Palladium catalyzed Nazarov-type cyclization of allyl diacetates

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Indian Institute of Science Education and Research Mohali
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Certificate of Examination

This is to certify that the dissertation titled "*Palladium catalyzed Nazarov cyclization of allyl diacetates*" submitted by Ms. Mrudula Nikam (Reg. No. MS14107) for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Declaration

The work presented in this dissertation has been carried out by me under the guidance of **Dr. S. S. V. Ramasastry** at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussion. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Notations and Abbreviations

NMR	Nuclear magnetic resonance
IR	Infra-red
HRMS	High resolution mass spectroscopy
TLC	Thin layer chromatography
δ	Chemical shift in ppm
ppm	Parts per million
EtOAc	Ethyl acetate
s	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet
dd	Doublet of doublets
dt	Doublet of triplets
td	Triplet of doublets
ddd	Doublet of doublet of doublets
M. P.	Melting point

Abstract

An efficient method of palladium catalyzed double Tsuji-Trost reaction of benzothiophene diacetates was investigated. Also Lewis acid mediated synthesis of dibenzoxanthene derivatives from geminal diacetates was accomplished. Attempts to perform chiral Nazarov cyclization of divinyl acetates were made.

Introduction

Cyclopenta-fused arenes and heteroarenes are ubiquitous in several important biologically active natural products as well as other useful plant metabolites. Designing various methodologies for synthesis of cyclopentanes has always attracted attention of synthetic community over the years. Variety of natural products bearing this skeleton have known to exhibit antiviral[1], antifungal[2], antiproliferative[3], *S*-adenosylhomocysteine hydrolase inhibitors[4], antibacterial[5], anti-microbial[6], antagonist [7], anti-HIV[8], anticancerous[9] activity etc.

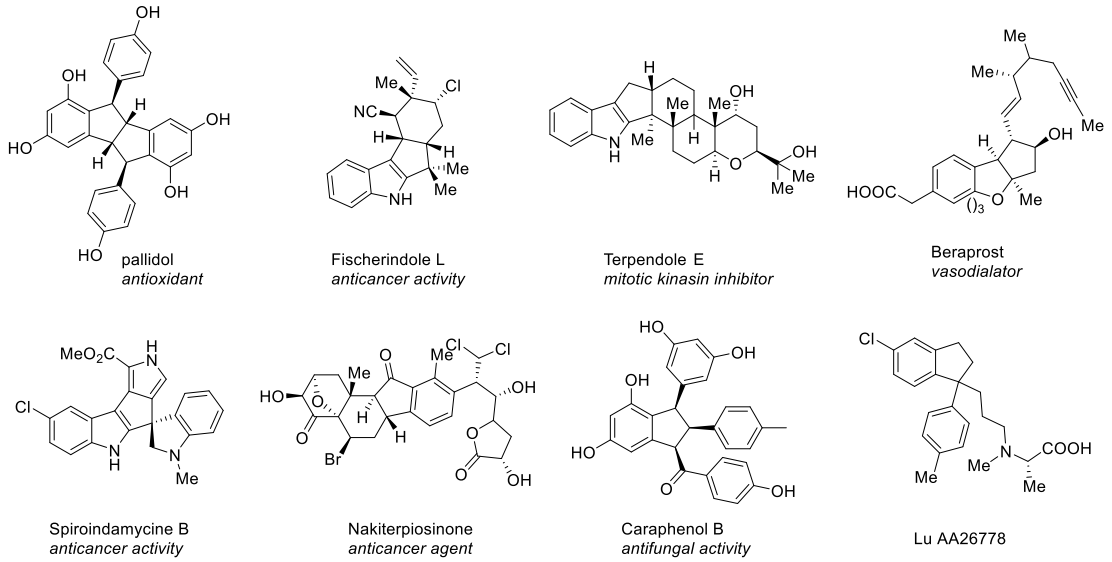


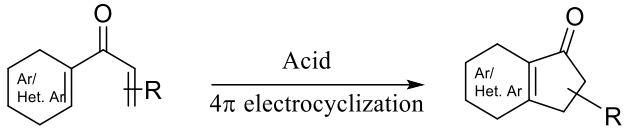
Figure 1: Representative examples of cyclopenta fused arenes and heteroarenes

For the construction of cyclopenta fused arene and heteroarene scaffold numerous strategies have been used which include organocatalytic as well as metal catalyzed techniques. Owing to their importance, a number of elegant methods for the preparation of cyclopentene derivatives were developed which mainly consists of aldol cyclocondensation[10], rearrangements of vinyl cyclopropanes[11], Nazarov cyclizations[12], phosphine-catalyzed [3 + 2] cycloaddition reactions[13], domino ring-opening cyclization of donor–acceptor cyclopropanes[14], cycloaddition of cyclopropanes with alkenes or alkynes[15], bimetallic catalyzed cycloaddition of

cyclopropylcarboxamide with alkynes[16], silver-catalyzed oxidative intermolecular [3 + 2] annulation of terminal alkynes with 4-vinyl acids[17], and allenic-ketone based multicomponent reactions[18].

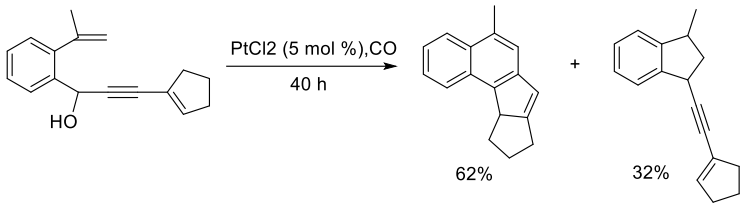
The Nazarov cylization is one of the most efficient and versatile synthetic tools for the stereoselective preparation of various cyclopentenone scaffolds. The Bronsted or Lewis acid catalyzed cyclization of divinyl ketones and their acid-labile precursors *via* pentadienylic cations is known as the Nazarov cyclization. In 1903, D. Vorlander and co-workers treated dibenzylideneacetone with concentrated sulfuric acid and acetic anhydride followed by hydrolysis by sodium hydroxide to afford cyclic ketol[20], the structure of which was later proposed in 1955[21]. Later, in the 1940s and 1950s, I. N. Nazarov revisited the topic and extensively studied the cyclization of the intermediate allyl vinyl ketones to give rise to the corresponding 2-cyclopentenones [22].

Classical acid catalyzed Nazarov cyclization of dienones to cyclopentenones:

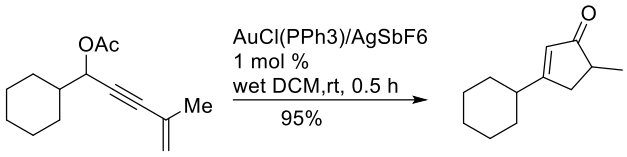


Various literature reports have been known regarding metal catalyzed Nazarov cyclization and its modified versions. Reports are also known about various transition metals such as Au(I)[23], Au(III)[24], Ag(I)[25], V(IV)[26], Re(0)[27], Pd(0)[28], Pt(II)[29], and Ir(III)[30] efficiently catalyzing the Nazarov Cyclization. In some cases, the Nazarov Cyclization may be induced by UV irradiation (photocyclization)[32].

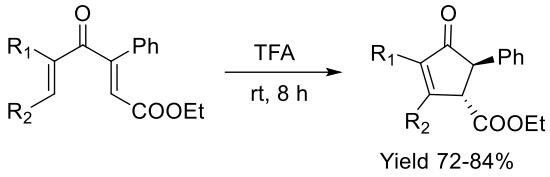
In 2006, Liu et al reported that in presence of $PtCl_2$/CO catalyst 2-alkenyl-(1′-hydroxyl-4-en-2-ynyl) benzenes undergo 6-exo-dig cyclization followed by Nazarov cyclization to yield 1*H*-



In 2007, Zhang and coworkers reported Au (I)-catalyzed synthesis of cyclopentenones from readily available enynyl esters *via* tandem 3,3-rearrangement and the Nazarov reaction.[34]

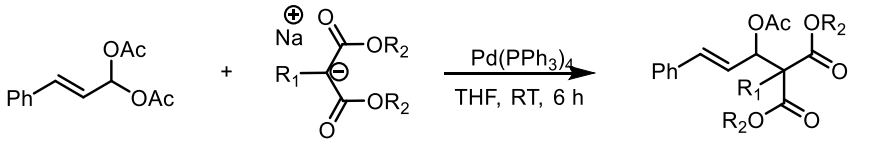


In 2016, Sudhakar and coworkers reported the TFA catalyzed regioselective Nazarov cyclization of dienone system bearing ester moiety at β-position [35].



R_1 = Me, R_2 = Ph, R_1 = Me, R_2 = PMP
R_1 = R_2 = Me, R_1 = Ph, R_2 = ^{i}Pr

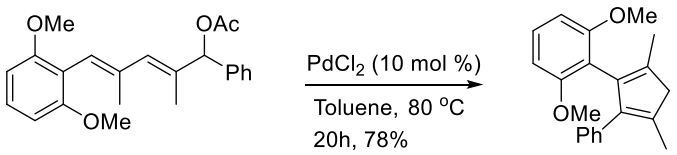
The palladium-catalyzed allylic alkylation reaction is efficient tool for the controlled introduction of carbon-carbon and carbon-heteroatom bonds into different organic compounds [36]. Allyl gem-diacetates are used as substrate for nucleophilic substitution reaction via palladium catalyzed Tsuji-Trost reaction [37].



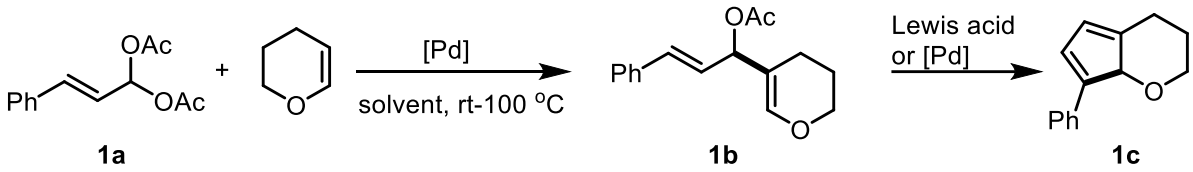
R_1= CH_3, R_2= $C(CH_3)_3$
R_1= NO_2, R_2= CH_2CH_3
R_1= NHAc, R_2= CH_2CH_3

Our group has recently published synthesis of cyclopentene scaffolds through palladium catalyzed intramolecular Trost–Oppolzer-Type Alder–Ene reaction of Dienyl Acetates. It features

generation of vinyl (π-allyl) palladium species which is then transformed to cyclopentadienyl cation by Alder–ene reaction. This approach, to access cyclopentadienes, combines electrophilic features of Tsuji-Trost reaction and nucleophilic features of Alder–ene reaction. The overall transformation represents a Pd-catalyzed (acid-free) iso-Nazarov-type reaction. [38]

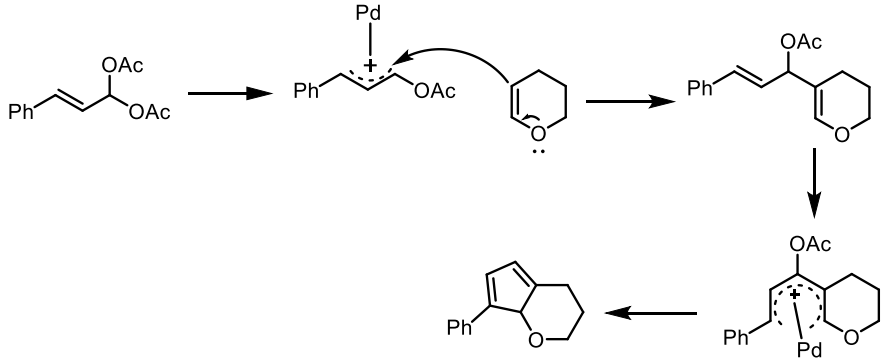


Therefore, motivated by literature reports and our lab work, we hypothesized that using geminal diacetate **1a** as our potential substrate and 2,4-H-dihydropyran as our nucleophile we can perform Tsuji-Trost reaction in presence of palladium catalyst to provide **1b**. Furthermore, **1b** can undergo cationic Nazarov cyclization to furnish cyclopenta[b]annulated scaffold **1c**.



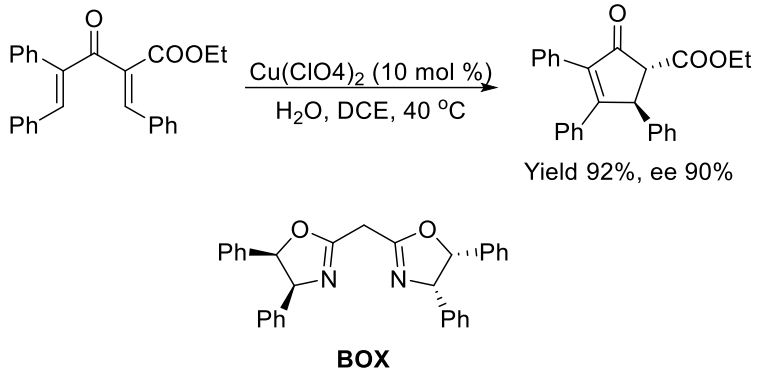
Scheme 1: Palladium catalyzed Tsuji-Trost reaction followed by Nazarov type cyclization

Plausible mechanism:



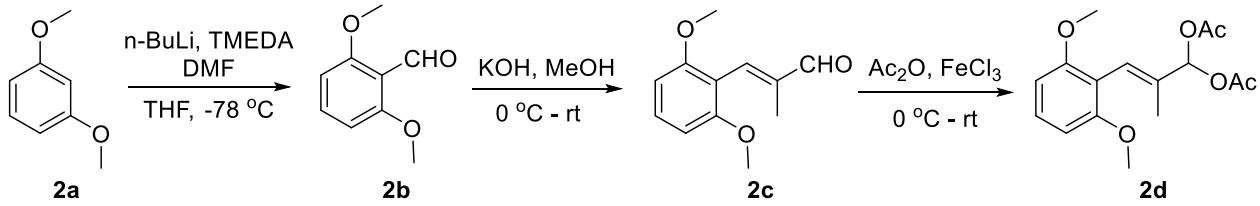
Also, our later plan was to carry out asymmetric Nazarov type cyclization of divinyl acetates. This can be accomplished by employing enantiomerically pure catalysts which can act as activators for our substrate and offer chiral induction.

An enatioselective copper catalyzed version of Nazarov cyclization of divinyl ketoesters was developed by Tang et al which uses BOX ligand for chiral induction[39].

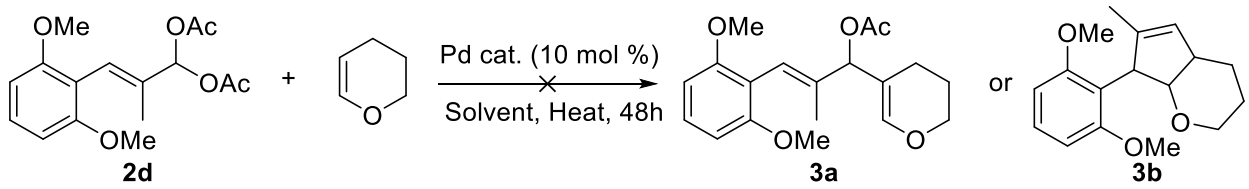


Results and Discussion

At the outset, we synthesized starting material for validation of our hypothesis and started screening various palladium catalysts in different solvents with different temperature combinations.



Scheme 2: Synthesis of (E)-3-(2,6-dimethoxyphenyl)-2-methylprop-2-ene-1,1-diyl diacetate



Scheme 3: Strategy for obtaining Nazarov type cyclization

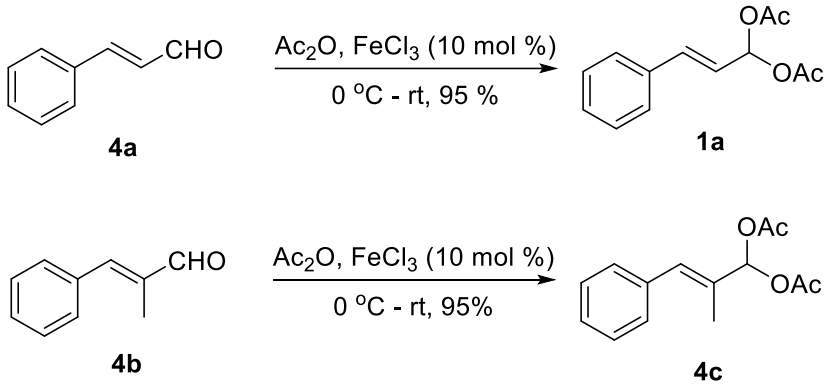
Table 1: Screening of reaction parameters for formation of **3a** or **3b**:

Entry	Solvent	Catalyst (10 mol %)	Temperature (°C)
1	Toluene, DMF	$PdCl_2$	60, 80, 100
2	Toluene, DMF	$Pd(OAc)_2$	60, 80, 100
3	Toluene, DMF	$Pd(PPh_3)_4$	60, 80, 100
4	Toluene, DMF	$Pd_2(dba)_3$	60, 80, 100
5	Toluene, DMF	Pd(π-allyl) Cl_2	60, 80, 100
6	Toluene, DMF	$Pd(PPh_3)_2Cl_2$	60, 80, 100
7	CH_3CN, 1,4-Dioxane, THF	$PdCl_2$	60, 80
8	CH_3CN, 1,4-Dioxane, THF	$Pd(OAc)_2$	60, 80

9	CH_3CN, 1,4-Dioxane, THF	$Pd(PPh_3)_4$	60, 80
10	CH_3CN, 1,4-Dioxane, THF	$Pd_2(dba)_3$	60, 80
11	CH_3CN, 1,4-Dioxane, THF	Pd(π-allyl) Cl_2	60, 80
12	CH_3CN, 1,4-Dioxane, THF	$Pd(PPh_3)_2Cl_2$	60, 80

After continuous monitoring of the reactions, we found that in all cases approximately after 5-6 h aldehyde **2c** started forming and several other spots were observed at 80 and 100 ^oC. But at 60 ^oC and room temperature, we observed that staring material was as such along with some amount of corresponding aldehyde **2c**. We conclude after extensive screening that starting material **2d** was not stable at these temperatures and decomposed.

We moved on to the more stable substrate design, cinnamyl diacetate **1a** and α-methyl-trans cinnamaldehyde **4c**, which is little explored in context of nucleophilic substitution via Tsuji-Trsost reaction. Synthesis of **1a** and **4c** was accomplished via single step from corresponding aldehyde.(Scheme **4**)We initiated screening of various palladium catalysts and solvent combinations at different temperatures with **1a** as the model substrate, with the intention to obtain the cyclopenta fused arene **1c**.



Scheme 4: General approach towards synthesis of allyl diacetates from corresponding aldehydes

Table 2: Screening of reaction conditions for **4a** and **4c**

Entry	Solvent	Catalyst (10 mol %)	Temperature (^oC)	Time (h)

1.	Toluene	$PdCl_2$	60, 80, 100, 130	24
2.	Toluene	$Pd(OAc)_2$	60, 80, 100, 130	24
3.	Toluene	$Pd(PPh_3)_4$	60, 80, 100, 130	24
4.	Toluene	$Pd_2(dba)_3$	60, 80, 100, 130	24
5.	DMF	$PdCl_2$	80, 100	24
6.	DMF	$Pd(OAc)_2$	80, 100	24
7.	DMF	$Pd(PPh_3)_4$	80, 100	24
8.	DMF	$Pd_2(dba)_3$	80, 100	24
9.	CH3CN	PdCl2	70, 85	24
10.	CH_3CN	$Pd(OAc)_2$	70, 85	24
11.	CH_3CN	$Pd(PPh_3)_4$	70, 85	24
12.	CH_3CN	$Pd_2(dba)_3$	70, 85	24
13.	1,4- Dioxane	$PdCl_2$	80	24
14.	1,4- Dioxane	$Pd(OAc)_2$	80	24
15.	1,4- Dioxane	$Pd(PPh_3)_4$	80	24
16.	1,4- Dioxane	$Pd_2(dba)_3$	80	24

Screening of reaction conditions with dry solvents:

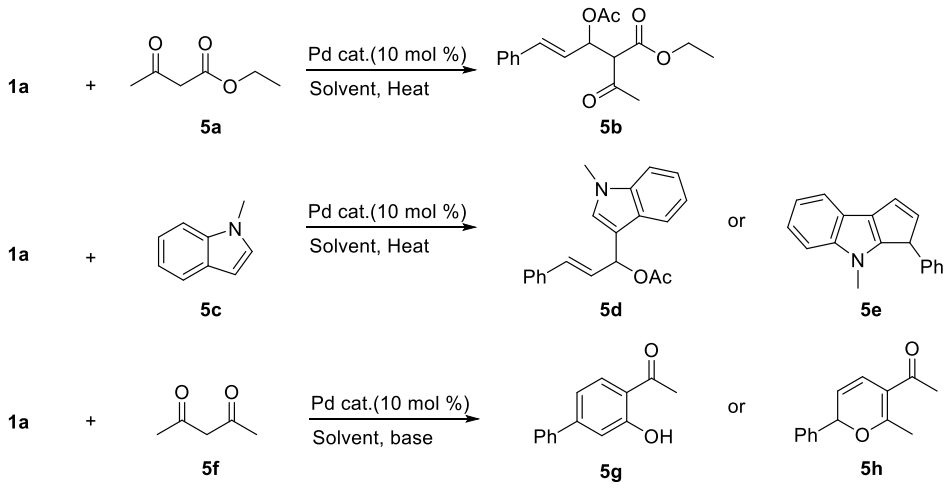
Table 3: Screening of **1a** with dry solvents

Entry	Dry Solvent	Catalyst (10 mol %)	Temperature (^oC)	Time (h)/ Yield
1.	Toluene	$PdCl_2$	100	48/-
2.	Toluene	$Pd(OAc)_2$	100	48/-
3.	Toluene	$Pd(PPh_3)_4$	100	48/-
4.	Toluene	$Pd_2(dba)_3$	100	48/-
5.	Toluene	PdI_2	100	48/-
6.	DCE, DCM, THF	$PdCl_2$	80	48/-
7.	DCE, DCM, THF	$Pd(OAc)_2$	80	48/-

8.	DCE, DCM, THF	$Pd(PPh_3)_4$	80	48/-
9.	DCE, DCM, THF	$Pd_2(dba)_3$	80	48/-
10.	DCE, DCM, THF	PdI_2	80	48/-

In case of **1a** and **4c**, we were unable to get neither the Tsuji-Trost product **1b** nor the cyclized product **1c**. The starting material **1a** and **4c** was converting to corresponding aldehyde **4a** and **4b** and some starting material was as such. No other spots were observed on TLC. Some screening was carried out using dry solvents (dry DCM, DCE, DMF, Toluene, THF) also. In that case, the time taken by aldehyde spot to appear was extended but no other spot was observed on TLC. Activation of starting material with Lewis acid was also considered to have some impact so few A brief screening of Lewis acids ($Bi(OTf)_3$, $Sc(OTf)_3$, $InCl_3$, AgOTf) was undertaken in different solvents to see whether it can activate the substrate and lead to the formation of product. But no product formation was observed.

We arrived at the conclusion that may be due to less reactivity of 2,4-H-dihydropyran we were unable to obtain expected product **1c**. So we thought of changing the nucleophile and began screening of different nucleophiles like ethyl acetoacetate **5a**, 1-methylindole **5c**, acetyl acetone **5f**, expecting to obtain **5b**, **5d** or **5e**, **5g** or **5h** respectively. (Scheme 5)

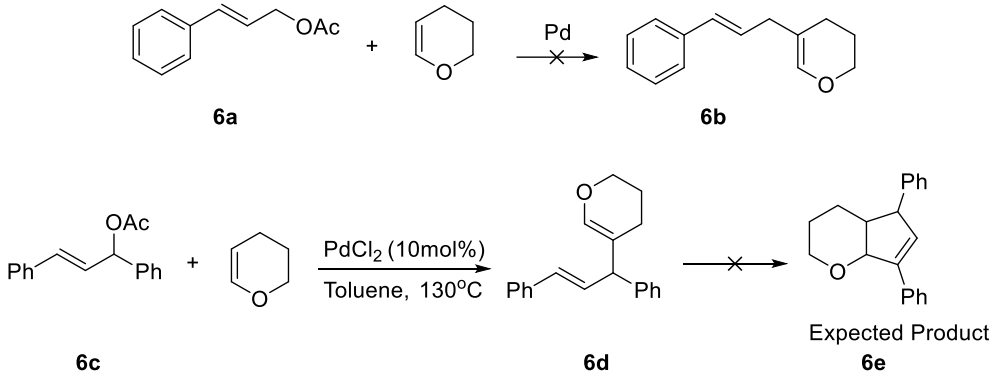


Scheme 5: Screening of different nucleophiles and expected products

Several subsequent efforts were directed to afford expected product thorough screening of various palladium catalysts along with equivalent amount of base (Et_3N, DMAP, NaH, Pyridine,

K_2CO_3) for acetyl acetone **5f** as well as ethyl acetoacetate **5a**. For 1-methylindole **5c**, extensive solvent screening with different catalyst and temperature combination was carried out. Unfortunately, we could not succeed to procure desired product.

Later, we thought of obtaining only nucleophile substituted product via Tsuji-Trost reaction and then finding suitable reaction condition to get it cyclized. **6a** and **6c** were synthesized using standard procedure and reacted with 3,4-dihydro-2-H-pyran with catalytic amount of $PdCl_2$, with **6c** we succeded to get pyran substituted product. For further cyclization, several Lewis and Brosted acids were screened. **6d** was unstable under Lewis acidic condition and after 1 – 2 h it decomposed completely in each case.

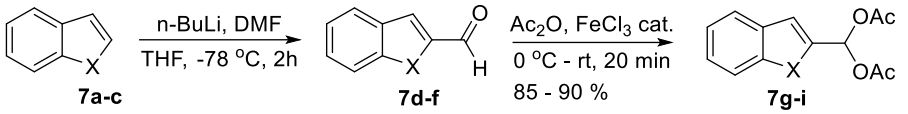


Scheme 6: Tsuji-Trost reaction of allyl mono-acetates

Table 4: Screening of Lewis acids for **6e** from **6e**

Entry	Solvent	LA/BA (10 mol %)	Temperature	Time(h)
1	DCM	$BF_3.OEt_2$	rt	1
2	DCM	$SnCl_4$	rt	1
3	DCM	Ag(OTf)	rt	1
4	DCM	$Sc(OTf)_3$	rt	1
5	DCM	PTSA	rt	1
6	DCM	$La(OTf)_3$	rt	1

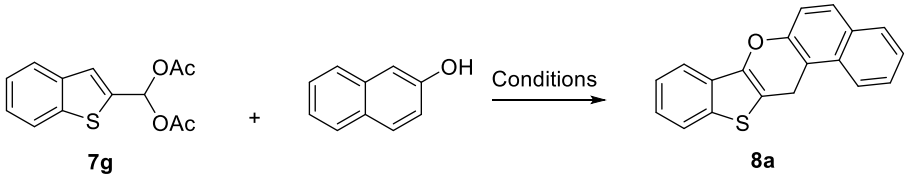
Inorder to verify our hypothesis, we moved on to heterocyclic geminal diacetates and began screening different nucleophiles in presence of palladium catalysts. The geminal diacetates **7g–7i** were synthesized from corresponding heterocycles in good to excellent yields.



X = S (**7a, 7d, 7f**), O **(7b, 7e, 7h)**, N-Ts (**7c,7f, 7i**)

Scheme 7: Synthesis of heterocyclic gem-diacetates

While screening different nucleophiles, to our surprise, the reaction of **7g** with 2-naphthol in presence of $PdCl_2$ (10 mol %) delivered **8a** in 45% yield (Table 5, entry 7), which is product obtained by Tsuji-Trost followed by Friedel-Crafts reaction. Further attempts were made to find out optimization condition for synthesis of **8a**. (Table 5)



Scheme 8: Palladium catalyzed double Tsuji-Trost reaction

Table 5: Optimization of reaction parameters for **8a** from **7g.**

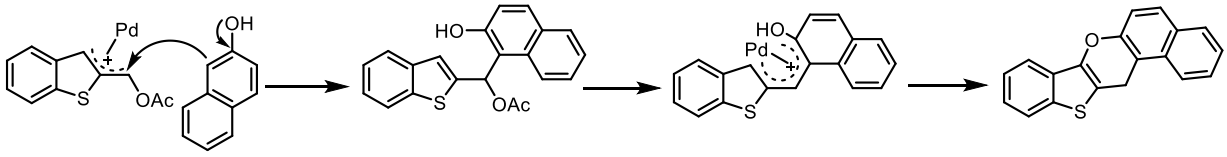
Entry	Catalyst (10 mol %)	Solvent	Temperature (°C)	Time (h)	Yield (%)
1.	$PdCl_2$	Toluene	100	35	45
2.	$Pd(OAc)_2$	Toluene	100	48	-
3.	$Pd(PPh3)_4$	Toluene	100	48	-
4.	$Pd_2(dba)_3$	Toluene	100	48	-
5.	PdI_2	Toluene	100	48	-
6.	$PdCl_2$	DCE	70	48	50
7.	$PdCl_2$	DCE	80	23	75
8.	$PdCl_2$	DCE	100	24	-

9.	$PdCl_2$	CH3CN	70	50	48
10.	$PdCl_2$	CH3CN	85	24	65
11.	$PdCl_2$	DMF	100	24	-
12.	$PdCl_2$	DMF	130	24	-
13.	$PdCl_2$	DMSO	100	24	-
14.	$PdCl_2$	DMSO	130	24	-

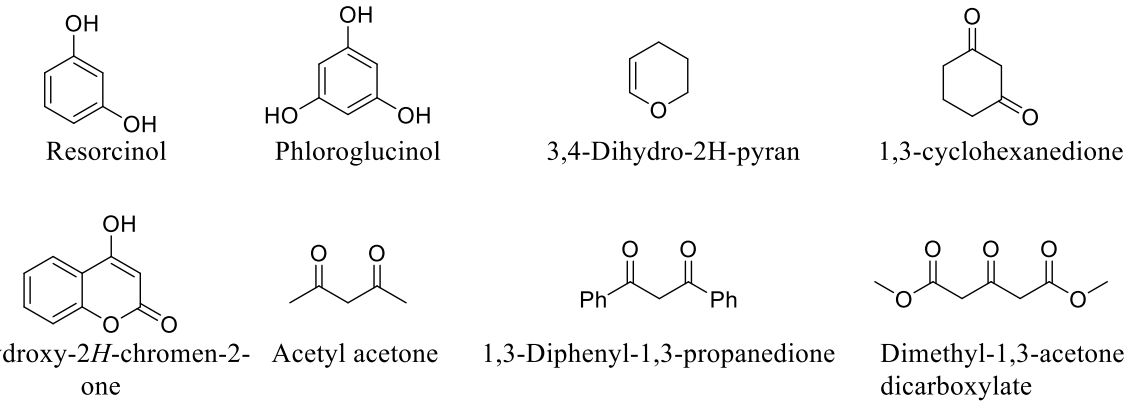
Therefore, among few other variations undertaken to increase the efficiency of the reaction, only the reaction of **7g** at moderate temperature provided **8a** with a much increased yield (Table 5, entry 7). Employing a few other Pd(II) salts proven to be unsuccessful (Table 5, entry 2-5). The low yield at higher temperature was found to be due to instability of product **8a**. At elevated temperature in DCE and toluene, formation of multiple non-polar spots was observed. In presence of molecular sieves and proton scavengers, no significant change in yield of **8a** was observed.

The mechanism for this transformation must be going through formation of π-allylpalladium species and then substitution with 2-naphthol to give substituted intermediate and after that Friedel-Crafts reaction to provide pentacyclic core **8a**.

Plausible mechanism:

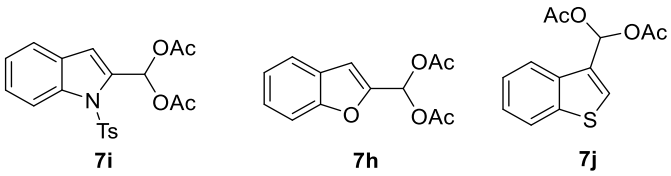


Several other nucleophiles were explored to react with **7g** (Scheme 9). But starting material was as such even after 48h with optimized parameters maintained.

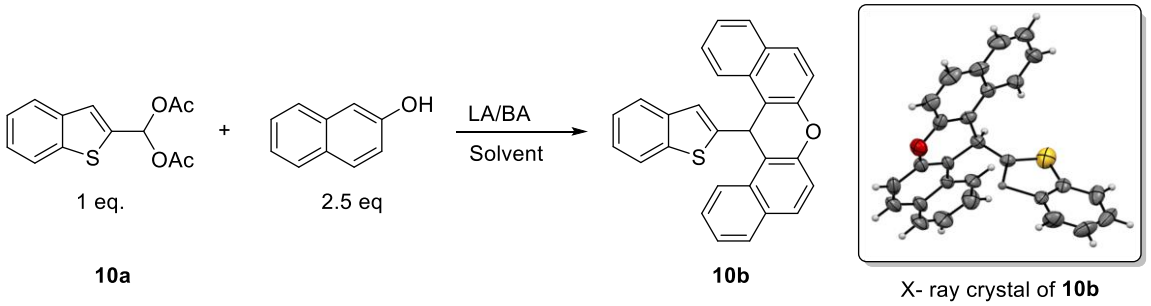


Scheme 9: Different nucleophiles used for **7g**

We tried other heterocyclic geminal diacetates **7h** and **7i** with 2-Naphthol. Interestingly, in each case xanthenes derivative was delivered which was confirmed by NMR and single crystal x-ray diffraction. From **7h** and **7i** we obtained similar compounds under Lewis acidic conditions with good to excellent yield.



To obtain **10b** exclusively from reaction, we screened Lewis acid and Bronsted acids which gave us favourable results in terms of yield of **10a**.



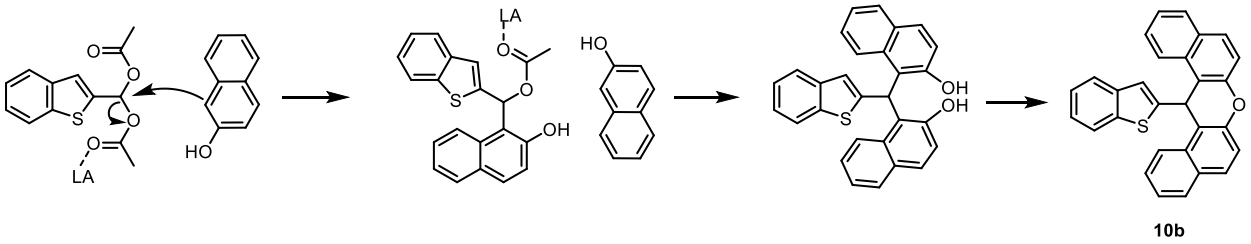
Scheme 10: Synthesis of dibenzoxanthene derivatives

Table 6: Screening of reaction condition for **10b** from **10a**

Entry	Solvent	Catalyst (10 mol %)	Time (h)	Yield (%)
1.	DCE	$Bi(OTf)_3$	11	55
2.	DCE	$In(OTf)_3$	10	65
3.	DCE	Ag(OTf)	15	50
4.	DCE	$Yb(OTf)_3$	-	-
5.	DCE	$Zn(OTf)_2$	26	-
6.	DCM	$Bi(OTf)_3$	10	79
7.	DryDCE	$Bi(OTf)_3$	10	70
8.	Dry DCM	$Bi(OTf)_3$	12	80
9.	DCE	PTSA	5	50

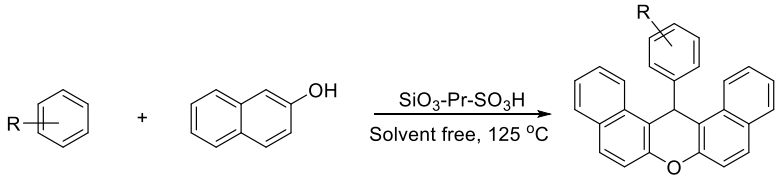
DCM and $Bi(OTf)_3$ afforded 80% yield at room temperature. The mechanism for this transformation goes via Lewis acid mediated activation of acetate group which facilitates nucleophilic attack of 2-naphthol. Two molecules of 2-naphthol are tethered to diacetate which further undergoes condensation to give diabezoxanthene derivative.

Plausible mechanism:



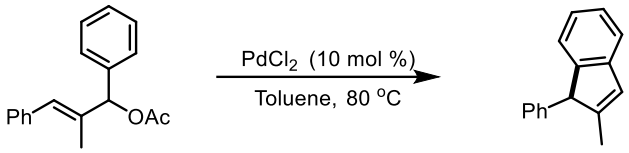
10b

Literature reports[40] are already known for the formation of xanthenes derivatives as they are very useful as fluorescence dyes for visualization of biomolecules. They are well known for their use in biological and pharmaceutical applications such as bactericidal activity[41], photodynamic therapy[41], anti-inflammatory[42] and anti-viral activity[43].

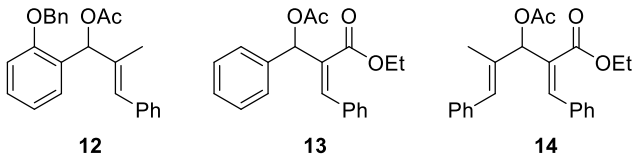


Scheme 11: The preparation of 14-aryloralkyl-14*H*-dibenzoxanthenes usingSiO_2-Pr-SO_3H.

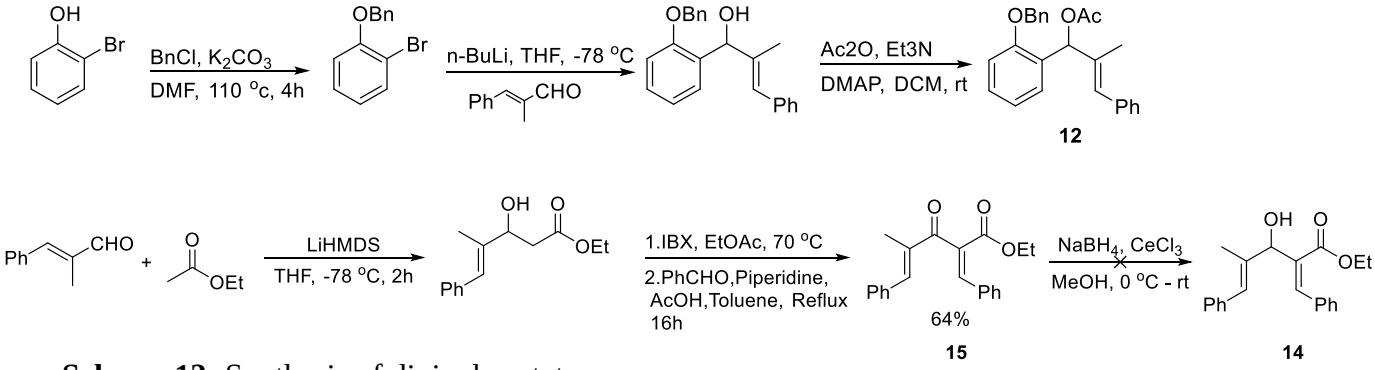
We then moved our attention to develop chiral version of Nazarov cyclization from the recemic protocol already established in our lab (Scheme 11a), by slight modification in substrate design. So we designed our substrate in such way that it would bear a functional moiety which will co-ordinate with chiral ligands of palladium catalyst to furnish enantioselectively pure Nazarov cyclized product. Our plan was to establish general chiral protocol for Nazarov cyclization divinyl acetates by screening several ligands with $PdCl_2$ along with any additives if required.



Scheme 11a: Palladium catalyzed Nazarov type cyclization of divinyl acetate.



Synthesis of starting material 12 and 14:



Scheme 12: Synthesis of divinyl acetates.

Considering the aforementioned rationale and to examine our hypothesis we synthesized **12** and started screening for racemic version first. In presence $PdCl_2$, the reaction worked but multiple spots with very close RF value were observed on TLC. After several failed attempts to get clean NMR data for the same, we moved on to the next substrate design **14**. Synthesis of **14**

started with α-methyl-trans-cinnamaldehyde which after three steps furnished **15** in 64% yield. We attempted $NaBH_4$ reduction in presence of $CeCl_3$ which ended up with formation multiple spots even at reduced temperatures.

Summary

In summary, the reactivity and scope of various geminal diacetates is examined through extensive screening with different nucleophiles for Palladium catalyzed Tsuji-Trost reaction. Several attempts were made to cyclize Tsuji-Trost product obtained from allyl acetates. Benzothiophene diacetate was screened for several nucleophiles and pentacyclic core was obtained from reaction of benzothiophene diacetate with 2-naphthol via $PdCl_2$ catalyzed double Tsuji-Trost reaction. Dibenzoxanthene derivatives were synthesized via Lewis acid catalyzed reaction of benzothiophene diacetate with 2 equivalents of 2-naphthol.

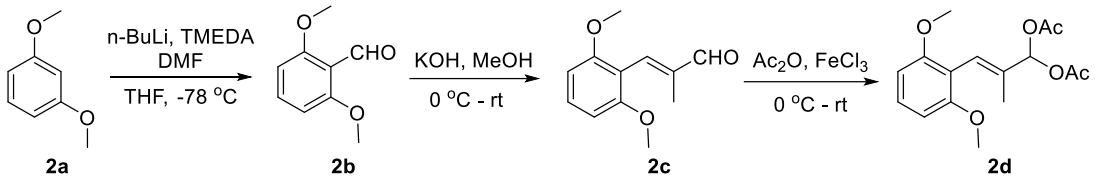
Experimental methods

General experimental methods: All the starting compounds and catalysts employed in this study were procured from Sigma-Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max} in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP30 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz BrukerBiospinAvance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$.Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ77.1 ppm). High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Enantiomeric excess was determined by using Waters Chiral HPLC.

General procedure for synthesis of geminal diacetate from corresponding aldehyde:

Aldehyde **4a** (500 mg, 3.78 mmol) was dissolved in acetic anhydride (2.15 ml, 22.69 mmol). The RB is cooled to 0 ^oC and $FeCl_3$ (61.23 mg, 0.378 mmol) was added to the reaction mixture and continued stirring for 20 min. Completion of reaction is confirmed by TLC. Reaction mixture was quenched by slow addition of dilute solution $NaHCO_3$ at 0 ^oC organic layer was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (5-10% EtOAc/hexane) to afford **1a** in 90-95% yields.

Procedure for preparation of 2d (scheme 2):



Step 1: An oven dried round bottom flask was charged with 1,3-dimethoxybenzene (1000 mg, 7.24 mmol), N,N,N,N-Tetramethyldiamine (106 µl, 0.36 mmol) and 5 mL dry THF placed at 0 °C. n-BuLi (4.98 ml, 7.96 mmol) was added drop wise at the same temperature and stirred for 1h. DMF (673 µl, 7.96 mmol) was added to the reaction mixture and continued stirring for another 1 h. Upon completion, the reaction mixture was quenched by adding water and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford **2b** in 80-85 % yields.

Step 2: In an oven dried round bottom flask charged with methanol, **2b** (1560 mg, 9.39 mmol) was dissolved and kept at 0 °C. KOH pellets (580 mg, 10.33 mmol) were added and reaction mixture was stirred for 5 min and propionaldehyde (600 mg, 10.33 mmol) and reaction mixture was stirred for 12h. Upon completion, reaction mixture was quenched and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20 % EtOAc/hexane) to afford **2c** in 80-85 % yields.

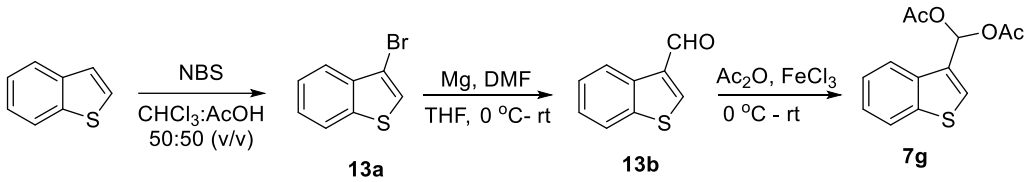
Step 3: 2c (1627 mg, 7.89 mmol) was dissolved in acetic anhydride (4.5 ml, 47.34 mmol). The RB is cooled to 0 °C and $FeCl_3$ (128 mg, 0.789 mmol) was added to the reaction mixture and continued stirring for 20 min. Completion of reaction is confirmed by TLC. Reaction mixture was quenched by slow addition of dilute solution $NaHCO_3$ at 0 °C organic layer was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20 % EtOAc/hexane) to afford **2d** in 90-95% yields.

Procedure for preparation of 7g-7i (Scheme 7):

Step 1: An oven dried round bottom flask was charged with Thianaphthene (500 mg, 3.73 mmol), dissolved in 5 mL dry THF placed at -78 ^{o}C. n-BuLi (3.5 ml, 5.59 mmol) was added drop wise at the same temperature and stirred for 1h. DMF (344 µl, 4.48 mmol) was added to the reaction mixture and continued stirring for another 1 h. Upon completion, the reaction mixture was quenched by adding water and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford 7**d** in 90-95 % yields.

Step 2: Corresponding aldehyde **7d** (545 mg, 3.37 mmol) was dissolved in acetic anhydride (1.91 ml, 20.19 mmol). The RB is cooled to 0 ^{o}C and $FeCl_3$ (55 mg, 0.337 mmol) was added to the reaction mixture and continued stirring for 20 min. Completion of reaction is confirmed by TLC. Reaction mixture was quenched by slow addition of dilute solution $NaHCO_3$ at 0 ^{o}C organic layer was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1-5 % EtOAc/hexane) to afford **7g** in 90-95% yields.

Procedure for preparation of 7j (Scheme 13):



Scheme 13: Synthesis of 7j

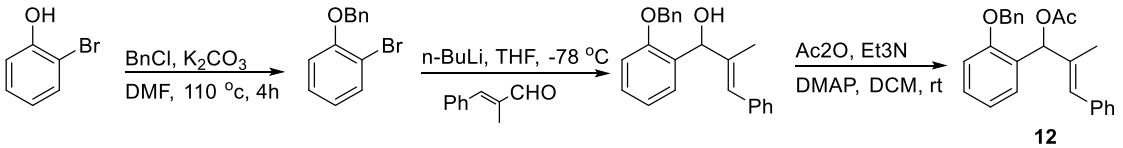
Step 1: Thianaphthene (3.73 mmol) was dissolved in 50:50 (v/v) mixture of chloroform and glacial acetic acid. N-bromosuccinamide (3.73 mmol) was added to the reaction mixture and stirred for 3 days at room temperature. After completion of reaction, reaction mixture was quenched by adding water. The combined organic layers were washed with brine, organic layer was extracted with DCM and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1-5 % EtOAc/hexane) to afford **13a** in 80-85 % yields.

Step 2: An oven dried round bottom flask was charged with magnesium turnings (1.0 mmol), catalytic amount of iodine and dry THF (0.5 mL). A solution of 3-bromobenzothiophene (1.1 mmol) in dry THF (1 mL) was slowly added to the suspension. At 0 ^{o}C, DMF was dissolved in dry THF mixture under inert atmosphere and to this the above reaction mixture was added. After 1h completion of reaction was confirmed by TLC. The reaction mixture was quenched by adding saturated aq. NH_4Cl (1 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (5 - 10 % EtOAc/hexane) to afford **13b** in 95% yield.

Step 3: Corresponding aldehyde (1090 mg, 6.73 mmol) was dissolved in acetic anhydride (3.81 ml, 40.37 mmol). The RB is cooled to 0 ^{o}C and $FeCl_3$ (109 mg, 0.673 mmol) was added to the reaction mixture and continued stirring for 20 min. Completion of reaction is confirmed by TLC. Reaction mixture was quenched by slow addition of dilute solution $NaHCO_3$ at 0 ^{o}C organic layer was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1-5 % EtOAc/hexane) to afford **7j** in 90-95% yields.

General procedure for the optimization of reaction parameters. An oven-dried 5 mL glass vial was charged with **7g-i** (0.076 mmol, 1 equiv), 2-naphthol (0.076 mmol, 1 equiv) and an appropriate solvent (1 mL). A catalyst (10 mol%, 0.1 equiv) was then introduced at room temperature. The reaction mixture was stirred at higher temperatures until starting material disappeared as monitored by TLC. The reaction mixture was quenched with aqueous sodium bicarbonate solution, diluted with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer further extracted with ethyl acetate (1-2 mL) The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the product **7g-i** as a pale orange solid**.**

Procedure for preparation of 12:



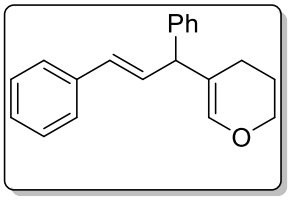
12

Step 1: In an oven dried round bottom flask 2-bromophenol (2.89 mmol) was taken and dissolved in DMF. Benzyl chloride (3.46 mmol) and K_2CO_3 (3.46 mmol) was added into it and reaction mixture was heated to 110 ^oC for 4h. After completion, reaction mixture was quenches with ice and extracted with EtOAc, concentrated and used for next step.

Step 2: The product from above step (2.66 mmol) was dissolved in 5 mL dry THF placed at -78 ^oC. n-BuLi (3.19 mmol) was added drop wise at the same temperature and stirred for 1h. α-methyl trans-cinnamaldehyde (2.66 mmol) was added to the reaction mixture and continued stirring for another 1 h. Upon completion, the reaction mixture was quenched by adding water and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexane) to afford alcohol in 85 % yields.

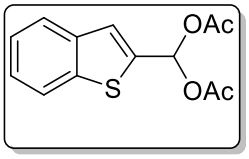
Step 3: The alcohol (2.26 mmol) from above step was taken in Oven dried round bottom flask charged with DCM. Acetic anhydride (2.26 mmol) and Et_3N (2.26 mmol) was added to the reaction mixture along with catalytic amount of DMAP (0.226 mmol). After 15 min, confirming completion of reaction, it was quenched and organic layer was washed with brine and extracted with DCM and dried over anhydrous Na_2SO_4.After concentration under reduced pressure, the residue was purified by silica gel chromatography (10-20 EtOAc/Hexane) to afford **12** in 90% yield.

Spectroscopic data of all new compounds reported in this study:



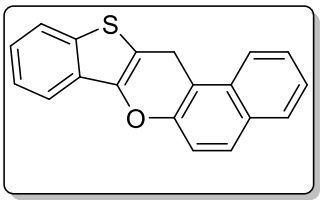
(*E*)-5-(1,3-diphenylallyl)-3,4-dihydro-*2H*-pyran

This compound was isolated as green oil following procedure mentioned above with 70% yield. **IR (thin film, neat):** ν_{max}/cm^{-1} **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.43-7.24 (m, 10H), 6.54-6.39 (m, 3H), 4.10(d, J = 7.14, 1H), 4.00 – 3.97 (m, 2H), 1.93 – 1.89 (m, 4H) **^{13}C NMR** (100 MHz, $CDCl_3$): δ142.4, 141.4, 137.4, 131.3, 130.9, 128.5 (2C), 128.39 (2C), 128.38 (2C), 127.2, 126.4, 126.2 (2C), 114.6, 65.5, 52.2, 22.6, 22.3 **HRMS (ESI):***m/z*calcdfor $C_{20}H_{20}O$: $(M)^+$: 276.1514 Found: 276.1521.



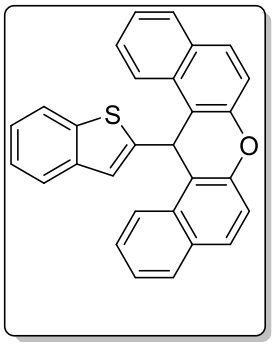
Benzo[*b*]thiophen-2-ylmethylene diacetate

This compound was isolated as pale orange solid. Following the general procedure, This compound was obtained in 75% yield. R_f= 0.6 (EtOAc/Hexane = 1/10). **IR (thin film, neat):** ν_{max}/cm^{-1} 2924,2853, 1766, 1372, 1235, 1198, 1008, 750. **^{1}H NMR** (400 MHz, $CDCl_3$): δ8.03 (s, 1H), 7.87 – 7.79 (m, 2H), 7.51 (s, 1H), 7.41 – 7.38 (m, 2H), 2.18 (s, 6H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.4 (2C), 139.8, 138.5, 138.2, 125.3, 124.6, 124.4, 124.1, 122.5, 86.7, 20.8 (2C) **HRMS (ESI):***m/z*calcdfor $C_{13}H_{12}NaO_4S$ $(M+Na)^+$: 287.0354. Found: 287.0368.



13H-benzo[f]benzo[4,5]thieno[3,2-b]chromene

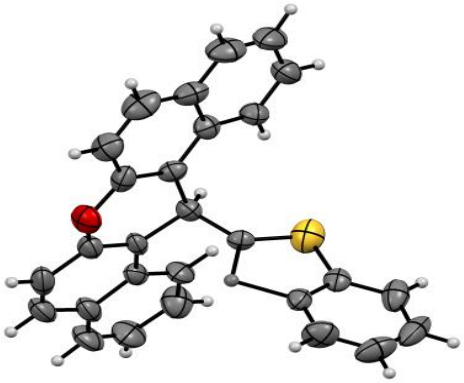
This compound was isolated as pale yellow solid. Following the general procedure, this compound was obtained in 75% yield. R_f = 0.6 (EtOAc/Hexane = 1/20). **IR (thin film, neat):** ν_{max}/cm^{-1} 2920, 2848, 1515, 1436, 1236, 811, 744. **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.94 – 7.80 (m, 5H), 7.66 – 7.62 (m, 1H), 7.53 – 7.39 (m, 4H), 4.53 (s, 2H) **^{13}C NMR** (100 MHz, $CDCl_3$): δ148.5, 140.9, 136.0, 132.1, 130.6, 130.5, 128.6, 128.4, 126.9, 124.8, 124.4, 124.3, 122.7, 122.45, 120.0, 118.3, 112.0, 109.8, 23.6, **HRMS (ESI):***m/z*calcdfor $C_{19}H_{11}OS$ $(M–H)^+$: 287.0528. Found: 287.0497.



14-(benzo[*b*]thiophen-2-yl)-14*H*-dibenzo[*a,j*]xanthenes

This compound was isolated as white solid. Following the general procedure, this compound was obtained in 80% yield. R_f = 0.5 (EtOAc/Hexane = 1/20). **IR (thin film, neat):** ν_{max}/cm^{-1}2925, 1622, 1593, 1458, 1247, 815, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ8.47 (d, J = 8.6 Hz, 2H),7.89 (dd, J = 11.2 and 8.8 Hz, 4H), 7.67 (t, J = 7.7, 2H), 7.55 – 7.44 (m, 6H), 7.20 – 7.12 (m, 2H), 7.06 (s, 1H), 6.93 (s, 1H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ149.1, 148.9, 139.3, 139.2, 131.3, 131.0, 129.3 (3C), 128.8 (3C), 127.0 (3C), 124.5 (2C), 124.0, 123.7, 123.2, 122.5 (3C), 122.0, 121.3, 117.9 (2C), 115.9, 33.1. **HRMS (ESI):***m/z*calcdfor $C_{29}H_{18}OS$ $(M–H)^+$: 413.0999. Found: 413.0993.

Crystal structure of 10b Structure of the **10b** was confirmed by single crystal X-ray diffraction analysis.



Mn01121P_0ma

Table 1 Crystal data and structure refinement for Mn01121P_0ma.

Identification code	Mn01121P_0ma
Empirical formula	$C_{29}H_{17}OS$
Formula weight	413.52
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	14.080(2)
b/Å	17.400(3)
c/Å	8.3603(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2048.2(6)
Z	4
ρ_{calc}g/cm^3	1.3409
μ/mm^{-1}	0.177
F(000)	860.8
Crystal size/mm^3	N/A × N/A × N/A
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	3.72 to 50.1
Index ranges	$-15 \leq h \leq 16$, $-20 \leq k \leq 20$, $-9 \leq l \leq 9$
Reflections collected	15555
Independent reflections	3609 [R_{int} = 0.0311, R_{sigma} = 0.0283]
Data/restraints/parameters	3609/1/276
Goodness-of-fit on F^2	2.116
Final R indexes [I>=2σ (I)]	R_1 = 0.0868, wR_2 = 0.2599
Final R indexes [all data]	R_1 = 0.0986, wR_2 = 0.2694
Largest diff. peak/hole / e $Å^{-3}$	1.13/-0.91
Flack parameter	7.85(3)

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Mn01121P_0ma. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O3	-4648(2)	-4857(2)	-1790(5)	54.6(10)
C4	-6610(3)	-6098(3)	-364(6)	39.2(11)
C5	-6595(3)	-4636(3)	-749(6)	37.6(12)
C6	-6097(4)	-3224(3)	-304(7)	42.7(12)
C7	-6114(3)	-5414(3)	-808(6)	37.3(12)
C8	-7271(3)	-4561(3)	-2130(6)	34.7(11)
C9	-4737(4)	-6200(4)	-1538(7)	58.4(16)
C10	-5188(4)	-5476(3)	-1359(7)	43.7(13)
C11	-5876(3)	-3996(3)	-773(6)	38.6(11)
C12	-7920(4)	-4593(3)	-4773(7)	41.3(13)
C13	-5648(5)	-1878(4)	23(9)	69.1(19)
C14	-7544(4)	-6100(3)	260(7)	49.0(14)
C15	-6164(4)	-6832(3)	-594(7)	50.6(14)
C16	-9566(4)	-4276(3)	-4432(9)	59.4(17)
C17	-6971(4)	-3025(3)	377(7)	45.6(12)
C18	-8682(4)	-4412(3)	-3777(7)	41.0(12)
C19	-5200(5)	-6834(4)	-1179(8)	57.6(16)
C20	-7976(5)	-6767(4)	662(9)	66.1(18)
C21	-4267(4)	-3572(4)	-1518(8)	54.3(14)
C22	-8898(5)	-4513(4)	-7035(8)	70(2)

C23	-4950(4)	-4132(4)	-1352(7)	47.0(13)
C24	-8053(5)	-4634(4)	-6410(8)	63.9(17)
C25	-5404(4)	-2634(3)	-459(7)	53.6(15)
C26	-6656(5)	-7494(3)	-120(9)	61.4(18)
C27	-9670(6)	-4338(4)	-6070(10)	77(2)
C28	-7508(5)	-7469(4)	516(9)	67.2(19)
C29	-7177(5)	-2292(3)	831(8)	59.1(17)
C30	-6473(5)	-1706(3)	662(10)	71(2)
C31	-4488(5)	-2825(4)	-1094(8)	66.3(18)
S1	-8419.9(12)	-4336.2(11)	-1826(2)	76.5(7)
C1	-6901(2)	-4752.3(19)	-3954(4)	12.7(7)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Mn01121P_0ma. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O3	42(2)	64(3)	58(3)	6.0(17)	15(2)	-4(2)
C4	50(3)	33(3)	34(3)	10(2)	-9(2)	2(2)
C5	41(3)	35(3)	37(3)	4.1(19)	3(2)	0(2)
C6	50(3)	36(3)	42(3)	1(2)	-6(2)	9(2)
C7	40(3)	38(3)	33(3)	16(2)	-2(2)	-2(2)
C8	39(3)	34(2)	30(2)	-2.0(18)	3(2)	-0.3(19)
C9	50(3)	77(4)	48(3)	29(3)	-8(3)	-7(3)
C10	42(3)	48(3)	41(3)	11(2)	-2(2)	-5(2)
C11	41(3)	44(3)	32(2)	-7(2)	0(2)	-1(2)
C12	40(3)	32(2)	52(3)	-1(2)	-10(2)	3(2)
C13	90(5)	42(3)	75(5)	-20(3)	-11(4)	3(3)
C14	59(3)	26(3)	62(4)	2(2)	-10(3)	0(2)
C15	61(3)	43(3)	48(3)	23(2)	-6(3)	-4(3)
C16	43(3)	53(4)	82(5)	-4(2)	-8(3)	22(3)
C17	47(3)	38(3)	51(3)	-2(2)	-1(3)	-3(2)
C18	39(3)	31(3)	53(3)	-7(2)	-3(2)	8(2)
C19	70(4)	42(3)	60(4)	23(3)	-7(3)	-8(3)
C20	63(4)	56(4)	79(5)	1(3)	-3(4)	19(3)
C21	43(3)	67(4)	53(3)	-8(3)	10(3)	0(3)
C22	90(6)	74(4)	46(4)	-24(4)	-20(4)	4(3)
C23	36(3)	65(4)	40(3)	5(2)	-4(2)	1(3)
C24	73(4)	77(4)	42(3)	0(3)	5(3)	-7(3)

C25	65(4)	51(3)	45(3)	-16(3)	-9(3)	1(3)
C26	81(5)	28(3)	75(4)	15(3)	-5(3)	0(3)
C27	76(5)	54(4)	100(6)	-21(3)	-53(4)	23(4)
C28	82(5)	33(3)	87(5)	0(3)	-10(4)	8(3)
C29	70(4)	44(3)	63(4)	10(3)	-10(3)	-7(3)
C30	91(5)	34(3)	88(5)	2(3)	-31(4)	-8(3)
C31	61(4)	74(5)	64(4)	-29(3)	1(3)	13(3)
S1	67.1(11)	81.7(13)	80.5(13)	3.5(9)	-7.5(9)	10.4(10)

Table 4 Bond Lengths for Mn01121P_0ma.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C10	1.366(7)	C12	C1	1.614(6)
O3	C23	1.382(7)	C13	C25	1.418(9)
C4	C7	1.428(7)	C13	C30	1.314(11)
C4	C14	1.415(7)	C14	C20	1.353(8)
C4	C15	1.437(7)	C15	C19	1.442(9)
C5	C7	1.514(6)	C15	C26	1.402(9)
C5	C8	1.502(7)	C16	C18	1.380(8)
C5	C11	1.505(7)	C16	C27	1.381(11)
C6	C11	1.433(7)	C17	C29	1.362(8)
C6	C17	1.400(8)	C18	S1	1.678(6)
C6	C25	1.422(7)	C20	C28	1.393(9)
C7	C10	1.386(7)	C21	C23	1.376(8)
C8	S1	1.684(5)	C21	C31	1.382(9)
C8	C1	1.645(6)	C22	C24	1.317(10)
C9	C10	1.420(8)	C22	C27	1.388(11)
C9	C19	1.316(9)	C25	C31	1.434(9)
C11	C23	1.411(7)	C26	C28	1.313(9)
C12	C18	1.394(8)	C29	C30	1.427(9)
C12	C24	1.383(9)			

Table 5: Bond Angles for Mn01121P_0ma.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C23	O3	C10	118.6(4)	C19	C15	C4	117.3(5)
C14	C4	C7	123.6(4)	C26	C15	C4	118.5(5)

C15	C4	C7	119.5(5)	C26	C15	C19	124.0(5)
C15	C4	C14	116.9(5)	C27	C16	C18	118.4(7)
C8	C5	C7	109.7(4)	C29	C17	C6	122.1(5)
C11	C5	C7	111.1(4)	C16	C18	C12	119.7(6)
C11	C5	C8	110.6(4)	S1	C18	C12	115.4(4)
C17	C6	C11	122.2(4)	S1	C18	C16	124.8(5)
C25	C6	C11	120.2(5)	C15	C19	C9	122.9(5)
C25	C6	C17	117.5(5)	C28	C20	C14	121.2(6)
C5	C7	C4	121.1(4)	C31	C21	C23	118.9(5)
C10	C7	C4	118.8(4)	C27	C22	C24	120.8(7)
C10	C7	C5	120.0(4)	C11	C23	O3	121.9(5)
S1	C8	C5	120.8(4)	C21	C23	O3	113.9(5)
C1	C8	C5	119.6(3)	C21	C23	C11	124.2(6)
C1	C8	S1	119.4(3)	C22	C24	C12	120.4(7)
C19	C9	C10	119.8(5)	C13	C25	C6	118.6(6)
C7	C10	O3	123.4(5)	C31	C25	C6	118.9(6)
C9	C10	O3	115.0(5)	C31	C25	C13	122.5(6)
C9	C10	C7	121.7(5)	C28	C26	C15	122.6(5)
C6	C11	C5	123.0(4)	C22	C27	C16	120.7(6)
C23	C11	C5	120.1(5)	C26	C28	C20	119.8(6)
C23	C11	C6	116.8(5)	C30	C29	C17	119.5(6)
C24	C12	C18	119.9(6)	C29	C30	C13	119.5(6)
C1	C12	C18	118.0(5)	C25	C31	C21	121.0(5)
C1	C12	C24	122.1(5)	C18	S1	C8	92.6(3)
C30	C13	C25	122.7(6)	C12	C1	C8	94.4(3)
C20	C14	C4	120.8(5)				

Table 6: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Mn01121P_0ma.

Atom	*x*	*y*	*z*	U(eq)
H5	-6959(3)	-4601(3)	248(6)	45.1(14)
H9	-4114(4)	-6227(4)	-1908(7)	70.1(19)
H13	-5204(5)	-1488(4)	-118(9)	83(2)
H14	-7865(4)	-5638(3)	396(7)	58.8(17)
H16	-10079(4)	-4145(3)	-3786(9)	71(2)
H17	-7426(4)	-3406(3)	525(7)	54.8(15)
H19	-4893(5)	-7303(4)	-1307(8)	69.1(19)

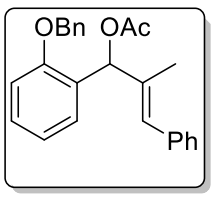
H20	-8597(5)	-6757(4)	1043(9)	79(2)
H21	-3667(4)	-3694(4)	-1908(8)	65.2(17)
H22	-8978(5)	-4545(4)	-8137(8)	84(2)
H24	-7542(5)	-4749(4)	-7074(8)	77(2)
H26	-6368(5)	-7970(3)	-262(9)	74(2)
H27	-10264(6)	-4261(4)	-6531(10)	92(3)
H28	-7798(5)	-7919(4)	868(9)	81(2)
H29	-7771(5)	-2173(3)	1248(8)	71(2)
H30	-6598(5)	-1208(3)	1002(10)	85(2)
H31	-4036(5)	-2441(4)	-1223(8)	80(2)

Experimental

Single crystals of $C_{29}H_{17}OS$ [Mn01121P_0ma] were []. A suitable crystal was selected and [] on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2 [1], the structure was solved with the Unknown [2] structure solution program using Unknown and refined with the Unknown [3] refinement package using Unknown minimisation.

Crystal structure determination of [Mn01121P_0ma]

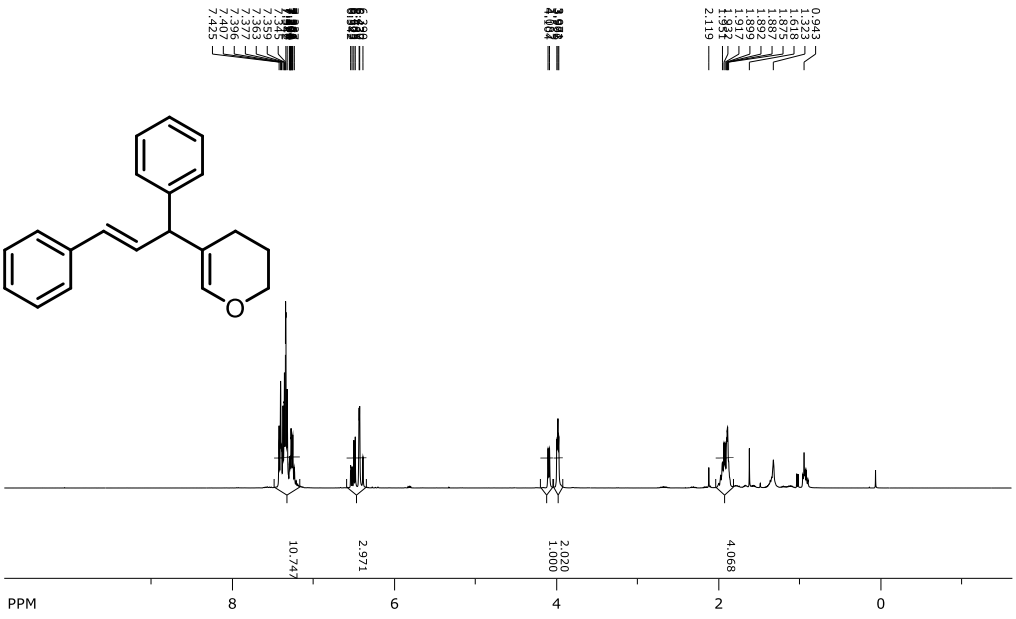
Crystal Data for $C_{29}H_{17}OS$ (M =413.52 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), a = 14.080(2) Å, b = 17.400(3) Å, c = 8.3603(15) Å, V = 2048.2(6) $Å^3$, Z = 4, T = 296.15 K, μ(Mo Kα) = 0.177 mm^{-1}, *Dcalc* = 1.3409 g/cm^3, 15555 reflections measured ($3.72° \leq 2\Theta \leq 50.1°$), 3609 unique ($R_{int}$ = 0.0311, R_{sigma} = 0.0283) which were used in all calculations. The final R_1 was 0.0868 (I>=2u(I)) and wR_2 was 0.2694 (all data).



(*E*)-1-(2-(benzyloxy)phenyl)-2-methyl-3-phenylallyl acetate

This compound was isolated as white solid. Following the general procedure, 30 mg of **xx** afforded 37.6 mg of **xx** (80% yield.) R_f= 0.6 (EtOAc/Hexane = 1/20). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 1738, 1490, 1452, 1231, 1017, 752, 697. **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.48 -7.24 (m, 12H), 7.04 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.84 (s, 1H), 6.62 (s, 1H), 5.12 (s, 2H), 2.18 (s, 3H), 1.87 (s, 3H) **^{13}C NMR** (100 MHz, $CDCl_3$): δ169.7, 155.9, 137.4, 136.9, 135.2, 129.08 (2C), 129.00, 128.5 (2C), 128.0 (2C), 127.8, 127.6, 127.5, 127.4, 127.3 (2C), 126.5, 120.7, 111.9, 74.5, 70.1, 21.3, 14.6 **HRMS (ESI):***m/z*calcdfor $C_{23}H_{21}O$:$(M–OAc)^+$: 313.1592 Found: 313.1579.

NMR spectra: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6
4
2
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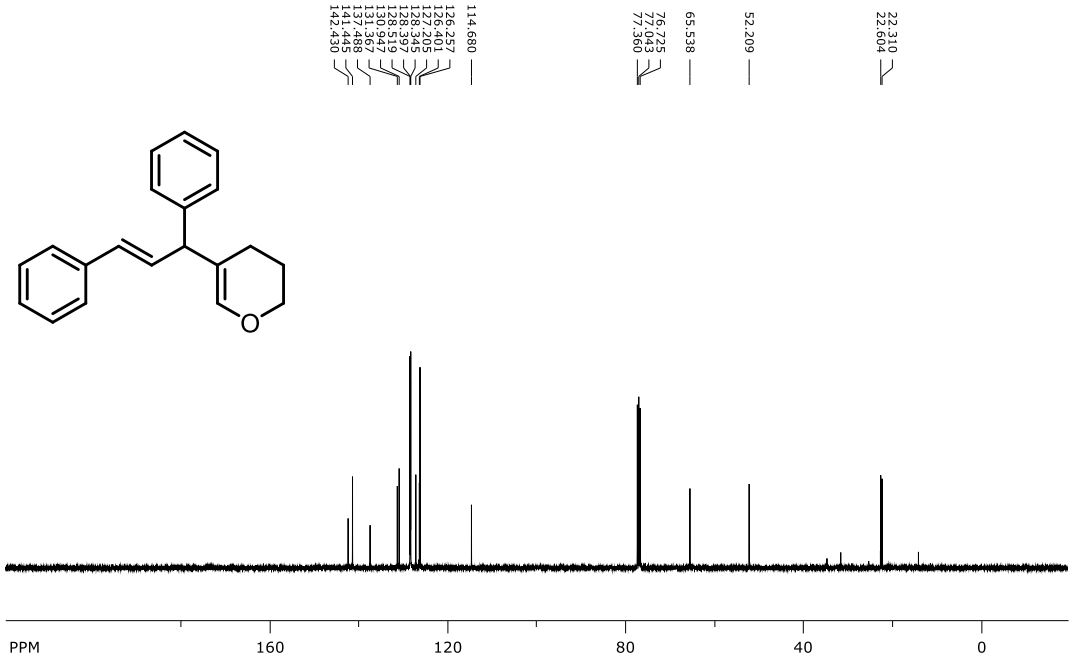
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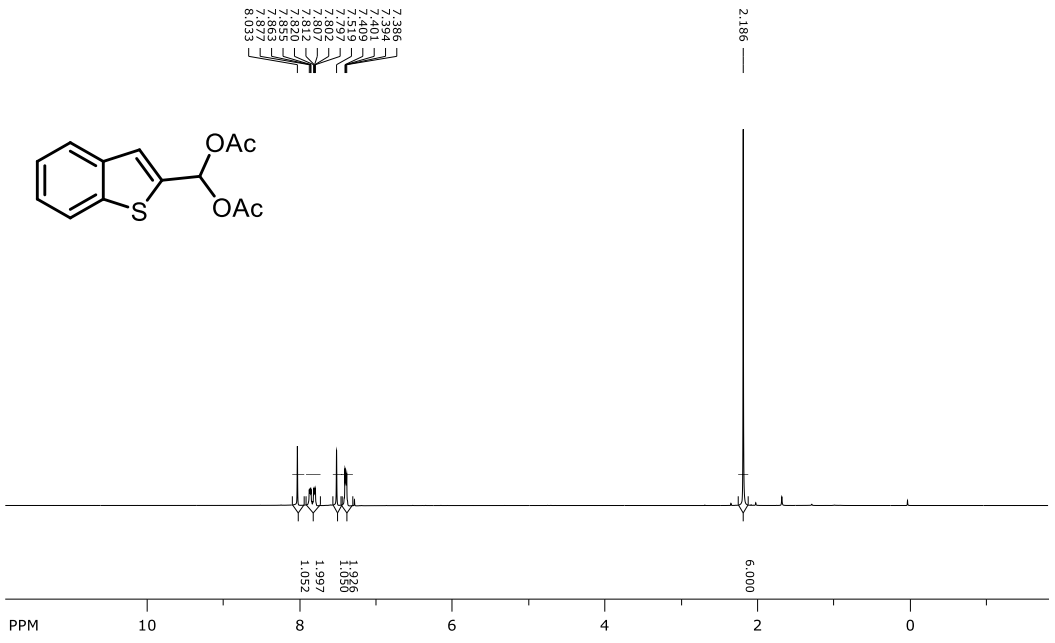
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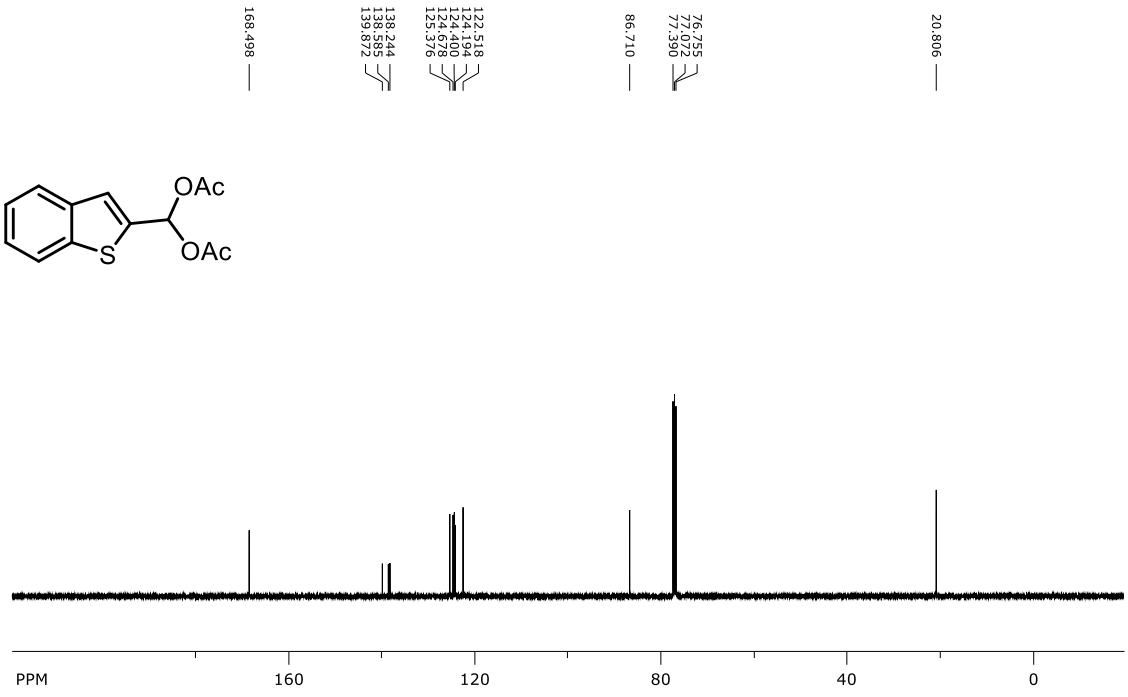
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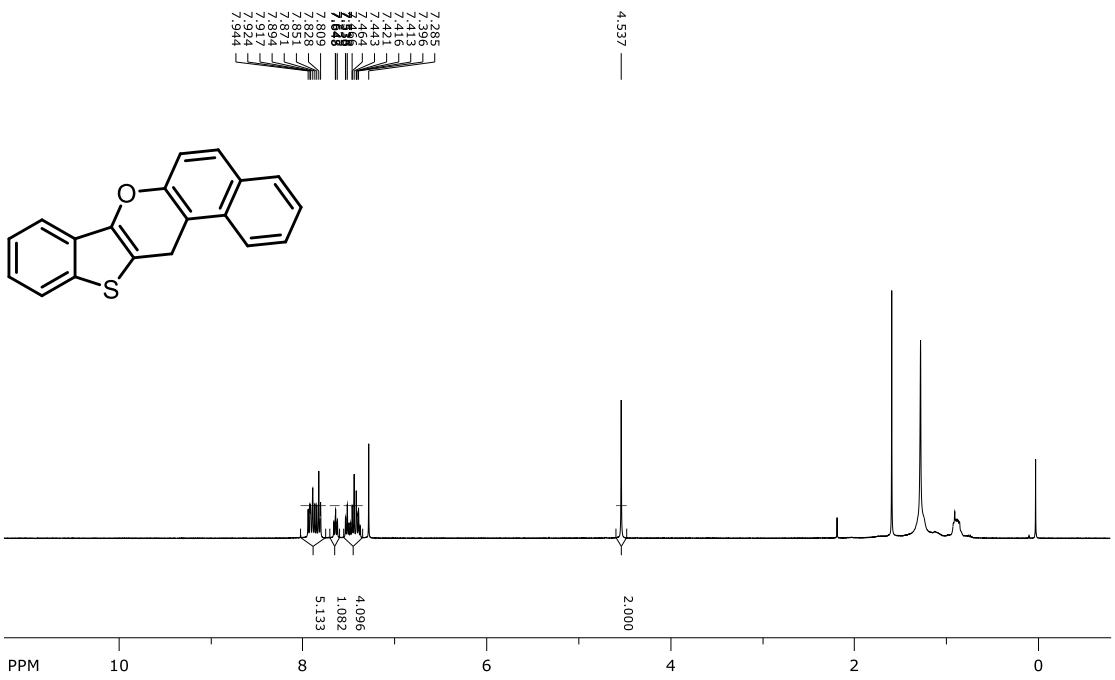
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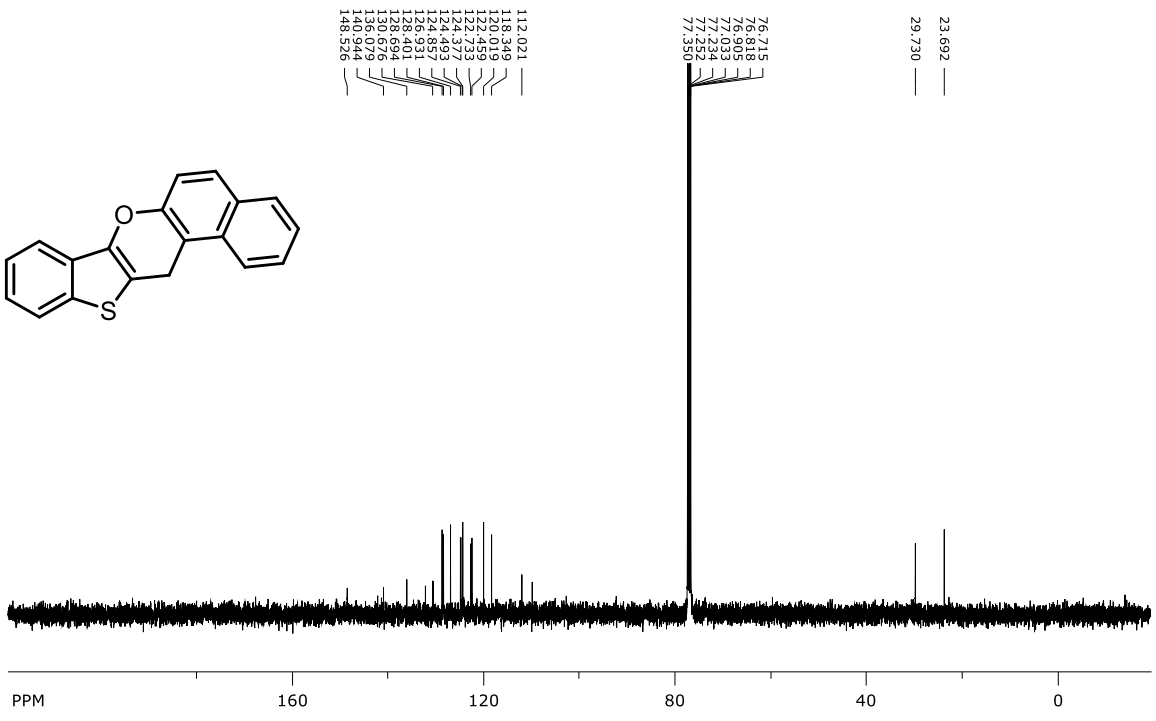
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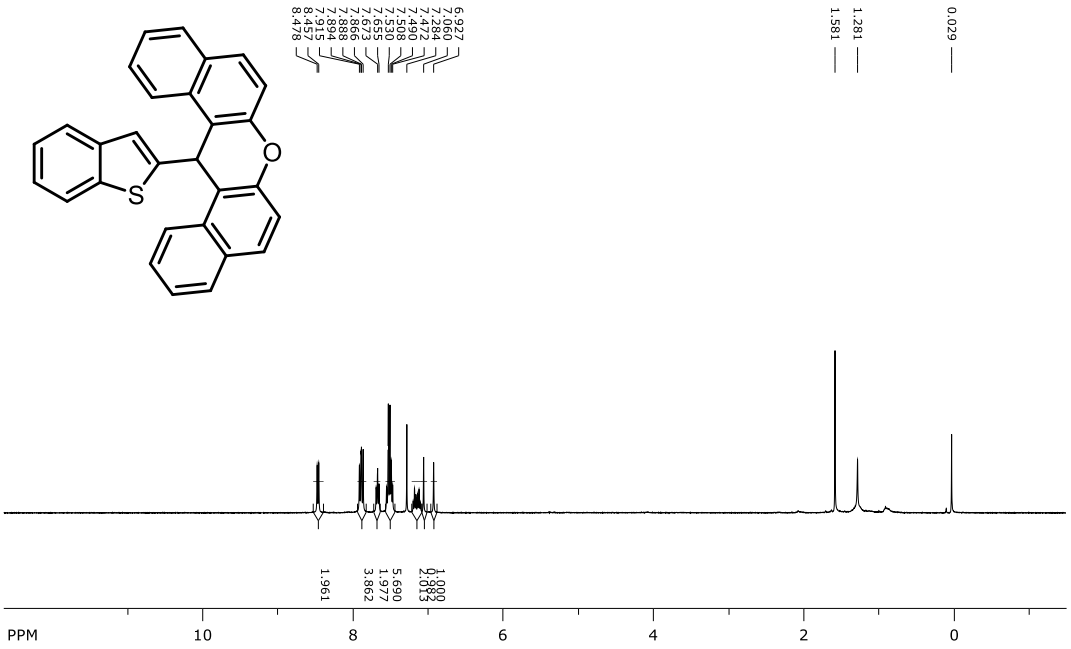
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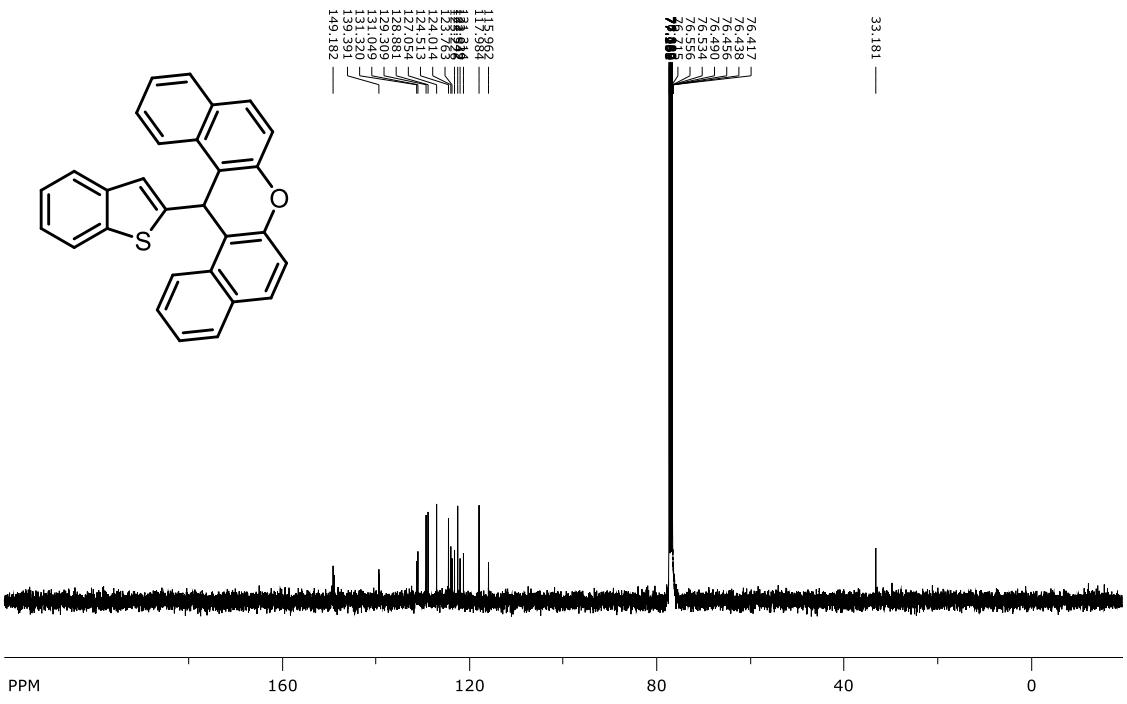
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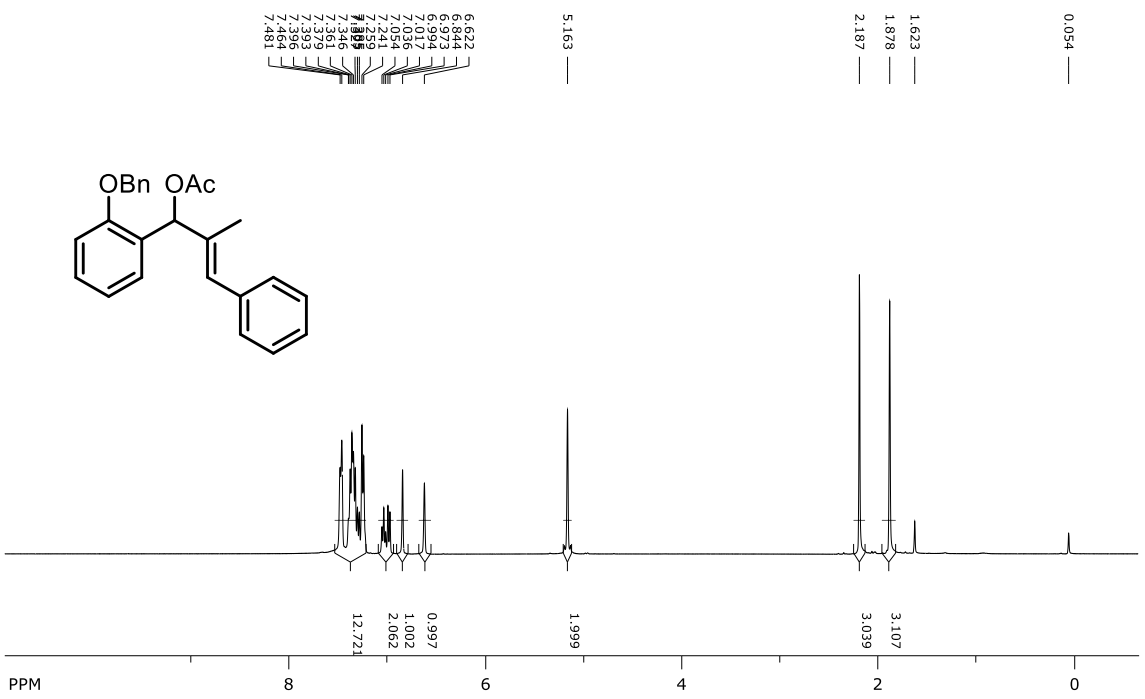
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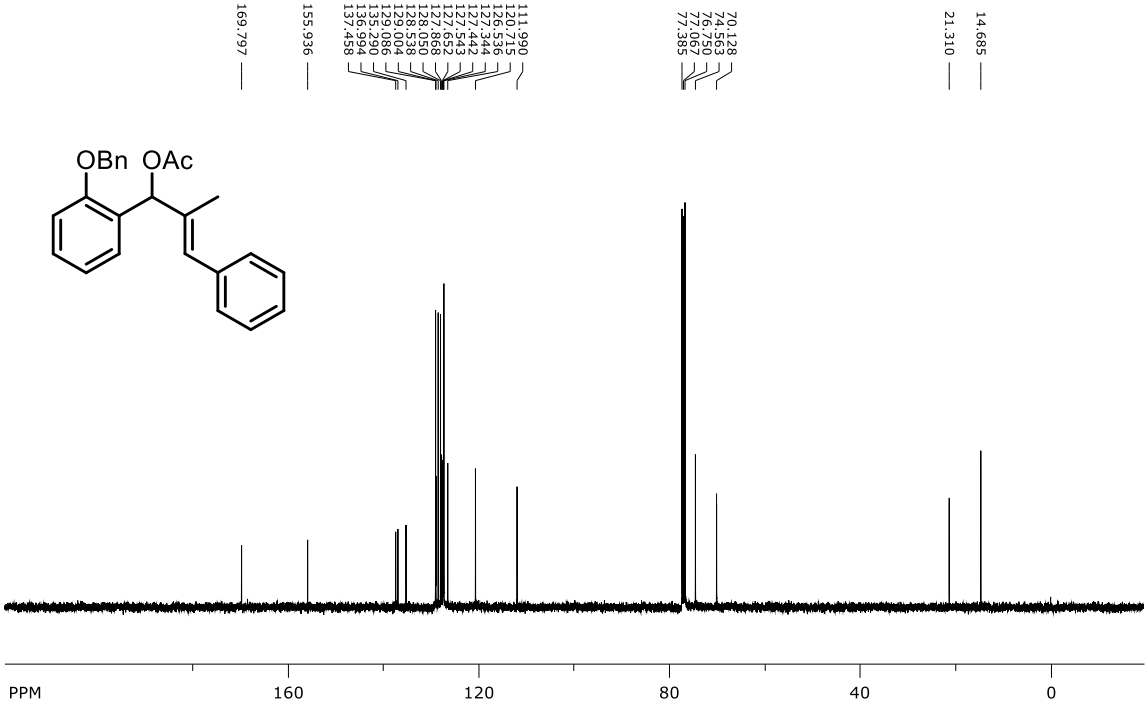
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Bibilography:

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