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Efficient nickel(II) naringenin-oxime complex catalyzed Mizoroki-Heck cross-coupling reaction in the presence of hydrazine hydrate

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A novel nickel(II) naringenin-oxime complex was designed, synthesized and characterized. Therein, nickel(II) naringenin oxime complex as an efficient catalyst was used in Mizoroki-Heck coupling reactions of aryl halides adhering electron-rich and electron-deficient substituents with styrene, methyl acrylate and divinylbenzene (DVB), respectively. The reaction proceeded efficiently under alkaline condition in the presence of 0.30 mol% of Ni(II) naringenin oxime complex, N₂H₄·H₂O as reductant in EtOH at 80 °C, and 32 alkenes products were afforded in moderate to excellent yields, containing four new olfeins. The new catalytic system not only provided an inexpensive and efficient process with greener condition, but also broadened the reaction scope.

Introduction

Alkenes constitute a series of key structural motifs presence in numerous pharmaceuticals,¹⁻² natural products,³⁻⁴ and flavors.⁵⁻⁶ Palladium-catalyzed Mizoroki-Heck have proven to be the most efficient method to synthesize products containing such motifs.⁷⁻¹² Traditionally, phosphine ligands/Pd(OAc)₂ can catalyze the coupling reaction in the protection of inert atmosphere, however, phosphine ligands are accompanied with limitations such as synthetic and handling difficulties, air and moisture sensitivity¹³⁻¹⁵ etc. Moreover, palladium catalysts are restricted with the poor solubility and the high cost.¹⁶⁻¹⁸ Therefore, it is necessary to develop a cheap and efficient catalytic system to solve above problems. On the basis of

School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China. E-mail address:<u>wenyichu@hliu.edu.cn</u>, TEL/FAX: +86-451-86609135. Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, Harbin 150080, P. R. China. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x the review of literatures, nickel not only shows good catalytic properties, but also more electropositive than palladium.¹⁹ And nickel complexes bearing N,O-based ligands as catalysts could accelerate the cross-coupling reaction as well.

In 2007, Wang et al.²⁰ synthesized nickel complexes bearing N,N,O-chelate anionic ligands and validated the good catalytic activity in the Heck coupling reaction of iodides with butyl acrylate. Ojwach's group²¹ prepared new nickel(II) complexes bearing N,O,Sligated imino-pyridyl derived ligands, which were active and stable for Heck reactions towards aryl halides with methyl acrylate. In 2012, nickel complexes of tridentate O,N,S-donors thiosemicarbazones catalyzed Heck coupling reactions was reported by Bhattacharya et al.²² And the activities of nickel complexes were found to be comparatively high than previously species. As reported by Sridevi et al.²³ in 2013, the use of nickel(II) thiosemicarbazone complex with low loading (0.5 mol%) as an efficient catalyst for the Heck reaction of aryl bromides with olefins. In addition,

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Wang/Zong²⁴ have shown a new type of Ni catalyst in Heck crosscoupling reaction, composed of N-(4,5-dihydrooxazol-2-yl) benzamide and the coupling of alkenes with aryl iodide or aryl bromide in DMF provided the corresponding products with moderate to good yields. Despite the good yields, there is a long time of reflux, a high boiling solvent is used, and a small methodological scope, only having tested bromobenzene derivatives.

Naringenin-oxime as a N,O-based ligand is broadly investigated in biological chemistry owing to its chelating capability.²⁵⁻²⁶ The need to abandon the use of the electron rich property of naringeninoxime, prompted us to employ it as an organic ligand in the coupling reaction. Herein, we reported a novel protocol for the Mizoroki-Heck reaction in the presence of Ni(II) naringenin-oxime complex, and it was the first time to use naringenin-oxime as ligand to promote the C-C cross-coupling reactions. The ligand was acquired in excellent yields by the oximation of naringenin, and the air-stable Ni(II) complex was synthesized by refluxing anhydrous NiCl₂ with naringenin oxime in the ration of 1:2 in the ethanol-ethyl ether (**Scheme 1**). The unique catalyst displays promising application in Mizoroki-Heck cross-coupling reaction with ultra-low Ni loading, meanwhile, the protocol is appropriate for heterocyclic substrates.



Scheme 1. Synthesis of the nickel(II) complex

Results and discussion

Complex have been fully characterized by spectroscopy (NMR, HRMS, FT-IR) and by elemental analysis. The elemental contents (C, H and N) of the synthesized complex were relatively close to its calculated based on molecular formulae proposed. Compared IR spectra of the synthesized ligand to complex, the strong band emerging at 3412 cm^{-1} in the IR spectra of ligand was assigned to the vibration of v_{O-H}. Upon complexation, the v_{O-H} band was increased to 3476 cm^{-1} , indicating the occurrence of coordination of oxygen to

Ni(II) ion. In the FT-IR spectra of ligand, the characteristic (C=N) band appeared at 1648 cm⁻¹, after the chelation leaded to the splitting of the characteristic (C=N) band in 1628 cm⁻¹, and the occurrence of red shift, as was reported in the literature.²³ Upon coordination with metal, the absorption bands near 545 and 465 cm⁻¹ were observed from the FT-IR spectra of the complex and ascribable to Ni-O and Ni-N bands. NMR spectra of the synthesized ligand and complex were measured in DMSO. For the complex, ¹H NMR peak at 10.38 ppm was assigned to C=N-OH proton, so compared to ligand (11.21 ppm), a shift of 0.83 ppm was observed. The disappearance of -OH on C5 in the ¹H NMR peak indicated that the -OH group of the ligand formed coordinate bond with metal resulting in the deprotonation, then the hydrogen bond between exposed oxygen atom and OH of oxime group was formed. Similar shifts of the aromatic protons and C atoms were observed in the ¹³C NMR spectrum of the complex, which consistent with the observations made by Volkov and co-workers.27

The catalytic activity of nickel(II) naringenin-oxime complex was verified by Mizoroki-Heck cross-coupling reaction. In a model reaction, the coupling of bromobenzene with styrene was studied in the presence of N_2H_4 · H_2O under air. The results were summarized in **Table 1**.

Comparing the Ni-based catalysts in the same quantity, $Ni(OAc)_2$ or $Ni(TFA)_2$ with good solubility catalyzed the reaction to give about 40% yield (**Table 1**, entries 1-2). When the reaction employed insoluble NiCl₂ as catalyst, only 23% yield was obtained (**Table 1**, entry 3). Surprisingly, with NiCl₂ and the ligand, the yield could be up to 69% (**Table 1**, entry 4). When the reaction was performed using NiCl₂/8-hydroxy-1-tetralone (L₁), and the yield obtained was lower than for the naringenin-oxime as ligand (**Table 1**, entry 5). To improve its solubility, the reaction was carried out in the presence of the complex in EtOH, and the highest yield could be achieved 88% (**Table 1**, entry 6). Various complex quantities were also screened. The results showed that 0.30 mol% of the complex was sufficient to catalyze the reaction more efficiently. When increased the amount of the complex, no marked difference in the yield was observed (**Table 1**, entries 8-9). The solvent had a

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dramatic influence on the Heck reaction, then polar and non-polar solvents were selected.

 Table 1 Effects of catalysts, solvents, bases and temperatures in the

 Heck cross-coupling reactions^a of bromobenzene with styrene

Catal. (mol%) Temp. N₂H₄ • H₂O Base Solvent

Entry	Catal.	Solvent	Base	Temp.	Reductant	Yield ^b		
	(mol%)		(equiv.)	(°C)		(%)		
1	Ni(OAc) ₂ (0.30)	EtOH	Na ₂ CO ₃ (2.0)	80	$N_2H_4{\cdot}H_2O$	38		
2	Ni(TFA)2 (0.30)	EtOH	$Na_2CO_3(2.0)$	80	$N_2H_4{\cdot}H_2O$	40		
3	NiCl ₂ (0.30)	EtOH	$Na_2CO_3(2.0)$	80	$N_2H_4{\cdot}H_2O$	23		
4	$NiCl_2(0.30) + L$ (0.60)	EtOH	Na ₂ CO ₃ (2.0)	80	$N_2H_4{\cdot}H_2O$	69		
5	$NiCl_2(0.30) + L_1(0.60)$	EtOH	Na ₂ CO ₃ (2.0)	80	$N_2H_4{\cdot}H_2O$	63		
6	Complex (0.30)	EtOH	Na ₂ CO ₃ (2.0)	80	$N_2H_4{\cdot}H_2O$	88		
7	Complex (0.10)	EtOH	Na ₂ CO ₃ (2.0)	80	$N_2H_4{\cdot}H_2O$	51		
8	Complex (0.50)	EtOH	Na ₂ CO ₃ (2.0)	80	N_2H_4 · H_2O	85		
9	Complex (1.0)	EtOH	Na ₂ CO ₃ (2.0)	80	N_2H_4 · H_2O	85		
10	Complex (0.30)	H_2O	Na ₂ CO ₃ (2.0)	reflux	N_2H_4 · H_2O	20		
11	Complex (0.30)	Toluene	Na ₂ CO ₃ (2.0)	reflux	N_2H_4 · H_2O	34		
12	Complex (0.30)	DMF	Na ₂ CO ₃ (2.0)	reflux	N_2H_4 · H_2O	75		
13	Complex (0.30)	DMSO	Na ₂ CO ₃ (2.0)	reflux	N ₂ H ₄ ·H ₂ O	65		
14	Complex (0.30)	MeOH	Na ₂ CO ₃ (2.0)	reflux	N_2H_4 · H_2O	66		
15	Complex (0.30)	PrOH	Na ₂ CO ₃ (2.0)	reflux	N ₂ H ₄ ·H ₂ O	61		
16	Complex (0.30)	EtOH:H ₂ O =1:1	Na ₂ CO ₃ (2.0)	reflux	$N_2H_4{\cdot}H_2O$	75		
17	Complex (0.30)	EtOH:H ₂ O =1:3	Na ₂ CO ₃ (2.0)	reflux	$N_2H_4{\cdot}H_2O$	73		
18	Complex (0.30)	EtOH:H ₂ O =3:1	Na ₂ CO ₃ (2.0)	reflux	$N_2H_4{\cdot}H_2O$	78		
19	Complex (0.30)	EtOH	N ₂ H ₄ ·H ₂ O (2.0)	80		82		
20	Complex (0.30)	EtOH	N ₂ H ₄ ·H ₂ O (2.5)	80		83		
21	Complex (0.30)	EtOH	Et ₃ N (2.0)	80	$N_2H_4{\cdot}H_2O$	25		
22	Complex (0.30)	EtOH	EDA (2.0)	80	$N_2H_4{\cdot}H_2O$	33		
23	Complex (0.30)	EtOH	Pyridine (2.0)	80	$N_2H_4{\cdot}H_2O$	30		
24	Complex (0.30)	EtOH	NaOH (2.0)	80	$N_2H_4{\cdot}H_2O$	78		
25	Complex (0.30)	EtOH	Na ₂ CO ₃ (2.5)	80	$N_2H_4{\cdot}H_2O$	87		
26	Complex (0.30)	EtOH	Na ₂ CO ₃ (1.5)	80	$N_2H_4{\cdot}H_2O$	80		
27	Complex (0.30)	EtOH	Na ₂ CO ₃ (1.0)	80	$N_2H_4{\cdot}H_2O$	66		
28	Complex (0.30)	EtOH	Na ₂ CO ₃ (2.0)	rt	$N_2H_4\!\cdot\!H_2O$	trace		
29	Complex (0.30)	EtOH	Na ₂ CO ₃ (2.0)	60	N_2H_4 · H_2O	54		
30	Complex (0.30)	EtOH	Na ₂ CO ₃ (2.0)	100	N_2H_4 · H_2O	86		
31	Complex (0.30)	EtOH	Na ₂ CO ₃ (2.0)	120	N_2H_4 · H_2O	85		
^a Rea	ction condition	s: bromobe	enzene (10 n	nmol 1	0 equiv)	styrene		
(1.3 equiv.), base, N_2H_4 · H_2O (0.5 equiv.), solvent (4 mL), under air,								
7.5 h. ^b Yield of isolated product.								

In water medium (even under reflux conditon), the yield of the reaction was very low (20%), owing to the poor solubility of the substrates (**Table 1**, entry 10). Non-polar solvent was adverse to the reaction, which only gave almost 34% yield (**Table 1**, entry 11). However, when chosen polar solvents like DMF, DMSO, MeOH and PrOH, approximately 70% yields of the products were isolated (**Table 1**, entries 12-15). A slight increase in yields was observed when different ration of EtOH/H₂O (1:1, 1:3, 3:1) were used as solvents (**Table 1**, entries 16-18). Results indicated that adding the polar protic solvent EtOH into the reaction, the yield was substantial increased to 88% (**Table 1**, entry 6).

The base also exerted a strong role in the reaction. With organic bases like Et₃N, ethylenediamine (EDA) and pyridine, trans-stilbene was obtained lower than 35% yield (Table 1, entries 20-22). Among the various inorganic bases used for the Mizoroki-Heck coupling reation (Table 1, entries 6, 24-27), Na₂CO₃ (2.0 equiv.) was the found to be the most suitable (88%, Table 1, entry 6). When experiments were carried out in the presence of N2H4 H2O as a reductant, the yield was significantly increased to 88%. When N₂H₄·H₂O was present as base (even increase the amount to 2.5 equiv.), the yield only reached 83% (Table 1, entries 6 and 20). It indicated adding a little amount of reductant under alkali conditon maybe activate the reducing ability of hydrazine so that promote the coupling process.²⁸⁻³⁰ Different temperatures in the range rt-120 °C showed that 80 °C was the optimal for the reaction, even raise to higher temperature, the yield had no significant change (Table 1, entries 30-31).

From the experimental data, we determined the optimized conditions: the complex (0.30 mol%), Na₂CO₃ (2.0 equiv.), N₂H₄·H₂O (0.5 equiv.) in EtOH (4 mL) at 80 °C under air. With the optimum reaction system, the Mizoroki-Heck coupling reations of various aryl halides with alkenes were examined to explore the scope. The results were summarized in **Table 2**. As shown in **Table 2**, the Mizoroki-Heck reaction of bromobenzene with styrene gave a 88% yield within 7.5 h (**Table 2**, entry 1). The properties and positions of the substituents of aryl bromides were in association with the yields.

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 Table 2 Heck cross-coupling reactions^a of aryl halides with alkenes

 catalyzed by using the complex

	Complex (0.30 mol%)	80°C	\mathbf{R}
$R_1 \longrightarrow R_2$	N ₂ H ₄ • H ₂ O Na ₂ CO ₃	EtOH	

F (D	Time	Yield ^b
Entry	Х	K_1	R_2	(h)	(%)
1	Br	Н	Ph	7.5	88
2	Br	4-NO ₂	Ph	7.5	90
3	Br	4-CHO	Ph	8.0	82
4	Br	4-CN	Ph	7.5	85
5	Br	4-Br	Ph	9.0	82
6	Br	4-Me	Ph	11.0	80
7	Br	4-OMe	Ph	12.5	78
8	Br	1-Naphthyl	Ph	10.5	85
9	Br	3-Me,4-COOEt	Ph	10.0	83
10	Br	2-NO ₂	Ph	16.0	73
11	Br	3-Pyridyl	Ph	14.5	70
12	Br	Н	CO ₂ Me	7.0	93
13	Br	4-NO ₂	CO ₂ Me	7.0	96
14	Br	4-CHO	CO ₂ Me	7.5	94
15	Br	4-CN	CO ₂ Me	7.0	95
16	Br	4-Me	CO ₂ Me	8.0	88
17	Br	4-OMe	CO ₂ Me	9.0	82
18	Br	2-NO ₂	CO ₂ Me	15.5	78
19	Br	3-Pyridyl	CO ₂ Me	13.0	71
20	Br	Н	4-CH ₂ =CH-C ₆ H ₄ -	10.5	88,85
21	Br	4-NO ₂	4-CH ₂ =CH-C ₆ H ₄ -	11.5	89
22	Br	4-CHO	4-CH ₂ =CH-C ₆ H ₄ -	12.0	86
23	Br	4-CN	4-CH ₂ =CH-C ₆ H ₄ -	12.0	88
24	Br	4-Me	4-CH ₂ =CH-C ₆ H ₄ -	13.5	80
25	Br	4-OMe	4-CH ₂ =CH-C ₆ H ₄ -	13.5	78
26	Br	4-CH ₂ CN	4-CH ₂ =CH-C ₆ H ₄ -	13.0	76
27	Br	3,4-(OBn) ₂	4-CH ₂ =CH-C ₆ H ₄ -	14.5	78
28	Br	3,5-(CF ₃) ₂	4-CH ₂ =CH-C ₆ H ₄ -	15.0	74
29	Cl	Н	Ph	9.5	66
30	Cl	4-CHO	Ph	10.5	68
31	Cl	4-Me	Ph	13.0	61
32	Cl	2-NO ₂	Ph	20.0	56

^a Reaction conditions: aryl halides (1.0 mmol, 1.0 equiv.), alkenes (1.3 equiv.), Na₂CO₃ (2.0 equiv.), N₂H₄·H₂O (0.5 equiv.), complex (0.30 mol%), EtOH (4 mL), 80 °C, under air. ^b Yield of isolated product. ^c bromobenzene (1.5 mmol), alkenes (1.3 equiv.), Na₂CO₃ (3.0 equiv.), N₂H₄·H₂O (0.5 equiv.), complex (0.30 mol%), EtOH (4 mL), 80 °C, t=11.5 h, under air.

It was observed that 4-substituted aryl bromides with electronwithdrawing substituents such as nitro, formyl, cyano and bromo groups (**Table 2**, entries 2-5) led to high yields of the corresponding products. 4-Substituted aryl bromides with electron-donating groups like methyl and methoxy groups (**Table 2**, entries 6-7) underwent the reaction smoothly to give moderate yields of products. The scope of the reaction was investigated further by synthesizing naphthyl olefin and ethyl-2-methyl-4-styrylbenzoate in good yields (85% and 83%, **Table 2**, entries 8-9). Furthermore, steric hindrance due to the *ortho*-substituents on the aryl bromides affected the reaction progress. *ortho*-Nitrobromobenzene needed longer reaction time and gave lower yield (73%) than *para*-nitrobromobenzene (**Table 2**, entries 2 and 10).

Then the reactions of aryl bromides with methyl acrylate were tolerated in order to show the originality of the complex. The coupling of bromobenzene with methyl acrylate afforded the methyl cinnamate in 93% yield (Table 2, entry 12). Similar to the reaction with styrene, the reactivity of aryl bromides adhering electronwithdrawing groups was found to be higher than those with electrondonating groups (Table 2, entries 13-17). Sterically hindered orthonitrobromobenzene could also react effectively with methyl acrylate in a moderate yield (Table 2, entry 18). We further investigated the Mizoroki-Heck reaction of heterocyclic bromide like 3-pyridyl bromide with styrene and methyl acrylate (Table 2, entries 11, 19), both of them gave the olefins products in medium yields, though the yields were lower compared to bromobenzene with electrondonating and electron-withdrawing substituent groups. Mizoroki-Heck cross-coupling reactions were also employed for the synthesis of p-phenylene vinylene. The results illustrated that both nonsubstituted and 4-substituted bromobenzene provided moderate yields with divinylbenzene during the reaction, and the mainly products were mono-coupling olefins (Table 2, entries 20-26). When increased the quantity of aryl bromides, the bis-coupling olefins products were also isolated in good yields (Table 2, entry 20). Bromobenzene with double substituents involved in the reaction, medium yields could be obtained as well. Especially, 3,4dibenzyloxybromobenzene as substrate coupled with divinylbenzene Published on 08 September 2017. Downloaded by Fudan University on 11/09/2017 02:15:49

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75% in vield, which is superior 3,5to ditrifluoromethylbromobenzene (Table 2, entries 27-28). Likewise, the reaction of aryl chlorides with styrene could also occurred in the optimal condition with mid-low yields (Table 2, entries 29-32). Therein, four new olefins products were produced under the catalytic system (Table 2, entries 9, 26-28), p-Phenylene vinvlene and its derivatives were the important units in the fields of the synthesis of light-emitting materials as well as studied on field-effect transistor and amphiphilic materials.³¹⁻³² Among the new isolated olefins, the product of (E)-1,3-bis(trifluoromethyl)-5-(4-vinylstyryl)benzene displays the better fluorescence (Table 2, entry 28).

Based on the above results, and also in accordance with previous literature reports,^{19, 33} a plausible mechanism as shown in **Scheme 2** is hypothesized.

Initially, LNi(0) catalyst (A) is formed by the activation of the nickel(II) naringenin oxime complex in the presence of hydrazine hydrate, and then the oxidative addition of bromobenzene to LNi(0) catalyst produces the intermediate(B), which undergoes the coordination-insertion of styrene into the bond of Ph-Ni to afford the intermediates (C). Then, β -hydrogen elimination provides the target compound *trans*-stilbene and the intermediate (D). Reductive elimination provides the regeneration of the LNi(0) catalyst in the alkaline condition.



Scheme 2. Proposed mechanism for the system

Conclusions

In conclucion, a novel nickel(II) naringenin oxime complex as the catalyst was successfully synthesized and applied in the Mizoroki-Heck cross-coupling reactions, where electron-rich and electron-poor functionalized aryl halides with alkenes were catalyzed to afford the corresponding products in moderate to high yields, including four new olefins. The methodology not only provided a simple and green reaction condition, but also enhanced good group tolerance to obtain abundant alkenes products.

Experimental section

General procedure for Heck cross-coupling reaction

In 10 mL reaction flask was charged with complex (0.30 mol %) and N_2H_4 ·H₂O (0.5 equiv.), then added aryl halides (1.0 mmol, 1.0 equiv.), olefin (1.3 equiv.), Na_2CO_3 (2.0 equiv.) and EtOH (4 mL). The reaction mixture was stirred at 80 °C and the progress was monitored by TLC analysis. After completion of the reaction, the reaction mixture was poured into water and the aqueous layer was extracted with ethyl acetate 3 times (3 × 10 mL), and the combined organic layer was dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1 as eluent) to afford the pure product. The characterizations of the synthesized products are all matched with the authentic samples (see the Supporting information).

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Notes and references

- S. N. Jadhav, A. S. Kumbhar, C. V. Rode and R. S. Salunkhe, Green Chem., 2016, 18, 1898-1911.
- [2] M. Larhed and A. Hallberg, Drug Discovery Today, 2001, 6, 406-416.

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Journal Name

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- [3] S. Q. Huo and E. Negishi, Org. Lett., 2001, 3, 3253-3256.
- [4] J. Prunet, Angew. Chem. Int. Ed., 2003, 42, 2826-2830.
- [5] K. Park and S. Lee, Org. Lett., 2015, 17, 1300-1303.
- [6] X. X. Sun, X. L. Shen, R. Jain, Y. H. Lin, J. Wang, J. Sun, J. Wang, Y. J. Yan and Q. P. Yuan, *Chem. Soc. Rev.*, 2015, 44, 3760-3785.
- [7] A. B. Dounay and L. E. Overman, *Chem. Rev.*, 2003, **103**, 2945-2964.
- [8] H. Zhang, P. H. Chen and G. S. Liu, Angew. Chem. Int. Ed., 2014, 53, 10174-10178.
- [9] C. L. Wu and J. R. Zhou, J. Am. Chem. Soc., 2014, 136, 650-652.
- [10] T. L. Yao, T. Liu and C. H. Zhang, Chem. Commun., 2017, 53, 2386-2389.
- [11] L. J. Zhang, Z. Jiang, C. N. Dong, X. Xue, R. Y. Qiu, W. J. Tang, H. R. Li, J. L. Xiao and L. J. Xu, *ChemCatChem.*, 2014, 6, 311-318.
- [12] B. Tamami, F. Farjadian, S. Ghasemi and H. Allahyari, *New. J. Chem.*, 2013, **37**, 2011-2018.
- [13] L. Wang, H. J. Li and P. H. Li, Tetrahedron, 2009, 65, 364-368.
- [14] K. Karami, Z. K. Moghadam and M. H. Kharat, *Catal. Commun.*, 2014, **43**, 25-28.
- [15] L. H. Yuan, Y. Xu, X. B. Hu, G. Q. Yang and Y. T. Wu, J. Mol. Catal. A Chem., 2015, 396, 55-60.
- [16] N. Nowrouzi and M. Zarei, Tetrahedron, 2015, 71, 7847-7852.
- [17] A. R. Hajipour and Z. Khorsandi, *Catal. Commun.*, 2016, 77, 1-4.
- [18] A. R. Hajipour and G. Azizi, Green Chem., 2013, 15, 1030-1034.
- [19] S. S. Wang and G. Y. Yang, Catal. Sci. Technol., 2016, 6, 2862-2876.

- [20] Z. X. Wang and Z. Y. Chai, Eur. J. Inorg. Chem., 2007, 2007, 4492-4499.
- [21] W. M. Motswainyana, M. O. Onani, S. O. Ojwach and B. Omondi, *Inorg. Chim. Acta.*, 2012, **391**, 93-97.
- [22] S. Datta, D. K. Seth, S. Gangopadhyay, P. Karmakar and S. Bhattacharya. *Inorg. Chim. Acta.*, 2012, **392**, 118-130.
- [23] P. K. Suganthy, R. N. Prabhu and V. S. Sridevi, *Tetrahedron Lett.*, 2013, 54, 5695-5698.
- [24] J. Wang, Y. X. Zong, S. L. Wei and Y. Pan, *Appl. Organometal. Chem.*, 2014, 28, 351-353.
- [25] D. H. Priscilla, D. Roy, A. Suresh, V. Kumar and K. Thirumurugan, *Chem. Biol. Interact.*, 2014, 210, 77-85.
- [26] M. Özyürek, D. Akpınar, M. Bener, B. Tükkan, K. Güclü and R. Apak, *Chem. Biol. Interact.*, 2014, **212**, 40-46.
- [27] V. V. Bon, S. I. Orysyk, V. I. Pekhnyo and S. V. Volkov, J. Mol. Struct., 2010, 984, 15-22.
- [28] S. S. Yi, D. H. Lee, E. Sin and Y. S. Lee, *Tetrahedron Lett.*, 2007, 48, 6771-6775.
- [29] A. M. Trzeciak, E. Mieczyńska, J. J. Ziółkowski, W. Bukowski, A. Bukowska, J. Noworól and J. Okal. *New. J. Chem.*, 2008, **32**, 1124-1130.
- [30] R. J. Kalbasi and N. Mosaddegh, J. Solid State Chem., 2011, 184, 3095-3103.
- [31] T. G. Jiu, Y. J. Li, H. Y. Gan, Y. L. Li, H. B. Liu, S. Wang, W.
 D. Zhou, C. R. Wang, X. F. Li, X. F. Liu and D. B. Zhu, *Tetrahedron*, 2007, 63, 232-240.
- [32] T. Lei, X. Xia, J. Y. Wang, C. J. Liu and J. Pei, J. Am. Chem. Soc., 2014, 136, 2135-2141.
- [33] B. L. Lin, L. Liu, Y. Fu, S. W. Luo, Q. Chen and Q. X. Guo, Organometallics, 2004, 23, 2114-2123.



 $R_2 = C_6H_5$, COOMe, 4-CH₂=CH-C₆H₄-

28 alkenes products 70~96% yields

Graphical abstract