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Cobalt-Catalyzed Addition of Styrylboronic Acids to 2-Vinylpyridine Derivatives

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Dedicated to Professor Eiichi Nakamura on the occasion of his 60th birthday

Abstract: Treatment of 2-vinyl nitrogen-containing heteroaromatic compounds with styrylboronic acid in the presence of a cobalt catalyst and a base results in an addition reaction to afford the corresponding 4-phenyl-3-butenyl heteroarenes. The adjacent nitrogen atom is essential for the promotion of the reaction because the nitrogen accelerates the addition of the styryl cobalt species, generated by transmetalation, onto the vinyl group. The reaction represents a rare example of cobalt catalysis in the reactions of organoboronic acids.

Keywords: addition reactions · alkenylation · cobalt · heterocycles · organoborons

Introduction

The transition metal catalyzed addition of organometallic reagents to activated alkenes is a useful carbon–carbon bond forming reaction in organic synthesis.[1] Organoboron reagents have been attracting increasing attention, owing to their easy handling, low toxicity, and widespread availability. Rhodium catalysis is now recognized as the most reliable method for 1,4-addition to α,β-unsaturated carbonyl compounds.[2] However, examples of addition onto alkenes activated by a heteroaromatic ring are limited.

Lautens and co-workers,[3,4] and Michelet, Genêt, and co-workers[5] have reported the rhodium-catalyzed addition of arylboronic acids to vinylpyridine derivatives in water. In these reports, there are no examples of the use of alkenylboronic acids. It is also noteworthy that rhodium is the only transition metal that can catalyze addition to vinyl heteroarenes. We are interested in the catalytic activity of cobalt in organic synthesis,[6–8] and report herein the cobalt-catalyzed addition of alkenylboronic acids to vinyl heteroarenes. The present reaction represents a rare example of cobalt catalysis in the addition reactions of organoboron reagents. To the best of our knowledge, cobalt-catalyzed addition of arylboronic acids to activated alkynes is the only precedent for the combined use of organoboronic acids and a cobalt catalyst.[9]

Results and Discussion

The reaction of 2-vinylpyridine (**1a**) with styrylboronic acid (**2a**, 3 equiv) proceeded very efficiently in the presence of potassium carbonate (2 equiv), cobalt(II) bromide (5 mol%), and triphenylphosphine (10 mol%) (Table 1, entry 1). The use of the excess of **2a** is important. The use of 2 equiv of **2a** gave **3a** in slightly lower (yet still high) yield (entry 2). A significant drop in yield was observed when 1 equiv of **2a** was employed (entry 3). In this case, all of the **2a** disappeared, and a large amount of styrene and a small amount of 1,4-diphenyl-1,3-butadiene were detected. Protonation of **2a** and the styryl cobalt species generated by transmetalation (see below) must compete to consume **2a**.

In the absence of base, the yield of **2a** was moderate (entry 4). While other potassium salts such as phosphate and hydroxide were also effective, sodium carbonate and cesium carbonate were inferior (entries 5–8). Interestingly, cesium fluoride was as effective as potassium bases (entry 9). The

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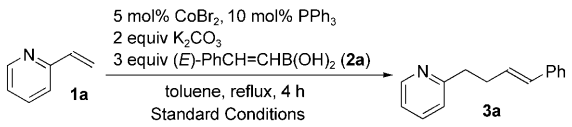
Table 1. Effects of amount of **2a**, base, and solvent.



Entry	Deviation from standard conditions	**3a** [%]
1	none	96
	amount of **2a**	
2	2 equiv **2a**	91
3	1 equiv **2a**	44
	base	
4	no base	38
5	K_3PO_4	88
6	KOH	71
7	Na_2CO_3	38
8	Cs_2CO_3	33
9	CsF	87
	solvent	
10	xylene, reflux	75
11	dioxane, reflux	64
12	acetonitrile, reflux	0
13	DMF, reflux	0

exact role of the base remains unclear. While a reaction in xylene or dioxane did proceed, more polar solvents, such as acetonitrile and dimethyl formamide, completely suppressed the reactions (entries 10–13). These highly polar solvents must strongly coordinate to cobalt and interrupt the coordination of the nitrogen atom of **1a** (see below).

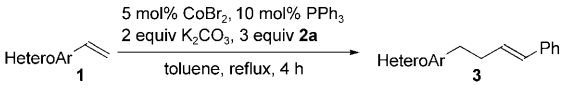
The scope of vinyl heteroarenes in these reactions is summarized in Table 2. The reactions of 2-vinylpyridine analogs such as 2-vinylpyrimidine (**1b**) and -pyrazine (**1c**) proceeded smoothly (entries 1–4). In contrast, 2-vinylthiophene (**1f**), 3-vinylpyridine (**1g**), and 4-vinylpyridine (**1h**) resisted the reaction (entries 5–7). 2-Vinylpyridine derivatives bearing a methyl group at the 3-, 4-, or 5-position underwent the addition reaction (entries 8–10). Interestingly, 6-methyl-2-vinylpyridine failed to react (entry 11). The nitrogen atom in the heteroaromatic ring clearly plays a key role in the addition reaction, probably coordinating to the cobalt, which then accelerates the addition reaction (see below). The corresponding 2-vinylpyridine *N*-oxides were too unstable to use as substrates, because they underwent polymerization.

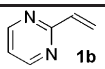
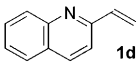
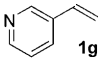
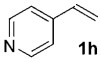
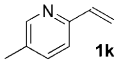
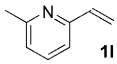
It is worth noting that the efficiency of the addition to 2-(1-propenyl)pyridine (**1m**) depended on the stereochemistry

Abstract in Japanese:

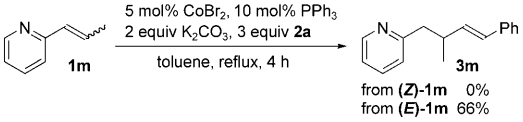
コバルト触媒と塩基の存在下、2位にビニル基を有する含窒素芳香族化合物に対してスチリルボロン酸を作用させると付加反応が進行し、対応する4-フェニル-3-ブテニル置換複素芳香族化合物が効率よく得られる。ビニル基に隣接する窒素原子は本反応の進行に必須である。本反応では、トランスメタル化によって生じるスチリルコバルト種のビニル基への付加が窒素原子によって加速されていると考えられる。本反応は有機ボロン酸の反応をコバルトが触媒する珍しい例である。

Table 2. Scope of vinyl heteroaromatic substrates.



Entry	**1**	Product	Yield [%]
1		**3b**	78
2		**3c**	45
3		**3d**	58
4		**3e**	76
5		**3f**	0
6		**3g**	0
7		**3h**	0
8		**3i**	78
9		**3j**	85
10		**3k**	71
11		**3l**	0

of the internal double bond (see Scheme 1). While (*Z*)-**1m** remained intact under the standard conditions, the reaction of the *E* isomer proceeded smoothly.



Scheme 1. Stereochemical control of the addition to **1m**.

An electron-neutral or -donating substituent at the *para* position of styrylboronic acids had little influence on the efficiency of the reaction (Table 3, entries 1, 3, and 5). In contrast, the *ortho* substituent of **2c** and the *para* electron-withdrawing group of **2e** diminished the yields of the corresponding adducts (entries 2 and 4), probably because of slower transmetalation (see below). 2-(2-Thienyl)ethenylboronic acid (**2g**) participated in the addition reaction (entry 6). Unfortunately, 1-phenylethenylboronic acid, phenylboronic acids, and 1-hexenylboronic acid failed to react. In these cases, small amounts of homocoupling products, such as 2,3-diphenyl-1,3-butadiene, biphenyl, and 5,7-dodecadiene were observed, which indicates that transmetalation from boron

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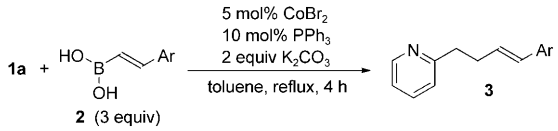
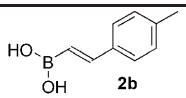
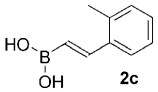
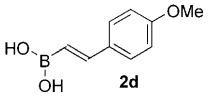
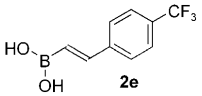
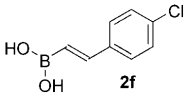
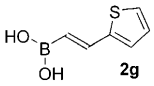
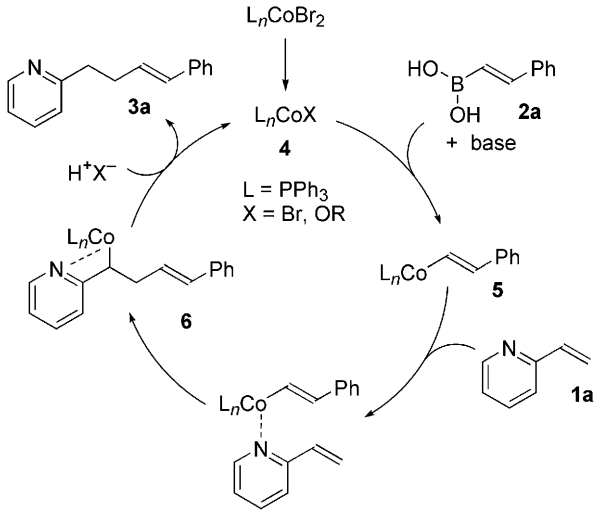
Table 3. Scope of organoboronic acids.



Entry	2	Product	Yield [%]
1		**3n**	86
2		**3o**	41
3		**3p**	75
4		**3q**	39
5		**3r**	72
6		**3s**	63

to cobalt proceeded, but that the subsequent addition to **1a** was sluggish.

It is possible that the reaction mechanism is similar to that of the well-known rhodium-catalyzed reaction (Scheme 2). Initially, a divalent cobalt species would be reduced in situ to monovalent cobalt **4** since the reaction of **1a** with **2a** proceeded in the presence of $CoCl(PPh_3)_3$ (80% yield).[10] The monovalent cobalt **4** would then undergo transmetalation with the aid of potassium carbonate to yield styryl cobalt **5**. The coordinating proximal nitrogen would accelerate the regioselective insertion of **1a** to yield **6**. Protonation of **6** with **2a** or other possible proton sources, such as potassium hydrogen carbonate, would afford product **3a** and regenerate **4**.



Scheme 2. A plausible mechanism.

Conclusions

We have developed a cobalt-catalyzed addition of alkenylboronic acids to vinyl heteroarenes. Cobalt is cheaper and more abundant than rhodium. In this report, cobalt proves to show similar catalytic activity to rhodium, and to catalyze the unprecedented assembly of organoboronic acids and activated alkenes.

Experimental Section

Typical Procedure

The reaction of 2-vinylpyridine (**1a**) with styrylboronic acid (**2a**) is representative (Table 1, entry 1). Cobalt(II) bromide (5.5 mg, 0.025 mmol), triphenylphosphine (13.1 mg, 0.050 mmol), potassium carbonate (138 mg, 1.0 mmol), and **2a** (222 mg, 1.5 mmol) were placed in a 20 mL reaction flask under argon. Toluene (2.0 mL) was added. A solution of **1a** (52.6 mg, 0.50 mmol) in toluene (1.5 mL) was then added at room temperature. The mixture was stirred for 4 h at reflux. Water (10 mL) was added, and the organic compounds were extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated. Silica gel column purification afforded 1-phenyl-4-(2-pyridyl)-1-butene (**3a**, 101 mg, 0.48 mmol, 96%).

Characterization Data for New Products

1-Phenyl-4-(2-pyridyl)-1-butene (3a): IR (neat): $\tilde{\nu}$=2924, 2855, 1588, 1458, 1373, 964 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.66 (dt, J=7.5, 7.5 Hz, 2H), 2.96 (t, J=7.5 Hz, 2H), 6.26 (dt, J=16.0, 7.5 Hz, 1H), 6.42 (d, J=16.0 Hz, 1H), 7.11 (dd, J=5.0, 7.5 Hz, 1H), 7.14–7.21 (m, 2H), 7.25–7.34 (m, 4H), 7.58 (dt, J=7.5, 2.0 Hz, 1H), 8.55 ppm (d, J=5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=33.21, 38.28, 121.25, 123.02, 126.14, 127.08, 128.60, 129.81, 130.70, 136.43, 137.80, 149.48, 161.44 ppm; elemental analysis: calcd (%) for $C_{15}H_{15}N$: C 86.08, H 7.22; found: C 86.16, H 7.29.

1-Phenyl-4-(2-pyrimidyl)-1-butene (3b): m.p.: 40–44 °C. IR (nujol): $\tilde{\nu}$= 2924, 2855, 2361, 1558, 1458 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.77 (dt, J=7.0, 7.0 Hz, 2H), 3.15 (t, J=7.0 Hz, 2H), 6.30 (dt, J=16.0, 7.0 Hz, 1H), 6.44 (d, J=16.0 Hz, 1H), 7.12 (dd, J=5.0, 5.0 Hz, 1H), 7.18 (dd, J=7.5, 7.5 Hz, 1H), 7.23 (dd, J=7.5, 7.5 Hz, 2H), 7.32 (d, J=7.5 Hz, 2H), 8.68 ppm (d, J=5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=31.93, 39.35, 118.71, 126.20, 127.11, 128.61, 129.60, 130.77, 137.80, 157.19, 170.82 ppm; HRMS (DI-EI$^+$) (m/z) observed: 210.1158 (Δ=+0.7 ppm); calcd for $C_{14}H_{14}N_2$ [M^+]: 210.1157.

1-Phenyl-4-(2-pyrazyl)-1-butene (3c): IR (neat): $\tilde{\nu}$=2924, 2855, 2361, 1458, 1373 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.68 (dt, J=7.0, 7.5 Hz, 2H), 3.00 (t, J=7.5 Hz, 2H), 6.24 (dt, J=16.0, 7.0 Hz, 1H), 6.42 (d, J=16.0 Hz, 1H), 7.20 (dd, J=2.0, 2.0 Hz, 1H), 7.25–7.35 (m, 4H), 8.41 (d, J=2.5 Hz, 1H), 8.48 (s, 1H), 8.52 ppm (d, J=2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ= 32.64, 35.41, 126.21, 127.31, 128.67, 128.93, 131.31, 137.55, 142.50, 144.30, 144.83, 157.04 ppm; elemental analysis: calcd (%) for $C_{14}H_{14}N_2$: C 79.97, H 6.71; found: C 79.82, H 6.75.

1-Phenyl-4-(2-quinolyl)-1-butene (3d): IR (neat): $\tilde{\nu}$=2924, 2855, 2731, 1458, 1373, 1034 cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.76 (dt, J=6.5, 7.5 Hz, 2H), 3.16 (t, J=7.5 Hz, 2H), 6.32 (dt, J=16.0, 6.5 Hz, 1H), 6.45 (d, J=16.0 Hz, 1H), 7.19 (dd, J=7.0, 7.0 Hz, 1H), 7.26–7.34 (m, 5H), 7.49 (dd, J=8.0, 8.0 Hz, 1H), 7.69 (dd, J=8.0, 8.0 Hz, 1H), 7.78 (d, J=8.0 Hz, 1H), 8.06 (d, J=8.0 Hz, 1H), 8.07 ppm (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=33.31, 39.20, 121.66, 125.97, 126.23, 127.01, 127.17, 127.71,

128.66, 129.12, 129.59, 129.83, 130.87, 136.44, 137.86, 148.24, 162.06 ppm; elemental analysis: calcd (%) for $C_{19}H_{17}N$: C 87.99, H 6.61; found: C 88.07, H 6.83.

1-Phenyl-4-(2-thiazolyl)-1-butene (3e): IR (neat): $\tilde{\nu}$ = 3024, 2847, 1705, 1497, 964, 741 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.73 (dt, J = 7.0, 7.0 Hz, 2H), 3.21 (t, J = 7.0 Hz, 2H), 6.26 (dt, J = 16.0, 7.0 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 7.19 (d, J = 3.0 Hz, 1H), 7.20–7.22 (m, 1H), 7.27–7.35 (m, 4H), 7.70 ppm (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 33.27, 33.29, 118.36, 126.26, 127.35, 128.53, 128.68, 131.59, 137.54, 142.47, 170.33 ppm; elemental analysis: calcd (%) for $C_{13}H_{13}NS$: C 72.52, H 6.09; found: C 72.73, H 6.13.

1-Phenyl-4-(3-methyl-2-pyridyl)-1-butene (3i): IR (neat): $\tilde{\nu}$ = 3024, 2932, 1582, 1450, 965, 741 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.33 (s, 3H), 2.65 (dt, J = 7.0. 8.0 Hz, 2H), 2.95 (t, J = 8.0 Hz, 2H), 6.32 (dt, J = 16.0, 7.0 Hz, 1H), 6.44 (d, J = 16.0 Hz, 1H), 7.04 (dd, J = 5.0, 7.5 Hz, 1H), 7.19 (dd, J = 7.0, 7.0 Hz, 1H), 7.26–7.35 (m, 4H), 7.41 (d, J = 7.5 Hz, 1H), 8.40 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 19.02, 32.25, 35.39, 121.39, 126.18, 127.09, 128.65, 130.25, 130.51, 131.15, 137.73, 137.92, 146.95, 159.74 ppm; elemental analysis: calcd (%) for $C_{16}H_{17}N$: C 86.05, H 7.67; found: C 85.80, H 7.74.

1-Phenyl-4-(4-methyl-2-pyridyl)-1-butene (3j): IR (neat): $\tilde{\nu}$ = 3024, 2924, 1605, 1443, 964, 741 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.32 (s, 3H), 2.65 (dt, J = 6.5, 7.5 Hz, 2H), 2.92 (t, J = 7.5 Hz, 2H), 6.27 (dt, J = 16.0, 6.5 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 6.94 (d, J = 5.0 Hz, 1H), 7.00 (s, 1H), 7.17–7.21 (m, 1H), 7.25–7.34 (m, 4H), 8.40 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.18, 33.31, 38.19, 122.34, 123.95, 126.18, 127.10, 128.64, 130.02, 130.63, 137.89, 147.53, 149.24, 161.23 ppm; HRMS (DI-EI$^+$) (m/z) observed: 223.1362 (Δ = +0.4 ppm); calcd for $C_{16}H_{17}N$ [M^+]: 223.1361.

1-Phenyl-4-(5-methyl-2-pyridyl)-1-butene (3k): IR (neat): $\tilde{\nu}$ = 2924, 2855, 1458, 1373, 964 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3H), 2.64 (dt, J = 6.8, 7.8 Hz, 2H), 2.92 (t, J = 7.8 Hz, 2H), 6.26 (dt, J = 16.0, 6.8 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.16–7.21 (m, 1H), 7.25–7.34 (m, 4H), 7.40 (d, J = 8.0 Hz, 1H), 8.37 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 18.23, 33.39, 37.84, 122.49, 126.17, 127.08, 128.63, 130.01, 130.48, 130.63, 137.08, 137.89, 149.85, 158.46 ppm; elemental analysis: calcd (%) for $C_{16}H_{17}N$: C 86.05, H 7.67; found: C 86.06, H 7.78.

3-Methyl-1-phenyl-4-(2-pyridyl)-1-butene (3m): IR (neat): $\tilde{\nu}$ = 3024, 2963, 1589, 1435, 964, 748 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.12 (d, J = 6.0 Hz, 3H), 2.81 (dd, J = 6.0, 12.0 Hz, 1H), 2.83–2.90 (m, 1H), 2.92 (dd, J = 6.0, 12.0 Hz, 1H), 6.18 (dd, J = 7.0, 16.0 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H), 7.08–7.13 (m, 2H), 7.14–7.20 (m, 1H), 7.25–7.32 (m, 4H), 7.57 (dt, J = 2.0, 7.5 Hz, 1H), 8.53 ppm (d, J = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 20.23, 37.92, 45.97, 121.25, 123.90, 126.20, 127.06, 128.61, 128.66, 135.72, 136.24, 137.89, 149.46, 160.71 ppm; HRMS (DI-EI$^+$) (m/z) observed: 223.1364 (Δ = +1.5 ppm); calcd for $C_{16}H_{17}N$ [M^+]: 223.1361.

1-(4-Methylphenyl)-4-(2-pyridyl)-1-butene (3n): IR (neat): $\tilde{\nu}$ = 3017, 2924, 2855, 1589, 1435, 964, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.31 (s, 3H), 2.65 (dt, J = 7.0, 7.5 Hz, 2H), 2.96 (t, J = 7.5 Hz, 2H), 6.21 (dt, J = 15.5, 7.0 Hz, 1H), 6.39 (d, J = 15.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 5.0, 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.58 (dd, J = 8.0, 8.0 Hz, 1H), 8.55 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.30, 33.24, 38.42, 121.25, 123.05, 126.08, 128.82, 129.33, 130.57, 135.08, 136.42, 136.83, 149.53, 161.59 ppm; elemental analysis: calcd (%) for $C_{16}H_{17}N$: C 86.05, H 7.67; found: C 86.24, H 7.84.

1-(2-Methylphenyl)-4-(2-pyridyl)-1-butene (3o): IR (neat): $\tilde{\nu}$ = 3402, 3017, 2361, 1589, 1435, 964, 748 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 3.26 (s, 3H), 2.68 (dt, J = 7.0, 7.5 Hz, 2H), 2.98 (t, J = 7.5 Hz, 2H), 6.12 (dt, J = 16.0, 7.0 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 7.09–7.15 (m, 4H), 7.17 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.59 (dd, J = 7.5, 7.5 Hz, 1H), 8.55 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 19.91, 33.49, 38.41, 121.25, 123.11, 125.71, 126.15, 127.07, 128.77, 130.28, 131.14, 135.17, 136.41, 137.03, 149.53, 161.53 ppm; HRMS (DI-EI$^+$) (m/z) observed: 223.1363 (Δ = +1.1 ppm); calcd for $C_{16}H_{17}N$ [M^+]: 223.1361.

1-(4-Methoxyphenyl)-4-(2-pyridyl)-1-butene (3p): m.p.: 56–58 °C. IR (nujol): $\tilde{\nu}$ = 2855, 2677, 2361, 1458, 1373, 1042 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.63 (dt, J = 7.0, 7.5 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 3.79 (s, 3H), 6.12 (dt, J = 15.5, 7.0 Hz, 1H), 6.36 (d, J = 15.5 Hz, 1H), 6.83 (d, J = 9.0 Hz, 2H), 7.11 (dd, J = 5.0, 7.5 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 9.0 Hz, 2H), 7.58 (dd, J = 7.5, 7.5 Hz, 1H), 8.55 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 33.25, 38.50, 55.45, 114.07, 121.24, 123.04, 127.25, 127.68, 130.07, 130.69, 136.42, 149.51, 158.92, 161.61 ppm; HRMS (DI-EI$^+$) (m/z) observed:239.1315 (Δ = +2.2 ppm); calcd for $C_{16}H_{17}NO$ [M^+]: 239.1310.

4-(2-Pyridyl)-1-(4-trifluoromethylphenyl)-1-butene (3q): m.p.: 66–69 °C. IR (nujol): $\tilde{\nu}$ = 2855, 2677, 2361, 1458, 1373, 1126 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.70 (dt, J = 6.5, 7.5 Hz, 2H), 2.98 (t, J = 7.5 Hz, 2H), 6.37 (dt, J = 16.0, 6.5 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 7.13 (dd, J = 5.0, 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.60 (dd, J = 7.5, 7.5 Hz, 1H), 8.56 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 33.17, 38.02, 121.38, 123.03, 123.37, 125.58 (q, J = 31.0 Hz), 126.29, 128.95 (q, J = 257 Hz), 129.57, 132.73, 136.51, 141.31, 149.58, 161.18 ppm; HRMS (DI-EI$^+$) (m/z) observed: 277.1074 (Δ = −1.7 ppm); calcd for $C_{16}H_{14}F_3N$ [M^+]: 277.1078.

1-(4-Chlorophenyl)-4-(2-pyridyl)-1-butene (3r): m.p.: 51–52 °C. IR (nujol): $\tilde{\nu}$ = 2924, 2855, 2700, 1458, 1373, 1304, 964 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.66 (dt, J = 7.0, 8.0 Hz, 2H), 2.96 (t, J = 8.0 Hz, 2H), 6.24 (dt, J = 16.0, 7.0 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 7.12 (dd, J = 4.5, 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.24 (s, 4H), 7.60 (dd, J = 8.0, 8.0 Hz, 1H), 8.55 ppm (d, J = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 33.18, 38.21, 121.35, 123.05, 127.39, 128.77, 129.59, 130.62, 132.69, 136.35, 136.49, 149.57, 161.35 ppm; elemental analysis: calcd (%) for $C_{15}H_{14}ClN$: C 73.92, H 5.79; found: C 73.88, H 5.82.

4-(2-Pyridyl)-1-(2-thienyl)-1-butene (3s): IR (neat): $\tilde{\nu}$ = 3071, 2845, 1589, 1435, 957, 694 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.62 (dt, J = 7.0, 7.5 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 6.11 (dt, J = 15.5, 7.0 Hz, 1H), 6.54 (d, J = 15.5 Hz, 1H), 6.85 (d, J = 3.5 Hz, 1H), 6.91 (dd, J = 3.5, 5.0 Hz, 1H), 7.07 (d, J = 5.0 Hz, 1H), 7.10 (dd, J = 5.0, 7.5 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.58 (dd, J = 7.5, 7.5 Hz, 1H), 8.54 ppm (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 32.97, 38.15, 121.29, 123.02, 123.42, 123.96, 124.58, 127.36, 129.81, 136.43, 143.01, 149.52, 161.32 ppm; HRMS (DI-EI$^+$) (m/z) observed: 215.0768 (Δ = −0.6 ppm); calcd for $C_{13}H_{13}NS$ [M^+]: 215.0769.

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