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Rhodium-Catalyzed Coupling Reactions of β- or α,β-Substituted Vinylpyridines with Alkenes via C–H Bond Activation

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ABSTRACT: *β- or α,β-Substituted vinylpyridines react with 3,3-dimethylbut-1-ene in the presence of Wilkinson catalyst [$RhCl(PPh_3)_3$] to give the corresponding alkylated products along with unusually isomerized products.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:346–350, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10045

INTRODUCTION

The development of transition metal catalysts for the activation of a π-unsaturated C—H bond has been intensively studied. Transition metal catalyzed C—C bond formation via C—H bond activation is currently one of the fields of great interest [1]. The efficient catalytic coupling reactions with alkenes through $C(sp^2)$—H bond activation have been reported [2–5]. Murai and coworkers [2] and Trost and co-workers [3] have reported that C—C bond formation by C—H bond activation with rhodium and ruthenium catalysts [$RuH_2(Ph_3P)_3(CO)$] [2,3] was successfully achieved. In connection with the formation of C—C bonds by activation of C—H bonds, we have recently studied the coupling reactions of α-substituted vinylpyridines, vinylquinolines, and phenylpyridines with alkenes utilizing rhodium catalysts [4]. Vinylpyridines are good substrates for cyclometallation [6], and vinylic C—H bond activation of alkenes by transition metal complexes has been well documented [7]. Alkylations of various vinylpyridines with terminal alkenes and a transition metal catalyst have been performed [4e]. However, to the best of our knowledge, a coupling of β-substituted vinylpyridines with alkenes has never been reported.

RESULTS AND DISCUSSION

We herein describe a rhodium(I)-catalyzed coupling reaction of β- and α,β-substituted vinylpyridines with 3,3-dimethylbut-1-ene in the presence of the Wilkinson catalyst (Scheme 1).

6-Methyl-2-(prop-1-enyl)pyridine (**1a**) (cis/trans = 58:42) reacted with 3,3-dimethylbut-1-ene (5 equiv.) in the presence of $RhCl(PPh_3)_3$ (**2**) (10 mol%) in toluene at 100°C for 20 h to give the alkylated products, 6-methyl-2-(2-neohexylprop-1-enyl)pyridine (**3a**) (31%, Z-isomer) and 6-methyl-2-(3-neopentyl-2-methylprop-2-enyl)pyridine (**5a** and **6a**) (7%). The coupled product **3a** was actually isomerized to **5a** and **6a**. The starting material was recovered as the

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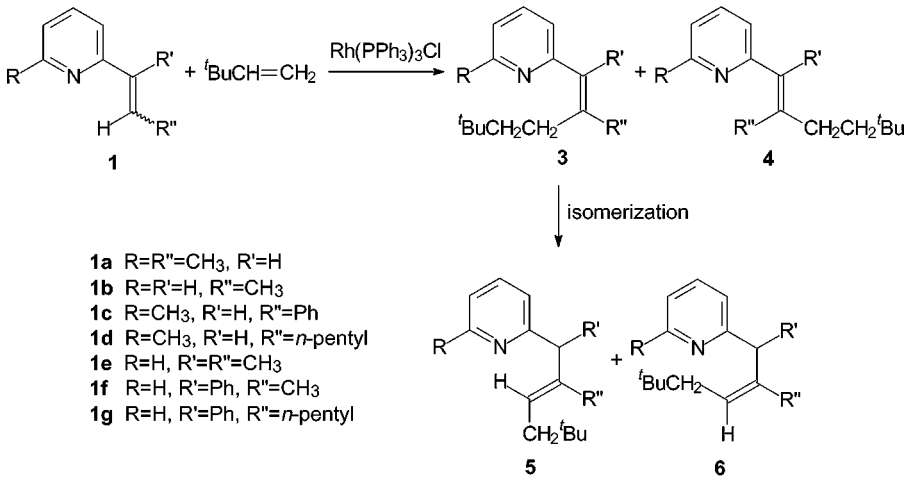


SCHEME 1 The coupling reaction of vinylpyridines with 3,3-dimethylbut-1-ene.

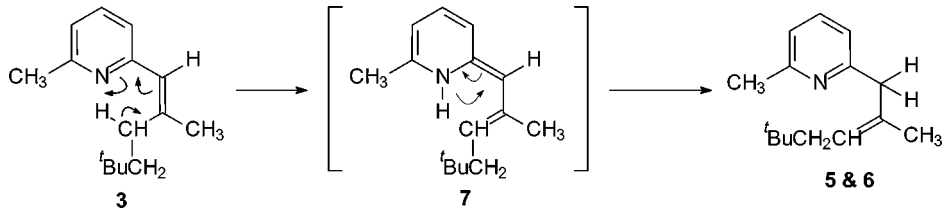
trans isomer of **1a** (49%), and **3a** could be easily separated by column chromatography (silica gel, hexane/ethylacetate = 10:1) (run 1 in Table 1). The unexpected products **5a** and **6a** were obtained as a mixture. The double bond had migrated into the alkyl moiety. It is noteworthy that α-substituted 2-vinylpyridines and 2-vinylpyridine do not provide such isomerized products [4a]. When the coupling reaction was carried out at 130–140°C, the starting material was consumed quantitatively and the double-bond-migrated product **5a** was obtained as the major isomer together with **3a, 4a**, and **6a** (89% yield; the ratio of **3a:4a:5a:6a** = 26:15:41:18). When the coupling reaction was carried out in benzene at a lower temperature, 95–100°C for 48 h, **3a** was obtained in higher yield (45%) (run 2 in Table 1).

In order to obtain additional evidence pertaining to the isomerization mechanism of **3** to **5** and **6, 3a** was heated in the absence of the Wilkinson catalyst in toluene at 130°C for 5 h to yield a mixture of **5a** (27%) and **6a** (10%), together with a small amount of **4a** (6%). Product **3a** was isomerized to **4a** (30%) in the presence of the Wilkinson catalyst at a lower temperature, 110°C. When a mixture of **3a** and **4a** was heated at 130°C for 5 h, about the same ratio of **5a:6a** was obtained, but the E isomer **4a** remained without isomerization. The isomerization appears to occur mainly by a thermal process, but a competitive isomerization by the allyl-hydrido mechanism in the presence of a transition metal [8] cannot be ruled out. A possible mechanism for thermal isomerization of the Z-isomer **3** can be proposed, as shown in

TABLE 1 Results of the Coupling Reaction of β- and α,β-Substituted Vinylpyridines[a]

Run	Substrate	Reaction Time (h)	Reaction Temperature[b] (°C)	Yield[c] (%)	Ratio of Isomers[d]			
					3	**4**	**5**	**6**
1	**1a**	20	100	38	82		13	5
2	**1a**	48	100	56	80		14	6
3	**1a**	20	130–140	89	25	12	41	22
4	**1b**	21	130	28[e]	61		32	7
5	**1c**	24	100–105	17	100			
6	**1c**	12	125	57	48	6	27	19
7	**1d**	22	120	75[f]	27	11	[g]	[g]
8	**1e**	20	100	84	4	94	1	1
9	**1e**	20	130	98	13	65	17	5
10	**1f**	20	130	66	–	>99	<1	–

[a]Substrate/3,3-dimethylbut-1-ene/$RhCl(PPh_3)_3$ = 1:5:0.1; the reactions were carried out in a screw-capped vial.
[b]Bath temperature.
[c]Isolated yield based on substrate.
[d]Ratio of isomers was determined by GC-MSD and ^1H NMR.
[e]Very volatile.
[f]Yields containing the remaining isomerized products.
[g]The structures of isomers could not be determined.



SCHEME 2 A possible mechanism for the thermal isomerization of **3** to **5** and **6** by double bond migration.

Scheme 2. First, the nitrogen atom in the pyridine ring may capture one of the two methylene hydrogens to form an intermediate **7**, followed by transformation to the products **5** and **6** aided by the recovery of aromaticity [9].

(*Z*)-6-Methyl-2-β-styrylpyridine (**1c**) reacted with 3,3-dimethylbut-1-ene in the presence of the Wilkinson catalyst (10 mol%) in toluene at 100°C for 24 h to give **3c** (17%) together with the starting material recovered as the *E*-isomer of **1c** (57%) (run 5). In order to evaluate a possible temperature effect, the coupling reaction of **1c** was carried out at 125°C for 12 h. The coupled products were obtained in 57% yield (run 6). However, (*E*)-6-methyl-2-β-styrylpyridine (isomer of **1c**) did not undergo the coupling reaction under the same conditions. It is noteworthy that the *Z*-isomer was more reactive than the *E*-isomer. The *Z*-isomer seems to be unfavorable for this coupling reaction, because the structure has the C—H bond located on the opposite site for C—H bond activation. This result implies that this coupling reaction is affected deeply by the ability of coordination of the double bond in the substrate to the rhodium complex. Coordination between rhodium and nitrogen of the pyridine moiety is essential to this coupling reaction [4]; however, coordination between rhodium and the double bond in the substrate must take place first. In the coupling reaction, the metal coordinated *Z*-isomer is isomerized to the *E*-isomer to allow for the coordination toward the pyridine moiety. The substrate **1d** gave the alkylated products as a mixture of **3d, 4d**, and others (run 7).

β-Substituted or α,β-substituted vinylpyridines (**1e** and **1f**) were applied to this coupling reaction. Substrate **1e** (*E*:*Z* = 1:2) was easily reacted with 3,3-dimethylbut-1-ene at 130°C to give the alkylated products as a mixture of isomers in excellent isolated yield (98%, run 9). But, in the reaction at 100°C, **1e** gave **4e** as the major product in 84% yield (**3e:4e:5e:6e** = 4:94:1:1, run 8). Under the same reaction conditions, **1f** (*E*:*Z* = 74:26) gave **4f** as the major product in 66% isolated yield (**4f:5f** = >99:1, run 10) together with the starting material (30%) recovered as the *E*-isomer. When the reaction time was prolonged, the proportion of **5f** and **6f** increased without increase of **4f**. The substrate **1g** containing an *n*-pentyl group instead of a methyl group in **1f** did not undergo the coupling reaction, probably because of the steric hindrance of the *n*-pentyl group. This result suggests that the coordination between Rh(I) and the substrates plays an important role for this coupling reaction.

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$on Bruker AC-300F (300 MHz) and a Bruker AC-200 (200 MHz) instruments, and the chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{13}C NMR spectra were recorded on a Bruker AC-300F (75 MHz) machine. IR spectra were run on a Nicolet magna 550 FT-IR instrument. Mass spectra were measured at 70 eV on an HP-5971A mass spectrometer equipped with a Hewlett-Packard 5890 series II gas chromatograph. The silica gel used in column chromatography was purchased from Aldrich (230–400 mesh). Analytical thin layer chromatography was performed on glass plates (0.25 mm) coated with silica gel 60F 254 from Aldrich. The purities of products were determined by gas chromatography (capillary column, HP 5890 series II attached to the mass analytical instrument). Elemental analyses were carried out by the Analytical Laboratory at the ADD.

General Procedure for the Alkylation

A screw-capped vial (5 ml) was charged with **1a** (53.3 mg, 0.4 mmol), 3,3-dimethylbut-1-ene (168 mg, 2 mmol, 5 equiv.) and **2** (37 mg, 0.04 mmol, 10 mol%) in toluene (3 ml). The stirred reaction mixture was heated at 100–140°C for 20–48 h and concentrated. The products were purified by column chromatography on silica gel (EtOAc–hexane, 1:10).

3a: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.47 (t, J = 7.8, 1H 4-H in py), 6.89–6.96 (m, 2H 3,5-H in py), 6.28 (s, 1H=C—H), 2.52 (s, 3H CH_3 in py), 2.43–2.50 (m, 2H=$CCH_2CH_2Bu^t$), 1.91 (s, 3H=CCH_3), 1.37–1.43 (m, 2H=$CCH_2CH_2Bu^t$), 0.91 (s, 9H Hs in Bu^t). ^{13}C NMR (75 MHz; $CDCl_3$): δ 157.53, 156.58, 144.97, 135.97, 124.84, 120.21, 119.92, 41.99, 30.63, 29.24, 28.21,

24.90, 24.55. MS: *m/z* 217 (M^+, 10%), 202 ($M^+ - CH_3$, 8), 160 ($M^+ - Bu^t$, 100), 146 ($M^+ - CH_2Bu^t$, 6), 145 (17), 132 ($M^+ - CH_2CH_2Bu^t$, 3). IR: ν_{max} (NaCl) cm^{-1} 3059w, 2954vs, 2865m, 1650m, 1582s, 1572s, 1474m, 1455s, 1392w, 1373w, 1364m, 1246w, 1219w, 1158w, 1095w, 892w, 851w, 783m, 746w, 736w, 652w. Anal Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44%. Found: C, 82.81; H, 10.48; N, 6.69%.

4a: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.50 (t, $J = 6.9$, 1H 4-H in py), 7.01 (d, $J = 7.8$, 1H 5-H in py), 6.92 (d, $J = 7.9$, 1H 3-H in py), 6.35 (s, 1H=C—H), 2.54 (s, 3H CH_3 in py), 2.11–2.18 (m, 2H=$CCH_2CH_2Bu^t$), 2.01 (s, 3H=CCH_3), 1.37–1.47 (m, 2H=$CCH_2CH_2Bu^t$), 0.93 (s, 9H Hs in Bu^t). ^{13}C NMR (75 MHz): δ 157.48, 156.77, 144.35, 135.94, 124.48, 120.51, 119.90, 42.28, 36.04, 30.23, 29.20, 28.17, 18.34. MS: *m/z* 217 (M^+, 37%), 202 ($M^+ - CH_3$, 70), 160 ($M^+ - Bu^t$, 100), 158 (8), 146 ($M^+ - CH_2Bu^t$, 32), 145 (24), 132 ($M^+ - CH_2CH_2Bu^t$, 19), 131 (24), 107 (30), 57 (Bu^{t+}, 6).

5a: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.47 (t, $J = 7.7$, 1H 4-H in py), 6.99 (t, $J = 8.7$, 2H 3,5-H in py), 5.37 (t, $J = 7.8$, 1H=C—H), 3.50 (s, 2H CH_2 in py), 2.53 (s, 3H CH_3in py), 1.93 (d, $J = 7.7$, 2H=CCH_2Bu^t), 1.58 (s, 3H=CCH_3), 0.90 (s, 9H Hs in Bu^t). ^{13}C NMR (75 MHz): δ 160.09, 157.41, 136.35, 134.30, 124.82, 120.39, 119.44, 49.01, 41.97, 31.70, 29.24, 24.42, 16.01. MS: *m/z* 217 (M^+, 2%), 202 ($M^+ - CH_3$, 83), 160 ($M^+ - Bu^t$, 100), 158 (14), 146 ($M^+ - CH_2Bu^t$, 65), 145 (23), 131 (14), 107 (26), 57 (Bu^{t+}, 7).

6a: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.46 (t, $J = 7.6$, 1H 4-H in py), 6.92 (t, $J = 7.8$, 2H 3,5-H in py), 5.46 (t, $J = 6.9$, 1H=C—H), 3.56 (s, 2H CH_2-py), 2.53 (s, 3H CH_3 in py), 2.01 (d, $J = 7.7$, 2H=CCH_2Bu^t), 1.72 (s, 3H=CCH_3), 0.92 (s, 9H Hs in Bu^t). ^{13}C NMR (75 MHz): δ 159.61, 157.50, 136.50, 133.44, 124.71, 120.39, 118.69, 49.01, 41.85, 40.50, 31.25, 29.24, 23.83. MS: *m/z* 217 (M^+, 4%), 202 ($M^+ - CH_3$, 73), 160 ($M^+ - Bu^t$, 100), 158 (11), 146 ($M^+ - CH_2Bu^t$, 48), 131 (11), 107 (18), 57 (Bu^{t+}, 6).

3b: ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.53–8.56 (m, 1H 6-H in py), 7.59 (dt, $J = 7.7$, 1.9, 1H 4-H of py), 7.14 (d, $J = 8.0$, 1H 3-H in py), 7.02–7.07 (m, 1H 5-H in py), 6.30 (s, 1H=CH), 2.42–2.48 (m, 2H=C—CH_2), 1.92 (d, $J = 1.4$, 3H=C—C**H**$_3$), 1.37–1.43 (m, 2H CH_2Bu^t), 0.91 (s, 9H Bu^t). ^{13}C NMR (75 MHz): δ 157.24, 149.04, 145.52, 135.73, 124.66, 123.19, 120.45, 42.01, 30.66, 29.22, 28.27, 25.01. MS: *m/z* 203 (M^+, 6%), 188 ($M^+ - CH_3$, 8), 146 ($M^+ - Bu^t$, 100), 132 ($M^+ - CH_2Bu^t$, 10), 131 (24). IR: ν_{max} (NaCl) cm^{-1} 3059w, 2954vs, 2864m, 1647m, 1585s, 1560w, 1472m, 1425w, 1363w, 1246w, 1148w, 854w, 771m, 741w. Anal Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89%. Found: C, 82.68; H, 10.17; N, 7.10%.

A mixture of **5b** and **6b:** ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.41–8.53 (m, 1H 6-H of py), 7.56–7.63 (m, 1H 4-H of py), 7.17–7.25 (m, 1H 3-H of py), 7.06–7.13 (m, 1H 3-H of py), 5.39 (t, $J = 7.2$, =C—H of **5b**), 3.58 (s, =$C(CH_3)CH_2$ of **6b**), 3.53 (s, =$C(CH_3)CH_2$ of **5b**), 1.93 (d, $J = 6.9$, 2H=C—CH_2Bu^t), 1.57 (s, =C—CH_3 of **5b**), 0.92 (s, Bu^t of **6b**), 0.90 (s, Bu^t of **5b**).

3c: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.24–7.55 (6H 4-H in py and Hs in ph), 7.07 (d, $J = 7.7$, 1H 3-H in py), 6.97 (d, $J = 7.6$, 1H 5-H in py), 6.67 (s, 1H=C—H), 3.04–3.10 (m, 2H=$CCH_2CH_2Bu^t$), 2.56 (s, 3H CH_3 in py), 1.34–1.40 (m, 2H=C—$CH_2CH_2Bu^t$), 0.92 (s, 9H Bu^t). ^{13}C NMR (75 MHz): δ 157.79, 156.49, 147.59, 143.32, 136.15, 128.27, 127.34, 126.91, 126.57, 121.31, 120.49, 42.43, 30.75, 29.24, 25.74, 24.62. MS: *m/z* 279 (M^+, 8%), 264 ($M^+ - CH_3$, 5), 223 (17), 222 ($M^+ - Bu^t$, 100), 208 ($M^+ - CH_2Bu^t$, 6), 207 (15), 194 ($M^+ - CH_2CH_2Bu^t$, 3), 84 (13), 57 (Bu^{t+}, 3). IR: ν_{max} (NaCl) cm^{-1} 3057m, 2953s, 2864s, 1672m, 1566s, 1493m, 1449s, 1391w, 1363m, 1246m, 1192w, 1158m, 1095w, 1077w, 1030w, 986w, 896w, 873w, 787s, 741m, 697s. Anal Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01%. Found: C, 85.82; H, 9.07; N, 5.09%.

4c: ^{1}H NMR (300 MHz; $CDCl_3$): δ 6.80–7.41 (8H Hs in py and ph), 6.59 (s, 1H=C—H), 2.50 (s, 3H CH_3 in py), 2.42–2.51 (m, 2H=$CCH_2CH_2Bu^t$), 1.32–1.40 (m, 2H=$CCH_2CH_2Bu^t$), 0.97 (s, 9H Bu^t). MS: *m/z* 279 (M^+, 7%), 264 ($M^+ - CH_3$, 6), 223 (15), 222 ($M^+ - Bu^t$, 80), 208 ($M^+ - CH_2Bu^t$, 8), 207 (12), 194 ($M^+ - CH_2CH_2Bu^t$, 4), 92 (61), 91 (100), 65 (15).

5c: ^{1}H NMR (300 MHz; $CDCl_3$): δ 6.83–7.44 (8H Hs in py and ph), 5.61 (t, $J = 7.5$, 1H=C—H), 3.84 (s, 2H C=CCH_2), 2.49 (s, 3H CH_3 in py), 1.89 (d, $J = 7.3$, 2H=CCH_2Bu^t), 0.83 (s, 9H Hs in Bu^t). MS: *m/z* 279 (M^+, 14%), 264 ($M^+ - CH_3$, 51), 223 (11), 222 ($M^+ - Bu^t$, 57), 208 ($M^+ - CH_2Bu^t$, 100), 107 (36), 92 (35), 91 (56), 65 (13), 57 (Bu^t, 9).

6c: ^{1}H NMR (300 MHz; $CDCl_3$): δ 6.83–7.44 (8H Hs in py and ph), 6.17 (t, $J = 7.6$, 1H=C—H), 4.07 (s, 2H C=CCH_2), 2.53 (s, 3H CH_3 in py), 2.14 (d, $J = 7.6$, 2H=CCH_2Bu^t), 0.96 (s, 9H Hs in Bu^t). MS: *m/z* 279 (M^+, 11%), 264 ($M^+ - CH_3$, 47), 222 ($M^+ - Bu^t$, 49), 208 ($M^+ - CH_2Bu^t$, 100), 194 (5), 107 (41), 91 (64), 65 (14), 57 (Bu^t, 10).

3d: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.47 (t, $J = 7.7$, 1H 4-H in py), 6.96 (d, $J = 7.7$, 1H 3-H in py), 6.90 (d, $J = 7.6$, 1H 5-H in py), 6.26 (s, 1H=CH), 2.52 (s, 3H CH_3), 2.45–2.52 (m, 2H=C—CH_2), 2.17 (t, $J = 7.6$, 2H=C—CH_2), 1.18–1.60 (m, 8H CH_2), 0.89 (s, 9H Bu^t), 0.85–0.93 (3H CH_3). ^{13}C NMR (75 MHz): δ 157.48, 156.77, 149.12, 135.89, 124.12, 120.37, 119.82, 42.14, 38.10, 31.71, 29.26, 27.73, 26.48, 24.53, 22.53, 13.98. MS: *m/z* 273 (M^+, 9%), 258 ($M^+ - CH_3$, 7), 230 (11), 216 ($M^+ - Bu^t$, 100), 202 (10), 158 (22), 144 (20), 131 (13), 107 (16).

3e: ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.55–8.59 (m, 1H 6-H of py), 7.60 (dt, $J = 7.7$, 1.8, 1H 4-H

of py), 7.06–7.13 (m, 2H 3,5-Hs of py), 2.11–2.17 (m, 2H=C–CH_2), 2.02 (s, 3H=C(py)CH_3), 1.63 (s, 3H=C–CH_3), 1.33–1.40 (m, 2H CH_2Bu^t), 0.95 (s, 9H Bu^t). MS: *m/z* 217 (M^+, 17%), 202 ($M^+ -$, CH_3, 18), 160 ($M^+ - Bu^t$, 100), 146 ($M^+ - CH_2Bu^t$, 37), 145 (43), 130 (39).

4e: ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.55–8.59 (m, 1H 6-H in py), 7.60 (dt, $J = 7.7$, 1.8, 1H 4-H in py), 7.06–7.13 (m, 2H 3, 5-Hs in py), 2.00 (s, 3H=C(py)CH_3), 1.84–1.90 (m, 2H=C–CH_2), 1.80 (s, 3H=C–CH_3), 1.24–1.31 (m, 2H CH_2Bu^t), 0.74 (s, 9H Bu^t). ^{13}C NMR (75 MHz): δ 162.84, 148.99, 135.63, 134.57, 129.88, 123.08, 120.78, 42.50, 30.44, 30.23, 28.96, 19.31, 18.33. MS: *m/z* 217 (M^+, 6%), 202 ($M^+ - CH_3$, 5), 160 ($M^+ - Bu^t$, 100), 146 ($M^+ - CH_2Bu^t$, 15), 145 (39), 130 (22). IR: ν_{max} (NaCl) cm^{-1} 3059w, 2953vs, 2864s, 1647w, 1586s, 1563m, 1466s, 1428m, 1392w, 1363m, 1280w, 1246m, 1147w, 1090w, 1074w, 1044m, 990w, 790s, 748s. Anal Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44%. Found: C, 82.79; H, 10.65; N, 6.51%.

A mixture of **5e** and **6e:** ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.52–8.57 (m, 1H 6-H in py), 7.55–7.61 (m, 1H 4-H in py), 7.06–7.20 (m, 2H 3,5-Hs in py), 5.47 (t, $J = 7.6$, =C–H in **5e**), 5.35 (t, $J = 7.6$, =C–H in **6e**), 4.18 (q, $J = 7.1$, =C(CH_3)C(CH_3)H in **6e**), 3.62 (q, $J = 7.0$, =C(CH_3)C(CH_3)H in **5e**), 1.94 (d, $J = 7.7$, 2H=C–CH_2Bu^t), 1.56 (s, =C–CH_3 of **6e**), 1.49 (s, =C–CH_3 of 5e), 1.43 (d, $J = 7.2$, =C–CH(py)CH_3), 0.93 (s, Bu^t of **6e**), 0.90 (s, Bu^t of **5e**).

4f: ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.57–8.60 (m, 1H 6-H of py), 7.57 (dt, $J = 7.8$, 1.8, 1H 4-H in py), 7.08–7.29 (m, 7H 3,5-Hs of py and Hs of ph), 2.03–2.09 (m, 2H=C–CH_2), 1.82 (s, 3H=C–CH_3), 1.36–1.43 (m, 2H CH_2Bu^t), 0.77 (s, 9H Bu^t). ^{13}C NMR (75 MHz): δ 161.31, 148.99, 141.82, 138.68, 135.82, 129.64, 127.94, 126.25, 124.43, 121.02, 42.45, 30.66, 30.36, 29.02, 19.90. MS: *m/z* 279 (M^+, 8%), 264 ($M^+ - CH_3$, 5), 222 ($M^+ - Bu^t$, 100), 208 ($M^+ - CH_2Bu^t$, 27), 194 ($M^+ - CH_2CH_2Bu^t$, 8), 193 (16), 167 (22). IR: ν_{max} (NaCl) cm^{-1} 3057w, 2954vs, 2864s, 1584s, 1561w, 1491w, 1467s, 1441m, 1425m, 1363m, 1245w, 991w, 788w, 763m, 746m, 710m, 701m. Anal Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01%. Found: C, 85.91; H, 9.09; N, 4.98%.

5f: ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.56–8.59 (m, 1H 6-H in py), 7.09–7.62 (m, 8H 3,4,5-Hs of py and Hs in ph), 5.03 (t, $J = 7.3$, 1H=CH), 4.95 (s, 1H=C(CH_3)CH), 1.95 (d, $J = 7.7$, 2H=C–CH_2), 1.66 (s, 3H=C–CH_3), 0.84 (s, 9H Bu^t). MS: *m/z* 279 (M^+, 32%), 278 ($M^+ - 1$, 37), 264 ($M^+ - CH_3$, 31), 222 ($M^+ - Bu^t$, 39), 208 ($M^+ - CH_2Bu^t$, 100), 193 (13), 168 (19).

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