Tetrahedron 69 (2013) 10940–10945

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Heck cross-coupling of vinyl heteroaromatic compounds with aryl and heteroaryl halides using Pd(II) complex under phosphine-free conditions

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ARTICLE INFO

Article history:
Received 6 August 2013
Received in revised form 17 October 2013
Accepted 21 October 2013
Available online 31 October 2013

Keywords:
C–C coupling
Heck reaction
Palladium
trans-2-Styrylpyridines
Vinyl heterocycles

ABSTRACT

The palladium-catalyzed cross-coupling reaction of vinyl heteroaromatic compounds with aryl bromides and heteroaryl bromides is described using air and moisture stable *N*,*N*′,*N*″,*O*-tetrafunctional Pd catalyst under phosphine-free conditions. As a result a variety of *trans*-1,2-disubstituted vinyl heterocycles were obtained in high to good yields.

1. Introduction

Heck reaction is one of the most popular catalytic processes used for the construction of $C(sp_2)$–$C(sp_2)$ bonds.[1] Traditionally, Heck reaction of aryl halides with alkenes is carried out using various palladium phosphine catalysts.[2] While, significant progress has been made in the field of Heck coupling of aryl halides or heteroaryl halides with styrene derivatives; the corresponding synthesis of *trans*-2-styrylpyridines derivatives or *trans*-1,2-disubstituted vinyl heterocycles by coupling of 2-vinylpyridines or vinyl functionalized heterocycles with aryl- or heteroaryl halides is challenging. Earlier, Doucet et al. reported the synthesis of few selected styrylpyridine derivatives by Heck reaction of aryl halides with vinylpyridines using $[Pd(C_3H_5)Cl]_2$/tedicyp catalyst.[3] Frech et al. used aminophosphine-based pincer complexes for the Heck coupling of vinylpyridines with aryl bromides.[4] Notably, Li and Hua demonstrated the synthesis of *trans*-2-styrylpyridines derivatives by $PdCl_2(PCy_3)_2$ catalyzed coupling of 2-vinylpyridine with aryl chlorides.[5] These processes represent important advancement made in this field; however, it is important to develop a convenient and efficient catalytic protocol with wide substrate scope under phosphine-free conditions mainly in view of the growing significance of styrylpyridine derivatives in material chemistry,[6] biologically active compounds,[7] amyloid imaging agents for Alzheimer's disease,[8] and as ligands in metal complexes.[9]

In recent years, much emphasis was given for the design and synthesis of air-stable palladium complexes, which can be used as an alternate to air-sensitive and toxic palladium phosphine catalysts. In these direction, many palladium complexes comprising *N*-, *O*- and *S*-centred ligands have been developed amongst, which *N*-heterocyclic carbene complexes,[10] *N*-based palladacycles,[11] and carbocyclic carbenes,[12] are remarkable. Earlier, we have shown that palladium complexes containing *N*-donor ligands with amide functionality; namely, tetradentate dicarboxyamidate/dipyridyl palladium, amido/pyridyl carboxylate ligated palladium and uridate/pyridyl palladium complexes, increases the thermal stability and activity of the palladium catalyst for the Heck reaction of deactivated aryl halides with high turnover number.[13] However, limitations remain with substrate scope of vinyl heterocycles, such as vinylpyridines, vinyl triazoles and vinyl thiazoles, which are reported with this communication.

More recently, we have reported the synthesis and application of palladium(II) complexes of multi-donor and multi-functional amido/pyridyl/phenolic/amine ligands for the Heck reaction of

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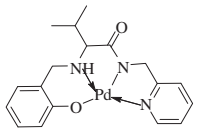
http://dx.doi.org/10.1016/j.tet.2013.10.078



Catalyst

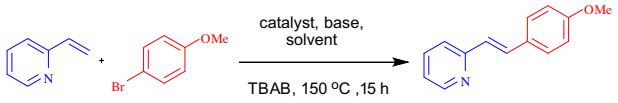
Fig. 1. *N*,*N*′,*N*″,*O*-Tetrafunctional palladium(II) complex.

aryl bromides with substituted styrenes.[14] In continuation of these studies; herein, we report the Heck reaction of vinyl heteroaromatic compounds with aryl bromides and heteroaryl bromides using *N*,*N*′,*N*″,*O*-tetrafunctional Pd(II) complex (Fig. 1).

2. Results and discussion

Initial studies to evaluate the catalytic activity of palladium complex for the Heck reaction were performed in a 0.5 mmol scale using 2-vinylpyridine and 4-bromoanisole as the model substrates at 150 °C. In the presence of 1.2 mol % catalyst (5.0 mg) and 0.7 mmol of LiO^tBu in DMF, the model substrates reacted well to afford the corresponding cross-coupled product: namely, (*E*)-2-(4-methoxystyryl)pyridine in 60% yield (Table 1, entry 1). Addition of phase transfer catalyst, TBAB enhanced the yield to 70% (Table 1, entry 2). Thereafter, optimization studies were performed altering the solvents and bases, and the corresponding results are summarized in Table 1. The solvent screening studies indicated that polar aprotic solvent like DMF and DMA are superior for this reaction (Table 1, entries 1–8), whereas non-polar solvents like toluene and *o*-xylene are less effective (Table 1, entries 9 & 10). In a similar way, base screening revealed Cs_2CO_3 as the best base (Table 1, entries 3–5, 9–11). When the reaction is conducted by using conventional catalysts for instance $Pd(CH_3CN)_2Cl_2$ and palladium(II)acetylacetonate ($Pd(C_5H_7O_2)_2$) poor yields were observed (Table 1, entries 12 & 13). Upon optimized reaction condition using uridate/pyridyl palladium complex nearly constant results were obtained in 42% yield (Table 1, entry 14). However, the present phosphine-free *N*,*N*′,*N*″,*O*-tetrafunctional Pd(II) complex system showed most promising results (Table 1, entry 5).

Table 1
Optimization studies for cross-coupling of 2-vinlypyridine with 4-bromoanisole[a]



Entry	Base	Solvent	Yield[b] (%)
1	LiO^tBu	DMF	60[c]
2	LiO^tBu	DMF	70
3	Cs_2CO_3	DMF	80
4	Cs_2CO_3	DMA	87
5	Cs_2CO_3	DMA	88[d]
6	K_2CO_3	DMA	47
7	$LiOH\cdot H_2O$	DMA	55
8	TEA	DMA	32
9	Cs_2CO_3	Toluene	45
10	Cs_2CO_3	*o*-Xylene	48
11	Cs_2CO_3	Cy_2NMe	35
12	Cs_2CO_3	DMA	44
13	Cs_2CO_3	DMA	35
14	Cs_2CO_3	DMA	42

[a] Unless otherwise stated, all reactions were performed using 2-vinylpyridine (0.5 mmol), 4-bromoanisole (0.8 mmol), catalyst (1.2 mol %), base (0.7 mmol), TBAB (0.5 mmol) in 2.0 mL solvent at 150 °C for 15 h.
[b] Isolated yield.
[c] Reaction performed in the absence of TBAB.
[d] Time 24 h.

Thus the optimum reaction conditions for Heck cross-coupling of vinyl heteroarenes with aryl halide and heteroaryl halide are Pd(II) complex/base as Cs_2CO_3, TBAB as additive and DMA used as solvent at 150 °C. The results obtained from optimized reaction conditions by using 2-vinylpyridine with various aryl and heteroaryl halides to explore the scope of the reaction and the results are presented in Table 2.

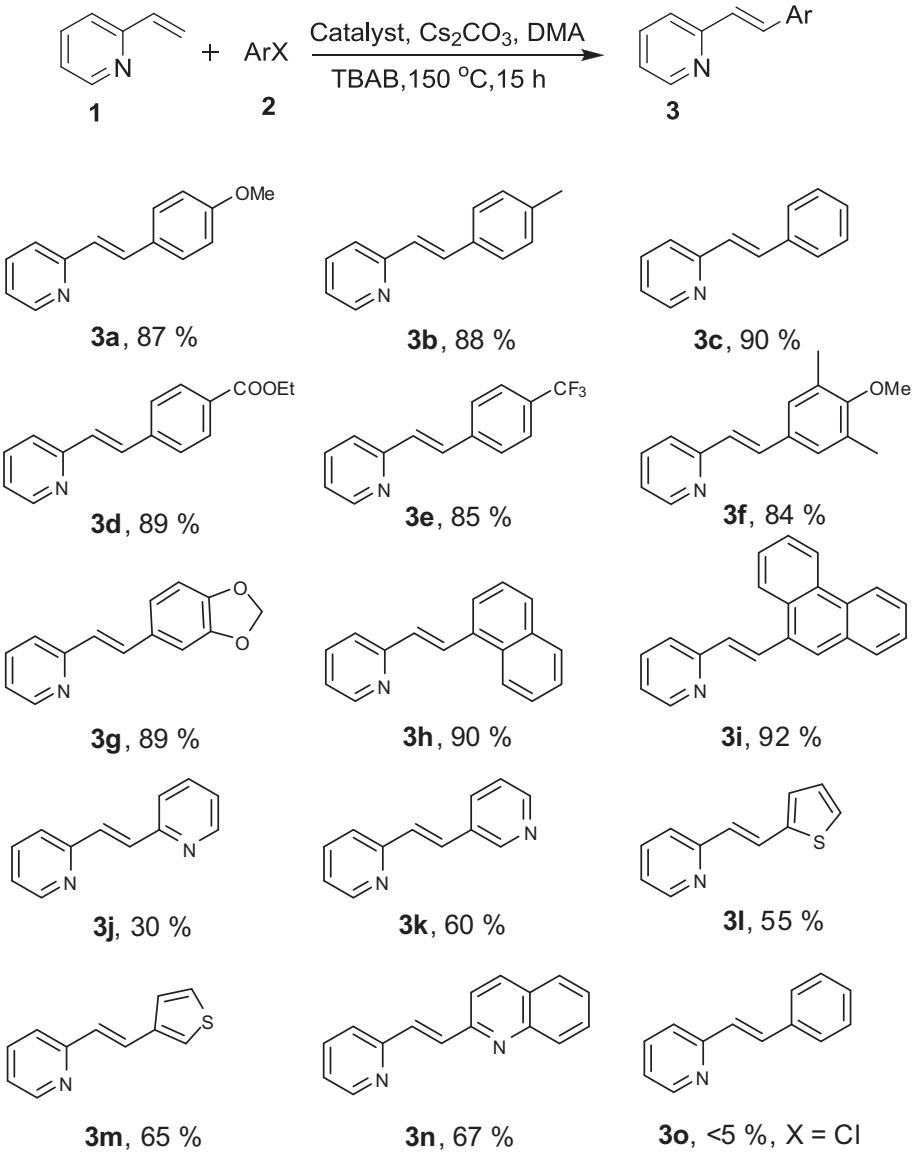
As can be seen in Table 2, when the reaction performed with 2-vinylpyridine and electron-rich aryl bromides, such as, *p*-bromoanisole and *p*-bromotoluene proceeded smoothly to afford the corresponding desired cross-coupled products as (*E*)-2-(4-methoxystyryl)pyridine and (*E*)-2-(4-methylstyryl)pyridine in good yields (Table 2, **3a**,**b**). When the reaction conducted with bromobenzene the product (*E*)-2-styrylpyridine was obtained in high yield 90% (Table 2, **3c**). Under similar reaction conditions the products were isolated as (*E*)-ethyl 4-(2-(pyridin-2-yl)vinyl)benzoate and (*E*)-2-(4-(trifluoromethyl)styryl)pyridine in 89% and 85% with electron-deficient aryl bromides like ethyl 4-bromobenzoate and 1-bromo-4-(trifluoromethyl)benzene (Table 2, **3d**,**e**). As like above, the reaction performed with 5-bromo-2-methoxy-1,3-dimethylbenzene and 5-bromobenzo[*d*][1,3]dioxole the products are isolated in 84% and 89% as (*E*)-2-(4-methoxy-3,5-dimethylstyryl)pyridine and (*E*)-2-(2-(benzo[*d*][1,3]dioxol-5-yl)vinyl)pyridine (Table 2, **3f**,**g**), respectively. Notably, the reaction also works for sterically rather hindered substrates like 1-bromonaphthalene and 9-bromophenanthrene gave good yields of coupled product, such as (*E*)-2-(2-(naphthalen-1-yl) vinyl)pyridine and (*E*)-2-(2-(phenanthren-9-yl)vinyl)pyridine with 90% and 92% (Table 2, **3h**,**i**). Afterwards, the scope of the reaction was tested for several deactivated heteroaryl bromides, such as 2-bromopyridine, 3-bromopyridine, 2-bromothiophene, 3-bromothiophene and 2-bromoquinoline has given the desired coupled products as (*E*)-1,2-di(pyridin-2-yl)ethene, (*E*)-2,5′-(ethene-1,2-diyl)dipyridine, (*E*)-2-(2-(thiophen-2-yl)vinyl)pyridine, (*E*)-2-(2-(thiophen-3-yl)vinyl)pyridine and (*E*)-2-(2-(pyridin-2-yl)vinyl)quinoline with moderate yields, respectively (Table 2, **3j**–**n**). However the reaction of chlorobenzene was sluggish and gave very poor yield of (*E*)-2-(4-methoxystyryl)pyridine (Table 2, **3o**).

Based on the palladium catalyzed Heck cross-coupling of 2-vinylpyridine with various aryl and heteroaryl halides we further investigated the palladium catalyzed cross-coupling of various regio-isomers of vinylpyridines and also vinyl-functionalized heterocycles with deactivated aryl halides, such as 4-bromoanisole and bromobenzene were performed and the corresponding results are summarized in Table 3.

It is noteworthy that the reactions of 3-vinylpyridine and 4-vinylpyridine with 4-bromoanisole proceeded smoothly and furnished the respective cross-coupled products as (*E*)-3-(4-methoxystyryl)pyridine and (*E*)-4-(4-methoxystyryl)pyridine in good yields, respectively (Table 3, **6a**,**b**). Importantly, the reaction of vinyl functionalized heterocycles like 1-vinyl-1*H*-1,2,4-triazole and 4-methyl-5-vinylthiazole with aryl bromides employing LiO^tBu base gave the corresponding coupling products as (*E*)-1-styryl-1*H*-1,2,4-trazole, (*E*)-1-(4-methoxystyryl)-1*H*-1,2,4-triazole, (*E*)-4-methyl-5-styrylthiazole and (*E*)-5-(4-methoxystyryl)-4-methylthiazole in moderate to good yields, respectively (Table 3, **6c**–**f**).

The catalytic species involves in the Heck cross-coupling reaction are Pd(0). Usually, the catalytic cycle involves between the Pd(0) and Pd(II) oxidation states during the reaction. In our case a precatalyst (Pd(II) complex) in the Pd(II) oxidation state is used, and it is presumed to be reduced to Pd(0) in situ, some relevant data has been obtained only for phosphine assisted catalytic processes.[15] In phosphine-free catalytic process reduction of Pd(II) to Pd(0) can be effected by amines and olefins,[16] or palladium can be reduced by quaternary phosphonium and ammonium salts,[17] Herrmann reported that the addition of TBABr eliminated the induction period in the reaction catalyzed by Pd carbene complex,[18] which acts as a reducing agent.

Table 2
Cross-coupling of 2-vinylpyridine with aryl bromides[a,b]



[a] All reactions were performed with 2-vinylpyridine (0.5 mmol), aryl halide (0.8 mmol), catalyst (1.2 mol %), Cs_2CO_3 (0.7 mmol), TBAB (0.5 mmol) in 2.0 mL DMA at 150 °C for 15 h.
[b] Yields are reported after isolation and purification by column chromatography.

3. Conclusion

We have developed palladium-catalyzed cross-coupling of vinyl heteroaromatic compounds with aryl halides and heteroaryl halides under phosphine-free conditions. This approach provides an efficient and convenient route to prepare a wide variety of styrylpyridine derivatives and novel *trans*-1,2-disubstituted vinyl heterocycles.

4. Experimental procedure

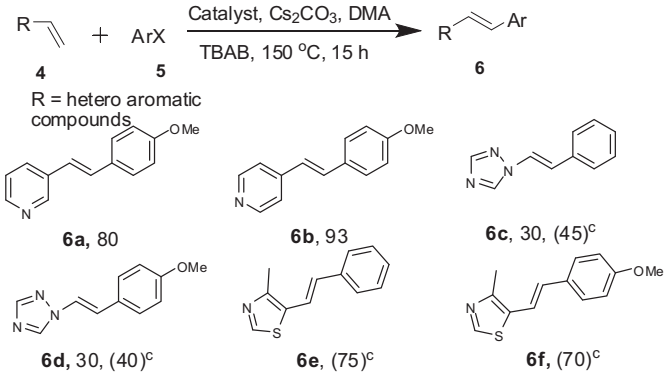
4.1. Typical procedure for Heck reaction of vinyl heterocycles with aryl bromides

The 15 mL sealed tube was charged with aryl bromides (0.8 mmol), alkenes (0.5 mmol), Cs_2CO_3 or LiO^tBu (0.7 mmol), TBAB (0.5 mmol) and the catalyst (1.2 mol %, 5.0 mg), in *N*,*N*-dimethylacetamide (2.0 mL). The reaction mixture was heated at 150 °C for 15 h and the progress of reaction was monitored by TLC. At the end of the reaction, the reaction mixture was cooled to room temperature and was diluted with EtOAc (20 mL), washed with 1 N aq HCl and water. The combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and hexane to afford the Heck product in high purity.

4.2. Characterization data for the products of the Heck reaction

*4.2.1. (E)-2-(4-Methoxystyryl)pyridine (**3a**).*[19a] White solid; mp 74–76 °C (lit.,[19b] 75.5–77 °C); R_f (30% EtOAc/Hexane) 0.54; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=3.83 (s, 3H, OCH_3), 6.91 (d, J=8.0 Hz, 2H, H-3″, 5″), 7.04 (d, J=16.0 Hz, 1H, H-1′), 7.10 (dd, J=7.0, 5.0 Hz, 1H, H-5), 7.35 (d, J=8.0 Hz, 1H, H-3), 7.52 (d, J=9.0 Hz, 2H, H-2″, 6″), 7.58

Table 3
Scope of vinyl heteroaromatic compounds with aryl bromides[a,b]



[a]Reaction performed with vinyl heteroaromatic compound (0.5 mmol), aryl halide (0.8 mmol), catalyst (1.2 mol %), Cs_2CO_3 (0.7 mmol) and TBAB (0.5 mmol) in 2.0 mL DMA at 150 °C for 15 h.
[b]Yields are reported after isolation and purification by column chromatography.
[c]Yield indicated in the parenthesis is for the reaction performed with LiO^{t}Bu.

(d, J=16.0 Hz, 1H, H-2′), 7.63 (td, J=6.0, 2.0 Hz, 1H, H-4), 8.58 (d, J=5.0 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.2, 114.1, 121.6, 121.7, 125.7, 128.4, 129.3, 132.2, 136.4, 149.5, 155.9, 159.8; IR (KBr, cm^{-1}): 3005, 2957, 2927, 2836, 1631, 1577, 1507, 1462, 1429, 1294, 1246, 1173, 1140, 1021, 982, 876, 826; ESI-MS (m/z): $(M+H)^+$=212; HRMS: calcd for $C_{14}H_{14}NO$ $(M+H)^+$=212.1069, found: 212.1065.

*4.2.2. (E)-2-(4-Methylstyryl)pyridine (**3b**).*[20] White solid; mp 77–79 °C (lit.,[20] 76–78 °C); R_f (30% EtOAc/Hexane) 0.69; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.37 (s, 3H, CH_3), 7.11–7.14 (m, 2H, H-1′, H-5), 7.18 (d, J=8.0 Hz, 2H, H-3″, 5″), 7.37 (d, J=8.0 Hz, 1H, H-3), 7.48 (d, J=8.0 Hz, 2H, H-2″, 6″), 7.60 (d, J=16.0 Hz, 1H, H-2′), 7.63–7.66 (m, 1H, H-4), 8.59 (d, J=4.0 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.3, 121.8, 121.9, 126.9, 127.0, 129.4, 132.6, 133.8, 136.5, 138.3, 149.6, 155.7; IR (KBr, cm^{-1}): 3001, 2922, 2853, 1630, 1577, 1556, 1507, 1463, 1425, 1299, 1174, 1088, 979, 811; ESI-MS (m/z): $(M+H)^+$=196; HRMS: calcd for $C_{14}H_{14}N$ $(M+H)^+$=196.1120, found: 196.1114.

*4.2.3. (E)-2-Styrylpyridine (**3c**).*[21] White solid; mp 88–90 °C (lit.,[19b] 90–90.5 °C); R_f (30% EtOAc/Hexane) 0.64; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.12–7.20 (m, 2H, H-1′, H-5), 7.29–7.40 (m, 4H, H-4, H-3″, 4″, 5″), 7.57–7.69 (m, 4H, H-3, H-2′, H-2″, 6″), 8.61 (d, J=4.7 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=122.0, 122.1, 127.0, 127.9, 128.3, 128.7, 132.6, 136.5, 149.6, 155.5; IR (KBr, cm^{-1}): 3034, 2924, 1629, 1576, 1491, 1465, 1422, 1299, 1142, 1070, 981, 778; ESI-MS (m/z): $(M+H)^+$=182; HRMS: calcd for $C_{13}H_{12}N$ $(M+H)^+$=182.0964, found: 182.0961.

*4.2.4. (E)-Ethyl 4-(2-(pyridin-2-yl)vinyl)benzoate (**3d**).* White solid; mp 92–94 °C; R_f (30% EtOAc/Hexane) 0.52; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=1.40 (t, J=7.1 Hz, 3H, CH_3), 4.39 (q, J=7.1 Hz, 2H, OCH_2), 7.16–7.20 (m, 1H, H-5), 7.26 (d, J=16.1 Hz, 1H, H-1′), 7.41 (d, J=7.7 Hz, 1H, H-3), 7.62–7.72 (m, 4H, H-4, H-2′, H-2″, 6″), 8.05 (d, J=8.3 Hz, 2H, H-3″, 5″), 8.63 (d, J=4.5 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.3, 60.9, 122.5, 126.8, 129.8, 129.9, 130.1, 131.5, 136.6, 140.9, 149.7, 155.0, 166.2; IR (KBr, cm^{-1}): 2930, 1702, 1600, 1580, 1465, 1278, 1175, 1101, 1018, 978, 846, 780; ESI-MS (m/z): $(M+H)^+$=254; HRMS: calcd for $C_{16}H_{16}NO_2$ $(M+H)^+$=254.1175, found: 254.1167.

*4.2.5. (E)-2-(4-(Trifluoromethyl)styryl)pyridine (**3e**).* White solid; mp 116–118 °C; R_f (30% EtOAc/Hexane) 0.66; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.17–7.20 (m, 1H, H-5), 7.24 (d, J=15.9 Hz, 1H, H-1′), 7.40 (d, J=8.0 Hz, 1H, H-3), 7.64–7.72 (m, H-4, H-2′, H-2″, 6″), 8.63 (d, J=4.2 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=122.5, 122.6, 124.1 (q, J_{C-F}=271.7 Hz), 125.6, (d, J_{C-F}=3.3 Hz), 127.1, 129.9, (q, J_{C-F}=32.4 Hz), 130.3, 131.1, 136.6, 140.1, 149.8, 154.9; IR (KBr, cm^{-1}): 2925, 1610, 1579, 1466, 1431, 1328, 1163, 1110, 1064, 979, 831, 740; ESI-MS (m/z): $(M+H)^+$=250; HRMS: calcd for $C_{14}H_{11}NF_3$ $(M+H)^+$=250.0838, found: 250.0830.

*4.2.6. (E)-2-(4-Methoxy-3,5-dimethylstyryl)pyridine (**3f**).* White solid; mp 85–87 °C; R_f (30% EtOAc/Hexane) 0.67; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=2.31 (s, 6H, CH_3), 3.74 (s, 3H, OCH_3), 7.06 (d, J=15.9 Hz, 1H, H-1′), 7.10–7.15 (m, 1H, H-5), 7.25 (s, 2H, H-2″, 6″), 7.36 (d, J=8.3 Hz, 1H, H-3), 7.53 (d, J=15.9 Hz, 2H, H-2′), 7.65 (td, J=7.6, 2.3 Hz, 1H, H-4), 8.59 (d, J=3.8 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.2, 59.7, 121.7, 121.8, 126.8, 127.6, 131.1, 132.1, 132.3, 136.4, 149.5, 155.8, 157.3; IR (KBr, cm^{-1}): 2995, 2914, 2857, 1633, 1582, 1560, 1470, 1427, 1270, 1218, 1139, 1092, 983, 855; ESI-MS (m/z): $(M+H)^+$=240; HRMS: calcd for $C_{16}H_{18}NO$ $(M+H)^+$=240.1382, found: 240.1376.

*4.2.7. (E)-2-(2-(Benzo[d][1,3]dioxol-5-yl)vinyl)pyridine (**3g**).*[19a] White solid; mp 83–85 °C; R_f (30% EtOAc/Hexane) 0.59; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=6.0 (s, 2H, OCH_2O), 6.81 (d, J=8.3 Hz, 1H, H-5″), 7.0–7.05 (m, 2H, H-1′, H-6″), 7.12 (td, J=6.0, 1.5 Hz, 2H, H-5, H-2″), 7.34 (d, J=7.6 Hz, 1H, H-3), 7.55 (d, J=15.9 Hz, 1H, H-2′), 7.64 (td, J=7.9, 1.5 Hz, 1H, H-4), 8.59 (d, J=4.5 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=101.2, 106.0, 108.4, 121.7, 121.9, 122.4, 126.2, 131.1, 132.4, 136.4, 147.9, 148.1, 149.6, 155.7; IR (KBr, cm^{-1}): 3056, 3007, 2905, 2788, 1629, 1583, 1558, 1498, 1441, 1362, 1310, 1249, 1193, 1104, 1033, 963, 924, 868, 806; ESI-MS (m/z): $(M+H)^+$=226; HRMS: calcd for $C_{14}H_{12}NO_2$ $(M+H)^+$=226.0862, found: 226.0860.

*4.2.8. (E)-2-(2-(Naphthalen-1-yl)vinyl)pyridine (**3h**).*[22] Off-white solid; mp 37–39 °C (lit.,[22] 38–40 °C); R_f (30% EtOAc/Hexane) 0.68; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.18–7.26 (m, 2H, H-1′, H-5), 7.44–7.58 (m, 4H, H-3, 3″, 6″, 7″), 7.71 (td, J=7.6, 1.5 Hz, 1H, H-4), 7.82–7.89 (m, 3H, H-2″, 4″, 5″), 8.32 (d, J=8.3 Hz, 1H, H-8″), 8.48 (d, J=15.9 Hz, 1H, H-2′), 8.66 (d, J=3.8 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=122.1, 122.3, 123.9, 125.6, 125.9, 126.2, 128.5, 128.6, 129.8, 130.8, 131.5, 133.7, 134.3, 136.5, 149.7, 155.7; IR (KBr, cm^{-1}): 3052, 3004, 2925, 2853, 1632, 1584, 1563, 1509, 1468, 1430, 1392, 1346, 1253, 1149, 976, 797; ESI-MS (m/z): $(M+H)^+$=232; HRMS: calcd for $C_{17}H_{14}N$ $(M+H)^+$=232.1120, found: 232.1114.

*4.2.9. (E)-2-(2-(Phenanthren-9-yl)vinyl)pyridine (**3i**).* Yellow solid; mp 82–84 °C; R_f (30% EtOAc/Hexane) 0.65; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.18–7.22 (m, 1H, H-5), 7.30 (d, J=15.7 Hz, 1H, H-1′), 7.47 (d, J=7.9 Hz, 1H, H-3), 7.58–7.74 (m, 5H, H-4, H-2″, H-3″, H-6″, H-7″), 7.92 (d, J=9.1 Hz, 1H, H-8″), 8.05 (s, 1H, H-10″), 8.35 (d, J=9.4 Hz, 1H, H-1″), 8.46 (d, J=15.7 Hz, 1H, H-2′), 8.68 (d, J=6.4 Hz, 2H, H-4″, H-5″), 8.75 (d, J=9.4 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=122.2, 122.3, 122.5, 123.0, 124.8, 125.0, 126.5, 126.6, 126.7, 126.8, 128.8, 130.35, 130.39, 130.43, 130.7, 131.2, 131.7, 133.3, 136.5, 149.7, 155.6; IR (KBr, cm^{-1}): 3060, 2924, 1632, 1579, 1557, 1467, 1425, 1385, 1321, 1265, 1147, 1047, 962, 884, 743; ESI-MS (m/z): $(M+H)^+$=282; HRMS: calcd for $C_{21}H_{16}N$ $(M+H)^+$=282.1277, found: 282.1269.

*4.2.10. (E)-1,2-Di(pyridin-2-yl)ethene (**3j**).*[23] Yellow solid; mp 118–120 °C (lit.,[23] 118–122 °C); R_f (30% EtOAc/Hexane) 0.18; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=7.17–7.19 (m, 2H, H-5, H-5″), 7.43 (d, J=8.0 Hz, 2H, H-3, H-3″), 7.66–7.70 (m, 4H, H-4, H-4″, H-1′, H-2′), 8.63 (d, J=4.0 Hz, 2H, H-6, H-6″); ^{13}C NMR (75 MHz, $CDCl_3$): δ=122.6, 123.3, 131.6, 136.6, 149.7, 154.9; IR (KBr, cm^{-1}): 3045, 2924, 2852, 1649, 1582, 1561, 1469, 1429, 1321, 1142, 1084, 988, 959, 888,

786; ESI-MS (m/z): $(M+H)^+$=183; HRMS: calcd for $C_{12}H_{11}N_2$ $(M+H)^+$=183.0916, found: 183.0912.

*4.2.11. (E)-2,5′-(Ethene-1,2-diyl)dipyridine (**3k**).* Yellow oil; R_f (30% EtOAc/Hexane) 0.08; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.17–7.25 (m, 2H, H-5, H-1′), 7.31 (dd, J=7.9 Hz, J=4.9 Hz, 1H, H-4), 7.40 (d, J=7.7 Hz, 1H, H-3), 7.63 (d, J=16.2 Hz, 1H, H-2′), 7.69 (td, J=7.6, 1.9 Hz, 1H, H-3″), 7.90 (dt, J=7.9, 1.9 Hz, 1H, H-4″), 8.52 (dd, J=1.5, 1.5 Hz, 1H, H-2″), 8.63 (d, J=4.5 Hz, 1H, H-6), 8.80 (br d, J=2.1 Hz, 1H, H-6″); ^{13}C NMR (75 MHz, $CDCl_3$): δ=122.4, 122.5, 123.6, 128.9, 129.8, 132.3, 133.3, 136.7, 148.9, 149.0, 149.7, 154.7; IR (KBr, cm^{-1}): 3051, 2923, 2851, 1640, 1585, 1564, 1472, 1432, 1151, 1024, 970, 804; ESI-MS (m/z): $(M+H)^+$=183; HRMS: calcd for $C_{12}H_{11}N_2$ $(M+H)^+$=183.0916, found: 183.0912.

*4.2.12. (E)-2-(2-(Thiophen-2-yl)vinyl)pyridine (**3l**).*[24] Yellow solid, mp 96–98 °C (lit.,[24] 99 °C); R_f (30% EtOAc/Hexane) 0.74; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=6.97 (d, J=15.9 Hz, 1H, H-1′), 7.01–7.04 (m, 1H, H-4″), 7.11–7.16 (m, 1H, H-5), 7.17 (d, J=3.0 Hz, 1H, H-3″), 7.26 (d, J=5.2 Hz, 1H, H-5″), 7.31 (d, J=7.6 Hz, 1H, H-3), 7.65 (dt, J=7.6, 1.5 Hz, 1H, H-4), 7.79 (d, J=15.9 Hz, 1H, H-2′), 8.58 (d, J=4.5 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=121.9, 122.0, 125.4, 125.7, 127.2, 127.7, 136.5, 142.1, 149.6, 155.2; IR (KBr, cm^{-1}): 3108, 3071, 3004, 1623, 1576, 1463, 1417, 1296, 1233, 1192, 1142, 1084, 1040, 971, 825, 769; ESI-MS (m/z): $(M+H)^+$=188; HRMS: calcd for $C_{11}H_{10}NS$ $(M+H)^+$=188.0528, found: 188.0524.

*4.2.13. (E)-2-(2-(Thiophen-3-yl)vinyl)pyridine (**3m**).*[24] Yellow solid; mp 82–84 °C (lit.,[24] 82 °C); R_f (30% EtOAc/Hexane) 0.64; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.0 (d, J=16.1 Hz, 1H, H-1′), 7.11–7.15 (m, 1H, H-5), 7.32–7.40 (m, 4H, H-3, H-4, H-2′, H-4″), 7.61–7.67 (m, 2H, H-2″, H-5″), 8.59 (d, J=4.7 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=121.7, 121.8, 124.1, 125.0, 126.3, 126.7, 127.8, 136.4, 139.5, 149.6, 155.7; IR (KBr, cm^{-1}): 3090, 3044, 3002, 1629, 1578, 1557, 1462, 1425, 1301, 1273, 1240, 1144, 1082, 976, 863, 788; ESI-MS (m/z): $(M+H)^+$=188; HRMS: calcd for $C_{11}H_{10}NS$ $(M+H)^+$=188.0528, found: 188.0525.

*4.2.14. (E)-2-(2-(Pyridin-2-yl)vinyl)quinoline (**3n**).*[25] Yellow solid; mp 94–96 °C (lit.,[25] 95–97 °C); R_f (30% EtOAc/Hexane) 0.29; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.20–7.23 (m, 1H, H-5), 7.52 (dd, J=8.3 Hz, J=6.8 Hz, 1H, H-4), 7.58 (d, J=7.5 Hz, 1H, H-3), 7.67–7.74 (m, 3H, H-3″, H-6″, H-7″), 7.78–7.89 (m, 3H, H-1′, H-2′, H-8″), 8.10 (d, J=8.3 Hz, 1H, H-5″), 8.16 (d, 9.1 Hz, 1H, H-4″), 8.66 (d, J=3.8 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=120.2, 122.7, 122.8, 126.4, 127.5, 129.3, 129.7, 132.5, 133.6, 136.4, 136.6, 148.2, 149.7, 155.0, 155.2; IR (KBr, cm^{-1}): 3053, 2997, 2923, 1642, 1587, 1557, 1500, 1426, 1342, 1137, 1116, 975, 824, 748; ESI-MS (m/z): $(M+H)^+$=233; HRMS: calcd for $C_{16}H_{13}N_2$ $(M+H)^+$=233.1073, found: 233.1071.

*4.2.15. (E)-3-(4-Methoxystyryl)pyridine (**6a**).*[26] White solid; mp 96–98 °C (lit.,[26] 98–99 °C); R_f (30% EtOAc/Hexane) 0.33; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=3.84 (s, 3H, OCH_3), 6.90–6.96 (m, 3H, H-3″, H-5″, H-1′), 7.12 (d, J=16.6 Hz, 1H, H-2′), 7.27 (dd, J=8.3 Hz, J=4.5 Hz, 1H, H-5), 7.47 (d, J=8.3 Hz, 2H, H-2″, H-6″), 7.81 (dt, J=7.6, 1.9 Hz, 1H, H-4) 8.46 (dd, J=4.5, 1.5 Hz, 1H, H-6), 8.70 (d, J=1.5 Hz, 1H, H-2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.3, 114.2, 122.6, 123.4, 127.9, 129.4, 130.3, 132.3, 133.3, 148.1, 148.2, 159.7; IR (KBr, cm^{-1}): 3013, 2959, 2839, 1600, 1570, 1508, 1451, 1416, 1248, 1172, 1106, 1023, 963, 823; ESI-MS (m/z): $(M+H)^+$=212; HRMS: calcd for $C_{14}H_{14}NO$ $(M+H)^+$=212.1069, found: 212.1067.

*4.2.16. (E)-4-(4-Methoxystyryl)pyridine (**6b**).*[27] White solid, mp 132–134 °C (lit.,[27] 133–135 °C); R_f (30% EtOAc/Hexane) 0.19; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=3.84 (s, 3H, OCH_3), 6.85–6.94 (m, 3H, H-1′, H-3″, H-5″), 7.26 (d, J=16.2 Hz, 1H, H-2′), 7.33 (d, J=6.0 Hz, 2H, H-2″, H-6″), 7.48 (d, J=8.7 Hz, 2H, H-3, H-5), 8.55 (d, J=6.2 Hz, 2H, H-2, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.3, 114.2, 120.5, 123.6, 128.3, 128.8, 132.6, 144.9, 150.0, 160.0; IR (KBr, cm^{-1}): 3018, 2966, 2932, 2841, 1633, 1585, 1508, 1456, 1412, 1258, 1171, 1115, 1022, 968, 832; ESI-MS (m/z): $(M+H)^+$=212; HRMS: calcd for $C_{14}H_{14}NO$ $(M+H)^+$=212.1069, found: 212.1065.

*4.2.17. (E)-1-Styryl-1H-1,2,4-triazole (**6c**).*[28] Yellow oil; R_f (30% EtOAc/Hexane) 0.25; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=7.19–7.27 (m, 2H, H-1′, H-4″), 7.32 (t, J=7.32 Hz, 2H, H-3″, H-5″), 7.39 (d, J=7.32 Hz, 2H, H-2″, H-6″), 7.46 (d, J=14.3 Hz, 1H, H-2′), 8.01 (s, 1H, H-5), 8.44 (s, 1H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=121.3, 121.8, 126.5, 128.5, 128.9, 133.7, 142.2, 152.3; IR (KBr, cm^{-1}): 3118, 3081, 3031, 2930, 1660, 1507, 1450, 1422, 1362, 1276, 1196, 1136, 1001, 946, 862, 780, 750; ESI-MS (m/z): $(M+H)^+$=172; HRMS: calcd for $C_{10}H_{10}N_3$ $(M+H)^+$=172.0869, found: 172.0871.

*4.2.18. (E)-1-(4-Methoxystyryl)-1H-1,2,4-triazole (**6d**).* White solid; mp 82–84 °C; R_f (30% EtOAc/Hexane) 0.24; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=3.84 (s, 3H, OCH_3), 6.92 (d, J=8.2 Hz, 2H, H-3″, H-5″), 7.21 (d, J=14.2 Hz, 1H, H-1′), 7.38–7.42 (m, 3H, H-2′, H-2″, H-6″), 8.03 (s, 1H, H-5), 8.29 (s, 1H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.3, 114.4, 120.2, 121.2, 126.3, 127.8, 141.9, 152.1, 159.9; IR (KBr, cm^{-1}): 3115, 3015, 2970, 2930, 2832, 1656, 1604, 1512, 1462, 1412, 1302, 1254, 1197, 1173, 1139, 1106, 1022, 1000, 932, 836, 803; ESI-MS (m/z): $(M+H)^+$=202; HRMS: calcd for $C_{11}H_{12}N_3O$ $(M+H)^+$=202.0974, found: 202.0974.

*4.2.19. (E)-4-Methyl-5-styrylthiazole (**6e**).* Yellow solid; mp 85–87 °C; R_f (30% EtOAc/Hexane) 0.75; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=2.55 (s, 3H, CH_3), 6.83 (d, J=16.0 Hz, 1H, H-1′), 7.18 (d, J=16.0 Hz, 1H, H-2′), 7.28 (d, J=7.3 Hz, 1H, H-4″), 7.37 (t, J=7.6 Hz, 2H, H-3″, H-5″), 7.48 (d, J=7.4 Hz, 2H, H-2″, H-6″) 8.60 (s, 1H, H-2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.3, 118.0, 126.3, 128.0, 128.7, 130.9, 131.4, 136.6, 149.5, 150.2; IR (KBr, cm^{-1}): 3064, 3028, 2924, 2854, 1639, 1514, 1491, 1443, 1404, 1324, 1255, 1181, 1072, 945, 821, 747; ESI-MS (m/z): $(M+H)^+$=202; HRMS: calcd for $C_{12}H_{12}NS$ $(M+H)^+$=202.0685, found: 202.0687.

*4.2.20. (E)-5-(4-Methoxystyryl)-4-methylthiazole (**6f**).* Yellow solid; mp 88–90 °C; R_f (30% EtOAc/Hexane) 0.51; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.53 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.78 (d, J=16.0 Hz, 1H, H-1′), 6.90 (d, J=8.0 Hz, 2H, H-3″, H-5″), 7.03 (d, J=16.0 Hz, 1H, H-2′), 7.41 (d, J=9.0 Hz, 2H, H-2″, H-6″), 8.53 (s, 1H, H-2); ^{13}C NMR (125 MHz, $CDCl_3$): δ=15.3, 55.2, 114.1, 116.0, 127.5, 129.4, 130.8, 131.1, 148.9, 149.7, 159.4; IR (KBr, cm^{-1}): 3069, 3026, 2924, 2839, 1654, 1599, 1507, 1461, 1404, 1325, 1250, 1170, 1109, 1026, 933, 850, 796; ESI-MS (m/z): $(M+H)^+$=232; HRMS: calcd for $C_{13}H_{14}NSO$ $(M+H)^+$=232.0790, found: 232.0787.

Acknowledgements

M.A. thanks University Grants Commission (UGC), New Delhi, India, for the award of Senior Research Fellowship (SRF).

Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2013.10.078.

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