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Palladium-Catalysed Hydroarylation and Hydrovinylation of 3,3-Dialkoxy-1-aryl-1-propynes. An Approach to 3-Aryl- and 3-Vinylquinolines

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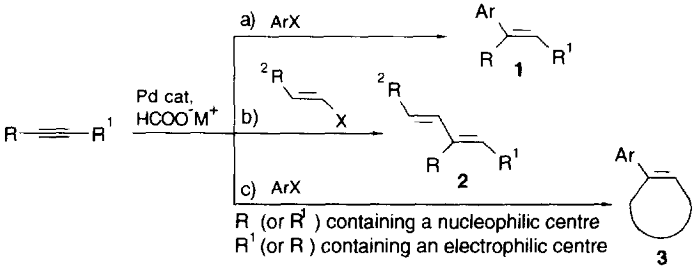
Abstract. Acetylenic acetals and ketals have been reacted with aryl and vinyl halides to generate hydroarylation and hydrovinylation products. The reaction proceeds with high regioselectivity. The carbopalladation step appears to be mainly controlled by steric effects and the new carbon-carbon bond is generated preferentially on the carbon bearing the acetal group. The reaction has been employed to develop a regioselective synthesis of 3-aryl and 3-vinylquinolines.

Introduction

The palladium-catalysed hydroarylation and hydrovinylation of disubstituted alkynes has proven to be a versatile method for the preparation of trisubstituted alkenes **1**[1] (Scheme 1a) and 1,3-dienes **2**[2] (Scheme 1b). The intramolecular version of the reaction has also been reported.[3] With alkynes bearing suitable nucleophilic and electrophilic centres near to the carbon-carbon triple bond the reaction provides a unique entry into cyclic derivatives **3** through a sequential addition/cyclization process[2,4] (Scheme 1c).

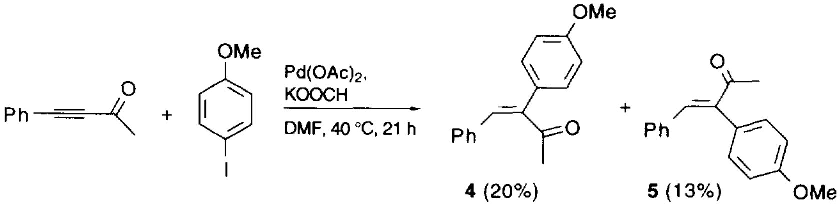


Scheme 1

Addition products in this reaction are stereoselectively *cis*[4,5] and, with disymmetric alkynes (Ar *vs.* ^{t}Bu[1b] and SiMe$_3$[1c]) and the C$_{sp^2}$ donors (aryl and vinyl halides) tested so far, the regiochemical outcome was found to be primarily controlled by steric effects directing the organic framework to the less hindered end of the alkyne and the hydrogen atom (the palladium moiety in the carbopalladation intermediate) to the more hindered end. With tertiary propargylic alcohols (Ar *vs.* CHR$_2$OH) hydroxyl coordination to palladium may reinforce steric effects in directing the addition of organopalladium intermediates to the carbon-carbon triple bond and lead to higher regioselectivity.[1b,2,4] Similar regioselectivity has been observed in other alkyne addition chemistry.[6] Electronic effects would appear to play a less important role as suggested by the formation of the two possible regioisomers in almost equimolar amounts in the hydroarylation of disymmetric diaryl acetylenes, such as (*p*-acetylphenyl)-2-phenylacetylene and (*p*-methoxyphenyl)-2-phenylacetylene, whereby one of the aryl groups bears a strong electron-withdrawing and -donating substituent.[1] A high regioselectivity would be expected in these cases if the hydroarylation proceeded through a charge controlled carbopalladation of the carbon-carbon-triple bond. With the exception of the *p*-nitro derivative, that produced a significant excess of one of the possible regioisomers, similar lack of regioselectivity has also been observed in the palladium-catalysed reaction of 1-iodo-8-dimethylaminonaphthalene with diarylacetylenes containing a variety of electron-withdrawing and -donating groups on one of the aromatic rings.[7]

To widen the scope of the methodology, we decided to investigate the reactivity of acetylenic systems containing functional groups amenable to further functional group modifications and alkynes with carbon-carbon triple bonds conjugated to ketonic and aldehydic functionalities appeared of particular interest. The hydroarylation of these substrates would provide an interesting approach to functionalised α,β-unsaturated carbonyl compounds. On the other hand, α,β-ynones have recently been reported to undergo a regioselective addition of σ-acyl- and σ-(8-dimethylaminonaphthyl)-palladium complexes to afford, respectively, substituted furans[8] and N-methylbenzo[*d,e*]quinolines.[7]

Exposure (DMF, 40 °C, 21 h) of the commercially available 4-phenyl-3-butyn-2-one to 4-methoxyphenyl iodide (2.4 equiv.) in the presence of catalytic amounts of $Pd(OAc)_2$ (5 mol %) and potassium formate (2.4 equiv.), however, produced a messy reaction mixture which contained the stereoisomeric derivatives **4** and **5**[9] as the main hydroarylation products (Scheme 2), along with other unidentified products. Compounds **4** and **5** are likely to arise from a sterically biased addition of the σ-(*p*-methoxyphenyl)-palladium complex, generated *in situ* through the oxidative addition of Pd^0 species with the organic halide, to the carbon-carbon triple bond. Electronic factors would be expected to influence the hydroarylation reaction in such a way that the added aryl unit ends up far from the carbonyl function. Our result is in agreement with the regiochemistry of other additions of "σ-arylpalladium halides" to 4-phenyl-3-butyn-2-one[7] and to related alkynes containing carbon-carbon triple bonds conjugated to electron withdrawing groups such as 3-phenyl-propynal[6a,7] and alkyl phenylpropynoate.[6a,7,13] The unusual formation of significant amounts of the overall trans derivative **5** in the hydroarylation reaction (there are, however, several known examples of overall *trans* additions of transition metal-hydride or -alkyl fragments to acetylenic compounds)[14] could be dependent on the strong electron-withdrawing effect of the ketonic function, favouring the isomerization of the σ-vinylpalladium intermediate resulting from the carbopalladation step.[15]



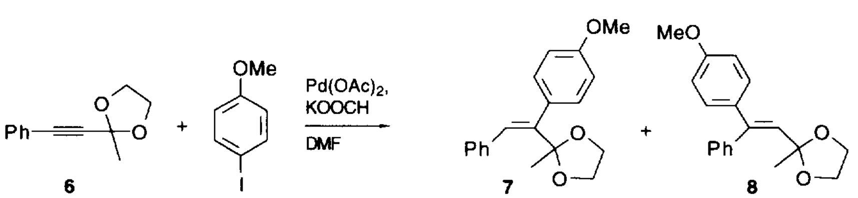
Scheme 2

Assuming that masking it with a suitable protecting group could lead to a better control of the stereochemical outcome and possibly to higher yields, we decided to investigate the reactivity of alkynes containing ketal and acetal functionalities on the propargylic carbon atom.

Hereafter we report the results of this study.

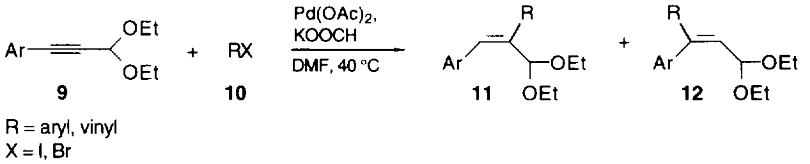
Results

Hydroarylation of 3,3-Ethylendioxy-1-phenyl-1-butyne (6) - First attempts were made subjecting to hydroarylation conditions 4-methoxyphenyl iodide and 3,3-ethylendioxy-1-phenyl-1-butyne **6**, prepared from 4-phenyl-3-butyn-2-one and ethylene glycol in 95% yield. The reaction (40 °C, 24 h) produced the regioisomeric hydroarylation products **7** and **8** in 82% overall yield as a 64/36 mixture according to ^1H NMR spectroscopic data (Scheme 3). Increasing the reaction temperature to 60 °C (7 h) led to a lower yield and to a lower regioselectivity. Compounds **7** and **8** were isolated in 73% yield as an about 1/1 mixture. The stereo- and regiochemistry of **7** and **8** were determined by NOESY experiments which showed that the vinyl proton and the *p*-methoxyphenyl unit are *cis*, that the *p*-methoxyphenyl unit and the ketal group are adjacent to each other in **7**, and that the vinyl proton is adjacent to the ketal group in **8**.



Scheme 3

Hydroarylation of 3,3-Diethoxy-1-aryl-1-propynes (9). Assuming that switching to the less steric demanding acetal group [Ph *vs.* $CH(OEt)_2$ compared with Ph *vs.* $CMe(OEt)_2$] could favour the directing effect of the aryl unit and allow a higher degree of regioselectivity, we next turned to acetylenic acetals. 3,3-Diethoxy-1-phenyl-1-propyne **9a**, readily prepared through the palladium-catalysed coupling of phenyl iodide with the commercially available 3,3-diethoxy-1-propyne,[20] was selected as the model system. According to the the regioselectivity generally observed in related alkyne addition processes of this alkyne.[7,21] its reaction with 4-methoxyphenyl iodide in the presence of potassium formate and $Pd(OAc)_2$ at 40 °C (20 h) afforded the hydroarylation derivative **11a** in 48% yield along with little of the regioisomeric hydroarylation product **12a**. The regio- and stereochemistry of **11a** was assigned on the basis of a NOE study which showed that the added aryl group is close to the acetal proton and on the same side of the carbon-carbon double bond as the vinyl proton. α,β-Unsaturated aldehydes, very likely derived from the adventitious hydrolysis of **11a** and **12a**, were also isolated. The recovery of **9a** in almost quantitative yield after its treatment with potassium formate in the absence of 4-methoxyphenyl iodide and $Pd(OAc)_2$ appears to rule out the possible formation of the above mentioned α,β-unsaturated aldehydes through the hydrolysis of **9a** followed by the hydroarylation of the resultant α,β-ynal. The formation of **11a** and **12a** through the palladium-catalysed vinylic substitution of the alkene derived from the reduction of the carbon-carbon triple bond was also excluded. In fact, treatment of **9a** under hydroarylation conditions (20 h), omitting 4-methoxyphenyl iodide, led to the isolation of 3,3-diethoxy-1-phenyl-1-propene in only 8% yield along with a mixture of other unidentified products, whose NMR spectra showed signals attributable to aldehyde derivatives. The starting alkyne was recovered in 67% yield. In addition, no reduction products were detected in the reaction mixture derived from the hydroarylation of **9a**. Most probably the hydroarylation reaction is faster than the hydrogenation reaction. The results obtained in the hydroarylation of some 3,3-diethoxy-1-aryl-1-propynes are summarised in Table 1.



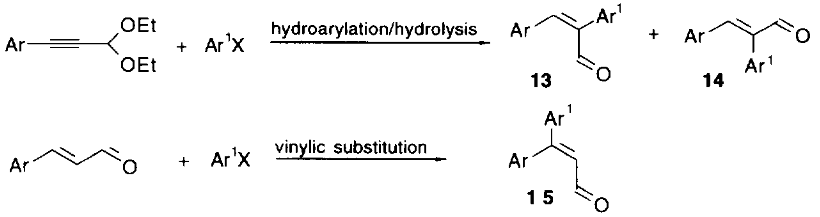
Scheme 4

Table1. Palladium-Catalysed Hydroarylation of 3,3-Diethoxy-1-aryl-1-propynes **9** with *p*-Methoxyphenyl Iodide.[a]

entry	3,3-diethoxy-1-aryl-1-propyne **9**[b,c,d] Ar			reaction time (h)	yield % of **11**[d]
1	C_6H_5	**a**	(75)	20	48
2	*o*-Me-C_6H_4	**b**	(89)	4	56
3	*p*-Me-C_6H_4	**c**	(74)	24	12
4	*o*-MeOCO-C_6H_4	**d**	(82)	3.75	58
5	*p*-MeOCO-C_6H_4	**e**	(74)	8.5	66

[a] Reactions have been carried out at 40 °C in DMF, under an argon atmosphere, by using the following molar ratios: **9**: **10**: $Pd(OAc)_2$: KOOCH = 1 : 2.4: 0.05: 2.4. [b] Compounds **9** have been prepared through the palladium-catalysed coupling of aryl iodides with 3,3-diethoxy-1-propyne in DMF at 25 °C (2-6 h), under an argon atmosphere, by using the following molar ratios: ArI: 3,3-diethoxy-1-propyne: $Pd(OAc)_2(PPh_3)_2$: CuI: Et_2NH = 1: 1: 0.02: 0.04: 10. [c] Figures in parentheses refer to the yield of **9**. [d] Yields are for pure, isolated products.

One-flask Hydroarylation/Hydrolysis of 3,3-Diethoxy-1-aryl-1-propynes 9. Synthesis of α-Substituted-α,β-unsaturated Aldehydes. The hydroarylation derivative **11a** was converted into the corresponding aldehyde **13a**, in 88% yield and with complete retention of configuration, on treatment with 5% TsH in EtOH at 0 °C for 4 h. The whole process (hydroarylation/hydrolysis) provides an interesting approach to the preparation of compounds complementary to the ones that can be prepared through the palladium-catalysed vinylic susbtitution of β-substituted-α,β-enals[10] (Scheme 5).



Scheme 5

Aldehydes **13** can be prepared even through a one-flask process without the isolation of **11**, subjecting to the hydrolysis conditions (5% TsH, EtOH, 0 °C) the crude reaction mixture derived from the hydroarylation step (see Table 2). Following this procedure, variable amounts of stereoisomeric aldehydes **14** have been isolated. Since the observed retention of configuration in the hydrolysis of **11a** at 0 °C would seem to argue against the possible formation of **14** under these conditions, it seems reasonable to envisage that the lack of stereochemistry at the carbon-carbon double bond is predominantly due to the adventitious hydrolysis of the acetal function of **11** that takes place under hydroarylation conditions. On the other hand, the configurational stability of the olefinic system in the conversion of the acetal function into the aldehydic function has been found to decrease by increasing the reaction temperature (Table 2, entries 4 -6) and hydroarylations (and consequently hydrolyses occurring in the hydroarylation step) have been run at 40 °C.

Table 2. One-flask Hydroarylation/Hydrolysis of **9** with *p*-Methoxyphenyl Iodide.[a]

entry	3,3-diethoxy-1-aryl-1-propyne **9** Ar		reaction temperature (hydrolysis)[b] (°C)	reaction time (hydrolysis) (h)	overall yield[c]	aldehyde relative percentages[d] **13**	**14**
1	C_6H_5	**a**	0	7	37	100	-
2	*o*-Me-C_6H_4	**b**	"	6	62	98	2
3	*p*-Me-C_6H_4	**c**	"	6	49	100	-
4	*o*-MeOCO-C_6H_4	**d**	"	4	60	100	-
5	"	**d**	20	4	54	95	5
6	"	**d**	40	1.5	44	85	15
7	*p*-MeOCO-C_6H_4	**e**	0	3	50	90	10

[a] The hydroarylation reactions of **9a-9e** with 4-methoxyphenyl iodide were carried out (15-24 h) on a 0.8-1.2 mmol scale, under an argon atmosphere, at 40 °C in DMF (2 mL) by using the following molar ratios: **9**: 4-methoxyphenyl iodide: KOOCH: $Pd(OAc)_2$ =. 1: 2.4: 2.4: 0.05. [b] Hydrolyses were carried out in EtOH in the presence of 5% TsH. [c] Yields are given for isolated products. [d] **13/14** ratios were calculated by NMR analysis.

Hydroarylation and Hydrovinylation of 3,3-Diethoxy-1-(*o*-acetamidophenyl)-1-propyne (9f). Synthesis of 3-Substituted Quinoline Derivatives - Because the *cis* stereochemistry of the reaction pushes the substituents of the two C_{sp} carbon atoms of the acetylenic system on the same side of the molecule, the present reaction appeared particularly promising for the construction of cyclic derivatives, providing that the aromatic ring of the starting alkyne contains a nucleophilic centre in the *ortho* position. Using 3,3-diethoxy-1-(*o*-acetamidophenyl)-1-propyne **9f** as the starting alkyne (prepared in 85% yield from *o*-acetamidophenyl iodide and 3,3-diethoxy-1-propyne), this strategy to the synthesis of cyclic derivatives has been attempted to develop a new approach to 3-substituted quinoline derivatives (Scheme 6). These compounds have recently been reported to act as potent inhibitors of platelet derived growth factor tyrosine kinase (PDGF-RTK).[22]

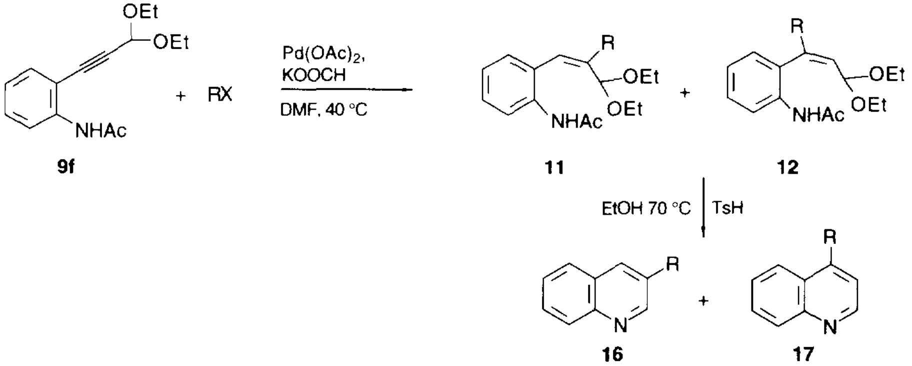
Treatment of **9f** with a variety of aryl and vinyl halides under usual conditions afforded hydroarylation and hydrovinylation products in good yield and high regioselectivity. Preferential formation of **11**, with the new carbon-carbon bond on the carbon bearing the acetal group, was invariably observed (Table 3). Poor results were obtained by using the corresponding *o*-amino derivative, at least in the reaction with *p*-methoxyphenyl iodide.

Table 3. Palladium-Catalysed Hydroarylation and Hydrovinylation of 3,3-Diethoxy-1-(*o*-acetamidophenyl)-1-propyne **9f**.[a]

entry	RX **10**	reaction time (h)		**11**	**12**
				yield (%)[b]	
1	*p*-MeO-C_6H_4-I	6	**f**	58	
2	PhI	6	**g**[c]	75	4
3	*p*-Me-C_6H_4-I	4	**h**[c]	56	5
4	*p*-MeCO-C_6H_4-I	16	**i**	72	
5	*m*-CF_3-C_6H_4-I	36	**j**[c]	62	8
6	*p*-MeOOC-C_6H_4-I	17	**k**[c]	57	6
7	*m*-F-C_6H_4-I	10	**l**[c]	74	4
8	PhCH=CHBr	24	**m**	33	
9	Me_3SiCH=CHBr	7	**n**	31	

[a] Reactions have been carried out at 40 °C in DMF, under an argon atmosphere, by using the following molar ratios: **9f**: **10**: $Pd(OAc)_2$: KOOCH = 1 : 2.4: 0.05: 2.4. [b] Yields refer to isolated products. [c] Isolated as regioisomeric mixture. Yields of **11** and **12** were calculated by NMR analysis.

The cyclization to the quinoline skeleton has been performed by reacting **11**, or the regioisomeric hydroarylation mixture, with TsH 5% in EtOH at 70 °C. As an example, treatment of **11f** with TsH 5% in EtOH at 70 °C for 0.75 h afforded the corresponding quinoline derivative **16f** in 89% yield.



Scheme 6

Quinoline derivatives **16**, however, have more conveniently been prepared from **9f** through a one-flask process, carrying out the cyclization reaction on the crude reaction mixture resulting from the palladium-catalysed hydroarylation or hydrovinylation after extraction and evaporation of the solvent. Regioisomeric quinolines **17** have been obtained in variable amounts, ranging from traces to 10% yield. Our results are summarised in Table 4.

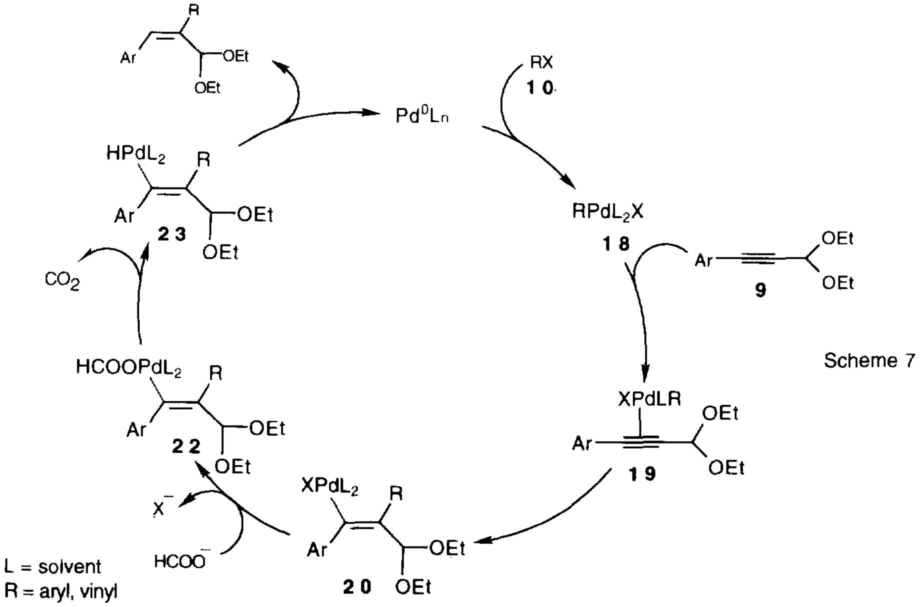
Table 4. One-Flask Preparation of 3-Aryl- and 3-Vinylquinolines **16** from 3,3-Diethoxy-1-(*o*-acetamidophenyl)-1-propyne **9f**.[a,b,c]

entry	aryl and vinyl halide **10**	ligand	reaction time (h)		quinoline **16** overall yield (%)[d]	
1	*p*-MeO-C_6H_4-I	-	7	1	**f**	56
2	PhI	-	8	1.5	**g**	51
3	*p*-Me-C_6H_4-I	-	9	1	**h**	51
4	*p*-MeCO-C_6H_4-I	-	16	0.75	**i**	61 (5)
5	*m*-F_3C-C_6H_4-I	-	22	2	**j**	52
6	*p*-MeOOC-C_6H_4-I	-	15	2	**k**	49
7	*m*-F-C_6H_4-I	-	19	0.75	**l**	54
8	PhCH=CHBr	PPh_3	6	24	**m**	55
9	Me_3SiCH=CHBr	-	7	0.5	**n**	29
10	*p*-H_2N-C_6H_4-I	PPh_3	4	18	**o**	34 (3)
11	*p*-AcNH-C_6H_4-I	-	18	2	**p**	50 (10)
12	*p*-HO-C_6H_4-I	-	16	2	**q**	63
13	*p*-HO-*m*-Me-C_6H_4-I	-	20	2	**r**	45 (6)[e]
14	*m*-$HOCH_2$-C_6H_4-I	-	7.5	2	**s**	65 (5)
15	*m*-O_2N-C_6H_4-I	-	48	1	**t**	46 (6)[e]
16	*m*-$AcNHCH_2$-C_6H_4-I	-	18	4	**u**	41 (6)

[a] Hydroarylation and hydrovinylation reactions have been carried out at 40 °C in DMF, under an argon atmosphere, by using the following molar ratios: **9f**: **10**: $Pd(OAc)_2$: KOOCH = 1 : 2.4: 0.05: 2.4. [b] Cyclization reactions have been carried out at 70 °C, in EtOH, in the presence of TsH (5 mol%). [c] Reaction mixtures were usually purified by column chromatography on silica gel used as it came. [d] Figures in parentheses refer to the yield of regioisomeric quinolines **17**. When quinoline derivatives have been isolated as regioisomeric mixtures, yields have been calculated by NMR analysis. [e] The pure regioisomer **16** was isolated by column chromatography on silica gel heated in the oven at 200 °C overnight.

Discussion

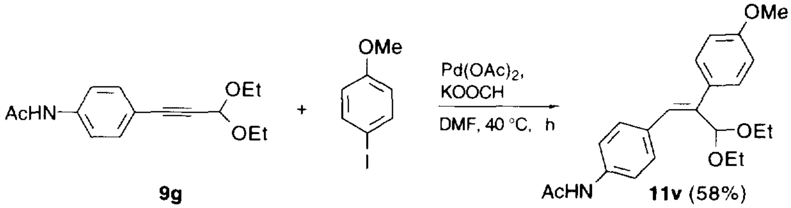
According to our previous studies, the present hydroarylation/hydrovinylation reaction can be supposed to proceed through a) formate induced reduction of $Pd(OAc)_2$ to Pd^0 species, b) stereo- and regioselective addition of the σ-C_{sp^2}-palladium complex, generated *in situ* from unsaturated halides and the palladium



Scheme 7

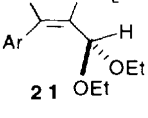
catalyst, to the carbon-carbon triple bond through the intermediacy of the η^2-palladium complex **19**, c) trapping of the resultant σ-vinylpalladium intermediate **20** by the formate anion to give **22**, d) carbon dioxide deinsertion, and e) reductive elimination of a low ligated zero-valent palladium complex[23] that produces the olefinic derivative and regenerates the catalyst (Scheme 7).

On the basis of the generally accepted idea that σ-vinylpalladium intermediates resulting from the carbopalladation of the carbon-carbon triple bond are generated from η^2-palladium complexes with the carbon unit and the acetylenic moiety *cis*[24] and assuming that under our standard conditions the formation of the new carbon-carbon bond is irreversible, the regiochemistry of the reaction ought to be dependent on electronic and steric effects controlling the migration of the organic framework and of the palladium moiety onto the coordinated acetylene. With 3,3-diethoxy-1-(*o*-acetamidophenyl)-1-propyne **9f**, coordination of the *ortho* nitrogen atom to palladium, favouring the formation of **20**, could also be considered. However, the result obtained in reaction of *p*-methoxyphenyl iodide with 3,3-diethoxy-1-(*p*-acetamidophenyl)-1-propyne **9g** (prepared in 78% yield) (Scheme 8), that showed the same regiochemical trend observed in the hydroarylation of the *o*-acetamido derivative, appears to rule out any significant influence of coordinating effects in the carbopalladation of **9f**.



(Scheme 8)

As for the electronic effects, semiempirical calculations made on the starting acetylenic acetals and ketals have shown that the negative charge on the acetylenic carbon bearing acetal and ketal groups are more than twice as high as on the acetylenic carbon linked to the aryl substituent.[25] Therefore, to the extent that the charge distribution in the starting noncoordinated alkyne can be taken as a measure of the charge distribution in the more polarised η^2-palladium complex or, more correctly, in the transition state leading to the σ-vinyl palladium complex (theoretical investigations on the acetylene system have shown that no intermediate is involved in the η^2-to-σ-vinyl conversion),[24b] electronic factors should favour the formation of **21**, in which the palladium is linked to the same atom as the acetal group. The hydroarylation and the hydrovinylation of acetylenic acetals and ketals with aryl and vinyl halides, however, invariably gave rise to the preferential formation of olefinic derivatives generated from the palladium complex **20**. This result suggests that in the present reaction electronic effects are not very important either and that the regiochemical outcome is mainly dependent on steric factors.

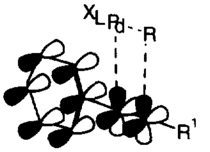


L = solvent
R = aryl, vinyl

21

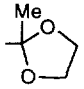
Most probably the addition of the σ-C_{sp^2}-palladium complex **18** to **9** proceeds preferentially through a transition state that minimises steric strain between the aromatic ring of the starting alkyne and the approaching unsaturated framework. The lower regioselectivity observed with the acetylenic ketal **6** (Scheme 3), where an acetylenic carbon bears a substituent the steric hindrance of which can compete more effectively with that of the aromatic ring, is in agreement with this view.

A working hypothesis to account for the effect of the aromatic ring ligated to the acetylenic carbon in dictating the orientation of the carbopalladation step in this reaction[26] is that the conversion of η^2-palladium complexes into the corresponding σ-vinylpalladium complexes occurs through a transition state where steric interactions between nonbonded groups and electronic effects resemble those roughly sketched in **23** (the likely bending of acetylenic substituents is not represented). This spatial arrangement, whereby the plane of the aromatic ring is coplanar, or nearly so, to the plane containing the acetylenic carbons and the palladium atom, could benefit by some overlapping of the aromatic π-electrons with the acetylenic π-electrons orthogonal to those coordinated to palladium. At the same time, it could allow the aromatic ring to provide a steric hindrance higher than that of the acetal substituent, favouring the migration of aryl or vinyl units onto the carbon linked to the acetal substituent.



23

$R^1 = -CH(OEt)_2$,



Experimental Section

Melting points were determined with a Büchi apparatus and are uncorrected. All the starting materials, catalysts, ligands, salts and solvents are commercially available and were used without further purification. Compound **9a** was prepared from phenyl iodide and commercially available 3,3-diethoxy-1-propyne according to reference 20. Reaction products were purified on axially compressed columns [packed with SiO_2 25-40 µm (Macherey Nagel) used as it came] connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/ethyl acetate mixtures. In cases where standard separation conditions led to the isolation of substituted quinolines as regioisomeric mixtures, pure 3-substituted-quinolines were obtained by employing silica gel heated in the oven at 200 °C overnight (see, for example, Table 4, entries 13 and 15). ^1H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra ($CDCl_3$, unless otherwise stated; TMS as internal standard) were recorded with a Bruker AM 200 spectrometer. IR spectra were recorded with a Nicolet 5DX FT/IR spectrometer. MS spectra were recorded with a Hewelett Packard HP 5980A spectrometer equipped with a Data System 5934A.

Preparation of 3,3-Ethylendioxy-1-phenyl-1-butyne (6). A benzene (5 mL) solution of *p*-toluenesulfonic acid (0.132 g, 0.69 mmol), 4-phenyl-3-butyn-2-one (1.0 g, 6.94 mmol), and ethylene glycol (1.93 mL, 34.68 mmol) in a Dean-Stark apparatus was heated at 100 °C with internal stirring for 2 h. During this period the benzene-water azeotrope was slowly removed and benzene was slowly added through a dropping funnel. After the mixture was cooled at room temperature, ethyl acetate and saturated $NaHCO_3$ were added, the organic layer was separated, washed with water, dried (K_2CO_3), and concentrated under reduced pressure. The residue was chromatographed on silica gel eluting with *n*-hexane/ethyl acetate (95/5 v/v) to afford 1.23 g (95%) of the title compound: mp 55-56 °C; IR (nujol) 2230, 859, 773 cm^{-1}; ^1H NMR δ 7.47-7.41 (m, 2 H), 7.34-7.26 (m, 3 H), 4.19-3.99 (m, 4 H), 1.80 (s, 3 H); ^{13}C NMR δ 134.26, 129.27, 129.02, 122.61, 101.80, 87.94, 83.42, 65.33, 27.07; MS (relative intensity) 188 (M^+, 100), 173 (71), 146 (63), 129 (68). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.89; H, 6.45.

General Procedure for the Preparation of 3,3-Diethoxy-1-aryl-1-propynes (9b-g). 3,3-Diethoxy-1-(*o*-Methylphenyl)-1-propyne (9b). To a solution of *o*-methylphenyl iodide (0.400 g, 1.83 mmol) and 3,3-diethoxy-1-propyne (0.235 g, 1.83 mmol) in diethylamine (4 mL) and DMF (1 mL) were added CuI (0.014 g, 0.07 mmol) and bis(triphenylphosphine)palladium diacetate (0.028 g, 0.04 mmol) under argon. The mixture was stirred at room temperature for 2 h. Then, the reaction mixture was diluted with ethyl acetate, washed with water, dried over Na_2SO_4, and evaporated under vacuum. The residue was chromatographed on silica gel eluting with *n*-hexane/ethyl acetate (98/2 v/v) to afford 0.356 g (89%) of **9b**: mp oil; IR (liquid film) 2238, 761 cm^{-1}; ^1H NMR δ 7.94 (dd, J = 7.3 Hz, J = 1.8 Hz, 1 H), 7.50-7.35 (m, 4 H), 5.55 (s, 1 H), 3.92 (s, 3 H), 3.95-3.55 (m, 4 H), 1.27 (t, J = 7.1 Hz, 6 H); ^{13}C NMR δ 134.43, 132.25, 131.56, 130.32, 128.44, 122.30, 91.85, 89.31, 83.64, 60.95, 52.12, 15.11; MS *m/e* (relative intensity) 218 (M^+, 2), 217 (5), 189 (18), 173 (77), 145 (100). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.73; H, 8.27.

The following compounds were prepared and isolated in a similar manner.

3,3-Diethoxy-1-(*p*-methylphenyl)-1-propyne (9c): mp oil; IR (liquid film) 2230, 818 cm^{-1}; ^1H NMR δ 7.36 (d, J = 8.0 Hz, 2 H), 7.10 (d, J = 8.0 Hz, 2 H), 5.47 (s, 1 H), 3.88-3.60 (m, 4 H), 2.33 (s, 3 H), 1.27 (t, J = 7.2 Hz, 6 H); ^{13}C NMR δ 138.96, 131.83, 129.04, 118.81, 91.86, 85.43, 83.72, 60.89, 21.50, 15.15; MS *m/e* (relative intensity) 218 (M^+, 3), 217 (7), 189 (11), 173 (61), 145 (100). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.71; H, 8.28.

3,3-Diethoxy-1-(*o*-carbomethoxyphenyl)-1-propyne (9d): mp oil; IR (liquid film) 2238, 1727, 761 cm^{-1}; ^1H NMR δ 7.42 (d, J = 8.0 Hz, 1 H), 7.28-7.10 (m, 3 H), 5.54 (s, 1 H), 3.88-3.63 (m, 4 H), 2.44 (s, 3 H), 1.26 (t, J = 7.0 Hz, 6 H); ^{13}C NMR δ 140.48, 132.34, 129.42, 126.79, 125.49, 121.72, 91.92, 88.27, 84.15, 80.93, 20.72, 15.17; MS *m/e* (relative intensity) 262 (M^+, 1), 217 (46), 189 (100), 173 (32), 157 (77). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.42; H, 6.89.

3,3-Diethoxy-1-(*p*-carbomethoxyphenyl)-1-propyne (9e): mp oil; IR (liquid film) 2238, 1727, 859, 769 cm^{-1}; ^1H NMR δ 8.00 (d, J = 9.2 Hz, 2 H), 7.55 (d, J = 9.2 Hz, 2 H), 5.50 (s, 1 H), 3.90 (s, 3 H), 3.80 (m, 2 H), 3.70 (m, 2 H), 1.25 (t, J = 6.1 Hz, 6 H); ^{13}C NMR δ 166.36, 131.86, 130.07, 129.39, 126.48, 91.66, 87.19, 84.26, 61.05, 52.25, 15.09; MS *m/e* (relative intensity) 262 (M^+, 1), 217 (72), 189 (100), 157 (14). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.99; H, 6.94.

3,3-Diethoxy-1-(*o*-acetamidophenyl)-1-propyne (9f): mp 101-102 °C; IR (KBr) 3271, 2238, 1663, 761 cm^{-1}; ^1H NMR δ 6.35 (d, J = 4.4 Hz, 1 H), 7.92 (bs, 1 H), 7.45-7.26 (m, 2 H), 7.03 (t, J = 7.5 Hz, 1 H), 5.54 (s, 1 H), 3.82 (m, 2 H), 3.65 (m, 2 H), 2.21 (s, 3 H), 1.29 (t, J = 7.1 Hz, 6 H); ^{13}C NMR δ 168.20, 139.36, 131.76, 130.21, 123.27, 119.38, 110.40, 91.84, 91.73, 80.52, 61.15, 24.78, 15.09; MS *m/e* (relative intensity) 261 (M^+, 9), 216 (89), 188 (72), 160 (75), 146 (100). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33, N, 5.36. Found: C, 69.26; H, 7.35; N, 5.39.

3,3-Diethoxy-1-(*p*-acetamidophenyl)-1-propyne (9g): mp 154-156 °C; IR (KBr) 3255, 2221, 1672, 843, 827, 761 cm^{-1}; ^1H NMR δ 8.03 (bs, 1 H), 7.47 (d, J = 8.7 Hz, 2 H), 7.36 (d, J = 8.7 Hz, 2 H), 5.46 (s, 1 H), 3.87-3.56 (m, 4 H), 2.13 (s, 3 H), 1.25 (t, J = 7.0 Hz, 6 H); ^{13}C NMR δ 168.87, 138.63, 132.71, 119.42, 117.29, 91.89, 85.09, 83.96, 61.08, 24.57, 15.14; MS *m/e* (relative intensity) 261 (M^+, 9), 216 (100), 188 (89), 146 (60). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33, N, 5.36. Found: C, 68.66; H, 7.31; N, 5.33.

General procedure for the Palladium-Catalysed Hydroarylation of 4-Phenyl-3-butyn-2-one, 3,3-Ethylendioxy-1-phenyl-1-butyne (6), and 3,3-Diethoxy-1-aryl-1-propynes (9). 3,3-Diethoxy-2-(*p*-Methoxyphenyl)-1-phenyl-1-propene (11a). To a suspension of 3,3-diethoxy-1-phenyl-1-propyne **9a** (0.150 g, 0.74 mmol), 4-methoxyphenyl iodide (0.413 g, 1.76 mmol) and potassium formate (0.148 g, 1.76 mmol) in DMF (2 mL) was added palladium diacetate (0.008 g, 0.04 mmol) under argon. The mixture was warmed at 40 °C and stirred for 20 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with water, dried over Na_2SO_4, and evaporated under vacuum. The residue was chromatographed on silica gel eluting with *n*-hexane/ ethyl acetate (97 / 3 v /v) to afford 0.100 g (48 %) of **11a**: mp oil; IR (liquid film) 1606, 1516, 827, 761, 736, 704 cm^{-1}; ^1H NMR δ 7.66 (d, J = 8.9 Hz, 2 H), 7.36 (m, 5 H), 6.94 (s, 1 H), 6.88 (d, J = 8.9 Hz, 2 H), 5.29 (s, 1 H), 3.82 (s, 3 H), 3.57 (m, 2 H), 3.42 (m, 2 H), 1.15 (t, J = 6.3 Hz, 6 H); ^{13}C NMR δ 158.94, 139.79, 136.61, 131.56, 131.44, 129.27, 129.11, 127.14, 126.17, 113.32, 101.07,62.60, 55.25, 15.21; MS *m/e* (relative intensity) 312 (M^+, 43), 267 (50), 209 (45), 165 (100). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 77.22; H, 7.76.

The following compounds were prepared and isolated in a similar manner.

(*Z*)-3-(*p*-Methoxyphenyl)-4-phenyl-3-buten-2-one (4): mp 60-61 °C; IR (KBr) 1698, 827, 762 cm^{-1}; ^1H NMR δ 7.35 (m, 7 H), 6.85 (s, 2 H), 3.85 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR δ 207.80, 159.74, 143.31, 135.85, 129.47, 128.62, 128.48, 128.08, 127.84, 127.58, 114.19, 55.35, 31.56; MS *m/e* (relative intensity) 252 (M^+, 67), 209 (100), 194 (30), 165 (46). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.54; H, 6.37.

(*E*)-4-(*p*-Methoxyphenyl)-4-phenyl-but-3-en-2-one (5): mp 79-80 °C; IR (KBr) 1655, 1605, 761, 695 cm^{-1}; ^{1}H NMR δ 7.60 (s, 1H), 7.40-6.85 (m, 9H), 3.85 (s, 3H), 2.35 (s,3H); ^{13}C NMR δ 199.95, 159.27, 140.57, 138.84, 114.53, 55.42, 29.77; MS *m/e* (relative intensity) 252 (M^+, 63), 209 (100), 194 (28), 165 (52). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.57; H, 6.36.

(*Z*)-3,3-Ethylendioxy-2-(*p*-methoxyphenyl)-1-phenyl-1-butene (7): mp oil; IR (liquid film) 1606, 1508, 950, 867, 818, 695 cm^{-1}; ^{1}H NMR δ 7.42-7.25 (m, 7 H), 6.87 (d, J = 8.9 Hz, 2 H), 6.58 (s, 1 H), 3.84 (s, 3 H), 3.79-3.71 (m, 2 H), 3.60-3.54 (m, 2 H), 1.64 (s, 3 H) ; ^{13}C NMR δ 158.95, 143.50, 138.45, 134.93, 132.05, 130.19, 129.98, 127.65, 126.70, 113.30, 109.35, 63.98, 55.44, 26.36; MS *m/e* (relative intensity) 296 (M^+, 45), 210 (46), 165 (100). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.73; H, 6.77.

(*E*)-3,3-Ethylendioxy-1-(*p*-methoxyphenyl)-1-phenyl-1-butene (8): mp oil; IR (liquid film) 1606, 1516, 950, 859 827, 761 cm^{-1}; ^{1}H NMR δ 7.20-7.00 (m, 5 H), 6.97-6.85 (m, 4 H), 6.90 (s, 1 H), 4.10-4.00 (m, 4 H), 3.62 (s, 3 H), 1.50 (s, 3 H); ^{13}C NMR δ 158.91, 141.37, 136.47, 131.06, 130.39, 129.62, 127.99, 126.94, 126.63, 113.98, 109.87, 64.70, 55.25, 24.71; MS *m/e* (relative intensity) 296 (M^+, 55), 210 (48), 165 (100). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.63; H, 6.82.

(*Z*)-3,3-Diethoxy-2-(*p*-methoxyphenyl)-1-(*o*-methylphenyl)-1-propene (11b): mp oil; IR (liquid film) 1688, 1606, 827, 786, 761, 695 cm^{-1}; ^{1}H NMR δ 7.75 (d, J = 9.5 Hz, 2 H), 7.25 (m, 5 H), 6.90 (d, J = 9.5 Hz, 2 H), 5.15 (s, 1 H), 3.80 (s, 3 H), 3.55 (m, 2 H), 3.35 (m, 2 H), 2.35 (s, 3 H), 1.15 (t, J = 6.2 Hz, 6 H); ^{13}C NMR δ 158.94, 139.44, 101.37, 62.63, 56.19, 20.08, 15.17; MS *m/e* (relative intensity) 326 (M^+, 68), 282 (72), 281 (55), 235 (53), 178 (49), 165 (63). Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.64; H, 8.06.

(*Z*)-3,3-Diethoxy-2-(*p*-methoxyphenyl)-1-(*p*-methylphenyl)-1-propene (11c): mp oil; IR (liquid film) 1606, 1516, 827, 730 cm^{-1}; ^{1}H NMR δ 7.65 (d, J = 8.0 Hz, 2 H), 7.35-7.10 (m, 4 H), 7.10 (s, 1 H), 6.80 (d, J = 8.0 Hz, 2 H), 5.30 (s, 1 H), 3.90 (s, 3 H), 3.60 (m, 2 H), 3.40 (m, 2 H), 2.40 (s, 3 H), 1.15 (t, J = 6.0 Hz, 6 H); ^{13}C NMR δ 156.66, 139.24, 101.17, 62.57, 55.36, 21.27, 15.24; MS *m/e* (relative intensity) 326 (M^+, 100), 282 (70), 281 (75), 235 (57), 165 (100). Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.66; H, 8.05.

(*Z*)-3,3-Diethoxy-2-(*p*-methoxyphenyl)-1-(*o*-carbomethoxyphenyl)-1-propene (11d): mp oil; IR (liquid film) 1726 cm^{-1}; ^{1}H NMR δ 8.05 (d, J = 8.5 Hz, 1 H), 7.75 (d, J = 9.0 Hz, 2 H), 7.50-7.30 (m, 2 H), 7.25 (d, J = 8.5 Hz, 1 H), 6.90 (d, J = 9.0 Hz, 2 H), 5.00 (s, 1 H), 3.90 (s, 3 H), 3.80 (s, 3 H), 3.50 (m, 2 H), 3.30 (m, 2 H), 1.10 (t, J = 5.8 Hz, 6 H); ^{13}C NMR δ 192.13, 101.38, 62.44, 55.31, 52.37, 15.13; MS *m/e* (relative intensity) 370 (M^+, 8), 326 (19), 267 (100), 235 (39), 165 (37). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 70.95; H, 7.05.

(*Z*)-3,3-Diethoxy-2-(*p*-methoxyphenyl)-1-(*p*-carbomethoxyphenyl)-1-propene (11e): mp oil; IR (liquid film) 1724 cm^{-1};^{1}H NMR δ 8.05 (d, J = 8.6 Hz, 2 H), 7.65 (d, J = 8.6 Hz, 2 H), 7.45 (d, J = 8.6 Hz, 2 H), 6.94 (s, 1 H), 6.85 (d, J = 8.6 Hz, 2 H), 5.20 (s, 1 H), 3.95 (s, 3 H), 3.85 (s, 3 H), 3.60 (m, 2 H), 3.40 (m, 2 H), 1.15 (t, J = 5.8 Hz, 6 H); ^{13}C NMR δ 166.50, 159.10, 110.93, 62.62, 55.12, 52.04, 15.10; MS *m/e* (relative intensity) 370 (M^+, 43), 326 (44), 267 (39), 237 (39), 165 (100). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 71.70; H, 7.09.

(*Z*)-3,3-Diethoxy-2-(*p*-methoxyphenyl)-1-(*o*-acetamidophenyl)-1-propene (11f): mp oil; IR (liquid film) 3310, 1671 cm^{-1};^{1}H NMR δ 8.12 (d, J = 9.4 Hz, 1 H), 7.93 (bs, 1 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.34-7.04 (m, 3 H), 6.91 (d, J = 8.6 Hz, 2 H), 6.76 (s, 1 H), 5.01 (s, 1 H), 3.82 (s, 3 H), 3.55 (m, 2 H), 3.32 (m, 2 H), 2.13 (s, 3 H), 1.10 (t, J = 7.4 Hz, 6 H); ^{13}C NMR δ 166.65, 101.34, 63.11, 55.27, 24.59, 15.04; MS *m/e* (relative intensity) 369 (M^+, 3), 278 (40), 236 (100). Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52; H, 7.37; N, 3.79. Found: C, 71.90; H, 7.39; N, 3.81.

(*Z*)-3,3-Diethoxy-2-phenyl-1-(*o*-acetamidophenyl)-1-propene (11g) and (*E*)-3,3-Diethoxy-1-phenyl-1-(*o*-acetamidophenyl)-1-propene (12g): IR (KBr) 3304, 1672, 910, 761, 736 cm^{-1};^{1}H

NMR δ 8.10 (d, J = 8.5 Hz, 1 H), 7.95 (bs, 1 H), 7.73-7.12 (m, 8 H), 6.80 (s, 0.95 H), 6.42 (d, J = 9.0 Hz, 0.05 H), 5.02 (s, 0.95 H), 4.70 (d, J = 9.0 Hz, 0.05 H), 3.55 (m, 2 H), 3.33 (m, 2 H), 2.13 (s, 3 H), 1.10 (t, J = 7.0 Hz, 6 H); ^{13}C NMR δ 168.37, 143.47, 138.09, 135.63, 101.32, 63.20, 24.63, 15.03; MS *m/e* (relative intensity) 294 (61), 248 (18), 206 (100).

(*Z*)-3,3-Diethoxy-2-(*p*-methylphenyl)-1-(*o*-acetamidophenyl)-1-propene (11h) and (*E*)-3,3-Diethoxy-1-(*p*-methylphenyl)-1-(*o*-acetamidophenyl)-1-propene (12h): IR (liquid film) 3296, 1672, 910, 810, 761, 736 cm^{-1};^{1}H NMR δ 8.15 (d, J = 8.6 Hz, 1 H), 7.95 (bs, 1 H), 7.60 (d, J = 8.2 Hz, 2 H), 7.45-7.00 (m, 5 H), 6.77 (s, 0.92 H), 6.44 (d, J = 7.6 Hz, 0.08 H), 5.08 (s, 0.92 H), 4.75 (d, J = 7.6 Hz, 0.08 H), 3.55 (m, 2 H), 3.33 (m, 2 H), 2.37 (s, 3 H), 2.12 (s, 3 H), 1.09 (t, J = 6.4 Hz, 6 H); ^{13}C NMR δ 168.38, 143.09, 137.68, 101.30, 63.12, 24.57, 21.20, 15.00; MS *m/e* (relative intensity) 307 (3), 262 (37), 220 (100).

(*Z*)-3,3-Diethoxy-2-(*p*-acetylphenyl)-1-(*o*-acetamidophenyl)-1-propene (11i): mp oil; IR (liquid film) 3291, 1715, 1672 cm^{-1};^{1}H NMR δ 7.92 (bs, 1 H), 7.95 - 7.70 (m, 4 H), 7.42 - 7.04 (m, 4 H), 6.82 (s, 1 H), 5.08 (s, 1 H), 3.55 (m, 2 H), 3.35 (m, 2 H), 2.61 (s, 3 H), 1.11 (t, J = 7.1 Hz, 6 H); ^{13}C NMR δ 196.08, 174.61, 101.05, 63.28, 26.65, 20.84, 15.02; MS *m/e* (relative intensity) 336 (64), 290 (21), 248 (100). Anal. Calcd for $C_{23}H_{27}NO_4$: C, 72.42; H, 7.13; N, 3.67. Found: C, 72.81; H, 7.18; N, 3.69.

(*Z*)-3,3-Diethoxy-2-(*m*-trifluoromethylphenyl)-1-(*o*-acetamidophenyl)-1-propene (11j) and (*E*)-3,3-Diethoxy-1-(*m*-trifluoromethylphenyl)-1-(*o*-acetamidophenyl)-1-propene (12j): IR (liquid film) 3304, 1672, 802, 761, 704 cm^{-1}; ^{1}H NMR δ 8.10 (d, J = 8.6 Hz, 1 H), 8.00 - 7.10 (m, 8 H), 6.84 (s, 0.88 H), 6.45 (d, J = 9.0 Hz, 0.12 H), 5.04 (s, 0.88 H), 4.70 (d, J = 9.0 Hz, 0.12 H), 3.54 (m, 2 H), 3.35 (m, 2 H), 2.15 (s, 3 H), 1.11 (t, J = 7.1 Hz, 6 H); ^{13}C NMR δ 168.40, 142.13, 139.98, 100.86, 63.23, 53.41, 30.90, 24.47, 14.95; MS *m/e* (relative intensity) 362 (73), 316 (25) 274 (100).

(*Z*)-3,3-Diethoxy-2-(*p*-carbomethoxyphenyl)-1-(*o*-acetamidophenyl)-1-propene (11k) and (*E*)-3,3-Diethoxy-1-(*p*-carbomethoxyphenyl)-1-(*o*-acetamidophenyl)-1-propene (12k): IR (liquid film) 3350, 1721, 1696, 786, 761 cm^{-1};^{1}H NMR δ 8.30-8.70 (m, 5 H), 7.50-7.05 (m, 4 H), 6.68 (s, 0.9 H), 6.50 (d, J = 7.7 Hz, 0.1 H), 4.65 (d, J = 7.7 Hz, 0.1 H), 3.94 (s, 3 H), 3.53 (m, 2 H), 3.34 (m, 2 H), 2.15 (s, 3 H), 1.10 (t, J = 7.0 Hz, 6 H); ^{13}C NMR δ 168.65, 166.95, 101.00, 63.15, 52.05, 24.30, 14.96; MS *m/e* (relative intensity) 352 (60), 306 (22), 264 (100).

(*Z*)-3,3-Diethoxy-2-(*m*-fluorophenyl)-1-(*o*-acetamidophenyl)-1-propene (11l) and (*E*)-3,3-Diethoxy-1-(*m*-fluorophenyl)-1-(*o*-acetamidophenyl)-1-propene (12l): IR (liquid film) 3288, 1663, 909, 786, 761, 695 cm^{-1};^{1}H NMR δ 8.10 (d, J = 8.5 Hz, 1 H), 7.87 (bs, 1 H), 7.50-6.80 (m, 7 H), 6.81 (s, 0.94 H), 6.40 (d, J = 7.6 Hz, 0.06 H), 5.01 (s, 0.94 H), 4.67 (d, J= 7.6 Hz, 0.06 H), 3.55 (m, 2 H), 3.34 (m, 2 H), 2.14 (s, 3 H), 1.11 (t, J = 7.1 Hz, 6 H); ^{13}C NMR δ 166.46, 101.06, 63.28, 24.53, 18.41, 15.01; MS (relative intensity) 312 (84), 266 (24), 224 (100).

(*Z*)-3,3-Diethoxy-2-[(*E*)-2-Phenylethenyl]-1-(*o*-acetamidophenyl)-1-propene (11m): mp oil; IR (liquid film) 3337, 1672, 753 cm^{-1}; ^{1}H NMR δ 8.05 (d, J = 9.0 Hz, 1 H), 7.65 (bs, 1 H), 7.50-7.00 (m, 9 H), 6.80 (d, J = 17.5 Hz, 1 H), 6.75 (s, 1 H), 4.95 (s, 1 H), 3.60 (m, 2 H), 3.35 (m, 2 H), 2.15 (s, 3 H), 1.10 (t, J = 7.0 Hz, 6 H); ^{13}C NMR δ 169.16, 101.08, 63.73, 25.30, 15.78; MS *m/e* (relative intensity) 365 (M$^+$, 7), 319 (9), 274 (15), 232 (100). Anal. Calcd for $C_{23}H_{27}NO_3$: C, 75.59; H, 7.45; N, 3.83. Found: C, 75.22; H, 7.42; N, 3.81.

3,3-Diethoxy-2-[(*E*)-2-trimethylsilylethenyl]-1-(*o*-acetamidophenyl)-1-propene (11n): mp oil; IR (liquid film) 3304, 1671, 867, 760 cm^{-1}; ^{1}H NMR δ 8.209-8.00 (m, 1 H), 7.70 (bs, 1 H), 7.60-7.00 (m, 3 H), 6.65 (s, 1 H), 6.62 (d, J = 19.0 Hz, 1 H), 6.45 (d, J = 19.0 Hz, 1 H), 4.87 (s, 1 H), 3.65-3.25 (m, 4 H), 2.15 (s, 3 H), 1.23 (t, J = 7.0 Hz, 3 H), 1.11 (t, J = 7.0 Hz, 3 H), 0.13 (s, 9 H); ^{13}C NMR δ 166.88, 142.97, 141.31, 133.82, 129.62, 100.98, 63.72, 24.80, 15.03, – 1.24; MS *m/e* (relative intensity) 361 (M$^+$, 2), 286 (16), 267 (59), 228 (100). Anal. Calcd for $C_{20}H_{31}NO_3Si$: C, 66.44 H, 8.64; N, 3.87. Found: C, 66.73; H, 8.67; N, 3.89.

3,3-Diethoxy-2-(*p*-methoxyphenyl)-1-(*p*-acetamidophenyl)-1-propene (11v): mp 125-126 °C; IR (KBr) 3295, 1672, 843 cm^{-1}; ^{1}H NMR δ 7.66 (bs, 1 H), 7.64 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.30 (s, 1 H), 3.80 (s, 3 H), 3.57-3.40 (m, 4 H), 2.16 (s, 3 H), 1.14 (t, J = 7.0 Hz, 6 H); ^{13}C NMR δ 168.83, 158.84, 139.40, 101.11, 62.63, 55.20, 24.49, 15.19; MS *m/e* (relative intensity) 369 (M$^+$, 18), 324 (14), 295 (24), 236 (26), 103 100). Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52 H, 7.37; N, 3.79. Found: C, 71.18; H, 7.35; N, 3.77.

One-flask Hydroarylation/Hydrolysis of 3,3-Diethoxy-1-aryl-1-propynes (9). (*Z*)-3-(*p*-Methylphenyl)-2-(*p*-methoxyphenyl)-2-propenal (13c) . To a suspension of 3,3-diethoxy-1-(*p*-methylphenyl)-1-propyne **9c** (0.150 g, 0.69 mmol), *p*-methoxyphenyl iodide (0.387 g, 1.66 mmol) and potassium formate (0.139 g, 1.66 mmol) in DMF (2.5 mL) was added palladium diacetate (0.008 g, 0.034 mmol) under argon. The mixture was warmed at 40 °C and stirred for 24 h. After cooling, ethyl acetate and water were added and the organic layer was separated, washed with water, dried over Na_2SO_4 and concentrated at reduced pressure. The residue was diluted with 2 mL of EtOH, cooled at 0 °C, added of 0.07 g of TsH, and stirred at 0 °C for 6 h. It was then worked-up as usual. After chromatography on silica gel, using *n*-hexane/ethyl acetate (90/10 v/v) as the eluant, 0.085 g (49% yield) of the aldehyde **13c** were isolated as a white solid: mp 106-108 °C; IR (KBr) 2935, 1680, 827 cm^{-1};^1H NMR δ 10.10 (s, 1 H), 7.80 (s, 1 H), 7.42-7.22 (m, 6 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.84 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR δ 192.65, 159.82, 146.17, 140.10, 139.90, 113.89, 55.38, 21.47; MS *m/e* (relative intensity) 252 (M$^+$, 100), 237 (52), 209 (44), 165 (46). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.30; H, 6.42.

The following aldehydes were prepared and isolated in a similar manner.

(*Z*)-3-Phenyl-2-(*p*-methoxyphenyl)-prop-2-enal (13a): mp 114-115 °C; IR (KBr) 1672, 1605, 827, 769, 712, 695 cm^{-1};^1H NMR δ 10.06 (s, 1 H), 7.80 (s, 1 H), 7.45-7.33 (m, 7 H), 6.91 (d, J = 6.7 Hz, 2 H), 3.81 (s, 3 H); ^{13}C NMR δ 192.66, 159.85, 146.01, 140.58, 55.37; MS *m/e* (relative intensity) 238 (M$^+$, 100), 210 (19), 209 (55), 195 (21), 194 (34), 165 (65). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.29; H, 5.90.

(*E/Z*)-3-(*o*-Methylphenyl)-2-(*p*-methoxyphenyl)-2-propenal (14b/13b): IR (KBr) 2844, 1680, 826, 761 cm^{-1};^1H NMR δ 9.98 (s, 0.98 H), 9.90 (s, 0.02 H), 7.90 (s, 1 H), 7.44 (d, J = 6.7 Hz, 2 H), 7.36-7.20 (m, 5 H), 6.99 (d, J = 6.7 Hz, 2 H), 3.85 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR δ 192.71, 166.06, 159.93, 145.66, 113.92, 59.83, 55.40; MS *m/e* (relative intensity) 252 (M$^+$, 49), 237 (100), 209 (24), 165 (27), 115 (53).

(*Z*)-3-(*o*-Carbomethoxyphenyl)-2-(*p*-methoxyphenyl)-2-propenal (13d): mp 93-94 °C; IR (KBr) 1712, 1663, 769 cm^{-1};^1H NMR δ 9.87 (s, 1 H), 8.32 (s, 1 H), 8.13 (dd, J = 7.4 Hz, J = 1.1 Hz, 1 H), 7.61-7.20 (m, 4 H), 6.81 (d, J = 8.6 Hz, 2 H), 3.96 (s, 3 H), 3.77 (s, 3 H); ^{13}C NMR δ 192.16, 166.71, 159.78, 147.47, 113.83, 55.36, 52.40; MS *m/e* (relative intensity) 296 (M$^+$, 15), 267 (100), 235 (75), 165 (40). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.32; H, 5.46.

(*E/Z*)-3-(*p*-Carbomethoxyphenyl)-2-(*p*-methoxyphenyl)-2-propenal (14e/13e): IR (liquid film) 1729, 1671, 1655, 827, 802, 769 cm^{-1};^1H NMR δ 10.08 (s, 0.88 H), 9.87 (s, 0.12 H), 8.10 (d, J = 8.2 Hz, 2 H), 7.81 (s, 1 H), 7.52-7.37 (m, 4 H), 6.95 (d, J = 8.6 Hz, 2 H), 3.84 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR δ 192.19, 165.97, 160.13, 144.13, 113.96, 61.33, 55.38, 53.47; MS *m/e* (relative intensity) 296 (M$^+$, 100), 281 (98), 267 (32), 237 (87), 209 (66), 165 (85).

One-flask Preparation of 3-Aryl and 3-Vinylquinolines (16) from 3,3-Diethoxy-1-(*o*-acetamidophenyl)-1-propyne (9f). 3-(*p*-Methoxyphenyl)-quinoline (16f). To a suspension of 3,3-diethoxy-1-(*o*-acetamidophenyl)-1-propyne **9f** (0.200 g, 0.77 mmol), *p*-methoxyphenyl iodide (0.430 g, 1.84 mmol) and potassium formate (0.155 g, 1.84 mmol) in DMF (2.5 mL) was added palladium diacetate (0.009 g, 0.004 mmol) under argon. The mixture was warmed at 40 °C and stirred for 7 h. After extraction as usual and evaporation of the solvent, the crude mixture was diluted with 2.5 mL of EtOH, added of TsH (0.007 g, 0.04 mmol), warmed at 70 °C and stirred for 1 h. It was then worked-up as usual and chromatographed on silica gel, eluting with *n*-hexane/ethyl acetate (70/30 v/v) to afford 0.101 g (56% yield) of **16f** as a white solid: mp 78-79 °C; IR (KBr) 1606, 827, 786, 744 cm^{-1} ; ^1H NMR δ 9.15 (d, J = 1.3 Hz, 1H), 8.21 (d, J = 1.3 Hz, 1 H), 8.15 (d, J = 8.5 Hz, 1 H), 7.81 (d, J = 8.5 Hz, 1 H), 7.75-7.40 (m, 4 H), 7.02 (d, J = 9.0 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR δ 159.76, 149.77, 146.97, 133.44, 132.34, 130.21, 55.37; MS *m/e* (relative intensity) 235 (M$^+$, 100), 220 (54), 192 (28). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 82.08; H, 5.59; N, 5.98.

The following quinoline derivatives were prepared and isolated in a similar manner.

3-Phenylquinoline (16g): mp 43-44 °C; IR (KBr) 1491, 1458, 949, 908,818, 785, 752 cm^{-1}; ^{1}H NMR δ 9.17 (d, J = 2.0 Hz, 1 H), 8.27 (d, J = 2.0 Hz, 1 H), 8.14 (d, J = 8.2 Hz, 1 H), 7.86 (d, J = 8.2 Hz, 1 H), 7.75-7.30 (m, 7 H); ^{13}C NMR δ 149.91, 147.31, 137.64, 133.80, 133.20; MS *m/e* (relative intensity) 205 (M$^+$, 100), 204 (55). Anal. Calcd for $C_{15}H_{11}N$: C, 87.77 H, 5.40; N, 6.82. Found: C, 87.39; H, 5.38; N, 6.79.

3-(*p*-Methylphenyl)-quinoline (16h): mp 72-73 °C; IR (KBr) 1491, 957, 900, 786, 761 cm^{-1}; ^{1}H NMR δ 9.16 (d, J = 2.0 Hz, 1 H), 1.24 (d, J = 2.0 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.75-7.25 (m, 6 H), 2.42 (s, 3 H); ^{13}C NMR δ 149.89, 147.15,136.04, 134.91, 21.17; MS *m/e* (relative intensity) 219 (M$^+$, 100), 204 (11). Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.10; H, 5.96; N, 6.36.

3-(*p*-Acetylphenyl)-quinoline (16i) and 4-(*p*-Acetylphenyl)-quinoline (17i): IR (KBr) 1680, 1597, 1031, 827, 753 cm^{-1}; ^{1}H NMR δ 8.32 (s, 0.92 H), 8.95 (d, J = 6.3 Hz, 0.08 H), 8.77 (s, 0.92 H), 8.65-8.25 (m, 6 H), 7.90 -7.76 (m, 1 H), 7.75-7.55 (m, 1 H), 7.50 (d, J = 6.3 Hz, 0.08 H), 2.65 (s, 3 H); ^{13}C NMR δ 197.55, 149.31, 147.52, 142.30, 26.71; MS *m/e* (relative intensity) 247 (M$^+$, 63), 232 (100), 204 (48).

3-(*m*-Trifluoromethylphenyl)-quinoline (16j): mp 86-87 °C; IR (KBr) 892, 807, 784, 753, 707 cm^{-1}; ^{1}H NMR δ 8.16 (d, J = 2.0 Hz, 1 H), 8.31 (d, J = 2.0 Hz, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 7.95 (s, 1 H), 7.92-7.55 (m, 6 H); ^{13}C NMR δ 149.30, 147.56,136.74, 133.80; MS *m/e* (relative intensity) 273 (M$^+$, 100), 204 (22). Anal. Calcd for $C_{16}H_{10}F_3N$: C, 70.33; H, 3.69; N, 5.13. Found: C, 70.63; H, 3.70; N, 5.15.

3-(*p*-Carbomethoxyphenyl)-quinoline (16k): mp 120-121 °C; IR (KBr) 1721, 1606, 1278, 851, 789, 703 cm^{-1}; ^{1}H NMR δ 8.19 (s, 1 H), 8.35 (s, 1 H), 8.20-8.10 (m, 3 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.85-7.75 (m, 3 H), 7.55 (t, J = 8.0 Hz, 1 H), 3.96 (s, 3 H); ^{13}C NMR δ 166.73, 149.31, 142.15, 133.95, 52.27; MS *m/e* (relative intensity) 263 (M$^+$, 93), 232 (100), 204 (51). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.94; H, 5.00; N, 5.34.

3-(*m*-Fluorophenyl)-quinoline (16l): mp 75-76°C; IR (KBr) 1581, 876, 786, 744 cm^{-1}; ^{1}H NMR δ 9.12 (s, 1 H), 8.21 (s, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 7.81 (d, J = 8.4 Hz, 1 H), 7.75-7.25 (m, 5 H), 7.20-7.05 (m, 1 H); ^{13}C NMR δ 165.71, 160.82, 149.45, 147.50, 139.95, 133.43, 130.80; MS *m/e* (relative intensity) 223 (M$^+$, 100). Anal. Calcd for $C_{15}H_{10}FN$: C, 80.70; H, 4.51; N, 6.27. Found: C, 81.07; H, 4.53; N, 6.25.

3-[(*E*)-2-Phenylethenyl]-quinoline (16m): mp 90-91 °C; IR (KBr) 1645, 958, 909, 786, 744, 687 cm^{-1}; ^{1}H NMR δ 9.07 (d, J = 1.9 Hz, 1 H), 8.10-8.06 (m, 2 H), 7.70 (d, J = 9.0 Hz, 1 H), 7.70-7.20 (m, 9 H); ^{13}C NMR δ 149.30, 136.34, 132.23, 130.62; MS *m/e* (relative intensity) 231 (M$^+$, 72), 230 (100). Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.70; H, 5.70; N, 6.09.

3-[(*E*)-2-Trimethylsilylethenyl]-quinoline (16n): mp oil ; IR (liquid film) 1245, 982, 867, 745 cm^{-1}; ^{1}H NMR δ 8.87 (d, J = 2.0 Hz, 1 H), 7.90-7.80 (m, 2 H), 7.55 (d, J = 9.0 Hz, 1 H), 7.45 (dt, J = 6.0 Hz, J = 2.0 Hz, 1 H), 6.80 (d, J = 18.0 Hz, 1 H), 6.50 (d, J = 18.0 Hz, 1 H), 0.01 (s, 9 H); ^{13}C NMR δ 141.46, 134.40, 133.91, 130.63; MS *m/e* (relative intensity) 227 (M$^+$, 45), 226 (59), 212 (100). Anal. Calcd for $C_{14}H_{17}NSi$: C, 73.95; H, 7.54; N, 6.16. Found: C, 73.59; H, 7.51; N, 6.12.

3-(*p*-Aminophenyl)-quinoline (16o) and 4-(*p*-Aminophenyl)-quinoline (17o): IR (KBr) 3443, 3320, 3205, 1605, 957, 826, 752 cm^{-1}; ^{1}H NMR δ 9.15 (s, 0.91 H), 8.90 (s, 0.09 H), 8.20-7.25 (m, 7 H), 6.79 (d, J = 11.9 Hz, 2 H), 4.35 (bs, 1.82 H), 2.17 (bs, 0.18 H); ^{13}C NMR δ 149.66, 149.59, 146.73, 146. 47, 131.83, 130.75; MS *m/e* (relative intensity) 220 (M$^+$, 100).

3-(*p*-Acetamidophenyl)-quinoline (16p) and 4-(*p*-Acetamidophenyl)-quinoline (17p): IR (KBr) 3238, 1663, 827, 753 cm^{-1}; ^{1}H NMR δ 9.14 (d, J = 2.0 Hz, 0.83 H), 8.92 (d, J = 4.5 Hz, 0.17 H), 8.27 (d, J = 2.0 Hz, 0.83 H), 8.20-7.45 (m, 9 H), 7.32 (d, J = 4.5 Hz, 0.17 H), 2.24 (s, 3 H); ^{13}C NMR δ 168.65, 149.57, 147.06, 138.20, 133.52, 132.93, 130.27, 24.66; MS *m/e* (relative intensity) 262 (M$^+$, 45), 220 (100).

3-(*p*-Hydroxyphenyl)-quinoline (16q): mp 221-222 °C; IR (KBr) 3156, 1606, 974, 787, 744 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.20 (d, J = 1.9 Hz, 1 H), 8.54 (d, J = 1.9 Hz, 1 H), 8.05 (d, J = 8.5 Hz, 2 H), 7.85-7.50 (m, 4 H), 6.99 (d, J = 8.5 Hz, 2 H), 2.58 (s, 1 H); ^{13}C NMR δ 157.65, 149.11, 145.96, 132.85; MS *m/e* (relative intensity) 221 (M$^+$, 100), 220 (27). Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.08; H, 4.99; N, 6.29.

3-(*p*-Hydroxy-*m*-methylphenyl)-quinoline (16r): mp 140-141 °C; IR (KBr) 3042, 2916, 1606, 1493, 1268, 1123, 829, 741 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.66 (s, 1 H), 9.21 (d, J = 2.0 Hz, 1 H), 8.50 (d, J = 2.0 Hz, 1H), 8.04-7.98 (m, 2 H), 7.75-7.52 (m, 4 H), 6.96 (d, J = 8.2 Hz, 1 H), 2.24 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 155.99, 149.38, 146.31, 131.20, 129.42, 128.88, 128.63, 128.16, 127.50, 126.86, 125.55, 124.85, 115.32, 16.15; MS *m/e* (relative intensity) 235 (M$^+$, 100), 220 (8). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 82.02; H, 5.59; N, 5.97.

3-(*m*-Hydroxymethylphenyl)-quinoline (16s) and 4-(*m*-Hydroxymethylphenyl)-quinoline (17s): IR (KBr) 3263, 794, 753, 703 cm^{-1}; ^{1}H NMR δ 8.86 (d, J = 2.0 Hz, 0.93 H), 8.67 (d, J = 5.3 Hz, 0.07 H), 8.11 (d, J = 2.0 Hz, 0.93 H), 8.05-7.20 (m, 8 H), 7.10 (d, J = 5.3 Hz, 0.12 H), 4.72 (s, 2 H), 3.59 (bs, 1 H); ^{13}C NMR δ 149.39, 149.34, 146.69, 142.63, 137.53, 133.64, 64.54; MS *m/e* (relative intensity) 235 (M$^+$, 100), 217 (17), 206 (50).

3-(*m*-Nitrophenyl)-quinoline (16t): mp 162-163 °C; IR (KBr) 1532, 1491, 1352, 884, 744, 687 cm^{-1}; ^{1}H NMR δ 9.16 (d, J = 2.2 Hz, 1 H), 8.54 (d, J = 1.6 Hz, 1 H), 8.35 (d, J = 1.8 Hz, 1 H), 8.29-7.57 (m, 7 H); ^{13}C NMR δ 148.88, 148.76, 147.68, 139.46, 133.80, 133.10, 131.21, 130.12, 129.20, 128.04, 127.57, 127.41, 122.70, 122.07; MS *m/e* (relative intensity) 250 (M$^+$, 100), 204 (78), 176 (25). Anal. Calcd for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03; N, 11.19. Found: C, 71.65; H, 4.04; N, 11.16.

3-(*m*-Acetamidomethylphenyl)-quinoline (16u) and 4-(*m*-Acetamidomethylphenyl)-quinoline (17u): IR (KBr) 3296, 1647, 1540, 802, 744, 704 cm^{-1}; ^{1}H NMR δ 9.25 (d, J = 2.2 Hz, 0.88 H), 8.95 (d, J = 5.3 Hz, 0.12 H), 8.65 (d, J = 2.2 Hz, 0.88 H), 8.50-8.35 (m, 1 H), 8.10 (d, j = 8.0 Hz, 1 H), 8.00-7.30 (m, 7.12 H), 4.38 (d, J = 6.4 Hz, 2 H), 1.92 (s, 3 H); ^{13}C NMR δ 170.36, 149.60, 147.21, 139.56, 138.08, 133.38, 129.57, 43.58, 23.22; MS *m/e* (relative intensity) 276 (M$^+$, 72), 233 (100), 217 (46).

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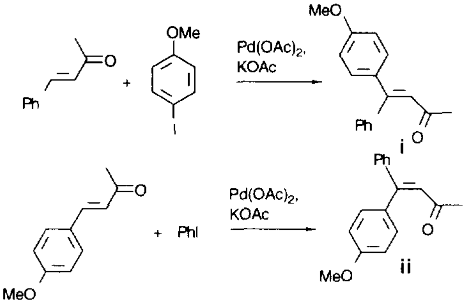
9. The regio- and stereochemistry of **4** and **5** was assigned on the basis of NMR and MS data and of chemical evidence. MS and NMR data suggested that **4** and **5** were hydroarylation products. None of them, however, resulted to be the hydroarylation derivative with the added aryl unit on the β-carbon, *i.e.* (*E*)-4-(*p*-methoxyphenyl)-4-phenyl-3-buten-2-one **i** or (*Z*)-4-(*p*-methoxyphenyl)-4-phenyl-3-buten-2-one **ii**.



This was unambiguously proved by comparison of **4** and **5** with authentic specimens of **i**[10] and **ii**[11] prepared through palladium-catalysed vinylic substitution reactions. Therefore, we inferred that **4** and **5** were the hydroarylation products with the added aryl unit on the carbon bearing the carbonyl group. The stereochemistry of **5** was assigned on the basis of a NOE study, which showed that the vinyl proton and the acyl group are *cis* (irradiation of the vinyl proton led to the enhancement of the methyl group). Compound **4**, whose NOE study was prevented by the close chemical shift of the vinylic and aromatic protons, was assumed to have the vinyl proton and the carbonyl group *trans*.

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11. (*Z*)-4-(*p* -methoxyphenyl)-4-phenyl-3-buten-2-one **ii** was prepared in 30% yield through the palladium-catalysed reaction of 4-(*p*-methoxyphenyl)-4-buten-2-one with phenyl iodide according to the procedure described in reference 12: mp oil; IR (liquid film) 1655, 835, 761, 695; ^{1}H NMR δ 7.36 (m, 5 H), 7.18 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 6.54 (s, 1 H), 3.89 s, 3 H), 1.95 (s, 3 H); ^{13}C NMR δ 200.56, 160.27, 154.06, 141.28, 113.78, 55.29, 30.31; MS *m/e* (relative intensity) 252 (M$^+$, 74), 251 (96), 237 (100), 194 (29), 165 (65), 135 (67). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.78; H, 5.90.
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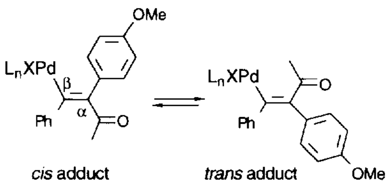
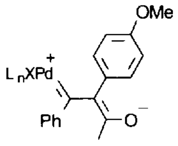
15. As the observed general predominance of *cis* hydroarylation/hydrovinylation products argues against the existence of a direct *trans* addition pathway paralleling the *cis* addition pathway, the appearance of both *E* and *Z* isomers of the products following the carbopalladation step should involve the formation of a *cis* addition intermediate capable of rotation about the C_α-C_β bond. According to Alper et al.,[16a] a possible rationale for this *cis-trans* isomerization of the addition intermediate could involve contributions from zwitterionic resonance forms of type **iii**, derived from the formal donation of an electron pair by a d^8 palladium centre.



cis adduct *trans* adduct



iii

The carbonyl group could play a pivotal role in lowering the C_α-C_β bond order to the point needed for the rotation that results in the formation of the *trans* addition product. In the absence of the carbonyl group, less or no *trans* isomer would be expected; this is what we have found in the present reaction. *Cis-trans* isomerization of σ-vinyl ligands has also been invoked by Werner et al.[17] (osmium complexes), Bergman et al.[18] (nickel complexes), and Hubbard et al.[19] (ruthenium complexes) to account for the formation of *trans* addition derivatives.

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23. Even though the low ligated zero-valent palladium complex has been represented as Pd^0L_n in Scheme 7, it seems reasonable to suppose that under our conditions (in the absence of phosphine and other strong ligands) the active palladium(0) species are stabilised by coordination to the acetylenic π-electrons. For example, the palladium catalyst was found to precipitate very quickly as a dark powder when diphenylacetylene was slowly added to a dimethylformamide solution containing a vinyl triflate, catalytic amounts of a palladium catalyst, and potassium formate (unpublished results).
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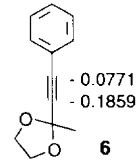
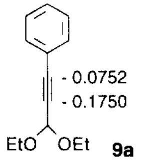
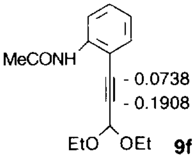
25. Mopac 6.0 data for acetylenic carbons of **6**, **9a** and **9f** using the Hamiltonian AM 1 of substructures with optimised bond lengths, bond angles, and torsional angles are as follows.



6



9a



9f

26. The same pronounced directing effect of the aryl group has been observed in other palladium-catalysed additions of aryl halides to 1-phenyl-1-propyne (Ph *vs.* Me).[6a,e, 7,13b]

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