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Oxidative Cyanation of Tertiary Amines with Ethyl Cyanoformate over a Niobia-Supported Iron-Exchanged Molybdophosphoric Acid Catalyst

Kasanneni Tirumala Venkateswara Rao, Bathula Haribabu, Potharaju S. Sai Prasad, and Nakka Lingaiah^{*[a]}

The oxidative cyanation of tertiary amines by using the less-toxic ethyl cyanoformate as the cyanating agent was achieved over heterogeneous iron-exchanged molybdophosphoric acid (FeMPA) supported on a niobia catalyst under mild reaction

conditions. The catalyst not only showed exceptional activity with variety of tertiary amines but also exhibited consistent activity upon reuse.

Introduction

The formation of C–C bonds by the direct and selective activation of C–H bonds is finding increasing use in synthetic organic chemistry.^[1] The direct functionalization of a C–H bond that is adjacent to a heteroatom avoids the need for pre-functionalization of starting materials, which shortens the reaction scheme.^[2] Among the important classes of reactions that fall under this C–H activation methodology is the oxidative cyanation of tertiary amines. The oxidative cyanation of tertiary amines has attracted much interest because α -amino nitriles are versatile intermediates in organic synthesis for the preparation of biologically active compounds, such as alkaloids, α -amino acids, and 1,2-diamines.^[3] The classical Strecker synthesis of α -amino nitriles, which involves the reaction between a carbonyl compound, an amine, and a cyanide is well-reported in the literature.^[4] On the other hand, these compounds can be prepared by the catalytic oxidation of tertiary amines into iminium ions, followed by the in-situ nucleophilic attack of a cyanide ion. In this regard, ruthenium-^[5] and vanadium-based catalysts^[6] have been reported for the oxidative cyanation of tertiary amines with NaCN and molecular oxygen in the presence of an acidic promoter. The coexistence of both the metal and the acidic promoter is mandatory to obtain the desired product. However, both of these methods have certain limitations, as they require the use of NaCN as a cyanide source. NaCN is highly toxic and difficult to handle. Alternatively, the combination of FeCl₂^[7] and a gold complex^[8] has been reported to catalyze the α -cyanation of amines with trimethylsilyl cyanide (TMSCN) as a cyanide source. However, these processes require homogeneous conditions and also TMSCN is highly volatile, hazardous, and expensive for commercial use. Thus, the development of alternative and cheaper heterogeneous catalytic systems for the cyanation of tertiary amines that use less-toxic cyanide sources remains an exciting challenge.

Recently, a few heterogeneous catalysts, such as polymer-supported Fe^{II}-phthalocyanine^[9] and starch-immobilized RuCl₃ catalysts^[10] have been reported for cyanation reactions. However, in these procedures, NaCN or TMSCN were used as a cy-

nide source. Therefore, it is necessary to look into less-toxic, easy-to-handle, and readily available cyanide sources for the oxidative cyanation of tertiary amines. In this context, ethyl cyanoformate is relatively less-toxic, cheap, and has only been used recently for the asymmetric cyanation of aldehydes^[11] and olefins.^[12] To the best of our knowledge, there are no reports on the oxidative cyanation of tertiary amines with ethyl cyanoformate (ECF) over heterogeneous catalysts. As part of our ongoing research on the use of modified Keggin-type heteropoly acid catalysts for various organic transformations,^[13] we explored these catalysts for the cyanation of tertiary amines.

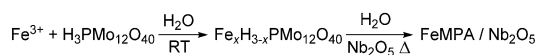
Herein, we report the use of iron-exchanged phosphomolybdic acid supported on niobia as an efficient catalyst for the oxidative cyanation of tertiary amines with ethyl cyanoformate as a cyanide source in MeOH/water solvent and *tert*-butyl hydroperoxide (TBHP) as an oxidant.

Results and Discussion

The catalyst was easily synthesized by the exchange of protons in the secondary structure of molybdophosphoric acid (MPA) with Fe³⁺ ions, followed by the addition of a niobia (Nb₂O₅) support (Scheme 1). To know the structural stability of this catalyst, it was characterized by XRD, FTIR, Raman spectroscopy, and temperature-programmed desorption of NH₃.

FTIR spectroscopy is the best tool for the characterization of the Keggin structure of heteropoly anions. The FTIR spectra of the catalysts are shown in Figure 1. Pure MPA and bulk FeMPA are also shown for comparison. The catalysts exhibited charac-

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Scheme 1. The preparation of a niobia-supported FeMPA catalyst.

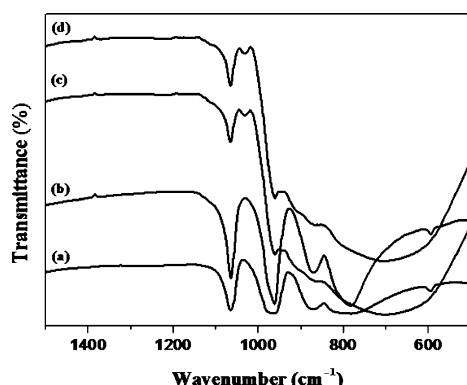


Figure 1. FTIR patterns of a) MPA, b) FeMPA, c) FeMPA/Nb₂O₅ (fresh), and d) FeMPA/Nb₂O₅ (used) catalysts.

teristic IR bands at 1065, 963, 871, and 782 cm⁻¹, which were attributed to the asymmetric stretching mode of the central oxygen (P–O) bond of the PO₄ tetrahedron, the asymmetric stretching mode of the peripheral terminal oxygen (M=O) bond, and the Mo–O–Mo stretch of the inter- and intra-octahedral bridges of the trimetallic group, respectively.^[14] Similar FTIR bands were observed when the MPA protons were exchanged with iron. This result indicated that the Keggin structure of MPA remained intact, even after modification with iron. In the case of FeMPA that was supported on niobia, the presence of two characteristic IR bands (1065 and 961 cm⁻¹) indicated the retention of the Keggin structure on niobia. The absence of two characteristic Keggin peaks in the range 700–900 cm⁻¹ was due to the strong absorbance of niobia in that region. In the supported catalyst, two IR bands at 690 cm⁻¹ and a shoulder at 865 cm⁻¹ were attributed to the amorphous nature of niobia.^[15]

The structural stability of these modified catalysts was further investigated by XRD (Figure 2). Strong characteristic peaks at 2θ = 10.5, 23.7, 26.1, 30.2, and 35.6° were assigned to the Keggin structure of MPA [JCPDS File 1-32]. The modification of

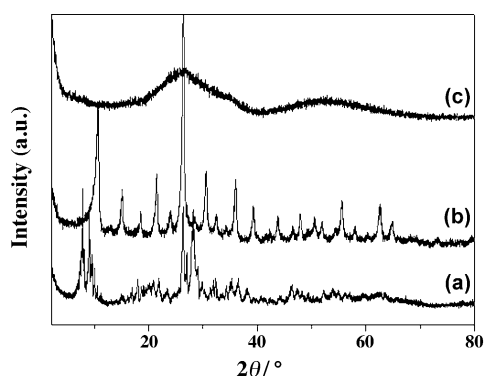


Figure 2. XRD patterns of a) MPA, b) FeMPA, and c) FeMPA/Nb₂O₅.

MPA with iron enhanced the crystalline nature of MPA in a similar manner to that of MPA that was modified with Cs salts.^[16] In the case of a FeMPA/Nb₂O₅ catalyst, no XRD patterns were observed that were related to the Keggin ion, presumably owing to the high dispersion of FeMPA on the Nb₂O₅ surface. XRD revealed the amorphous nature of the catalyst.

Figure 3 shows the laser Raman spectra of MPA and its modified catalysts. The Raman spectra of MPA and FeMPA showed Raman bands at 1009, 996, 901, 620, and 246 cm⁻¹,

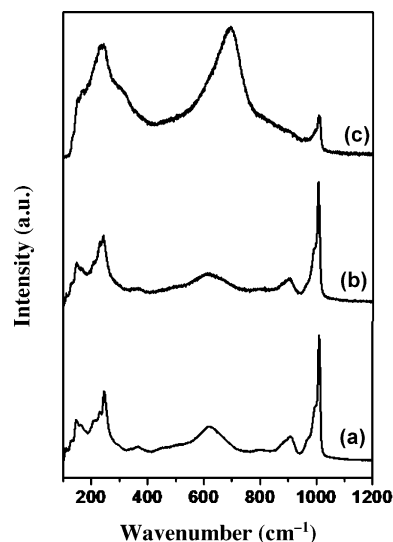


Figure 3. Raman spectra of a) MPA, b) FeMPA, and c) FeMPA/Nb₂O₅.

which were due to the presence of the Keggin structure of heteropoly molybdate.^[17] The strong band at 1009 cm⁻¹ and the shoulder at 996 cm⁻¹ were due to the symmetric and asymmetric stretching modes of the Mo=O_t bond, respectively. The broad bands at 901 and 620 cm⁻¹ were related to the asymmetric stretching vibrational mode of the bridging Mo–O_b–Mo and the bending mode of the O–P–O bonds, respectively. The strong band at 246 cm⁻¹ corresponded to the Mo–O–Mo bending mode of the intact Keggin structure. Raman bands that were related to the Keggin structure were observed in the case of the FeMPA/Nb₂O₅ catalyst, which indicated that the Keggin structure was well-preserved after the impregnation of FeMPA onto niobia. Apart from the Keggin ion peaks, a broad band at around 700 cm⁻¹ was observed, which was related to Nb₂O₅.^[18]

The acidity of the catalyst was measured by using the temperature-programmed desorption of NH₃ (Figure 4). The bulk FeMPA catalyst exhibited two NH₃-desorption patterns in the temperature ranges 200–370 °C and 400–650 °C. The low-temperature desorption peak corresponded to weakly acidic sites whilst the high-temperature desorption peak was attributed to the strongly acidic sites on the catalyst. The supported niobia exhibited broad desorption in the low-temperature region, which indicated the weak acidity of the support. Three distinct NH₃-desorption peaks were observed in the case of the FeMPA/Nb₂O₅ catalyst. This catalyst showed a high-tempera-

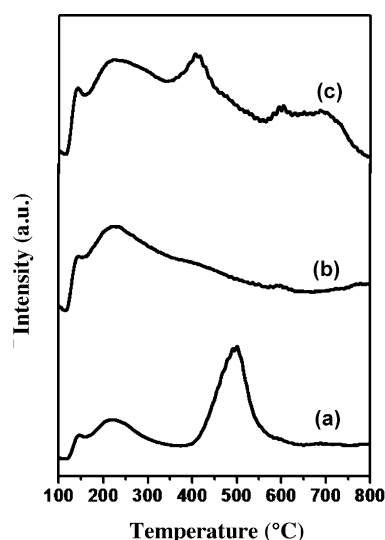
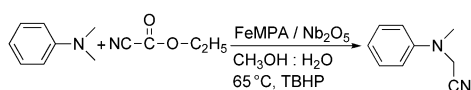


Figure 4. TPD patterns of a) FeMPA, b) Nb₂O₅, and c) FeMPA/Nb₂O₅.

ture desorption peak, which corresponded to strongly acidic sites. Although the total acidity of the supported catalyst was low compared to the bulk FeMPA catalyst, distinct strongly acidic sites were observed for the FeMPA/Nb₂O₅ catalyst.

FTIR, XRD, and Raman analysis suggested the retention of the Keggin structure, even after exchange of Fe with the MPA protons. FTIR further suggested the existence of an FeMPA Keggin structure on a Nb₂O₅ support.

Subsequently, the activity of the catalyst was evaluated by performing the oxidative cyanation of various tertiary amines to afford α -amino nitriles with TBHP as an oxidant, ethyl cyanoformate as a cyanide source, and MeOH/water as a co-solvent (Scheme 2).



Scheme 2. The niobia-supported FeMPA-catalyzed oxidative cyanation reaction.

Initially, *N,N*-dimethylaniline was chosen as a model substrate for investigating the catalysts and the reaction conditions. The reaction of *N,N*-dimethylaniline with ethyl cyanoformate as a cyanide source and TBHP/water (70%) as a terminal oxidant in a MeOH/water solvent system at 65 °C was performed over different Keggin-type heteropoly acid catalysts (Table 1). Under these reaction conditions, we anticipated that CN[−] was generated in situ from the reaction of ethyl cyanoformate with water to produce HCN, CO₂, and EtOH.^[19]

Tungstophosphoric acid (TPA) and silicotungstic acid (STA) are both strong solid-acid catalysts but showed poor activity for the formation of *N*-methyl-*N*-phenylamino acetonitrile, which was obtained in low yield, even after the reaction was performed for 14 h (Table 1, entries 1 and 2). Molybdophosphoric acid (MPA), which is known for its oxidizing ability

Table 1. Effect of the catalyst and the cyanide source on the oxidative cyanation of *N,N*-dimethylaniline.^[a]

Entry	Catalyst	Cyanide source (equiv)	t [h]	Yield [%] ^[b]
1	H ₃ PW ₁₂ O ₄₀ (TPA)	ECF (2)	14	10
2	H ₄ SiW ₁₂ O ₄₀ (STA)	ECF (2)	14	12
3	H ₃ PMo ₁₂ O ₄₀ (MPA)	ECF (2)	10	50
4	H ₄ SiMo ₁₂ O ₄₀ (SMA)	ECF (2)	10	38
5	FeMPA	ECF (2)	10	85
6	CuMPA	ECF (2)	10	67
7	AgMPA	ECF (2)	10	62
8	1	ECF (2)	7	96
9	1	K ₃ [Fe(CN) ₆](0.25)	7	20
10	1	CH ₂ (CN) ₂ (2)	7	15
11	1	ECA (2)	7	13
12	Fe(NO ₃) ₃ ·9H ₂ O	ECF (2)	7	30
13	Fe ₂ O ₃	ECF (2)	7	50
14	Nb ₂ O ₅	ECF (2)	7	5

[a] Reaction conditions: *N,N*-dimethylaniline (1 mmol), TBHP/H₂O (70%, 2 mmol), MeOH/water (2 mL, 1:1 v/v), catalyst (50 mg), 65 °C; [b] Yield of isolated product.

owing to an appended Mo atom, afforded a moderate yield of the product (Table 1, entry 3). In contrast, with silicomolybdic acid (SMA), the yield of the product was considerably lower than that of MPA (Table 1, entry 4). No product was detected in the absence of any catalyst. Intriguingly, the exchange of MPA protons with Fe enhanced the α -cyanation of the tertiary amine several-fold compared to MPA itself (Table 1, entry 5), possibly owing to the synergetic effect of both iron and molybdenum. Importantly, MPA that was modified with other transition metals, such as copper and silver, did not accelerate the reaction as markedly as iron (Table 1, entries 6 and 7). Different iron sources (Table 1, entries 12 and 13) were also tested, but none of these were as effective as FeMPA.

Despite the high activity of the FeMPA catalyst, it was homogeneous under these reaction conditions. FeMPA was made into a heterogeneous catalyst by dispersing it over a niobia support. Interestingly, when FeMPA was supported on niobia, the α -amino nitrile product was formed in much-higher yield (Table 1, entry 8) compared to the bulk catalyst. Niobia itself was not active for this reaction, as it gave <5% yield of the desired product (Table 1, entry 14). Of all of the catalysts studied, FeMPA on Nb₂O₅ (20 wt.%) was the best catalyst for the oxidative cyanation of tertiary amines. The effect of the cyanide source was also studied and ECF was found to be better than malonitrile, potassium hexacyano ferrate (III), and ethyl cyanoacetate (ECA; Table 1, entries 9–11).

Subsequently, the reaction was performed over FeMPA/Nb₂O₅ in different solvents and at different temperatures (Table 2). MeOH/water (1:1) was a superior solvent system than MeOH, water, and EtOH alone. When the reaction was performed in MeCN, there was no formation of the product. At room temperature, a longer time was required to obtain a reasonable yield of the product; 65 °C was the optimum temperature for this reaction.

Different oxidants were used for the oxidative cyanation of tertiary amines under the optimal reaction conditions. In the

Table 2. Effect of the solvent and the reaction temperature on the oxidative cyanation of *N,N*-dimethylaniline.^[a]

Entry	Solvent	Yield [%] ^[b]
1	MeOH	60
2	EtOH	49
3	MeCN	–
4	water	45
5	MeOH/water	96, ^[c] 60, ^[d] 71 ^[e]

[a] Reaction conditions: *N,N*-dimethylaniline (1 mmol), ethyl cyanoformate (2 mmol), TBHP/H₂O (70%, 2 mmol), FeMPA/Nb₂O₅ (50 mg), solvent (2 mL); [b] yield of isolated product; [c] at 65 °C; [d] at RT; [e] at 40 °C.

presence of molecular oxygen, the reaction did not proceed. With H₂O₂ only trace amount of product (<10%) were detected. The best result was achieved with aqueous TBHP as the oxidant.





























Subsequently, we tested the scope of the catalyst for the oxidative cyanation reaction of various tertiary amines (Table 3). Substituted *N,N*-dimethylanilines that contained electron-donating and -withdrawing groups on the aromatic ring gave their corresponding cyanated products in excellent yields (Table 3, entries 2–6). *N,N*-dimethylnaphthalene-1-amine only gave 30% yield of 2-(methyl(naphthalen-1-yl)amino)acetonitrile after a prolonged reaction time (Table 3, entry 7). In the case of unsymmetrical tertiary amines, the nucleophile CN[–] was attacked chemoselectively (Table 3, entries 8–10). This catalyst was also effective for the transformation of cyclic amines, such as *N*-phenylpiperidine, *N*-phenylpyrrolidine, and *N*-phenyltetrahydroisoquinoline, which gave their corresponding α -cyanoamines in excellent yields (Table 3, entries 11–13). *N,N*-Dimethyl-*p*-nitrosoaniline was unreactive under these reaction conditions (Table 3, entry 14).

Next, the reusability of the catalyst was studied. After the completion of the reaction, the catalyst was recovered by adding EtOAc to the reaction mixture, followed by simple filtration. The retrieved catalyst was washed two to three times with EtOAc and dried in an oven at 120 °C for 2 h. Oxidative cyanation of *N,N*-dimethylaniline with ECF and TBHP afforded *N*-methyl-*N*-phenylamino acetonitrile after the fourth cycle in an almost identical yield as with the fresh catalyst, with no appreciable change in the activity (Table 3, entry 1). This consistent activity may have been due to the intact Keggin structure of FeMPA. FTIR measurements confirmed that the Keggin structure of FeMPA remained unchanged after the reaction (Figure 1).

To investigate the reaction mechanism, a catalytic amount of radical scavenger 4-*tert*-butylpyrocatechol was added to the reaction mixture. However, the scavenger had no influence on the reaction, which indicated that the reaction did not proceed through a radical pathway. This result was in agreement with the FeCl₂-catalyzed oxidative cyanation of tertiary amines with TMSCN report by Han and Ofial.^[7] A plausible reaction mechanism that involved both iron and molybdenum is shown in Scheme 3.

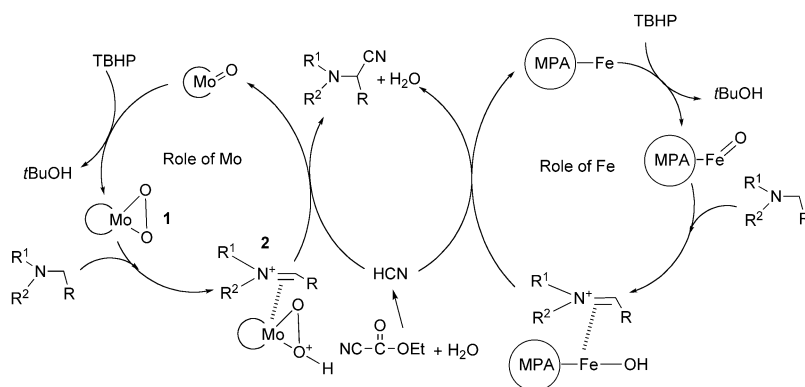
First, molybdenum reacted with TBHP to produce molybdenum peroxo species 1.^[20] Subsequently, this species reacted

Table 3. Oxidative cyanation of various tertiary amines over a FeMPA/Nb₂O₅ catalyst.^[a]

Entry	Substrate	Product	Yield [%] ^[a]
1			96, 90 ^[c]
2			98
3			97
4			93
5			92
6			98
7			30 ^[b]
8			87
9			70
10			75
11			91
12			87
13			90
14			0

[a] Reaction conditions: tertiary amine (1 mmol), ethyl cyanoformate (2 mmol), TBHP/H₂O (70%, 2 mmol), FeMPA/Nb₂O₅ (50 mg), MeOH/water (2 mL, 1:1 v/v), 65 °C, 7 h; [b] yield of isolated product; [c] 14 h; [d] yield after the fourth cycle.

with a tertiary amine to produce iminium ion intermediate 2. The CN[–] nucleophile, which was generated in situ by the reaction of ethyl cyanoformate and water, subsequently reacted with the intermediate iminium ion to yield the corresponding



Scheme 3. Plausible reaction mechanism.

α -amino nitrile. The participation of iron could be explained as a reaction with TBHP to form an oxo-iron species.^[21] Then, the next steps were assumed to proceed along the same pathway as that proposed by Sain and co-workers.^[9] Fe was present in the secondary structure of the Keggin ion and where the primary structure consisted of a molybdenum anion. Both of these structured were catalytically active in this reaction. The higher activity of FeMPA compared to MPA reiterated the involvement of both iron and molybdenum in this reaction. Further investigation into the reaction mechanism is underway in our laboratory.

Conclusions

We have developed a simple and highly efficient heterogeneous hetero-poly-acid-based catalyst for the oxidative cyanation of tertiary amines with ethyl cyanoformate as a cyanide source under mild reaction conditions. The advantage of this method is that it evades the use of highly toxic cyanide reagents. This catalytic system has been demonstrated to be an efficient, environmental friendly, and reusable catalyst for the cyanation of various tertiary amines.

Experimental Section

Iron-exchanged molybdophosphoric acid (FeMPA) was prepared by dissolving MPA (5 g) in distilled water, followed by the slow addition of an aqueous solution of iron nitrate (1.134 g) under stirring. Excess water was removed on a hot plate and the resultant solid was dried in an oven at 120 °C for 12 h. Finally, the catalyst was obtained by calcination at 300 °C for 2 h in air. The final composition of the catalyst was determined by ICP-AES as $\text{Fe}_{0.64}\text{H}_{0.36}\text{PMo}_{12}\text{O}_{40}$.

The niobium-supported FeMPA catalyst was prepared by using an impregnation method. The required quantity of FeMPA was dissolved in distilled water and this solution was added to the support under constant stirring. Excess water was removed on a water bath followed by drying at 120 °C for 12 h. Finally, the catalyst was obtained by calcination at 300 °C for 2 h in air. The FeMPA content on niobia was kept at 20 wt.%. This catalyst was denoted as FeMPA/Nb₂O₅.

FTIR spectra of the catalysts were recorded by using a DIGILAB (USA) IR spectrometer by using the KBr-disc method. XRD patterns were measured on a SIEMENS D-500 diffractometer by using $\text{Cu}_{K\alpha}$ radiation ($\lambda = 0.154 \text{ nm}$). The 2θ angles were scanned from 2–80° at a rate of 2° min⁻¹.

Raman spectra of the samples were recorded by using a Horiba-Jobin Yvon LabRam-HR spectrometer that was equipped with a confocal microscope, 2400/900 grooves mm⁻¹ gratings, and a notch filter. Visible laser excitation at 532 nm (visible/green) was used as

the laser source. The scattered photons were directed and focused onto a single-stage monochromator and measured with a UV-sensitive LN₂-cooled CCD detector.

Temperature-programmed desorption (TPD) of NH₃ was performed on a laboratory-built apparatus. In a typical experiment, about 0.1 g of the sample was pretreated at 300 °C for 1 h under a flow of helium (99.9%, 50 mL min⁻¹). After pretreatment, the sample was saturated with anhydrous ammonia (10% NH₃ balanced with He) at 100 °C for 1 h and subsequently flushed with He at the same temperature to remove any physisorbed ammonia. Then, TPD analysis was performed from ambient temperature to 800 °C at a heating rate of 10 °C min⁻¹ and the desorbed ammonia was measured by GC that was equipped with a thermal conductivity detector.

General reaction procedure for the oxidative cyanation of tertiary amines

A 10 mL round-bottomed flask that was equipped with a magnetic stirrer bar was charged with *N,N*-dimethylaniline (1 mmol), ethyl cyanoformate (2 mmol), TBHP/water (70%, 2 mmol), MeOH/water (2 mL, 1:1 v/v), and FeMPA/Nb₂O₅ catalyst (20%, 50 mg). The reaction mixture was stirred at 65 °C for 7 h. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and poured into an aqueous solution of NaHCO₃ and extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (5% ethyl acetate/hexane eluent). The identity and purity of the product was confirmed by using ¹H NMR and ¹³C NMR spectroscopy and by GCMS; the data were compared with literature values.

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[1] C. J. Li, *Acc. Chem. Res.* **2009**, *42*, 335–344.

- [2] a) D. H. Wang, M. Was, R. Giri, J. Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 7190–7191; b) O. Basle, C.-J. Li, *Org. Lett.* **2008**, *10*, 3661–3663.
- [3] a) R. H. Crabtree, *J. Organomet. Chem.* **2004**, *689*, 4083–4091; b) V. Rittling, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770; c) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633–639; d) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808–1822; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698–1712; e) E. J. Martinez, E. J. Corey, *Org. Lett.* **1999**, *1*, 75–78.
- [4] a) H. Ishitani, S. Komiya, S. Kobiyashi, *Angew. Chem.* **1998**, *110*, 3369–3372; *Angew. Chem. Int. Ed.* **1998**, *37*, 3186–3188; b) K. Surendra, N. S. Krishnavani, N. Mahesh, K. R. Rao, *J. Org. Chem.* **2006**, *71*, 2532–2534; c) F. Cruz-Acosta, A. Santos-Exposito, P. Tellado, *Chem. Commun.* **2009**, 6839–6841; d) J. Wang, Y. Masui, M. Onaka, *Eur. J. Org. Chem.* **2010**, 1763–1771; e) P. Galletti, M. Pori, D. Giacomini, *Eur. J. Org. Chem.* **2011**, 3896–3903; f) G. K. S. Prakash, T. Mathew, C. Panja, S. Alconcel, H. Vaghoo, C. Do, G. A. Olah, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 3703–3706.
- [5] a) S. I. Murahashi, N. Komiya, H. Terai, T. Nakae, *J. Am. Chem. Soc.* **2003**, *125*, 15312–15313; b) S. I. Murahashi, N. Komiya, H. Terai, *Angew. Chem.* **2005**, *117*, 7091–7093; *Angew. Chem. Int. Ed.* **2005**, *44*, 6931–6933.
- [6] S. Singhal, S. J. Jain, B. Sain, *Chem. Commun.* **2009**, 2371–2372.
- [7] W. Han, A. R. Ofial, *Chem. Commun.* **2009**, 5024–5026.
- [8] Y. Zhang, Y. Peng, M. Zhang, Y. Cheng, *Chem. Commun.* **2011**, *47*, 2354–2356.
- [9] S. Singhal, S. J. Jain, B. Sain, *Adv. Synth. Catal.* **2010**, *352*, 1338–1344.
- [10] S. Verma, S. J. Jain, B. Sain, *ChemCatChem* **2011**, *3*, 1329–1332.
- [11] S. Lundgren, E. Wingstrand, M. Penhoat, C. Moberg, *J. Am. Chem. Soc.* **2005**, *127*, 11592–11593.
- [12] J. Wang, W. Li, Y. Liu, X. Liu, X. Feng, *Org. Lett.* **2010**, *12*, 1280–1283.
- [13] a) N. Lingaiah, N. S. Babu, K. M. Reddy, P. S. S. Prasad, I. Suryanarayana, *Chem. Commun.* **2007**, 278–279; b) N. Pasha, N. S. Babu, K. T. V. Rao, P. S. S. Prasad, N. Lingaiah, *Tetrahedron Lett.* **2009**, *50*, 239–242; c) P. Nagaraju, N. Pasha, P. S. S. Prasad, N. Lingaiah, *Green Chem.* **2007**, *9*, 1126–1129; d) K. T. V. Rao, P. S. S. Prasad, N. Lingaiah, *J. Mol. Catal. A* **2009**, *312*, 65–69.
- [14] C. Marchal-Roch, N. Loronze, N. Guillou, A. Teze, G. Herve, *Appl. Catal. A* **2000**, *199*, 33–44.
- [15] M. Paulis, M. Martin, D. B. Soria, A. Diaz, J. A. Odrizola, M. A. Montes, *Appl. Catal. A* **1999**, *180*, 411–420.
- [16] A. Corma, A. Martinez, C. Martinez, *J. Catal.* **1996**, *164*, 422–432.
- [17] C. Rocchiccioli-Deltcheff, M. Fournier, R. Frank, R. Thouvenot, *Inorg. Chem.* **1983**, *22*, 207–216.
- [18] T. Ohuchi, T. Miyatake, Y. Hitomi, T. Tanaka, *Catal. Today* **2007**, *120*, 233–239.
- [19] T. Purkharthofer, W. Skranc, H. Weber, H. Griengel, M. Webbols, G. Scholz, P. Pochlauer, *Tetrahedron* **2004**, *60*, 735–739.
- [20] A. O. Chong, K. B. Sharples, *J. Org. Chem.* **1977**, *42*, 1587–1590.
- [21] T. G. Traylor, C. Kim, J. L. Richrds, F. Xu, C. L. Perrin, *J. Am. Chem. Soc.* **1995**, *117*, 3468–3474.

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