PALLADIUM CATALYZED SYNTHESIS OF ALKENE AND ALKYNE DERIVATIVES FROM TERMINAL ALKYNES

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF PHILOSOPHY (M. PHIL) IN CHEMISTRY

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Farhana Hoque

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Farhana Hoque
Author

Dedicated
to
my parents

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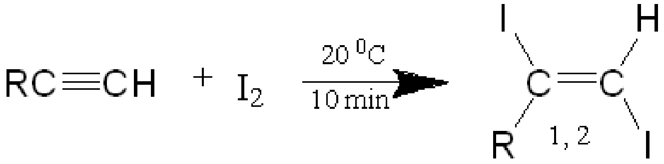
Thesis title: Palladium catalyzed synthesis of alkene and alkyne derivatives from terminal alkynes.

Abstract

Arylalkynes are very useful intermediates for the preparation of important compounds including natural products, pharmaceuticals, oligomers, polymers. Their derivatives are versatile compounds in synthetic organic chemistry, and hence, various methods for their synthesis have been explored. Palladium-catalyzed carbon-carbon bond formations are very useful methods for constructing higher molecules such as materials and drugs for modern chemical and medical applications. Here, it is desired to develop the methods of synthesis of alkene and alkyne derivatives through palladium catalyzed reactions. For this purpose, iodo compounds [1,2-diiodo-1-phenylethene; 1,2-diiodo-1-heptene and 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene] were synthesized by the iodination of their parent corresponding alkynes using molecular iodine (I_2). The palladium-catalyzed cross-coupling reaction of the starting materials (1,2-diiodo-1-phenylethene and 1,2-diiodo-1-heptene) with terminal alkynes (phenylacetylene, 1-hexyne, 1-heptyne) or alkyl acrylate (methyl acrylate, ethyl acrylate) were carried out in the presence of bis (triphenyl phosphine) palladium (II) chloride, copper (I) iodide, and triethylamine in DMF or CH_2Cl_2 at 80°C for 24 h under nitrogen atmosphere to yield alkenyne and alkenoate derivatives. Copper (I) iodide was not used for the synthesis of alkenoate derivatives,

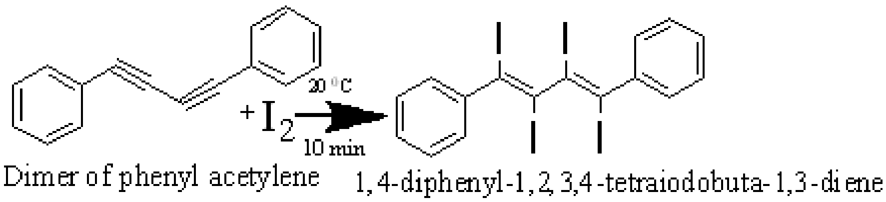
The iodination reaction of terminal alkynes is shown in Scheme-1



Scheme-1

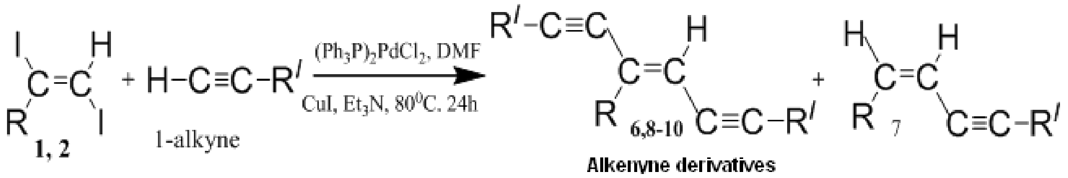
Here, R = C_6H_5, and $CH_3(CH_2)_4$

The 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene can be prepare as the same way (Scheme-2).



Scheme-2

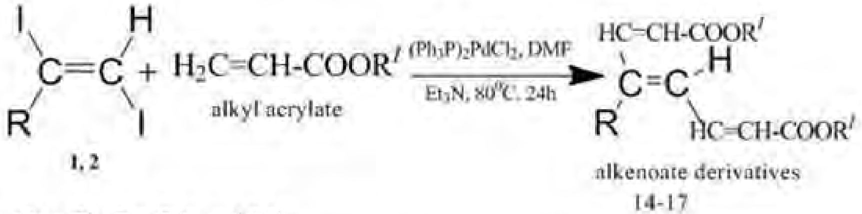
The coupling reactions are shown in Scheme-3 (for alkenyne products) and Scheme-4 (for alkenoate products).



Here, R = C_6H_5, $CH_3(CH_2)_4$; $R^{/}$ = C_6H_5, $CH_3(CH_2)_3$ and $CH_3(CH_2)_4$
1-alkynes are phenylacetylene, 1-hexyne and 1-heptyne.

Compound	R	$R^{/}$
6	C_6H_5	C_6H_5
7	C_6H_5	C_6H_5
8	C_6H_5	CH_3-$(CH_2)_3$
9	C_6H_5	CH_3-$(CH_2)_4$
10	CH_3-$(CH_2)_4$	C_6H_5

Scheme-3



Here, $R^{/}$ = CH_3, C_2H_5 and C_4H_9.
The alkyl acrylates are methyl acrylate, ethyl acrylate and butyl acrylate.

Compound	R	$R^{/}$
14	C_6H_5	CH_3
15	C_6H_5	CH_2-CH_3
16	C_6H_5	CH_3-$(CH_2)_3$
17	CH_3-$(CH_2)_4$	CH_2-CH_3

Scheme-4

The synthesized compounds were characterized based on analytical data obtained from IR, UV, ^{1}HNMR, ^{13}CNMR spectra and melting point.

Summary

Investigation incorporated in this dissertation titled, "Palladium catalyzed synthesis of alkene and alkyne derivatives from terminal alkynes" have been presented in three chapters. The first chapter is introductory section, in which the back ground, biological action and the important synthesis are presented. The second chapter deals with rationale, results and discussion, mechanism, and conclusion for the synthesis of iodo compounds [1,2-diiodo-1-phenylethene; 1,2-diiodo-1-heptene and 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene] and their palladium-catalyzed coupling products (alkenyne and alkenoate derivatives). The third chapter deals with the detailed methodologies and experimental procedure for the synthesis of the starting materials, their coupling products, spectra, and reference.

Chapter I

It represents the importance and synthesis of 1,2-diiodo-1-phenylethene; 1,2-diiodo-1-heptene and 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene; and their palladium-catalyzed coupling products (and alkenoate derivatives). The palladium-catalyzed coupling of haloarenes and haloalkenes with alkenes known as Heck reaction is well established. The Sonogashira coupling reaction of terminal alkynes with synthesis provides an efficient route of arylalkynes. Numerous applications to terminal product synthesis have been reported including the construction of complex enediyne antibiotic. Palladium catalysts are the pathway to compounds that cannot otherwise be easily synthesized. They can synthesize industrial compounds: pharmaceuticals anti-cancer, anti-oxidant, anti-fungal, UV absorbers.

Chapter II

In this section the results and discussion are presented. Here a convenient approach is discussed for the synthesis of alkene and alkyne derivatives through palladium catalyzed reaction of starting materials or iodo compounds [1,2-diiodo-1-phenylethene (**1**); 1,2-diiodo-1-heptene (**2**) and 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene (**18**)] with terminal alkynes (phenylacetylene, 1-hexyne, 1-heptyne) or alkyl acrylate (methyl acrylate, ethyl acrylate). The yields (%) of the condensation reactions are slightly higher for phenyl acetylene compared with 1-hexyne and 1-heptyne with different aryl and alkyl iodide. For the condensation reaction between aryl iodide and phenyl acetylene showed faster reaction compared with 1-hexyne or 1-heptyne in the

identical condition. The spectral data of the alkenyne and alkenoate derivatives are discussed in this chapter.

Chapter III

In the experimental section the general procedure for the synthesis of palladium catalyzed alkene and alkyne derivatives is described. For this purpose first of all, different aryl iodide and alkyl iodide were synthesized from their corresponding alkynes. The palladium catalyzed coupling reactions were carried out by stirring the mixture of starting material (any one of the compound **1, 2**) and 1-alkyne (phenylacetylene, 1-hexyne, 1-heptyne) or alkyl acrylate (methyl acrylate, ethyl acrylate) (3 equiv.) in dichloromethane (10 ml) or DMF (4 ml) in the presence of bis (triphenyl phosphine) palladium(II) chloride (3.5 mol%), copper (I) iodide (8 mol%), and triethylamine (4 equiv.) for 24 hr at 80ºC. After usual work up purification on column chromatography over silica gel the final products **6-10** (alkenyne derivatives) and **14-17** (alkenoate derivatives) were obtained in good yields. For alkyl acrylate, copper (I) iodide was not used.

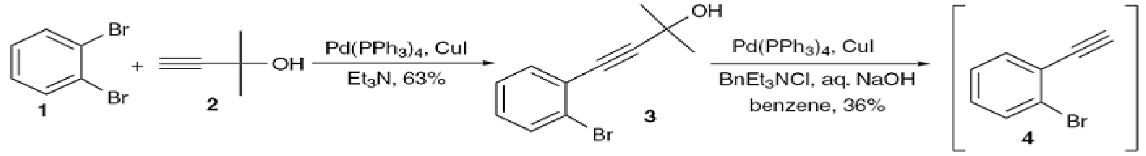
The synthesized compounds were characterized based on analytical data obtained from IR, UV, ^{1}HNMR, ^{13}CNMR spectra and melting point.

1.0 Introduction

The palladium-catalyzed carbon-carbon bond formations are very useful methods for constructing higher molecules such as materials and drugs for modern chemical and medical applications [1]. There are several types of reactions that depend on a variety of organometallic nucleophiles, such as the Kumada, Negishi, Stille, Suzuki, Hiyama, Sonogashira, and other related couplings [2].

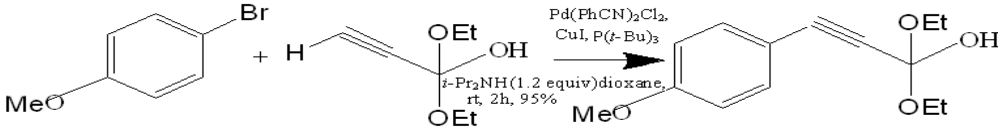
The palladium-catalyzed coupling of haloarenes and haloalkenes with alkenes known as Heck reaction is well established [3]. The Sonogashira coupling reaction of terminal alkynes with synthesis provides an efficient route of arylalkynes [4]. Numerous applications to terminal product synthesis have been reported including the construction of complex enediyne antibiotic [5].

Another protected acetylenes are propargyl alcohol and 2-methyl-3-butyn-2-ol. After coupling with halides, deprotection by alkaline hydrolysis gives 1-alkynes. Monocoupling of *o*-dibromobenzene (**1**) with **2** afforded the protected alkyne **3**. Treatment of **3** with Pd(0)-CuI catalyst, NaOH, and quaternary ammonium chloride generates the deprotected 1-alkyne[6] **4** ashown in Scheme-1.



Scheme-1

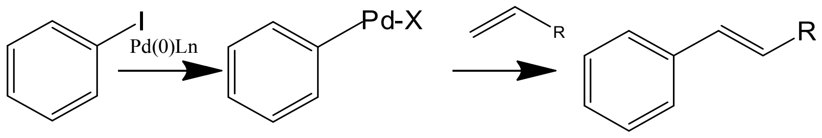
Buchwald and Fu *et al.* reported that coupling of inactivated 4-bromoanisole **5** could be carried out at room temperature by using Pd(PhCN)$_2$Cl$_2$ as a catalyst, p-(t-Bu)$_3$ *as a ligand* and only 1.2 equivalent of di-isopropyl-amine. Poor results are obtained when PPh$_3$, PCy$_3$, P(o-Tol)$_3$ and DPPF are used instead of p-(t-Bu)$_3$ under similar conditions [7] as shown in scheme-2.



5 **6** **7**

Scheme-2

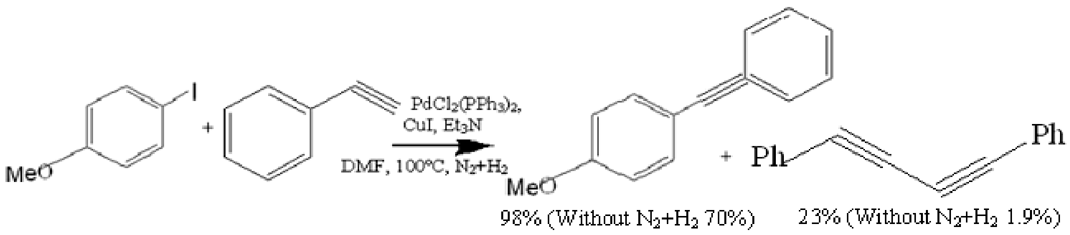
The phenyl palladium halides **9** were formed by oxidative addition of aryl iodide with palladium(0) in which alkene insertion underwent followed by *β*-H elimination to yield arylalkenes[8] **10** (Scheme-3).



8 9 10

Scheme-3: Insertion to phenyl palladium intermediates

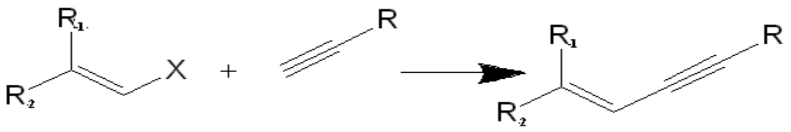
Ho *et al.* reported that the phase transfer halocoupling of phenyl acetylene with 4-iodanisole **11** can be reduced drastically by carrying out the reaction in an atmosphere of H_2 diluted with N_2 or argon[9] as shown in scheme-4.



11 12 13 14

Scheme-4

From the reaction of vinyl halides **15** (R_1R_2 C=CHX) with terminal alkynes **16** (*E*)-β-bromostyrene (PhCH=CHBr) smoothly afforded with alkynes **17** in good yields, irrespective of alkynes employed[10].



15 16 17

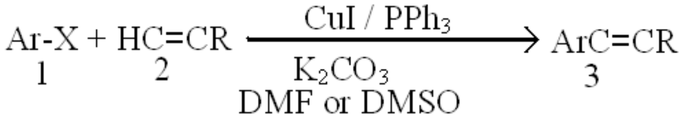
Scheme-5

As expected *(E*)-β-iodostyrene (PhCH=CHI) was more reactive than (*E*)-β-bromostyrene (**19a**), and the reaction could be completed at 80ºC.

From the coupling reaction of aryl halides with terminal alkynes by using a catalyst system of CuI-PPh_3 in the presence of K_2CO_3 as base the corresponding arylated alkynes is produced in excellent yields. Addition of PPh_3 is essential for the reaction to proceeded catalytically [10].

Synthesis of acetylene derivatives have been explored [11]. Palladium-catalyzed coupling of aryl and vinyl halides with terminal alkynes [12-14] and with alkynylmetals has also been developed and is now widely used for the synthesis of biologically active enyne compounds [15,16]. The reaction with terminal alkynes is often carried out using copper (I) iodide as a cocatalyst [17].

On the other hand, Suzuki *et al.* have demonstrated that copper (I) species can promote the reaction of vinyl halides with terminal alkynes without employing palladium catalysts [18], However as in the Castro reaction a stoichiometric amount of copper salt is needed. It is found that aryl and vinyl iodides smoothly react with terminal alkynes in the presence of catalyst potassium carbonate as been when an appropriate amount of triphenylphosphine is added [19], giving the corresponding coupling products in good yield (Schene-6).



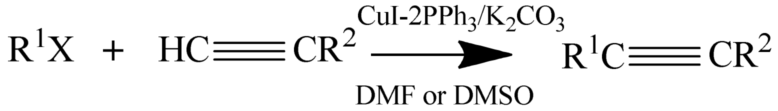
$$\underset{1}{\text{Ar-X}} + \underset{2}{\text{HC=CR}} \xrightarrow[\substack{K_2CO_3 \\ \text{DMF or DMSO}}]{\text{CuI / PPh}_3} \underset{3}{\text{ArC=CR}}$$

Scheme-6

Here, Ar = aryl or substituted aryl; X = I, Br; R = alkyl or substituted alkyl or substituted aryl.

Allenes have become very important in organic synthesis[20-25]. Thus, efficient new methods for the synthesis of allenes from the commonly used starting materials are highly desirable[26]. Terminal alkynes are readily available organic compounds and can be converted to terminal allenes by the reaction with paraformaldehyde in the presence of *i*-Pr_2NH and CuBr in dioxane[27]. However, in many cases the reaction provides the products in relatively low yields. To further improve this one step procedure, the ammine can be crucial for this transformation since the *i*-Pr_2NH used also provides the "H" for the reduction of the in situ formed propergylic amine from the Mannich-type reaction of terminal 1-alkyne, paraformaldehyde, and *i*-Pr_2NH

Kazumi Okuro *et al.* reported that coupling reaction of aryl and vinyl halides with terminal alkynes using a catalyst system of copper(I) iodide - triphenylphosphine proceeds efficiently in the presence of potassium carbonate to give the corresponding unsymmetrical acetylenes in good yield (Sheme-7)



$$R^1X + HC\equiv CR^2 \xrightarrow[\text{DMF or DMSO}]{\text{CuI-2PPh}_3/\text{K}_2\text{CO}_3} R^1C\equiv CR^2$$

Scheme-7

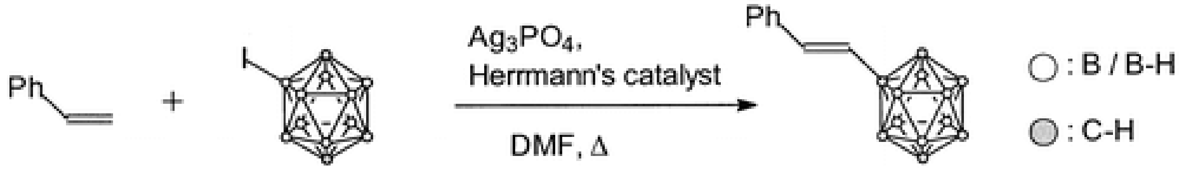
Here, R^1 = aryl, vinyl; and R^2 = phenyl, n-pentyl.

Palladium-catalyzed reactions are very useful because palladium catalysts are relatively inert, Usually has high yield and selectivity; and they are less expensive than Platinum, which has similar properties.

Palladium can be used in a wide variety of reactions[29,30] as a catalyst such as Stille combines organohalides and organotin compounds to make a new organic compund. Buchwald-Hartwig combines aryl halides and either amines or aryl alcohol to make aryl amines or diaryl ethers. The Tsuji-Trost reaction adds a nucleophile to an alkene, and the Heck reaction combines alkenes and alkyl halides to form a hydrocarbon. All the reactions mentioned here are palladium-catalyzed cross-coupling reactions. In general, the palladium catalyst would first bind to one of the substituents. The second substituent would then bind or coordinate to the metal complex; this step could either occur through a transmetalation or nucleophilic attack. The metal complex then undergoes reductive elimination to form a new compound that consists of the two substituents, and the catalyst is reformed in the process.

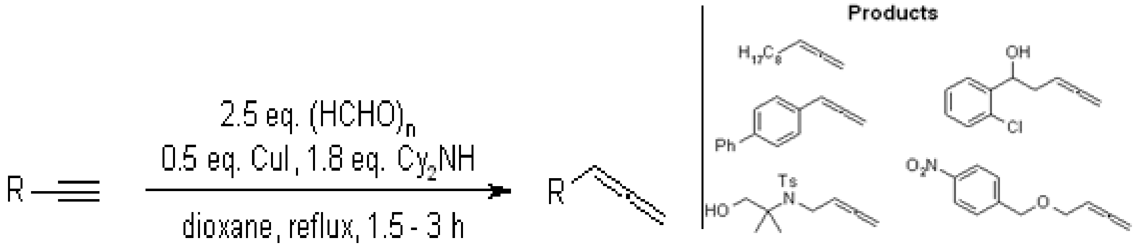
Allenes have become very important in organic synthesis [20-25]. Thus, efficient new methods for the synthesis of allenes from the commonly used starting materials are highly desirable [26]. Terminal alkynes are readily available organic compounds and can be converted to terminal allenes by the reaction with paraformaldehyde in the presence of i-Pr_2NH and CuBr in dioxane[27,31-33]. However, in many cases the reaction provides the products in relatively low yields. To further improve this one step procedure, the amine can be crucial for this transformation since the i-Pr_2NH used also provides the “H” for the reduction of the in situ formed propergylic amine from the Mannich-type reaction of terminal 1-alkyne, paraformaldehyde, and i-Pr_2NH[32]. In addition, recently, Nakamura *et al.* reported the Pd-catalyzed hydride-transfer reation of propergylic diisopropyl or dicyclohexyl amines for the formation of allenes[34-38].

Ludvig Eriksson *et al.* reported that *p*-Carborane has been vinylated on the 2- β -atom in high yields using the Heck reaction. Thus, the reaction between 2-iodo-p-carborane and various styrenes [4-H-, 4-C_6H_4-, 4-Cl-, 4-Br-, 4-NO_2-, 4-CH_3O-, and 4-CH_3-] resulted in the production of the corresponding *trans*-β-(2-*B*-*p*-carboranyl)styrene in DMF solution when reacted in the presence of silver phosphate and the palladacycle Herrmann's catalyst [39].



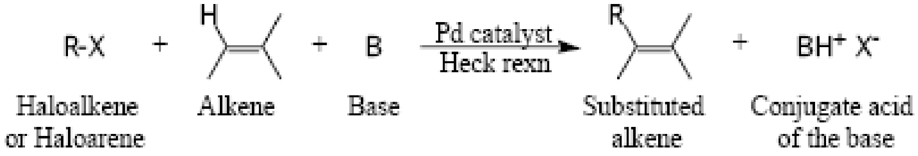
Scheme-8

J. Kuang, S. Ma reported that terminal allenes produces in much higher yields than previously reported protocols from the reaction of 1-alkynes with Cy_2NH and paraformaldehyde mediated by CuI in refluxing dioxane and many functional groups such as mesylate, hydroxyl group, ether, amide, etc. are tolerated[40(a)].



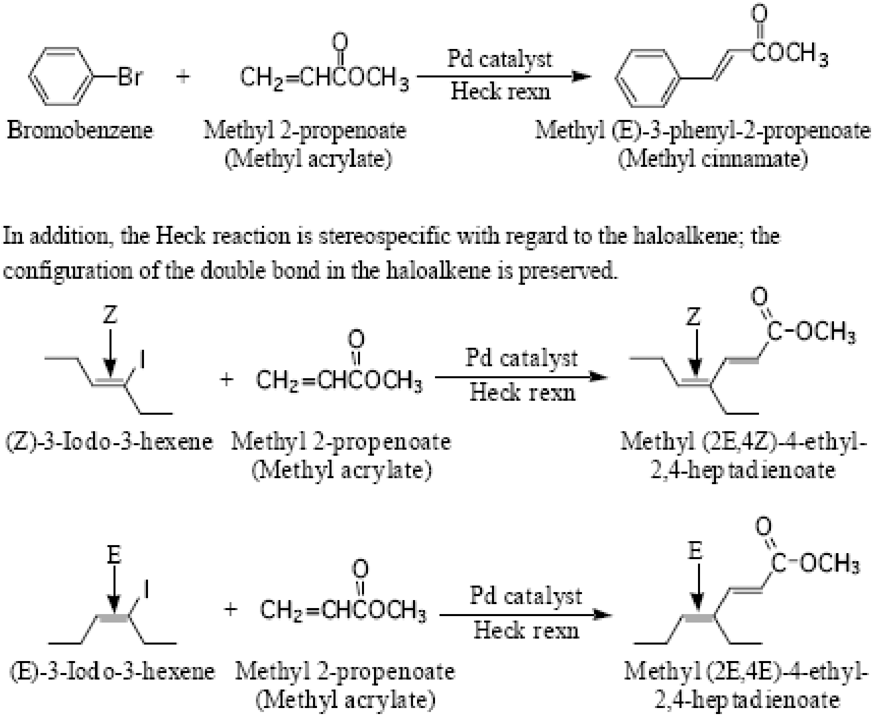
Scheme-9

In the early 1970s, Richard Heck at the Hercules Co. and later at the University of Delaware discovered a palladium-catalyzed reaction in which the carbon group of a haloalkene or haloarene is substituted for a hydrogen on the carbon-carbon double bond (a vinylic hydrogen) of an alkene. This reaction, now known as the Heck reaction, is particularly valuable in synthetic organic chemistry because it is the only general method yet discovered for the type of substitution.[40(b)]



Scheme-10

Substitution for a vinylic hydrogen by the Heck reaction is highly regioselective; formation of the new carbon-carbon bond most commonly occurs at the less substituted carbon of the double bond. In addition, where a *cis* or *trans* configuration is possible at the new carbon-carbon double bond of the product, the Heck reaction is highly stereoselective, often giving almost exclusively the *E* configuration of the resulting alkene.



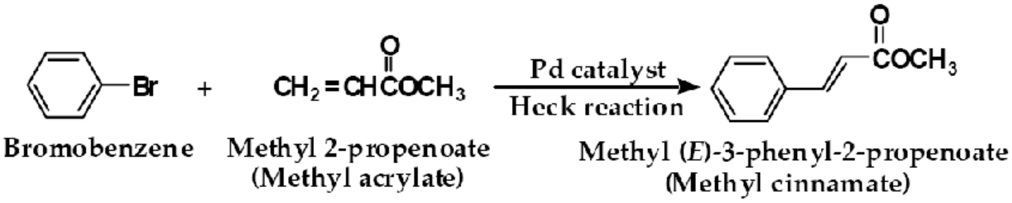
In addition, the Heck reaction is stereospecific with regard to the haloalkene; the configuration of the double bond in the haloalkene is preserved.

Scheme-11

The reactivity of the alkene is a function of steric crowding about the carbon carbon double bond. Ethylene and monosubstituted alkenes are the most reactive; the greater the degree of substitution on the double bond the slower the reaction and the lower the yield of product.

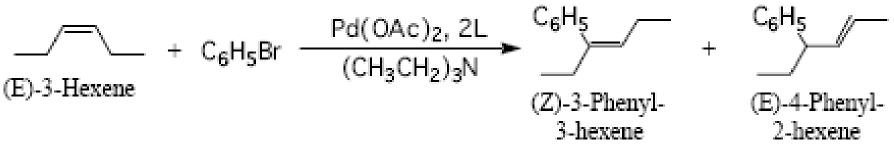
As has been demonstrated in the text, when the starting alkene has CH_2 as its terminal group, the Heck reaction is highly stereoselective for formation of the *E* isomer as illustrated in this example. Here, the benzene ring is abbreviated C_6H_5-.

Where a *E, Z* isomer is possible at the new carbon-carbon double bond of the product, the Heck reaction is highly stereoselective, often giving almost exclusively the *E* configuration of the resulting alkene.[40(b)]



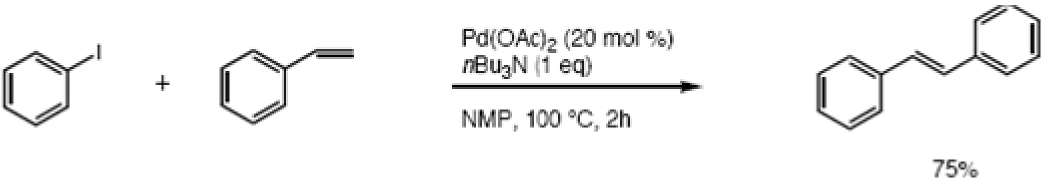
Scheme-12

Heck reaction of bromobenzene and *(E)*-3-hexene gives a mixture of 3-phenyl-3-hexene and 4-phenyl-2-hexene in roughly equal amounts. Account for the formation of these two products.



Scheme-13

The first intermolecular Heck reaction was reported by Heck in 1972[41].



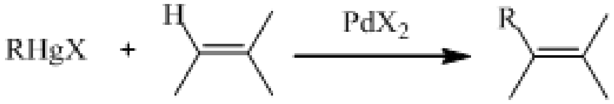
Scheme-14

Development of the general intermolecular reaction suffered due to poor regiocontrol of the addition and elimination steps for electronically neutral unsymmetrical olefins.

The 2010 Nobel Prize in Chemistry was awarded jointly to Richard Heck, Ei-ichi Negishi and Akira Suzuki for their pioneering work on palladium-catalysed cross-couplings in organic synthesis.

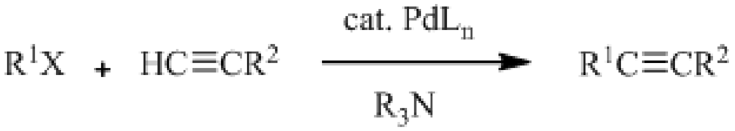
The interest of Richard Heck was piqued by the notion of using palladium more widely. He began experimenting with different reaction conditions and his successful results culminated in a series of scientific papers published in 1968 in which he showed that it was relatively straightforward to link a ring of carbon atoms to a shorter fragment of carbons to make styrene, the monomer used to make polystyrene. The styrene synthesis was just one of several palladium-catalysed reactions, which became known generally as the Heck reaction, which share a common feature in creating single bonds between carbon atoms.

Heck was able to regenerate the palladium catalysts and thus this reaction became extremely appealing. From this point many studies were preformed to determine the potential applications in organic synthesis and other valuable versions of the reaction. This led to the current Heck reaction displayed stoichiometrically as shown in scheme-15.



Scheme-15

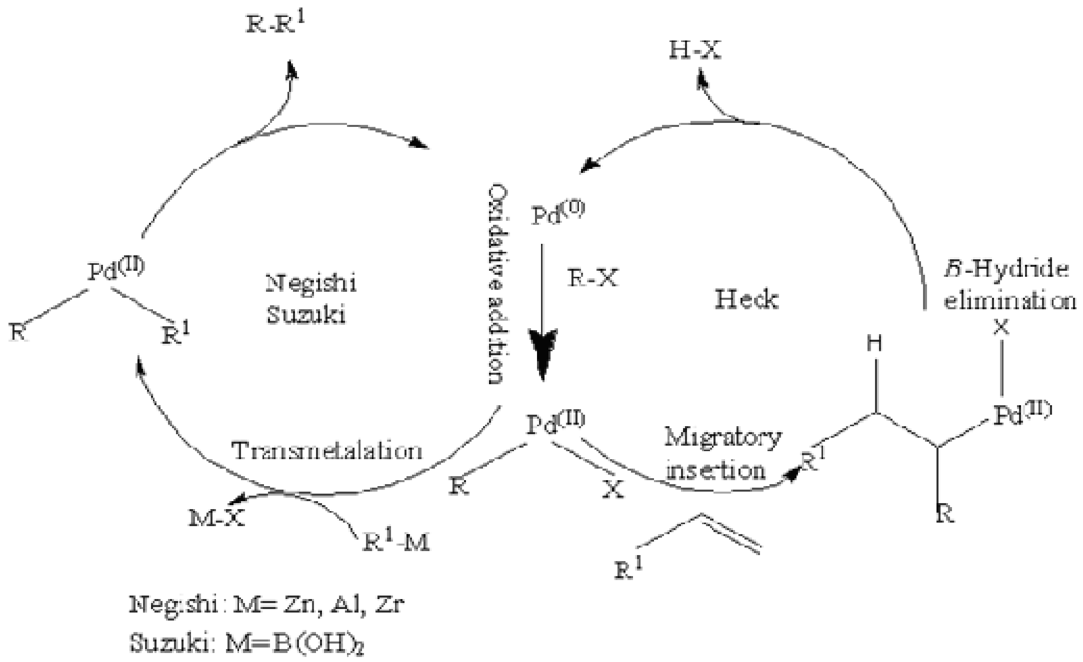
Through further study Heck was able to regenerate the palladium catalysts alkynes synthesis as shown in scheme-16.



$$R^1X + HC{\equiv}CR^2 \xrightarrow[R_3N]{\text{cat. }PdL_n} R^1C{\equiv}CR^2$$

Scheme-16

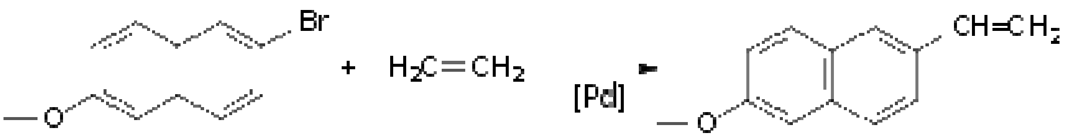
The Heck reaction involves the reaction of an unsaturated halide or triflate with an electron-deficient alkene (such as an acrylate ester or an acrylonitrile) and a base and the organopalladium catalyst (eg the catalyst can be tetrakis (triphenylphosphine) palladium (0), palladium chloride or palladium(II) acetate), to form a substituted alkene.



Scheme-17

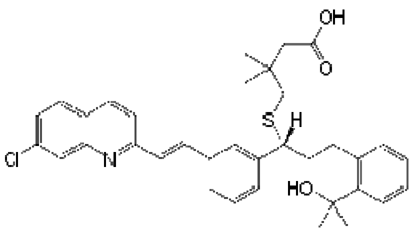
Today, the Heck reaction is used to manufacture the anti-inflammatory drug naproxen[42], the painkiller drug morphine, etc.

The coupling reaction is stereoselective with a propensity for trans coupling as the palladium halide group and the bulky organic residue move away from each other in the reaction sequence in a rotation step. The Heck reaction is applied industrially in the production of naproxen and the sunscreen component octyl methoxycinnamate. The naproxen synthesis includes a coupling between a brominated naphthalene compound with ethylene[42(a).]



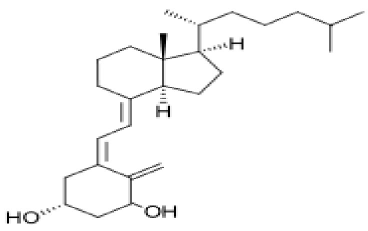
The Heck reaction in Naproxen production

Scheme-18 (a)



Singulair

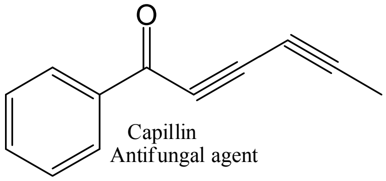
Montelukast (trade names Singulair and Montelo-10): It is used for the maintenance treatment of asthma and to relieve symptoms of seasonal allergies.



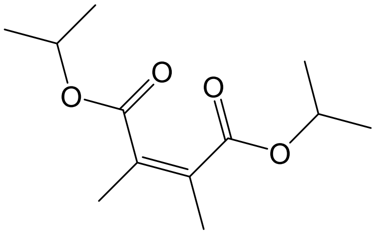
(+)-calcidiol

The blood concentration of calcidiol is considered the best indicator of vitamin D status.

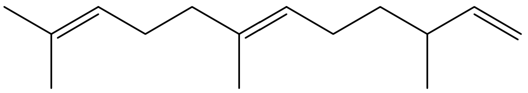
Scheme-18 (b): Synthetic coupling products[42(b)]



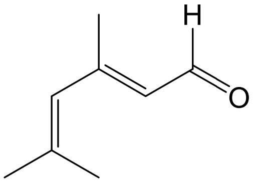
Capillin
Antifungal agent



A synthetic cockroach repellent



Farnerene is a compound found in the waxy coating of apples

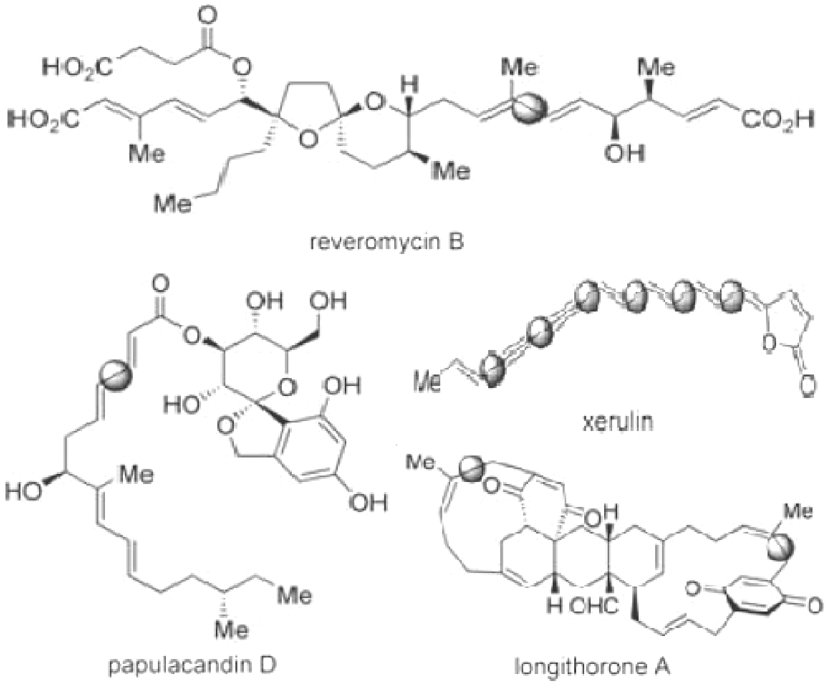


Geranial is a component of Lemongrass oil

$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}CH_2{-}C({=}CH_2){-}CH{=}CH_2$

3-methylene-7,11-dimethyl-1,6,10-dodecatriene
an aphid alarm pheromone
an example of insect pheromone

Scheme-18 (C$_1$): Selected examples of synthetic natural products.[42(c)]



Scheme-18 (C_2): Selected examples of synthetic natural products.[42(d)]

The palladium-catalyzed cross-coupling of an organometal (R^1M) with an organic electrophile (R^2X) has emerged over the past thirty years as one of the most general and selective methods for carbon–carbon-bond formation[43].

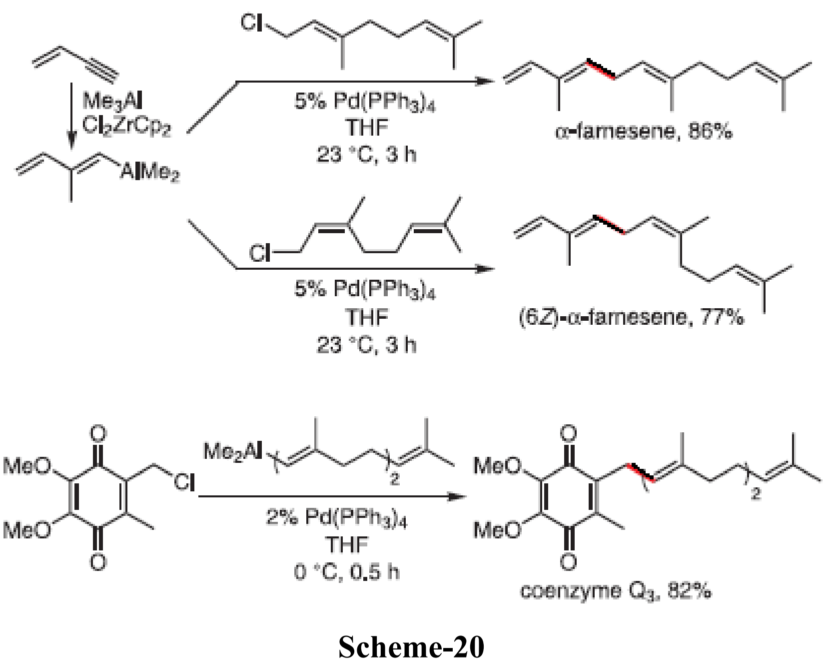
$$R^1M + R^2X \xrightarrow{PdL_n(cat.)} R^1\text{-}R^2 + MX$$

Scheme-19

Currently, it appears to be generally superior to related methods involving the use of Ni, Cu, or Fe catalysts in its scope and stereo-, regio-, and chemoselectivities. The R^1 group of R^1M can be aryl, alkenyl, alkynyl, allyl, benzyl, propargyl, alkyl, cyano, or enoxy; while the R^2 group of R^2X can be aryl, alkenyl, alkynyl, allyl, benzyl, propargyl, alkyl, or acyl. Use of other related carbon groups as R^1 and/or R^2 is not only conceivable, but also known in the literature. Even if only those nine types of organometals (R^1M) and eight types of organic electrophiles (R^2X) mentioned above are considered, their binary combinations lead to 72 different types of cross-coupling reactions, and most of these reactions have indeed been developed. Until recently, the use of alkyl electrophiles lacking proximal π bonds had been considered to be categorically very difficult, and the task of Pd-catalyzed alkylation had been achieved by using alkylmetals. The latter is still of much broader synthetic applicability. However, some recent developments suggest that this generalization may have to be significantly modified in the future, as discussed in Section 2.6. Another group of categorically difficult Pd-catalyzed crosscoupling reactions are those involving cross-coupling between allyl, benzyl, and/or propargyl groups. In addition, a more promising, direct, and selective α alkenylation and α alkynylation of metal enolates need to be further developed.

Despite the fact that the reaction of allyl(tributyl)stannane with bromobenzene in the presence of $Pd(PPh_3)_4$, reported in 1977, is probably the first example of Pd-catalyzed allylation of organic halides, the allyl–alkenyl coupling is generally to be avoided in favor of the alkenyl–allyl coupling for a couple of reasons[43].

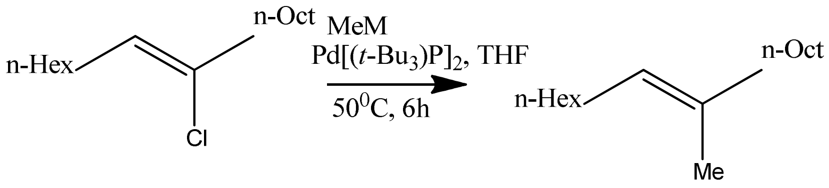
The number of natural products synthesized by the Pd-catalyzed alkenyl–allyl coupling is still relatively small. Nonetheless, strictly regio- and stereospecific syntheses of α-farnesene and its 6Z isomer, (+)-hennoxazole A, as well as a series of coenzyme Q's and menaquinones, persuasively point to its synthetic potential (Scheme 20). Both Pd and Ni complexes are highly satisfactory for catalyzing the alkenyl–benzyl and alkenyl–allyl coupling reactions.[44-47]



Scheme-20

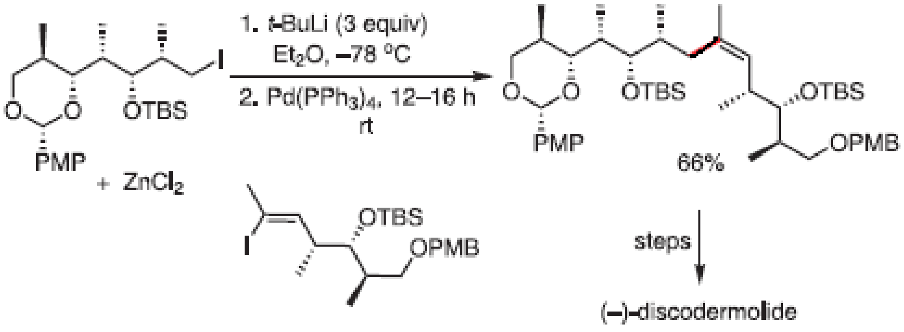
Despite recent promising developments such as those mentioned above, the Pd-catalyzed alkylation of alkenyl derivatives is still achieved mostly by the alkyl–alkenyl coupling protocol. In this regard, alkylzincs are generally superior to the other alkylmetals that have been examined to date, although alkylborons[45] and alkylmagnesiums[49-51] are satisfactory in many cases.

One should bear in mind that, in the Pd-catalyzed alkylation with alkylzincs or perhaps organozincs in general, the precise composition of alkylzincs, which significantly depends on the methods of their generation, affects the course of the subsequent cross-coupling process. One important determining factor is the alkyl/Zn/Li (or Mg) ratio. In a synthesis of (–)-discodermolide, it was shown to be desirable to add 3 equiv of t-BuLi to an alkyl iodide premixed with $ZnCl_2$ (Scheme 22).[52-54]



M= ZnBr, MgBr

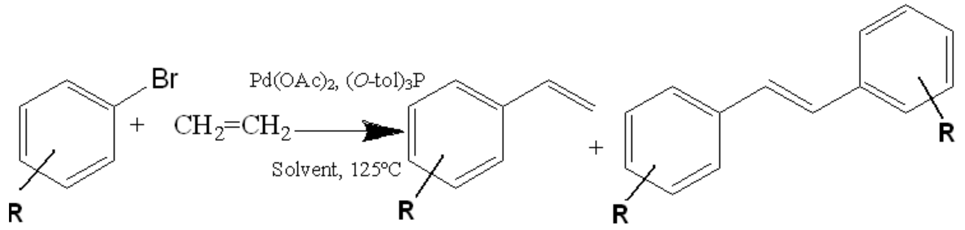
Scheme-21



Scheme-22

Ethylene is the ideal vinyl source for a vinylation reaction, as only one hydrogen atom is lost from the ethylene group[55]. Accordingly, the successful incorporation of a vinyl unit using ethylene generates as waste only HX (from an aryl halide). In practice, ethylene was initially demonstrated to be an effective vinyl donor by Heck in 1968[56]. Subsequent optimization by

Heck allowed the conversation of a range of substituted aryl bromides into the corresponding styrenes in moderate yields[57](Scheme-23).



Scheme-23

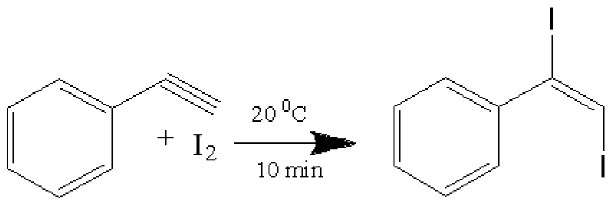
Here, R = 2-CH_3, 2-NO_2, 4NHAc, 2-NH_2, 3-COH, 2-Br.

A number of methods have been developed for the synthesis of conjugated acetylenic ketones[58-60]. Recently, t he synthesis of α,β-acetylenic ketones by palladium-catalysis from 1-alkynes and acyl chloride[61] or from i-alkynes and aryl and vinyl halides in the presence of carbon monoxide[62-63] have been reported. A very facile method for the synthesis of α,β-acetylenic ketones by the reaction of 1-alkynes with acyl halides in the presence of catalytic amounts of copper (I) salts only (Scheme-24)[64]·have also been reported.

$$R\text{—}C\equiv CH + R^1\text{-CO-Cl} \xrightarrow{\text{CuI, Et}_3\text{N, rt, 30h}} R\text{—}C\equiv C\text{-CO-}R^1$$

Scheme-24

Recently, the development of the "Green Chemistry" principles has stimulated studies on organic processes occurring in absence of a solvent[65]. E. N. Tveryakova *et al.* reported that phenylacetylene racts with molecular iodine on grinding in a mortar without a solvent for 2-10 min to give 45-90% of *trans*-1,2-diiodophenylethylne [66]. (Scheme-25)



Phenylacetylene Diiodophenylethylne

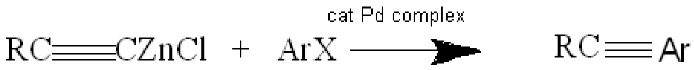
Scheme25

Green chemistry, also called sustainable chemistry, which has some principles[67] and it is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.

Arylalkynes are very useful intermediates for the preparation of important compounds including natural products, pharmaceuticals, oligomers, polymers[68]. Their conjugated systems also have received much more attention in optical and electronic applications[68].

Arylalkynes represents a number of natural products such as freelingyne, junipal, dectylyne, *(3E)*-laureatin, and capillin[69]. The presence of enynes in natural products such as *cis*-jasmone, muscalure, geranial, and farnesene and their utility as building blocks for further structural elaboration stimulate the interest in seeking simple synthetic routes to them[70].

Neigishi *et al.* reportd that a procedure is developed for aryl-alkenyl coupling applicable even to the direct and selective synthesis of terminal arylalkynes [71] (Scheme-26).



$$RC\equiv CZnCl + ArX \xrightarrow{\text{cat Pd complex}} RC\equiv Ar$$

Scheme-26

Here R=H, alkyl, or aryl; X= I or Br.

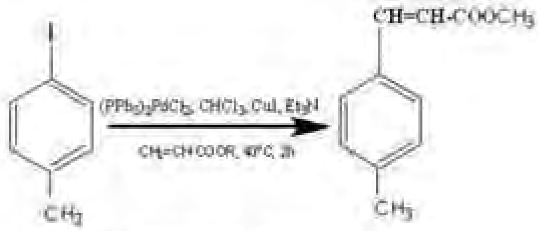
The synthesis of methyl enynoates and *(E)*-enynones is of interest as the alkyl enynoate moiety has been found in naturally occurring compounds[72], and because of their use as synthetic intermediates.

T. Jeffery reported the synthesis of enynoates and enynone derivatives under solid-liquid phase-transfer conditions[73]. The carbon-carbon double bond is arguably the most diversifiable functional group in organic chemistry[74]. The variety of reactions available to functionalize olefins extends the range of reductive (hydrogenation, hydroboration, hydrosilylation), oxidative (epoxidation, dihydroxylation, halogenation) and constructive transformations[75].

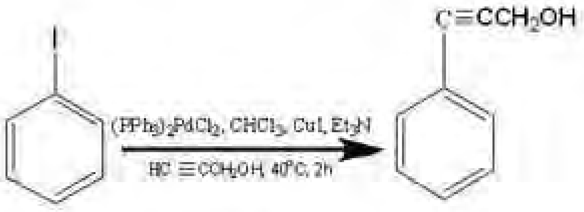
Acetylene derivatives are versatile compounds in synthetic organic chemistry, and hence, various methods for their synthesis have been explored[76].

In recent years, our research group has reported the synthesis of various aromatic heterocyclic compounds such as isoquinolinones[77] and 2-acylbenzofurans[78] through palladium catalyzed reactions. It is desired to develop the methods of synthesis of alkene and alkyne derivatives through palladium catalyzed reactions.

Recently, our research group has synthesized arylpropenoate, alkenyl alcohol, etc. from iodobenzene and its derivatives (Scheme-27).[79,80]



Arylpropenoate preparation



Alkenyl alcohol preparation

Scheme-27

In this literature, it is desired to develop the methods of synthesis of alkene and alkyne derivatives from terminal alkynes through palladium catalyzed reactions.

2.0 Present Work

Palladium catalyzed synthesis of alkene and alkyne derivatives from terminal alkynes.

2.1 Rationale

For the formation of a new carbon-carbon bond, the palladium catalyzed coupling of heloarenes and heloalkenes with alkenes known as Heck reaction is well established[10]. Acetylene derivatives (Arylalkynes, alkylalkynes, etc.) are versatile compounds in synthetic organic chemistry and hence several methods for their synthesis have been explored.

Today, the Heck reaction is used to manufacture the anti-inflammatory drug naproxen[42], the asthma drug montelukast and the painkiller morphine.

Allenes have become very important in organic synthesis[20-25]. Thus, efficient new methods for the synthesis of allenes from the commonly used starting materials are highly desirable[26]. Terminal alkynes are readily available organic compounds and can be converted to terminal allenes[27,31-33].

Arylalkynes are very useful intermediates for the preparation of important compounds including natural products, pharmaceuticals, oligomers, polymers[68]. Their conjugated systems also have received much more attention in optical and electronic applications[68].

For the importance of palladium catalyzed coupling products of alkenes and alkynes it is planned to develop the methods of synthesis of alkene and alkyne derivatives from terminal alkynes through palladium catalyzed reactions.

2.2 Results and Discussion

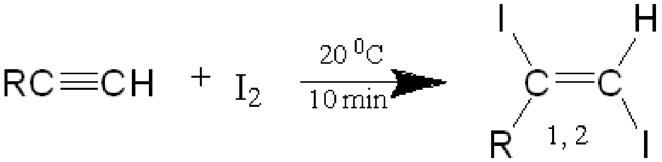
Here a convenient approach for the synthesis of alkenyne and alkenoate derivatives from terminal alkynes through palladium catalyzed is reported.

The required iodo compounds were prepared from their corresponding terminal alkynes (Scheme-1). After usual workup, the iodo compounds **1, 2** and **18** (Scheme-1, Scheme-2) were isolated. Coupling products alkenyne and alkenoate derivatives were prepared from these starting materials by the palladium catalyzed coupling reaction with terminal alkynes and alkyl acrylates. The palladium catalyzed cross-coupling reactions were carried out by stirring the mixture of a starting material with a terminal alkyne or an alkyl acrylate (3 mol equiv.), bis(triphenylphosphine) palladium(II) chloride (3.5 mol %), copper(I) iodide (8 mol %) and triethylamine(4 mol equiv.) under nitrogen atmosphere in DMF (4 mL) or CH_2Cl_2 (10 mL) at 80°C for 24 hours. After usual workup, the crude product was purified by column chromatography on silica gel using n-hexane /ethyl acetate and products alkenyne and alkenoate derivatives were isolated in good yield (Scheme-3- Scheme-4).

2.3 Synthesis iodo compounds from corresponding alkynes

1,2-diiodo-1-phenylethene (**1**) and 1,2-diiodo-1-heptene (**2**) have been used as starting materials which were prepared from corresponding terminal alkynes using molecular iodine under mild condition (scheme-1). The iodo compound 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene (**18**) was prepared as the same way from 1,4-diphenylbuta-1,3-diyne (dimer of phenyl acetylene, Scheme-2). The results are demonstrated in **Tabe-2.3**.

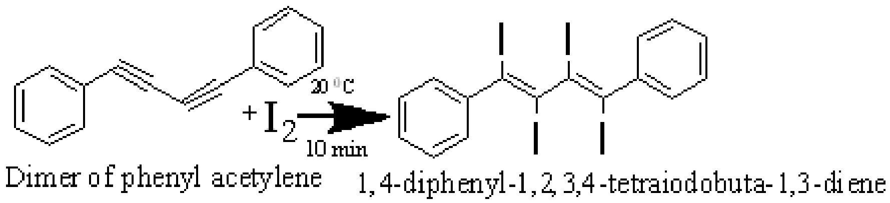
Here phenylacetylene and alkyl 1-heptyne were reacted with molecular iodine on grinding in a mortar without a solvent for 10 minutes at 20ºC to give *trans*-1,2-diiodophenylethylne [66] and *trans*-1,2-diiodoalkylethylnes respectively (Scheme-1).



Scheme-1

For the preparation of 1,2-diiodo-1-phenylethene, phenyl acetylene (2 mmol) was added in portions over a period of 10 minutes to I_2 (1mmol) under grinding in an agate mortar at 20°C. The mixture then extracted by 10 ml dichloromethane (or diethylether). The extract was washed with 5ml of 5% $Na_2S_2O_3$ solution, 10ml of water and 50 ml of saturated solution of NaCl. The solvent was distilled off to obtain 1,2-diiodo-1-phenylethene (**1**).

In this way 1,2-diiodo-1-heptene was prepared from 1-heptyne (Scheme-1).



Scheme-2

From the Lassaigne's test it was proved that iodide was present in each of iodo compounds (**1, 2, 18**).

$$Na + I \text{ ------------------> } NaI$$

$$Ag^{+}_{(aq)} + I^{-}_{(aq)} \longrightarrow AgI_{(s)}$$

AgI (very pale yellow precipitate) is insoluble in ammonia solution of any concentration.

As the same way 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene **18** was also prepared from the dimer of phenylacetylene (Scheme-2).

Table-2.3: Synthesis of iodo compounds **1, 2** and **18**

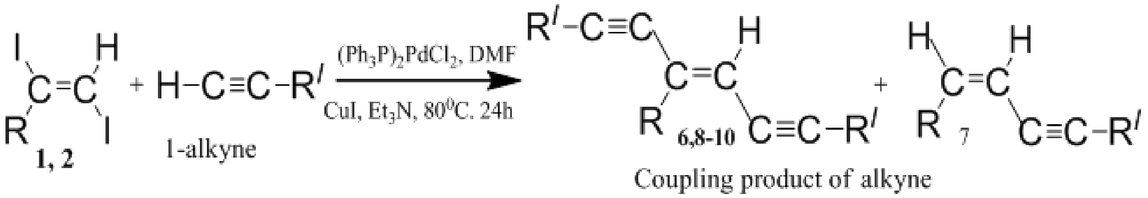
Alkyne	Iodine	Iodo compound 1, 2 and 18	Yield (%)
C_6H_5-C≡CH 1-phenylacetylene	I_2	C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	66%
1-heptyne CH_3-$(CH_2)_4$-C≡CH	I_2	CH_3-$(CH_2)_4$-CI=CHI 1,2-diiodo-1-heptene **2**	50%
C_6H_5-C≡C-C≡C-C_6H_5 1,4diphenyl-1,3-butadiyne	I_2	C_6H_5-CI=CI-CI=CI-C_6H_5 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene (**18**)	55%

2.4 Synthesis of palladium catalyzed alkenyne derivatives 6-10

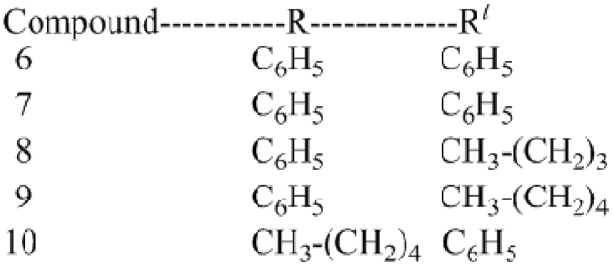
A facile method for the synthesis of alkenyne derivatives through palladium catalyzed coupling reaction of 1,2-diodo-1-phenylethene, 1,2-diiodo-1-heptene with phenylacetylene, 1-hexyne, and 1-heptyne as shown in **scheme-3** is reported and the results are demonstrate in the **Table-2.4**.

For the preparation of alkenyne derivatives **6-10,** the mixture of starting material (1,2-diiodo-1-alkene), bis (triphenyl phosphine)palladium (II) chloride (3.5 mol%), copper (I) iodide (8 mol%)

and triethylamine (4 equiv.) was stirred in DMF (4mL) under nitrogen atmosphere for 1 hour. Then and 1-alkyne (phenylacetylene, 1-hexyne or 1-heptyne) (3 equiv.) was added to the reaction mixture. The solution was heated hr at 80ºC for 24 h (**Scheme-3**). the progress of the reaction was monitored by TLC (n-hexane). After completion of the reaction the mixture was then evaporated to dryness under reduced pressure and the residue was extracted with chloroform. The combined chloroform extracts were washed with distilled water, dried over anhydrous Na_2S0_4, filtered and concentrated under reduced pressure to obtained the gummy alkenyne products. The latter was purified by chromatography on a column of silica gel (60-120 mesh) with n hexane and ethyl acetate. Then the pure products were obtained.



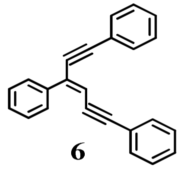
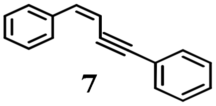
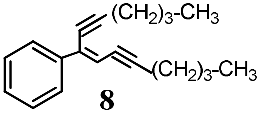
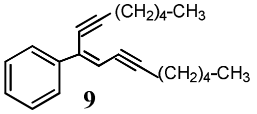
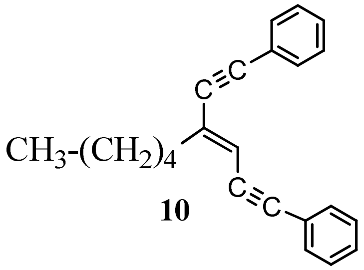
Here, R = C_6H_5, $CH_3(CH_2)_4$; R ^{l}= C_6H_5, $CH_3(CH_2)_3$ and $CH_3(CH_2)_4$
1-alkynes are phenylacetylene, 1-hexyne and 1-heptyne.



Compound-----------	R-------------	R^{l}
6	C_6H_5	C_6H_5
7	C_6H_5	C_6H_5
8	C_6H_5	CH_3-$(CH_2)_3$
9	C_6H_5	CH_3-$(CH_2)_4$
10	CH_3-$(CH_2)_4$	C_6H_5

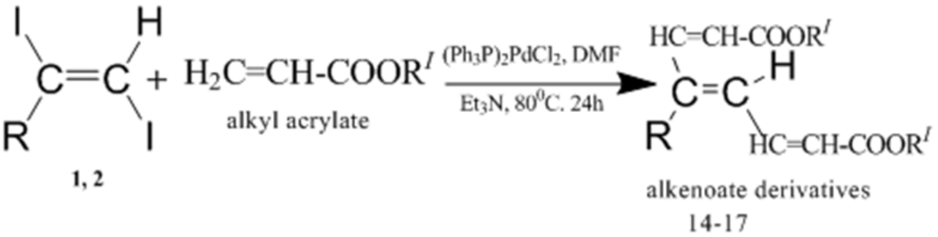
Scheme-3

Table-2.4: Coupling of **A** (starting materials **1, 2**) with **B** (1-alkyne)

Starting materials A (1, 2)	**1-Alkyne B**	**Solvent**	**Product (Alkenyne derivatives) 6-10**	**Yield (%)**
C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	C_6H_5-C≡CH 1-phenylacetylene	DMF	 **6** **1,3,6-triphenylhex-3-en-1,5-diyne**  **7** **1,4-diphenylbut-1-en-3-yne**	60
C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	CH_3-$(CH_2)_3$-C≡CH 1-hexyne	DMF	 **8** **7-phenyl-7-tetradecen-5,9-diyne**	55
C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	CH_3-$(CH_2)_4$-C≡CH 1-heptyne	DMF	 **9** **8-phenyl-8-hexadecen-6,10-diyne**	55
CH_3-$(CH_2)_4$-CI=CHI 1,2-diiodo-1-heptene **2**	C_6H_5-C≡CH 1-phenylacetylene	DMF	 **10** **3-pentyl-1,6-diphenyl-3-hexen-1,5-diyne**	50

2.5 Synthesis of palladium catalyzed alkenoate derivatives 14-17

As the above mentioned procedure, alkenoate derivatives were synthesized through palladium catalyzed coupling reaction of 1,2-diodo-1-phenylethene or 1,2-diiodo-1-heptene with alkyl acrylate (methyl acrylate, ethyl acrylate, butyl acrylate) as shown in **scheme-4**. The results are demonstrate in the **Table-2.5**. For the synthesis of alkenoate derivatives, copper (I) iodide was not used.



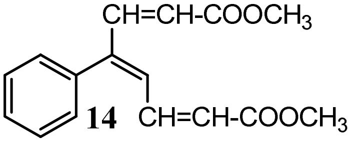
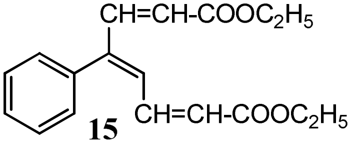
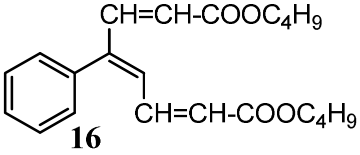
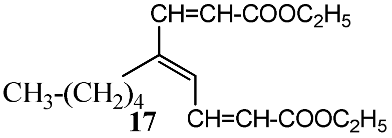
Here, $R^{l} = CH_3$, C_2H_5 and C_4H_9.

The alkyl acrylates are methyl acrylate, ethyl acrylate and butyl acrylate.

Compound	R	R^{l}
14	C_6H_5	CH_3
15	C_6H_5	CH_2-CH_3
16	C_6H_5	CH_3-$(CH_2)_3$
17	CH_3-$(CH_2)_4$	CH_2-CH_3

Scheme-4

Table-2.5: Coupling of **A** (starting materials **1, 2**) with **B** (alkyl acrylate)

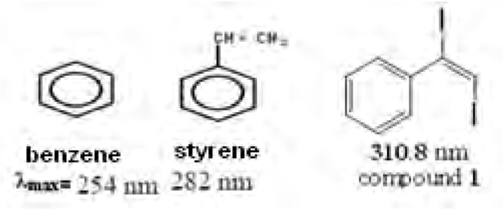
Starting materials A (1, 2)	Alkyl acrylate B	Solvent	Product (Alkenoate derivatives) 14-17	Yield (%)
C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	CH_2=CH-$COOCH_3$ methyl acrylate	DMF	 **14** **4-phenyl-1,8-dimethylocta-2,4,6-trienoate**	52
C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	CH_2=CH-$COOC_2H_5$ ethyl acrylate	DMF	 **15** **4-phenyl-1,8-diethylocta-2,4,6-trienoate**	55
C_6H_5-CI=CHI 1,2-diiodo-1-phenylethene **1**	CH_2=CH-$COOC_4H_9$ butyl acrylate	DMF	 **16** **4-phenyl-1,8-dibutylocta-2,4,6-trienoate**	50
CH_3-$(CH_2)_4$-CI=CHI 1,2-diiodo-1-heptene **2**	CH_2=CH-$COOC_2H_5$ ethyl acrylate	DMF	 **17** **4-pentyl-1,8-dibutylocta-2,4,6-trienoate**	45

2.6 Characterization of iodo compounds

The iodo compounds **1, 2** and **18** (1,2-diiodo-1-phenylethene and 1,2-diiodo-1-heptene and 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene) were characterized by their melting points, IR spectra, UV spectra and NMR spectra (**Table-2.6**). The presence of iodide of all the starting materials was confirmed by Lassaigne test.

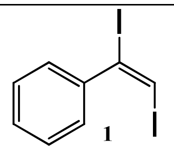
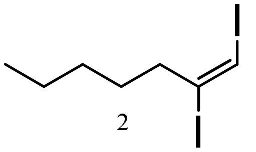
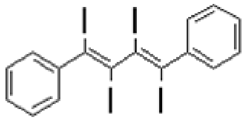
In IR spectra of compounds **1** and **18**, the absorption band was found at 3080 and 3047.3 cm^{-1} due to the presence of aromatic C-H; for the compounds **1, 2** and **18** 594, 550 and 522.7 cm^{-1} due to the presence of C-I group respectively. The 1566.1, 1601 and 1546.8 cm-1 bands indicated the presence of aromatic C=C for starting compounds **1, 2** and **18** respectively.

From the UV spectra, the absorption bands at λ_{max} 310.8 for the compound **1** and 305, 327.2, 334.2 nm of the compound **18** respectively due to electronic transition of C = C of benzene ring, double bond extending conjugation and –I group. The absorption bands at 312.8 nm of the compound **2** due to electronic transition of C = C of aliphatic alkene and –I group. The electronic absorption maxima were found at higher wavelength range (comparing with benzane, λ_{max}=254 nm) due to the extending conjugation of double bond. We know that styrene shows the absorption band at λmax 282 nm (where by using Woodward-Fieser rules, the calculated value is 254+30 = 284 nm) and from the compound **1**, experimentally the absorption band was found at λmax 310.8 nm. This bathochromic and hyperchromic shift was caused for the presence of iodo group in this compound. This was caused for the n-π* transition of the –I group.



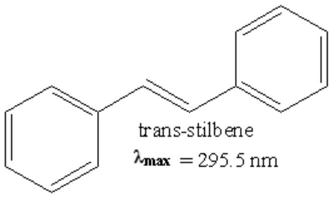
In ^{I}H NMR spectra of the compound **1,** the chemical shift at δ 7.29-7.34 was found as a multiplet for five hydrogen in an aromatic proton and at δ 7.25 (s, 1H, =CH) for a vinyl proton. In the compound **18**, the chemical shift at δ7.54-7.51 (m, 4H, Ar-H) was found as a multiplet for four hydrogen of aromatic proton and δ7.40-7.31 (m, 6H, Ar-H) was found as a multiplet for six hydrogen of aromatic proton.

Table-2.6: Comparison of some spectral data and melting point of the iodo compounds 1, 2, 18

Starting materials	^{1}HNMR (δ ppm, J Hz)	UV (nm)	IR (cm^{-1})	Melting point
 1 1,2-diiodo-1-phenylethene	7.29-7.34 (m, 5H, Ar-H), 7.25 (s, 1H, =CH)	310.8	1566.1 & 1479.3 (Ar C=C), 1566.1 (alkene C=C), 3080 (Ar C-H), 594(C-I)	76-77ºC
 2 1,2-diiodo-1-heptene	--	312.8	1600.1 (alkene C=C), 2960 (Aliphatic C-H), 550(C-I)	Semi-solid
 1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene 14	7.54-7.51 (m, 4H, Ar-H), 7.40-7.31 (m, 6H, Ar-H)	305 327.2 334.2	1546.8 & 1485.1(Ar C=C), 1546.8 (alkene, C=C), 3047.3 (Ar C-H), 522.7 (C-I)	82-83ºC

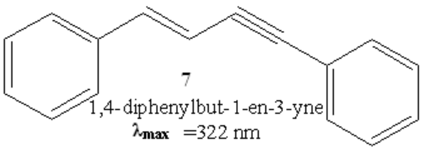
In IR spectra of compounds **6-10** (alkenyne derivatives), the absorption band was found at 3047.3-3055 cm^{-1} due to the aromatic C-H, 1575-1637.2 cm^{-1} due to alkene C=C and 2125.5-2185.2 cm^{-1} due to the C≡C group. The absorption bands at 1575-1637.2 and 1465-1488 cm^{-1} were found due to aromatic C=C group. For the compound **8** and **9** absorption bands at 2850.6 and 2921.9 cm^{-1} were found due to the aliphatic C-H (**Table-2.7**).

From the UV spectra, the absorption bands (λ_{max}) of the coupling products **6-10** were shifted to the higher wavelength range comparing to their corresponding stating materials due to their extension of conjugation of the unsaturated bonds. As for example, stilbene experimentally shows the absorption bands at λmax 295.5 nm.[81,82] Comparing with *trans*-stilbene, for the one triple bond extension in the conjugation system the calculated absorption value λmax of the compound **7** is 320.1 nm. From the compound **7**, the observed value was found at 322 nm.



trans-stilbene

λ_{max} = 295.5 nm



7

1,4-diphenylbut-1-en-3-yne

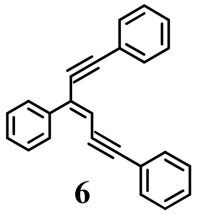
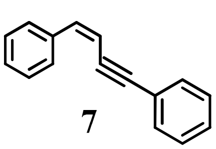
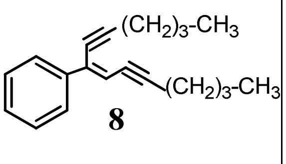
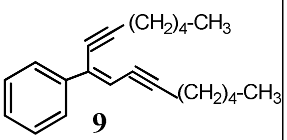
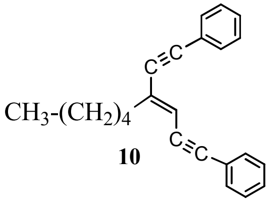
λ_{max} =322 nm

In ^{I}H NMR spectra of the compound **6,** the chemical shift at δ7.53 -7.30 (m, 6H Ar-H) was found for six aromatic protons; and at δ7.39-7.31 (m, 9H, Ar-H; 1H,=CH) for nine aromatic protons and one vinyl proton. For compound **7,** the chemical shift at δ 6.016-7.855 (m, 10H, Ar-H; 2H =CH) for ten aromatic protons and two vinyl protons. For compound **8,** the chemical shift at δ7.26- 7.47 (5H, Ar-H, 1H =CH) for five aromatic protons and one vinylic proton; δ0.92 (t, 6H, J= 6.98-7.19, CH_3) for six methyl protons; δ 1.53-1.51 (m, 8H, CH_2) for eight methylene proton.

For the compound **9,** the chemical shift at δ 7.54 (d, 2H J= 6.33, Ar-H) and 7.35 (m, J= 7.37, 3H Ar-H; 1H, =CH) caused by ten aromatic protons and one vinyl proton; δ 0.923 (t, 3H, J= 7.26, CH_3) for three methyl protons, δ 1.39 (m, 6H, J= 7.08, CH2) for six methylene protons, δ 2.30 (2t, 2H, J= 7.05, CH_2-C=C) caused by methylene protons which are adjacent to alkene group.For compound **9,** the chemical shift at δ 7.47-7.25- (5H, Ar-H, 1H =CH)) for five aromatic protons and one vinylic proton; δ0.88 (t, 6H, J= 6.98, CH_3) for six methyl protons; δ 1.59-1.48 (m, 12H, CH_2) for twelve methylene proton; δ 2.29 (t, 4H, J= 6.75, CH_2) caused four by methylene protons..

In the ^{13}C NMR spectrum of the compound **6** showed the chemical shifts at δ_c 81.533 & 73.890 were found due to the presence of C≡C (δ_c 73.89 for two carbon C-1 and C-6; and δ_c 81.633 for two carbon C-2 and C-5). The chemical shifts at δ_c 133.476 (for C-3) and 121.766 (for C-4) were designed for C=C (vinylic carbon). From the ^{13}NMR spectrum, the chemical shifts for the Ar-C of three phenyl group were found at δ_c 133.48, 129.19, 128.42, and 121.77.

Table-2.7: Comparison of some spectral data and melting point of the alkenyne derivatives

Coupling compound	^{1}HNMR (δ ppm, J Hz)	UV (nm)	IR (cm^{-1})	Melting point
 **6**	7.53 -7.51 (m, 6H Ar-H), 7.39-7.31 (m, 9H, Ar-H; 1H,=CH)	329.6 327.4 324.4 307	1591.2 & 1485.1 (Ar C=C), 1591.2 (alkene C=C), 3050 (ArC-H), 2135.1 (C≡C)	86-87ºC
 **7**	7.86-6.02 (m, 10H, Ar-H; 2H =CH)	356.6 346.4 322, 305.2	1598.9 & 1483(Ar C=C), 1598.9 (alkene C=C), 3055(ArC-H), 21852 (C≡C)	Liquid
 **8**	7.26- 7.47 (5H, Ar-H, 1H =CH), 0.92 (t, 6H, J= 7.19, CH_3), 1.53-1.51 (m, 8H, CH_2), 2.29 (t, 4H, J= 6.75, CH_2)	310.6 292.6 274.4	1575& 1488.9(Ar C=C), 1575 (alkene C=C), 3055 (ArC-H), 2850.6 (aliphatic C-H), 2144.7 (C≡C)	Liquid
 **9**	7.47-7.25- (5H, Ar-H, 1H =CH), 0.88 (t, 6H, J= 6.98, CH_3), 1.59-1.48 (m, 12H, CH_2), 2.29 (t, 4H, J= 6.93, CH_2)	328.8 311.2 305.4 266.6	1591.2 & 1485.1(Ar C=C), 1591.2 (alkene C=C), 3047.3 (ArC-H), 2921.9 (aliphatic C-H), 2144.7 (C≡C)	Liquid
 **10**	7.54 -7.26 (m, 10H, Ar-H; 1H, =CH), 0.923 (t, 3H, J= 7.26, CH_3), 1.44-1.26 (m, 6H, CH_2), 2.30 (2t, 2H, J= 7.05, CH_2)	335 325.4 306.8	1654.4 & 1485(Ar C=C), 1637.2 (s,alkene C=C), 3055(ArC-H), 2921.9 (aliphatic C-H), 2125.05 (C≡C)	76-78 ºC

2.8 Characterization of alkenoate derivatives

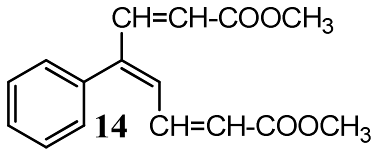
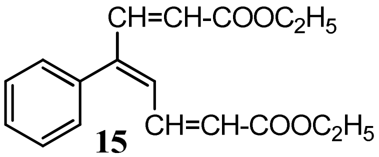
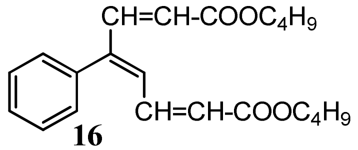
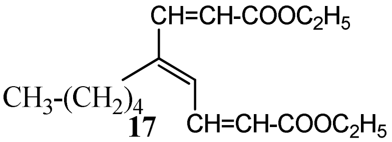
In IR spectra of compounds **14-17** (alkenoate derivatives), the absorption band was found at 3047.3-3055 cm^{-1} due to the aromatic C-H, 1589-1620.7 cm-1 due to alkene C=C. The absorption bands at 1589-1654.2 and 1470-1485.1 cm^{-1} were found due to aromatic C=C group; 2941.2-2977.9 cm^{-1} were found due to the aliphatic C-H; and 1730-1741 cm^{-1} were found due to the presence of ester group (COOR) (**Table-2.8**). For the compounds **17**, the absorption band was found at 1620.7 cm-1 due to alkene C=C; 2925.8 cm^{-1} due to the aliphatic C-H; and 1710.7 cm^{-1} due to the presence of ester group (COOR).

From the UV spectra, the absorption bands (λ_{max}) of the coupling products **14-17** were shifted to the higher wavelength range comparing to their corresponding stating materials due to their extension of conjugation of the unsaturated bonds and chromophoric group (C=C and >CO).

In ^{I}H NMR spectra of the compound **14-16,** the chemical shifts at 7.67-7.29 (5H, Ar-H; 5H, =CH)) were found due to the five aromatic protons and five vinyl protons. For compound **14**, a singlet chemical shift at δ 1.523 ppm was found due to the presence or six protons of methyl group. For the compound **15** and**16**, the chemical shift at δ 0.87-1.113 (t, J= 6.76-6.97, 6H, CH_3), 4.14 (q, J= 6.76-6.79, 4H, CH_2) ppm were fond due to the presence of six methyl protons and four methylene protons (OCH_2) respectively. The chemical shift at δ 1.25 ppm (m) was fond for eight methylene protons (CH_2) of the compound **16**.

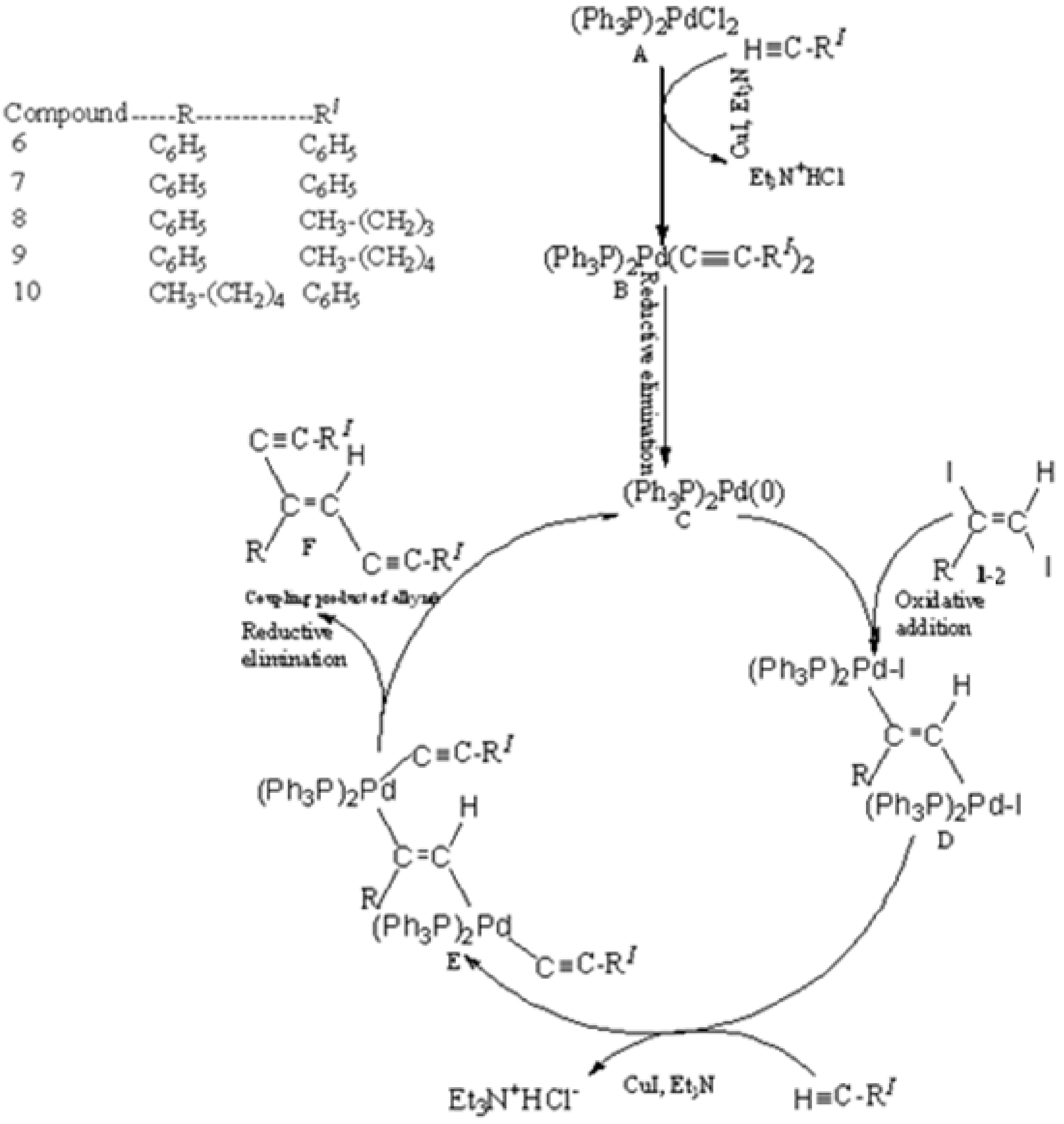
For the compound **17,** the chemical shift at δ 7.25-7.21 (m, 1H, =CH), 6.75 (d, 2H, =CH, J=15.7) and 6.13 (d, 2H, =CH, J=12.4) ppm were found as multiplet, doublet, doublet respectively due to the presence of five vinylic protons (=CH); a triplet were found at δ 0.89 (J= 7.66) due to the presence of three methyl proton, one more triplet were found at 1.40 ppm (J= 7.56) due to the presence of six methyl proton; a multiplet was found at δ 1.22-1.26 for the presence of methylene group (CH_2); and a quartet was found at δ 4.09 for the presence of methylene group (J= 7.25, O CH_2).

Table-2.8: Comparison of some spectral data and melting point of the alkenoate derivatives

Coupling compound	^{1}HNMR (δ ppm, J Hz)	UV (nm)	IR (cm^{-1})	Melting point
 **14**	7.54-7.51 & 7.38-7.29 (2m, 5H, Ar-H; 5H, =CH), 1.523 (s, 6H, CH$_3$)	329, 319.8, 305.2	1591.2 & 1485 (Ar C=C), 1591.2 (alkene C=C), 3448 (ArC-H), 2930 (aliphatic C-H), 1730 (ester)	53-55ºC
 **15**	7.53-7.31 (m, (5H, Ar-H; 5H, =CH), 1.113 (t, J= 6.97, 6H, CH$_3$), 4.14 (q, J= 6.76, 4H, CH$_2$)	329, 315	1610.4 & 1485.1(Ar C=C), 1610.4 (s,alkene C=C), 3055(Ar C-H), 2977.9 (aliphatic C-H), 1730 (ester)	78-79ºC
 **16**	7. 69-7.45 (m, (5H, Ar-H; 5H, =CH) 0.87 (t, J= 6.76, 6H, CH$_3$), 1.2-1.4 (m, 8H, CH$_2$), 4.14 (q, J= 6.79, 4H, CH$_2$)	330, 305.4, 277	1589.2 & 1470 (Ar C=C), 1589.2 (alkene C=C), 3047.3(Ar C-H), 2941.2 (aliphatic C-H) 1741 (ester)	102 - 105ºC
 **17**	7.25-7.21 (m, 1H, =CH), 6.75 (d, 2H, =CH, J=15.7), 6.13 (d, 2H, =CH, J=12.4), 0.89 (t, J= 7.66, 3H, CH$_3$), 1.40 (t, J= 7.56, 6H, CH$_3$), 1.22-1.26 (m, 8H, CH$_2$) , 4.09 (q, J= 7.25, 4H, CH$_2$)	329.2, 310.2	1620.7 (alkene C=C), 1498.6 (CH$_2$), 1458 & 1301.9 (CH$_3$), 2925.8 (aliphatic C-H) , 1710.7 (ester)	Liquid

2.9 Mechanism of palladium-catalyzed coupling reaction of 1,2-diiodo-1-alkene with 1-alkyness

The mechanism of the synthesis of alkenyne derivatives was followed the Sonogashira coupling reaction. The presumed catalytic cycle of the synthesis of alkenyne derivatives is shown in **Scheme-5**. Bis (triphenyl phosphine) palladium (0) (see C), the putative active catalyst, could conceivably bis-alkynylation and reductive elimination reactions (see A→B→C, Scheme-5). Once formed, the highly coordinatively unsaturated 14-electron palladium (0) complex C was participated in an oxidative addition reaction with the 1,2-diiodo-1-alkene to give the 16-electron palladium (II) complex D. A copper (I) - catalyzed alkynylation of D then furnished an alkenyl palladium (II) complex E. Finally, the terminating reductive elimination step revealed the coupling product F and the active palladium (0) catalyst was regenerated.

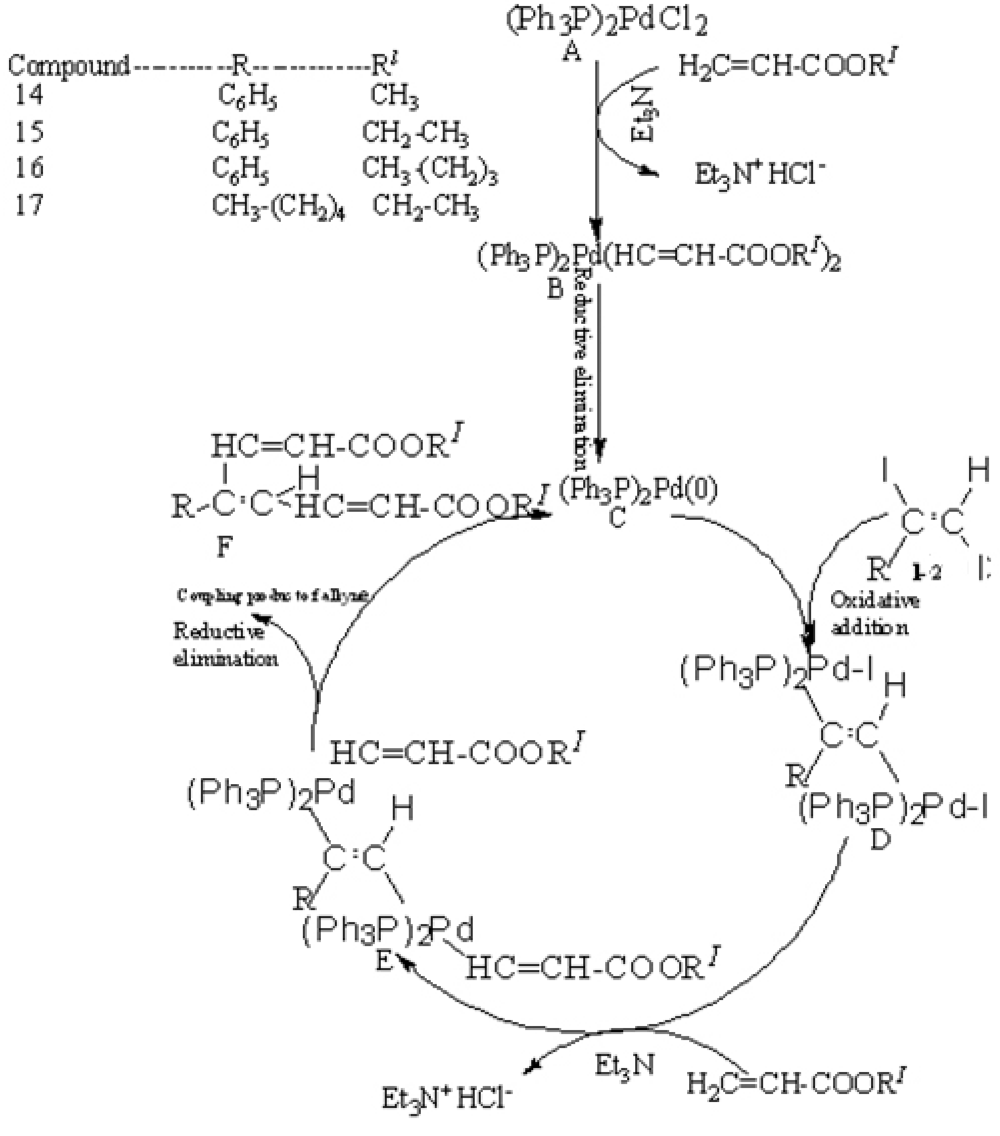


Scheme-5

2.10 Mechanism of palladium-catalyzed coupling reaction of 1,2-diiodo-1-alkene with alkyl acrylates

Although the detailed mechanism of the coupling reaction is yet to be clarified, it can be perceived that the reactions proceed according to **Scheme-6**. From our observation, it was clear that the presence of palladium catalyst was very essential for the success of the coupling reactions.

The key steps of the mechanism were based on the following observations. It could be suggest that Pd (0) could be the intermediate involved in the catalytic process. The reaction of Pd (II) to Pd (0) in the presence of Et_3N and terminal alkynes took place. The Heck reaction produced the expected products, presumably by the classic catalytic cycle.



Scheme-6

2.11 Conclusion

Here we have developed a convenient and facile method for the synthesis of alkene and alkyne derivatives from terminal alkynes through palladium catalyzed coupling reaction.

The most important features of the synthesis were that –

1) Readily available starting materials were used under relatively mild conditions.

2) The iodo compounds were prepared from their corresponding terminal alkynes; and their alkene and alkyne derivatives were synthesized through palladium- catalyzed cross-coupling reaction with terminal alkynes and alkyl acrylates.

3) One of the most important features is that there is no toxic or hazardous compounds is prepared in this procedure.

4) The coupling products were prepared from the freshly prepared starting materials and temperature was maintained carefully. Because the iodo compounds and their coupling products can be deiodinated or decomposed easily.

5) The iodo compounds and their coupling products were very sensitive to heat and light. For this after preparing them these were kept in a dark place at cool temperature.

6) By using this methodology researchers will be able to synthesize alkene and alkyne derivatives from their terminal alkynes which might have versatile synthetic importance.

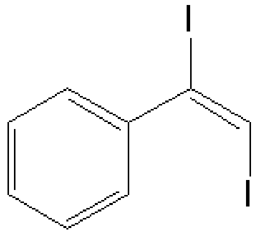
3.0 Experimental

Melting points were determined in open capillary tubes on Stuart SMP10 melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrophotometer (400MHz) using tetramethylsilane as internal reference. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60F-254 (E. Merck), and the spots were visualized with UV light. Column chromatography was performed on silica gel (60–120 mesh). Bis (triphenyl phosphine) palladium(II) chloride and other reagents were purchased from E. merck (Germany) and Fluka (Switzerland).

3.1 Synthesis and characterization of iodo compounds

3.1.1 Preparation of iodo compounds

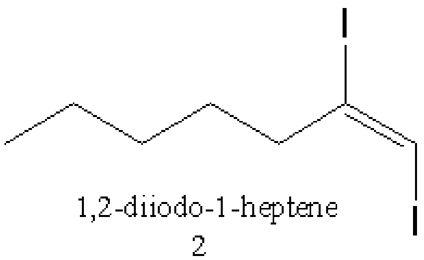
The starting material 1,2-diiodo-1-phenylethene was prepared from phenylacetylene using molecular iodine under mild condition.



1,2-diiodophenylethene

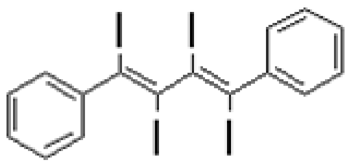
1

In this way 1,2-diiodo-1-heptene was prepared from 1-heptyne; and 1,4-diphenyl-1,2,3,4-tetraiodo-1,3-butadiene was prepared from the dimer of phenylacetylene.



1,2-diiodo-1-heptene

2



1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene

14

3.1.2 The characteristic data of iodo compounds 1, 2 and 18

1,2-diiodo-1-phenylethene

Physical state: Yellow solid.

mp: 76-77° C.

R_f Value: 0.90 (n-hexane)

IR (KBr): ν_{max} 1566.1 & 1479.3 (Ar C=C), 1566.1 (alkene C=C), 3080 (Ar C-H), 594 (C-I) cm^{-1}.

UV: λ_{max} 310.8 nm.

^{1}HNMR: (400 MHz, $CDCl_3$): δ_H 7.286-7.3414 (m, 5H, Ar-H), 7.25 (s, 1H, =CH) ppm

1,2-diiodo-1-heptene

Physical state: Orange solid.

R_f Value: 0.93(n-hexane)

IR (KBr): ν_{max} 1600.1 (alkene C=C), 2960 (Aliphatic C-H), 550 (C-I) cm^{-1}

UV: λ_{max} 312.80 nm.

1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene

Physical state: Yellow solid.

mp: 82-83°C.

R_f Value: 0.85 (n-hexane)

IR (KBr): ν_{max} 1546.8 & 1485.1(Ar C=C), 1546.8 (alkene, C=C), 3047.3 (Ar C-H), 522.7 (C-I) cm^{-1}.

UV: λ_{max} 305, 327.2, 334.2 nm.

^{1}HNMR: (400 MHz, $CDCl_3$): δ_H 7 7.54-7.51 (m, 4H, Ar-H), 7.40-7.31 (m, 6H, Ar-H) ppm

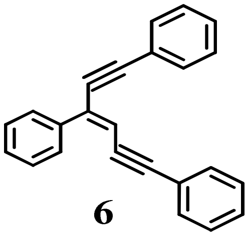
3.2 Synthesis and characterization of alkenyne derivatives 6-10

3.2.1 General procedure for the synthesis of alkenyne derivatives 6-10

For the preparation of alkenyne compounds **6-10** the coupling reaction was carried out by stirring the mixture of starting material **1** or **2** and one of the 1-alkyne (**3-5**) (3 equiv.) in dichloromethane (10 ml) or DMF (4 ml) in the presence of bis (triphenylhosphine) palladium(II) chloride (3.5 mol%), copper iodide (8 mol%), and triethylamine (4 equ.) for 24 hr at 80ºC. After usual work up purification on column chromatography over silica gel the final products **6-10** were obtained in good yield.

3.2.2 The characteristic data of alkenyne derivatives 6-10

1,3,6-triphenylhex-3-en-1,5-diyne 6



6

Physical state: Light yellow solid

mp: 86-87°C

R_f Value: 0.6 (n-hexane)

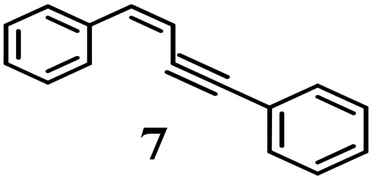
IR (KBr): 1591.2 & 1485.1 (Ar C=C), 1591.2 (alkene C=C), 3050 (Ar C-H), 2135.1 (C≡C) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53 -7.51 (m, 6H Ar-H), 7.39-7.31 (m, 9H, Ar-H; 1H, =CH) ppm.

^{1}C NMR (100 MHz, $CDCl_3$): δ_C 133.48, 129.19, 128.42, and 121.77 (Ar-C); 73.89, 81.63 (C≡C); 133.48, 121.77 (vinylic carbon, C=C)

UV: λ_{max} 329.6, 327.4, 324.4, 307 nm.

1,4-diphenylbut-1-en-3-yne 7



7

Physical state: Orange liquid

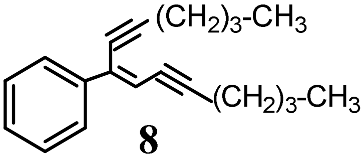
R_f Value: 0.32 (n-hexane)

IR (KBr): 1598.9 & 1483(Ar C=C), 1598.9 (alkene C=C), 3055 (Ar C-H), 21852 (C≡C) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86-6.02 (m, 10H, Ar-H; 2H =CH) ppm.

UV: λ_{max} 356.6, 346.4, 322, 305.2nm.

7-phenyl-7-tetradecen-5,9-diyne 8



8

Physical state: Light yellow liquid

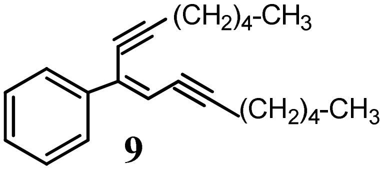
R_f Value: 7.3 (n-hexane)

IR (KBr): 1575& 1488.9(Ar C=C), 1575 (alkene C=C), 3055 (Ar C-H), 2850.6 (aliphatic C-H), 2144.7 (C≡C) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26- 7.47 (5H, Ar-H, 1H =CH), 0.92 (t, 6H, J= 7.19 Hz, CH_3), 1.53-1.51 (m, 8H, CH_2), 2.29 (t, 4H, J= 6.75 Hz, CH_2) ppm.

UV: λ_{max} 310.6, 292.6, 274.4 nm.

8-phenyl-8-hexadecen-6,10-diyne 9



9

Physical state: Orange liquid

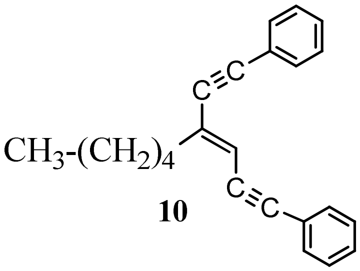
R_f Value: 0.80 (n-hexane)

IR (KBr): 1591.2 & 1485.1(Ar C=C), 1591.2 (alkene C=C), 3047.3 (Ar C-H), 2921.9 (aliphatic C-H), 2144.7 (C≡C) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47-7.25- (5H, Ar-H, 1H =CH), 0.88 (t, 6H, J= 6.98 Hz, CH_3), 1.59-1.48 (m, 12H, CH_2), 2.29 (t, 4H, J= 6.93 Hz, CH_2) ppm.

UV: λ_{max} 328.8, 311.2, 305.4, 266.6 nm.

3-pentyl-1,6-diphenyl-3-hexen-1,5-diyne 10



10

Physical state: Light yellow solid

mp: 76-78°C

R_f Value: 0.7 (n-hexane)

IR (KBr): 1654.4 & 1485(Ar C=C), 1637.2 (alkene C=C), 3055(Ar C-H), 2921.9 (aliphatic C-H), 2125.05 (C≡C) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 -7.26 (m, 10H, Ar-H; 1H, =CH), 0.923 (t, 3H, J= 7.26 Hz, CH_3), 1.44-1.26 (m, 6H, CH_2), 2.30 (2t, 2H, J= 7.05 Hz, CH_2) ppm.

UV: λ_{max} 335, 325.4, 306.8 nm.

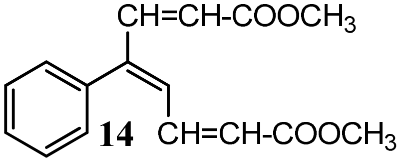
3.3 Synthesis and characterization of alkenoate derivatives 14-17

3.3.1 General procedure for the synthesis of alkenyne derivatives 14-17

For the preparation of alkenoate derivatives **14-17,** the coupling reaction was carried out by stirring the mixture of starting material **1** or **2** and one of the 1-alkyne (**3-5**) (3 equiv.) in For the preparation of alkenoate compounds **14-17** the coupling reaction was carried out by stirring the mixture of starting material **1** or **2** and one of the alkyl acrylate (**11-13**) (3 equ.) in dichloromethane (10 ml) or DMF (4 ml) in the presence of bis (triphenylhosphine) palladium(II) chloride (3.5 mol%) and triethylamine (4 equ.) for 24 hr at 80ºC. After usual work up purification on column chromatography over silica gel the final products **14-17** were obtained in good yield.

3.3.2 The characteristic data of alkenoate derivatives 14-17

4-phenyl-1,8-dimethylocta-2,4,6-trienoate 14



Physical state: Light yellow solid

mp: 53-55°C

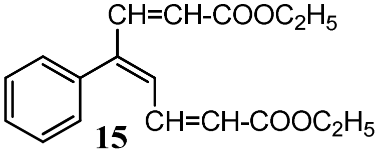
R_f Value: 0.87 (n-hexane)

IR (KBr): 1591.2 & 1485 (Ar C=C), 1591.2 (alkene C=C), 3448 (Ar C-H), 2930 (aliphatic C-H), 1730 (ester, COOR) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 77.54-7.51 & 7.38-7.29 (2m, 5H, Ar-H; 5H, =CH), 1.52 (s, 6H, CH_3) ppm.

UV: λ_{max} 329, 319.8, 305.2 nm.

4-phenyl-1,8-diethylocta-2,4,6-trienoate 15



Physical state: white solid

mp: 78-79ºC

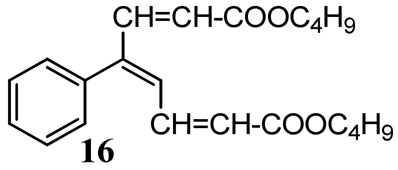
R_f Value: 0.86 (n-hexane)

IR (KBr): 1610.4 & 1485.1(Ar C=C), 1610.4 (alkene C=C), 3055(Ar C-H), 2977.9 (aliphatic C-H), 1730 (ester, COOR) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53-7.31 (m, (5H, Ar-H; 5H, =CH), 1.113 (t, J= 6.97 Hz, 6H, CH_3), 4.14 (q, J= 6.76 Hz, 4H, CH_2) ppm.

UV: λ_{max} 329, 315 nm.

4-phenyl-1,8-dibutylocta-2,4,6-trienoate 16



16

Physical state: Light yellow solid

mp: 102 -105ºC

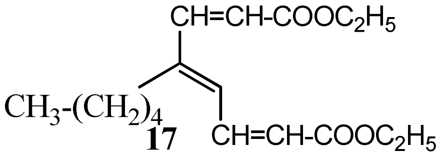
R_f Value: 0.68 (n-hexane)

IR (KBr): 1589.2 & 1470 (Ar C=C), 1589.2 (alkene C=C), 3047.3(Ar C-H), 2941.2 (aliphatic C-H), 1741 (ester, COOR) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7. 69-7.45 (m, (5H, Ar-H; 5H, =CH), 0.87 (t, J= 6.76 Hz, 6H, CH_3), 1.2-1.4 (m, 8H, CH_2), 4.14 (q, J= 6.79 Hz, 4H, CH_2) ppm.

UV: λ_{max} 330, 305.4, 277 nm.

4-pentyl-1,8-dibutylocta-2,4,6-trienoate 17



17

Physical state: Light yellow liquid

mp: 102 -105ºC

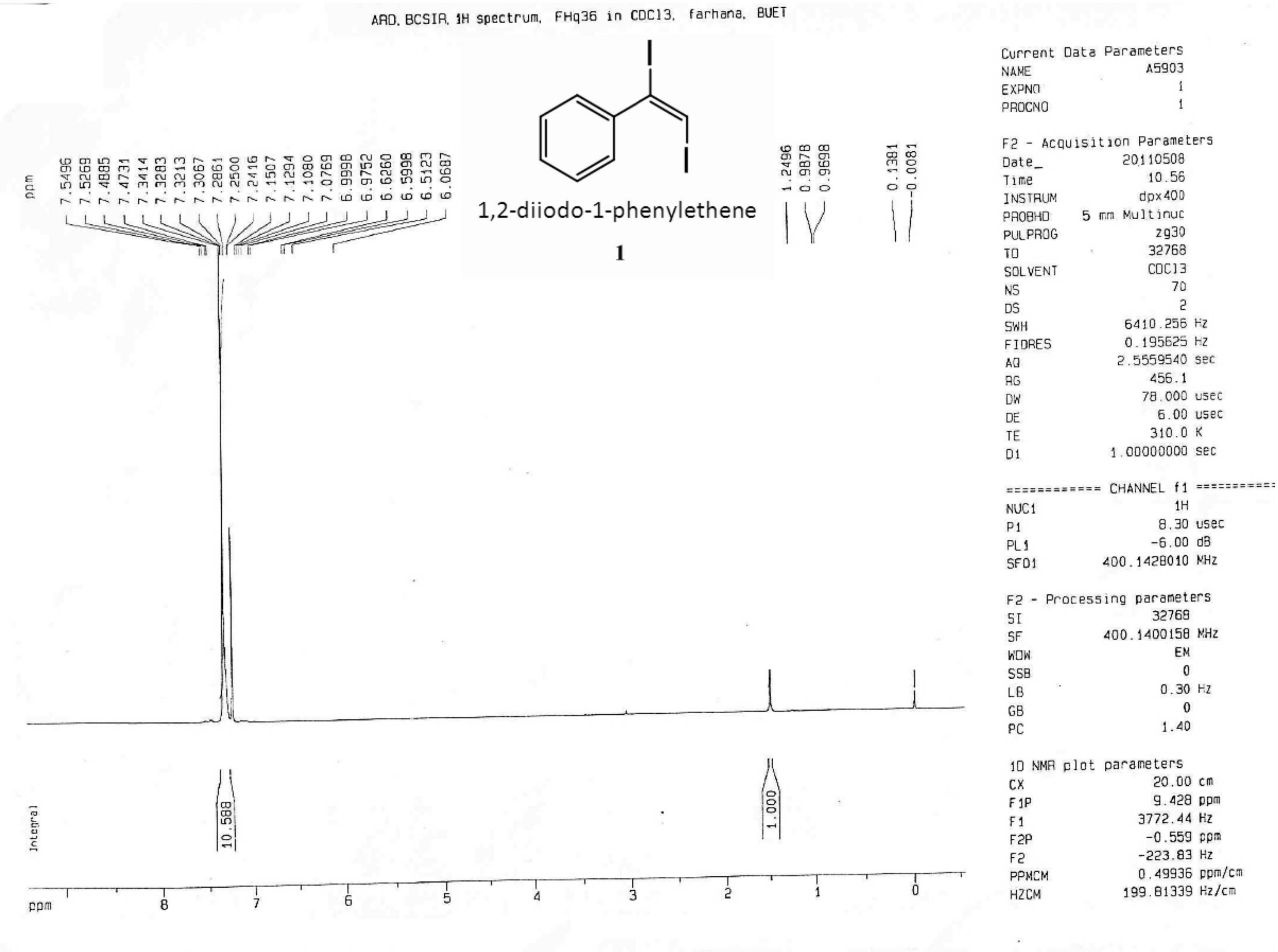
R_f Value: 0.14 (n-hexane)

IR (KBr): 1620.7 (alkene C=C), 1498.6 (CH2), 1458 & 1301.9 (CH3), 2925.8 (aliphatic C-H), 1710.7 (ester, COOR) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25-7.21 (m, 1H, =CH), 6.75 (d, 2H, =CH, J=15.7), 6.13 (d, 2H, =CH, J=12.4), 0.89 (t, J= 7.66 Hz, 3H, CH_3), 1.40 (t, J= 7.56 Hz, 6H, CH_3), 1.22-1.26 (m, 8H, CH_2) , 4.09 (q, J= 7.25 Hz, 4H, CH_2 ppm.

UV: λ_{max} 329.2, 310.2 nm.

ARD, BCSIR, 1H spectrum, FHq36 in CDC13, farhana, BUET



1,2-diiodo-1-phenylethene

1

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EXPNO                   1
PROCNO                  1

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PULPROG              zg30
TD                  32768
SOLVENT             CDC13
NS                     70
DS                      2
SWH              6410.256 Hz
FIDRES           0.195625 Hz
AQ              2.5559540 sec
RG                  456.1
DW                 78.000 usec
DE                   6.00 usec
TE                  310.0 K
D1             1.00000000 sec

============ CHANNEL f1 ==========
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P1                   8.30 usec
PL1                 -6.00 dB
SFO1          400.1428010 MHz

F2 - Processing parameters
SI                  32768
SF            400.1400158 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
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F2P                -0.559 ppm
F2                -223.83 Hz
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HZCM            199.81339 Hz/cm
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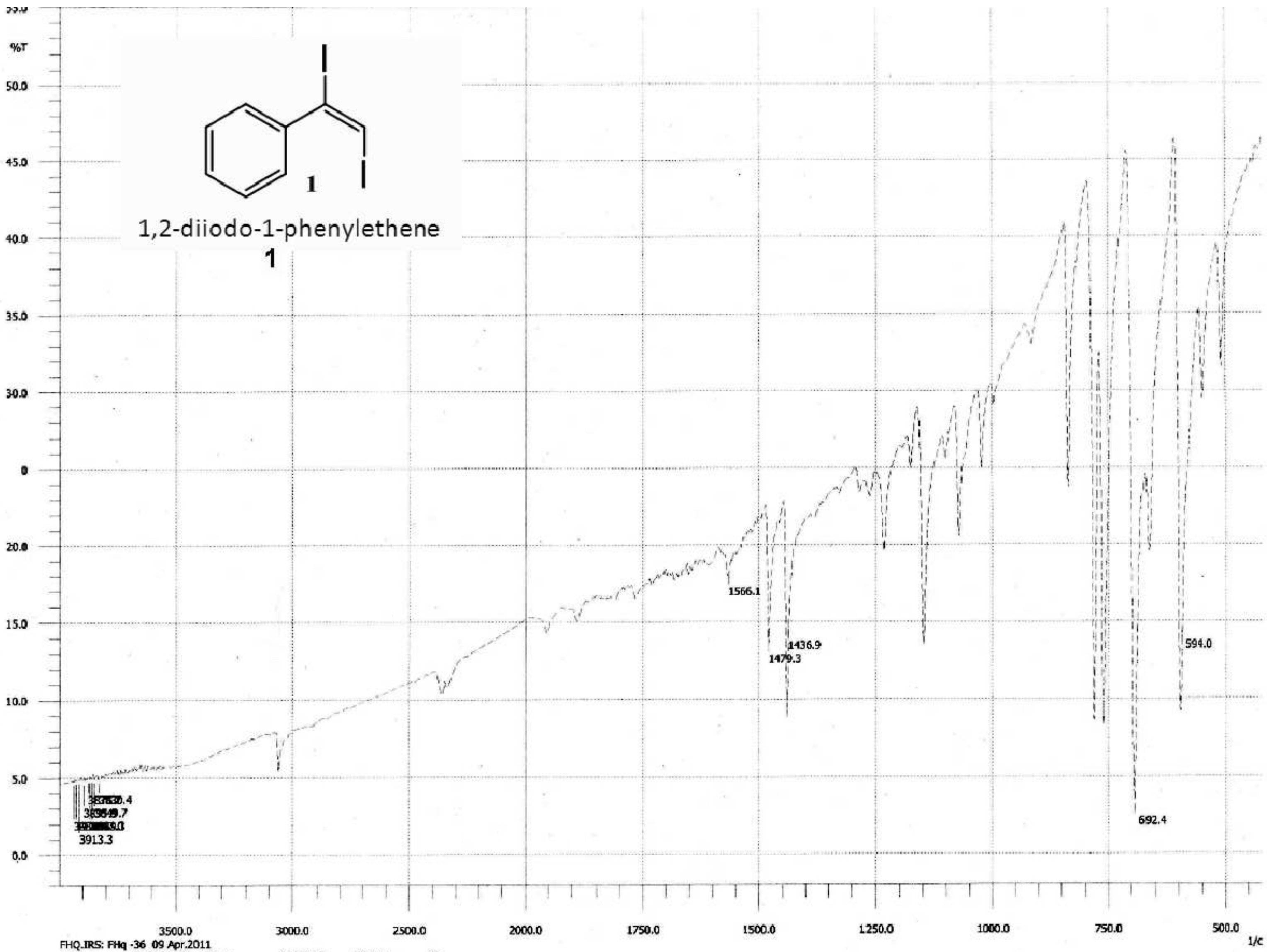

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Min:        401.17       Max:            3998.16     Range:         1/cm
Ndp:        1866         Data Interval:  1.92868     Resolution:    4.0
Gain:       auto         Aperture:       auto        Mirror Speed:  2.8(low)
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Created: 11:53 06/19/12
Data: Original

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Scan Speed: Fast
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Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
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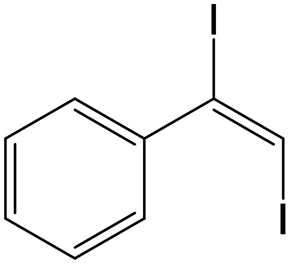
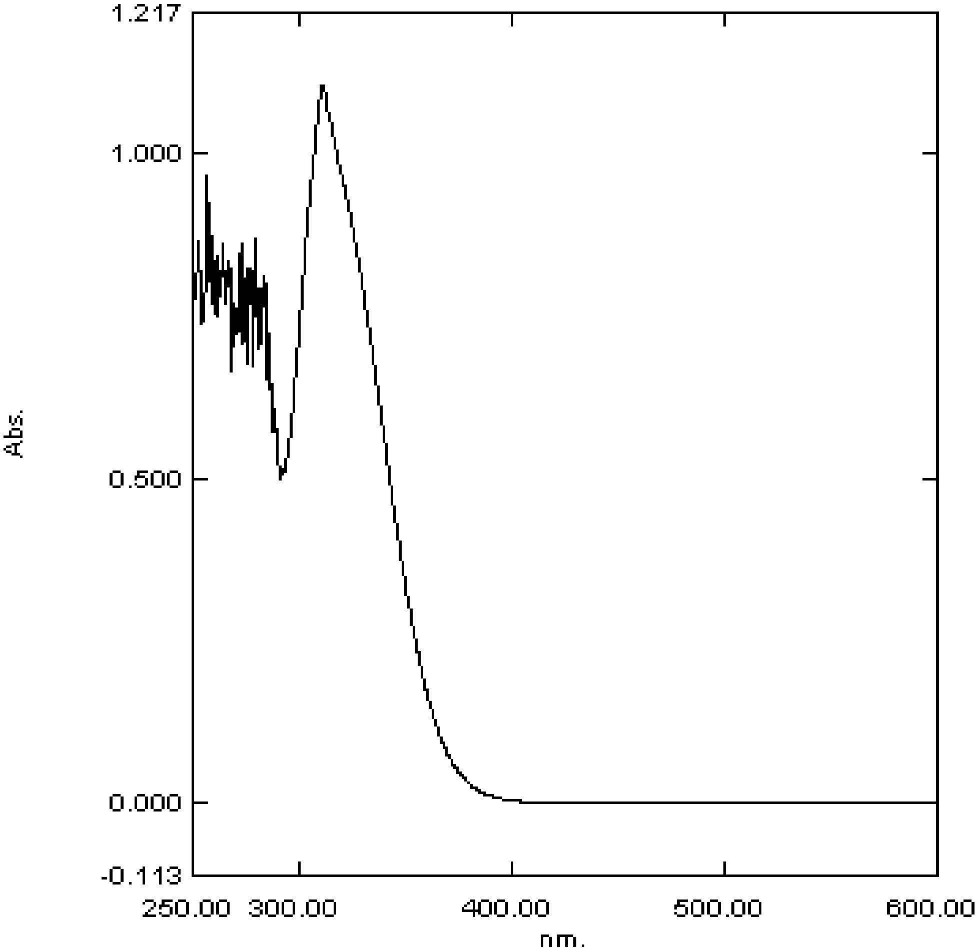
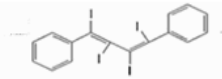


1
1,2-diiodo-1-phenylethene

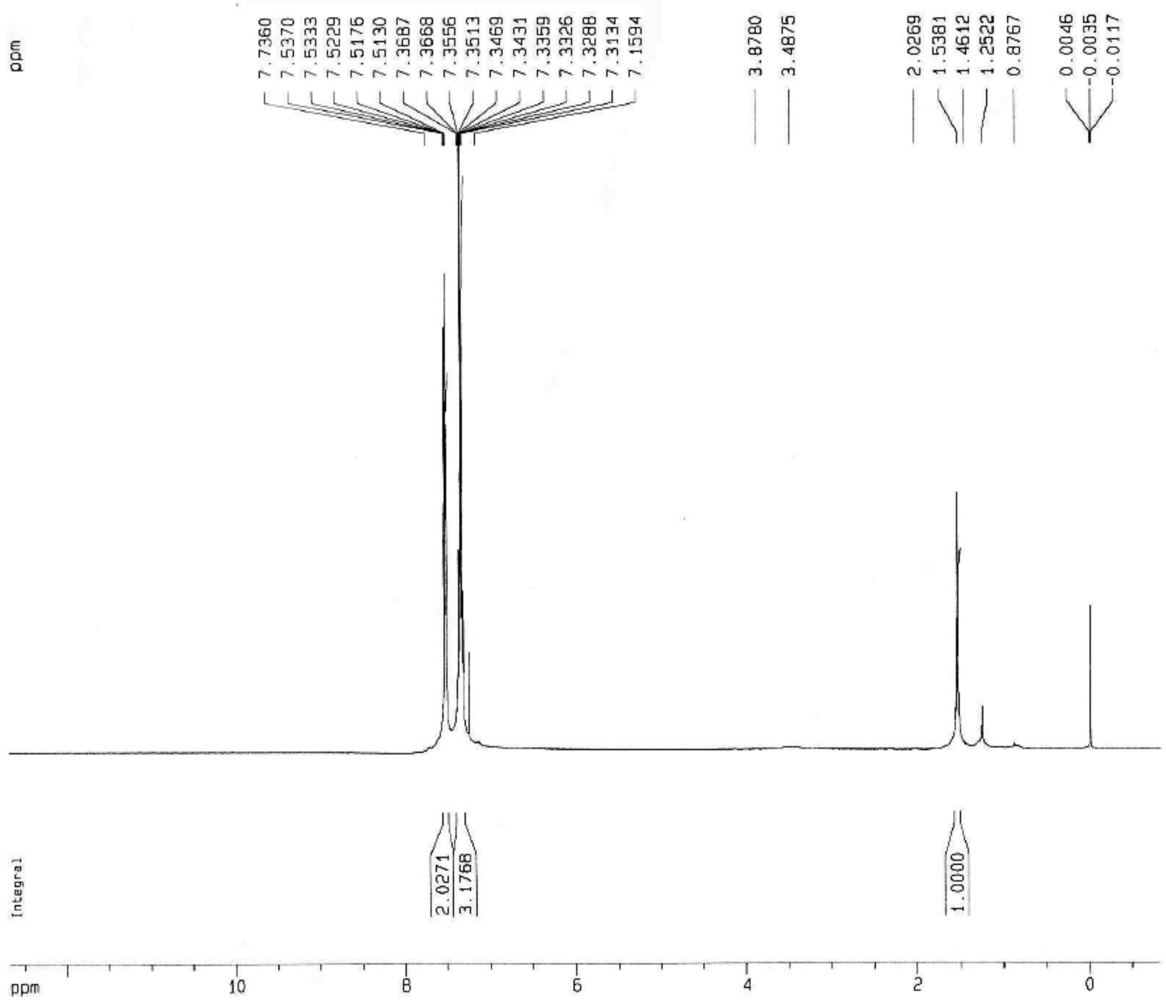
1



ARD, BCSIR, 1H Spectrum, FHq2 in cdcl3.



1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene
18



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EXPNO                1
PROCNO               1

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PULPROG             zg
TD               32768
SOLVENT          CDCl3
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DS                   2
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FIDRES        0.195625 Hz
AQ           2.5559540 sec
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DW              78.000 usec
DE                6.00 usec
TE               310.0 K
D1          1.00000000 sec

============ CHANNEL f1 ============
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P1                8.50 usec
PL1              -6.00 dB
SFO1       400.1428010 MHz

F2 - Processing parameters
SI               32768
SF         400.1400126 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P             12.680 ppm
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F2P             -0.820 ppm
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HZCM         270.10272 Hz/cm
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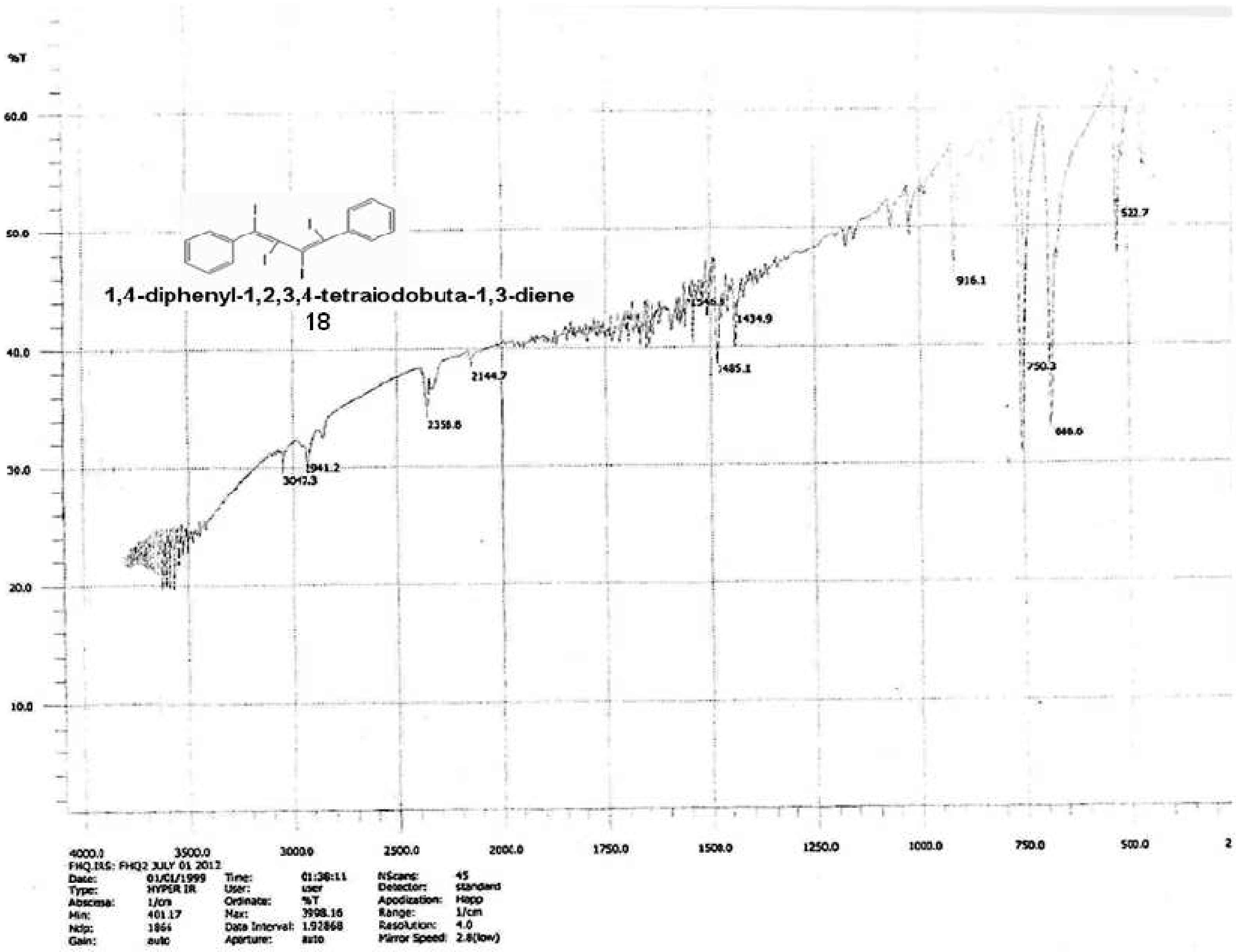

1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene

18

File Name: **FHQ2**

Created: 12:20 06/19/12
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Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

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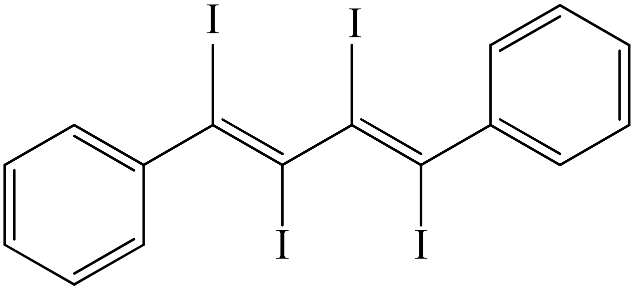
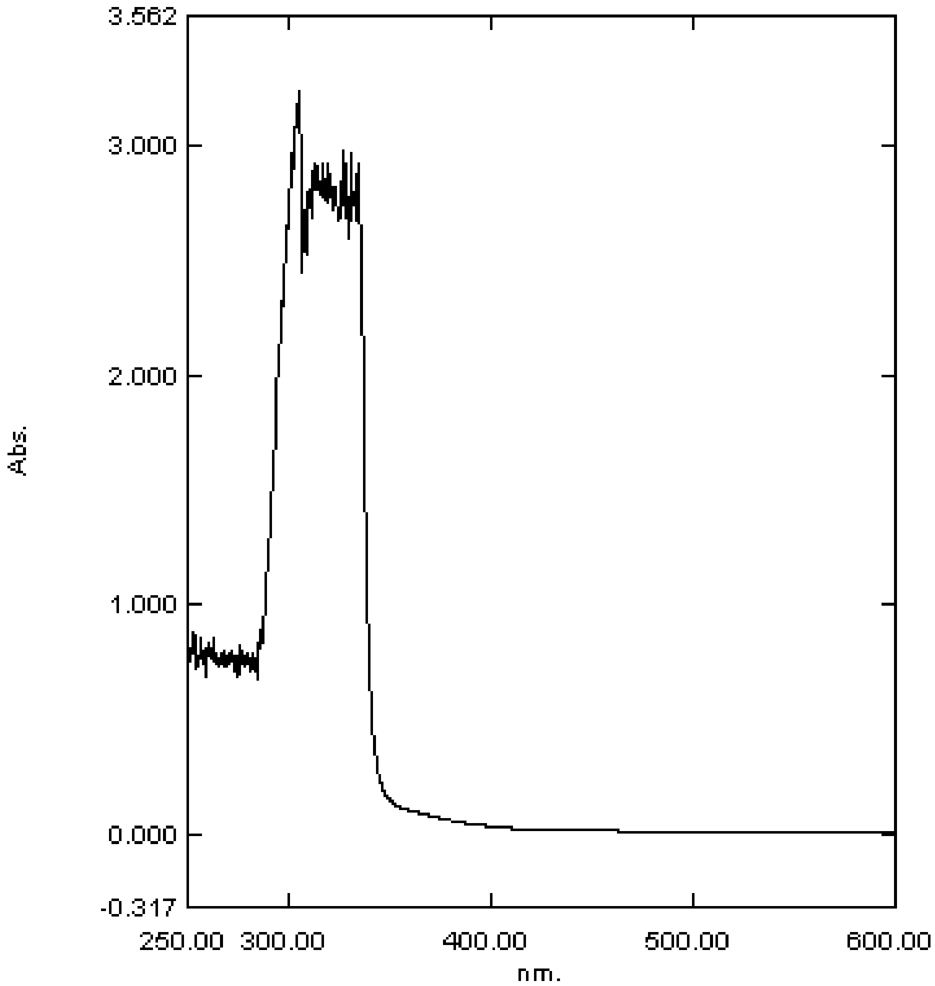
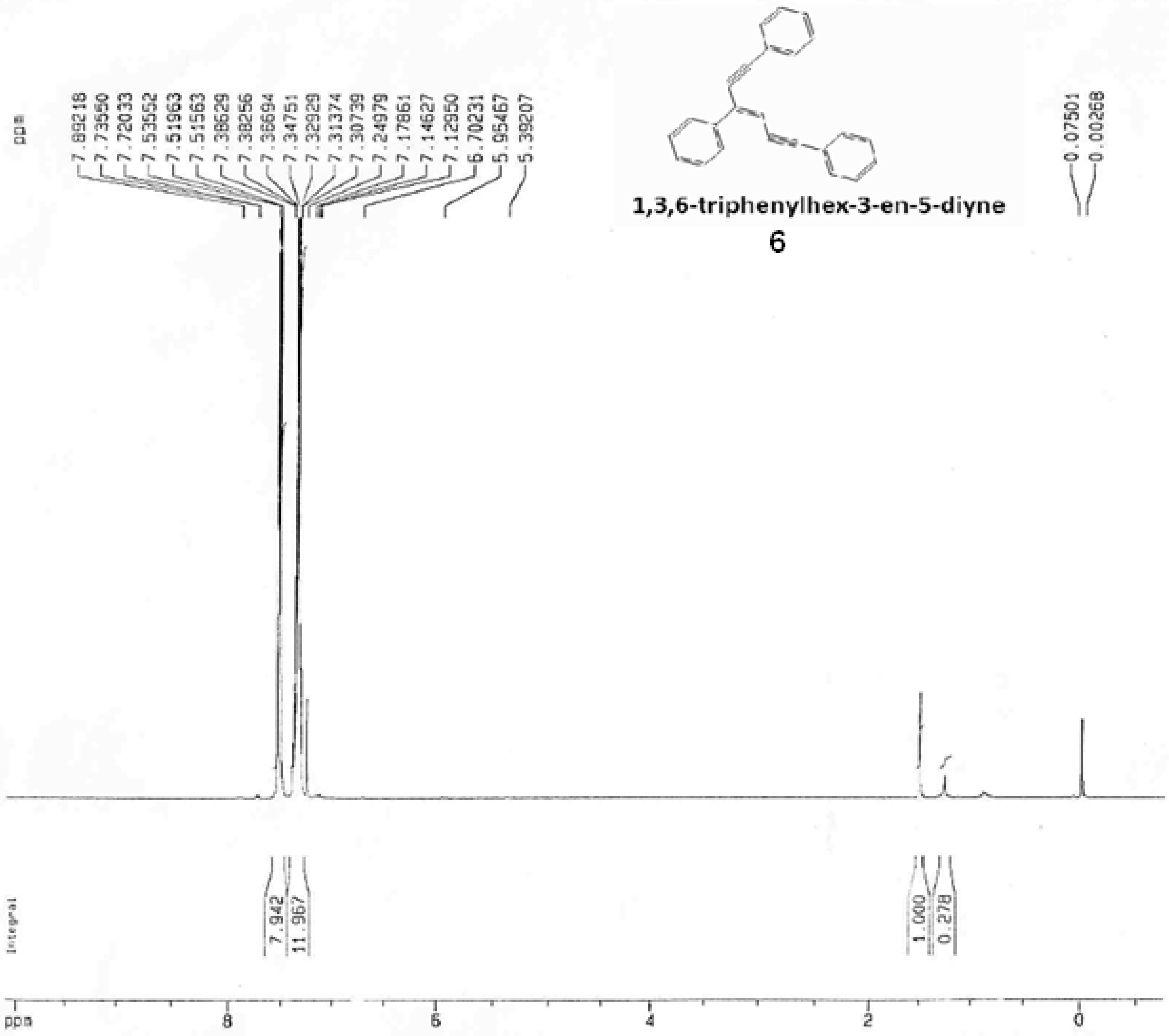


18
1,4-diphenyl-1,2,3,4-tetraiodobuta-1,3-diene



ARD, BCSIR, 1H spectrum, FHq 34 P1 in CDC13, Farhana, BUET



1,3,6-triphenylhex-3-en-5-diyne

6

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EXPNO                    1
PROCNO                   1

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FIDRES            0.195625 Hz
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RG                   322.5
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DE                    6.00 usec
TE                   310.0 K
D1              1.00000000 sec

============ CHANNEL f1 ============
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P1                    8.30 usec
PL1                  -6.00 dB
SFO1           400.1428010 MHz

F2 - Processing parameters
SI                   32768
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WDW                     EM
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GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
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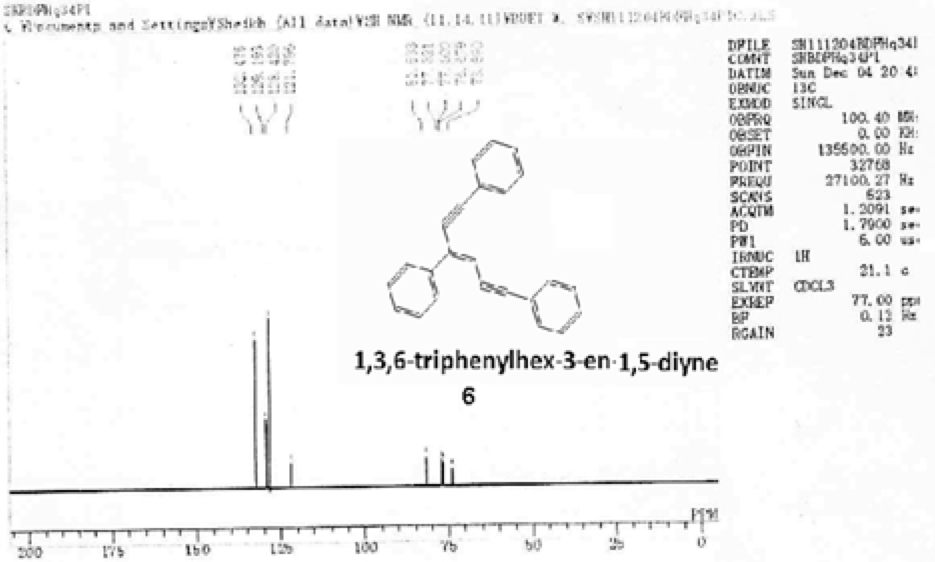

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SHBDPHq34P1
C ¥Documents and Settings¥Sheikh (All data)¥SH NMR (11.14.11)¥BUET ¥. S¥SH111204BDPHq34P1C.ALS
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1,3,6-triphenylhex-3-en-1,5-diyne

6

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EXMOD   SINGL
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OBSET             0.00 KH
OBFIN        135500.00 Hz
POINT            32768
FREQU         27100.27 Hz
SCANS              523
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RGAIN               23
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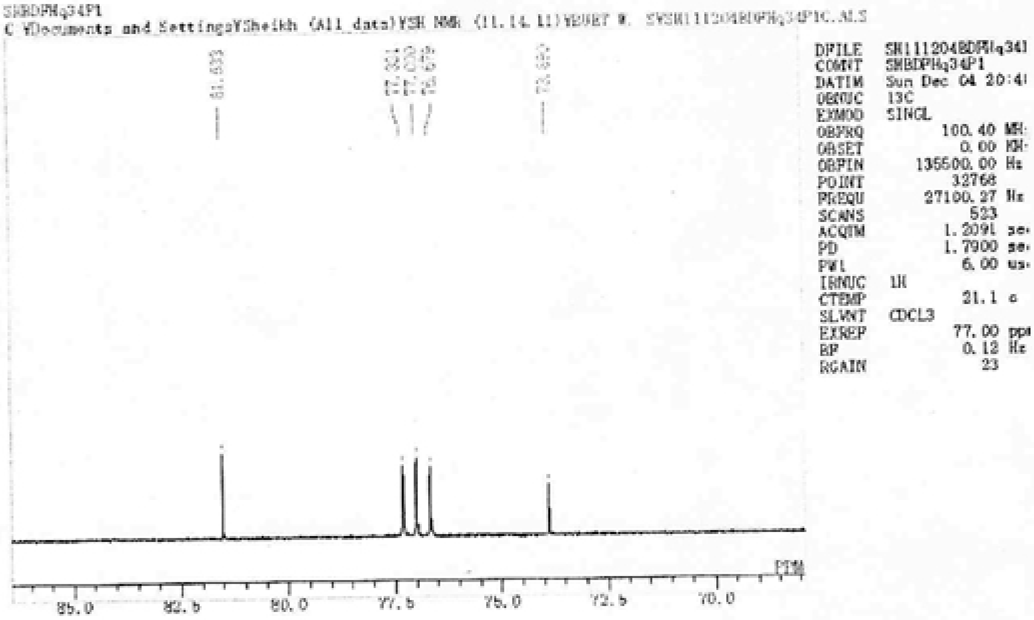

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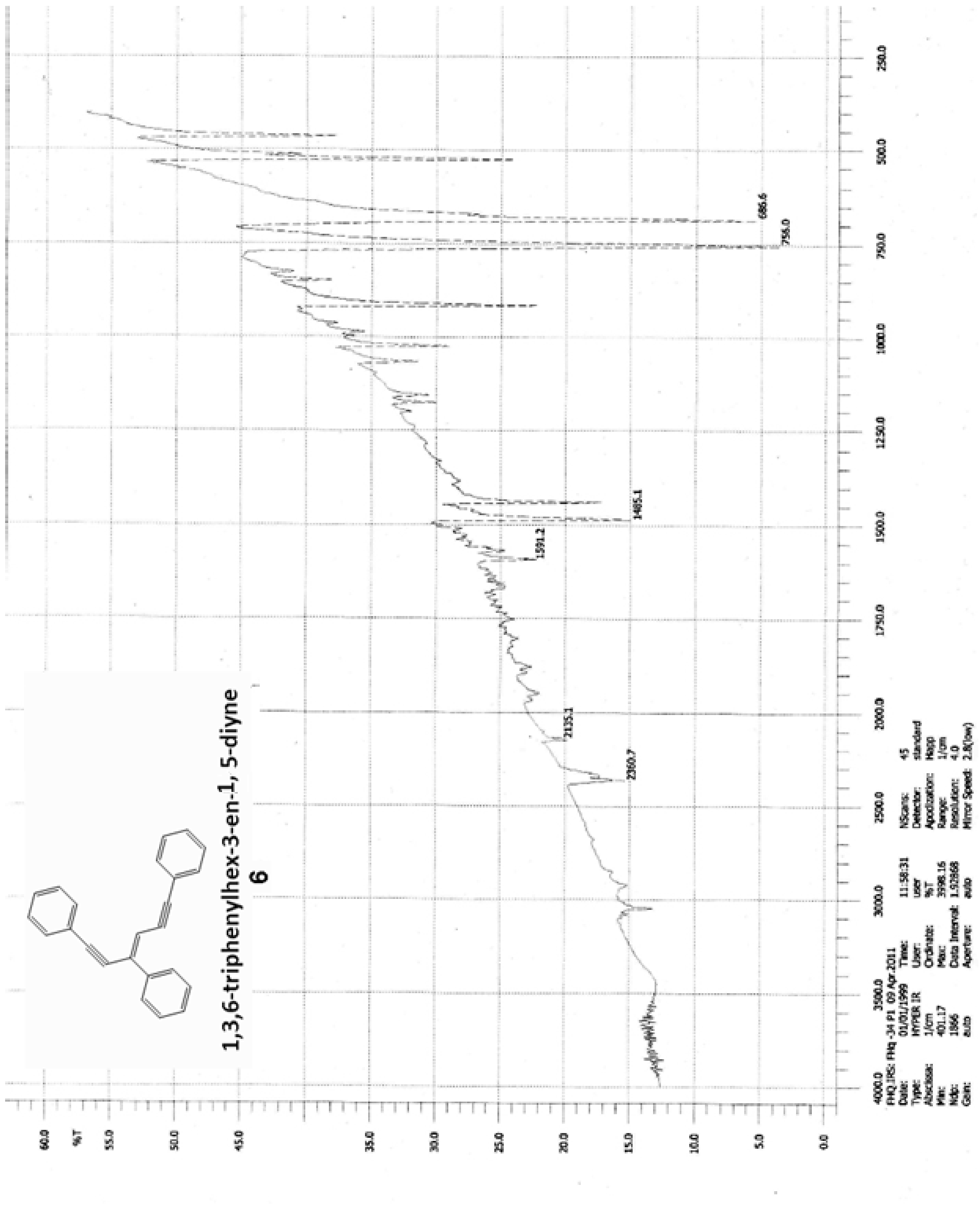

1,3,6-triphenylhex-3-en-1, 5-diyne

6

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Ndp: 1866 Data Interval: 1.92868
Gain: auto Aperture: auto
NScans: 45
Detector: standard
Apodization: Happ
Range: 1/cm
Resolution: 4.0
Mirror Speed: 2.8(low)

File Name: **FHQ34P1**

Created: 11:59 06/19/12
Data: Original

Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
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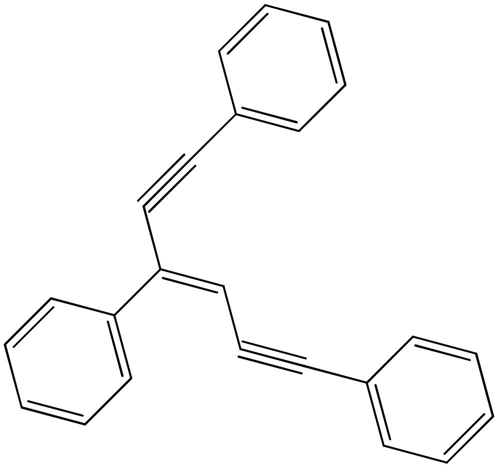
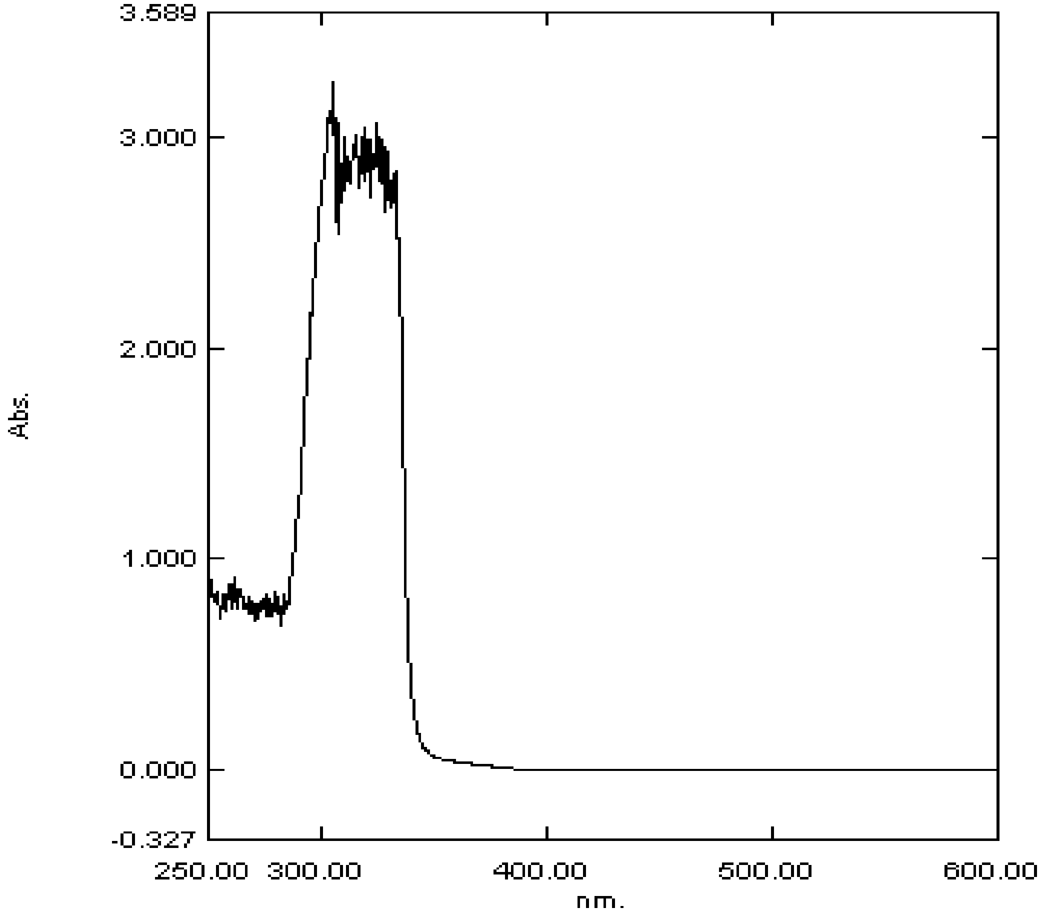
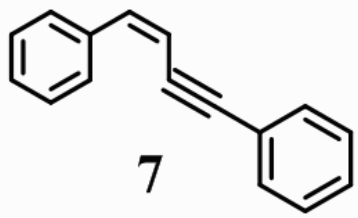
2	327.40	2.9850
3	324.40	3.0602
4	307.00	3.0941



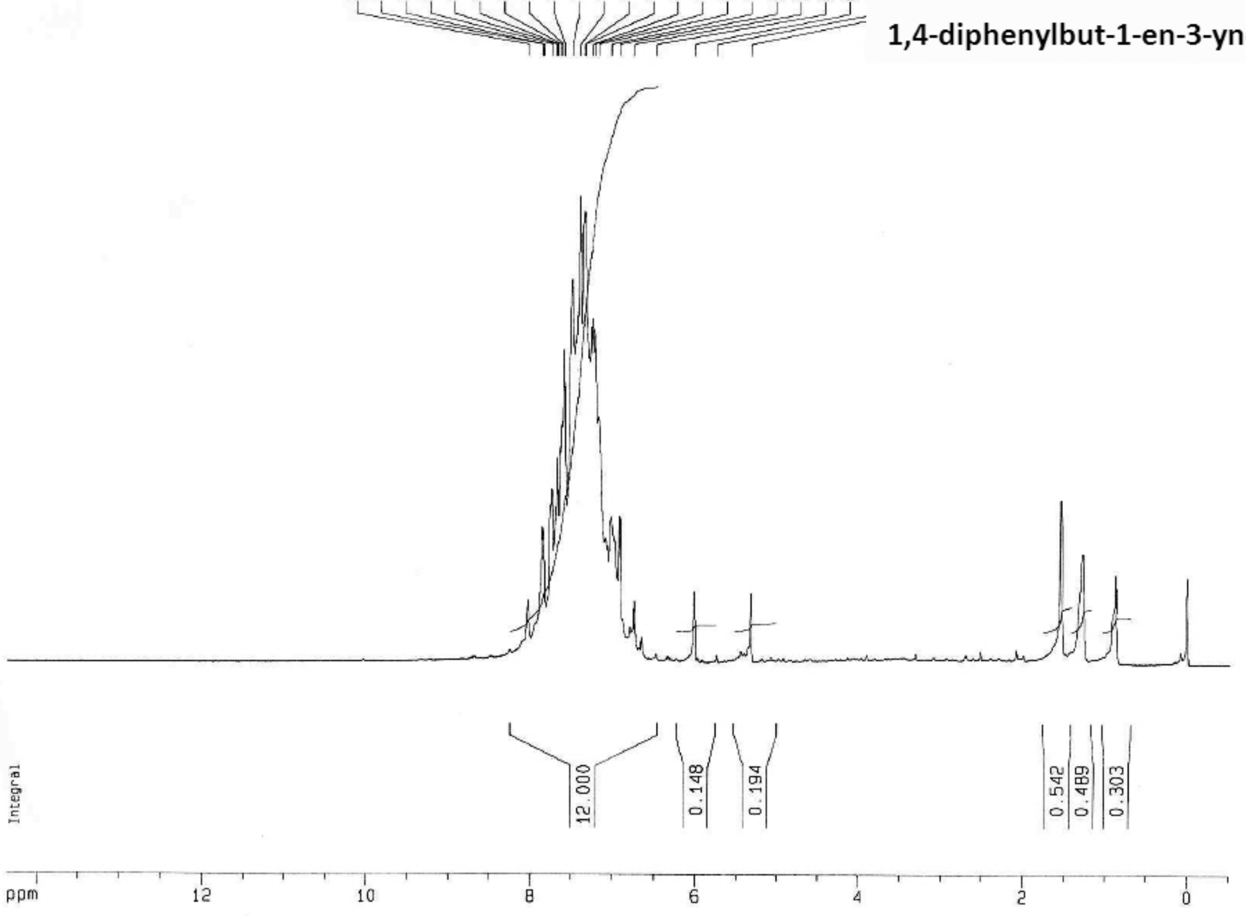
6
1,3,6-triphenyl-hex-3-en-1,5-diyne





7

1,4-diphenylbut-1-en-3-yne



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PROCNO                1

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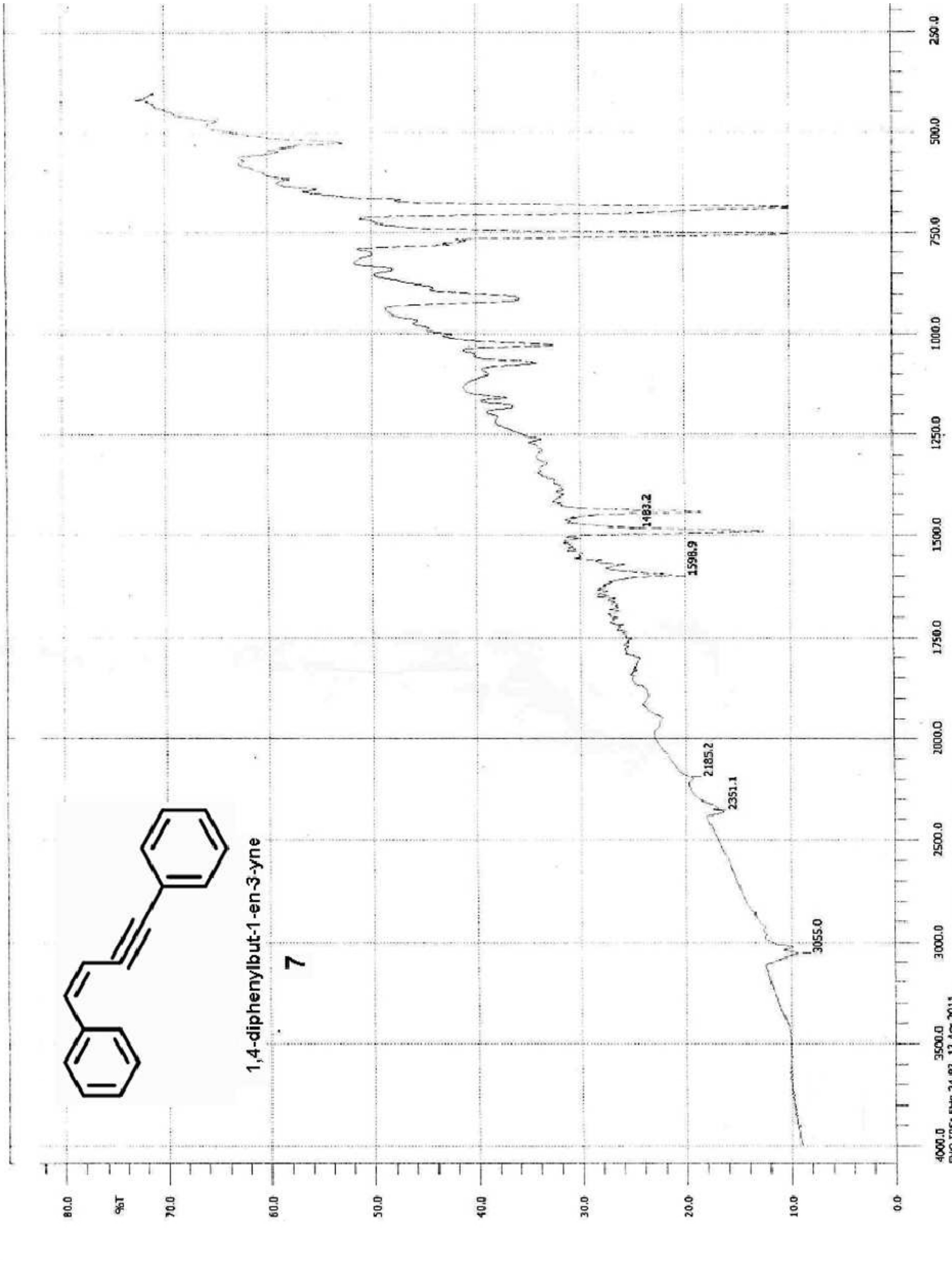
DE                 6.00 usec
TE                310.0 K
D1           1.00000000 sec

============ CHANNEL f1 ============
NUC1                 1H
P1                 8.50 usec
PL1               -6.00 dB
SFO1        400.1428010 MHz

F2 - Processing parameters
SI                32768
SF          400.1400112 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              14.369 ppm
F1              5749.71 Hz
F2P              -0.510 ppm
F2              -204.13 Hz
PPMCM           0.74397 ppm/cm
HZCM          297.69205 Hz/cm
```

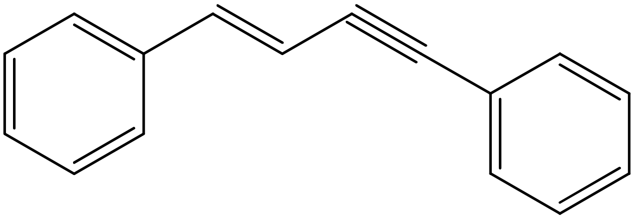

1,4-diphenylbut-1-en-3-yne
7
%T
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
4000.0
3500.0
3000.0
2500.0
2000.0
1750.0
1500.0
1250.0
1000.0
750.0
500.0
250.0
3055.0
2351.1
2185.2
1598.9
1483.2
FHQ.IRS: FHq-34 P3 13 Apr 2011
Date: 01/01/1999
Type: HYPER IR
Time: 11:23:12
User: user
NScans: 45
Detector: standard

File Name: **FHQ34P3**

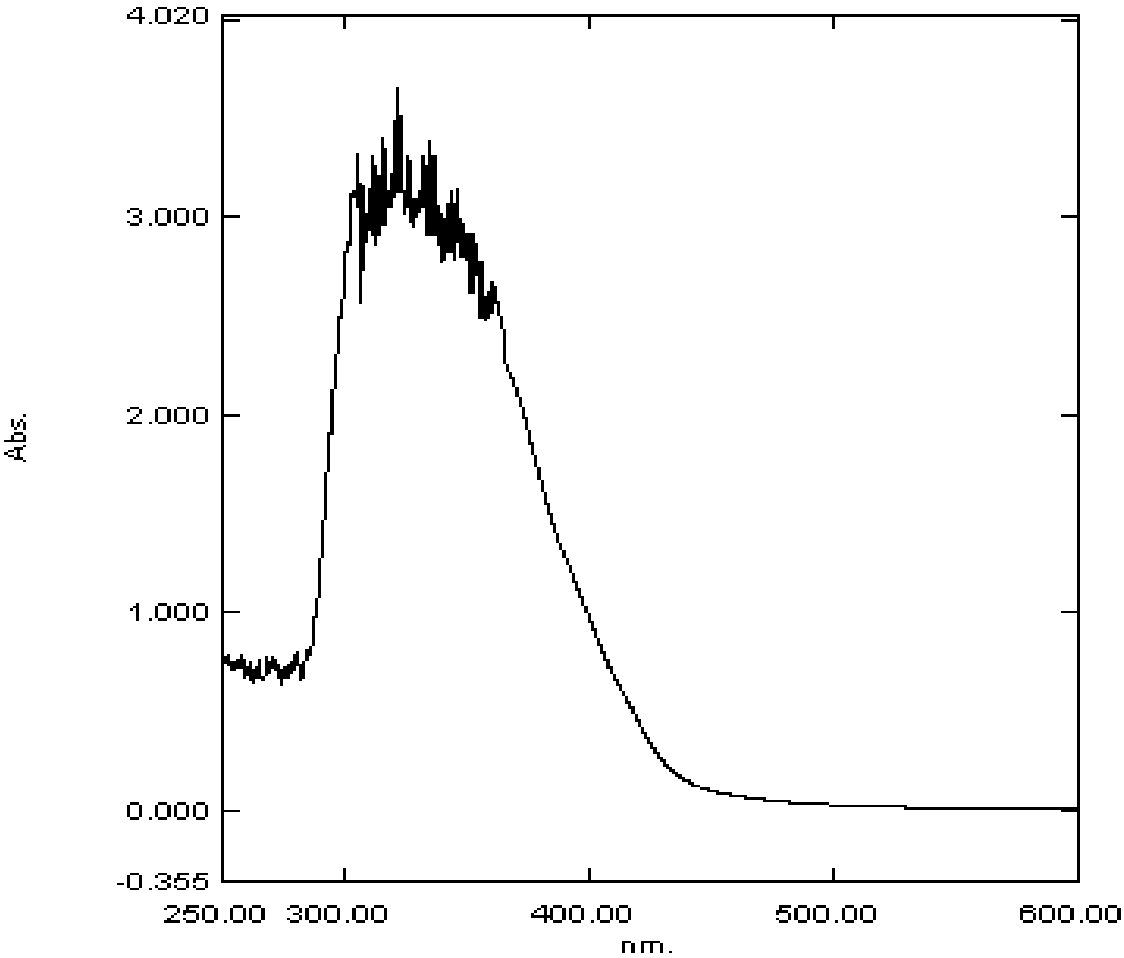
Created: 12:02 06/19/12
Data: Original

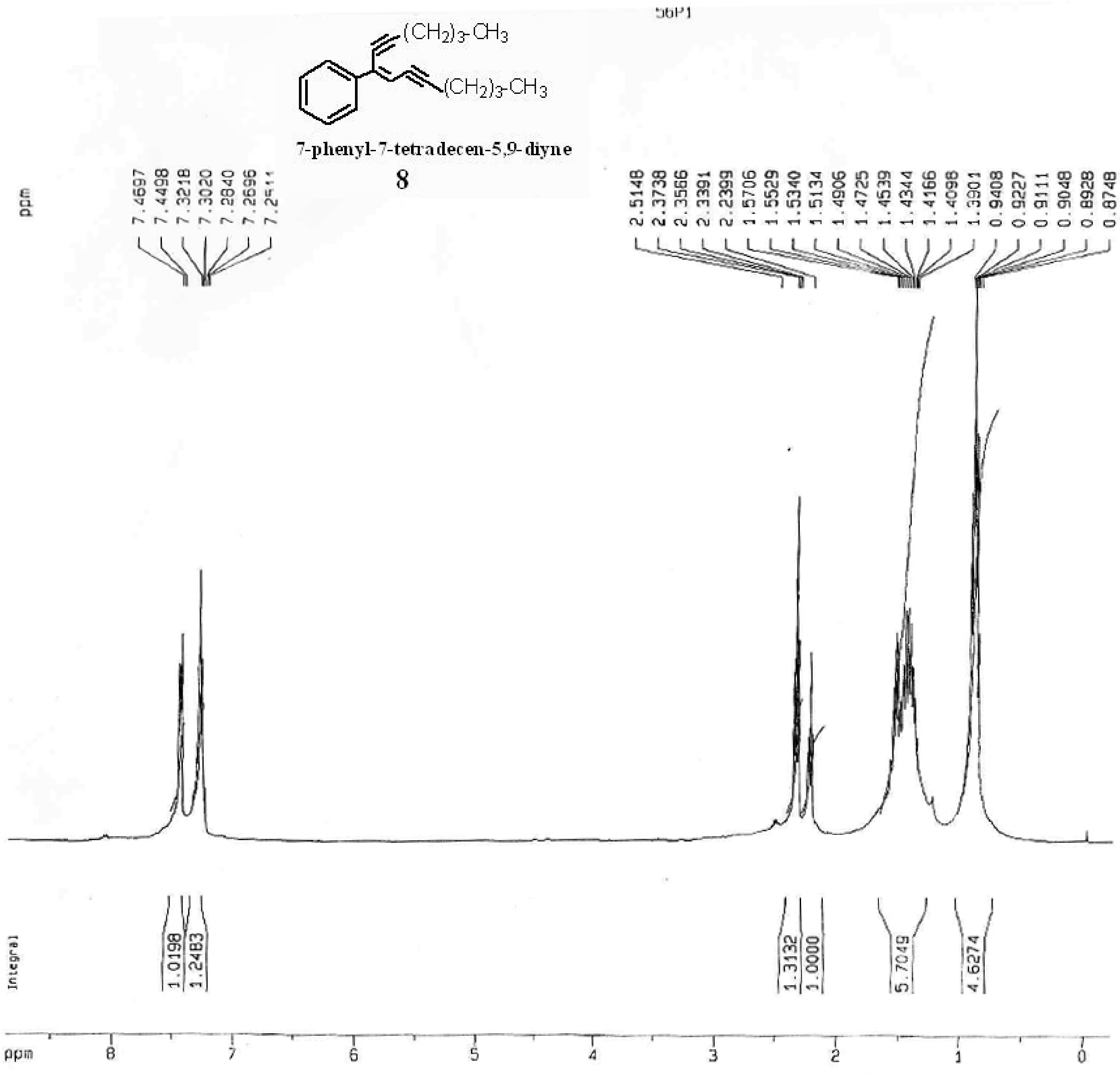
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	356.60	2.7756
2	346.40	3.1395
3	322.00	3.6555
4	305.20	3.3184



7
1,4-diphenylbut-1-en-3-yne





7-phenyl-7-tetradecen-5,9-diyne

8

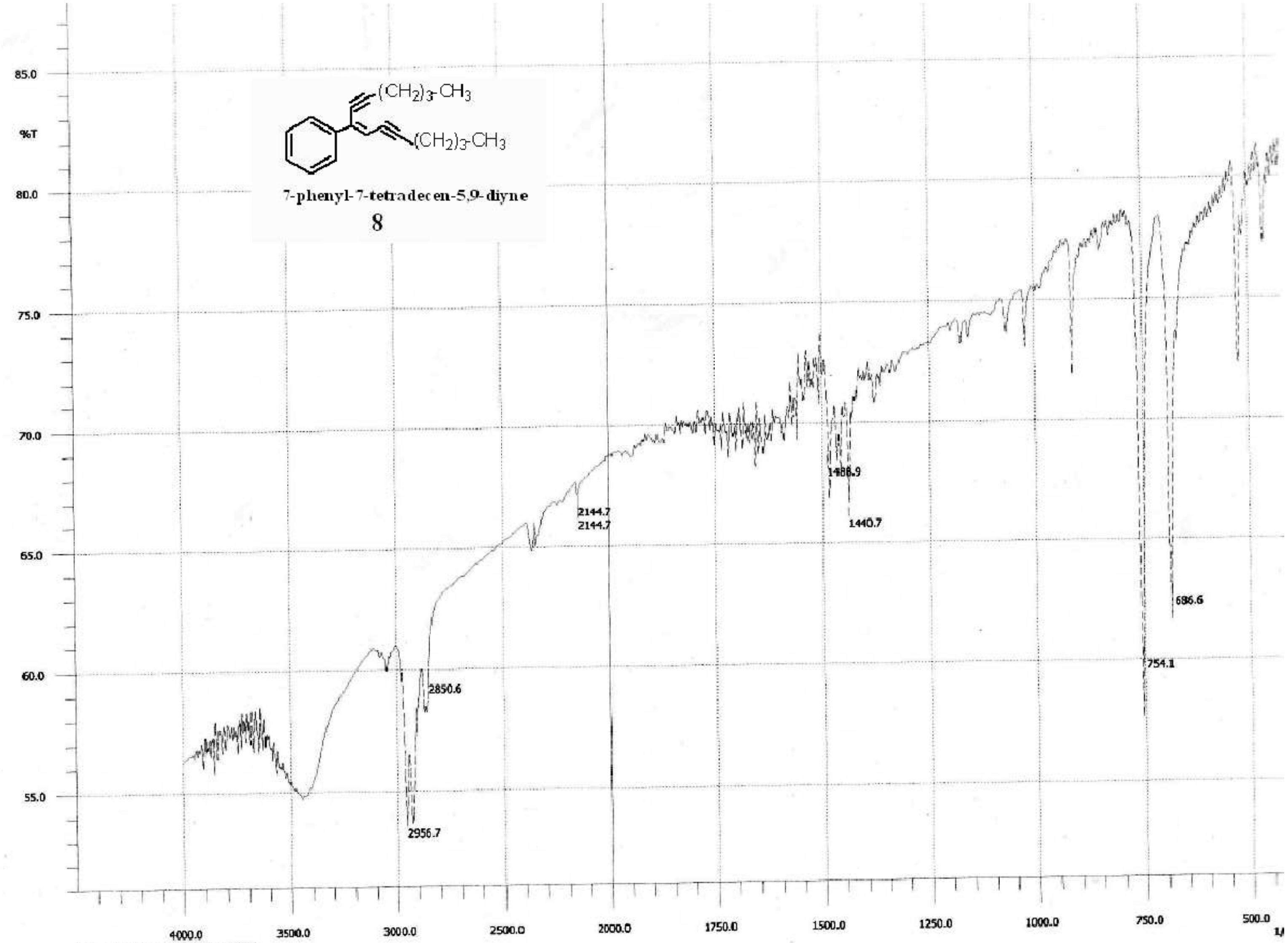
```
Current Data Parameters
NAME              A5965
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20111128
Time              10.46
INSTRUM          dpx400
PROBHD   5 mm Multinuc
PULPROG              zg
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH            6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                   64
DW               78.000 usec
DE                 6.00 usec
TE                310.0 K
D1           1.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                 8.50 usec
PL1               -6.00 dB
SFD1        400.1428010 MHz

F2 - Processing parameters
SI                32768
SF          400.1400128 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P               8.870 ppm
F1              3549.09 Hz
F2P              -0.231 ppm
F2               -92.25 Hz
PPMCM           0.45501 ppm/cm
HZCM          182.06702 Hz/cm
```


7-phenyl-7-tetradecen-5,9-diyne

8

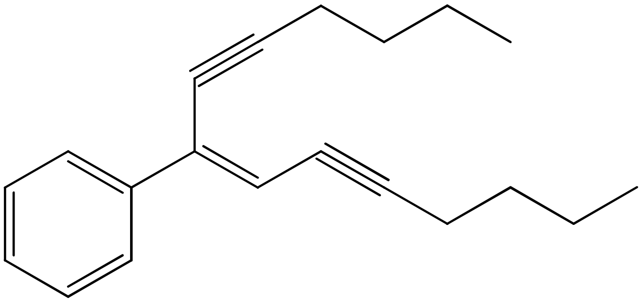
NONAME.IRS: FHq 56p2 May.6.2011
Date: 01/01/1999
Type: HYPER IR
Abscissa: 1/cm
Min: 401.17
Ndp: 1866
Gain: auto
Time: 01:13:19
User: user
Ordinate: %T
Max: 3998.16
Data Interval: 1.92868
Aperture: auto
NScans: 45
Detector: standard
Apodization: Happ
Range: 1/cm
Resolution: 4.0
Mirror Speed: 2.8(low)

File Name: **FHQ56P1**

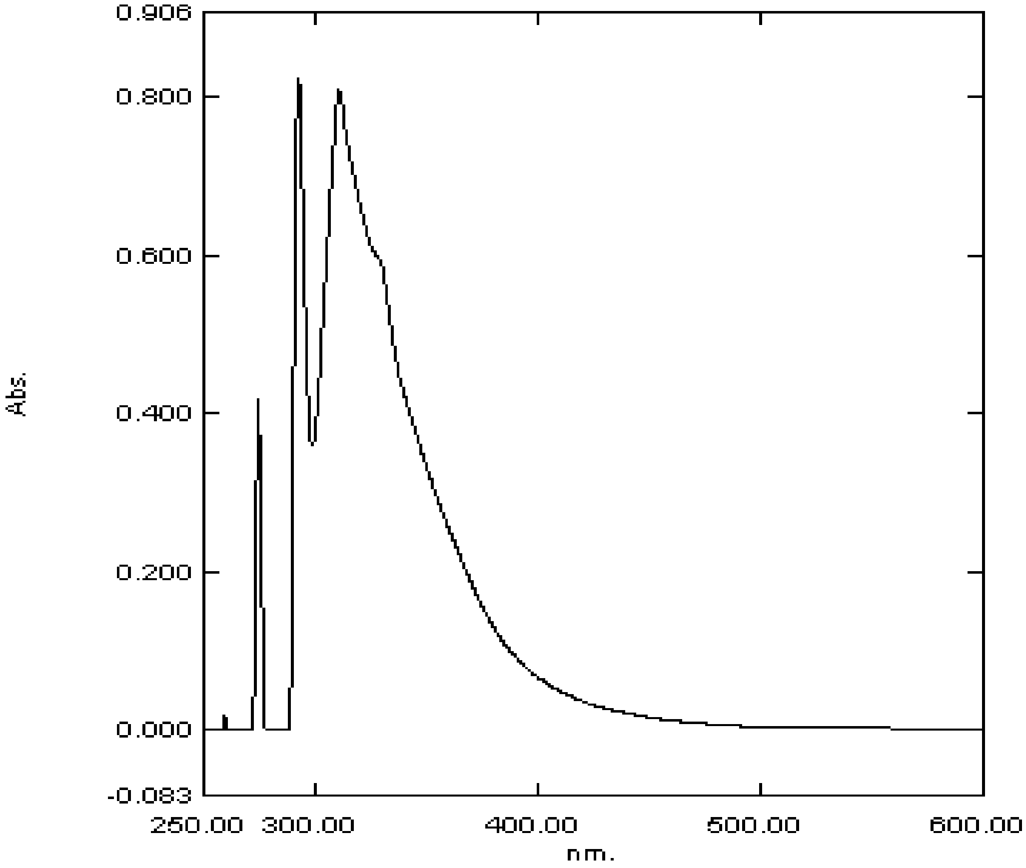
Created: 12:37 06/19/12
Data: Original

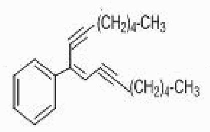
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	310.60	0.8094
2	292.60	0.8240
3	274.40	0.4180



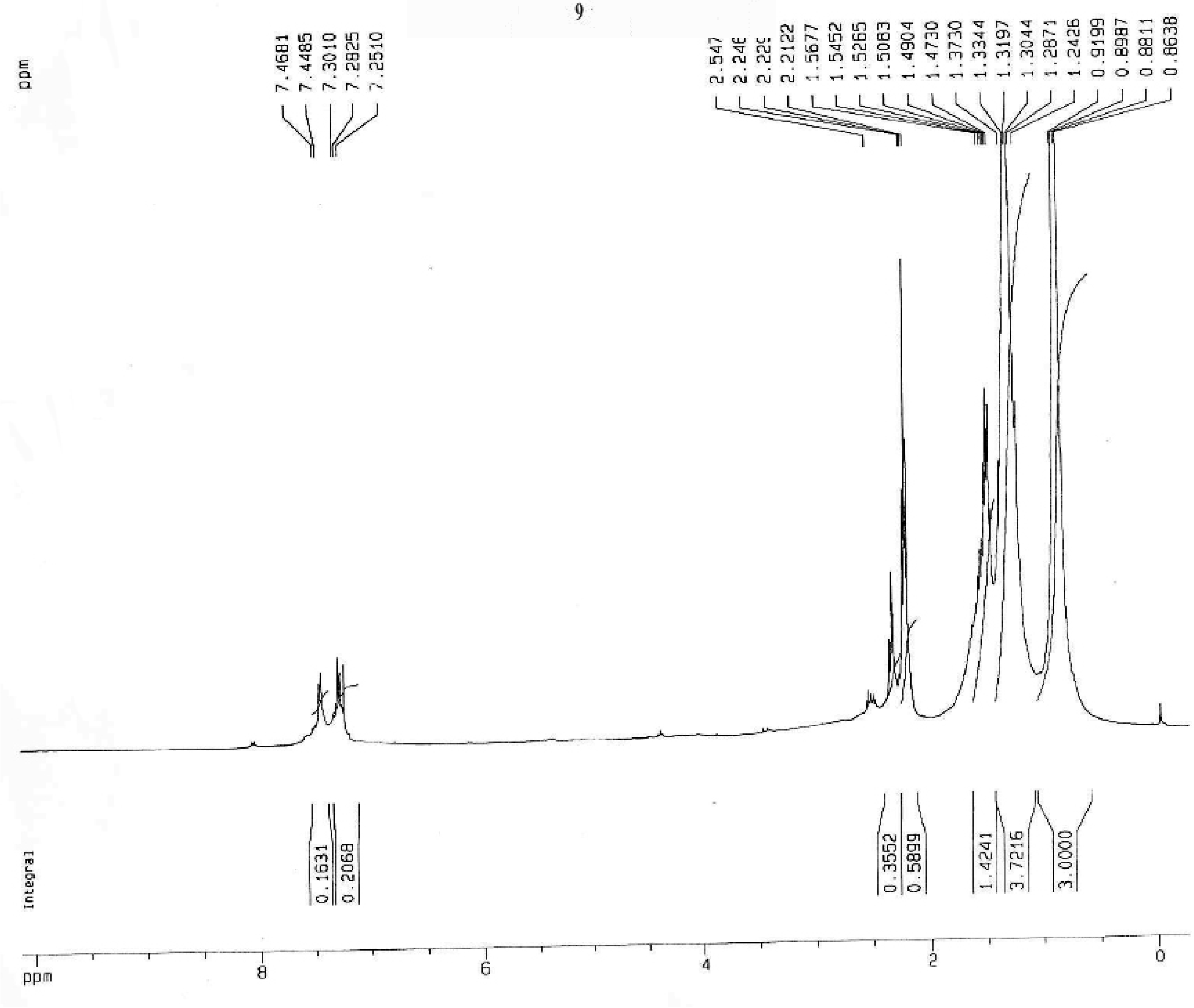
8
7-phenyl-7-tetradecen-5,9-diyne





8-phenyl-8-hexadecen-6,10-diyne

9



FHq - 44P1

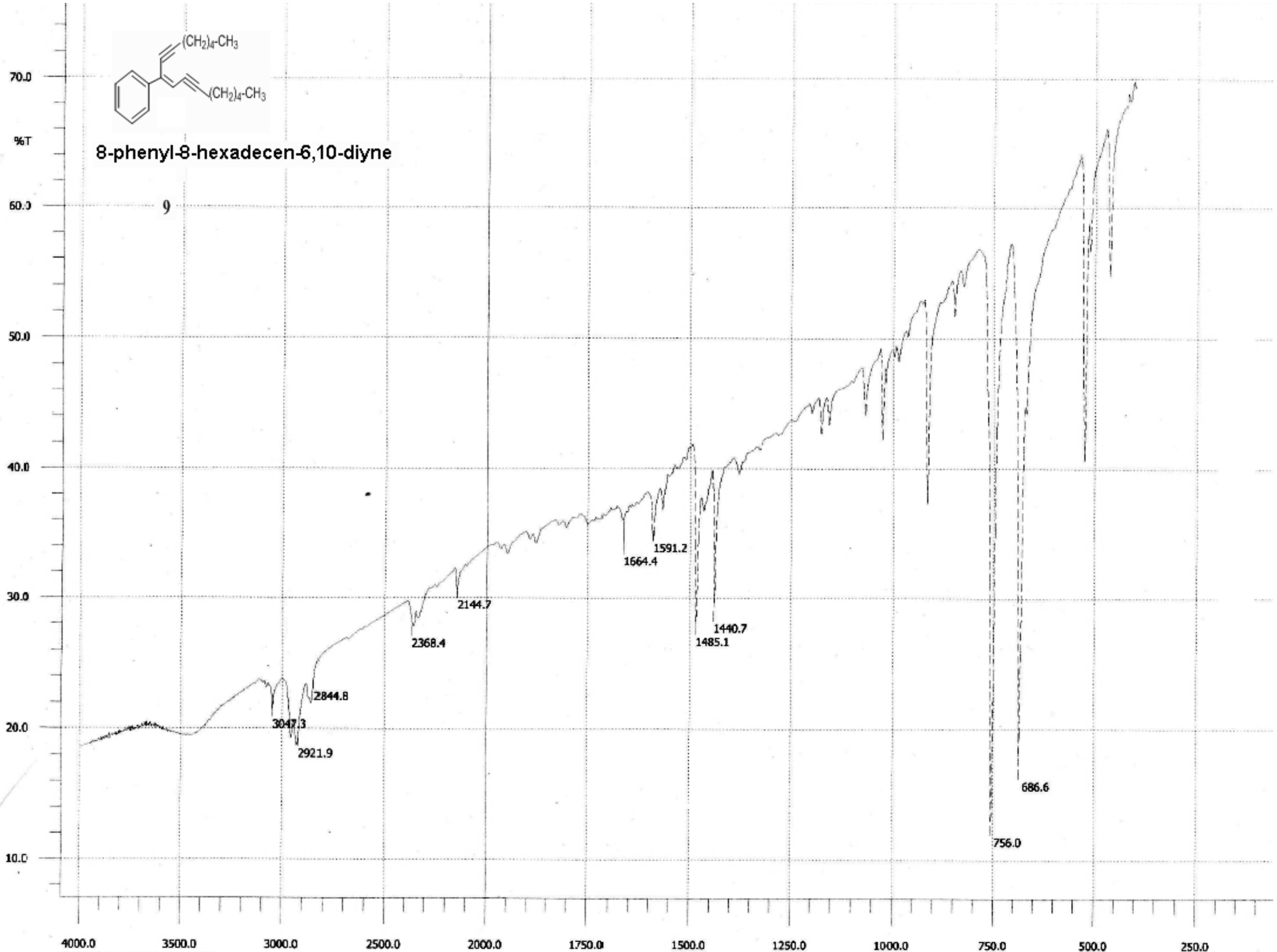
```
Current Data Parameters
NAME                A5964
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20111128
Time                10.27
INSTRUM            dpx400
PROBHD      5 mm Multinuc
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                    128
DS                      2
SWH              6410.256 Hz
FIDRES           0.195625 Hz
AQ              2.5559540 sec
RG                     64
DW                 78.000 usec
DE                   6.00 usec
TE                  310.0 K
D1             1.00000000 sec

============ CHANNEL f1 =====
NUC1                   1H
P1                   8.50 usec
PL1                 -6.00 dB
SFO1          400.1428010 MHz

F2 - Processing parameters
SI                  32768
SF            400.1400126 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P                10.134 ppm
F1                4055.12 Hz
F2P                -0.263 ppm
F2                -105.40 Hz
PPMCM             0.51988 ppm/
HZCM            208.02603 Hz/c
```



8-phenyl-8-hexadecen-6,10-diyne

9

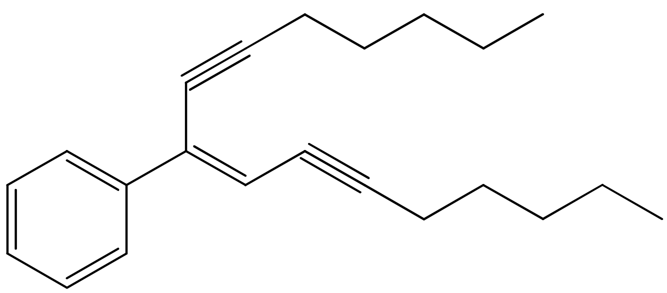
FHQ.IRS: FHq 44 P2 May.4.2011

Date:	01/01/1999	Time:	11:17:38	NScans:	45
Type:	HYPER IR	User:	user	Detector:	standard
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ
Min:	401.17	Max:	3998.16	Range:	1/cm
Ndp:	1866	Data Interval:	1.92868	Resolution:	4.0
Gain:	auto	Aperture:	auto	Mirror Speed:	2.8(low)

File Name: **FHQ44P1**

Created: 12:16 06/19/12
Data: Original

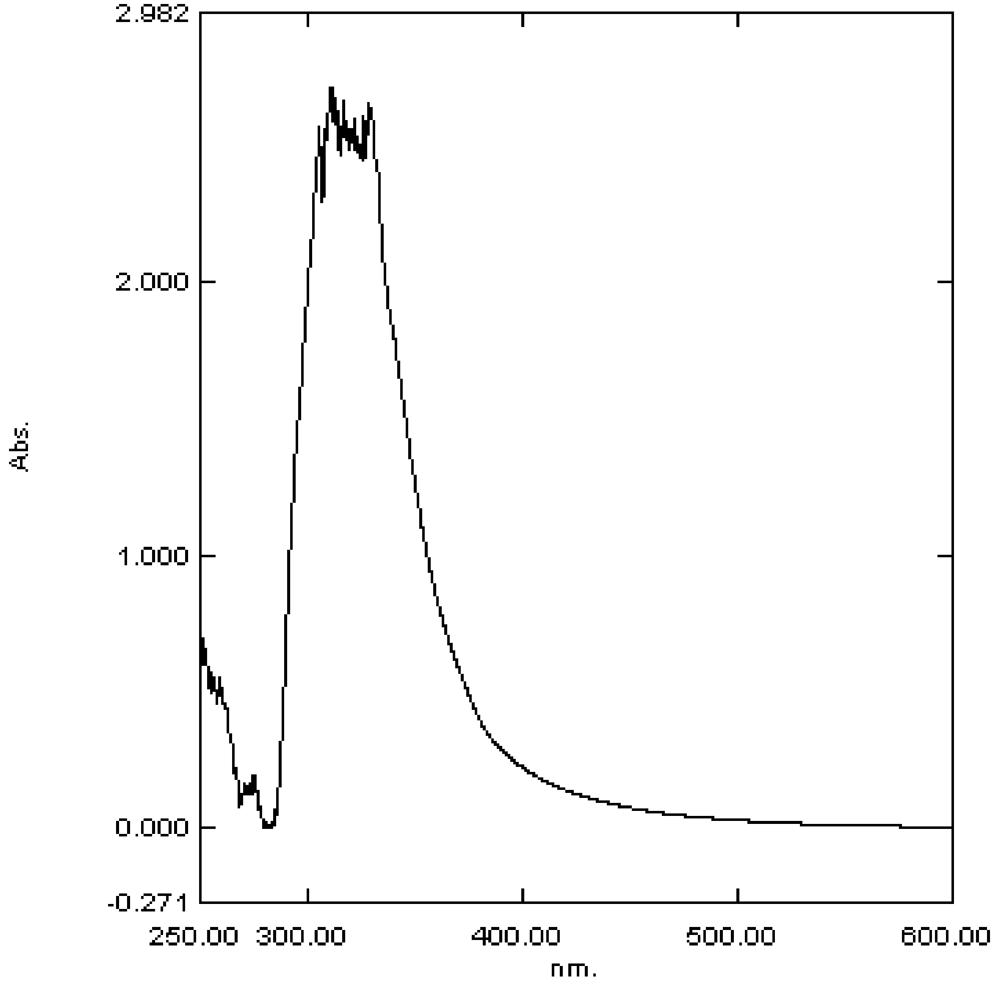
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

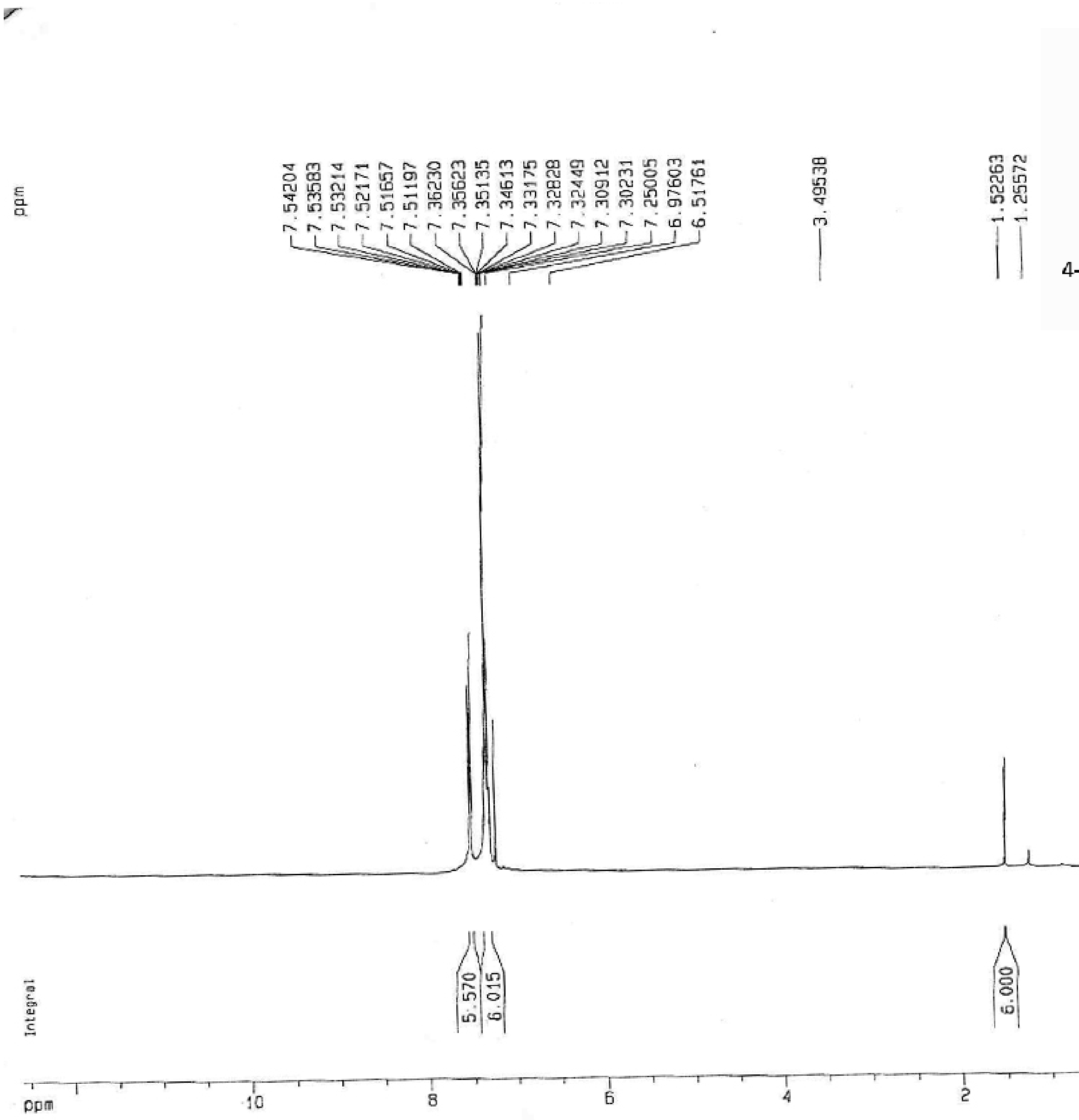


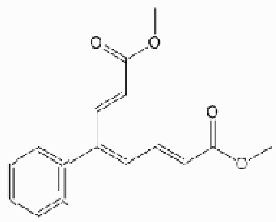
9

8-phenyl-8-hexadecen-6,10-diyne

No.	Wavelength (nm.)	Abs.
1	328.80	2.6531
2	311.20	2.7107
3	305.40	2.5673
4	266.60	0.2207
5	258.60	0.5486







4-phenyl-1,8-dimethylocta-2,4,6-trienoate

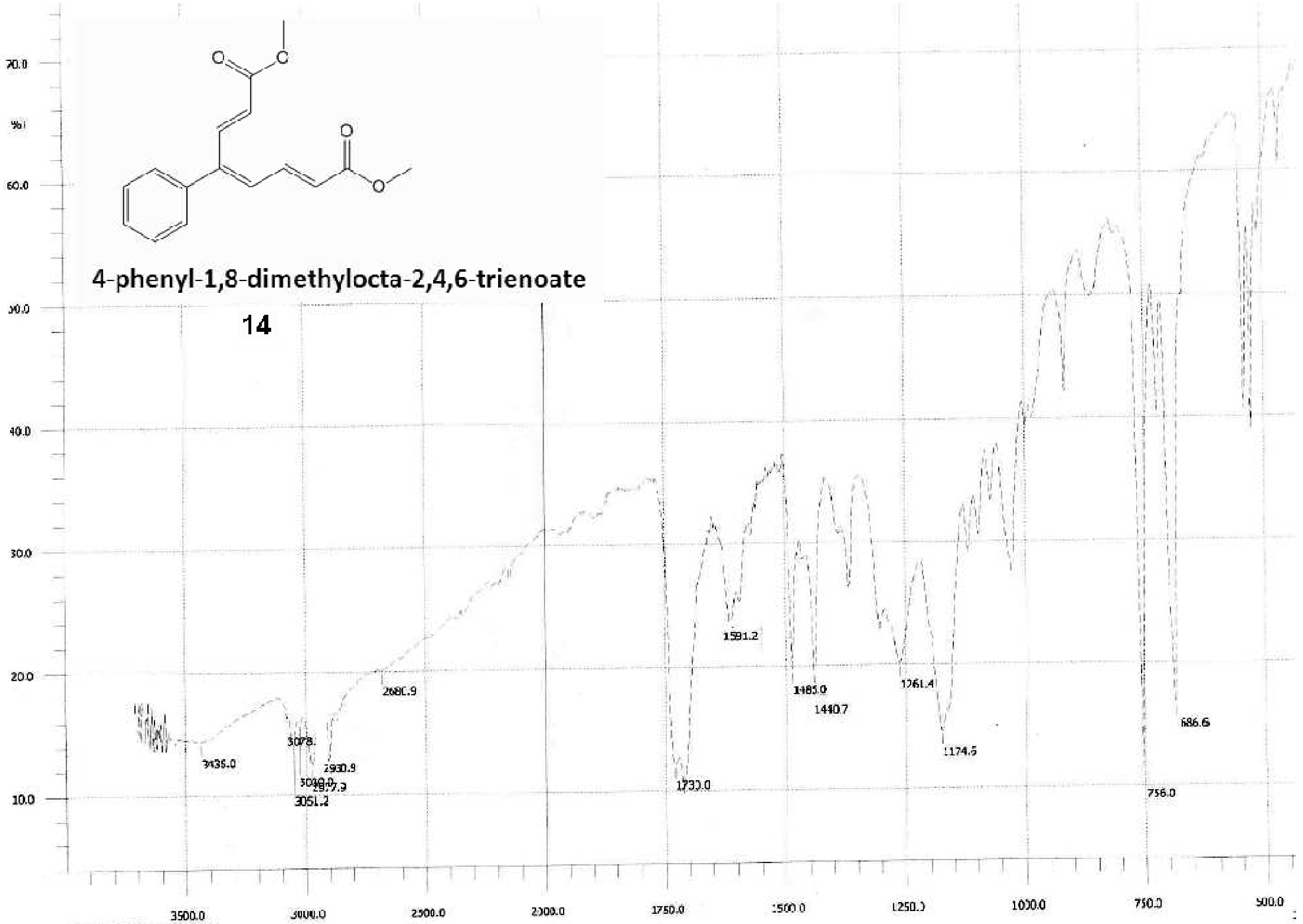
14

```
NS                     42
DS                      2
SWH              6410.256 Hz
FIDRES           0.195625 Hz
AQ              2.5559540 se
RG                   90.5
DW                 78.000 us
DE                   6.00 us
TE                  310.0 K
D1             1.00000000 se

============ CHANNEL f1 ==
NUC1                   1H
P1                   8.50 us
PL1                 -6.00 dE
SF01          400.1428010 MH

F2 - Processing parameters
SI                  32768
SF            400.1400169 MH
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cı
F1P                12.601 pı
F1                5042.27 H
F2P                -0.712 pı
F2                -284.85 H
PPMCM             0.66566 pı
HZCM            266.35605 H
```



4-phenyl-1,8-dimethylocta-2,4,6-trienoate

14

FHQ48.IRS: FHq52 Apr.2011

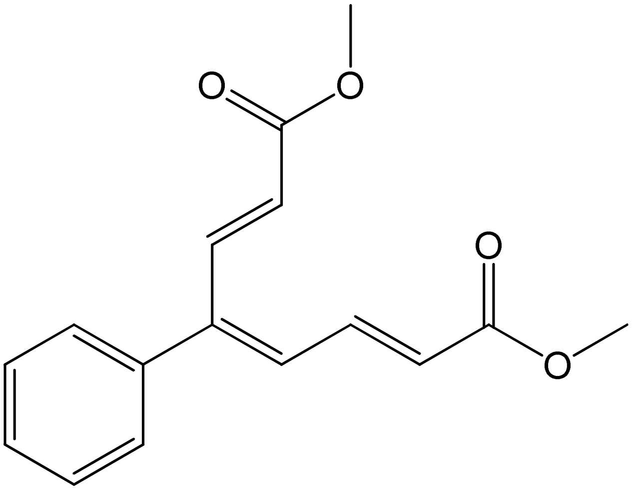
Date:	01/01/1999	Time:	01:26:10	Nscans:	95
Type:	HYPER IR	User:	user	Detector:	standard
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ
Min:	401.17	Max:	3993.16	Range:	1/cm
Nrp:	1866	Data Interval:	1.92868	Resolution:	4.0
Gain:	auto	Aperture:	auto	Mirror Speed:	2.8(low)

File Name: **FHQ52**

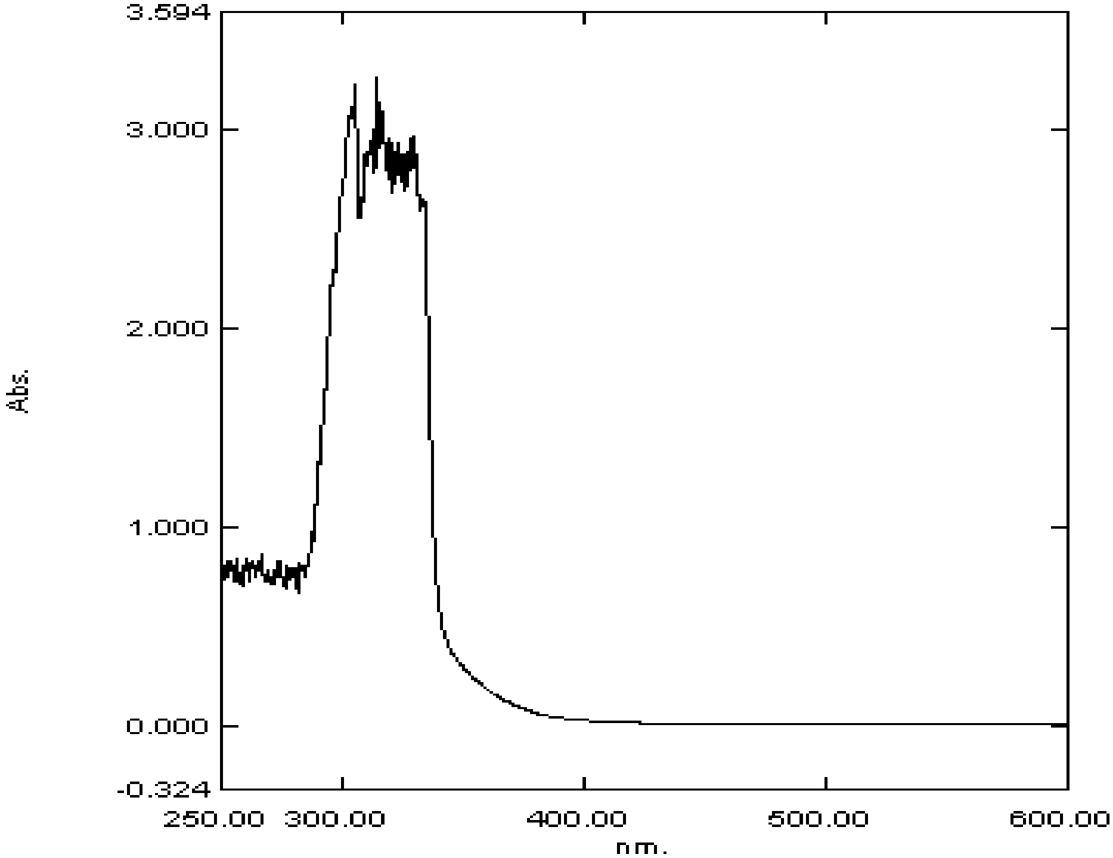
Created: 12:27 06/19/12
Data: Original

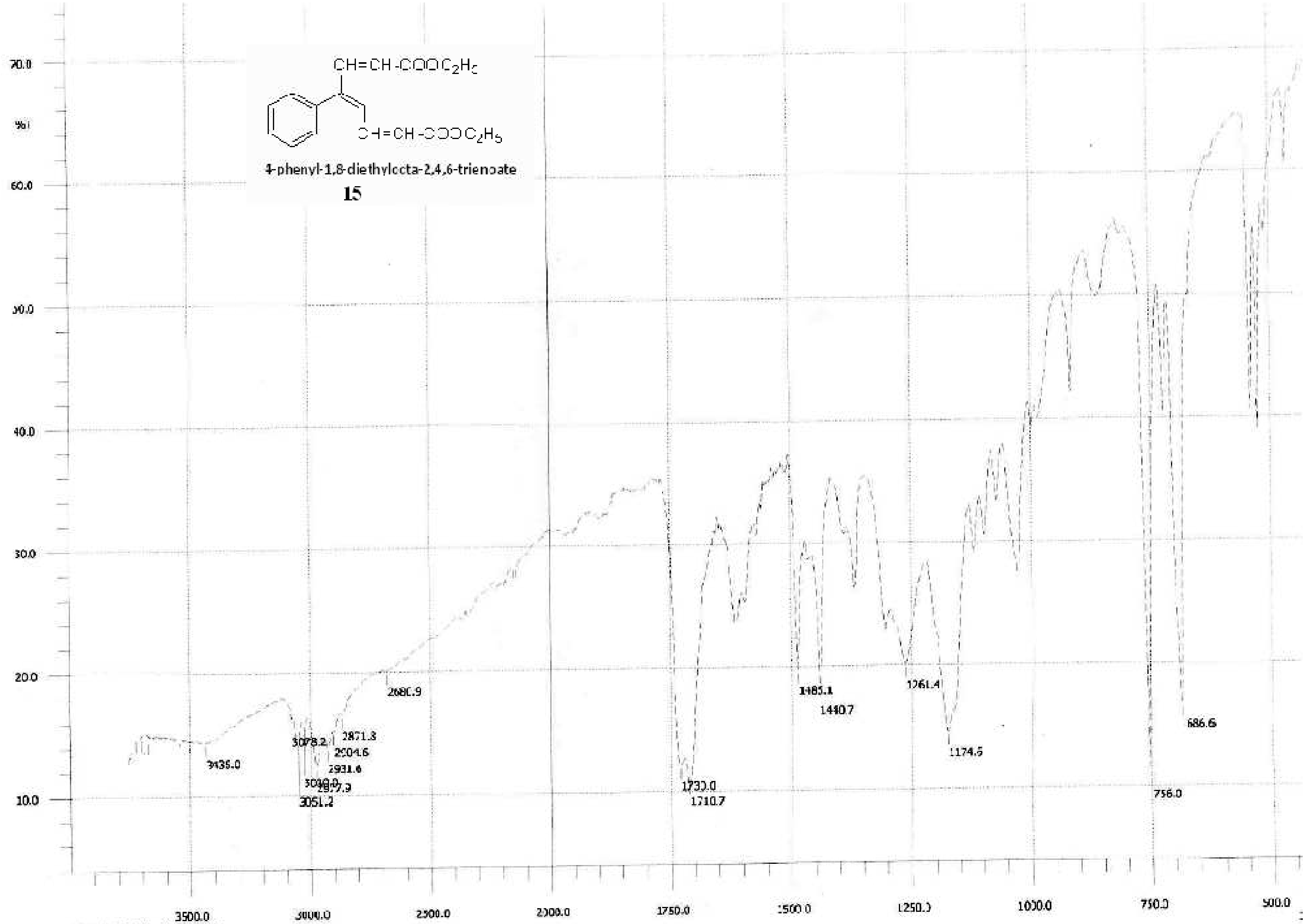
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	329.00	2.9664
2	319.80	2.9597
3	305.20	3.2334



14
4-phenyl-1,8-dimethylocta-2,4,6-trienoate





4-phenyl-1,8-diethylocta-2,4,6-trienoate

15

FHQ48.IRS: FHq 48 Apr.2011

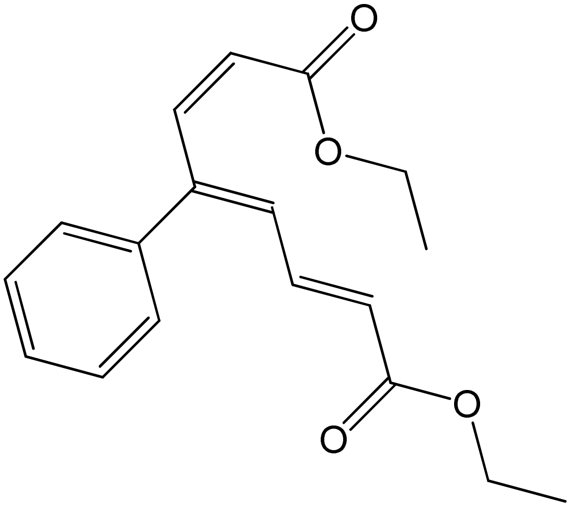
Date:	01/01/1999	Time:	01:26:10	Nscans:	45
Type:	HYPER IR	User:	user	Detector:	standard
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ
Min:	401.17	Max:	3993.16	Range:	1/cm
NPn:	1866	Data Interval:	1.92868	Resolution:	4.0
Gain:	auto	Aperture:	auto	Mirror Speec:	2.8(low)

File Name: **FHQ48N**

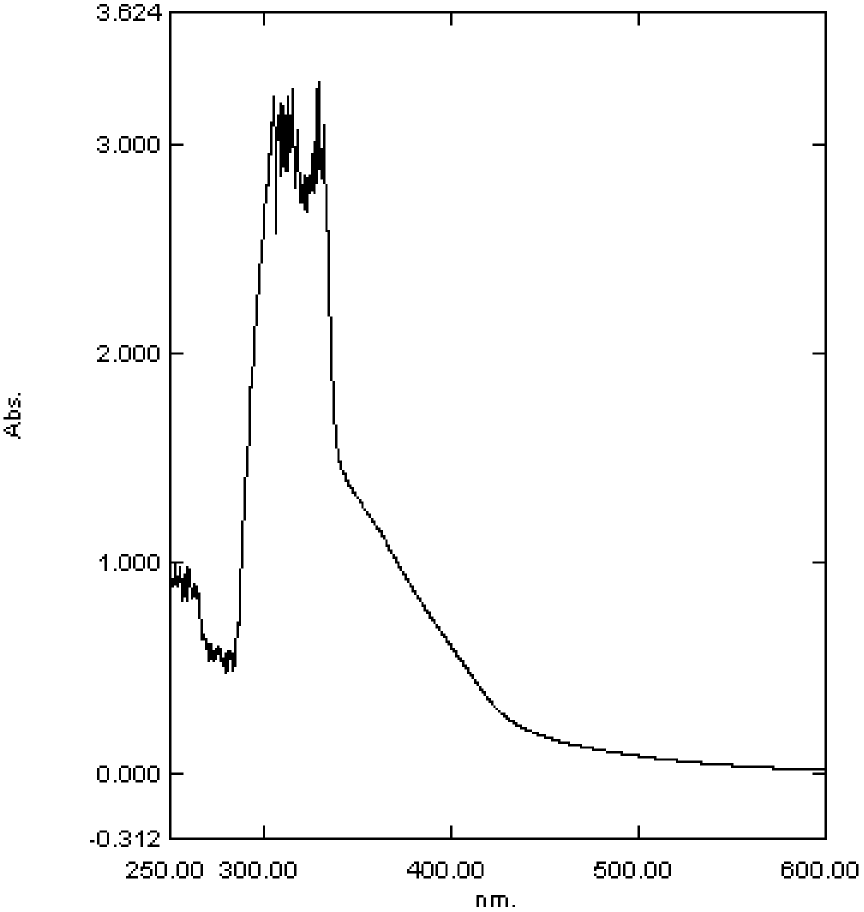
Created: 12:06 06/19/12
Data: Original

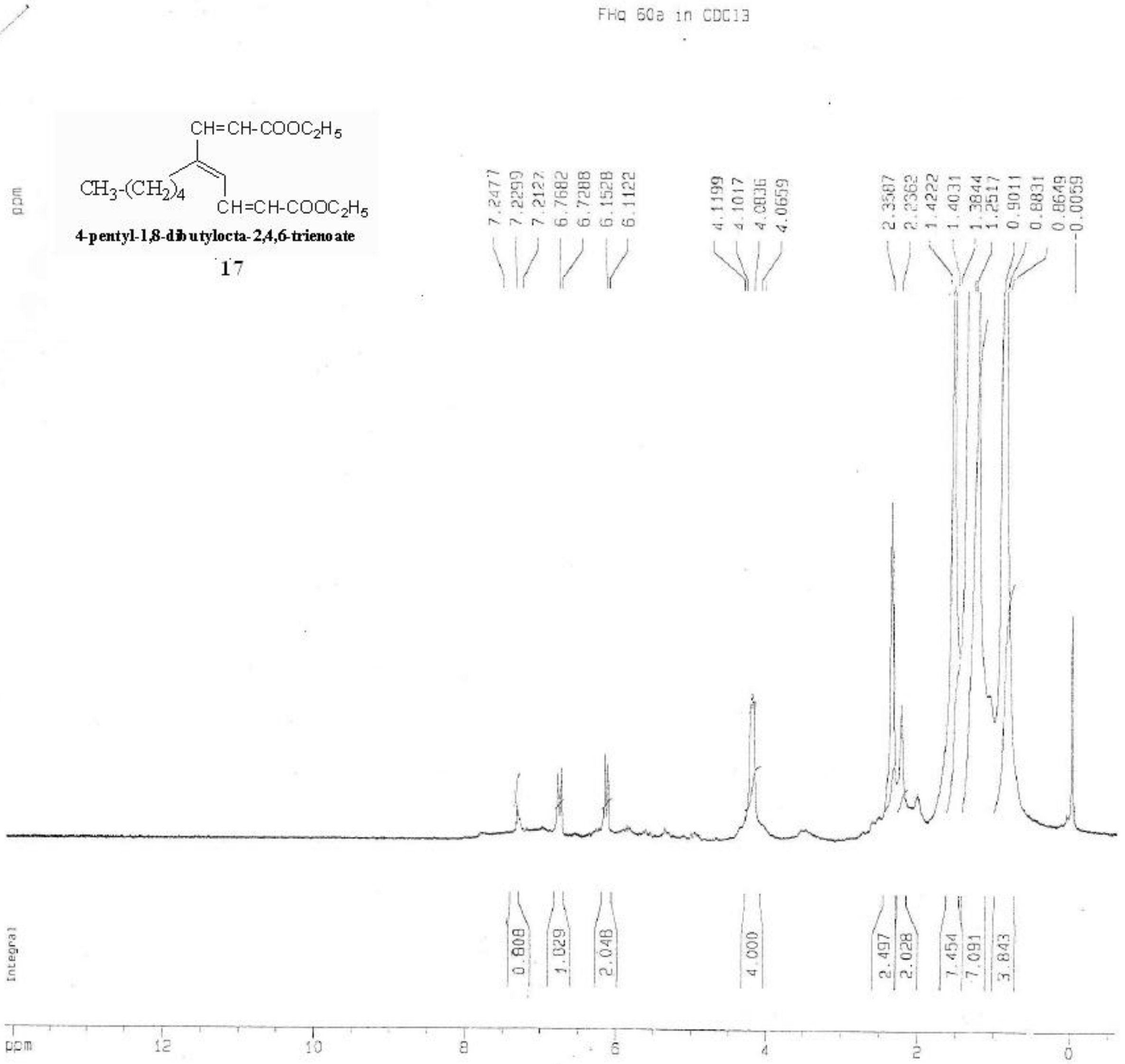
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2

No.	Wavelength (nm.)	Abs.
1	329.00	3.2961
2	315.00	3.2594
3	259.60	0.9817
4	252.20	0.9910



15
4-phenyl-1,8-diethylocta-2,4,6-trienoate





4-pentyl-1,8-dibutylocta-2,4,6-trienoate

17

```
Current Data Parameters
NAME              A6260
EXPNO                 1
PROCNO                1

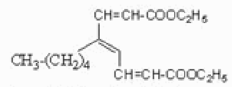
F2 - Acquisition Parameters
Date_          20120621
Time              12.37
INSTRUM          dpx400
PROBHD   5 mm Multinuc
PULPROG              zg
TD                32768
SOLVENT           CDC13
NS                  128
DS                    2
SWH            6410.256 Hz
FIDRES         0.195625 Hz
AQ            2.5559540 sec
RG                  128
DW               78.000 usec
DE                 6.00 usec
TE                310.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                 1H
P1                 8.50 usec
PL1               -5.00 dB
SFO1        400.1428010 MHz

F2 - Processing parameters
SI                32768
SF          400.1400112 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.40

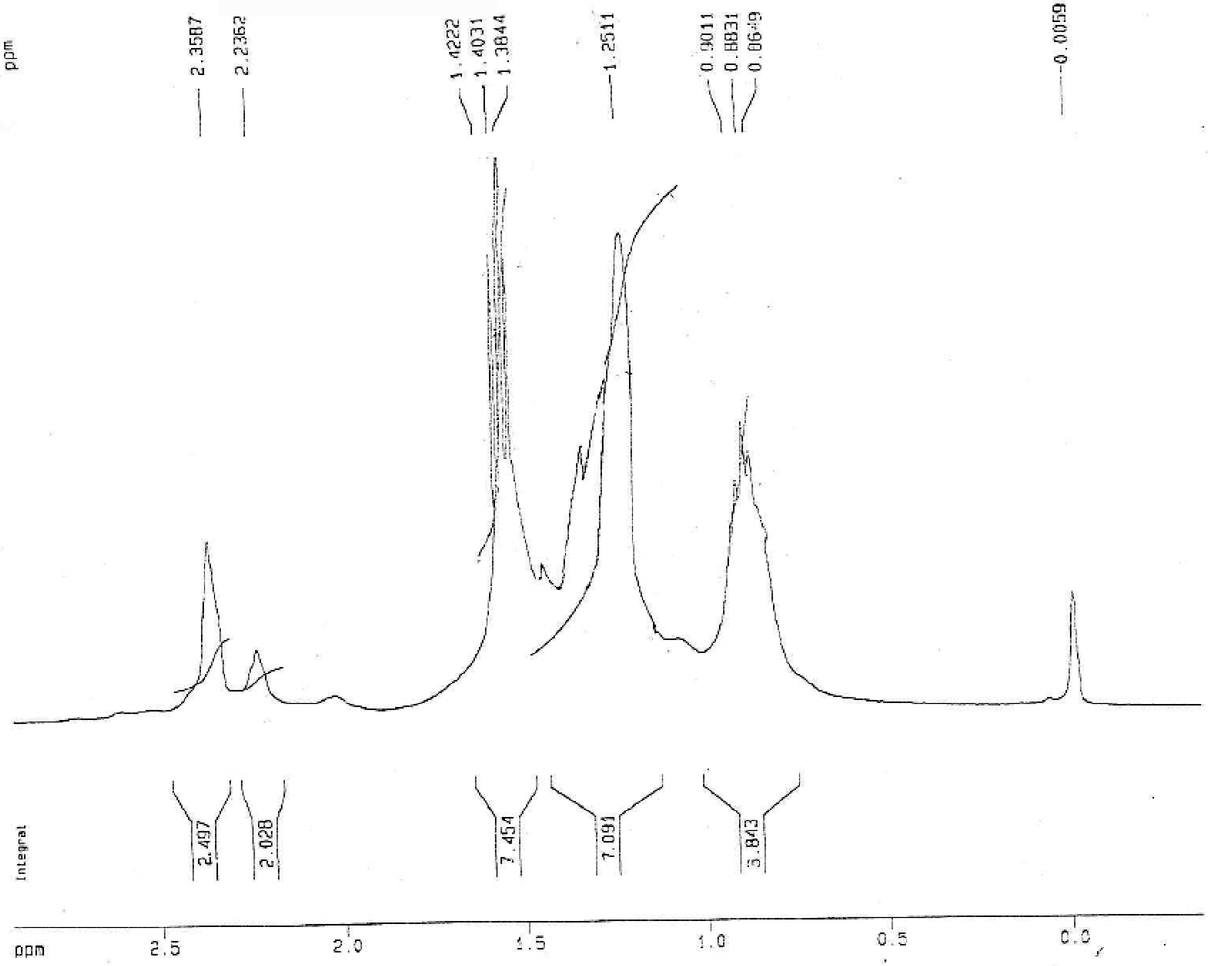
1D NMR plot parameters
CX                20.00 cm
F1P              14.114 ppm
F1              5647.52 Hz
F2P              -0.595 ppm
F2              -238.19 Hz
PPMCM           0.73546 ppm/cm
HZCM          294.28595 Hz/cm
```

FHq 60a in CDCl3



4-pentyl-1,8-dibutylocta-2,4,6-trienoate

17



```
Current Data Parameters
NAME                 A6260
EXPNO                    1
PROCNO                   1

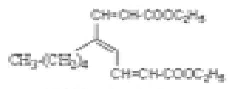
F2 - Acquisition Parameters
Date_             20120521
Time                 12.37
INSTRUM             dpx400
PROBHD     5 mm Multinuc
PULPROG                 zg
TD                   32768
SOLVENT              CDC13
NS                     128
DS                       2
SWH               6410.256 Hz
FIDRES            0.195625 Hz
AQ               2.5559540 sec
RG                     128
DW                  78.000 usec
DE                    6.00 usec
TE                   310.0 K
D1              1.00000000 sec

============ CHANNEL f1 =========
NUC1                    1H
P1                    8.50 usec
PL1                  -6.00 dB
SFO1           400.1428010 MHz

F2 - Processing parameters
SI                   32768
SF             400.1400112 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.40

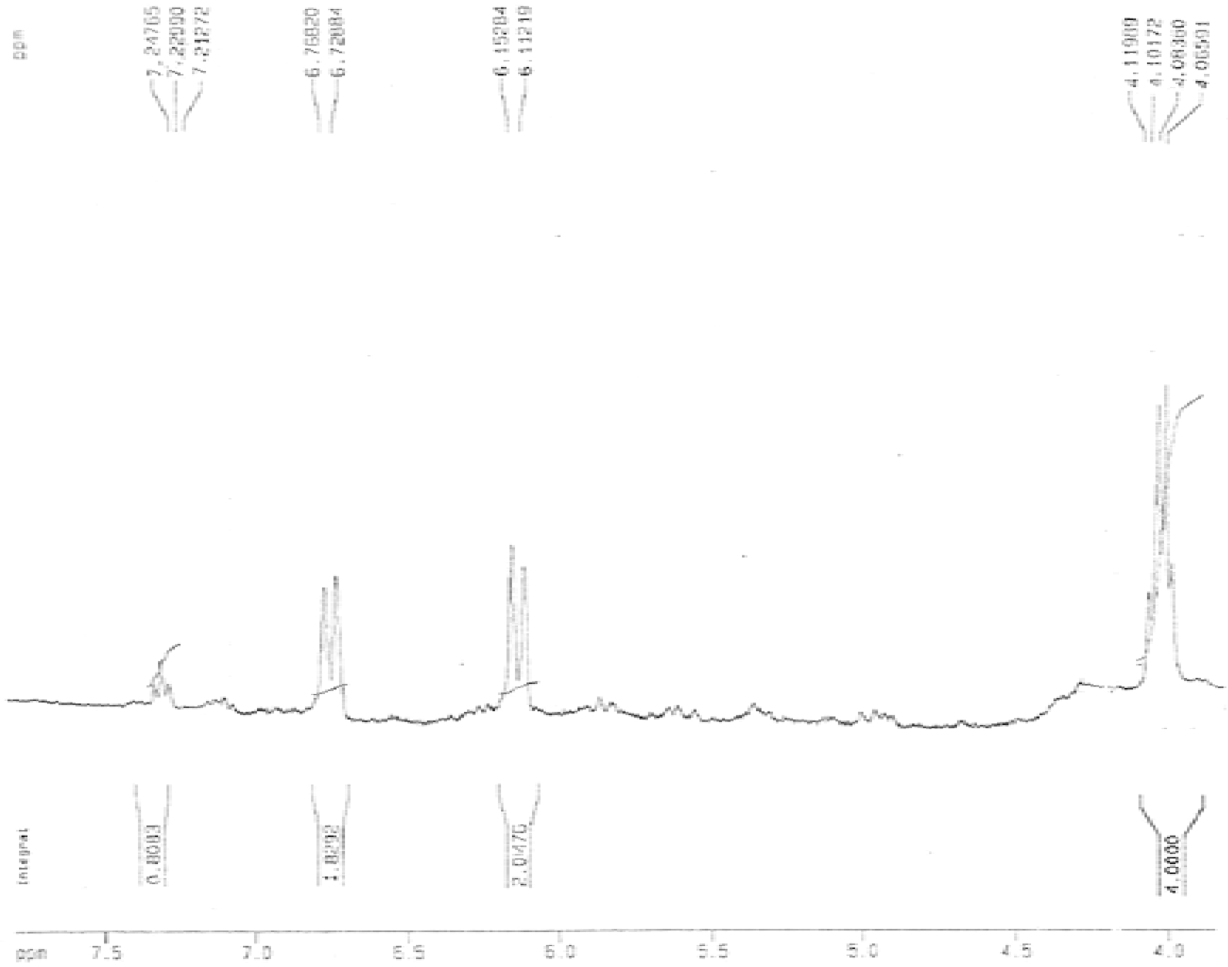
1D NMR plot parameters
CX                   20.00 cm
F1P                  2.912 ppm
F1                 1165.11 Hz
F2P                 -0.357 ppm
F2                 -142.82 Hz
PPMCM              0.16344 ppm/cm
HZCM              65.39669 Hz/cm
```

FHq 60a in CDCl3



4-pentyl-1,8-dibutylocta-2,4,6-trienoate

17



```
Current Data Parameters
NAME               A6250
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120621
Time               12.37
INSTRUM           dpx400
PROBHD    5 mm Multinuc
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     2
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5559540 sec
RG                   128
DW                78.000 usec
DE                  6.00 usec
TE                 310.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                  6.50 usec
PL1                -6.00 dB
SFO1         400.1428010 MHz

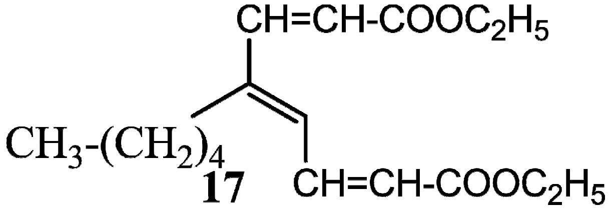
F2 - Processing parameters
SI                 32768
SF           400.1400112 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P                7.802 ppm
F1               3121.80 Hz
F2P                3.846 ppm
F2               1538.50 Hz
PPMCM            0.19779 ppm/cm
HZCM            79.14485 Hz/cm
```

File Name: **FHQ60a**

Created: 12:48 06/19/12
Data: Original

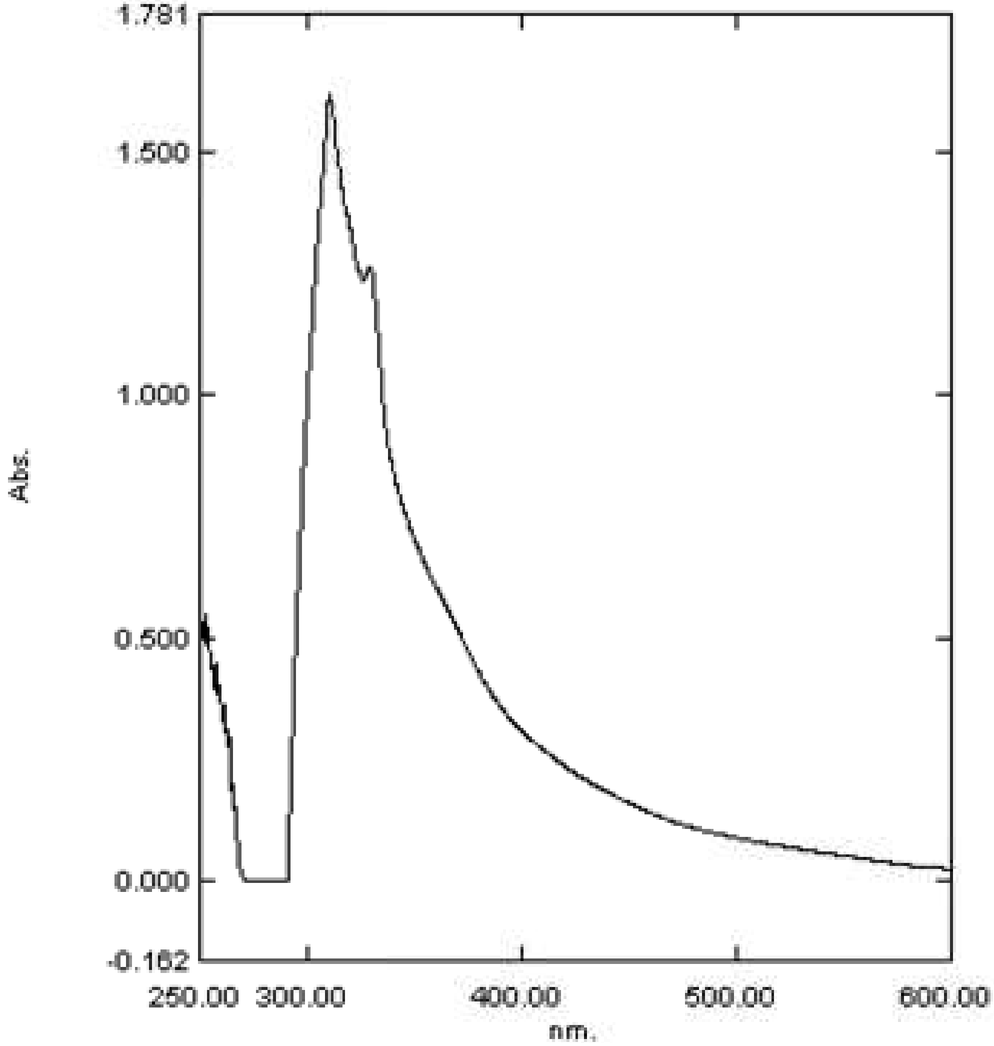
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 2.0
Sampling Interval: 0.2



17

4-phenyl-1,8-diethylocta-2,4,6-trienoate

No.	Wavelength (nm.)	Abs.
1	329.20	1.2605
2	310.20	1.6188



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