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Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

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To cite this article: Pronnoy G. Bangar , Priyanka R. Jawalkar , Swapnil R. Dumbre , Pallavi K. Raut , Dharmaraj J. Patil , Neethu Tv , Shana Sudhakaran & Suresh Iyer (2020): Mizoroki–Heck reaction of 1,2-disubstituted aryl alkenes: Variables of synthesis, solvent and ligand modulation of reactivity, Synthetic Communications, DOI: 10.1080/00397911.2020.1811986

To link to this article: https://doi.org/10.1080/00397911.2020.1811986

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https://doi.org/10.1080/00397911.2020.1811986

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Mizoroki–Heck reaction of 1,2-disubstituted aryl alkenes: Variables of synthesis, solvent and ligand modulation of reactivity

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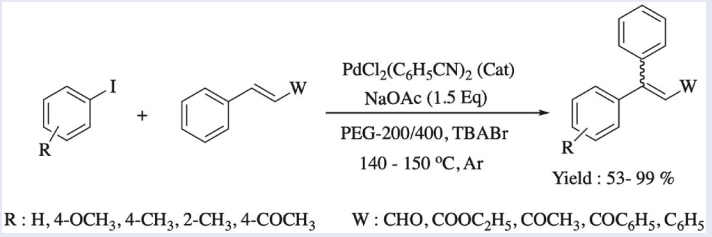
ABSTRACT

Reaction of aryl iodides with 1,2-disubstituted aryl alkenes in the presence of TBABr/TBACl gave high yields of the Mizoroki–Heck product. Phosphine ligands were used for the modulation of reactivity and stereoselectivity, for the reaction of 4-iodoanisole with cinnamaldehyde. tert-$Bu_3P.HBF_4$ gave the highest E:Z ratio of 1:0.08. The use of PEG-200 and PEG-400 as solvent could activate the reaction of aryl iodides with various 1,2-disubstituetd aryl alkenes.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 22 May 2020

KEYWORDS
12-Disubstituted aryl alkenes; ligand effect; Mizoroki–Heck reaction; PEG 200/400; TBABr

Introduction

The Mizoroki–Heck is a versatile and fast reaction of monosubstituted alkenes with aryl iodides, giving E-isomer products in very high yields and regioselectivity.[1–4] 1,1 and 1,2 disubstituted alkenes are difficult substrates requiring long reaction times and special reagents.[5–13] The resulting 1,1,2-trisubstituted aryl alkene scaffolds have been shown to be important bioactive molecules and drugs like Tamoxifen also synthesized from them.[14–18] The 1,1-diaryl substitution pattern is present in several drug molecules like fenpiprane and tolterodine.[18] The core pi structure of various molecules exhibit OLED and other properties and has been the subject of platform synthesis.[19–21] The 1,1′,2,2′,-pi scaffold is a difficult to construct molecular architecture. A user-friendly reaction is required for arylation and vinylation of disubstituted alkenes and it is also necessary to address stereoselectivity in these reactions.

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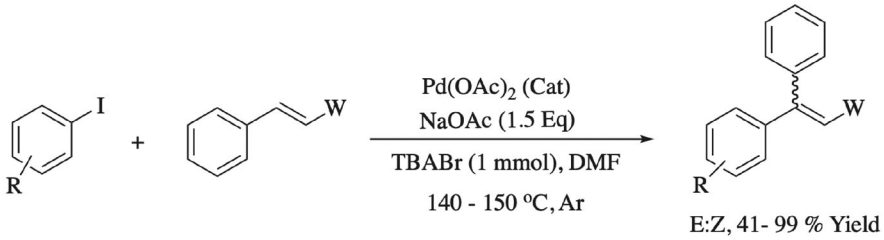


R : H, 4-OCH_3, 4-CH_3, 4-F, 2-CH_3 W : CHO, $COOC_2H_5$, $COCH_3$, COC_6H_5, C_6H_5

Scheme 1. TBABr additive for the $PdOAc_2$ catalyzed Mizoroki–Heck reaction of 1,2 disubstituted aryl alkenes.

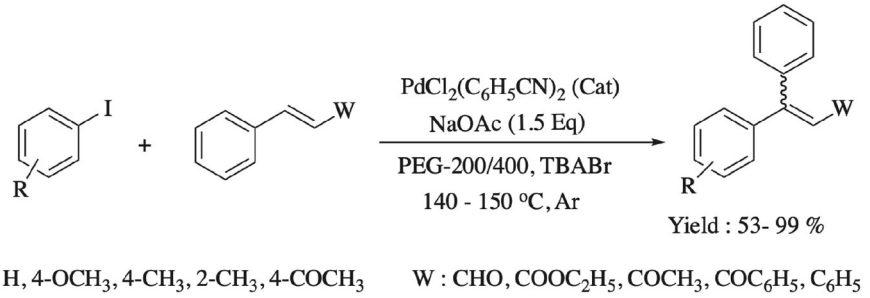
There are a few standard protocols for the arylation of disubstituted alkenes, though limited in the generality of application; they typically are sluggish reactions and requiring long reaction times, special bases, reagents or ligands.[5–13] Ciufolini and coworkers describe the reactions to be limited to electron rich aryl iodides, specifically 4-iodo anisole and 4-N, N-dimethyl amino iodo benzene.[22,23] Other reactions require the use of Ionic Liquids.[24–26]

Monteiro and coworkers have reported the Mizoroki–Heck reaction of aryl bromides with stilbenes, requiring 48 h for completion.[27] The silver sequestration of halides has been used in the asymmetric Mizoroki–Heck reaction and vinylation of allyl alcohols.[28–33] Stoichiometric Ag_2CO_3 has been used for the Pd catalyzed arylation of fluoro acrylates.[34] Chen et al have reported AgOAc mediated disubstitution of mono-substituted alkenes, ethyl acrylate and styrene.[35] More recently the arylation of aryl vinyl MIDA boronates followed by Suzuki coupling for the synthesis of triarylethylene units have been described.[36] We have communicated the silver sequestration of aryl iodides for reaction with various 1,1 and 1,2 disubstituted aryl alkenes, providing 1,1,2- trisubstituted aryl alkenes in very high yields in short reaction times.[37] Ligands and reagents ramp up the magical activity of the catalyst marvel, Pd. Stoichiometric silver salts being expensive, we investigated ligand alternatives for silver as well as solvent variations. We now report in this article the studies conducted on the silver free arylation of various 1,2-disubstituted alkenes.

Results and discussion

In a preliminary communication, we described the Pd catalyzed arylation of diphenylethene, ethyl atropate, itaconate and several 1,2-disubstituted aryl alkenes in very high yields, using stoichiometric AgOAc.[37] We report here a silver free, user-friendly protocol for the high yielding arylation of 1,2-disubstituted aryl alkenes (Schemes 1 and 2). This is thus an easy entry into drug molecules like Tamoxifen, Fenpiprane, and Tolterodine. While the original Mizoroki–Heck reaction is E-selective, 1,2-disubstituted aryl alkenes give E: Z mixtures.

The use of silver salts being stoichiometric and expensive, the search for inexpensive alternatives was essential. Molten TBABr has been used as a solvent for the arylation of ethyl cinnamate.[5] N-Phenyl urea as ligand promotes the Pd catalyzed reaction of various 1, 2-disubstituted alkenes but limited to 4-iodo anisole and 4-N,N-dimethyl amino iodo benzene.[22,23] Jeffery Tuyet has reported the first use of TBACl and TBABr for the Mizoroki–Heck reaction of mono-substituted alkenes giving high yields and reactions at RT.[38] The use of Ionic liquids, TBAA and TBABr demonstrates enhanced reactivity for



Scheme 2. [Pd] (Cat) Mizoroki–Heck reaction of disubstituted alkenes in PEG-200 and PEG-400.

1,2-disubstituted alkenes.[24–26] In this study, reaction of 1,2-disubstituted aryl alkenes in DMF as solvent and TBABr as additive, gave reasonably fast reactions and high yields without the addition of silver salts (Scheme 1; Table 1). TLC monitoring of these reactions was difficult due to the close Rf value of the product and starting materials. Repeated elutions of the TLC gave visible separations and thus reactions could be concluded.

Having established the reactivity of 4-iodoanisole with cinnamaldehyde, we explored randomly the reactivities of several aryl iodides with various 1,2-disubstituted alkenes using OTP, BINAP and acetophenone oxime as ligands in conjunction with $Pd(OAc)_2$ as catalyst (Scheme 1; Table 1). Exceptionally good yields were obtained with several aryl iodides and alkenes compared to the results of Ciufolini where only electron-rich aryl iodides were productive. 4-FC_6H_4I reacted with ethyl cinnamate to give 86% yield and a E:Z ratio of 9: 1.

In several publications, the use of TBABr and TBACl as an additive has been shown to be conducive for high yields in the Mizoroki–Heck reactions and also for some examples with 1,2-disubstituted alkenes.[8] This effect along with variations in ligands in the reaction of different aryl iodides and several 1,2-disubstituted alkenes was explored (Scheme 1; Table 1). Very good yields were obtained but low E:Z ratios. Reactions were comparable with the use of additives like AgOAc and $AgBF_4$.

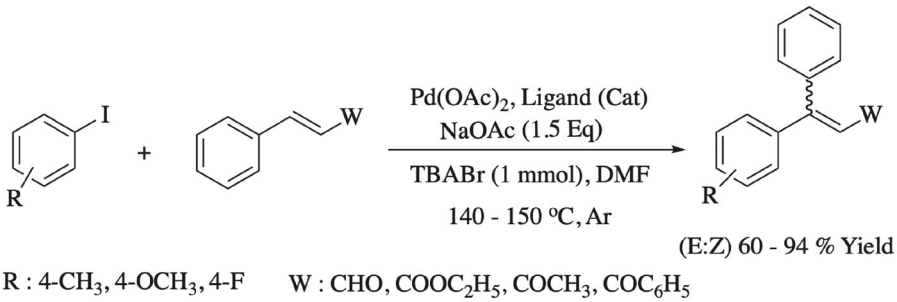
Search for increased reactivity and inexpensive silver alternatives led us to examine solvent variations. The Mizoroki–Heck reaction has been shown to be especially facile in PEG-400.[39] PEG has also been shown to be a good solvent for the Mizoroki–Heck reaction with various other catalysts.[40–47] The reaction of disubstituted aryl alkenes in PEG-400/200 catalyzed by $PdCl_2(C_6H_5CN)_2$, with an inorganic base and in the absence of Ag salts was explored (Scheme 2; Table 1). To our delight, most of these reactions were very high yielding with moderate reaction times of $2.1 - 34$ h, but mixtures of E:Z isomers.

Ligands conjure the magical wizardry associated with Pd catalysis. So the reaction of 4-iodo anisole with E-cinnamaldehyde for the effect of various ligands on reactivity, yields and stereoselectivity was investigated (Scheme 3; Table 2). All the ligands studied gave high yields of the substituted alkenes. Best result was obtained with tert-$Bu_3P.HBF_4$ with a yield of 96%, reaction time of 5 h and E:Z ratio of 1:0.08.[48] PCy_3 was second with a yield of 90% in 3 h and E:Z ratio of 1: 0.24. Nonphosphine ligands—acetophenone oxime, ThCOOH and proline gave good yields in $16 - 24$ h, but low E:Z ratios. Palladacycle catalysts also gave high yields in $20 - 24$ h, but low E:Z ratios.

The effect of OTP was then studied for the reaction of substituted aryl iodides with 1,2-disubstituted aryl alkenes in DMF solvent with TBABr additive and NaOAc as base.

Table 1. TBABr/TBACl additive & solvent (PEG-200, PEG-400) effects for the Pd-catalyzed Mizoroki–Heck reaction of 1,2 disubstituted aryl alkenes with aryl iodides.

S. No	Aryl Halide	Alkene	Ligand/Reagent/Solvent	Catalyst	Time, h	Yield %	Product (E:Z Ratio)
1	C_6H_5I	PhCH = CH.CHO (E)	Acetophenone Oxime	$Pd(OAc)_2$	24	99	—
2	4-$CH_3OC_6H_4I$	PhCH = CH.CHO (E)	Acetophenone Oxime	$Pd(OAc)_2$	24	93	1.5:1
3	4-$CH_3C_6H_4I$	PhCH = CH.CHO (E)	OTP	$Pd(OAc)_2$	24	91	1.3:1
4	4-$CH_3OC_6H_4I$	PhCH = CH.COOEt (E)	Acetophenone Oxime	$Pd(OAc)_2$	39	64	2.4:1
5	4-FC_6H_4I	PhCH = CH.COOEt (E)	OTP	$Pd(OAc)_2$	25	86	9:1
6	4-$CH_3OC_6H_4I$	PhCH = CH.COOEt (E)	OTP	$Pd(OAc)_2$	24	83	2.4:1
7	4-$CH_3OC_6H_4I$	PhCH = CH.COOEt (E)	BINAP (R)	$Pd(OAc)_2$	26	60	1.8:1
8	4-FC_6H_4I	PhCH = CH.COOEt (E)	OTP	$Pd(OAc)_2$	24	99	1.1:1
9	4-$CH_3OC_6H_4I$	PhCH = CH.COOEt (E)	AgOAc	$Pd(OAc)_2$	10	68	2:1
10	4-$CH_3OC_6H_4I$	PhCH = CH.COOEt (E)	$AgBF_4$	$Pd(OAc)_2$	3	99	2.1:1
11	4-$CH_3OC_6H_4I$	PhCH = CH.$COCH_3$ (E)	OTP	$Pd(OAc)_2$	16	87	1.1:1
12	4-$CH_3OC_6H_4I$	Chalcone (E)	OTP	$Pd(OAc)_2$	21	94	2.8:1
13	C_6H_5I	Stilbene (E)	Acetophenone oxime	$Pd(OAc)_2$	44	41	–
14	4-$CH_3OC_6H_4I$	Stilbene (E)	Acetophenone oxime	$Pd(OAc)_2$	48	49	2:1
15	4-$CH_3OC_6H_4I$	C_6H_5CH = CH.COC_6H_5 (E)	TBABr, no ligand	$Pd(OAc)_2$	4.5	83	1:0.37
16	4-$CH_3OC_6H_4I$	C_6H_5CH = CH.$COCH_3$ (E)	TBABr, no ligand	$Pd(OAc)_2$	2.15	83	1:0.34
17	2-$CH_3C_6H_4I$	C_6H_5CH = CH.CHO (E)	TBACl, no ligand	$Pd(OAc)_2$	7.5	95	1: 0.17
18	4-$CH_3C_6H_4I$	PhCH = CH.$COCH_3$ (E)	TBACl, no ligand	$Pd(OAc)_2$	18	92	1:1
19	C_6H_5I	Cinnamaldehyde (E)	PEG-400	$PdCl_2(PhCN)_2$	15	83	–
20	4-$CH_3O.C_6H_4I$	Ethyl Cinnamate (E)	PEG-400	$PdCl_2(PhCN)_2$	9.5	73	2:1
21	4-$CH_3C_6H_4I$	Cinnamaldehyde (E)	PEG-400	$PdCl_2(PhCN)_2$	2.1	99	2:1
22	2-$CH_3C_6H_4I$	Stilbene (E)	PEG-400	$PdCl_2(PhCN)_2$	17.1	Traces	–
23	4-$CH_3O.C_6H_4I$	Stilbene (E)	PEG-400	$PdCl_2(PhCN)_2$	32	79	2:1
24	4-$CH_3O.C_6H_4I$	Chalcone (E)	PEG-400	$PdCl_2(PhCN)_2$	34	82	3:1
25	4-$CH_3CO.C_6H_4I$	Chalcone (E)	PEG-400	$PdCl_2(PhCN)_2$	5	74	2:1
26	4-$CH_3C_6H_4I$	Benzalacetone (E)	PEG-400	$PdCl_2(PhCN)_2$	2 h	99	1:1
27	4-$CH_3O.C_6H_4I$	Cinnamaldehyde (E)	PEG-400	$PdCl_2(PhCN)_2$	16	79	1.5:1
28	C_6H_5I	Cinnamaldehyde (E)	PEG-200	$PdCl_2(PhCN)_2$	12	75	–
29	4-$CH_3O.C_6H_4I$	Ethyl Cinnamate (E)	PEG-200	$PdCl_2(PhCN)_2$	5	53	2:1
30	4-$CH_3C_6H_4I$	Benzalacetone (E)	PEG-200	$PdCl_2(PhCN)_2$	4.2	89	1:1
31	2-$CH_3C_6H_4I$	Cinnamaldehyde (E)	PEG-200	$PdCl_2(PhCN)_2$	10	78	3:1
32	4-$CH_3O.C_6H_4I$	Cinnamaldehyde (E)	PEG-200	$PdCl_2(PhCN)_2$	14	73	1.5:1
33	4-$CH_3CO.C_6H_4I$	Chalcone (E)	PEG-200	$PdCl_2(PhCN)_2$	8	69	2:1



Scheme 3. Ligand effect on the Mizoroki–Heck reaction of aryl iodides with 1,2-disubstituted aryl alkenes.

Extremely high yields were obtained in $16-24$ h reaction time. But the products were obtained as E:Z mixtures with only 4-FC_6H_4I giving a moderately high ratio of 9: 1.

The enhanced reactivity of the catalyst systems described could be attributed to the formation of Pd nano particles. TBABr addition stabilizes such nanoparticles.[5,8,28,49] PEG is also known to stabilize Pd NPs which explains the enhanced reactivity in PEG-

Table 2. Ligand–catalyst effects for the Mizoroki–Heck reaction of aryl iodides with 1,2-disubstituted aryl alkenes.

S. no	Ligand/catalyst	ArI	Alkene	Time, h	Yield %	Product (E:Z Ratio)
1	Triphenylphosphine (2 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	4	86	1:0.6
2	Tri(o-tolyl)phosphine (4 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	24	99	1.7:1
3	Dppe—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	20	85	1.61:1
4	Dppf—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	20	72	1.6:1
5	Johnphos (4 mol %)—$Pd(OAc)_2$	4-$CH_3OC_6H_4I$	Cinnamaldehyde (E)	21	65	1.37:1
6	Xphos—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	20	71	1.6:1
7	Sphos—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	20	81	1.5:1
8	BINAP (R)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	24	60	1.8:1
9	Xantphos (2.1 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	19	91	1.5:1
10	Acetophenone oxime (2.5 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	24	93	1.5:1
11	Proline (l) (2 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	16	64	1:0.86
12	2-Thiophene carboxylic acid (2 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	19	71	1:0.26
13	PCy_3 (2 mol %)—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	3	90	1:0.24
14	Tert-$Bu_3P.HBF_4$—$Pd(OAc)_2$	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	5	96	1:0.08
15	Acetophenone oxime palladacycle	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	23	66	1.6:1
16	Herrmann–Beller palladacycle	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	22	79	1.6:1
17	Tris(2,4-di-tert-butylphenyl)phosphite palladacycle	4-CH_3O·C_6H_4I	Cinnamaldehyde (E)	24	92	2:1
18	OTP	4-CH_3·C_6H_4I	Cinnamaldehyde (E)	24	91	1.3:1
19	OTP	4-CH_3O·C_6H_4I	Ethyl cinnamate (E)	24	83	2.4:1
20	OTP	4-F·C_6H_4I	Ethyl cinnamate (E)	24	86	9:1
21	OTP	4-CH_3O·C_6H_4I	Benzalacetone (E)	16	87	1.1:1
22	OTP	4-CH_3O·C_6H_4I	Chalcone (E)	21	94	2.8:1

Reaction conditions: Aryliodide (1.2 mmol), 1,2-Disubstituted alkene (1 mmol), NaOAc (1.5 mmol), TBABr (1 mmol), $Pd(OAc)_2$/Cat (1 mol %), Ligand (2–4 mol %), DMF (10 ml), Argon, 140–150 °C.

200 and PEG-400.[39,46,51,52] DMF solvent and base—NaOAc used, also shows the similar activity as described by Chakraborti and coworkers.[50] Pd (II) is readily converted–reduced to Pd(0) which enhances the oxidative addition to aryl halides and then readily adds to the 1,2-disubstituted alkenes. Ligands especially, tert-$Bu_3P.HBF_4$ and PCy_3 demonstrated high reactivity and also stereoselectivity which could be due to Pd NPs stabilized by the ligands described. High reaction temperatures used might be the cause of NPs formation, E: Z isomerization and formation of mixtures as noted earlier.

Experimental procedure

General procedure for Mizoroki–Heck reaction of 1,2-disubstituted aryl alkenes in PEG-200 or PEG-400

The aryl halide (1.2 mmol), alkene (1 mmol), NaOAc (1.5 mmol), $PdCl_2(PhCN)_2$ (2.5 mol%), *n*-Bu_4NBr or *n*-Bu_4NCl (1 mmol) and solvent (PEG-400 or PEG-200), 3 ml were added to an oven-dried 25 ml single neck round bottom flask which was then sealed with reflux condenser and two-way stopcock above it. The mixture was purged

with argon and heated at 140 – 150 °C for 2 – 34 h. When the starting materials were completely consumed as determined by TLC, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc and washed three times with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. Purification by column chromatography afforded the analytically pure product.

Ethene-1,1,2-triyltribenzene (3a) (2 h, 74%) CAS Registry Number 58-72-0 ^{1}H NMR (200 MHz, $CDCl_3$, δ)—7.39–7.23 (m, 10H), 7.19 – 7.05 (m, 5H), 7.02 (s, 1H) ^{13}C NMR (200 MHz, $CDCl_3$, δ)—143.4, 142.6, 140.3, 137.4, 130.4, 129.5, 128.6, 128.2, 127.9, 127.6, 127.5, 127.4, 126.7, 116.5, 87.5, 83.1, 68.8, 65.1, 64.6 IR (cm^{-1})—3023, 2402, 1597, 1522, 1428, 1216, 1028, 928, 768, 671 HRMS-ESI: $[M^+ + H]^+$ calcd for $C_{20}H_{17}$ $[M^+ + H]^+$ 257.1325, found: 257.1326

Conclusions

Inexpensive silver free protocols were developed for the Mizoroki–Heck reaction of 1,2-disubstituted alkenes. Use of TBABr or n-Bu_4NCl in DMF, ramped up the Mizoroki–Heck reaction of aryl iodides with various 1,2-disubstituted aryl alkenes. PEG 200/400 as solvent conjured magically, high yields of the Mizoroki–Heck product in short reaction times. Several phosphine ligands also gave excellent results, with various 1,2-disubstituted alkenes and aryl iodides, though the E:Z ratios were low. Preliminary studies with tert$Bu_3P{\cdot}HBF_4$ as ligand show high reactivity and E-isomer selectivity. Further studies with such ligand variations are expected to show the desired modulation of reactivity.

Supplementary information associated with this article can be found online.

Acknowledgments

Financial support is gratefully acknowledged from the CSIR Network Project, ORIGIN – under the XII Five year plan CSC 0108 and PGB thanks the UGC for a SRF.

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