Tetrahedron Letters xxx (2017) xxx-xxx

Contents lists available at ScienceDirect



Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Mono- and dinuclear cyclopalladates as catalysts for Suzuki–Miyaura cross-coupling reactions in predominantly aqueous media

G. Narendra Babu, Samudranil Pal*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

ARTICLE INFO

Article history: Received 28 December 2016 Revised 23 January 2017 Accepted 25 January 2017 Available online xxxx

Keywords: Cyclopalladates Mono- and dinuclear Suzuki-Miyaura cross-coupling Aqueous media

ABSTRACT

Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids were performed in predominantly aqueous media employing two mono- and two dinuclear cyclopalladated complexes as catalysts. These complexes are [Pd(HL)Cl] (I), [Pd(L)(PPh₃)] (II), [Pd₂(μ -dppb)(L)₂] (III) and [Pd₂(μ -dppf)(L)₂] (IV); where H₂L, dppb and dppf represent 4-methoxy-N'-(mesitylidene)benzohydrazide, 1,4-bis (diphenylphosphino)butane and 1,1'-bis(diphenylphosphino)ferrocene, respectively. The reactions were conducted using potassium carbonate as base in presence of tetrabutylammonium bromide (TBAB) at 70/90 °C in dimethylformamide–water (1:20) mixture. Among the four catalysts used, the dinuclear complex IV turned out to be the most effective and afforded moderate to excellent yields with broad substrate scope.

© 2017 Elsevier Ltd. All rights reserved.

Biaryls and biheteroaryls are an important class of compounds as they are significant building blocks for a variety of natural products, pharmaceuticals, agrochemicals and functional materials such as sensors and liquid crystals.¹ The most convenient and useful method for the single step synthesis of a biaryl or biheteroaryl is the Csp²–Csp² Suzuki–Miyaura cross-coupling reaction.² Since the discovery of this catalytic coupling reaction, there is a continuous effort to develop new catalyst systems which will be effective for a wide range of products. Generally organic media are more common for this coupling reaction. However, due to the environmental concerns necessity for the use of the benign solvent water as the medium for chemical reactions is continuously growing. Thus, in recent times, there is a particular emphasis on the development of catalyst systems that will be effective for Suzuki-Miyaura cross-coupling reactions in aqueous media.³ So far, among the various catalyst systems used for Suzuki-Miyaura reaction in aqueous or aqueous-organic media, very few are based on cyclopalladated complexes.⁴ These complexes are either water soluble for use in homogeneous reactions or anchored to silica or nano-particles for applications in heterogeneous reactions. We have been working on coordination⁵ and cyclometallated⁶ complexes of transition metal ions with Schiff bases and reduced Schiff bases and their applications as catalysts in synthetic organic reactions for the past couple of years. Recently we have reported a series of mononuclear and dinuclear cyclometallated palladium(II)

* Corresponding author. E-mail address: spal@uohyd.ac.in (S. Pal).

http://dx.doi.org/10.1016/j.tetlet.2017.01.089 0040-4039/© 2017 Elsevier Ltd. All rights reserved. complexes with the Schiff base 4-methoxy-*N*'-(mesitylidene)benzohydrazide (H₂L).⁷ In these complexes having the formulas [Pd (HL)Cl] (**I**), [Pd(L)(PPh₃)] (**II**), [Pd₂(μ -dppb)(L)₂] (**III**) and [Pd₂(μ dppf)(L)₂] (**IV**) (dppb = 1,4-bis(diphenylphosphino)butane and dppf = 1,1'-bis(diphenylphosphino)ferrocene); the ligands ((HL)⁻ and (L)²⁻) have the 5,6-membered fused chelate rings forming pincer-like ONC-coordinating mode (Chart 1). In the present work, we have examined the catalytic properties of these four complexes in Suzuki–Miyaura cross-coupling reactions of phenyl- and 2-naphthylboronic acids with electronically diverse types of aryl halides in predominantly aqueous media.

4-bromobenzaldehyde and phenylboronic acid were chosen as the model substrates for optimization of the reaction conditions. The reactions were performed in water (2 ml) under aerobic conditions at 70 °C in presence of tetrabutylammonium bromide (TBAB) by varying the catalyst (I-IV) (taken in 0.1 ml of dimethylformamide (DMF)), catalyst loading (mol% of the metal complex), base, and the amounts of base and TBAB (Table 1). Among the four catalysts I-IV assessed (entries 1-4), catalyst IV provided the highest yield in shortest reaction time (entry 4). Decrease in the mol% of IV resulted into significant decrease in the yield and increase in the reaction time (entries 5-7). Considering the dinuclearity of IV, it is expected to be more productive than either of the two mononuclear complexes (I and II). But, the performances of IV with significantly lower loadings of 0.01-0.0001 mol% were better than the performances of 0.1 mol% of both I and II (entries 1 and 2). Variation of reaction temperature (entries 8-10) showed that at elevated temperature (90 °C) though same yield was obtained

G.N. Babu, S. Pal/Tetrahedron Letters xxx (2017) xxx-xxx



Chart 1. Chemical structures of I-IV.

Table 1Optimization of reaction conditions.^a

but there was no significant decrease in the reaction time (entry 10). K_2CO_3 turned out to be the best base when compared with the other inorganic bases and triethylamine (entries 11-16). Lowering of the amount of K₂CO₃ from 2 mmol to 1.5 mmol increased the reaction time by 1 h for the same yield (99%) (entry 17). However, further lowering resulted into significant decrease in the yields (entries 18 and 19). Similarly decrease in the amount of TBAB or its absence resulted into significantly reduced yields in longer durations of the reactions (entries 20-22). The requirement of TBAB is perhaps due to the formation of $[Bu_4N][BPh(OH)_3]$ which helps to increase the rate of the reaction and hence more yield of the cross-coupling product.^{4b,8} The control experiments showed no detectable product formation without catalyst (entry 23), while yields were 29 or 21% in presence of catalyst but without base (entry 24) or both base and TBAB (entry 25), respectively. Thus the conditions used for entry 17 were found to be optimal and used for subsequent reactions with various substrates.9

The optimized conditions as described above were then employed for Suzuki–Miyaura cross-coupling reactions of substituted phenyl bromides with phenylboronic acid. The products¹⁰ obtained with the required reaction times and the yields are listed in Table 2. Phenyl bromides bearing electron withdrawing groups at *para* position were more reactive and provided excellent yields (\geq 98%) in 6 h (entries 1, 4 and 5). In comparison, reactions involving phenyl bromides containing electron withdrawing groups at



Entry	Catalyst (mol%)	Base (mmol)	TBAB (mmol)	Time (h)	Yield ^b (%)
1	I (0.1)	$K_2CO_3(2)$	1	12	63
2	II (0.1)	$K_2CO_3(2)$	1	8	77
3	III (0.1)	$K_2CO_3(2)$	1	8	95
4	IV (0.1)	$K_2CO_3(2)$	1	5	99
5	IV (0.01)	$K_2CO_3(2)$	1	6	84
6	IV (0.001)	$K_2CO_3(2)$	1	6	71
7	IV (0.0001)	$K_2CO_3(2)$	1	10	59
8	IV (0.1)	$K_2CO_3(2)$	1	24	76 ^c
9	IV (0.1)	$K_2CO_3(2)$	1	18	88 ^d
10	IV (0.1)	$K_2CO_3(2)$	1	4.5	99 ^e
11	IV (0.1)	NaOH (2)	1	12	92
12	IV (0.1)	KOH (2)	1	12	93
13	IV (0.1)	$K_{3}PO_{4}(2)$	1	12	84
14	IV (0.1)	$CS_2CO_3(2)$	1	12	86
15	IV (0.1)	Et ₃ N (2)	1	12	75
16	IV (0.1)	$Na_2CO_3(2)$	1	6	94
17	IV (0.1)	K_2CO_3 (1.5)	1	6	99
18	IV (0.1)	$K_2CO_3(1)$	1	6	82
19	IV (0.1)	K_2CO_3 (0.5)	1	6	71
20	IV (0.1)	K_2CO_3 (1.5)	0.5	12	80
21	IV (0.1)	K_2CO_3 (1.5)	0.2	12	64
22	IV (0.1)	K_2CO_3 (1.5)	-	12	49
23	-	K_2CO_3 (1.5)	1	24	-
24	IV (0.1)	_	1	24	29
25	IV (0.1)	_	-	24	21

^a 4-Bromobenzaldehyde (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (I-IV) in 0.1 ml of dimethylformamide, tetrabutylammonium bromide (TBAB) (1.0 mmol), H₂O (2 ml).

^b GC-MS yield (based on 4-bromobenzaldehyde).

° At 25 °C.

^d At 50 °C.

^e At 90 °C.

G.N. Babu, S. Pal/Tetrahedron Letters xxx (2017) xxx-xxx

Table 2

Suzuki-Miyaura reactions of aryl bromides with phenylboronic acid.^a



Entry	R	Product	Time (h)	Yield ^b (%)	Ref.
1	р-СНО	Рh	6	99	10a
2	o-CHO	онс	6, 8	82, 91	10a
		Ph			
3	т-СНО	СНО	6	92	10b
		Ph			
4	p-NO ₂	Ph-NO ₂	5	99	10b
5	р-СООН	Ph-COOH	6	98	10c
6	т-соон	СООН	6	94	10c
		Ph			
7	<i>p</i> -OMe	Ph-	8	94	10a
8	<i>m</i> -OMe	OMe	8	90	10a
		Ph			
9	o-OMe	MeO	8	84	10a
		Ph			
10	p-OH	PhOH	8	91	10c
11	<i>m</i> -OH	ОН	8	85	10c
		Ph-			
12	o-OH	HO	8	78	10d
10		Ph-	<u>,</u>	20	10
13	<i>р</i> -NH ₂		8	86	10e
14	o-NH ₂	H ₂ N	8	74	10e
		Ph—			

^a Aryl bromide (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst **IV** (0.1 mol%) in 0.1 ml of dimethylformamide, K₂CO₃ (1.5 mmol), TBAB (1.0 mmol), H₂O (2 ml). ^b GC-MS yield (based on aryl bromide).

meta position produced slightly lower yields (~93%) in the same reaction time of 6 h (entries 3 and 6). In contrast, due to steric effect ortho-bromobenzaldehyde gave a relatively modest yield of 82% in 6 h and 91% when the reaction was allowed for longer time of 8 h (entry 2). In contrast, phenyl bromides containing electron donating groups showed somewhat low reactivities and gave moderate to excellent yields in longer reaction durations (entries 7-14). In the cases of para- and meta-bromoanisoles, yields of coupling products were \geq 90%, while the yield was 84% for *ortho*-anisole in 8 h of reaction time for each (entries 7–9). Similarly, in 8 h, yields were 85-91% for both para- and meta-bromophenols and para-bromoaniline (entries 10, 11 and 13). However, because of steric effect both ortho-bromophenol and ortho-bromoaniline provided the corresponding coupling products in lower yields of 78 and 74%, respectively in 8 h (entries 12 and 14). Thus, in general, presence of electron withdrawing substituents enhances the reactivities of the aryl bromides in comparison to the electron donating substituents, as reported earlier.¹¹

The same approach as described above for phenylboronic acid was employed for the cross-coupling reactions of 2-naphthylboronic acid with a variety of aryl bromides using the catalyst **IV**. **Table 3** lists the products¹² isolated with the corresponding reaction times and the yields. Results were very similar to those observed for phenylboronic acid. Excellent yields (96%) of the coupling products were obtained in 6 h for phenyl bromides having electron withdrawing groups at *para* position (entries 1 and 2). On the other hand, yields were relatively less (91 and 86%) even in longer reaction time (8 h) for phenyl bromides having electron donating groups at the same *para* position (entries 3 and 4). Similar or even less yields of 88 and 80% were obtained in 8 h for two electron donating atoms/groups containing aryl bromides such as 5-bromo-1,3-benzodioxole and 4-bromo-1,2-dimethoxybenzene,

Please cite this article in press as: Babu G.N., Pal S. Tetrahedron Lett. (2017), http://dx.doi.org/10.1016/j.tetlet.2017.01.089

4

G.N. Babu, S. Pal/Tetrahedron Letters xxx (2017) xxx-xxx

Table 3

Suzuki-Miyaura reactions of aryl bromides with 2-naphthylboronic acid.^a



Entry	Aryl bromide	Product ^b	Time (h)	Yield ^c (%)	Ref.
1	ВгСНО	Np-	6	96	12a
2	Br-NO ₂		6	96	12b
3	Br	Np	8	91	12b
4	Br-NH ₂		8	86	12c
5			8	88	12d
6	OMe	OMe	8	80	12e
	Br	Np			
7	СНО	СНО	10, 16	62, 80	12c
	Br————————————————————————————————————	Np{ОН			
8	Br	Np	10	90	12c
9	Br		6	92	12f
10	Br —		8	94	12g
	Ň	· ``N			

^a Aryl bromide (1.0 mmol), 2-naphthylboronic acid (1.2 mmol), catalyst **IV** (0.1 mol%) in 0.1 ml of dimethylformamide, K₂CO₃ (1.5 mmol), TBAB (1.0 mmol), H₂O (2 ml).

^b Np represents the 2-naphthyl group.

^c Isolated yield.

respectively (entries 5 and 6). Interestingly, among all the aryl bromides, 5-bromo-2-hydroxybenzaldehyde having an electron donating group as well as an electron withdrawing group was least reactive and provided comparatively very low yields of 62 and 80% yields in significantly longer reaction durations of 10 and 16 h, respectively (entry 7). Furthermore, catalyst **IV** was also very effective for heteroaryl bromides such as 2-bromothiophene, 2-acetyl-5-bromothiophene and 2-bromopyrimidine, and the reactions afforded >90% yields of the corresponding aryl-heteroaryl crosscoupling products in 6–10 h (entries 8, 9 and 10). Here also presence of electron withdrawing substituent on the heteroaryl bromide enhances its reactivity (entries 8 and 9).

The aryl chlorides are less reactive than the aryl bromides because of the stronger C–Cl bond than the C–Br bond.¹³ Hence, previously reported cyclopalladate catalyzed Suzuki–Miyaura coupling reactions involving aryl chlorides in water or water–organic mixed solvents were generally performed at rather higher temperatures ($\geq 100 \text{ °C}$).⁴ However, somewhat related complexes of {Pd (CH₃)(PR₃)}⁺ with NN-coordinating β -dikitiminate ligands were shown to effectively catalyze coupling of aryl chlorides with arylboronic acids in ethanol-water (1:1) mixture at lower temperatures ranging from 50–80 °C.¹⁴ We also examined the catalytic effectiveness of complex **IV** in the cross-coupling reactions of phenylboronic acid with a range of aryl chlorides. The products^{10,15} formed, reaction durations and the yields are summarized in **Table 4**. Under the same optimized conditions as used for aryl bromides (**Table 1**, entry 17), the yields were 63 and 74% in reaction

times of 10 and 18 h, respectively for para-nitrochlorobenzene. Increase of reaction temperature from 70 to 90 °C led to the improved yields of 71 and 82% in 10 and 18 h, respectively. The yield improved further to 98% in 10 h reaction time when the catalyst loading was also increased from 0.1 to 0.2 mol% with the increase of temperature to 90 °C. Thus the conditions used for entry 1 in Table 4 were found to be the best and applied for the remaining aryl chloride substrates. Chlorobenzenes substituted at para position by electron withdrawing groups provided excellent yields (95-99%) of the corresponding coupling products in 10 h (entries 1-3). In slightly longer reaction time of 12 h, chlorobenzenes with electron withdrawing substituents at meta position also gave very good yields (91 and 94%) (entries 4 and 5). Whereas, a comparatively moderate yield of 84% was obtained for orthochlorobenzonitrile in 12 h (entry 6). In contrast, the coupling reactions of chlorobenzenes having electron donating groups at the para position required somewhat longer reaction time (14 h) for moderate to very good yields (83–91%) (entries 7–9). The reaction with the heteroaryl chloride 2-chloropyrimidine was also successful and a yield of 85% was obtained in a reaction time of 12 h. Not surprisingly, as observed before⁴ here also the aryl chlorides required higher reaction temperature as well as higher catalyst loading and longer reaction durations for moderate to excellent vields of the cross-coupling products in comparison to the aryl bromides due to the difference in the C–Cl and C–Br bond strengths.¹³

In summary, the catalytic properties of a series of mono- and dinuclear cyclometallated palladium(II) complexes having the

G.N. Babu, S. Pal/Tetrahedron Letters xxx (2017) xxx-xxx

Table 4

Suzuki-Miyaura reactions of aryl chlorides with phenylboronic acid.^a



Entry	Aryl chloride	Product	Time (h)	Yield ^b (%)	Ref.
1	O ₂ N-CI	O ₂ N-Ph	10	98	10b,15a
2	PhOC — Cl	PhOC Ph	10	99	15a
3	ноос	HOOC-	10	95	10c,15a
4	онс	онс	12	91	10b
	CI CI	Ph			
5	NC	NC	12	94	15b
C	CI	Ph	10	84	15b
0			12	84	
	СІ	Ph Ph			
7		H ₂ N-Ph	14	83	10e,15a
8	HO	HO	14	87	10c,15a
9	MeO	MeO	14	91	10a,15a
10			12	85	12g
	\N C'				

^a Aryl chloride (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst **IV** (0.2 mol%) in 0.1 ml of dimethylformamide, K₂CO₃ (1.5 mmol), TBAB (1.0 mmol), H₂O (2 ml). ^b GC-MS yield (based on aryl chloride).

pincer-like ONC-donor $(L)^{2-}$ (H₂L = 4-methoxy-*N*-(mesitylidene) benzohydrazide) as primary and monodentate chloride or monophosphine or bidentate bridging diphosphines as ancillary ligands in Suzuki-Miyaura cross-coupling reactions of a diverse range of aryl bromides and chlorides with arylboronic acids in predominantly aqueous media were investigated. Out of the four complexes evaluated, the dinuclear [Pd₂(µ-dppf)(L)₂] containing the 1,1'-bis(diphenylphosphino)ferrocene (dppf) as the bridging ligand turned out to be the best performing catalyst. The catalytic reactions exhibited a broad substrate scope and afforded a wide variety of biaryl and aryl-heteroaryl products. The yields were moderate to excellent in reasonably short duration reactions.

Acknowledgments

G.N. Babu thanks the Council of Scientific and Industrial Research, New Delhi for a research fellowship (No. 09/414 (1025)/2012-EMR-I). Financial support and instrumental facilities provided by the Department of Science and Technology, New Delhi through the FIST and the PURSE programs and by the University Grants Commission, New Delhi through the CAS and the UPE programs are gratefully acknowledged.

References

(a) Aldemir H, Richarz R, Gulder TAM. Angew Chem Int Ed. 2014;53:8286–8293;
 (b) Zhong G-X, Chen L-L, Li H-B, Liu F-J, Hu J-Q, Hu W-X. Biorg Med Chem Lett. 2009;19:4399–4402;
 (c) Dadibovena S. Eur J Med Chem. 2012;51:17–34;

(d) Chai T, Yang W, Qiu J, Hou S. *Chirality*. 2015;27:32–38; (e) Pu L. *Acc Chem Res*. 2012;45:150–163;

- (f) Solladie G, Gottarelli G. Tetrahedron. 1987;43:1425–1437.
- (a) Miyaura N, Suzuki A. Chem Rev. 1995;95:2457–2483;
- (b) Kotha S, Lahiri K, Kashinath D. *Tetrahedron*. 2002;58:9633–9695;
- (c) Molander GA, Canturk B. Angew Chem, Int Ed. 2009;48:9240–9261; (d) Suzuki A. Angew Chem, Int Ed. 2011;50:6722–6737;
- (e) Han F-S. Chem Soc Rev. 2013;42:5270–5298;
- (f) Lennox AJJ, Lloyd-Jones GC. Chem Soc Rev. 2014;43:412–443;
- (g) Paul S, Islam MdM, Islam SkM. *RSC Adv.* 2015;5:42193–42221;
- (h) Maluenda I, Navarro O. *Molecules*. 2015;20:7528–7557.
- (a) Polshettiwar V, Decottignies A, Len C, Fihri A. *ChemSusChem.*
- 2010;3:502–522; (b) Li X Zhau X Cua M Ora Diamal Cham
- (b) Liu S, Lv M, Xiao D, Li X, Zhou X, Guo M. Org Biomol Chem. 2014;12:4511-4516;
- (c) Liu Y, Gu N, Liu P, Ma X, Xie J, Dai B. Tetrahedron. 2015;71:7985-7989;
- (d) Wang S, Guo R, Li J, Zou D, Wu Y, Wu Y. Tetrahedron Lett. 2015;56:3750-3753;
- (e) Dewan A, Bharali P, Bora U, Thakur AJ. RSC Adv. 2016;6:11758–11762;
- (f) Chatterjee A, Ward TR. *Catal Lett.* 2016;146:820–840.
 (a) Alonso DA, Nájera C, Pacheco MC. J Org Chem. 2002;67:5588–5594;
 (b) Botella L, Nájera C. *Angew Chem Int Ed.* 2002;41:179–181;
 (c) Chen C-L, Liu Y-H, Peng S-M, Liu S-T. *Tetrahedron Lett.* 2005;46:521–523;
- (d) Huang R, Shaughnessy KH. Organometallics. 2006;25:4105–4112; (e) Li H, Wu Y. Appl Organomet Chem. 2008;22:233–236;
- (f) Zhang G, Zhang W, Luan Y, Han X, Ding C. Chin J Chem. 2015;33:705–710.
- 5. (a) Kurapati SK, Maloth S, Pal S. Inorg Chim Acta. 2015;430:66–73; (b) Prabhu RN, Pal S. Tetrahedron Lett. 2015;56:5252–5256;
 - (c) Kurapati SK, Pal S. Appl Organomet Chem. 2016;30:116–124;
 - (d) Prabhu RN, Babu GN, Pal S. Appl Organomet Chem. 2017;31:e3544;
 - (e) Ghosh S, Kurapati SK, Pal S, Polyhedron, http://dx.doi.org/10.1016/j.poly. 2016.08.025.
- 6. (a) Babu GN, Pal S. J Organomet Chem. 2016;824:42–47;
 (b) Keesara S, Babu GN, Pal S, Appl Organomet Chem, http://dx.doi.org/10.1002/ aoc 3778
- 7. Babu GN, Pal S. J Organomet Chem. 2016;805:19-26.

6

G.N. Babu, S. Pal/Tetrahedron Letters xxx (2017) xxx-xxx

8. Badone D, Baroni M, Cardamone R, Ielmini A, Guzzi U. J Org Chem. 1997;62:7170–7173.

- 9. General procedure: An oven-dried round bottom flask (10 ml) was charged with 0.1 ml dimethylformamide solution of complex **IV** (0.1 mol% for aryl bromides and 0.2 mol% for aryl chlorides), aryl boronic acid (1.2 mmol), aryl halide (1.0 mmol), K₂CO₃ (1.5 mmol), TBAB (1.0 mmol) and 2 ml water. The reaction mixture was then heated (to 70 °C for aryl bromides and 90 °C for aryl chlorides) with stirring under aerobic conditions for the required time. At the end of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (2×5 ml). The combined extract was washed with water (2×10 ml), dried over anhydrous sodium sulfate and then subjected to GC-MS analysis for identification and yield determination (from the areas under the peaks) of the products. In the case of reactions with 2-naphthylboronic acid, the combined extract was evaporated to dryness under reduced pressure and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane) to afford the coupling products. The products were identified by ¹H and ¹³C NMR and HR-MS analysis.
- (a) Mino T, Shirae Y, Sakamoto M, Fujita T. J Org Chem. 2005;70:2191–2194;
 (b) Srimani D, Sarkar A. Tetrahedron Lett. 2008;49:6304–6307;
 - (c) Li L, Wu T, Wang J, Wang R. ChemPlusChem. 2014;79:257-265;
 - (d) Okamoto K, Akiyama R, Kobayashi S. Org Lett. 2004;6:1987-1990;
 - (e) Li Z, Gelbaum C, Heaner WL, et al. Org Process Res Dev. 2016;20:1489-1499.

- (a) Saito S, Oh-tani S, Miyaura N. J Org Chem. 1997;62:8024–8030;
 (b) Weissman H, Milstein D. Chem Commun. 1999;1901–1902;
 (c) Zim D, Gruber AS, Ebeling G, Dupont J, Monteiro AL. Org Lett. 2000;2:2881–2884.
 (c) Alace N, Ander T. Shiharaki E et al. Tatrahadram Lett. 2014;55:1046–1049;
- (a) Mase N, Ando T, Shibagaki F, et al. *Tetrahedron Lett.* 2014;55:1946–1948;
 (b) Sultana T, Mandal BH, Rahman MdL, Sarkar SM. *ChemistrySelect.* 2016;1:4108–4112;
 (c) Bolligera JL, Frecha CM. *Adv Synth Catal.* 2010;352:1075–1080;
 - (d) Bei X, Turner HW, Weinberg WH, Guran AS. J Org Chem. 1999;64:6797–6803; (e) Zotto AD, Amoroso F, Baratta W, Rigo P. Eur J Org Chem. 2009;110–116;
 - (f) Dang TT, Bonneau M, Williams JAG, Bozec HL, Doucet H, Guerchais V. Eur J Inorg Chem. 2015;2956–2964;
 - (g) Bhadra S, Matheis C, Katayev D, Gooßen LJ. Angew Chem Int Ed. 2013;52:9279–9283.
- 13. Luo Y-R. Handbook of Bond Dissociation Energies in Organic Compounds. Boca Raton: CRC Press LLC; 2003.
- 14. Lee D-H, Jin M-J. Org Lett. 2011;13:252-255.
- (a) Rao GK, Kumar A, Ahmedz J, Singh AK. *Chem Commun.* 2010;46:5954–5956;
 (b) Ke H, Chen X, Zou G. *Appl Organomet Chem* 2014;28:54–60.