Chapter - 4

Introduction: One-Pot methodologies in Organic Synthesis

Present Work:

Part-1: Dehydrohalogenation-Heck Olefination and Multi-component Wittig-Heck Reaction

Part-2: Oxidation-Wittig Reaction
Introduction

Synthetic protocols in which more than one steps are carried out simultaneously or as one-pot process, offer a number of advantages to the chemists. Mainly the combination of operations results in the lower overall consumption of reagents for reaction/work-up. Moreover, there is a reduction in the total reaction time, avoids purification of unstable, toxic or volatile intermediates and often fulfill some of the requirements of the alternative greener synthesis. In a way they are often referred as “Greener Synthetic Procedures”. In recent decades several procedures are developed for making useful molecules and intermediates by adopting one-pot or domino or tandem synthetic schemes.¹

Number of one-pot multi step reactions have been developed during last decade owing to their practical advantages. Due to their various applications in organic synthesis, we have developed three different one-pot methodologies for the synthesis of variety of stilbene derivatives. These synthetic developments will be presented in this chapter. Discussion will be divided in to two parts, one will comprise of one-pot dehydrohalogenation-Heck olefination and multicomponent Wittig-Heck reaction for preparation of stilbene derivatives while the second part will have discussion about the oxidation-Wittig sequence for the synthesis of symmetrical as well as unsymmetrical stilbenes.

Interesting one-pot strategy has been developed combining catalytic Hunsdiecker reaction (using tetrabutylammonium trifluoroacetate in dichloroethane) and Heck coupling (using palladium acetate/triethylamine/triphenylantimony/dichloroethane) for the synthesis of 5-aryl-2,4-pentadienoic acids, esters and amides in moderate to good yields [Scheme 1].²

![Scheme 1: One-pot Hunsdiecker-Heck coupling reaction](image)

During the course of the reaction, the first step was halodecarboxylation reaction which upon successive palladium catalyzed Heck reaction with variety of acrylates or acrylamides gave corresponding conjugated dienes with good conversion.

Since the discovery of electroluminescence from poly(phenylenevinylene) (PPV), continuous research efforts have been devoted to the synthesis of differently structured PPV derivatives, which can be considered the most promising organic materials to be used in light-emitting diodes (LEDs). As a contributing part of this study, poly(fluorenylenvinylene)s P₁–P₃ can be synthesized by one-pot cascade Suzuki–Heck reaction from dibromofluorene derivative 1 and variety of aryldibromides [Scheme 2].³ This approach differs from the known syntheses of PFVs, which require a multistep approach for the synthesis of the
monomers, inevitably leading to unsatisfactory overall yields, the most important advantage of this method is the use of easily accessible substrates and potassium vinyltrifluoroborate as ethylene equivalent in a high-yield reaction.

![Scheme 2: one-pot cascade Suzuki–Heck reaction for the synthesis of poly(fluorenylenevinylene)](image)

Beck and co-workers have developed the synthesis of substituted indoles from 2-haloanilines via palladium catalyzed one-pot N-alkylation-Heck cascade reaction. As the indole derivatives have been useful moiety for contributing to the pharmacological activities, this methodology could be widely accepted for the synthesis of the indole derivative of interest.

Inspired by the variety of applications of oligo (p-phenylenevinylene)s (OPVs) studied in recent years, number of routes have been reported for the synthesis of such type of useful molecules, which involved Wittig olefination of benzaldehydes with bisdiethylphosphonates (obtained from xylenes through bromination-phonation) followed by deprotection. In addition to that new approach for one step olefination of benzaldehydes into hydroxy functionalized OPVs was achieved through the first domino Knoevenagel-decarboxylation-Heck sequence using a single catalyst system. The methodology also led to new oxygen based OPV scaffolds capable of selective and visible fluoride recognition in organic or aqueous medium. The application of this methodology was proved by the preparation of more complex molecule like octupolar OPV 5 via reaction of hydroxyl benzaldehyde derivative 3, malonic acid and the 1,3,5-tribromobenzene 4 in 39% yield [Scheme 3].

232
Scheme 3: Domino Knoevenagel-decarboxylation-Heck sequence for octupolar OPV 5

Vennerstrøm and co-workers were the first to report one-pot synthesis of unsymmetrical bis-styrylbenzenes using a Heck/HWE sequence. The yields were shown to be comparable or higher than those reported from HWE/Heck stepwise reactions. This method should be applicable to the synthesis of structurally diverse unsymmetrical bis-styrylbenzenes [Scheme 4].

Scheme 4: Heck-HWE one-pot synthesis of unsymmetrical bis-syrylbenzenes

Interestingly, Taylor has developed a new tandem sequence involving HWE olefination followed by a palladium-catalysed intramolecular Heck reaction which provides rapid access to isomeric mixture of 3-alkenyl-oxindoles from readily available α-bromoanilides and aldehydes. The one-pot, micro-wave accelerated process have been employed with a range of aldehyde trapping reagents and N-alkylated as well as N-H oxindoles have been prepared using this sequence [Scheme 5].

Scheme 5: Tandem HWE-Heck route for 3-alkenyl-oxindoles
A new and versatile one-pot synthesis of indol-2-ones by a novel Ugi-four-component-Heck reaction was developed by Umkehrer and co-workers because compounds containing the indol-2-one scaffold constitute an important pharmacophoric moiety, which exhibits important biological effects such as antitumor activity, phosphodiesterase inhibitor activity and tyrosine kinase inhibitor activity [Figure 1].

![Scheme 6: One-Pot four-component Ugi-Heck reaction](image)

Multicomponent reactions like the Ugi reaction allow rapid generation of compound libraries and the final intramolecular Heck reaction is used for a defined ring-closing. The products, high substituted indol-2-ones have four points of potential diversity. The aldehydes, anilines, isocyanides, and acrylic acids can be varied broadly, producing products with four potential combination units. Reaction of 2-bromoaniline, benzaldehyde, isocyanid ester and cinnamic acid undergo Ugi reaction which produced. The formation of the acyclic products was originally reported by Ugi et al. and the final ring-closing was performed by a classical intramolecular Heck reaction using palladium(II)acetate:PPh₃ as catalyst system which afforded the isomeric mixture of indol-2-one derivative in moderate yield [Scheme 6].

![Figure 1: Indol-2-one scaffold in biologically active molecules](image)
It is also noteworthy that a number of stilbenes have been isolated from natural sources. Among them, hydroxylated (E)-stilbenoids, such as resveratrol 18 (3,4,5-trihydroxystilbene, a phytoalexin found in grapes and other food products), have attracted considerable attention because of their potential therapeutic value as chemopreventive and chemotherapeutic agents. Various synthetic routes have been developed, including a large number based on Heck methodologies. Recently, cross-metathesis reactions have also been successfully used to prepare hydroxylated (E)-stilbenoids. However, in all cases, it is required to have a styrene derivative as the substrate. Using a multicatalytic strategy combining a methylation reaction with a coupling reaction avoids the need for isolating the styrene intermediate (which can potentially polymerize), thereby decreasing the amount of required reagents and solvents (for workup and purification procedures), while producing less waste. Lebel has explored the combination of the rhodium- or copper-catalyzed methylation reaction with a palladium-catalyzed Heck cross-coupling reaction for the synthesis of some useful stilbene derivatives. The one-pot process was developed by performing Cu-catalyzed methylation of aldehydes to generate variety of styrene derivatives in situ, followed by Pd-catalyzed Heck cross coupling. The applicability of this tandem method was justified by the synthesis of biologically active compound such as resveratrol 18 from 3,5-dimethoxybenzaldehyde 17 in good overall yield [Scheme 7].

![Scheme 7: Synthesis of resveratrol 18 via one-pot methylation-Heck method](image)

In addition to these complex methodologies, we have developed comparatively simpler procedures to generate in situ styrenes from easily accessible precursors which will be discussed in first part of this chapter.

In recent decades several procedures were developed for making useful molecules and intermediates by adopting one-pot or domino or tandem synthetic schemes. Functional groups such as aldehydes and ketones are critical starting materials for building many products by a number of important reactions. Several of these starting materials are commercially available or can be easily synthesized. Oxidation of primary alcohols give inherently unstable aldehydes and the strategy of their in situ one-pot reaction is an attractive option. In this
connection several reagents have been applied for in situ oxidation of alcohols for subsequent wide variety of organic transformations.

In mid 80’s, Norbeck has attempted to developed the synthesis of some important carbonyl compounds from its corresponding alcohols via swern oxidation. But particularly in case of the bicyclic primary alcohol 19 which upon Swern oxidation yielded corresponding aldehyde 20 which was proved to be unstable because it could not be isolated even as impure sample. Hence this unstable aldehyde 20 was then trapped by addition of methyl (triphenylphosphoranylidene)acetate to the crude Swern oxidation mixture which provided the unsaturated ester 21 in the form of isomeric mixture in excellent yield [Scheme 8]. This oxidation-Wittig sequence was then applied to a variety of primary alcohols for several applications in organic synthesis.

![Scheme 8: One-pot oxidation-Wittig olefination reaction](image)

Number of the in situ oxidation-Wittig reactions have been reported by several groups using stabilized Wittig reagent, Barrett’s group used the Dess-Martin periodinane as an oxidant, Matsuda’s group used barium permanganate, and Taylor’s group utilized manganese dioxide.

Shing and co-workers have developed efficient and facile glycol cleavage oxidation using improved silica gel-supported sodium metaperiodate under non-aqueous condition. Interestingly, the Boc-protected alcohol 22 was subjected to the oxidation using silica based sodium metaperiodate which in situ resulted in to the formation of aldehyde followed by Wittig reaction with triphenylphosphoranylidene acetone as ylide to afford corresponding unsaturated ketone 23 in excellent yield of 97% [Scheme 9]. It was noteworthy that throughout the course of reaction the Bdh-protection remain intact, in a way it offered relatively mild condition for the oxidation-Wittig sequence for such sensitive precursors.

![Scheme 9. Silica supported NaIO₄ as oxidant for one-pot oxidation-Wittig reaction.](image)
Inspired by the results, Dunlap has utilized this reagent system for the oxidative cleavage/Wittig reaction on some carbohydrate derived glycols exhibited good results.\textsuperscript{21b}

A convenient sequential oxidation–Wittig olefination protocol was reported by Ley using tetra-$n$-propylammonium persulfenate (TPAP) 24 as oxidant and phosphonium salts as olefin source.\textsuperscript{24} It was widely applicable to a range of alcohols, including aromatic, aliphatic, heterocyclic, secondary, and chiral alcohols, with both stabilised and nonstabilised Wittig reagents to synthesise ethylenes, vinyl halides, and esters. This method has potential for use in natural product synthesis [Figure 2].

![Figure 2: oxidising reagent used for one-pot oxidation-Wittig reaction](image)

After the development of a versatile and highly selective hypervalent iodine bis(acetoxy)iodobenzene (BAIB) 25 and 2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO) 26 mediated oxidation of alcohols to carbonyl compounds by Piancatelli and co-workers,\textsuperscript{25} Vatele has implemented this system for the tandem oxidation-Wittig olefination reaction for variety of alcohols to give unsaturated esters. This oxidative process is very attractive because of its mild nature, commercially available reagents, compatibility with many functional and protecting groups and high selectivity in the oxidation of primary alcohols in the presence of secondary ones. This method involves the rapid oxidation of alcohols in dichloromethane at room temperature using BAIB in the presence of catalytic amount of TEMPO followed by the addition of stabilized phosphoranes to afford unsaturated esters in good yields.\textsuperscript{26}

Besides these developments in one-pot oxidation-Wittig olefination reactions, we have attempted to develop the use of the simpler reagents and facile conditions for such reaction combinations for one-pot synthesis of olefins.
Result and Discussion

Part-1: Dehydrohalogenation-Heck Olefination and Multi-component Wittig-Heck Reaction

In this part of the chapter we present two different approaches of olefination forming processes, followed by their Mizoroki-Heck reaction as one-pot methods. The prerequisite of planning the one-pot multi step reactions is the compatibility of the reagent system and reaction conditions. In the present effort the second reaction, the Mizoroki-Heck is carried out with Pd-catalyst and a suitable base. The required olefin is envisaged to be prepared either by dehydrohalogenation of suitable alkyl halide [Approach A] or alternatively from Wittig reaction of aldehyde [Approach B], both being carried out in the basic medium. The two approaches are outlined in [Scheme-10] while taking the example of the in situ synthesis of styrene 27 and then subjected to Mizoroki-Heck conditions to form stilbene 28. In the approach A-1 the styrene is prepared by dehydrohalogenation of (2-bromoethyl)benzene 29, and in A-2 from (1-bromoethyl)benzene 30 using same base which will also work for subsequent Mizoroki-Heck reaction. Elimination reaction of 29 may be more favorable compared to 30 if it follows the E1cB mechanism\(^{27}\) and hence the availability of styrene will be more for further Mizoroki-Heck reaction.

\[ \text{Ph} \quad \text{Br} \quad 29 \quad \xrightarrow{\text{A-1}} \quad \text{Ph} \quad \xrightarrow{\text{Heck}} \quad \text{Ph} \quad \text{Br} \quad \text{Ph} \quad 30 \quad \xrightarrow{\text{A-2}} \quad \text{Ph} \quad \xrightarrow{\text{Heck}} \quad \text{Ph} \quad \xrightarrow{\text{HCHO}} \quad \text{Ph} \quad \xrightarrow{\text{Pd-L}} \quad \text{Ph} \quad \text{Ph} \quad 28 \]

**Scheme-10**: One-Pot Dehydrohalogenation-Heck and Wittig-Heck Reaction

Alternatively the intermediate styrene may also be prepared by Wittig reaction of an aldehyde and suitable phosphonium salt, Approach B of Scheme-10. Since the Wittig reaction involves two components i.e. an aldehyde and a phosphonium salt, synthesis of styrene can be achieved either by approach B-1 using benzaldehyde 31 and phosphonium salt.
obtained from methyl iodide or by B-2 using formaldehyde and phosphonium salt 32 obtained from benzyl bromide and triphenylphosphine.

As discussed earlier, we are exploring the oxazolinyl ligands for catalytic reactions for the phosphine free ligands for Pd mediated Mizoroki-Heck reaction, we have chosen ligands shown in Figure-3 for the present study, 33-35 being synthesized as described in chapter 2.

![Figure-3: Ligands investigated for the present study.](image)

**Approach-A: One-Pot Dehydrohalogenation-Heck Reaction**

In order to demonstrate the generality of this approach to prepare variety of stilbenes a series of alkyl bromides were used which are listed in Figure-4. The mixture of suitable aryl halide, an alkyl halide, an excess of K$_2$CO$_3$, catalytic quantity of Pd(OAc)$_2$-ligand in dry DMA was heated at 140 °C. Careful thin layer chromatography analysis indicated the formation of corresponding stilbenes [Scheme 11], which were isolated and characterized. The results are presented in Table-1, which consists of some combinations of aryl and alkyl halides to give a series of stilbenes.

![Figure-4: Alkyl halides used for in situ generation of olefins by dehydrohalogenation for Mizoroki-Heck reaction.](image)
Scheme 11: General synthetic scheme for one-pot dehydrohalogenation-Heck reaction (Approach-A)

In most of the cases the isolated yields of olefin were good with just 1.2 equivalent quantity of alkyl halide. As expected the formation of trans-stilbene 28 with alkyl halide 29 with iodobenzene was more favored due to facile elimination, as compared with that of with alkyl halide 30. However, it will be more logical and practical to use alkyl halides of the type 30 and 37 for this type of reactions, as they can be easily accessible from ethyl aryls by benzylic bromination [conditions: NBS-Bz₂O₂-light], as we did.
<table>
<thead>
<tr>
<th>No.</th>
<th>Alky halides</th>
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<th>Yield (%)</th>
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<td><img src="image2" alt="image" /></td>
<td><img src="image3" alt="image" /></td>
<td>80</td>
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<td></td>
<td><img src="image4" alt="image" /></td>
<td><img src="image5" alt="image" /></td>
<td><img src="image6" alt="image" /></td>
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<td><img src="image7" alt="image" /></td>
<td><img src="image8" alt="image" /></td>
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<td>54</td>
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<td><img src="image11" alt="image" /></td>
<td><img src="image12" alt="image" /></td>
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<td><img src="image17" alt="image" /></td>
<td><img src="image18" alt="image" /></td>
<td>78</td>
</tr>
</tbody>
</table>
All reactions run with aryl halide (1 eq.), alkyl halide (1.2 eq.), K₂CO₃ (3 eq.), Pd(OAc)₂ (0.5 %), 33 or 34 (0.55 %) in DMA at 140 °C for 40 h.
For entry 7: 29 (3 eq.), K₂CO₃ (4.0 eq.), Fd (1.0 %)-34 (2.5 %). *Isolated Yield, †With L-36, ‡With L-35.
Approach-B: One-Pot Three-Component Wittig-Heck Reaction

The second approach under consideration to develop a one-pot procedure to generate styrene involves its *in situ* synthesis by the classical Wittig olefination.\(^\text{29}\) Reaction of aromatic aldehyde with phosphonium salts undergo Wittig reaction even with weak base like potassium carbonate,\(^\text{30}\) which is available in the present Mizoroki-Heck conditions. Hence a concoction of equimolar amount of benzaldehyde, \(\text{Ph}_3\text{P}\text{CH}_2\text{I}\), iodobenzene, excess of \(\text{K}_2\text{CO}_3\), catalytic quantity of \(\text{Pd(OAc)}_2\cdot\text{oxazolinyl ligand 33 or 34, TBAB as PTC was heated in DMA and trans-stilbene 28 was isolated in good yield. A series of experiments are reported in Table-2 where this concept was clearly established for a number of aldehydes, three representative phosphonium salts and another set of aryl halides. One carbon aldehyde unit was accessed by selecting paraformaldehyde (0.34 eq) in the reaction. This is a three component reaction and hence with the same number of variations available for the facile generation of substituted stilbenes [Scheme 12]. Utilizing the well established, transition metal free, high yielding Wittig reaction for the *in situ* olefination is an attractive option. It is significant to mention that good yields of olefins were obtained by equimolar ratios of three reagents compared to the use of excess of olefin in normal Mizoroki-Heck reaction protocol.

\[
\begin{align*}
\text{O} & \quad \text{Wittig Reaction} \\
\text{Ar} & \quad \text{Ph}_3\text{P}\text{CH}_2\text{I} & \quad \text{K}_2\text{CO}_3 \\
\text{H} & \quad \text{Wittig Reaction} \\
\text{Ar} & \quad \text{ArPh}_3\text{P}\text{CH}_2\text{X} & \quad \text{K}_2\text{CO}_3 \\
\text{Heck Condition} & \quad X = \text{Br or I} \\
\text{Ar} & \quad \text{Ar'} \\
56 - 97\% &
\end{align*}
\]

**Scheme 12**: One-Pot three component Wittig-Heck reaction
<table>
<thead>
<tr>
<th>No.</th>
<th>Aldehyde</th>
<th>Phosphonium Salt</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Arényliden</td>
<td>Pt$_3$P·CH$_3$I</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>Arényliden</td>
<td>Pt$_3$P·CH$_3$I</td>
<td>94 (85)</td>
</tr>
<tr>
<td>3</td>
<td>Arényliden</td>
<td>Pt$_3$P·CH$_3$I</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>Arényliden</td>
<td>Pt$_3$P·CH$_3$I</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Arényliden</td>
<td>Pt$_3$P·CH$_3$I</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 2: Synthesis of stilbene by one-pot three component procedure of Wittig-Heck reaction.
<table>
<thead>
<tr>
<th>No.</th>
<th>Structure 1</th>
<th>PL₃P⁺CH₃ I</th>
<th>Structure 2</th>
<th>Structure 3</th>
<th>Percentage</th>
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</thead>
<tbody>
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<td>PL₃P⁺CH₃ I</td>
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<td>7</td>
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<td>PL₃P⁺CH₃ I</td>
<td><img src="#" alt="Structure 39" /></td>
<td><img src="#" alt="Structure 66" /></td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td><img src="#" alt="Structure 67" /></td>
<td>PL₃P⁺CH₃ I</td>
<td><img src="#" alt="Structure 39" /></td>
<td><img src="#" alt="Structure 68" /></td>
<td>92</td>
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<tr>
<td>9</td>
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<td>PL₃P⁺CH₃ I</td>
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<td>82</td>
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<td>10</td>
<td><img src="#" alt="Structure 60" /></td>
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<tr>
<td>11</td>
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<td>PL₃P⁺CH₃ I</td>
<td><img src="#" alt="Structure 39" /></td>
<td><img src="#" alt="Structure 71" /></td>
<td>82</td>
</tr>
</tbody>
</table>
All reactions were run in DMA, with Pd(OAc)$_2$ (0.5 mol%), ligand 33 or 34 (1.0 mol%), K$_2$CO$_3$ (3.5 eq.), TBAB (2C, %) at 130-40°C for 40 h.

Approach-C: One-Pot Five-Component Wittig-Heck Reaction

Development of efficient synthesis of conjugated molecules is important for the preparation of several new materials capable of having unique properties due to the delocalization of electrons over several multiple bonds. Among such entities the molecules with alternate double bonds and aromatic rings are prominent and have received some attention. The present strategy of in situ generation of stilbene was further extended to synthesize distyryl benzenes from easily available stable starting materials. The approach involves simultaneous formation of two double bonds between three aromatic rings via a combination of Wittig and Mizoroki-Heck reaction between five reactants molecules in a single step process. This one-pot five component process can be done in two ways. The 1,4-divinyl benzene 77 was in situ prepared by reaction of terephthalaldehyde 75 and two equivalents of Wittig reagent and subsequently reacted with Pd catalyzed Heck reaction with two equivalent of iodobenzene 39 [approach C-1, scheme-13] or by making the two molecules of styrene (in situ) and then reacting with a single molecule of 1,4-dibromo benzene 76 [approach C-2, scheme-13]. The combined yield of the reactions conducted in a single pot was very good, both with ligand 33 or 34 and with dppp, 36 [Table-3].

Scheme-13: One-pot five component approach for 1,4-distyryl benzene 77

The route involving in situ synthesis of 1,4-divinyl benzene from terephthalaldehyde (route C-1, Scheme-5) was less effective since this compound has a tendency towards cross linking polymerization. On the other haln intermediate styrene is formed in route C-2, which appears to be more stable for polymerisation or side reactions.
<table>
<thead>
<tr>
<th>No.</th>
<th>Aldehyde</th>
<th>Ar/Halide</th>
<th>Route</th>
<th>Product</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Aldehyde" /></td>
<td><img src="image2" alt="Ar/Halide" /></td>
<td>C-1</td>
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<td><img src="image4" alt="Aldehyde" /></td>
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<td>C-2</td>
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<td>C-2</td>
<td><img src="image15" alt="Product" /></td>
<td>77b</td>
</tr>
</tbody>
</table>

All reactions carried out with $\text{Ph}_3\text{P}^+\text{CH}_3^-$(2.3 eq), TBAB (40%), $\text{K}_2\text{CO}_3$ (7.0 eq), DMA, 140 °C, 48 h. \(^{\text{b}}\) Entry 1,3 to 5: Pc (1.0%), 33 (2.0%); \(^{\text{b}}\) Entry 2 Pd (1.0%), dppp (2.0%).
We have prepared styrene from alkyl halides or aldehydes by base mediated dehydrohalogenation or Wittig reaction and subjected it to in situ palladium catalyzed one-pot Heck reaction to efficiently access substituted stilbenes. Alkyl halides can also be valuable precursors of aldehydes for further olefination procedures which will be discussed in next part of this chapter.

**Part 2: One-Pot Oxidation-Wittig Olefination Reaction**

To the best of our knowledge synthesis of symmetrical olefins by coupling of alkyl halides via its in situ generated aldehyde by vanadium catalyzed oxidation of the ylide is the only reported example. In this portion we have documented access of aromatic aldehydes by in situ oxidation of benzyl halides and subject it further to one-pot Wittig reaction towards stilbenes. The approach in this direction is based on the well known Kornblum oxidation of benzyl halides to the corresponding aromatic aldehydes [Scheme 14]. The combinations of domino reactions with Kornblum type oxidation as one of the steps are relatively rare. In the **Approach D** one molecule of benzyl halide will undergo Kornblum oxidation to an aldehyde, while the second one will form a phosphonium salt with triphenyl phosphine. Both of them will subsequently combine to give a symmetrical stilbene as the Wittig product. Further modification in **Approach E** will give unsymmetrical stilbene when one equivalent of a preformed phosphonium salt of a different benzyl halide is added in the reaction mixture.

**Scheme 14:** Synthesis of symmetrical / unsymmetrical stilbenes from benzyl halide by one-pot oxidation-Wittig sequence.

The concept is investigated by conducting the one-pot reaction of benzyl halides with half equivalent of Ph₃P in dry DMSO, catalytic amount of additive, excess of base at higher
temperature for appropriate reaction time. Number of experiments have been performed to meet the standard reaction parameters for this study [Table 4].

**Table 4:** Experiments for the search of standard condition for one-pot oxidation-Wittig reaction.

<table>
<thead>
<tr>
<th>No.</th>
<th>Benzyl halide</th>
<th>Base</th>
<th>Additive</th>
<th>Solvent</th>
<th>Yield of Stilbene 28 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzyl chloride 81</td>
<td>K$_2$CO$_3$</td>
<td>TBAB</td>
<td>DMSO</td>
<td>43</td>
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<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Benzyl chloride 81</td>
<td>NaHCO$_3$</td>
<td>TBAB</td>
<td>DMSO</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Benzyl chloride 81</td>
<td>Cs$_2$CO$_3$</td>
<td>TBAB</td>
<td>DMSO</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Benzyl chloride 81</td>
<td>DBU</td>
<td>TBAB</td>
<td>DMSO</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Benzyl chloride 81</td>
<td>NaHCO$_3$</td>
<td>KI</td>
<td>DMSO</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Benzyl chloride 81</td>
<td>NaHCO$_3$</td>
<td>18-crown-6</td>
<td>DMSO</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Benzyl chloride 81</td>
<td>NaHCO$_3$</td>
<td>KI</td>
<td>DMA</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12 ml</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Benzyl bromide 82</td>
<td>NaHCO$_3$</td>
<td>TBAB</td>
<td>DMSO</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Benzyl bromide 82</td>
<td>NaHCO$_3$</td>
<td>KI</td>
<td>DMSO</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 ml</td>
<td></td>
</tr>
</tbody>
</table>

*aCondition: PPh$_3$ (0.5 eq), DMSO as oxidant and solvent, 140°C, 40h; bDMSO (20 eq) and N,N- dimethyl acetamide (DMA) as solvent.

We have performed experiments using benzyl bromide as well as benzyl chloride and variety of bases such as Cs$_2$CO$_3$, K$_2$CO$_3$, NaHCO$_3$ as well as organic base like DBU [Entry 1-4, Table 4]. Also the effect of additives like KI, TBAB and crown ether [Entry 4-6, Table
was studied. We have also tried to minimize the amount of oxidant but it gave lower conversion. During this investigation we found NaHCO₃ as a best base, KI as efficient additive and DMSO as oxidant as well as solvent for this reaction to afford best results. Irrespective of the benzyl halide, product 28 was isolated in excellent yield up to 87% [Entry 5 and 9, Table 4]. The product stilbene 28 was isolated from the reaction mixture by column chromatography and the ratio of its $Z:E$ isomer established by $^1$H-NMR analysis.

Encouraged by the reaction a series of benzyl halides were subjected for the one-pot reaction sequence and the products were obtained in good yield, with considerable amount of $Z$ isomer as expected for the unstabilized Wittig reagent [Table 5].

This reaction worked well with most benzylic halides, although oxidation of aliphatic bromides did take place. A controlled experiment with benzyl bromide 82 and dodecyl bromide 83 gave stilbene 28 in 67% yield; no significant olefin containing dodecyl unit was isolated, although dodecanal was detected by GC-MS of the crude mixture [Scheme 15].

![Scheme 15: Controlled experiment for the selectivity of Benzylhalides than alkylhalide](image-url)
Table 5: Examples for the synthesis of symmetrical stilbenes.\(^a\)

<table>
<thead>
<tr>
<th>No</th>
<th>ArCH₂X</th>
<th>Stilbene</th>
<th>% Y</th>
<th>[Z:E](^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅CH₂Cl</td>
<td><img src="image1.png" alt="Image" /></td>
<td>87</td>
<td><img src="image2.png" alt="Image" /> [45:55]</td>
</tr>
<tr>
<td>2</td>
<td>4-FC₆H₄CH₂Br</td>
<td><img src="image3.png" alt="Image" /></td>
<td>86</td>
<td><img src="image4.png" alt="Image" /> [53:47]</td>
</tr>
<tr>
<td>3</td>
<td>4-ClC₆H₄CH₂Br</td>
<td><img src="image5.png" alt="Image" /></td>
<td>60</td>
<td><img src="image6.png" alt="Image" /> [55:45]</td>
</tr>
<tr>
<td>4</td>
<td>4-BrC₆H₄CH₂Br</td>
<td><img src="image7.png" alt="Image" /></td>
<td>63</td>
<td><img src="image8.png" alt="Image" /> [23:77]</td>
</tr>
<tr>
<td>5</td>
<td>3-FC₆H₄CH₂Cl</td>
<td><img src="image9.png" alt="Image" /></td>
<td>75</td>
<td><img src="image10.png" alt="Image" /> [46:54]</td>
</tr>
<tr>
<td>6</td>
<td>2-ClC₆H₄CH₂Cl</td>
<td><img src="image11.png" alt="Image" /></td>
<td>58</td>
<td><img src="image12.png" alt="Image" /> [39:61]</td>
</tr>
<tr>
<td>7</td>
<td>2-NO₂C₆H₄CH₂Br</td>
<td><img src="image13.png" alt="Image" /></td>
<td>69</td>
<td><img src="image14.png" alt="Image" /> [46:54]</td>
</tr>
</tbody>
</table>

\(^a\)Condition: Benzylhalide (1.0 eq.), PPh₃ (0.5 eq.), NaHCO₃ (3.0 eq.), KI (0.1 eq.), DMSO, 140°C;
\(^b\)Isolated yield. (Z:E) Ratio determined by \(^1\)H-NMR.

The modified **Approach E** involves a one-pot Wittig reaction between a preformed phosphonium salt from one benzyl halide and the aldehyde formed by the Kornblum oxidation from a different benzyl halide. A variety of unsymmetrical stilbenes have been prepared by this route [Scheme 14, Table 6].
<table>
<thead>
<tr>
<th>No</th>
<th>ArCH₂X and Ar’CH₃PPh₃X’</th>
<th>Stilbene Ar-CH=CH-Ar’</th>
<th>% Y</th>
<th>[Z:E]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅CH₂Cl 81</td>
<td><img src="81" alt="Chemical Structure" /></td>
<td>84</td>
<td>[46:54]ᵇ</td>
</tr>
<tr>
<td></td>
<td>C₆H₅CH₂PPh₃Cl 32</td>
<td><img src="32" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4-BrC₆H₅CH₂Br 88</td>
<td><img src="88" alt="Chemical Structure" /></td>
<td>81</td>
<td>[31:69]ᵇ</td>
</tr>
<tr>
<td></td>
<td>4-BrC₆H₅CH₂PPh₃Br 72</td>
<td><img src="72" alt="Chemical Structure" /></td>
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</tr>
<tr>
<td>3</td>
<td>4-ClC₆H₅CH₂Br 86</td>
<td><img src="86" alt="Chemical Structure" /></td>
<td>73</td>
<td>[51:49]ᵇ</td>
</tr>
<tr>
<td></td>
<td>C₆H₅CH₂PPh₃Cl 32</td>
<td><img src="32" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4-BrC₆H₅CH₂Br 88</td>
<td><img src="88" alt="Chemical Structure" /></td>
<td>75</td>
<td>[47:53]ᵇ</td>
</tr>
<tr>
<td></td>
<td>C₆H₅CH₂PPh₃Cl 32</td>
<td><img src="32" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4-NO₂C₆H₅CH₂Br 97</td>
<td><img src="97" alt="Chemical Structure" /></td>
<td>65</td>
<td>[43:57]ᵇ</td>
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<tr>
<td></td>
<td>C₆H₅CH₂PPh₃Cl 32</td>
<td><img src="32" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4-BrC₆H₅CH₂Br 88</td>
<td><img src="88" alt="Chemical Structure" /></td>
<td>54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-RC₆H₅CH₂PPh₃Br 98</td>
<td><img src="98" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R = COOMe)</td>
<td><img src="99" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>C₆H₅CH₂Cl 81</td>
<td><img src="81" alt="Chemical Structure" /></td>
<td>81</td>
<td>[59:41]ᵇ</td>
</tr>
<tr>
<td></td>
<td>Ar’CH₂PPh₃Brᵈ 100</td>
<td><img src="100" alt="Chemical Structure" /></td>
<td></td>
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<td>4-FC₆H₄CH₂Br 84</td>
<td><img src="84" alt="Chemical Structure" /></td>
<td>79</td>
<td>[52:48]ᶜ</td>
</tr>
<tr>
<td></td>
<td>Ar’CH₂PPh₃Brᵉ 100</td>
<td><img src="101" alt="Chemical Structure" /></td>
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<td></td>
</tr>
<tr>
<td>9</td>
<td>4-BrC₆H₅CH₂Br 88</td>
<td><img src="88" alt="Chemical Structure" /></td>
<td>74</td>
<td>[51:49]ᵇ</td>
</tr>
<tr>
<td></td>
<td>Ar’CH₂PPh₃Brᵉ 100</td>
<td><img src="102" alt="Chemical Structure" /></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃCondition: ArCH₂X (1.0 eq.), Ar’CH₂PPh₃X’ (1.0 eq.), NaHCO₃ (3.0 eq.), KI (0.2 eq.), DMSO, 140°C, 40h; ᶘIsolated yield. (Z:E) Ratio determined by H-NMR; ᵃ(Z:E) Ratio determined by HPLC analysis. ᵇMostly E isomer formed. ᵆAr’ = 2-Naphthyl.
Polyaromatic hydrocarbons are important class of compounds and many derivatives find applications in material chemistry. Synthesis of phenanthrene and its derivatives is achieved by one-pot Suzuki-aldol condensation\(^{37a}\) and Ullmann-Pinacol coupling\(^{37b}\) involving cyclization methodology. The present approach of oxidation-Wittig reaction is extended to the intramolecular version. In this attempt sample of 2,2’-dibromomethyl biphenyl \(103\) was subjected to partial oxidation of one \(\text{ArCH}_2\text{Br}\) and phophonium salt formation with the other, subsequent intramolecular Wittig reaction leads to \(104\) in moderate yield [Scheme 16]. Initial experiments indicate better conversion with higher dilution to favour intramolecular reaction with fewer side products.

**Scheme 16**: Synthesis of phenanthrene \(104\) by oxidation-intramolecular Wittig approach.
Experimental Section

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Purification of reaction products was carried out by column chromatography using silica gel (60-120 mesh). Thin layer chromatography was performed on TLC Silica Gel 60 F$_{254}$ (Merck). The spots were visualized under UV light or with iodine vapour. $^1$H-NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer (400 MHz) and were run in CDCl$_3$ unless otherwise stated. Signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument; IR spectra were recorded on Perkin-Elmer FTIR RXI spectrometer as KBr pallets. Melting points were recorded in Thiele’s tube using paraffin oil and are uncorrected. For the HPLC analysis CHIRALPAK AD-H column was used on Waters 996 photodiode Array Detector and Waters 2690 Separation Module HPLC system.

Solvents were dried and purified by distillation under reduced pressure and stored on molecular sieves. Palladium (II) acetate [Pd(OAc)$_2$] was purchased from the Aldrich Chemicals, stored in an inert atmosphere desiccator. All aldehydes, triphenylphosphine, Methyl iodide and Iodobenzene were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc., and used without further purification.

Part-1: Dehydrohalogenation-Heck Olefination and Multi-component Wittig-Heck Reaction

Approach-A: One-Pot Dehydrohalogenation-Heck Reaction

*Synthetic Procedures:*

*(E)-1,2-Diphenylethene or trans-Stilbene (28) from (2-bromoethyl)benzene (29):*

![Chemical structure of (E)-1,2-Diphenylethene or trans-Stilbene (28)](image)

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.50 mol %), 33 (0.0010 g, 0.0054 mmol, 0.55 mol %) in dry N,N-
dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of iodobenzene 39 (0.20 g, 0.98 mmol), dry K₂CO₃ (0.40 g, 2.94 mmol) and TBAB (0.031 g, 0.098 mmol, 10 mol %) in dry N,N-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N₂ gas. Then the solution was heated to 60 °C and (2-bromoethyl)benzene 29 (0.217 g, 1.17 mmol) was slowly added. Then the temperature was increased to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 × 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulphate. The solution was concentrated under reduced pressure to obtain a crude mass, which was purified by column chromatography using silica gel and petroleum ether as eluent to give stilbene as white solid (0.141 g, 80%).

**M.P.** 120 - 122 °C (Lit. 121 - 123 °C).

**¹H-NMR (400MHz, CDCl₃):** δ 7.57 – 7.55 (m, 4H), 7.42 – 7.38 (m, 4H), 7.32 – 7.28 (m, 2H), 7.16 (s, 2H).

*(E)-1,2-Diphenylethene or trans-Stilbene (28) from (1-bromoethyl)benzene (30):*

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.50 mol %), 33 (0.0010 g, 0.0054 mmol, 0.55 mol %) in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of iodobenzene 39 (0.20 g, 0.98 mmol), dry K₂CO₃ (0.40 g, 2.94 mmol) and TBAB (0.031 g, 0.098 mmol, 10 mol %) in dry N,N-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N₂ gas. Then the solution was heated to 60 °C and (1-bromoethyl)benzene 30 (0.217 g, 1.17 mmol) was slowly added. Then the temperature increased to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and
extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a crude mass, which was purified by column chromatography using silica gel and petroleum ether as eluent to give stilbene as white solid (0.118 g, 67%).

**M.P.** 120 - 122 °C (Lit. 121 - 123 °C).

**H-NMR** *(CDCl₃)*: δ 7.57 - 7.55 (m, 4H), 7.42 - 7.38 (m, 4H), 7.32 - 7.28 (m, 2H), 7.16 (s, 2H).

*(E)-1-Methoxy-4-styrylbenzene (41) from (2-bromoethyl)benzene (29):*

![Molecule Image]

Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol %) and 33 (0.0011 g, 0.0058 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another two neck round bottom flask 4-iodoanisole (40) (0.250g, 1.06 mmol), K₂CO₃ (0.44 g, 3.18 mmol) and TBAB (0.034 g, 0.106 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the solution was heated up to 60 °C and (2-bromoethyl)benzene 29 (0.24 g, 1.28 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 41 (0.120 g, 54%) as white solid.

**M.P.** 134 - 135 °C (Lit. 135 - 136 °C).

**H-NMR** *(CDCl₃, 400 MHz):* δ 7.50 - 7.44 (m, 4 H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, J = 16.31 Hz, 1H), 6.97 (d, J = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

**IR** *(KBr):* 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm⁻¹.

**MS** *(EI):* (m/z) 210 (M⁺, 100), 179 (14), 167 (27), 105 (7), 76(3).
(E)-1-Methoxy-4-styrylbenzene (41) from (1-bromoethyl)benzene (30):

Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol %) and 34 (0.0016 g, 0.0058 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another two neck round bottom flask 4-iodoanisole (40) (0.250 g, 1.06 mmol), K₂CO₃ (0.44 g, 3.18 mmol) and TBAB (0.034 g, 0.106 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the solution was heated up to 60 °C and (1-bromoethyl)benzene 30 (0.24 g, 1.28 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 41 (0.188 g, 84%) as white solid.

**M.P.** 134 - 135 °C (Lit. 39 135 - 136 °C).

**¹H-NMR (CDCl₃, 400 MHz):** δ 7.50 - 7.44 (m, 4 H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, J = 16.31 Hz, 1H), 6.97 (d, J = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

**IR (KBr):** 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm⁻¹

**MS (EI):** (m/z) 210 (M⁺, 100), 179 (14), 167 (77), 105 (7), 76(3).

(E)-1-Nitro-4-styrylbenzene (43) from (2-bromoethyl)benzene (29):
Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0014 g, 0.0062 mmol, 0.50 mol %), 33 (0.0013 g, 0.0068 mmol, 0.55 mol %) in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another two neck round bottom flask 4-bromonitrobenzene 42 (0.25 g, 1.23 mmol), dry K₂CO₃ (0.51 g, 3.71 mmol) and TBAB (0.039 g, 0.12 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the solution was heated up to 60 °C, and (2-bromoethyl)benzene 29 (0.274 g, 1.48 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured into water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 43 (0.187 g, 67%) as yellow solid.

**M.P.** 159-60 °C (Lit. ¹⁰ 157 °C).

**¹H-NMR (CDCl₃, 400 MHz):** δ 8.74 (d, J = 9.2 Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, J = 16.3 Hz, 1H), 7.14 (d, J = 16.3 Hz, 1H).

**IR (KBr) 2922, 1590, 1340, 1107, 970, 694 cm⁻¹**

**MS (EI):** (m/z) 225 (M⁺, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

**(E)-1-Nitro-4-styrylbenzene (43) from (1-bromoethyl)benzene (30).**

![Chemical Structure](image_url)

Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0062 mmol, 0.5 mol %) and 34 (0.0019 g, 0.0068 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another two neck round bottom flask 4-bromonitrobenzene 42 (0.25 g, 1.23 mmol), dry K₂CO₃ (0.51 g, 3.71 mmol) and TBAB (0.039 g, 0.12 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the
solution was heated up to 60 °C, and (1-bromoethyl)benzene 30 (0.274 g, 1.48 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 43 (0.223 g, 80%) as yellow solid.

**M.P.** 159-60 °C (Lit. 40 157 °C).

**¹H-NMR (CDCl₃, 400 MHz):** δ 8.74 (d, J = 9.2 Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, J = 16.3 Hz, 1H), 7.14 (d, J = 16.3 Hz, 1H).

**IR (KBr)** 2922, 1590, 1340, 1107, 970, 694 cm⁻¹

**MS (EI):** (m/z) 225 (M⁺, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

(E) 1 Nitro 4 styrylbenzene (43) from 1 (2 bromoethyl) 1 nitrobenzene (38):

![Chemical Structure](image)

Catalyst Solution: A solution of palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and 34 (0.0015 g, 0.0054 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another two neck round bottom flask iodosobenzene 39 (0.20 g, 0.98 mmol), dry K₂CO₃ (0.40 g, 2.94 mmol) and TBAB (0.031 g, 0.098 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the solution was heated up to 60 °C, and 1-(2-bromoethyl)-4-nitrobenzene 38 (0.270 g, 1.17 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified...
by column chromatography using silica gel and petroleum ether as eluent to afford 43 (0.163 g, 76%) as yellow solid.

**M.P.** 159-60 °C (Lit.\(^{40}\) 157 °C).

\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.74 (d, \(J = 9.2\) Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, \(J = 16.3\) Hz, 1H), 7.14 (d, \(J = 16.3\) Hz, 1H).

**IR (KBr)** 2922, 1590, 1340, 1107, 970, 694 cm\(^{-1}\)

**MS (EI):** (m/z) 225 (M\(^+\), 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

(E)-1-Nitro-3-styrylbenzene (45) from (2-bromoethyl)benzene (29):

![Chemical structure](image)

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.50 mol %), 34 (0.0015 g, 0.0054 mmol, 0.55 mol %) in dry N,N-dimethylacetamide (5 mL) under N\(_2\) atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another two neck round bottom flask 3-bromonitrobenzene 44 (0.20 g, 0.99 mmol), dry K\(_2\)CO\(_3\) (0.41 g, 2.97 mmol) and TBAB (0.032 g, 0.099 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N\(_2\) gas. Then the solution was heated up to 60 °C, and (2-bromoethyl)benzene 29 (0.220 g, 1.19 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 45 (0.174 g, 78%) as light yellow solid.

**M.P.** 108-110 °C (Lit.\(^{41}\) 111-12 °C)

\(^1\)H-NMR (DMSO, 400 MHz): \(\delta\) 8.44 (s, 1H), 8.12 – 8.07 (m, 2H), 7.70 – 7.66 (m, 3H), 7.53 – 7.40 (m, 4H), 7.34 – 7.31 (m, 1H).

262
IR (KBr): 2925, 1588, 1355, 1117, 980, 714 cm\(^{-1}\).

MS (EI): \((m/z)\) 225 (M\(^+\), 60), 178 (100), 152 (23), 76(12).

\((E)-2\text{-Styrylbenzo[}\text{c}\text{]phenanthrene (75) from (2-bromoethyl)benzene (29):}\)

\[\text{Ph}\]

In a typical procedure a catalyst solution was separately prepared in an oven dry. \(N_2\) flushed two neck round bottom flask. A solution of palladium acetate (0.0009 g, 0.0041 mmol, 0.5 mol \%) and ligand 34 (0.0012 g, 0.0044 mmol, 0.55 mol \%) was prepared in dry \(N,N\)-dimethylacetamide (5 mL), under \(N_2\) atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 2-bromobenzo[c]phenanthrene 46 (0.25 g, 0.81 mmol), dry \(K_2CO_3\) (0.34 g, 2.44 mmol) and TBAB (0.026 g, 0.081 mmol, 10 mol\%) in dry \(N,N\)-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with \(N_2\) gas. The solution was heated to 60 \(^\circ\)C and (2-bromoethyl)benzene 29 (0.18 g, 0.97 mmol) was slowly added. After the addition temperature was increased (100 \(^\circ\)C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 \(^\circ\)C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 40 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure 47 (0.230 g, 69 \%) as white solid.

M.P. 142 \(^\circ\)C (Lit.\(^{42}\) 140 \(^\circ\)C).

\(^1\text{H-NMR (CDCl}_3, 400 \text{MHz):}\) \(\delta\) 9.19 (d, \(J = 3.6\) Hz, 1H), 9.18 (s, 1H), 8.07 – 8.04 (m, 2H), 7.94 – 7.89 (m, 3H), 7.86 – 7.81 (m, 2H), 7.78 – 7.43 (m, 1H), 7.69 – 7.63 (m, 3H), 7.45 - 7.41 (m, 3H), 7.35 - 7.28 (m, 3H).

IR (KBr): 3017, 1600, 1499, 1072, 1043, 982, 902, 782, 744 cm\(^{-1}\).

MS (EI): \((m/z)\) 331 (M\(^+\), 28), 330 (M\(^+\), 100), 226 (12.3), 164 (23.6).
((1E,1′E)-(2,5-Dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene (49) from (2-bromoethyl)benzene (29):

Catalys solution was separately prepared in an oven dry N₂ flushed two neck round bottom flask. A solution of palladium acetate (0.0014 g, 0.0064 mmol, 1.0 mol %) and ligand 34 (0.0030 g, 0.016 mmol, 2.5 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N₂ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 1,4-diiodo-2,5-dimethoxybenzene 48 (0.25 g, 0.64 mmol), dry K₂CO₃ (0.35 g, 2.56 mmol) and TBAB (0.041 g, 0.127 mmol, 20 mol %) in dry N,N-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N₂ gas. The solution was heated to 60 °C and (2-bromoethyl)benzene 29 (0.35 g, 1.92 mmol) was slowly added. After the addition temperature was increased (100 °C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure 49 (0.162 g, 74 %) as light yellow crystals.

M.P. 184 - 186 °C (Lit. 43 177 - 178 °C)

¹H-NMR (CDCl₃, 400 MHz): δ 7.85 - 7.77 (m, 4H), 7.75 - 7.73 (dd, J = 1.3 & 8.6 Hz, 2H), 7.57 - 7.55 (dd, J = 1.3 & 8.6 Hz, 4H), 7.49 - 7.42 (m, 4H), 7.40 - 7.34 (m, 4H), 7.12 (d, J = 16 Hz, 4H), 3.93 (s, 6H).

MS (EI): (m/z) 343 (M⁺, 25), 342 (M⁺, 100), 171 (11), 105 (35).

(E)-2-Styrylnaphthalene (50) from 2-(1-bromoethyl)naphthalene (37):

264
In a typical procedure a catalyst solution was separately prepared in an oven dry, N₂ flushed two neck r.b. flask. A solution of palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0015 g, 0.0054 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N₂ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of iodosobenzene 39 (0.20 g, 0.98 mmol), dry K₂CO₃ (0.41 g, 2.94 mmol) and TBAB (0.032 g, 0.098 mmol, 10 mol %) in dry N,N-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N₂ gas. The solution was heated to 60 °C and 2-(1-bromoethyl)naphthalene 37 (0.27 g, 1.17 mmol) was slowly added. After the addition temperature was increased (100 °C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure 50 (0.144 g, 64 %) as white solid.

**M.P.** 146 – 147 °C (Lit.⁴⁴ 147 – 149 °C).

\(^1\)H-NMR (CDCl₃, 400 MHz): \(\delta 7.85 – 7.77\) (m, 4H), \(7.75 – 7.73\) (dd, \(J = 1.3 \& 8.6\) Hz, 1H), \(7.57 – 7.55\) (dd, \(J = 1.3 \& 8.6\) Hz, 2H), \(7.49 – 7.42\) (m, 2H), \(7.40 – 7.34\) (m, 2H), \(7.30 – 7.24\) (m, 3H).

IR (KBr): 3077, 3045, 1595, 1510, 1496, 1448, 1350, 1074, 957, 794, 775 cm⁻¹

MS (EI): (m/z) 230 (M⁺, 100), 215 (21), 115 (15), 107 (9).

\((E)-2-(4-Methoxystyryl)-naphthalene (51) from 2-(1-bromoethyl)naphthalene (37):\)

\[\text{Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol %) and 34 (0.0016 g, 0.0058 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.}\]

In another two neck round bottom flask 4-iodoanisole (40) (0.250 g, 1.06 mmol), dry K₂CO₃ (0.44 g, 3.18 mmol) and TBAB (0.034 g, 0.106 mmol, 10 mol %) were mixed in dry N,N-
dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the solution was heated up to 60 °C and 2-(1-bromoethyl)naphthalene 37 (0.30 g, 1.28 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 51 (0.238 g, 86%) as white solid.

**M.P.** 170-172 °C (Lit.¹⁵ 172 – 173 °C)

¹H-NMR (DMSO, 400 MHz):  δ 7.76 – 7.83 (m, 5H), 7.45 – 7.52 (m, 4H), 7.12 – 7.23 (m, 2H), 6.9 (m, 2H), 3.8 (s, 3H).

**MS (EI):** (m/z) 260 (M⁺, 100), 229 (20), 201 (24), 107 (15).

**N-[4-(2-Naphthalen-2-yl-vinyl)-phenyl]-acetamide (53) from 2-(1-bromoethyl)naphthalene (37):**

In a typical procedure a catalyst solution was separately prepared in an oven dry, N₂ flushed two neck round bottom flask. A solution of palladium acetate (0.0013 g, 0.0057 mmol, 0.5 mol %) and ligand 34 (0.0018 g, 0.0063 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N₂ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 4-iodoacetanilide 52 (0.30 g, 1.15 mmol), dry K₂CO₃ (0.47 g, 3.44 mmol) and TBAB (0.037 g, 0.115 mmol, 10 mol %) in dry N,N-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N₂ gas. The solution was heated to 60 °C and 2-(1-bromoethyl)naphthalene 37 (0.32 g, 1.38 mmol) was slowly added. After the addition temperature was increased (100 °C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with
water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure 53 (0.179 g, 54 %) as off white solid.

**M.P.** 256 - 257 °C

**¹H-NMR (DMSO, 400 MHz):** δ 10.00 (s, 1H), 7.98 (s, 1H), 7.83 – 7.91 (m, 5H), 7.57 – 7.64 (m, 4H), 7.45 – 7.53 (m, 2H), 7.28 – 7.38 (m, 2H), 2.07 (s, 3H).

**IR (KBr):** 3077, 3045, 1595, 1510, 1496, 1448, 1350, 1074, 957, 794, 775 cm⁻¹

**MS (EI):** (m/z) 287 (M⁺, 100), 245 (82), 228 (13.8), 215 (12.8), 43 (14).

*(E)-2-(4-Chlorostyryl)-naphthalene (55) from 2-(1-bromoethyl)naphthalene (37):*

![Chemical Structure](image)

Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0052 mmol, 0.5 mol %) and 34 (0.0016 g, 0.0057 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another two neck round bottom flask 4-bromochlorobenzene (54) (0.20 g, 1.04 mmol), K₂CO₃ (0.43 g, 3.13 mmol) and TBAB (0.033 g, 0.104 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N₂ gas. Then the solution was heated up to 60 °C and 2-(1-bromoethyl)naphthalene 37 (0.29 g, 1.25 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured into water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 55 (0.244 g, 88%) as white solid.

**M.P.** 180 – 184 °C
\[\text{\textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): } \delta 7.12 - 7.51 \text{ (m, 9H), 7.64 - 7.85 \text{ (m, 4H) with an overlapping of two doublets at 7.33 and 7.47 for two protons having } J = 16 \text{ Hz.}}\]

**MS (EI):** (m/z) 266 (M\textsuperscript{+}, 32), 264 (M\textsuperscript{+}, 100), 228 (99), 114 (36), 101 (19).

\textit{(E)-1-(4-Methoxystyryl)-4-nitrobenzene (56) from 1-(2-bromoethyl)-4-nitrobenzene (38):}

Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol %) and 34 (0.0016 g, 0.0058 mmol, 0.55 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another two neck round bottom flask 4-idoanisole 40 (0.25 g, 1.07 mmol), dry K\textsubscript{2}CO\textsubscript{3} (0.44 g, 3.20 mmol) and TBAB (0.034 g, 0.107 mmol, 10 mol %) were mixed in dry N,N-dimethylacetamide (5 mL) and repeatedly degassed by purging with N\textsubscript{2} gas. Then the solution was heated up to 60 °C, and 1-(2-bromoethyl)-4-nitrobenzene 38 (0.295 g, 1.28 mmol) was added. After 15 mins temperature was raised to 100 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 140 °C for 40 hrs. The cooled mixture was poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford 56 (0.210 g, 77%) as yellow solid.

**M.P.** 128 °C (Lit.\textsuperscript{46} 129-130 °C)

\[\text{\textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz): } \delta 8.19 - 8.22 \text{ (m, 2H), 7.59 - 7.62 \text{ (m, 2H), 7.49 - 7.52 \text{ (m, 2H), 7.23 \text{ (d, } J = 16.32 \text{ Hz, 1H), 7.01 \text{ (d, } J = 16.32 \text{ Hz, 1H), 6.92 - 6.95 \text{ (m, 2H), 3.85 \text{ (s, 3H).}}}\]

**IR (KBr):** 3021, 2962, 1587, 1461, 1421, 970, 875, 821, 749, 717 cm\textsuperscript{-1}

**MS (EI):** (m/z) 256 (M\textsuperscript{+}, 16), 255 (M\textsuperscript{+}, 100), 178 (15.9), 97 (7.16), 71 (6.6), 43 (8.39).
Synthetic Procedures:

*(E)-1,2-Diphenylethene or trans-Stilbene (28):*

Preparation of catalyst solution: In a dry two neck flask a solution of palladium acetate (0.0027 g, 0.0122 mmol, 0.5 mol %), ligand 36 (0.0101 g, 0.0245 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of iodobenzene 39 (0.50 g, 2.45 mmol), benzaldehyde 31 (0.260 g, 2.45 mmol), methyltriphenylphosphonium iodide (0.995 g, 2.45 mmol), TBAB (0.158 g, 0.49 mmol, 20 mol %) and dry K₂CO₃ (1.18 g, 8.57 mmol) in dry N,N-dimethylacetamide (10 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give trans-stilbene 28 (0.403 g, 91%) as white solid.

**M.P.** 120 - 122 °C (Lit. 38 121 - 123 °C).

**¹H-NMR (400MHz, CDCl₃):**  δ 7.57 – 7.55 (m, 4H), 7.42 – 7.38 (m, 4H), 7.32 – 7.28 (m, 2H), 7.16 (s, 2H).

*(E)-1,2-Diphenylethene or trans-Stilbene (28):*
Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0061 mmol, 0.5 mol %) and 34 (0.0034 g, 0.0122 mmol, 1.0 mol%) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of iodobenzene 39 (0.250 g, 1.22 mmol), paraformaldehyde (0.013 g, 0.416 mmol), benzyl triphenylmethylphosphonium chloride 32 (0.476 g, 1.22 mmol), TBAD (0.079 g, 0.24 mmol, 20 mol %) and dry K₂CO₃ (0.590 g, 4.27 mmol) in dry N,N-dimethylacetamide (7 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give 28 (0.194 g, 88%) as white solid.

**M.P.** 120 - 122 °C (Lit. 38 121 - 123 °C).

**¹H NMR (400MHz, CDCl₃):** δ 7.57 7.55 (m, 4H), 7.42 7.38 (m, 4H), 7.32 7.28 (m, 2H), 7.16 (s, 2H).

(E)-1-Methoxy-4-styrylbenzene (41):

![Diagram](Image)

Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0061 mmol, 0.5 mol%) and 34 (0.0034 g, 0.0122 mmol, 1.0 mol%) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of iodobenzene 39 (0.250 g, 1.22 mmol), 4-methoxybenzaldehyde 60 (0.166 g, 1.22 mmol), methyltriphenylphosphonium iodide (0.495 g, 1.22 mmol), TBAB (0.079 g, 0.24 mmol, 20 mol %) and dry K₂CO₃ (0.590 g, 4.27 mmol) in dry N,N-dimethylacetamide (7 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The
solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give 41 (0.226 g, 88%) as white solid.

**M.P.** 134 - 135 °C (Lit.$^{39}$ 135 - 136 °C).

**$^1$H-NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.50 - 7.44 (m, 4 H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, $J$ = 16.3 Hz, 1H), 6.97 (d, $J$ = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

**IR (KBr):** 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm.$^{-1}$

**MS (EI):** ($m/z$) 210 (M$^+$, 100), 179 (14), 167 (27), 105 (7), 76(3).

*(E)-1-Nitro-4-styrylbenzene (43)*:

In a typical procedure a catalyst solution was separately prepared in an oven dry, N$_2$ flushed two neck r.b. flask. A solution of palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0027 g, 0.0098 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N$_2$ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of iodobenzene 39 (0.20 g, 0.980 mmol), 4-nitrobenzaldehyde 57 (0.148 g, 0.980 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.980 mmol), TBAB (0.063 g, 0.196 mmol, 20 mol%) and dry K$_2$CO$_3$ (0.47 g, 3.43 mmol) in dry N,N-dimethylacetamide (5 mL) was taken and stirred under N$_2$ gas. The solution was heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to produce 43 (0.207 g, 94%) as yellow solid.

**M.P.** 159-60 °C (Lit.$^{40}$ 157 °C).
\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.74 (d, \(J = 9.2\) Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, \(J = 16.3\) Hz, 1H), 7.14 (d, \(J = 16.3\) Hz, 1H).

IR (KBr) 2922, 1590, 1340, 1107, 970, 694 cm\(^{-1}\).

MS (EI): (m/z) 225 (M\(^+\), 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

\((E)-1-(4-Methoxy styryl)-4-nitrobenzene (56):\)

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0028 g, 0.0099 mmol, 1.0 mol %) in dry \(N,N\)-dimethylacetamide (5 mL) under \(N_2\) atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another two neck round bottom flask 4-bromonitrobenzene 42 (0.20 g, 0.990 mmol), 4-methoxybenzaldehyde 60 (0.134 g, 0.990 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.990 mmol), TBAB (0.064 g, 0.198 mmol, 20 mol %) and dry \(K_2CO_3\) (0.479 g, 3.46 mmol) were mixed in dry \(N,N\)-dimethylacetamide (5 mL) and stirred under \(N_2\) gas. Then the solution was heated up to to 100 °C and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to produce 56 (0.206 g, 82%) as yellow solid.

M.P. 128 °C (Lit.\(^{46}\) 129-130 °C)

\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.19 – 8.22 (m, 2H), 7.59 – 7.62 (m, 2H), 7.49 – 7.52 (m, 2H), 7.23 (d, \(J = 16.32\) Hz, 1H), 7.01 (d, \(J = 16.32\) Hz, 1H), 6.92 – 6.95 (m, 2H), 3.85 (s, 3H).

IR (KBr): 3021, 2962, 1587, 1461, 1421, 970, 875, 821, 749, 717 cm\(^{-1}\).

MS (EI): (m/z) 256 (M\(^+\), 16), 255 (M\(^-\), 100), 178 (15.9), 97 (7.16), 71 (6.6), 43 (8.39).
(E)-1-Chloro-4-styrylbenzene (59):

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0027 g, 0.0098 mmol, 1.0 mol %) in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another two neck round bottom flask iodobenzene 39 (0.20 g, 0.980 mmol), 4-chlorobenzaldehyde 58 (0.137 g, 0.980 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.980 mmol), TBAB (0.063 g, 0.196 mmol, 20 mol %) and dry K₂CO₃ (0.47 g, 3.43 mmol) were mixed in dry N,N-dimethylacetamide (5 mL) and stirred under N₂ gas. Then the solution was heated up to to 100 °C and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to afford 59 (0.190 g, 90%) as white solid.

M.P. 130 °C (Lit.¹ 129-30 °C)

¹H-NMR (CDCl₃, 400 MHz):  δ 7.54 - 7.52 (m, 2H), 7.47 - 7.45 (m, 2H), 7.41 - 7.30 (m, 5H), 7.11 (d, J = 16.2 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H).

IR (KBr): 2925, 1588, 1355, 1117, 980, 714 cm⁻¹

MS (EI): (m/z) 214 (M⁺, 80), 179 (100), 89 (33), 76 (20).

(E)-N,N-Dimethyl-4-styrylaniline (62):

273
In a typical procedure a catalyst solution was separately prepared in an oven dry, N₂ flushed two neck r.b. flask. A solution of palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0027 g, 0.0098 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N₂ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of iodobenzene 39 (0.20 g, 0.980 mmol), 4-N,N-dimethylaminobenzaldehyde 61 (0.146 g, 0.980 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.980 mmol), TBAB (0.063 g, 0.196 mmol, 20 mol %) and dry K₂CO₃ (0.47 g, 3.43 mmol) in dry N,N-dimethylacetaminc (5 mL) was taken and stirred under N₂ gas. The solution was heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give 62 (0.181 g, 83%) as yellow solid.

**M.P.** 146-148 °C (Lit.⁴⁵ 144-146 °C)

**¹H-NMR** (CDCl₃, 400 MHz): δ 7.47 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.31 – 7.35 (m, 2H), 7.20 – 7.22 (m, 1H), 7.05 (d, J = 16.4 Hz, 1H), 6.92 (d, J = 16.4 Hz, 1H), 6.76 (m, 2H), 2.99 (s, 6H).

**IR (KBr):** 3020, 2923, 2796, 1599, 1518, 1477, 1347, 1162, 1061, 962, 809, 748 cm⁻¹

**(E)-1-Methyl-4-styrylbenzene (64):**

![Chemical structure](image)

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0027 g, 0.0098 mmol, 1.0 mol %) in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.
In another two neck round bottom flask iodobenzene 39 (0.20 g, 0.980 mmol), 4-methylbenzaldehyde 63 (0.117 g, 0.980 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.980 mmol), TBAB (0.063 g, 0.196 mmol, 20 mol %) and dry K$_2$CO$_3$ (0.47 g, 3.43 mmol) were mixed in dry N,N-dimethylacetamide (5 mL) and stirred under N$_2$ gas. Then the solution was heated up to 100 °C and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to produce 64 (0.185 g, 97%) as white solid.

**M.P.** 112 -114 °C (Lit. 114-116 °C)

**$^1$H-NMR (CDCl$_3$, 400 MHz):** $\delta$ 7.54 – 7.52 (m, 2H), 7.44 (d, $J=8$ Hz, 2H), 7.40 – 7.36 (m, 2H), 7.29 – 7.25 (m, 1H), 7.20 (d, $J=8$ Hz, 2H), 7.12 (d, $J=16.2$ Hz, 1H), 7.08 (d, $J=16.2$ Hz, 1H), 2.38 (S, 3H).

**IR (KBr):** 2925, 1588, 1355, 1117, 980, 714 cm$^{-1}$

**MS (EI):** ($m/z$) 195 (M$^+$, 93.5), 179 (100), 89 (11), 76 (5.3).

(E)-3-Styrylpyridine (66):

![Image](image.png)

In a typical procedure a catalyst solution was separately prepared in an oven dry, N$_2$ flushed two neck r.b. flask. A solution of palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0027 g, 0.0098 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N$_2$ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of iodobenzene 39 (0.20 g, 0.980 mmol), pyridin-3-aldehyde 65 (0.105 g, 0.980 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.980 mmol), TBAB (0.063 g, 0.196 mmol, 20 mol %) and dry K$_2$CO$_3$ (0.47 g, 3.43 mmol) in dry N,N-dimethylacetamide (5 mL) was taken and stirred under N$_2$ gas. The solution was heated to 100 °C and previously prepared palladium catalyst solution was added drop wise.
and the reaction mixture heated to 130 - 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to produce 66 (0.160 g, 90 %) as off white solid.

**M.P.** 78-80 °C (Lit46 81-83 °C)

^1H-NMR (CDCl₃, 400 MHz): δ 8.21 – 8.23 (m, 2H), 7.62 – 7.65 (m, 2H), 7.54 – 7.56 (m, 2H), 7.31 – 7.42 (m, 3H), 7.27 (d, J = 16.4 Hz, 1H), 7.14 (d, J = 16.4 Hz, 1H).

IR (KBr): 3022, 1590, 1564, 1485, 1309, 1187, 1022, 962, 800, 752 cm⁻¹

**MS (EI):** (m/z) 181 (M, 80.57), 180 (M⁺, 100), 97 (29), 71 (21).

**(E)-1-(3,4-Methylenedioxyphenyl)-2-phenylethene (68):**

![Chemical structure](image)

Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0061 mmol, 0.5 mol %) and 34 (0.0034 g, 0.0122 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of iodosobenzene 39 (0.250 g, 1.22 mmol), piperonal 67 (0.183 g, 1.22 mmol), methyltriphenylphosphonium iodide (0.495 g, 1.22 mmol), TBAB (0.079 g, 0.24 mmol, 20 mol %) and dry K₂CO₃ (0.590 g, 4.27 mmol) in dry N,N-dimethylacetamide (7 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give 68 (0.247g, 92%) as white solid.

**M.P.** 96 °C (Lit.47 97 °C)
\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.47 – 7.49 (m, 2H), 7.32 – 7.36 (m, 2H), 7.22 – 7.25 (m, 1H), 7.07 (d, \(J = 1.6\) Hz, 1H), 7.03 (d, \(J = 16\) Hz, 1H), 6.93 (d, \(J = 1.6\) Hz, 1H), 6.94 (d, \(J = 16\) Hz, 1H), 6.80 (d, \(J = 8\) Hz, 1H), 5.97 (s, 2H).

IR (KBr): 3031, 2895, 2783, 1595, 1501, 1442, 1251, 1040, 931, 871, 750 cm\(^{-1}\).

MS (EI): \((m/z)\) 225 (M\(^+\), 26), 224 (M\(^+\), 100), 193 (14.2), 165 (64).

\((E)-1-(4\text{-}\text{Methoxystyryl})-4\text{-}\text{chlorobenzene (69)}:\)

Preparation of catalyst solution: In a dry two neck flask a solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol %), ligand 34 (0.0030 g, 0.0107 mmol, 1.0 mol %) was prepared in dry \(N,N\)-dimethylacetamide (5 mL) under \(N_2\) atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry \(N_2\) flushed two neck round bottom flask a mixture of 4-iodoanisole 40 (0.250 g, 1.07 mmol), 4-chlorobenzaldehyde 58 (0.150 g, 1.07 mmol), methyltriphenylphosphonium iodide (0.434 g, 1.07 mmol), TBAB (0.069 g, 0.214 mmol, 20 mol %) and dry K\(_2\)CO\(_3\) (0.517 g, 3.74mmol) in dry \(N,N\)-dimethylacetamide (7 mL) was taken and kept under \(N_2\) atmosphere. The solution was then heated to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 \(\times\) 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give 69 (0.215 g, 82%) as white solid.

**M.P.** 178-180 °C (Lit.\(^{45}\) 181-183 °C)

\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.39 – 7.45 (m, 4H), 7.29 – 7.31 (m, 2H), 7.03 (d, \(J = 16.0\) Hz, 1H), 6.91 (d, \(J = 16.0\) Hz, 1H), 6.90 (d, \(J = 8.8\) Hz, 2H), 3.83 (s, 3H).

IR (KBr): 3018, 2931, 1604, 1511, 1406, 1255, 1098, 1031, 967, 831, 722 cm\(^{-1}\).

MS (EI): \((m/z)\) 246 (M\(^+\), 32), 244 (M\(^+\), 100), 229 (21), 178 (9).
(E)-2-Styrylfuran (71):

In a typical procedure a catalyst solution was separately prepared in an oven dry, N₂ flushed two neck round bottom flask. A solution of palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0027 g, 0.0098 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N₂ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of iodosobenzene 39 (0.20 g, 0.980 mmol), 2-furfural 70 (0.097 g, 0.980 mmol), methyltriphenylphosphonium iodide (0.398 g, 0.980 mmol), TBAB (0.063 g, 0.196 mmol, 20 mol %) and dry K₂CO₃ (0.47 g, 3.43 mmol) in dry N,N-dimethylacetamide (5 mL) was taken and stirred under N₂ gas. The solution was heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to produce 71 (0.136 g, 82%) as off white solid.

M.P. 61 °C (Lit.⁴⁸ 55-56 °C)

¹H-NMR (CDCl₃, 400 MHz): δ 7.45 – 7.53 (m, 2H), 7.40 (d, J = 1.6 Hz, 1H), 7.32 – 7.36 (m, 2H), 7.22 – 7.26 (m, 1H), 7.04 (d, J = 16.28 Hz, 1H), 6.89 (d, J = 16.28 Hz, 1H), 6.42 (m, 1H), 6.35 (d, J = 3.28 Hz, 1H).

IR (KBr): 3041, 1957, 1595, 1444, 1200, 1072, 924, 802, 742 cm⁻¹

MS (EI): (m/z) 170 (M⁺, 88), 141 (94), 109 (29), 85 (67), 57 (100).

(E)-1-(4-Methoxystyryl)-4-bromobenzene (73):
Preparation of catalyst solution: In a dry two neck flask a solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol %), ligand 34 (0.0030 mg, 0.0107 mmol, 1.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of 4-iodoanisole 40 (0.250 g, 1.07 mmol), paraformaldehyde (0.011 g, 0.363 mmol), (4-bromobenzyl)triphenylphosphonium bromide 72 (0.548 g, 1.07 mmol), TBAB (0.069 g, 0.214 mmol, 20 mol %) and dry K₂CO₃ (0.517 g, 3.74 mmol) in dry N,N-dimethylacetamide (7 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and mixture petroleum ether:ethyl acetate as eluent to give 73 (0.173 g, 56%) as white solid.

**M.P.** 200 – 202 °C (Lit⁴⁵ 200 - 201 °C)

**¹H-NMR (CDCl₃, 400 MHz):** δ 7.43 – 7.46 (m, 4H), 7.33 – 7.36 (m, 2H), 7.04 (d, J = 16.3 Hz, 1H), 6.88 – 6.90 (m, 2H), 6.89 (d, J = 16.3 Hz, 1H), 3.83 (s, 3H).

**(E)-1-(4-Nitrostyryl)-4-bromobenzene (74):**

Initially, in an oven dry flask the catalyst solution was prepared by stirring palladium acetate (0.0011 g, 0.0049 mmol, 0.5 mol %) and ligand 34 (0.0028 g, 0.0099 mmol, 1.0 mol %) in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.
In another two neck round bottom flask 4-bromonitrobenzene 42 (0.20 g, 0.990 mmol), paraformaldehyde (0.010 g, 0.336 mmol), (4-bromobenzyl)triphenylphosphonium bromide 72 (0.507 g, 0.990 mmol), TBAB (0.064 g, 0.198 mmol, 20 mol %) and dry K$_2$CO$_3$ (0.479 g, 3.46 mmol) were mixed in dry N,N-dimethylacetamide (5 mL) and stirred under N$_2$ gas. Then the solution was heated up to 100 °C and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 130 - 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to produce 74 (0.202 g, 67%) as off white solid.

**M.P.:** 218 – 220 °C (Lit. 215 - 217 °C)

$^1$H-NMR (CDCl$_3$, 400 MHz): δ 8.20 – 8.24 (m, 2H), 7.61 – 7.64 (m, 2H), 7.50 – 7.54 (m, 2H), 7.39 – 7.43 (m, 2H), 7.20 (d, $J = 16.36$ Hz, 1H), 7.12 (d, $J = 16.36$ Hz, 1H),

IR (KBr): 3015, 2922, 1595, 1501, 1387, 1230, 1088, 1021, 957, 822, 712 cm$^{-1}$

MS (EI): (m/z) 306 (M$^+$, 9), 304 (M$^+$, 9), 256 (11), 178 (20), 83 (89), 57 (100).

**Approach C: One-Pot Five-component Wittig-Heck Olefination Reaction**

**Synthetic Procedures:**

1,4-di((E)-Styryl)benzene (77) using ligand 36:

![Image of 1,4-di((E)-Styryl)benzene (77)]

Preparation of catalyst solution: In a dry two neck flask a solution of palladium acetate (0.0033 g, 0.0149 mmol, 1.0 mol %), ligand 36 (0.012 g, 0.0298 mmol, 2.0 mol %) was prepared in dry N,N-dimethylacetamide (3 mL) under N$_2$ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry N$_2$ flushed two neck round bottom flask a mixture of terephthaldehyde 75 (0.200 g, 1.49 mmol), iodobenzene 39 (0.609 g, 2.98 mmol), methyltriphenylphosphonium iodide (1.21 g, 2.98 mmol), TBAB (0.192 g, 0.597 mmol, 40 mol %) and dry K$_2$CO$_3$ (1.44 g,
10.44 mmol) in dry N,N-dimethylacetamide (10 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 48 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a crude mass, which was purified by column chromatography using silica gel and petroleum ether/EtOAc as eluent to give 77 (0.208 g, 49%) as yellow crystals.

M.P. 262 °C (Lit.⁵⁰a 264 - 266 °C)

¹H-NMR (200 MHz, DMSO-CDCl₃): δ 7.40 – 7.55 (m, 10H), 7.29 – 7.37 (m, 4H), 7.10 (s, 4H).

MS (EI): (m/z) 283 (M⁺, 19.7), 282 (M⁺, 100), 203 (13), 178 (21), 141 (9.6).

1,4-di((E)-Styryl)benzene (77) using liganá 33:

![Structure of 1,4-di((E)-Styryl)benzene (77)]

Preparation of catalyst solution: In a dry two neck flask a solution of palladium acetate (0.0019 g, 0.0084 mmol, 1.0 mol %), ligand 33 (0.0032 g, 0.0169 mmol, 2.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL) under N₂ atm. The mixture was stirred at room temperature until homogeneous (15 min) and degassed several times prior to use.

In another dry N₂ flushed two neck round bottom flask a mixture of 1,4-dibromobenzene 76 (0.200 g, 0.847 mmol), benzaldehyde 31 (0.179 g, 1.69 mmol), methyltriphenylphosphonium iodide (0.688 g, 1.69 mmol), TBAB (0.109 g, 0.338 mmol, 40 mol %) and dry K₂CO₃ (0.819 g, 5.93 mmol) in dry N,N-dimethylacetamide (10 mL) was taken and kept under N₂ atmosphere. The solution was then heated to 100 °C, and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether/EtOAc as eluent to afford 77 (0.203 g, 85%) as yellow crystls.

M.P. 262 °C (Lit.⁵⁰a 264 - 266 °C)
**1H-NMR (200 MHz, DMSO-CDCl3):** δ 7.40 – 7.55 (m, 10H), 7.29 – 7.37 (m, 4H), 7.10 (s, 4H).

**MS (EI):** (m/z) 283 (M⁺, 19.7), 282 (M⁺, 100), 203 (13), 178 (21), 141 (9.6).

*1,4-bis((E)-4-Nitrostyryl)benzene (78):*

In a typical procedure a catalyst solution was separately prepared in an oven dry, N₂ flushed two neck round bottom flask. A solution cf palladium acetate (0.0019 g, 0.0084 mmol, 1.0 mol %), ligand 33 (0.0032 g, 0.0169 mmol, 2.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL), under N₂ atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 1,4-dibromobenzene 76 (0.200 g, 0.847 mmol), 4-nitrobenzaldehyde 57 (0.255 g, 1.69 mmol), methyltriphenyolphosphonium iodide (0.688 g, 1.69 mmol), TBAB (0.109 g, 0.338 mmol, 40 mol %) and dry K₂CO₃ (0.819 g, 5.93 mmol) in dry N,N-dimethylacetamide (5 mL) was taken and stirred under N₂ gas. The solution was heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 40 h. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether/EtOAc as eluent to afford 78 (0.197 g, 63%) as orange solid.

**M.P. >280 °C (Lit.⁵⁰b 288 – 290 °C)**

**1H-NMR (200 MHz, DMSO-CDCl3):** δ 8.16 (d, J = 8.76 Hz, 4H), 7.65 (d, J = 8.70 Hz, 4H), 7.56 – 7.54 (m, 4H), 7.28 (d, J = 16.4 Hz, 2H), 7.18 (d, J = 16.4 Hz, 2H).

**MS (EI):** (m/z) 373 (M⁺, 24), 372 (M⁺, 100), 342 (36), 263 (11), 178 (9).

*1,2-dii((E)-Styryl)benzene (85):*
Catalyst Solution: A solution of palladium acetate (0.0019 g, 0.0084 mmol, 1.0 mol %), ligand 33 (0.0032 g, 0.0169 mmol, 2.0 mol %) was prepared in dry N,N-dimethylacetamide (5 mL). The mixture was stirred for 15 min and degassed several times prior to use.

In another dry N_2 flushed two neck round bottom flask a mixture of 1,2-dibromobenzene 79 (0.200 g, 0.847 mmol), benzaldehyde 31 (0.179 g, 1.69 mmol), methyltriphosphonium iodide (0.688 g, 1.69 mmol), TBAD (0.109 g, 0.338 mmol, 40 mol %) and dry K_2CO_3 (0.819 g, 5.93 mmol) in dry N,N-dimethylacetamide (10 mL) was taken and kept under N_2 atmosphere. The solution was then heated to 100 °C and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 °C for 48 hrs. The cooled mixture was then poured in water (25 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography using silica gel and petroleum ether as eluent to give 80 (0.185 g, 77%) as yellow crystals.

**M.P.** 115 °C (Lit. 111-12 °C)

**^1H-NMR** (CDCl_3, 400 MHz): δ 7.60 – 7.58 (m, 2H), 7.54 – 7.51 (m, 4H), 7.46 (d, J = 16.4 Hz, 2H), 7.38 – 7.34 (m, 4H), 7.30 – 7.24 (m, 4H), 7.00 (d, J = 16.4 Hz, 2H).

**IR (KBr):** 3086, 3053, 3019, 1600, 1491, 1213, 1158, 1071, 956, 758, 691 cm^{-1}

**MS (EI):** (m/z) 223 (M^+, 8.9), 282 (M^+ 38), 191 (100), 178(5.6), 91 (12.3).

**Part-2: One-Pot Oxidation-Wittig Olefination Reaction**

**Synthetic Procedures:**

**Stilbene (28):**

\[
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    \text{Ph} \\
    \text{Ph}
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\]

In two neck round bottom flask a mixture of benzyl chloride (0.241 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO_3 (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was stirred at 140 °C under N_2 atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and
dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure stilbene 28 (0.148 g, 87 %) (The ratio of Z:E isomers was determined to be 45:55 by $^1$H-NMR).

**M.P.** (E-isomer): 122 °C (Lit.$^{38}$ 121 - 123 °C).

$^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.22 – 7.4 (complex m, aromatic protons of both isomers), 7.18 (s, E olefinic protons), 6.66 (s, Z olefinic protons).

**4-Nitrostilbene (43):**

![4-Nitrostilbene](image)

To the oven dry two neck round bottom flask Benzyltriphenylphosphonium chloride 32 (0.450 g, 1.16 mmol), 4-Nitrobenzyl bromide 97 (0.25 g, 1.16 mmol), NaHCO$_3$ (0.292 g, 3.648 mmol) and potassium iodide (0.038 g, 0.23 mmol) in dimethylsulfoxide (7 mL) was mixed and stirred at 140 °C under N$_2$ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to afford 43 (0.170 g, 65 %) (The ratio of Z:E isomers was determined to be 43:57 by $^1$H-NMR).

**M.P.** (E-isomer): 159-60 °C (Lit.$^{40}$ 157 °C).

$^1$H-NMR (CDCl$_3$, 400MHz): δ 8.20 – 8.22 (m, aromatic protons of both the isomers), 8.05 – 8.07 (m, aromatic protons of both the isomers), 7.61 – 7.64 (m, aromatic protons of both the isomers), 7.54 – 7.56 (m, aromatic protons of both the isomers), 7.33 – 7.42 (m, aromatic protons of both the isomers), 7.18 – 7.29 (complex m, aromatic protons of both the isomers), 7.14 (d, J = 16.4 Hz, E olefinic proton), 6.81 (d, J = 12.4 Hz, Z olefinic proton), 6.60 (d, J = 12.4 Hz, Z olefinic proton).

**IR (KBr):** 2922, 1590, 1340, 1107, 970, 694 cm.$^{-1}$

**MS (EI):** (m/z) 225 (M$^+$, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

**2-Styrylnaphthalene (50):**
(2-Naphthyl)triphenylphosphonium bromide 100 (0.955 g, 1.97 mmol), benzyl chloride 81 (0.25 g, 1.97 mmol), NaHCO₃ (0.496 g, 5.91 mmol) and potassium iodide (0.065 g, 0.39 mmol) in dimethylsulfoxide (10 mL) was added to the two neck oven dry flask and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give 50 (0.300 g, 66 %) (The ratio of Z:E isomers was determined to be 59:41 by HPLC analysis).

**M.P.** (*E*-isomer): 146-148 °C (Lit.⁴⁵ 147-148 °C)

**¹H-NMR (CDCl₃, 400 MHz):** δ 8.02 (s, 1H), 7.76 - 7.91 (m, 9H), 7.17 - 7.60 (m, 17H, siganals for E olefinic protons are merged in it), 6.86 (d, J = 12Hz, 1H for Z olefinic proton), 6.68 (d, J = 12Hz, 1H for Z olefinic proton).

**IR (KBr):** 3077, 3045, 1595, 1510, 1496, 1448, 1350, 1074, 957, 794, 775 cm⁻¹

**MS (EI):** (m/z) 230 (M⁺, 100), 215 (21), 115 (15), 107 (9).

**HPLC Analysis for Z:E ratio of (50): Z:E :: 59:41; [Column: CHIRALPAK AD-H; Solvent system: Hexane/Isopropanol/TFA (95:5:0.25); Flow rate: 1.0 mL/min; λmax = 254 nm; tR = 4.05 min (major, Z isomer), tR = 5.75 min (minor, E isomer).**

**4-Chlorostilbene (59):**

In two neck round bottom flask a mixture of Benzyltriphenylphosphonium chloride 32 (0.473 g, 1.22 mmol), 4-Chlorobenzyl bromide 86 (0.25 g, 1.22 mmol), NaHCO₃ (0.307 g, 3.66 mmol) and potassium iodide (0.040 g, 0.24 mmol) in dimethylsulfoxide (7 mL) was stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under
reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to produce 59 (0.190 g, 73 %) (The ratio of Z:E isomers was determined to be 51:49 by $^1$H-NMR).

**M.P.** $(E$-isomer): 130 °C (Lit.$^{45}$ 129-130 °C)

$^1$H-NMR (CDCl$_3$ 400 MHz): $\delta$ 7.54 – 7.56 (m, aromatic protons of both the isomers), 7.47 – 7.49 (m, aromatic protons of both the isomers), 7.22 – 7.43 (m, aromatic protons for both the isomers), 7.13 (d, $J = 16.4$ Hz, $E$ olefinic proton), 7.09 (d, $J = 16.4$ Hz, $E$ olefinic proton), 6.75 (d, $J = 12.0$ Hz, $Z$ olefinic proton), 6.57 (d, $J = 12.0$ Hz, $Z$ olefinic proton).

**IR (KBr):** 2925, 1588, 1355, 1117, 980, 714 cm.$^{-1}$

**MS (EI):** (m/z) 214 (M$^+$, 80), 179 (100), 89 (33), 76 (20).

4-Bromostilbene (96):

![4-Bromostilbene](image)

In two neck round bottom flask a mixture of benzyltriphenylphosphonium chloride 32 (0.39 g, 1.0 mmol), 4-bromobenzyl bromide 88 (0.25 g, 1.0 mmol), NaHCO$_3$ (0.252 g, 3.0 mmol) and potassium iodide (0.033 g, 0.2 mmol) in dimethylsulfoxide (7 mL) was stirred at 140 °C under N$_2$ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid. which was purified by column chromatography on silica gel and petroleum ether as eluent to give 96 (0.193 g, 75 %). (The ratio of Z:E isomers was determined to be 47:53 by $^1$H-NMR).

**M.P.** $(E$-isomer): 138 °C (Lit.$^{56}$ 135-136.5 °C)

$^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 7.51 – 7.57 (complex m, aromatic protons of both isomers), 7.33 – 7.44 (complex m, aromatic protons of both isomers), 7.26 - 7.32 (complex m, aromatic protons of both isomers), 7.13 – 7.17 (m, signals for $E$ olefinic proton are merged in it $J = 16.0$ Hz), 7.08 (d, $J = 16.0$ Hz, $E$ olefinic proton), 6.88 (d, $J = 12.4$Hz, $Z$ olefinic proton), 6.56 (d, $J = 12.4$Hz, $Z$ olefinic proton).

**IR (KBr):** 3021, 2926, 1637, 1490, 1446, 1329, 1216, 1179, 1088, 864, 751, 528 cm.$^{-1}$

**MS (EI):** (m/z) 261 (M$^{12}$, 48), 259 (M$^+$, 49), 179 (69), 178 (100), 89 (68), 76 (45).
**4,4'-Difluorostilbene (85):**

![Chemical structure of 4,4'-Difluorostilbene](image)

To the oven dry two neck round bottom flask 4-Fluorobenzyl bromide 84 (0.360 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO₃ (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was mixed and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to afford 85 (0.177 g, 86 %) (The ratio of Z:E isomers was determined to be 53:47 by ¹H-NMR).

**M.P.** (E-isomer): 148-151 °C (Lit.⁵² 148 °C)

**¹H-NMR (CDCl₃, 400 MHz):** δ 7.43 – 7.48 (m, aromatic protons of both isomers), 7.15 – 7.20 (m, aromatic protons of both isomers), 7.02 – 7.08 (m, aromatic protons of both isomers), 6.97 (s, E olefinic protons), 6.89 – 6.95 (m, aromatic protons), 6.53 (s, Z olefinic protons).

**IR (KBr):** 3102, 2963, 1631, 1487, 1396, 12014, 1176, 1079, 997, 753, 678, 525 cm⁻¹

**MS (EI):** (m/z) 217 (M⁺, 15), 216 (M⁺, 100), 196 (14), 195 (18), 178 (35), 102 (19), 76(9).

**E) 4,4'-Dichlorostilbene (87):**

![Chemical structure of 4,4'-Dichlorostilbene](image)

4-Chlorobenzyl bromide 86 (0.391 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO₃ (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was added to the two neck oven dry flask and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on
silica gel and petroleum ether as eluent to produce 87 (0.142 g, 60 %) (The ratio of Z:E isomers was determined to be 55:45 by 1H-NMR).

**M.P.** (E-isomer): 176 °C (Lit.53 178 °C)

**1H-NMR (CDCl₃, 400 MHz):** δ 7.44 (d, J = 8.8 Hz, 4H, aromatic protons of E isomer), 7.35 (d, J = 8.4 Hz, 4H, aromatic protons of E isomer), 7.23 (d, J = 8.4 Hz, 4H, aromatic protons of Z isomer), 7.17 (d, J = 8.4 Hz, 4H, aromatic protons of Z isomer), 7.03 (s, E olefinic protons, 2H), 6.58 (s, Z olefinic protons).

**IR (KBr):** 3045, 2834, 1598, 1499, 1426, 1386, 1296, 1179, 987, 688, 754, 564 cm⁻¹

**MS (EI):** (m/z) 250 (M⁺², 70), 248 (M⁺, 31), 212 (75), 176 (100), 151 (15), 106 (25), 88 (62), 76(23).

*4,4’-Dibromostilbene (89):*

![4,4’-Dibromostilbene](image)

In two neck round bottom flask a mixture of 4-Bromobenzyl bromide 88 (0.476 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO₃ (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give 89 (0.192 g, 63 %) (The ratio of Z:E isomers was determined to be 23:77 by 1H-NMR).

**M.P.** (E-isomer): 210-212 °C (Lit.53 212 °C)

**1H-NMR: (CDCl₃, 400 MHz):** δ 7.36 – 7.51 (m, aromatic protons of both isomers), 7.09 – 7.11 (m, aromatic protons of both isomer), 7.04 (s, E olefinic protons), 6.56 (s, Z olefinic protons).

**IR (KBr):** 3049, 3102, 2883, 1678, 1621, 1565, 1499, 1416, 1394, 1286, 1149, 1049, 979, 876, 788, 662 cm⁻¹

**MS (EI):** (m/z) 338 (M⁺², 51), 336 (M⁺, 27), 256 (4), 178 (100), 151 (12), 88 (14), 76(8).

288
3,3'-Difluorostilbene (91):

![Structural diagram]

To the oven dry two neck round bottom flask 3-Fluorobenzyl chloride 90 (0.275 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO₃ (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was mixed and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to afford 91 (0.156 g, 75 %) (The ratio of Z:E isomers was determined to be 46:54 by ¹H-NMR).

M.P. (E-isomer): 86-888°C (Lit.⁵⁴ 86-87 °C)

¹H-NMR (CDCl₃, 400 MHz): δ 7.20 – 7.37 (m, aromatic proton for both isomers). 7.08 (s, E olefinic proton), 6.91 – 7.02 (m, aromatic protons of both isomers), 6.61 (s, Z olefinic proton).

IR (KBr): 3101, 2883, 1623, 1541, 1424, 1284, 1196, 1099, 964, 865, 745, 566 cm⁻¹

MS (EI): (m/z) 217 (M¹⁺, 23), 216 (M⁺, 100), 196 (20), 195 (10), 179 (25), 101 (17), 76(8).

2,2'-Dichlorostilbene (93):

![Structural diagram]

2-Chlorobenzyl chloride 92 (0.307 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO₃ (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was added to the two neck oven dry flask and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to produce 93 (0.137 g, 58 %) (The ratio of Z:E isomers was determined to be 39:61 by ¹H-NMR).
M.P. (E-isomer): 96-98 °C (Lit. 54 98-99 °C)

1H-NMR (CDCl₃, 400 MHz): δ 7.76 – 7.79 (m, aromatic protons of both isomers), 7.53 (s, E olefinic protons), 7.39 – 7.44 (m, aromatic protons of both isomers), 7.30 -7.34 (m, aromatic protons of both isomers), 7.20 – 7.28 (m, aromatic protons of both isomers), 7.14 – 7.19 (m, aromatic protons of both isomers), 6.98 – 7.07 (m, aromatic protons of both isomers), 6.89 (s, Z olefinic protons).

IR (KBr): 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm⁻¹

MS (EI): (m/z) 250 (M⁺, 75), 248 (M⁺, 30), 212 (78), 177 (51), 176 (100), 151 (31), 106 (26), 88 (57), 76(40).

2,2'-Dinitrostilbene (95):

![2,2'-Dinitrostilbene](image)

In two neck round bottom flask a mixture of 2-Nitrobenzyl bromide 94 (0.411 g, 1.906 mmol), triphenylphosphine (0.25 g, 0.953 mmol), NaHCO₃ (0.240 g, 2.86 mmol) and potassium iodide (0.032 g, 0.191 mmol) in dimethylsulfoxide (7 mL) was stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give 89 (0.177 g, 69 %) (The ratio of Z:E isomers was determined to be 46:54 by ¹H-NMR).

M.P. (E-isomer): 196 °C (Lit. 55 197.5-198 °C)

1H-NMR (DMSO-d₆, 400 MHz): δ 8.09 – 8.10 (m, aromatic protons of both isomers), 7.90 – 7.92 (m, aromatic protons of both isomers), 7.78 – 7.82 (m, aromatic protons of both isomers), 7.59 – 7.63 (m, aromatic protons of both isomers), 7.52 (s, E olefinic protons), 7.46 – 7.48 (m, aromatic protons), 7.09 (s, Z olefinic protons), 7.02 – 7.04 (m, aromatic protons).

IR (KBr): 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm⁻¹

MS (EI): (m/z) 271 (M⁺¹, 21), 270 (M⁺, 100), 178 (49), 176 (55), 152 (34).

(E)- 4-[2-(4-Bromo-phenyl)-vinyl]-benzoic acid methyl ester (99):
4-Bromomethyl-benzolic acid methylester phosphonium bromide salt 98 (0.491 g, 1.0 mmol), 4-bromobenzyl bromide 88 (0.25 g, 1.0 mmol), NaHCO₃ (0.252 g, 3.0 mmol) and potassium iodide (0.033 g, 0.2 mmol) in dimethylsulfoxide (7 mL) was added to the two neck oven dry flask and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to produce 99 (0.172 g, 54 %) (Mostly E-isomer was formed).

**M.P.** (E-isomer): 182 °C (Lit. 57 179-180 °C).

**¹H-NMR (CDCl₃, 400 MHz):** δ 8.03 – 8.06 (m, 2H), 7.56 – 7.58 (m, 2H), 7.50 – 7.53 (m, 2H), 7.41 – 7.43 (m, 2H), 7.17 (d, J = 16.4Hz, 1H for E olefinic proton), 7.12 (d, J = 16.4Hz, 1H for E olefinic proton), 3.94 (s, 3H).

**IR (KBr):** 2977, 1714, 1406, 1273, 1060, 713 cm⁻¹.

**MS (EI):** (m/z) 319 (M⁺, 67), 317 (M⁺, 64), 287 (13), 285 (14), 238 (39), 171 (96), 169 (100).

2-(4-Fluorostyryl)-napthahene (101):  

(2-Naphthyl)triphenylphosphonium bromide 100 (0.645 g, 1.32 mmol), 4-Fluorobenzyl bromide 84 (0.25 g, 1.32 mmol), NaHCO₃ (0.33 g, 3.96 mmol) and potassium iodide (0.044 g, 0.26 mmol) in dimethylsulfoxide (10 mL) was added to the two neck oven dry flask and stirred at 140 °C under N₂ atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give 101 (0.260 g, 79 %) (The ratio of Z:E isomers was determined to be 52:48 by HPLC analysis).
**M.P.** (E-isomer): 150 °C (Lit.\textsuperscript{58} 151-152 °C)

\(^1\text{H}-\text{NMR} \ (\text{CDCl}_3, \text{ 400 MHz}): \delta \ 7.65 - 7.84 \ \text{(complex m, aromatic protons of both the isomers)}, \ 7.42 - 7.54 \ \text{(complex m, aromatic protons of both the isomers)}, \ 7.30 - 7.32 \ \text{(m, aromatic protons of both the isomers)}, \ 7.18 - 7.25 \ \text{(siganals for E olefinic protons are merged with aromatic protons of both isomers)}, \ 7.05 - 7.09 \ \text{(m, aromatic protons of both isomers)}, \ 6.87 - 6.91 \ \text{(m, aromatic protons of both isomers)}, \ 6.82 \ \text{(d, } J = 12.0 \text{ Hz, Z olefinic proton)}, \ 6.62 \ \text{(d, } J = 12.0 \text{ Hz, Z olefinic proton}).

**IR (KBr):** 3062, 1383, 1204, 1117, 987, 790, 672, 589 cm\(^{-1}\)

**MS (EI):** (m/z) 249 (M\(^+\) 13), 248 (M\(^+\) 100), 233 (15), 152 (4), 77 (4).

**HPLC Analysis for Z:E ratio of (50):** \(Z:E:: 52:48\); Column: CHIRALPAK AD-H; Solvent system: Hexane/Iso-propanol/TFA (95:5:0.25); Flow rate: 1.0 mL/min; \(\lambda_{max} = 254 \text{ nm}\); \(t_R = 4.18 \text{ min (major, Z isomer)}, t_R = 6.27 \text{ min (minor, E isomer)}\).

**2-(4-Bromostyryl)-naphthalene (102):**

![2-(4-Bromostyryl)-naphthalene (102)](image)

To the oven dry two neck round bottom flask (2-Naphthyl)triphenylphosphonium bromide \textbf{100} (0.483 g, 1.00 mmol), 4-Bromobenzyl bromide \textbf{88} (0.25 g, 1.00 mmol), NaHCO\(_3\) (0.25 g, 3.00 mmol) and potassium iodide (0.033 g, 0.20 mmol) in dimethylsulfoxide (7 mL) was mixed and stirred at 140 °C under N\(_2\) atmosphere for 40 h. The cooled mixture was then poured in water (100 mL) and extracted with dichloromethane (3 x 50 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to afford \textbf{102} (0.230 g, 74 %) (The ratio of Z:E isomers was determined to be 51.49 by HPLC analysis).

**M.P.** (E-isomer): 186-188 °C (Lit.\textsuperscript{11} 188.5-189 °C)

\(^1\text{H}-\text{NMR} \ (\text{DMSO, 400 MHz}): \delta \ 8.02 \ \text{(s, aromatic protons of both isomer)}, \ 7.76 - 7.91 \ \text{(m, aromatic protons of both isomer)}, \ 7.17 - 7.60 \ \text{(complex m, siganals for E olefinic protons are merged with aromatic protons of both isomers)}, \ 6.86 \ \text{(d, } J = 12.0 \text{ Hz, Z olefinic protons)}, \ 6.68 \ \text{(d, } J = 12.0 \text{ Hz, Z olefinic protons}).

**IR (KBr):** 3049, 1583, 1483, 1396, 1072, 965, 853, 820, 741 cm\(^{-1}\).
**MS (EI):** \((m/z)\) 311 (13), 310 (61), 309 (15), 308 (70), 230 (15), 229 (89), 228 (100), 226 (33), 202 (15), 152 (6), 114 (57), 101 (26).

**HPLC Analysis for Z:E ratio of (50):** \(Z:E :: 51:49\); [Column: CHIRALPAK AD-H; Solvent system: Hexane/Iso-propanol/TFA (95:5:0.25); Flow rate: 1.0 mL/min; \(\lambda_{\text{max}} = 254\) nm; \(t_R = 4.52\) min (major, \(Z\) isomer), \(t_R = 7.45\) min (minorr, \(E\) isomer).]

**Phenantherne (104):**

![Phenantherne (104)](image)

In two neck round bottom flask a mixture of 2,2'-bis-bromomethyl-biphenyl 103 (0.20 g, 0.588 mmol), triphenylphosphine (0.155 g, 0.588 mmol), NaHCO₃ (0.296 g, 3.54 mmol) and potassium iodide (0.020 g, 0.117 mmol) in dimethysulfoxide (30 mL) was stirred at 140 °C under \(N_2\) atmosphere for 40 h. The cooled mixture was then poured in water (150 mL) and extracted with dichloromethane (3 x 100 mL). The organic layer was washed with water (2 x 100 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a crude product, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure phenantherne 104 (0.073 g, 70 %) as White solid.

**M.P.** 96 °C (Lit. 60 98 – 100 °C)

**\(^1\)H-NMR (400 MHz, CDCl₃):** \(\delta 8.69\) (d, \(J = 7.96\) Hz, 2H), 7.89 (m, 2H), 7.74 (s, 2H), 7.66 (m, 7.0 Hz & 8.4 Hz, 2H), 7.60 (m, 1H).

**IR (KBr):** 3432, 3050, 2926, 1600, 1524, 1497, 1452, 1426, 1299, 1241, 1139, 948, 869, 817, 731, 712 cm.-1

**MS (EI):** \((m/z)\) (%) 178 (92), 177 (90), 176 (24), 175 (21), 149 (27), 137 (21), 136 (18), 97 (27), 83 (32), 81 (89), 71 (37), 69 (100), 68 (86), 57 (39).
Spectral Data

Part-1: Dehydrohalogenation-Heck Olefinatio and Multi-component Wittig-Heck Reaction

$^1$H-NMR of compound 28 (400 MHz, CDCl$_3$)

$^1$H-NMR of compound 41 (400 MHz, CDCl$_3$)

294
EI-Mass Spectra of Compound 41

\[ ^1\text{H-NMR of Compound 43 (400 MHz, CDCl}_3\text{)} \]

295
El-Mass Spectra of Compound 43

$^1$H-NMR of Compound 45 (400 MHz, DMSO)
EI-Mass Spectra of Compound 45

\[ ^1\text{H-NMR of Compound 47 (400 MHz, CDCl}_3) \]
EI-Mass Spectra of Compound 49

$^1$H-NMR of Compound 50 (400 MHz, CDCl$_3$)
EI-Mass Spectra of Compound 50

$^1$H-NMR of Compound 51 (400 MHz, DMSO)
EI-Mass Spectra of Compound 51

$^1$H-NMR of Compound 53 (400 MHz, DMSO)

301
EI-Mass Spectra of Compound 53

$^1$H-NMR of Compound 55 (400 MHz, CDCl$_3$)
E.I-Mass Spectra of Compound 55

$^1$H-NMR of Compound 56 (400 MHz, CDCl$_3$)
EI-Mass Spectra of Compound 56

$^1$H-NMR of Compound 59 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 62 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 64 (400 MHz, CDCl$_3$)

305
EI-Mass Spectra of Compound 64

$^1$H-NMR of Compound 66 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 68 (400 MHz, CDCl$_3$)

El-Mass Spectra of Compound 68
$^1$H-NMR of Compound 69 (400 MHz, CDCl$_3$)

EI-Mass Spectra of Compound 69

308
$^1$H-NMR of Compound 71 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 77 (300 MHz, CDCl$_3$:DMSO)
EI-Mass Spectra of Compound 77

$^1$H-NMR of Compound 78 (300 MHz, CDCl$_3$:DMSO)
EI-Mass Spectra of Compound 78

1H-NMR of Compound 80 (400 MHz, CDCl₃)
El-Mass Spectra of Compound 80

Spectral Data for Part-2: Oxidation-Wittig Olefination reaction

$^1$H-NMR of Compound 28 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 43 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 50 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 59 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 85 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 87 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 89 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 91 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 93 (400 MHz, CDCl$_3$)
$^{1}$H-NMR of Compound 95 (400 MHz, DMSO)

$^{1}$H-NMR of Compound 96 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 99 (400 MHz, CDCl$_3$)

$^1$H-NMR of Compound 101 (400 MHz, CDCl$_3$)
$^1$H-NMR of Compound 102 (400 MHz, DMSO)

$^1$H-NMR of Compound 104 (400 MHz, CDCl$_3$)
EI-Mass Spectra of Compound 104

HPLC data for determination of Z:E ratio

Method For HPLC Analysis of the compound 50:
Solvent System: n-Hexane: Iso-propanol: TFA (95:5:0.2:5)
Flow rate: 1.0 mL/min.
Detector: UV-Vis (λ.max – 254 nm)
Chiral Column: CHIRALPAK AD-H
Method For HPLC Analysis of the compound 101:
Solvent System: *n*-Hexane: *Iso*-propanol: TFA (95:5:0.2.5)
Flow rate: 1.0 mL/min.
Detector: UV-Vis ($\lambda_{max} – 254$ nm)
Chiral Column: CHIRALPAK AD-H

Method For HPLC Analysis of the compound 102:
Solvent System: *n*-Hexane: *Iso*-propanol: TFA (95:5:0.2.5)
Flow rate: 1.0 mL/min.
Detector: UV-Vis ($\lambda_{max} – 254$ nm)
Chiral Column: CHIRALPAK AD-H
Conclusion

- A variant of olefination reaction involving in situ generation of styrene by either one-pot dehydrohalogenation - Heck or one-pot multicomponent Wittig – Heck reaction is developed which can be advantageous when unstable styrenes are one of the reactants for reaction.

- We have also developed two different variants of oxidation-Wittig one-pot procedures for the efficient synthesis of stilbenes with many possible substitution options.

- We have also synthesised phenanthrene via intramolecular version of oxidation-Wittig reaction. This methodology can be further applied for the synthesis of higher helicenes.
References


324


List of Publications


2. Amino oxazolines as easily accessible water stable ligands for palladium catalysed aqueous Heck reaction.


4. Amino oxazoline as new class of organocatalyst for direct intermolecular asymmetric aldol reaction between acetone and aromatic aldehydes.