HECK COUPLING STYRENE WITH ARYL HALIDES CATALYZED BY PALLADIUM COMPLEXES IN BIPHASIC MEDIA

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ABSTRACT: In this work, we have studied the effect of the halide nature in the coupling of styrene with halide benzene catalysed by palladium acetate or chloride. The activation by a catalyst of phase-transfer type Aliquat-336 improves the reactivity in N, N-dimethylformamide-water mixture. The presence of electron-donating groups on the aromatic nucleus of aryl halide involves a decrease of yields. We have also tested the effectiveness of the catalytic system $PdCl\{C_6H_3\text{-}2,6\text{-}(OP^iPr_2)_2\}$ in the coupling of styrene with aromatic chlorides. In this context, a reactional mechanism is proposed.

Keywords: Palladium complexes, phase transfer catalysis, Heck reaction, Aliquat-336, arylation.

I- INTRODUCTION

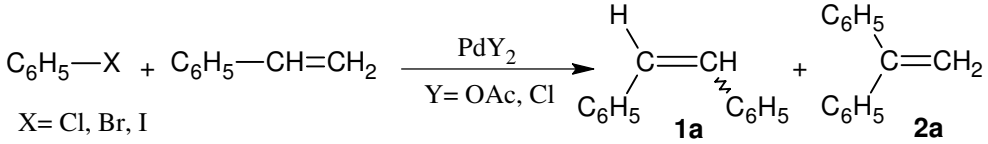
Arylation of olefins by Heck coupling is an important synthetic method for the formation of carbon-carbon bonds [1-12]. They are usually catalysed by palladium catalysts complexed or not with ligands [5,13-20].To restore the catalyst and quench the acid liberated during the reaction various organic (Et_3N) or inorganic (K_2CO_3, Cs_2CO_3, NaOAc, K_3PO_4, Na_3PO_4…) bases have been employed [1,19,21-23]. These reactions afford coupling products from olefins and aryl halides which are widely used in organic synthesis as intermediates in fine and pharmaceutical chemistry [3,6,24-27]. Still closer to our study, Peroza found that the presence of Aliquat-336 in conjunction with a supported metal catalyst promotes the Heck reaction, and allows interesting rates to be achieved and selectivity in reactions which involve aryl-halogen bond activation by palladium [28]. Furthermore, Perosa reported that Aliquat-336 was found to be crucial for the Heck reaction. Its presence in catalytic amounts accelerates the reaction in a triphasic system [28].

The present work reports comparative studies of the synthesis of stilbene and derivatives by coupling styrene with aryl halides in organic and aqueous media in the presence of Pd chloride or acetate. The effect of the substituent on the aromatic ring of the halobenzene is also examined. Our recent results [29,30] emphasized the role of phase transfer catalysis in anionic reactions. We, therefore, applied PTC also in arylation reactions leading to stilbenes [3,31] in the presence of palladium complexes which are known as performant catalysts in the formation of carbon-carbon bonds [32,33].

II- RESULTS AND DISCUSSION

1- Coupling of styrene with halobenzenes:

In a first step we studied the nature of the halide in the coupling of styrene and halobenzenes (Table I).



Scheme 1. Coupling of styrene with halobenzenes.

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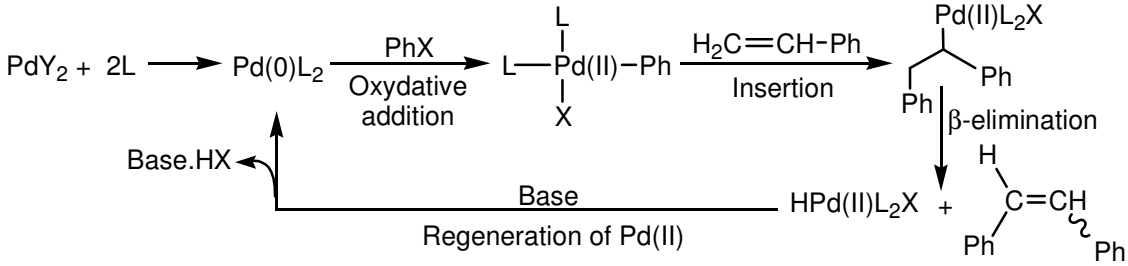
Table I. Effect of the halide on the yield of the coupling of styrene.

	Yield %											
Y	OAc						Cl					
X	Cl		Br		I		Cl		Br		I	
Base	Et_3N	K_2CO_3	Et_3N	K_2CO_3	Et_3N	K_2CO_3	Et_3N	K_2CO_3	Et_3N	K_2CO_3	Et_3N	K_2CO_3
DMF [a]	17	22	84	44	92	54	15	18	61	38	73	39
Water [b]	15	20	38	39	40	42	12	10	31	33	35	35
Water + DMF [c]	-	22	-	42	45	-	-	20	-	40	-	41

[a] Procedure A: Halobenzene (10 mmol), styrene (12 mmol), PPh_3 (0.4 mmol), PdY_2 (0.1 mmol), Et_3N or K_2CO_3 (15 mmol), DMF (5 mL), T = 100°C, time : 12 h. [b] Procedure B: water was used instead of DMF as solvent.
[c] Procedure C: mixture of water and DMF was used instead of DMF as solvent.

In the reaction products 1,1-diphenylethylene **2a** could not be detected. The only product was **1a** formed by arylation on sp^2 carbon in position β. In fact, the electroattracting phenyl group in styrene involves steric hindrance on α carbon. The phenyl is therefore, bounded on the less substituted carbon while Pd is fixed to the hindered substituted carbon. A σ-complex is formed affording **1a** via β-elimination of H-Pd^{II}-X complex. The results are in agreement with the literature [5,34-36] (Scheme 2).



Scheme 2. Simplified catalytic cycle for the coupling reaction.

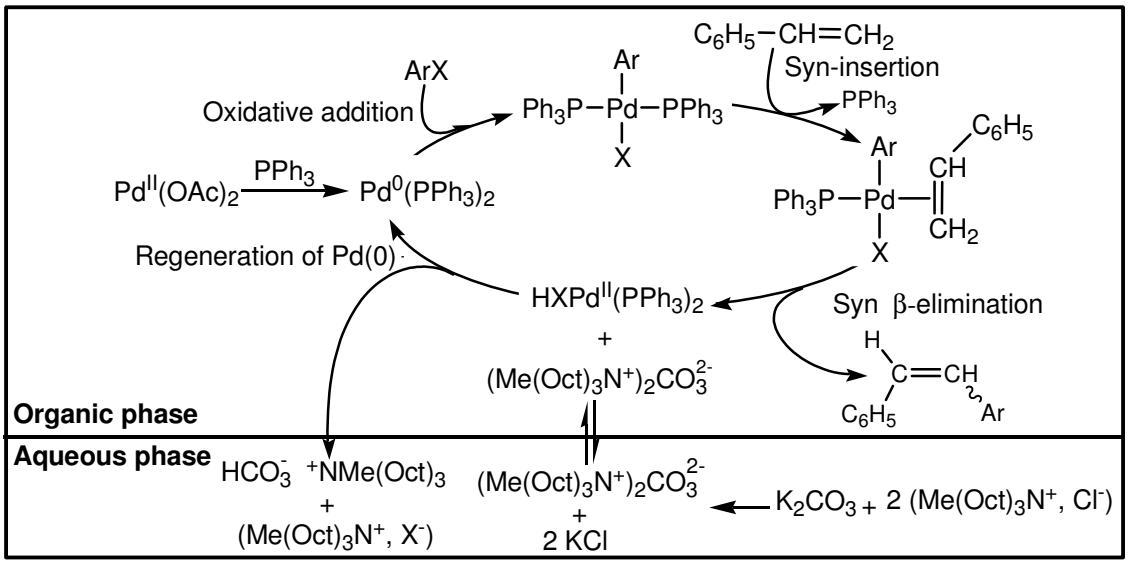
The results of Table I show that the reactivity of iodo- and bromobenzene are similar but slightly higher than the reactivity of the corresponding chloro derivative. The trend can be correlated with several physical properties of the C-halide bond such as the dissociation energy and the interatomic distance [37-39]. An easier breaking of the bond corresponds to a higher reactivity of the aromatic halide for a reduction reaction.

The low reactivity observed in aqueous solution may be ascribed to the low solubility of reactants and catalysts: Pd acetate and chloride are insoluble in water [40].This is also the reason of the poor yields obtained with potassium carbonate which is insoluble in N, N-dimethylformamide. In fact, the Pd catalyst is regenerated under the active form in basic media. Operating in DMF-water mixtures increases the solubility of K_2CO_3. The addition of the PTC catalyst Aliquat-336 has a beneficial effect on yields (Table II). The PTC catalyst increases the hydrophobic force and, consequently, activates the formation of the active zerovalent palladium catalyst [17]. It also facilitates the transfer of the carbonate anion from the aqueous to the organic phase. From a stereochemical point of view, the reaction affords a high percentage of *E*-isomer. The results are possibly rationalized by Scheme 3.

Table II. Effect of the addition of Aliquat-336 on the yield of Heck coupling styrene with halobenzenes.

Y	OAc			Cl		
X	Cl	Br	I	Cl	Br	I
Yield %	51	84	96	52	81	84

Procedure D: Halobenzene (10 mmol), styrene (12 mmol), PPh_3 (0.4 mmol), PdY_2 (0.1 mmol), K_2CO_3 (15 mmol), Aliquat-336 (0.5 mmol), DMF (2.5 mL), water (2.5 mL), T = 100°C, time : 12 h.

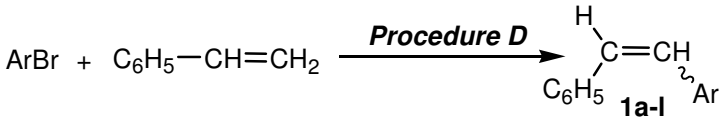


Scheme 3. Suggested mechanism for the Heck coupling in biphasic system Water-DMF in presence of Aliquat-336.

The mechanism begins with the pre-activation step in the Heck catalytic cycle. This step requires the reduction of Pd^{II} to Pd^{0} forming active species through multiple ligand exchange equilibria. It has been described via electrochemistry studies by Amatore and Jutand [41,42] who demonstrated the role of the phosphine in Pd^{II} reduction. The first step is the oxidative addition of the C-X bond onto the Pd^{0} complex. In most cases, except for complexes involving chelating ligands, the product of oxidative addition has the *trans* geometry. The complex $ArPdX(PPh_3)_2$, however, which forms first, leads to the *E*-isomer, the more thermodynamically stable. In a second step, the alkene coordinates to the Pd^{II} catalyst. A Pd^{II} complex is formed leading to a σ-complex via a *syn*-insertion of $[PdHX(PPh_3)_2]$ reaction into the Pd-Ar bond. This step is crucial for the regioselectivity since it is controlled through steric and electronic factors. When an H-atom is located in β-position of Pd, a rotation brings it back to an antiparallel position, making possible β-elimination or *syn*-elimination of the palladium complex and affording, subsequently, the coupling product. The Pd^{0} complex is regenerated by reaction of a base on the $[PdHX(PPh_3)_2]$ complex. The carbonate ion migrates from the aqueous to the organic phase in the presence of the quaternary ammonium salt Aliquat-336.

2- Coupling of styrene and aryl bromides:

In a further step we have studied the effect of the substituents on the reactivity of the aromatic halide by coupling styrene with diversely substituted bromobenzenes in the presence of palladium acetate in DMF-water (Table III).



Scheme 4. Coupling of styrene with aryl bromides.

The results show that the yields of the arylation reaction depend on the nature of the substituent in bromobenzene. In fact, the strength of the aromatic carbon-halide bond is correlated, at least partly, with the electronic properties of the substituent. An electroattracting group may weaken the C-Br bond whereas, inversely, an electrodonating group enhances it. As a result, the yield is increased with electroattracting groups and decreased with electrodonating groups.

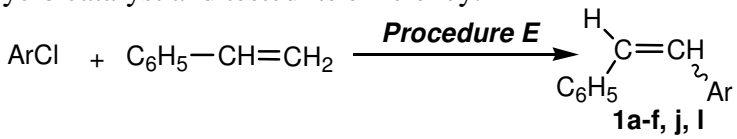
Table III. Influence of the nature of the substituent in coupling styrene with aryl bromides.

Ar-Br	Product	Yield %	E/Z	Ar-Br	Product	Yield %	E/Z
C_6H_5Br	**1a**	84	87/13	o-CNC_6H_4Br	**1g**	97	88/12
p-$CH_3C_6H_4Br$	**1b**	75	90/10	p-$CHOC_6H_4Br$	**1h**	87	84/16
o-$CH_3C_6H_4Br$	**1c**	73	90/10	p-HOC_6H_4Br	**1i**	62	86/14
p-$CH_3OC_6H_4Br$	**1d**	58	90/10	p-$NO_2C_6H_4Br$	**1j**	95	88/12
p-$CH_3COC_6H_4Br$	**1e**	92	90/10	p-$NH_2C_6H_4Br$	**1k**	60	86/14
p-CNC_6H_4Br	**1f**	96	86/14	p-$N(Me)_2C_6H_4Br$	**1l**	53	88/12

Procedure D: Halobenzene (10 mmol), styrene (12 mmol), PPh_3 (0.4 mmol), PdY_2 (0.1 mmol), K_2CO_3 (15 mmol), Aliquat-336 (0.5 mmol), DMF (2.5 mL), water (2.5 mL), T = 100°C, time12 h.

3- Coupling of styrene with aryl chlorides:

In order to increase the yield in the coupling reactions of styrene with aryl chlorides we synthesized a palladocyclo catalyst and tested its efficiency.

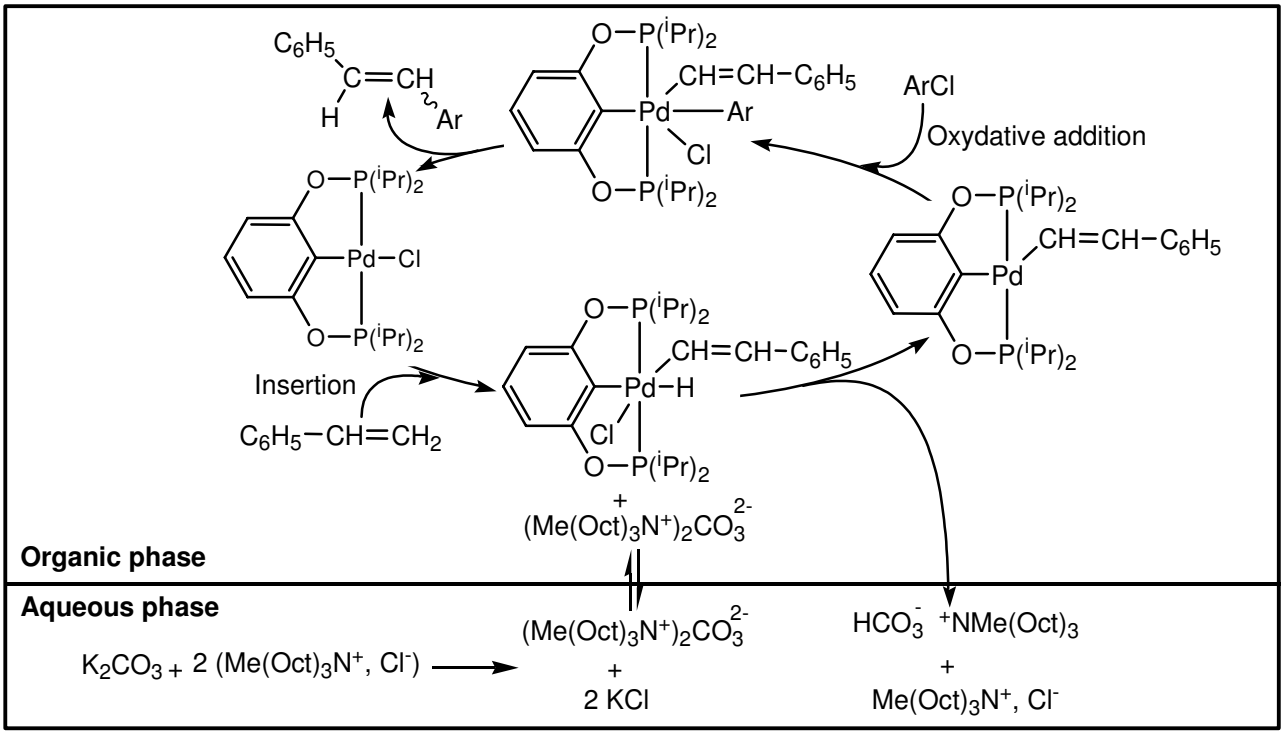


Scheme 5. Coupling of styrene with aryl chlorides.

Table IV. Heck coupling of aryl chlorides with $PdCl\{C_6H_3\text{-}2,6\text{-}(OP^iPr_2)_2\}$.

Ar-Cl	Product	Yield %	E/Z	Ar-Cl	Product	Yield %	E/Z
C_6H_5Cl	**1a**	89	88/12	p-$CH_3COC_6H_4Cl$	**1e**	81	80/20
p-$CH_3C_6H_4Cl$	**1b**	84	80/20	p-CNC_6H_4Cl	**1f**	92	80/20
o-$CH_3C_6H_4Cl$	**1c**	82	80/20	p-$NO_2C_6H_4Cl$	**1j**	75	76/24
p-$CH_3OC_6H_4Cl$	**1d**	73	76/24	p-$N(Me)_2C_6H_4Cl$	**1l**	70	76/24

Procedure E: Styrene (12 mmol), aryl chloride (10 mmol), K_2CO_3 (15 mmol), DMF (2.5 mL), water (2.5 mL), $PdCl\{C_6H_3\text{-}2,6\text{-}(OP^iPr_2)_2\}$ (0.06mmol), Aliquat-336 (0.5mmol), T = 120°C, 12h.



Scheme 6. Proposed mechanism for Heck coupling catalysed by $PdCl\{C_6H_3\text{-}2,6\text{-}(OP^iPr_2)_2\}$ in presence of Aliquat-336.

The results listed in Table IV confirm the efficiency of the catalytic system in arylation reactions. There is, however, a drawback as the reactions require a relatively high temperature (140°C during 20 hours). The results stay in agreement with those taken from literature Jensen and al. [43]. Jensen proposed a catalytic cycle that proceeds via the C H activation of the olefin at a Pd(II) centre followed by oxidative addition [43]. It is noteworthy that the stability of palladacycles suppress aggregation and give them a high efficiency as catalysts in Heck reactions [44], and several reports dealt with the exclusive use of palladacycles [45-47].

The mechanism must take into account the nature of the precursor as well as every chemical specie formed during the reaction. Based on a palladium^{II}/ palladium^{IV} type process it begins with oxidative addition of the alkene followed by elimination of H and Cl with the aid of carbonate ions transferred to the organic phase. The two vacant sites on Pd are then filled during the oxidative addition of the aromatic halide. The reductive elimination of the coupling product regenerates the catalyst (Scheme 6).

III- CONCLUSION

Our study of the coupling of styrene with halide benzene catalysed by palladium catalysts shows a higher reactivity with the addition of a catalytic amount of Aliquat-336 in water-DMF mixtures. The reaction occurs according to a biphasic catalysis process in the presence of carbonate ions. The introduction, however, of electrodonating groups on the aromatic ring of the aryl halide decreases the yield. At last, the results show that the palladium complex PdCl{C_6H_3-2,6-(OP^iPr_2)$_2$} can be an excellent catalytic system for the coupling reaction of styrene and aryl chlorides.

IV- EXPERIMENTAL

- **Method A :** Halobenzene (10 mmol), styrene (1.25g, 12 mmol), triphenylphosphine (0,26g, 0.4 mmol) and PdY_2 (0.1 mmol) are introduced in a tubular reactor fitted with a septum. Vacuum is applied for 30 min then the reactor is flushed with argon. Base (Et_3N or K_2CO_3) (15 mmol) and N,N-dimethylformamide (5 mL) are added. The reactor is then placed in an oil bath preheated to 100°C for 12 h. After reaction, the reaction mixture is filtered and the solvent removed in vacuo. The coupling product is isolated by chromatography on silica gel with hexane/ether as eluent.
- **Method B:** The same protocol that in procedure A, but with water as solvent. At the end of the reaction, an extraction is carried out. The organic phase is dried on the anhydrous magnesium sulphate. The product was purified by chromatography on silica gel column using a mixture hexane/ether as eluent.
- **Method C:** Protocol is the same as the one used in procedure A. The only difference is in a mixture of water (2.5 mL) and DMF (2.5 mL) as solvent. At the end of the reaction, an extraction is carried out. The organic phase is dried on the anhydrous magnesium sulphate. The product was purified by chromatography on silica gel column using a mixture hexane/ether as eluent.
- **Method D:** The same protocol that in procedure C, but with K_2CO_3 as base. However, 0.5 mmol (5mol %) of Aliquat-336 is added to the initial mixture.
- **Method E:** A mixture of styrene (12 mmol), aryl chloride (10 mmol), K_2CO_3 (15 mmol), DMF (2.5 mL), water (2.5 mL), PdCl{C_6H_3-2,6-(OP^iPr_2)$_2$} (0.06mmol) and Aliquat-336 (0.5mmol) was refluxed in an oil bath at 120°C for 12h. After cooling to room temperature, the reaction mixture was extracted with ether (5 x 20 mL). The ethereal solution was washed with brine (3 x 10 mL) and dried ($MgSO_4$) and filtered. After removing the solvent under vacuum, the product was purified by chromatography on a silica gel column using a mixture hexane/ether as eluent.

NMR spectra ^{1}H (300 MHz) and ^{13}C (75MHz) NMR spectra are recorded on a AC 300 Brüker spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal reference. All chemical shifts (δ) were reported in ppm from internal TMS. IR spectra are recorded on a JASCO FT–IR-420 device in KBr pellets. Melting points were taken on a Reichert-Heizbank apparatus.

Synthesis of PdCl{C_6H_3-2,6-(OP^iPr_2)$_2$}:

Preparation of C_6H_4-2,6-(OP^iPr_2)$_2$ [48]**:** A solution of resorcinol (3 mmol) and 4-dimethylamino pyridine (6.1 mmol) in THF (25 mL) was added a solution of ClP(i-Pr)$_2$ (6 mmol) in THF (20 mL), while stirring at 0°C. The resulting mixture was allowed to reach room temperature and stirred for an additional 24 h. Following removal of the solvent in vacuo, the solid residue was extracted with toluene (3 x 20 mL). The combined extracts were filtered through a short plug of Celite and the toluene removed in vacuo to yield the product (95%) as colourless oil.
^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.00-1.39 (m, 24H), 1.83-2.02 (m, 4H), 6.82-7.15 (m, 4H).
^{13}C-NMR ($CDCl_3$) (δ/ppm) 16.80, 17.71, 28.42, 108.85, 112.70, 129.41, 160.32.

Preparation of PdCl{C_6H_3-2,6-(OP^iPr_2)$_2$} [48] **:** In a 250 mL two-necked flask equipped with a cooling system and magnetic stirrer, 1.5mmol of C_6H_4-2,6-(OP^iPr_2) and 1.5mmol de $PdCl_2$(COD) are introduced into 50 mL of toluene. The mixture was refluxed during 5 h. The solvent was removed *in vacuo*. The crude product was extracted with pentane (3 x 20 mL). The product was purified by crystallization from diethyl ether (Yield 87%).
^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.15-1.47 (m, 24H), 2.42-2.55 (m, 4H), 6.54 (d, 2H, *J* = 8.1 Hz), 6.96 (t, 1H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 16.75, 17.40, 28.82, 106.04, 129.00, 150.24, 166.31.

(*E*)-1,2-Diphenylethene (1a): mp = 123-124°C. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 7.09 (d, 2H, *J* = 15.9 Hz), 7.11-7.30 (m, 6H), 7.44 (d, 4H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 124.80, 126.51, 127.75, 128.04, 135.01.

(*Z*)-1,2-Diphenylethene (1a): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 6.88 (d, 2H, *J* = 11.7 Hz), 7.09-7.33 (m, 6H), 7.42 (d, 2H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 125.05, 126.77, 127.81, 128.40, 135.10.

(*E*)-1-(4-Methylphenyl)-2-phenylethene (1b): mp = 119-121°C. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.35 (s, 3H,) 7.06 (d, 1H, *J* = 15.3 Hz), 7.10 (d, 1H, *J* = 15.3 Hz), 7.16 (d, 2H, *J* = 8.1 Hz), 7.21-7.26 (m, 3H), 7.33 (d, 2H, *J* = 8.1 Hz), 7.48 (d, 2H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 21.31, 126.52, 126.85, 127.56, 127.66, 127.85, 128.79, 129.34, 129.57, 134.65, 137.62.

(*Z*)-1-(4-Methylphenyl)-2-phenylethene (1b): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.34 (s, 3H), 7.03 (d, 1H, *J* = 11.4 Hz), 7.09 (d, 1H, *J* = 11.4 Hz), 7.14 (d, 2H, *J* = 8.1 Hz), 7.21-7.28 (m, 3H), 7.37 (d, 2H, *J* = 8.1 Hz), 7.48 (d, 2H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 21.55, 127.21, 128.42, 129.00, 129.19, 129.28, 129.89, 130.44, 134.51, 137.11, 137.75.

(*E*)-1-(2-Methylphenyl)-2-phenylethene (1c): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.30 (s, 3H), 7.08 (d, 1H, *J* = 16.2 Hz), 7.13 (d, 1H, *J* = 16.2 Hz), 7.19 (d, 2H, *J* = 8.4 Hz), 7.29-7.39 (3H, m), 7.59 (d, 2H, *J* = 8.4 Hz), 7.67 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 20.20, 125.78, 126.67, 126.75, 126.98, 127.99, 129.00, 130.47, 130.84, 136.11, 136.74, 138.09.

(*Z*)-1-(2-Methylphenyl)-2-phenylethene (1c): mp = 135-136°C**.** ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.26 (s, 3H), 6.59 (d, 1H, *J* = 11.1 Hz), 7.05 (d, 1H, *J* = 11.1 Hz), 7.11 (d, 2H, *J* = 8.4 Hz), 7.21-7.31 (m, 3H), 7.62 (d, 2H, *J* = 8.4 Hz), 7.68 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 19.84, 125.54, 127.01, 127.25, 128.00, 128.78, 128.89, 129.65, 130.09, 130.51, 136.10, 137.05, 137.11.

(*E*)-1-(4-Methoxyphenyl)-2-phenylethene (1d): mp = 135-136°C**.** ^{1}H-NMR ($CDCl_3$) (δ/ppm) 3.75 (s, 3H), 6.84 (d, 1H, *J* = 16.2 Hz), 7.00 (d, 1H, *J* = 16.2 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 7.36-7.46 (s, 3H), 7.62 (d, 2H, *J* = 8.4 Hz), 7.68 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 55.50, 114.43, 126.52, 126.89, 127.65, 128.00, 128.45, 128.89, 130.44, 137.98, 159.56.

(*Z*)-1-(4-Methoxyphenyl)-2-phenylethene (1d): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 3.72 (s, 3H), 6.74 (d, 1H, *J* = 12.0 Hz), 7.10 (d, 1H, *J* = 12.0 Hz), 7.30 (d, 2H, *J* = 7.8 Hz), 7.28-7.36 (m, 3H), 7.71 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 54.50, 114.37, 126.61, 126.78, 127.54, 128.13, 128.56, 128.89, 129.03, 138.78, 156.44.

(*E*)-1-(4-Methylcarbonylphenyl)-2-phenylethene (1e): I.R. $\nu_{C=O}$ = 1805 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.58 (s, 3H,), 7.11 (d, 1H, *J* = 16.5 Hz), 7.22 (d, 1H, *J* = 16.5 Hz), 7.24-7.40 (m, 3H), 7.53 (d, 2H, *J* = 7.2 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 7.94 (d, 2H, *J* = 8.7 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 26.91, 126.63, 126.90, 127.45, 128.34, 128.89, 129.00, 131.53, 136.01, 136.78, 142.11, 197.55.

(*Z*)-1-(4-Methylcarbonylphenyl)-2-phenylethene (1e): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.60 (s, 3H), 6.93 (d, 1H, *J* = 12.3 Hz), 7.09 (d, 1H, *J* = 12.3 Hz), 7.18-7.35 (m, 3H), 7.48 (d, 2H, *J* = 7.2 Hz), 7.55 (d, 2H, *J* = 8.7 Hz), 7.90 (d, 2H, *J* = 8.7 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 26.55, 126.75, 126.90, 127.25, 128.54, 128.96, 129.09, 131.55, 136.02, 136.78, 142.11, 197.55.

(*E*)-1-(4-Cyanophenyl)-2-phenylethene (1f): mp = 120-121°C. I.R: $\nu_{C=C}$ = 1610cm^{-1}, ν_{CN} = 2225cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 27.09 (d, 1H, *J* = 16.2 Hz), 7.11-7.21 (m, 3H), 7.22 (d, 1H, *J* = 16.2 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 8.1 Hz), 7.64 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 111.71, 117.00, 124.88, 124.91, 126.33, 126.95, 127.82, 128.55, 131.97, 134.91, 139.49.

(*Z*)-1-(4-Cyanophenyl)-2-phenylethene (1f): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 7.01 (d, 1H, *J* = 11.7 Hz), 7.12-7.25 (m, 3H), 7.26 (d, 1H, *J* = 11.7 Hz), 7.32 (d, 2H, *J* = 8.1 Hz), 7.49 (d, 1H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 111.92, 116.54, 124.88, 124.96, 126.33, 124.91, 126.33, 126.96, 127.82, 128.55, 131.97, 134.77, 139.51.

(*E*)-1-(2-Cyanophenyl)-2-phenylethene (1g): mp = 121-122°C ^{1}H-NMR ($CDCl_3$) (δ/ppm) 7.00 (d, 1H, *J* = 16.2 Hz), 7.11-7.21 (m, 3H), 7.24 (d, 1H, *J* = 16.2 Hz), 7.36 (d, 2H, *J* = 8.1 Hz), 7.48 (d, 2H, *J* = 8.7 Hz), 7.55 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 110.61, 118.10, 124.48, 124.71, 126.19, 127.04, 127.79, 128.66, 132.06, 134.93, 139.96.

(*Z*)-1-(2-Cyanophenyl)-2-phenylethene (1g): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 6.88 (d, 1H, *J* = 11.4 Hz), 7.11-7.21 (m, 3H), 7.22 (d,1H, *J* = 11.4 Hz), 7.30 (d, 2H, *J* = 8.1 Hz), 7.42 (d, 2H, *J* = 8.1 Hz), 7.43 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 110.30, 118.93, 124.78, 124.98, 126.22, 127.14, 127.66, 128.74, 132.17, 134.27, 140.04.

(*E*)-1-(4-aldehydophenyl)-2-phenylethene (1h): I.R. $\nu_{C=O}$ = 1717 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 6.99 (d, 1H, *J* = 16.8 Hz), 7.08 (d, 1H, *J* = 16.8 Hz), 7.11-7.28 (m, 3H), 7.43 (d, 2H, *J* = 8.1 Hz), 7.62 (d, 2H, *J* = 7.8 Hz), 7.90 (d, 2H, *J* = 8.1 Hz), 9.89 (s, 1H). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 124.00, 124.74, 126.32, 126.95, 127.71, 128.55, 129.54, 135.48, 141.11, 190.33.

(*Z*)-1-(4-aldehydophenyl)-2-phenylethene (1h): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 6.93 (d, 1H, *J* = 11.7 Hz), 7.11 (d, 1H, *J* = 11.7 Hz), 7.18-7.28 (m, 3H), 7.48 (d, 2H, *J* = 8.1 Hz), 7.55 (d, 2H, *J* = 7.8 Hz), 7.80 (d, 2H, *J* = 8.4 Hz), 9.91 (s, 1H). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 26.55, 126.75, 126.90, 127.25, 128.54, 128.96, 129.09, 131.55, 136.02, 136.78, 142.11, 197.55.

(*E*)-1-(4-hydroxyphenyl)-2-phenylethene (1i): I.R: $\nu_{C\text{-}OH}$ = 3550 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 4.99 (b, 1H), 6.74 (d, 2H, *J* = 7.8 Hz), 6.97 (d, 1H, *J* = 15.6 Hz), 7.01 (d, 1H, *J* = 15.6 Hz), 7.07-

7.24 (m, 3H), 7.26 (d, 2H, *J* = 8.1 Hz), 7.4 (d, 2H, *J* = 7.8 Hz). ^{3}C-NMR ($CDCl_3$) (δ/ppm) 115.60, 124.88, 126.98, 126.33, 127.41, 127.55, 127.96, 128.56, 134.97, 157.00.

(*Z*)-1-(4-hydroxyphenyl)-2-phenylethene (1i): I.R. $\nu_{C=O}$ = 1717 cm^{-1}; $\nu_{C\text{-}NO_2}$ = 1548 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 4.75 (b, 1H), 6.88 (d, 2H, *J* = 7.8 Hz), 6.77 (d, 1H, *J* = 11.4 Hz), 7.01 (d, 1H, *J* = 11.4 Hz), 7.07-7.24 (m, 3H), 7.33 (d, 2H, *J* = 8.1 Hz), 7.4 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 115.50, 124.44, 126.88, 126.55, 127.57, 127.84, 127.96, 128.90, 135.07, 157.71.

(*E*)-1-(4-Nitrophenyl)-2-phenylethene (1j): mp = 156-157°C. I.R. $\nu_{C\text{-}NO_2}$ = 1548 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 7.10-7.26 (m, 3H), 7.30 (d, 1H, *J* = 15.9 Hz), 7.39 (d, 1H, *J* = 15.9 Hz), 7.42 (d, 2H, *J* = 8.4 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 8.19 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 123.51, 124.74, 125.09, 126.34, 127.00, 127.85, 128.55, 135.00, 141.00, 147.75.

(*Z*)-1-(4-Nitrophenyl)-2-phenylethene (1j): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 6.70 (d, 1H, *J* = 11.4 Hz), 6.85 (d, 1H, *J* = 11.4 Hz), 7.11-7.26 (m, 3H), 7.44 (d, 2H, *J* = 8.1 Hz), 7.67 (d, 2H, *J* = 7.8 Hz), 8.20 (d, 2H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 23.10, 124.59, 125.44, 126.33, 127.21, 127.74, 128.47, 135.51, 141.33, 147.40.

(*E*)-1-(4-aminophenyl)-2-phenylethene (1k): I.R. ν_{NH_2} = 3520 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 4.10 (b, 2H), 6.45 (d, 2H, *J* = 7.8 Hz), 6.97 (d, 1H, *J* = 15.9 Hz), 7.02 (d, 1H, *J* = 15.9 Hz), 7.11-7.27 (m, 5H), 7.43 (d, 2H, *J* = 7.8 Hz)). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 115.00, 124.61, 124.84, 124.98, 126.22, 127.00, 127.85, 128.41, 134.88, 146.01.

(*Z*)-1-(4-aminophenyl)-2-phenylethene (1k): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 4.10 (b, 2H), 6.55 (d, 2H, *J* = 7.8 Hz), 6.87 (d, 1H, *J* = 11.4 Hz), 6.99 (d, 1H, *J* = 11.4 Hz), 7.09-7.22 (m, 3H), 7.27 (d, 2H, *J* = 8.1 Hz), 7.43(d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 115.00, 124.40, 124.65, 124.85, 125.80, 127.00, 127.75, 128.47, 133.70, 145.95.

(*E*)-1-(4-N,N-dimethylaminophenyl)-2-phenylethene (1l): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.87 (6H, s), 6.60 (d, 2H, *J* = 8.1 Hz), 6.98 (d, 1H, *J* = 16.2 Hz), 7.00 (d, 1H, *J* = 16.2 Hz), 7.11-7.23 (m, 3H), 7.24 (d, 2H, *J* = 7.8 Hz), 7.43 (d, 2H, *J* = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 43.66, 113.21, 124.45, 124.95, 125.54, 126.44, 127.11, 127.79, 128.44, 134.98, 143.77.

(*Z*)-1-(4-N,N-dimethylaminophenyl)-2-phenylethene (1l): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 2.88 (s, 6H), 6.61 (d, 2H, *J* = 7.8 Hz), 6.96 (d, 1H, *J* = 11.1 Hz), 6.99 (d, 1H, *J* = 11.1 Hz), 7.09-7.22 (m, 3H), 7.25 (d, 2H, *J* = 8.7 Hz), 7.40 (d, 2H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 43.68, 113.29, 124.65, 124.90, 125.56, 126.46, 127.22, 127.76, 128.32, 134.25, 142.95.

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