Tetrahedron Vol. 47, No 32, pp. 6449-6456, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

Preparative and Regiochemical Aspects of the Palladium-Catalyzed Carbonylative Coupling of 2-Hydroxyaryl Iodides with Ethynylarenes

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(*Received in UK* 15 *March* 1991)

Abstract: The title reaction has been conveniently carried out in DMF at 60°C under 1 atm of CO pressure using DBU as the base and $Pd(OAc)_2(DPPF)_2$ as the catalyst to afford generally mixtures of flavones 4 and aurones 5 in varying yields, depending on the substituents in the both reactants. Factors controlling the regioselectivity for 4 or 5 formation in this and in similar, previously reported, coupling procedures have been examined.

The discovery in 1981 that aryl halides reacted with carbon monoxide and terminal acetylenes in the presence of triethylamine and a palladium catalyst to give acetylenic ketones in useful yields[1] suggested that alkynyl ketones such as **3** might be obtained by an analogous process from 2-hydroxyaryl iodides **1** and ethynylarenes **2**. Their subsequent 'in situ' cyclization[2] would provide a new, direct entry to the basic skeleton of naturally occurring and/or biologically active flavones **4** and/or aurones **5**.[3]

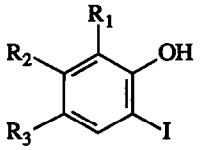
Last year, indeed, Chiusoli's group has briefly reported the reaction of 2-iodophenol (**1a**), carbon monoxide, and phenylacetylene (**2a**) in anisole using potassium acetate as the base and $Pd(PPh_3)_4$ as the catalyst to give (Z)-aurone (**5a**) in 82% yield.[4]

Since the scope of the carbonylative coupling between **1** and **2** would be considerably broadened if, by proper selection of experimental conditions, the preferential formation of flavones **4** could be alternatively induced, we undertook a study of the reaction to achieve this goal.

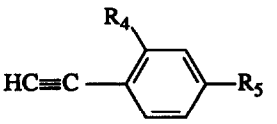
While this work was in progress, a palladium-catalyzed carbonylative coupling of *o*-iodophenols **1a, b** with terminal acetylenes **2a,b** in diethylamine at 120°C and 20 atm CO pressure to give flavones **4a, b, e** in 81, 54, and 67% TLC and UV yields, respectively, has been described.[5] No mention has been made in this case of the formation as by-products of the corresponding aurones **5a, b, e.**

From a synthetic point of view, the usefulness of the procedure described by Russian workers appears to be limited by the rather drastic conditions employed and by the apparent need to manipulate pressurized CO in an autoclave to secure useful yields. Only a 28% yield of **4a** has been in fact reported under 1 atm of CO. We wish to describe now our results in the carbonylative coupling of **1** with **2** under milder conditions and ambient CO pressure and more clearly define the scope and the limitations of the reaction, and the influence of various parameters affecting **4/5** selectivity.

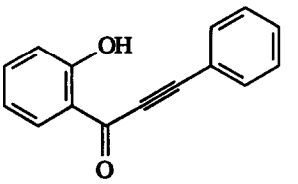
When 2-hydroxyphenyl iodide (**1a**) was reacted under atmospheric CO pressure with phenylacetylene (**2a**) in DMF at 60°C, the best result in terms of both overall (i.e. **4+5**) yield and **4/5** selectivity was obtained using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base and a catalyst generated in situ from 3 mol% of $Pd(OAc)_2$ and 6 mol% of 1,1'-bis(diphenylphosphino)ferrocene (DPPF). Under these conditions, 64% of **4a** and 19% of **5a** were isolated after completion of the reaction (6 h).[6] The use of PPh_3 as ligand or of Et_3N and AcOK as bases resulted in lower overall yields and **4/5** ratios. Thus, **4a** and **5a** were formed in 29 and 11, 10



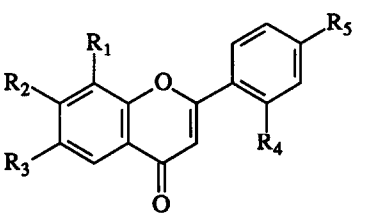
1a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = H$; $R_3 = CH_3$
c, $R_1 = R_3 = H$; $R_2 = CH_3$
d, $R_1 = R_3 = CH_3$; $R_2 = H$
e, $R_1 = R_3 = H$; $R_2 = OCH_3$
f, $R_1 = R_3 = H$; $R_2 = Cl$



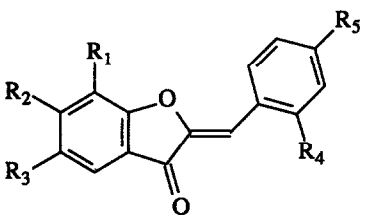
2a, $R_4 = R_5 = H$
b, $R_4 = H$; $R_5 = OCH_3$
c, $R_4 = H$; $R_5 = CO_2CH_3$
d, $R_4 = OCH_3$; $R_5 = H$



3



4a - i



5a - i

a, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
b, $R_1 = R_2 = R_3 = R_4 = H$; $R_5 = OCH_3$
c, $R_1 = R_2 = R_3 = R_4 = H$; $R_5 = CO_2CH_3$
d, $R_1 = R_2 = R_3 = R_5 = H$; $R_4 = OCH_3$
e, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = CH_3$
f, $R_1 = R_2 = R_4 = H$; $R_3 = CH_3$; $R_5 = OCH_3$
g, $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = CH_3$
h, $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = OCH_3$
i, $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = Cl$

and 26, and 38 and 24% yields by substituting PPh_3 for DPPF or Et_3N and AcOK for DBU, respectively. The optimal procedure was then extended to the 2-hydroxyaryl iodides **1b-f** and to the ethynylarenes **2b-d**. The results obtained are summarized in Table 1.

Only one of the two possible geometric aurone isomers was invariably isolated. Evidence for the depicted Z configuration of aurones **5** was obtained by comparison of their physical (mp, IR, ^1H NMR) data with those reported in the literature for Z-isomers (Tables 1 and 2). In this connection, it may be recalled that the thermodynamically less stable E-isomers have been so far obtained only by photoisomerization (UV irradiation) of Z-isomers.[7]

Generally, products of apparent both 6-endo-dig and 5-exo-dig ring closure [2a] of postulated intermediate diarylpropynones such as **3** were isolated, although the 6-endo mode was in most cases preferred (entries 1, 2, 5-9), thus being obtained the flavones **4a**, **b**, **e-i** as major products. This trend was in good agreement with the results obtained by Miranda et al.[2a] on the influence of the reaction conditions on the cyclization of 1-(2-hydroxyaryl)-3-aryl-2-propyn-1-ones. When the ethynylarene **2d** was used, the 5-exo-dig ring closure became however clearly enhanced (entry 4) and the aurone **5d** was obtained as the major product. The substitution at the ortho-carbon of **2** evidently introduced an unfavourable steric factor towards the 6-endo-dig process.

As expected, the nature and position of substituents significantly affected the overall yield as well as the **4/5** ratio. An electron-donating group in the 4-position of **1** hindered the reaction (entries 7 and 8) while its presence in para to the ethynyl group raised the **4/5** ratio (compare entries 1, 2 and 5, 6). Less than 10% yield of both flavone and aurone were obtained with **1e** and **2b** as reactants while **1d** failed to react at all with **2a**.

The question of the different regiochemical outcome of various carbonylative coupling procedures was then explored. It has been already pointed out by different authors[21] that the carbonylative coupling between aryl

Table 1. Flavones **4** and Aurones **5** Prepared[a]

Entry	Starting Compounds[b]	Products	Yield[c] (%)	mp (°C)	Lit. mp (°C)
1	**1a + 2a**	**4a**	64	95-96	99[8]
		5a	19	109-110	110-111[9]
2	**1a + 2b**	**4b**	61	158	158-159[10]
		5b	12	139	139[7b]
3	**1a + 2c**	**4c**	10	178-179	182[11]
		5c	14	205-206	204[12]
4	**1a + 2d**	**4d**	19	100-101	105[13]
		5d	69	173-175	175[14]
5	**1b + 2a**	**4e**	60	120	120[15]
		5e	22	118-119	119[16]
6	**1b + 2b**	**4f**	52	171-172	173-175[17]
		5f	13	151-152	152-153[16]
7	**1c + 2a**	**4g**	38	121-122	123[18]
		5g	9	152-153	153[19]
8	**1e + 2a**	**4h**	35	105-106	111-112[20]
		5h	18	145-147	145-146[16]
9	**1f + 2a**	**4i**[d]	62	158-159	158[18]

[a] The preparation of compounds **4** and **5** was carried out as described in the experimental section. [b] 2-Hydroxyaryl iodides **1a-f** were prepared from the corresponding aryl iodides according to: Cambie, R.C.; Rutledge, P.S.; Smith-Palmer, T.; Woodgate, P.D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1161-1164. Ethynylarenes **2b-d** were prepared from the corresponding aryl iodides according to: Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627-630. [c] Yields of isolated products. [d] The corresponding aurone **5i** was formed in trace amounts.

Table 2. Spectral Data of Flavones **4** and Aurones **5**

Compound	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ (ppm)
4a	1642 (C=O) 1605 (C=C)	6.84 (1H, s, 3-H), 7.41-7.74 (6H, m, 6, 7, 8, 3', 4', and 5'-Hs), 7.94 (2H, m, 2' and 6'-Hs), 8.24 (1H, dd, J = 7.8 and 1.7 Hz, 5-H)
5a	1710 (C=O) 1658 (C=C)	6.91 (1H, s, 10-H), 7.21-7.69 (6H, m, 5, 6, 7, 3', 4', and 5'-Hs), 7.81 (1H, dd, J = 7.6 and 1.0 Hz, 4-H), 7.93 (2H, dd, J = 7.8 and 1.0 Hz, 2' and 6'-Hs)
4b	1645 (C=O) 1608 (C=C)	3.89 (3H, s, 4'-OMe), 6.75 (1H, s, 3-H), 7.02-7.72 (5H, m, 6, 7, 8, 3' and 5'-Hs), 7.89 (2H, d, J = 8.5 Hz, 2' and 6'-Hs), 8.23 (1H, dd, J = 8.0 and 1.7 Hz, 5-H)
5b	1697 (C=O) 1648 (C=C)	3.88 (3H, s, 4'-OMe), 6.90 (1H, s, 10-H), 6.98-7.65 (5H, m, 5, 6, 7, 3', and 5'-Hs), 7.81 (1H, dd, J = 7.7 and 1.5 Hz, 4-H), 7.90 (2H, d, J = 9.0 Hz, 2' and 6'-Hs)
4c	1728 (CO_2CH_3) 1659 (C=O) 1605 (C=C)	3.98 (3H, s, 4'-CO_2Me), 6.90 (1H, s, 3-H), 7.43-7.77 (3H, m, 6, 7, and 8-Hs), 8.01 (2H, d, J = 8.3 Hz, 2' and 6'-Hs), 8.20 (2H, d, J = 8.3 Hz, 3' and 5'-Hs), 8.25 (1H, dd, J = 8.2 and 1.6 Hz, 5-H)

(continued)

Table 2. (continued)

Compound	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ (ppm)
5c	1713 (CO_2CH_3) 1703 (C=O) 1648 (C=C)	3.95 (3H, s, 4'-CO_2Me), 6.89 (1H, s, 10-H), 7.23-7.72 (3H, m, 5, 6, and 7-Hs), 7.82 (1H, dd, J = 7.6 and 1.5 , Hz, 4-H), 7.98 (2H, d, J = 8.0 Hz, 2' and 6'-Hs), 8.11 (2H, d, J = 8.0 Hz, 3' and 5'-Hs)
4d	1632 (C=O) 1605 (C=C)	3.94 (3H, s, 2'-OMe), 7.04-7.14 (2H, m, 3' and 5'-Hs), 7.15 (1H, s, 3-H), 7.38-7.71 (4H, m, 6, 7, 8, and 4'-Hs), 7.91 (1H, dd, J = 7.8 and 1.7 Hz, 6'-H), 8.24 (1H, dd, J = 8.2 and 1.8 Hz, 5-H)
5d	1696 (C=O) 1644 (C=C)	3.91 (3H, s, 2'-OMe), 6.92-7.41 (5H, m, 6, 7, 3', 4' and 5'-Hs), 7.49 (1H, s, 10-H), 7.64 (1H, m, 5-H), 7.82 (1H, dd, J = 8.2 and 1.4 Hz, 4-H), 8.32 (1H, dd, J = 7.8 and 1.7 Hz, 6'-H)
4e	1633 (C=O) 1613 (C=C)	2.47 (3H, s, 6-Me), 6.82 (1H, s, 3-H), 7.49-7.94 (7H, m, 6, 7, 2', 3', 4', 5', and 6'-Hs), 8.02 (1H, d, J = 2.0 Hz, 5-H)
5e	1698 (C=O) 1649 (C=C)	2.41 (3H, s, 5-Me), 6.88 (1H, s, 10-H), 7.21-7.48 (5H, m, 6, 7, 3', 4', and 5'-Hs), 7.59 (1H, d, J = 1.0 Hz, 4-H), 7.92 (2H, dd, J = 7.9 and 1.0 Hz, 2' and 6'-Hs)
4f	1643 (C=O) 1604 (C=C)	2.46 (3H, s, 6-Me), 3.89 (3H, s, 4'-OMe), 6.73 (1H, s, 3-H), 7.01-7.51 (4H, m, 7, 8, 3', and 5'-Hs), 7.88 (2H, d, J = 9.1 Hz, 2' and 6'-Hs), 8.01 (1H, d, J = 2.0 Hz, 5-H)
5f	1698 (C=O) 1644 (C=C)	2.40 (3H, s, 5-Me), 3.87 (3H, s, 4'-OMe), 6.86 (1H, s, 10-H), 6.97-7.47 (4H, m, 6, 7, 3', and 5'-Hs), 7.58 (1H, d, J = 0.7 Hz, 4-H), 7.89 (2H, d, J = 8.8 Hz, 2' and 6'-Hs)
4g	1633 (C=O) 1606 (C=C)	2.52 (3H, s, 7-Me), 6.81 (1H, s, 3-H), 7.23-7.54 (5H, m, 6, 8, 3', 4', and 5'-Hs), 7.92 (2H, m, 2' and 6'-Hs), 8.12 (1H, d, J = 8.1 Hz, 5-H)
5g	1702 (C=O) 1651 (C=C)	2.50 (3H, s, 6-Me), 6.87 (1H, s, 10-H), 7.03-7.49 (5H, m, 5, 7, 3', 4', and 5'-Hs), 7.69 (1H, d, J = 7.9 Hz, 4-H), 7.92 (2H, dd, J = 6.8 and 1.0 Hz, 2' and 6'-Hs)
4h	1650 (C=O) 1607 (C=C)	3.94 (3H, s, 7-OMe), 6.77 (1H, s, 3-H), 6.98-7.54 (5H, m, 6, 8, 3', 4', and 5'-Hs), 7.91 (2H, m, 2' and 6'-Hs), 8.14 (1H, d, J = 9.1 Hz, 5-H)
5h	1694 (C=O) 1650 (C=C)	3.93 (3H, s, 6-OMe), 6.75-6.78 (2H, m, 5 and 7-Hs), 6.83 (1H, s, 10-H), 7.36-7.48 (3H, m, 3', 4', and 5'-Hs), 7.72 (1H, d, J = 8.2 Hz, 4-H), 7.90 (2H, dd, J = 7.7 and 0.8 Hz, 2' and 6'-Hs)
4i	1640 (C=O) 1606 (C=C)	6.82 (1H, s, 3-H), 7.38-7.62 (5H, m, 6, 8, 3', 4', and 5'-Hs), 7.91 (2H, m, 2' and 6'-Hs), 8.17 (1H, d, J = 8.5 Hz, 5-H)

halides and terminal acetylenes presumably involves a nucleophilic attack of an acetylide anion on an aroylpalladium iodide, even though the precise nature of this attack, e.g. Pd attack (followed by rapid 1,1-reductive elimination of the resulting aroylethynylpalladium species) *vs* CO attack with concomitant σ-acyl-metal bond cleavage, still remains to be ascertained.[22]

On the reasonable assumptions that an analogous pathway is followed by 2-hydroxyaryl iodides **1** and that the 1,1-reductive elimination process, if occurring, is faster than the cyclization step, the ethynyl ketone **3** was chosen as model intermediate and its cyclization under conditions summarized in Table 3 was examined.

As concerns the carbonylative coupling procedure described by Kalinin et al.,[5] the cyclization step most probably involves an addition-substitution mechanism with β-aminovinyl ketones as intermediates. Formation of flavones from diarylpropynones such as **3** and secondary amines through β-aminovinyl ketones has been previously established.[2b]

Table 3. Cyclization of 3-Phenyl-1-(2-hydroxyphenyl)-2-propyn-1-one (**3**)[a]

Entry	Reagents	Solvent	% Unchanged **3**[b]	Yield%[b]	
				4a	**5a**
1	$Pd(PPh_3)_4$, AcOK, CO	Anisole	25	-	75
2	$Pd(PPh_3)_4$, CO	"	24	-	76
3	$Pd(PPh_3)_4$	"	32	-	68
4	$Pd(OAc)_2(DPPF)_2$, CO	"	-	-	100
5	AcOK	"	100	-	-
6	AcOK, 18-Crown-6	"	-	63	37
7	$Pd(PPh_3)_4$, DBU, CO	"	-	69	31
8	DBU	"	-	78	22
9	$Pd(OAc)_2(DPPF)_2$, DBU, CO	DMF	-	92	8
10	$Pd(OAc)_2(DPPF)_2$, CO	"	-	68	32
11	$Pd(PPh_3)_4$	"	-	55	45
12	DBU	"	-	91	9

[a] Reactions were carried out for 4 h at 80°C (in anisole) or 60°C (in DMF) under N_2 or, when employed, 1 atm CO using 0.5 mmol of **3**, 0.01 mmol of $Pd(PPh_3)_4$, 0.015 mmol of $Pd(OAc)_2$, 0.03 mmol of DPPF, 1.25 mmol of AcOK or DBU, 0.12 mmol of 18-crown-6, and 2 mL of anisole or DMF. [b] Relative yields determined by ^1H NMR analysis of the reaction residue.

The experimental results summarized in Table 3 indicate that the cyclization step under Chiusoli's carbonylative coupling conditions[4] is likely to be catalyzed by a palladium (0) complex (cf. entries 1-3). AcOK has practically no influence on the course of the reaction as demonstrated also by the unability of AcOK itself to significantly promote the cyclization of **3** (entry 5).

When 18-crown-6 is added to a mixture of **3** and AcOK in anisole, a base-catalyzed process with a moderate selectivity for flavone (**4a**) takes place instead (entry 6).

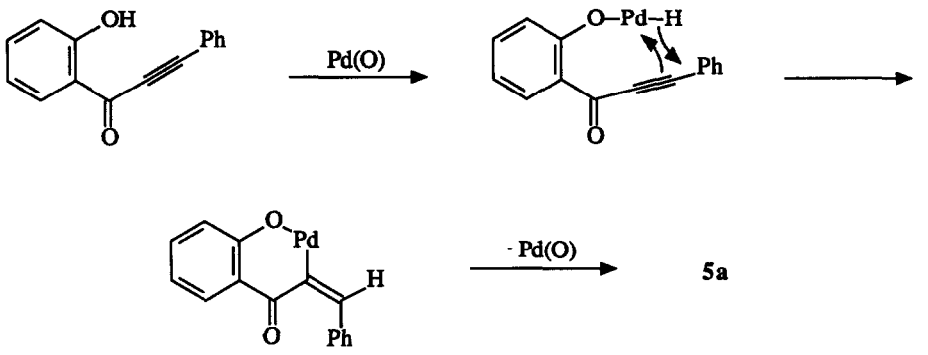
Substitution of DBU for AcOK gives **4a** as the main cyclization product, regardless of the presence of $Pd(PPh_3)_4$ as a result of a prevailing base-catalyzed, 6-endo-dig process (entries 7 and 8). A palladium-catalyzed process is however still operating even using DBU as the base, as indicated by the shift of the **4a/5a** ratio from 2.2 to 3.5 when $Pd(PPh_3)_4$ is absent.

The use of $Pd(OAc)_2(DPPF)_2$ as the catalyst again affords **5a** exclusively and, interestlingly, appears to increase the rate of cyclization relatively to $Pd(PPh_3)_4$ (entry 4).

According to a subsequent suggestion of Chiusoli himself,[23] the pathway leading to aurone **5a** under conditions of entries 1-4 presumably consists of an oxidative addition of the OH group to palladium(0), followed by intramolecular acetylene insertion and 1,1-reductive elimination (Scheme).

The exclusive formation of **5a** appears to be the consequence of a concerted, cis addition of ArOPdH to the triple bond since it can only proceed in the direction indicated in the Scheme (the opposite direction of addition would form an impossibly strained seven-membered ring containing a trans double bond).

In contrast with a Chiusoli's assumption,[23] formation of the more stable Z-isomer cannot be however attributed to an isomerization of the initially formed E-isomer since this latter[24] was recovered unchanged in 90% yield (^1H NMR analysis) when heated for 4 h at 80°C in anisole under 1 atm of CO in the presence of **3**, $Pd(PPh_3)_4$, and AcOK. This result seems to suggest that, in the event of a concerted, cis acetylene insertion, the



Scheme

reductive elimination process is likely to occur with a predominant and unusual[25] inversion of geometry of the double bond. The possibility of a regioselective, non concerted addition of ArOPdH to the triple bond, although less plausible, because invoking the formation of high-energy intermediates, cannot be however entirely ruled out.

Turning eventually to our carbonylative coupling procedure, the regiochemical outcome of the reaction can be accounted for by the intervention of concomitant DBU- and palladium-catalyzed cyclization processes (entries 9, 10, 12). A 6 -endo-dig ring closure to give **4a** is strongly promoted by DBU (entry 12) but palladium itself catalyzes the preferential formation of flavone (entry 10). The **4a/5a** ratio in the palladium-catalyzed process is however significantly dependent on the nature of the catalyst (compare entries 10 and 11). A possible explanation for the palladium-catalyzed route to **4a** is that an electrophilic assistance by a palladium species of the attack by the oxygen nucleophile at the more electron-deficient carbon of the acetylenic linkage may be involved. This process would be in competition in DMF with the aforementioned intramolecular addition of ArOPdH to the triple bond leading to aurone, whilst in anisole the reduced nucleophilicity of the phenolic OH group would render it ineffective.

The discrepancy between **4a/5a** ratios in the carbonylative coupling of **1a** with **2a** (Table1, entry 1) and in the cyclization of **3** under the same conditions (Table 3, entry 9) can be reconciled if one considers that in the former case **3**, when formed, is likely to experience a much higher "local" concentration of palladium. This fact would result in an increased proportion of aurone **5a**.

EXPERIMENTAL SECTION

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^{1}H NMR spectra were run on a Varian XL-300 spectrometer.

*General Procedure for the Palladium-Catalyzed Carbonylative Coupling of 2-Hydroxyaryl Iodides **1a-f** with Ethynylarenes **2a-d**.*

A mixture of 2-hydroxyaryl iodide (1 mmol), ethynylarene (1.2 mmol), DBU (0.37 mL, 2.5 mmol), palladium acetate (7 mg, 0.03 mmol), and DPPF (33 mg, 0.06 mmol) in DMF (3 mL) was purged with carbon monoxide for 5 min and stirred under a CO balloon at 60°C for 6 h. The reaction mixture was then diluted with brine, extracted with ether, washed with 2N HCl and then brine until neutral, dried (Na_2SO_4), and evaporated.

Chromatography of the residue on silica gel using hexane/AcOEt mixtures as eluent gave aurones **5a-i** followed by flavones **4a-i**.

Cyclization of 3. General Procedure

A mixture of **3**, the appropriate palladium complex, base, and solvent was stirred at the temperature and for the time indicated under CO or N_2 atmosphere (see Table 3 for details). For entries 1, 5-12, the reaction mixture was then diluted with brine, extracted with ether, washed with 2N HCl (when DBU was used) and then brine until neutral, dried (Na_2SO_4), and evaporated. For entries 2-4, the reaction mixture was directly evaporated.

The residue was dissolved in CH_2Cl_2 and filtered through a short pad of silica gel. The filtrate was evaporated and subjected to ^1H NMR analysis.

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