Bull. Chem. Soc. Ethiop. **2024**, 38(5), 1405-1412.
DOI: https://dx.doi.org/10.4314/bcse.v38i5.16

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

A SYNTHESIS OF 1,3-DIENES USING A Ni(II) MEDIATED SUZUKI-MIYAURA REACTION

Yassir S. Al-Jawaheri* and Nameer S. Ezzat

College of Education, Department of Chemistry, Mosul University, Iraq

(Received March 23, 2024; Revised June 11, 2024; Accepted June 13, 2024)

ABSTRACT. Synthesis of the 1,3-dienes from arylboronic acids with propargyl alcohols using a Ni(II) precatalysts is presented. Through detailed reaction screening $NiCl_2(PCy_3)_2$ has been identified as the optimal catalyst for this transformation. The reaction is thought to proceed through a Ni(II) allenyl complex, which undergoes a base free Suzuki-Miyaura cross-coupling through arylboronic acids, with the resultant aryl allene rearranging to its 1,3-diene. Application of these optimized reaction conditions then provides several dienes in reasonable to good, isolated yields.

KEY WORDS: Suzuki-Miyaura, $NiCl_2(PCy_3)_2$, 1,3-Dienes, Allenyl, Base free

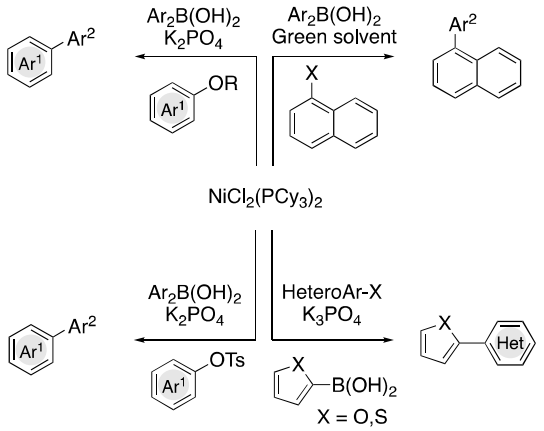
INTRODUCTION

The Suzuki-Miyaura (SM) coupling reaction, a well-known process, employs $NiCl_2(PCy_3)_2$ as a precatalyst. It involves cross-coupling an aryl or vinyl boronic acid using an aryl or vinyl halide to facilitate a vital tool in organic synthesis for building carbon-carbon bonds. By replacing the valuable metal palladium with abundant first-row nickel [1, 2]. Nickel complexes, due to their high reactivity, enable some interesting coupling reactions to happen with catalysts having ligands. Also known as nickel(II) chloride bis (tricyclohexylphosphine), $NiCl_2(PCy_3)_2$ finds widespread use as a pre-catalyst in various coupling cross-coupling processes. The PCy_3 ligand (tricyclohexylphosphine) stabilizes the nickel centre and enhances its reactivity during catalysis. In these coupling reactions, $NiCl_2(PCy_3)_2$ facilitates the oxidative addition of organic halides or pseudohalides to the nickel centre, followed by transmetallation with organoboron reagents, and ultimately, reductive elimination to yield the desired coupling product [3-5].

The stability and tolerance to various functional groups make $NiCl_2(PCy_3)_2$ an advantageous precatalyst, enabling its use in complex molecule synthesis [6]. However, it is important to note that other nickel precatalysts, such as $NiCl_2(PPh_3)_2$ can also be employed [7].

The $NiCl_2(PCy_3)_2$-catalyzed SM coupling reaction has proven effective in overcoming various reaction obstacles and limitations. Notable advantages are the broad availability of boronic acids in these reactions, and the tolerance of nucleophiles outside the usual halide window, such as tosylates. For example, in 2001 Menteiro [8] successfully substituted aryl halides with aryl tosylates, while in 2008, Garg [9] introduced halo naphthyl compounds in environmentally friendly solvents such as methyl tetrahydrofuran, then in 2009, they utilized carbamates, carbonates, and sulfamates with toluene as a solvent [10]. Furthermore, in 2013, Hartwig [11] employed heteroaryl boronic acids in combination with heteroaryl halides in green solvents (Scheme 1). Overall, these advancements demonstrate the continuous efforts to enhance and diversify the SM coupling reaction using $NiCl_2(PCy_3)_2$ as the catalyst, opening new possibilities for organic synthesis.

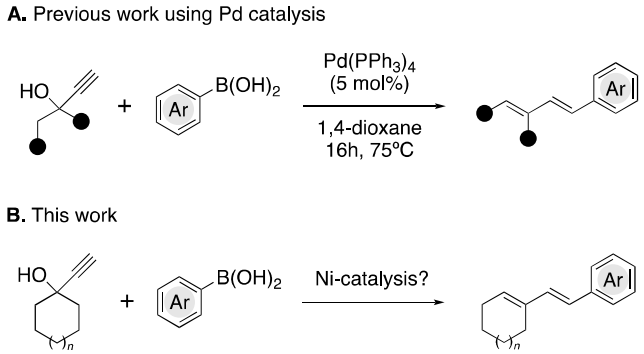
*Corresponding authors. E-mail: yassir_chem71@uomosul.edu.iq



Scheme 1. Examples of the Suzuki-Miyaura reaction using $NiCl_2(PCy_3)_3$.

In addition of SM coupling, $NiCl_2(PCy_3)_2$ is utilized as a precatalyst in several coupling reactions: including the Buchwald-Hartwig amination [12] for forming arylamines or alkylamines, the Sonogashira coupling [13, 14] to produce substituted alkynes, the Heck reaction [15] for substituted alkenes synthesis, and the Stille coupling [16] to form carbon-carbon bonds with organostannanes.

In 2016, we reported the use of a Pd^0 catalysis in the formation of 1,3-dienes. This reaction used a base free Suzuki-Miyuara reaction between boronic acids with propargyl alcohols to initially form the allene, which subsequently underwent rearrangement to the 1,3-diene (Scheme 2a) [17, 18]. In continuation of this, we wished to examine the feasibility of replacing palladium (Pd) with various readily available nickel (Ni) catalysts (Scheme 2b). This survey aims to investigate which nickel catalysts, if any, can effectively catalyse the production of conjugated dienes compounds using propargyl alcohols in the absence of a base.



Scheme 2. Previous work using Pd catalysis and this work.

RESULTS AND DISCUSSION

In Table 1, we selected 1,3-diene **3** as it had been previously prepared [18] and readily detected by ^{1}H-NMR. Using three equivalents of boronic acid at a temperature of 85 ºC, with a catalyst of 5% $NiCl_2.6H_2O$, and a reaction time of 16 hours, the conversion of boronic acid into the desired product resulted in no detectable yield of 1 (Entry 1). Using three equivalents of boronic acid at a temperature of 85 ºC, with a catalyst of 10% $NiCl_2.6H_2O$, and a reaction time of 24 hours, the conversion of boronic acid into the desired product also resulted in no detectable yield. Entry 3: Using two equivalents of boronic acid at a temperature of 85 ºC, with a catalyst of 10% $NiCl_2.6H_2O$, and a reaction time of 24 hours, the conversion of boronic acid into the desired product also resulted in no detectable yield. Entry 4: Consuming three equivalents of boronic acid with temperature at 85 ºC, in presence of 5% Raney Ni as a catalyst, with reaction time of 16 hours, resulted again in no noticeable yield. Entry 5: For two equivalents of boronic acid with a temperature of 75 ºC, and 5% of a catalyst $NiCl_2(Pcy_3)_2$, with 16 hours reaction time, the conversion also resulted in no yield detectable. Entry 6: Utilising three equivalents of boronic acid with a temperature of 85 ºC, and a catalyst of 5% $NiCl_2(Pcy_3)_2$, with a reaction time of 24 hours, the favourite product generated a 14% conversion. Entry 7: Using three equivalents of boronic acid at a temperature of 60 ºC, with a catalyst of 5% $NiCl_2(Pcy_3)_2$, and a reaction time of 24 hours, the conversion of boronic acid into the desired product again resulted in no detectable yield.

Table 1 presents the optimal experimental results for $NiCl_2(PCy_3)_2$, with the most favourable outcome observed in (Entry 6). As a result, the focus has now shifted towards optimizing this catalyst concerning the solvent, reaction time, temperature, and the percentage of the catalyst parameters, as depicted in Table 2.

In Table 2, Entry 1, using a 5% $NiCl_2(Pcy_3)_2$ catalyst in dioxane and a reaction time of 24 hours at a temperature of 95 ºC resulted in a conversion of boronic acid into the desired product with a yield of 22%. Entry 2: Continuing with a 5% $NiCl_2(Pcy_3)_2$ catalyst in dioxane as the solvent, extending the reaction time to 36 hours at a temperature of 95 ºC improved the conversion, leading to a higher yield of 53%. Entry 3: Increasing the catalyst concentration to 10% $NiCl_2(Pcy_3)_2$ in dioxane as the solvent and conducting the reaction for 48 hours at a temperature of 95 ºC significantly enhanced the conversion, resulting in an impressive yield of 95%. Entry 4: Maintaining the catalyst concentration at 10% $NiCl_2(Pcy_3)_2$ in Dioxane as the solvent but reducing the temperature to 90 ºC and maintaining a reaction time of 48 hours, the conversion of boronic acid yielded a slightly lower but still substantial yield of 73%. Entry 5: Using 10% $NiCl_2(Pcy_3)_2$ catalyst in dioxane as the solvent, increasing the reaction temperature to 100 ºC while keeping the reaction time at 48 hours, resulted in an improved yield of 72% for the conversion of boronic acid. Entry 6: Shifting the solvent to Toluene while maintaining the catalyst concentration at 10% $NiCl_2(Pcy_3)_2$, conducting the reaction for 24 hours at a temperature of 85 ºC a slight yield detectable conversion (7% yield). Entry 7: Continuing with Toluene as the solvent, extending the reaction time to 48 hours at a temperature of 95 ºC still slightly yield detectable conversion (10% yield). Entry 8: Finally, utilizing THF as the solvent with 10% $NiCl_2(Pcy_3)_2$ catalyst, conducting the reaction for 24 hours at a temperature of 95 ºC also slight resulted detectable conversion (5% yield).

After the general reaction optimised condition, we applied it to various boronic acids and propagyl alcohol (Table 3).

Table 3 displays the quantities of prepared dienes derived from ethynyl cyclohexanol, with variations of boronic acids in the reactions. Initially, *m*-methyl boronic acid was utilized in the optimization process, resulting in an excellent yield of 95% (Entry 1). When the electron-rich m-methoxy boronic acid was employed, it produced moderate dienes (2), with the percentage of the yield showing an increase (Entry 2). The use of furane boronic acid (Entry 3) further improved the yield percentage of the desired dienes. Conversely, pyridyl boronic acid resulted in a poor yield of less than 5%, requiring further investigation (Entry 4). Replacement the alkyne six with

five membered rings with 3,5-dimethyl boronic acid give good result 83% (entry 5). Substituting the propagyl alcohol with 8-ethynyl-1,4-dioxa spiro [4, 5] decan-8-ol and using m-methyl boronic acid led to a yield of 75% (Entry 6). Similarly, employing the electron-rich 3,4-dimethoxy boronic acid with 8-ethynyl-1,4-dioxa spiro [4, 5] decan-8-ol resulted in a yield of 47% (Entry 7). Exceptional results in the final variation of 91% were obtained when five-membered heterocyclic furane boronic acid was utilized (Entry 8). These results indicate the impact of different boronic acids and substrates on the formation of dienes and highlight potential avenues for further exploration and optimization. The mechanism of the reaction could be proposed according to our previous work [19-21].

The structure of the prepared compounds was characterised by their distinctive signals in ^{1}H NMR belong to the two protons of the double bond as a doublet-doublet at (6.8-6.3) ppm with coupling constant (J = 16 Hz) which indicate that exist in trans configuration. The next double bond has one proton appear as triplet signal at (5.7-5.8) ppm. In addition, the ^{13}C NMR used to prove the structures of dienes. All signals were in perfect position. Also, the Mass spectrometric charts give exact mass in four decimals.

EXPERIMENTAL

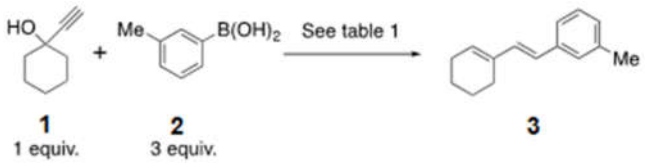
Materials and methods

All chemicals were purchased from commercially available companies such as Sigma Aldrich and Flourochem. These chemicals were used without additional purification. ^{1}H-NMR data was verified at 400 MHz and the ^{13}C NMR noted at 100 MHz, Bruker Avance 400 MHz spectrometer was used with $CDCl_3$ as a solvent.

Optimisation of the Ni catalysis

We began this study investigating the reaction of propargyl alcohol **1** with aryl boronic acid **2** with several Ni-catalysts (Table 1). These substrates were selected given the success of this transformation in the previous work and the ease of ^{1}H NMR detection of the product 1,3-diene **3**.

Table 1. Ni-catalysis optimisation.



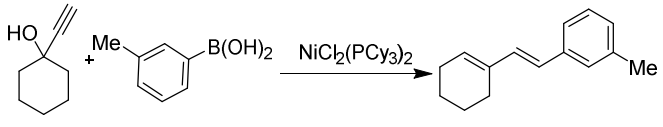
Entry	$RB(OH)_2$	Temperature	Catalyst	Time (h)	Conversion[b] [%]
1	3	85	5% $NiCl_2.6H_2O$	16	0
2	3	85	10% $NiCl_2.6H_2O$	24	0
3	2	85	10% $NiCl_2.6H_2O$	24	0
4	3	85	5%Raney Ni	16	0
5	2	75	5% $NiCl_2(PCy_3)_2$	16	0
6	3	85	5% $NiCl_2(PCy_3)_2$	24	14
7	3	60	5% $NiCl_2(PCy_3)_2$	24	0

[a]Reaction occurred under argon atmosphere, [b]Detected by ^{1}H NMR.

Optimisation of the $NiCl_2(PCy_3)_2$

In Table 1, we found that the $NiCl_2(PCy_3)_2$ successfully gave product in Entry 6. Table 2 gives the optimization condition of the selected catalyst.

Table 2. Optimization condition $NiCl_2(PCy_3)_2$.



1 1 equiv. 2 3equiv. 3

Entry	Catalyst (mol%)[b]	Solvent	Time [h]	Temp [ºC].	Yield [%][c]
1	5	1,4-Dioxane	24	85	14
2	5	1,4-Dioxane	24	95	22
3	5	1,4-Dioxane	36	95	53
4	10	1,4-Dioxane	48	95	95
5	10	1,4-Dioxane	48	90	78
6	10	1,4-Dioxane	48	100	72
7	10	Toluene	48	95	10
8	10	THF	24	95	5
9	10[d]	1,4-Dioxane	24	85	-

General procedure for preparation 1,3-dienes

In this preparation process boronic acid (3 equiv.) and alkyne (1 equiv.) are mixed in (5 mL) 1,4-dioxane. The resulted mixture heated at 95 ºC under reflux conditions in an argon atmosphere for 10 min. After this heating time, 10% $NiCl_2(PCy_3)_2$ (69 mg. 0.1 mmol, 10 mol%) is added into the reaction combination, then the resulted mixture was heated for 48 hours. After this period, the mixture was cooled to room mixture, then diethyl ether (30 mL) was added to it. The mixture was washed with sodium bicarbonate solution (30 mL) then extraction with extra diethyl ether (15 mL). The mixed organic layers were rinsed with brine (30 mL), dry out with magnesium sulfate, filtered, and the solvents was removed under reduced pressure. Column chromatography was used to purify resulted crude, to give 1,3-diene compounds (Table 3).

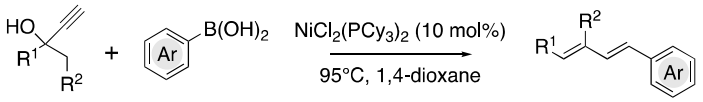
*1-(2-(Cyclohex-1-en-1-yl)vinyl)-3-methylbenzene (**3**).* Oil colorless ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.19 (m, 3H), 7.00 (m, 1H), 6.77-6.73 (d, *J* = 16 Hz, 1H), 6.42-6.38 (d, *J* = 16 Hz, 1H), 5.88 (t, 1H), 2.33 (s, 3H), 2.27 (t, 2H), 2.17 (t, 2H), 1.71 (m, 2H), 1.63 (m, 2H) ppm. ^{13}C NMR δ 138.1, 138.03, 135.94, 132.24. 130.74, 128.48, 127.71, 126.64, 124.76, 123.36 26.21, 24.61, 22.63, 22.58, 21.51; HRMS [M+H$^+$] computed for $C_{15}H_{19}$ 199.1481, found 199.1481.

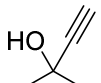
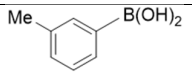
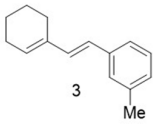
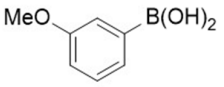
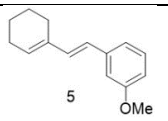
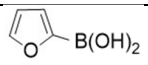
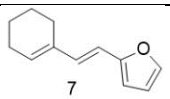
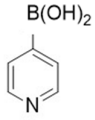
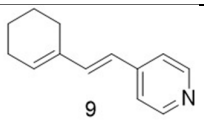
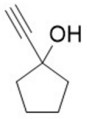
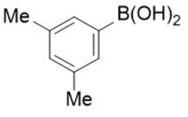
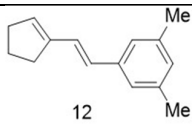
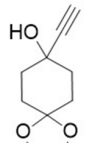
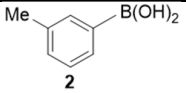
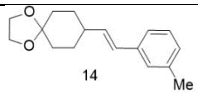
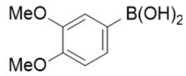
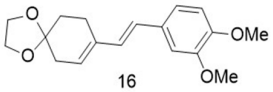
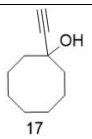
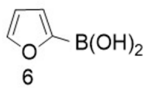
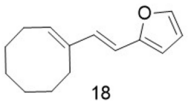
*1-(2-(Cyclohex-1-en-1-yl)vinyl)-3-methoxybenzene (**5**).* Oil colorless, ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.20 (t, 1H), 6.98 (d, 1H), 6.92 (s, 1H), 6.74 (t, 2H) 6.40 (d, 1H), 5.89 (t, 1H), 3.08 (s, 3H), 2.25 (t, 2H), 2.18 (t, 2H), 1.71 (m, 2H), 1.63 (m, 2H) ppm; ^{13}C NMR δ 159.8, 139.6, 135.8, 133.0, 131.1, 129.5, 124.4, 118.9, 112.6, 111.4, 55.27, 26.2, 24.60, 22.62, 22.57; HRMS [M+H$^+$] computed for $C_{15}H_{19}O$ 215.1430, found 215.1437.

*2-(2-(Cyclohex-1-en-1-yl)vinyl) furan (**7**).* Oil colourless; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.30 (d, J = 16 Hz, 1H), 6.8 (d, *J* = 16 Hz, 1H), 6.35 (d, 1H), 6.25 (d, *J* = 16 Hz, 1H), 6.2 (d, 1H), 5.88 (t, 1H), 2.17 (m, 4H), 1.69 (m, 2H), 1.60 (m, 2H) ppm; ^{13}C NMR δ 154.0, 141.5, 135.5, 131.3, 131.0,

113.0, 111.4, 107.0, 26.2, 24.3, 22.5, 22.51; HRMS [M+H$^+$] computed for $C_{12}H_{15}O$ 175.1117, found 175.1111.

Table 3. Synthesis of 1,3 dienes.



Entry	Alkyne	Boronic acid/R	1,3-Diene	Yield%
1	 1	 2	 3	95
2		 4	 5	61
3		 6	 7	69
4		 8	 9	5[a]
5	 10	 11	 12	83
6	 13	 2	 14	75
7		 15	 16	47
8	 17	 6	 18	91

[a]Detected by ^{1}H NMR.

*(E)-1-(2-(Cyclopent-1-en-1-yl)vinyl)-3,5-dimethylbenzene (**12**).* IR (CH_2Cl_2)ν_{max} 3054, 2986, 1422, 1261 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.03 (s, 2H), 7.00-6.96(d, *J* =16 Hz, 1H), 6.84 (s, 1H), 6.34 (d, *J* = 16 Hz, 1H), 5.826 (t, 1H), 2.54-2.50 (t, 2H), 2.47-2.44 (t, 2H), 2.29 (s, 6H), 1.97-1.93 (m, 2H) ppm. ^{13}C NMR δ 142.98, 138.04, 137.77, 131.71, 129.00, 128.94, 125.49, 124.24. 33.11, 31.28, 23.24, 21.37 ppm; HRMS [M+H^+] computed for $C_{15}H_{19}$ 199.1481, found 199.1445.

*8-(3-Methylstyryl)-1,4-dioxaspiro[4.5]dec-7-ene (**14**).* Oil colourless (R_f 0.47 petroleum ether: DCM:ether/50:40:10, respectively); IR (CH_2Cl_2)ν_{max} 3050, 2978, 1499, 1445, 1266 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.20- 7.18 (m, 3H), 7.01 (s, 1H), 6.78- 6.74 (d, *J* = 16 Hz, 1H), 6.44-6.40 (d, *J* = 16 Hz, 1H), 5.77 (t, 1H), 3.98 (s, 4H), 2.50 (t, 2H), 2.44 (d, 2H), 2.33 (s, 3H), 1.87 (t, 2H) ppm; ^{13}C NMR δ 138.14, 137.78, 135.45, 131.04, 128.527, 127.97, 127.07, 126.83, 126.31, 123.49, 108.143, 64.57, 36.44, 30.93, 23.78, 21.52 ppm; HRMS [M+H^+] computed for $C_{17}H_{21}O_2$ 257.1536, found 257.1535.

*8-(3,4-Dimethoxystyryl)-1,4-dioxaspiro[4.5]dec-7-ene (**16**).* Oil colorless (R_f 0.41 petroleum ether: DCM: ether/50:40:10, respectively); IR (CH_2Cl_2)ν_{max} 3009. 2932, 1600, 1578, 1509, 1462, 1247 cm^{-1}. ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.08-7.04 (m, 1H), 6.92 (s, 1H), 6.80 (d, 1H), 6.68-6.62 (d, *J* = 16 Hz, 1H), 5.71 (t, 1H), 3.98 (s, 4H), 3.93 (s, 3H), 3.85 (s, 3H), 2.49(t, 2H), 2.42 (d, 2H), 1.86 (t, 3H) ppm; ^{13}C NMR δ 149.17, 148.38, 135.40, 129.54, 126.15, 119.45, 111.53, 111.25, 110.44, 108.73, 108.14, 64.56, 56.08, 36.41, 30.96, 23.83 ppm; HRMS [M] computed for $C_{18}H_{21}O_4$ 302.1513, found 302.1468.

*2-((2-(Cyclooct-1-en-1-yl)vinyl)furan (**18**).* Oil colorless (R_f 0.41, 100% petroleum ether), ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.33-7.29 (d, 1H), 6.69- 6.64 (d, *J* = 20 Hz, 1H), 6.40- 6.35 (d, J = 20 Hz, 1H), 6.3-6.26(d, *J* = 16 Hz, 1H), 6.19 (t,1H), 5.85 (t,1H), 2.62 (t, 1H), 2.49 (t, 1H), 2.44 (t, 2H), 2.30-2.21 (m, 4H), 1.67- 1.61 (m, 2H), 1.50-1.44 (m, 2H) ppm; ^{13}C NMR δ 149.16, 146.48, 143.04, 134.27, 130.07, 127.07, 112.57, 112.46, 28.52, 28.49, 28.09, 27.89, 27.34, 27.18; HRMS [M-H^+] computed for $C_{14}H_{17}O$ 201.1274, found 201.1287.

CONCLUSION

This paper describes a new approach for the preparation of 1,3-dienes through a direct coupling between propargyl alcohols and boronic acids. The catalytic reaction utilizes $NiCl_2(PCy_3)_2$ in a free-base Suzuki-Miyaura coupling reaction. Through careful optimization of reaction conditions, a range of 1,3-dienes was successfully prepared, achieving moderate to excellent yields. This methodology offers a promising and efficient strategy for accessing valuable 1,3-diene compounds with potential applications in various fields of organic synthesis**.**

ACKNOWLEDGEMENTS

We would like to express our sincere thanks and appreciation to the University of Mosul for their support and the significantly contributed to the success of this project. In addition, We are deeply thankful for Dr. Marc C. Kimber from Loughborough University for his effort in this research and for the occasion to have been a part of his research group.

REFERENCES

1. Hazari, N.; Melvin, P.R.; Beromi, M.M. Well-defined nickel and palladium precatalysts for cross-coupling. *Nat. Rev. Chem*. **2017**, 1, 0025.

2. Shoma, M.; Yusuke, Y. Catalyst recycling in the suzuki coupling reaction: toward a greener synthesis in the pharmaceutical industry. *Knowledge* **2023**, 3, 1–17.
3. Yoshida, M.; Gotou, T.; Ihara, M. Palladium-catalyzed direct coupling reaction of propargylic alcohols with arylboronic acids. *Tetrahedron Lett.* **2004**, 45, 5573–5575.
4. Hany, M.E.; Nadia, A.E.; Alaa, M.A.; Ibtisam, K.A.; Faeza, A.; Rasha, M.R.; El Sayed, A.S.; Ali, M.A. Nickle oxide nanoparticales as sustainable catalysts for efficient synthesis and anti-microbial evaluation of 2-amino-4H-pyran derivatives. *Bull. Chem. Soc. Ethiop*. **2024**, 38, 657–670.
5. Hussein, A.H.; Saad, M.M.; Hanaa, A.A. Tetradentate azo Schiff base Ni(II), Pd(II) and Pt(II) complexes: Synthesis, spectral properties, antibacterial activity, cytotoxicity and docking studies. *Bull. Chem. Soc. Ethiop*. **2024**, 38, 99–111.
6. Alasdair, K.C.; Paul, M.B.; David, J.N. Nickel versus palladium in cross-coupling catalysis: On the role of substrate coordination to zerovalent metal complexes. *Synth.* **2020**, 52, 565–573.
7. Moran, J. Synthesis review / short review recent advances in nickel catalysis enabled by stoichiometric metallic reducing agents. *Synth*. **2018**, 50, 499–513.
8. Zim, D.; Lando, V.R.; Dupont, J.; Monteiro, A.L. $NiCl_2(PCy_3)_2$: A simple and efficient catalyst precursor for the suzuki cross-coupling of aryl tosylates and arylboronic acids. *Org. Lett.* **2001**, 3, 3049–3051.
9. Ramgren, S.D.; Hie, L.; Ye, Y.; Garg, N.K. Nickel-catalyzed Suzuki-Miyaura couplings in green solvents. *Org. Lett.* **2013**, 15, 3950–3953.
10. Quasdorf, K.W.; Riener, M.; Petrova, K.V.; Garg, N.K. Suzuki-Miyaura coupling of aryl carbamates, carbonates, and sulfamates. *J. Am. Chem. Soc.* **2009**, 131, 17748–17749.
11. Ge, S.; Hartwig, J.F. Highly reactive, single-component nickel catalyst precursor for Suzuki-Miyuara cross-coupling of heteroaryl boronic acids with heteroaryl halides. *Angew. Chem.* **2012**, 51, 12837–12841.
12. Fine N.F.; Kim, J.; Hie, L.; Jiang, X.; Garg, N.K. Nickel-catalyzed amination of aryl chlorides and sulfamates in 2-methyl-THF. *ACS Catal*. **2014**, 4, 3289–3293.
13. Nair, P.P.; Philip, R.M.; Anilkumar, G. Nickel catalysts in sonogashira coupling reactions. *Org. Biomol. Chem.* **2021**, 19, 4228–4242.
14. Anwar, A.F.; Yassir, S.J.; Shaimaa, S.I. Synthesis of some new substituted imines from aldehydes and ketones derived from quinolinic acid. *Eclet. Quim*. **2023**, 48, 49–65.
15. Mishra, S.; Halpani, C.G.; Patel, S. Nickel-catalyzed Heck Reaction of aryl halides and terminal olefins using zinc/triflate ligand/DMA/TBAB. *ChemistrySelect* **2019**, 4, 6913–6916.
16. Russell, J.E.A.; Entz, E.D.; Joyce, I.M.; Neufeldt, S.R. Nickel-catalyzed stille cross coupling of C-O electrophiles. *ACS Catal*. **2019**, 9, 3304–3310.
17. Al-Jawaheri, Y.; Elsegood, M.R.J.; Mistry, J.R.; Kimber, M.C. Concise synthesis of moracin M using appel mediated dehydration of a bioinspired endoperoxide. *Tetrahedron Lett.* **2023**, 114, 1–4.
18. Al-Jawaheri, Y.; Kimber, M.C. Synthesis of 1,3-dienes via a sequential Suzuki-Miyaura coupling/palladium-mediated allene isomerization sequence. *Org. Lett.* **2016**, 18, 3502–3505.
19. Al-Jawaheri, Y.; Kimber, M.C. The rearrangement of alkylallenes to 1,3-dienes. *React.* **2022**, 3, 70–86.
20. Al-Jawaheri, Y.; Turner, M.; Kimber, M.C. Enabling the rearrangement of unactivated allenes to 1,3-dienes by use of a palladium (0)/boric acid system. *Synthesis (Germany)* **2018**, 50, 2329–2336.
21. Farshadfar, K.; Chipman, A.; Hosseini, M.; Yates, B.F.; Ariafard, A. A modified cationic mechanism for $PdCl_2$-catalyzed transformation of a homoallylic alcohol to an allyl ether. *Organomet*. **2019**, 38, 2953–2962.