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Synthesis of N-Methyl Piperidine Substituted Vinyl Benzenes *Via* Heck Reaction

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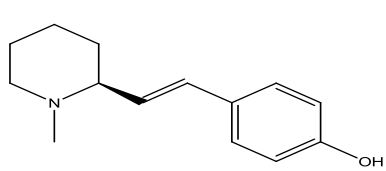
ABSTRACT

A new, simple and convenient procedure for the synthesis of novel analogues of piperidine substituted vinyl benzenes via Ni(II)/NHC catalyzed Heck cross-coupling by the reaction of 2-vinyl-N-Tosyl-piperidine (3) with substituted iodo benzene (4). The deprotection of the all (E)-olefin 6(a-f) was obtained with MCM-41 zeolite as catalyst in MeOH was found to be effective than the reported methods. During the preparation of compounds 5(a-f) we applied an easy protocol to a catalytic system consisting of 1:2 Ni(OAc)2+ NHC Ligands and slightly excess of base (Et3N) in DMF. All the synthesized compounds were characterized by the spectral studies i.e., I R, 1H NMR and Mass and elemental analyses data.

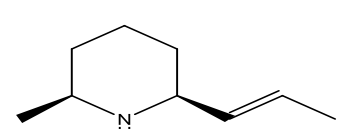
KEYWORDS Piperidine, Iodo benzenes, Nickel acetate, MCM-41 Zeolite

Introduction:

Cancer remains a major public health problem in the developed countries. One in four deaths on earth is caused by cancer, which stood as the utmost dangerous disease and needs more attention towards its therapy. Substituted piperidine structural motifs are present in numerous bioactive natural alkaloids,[1–5] these are most widely prescribed drug categories and their synthesis in a stereo defined manner with appropriate building blocks represents a significant synthetic task.[6–9] In this context, the stereoselective synthesis of alkene substituted piperidines would be worth studying since both the functionalities are known to be highly selective against various drug metabolizing enzymes like cytochrome P450 and provides combined effect.[10–12] The important metabolic pathways of piperidine and alkenes include hydration, oxidation, peroxidation, and reduction. Besides, the alkene group can undergo many useful synthetic transformations such as cycloaddition, Wacker oxidation, metathesis and polymerization[13–17] that can further enhance the application of piperidine–alkene derivatives vastly in fine chemicals, medicine and material science. There is some natural piperidine alkaloids[18–22] composed of either terminal or internal alkene linkage shown in **Figure 1.**



(+)-Caulophyllumine B



(+)-Pinidine

Herein we describe the suitability of Heck and Negishi cross-coupling reactions, catalyzed by in situ generated Ni-NHCs, as key step in the stereoselective synthesis of a variety of piperidine alkene alkaloids.

Results and discussion:

The design of the synthesis of piperidine alkene alkaloids **3(a-f)** is presented in the **Scheme 1.** At first we have synthesized (S)-2-vinyl-N-Boc-pepiridine **(2),** a critical starting material for Heck coupling by treating N-Tosyl-piperidine with s-BuLi/(+)-Sparteine.[21] After having, (S)-2-vinyl-N-Tosyl-pepiridine in hand, we have then worked on the optimization of conditions for catalytic Heck coupling with 4-acetoxy iodo benzene **(3a)** in aqueous ethanol to obtain (E)-olefin **(4a)** (**Table 1**).

Table 1: Optimization of reaction condition for the Ni(II)/NHC-catalyzed Heck cross coupling of 2-vinyl-N-Tosyl-piperidine (**3a′**) with 4-acetoxy Iodo benzene (**4a′**)[a].

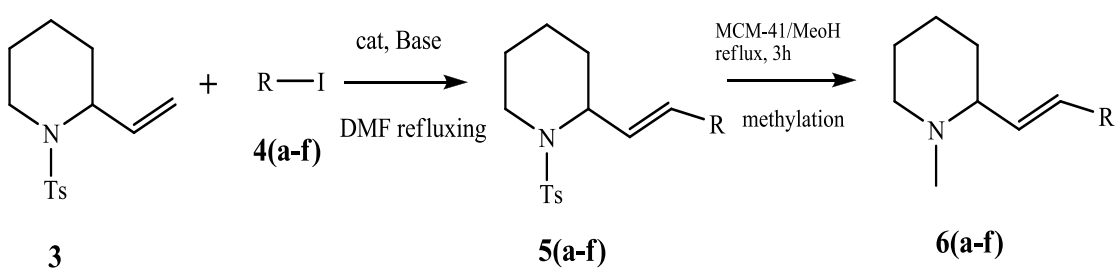
Entry	Cat. (Ni(II)/NHC (1:2)	Base	Time (h)	Yield(%)[b]
1	$Ni(OAc)_2$	--	24	0
2	$Ni(OAc)_2$	Et_3N	24	45
3	$NI(OAc)_2$ /L	Et_3N	12	91

[a] Reaction conditions: 2-vinyl-*N*-Tosyl-piperidine (1 mmol), 4-acetoxy iodo benzene (1.2 mmol), DMF(10 ml) at refluxing. [b] Determined by G.C

We applied an easy protocol to a catalytic system consisting of 1:2 $Ni(OAc)_2$+ NHC Ligand, and slightly excess of base (Et_3N), in DMF. This system proved to be highly efficient in Heck coupling of (**3a′**) with (**4a′**) than ligand free Ni(II) catalytic system and reached almost completion in ~12h to give >90% yield (GC) of selectively E-olefin (**5a).** The deprotection of the all (*E*)-olefin (**5a**) was obtained with MCM-41(zeolite) catalyst in MeOH was found to be effective than the reported

methods. At first we have studied an independent Heck-coupling experiment without the addition of Ni(II). In this experiment there was no Heck activity occurred **(Table 1, entry 1).** A ligand free $Ni(OAc)_2$/base (Et_3N) catalytic system shows the occurrence of the Heck reaction to produce selectively the desired (*E*)-olefin (**5a**), but the reaction was slow and yields were low **(Table 5, entry2).** After this, the combination of $Ni(OAc)_2$/NHC-Ligand/base/Et_3N has been used as catalytic system. It is well known that the presence of ligands will improve the efficiency of Ni(II) in Heck coupling by accelerating the oxidative addition of the catalyst to the substrate during the cross-coupling. Based on this subject, in order to improve the yield of **5a** and the reaction time, we have introduced imidazolium chloride with Ni(II) salt [23] during the Heck-coupling.

Scheme 1: Synthesis of vinyl substituted piperidine *via* Ni(II)/NHC catalyzed Heck cross-coupling reaction



R= a) 4-iodophenyl acetate; b) 4-iodo benzene; c) 4-methyl iodobenzene: d) 4-methoxy iodo benzene; e) 2-methoxy iodobenzene f) 2, 3- dimethyl iodobenzene

Experimental:

Melting points were recorded on a Stuart SMP30 melting point apparatus and were uncorrected. Column chromatography was performed using silica–gel (100–200 mesh size) purchased from Thomas Baker, and thin layer chromatography (TLC) was carried out using aluminium sheets

pre-coated with silica gel 60F254 purchased from Merck. IR spectra (KBr) were obtained using a Perkin Elmer Spectrum100 FTIR Spectrometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker WM-400 spectrometer in DMSO-d_6 with TMS as an internal standard. Mass spectra (ESI) were carried out on a JEOL SX-102 spectrometer. CHN analysis was done by Carlo Erba EA 1108 automatic elemental analyzer. The chemicals and solvents used were of commercial grade and were used without further purification unless otherwise stated.

General procedure:

Synthesis of N-methyl substituted viny benzenes *via* Heck cross-coupling 5(a-f) & 6(a-f):

Heck coupling reactions were carried out using aryl iodides **4(a-f)** (1 mmol), 2-Vinyl-*N*-Tosyl-piperidine **(3)** (1.2 mmol), and Et_3N as base (2 mmol) dissolved in 10 ml of ethanol (water/ethanol = 9:1). An appropriate amount of NHC (0.1 mmol), and $Ni(OAc)_2$ (0.05 mmol), and TBAB (0.025 mmol) were added to this mixture. The reaction mixture was heated to 80 °C for 5 h. The coupled product was extracted with DCM (2 x 20 ml). The combined organic layers were dried (anhydrous Na_2SO_4) and evaporated under reduced pressure to afford a crude product which was subjected to column chromatography to afford pure *E*-Olefins **5(a-f)**. The de-protection of the all (*E*)-olefin 6(**a-f**) was obtained by the reaction of compounds **5(a-f)** with MCM-41(zeolite) catalyst in methanol.

4-(2-(1-tosylpiperidin-2-yl)vinyl)phenylacetate (5a): ^{1}H NMR (200 MHz, $CDCl_3$): δ =, 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.27 (s, 3H), 2.84 (td, 1H), 2.34 (s,3H), 3.93 (d, 1H), 4.90 (bs, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.94 (d, 2H, Ar-H), 7.35 (d, 2H, Ar-H), 7.46-7.48 (dd, 2H, Ar-H), 7.72-7.74 (dd, 2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.4, 25.20, 28.51, 29.30, 32.40, 40.22, 52.52, 79.65, 121.72, 127.20, 128.62, 129.12, 129.54, 132.59**,** 33.62, 139.82, 142.42, 149.20, 156.60, 169.52. IR (KBr, cm^{-1}): 2931, 2857, 1687, 1599, 1545, 1492, 1448, 1407, 1364,

1321, 1269, 1250, 1161, 1094, 1072, 1039. MS: m/z (%) 400 [M+]; Mol. Formula: $C_{22}H_{25}NO_4S$: Calcd (%): C 66.14, H 6.31, N 3.51; found C 66.02, H 6.27, N 3.26.

2-Styryl-1-tosylpiperidine (5b): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 7.20-7.12 (m, 1H), 7.20-7.32 (m, 4H, Ar-H), 7.40-7.44 (dd, 2H, Ar-H), 7.72-7.74 (dd,2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.40, 28.52, 29.72, 40.15, 52.40, 79.60, 126.35, 127.52, 128.62, 128.70, 128.94, 130.90, 132.50, 137.25, 139.43, 142.45, 155.42 ppm. IR (KBr, cm^{-1}): 2930, 2857, 1542, 1492, 1445, 1409, 1367, 1319, 1262, 1252, 1161, 1098, 1077, 1042. MS: *m*/*z* (%) = 341 [M+]. Mol. Formula: $C_{20}H_{23}NO_2S$: Calcd (%): C 70.35, H 6.79, N 4.10; found C 75.25, H 6.72, N 4.07.

2-(4-Methylstyryl)-1-tosylpiperidine (5c): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.36 (s,3H), 2.46 (s, 3H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.92 (d, 2H, Ar-H), 7.24 (d, 2H, Ar-H), 7.42-7.44 (dd, 2H, Ar-H), 7.76-7.78 (dd, 2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ =19.65, 25.40, 26.24, 28.52, 29.72, 40.15, 52.40, 79.60, 126.35, 127.52, 128.56, 128.70, 128.94, 130.90, 132.34, 137.25, 139.24, 143.23**,** 155.42 ppm. IR (KBr, cm^{-1}): 2931, 2857, 1548, 1492, 1445, 1407, 1364, 1322, 1269, 1250, 1161, 1094, 1070, 1039. MS: *m*/*z* (%) = 358 [M+]. Mol. Formula: $C_{21}H_{25}NO_2S$: Calcd (%): C 70.95, H 7.09, N 3.94; found C 70.69, H 7.05, N 3.92.

(2-(4-Methoxystyryl)-1-tosylpiperidine (5d): ^{1}H NMR (200 MHz, $CDCl_3$): δ =1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.54 (s, 3H), 2.84 (td, 1H), 3.58 (s, 3H), 3.93 (d, 1H), 4.90 (bs, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.92 (d, 2H, Ar-H), 7.24 (d, 2H, Ar-H), 7.48-7.50 (dd, 2H, Ar-H), 7.74-7.78 (dd, 2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.40, 28.52, 29.72, 36.45, 40.15, 52.40, 58.72, 79.60, 126.35, 127.52, 128.70, 128.94, 129.34, 130.90, 132.45, 137.25,142.24,

143.46**,** 155.42 ppm. IR (KBr, cm^{-1}): 2931, 2857, 1544, 1492, 1440, 1412, 1362, 1325, 1269, 1250, 1161, 1094, 1070, 1039. MS: *m*/*z* = 372 [M+]. Mol. Formula: $C_{21}H_{25}NO_3S$: Calcd (%): C 67.89, H 6.78, N 3.77; Found: C 67.86, H 6.69, N 3.72.

(2-(2-Methoxystyryl)-1-tosylpiperidine (5e): ^1H NMR (200 MHz, $CDCl_3$): δ =1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.53 (s,3H), 3.58 (s, 3H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.92 (d, 2H, Ar-H), 7.24 (d, 2H, Ar-H), 7.42-7.44 (dd, 2H, Ar-H), 7.76-7.78 (dd, 2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.42, 28.52, 29.72, 36.46, 40.15, 52.40, 58.72, 79.60, 126.35, 127.52, 128.70, 128.94, 129.36, 130.90, 132.48, 137.25, 142.24, 143.46,155.42 ppm. IR (KBr, cm^{-1}): 2931, 2857, 1544, 1492, 1440, 1412, 1362, 1325, 1269, 1250, 1161, 1094, 1070, 1039. MS: *m*/*z* = 372 [M+]. Mol. Formula: $C_{21}H_{25}NO_3S$: Calcd (%): C 67.89, H 6.78, N 3.77; Found: C 67.86, H 6.69, N 3.72.

(2-(2,3-Dimethylstyryl)-1-tosylpiperidine(5f): ^1H NMR (200 MHz, $CDCl_3$): δ =1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.48(s, 3H), 2.54 (s, 6H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.82-6.96 (m, 3H, Ar-H), 7.40-7.45 (dd, 2H, Ar-H), 7.70-7.74 (dd, 2H, Ar-H) ppm. MS: *m*/*z* = 370 [M+]. Mol. Formula: $C_{22}H_{27}NO_2S$: Calcd (%): C 71.51, H 7.36, N 3.79; Found: C 71.48, H 7.31, N 3.72.

4-(2-(1-Methylpiperidin-2-yl)-vinyl)-phenol (6a): $[\alpha]_D^{25} = -9.7$ (*c* = 0.24 in MeOH), ^1H NMR (200 MHz, $CDCl_3$): δ = 1.22-1.43 (m, 2H), 1.60-1.84 (m, 5H), 2.22-2.32 (m, 1H), 2.36 (s, 3H), 2.62 (m, 1H), 3.08 (br d, 1H), 5.94 (dd, 1H), 6.43 (d, 1H), 6.76 (d, 2H, Ar-H), 7.17 (d, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.65, 24.90, 32.52, 43.56, 56.42, 68.50, 116.21, 127.32, 127.82, 128.24, 132.20, 157.15 ppm. IR (KBr, cm^{-1}): 3442, 2931, 2857, 1545, 1492, 1407, 1321, 1269, 1250, 1165, 1094, 1070, 1032. MS (m/z): 240 $[M+Na]^+$. EA calcd (%) for $C_{14}H_{19}NO$: (217.15): C 77.38, H 8.81, N 6.45; found C 77.36, H 8.80, N 6.43.

2-Styrylpiperidine (6b): $[\alpha]_D^{25} = -9.2$ (*c* = 0.24 in MeOH), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 5.56 (dq, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 7.20-7.12 (m, 1H), 7.20-7.32 (m, 4H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 25.43, 28.52, 30.40, 42.02, 52.24, 126.35, 127.04, 127.94, 128.94, 130.20, 130.82, 140.10 ppm. MS: (*m/z)* = 210 $[M+Na]^+$. EA calcd (%) for $C_{13}H_{17}N$: (187.14): C 83.37, H 9.15, N 7.48; found C 83.35, H 9.13, N 7.46.

2-(2-*p*-Tolylvinyl)-piperidine (6c): $[\alpha]_D^{25} = -9.4$ (*c* = 0.24 in MeOH), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.46 (s, 3H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 5.56 (dq, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.92 (d, 2H, Ar-H), 7.24 (d, 2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 18.22, 25.43, 28.52, 30.40, 42.02, 52.24, 126.35, 127.04, 128.94, 129.32, 130.82, 140.10 ppm. MS (*m/z)* = 224 $[M+Na]^+$. EA calcd (%) for $C_{14}H_{19}N$: (201.15): C 83.53, H 9.51, N 6.96; found C 83.51, H 9.50, N 6.94.

2-(2-(4-Methoxyphenyl)-vinyl)-piperidine (6d): $[\alpha]_D^{25} = -10.1$ (*c* = 0.24 in MeOH), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 3.58 (s, 3H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 5.57 (dq, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.92 (d, 2H, Ar-H), 7.24 (d, 2H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 25.43, 28.52, 30.40, 42.02, 52.24, 58.72, 126.35, 127.04, 128.94, 129.32, 130.82, 152.26 ppm. MS (*m/z)* = 240 $[M+Na]^+$. EA calcd (%) for $C_{14}H_{19}NO$: (217.15): C 77.38, H 8.81, N 6.45; found C 77.36, H 8.80, N 6.42.

2-(2-(2-Methoxyphenyl)-vinyl)-piperidine (6e): $[\alpha]_D^{25} = -12.4$ (*c* = 0.24 in MeOH), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.84 (td, 1H), 3.64 (s, 3H), 3.93 (d, 1H), 4.90 (bs, 1H), 5.56 (dq, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.86-7.05 (m, 4H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 25.43, 28.52, 30.40, 42.02, 52.24, 58.20, 116.92, 122.34, 122.82,

126.35, 128.12, 128.54, 129.32, 163.56 ppm. MS (*m/z)* = 240 $[M+Na]^+$. EA calcd (%) for $C_{14}H_{19}NO$: (217.15): C 77.38, H 8.81, N 6.45; found C 77.36, H 8.80, N 6.42.

2-(2-(2,6-Dimethylphenyl)-vinyl)-piperidine (6f): $[\alpha]_D^{25} = -9.8$ (*c* = 0.24 in MeOH), ^1H NMR (200 MHz, $CDCl_3$): δ = 1.44-1.62 (m, 4H), 1.64-1.81 (m, 2H), 2.54 (s, 6H), 2.84 (td, 1H), 3.93 (d, 1H), 4.90 (bs, 1H), 5.56 (dq, 1H), 6.12 (dd, 1H), 6.34 (dd, 1H), 6.82-6.96 (m, 3H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 17.55, 25.43, 28.52, 30.40, 42.02, 52.24, 125.46, 126.35, 128.62, 129.32, 134.20, 136.02 ppm. MS (*m/z)* = 238 $[M+Na]^+$. EA calcd (%) for $C_{15}H_{21}N$: (215.17): C 83.67, H 9.83, N 6.50; found C 83.65, H 9.82, N 6.48.

Conclusions:

In conclusion, we have optimized the conditions for Heck coupling catalyzed by simple in situ formed Ni(II)-NHCs as key step to obtained piperidine containing olefin intermediate of both natural and synthetic piperdine alkene–alkaloids in high yields and their application as promising anti-cancer agents for a panel of human cancer cell lines in future study.

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