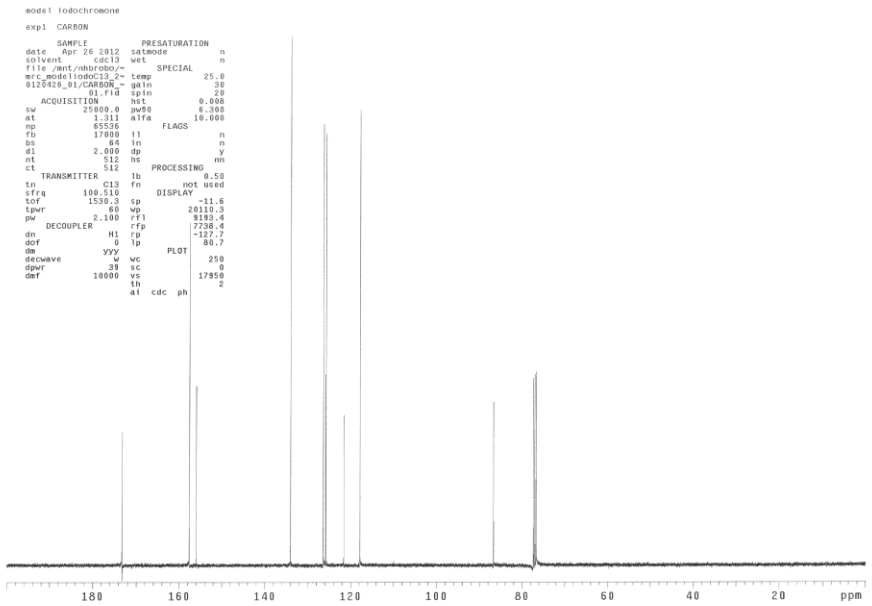
 Relax. delay 2.000 sec
 Pulse 30.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 512 repetitions
OBSERVE C13, 100.4987162 MHz
DECOUPLE H1, 399.6783771 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 6 sec

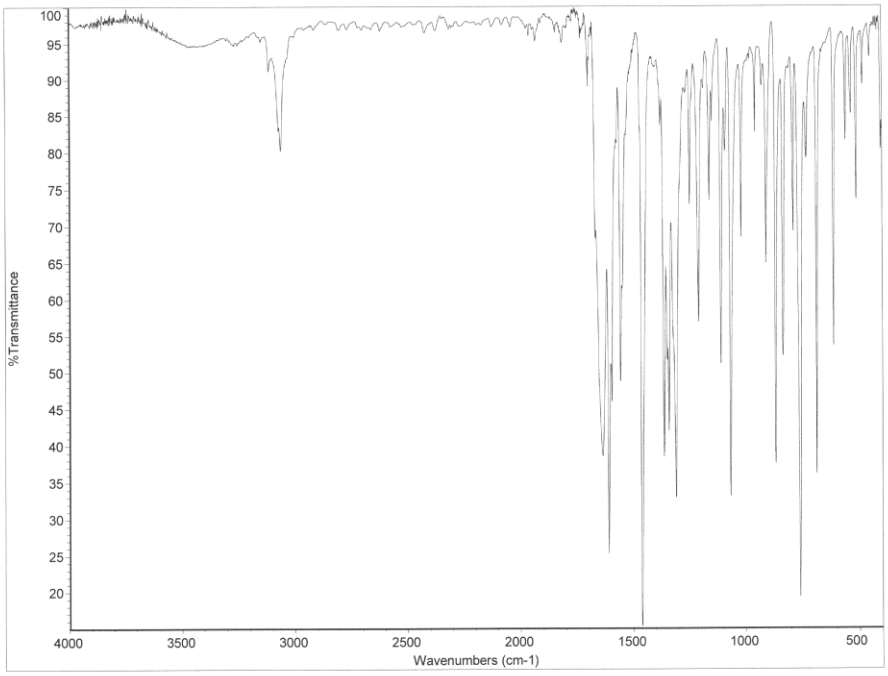


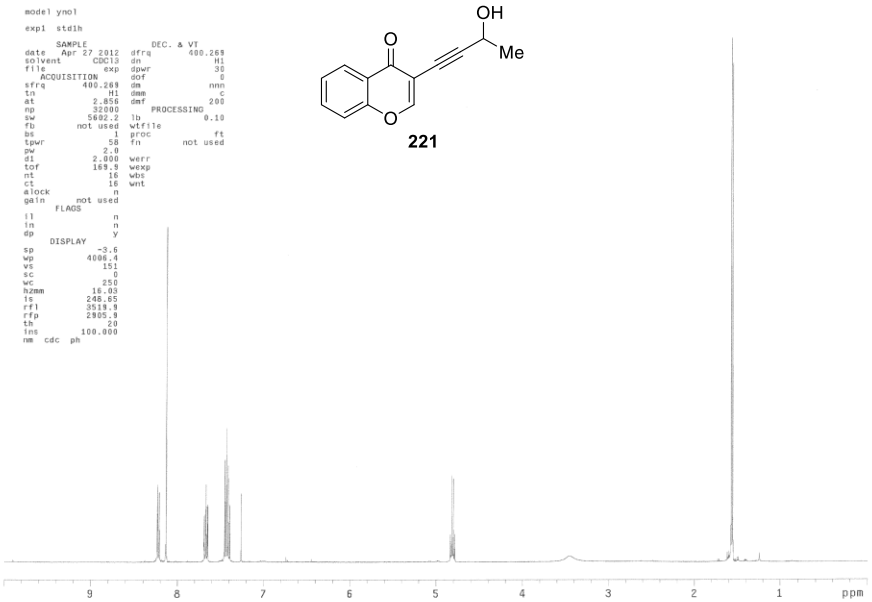

100
95
90
85
80
75
70
65
60
55
50
45
40
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

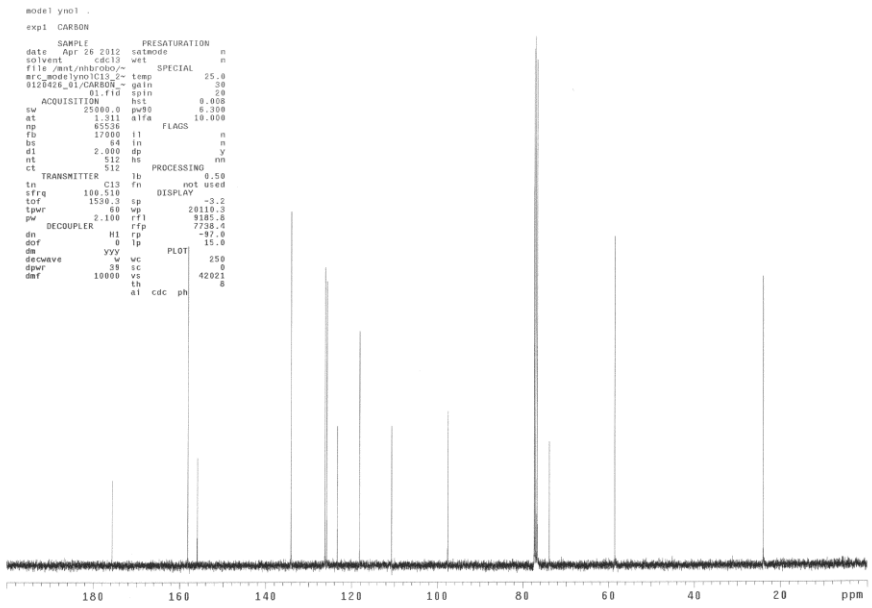

model iodochromone
exp1 stdlh
SAMPLE
date Apr 27 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4008.4
vs 151
sc 0
wc 250
hzmm 16.03
is 3414.14
rfl 3519.9
rfp 2805.9
th 3
ins 1.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
9
8
7
6
5
4
3
2
1
ppm

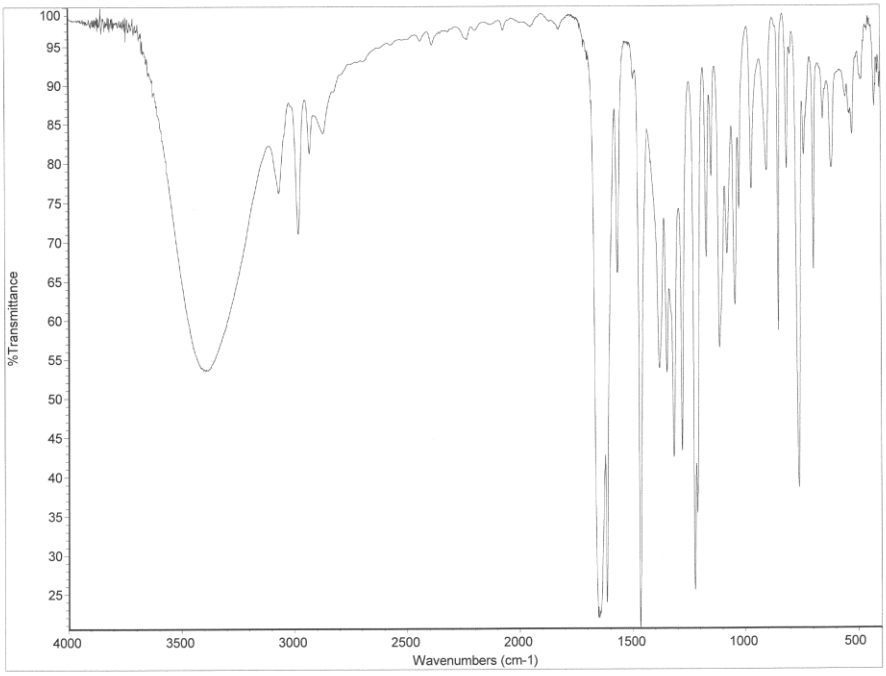
207

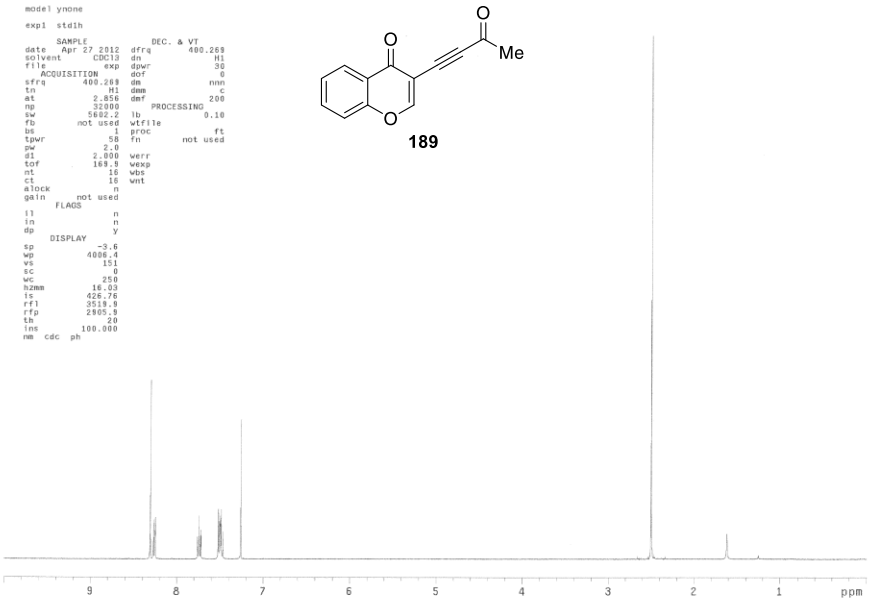

model iodochromone
exp1 CARBON
SAMPLE
date Apr 26 2012
solvent cdcl3
file /mnt/nmrobo/mrc_modeliodoC13_2/0120426_01/CARBON_1/01.fid
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 64
d1 2.000
nt 512
ct 512
TRANSMITTER
tn C13
sfrq 100.510
tof 1530.3
tpwr 60
pw 2.100
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 39
dmf 10000
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -11.6
wp 20110.3
rfl 9193.4
rfp 7738.4
rp -127.7
lp 80.7
PLOT
wc 250
sc 0
vs 17950
th 2
ai cdc ph
180
160
140
120
100
80
60
40
20
ppm

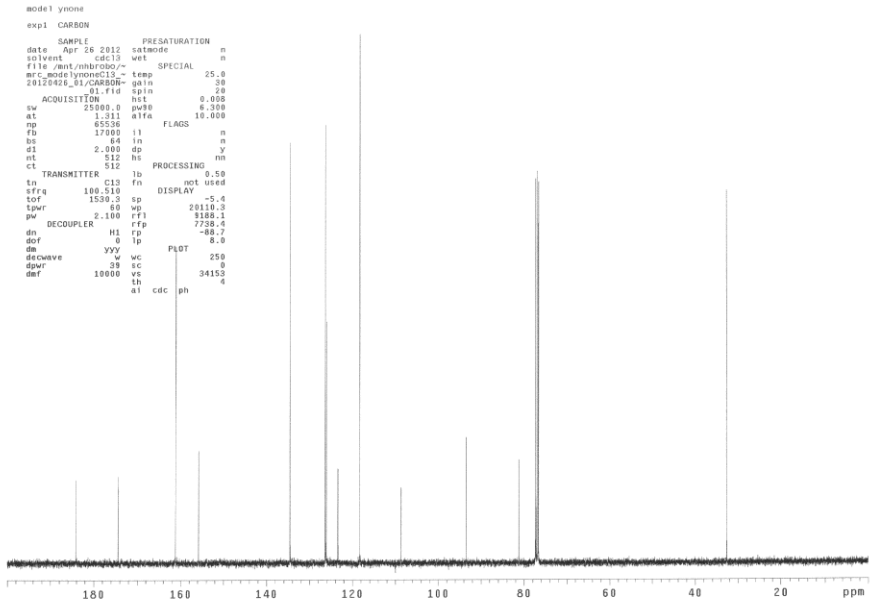

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

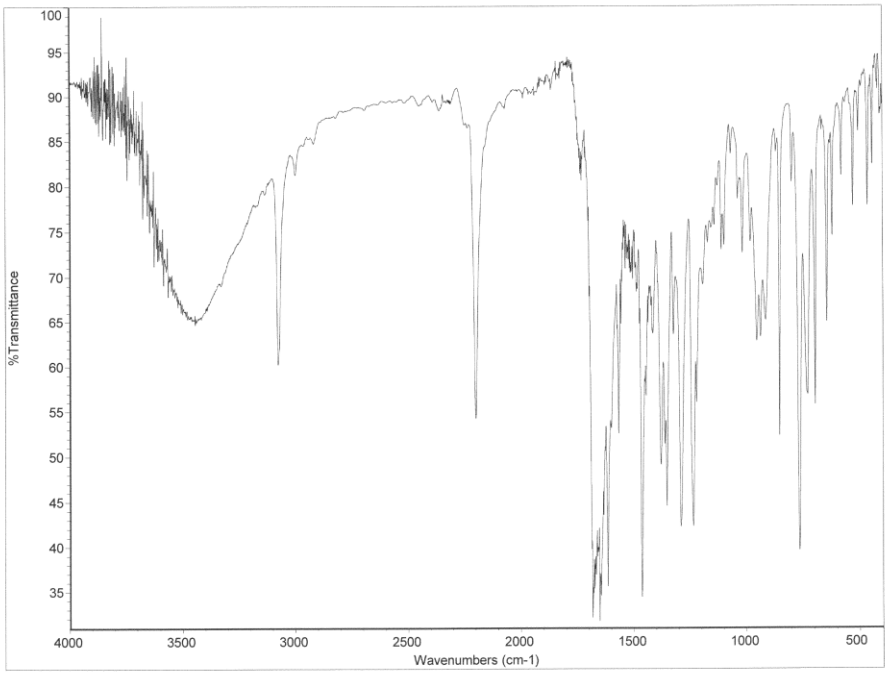

model ynol
exp1 stdlh
SAMPLE
date Apr 27 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 246.65
rfl 3519.9
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 38
dof 0
dm nnn
dmm C
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexg
wbs
wnt
OH
Me
O
O
221
9
8
7
6
5
4
3
2
1
ppm

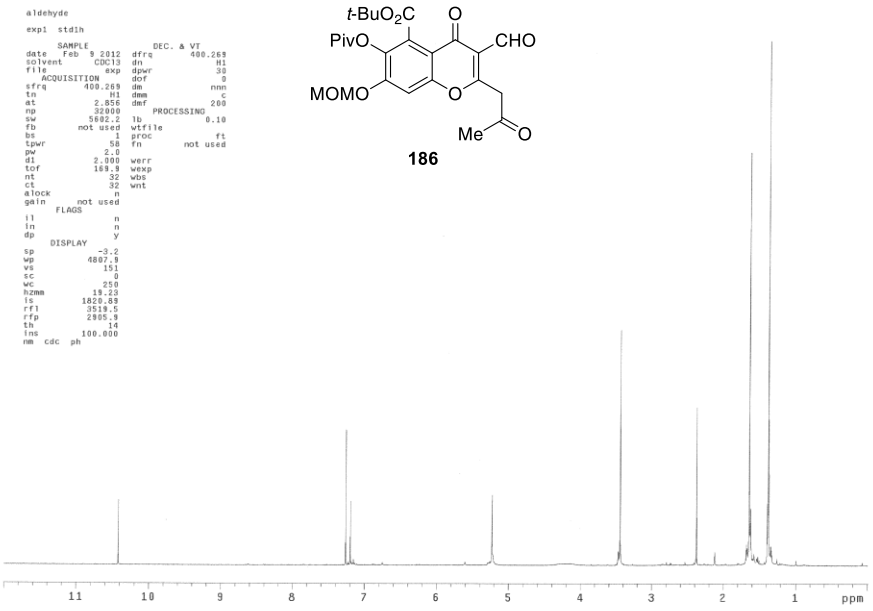

model ynol .
exp1 CARBON
SAMPLE
date Apr 26 2012
solvent cdcl3
file /mnt/nmrobo/~
mrc_modelynol13_2~
0120426_01/CARBON_~
01.fid
ACQUISITION
sw 25080.0
at 1.311
np 65536
fb 17000
bs 64
d1 2.000
nt 512
ct 512
TRANSMITTER
tn C13
sfrq 100.510
tof 1530.3
tpwr 60
pw 2.100
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 38
dmf 10000
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -3.2
wp 20110.3
rfl 9185.8
rfp 7738.4
rp -97.0
lp 15.0
PLOT
wc 250
sc 0
vs 42021
th 8
al cdc ph
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


model ynone
exp1 std1h
SAMPLE
date Apr 27 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.288
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.5
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 426.76
rfl 3519.9
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
O
O
Me
O
189
9
8
7
6
5
4
3
2
1
ppm

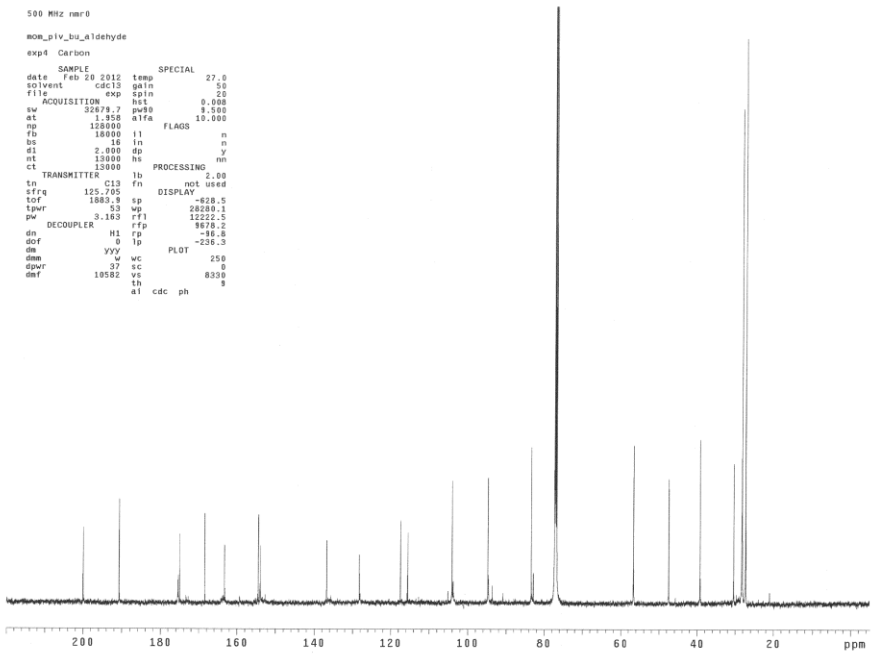

model ynone
exp1 CARBON
SAMPLE
date Apr 26 2012
solvent cdcl3
file /mnt/nmrobo/~
mrc_modelynone613_~
20120426_01/CARBON~
_01.fid
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 64
d1 2.000
nt 512
ct 512
TRANSMITTER
tn C13
sfrq 100.510
tof 1530.3
tpwr 60
pw 2.100
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 39
dmf 10000
PRESATURATION
satmode n
wet n
SPECIAL
temp 25.0
gain 30
spin 20
hst 0.008
pw90 6.300
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -5.4
wp 20110.3
rfl 9188.1
rfp 7738.4
rp -88.7
lp 8.0
PLOT
wc 250
sc 0
vs 34153
th 4
ai cdc ph
180
160
140
120
100
80
60
40
20
ppm

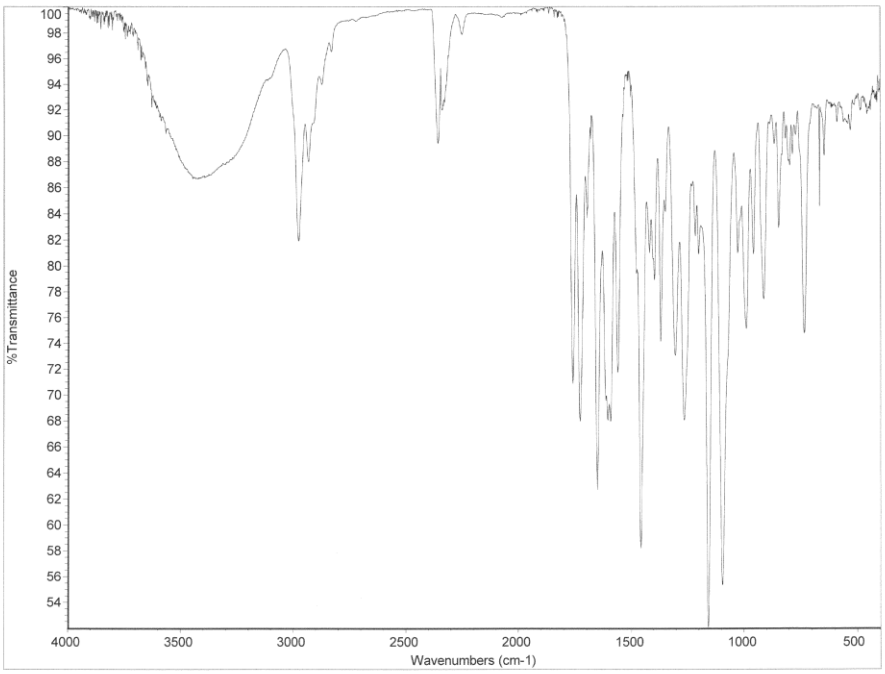

100
95
90
85
80
75
70
65
60
55
50
45
40
35
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

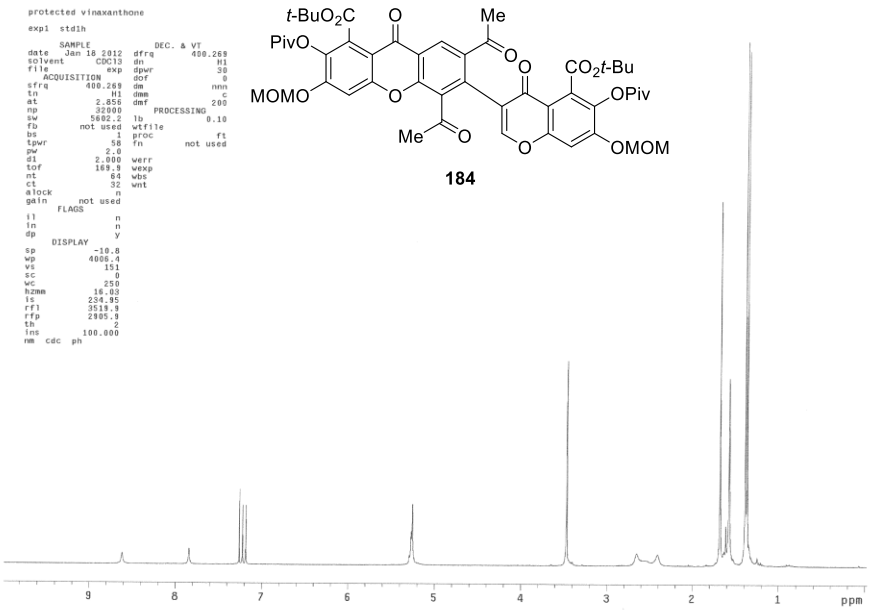

aldehyde
exp1 std1h
SAMPLE
date Feb 9 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5802.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4807.9
vs 151
sc 0
wc 250
hzmm 18.23
is 1820.89
rf1 3519.5
rfp 2905.9
th 14
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
11
10
9
8
7
6
5
4
3
2
1
ppm

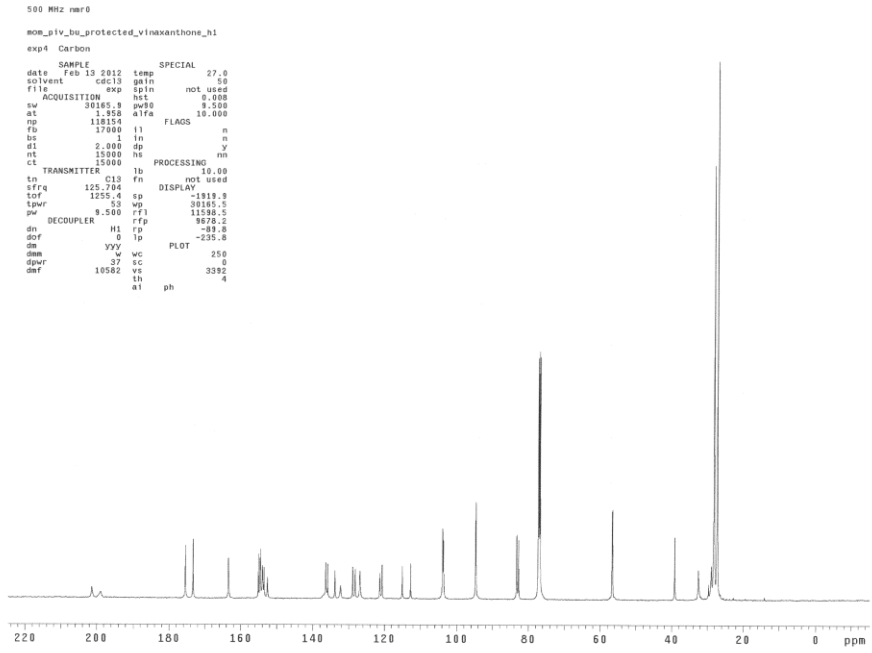
t-BuO2C
O
PivO
CHO
MOMO
O
Me
O

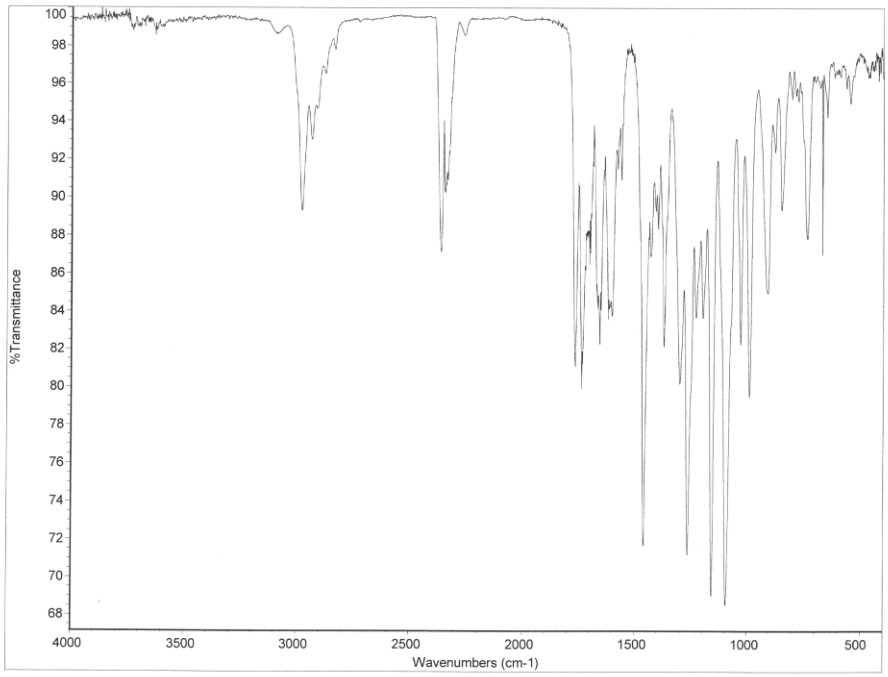
186

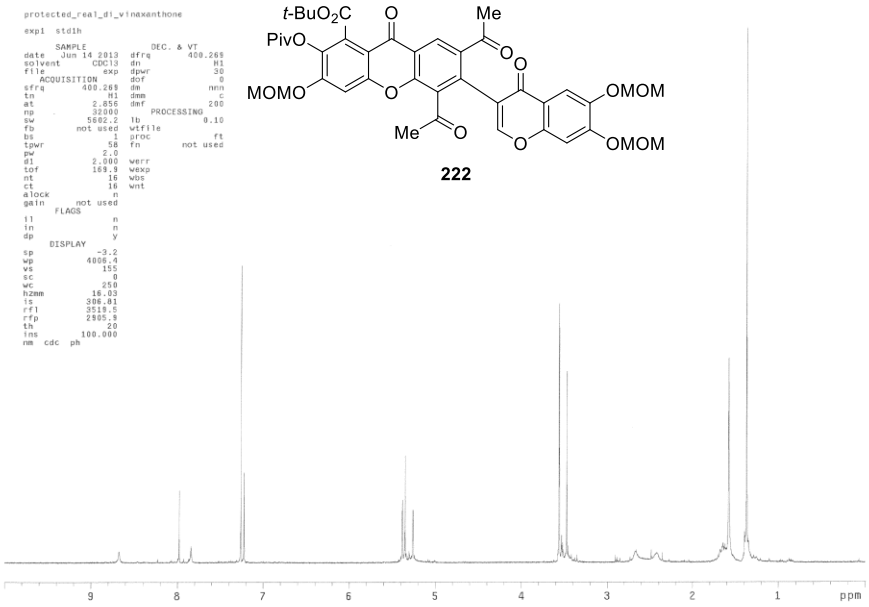

500 MHz nmr0
mom_piv_bu_aldehyde
exp4 Carbon
SAMPLE
date Feb 20 2012
solvent cdcl3
file exp
ACQUISITION
sw 32679.7
at 1.958
np 128000
fb 18000
bs 16
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 125.705
tof 1883.9
tpwr 53
pw 3.163
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 37
dmf 10582
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 9.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 2.00
fn not used
DISPLAY
sp -628.5
wp 28280.1
rf1 12222.5
rfp 9678.2
rp -96.8
lp -236.3
PLOT
wc 250
sc 0
vs 8330
th 9
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

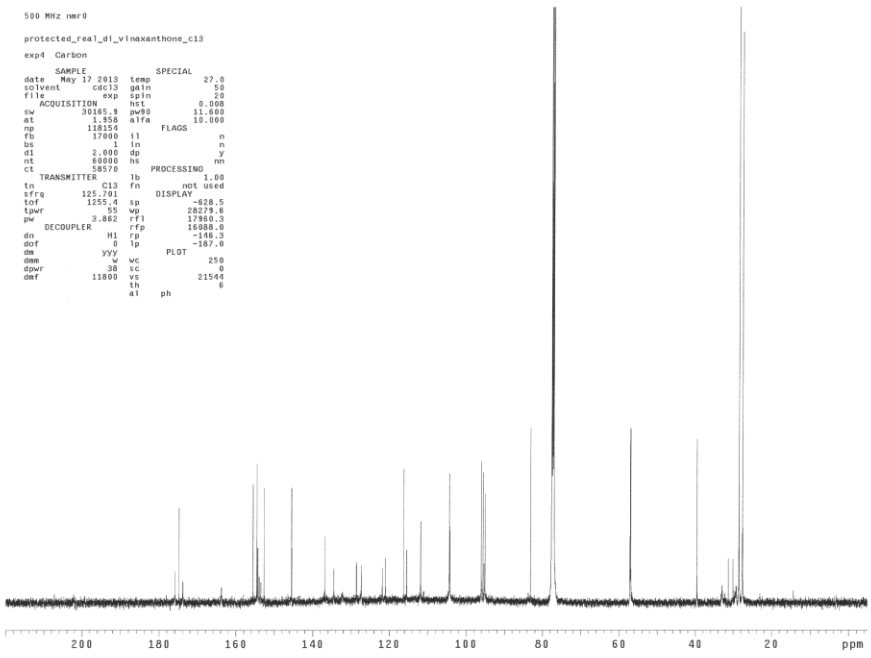

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

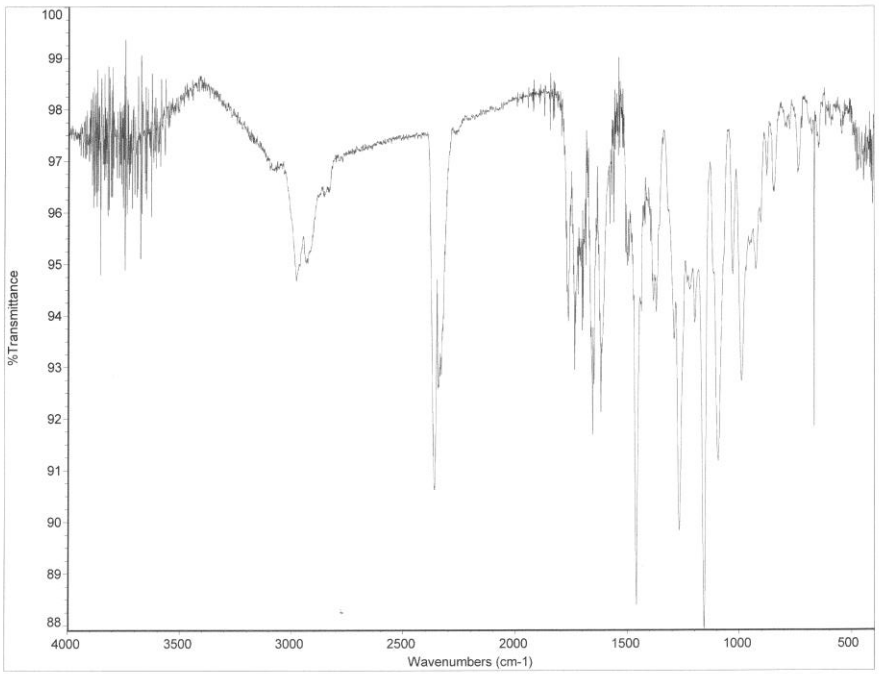

protected vinaxanthone
exp1 std1h
SAMPLE
date Jan 18 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5802.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 64
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -10.8
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 234.95
rfl 3519.9
rfp 2805.9
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
t-BuO2C
O
Me
PivO
O
O
CO2t-Bu
MOMO
O
OPiv
Me
O
O
OMOM
184
9
8
7
6
5
4
3
2
1
ppm

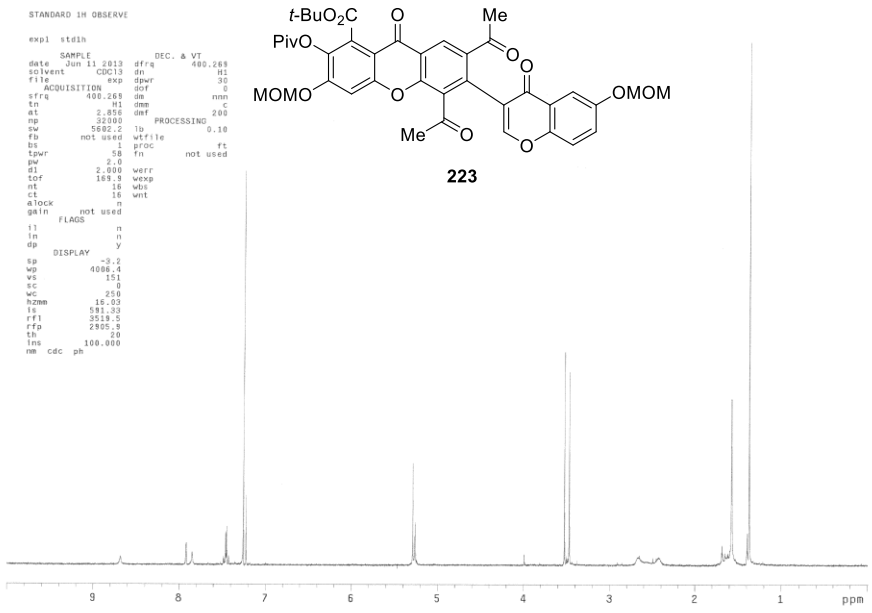

500 MHz nmr0
mom_piv_bu_protected_vinaxanthone_h1
exp4 Carbon
SAMPLE
date Feb 13 2012
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 15000
TRANSMITTER
tn C13
sfrq 125.704
tof 1255.4
tpwr 53
pw 9.500
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 37
dmf 10582
SPECIAL
temp 27.0
gain 50
spin not used
hst 0.008
pw90 9.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 10.00
fn not used
DISPLAY
sp -1919.9
wp 30165.5
rfl 11598.5
rfp 9678.2
rp -89.8
lp -235.8
PLOT
wc 250
sc 0
vs 3392
th 4
ai ph
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


protected_real_di_vinaxanthone
exp1 stdih
SAMPLE
date Jun 14 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4006.4
vs 155
sc 0
wc 250
hzmm 16.03
is 306.01
rfl 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
t-BuO2C
PivO
MOMO
Me
OMOM
OMOM
222
9
8
7
6
5
4
3
2
1
ppm

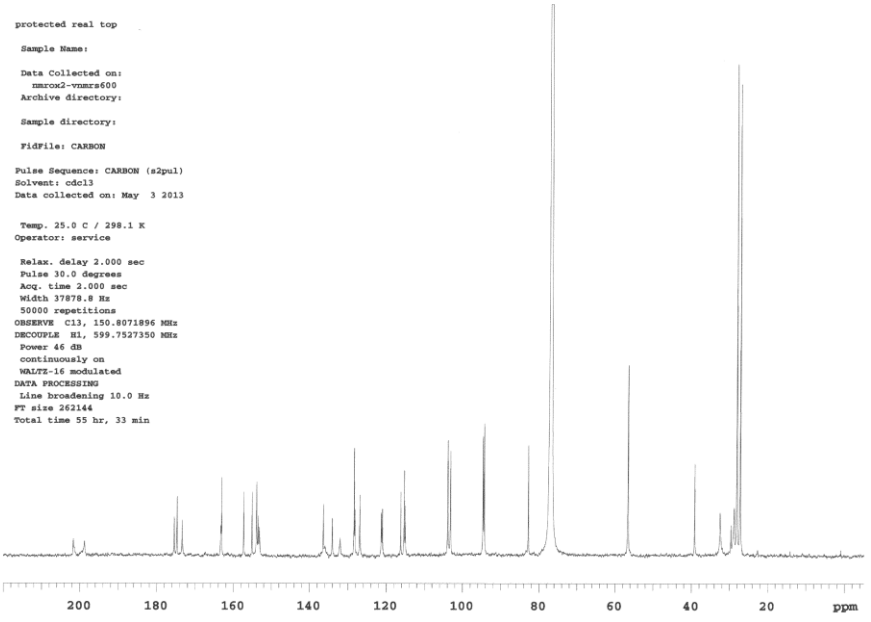

500 MHz nmr0
protected_real_di_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 17 2013
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.358
np 118154
fb 17000
bs 1
d1 2.000
nt 60000
ct 58570
TRANSMITTER
tn C13
sfrq 125.701
tof 1255.4
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.5
wp 28279.8
rfl 17960.3
rfp 16088.0
rp -146.3
lp -187.0
PLOT
wc 250
sc 0
vs 21544
th 8
al ph
200
180
160
140
120
100
80
60
40
20
ppm

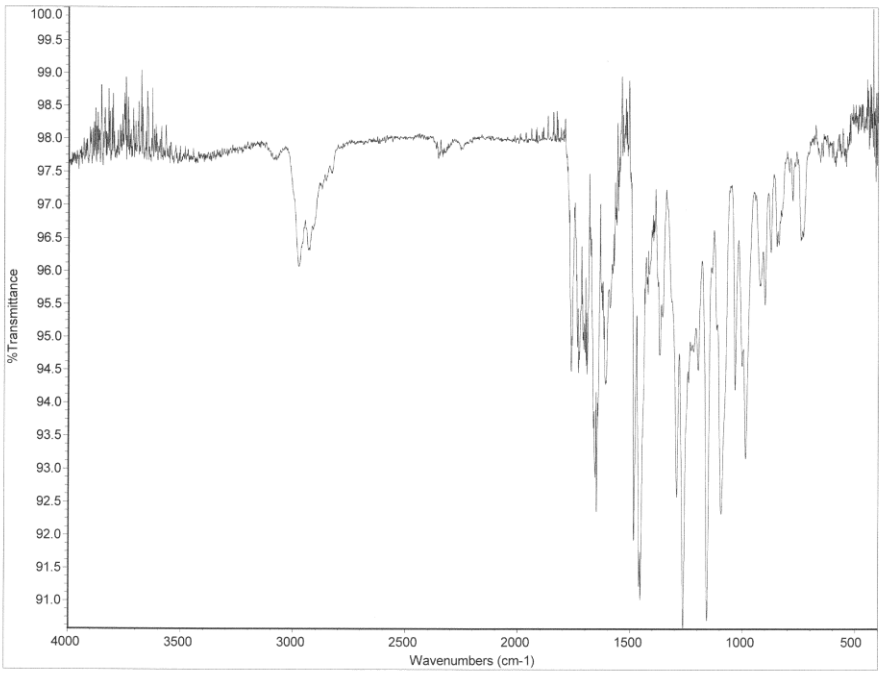

100
99
98
97
96
95
94
93
92
91
90
89
88
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

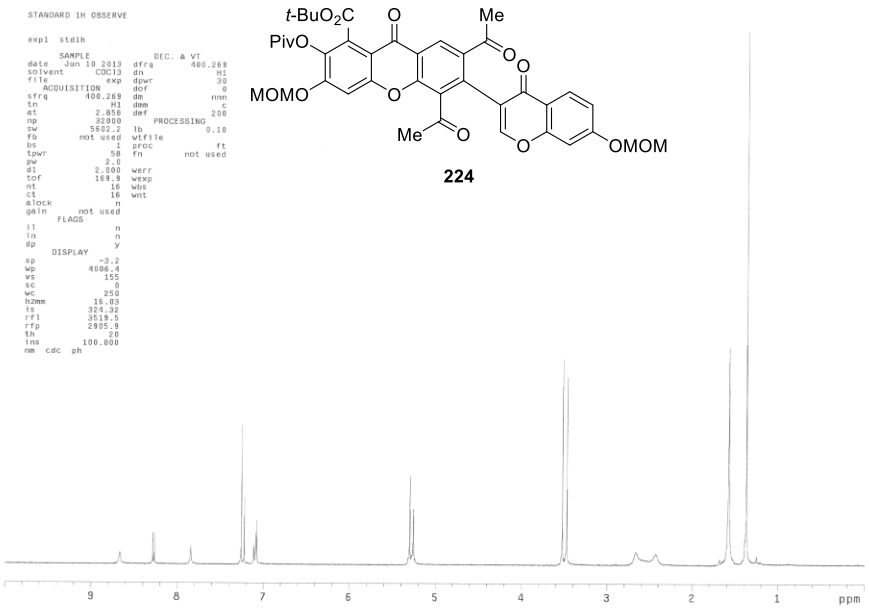

STANDARD 1H OBSERVE
expl stdih
SAMPLE
date Jun 11 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.265
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
ws 151
sc 0
wc 250
hzmm 15.03
is 591.33
rf1 3519.5
rfp 2905.9
th 20
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.265
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
9
8
7
6
5
4
3
2
1
ppm

t-BuO2C
O
Me
PivO
O
O
MOMO
O
OMOM
Me
O
O

223

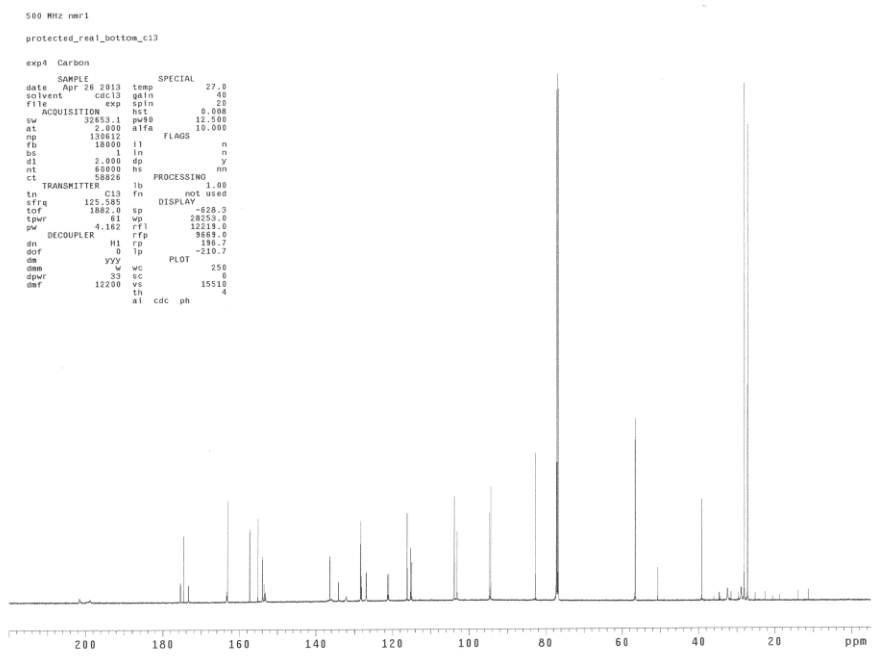

protected real top
Sample Name:
Data Collected on:
nmrox2-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 3 2013
Temp. 25.0 C / 298.1 K
Operator: service
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.000 sec
Width 37878.8 Hz
50000 repetitions
OBSERVE C13, 150.8071896 MHz
DECOUPLE H1, 599.7527350 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 10.0 Hz
FT size 262144
Total time 55 hr, 33 min
200
180
160
140
120
100
80
60
40
20
ppm

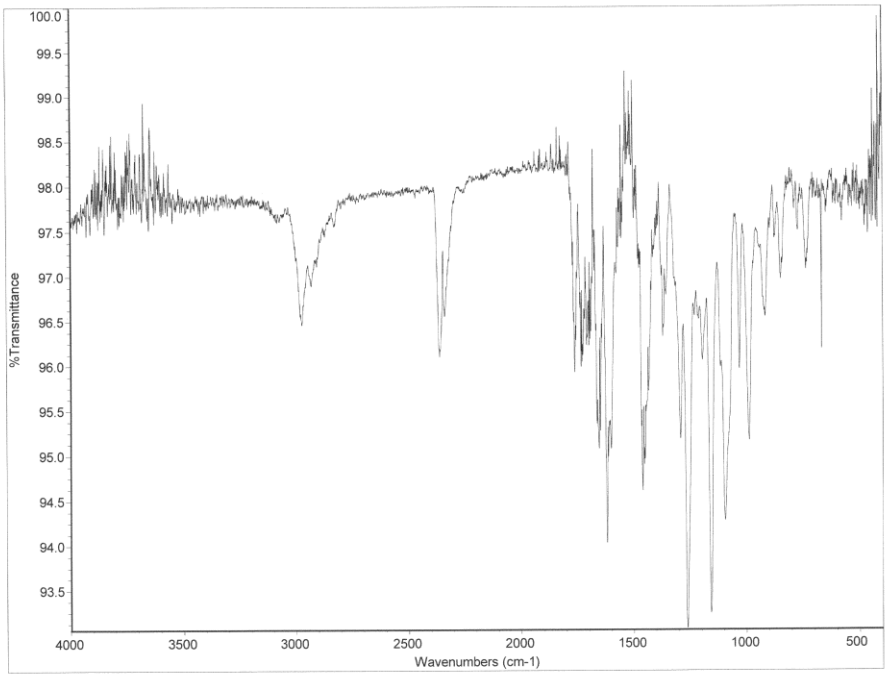

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

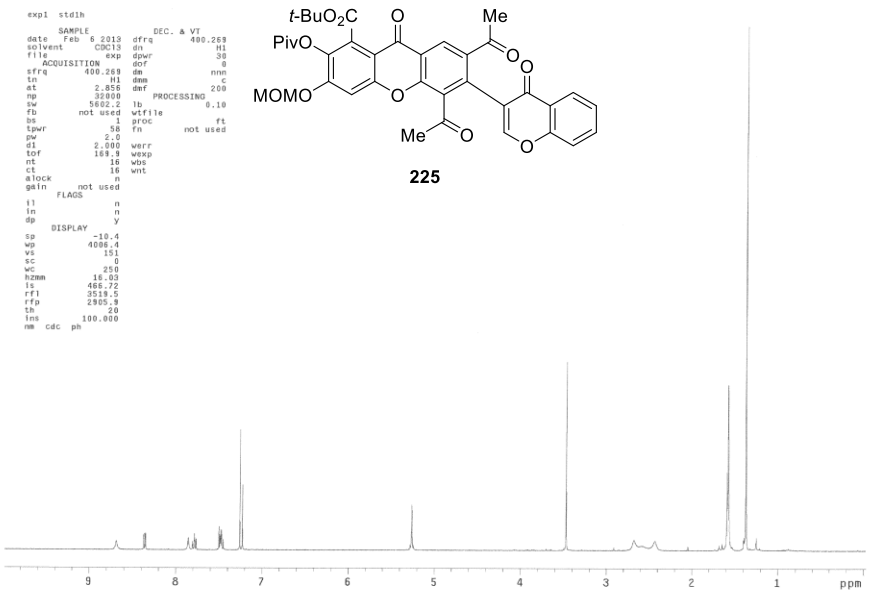

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jun 10 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
vs 155
sc 0
wc 250
hzmm 15.03
is 324.92
rfl 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
def 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
9
8
7
6
5
4
3
2
1
ppm

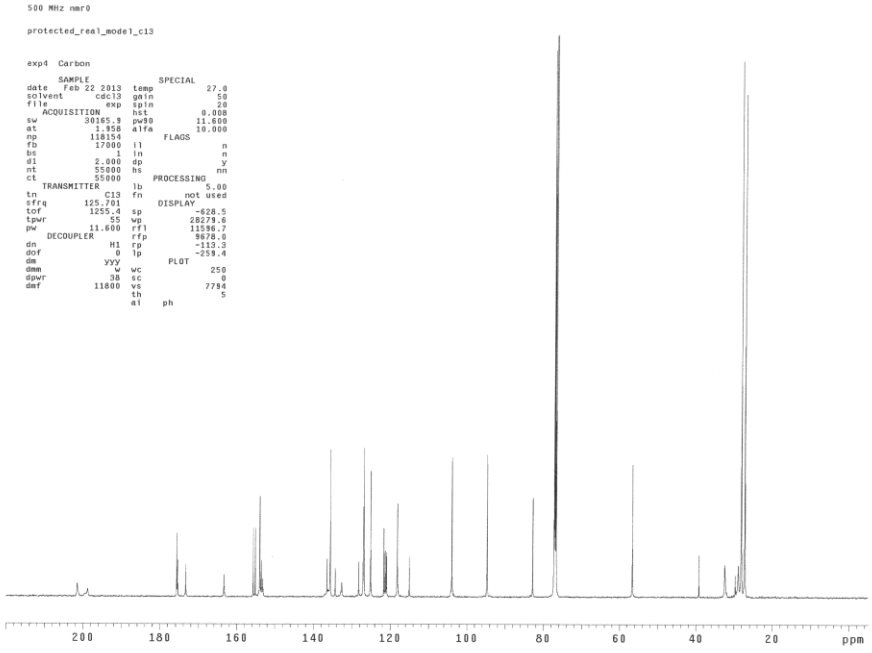
t-BuO2C
PivO
MOMO
Me
Me
OMOM

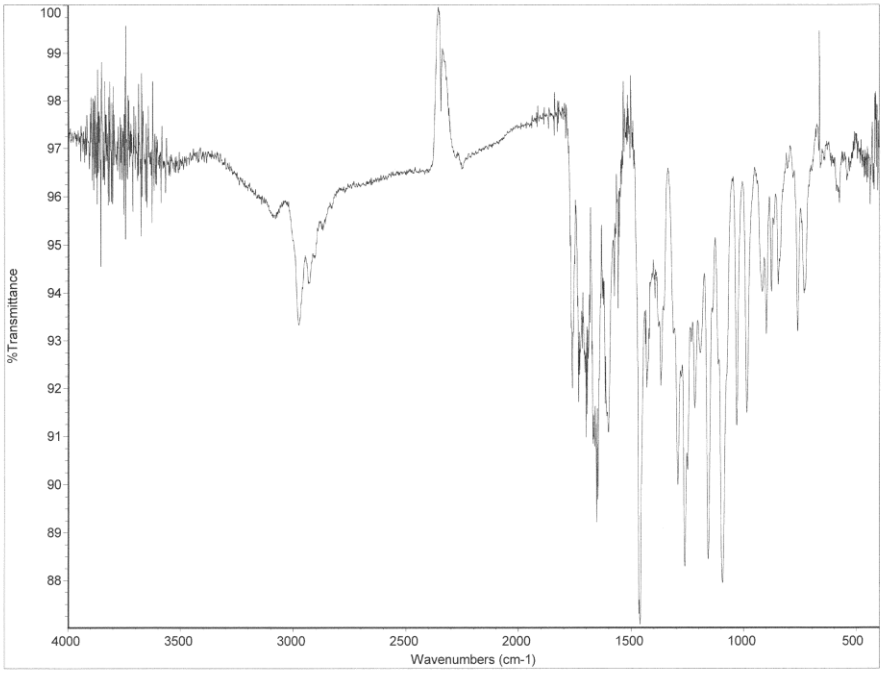
224

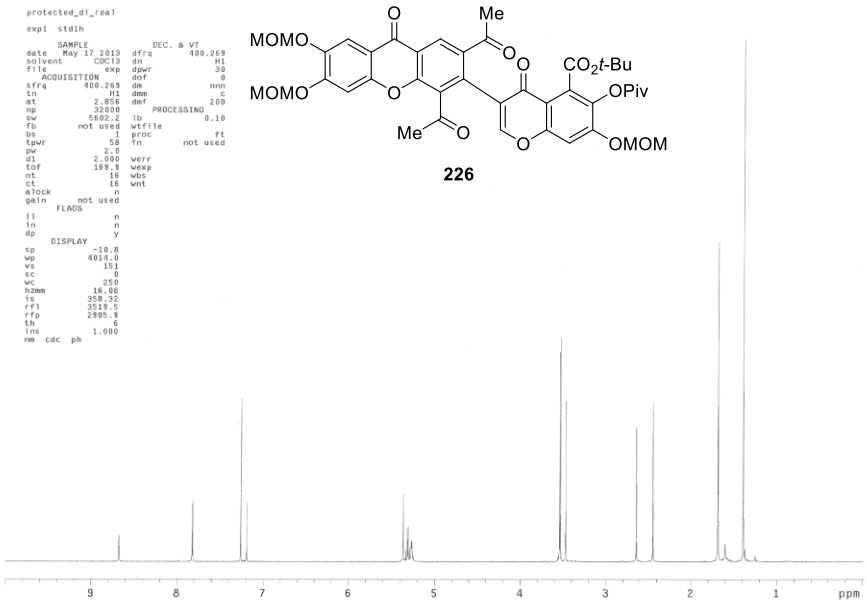

500 MHz nmr1
protected_real_bottom_c13
exp4 Carbon
SAMPLE
date Apr 26 2013
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 60000
ct 58826
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.3
wp 28253.0
rfl 12219.0
rfp 9669.0
rp 196.7
lp -210.7
PLOT
wc 250
sc 0
vs 15510
th 4
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

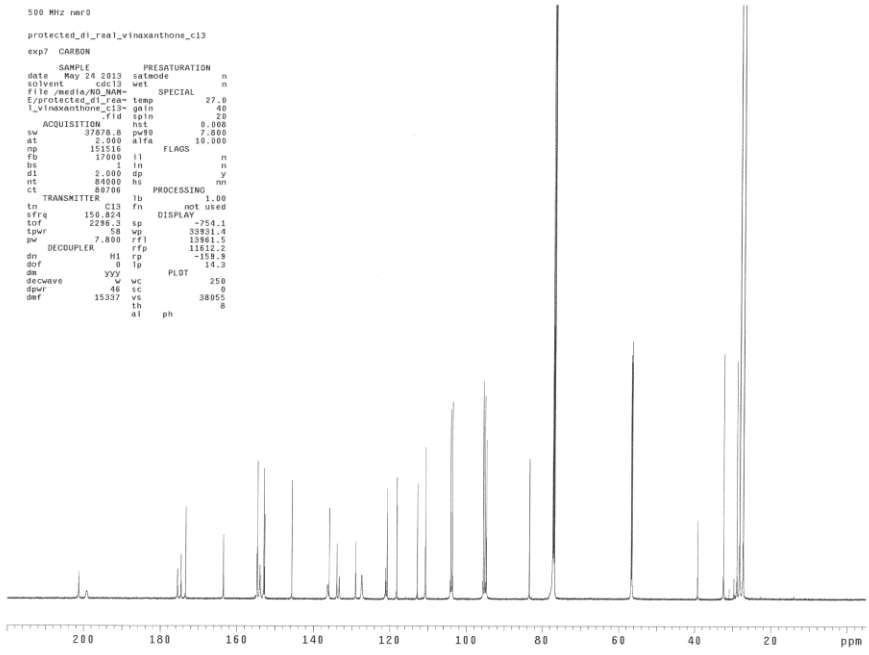

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

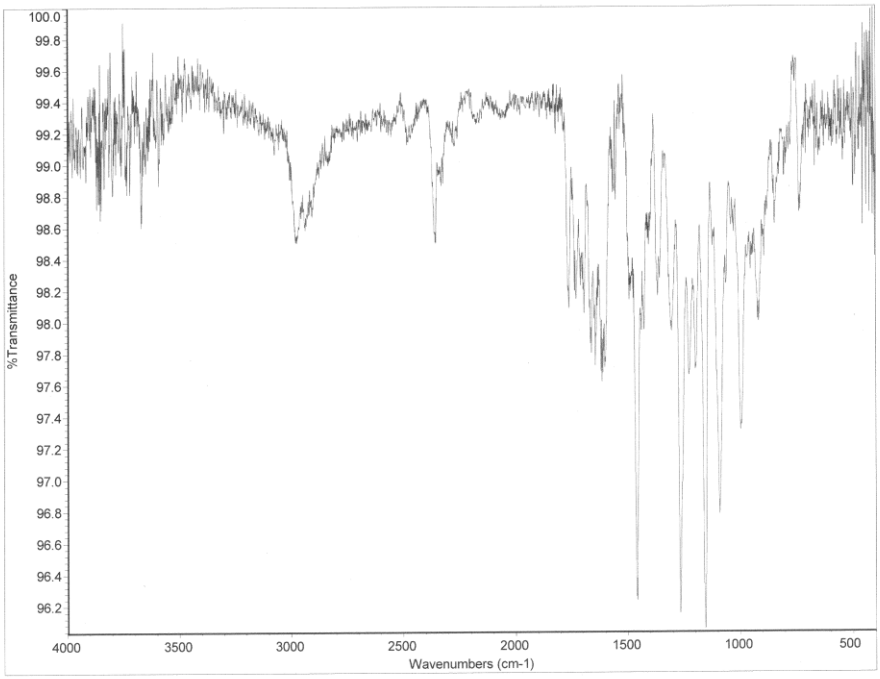

exp1 std1h
SAMPLE
date Feb 6 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.268
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -10.4
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 466.72
rfl 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.268
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
t-BuO2C
PivO
MOMO
Me
Me
O
O
O
O
O
O
225
9
8
7
6
5
4
3
2
1
ppm

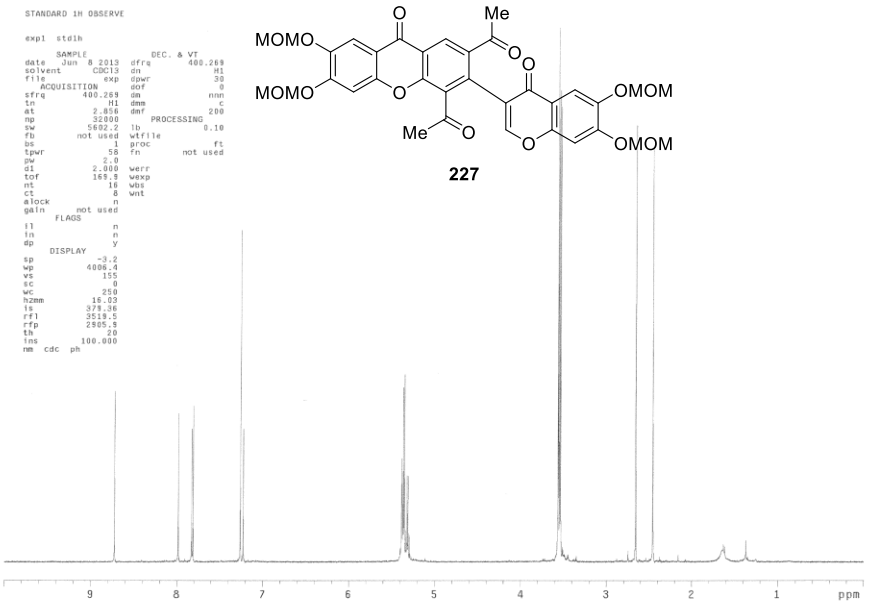

500 MHz nmr0
protected_real_model_c13
exp4 Carbon
SAMPLE
date Feb 22 2013
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.358
np 118154
fb 17000
bs 1
d1 2.000
nt 55000
ct 55000
TRANSMITTER
tn C13
sfrq 125.701
tof 1255.4
tpwr 55
pw 11.600
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 5.00
fn not used
DISPLAY
sp -628.5
wp 28279.6
rfl 11596.7
rfp 9678.0
rp -113.3
lp -259.4
PLOT
wc 250
sc 0
vs 7794
th 5
al ph
200
180
160
140
120
100
80
60
40
20
ppm

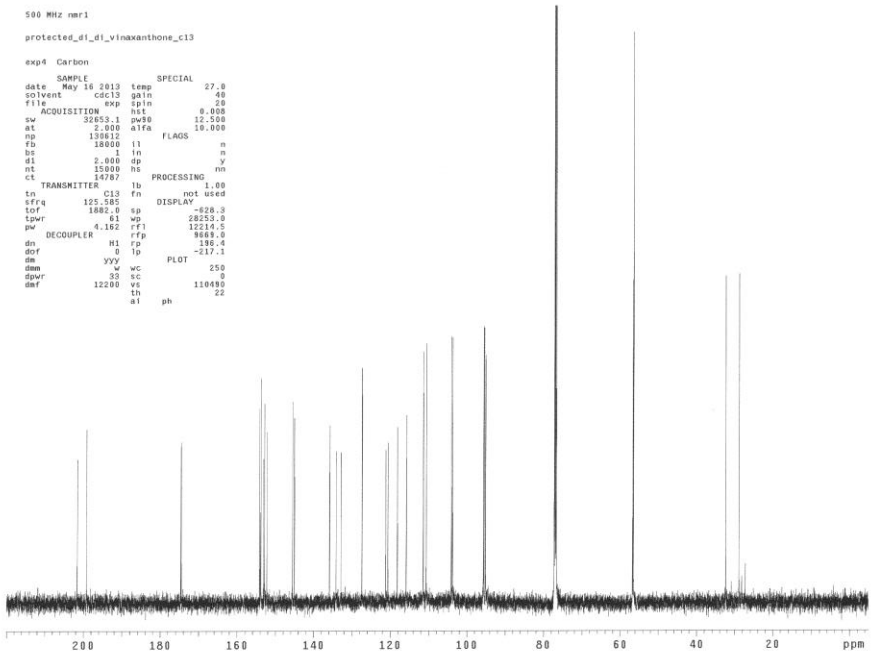

100
99
98
97
96
95
94
93
92
91
90
89
88
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

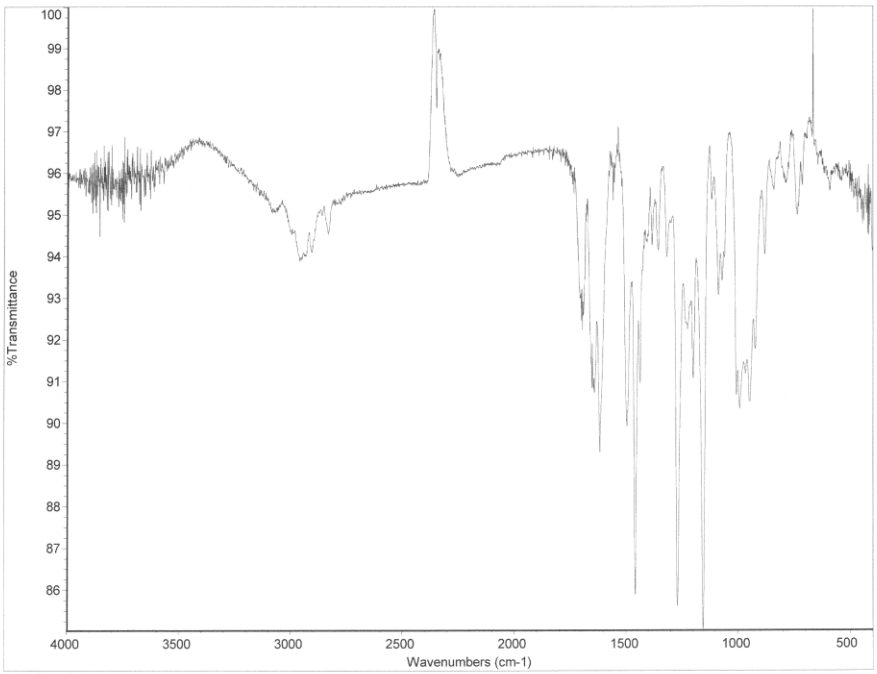

protected_di_real
exp1 stdih
SAMPLE
date May 17 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.8
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -10.8
wp 4014.0
vs 151
sc 0
wc 250
hzmm 16.06
is 358.32
rfl 3519.5
rfp 2805.9
th 6
ins 1.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 58
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
MOMO
Me
Me
CO2t-Bu
OPiv
OMOM
226
9
8
7
6
5
4
3
2
1
ppm

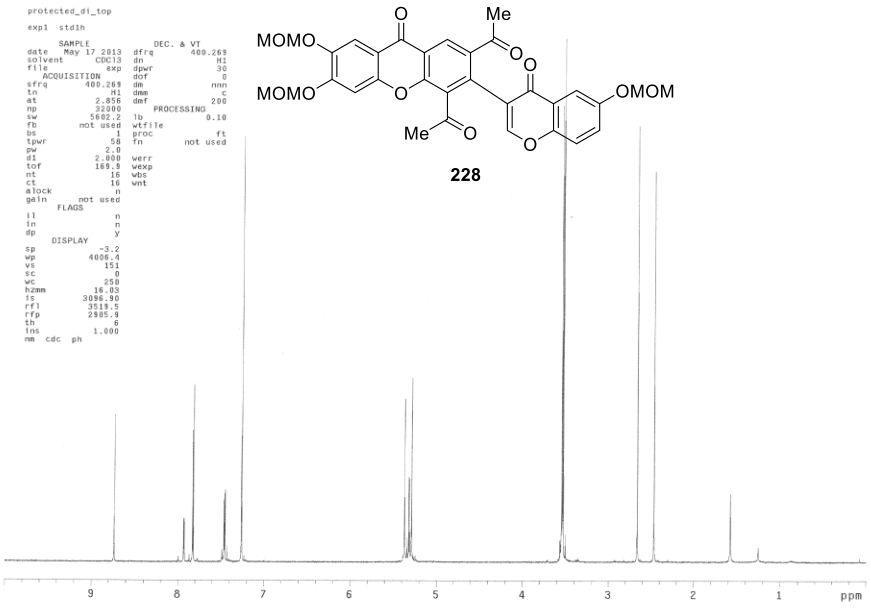

500 MHz nmr0
protected_di_real_vinaxanthone_c13
exp7 CARBON
SAMPLE
date May 24 2013
solvent cdcl3
file /media/NO_NAM~
E/protected_di_rea~
l_vinaxanthone_c13~
.fid
ACQUISITION
sw 37878.8
at 2.000
np 151516
fb 17000
bs 1
d1 2.000
nt 84000
ct 80706
TRANSMITTER
tn C13
sfrq 150.824
tof 2296.3
tpwr 58
pw 7.800
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 46
dmf 15337
PRESATURATION
satmode n
wet n
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 7.800
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -754.1
wp 33931.4
rfl 13861.5
rfp 11612.2
rp -159.9
lp 14.3
PLOT
wc 250
sc 0
vs 38055
th 8
al ph
200
180
160
140
120
100
80
60
40
20
ppm

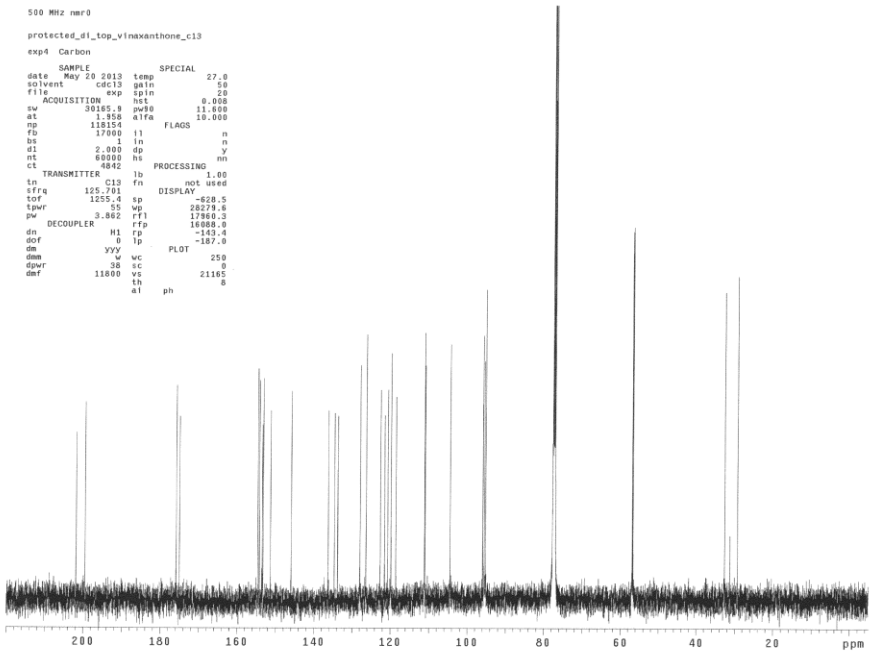

100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
96.6
96.4
96.2
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

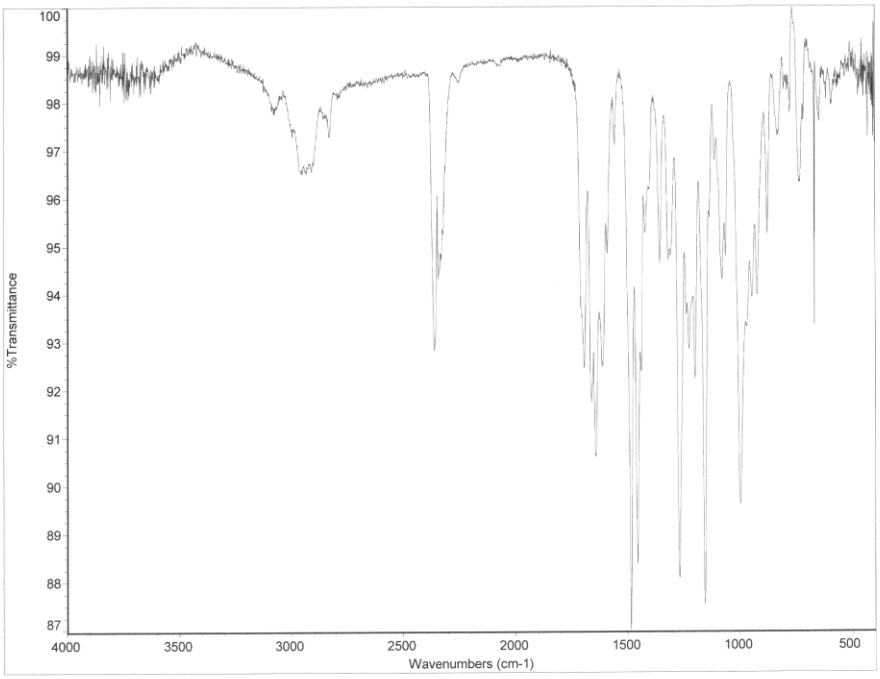

STANDARD 1H OBSERVE
expl stdih
SAMPLE
date Jun 8 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.8
nt 16
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
vs 155
sc 0
wc 250
hzmm 16.03
is 379.96
rf1 3519.5
rfp 2905.8
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
MOMO
Me
Me
OMOM
OMOM
227
9
8
7
6
5
4
3
2
1
ppm

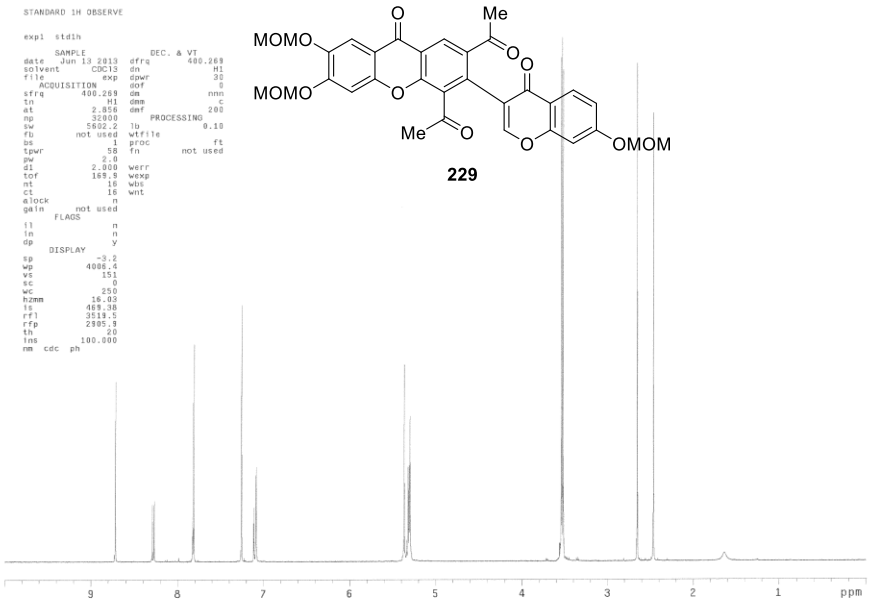

500 MHz nmr1
protected_di_di_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 16 2013
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 15000
ct 14787
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -626.3
wp 28253.0
rf1 12214.5
rfp 9669.0
rp 198.4
lp -217.1
PLOT
wc 250
sc 0
vs 110490
th 22
al ph
200
180
160
140
120
100
80
60
40
20
ppm

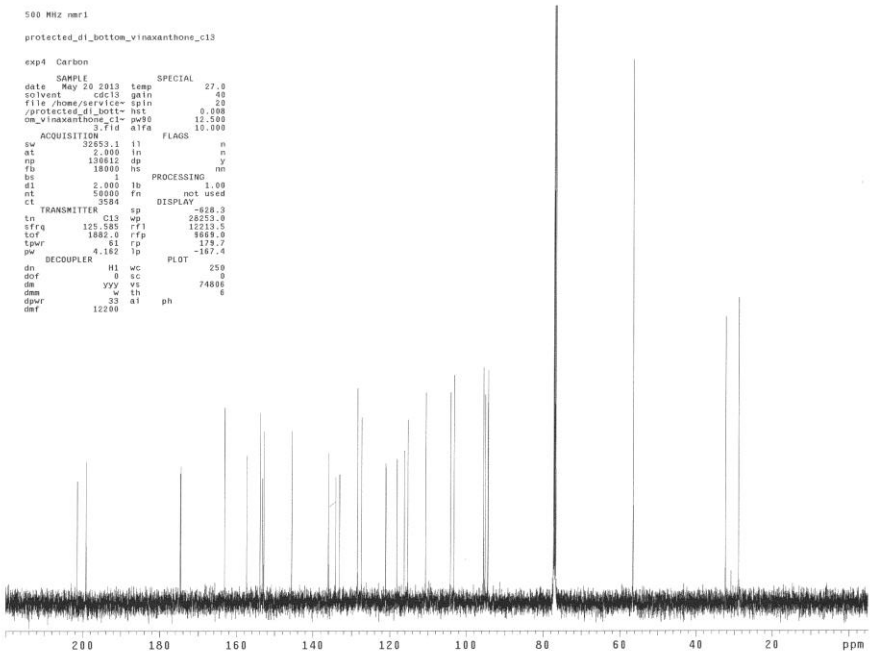

100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

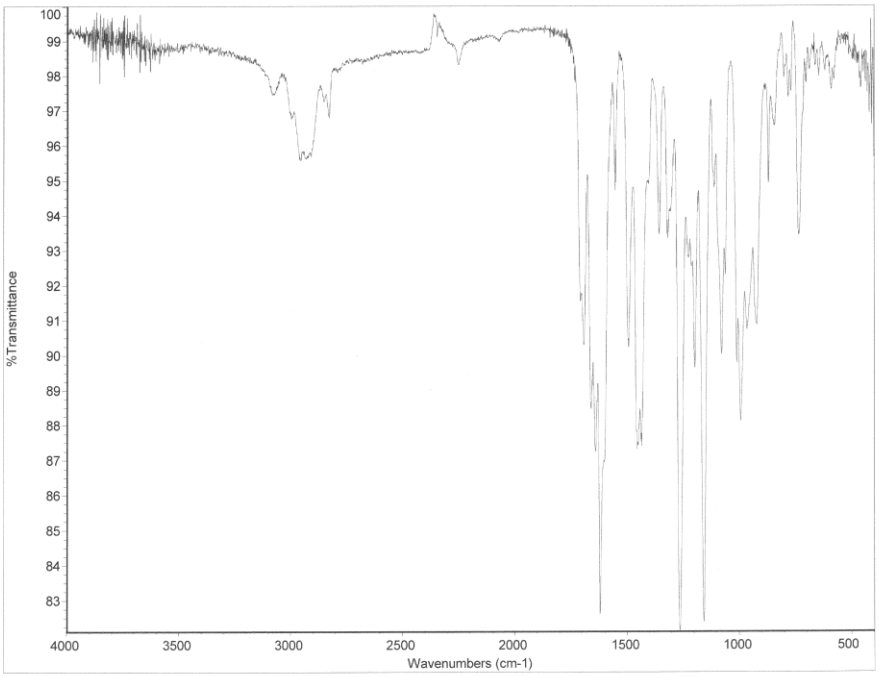

protected_di_top
exp1 std1h
SAMPLE
date May 17 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.5
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 3096.90
rfl 3519.5
rfp 2905.9
th 6
ins 1.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm C
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
MOMO
Me
Me
OMOM
228
9
8
7
6
5
4
3
2
1
ppm

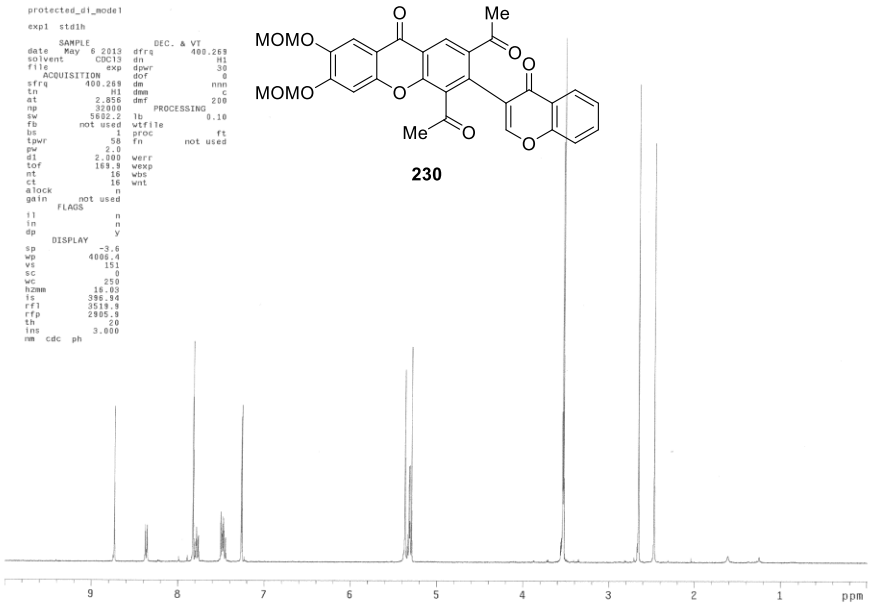

500 MHz nmr0
protected_di_top_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 20 2013
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.956
np 118154
fb 17000
bs 1
d1 2.000
nt 60000
ct 4842
TRANSMITTER
tn C13
sfrq 125.701
tof 1255.4
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.5
wp 28279.6
rfl 17960.3
rfp 16088.0
rp -143.4
lp -187.0
PLOT
wc 250
sc 0
vs 21165
th 8
al ph
200
180
160
140
120
100
80
60
40
20
ppm


100
99
98
97
96
95
94
93
92
91
90
89
88
87
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

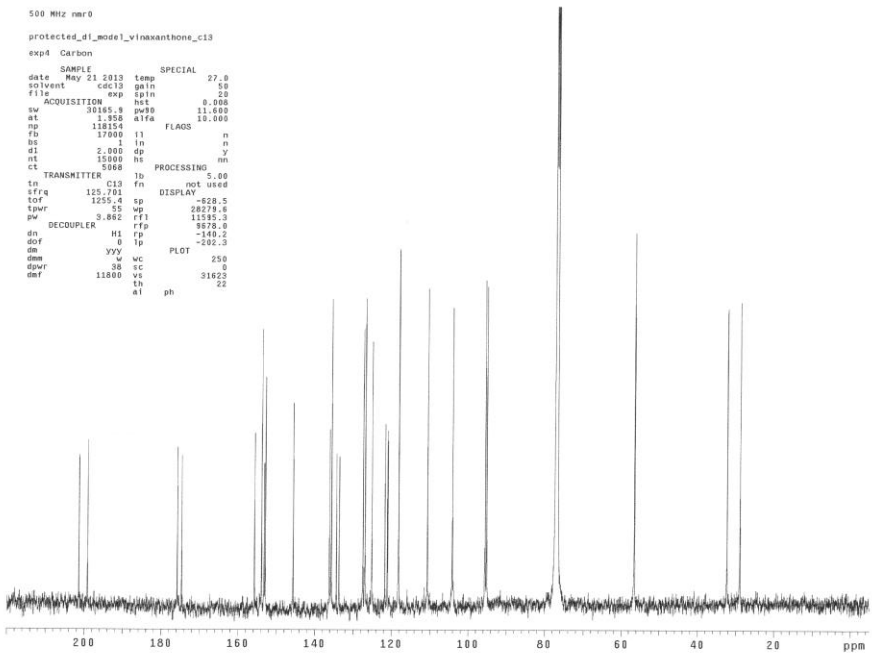

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jun 13 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32800
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
vs 151
sc 0
wc 250
hzmm 16.03
is 469.38
rf1 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.18
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
MOMO
Me
Me
O
OMOM
229
9
8
7
6
5
4
3
2
1
ppm

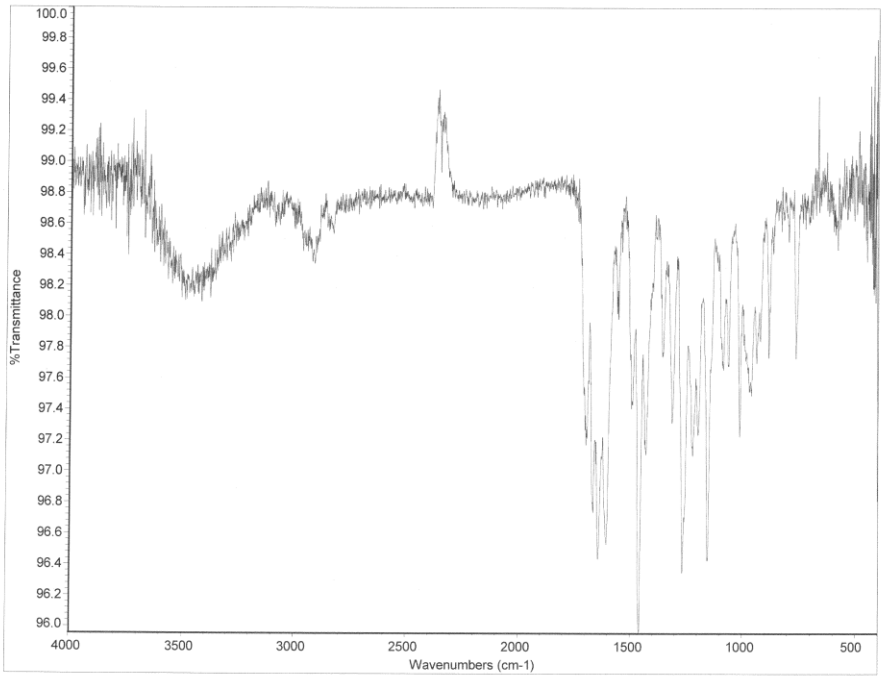

500 MHz nmr1
protected_di_bottom_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 20 2013
solvent cdcl3
file /home/service~
/protected_di_bott~
om_vinaxanthone_c1~
3.fid
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 58000
ct 3584
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.3
wp 28253.0
rf1 12213.5
rfp 9869.0
rp 179.7
lp -167.4
PLOT
wc 250
sc 0
vs 74806
th 6
ai ph
200
180
160
140
120
100
80
60
40
20
ppm

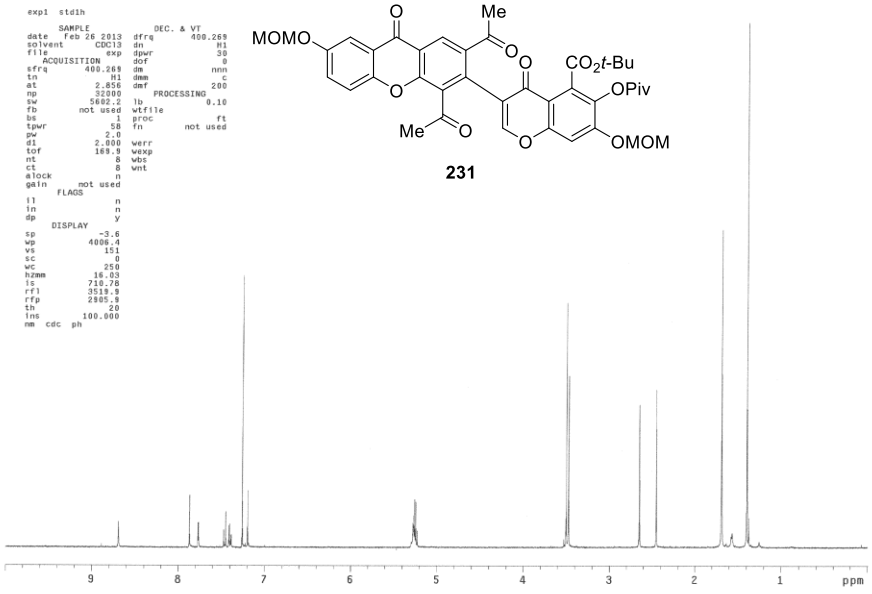

100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

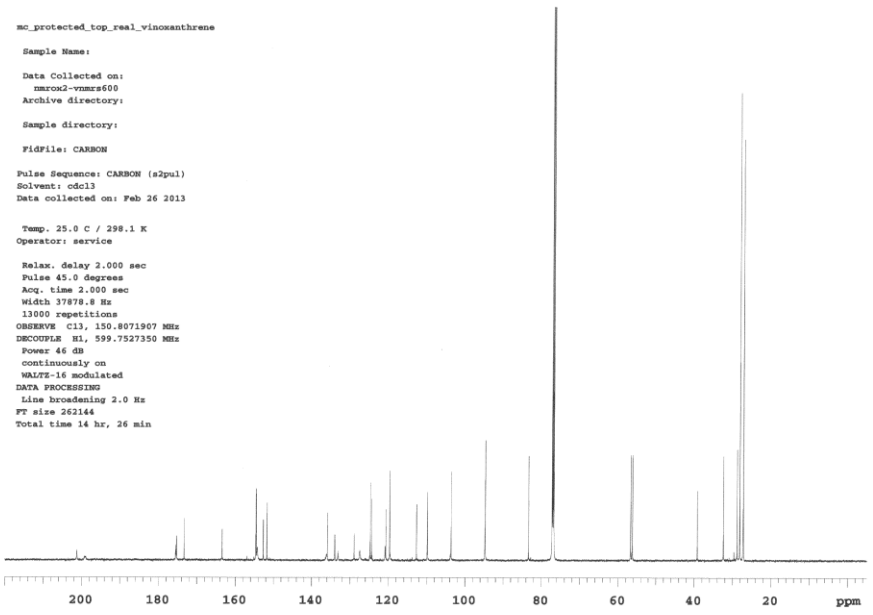

protected_di_model
exp1 std1h
SAMPLE
date May 6 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 56
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 396.94
rf1 3519.9
rfp 2905.9
th 20
ins 3.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
MOMO
Me
Me
O
O
O
O
O
O
O
9
8
7
6
5
4
3
2
1
ppm

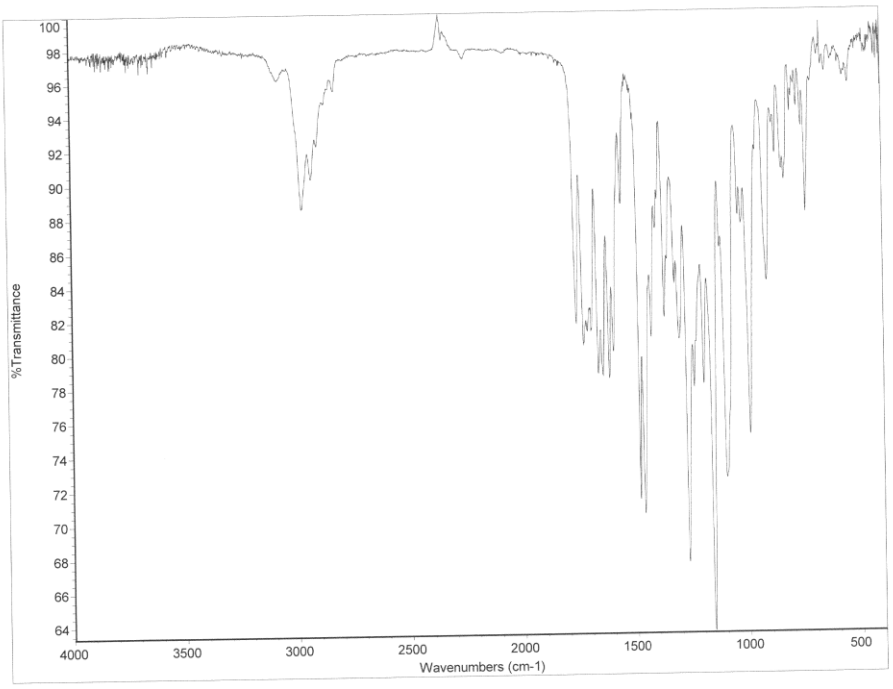
230

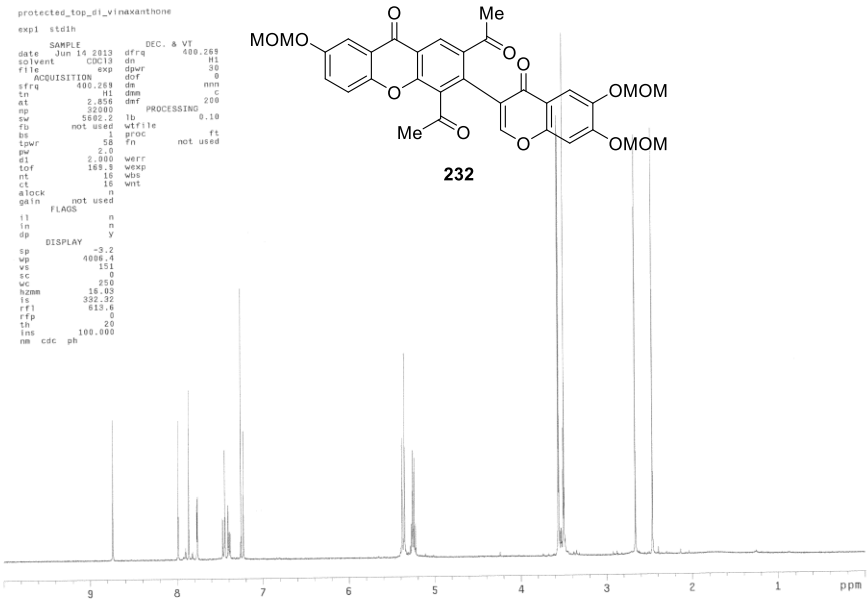

500 MHz nmr0
protected_di_model_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 21 2013
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.358
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 5068
TRANSMITTER
tn C13
sfrq 125.701
tof 1255.4
tpwr 55
pw 9.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 5.00
fn not used
DISPLAY
sp -628.5
wp 28279.8
rf1 11595.3
rfp 9578.0
rp -140.2
lp -202.3
PLOT
wc 250
sc 0
vs 31623
th 22
al ph
200
180
160
140
120
100
80
60
40
20
ppm

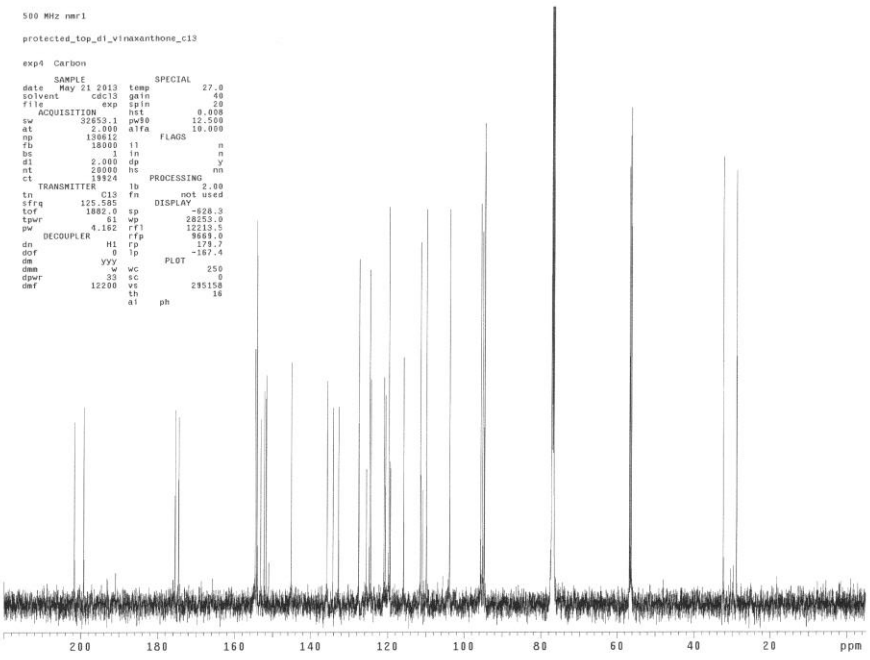

100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
96.6
96.4
96.2
96.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

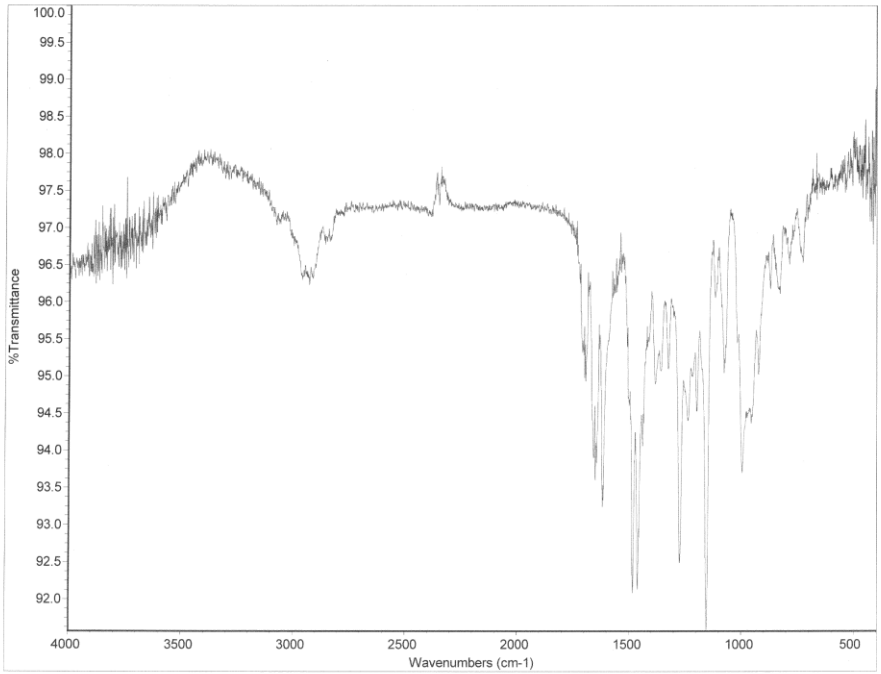

exp1 std1h
SAMPLE
date Feb 26 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 8
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 710.78
rfl 3519.9
rfp 2805.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
Me
Me
CO2t-Bu
OPiv
OMOM
231
9
8
7
6
5
4
3
2
1
ppm

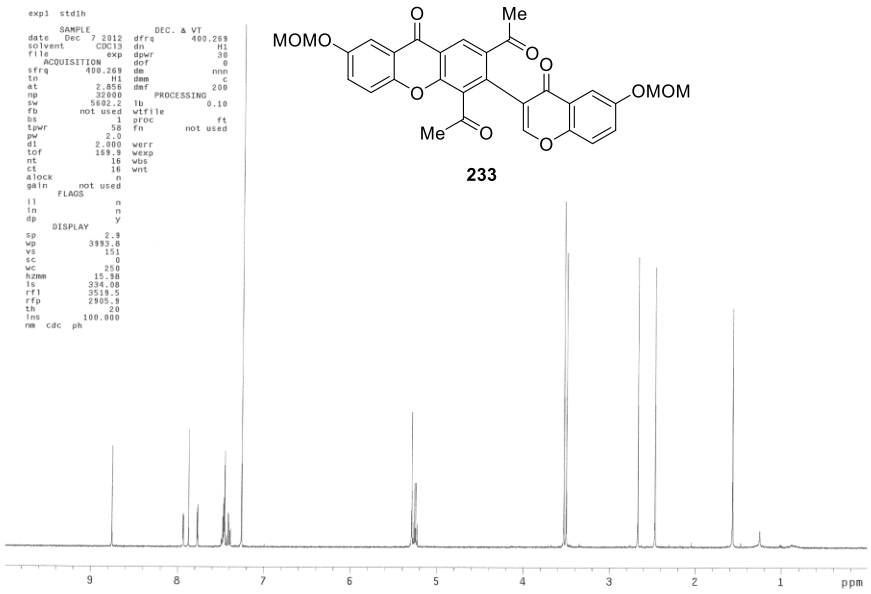

mc_protected_top_real_vinoxanthrene
Sample Name:
Data Collected on:
nmrox2-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 26 2013
Temp. 25.0 C / 298.1 K
Operator: service
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.000 sec
Width 37878.8 Hz
13000 repetitions
OBSERVE C13, 150.8071907 MHz
DECOUPLE H1, 599.7527350 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 262144
Total time 14 hr, 26 min
200
180
160
140
120
100
80
60
40
20
ppm

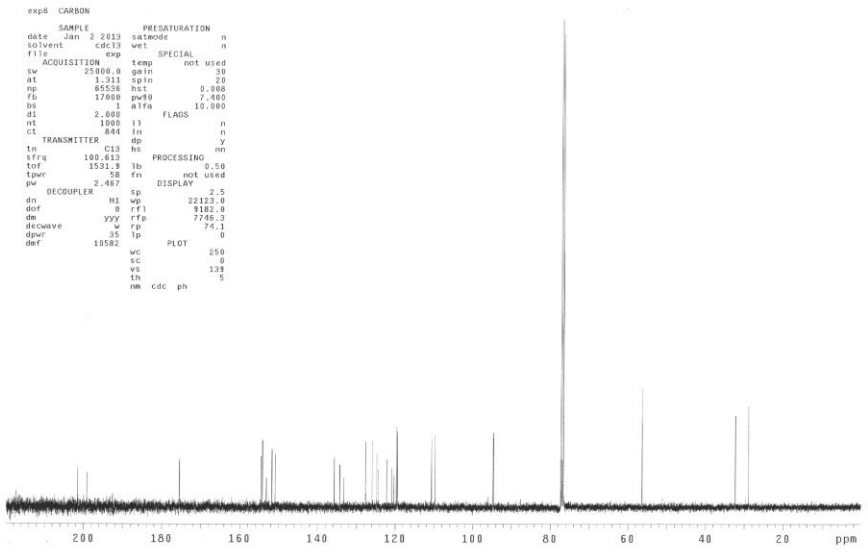

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

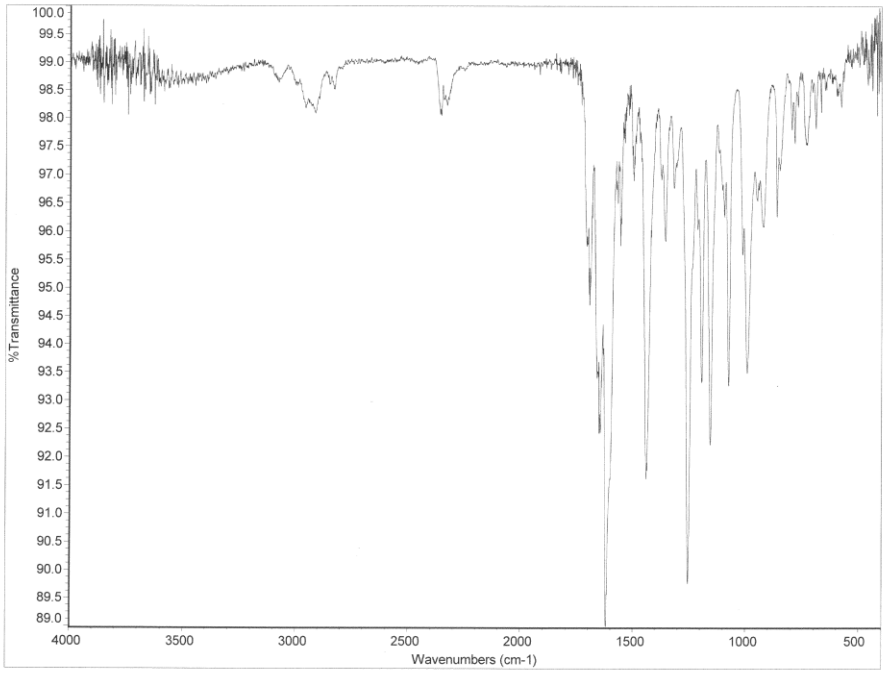

protected_top_di_vinaxanthone
exp1 std1h
SAMPLE
date Jun 14 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.5
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
vs 151
sc 0
wc 250
hzmm 16.03
is 332.32
rf1 613.6
rfp 0
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 38
dof 0
dm nnn
dmm C
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
Me
OMOM
OMOM
232
9
8
7
6
5
4
3
2
1
ppm

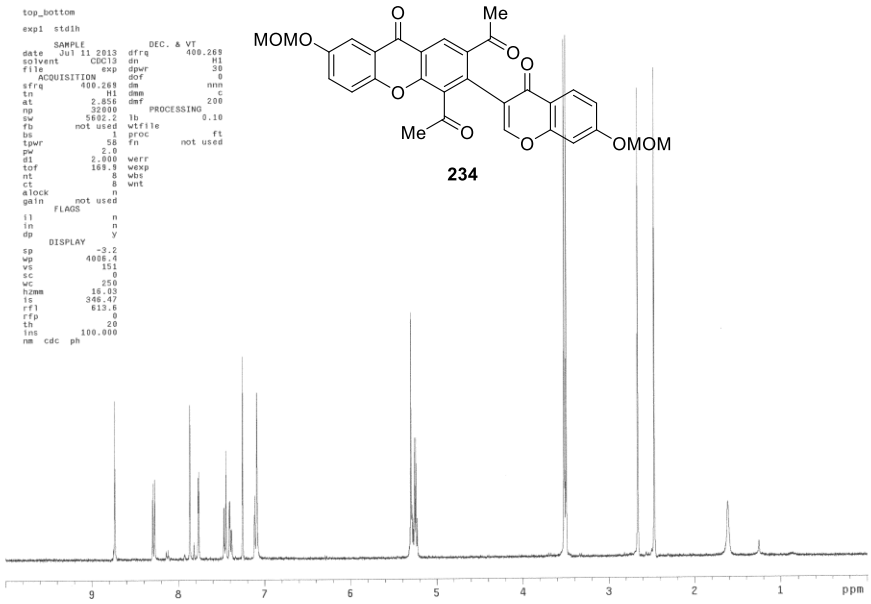

500 MHz nmr1
protected_top_di_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 21 2013
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 28000
ct 19924
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 2.00
fn not used
DISPLAY
sp -628.3
wp 28253.0
rf1 12213.5
rfp 9669.0
rp 179.7
lp -167.4
PLOT
wc 250
sc 0
vs 295158
th 16
al ph
200
180
160
140
120
100
80
60
40
20
ppm

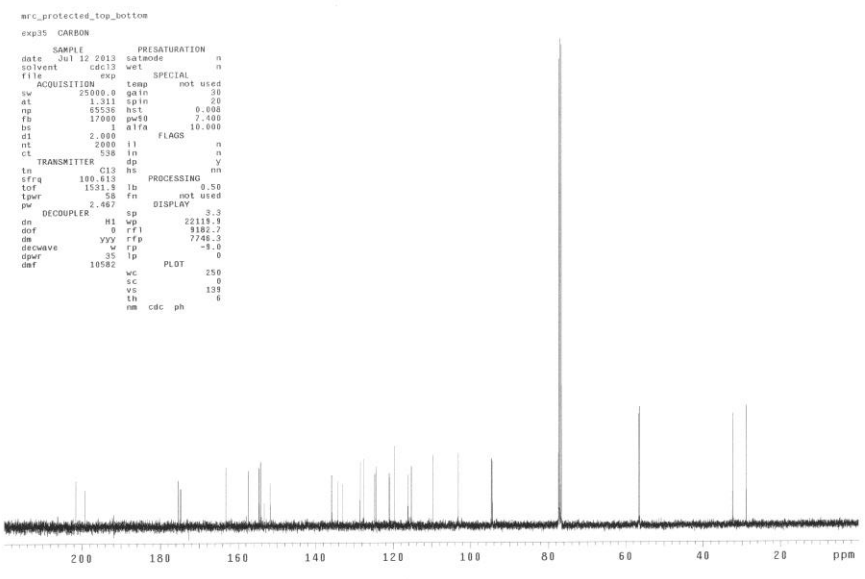

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

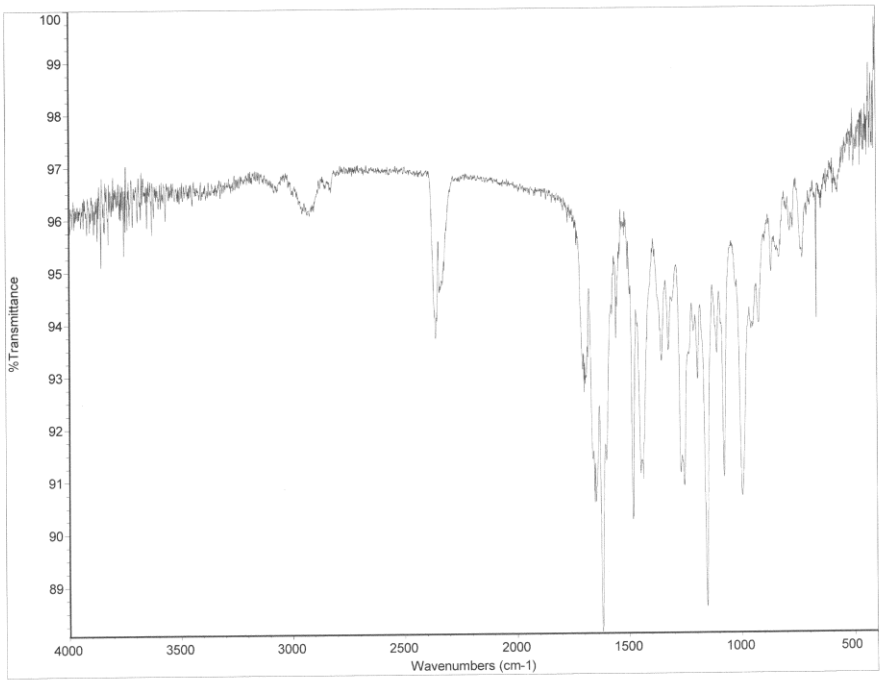

exp1 stdlh
SAMPLE
date Dec 7 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 2.9
wp 3993.8
vs 151
sc 0
wc 250
hzmm 15.98
is 334.08
rfl 3519.5
rfp 2905.9
th 20
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
Me
Me
OMOM
233
9
8
7
6
5
4
3
2
1
ppm

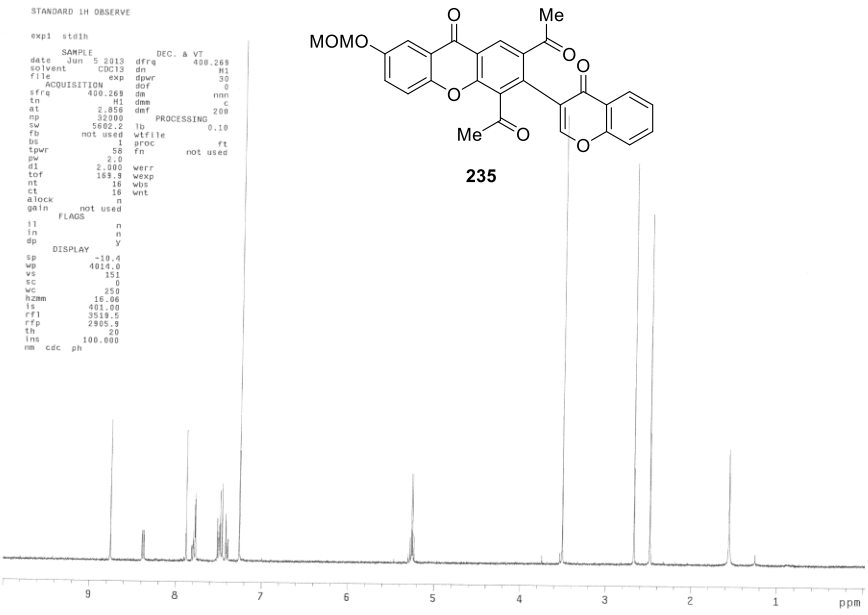

exp8 CARBON
SAMPLE
date Jan 2 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 844
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 2.5
wp 22123.0
rfl 9182.0
rfp 7746.3
rp 74.1
lp 0
PLOT
wc 250
sc 0
vs 139
th 5
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

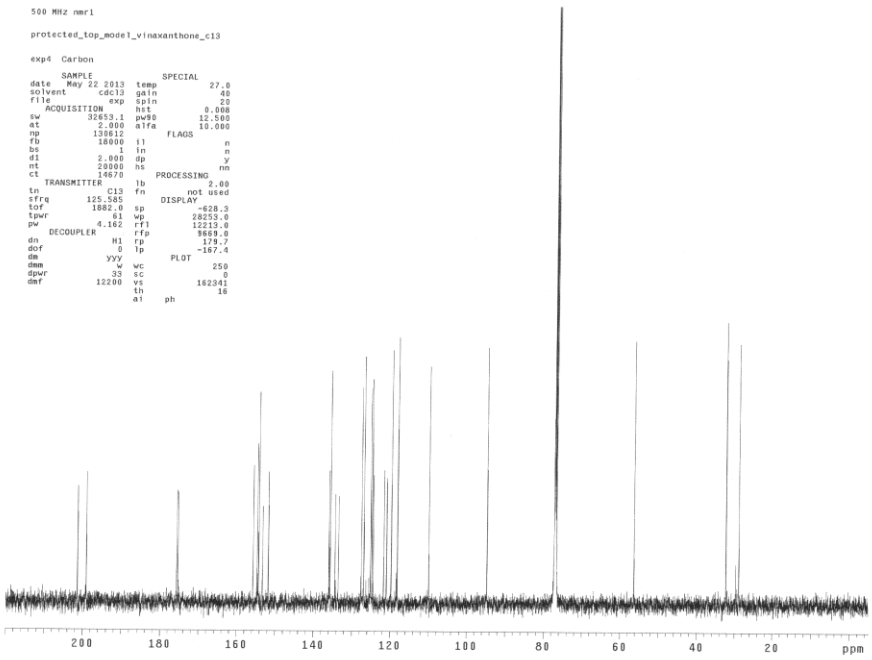

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
90.0
89.5
89.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

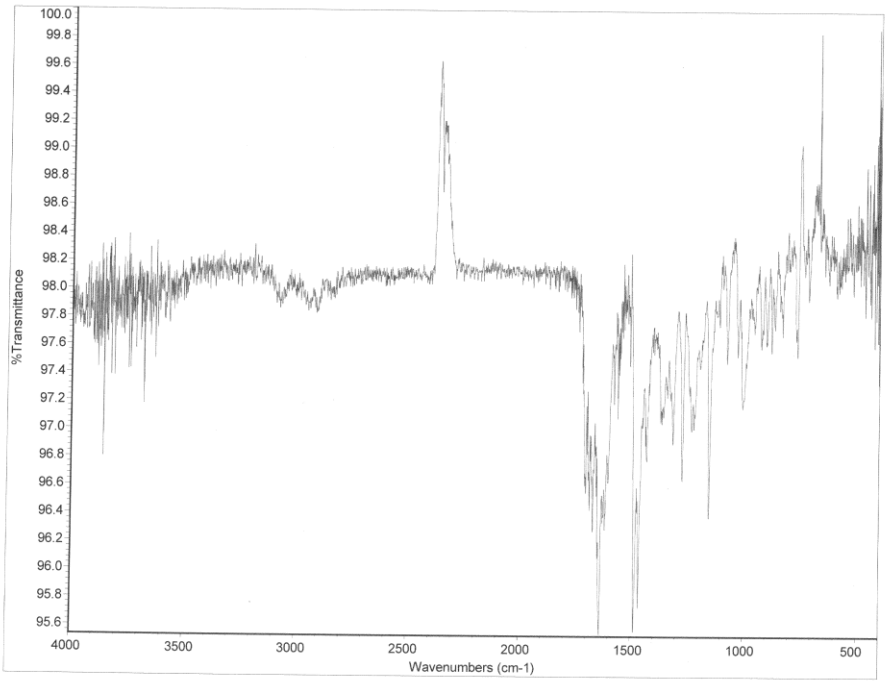

top_bottom
exp1 stdih
SAMPLE
date Jul 11 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.268
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 8
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4086.4
vs 151
sc 0
wc 250
hzmm 16.03
is 346.47
rfl 613.6
rfp 0
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
Me
Me
OMOM
234
9
8
7
6
5
4
3
2
1
ppm

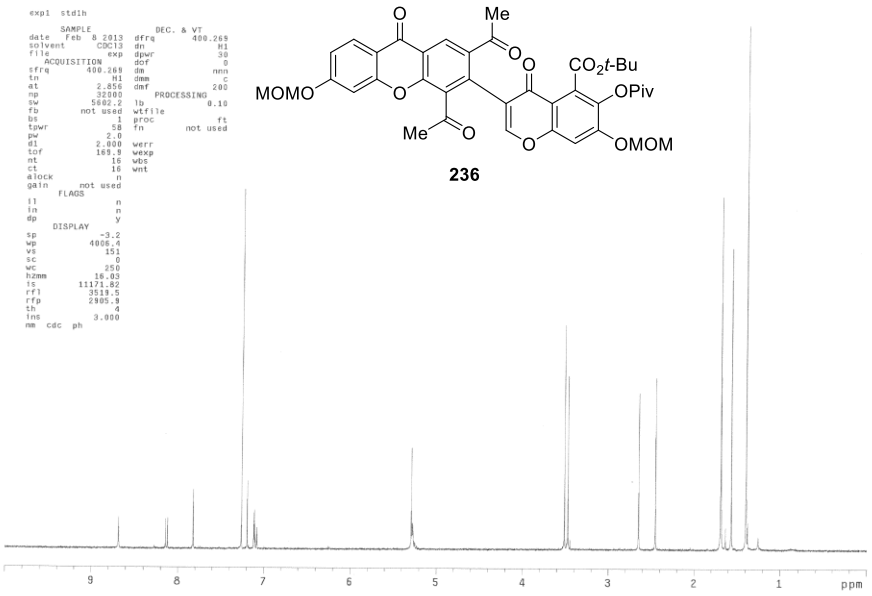

mrc_protected_top_bottom
exp35 CARBON
SAMPLE
date Jul 12 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 2000
ct 538
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp Y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 3.3
wp 22119.9
rfl 9182.7
rfp 7746.3
rp -5.0
lp 0
PLOT
wc 250
sc 0
vs 139
th 6
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

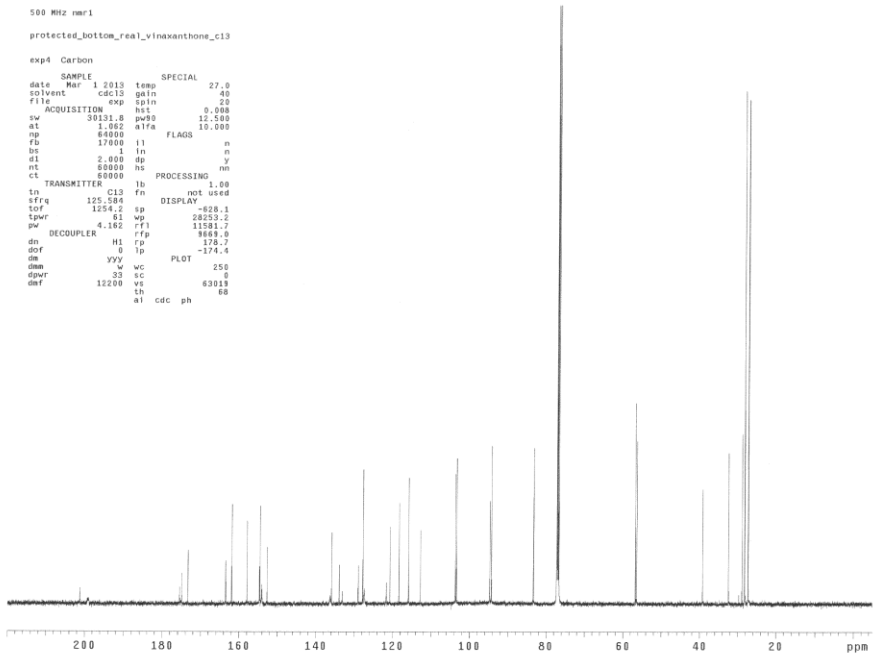

100
99
98
97
96
95
94
93
92
91
90
89
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

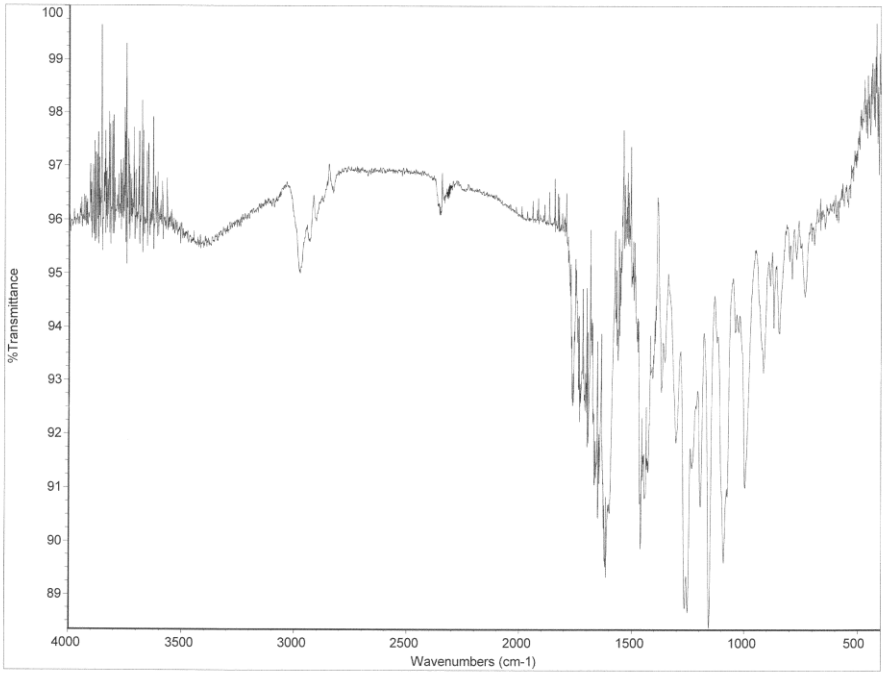

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jun 5 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 163.8
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -18.4
wp 4014.0
vs 151
sc 0
wc 250
hzmm 16.06
is 401.00
rf1 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
Me
Me
O
O
O
O
O
O
235
9
8
7
6
5
4
3
2
1
ppm

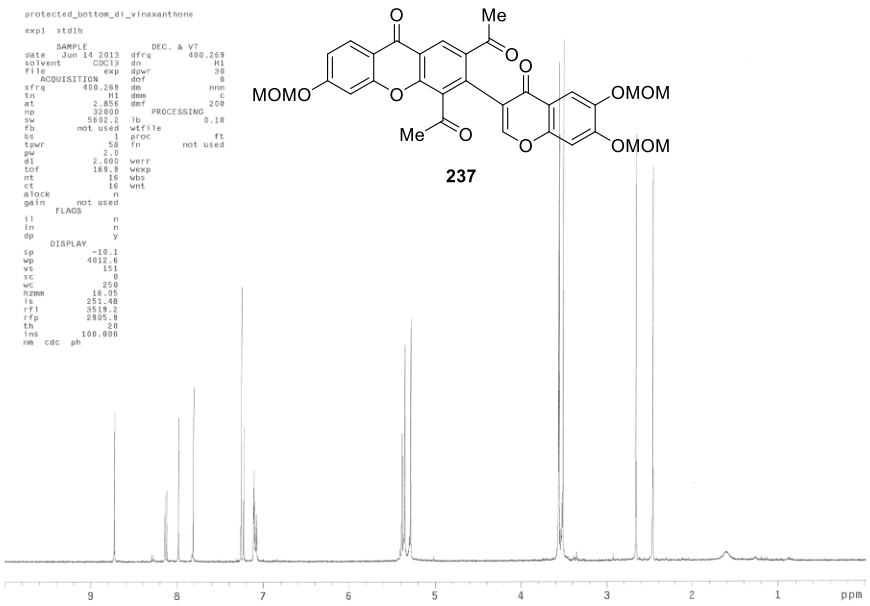

500 MHz nmr1
protected_top_model_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 22 2013
solvent cdcl3
file exp
ACQUISITION
sw 32853.1
at 2.000
np 138612
fb 10000
bs 1
d1 2.000
nt 20000
ct 14670
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 2.00
fn not used
DISPLAY
sp -628.3
wp 28253.0
rf1 12213.0
rfp 9669.0
rp 179.7
lp -167.4
PLOT
wc 250
sc 0
vs 162341
th 16
al ph
200
180
160
140
120
100
80
60
40
20
ppm

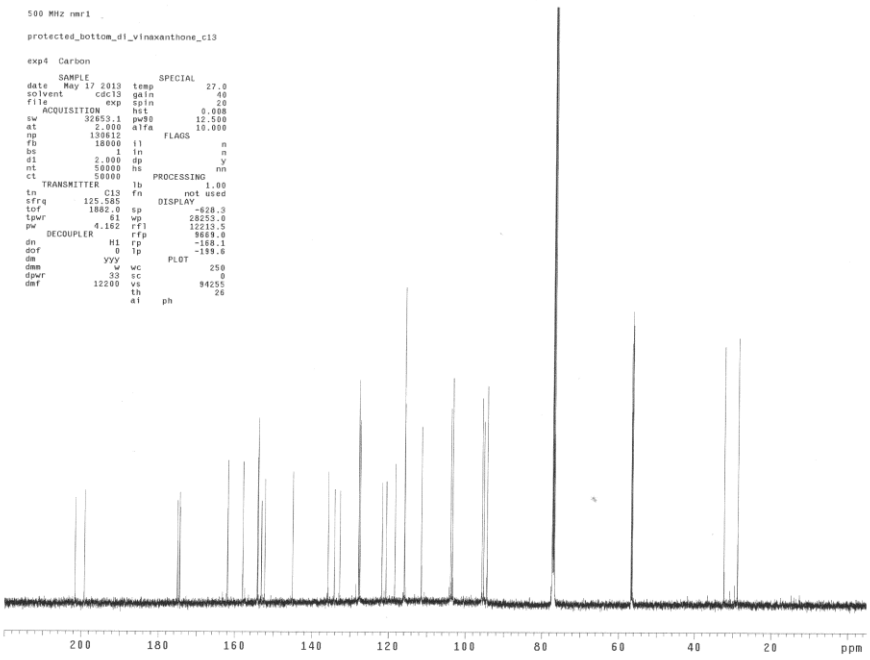

100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
96.6
96.4
96.2
96.0
95.8
95.6
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

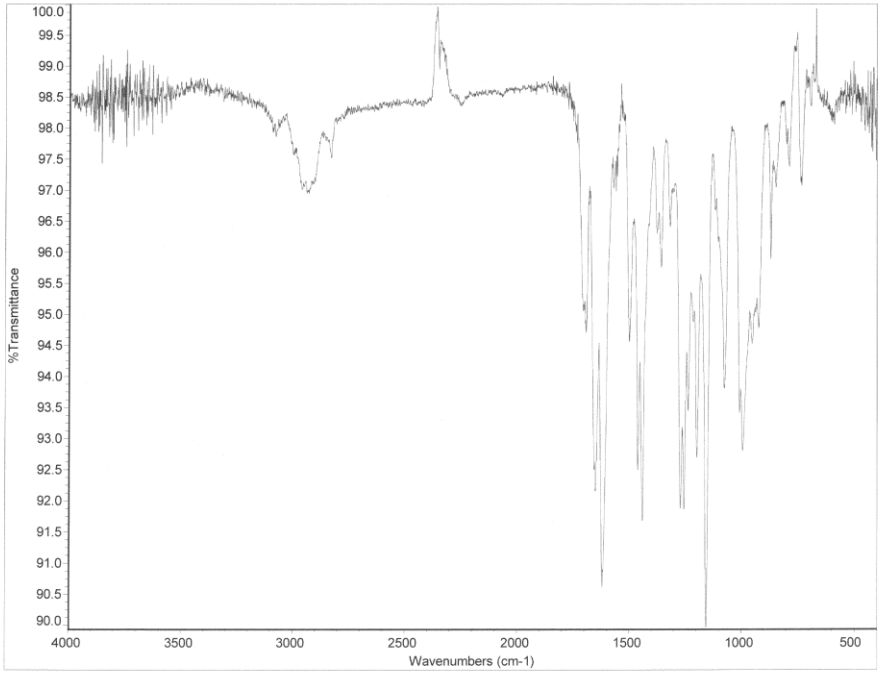

exp1 stdlh
SAMPLE
date Feb 8 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
fs 11171.82
rf1 3519.5
rfp 2905.9
th 4
ins 3.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
O
O
O
CO2t-Bu
MOMO
O
OPiv
Me
O
O
OMOM
236
9
8
7
6
5
4
3
2
1
ppm

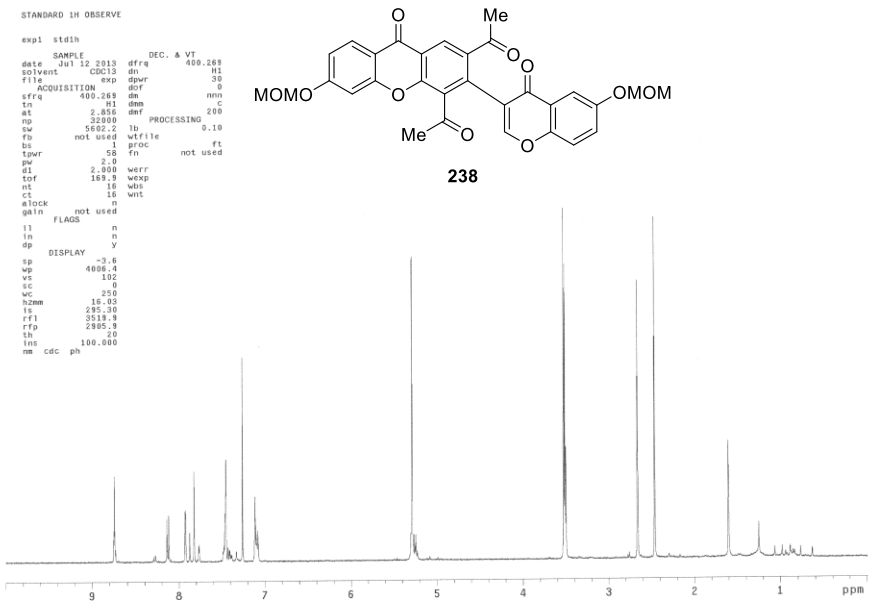

500 MHz nmr1
protected_bottom_real_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Mar 1 2013
solvent cdcl3
file exp
ACQUISITION
sw 30131.8
at 1.062
np 64000
fb 17000
bs 1
d1 2.000
nt 80000
ct 60000
TRANSMITTER
tn C13
sfrq 125.584
tof 1254.2
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.1
wp 28253.2
rf1 11581.7
rfp 9669.0
rp 178.7
lp -174.4
PLOT
wc 250
sc 0
vs 63019
th 68
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm


100
99
98
97
96
95
94
93
92
91
90
89
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

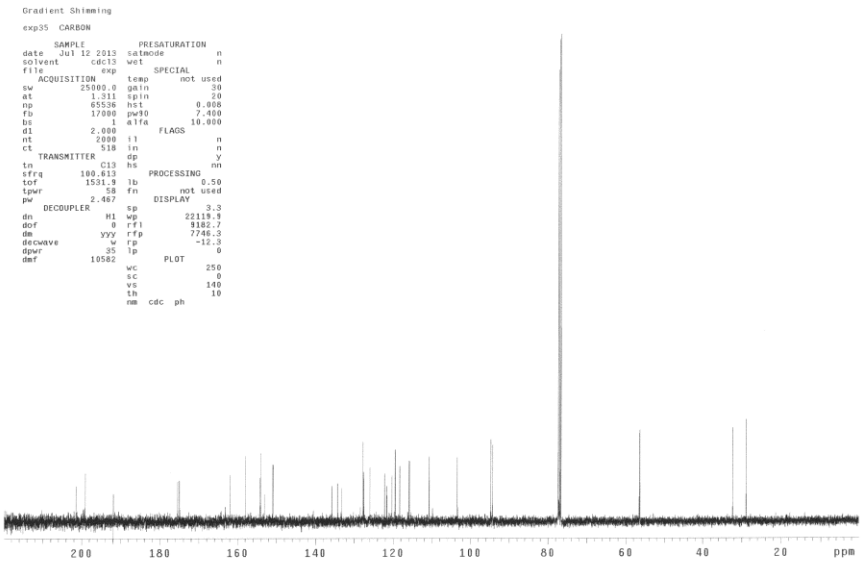

protected_bottom_di_vinaxanthone
exp1 std1h
SAMPLE
date Jun 14 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.8
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -10.1
wp 4012.6
vs 151
sc 0
wc 250
hzmm 16.05
is 251.48
rf1 3519.2
rfp 2905.9
th 20
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
O
Me
O
O
MOMO
O
OMOM
Me
O
O
OMOM
237
9
8
7
6
5
4
3
2
1
ppm

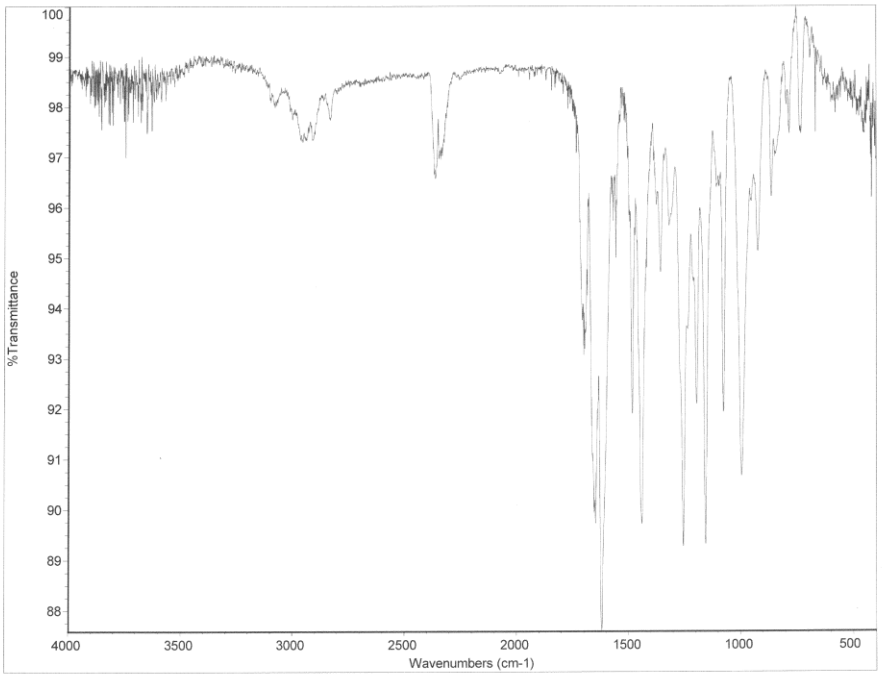

500 MHz nmr1
protected_bottom_di_vinaxanthone_c13
exp4 Carbon
SAMPLE
date May 17 2013
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 50000
ct 30000
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.3
wp 28253.0
rf1 12213.5
rfp 9669.0
rp -168.1
lp -199.6
PLOT
wc 250
sc 0
vs 94255
th 26
at
ph
200
180
160
140
120
100
80
60
40
20
ppm

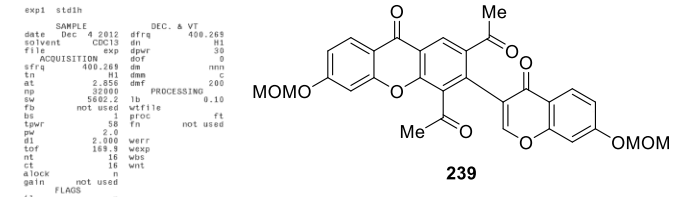

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
90.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jul 12 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 102
sc 0
wc 250
hzmm 16.03
is 295.30
rfl 3519.9
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MOMO
OMOM
Me
Me
O
O
O
O
O
O
9
8
7
6
5
4
3
2
1
ppm

238

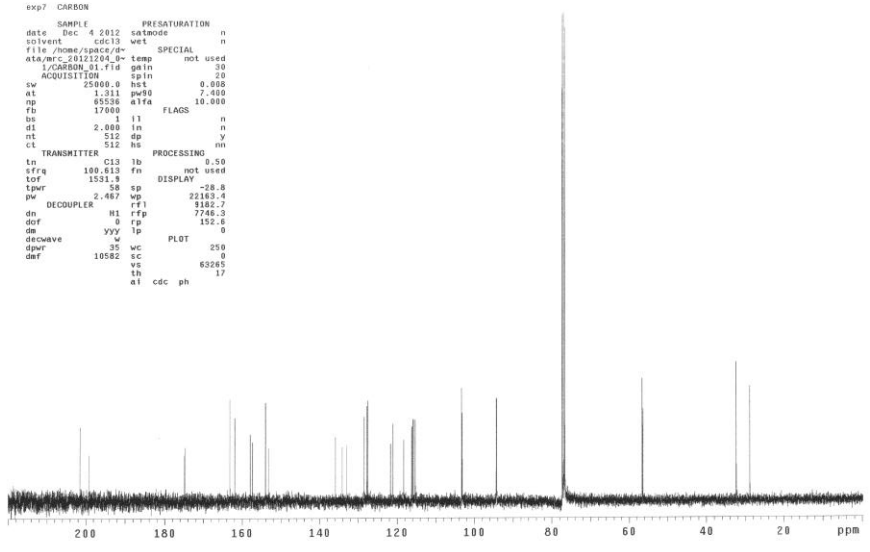

Gradient Shimming
exp35 CARBON
SAMPLE
date Jul 12 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 2000
ct 518
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp 3.3
wp 22119.9
rfl 9182.7
rfp 7746.3
rp -12.3
lp 0
PLOT
wc 250
sc 0
vs 140
th 10
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

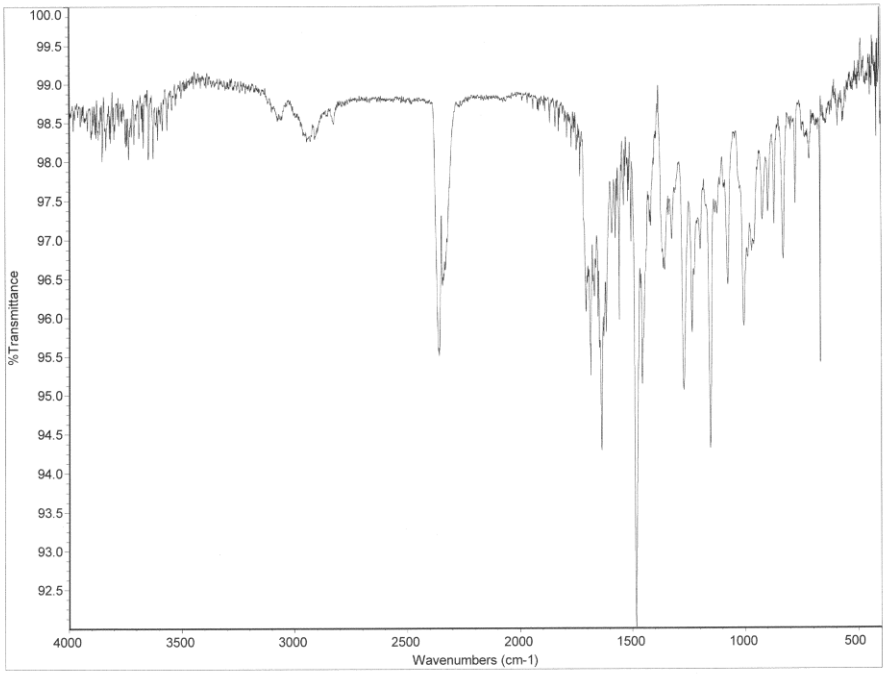

100
99
98
97
96
95
94
93
92
91
90
89
88
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

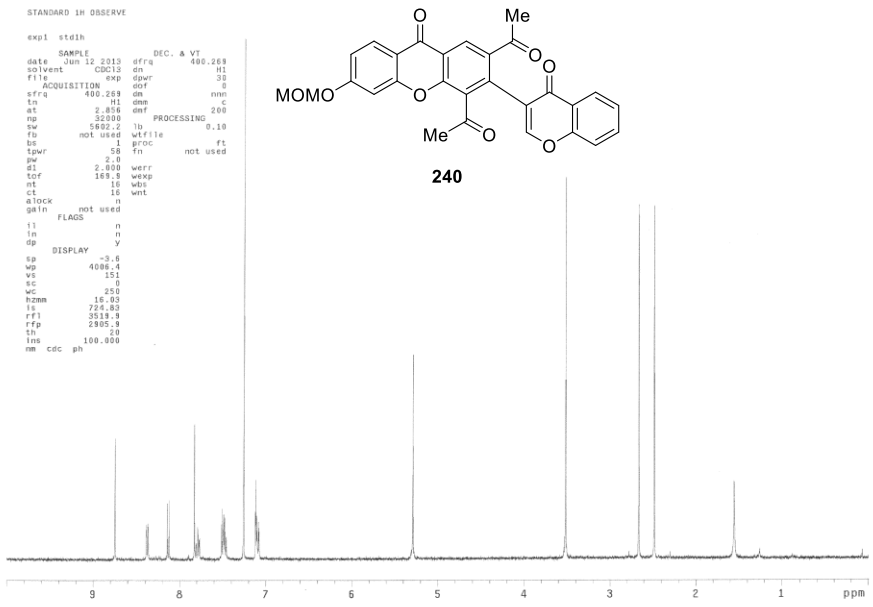

O
Me
O
O
MOMO
O
Me
O
O
OMOM

239

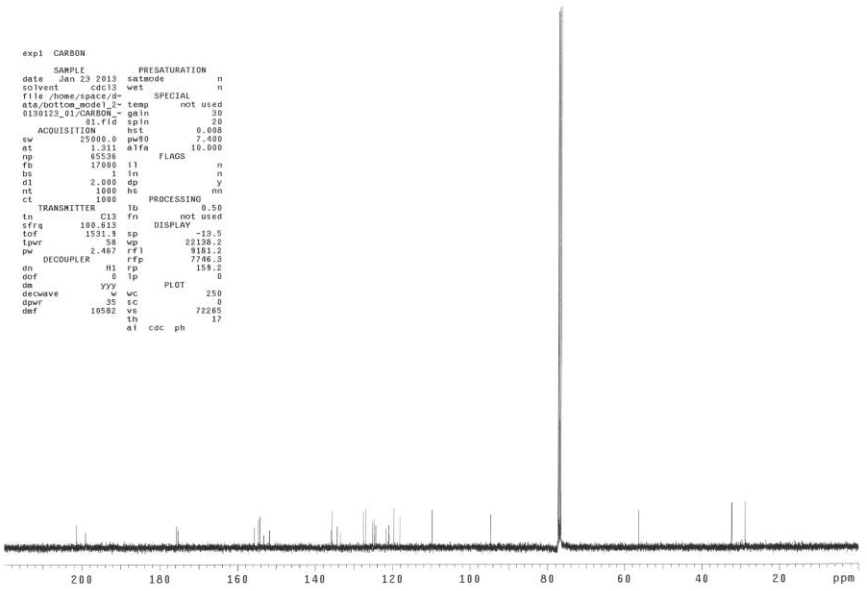
exp1 stdih
SAMPLE
date Dec 4 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -4.3
wp 4000.3
vs 76
sc 0
wc 250
hzmm 16.00
is 662.31
rfl 3519.5
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
9
8
7
6
5
4
3
2
1
ppm

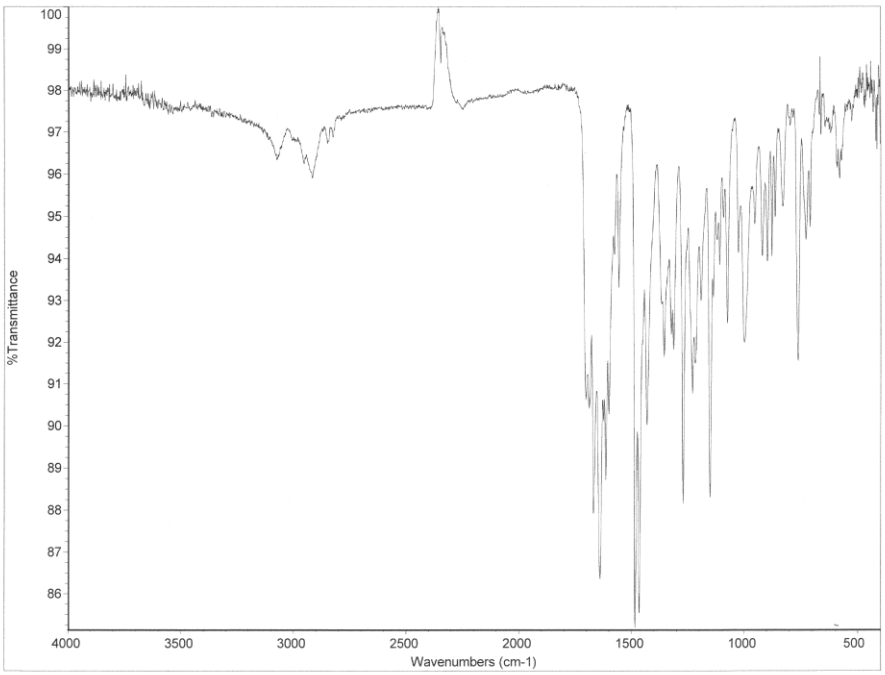

exp7 CARBON
SAMPLE
date Dec 4 2012
solvent cdcl3
file /home/space/d~
ata/mrc_20121204_0~
1/CARBON_01.ffd
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 512
ct 512
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
dmwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -28.8
wp 22163.4
rfl 9182.7
rfp 7746.3
rp 152.6
lp 0
PLOT
wc 250
sc 0
vs 63265
th 17
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

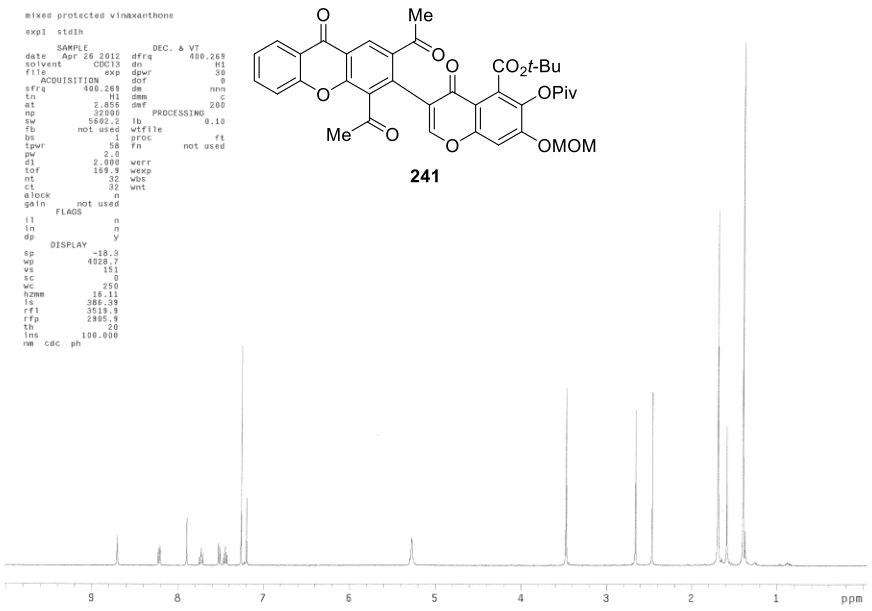

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

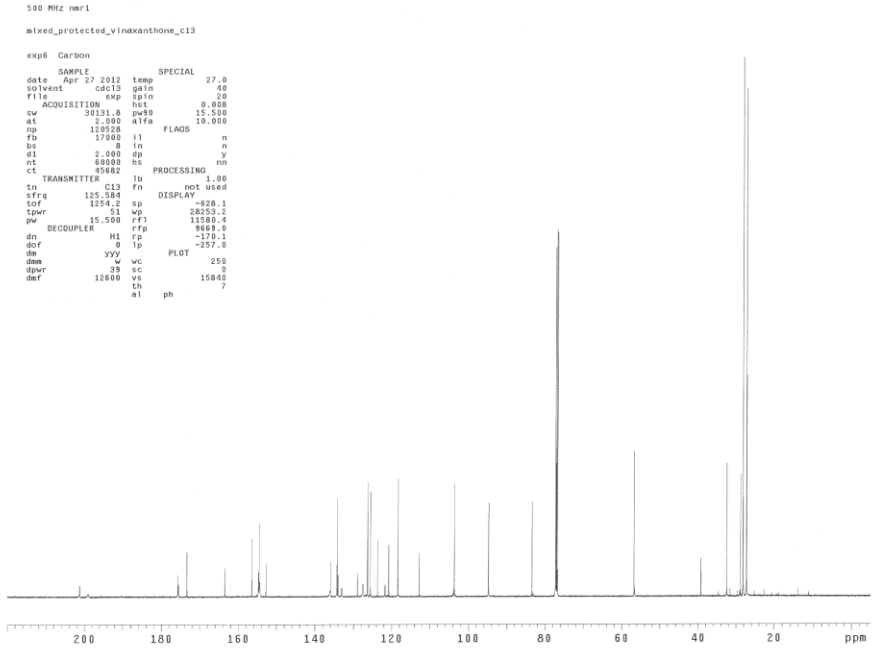

STANDARD 1H OBSERVE
exp1 stdlh
SAMPLE
date Jun 12 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4086.4
vs 151
sc 0
wc 250
hzmm 15.03
is 724.83
rf1 3519.9
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
O
Me
O
O
MOMO
O
Me
O
O
9
8
7
6
5
4
3
2
1
ppm

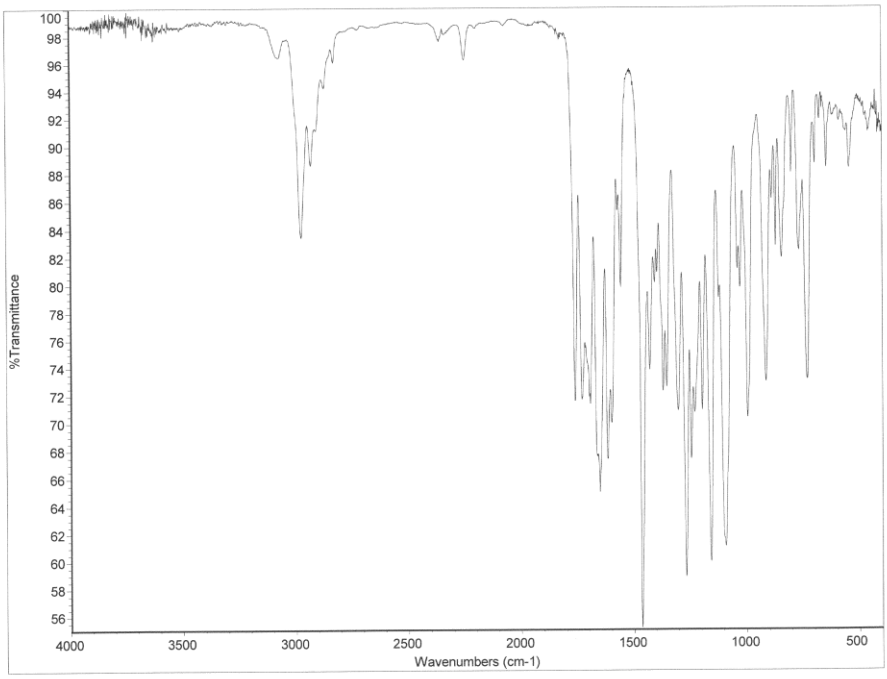
240

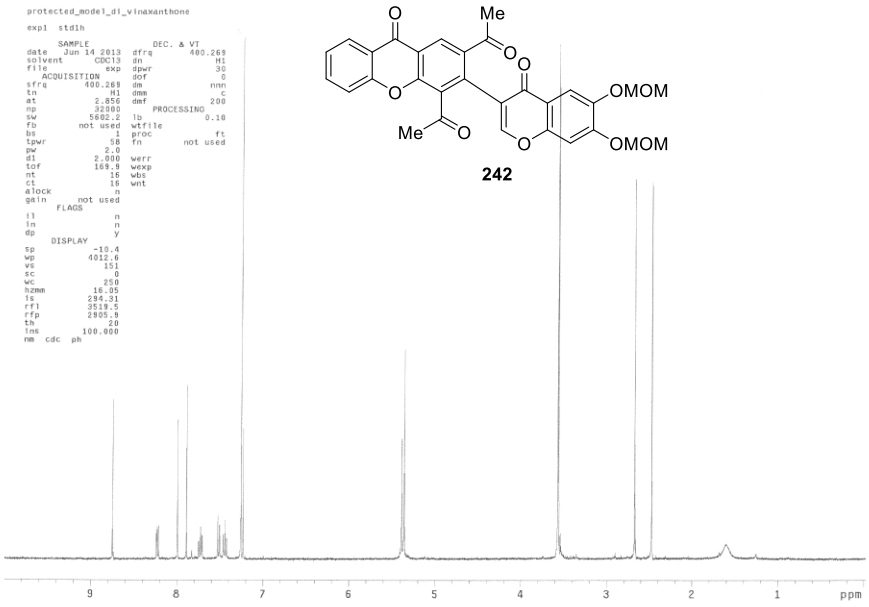

exp1 CARBON
SAMPLE
date Jan 23 2013
solvent cdcl3
file /home/space/d-
ata/bottom_model_2-
0130123_01/CARBON_-
01.fid
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 1000
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -13.5
wp 22138.2
rf1 9181.2
rfp 7746.3
rp 159.2
lp 0
PLOT
wc 250
sc 0
vs 72265
th 17
ai cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

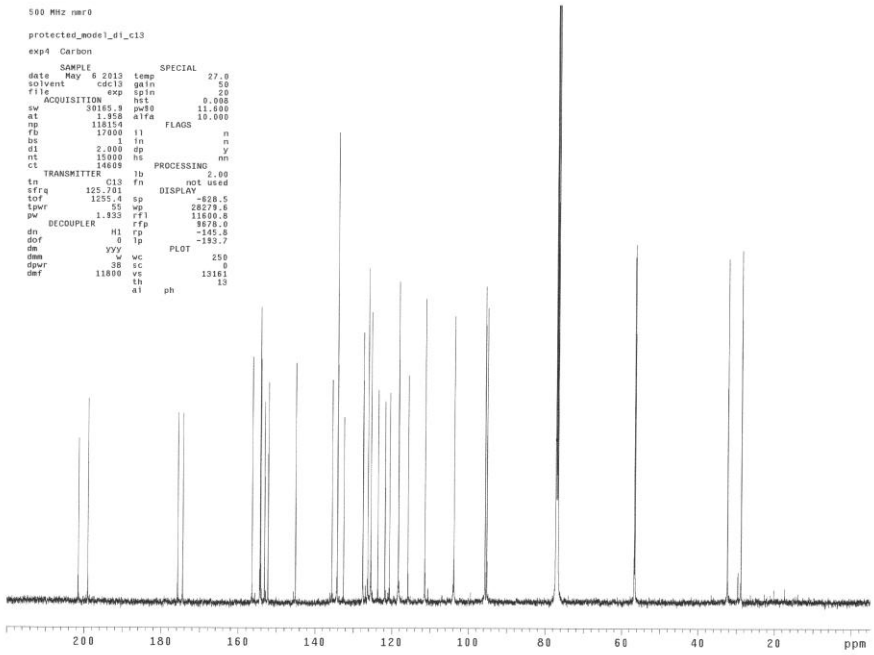

100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

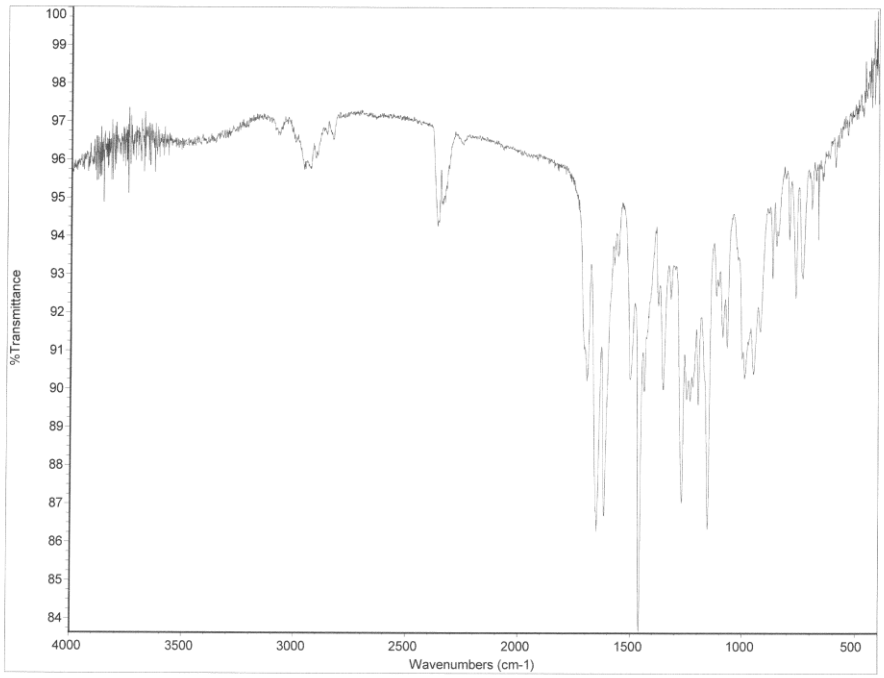

mixed protected vinaxanthone
exp1 stdlh
SAMPLE
date Apr 26 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -18.3
wp 4028.7
ws 151
sc 0
wc 250
hzmm 16.11
is 386.39
rf1 3519.9
rfp 2905.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
O
O
O
O
CO2t-Bu
OPiv
OMOM
Me
O
O
241
9
8
7
6
5
4
3
2
1
ppm

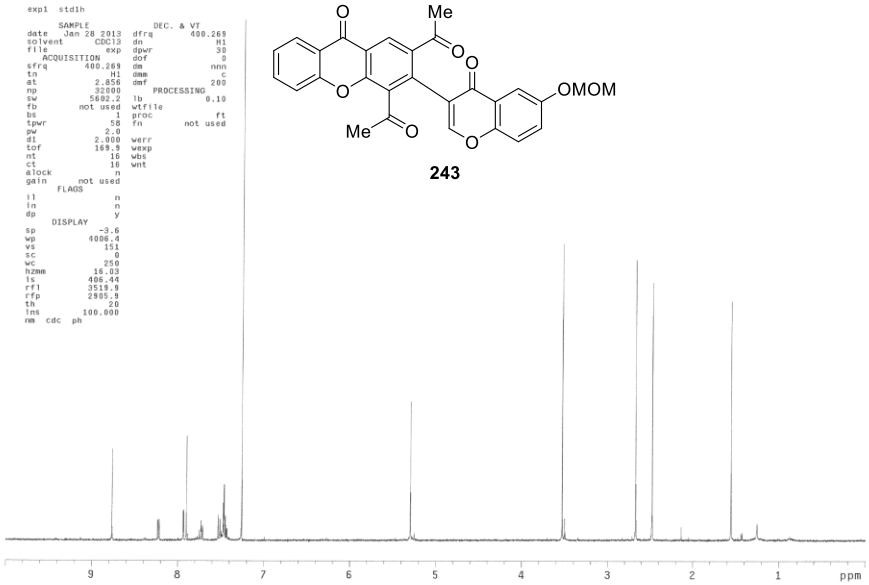

500 MHz nmr1
mixed_protected_vinaxanthone_c13
exp6 Carbon
SAMPLE
date Apr 27 2012
solvent cdcl3
file exp
ACQUISITION
sw 30131.8
at 2.000
np 120528
fb 17000
bs 8
d1 2.000
nt 80000
ct 45682
TRANSMITTER
tn C13
sfrq 125.584
tof 1254.2
tpwr 51
pw 15.500
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 12600
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 15.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.1
wp 28253.2
rf1 11580.4
rfp 9669.8
rp -170.1
lp -257.0
PLOT
wc 250
sc 0
vs 15840
th 7
ai ph
200
180
160
140
120
100
80
60
40
20
ppm

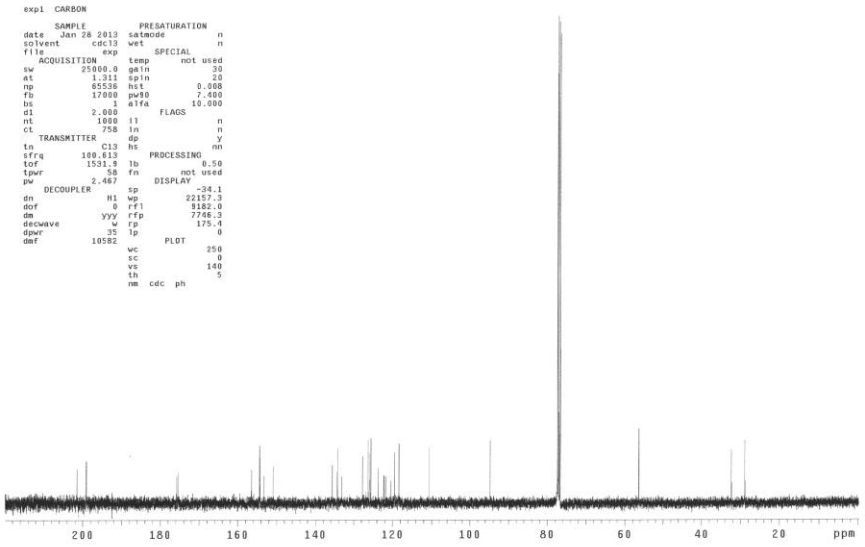

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

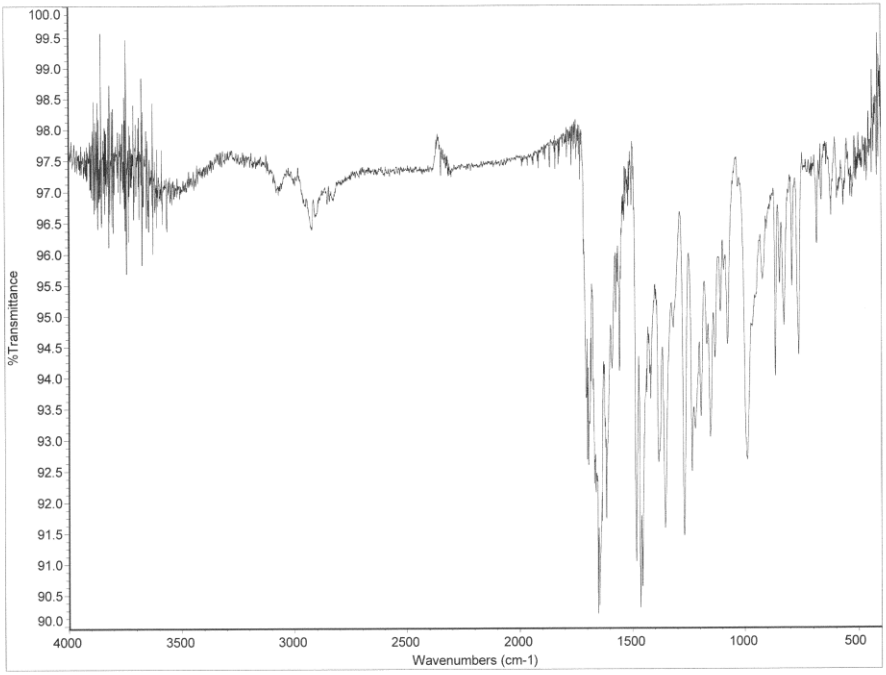

protected_model_di_vinaxanthone
exp1 stdlh
SAMPLE
date Jun 14 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -10.4
wp 4012.6
vs 151
sc 0
wc 250
hzmm 16.05
is 294.31
rfl 3519.5
rfp 2805.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm C
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
O
O
O
O
Me
O
OMOM
OMOM
242
9
8
7
6
5
4
3
2
1
ppm

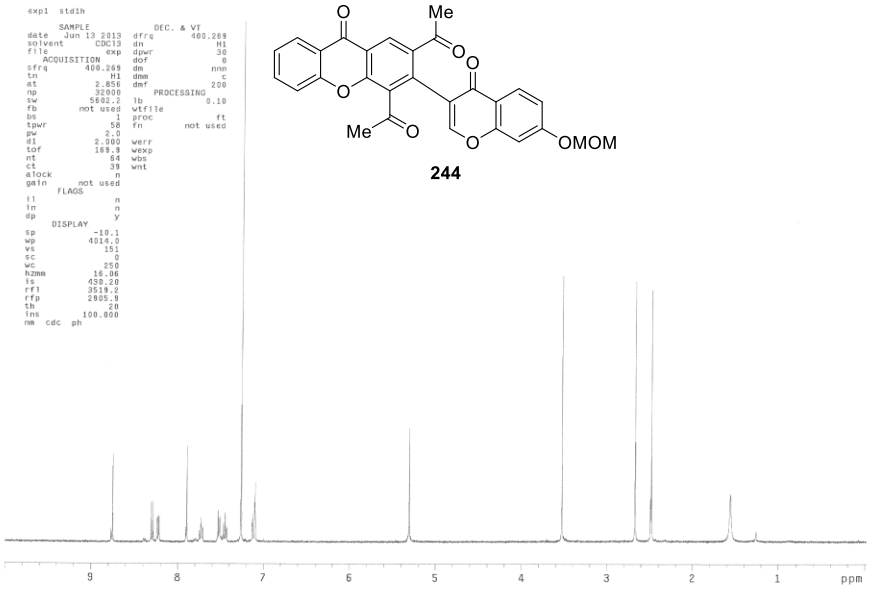

500 MHz nmr0
protected_model_di_c13
exp4 Carbon
SAMPLE
date May 6 2013
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 14609
TRANSMITTER
tn C13
sfrq 125.701
tof 1255.4
tpwr 55
pw 1.933
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 2.00
fn not used
DISPLAY
sp -626.5
wp 28279.6
rfl 11600.8
rfp 9678.0
rp -145.8
lp -193.7
PLOT
wc 250
sc 0
vs 13161
th 13
al ph
200
180
160
140
120
100
80
60
40
20
ppm

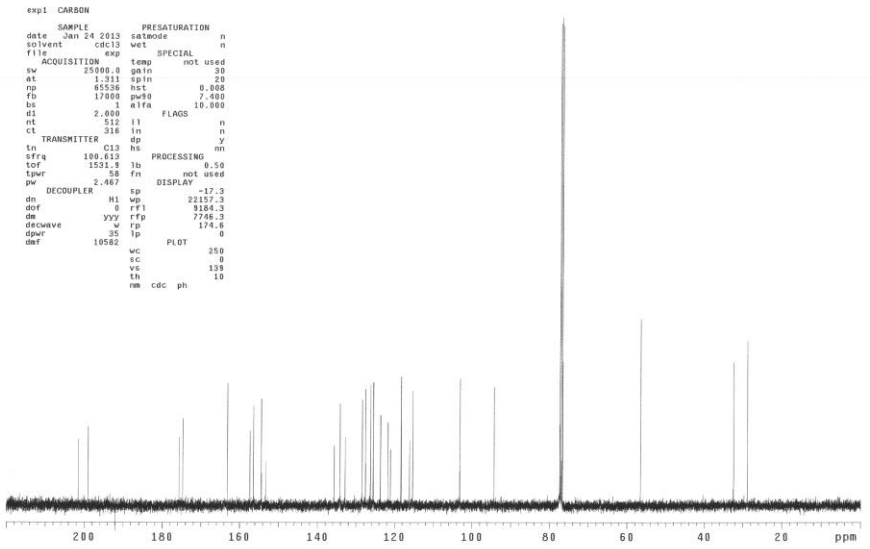

100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

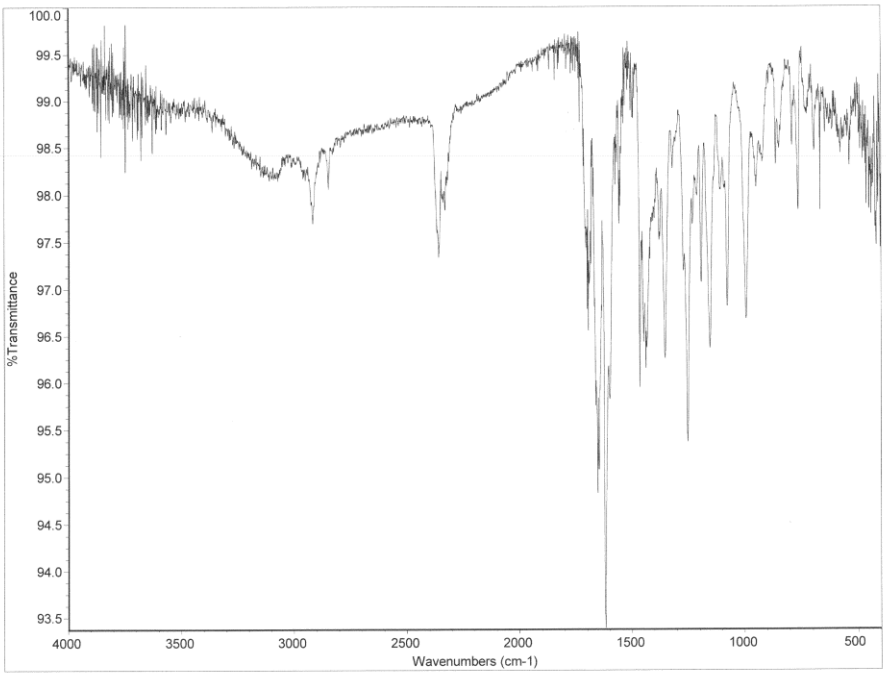

exp1 stdih
SAMPLE
date Jan 28 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.6
wp 4006.4
vs 151
sc 0
wc 250
hzmm 16.03
is 405.44
rfl 3519.9
rfp 2805.9
th 20
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
O
O
O
O
Me
O
OMOM
243
9
8
7
6
5
4
3
2
1
ppm

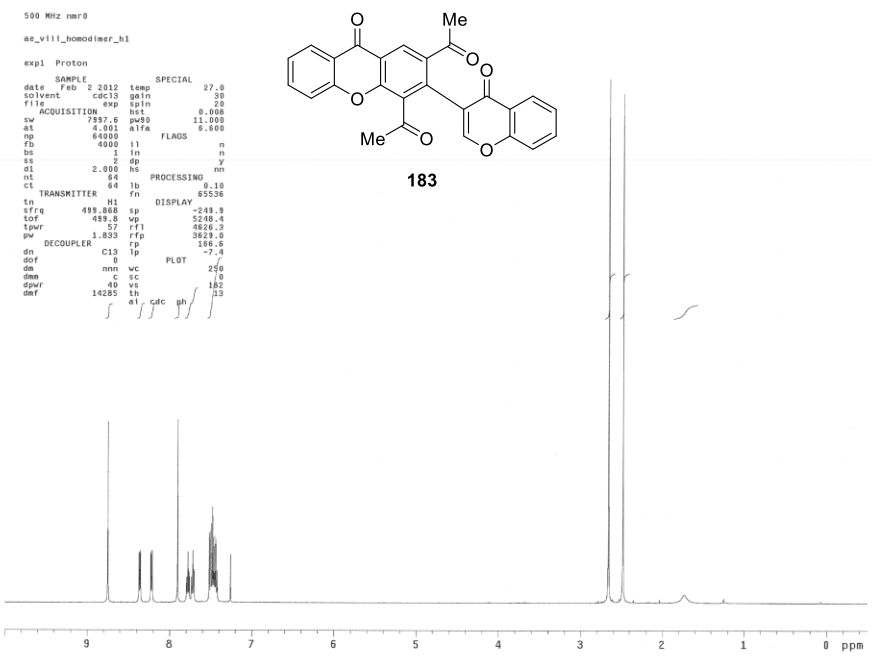

exp1 CARBON
SAMPLE
date Jan 28 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 1000
ct 758
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp Y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -34.1
wp 22157.3
rfl 9182.0
rfp 7746.3
rp 175.4
lp 0
PLOT
wc 250
sc 0
vs 140
th 5
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm


100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
90.0
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

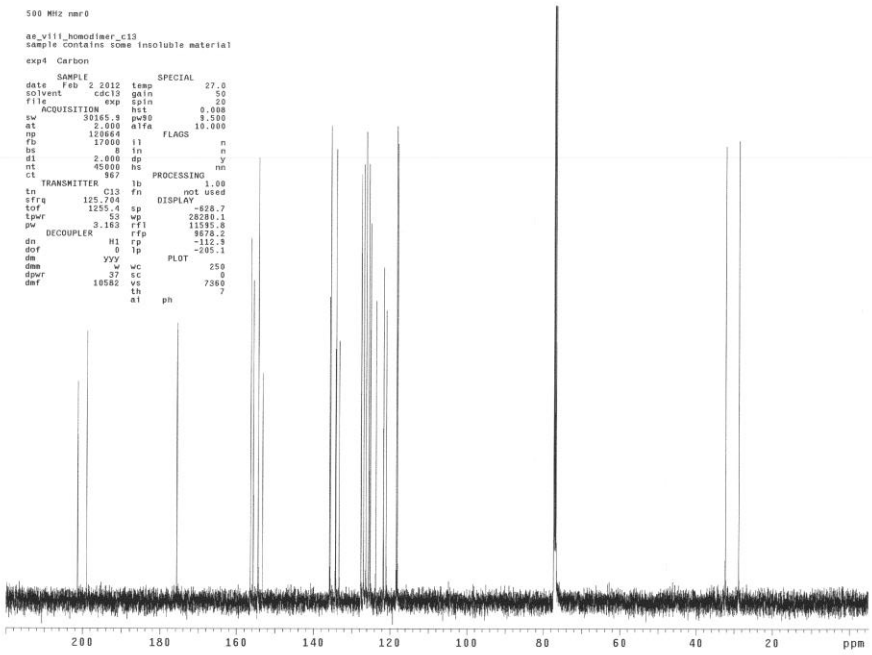

exp1 stdih
SAMPLE
date Jun 13 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.269
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 64
ct 39
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -10.1
wp 4014.0
vs 151
sc 0
wc 250
hzmm 16.06
is 430.20
rf1 3519.2
rfp 2805.9
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.269
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 208
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
O
O
O
O
Me
O
OMOM
244
9
8
7
6
5
4
3
2
1
ppm

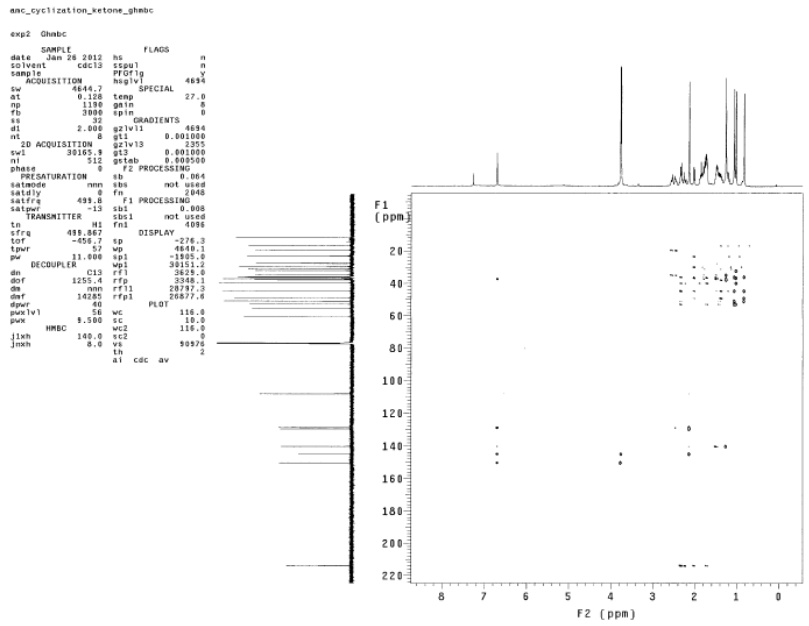

exp1 CARBON
SAMPLE
date Jan 24 2013
solvent cdcl3
file exp
ACQUISITION
sw 25000.0
at 1.311
np 65536
fb 17000
bs 1
d1 2.000
nt 512
ct 316
TRANSMITTER
tn C13
sfrq 100.613
tof 1531.9
tpwr 58
pw 2.467
DECOUPLER
dn H1
dof 0
dm yyy
decwave w
dpwr 35
dmf 10582
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 30
spin 20
hst 0.008
pw90 7.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -17.3
wp 22157.3
rf1 9184.3
rfp 7746.3
rp 174.6
lp 0
PLOT
wc 250
sc 0
vs 139
th 10
nm cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

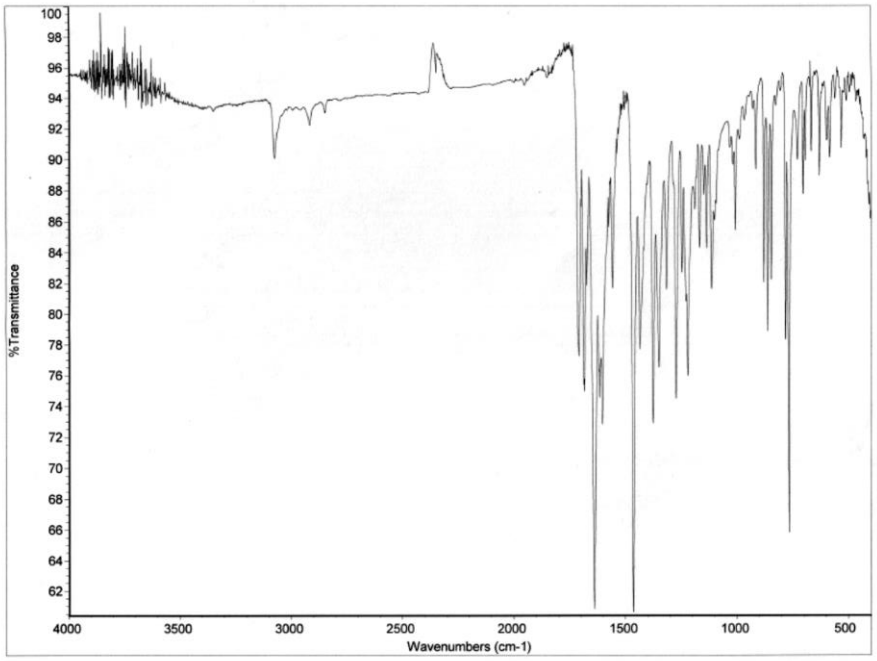

100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

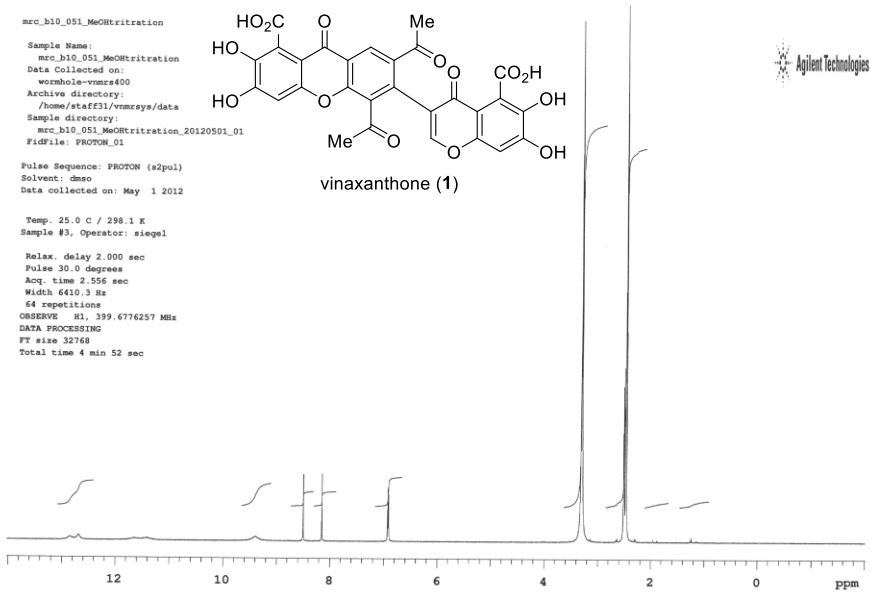

500 MHz nmr0
ae_viii_homodimer_h1
exp1 Proton
SAMPLE
date Feb 2 2012
solvent cdcl3
file exp
ACQUISITION
sw 7597.6
at 4.001
np 64000
fb 4000
bs 1
ss 2
d1 2.000
nt 64
ct 64
TRANSMITTER
tn H1
sfrq 499.868
tof 459.8
tpwr 57
pw 1.833
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 40
dmf 14285
SPECIAL
temp 27.0
gain 30
spin 20
hst 0.008
pw90 11.000
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.10
fn 65536
DISPLAY
sp -249.9
wp 5248.4
rf1 4626.3
rfp 3629.0
rp 166.6
lp -7.4
PLOT
wc 250
sc 0
vs 182
th 13
al gdc ph
9 8 7 6 5 4 3 2 1 0 ppm

183

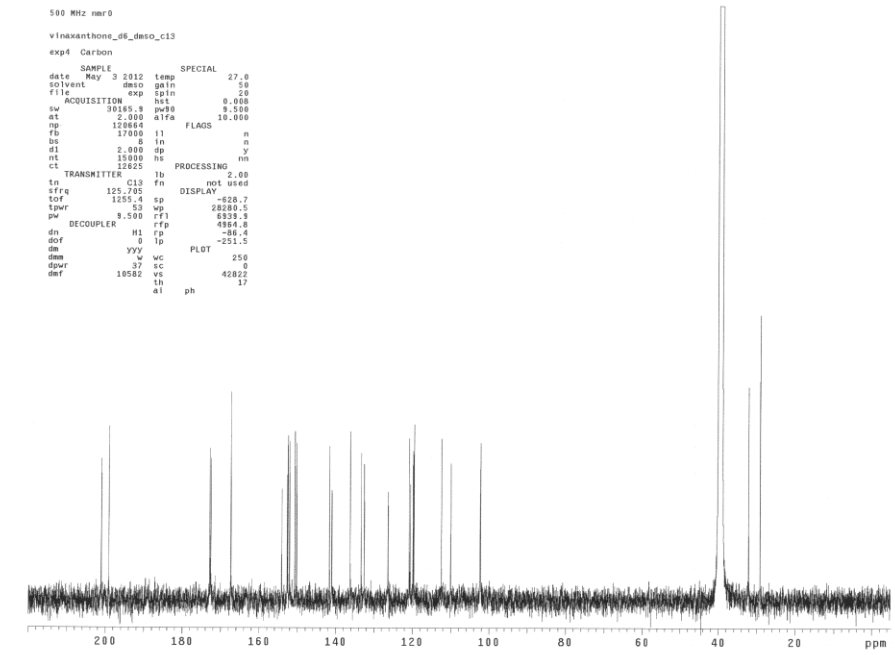

500 MHz nmr0
ae_viii_homodimer_c13
sample contains some insoluble material
exp4 Carbon
SAMPLE
date Feb 2 2012
solvent cdcl3
file exp
ACQUISITION
sw 30165.9
at 2.000
np 120664
fb 17000
bs 8
d1 2.000
nt 45000
ct 967
TRANSMITTER
tn C13
sfrq 125.704
tof 1255.4
tpwr 53
pw 3.163
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 37
dmf 10582
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 9.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.7
wp 28280.1
rf1 11595.8
rfp 9678.2
rp -112.9
lp -205.1
PLOT
wc 250
sc 0
vs 7360
th 7
al ph
200 180 160 140 120 100 80 60 40 20 ppm

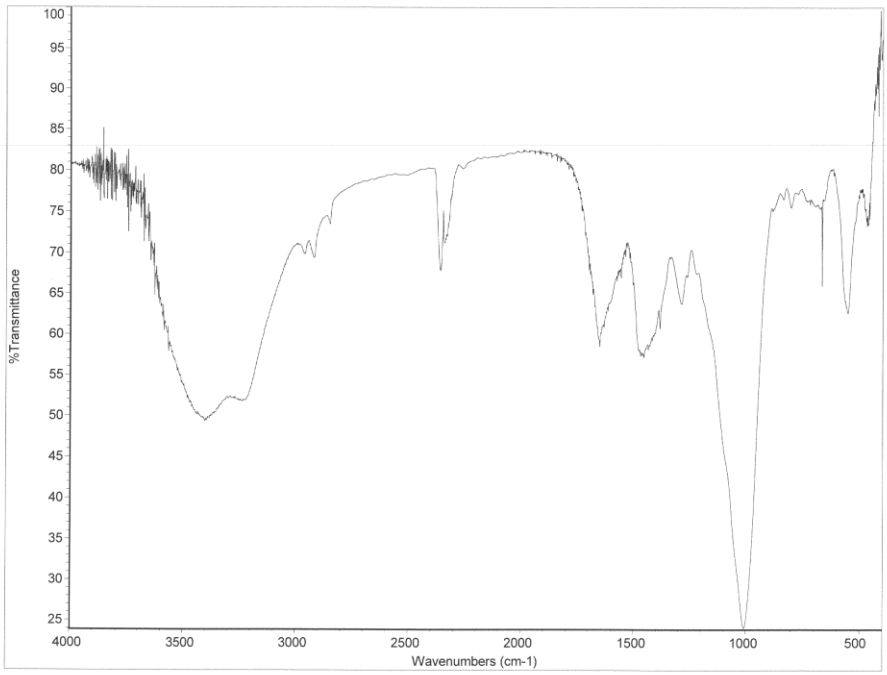

amc_cyclization_ketone_ghmbc
exp2 Ghmbc
SAMPLE
date Jan 26 2012
solvent cdcl3
sample
ACQUISITION
sw 4644.7
at 0.128
np 1190
fb 3000
ss 32
d1 2.000
nt 8
2D ACQUISITION
sw1 30165.9
ni 512
phase 0
PRESATURATION
satmode nnn
satdly 0
satfrq 499.8
satpwr -13
TRANSMITTER
tn H1
sfrq 499.867
tof -456.7
tpwr 57
pw 11.000
DECOUPLER
dn C13
dof 1255.4
dm nnn
dmf 14285
dpwr 40
pwx1v1 56
pwx 5.500
HMBC
j1xh 140.0
jnxh 8.0
FLAGS
hs n
sspul n
PFGflg y
hsglvl 4694
SPECIAL
temp 27.0
gain 8
spin 0
GRADIENTS
gz1v11 4694
gt1 0.001000
gz1v13 2355
gt3 0.001000
gstab 0.000500
F2 PROCESSING
sb 0.064
sbs not used
fn 2048
F1 PROCESSING
sb1 0.008
sbs1 not used
fn1 4096
DISPLAY
sp -276.3
wp 4640.1
sp1 -1985.0
wp1 30151.2
rf1 3625.0
rfp 3348.1
rf11 28797.3
rfp1 26877.6
PLOT
wc 116.0
sc 19.0
wc2 116.0
sc2 0
vs 90576
th 2
al cdc av
F1 (ppm)
F2 (ppm)

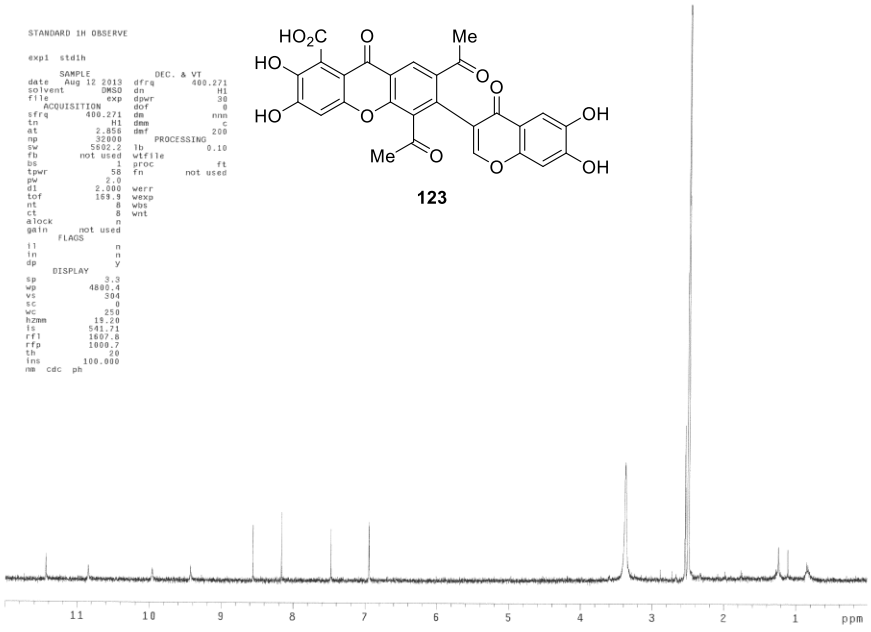

%Transmittance
Wavenumbers (cm-1)



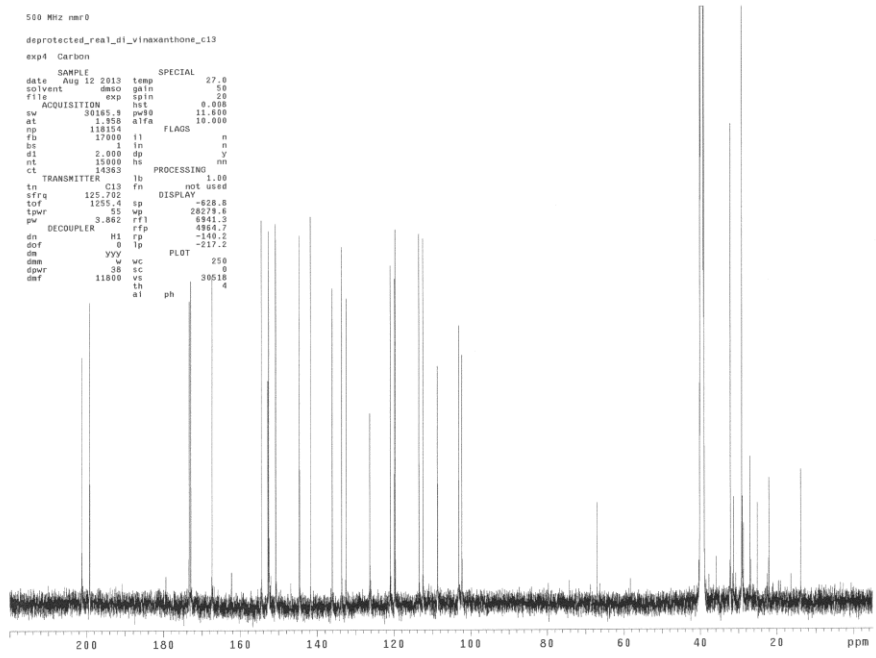
Plotname: PROTON_01_plot01

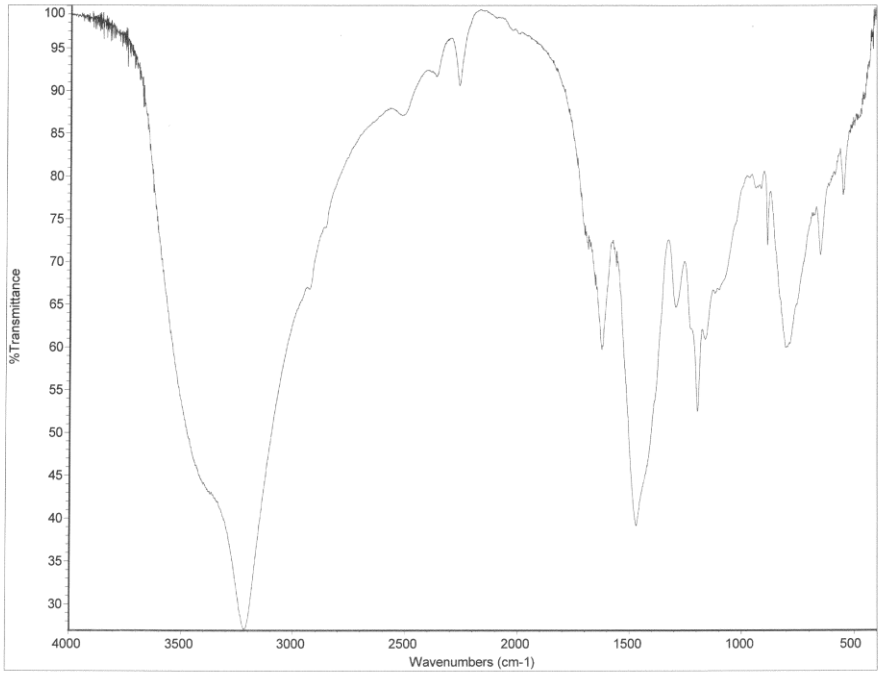


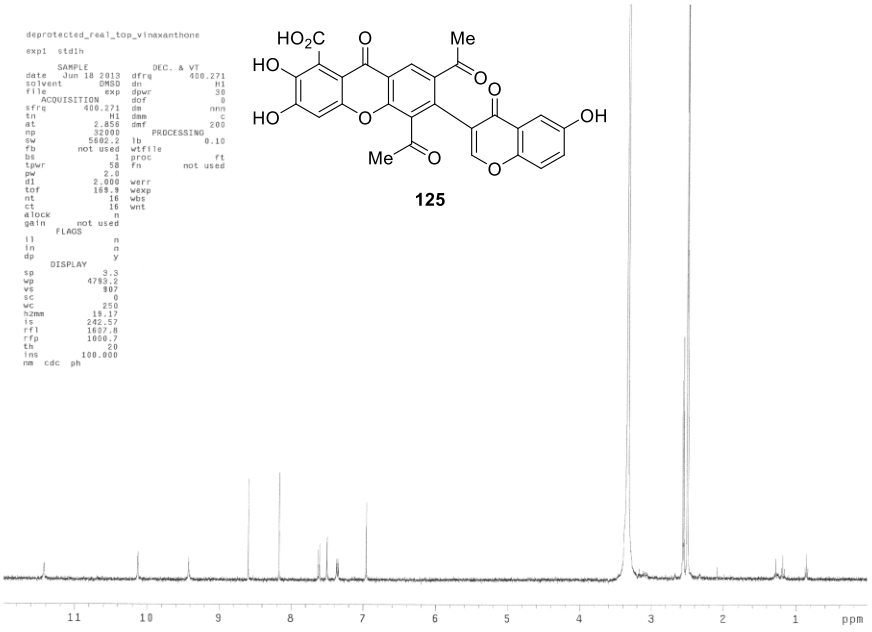

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

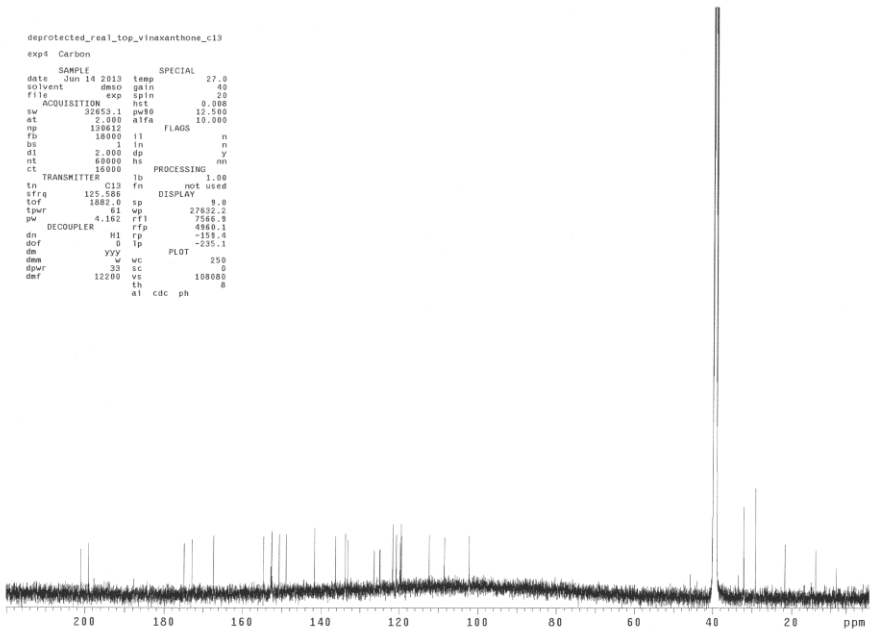

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Aug 12 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 8
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 3.3
wp 4800.4
vs 304
sc 0
wc 250
hzmm 15.20
is 541.71
rfl 1607.8
rfp 1009.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO2C
O
Me
HO
HO
O
O
O
OH
Me
O
O
OH
11
10
9
8
7
6
5
4
3
2
1
ppm

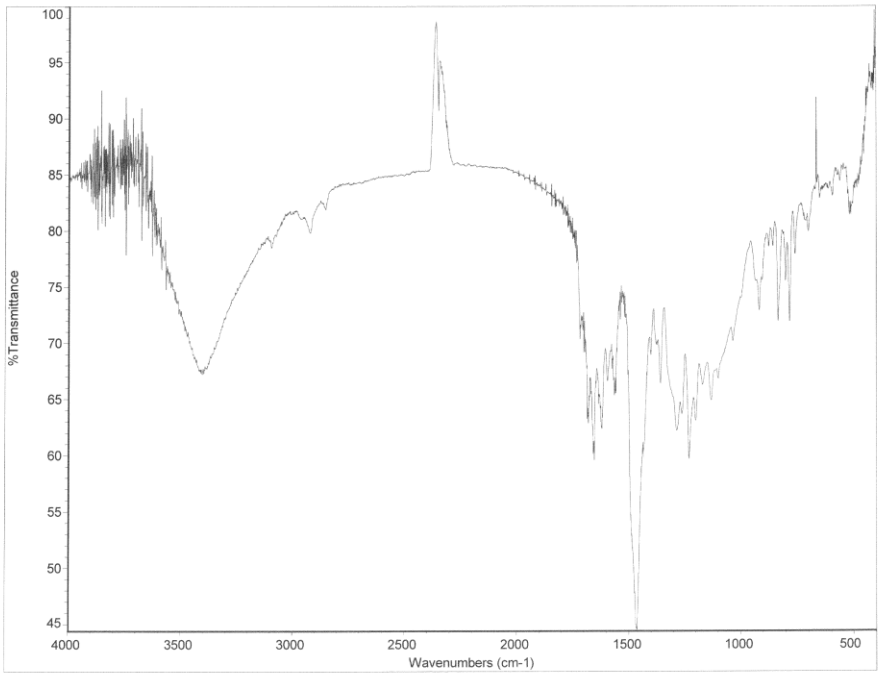
123

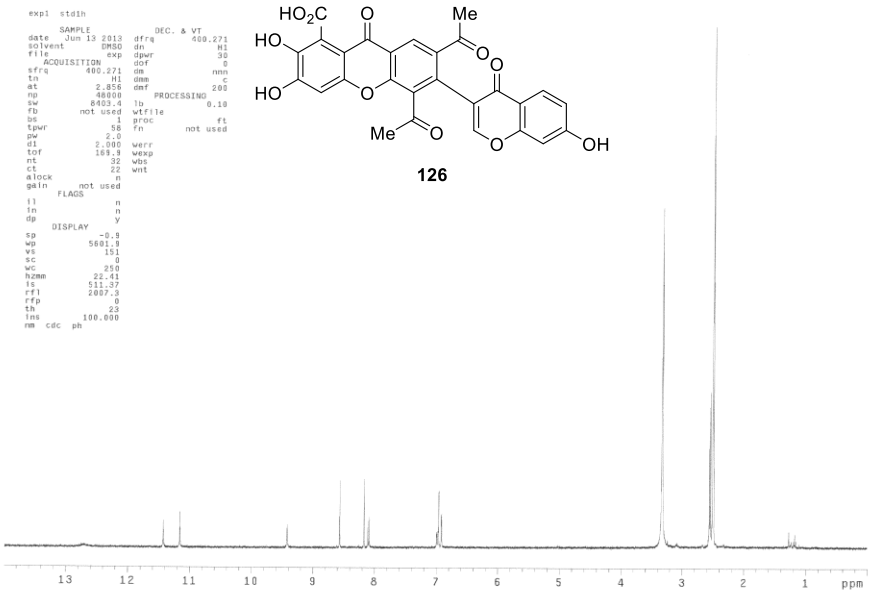

500 MHz nmr0
deprotected_real_di_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Aug 12 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.358
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 14363
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.8
wp 28279.6
rfl 6941.3
rfp 4864.7
rp -140.2
lp -217.2
PLOT
wc 250
sc 0
vs 30518
th 4
al ph
200
180
160
140
120
100
80
60
40
20
ppm

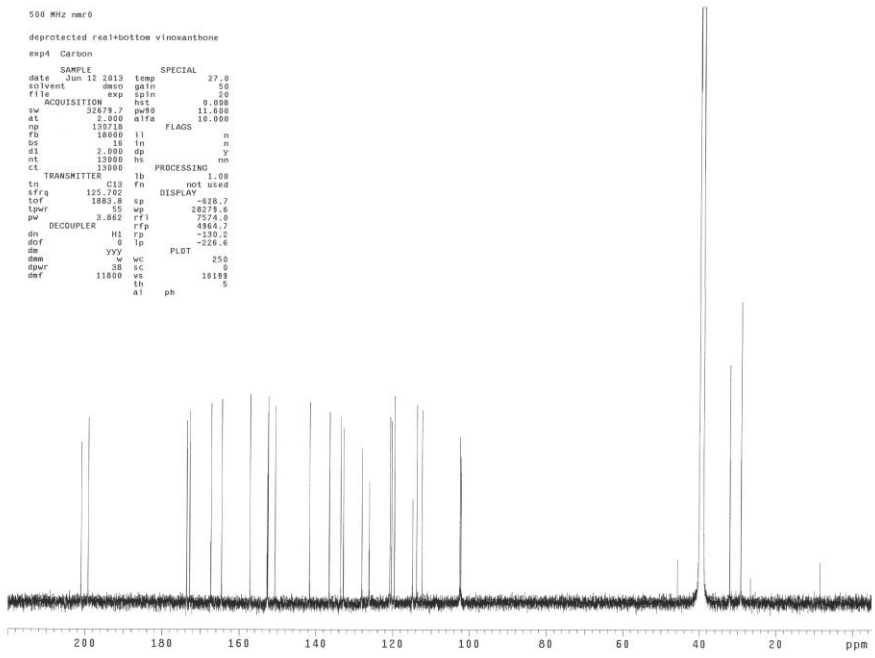

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

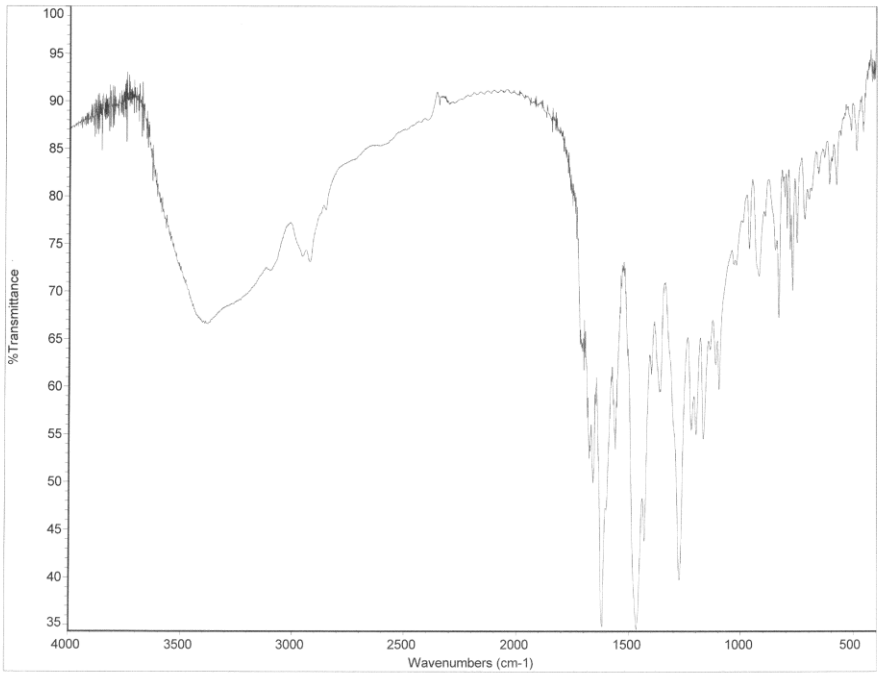

deprotected_real_top_vinaxanthone
exp1 stdlh
SAMPLE
date Jun 18 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 3.3
wp 4783.2
vs 907
sc 0
wc 250
hzmm 18.17
is 242.57
rfl 1607.8
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO2C
HO
HO
O
Me
O
O
O
OH
Me
O
O
125
11
10
9
8
7
6
5
4
3
2
1
ppm

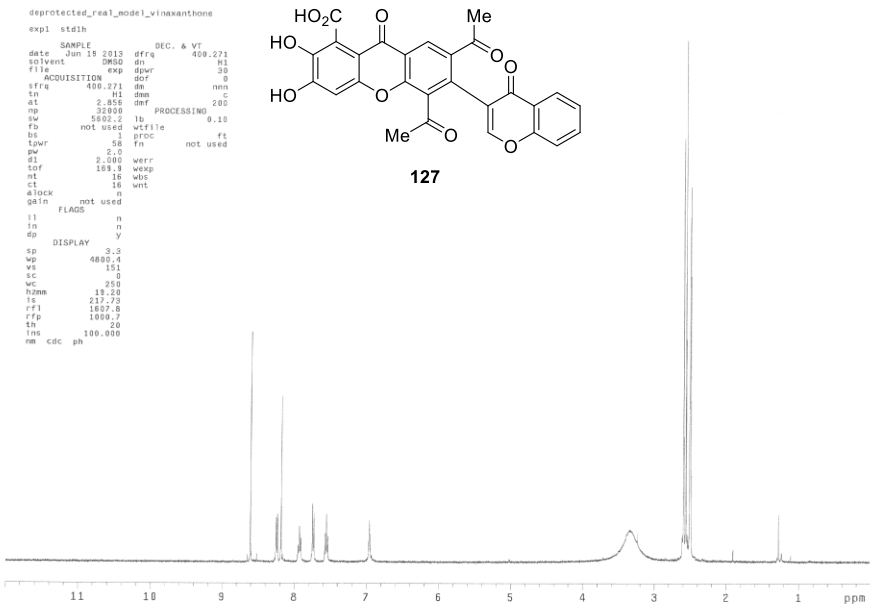

deprotected_real_top_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jun 14 2013
solvent dmso
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 60000
ct 16000
TRANSMITTER
tn C13
sfrq 125.586
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 9.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 9.0
wp 27632.2
rfl 7566.9
rfp 4960.1
rp -158.4
lp -235.1
PLOT
wc 250
sc 0
vs 108080
th 8
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

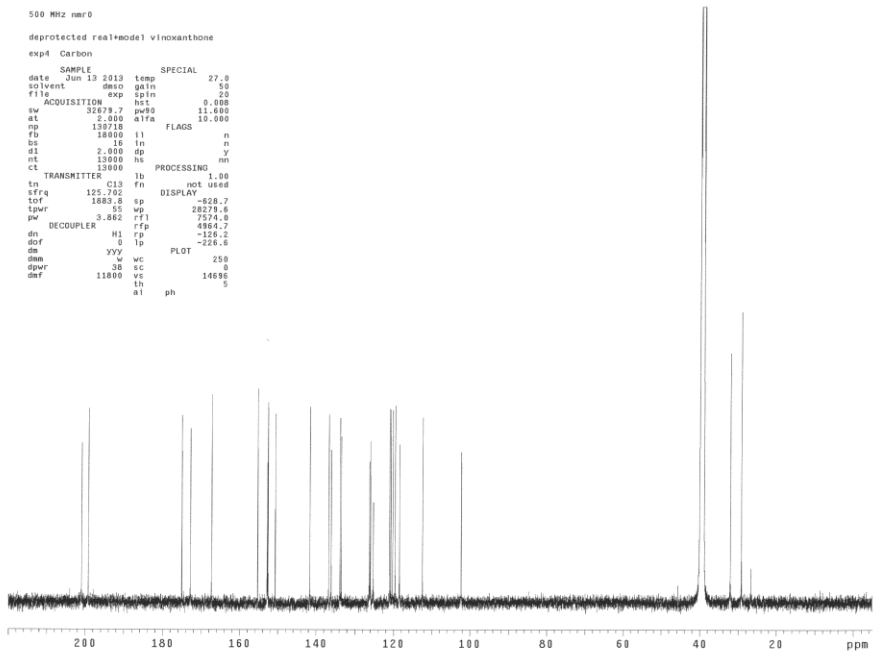

100
95
90
85
80
75
70
65
60
55
50
45
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

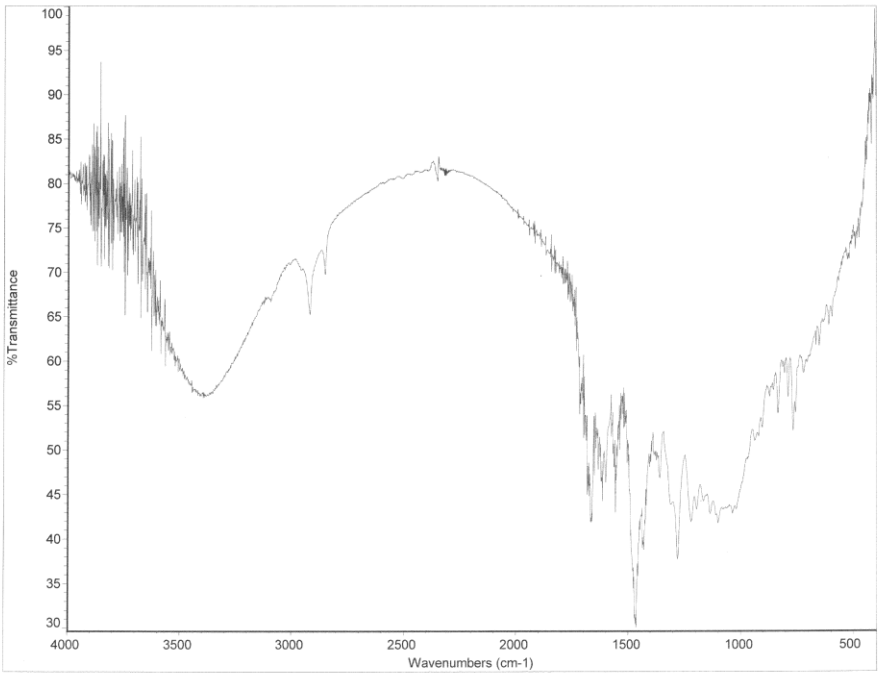

exp1 std1h
SAMPLE
date Jun 13 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 48000
sw 8403.4
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 32
ct 22
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -0.9
wp 5601.9
vs 151
sc 0
wc 250
hzmm 22.41
is 511.37
rfl 2007.3
rfp 0
th 23
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO2C
O
Me
HO
HO
O
O
O
Me
O
O
OH
126
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

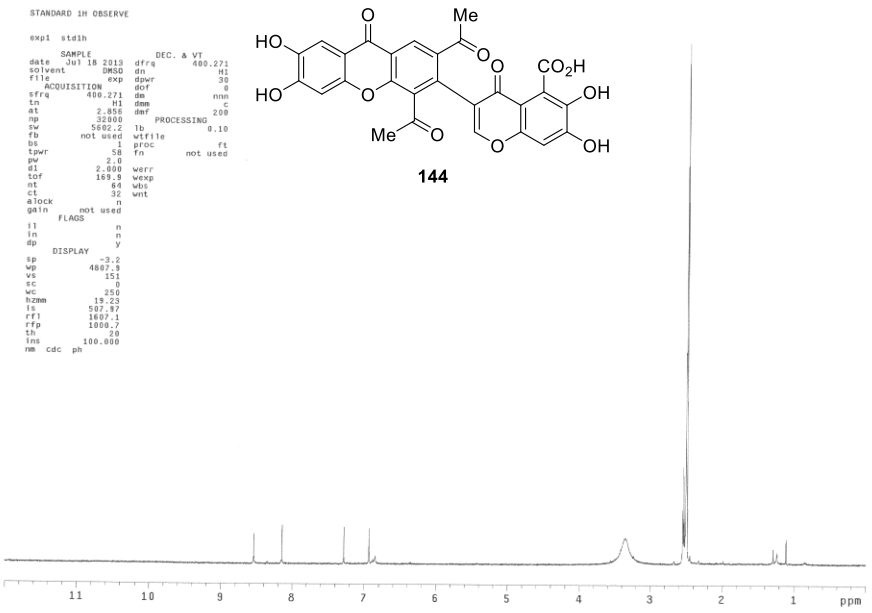

500 MHz nmr0
deprotected real+bottom vinoxanthone
exp4 Carbon
SAMPLE
date Jun 12 2013
solvent dmso
file exp
ACQUISITION
sw 32679.7
at 2.000
np 130718
fb 18000
bs 16
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 125.702
tof 1883.8
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -928.7
wp 28275.6
rfl 7574.0
rfp 4964.7
rp -130.2
lp -226.6
PLOT
wc 250
sc 0
vs 16199
th 5
al ph
200
180
160
140
120
100
80
60
40
20
ppm

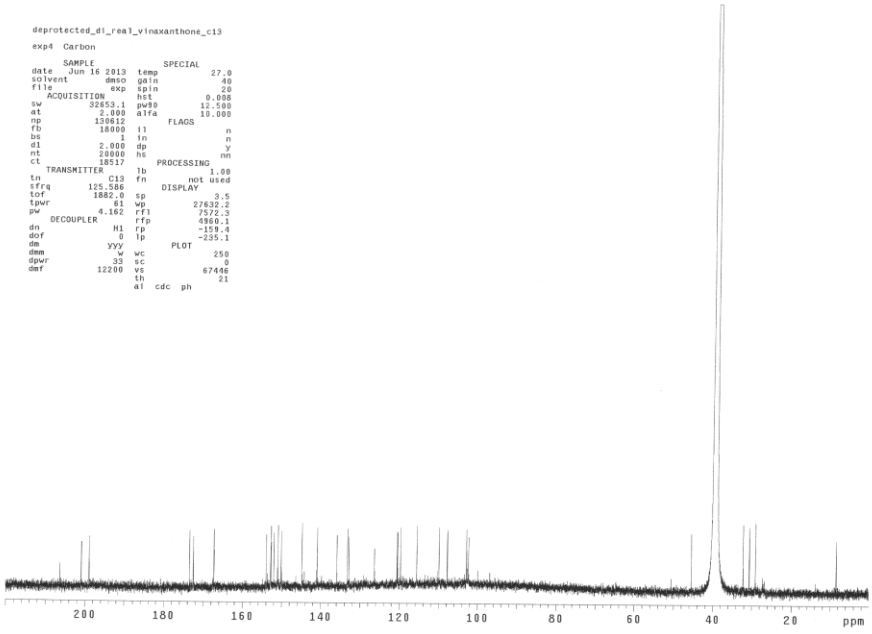

100
95
90
85
80
75
70
65
60
55
50
45
40
35
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

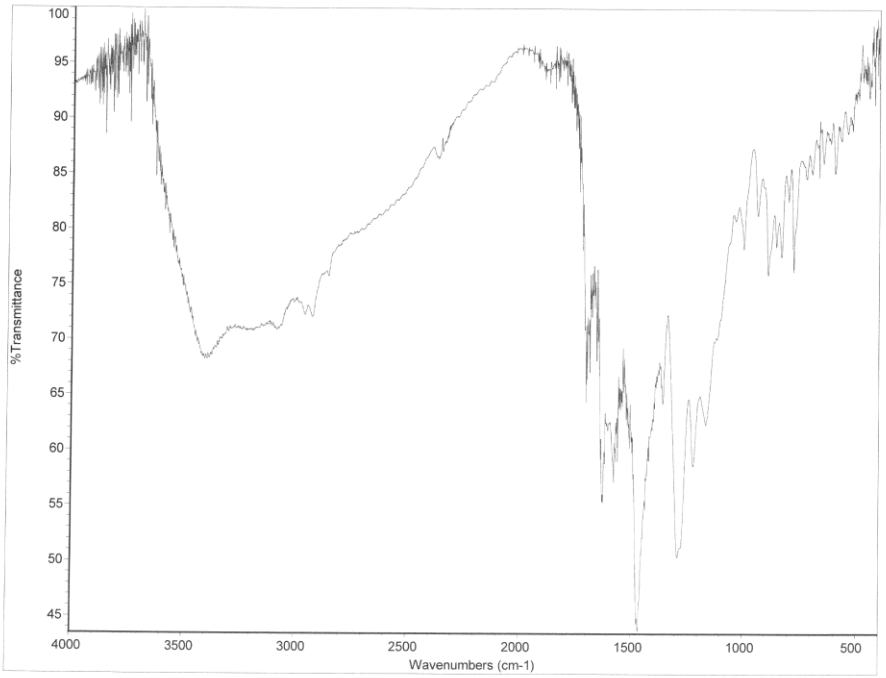

deprotected_real_model_vinaxanthone
exp1 std1h
SAMPLE
date Jun 18 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5802.2
fb not used
bs 1
tpwr 56
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 3.3
wp 4800.4
vs 151
sc 0
wc 250
hzmm 18.20
is 217.73
rfl 1607.8
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO2C
O
Me
HO
O
O
HO
O
Me
O
O
127
11
10
9
8
7
6
5
4
3
2
1
ppm


500 MHz nmr0
deprotected real+model vinoxanthone
exp4 Carbon
SAMPLE
date Jun 13 2013
solvent dmso
file exp
ACQUISITION
sw 32679.7
at 2.000
np 130718
fb 18000
bs 16
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 125.702
tof 1883.8
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.7
wp 28279.6
rfl 7574.8
rfp 4964.7
rp -126.2
lp -226.6
PLOT
wc 250
sc 0
vs 14696
th 5
al ph
200
180
160
140
120
100
80
60
40
20
ppm


100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


STANDARD 1H OBSERVE
exp1 stdih
SAMPLE
date Jul 18 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 64
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4807.9
vs 151
sc 0
wc 250
hzmm 15.23
is 507.97
rf1 1607.1
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
HO
O
O
Me
O
Me
O
O
CO2H
OH
OH
144
11
10
9
8
7
6
5
4
3
2
1
ppm

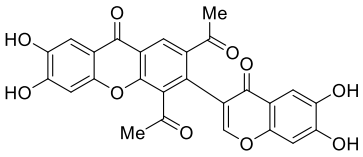

deprotected_di_real_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jun 16 2013
solvent dmso
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 20000
ct 18517
TRANSMITTER
tn C13
sfrq 125.586
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 9.5
wp 27632.2
rf1 7572.3
rfp 4960.1
rp -159.4
lp -235.1
PLOT
wc 250
sc 0
vs 67446
th 21
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm


100
95
90
85
80
75
70
65
60
55
50
45
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

STANDARD 1H OBSERVE

expl std1h

SAMPLE		DEC. & VT	
date	Jul 9 2013	dfrq	400.271
solvent	DMSO	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	400.271	dm	nnn
tn	H1	dmm	c
at	2.856	dmf	200
np	32000	PROCESSING	
sw	5802.2	lb	0.10
fb	not used	wtfile	
bs	1	proc	ft
tpwr	58	fn	not used
pw	2.0		
d1	2.000	werr	
tof	169.8	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	2.6		
wp	4800.4		
vs	151		
sc	0		
wc	250		
hzmm	18.20		
ls	2558.67		
rf1	1608.1		
rfp	1000.7		
th	7		
ins	1.000		
nm ph			

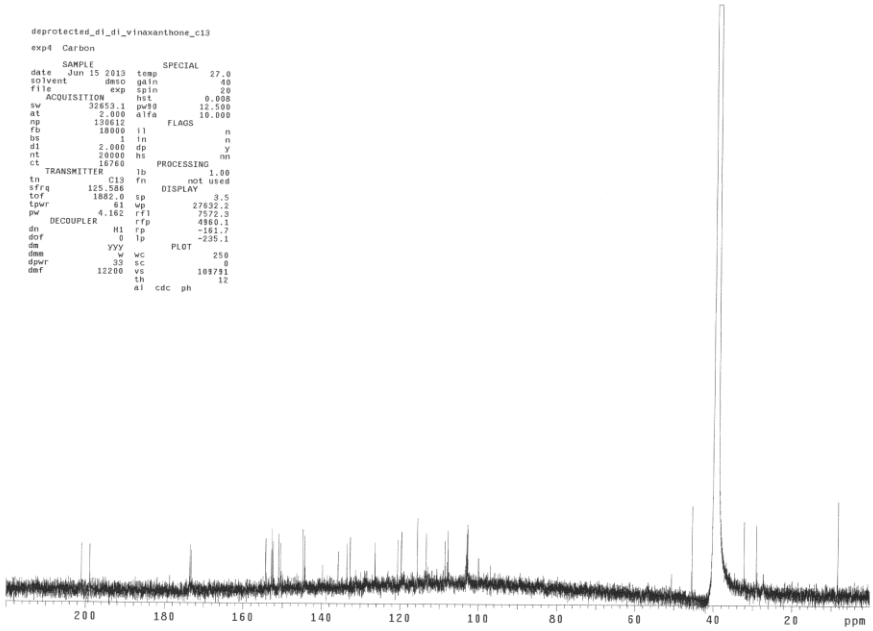


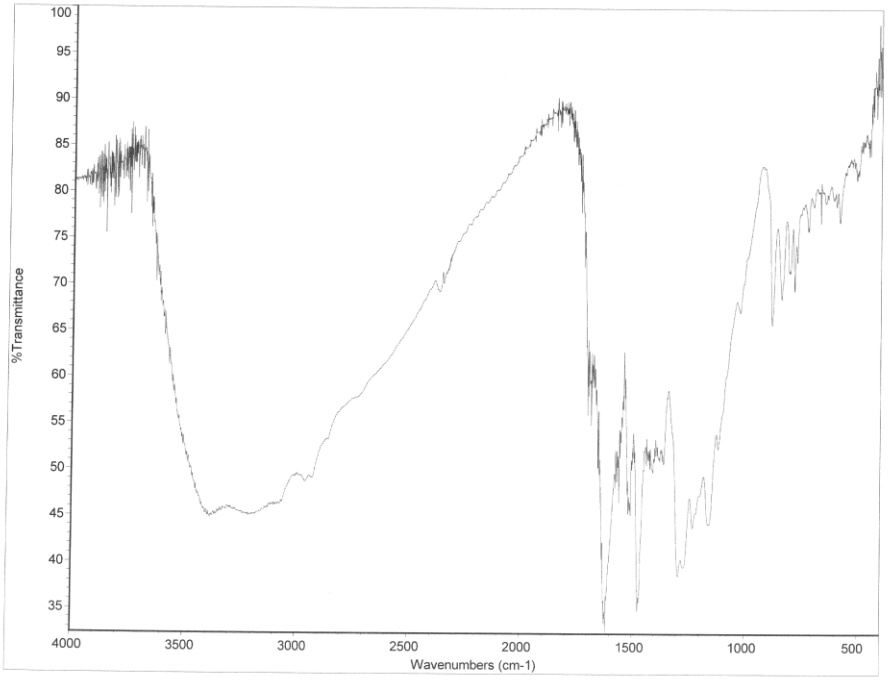
147

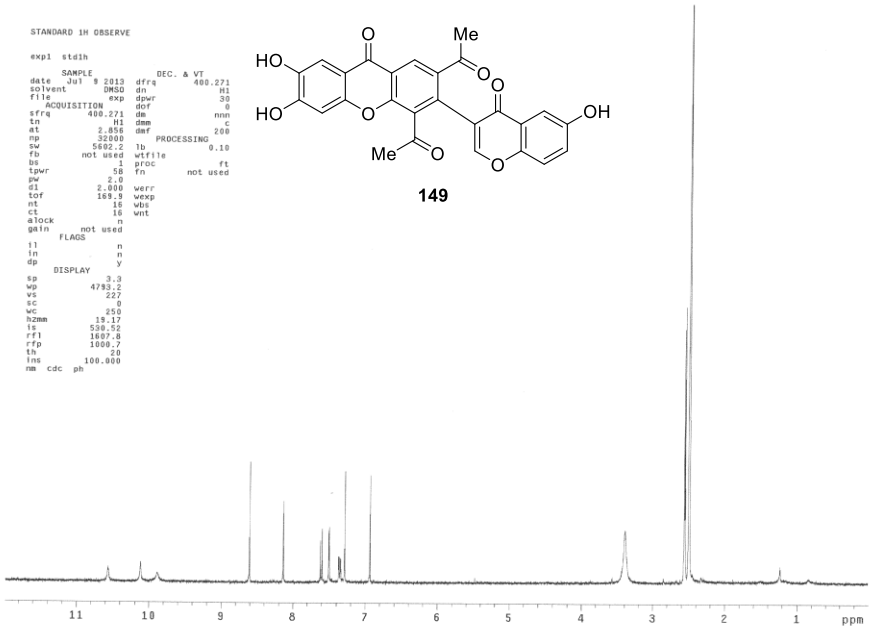
deprotected_di_di_vinaxanthone_c13

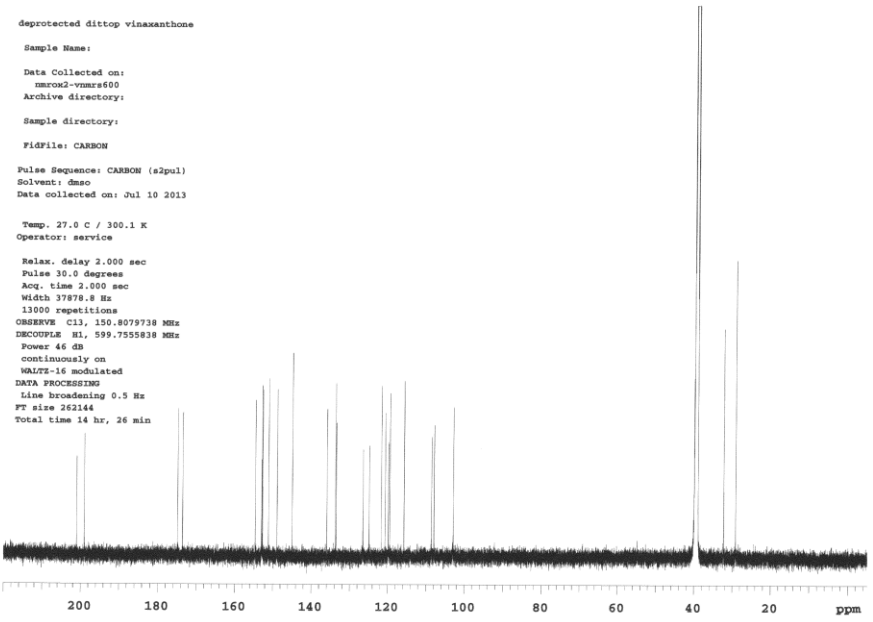
exp4 Carbon

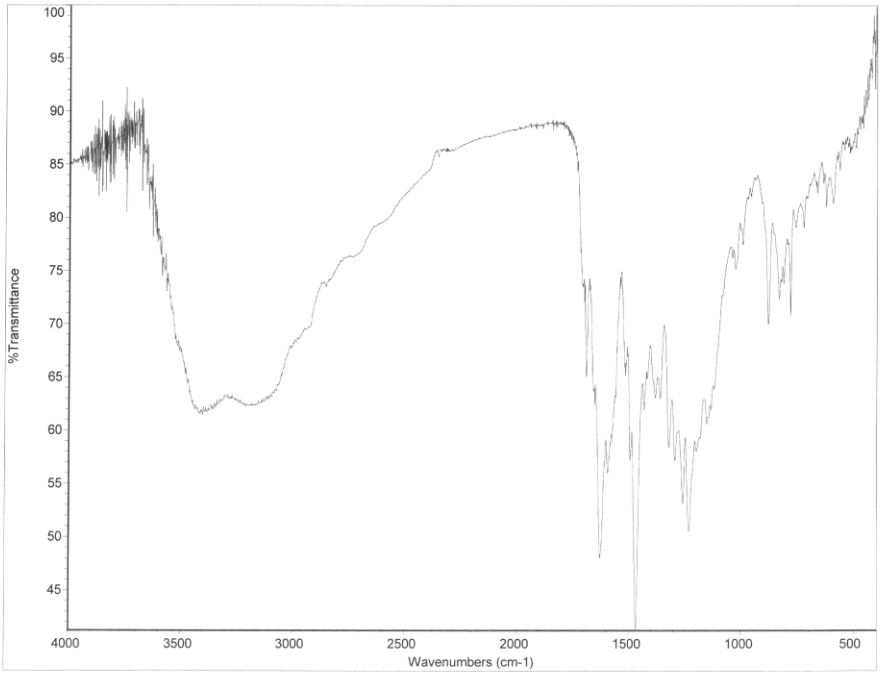
SAMPLE		SPECIAL	
date	Jun 15 2013	temp	27.0
solvent	dmso	gain	40
file	exp	spin	20
ACQUISITION		hst	0.008
sw	32653.1	pw90	12.500
at	2.000	alfa	10.000
np	130612	FLAGS	
fb	18000	il	n
bs	1	in	n
d1	2.000	dp	y
nt	28000	hs	nn
ct	16760	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	125.586	DISPLAY	
tof	1882.0	sp	3.5
tpwr	61	wp	27632.2
pw	4.162	rf1	7572.3
DECOUPLER		rfp	4960.1
dn	H1	rp	-161.7
dof	0	lp	-235.1
dm	YYY	PLOT	
dmm	w	wc	250
dpwr	33	sc	0
dmf	12200	vs	109731
		th	12
		ai cdc ph	

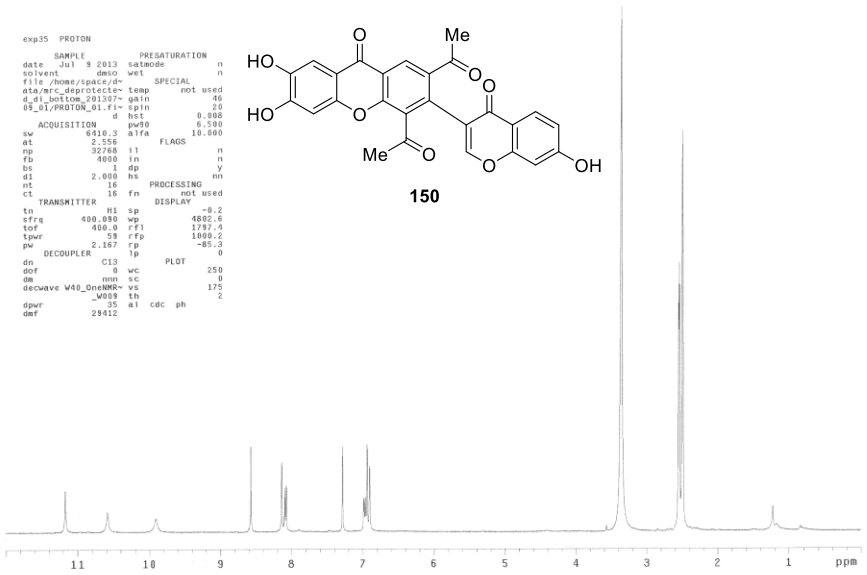


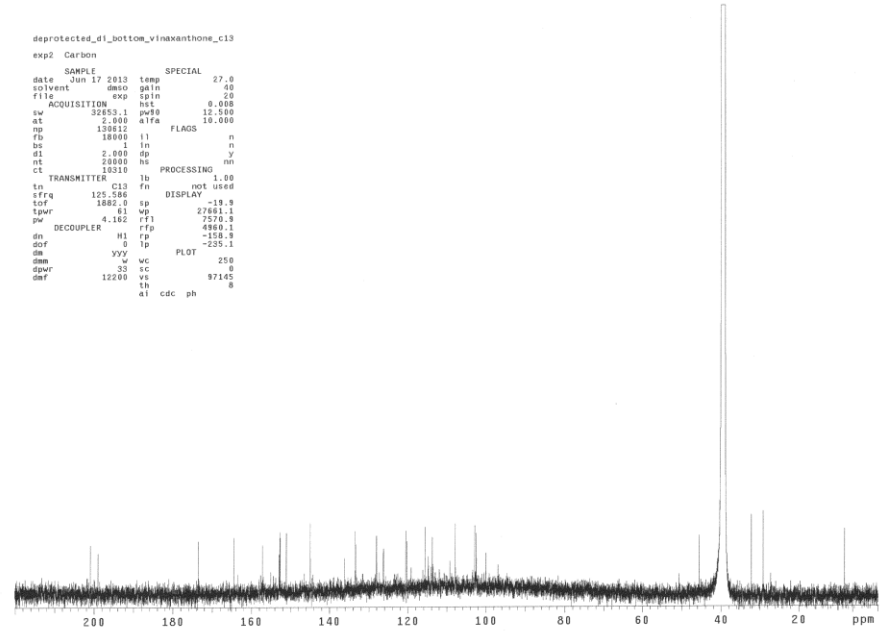

100
95
90
85
80
75
70
65
60
55
50
45
40
35
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

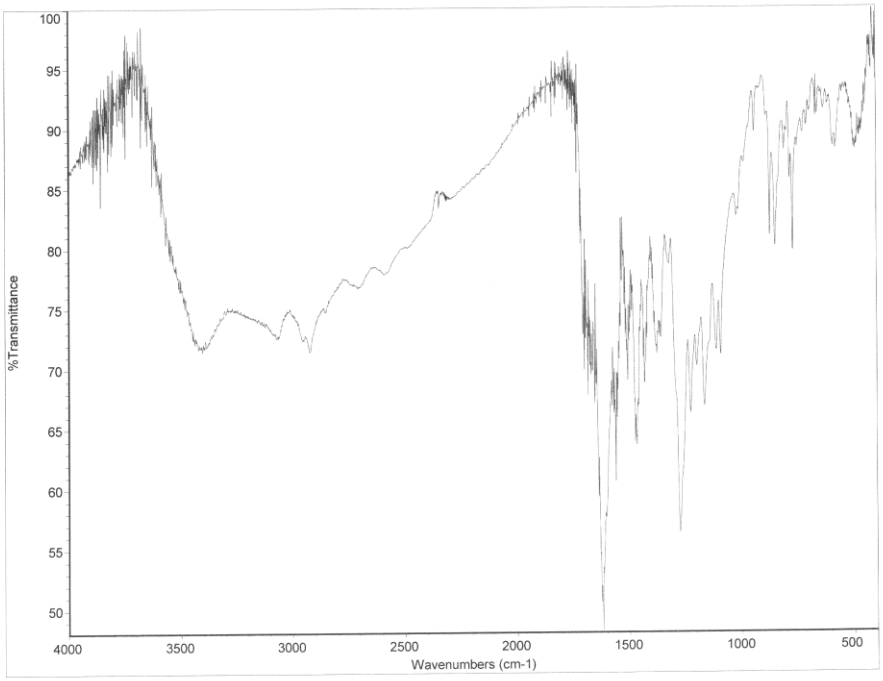

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jul 9 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 3.3
wp 4793.2
vs 227
sc 0
wc 250
hzmm 19.17
fs 530.52
rf1 1607.8
rfp 1000.7
th 20
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
HO
O
Me
O
O
OH
Me
O
O
149
11
10
9
8
7
6
5
4
3
2
1
ppm

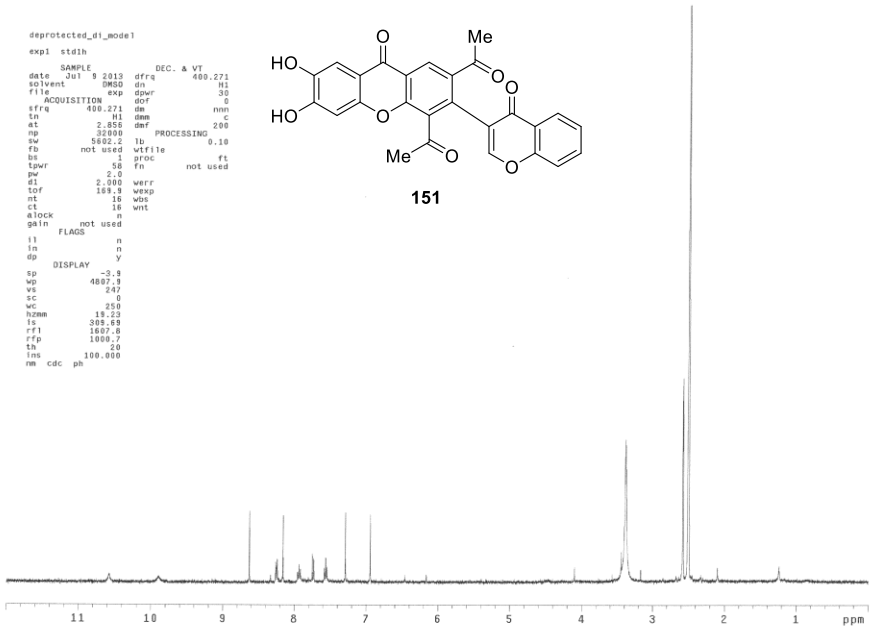

deprotected dittop vinaxanthone
Sample Name:
Data Collected on:
nmroa2-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: dmso
Data collected on: Jul 10 2013
Temp. 27.0 C / 300.1 K
Operator: service
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.000 sec
Width 37878.8 Hz
13000 repetitions
OBSERVE C13, 150.8079738 MHz
DECOUPLE H1, 599.7555838 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 14 hr, 26 min
200
180
160
140
120
100
80
60
40
20
ppm


100
95
90
85
80
75
70
65
60
55
50
45
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

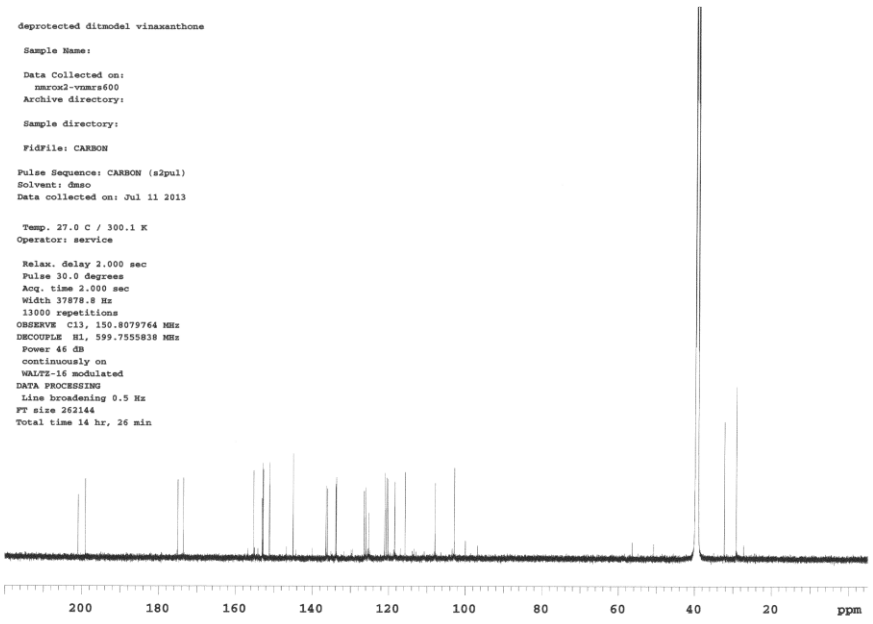

exp35 PROTON
SAMPLE
date Jul 9 2013
solvent dmso
file /home/space/d~
ata/mrc_deprotecte~
d_di_bottom_201307~
09_01/PROTON_01.fi~
d
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
di 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.090
tof 400.0
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR~
_W009
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 46
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -0.2
wp 4802.6
rf1 1797.4
rfp 1000.2
rp -85.3
lp 0
PLOT
wc 250
sc 0
vs 175
th 2
al cdc ph
HO
HO
O
O
O
Me
Me
O
O
OH
150
11
10
9
8
7
6
5
4
3
2
1
ppm

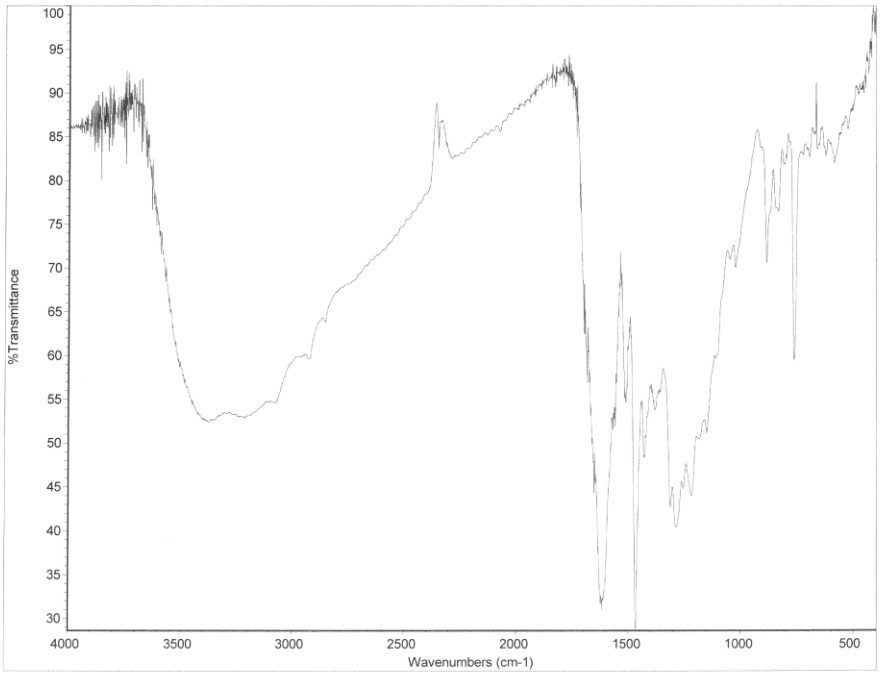

deprotected_di_bottom_vinaxanthone_c13
exp2 Carbon
SAMPLE
date Jun 17 2013
solvent dmso
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
di 2.000
nt 20000
ct 16310
TRANSMITTER
tn C13
sfrq 125.586
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm YYY
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -19.9
wp 27661.1
rf1 7570.9
rfp 4960.1
rp -158.9
lp -235.1
PLOT
wc 250
sc 0
vs 97145
th 8
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

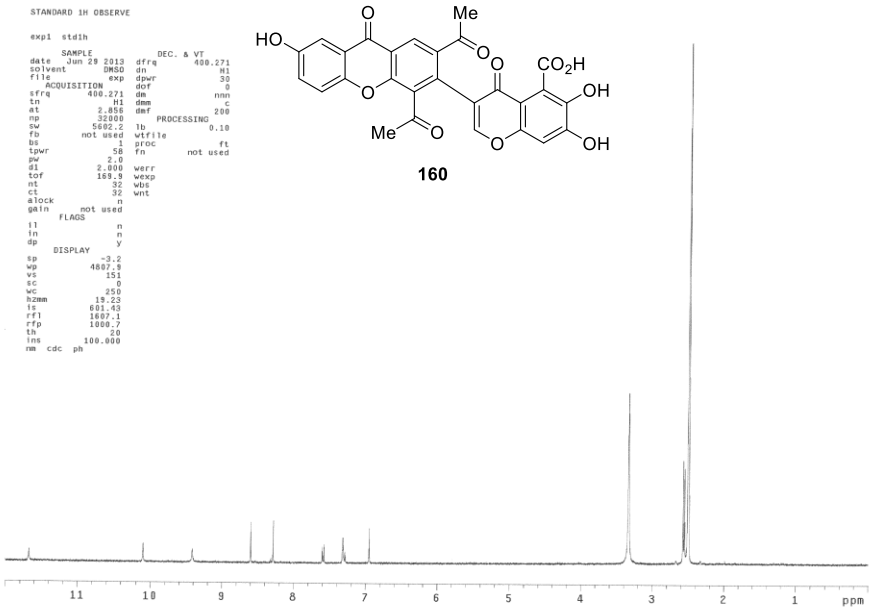

100
95
90
85
80
75
70
65
60
55
50
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

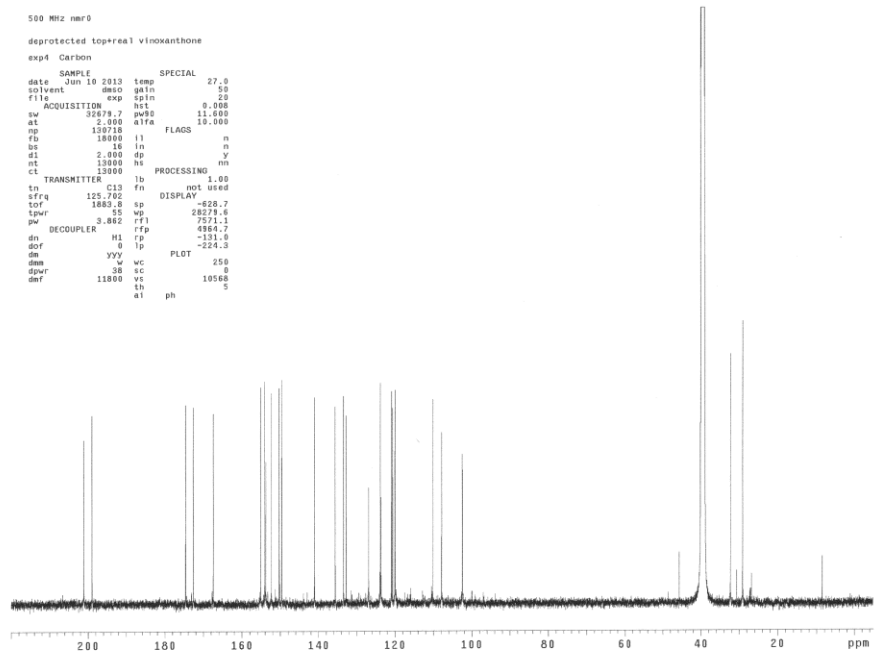

deprotected_d1_model
exp1 stdlh
SAMPLE
date Jul 9 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5802.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.9
wp 4807.9
vs 247
sc 0
wc 250
hzmm 15.23
is 305.68
rf1 1607.6
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
HO
O
Me
O
O
Me
O
O
11
10
9
8
7
6
5
4
3
2
1
ppm

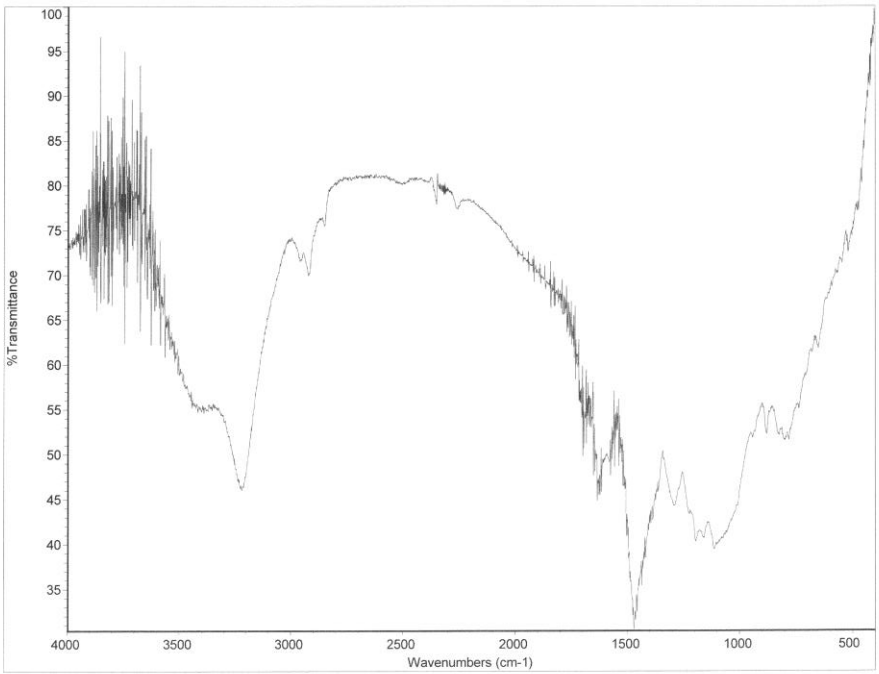
151

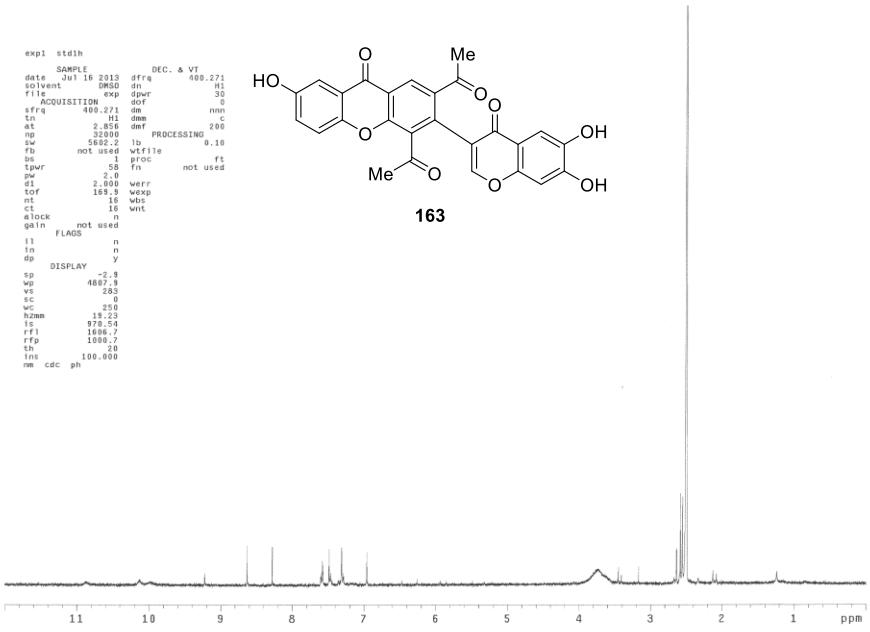

deprotected ditmodel vinaxanthone
Sample Name:
Data Collected on:
nmrox2-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: dmso
Data collected on: Jul 11 2013
Temp. 27.0 C / 300.1 K
Operator: service
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.000 sec
Width 37878.8 Hz
13000 repetitions
OBSERVE C13, 150.8079764 MHz
DECOUPLE H1, 599.7555838 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 14 hr, 26 min
200
180
160
140
120
100
80
60
40
20
ppm

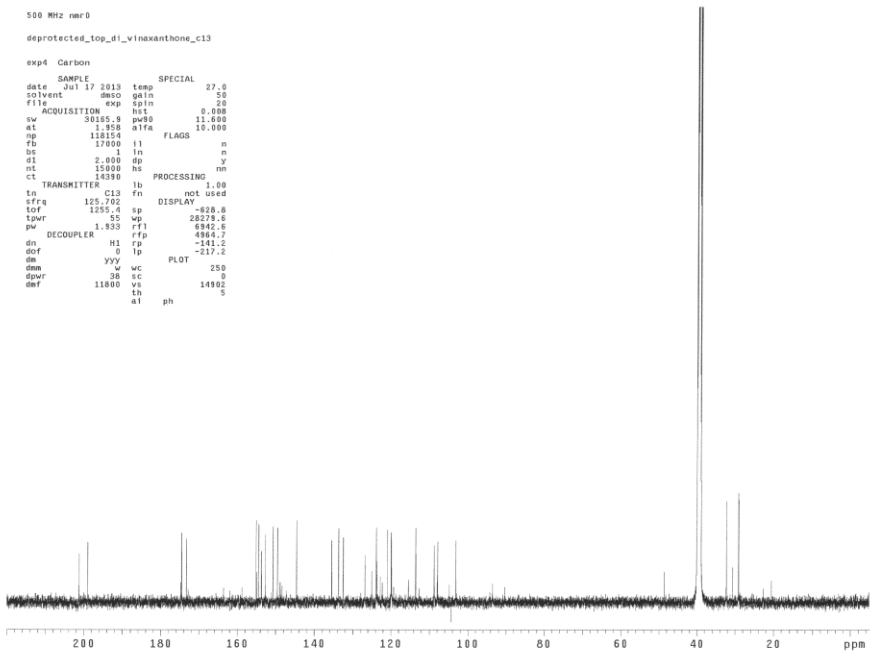

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

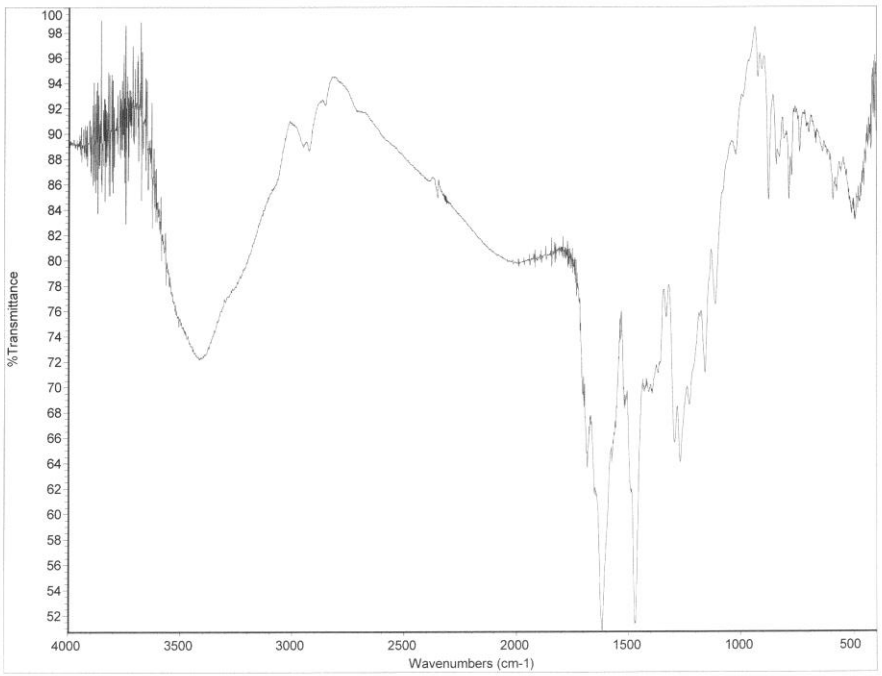

STANDARD 1H OBSERVE
exp1 stdlh
SAMPLE
date Jun 29 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 163.9
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4807.9
vs 151
sc 0
wc 250
hzmm 15.23
fs 601.43
rf1 1607.1
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
CO2H
OH
O
Me
O
O
OH
160
11
10
9
8
7
6
5
4
3
2
1
ppm

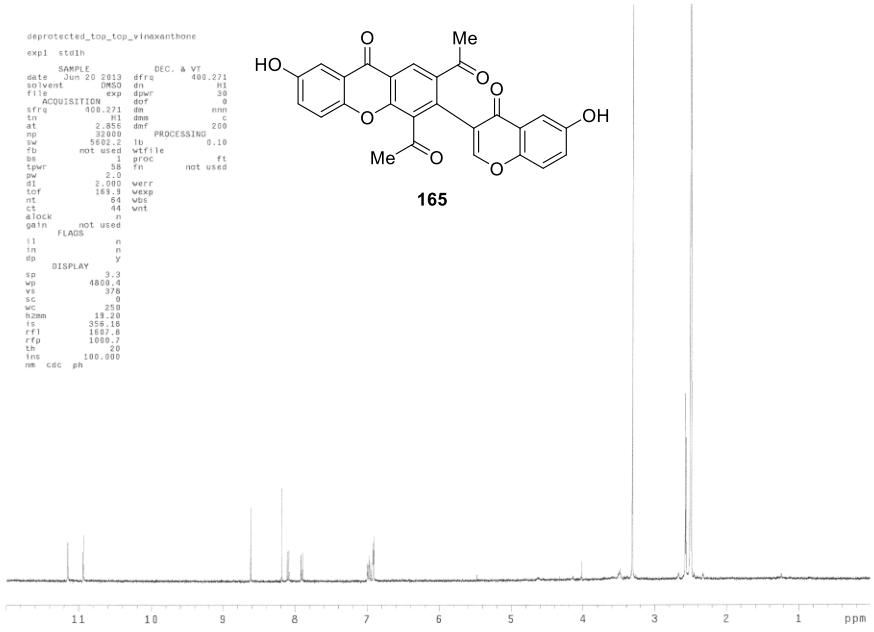

500 MHz nmr0
deprotected top+real vinoxanthone
exp4 Carbon
SAMPLE
date Jun 10 2013
solvent dmso
file exp
ACQUISITION
sw 32679.7
at 2.000
np 130718
fb 18000
bs 16
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 125.702
tof 1883.8
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.7
wp 28279.6
rf1 7571.1
rfp 4964.7
rp -131.0
lp -224.3
PLOT
wc 250
sc 0
vs 10568
th 5
al ph
200
180
160
140
120
100
80
60
40
20
ppm

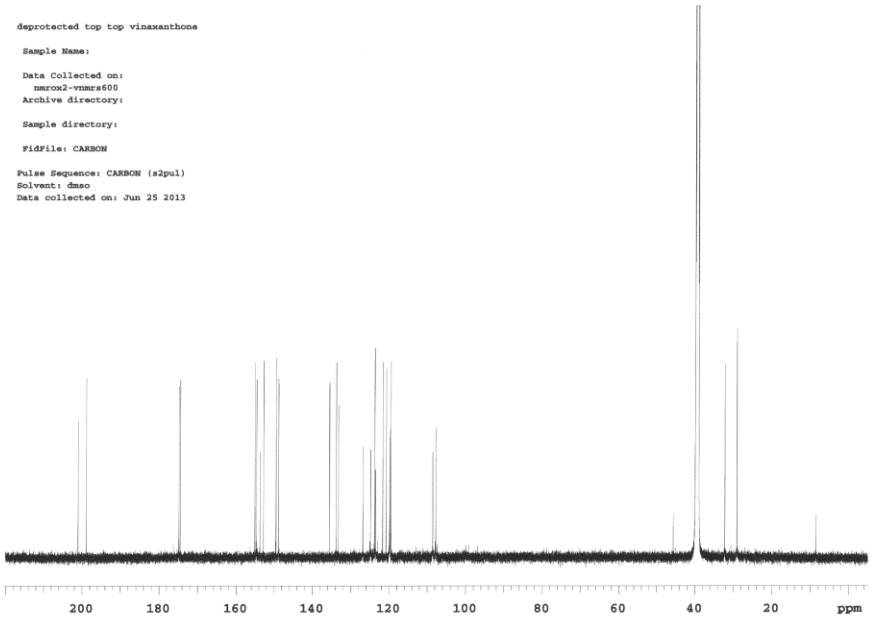

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

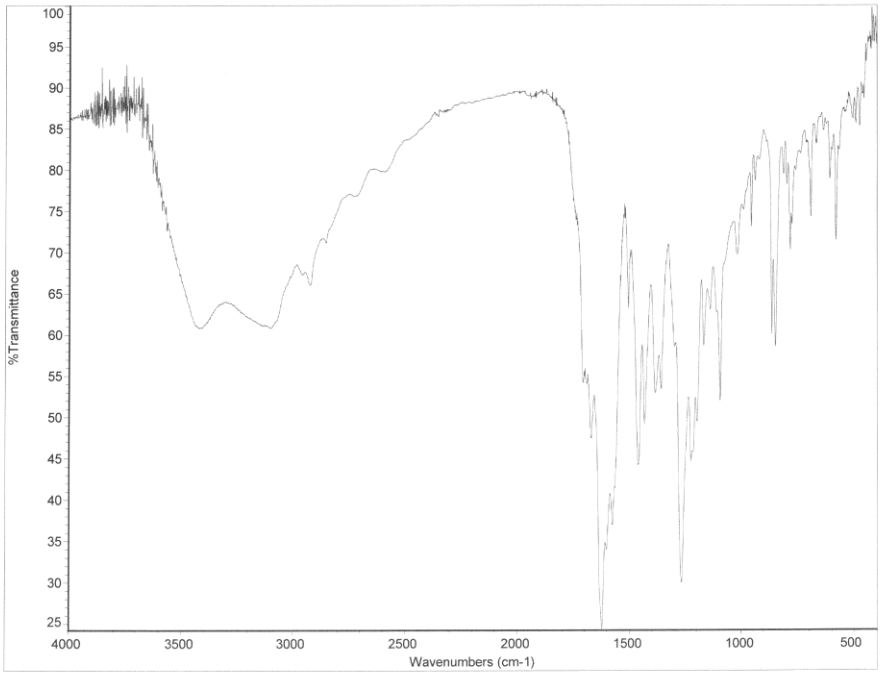

exp1 std1h
SAMPLE
date Jul 16 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2.9
wp 4807.9
vs 283
sc 0
wc 250
hzmm 15.23
is 970.54
rfl 1686.7
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
O
OH
Me
O
O
OH
163
11
10
9
8
7
6
5
4
3
2
1
ppm

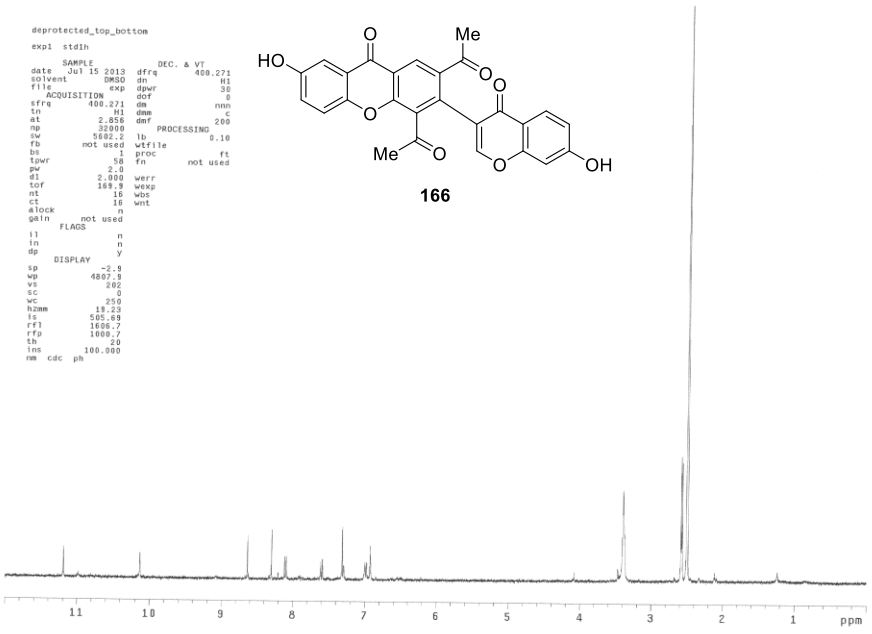

500 MHz nmr0
deprotected_top_di_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jul 17 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.358
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 14390
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 1.933
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 58
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.8
wp 28279.6
rfl 6942.6
rfp 4964.7
rp -141.2
lp -217.2
PLOT
wc 250
sc 0
vs 14902
th 5
ai ph
200
180
160
140
120
100
80
60
40
20
ppm

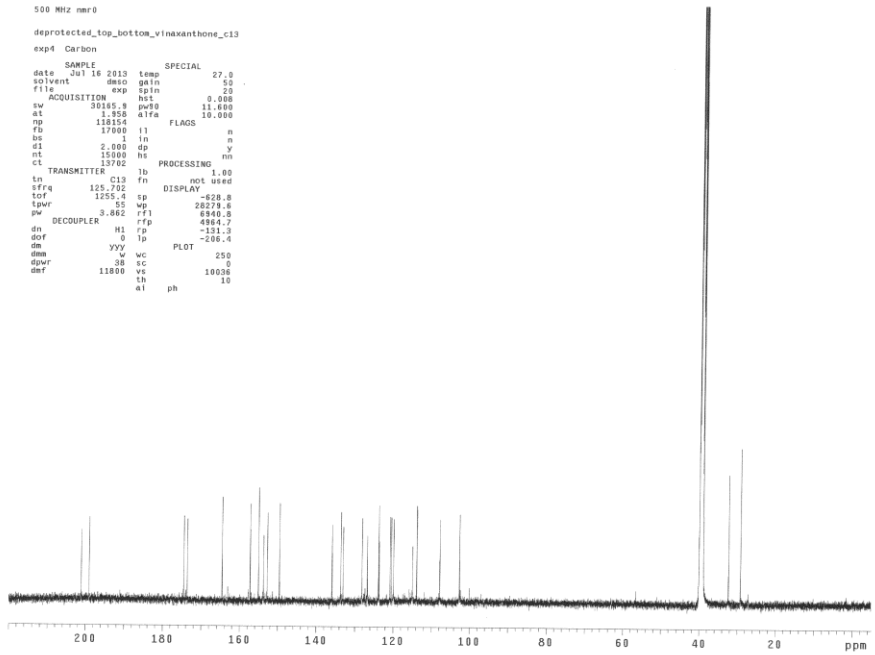

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

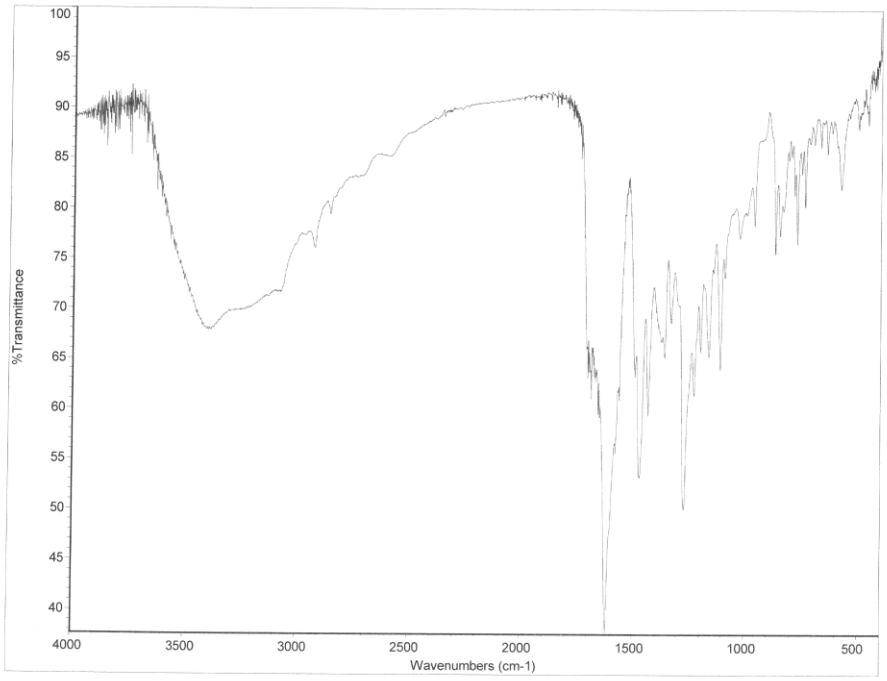

deprotected_top_top_vinaxanthone
exp1 std1h
SAMPLE
date Jun 20 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 64
ct 44
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 3.3
wp 4800.4
vs 378
sc 0
wc 250
hzmm 18.20
is 355.18
rfl 1687.8
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
HO
O
Me
O
O
OH
Me
O
O
165
11
10
9
8
7
6
5
4
3
2
1
ppm

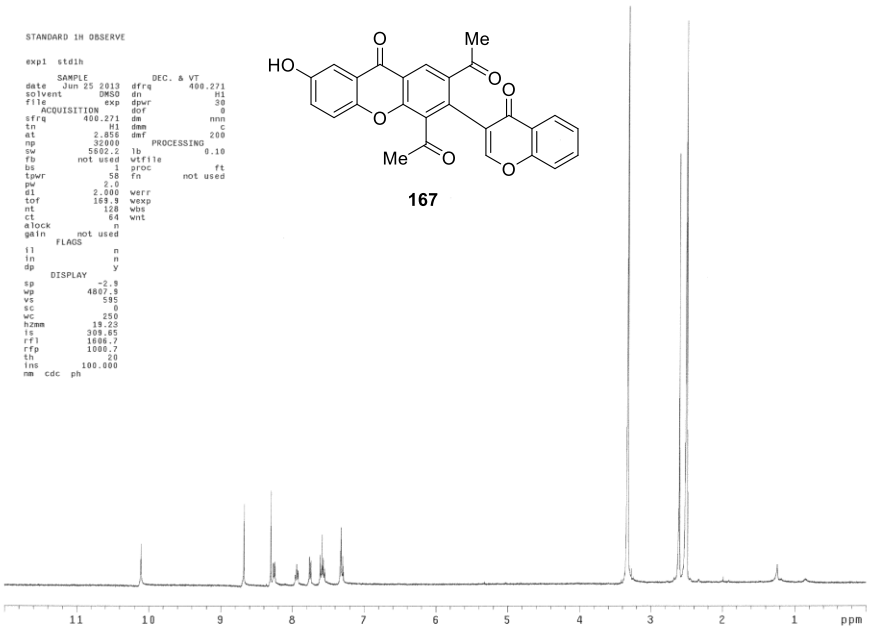

deprotected top top vinaxanthone
Sample Name:
Data Collected on:
nmrox2-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: dmso
Data collected on: Jun 25 2013
200
180
160
140
120
100
80
60
40
20
ppm

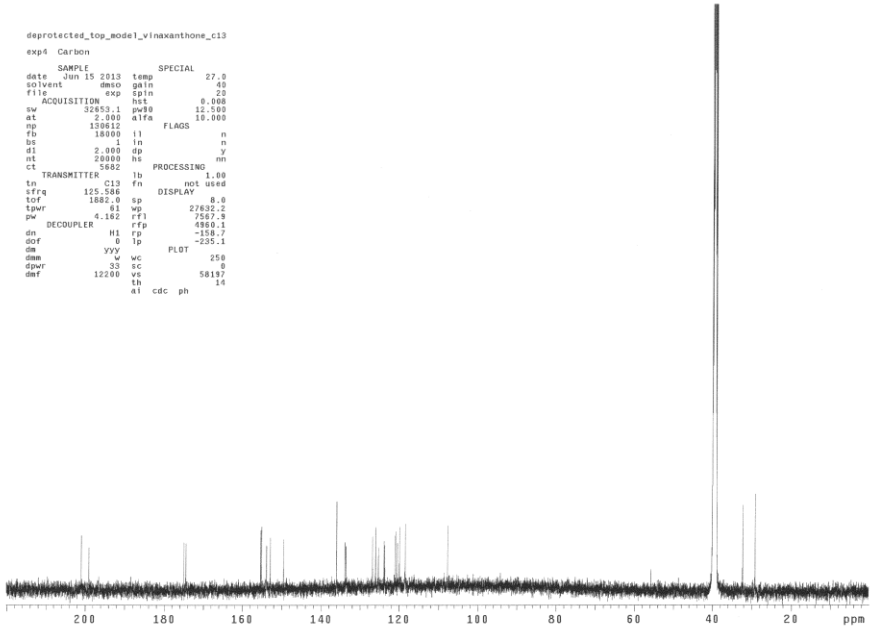

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

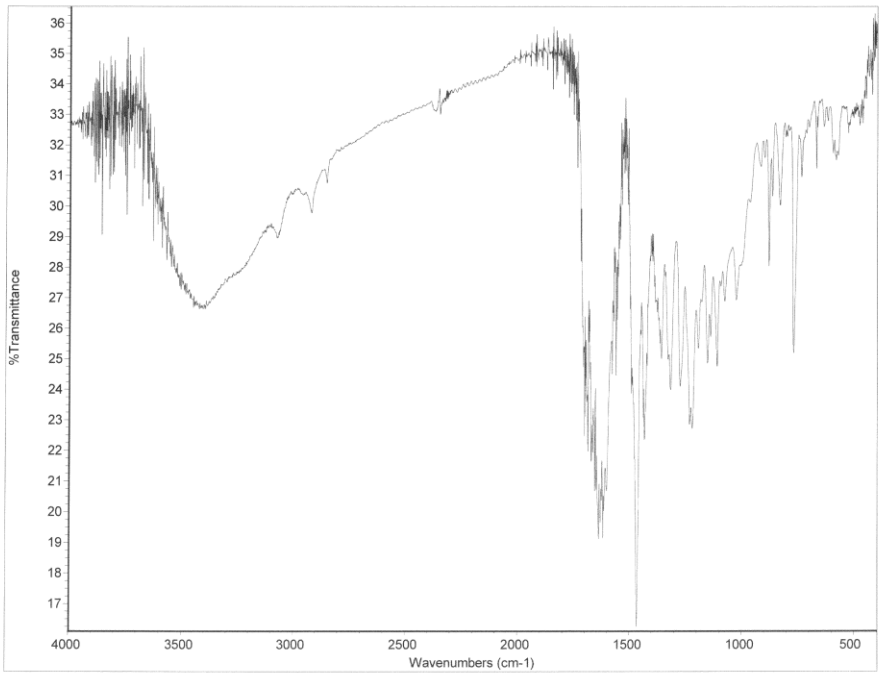

deprotected_top_bottom
exp1 std1h
SAMPLE
date Jul 15 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5802.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2.9
wp 4807.9
vs 202
sc 0
wc 250
hzmm 18.23
is 505.68
rf1 1606.7
rf2 1008.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
Me
O
O
OH
166
11
10
9
8
7
6
5
4
3
2
1
ppm

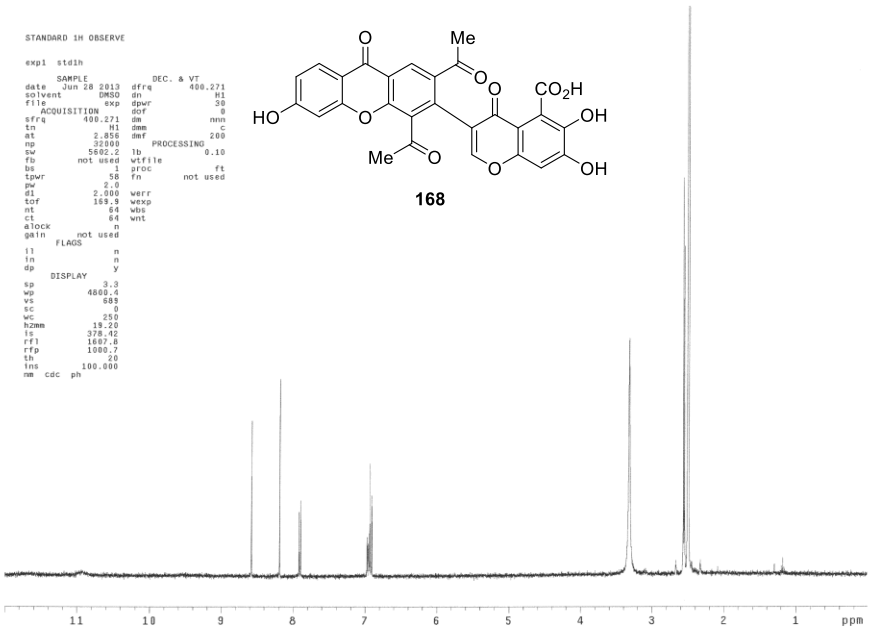

500 MHz nmr0
deprotected_top_bottom_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jul 16 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.956
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 13702
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw80 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.8
wp 28279.6
rf1 6940.8
rfp 4964.7
rp -131.3
lp -206.4
PLOT
wc 250
sc 0
vs 10036
th 10
al ph
200
180
160
140
120
100
80
60
40
20
ppm

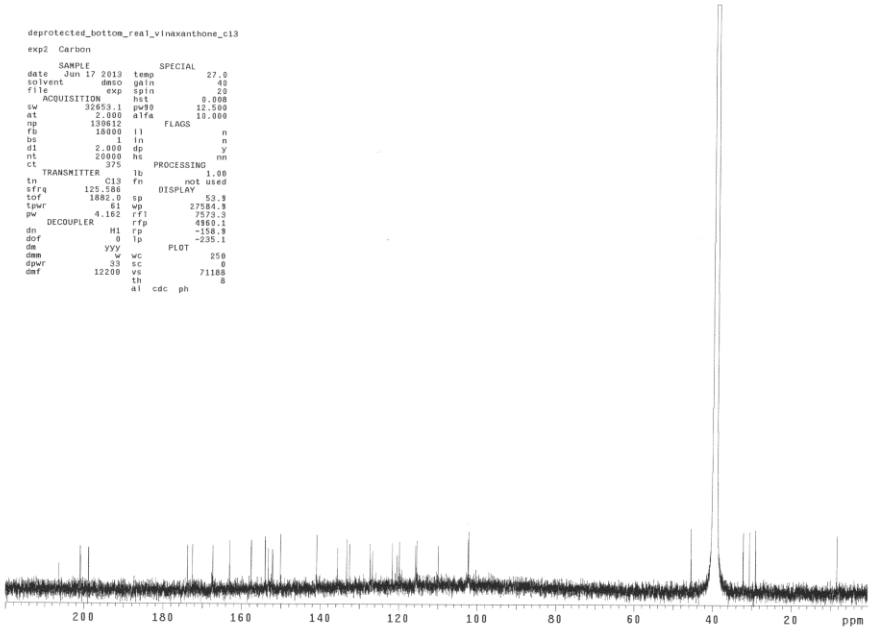

100
95
90
85
80
75
70
65
60
55
50
45
40
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

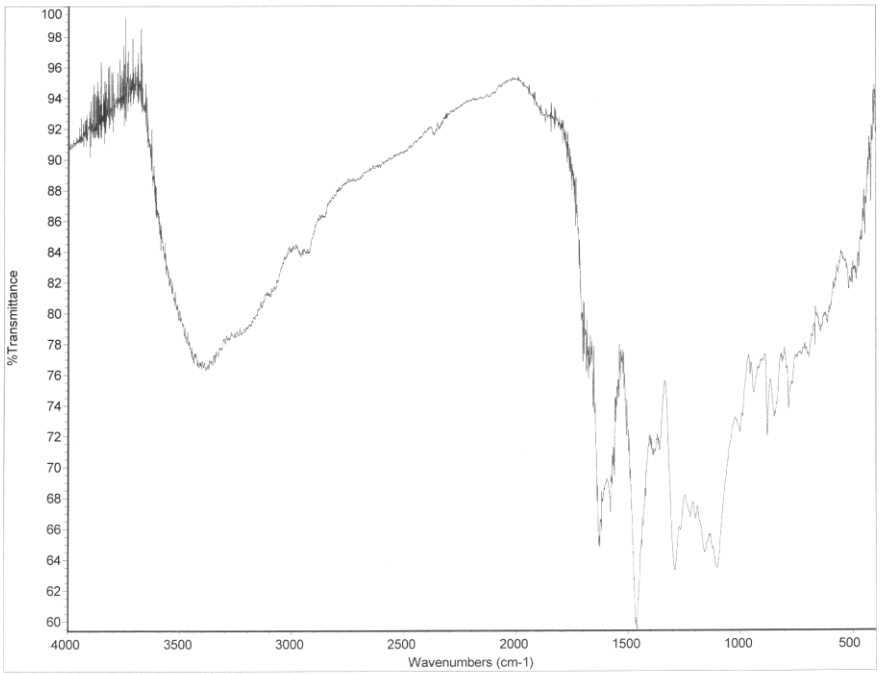

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jun 25 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 163.9
nt 128
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2.9
wp 4807.9
vs 595
sc 0
wc 250
hzmm 19.23
is 309.65
rfl 1606.7
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
Me
O
O
167
11
10
9
8
7
6
5
4
3
2
1
ppm

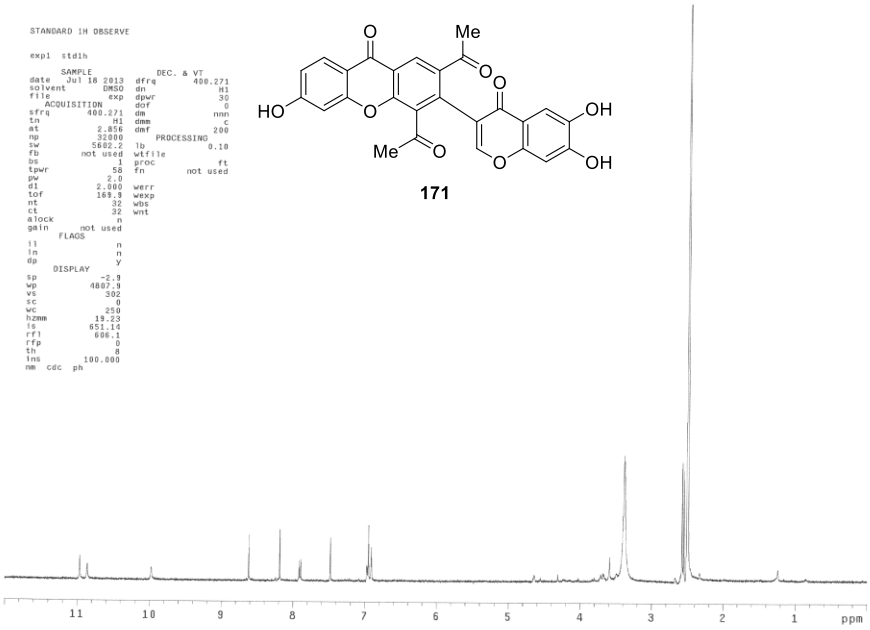

deprotected_top_model_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jun 15 2013
solvent dmso
file exp
ACQUISITION
sw 32853.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 20000
ct 5682
TRANSMITTER
tn C13
sfrq 125.586
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 8.0
wp 27632.2
rfl 7567.9
rfp 4960.1
rp -158.7
lp -235.1
PLOT
wc 250
sc 0
vs 58197
th 14
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

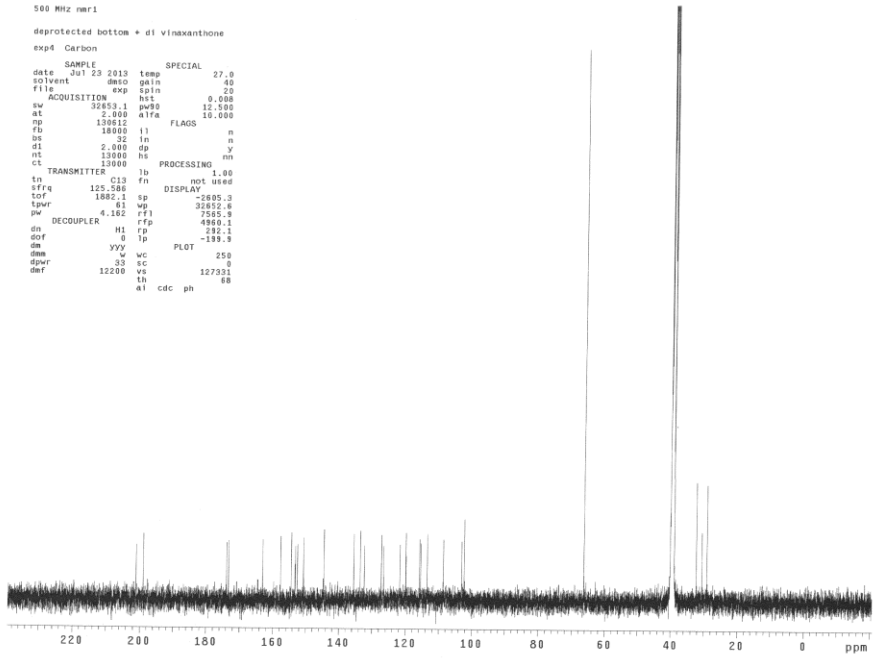

%Transmittance
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

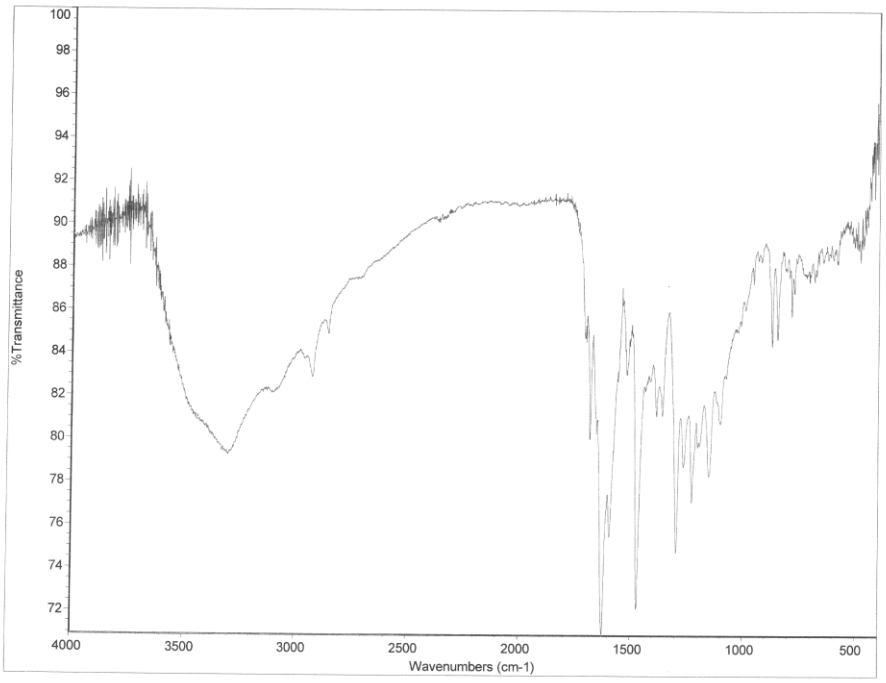

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jun 28 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 163.9
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 3.3
wp 4800.4
vs 689
sc 0
wc 250
hzmm 19.20
fs 378.42
rfl 1607.8
rfp 1080.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
CO2H
OH
Me
O
O
OH
168
11
10
9
8
7
6
5
4
3
2
1
ppm

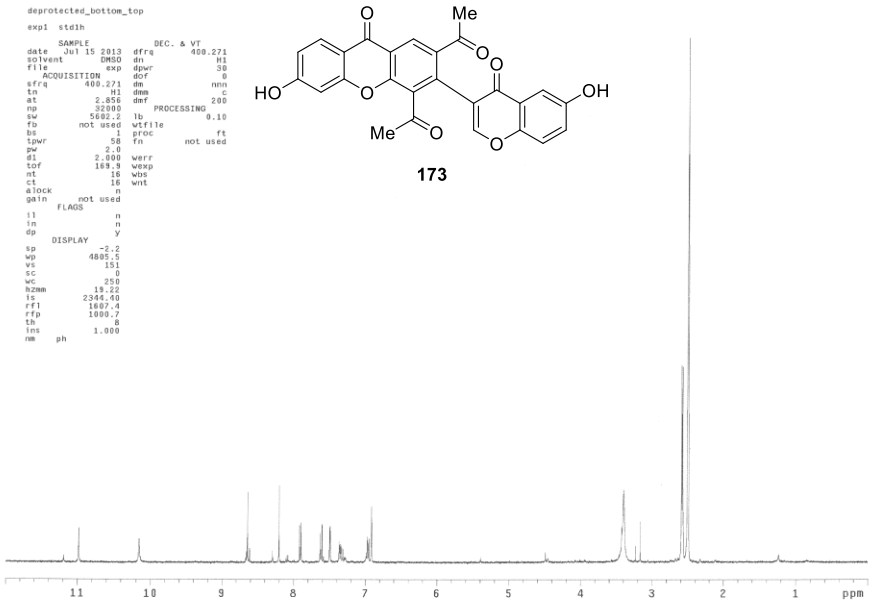

deprotected_bottom_real_vinaxanthone_c13
exp2 Carbon
SAMPLE
date Jun 17 2013
solvent dmso
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 1
d1 2.000
nt 20000
ct 375
TRANSMITTER
tn C13
sfrq 125.586
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 53.8
wp 27584.9
rfl 7573.3
rfp 4960.1
rp -158.9
lp -235.1
PLOT
wc 250
sc 0
vs 71188
th 8
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

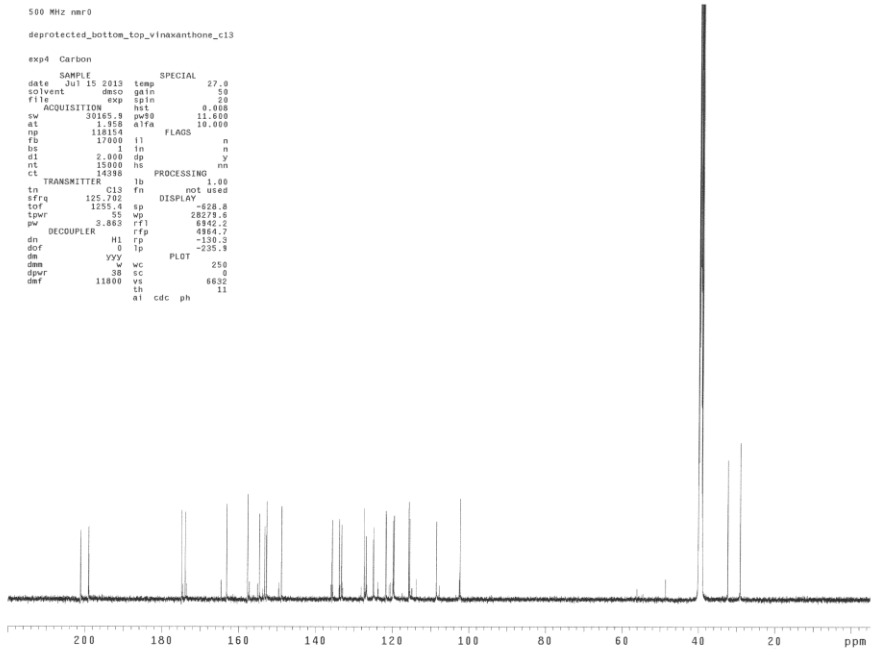

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

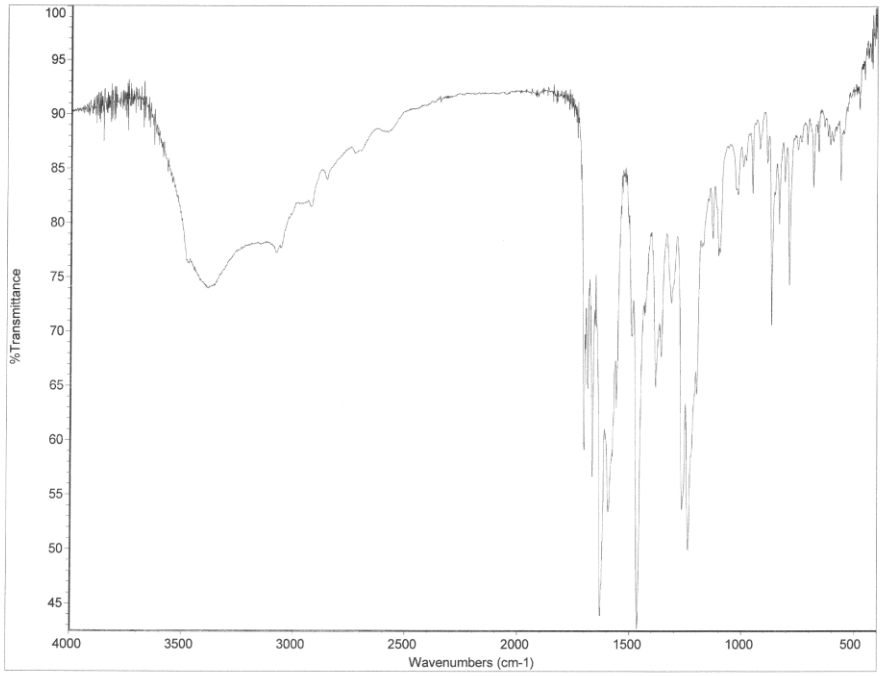

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jul 16 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2.9
wp 4807.9
vs 302
sc 0
wc 250
hzmm 19.23
is 651.14
rfl 606.1
rfp 0
th 8
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
Me
O
OH
OH
O
171
11
10
9
8
7
6
5
4
3
2
1
ppm

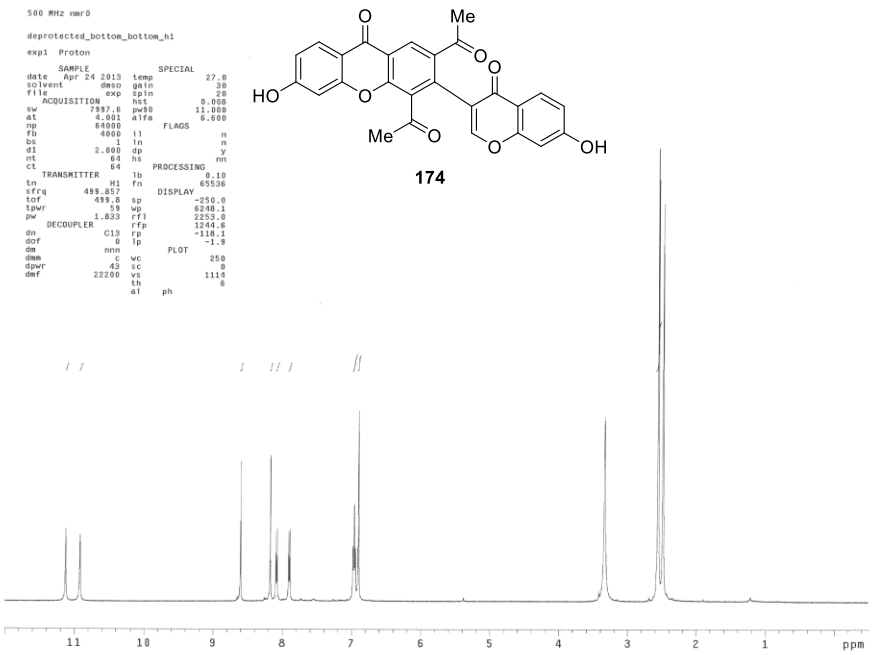

500 MHz nmr1
deprotected bottom + d1 vimaxanthone
exp4 Carbon
SAMPLE
date Jul 23 2013
solvent dmso
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 32
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 125.586
tof 1882.1
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -2605.3
wp 32652.6
rfl 7565.9
rfp 4960.1
rp 292.1
lp -198.9
PLOT
wc 250
sc 0
vs 127331
th 68
ai cdc ph
220
200
180
160
140
120
100
80
60
40
20
0
ppm

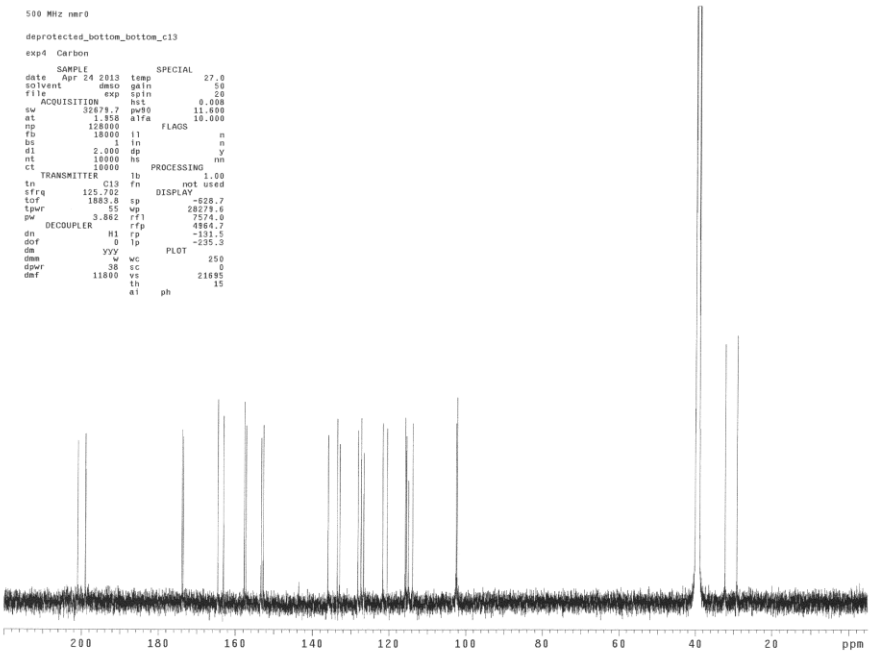

100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

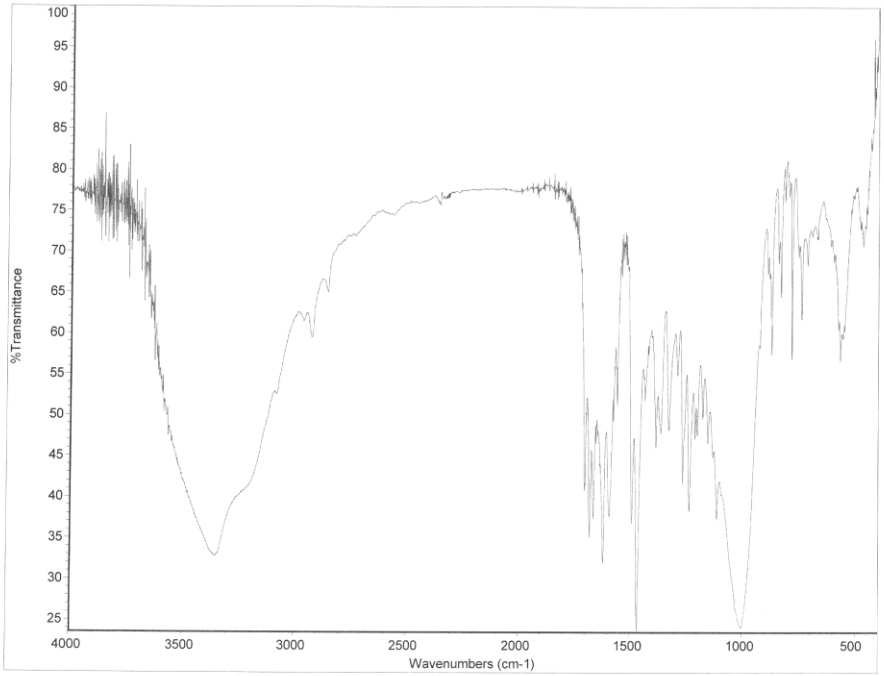

deprotected_bottom_top
exp1 std1h
SAMPLE
date Jul 15 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2.2
wp 4805.5
vs 151
sc 0
wc 250
hzmm 19.22
is 2344.40
rfl 1607.4
rfp 1000.7
th 8
ins 1.000
nm ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
OH
173
11
10
9
8
7
6
5
4
3
2
1
ppm

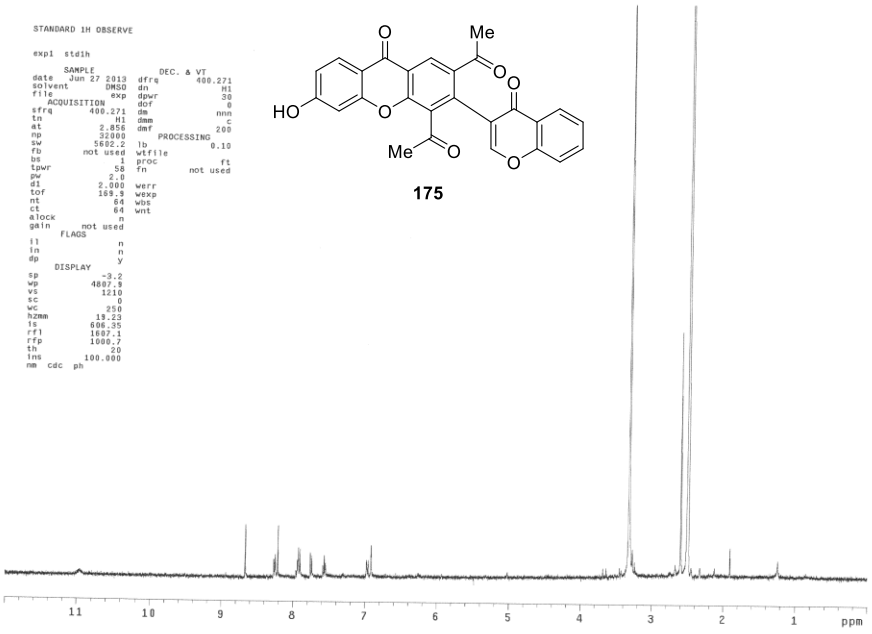

500 MHz nmr0
deprotected_bottom_top_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jul 15 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118154
fb 17000
bs 1
d1 2.000
nt 15000
ct 14398
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 3.863
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.8
wp 28279.6
rfl 6942.2
rfp 4964.7
rp -130.3
lp -235.9
PLOT
wc 250
sc 0
vs 6632
th 11
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm

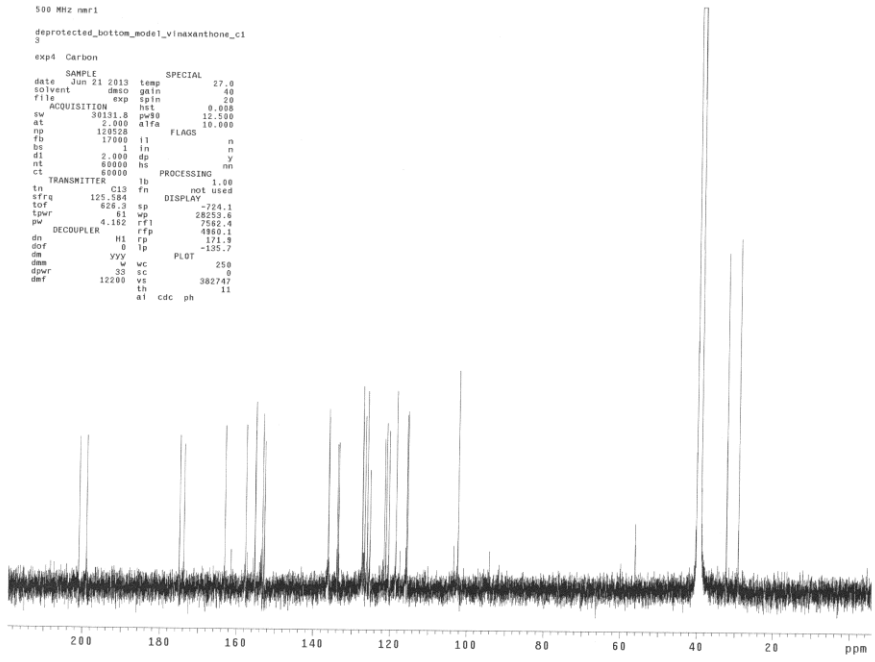

100
95
90
85
80
75
70
65
60
55
50
45
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

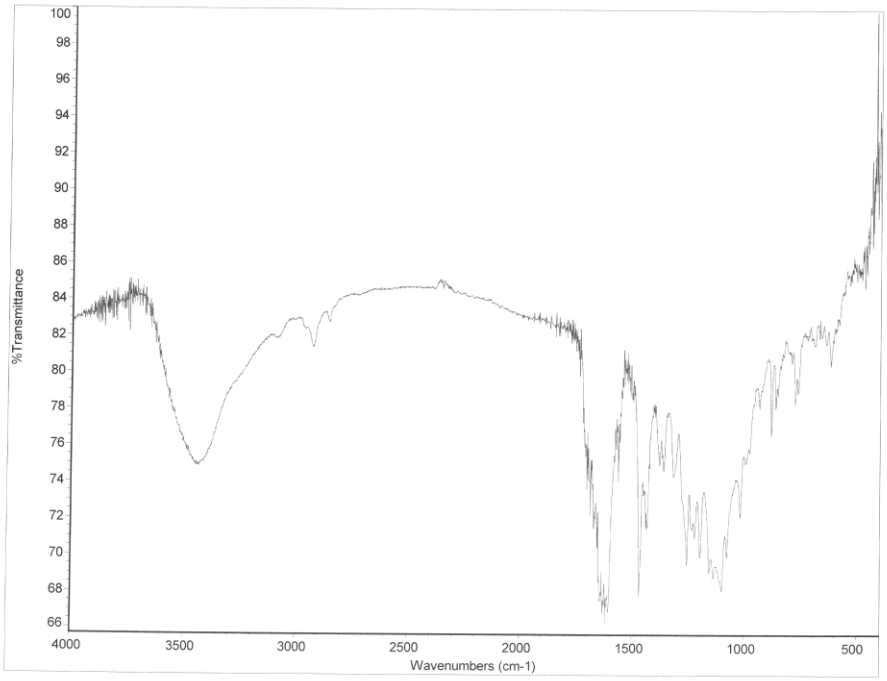

500 MHz nmr0
deprotected_bottom_bottom_h1
exp1 Proton
SAMPLE
date Apr 24 2013
solvent dmso
file exp
ACQUISITION
sw 7997.6
at 4.001
np 64000
fb 4000
bs 1
d1 2.000
nt 64
ct 64
TRANSMITTER
tn H1
sfrq 499.857
tof 499.8
tpwr 59
pw 1.833
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 43
dmf 22200
SPECIAL
temp 27.0
gain 30
spin 20
hst 0.008
pw90 11.000
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.10
fn 65536
DISPLAY
sp -250.0
wp 6248.1
rf1 2253.0
rfp 1244.6
rp -118.1
lp -1.9
PLOT
wc 250
sc 0
vs 1114
th 6
al ph
O
Me
O
O
HO
O
Me
O
O
OH
174
11
10
9
8
7
6
5
4
3
2
1
ppm

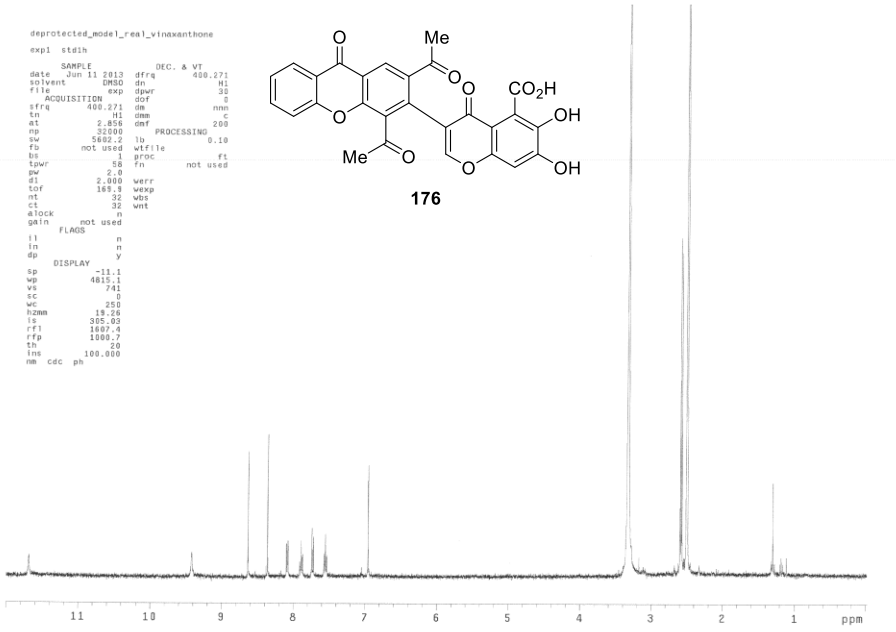

500 MHz nmr0
deprotected_bottom_bottom_c13
exp4 Carbon
SAMPLE
date Apr 24 2013
solvent dmso
file exp
ACQUISITION
sw 32679.7
at 1.358
np 128000
fb 18000
bs 1
d1 2.000
nt 10000
ct 10000
TRANSMITTER
tn C13
sfrq 125.702
tof 1883.8
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.7
wp 28279.6
rf1 7574.0
rfp 4964.7
rp -131.5
lp -235.3
PLOT
wc 250
sc 0
vs 21695
th 15
al ph
200
180
160
140
120
100
80
60
40
20
ppm

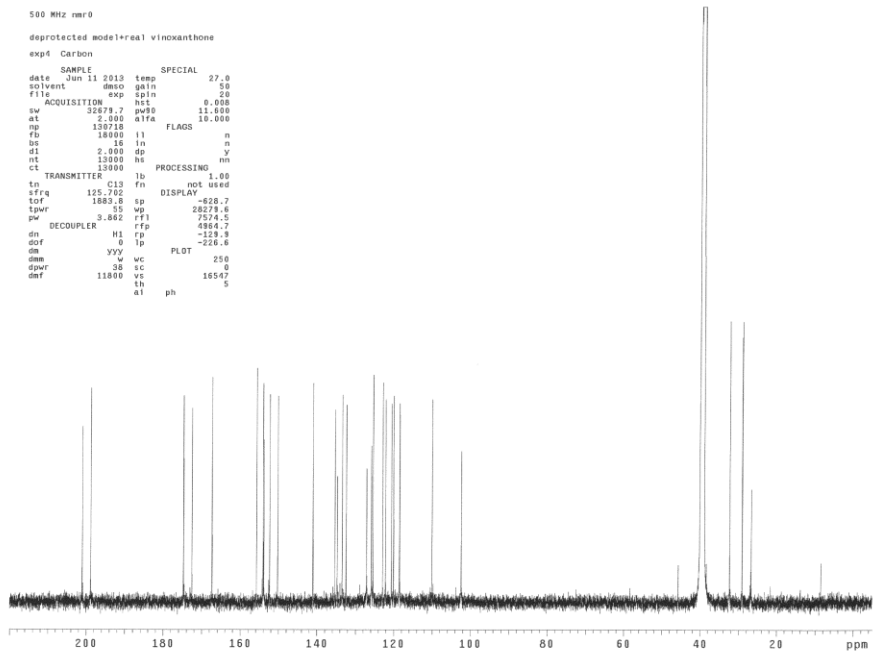

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

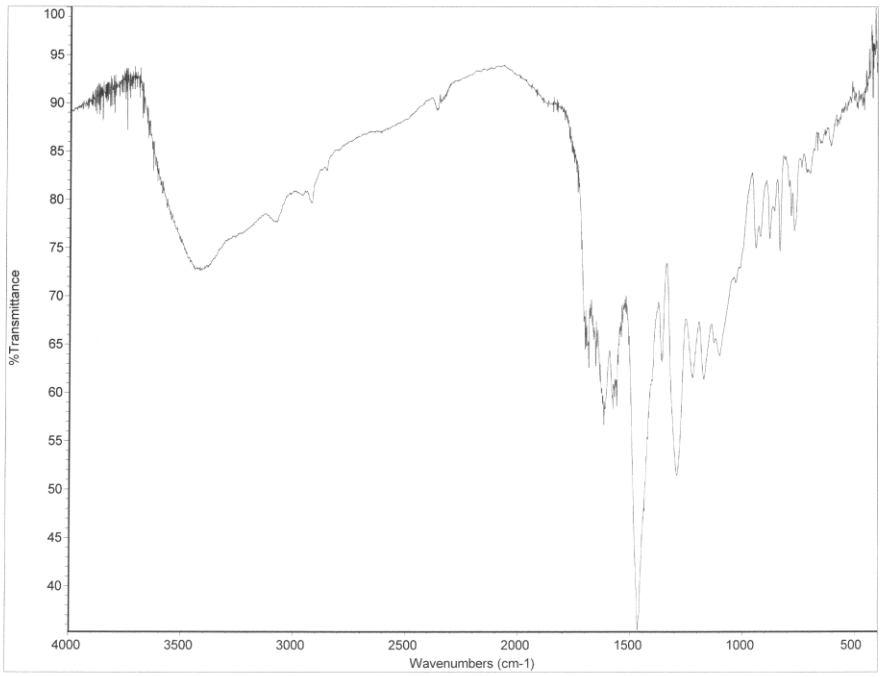

STANDARD 1H OBSERVE
exp1 std1h
SAMPLE
date Jun 27 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 169.9
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -3.2
wp 4807.9
vs 1210
sc 0
wc 250
hzmm 19.23
is 606.35
rf1 1607.1
rfp 1000.7
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
HO
O
Me
O
O
Me
O
O
175
11
10
9
8
7
6
5
4
3
2
1
ppm

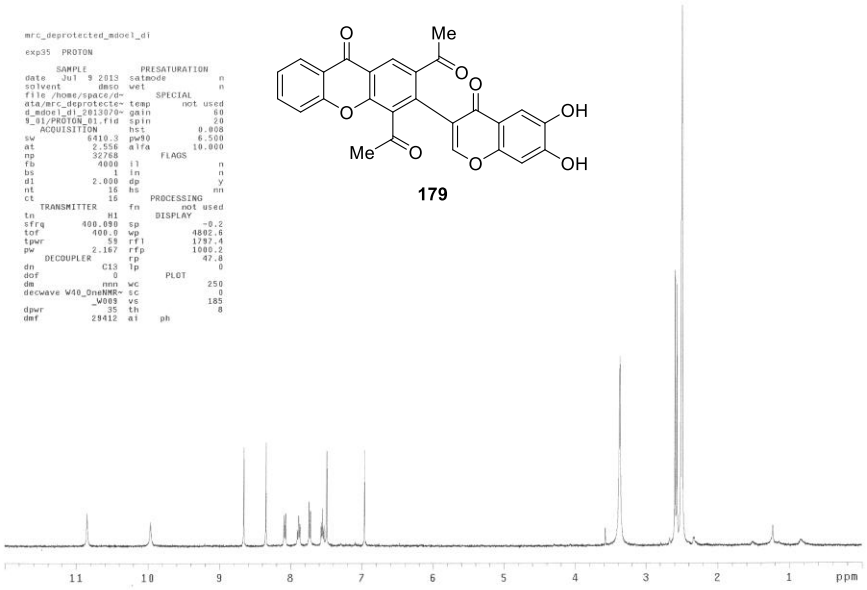

500 MHz nmr1
deprotected_bottom_model_vinaxanthone_c1
3
exp4 Carbon
SAMPLE
date Jun 21 2013
solvent dmso
file exp
ACQUISITION
sw 30131.8
at 2.000
np 120528
fb 17000
bs 1
d1 2.000
nt 60000
ct 60000
TRANSMITTER
tn C13
sfrq 125.584
tof 626.3
tpwr 61
pw 4.182
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -724.1
wp 28253.6
rf1 7562.4
rfp 4860.1
rp 171.9
lp -135.7
PLOT
wc 250
sc 0
vs 382747
th 11
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

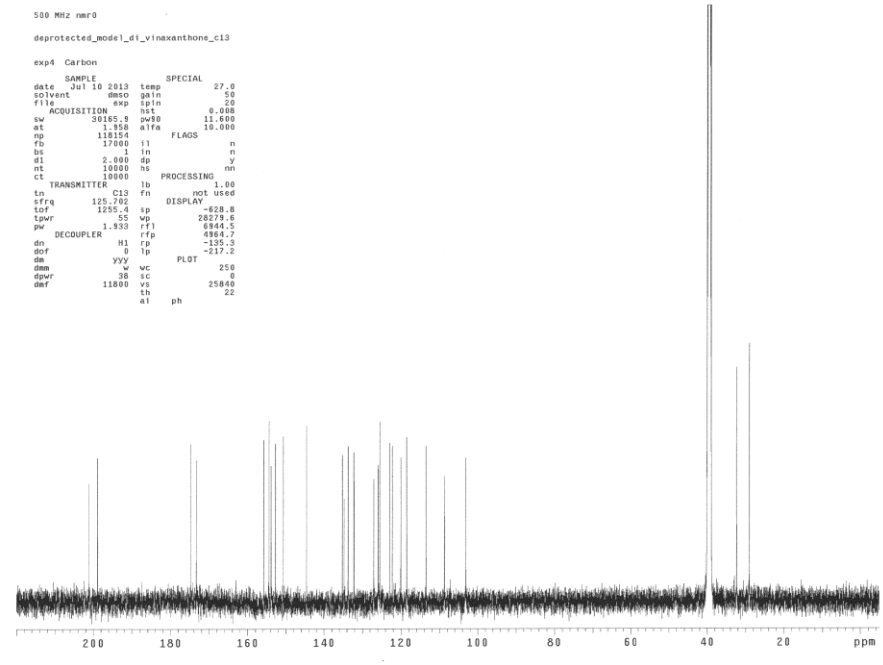

deprotected_model_real_vinaxanthone
exp1 std1h
SAMPLE
date Jun 11 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 32000
sw 5602.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 165.5
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -11.1
wp 4815.1
vs 741
sc 0
wc 250
hzmm 19.26
is 305.03
rf1 1607.4
rfp 1000.7
th 20
ins 100.000
nm cdc ph
OEC. & VT
dfrq 400.271
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
CO2H
OH
176
11
10
9
8
7
6
5
4
3
2
1
ppm

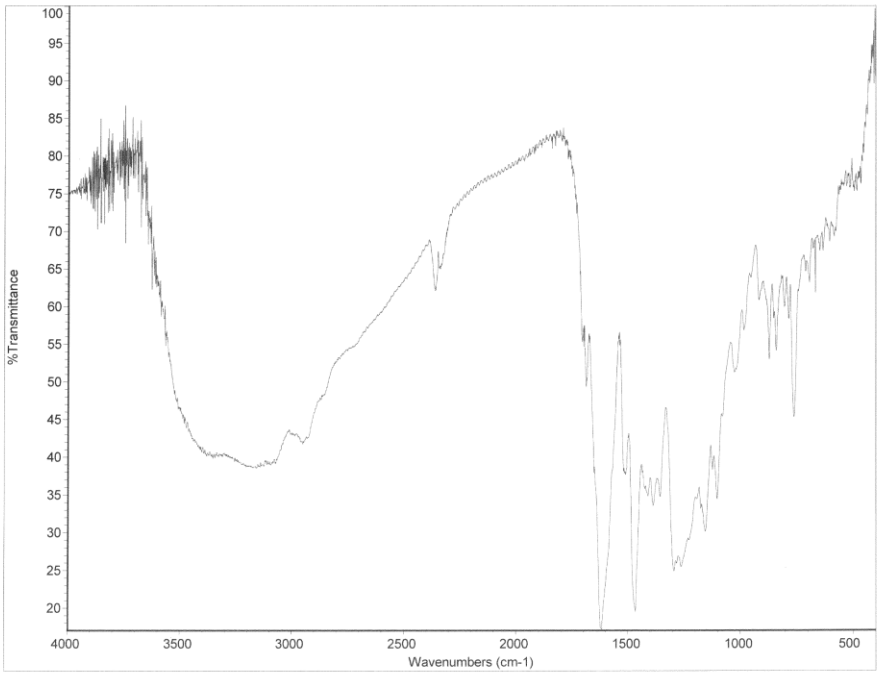

500 MHz nmr0
deprotected model+real vinoxanthone
exp4 Carbon
SAMPLE
date Jun 11 2013
solvent dmso
file exp
ACQUISITION
sw 32679.7
at 2.000
np 130718
fb 18000
bs 16
d1 2.000
nt 13000
ct 13000
TRANSMITTER
tn C13
sfrq 125.702
tof 1883.8
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.7
wp 28278.6
rf1 7574.5
rfp 4964.7
rp -129.9
lp -226.6
PLOT
wc 250
sc 0
vs 16547
th 5
al ph
200
180
160
140
120
100
80
60
40
20
ppm

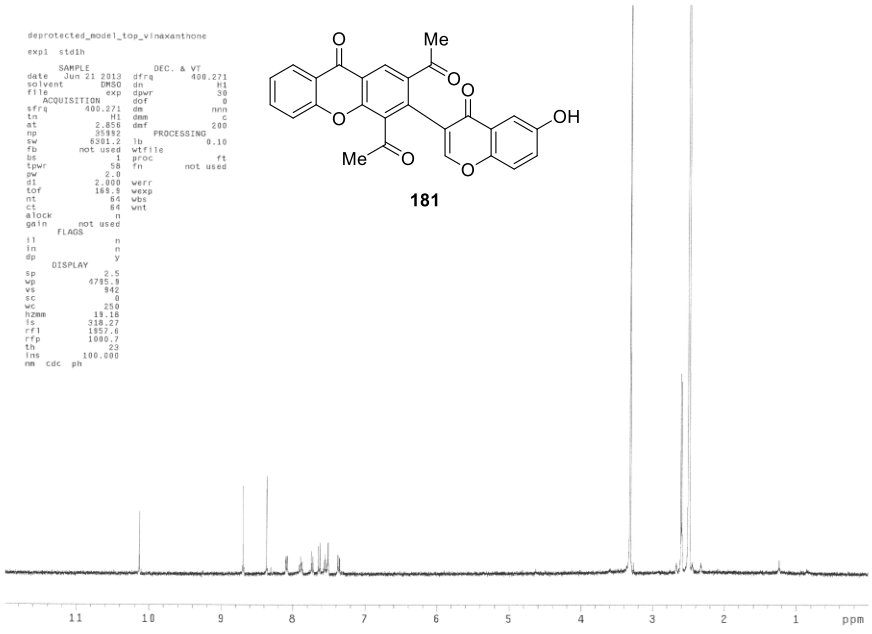

100
95
90
85
80
75
70
65
60
55
50
45
40
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

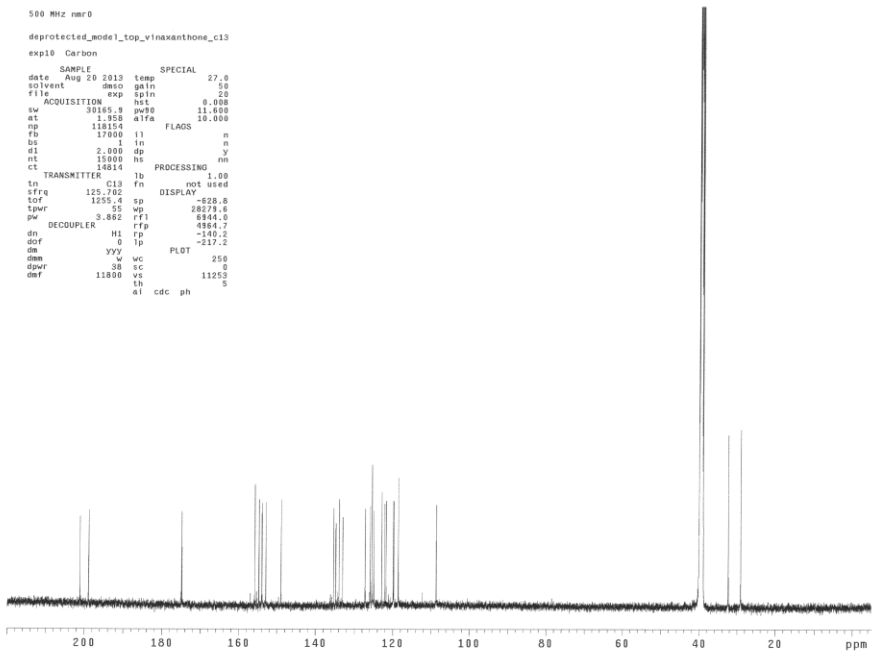

mrc_deprotected_mdoel_d1
exp35 PROTON
SAMPLE
date Jul 9 2013
solvent dmso
file /home/space/d~
ata/mrc_deprotecte~
d_mdoel_d1_2013070~
9_01/PROTON_01.fid
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.090
tof 400.0
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR~
_W989
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 60
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -0.2
wp 4882.6
rf1 1797.4
rfp 1080.2
rp 47.8
lp 0
PLOT
wc 250
sc 0
vs 185
th 8
al ph
O
Me
O
O
OH
Me
O
O
OH
11
10
9
8
7
6
5
4
3
2
1
ppm

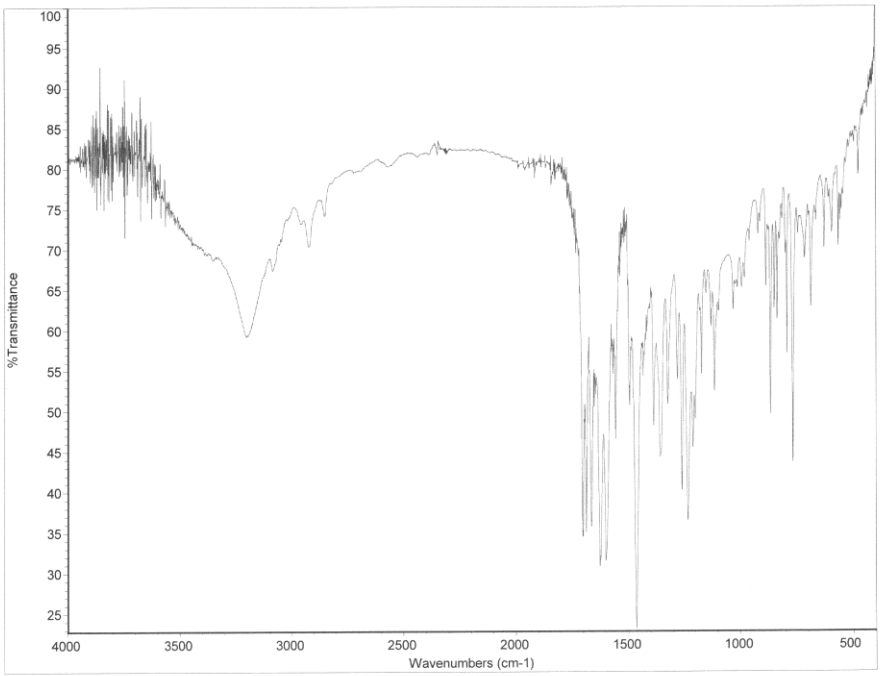
179

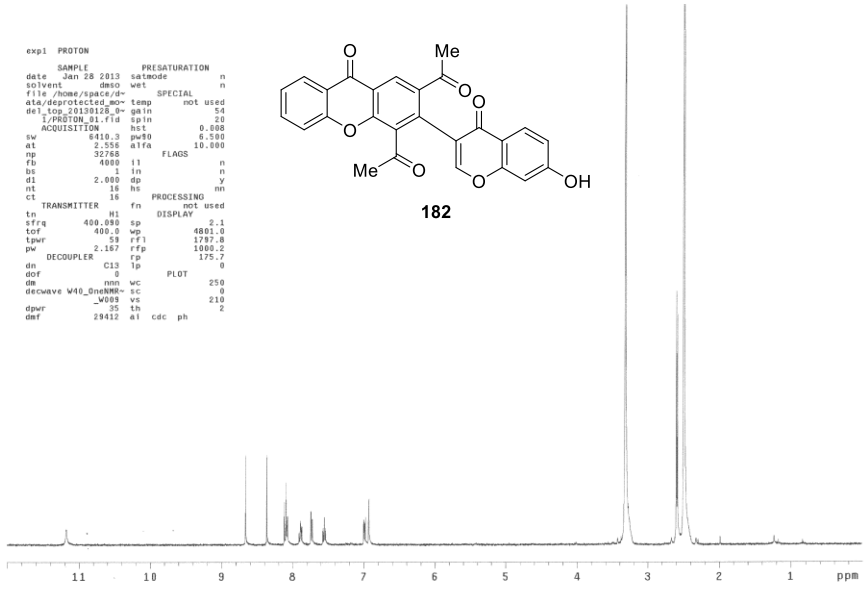

500 MHz nmr0
deprotected_model_d1_vinaxanthone_c13
exp4 Carbon
SAMPLE
date Jul 10 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.358
np 118154
fb 17000
bs 1
d1 2.000
nt 10000
ct 10000
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 1.933
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.8
wp 28279.6
rf1 6944.5
rfp 4864.7
rp -135.3
lp -217.2
PLOT
wc 250
sc 0
vs 25840
th 22
al ph
200
180
160
140
120
100
80
60
40
20
ppm

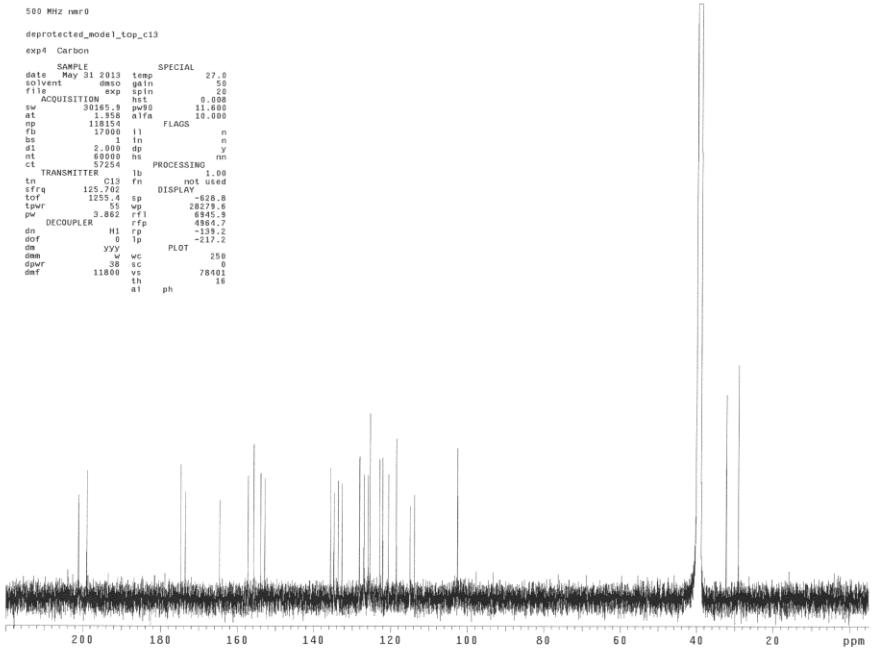

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

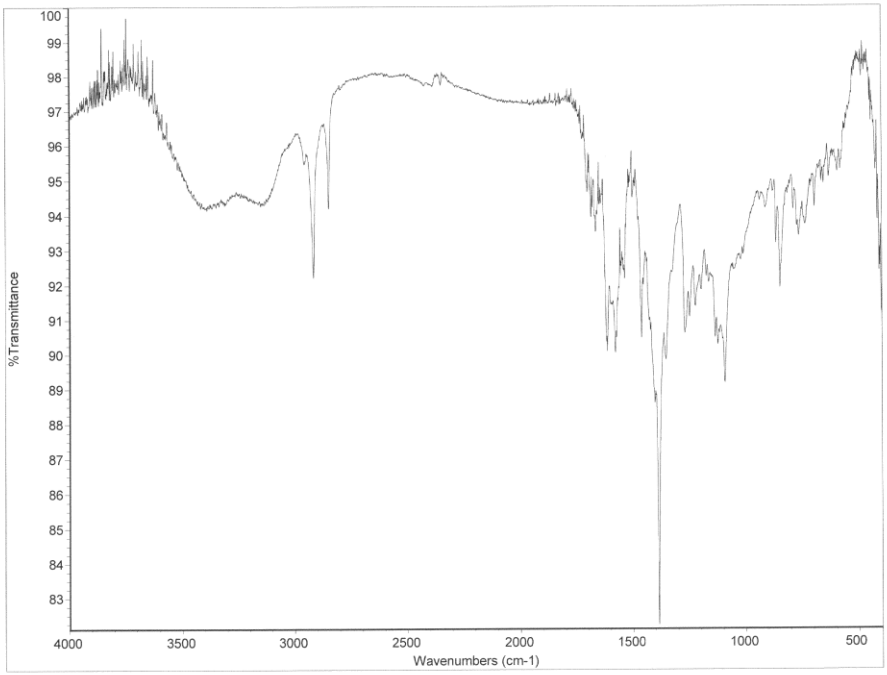

deprotected_model_top_vinaxanthone
exp1 std1h
SAMPLE
date Jun 21 2013
solvent DMSO
file exp
ACQUISITION
sfrq 400.271
tn H1
at 2.856
np 35992
sw 6381.2
fb not used
bs 1
tpwr 58
pw 2.0
d1 2.000
tof 165.5
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 2.5
wp 4785.9
vs 942
sc 0
wc 250
hzmm 19.16
fs 318.27
rf1 1857.6
rfp 1000.7
th 23
lns 100.000
nm cdc ph
DEC. & VT
dfrq 400.271
dn H1
dpwr 50
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
O
Me
O
O
O
OH
Me
O
O
181
11
10
9
8
7
6
5
4
3
2
1
ppm


500 MHz nmr0
deprotected_model_top_vinaxanthone_c13
exp10 Carbon
SAMPLE
date Aug 20 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118154
fb 17000
bs 1
d1 2.000
nt 15800
ct 14814
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -528.8
wp 28279.8
rf1 6944.0
rfp 4964.7
rp -140.2
lp -217.2
PLOT
wc 250
sc 0
vs 11253
th 5
al cdc ph
200
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


exp1 PROTON
SAMPLE
date Jan 28 2013
solvent dmso
file /home/space/d~
ata/deprotected_mo~
del_top_20130128_0~
1/PROTON_01.fid
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.090
tof 400.0
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR~
_W009
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 54
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 2.1
wp 4801.0
rf1 1787.8
rfp 1000.2
rp 175.7
lp 0
PLOT
wc 250
sc 0
vs 210
th 2
al cdc ph
O
Me
O
O
Me
O
O
OH
182
11
10
9
8
7
6
5
4
3
2
1
ppm


500 MHz nmr0
deprotected_model_top_c13
exp4 Carbon
SAMPLE
date May 31 2013
solvent dmso
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118156
fb 17000
bs 1
d1 2.000
nt 68000
ct 57254
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 3.862
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 0.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -626.8
wp 28279.6
rf1 6945.9
rfp 4964.7
rp -139.2
lp -217.2
PLOT
wc 250
sc 0
vs 78401
th 18
al ph
200
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

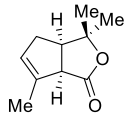
bicycle

Sample Name:
bicycle
Data Collected on:
nhb400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
bicycle_20140807_01
FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 7 2014

Operator: siegel

Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.0861305 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 13 sec



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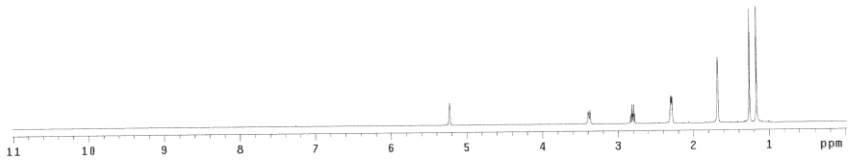


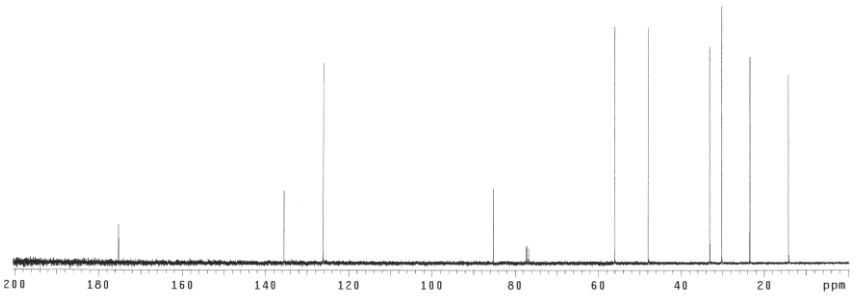
STANDARD CARBON PARAMETERS

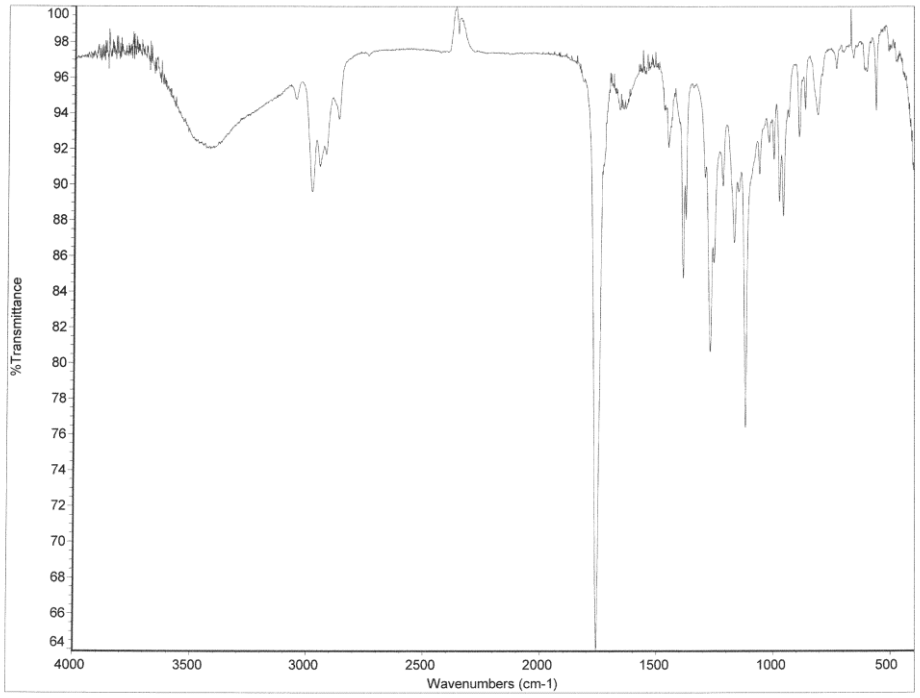
Sample Name:
bicycle
Data Collected on:
nhb400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
bicycle_20140807_02
FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 7 2014

Operator: siegel

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
52 repetitions
OBSERVE C13, 100.6017755 MHz
DECOUPLE H1, 400.0881319 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 52 sec




%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

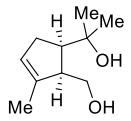
diol

Sample Name:
diol
Data Collected on:
nhb400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
diol_20140807_01
FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 7 2014

Operator: siegel

Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.0861309 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 13 sec



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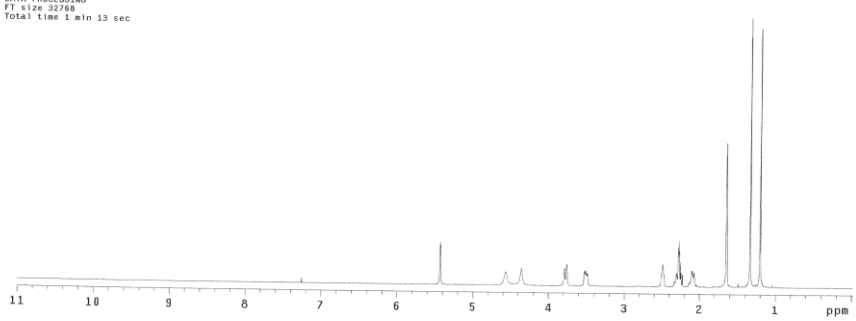


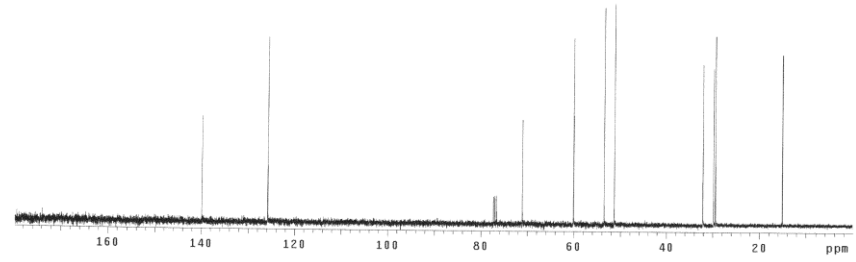
STANDARD CARBON PARAMETERS

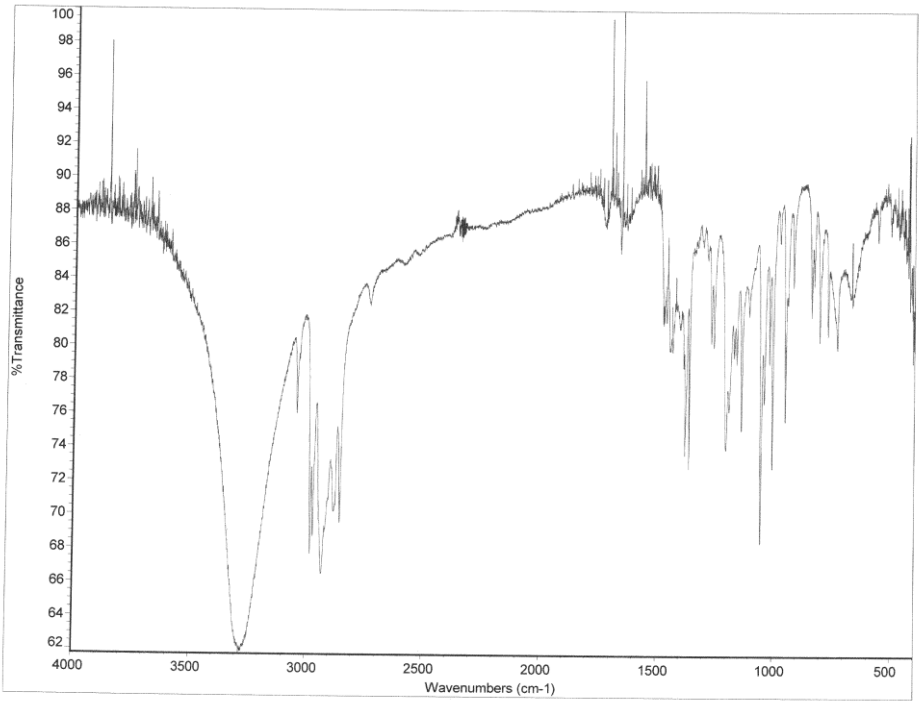
Sample Name:
diol
Data Collected on:
nhb400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
diol_20140807_02
FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 7 2014

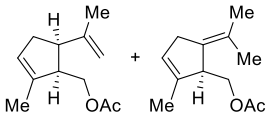
Operator: siegel

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
52 repetitions
OBSERVE C13, 100.6017503 MHz
DECOUPLE H1, 400.0881319 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 52 sec




%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

Parameter		Value
1	Data File Name	C:/ Users/ mchin318/ Desktop/ NMR FIDS/ mrc_eupalinilde/ 19/ fid
2	Title	1D 1H with 30o pulse 5 mm CP-TCI, 298K UCSD_PROTON
3	Origin	Bruker BioSpin GmbH
4	Owner	siegel
5	Solvent	CDCl3
6	Pulse Sequence	zg30
7	Acquisition Date	2015-01-17T18:14:08
8	Modification Date	
9	Temperature	298.0
10	Number of Scans	8
11	Spectrometer Frequency	600.11
12	Spectral Width	7211.5
13	Lowest Frequency	-622.9
14	Nucleus	1H
15	Acquired Size	8192
16	Spectral Size	16384



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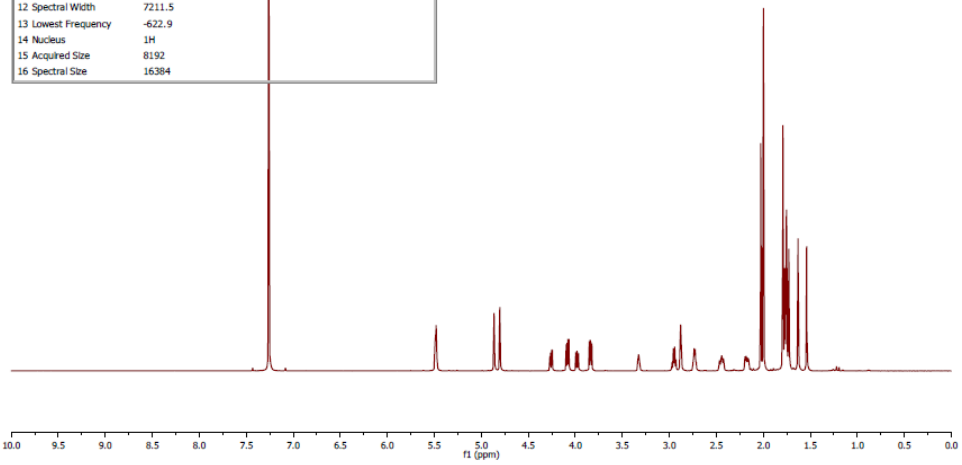
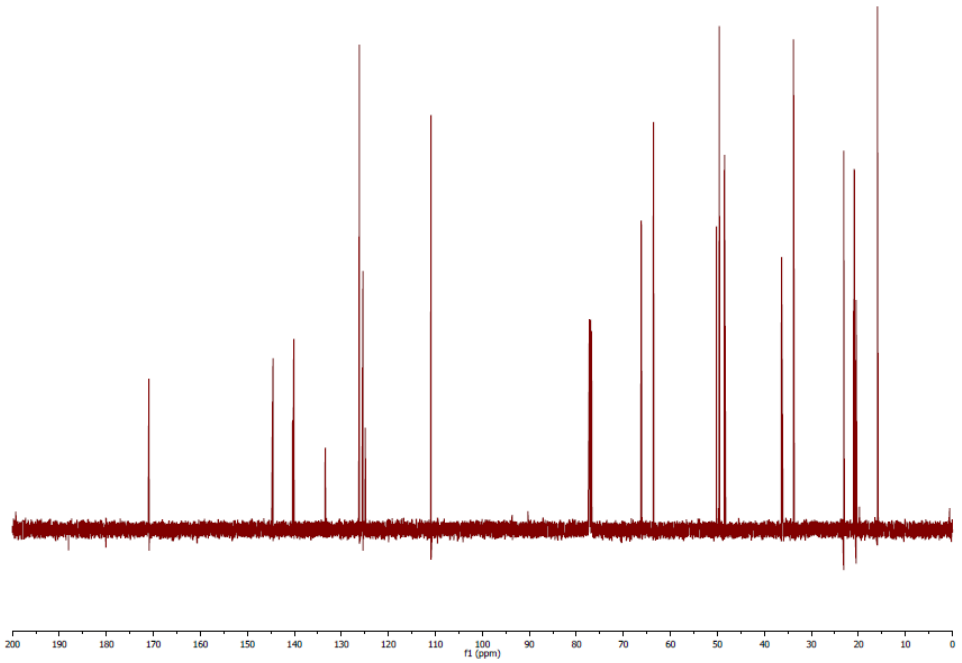
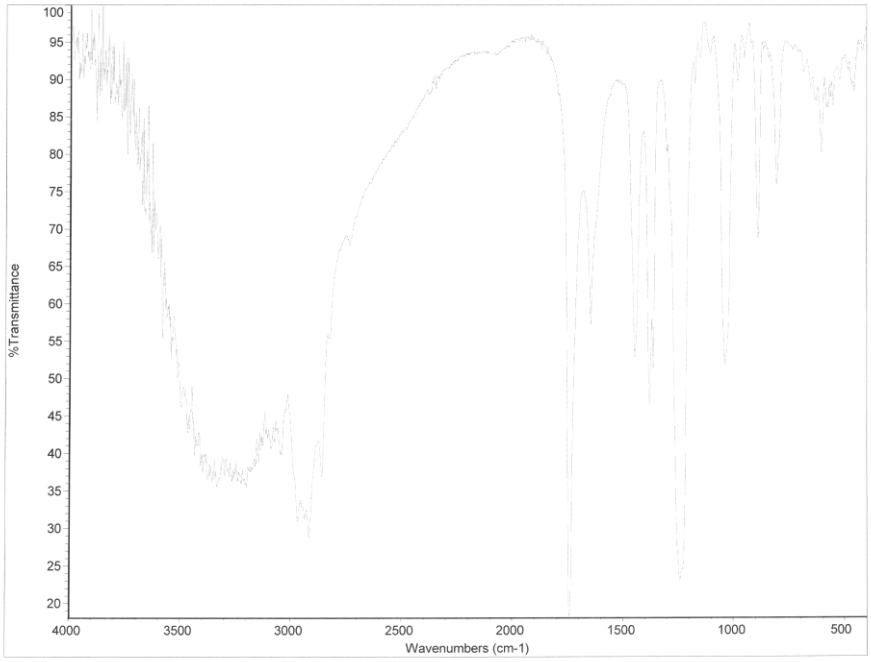
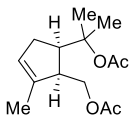





100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

	Parameter	Value
1	Data File Name	C:/ Users/ mchin318/ Desktop/ 39/ fid
2	Title	1D 1H with 30o pulse 5 mm CP-TCI, 298K UCSD_PROTON
3	Origin	Bruker BioSpin GmbH
4	Owner	siegel
5	Solvent	CDCl3
6	Pulse Sequence	zg30
7	Acquisition Date	2015-01-27T20:11:41
8	Modification Date	
9	Temperature	298.0
10	Number of Scans	8
11	Spectrometer Frequency	600.11
12	Spectral Width	7211.5
13	Lowest Frequency	-622.3
14	Nucleus	1H
15	Acquired Size	8192
16	Spectral Size	16384



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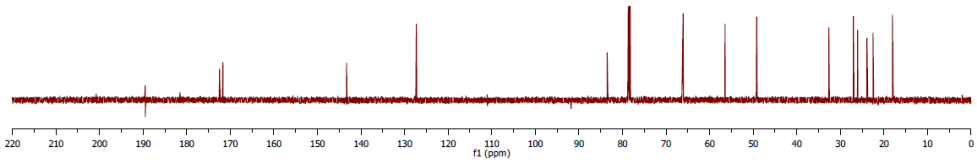
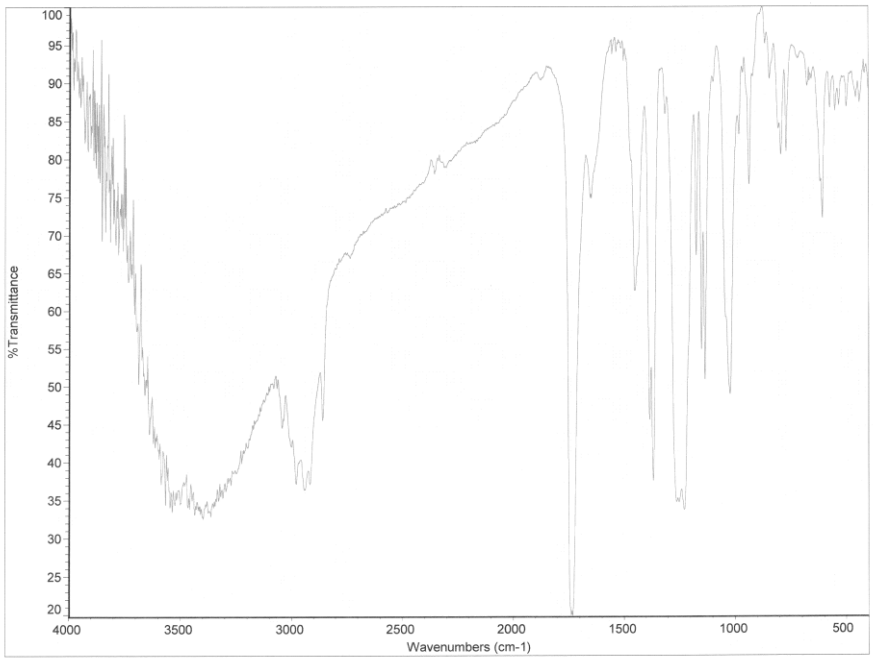
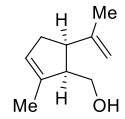
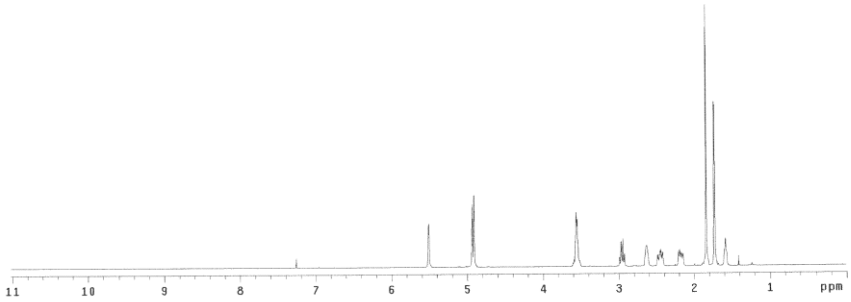



%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

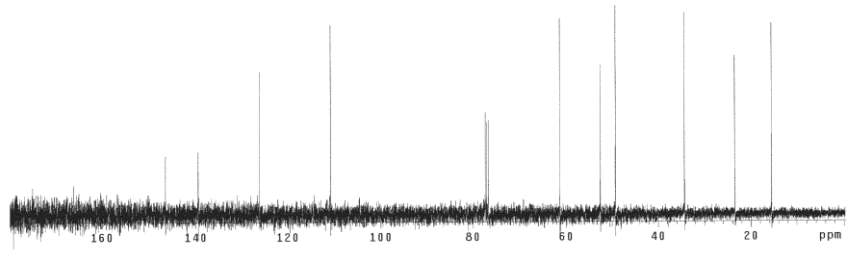
```
STANDARD PROTON PARAMETERS

 Sample Name:
   terminal_olefin
 Data Collected On:
   nhb400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   terminal_olefin_20140808_01
 FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug  8 2014

Operator: siegel

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 400.0861309 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
```

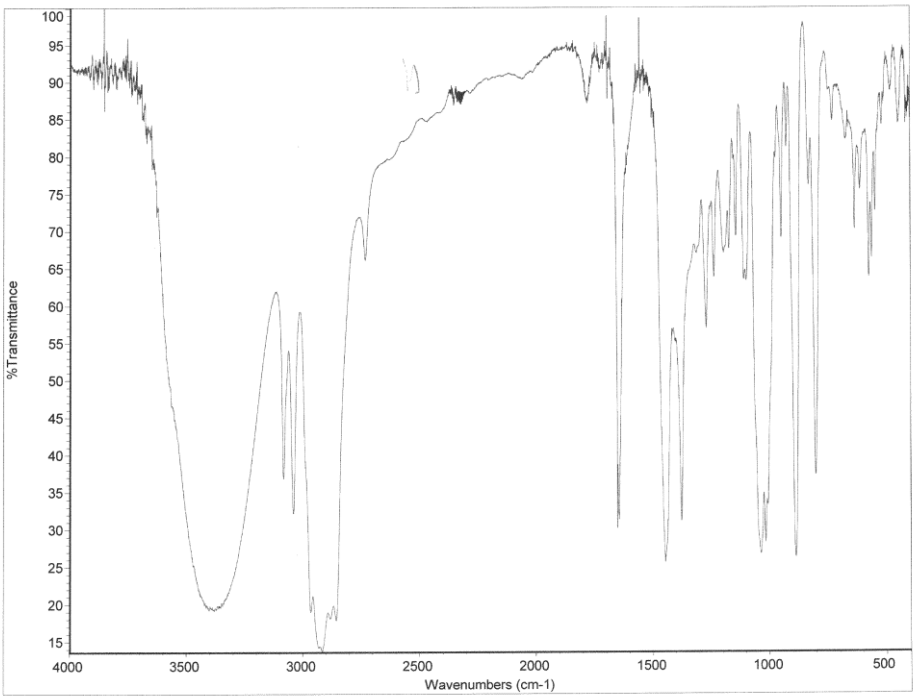


397

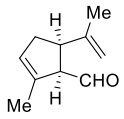



```
terminal_olefin

 Sample Name:
   terminal_olefin
 Data Collected On:
   nhb400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   terminal_olefin_20140808_02
 FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug  8 2014

Operator: siegel

 Relax. delay 2.000 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 128 repetitions
OBSERVE   C13, 100.6017450 MHz
DECOUPLE  H1, 400.0861319 MHz
 Power 35 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 28 min
```

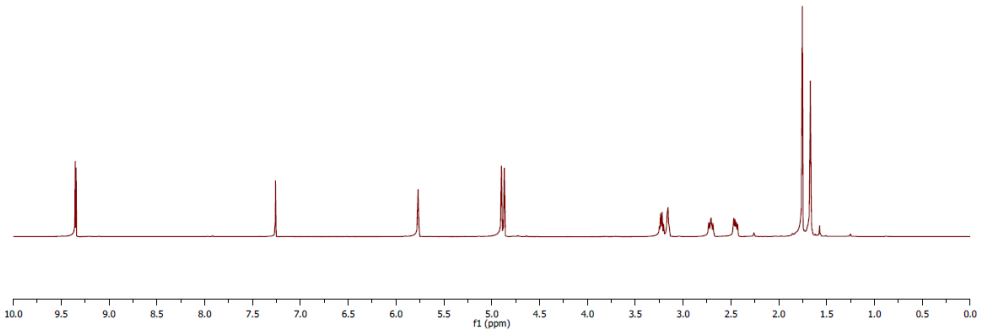



%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

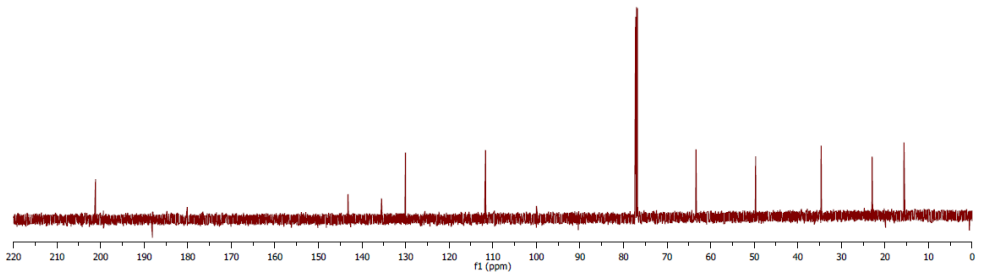
	Parameter	Value
1	Data File Name	C:/ Users/ mchin318/ Desktop/ 9/ fid
2	Title	1D 1H with 30o pulse 5 mm CP-TCI, 298K UCSD_PROTON
3	Origin	Bruker BioSpin GmbH
4	Owner	siegel
5	Solvent	CDCl3
6	Pulse Sequence	zg30
7	Acquisition Date	2015-02-24T21:11:51
8	Modification Date	
9	Temperature	298.0
10	Number of Scans	8
11	Spectrometer Frequency	600.11
12	Spectral Width	7211.5
13	Lowest Frequency	-621.7
14	Nucleus	1H
15	Acquired Size	8192
16	Spectral Size	16384

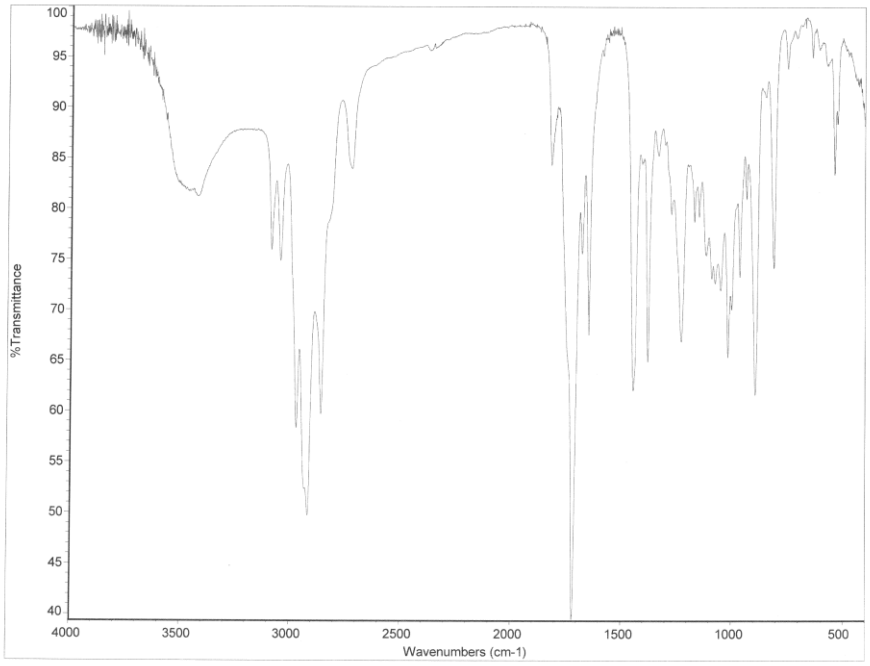


398

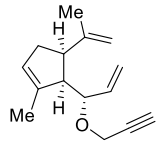


	Parameter	Value
1	Data File Name	C:/ Users/ mchin318/ Desktop/ 10/ fid
2	Title	1D 1H with 30o pulse 5 mm CP-TCI, 298K UCSD_PROTON
3	Origin	Bruker BioSpin GmbH
4	Owner	siegel
5	Solvent	CDCl3
6	Pulse Sequence	zgpg30
7	Acquisition Date	2015-02-24T21:20:44
8	Modification Date	
9	Temperature	298.0
10	Number of Scans	257
11	Spectrometer Frequency	150.90
12	Spectral Width	37878.8
13	Lowest Frequency	-3853.7
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

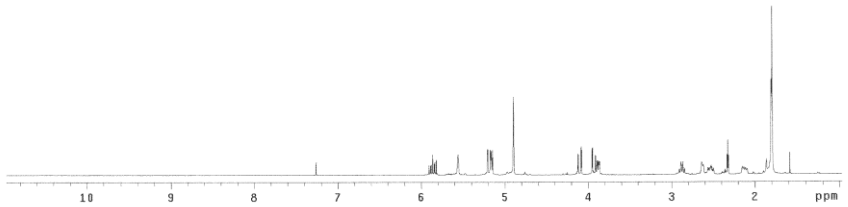



100
95
90
85
80
75
70
65
60
55
50
45
40
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

```
STANDARD PROTON PARAMETERS

 Sample Name:
   enyne
 Data Collected on:
   nhb400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   enyne_20140809_02
 FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug  9 2014

Operator: siegel

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 400.0861305 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
```

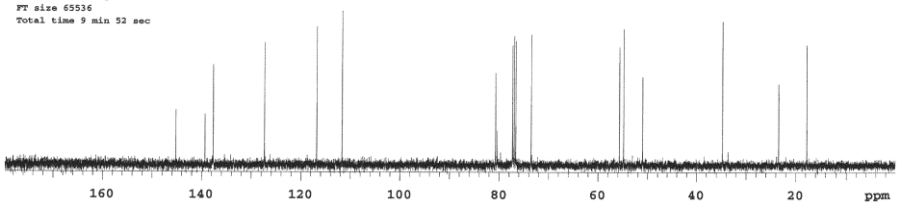


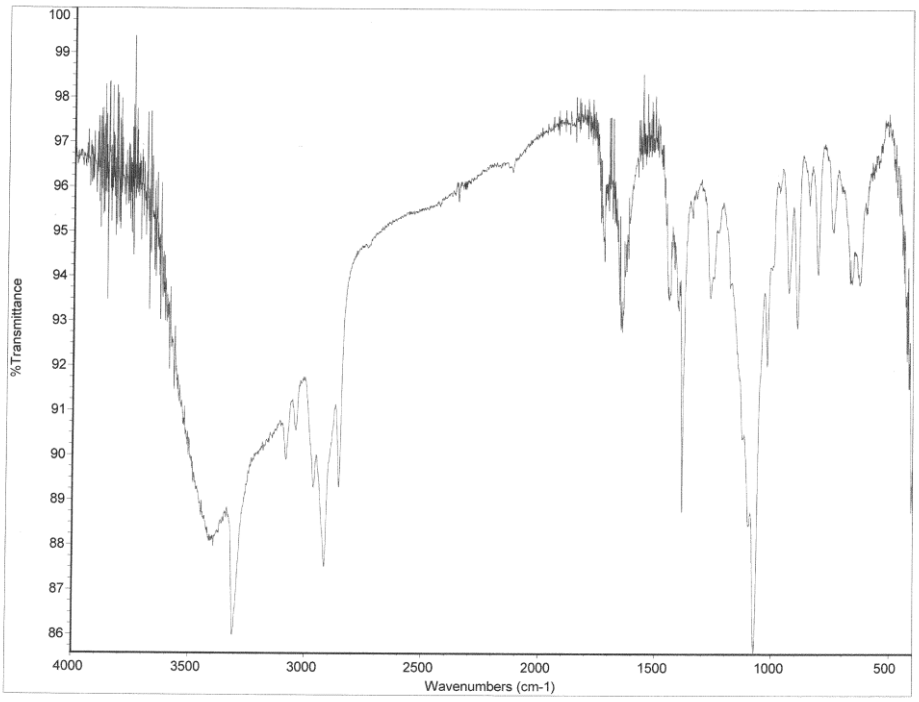
421




```
STANDARD CARBON PARAMETERS

 Sample Name:
   enyne
 Data Collected on:
   nhb400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   enyne_20140809_02
 FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug  9 2014

Operator: siegel

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 56 repetitions
OBSERVE  C13, 100.6017396 MHz
DECOUPLE  H1, 400.0881319 MHz
 Power 35 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 9 min 52 sec
```

Agilent Technologies




100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

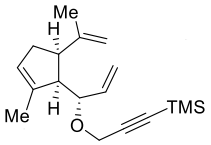
STANDARD PROTON PARAMETERS

Sample Name:
tms_enyne
Data Collected on:
nhb400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
tms_enyne_20140808_03
FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 8 2014

Operator: siegel

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.0861313 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec



400

STANDARD CARBON PARAMETERS

Agilent Technologies

Sample Name:
tms_enyne
Data Collected on:
nhb400-vnmrs400
Archive directory:

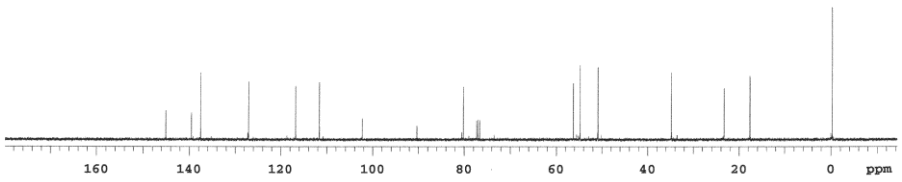
Sample directory:

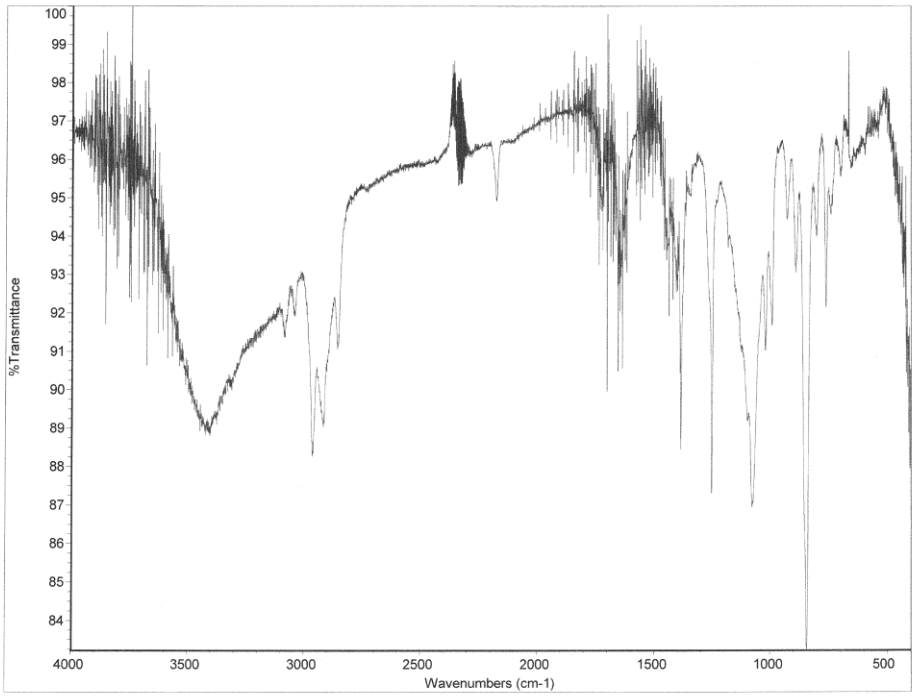
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 8 2014

Operator: siegel

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
24 repetitions
OBSERVE C13, 100.6017457 MHz
DECOUPLE H1, 400.0881319 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min




%Transmittance
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

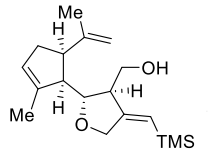
enyne_product

Sample Name:
enyne_product
Data Collected on:
we1400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
enyne_product_20140808_01
FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 8 2014

Temp. 25.0 C / 298.1 K
Operator: siegel

Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7714877 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 13 sec



401

STANDARD CARBON PARAMETERS

Sample Name:
enyne_product
Data Collected on:
we1400-vnmrs400
Archive directory:

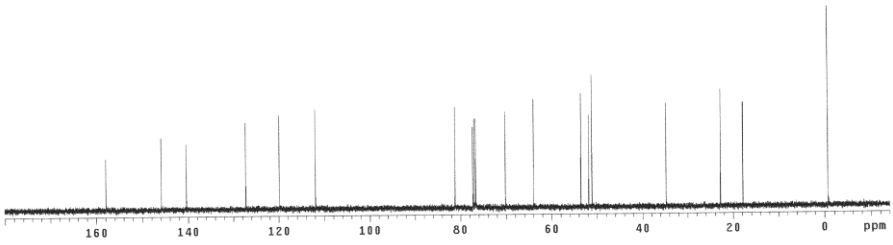
Sample directory:

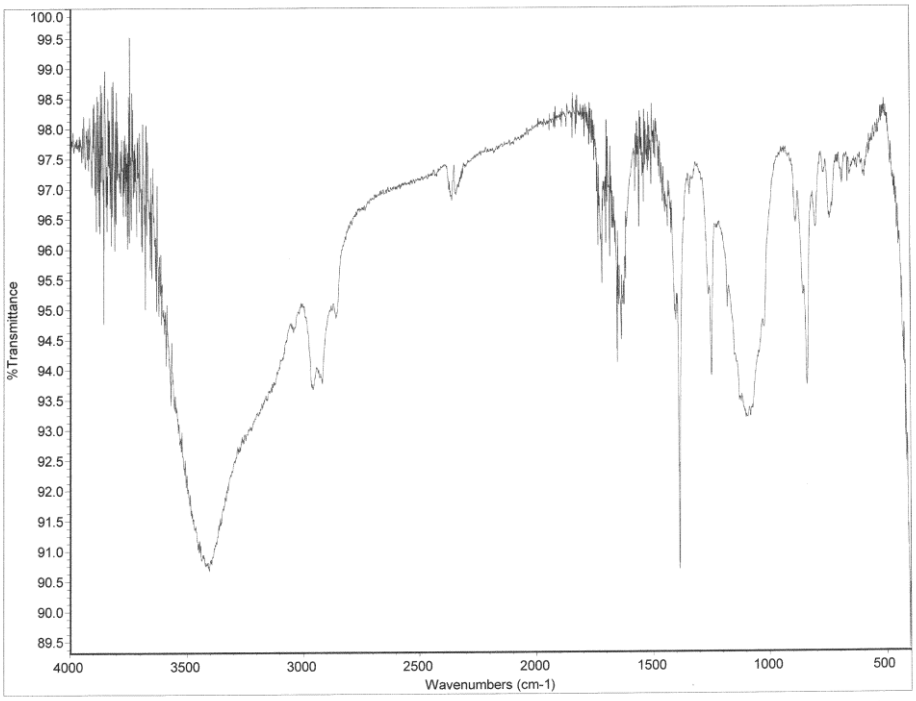
FidFile: CARBON

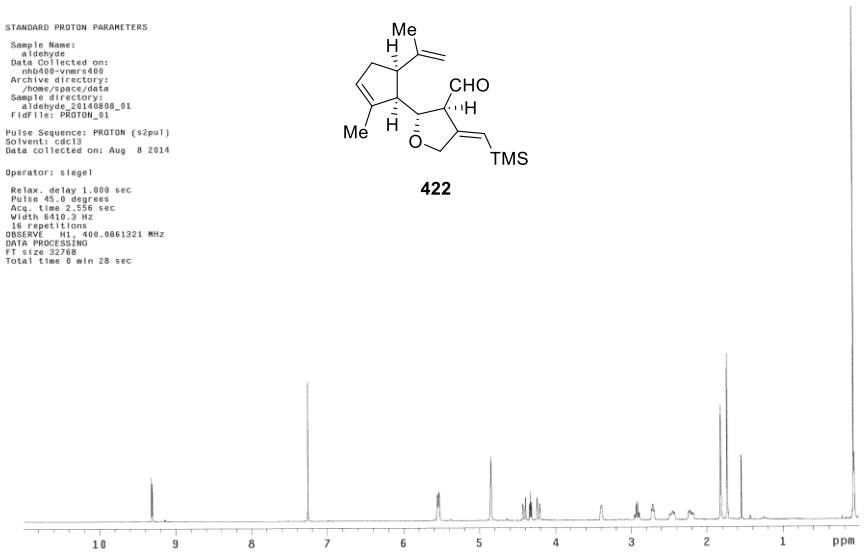
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 8 2014

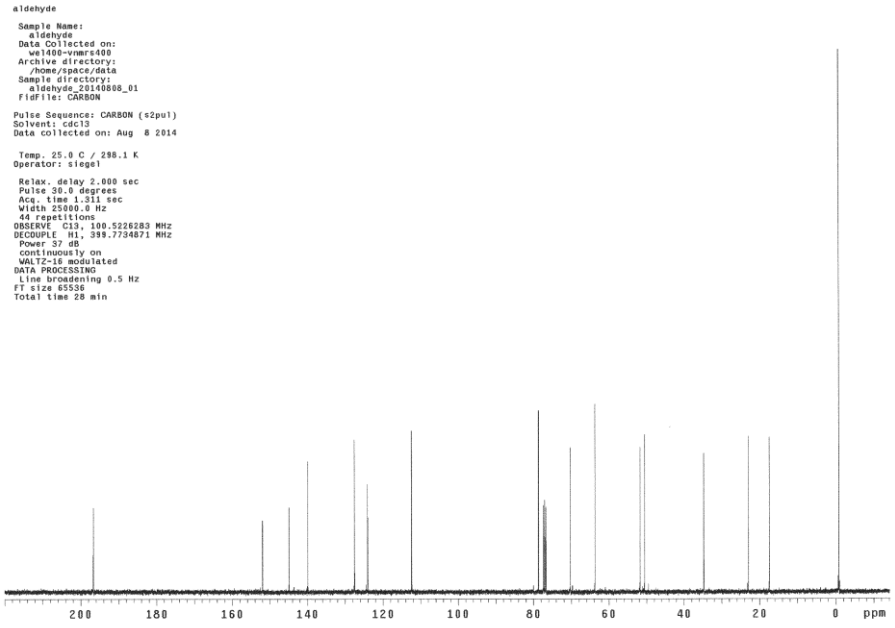
Temp. 25.0 C / 298.1 K
Operator: siegel

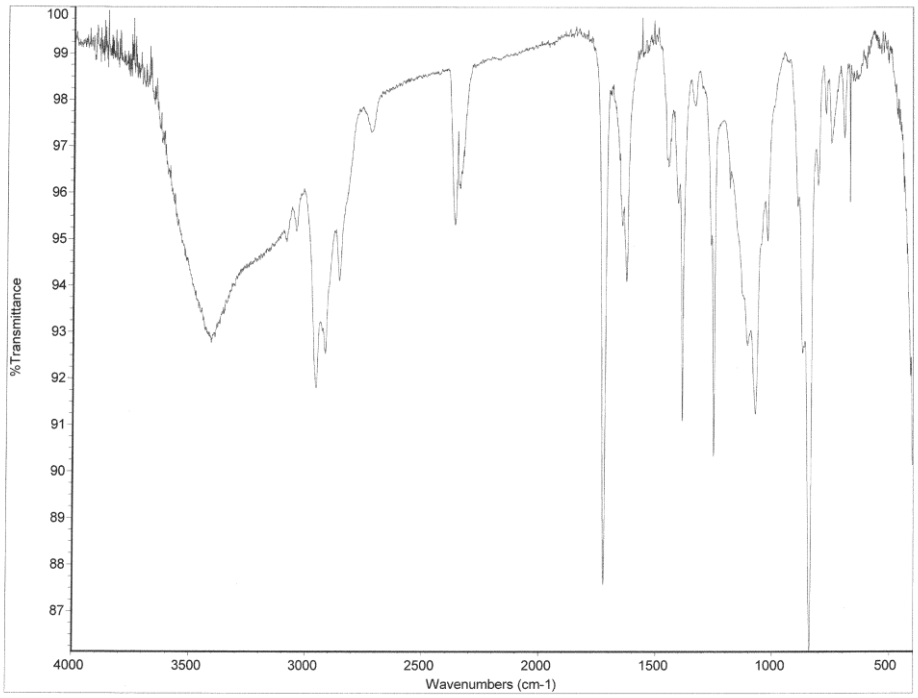
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
44 repetitions
OBSERVE C13, 100.5226237 MHz
DECOUPLE H1, 399.7734871 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min




100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
96.0
95.5
95.0
94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
90.0
89.5
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

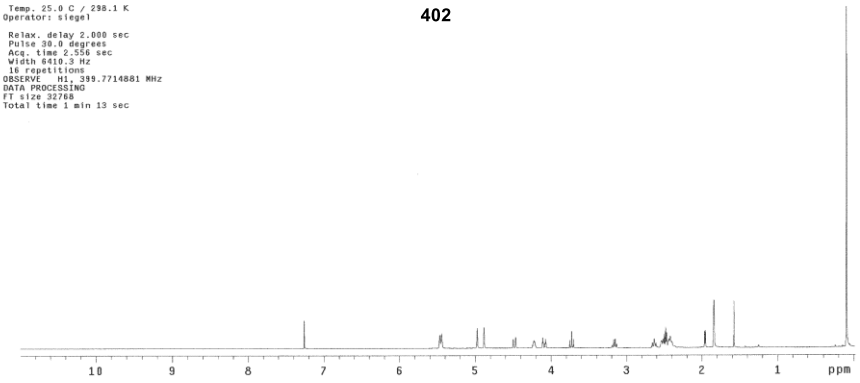

STANDARD PROTON PARAMETERS
Sample Name:
aldehyde
Data Collected on:
nmb400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
aldehyde_20140808_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 8 2014
Operator: siegel
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.0861321 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
Me
H
CHO
H
Me
H
O
TMS
422
10
9
8
7
6
5
4
3
2
1
ppm


aldehyde
Sample Name:
aldehyde
Data Collected on:
wel400-vnmrs400
Archive directory:
/home/space/data
Sample directory:
aldehyde_20140808_01
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 8 2014
Temp. 25.0 C / 298.1 K
Operator: siegel
Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
44 repetitions
OBSERVE C13, 100.5226283 MHz
DECOUPLE H1, 398.7734871 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min
200
180
160
140
120
100
80
60
40
20
0
ppm


100
99
98
97
96
95
94
93
92
91
90
89
88
87
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

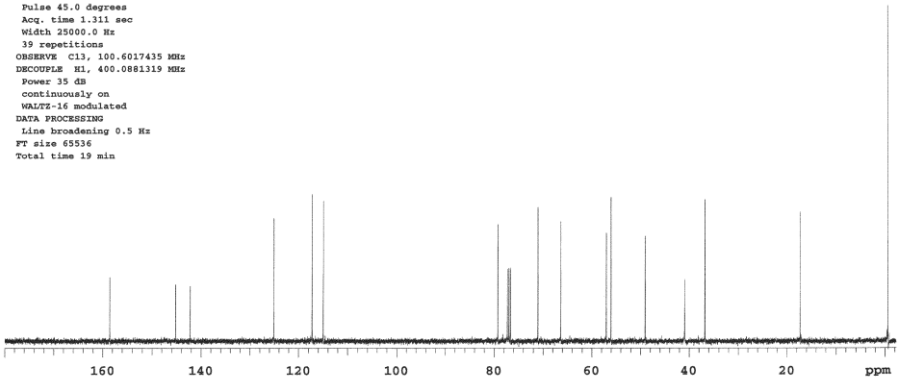
402

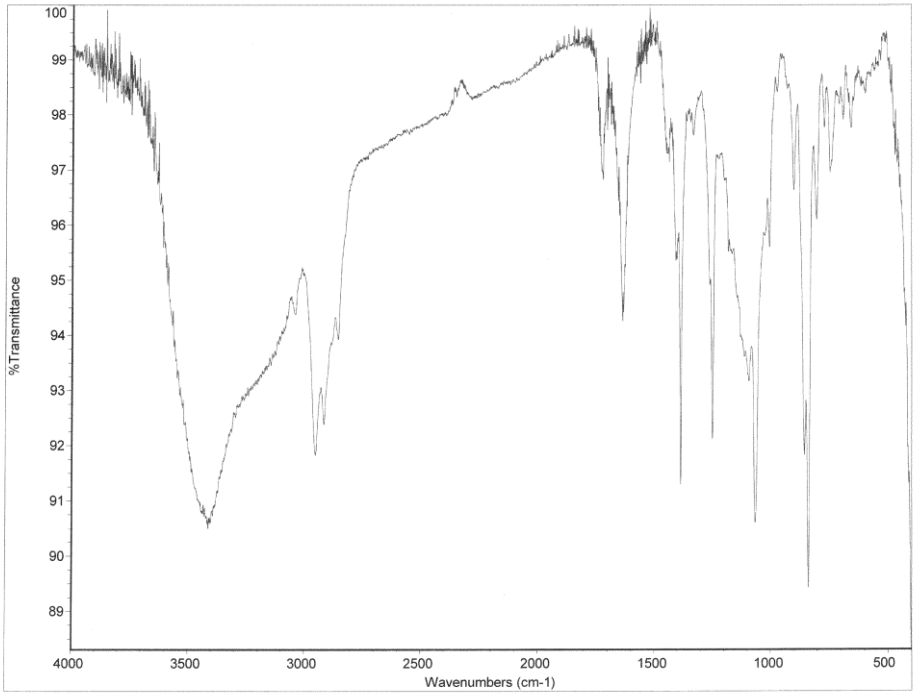
```
5_7_5

 Sample Name:
   5_7_5
 Data Collected on:
   we1400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   5_7_5_20140809_01
 FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug  9 2014

 Temp. 25.0 C / 298.1 K
Operator: siegel

 Relax. delay 2.000 sec
 Pulse 30.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.7714881 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 13 sec
```

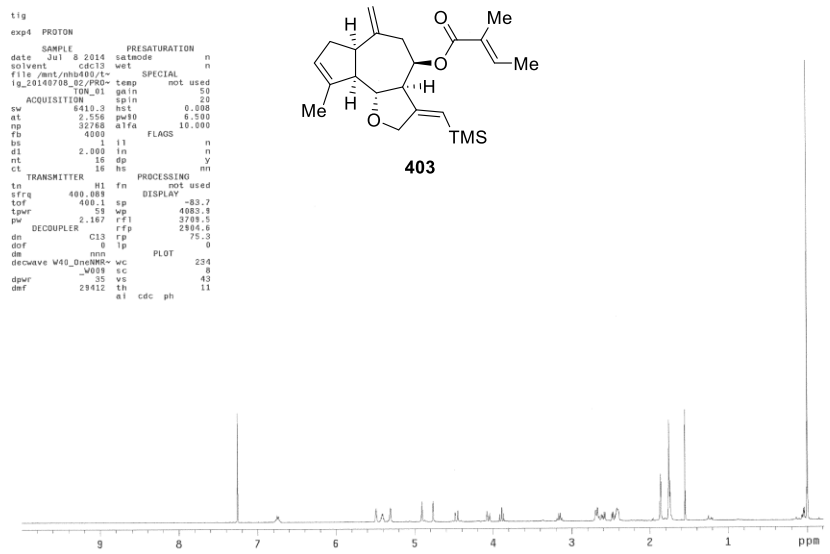


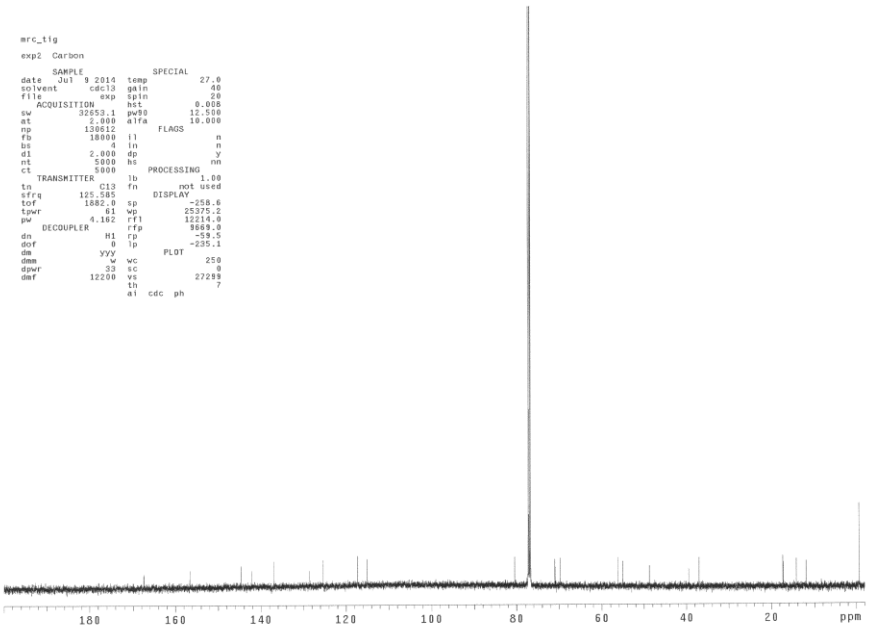

```
STANDARD CARBON PARAMETERS

 Sample Name:
   5_7_5
 Data Collected on:
   nhb400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   5_7_5_20140808_02
 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug  8 2014

Operator: siegel

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 39 repetitions
OBSERVE  C13, 100.6017435 MHz
DECOUPLE  H1, 400.0881319 MHz
 Power 35 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 19 min
```

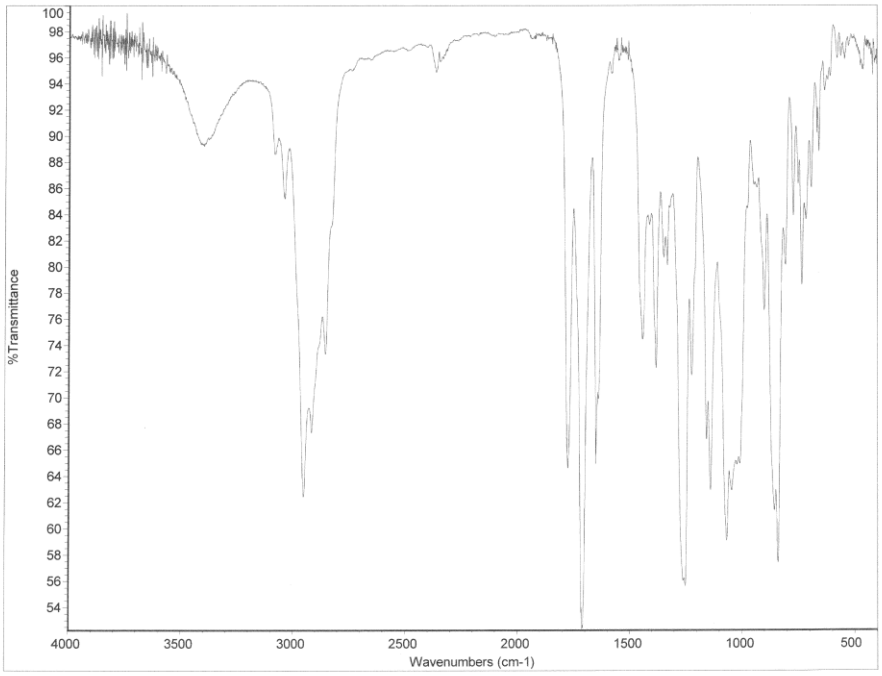
Agilent Technologies

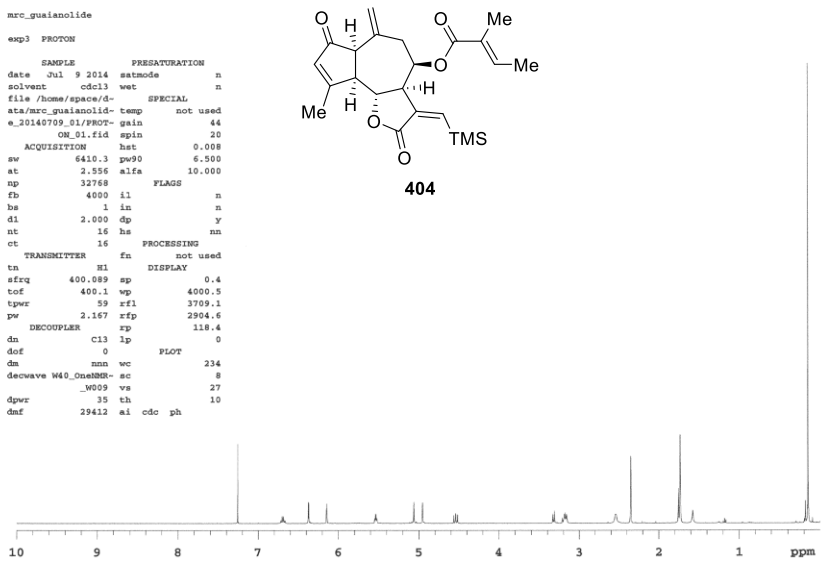



100
99
98
97
96
95
94
93
92
91
90
89
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

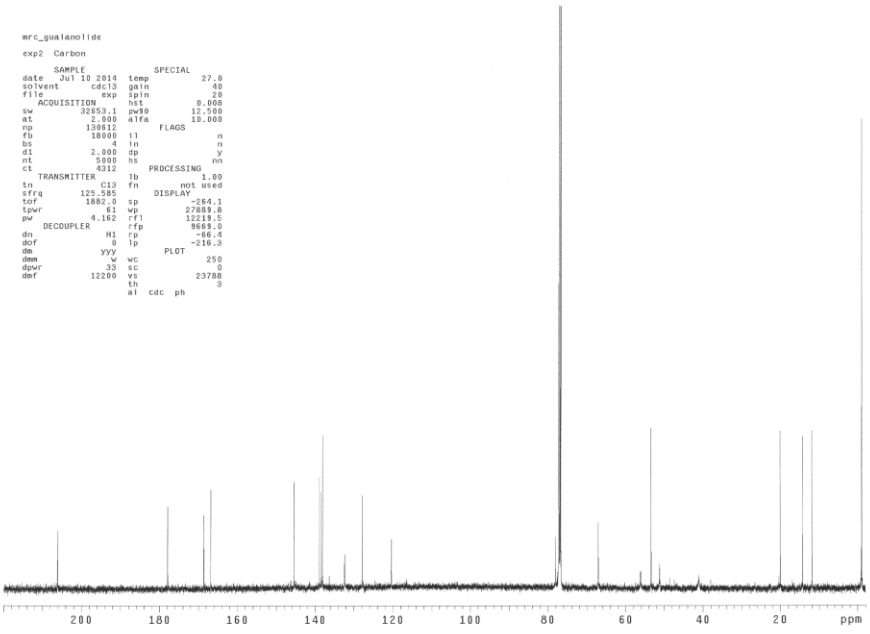

tig
exp4 PROTON
SAMPLE
date Jul 8 2014
solvent cdcl3
file /mnt/nhb400/t-
ig_20140708_02/PRD-
TON_01
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR-
_W898
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 50
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -83.7
wp 4083.9
rf1 3709.5
rfp 2804.6
rp 75.3
lp 0
PLOT
wc 234
sc 0
vs 43
th 11
al cdc ph
H
O
Me
Me
O
H
Me
H
O
TMS
403
9
8
7
6
5
4
3
2
1
ppm

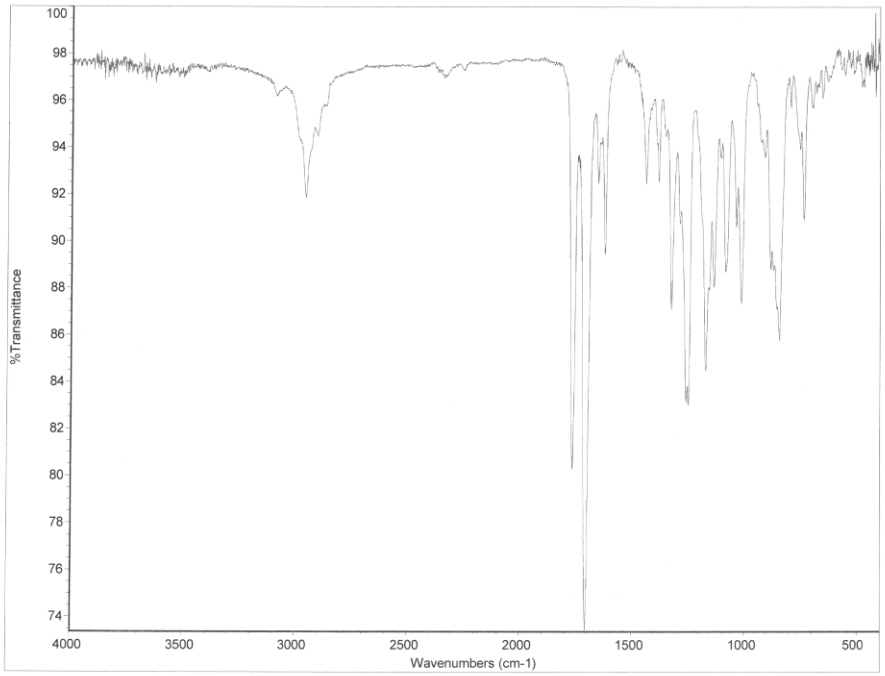

mrc_tig
exp2 Carbon
SAMPLE
date Jul 9 2014
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 1.000
np 130612
fb 18000
bs 4
d1 2.000
nt 5000
ct 5000
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -258.6
wp 25375.2
rf1 12214.0
rfp 9669.0
rp -59.5
lp -235.1
PLOT
wc 250
sc 0
vs 27299
th 7
al cdc ph
180
160
140
120
100
80
60
40
20
ppm

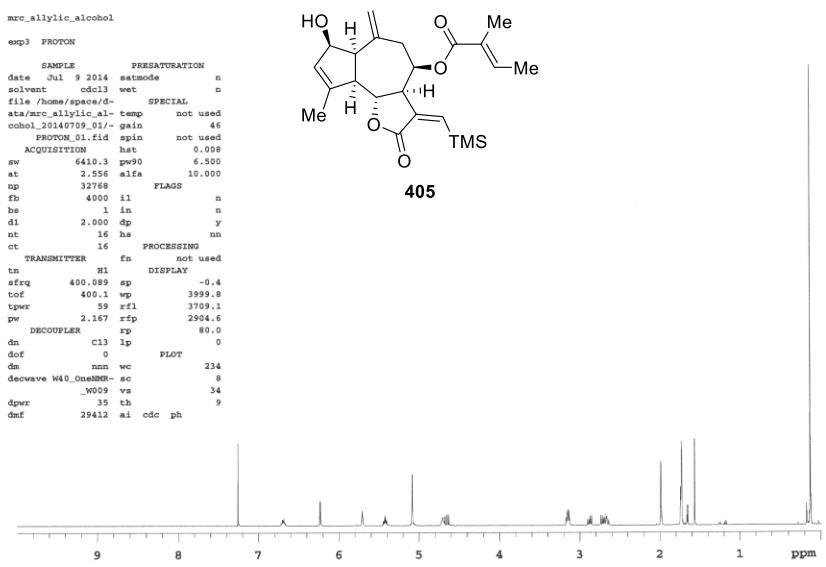

%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

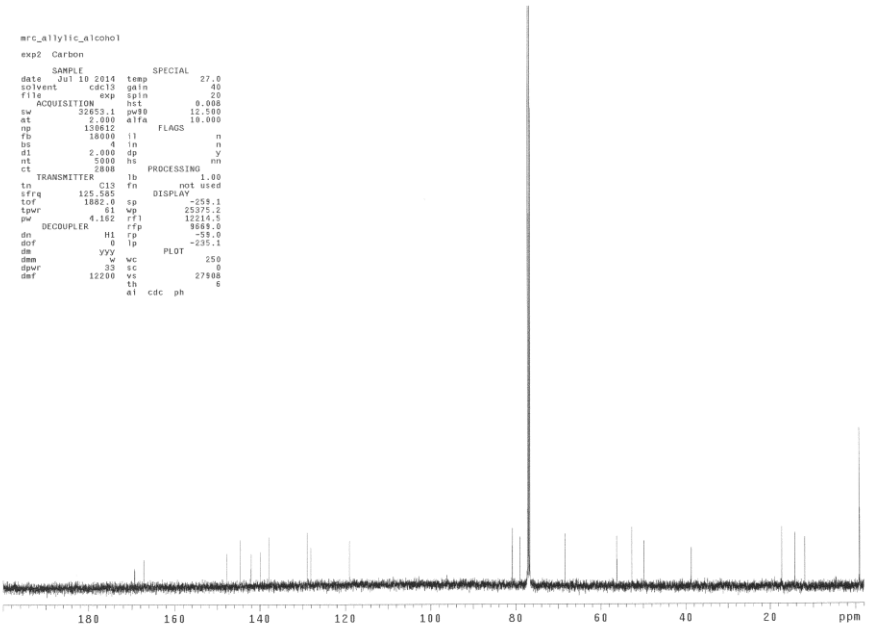

mrc_guaianolide
exp3 PROTON
SAMPLE
date Jul 9 2014
solvent cdcl3
file /home/space/data/mrc_guaianolide_20140709_01/PROTON_01.fid
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR_W009
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 44
spin 20
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp 0.4
wp 4000.5
rfl 3709.1
rfp 2904.6
rp 118.4
lp 0
PLOT
wc 234
sc 8
vs 27
th 10
ai cdc ph
10
9
8
7
6
5
4
3
2
1
ppm

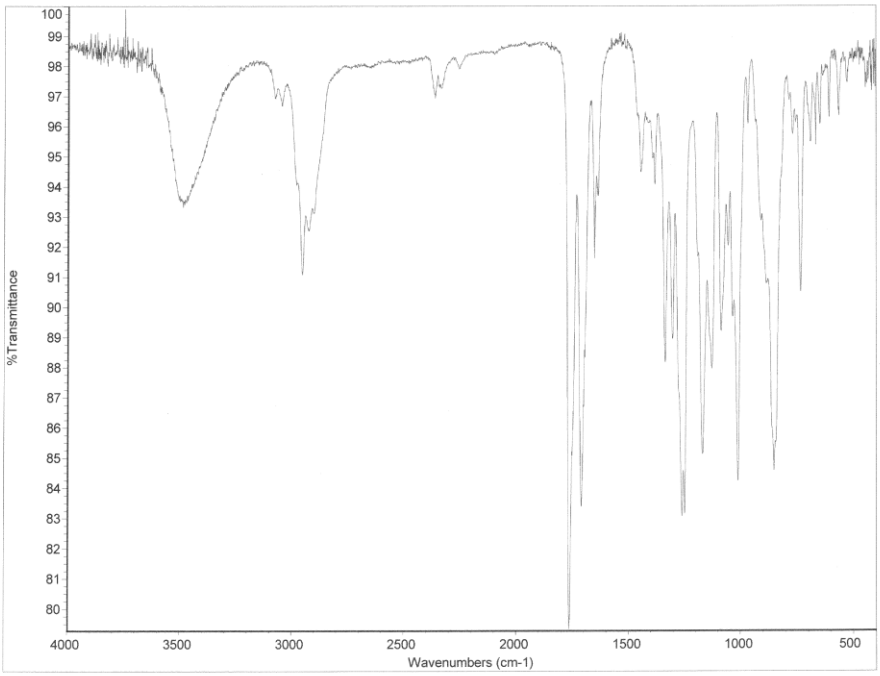
404


mrc_guaianolide
exp2 Carbon
SAMPLE
date Jul 10 2014
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 4
d1 2.000
nt 5000
ct 4312
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -264.1
wp 27889.8
rfl 12219.5
rfp 9669.0
rp -66.4
lp -216.3
PLOT
wc 250
sc 0
vs 23788
th 3
ai cdc ph
200
180
160
140
120
100
80
60
40
20
ppm


100
98
96
94
92
90
88
86
84
82
80
78
76
74
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


mrc_allylic_alcohol
exp3 PROTON
SAMPLE
date Jul 9 2014
solvent cdcl3
file /home/space/d-
ata/mrc_allylic_al-
cohol_20140709_01/~
PROTON_01.fid
ACQUISITION
sw 6410.3
at 2.556
np 32768
fb 4000
bs 1
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.089
tof 400.1
tpwr 59
pw 2.167
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_OneNMR-
_W009
dpwr 35
dmf 29412
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 46
spin not used
hst 0.008
pw90 6.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -0.4
wp 3999.8
rfl 3709.1
rfp 2904.6
rp 80.0
lp 0
PLOT
wc 234
sc 8
vs 34
th 9
ai cdc ph
HO
H
O
Me
Me
O
H
Me
H
O
TMS
O
405
9
8
7
6
5
4
3
2
1
ppm


mrc_allylic_alcohol
exp2 Carbon
SAMPLE
date Jul 10 2014
solvent cdcl3
file exp
ACQUISITION
sw 32653.1
at 2.000
np 130612
fb 18000
bs 4
d1 2.000
nt 5000
ct 2808
TRANSMITTER
tn C13
sfrq 125.585
tof 1882.0
tpwr 61
pw 4.162
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 33
dmf 12200
SPECIAL
temp 27.0
gain 40
spin 20
hst 0.008
pw90 12.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -255.1
wp 25375.2
rf1 12216.5
rfp 9869.0
rp -55.0
lp -235.1
PLOT
wc 250
sc 0
vs 27908
th 6
ai cdc ph
180
160
140
120
100
80
60
40
20
ppm


%Transmittance
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
82
81
80
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

STANDARD PROTON PARAMETERS

Sample Name:
lactone
Data Collected on:
nhb400-vmrs400
Archive directory:

Sample directory:

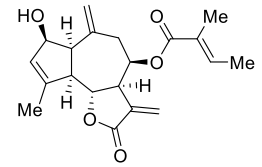
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 12 2014

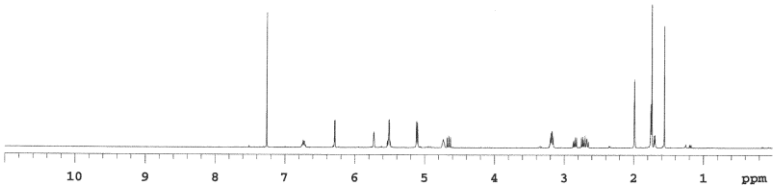
Operator: siegel

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
64 repetitions
OBSERVE H1, 400.0861309 MHz
DATA PROCESSING
FT size 32768
Total time 3 min 48 sec

Agilent Technologies



415

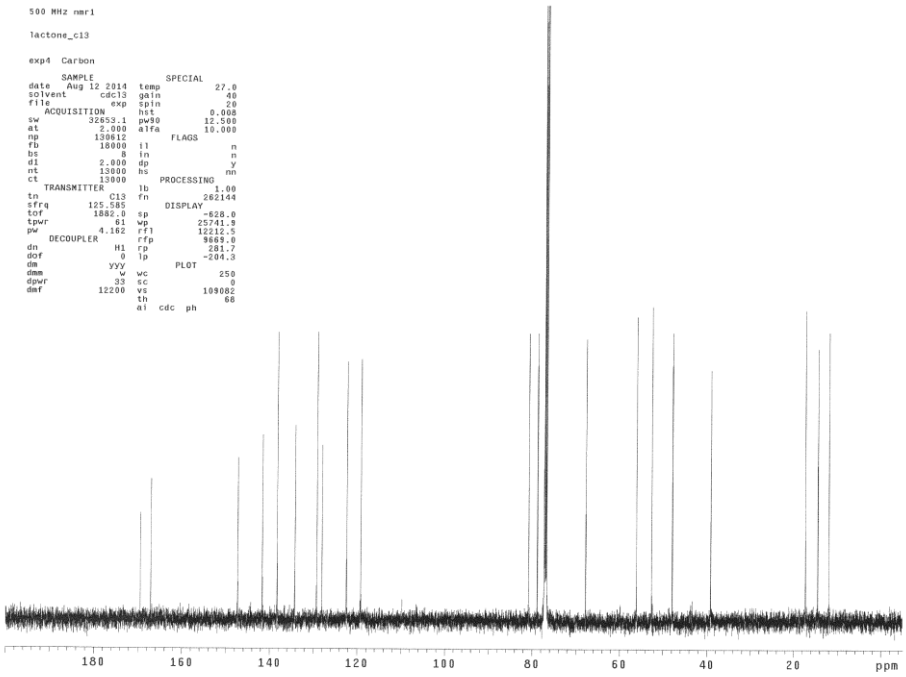


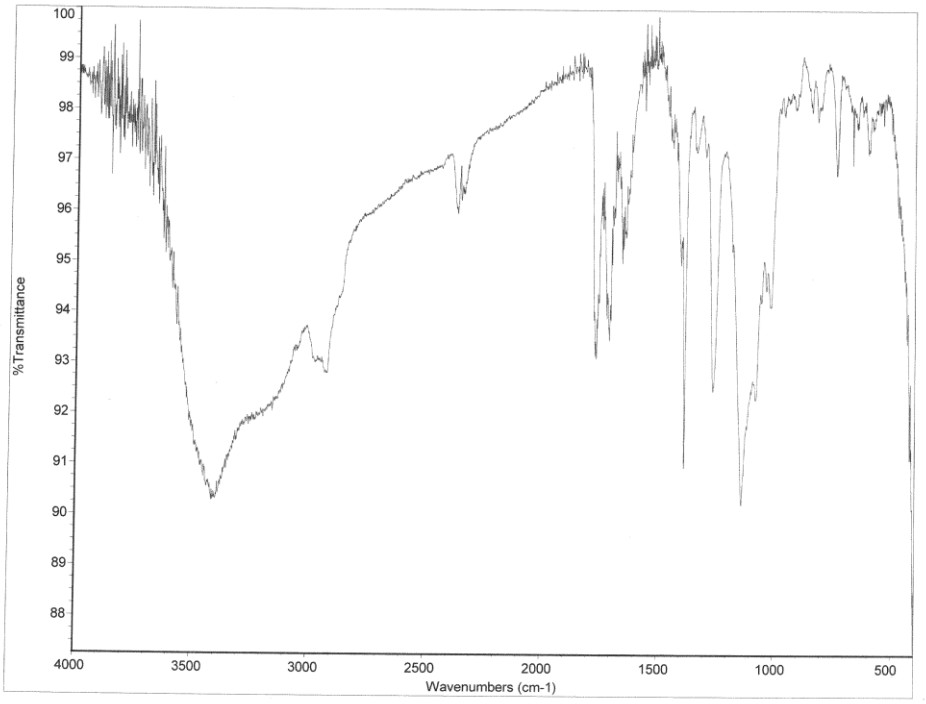
500 MHz nmr1

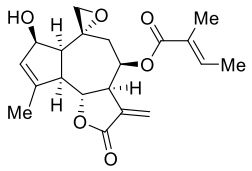
lactone_c13

exp4 Carbon

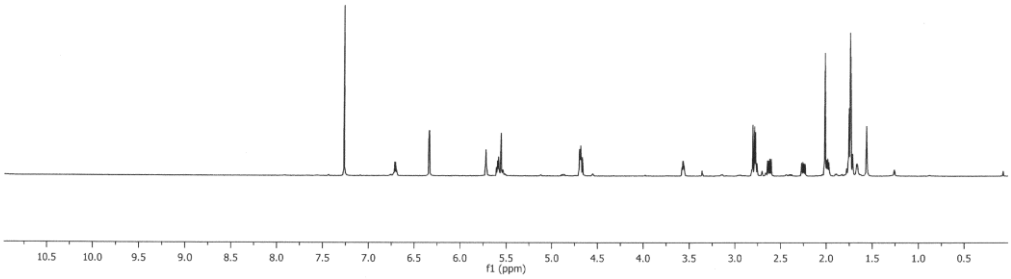
SAMPLE		SPECIAL	
date	Aug 12 2014	temp	27.0
solvent	cdcl3	gain	40
file	exp	spin	20
ACQUISITION		hst	0.008
sw	32653.1	pw90	12.500
at	2.000	alfa	10.000
np	130612	FLAGS	
fb	18000	il	n
bs	8	in	n
d1	2.000	dp	y
nt	13000	hs	nn
ct	13000	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	262144
sfrq	125.585	DISPLAY	
tof	1882.0	sp	-628.0
tpwr	61	wp	25741.9
pw	4.162	rf1	12212.5
DECOUPLER		rfp	9669.0
dn	H1	rp	281.7
dof	0	lp	-204.3
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	33	sc	0
dmf	12200	vs	109082
		th	68
		al cdc ph	

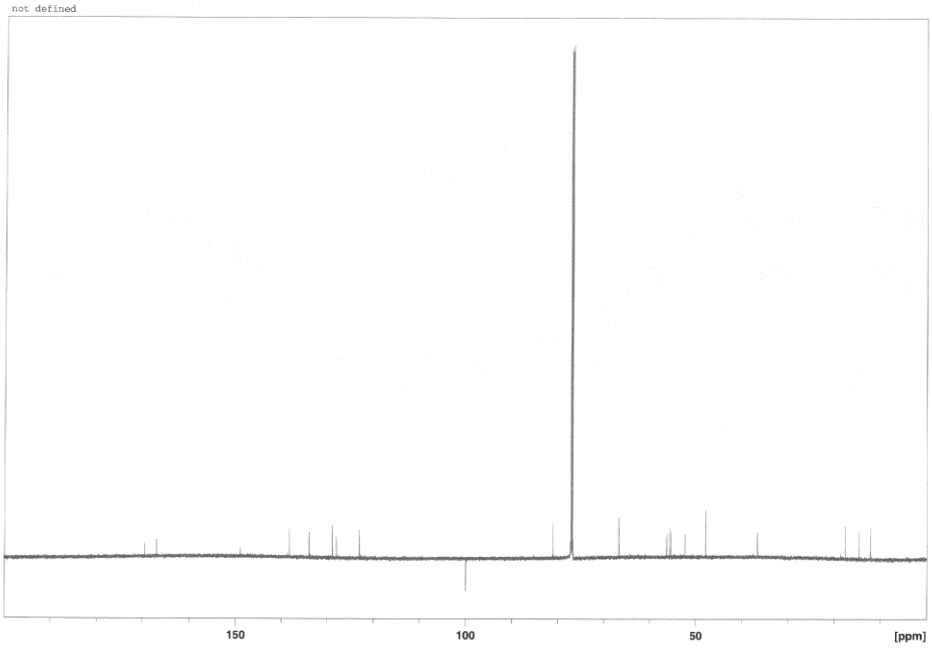


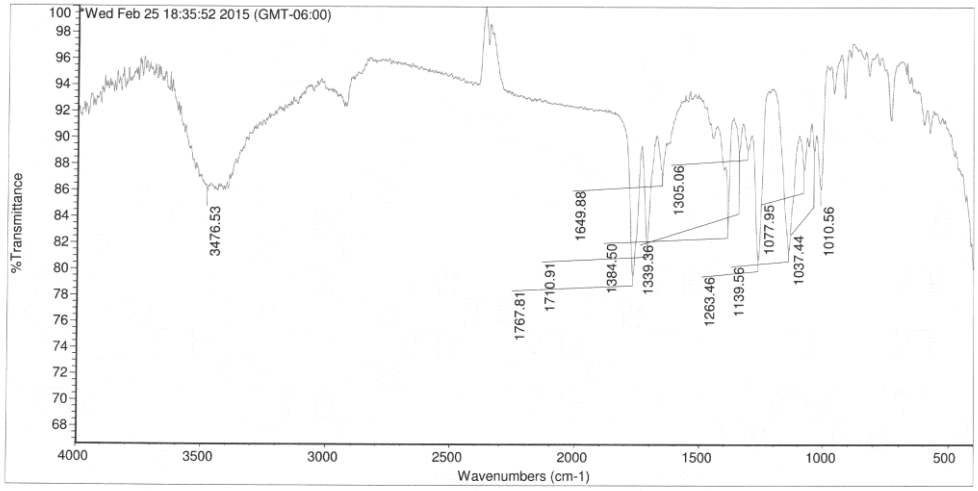

100
99
98
97
96
95
94
93
92
91
90
89
88
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


HO
H
O
O
Me
O
Me
H
Me
H
O
O

418


10.5
10.0
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
f1 (ppm)


not defined
150
100
50
[ppm]



Wed Feb 25 18:37:49 2015 (GMT-06:00)
FIND PEAKS:

Spectrum:	*Wed Feb 25 18:35:52 2015 (GMT-06:00)		
Region:	4000.00	400.00	
Absolute threshold:	89.790		
Sensitivity:	50		
Peak list:			

Position:	1010.56	Intensity:	86.155
Position:	1037.44	Intensity:	88.985
Position:	1077.95	Intensity:	87.602
Position:	1139.56	Intensity:	81.436
Position:	1263.46	Intensity:	80.731
Position:	1305.06	Intensity:	89.193
Position:	1339.36	Intensity:	89.017

STANDARD PROTON PARAMETERS

Sample Name:
lactone
Data Collected on:
nhb400-vmrs400
Archive directory:

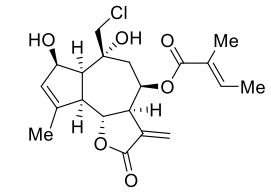
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 12 2014

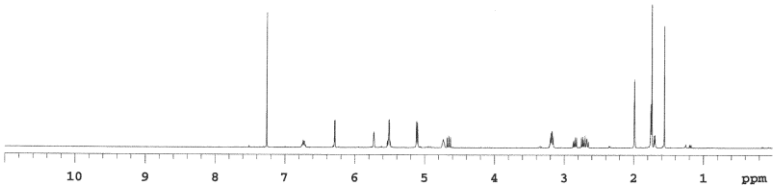
Operator: siegel

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
64 repetitions
OBSERVE H1, 400.0861309 MHz
DATA PROCESSING
FT size 32768
Total time 3 min 48 sec



eupalinilide E (**256**)

Agilent Technologies

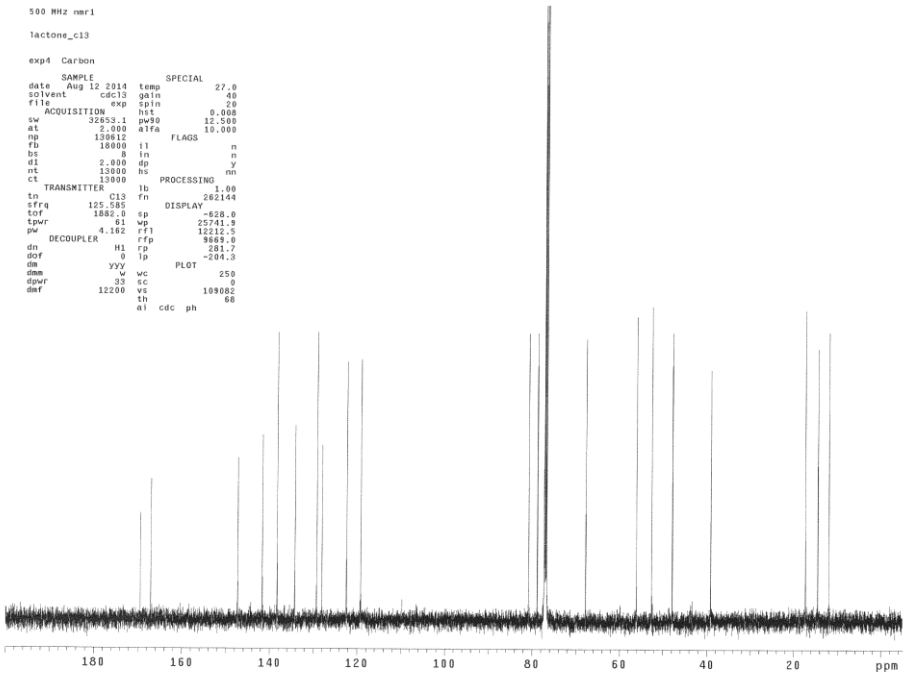


500 MHz nmr1

lactone_c13

exp4 Carbon

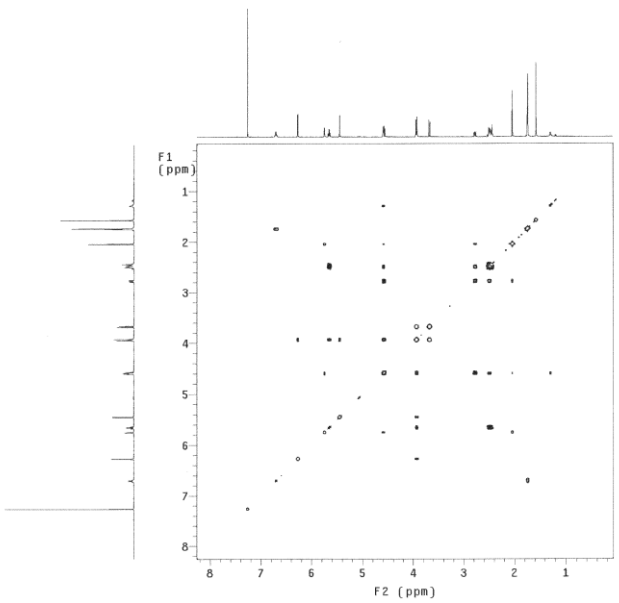
SAMPLE		SPECIAL	
date	Aug 12 2014	temp	27.0
solvent	cdcl3	gain	40
file	exp	spin	20
ACQUISITION		hst	0.008
sw	32653.1	pw90	12.500
at	2.000	alfa	10.000
np	130612	FLAGS	
fb	18000	il	n
bs	8	in	n
d1	2.000	dp	y
nt	13000	hs	nn
ct	13000	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	262144
sfrq	125.585	DISPLAY	
tof	1882.0	sp	-628.0
tpwr	61	wp	25741.9
pw	4.162	rf1	12212.5
DECOUPLER		rfp	9669.0
dn	H1	rp	281.7
dof	0	lp	-204.3
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	33	sc	0
dmf	12200	vs	109082
		th	68
		al cdc ph	



eupalinilide_e

exp3 Gcosy

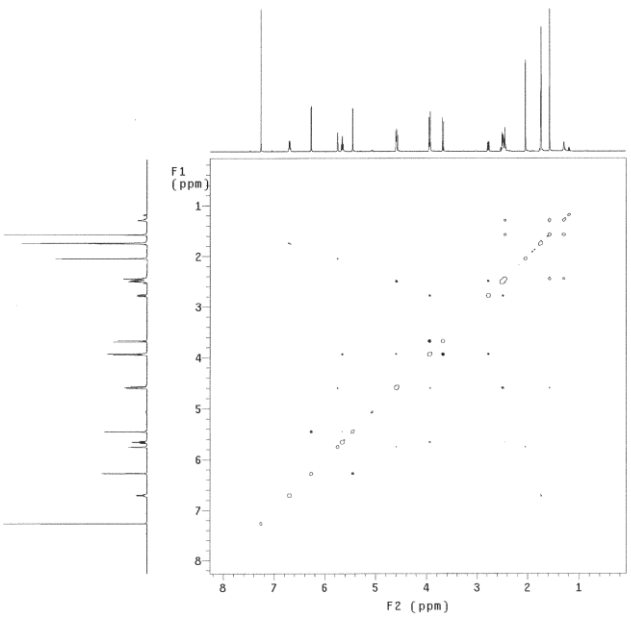
SAMPLE		FLAGS	
date	Aug 19 2014	hs	nn
solvent	cdcl3	sspul	n
sample		hsglvl	4694
ACQUISITION		SPECIAL	
sw	4080.2	temp	27.0
at	0.125	gain	30
np	1024	spin	0
fb	2000	F2 PROCESSING	
ss	8	sb	-0.063
d1	2.000	sbs	not used
nt	2	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	4080.2	sb1	-0.125
ni	512	sbs1	not used
PRESATURATION		proc1	lp
satmode	nnn	fn1	4096
satdly	0	DISPLAY	
satfrq	499.8	sp	38.0
satpwr	-13	wp	4088.2
TRANSMITTER		sp1	38.6
tn	H1	wp1	4088.2
sfrq	499.854	rf1	3593.0
tof	-405.0	rfp	3628.9
tpwr	59	rf11	3592.3
pw	11.000	rfp1	3628.9
tpwr_cf	1.000	PLOT	
GRADIENTS		wc	116.0
gzlvl1	4694	sc	10.0
gt1	0.001000	wc2	116.0
gstab	0.000500	sc2	0
DECOUPLER		vs	872
dn	C13	th	2
dm	nnn	al cdc av	



eupalinilide_e

exp8 Noesy

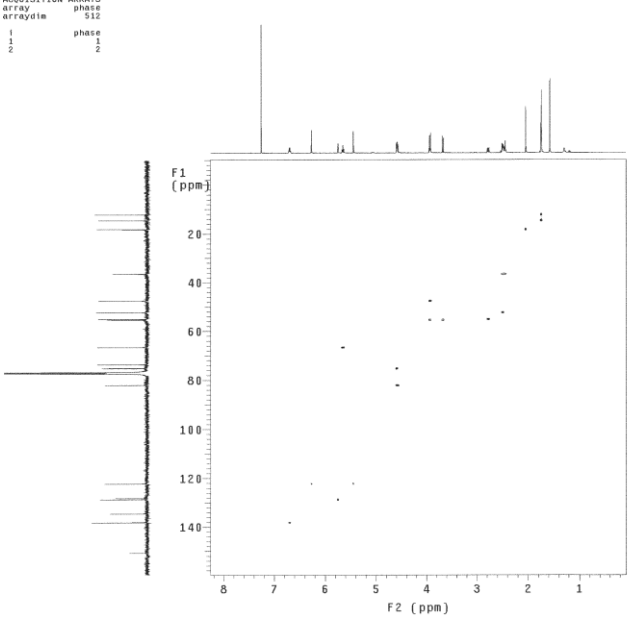
SAMPLE		FLAGS	
date	Aug 19 2014	hs	n
solvent	cdcl3	sspul	y
sample		PFGflg	y
ACQUISITION		hsglvl	4694
sw	4080.2	SPECIAL	
at	0.125	temp	27.0
np	1024	gain	30
fb	2000	spin	0
ss	32	F2 PROCESSING	
d1	2.000	gf	0.058
nt	8	gfs	not used
2D ACQUISITION		fn	2048
sw1	4080.2	F1 PROCESSING	
ni	256	gf1	0.058
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.854	fn1	2048
tof	-405.0	DISPLAY	
tpwr	59	sp	40.0
pw	11.000	wp	4086.2
NOESY		sp1	41.1
mix	0.800	wp1	4086.2
PRESATURATION		rf1	3592.9
satmode	nnn	rfp	3628.9
satpwr	-13	rf11	3591.8
satdly	0	rfp1	3628.9
satfrq	499.8	PLOT	
DECOUPLER		wc	116.0
dn	C13	sc	10.0
dm	nnn	wc2	116.0
		sc2	0
		vs	7540
		th	2
		al cdc ph	



eupalinilide_e

exp6 Ghsqc

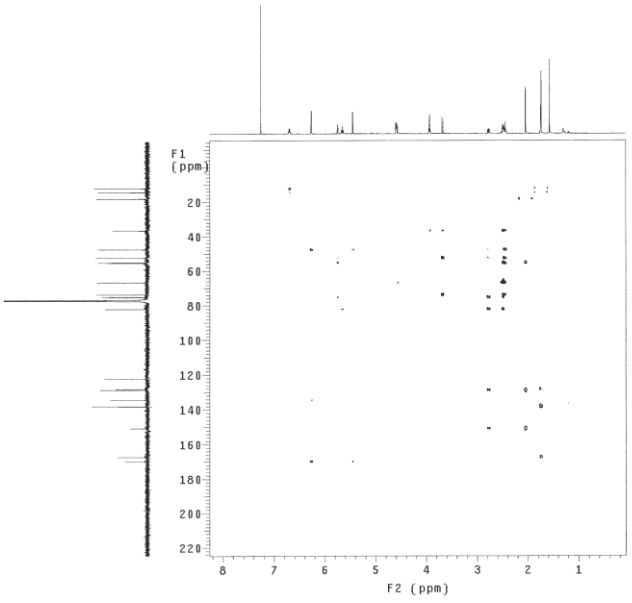
SAMPLE		FLAGS		ACQUISITION ARRAYS	
date	Aug 19 2014	hs	n	array	phase
solvent	cdcl3	sspul	y	arraydim	512
sample		PFGflg	y		
ACQUISITION		hsglvl	4694	i	phase
sw	4050.2	SPECIAL		1	1
at	0.199	temp	27.0	2	2
np	1630	gain	30		
fb	2000	spin	0		
ss	32	GRADIENTS			
d1	2.000	gzlvl1	4694		
nt	4	gt1	0.002000		
2D ACQUISITION		gzlvl3	2347		
sw1	21367.5	gt3	0.001000		
ni	256	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
PRESATURATION		gf	0.092		
satmode	nnn	gfs	not used		
satdly	0	fn	4096		
satfrq	499.8	F1 PROCESSING			
satpwr	-13	gf1	0.011		
TRANSMITTER		gfs1	not used		
tn	H1	proc1	lp		
sfrq	499.854	fn1	2048		
tof	-405.0	DISPLAY			
tpwr	59	sp	39.1		
pw	11.000	wp	4088.2		
DECOUPLER		sp1	-1266.9		
dn	C13	wp1	21346.7		
dof	-2515.2	rf1	981.6		
dm	nny	rfp	1018.7		
dmf	22200	rf11	18641.7		
dpwr	43	rfp1	17353.9		
pwx1v1	55	PLOT			
pwx	10.500	wc	116.0		
HSQC		sc	10.0		
jlxh	140.0	wc2	116.0		
nullflg	y	sc2	0		
mult	2	vs	872		
		th	2		
		al cdc ph			

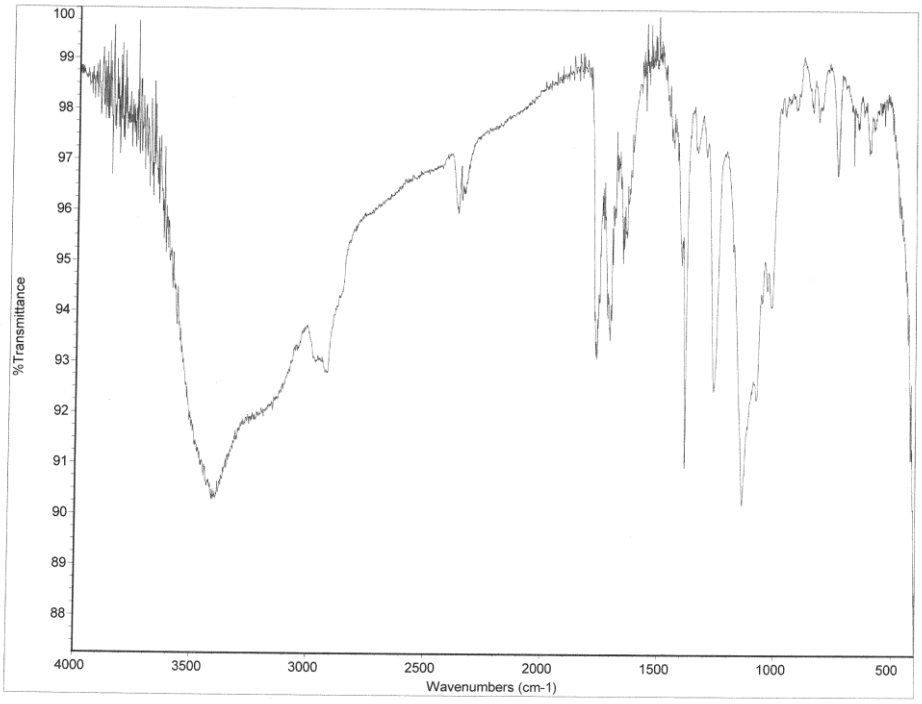


eupalinilide_e

exp7 Ghmbc

SAMPLE		FLAGS	
date	Aug 19 2014	hs	n
solvent	cdcl3	sspul	n
sample		PFGflg	y
ACQUISITION		hsglvl	4694
sw	4050.2	SPECIAL	
at	0.128	temp	27.0
np	1048	gain	30
fb	2000	spin	0
ss	32	GRADIENTS	
d1	2.000	gzlvl1	4694
nt	16	gt1	0.001000
2D ACQUISITION		gzlvl3	2347
sw1	30165.9	gt3	0.001000
ni	256	gstab	0.000500
phase	0	F2 PROCESSING	
PRESATURATION		sb	0.064
satmode	nnn	sbs	not used
satdly	0	fn	2048
satfrq	499.8	F1 PROCESSING	
satpwr	-13	sb1	0.008
TRANSMITTER		sbs1	not used
tn	H1	proc1	lp
sfrq	499.854	fn1	2048
tof	-405.0	DISPLAY	
tpwr	59	sp	40.5
pw	11.000	wp	4086.2
DECOUPLER		sp1	-1830.9
dn	C13	wp1	30136.5
dof	1255.4	rf1	982.2
dm	nnn	rfp	1018.7
dmf	22200	rf11	22931.5
dpwr	43	rfp1	21011.1
pwx1v1	55	PLOT	
pwx	10.500	wc	116.0
HMBC		sc	10.0
jlxh	140.0	wc2	116.0
jnxh	8.0	sc2	0
		vs	328
		th	2
		al cdc av	




100
99
98
97
96
95
94
93
92
91
90
89
88
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

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