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DIPLOMARBEIT

Investigating the asymmetric Claisen-Cope rearrangement

ausgeführt am

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Datum

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I'm an early bird and I'm a night owl so I am wise and I have worms.

-Michael Scott

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Abstract

Since its discovery more than a century ago, the Claisen rearrangement has become a valuable tool in organic synthesis for carbon-carbon bond formation. Therefore, an asymmetric version of this [3,3]-sigmatropic rearrangement that is enantioselective during bond formation is of great interest. Although the catalytic asymmetric aromatic *ortho*-Claisen rearrangement has been successfully reported, the *para*-rearrangement has been largely neglected and underdeveloped. This study focuses on the optimization of the asymmetric aromatic Claisen-Cope rearrangement of chiral allyl-aryl ethers.

In the course of this work, we were able to find a working protocol using a Europium(III) catalyst. A series of 2,6-disubstituted allyl-aryl ethers with different functionalities was investigated. The rearrangement of these substrates consistently showed exceptional chirality transfer and excellent yields. In addition, the rearrangement of a monosubstituted allyl-aryl ether gave promising results, providing a good basis for further investigation of the Claisen-Cope rearrangement and its application to a wider range of chiral substrates.

In addition, by optimizing the preparation of the chiral allyl-aryl ethers, it was found that the carbonate has an influence on the enantiomeric excess, improving not only our results but also literature precedents. A variety of 2,6-disubstituted allyl-aryl ethers was prepared, achieving up to 99% *ee*.

Furthermore, studies were performed to gain a deeper understanding of this reaction. A crossover experiment was performed to investigate the intramolecularity of the rearrangement. In addition, the stereochemistry of the starting materials and products was determined to find evidence for the Claisen-Cope mechanism.

Deutsche Kurzfassung

Die Claisen-Umlagerung ist seit ihrer Entdeckung vor mehr als einem Jahrhundert eine wertvolle Methode in der organischen Synthese für die Bildung von Kohlenstoff-Kohlenstoff-Bindungen geworden. Daher ist eine asymmetrische Version dieser [3,3]-sigmatropen Umlagerung, welche während der Bindungsbildung enantioselektiv verläuft, von großem Interesse. Obwohl über die katalytische asymmetrische aromatische *ortho*-Claisen-Umlagerung bereits erfolgreich berichtet wurde, wurde die Umlagerung in die *para*-Position weitgehend vernachlässigt. Diese Arbeit konzentriert sich auf die Optimierung der asymmetrischen aromatischen Claisen-Cope-Umlagerung von chiralen Allyl-Aryl-Ethern.

Im Zuge dieser Arbeit gelang es uns, ein neues Protokoll, unter Verwendung eines Europium(III)-Katalysators, zu entwickeln. Eine Reihe von 2,6-disubstituierten Allyl-Aryl-Ethern mit verschiedenen Funktionalitäten wurde untersucht. Die Umlagerung dieser Substrate zeigte durchweg ausgezeichneten Chiralitätstransfer und sehr gute Ausbeuten. Darüber hinaus lieferte die Umlagerung eines monosubstituierten Allyl-Aryl-Ethers vielversprechende Ergebnisse und damit eine Grundlage für weitere Untersuchungen der Claisen-Cope-Umlagerung und deren Anwendung auf ein breiteres Spektrum chiraler Substrate.

Zusätzlich wurde bei der Optimierung der Herstellung der chiralen Allyl-Aryl-Ether festgestellt, dass das Carbonat einen Einfluss auf den enantiomeren Überschuss ausübt, was nicht nur zur Verbesserung unserer Ergebnisse, sondern auch der von literaturbekannten Beispielen führte. Es wurde eine Vielzahl von 2,6-disubstituierten Allyl-Aryl-Ethern hergestellt, wobei bis zu 99% *ee* erzielt wurde.

Darüber hinaus wurden Experimente durchgeführt, um ein tieferes Verständnis dieser Reaktion zu erlangen. Ein Crossover-Experiment wurde durchgeführt, um die Intramolekularität der Umlagerung zu untersuchen. Zusätzlich wurde die Stereochemie der Ausgangsmaterialien und Produkte bestimmt, um Beweise für den Claisen-Cope-Mechanismus zu finden.

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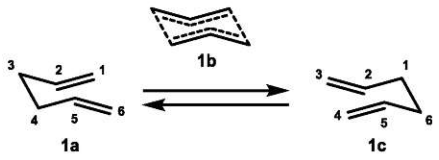
Introduction

[3,3]-Sigmatropic rearrangements

All organic reactions can be categorized into three groups of reactions: ionic, radical and pericyclic reactions. While ionic reactions include the movement of electron pairs in one direction, radical reactions involve the movement of single electrons. Pericyclic reactions distinguish themselves by having cyclic transition states where all bond-forming and bond-breaking happens concertedly and no intermediate is formed.[1]

Pericyclic reactions can be further categorized into four classes: *cycloadditions*, *electrocyclic reactions*, *group transfer reactions* and *sigmatropic rearrangements*. Sigmatropic rearrangements are characterized by a concerted pericyclic *intramolecular* bond-reorganization process. The transition state features a cyclic array of continuously bonded atoms, leading to predictable products in terms of connectivity and configuration. They formally involve the movement of a σ-bond from one position to another, while the conjugated system moves to accommodate the new bond. The filling of the vacancy left behind, results in the overall number of σ- and -bonds remaining the same. Through this bond reorganization process **1a** can be transformed to **1c** *via* a cyclic transition state **1b** (Scheme 1). Sigmatropic rearrangements are named based on the number of atoms each end of the bond shifts along the carbon chain. In a [3,3]-sigmatropic rearrangement, the single bond effectively moves three atoms along one carbon chain and three atoms along the other.[1,2]



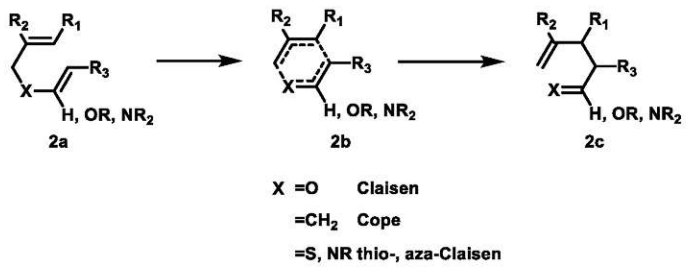
Scheme 1 General mechanism [3,3] sigmatropic rearrangement.

One sigmatropic reaction, which has proven to be among the most useful, is the Claisen rearrangement (Scheme 2). In 1912, Ludwig Claisen was the first to observe the thermally induced rearrangement of allyl-vinyl and allyl-aryl ethers to their corresponding C-homoallyl isomers upon sufficient heating, describing it as the "thermal isomerization of an allyl-vinyl ether to give a

bifunctionalized molecule", meaning that a carbonyl group and a new olefine moiety were formed in the process.[3,4]

In 1940, Cope *et al.* reported the-all carbon equivalent (X=CH_2, Scheme 2). Both transformations are the most common examples of [3,3]-sigmatropic rearrangements, and have proven to be useful methods due to their chemo-, regio-, diastereo- and enantioselective properties not only for the formation of carbon-carbon bonds, but are also established protocols for the generation of defined stereogenic centres.[5]

The Claisen rearrangement can also occur for other allyl-vinyl substrates, such as thioethers or amines.[4] All these rearrangements start with the respective starting compound **2a** and then, featuring a cyclic transition state **2b**, produce the rearranged product **2c**.

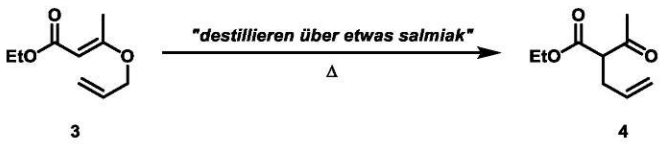


Scheme 2 Claisen rearrangement and analogues.

Because of its synthetic utility, several generations of chemists have been trying to find the most suitable experimental conditions to enhance the scope, selectivity and yield to afford potentially useful polyfunctionalized products.[6]

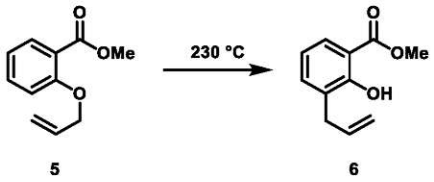
The Beginnings...

In 1912 Claisen reported the first examples of aliphatic and aromatic [3,3]-sigmatropic rearrangements, undoubtedly revealing a new and powerful tool for carbon-carbon bond formation, which is still of great significance to this day. The *O*-allylated derivative of acetoacetic ester **3** was observed to undergo a rearrangement to its corresponding C-isomer **4** upon distillation in the presence of ammonium chloride (Scheme 3).[3]



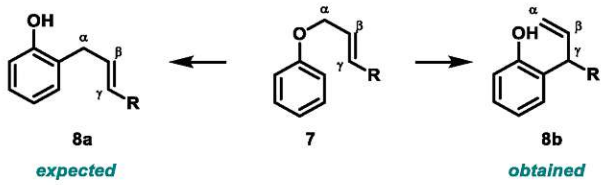
*Scheme 3 Rearrangement of **3**.*

In this seminal work, the transformation of *O*-allylphenol **5** by heating it to 230 °C to the corresponding *ortho*-rearranged product **6** was described, representing the first example for the aromatic Claisen rearrangement (Scheme 4).[3]



*Scheme 4 Rearrangement of **5**.*

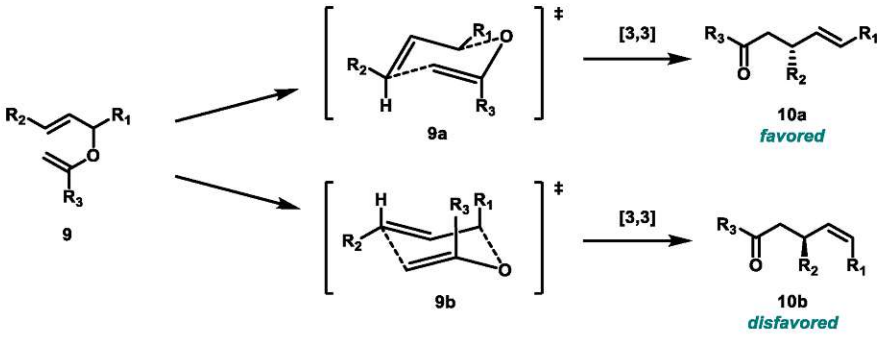
Claisen and Tietze established the regioselective properties of the Claisen rearrangement by proving that the carbon atom attaching to the aromatic system is the one in the γ-position of the allyl group, rather than the expected α-carbon. During the course of this transformation, the double bond is reorganized from the β,γ- to the α,β-position. Cinnamyl phenyl ether **7**, along with other allyl-phenyl ether derivatives, was found to rearrange to the branched allyl phenol **8b**, rather than the linear phenol **8a**, exhibiting an 'inversion' for the allyl group (Scheme 5). This is in accordance with the now established consensus of the Claisen and the Cope rearrangement belonging to the group of [3,3]-sigmatropic rearrangements.[7,8]



Scheme 5 Demonstration of regioselectivity.

In regard of acyclic systems, they tend to adopt a chair-like transition state, whereas cyclic systems are proposed to proceed *via* boat-like transition states. These highly ordered transition states facilitate a high degree of stereocontrol in the Claisen rearrangements by allowing efficient transfer of stereochemical information to the products. Starting from racemic starting materials **9**, different

outcomes are possible (Scheme 6). Through minimizing unfavorable 1,3-diaxial interactions, certain isomers are preferentially formed over others, for example transition state **9a** being favored over **9b**. The reaction therefore delivers **10a** as the major and **10b** as the minor product.[9,10]



Scheme 6 Transition states of the Claisen rearrangement.

Having established the chemo-, regio-, diastereo-, and enantioselective properties of the Claisen reaction, its synthetic potential becomes evident. As the rearrangement under thermal conditions requires high temperatures, a catalytic variant to enable milder reaction conditions has been subject of extensive interest. Milder conditions might omit undesired side product formation and/or decomposition of starting materials and products. Numerous Lewis and Brønsted acids, bases, and transition metal complexes have been investigated to show their catalytic effect on the rearrangement, Claisen himself being the first example.[6,11]

The ability to introduce two new functionalities, a carbonyl group and an olefine, makes it a valuable tool in organic synthesis. These functional groups are typically useful for subsequent chemical transformations, such as carbon chain elongation. As a result, the Claisen rearrangement is frequently employed in the synthesis of natural products, particularly for forming essential carbon-carbon bonds and building the carbon framework. Given its importance to synthetic chemistry, numerous enhancements and variations of the Claisen rearrangement have been developed. [4–6,12,13]

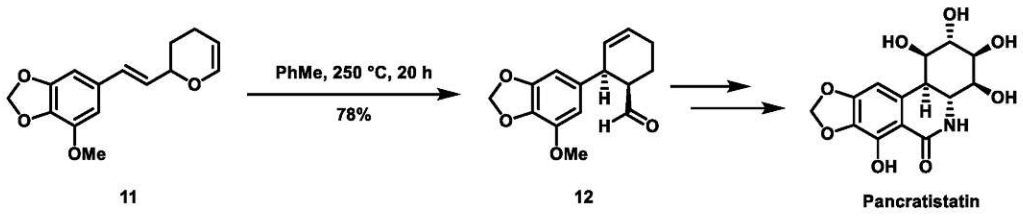
Selected examples and their application will be briefly discussed to demonstrate the value of these rearrangement reactions for the scientific community.

The Claisen rearrangement & selected variants: Applications in total synthesis and medicinal chemistry

Aliphatic Claisen rearrangement

Many natural products have been synthesized by applying the Claisen rearrangement or variants of it as a key step in the total synthesis.

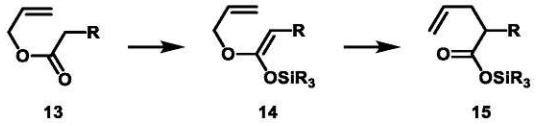
Pancratistatin, an alkaloid exhibiting antitumor activity, has been synthesized by Kim *et al.* from readily available staring materials, including an aliphatic Claisen rearrangement as key step. Cyclic ether **11** rearranged under thermal conditions giving the *cis*-disubstituted cyclohexene **12** as single isomer (Scheme 7). The rearrangement is proposed to proceed *via* a boatlike transition state, as the starting material is of cyclic nature. Going forward, this compound was converted to the natural product in several steps.[14]



Scheme 7 Claisen rearrangement in the synthesis of Pancratistatin.

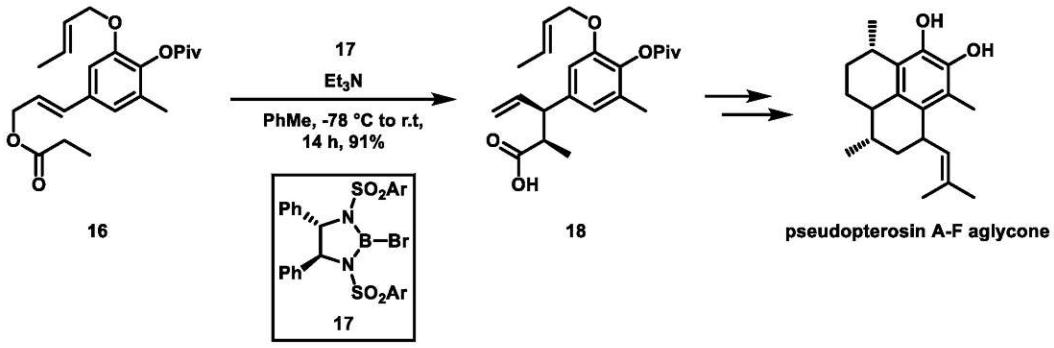
Ireland-Claisen rearrangement

The Ireland-Claisen rearrangement involves a [3,3]-sigmatropic shift of an allylic silyl ketene acetal. An acylated allylic alcohol **13** is deprotonated by a base, forming an enolate which is trapped by a silylating reagent, affording the *O*-allyl-*O*-silylketeneacetal **14** (Scheme 8). Upon heating, compound **14** undergoes rearrangement, furnishing a γ,δ-unsaturated silylester **15**. This silyl ester is typically converted into a carboxylic acid or a methyl ester in subsequent steps.[13]



Scheme 8 General mechanism of the Ireland-Claisen rearrangement.

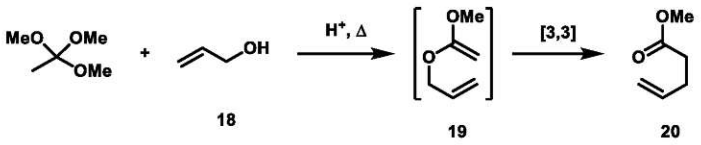
Cooksey *et al.* applied a modified Ireland-Claisen rearrangement in the total synthesis of the marine metabolite pseudopterosin A–F aglycone. Treatment of the precursor **16** with triethylamine and chiral Lewis acid **17** and subsequent aqueous work up produced the desired carboxylic acid **18** enantioselectively. This material was further elaborated to pseudopterosin A-F aglycone over several steps (Scheme 9).[15]



Scheme 9 Modified Ireland-Claisen in the synthesis of pseudopterosin A–F.

Johnson-Claisen rearrangement

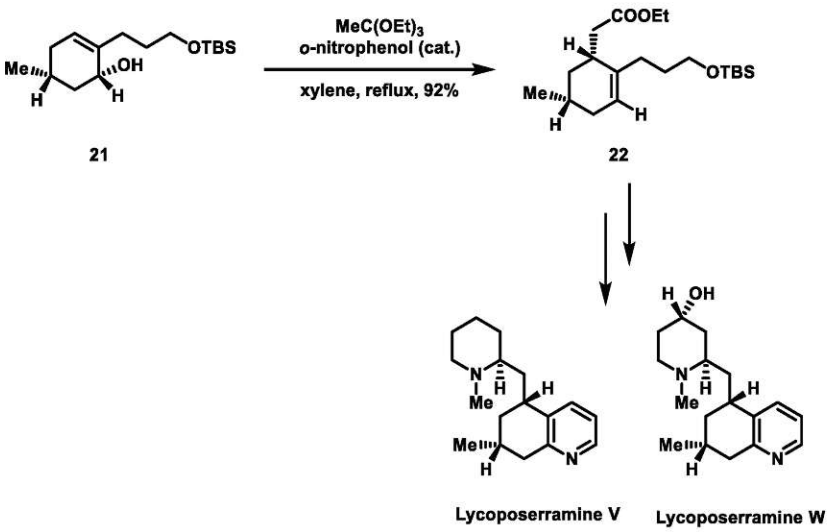
The Johnson-Claisen rearrangement is also a derivative of the aliphatic Claisen rearrangement. Here a ketene acetal is generated through the condensation of trimethyl orthoacetate with allylic alcohol **18**, leading to the formation of a mixed orthoester **19** (Scheme 10). The subsequent rearrangement of the ketene intermediate results in the formation of the γ,δ-unsaturated ester **20**.[13,16]



Scheme 10 General mechanism of the Johnson-Claisen rearrangement.

The rearrangement found its application in the total synthesis of Lycoposerramines-V and -W, phlegmarine-type alkaloids, exhibiting biological activities, reported by Takayama *et al.* The Johnson-Claisen rearrangement of precursor **21**, using triethyl orthoacetate and catalytic amounts of *o*-nitrophenol, afforded the γ,δ-unsaturated ester **22** stereoselectively (Scheme 11).

Compound **22** could be converted to the natural products Lycoposerramines-V and -W in a few steps.[16,17]

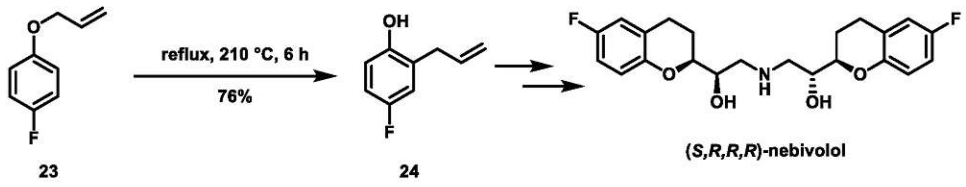


Scheme 11 Johnson-Claisen rearrangement in the synthesis of Lycoposerramines-V and -W.

Aromatic Claisen rearrangement

The aromatic Claisen rearrangement is a crucial tool in the synthesis of natural products as well. Its value lies in its ability to produce both *ortho*- and *para*-substituted products, as will be elaborated in the following chapter. These rearranged products can be easily functionalized further to furnish a variety of bioactive natural compounds, either in a single or through multiple steps. Due to its high regioselectivity at the *ortho*-position of the aromatic ring, this rearrangement is particularly effective in natural product synthesis.[16]

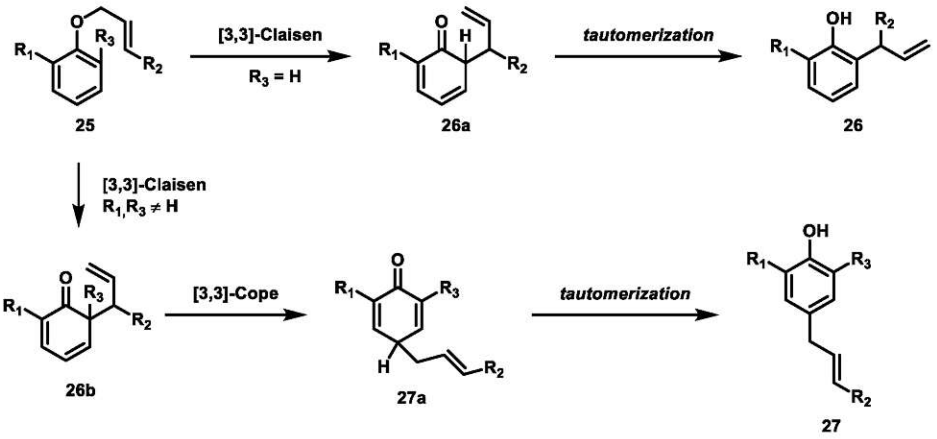
The aromatic Claisen rearrangement is one of the first steps in the synthesis by Chandrasekhar *et al.* of (*S,R,R,R*)-nebivolol, a β_1-adrenergic blocker with antihypertensive activity. Starting from commercially available *p*-fluorophenol, precursor **23** was obtained. Thermal rearrangement of this compound produced the *ortho*-Claisen product **24**, which subsequently could then be converted to the desired product (Scheme 12).[18]



Scheme 12 Aromatic Claisen rearrangement in the synthesis of (S,R,R,R)-nebivolol.

Claisen-Cope rearrangement

The aromatic Claisen rearrangement of allyl-aryl ether **25** (R_3=H) usually proceeds *via* intermediate **26a** which after tautomerization provides the *ortho*-allylated phenol **26** (Scheme 13). If both *ortho*-positions of **25** are occupied (R_1,R_3≠H), intermediate **26b** cannot tautomerize to re-establish aromaticity after the first rearrangement. Hence, a second rearrangement takes place, positioning the olefine moiety in the *para*-position. Upon tautomerization of intermediate **27a**, the *para*-alkylated phenol **27** is formed.



Scheme 13 Claisen vs. Claisen-Cope.

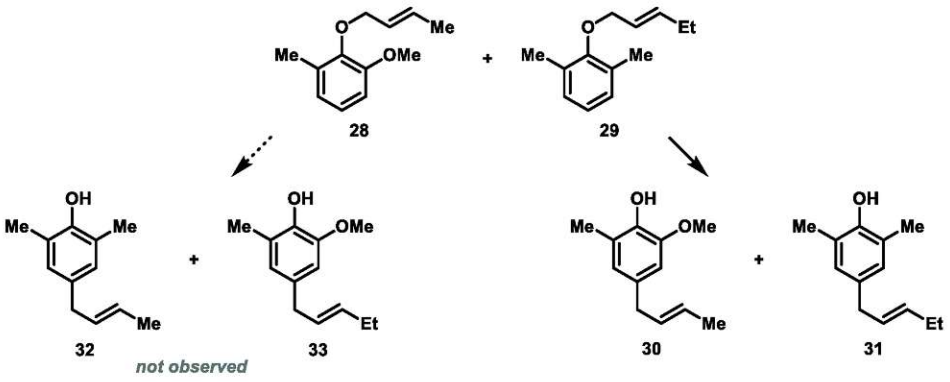
The *ortho*-Claisen rearrangement predominates in most cases, although the *para*-process can compete for some examples even when there are no substituents present in the *ortho*-position. If both *ortho*- and the *para*-positions are blocked complex decomposition follows.[4,7,11]

The rearrangement of systems in which both *ortho*- and *para*-positions are unoccupied has been shown to give mixed products due to the competitive nature of both possible reaction pathways. The ratio of *ortho*- to *para*-product depends on various factors, including the steric demand, number, and position of substituents on the ring, as well as the steric demand of substituents in the migrating

allyl moiety. Moreover, the polarity of the solvent can significantly impact the product ratio. More polar solvents facilitate the enolization of the initially formed *ortho*-dienone **26a**, resulting in a preference for the *ortho*-rearrangement. Conversely, less polar solvents impede this enolization step, making the *para*-position more competitive. Nevertheless, the *para*-product is predominantly a by-product, which is also the reason why the Claisen-Cope process has been largely disregarded as an undesired side reaction.[5]

The Claisen-Cope reaction on its own has largely been overlooked, it has been primarily studied within the framework of the Claisen rearrangement. The literature on this double [3,3]-reaction is scarce, focusing mainly on mechanistic studies, with relatively little research dedicated to optimizing reaction conditions compared to its *ortho*-counterpart.

Various groups conducted mechanistic studies to elucidate the underlying mechanism of the Claisen-Cope rearrangement. Rhodes and Crecelius performed cross over experiments to investigate whether the thermal rearrangement of a mixture of **28** and **29** would follow an inter- or an intramolecular pathway (Scheme 14).

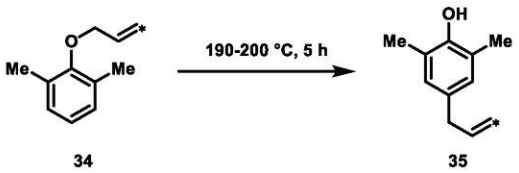


Scheme 14 Crossover experiments by Rhodes and Crecelius.

They chose this pair of substrates, as their reactivities were shown to be nearly the same, which made it a reasonable choice. The mixture of **28** and **29** was heated to reflux in DEA for three hours and the only products obtained were phenols **30** and **31**, respectively, both derived *via* an intramolecular reaction. Mixed products **32** and **33**, possibly obtained *via* an intermolecular reaction, were not observed. This observation allowed the authors to conclude that the thermal rearrangement of 2,6-disubstituted allyl-aryl ethers proceeds in an intramolecular fashion.[19]

Similarly, Ryan and O'Connor investigated the mechanistic aspects of the rearrangement, by Carbon-14 labelling experiments (Scheme 15, asterisk donates ^{14}C).

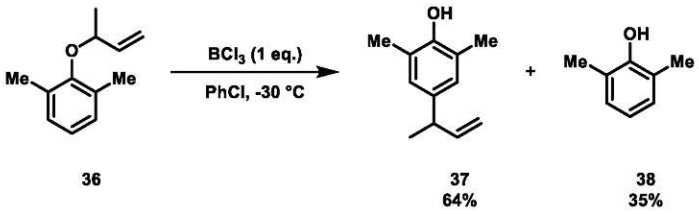
Thermal rearrangement of C-14 labelled **34** delivered *para*-allylated phenol **35** after five hours at 190-200 °C. Hereby, they could show that the *para*-rearrangement proceeds with no inversion of the allyl group.[20]



34 35

*Scheme 15 Mechanistic studies using C-14 labelled **34**.*

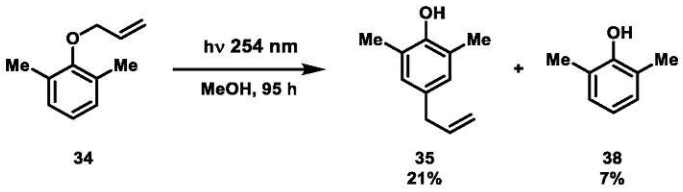
Borgulya *et al.* studied the BCl_3-induced rearrangement of a wide range of *ortho*-disubstituted allyl-aryl ethers. In this work, they achieved moderate to good yields for the *para*-Claisen-Cope rearrangement for most 2,6-disubstituted substrates. Exemplified by 2,6-dimethyl substrate **36**, the product **37** was obtained in 64% yield (Scheme 16). It is noteworthy, however, that they also observed significant formation of cleaved product **38**. This can be attributed to the strong Lewis acidic nature of the catalyst.[21]



36 37 64% 38 35%

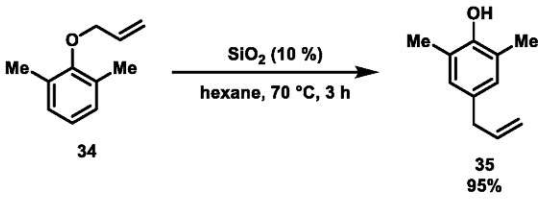
Scheme 16 Lewis acid mediated Claisen-Cope rearrangement.

Schmid *et al.* investigated the photochemically induced Claisen-Cope rearrangement of various allyl-aryl ethers. The most favorable results for the *para*-allylated product were achieved by irradiating compound **34** in methanol for 95 hours, affording the product **35** and phenol **38** (Scheme 17). Despite this, the reaction resulted in a mixture of products, with overall less-than-ideal outcomes.[22]



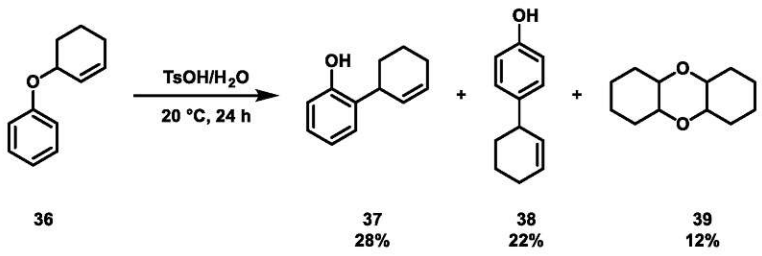
Scheme 17 Photochemical Claisen-Cope rearrangement.

A noteworthy improvement of the Claisen-Cope reaction, however, was made by Krimer *et al.*, who reported milder conditions for the rearrangement. They obtained the *para*-rearranged product **35** of 2,6-disubstituted allyl ether **34** in good yields after just 3.5 hours by depositing the starting material on silica gel and heating it to 70 °C (Scheme 18). Unfortunately, the reported examples are limited in both complexity and number.[23]



Scheme 18 Claisen-Cope rearrangement mediated by silica gel.

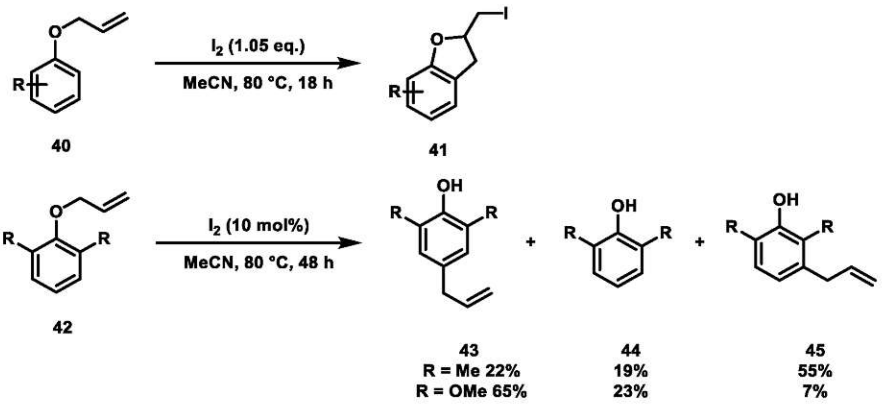
Novak *et al.* reported on the sigmatropic rearrangements of cycloalkenyl-aryl ethers, bearing differently sized cycloalkene residues on the oxygen. The rearrangement was performed under Brønsted mediated reaction conditions. Starting with representative **36**, a mixture of products, containing *ortho*-allyl phenol **37**, desired product **38** and sideproduct **39** was obtained (Scheme 19). The *para*-substituted phenol **38** was found to be the minor product. Additionally, decomposition of the cyclohexenyl-aryl ethers was observed under the strong acidic reaction conditions.[24]



*Scheme 19 Brønsted acid mediated Claisen-Cope rearrangement of **36**.*

The Breugst group explored the iodine-mediated one-pot Claisen rearrangement of compound **40** followed by iodocyclization. When treated with stoichiometric amounts of iodine, the Claisen

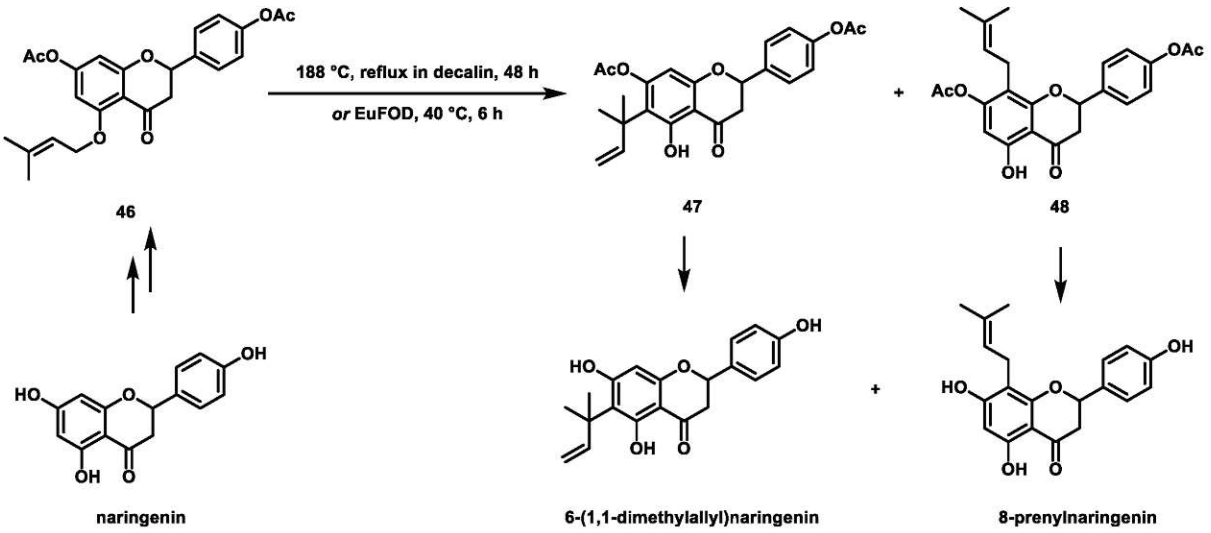
rearrangement occurred, and the resulting *ortho*-allylated product swiftly underwent iodocyclization, yielding compound **41** (Scheme 20). The group also sought evidence for the Claisen rearrangement through an iodine-catalyzed Claisen-Cope rearrangement. Conducting this reaction under catalytic conditions on the 2,6-disubstituted substrate **42** resulted in a mixture of products. Among these, phenol **43**, derived from the Claisen-Cope rearrangement, was obtained in poor to moderate yields and was accompanied by the formation of undesired side products **44** and **45**.[25]



Scheme 20 Iodine mediated Claisen-Cope rearrangement.

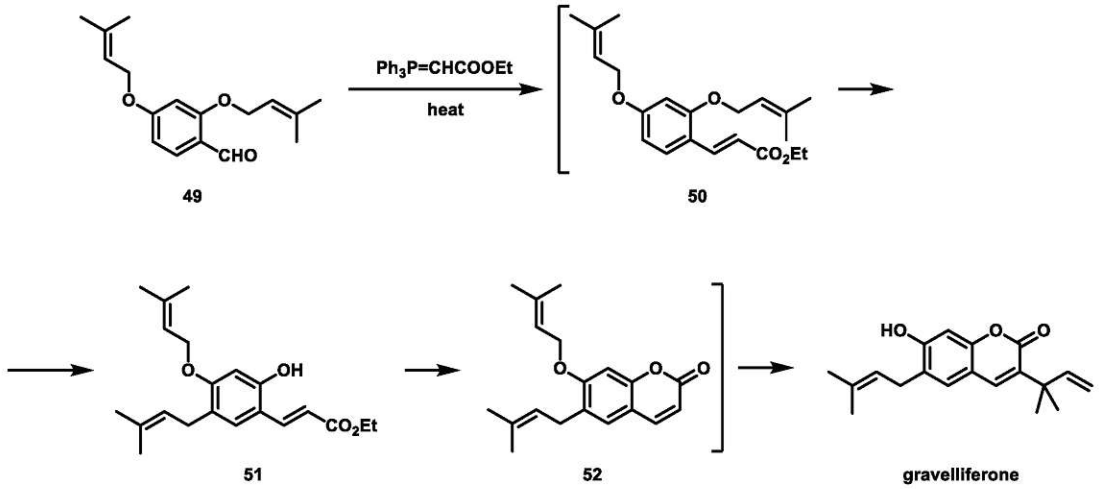
These examples illustrate that the exploration of the Claisen-Cope rearrangement, particularly in terms of catalysis, is still in its early stages. Most reported rearrangements have been conducted under harsh thermal conditions, requiring very high temperatures, harsh Lewis acidic or catalytic conditions that give only poor to moderate yields. The available literature on feasible reaction conditions remains limited, each possessing certain drawbacks. Nevertheless, there are examples of Claisen-Cope reactions used as key steps in total synthesis of natural products.

The Vollmer group reported the total synthesis of bioactive flavonoids, 8-prenylnaringenin and 6-(1,1-dimethylallyl)naringenin, starting from commercially available naringenin. While applying different sets of conditions on prenyl ether **46** for the Claisen-Cope rearrangement, a significant influence on the regioselectivity was observed. Performing the reaction under thermal conditions (188 °C, reflux in decalin, 48 h) gave the *para*-prenylated product in high selectivity (>20:1, **48:47**). In contrast, when using lanthanide catalysis (EuFOD, 40 °C, 6 h), the reaction resulted in lower regioselectivity (1.2:1, **48:47**) (Scheme 21).[26]



Scheme 21 Claisen-Cope rearrangement in the synthesis of flavanoids by Vollmer et al.

Tilve *et al.* reported an interesting one pot synthesis of naturally occurring coumarin gravelliferone. Coumarins are a group of natural products renowned for their wide range of bioactivities, including significant anti-cancer, -viral and -bacterial properties. Upon salt free Wittig conditions, aldehyde **49** was transformed into desired compound **50** in one step. It was hypothesized that the first Claisen-Cope rearrangement afforded **51**, which in turn forms the coumarine moiety **52**. Then a second Claisen-Cope rearrangement places the prenyl chain in the γ-position with respect to the α,β-unsaturated coumarine (C10 of the coumarin backbone). A third rearrangement positions the prenyl chain in the desired position, forming the natural product (Scheme 22).[27]



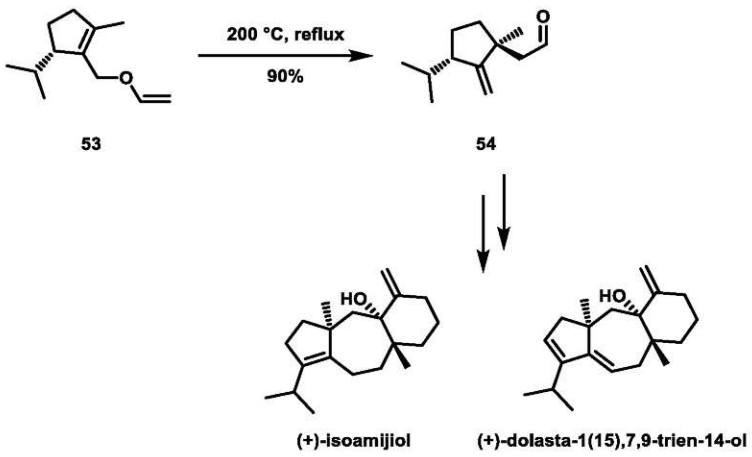
Scheme 22 Claisen-Cope rearrangement in the synthesis of gravelliferone.

State of the Art

Asymmetric Claisen rearrangement in total synthesis

The aliphatic Claisen rearrangement has become a crucial tool for stereoselective carbon-carbon bond formation. Numerous natural products have been synthesized using variants of this rearrangement as a key step to achieve both regio- and stereoselectivity.

Mehta *et al.* synthesized dolastane-type tricyclic marine natural products, (+)-isoamijiol and (+)-dolasta-1(15),7,9-trien-14-ol, utilizing the Claisen rearrangement as one of the essential steps. The precursor **53**, readily available from limonene, was stereospecifically rearranged under thermal conditions to **54**, from which the natural products could be afforded after multiple steps (Scheme 23).[28]



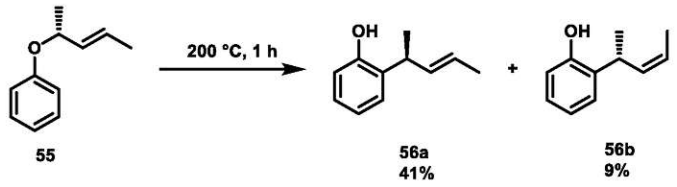
Scheme 23 Asymmetric Claisen rearrangement in the synthesis of marine natural products.

Asymmetric aromatic Claisen rearrangement

As the asymmetric aliphatic Claisen rearrangement was established to be a powerful tool in organic chemistry for the control of stereochemistry in carbon-carbon bond formation early on, the development of the aromatic equivalent was desirable. However, this was hindered by numerous issues, including selectivity of migration, abnormal Claisen rearrangements based on the

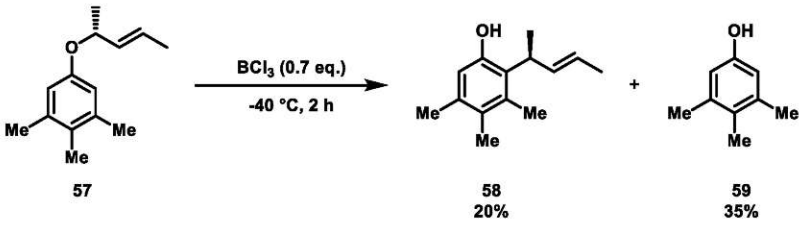
1,5 sigmatropic hydrogen shift, and the rearrangement *via* an allylic cation mechanism, which results in a loss of stereospecificity and regioselectivity.[5,12]

To this date, the number of reports of asymmetric *ortho*-Claisen rearrangements is relatively limited, with only a few accounts having been documented. One of the first examples reported is the rearrangement of neat **55** under thermal conditions to a mixture of **56a** and **56b**, however, enantiomeric excess of each product was not stated, only optical rotation being described (Scheme 24).[29]



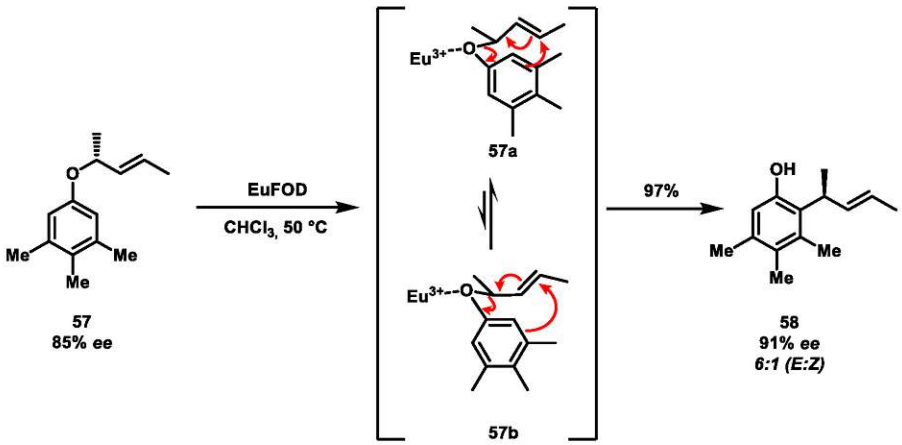
Scheme 24 Thermal asymmetric aromatic Claisen rearrangement.

Borgulya *et al.* observed chirality transfer in a BCl_3-catalyzed rearrangement of chiral starting material **57** to compound **58**, albeit significant cleavage to **59** (Scheme 25). These results are analogous to the rearrangement of **36** presented in Scheme 16. Again only optical rotation was reported.[11,21]



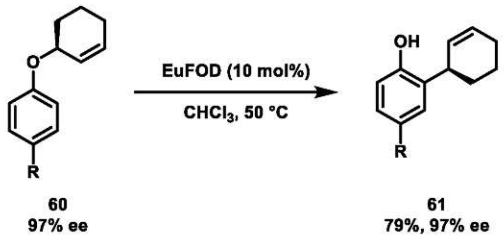
Scheme 25 Lewis acid mediated asymmetric aromatic Claisen rearrangement.

A significant breakthrough was achieved by Trost *et al.*, as they successfully transferred chirality intramolecularly from a *para*-substituted chiral allyl-aryl ether **57** to the corresponding *ortho*-substituted phenol **58** (Scheme 26). The Europium-catalyzed rearrangement proceeded under mild conditions, with good point-to-point chirality transfer. However, the formation of *(Z)*-**58** was observed, suggesting a small amount of isomerization. This is attributed to the equilibrium between the boat- (**57a**) and the chair-like (**57b**) conformation of the transition state.[12,30]



Scheme 26 Europium-catalyzed asymmetric aromatic Claisen rearrangement.

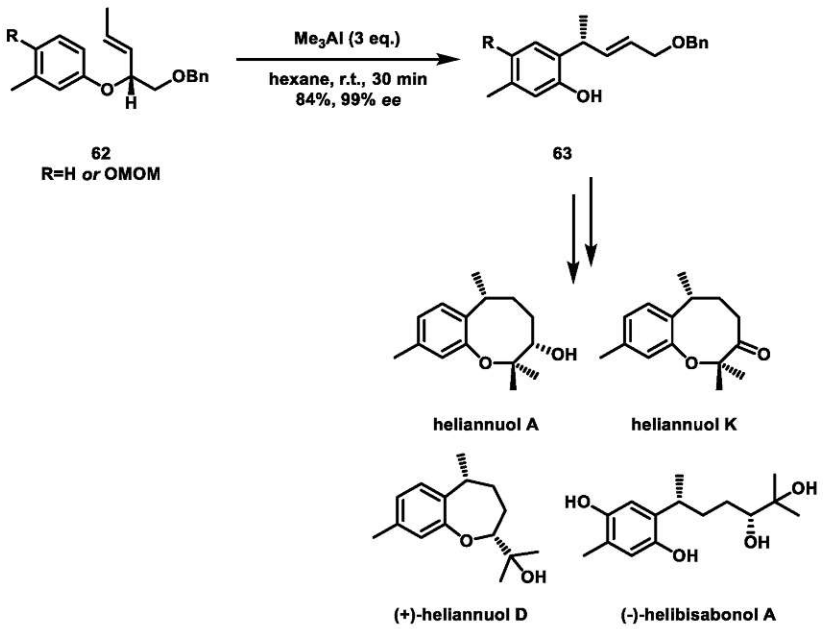
Trost and Toste also investigated the asymmetric *ortho*-Claisen rearrangement of cycloalkenyl-aryl ethers, bearing a *para*-substituent. This transformation proceeded again under mild conditions and with good point-to-point chirality transfer under EuFOD catalysis, starting with **60** and producing phenol **61** in good yield and excellent enantiomeric excess (Scheme 27).[30]



*Scheme 27 Europium-catalyzed asymmetric aromatic Claisen rearrangement of **60**.*

Other methods for enantioselective aromatic *ortho*-Claisen rearrangements have been reported since. However, these methods are limited in number and complexity, and further development remains one of the future objectives. Nevertheless, the asymmetric aromatic Claisen rearrangement found some applications in the total synthesis of natural products as well.

Shishido *et al.* reported the total synthesis of heliannuol A, K, D and helibisabonol A using Lewis acid mediated aromatic Claisen rearrangement as one of the first steps. Starting from readily available chiral ether **62**, the desired asymmetric rearrangement was realized by treatment with Me_3Al in hexane at ambient temperature. Compound **63** was obtained in high yield and excellent enantiomeric purity. This advanced intermediate was further elaborated to the four respective natural products (Scheme 28).[31,32]

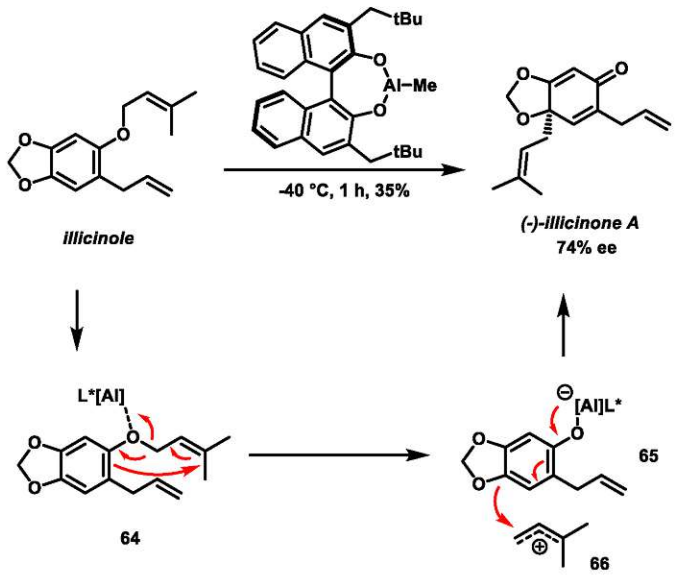


Scheme 28 Asymmetric aromatic Claisen rearrangement in the synthesis of heliannuols A, K, D and helibisabonol A.

Asymmetric *para*-alkylation

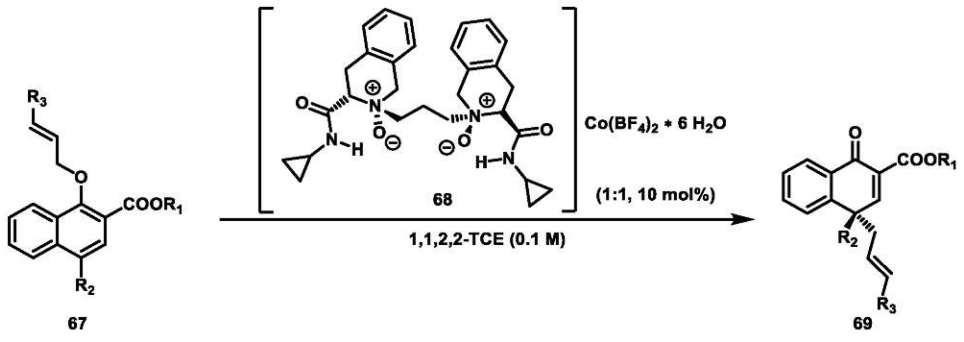
The development of the asymmetric *para*-Claisen-Cope rearrangement has been utterly neglected, the *para*-rearrangement in general being highly disregarded. Only in recent years the first examples of this previously overlooked approach have been reported.

In 2021, Lawrence *et al.* reported the first enantioselective *para*-Claisen rearrangement, which enabled the synthesis of (-)-Illicinone A. The authors' initial approach was based on the established [3,3]-Claisen/[3,3]-Cope mechanism for *para*-rearrangements. They assumed that enantioselectivity could be achieved by merely extending the asymmetric *ortho*-Claisen methodology, thus do a point-to-point chirality transfer. Application of chiral catalysis enabled the introduction of chirality into their compound during the transformation. The aluminum-based Lewis acid can coordinate to the ether-oxygen of illicinole and polarize the electrically neutral substrate forming a stabilized enolate **65** and a positively polarized allyl species **66**, *via* **64**. The chiral ligand can influence the recombination step and therefore induce chirality (Scheme 29).[33]



Scheme 29 Asymmetric para-alkylation in the synthesis of illicinone A.

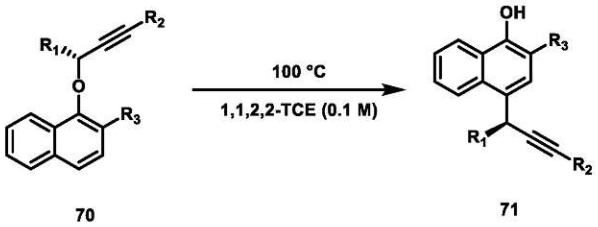
In 2023, Feng *et al.* described the *para*-Claisen rearrangement-based asymmetric dearomatization of allyl α-naphthol ethers **67** using chiral *N,N'*-dioxide/Co(II) **68** complex as the catalyst. The researchers achieved up to 99% *ee* and 94% yield, describing 43 examples for **69** (Scheme 30). However, in this instance, the rearrangement was again not of the Claisen-Cope type. Instead, the ether again underwent disconnection, forming an allylic cation and an enolate. The latter was coordinated to the Cobalt-catalyst *via* the ester group in the *ortho*-position. Similar to the mechanism presented in Scheme 29, the ligand shields one side of the substrate and introduces chirality into the product.[34]



*Scheme 30 Asymmetric para-alkylation using chiral Co-catalyst **68**.*

Liu *et al.* investigated the thermal *para*-Claisen rearrangement of chiral naphthyl 1-propargyl ethers **70** to their corresponding *para*-propargylated products **71**. The transformation also proceeds asymmetrically (Scheme 31). Chirality was transferred well during this reaction, facilitated by the

formation of a chiral allene intermediate. The desired products were obtained in both excellent yield and enantiomeric purity, affording up to 98% *ee* and 95% yield, describing 9 examples.[35]



70 71

Scheme 31 Asymmetric para-Claisen rearrangement of naphtyl-propargyl ethers.

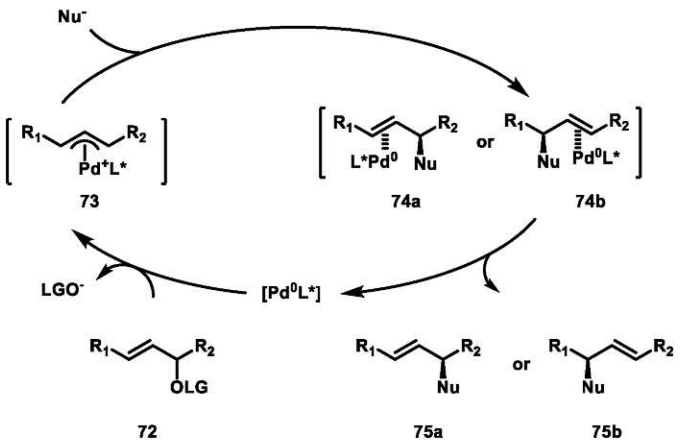
The aforementioned examples illustrate the absence of literature on the Claisen-Cope rearrangement, especially the asymmetric version. The literature methods available describe a thermal rearrangement under harsh conditions accompanied by a lack of selectivity. Application of Lewis acid suffers from severe racemization or even decomposition.

Chiral Claisen-Cope rearrangements of allyl-aryl based systems were - to the best of our knowledge - never reported. The *para*-alkylations are based on a disconnective ionic approach, whereas the Claisen-Cope mechanism would be entirely intramolecular and pericyclic in nature. Only recently, the first account of a Claisen-Cope rearrangement was reported by Liu *et al.* yet limited to propargyl-aryl systems. The asymmetric transformation of the naphtyl-propargyl follows an intramolecular mechanism. Nonetheless, the Claisen-Cope rearrangement of allyl-aryl ethers remains a blind spot in current literature.

Asymmetric allylic alkylation (Tsuji-Trost reaction)

One of the most efficient methods for preparing enantioenriched allyl-aryl ethers is the Tsuji-Trost reaction. It employs a chiral palladium catalyst to form asymmetric allylic C-C, C-O, C-N, C-S, and C-P bonds, thereby introducing chirality into a racemic starting material. This synthetic tool tolerates a broad range of olefins that contain a leaving group in the allylic position. It performs well under mild reaction conditions and forms the desired products with exemplary yields. Several chiral ligands have been described in literature that induce high enantiomeric excesses in various reactions of achiral substrates with different nucleophiles.[36–38]

The catalytic cycle commences with the coordination of the Palladium catalyst to the allylic substrate **72** to form two equilibrating Palladium-η^3-allyl complexes **73**, which can interconvert *via* -σ- isomerization (Scheme 32). The allylic substrate contains a leaving group, such as acetates and carbonates which dissociates in an oxidative addition step. The nucleophilic attack follows, forming intermediates **74a** and **74b**, subsequent dissociation liberates the Palladium catalyst and the chiral product **75a** and **75b.** Chiral ligands influence the -σ- isomerization and with that enantioselectivity of the nucleophilic attack. In this way one enantiomer of product can be formed preferentially. [38,39]



Scheme 32 General mechanism of the Tsuji-Trost reaction.

1,3-Disubstituted allyl carbonates, which result in a symmetrical allyl intermediate (R_1=R_2), are the most commonly employed substrates in asymmetric allylic alkylation (AAA). They are among the most extensively studied and successful, which can be attributed to the regioselectivity not being

an issue. The enantioselective step for these compounds is the nucleophilic attack which occurs at one of the diastereotopic sites. For 1,3-disubstituted allyl carbonates with different substituents ($R_1 \neq R_2$) oxidative addition is where the enantiodiscrimination occurs.[38,39]

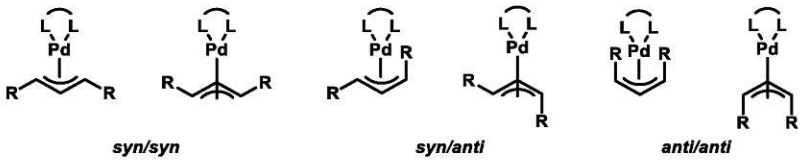


Figure 1 Possible allyl-Palladium intermediates.

Enantioselectivity is strongly influenced by the R-substituents (Figure 1). 1,3-Diphenylallyl acetate is frequently used as a model substrate in studies of palladium-catalyzed allylic substitution reactions, as the *syn/syn* isomer is sterically favored over the *syn/anti* and *anti/anti* isomers. In contrast, for less sterically hindered linear 1,3-dialkyl substrates, the *syn/anti* isomer becomes energetically more favored and competitive, and must be considered as an undesired intermediate, which makes enantioselectivity harder to control. For cyclic substrates, only the *anti/anti* geometry can occur. Since enantiodiscrimination is guided by small hydrogen atom, controlling enantioselectivity is more challenging compared to the linear substrates. However, Trost-type ligands have proven to be effective for both of these substrate classes.[38]

This work

The aforementioned knowledge built the basis for this thesis. It has been demonstrated that both the racemic and the asymmetric aliphatic Claisen rearrangement have been applied extensively in total synthesis. Similarly, the aromatic Claisen rearrangement has been shown to be a valuable technique, with the asymmetric version having been successfully employed in the past few decades as well. The Claisen-Cope rearrangement has likewise been demonstrated to be a crucial approach in natural product synthesis. However, it is evident that the *asymmetric* Claisen-Cope rearrangement is an area that has been insufficiently explored in the current literature. The objective was to develop a viable protocol for this method.

The idea was based on the utilization of the highly ordered transition states of the sigmatropic rearrangements and their ability for stereocontrol. It has been demonstrated that chirality can be transferred into the *ortho*-position. Accordingly, extending this methodology with the Cope mechanism to the *para*-position appeared to be a viable approach. The development of a viable protocol would be of significant interest, as it would represent a novel approach to the generation of defined stereogenic centers.

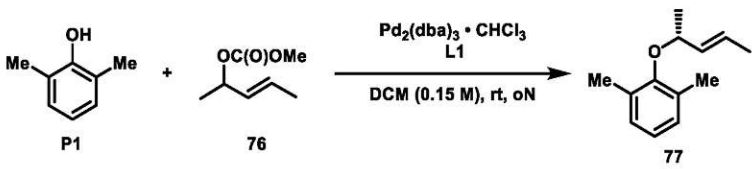
To achieve this, additionally highly enantioenriched starting materials were required. For the preparation of these chiral starting materials, it was necessary to identify the optimal conditions for achieving the highest enantiomeric excess possible. Moreover, if a protocol for the asymmetric Claisen-Cope rearrangement could be identified, evidence for the Claisen-Cope mechanism would also be of great value.

Results and Discussion

Rearrangement

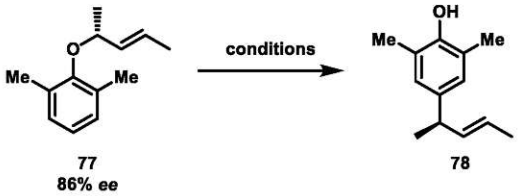
First results

In order to investigate the asymmetric Claisen-Cope rearrangement, the first task was the preparation of enantioenriched precursor. Hence, 2,6-dimethylphenol **P1** was chosen as starting material and subjected to an adapted Tsuji-Trost procedure.[30,38] To our delight, this first attempt proved successful and compound **77** was obtained in good yield and 86% *ee* from starting material **76** (Scheme 33).



*Scheme 33 Preparation of chiral starting material **77**.*

With a working protocol for the preparation of chiral precursor material at hand, we then turned our attention towards the exploration of the asymmetric Claisen-Cope rearrangement. We wanted to find appropriate conditions for the rearrangement of **77** to **78** (Scheme 34).



Scheme 34 Model reaction for the rearrangement investigation.

Based on the aforementioned literature precedents, we initially chose thermal conditions as the starting point for our investigations. Heating in DEA[19,31] (table 1, entry 1) produced the *para*-allylated product with excellent chirality transfer, demonstrating potential for further optimization. However, a significant drawback was the requirement for high reaction temperatures. Reducing the temperature to 140 °C, though still relatively high, resulted in a considerable increase in reaction time (entry 2). Similar outcomes, good chirality transfer and long reaction times, were observed

with other solvents, such as *o*-xylene (entry 3) and dichlorobenzene (entry 4), making this approach unsuitable. Further lowering the temperature to 100 °C led to no conversion of starting material (entry 5). These results, however, pose a promising starting point, as chirality was transferred successfully for entries 1-4.

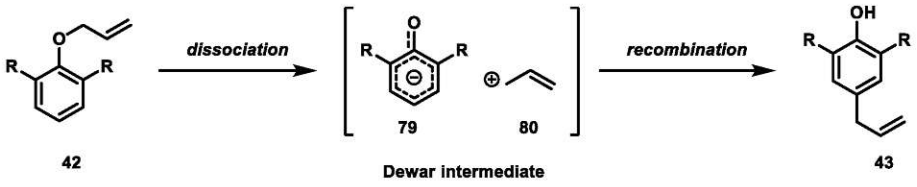
Table 1 Thermal rearrangements.

entry	Conditions	T (°C)[a]	t	% *ee*[b,c]
1	*N,N*-Diethylaniline (0.5 M)	190	3.5 h	86
2	*N,N*-Diethylaniline (0.5 M)	140	23 h	86
3	*o*-Xylene (0.5 M)	140	23 h	86
4	1,2-Dichlorobenzene (0.5 M)	140	23 h	86
5	*N,N*-Diethylaniline (0.5 M)	100	5 h	no conversion

[a]reaction block/bath temperature.
[b]starting material 86% *ee*.
[c]determined from the crude mixture.

Subsequently, a series of Lewis acids, which are frequently employed in the Claisen rearrangement, were subjected to investigation. Inspired by literature, BF_3-Et_2O was initially tested.[40] Although the rearrangement was completed quickly, there was a significant reduction in enantiomeric excess (table 2, entry 1). Lowering both the reaction temperature and the quantity of reagent from stoichiometric to catalytic amounts resulted in a modest improvement in enantiomeric excess (entry 2), suggesting that milder conditions favor the intramolecular pathway more significantly.

Lewis acids have been reported to lead to either decomposition or at least some level of racemization. This phenomenon can be attributed to the *Dewar intermediate*, which describes the disconnection of the ether **42** into the phenolic anion **79** and an allylic cation **80**, which subsequently recombine, forming phenol **43**.[41] This recombination results in the loss of stereoinformation.



Scheme 35: Dewar intermediate mechanism.

Entry 1 and 2 highlight that varying the reaction conditions may influence the relative prevalence of the dissociative mechanism, *i.e.* disfavor the formation of the Dewar intermediate, and in turn favor the intramolecular Claisen-Cope pathway. When Et_2AlCl[42] was used (entry 3), there was a complete loss of enantiomeric excess.

Table 2 Rearrangement under Lewis acidic conditions.

entry	Conditions	T (°C)[a]	t	% *ee*[b,c]
1	BF_3-etherate (1.2 eq.), DCM (0.1 M)	-40	5 min	20
2	BF_3-etherate (0.1 eq.), DCM (0.1 M)	-80	5 min	32
3	Et_2AlCl (1.5 eq.), hexane (0.2 M)	0	5 min	2
4	Me_3Al (3 eq.), hexane (0.15 M)	0	5 min	decomposition
5	$CeCl_3$ (0.1 eq.), PhMe (0.15 M)	r.t.	21.5 h	no conversion
6	$ZnCl_2$ (1.05 eq.), DCE (0.15 M)	80	2.5 h	14
7	$SnCl_4$ (1.2 eq.), DCM (0.5 M)	0	5 min	16
8	$Bi(OTf)_3$ (20 mol%), PhMe (0.1 M)	0	4 h	10
9	AcOH (1.5 eq.), PhMe (1 M)	r.t.	22 h	no conversion
10	EuFOD (5 mol%), hexane (0.5 M)	40	24 h	86

[a]reaction block/bath temperature.
[b]starting material 86% *ee*.
[c]determined from the crude mixture.

Inspired by Shishido's synthesis of heliannuols[31,32], which achieved excellent chirality transfer, Me_3Al was also investigated but resulted in the complete decomposition of the starting material (entry 4). Rearrangement applying catalytic amounts of $CeCl_3$ failed to deliver any conversion (entry 5). Subsequent trials with $ZnCl_2$[43] (entry 6), $SnCl_4$[44] (entry 7) and $Bi(OTf)_3$[45] (entry 8) led to significant racemization and reduced enantiomeric excess on a similar level. These results remained unsatisfactory, reinforcing the necessity for a novel approach. Notably, the rearrangement was also attempted using Brønsted acid catalysis (entry 9), but no conversion was observed.

Based on work previously reported by our group and encouraged by various literature precedents, we then turned our attention towards lanthanoid complexes.[26,30,31,46–48] EuFOD delivered the most

promising results yet, achieving complete retention of enantiomeric excess in the product, though only 75% conversion of starting material was achieved (entry 10).

Fortunately, we had a range of different Lanthanide FOD-catalysts available, all of which demonstrated excellent chirality transfer (table 3, entries 1-3). The obtained enantiomeric excess of the product was comparable to that observed in the thermal rearrangement, albeit at significantly lower reaction temperatures. A slight reduction in enantiomeric excess was obtained with HoFOD (entry 2). As a result, we decided to focus on EuFOD (entry 1), given the promising results and its extensive use in previous work within our research group.[46]

Table 3 Lanthanide-catalyzed rearrangements.

entry	Conditions	T (°C)[a]	t (h)	% *ee*[b,c]
1	EuFOD (10 mol%), hexane (0.5 M)	40	16	**86**
2	HoFOD (10 mol%), hexane (0.5 M)	40	16	**84**
3	PrFOD (10 mol%), hexane (0.5 M)	40	16	**86**
4	$Eu(hfc)_3$ (10 mol%), PhMe (0.1 M)	60	23	racemic[d]

[a]reaction block/bath temperature.
[b]starting material 86% *ee*.
[c]determined from the crude mixture.
[d]starting material racemic.

Furthermore, chiral camphor-based Europium catalyst $Eu(hfc)_3$ was tested on racemic starting material (entry 4) at higher reaction temperatures. This experiment aimed to determine whether chirality could be induced during the rearrangement. Although the reaction did proceed under these conditions, no effect on enantiomeric excess was observed. If the reaction had involved a charge separated mechanism the chiral ligand might have been able to introduce chirality into the substrate. A higher temperature was chosen for this rearrangement as it has been shown that a higher temperature can facilitate the charge separated process (table 2, entries 1-2). This observation is a first hint that the Europium(III)-catalyzed rearrangement is likely entirely intramolecular in nature.

Optimization

Continuing with EuFOD, the objective was to identify the optimal reaction conditions. To achieve this, the reaction conditions were systematically examined in greater detail, with different factors being considered. Multiple parameters were changed simultaneously to gather as much information as possible while keeping the number of required experiments to a minimum.

Table 4 Reaction concentration & catalyst loading.

entry	EuFOD (mol%)	Solvent (conc.)	T (°C)	t (h)	comment	% *ee*[a]
1	5	PhMe (0.2 M)	40	22	*48% conv.*[b]	n. d.
2	5	PhMe (1 M)	40	22	*81% conv.*[b]	n. d.

[a]*ee* not determined (n. d.).
[b]determined by NMR analysis. The conversion was determined by the relative amount of starting material and product.

Initially, a reduced catalyst loading of 5 mol% was tested while varying the reaction concentrations (table 5). At a concentration of 0.2 M (entry 1), only 48% conversion was achieved, as determined by NMR. Since the Claisen-Cope mechanism is an intramolecular reaction, it was hypothesized that increasing the concentration will have a beneficial effect on reaction kinetics This hypothesis was confirmed (entry 2; table 3, entry 10); however, even at the highest concentration, the reaction time remained quite lengthy, prompting us to increase in the catalyst amount.

Table 5 Catalyst loading.

entry	EuFOD (mol%)	Solvent (conc.)	T (°C)	t (h)	comment	% *ee*[a]
1	5	PhMe (1 M)	40	14	*75% conv.*[b]	n. d.
2	10	PhMe (1 M)	40	14	*full conv.*[b]	n. d.
3	100	PhMe (1 M)	40	1	Quant.[c]	88

[a]starting material 88% *ee*.
[b]determined by NMR analysis. The conversion was determined by the relative amount of starting material and product.
[c]isolated yield.

With respect to catalyst loading, it was demonstrated that 5 mol% proved to be insufficient to achieve full conversion within a reasonable timeframe (table 6, entry 1). Application of 10 mol% EuFOD on the other hand allowed the reaction to reach full conversion overnight (entry 2). As previously discussed, reducing the quantity of reagent from stoichiometric to catalytic amounts

resulted in a minor increase of enantiomeric excess (table 2, entry 1-2). Vice versa this led to the question whether the enantiomeric excess would decrease if the amount of EuFOD is increased from a catalytic to a stochiometric amount. However, as shown in entry 3, this appeared not to be the case, and the desired product was obtained in quantitative yield with virtually perfect chirality transfer. This suggests that the rearrangement catalyzed by EuFOD occurs exclusively through the Claisen-Cope pathway, indicating that racemization is not a concern.

Table 6 Solvents & reaction temperature.

entry	EuFOD (mol%)	Solvent (conc.)	T (°C)	t (h)	Isolated yield	% *ee*[a]
1	10	Hexane (1 M)	60	3	Quant.	86
2	10	$CHCl_3$ (1 M)	60	3	Quant.	86
3	10	PhMe (1 M)	60	3	Quant.	86

[a]starting material 86% *ee*.

Although having a promising protocol at hand, we investigated various solvents. We were curious if the results obtained were due to a solvent-effect limited to toluene or if this observation was general. We were delighted to find that the desired transformation performed nicely in hexane (table 7, entry 1), chloroform (entry 2) and toluene (entry 3) even at elevated temperatures to furnish the product in each case in quantitative yield and excellent *ee*. Therefore, toluene was chosen as solvent going forward, as it exhibits the broadest possible temperature range.

Table 7 Reaction temperatures.

entry	EuFOD (mol%)	Solvent (conc.)	T (°C)	t (h)	Isolated yield	% *ee*[a]
1	10	PhMe (1 M)	50	3	Quant.	86
2	10	**PhMe (1 M)**	**40**	**3**	**Quant.**	**86**
3	10	PhMe (1 M)	r.t.	21	Quant.	86

[a]starting material 86% *ee*.

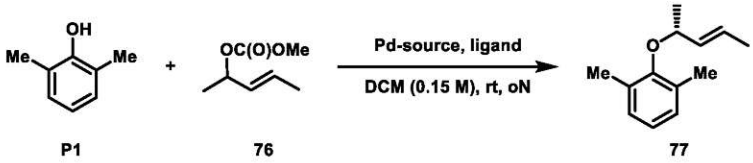
Regarding temperature and duration, the objective was to identify the lowest reaction temperature for the rearrangement to the *para*-allylated product, within the shortest possible timeframe. As shown above, the reaction at 60 °C (table 6, entry 3) gave full conversion of the starting material. Lowering the temperature to 50 °C led to full conversion of the starting material within three hours

and the product was obtained in quantitative yield as well (Table 7, entry 1). Furthermore, quantitative yield with full chirality transfer was also accomplished within a three-hour period at 40 °C (entry 2). The same results were achieved at room temperature although the reaction took place overnight (entry 3). Therefore, the objective of developing a viable protocol for the asymmetric Claisen-Cope rearrangement has been successfully achieved, and the optimal conditions identified. With a working protocol for the Claisen-Cope rearrangement at hand, the attention was then turned towards the optimization of starting material preparation.

Tsuji-Trost reaction

Reaction optimization

Our initial attempt at the Tsuji-Trost reaction successfully produced compound **77** with a good yield and 86% *ee* from 2,6-dimethylphenol **P1** (Scheme 36). However, we aimed to see if these results could be improved further, before focusing on investigations of scope. A series of experiments was conducted to evaluate the performance of various chiral Trost-ligands and palladium sources.



Scheme 36 Test reaction for optimization.

These bidentate ligands **L1**-**L4** are commonly employed in the Tsuji-Trost reaction and share a similar structural backbone (Figure 2).

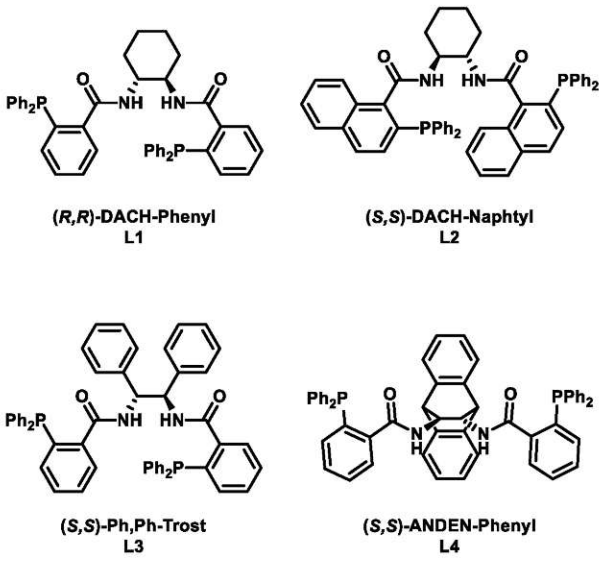


Figure 2 Ligands for the Tsuji-Trost reaction.

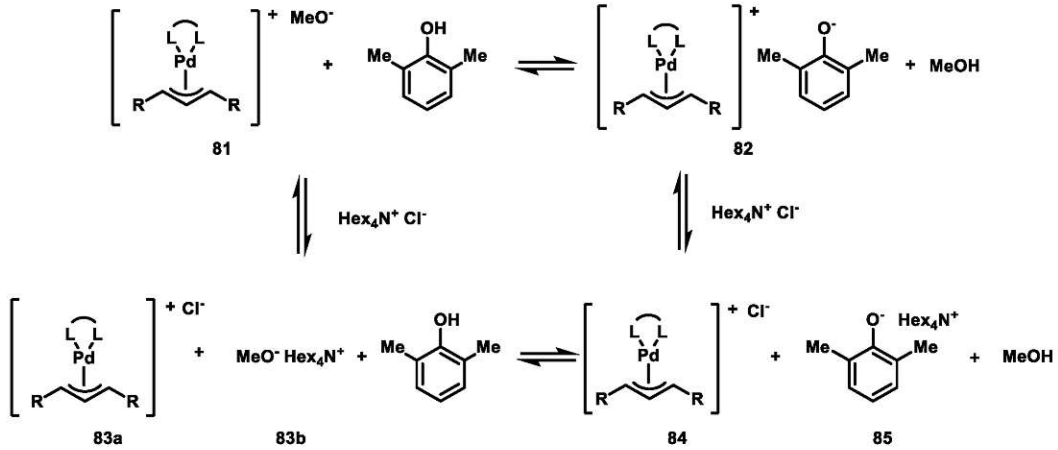
Our standard conditions, already applied in Scheme 33, served as the starting point for the attempted optimization (table 8, entry 1). **L1**, when combined with $Pd_2(dba)_3{\cdot}CHCl_3$ as the palladium source, produced the most favorable outcomes. The first parameter investigated was the ligand. Other literature known bidentate ligands, **L2, L3** and **L4** were tested, however, all led to

diminished enantiomeric excesses (entry 2-4).[49] Next, we envisioned to further increase the *ee* of the most promising results yet (entry 1) by addition of Hex_4NCl.

Table 8 Optimization Tsuji-Trost reaction.

entry	Pd-species (2 mol%)	Ligand (6 mol%)	Additives	% *ee*
1	**$Pd_2(dba)_3$·$CHCl_3$**	**L1**	-	**86**
2	$Pd_2(dba)_3$·$CHCl_3$	L2	-	64
3	$Pd_2(dba)_3$·$CHCl_3$	L3	-	40
4	$Pd_2(dba)_3$·$CHCl_3$	L4	-	62
5	$Pd_2(dba)_3$·$CHCl_3$	L1	Hex_4NCl (30 mol%)	68
6	$[PdCl(C_3H_5)]_2$	L1	-	60
7	$[PdCl(C_3H_5)]_2$	L3	-	16

Literature precedents indicate, that the addition of additives, such as tetrahexylammonium chloride, can enhance the enantiomeric excess of the product to some extent.[39]



Scheme 37 Influence of additives.

Looking at the Tsuji-Trost reaction mechanism it can be reasoned that without tetraalkylammonium additives, **81** can either interconvert *via* -σ- isomerization or undergo deprotonation of the phenol, resulting in ion pair **82** (Scheme 37). This may then either further isomerize or react to give the final product. The rates at which these processes occur impact the enantioselectivity of the allylic alkylation. When tetraalkylammonium salts are introduced, both ion pairs **81** and **82** can interact

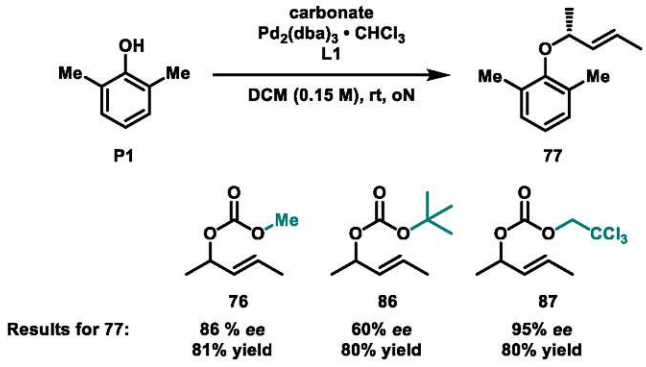
with the ammonium salt. The newly formed ion pairs **83a** and **84** can isomerize more easily, as the chloride ion can additionally coordinate with palladium. Furthermore, ion pair **83b** can delay the deprotonation of the phenol and **85** can stabilize the phenolate. Both **83b** and **85** potentially slow down the nucleophilic attack. These processes can impact enantioselectivity in a positive manner.[39] However, this phenomenon was not observed in our case and the obtained enantiomeric excess was only moderate (entry 5).

A different palladium source was also investigated to see if it could improve the enantiomeric excess. However, both the best-performing ligand, **L1** (entry 6), and the poorest-performing ligand, **L3** (entry 7), showed only a decrease in enantiomeric excess.

Investigation of carbonates

Leaving groups

Nevertheless, an additional component of this reaction, namely the carbonate, could be investigated to evaluate its potential influence on enantiomeric excess. For this purpose, two additional carbonates were prepared (Scheme 38).



Scheme 38 Influence of different carbonates on ee.

The methyl-carbonate **76** was initially examined, and it delivered promising outcomes with an enantiomeric excess of 86%, upon subjection to the optimized Tsuji-Trost conditions. The use of the *tert*-butyl-carbonate **86** resulted in a decreased enantiomeric excess, proving that it was not a viable option, and it was disregarded immediately. Nevertheless, utilizing the Troc-carbonate **87** resulted in a considerable increase in the enantiomeric excess, affording **77** in 95% *ee*.

We aimed to determine whether this improvement holds true for different substrates (Figure 3). The increase in enantiomeric excess is observed for the dimethyl- **77**, diethyl- **88** and diisopropyl **89** ethers, however not for the trimethyl substrate **90**.

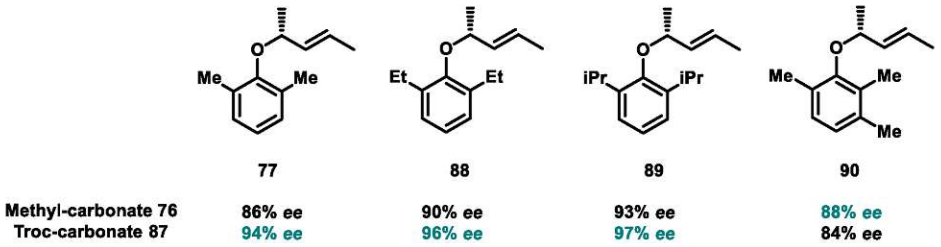


Figure 3 Comparison of enantiomeric excess.

To compare the modified carbonate with literature precedent, we synthesized ether **57**. In 1998, Trost and Toste reported the preparation of **57** with 85% *ee*.[30] In our hands, the use of carbonate **87** furnished the desired compound in slightly improved *ee* of 87% (Figure 4).

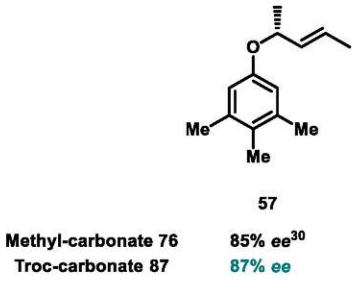


*Figure 4 Improvement of ee by carbonate **87**.*

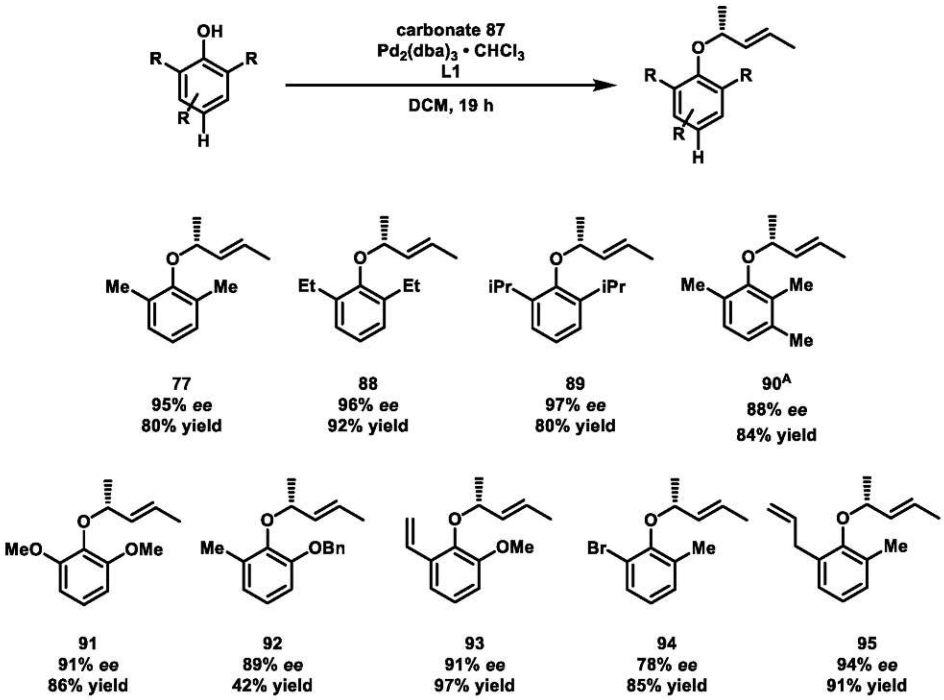
The origin of this influence remains uncertain, although it can be hypothesized. As previously discussed, the nucleophilic attack has been established as the regio- and enantioselective step[38]. As the formed allylic palladium complex is symmetrical, regioselectivity can be discounted. An examination of the catalytic cycle of the Tsuji-Trost reaction reveals that the carbonate should not exert a direct influence on the nucleophilic attack, as the allyl palladium complex is formed well before the enantiodetermining step. Therefore, it is necessary to consider how the carbonate leaving group can influence the reaction. Upon allyl complex formation the carbonate decarboxylates, liberating the corresponding base ($^-$OMe, $^-$OtBu, $^-$OTroc), which in turn can deprotonate the phenol. Due to the different basicities of the resulting anions the deprotonation occurs at different rates, in turn influencing the rate of the nucleophilic attack. Comparing the p*K*a-values of the generated counterions ($^-$OtBu>$^-$OMe>$^-$OTroc), this trend seems to fit well with respect to the obtained

enantiomeric excesses during the asymmetric allylic alkylation. Furthermore, the counteranions may influence the -σ- isomerization, thereby enhancing enantioselectivity. Nevertheless, this is all speculation, and this matter remains to be determined.

Scope

Tsuji-Trost alkylation

With the optimized protocol for the Tsuji Trost reaction in hand the next step was the determination of the scope of the reaction. A variety of different 2,6-disubstituted phenols was subjected to the optimized asymmetric allylic alkylation conditions and the results are summarized below (Scheme 39).



Scheme 39 Scope Tsuji-Trost.[A]

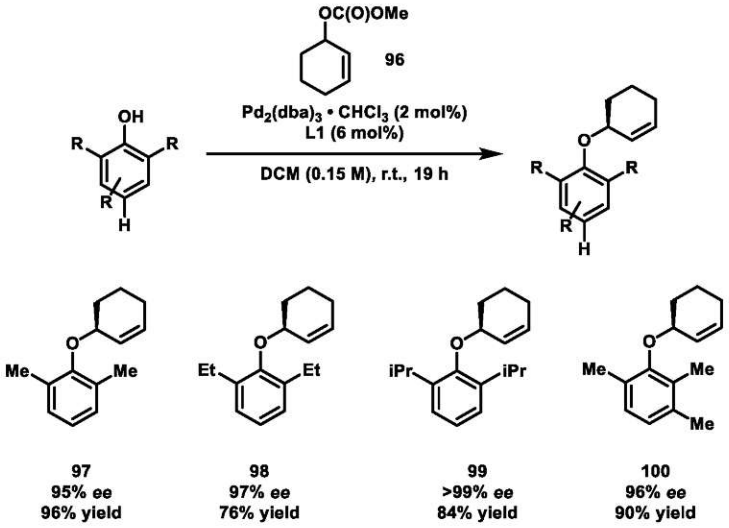
The 2,6-dialkyl-substituted ethers **77**, **88**, and **89** were produced with similar high enantiomeric excesses, with up to 97% *ee* and good to excellent yields. As mentioned above the best results for compound **90** were achieved with carbonate **76** and the 2,3,6-methylated ether was obtained with an enantiomeric excess of 88%. Besides alkyl substituted substrates we were able to demonstrate that also methoxy- and O-benzyl substituted compounds **91** and **92** were produced in excellent enantiomeric excesses although the later in only moderate yields. Further, vinyl compound **93** was also accessible in excellent yield and comparable enantiomeric purity.

[A]compound **90** was prepared with carbonate **76**.

It turned out that bromides were also well tolerated by this procedure, and compound **94** was obtained in very good yield, though with a slightly reduced enantiomeric excess. Finally, compound **95** was obtained with excellent enantiomeric excess and yield, respectively.

Cyclic allyl carbonate

Building on the successful outcomes with the linear carbonate, we sought to extend our investigation to include cyclic substrates as well. The optimized conditions were employed to prepare chiral 2,6-disubstituted ethers using a cyclic allyl carbonate **96**. This procedure was successful, with no complications, which was to be expected given that these carbonates have been used previously and the results are summarized below (Scheme 40).



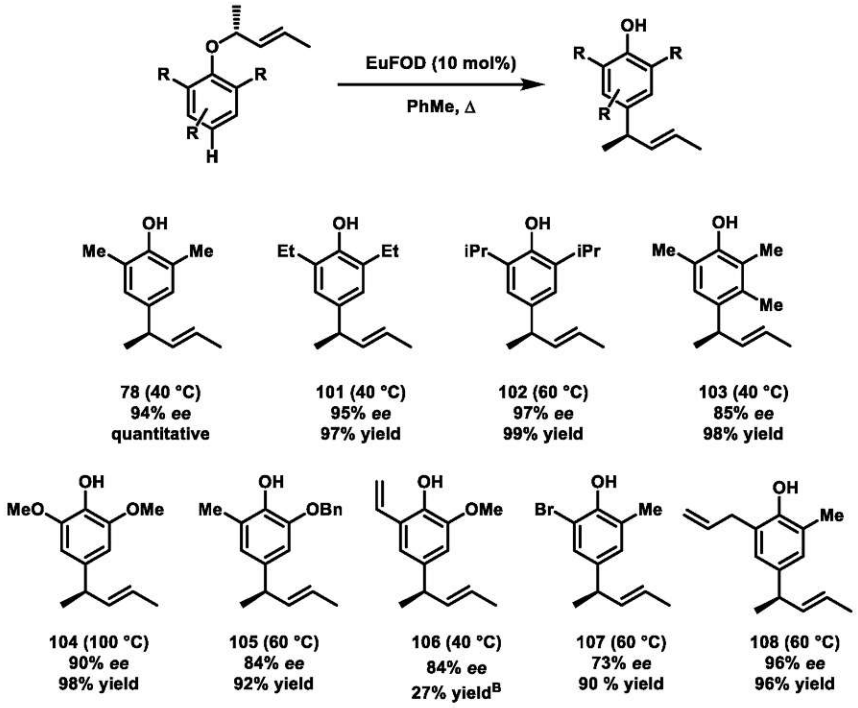
Scheme 40 Scope Tsuji-Trost with cyclic allyl carbonate.

Compound **97** was synthesized with excellent yield and enantiomeric excess, respectively. Compound **98** achieved exceptional enantiomeric excess, although with slightly diminished yields. The highest *ee* was obtained for compound **99**, which yielded an enantiomeric excess greater than 99%. Compound **100** was again afforded with comparable yield and enantiomeric excess.

It is noteworthy that the reaction with the cyclic allyl carbonate typically yielded a higher enantiomeric excess compared to the linear analogues. This is surprising as, in literature it has been reported that enantiodiscrimination for cyclic substrates furnished poorer results than for its linear counterpart.[38]

Asymmetric Claisen-Cope rearrangement

After the successful preparation of a variety of chiral allyl-aryl ethers, they were subjected to the optimized protocol for the asymmetric Claisen-Cope rearrangement. The reaction was conducted with 10 mol% EuFOD, 1 Molar in toluene. Depending on substrate the temperature ranges from 40 to 100 °C. The results of the investigations are summarized below (Scheme 41).



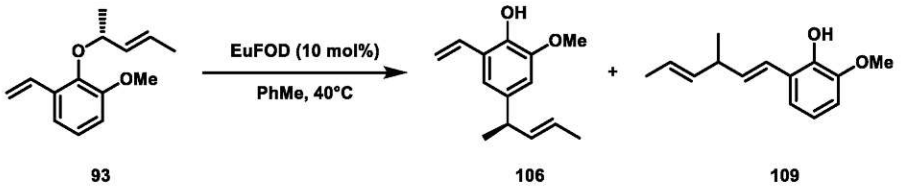
Scheme 41 Scope asymmetric Claisen-Cope rearrangement.[B]

The compounds were successfully rearranged to their *para*-allylated isomers using the optimized protocol, giving very good to excellent yields and an exceptional degree of chirality transfer. Enantiomeric excesses of up to 97% *ee* and yields up to quantitative were achieved. However, it was found that not all the compounds rearranged at 40 °C within a three-hour period, but a higher temperature was required. At the specified temperatures, nearly all allyl-aryl ethers rearranged to their *para*-substituted counterparts within three to four hours. With our method generally no undesired side reactions were observed. The *para*-rearrangement proceeded selectively, neither giving the *meta*-substituted nor cleaved products. Also, no evidence for isomerization, leading to the Z-isomer, was found.

[B]27% of **106** separated, mixture of product and unidentified sideproduct not taken into account.

The 2,6-dialkyl substituted phenols **78**, **101**-**103** were obtained with excellent chirality transfer under mild conditions. For compounds **78**, **101** and **103** the reaction proceeds at 40 °C, **102** requires 60 °C for the same reaction time. This fact can be attributed to the more sterically demanding iPr-substituents. Compound **104**, already requiring high reaction temperatures additionally needed a longer reaction time, the rearrangement taking over night. However, **105** was again obtained with exceptional chirality transfer and high yields.

For compounds **106** and **107**, enantiomeric excess decreased slightly during the rearrangement. The reason for the drop is unclear, as alkyl- and alkyloxy-substituents did not appear to influence chirality transfer for compounds **78**, **101**-**105**. Additionally, the rearrangement of compound **106** produced an unidentified side product. The rearrangement was initially conducted at 60 °C. Lowering the temperature and extending the reaction time, in an attempt to eliminate this unwanted side reaction, had no effect. However, after three hours at 40 °C the rearrangement of **93** was complete. Purification of compound **106** proved challenging and only minor amounts were obtained in pure form. It can be hypothesized that a second rearrangement onto the vinyl moiety may be competing with the aromatic Claisen-Cope reaction affording compound **109** (Scheme 42).

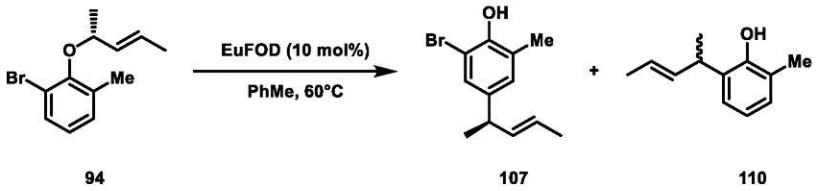


*Scheme 42 Hypothesized side product for the rearrangement of **93**.*

This could not be confirmed, however, due to the difficulty in isolating the side product and the significant overlap in the NMR spectra. The unknown side reaction could also be a reason for the decrease in enantiomeric excess in the product.

We were delighted to find that Br-containing compound **107** was also accessible *via* this method, although the enantiomeric excess of the product dropped slightly. The reason for the diminished *ee* could be the following: as separation of **107** on chiral HPLC proved impossible, enantiomeric excess was determined by converting **107** into the corresponding dehalogenated phenol **116**, by treatment with *n*BuLi, (see Scheme 58 for details). It can be hypothesized the use of the strong base to be the reason for the decrease in enantiomeric excess.

Furthermore, the reaction yielded 5-6% of the *ortho*-allylated product **110** as a result of a side reaction (Scheme 43). This could be confirmed by isolation and NMR analysis of the side product **110**. Reducing the temperature to 40 °C and extending the reaction time overnight yet again did not improve the outcome, resulting in similar results.

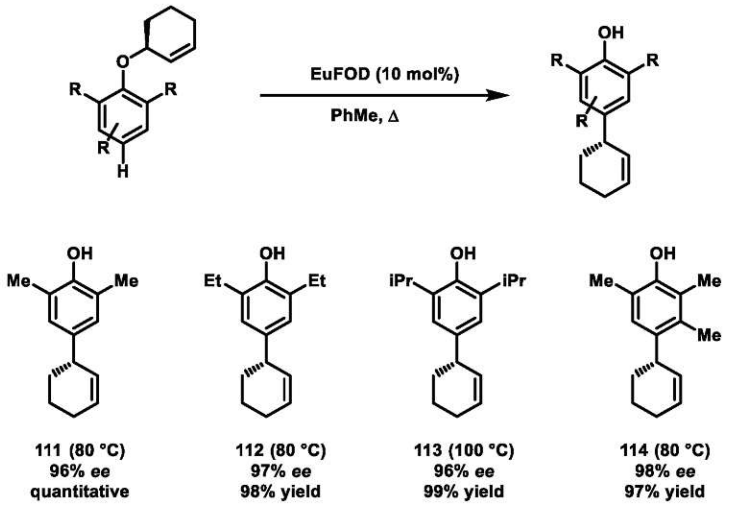


*Scheme 43 Side product formation during rearrangement of **94**.*

Allylic substituted compound **108** was again afforded with excellent chirality transfer and in high yield.

Cycloalkenyl-aryl ethers

Next, we applied our optimized Claisen-Cope rearrangement conditions to a series of 2,6-dialkylsubstituted substrates containing a chiral cyclic allyl ether moiety.



Scheme 44 Scope of asymmetric Claisen-Cope rearrangement for cyclic allyl ethers.

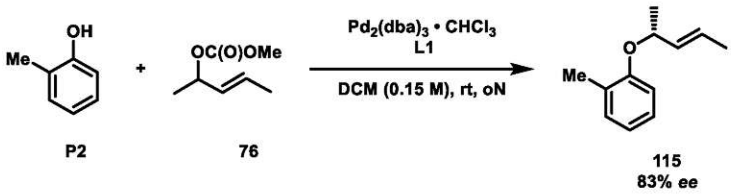
The chiral cycloalkenyl-aryl ethers were successfully rearranged to their *para*-allylated isomers **111**-**114** using the optimized protocol, giving excellent yields and demonstrating an exceptional degree of chirality transfer (Scheme 44). It was observed that these cyclic compounds generally require

higher temperatures for the rearrangement than their linear counterparts. This phenomenon is likely caused by steric effects. Thereby using toluene as a solvent was an appropriate choice.

In general, it should be noted that all of the rearrangements could also be performed at lower temperatures with increased reaction times, achieving comparable results in terms of yield and enantiomeric excess. This shows that the rearrangement can be performed at milder temperatures, if required. For instance, products **111**-**114** were successfully obtained overnight at reduced temperatures (**111**, **112**, and **114** at 60 °C; **113** at 80 °C overnight) with satisfactory results as well (compare table 7, entry 3).

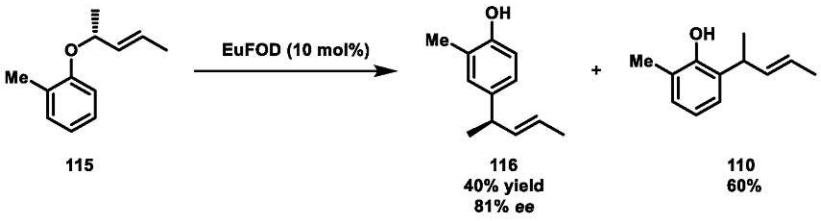
Mono-substituted allyl-aryl ethers

With our outstanding results for both the asymmetric allylic alkylation and the asymmetric Claisen-Cope rearrangement, we wanted to turn our focus on mono-substituted substrates. To explore chirality transfer in the Claisen-Cope reaction of mono-substituted ethers, starting material **115** was synthesized following the established protocol from **P2**, delivering the product with an enantiomeric excess of 83% (Scheme 45).



*Scheme 45 Preparation of **115**.*

The rearrangement of **115** was performed at 80 °C over three hours or at 60 °C overnight, respectively (Scheme 46). In both cases, the reaction afforded a 1.5:1 mixture of products, the *ortho*-allylated Claisen product **110** being predominantly formed. The desired *para*-allylated phenol **116** was obtained in a 40% yield with 81% *ee*. The enantiomeric excess of **110** was not determined.



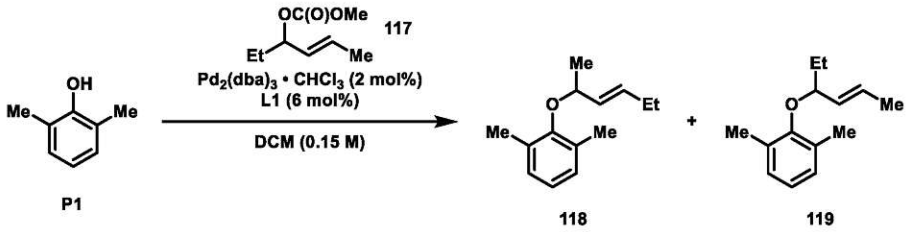
*Scheme 46 Rearrangement of **115**.*

These results demonstrate that our protocol of the Claisen-Cope rearrangement can effectively transfer chirality in mono-substituted substrates as well. However, the regioselectivity of the reaction remains an issue. Further investigation is needed to determine if the product ratio can be shifted more favorably towards the *para*-product.

Limitations

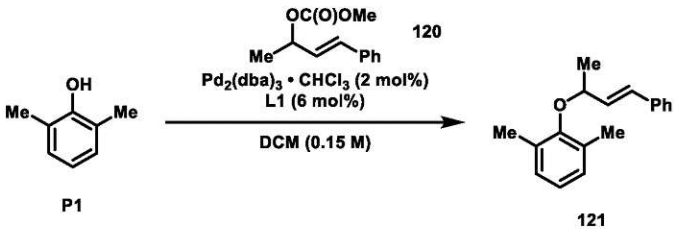
1,3-Disubstituted carbonates with non-identical substituents ($R_1 \neq R_2$)

We also wanted to investigate our optimized reaction conditions with asymmetrically substituted 1,3-carbonates. The reaction with 1,3-dialkyl carbonate **117** gave an inseparable mixture of products **118** and **119** (4:1) (Scheme 47). It was shown that the catalyst exerts an influence only on regioselectivity in this.



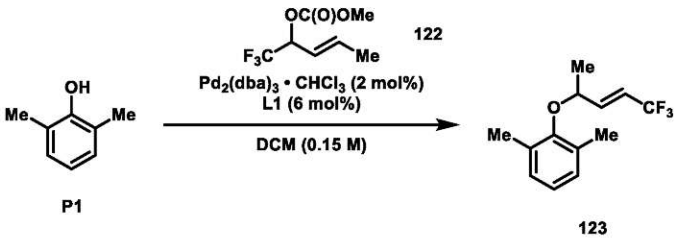
*Scheme 47 Tsuji-Trost reaction with carbonate **117**.*

In the reaction with carbonate **120**, an influence on regioselectivity by the catalyst was not observed anymore (Scheme 48). It seems that in this reaction the substrate directs the reaction outcome by sterical demand of its substituents. Only the formation of one racemic product **121** was observed.



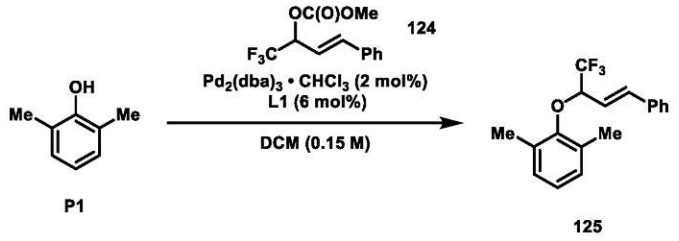
*Scheme 48 Tsuji-Trost reaction with carbonate **120**.*

We also attempted the reaction with fluorinated carbonates. The idea was to generate a chiral center bearing a trifluormethyl moiety. However, the only obtained product was the undesired regioisomer **123**, indicating that the methyl-side is the less sterically hindered side of the allyl-complex and or potentially the electronically more favorable. Therefore, attack of the phenol occurred exclusively at the methyl position (Scheme 49).



*Scheme 49 Tsuji-Trost with carbonate **122**.*

We hypothesized that the steric demand would follow the order Ph > CF_3 > Me, potentially allowing for the introduction of a chiral CF_3 group (R_1) when combined with a phenyl group (R_2). To test this theory, carbonate **124** was reacted with 2,6-dimethylphenol under standard conditions (Scheme 50). Unfortunately, the reaction did not proceed cleanly, and the desired product **125** could not be obtained in pure form.



*Scheme 50 Tsuji-Trost reaction with carbonate **124**.*

Moreover, HPLC analysis confirmed that no chirality was introduced in this reaction with either carbonate **122** and **124**, affording ethers **123** and **125** as racemates. All these examples

(Scheme 47-50) demonstrate that unfortunately with asymmetrically substituted 1,3-allyl-carbonates, our standard conditions failed to induce chirality.

Troublesome compounds

While exploring the reaction scope, we faced some obstacles, including difficulties in preparing certain substrates as intended.

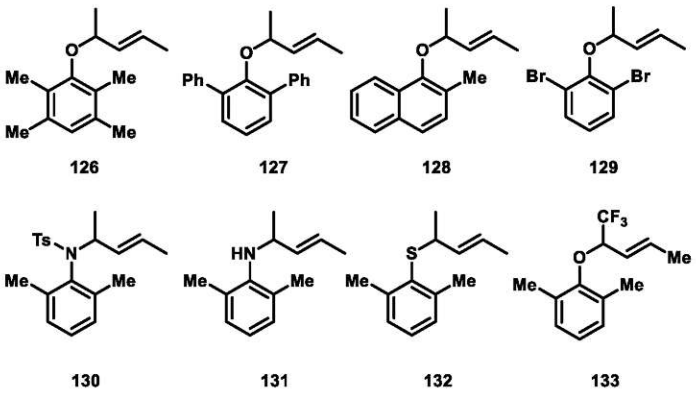


Figure 5 Racemic Scope - No rearrangement.

Before synthesizing the substrates in an enantiomerically enriched form, the compounds are prepared in a racemic fashion. Compounds **126** through **133** were successfully synthesized as racemates (Figure 5). However, the subsequent rearrangement did not provide satisfactory results. As a consequence, these compounds were not further pursued, and no asymmetric synthesis was attempted. All these compounds gave either no conversion (**126**, **130**-**133**) or decomposed under the reaction conditions (**127**-**129**). For compound **129**, this was to be expected as in literature it was shown previously that 2,6-disubstituted allyl-aryl ethers bearing electron withdrawing substituents, such as halogens, are prone to ether cleavage.[21]

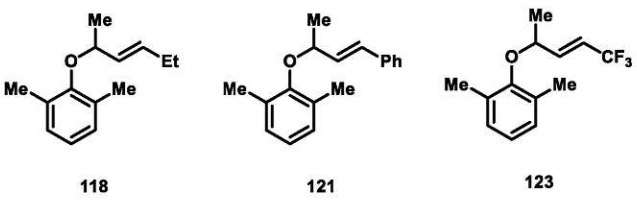
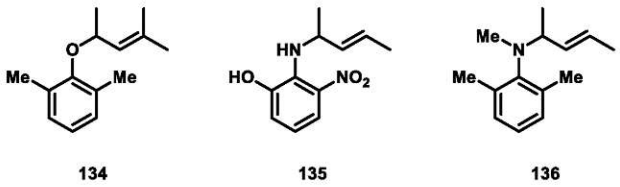


Figure 6 Racemic Scope - No AAA.

As discussed in the previous chapter, racemic compounds **118**, **121** and **123** were successfully synthesized using the Tsuji-Trost reaction (Figure 6). However, no enantioselectivity was achieved, as for asymmetrically substituted 1,3-carbonates, the catalyst is no longer able to induce chirality.

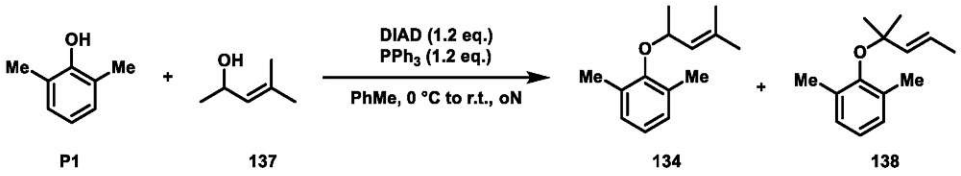


134 **135** **136**

Figure 7 No alkylation reaction.

Furthermore, compounds **134**-**136** could not be prepared using palladium-catalyzed allylic alkylation (Figure 7).

Compound **134** was successfully accessible from 2,6-dimethylphenol and alcohol **137** *via* Mitsunobu reaction, though it afforded an inseparable 2:1 mixture, favoring the desired product **134** over compound **138** (Scheme 51). This mixture was then subjected to the rearrangement, which proceeded, delivering products in the same ratio.



P1 **137** **134** **138**

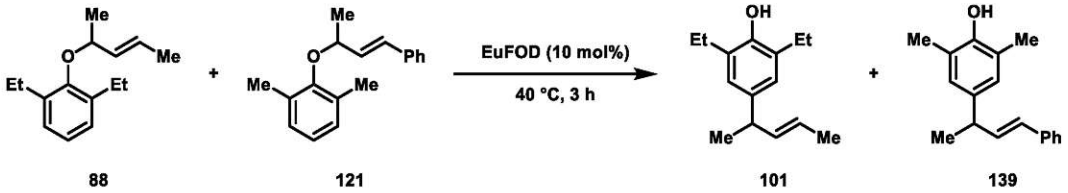
Scheme 51 Sideproduct of the Mitsunobu reaction.

Although there are literature[38] examples of the Tsuji-Trost reaction being successfully employed with anilines, our attempts with **135** and **136** resulted in no reaction. This lack of reactivity may be attributed to the choice of ligands, as different ligands were used in the literature examples, as well as solvents, temperature etc. However, further investigation into this was not pursued in the course of this work as no rearrangement was observed for racemic **130** and **131** anyhow.

Mechanistic studies

Crossover experiment

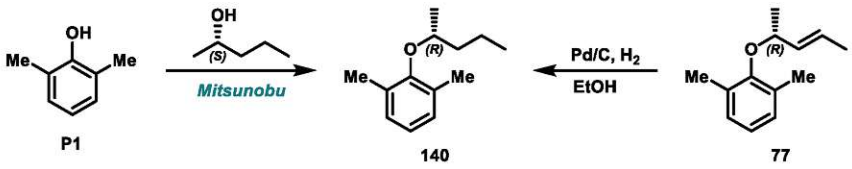
Our excellent chirality transfer strongly suggests an intramolecular mechanism; however, we sought additional evidence to support this hypothesis and rule out any possibility of an intermolecular process. Inspired by literature[19] we conducted a crossover experiment (Scheme 52). For this a mixture of compounds **88** and **121** was rearranged. This pair was chosen as their reaction temperature and time were similar and the anticipated reaction products were easily separable by column chromatography. Consistent with literature and the mechanism of the Claisen-Cope reaction, the outcome did not show any evidence of crossover reactions and only products **101** and **139** were isolated.



*Scheme 52 Crossover experiment of **88** and **121**.*

Stereochemistry determination

The configuration of the chiral linear ether was assumed to be in agreement with literature reports. Although this seemed plausible, we wanted to pinpoint the stereochemistry introduced during the asymmetric allylic alkylation. This was seen necessary to correctly interpret the results obtained during the Claisen-Cope rearrangement.



Scheme 53 Stereochemistry determination.

Therefore, chiral ether **77** was converted to compound **140** by catalytic hydrogenation. Additionally, chiral compound **140** was obtained *via* Mitsunobu reaction of 2,6-dimethylphenol with *(S)*-2-pentanol which under inversion gives the *(R)*-enantiomer (Scheme 53).

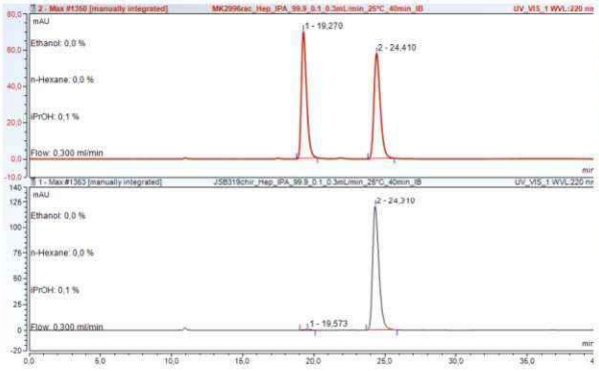


*Figure 8 Mitsunobu HPLC (**140m**).*

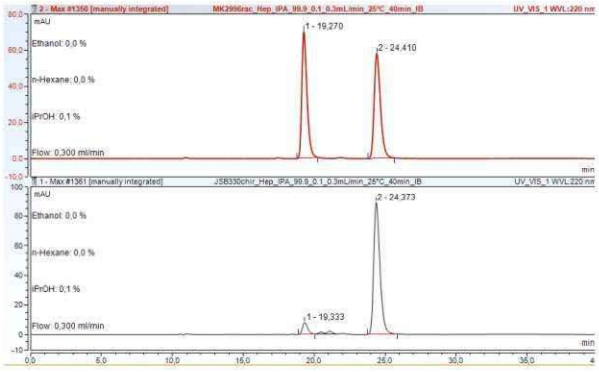
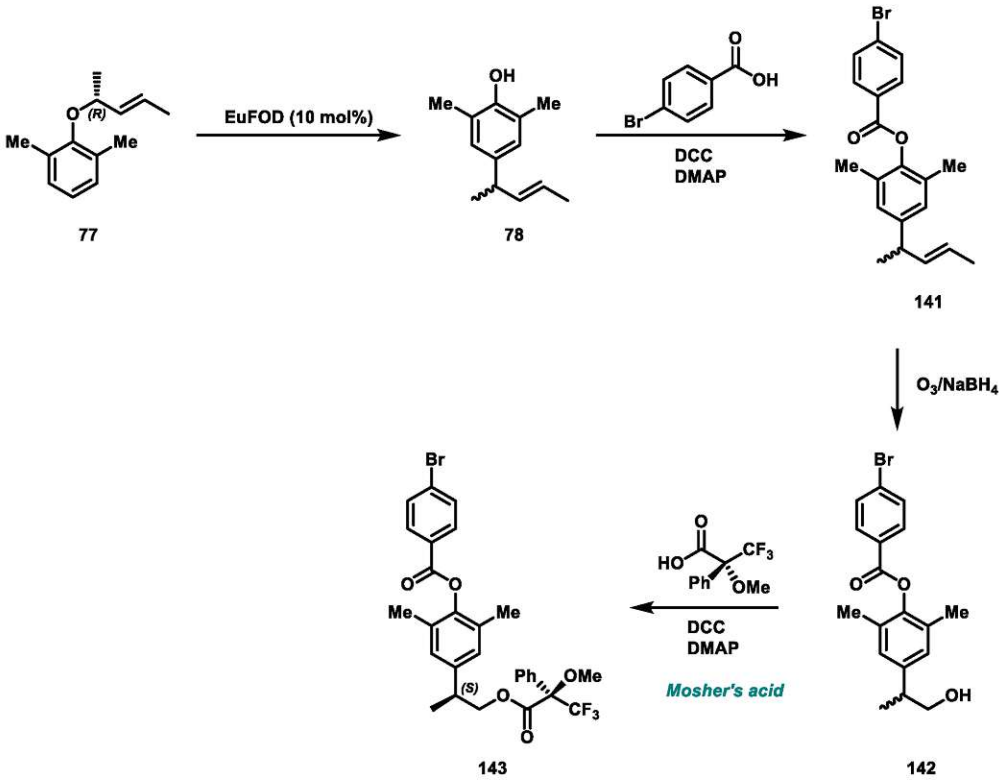


*Figure 9 Hydrogenation HPLC (**140h**).*

Comparing the chiral HPLC chromatograms (Figure 8 and 9) one can clearly see the two enantiomers of the racemic substrate (orange). Comparing this to the products of Mitsunobu reaction **140m** (Figure 8, grey) and the hydrogenation reaction **140h** (Figure 9, grey), HPLC analysis confirms that both reactions result in the same enantiomer. This demonstrates that ligand **L1** gives the *(R)*-enantiomer.

Mosher's acid analysis

Unfortunately, for the exact determination of the stereochemistry of the rearranged products, no such straightforward way exists. Therefore, phenol **77** was subjected to a number of reactions (Scheme 54). Initial efforts to determine the product's configuration included crystallization of *para*-bromobenzoic ester **141**. Unfortunately, this proved unsuccessful and the said compound was subjected to further derivatization. In this sense, reductive ozonolysis provided primary alcohol **142**. Again, no suitable crystal for X-ray analysis was obtained and the attention was then turned towards the preparation of the corresponding Mosher ester. Esterification of **142** with Mosher's acid (MTPA) under Steglich conditions furnished compound **143**.



Scheme 54 Derivatization using Mosher's acid.

Mosher's method has been established as a reliable method for the determination of absolute configuration of secondary alcohols. However, assigning absolute stereochemistry of primary alcohols is not as widely recognized, as Δδ values are usually irregular. Tsuda *et al.*[50] developed a method to assign the absolute configurations at C2 of chiral primary alcohols by analyzing the chemical shift differences of the geminal protons in the methylene group that connects the chiral benzylic position to the Mosher's ester.

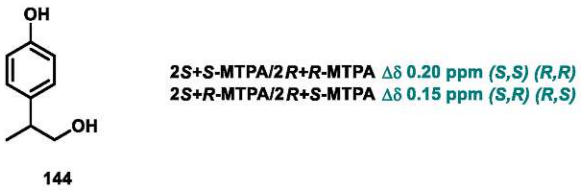


*Figure 10 Δδ values for literature example **144**.*

They provided chemical shift data for the Mosher's esters of primary alcohol **144** (Figure 10), which corresponds to the substructure of compound **142**. The study reported the chemical shifts for both enantiomers/diastereomers, using both enantiomers of alcohol **144** and Mosher's acid, respectively.

The *(R,R)/(S,S)*-enantiomers were reported to show a greater distance between the methylene-signals compared to the *(R,S)/(S,R)*-enantiomers.

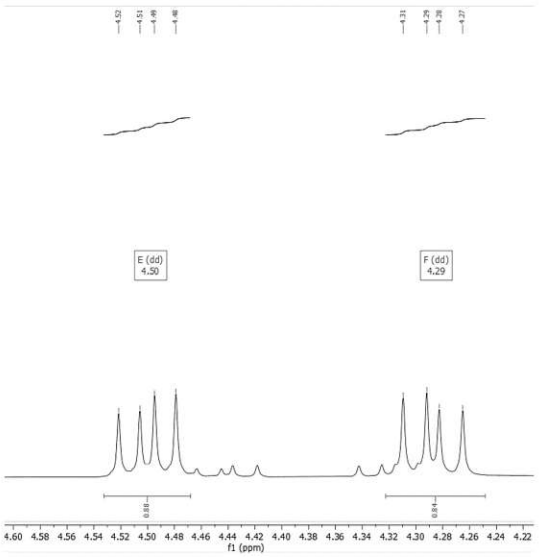


*Figure 11 NMR spectrum of **143s**.*

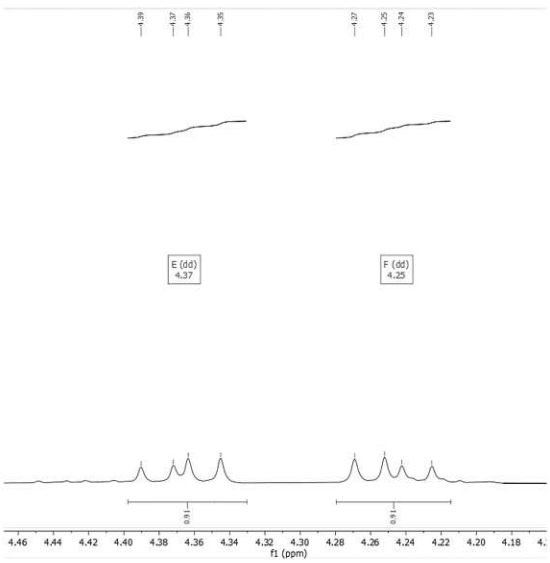


*Figure 12 NMR spectrum of **143r.***

Comparing NMR results of **143s** (Figure 11) and **143r** (Figure 12) the spectra unambiguously demonstrate the difference in the shifts of the geminal hydrogens. For **143s** a greater Δδ was shown than for **143r** (Figure 13). The Δδ values were very comparable with those reported by Tsuda *et al.*

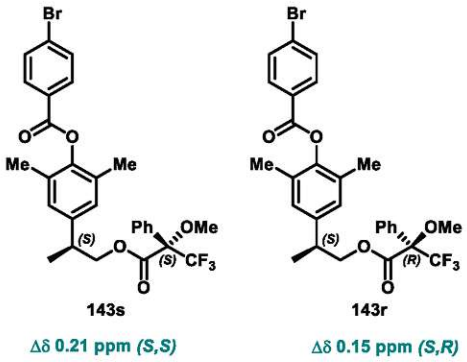


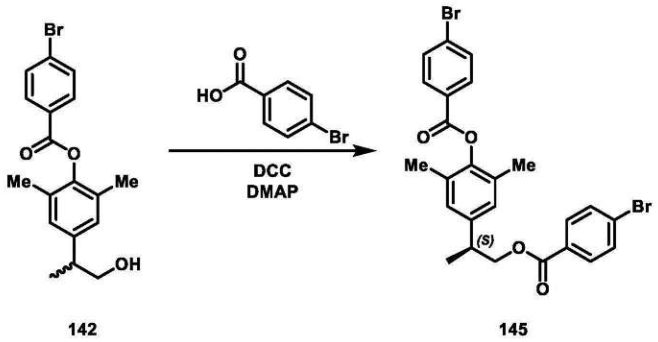
*Figure 13 Δδ values for compounds **143s** and **143r**.*

This ultimately led to the deduction that the **143s** was the *(S,S)*- and **143r** the *(S,R)*-enantiomer. With that, the stereochemistry of **142** can be determined being *(S)*. Since the priorities of the substituents on the stereocenter change after the ozonolysis, this leads to the conclusion that the stereochemistry of the rearranged phenol **78** is the *(R)*-configuration.

In conclusion, it was shown that both the starting material and the rearranged phenols were of *(R)*-configuration. This result is consistent with the established mechanisms of two [3,3]-sigmatropic rearrangements, with inversion for Claisen and inversion for Cope, resulting in the overall retention of absolute configuration.[50]

X-Ray Analysis

This devised stereochemistry was later confirmed through X-ray analysis of the bromoester **145** of the ozonolysis product **142**, which was prepared through a second ester formation reaction (Scheme 55).



142 145

*Scheme 55 Preparation of **145**.*

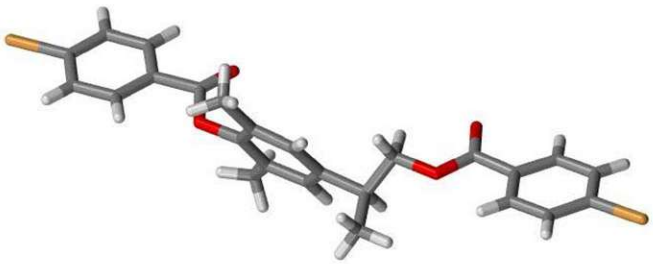


*Figure 14 Crystal structure of **145**.*

The crystal structure confirms *(S)*-configuration of **145** and with that, *(R)*-configuration of the rearranged product **78** (Figure 14).

The stereochemistry of the cyclic allyl ethers was also confirmed by crystallization of compound **99** (Figure 15).

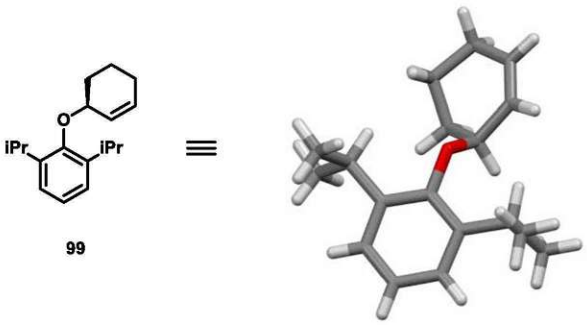


*Figure 15 Crystal structure of **99.***

X-ray analysis confirmed that the Tsuji-Trost reaction delivers the cycloalkenyl-aryl ethers in *(S)*-configuration.

Derivatization

For the determination of enantiomeric excess, it is necessary to achieve sufficient separation on the chiral HPLC, which ideally would give two distinguishable peaks. However, this was not the case for six compounds (Figure 16), as they were too apolar for any separation to be possible. Consequently, it was necessary to find an alternative method for the determination of enantiomeric excess for the compounds in question. The goal was to derivatize the six compounds, to achieve effective separation of the derivatives on the chiral HPLC.

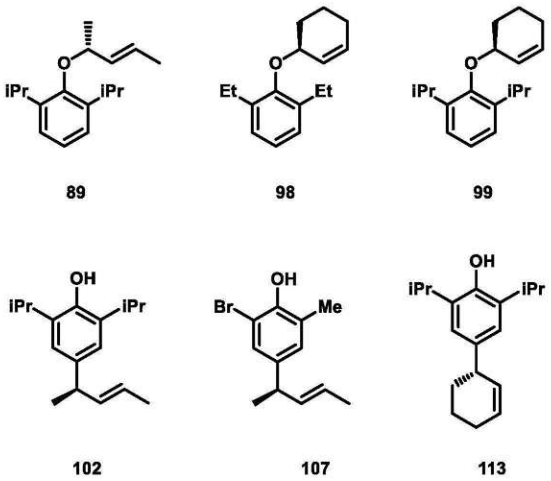
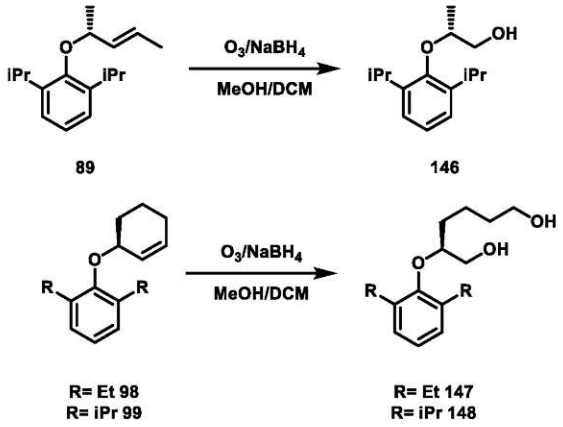


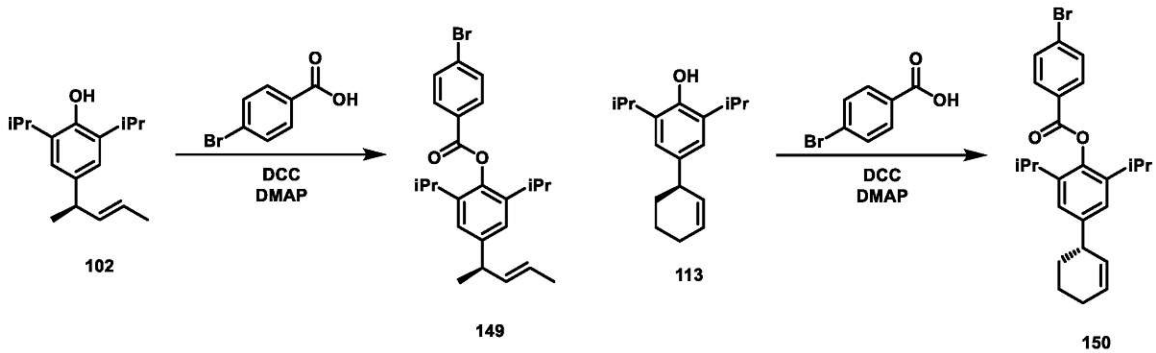
Figure 16 Compounds not separable on HPLC.

The initial approach involved reductive ozonolysis, which proved effective for ethers **89**, **98** and **99** (Scheme 56). The alcohols **146**, **147** and **148** could be separated on chiral HPLC, allowing the enantiomeric excess to be determined for the three compounds.



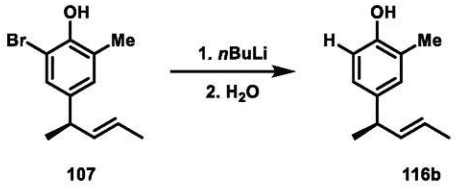
*Scheme 56 Derivatization of **89**, **98** and **99**.*

However, reductive ozonolysis led to decomposition of the rearranged phenols **102** and **113**. Likely, the high electron density led to oxidation of the aromatic core and subsequent decomposition. Therefore, an alternative method was required for **102** and **113**. Next, compound **102** was transformed into the *para*-bromobenzoate **149** (Scheme 57). This shall serve two purposes, first the obtained material should now be separable on chiral HPLC, secondly, it was speculated that the product might provide suitable crystals for X-ray analysis. The latter, unfortunately, did not come true, but enantiomeric excess was determined by chiral HPLC. Similarly, conversion of compound **113** into its *para*-bromobenzoic ester **150** allowed the determination of *ee* by separation on chiral HPLC.



*Scheme 57 Derivatization of **102** and **113**.*

Still, compound **107** presented the greatest challenge. Ozonolysis was ruled out as an option since it had already proven ineffective for phenols **102** and **113**. We then tried the same method using nitrobenzoic acid, in hopes this would change the outcome, but this also failed to achieve separation on HPLC. Finally, treating compound **107** with *n*BuLi followed by an aqueous workup (Scheme 58) afforded compound **116b**, which we had successfully separated on HPLC previously for the mono-substituted substrate (Scheme 46).



*Scheme 58 Derivatization of **107**.*

The measured enantiomeric excess, however, was a bit lower than that of the starting material. It is unclear whether this decrease is due to the treatment with strong base during the derivatization process or if some loss of chirality occurs during the rearrangement of **94** to **107**. This requires further investigation. Nonetheless, the obtained *ee* remains within a good range, comparable to that of the starting material.

Consequently, all enantiomeric excesses were successfully determined.

Experimental section

General information

The reactions were performed as described in the general procedures. All reactions were stirred magnetically.

Phenols were purchased from commercial suppliers and used as received.

General procedure T is a modification of a known literature procedure.

Dry toluene, dichloromethane and tetrahydrofuran were retrieved from an Innovative Technologies PureSolv system. Dichloromethane was degassed by two freeze-thaw cycles.

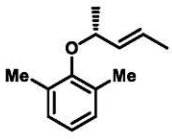
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 at 400 and 101 MHz; AC 600 at 600 and 151 MHz using the solvent peak as reference. ^{13}C NMR spectra were run in proton-decoupled mode. Multiplicities of 1H signals were referred to as s (singlet), d (doublet), t (triplet), q (quartet) and more complex patterns or m (multiplet). TLC-analysis was done with precoated aluminum-backed plates (Silica gel 60 F254, Merck). Compounds were visualized by submerging in: an acidic phosphomolybdic acid / Cerium sulphate solution, $KMnO_4$, Vanillin or Anisaldehyde and dried with a heat gun. Column chromatography was carried out with silica gel Merck 60. Eluent systems refer to volumetric ratios, e.g., 4:1 =80%: 20%. HRMS measurements were carried out in acetonitrile, methanol, water or a mixture on an Agilent 1100/1200 HPLC with binary pumps, a degassed and a column thermostat and an Agilent 6230 AJS ESI-TOF mass spectrometer.

Specific rotations were measured on an Anton Parr MCP 500 polarimeter at 20 °C and 589 nm. Melting points were determined with a Leica Galen III Kofler hot stage apparatus.

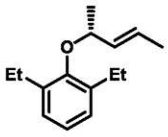
General procedures

General procedure T – Tsuji-Trost reaction by modified literature procedure[30]

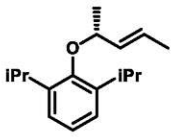
A flame dried Schlenk flask was charged with the respective carbonate (1.1 eq.), $Pd_2dba_3{*}CHCl_3$ (2 mol%), *R,R*-DACH- ligand (6 mol%) and dissolved in dry degassed DCM (0.3 M). After 15 minutes, during which a color change from red to green was observed, phenol (1 eq.) in dry degassed DCM (0.3 M) was added. The mixture was stirred under argon atmosphere for 19 hours. After TLC control confirmed full consumption of starting material, the reaction was filtered over silica (petroleum ether/ethyl acetate 10:1) and concentrated in vacuo. The crude material was subjected to column chromatography.



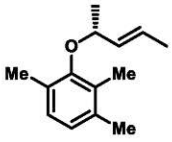
1a
95% *ee*
80% yield



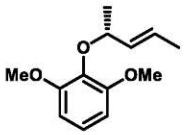
1a
96% *ee*
92% yield



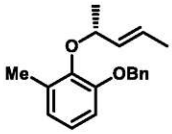
1a
97% *ee*
80% yield



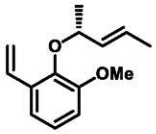
1a
88% *ee*
84% yield



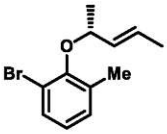
1a
91% *ee*
86% yield



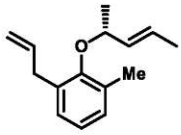
1a
89% *ee*
42% yield



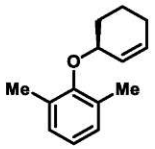
1a
91% *ee*
97% yield



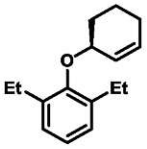
1a
78% *ee*
85% yield



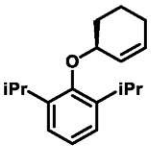
1a
94% *ee*
91% yield



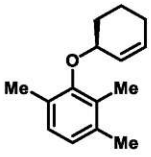
1e
95% *ee*
96% yield



1e
97% *ee*
76% yield



1e
>99% *ee*
84% yield



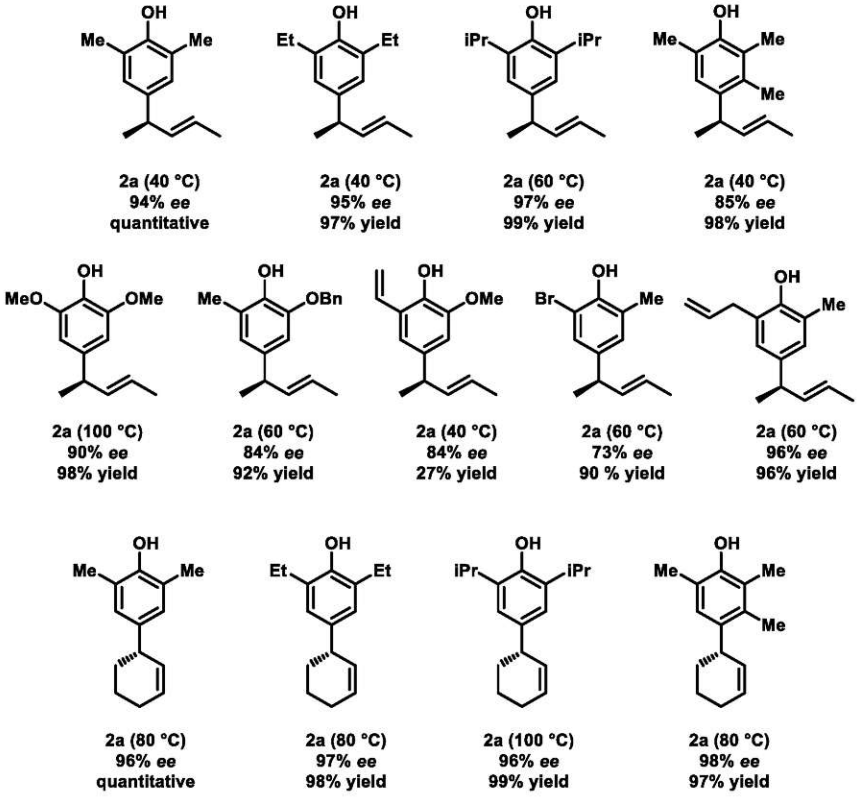
1e
96% *ee*
90% yield

General procedure R – racemic ethers

A flame dried Schlenk flask was charged with phenol (1 eq.), the respective carbonate (1.1 eq.), $Pd(PPh_3)_4$ (4 mol%) and dissolved in dry degassed DCM (0.1 M). The mixture was stirred under argon atmosphere until TLC confirmed full consumption of starting material. The reaction was filtered over silica (petroleum ether/ethyl acetate 10:1) and concentrated *in vacuo*. The crude material was purified by column chromatography.

General procedure C – Claisen-Cope Rearrangement

An 8 mL screw neck vial was charged with starting material (1 eq.) and EuFOD (10 mol%) in dry toluene (1 M). The reaction was heated to a given temperature in a metal heating block until TLC showed full conversion. The reaction was directly purified by column chromatography.



General procedure O – Ozonolysis

A Schlenk flask was charged with the compound (1 eq.) dissolved in DCM/MeOH (1:1, 0.05 M) and cooled to -80 °C. A stream of ozone was bubbled through the solution until it took on a deep blue color. After 7 minutes of further stirring, a stream of oxygen was bubbled through the solution until the blue color disappeared. Subsequently, sodium borohydride (4 eq.) was added at -80 °C and the reaction was allowed to reach room temperature. After stirring at room temperature for 30 minutes, saturated NH_4Cl solution was added. The aqueous phase was extracted with DCM three times, the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was received either sufficiently pure or was subjected to column chromatography.

General procedure C – Bromobenzoic acid

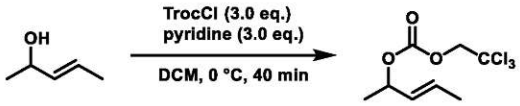
A 8 mL screw neck vial was charged with starting material (1 eq.), DCC (1.2 eq.), DMAP (0.2 eq.) and bromobenzoic acid (1.2 eq.). The mixture was schlenked five times, then dry DCM was added (0.1 M) and the reaction was stirred at room temperature until TLC confirmed full consumption of starting material. The solvent was removed *in vacuo* and the crude material was directly purified by column chromatography (petroleum ether/ethyl acetate 40:1).

General procedure M – Mosher's esters

A 8 mL screw neck vial was charged with starting material (1 eq.), DCC (1.2 eq.), DMAP (0.2 eq.) and the respective MTPA-stereoisomer (1.2 eq.). The mixture was schlenked five times, then dry DCM was added (0.1 M) and the reaction was stirred at room temperature until TLC confirmed full consumption of starting material. The solvent was removed *in vacuo* and the crude material was directly purified by column chromatography (petroleum ether/ethyl acetate 40:1).

Synthetic Procedures

(E)-pent-3-en-2-yl (2,2,2-trichloroethyl) carbonate (**87**)



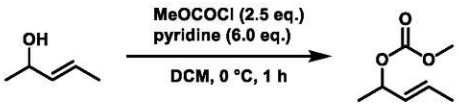
The preparation was carried out following a modified literature procedure[15].

To an ice cooled solution of *(E)*-pent-3-en-2-ol (1.5 g, 17.4 mmol, 1 eq.) and pyridine (4.2 mL, 52.2 mmol, 3.0 eq.) in 70 mL dry DCM, 2,2,2-trichloroethyl chloroformate (4.1 mL, 52.2 mmol, 3 eq.) was added dropwise. The formation of white precipitate was observed, and the reaction mixture was stirred for 40 minutes at 0 °C. After TLC (petroleum ether/ethyl acetate 10:1) confirmed full conversion, the reaction was washed with 1 N HCl three times and the aqueous layer was extracted with DCM. The combined organic layers were then washed with saturated aqueous $NaHCO_3$ solution, brine and dried over $MgSO_4$, filtrated and concentrated. The crude material was purified by distillation and the title compound was obtained as colorless oil in 98% yield (2.47 g, 16.6 mmol, b.p. 104-106 °C @ 6-7 mbar).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (dqd, J = 15.3, 6.6, 0.9 Hz, 1H), 5.46 (ddq, J = 15.3, 7.3, 1.7 Hz, 1H), 5.20 – 5.09 (m, 1H), 4.75 – 4.62 (m, 2H), 1.71 – 1.60 (m, 3H), 1.33 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.43, 130.12, 129.72, 94.71, 77.23, 76.74, 20.42, 17.81.

(E)-pent-3-en-2yl methyl carbonate (**76**)



The preparation was carried out following a modified literature procedure:[51]

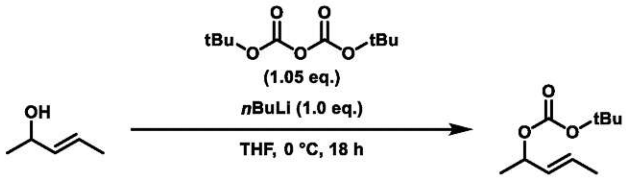
To an ice cooled solution of *(E)*-pent-3-en-2-ol (10 g, 116.1 mmol, 1 eq.) and pyridine (56 mL, 696.6 mmol, 6.0 eq.) in 390 mL dry DCM, methyl chloroformate (22.5 mL, 290.3 mmol, 2.5 eq.) was added dropwise. Formation of white precipitate was observed and the reaction mixture was

stirred for 1 hour at 0 °C. After TLC (petroleum ether/ethyl acetate 10:1) confirmed full conversion, the reaction was quenched with 1 N HCl. The organic phase was washed three times with 1 N HCl, then with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by distillation to give the title compound as colorless oil in 85% yield (14.4 g, 98 mmol, b.p. 62-63 °C@20mbar).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dqd, J = 15.3, 6.5, 1.0 Hz, 1H), 5.49 (ddq, J = 15.3, 7.2, 1.6 Hz, 1H), 5.20 – 5.08 (m, 1H), 3.75 (s, 3H), 1.69 (ddd, J = 6.5, 1.7, 0.7 Hz, 3H), 1.34 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.21, 130.27, 129.11, 75.47, 54.45, 20.39, 17.67.

(E)-tert-butyl pent-3-en-2-yl carbonate (**86**)

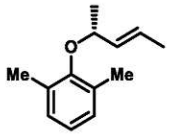


The preparation was carried out following a literature procedure[52].

To an ice cooled solution of *(E)*-pent-3-en-2-ol (1.5 g, 17.4 mmol, 1 eq.) in 24 mL dry THF, *n*BuLi (2.5 M in hexanes, 7.0 mL, 17.4 mmol, 1 eq.) was added dropwise. The formation of white precipitate was observed. The reaction mixture was stirred for 10 minutes and di-*tert*-butyldicarbonate (3 M in THF, 6.1 mL, 18.3 mmol, 1.05 eq.) in dry THF was added quickly. The reaction mixture was allowed to warm to room temperature and was stirred for 18 hours. After TLC (petroleum ether/ethyl acetate 10:1) confirmed full conversion, the mixture was partitioned between Et_2O and water. The organic layer was extracted washed with brine and dried over $MgSO_4$, filtrated and concentrated. After distillation the title compound was obtained as colorless oil in 92% yield (2.98 g, 16.0 mmol, b.p. 85-87 °C @ 20 mbar).

The obtained analytical data is in accordance with literature.

(R,E)-1,3-dimethyl-2-(pent-3-en-2-yloxy)benzene (**77**)



The title compound was synthesized from 2,6-dimethylphenol (100 mg, 0.82 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **77** as colorless oil in 80% yield (124 mg, 0.65 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.03 (m, 2H), 7.03 – 6.92 (m, 1H), 5.80 – 5.67 (m, 1H), 5.64 – 5.50 (m, 1H), 4.50 – 4.40 (m, 1H), 2.45 – 2.27 (m, 6H), 1.78 – 1.70 (m, 3H), 1.51 (ddd, J = 6.4, 2.3, 1.4 Hz, 3H).

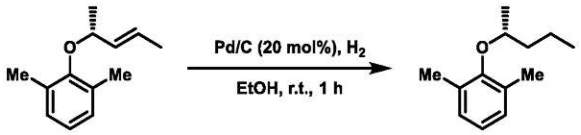
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.73, 132.69, 131.38, 128.72, 127.46, 123.27, 79.21, 21.27, 17.62, 17.27.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$ = +55,96 (c 1.00, CH_2Cl_2).

95% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 14.25 min, major enantiomer. t_r = 16.04 min.

(R)-1,3-dimethyl-2-(pentan-2-yloxy)benzene (**140h**)



A 8 mL screw neck vial was charged with starting material starting material **77** (50 mg, 0.26 mmol, 1 eq.) in 2.6 mL EtOH. The colorless solution was schlenked 10 times then Pd/C (10 wt.%, 59 mg,

53 µmol, 20 mol %) was added. The atmosphere was exchanged to H_2 *via* vacuum/H_2 backfill (5 times) and the mixture was stirred for 1 hour, until TLC showed full conversion. The atmosphere was exchanged to argon by vacuum/argon backfill (5 times) and the black suspension was filtered over silica. The desired product **140h** was obtained as pale-yellow oil in quantitative yield (50 mg, 0.26 mmol) and was used without further purification for HPLC analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 7.4 Hz, 2H), 6.90 (m, 1H), 4.09 (m, 1H), 2.28 (s, 6H), 1.84 – 1.69 (m, 1H), 1.66 – 1.54 (m, 1H), 1.53 – 1.41 (m, 2H), 1.20 (dd, J = 6.2, 0.8 Hz, 3H), 1.01 – 0.92 (m, 3H).

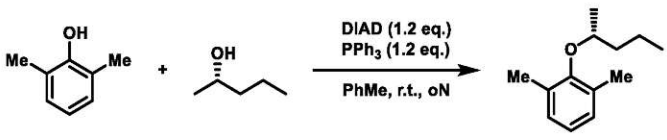
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.73, 131.50, 128.95, 123.18, 77.77, 39.33, 19.85, 19.08, 17.39, 14.42.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$= +7.43 (c 1.10, CH_2Cl_2).

86% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 19.33 min, major enantiomer. t_r = 24.37 min.

(R)-1,3-dimethyl-2-(pentan-2-yloxy)benzene (**140m**)



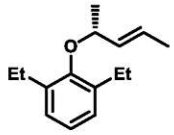
A solution of 2,6-dimethylphenol (40 mg, 0.45 mmol, 1 eq.) and PPh_3 (143 mg, 0.55 mmol, 1.2 eq.) in 0.9 mL dry toluene was cooled by ice bath was added and the mixture was stirred for 15 minutes. Then, DIAD (0,11 mL, 0.55 mmol, 1.2 eq.) was added dropwise and the mixture was allowed to slowly warm up. After stirring over night the solvent was removed *in vacuo* and the crude residue was subjected to column chromatography (petroleum ether/ethyl acetate 30:1). The title compound was obtained as colorless oil in 31% unoptimized yield (27 mg, 0.14 mmol).

The obtained analytical data is in accordance with **140m**.

$[\alpha]_D^{20}$= +10.80 (c 1.35, CH_2Cl_2).

99% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 19.57 min, major enantiomer. t_r = 24.31 min.

(R,E)-1,3-diethyl-2-(pent-3-en-2-yloxy)benzene (**88**)



The title compound was synthesized from 2,6-diethylphenol (50 mg, 0.33 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **88** as colorless oil in 92% yield (67 mg, 0.31 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.02 (m, 2H), 7.02 – 6.95 (m, 1H), 5.60 (ddq, J = 15.3, 7.5, 1.5 Hz, 1H), 5.45 (dqd, J = 15.3, 6.4, 0.7 Hz, 1H), 4.34 – 4.25 (m, 1H), 2.66 (q, J = 7.6 Hz, 4H), 1.67 – 1.59 (m, 3H), 1.39 (d, J = 6.3 Hz, 3H), 1.21 (t, J = 7.6 Hz, 6H).

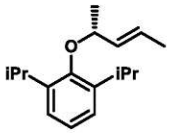
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.58, 137.62, 132.71, 127.70, 126.67, 123.74, 80.26, 23.28, 21.39, 17.76, 14.77.

HRMS (ESI): exact mass calculated for $C_{15}H_{23}O^+$ [(M + H)$^+$], 219.1743; found 219.1749.

$[\alpha]_D^{20}$= +51,18 (c 1.00, CH_2Cl_2).

96% *ee* (determined by chiral HPLC: Chiralpak® OD column, n-Heptane/EtOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 13.46 min, major enantiomer. t_r=14.10 min.

(R,E)-1,3-diisopropyl-2-(pent-3-en-2-yloxy)benzene (**89**)



The title compound was synthesized from 2,6-diisopropylphenol (400 mg, 2.24 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **89** as colorless oil in 90% yield (500 mg, 2.03 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.03 (m, 3H), 5.60 (ddq, J = 15.2, 7.8, 1.6 Hz, 1H), 5.43 (dq, J = 15.2, 6.4 Hz, 1H), 4.28 – 4.17 (m, 1H), 3.35 (hept, J = 7.0 Hz, 2H), 1.64 (dd, J = 6.4, 1.5 Hz, 3H), 1.42 (d, J = 6.3 Hz, 3H), 1.19 (t, J = 6.8 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.57, 142.54, 132.66, 128.08, 124.16, 123.84, 81.29, 26.78, 24.32, 24.11, 21.39, 17.84.

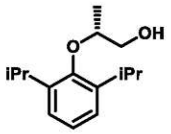
HRMS (ESI): exact mass calculated for $C_{17}H_{27}O^+$ [(M + H)$^+$], 247.2056; found 247.2061.

$[\alpha]_D^{20}$= +61,92 (c 1.00, CH_2Cl_2).

97% *ee* (determined by chiral HPLC of derivative **146**).

m.p. 55-57 °C

(R)-2-(2,6-diisopropylphenoxy)propan-1-ol (**146**)



The title compound was synthesized from **89** (100 mg, 0.41 mmol) following **general procedure O**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide the desired product **146** as colorless oil in 76% yield (73 mg, 0.31 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 3H), 4.23 – 4.09 (m, 1H), 3.86 – 3.71 (m, 2H), 3.38 (hept, J = 6.9 Hz, 2H), 2.12 (dd, J = 7.8, 5.2 Hz, 1H), 1.20 (dd, J = 6.9, 6.2 Hz, 12H), 1.14 (d, J = 6.4 Hz, 3H).

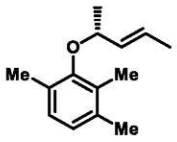
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.53, 142.41, 124.55, 124.13, 79.48, 67.11, 26.61, 24.44, 23.87, 15.92.

HRMS (ESI): exact mass calculated for $C_{15}H_{24}NaO_2^+$ [(M + Na)$^+$], 259.1669; found 259.1642.

$[\alpha]_D^{20}$= -6.52 (c 1.00, CH_2Cl_2).

97% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/EtOH = 99.7:0.3, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 20.95 min, major enantiomer. t_r = 22.19 min.

(R,E)-1,2,4-trimethyl-3-(pent-3-en-2-yloxy)benzene (**90**)



The title compound was synthesized from 2,3,6-trimethylphenol (200 mg, 1.47 mmol) with carbonate **76** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **90** as colorless oil in 84% yield (265 mg, 1.30 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 5.70 – 5.56 (m, 1H), 5.48 (dq, J = 15.4, 6.3 Hz, 1H), 4.36 – 4.24 (m, 1H), 2.22 (s, 6H), 2.16 (s, 3H), 1.65 (dd, J = 6.4, 1.5 Hz, 3H), 1.38 (d, J = 6.4 Hz, 3H).

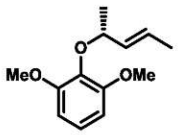
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.57, 135.60, 132.73, 130.21, 128.78, 127.79, 127.51, 124.80, 79.55, 21.21, 20.17, 17.77, 17.31, 13.69.

HRMS (ESI): exact mass calculated for $C_{14}H_{20}NaO^+$ [(M + Na)$^+$], 227.1406; found 227.1409.

$[\alpha]_D^{20}$= +64,07 (c 1.00, CH_2Cl_2).

88% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Hexane/EtOH = 99.9:0.1, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 7.90 min, major enantiomer. t_r = 8.76 min

(R,E)-1,3-dimethoxy-2-(pent-3-en-2-yloxy)benzene (**91**)



The title compound was synthesized from 2,6-dimethoxyphenol (100 mg, 0.65 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide the desired product **91** as yellow oil in 86% yield (124 mg, 0.56 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (t, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 2H), 5.65 (ddq, *J* = 15.2, 7.6, 1.5 Hz, 1H), 5.50 (dqd, *J* = 15.3, 6.4, 0.8 Hz, 1H), 4.65 – 4.54 (m, 1H), 3.82 (s, 6H), 1.66 – 1.57 (m, 3H), 1.38 (d, *J* = 6.4 Hz, 3H).

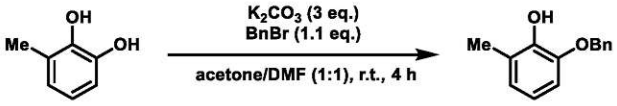
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.24, 136.00, 133.09, 127.42, 123.40, 105.34, 79.42, 56.15, 21.11, 17.73.

HRMS (ESI): exact mass calculated for $C_{13}H_{19}O_3^+$ [(M + H)$^+$], 223.1329; found 223.1333.

$[\alpha]_D^{20}$= +54.08 (c 1.25, CH_2Cl_2).

91% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hextane/iPrOH = 97:3, 0.7 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 18.50 min, major enantiomer. t_r = 21.66 min.

2-(benzyloxy)-6-methylphenol (**151**)

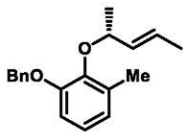


The preparation was carried out following a modified literature procedure.[53]

To a solution of 3-methylbenzene-1,2-diol (1.00 g, 8.1 mmol, 1 eq.) in 24 mL DMF/acetone (2:1) were added K_2CO_3 (3.34 g, 24.2 mmol, 3 eq.) and benzyl bromide (1.52 g, 8.86 mmol, 1.1 eq.). After stirring at room temperature for 4 hours, the reaction mixture was filtered and the solid washed with ethyl acetate. The filtrate was collected and concentrated *in vacuo*. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide the desired product **151** as white solid in 30% yield (523 mg, 2.44 mmol).

The obtained analytical data is in accordance with literature.

(R,E)-1-(benzyloxy)-3-methyl-2-(pent-3-en-2-yloxy)benzene (**92**)



The title compound was synthesized from **151** (100 mg, 0.47 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **92** as clear oil in 42% yield (59 mg, 0.21 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.29 (m, 1H), 6.89 (dd, J = 8.2, 7.4 Hz, 1H), 6.84 – 6.72 (m, 2H), 5.60 (ddq, J = 15.3, 7.6, 1.5 Hz, 1H), 5.52 – 5.35 (m, 1H), 5.08 (s, 2H), 4.80 – 4.66 (m, 1H), 2.25 (s, 3H), 1.60 (dd, J = 6.4, 1.5 Hz, 3H), 1.35 (d, J = 6.3 Hz, 3H).

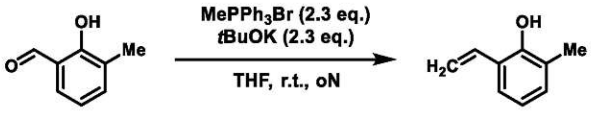
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.22, 145.68, 137.55, 133.18, 133.03, 128.57, 127.89, 127.65, 127.51, 123.41, 123.25, 112.04, 79.07, 70.91, 21.36, 17.76, 17.00.

HRMS (ESI): exact mass calculated for $C_{19}H_{22}NaO_2^+$ [(M + Na)$^+$], 305.1512; found 305.1510.

$[\alpha]_D^{20}$= +48.08 (c 1.30, CH_2Cl_2).

89% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/EtOH = 99.9:0.1, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 29.82 min, major enantiomer. t_r = 31.19 min.

2-methyl-6-vinylphenol (**152**)

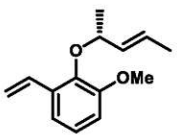


The preparation was carried out following a modified literature procedure[54].

To a solution of methyltriphenylphosphonium bromide (6.03 g, 16.89 mmol, 2.3 eq.) and potassium *tert*-butoxide (1.90 g, 16.89 mmol, 2.3 eq.), in 42 mL anhydrous THF, a solution of 2-hydroxy-3-methylbenzaldehyde (1.00 g, 7.34 mmol, 1 eq.) in 73 mL anhydrous THF was added dropwise. The reaction mixture was stirred overnight. After TLC confirmed full consumption of starting material, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with Et_2O three times. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 10:1), providing the product as colorless oil in 39% yield (386 mg, 2.88 mmol).

The obtained analytical data is in accordance with literature.

(R,E)-1-methoxy-2-(pent-3-en-2-yloxy)-3-vinylbenzene (**93**)



The title compound was synthesized from **152** (100 mg, 0.67 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **93** as colorless oil in 97% yield (142 mg, 0.65 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 1H), 7.06 (dd, J = 17.8, 11.1 Hz, 1H), 6.99 (td, J = 8.0, 0.6 Hz, 1H), 6.80 (dd, J = 8.1, 1.5 Hz, 1H), 5.68 (dd, J = 17.8, 1.5 Hz, 1H), 5.59 (dddd, J = 15.3, 7.3, 2.7, 1.3 Hz, 1H), 5.54 – 5.41 (m, 1H), 5.24 (dd, J = 11.1, 1.5 Hz, 1H), 4.68 – 4.56 (m, 1H), 3.83 (s, 3H), 1.64 – 1.59 (m, 3H), 1.37 (d, J = 6.3 Hz, 3H).

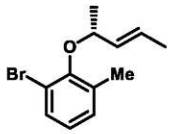
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.38, 144.43, 132.87, 132.64, 132.46, 127.85, 123.57, 117.65, 114.17, 111.49, 79.76, 55.86, 21.14, 17.74.

HRMS (ESI): exact mass calculated for $C_{14}H_{18}NaO^+$ [(M + Na)$^+$], 241.1199; found 241.1170.

$[\alpha]_D^{20}$= +13.85 (c 1.30, CH_2Cl_2).

91% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/iPrOH = 99.4:0.6, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 15.67 min, major enantiomer. t_r = 17.79 min.

(R,E)-1-bromo-3-methyl-2-(pent-3-en-2-yloxy)benzene (**94**)



The title compound was synthesized from 2-bromo-6-methylphenol (100 mg, 0.53 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **94** as colorless oil in 85% yield (115 mg, 0.45 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (ddd, J = 8.0, 1.7, 0.7 Hz, 1H), 7.07 (ddq, J = 7.5, 1.5, 0.7 Hz, 1H), 6.83 (t, J = 7.7 Hz, 1H), 5.63 (ddq, J = 15.3, 8.0, 1.5 Hz, 1H), 5.46 (dqd, J = 15.3, 6.4, 0.7 Hz, 1H), 4.67 (dq, J = 8.3, 6.3 Hz, 1H), 2.26 (d, J = 0.8 Hz, 3H), 1.62 (dd, J = 6.3, 1.5 Hz, 3H), 1.45 (d, J = 6.3 Hz, 3H).

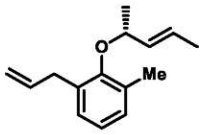
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.22, 134.30, 132.06, 131.16, 130.24, 128.69, 124.64, 118.30, 80.41, 21.26, 17.70.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$= +47.71 (c 1.70, CH_2Cl_2).

78% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 22.59 min, major enantiomer. t_r = 24.00 min.

(R,E)-1-allyl-3-methyl-2-(pent-3-en-2-yloxy)benzene (**95**)



The title compound was synthesized from 2-allyl-6-methylphenol (100 mg, 0.67 mmol) with carbonate **87** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **95** as colorless oil in 91% yield (130 mg, 0.60 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 6.97 (m, 2H), 6.97 – 6.89 (m, 1H), 5.94 (ddt, *J* = 16.8, 6.6, 1.2 Hz, 1H), 5.60 (ddq, *J* = 15.2, 7.6, 1.4 Hz, 1H), 5.52 – 5.39 (m, 1H), 5.14 – 5.02 (m, 2H), 4.33 (p, *J* = 6.6 Hz, 1H), 3.40 (dt, *J* = 6.6, 1.5 Hz, 2H), 2.26 (s, 3H), 1.63 (dd, *J* = 6.3, 1.5 Hz, 3H), 1.39 (dd, *J* = 6.4, 1.2 Hz, 3H).

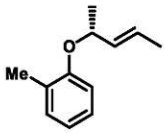
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.24, 137.66, 133.50, 132.55, 131.73, 129.25, 127.89, 123.50, 115.77, 79.90, 34.64, 21.35, 17.75, 17.50.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$= +59.53 (c 1.05, CH_2Cl_2).

94% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 16.41 min, major enantiomer. t_r = 17.72 min.

(R,E)-1-methyl-2-(pent-3-en-2-yloxy)benzene (**115**)



The title compound was synthesized from 2-methylphenol (300 mg, 2.77 mmol) with carbonate **76** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **115** as colorless oil in 98% yield (479 mg, 2.72 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.04 (m, 2H), 6.83 (t, J = 7.3 Hz, 2H), 5.69 (dqd, J = 15.5, 6.3, 0.9 Hz, 1H), 5.55 (ddq, J = 15.5, 6.3, 1.5 Hz, 1H), 4.73 (p, J = 6.3 Hz, 1H), 2.22 (s, 3H), 1.69 (ddd, J = 6.4, 1.5, 0.8 Hz, 3H), 1.40 (d, J = 6.3 Hz, 3H).

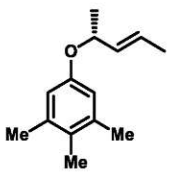
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 131.56, 129.60, 126.67, 125.66, 125.41, 119.20, 112.58, 73.60, 20.65, 16.67, 15.42.

HRMS (ESI): exact was not found after multiple attempts.

81% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/EtOH = 99.9:0.1, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 9.86 min, major enantiomer. t_r = 11.64 min.

$[\alpha]_D^{20}$= +17.15 (c 0.67, CH_2Cl_2).

(R,E)-1,2,3-trimethyl-5-(pent-3-en-2-yloxy)benzene (**57**)



The title compound was synthesized from 3,4,5-trimethylphenol (150 mg, 1.10 mmol) with carbonate 87 following **general procedure T**. The crude material was purified by column

chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **57** as colorless oil in 76% yield (171 mg, 0.84 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 5.77 – 5.64 (m, 1H), 5.55 (ddq, J = 15.4, 6.4, 1.6 Hz, 1H), 4.77 – 4.66 (m, 1H), 2.24 (s, 6H), 2.09 (s, 3H), 1.78 – 1.66 (m, 3H), 1.37 (dd, J = 6.3, 1.8 Hz, 3H).

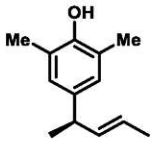
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.48, 137.49, 132.65, 126.96, 115.39, 74.18, 21.56, 20.98, 17.89, 14.72

HRMS (ESI): exact mass calculated for $C_{14}H_{21}O^+$ [(M + H)$^+$], 205.1587; found 205.1588.

$[\alpha]_D^{20}$= +29.32 (c 1.20, CH_2Cl_2).

87% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 ML/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r =30.35 min, major enantiomer. t_r = 34.17 min.

(R,E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenol (**78**)



The title compound was synthesized from **77** (100 mg, 0.53 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **78** as clear oil in quantitative yield (100 mg, 0.53 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 5.58 (ddq, J = 15.2, 6.7, 1.5 Hz, 1H), 5.49 – 5.38 (m, 1H), 4.61 (s, 1H), 3.29 (p, J = 7.0 Hz, 1H), 2.25 (s, 6H), 1.71 – 1.62 (m, 3H), 1.29 (d, J = 7.0 Hz, 3H).

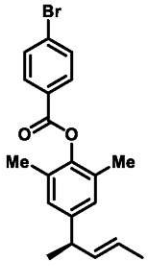
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.63, 138.38, 136.90, 127.34, 123.22, 123.06, 41.74, 21.83, 18.07, 16.20.

HRMS (ESI): exact mass calculated for $C_{13}H_{17}O^-$ [(M - H)$^-$], 189.1285; found 189.1284.

$[\alpha]_D^{20}$= -6.02 (c 1.00, CH_2Cl_2).

94% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/EtOH = 99.5:0.5, 0.7 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 19.37 min, major enantiomer. t_r = 20.38 min.

(R,E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (**141**)



The title compound was synthesized from **78** (41 mg, 0.21 mmol) following **general procedure B**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **141** as colorless oil in 88% yield (71 mg, 0.19 mmol).

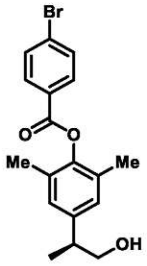
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.70 – 7.63 (m, 2H), 6.93 (d, J = 1.1 Hz, 2H), 5.60 (ddd, J = 15.2, 6.8, 1.5 Hz, 1H), 5.54 – 5.40 (m, 1H), 3.36 (q, J = 7.0 Hz, 1H), 2.15 (d, J = 0.7 Hz, 6H), 1.68 (dt, J = 6.2, 1.3 Hz, 3H), 1.32 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.93, 146.36, 144.21, 136.34, 132.12, 131.77, 129.96, 128.89, 128.41, 127.50, 123.74, 41.96, 21.65, 18.07, 16.59.

HRMS (ESI): exact mass calculated for $C_{20}H_{22}BrO_2^+$ [(M + H)$^+$], 373.0798; found 373.0802.

$[\alpha]_D^{20}$= -6.37 (c 0.67, CH_2Cl_2).

(S)-4-(1-hydroxypropan-2-yl)-2,6-dimethylphenyl 4-bromobenzoate (**142**)



The title compound was synthesized from **141** (1.00 g, 2.68 mmol) following **general procedure O**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **142** as colorless oil in 56% yield (974 mg, 1.69 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.73 – 7.62 (m, 2H), 6.97 (s, 2H), 3.70 (t, J = 5.7 Hz, 2H), 2.91 (h, J = 6.9 Hz, 1H), 2.16 (s, 6H), 1.27 (d, J = 7.0 Hz, 3H).

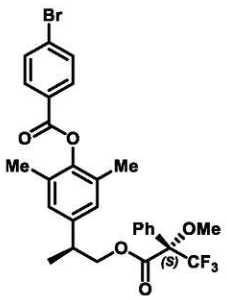
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.95, 146.89, 141.49, 132.14, 131.75, 130.34, 128.99, 128.22, 127.85, 68.77, 42.02, 17.73, 16.57.

HRMS (ESI): exact mass calculated for $C_{18}H_{19}BrNaO_3^+$ [(M + Na)$^+$], 385.0410; found 385.0416.

$[\alpha]_D^{20}$= -8.73 (c 1.00, CH_2Cl_2).

80% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/EtOH = 99:1, 0.7 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 57.46 min, major enantiomer. t_r = 62.26 min.

2,6-dimethyl-4-((*S*)-1-(((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)propan-2-yl)phenyl 4-bromobenzoate (**143s**)



The title compound was synthesized from **142** (16 mg, 44 µmol) following **general procedure M** using *(S)*-MTPA. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **143s** as colorless oil in 47% yield (12 mg, 21 µmol).

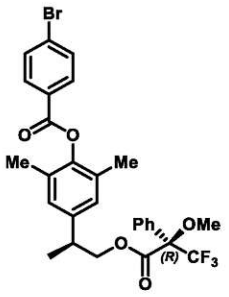
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 2H), 7.70 – 7.65 (m, 2H), 7.45 – 7.35 (m, 5H), 6.93 (d, J = 4.6 Hz, 2H), 4.50 (dd, J = 10.7, 6.3 Hz, 1H), 4.29 (dd, J = 10.8, 7.0 Hz, 1H), 3.46 (q, J = 1.3 Hz, 3H), 3.15 (dt, J = 13.7, 6.8 Hz, 1H), 2.12 (d, J = 1.8 Hz, 6H), 1.29 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.56, 163.70, 147.00, 139.92, 132.21, 132.06, 131.65, 130.28, 129.55, 128.90, 128.39, 128.13, 127.65, 127.32, 71.34, 55.39, 38.16, 17.85, 16.41.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$= -26.74 (c 1.00, CH_2Cl_2).

2,6-dimethyl-4-((*S*)-1-(((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)propan-2-yl)phenyl 4-bromobenzoate (**143r**)



The title compound was synthesized from **142** (25 mg, 69 µmol) following **general procedure M** using *(R)*-MTBA. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **143r** as colorless oil in 83% yield (33 mg, 57 µmol).

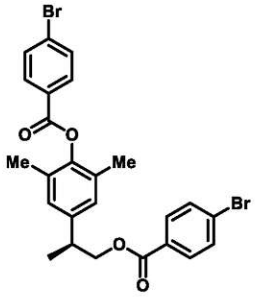
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H), 7.73 – 7.63 (m, 2H), 7.46 – 7.31 (m, 5H), 6.94 (d, J = 4.7 Hz, 2H), 4.45 (dd, J = 10.7, 7.4 Hz, 1H), 4.33 (dd, J = 10.7, 6.8 Hz, 1H), 3.47 – 3.40 (m, 3H), 3.18 – 3.05 (m, 1H), 2.12 (s, 6H), 1.30 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 163.84, 147.13, 140.05, 132.20, 131.79, 130.42, 129.68, 129.04, 128.52, 128.27, 127.78, 127.45, 71.48, 55.52, 38.30, 17.99, 16.54.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$= +7.2799 (c 0.67, CH_2Cl_2).

(S)-2-(4-((4-bromobenzoyl)oxy)-3,5-dimethylphenyl)propyl 4-bromobenzoate (**145**)



The title compound was synthesized from **142** (112 mg, 0.31 mmol) following **general procedure B**. The crude material was purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to provide the desired product **145** as colorless oil in 91% yield (154 mg, 0.28 mmol).

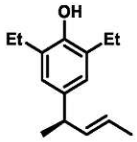
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.02 (m, 2H), 7.89 – 7.82 (m, 2H), 7.73 – 7.64 (m, 2H), 7.62 – 7.54 (m, 2H), 7.01 (s, 2H), 4.48 – 4.26 (m, 2H), 3.19 (h, J = 7.0 Hz, 1H), 2.16 (s, 6H), 1.38 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.92, 163.88, 147.03, 140.71, 132.18, 131.86, 131.79, 131.24, 130.38, 129.36, 129.03, 128.26, 128.17, 127.74, 70.26, 38.63, 18.17, 16.60.

HRMS (ESI): exact was not found after multiple attempts.

$[\alpha]_D^{20}$= -25.01 (c 1.00, CH_2Cl_2).

(R,E)-2,6-diethyl-4-(pent-3-en-2-yl)phenol (**101**)



The title compound was synthesized from **88** (100 mg, 0.46 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **101** as clear oil in 97% yield (97 mg, 0.45 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.60 (ddq, J = 15.2, 6.8, 1.5 Hz, 1H), 5.45 (dqd, J = 15.2, 6.3, 1.2 Hz, 1H), 4.51 (s, 1H), 3.32 (p, J = 7.1 Hz, 1H), 2.61 (q, J = 7.6 Hz, 4H), 1.67 (ddd, J = 6.3, 1.5, 1.0 Hz, 3H), 1.30 (d, J = 7.0 Hz, 3H), 1.25 (t, J = 7.6 Hz, 6H).

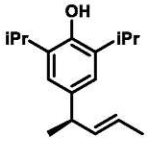
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.49, 138.56, 136.97, 129.15, 125.48, 123.18, 41.97, 23.41, 21.89, 18.08, 14.21.

HRMS (ESI): exact mass calculated for $C_{15}H_{21}O^-$ [(M - H)$^-$], 217.1598; found 217.1595.

$[\alpha]_D^{20}$= -4.60 (c 1.00, CH_2Cl_2).

95% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 34.09 min, major enantiomer. t_r = 35.71 min.

(R,E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenol (**102**)



The title compound was synthesized from **89** (100 mg, 0.41 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **102** as clear oil in 99% yield (99 mg, 0.41 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 5.61 (ddq, J = 15.2, 6.9, 1.5 Hz, 1H), 5.45 (dqd, J = 15.3, 6.3, 1.3 Hz, 1H), 4.70 (s, 1H), 3.34 (p, J = 6.9 Hz, 1H), 3.15 (hept, J = 6.9 Hz, 2H), 1.67 (d, J = 6.3 Hz, 3H), 1.31 (d, J = 7.0 Hz, 3H), 1.27 (d, J = 6.9 Hz, 12H).

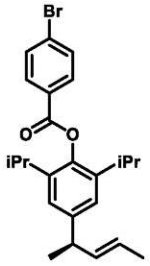
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.26, 138.50, 137.02, 133.54, 123.15, 122.17, 42.36, 27.52, 22.91, 21.97, 18.07.

HRMS (ESI): exact mass calculated for $C_{17}H_{25}O^-$ [(M - H)$^-$], 245.1911; found 245.1906.

$[\alpha]_D^{20}$= -5.39 (c 1.00, CH_2Cl_2).

97% *ee* (determined by chiral HPLC of derivative **149**).

(R,E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (**149**)



The title compound was synthesized from **102** (20 mg, 0.08 mmol) following **general procedure B**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **149** as colorless oil in 77% yield (27 mg, 0.06 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.73 – 7.63 (m, 2H), 7.02 (s, 2H), 5.70 – 5.57 (m, 1H), 5.57 – 5.43 (m, 1H), 3.42 (p, J = 7.0 Hz, 1H), 2.91 (hept, J = 6.7 Hz, 2H), 1.70 (dt, J = 6.3, 1.3 Hz, 3H), 1.35 (d, J = 7.0 Hz, 3H), 1.20 (d, J = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.83, 144.62, 143.91, 140.05, 136.49, 132.20, 131.82, 128.93, 128.57, 123.68, 122.96, 122.78, 42.56, 27.96, 24.03, 22.80, 21.83, 18.07.

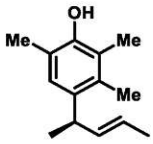
HRMS (ESI): exact mass calculated for $C_{24}H_{30}BrO_2^+$ [(M + H)$^+$], 429.1424; found 429.1434.

$[\alpha]_D^{20}$= -4.83 (c 1.30, CH_2Cl_2).

97% *ee* (determined by chiral HPLC: Chiralpak® OD column, n-Heptane/EtOH = 99.9:0.1, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 20.89 min, major enantiomer. t_r = 22.28 min.

m.p. 85-87 °C

(R,E)-2,3,6-trimethyl-4-(pent-3-en-2-yl)phenol (**103**)



The title compound was synthesized from **90** (100 mg, 0.49 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **103** as white solid in 98% yield (98 mg, 0.49 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 5.59 (ddq, *J* = 15.2, 6.2, 1.6 Hz, 1H), 5.41 (dqd, *J* = 15.3, 6.4, 1.4 Hz, 1H), 4.79 (s, 1H), 3.63 (ddt, *J* = 8.4, 7.0, 5.7 Hz, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H), 1.68 (dt, *J* = 6.3, 1.4 Hz, 3H), 1.29 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.36, 136.47, 136.32, 133.12, 125.89, 123.23, 122.33, 120.09, 37.73, 21.20, 18.11, 16.25, 15.19, 12.64.

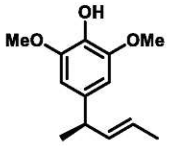
HRMS (ESI): exact mass calculated for $C_{14}H_{19}O^-$ [(M - H)$^-$], 203.1441; found 203.1443.

$[\alpha]_D^{20}$= -2.28 (c 1.00, CH_2Cl_2).

85% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/EtOH = 99.8:0.2, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 25.02 min, major enantiomer. t_r = 26.59 min.

m.p. 56-58 °C

(R,E)-2,6-dimethoxy-4-(pent-3-en-2-yl)phenol (**104**)



The title compound was synthesized from **91** (100 mg, 0.41 mmol) following **general procedure C** at 100 °C overnight. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide the desired product **104** as yellow oil in 98% yield (98 mg, 0.41 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (s, 2H), 5.59 (ddq, J = 15.2, 6.5, 1.5 Hz, 1H), 5.47 (dqd, J = 15.2, 6.2, 1.3 Hz, 1H), 5.36 (s, 1H), 3.88 (s, 6H), 3.33 (p, J = 7.0 Hz, 1H), 1.68 (dt, J = 6.2, 1.3 Hz, 3H), 1.31 (dd, J = 7.0, 1.5 Hz, 3H).

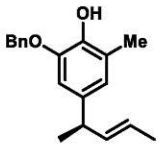
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.00, 137.81, 136.40, 132.99, 123.65, 103.84, 56.36, 42.56, 21.77, 18.02.

HRMS (ESI): exact mass calculated for $C_{13}H_{19}O_3^+$ [(M + H)$^+$], 223.1329; found 223.1333.

$[\alpha]_D^{20}$= +2.05 (c 1.00, CH_2Cl_2).

90% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/EtOH = 96.5:3.5, 0.7 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 21.66 min, minor enantiomer. t_r = 27.59 min.

(R,E)-2-(benzyloxy)-6-methyl-4-(pent-3-en-2-yl)phenol (**105**)



The title compound was synthesized from **92** (50 mg, 0.18 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum

ether/ethyl acetate 40:1) to provide the desired product **105** as clear oil in 92% yield (46 mg, 0.16 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 5H), 6.66 (dd, J = 11.3, 2.0 Hz, 2H), 5.64 (d, J = 1.5 Hz, 1H), 5.63 – 5.56 (m, 1H), 5.47 (dqd, J = 15.3, 6.3, 1.2 Hz, 1H), 5.11 (s, 2H), 3.33 (p, J = 7.0 Hz, 1H), 2.28 (s, 3H), 1.71 (dt, J = 6.3, 1.3 Hz, 3H), 1.33 (d, J = 7.0 Hz, 3H).

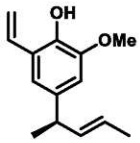
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.41, 142.20, 137.54, 136.79, 136.71, 128.79, 128.42, 128.04, 123.85, 123.39, 121.96, 108.85, 71.30, 42.10, 21.80, 18.07, 15.73.

HRMS (ESI): exact mass calculated for $C_{19}H_{21}O_2^-$ [(M - H)$^-$], 281.1547; found 281.1552.

$[\alpha]_D^{20}$= -4.49 (c 1.00, CH_2Cl_2).

84% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/EtOH = 99.8:0.2, 0.5 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 42.53 min, minor enantiomer. t_r = 48.13 min.

(R,E)-2-methoxy-4-(pent-3-en-2-yl)-6-vinylphenol (**106**)



The title compound was synthesized from **93** (100 mg, 0.49 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **106** as clear oil in 27% unoptimized yield (27 mg, 0.13 mmol) together with a mixture of the product and an unidentified sideproduct.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dd, J = 17.8, 11.2 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H), 6.62 (d, J = 1.9 Hz, 1H), 5.81 (dd, J = 17.8, 1.6 Hz, 1H), 5.76 (s, 1H), 5.61 (ddq, J = 15.2, 6.5, 1.5 Hz, 1H), 5.47 (dqd, J = 15.3, 6.3, 1.2 Hz, 1H), 5.29 (dd, J = 11.2, 1.5 Hz, 1H), 3.89 (s, 3H), 3.34 (p, J = 7.0 Hz, 1H), 1.69 (dt, J = 6.2, 1.3 Hz, 3H), 1.32 (d, J = 7.0 Hz, 3H).

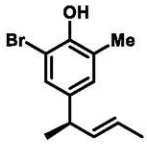
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.65, 141.62, 137.76, 136.54, 131.48, 123.64, 123.54, 117.11, 114.75, 108.93, 56.23, 42.28, 21.76, 18.06.

HRMS (ESI): exact mass calculated for $C_{14}H_{17}O_2^-$ [(M - H)$^-$], 217.1234; found 217.1241.

$[\alpha]_D^{20}$= -6.50 (c 1.10, CH_2Cl_2).

84% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/EtOH = 98:2, 0.5 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 16.00 min, minor enantiomer. t_r = 18.42 min.

(R,E)-2-bromo-6-methyl-4-(pent-3-en-2-yl)phenol (**107**)



The title compound was synthesized from **94** (70 mg, 0.27 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **107** as clear oil in 90% yield (63 mg, 0.25 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 2.1 Hz, 1H), 6.92 – 6.88 (m, 1H), 5.59 – 5.50 (m, 1H), 5.50 – 5.41 (m, 1H), 5.40 (d, J = 6.9 Hz, 1H), 3.29 (p, J = 6.9 Hz, 1H), 2.27 (d, J = 0.7 Hz, 3H), 1.68 (dt, J = 6.1, 1.2 Hz, 3H), 1.28 (d, J = 7.0 Hz, 3H).

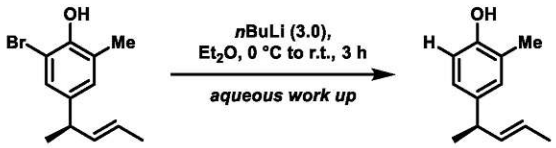
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.60, 139.69, 136.08, 129.43, 127.76, 125.66, 124.00, 110.07, 41.47, 21.65, 18.05, 16.88.

HRMS (ESI): exact mass calculated for $C_{12}H_{14}BrO^-$ [(M - H)$^-$], 253.0234; found 253.0243.

$[\alpha]_D^{20}$= -7.87 (c 0.70, CH_2Cl_2).

72% *ee* (determined by chiral HPLC of derivative **116b**).

(R,E)-2-methyl-4-(pent-3-en-2-yl)phenol (**116b**)



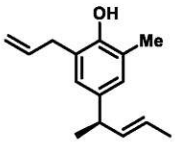
The preparation was carried out following a modified literature procedure[55].

To an ice cooled solution of **107** (15 mg, 58 µmol, 1 eq.) in 24 mL dry Et_2O, *n*BuLi (2.5 M in hexanes, 0.1 mL, 176 µmol, 3 eq.) was added dropwise. The reaction was allowed to warm to room temperature. After three hours TLC (petroleum ether/ethyl acetate 10:1) confirmed full conversion, the reaction was quenched with water. The mixture was partitioned between Et_2O and water. The organic layer was extracted washed with brine and dried over $MgSO_4$, filtrated and concentrated affording as colorless oil in 77% yield (8 mg, 45 µmol).

The obtained analytical data is in accordance with **116**.

72% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/EtOH = 97:3, 0.7 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 22.12 min, major enantiomer. t_r = 23.50 min.

(R,E)-2-allyl-6-methyl-4-(pent-3-en-2-yl)phenol (**108**)



The title compound was synthesized from **95** (50 mg, 0.23 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **108** as clear oil in 96% yield (48 mg, 0.22 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 2.3 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.11 – 5.97 (m, 1H), 5.61 (ddt, J = 15.2, 6.8, 1.4 Hz, 1H), 5.54 – 5.38 (m, 1H), 5.27 – 5.14 (m, 2H), 4.88 (dd, J =

3.0, 1.1 Hz, 1H), 3.42 (dt, J = 6.4, 1.5 Hz, 2H), 3.32 (p, J = 7.0 Hz, 1H), 2.25 (s, 3H), 1.70 (dq, J = 6.2, 1.3 Hz, 3H), 1.31 (dd, J = 7.0, 1.1 Hz, 3H).

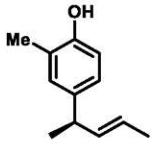
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.88, 138.50, 136.88, 136.84, 128.07, 126.73, 124.45, 124.21, 123.27, 116.65, 41.74, 36.01, 21.83, 18.06, 16.12.

HRMS (ESI): exact mass calculated for $C_{15}H_{19}O^-$ [(M - H)$^-$], 215.1441; found 215.1453.

$[\alpha]_D^{20}$= -4.28 (c 1.00, CH_2Cl_2).

96% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 36.08 min, major enantiomer. t_r = 37.44 min.

(R,E)-2-methyl-4-(pent-3-en-2-yl)phenol (**116**)



The title compound was synthesized from **115** (30 mg, 0.17 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **116** as clear oil in 40% yield (12 mg, 68 µmol) accompanied by 60% (18 mg, 102 µmol) of compound **110**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.94 (d, J = 7.9 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 5.59 (ddq, J = 15.2, 6.7, 1.5 Hz, 1H), 5.44 (dqd, J = 15.3, 6.3, 1.3 Hz, 1H), 3.34 (q, J = 7.1 Hz, 1H), 2.32 (s, 3H), 1.67 (dt, J = 6.3, 1.3 Hz, 3H), 1.30 (d, J = 7.0 Hz, 3H).

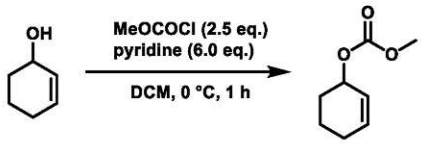
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.36, 138.92, 136.80, 129.90, 125.73, 123.72, 123.37, 115.05, 41.69, 21.78, 18.05, 16.09.

HRMS (ESI): exact mass calculated for $C_{12}H_{15}O^-$ [(M - H)$^-$], 175.1128; found 175.1133.

83% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/EtOH = 97:3, 0.7 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 21.49 min, major enantiomer. t_r = 22.61 min.

$[\alpha]_D^{20}$= -3,26 (c 0.67, CH_2Cl_2).

(±)-cyclohex-2-enyl methyl carbonate (**96**)



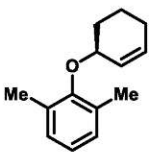
The preparation was carried out following a modified literature procedure:[51]

Methyl chloroformate (9.9 mL, 127.4 mmol, 2.5 eq.) was added dropwise to an ice cooled solution of 2-cyclohexene-1-ol (5 g, 51.0 mmol, 1 eq.) and pyridine (25 mL, 305.7 mmol, 6.0 eq.) in 160 mL dry DCM. Formation of white precipitate was observed and the reaction mixture was stirred for one hour at 0 °C. After TLC (petroleum ether/ethyl acetate 10:1) confirmed full conversion reaction was quenched with 1 N HCl. The organic phase was washed three times with 1 N HCl, then with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated, and concentrated under reduced pressure affording a colorless oil. The desired carbonate was obtained in 97% yield, without the need for further purification (7.7 g, 49.3 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 – 5.05 (m, 1H), 5.83 – 5.71 (m, 1H), 5.12 (td, J = 5.2, 3.3 Hz, 1H), 3.77 (s, 3H), 2.17 – 1.58 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.64, 133.50, 125.07, 72.04, 54.66, 28.34, 24.97, 18.70.

(S)-2-(cyclohex-2-en-1-yloxy)-1,3-dimethylbenzene (**97**)



The title compound was synthesized from 2,6-dimethylphenol (150 mg, 1.24 mmol) with carbonate **96** following **general procedure T**. The crude material was purified by column chromatography

(petroleum ether/ethyl acetate 30:1) to provide the desired product **97** as colorless oil in 96% yield (239 mg, 1.19 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 7.8 Hz, 2H), 6.96 – 6.84 (m, 1H), 5.92 (dtd, J = 10.2, 3.6, 1.2 Hz, 1H), 5.85 (ddt, J = 10.1, 3.8, 2.0 Hz, 1H), 4.37 (td, J = 5.1, 3.3 Hz, 1H), 2.29 (s, 6H), 2.20 – 2.08 (m, 1H), 2.05 – 1.77 (m, 4H), 1.68 – 1.56 (m, 1H).

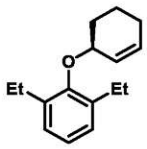
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.27, 131.55, 131.43, 128.95, 127.51, 123.39, 75.46, 29.41, 25.41, 19.32, 17.41.

HRMS (ESI): exact mass calculated for $C_{14}H_{19}O$ [(M + H)$^+$], 203.1430; found 203.1432.

$[\alpha]_D^{20}$= -133.82 (c 1.00, CH_2Cl_2).

95% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 29.06 min, minor enantiomer. t_r = 31.56 min.

(S)-2-(cyclohex-2-en-1-yloxy)-1,3-diethylbenzene (**98**)



The title compound was synthesized from 2,6-diethylphenol (200 mg, 1.33 mmol) with carbonate **96** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **98** as colorless oil in 76% yield (232 mg, 1.01 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.04 (m, 2H), 7.04 – 6.98 (m, 1H), 5.91 (dtd, J = 10.2, 3.6, 1.2 Hz, 1H), 5.83 (ddt, J = 10.1, 3.3, 2.0 Hz, 1H), 4.41 – 4.28 (m, 1H), 2.70 (q, J = 7.6 Hz, 4H), 2.22 – 2.09 (m, 1H), 2.04 – 1.78 (m, 4H), 1.68 – 1.56 (m, 1H), 1.22 (t, J = 7.6 Hz, 6H).

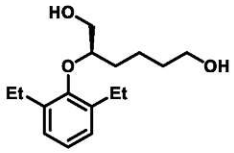
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.06, 137.55, 131.41, 127.55, 126.86, 123.81, 76.39, 29.35, 25.43, 23.40, 19.42, 14.80.

HRMS (ESI): exact mass calculated for $C_{17}H_{27}O$ [(M + H)$^+$], 247.2062; found 247.2061.

97% *ee* (determined by chiral HPLC of derivative **147**).

$[\alpha]_D^{20}$= -122.33 (c 1.00, CH_2Cl_2).

(R)-2-(2,6-diethylphenoxy)hexane-1,6-diol (**147**)



The title compound was synthesized from **98** (50 mg, 0.22 mmol) following **general procedure O**. The desired product was obtained in sufficient purity as colorless oil in 92% yield (53 mg, 0.20 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 6.94 (m, 3H), 4.02 (ddd, J = 8.7, 5.1, 3.5 Hz, 1H), 3.83 (dd, J = 11.8, 3.4 Hz, 1H), 3.71 (dd, J = 11.8, 5.4 Hz, 1H), 3.59 (t, J = 6.4 Hz, 2H), 2.68 (q, J = 7.5 Hz, 4H), 1.80 – 1.25 (m, 8H), 1.21 (t, J = 7.6 Hz, 6H).

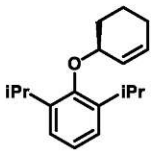
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.65, 137.29, 127.08, 124.11, 82.53, 64.21, 62.42, 32.75, 29.94, 23.28, 21.89, 14.80.

HRMS (ESI): exact mass calculated for $C_{16}H_{26}NaO_3^+$ [(M + Na)$^+$], 289.1774; found 289.1777.

$[\alpha]_D^{20}$= +8.76 (c 0.50, CH_2Cl_2).

97% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/EtOH = 98.5:1.5, 0.5 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 67.69 min, minor enantiomer. t_r = 71.79 min.

(S)-2-(cyclohex-2-en-1-yloxy)-1,3-diisopropylbenzene (**99**)



The title compound was synthesized from 2,6-diisopropylphenol (200 mg, 1.12 mmol) with carbonate **96** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **99** as white solid in 84% yield (243 mg, 0.94 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 3H), 5.92 (dtd, J = 10.2, 3.5, 1.3 Hz, 1H), 5.83 (ddt, J = 10.1, 3.9, 2.1 Hz, 1H), 4.33 – 4.24 (m, 1H), 3.40 (hept, J = 6.9 Hz, 2H), 2.23 – 2.08 (m, 1H), 2.07 – 1.79 (m, 4H), 1.69 – 1.57 (m, 1H), 1.21 (d, J = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.01, 142.44, 131.41, 127.42, 124.22, 123.99, 77.23, 29.17, 26.78, 25.43, 24.30, 24.11, 19.44.

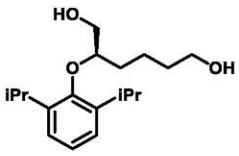
HRMS (ESI): exact mass calculated for $C_{18}H_{27}O^+$ [(M + H)$^+$], 259.2056; found 259.2061.

$[\alpha]_D^{20}$= -117.23 (c 1.00, CH_2Cl_2).

>99% *ee* (determined by chiral HPLC of derivative **148**).

m.p. 55-57 °C

(R)-2-(2,6-diisopropylphenoxy)hexane-1,6-diol (**148**)



The title compound was synthesized from **99** (200 mg, 0.77 mmol) following **general procedure O**. The desired product was obtained in sufficient purity as colorless oil in 57% yield (131 mg, 0.44 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 3H), 3.97 (dtd, J = 8.7, 5.1, 3.3 Hz, 1H), 3.88 (ddd, J = 11.8, 7.2, 3.2 Hz, 1H), 3.75 (dt, J = 11.5, 5.6 Hz, 1H), 3.61 (q, J = 6.2 Hz, 2H), 3.36 (hept, J = 6.9 Hz, 2H), 2.01 (dd, J = 7.3, 5.5 Hz, 1H), 1.75 – 1.57 (m, 2H), 1.54 – 1.49 (m, 1H), 1.46 – 1.23 (m, 3H), 1.20 (dd, J = 6.9, 4.2 Hz, 12H).

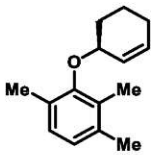
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.54, 142.30, 124.55, 124.16, 83.48, 64.39, 62.59, 32.80, 29.72, 26.62, 24.36, 23.96, 22.02.

HRMS (ESI): exact mass calculated for $C_{18}H_{31}O_3^+$ [(M + H)$^+$], 295.2268; found 295.2270.

$[\alpha]_D^{20}$= +5.08 (c 0.25, CH_2Cl_2).

>99% *ee* (determined by chiral HPLC: Chiralpak® IA-3 column, n-Hexane/iPrOH = 98:2, 0.7 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 59.47 min, minor enantiomer. t_r = 67.12 min.

(S)-2-(cyclohex-2-en-1-yloxy)-1,3,4-trimethylbenzene (**100**)



The title compound was synthesized from 2,3,6-trimethylphenol (200 mg, 1.47 mmol) with carbonate **96** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **100** as clear oil in 90% yield (287 mg, 1.33 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 5.92 (dtd, J = 10.2, 3.5, 1.2 Hz, 1H), 5.85 (ddt, J = 10.1, 3.7, 1.9 Hz, 1H), 4.35 – 4.27 (m, 1H), 2.26 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 2.17 – 1.55 (m, 6H).

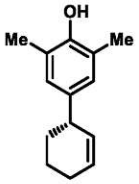
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.09, 135.82, 131.42, 130.10, 128.69, 127.98, 127.63, 124.86, 75.82, 29.28, 25.43, 20.20, 19.42, 17.37, 13.71.

HRMS (ESI): exact mass calculated for $C_{16}H_{20}NaO^+$ [(M + Na)$^+$], 239.1406; found 239.1409.

$[\alpha]_D^{20}$= -121,03 (c 1.00, CH_2Cl_2).

96% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), major enantiomer t_r = 31.21 min., minor enantiomer. t_r = 33.62 min.

(S)-3,5-dimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**111**)



The title compound was synthesized from **97** (100 mg, 0.49 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **111** as white solid in quantitative yield (100 mg, 0.49 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.92 – 5.80 (m, 1H), 5.73 – 5.62 (m, 1H), 4.49 (s, 1H), 3.28 (m, 1H), 2.24 (m, 6H), 2.13 – 2.04 (m, 2H), 2.04 – 1.92 (m, 1H), 1.81 – 1.68 (m, 1H), 1.68 – 1.46 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.58, 138.53, 130.96, 128.08, 127.97, 122.92, 41.23, 32.99, 25.19, 21.44, 16.13.

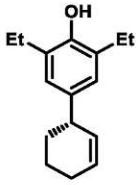
HRMS (ESI): exact mass calculated for $C_{14}H_{17}O^-$ [(M - H)$^-$], 201.1285; found 201.1283.

$[\alpha]_D^{20}$= -151.80 (c 1.00, CH_2Cl_2).

96% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/iPrOH = 99.5:0.5, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 38.98 min, major enantiomer. t_r = 40.66 min.

m.p. 53-56 °C

(S)-3,5-diethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**112**)



The title compound was synthesized from **98** (100 mg, 0.43 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **112** as clear oil in 98% yield (98 mg, 0.43 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 5.91 – 5.79 (m, 1H), 5.79 – 5.63 (m, 1H), 4.52 (s, 1H), 3.31 (m, 1H), 2.62 (q, J = 7.6 Hz, 4H), 2.14 – 2.03 (m, 2H), 2.03 – 1.94 (m, 1H), 1.81 – 1.68 (m, 1H), 1.67 – 1.47 (m, 3H), 1.25 (t, J = 7.6 Hz, 6H).

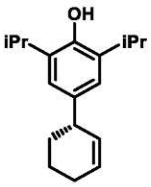
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.55, 138.74, 131.04, 129.09, 128.04, 126.12, 41.47, 33.02, 25.19, 23.37, 21.49, 14.24.

HRMS (ESI): exact mass calculated for $C_{16}H_{21}O^-$ [(M - H)$^-$], 229.1598; found 229.1597.

$[\alpha]_D^{20}$= -99.73 (c 1.00, CH_2Cl_2).

97% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Hexane/EtOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 38.63 min, major enantiomer. t_r = 41.13 min.

(S)-3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**113**)



The title compound was synthesized from **99** (100 mg, 0.39 mmol) following **general procedure C** for 3 hours at 100 °C. The reaction was directly purified by column chromatography (petroleum

ether/ethyl acetate 30:1) to provide the desired product **113** as clear oil in 99% yield (99 mg, 0.39 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 5.86 (dtd, J = 9.8, 3.7, 2.7 Hz, 1H), 5.79 – 5.66 (m, 1H), 4.73 (s, 1H), 3.38 – 3.28 (m, 1H), 3.17 (hept, J = 6.9 Hz, 2H), 2.19 – 2.04 (m, 2H), 2.05 – 1.94 (m, 1H), 1.82 – 1.70 (m, 1H), 1.69 – 1.49 (m, 2H), 1.28 (dd, J = 6.9, 0.9 Hz, 12H).

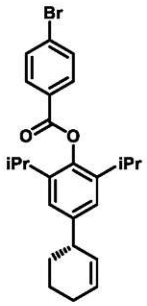
^{13}C NMR (151 MHz, $CDCl_3$) δ 148.30, 138.68, 133.49, 131.08, 128.03, 41.87, 33.06, 27.49, 25.19, 22.96, 22.92, 21.55.

HRMS (ESI): exact mass calculated for $C_{18}H_{25}O^-$ [(M - H)$^-$], 257.1911; found 257.1907.

$[\alpha]_D^{20}$= -80.43 (c 1.00, CH_2Cl_2).

96% *ee* (determined by chiral HPLC of derivative **150**).

(S)-3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl 4-bromobenzoate (**150**)



The title compound was synthesized from **113** (40 mg, 0.15 mmol) following **general procedure B**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **150** as colorless oil in 73% yield (50 mg, 0.11 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 2H), 7.73 – 7.65 (m, 2H), 7.04 (s, 2H), 5.95 – 5.86 (m, 1H), 5.81 – 5.70 (m, 1H), 3.48 – 3.37 (m, 1H), 3.03 – 2.84 (m, 2H), 2.16 – 2.01 (m, 3H), 1.84 – 1.75 (m, 1H), 1.69 – 1.52 (m, 2H), 1.25 – 1.19 (m, 12H).

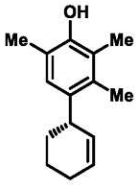
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.82, 144.82, 143.96, 140.01, 132.18, 131.81, 130.51, 128.92, 128.56, 128.43, 123.45, 42.07, 32.87, 27.93, 25.16, 24.04, 22.80, 21.48.

HRMS (ESI): exact mass calculated for $C_{25}H_{33}BrNO_2^+$ [(M + NH_4)$^+$], 458.1689; found 458.1692.

$[\alpha]_D^{20}$= -67.42 (c 1.20, CH_2Cl_2).

96% *ee* (determined by chiral HPLC: Chiralpak® IB column, n-Heptane/EtOH = 99.9:0.1, 0.5 mL/min, λ = 287.3 nm, 25 °C), minor enantiomer. t_r = 14.72 min, major enantiomer. t_r = 16.61 min.

(S)-2,3,5-trimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**114**)



The title compound was synthesized from **100** (100 mg, 0.46 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **114** as white solid in 97% yield (97 mg, 0.46 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 5.97 – 5.86 (m, 1H), 5.68 (dq, *J* = 10.1, 2.3 Hz, 1H), 4.54 (d, *J* = 3.2 Hz, 1H), 3.68 – 3.52 (m, 1H), 2.23 (s, 6H), 2.22 (s, 3H), 2.15 – 2.02 (m, 2H), 2.02 – 1.90 (m, 1H), 1.78 – 1.57 (m, 2H), 1.51 – 1.40 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.21, 136.20, 133.08, 131.39, 128.07, 127.34, 122.28, 119.71, 37.85, 31.30, 25.26, 21.34, 16.05, 15.16, 12.52.

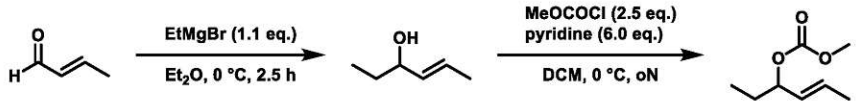
HRMS (ESI): exact mass calculated for $C_{15}H_{20}O^+$ [(M + H)$^+$], 217.1587; found 217.1591.

$[\alpha]_D^{20}$= -67.56 (c 1.00, CH_2Cl_2).

98% *ee* (determined by chiral HPLC: Chiralcel® OJ-3 column, n-Heptane/iPrOH = 99.9:0.1, 0.3 mL/min, λ = 287.3 nm, 25 °C), major enantiomer. t_r = 75.81 min, minor enantiomer. t_r = 81.76 min.

m.p. 132-133 °C

(E)-hex-4-en-3-yl methyl carbonate (**117**)



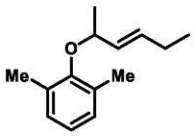
To an ice cooled solution of crotonaldeyde (1.00 g, 14.3 mmol, 1 eq.) in 21 mL dry Et_2O, EtMgBr (3.0 M in Et_2O, 5.3 mL, 15.7 mmol, 1.1 eq.) was added dropwise and precipitation was observed. After stirring the reaction mixture for 2.5 hours at 0 °C, TLC (petroleum ether/ethyl acetate 2:1) confirmed full consumption of starting material. The reaction was quenched by slow addition of water (30 mL) and the aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated *in vacuo*. The obtained material was used in the next reaction without further purification.

To the solution of *(E)*-hex-4-en-3-ol in 48 mL dry DCM, pyridine (6.9 mL, 85.7 mmol, 6.0 eq.) was added and the reaction mixture was cooled by an ice bath. Methyl chloroformate (2.8 mL, 35.7 mmol, 2.5 eq.) was added dropwise, accompanied by the formation of white precipitate. The reaction mixture was allowed to warm to room temperature overnight. After TLC (petroleum ether/ethyl acetate 5:1) confirmed full conversion, the reaction was quenched with 1 N HCl and the organic phase was washed with 1 N HCl three times, followed by saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by distillation to give the title compound as colorless oil in 66% yield over two steps (1.35 g, 9.4 mmol, b.p. 84-86 °C@35mbar).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (dqd, J = 15.4, 6.5, 0.9 Hz, 1H), 5.42 (ddq, J = 15.3, 7.7, 1.7 Hz, 1H), 4.93 (q, J = 7.0 Hz, 1H), 3.76 (s, 3H), 1.76 – 1.57 (m, 5H), 0.90 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.50, 130.41, 128.99, 80.85, 54.63, 27.65, 17.90, 9.63.

(E)-2-(hex-3-en-2-yloxy)-1,3-dimethylbenzene (**118**)



The title compound was synthesized from 2,6-dimethylphenol (150 mg, 1.23 mmol) with carbonate **117** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the product as colorless oil in 70% yield (176 mg, 0.86 mmol) as a mixture of isomers in a 4:1 ratio favoring the desired title compound **118**.

MAJOR (**118**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.94 (m, 2H), 6.94 – 6.81 (m, 1H), 5.62 – 5.31 (m, 1H), 4.35 (p, J = 6.5 Hz, 1H), 2.25 (s, 6H), 2.04 – 1.93 (m, 2H), 1.40 (d, J = 6.3 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H).

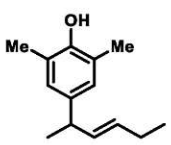
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.47, 138.45, 134.58, 130.41, 127.66, 127.34, 124.22, 122.96, 41.62, 25.67, 21.94, 16.16, 14.02.

MINOR (**119**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.94 (m, 2H), 6.94 – 6.81 (m, 1H), 5.62 – 5.31 (m, 2H), 4.09 (m, 1H), 2.24 (s, 3H), 1.88 (dt, J = 15.0, 7.5, 5.3 Hz, 1H), 1.70 (dt, J = 13.3, 7.6 Hz, 1H), 1.61 (dd, J = 6.3, 1.4 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.45, 137.28, 135.79, 127.34, 124.22, 50.21, 29.18, 18.13, 16.18, 12.47.

(E)-4-(hex-3-en-2-yl)-2,6-dimethylphenol (**153**)



The title compound was synthesized from **118** (40 mg, 0.20 mmol) following **general procedure C** for 1.5 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the product as colorless oil in quantitative yield (40 mg, 0.20 mmol) as a mixture of isomers in a 4:1 ratio favoring the desired title compound **153**.

MAJOR

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.63 – 5.37 (m, 2H), 4.58 (s, 1H), 3.30 (q, $J = 6.9$ Hz, 1H), 2.25 (s, $J = 6$H), 2.08 – 1.98 (m, 2H), 1.30 (d, $J = 7.0$ Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H).

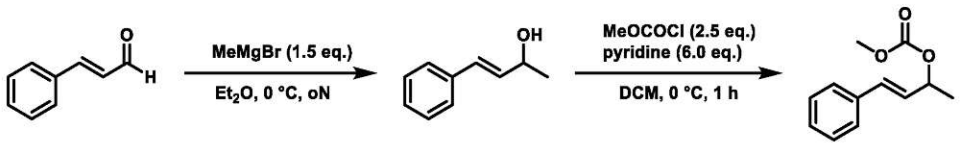
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.79, 134.65, 131.57, 130.26, 128.75, 123.33, 79.44, 25.24, 21.44, 17.42, 13.28.

MINOR

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 2H), 5.63 – 5.37 (m, 2H), 4.58 (s, 1H), 2.95 (q, $J = 7.5$ Hz, 1H), 2.25 (s, 6H), 1.69 – 1.65 (m, 3H), 0.85 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.65, 134.65, 130.97, 129.44, 128.75, 123.24, 84.96, 28.35, 17.79, 17.48, 10.03.

(E)-methyl (1-phenylbut-2-en-1-yl) carbonate (**120**)



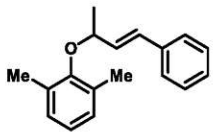
To an ice cooled solution of cinnamyl aldehyde (2.00 g, 15.1 mmol, 1 eq.) in 45 mL dry Et_2O cooled, methyl magnesium bromide (3.0 M in Et_2O, 7.8 mL, 22.7 mmol, 1.5 eq.) was added dropwise. The reaction was stirred overnight and allowed to warm to room temperature. TLC (petroleum ether/ethyl acetate 2:1) confirmed full consumption of starting material and the reaction was quenched with addition of saturated NH_4Cl solution. The aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated

and concentrated *in vacuo*. NMR confirmed product formation and the crude product was used for the next step without further purification.

To the solution of *(E)-4-phenylbut-3-en-2-ol* in 50 mL dry DCM, pyridine (7.4 mL, 90.6 mmol, 6.0 eq.) was added and the reaction was cooled by an ice bath. Methyl chloroformate (2.9 mL, 37.8 mmol, 2.5 eq.) was added dropwise. Formation of white precipitate was observed. The reaction mixture was stirred at 0 °C for 1 hour. After TLC (petroleum ether/ethyl acetate 5:1) confirmed full conversion, the reaction was washed with 1 N HCl three times, then with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The product was obtained in sufficient purity as yellow oil in 93% yield over two steps (2.89 g, 14.0 mmol).

The obtained analytical data is in accordance with literature.

(E)-1,3-dimethyl-2-((4-phenylbut-3-en-2-yl)oxy)benzene (**121**)



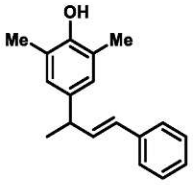
The title compound was synthesized from 2,6-dimethylphenol (120 mg, 0.98 mmol) with carbonate **120** following **general procedure T**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **121** as colorless oil in 57% yield (142 mg, 0.56 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 6.98 (d, $J = 7.8$ Hz, 2H), 6.89 (dd, $J = 8.2, 6.7$ Hz, 1H), 6.42 – 6.28 (m, 2H), 4.54 (p, $J = 6.4$ Hz, 1H), 2.28 (s, 6H), 1.52 (d, $J = 6.4$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.80, 136.79, 131.47, 131.04, 130.88, 128.94, 128.70, 127.83, 126.64, 123.58, 79.49, 21.56, 17.39.

HRMS (ESI): exact was not found after multiple attempts.

(E)-2,6-dimethyl-4-(4-phenylbut-3-en-2-yl)phenol (**154**)



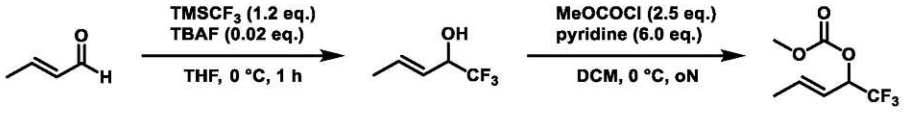
The title compound was synthesized from **121** (100 mg, 0.40 mmol) following **general procedure C** for 4 hours at 40 °C. The reaction mixture was directly subjected to column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **154** as clear oil in quantitative yield (100 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, $J = 7.3$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.23 – 7.17 (m, 1H), 6.44 – 6.32 (m, 2H), 4.53 (m, 1H), 3.57 – 3.46 (m, 1H), 2.25 (s, 6H), 1.43 (d, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.69, 137.84, 137.43, 135.91, 128.60, 128.13, 127.49, 127.08, 126.27, 123.10, 41.92, 21.53, 16.14.

HRMS (ESI): exact was not found after multiple attempts.

(E)-methyl (1,1,1-trifluoropent-3-en-2-yl) carbonate (**122**)



To an ice cooled solution of crotonaldehyde (3.00 g, 42.80 mmol, 1 eq.) in 125 mL dry THF, trifluoromethyltrimethylsilane (7.58 mL, 51.36 mmol, 1.2 eq.) was added slowly. Subsequently TBAF (1.0 M in THF, 0.86 mL, 0.86 mmol, 0.02 eq.) was added dropwise, upon which the reaction mixture turned brown. After stirring the reaction mixture for 1 hour at 0 °C, TLC (petroleum ether/ethyl acetate 2:1) showed full consumption of starting material. Cooling was removed and 1 N HCl was added. The mixture was stirred for an additional hour, then phases were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ solution, water, brine and dried over

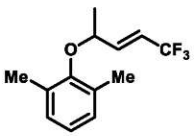
$MgSO_4$, filtrated and concentrated *in vacuo*. The obtained material was used in the next reaction without purification.

To a solution of *(E)*-1,1,1-trifluoropent-3-en-2-ol in 143 mL dry DCM, pyridine (20.7 mL, 257.0 mmol, 6.0 eq.) was added and the reaction was cooled by an ice bath. Methyl chloroformate (8.3 mL, 107.1 mmol, 2.5 eq.) was added dropwise over five minutes and formation of white precipitate was observed. The reaction mixture was allowed to warm to room temperature and stirred overnight. After TLC (petroleum ether/ethyl acetate 5:1) confirmed full conversion, the reaction was quenched with 1 N HCl. The organic phase was washed three times with 1 N HCl, followed by saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM three times and the combined organic layer was subsequently washed with brine, dried over $MgSO_4$, filtrated and concentrated. The product was obtained in sufficient purity as yellow-orange oil in 48% yield over two steps (4.10 g, 20.69 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (dq, J = 15.4, 6.6 Hz, 1H), 5.56 – 5.43 (m, 1H), 5.43 – 5.33 (m, 1H), 3.83 (s, 3H), 1.79 (dd, J = 6.6, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.42, 137.44, 119.72, 75.08 (q, J = 33.7 Hz)., 55.58, 18.07.

(E)-1,3-dimethyl-2-((5,5,5-trifluoropent-3-en-2-yl)oxy)benzene (**123**)



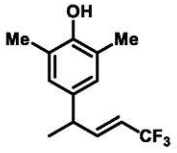
The title compound was synthesized from 2,6-dimethylphenol (100 mg, 0.82 mmol) with carbonate **122** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **123** as clear oil in 58% yield (116 mg, 0.48 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.00 (m, 2H), 6.95 (ddd, J = 8.2, 6.8, 1.6 Hz, 1H), 6.59 – 6.45 (m, 1H), 5.97 – 5.83 (m, 1H), 4.54 (ddtd, J = 10.6, 6.7, 4.6, 1.9 Hz, 1H), 2.34 – 2.19 (m, 6H), 1.42 (dt, J = 6.5, 1.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.16, 140.73 (q, J = 6.3 Hz), 131.20, 129.19, 124.07, 118.77 (q, J = 34.0 Hz).76.28, 20.33, 17.14.

HRMS (ESI): exact mass calculated for $C_{13}H_{16}F_3O^+$ [(M + H)$^+$], 245.1148; found 245.1120.

(E)-2,6-dimethyl-4-(5,5,5-trifluoropent-3-en-2-yl)phenol (**155**)



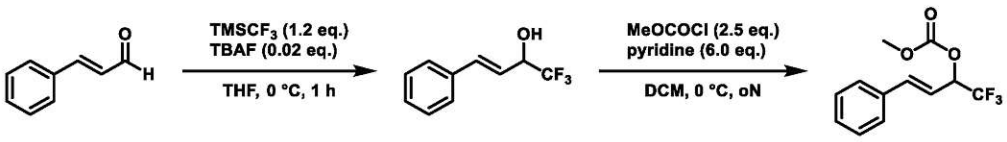
The title compound was synthesized from **123** (50 mg, 0.21 mmol) following **general procedure C.** After 2 days at 110 °C the reaction did not reach full conversion. The crude mixture was directly purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **155** as clear oil in 30% yield (15 mg, 0.06 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 6.51 (ddq, J = 15.8, 6.5, 2.2 Hz, 1H), 5.56 (dqd, J = 14.6, 6.4, 1.6 Hz, 1H), 4.59 (s, 1H), 3.52 – 3.39 (m, 1H), 2.24 (s, 6H), 1.37 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.16, 145.30 (q, J = 6.0 Hz), 134.70, 127.47, 123.41, 117.03 (q, J = 33.3 Hz). 40.68, 20.48, 16.11.

HRMS (ESI): exact mass calculated for $C_{13}H_{14}F_3O^-$ [(M - H)$^-$], 243.1002; found 243.1012.

(E)-methyl (1,1,1-trifluoropent-3-en-2-yl) phenyl carbonate (**124**)



To an ice cooled solution of cinnamyl aldehyde (1.32 g, 9.99 mmol, 1 eq.) in 125 mL dry THF, trifluoromethyltrimethylsilane (1.77 mL, 11.99 mmol, 1.2 eq.) was added slowly. Subsequently TBAF (1.0 M in THF, 0.86 mL, 0.86 mmol, 0.02 eq.) was added dropwise, upon which the reaction mixture turned brown. After stirring the reaction mixture for 1 hour at 0 °C, TLC (petroleum

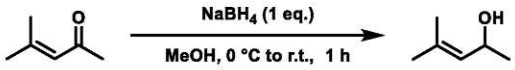
ether/ethyl acetate 2:1) showed full consumption of starting material. Cooling was removed and 1 N HCl was added. The mixture was stirred for an additional hour, then phases were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ solution, water, brine and dried over $MgSO_4$, filtrated and concentrated *in vacuo*. The obtained material was used in the next reaction without purification.

To the solution of *(E)*-1,1,1-trifluoro-4-phenylbut-3-en-2-ol in 32 mL dry DCM, pyridine (4.6 mL, 56.68 mmol, 6.0 eq.) was added and the reaction was cooled by an ice bath. Methyl chloroformate (1.8 mL, 23.62 mmol, 2.5 eq.) was added dropwise. Formation of white precipitate was observed. The reaction mixture was stirred overnight and allowed to warm to room temperature. After TLC (petroleum ether/ethyl acetate 5:1) confirmed full conversion, the reaction was quenched with 1 N HCl. The organic phase was washed three times with 1 N HCl, then with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The product was obtained in sufficient purity as yellow solid in 86% yield over two steps (2.23 g, 8.57 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.40 – 7.28 (m, 3H), 6.91 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 7.9 Hz, 1H), 5.63 (dqd, J = 7.5, 6.4, 1.0 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.39, 139.47, 134.96, 129.35, 128.91, 127.24, 116.72,75.14 (q, J = 33.9 Hz). 55.76.

4-methylpent-3-en-2-ol (**137**)



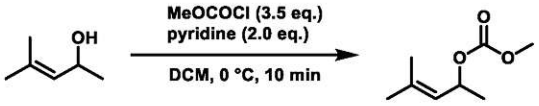
The preparation of **137** was carried out following a literature procedure[56].

To an ice cooled solution of mesityloxide (5.00 g, 50.95 mmol, 1 eq.) in 20 mL methanol, sodium borohydride (1.93 g, 50.95 mmol, 1.0 eq.) was added in small portions. After stirring the reaction mixture for 1 hour and allowing it to warm to room temperature, TLC showed full consumption of starting material. The solvent was evaporated and the residue was taken up in Et_2O and washed

with water, brine and dried over $MgSO_4$, filtrated and reduced *in vacuo*. The product **137** was obtained in sufficient purity as colorless oil in 92% yield (6.49 g, 46.62 mmol).

The obtained analytical data is in accordance with literature.

methyl (4-methylpent-3-en-2-yl) carbonate (**157**)

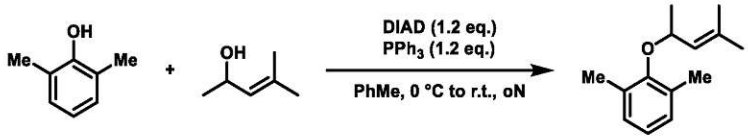


To the solution of **137** (2.16 g, 21.57 mmol, 1 eq.) in 55 mL dry DCM, pyridine (3.48 mL, 43.13 mmol, 2.0 eq.) was added and the reaction was cooled by an ice bath. Methyl chloroformate (5.9 mL, 75.48 mmol, 3.5 eq.) was added dropwise and a color change to yellow was observed. After 10 minutes TLC (petroleum ether/ethyl acetate 10:1) confirmed full conversion, the reaction was quenched with 1 N HCl. The organic phase was washed three times with 1 N HCl, then with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. After distillation the title compound was obtained as colorless oil in 64% yield (2.17 g, 13.72 mmol, b.p. 61-62 °C @ 11 mbar).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 – 5.37 (m, 1H), 5.16 (ddt, J = 9.1, 2.7, 1.3 Hz, 1H), 3.77 – 3.70 (m, 3H), 1.75 – 1.67 (m, 6H), 1.30 (dt, J = 6.4, 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.41, 137.05, 124.51, 72.50, 54.51, 25.79, 20.98, 18.37.

1,3-dimethyl-2-((4-methylpent-3-en-2-yl)oxy)benzene (**134**)



To an ice cooled solution of 2,6-dimethylphenol (117 mg, 0.96 mmol, 1.2 eq.), PPh_3 (251 mg, 0.96 mmol, 1.2 eq.) and **137** (80 mg, 0.80 mmol, 1 eq.) in 1.6 mL dry toluene. Then, DIAD

(0.19 mL, 0.96 mmol, 1.2 eq.) was added dropwise and the mixture was allowed to slowly warm up. After stirring over night, the solvent was removed in vacuo and the crude residue was subjected to column chromatography (petroleum ether/ethyl acetate 30:1) to provide the product as colorless oil in 55% yield (90 mg, 0.44 mmol) as a mixture of isomers in a 2:1 ratio favoring the desired title compound **134**.

MAJOR

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (ddd, J = 7.2, 1.4, 0.7 Hz, 2H), 6.87 (dd, J = 8.1, 6.6 Hz, 1H), 5.31 (dp, J = 9.2, 1.4 Hz, 1H), 4.69 (dq, J = 9.3, 6.3 Hz, 1H), 2.26 (s, 6H), 1.66 (d, J = 1.4 Hz, 3H), 1.41 (s, 3H), 1.31 (d, J = 1.4 Hz, 3H).

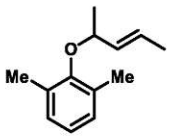
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.87, 135.10, 131.61, 128.70, 126.81, 123.31, 74.89, 25.86, 21.71, 19.09, 17.76.

MINOR

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (ddd, J = 7.2, 1.4, 0.7 Hz, 6H), 6.87 (dd, J = 8.1, 6.6 Hz, 3H), 5.76 (dq, J = 15.7, 1.6 Hz, 1H), 5.54 (dq, J = 15.7, 6.4 Hz, 1H), 2.24 (s, 6H), 1.67 (d, J = 1.6 Hz, 3H), 1.38 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.49, 137.91, 133.42, 128.62, 123.23, 122.88, 81.37, 27.89, 17.90, 17.28.

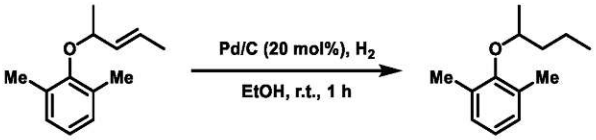
(E)-1,3-dimethyl-2-(pent-3-en-2-yloxy)benzene (**77rac**)



The title compound was synthesized from 2,6-dimethylphenol (300 mg, 2.46 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **77rac** as colorless oil in 96% yield (449 mg, 2.36 mmol).

The obtained analytical data is in accordance with **77**.

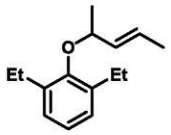
1,3-dimethyl-2-(pentan-2-yloxy)benzene (**140rac**)



A 8 mL screw neck vial was charged with starting material starting material **77rac** (17 mg, 89 µmol, 1 eq.) in 0.9 mL EtOH. The colorless solution was schlenked ten times then Pd/C (10 wt.%, 19 mg, 18 µmol, 20 mol %) was added. The atmosphere was exchanged to H_2 *via* vacuum/H_2 backfill (5 times) and the mixture was stirred for 2 hours, until TLC showed full conversion. The atmosphere was exchanged to argon by vacuum/agon backfill (5 times) and the black suspension was filtered over celite. The desired product was obtained as pale-yellow oil in 99% yield (17 mg, 88 µmol) and was used without further purification for HPLC analysis.

The obtained analytical data is in accordance with **140h**.

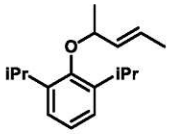
(E)-1,3-diethyl-2-(pent-3-en-2-yloxy)benzene (**88rac**)



The title compound was synthesized from 2,6-diethylphenol (200 mg, 1.33 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **88rac** as colorless oil in 91% yield (264 mg, 1.21 mmol).

The obtained analytical data is in accordance with **88**.

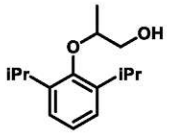
(E)-1,3-diisopropyl-2-(pent-3-en-2-yloxy)benzene (**89rac**)



The title compound was synthesized from 2,6-diisopropylphenol (150 mg, 0.84 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **89rac** as colorless oil in 88% yield (183 mg, 0.74 mmol).

The obtained analytical data is in accordance with **89**.

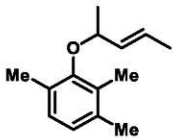
2-(2,6-diisopropylphenoxy)propan-1-ol (**146rac**)



The title compound was synthesized from **89rac** (100 mg, 0.41 mmol) following **general procedure O**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide the desired product **146rac** as colorless oil in 73% yield (73 mg, 0.30 mmol).

The obtained analytical data is in accordance with **146**.

(E)-1,2,4-trimethyl-3-(pent-3-en-2-yloxy)benzene (**90rac**)

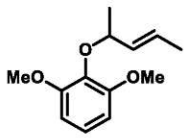


The title compound was synthesized from 2,3,6-trimethylphenol (150 mg, 1.10 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column

chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **90rac** as colorless oil in 89% yield (200 mg, 0.98 mmol).

The obtained analytical data is in accordance with **90**.

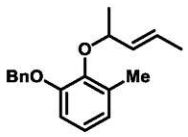
(E)-1,3-dimethoxy-2-(pent-3-en-2-yloxy)benzene (**91rac**)



The title compound was synthesized from 2,6-dimethoxyphenol (100 mg, 0.65 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 10:1) to provide the desired product **91rac** as yellow oil in 96% yield (139 mg, 0.63 mmol).

The obtained analytical data is in accordance with **91**.

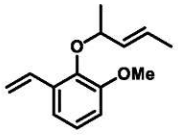
(E)-1-(benzyloxy)-3-methyl-2-(pent-3-en-2-yloxy)benzene (**92rac**)



The title compound was synthesized from **151** (100 mg, 0.47 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **92rac** as clear oil in 92% yield (121 mg, 0.43 mmol).

The obtained analytical data is in accordance with **92**.

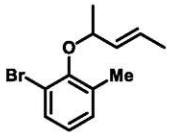
(E)-1-methoxy-2-(pent-3-en-2-yloxy)-3-vinylbenzene (**93rac**)



The title compound was synthesized from **152** (100 mg, 0.67 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **93rac** as colorless oil in 90% yield (131 mg, 0.60 mmol).

The obtained analytical data is in accordance with **93.**

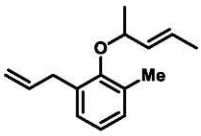
(E)-1-bromo-3-methyl-2-(pent-3-en-2-yloxy)benzene (**94rac**)



The title compound was synthesized from 2-bromo-6-methylphenol (150 mg, 0.80 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **94rac** as colorless oil in 88% yield (180 mg, 0.71 mmol).

The obtained analytical data is in accordance with **94**.

(E)-1-allyl-3-methyl-2-(pent-3-en-2-yloxy)benzene (**95rac**)

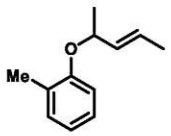


The title compound was synthesized from 2-allyl-6-methylphenol (100 mg, 0.67 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column

chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **95rac** as colorless oil in 77% yield (113 mg, 0.52 mmol).

The obtained analytical data is in accordance with **95**.

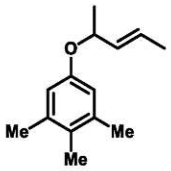
(E)-1-methyl-2-(pent-3-en-2-yloxy)benzene (**115rac**)



The title compound was synthesized from 2-methylphenol (100 mg, 0.92 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **115rac** as colorless oil in 98% yield (159 mg, 0.90 mmol).

The obtained analytical data is in accordance with **115**.

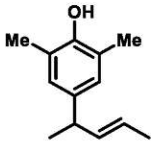
(E)-1,2,3-trimethyl-5-(pent-3-en-2-yloxy)benzene (**57rac**)



The title compound was synthesized from 3,4,5-trimethylphenol (150 mg, 1.10 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **57rac** as colorless oil in 85% yield (192 mg, 0.94 mmol).

The obtained analytical data is in accordance with **57**.

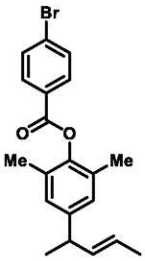
(E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenol (**78rac**)



The title compound was synthesized from **77rac** (100 mg, 0.53 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction mixture was directly subjected to column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **78rac** as clear oil in quantitative yield (100 mg, 0.53 mmol).

The obtained analytical data is in accordance with **78**.

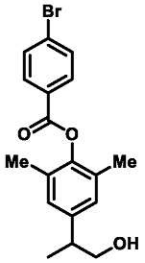
(E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (**141rac**)



The title compound was synthesized from **78rac** (1.00 g, 5.27 mmol) following **general procedure C**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **141rac** as colorless oil in 88% yield (1.72 g, 4.61 mmol).

The obtained analytical data is in accordance with **141**.

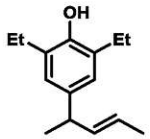
4-(1-hydroxypropan-2-yl)-2,6-dimethylphenyl 4-bromobenzoate (**142rac**)



The title compound was synthesized from **141rac** (50 mg, 0.13 mmol) following **general procedure O**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **142rac** as colorless oil in 76% yield (49 mg, 0.10 mmol).

The obtained analytical data is in accordance with **142**.

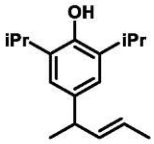
(E)-2,6-diethyl-4-(pent-3-en-2-yl)phenol (**101rac**)



The title compound was synthesized from **88rac** (100 mg, 0.46 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **101rac** as clear oil in 98% yield (98 mg, 0.46 mmol).

The obtained analytical data is in accordance with **101**.

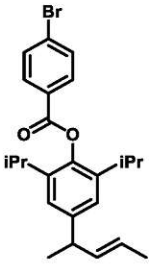
(E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenol (**102rac**)



The title compound was synthesized from **89rac** (100 mg, 0.41 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **102rac** as clear oil in 97% yield (97 mg, 0.41 mmol).

The obtained analytical data is in accordance with **102**.

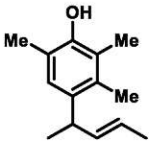
(E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (**149rac**)



The title compound was synthesized from **102rac** (20 mg, 0.08 mmol) following **general procedure B**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **149rac** as colorless oil in 71% yield (25 mg, 0.06 mmol).

The obtained analytical data is in accordance with **149**.

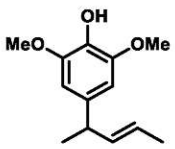
(E)-2,3,6-trimethyl-4-(pent-3-en-2-yl)phenol (**103rac**)



The title compound was synthesized from **90rac** (100 mg, 0.49 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **103rac** as white solid in 99% yield (99 mg, 0.49 mmol).

The obtained analytical data is in accordance with **103**.

(E)-2,6-dimethoxy-4-(pent-3-en-2-yl)phenol (**104rac**)

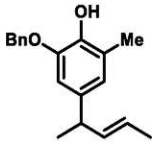


The title compound was synthesized from **91rac** (90 mg, 0.40 mmol) following **general procedure C** at 100 °C over night. The reaction was directly purified by column chromatography (petroleum

ether/ethyl acetate 10:1) to provide the desired product **104rac** as yellow oil in 87% yield (78 mg, 0.35 mmol).

The obtained analytical data is in accordance with **104**.

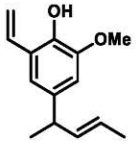
(E)-2-(benzyloxy)-6-methyl-4-(pent-3-en-2-yl)phenol (**105rac**)



The title compound was synthesized from **92rac** (50 mg, 0.18 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **105rac** as clear oil in 90% yield (45 mg, 0.16 mmol).

The obtained analytical data is in accordance with **105**.

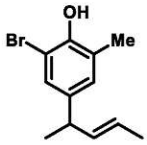
(E)-2-methoxy-4-(pent-3-en-2-yl)-6-vinylphenol (**106rac**)



The title compound was synthesized from **93rac** (50 mg, 0.23 mmol) following **general procedure C** for 3 hours at 40 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **106rac** as clear oil in 26% unoptimized yield (13 mg, 0.06 mmol) together a mixture of the product and an unidentified sideproduct.

The obtained analytical data is in accordance with **106**.

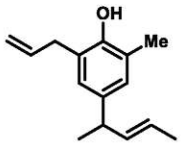
(E)-2-bromo-6-methyl-4-(pent-3-en-2-yl)phenol (**107rac**)



The title compound was synthesized from **94rac** (72 mg, 0.28 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **107rac** as clear oil in 93% yield (67 mg, 0.26 mmol).

The obtained analytical data is in accordance with **107**.

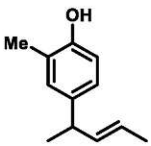
(E)-2-allyl-6-methyl-4-(pent-3-en-2-yl)phenol (**108rac**)



The title compound was synthesized from **95rac** (50 mg, 0.23 mmol) following **general procedure C** for 3 hours at 60 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **108rac** as clear oil in 92% yield (46 mg, 0.21 mmol).

The obtained analytical data is in accordance with **108**.

(E)-2-methyl-4-(pent-3-en-2-yl)phenol (**116rac**)

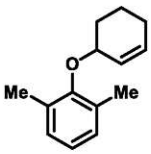


The title compound was synthesized from **115rac** (20 mg, 0.11 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum

ether/ethyl acetate 30:1) to provide the desired product **116rac** as clear oil in 40% yield (8 mg, 45 µmol) accompanied by 60% (12 mg, 68 µmol) of compound **110rac**.

The obtained analytical data is in accordance with **116**.

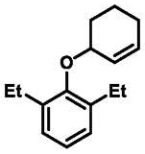
2-(cyclohex-2-en-1-yloxy)-1,3-dimethylbenzene (**97rac**)



The title compound was synthesized from 2,6-dimethylphenol (150 mg, 1.23 mmol) with carbonate **96** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **97rac** as colorless oil in 80% yield (197 mg, 0.97 mmol).

The obtained analytical data is in accordance with **97**.

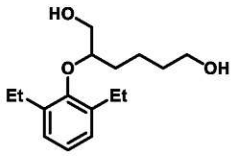
2-(cyclohex-2-en-1-yloxy)-1,3-diethylbenzene (**98rac**)



The title compound was synthesized from 2,6-diethylphenol (200 mg, 1.33 mmol) with carbonate **96** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **98rac** as colorless oil in 91% yield (264 mg, 1.21 mmol).

The obtained analytical data is in accordance with **98**.

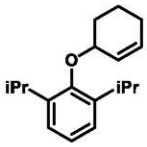
2-(2,6-diethylphenoxy)hexane-1,6-diol (**147rac**)



The title compound was synthesized from **98rac** (50 mg, 0.22 mmol) following **general procedure O**. The desired product was obtained in sufficient purity as white oil in 88% yield (51 mg, 0.19 mmol).

The obtained analytical data is in accordance with **147**.

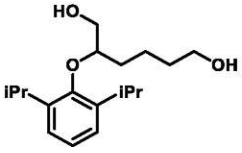
2-(cyclohex-2-en-1-yloxy)-1,3-diisopropylbenzene (**99rac**)



The title compound was synthesized from 2,6-diisopropylphenol (150 mg, 0.84 mmol) with carbonate **96** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **99rac** as white solid in 74% yield (161 mg, 0.62 mmol).

The obtained analytical data is in accordance with **99**.

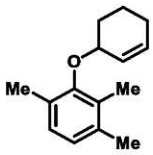
2-(2,6-diisopropylphenoxy)hexane-1,6-diol (**148rac**)



The title compound was synthesized from **99rac** (60 mg, 0.23 mmol) following **general procedure O**. The desired product **148rac** was obtained in sufficient purity as white oil in 80% yield (55 mg, 0.19 mmol).

The obtained analytical data is in accordance with **148**.

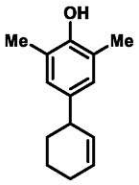
2-(cyclohex-2-en-1-yloxy)-1,2,4-trimethylbenzene (**100rac**)



The title compound was synthesized from 2,3,6-trimethylphenol (150 mg, 1.10 mmol) with carbonate **96** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **100rac** as clear oil in 68% yield (162 mg, 0.75 mmol).

The obtained analytical data is in accordance with **100**.

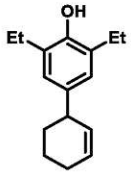
3,5-dimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**111rac**)



The title compound was synthesized from **97rac** (100 mg, 0.49 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **111rac** as white solid in 97% yield (97 mg, 0.49 mmol).

The obtained analytical data is in accordance with **111**.

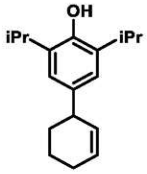
3,5-diethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**112rac**)



The title compound was synthesized from **98rac** (100 mg, 0.43 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **112rac** as yellowish oil in 99% yield (99 mg, 0.43 mmol).

The obtained analytical data is in accordance with **112**.

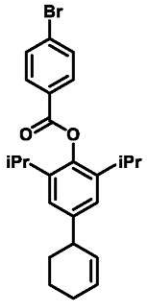
3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**113rac**)



The title compound was synthesized from **99rac** (100 mg, 0.39 mmol) following **general procedure C** for 3 hours at 100 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **113rac** as clear oil in 98% yield (98 mg, 0.39 mmol).

The obtained analytical data is in accordance with **113**.

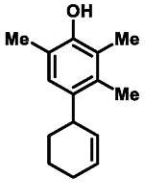
3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl 4-bromobenzoate (**150rac**)



The title compound was synthesized from **113rac** (20 mg, 0.08 mmol) following **general procedure B**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **150rac** as colorless oil in 82% yield (28 mg, 0.06 mmol).

The obtained analytical data is in accordance with **150**.

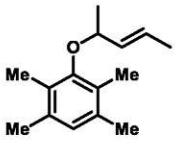
2,3,5-trimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (**114rac**)



The title compound was synthesized from **xyz** (100 mg, 0.46 mmol) following **general procedure C** for 3 hours at 80 °C. The reaction was directly purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **114rac** as white solid in 97% yield (97 mg, 0.46 mmol).

The obtained analytical data is in accordance with **114**.

(E)-1,2,4,5-tetramethyl-3-(pent-3-en-2-yloxy)benzene (**126**)



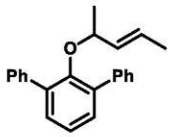
The title compound was synthesized from 2,3,5,6-tetramethylphenol (150 mg, 1.00 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **126** as colorless oil in 87% yield (200 mg, 0.87 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 5.63 (ddq, J = 15.3, 7.3, 1.6 Hz, 1H), 5.48 (dqd, J = 15.3, 6.4, 0.8 Hz, 1H), 4.29 – 4.17 (m, 1H), 2.19 (s, 6H), 2.12 (s, 6H), 1.65 (ddd, J = 6.4, 1.6, 0.6 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.43, 134.57, 132.77, 127.40, 127.37, 126.50, 79.75, 21.08, 20.03, 17.81, 13.63.

HRMS (ESI): exact was not found after multiple attempts.

(E)-2'-(pent-3-en-2-yloxy)-1,1':3',1''-terphenyl (**127**)



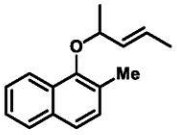
The title compound was synthesized from 2,6-diphenylphenol (300 mg, 1.24 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **127** as colorless oil in 80% yield (263 mg, 0.84 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4H), 7.46 – 7.38 (m, 4H), 7.38 – 7.29 (m, 4H), 7.21 (dd, J = 8.2, 6.9 Hz, 1H), 4.88 (dq, J = 15.3, 6.5 Hz, 1H), 4.59 (ddq, J = 15.2, 8.4, 1.6 Hz, 1H), 3.63 (dq, J = 8.5, 6.3 Hz, 1H), 1.32 (dd, J = 6.4, 1.7 Hz, 3H), 0.77 (d, J = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.44, 139.85, 137.31, 132.18, 130.04, 129.98, 128.01, 127.37, 126.94, 124.08, 80.33, 20.89, 17.58.

HRMS (ESI): exact mass calculated for $C_{23}H_{22}NaO^+$ [(M + Na)$^+$], 337.1563; found 337.1590.

(E)-2-methyl-1-(pent-3-en-2-yloxy)naphthalene (**128**)



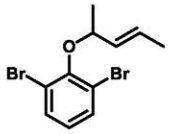
The title compound was synthesized from 2-methyl-naphtol (100 mg, 0.63 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 40:1) to provide the desired product **128** as colorless oil in 96% yield (138 mg, 0.61 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 1H), 7.87 – 7.77 (m, 1H), 7.61 – 7.38 (m, 3H), 7.33 (d, J = 8.4 Hz, 1H), 5.77 (ddq, J = 15.2, 7.5, 1.6 Hz, 1H), 5.60 – 5.46 (m, 1H), 4.72 – 4.58 (m, 1H), 2.49 (s, 3H), 1.70 – 1.62 (m, 3H), 1.54 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.22, 133.69, 132.50, 129.43, 129.34, 127.91, 127.85, 126.97, 125.40, 125.05, 123.37, 122.81, 80.62, 21.44, 17.71, 17.27.

HRMS (ESI): exact was not found after multiple attempts.

(E)-1,3-dibromo-2-(pent-3-en-2-yloxy)benzene (**129**)



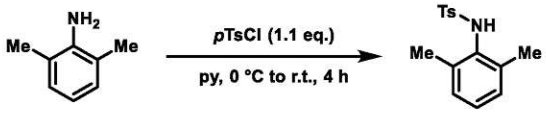
The title compound was synthesized from 2,6-dibromophenol (310 mg, 1.25 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **129** as colorless oil in 32% unopimized yield (107 mg, 0.33 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 6.80 (t, J = 8.0 Hz, 1H), 5.70 (ddq, J = 15.3, 8.5, 1.6 Hz, 1H), 5.55 – 5.39 (m, 1H), 4.92 (dq, J = 8.5, 6.3 Hz, 1H), 1.60 (dd, J = 6.5, 1.6 Hz, 3H), 1.49 (dd, J = 6.3, 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.18, 132.76, 131.57, 129.58, 125.69, 119.71, 81.54, 21.28, 17.67.

HRMS (ESI): exact was not found after multiple attempts.

N-(2,6-dimethylphenyl)-4-methylbenzenesulfonamide (**158**)

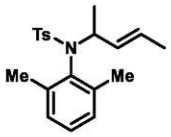


The preparation was carried out following a modified literature procedure.[57]

To a solution of 2,6-dimethylaniline (2.00 g, 16.50 mmol, 1 eq.) in 83 mL pyridine was added *para*-toluenesulfonyl chloride (3.46 g, 18.15 mmol, 1.1 eq.) at 0 °C. The reaction was allowed to room temperature and stirred for 4 hours. Pyridine was largely removed by rotary evaporator, then 1 N HCl was added to reaction mixture. The product was extracted with DCM, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide the desired product **158** as colorless oil in 88% yield (4.00 g, 14.53 mmol).

The obtained analytical data is in accordance with literature.

(*E*)-*N*-(2,6-dimethylphenyl)-4-methyl-*N*-(pent-3-en-2-yl)benzenesulfonamide (**130**)



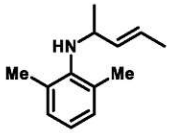
The title compound was synthesized from **158** (150 mg, 0.54 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **130** as colorless oil in 31% yield (58 mg, 017 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.18 – 7.11 (m, 2H), 7.09 – 6.90 (m, 3H), 5.60 – 5.46 (m, 1H), 5.29 (ddq, J = 15.2, 8.8, 1.6 Hz, 1H), 4.52 (dq, J = 8.8, 6.9 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H), 1.94 (s, 3H), 1.53 (dd, J = 6.5, 1.6 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.86, 140.93, 140.06, 140.02, 136.64, 132.13, 129.20, 128.89, 128.86, 128.11, 128.00, 127.71, 60.45, 21.64, 21.13, 20.32, 20.15, 17.68.

HRMS (ESI): exact mass calculated for $C_{20}H_{26}NO_2S^+$ [(M + H)$^+$], 344.1679; found 334.1683.

(E)-2,6-dimethyl-N-(pent-3-en-2-yl)aniline (**131**)



The title compound was synthesized from 2,6-dimethylanilin (100 mg, 0.83 mmol) with carbonate **76** following **general procedure R**. The crude material was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to provide the desired product **131** as orange oil in 52% yield (81 mg, 0.43 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, $J = 7.4$ Hz, 2H), 6.80 (t, $J = 7.5$ Hz, 1H), 5.52 – 5.44 (m, 2H), 3.74 – 3.66 (m, 1H), 2.25 (s, 6H), 1.66 – 1.60 (m, 3H), 1.21 (d, $J = 6.5$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.10, 134.95, 129.63, 128.82, 124.64, 121.62, 54.51, 21.93, 19.10, 17.85.

HRMS (ESI): exact was not found after multiple attempts.

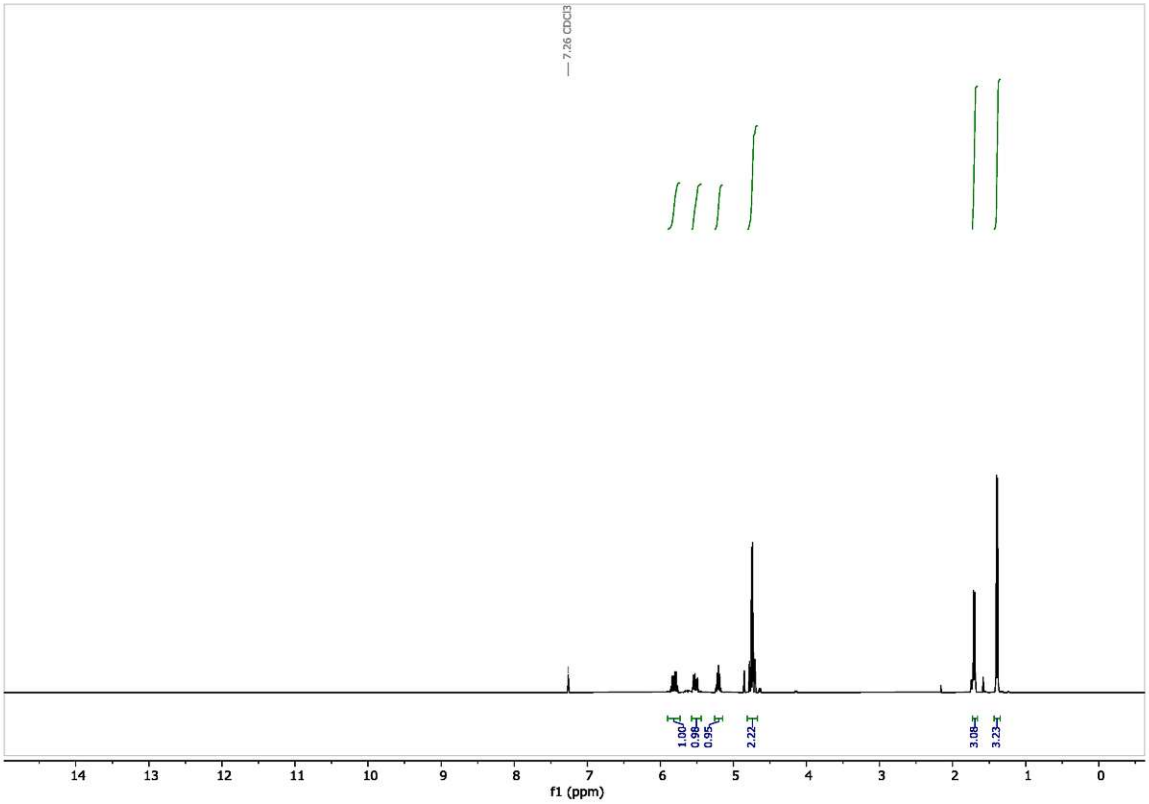
Abbreviations

1,1,2,2-TCE	1,1,2,2-tetrachloroethane
AAA	asymmetric allylic alkylation
Ac	acetyl
Bn	benzyl
b.p.	boiling point
dba	dibenzylideneacetone
DCC	*N,N'*-dicyclohexylcarbodiimide
DCM	dichloromethane
DEA	*N,N*-diethylaniline
DIAD	diisopropyl azodicarboxylate
DMAP	4-dimethylaminopyridine
ee	enantiomeric excess
ESI	electrospray ionization
Et	ethyl
Eu(hfc)$_3$	europium(III)-tris-[3-(heptafluorpropyl-hydroxymethylen)-d-camphorat]
EuFOD	tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium
Hex	hexyl
HMDS	hexamethyldisilazane
HoFOD	tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)holmium
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectroscopy
iPr	*iso*-Propyl
Me	methyl
MOM	methoxymethyl
m.p.	melting point
MTPA	Mosher's acid, or α-methoxy-α-trifluoromethylphenylacetic acid
NMR	nuclear magnetic resonance
Nu	nucleophile
oN	over night
OTf	trifluoromethanesulfonate
Ph	phenyl
PhCl	chlorobenzol
PhMe	toluene
PrFOD	tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)praseodym
py	pyridine
r.t.	room temperature
tBu	*tert*-Butyl
TLC	thin layer chromatography
TOF	time of flight
Troc	trichloroethoxycarbonyl-
Ts	toluenesulfonyl

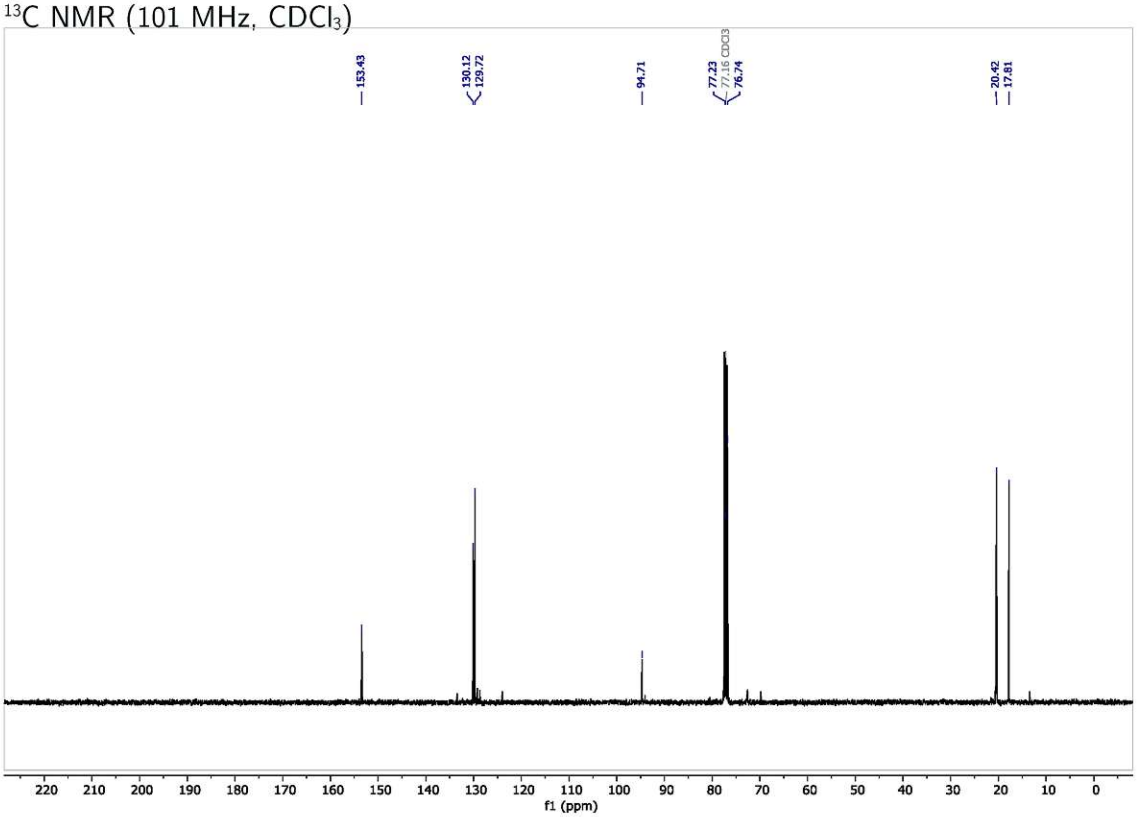
NMR-spectra

(E)-Pent-3-en-2-yl (2,2,2-trichloroethyl) carbonate (87)

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

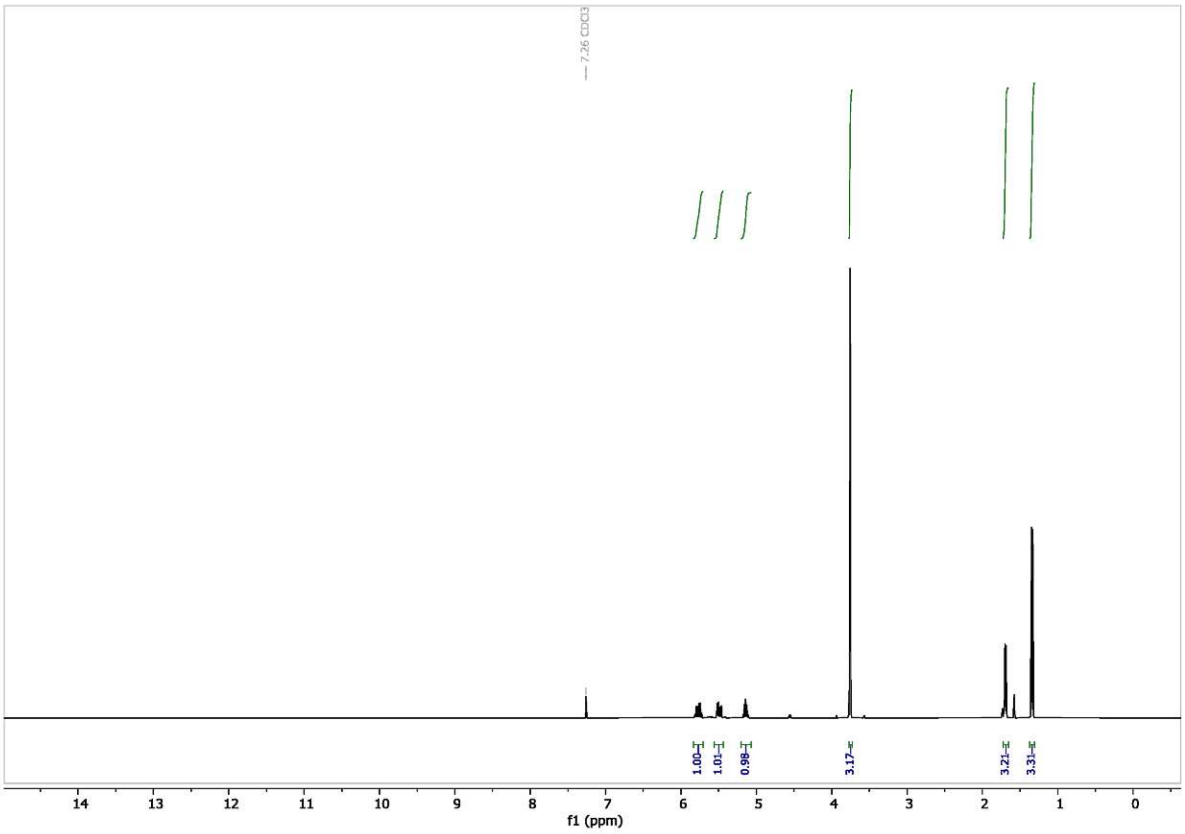


^{13}C NMR (101 MHz, $CDCl_3$)

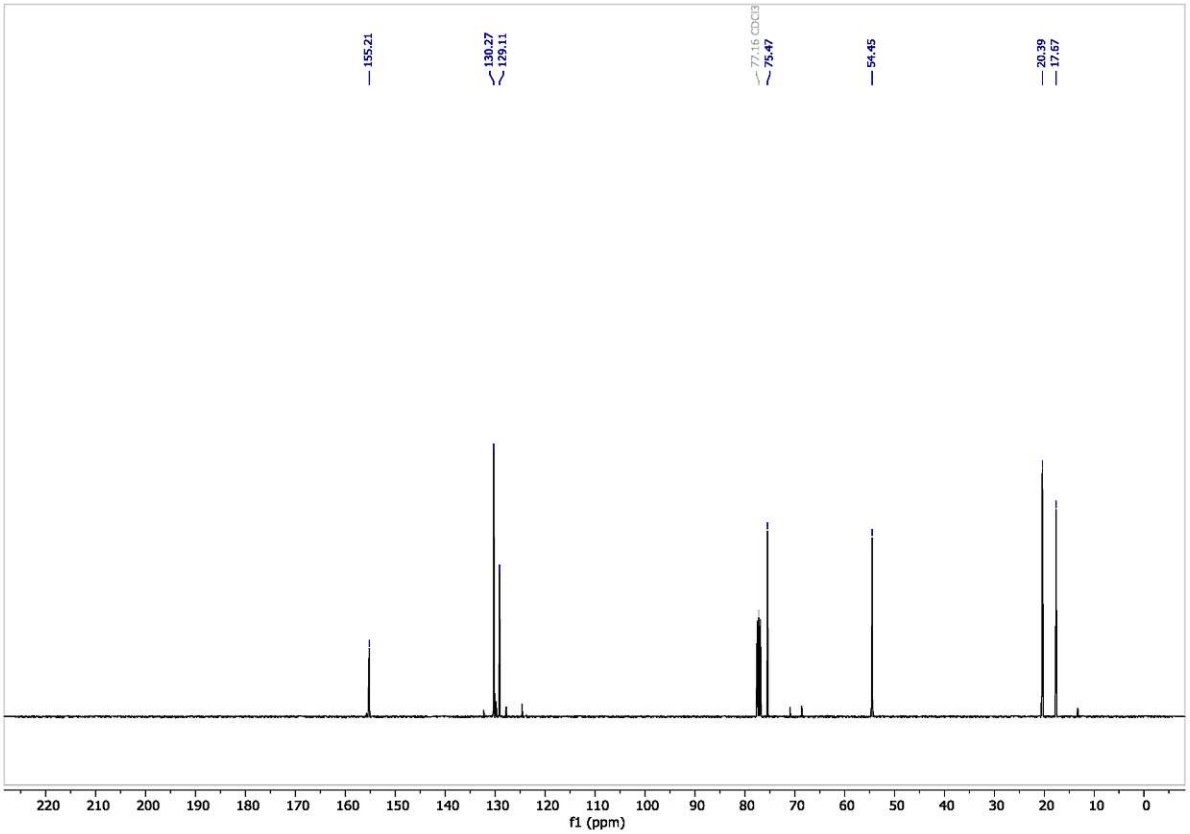


(E)-Pent-3-en-2yl methyl carbonate (76)

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

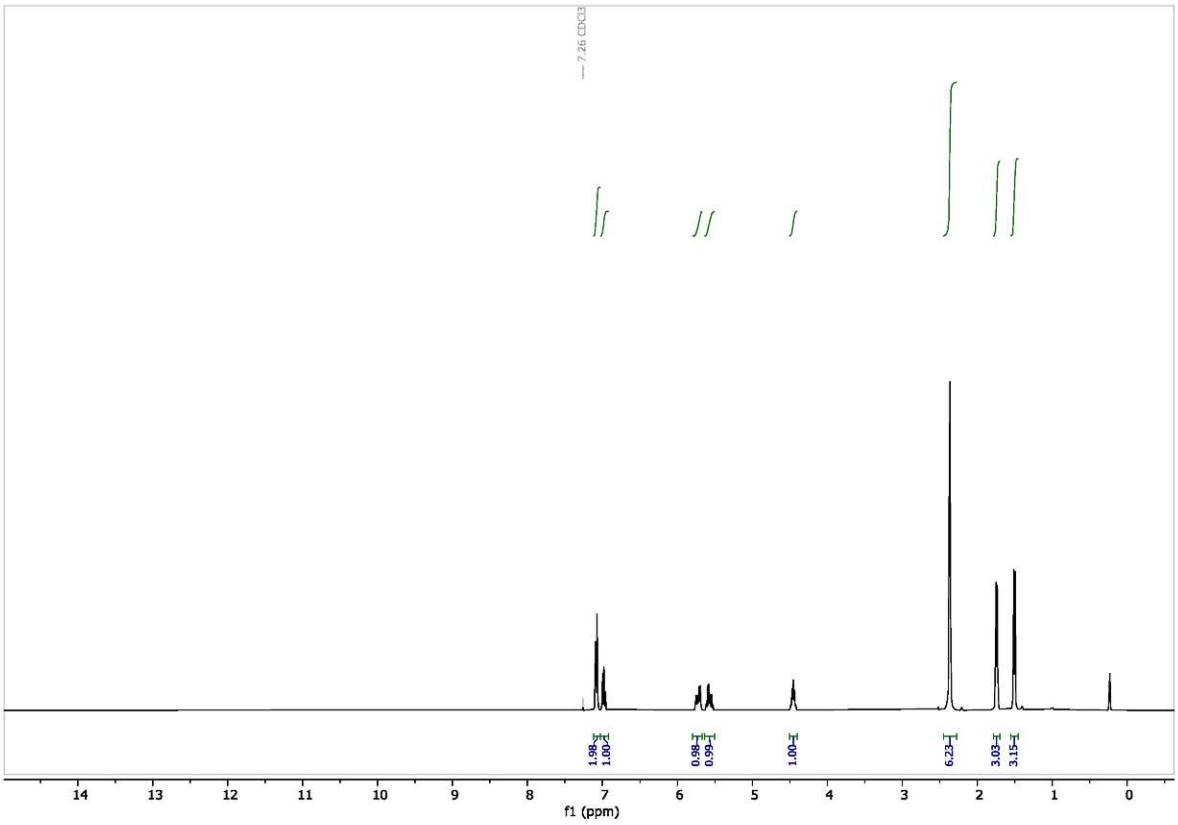


^{13}C NMR (101 MHz, $CDCl_3$)

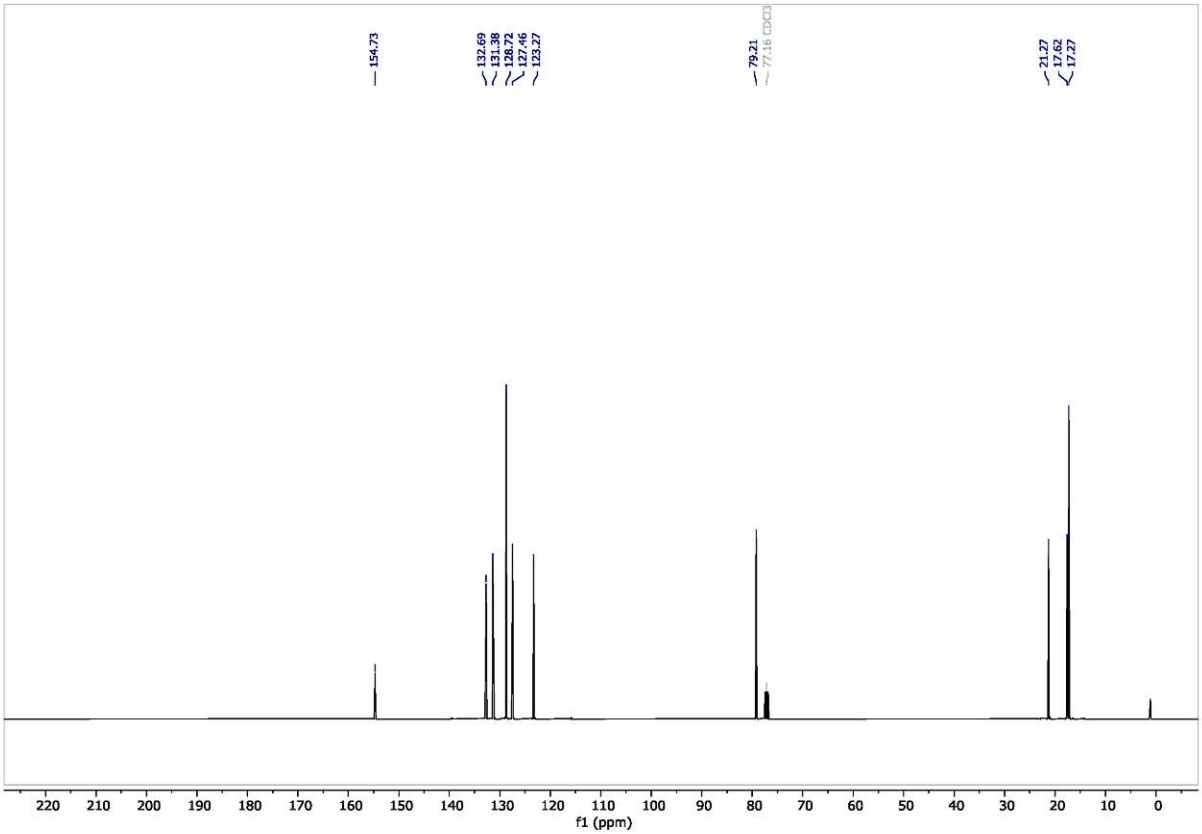


(R,E)-1,3-dimethyl-2-(pent-3-en-2-yloxy)benzene (77)

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

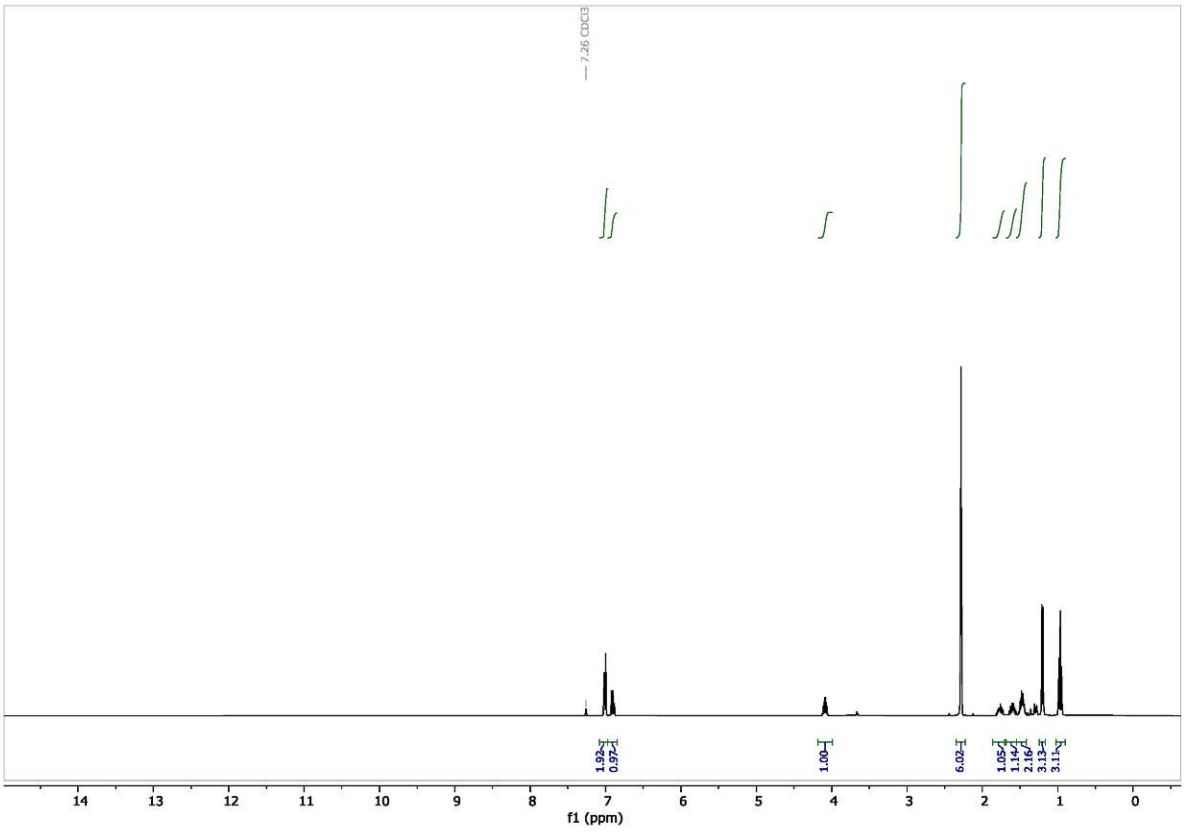


^{13}C NMR (101 MHz, $CDCl_3$)

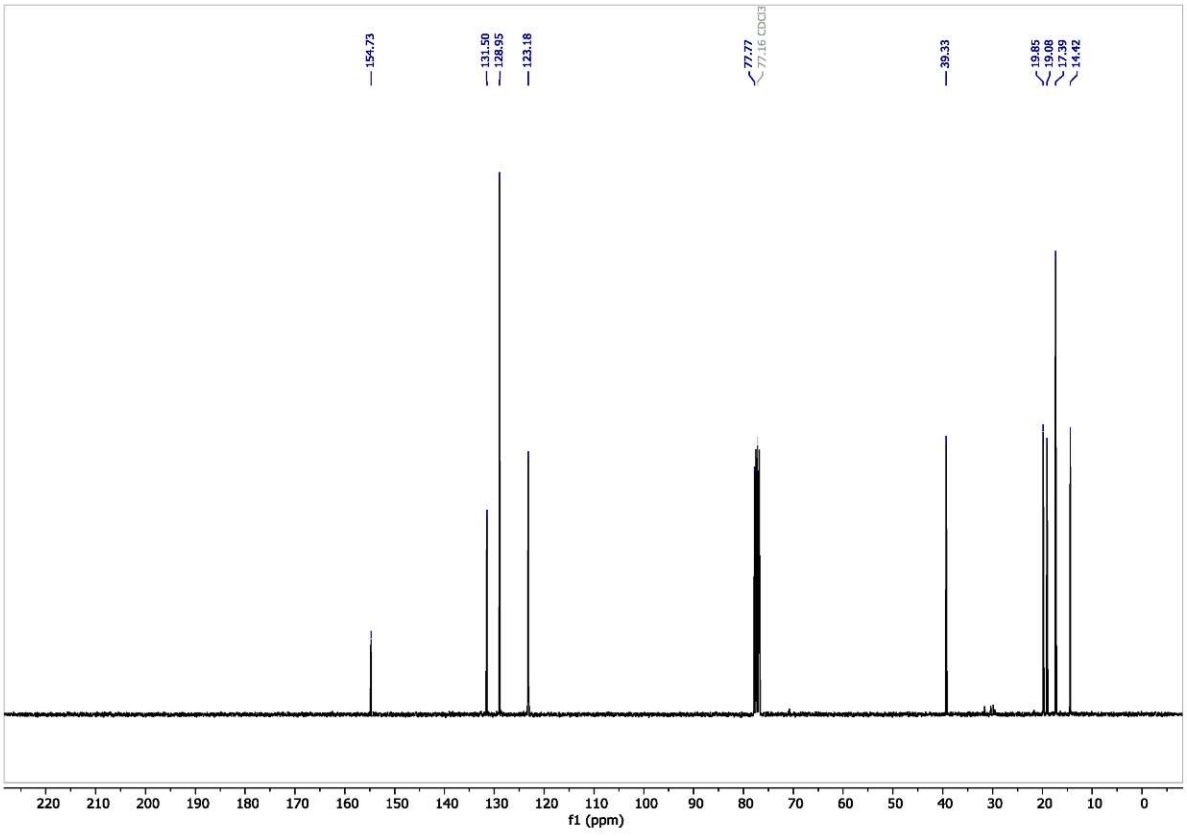


(R)-1,3-dimethyl-2-(pentan-2-yloxy)benzene (140)

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

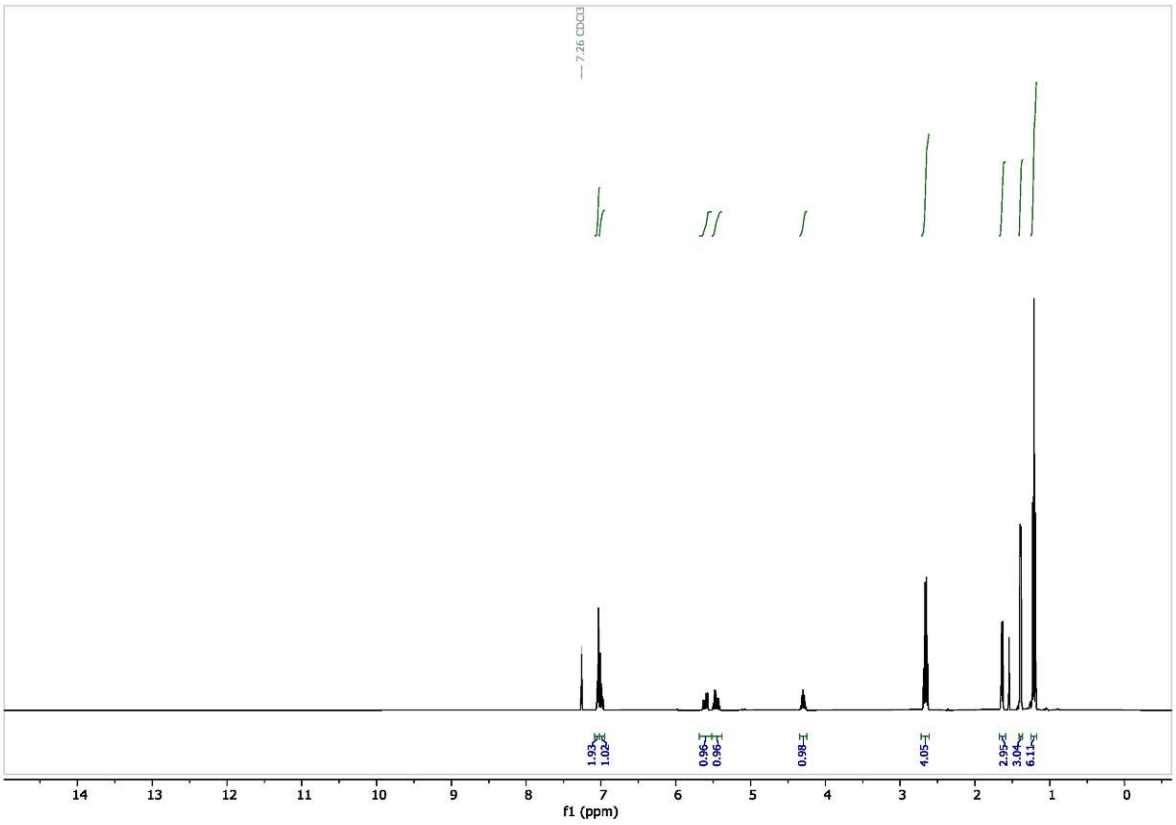


^{13}C NMR (101 MHz, $CDCl_3$)

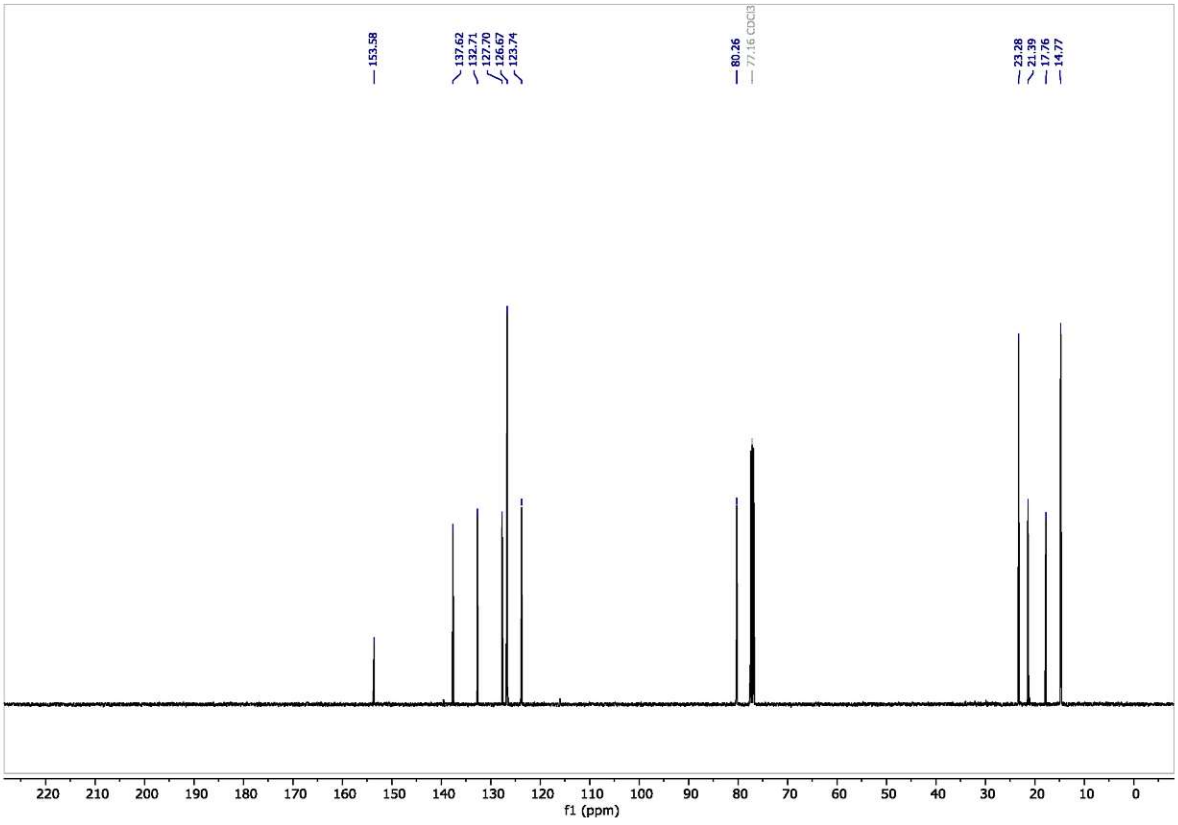


(R,E)-1,3-diethyl-2-(pent-3-en-2-yloxy)benzene (88)

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

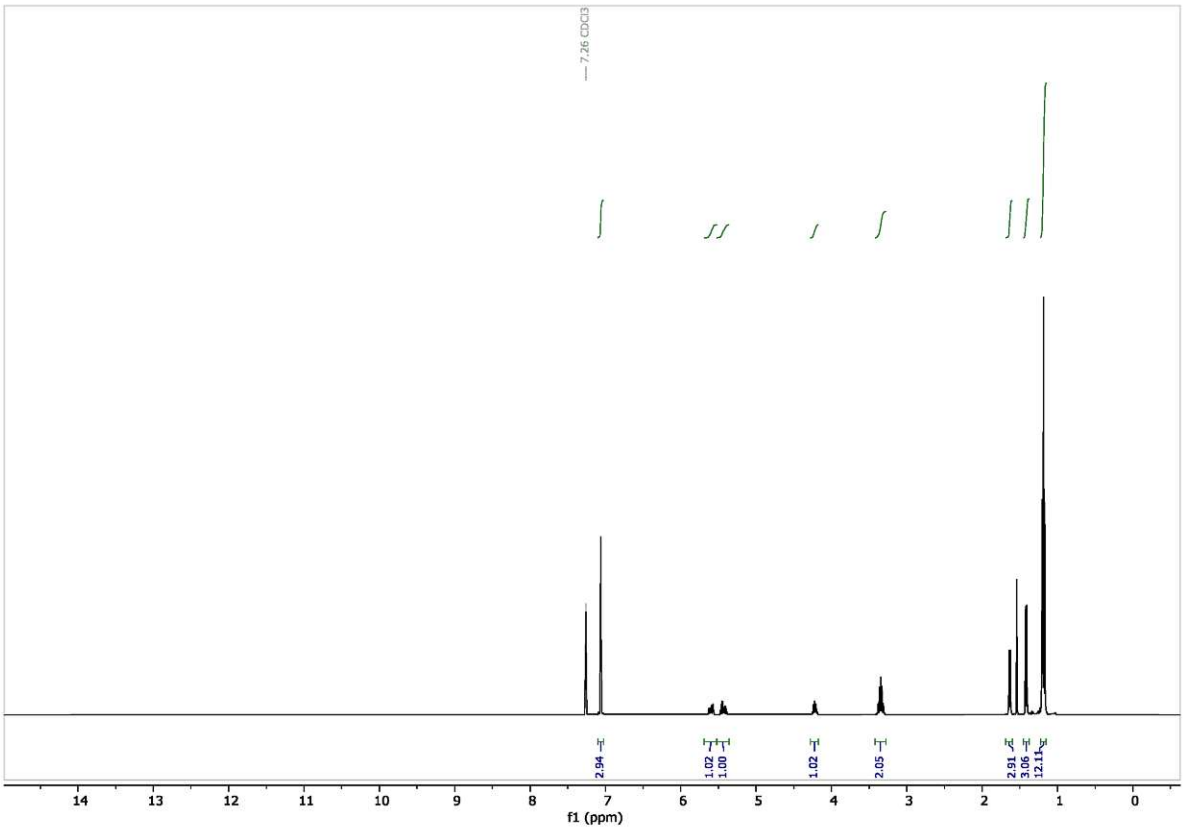


^{13}C NMR (101 MHz, $CDCl_3$)

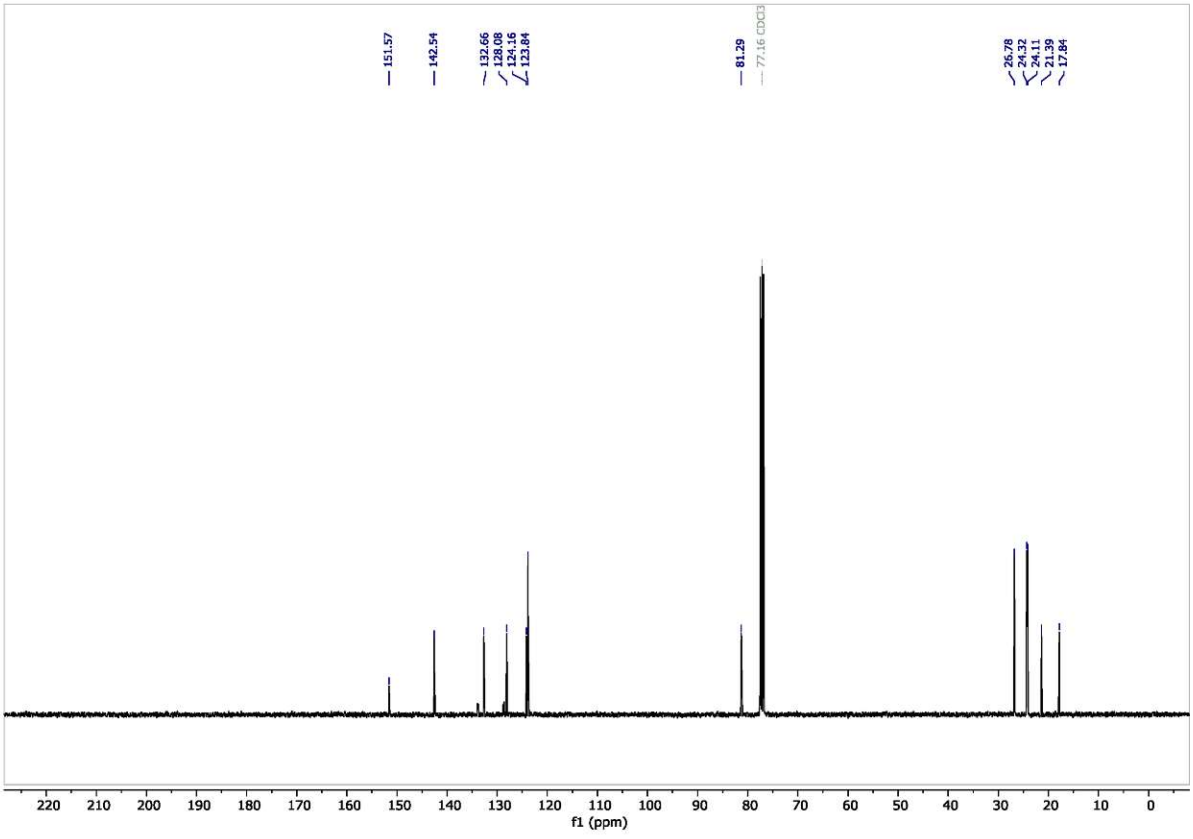


(R,E)-1,3-diisopropyl-2-(pent-3-en-2-yloxy)benzene (89)

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

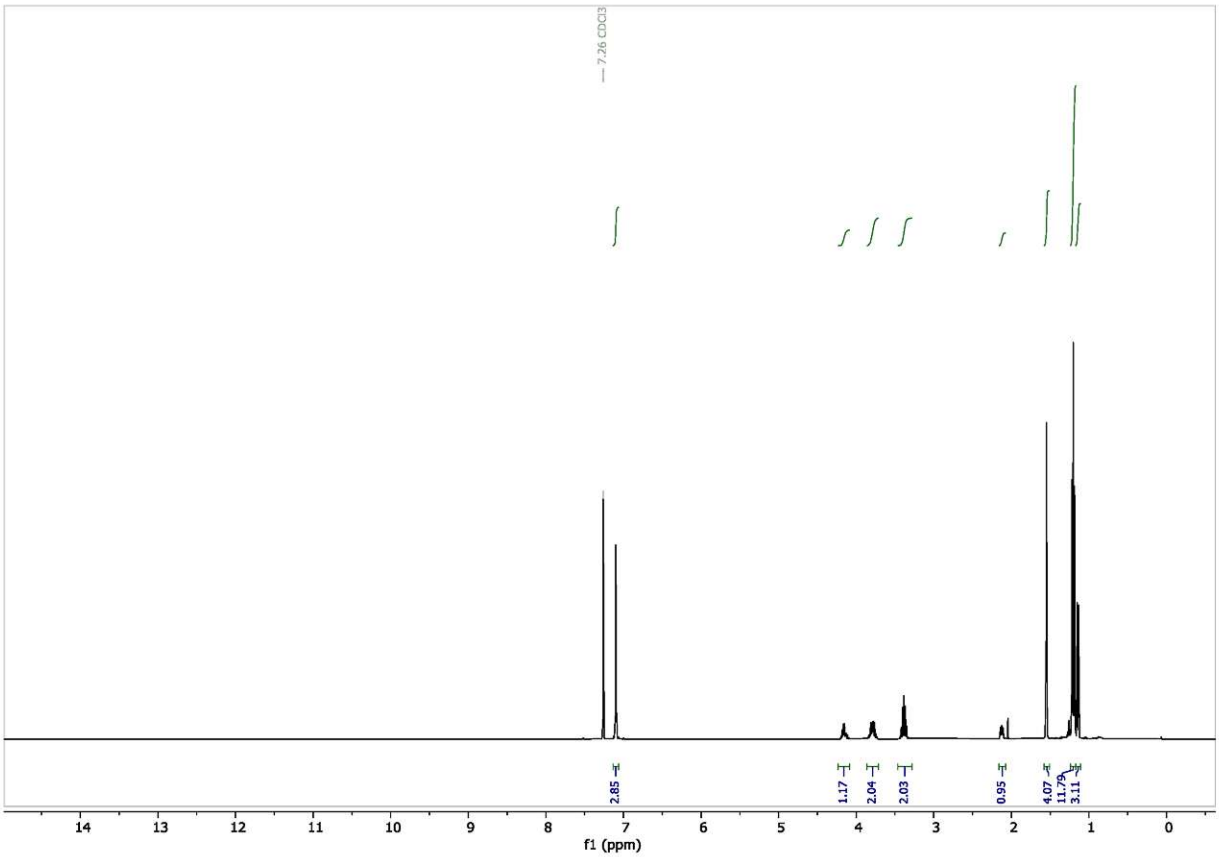


^{13}C NMR (101 MHz, $CDCl_3$)

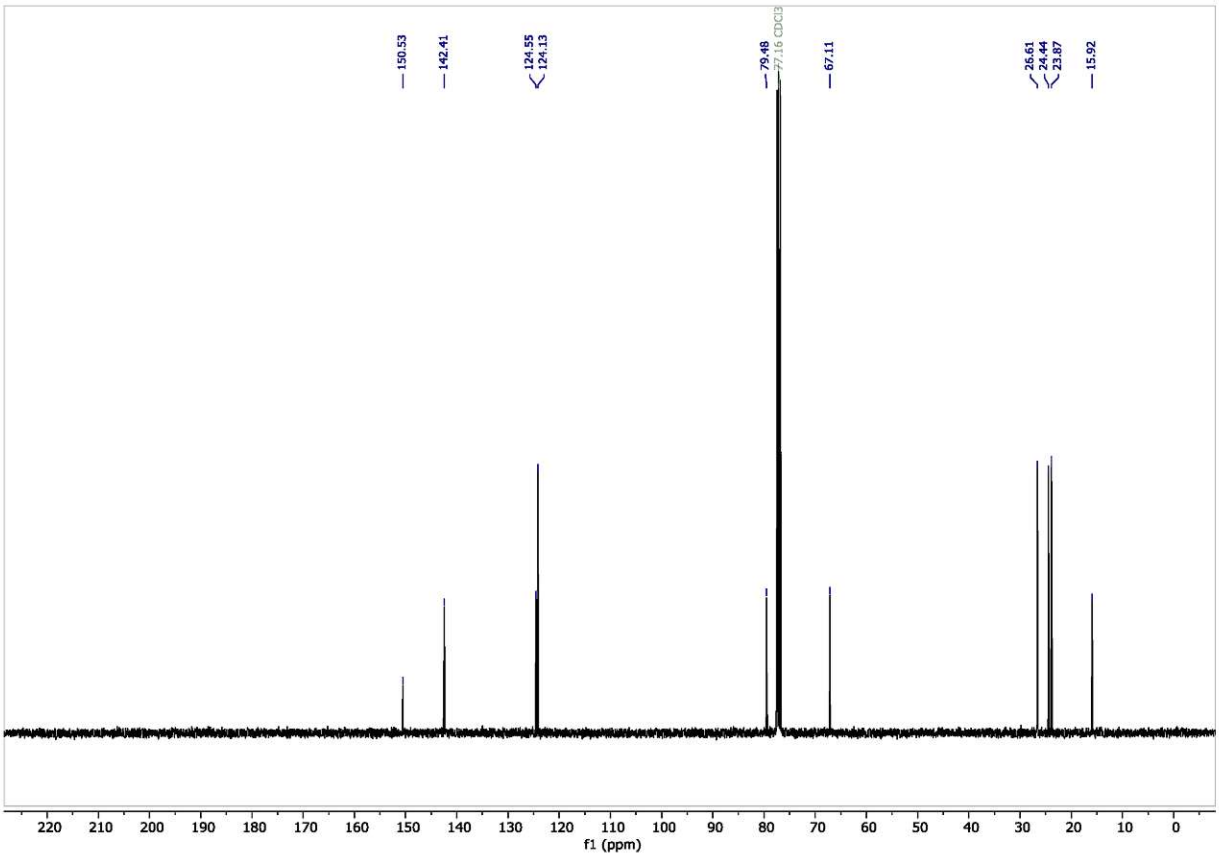


(R)-2-(2,6-diisopropylphenoxy)propan-1-ol (146)

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

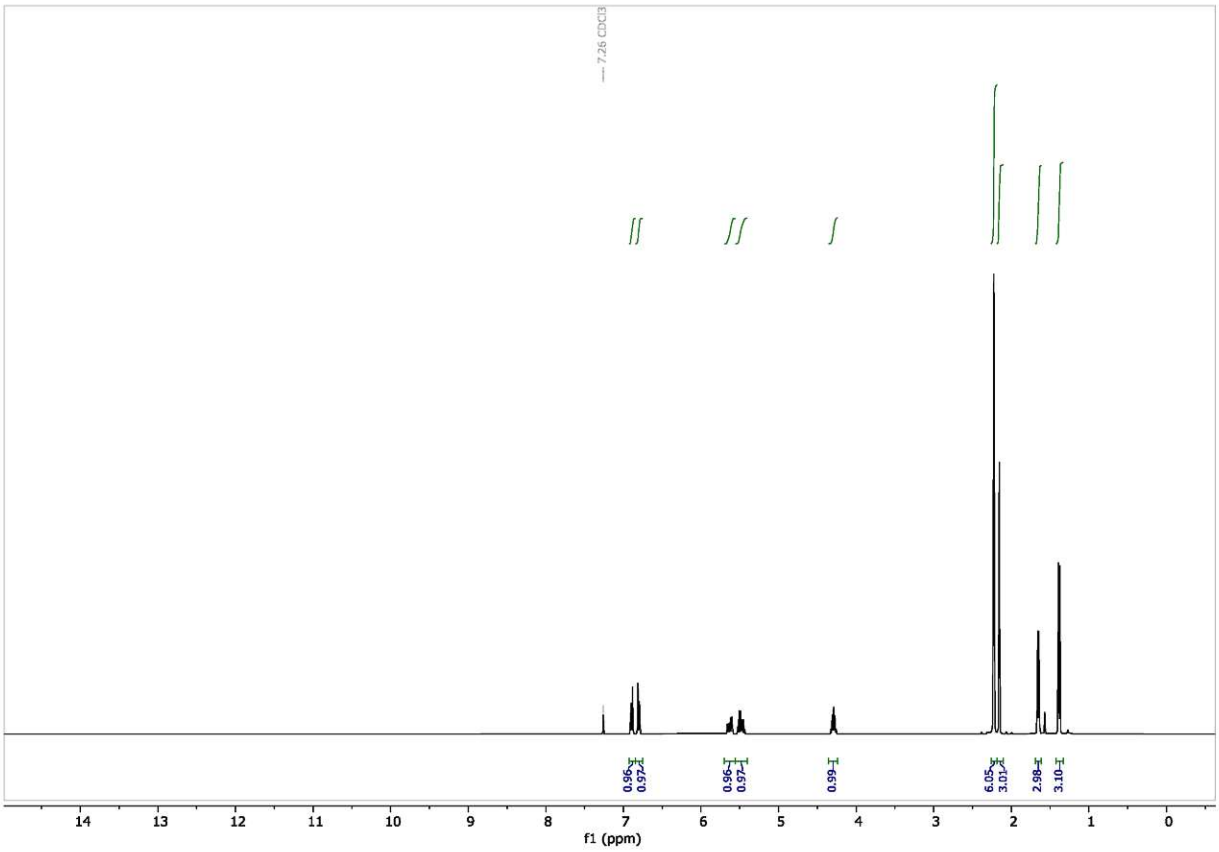


^{13}C NMR (101 MHz, $CDCl_3$)

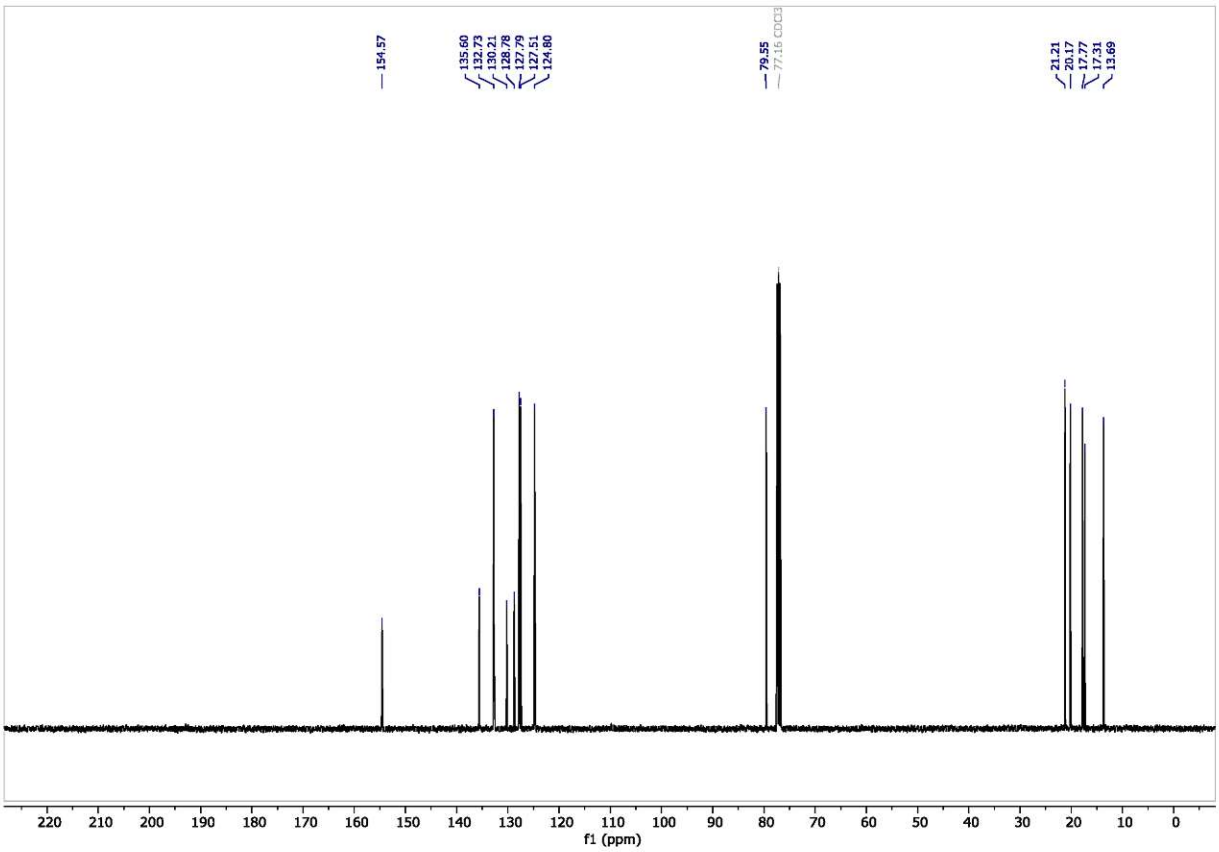


(R,E)-1,2,4-trimethyl-3-(pent-3-en-2-yloxy)benzene (90)

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

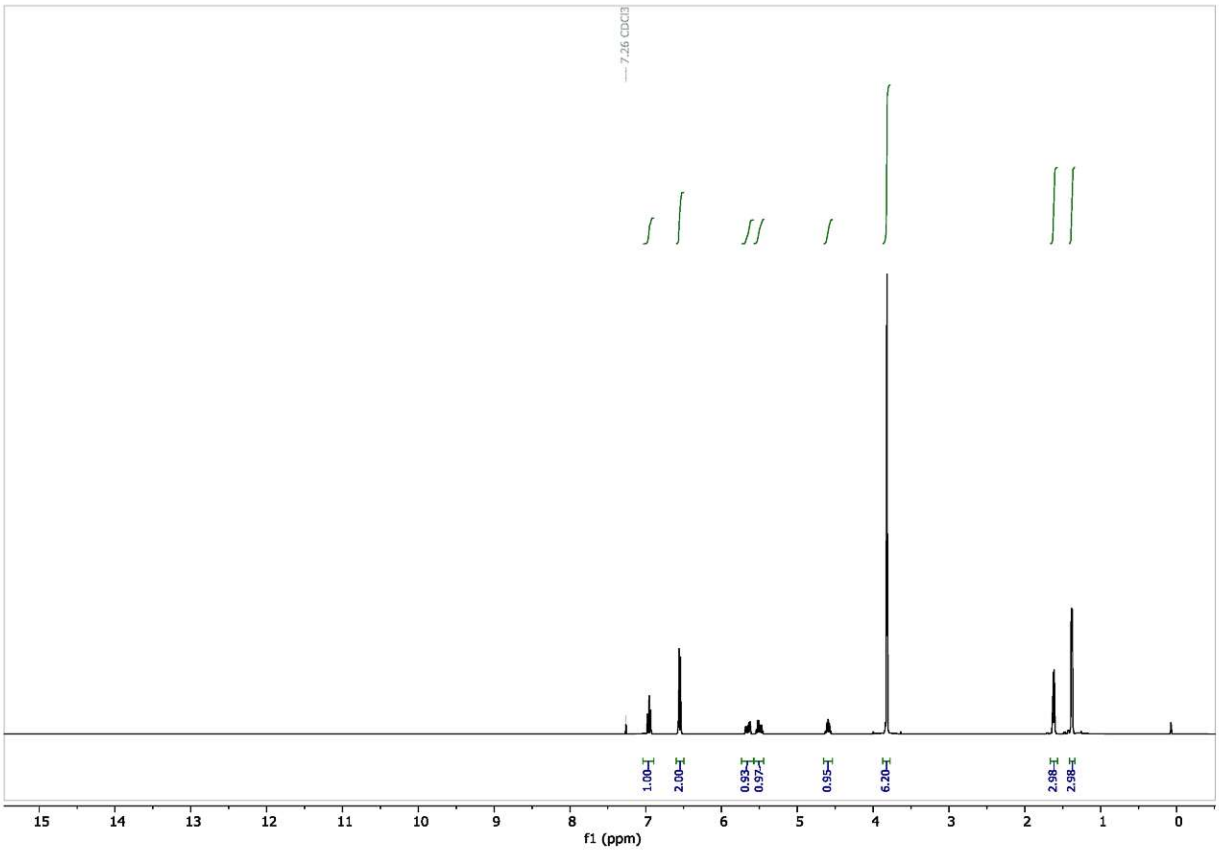


^{13}C NMR (101 MHz, $CDCl_3$)

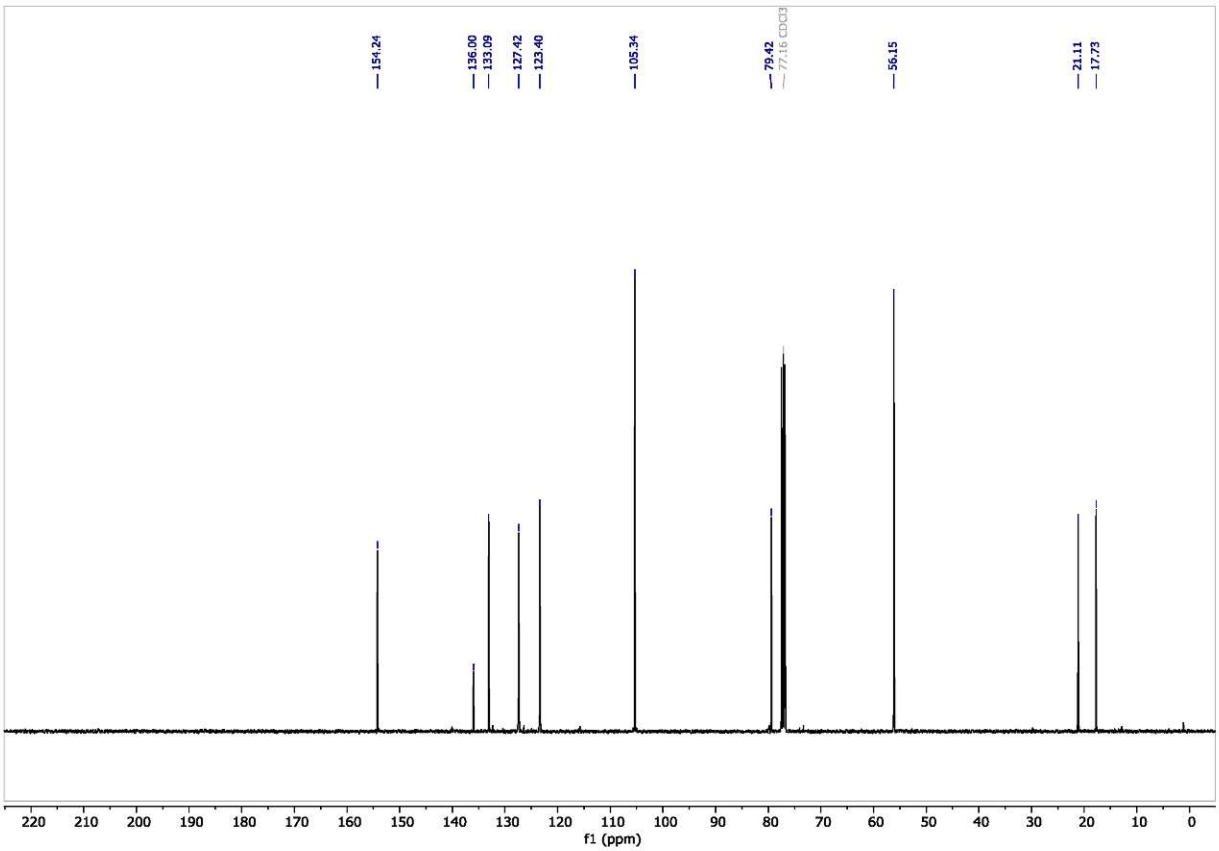


(R,E)-1,3-dimethoxy-2-(pent-3-en-2-yloxy)benzene (91)

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

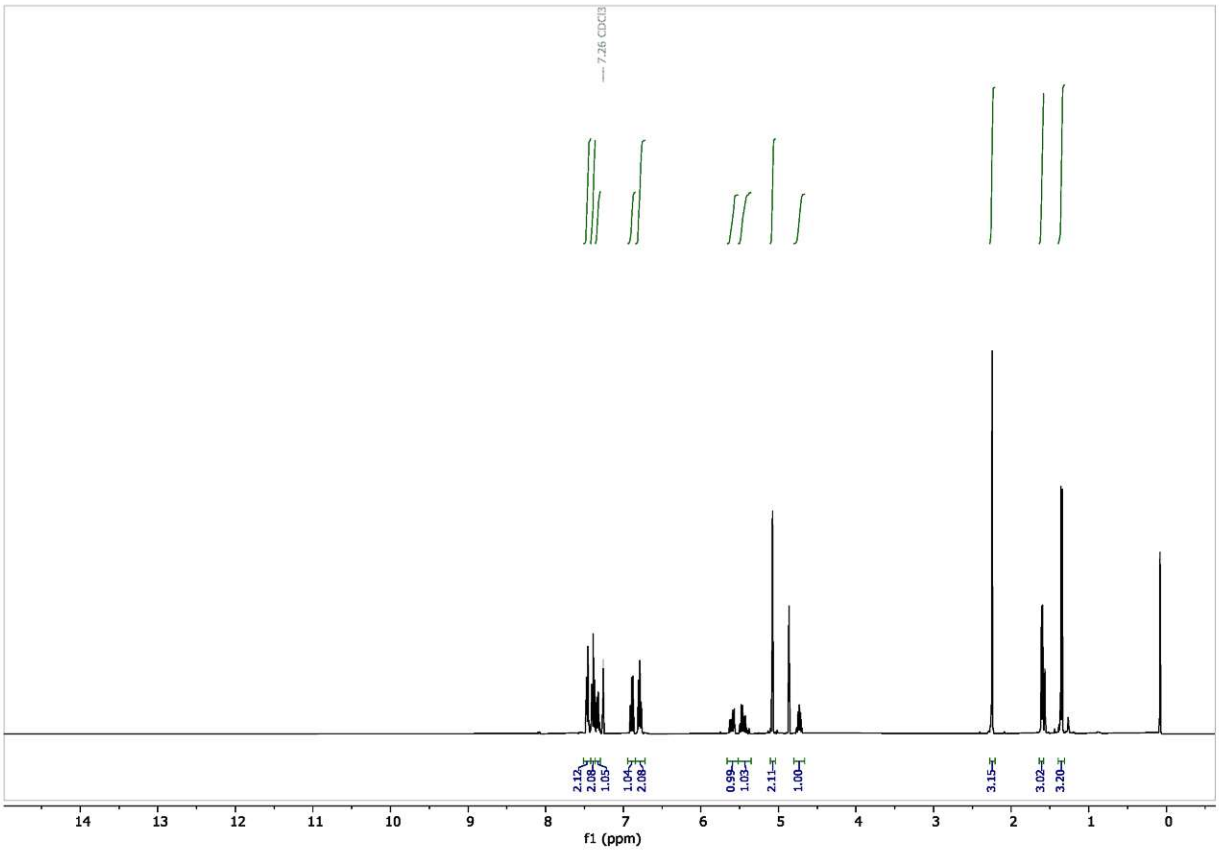


^{13}C NMR (101 MHz, $CDCl_3$)

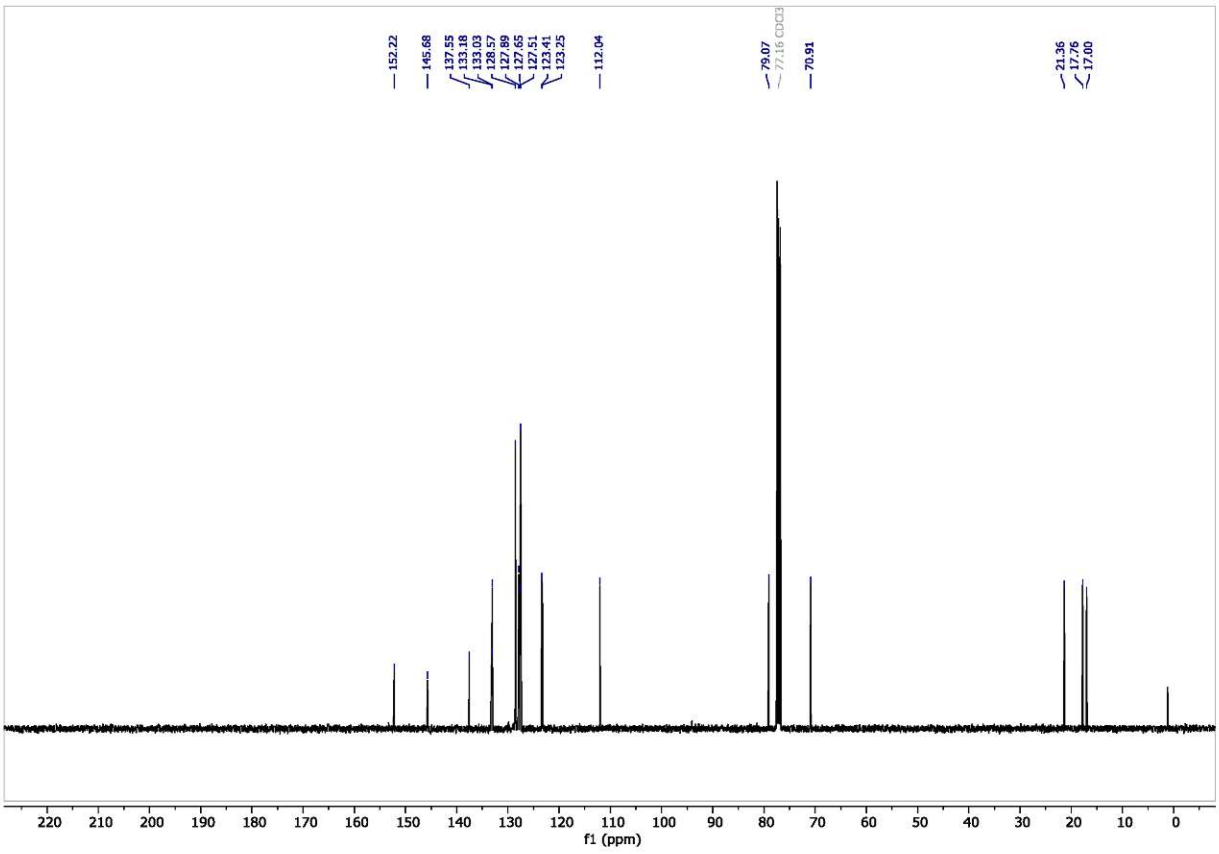


(E)-1-(benzyloxy)-3-methyl-2-(pent-3-en-2-yloxy)benzene (92)

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

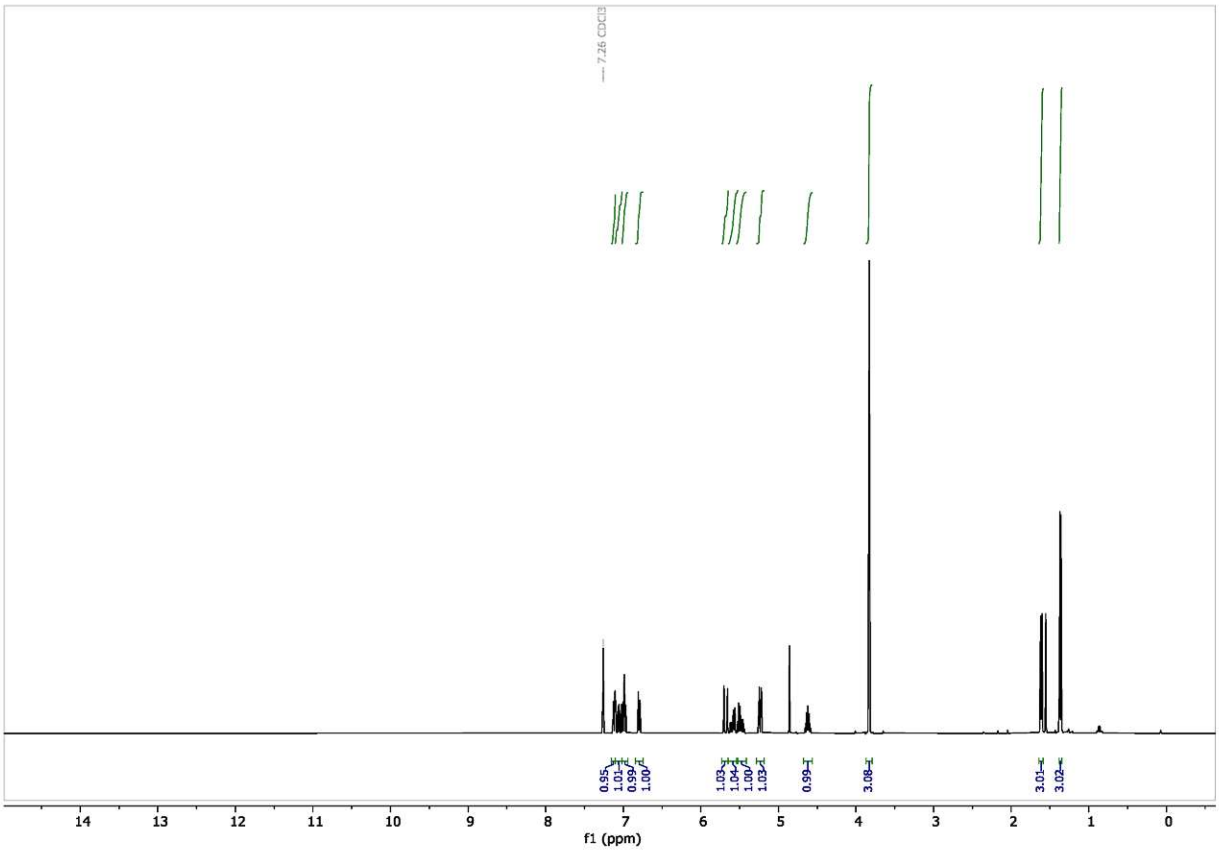


^{13}C NMR (101 MHz, $CDCl_3$)

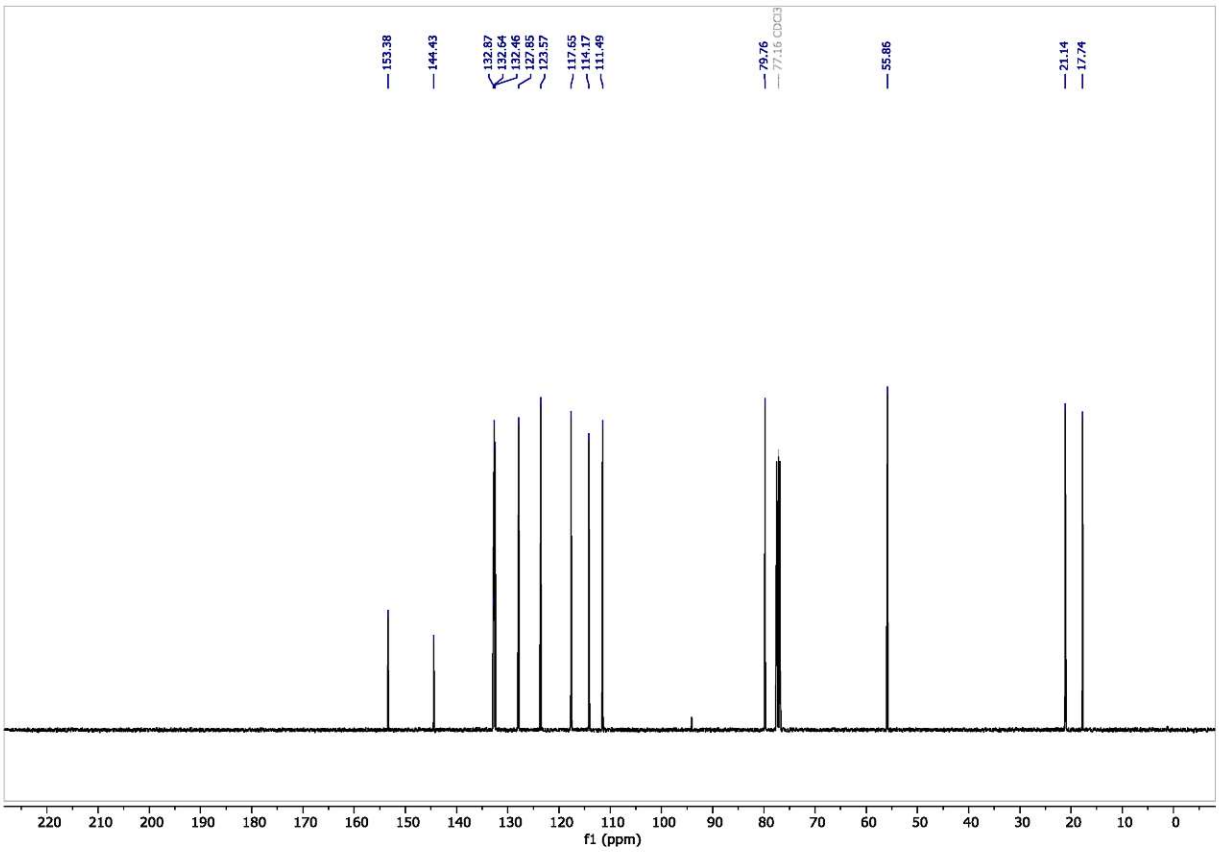


(R,E)-1-methoxy-2-(pent-3-en-2-yloxy)-3-vinylbenzene (93)

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

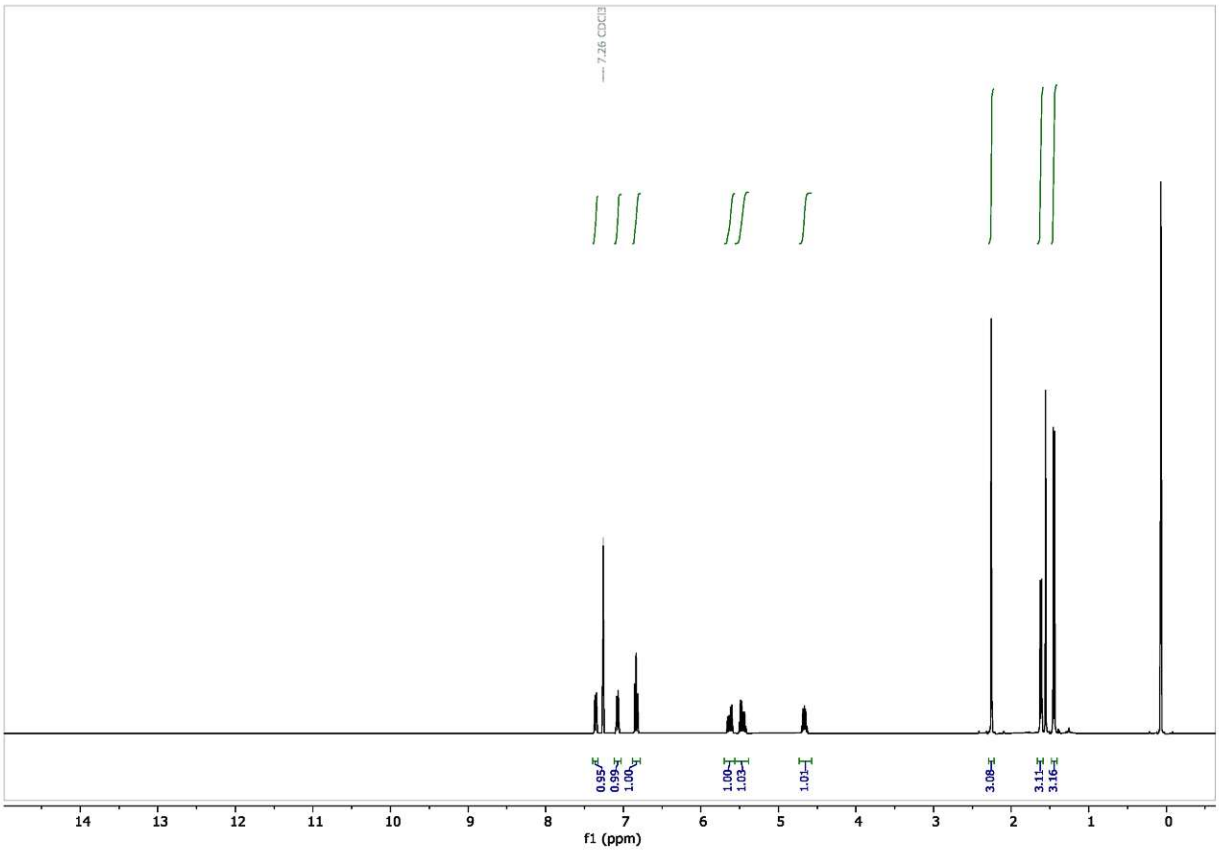


^{13}C NMR (101 MHz, $CDCl_3$)

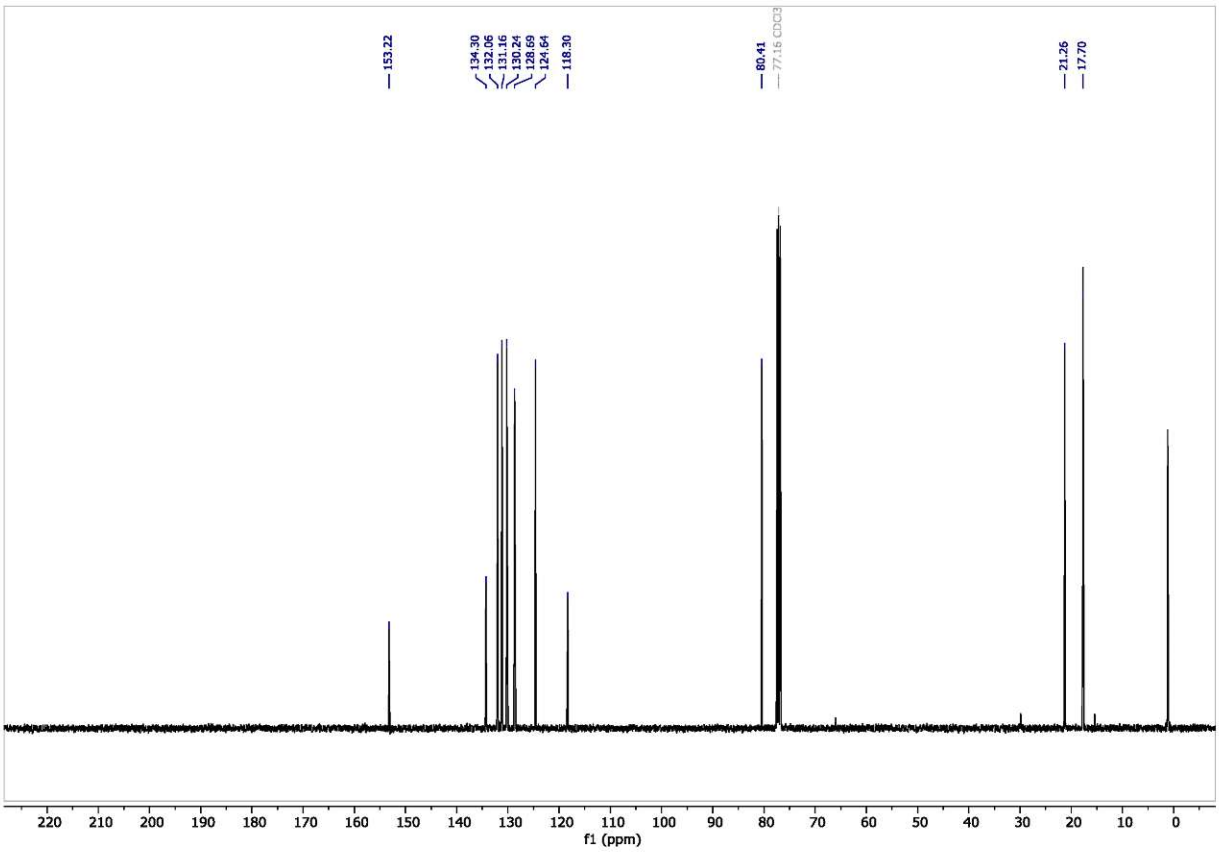


(R,E)-1-bromo-3-methyl-2-(pent-3-en-2-yloxy)benzene (94)

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

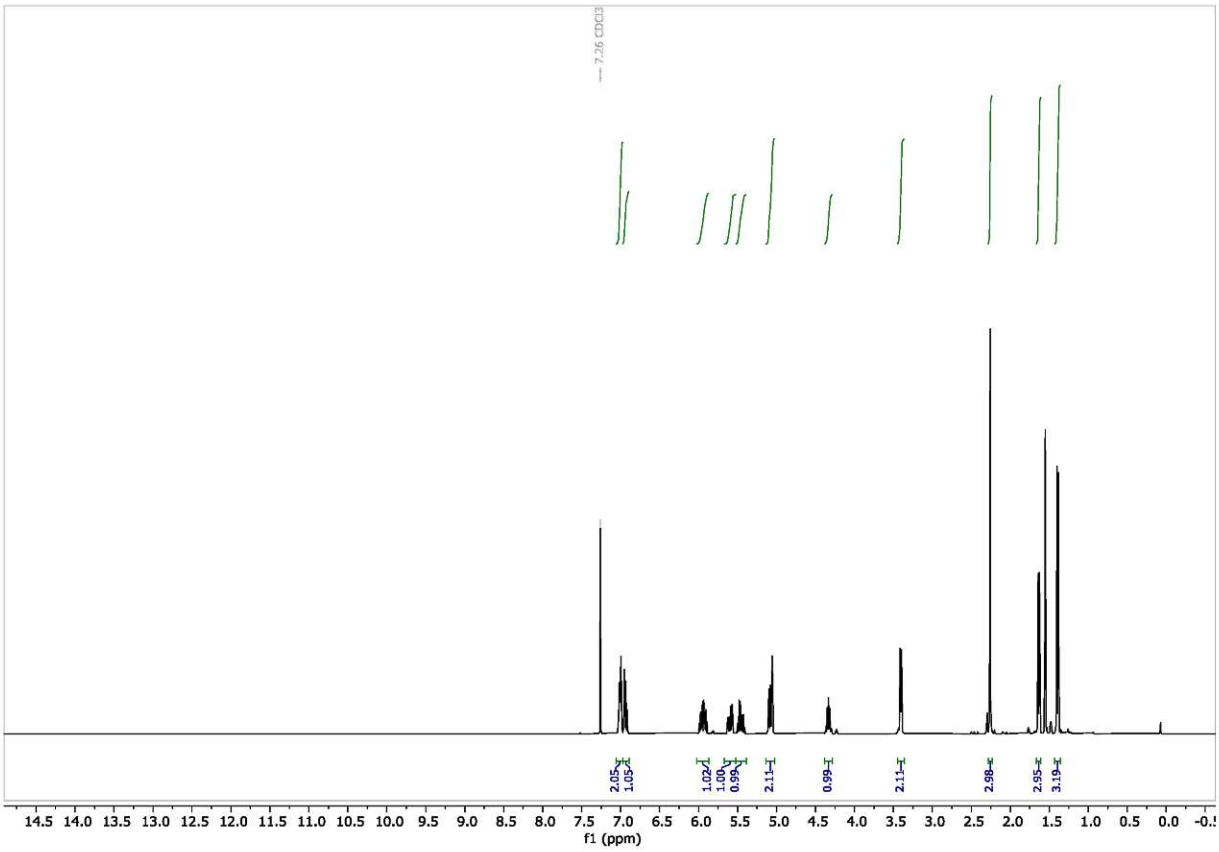


^{13}C NMR (101 MHz, $CDCl_3$)

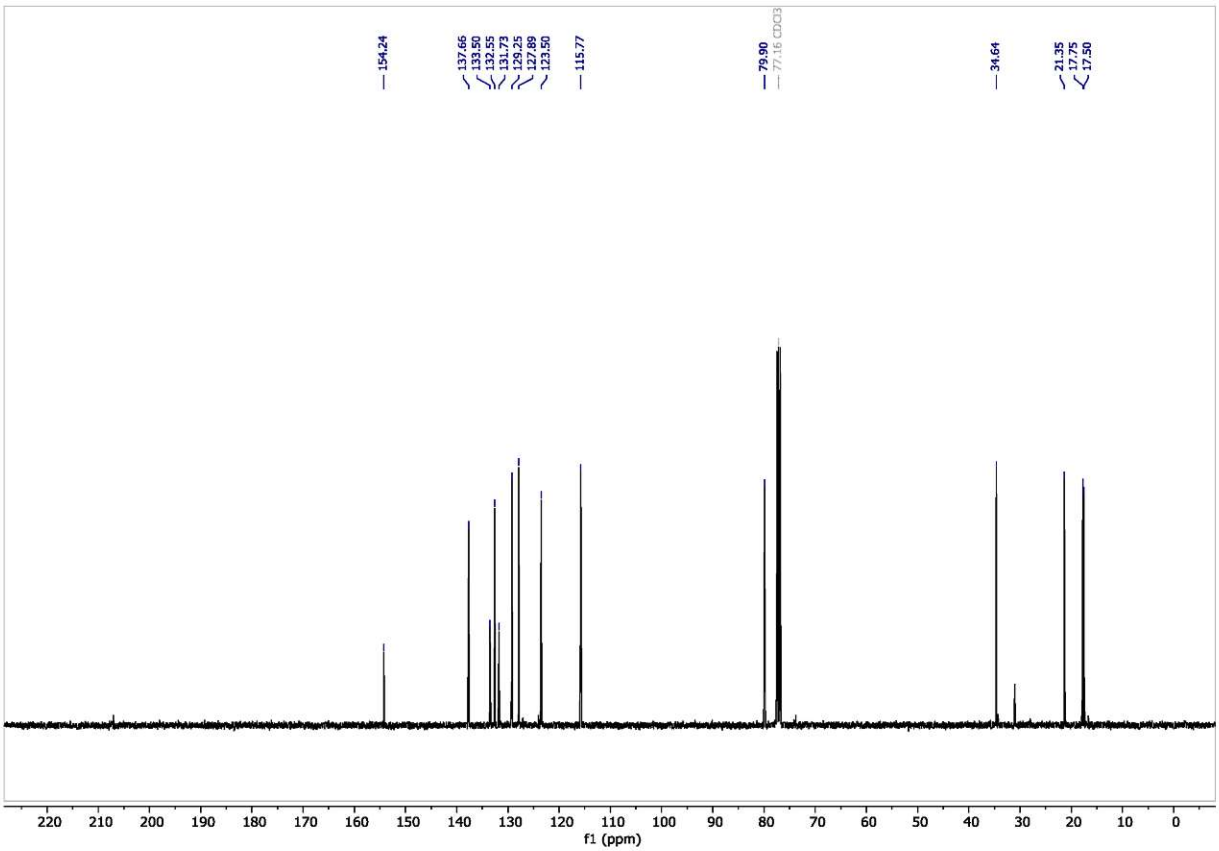


(R,E)-1-allyl-3-methyl-2-(pent-3-en-2-yloxy)benzene (95)

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

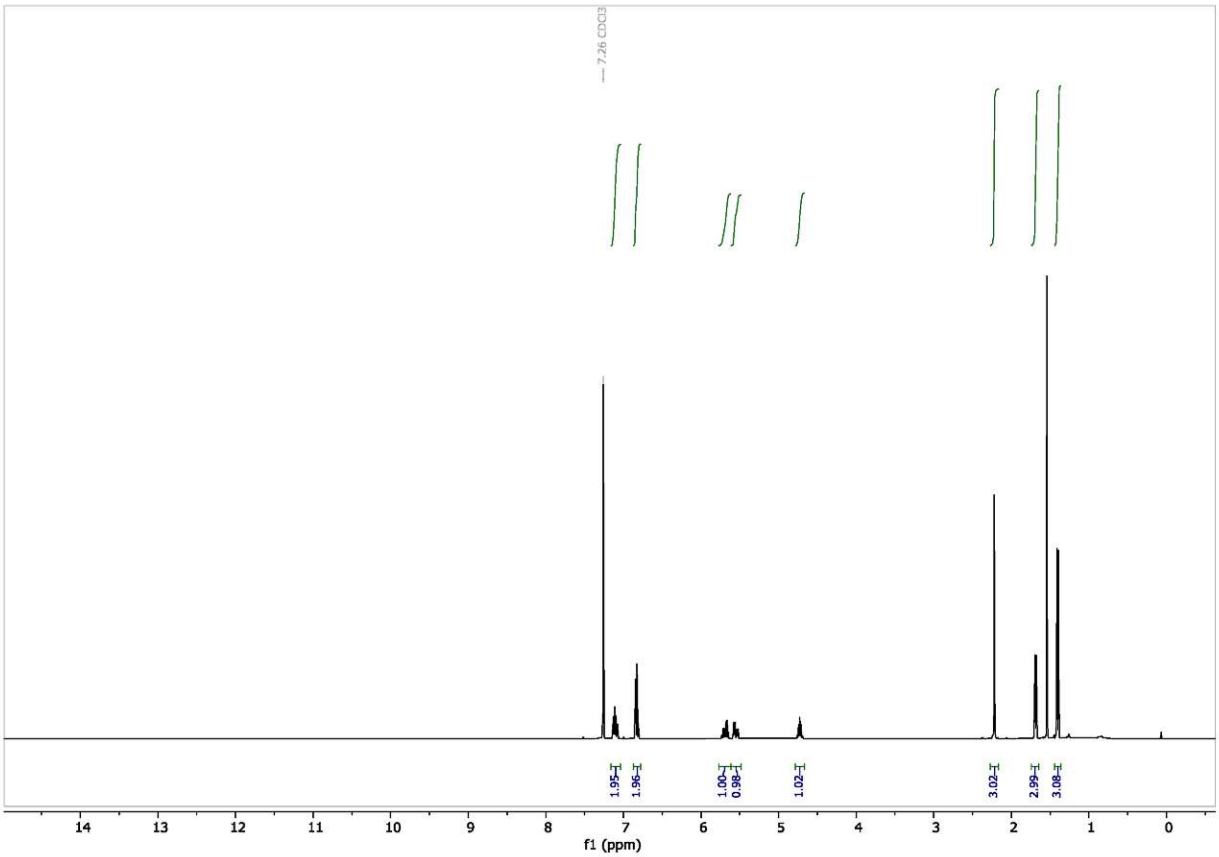


^{13}C NMR (101 MHz, $CDCl_3$)

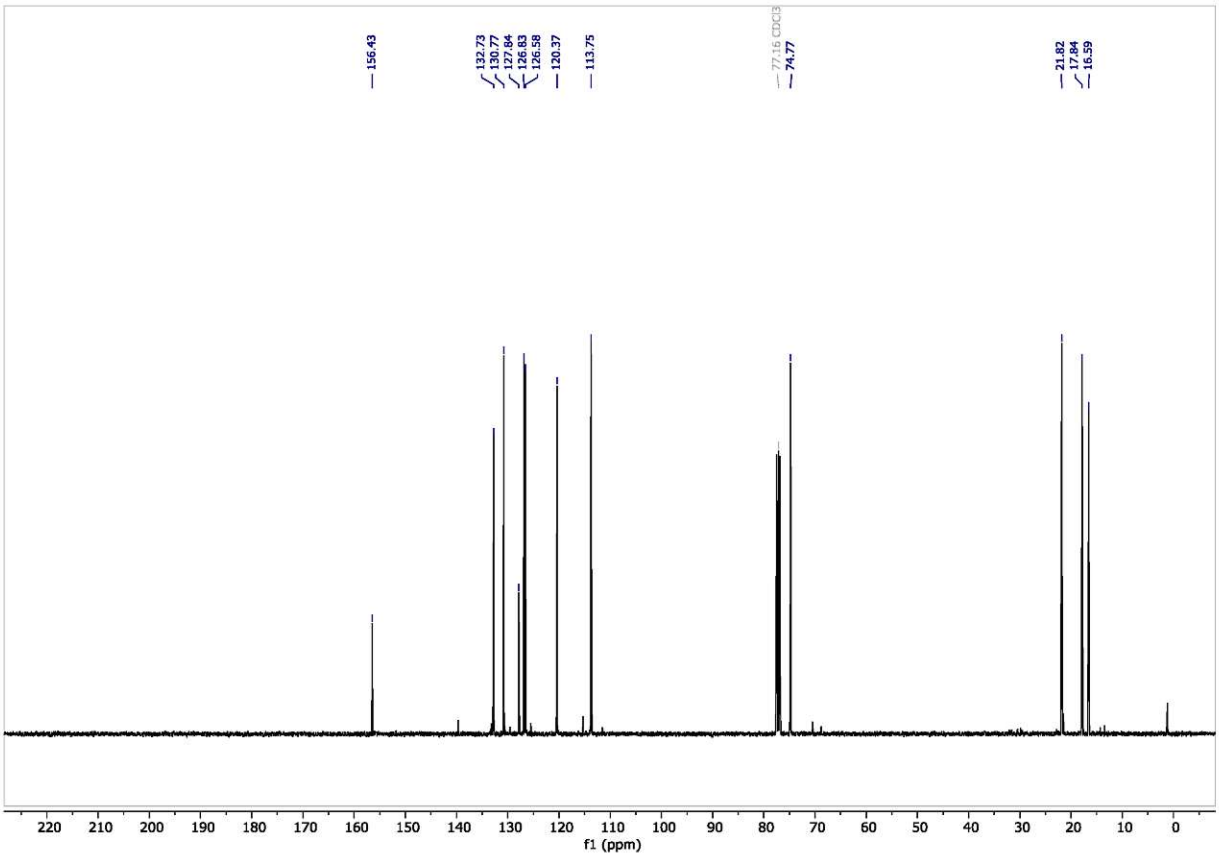


(R,E)-1-methyl-2-(pent-3-en-2-yloxy)benzene (115)

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

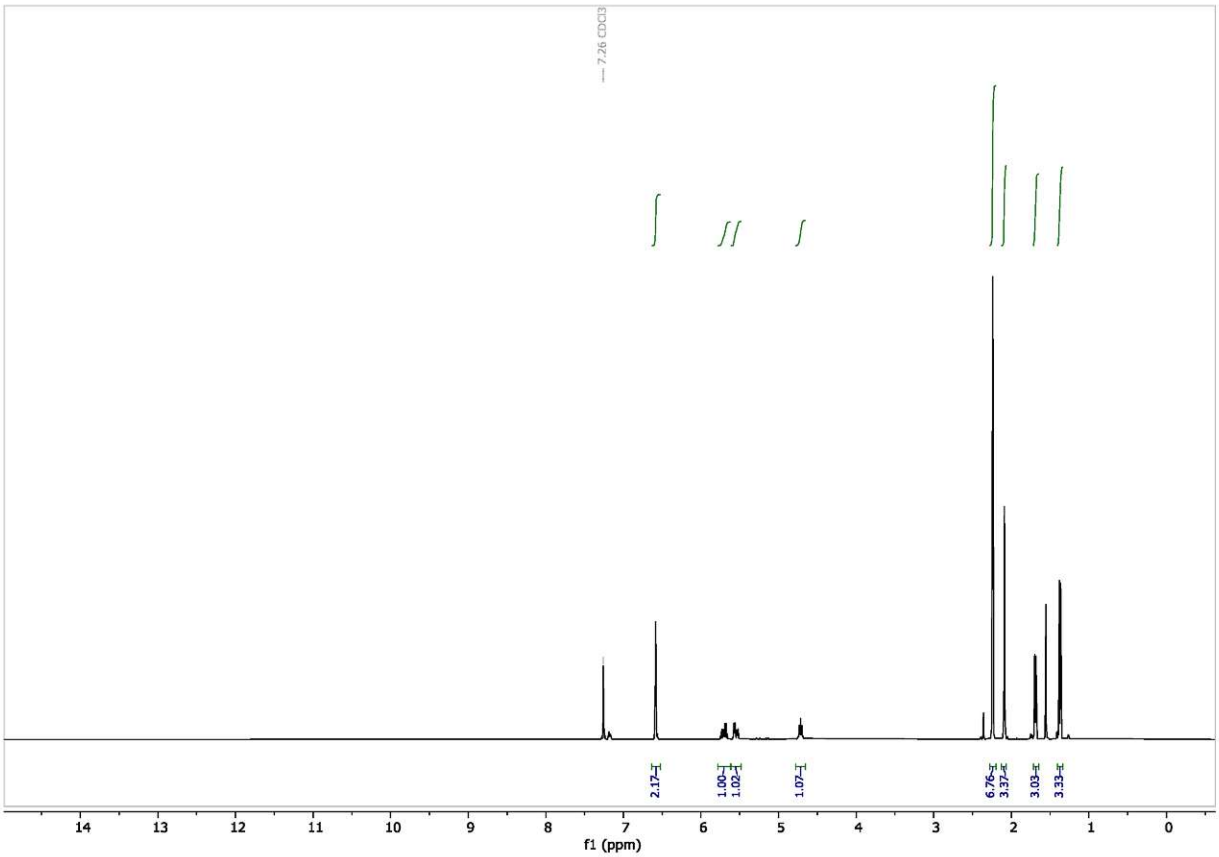


^{13}C NMR (101 MHz, $CDCl_3$)

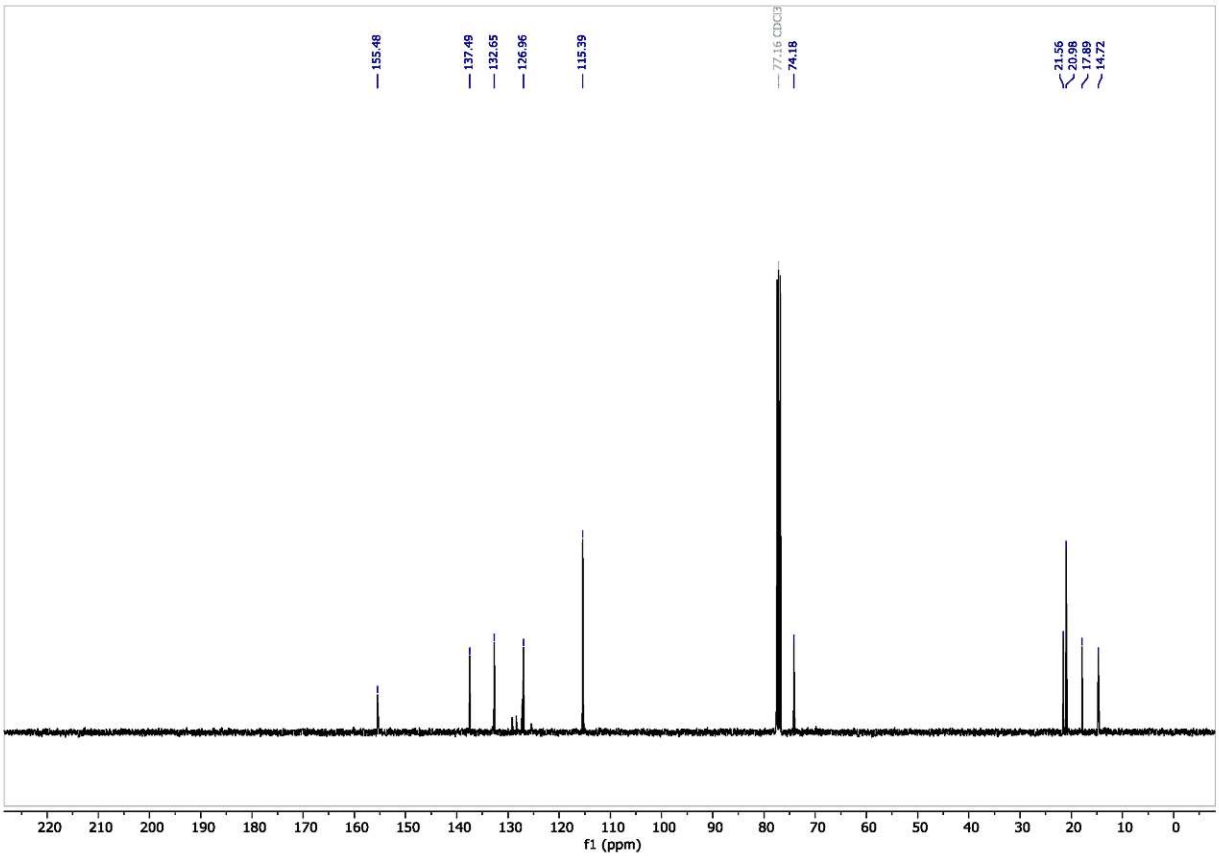


(R,E)-1,2,3-trimethyl-5-(pent-3-en-2-yloxy)benzene (57)

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

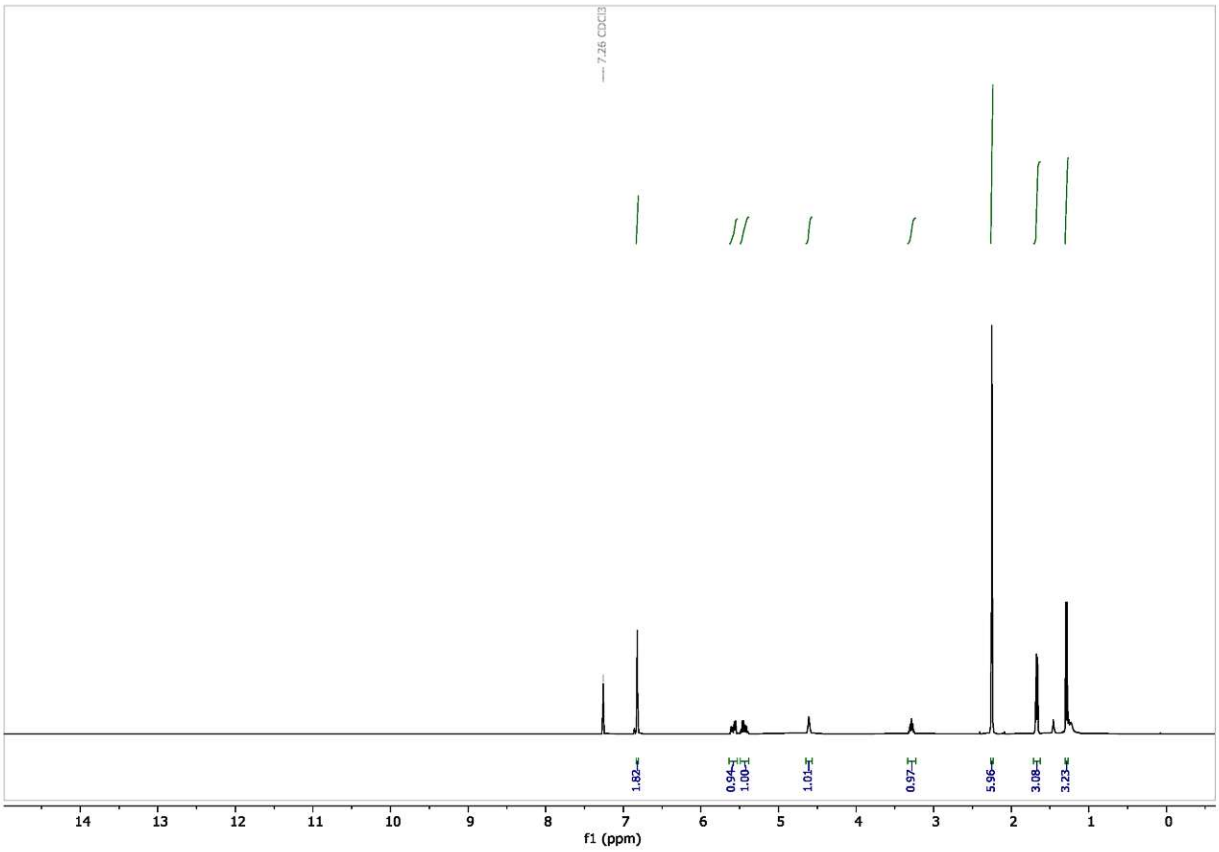


^{13}C NMR (101 MHz, $CDCl_3$)

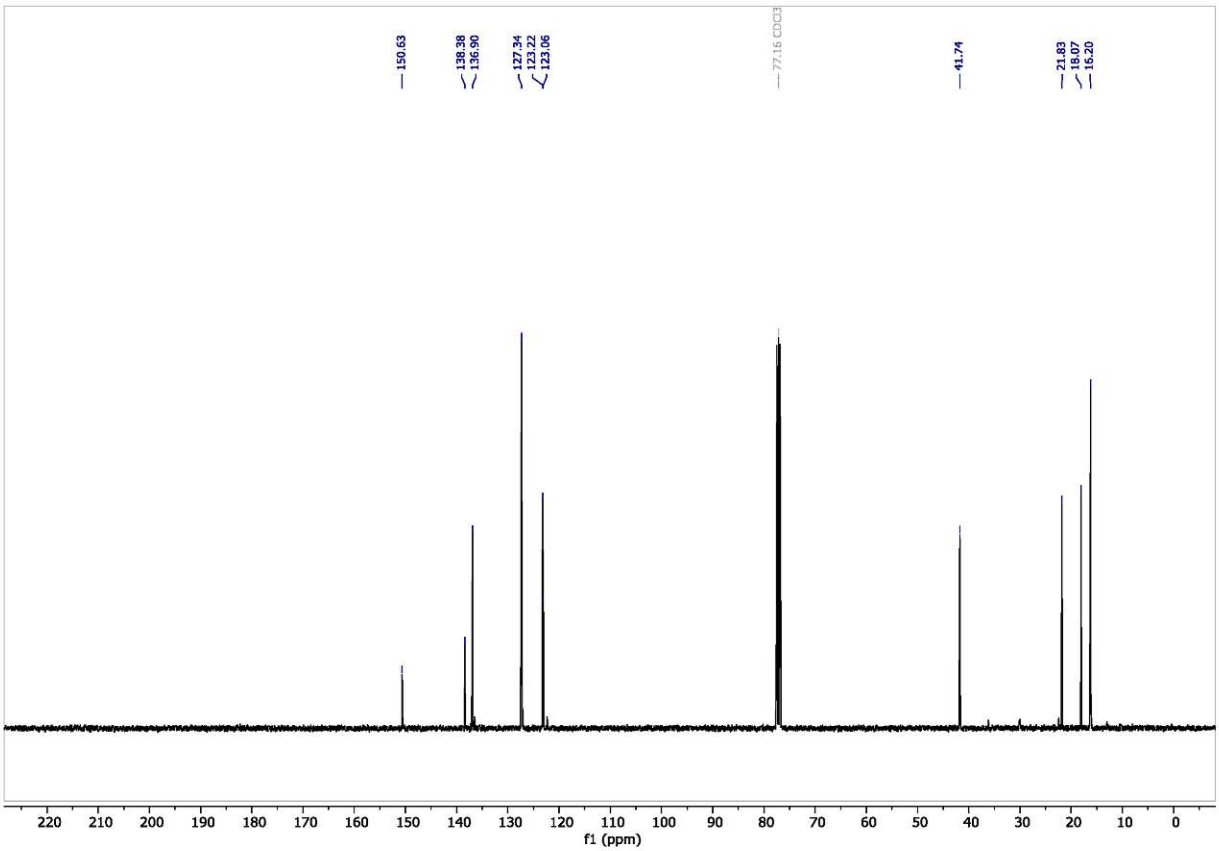


(R,E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenol (78)

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

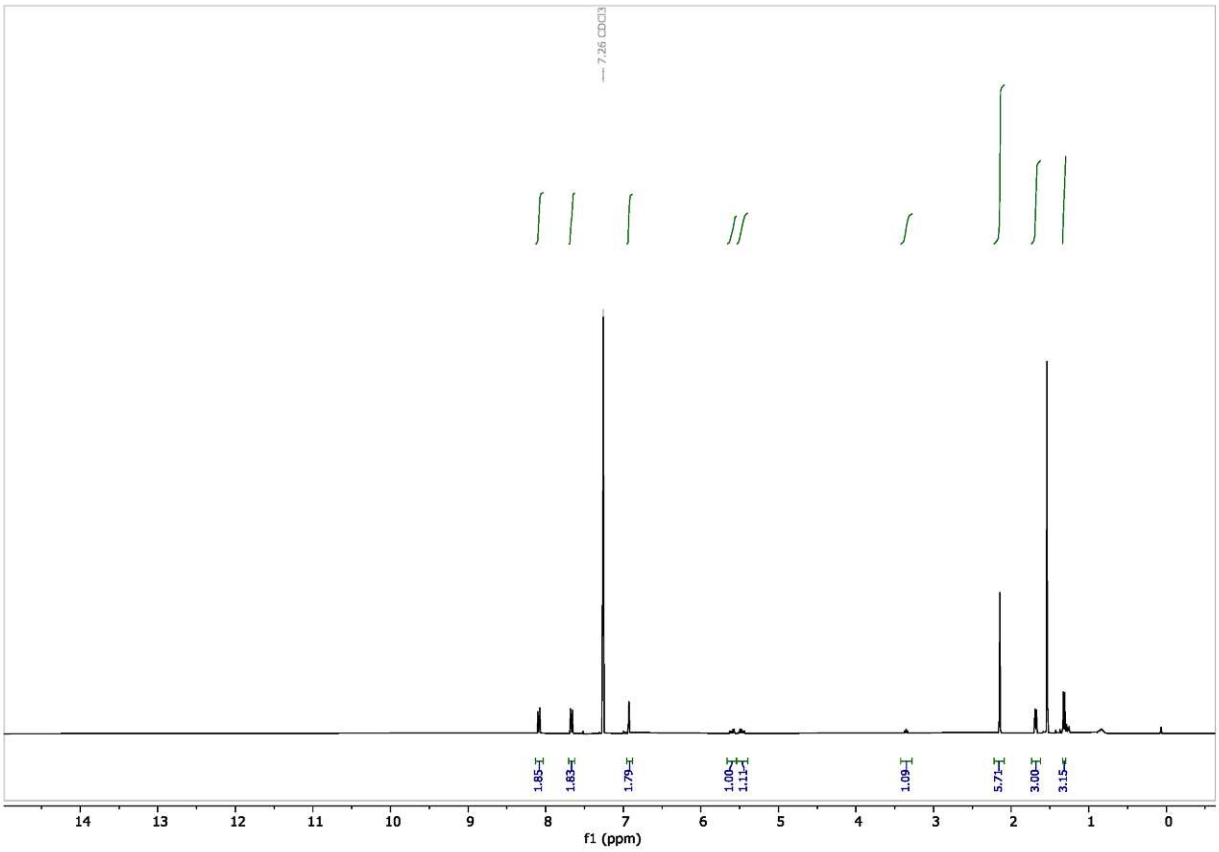


^{13}C NMR (101 MHz, $CDCl_3$)

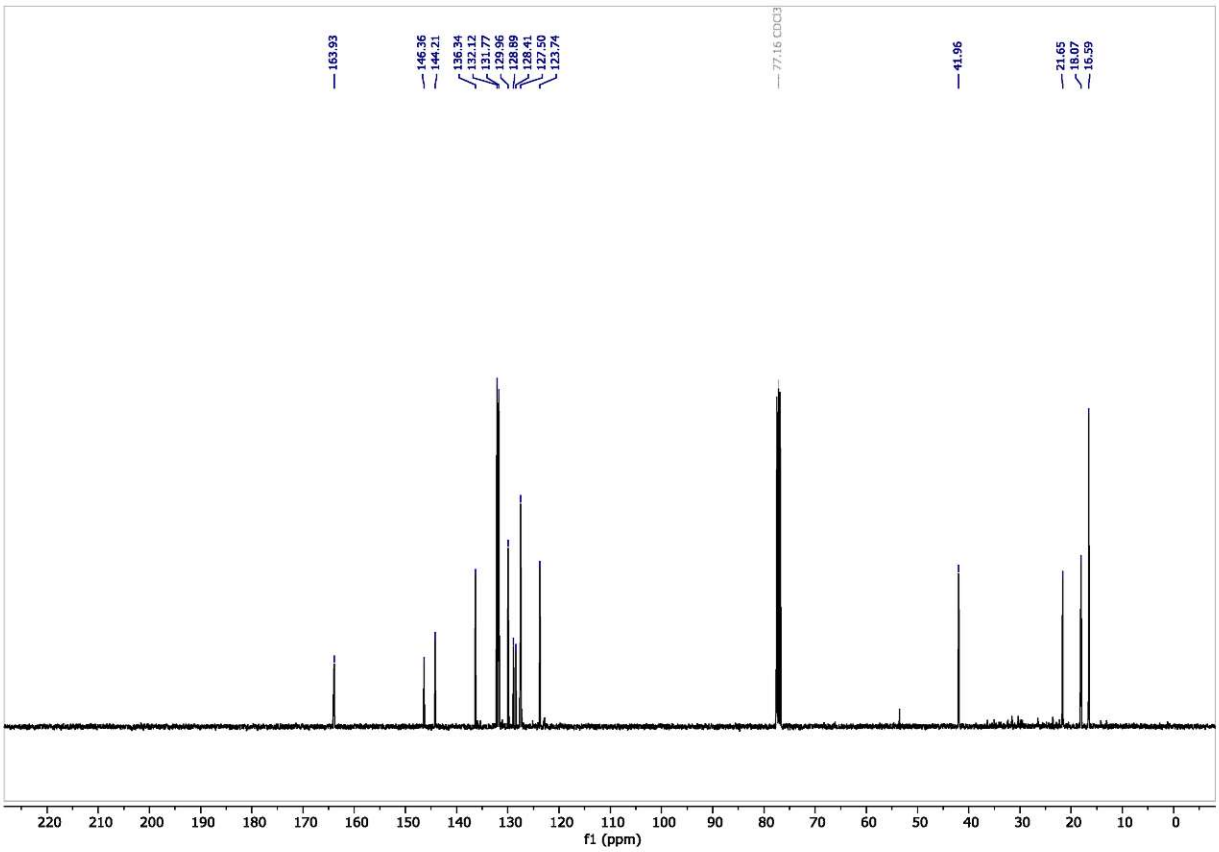


(R,E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (141)

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

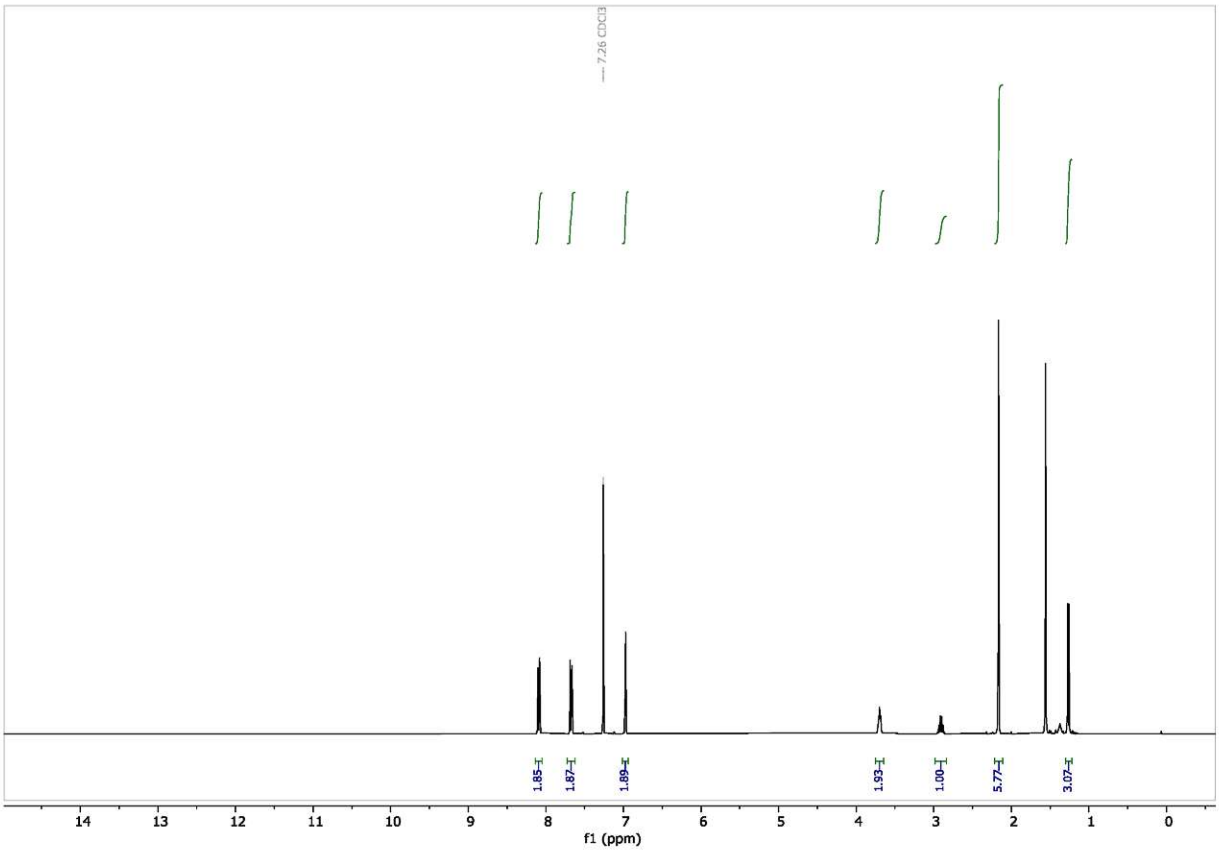


^{13}C NMR (101 MHz, $CDCl_3$)

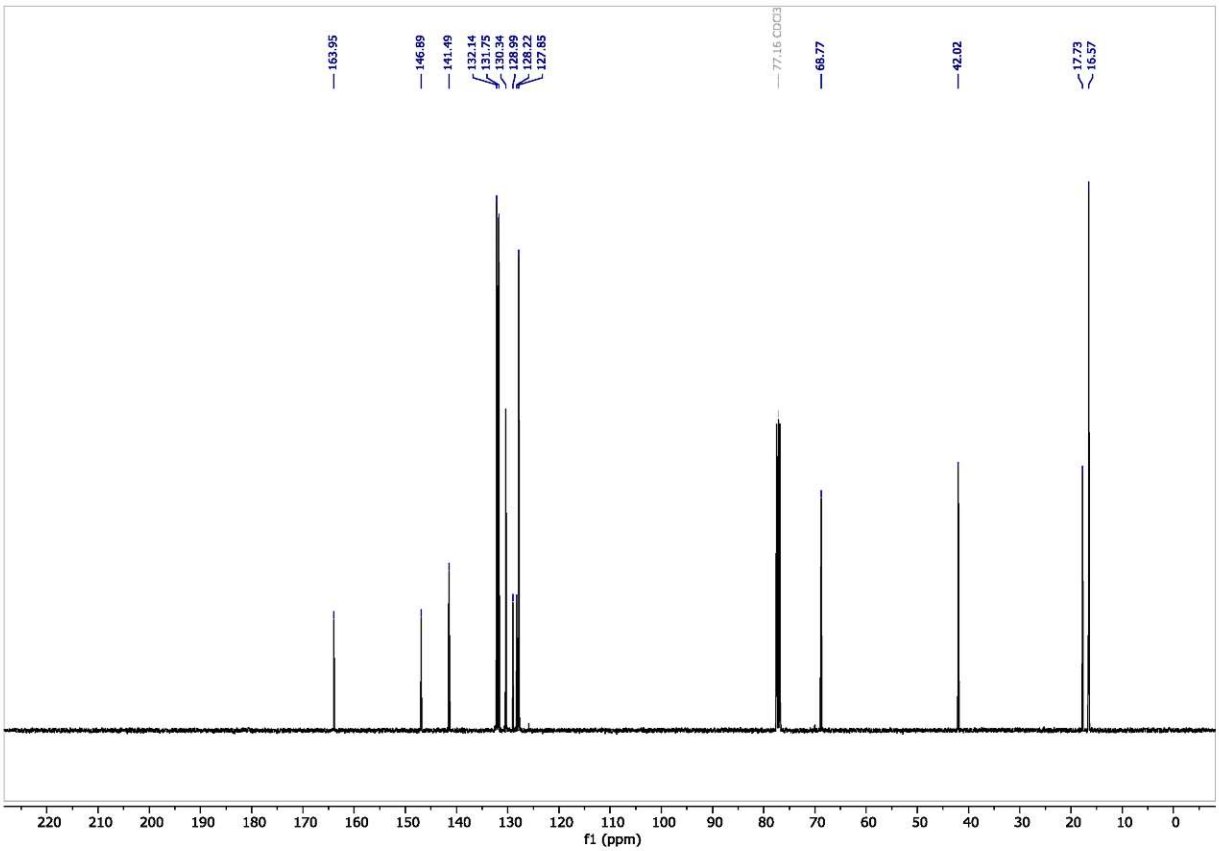


(S)-4-(1-hydroxypropan-2-yl)-2,6-dimethylphenyl 4-bromobenzoate (142)

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

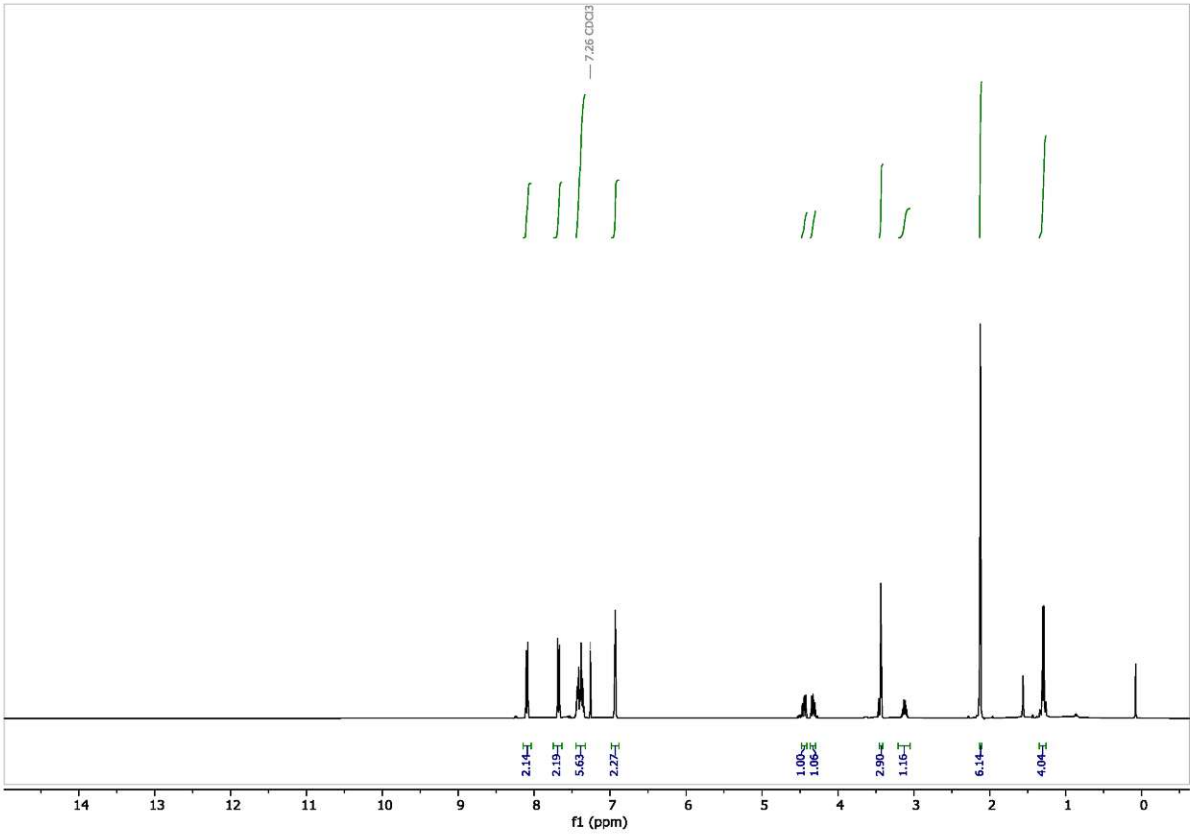


^{13}C NMR (101 MHz, $CDCl_3$)

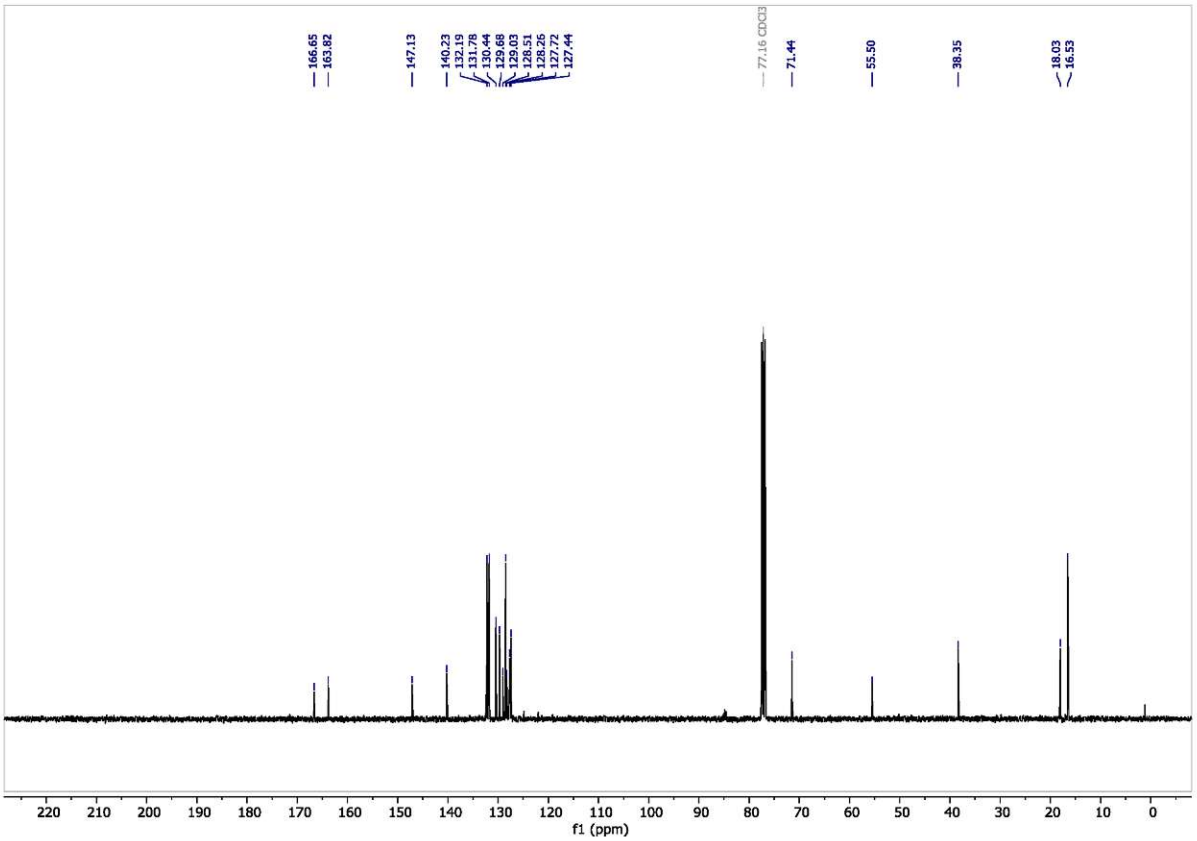


2,6-dimethyl-4-((*(S)*-1-(((*(S)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)propan-2-yl)phenyl 4-bromobenzoate (143s)

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

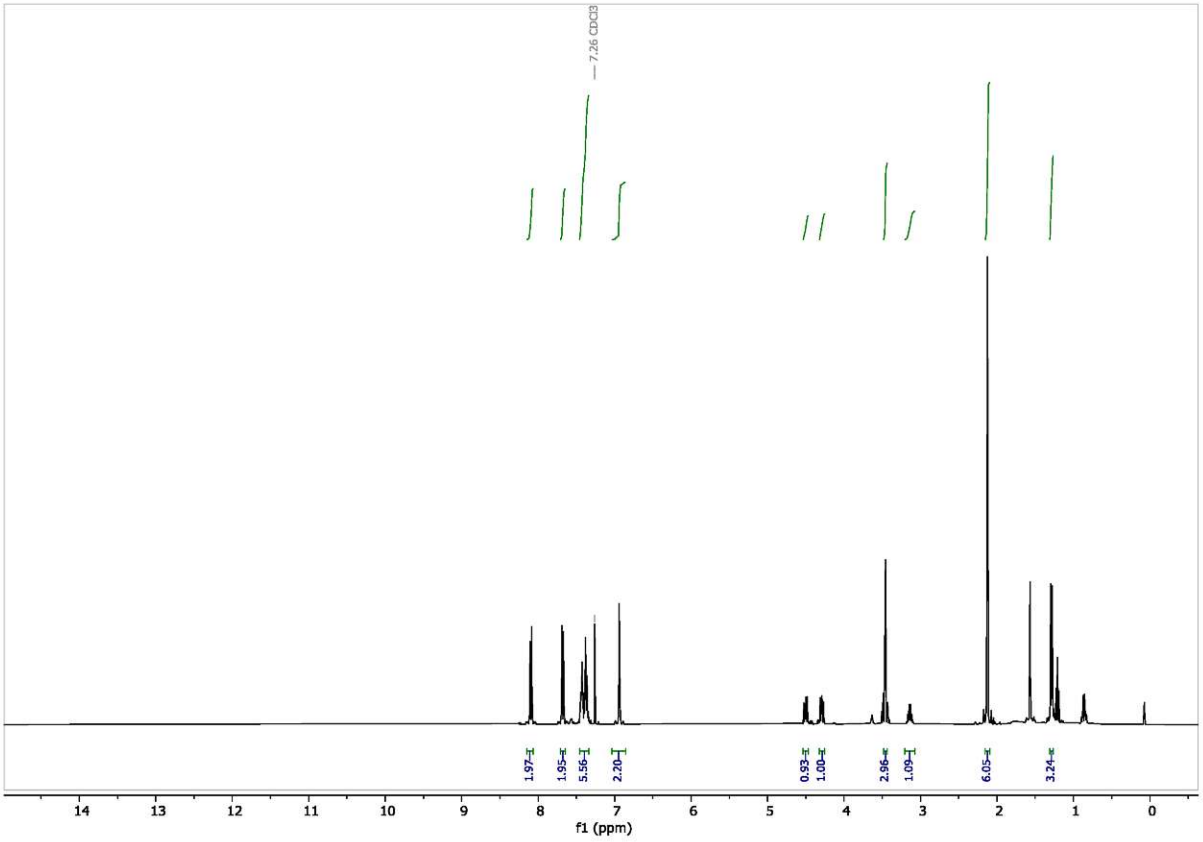


^{13}C NMR (101 MHz, $CDCl_3$)

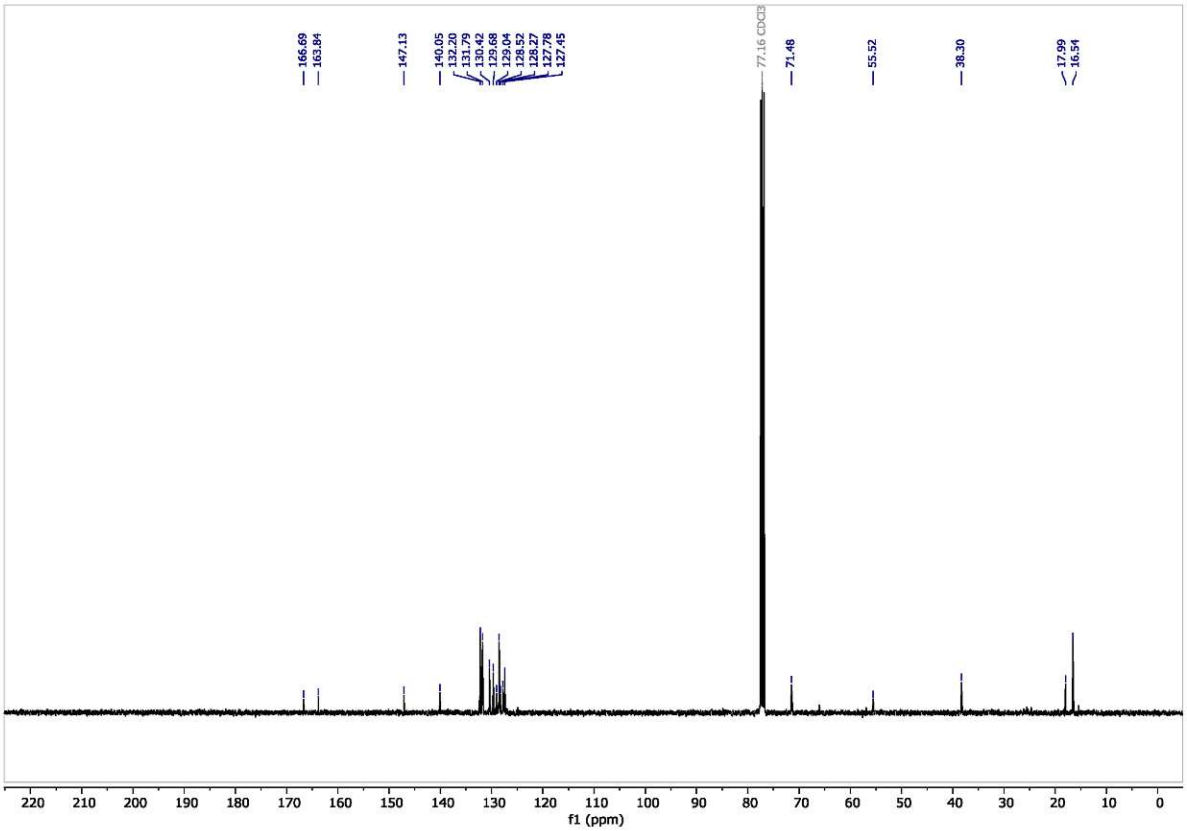


2,6-dimethyl-4-((*(S)*-1-(((*(R)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)propan-2-yl)phenyl 4-bromobenzoate (143r)

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

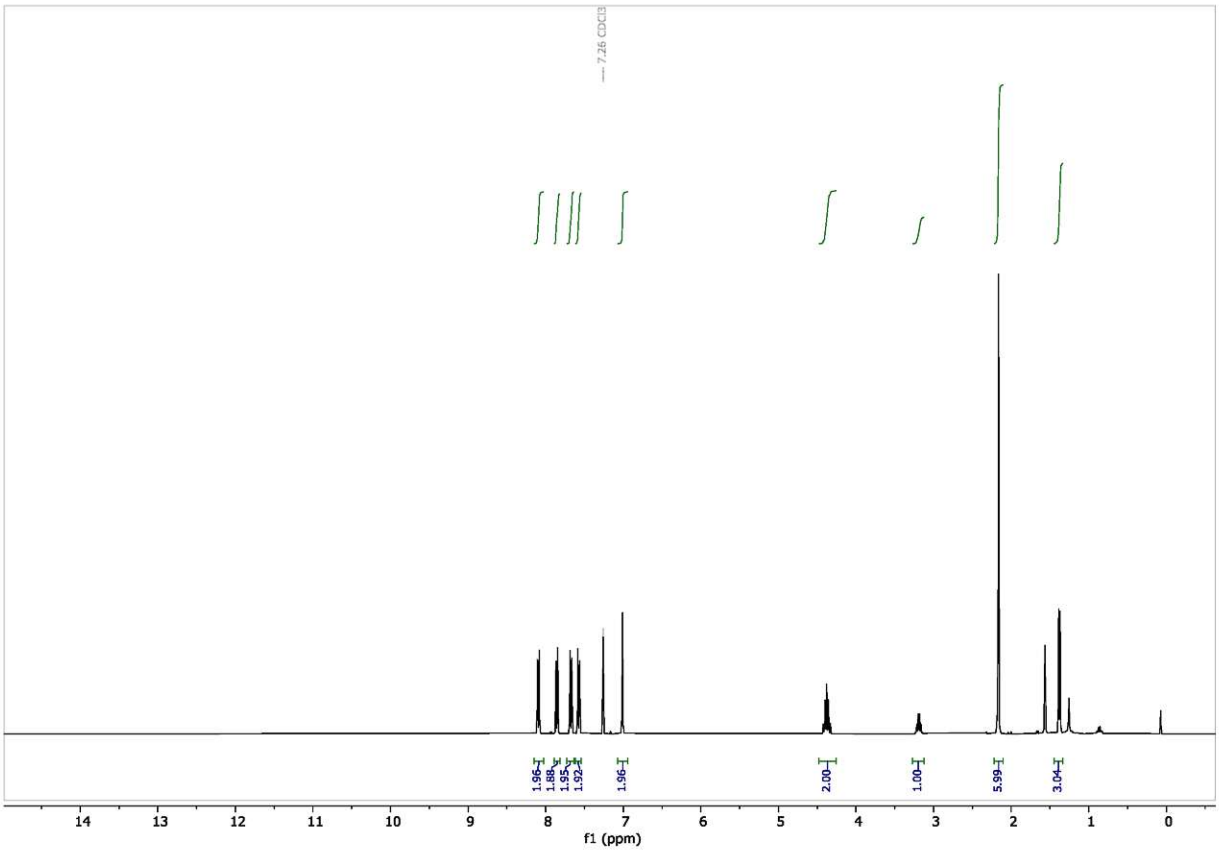


^{13}C NMR (101 MHz, $CDCl_3$)

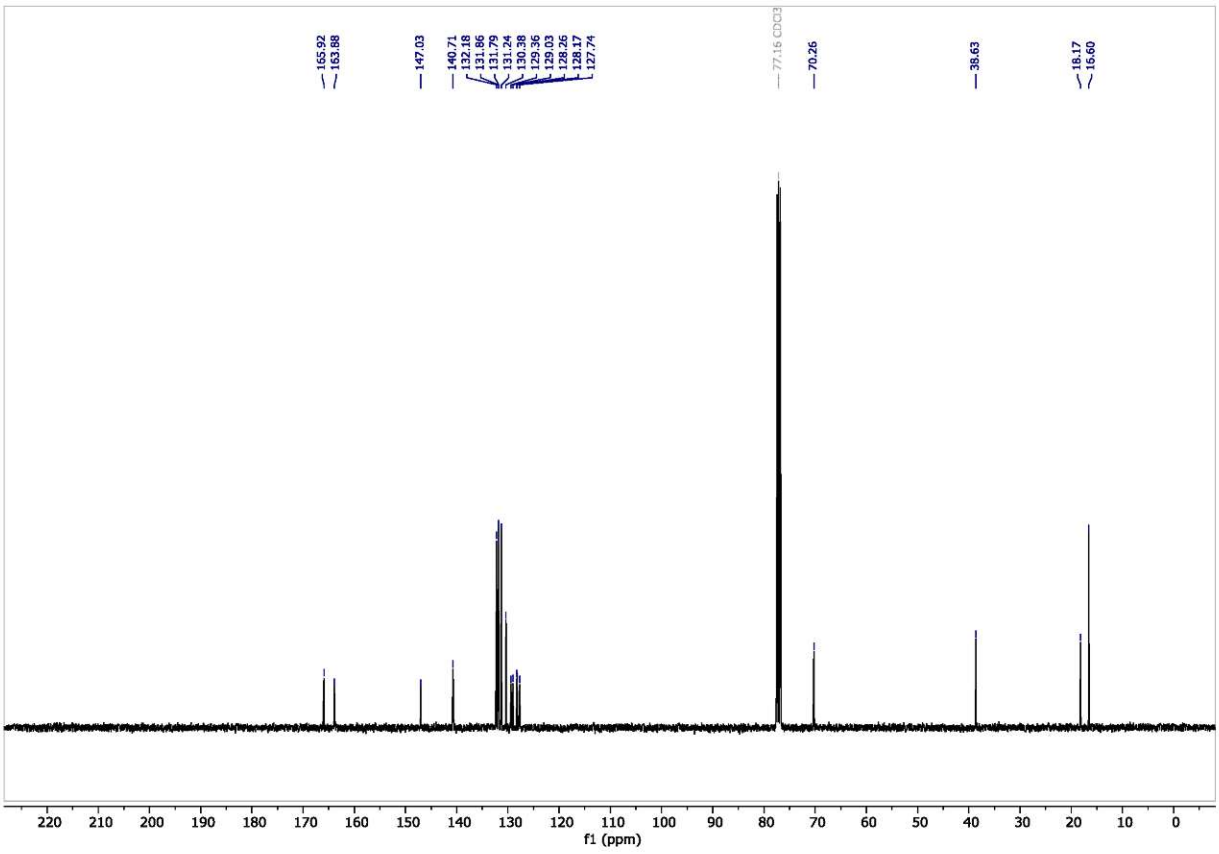


(S)-2-(4-((4-bromobenzoyl)oxy)-3,5-dimethylphenyl)propyl 4-bromobenzoate (145)

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

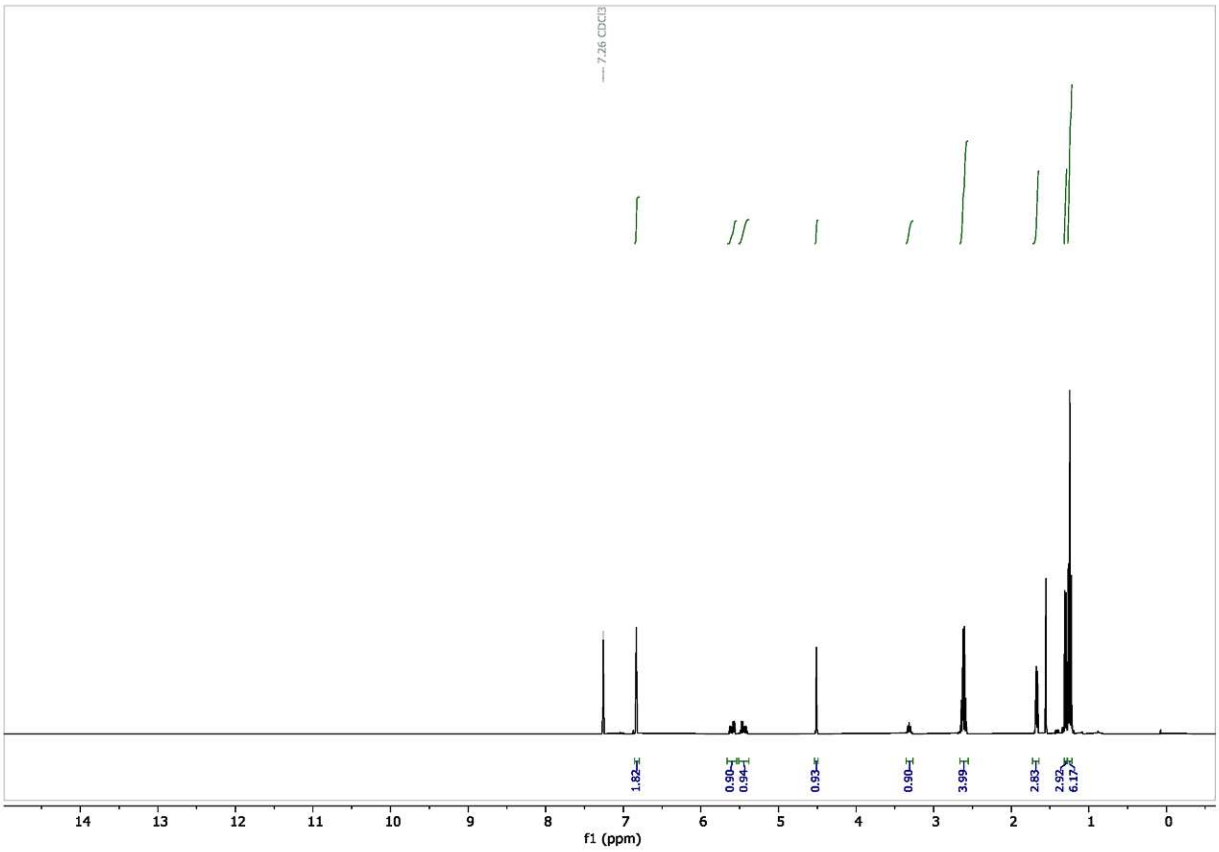


^{13}C NMR (101 MHz, $CDCl_3$)

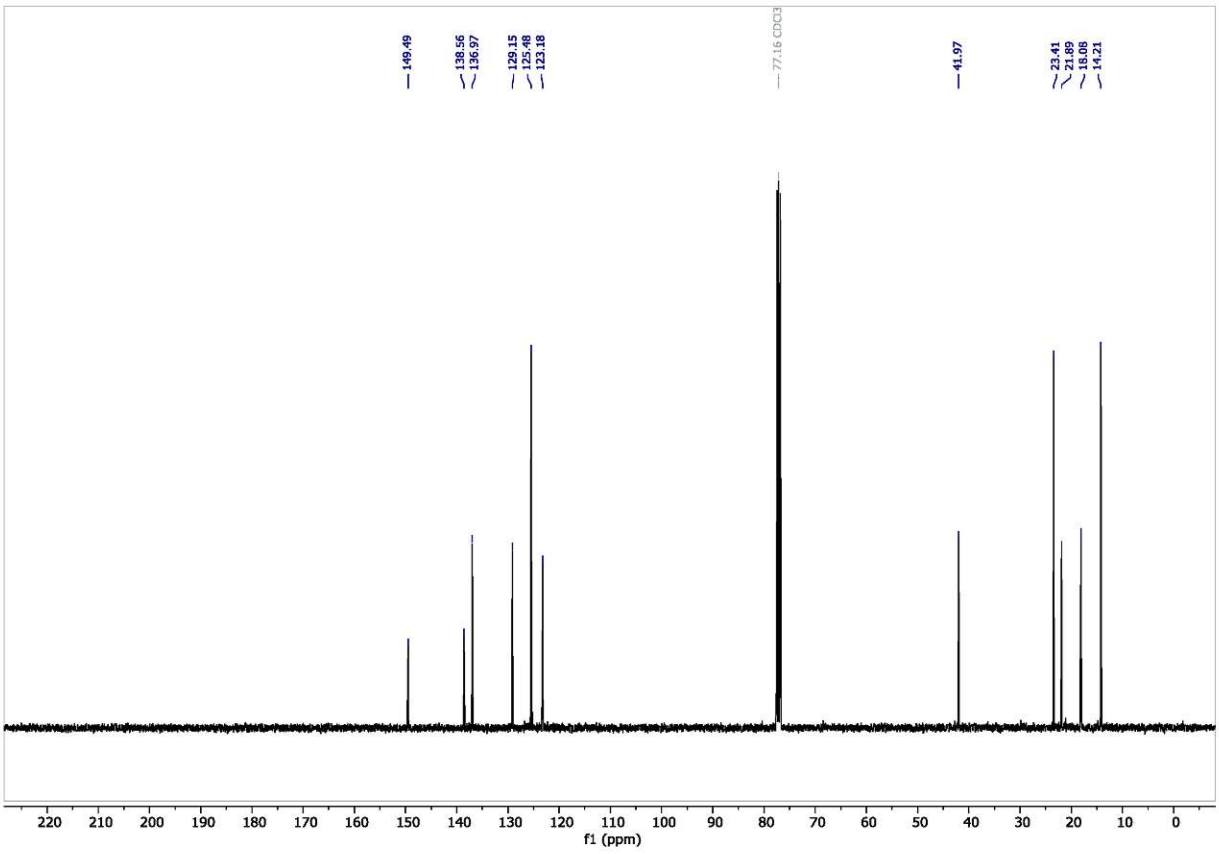


(R,E)-2,6-diethyl-4-(pent-3-en-2-yl)phenol (101)

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

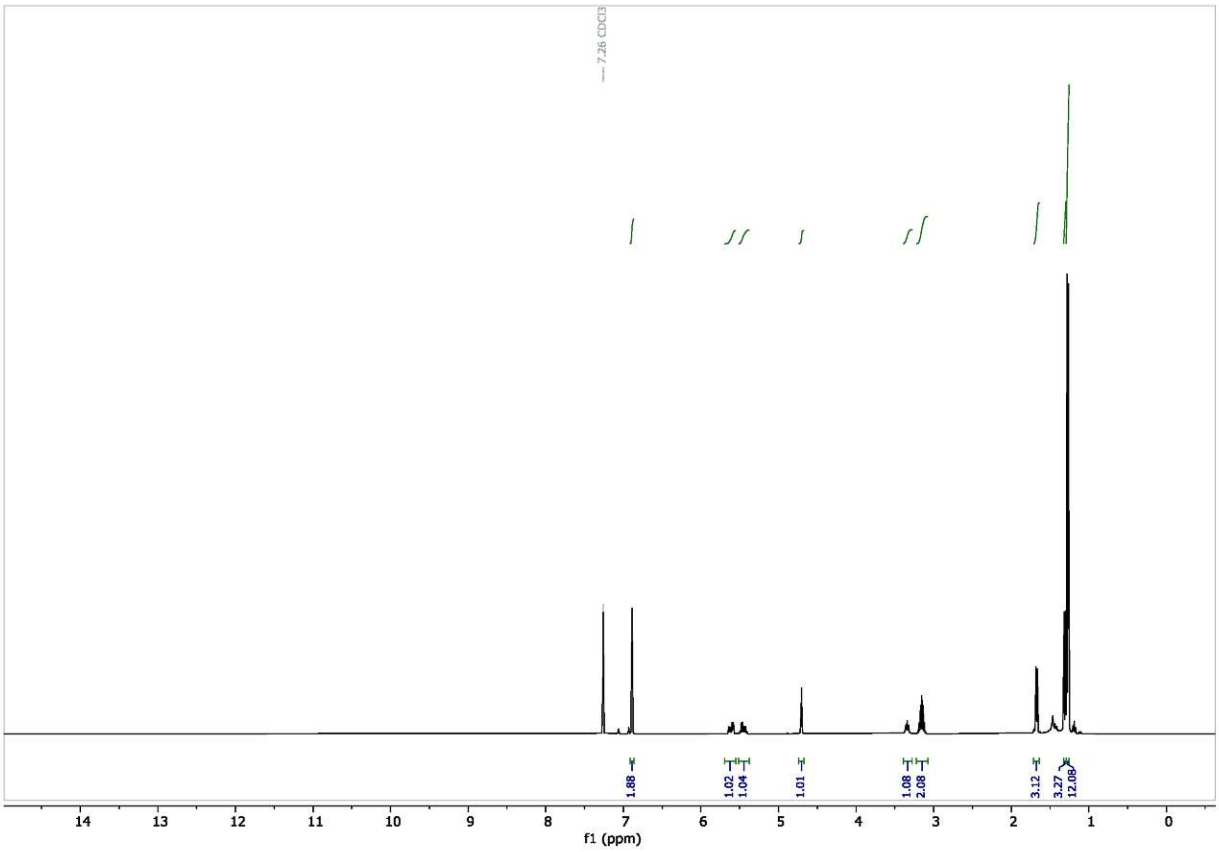


^{13}C NMR (101 MHz, $CDCl_3$)

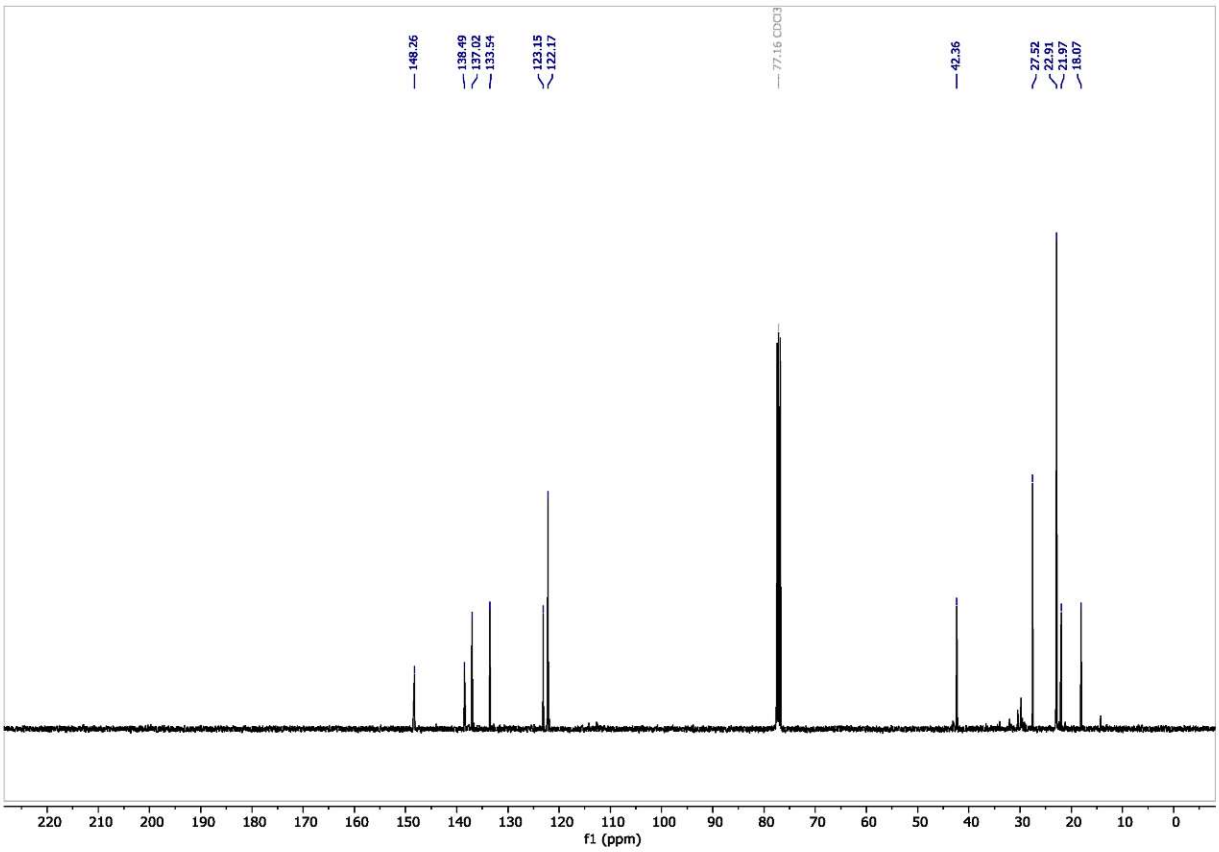


(R,E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenol (102)

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

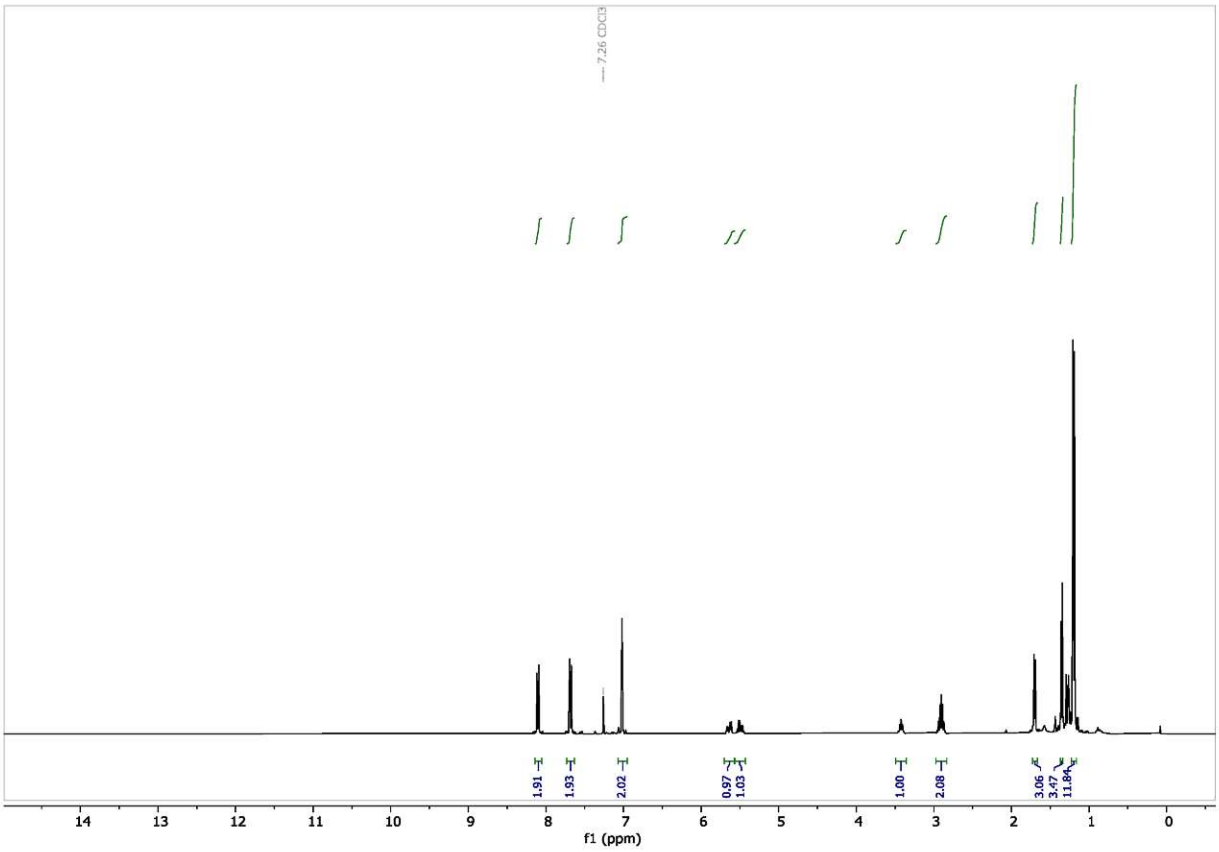


^{13}C NMR (101 MHz, $CDCl_3$)

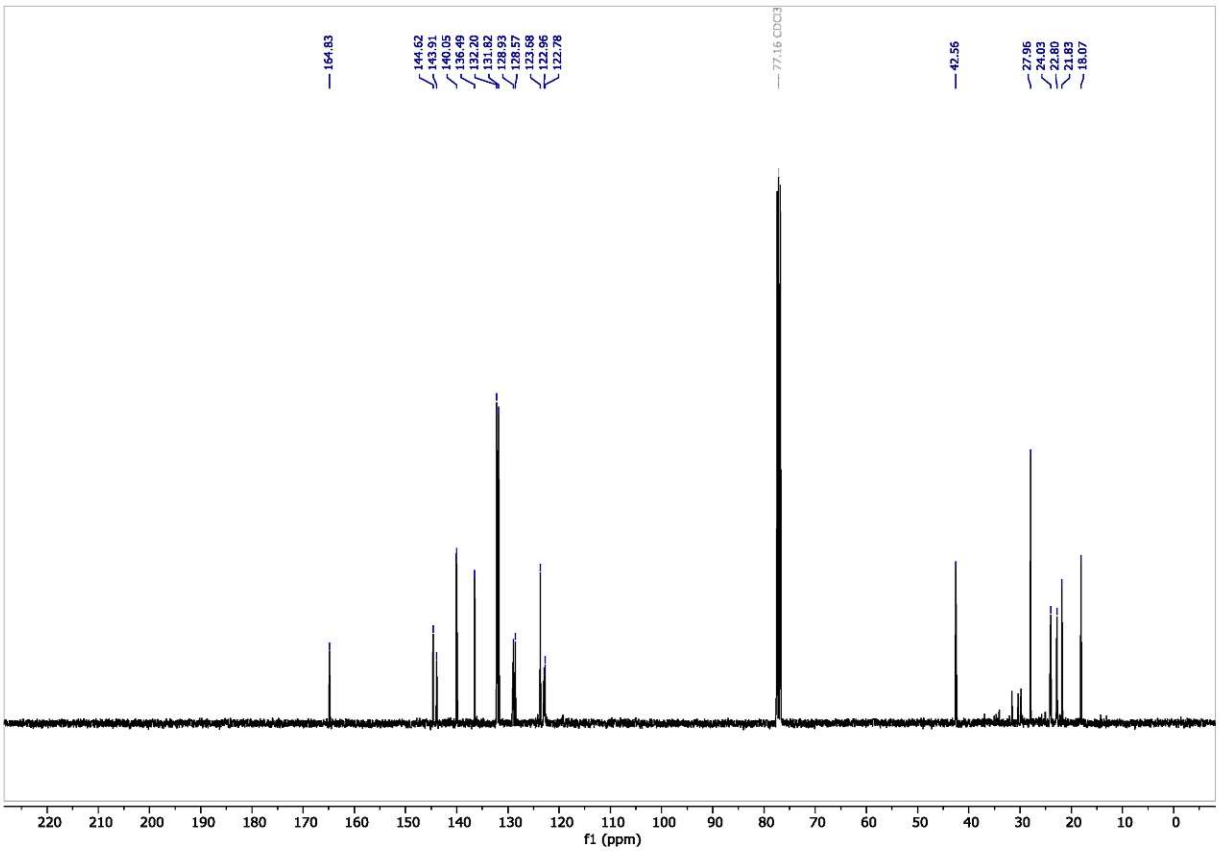


(R,E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (149)

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

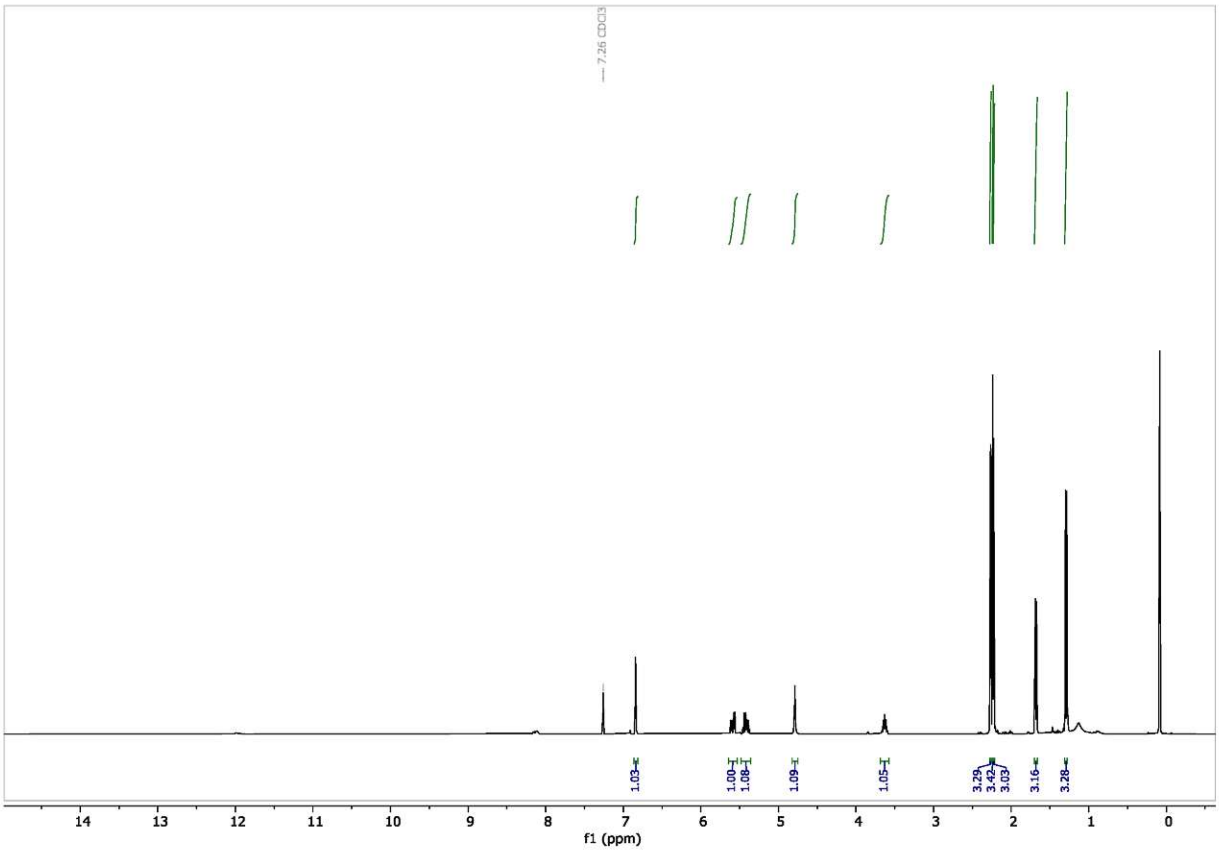


^{13}C NMR (101 MHz, $CDCl_3$)

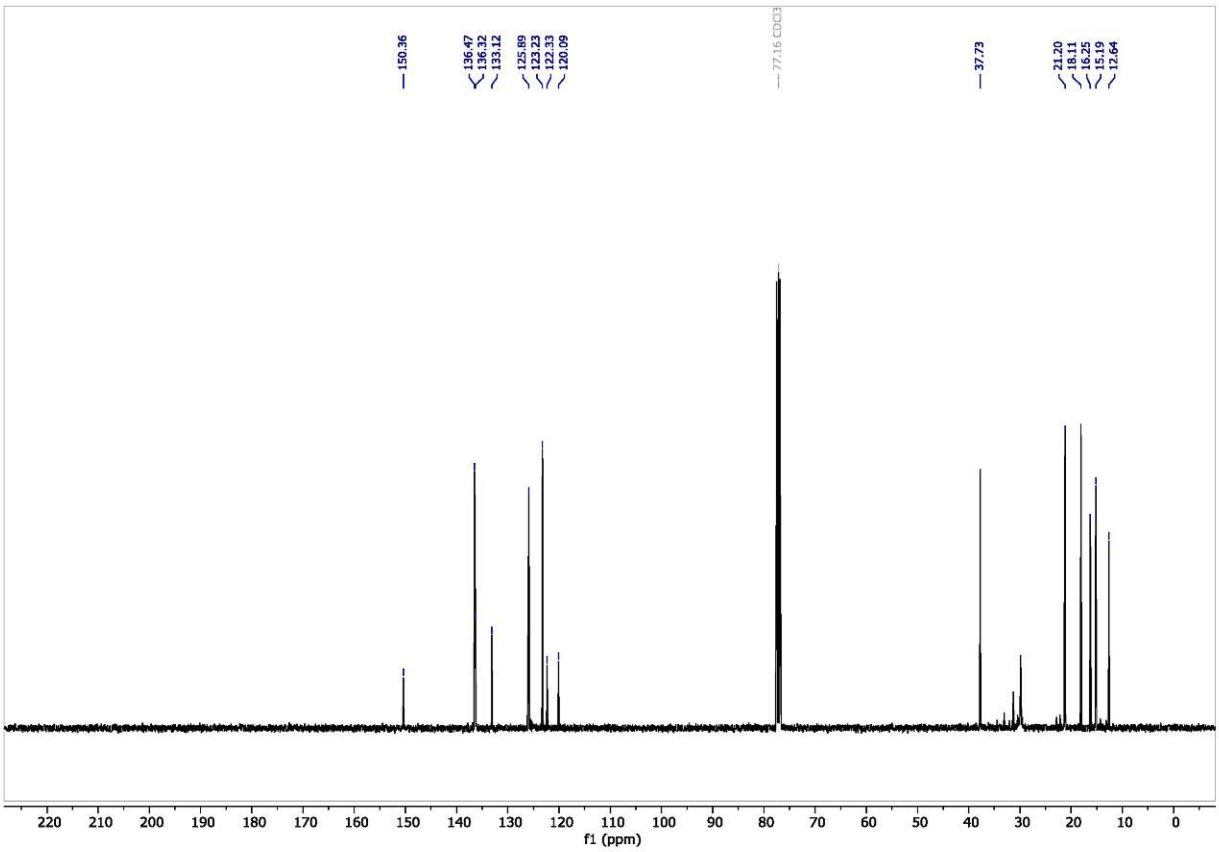


(R,E)-2,3,6-trimethyl-4-(pent-3-en-2-yl)phenol (103)

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

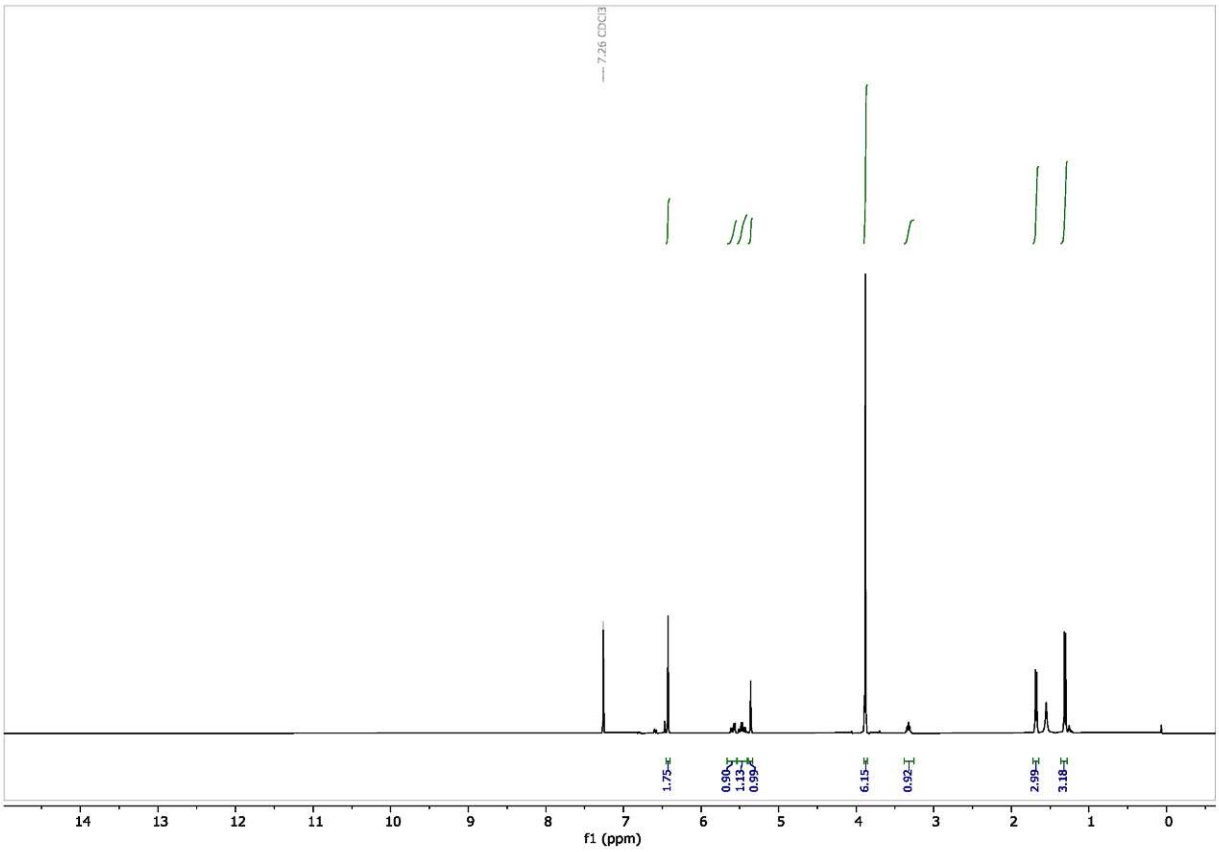


^{13}C NMR (101 MHz, $CDCl_3$)

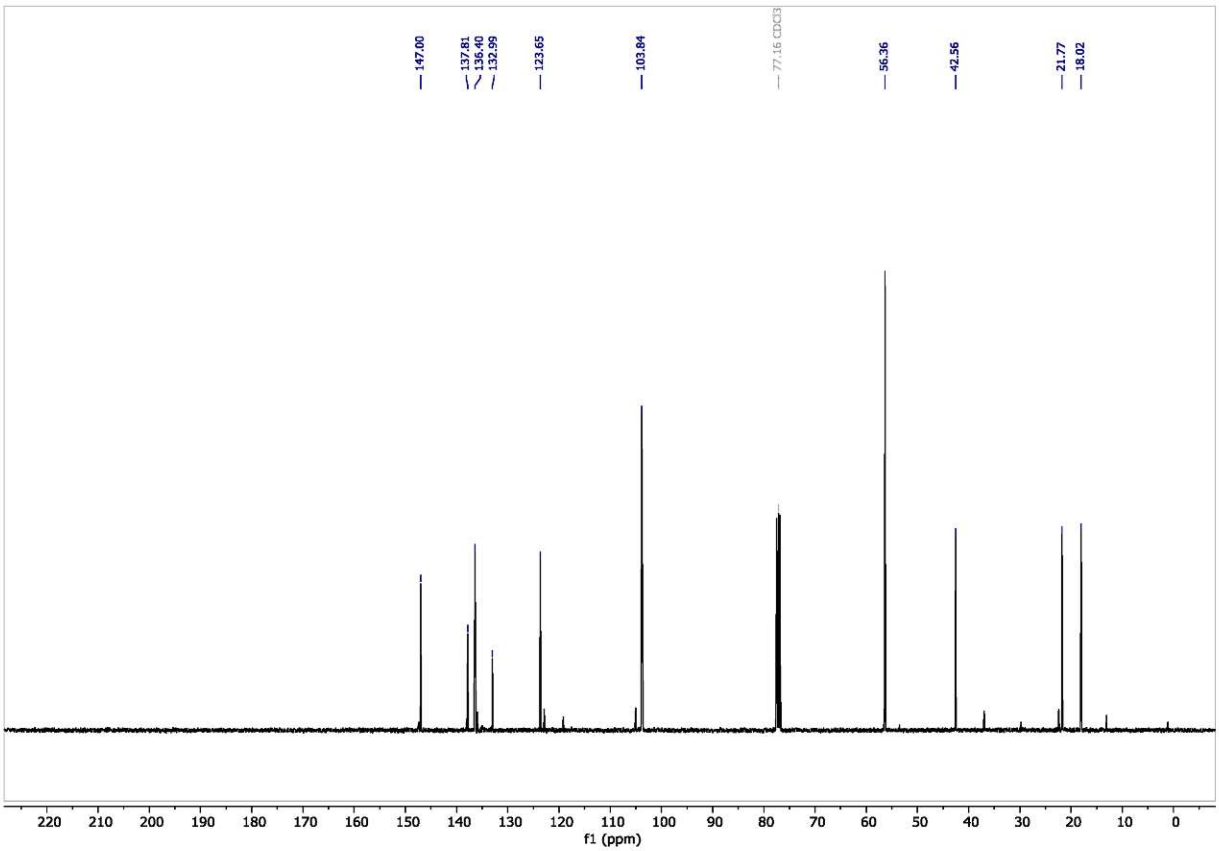


(R,E)-2,6-dimethoxy-4-(pent-3-en-2-yl)phenol (104)

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

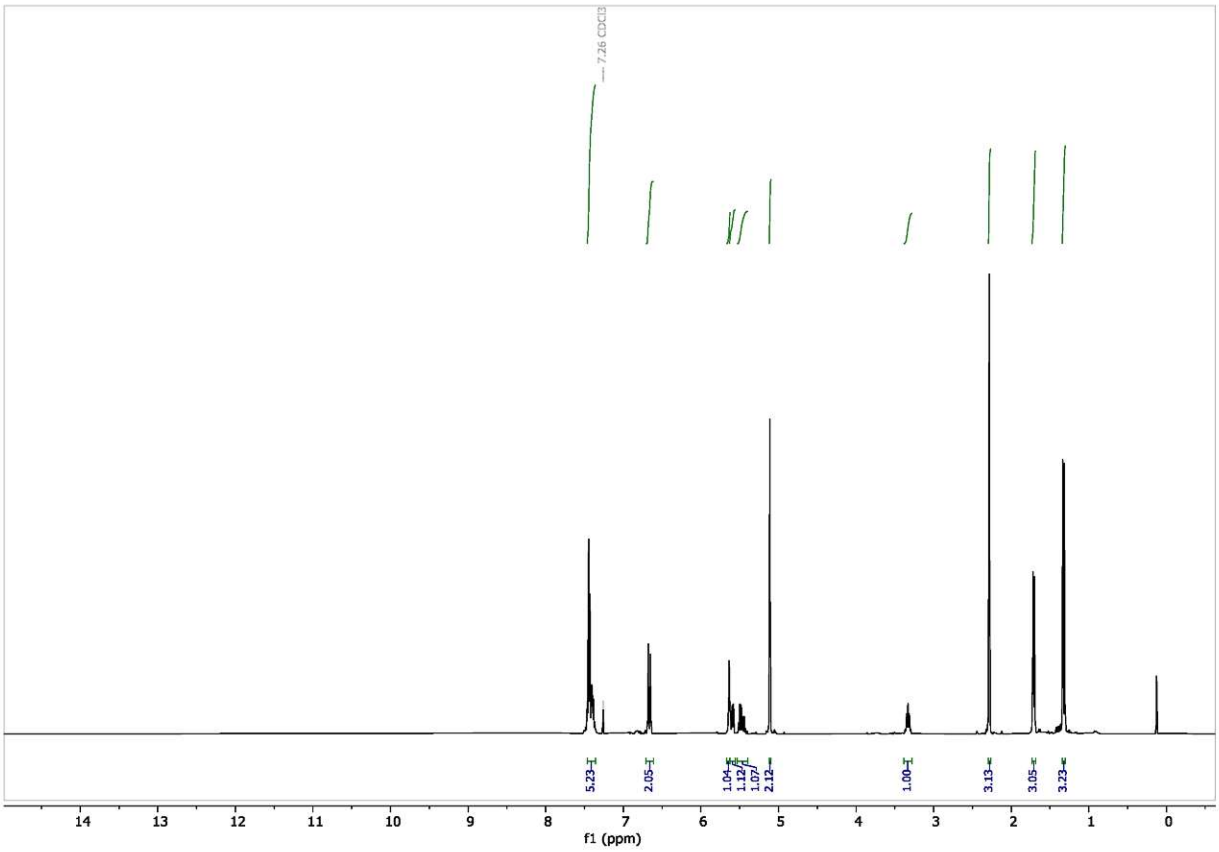


^{13}C NMR (101 MHz, $CDCl_3$)

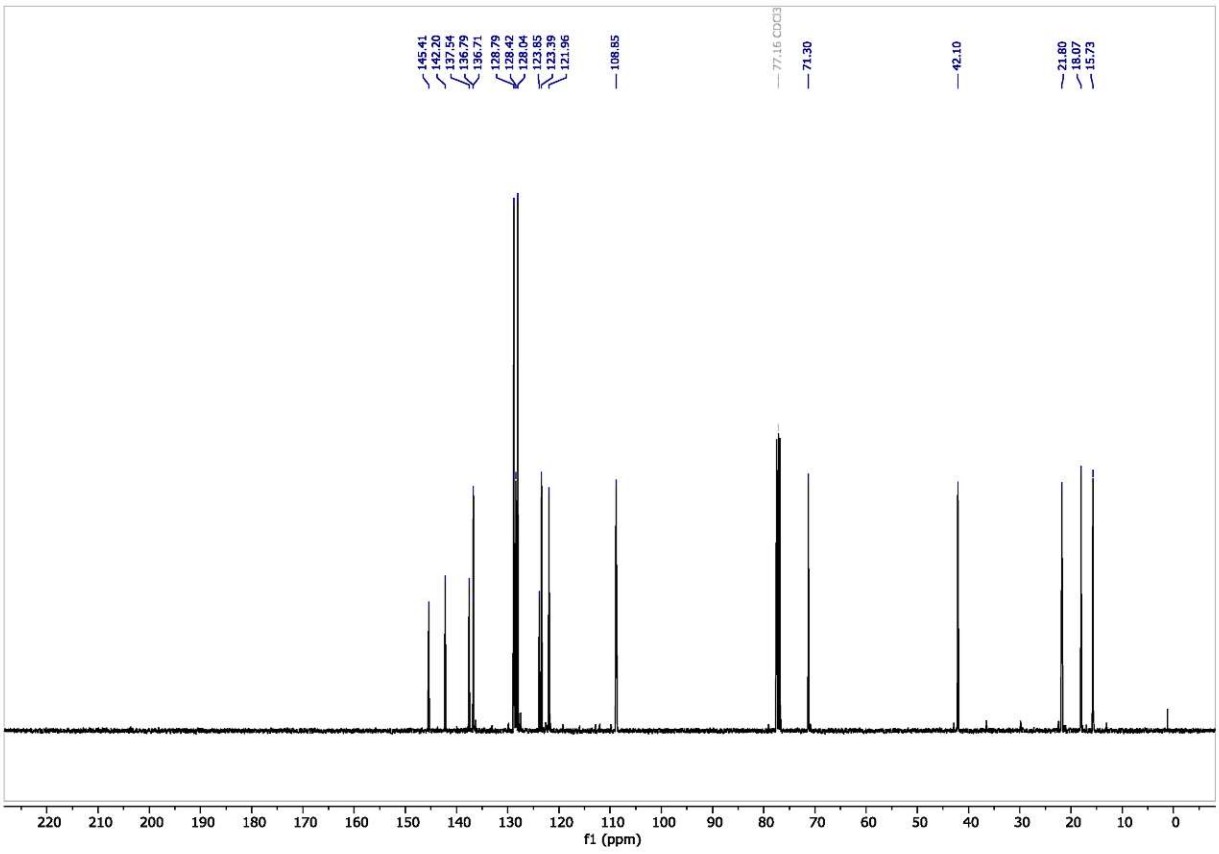


(R,E)-2-(benzyloxy)-6-methyl-4-(pent-3-en-2-yl)phenol (105)

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

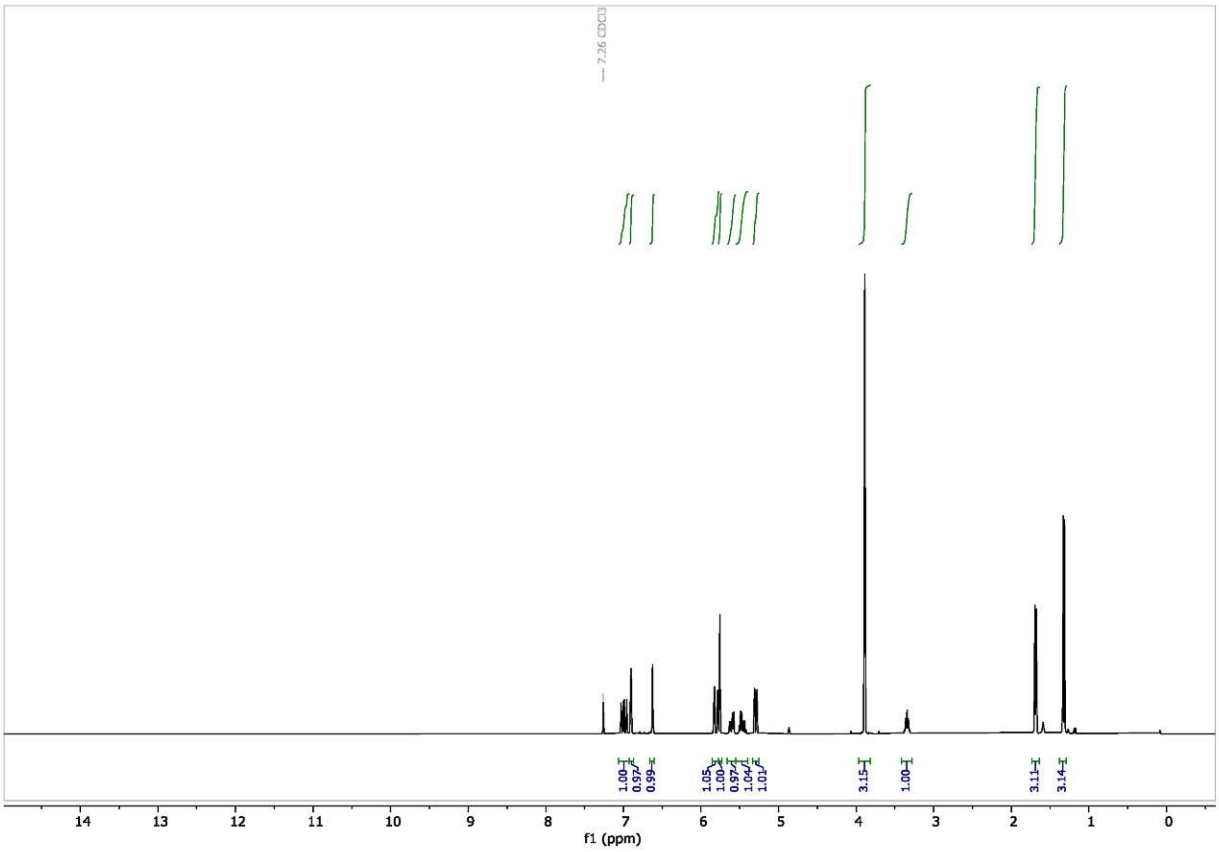


^{13}C NMR (101 MHz, $CDCl_3$)

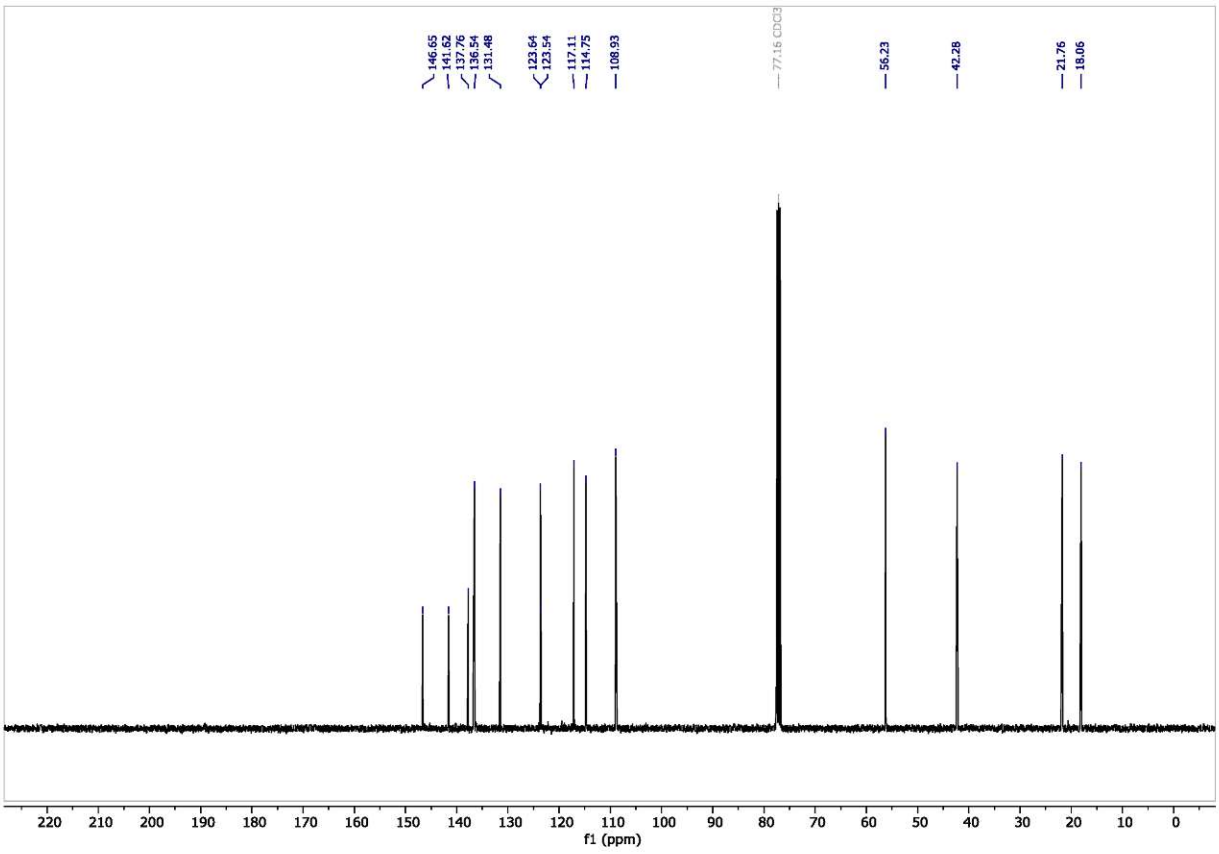


(R,E)-2-methoxy-4-(pent-3-en-2-yl)-6-vinylphenol (106)

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

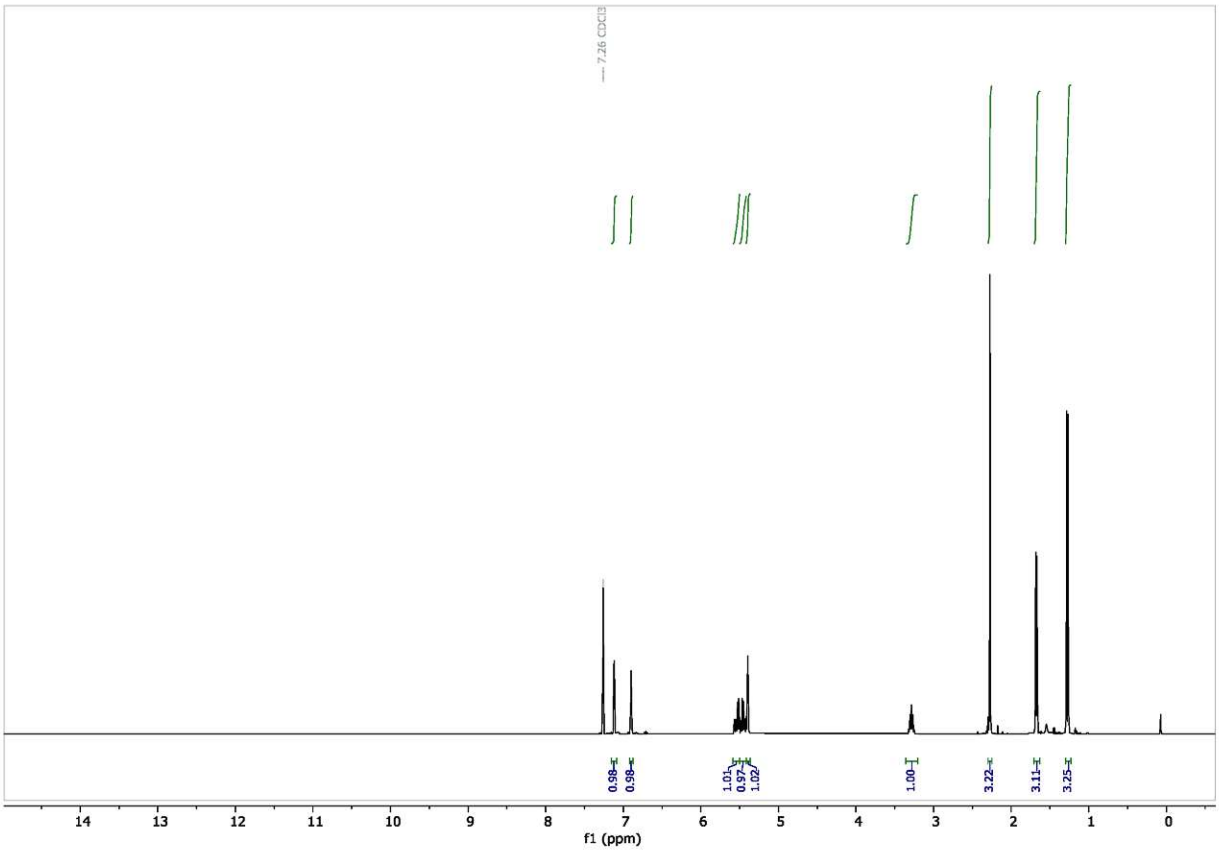


^{13}C NMR (101 MHz, $CDCl_3$)

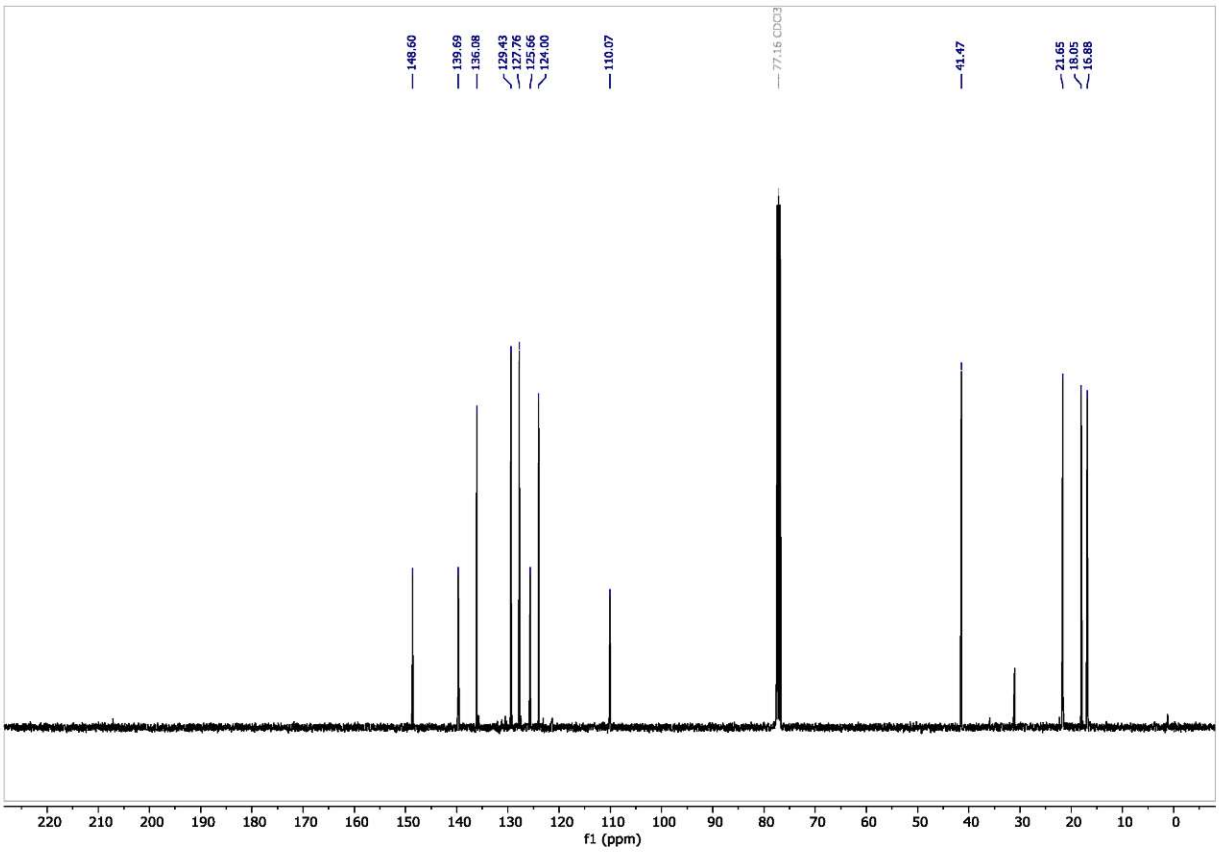


(R,E)-2-bromo-6-methyl-4-(pent-3-en-2-yl)phenol (107)

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

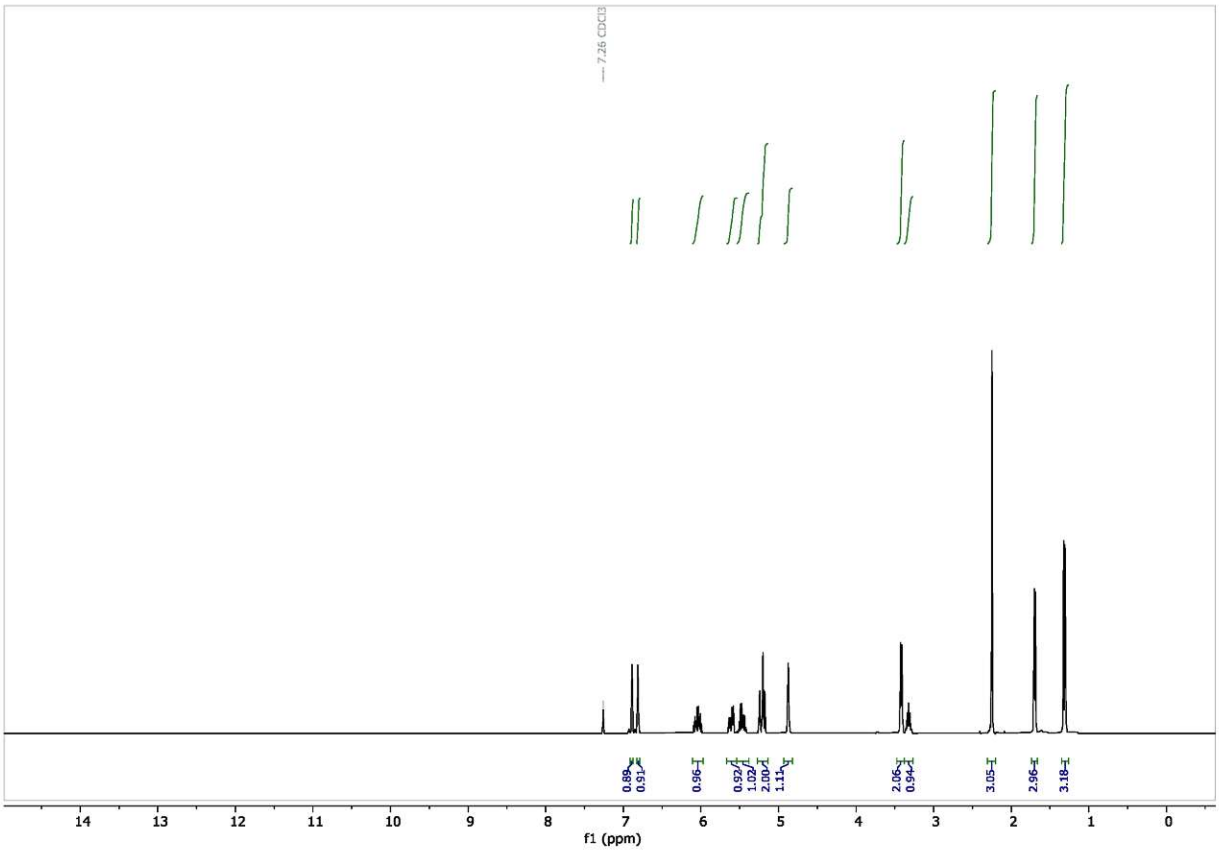


^{13}C NMR (101 MHz, $CDCl_3$)

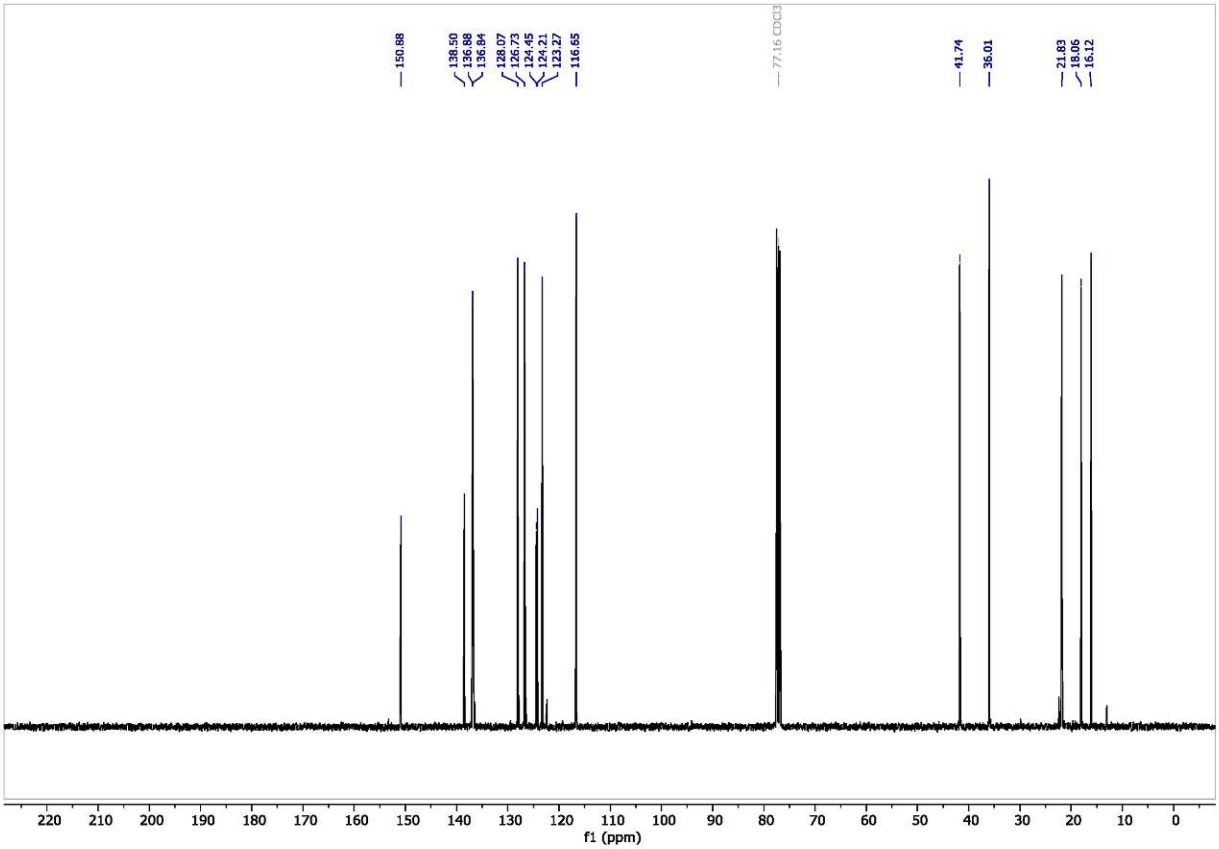


(R,E)-2-allyl-6-methyl-4-(pent-3-en-2-yl)phenol (108)

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

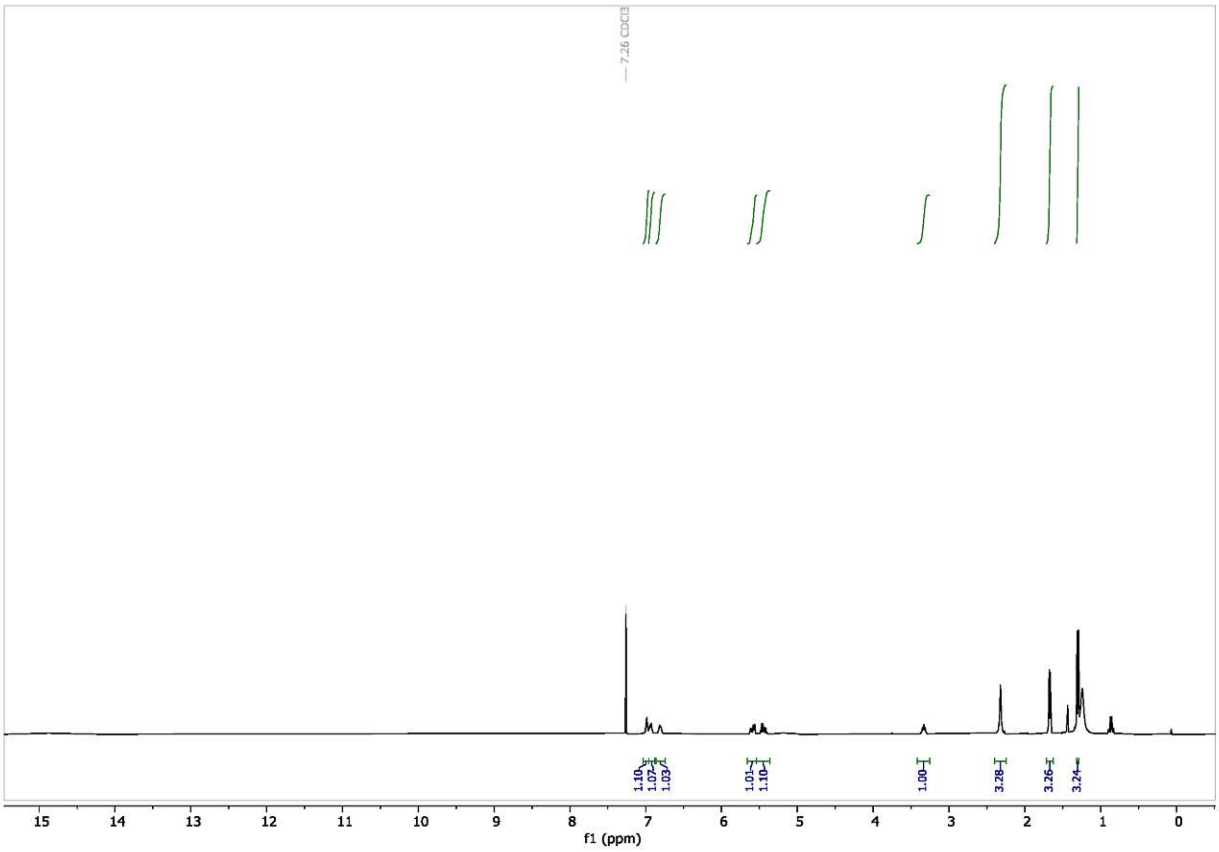


^{13}C NMR (101 MHz, $CDCl_3$)

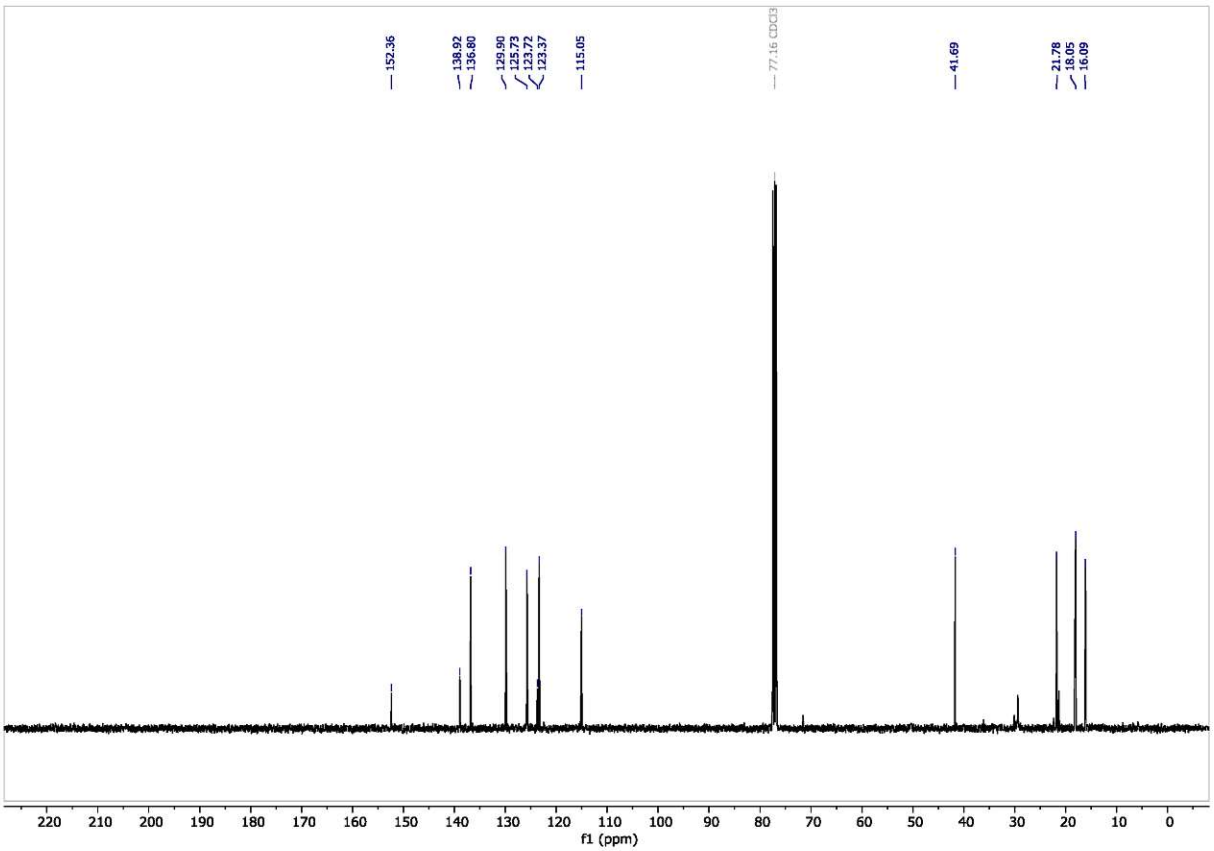


(R,E)-2-methyl-4-(pent-3-en-2-yl)phenol (116)

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

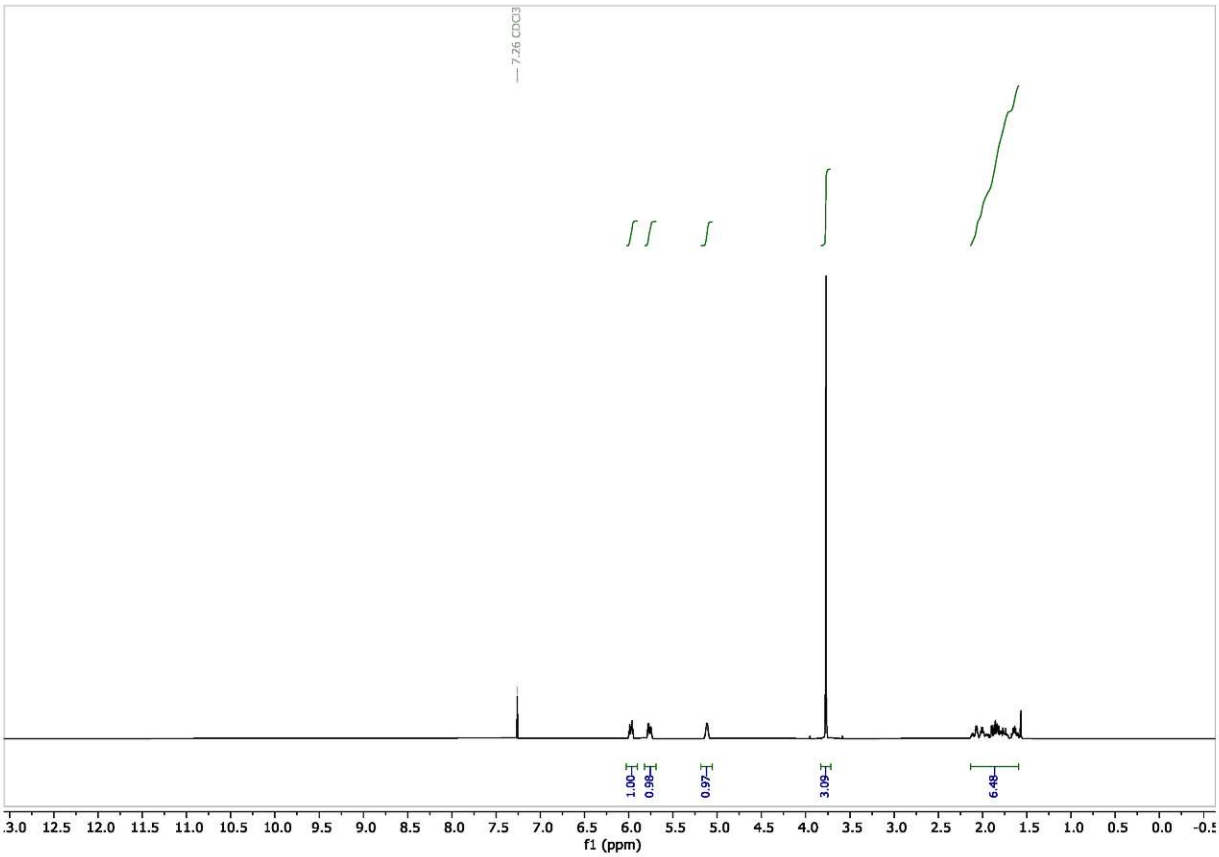


^{13}C NMR (101 MHz, $CDCl_3$)

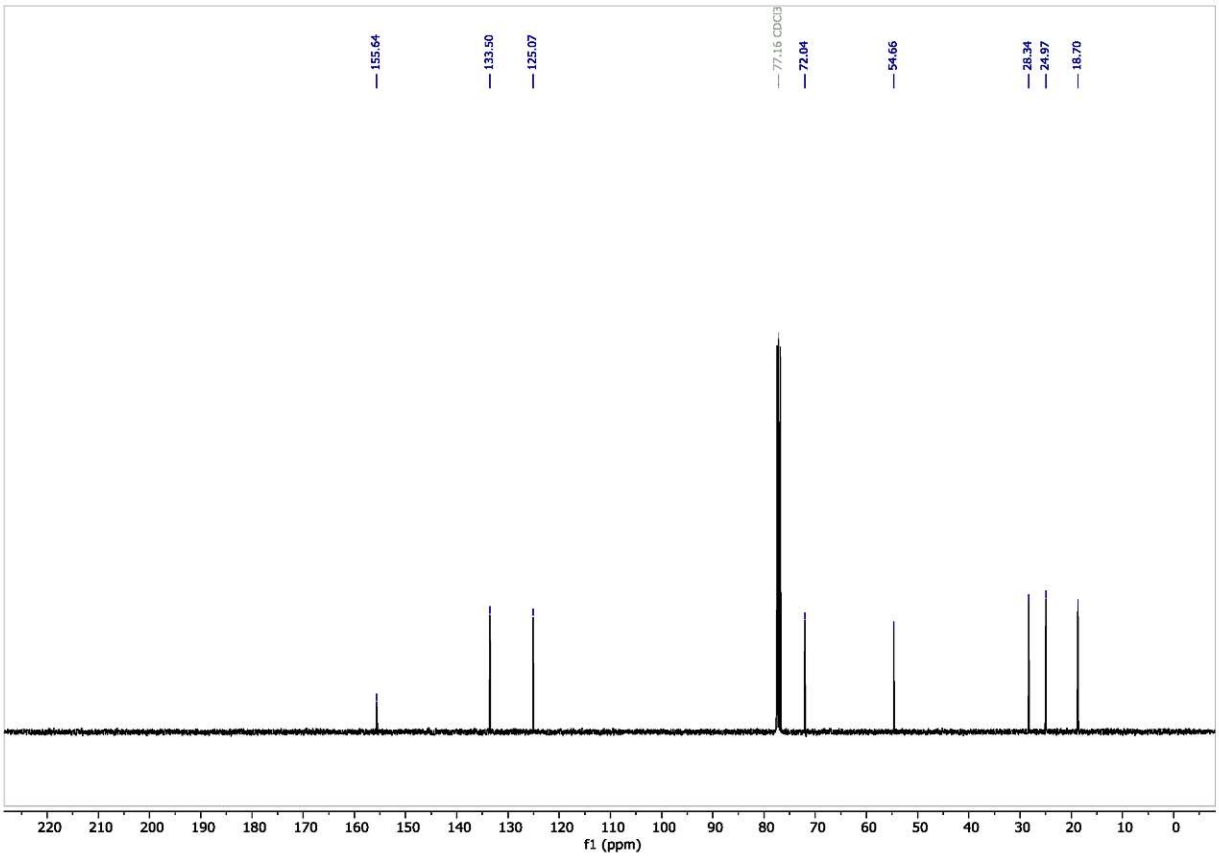


(±)-Cyclohex-2-enyl methyl carbonate (96)

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

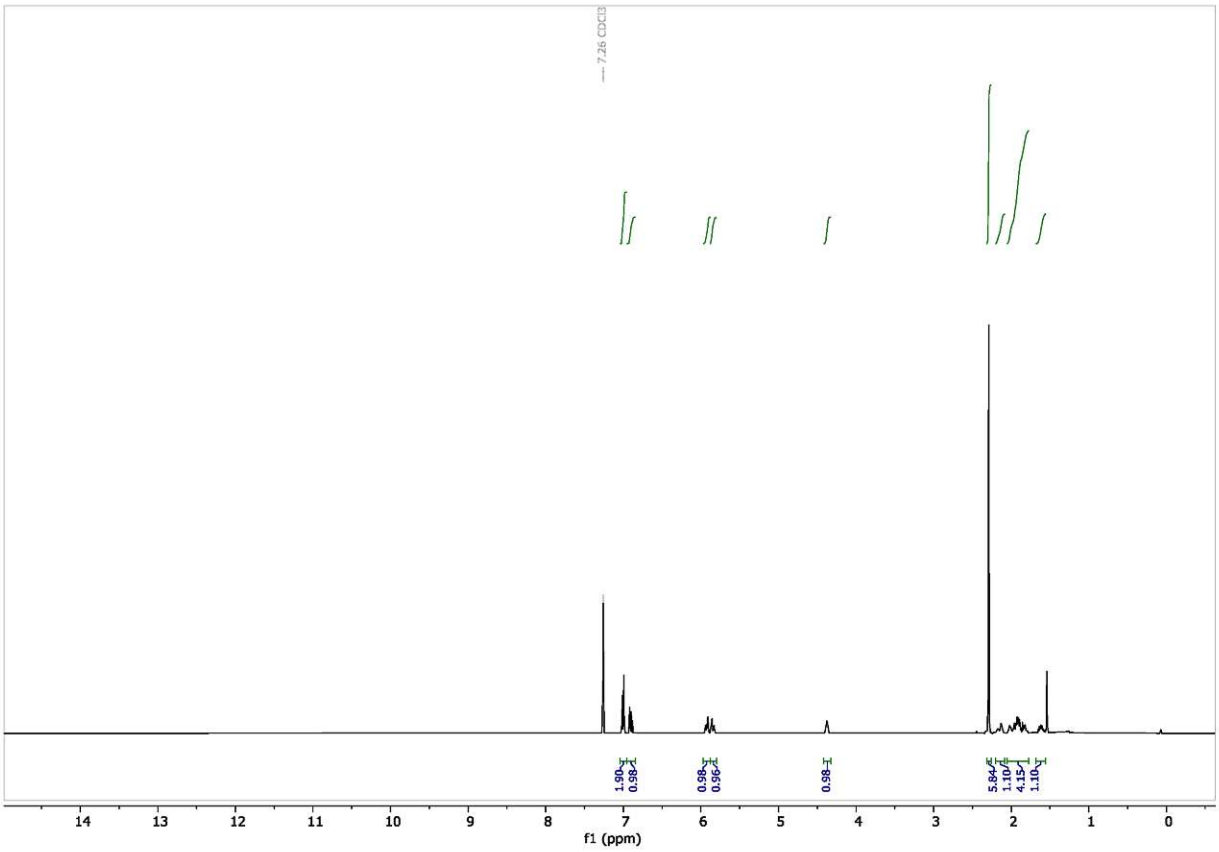


^{13}C NMR (101 MHz, $CDCl_3$)

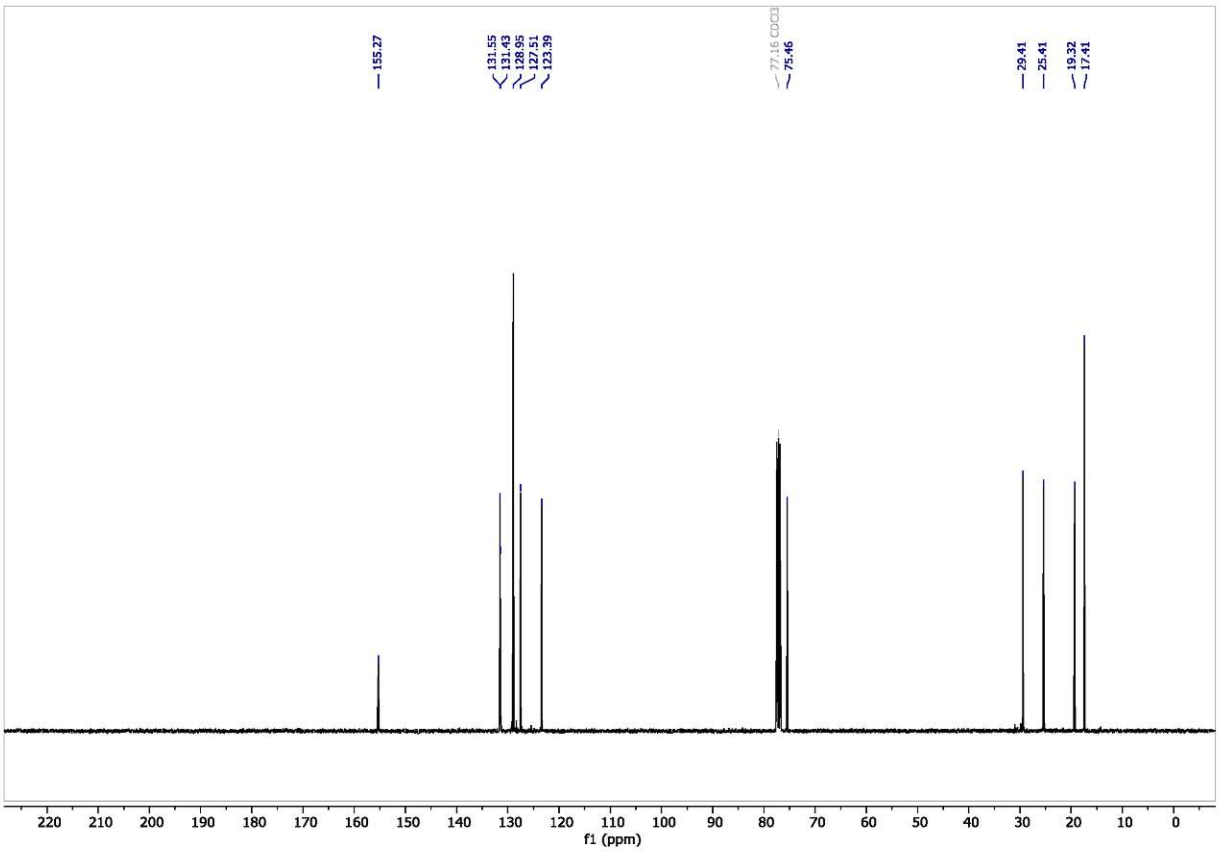


(S)-2-(cyclohex-2-en-1-yloxy)-1,3-dimethylbenzene (97)

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

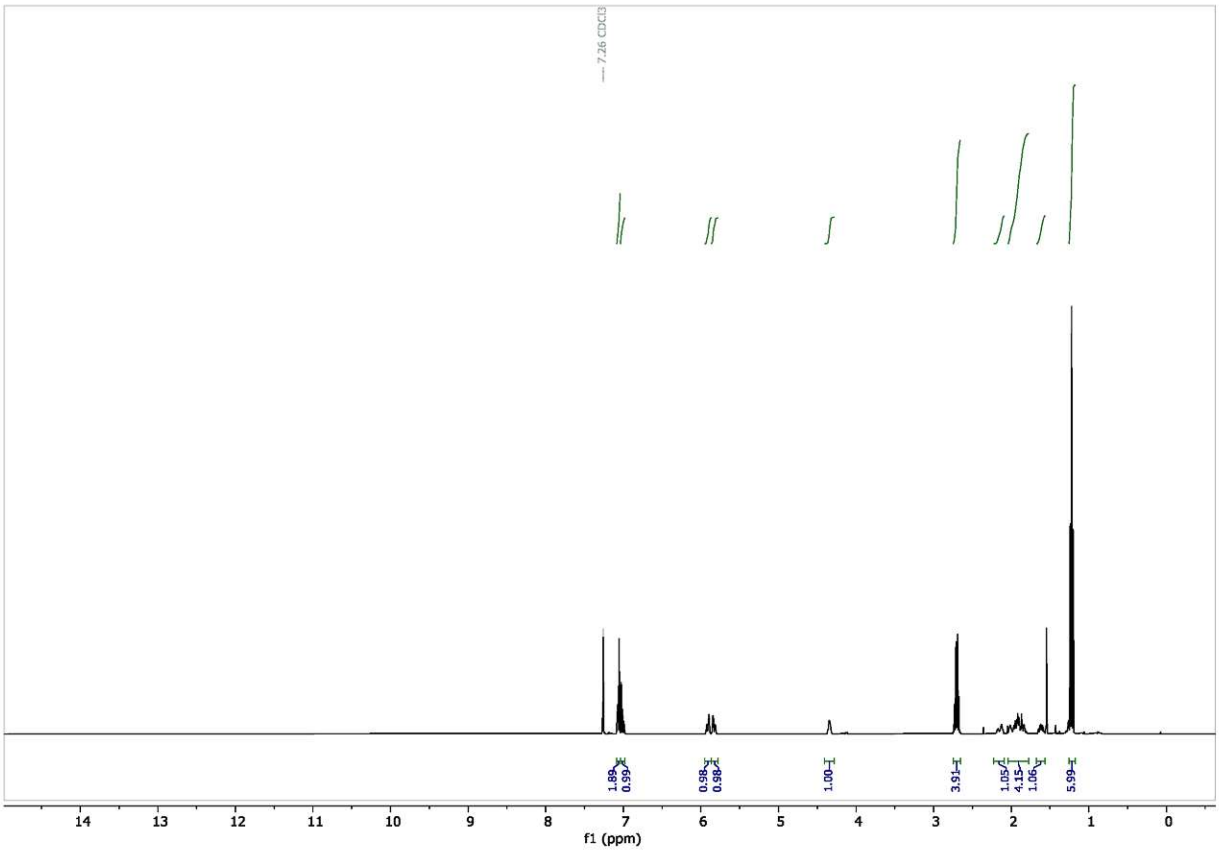


^{13}C NMR (101 MHz, $CDCl_3$)

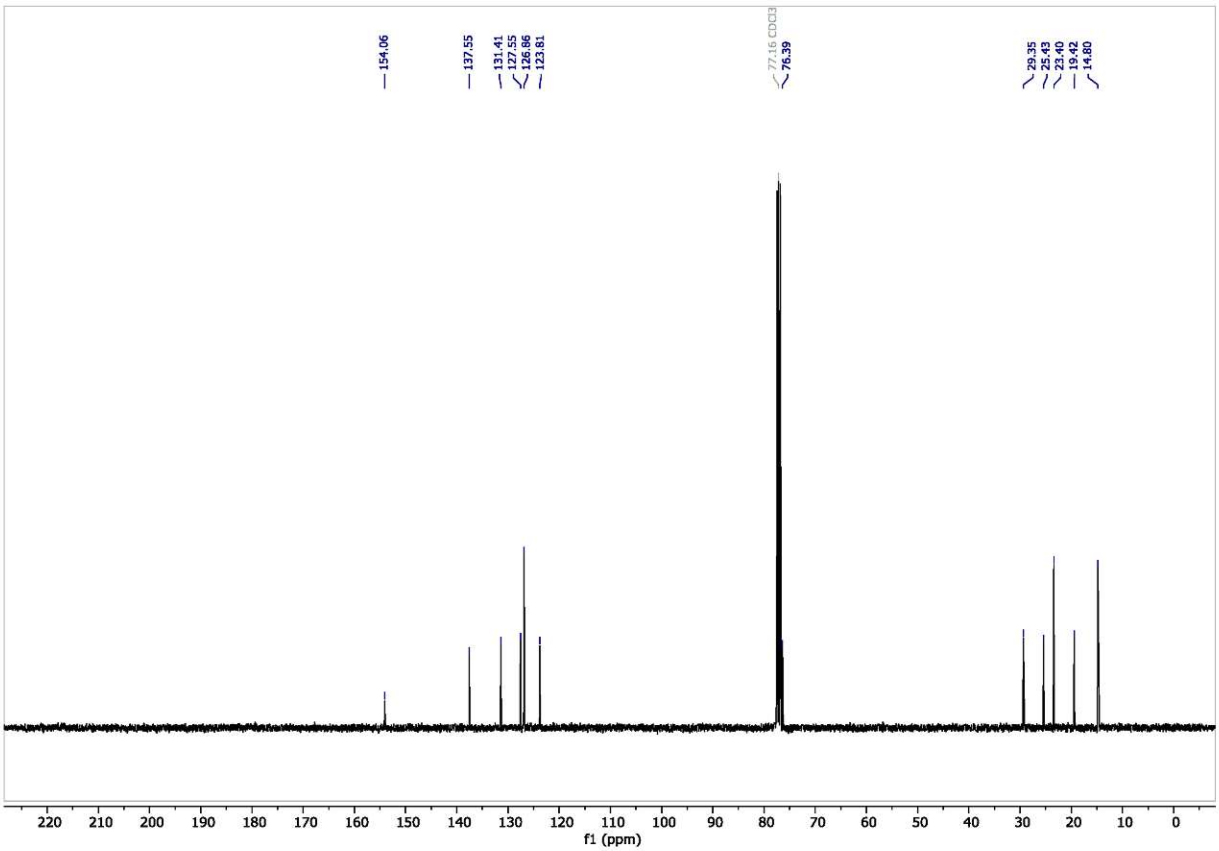


(S)-2-(cyclohex-2-en-1-yloxy)-1,3-diethylbenzene (98)

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

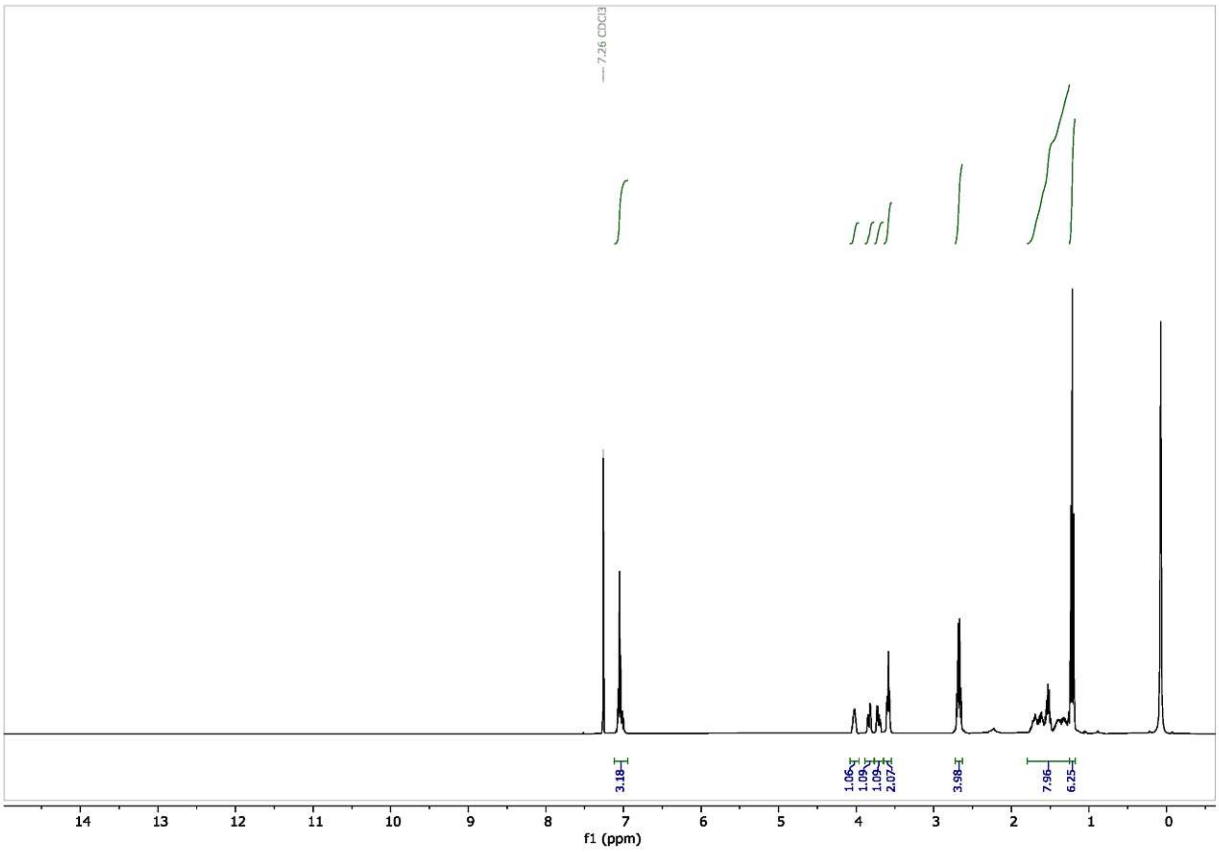


^{13}C NMR (101 MHz, $CDCl_3$)

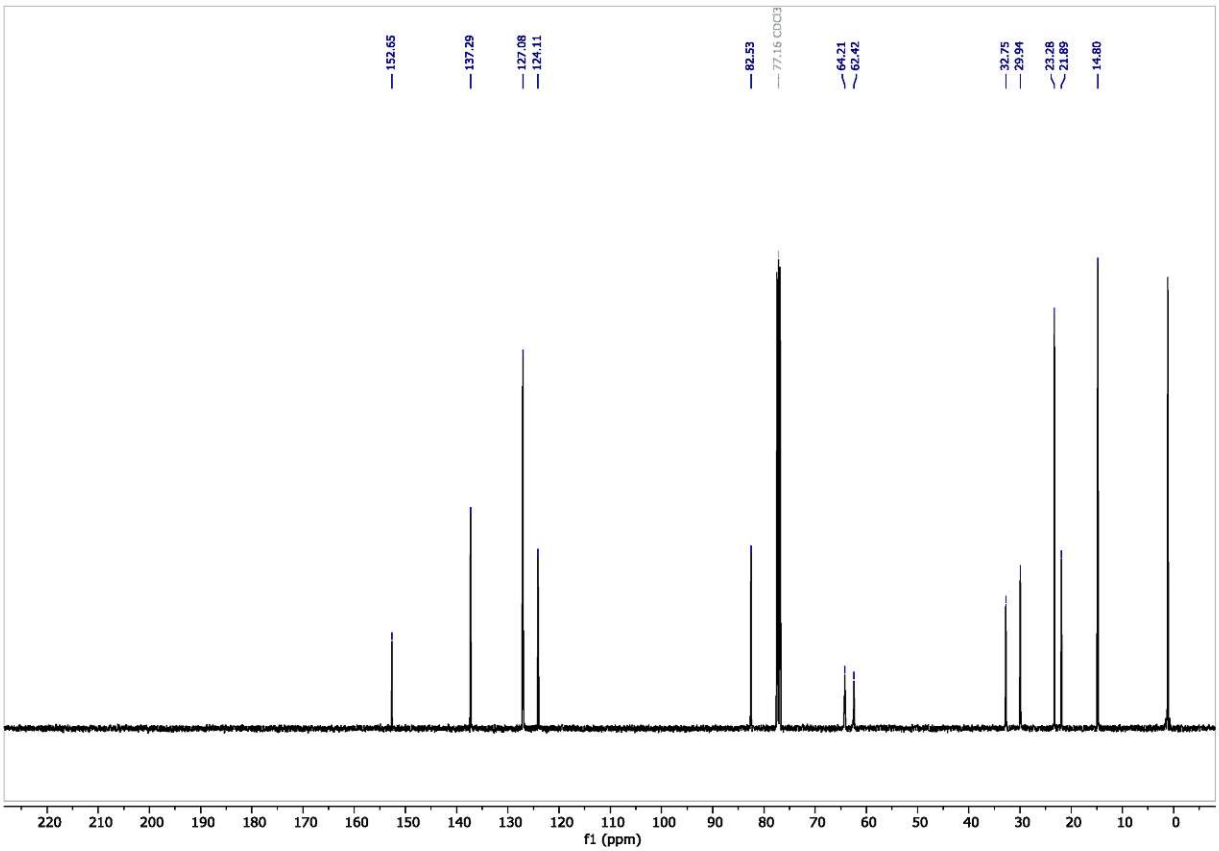


(R)-2-(2,6-diethylphenoxy)hexane-1,6-diol (147)

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

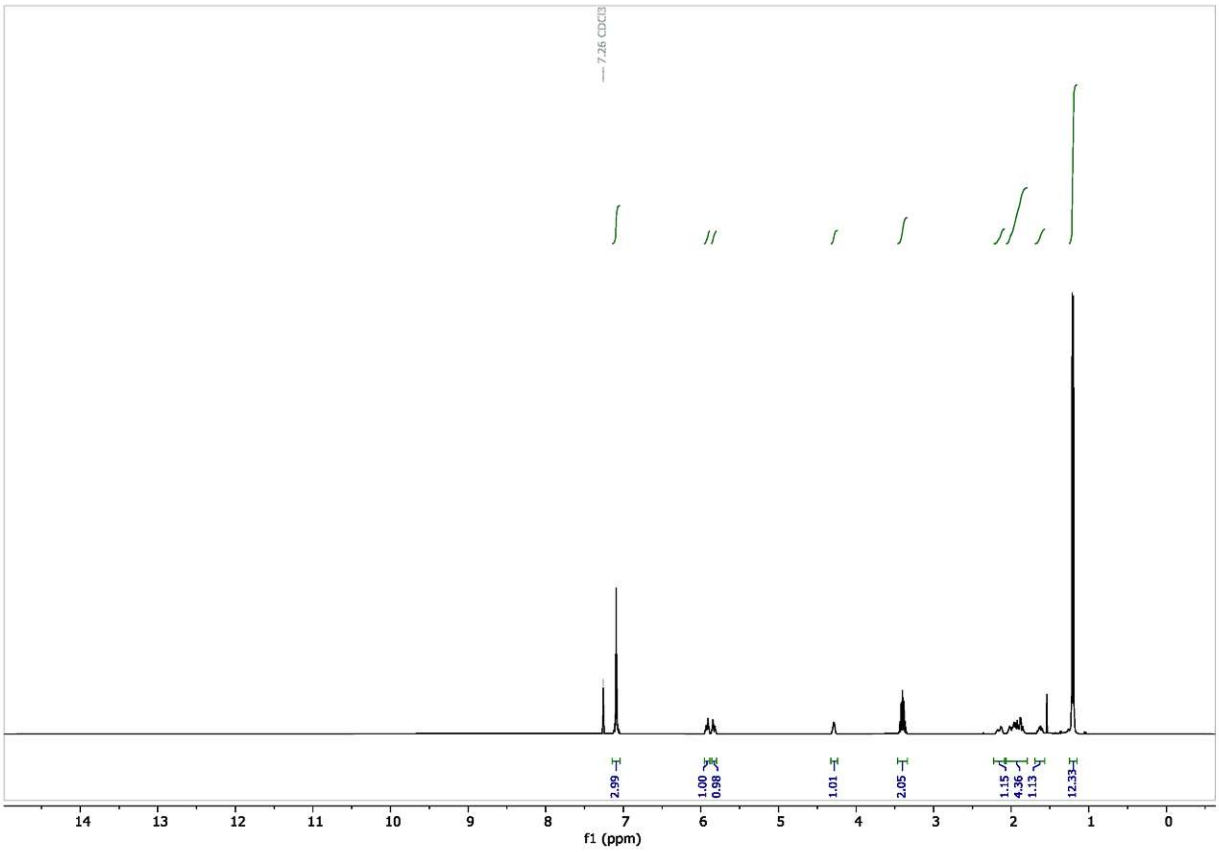


^{13}C NMR (101 MHz, $CDCl_3$)

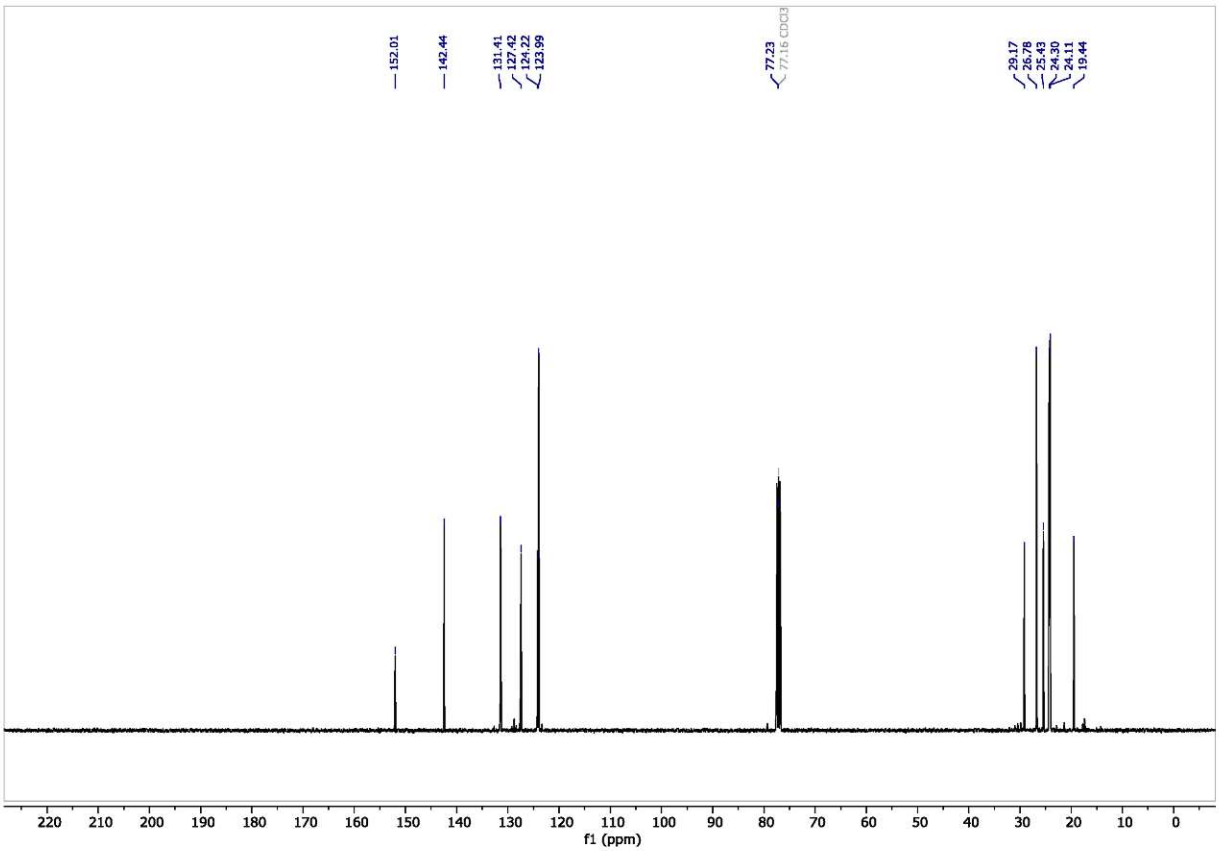


(S)-2-(cyclohex-2-en-1-yloxy)-1,3-diisopropylbenzene (99)

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

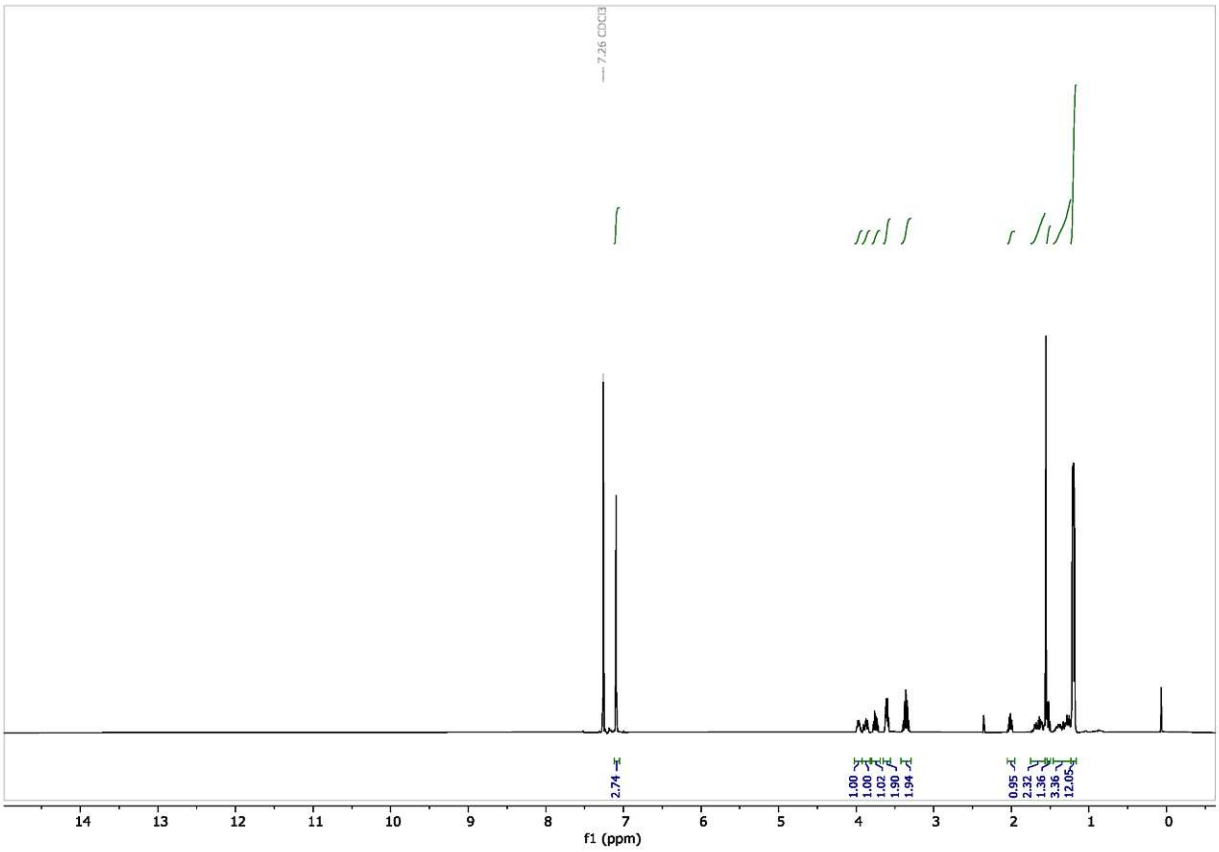


^{13}C NMR (101 MHz, $CDCl_3$)

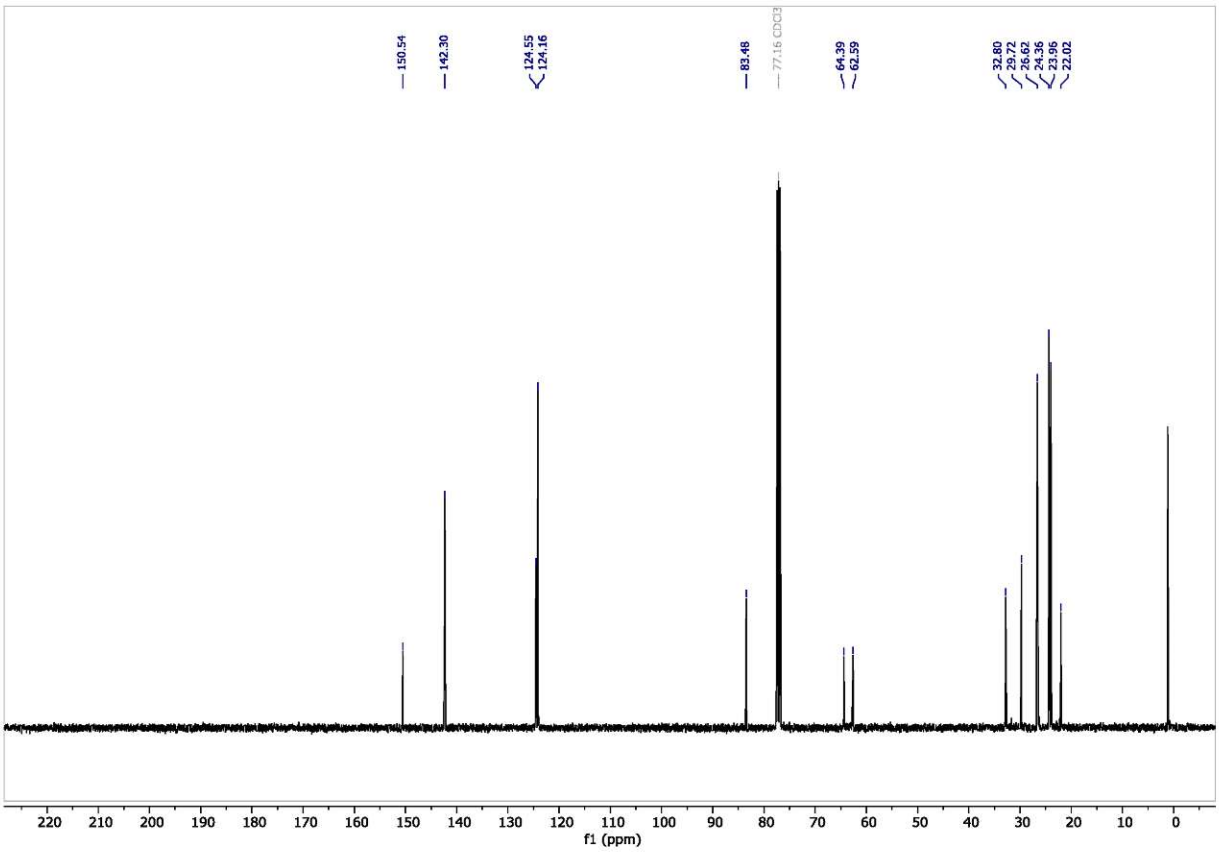


(R)-2-(2,6-diisopropylphenoxy)hexane-1,6-diol (148)

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

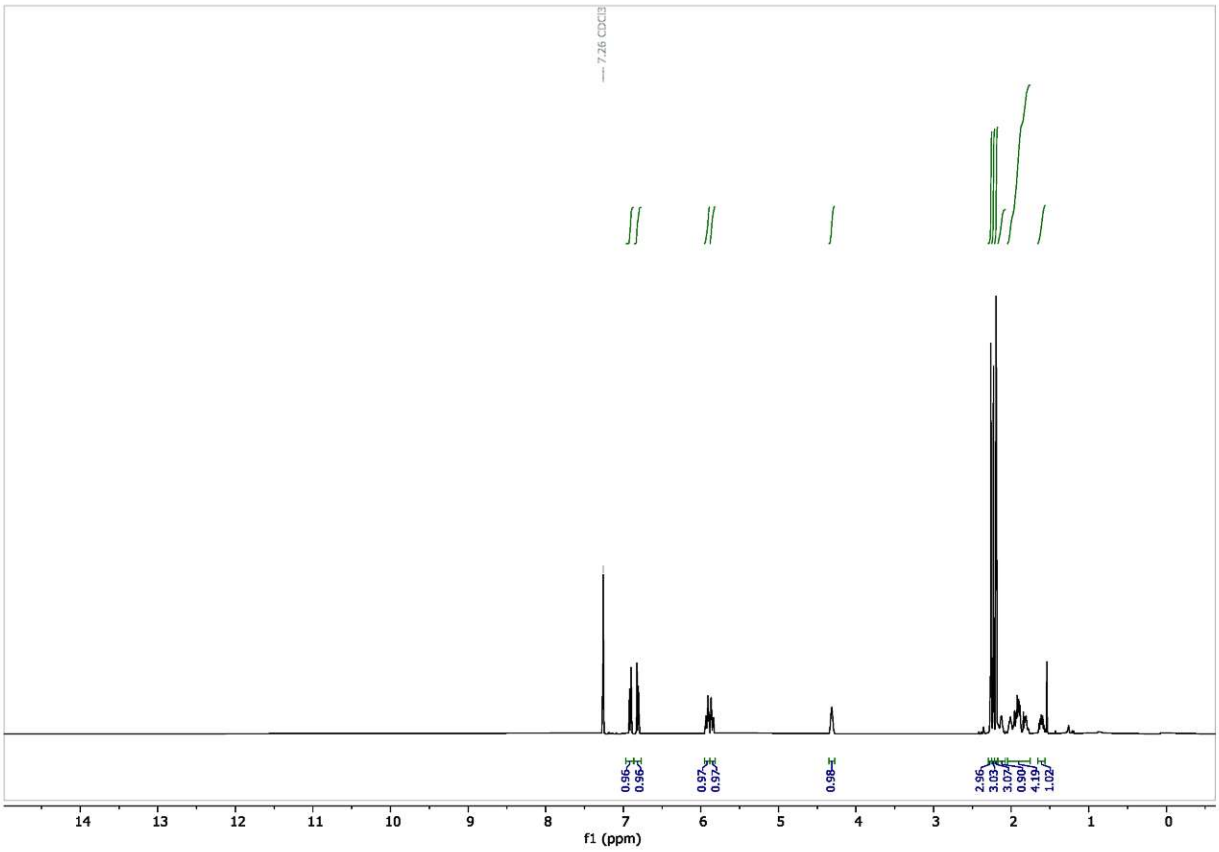


^{13}C NMR (101 MHz, $CDCl_3$)

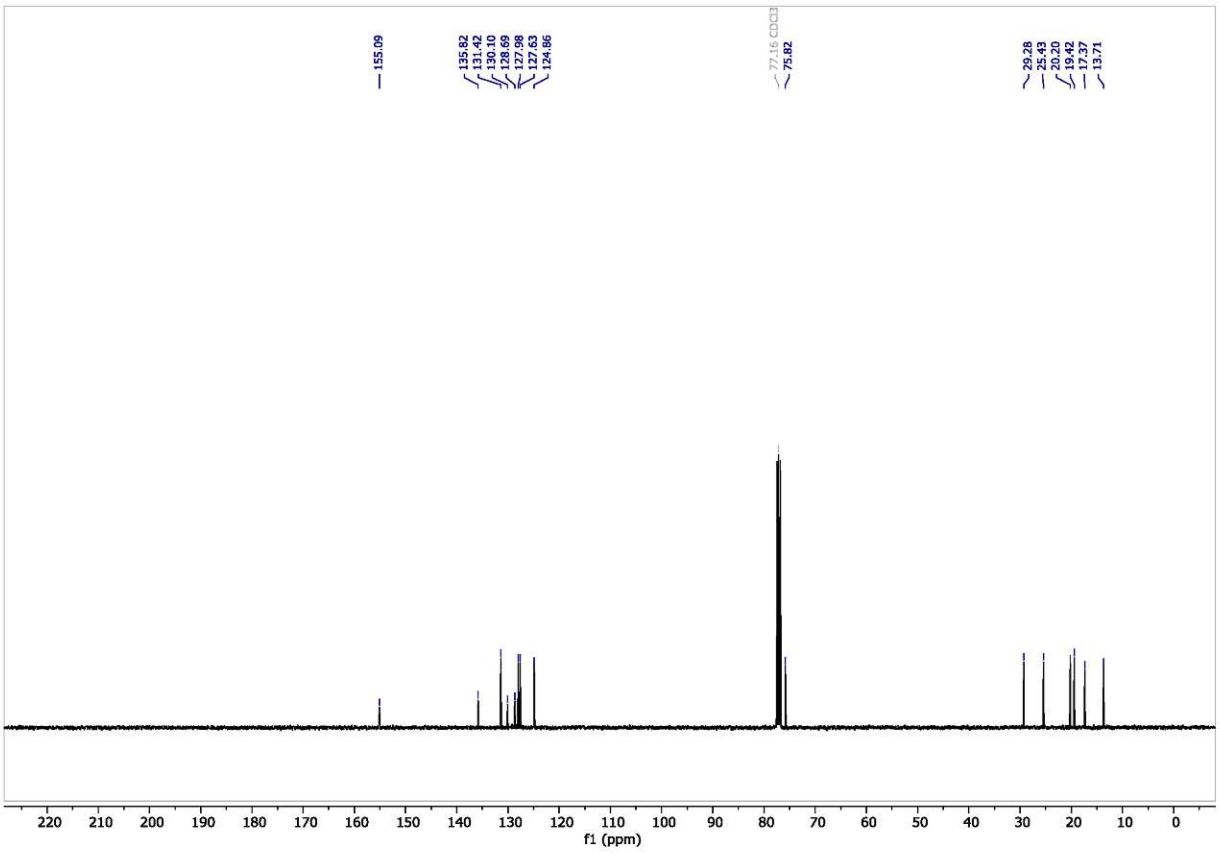


(S)-2-(cyclohex-2-en-1-yloxy)-1,3,4-trimethylbenzene (100)

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

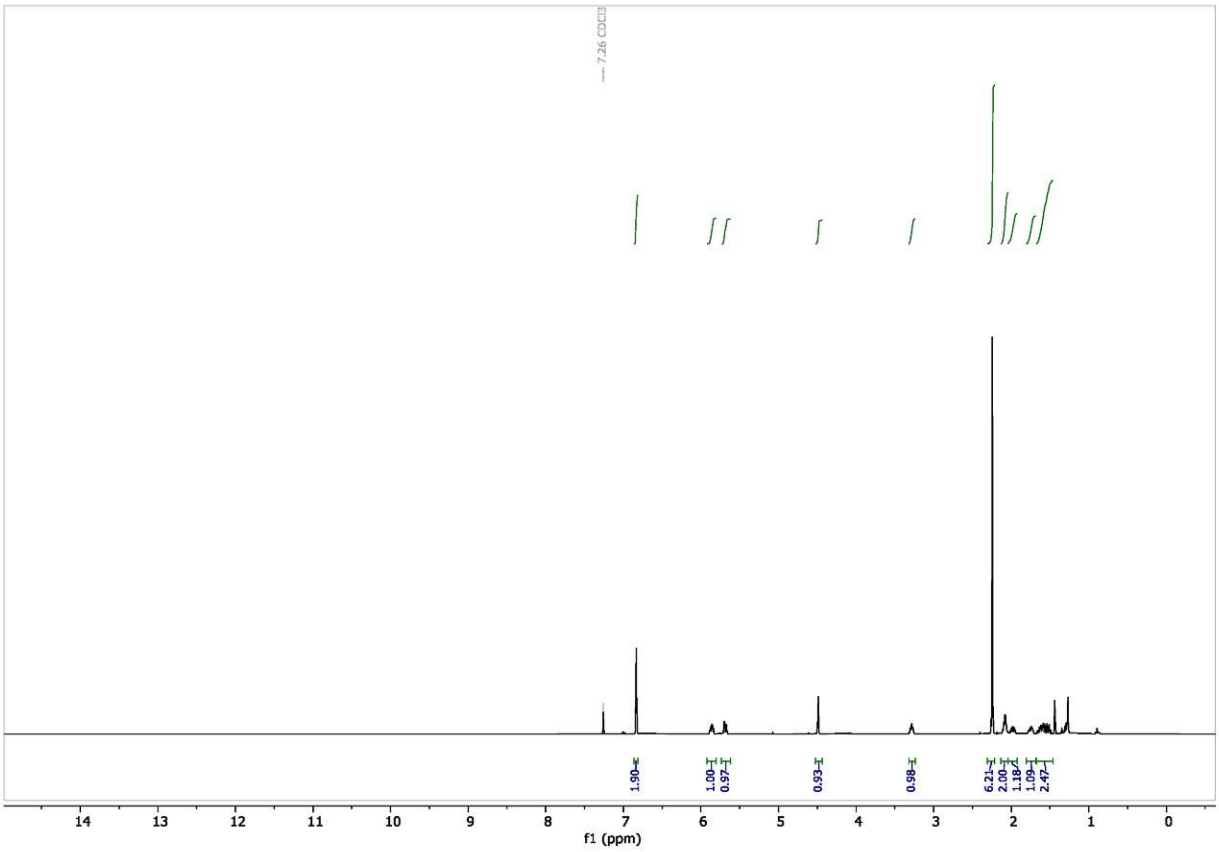


^{13}C NMR (101 MHz, $CDCl_3$)

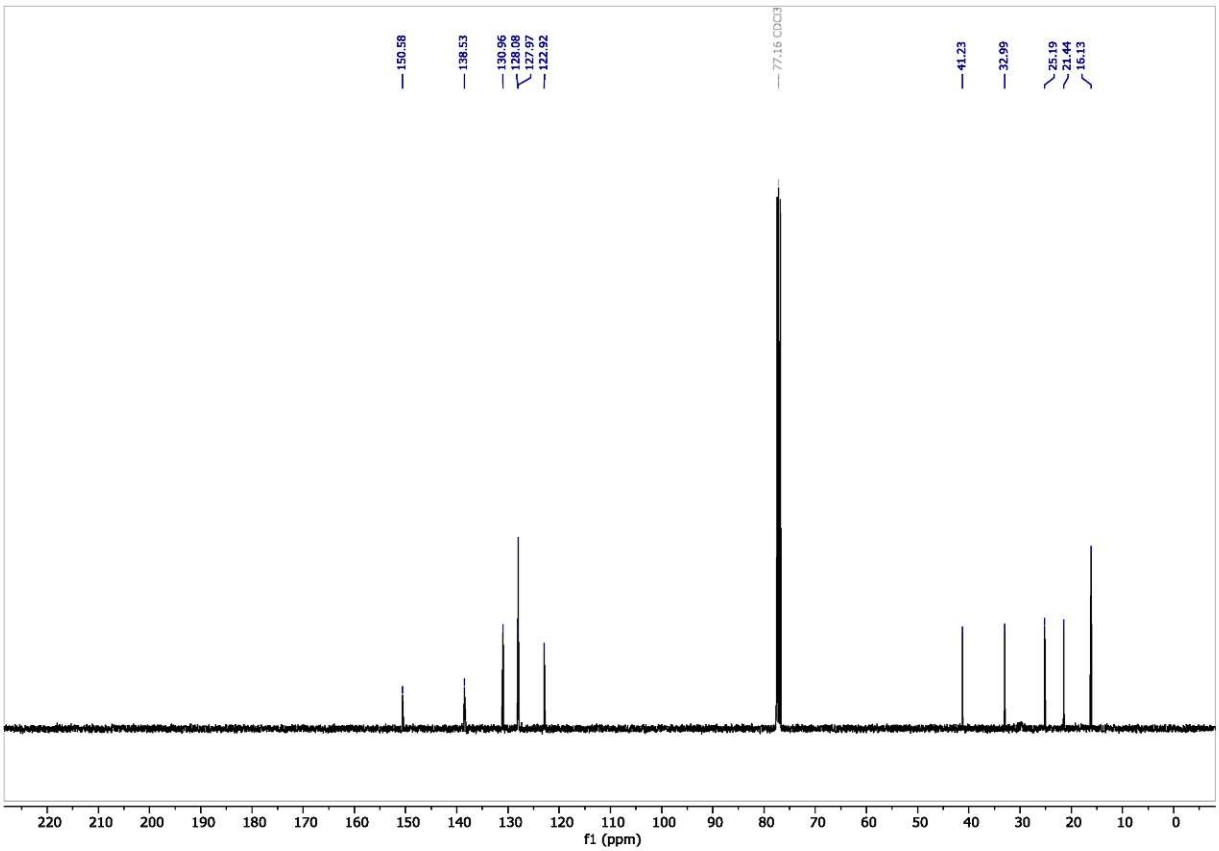


(S)-3,5-dimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (111)

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

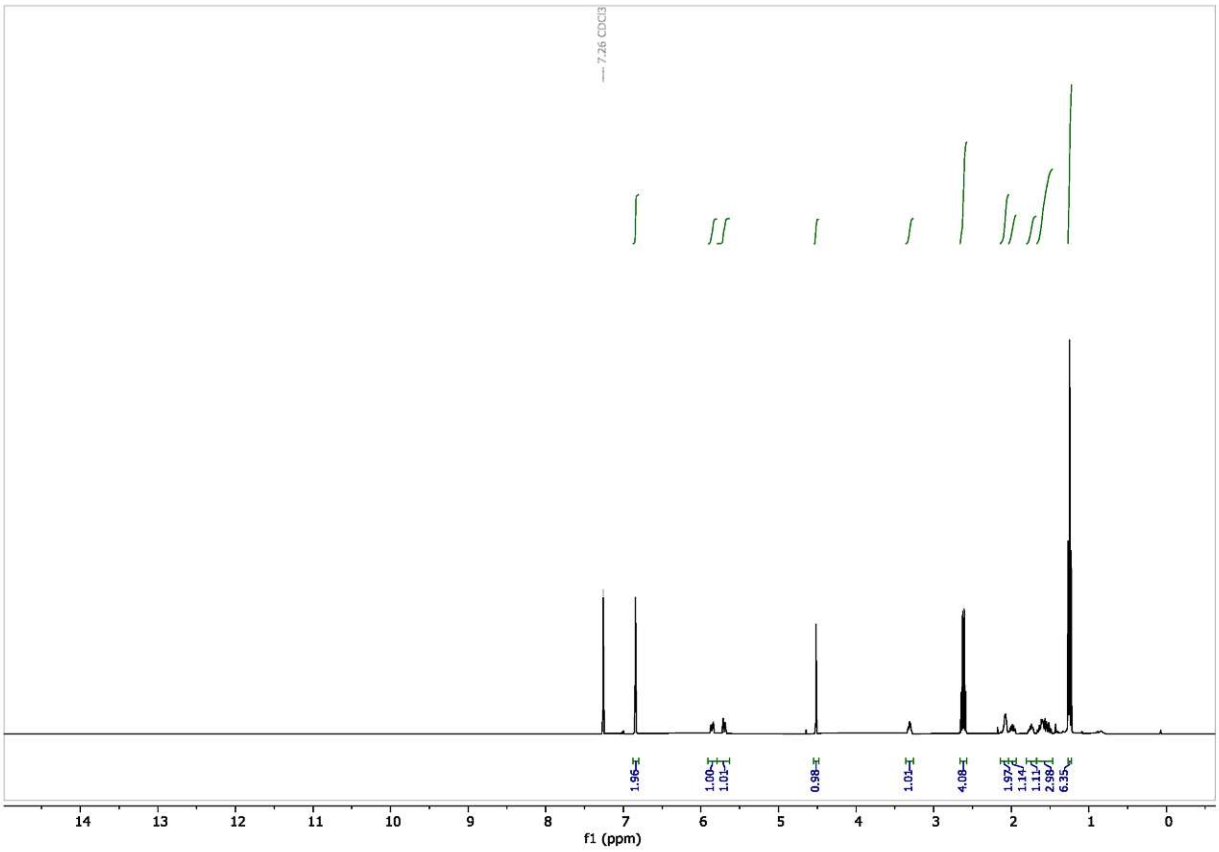


^{13}C NMR (101 MHz, $CDCl_3$)

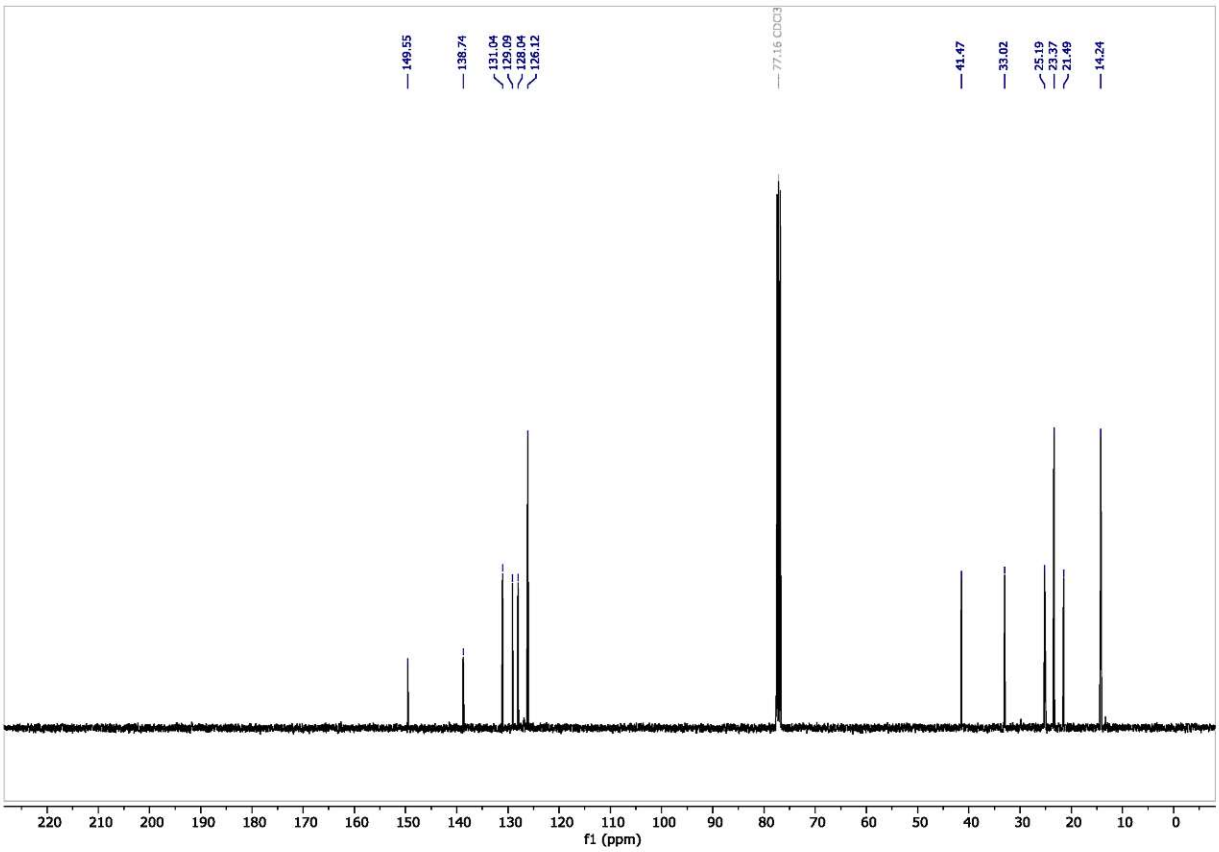


(S)-3,5-diethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (112)

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

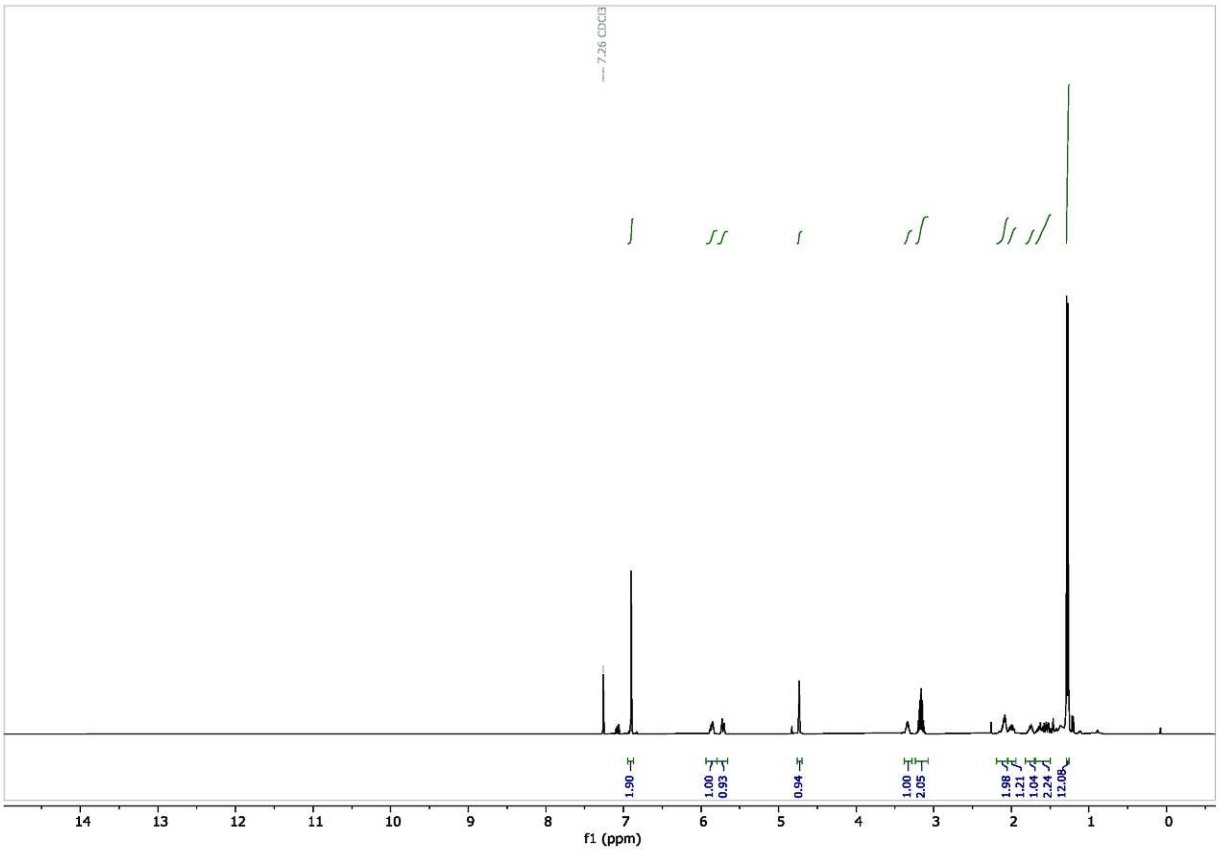


^{13}C NMR (101 MHz, $CDCl_3$)

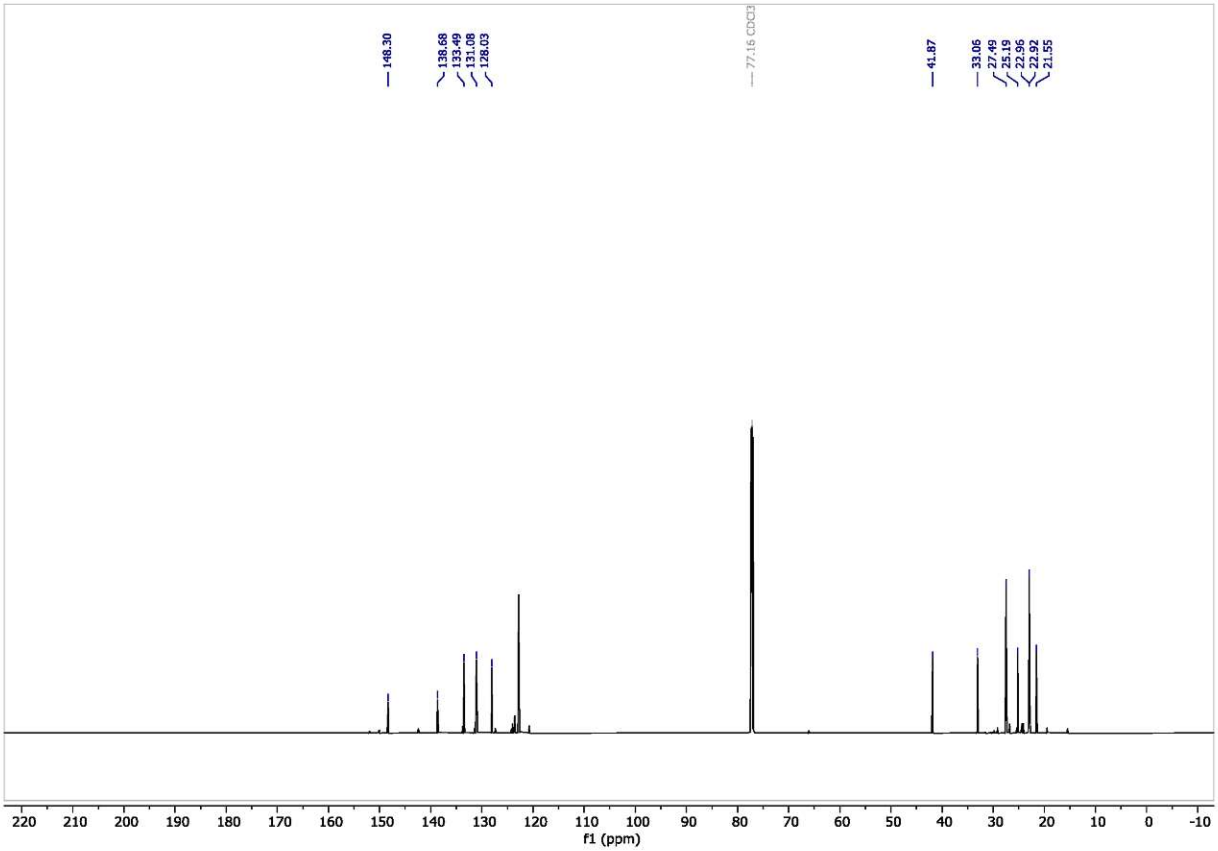


(S)-3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (113)

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

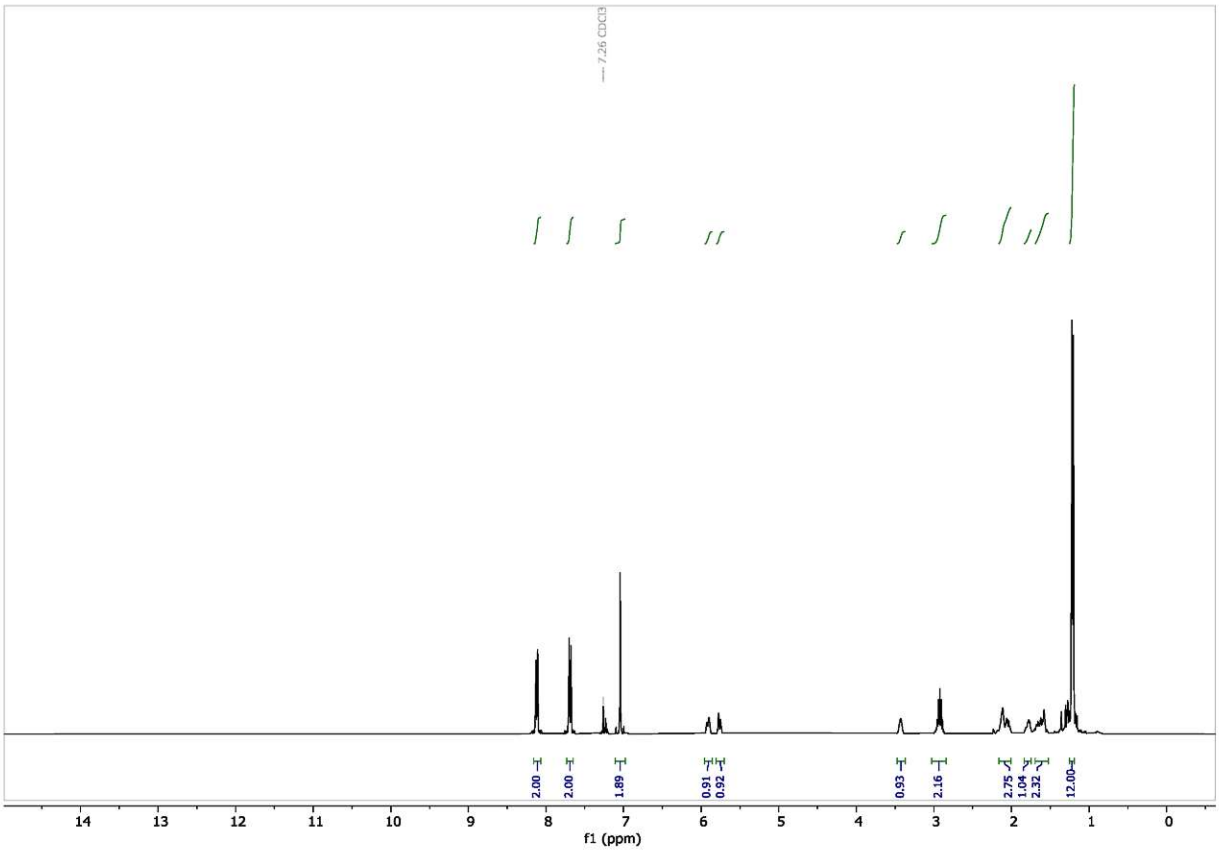


^{13}C NMR (101 MHz, $CDCl_3$)

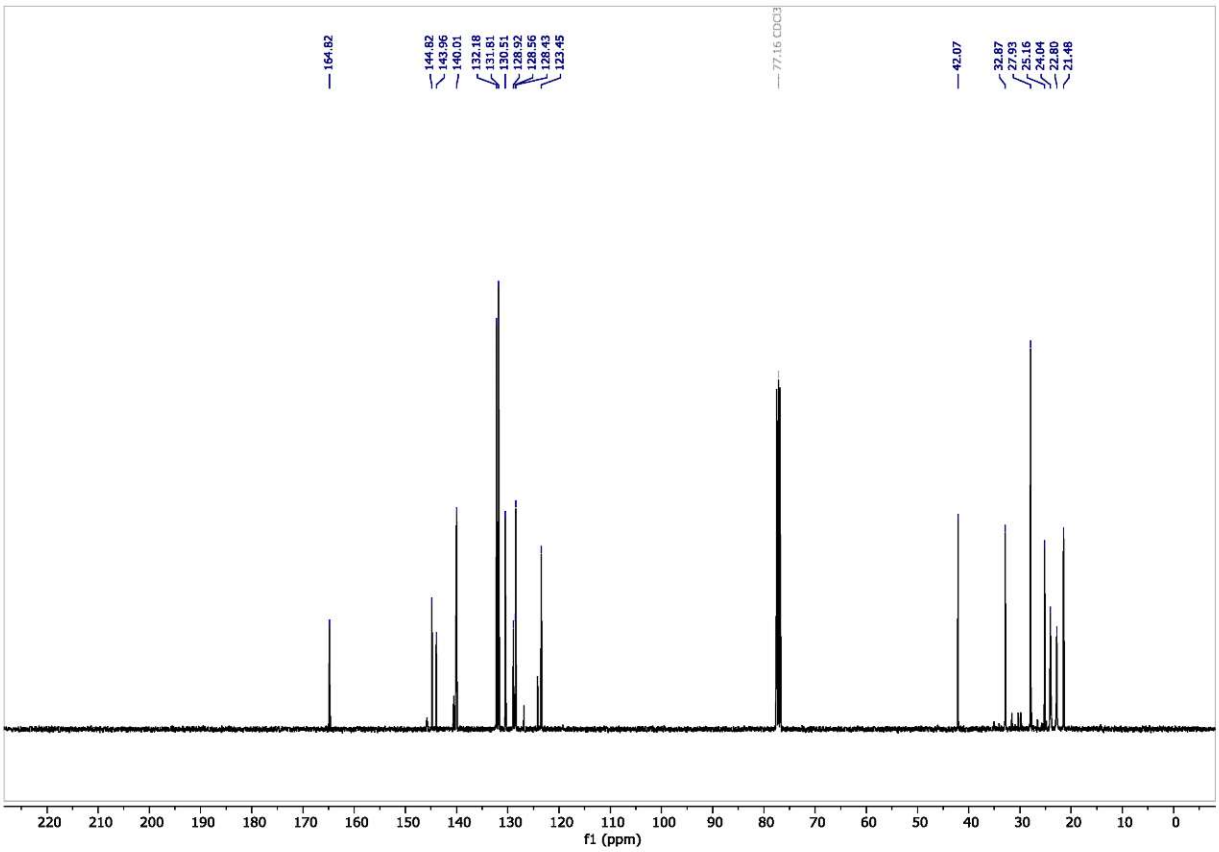


(S)-3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl 4-bromobenzoate (150)

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

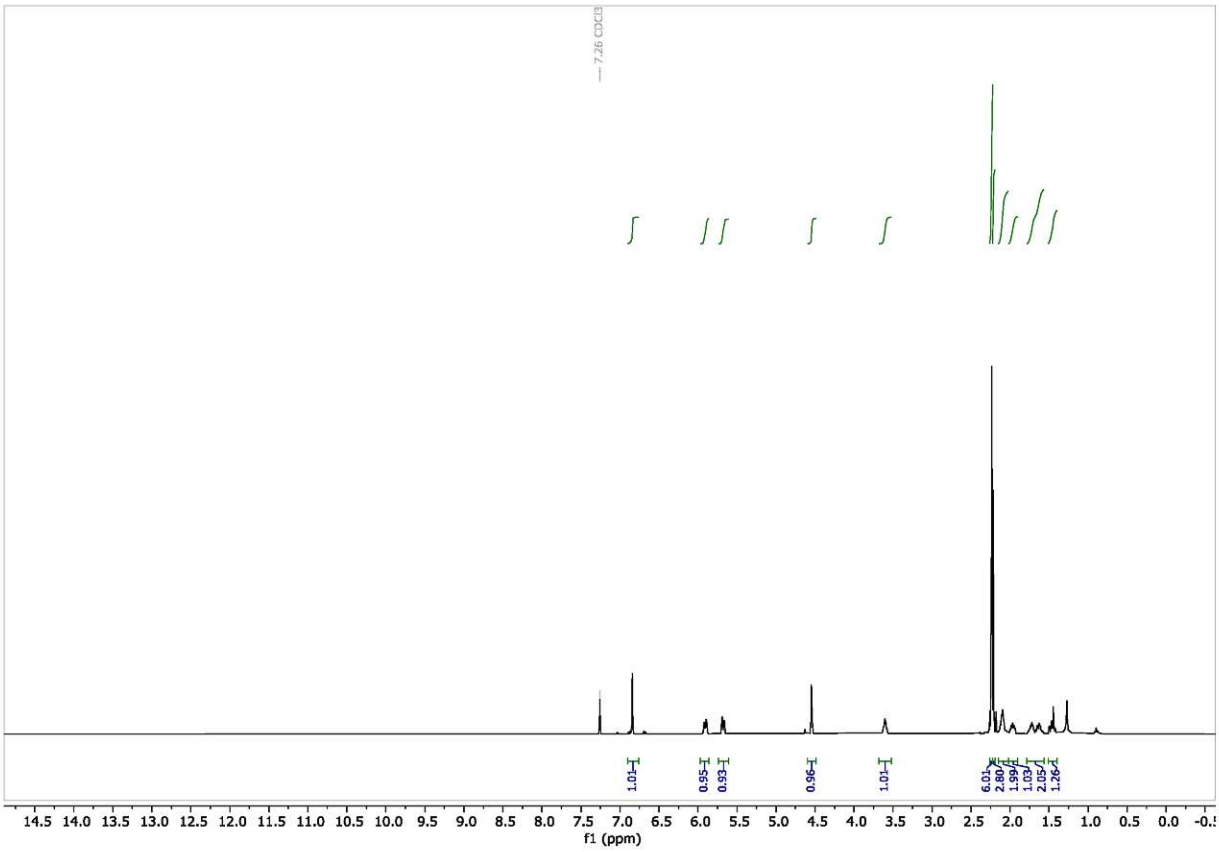


^{13}C NMR (101 MHz, $CDCl_3$)

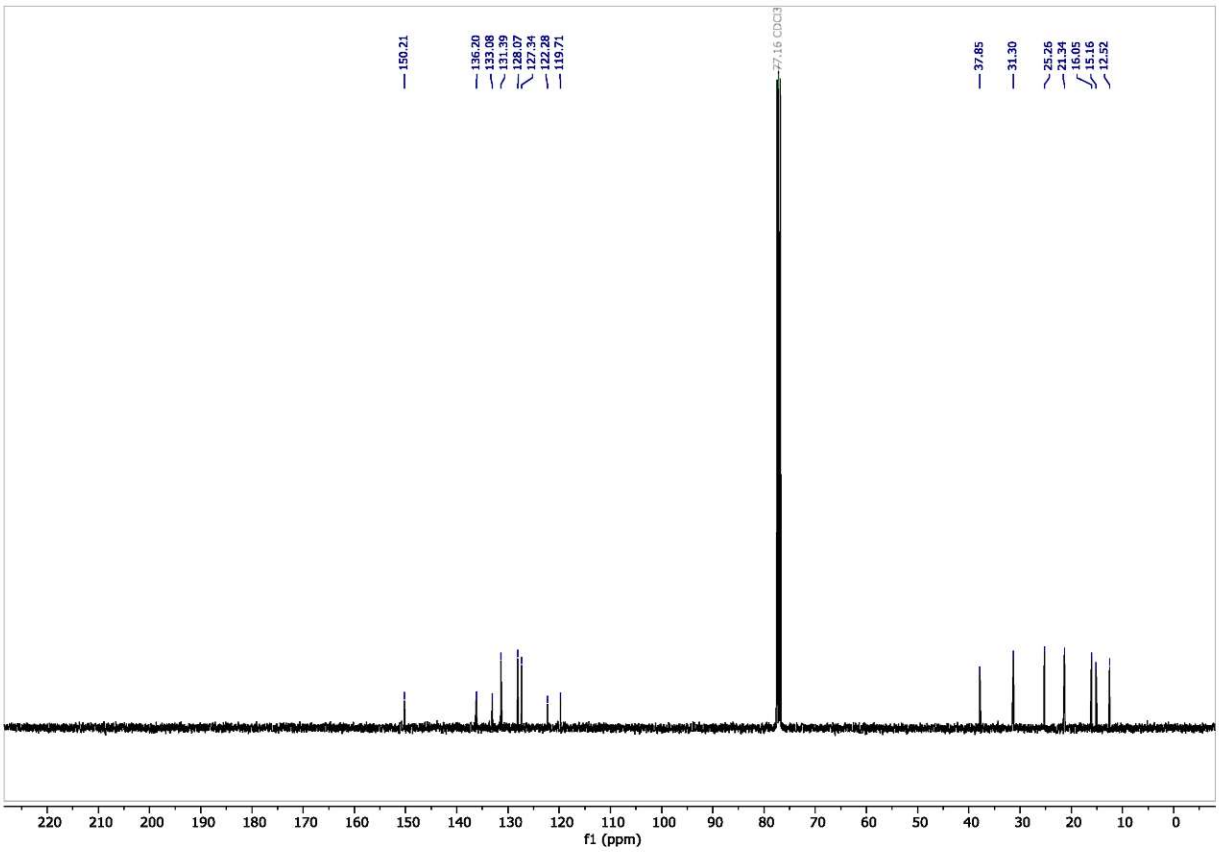


(S)-2,3,5-trimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (114)

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

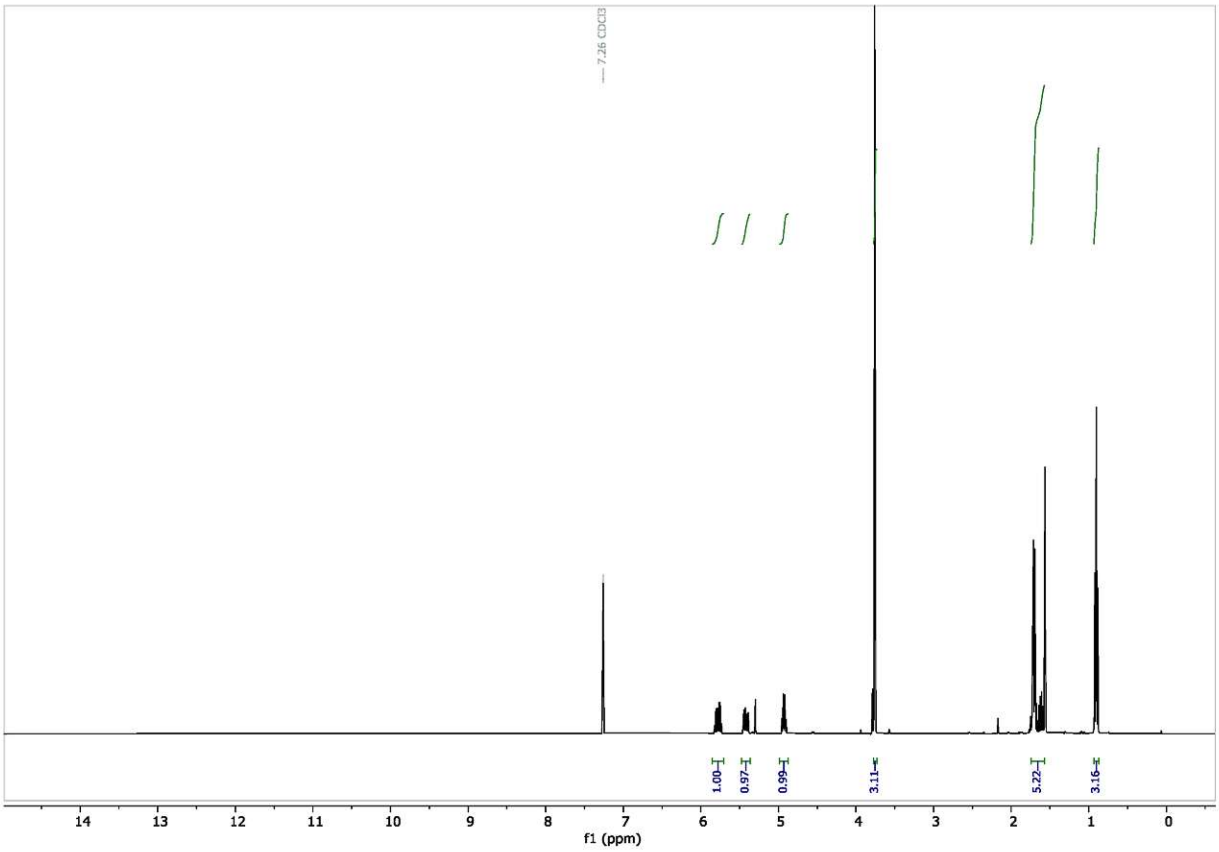


^{13}C NMR (101 MHz, $CDCl_3$)

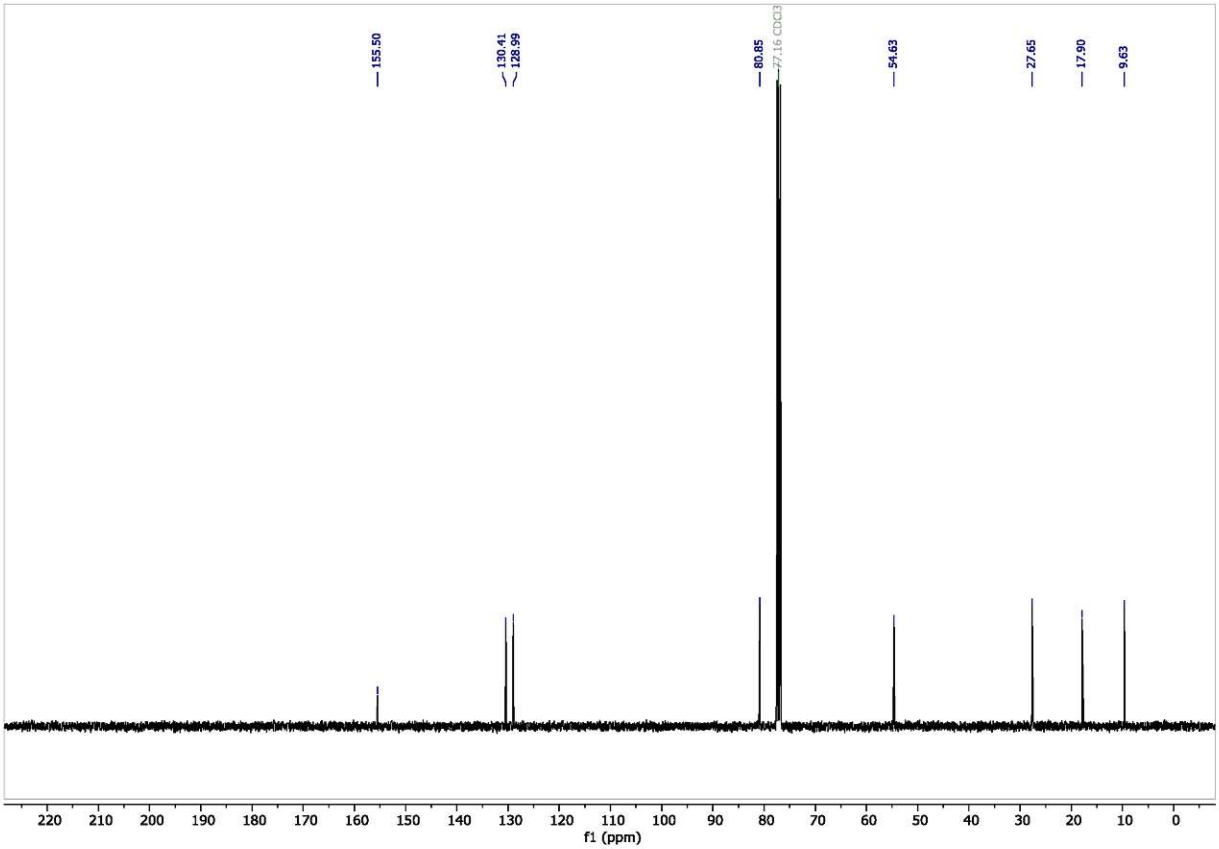


(E)-hex-4-en-3-yl methyl carbonate (117)

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

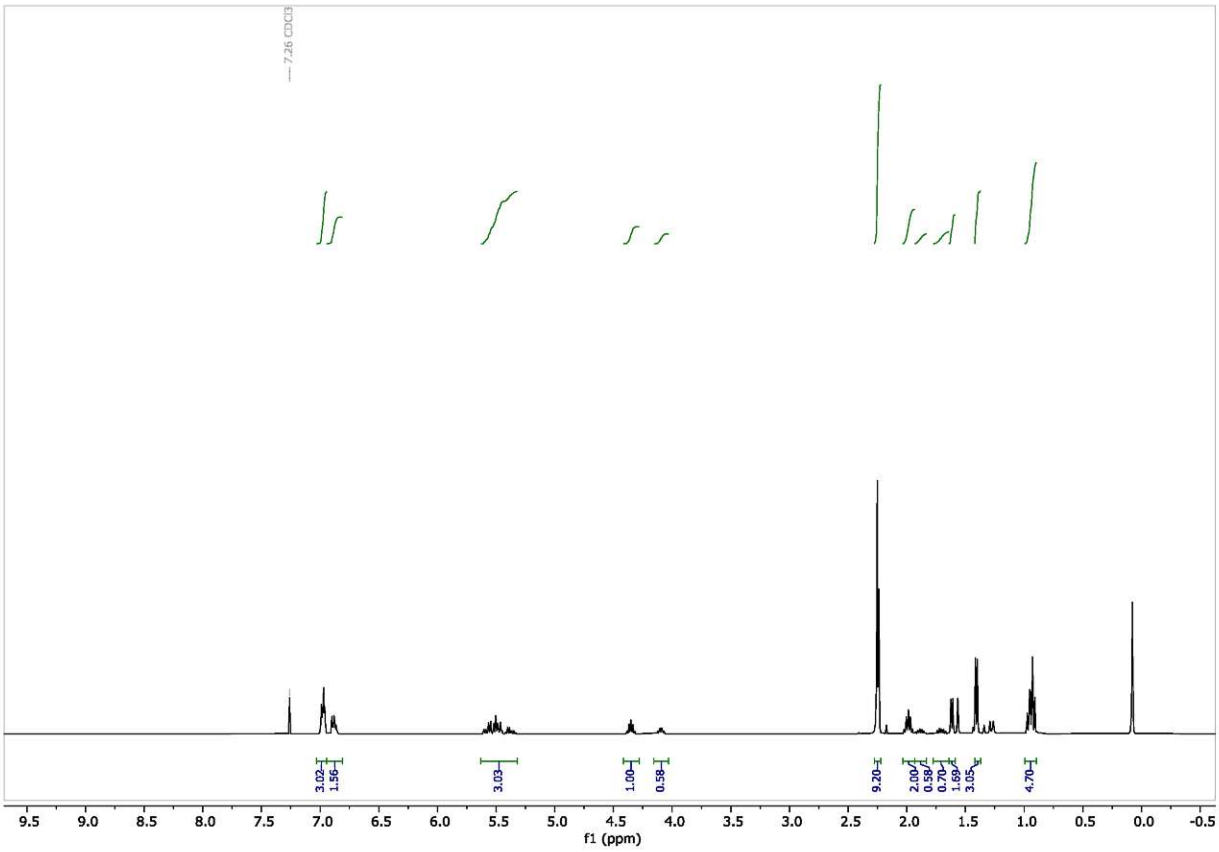


^{13}C NMR (101 MHz, $CDCl_3$)

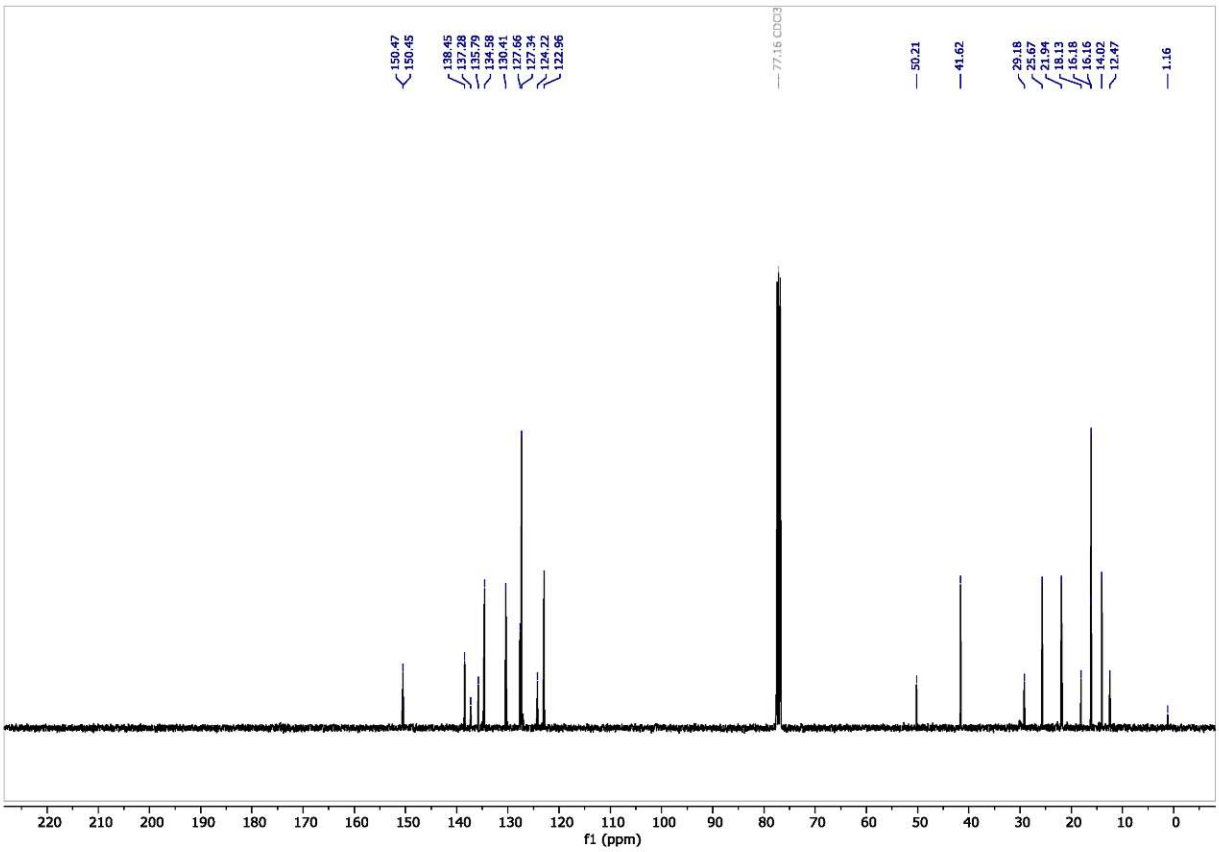


(E)-2-(hex-3-en-2-yloxy)-1,3-dimethylbenzene (118)

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

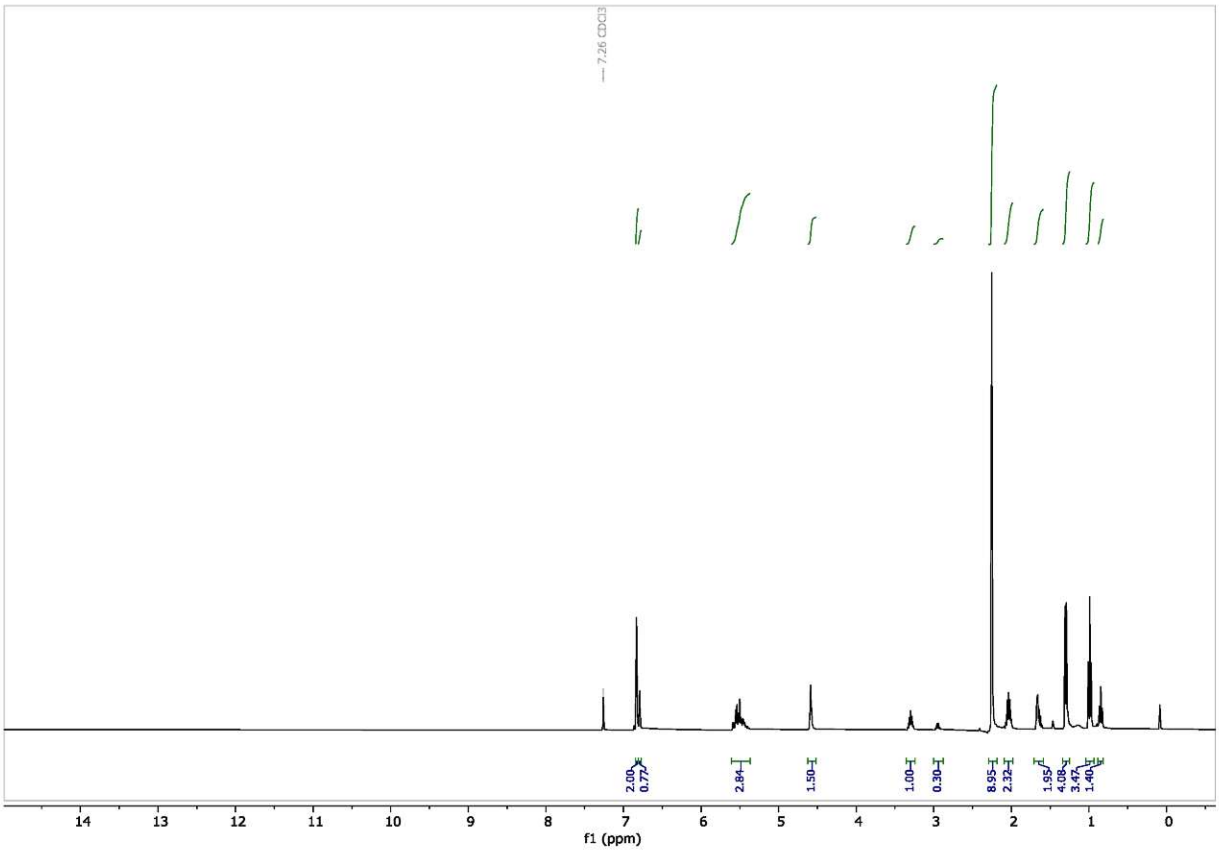


^{13}C NMR (101 MHz, $CDCl_3$)

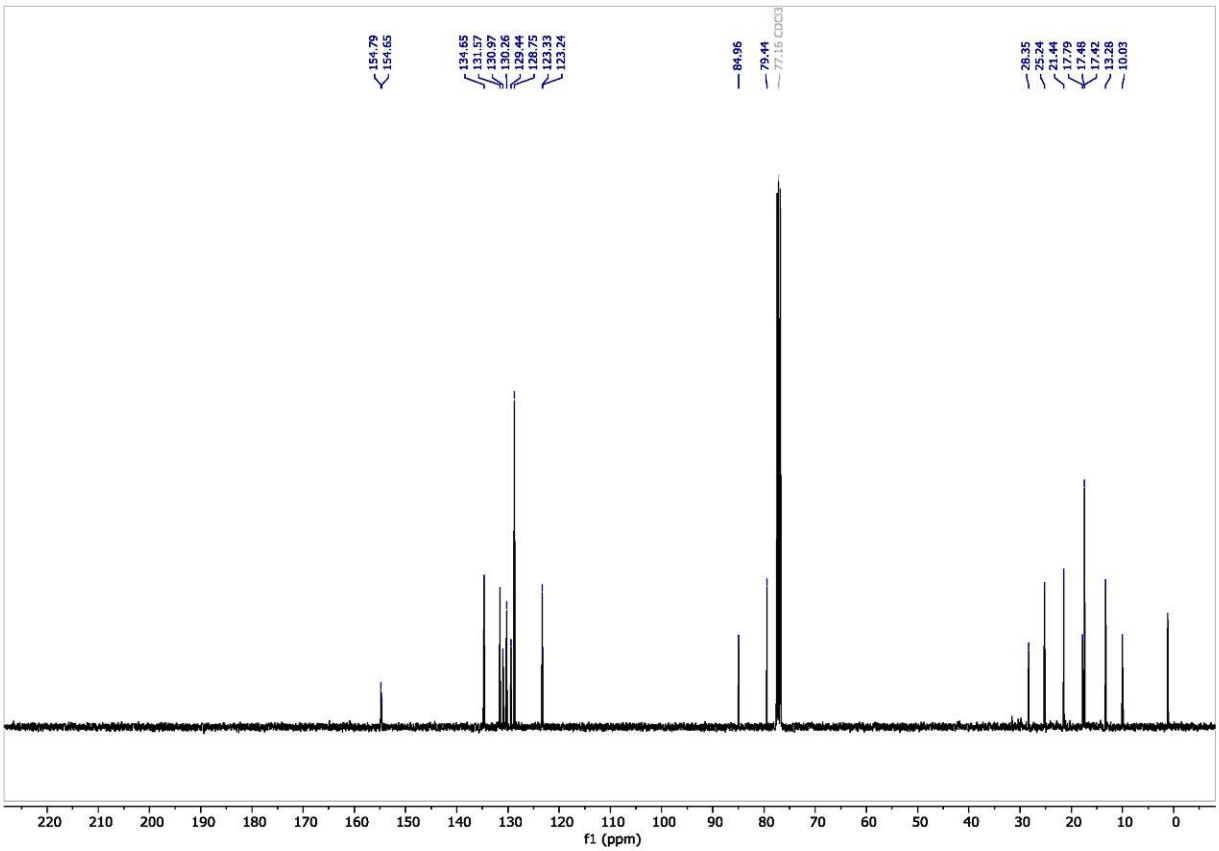


(E)-4-(hex-3-en-2-yl)-2,6-dimethylphenol (153)

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

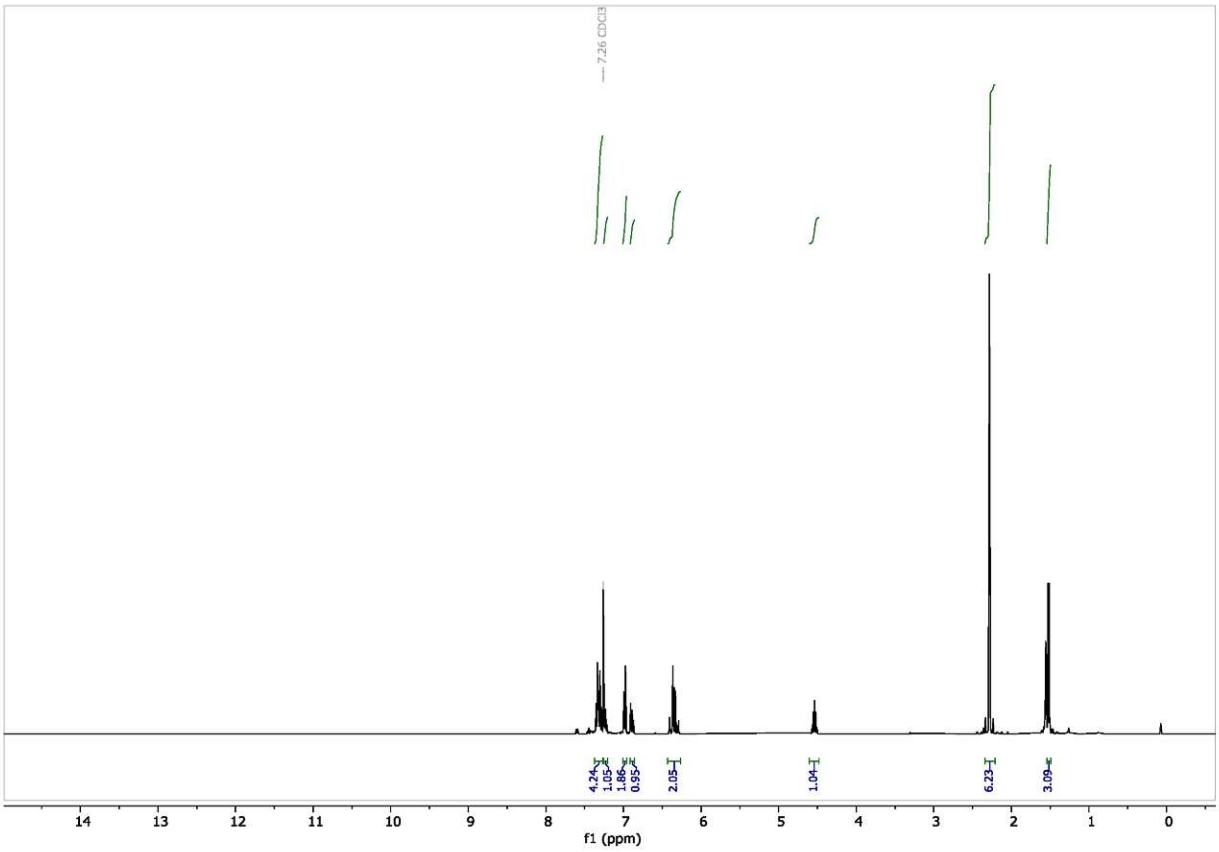


^{13}C NMR (101 MHz, $CDCl_3$)

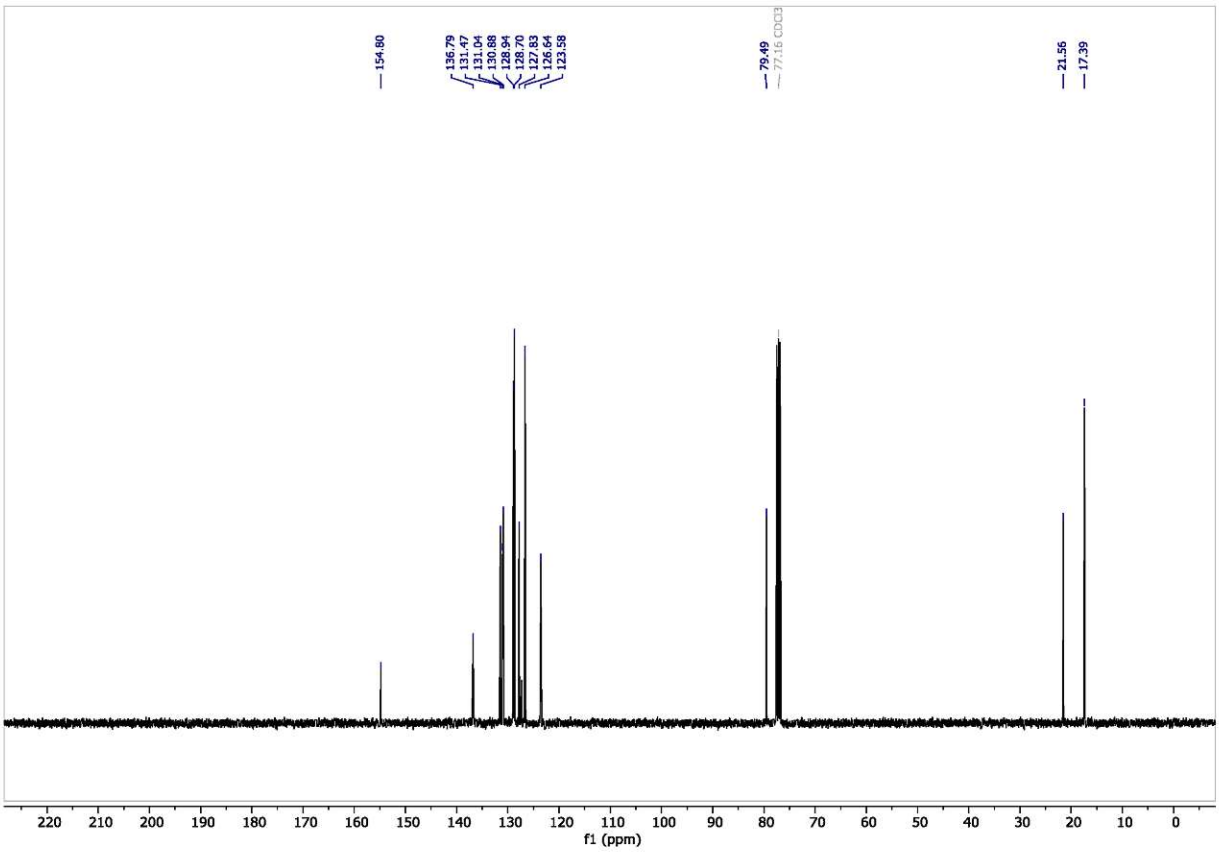


(E)-1,3-dimethyl-2-((4-phenylbut-3-en-2-yl)oxy)benzene (121)

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

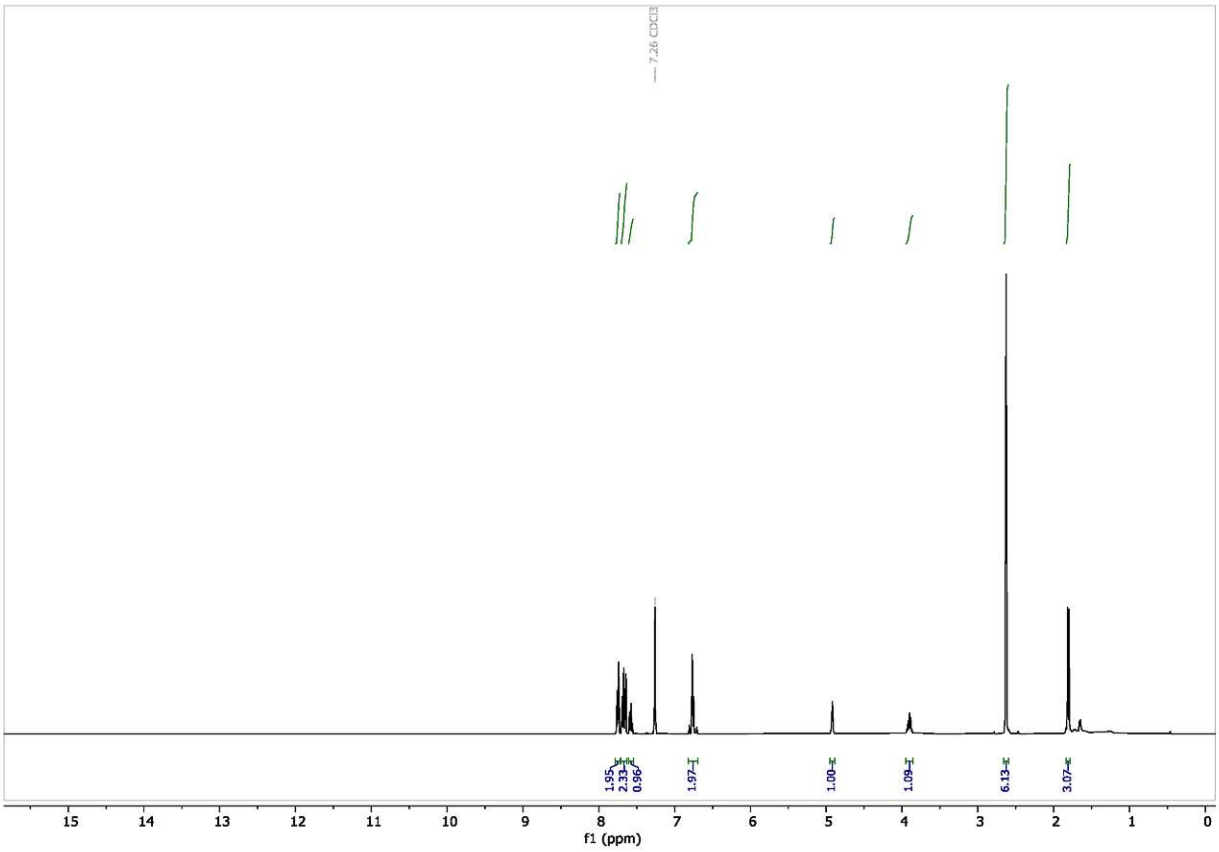


^{13}C NMR (101 MHz, $CDCl_3$)

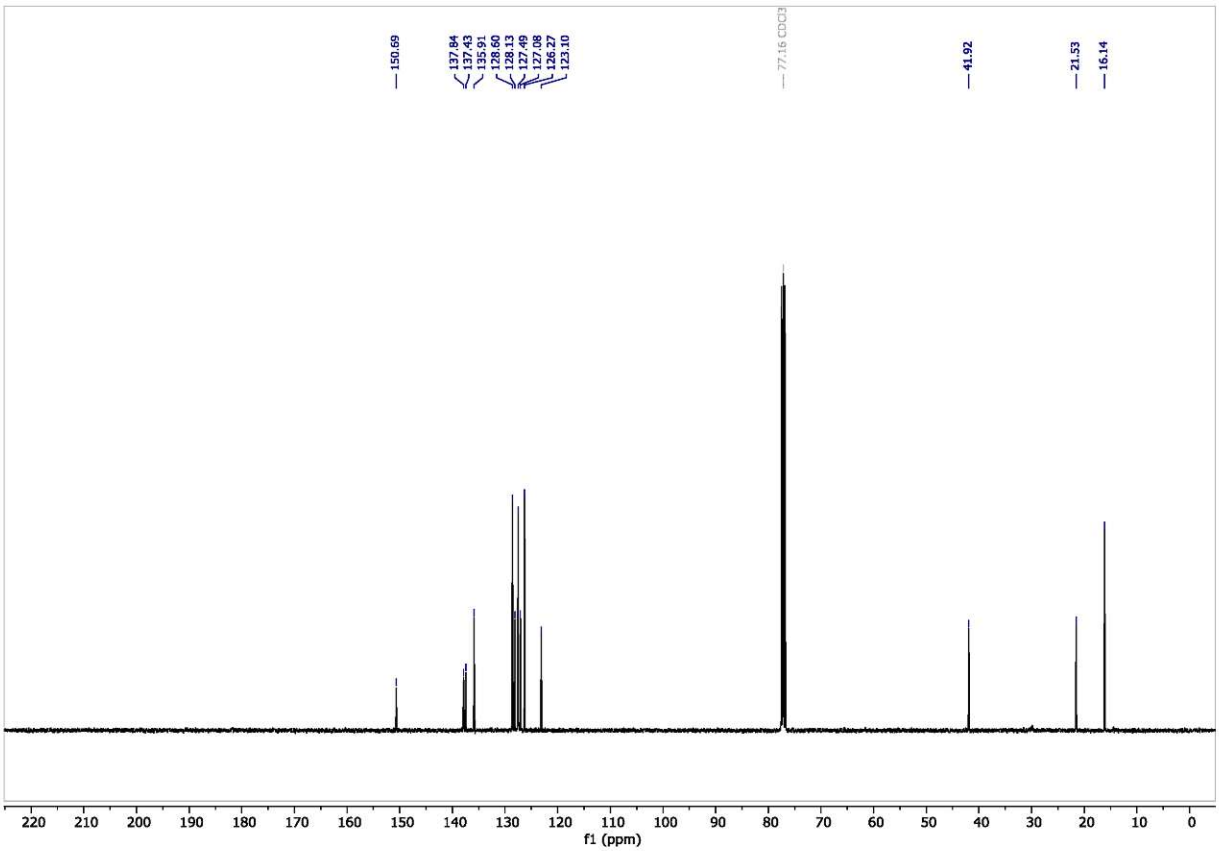


(E)-2,6-dimethyl-4-(4-phenylbut-3-en-2-yl)phenol (154)

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

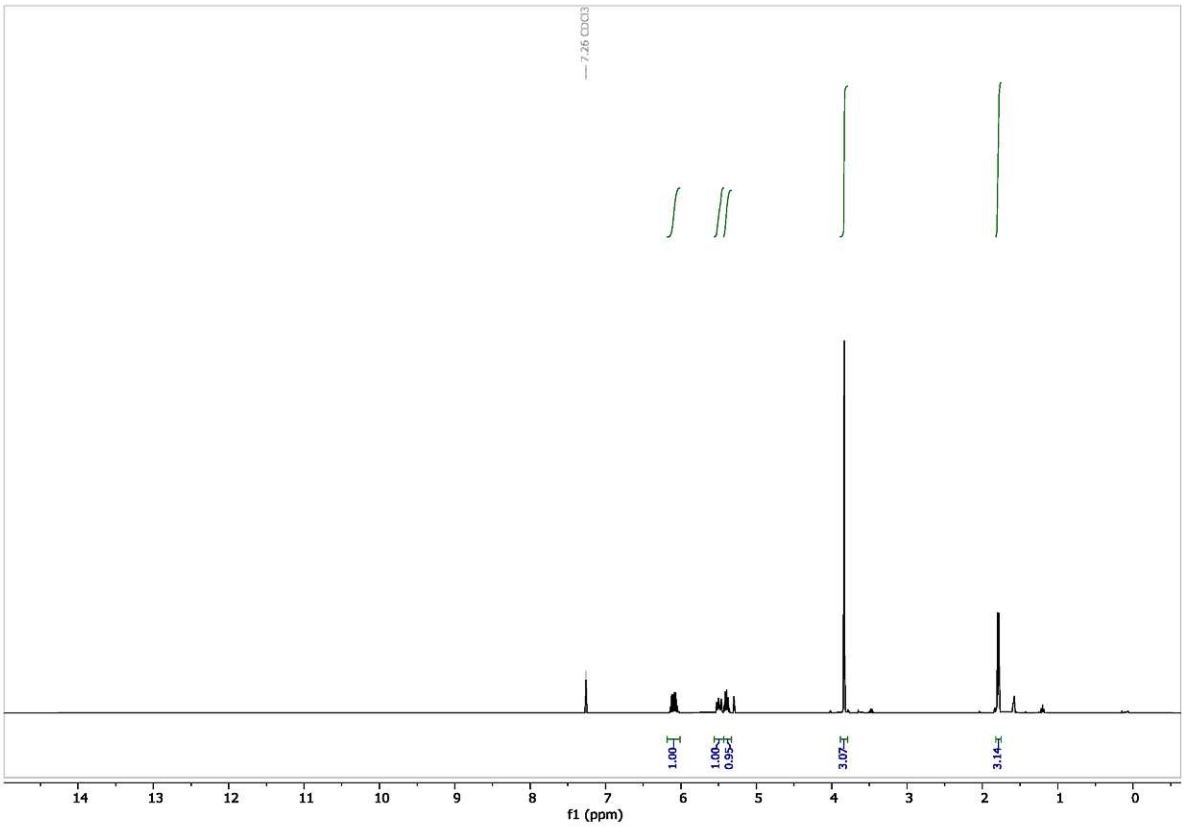


^{13}C NMR (101 MHz, $CDCl_3$)

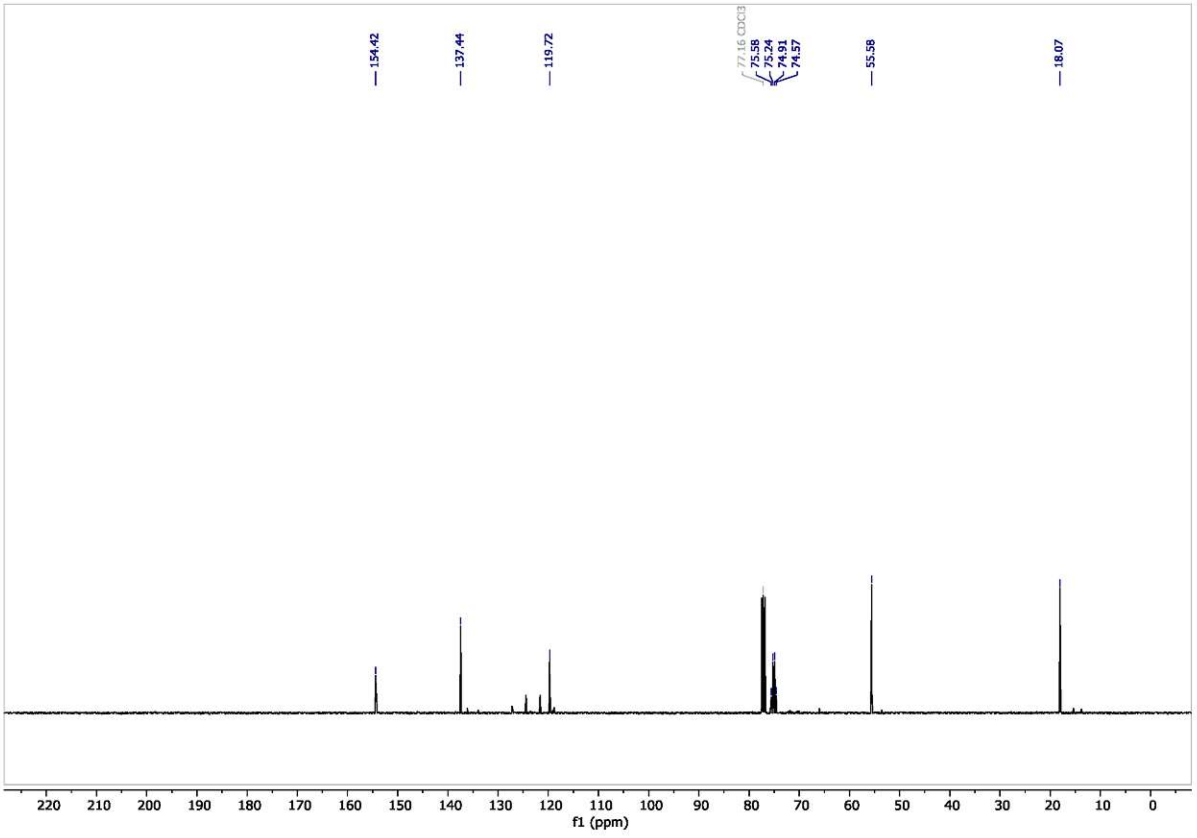


(E)-methyl (1,1,1-trifluoropent-3-en-2-yl) carbonate (122)

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

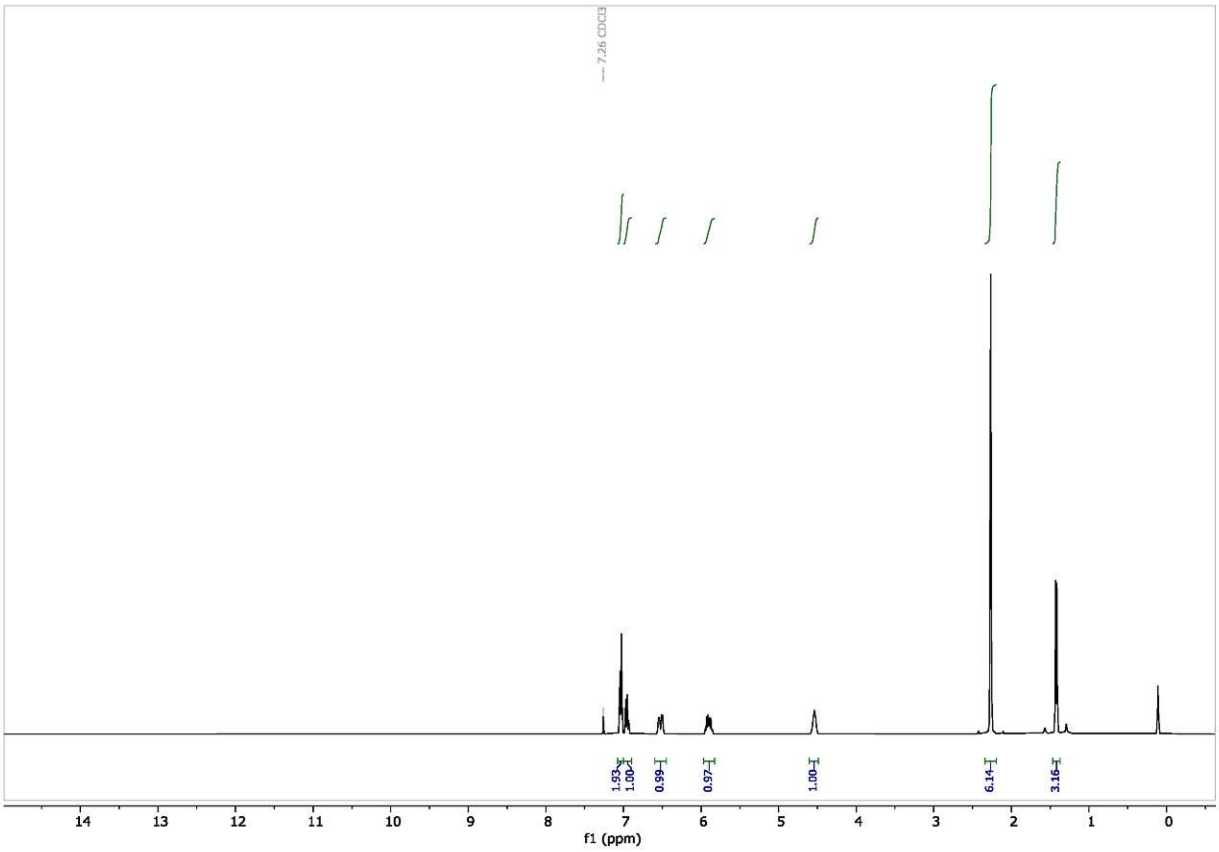


^{13}C NMR (101 MHz, $CDCl_3$)

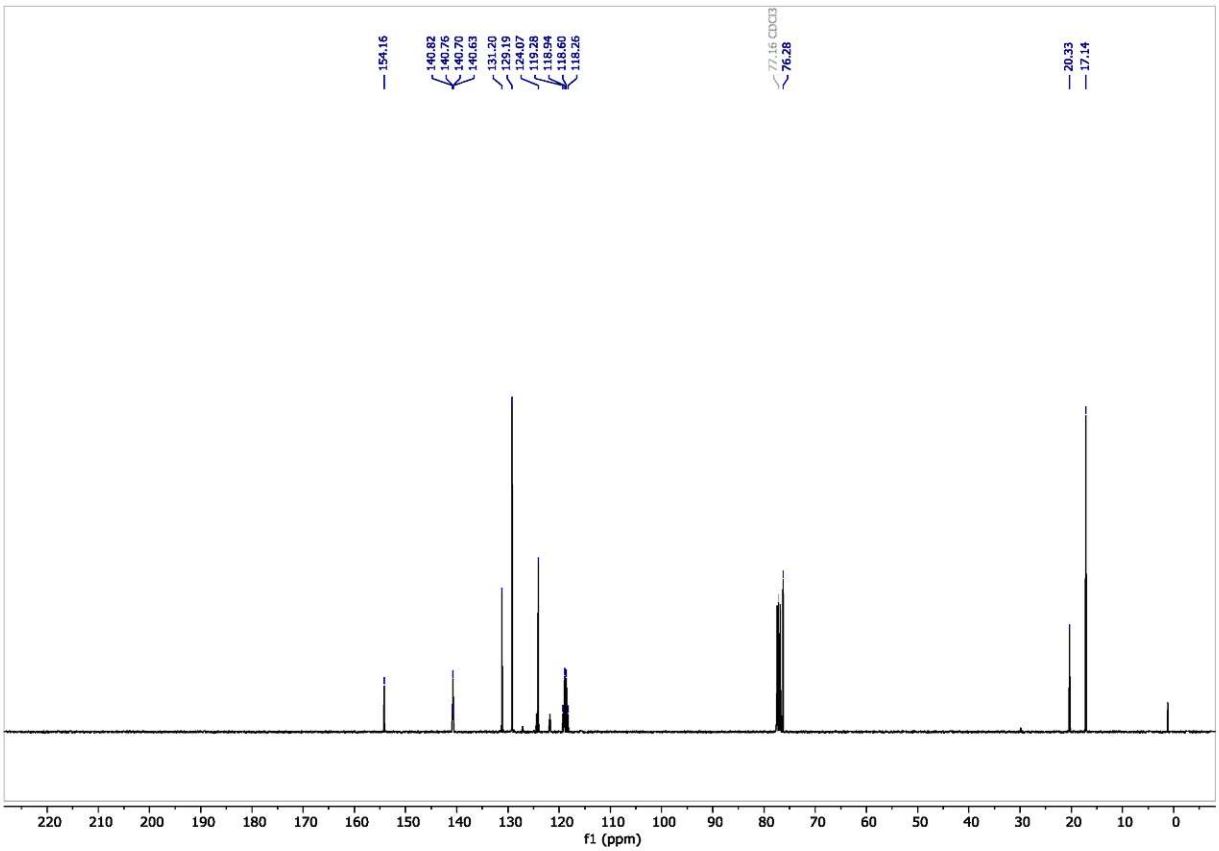


(E)-1,3-dimethyl-2-((5,5,5-trifluoropent-3-en-2-yl)oxy)benzene (123)

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

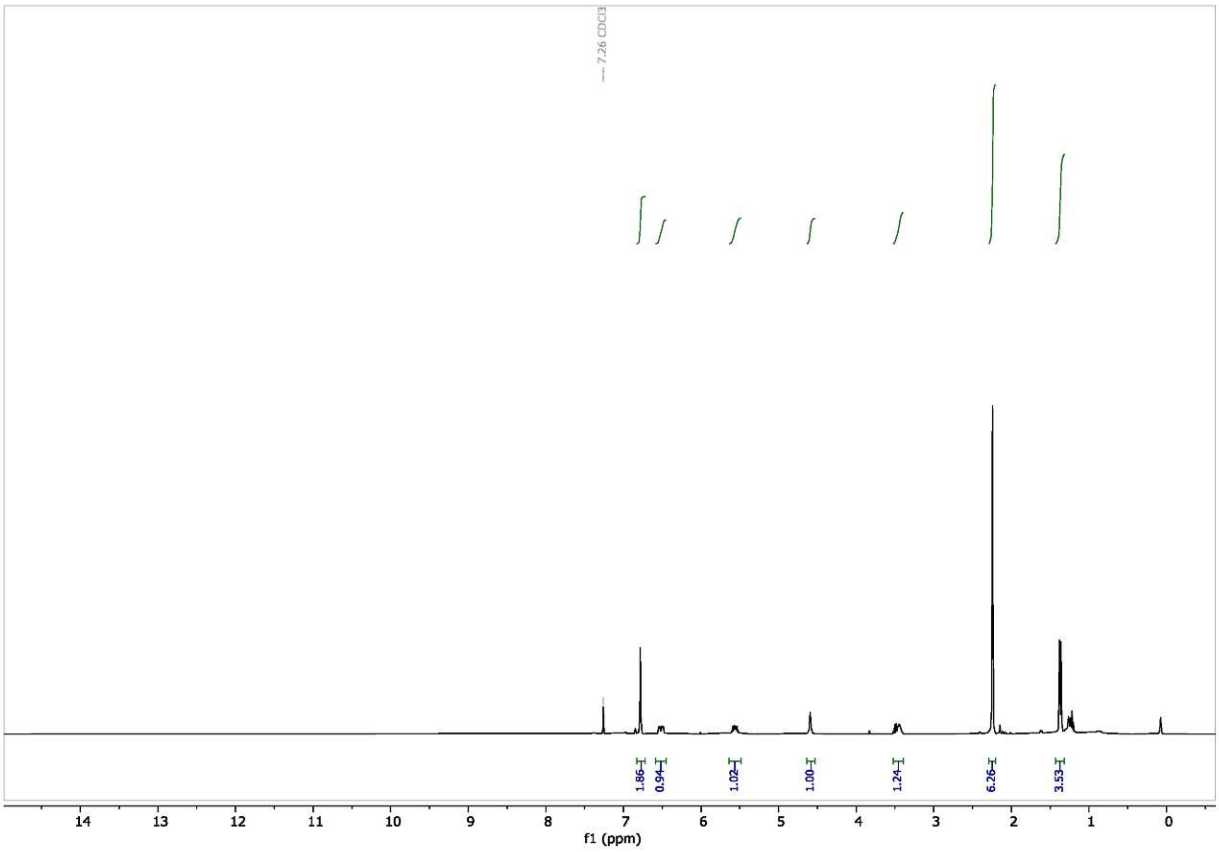


^{13}C NMR (101 MHz, $CDCl_3$)

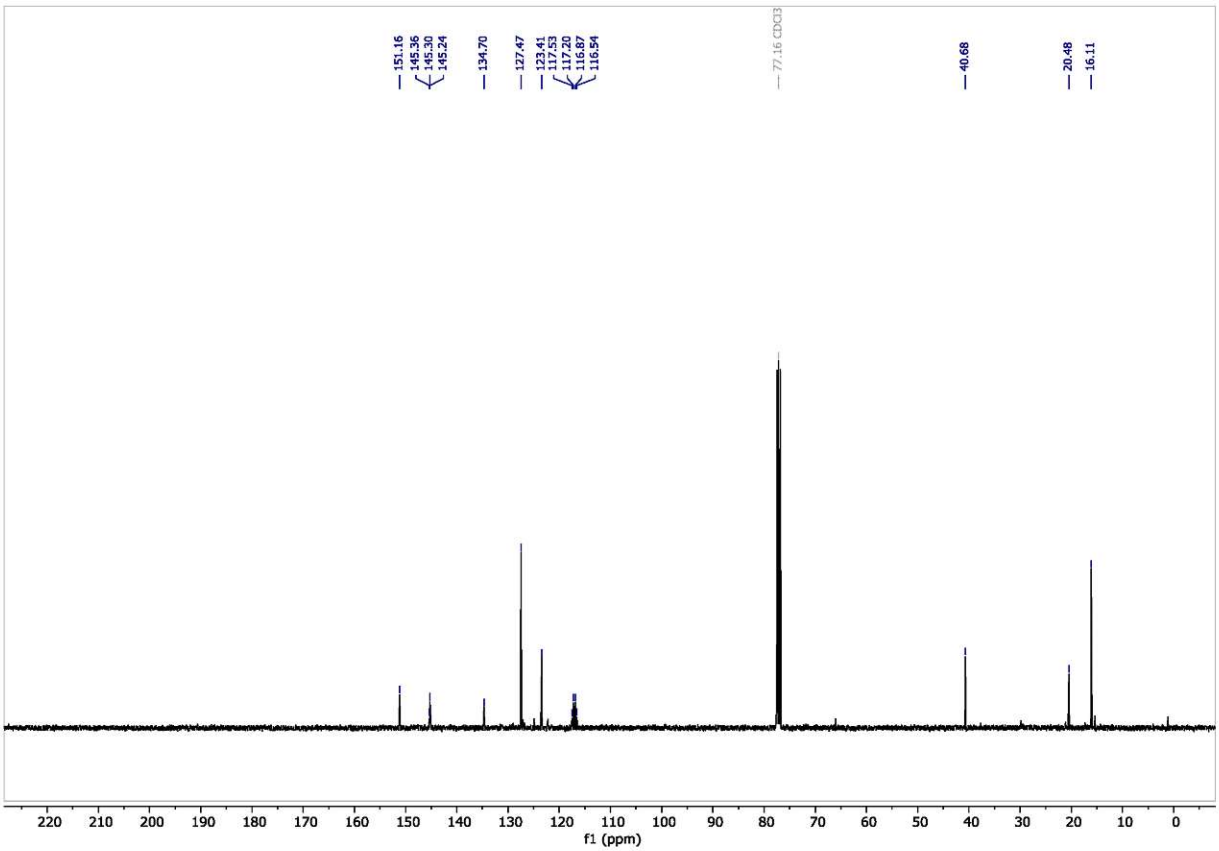


(E)-2,6-dimethyl-4-(5,5,5-trifluoropent-3-en-2-yl)phenol (155)

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

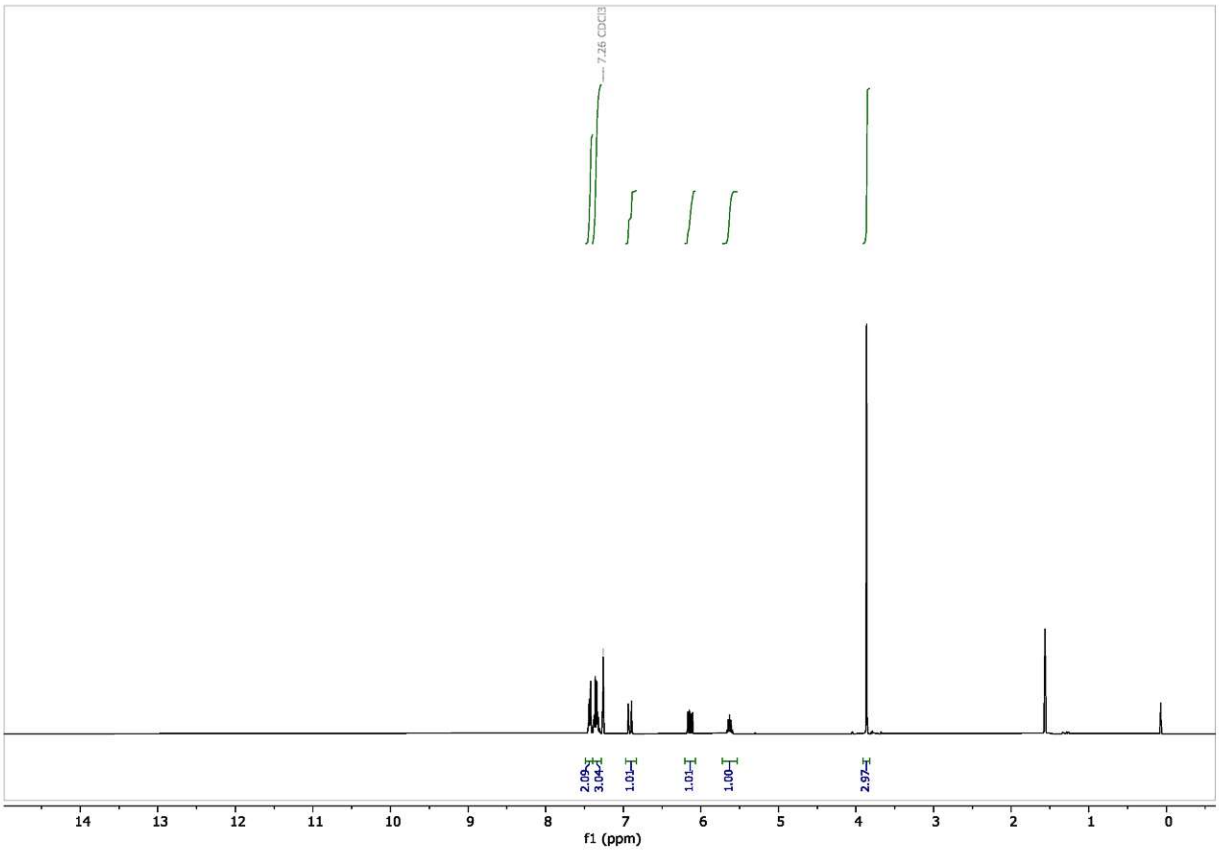


^{13}C NMR (101 MHz, $CDCl_3$)

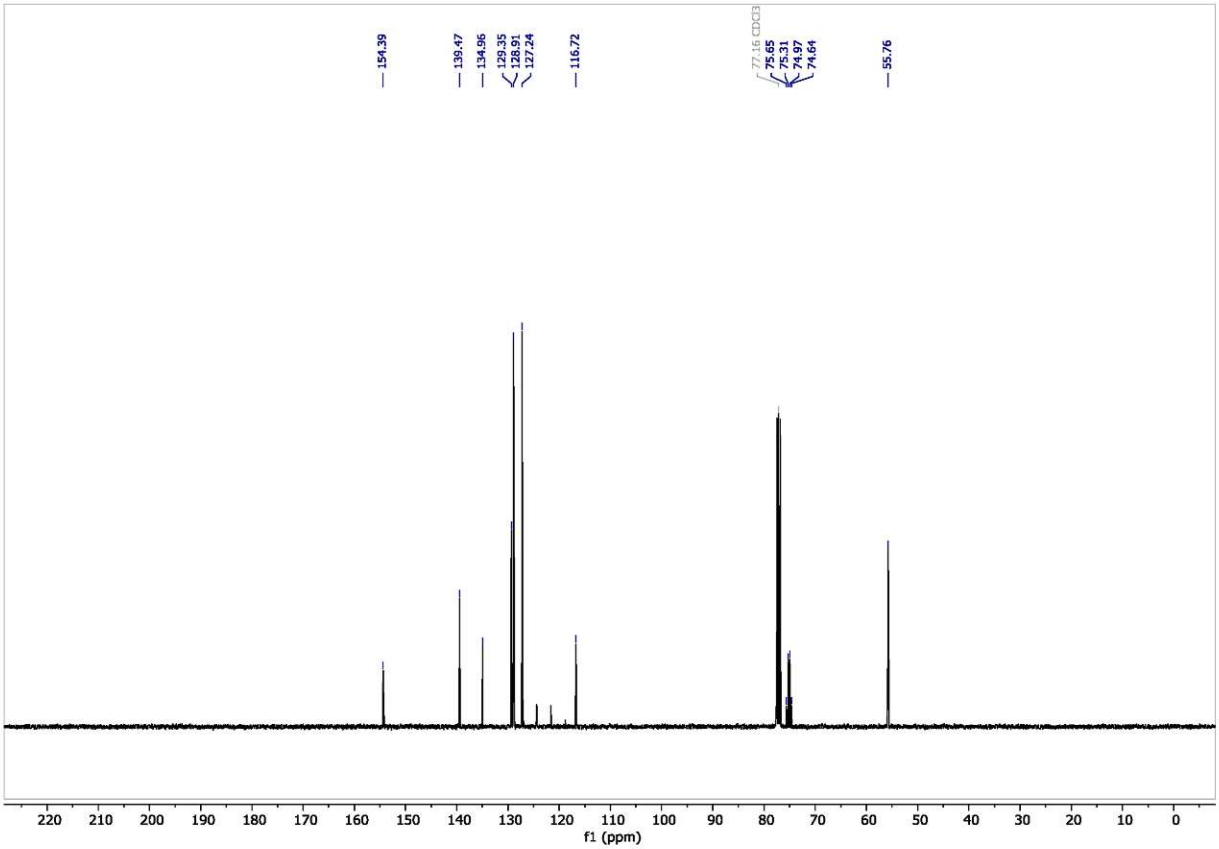


(E)-methyl (1,1,1-trifluoropent-3-en-2-yl) phenyl carbonate (124)

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

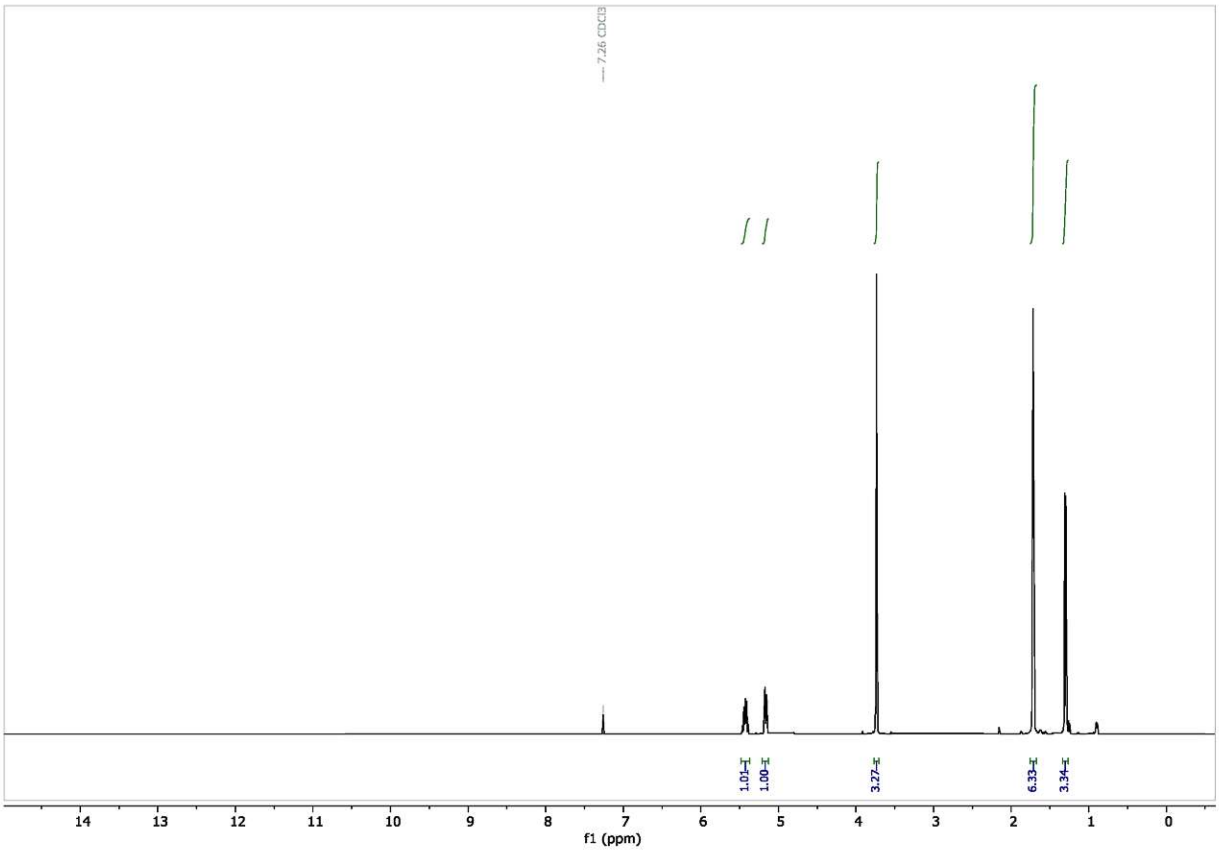


^{13}C NMR (101 MHz, $CDCl_3$)

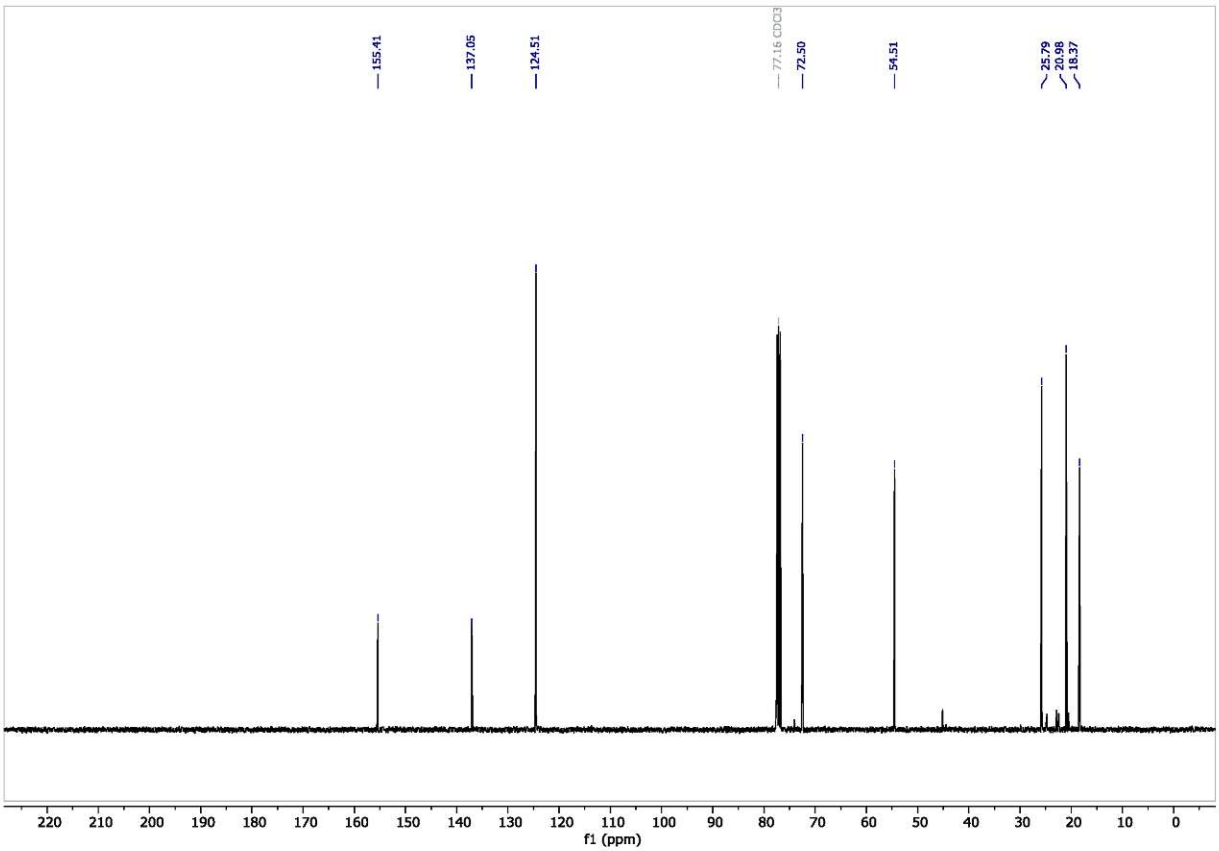


Methyl (4-methylpent-3-en-2-yl) carbonate (157)

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

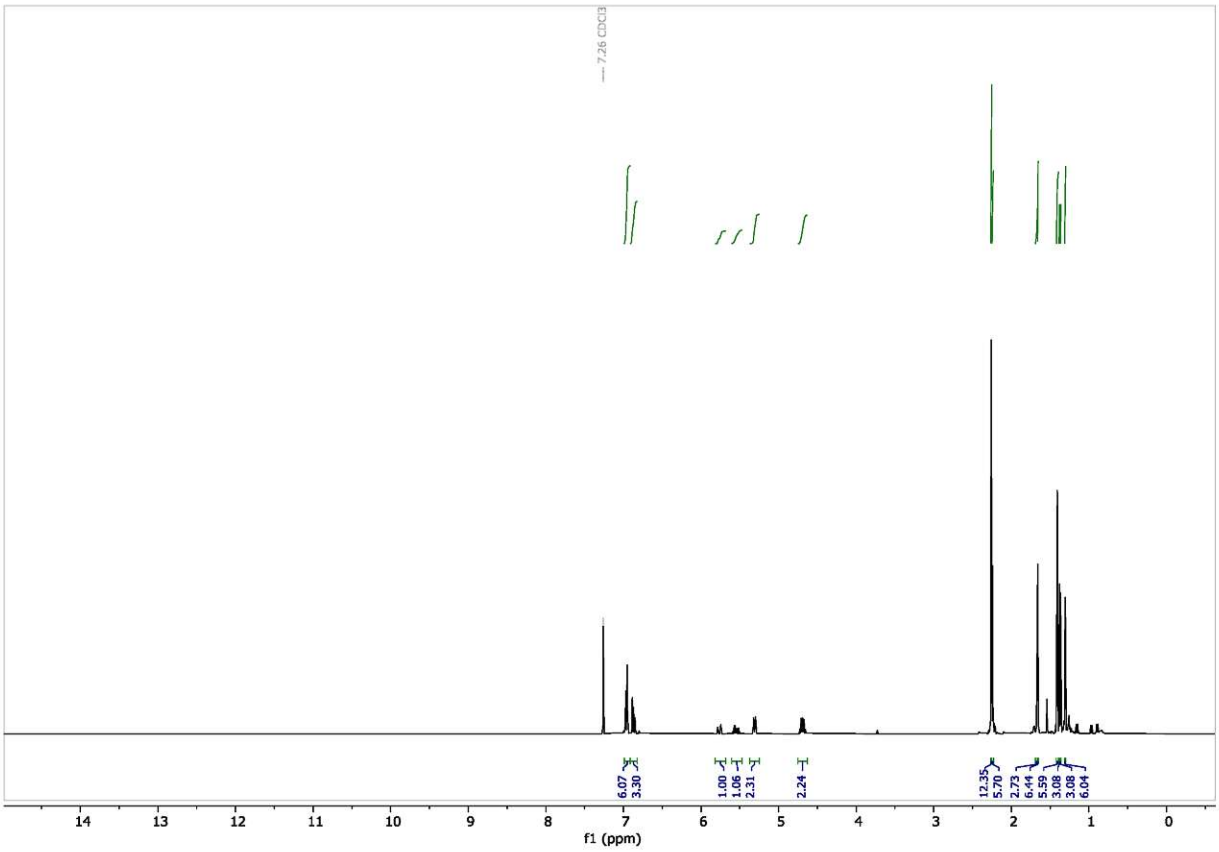


^{13}C NMR (101 MHz, $CDCl_3$)

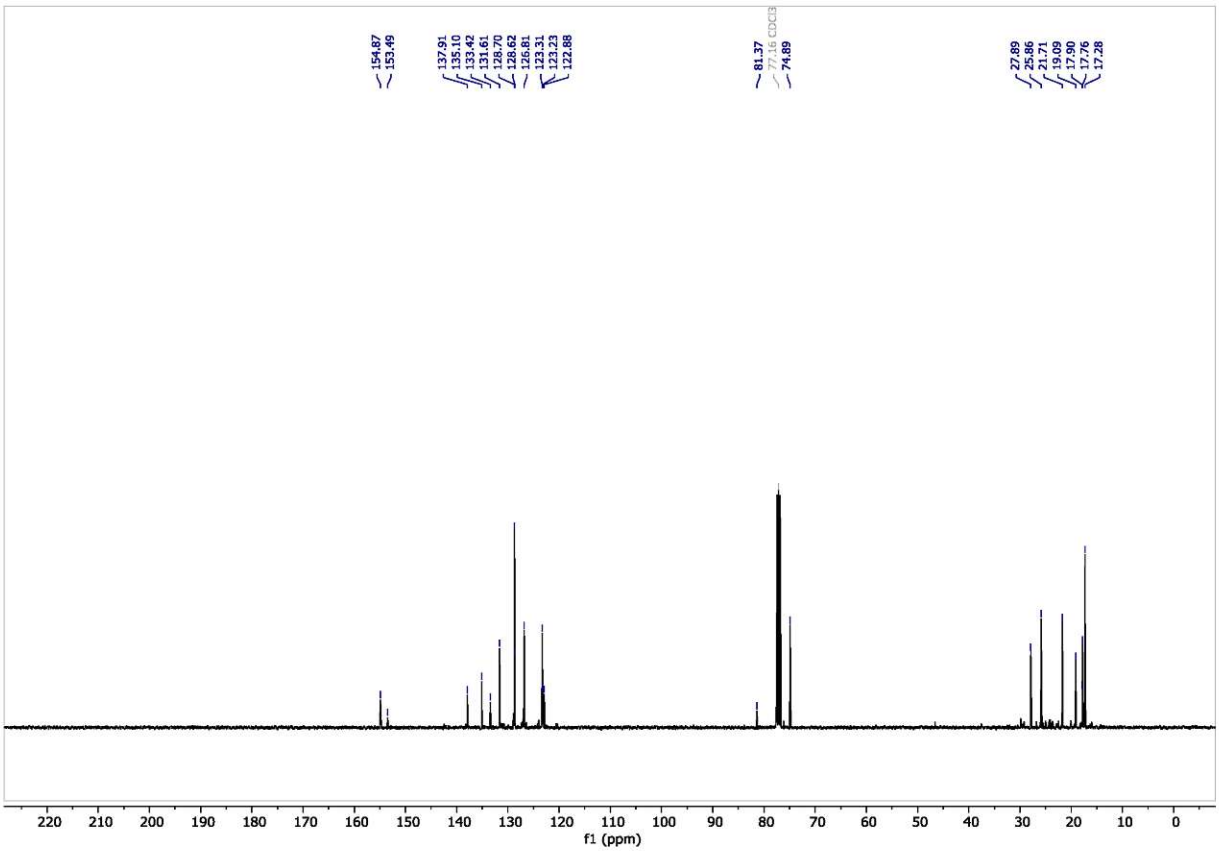


1,3-dimethyl-2-((4-methylpen-3-en-2-yl)oxy)benzene (134)

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

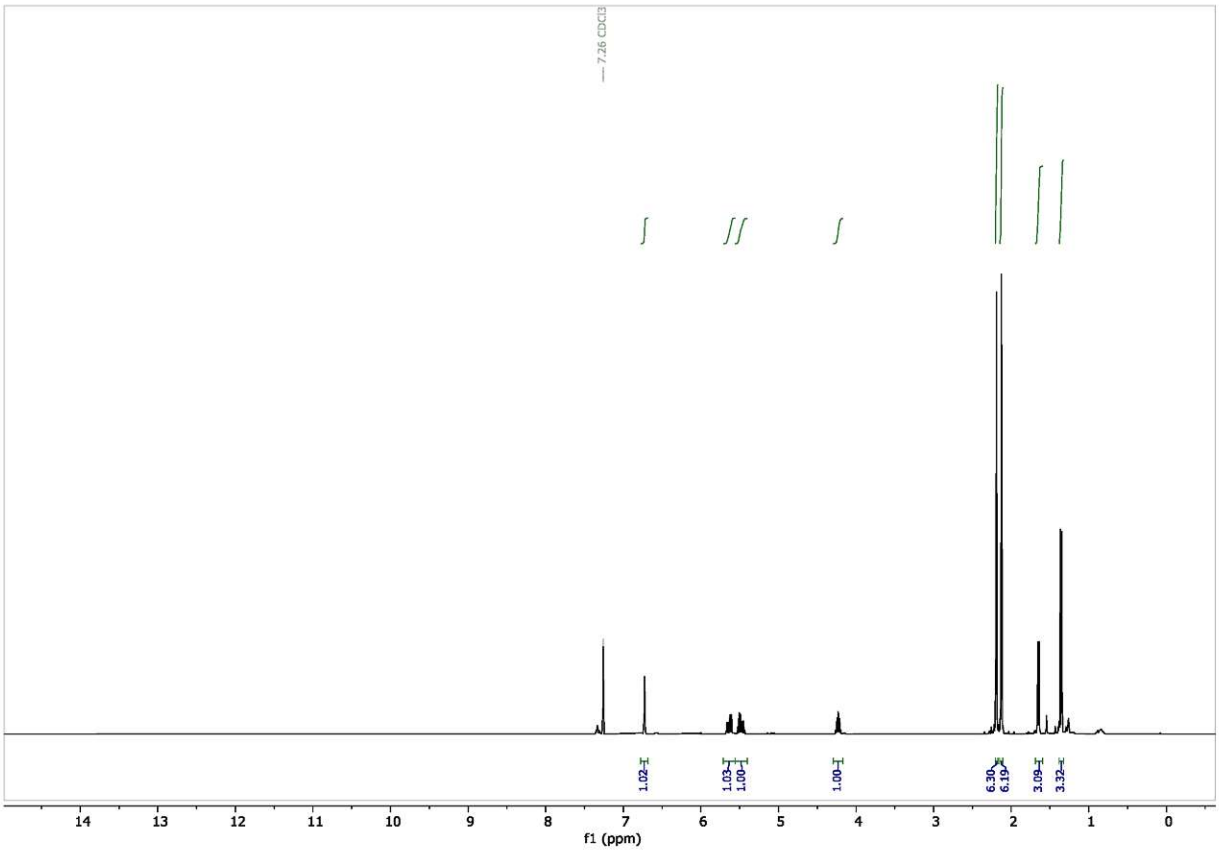


^{13}C NMR (101 MHz, $CDCl_3$)

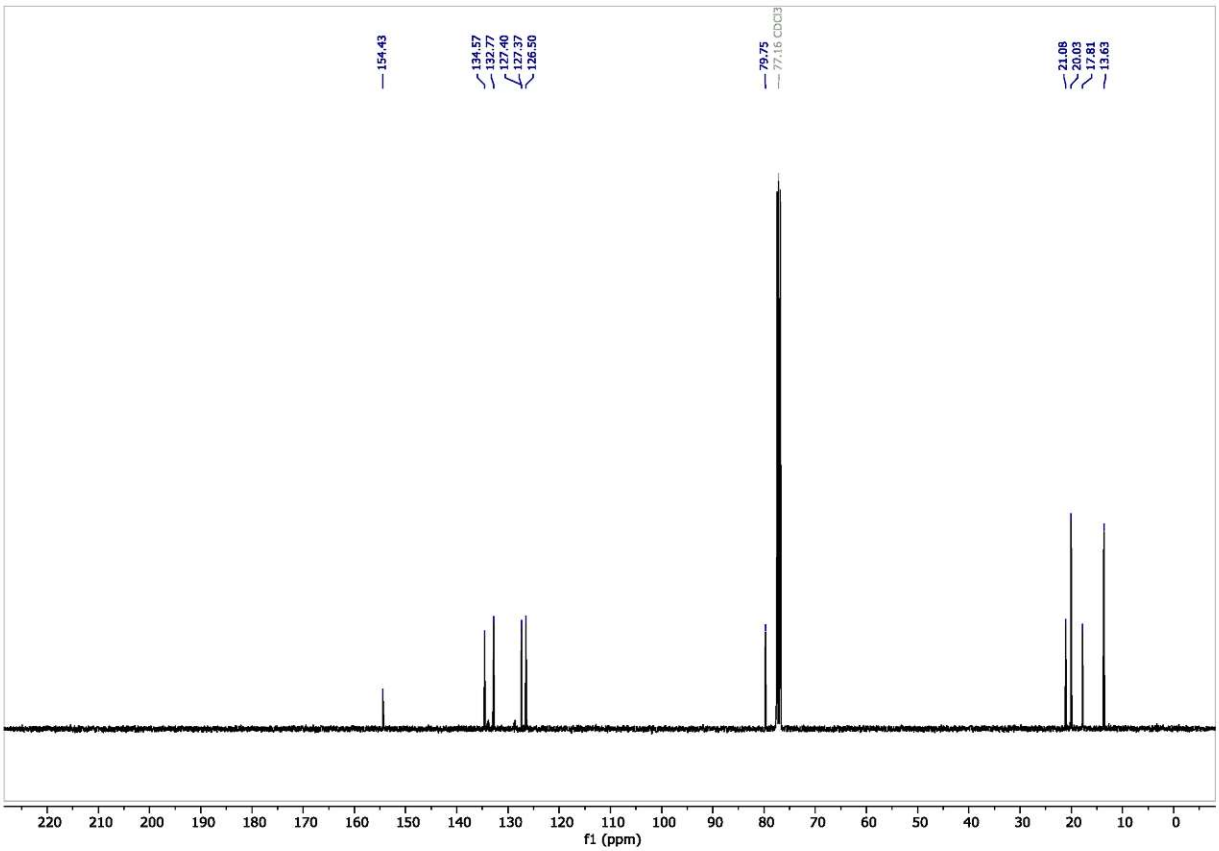


(E)-1,2,4,5-tetramethyl-3-(pent-3-en-2-yloxy)benzene (126)

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

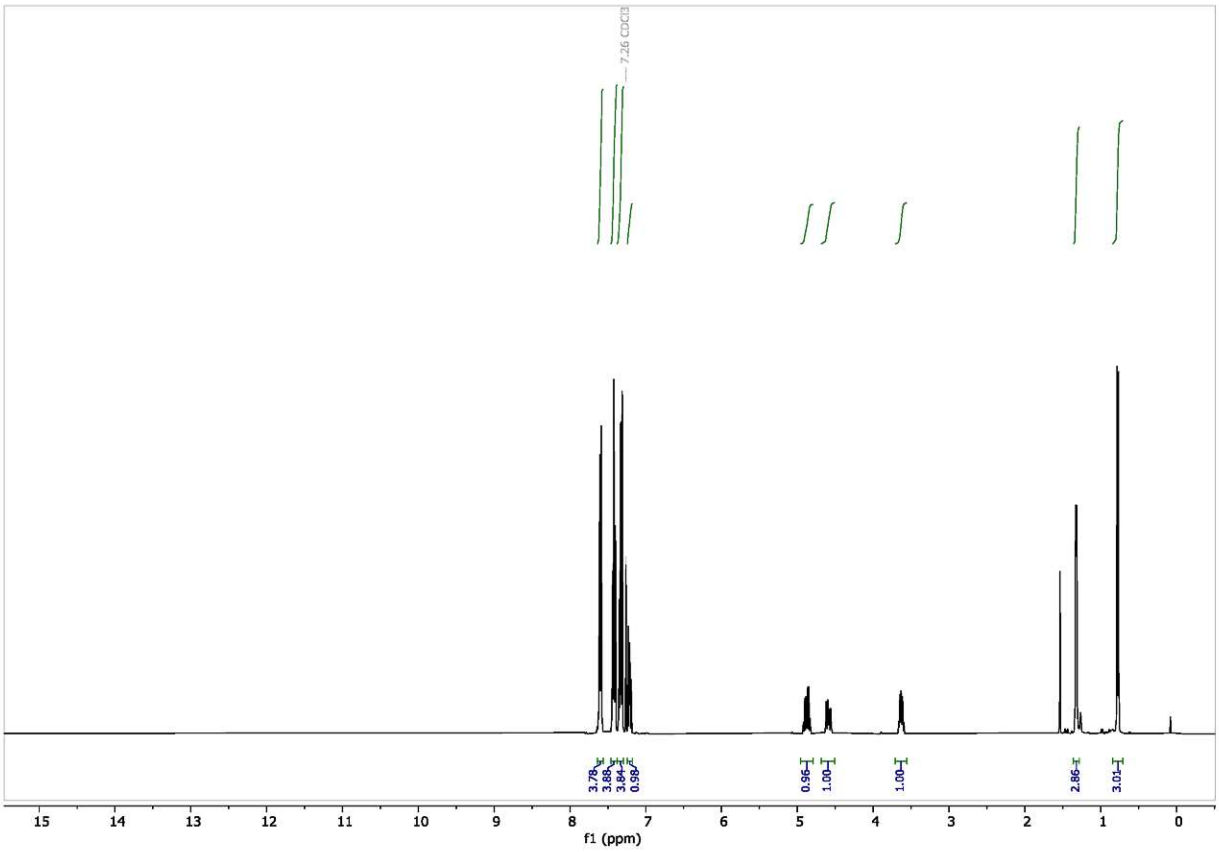


^{13}C NMR (101 MHz, $CDCl_3$)

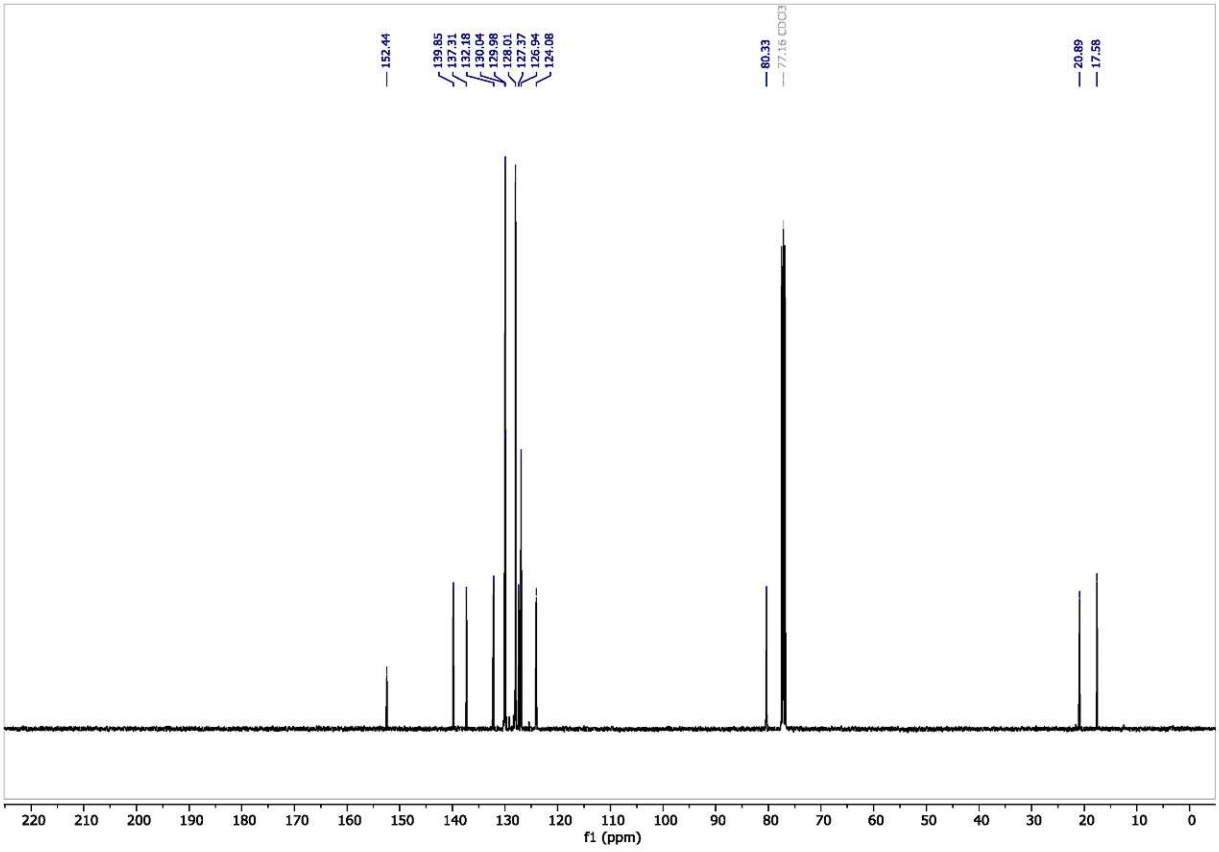


(E)-2'-(pent-3-en-2-yloxy)-1,1':3',1''-terphenyl (127)

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

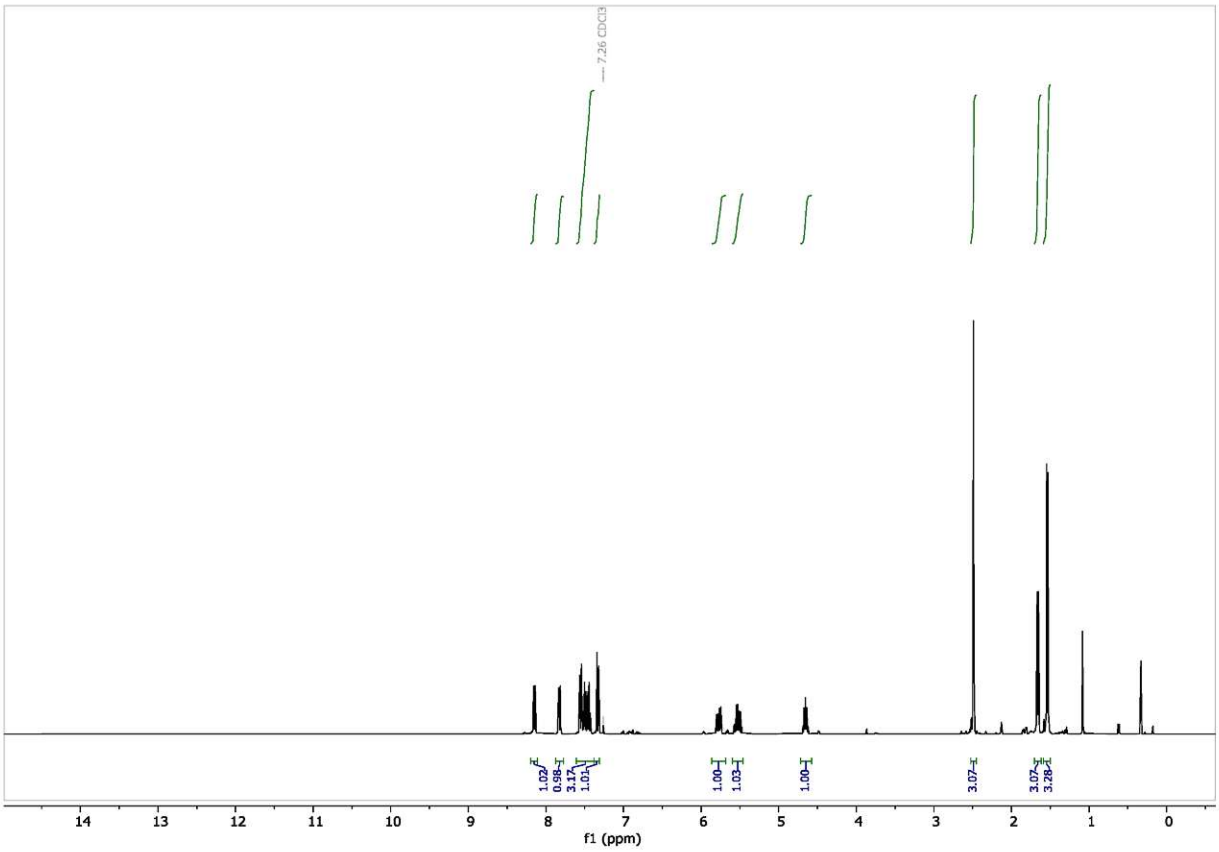


^{13}C NMR (101 MHz, $CDCl_3$)

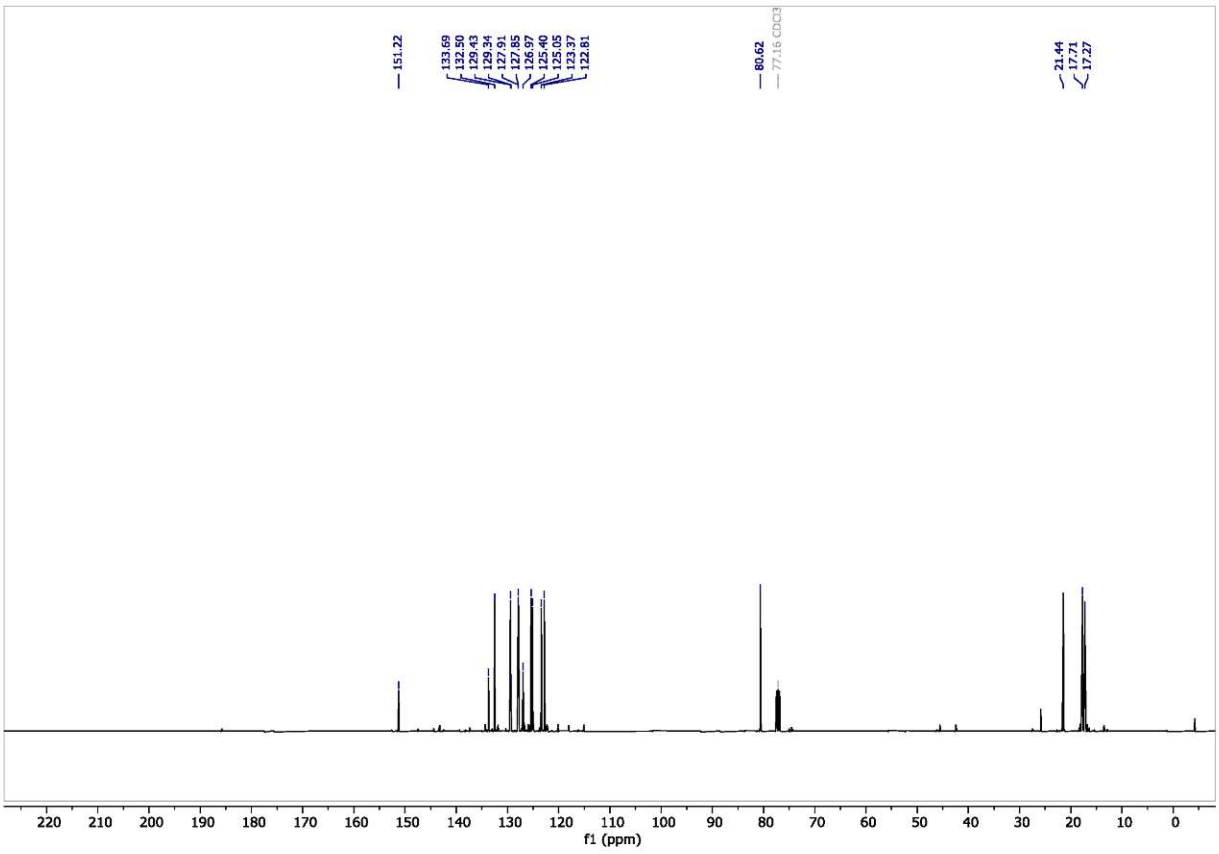


(E)-2-methyl-1-(pent-3-en-2-yloxy)naphthalene (128)

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

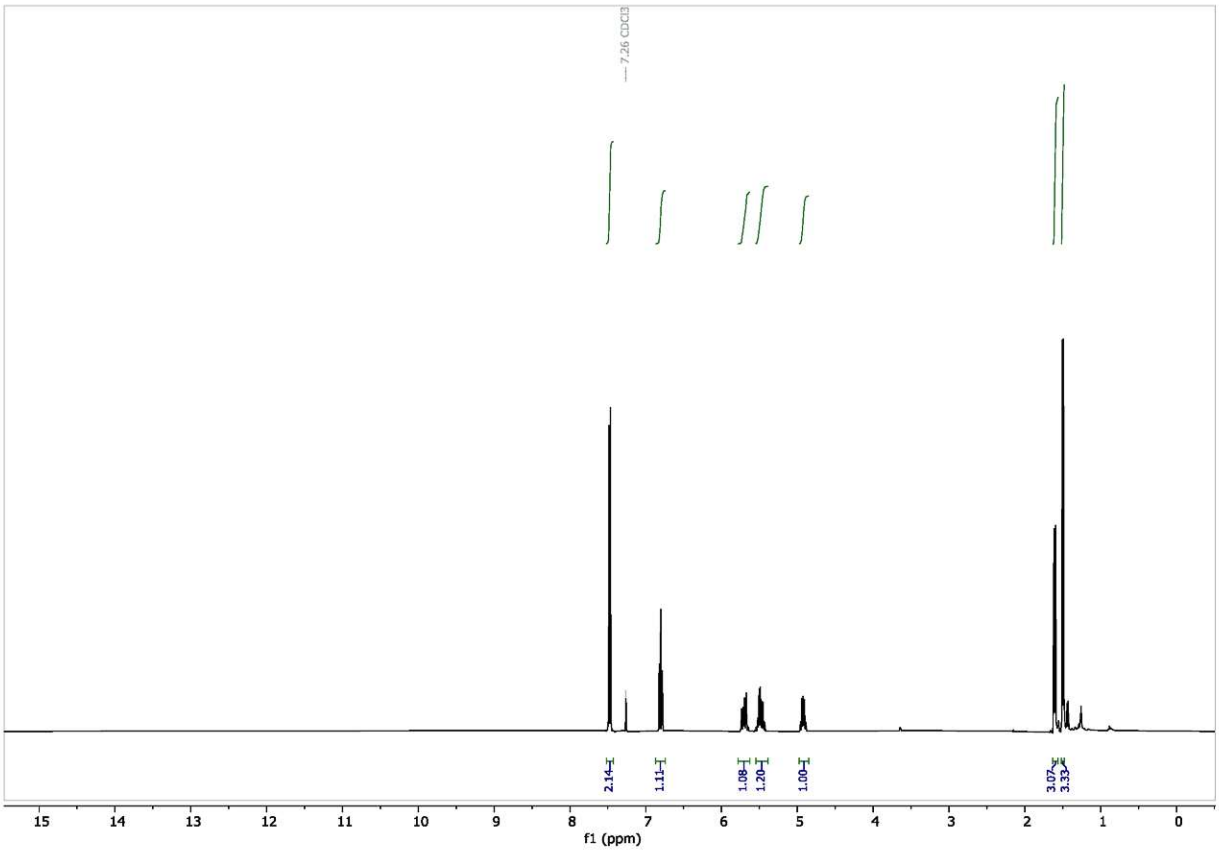


^{13}C NMR (101 MHz, $CDCl_3$)

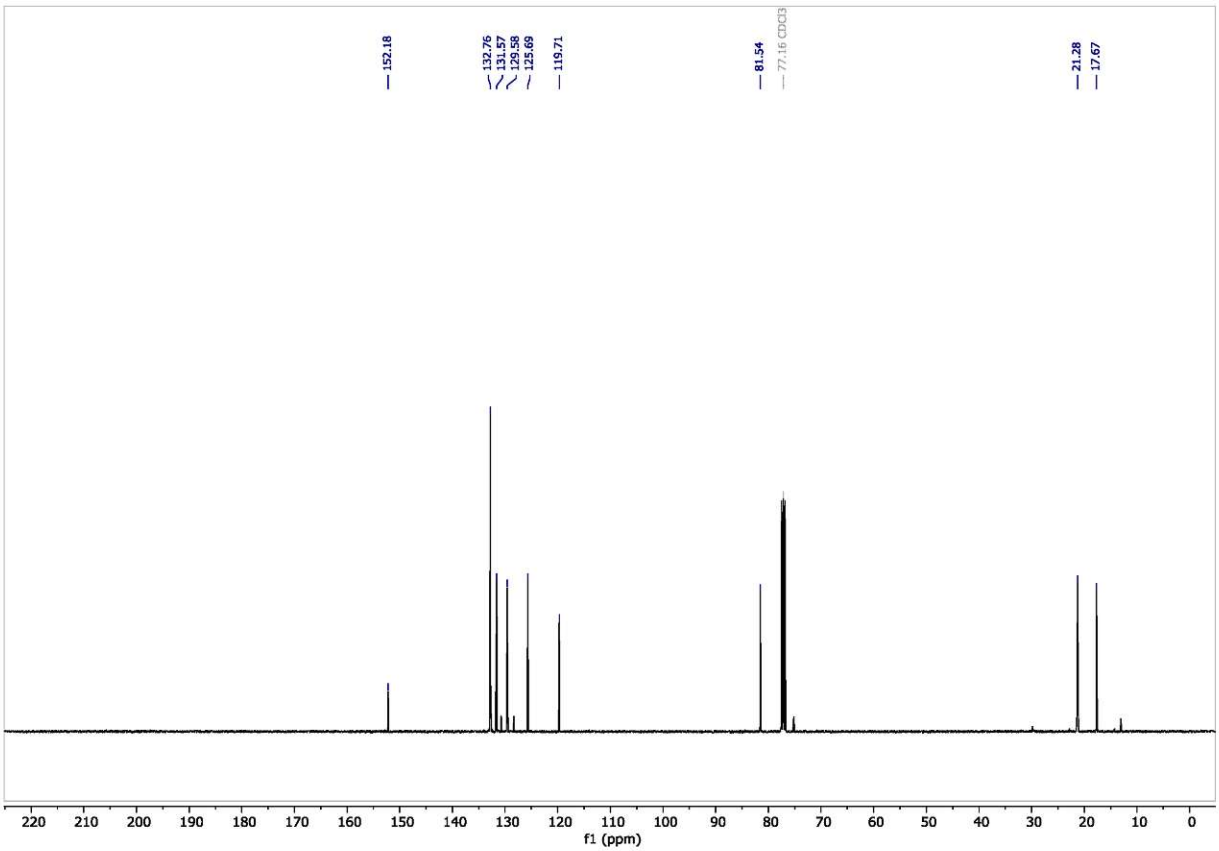


(E)-1,3-dibromo-2-(pent-3-en-2-yloxy)benzene (129)

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

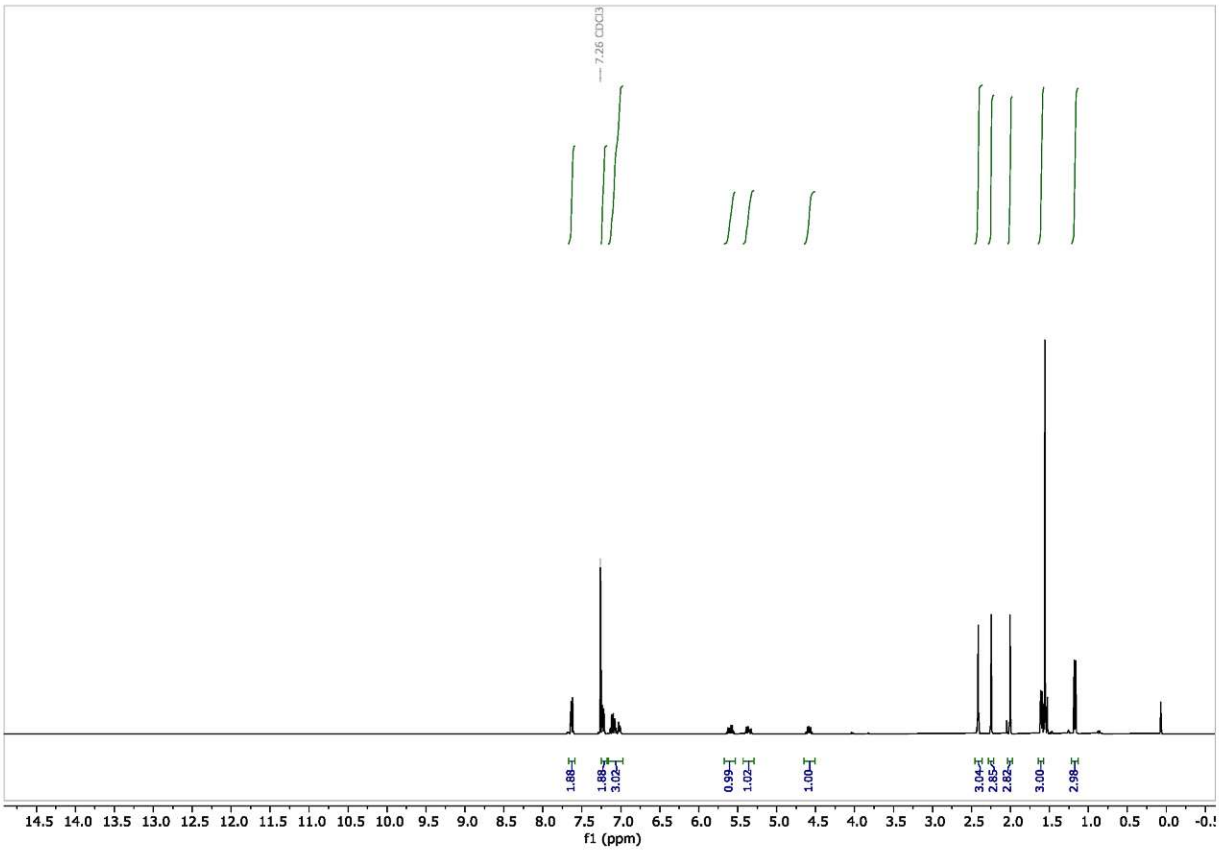


^{13}C NMR (101 MHz, $CDCl_3$)

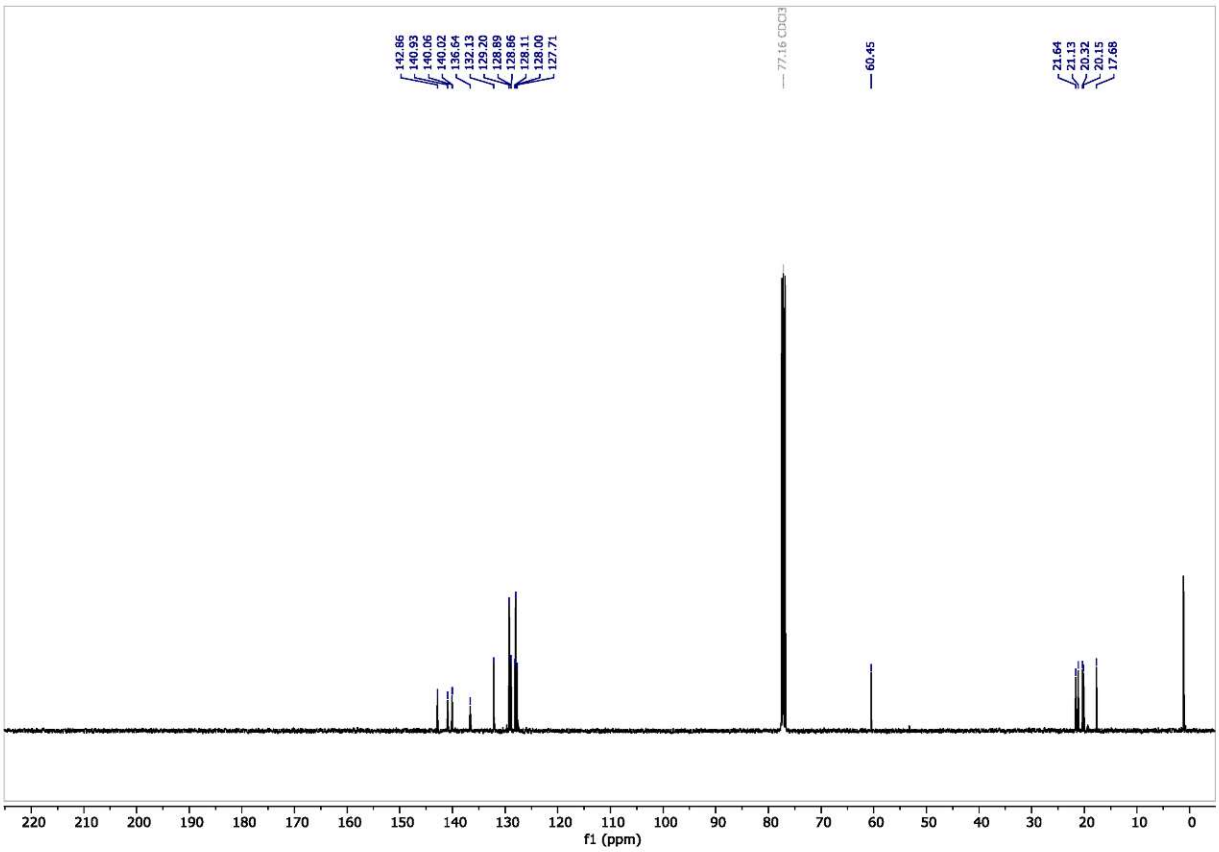


(E)-N-(2,6-dimethylphenyl)-4-methyl-N-(pent-3-en-2-yl)benzenesulfonamide (130)

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

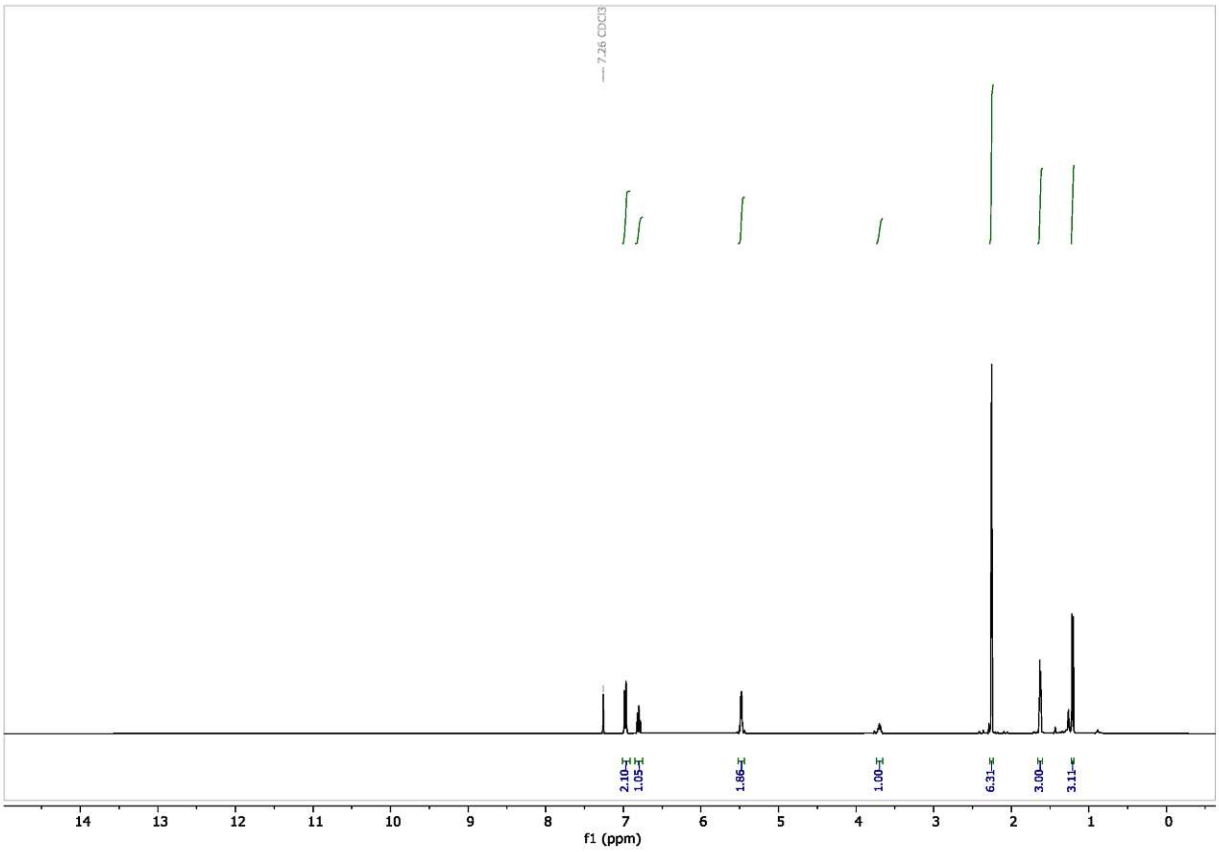


^{13}C NMR (101 MHz, $CDCl_3$)

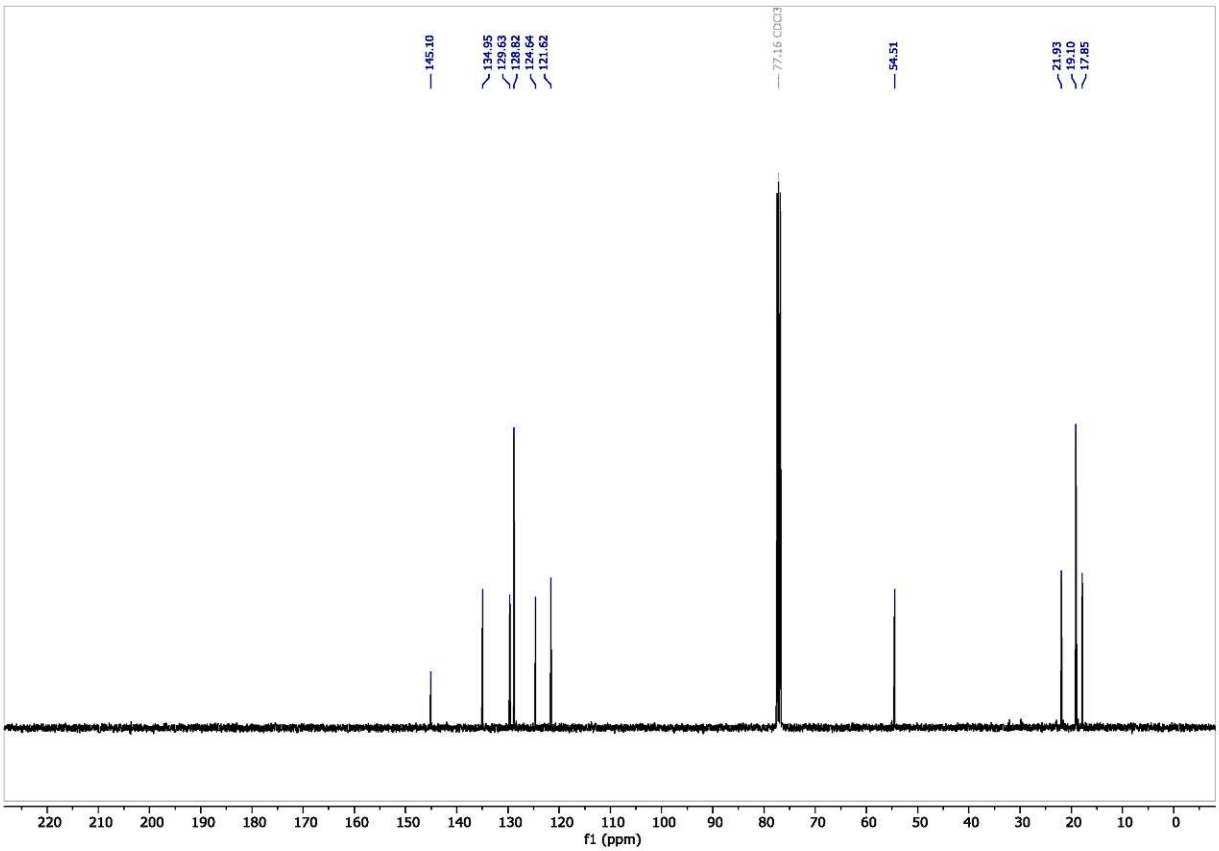


(E)-2,6-dimethyl-N-(pent-3-en-2-yl)aniline (131)

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



^{13}C NMR (101 MHz, $CDCl_3$)



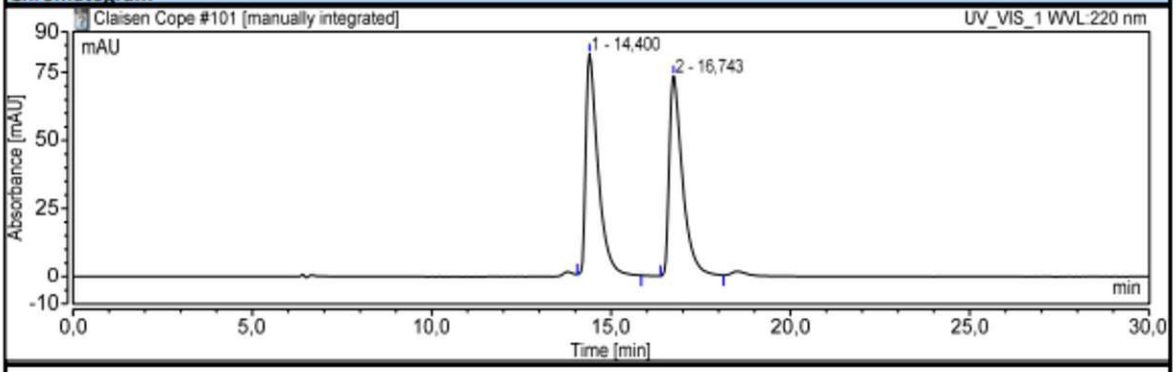
HPLC

***(E)*-1,3-dimethyl-2-(pent-3-en-2-yloxy)benzene (77rac)**

Chromatogram and Results

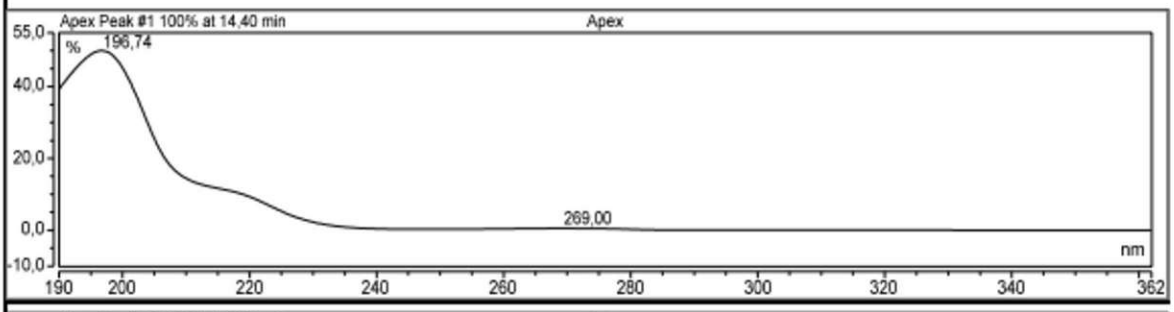
Instrument Method:	**Heptane_IPA_99.9_0.1_0.5mlmin_25C_30min-MK**	*B %:*	**0,1**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

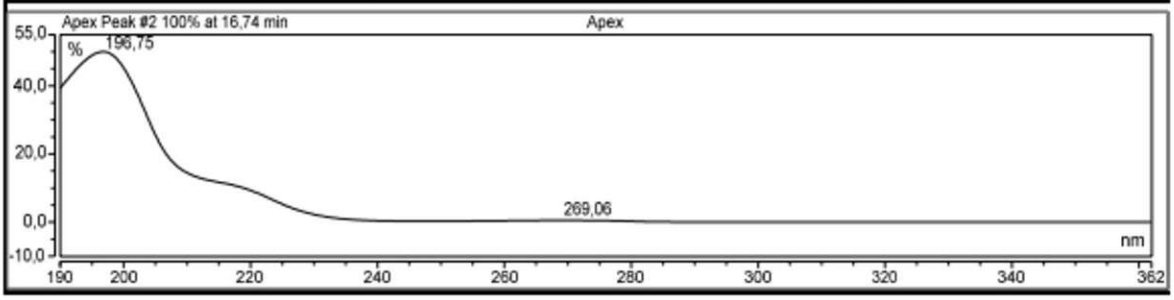
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14,400	32,130	81,485	50,69	52,61
2		16,743	31,254	73,385	49,31	47,39
Total:			**63,384**	**154,870**	**100,00**	**100,00**



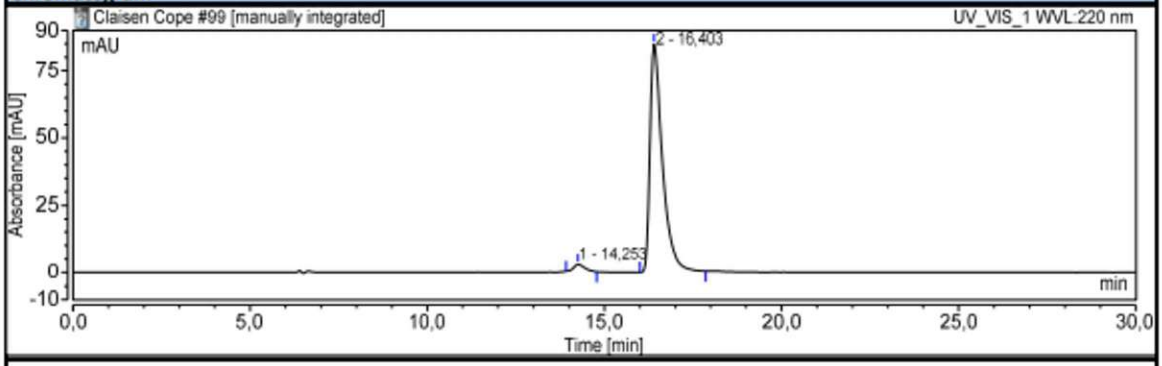


(R,E)-1,3-dimethyl-2-(pent-3-en-2-yloxy)benzene (77)

Chromatogram and Results

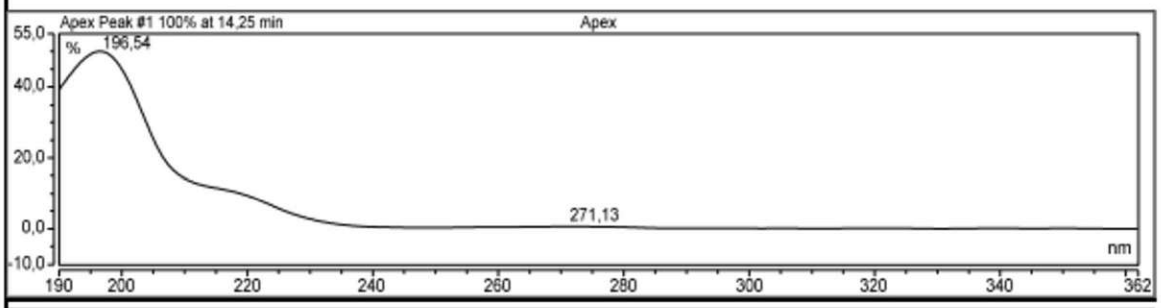
Instrument Method:	**Heptane_IPA_99.9_0.1_0.5mlmin_25C_30min-MK**	*B %:*	**0,1**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

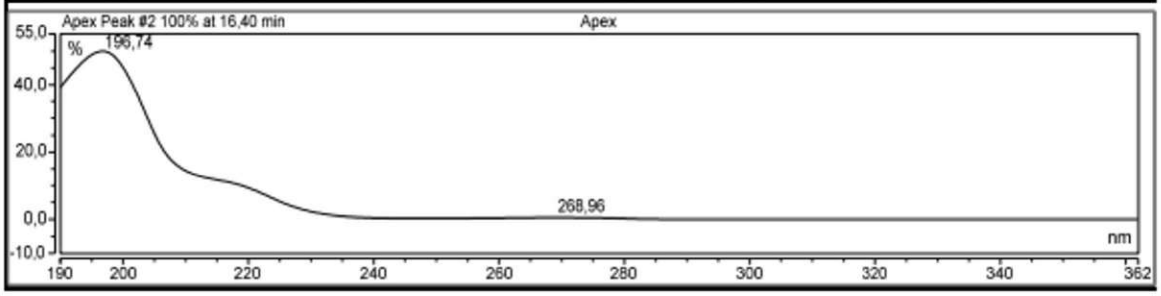
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14,253	0,941	2,656	2,66	3,04
2		16,403	34,482	84,730	97,34	96,96
Total:			**35,422**	**87,386**	**100,00**	**100,00**



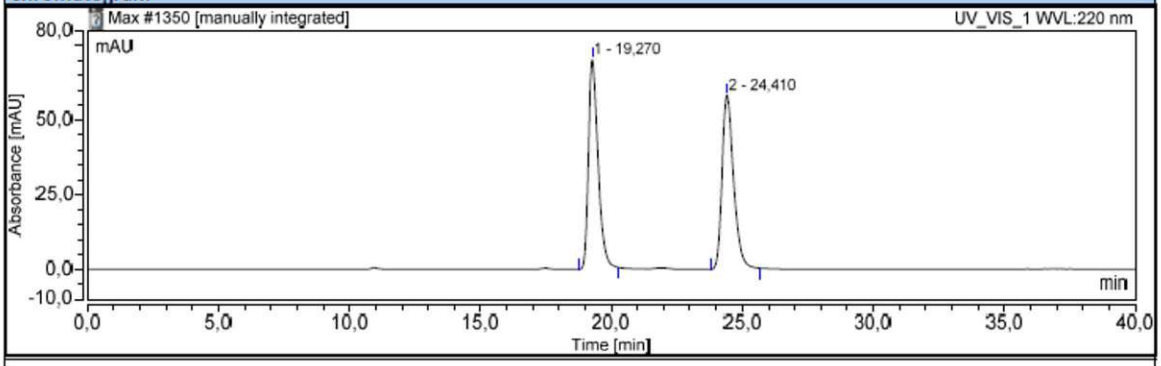


1,3-dimethyl-2-(pentan-2-yloxy)benzene (140rac)

Chromatogram and Results

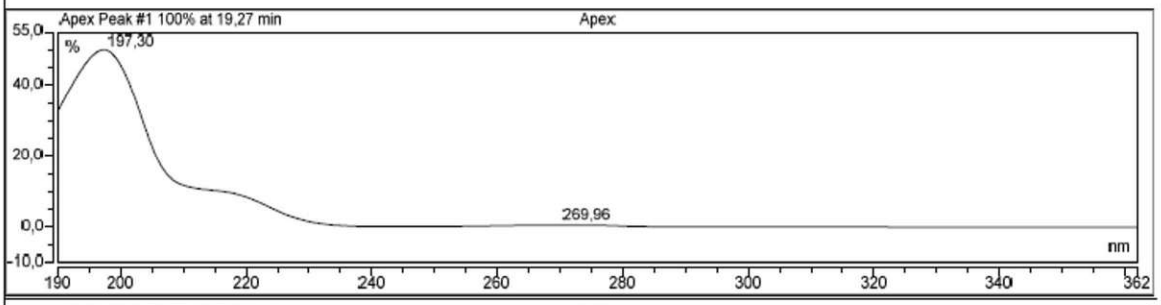
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_40min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	40,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

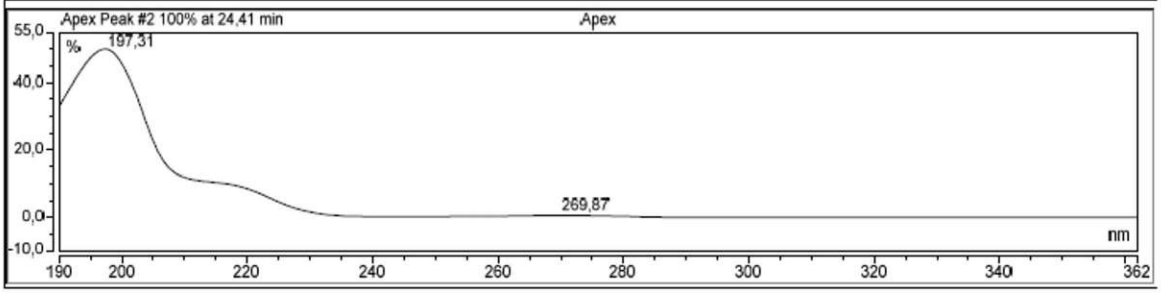
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		19,270	29,625	70,232	49,87	54,62
2		24,410	29,785	58,360	50,13	45,38
Total:			**59,410**	**128,593**	**100,00**	**100,00**



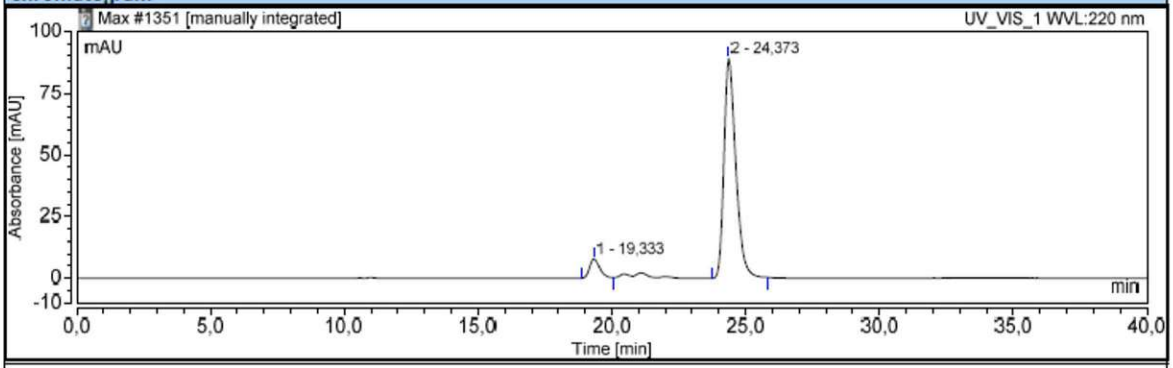


(R)-1,3-dimethyl-2-(pentan-2-yloxy)benzene (140h)

Chromatogram and Results

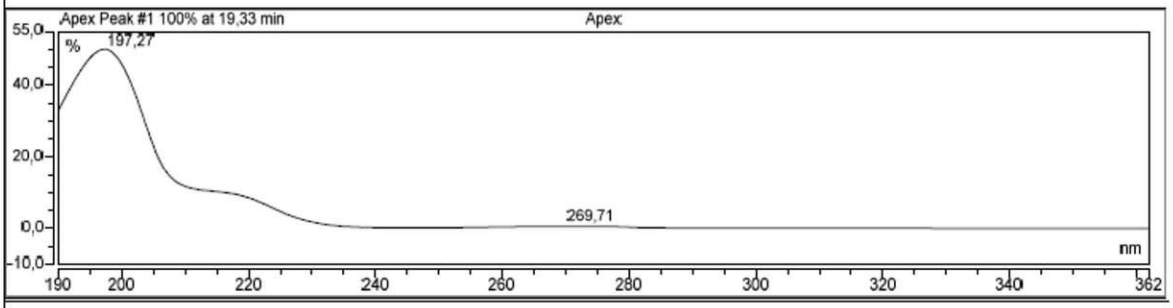
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_40min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	40,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

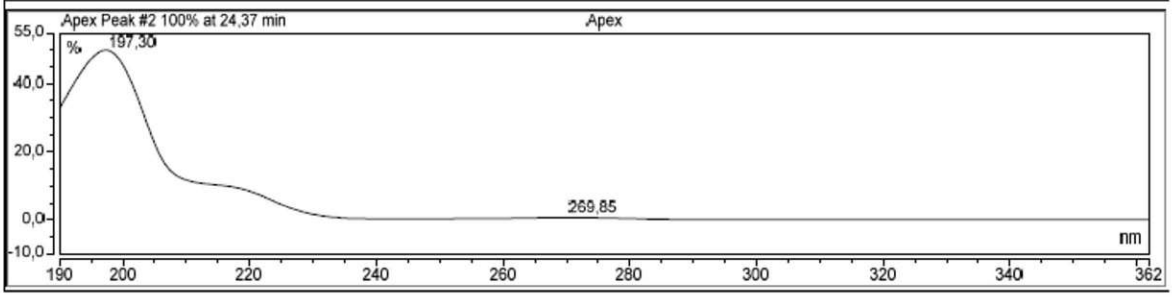
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		19,333	3,516	8,094	7,16	8,33
2		24,373	45,578	89,092	92,84	91,67
Total:			**49,094**	**97,186**	**100,00**	**100,00**



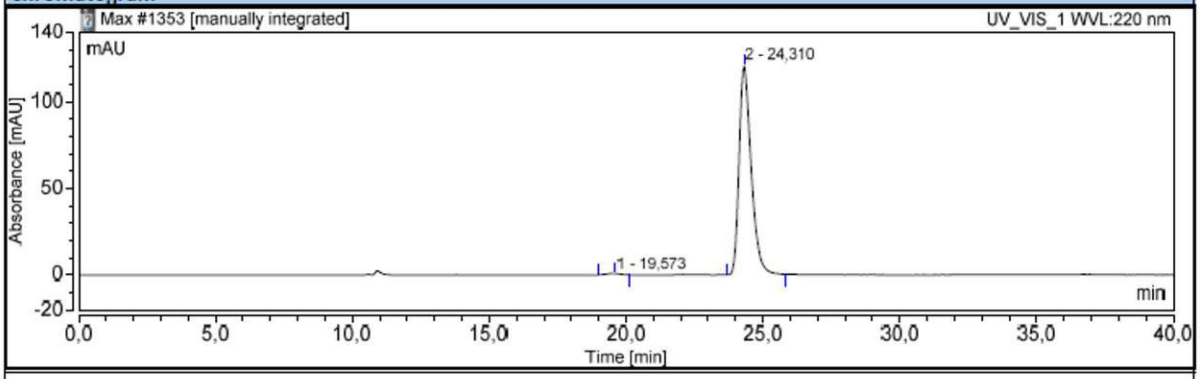


(R)-1,3-dimethyl-2-(pentan-2-yloxy)benzene (140m)

Chromatogram and Results

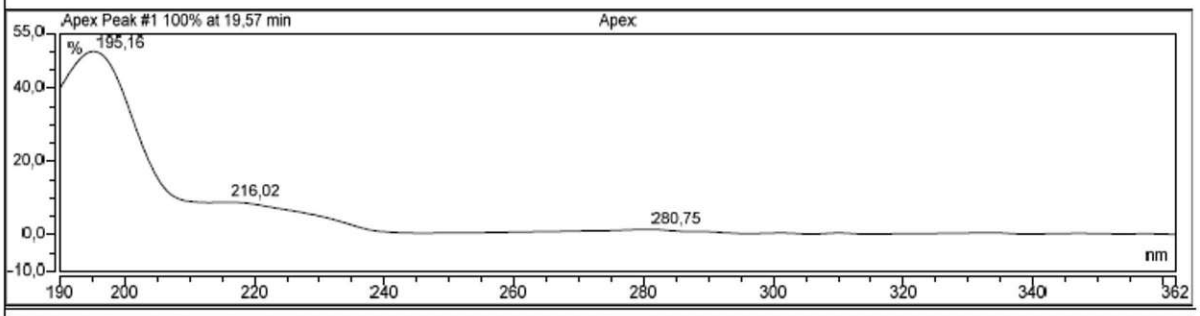
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_40min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	40,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

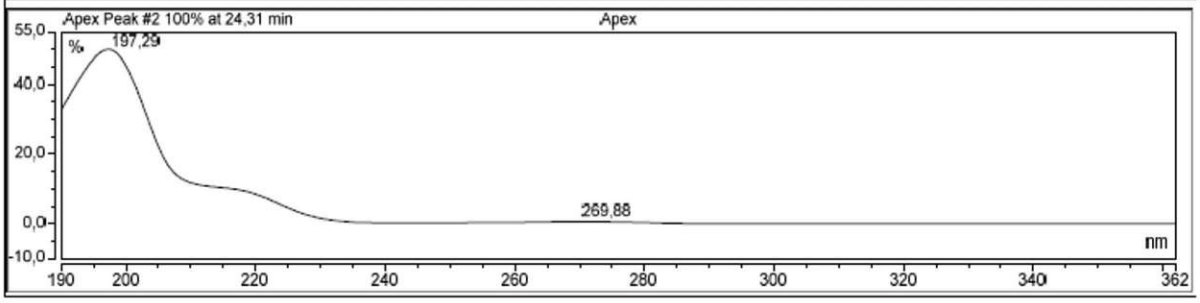
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		19,573	0,468	0,793	0,75	0,65
2		24,310	61,753	120,820	99,25	99,35
Total:			**62,221**	**121,613**	**100,00**	**100,00**



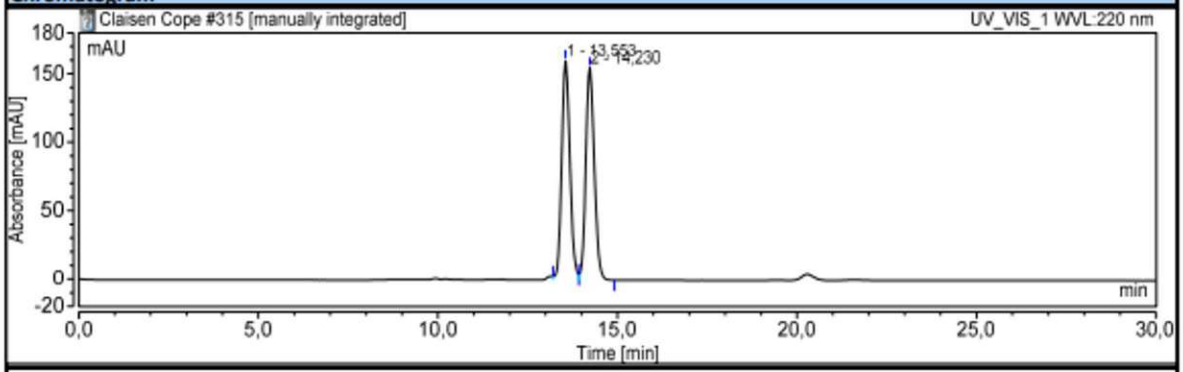


(E)-1,3-diethyl-2-(pent-3-en-2-yloxy)benzene (88rac)

Chromatogram and Results

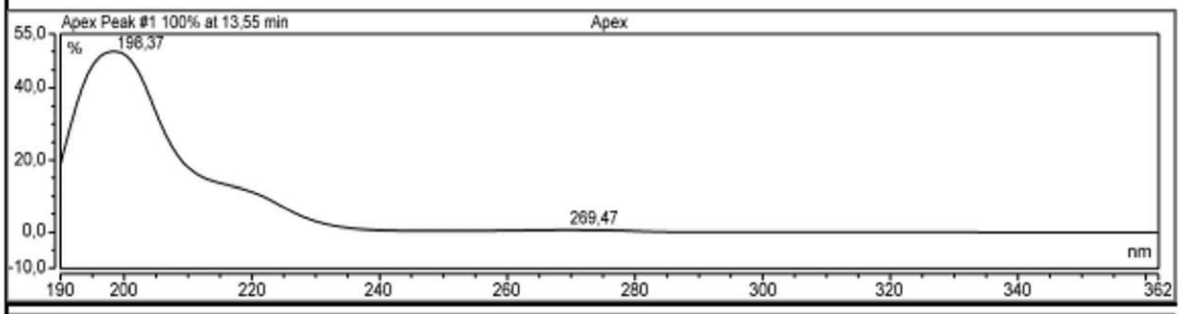
Instrument Method:	**Heptane_EtOH_99.9_0.1_0.3mlmin_25C_30min**	*B %:*	**0,0**
Column:	**OD**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**0,1**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

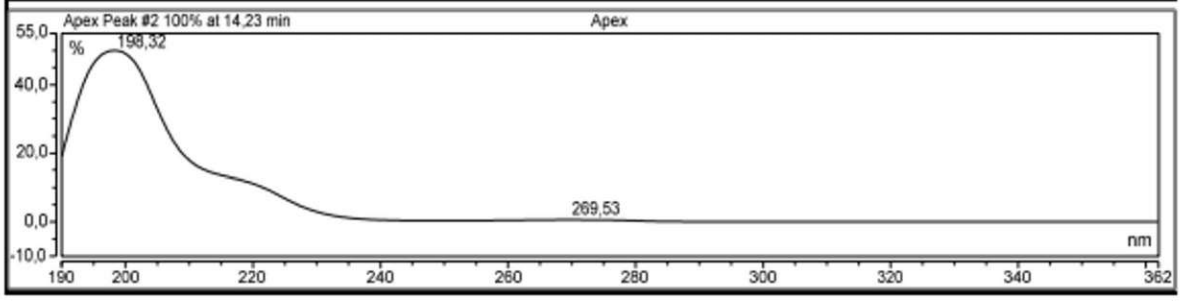
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		13,553	42,079	160,226	49,72	50,82
2		14,230	42,545	155,064	50,28	49,18
Total:			**84,624**	**315,290**	**100,00**	**100,00**



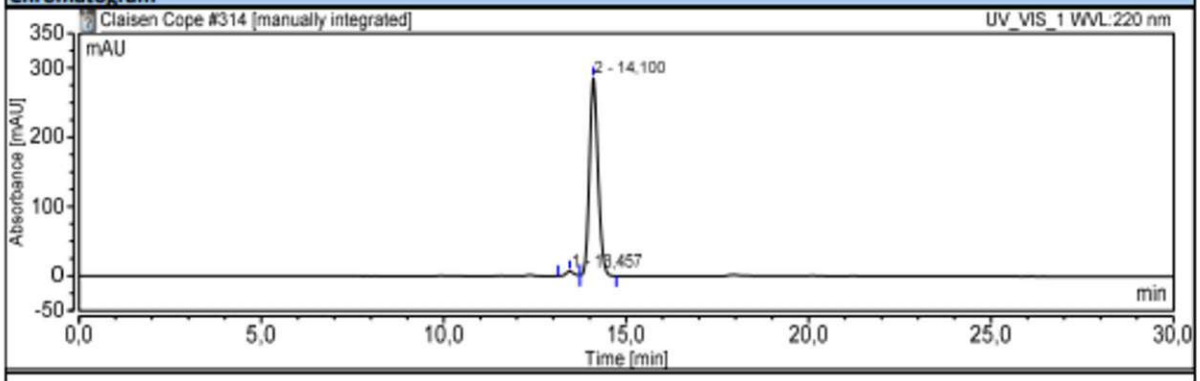


(R,E)-1,3-diethyl-2-(pent-3-en-2-yloxy)benzene (88)

Chromatogram and Results

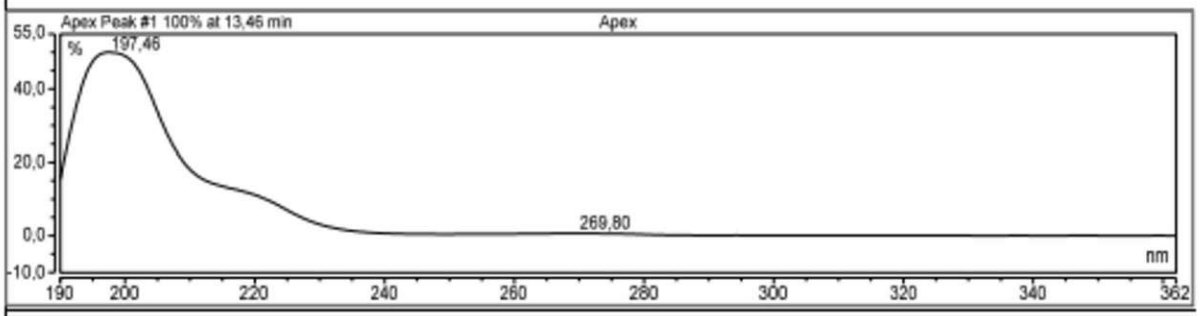
Instrument Method:	**Heptane_EtOH_99.9_0.1_0.3mlmin_25C_30min**	*B %:*	**0,0**
Column:	**OD**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**0,1**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

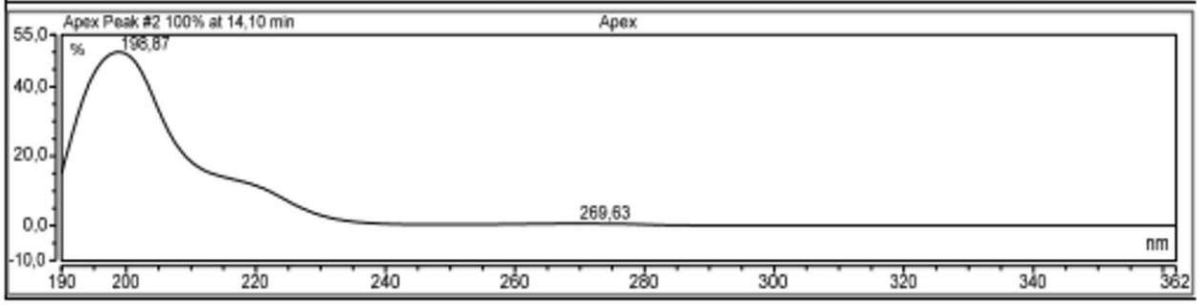
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		13,457	1,737	6,692	2,17	2,29
2		14,100	78,269	286,045	97,83	97,71
Total:			**80,005**	**292,737**	**100,00**	**100,00**



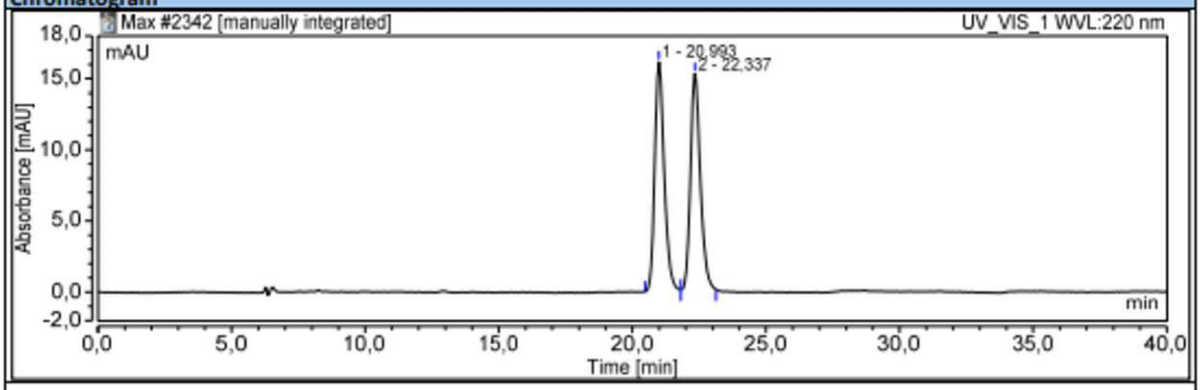


2-(2,6-diisopropylphenoxy)propan-1-ol (146rac)

Chromatogram and Results

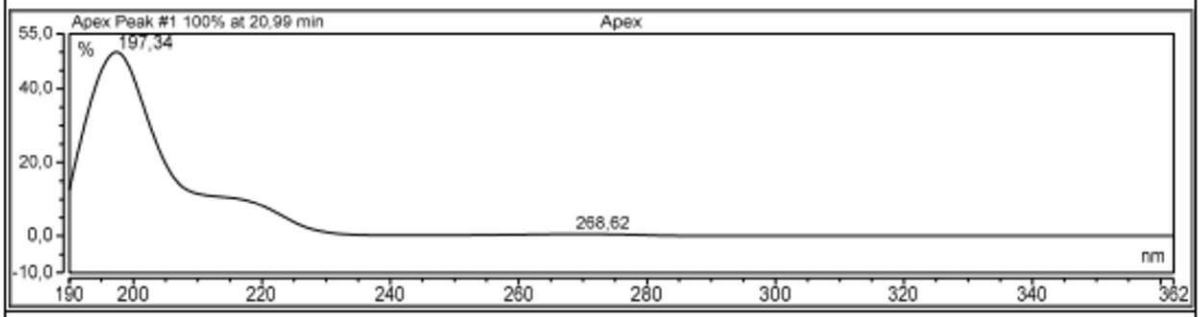
Injection Name:	**MK2943rac_Hep_EtOH_99.7_0.3_0.5mL/min_25°C_40min_IB**	*Run Time (min):*	**40,00**
Vial Number:	**BA1**	*Report Template:*	**Reports IJD**
Injection Volume:	**0,30**	*Channel:*	**UV_VIS_1**
Column:	**IB**	*Wavelength:*	**287,26**
Instrument Method:	**Heptane_EtOH_99.7_0.3_0.5mlmin_25C_40min**	*B %:*	**0,0**
Processing Method:	**Long alcohol**	*C %:*	**0,0**
Injection Date/Time:	**28.Mai.24 18:57**	*D %:*	**0,3**
Operator:	**Irena Jelenkovic - Didic**		

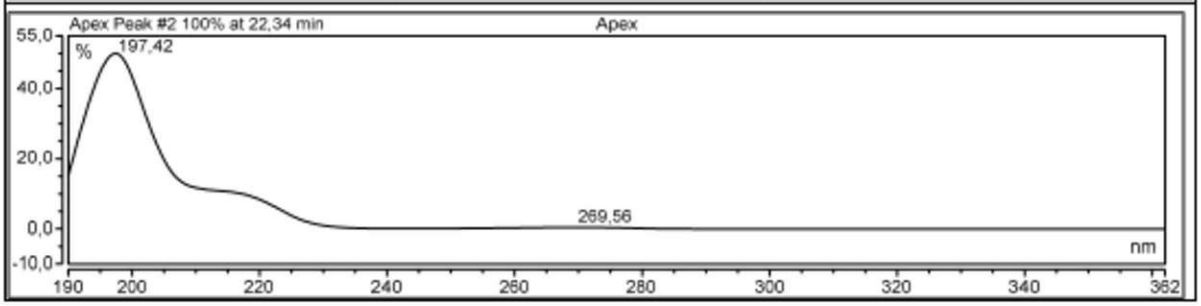
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
n.a.	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		20,993	6,616	16,125	50,31	51,42	n.a.
2		22,337	6,536	15,236	49,69	48,58	n.a.
Total:			**13,152**	**31,361**	**100,00**	**100,00**	



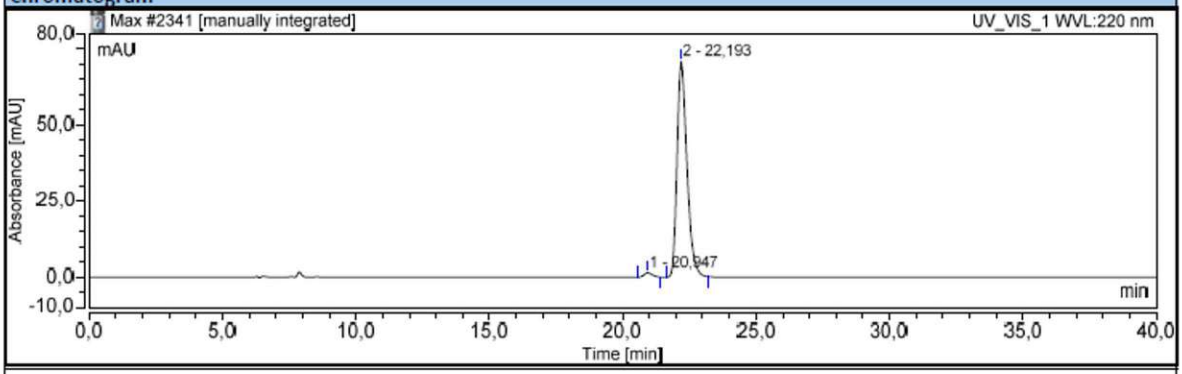


(R)-2-(2,6-diisopropylphenoxy)propan-1-ol (146)

Chromatogram and Results

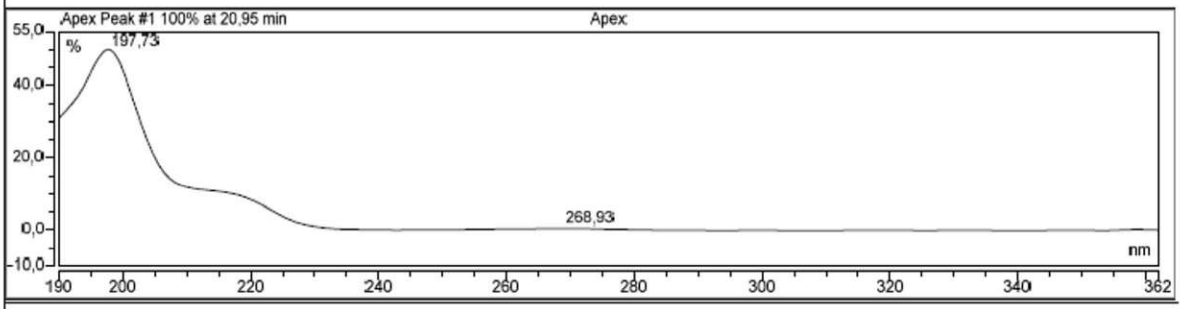
Instrument Method:	Heptane_EtOH_99.7_0.3_0.5mlmin_25C_40min	*B %:*	0,0
Column:	IB	*C %:*	0,0
Run Time (min):	40,00	*D %:*	0,3
Channel:	UV_VIS_1		
Wavelength:	287,26		

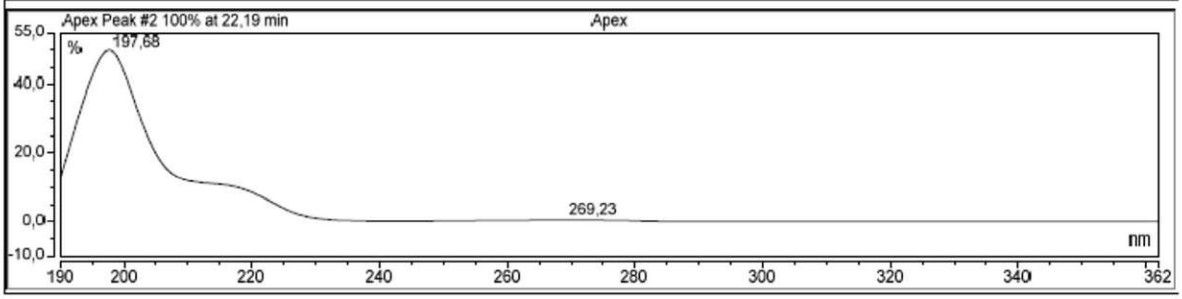
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		20,947	0,529	1,430	1,71	1,97
2		22,193	30,413	71,030	98,29	98,03
Total:			**30,942**	**72,460**	**100,00**	**100,00**



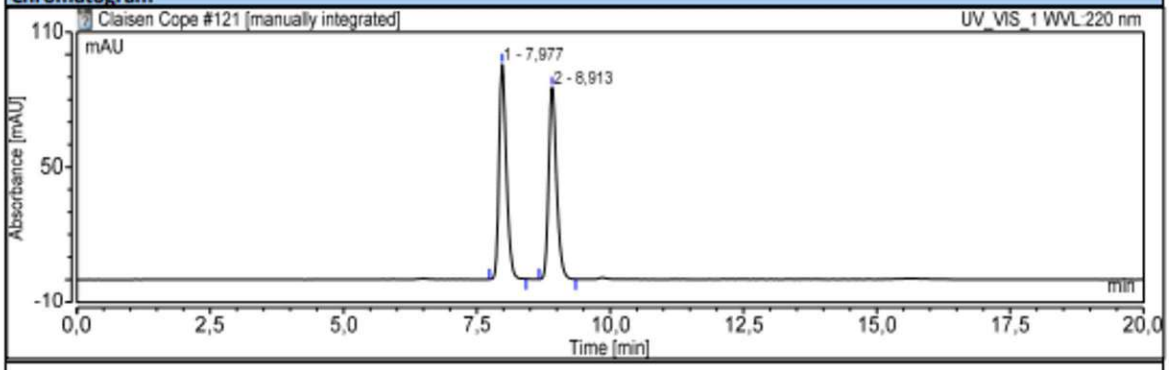


(E)-1,2,4-trimethyl-3-(pent-3-en-2-yloxy)benzene (90rac)

Chromatogram and Results

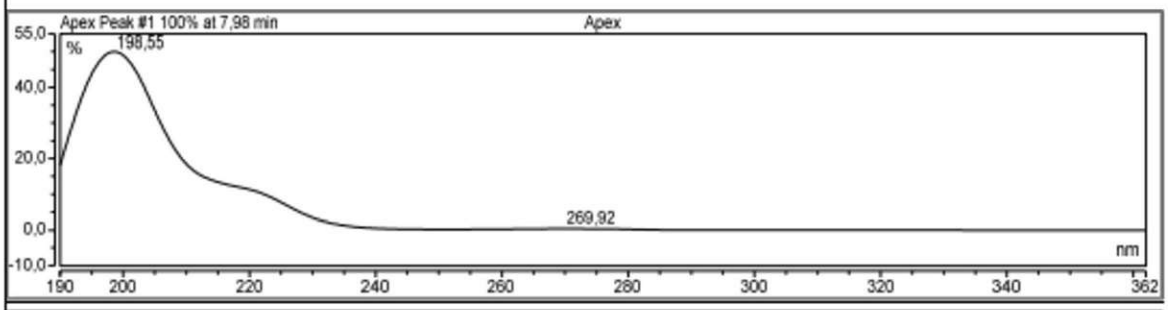
Instrument Method:	**Hexane_EtOH_99.9_0.1_0.5mlmin_25C_20min-MK**	*B %:*	**0,0**
Column:	**IB**	*C %:*	**99,9**
Run Time (min):	**20,00**	*D %:*	**0,1**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

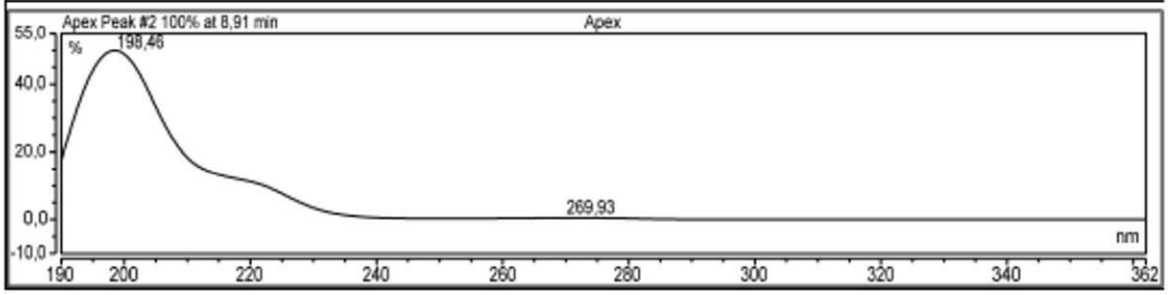
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7,977	15,111	95,459	50,86	52,85
2		8,913	14,600	85,164	49,14	47,15
Total:			**29,711**	**180,624**	**100,00**	**100,00**



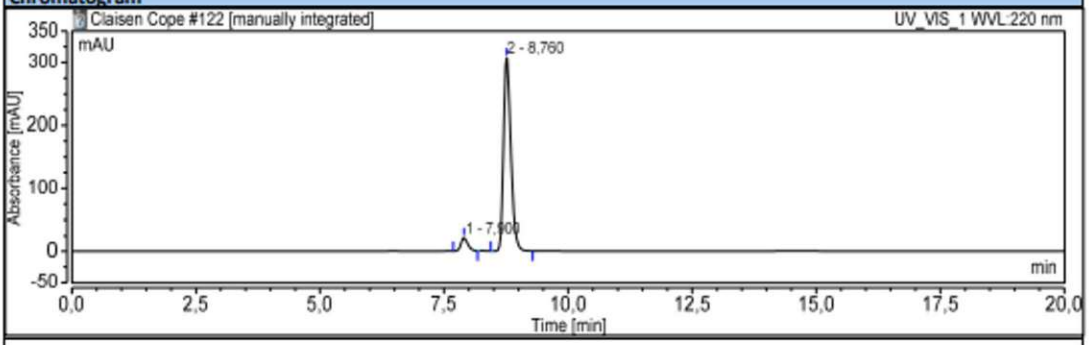


(R,E)-1,2,4-trimethyl-3-(pent-3-en-2-yloxy)benzene (90)

Chromatogram and Results

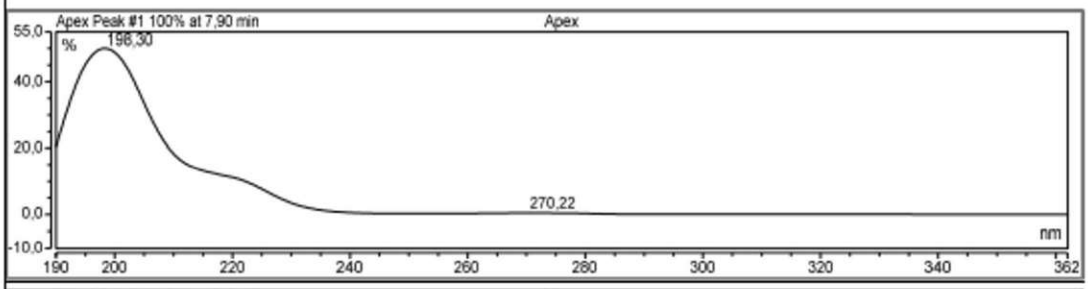
Instrument Method:	**Hexane_EtOH_99.9_0.1_0.5mlmin_25C_20min-MK**	*B %:*	**0,0**
Column:	**IB**	*C %:*	**99,9**
Run Time (min):	**20,00**	*D %:*	**0,1**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

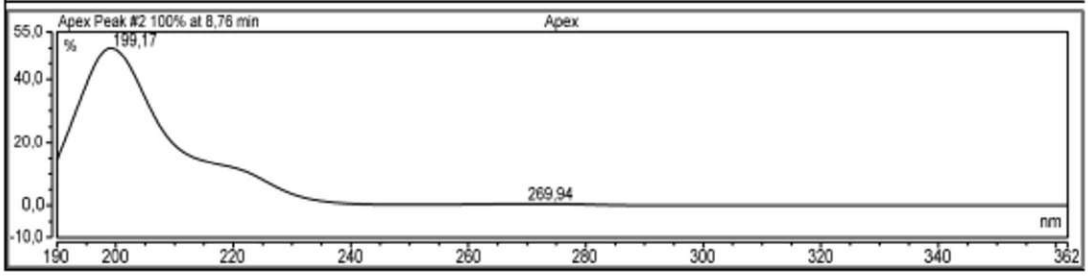
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7,900	3,509	22,164	6,29	6,73
2		8,760	52,323	307,308	93,71	93,27
Total:			**55,832**	**329,472**	**100,00**	**100,00**



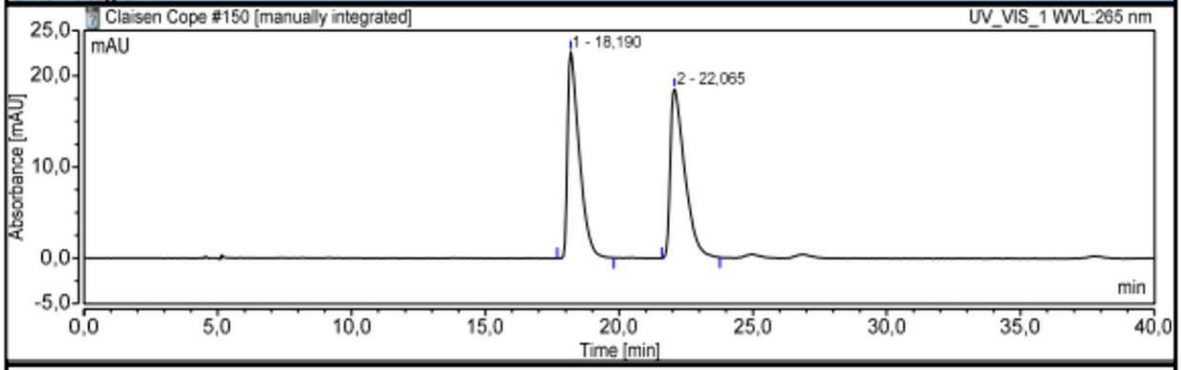


(E)-1,3-dimethoxy-2-(pent-3-en-2-yloxy)benzene (91rac)

Chromatogram and Results

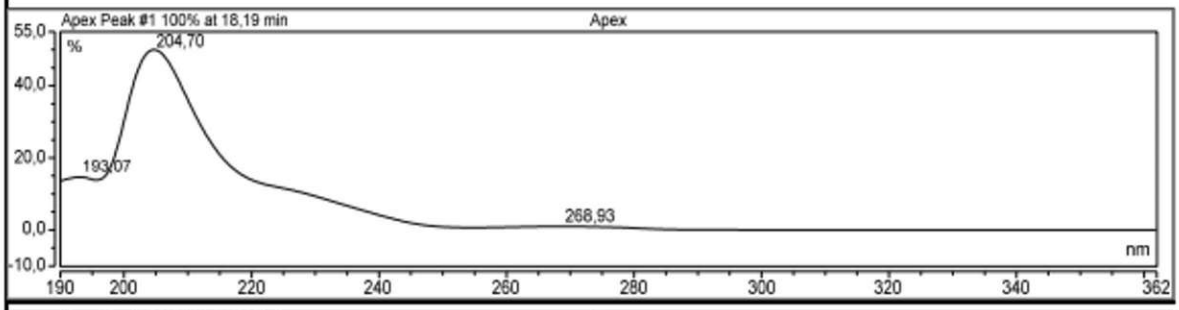
Instrument Method:	**Hexane_IPA_97_3 _0.7mLmin_25C_40min-MK**	*B %:*	**3,0**
Column:	**OJ3**	*C %:*	**97,0**
Run Time (min):	**40,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

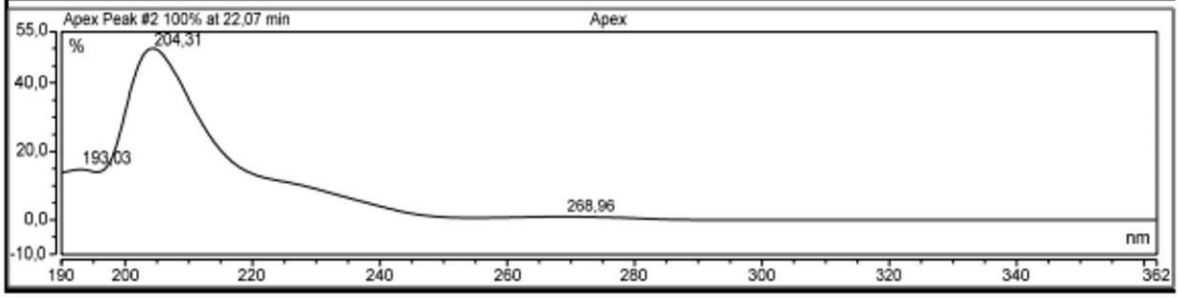
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		18,190	11,485	22,695	49,79	55,03
2		22,065	11,580	18,547	50,21	44,97
Total:			**23,065**	**41,242**	**100,00**	**100,00**



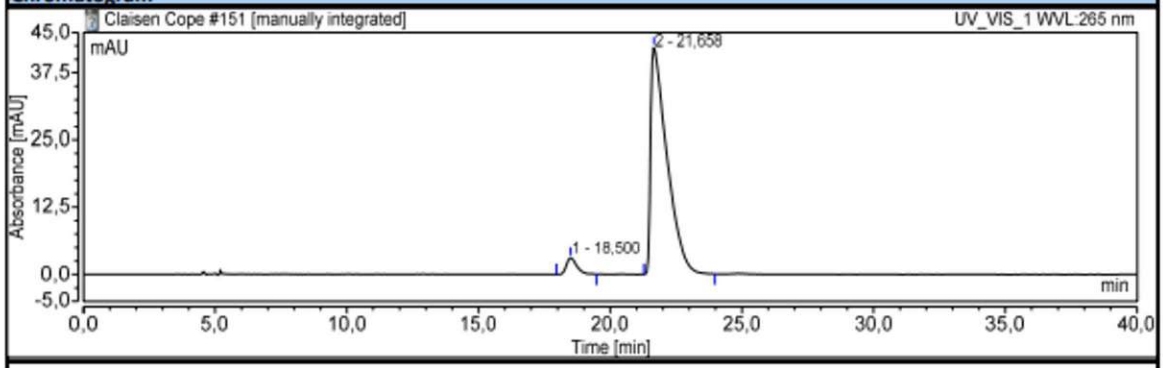


(R,E)-1,3-dimethoxy-2-(pent-3-en-2-yloxy)benzene (91)

Chromatogram and Results

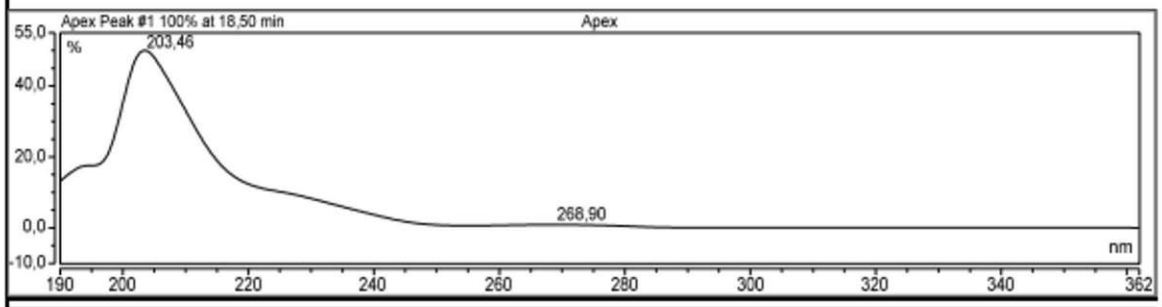
Instrument Method:	**Hexane_IPA_97_3 _0.7mLmin_25C_40min-MK**	*B %:*	**3,0**
Column:	**OJ3**	*C %:*	**97,0**
Run Time (min):	**40,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

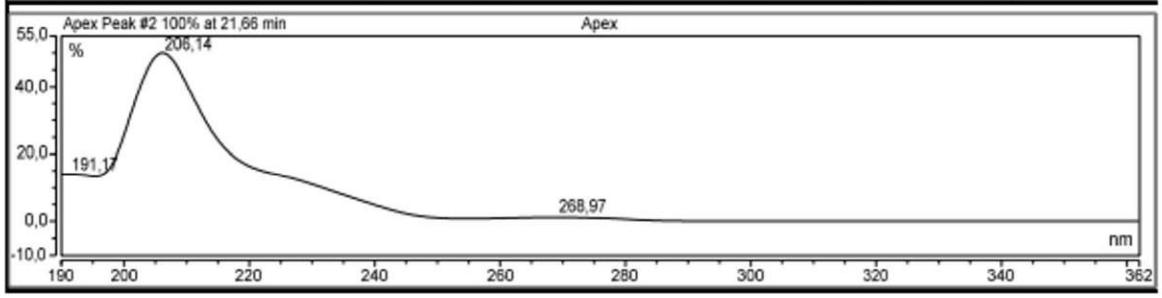
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		18,500	1,384	3,055	4,36	6,75
2		21,658	30,389	42,207	95,64	93,25
Total:			**31,773**	**45,261**	**100,00**	**100,00**



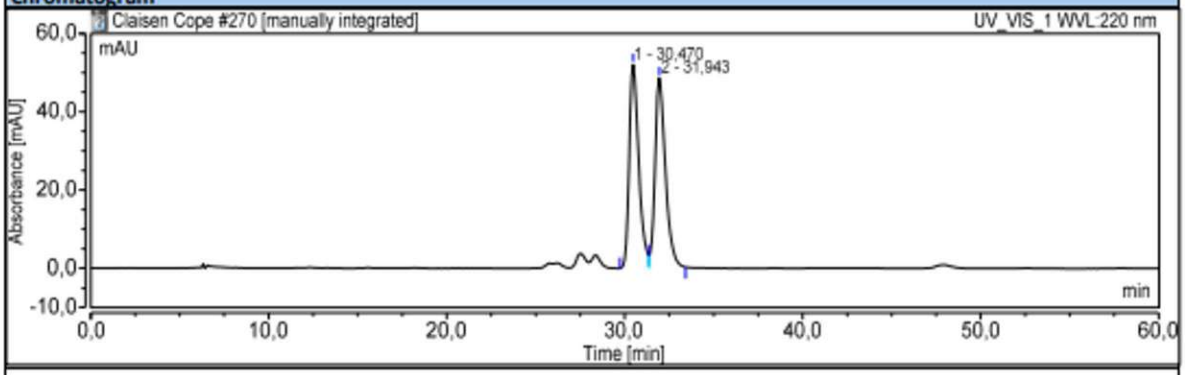


(E)-1-(benzyloxy)-3-methyl-2-(pent-3-en-2-yloxy)benzene (92rac)

Chromatogram and Results

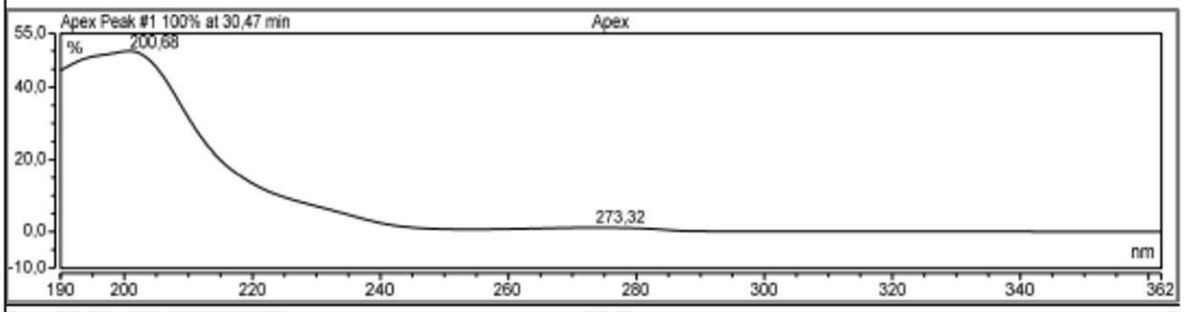
Instrument Method:	**Heptane_EtOH_99.9_0.1_0.5mlmin_25C_60min**	*B %:*	**0,0**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**60,00**	*D %:*	**0,1**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

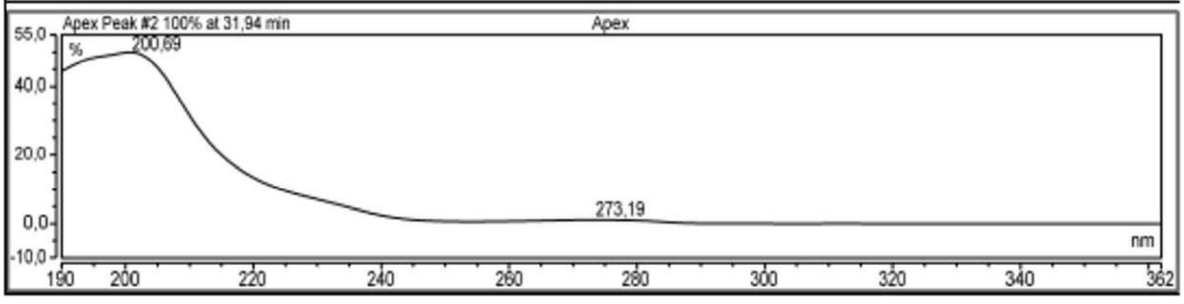
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		30,470	32,150	52,070	49,61	51,75
2		31,943	32,662	48,546	50,39	48,25
Total:			**64,812**	**100,616**	**100,00**	**100,00**



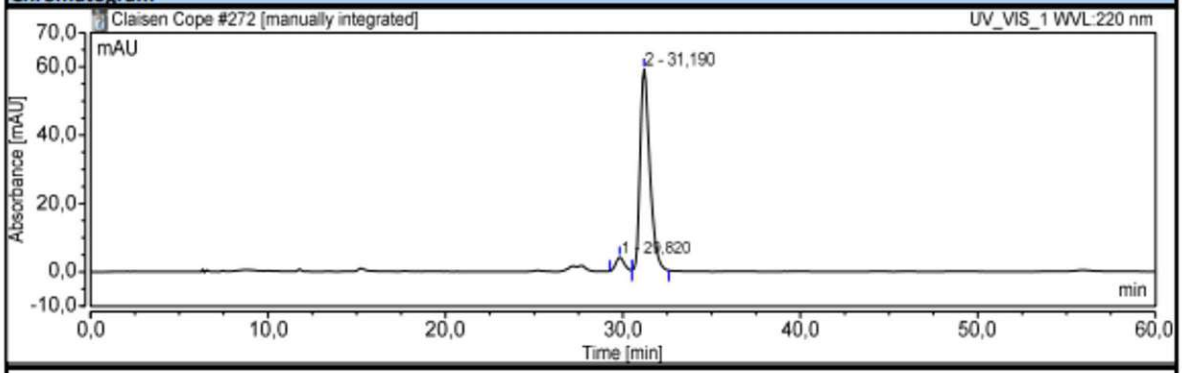


(E)-1-(benzyloxy)-3-methyl-2-(pent-3-en-2-yloxy)benzene (92)

Chromatogram and Results

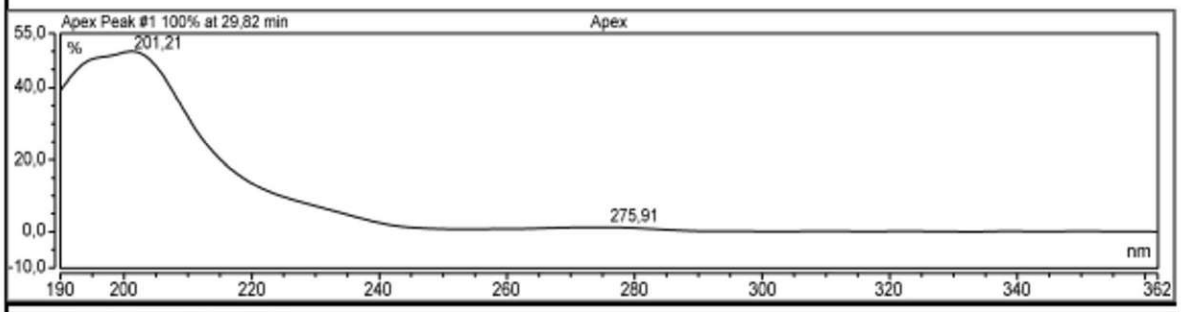
Instrument Method:	**Heptane_EtOH_99.9_0.1_0.5mlmin_25C_60min**	*B %:*	**0,0**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**60,00**	*D %:*	**0,1**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

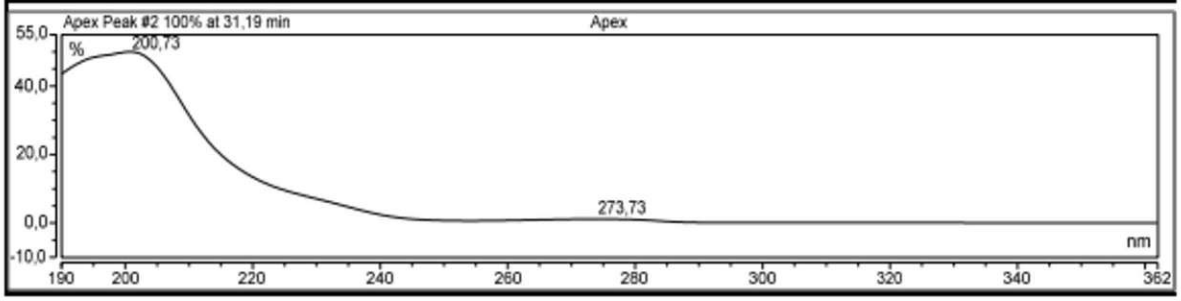
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		29,820	2,193	4,047	5,57	6,42
2		31,190	37,159	59,008	94,43	93,58
Total:			**39,351**	**63,055**	**100,00**	**100,00**



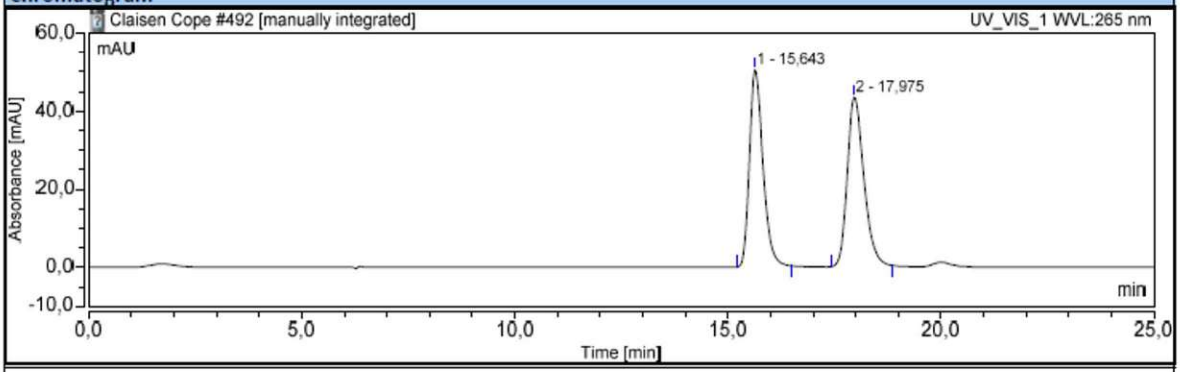


(E)-1-methoxy-2-(pent-3-en-2-yloxy)-3-vinylbenzene (93rac)

Chromatogram and Results

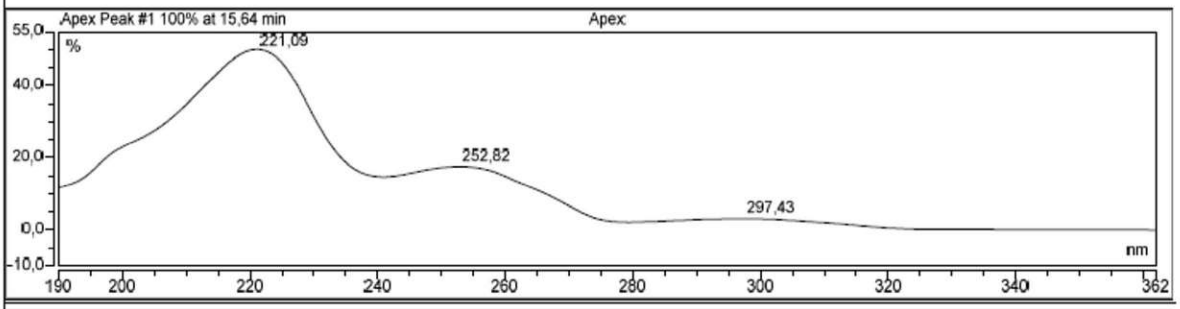
Instrument Method:	Hexane_IPA_99.4_0.6_0.5mLmin_25C_25min-MK	*B %:*	0,6
Column:	OJ3	*C %:*	99,4
Run Time (min):	25,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

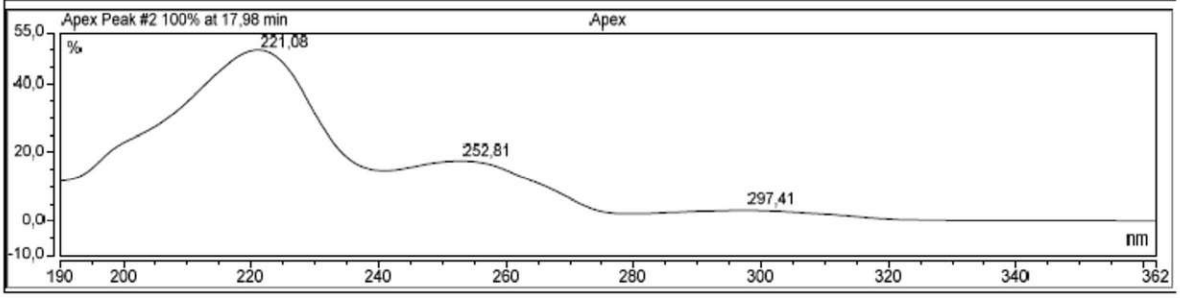
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		15,643	18,497	50,401	48,71	53,75
2		17,975	19,478	43,369	51,29	46,25
Total:			**37,975**	**93,770**	**100,00**	**100,00**



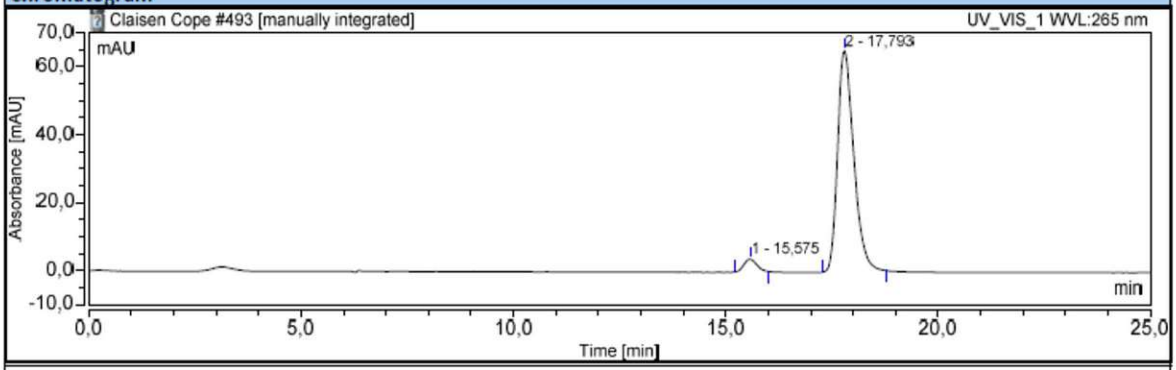


(R,E)-1-methoxy-2-(pent-3-en-2-yloxy)-3-vinylbenzene (93)

Chromatogram and Results

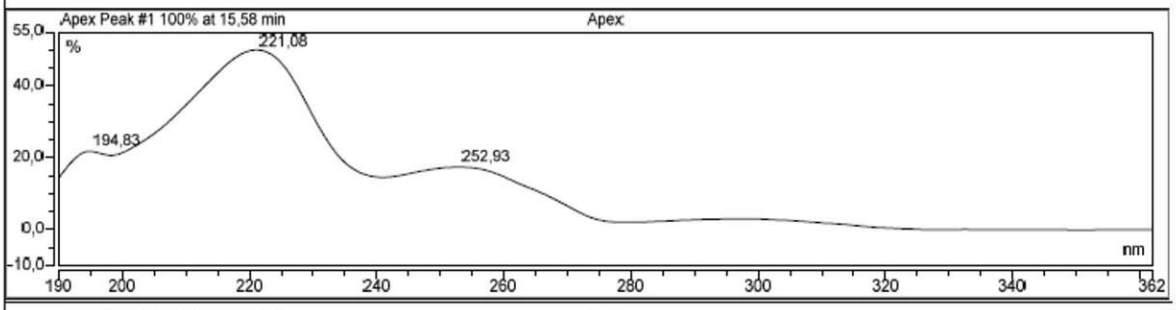
Instrument Method:	Hexane_IPA_99.4_0.6_0.5mLmin_25C_25min-MK	*B %:*	0,6
Column:	OJ3	*C %:*	99,4
Run Time (min):	25,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

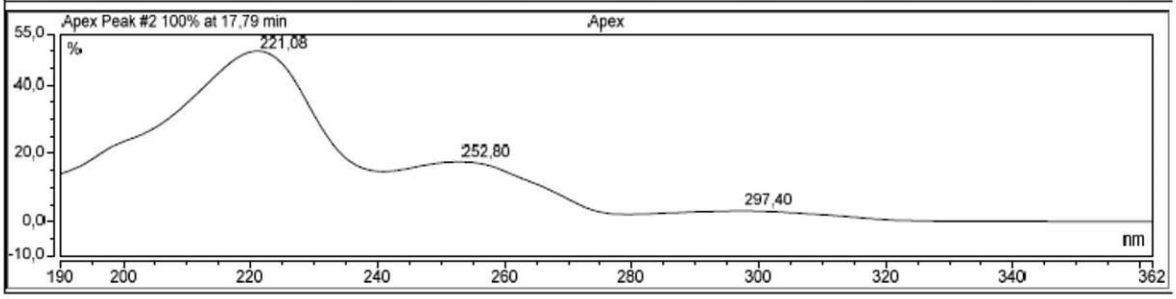
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		15,575	1,298	3,742	4,34	5,44
2		17,793	28,604	65,018	95,66	94,56
Total:			**29,902**	**68,759**	**100,00**	**100,00**



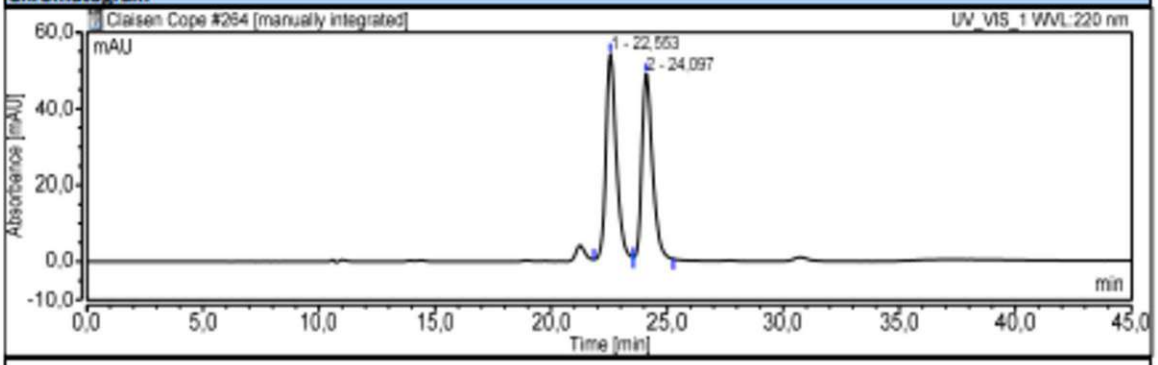


(E)-1-bromo-3-methyl-2-(pent-3-en-2-yloxy)benzene (94rac)

Chromatogram and Results

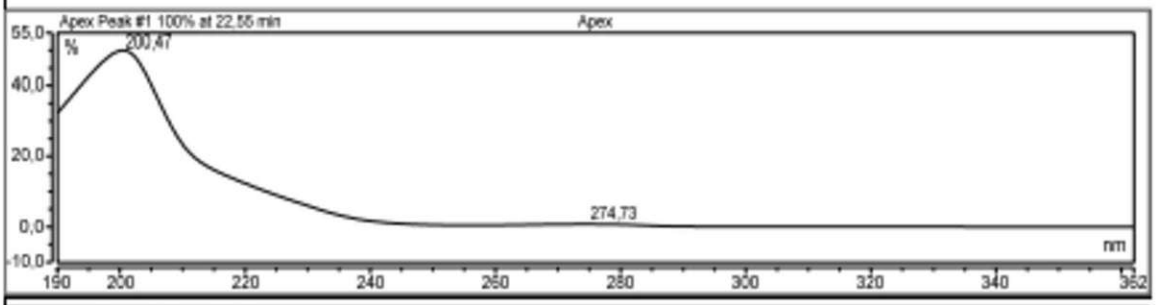
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min-MK	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

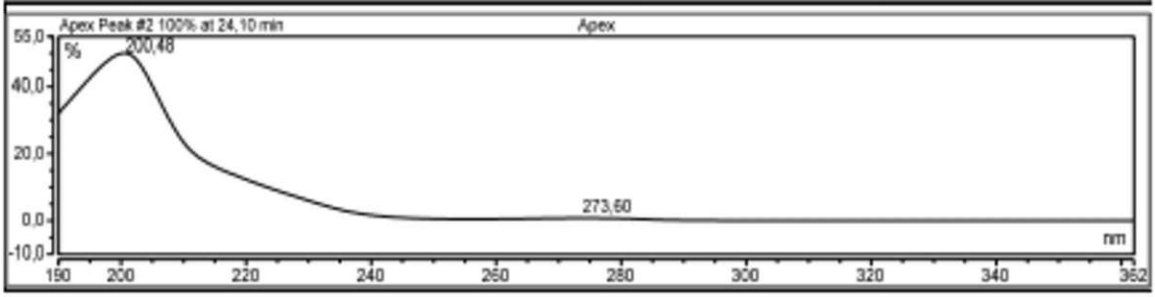
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		22,553	28,050	54,054	52,31	52,68
2		24,097	25,573	48,551	47,69	47,32
Total:			**53,624**	**102,605**	**100,00**	**100,00**



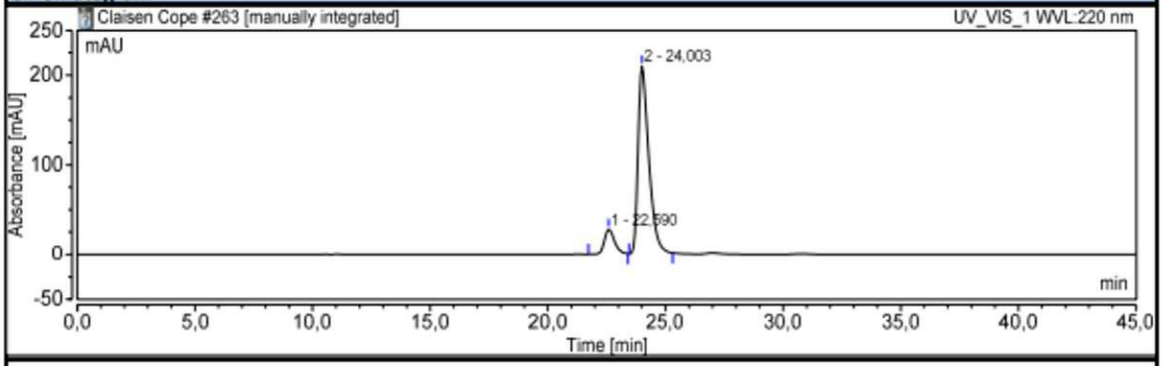


(R,E)-1-bromo-3-methyl-2-(pent-3-en-2-yloxy)benzene (94)

Chromatogram and Results

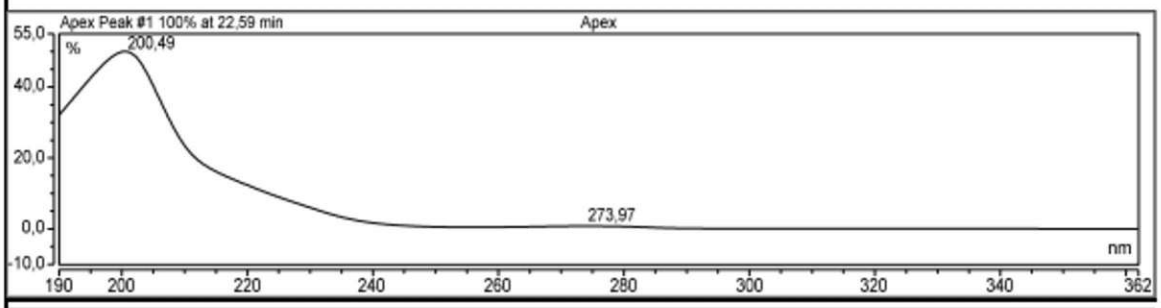
Instrument Method:	**Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min-MK**	*B %:*	**0,1**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**45,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

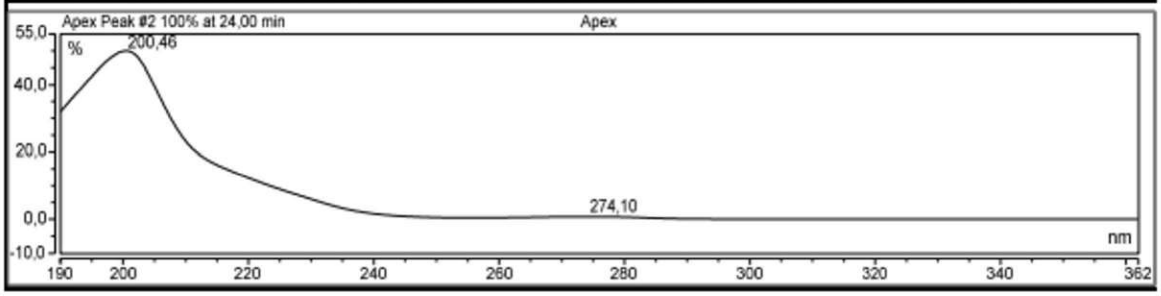
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		22,590	13,458	27,589	10,86	11,64
2		24,003	110,456	209,380	89,14	88,36
Total:			**123,914**	**236,969**	**100,00**	**100,00**



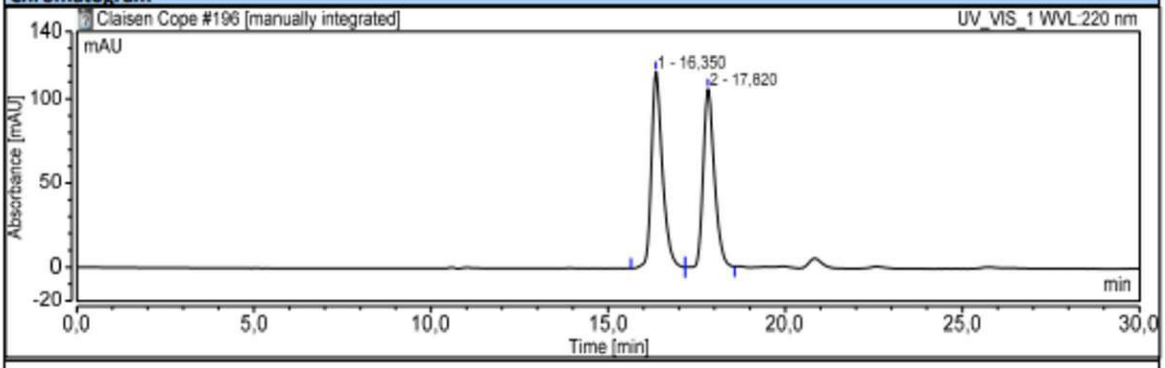


(E)-1-allyl-3-methyl-2-(pent-3-en-2-yloxy)benzene (95rac)

Chromatogram and Results

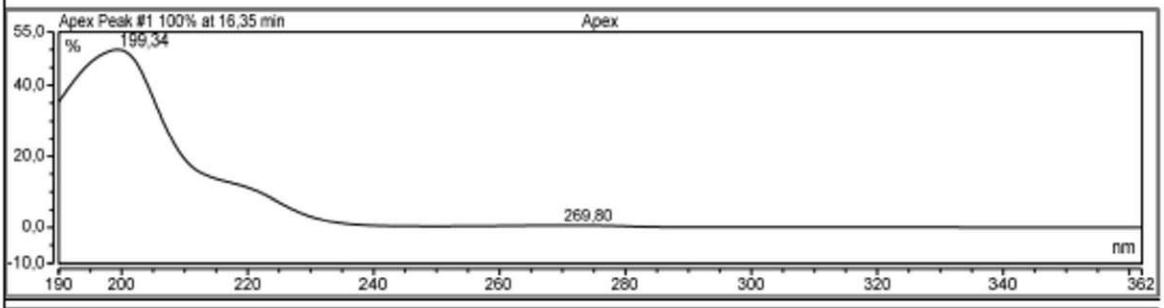
Instrument Method:	**Heptane_IPA_99.9_0.1_0.3mlmin_25C_30min-MK**	*B %:*	**0,1**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

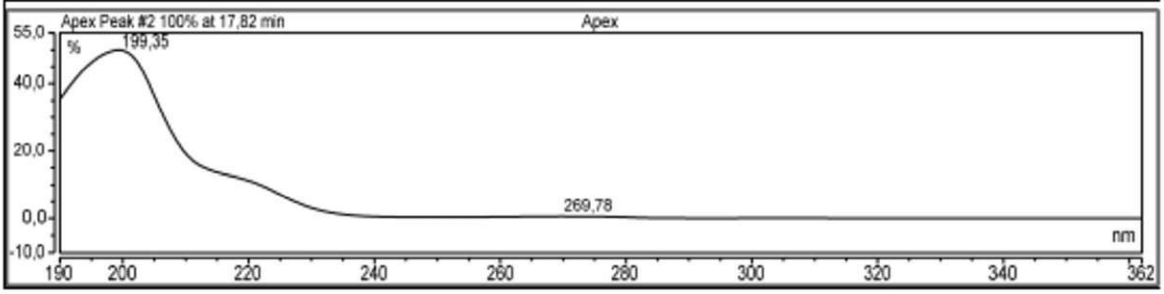
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		16,350	42,030	116,673	52,18	52,50
2		17,820	38,516	105,582	47,82	47,50
Total:			**80,546**	**222,255**	**100,00**	**100,00**



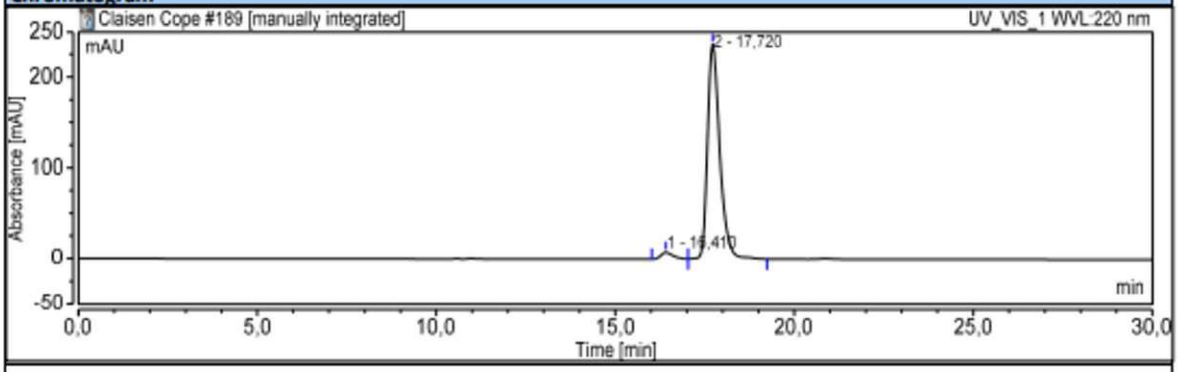


(R,E)-1-allyl-3-methyl-2-(pent-3-en-2-yloxy)benzene (95)

Chromatogram and Results

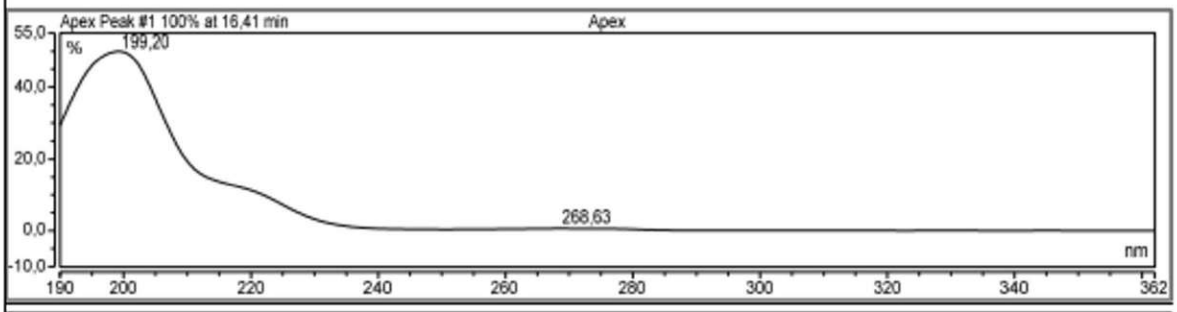
Instrument Method:	**Heptane_IPA_99.9_0.1_0.3mlmin_25C_30min-MK**	*B %:*	**0,1**
Column:	**IB**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**0,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

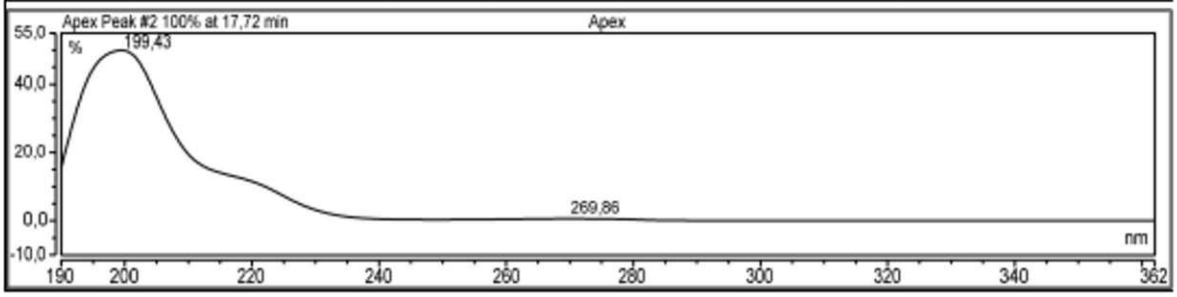
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		16,410	2,849	7,349	2,96	3,01
2		17,720	93,476	236,913	97,04	96,99
Total:			**96,325**	**244,262**	**100,00**	**100,00**



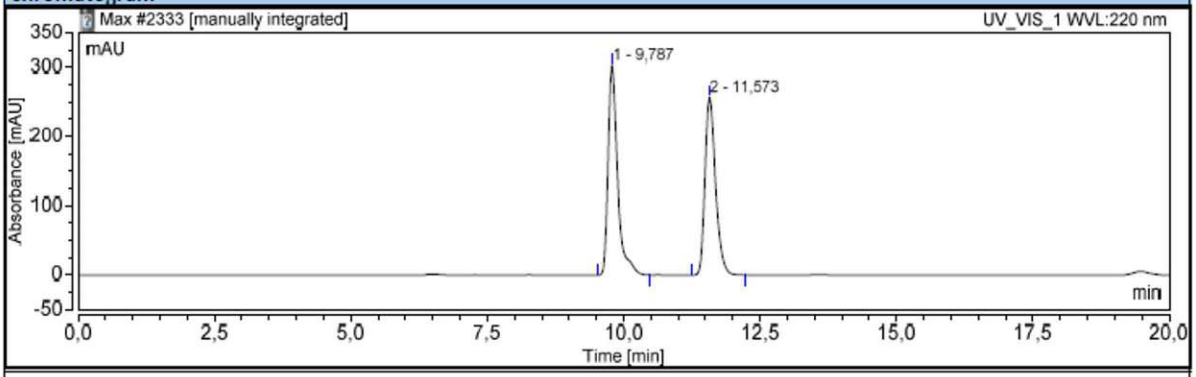


(E)-1-methyl-2-(pent-3-en-2-yloxy)benzene (115rac)

Chromatogram and Results

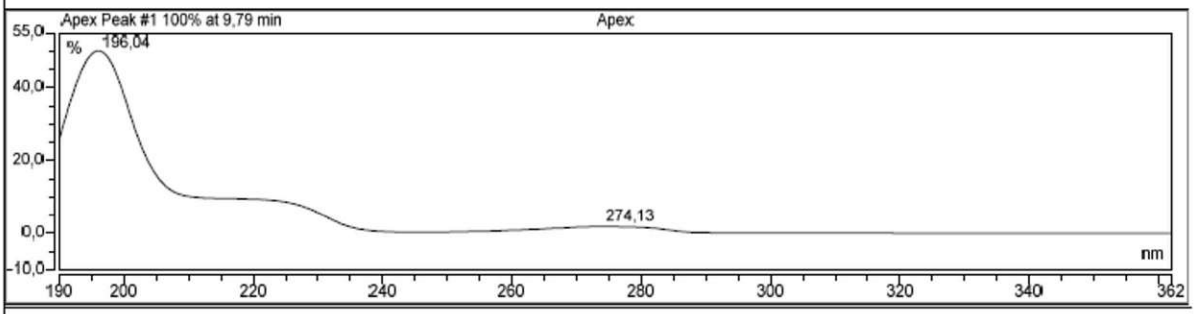
Instrument Method:	Heptane_EtOH_99.9_0.1_0.5mlmin_25C_20min	*B %:*	0,0
Column:	IB	*C %:*	0,0
Run Time (min):	20,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

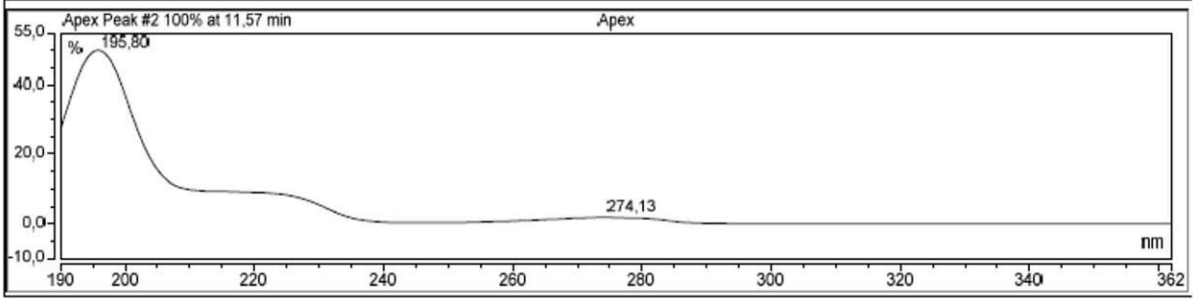
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		9,787	60,829	302,598	51,43	54,01
2		11,573	57,457	257,638	48,57	45,99
Total:			**118,286**	**560,236**	**100,00**	**100,00**



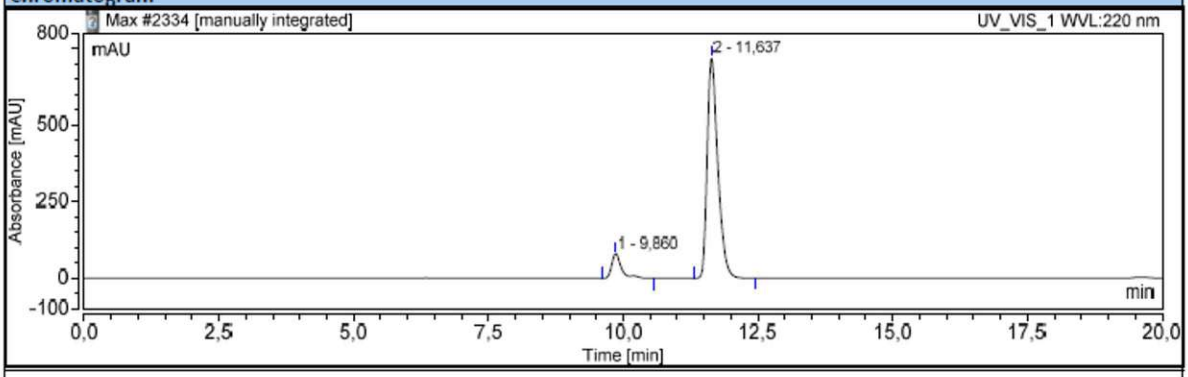


(R,E)-1-methyl-2-(pent-3-en-2-yloxy)benzene (115)

Chromatogram and Results

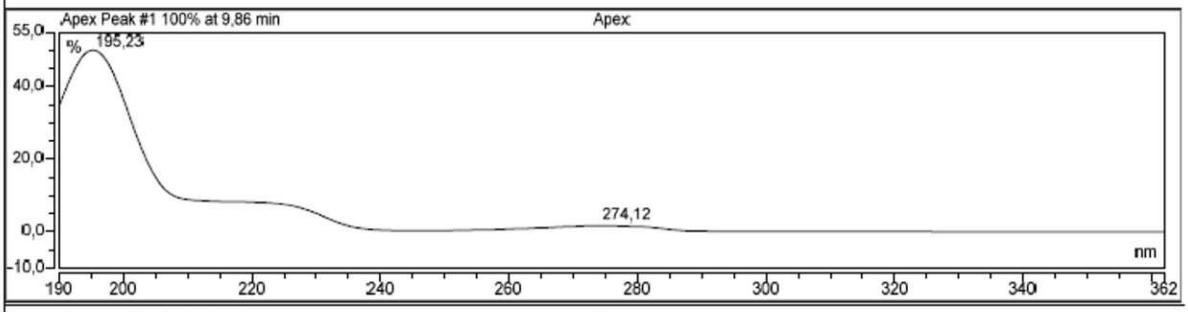
Instrument Method:	Heptane_EtOH_99.9_0.1_0.5mlmin_25C_20min	*B %:*	0,0
Column:	IB	*C %:*	0,0
Run Time (min):	20,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

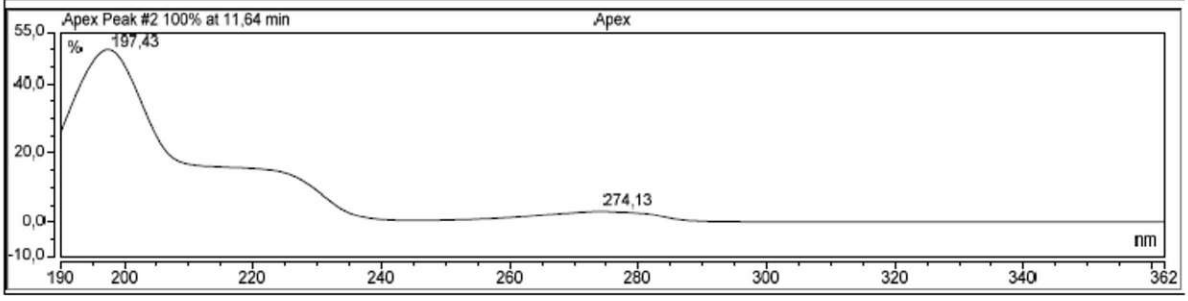
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		9,860	16,842	81,414	9,32	10,16
2		11,637	163,807	719,939	90,68	89,84
Total:			**180,648**	**801,353**	**100,00**	**100,00**



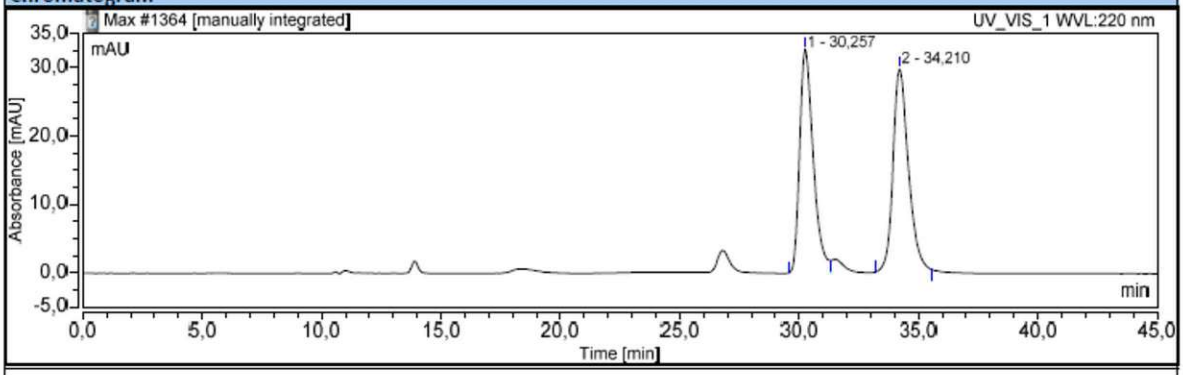


(E)-1,2,3-trimethyl-5-(pent-3-en-2-yloxy)benzene (57rac)

Chromatogram and Results

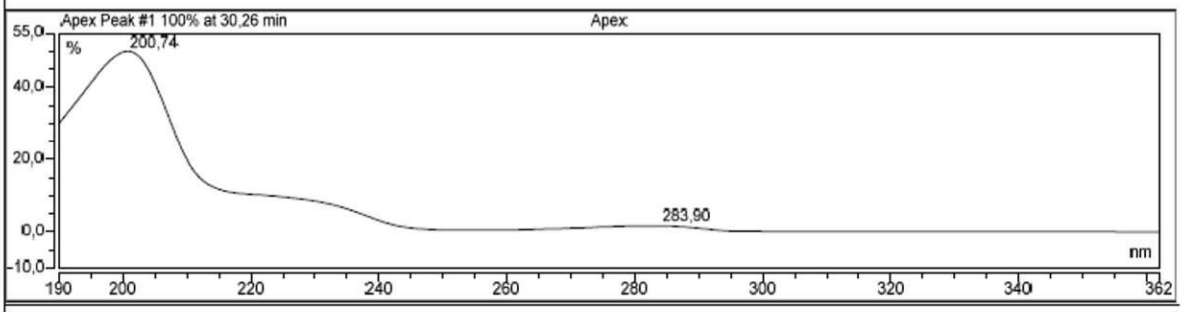
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

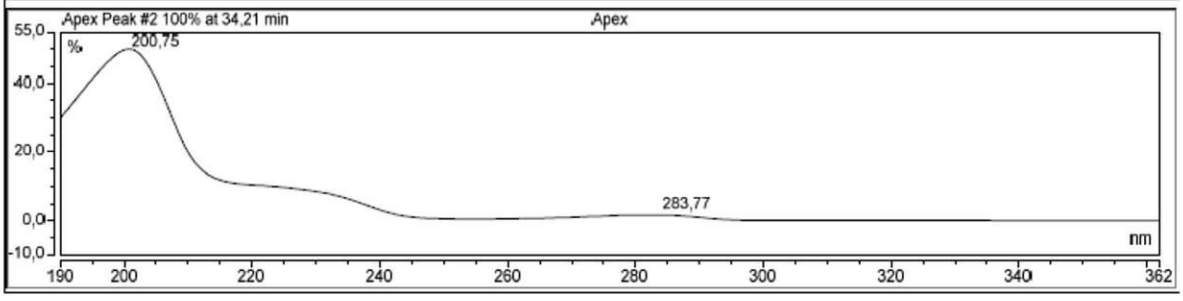
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		30,257	21,442	32,703	49,45	52,52
2		34,210	21,920	29,568	50,55	47,48
Total:			**43,362**	**62,270**	**100,00**	**100,00**



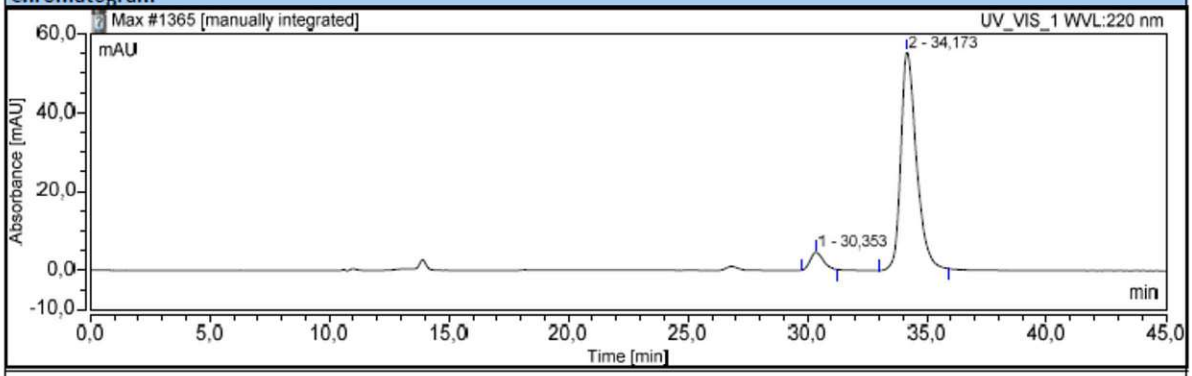


(R,E)-1,2,3-trimethyl-5-(pent-3-en-2-yloxy)benzene (57)

Chromatogram and Results

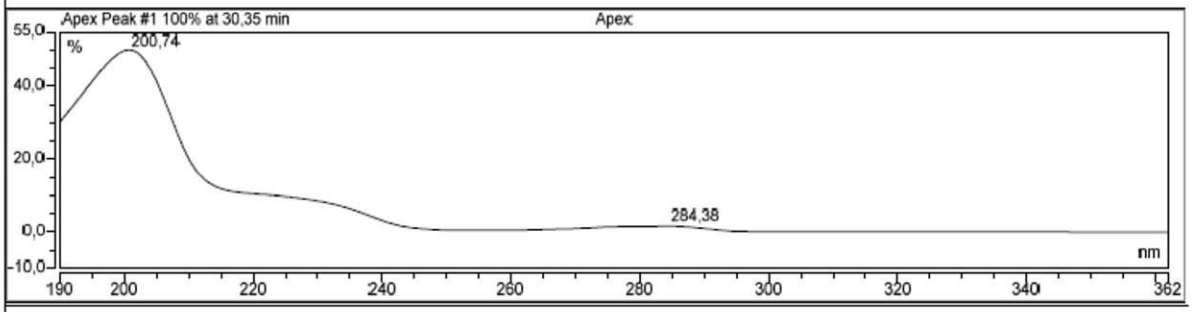
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

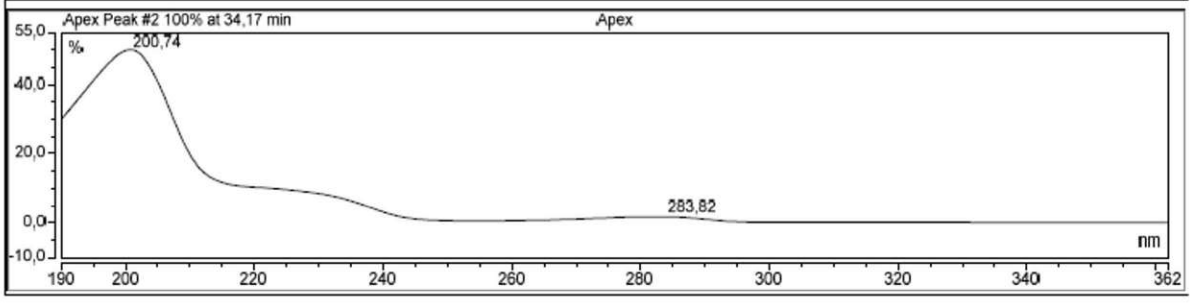
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		30,353	2,823	4,524	6,35	7,55
2		34,173	41,604	55,431	93,65	92,45
Total:			**44,427**	**59,955**	**100,00**	**100,00**



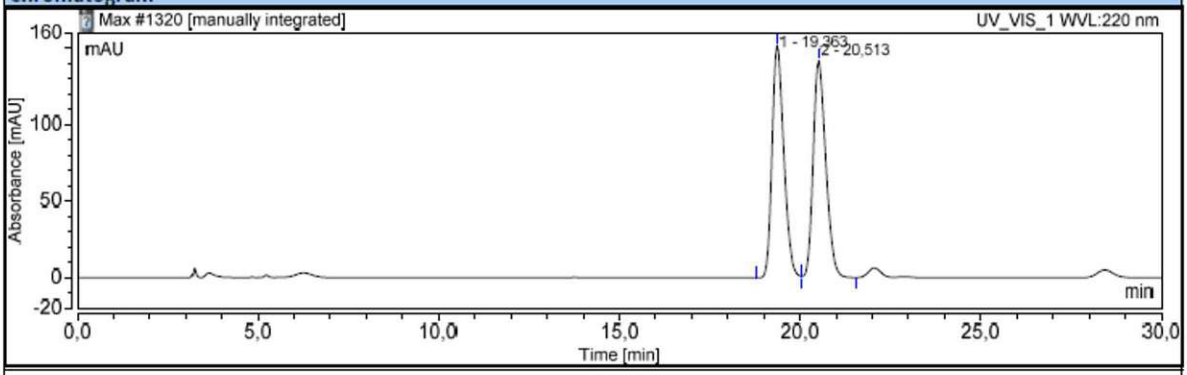


(E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenol (78rac)

Chromatogram and Results

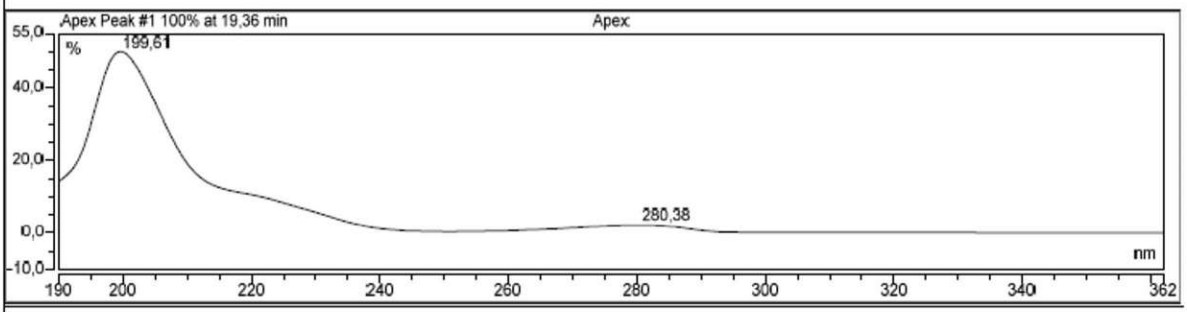
Instrument Method:	Heptane_EtOH_99.5_0.5_0.7mlmin_25C_30min	*B %:*	0,0
Column:	OJ-3	*C %:*	0,0
Run Time (min):	30,00	*D %:*	0,5
Channel:	UV_VIS_1		
Wavelength:	287,26		

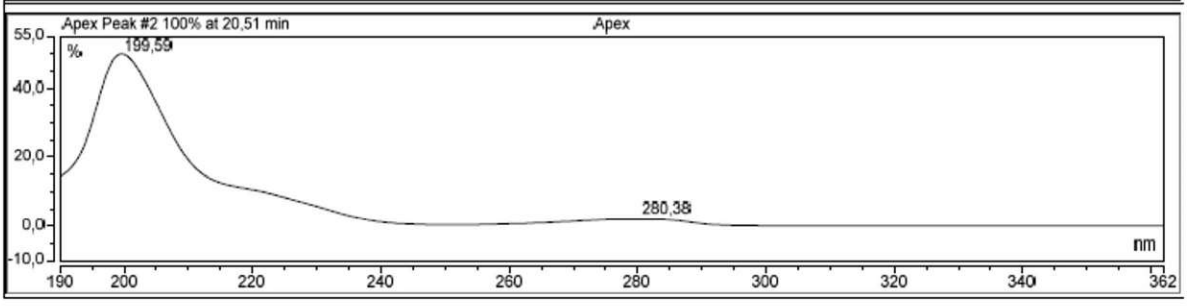
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		19,363	57,219	152,240	49,96	51,71
2		20,513	57,320	142,175	50,04	48,29
Total:			**114,539**	**294,415**	**100,00**	**100,00**



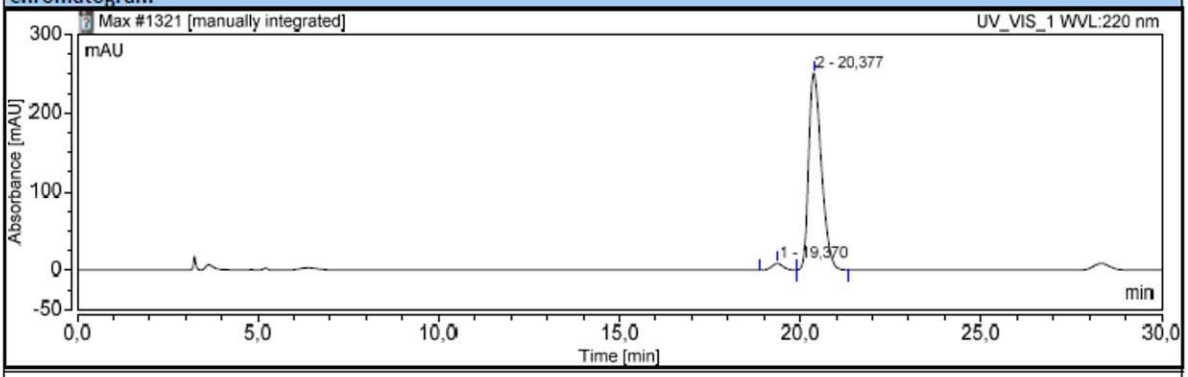


(R,E)-2,6-dimethyl-4-(pent-3-en-2-yl)phenol (78)

Chromatogram and Results

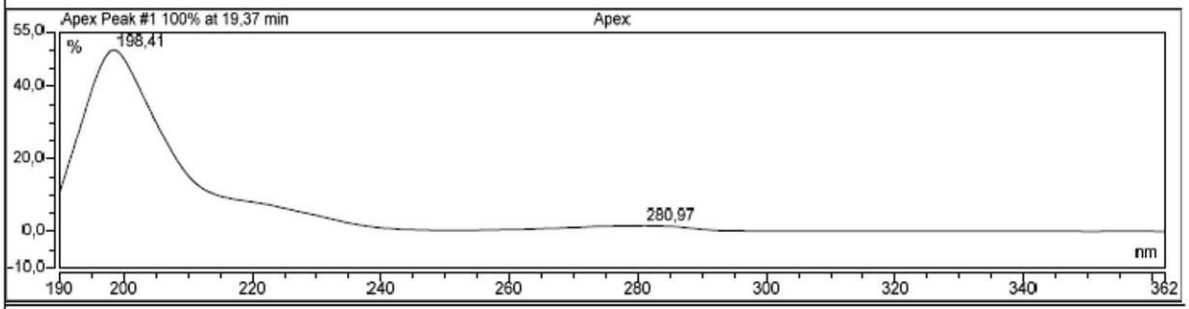
Instrument Method:	Heptane_EtOH_99.5_0.5_0.7mlmin_25C_30min	*B %:*	0,0
Column:	OJ-3	*C %:*	0,0
Run Time (min):	30,00	*D %:*	0,5
Channel:	UV_VIS_1		
Wavelength:	287,26		

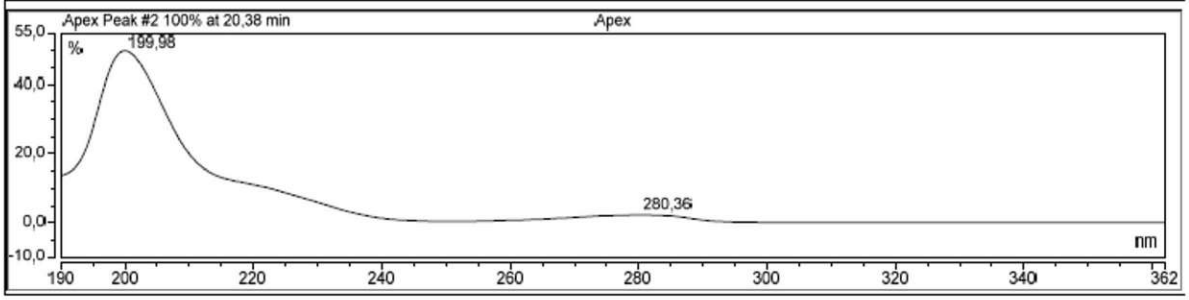
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		19,370	3,154	8,681	3,00	3,34
2		20,377	102,163	251,551	97,00	96,66
Total:			**105,317**	**260,232**	**100,00**	**100,00**



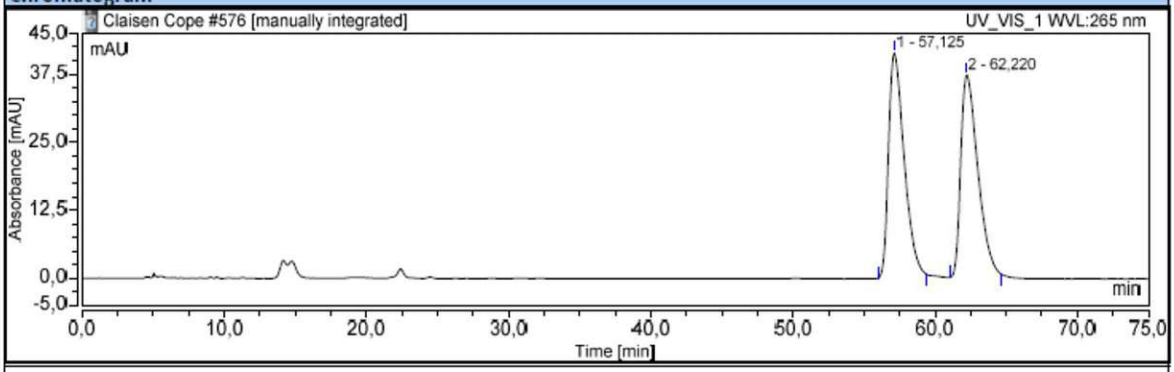


4-(1-hydroxypropan-2-yl)-2,6-dimethylphenyl 4-bromobenzoate (142rac)

Chromatogram and Results

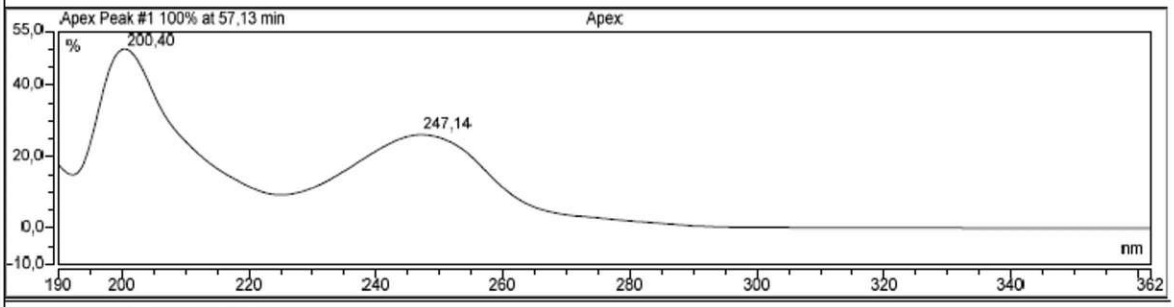
Instrument Method:	Hexane_EtOH_99_1 _0.7mLmin_25C_75min-MK	*B %:*	0,0
Column:	OJ3	*C %:*	99,0
Run Time (min):	75,00	*D %:*	1,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

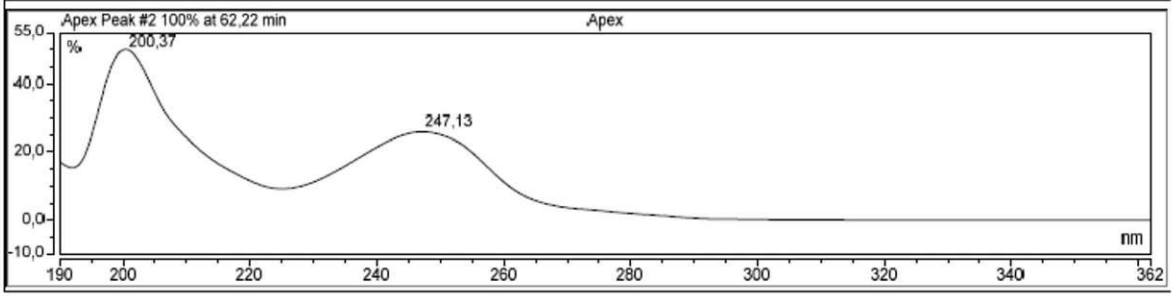
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		57,125	51,879	41,254	50,55	52,66
2		62,220	50,744	37,091	49,45	47,34
Total:			**102,623**	**78,345**	**100,00**	**100,00**



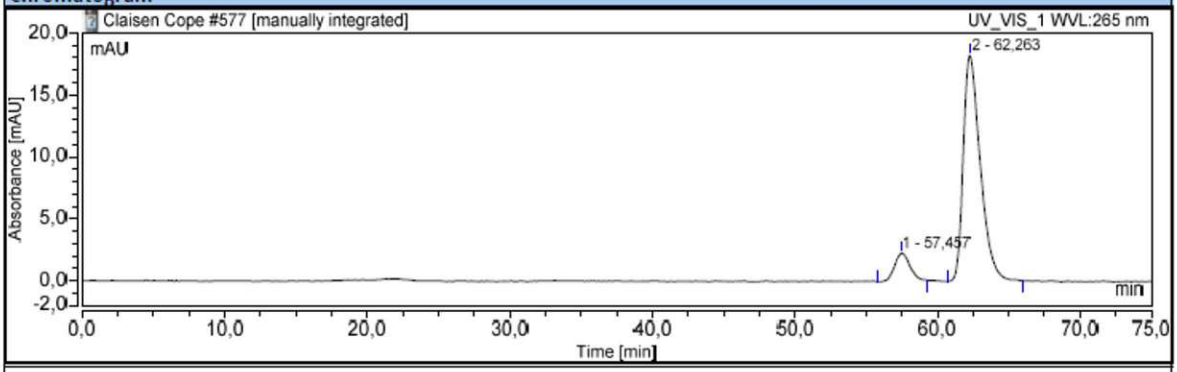


(S)-4-(1-hydroxypropan-2-yl)-2,6-dimethylphenyl 4-bromobenzoate (142)

Chromatogram and Results

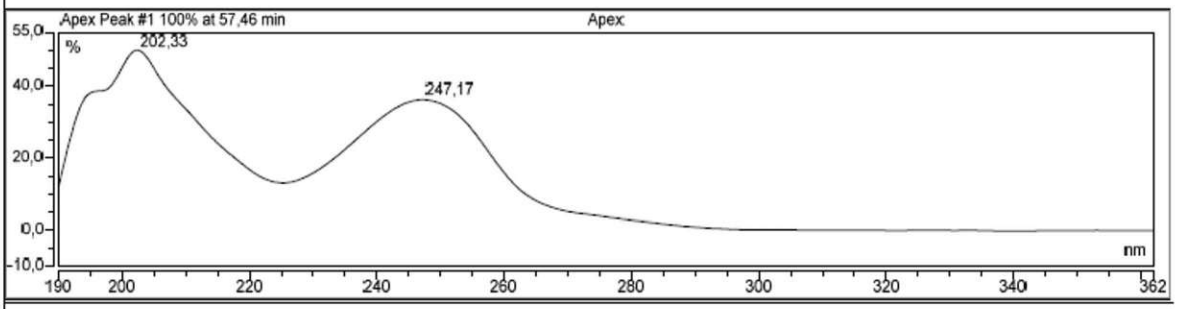
Instrument Method:	Hexane_EtOH_99_1 _0.7mLmin_25C_75min-MK	*B %:*	0,0
Column:	OJ3	*C %:*	99,0
Run Time (min):	75,00	*D %:*	1,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

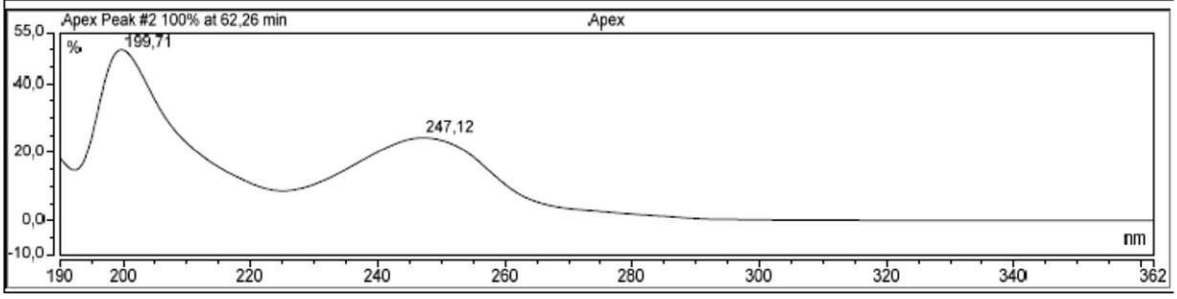
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		57,457	2,809	2,280	10,02	11,09
2		62,263	25,237	18,271	89,98	88,91
Total:			**28,046**	**20,551**	**100,00**	**100,00**



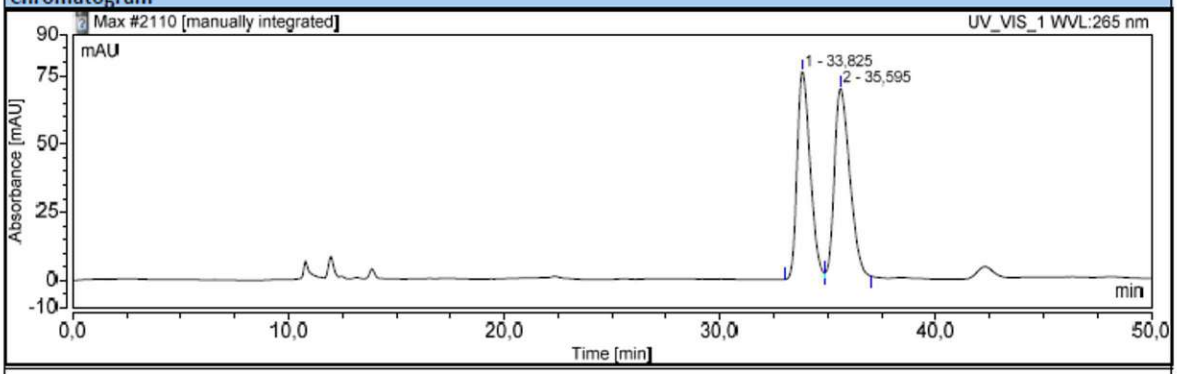


(E)-2,6-diethyl-4-(pent-3-en-2-yl)phenol (101rac)

Chromatogram and Results

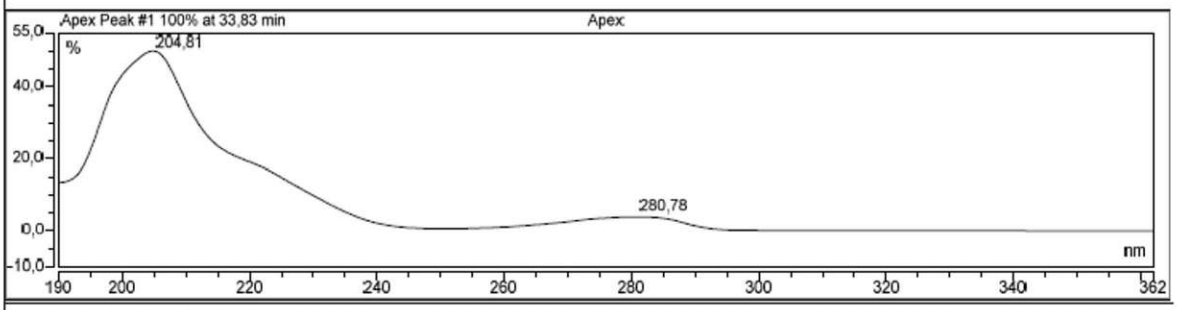
Instrument Method:	Hexane_IPA_99.9_0.1_0.3mLmin_25C_50min-MK	*B %:*	0,1
Column:	OJ3	*C %:*	99,9
Run Time (min):	50,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

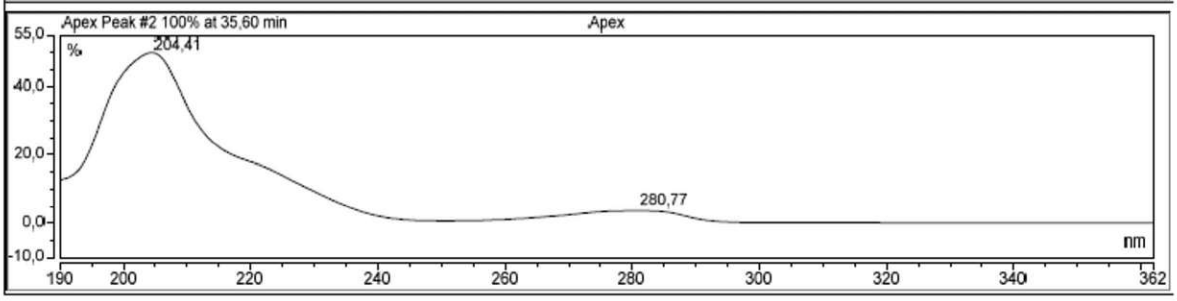
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		33,825	53,165	76,277	48,28	52,35
2		35,595	56,947	69,438	51,72	47,65
Total:			**110,111**	**145,714**	**100,00**	**100,00**



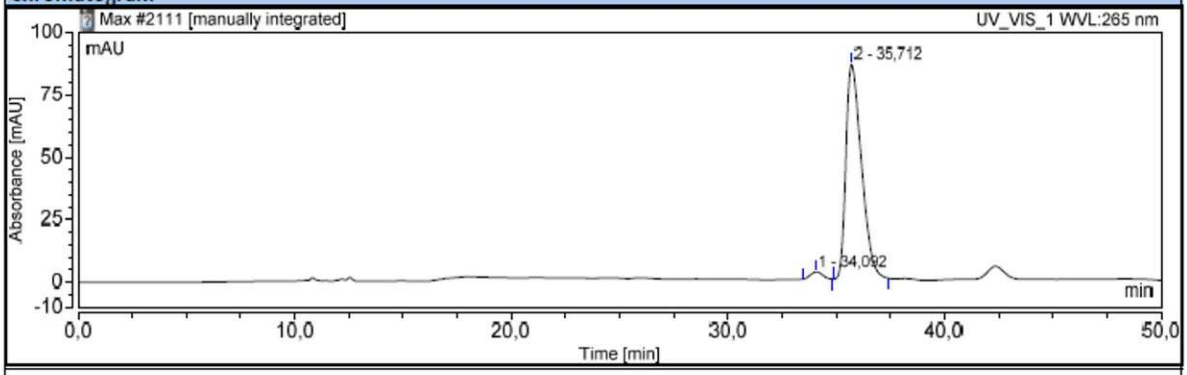


(R,E)-2,6-diethyl-4-(pent-3-en-2-yl)phenol (101)

Chromatogram and Results

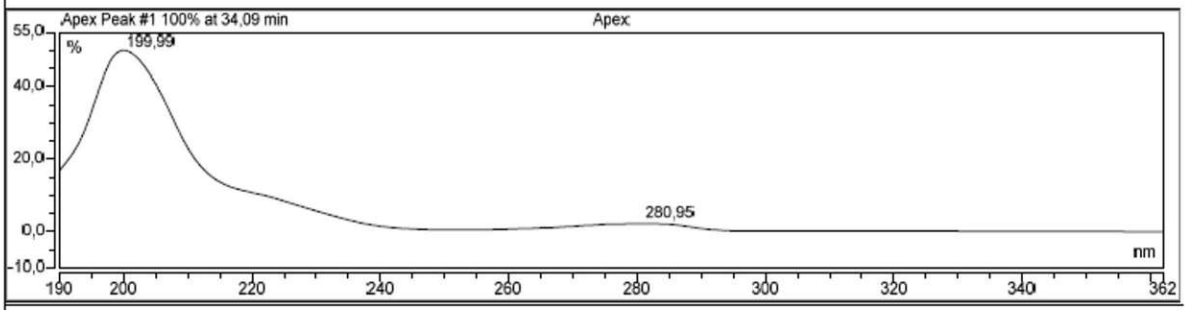
Instrument Method:	Hexane_IPA_99.9_0.1_0.3mLmin_25C_50min-MK	*B %:*	0,1
Column:	OJ3	*C %:*	99,9
Run Time (min):	50,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

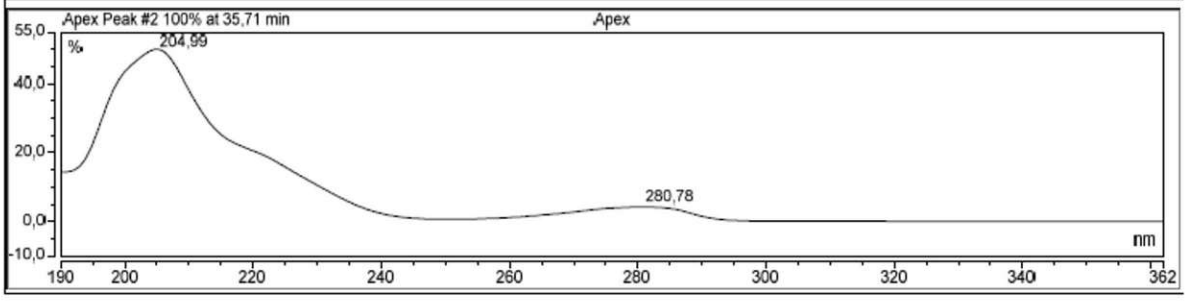
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		34,092	1,832	2,916	2,51	3,28
2		35,712	71,294	86,061	97,49	96,72
Total:			**73,126**	**88,977**	**100,00**	**100,00**



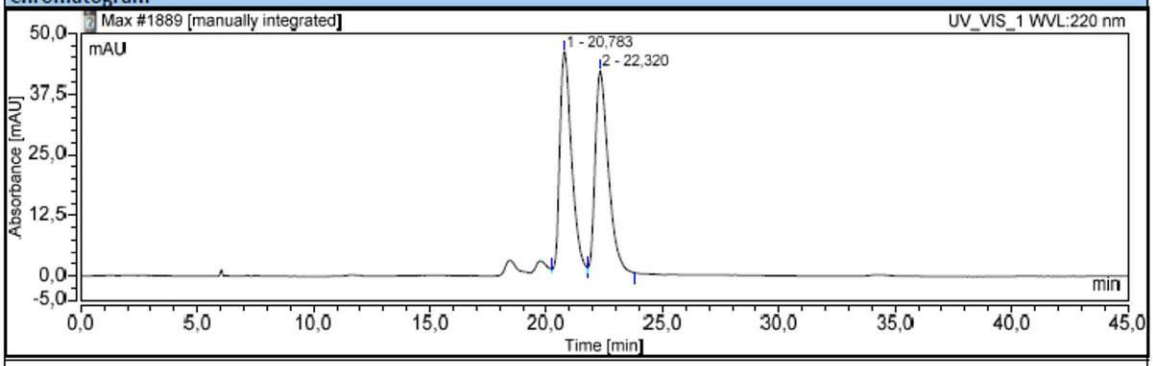


(E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (149rac)

Chromatogram and Results

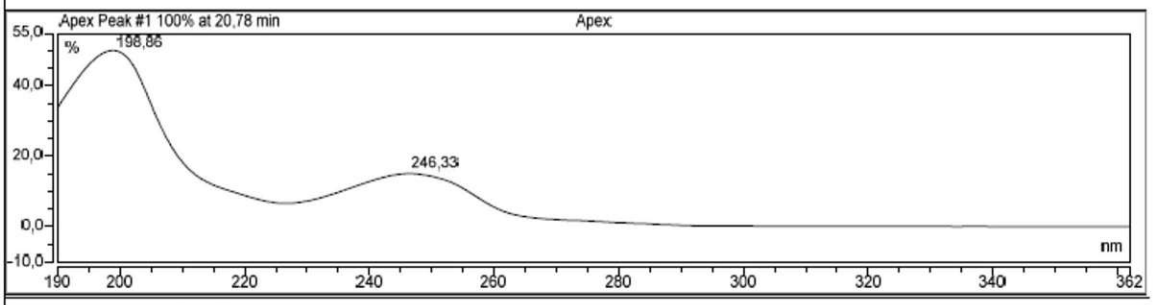
Instrument Method:	Heptane_EtOH_99.9_0.1_0.5mlmin_25C_45min	*B %:*	0,0
Column:	OD	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

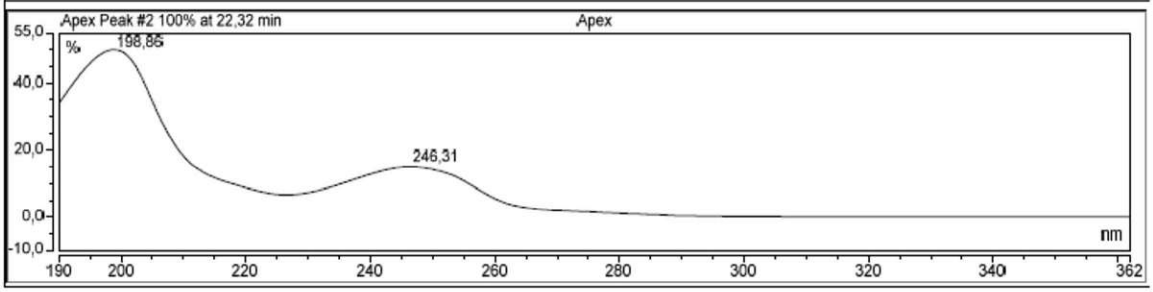
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		20,783	26,919	45,619	49,65	52,26
2		22,320	27,296	41,676	50,35	47,74
Total:			**54,215**	**87,296**	**100,00**	**100,00**



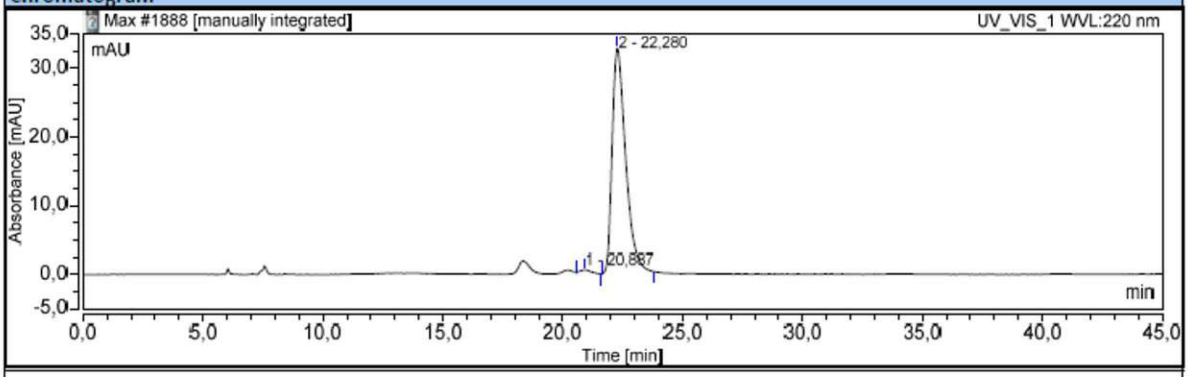


(R,E)-2,6-diisopropyl-4-(pent-3-en-2-yl)phenyl 4-bromobenzoate (149)

Chromatogram and Results

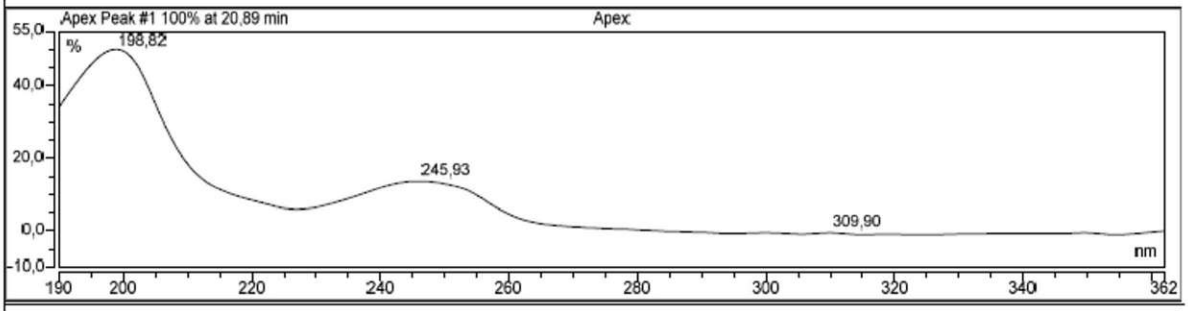
Instrument Method:	Heptane_EtOH_99.9_0.1_0.5mlmin_25C_45min	*B %:*	0,0
Column:	OD	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

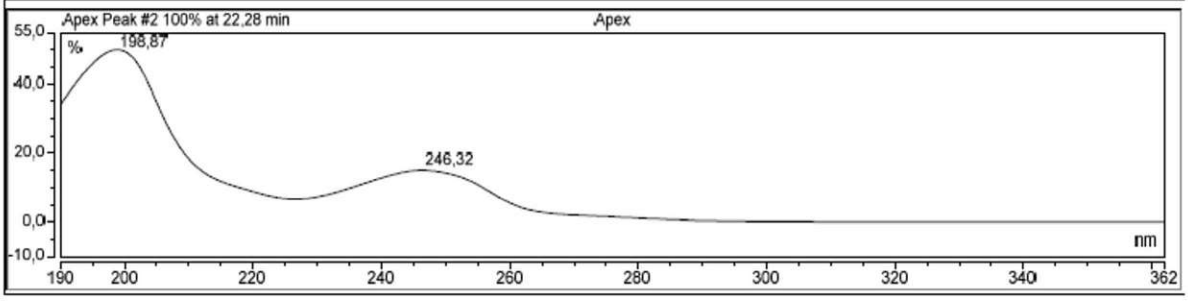
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		20,887	0,326	0,587	1,51	1,76
2		22,280	21,292	32,758	98,49	98,24
Total:			**21,618**	**33,346**	**100,00**	**100,00**



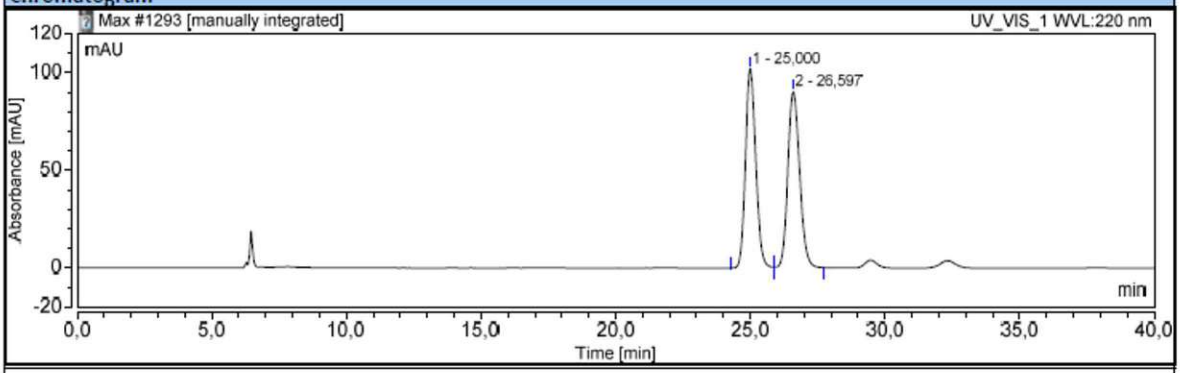


(E)-2,3,6-trimethyl-4-(pent-3-en-2-yl)phenol (103rac)

Chromatogram and Results

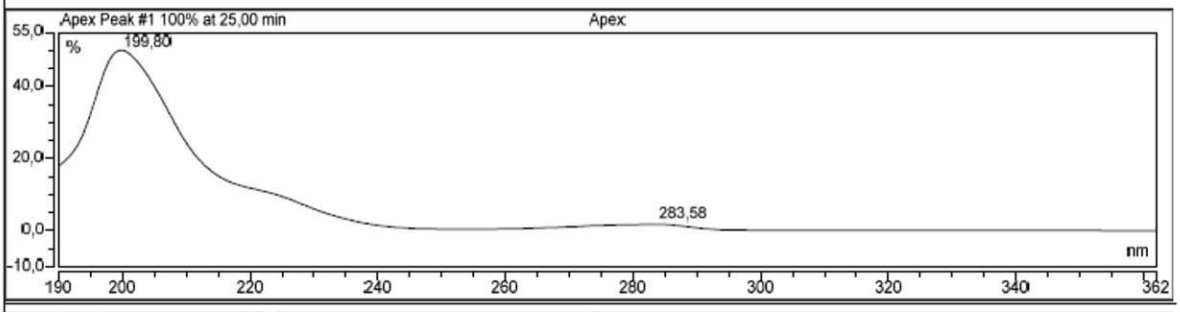
Instrument Method:	Hexane_EtOH_99.8_0.2_0.5mlmin_25C_40min	*B %:*	0,0
Column:	OJ-3	*C %:*	99,8
Run Time (min):	40,00	*D %:*	0,2
Channel:	UV_VIS_1		
Wavelength:	287,26		

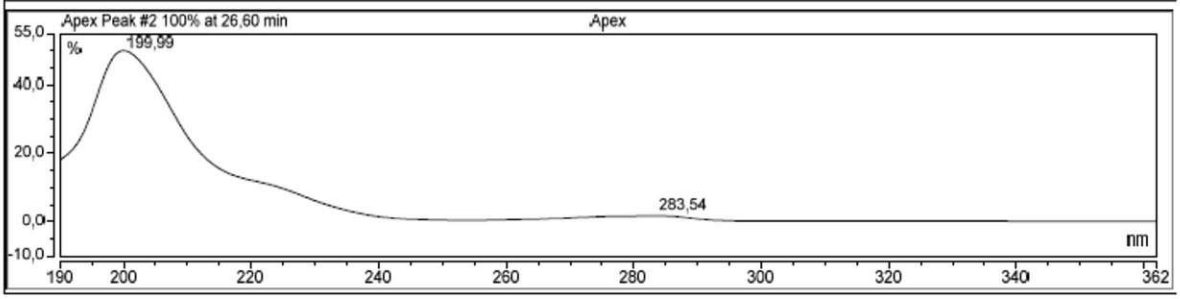
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		25,000	45,281	102,247	49,73	53,03
2		26,597	45,775	90,570	50,27	46,97
Total:			**91,056**	**192,817**	**100,00**	**100,00**



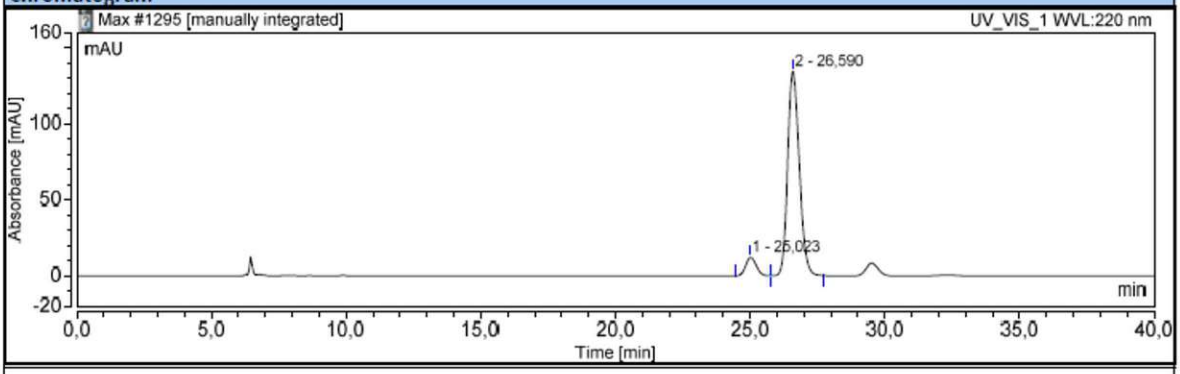


(R,E)-2,3,6-trimethyl-4-(pent-3-en-2-yl)phenol (103)

Chromatogram and Results

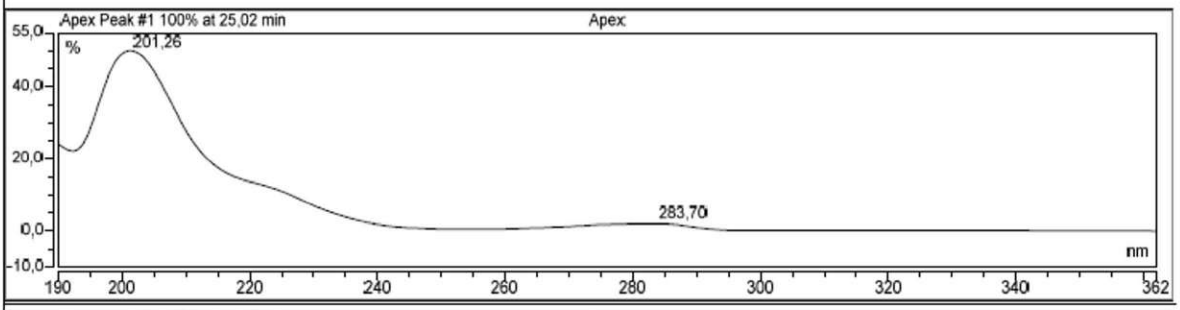
Instrument Method:	Hexane_EtOH_99.8_0.2_0.5mlmin_25C_40min	*B %:*	0,0
Column:	OJ-3	*C %:*	99,8
Run Time (min):	40,00	*D %:*	0,2
Channel:	UV_VIS_1		
Wavelength:	287,26		

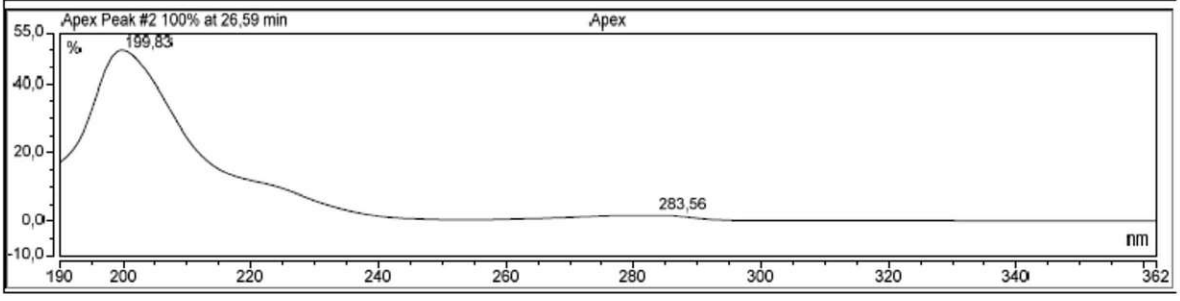
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		25,023	5,552	12,193	7,64	8,30
2		26,590	67,143	134,641	92,36	91,70
Total:			**72,695**	**146,834**	**100,00**	**100,00**



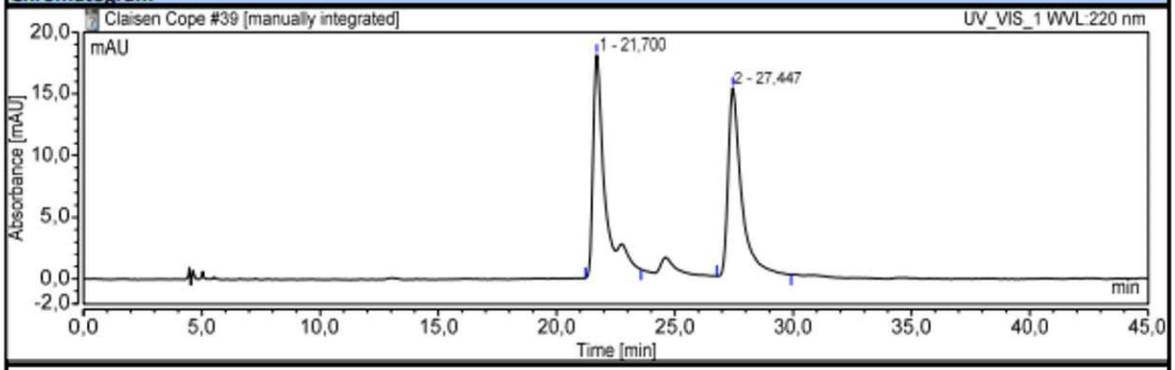


(E)-2,6-dimethoxy-4-(pent-3-en-2-yl)phenol (104rac)

Chromatogram and Results

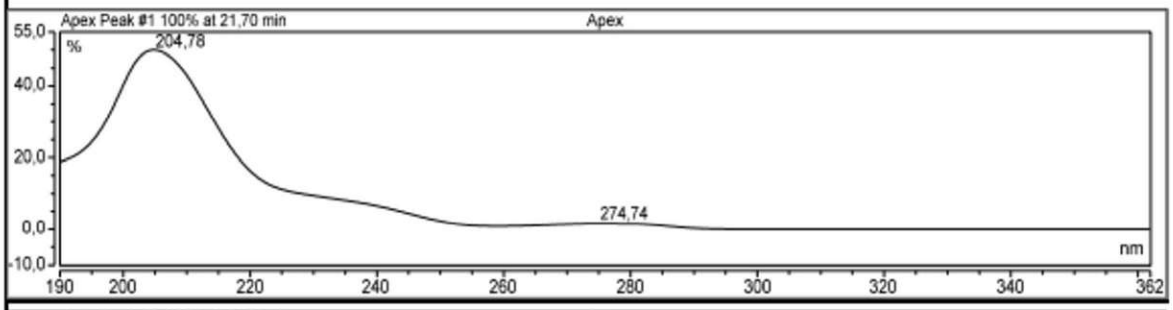
Instrument Method:	Heptane_EtOH_96.5_3.5_0.7mlmin_25C_45min-MK	*B %:*	0,0
Column:	OJ3	*C %:*	0,0
Run Time (min):	45,00	*D %:*	3,5
Channel:	UV_VIS_1		
Wavelength:	287,26		

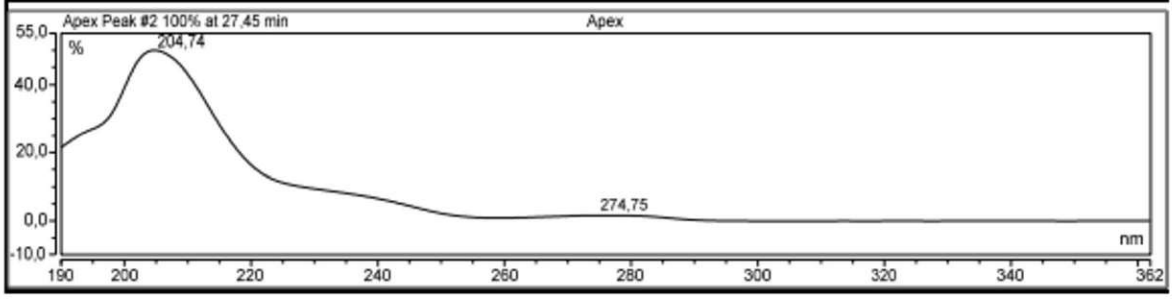
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21,700	10,243	17,973	50,91	54,09
2		27,447	9,877	15,256	49,09	45,91
Total:			**20,120**	**33,228**	**100,00**	**100,00**



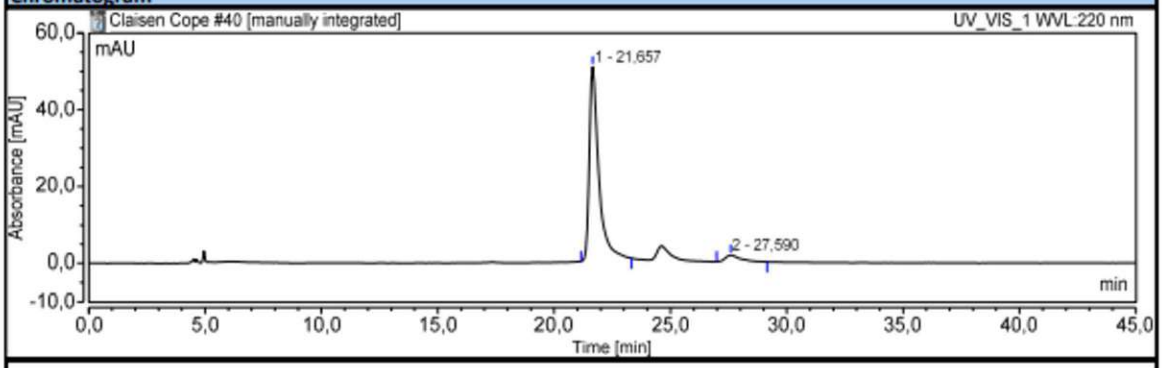


(R,E)-2,6-dimethoxy-4-(pent-3-en-2-yl)phenol (104)

Chromatogram and Results

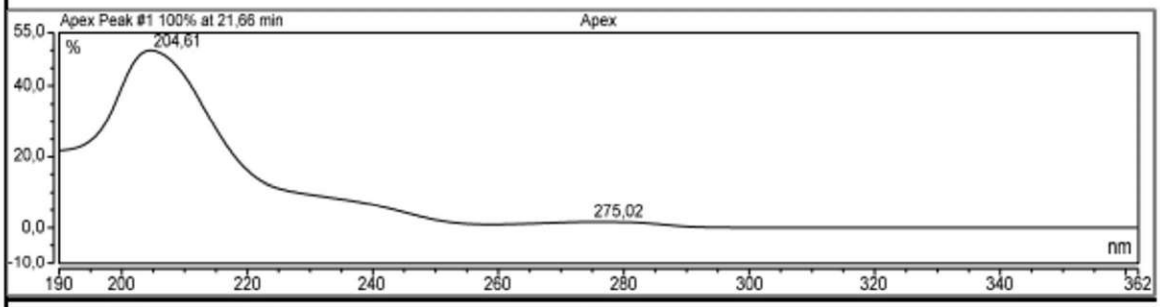
Instrument Method:	**Heptane_EtOH_96.5_3.5_0.7mlmin_25C_45min-MK**	*B %:*	**0,0**
Column:	**OJ3**	*C %:*	**0,0**
Run Time (min):	**45,00**	*D %:*	**3,5**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

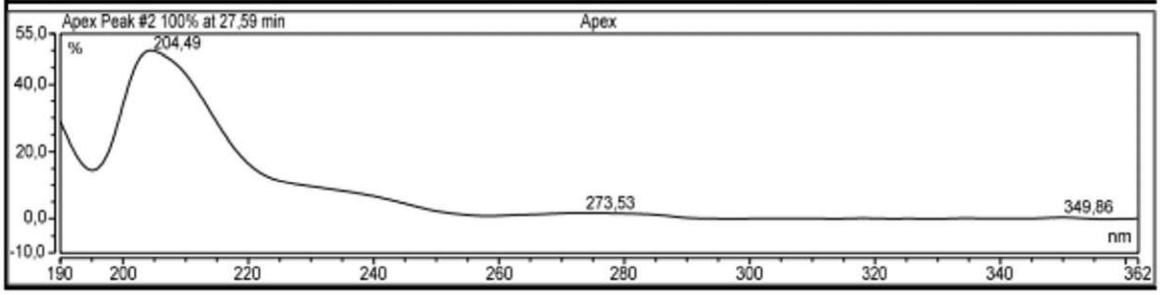
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21,657	23,754	50,561	95,04	96,73
2		27,590	1,239	1,708	4,96	3,27
Total:			**24,993**	**52,270**	**100,00**	**100,00**



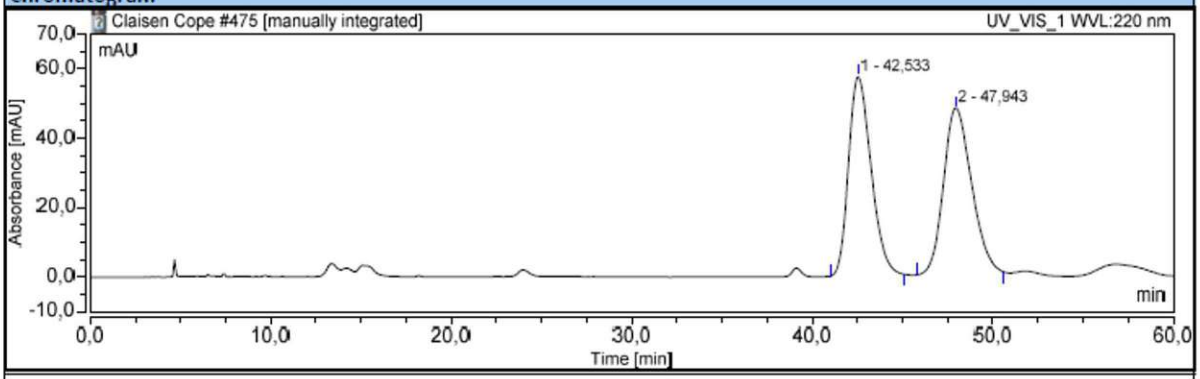


(E)-2-(benzyloxy)-6-methyl-4-(pent-3-en-2-yl)phenol (105rac)

Chromatogram and Results

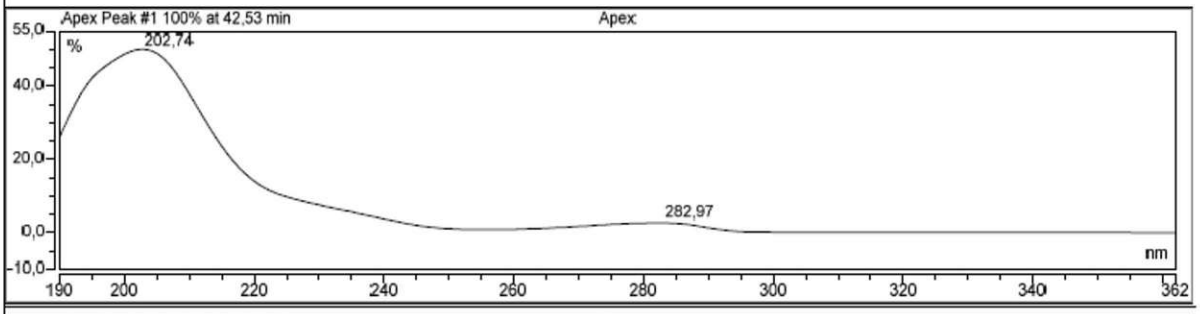
Instrument Method:	Heptane_EtOH_99.8_0.2_0.7mlmin_25C_60min	*B %:*	0,0
Column:	OJ3	*C %:*	0,0
Run Time (min):	60,00	*D %:*	0,2
Channel:	UV_VIS_1		
Wavelength:	287,26		

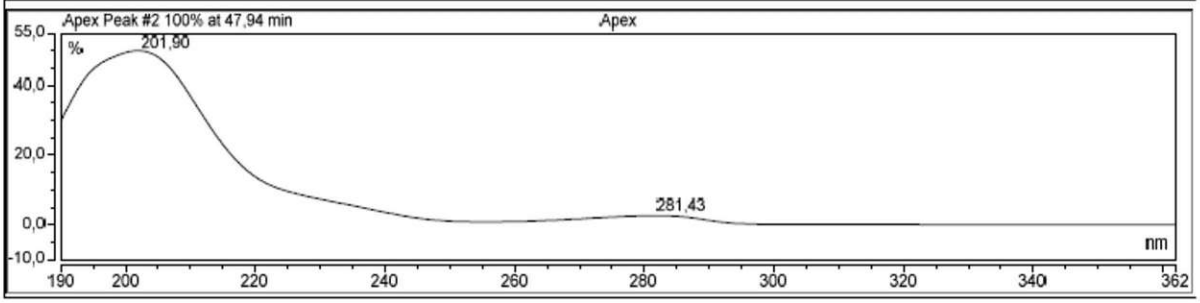
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		42,533	82,672	57,232	49,30	54,53
2		47,943	85,034	47,717	50,70	45,47
Total:			**167,706**	**104,949**	**100,00**	**100,00**



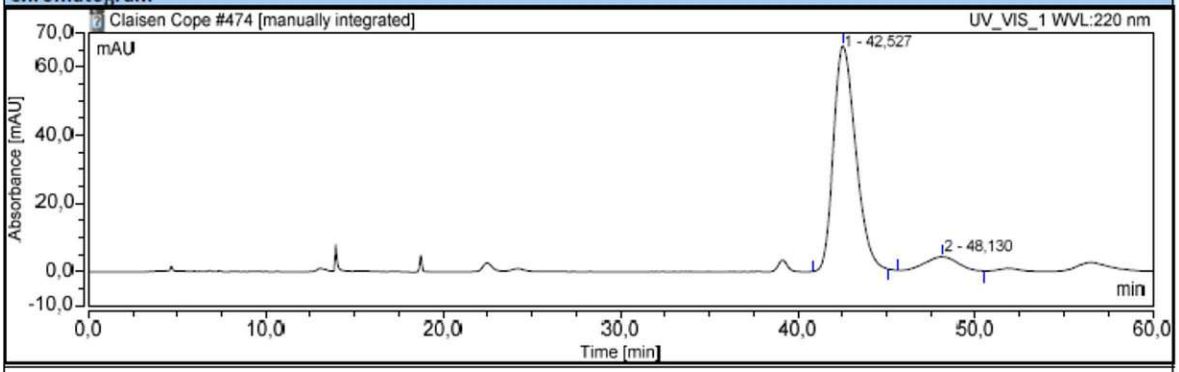


(R,E)-2-(benzyloxy)-6-methyl-4-(pent-3-en-2-yl)phenol (105)

Chromatogram and Results

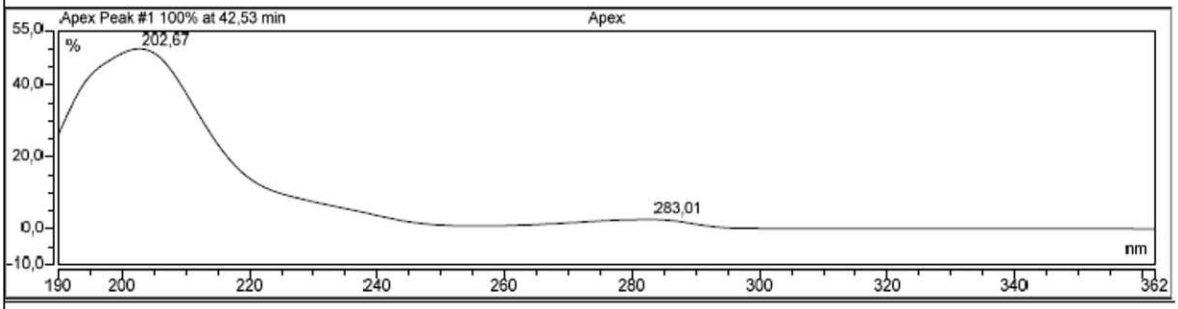
Instrument Method:	Heptane_EtOH_99.8_0.2_0.7mlmin_25C_60min	*B %:*	0,0
Column:	OJ3	*C %:*	0,0
Run Time (min):	60,00	*D %:*	0,2
Channel:	UV_VIS_1		
Wavelength:	287,26		

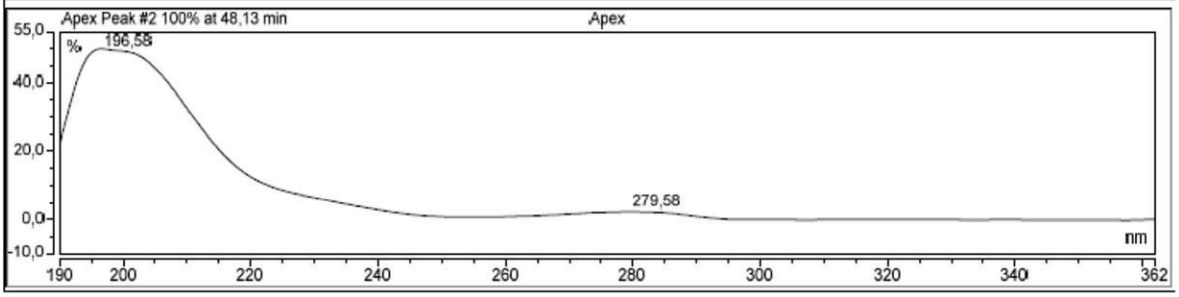
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		42,527	95,298	65,858	91,91	94,17
2		48,130	8,389	4,075	8,09	5,83
Total:			**103,686**	**69,933**	**100,00**	**100,00**



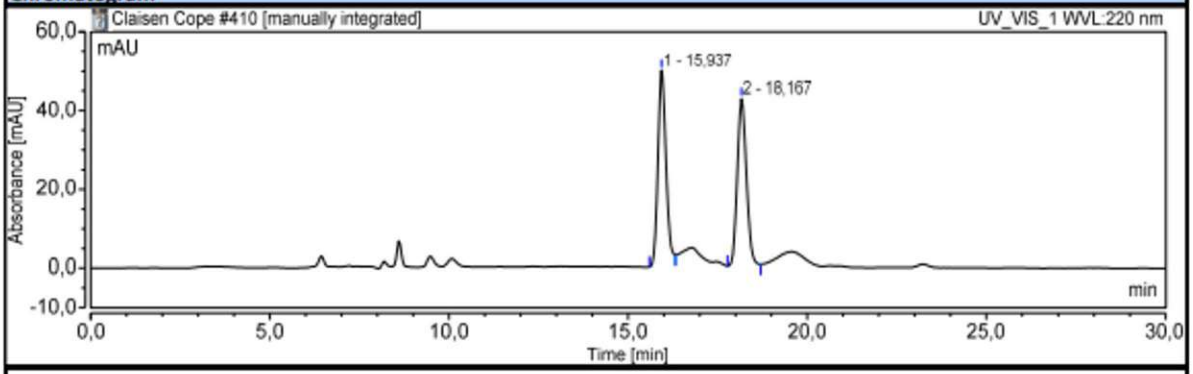


(E)-2-methoxy-4-(pent-3-en-2-yl)-6-vinylphenol (106rac)

Chromatogram and Results

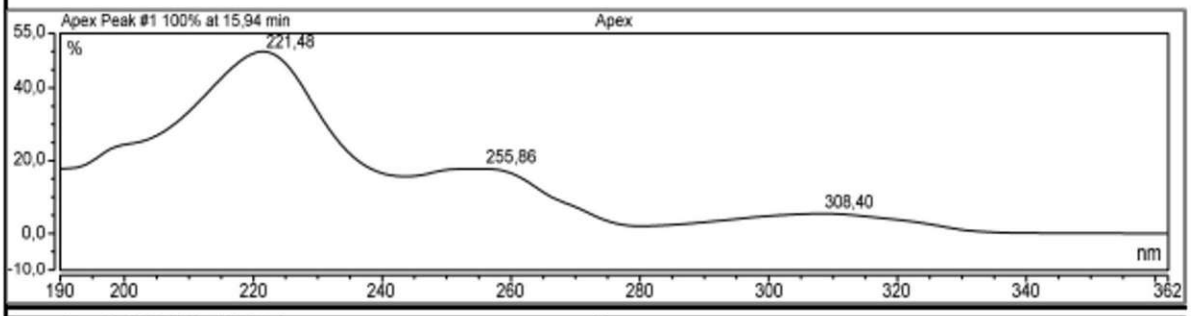
Instrument Method:	**Heptane_EtOH_98_2_0.5mlmin_25C_30min-MK**	*B %:*	**0,0**
Column:	**OJ3**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**2,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

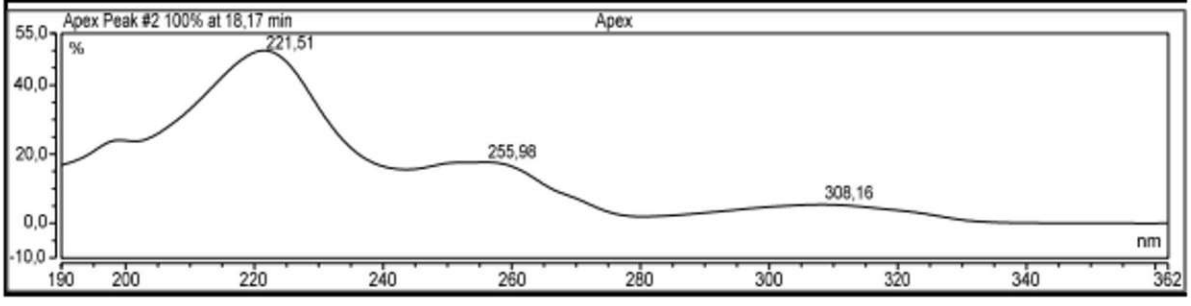
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		15,937	13,039	49,737	50,75	53,90
2		18,167	12,655	42,533	49,25	46,10
Total:			**25,694**	**92,270**	**100,00**	**100,00**



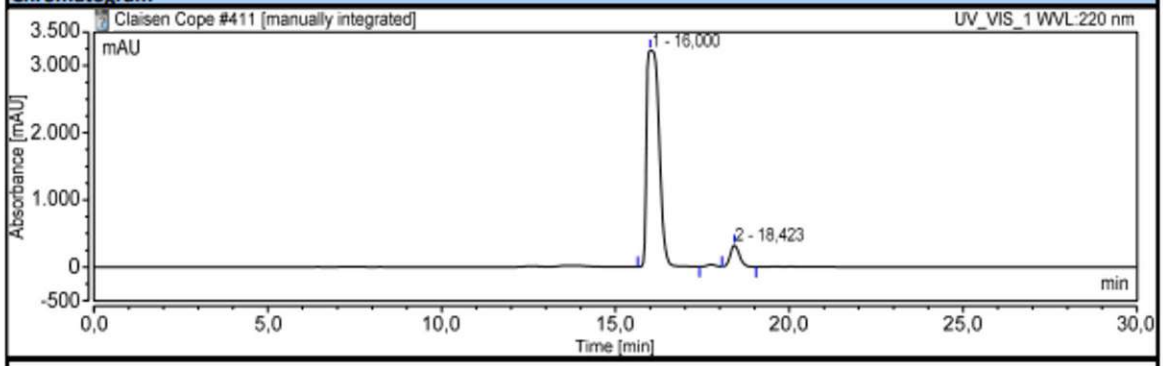


(R,E)-2-methoxy-4-(pent-3-en-2-yl)-6-vinylphenol (106)

Chromatogram and Results

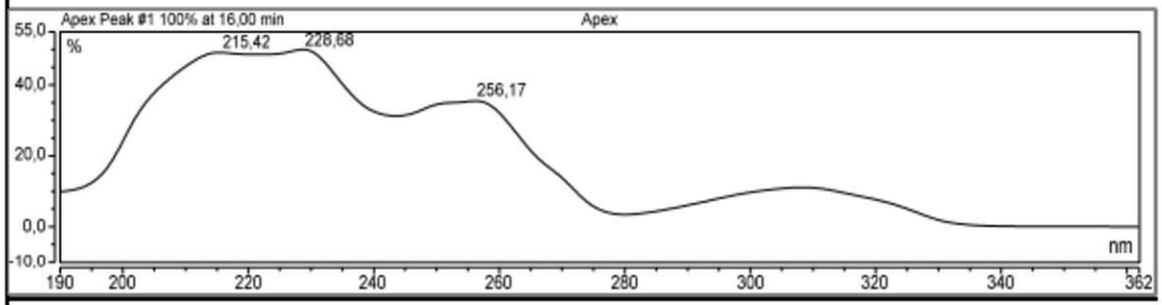
Instrument Method:	**Heptane_EtOH_98_2_0.5mlmin_25C_30min-MK**	*B %:*	**0,0**
Column:	**OJ3**	*C %:*	**0,0**
Run Time (min):	**30,00**	*D %:*	**2,0**
Channel:	**UV_VIS_1**		
Wavelength:	**287,26**		

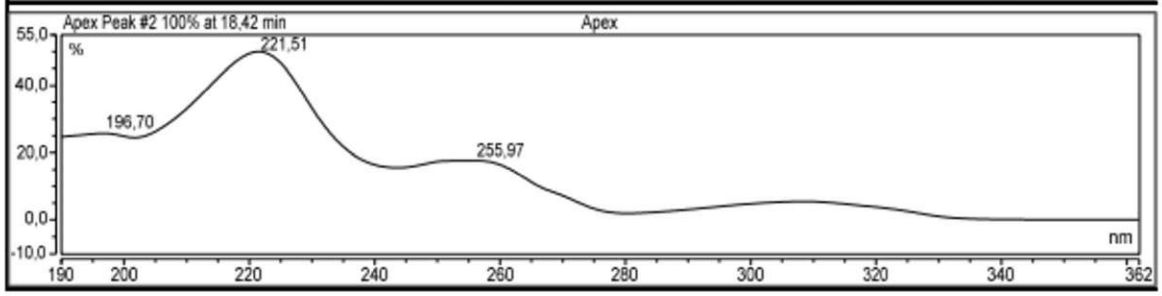
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		16,000	1334,588	3226,743	93,14	90,90
2		18,423	98,289	322,877	6,86	9,10
Total:			**1432,877**	**3549,620**	**100,00**	**100,00**



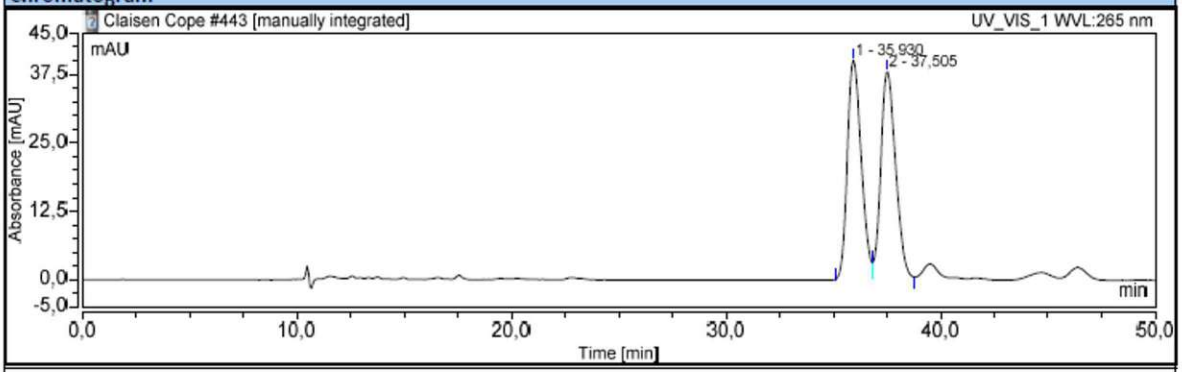


(E)-2-allyl-6-methyl-4-(pent-3-en-2-yl)phenol (108rac)

Chromatogram and Results

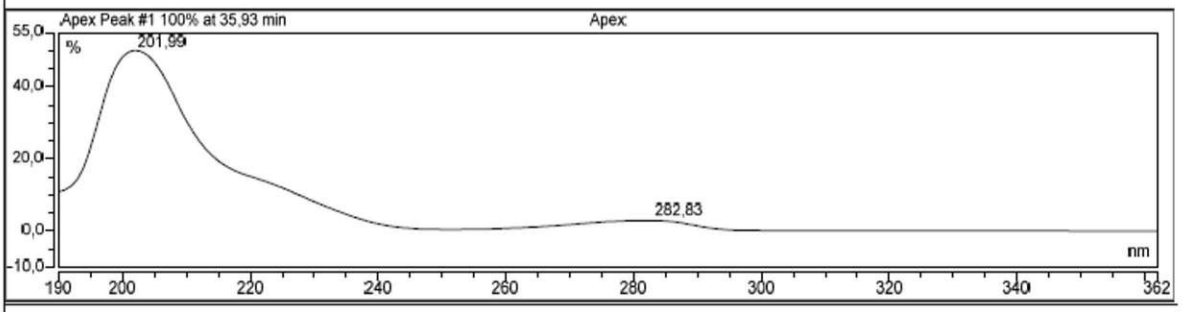
Instrument Method:	Hexane_IPA_99.9_0.1 _0.3mLmin_25C_50min-MK	*B %:*	0,1
Column:	OJ3	*C %:*	99,9
Run Time (min):	50,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

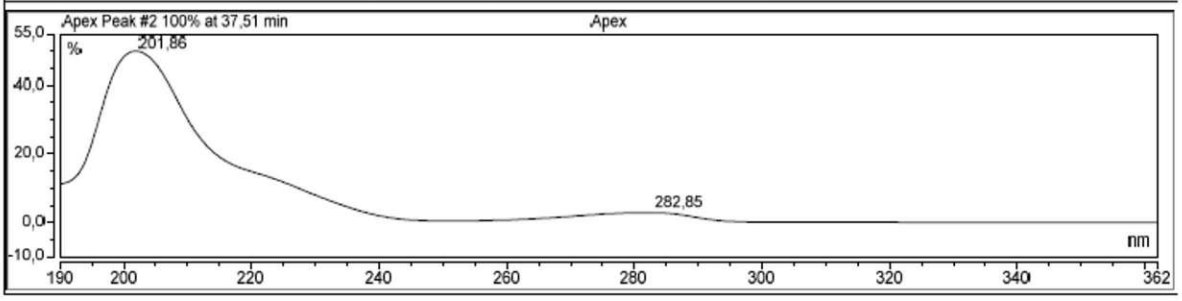
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		35,930	29,894	39,999	49,94	51,42
2		37,505	29,968	37,790	50,06	48,58
Total:			**59,862**	**77,789**	**100,00**	**100,00**



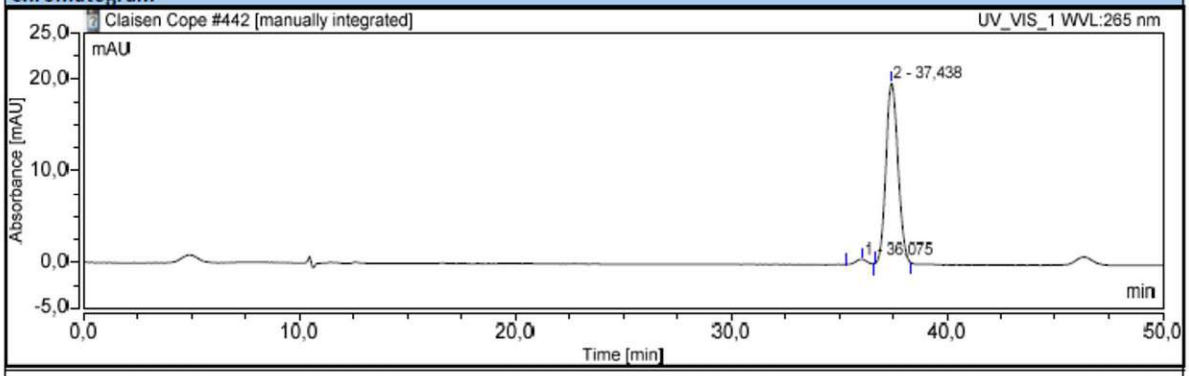


(R,E)-2-allyl-6-methyl-4-(pent-3-en-2-yl)phenol (108)

Chromatogram and Results

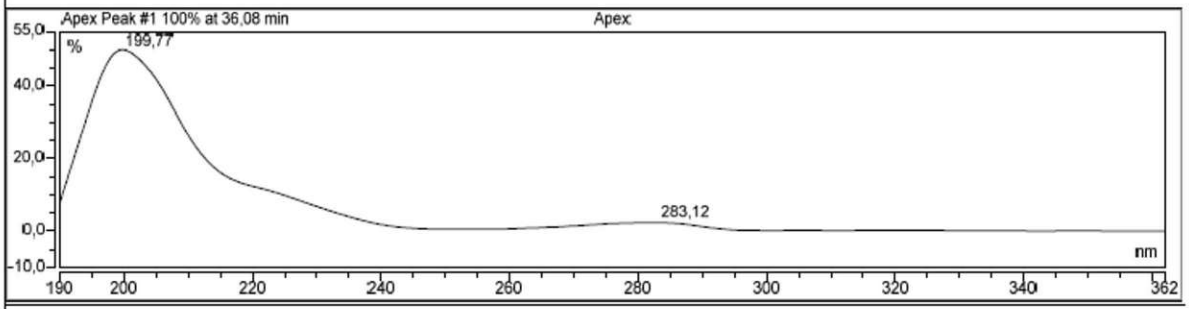
Instrument Method:	Hexane_IPA_99.9_0.1 _0.3mLmin_25C_50min-MK	*B %:*	0,1
Column:	OJ3	*C %:*	99,9
Run Time (min):	50,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

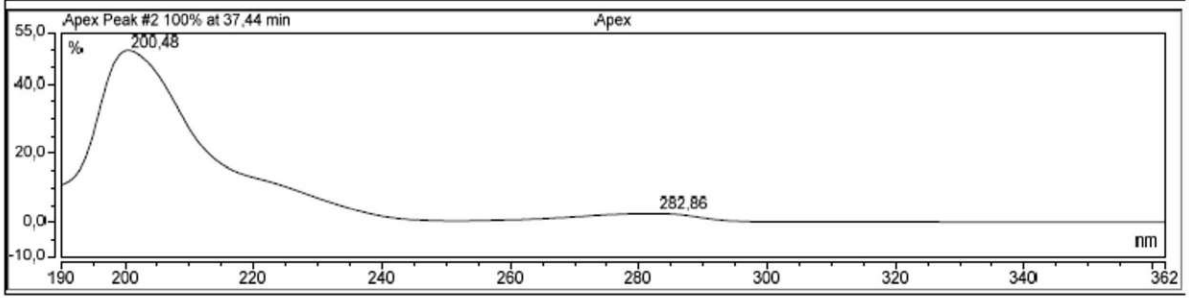
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		36,075	0,284	0,525	2,19	2,60
2		37,438	12,676	19,629	97,81	97,40
Total:			**12,960**	**20,154**	**100,00**	**100,00**



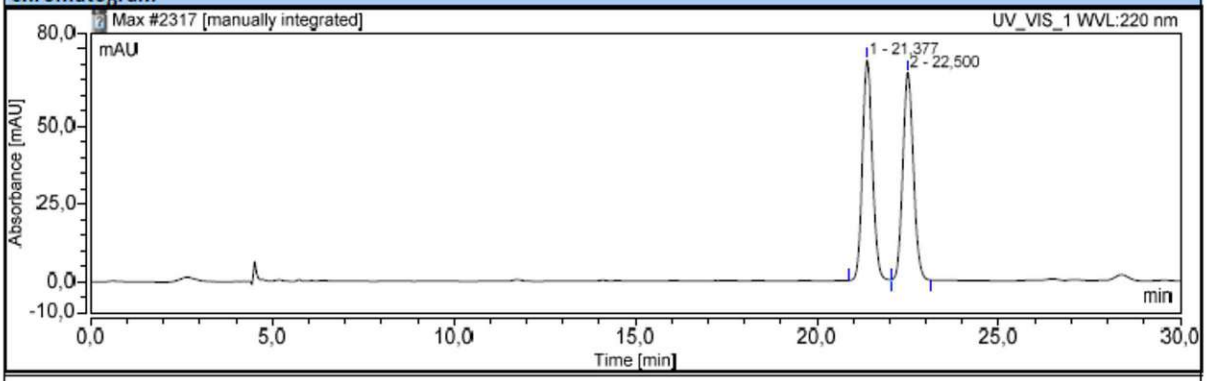


(E)-2-methyl-4-(pent-3-en-2-yl)phenol (116rac)

Chromatogram and Results

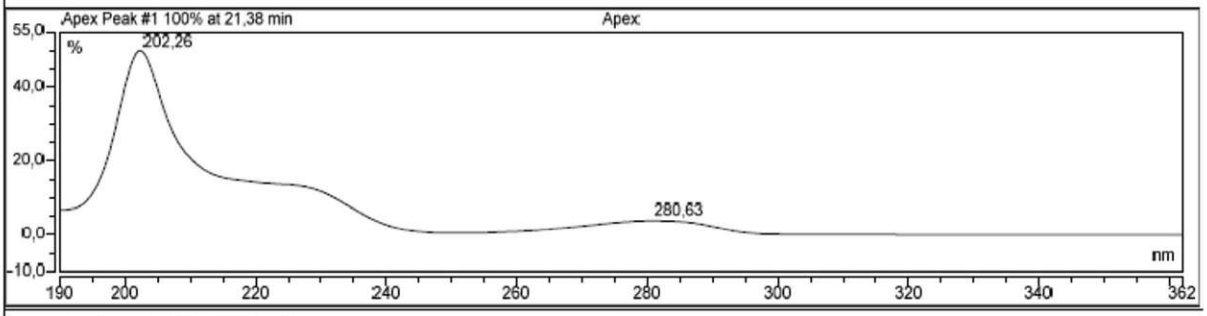
Instrument Method:	Hexane_EtOH_97_3_0.7mlmin_25C_30min-MK	*B %:*	0,0
Column:	OJ3	*C %:*	97,0
Run Time (min):	30,00	*D %:*	3,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

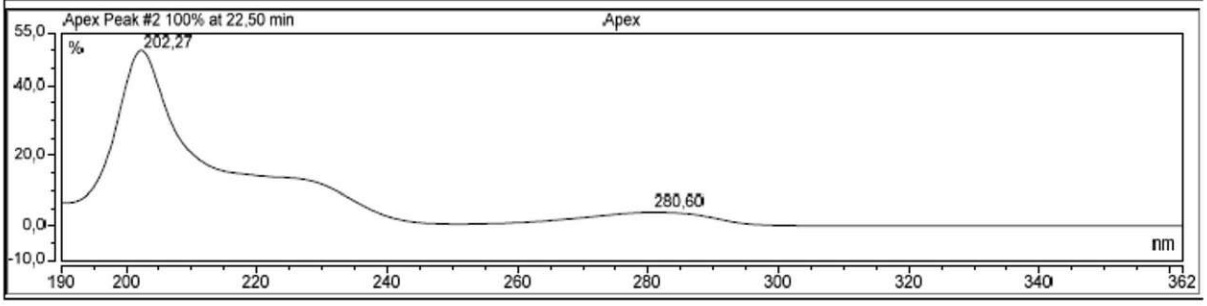
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21,377	22,681	70,986	50,04	51,48
2		22,500	22,646	66,902	49,96	48,52
Total:			**45,327**	**137,887**	**100,00**	**100,00**



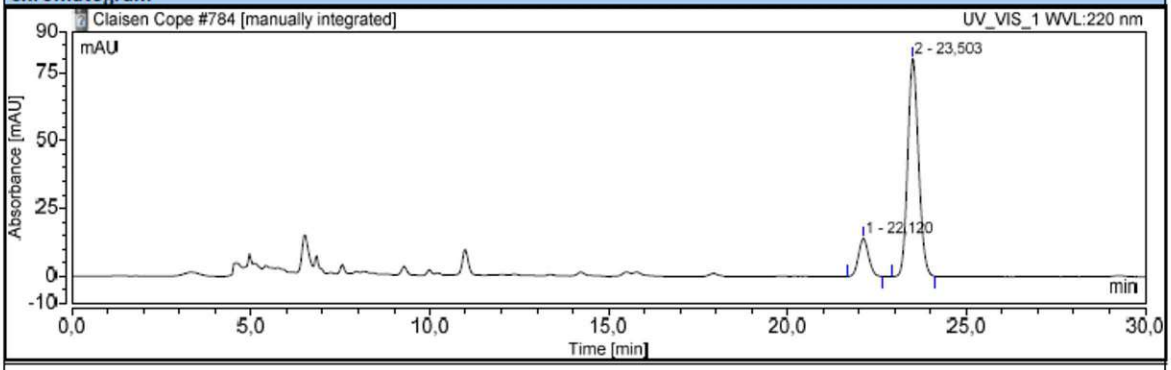


(R,E)-2-methyl-4-(pent-3-en-2-yl)phenol (116b)

Chromatogram and Results

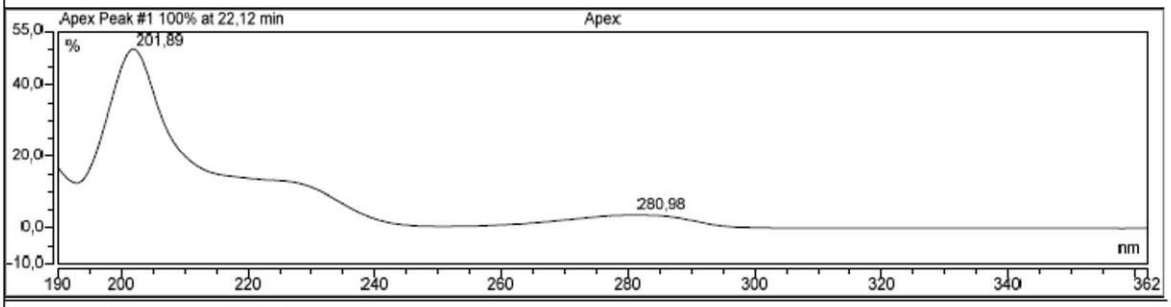
Instrument Method:	Hexane_EtOH_97_3_0.7mlmin_25C_30min-MK	*B %:*	0,0
Column:	OJ-3	*C %:*	97,0
Run Time (min):	30,00	*D %:*	3,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

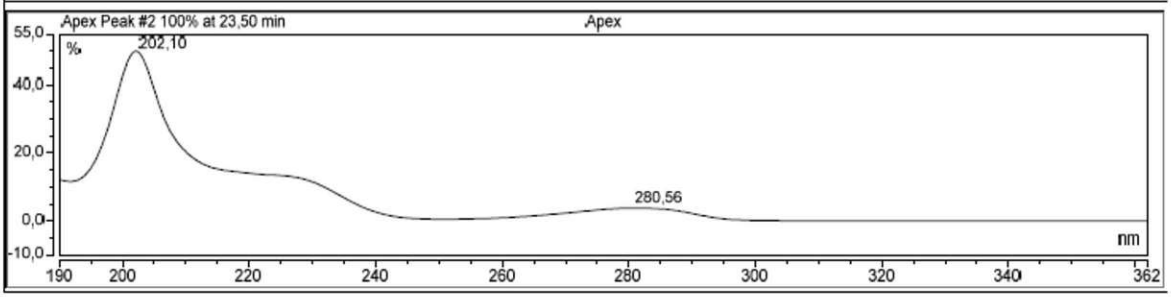
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		22,120	4,620	14,083	14,04	14,93
2		23,503	28,289	80,276	85,96	85,07
Total:			**32,909**	**94,359**	**100,00**	**100,00**



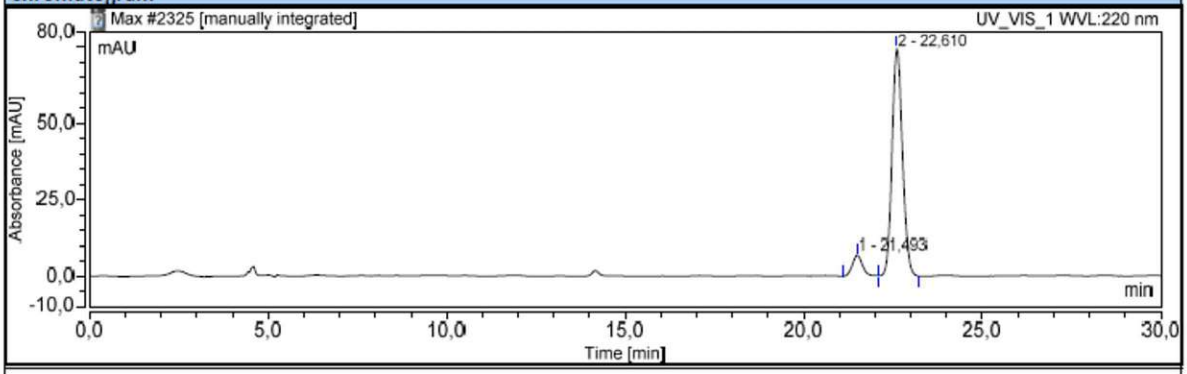


(R,E)-2-methyl-4-(pent-3-en-2-yl)phenol (116)

Chromatogram and Results

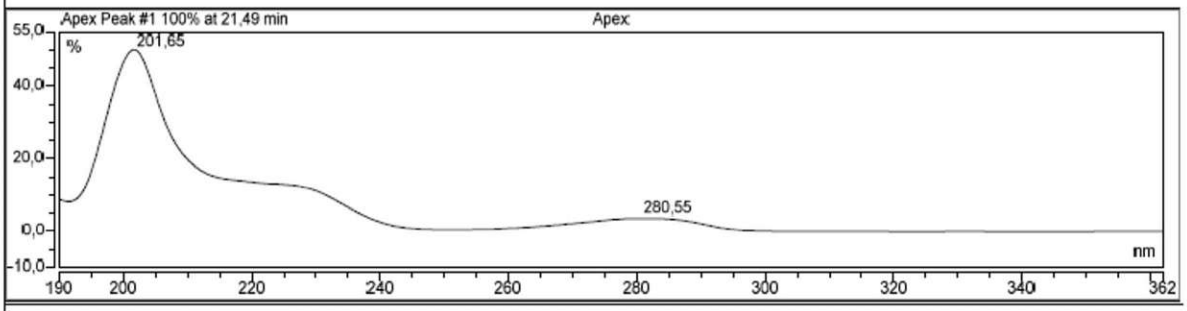
Instrument Method:	Hexane_EtOH_97_3_0.7mlmin_25C_30min-MK	*B %:*	0,0
Column:	OJ3	*C %:*	97,0
Run Time (min):	30,00	*D %:*	3,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

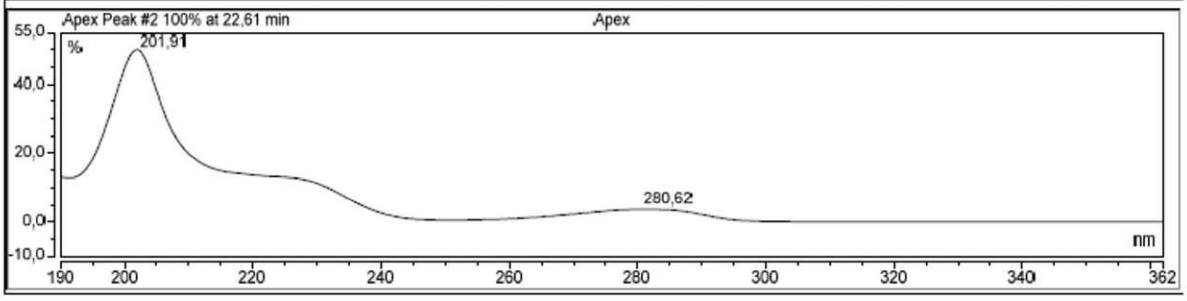
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21,493	2,329	7,093	8,42	8,68
2		22,610	25,321	74,646	91,58	91,32
Total:			**27,650**	**81,739**	**100,00**	**100,00**



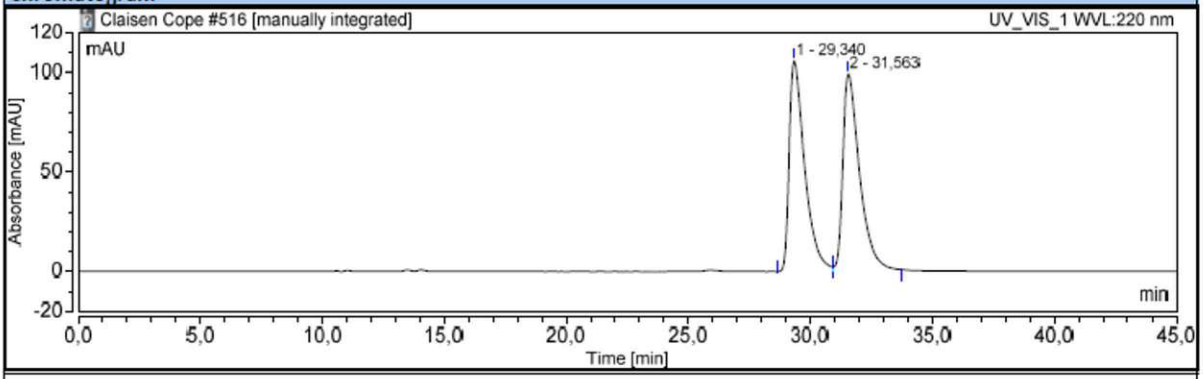


2-(cyclohex-2-en-1-yloxy)-1,3-dimethylbenzene (97rac)

Chromatogram and Results

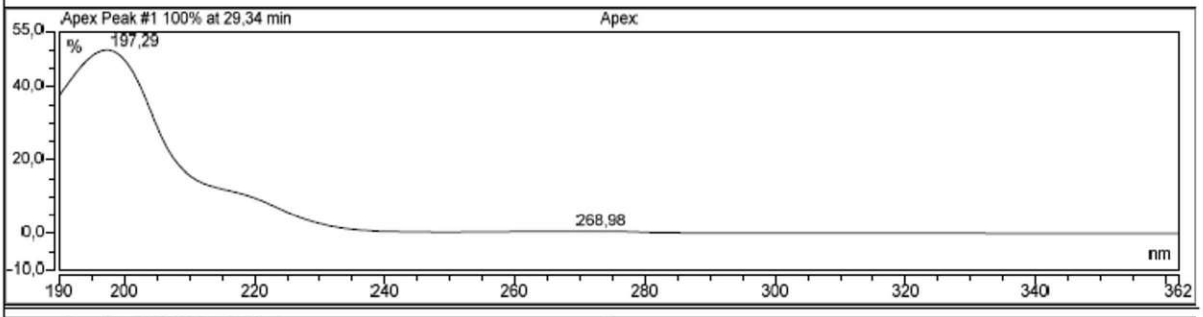
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min-MK	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

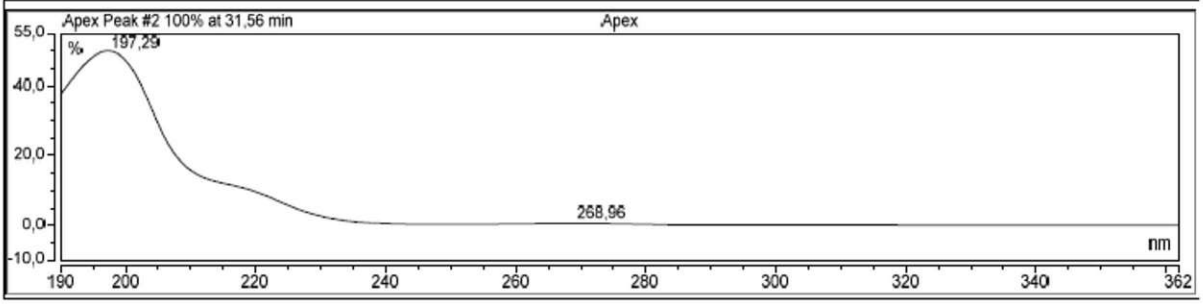
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		29,340	77,652	105,966	49,78	51,65
2		31,563	78,349	99,205	50,22	48,35
Total:			**156,001**	**205,170**	**100,00**	**100,00**



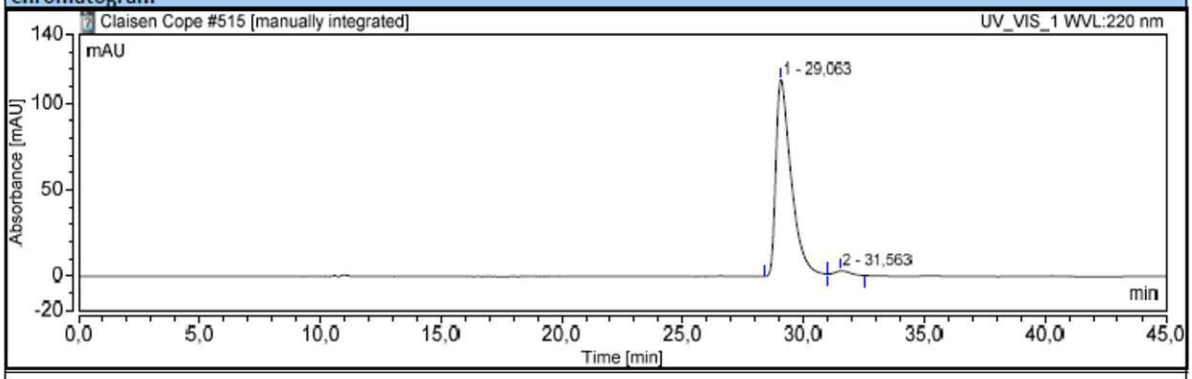


(S)-2-(cyclohex-2-en-1-yloxy)-1,3-dimethylbenzene (97)

Chromatogram and Results

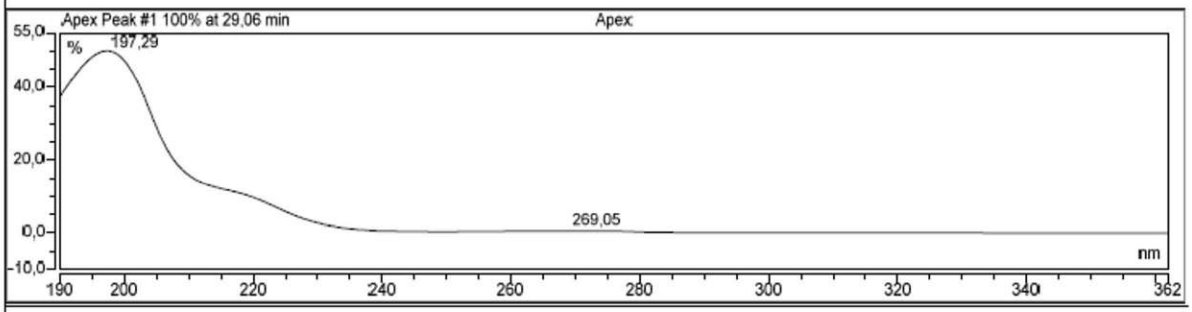
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min-MK	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

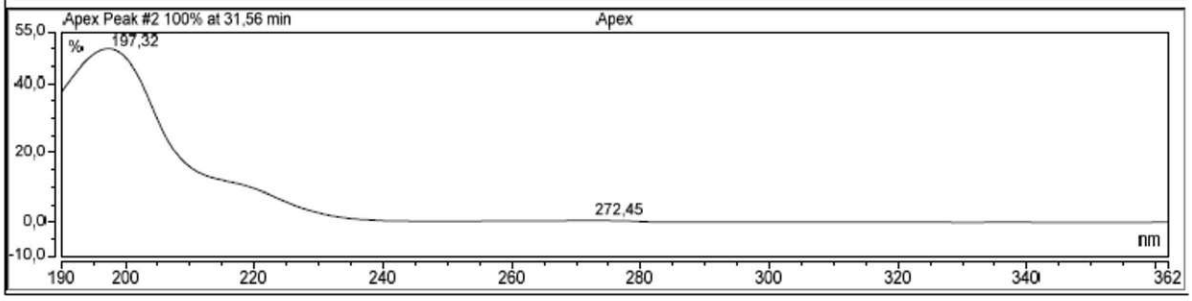
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		29,063	84,258	114,436	97,37	97,53
2		31,563	2,277	2,895	2,63	2,47
Total:			**86,535**	**117,330**	**100,00**	**100,00**



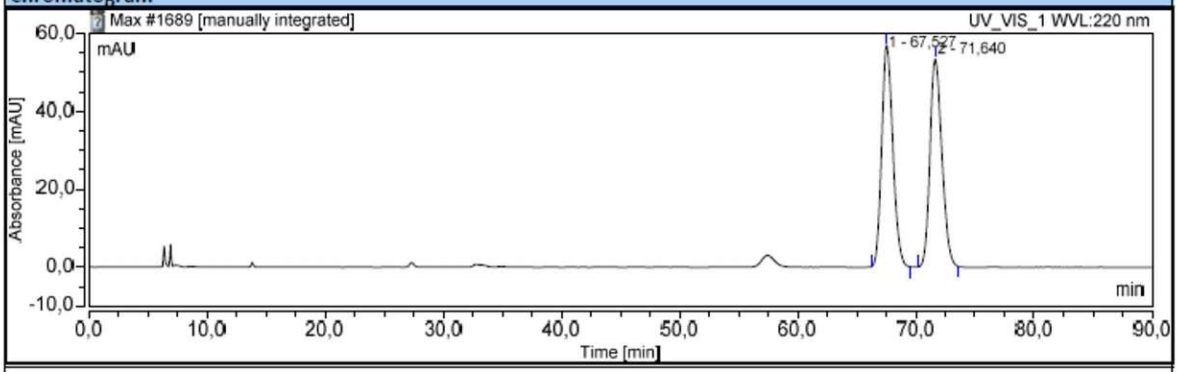


2-(2,6-diethylphenoxy)hexane-1,6-diol (147rac)

Chromatogram and Results

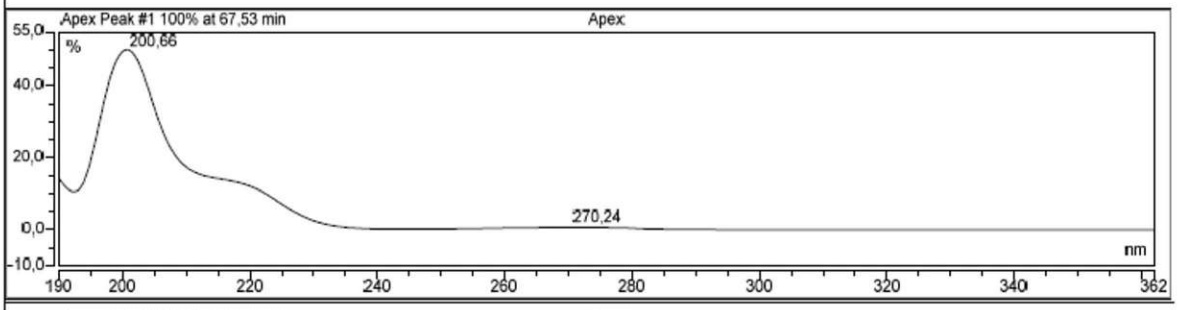
Instrument Method:	Heptane_EtOH_98.5_1.5_0.5mlmin_25C_90min	*B %:*	0,0
Column:	OJ3	*C %:*	0,0
Run Time (min):	90,00	*D %:*	1,5
Channel:	UV_VIS_1		
Wavelength:	287,26		

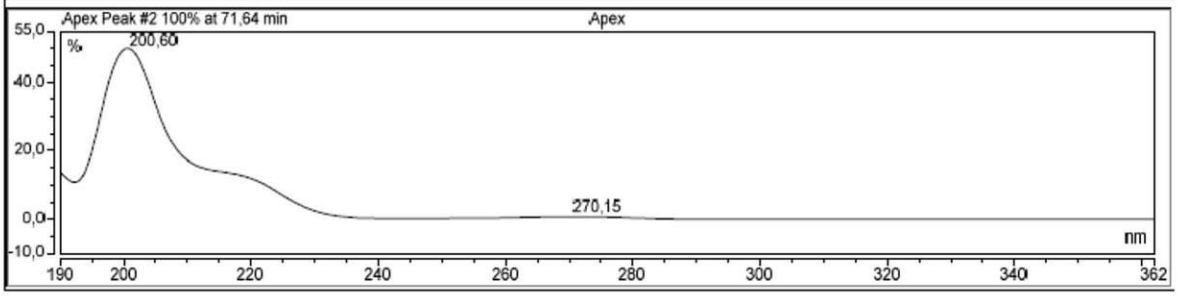
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		67,527	62,263	56,890	50,00	51,61
2		71,640	62,256	53,333	50,00	48,39
Total:			**124,519**	**110,223**	**100,00**	**100,00**



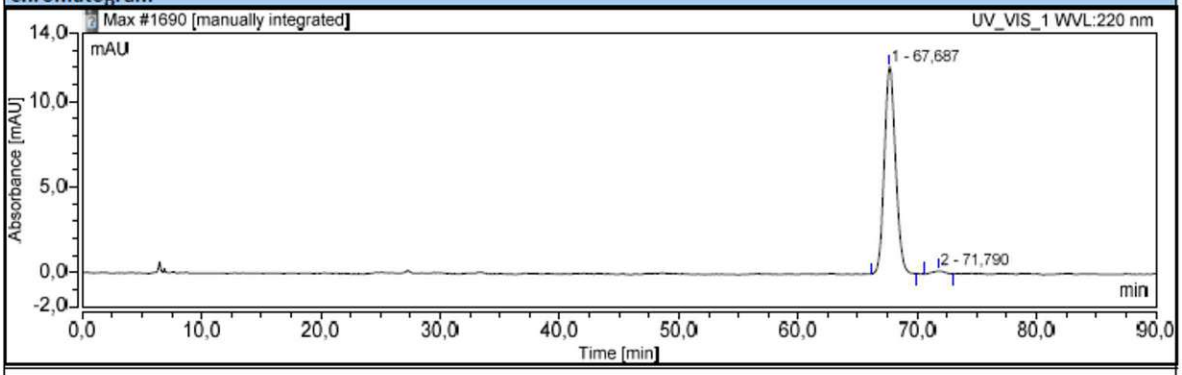


(R)-2-(2,6-diethylphenoxy)hexane-1,6-diol (147)

Chromatogram and Results

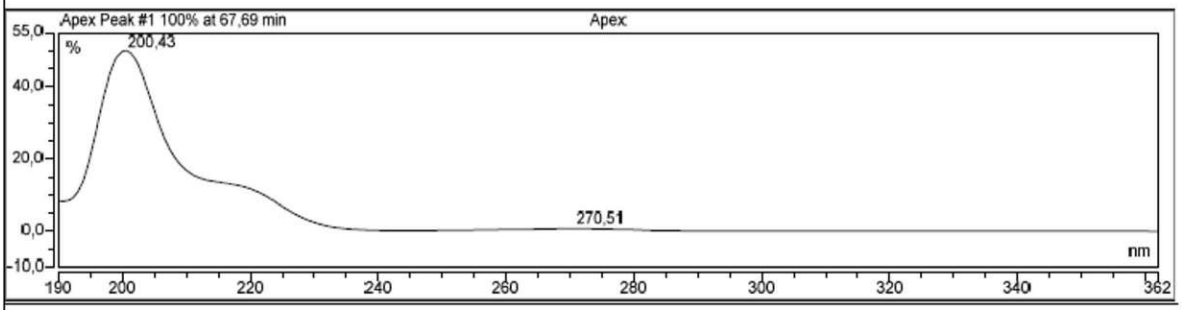
Instrument Method:	Heptane_EtOH_98.5_1.5_0.5mlmin_25C_90min	*B %:*	0,0
Column:	OJ3	*C %:*	0,0
Run Time (min):	90,00	*D %:*	1,5
Channel:	UV_VIS_1		
Wavelength:	287,26		

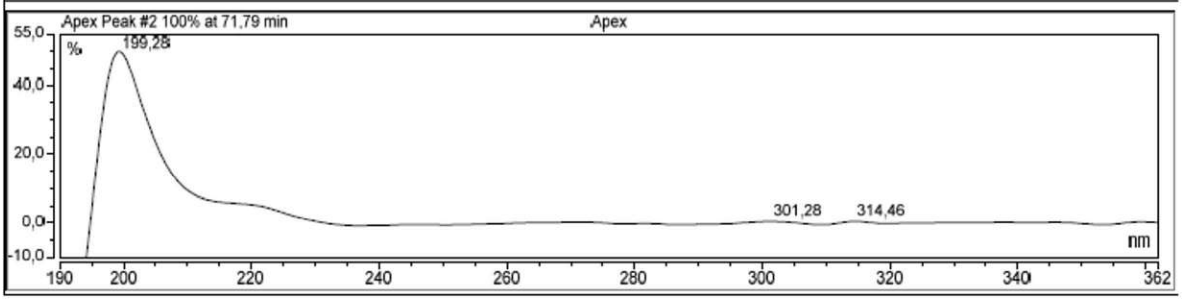
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		67,687	13,192	12,154	98,49	98,42
2		71,790	0,203	0,196	1,51	1,58
Total:			**13,395**	**12,350**	**100,00**	**100,00**



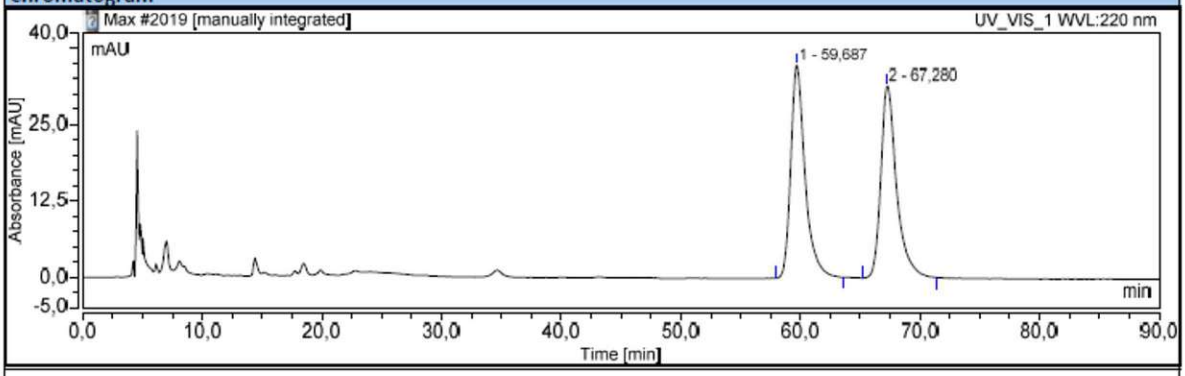


2-(2,6-diisopropylphenoxy)hexane-1,6-diol (148rac)

Chromatogram and Results

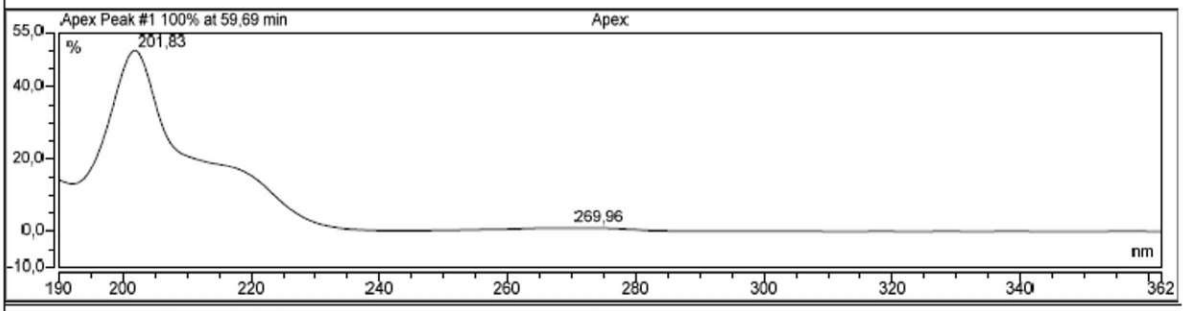
Instrument Method:	Hexane_IPA_98_2_0,7mlmin_25°C_90min	*B %:*	2,0
Column:	IA-3	*C %:*	98,0
Run Time (min):	90,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

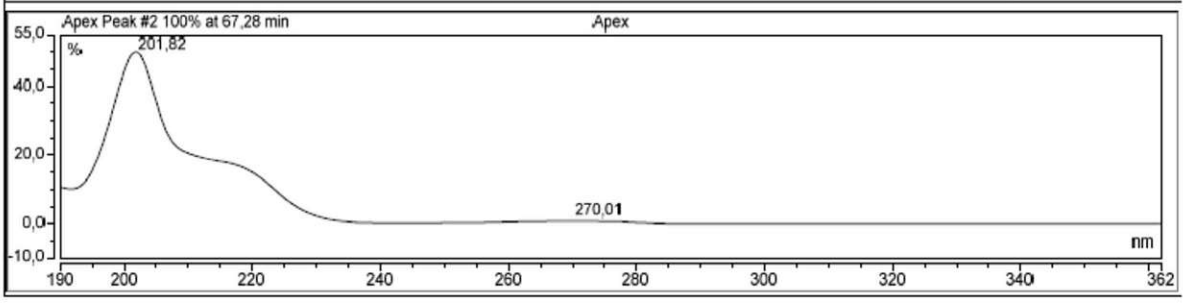
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		59,687	48,165	34,790	50,11	52,45
2		67,280	47,955	31,543	49,89	47,55
Total:			**96,120**	**66,333**	**100,00**	**100,00**



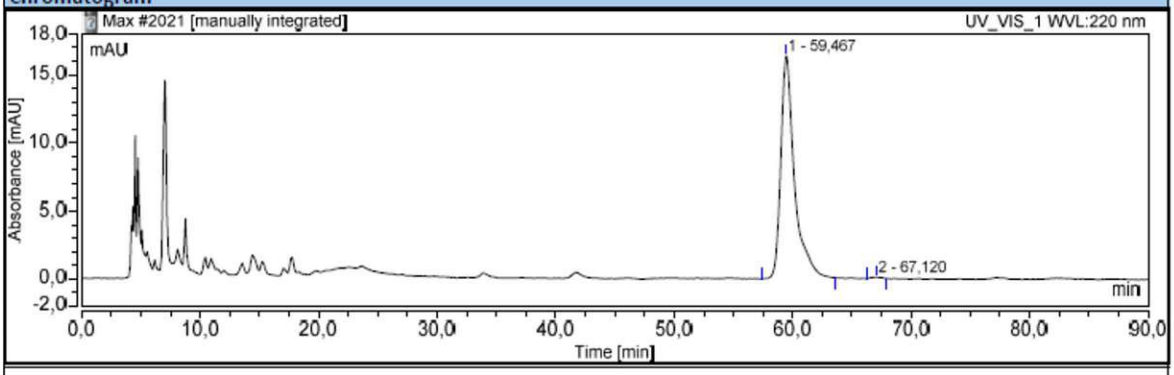


(R)-2-(2,6-diisopropylphenoxy)hexane-1,6-diol (148)

Chromatogram and Results

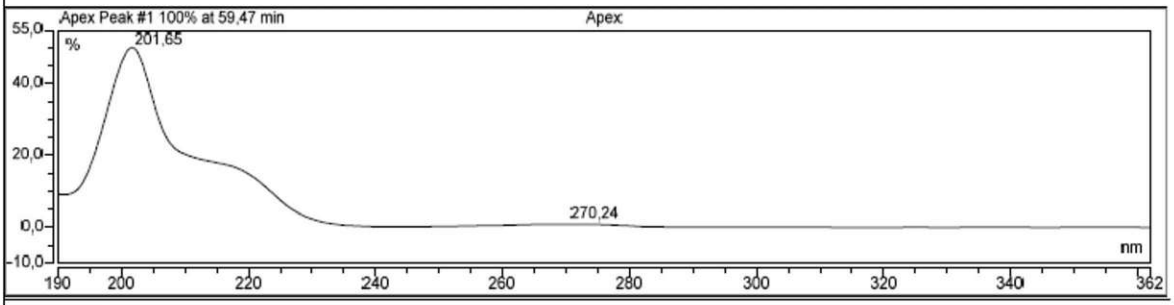
Instrument Method:	Hexane_IPA_98_2_0,7mlmin_25°C_90min	*B %:*	2,0
Column:	IA-3	*C %:*	98,0
Run Time (min):	90,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

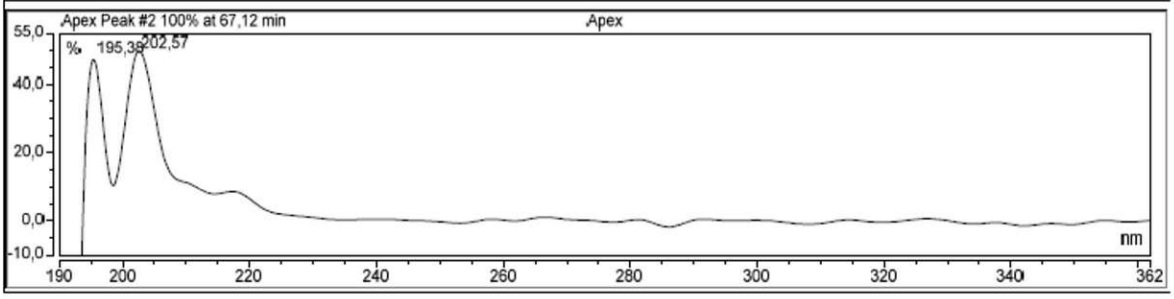
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		59,467	21,827	16,363	99,63	99,40
2		67,120	0,082	0,099	0,37	0,60
Total:			**21,909**	**16,462**	**100,00**	**100,00**



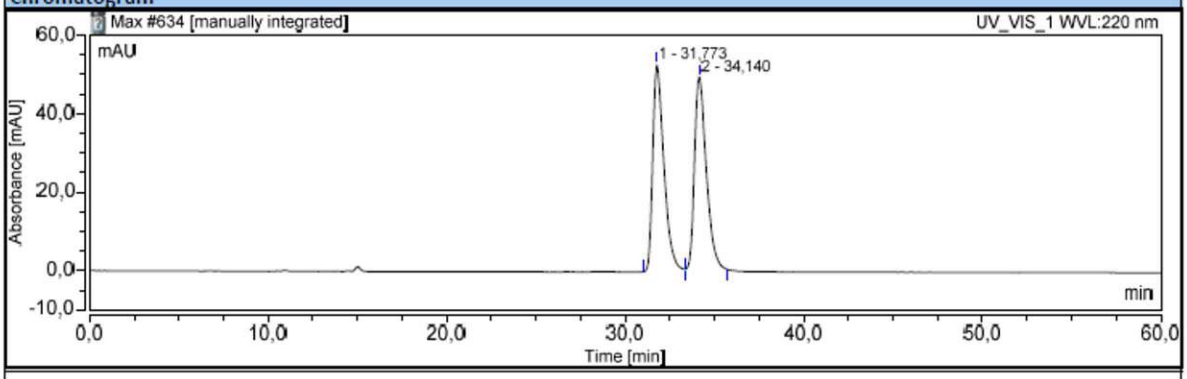


2-(cyclohex-2-en-1-yloxy)-1,2,4-trimethylbenzene (100rac)

Chromatogram and Results

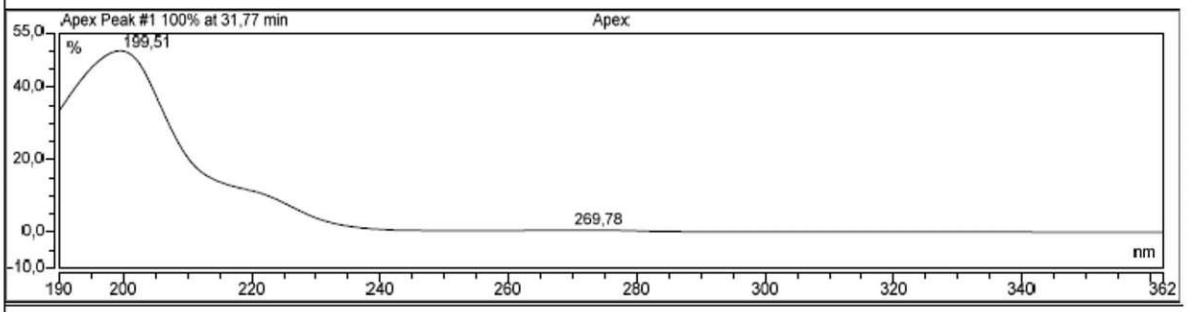
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_60min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	60,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

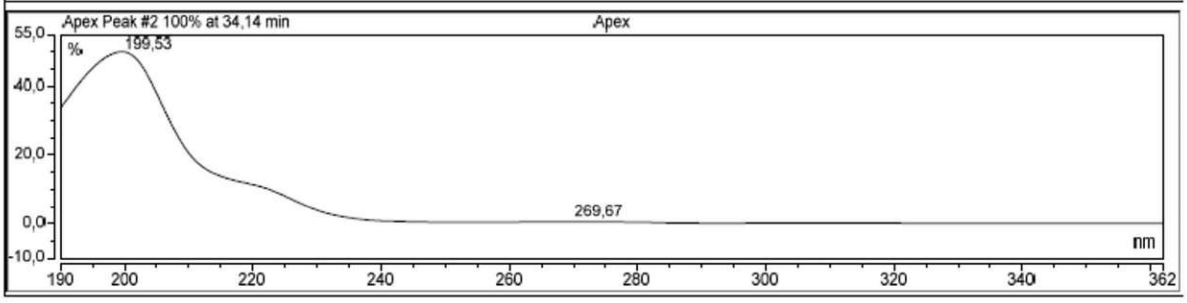
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		31,773	38,034	52,777	50,25	51,72
2		34,140	37,653	49,264	49,75	48,28
Total:			**75,687**	**102,041**	**100,00**	**100,00**



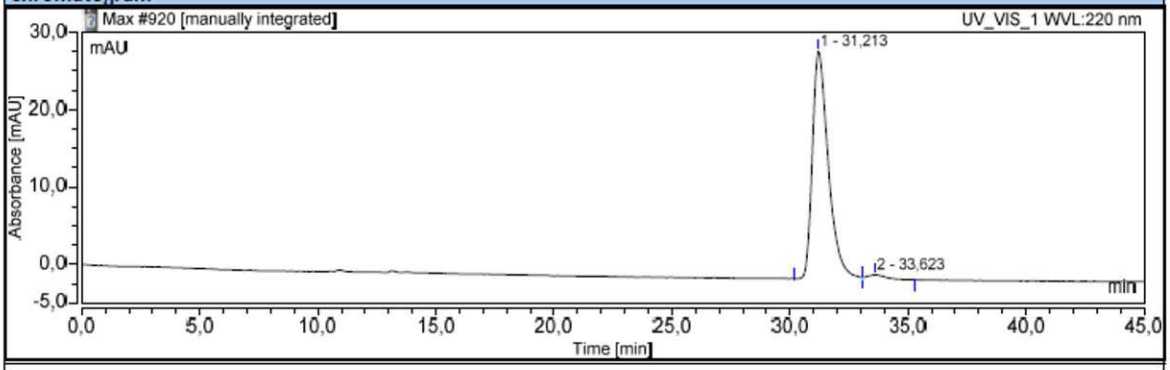


(S)-2-(cyclohex-2-en-1-yloxy)-1,3,4-trimethylbenzene (100)

Chromatogram and Results

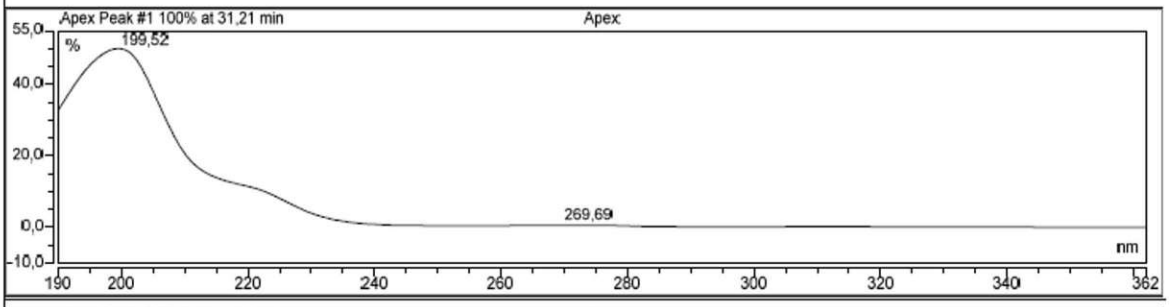
Instrument Method:	Heptane_IPA_99.9_0.1_0.3mlmin_25C_45min	*B %:*	0,1
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

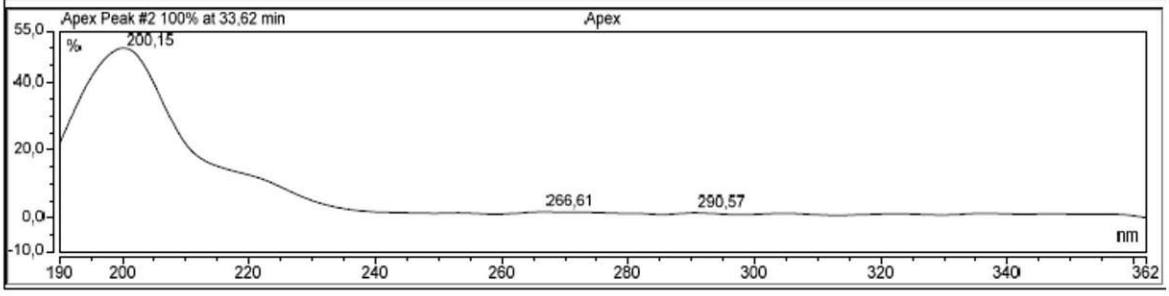
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		31,213	23,055	29,485	97,77	98,02
2		33,623	0,526	0,597	2,23	1,98
Total:			**23,581**	**30,082**	**100,00**	**100,00**



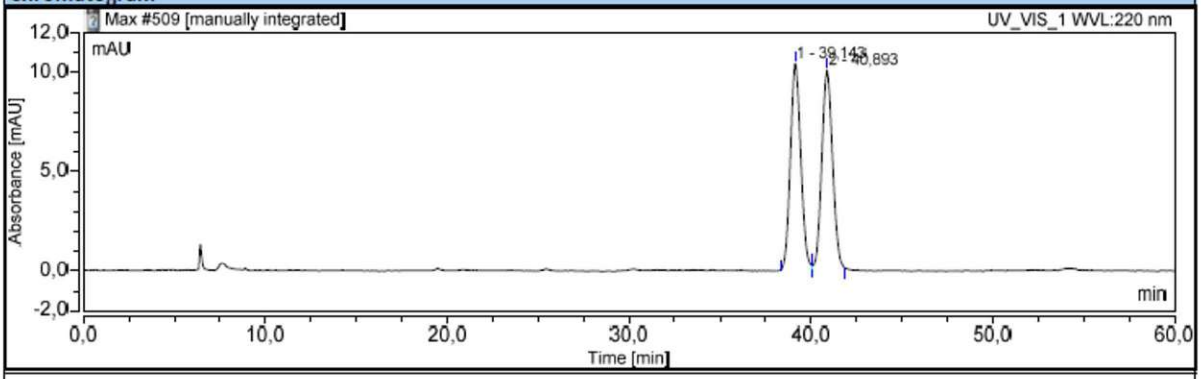


3,5-dimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (111rac)

Chromatogram and Results

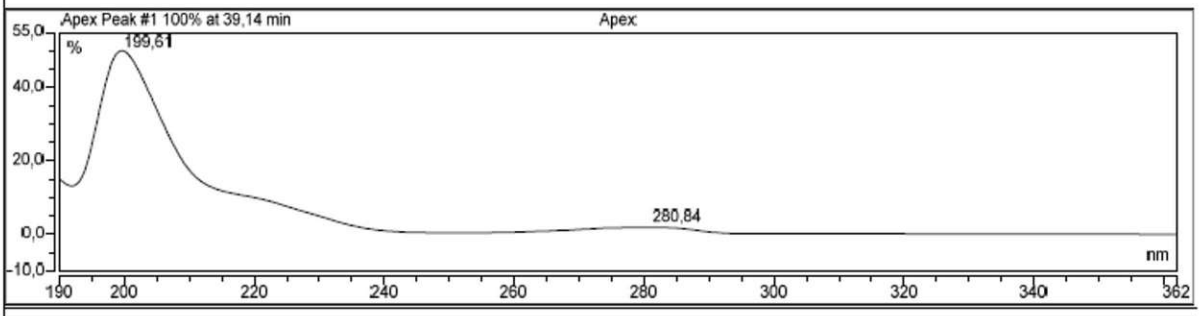
Instrument Method:	Hexane_IPA_99,5_0,5_05mlmin_25C_60min	*B %:*	0,5
Column:	OJ3	*C %:*	99,5
Run Time (min):	60,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

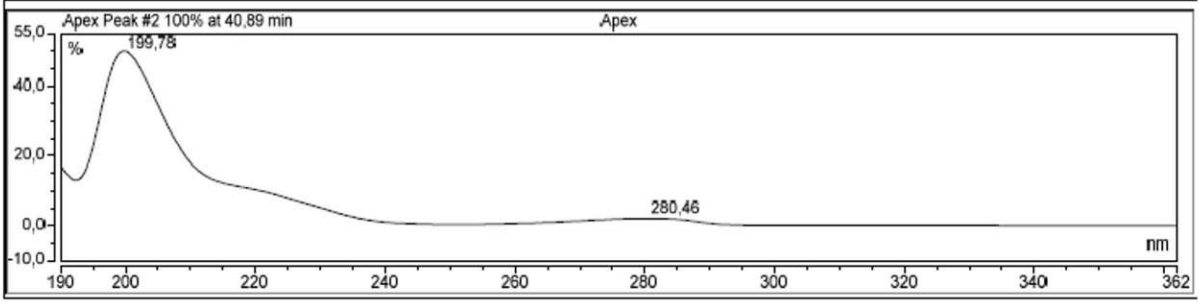
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		39,143	6,913	10,423	50,13	50,93
2		40,893	6,876	10,042	49,87	49,07
Total:			**13,789**	**20,464**	**100,00**	**100,00**



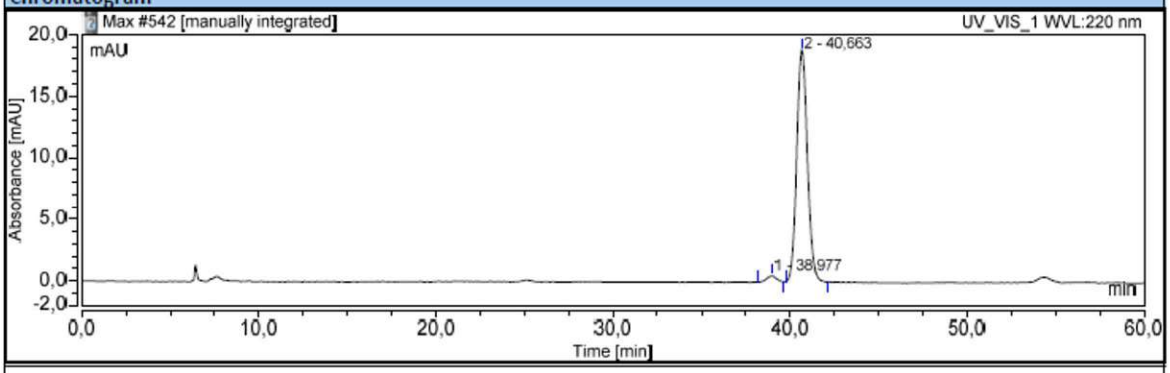


(S)-3,5-dimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (111)

Chromatogram and Results

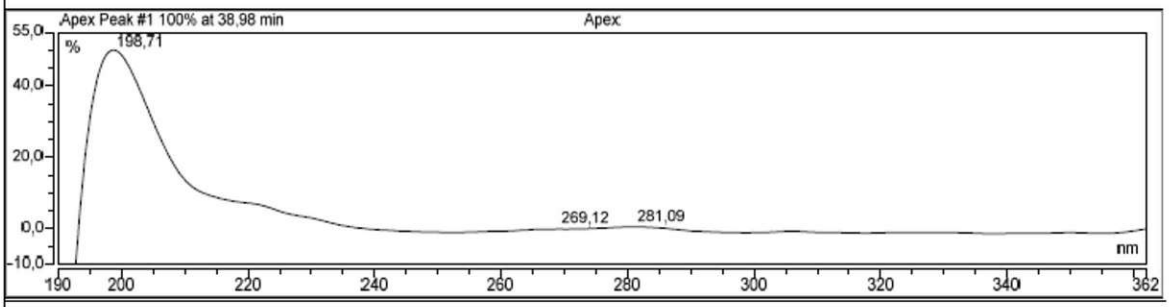
Instrument Method:	Hexane_IPA_99,5_0,5_05mlmin_25C_60min	*B %:*	0,5
Column:	OJ3	*C %:*	99,5
Run Time (min):	60,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

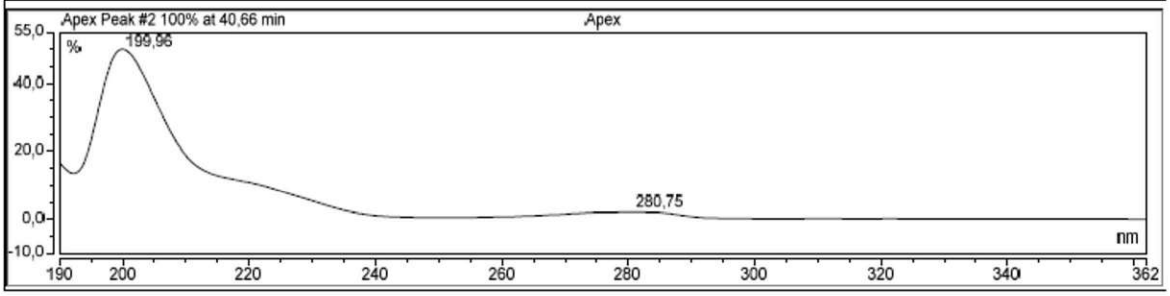
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		38,977	0,295	0,507	2,20	2,62
2		40,663	13,131	18,852	97,80	97,38
Total:			**13,426**	**19,359**	**100,00**	**100,00**



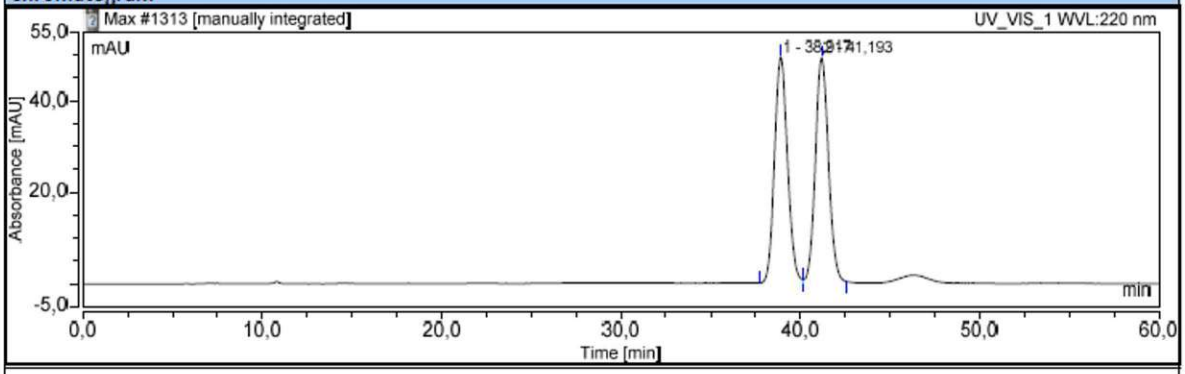


3,5-diethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (112rac)

Chromatogram and Results

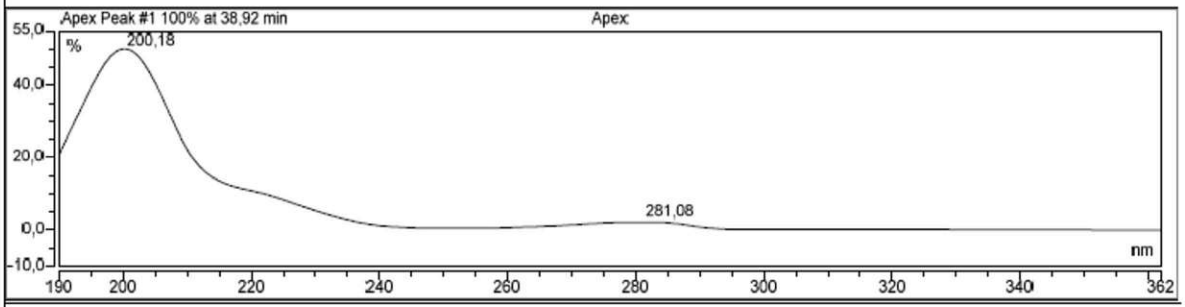
Instrument Method:	Hexane_EtOH_99.9_0.1_0.3mlmin_25C_60min	*B %:*	0,0
Column:	OJ-3	*C %:*	99,9
Run Time (min):	60,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

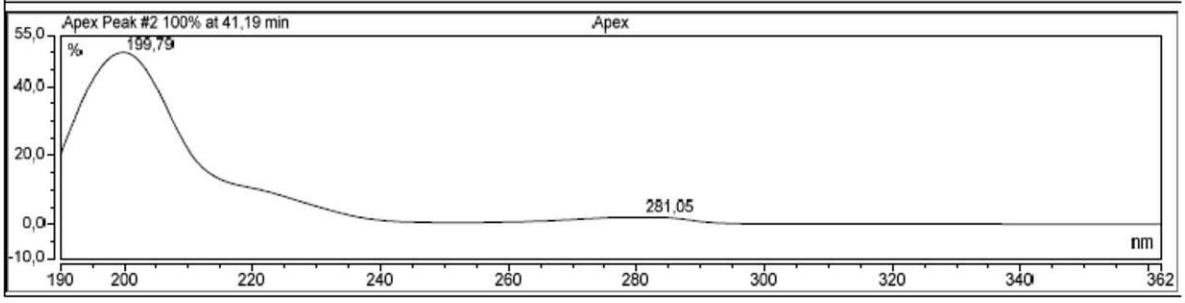
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		38,917	41,407	49,398	50,01	50,11
2		41,193	41,383	49,178	49,99	49,89
Total:			**82,790**	**98,576**	**100,00**	**100,00**



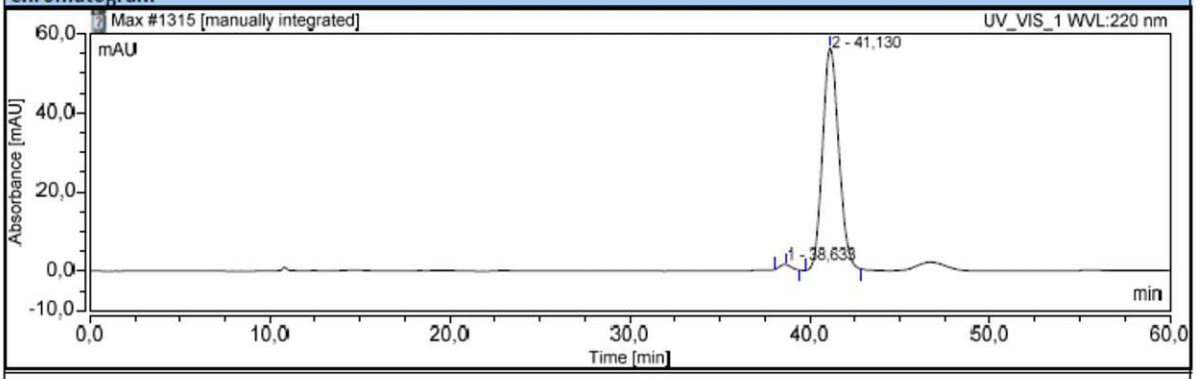


(S)-3,5-diethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (112)

Chromatogram and Results

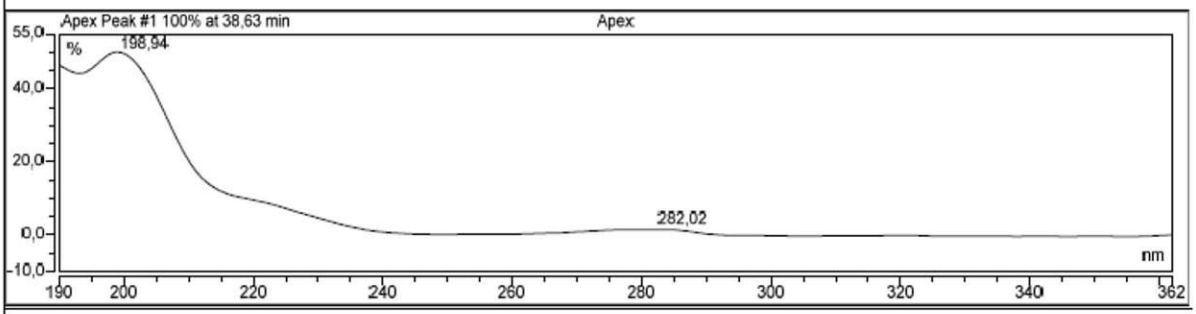
Instrument Method:	Hexane_EtOH_99.9_0.1_0.3mlmin_25C_60min	*B %:*	0,0
Column:	OJ-3	*C %:*	99,9
Run Time (min):	60,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

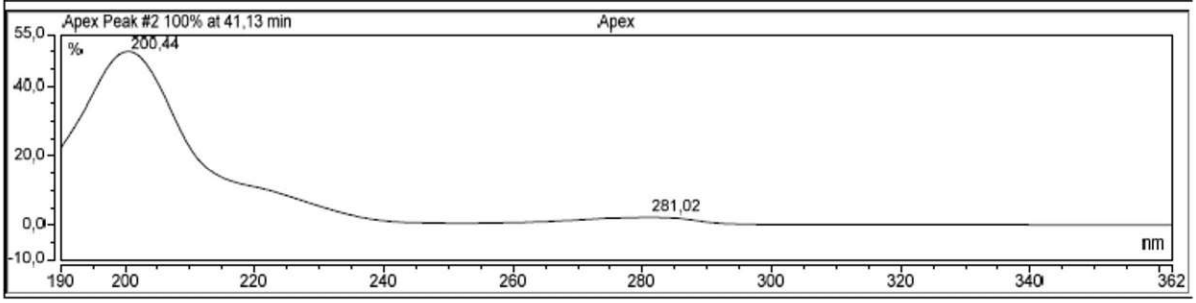
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		38,633	0,911	1,311	1,53	2,29
2		41,130	58,581	56,044	98,47	97,71
Total:			**59,492**	**57,356**	**100,00**	**100,00**



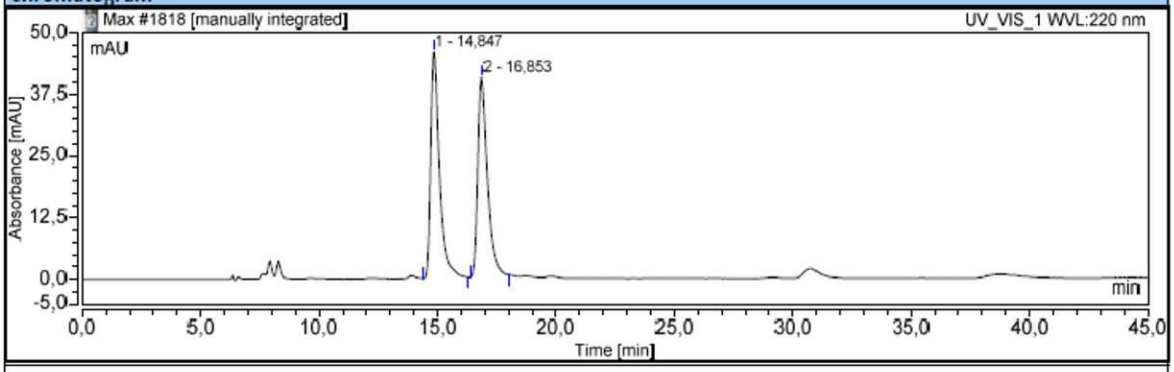


3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl 4-bromobenzoate (150rac)

Chromatogram and Results

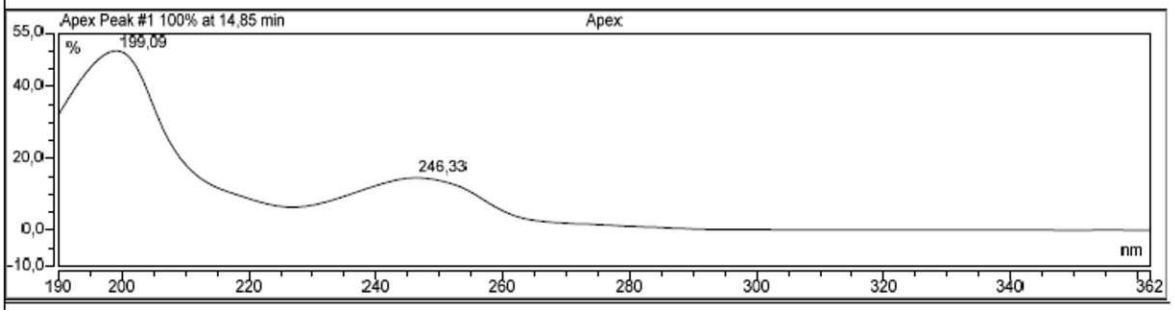
Instrument Method:	Heptane_EtOH_99.9_0.1_0.5mlmin_25C_45min	*B %:*	0,0
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

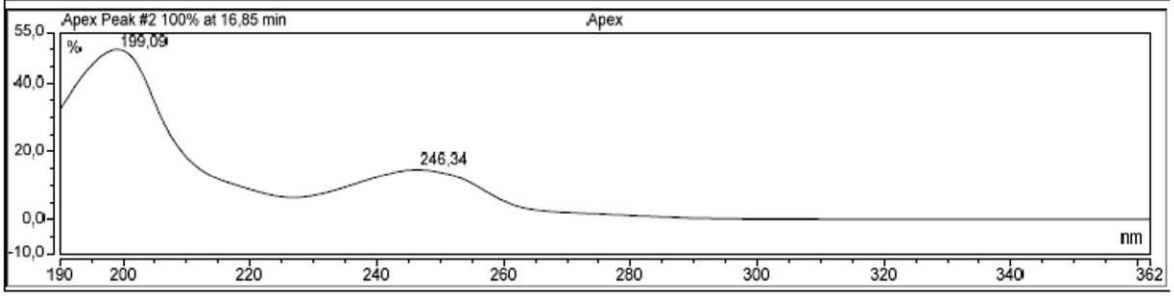
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14,847	19,382	45,940	50,86	53,15
2		16,853	18,724	40,500	49,14	46,85
Total:			**38,105**	**86,441**	**100,00**	**100,00**



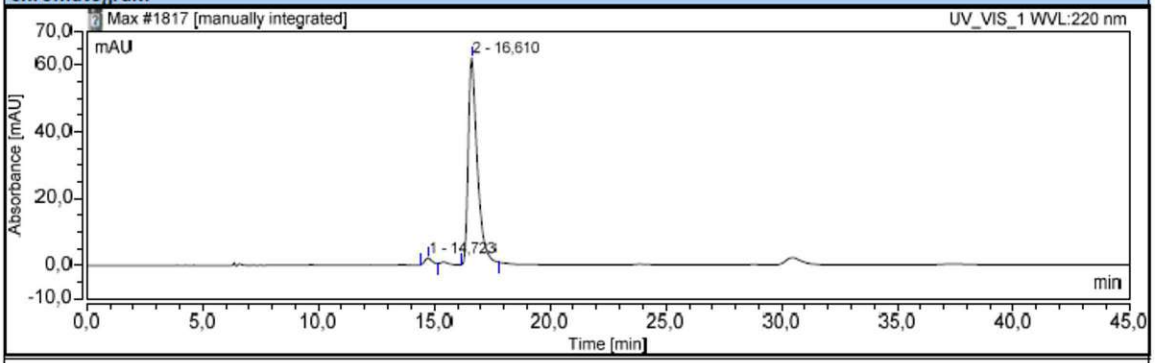


(S)-3,5-diisopropyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl 4-bromobenzoate (150)

Chromatogram and Results

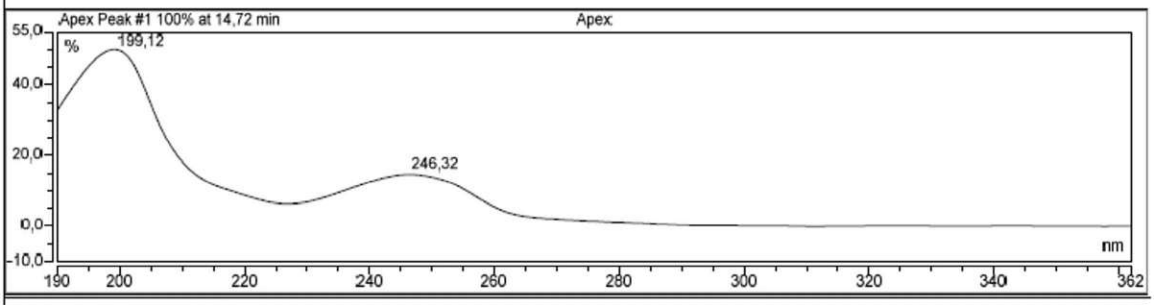
Instrument Method:	Heptane_EtOH_99.9_0.1_0.5mlmin_25C_45min	*B %:*	0,0
Column:	IB	*C %:*	0,0
Run Time (min):	45,00	*D %:*	0,1
Channel:	UV_VIS_1		
Wavelength:	287,26		

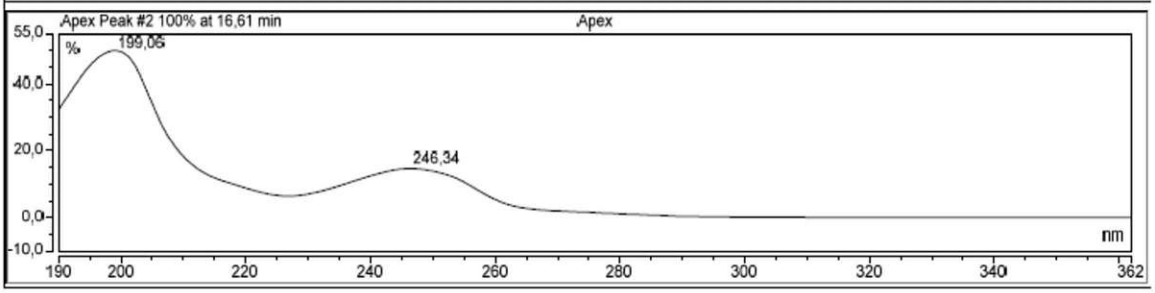
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14,723	0,784	2,114	2,75	3,31
2		16,610	27,764	61,766	97,25	96,69
Total:			**28,548**	**63,880**	**100,00**	**100,00**



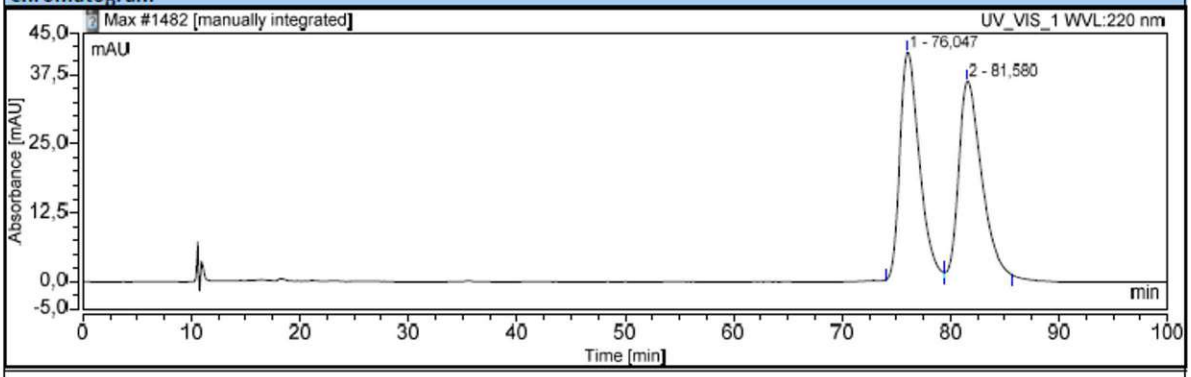


2,3,5-trimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (114rac)

Chromatogram and Results

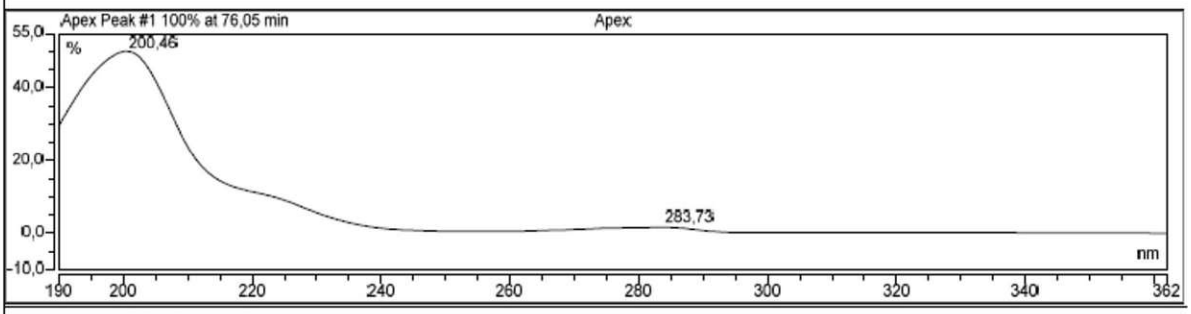
Instrument Method:	Heptane_IPA_99.8_0.2_0.3mlmin_25C_100min	*B %:*	0,2
Column:	OJ-3	*C %:*	0,0
Run Time (min):	100,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

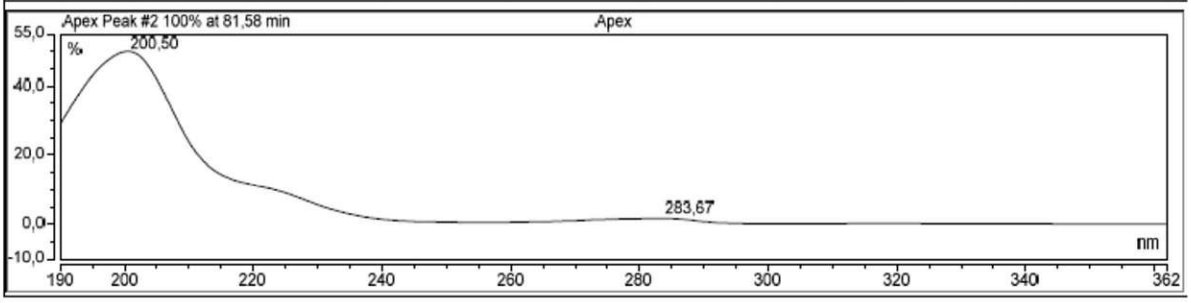
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		76,047	85,185	41,207	50,05	53,78
2		81,580	85,023	35,420	49,95	46,22
Total:			**170,208**	**76,627**	**100,00**	**100,00**



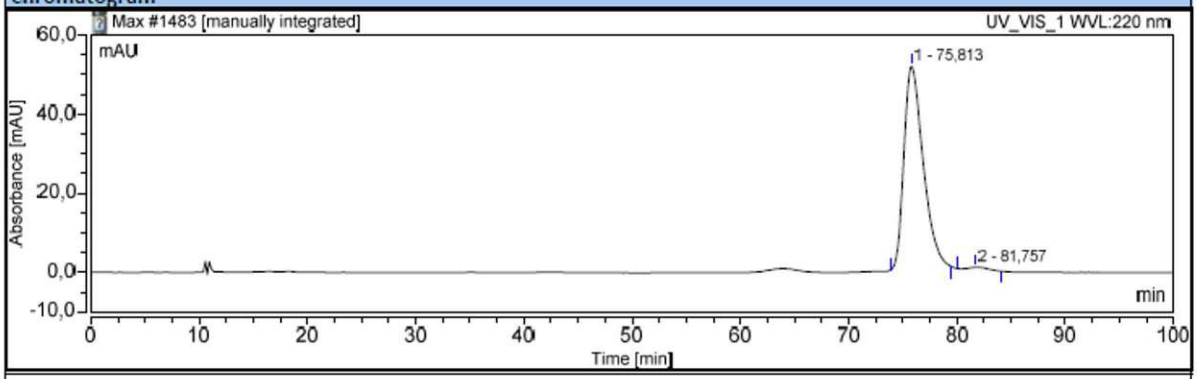


(S)-2,3,5-trimethyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-ol (114)

Chromatogram and Results

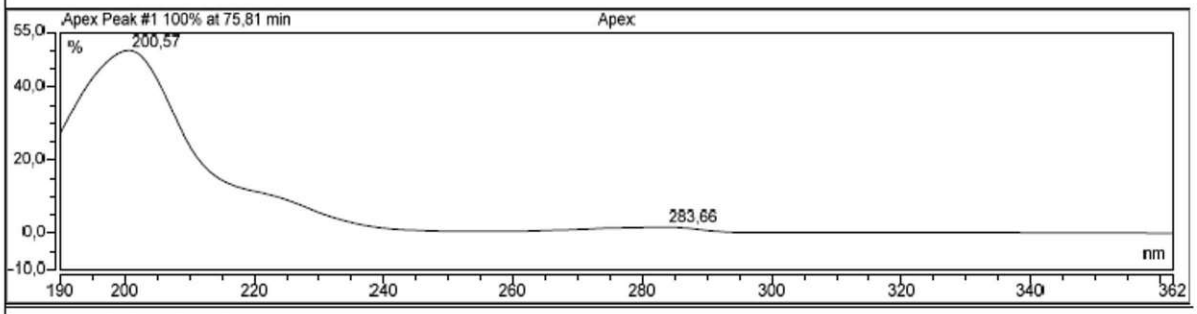
Instrument Method:	Heptane_IPA_99.8_0.2_0.3mlmin_25C_100min	*B %:*	0,2
Column:	OJ-3	*C %:*	0,0
Run Time (min):	100,00	*D %:*	0,0
Channel:	UV_VIS_1		
Wavelength:	287,26		

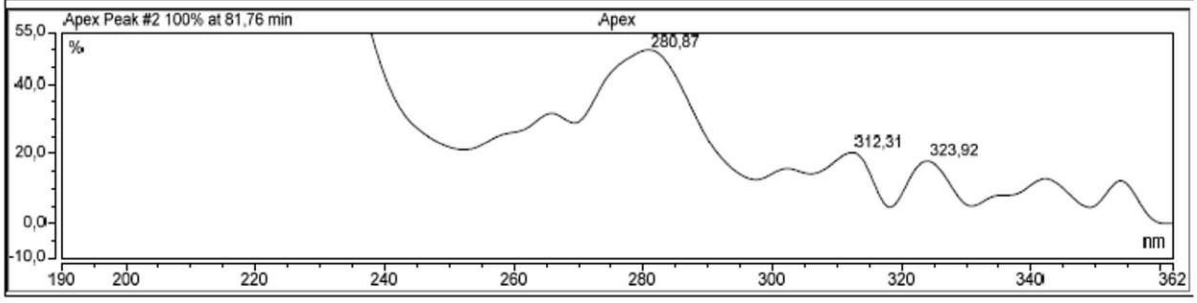
Chromatogram

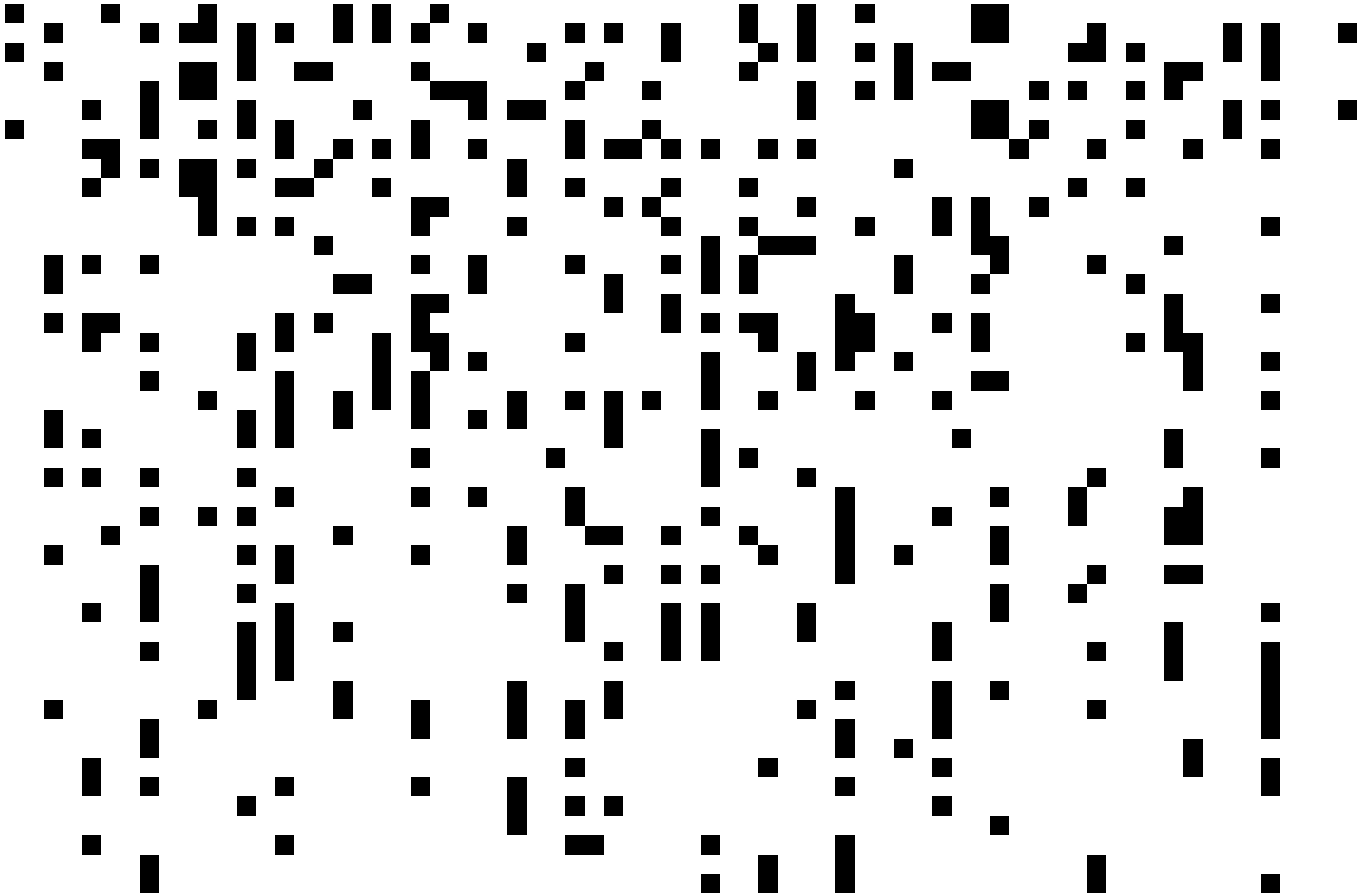


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		75,813	105,418	51,314	98,83	98,75
2		81,757	1,246	0,648	1,17	1,25
Total:			**106,664**	**51,962**	**100,00**	**100,00**







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