Facile and Efficient Synthesis of Simple Coumarins via the Pd(II)/$KHCO_3$ Catalyzed Heck Reaction under MW-Assisted Neat Conditions

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ABSTRACT:

An efficient and fast Pd(II)-catalyzed cross-coupling of aryl halides with olefins has been developed. In the presence of $Pd(OAc)_2$ and $PdCl_2$ cross-coupling of various aryl halides with olefins underwent smoothly to afford the corresponding products in moderate to high yields under MW mediated neat conditions. Simple coumarins were synthesized in good yields using 2-halophenoles in this procedure. Furthermore no solvent, solid support, expensive or/and toxic ligand is required.

Keywords: coumarin, aryl halides, cross-coupling, microwaves, $Pd(OAc)_2$, $PdCl_2$

INTRODUCTION

Carbon–carbon bond-forming reactions with aryl halides such as Kumada, Heck, Stille, Suzuki, and Negishi reactions have been recognized as one of the most important synthetic transformations in modern organic chemistry.[1-2] Palladium-catalyzed carbon-carbon bond forming reactions such as the Suzuki-Miyaura cross-coupling of organic halides with organoboron compounds[3-4] have been widely used in the synthesis of building blocks for active pharmaceutical components and natural products,[5] polymers and electronic materials,[6] and catalysts.[7] The traditional Heck reaction is typically performed with a palladium catalyst along with phosphine ligands in the presence of suitable base under an inert atmosphere.[8-9] Phosphin ligands are often toxic and sensitive to water and air. Consequently, several ligand-free methods have been developed.[10-13] Several methods were reported for the Palladium-catalyzed homocoupling reactions.[14-17] Most of these transformations require long reaction times (>20 h), polar solvents (DMSO, DMF, NMP), and elevated temperatures.

The use of microwave irradiation has been employed for a number of organic syntheses to reduce the reaction time, rate enhancement and to increase the selectivity and yields.[18-23] MW technology has attained an importance, especially when combined with neat procedures.[24-25] In other words, the absence of solvents coupled with the high yields and short reaction times often associated with MW reactions make these procedures very attractive. The objective of this work is to study the $Pd(OAc)_2$ and $PdCl_2$ catalyzed cross-coupling of aryl halides with olefins under conventional heating and MW irradiation in different conditions. Herein we wish to report our results.

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EXPERIMENTAL

General remarks

All reagents were purchased from Merck Company and used without further purification. ^{1}H NMR spectra were obtained in $CDCl_3$ solution with Bruker Avance AC-400MHz and ^{13}C NMR spectra at 100 MHz on the aforementioned instruments. Mass spectra were recorded on Shimadzu GCMS-QP-2000A mass spectrometer. All melting points are uncorrected and measured in an open glass-capillaries using Stuart melting point apparatus. Analytical thin-layer chromatography was performed using precoated silica gel 60 F254 plates (Merck, Darmstadt), and the spots were visualized with UV light at 254 nm. Merck silica gel 60 (230-400 mesh) was used for flash column chromatography. Microwave experiments were conducted in a Milestone MicroSYNTH apparatus.

Heck cross-coupling in ionic liquid

The iodobenzene (1 mmol) and the methylacrylate (1.15 mmol), Pd(II) catalyst (10 mol%), $KHCO_3$ (1 mmol) and ionic liquid (2 mL) were mixed in a round-bottom flask (5 cm^3). The mixture was heated under air to 140°C for the given reaction time listed in Table 1. The completion of reaction was monitored by TLC using (EtOAc/petroleum 3:8) as eluent. After completion of the reaction, the mixture was extracted with ether (10ml×3). The combined ether extracts were concentrated on a rotary evaporator and the crude mixture was purified by flash column chromatography on silica gel to afford methyl (*E*)-cinnamate **2a**.

Heck cross-coupling over solid support under MW irradiation

The iodobenzene (1 mmol) and the methylacrylate (1.15 mmol), Pd(II) catalyst (10 mol%), and $KHCO_3$ (1 mmol) absorbed on solid support were mixed thoroughly. The mixture was heated under MW irradiating conditions at 140°C and 200 W for the appropriate reaction time as listed in Table 1. The product was purified as described above.

Heck cross-coupling under MW mediated neat conditions

A mixture of the appropriate aryl or heteroaryl halide (1 mmol), the appropriate olefin (1.15 mmol), Pd(II) catalyst (10 mol%), and $KHCO_3$ (1 mmol) were mixed thoroughly in a 10 ml glass microwave vessel. The vessel was capped properly, and thereafter the mixture was heated under MW irradiating conditions at 140°C and 200 W for the appropriate reaction time as listed in Tables 2-3. The products were purified as described above.

Selected spectroscopic data

(*E*)-*tert* Butyl 3-(4-acetylphenyl)prop-2-enoate (2c): m.p.=99-100°C (lit.[26] m.p. is not given); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.61 (s, 9H, $C(CH_3)_3$), 2.63 (s, 3H, CH_3CO), 6.47 (d, *J* = 16.01 Hz, 1H), 7.58 (d, *J* = 16.01 Hz, 1H), 7.60 (d, *J* = 8.41 Hz, 2H), 7.95 (d, *J* = 8.41 Hz, 2H); ^{13}C NMR (100 MHz) δ: 27.8, 28.2, 80.2, 123.7, 127.4, 129.8, 137.5, 138.9, 142.7, 165.7, 196.5; MS (*m/e*) 246 (M+).

4-(Phenylethynyl)acetophenone (2d): m.p. = 143-144°C (lit.[27] 141-142°C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.56 (s, 3H, CH_3CO), 7.09 (d, *J* = 16.12 Hz, 1H), 7.15 (d, *J* = 16.12 Hz, 1H), 7.27-7.31 (m, 1H), 7.37 (m, 2H), 7.51-7.53 (m, 2H), 7.52 (d, *J* = 8.34 Hz, 1H), 7.89 (d, *J* = 8.34 Hz, 1H); ^{13}C NMR (100 MHz) δ: 25.5, 124.5, 127.0, 127.7, 128.2, 128.1, 129.1, 131.6, 135.9, 136.3, 141.3, 196.2; MS (*m/e*) 222 (M+).

(*E*)-*tert* Butyl 3-(3-pyridyl)prop-2-enoate (2e): m.p. = 57-58°C (lit.[28] 58°C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.51 (s, 9H, $C(CH_3)_3$), 6.39 (d, *J* = 16.04 Hz, 1H), 7.27-7.34 (dd, *J* = 7.84, 7.80 Hz, 1H), 7.49 (d, *J* = 16.04 Hz, 1H), 7.75-7.80 (ddd, *J* = 7.80, 2.02, 1.72 Hz, 1H), 8.57 (dd, *J* = 7.84, 1.72 Hz, 1H), 8.72 (d, *J* = 2.02 Hz, 1H); ^{13}C NMR (100 MHz) δ: 27.5, 82.2, 123.3, 124.3, 131.1, 134.1, 141.2, 149.2, 152.1, 165.1; MS (*m/e*) 205 (M+).

(*E*)-3-(β-Styryl)pyridine (2f): m.p. = 80-82°C (lit.[29] 81-83°C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.04 (d, *J* = 16.3 Hz, 1H), 7.14 (d, *J* = 16.3 Hz, 1H), 7.22-7.27 (m, 2H), 7.28-7.35 (dd, *J* = 7.84, 7.79 Hz, 1H), 7.37 (dd, *J* = 7.80, 7.20 Hz, 2H), 7.75-7.80 (ddd, *J* = 7.84, 2.04, 1.74 Hz, 1H), 7.81-7.83 (m, 1H), 8.57 (dd, *J* = 7.79, 1.74 Hz, 1H), 8.72 (d, *J* = 2.04 Hz, 1H); ^{13}C NMR (100 MHz) δ: 123.6, 124.1, 126.5, 127.5, 128.2, 131.9, 131.9, 134, 136, 149.1; MS (*m/e*) 181 (M+).

2-Oxo-2H-chromene (4a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.70 (d, J=8.87, 1H), 7.35-7.55 (m, 4H), 7.85 (d, J=8.87, 1H). ^{13}C NMR (100 MHz) δ: 108, 111.1, 113.3, 126, 127.2, 146.8, 148.8, 157.1, 160.9; IR ν_{max}/cm^{-1}: 3020, 1710, 1415.

7-Hydroxy-2-oxo-2H-chromene (4b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.59 (d, J=8.78, 1H), 7.00 (d, J=7.18, 1H), 7.85 (d, J=8.78, 1H), 7.05 (dd, J=1.30 Hz, J=7.18 1H), 7.12 (d, 1.30 Hz, 1H); ^{13}C NMR (100 MHz) δ: 108, 111.1, 113.3, 126, 127.2, 146.8, 148.8, 157.1, 160.9; IR ν_{max}/cm^{-1}: 3313, 3025, 1719, 1435;

7-Methoxy-2-oxo-2H-chromene (4c): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.39 (d, J=8.98, 1H), 7.01 (d, J=7.28, 1H), 7.95 (d, J=8.98, 1H), 7.15 (dd, J=1.31 Hz, J=7.28 1H), 7.32 (d, 1.31 Hz, 1H); ^{13}C NMR (100 MHz) δ: 108, 111.1, 113.3, 126, 127.2, 146.8, 148.8, 157.1, 160.9; IR ν_{max}/cm^{-1}: 3035, 1726, 1445.

6-Bromo-2-oxo-2H-chromene (4d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.49 (d, J=8.95, 1H), 7.15 (d, J=7.24, 1H), 7.75 (d, J=8.95, 1H), 7.75 (d, J=1.36 Hz, 1H), 7.82 (dd, J=7.24 and 1.36 Hz, 1H); ^{13}C NMR (100 MHz) δ: 111, 115.1, 118.3, 129, 130.2, 149.8, 151.8, 160.1, 163.9; IR ν_{max}/cm^{-1}: 3035, 1726, 1385.

6-Nitro-2-oxo-2H-chromene (4e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.40 (d, J=9.15, 1H), 7.25 (d, J=7.34, 1H), 7.78 (d, J=9.15, 1H), 7.90 (d, J=1.35 Hz, 1H), 8.04 (dd, J=7.34 and 1.35 Hz, 1H); ^{13}C NMR (100 MHz) δ: 111.5, 112.1, 113.3, 129.1, 129.2, 148.6, 150.5, 159.1, 163.3; IR ν_{max}/cm^{-1}: 3035, 1726, 1349, 1545.

8-Nitro-2-oxo-2H-chromene (4f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.43 (d, J=9.4, 1H), 7.15 (t, J=7.84, 1H), 7.68 (d, J=9.4, 1H), 7.94 (dd, J=7.3 and 1.3 Hz, 1H), 8.15 (dd, J=7.3 and 1.3 Hz, 1H); ^{13}C NMR (100 MHz) δ: 110.4, 111.5, 112, 128, 129.8, 148, 149.5, 159.8, 165.9; IR ν_{max}/cm^{-1}: 3041, 1739, 1345, 1535.

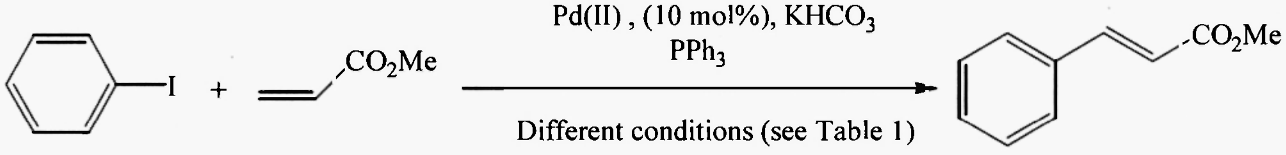
8-Bromo-2-oxo-2H-chromene (4g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.45 (d, J=9.4, 1H), 7.15 (t, J=7.4, 1H), 7.44 (dd, J=7.6 and 1.4 Hz, 1H), 7.70 (d, J=9.4, 1H), 7.75 (dd, J=7.6 and 1.4 Hz, 1H); ^{13}C NMR (100 MHz) δ: 110.4, 111.5, 112, 132, 132.8, 150, 150.5, 163.8, 165.9; IR ν_{max}/cm^{-1}: 3041, 1739, 1385.

7-Bromo-2-oxo-2H-chromene (4h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.49 (d, J=8.88, 1H), 7.21 (d, J=7.28, 1H), 7.80 (d, J=8.88, 1H), 7.35 (dd, J=1.31 Hz, J=7.28 1H), 7.27 (d, 1.31 Hz, 1H); ^{13}C NMR (100 MHz) δ: 109, 110.8, 114.7, 127.3, 128.2, 145.1, 149, 159, 160; IR ν_{max}/cm^{-1}: 3035, 1726, 1445.

5-Bromo-2-oxo-2H-chromene (4i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.66 (d, J=9.05, 1H), 7.25 (t, J=7.32, 1H), 7.34 (dd, J=7.2 and 1.35 Hz, 1H), 7.90 (d, J=9.05, 1H), 7.71 (dd, J=7.2 and 1.35 Hz, 1H); ^{13}C NMR (100 MHz) δ: 109.4, 110.21, 111.11, 130, 130.8, 151, 151.1, 160.6, 161.9; IR ν_{max}/cm^{-1}: 3021, 1730, 1365.

RESULTS AND DISCUSSION

Our initial attempts used iodobenzene and methylacrylate as the coupling partners in the presence of Pd(II) catalyst and triphenylphosphine in different conditions. 2-Iodobenzene under these conditions produces the coupling product methyl (E)-cinnamate **2a** (**Scheme 1**). This observation is in agreement with the reported methods in the literature for aryl iodides [30-31]. We tried different reaction conditions to carry out this reaction using several ionic liquids and found when the 1:1.15 (iodobenzene:methylacrylate) starting material ratio was carried out in butylmethylimidazolium hexaflorophosphate, [bmim] PF_6, at 140°C the product was prepared in 24h in 62% yield (**Table 1**). Elution of the reaction mixture with ether followed by the evaporation of solvent furnished the crude product which was purified by column chromatography. We also have explored the use of microwaves in this procedure. It can be seen from the Table 1 that when the reaction was conducted under microwave irradiation in ionic liquids the reaction times were decreased considerably (entries 7-8). We tried different reaction conditions using different solid supports to carry out this reaction under microwave irradiation and found when the irradiation of reactants was carried out under neat conditions without any solvent and solid support the cross-coupling was carried out smoothly in shorter reaction time and good yield (entries 13-14). We also report our studies on comparison of yield of the cross-coupling product when synthesized in the presence of different combinations of the catalysts ($Pd(OAc)_2$ or $PdCl_2$) and the base $KHCO_3$. Evidently, ($Pd(OAc)_2$/ $KHCO_3$, 1/10) was found to be superior in terms of yield (91%) and reaction time (12 min) as compared with other combinations, under MW mediated neat conditions. We examined the procedure in the absence of triphenylphosphine and found that the reaction was carried out smoothly in this condition.



2a

Scheme 1.

Table 1

Cross-coupling of iodobenzene with methylacrylate under various conditions

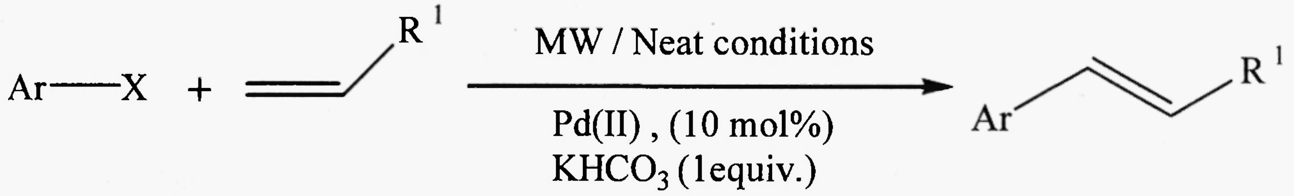
Entry	Ionic liquid	Solid support	Catalyst	Method	Time/ h or min	Yield[c]/%
1	[bmim] BF_4	-	$Pd(OAc)_2$	A[a]	26 h	58
2	[bmim] BF_4	-	$PdCl_2$	A	34 h	55
3	[bmim] PF_6	-	$Pd(OAc)_2$	A	24 h	62
4	[bmim] PF_6	-	$PdCl_2$	A	30 h	54
5	[bmim] CI	-	$Pd(OAc)_2$	A	36 h	43
6	[bmim] CI	-	$PdCl_2$	A	32 h	42
7	[bmim] PF_6	-	$Pd(OAc)_2$	B[b]	17min	73
8	[bmim] PF_6	-	$PdCl_2$	B	17min	60
9	-	silica gel	$Pd(OAc)_2PdCl_2$	C[c]	35 min	58
10	-	silica gel	$Pd(OAc)_2$	C	35 min	70
11	-	alumina	$PdCl_2$	C	40 min	57
12	-	alumina	$Pd(OAc)_2$	C	35 min	78
13	-	-	$PdCl_2$	D[d]	12 min	91
14	-	-		D	14 min	83

[a] Reaction was done at 140°C by conventional heating in ionic liquid. [b] Reaction was done in a microwave reactor at 140 C and 200 W in ionic liquid. [c] Reaction was done in a microwave reactor at 140°C and 200 W over solid support. [d] Reaction was done in a microwave reactor at 140 C and 200 W under neat conditions. [e] Yields of product **2a** were determined after column chromatography.

With optimal conditions in hand, wide ranges of aryl halides were coupled with olefins by this procedure to produce the corresponding·products (**Scheme 2**). Interestingly, the cross-coupling reaction was successful for electron-poor as well as for electron-rich aryl halide (**Table 2**). The results showed that the palladium-catalyzed cross-coupling reaction tolerated a variety of functional groups, and the yields and rates depended upon the substrates. The cross-coupling reaction of aryl and heteroaryl halides was highly regio- and stereoselective and provided only the thermodynamically more stable *E*-isomer of β-substituted alkylacrylates where GC-MS and ^{1}H NMR spectra of the crude reaction mixture did not reveal any evidence for α-arylation or the formation of *Z*-isomers. In addition, we also did not encounter the formation of carboxylic acids in the crude products which would have originated from ester hydrolysis under the basic conditions. All products of C–C coupling were obtained pure and were identical to authentic samples (^{1}H, ^{13}C NMR spectra).

Using the 2-halophenoles in this procedure afforded to related simple coumarins (**Scheme 3**). A variety of simple coumarins were synthesized in this procedure and the results were shown in **Table 3**. As it can be seen from **Table 3**, the synthesis of coumarins was successful for electron-poor as well as for electron-rich 2-halophenole.

In summary, we have developed a rapid, mild and efficient protocol for the synthesis of simple coumarins and (*E*)-cinamates via the cross-coupling Heck reaction in the presence of Pd(II)/$KHCO_3$ under MW mediated neat conditions. This Pd(II)-catalyzed procedure not only tolerates a range of functional groups, but also does not require any phosphine ligands.



1 X = Cl, Br, I **2**

2a:Ar= phenyl, R^2=CO_2Me
2b:Ar= phenyl, R^2=phenyl
2c:Ar= 4-COMe-phenyl, R^2=CO_2t-Bu
2d:Ar= 4-COMe-phenyl, R^2=phenyl
2e:Ar= 3-pyridyl, R^2=CO_2t-Bu
2f:Ar= 3-pyridyl, R^2=phenyl
2g:Ar= 4-Me-phenyl, R^2=CO_2Me
2h:Ar= 4-Me-phenyl, R^2=phenyl
2i:Ar= 4-OMe-phenyl, R^2=CO_2Me

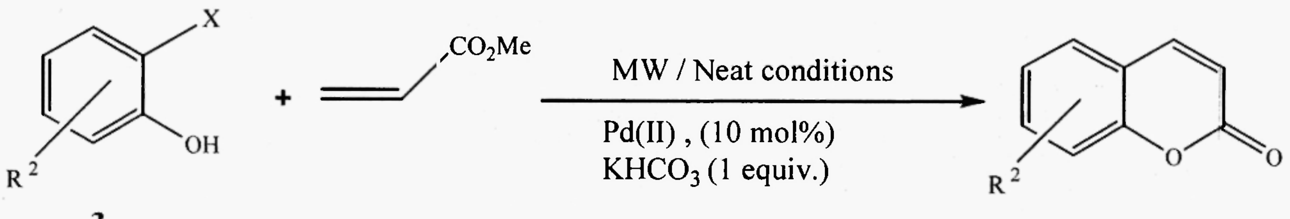
Scheme 2.

Table 2

MW mediated Pd(II)/$KHCO_3$ catalyzed cross-coupling Heck reaction under neat conditions

Entry	Ar-X	R^2	Time/ min	Product	Yield[a]/%	
					$Pd(OAc)_2$	$PdCl_2$
1	Ph-I	CO_2Me	12	**2a**	91	83
2	Ph-Br	CO_2Me	10	**2a**	93	84
3	Ph-Cl	CO_2Me	25	**2a**	69	61
4	Ph-I	Ph	10	**2b**	93	83
5	Ph-Br	Ph	11	**2b**	90	86
6	4-COMe-Ph-I	CO_2t-Bu	13	**2c**	92	83
7	4-COMe-Ph-Br	CO_2t-Bu	14	**2c**	89	82
8	4-COMe-Ph-Cl	CO_2t-Bu	21	**2c**	67	60
9	4-COMe-Ph-I	Ph	9	**2d**	91	86
10	4-COMe-Ph-Br	Ph	12	**2d**	90	84
11	3-I-pyr	CO_2t-Bu	10	**2e**	93	87
12	3-Br-pyr	CO_2t-Bu	14	**2e**	89	80
13	3-I-pyr	Ph	11	**2f**	94	88
14	3-Cl-pyr	Ph	19	**2f**	61	56
15	4-Me-Ph-I	CO_2Me Ph	9	**2g**	93	87
16	4-Me-Ph-Br	CO_2Me	12	**2h**	90	85
17	4-OMe-Ph-Br		12	**2i**	81	76

[a] Yields were determined after column chromatography.



3

4

4a: R^2=H
4b: R^2=7-OH
4c: R^2=7-OH
4d: R^2=6-Br
4e: R^2=6-NO_2
4f: R^2=8-NO_2
4g: R^2=8-Br
4h: 7-Br
4i: 5-Br

Scheme 3.

Table 3

MW mediated Pd(II)/$KHCO_3$ catalyzed synthesis of coumarins

					M.p (°C)		Yield[a]/%	
Entry	X	R^2	Time/min	Product	Found	Reported[Ref.]	$Pd(OAc)_2$	$PdCl_2$
1	I	H	15	**4a**	66-69	68-70[32]	71	69
2	Br	7-OH	14	**4b**	232-234	234-235[33]	70	68
3	Br	7-OMe	22	**4c**	117-120	118-119[34]	69	67
4	I	6-Br	20	**4d**	162-165	165-167[35]	72	71
5	I	6-NO_2	14	**4e**	181-183	181-182[36]	74	73
6	I	8-NO_2	14	**4f**	188-190	190-191[37]	75	72
7	Br	8-Br	16	**4g**	135-138	136.5-137[35]	72	70
8	I	7-Br	21	**4h**	120-124	122-124[35]	70	67
9	I	5-Br	20	**4i**	93-95	94.5-96.5[35]	71	69

[a] Yields were determined after column chromatography.

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REFERENCES

1. E.I. Negishi, F. Liu, in: F. Diedrich, Stang P. J. (Eds.), *Metal-catalyzed Cross-coupling Reactions,* Wiley-VCH, Weinheim, (1998).
2. W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds,* Wiley-VCH, Weinheim, (1996).
3. A. Suzuki, in: F. Diederich, P. Stang, (Eds.), *Metal-Catalyzed Cross-Coupling Reaction, Wiley-VCH: Weinheim,* (1998).
4. A. Suzuki, *J. Organometal. Chem.* **576**, 147 (1999).
5. K.C. Nicolaou, C.N.C. Boddy, S. Braso, N. Winssinger, *Angew. Chem. Int. Ed.* **38,** 2096 (1999).
6. P.N. Taylor, M.J. O'Connell, L.A. McNeill, M.J. Hall, R.T. Aplin, H.L. Anderson, *Angew. Chem. Int. Ed.*, **39**, 3456 (2000).
7. C.J. Stearman, V. Behar, *Tetrahedron Lett.*, **43**, 1943 (2002), and references cited therein.
8. B. Cornild, W.A. Herramann, *Applied homogenous catalysis with organometallic compounds,* VCH: Weinheim, Germany, (1996).
9. M. Beller, C. Bolm, *Transition metals for organic synthesis,* Wiley-VCH: Weinheim, Germany, (1998).
10. B.M. Choudary, M.R. Sarma, K.K. Rao, *Tetrahedron Lett.*, **31**, 5781 (1990).
11. L. Djakovitch, K. Koehler, *J. Am. Chem. Soc.* **123**, 5990 (2001).
12. R.S. Varma, K.P. Naicker, P.J. Leisen, *Tetrahedron Lett.* **40**, 2075 (1999).
13. L.-H. Du, Y.-G. Wang, *Synth. Commun.*, **37**, 217 (2007).
14. J.P. Parrish, Y.C. Jung, R.J. Floyd, K.W. Jung, *Tetrahedron Lett.* **43**, 7899 (2002) and references therein.
15. H. Fang, J. Yan, B. Wang, *Molecules* **9**, 178 (2004).

16. H. Yoshida, Y. Yamaryo, J. Ohshita, A. Kunai, *Tetrahedron Lett.* 44, 1541 (2003).
17. H. Yoshida, Y. Yamaryo, J. Ohshita, A. Kunai, *Chem. Commun.* 1510 (2003).
18. K. Li, W. Chen, *Heteroatom Chem.* **19**, 621 (2008).
19. G. Keglevich, A. Szekrényi, M. Sipos, K. Ludányi, I. Greiner, *Heteroatom Chem.* **19**, 207 (2008).
20. B. Kahveci, M. Özil, M. Serdar *Heteroatom Chem.* **19**, 38 (2008).
21. H.A. Oskooie, Z. Alimohammadi, M.M. Heravi, *Heteroatom Chem.* **17**, 699 (2008).
22. A.R. Katritzky, C. Cai, K. Suzuki, S.K. Singh, *J. Org. Chem.* **69**, 811 (2004).
23. M.P. Surpur, P.R. Singh, S.B. Patil, S.D. Samant, *Synth. Commun.* **37**, 1973 (2007).
24. M. Kidwai, *Pure Appl. Chem.* **73**, 147 (2001).
25. J. Hren, K. Kranjc, S. Polanc, M. Kocevar, *Synthesis* 452 (2008).
26. G.Y. Li, G. Zheng, A.F. Noonan, *J. Org. Chem.* 66, 8677 (2001).
27. S.E. Denmark, Z. Wang, *Org. Lett.* **3**, 1073 (2001).
28. Bull, S.D. Davies, S.G. Fox, D.J. Gianotti, M. Kelly, P.M. Pierres, C. Savory, E.D. Smith, A.D. *J. Chem. Soc. Perkin Trans.* **1**, 1858 (2002).
29. K. Kikukawa, K. Maemura, Y. Kiseki, F. Wada, T. Matsuda, C.S. Giam, *J. Org. Chem.* **46**, 4885 (1981).
30. C.B. Ziegler, R.F. Heck, *J. Org. Chem.* **43**, 2941 (1978).
31. L. Mats, H. Anders, *J. Org. Chem.* **61**, 9582 (1996).
32. J. Villieras, M. Ramband M. Graft La, *Tetrahedron Lett.* **26**, 53 (1985).
33. F.D. Gramer, H. Windel *Chem. Ber.* **89**, 354 (1956).
34. A. Shockravi, H. Valizadeh, M.M. Heravi, *Phosphorus, Sulfur, and Silicon and the Related Elements* **178**, 2555 (2003).
35. T. Harayama, K. Nakatsuka, H. Nishioka, K. Murakami, N. Hayashida, H. Ishii, *Chem. Pharm. Bull.* **42**, 2170 (1994).
36. G.T. Morgan, M.G.F. Mickletwait, *J. Chem. Soc.* **85**, 1230 (1904).
37. T. Harayama, K. Nakatsuka, H. Nishioka, K. Murakami, Y. Ohmori, Y. Takeuchi, H. Ishii, K. Kenmotsu, *Heterocycles* **38**, 2729 (1994).