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Transition metal catalyzed cross-coupling of aryl Grignard reagents with aryl fluorides via Pd- or Ni-activation of the C–F bond: an efficient synthesis of unsymmetrical biaryls – application of microwave technology in ligand and catalyst screening

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Abstract

Biaryl compounds are prevalent in both nature and in active pharmaceutical ingredients. The palladium and nickel catalyzed cross-coupling of aryl Grignard reagents with aryl fluorides reported herein affords moderate to excellent yields of the corresponding unsymmetrical biaryls. In addition, the first example of a biaryl cross-coupling utilizing unactivated aryl fluorides under phosphine free palladium conditions is reported. Microwave technology allowed rapid optimization of catalyst systems, which identified several ligands for this cross-coupling reaction.

Keywords: Palladium; Nickel; Biaryls; Cross-coupling; Homogeneous catalysis

1. Introduction

Unsymmetrical biaryls represent an important class of compounds in drug discovery [1] natural product [2], and material science [3]. These biaryls have been typically prepared via cross-coupling of aryl metal compounds with aryl halides (aryl iodides, bromides, and chlorides) mediated by transition metal catalysts [4]. Efforts have been made to expand the synthetic scope of these coupling reactions to include aryl electrophiles such as benzonitriles [5], anisoles [6], and aryl carbamates [7], which were previously regarded as unreactive in these transition-metal cross-coupling procedures. Within the aryl halide series of compounds, aryl fluorides have been known to be the least reactive toward standard cross-coupling protocols [9–13]. Indeed, activation of a C–F bond is an extremely challenging process due to the inherent strength of this bond [8]. Kumada and co-workers [9] demonstrated for the first time a C–F activation process involving the reaction of fluorobenzene and *i*-PrMgCl mediated by $NiCl_2(dmpe)_2$. In a significant extension of this initial report, Herrmann and co-workers [10] expanded the use of aryl fluorides as synthetically useful substrates in these couplings by the application of *N*-heterocyclic carbenes as ligands in a nickel catalyzed cross-coupling with aryl Grignard reagents. Most recently, Mongin et al. [11]. has reported the C–F activation chemistry of fluoroazine and diazine compounds using $NiCl_2L_2$ (L = dppe, dppp, and dppf) as the catalyst precursor. In the palladium catalysis arena, there have been several reports describing both the Suzuki and Stille biaryl cross-coupling protocols of highly activated substrates such as substituted

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fluoronitrobenzene derivatives and (fluoroarene) tricarbonylchromium(0) complexes [13]. However, mechanistically these cross-coupling reactions utilizing activated substrates probably proceed via an S_NAr type oxidative addition process.

Herein, our results concerning the application of both nickel and palladium mediated Kumada–Corriu coupling reactions of unactivated aryl fluorides is reported.

2. Results and discussion

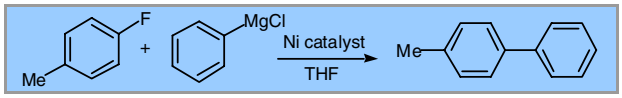
2.1. Ligand screening

A key to the development of this aryl fluoride cross-coupling chemistry was the use of microwave conditions to rapidly screen ligands and catalysts [14]. Utilization of microwave screening allows for a rational high throughput screening (HTS) protocol thus minimizing the number of experiments that need to be carried out (thereby distinguishing this technique from classical HTS). This allowed the rapid identification of several ligands that are active in both the nickel and palladium cross-coupling reactions of aryl fluorides with aryl Grignard reagents (Tables 1 and 2). Reactions using catalyst systems that performed well under the microwave conditions were also subjected to thermal (80 °C) conditions. In general, preferred ligands identified under microwave conditions were also the best under thermal conditions.

2.2. Nickel catalyzed cross-coupling

In the screening effort, two ligands with exceptional activity were identified (Table 1, entries 7 and 24). From these studies, it was determined that in the nickel catalyzed reactions the structure of the ligand plays an important role (Table 1). The reaction of PhMgBr and 4-fluorotoluene with $Ni(acac)_2$ under ligandless conditions or in conjunction with non-hindered phosphites provided low yields of 4-phenyltoluene (Table 1, entries 1–6). However, the more sterically hindered, tris(2, 4-di-t-butylphenyl)phosphite proved to be a outstanding ligand in this cross-coupling, providing 93% yield of 4-phenyltoluene (Table 1, entry 7). Electron rich ligands, such as trialkylphosphines, with either small or large cone angles, performed poorly in the cross-coupling (Table 1, entries 8–10 and 14). Nickel complexes with phosphine ligands of intermediate size, such as *t*-Bu_2PMe, produced 4-phenyltoluene in moderate yields. (Table 1, entry 13) Triarylphosphine ligands, in general, gave low yields in this coupling procedure (Table 1, 18–23). Remarkably, the more electron rich tris(*N*,*N*-dimethylaminophenyl)phosphine had furnished the desired 4-phenyltoluene in 82% yield (Table 1, entry 24). Bisphosphine ligands were less successful in the cross-coupling. Only $NiCl_2(dppp)$ had delivered reasonable yields of 4-phenyltoluene (Table 1, entries 25–29) in accordance with previous results [11]. Generally, it was found that nickel catalysts that proceed efficiently (Table 1, entries 7, 13 and 24) to afford the desired 4-phenyltoluene also produced small amounts bitoluene (5–15%) derived from homocoupling of the aryl fluoride. Addition of lithium salts, such as LiBr, did not reduce the amount of aryl fluoride homocoupling product [15].

Table 1
Cross-coupling of aryl fluorides and Grignard reagents. Microwave screening of nickel catalysts[a]



Entry	Catalyst	Yield of biaryl %
1	$Ni(acac)_2$	17
2	$Ni(acac)_2/P(OPh)_3$	8
3	$Ni(P(OEt)_3P)_4$	15
4	$Ni(acac)_2/P(OCH_2t\text{-}Bu)_3$	25
5	$Ni(acac)_2/P(Oi\text{-}Bu)_3$	3
6	$Ni(acac)_2/P(MeO)(OPh)_2$	2
7[b]	**$Ni(acac)_2P(OAr)_3$**	**93 (79)**
8	$NiCl_2(PMe_3)_2$	38
9	$NiCl_2(Pi\text{-}Bu_3)_2$	36 (80)
10	$Ni(acac)_2/Bn_3P$	30
11	$Ni(acac)_2/P(i\text{-}Pr)_3$	(55)
12	$NiCl_2(PCy_3)_2$	28
13	$NiCl_2/t\text{-}Bu_2PMe$	54
14	$Ni(acac)_2/P(t\text{-}Bu)_3$	26
15	$NiCl_2(PhPCy_2)_2$	45
16	$Ni(acac)_2/Cy_2P(2\text{-}PhC_6H_4)$	14
17	$NiCl_2(Ph_2PCy)_2$	20
18	$NiCl_2(PPh_3)_2$	14
19	$Ni(acac)_2/2\text{-}tol_3P$	14
20	$NiCl_2(p\text{-}tol_3P)_2$	32
21	$Ni(acac)_2/(2,4,6\text{-}Me_3C_6H_2)_3P$	27
22	$Ni(acac)_2/Ph_2P(2\text{-}MeOC_6H_4)$	20
23	$Ni(acac)_2/(4\text{-}MeOC_6H_4)_3P$	27
24	**$Ni(acac)_2/(4\text{-}Me_2NC_6H_4)_3P$**	**82**
25	$NiCl_2(dppf)$	48 (38)
26	$Ni(acac)_2/DIPF$	34
27	$Ni(acac)_2/DPPB$	22
28	$Ni(acac)_2/DCPP$	25
29	$NiCl_2(dppp)$	65

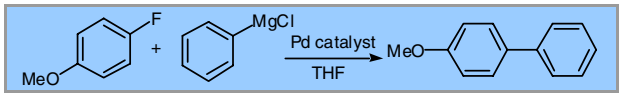
[a] Yields of the corresponding thermal reactions are in parenthesis. Thermal reactions were carried out at 80 °C for 15 h. Microwave reactions (Smith Creator, 2.45 GHz) were carried out at 100 °C for 15 min. GC yields are based on tridecane as an internal standard.

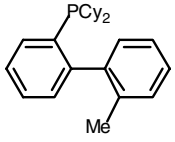
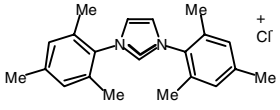
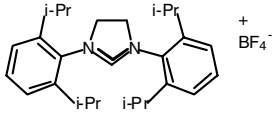
[b] Ar = 2,4-*t*-$Bu_2C_6H_3$.

2.3. Palladium catalyzed cross-coupling

It is well known that palladium catalysts are less reactive in the oxidative addition chemistry when compared to their nickel counterparts. Application of palladium complexes in cross-coupling reactions with organometallic reagents and fluoroarenes are rare in the literature. In any event, as part of the catalyst screening effort, palladium complexes were also studied and it was

Table 2
Cross-coupling of aryl fluorides and Grignard reagents. Microwave and thermal screening of palladium catalysts[a]



Entry	Catalyst	Yield of biaryl %
1	$Pd(dba)_2$	(45)
2	$Pd_2(dba)_3$	(43)
3	$Pd(acac)_2$	(43)
4	$(PdCl(\pi\text{-}C_3H_5))_2$	(33)
5	$Pd(OAc)_2$	(40)
6	$Pd(dba)_2/4PEt_3$	27
7	$Pd(dba)_2/PCy_3$	41 (30)
8	$Pd(dba)_2/2PCy_3$	20 (29)
9	$Pd(dba)_2/3PCy_3$	(28)
10	$Pd(dba)_2/4PCy_3$	21 (19)
11	$Pd(dba)_2/2P\textit{i}\text{-}Pr_3$	17
12	$Pd(dba)_2/4P\textit{i}\text{-}Pr_3$	34
13	$Pd(dba)_2/\textit{t}\text{-}Bu_2PCy$	22 (43)
14	$(PdBr(\textit{t}\text{-}\ Bu_3P))_2$	41 (14)
15	$Pd(dba)_2/2Et_2PPh$	15
16	$Pd(dba)_2/Cy_2PPh$	21
17	**$Pd(dba)_2/2Cy_2PPh$**	**55 (60)**
18	**$Pd(dba)_2/4Cy_2PPh$**	**64 (13)**
19		33
20	$Pd(dba)_2$/ $Pd(dba)_2/2Ph_2PCy$	18 (22)
21	$Pd(dba)_2/4Ph_2PCy$	44
22	$Pd(dba)_2/(Me_2NC_6H_4)_3P$	18
23	$Pd(dba)_2/Cy_2P(CH_2)_3PCy_2$	36
24[b]	$Pd_2(dba)_3$/ 	38
25[c]	$Pd(OAc)_2$/ $Pd(OAc)_2$/ 	35

[a] Yields of the thermal reactions are in parenthesis. Thermal reactions were carried out at 80 °C for 15 h. Microwave reactions (Personal Chemistry, 2.45 GHz) were carried out at 150 °C for 10 min. GC yields are based on tridecane as an internal standard.
[b] 15% of the homocoupling product was identified by GC/MS (entry 24).
[c] 20% of the homocoupling product was identified by GC/MS (entry 25).

discovered that phosphine free $Pd(dba)_2$ was able to catalyze the biaryl cross-coupling of aryl fluorides under both microwave (150 °C, 10 min) and thermal conditions (Table 2, entry 1). *This is the first example of a Kumada–Corriu coupling of an unactivated aryl fluoride utilizing a palladium catalyst under ligandless conditions*! A control experiment with no palladium catalyst present in the reaction mixture produced none of the desired biaryl and returned only the starting aryl fluoride as detected by GC. Screening of other phosphine free palladium catalysts did not improve the yields (35–43%) of the desired cross-coupling product (Table 2, entries 2–5). Palladium mediated cross-coupling utilizing electron rich ligands (Table 2, entries 6–14) furnished

4-methoxybiphenyl in moderate yields. The more active palladium catalyst systems using PCy_3 or t-Bu_2PCy provided reaction mixtures containing 4-fluoroanisole, 4-methoxybiphenyl and 4,4′-dimethoxybiphenyl (Table 2, entries 7 and 13). The relative amounts of these materials were a function of the Pd:phosphine ligand ratio. A 1:1 mixture of palladium and electron rich phosphine ligands (PCy_3 or t-Bu_2PCy) produced the highest conversions of the desired biaryl; however, large amounts of the homocoupling adduct derived from 4-fluoroanisole was observed in the reaction mixture. When the amount of ligand was increased (1:4 Pd: ligand) the reaction gave lower amounts of both 4-methoxybiphenyl and 4,4′-dimethoxybiphenyl. In addition, $(PdBr(t\text{-}Bu_3P))_2$ also provided 4-methoxybiphenyl with comparable yields to PCy_3 (Table 2, entry 14). From these screening studies, the best ligand was determined to be $PhPCy_2$ (Table 2, entries 16–18). The reactions with this ligand were optimal when 2–4 equivalents of ligand were utilized per equivalent of palladium catalyst. This ligand provided the cleanest reactions with only small amounts of the aryl fluoride derived homocoupling adduct, although long reaction times (3 days) were necessary to obtain acceptable levels of conversion under thermal conditions.

It was also determined that both Buchwalds biarylphosphine ligand and imidazolium salts showed no improvement in this palladium mediated C–C bond forming reaction (Table 2, entries 19, 24 and 25).

Several solvents were screened using the microwave. The best solvent for the cross-coupling was found to be THF. Nonpolar solvents such as toluene and t-AmOMe (t-Am = $EtCMe_2$) provided no biaryl adduct. Reaction in diethyl ether provided a small amount (4% yield of 4-methoxybiphenyl) of the biaryl cross-coupling product under thermal conditions ($Pd(dba)_2$, PCy_3, 40 °C).

2.4. Reaction scope

Generally speaking, relative activities of the nickel or palladium based catalyst systems observed under microwave conditions translated well to the corresponding thermal reactions. Thus, effective catalyst systems were developed that furnished a variety of biaryl compounds under thermal or microwave conditions (Table 3, entries 1–19). The cross-coupling could be performed with nickel or palladium catalyst systems using an assortment of aryl Grignard reagents (Table 3). In general, reactions mediated by nickel catalyst systems were superior to the respective reactions using palladium catalysts. Even the sterically encumbered organomagnesium reagent, MesMgBr, reacts with 4-fluorotoluene in the presence of $Pd(dba)_2$/$2PhPCy_2$ to provide the mesityltoluene derivative (Table 3, entry 5). Aryl fluorides bearing an *ortho* alkyl or aryl substituent were found to be more sensitive in the coupling reaction resulting in lower yields. 2-Fluorotoluene provided synthetically useful yields under nickel catalysis; however, this cross-coupling was not as efficient when mediated by a palladium catalyst (Table 3, entries 11–13). A more challenging substrate was 2-fluorobiphenyl, which provided moderate yields (21–47% yield, Table 3, entries 14–16) in the cross-coupling. Surprisingly, the cross-coupling of 2-fluoroanisole had achieved extremely high yields in both the nickel and palladium mediated reactions. Presumably, the positioning of the *ortho*-methoxy group provides either some stabilization of the oxidative addition adduct or perhaps coordination of the Grignard to the *ortho*-methoxy group entropically enhances the C–C bond forming process via transmetallation and reductive elimination.

In conclusion, we have discovered a series of ligands that have the ability to activate the C–F bond of aryl fluorides in the presence of nickel or palladium catalysts. Moreover, we have demonstrated that a laboratory microwave reactor can be a very useful tool to quickly identify nickel or palladium based catalyst systems for the cross-coupling of aryl fluorides with aryl Grignard reagents. With the increasing commercial availability of fluoroarenes, this biaryl cross-coupling should find use in the synthesis of natural products as well as in drug discovery programs.

3. Experimental

All compounds listed in this paper are known in the chemical literature. All reaction mixtures were identified by GC/MS and compared to authentic materials where possible. The yields, reported in Tables 1–3, are GC yields based on tridecane as an internal standard.

Thermal Ni-catalyzed cross-coupling (Table 1, entry 7): In a reaction flask was placed $Ni(acac)_2$ (15.6 mg, 0.0607 mmol), tris(2,4-di-t-butylphosphite) (39.3 mg, 0.0607 mmol), tridecane (104.8 mg, 0.568 mmol, as an internal standard), and 4-fluorotoluene (137.2 mg, 1.246 mmol). The reaction was charged with PhMgBr (1.90 mL, 2 M in THF, 3.80 mmol) and the reaction was heated to 80 °C for 15.5 h. A sample was withdrawn and quenched into dilute 0.5 M aqueous HCl and was extracted with MTBE. GC analysis of the organic phase showed the presence of 4-phenyltoluene (0.983 mmol, 79% yield).

The Ni-catalyzed cross-coupling under microwave conditions (Table 1, entry 7): A sealed thick-walled Pyrex tube was charged with p-tolylfluoride (114.1 mg, 1.037 mmol), $Ni(acac)_2$ (13.8 mg, 0.0537 mmol), *tris*(2,4-di-t-butylphosphite) (69.0 mg, 0.1066 mmol), PhMgCl (2.0 mL, 4.0 mmol) and tridecane (213.0 mg, 1.155 mmole) in THF (1.0 mL). The contents were placed in Smith Creator™ (Personal Chemistry, 2.45

Table 3
Ni- and Pd-catalyzed cross-coupling of aryl fluorides and Grignard reagents[a]

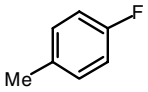
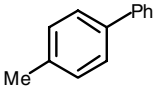
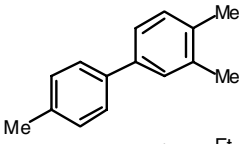
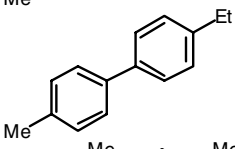
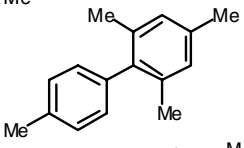
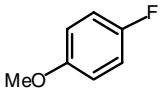
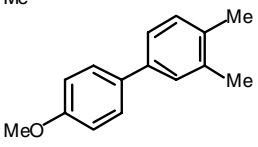
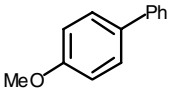
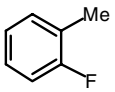
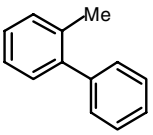
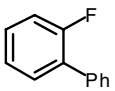
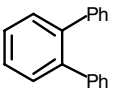
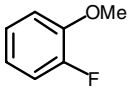
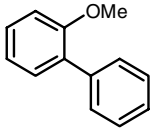
Entry	Aryl fluoride	Catalyst	Conditions	Biaryl	Yield %
1		$Pd(dba)_2$, $PhPCy_2$	80 °C, 65 h		65
2		$Pd(acac)_2$	80 °C, 65 h		43
3		$Pd(dba)_2$, $PhPCy_2$	80 °C, 65 h		49
4		$Pd(dba)_2$, $PhPCy_2$	80 °C, 65 h		52
5		$Pd(dba)_2$, $PhPCy_2$	80 °C, 65 h		21
6		$Pd(dba)_2$	80 °C, 65 h		33
7		$Pd(dba)_2$, $PhPCy_2$	80 °C, 65 h		49
8[b]		$Ni(acac)_2$, $(ArO)_3P$	MW 30 min.		80
9		$Ni(acac)_2$,$(4\text{-}Me_2NC_6H_4)_3P$	80 °C, 15 h		75
10[b]		$Ni(acac)_2$, $(ArO)_3P$	80 °C, 15 h		78
11[b]		$Ni(acac)_2$, $(ArO)_3P$	80 °C, 15 h		59
12[b]		$Ni(acac)_2$, $(ArO)_3P$	MW		35
13		$Pd(dba)_2$, $PhPCy_2$	80 °C, 48 h		40
14[b]		$Ni(acac)_2$, $(ArO)_3P$	MW, 160 °C		25
15[b]		$Ni(acac)_2$, $(ArO)_3P$	80 °C, 15 h		47

Table 3 (*continued*)

Entry	Aryl fluoride	Catalyst	Conditions	Biaryl	Yield %
16		$Pd(dba)_2$, $PhPCy_2$	MW 150 °C 30 min		21
17[b]		$Ni(acac)_2$, $(ArO)_3P$	MW		80
18[b]		$Ni(acac)_2$, $(ArO)_3P$	Thermal		42
19		$Pd(dba)_2$, $PhPCy_2$	MW, 150 °C		98

[a] All microwave reactions (Personal Chemistry, 2.45 GHz) were performed at 130 °C for 10 min except where noted. All thermal reactions were heated at 80 °C. GC yields are based on tridecane as an internal standard.

[b] Ar = 2,4-*t*-$Bu_2C_6H_3$.

GHz) and heated to 100 °C, without using inert gas, by microwave irradiation for 900 s. The cooled reaction mixture was quenched into dilute 0.5 M aqueous HCl and was extracted with MTBE (3 × 10 mL). GC analysis of the organic phase showed the presence of 4-phenyltoluene (0.964 mmol, 93% GC yield).

Thermal Pd-catalyzed cross-coupling (Table 3, entry 1): In a reaction flask was placed $Pd(dba)_2$ (37.3 mg, 0.0649 mmol), $PhPCy_2$ (37.1 mg, 0.1352 mmol), tridecane (72.4 mg, 0.393 mmol, as an internal standard), and 4-fluorotoluene (139.5 mg, 1.267 mmol). The reaction was charged with PhMgBr (1.90 mL, 2M in THF, 3.80 mmol) and the reaction was heated to 80 °C for 62 h. A sample was withdrawn and quenched into dilute 0.5 M aqueous HCl and was extracted with MTBE. GC analysis of the organic phase showed the presence of 4-phenyltoluene (0.823 mmol, 65% yield).

The Pd-catalyzed cross-coupling under microwave conditions (Table 2, entry 17): A sealed thick-walled Pyrex tube was charged with *p*-fluoroanisole (124.7 mg, 0.987 mmol), $Pd(dba)_2$ (35.0 mg, 0.069 mmol), $PhPCy_2$ (34.1 mg, 0.1243 mmol), PhMgCl in THF (1.5 mL, 3.0 mmol) and tridecane (117.2 mg, 0.636 mmol). The contents were placed in Smith Creator™ (Personal Chemistry, 2.45 GHz) and heated to 150 °C, without using inert gas, by microwave irradiation for 600 s. The cooled reaction mixture was quenched into dilute 0.5 M aqueous HCl and was extracted with MTBE (3 × 10 mL). GC analysis of the organic phase showed the presence of 4-methoxybiphenyl (0.542 mmol, 55% GC yield).

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References

[1] The biaryl ring system is regarded as a "privileged structure" comprising about 4.3% of marketed drug compounds. See P.J. Hajduk, M. Bures, J. Praestgaard, S.W. Fesik, J. Med. Chem. 43 (2000) 3443.
[2] G. Bringmann, D. Menche, Acc. Chem. Res. 34 (2001) 615.
[3] T. Yamamoto, Synlett (2003) 425.
[4] (a) For general references, see: E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, vols. 1 and 2. Wiley–Interscience, New York, 2002;
(b) E.-i. Negishi, F. Liu, in: F. Diederich, P.J. Stang (Eds.), Metal-Catalyzed Cross-Coupling reactions, vol. 1, Wiley–VCH, Weinheim, 1998, pp. 1–48;
(c) V. Farina, in: E.W. Abel, F.G.A. Stone, G. Wilkinson, L.S. Hegedus (Eds.), Comprehensive Organometallic Chemistry II, vol. 3.4, Pergamon, Oxford, 1995, pp. 161–240;
(d) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359;
(e) S.P. Stanforth, Tetrahedron 54 (1998) 263;
(f) A.F. Littke, G.C. Fu, Angew. Chem., Int. Ed. Engl. 41 (2002) 4176;
(g) R.J.P. Corriu, J.P. Masse, Chem. Commun (1972) 144;
(h) K. Tamao, K. Sumitani, M. Kumada, J.Am. Chem. Soc. 94 (1972) 4374;
(i) For a review on nickel catalyzed cross-coupling of Grignard reagents and aryl halides, see: M. Kumada, Pure Appl. Chem. 52 (1980) 669.
[5] (a) J.A. Miller, Tetrahedron Lett. 42 (2001) 6991;
(b) J.A. Miller, J.W. Dankwardt, Tetrahedron Lett. 44 (2003) 1907;
(c) J.A. Miller, J.W. Dankwardt, J.M. Penney, Synthesis (2003) 1643.
[6] (a) E. Wenkert, E.L. Michelotti, C.S. Swindell, J. Am. Chem. Soc. 101 (1979) 2246;
(b) E. Wenkert, E.L. Michelotti, C.S. Swindell, M. Tingoli, J. Org. Chem. 49 (1984) 4894;
(c) J.W. Dankwardt, Angew. Chem., Int. Ed. 43 (2004) 2428.
[7] S. Sengupta, M. Leite, D.S. Raslan, C. Quesnelle, V. Snieckus, J. Org. Chem. 57 (1992) 4066.
[8] M. Hudlicky, Chemistry of Organic Fluorine Compounds, Prentice-Hall, New York, 1992.
[9] Y. Kiso, K. Tamao, M. Kumada, J. Organomet. Chem. 50 (1973) C12.
[10] V.P.W. Böhm, C.W.K. Gstöttmayer, T. Weskamp, W.A. Herrmann, Angew. Chem. Int. Ed. 40 (2001) 3387.

[11] F. Mongin, L. Mojovic, B. Guillamet, F. Trécourt, G. Quéguiner, J. Org. Chem. 67 (2002) 8991.
[12] K. Lamm, M. Stollenz, M. Meier, H. Görls, D. Walther, J. Organomet. Chem. 681 (2003) 24.
[13] (a) Y.M. Kim, S. Yu, J. Am. Chem. Soc. 125 (2003) 1696;
(b) D.A. Widdowson, R. Wilhelm, Chem. Commun. (2003) 578;
(c) D.A. Widdowson, R. Wilhelm, J. Chem. Soc., Perkin Trans. I (2000) 1308;
(d) M. Jakt, L. Johannissen, H.S. Rzepa, D.A. Widdowson, R. Wilhelm, J. Chem. Soc., Perkin Trans. 2 (2002) 576;
(e) T. Braun, R.N. Perutz, M.I. Sladek, Chem. Commun. (2001) 2254.
[14] M. Larhed, C. Moberg, A. Hallberg, Acc. Chem. Res. 35 (2002) 717.
[15] (a) B.H. Lipshutz, T. Tomioka, P.A. Blomgren, J.A. Sclafani, Inorg. Chim. Acta 296 (1999) 164;
(b) S. Tasler, B.H. Lipshutz, J. Org. Chem. 68 (2003) 1190.