

A short review on synthesis of dihydrophenanthrene, phenanthrene and its analogues by palladium-catalyzed reaction

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Abstract

Use of transition metal compounds or complexes as catalysts or reagents in organic synthesis is an exciting field in research and numerous novel reactions which are impossible to achieve by conventional synthetic methods have already been discovered. Palladium catalysed C-C bond forming reaction is very important for the synthesis of carbocyclic compounds. In this mini review we have reviewed of some efficient methods for the construction of a dihydrophenanthrene, phenanthrene and its analogues by palladium-catalyzed reaction.

Keywords: Phenanthrene, palladium-catalyzed reaction, 9, 10 dihydrophenanthrenes electrocyclic reaction

Palladium catalyzed C-C bond forming reaction is important for the synthesis of heterocyclic and carbocyclic compounds. Polycyclic aromatic hydrocarbons (PAHs), more simply known as polyarenes, constitute an extraordinary large and diverse class of organic molecules.^{1,2} Within the chemical class of polycyclic aromatic compounds phenanthrene is an important core structure. The phenanthrene moiety can not only be found in several natural products, of which many exhibit interesting biological activity,³ but more recently phenanthrenes have also been shown as interesting ligands for novel catalyst systems.⁴ The discovery of the carcinogenic prosperities of polyarenes stimulated wide-ranging investigations of their structure activity relationships. Previously it was thought that PAHs are direct acting carcinogens, but this was proved to be wrong in latter stage. It is now recognized that PAHs require metabolic activation in order to express tumorigenic reactivity.^{5,6} It is believed that principal primary metabolites are arene oxides which are formed by enzymatic addition of an atom of oxygen to an aromatic C=C bond. These relatively unstable intermediates may then i) undergo hydration catalysed by epoxide hydrolase to form dihydrodiols, ii) rearrange spontaneously to phenols, iii) undergo addition of glutathione catalysed by glutathione-s-transferase, iv) from covalent binding with DNA, RNA, and proteins (Figure 1).

Evidences indicate that principal biologically active metabolites are dihydrodiol epoxide derivatives. These metabolically formed diol epoxides exert their carcinogenic and other genotoxic effects through covalent binding to DNA.

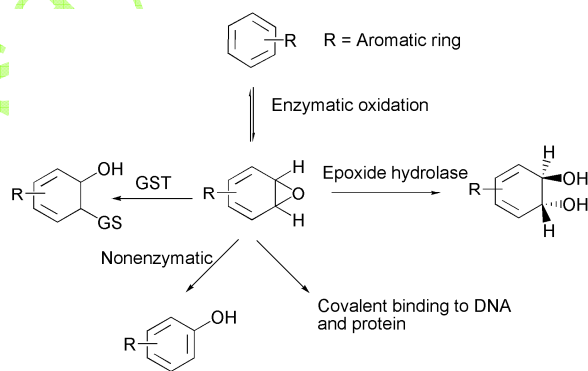
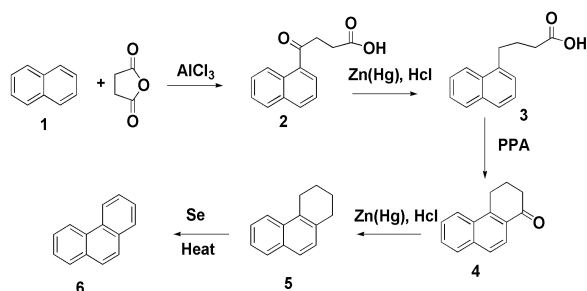


Figure 1

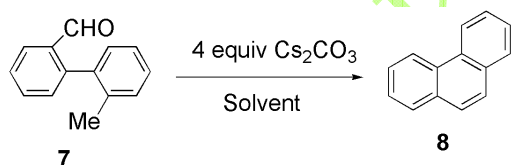
Therefore, the development of new short synthetic methods for this important class of organic compounds has regained importance. Several synthetic efforts for the preparation of PAH have been reported by different groups, of which most common procedure involves the classical oxidative photocyclization of stilbene derivatives.⁷ Among other methods intramolecular Diels-Alder reaction,⁸ flash vacuum pyrolysis,^{9,10,11,12} olefin metathesis,¹³ Friedel-Crafts type cyclization,¹⁴ dimerisation or trimerisation of acetylenes and arynes,^{15,16} transition metal catalyzed cycloisomerisation^{17,18} etc. are used as the key step for construction of a benzene ring for the synthesis of PAH. We also contributed in this field by synthesizing tri-substituted benzene derivatives via base catalyzed condensation and aromatization of various bromoaldehydes with active methylene compound.¹⁹

Palladium catalyzed activation of aromatic C-H bond has been used extensively in many organic synthesis since this reaction gives a solution for the construction of carbo- and heterocycles from the corresponding halides and triflates.^{20,21,22,23,24,25,26} Larock *et al* have developed a novel Palladium-catalyzed migration/C-H activation methodology for the synthesis of complex fused polycycles.^{27,28} The major sources of PAHs are crude oil, coal, oil shale. Methyl phenanthrene, belong to an important group alkyl-aromatic hydrocarbons which are present in natural environments. Methyl phenanthrene arises through the combustion of wood, coal; etc. There is a great variety of methods which are available for the synthesis of phenanthrene and its derivatives. Perhaps the most extensive method is the classical Haworth synthesis.



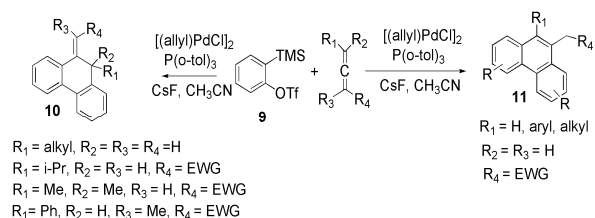
Scheme-1

Maes *et al.* synthesized phenanthrene²⁹ and substituted phenanthrene molecules by using only a weak, non-nucleophilic base for the ring closure of 2-methylbiphenyl-2-carbaldehydes under microwave heating (Scheme 2)



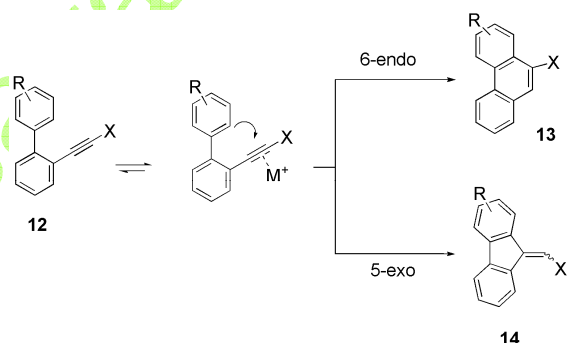
Scheme 2

There are several palladium catalyzed synthesis of phenanthrene have been reported. Pellet-roasting and Lemaire *et al.* reported Palladium-catalyzed cyclotrimerization³⁰ of allenes with arynes for selective synthesis of phenanthrenes. In the presence of $[(allyl)PdCl]_2$ and $P(o-tol)_3$, a variety of allenes, including internal and terminal allenes, underwent the cyclotrimerization with arynes to afford the corresponding phenanthrene in moderate to good yields which is shown in Scheme 3



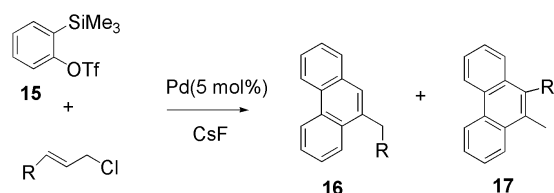
Scheme-3

Alois Furstner *et al.* reported the synthesis of substituted phenanthrenes³¹ from readily available biphenyl derivatives containing an alkyne unit at one of their ortho-positions on exposure to catalytic amounts of either $PtCl_2$, $AuCl$, $AuCl_3$, $GaCl_3$ or $InCl_3$ in toluene. This 6-endo-dig cyclization likely proceeds through initial π -complexation of the alkyne unit followed by interception of the resulting η^2 -metal species by the adjacent arene ring (Scheme 4).



Scheme-4

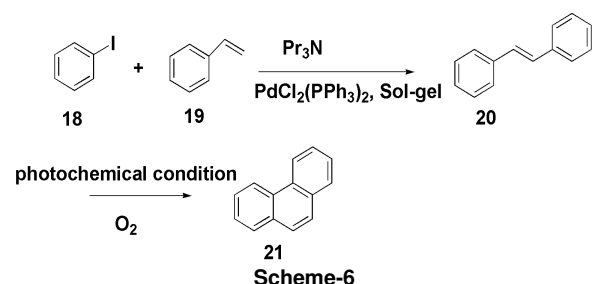
Benzynes are actually very reactive as a carbopalladation partner of π -allyl palladium chloride. Yamamoto *et al.* reported that the palladium-catalyzed³² reaction of allyl chlorides with benzyne precursor 15 produces phenanthrene derivatives 16, along with the minor regioisomers 17, in good yields. The reaction of allyl chloride (1.0 equiv) and benzyne precursor 15 (2.0 equiv) in the presence of $[Pd_2(dba)_3] \cdot CHCl_3$ (2.5 mol%), dppf (5 mol%), and CsF (4.0 equiv) in CH_3CN/THF (1/1) at 60 °C gave 16 in 69% yield (Scheme 5).



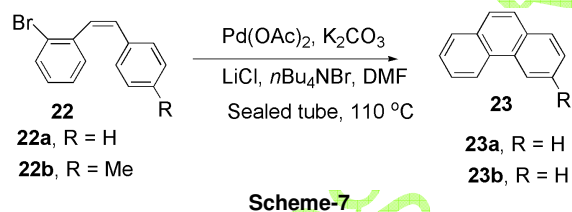
Scheme-5

Blum *et al.* have employed for the first time a sol gel physically entrapped version of the $PdCl_2(PPh_3)_2$ catalyst for

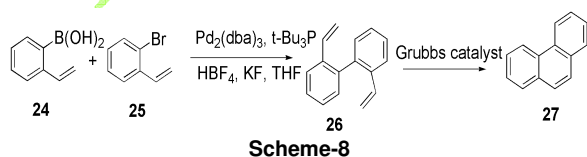
the Heck coupling process.³³ This heterogeneous catalyst is a perfectly leach proof, highly porous material and completely air stable for many months. When a solution of freshly distilled styrene **19**, iodobenzene **18**, and tripropylamine in 15 mL of toluene was refluxed for 12 h in the presence of a sol-gel encapsulated catalyst containing of $\text{PdCl}_2(\text{PPh}_3)_2$, the resulting solution containing *trans*- and *cis*-stilbene were found. Finally this stilbene under photocyclization yielded phenanthrene molecules (Scheme 6).



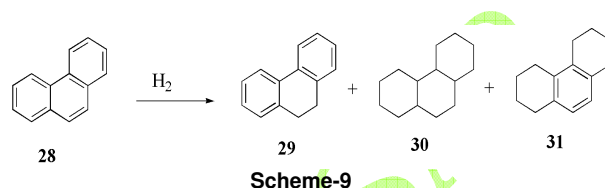
Meijere *et al.* synthesized phenanthrene molecules by palladium catalyzed intramolecular arylation reaction.³⁴ The *o*-bromo-*cis*-stilbenes **22a, b** when subjected to react with Pd(0) in sealed tube at 110 °C only phenanthrene (**23a**), and 3-methylphenanthrene (**23b**) in 70 and 71% yield, respectively, arising from an intramolecular aryl bromide to arene coupling (Scheme 7).



Barrett *et al.* examined the model coupling of 2-vinylphenylboronic acid **24** with 2-bromostyrene **25** under the Suzuki coupling conditions.³⁵ This gave biphenyl **26** in moderate yield (40%). Subsequent RCM using the second generation Grubbs catalyst gave phenanthrene **27**, in moderate yield (Scheme 8).

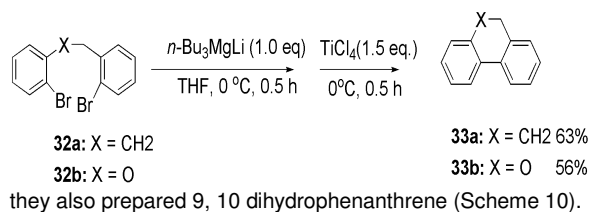


There are several methods that have been reported for the synthesis of 9,10-dihydrophenanthrene. Phenanthrene under catalytic hydrogenation yielded 9,10-dihydrophenanthrene **29** along with 1,2,3,4,5,6,7,8-octahydrophenanthrene **30**, and tetradecahydrophenanthrene **31** (Scheme-9).³⁶



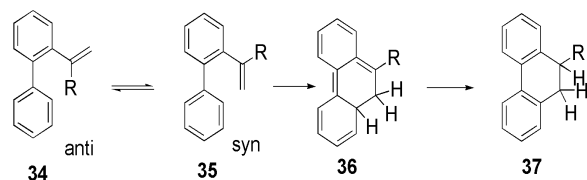
Burger and Mosettig took advantage of the greater activity of copper-chromium oxide toward olefinic double bonds as compared with benzenoid nuclei and selectively hydrogenated phenanthrene at 220 °C, obtaining 9, 10-dihydrophenanthrene in yields of about 80%.

Koichiro Oshima *et al.* synthesized biaryls³⁷ compound by titanium tetrachloride from aryl magnesium compound. They have developed a coupling method starting from aryl halides. They reported the halogen-magnesium exchange reaction of aryl bromides and aryl iodides with lithium trialkylmagnesate (R_3MgLi). This exchange reaction can generate an arylmagnesium ate-complex which would be a promising precursor for the oxidative coupling reaction. Indeed, the addition of TiCl_4 to the resulting arylmagnesium species provided biaryls in good yields. By using this methodology



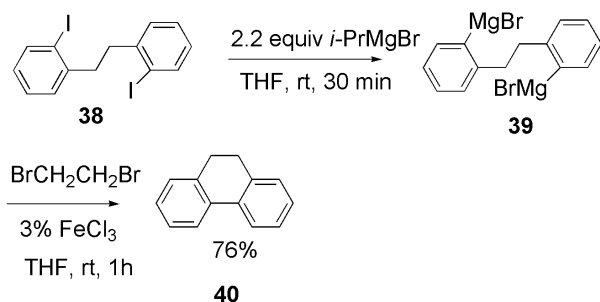
Scheme-10

The photochemical conversion of 2-vinylbiphenyl (**34**) to 9, 10-dihydrophenanthrene (**37**) was reported by Horgan *et al.* They proposed a two-step mechanism: photocyclization to yield the unstable 8a,9-dihydrophenanthrene intermediate **36**, which then underwent a thermal [1, *n*] sigmatropic hydrogen shift [*n* = 5, 9, or 13] to yield the observed product in both the absence and the presence of oxygen (Scheme 11).³⁸



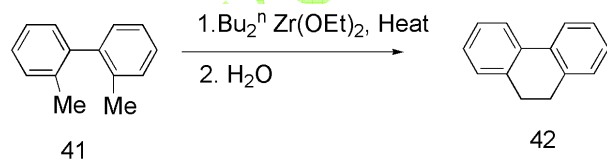
Scheme-11

Ge'ard Cahiez *et al.* have reported to synthesis of 9, 10-dihydrophenanthrene by intramolecular coupling reactions from di-Grignard reagents such as **39** (Scheme 12). The diiodo compound **38** reacted with *i*-PrMgBr at room temperature for 30 min to give **39**. Then, the treatment of the di-Grignard **39** with 1, 2-dibromoethane in the presence of 3% FeCl₃ provided the dihydrophenanthrene **40** in 76% overall yield.³⁹



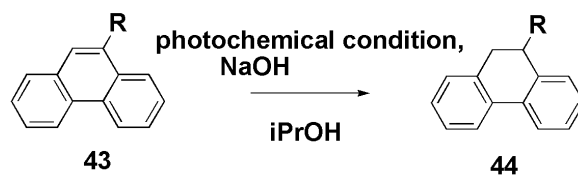
Scheme-12

Leter John J. Eisch *et al.* have made C-C Bond formation via C-H bond activation by Prior Zirconation reaction. By using this methodology (Scheme 13) they have synthesized 9, 10-dihydrophenanthrene from 2, 2 dimethyl biphenyl in moderate yield.⁴⁰



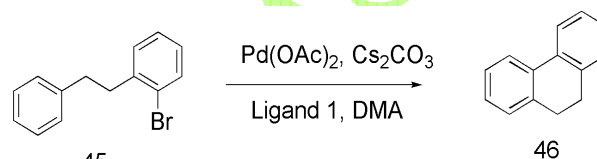
Scheme-13

Yasuharu Yoshimi synthesized dihydrophenanthrene by photochemical Birch reduction where sodium hydroxide used as electron source and Jackson also obtained dihydrophenanthrene by Birch reductions at room temperature with alkali metals in silica gel (Scheme 14).⁴¹



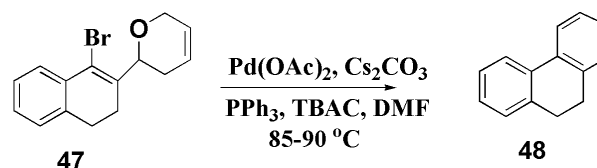
Scheme-14

Palladium catalyzed reaction also useful reaction for the synthesis of various type carbocyclic molecules. Fagnou synthesized 9, 10-dihydrophenanthrene by a C-H bond activation process, but the reaction condition was more vigorous (Scheme-15).⁴²



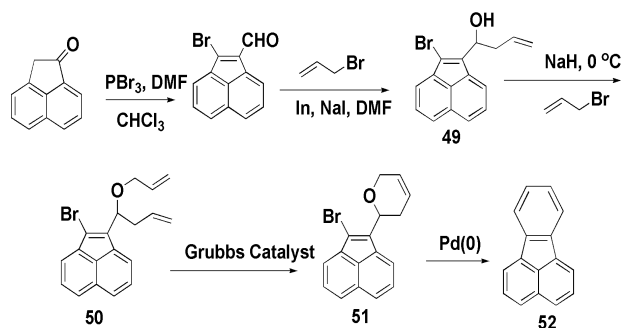
Scheme-15

We reported a novel and rapid convenient approach to the synthesis of substituted 9, 10-dihydrophenanthrene along with its analogues by a palladium-catalyzed 6π electrocyclic reaction.⁴³



Scheme-16

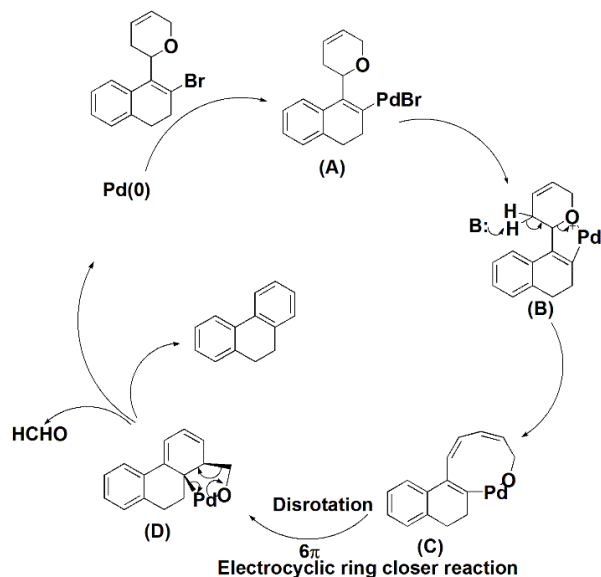
When we treated substrates **47** with Pd(OAc)₂ (10 mol %), Cs₂CO₃ (2 equiv), PPh₃ (0.5 equiv), TBAC (1 equiv), in DMF solvent, heated it at 85 °C-90 °C for 1.5h-2h, the unexpected products **48** resulted in 70% yield. A fused aromatic ring resulted from cleavage of the pyran ring present in the substrate followed by ring closer and aromatization. By using this methodology we have synthesized Fluoranthene in the following way



Scheme-17

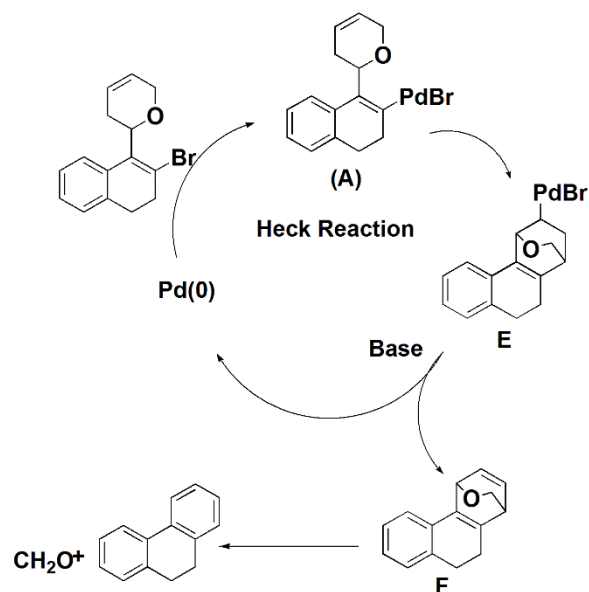
The reaction mechanism (Scheme 18) presumably involves a 6π electrocyclic ring closer reaction followed by formaldehyde elimination. The catalytic cycle involves initial oxidation of the Pd(0) to generate alkenyl palladium (II) intermediate (A) via oxidative addition of the Pd (0) to the substrate, which then co-ordinates with oxygen to generate the intermediate (B),

This undergoes proton abstraction followed by rearrangement to afford a nine membered cyclic Pd-O complex (C). This complex undergoes 6π electrocyclic ring closer reaction forming complex (D), followed by formaldehyde elimination to afford 9, 10 dihydro phenanthrene.



Scheme-18

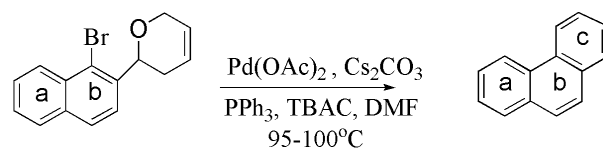
Recently Lan *et al.* proposed an alternative mechanism that occurs through an intramolecular Heck reaction. Using theoretical calculations they investigated both,



Scheme-19

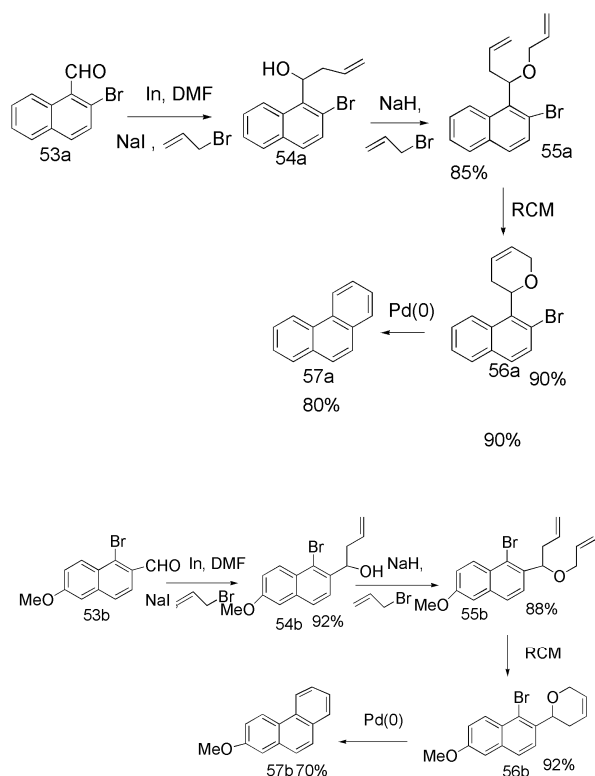
Mechanisms and find that the intramolecular Heck mechanism (Scheme 19)⁴⁴ is lower in energy than the electrocyclic pathway (Scheme 18).

Initially we have synthesized 9, 10 dihydrophenanthrenes by palladium catalyzed electrocyclic reaction starting from vinyl bromoaldehydes. Then we have employed our methodology to the aromatic bromoaldehydes system, we got successful result to synthesize phenanthrene and alkyl phenanthrene in good yield^{45,46}. Importance of this methodology is that we can introduce alkyl group in any one or two position of newly formed benzene ring(c) of phenanthrene (Scheme 20).



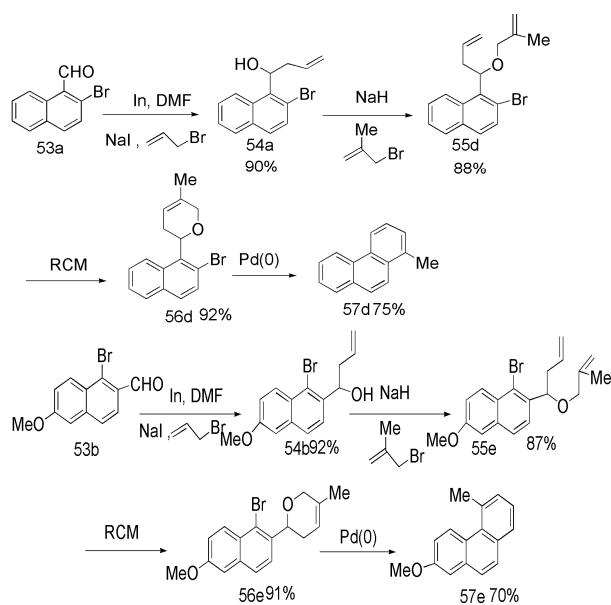
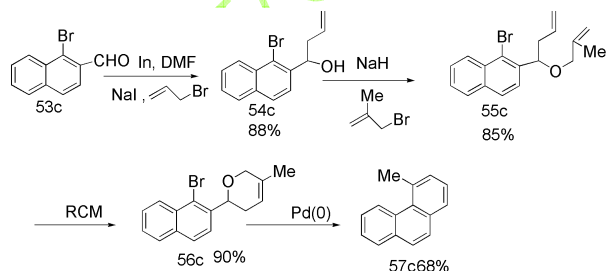
Scheme-20

First aromatic bromoaldehydes **53a**, **53b** were treated with allyl bromide, sodium iodide in presence of indium metal to obtained corresponding alcohols **54a** and **54b**. These alcohols were allylated in presence of sodium hydride in THF medium at 0 °C to obtained diallylated compound **55a** and **55b** which were subjected to 2nd generation Grubbs catalyst to Obtain desired cyclic precursor **56a** and **56b** respectively. Then these cyclic precursor were finally treated with Pd(OAc)₂, PPh₃, Cs₂CO₃ in DMF solvent at 85-90 °C to afforded phenanthrenes **57a** and 2-methoxy phenanthrene **57b** in good yield which is shown in Scheme 21.



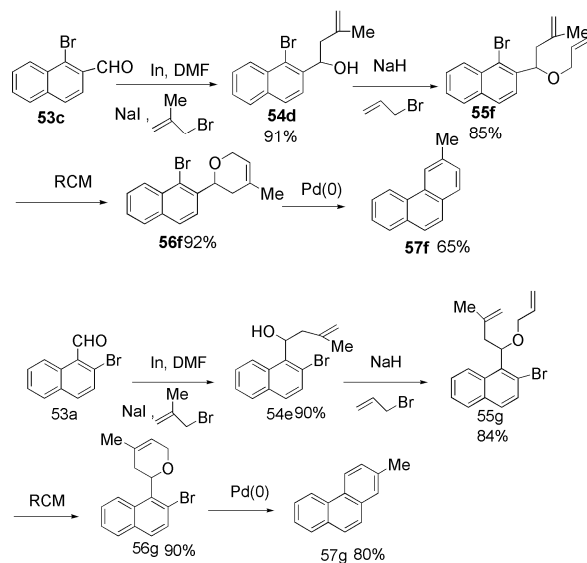
Scheme-21

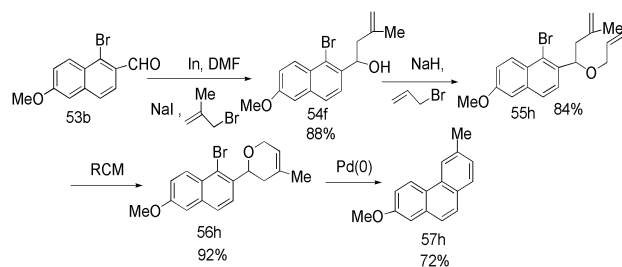
To introduce alkyl group in phenanthrene ring aromatic bromoaldehydes **53a**, **53b**, **53c** were treated with allyl bromide, sodium iodide in presence of indium metal to obtain corresponding alcohols **54a**, **54b** and **54c**. These alcohols were methylated in presence of sodium hydride in THF medium at 0°C to obtain diallylated compound **55c**, **55d** and **55e** which were subjected to 2nd generation Grubbs catalyst to obtain desired cyclic precursor **56c**, **56d** and **56e** respectively. Then these cyclic precursor were finally treated with Pd(OAc)₂, PPh₃, Cs₂CO₃ in DMF solvent at 85-90°C to afford alkyl phenanthrenes **57c**, **57d** and **57e** respectively which is shown below (Scheme 22).



Scheme-22

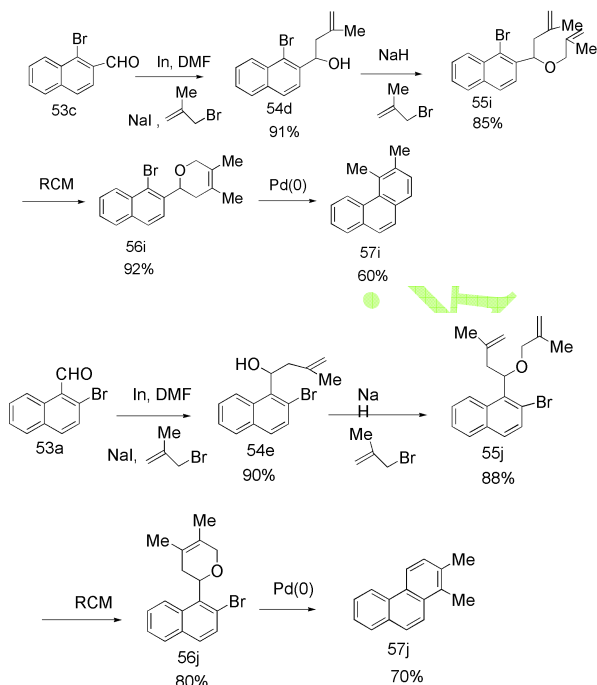
To alternate the position of methyl group, same aromatic bromoaldehydes **53a**, **53b** and **53c** were first treated with methylallyl bromide, sodium iodide in presence of indium metal to obtain compounds **54d**, **54e** and **54f**. These alcohols were then allylated in presence of sodium hydride in THF medium at 0°C to obtain diallylated compounds **55f**, **55g** and **55h** which were subjected to 2nd generation Grubbs catalyst to obtain desired cyclic precursor **56f**, **56g** and **56h** respectively. Then these cyclic precursor were finally treated with Pd(OAc)₂, PPh₃, Cs₂CO₃ in DMF solvent at 85-90°C to afford alkyl phenanthrenes **57f**, **57g** and **57h** respectively (Scheme 23).





Scheme-23

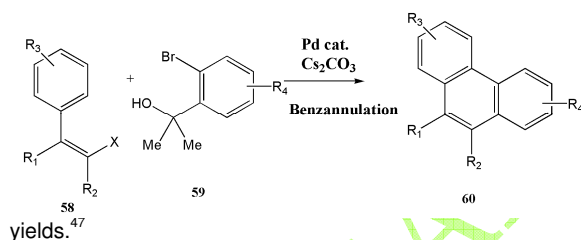
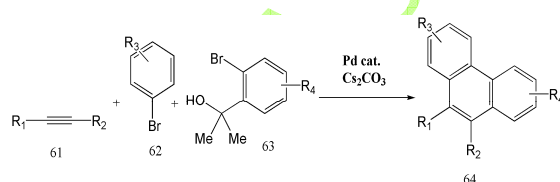
We can introduce two alkyl groups in phenanthrene ring. Few methods are known for the introduction of two alkyl group. First Aromatic bromoaldehydes **53a**, **53c** were treated with methylallyl bromide, sodium iodide in presence of indium metal to obtained corresponding alcohols **54d** and **54e**. These alcohols were methylated in presence of sodium hydride in THF medium at 0 °C to obtained diallylated compound **55i** and **55j** which were subjected to 2nd generation Grubbs catalyst to obtained desired cyclic precursor **56i** and **56j** respectively. Then these cyclic precursor were finally treated with Pd(OAc)₂, PPh₃, Cs₂CO₃ in DMF solvent at 85-90 °C to afforded dialkyl phenanthrenes **57i** and **57j** in good yield (Scheme 24).



Scheme-24

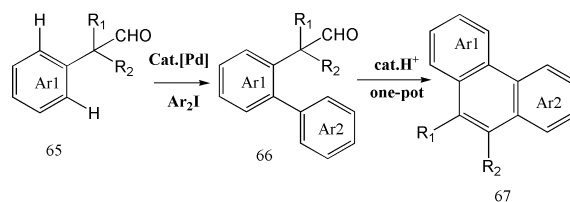
A palladium-catalyzed benzannulation with *o*-bromobenzyl alcohols enabled the facile construction of phenanthrene skeletons via the sequential multiple carbon-carbon bond formations. A variety of multi-substituted phenanthrenes were synthesized by the reaction of (*Z*)- β -halostyrenes with *o*-bromobenzyl alcohols as well as by the three-component coupling of alkynes, aryl bromides, and *ortho*-bromobenzyl

alcohols. The electron-deficient phosphine ligand played an important role to control the sequential oxidative addition of two different organic halides employed, which realized the selective formation of the desired phenanthrenes in good

yields.⁴⁷

Scheme-25

Ling Zhou envisioned that Pd-catalyzed γ -C(sp²)-H arylation of phenylacetaldehydes with aryl iodide by using an amino acid as a transient directing group would produce compound **66** undergo sequential intramolecular cationic cyclization, dehydration, and 1,2-migration in the presence of an acid to generate phenanthrenes **67** (Scheme 26). The major challenges of this strategy arise from questions regarding whether the acid generated during the course of the reaction is sufficiently reactive to activate the following cascade reaction and selective 1,2-migration to give a single isomer of phenanthrenes.⁴⁸



Scheme-26

Conclusion:

We have discussed different method for synthesis of phenanthrene, mono and dialkylated phenanthrene derivatives by using palladium catalyzed reaction. These methods are also useful for the synthesis of higher homologous of polynuclear aromatic hydrocarbons provided the efficient route to synthesis of suitable starting material.

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