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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 , Pradip D. Nahide , Heena K. Meroliya , Shobha A. Waghmode & Suresh Iyer (2020): Oxime ligands for Pd catalysis of the Mizoroki–Heck reaction, Suzuki–Miyaura coupling & annulation reactions, Synthetic Communications, DOI: 10.1080/00397911.2020.1826969

To link to this article: https://doi.org/10.1080/00397911.2020.1826969

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https://doi.org/10.1080/00397911.2020.1826969

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Oxime ligands for Pd catalysis of the Mizoroki–Heck reaction, Suzuki–Miyaura coupling & annulation reactions

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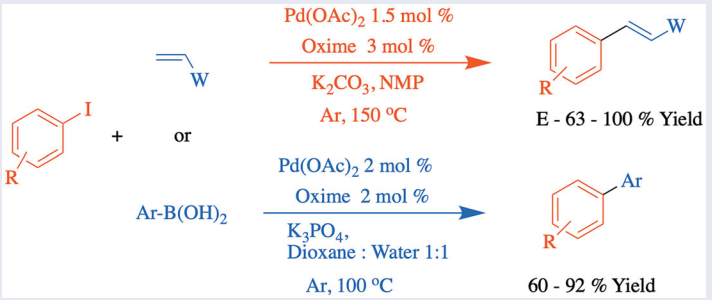
ABSTRACT

Monodentate and bidentate chelating oximes are readily available ligands for the Pd catalysis of the Mizoroki–Heck reaction and the Suzuki coupling. High yields were obtained in the Suzuki coupling in aqueous dioxane with TBABr as additive. The oximes can be easily synthesized from the corresponding ketones or aldehydes and thus provide a very large number of nitrogen-based ligands. They have the advantage of not undergoing oxidative degradation, common for phosphine ligands. Chelating oximes with $Pd(OAc)_2$, activate aryl iodides to give high yields of the substitution products in the Mizoroki–Heck reactions as well as the Suzuki coupling. Acetophenone oxime ligand with $Pd(OAc)_2$, catalyzed the reaction of aryl iodides with 1,2-disubstituted alkenes in moderate to high yields. As a test example, the LaRock indole annulation and synthesis of isocoumarin were achieved with acetophenone oxime ligand and $Pd(OAc)_2$ in high yields.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 19 May 2020

KEYWORDS
Isocoumarin; LaRock annulation; Mizoroki–Heck reaction; oximes; Suzuki coupling

Introduction

Though nano catalysts are state of the art, the dynamic association, dissociation of ligands conjures the magical wizardry associated with homogeneous catalysis. Thus, ligand-based homogeneous catalysis attributes activities and selectivities otherwise unachievable through normal organic synthesis. While huge reactivity is attributed to

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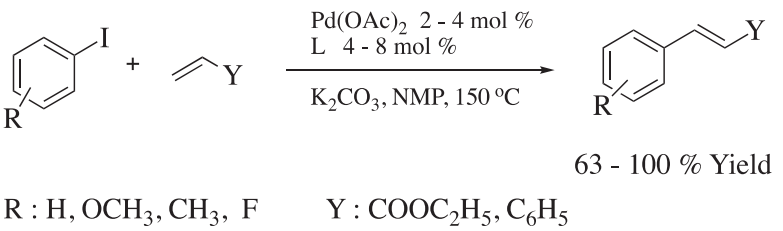
nano catalysts, ligand complexation ramps up homogeneous catalysis to even greater heights of selectivity, reactivity and efficiency. Ligand complexation entwined with metal co-ordination and oxidation states, enhances the homogeneous catalysis of organic transformations. Ligand accelerated catalysis is a well-established phenomena exemplified by the Sharpless dihydroxylation. Here, the life cycle of catalyst metal elements is highly enhanced by co-ordination. Ligand architecture and engineering are a complex arena of organometallic catalysis and a vast and fruitful exercise in organic synthesis. Thus, by the virtue of their design and nature, ligands induce magical properties to metal atoms in homogeneous catalysis. Phosphine ligands are a synthetic wizardry leading to vast complex structures which are though tedious synthesis in nature. Nitrogen compounds are excellent alternatives for phosphine ligands, which have become ubiquitous and synonymous with Pd and homogeneous catalysis, including industrial applications.[1] We and several other authors have earlier reported the use of easily obtainable nitrogen ligands for the Mizoroki–Heck reaction, the Suzuki–Miyaura coupling and other reactions.[2] Complexation of metals with oximes is well known and their ready availability from the corresponding ketones and aldehydes by simple derivatization or other methods make them very attractive.[3,4] Aromatic oximes due to their directed ortho palladation lead to molecular marvels, palladacycles; which are exciting catalysts as well as possessing other properties.[4] They provide competitive phosphine ligand alternatives for the Mizoroki–Heck reaction, Suzuki–Miyaura and related cross-coupling reactions.[5] Simpler complexes with mono or bidentate co-ordinating oximes are waiting to be explored. Unlike phosphines, NHCs, SALEN, di-imines, cyclopentadienes, and many other ligands, oximes are easy to synthesize and metal complexation simple to do in the laboratory and little studied in organometallic catalysis for organic synthesis, like cross-coupling reactions, though their ligating properties and co-ordination chemistry are well known. Oximes possess strong coordinating property as well as facile dissociation for attenuation of metal reactivity. They are excellent coordinating groups for various transition metals forming extremely stable metal complexes in very high yields.[4] While ligands can be spectatorial, fruitful ligand intervention is an essential feature of homogeneous catalysis, affecting stereo selectivities, activity, and efficiency.

The use of DMG, DAB, Salen, 8-HQ, Imines, Oxazolidines, nitrogen Pd cycles, and several other N-based ligands gives high yields in the Mizoroki–Heck reaction and Suzuki coupling.[6] $PdCl_2$DMG showed promising activity for the Mizoroki–Heck reaction of aryl iodides and some bromides.[2a] A novel 2-(diphenylphosphino)benzaldoxime ligand has been used for the Suzuki coupling of aryl bromides.[7]

Phosphines have been shown to inhibit the Suzuki–Miyaura coupling of aryl halides, thus limiting catalyst efficiency. Also, when using $Pd(PPh_3)_4$, significant incorporation of phenyl groups from the PPh_3 has been shown to occur. So ligand free, non-phosphine alternatives have been explored successfully and TBABr or PEG found to be an excellent additive-solvents for high yielding reactions in aqueous media.[8] Bora and coworkers have reported the use of oxime ethers as ligands in the aqueous phase Pd catalysis of the Suzuki–Miyaura coupling. Their catalytic activity is based on the *in situ* generation of palladacycles.[8g] Continuing in this concept, we explored oxime & other N, O compound themes for ligands in the Mizoroki–Heck and Suzuki–Miyaura coupling. While a vast number of N, O compounds are indeed readily available, some are



Scheme 1. Oxime ligand–Pd catalysis of the Mizoroki–Heck reaction.

also easily synthesizable using well-known reactions in high yields. Here, we experimented on the use of oximes and tertiary amines as well as ketones as ligands.

Results and discussion

In preliminary studies, we used DMG, which is commercially available, as the ligand with $Pd(OAc)_2$, to give high yields of the Mizoroki–Heck reaction product in short reaction times[2] (Scheme 1). While palladacycles have been derived from the aromatic oximes, we were curious about the catalytic activity of simple coordinating monodentate and bidentate oximes which would not undergo cyclopalladation. Several ketones and aldehydes are readily available for the derivatization of mono dentate oximes. We also prepared a bidentate amino oxime from the Mannich base of acetophenone. High yields are reported in the ligand free $Pd(OAc)_2$ catalysis of the Mizoroki–Heck reaction of aryl halides, though requiring long (19–44 h) reaction times (Fig. 1).[9]

The results of the Mizoroki–Heck reaction is shown in Table 1. Very high yields of the E-substituted product were readily obtained from the different aryl iodides and $Pd(OAc)_2$ as catalyst under standard Mizoroki–Heck reaction conditions. Though the reactions were carried out under argon, the reactions could be performed under ambient conditions in presence of air, without much depletion of the reaction or the yield. NMP and K_2CO_3 were the solvent and base of choice for the reaction.

Monodentate oximes gave high yields of the reaction substitution product as expected. We had anticipated some steric acceleration from hindered ketone oximes but surprisingly camphor oxime gave reduced yield. The chelating oximes also gave high yields. Similarly, the dimethyl amine group was easily incorporated by the Mannich reaction of acetophenone and the derived chelating oxime, gave excellent yields of the Mizoroki–Heck product.

The reaction of 1,2-disubstituted alkene was also tested with the acetophenone oxime ligand. We have reported silver sequestration of aryl halides for high yielding Mizoroki–Heck reaction of 1,1-and 1,2-disubstituted alkenes.[10] Cinnamaldehyde reacted with 4-iodoanisole catalyzed by $Pd(OAc)_2$ and acetophenone oxime ligand under standard conditions (with addition of 1 Eq TBABr, Scheme 2, Table 2, footnote), to provide the product in 99% isolated yield. TBABr is essential for good yields acting as solid–liquid phase transfer agent.[11] Preliminary experiments report the reaction to be successful with other 1, 2-disubstituted alkenes like ethyl cinnamate and stilbene. Iodobenzene reacted with stilbene providing product in 41% yield (Scheme 2). DMF was used as solvent for all the reactions while the base was NaOAc or K_2CO_3. With 4-iodoanisole the *E*:*Z* ratios were low, between 2: 1 and 3: 1 (Table 2).

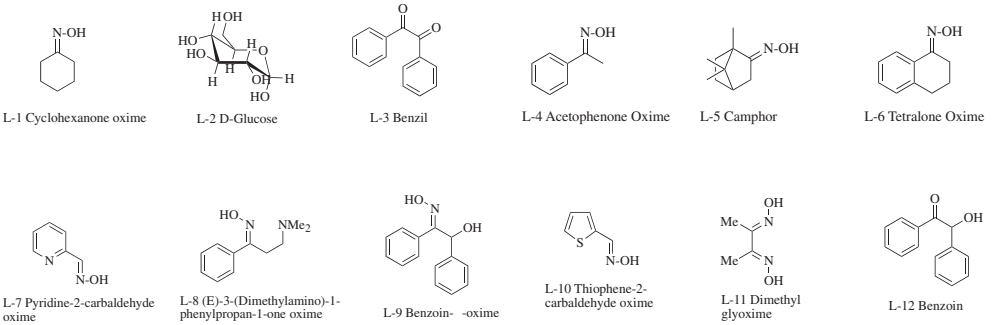
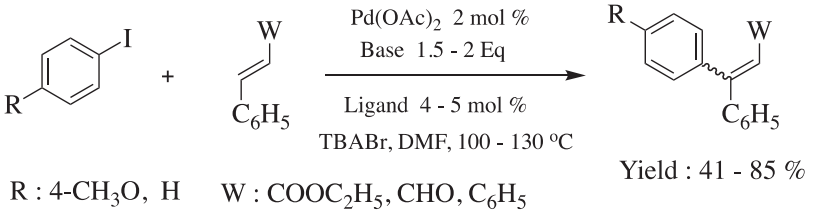


Figure 1. Structures of various oxime & N, O – ligands.

Table 1. Oxime ligands in Pd catalysts of the Mizoroki–Heck reaction.

S. no.	Aryl iodide	Alkene	Ligand	Time (h)	Yield (%)
1	C_6H_5I	Ethyl acrylate	CyOxime – L1	5	96
2	C_6H_5I	Ethyl acrylate	D-Glucose – L2	7	85
3	C_6H_5I	Ethyl acrylate	CyOxime – L1	4	100
4	C_6H_5I	Ethyl acrylate	Benzil – L3	4	94
5	C_6H_5I	Ethyl acrylate	Acetophenone oxime – L4	5	63
6	C_6H_5I	Styrene	Acetophenone oxime – L4	5	79
7	C_6H_5I	Ethyl acrylate	Camphor oxime – L5	15	65
8	C_6H_5I	Styrene	Tetralone oxime – L6	19	82
9	C_6H_5I	Styrene	Pyridine-2-carbaldehyde oxime – L7	19	65
10	C_6H_5I	Ethyl acrylate	(*E*)-3-(Dimethylamino)-1-phenylpropan-1-one oxime – L8	22	90
11	C_6H_5I	Ethyl acrylate	Benzoin-α-oxime – L9	22	87
12	C_6H_5I	Ethyl acrylate	Tetralone oxime – L6	24	77
13	C_6H_5I	Ethyl acrylate	Pyridine-2-carbaldehyde oxime – L7	24	65
14	C_6H_5I	Ethyl acrylate	Thiophene-2-carbaldehyde oxime – L10	24	91
15	4-CH_3O·C_6H_4I	Ethyl acrylate	(*E*)-3-(Dimethylamino)-1-phenylpropan-1-one oxime – L8	22	84
16	4-CH_3O·C_6H_4I	Ethyl acrylate	Tetralone oxime – L6	24	88
17	4-CH_3O·C_6H_4I	Ethyl acrylate	Thiophene-2-carbaldehyde oxime – L10	24	94
18	4-CH_3O·C_6H_4I	Ethyl acrylate	Pyridine-2-carbaldehyde oxime – L7	24	78
19	4-CH_3O·C_6H_4I	Styrene	DMG – L11	3	80
20	4-CH_3·C_6H_4I	Ethyl acrylate	DMG – L11	2	97
21	4-F·C_6H_4I	Ethyl acrylate	DMG – L11	3	92

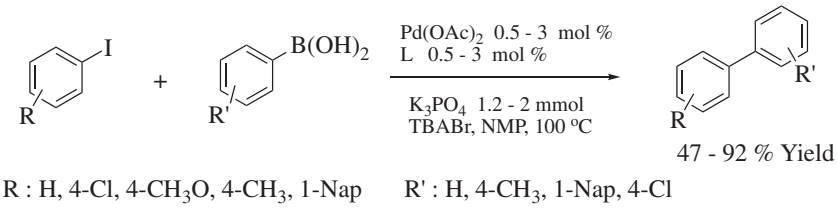


Scheme 2. Mizoroki–Heck reaction of 1,2-disubstituted alkenes.

Table 2. Acetophenone oxime as ligand for the Mizoroki–Heck reaction of 1,2-disubstituted alkenes.

S. no.	Aryl iodide	Alkene	Base	Time (h)	Yield (%)	*E:Z* ratio[a]
1	4-CH_3O·C_6H_5I	Ethyl cinnamate (E)	NaOAc	40	64	(3:1)
2	C_6H_5I	Cinnamaldehyde (E)	NaOAc	24	99	–
3	C_6H_5I	Stilbene (E)	K_2CO_3	44	41	–
4	4-CH_3O·C_6H_5I	Stilbene (E)	K_2CO_3	48	49	(2:1)

Reaction conditions: Aryl iodide (1.5 mmol), alkene (1 mmol), $Pd(OAc)_2$ (2 mol%), acetophenone oxime (4–5 mol%), NaOAc (1.5 mmol), TBABr (1 mmol), 10 ml DMF, temp: 100 °C then increased to 130 °C after 7 h.
[a]*E:Z* ratio was determined by ^{1}H NMR.

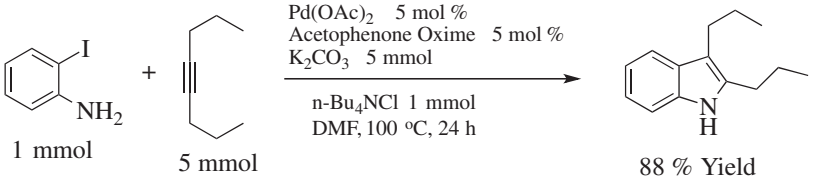


Scheme 3. Oxime ligands–$Pd(OAc)_2$ catalyzed Suzuki coupling.

Table 3. Oxime & other ligands in Pd catalysis of the Suzuki coupling.

S. no.	Aryl iodide	Boronic acid	Ligand	Time (h)	Yield (%)
1	4-Cl·C_6H_4I	$C_6H_5B(OH)_2$	CyOxime – L1	24	92[a]
2	C_6H_5I	$C_6H_5B(OH)_2$	Benzil – L3	10	69[a]
3	C_6H_5I	$C_6H_5B(OH)_2$	Benzoin – L12	10	47[a]
4	4-Cl·C_6H_5I	4-$CH_3C_6H_5B(OH)_2$	Benzoin – L12	14	60[a]
5	C_6H_5I	4-Cl.$C_6H_5B(OH)_2$	DMG – L11	2.15	83[b]
6	4-CH_3O·C_6H_5I	1-Nap.$B(OH)_2$	DMG – L11	1	89[b]
7	4-CH_3O·C_6H_5I	$C_6H_5B(OH)_2$	DMG – L11	2	88[b]
8	4-CH_3·C_6H_5I	$C_6H_5B(OH)_2$	CyOxime – L1	30 min	75[b]
9	1-Nap·Br	$C_6H_5B(OH)_2$	Acetophenone oxime – L4	1.30	79[b]

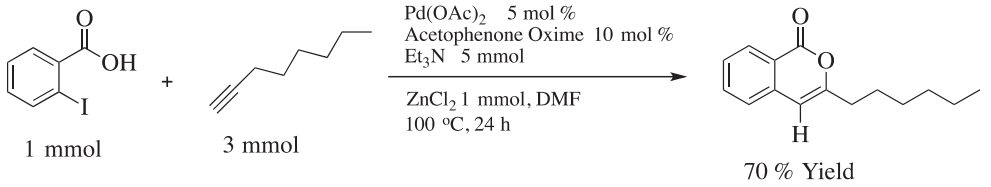
Reactions conditions: ArI (0.5 mmol), $ArB(OH)_2$ (0.6 mmol), K_3PO_4 (0.6 mmol), TBABr (0.6 mmol), $Pd(OAc)_2$ (0.5–3 mol%), ligand (0.5–3 mol%).
[a]NMP: 100 °C, time: 10–24 h.
[b]Dioxane:water (1:1), 100 °C, time: 30 min–2.5 h.



Scheme 4. The LaRock indole annulation.

We also tested these oxime ligands for the catalysis of the Suzuki coupling by $Pd(OAc)_2$. Under unoptimized conditions, good yields of the various biaryls were obtained (Scheme 3, Table 3).

Suzuki couplings of aryl halides have been reported to be high yielding in aqueous solvents.[8] The use of oxime ether ligands for Suzuki coupling with Pd catalysis is reported where the *in situ* generation of Pd cycles is proposed to be the real catalyst.[8g] Compared to this our study discusses the effect of oxime ligands for both the Mizoroki–Heck reaction and Suzuki coupling and related annulations. Some of the oximes we have studied do not form Pd cycles as evidenced by the activity of cyclohexanone oxime as ligand. Our experiments for the Suzuki coupling in 1:1 dioxane water mixture gave excellent results. The reactions with different aryl iodides and boronic acids using TBABr as additive were complete in 30 min to 2.5 h. Cyclohexanone oxime and DMG were representative oxime ligands and gave very high yields. Comparative studies were carried out with benzil, benzoin as ligands, which gave relatively lower yields. 1-Bromo naphthalene gave the Suzuki coupling in high yields. But, the reaction of 4-bromo anisole with phenyl boronic acid, both in



Scheme 5. The isocoumarin annulation.

the presence or absence of TBABr gave multiple products, due to homo coupling and cross-coupling.

The LaRock indole annulation was carried out with acetophenone oxime as ligand[12] (Scheme 4). The reaction of 2-iodoaniline with 3-octyne gave the indole in 88% yield. Similarly, 2-iodobenzoic acid reacted with 1-octyne to give the isocoumarin in 70% yield[13] (Scheme 5).

Conclusion

Oximes are excellent ligands for the Pd catalyzed Mizoroki–Heck reaction and Suzuki coupling. The oxime ligands can be readily derived from a vast library of aldehydes and ketones. The less reactive 1,2-disubstituted alkenes also provided high yields of trisubstituted products. The LaRock indole annulation and synthesis of isocoumarin could be carried out in very high yields in the presence of the acetophenone oxime ligand.

Experimental procedures

General procedure for the Mizoroki–Heck reaction

To an oven-dried 25 ml round bottom flask equipped with magnetic stirrer bar was charged palladium acetate (1.5–4 mol%) and ligand (3–8 mol%) in NMP (1 ml). The reaction mixture was stirred for 3 min. To this reaction mixture base K_2CO_3 (2 mmol), aryl iodide (1 mmol), olefin (1–2.5 mmol), and NMP (3 ml) were added and the reaction mixture was stirred at the indicated temperature for the indicated amount of time. At the conclusion of the reaction as monitored by TLC, the crude reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to give the desired product.

A1 2-Propenoic acid-3-phenyl, ethyl ester (2E) (4 h) (2 h, 0.126 g, 0.72 mmol, 72% yield, colorless oil) CAS Registry Number 103-36-6, ^{1}H NMR (CHLOROFORM-d, 200 MHz): δ (ppm) 7.65–7.73 (d, $J = 16$ Hz, 1H), 7.32–7.57 (m, 5H), 6.40–6.48 (d, $J = 16$ Hz, 1H), 4.14–4.38 (q, $J = 7.2$ Hz, 2H), 1.20–1.44 (t, $J = 7.1$ Hz, 3H) ^{13}C NMR ($CDCl_3$, d, 200 MHz): d 166.9, 144.48, 134.36, 130.13, 126.76, 127.96, 118.18, 60.40, 14.24; IR (cm^{-1}) 3399, 3021, 2976, 2404, 1706, 1636, 1482, 1453, 1372, 1315, 1272, 1214, 1176, 1089, 1036, 984, 829, 871, 765, 675; HRMS-ESI: $[M^+ + H]^+$ calcd for $C_{11}H_{12}O_2$ $[M + H]^+$ 177.0910, found: 177.0912.

General procedure for the catalysis of Suzuki coupling

To a solution of aryl halide (0.078 g, 0.5 mmol), aryl boronic acid (0.073 g, 0.6 mmol), TBABr (0.161 g, 0.5 mmol), and K_3PO_4 (0.127 g, 0.6 mmol) in dioxane and water (1:1, 10 ml) was added $Pd(OAc)_2$ (0.0022 g, 0.01 mmol) and ligand (0.01 mmol). The resulting mixture was heated with stirring at 130 °C for 2–6 h under argon. After completion of reaction (monitored by TLC), the reaction mixture was quenched by adding water. The solution was extracted with ethyl acetate (3 × 20 ml) the combined extract was washed with saturated brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuum and the crude product purified by column chromatography on silica gel (100–200 mesh, petroleum ether: 2% ethyl acetate) to give pure product.

B1 1,1-Biphenyl-4-chloro (5i) (2 h, 0.089 g, 0.94 mmol, 95% yield, white solid, MP: 79 °C) CAS Registry Number 2051-62-9, ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.60 − 7.37 (m, 9 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ): 139.98, 139.65, 133.35, 128.88, 128.37, 126.97; IR (cm^{-1}): 3022, 2923, 2403, 1894, 1755, 1657, 1597, 1480, 1398, 1218, 1091, 1012, 924, 834, 768, 677; HRMS-ESI: $[M]^+$ calcd for $C_{12}H_9Cl$ $[M]^+$ 188.0387, found: 188.0386.

Procedure for LaRock indole annulation using acetophenone oxime ligand – Palladium acetate (0.011 g, 5 mol%), acetophenone oxime (0.007 g, 5 mol%), n-Bu_4NCl (0.277 g, 1 mmol), K_2CO_3 (0.691 g, 5 mmol), 2-iodoaniline (0.219 g, 1 mmol), 4-octyne (0.551 g, 5 mmol), and DMF (10 ml) were added to an oven-dried 25 ml round bottom flask equipped with magnetic stirrer bar. The system was degassed and heated at 100 °C for 24 h. At the conclusion of the reaction as monitored by TLC, the reaction mixture was diluted with ethyl acetate and washed with saturated aqueous ammonium chloride and water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel to give analytically pure product (0.177 g, 88%).

2,3-Dipropyl-1H-indole – ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.71$ (s, 1H), 7.54–7.50 (m, 1H), 7.30–7.26 (m, 1H), 7.14–7.02 (m, 2H), 2.74–2.63 (m, 4H), 1.78–1.57 (m, 4H), 0.97 (q, $J = 7.33$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) $\delta = 135.23$, 135.14, 128.79, 120.73, 118.81, 118.35, 112.10, 110.14, 29.68, 28.12, 26.23, 24.09, 23.14, 14.23, 13.97; IR ($CHCl_3$) ν_{max}=3412, 2961, 2931, 1608, 1575, 1462, 1352, 903, 752, 735; HRMS: *m/z*=calcd for $C_{14}H_{19}N$ $[M]^+$ 201.1517, found: 201.1513.

Procedure for isocoumarin synthesis using acetophenone oxime ligand – To a solution consisting of 2-iodobenzoic acid (0.248 g, 1 mmol), 1-octyne (0.330 g, 3 mmol), and Et_3N (0.69 ml, 5 mmol) in DMF (1 ml) under argon were added $Pd(OAc)_2$ (0.011 g, 5 mol%), acetophenone oxime (0.014 g, 10 mol%), and zinc chloride (0.136 g, 1 mmol). The mixture was heated at 100 °C for 24 h. At the conclusion of the reaction as monitored by TLC, the reaction mixture was diluted with ethyl acetate and washed with saturated aqueous ammonium chloride and water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel to give analytically pure product (0.161 g, 70%).

3-Hexyl-1H-isochromen-1-one – ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 8.25$ (d, $J = 7.96$ Hz, 1H), 7.71–7.63 (m, 1H), 7.48–7.33 (m, 2H), 6.26 (s, 1H), 2.52 (t, $J = 7.71$ Hz, 2H), 1.78–1.63 (m, 2H), 1.44–1.26 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) $\delta = 163.07$, 158.29, 137.60, 134.64, 129.43, 127.46, 124.96, 120.06, 102.81, 33.48, 31.45,

28.63, 26.81, 22.46, 13.99; IR ($CHCl_3$) ν_{max}=3066, 2932, 2860, 1806, 1732, 1656, 1473, 1318, 1213, 1155, 1028, 826, 754, 688; HRMS: *m/z*=calcd for $C_{15}H_{18}NaO_2$ $[M + Na]^+$ 253.1199; found: 253.1204.

Funding

CSIR is acknowledged for scholarships, SRF to PGB and Dr. H. V. Thulasiram for CSC NAPA PA-II to Pradip Nahide.

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References

[1] (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461–1473. DOI: 10.1021/ar800036s.; (b) Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 6338–6361. DOI: 10.1002/anie.200800497.(c) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348. DOI: 10.1021/cr60307a002.(d) Rios, G. I.; Rosas-Hernandez, A.; Martin, E. *Molecules*. **2011**, *16*, 970–1010. DOI: 10.3390/molecules16010970;.(e) Suzuki, K.; Hori, Y.; Nakayama, Y.; Kobayashi, T. *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 1231–1246. DOI: 10.5059/yukigoseikyokaishi.69.1231.(f) *Organotransition Metal Chemistry, From Bonding to Catalysis*; John, F. Hartwig., Ed.; University Science Books: Sausalito, 2010; pp. 1160. (g) Allen, D. W. Chapter 1: Phosphines and Related P–C-Bonded Compounds. In *Organophosphorus Chemistry: Volume 43*; David W. Allen, John C. Tebby, David Loakes, Ed.,The Royal Society of Chemistry: London, 2014; Vol. 43; pp 1–51 .(h) Rauchfuss, T. B. Homogeneous Catalysis with Metal Phosphine Complexes. In *Modern Inorganic Chemistry*; Pignolet, L. H., Ed.; Springer: Boston, MA, 1983; pp 239–256;(i) Wauters, I.; Debrouwer, W.; Stevens, C. V.; Beilstein, J. *Beilstein J. Org. Chem.* **2014**, *10*, 1064–1096. DOI: 10.3762/bjoc.10.106.(j) Li, Y.; Kwong, F.; Yu, W.; Chan, A. *Coord. Che. Rev.* **2007**, *251*, 2119–2144. DOI: 10.1016/j.ccr.2007.07.020.

[2] (a) Iyer, S.; Kulkarni, G. M.; Ramesh, C. *Tetrahedron* **2004**, *60*, 2163–2172. DOI: 10.1016/j.tet.2003.12.012. (b) Iyer, S.; Kulkarni, G. M.; Ramesh, C.; Sattar, A. K. *Ind. J. Chem.* **2005**, *44B*, 1894–1908;(c) Gerasimchuk, N. Dalton Trans. **2019**, *48*, 7985–8013. DOI: 10.1039/c9dt01057b.(d) Caipa, C. M. A. Eindhoven Technische Universiteit Eindhoven. DOI: 10.6100/IR594547.(e) Pombeiro, A. J. L. *Dalton Trans.* **2019**, *48*, 13904–13906. DOI: 10.1039/c9dt90195g.

[3] (a) Kukushkin, V. Y.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1999**, *181*, 147–175. DOI: 10.1016/S0010-8545(98)00215-X. (b) Milios, C. J.; Stamatatos, T. C.; Perlepes, S. P. *Polyhedron*. **2006**, 2, 134–194; DOI: 10.1016/j.poly.2005.07.022.(c) Kukushkin, V. Y., Tudela, A. J. L., Pombeiro, A. J. L. *Coord. Chem. Rev.* **1996**, 156, 333–362; DOI: 10.1016/0010-8545(95)01234-6.(d) Smith, A.; Tasker, P. A.; White, D. J. *Coord. Chem. Rev.* **2003**, *241*, 61–85. DOI: 10.1016/S0010-8545(02)00310-7.(e) Milios, C. J.; Stamatatos, T. C.; Perlepes, S. P. *Polyhedron*. **2006**, *25*, 134–194. DOI: 10.1016/j.poly.2005.07.022.(f) Beirakhov, A. G.; Orlova, I. M.; Mikhailov, Y. N. *Russ. J. Inorg. Chem.* **2014**, *59*, 1679–1690. DOI: 10.1134/S0036023614140022.(g) Sandler, S.; Karo, W. Organic Functional Group Preparations, 2nd ed.; Academic Press: New York, 2012; pp 552;(h) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. J.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: London, 1989; p 922.

[4] (a) Brisdon, B. J.; Nair, P.; Dyke, S. F. *Tetrahedron.* **1981**, *37*, 173–177. DOI: 10.1016/S0040-4020(01)97731-2. (b) Onoue, H.; Minami, K.; Nakagawa, K. *BCSJ.* **1970**, *43*, 3480–3485. DOI: 10.1246/bcsj.43.3480.(c) Alacid, E.; Alonso, D. A.; Botella, L.; Najera, C.; Pacheco, M. C. *Chem. Rec.* **2006**, *6*, 117–132. DOI: 10.1002/tcr.20077.

[5] (a) Alonso, D. A.; Najera, C.; Pacheco, M. C. *Org. Lett.* **2000**, *2*, 1823–1826. DOI: 10.1021/ol0058644. (b) Iyer, S.; Ramesh, C. *Tetrahedron Lett.* **2000**, *41*, 8981–8984. DOI: 10.1016/S0040-4039(00)01594-X.(c) Iyer, S.; Jayanthi, A. *Tetrahedron Lett.* **2001**, *42*, 7877–7878. DOI: 10.1016/S0040-4039(01)01604-5.(d) Iyer, S.; Jayanthi, A. *Synlett* **2003**, *8*, 1125–1128. DOI: 10.1055/s-2003-39881..

[6] (a) Gruber, A. S.; Zim, D.; Ebeling, G.; Monteiro, A. L.; Dupont, J. *Org. Lett.* **2000**, *2*, 1287–1290. DOI: 10.1021/ol0057277. (b) Ohff, M.; Ohff, A.; Milstein, D. *Chem. Commun.* **1999**, 357–358. DOI: 10.1039/a809883b.(c) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374. DOI: 10.1002/anie.199523711.(d) Peris, E.; Mata, M.; Loch, J. A.; Crabtree, R. H. *Chem. Commun.* **2001**, 201–202. DOI: 10.1039/b008038l.

[7] Xu, L.; Zhu, D.; Wu, F.; Wang, R.; Wan, B. *J. Mol. Cat. A Chem.* **2005**, *237*, 210–214. DOI: 10.1016/j.molcata.2005.05.007.

[8] (a) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034–5037. DOI: 10.1021/jo00096a056. (b) Bedford, R. B.; Blake, M. E.; Butts, C. B.; Holder, D. *Chem. Commun.* **2003**, 466–467. DOI: 10.1039/b211329e.(c) Leadbeater, N. E.; Marco, M. *Org. Lett.* **2002**, *4*, 2973–2976. DOI: 10.1021/ol0263907.(d) Campi, E. M.; Jackson, W. R.; Marcuccio, S. M. ; Naeslund, C. G. M. *J. Chem. Soc., Chem. Commun.* **1994**, *20*, 2395–2395. DOI: 10.1039/C39940002395.(e) Badone, D.; Baroni, M.; Cardamone, R.; Ielmini, A.; Guzzi, U. *J. Org. Chem.* **1997**, *62*, 7170–7173. DOI: 10.1021/jo970439i.(f) Liu, L.; Zhang, Y.; Wang, Y. *J. Org. Chem.* **2005**, *70*, 6122–6125. DOI: 10.1021/jo050724z.(g) Mondal, M.; Bora, U. *Tetrahedron Lett.* **2014**, *55*, 3038–3040. DOI: 10.1016/j.tetlet.2014.03.113.

[9] Yao, Q.; Kinney, E. P.; Yang, Z. *J. Org. Chem.* **2003**, *68*, 7528–7531. DOI: 10.1021/jo034646w.

[10] Bangar, P.; Jawalkar, P.; Dumbre, S.; Patil, D.; Iyer, S. *Appl. Organometal. Chem.* **2018**, *32*, 1–6. DOI: 10.1002/aoc.4159.

[11] Jeffery, T.; Galland, J.-C. *Tetrahedron Lett.* **1994**, *35*, 4103–4106. DOI: 10.1016/s0040-4039(00)73124-8.

[12] LaRock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem.* **1998**, *63*, 7652–7662. DOI: 10.1021/jo9803277.

[13] Liao, H.-Y.; Cheng, C.-H. *J. Org. Chem.* **1995**, *60*, 3711–3716. DOI: 10.1021/jo00117a023.