PERKIN 1

Rhodium(I)-catalysed alkylation of 2-vinylpyridines with alkenes as a result of C–H bond activation

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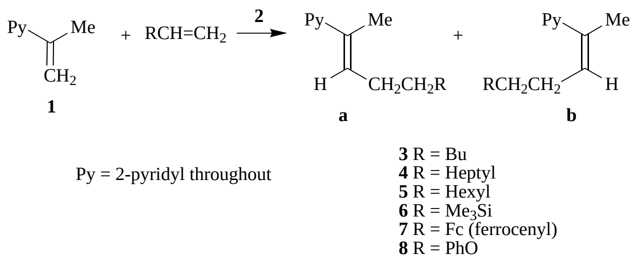
2-Vinylpyridines undergo regioselective β-alkylation with alkenes in the presence of a rhodium(I) complex as a catalyst to give products resulting from an anti-Markownikoff reaction. These results show the feasibility of alkylation of an alkenic position as a result of C–H bond activation. 2-(Prop-1-en-2-yl)pyridine 1 and 1-phenyl-1-(2-pyridyl)ethylene 15 react with linear terminal alkenes to give the corresponding alkylated products in high yields. Cyclic alkenes, allyl alcohol, but-3-en-1-ol and methyl vinyl ketone, however, fail to react with 1. Pent-2-ene gives the linear alkylated product in low yield. 6-Methyl-2-vinylpyridine 24 and 2-vinylpyridine 32 give the alkylated products in low yield together with their dimeric products. The alkenic C–H bond of 2-(cyclohex-1-enyl)pyridine 36 has been regioselectively alkylated. 2-(Cyclohex-1-enyl)pyridine 36 with alkenes in the presence of the Rh^{I} catalyst undergoes regiospecific alkylation at the alkenic position.

In connection with the formation of C–C bonds by activation of C–H bonds, we,[1] together with other groups[2–4] have recently studied the alkylation of aromatic rings with alkenes in the presence of a transition metal complex (Rh, Ru). Nevertheless, transition metal-catalysed, catalytic alkylation at the vinylic position of alkenes as a result of C–H bond activation by transition metal complexes is still rare.[5–7] Recently, Murai *et al.*[6] and Trost *et al.*[7] independently reported that addition of trisubstituted α,β-enones to alkenes was successfully achieved with $[RuH_2(Ph_3P)_3(CO)]$ as a catalyst. Vinylpyridines are known to be good substrates for cyclometallation[8] and vinylic C–H bond activation of alkenes by transition metal complexes has been well investigated.[9] We reported the original paper on rhodium-catalysed cross-coupling of alkenes as a result of C–H bond activation. Alkylation of various vinylpyridines with terminal alkenes and a transition-metal catalyst was then attempted. 2-Vinylpyridines reacted with various alkenes at the β-position in the presence of the Rh^{I} complex as a catalyst to give highly selectively cross-coupled β-alkylated products. Some preliminary results of this work have already been communicated.[5]

Results and discussion

2-(Prop-1-en-2-yl)pyridine **1** was chosen as a substrate for the alkylations with various alkenes, the C–H bond activation being induced by a Wilkinson complex **2** (Scheme 1).



Scheme 1

2-(Prop-1-en-2-yl)pyridine **1** reacted with hex-1-ene (5-fold excess) in toluene (110 °C for 19 h) in the presence of Wilkinson complex **2** (10 mol%) as a catalyst to give quantitatively the alkylated product, a mixture of (*E*)- and (*Z*)-2-(non-2-enyl)-pyridines **3**. This result was confirmed by a NOE difference experiment between the methyl group and one proton of the vinyl group.[10] No dimeric or polymeric form of **1** was detected in the reaction mixture. To see how temperature affected the alkylation, a reaction was carried out at 80 °C: this gave the *E* isomer **3a** of 2-(non-2-enyl)pyridine as the major product (*E*:*Z* = 93:7) in 73% isolated yield as shown in run 4 (Table 3). There was no reaction at room temperature. The alkylation of **1** with alkenes proceeded well at 110 °C. In order to check the relationship between the reactivity and the amount of alkenes employed, 2 and 5 equiv. of hex-1-ene were used. As shown in Table 1 and Table 2, use of 5 equiv. of hex-1-ene shortened the reaction time compared with that when 2 equiv. of alkene were employed. In the initial stage of the reaction the *Z* isomer was the major product, the proportion of the *E* isomer increasing with time. Use of 10 equiv. of hex-1-ene resulted in completion of the reaction in 4 h; the rate of isomerization of the *Z* isomer to the *E* isomer was slow (*E*:*Z* = 6:4) as shown in run 5 (Table 3). The results obtained from the alkylation of **1** with various alkenes are listed in Table 3.

Table 1 The change of ratio of isomers *vs.* time with 2 equiv. of hex-1-ene in the alkylation of **1**

Time (h)	*Z* Isomer	*E* Isomer	Conversion (%)
0.5	72	28	8
1.5	44	56	61
2.3	20	80	72
3.25	17	83	76
4	15	85	80

Table 2 The change of ratio of isomers *vs.* time with 5 equiv. of hex-1-ene in the alkylation of **1**

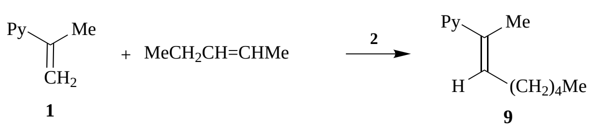
Time (h)	*Z* Isomer	*E* Isomer	Conversion (%)
0.5	65	35	18
1.25	74	26	78
2.0	60	40	89
2.83	52	48	96
3.5	43	57	98

Table 3 The results of the alkylation of **1** [a]

Run	Alkene	Reaction temp. (°C) [b]	Reaction time (h)	Product	Yield (%) [c]	*E*:*Z*
1	Hex-1-ene	110	19	**3**	96	93:7
2	Non-1-ene	115	20	**4**	99	92:8
3	Oct-1-ene	115	20	**5**	99	90:10
4	Hex-1-ene	80	20	**3**	73	93:7
5	Hex-1-ene [d]	110	4	**3**	100	60:40
6	Pent-2-ene	100	48	**9a**	6	100:0
7	$Me_3SiCH{=}CH_2$	110	19	**6**	64 [e]	90:10
8	$FcCH{=}CH_2$ [f]	110	19	**7a**	20	100:0
9	Allyl phenyl ether	110	20	**8**	65	90:10

[a] **1**:**2**:Alkene = 1:0.1:5 in toluene. [b] Oil bath. [c] Isolated yield. [d] 10 Equiv. of alkene was used. [e] Isolated yield including the bisalkylated product (44%). [f] Fc = ferrocenyl; 2 equiv. of the alkene was used.

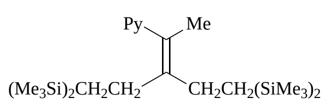
Pent-2-ene provided only the alkylated product **9a**, the *E* isomer, in 6% yield after 48 h as shown in run 6, most of the starting materials being recovered (see Scheme 2). Neither



Scheme 2

branched-chain products nor the *Z* isomer were observed in the reaction mixture, probably because of the instability of the secondary alkylmetal complex. Generally, internal alkenes give low product yields, the reactions being very sluggish because of the difficulty of coordination between the metal and internal alkenes.[11] Although isomerization of an internal alkene to a terminal alkene is rare, one example is the formation of a linear terminal product from pent-2-ene during hydroformylation.[11]

Cyclic alkenes such as cyclohexene and cyclopentene gave only trace amounts of the alkylated product, starting material being recovered. The vinyl(trimethyl)silane gave the doubly alkylated product **10** as the major product (44%) together with



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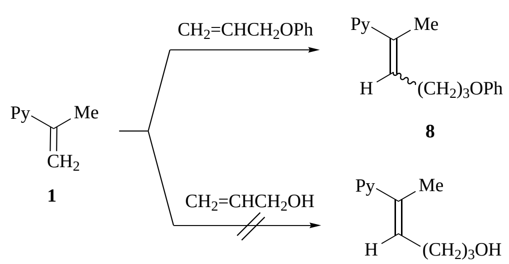
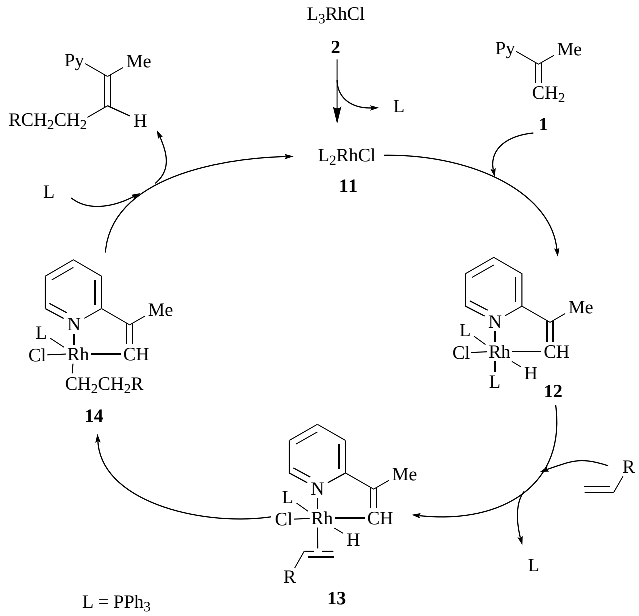
mono alkylated product **6** (20%) (see run 7). The rate of alkylation in vinyl(trimethyl)silane was faster than that of aliphatic alk-1-enes probably because it was unable to isomerize.[12] Methyl vinyl ketone failed to react to give alkylated products at 70 °C during 45 h, Diels–Alder product being detected in the reaction mixture together with starting material **1**. Allyl alcohol and but-3-en-1-ol were also unreactive, starting materials being recovered. On the other hand, allyl phenyl ether gave the alkylated product **8** in good yield (65%) together with trace amounts of 2-(hex-2-en-2-yl)pyridine as shown in run 10 (Scheme 3).



Scheme 3

A possible mechanism for the reaction may be postulated as shown in Scheme 4. The reaction appears to be initiated by formation of the highly reactive rhodium complex **11** by liber-



Scheme 4 A possible mechanism for the alkylation by C–H bond activation of **1**

ation of one ligand which reacts with **1** to form the rhodium(III) hydride complex **12** by cleavage of a vinyl C–H bond. Formation of the reactive metal complex **11** from the Wilkinson complex **2** in solution is well known.[13] The insertion of a hydride from the vinyl hydride rhodium(III) complex **13** into the coordinated alkene should form the hydrometallated complex intermediate **14** according to the anti-Markownikoff rule. This intermediate complex **14** then gives the alkylated product and **11** for the catalytic cycle by external ligand. Subsequently, the alkylated product couples with the external alkene to give the doubly alkylated product. No Markownikoff addition product could be detected.

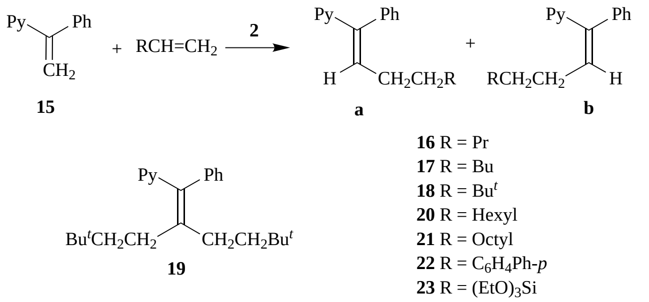
1-Phenyl-1-(2-pyridyl)ethylene **15** containing an α-phenyl group reacted with pent-1-ene (5 equiv.) in toluene (90 °C for 18 h) in the presence of Wilkinson complex **2** (10 mol%) to give a mixture of *E* **16a** and *Z* **16b** isomers of the alkylated product, 1-phenyl-1-(2-pyridyl)hept-1-ene (77%; *E*:*Z*, 73:27) (Scheme 5).

In order to see the effects of reaction temperature, compound **15** was treated with hex-1-ene in the presence of Wilkinson complex (10 mol%) in toluene at various temperatures[5] (Scheme 6). No alkylation occurred at 21 °C, starting material being quantitatively recovered. Alkylation occurred, however, at 60–67 °C to give the *Z* isomer **17b** of 1-phenyl-1-pyridyloct-1-ene (8%). This result provides evidence for concerted reductive elimination.[14] At 100 °C the reaction gave both isomers of 1-phenyl-1-(2-pyridyl)oct-1-ene **17** (83%; *E*:*Z*, 80:20). Similarly at 130 °C the reaction gave **17a** and **17b** quantitatively (*E*:*Z* = 70:30). As the reaction temperature increases, the reaction rate

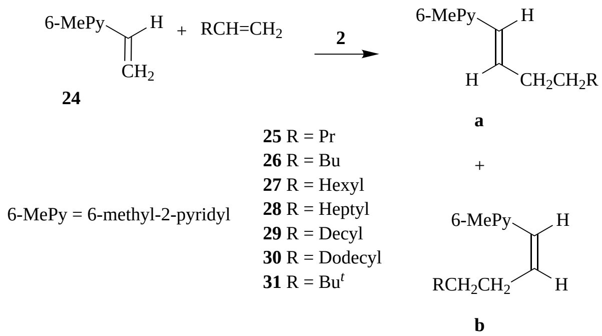
Table 4 The results of the alkylation of **15**[a]

Run	Alkene	Reaction temp. (°C)	Reaction time (h)	Product	Yield (%)[b]	E:Z
1	Pent-1-ene	90	18	**16**	77	73:27
2	Hex-1-ene	100	24	**17**	83	80:20
3	Hex-1-ene	60–67	18	**17b**	8	0:100
4	Hex-1-ene	130	24	**17**	99	70:30
5	Oct-1-ene	100	24	**20**	86	76:24
6	Dec-1-ene	110	18	**21**	78	75:25
7	$Bu^tCH{=}CH_2$	110	12	**18**	61[c]	76:24
8	$Bu^tCH{=}CH_2$	100	16	**18**	92[d]	64:36
9	*p*-Methylstyrene	120–130	42	**22**	31	76:24
10	$(EtO)_3SiCH{=}CH_2$	110	18	**23**	73	50:50

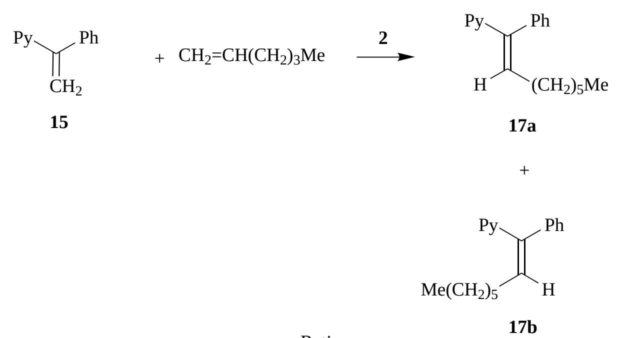
[a] **13**:**2**:Alkene = 1:0.1:5 in toluene. [b] Isolated yield. [c] Isolated yield including the bisalkylated product **19** (28%). [d] Isolated yield including the bisalkylated product **19** (13%).



Scheme 5



Scheme 7



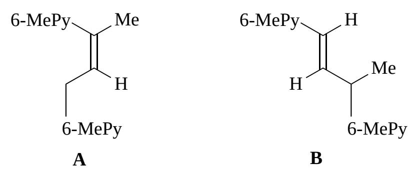
t/°C	% Yield	Ratio **17a**	: **17b**
21	–	–	–
65	8	0	100
100	83	80	20
130	99	70	30

Scheme 6

is accelerated. With 5 mol% of Wilkinson complex at 130–140 °C, the maximum turnover figure was 13 (67%; E:Z, 79:21). The structures of the Z and E isomers were confirmed by NOESY. Results for the alkylation of 1-phenyl-1-(2-pyridyl)-ethylene **15** with a variety of alkenes are listed in Table 4.

Linear long-chain alkenes such as oct-1-ene and dec-1-ene gave excellent product yields (runs 5 and 6). In particular, 3,3-dimethylbut-1-ene gave a doubly alkylated product **19** with both isomers of the mono alkylated product **18** (92%; run 8). *p*-Methylstyrene required a longer reaction time (42 h) to give a low product yield (31%; run 9). Alkylation of **15** and vinyltriethoxysilane gave the same ratio of Z and E isomers of the mono alkylated product **23** (73%). Methyl vinyl ketone and allyl alcohol were inert under the same reaction conditions.

6-Methyl-2-vinylpyridine **24** reacted with pent-1-ene (100–110 °C for 74 h) in toluene in the presence of Wilkinson complex **2** (10 mol%) to afford a mixture of *trans* (**a**) and *cis* (**b**) products (Scheme 7). After disappearance of the starting material, GC–MS analysis showed the presence of 2 sets of products having different molecular weight (189 and 238) in the reaction mixture. The products were easily separated by column chromatography (silica gel, 70–230 mesh). In order to elucidate the structure of the first-eluted compound (R_F 0.57, hexane–EtOAc, 10:1; 30% isolated yield) its ^{1}H NMR spectrum was recorded: whilst three pyridine ring proton signals remained, those for the vinylic protons of the vinylpyridine had disappeared and been replaced by alkenic proton and pentyl group signals at 5.86 ppm (double triplets, J 11.8, 7.4 Hz) and in the aliphatic region. This compound was identified as the *cis* isomer **25b** of 6-methyl-2-(hept-1-enyl)pyridine, the desired alkylation product (*cis*:*trans*, 95:5; run 1 in Table 5). The second-eluted material was identified as a dimer of **24** (69% isolated yield; **A**:**B** = 54:46). Brookhart and co-workers reported that attempts to catalyse the dimerization of 2-vinylpyridine by rhodium complex $[RhCp^*(C_2H_4)(CH_2CH_2\text{-}\mu\text{-}H)]^+$ was unsuccessful.[15] But, in this system, the major product was a mixture of dimers of **24**, the structures of which were identified as **A** and **B** from ^{1}H NMR and mass spectroscopic evidence.



6-MePy = 6-methyl-2-pyridyl

An attempt to increase the yield of the alkylated product, by carrying out the reaction at a higher reaction temperature (160 °C) gave the *trans* isomer **25a** (J 15.8) of the alkylated product as the major product but without the expected yield enhancement. The structure of the alkylated product **25a** confirmed by comparison of its ^{1}H NMR signals with those of 6-methyl-2-(hept-1-enyl)pyridine prepared from 6-methylpyridine-2-carbaldehyde and hexyl(triphenyl)phosphonium bromide by a Wittig reaction (*trans*:*cis* = 98:2; 53% yield). In the case of hex-1-ene, the alkylation gave the *cis* isomer **26b** as the major product (*cis*:*trans* = 96:4; 17% yield) at 120 °C but the *trans* isomer **26a** as the major product (*cis*:*trans* = 2:98; 19% yield) at 157–160 °C. To understand the effects of the temperature dependence, the reaction was carried out at 90–100 °C.

Table 5 Alkylation of **24** with various alkenes[a]

Run	Alkene	Reaction time (h)	Reaction temp. (°C)	Solvent	Product	Yield (%)[b]	*cis* : *trans*
1	Pent-1-ene	74	100–110	Toluene	**25**	30	95 : 5
2	Oct-1-ene	95	90–95	Benzene	**27**	15	93 : 7
3	Non-1-ene	96	140	Toluene	**28**	25	19 : 81
4	Non-1-ene	96	90–100	Toluene	**28**	15	100 : 0
5	Dodec-1-ene	96	140	Toluene	**29**	22	14 : 86
6	Hex-1-ene	96	157–160	Toluene	**26**	19	2 : 98
7	Tetradec-1-ene	96	157–160	Toluene	**30**	17	1 : 99
8	Penta-1,3-diene	24	110	Toluene		11[c]	
9	3,3-Dimethylbut-1-ene			Toluene	**31**	20	65 : 35
10	Pent-1-ene	72	100–110	Dioxane	**25**	26	71 : 29

[a] **24** : **2** : Alkene = 1 : 0.1 : 5. [b] Isolated yield. [c] Isolated as a mixture of isomers.

Table 6 Alkylation of **32** with alkenes[a]

Run	Alkene	Reaction time (h)	Reaction temp. (°C)	Product	Yield (%)[b]	*cis* : *trans*
1	Hex-1-ene	96	100	**33**	15	57 : 43
2	Pent-1-ene	96	100	**34**	11	68 : 32
3	Non-1-ene	49	110	**35**	15	36 : 64

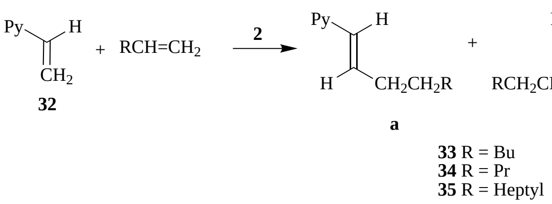
[a] **32** : **2** : Alkene = 1 : 0.1 : 5. [b] Isolated yield.

Surprisingly, the reaction gave exclusively the *cis* isomer **26b**, the *trans* isomer **26a** not being detected by GC in the reaction mixture.

In an attempt to understand the isomerization mechanism, the *cis*-isomer **25b** was first heated (3 h at 150–180 °C) in toluene in the absence of the Rh^I catalyst; it easily isomerized to the *trans*-isomer **25a** (>97% purity). When heated at 100 °C in the presence of alkene and Rh^I catalyst for 22 h in toluene **25b** gave a mixture of **25a** : **25b** in the ratio of 89 : 11. These results show that *cis* to *trans* isomerization easily occurs under thermal conditions both in the absence and the presence of a Rh^I catalyst.

Various terminal alkenes were subjected to the alkylation. Long-chain linear alkenes such as oct-1-ene, non-1-ene, dec-1-ene and tetradec-1-ene gave mixtures of *cis* and *trans* isomers in low yields (runs 2, 3, 5, 7 in Table 5). Excess of a phosphine ligand or silver salts ($AgBF_4$ or $AgClO_4$) failed to increase the yield of the alkylated product. Of the various solvents employed, toluene was found to be the best. Use of dioxane instead of toluene at the same reaction temperature, increased the proportion of *trans* isomer obtained without increasing the yield of the alkylated products (run 10 in Table 5). The results of alkylation of **24** are listed in Table 5.

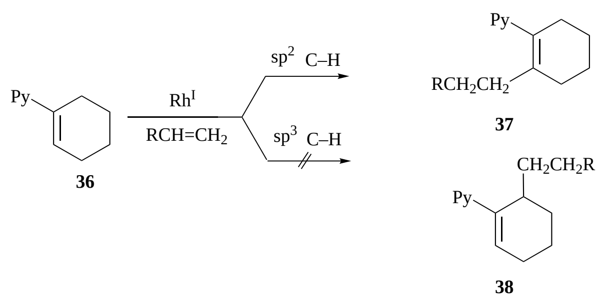
In order to compare the reactivity of **32** and **24**, the former was treated with hex-1-ene in the presence of Wilkinson catalyst (10 mol%) at 100 °C for 96 h to give the alkylated product **33** (15%) (Scheme 8). The results obtained are listed in Table 6.



Scheme 8

Under stoichiometric conditions, the proportion of *trans* isomer increased; the ratio of *trans* : *cis* = 69 : 31 (36%).

2-Cyclohex-1-enylpyridine **36**, which has two types of C–H bond (sp^2 and sp^3 C–H) at the reaction site, upon treatment with 3,3-dimethylbut-1-ene in the presence of Rh^I complex[16] (10 mol%) {prepared from $[(C_8H_{14})_2RhCl]_2$ and tricyclohexylphosphine (Cy_3P)} gave 2-[2-(3′,3′-dimethylbutyl)cyclohex-1-enyl]pyridine **37** (R = Bu^t) as the alkylated product by sp^2 C–H bond activation (Scheme 9). Compound **38**, 2-[6-(3′,3′-dimethylbutyl)cyclohex-1-enyl]pyridine, the putative product of sp^3 C–H bond activation, was not obtained. Wilkinson complex **2** gave a trace of the alkylated product. Use of 10 mol% of Rh^I catalyst and 3,3-dimethylbut-1-ene (3 equiv.) gave a 75% conversion, while use of more (5 equiv.) 3,3-dimethylbut-1-ene gave a lower yield (73%). Use of 15 mol% of Rh^I catalyst gave a 95% conversion of **36** (isolated yield, 85%) at 110 °C for 22 h.



Scheme 9

Experimental

^1H NMR spectra were recorded on Bruker AC-300F (300 MHz) and Bruker AC-200 (200 MHz) instruments. The chemical shifts are reported in ppm relative to internal tetramethylsilane in $CDCl_3$. ^{13}C NMR spectra were recorded on Bruker AC-300F (75 MHz) and Bruker AC-200 (50.3 MHz) machines. IR spectra were run on a Nicolet magna 550 FT-IR instrument. Mass spectra were measured with a HP-5971A mass spectrometer which was equipped with a Hewlett-Packard 5890 series II gas chromatograph using the electron impact method (70 eV). The silica gel used in column chromatography was from Aldrich (Merck, 230–400 mesh). Analytical thin layer chromatography was performed on glass plates (0.25 mm) coated with silica gel 60F 254 from Aldrich. Elemental analyses were carried out by the Analytical Laboratory at the ADD.

General procedure for the alkylation of 2-vinylpyridines

A screw-capped pressure vial (2.5 ml) was charged with **1** (50 mg, 0.4196 mmol), alkene (2.1 mmol, 5 equiv.) and **2** (38.8 mg, 0.042 mmol, 10 mol%) in toluene (2 ml). The stirred reaction mixture was heated at 80–160 °C for 4–96 h and then concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc–hexane, 1 : 10).

2-(Non-2-enyl)pyridine 3a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.46; δ_H(300 MHz; $CDCl_3$) 8.54 (1H, d, *J* 4.9, 6-H in Py), 7.58 (1H, t, *J* 7.6, 4-H in Py), 7.37 (1H, d, *J* 7.9, 3-H in Py), 7.06 (1H, t, *J* 7.3, 5-H in Py), 6.38 (1H, t, *J* 7.7, =CH), 2.25 (2H, q, *J* 7.3, =CHCH_2), 2.09 (3H, s, =CCH_3), 1.30–1.51 [8H, $(CH_2)_4$] and 0.89 (3H, t, *J* 5.9, CH_3); δ_C(75 MHz; $CDCl_3$) 160.02, 148.59, 136.01, 134.18, 131.99, 121.06, 119.42, 31.69, 29.25, 29.07, 28.78, 22.54, 14.11 and 13.99; *m*/*z* 203 (M^+, 22%), 202 ($M^+ - 1$, 8), 188 ($M^+ - CH_3$, 9), 174 (M^+ − Et, 10), 160 (M^+ − Pr, 16), 146 (M^+ − Bu, 100), 133 (27), 132 (M^+ − pentyl, 71), 117 (57) and 106 (16); ν_{max}(NaCl)/cm^{-1} 3082w, 3049w, 2999m, 2956s, 2926vs, 2871s, 2856s, 1645w, 1585s, 1564m, 1467s, 1431s, 1379m, 1281w, 1154w, 1099w, 1071w, 1047w, 990w, 776s, 743m, 723w and 617w (Found: C, 83.03; H, 10.50; N, 6.47. $C_{14}H_{21}N$ requires C, 82.70; H, 10.41; N, 6.89%); **3b** (*Z* isomer); R_F (EtOAc–hexane, 1 : 10) 0.38; δ_H(300 MHz; $CDCl_3$) 8.61 (1H, d, *J* 4.9, 6-H in Py), 7.63 (1H, t, *J* 7.7, 4-H in Py), 7.18 (1H, d, *J* 7.9, 3-H in Py), 7.12 (1H, dd, *J* 7.6, 4.9, 5-H in Py), 5.63 (1H, t, *J* 7.4, =CH), 2.11 (3H, s, =CCH_3), 2.00–2.09 (2H, =CHCH_2), 1.18–1.38 [8H, $(CH_2)_4$] and 0.85 (3H, t, *J* 7.0, CH_3); δ_C(75 MHz; $CDCl_3$) 160.20, 149.16, 135.68, 135.38, 130.60, 123.17, 121.26, 31.66, 29.90, 29.04, 28.91, 23.74, 22.55 and 14.03; *m*/*z* 203 (M^+, 16%), 188 ($M^+ - CH_3$, 3), 174 (M^+ − Et, 2), 160 (M^+ − Pr, 7), 147 (12), 146 (M^+ − Bu, 100), 144 (7), 132 (M^+ − pentyl, 19), 131 (28), 130 (20), 118 (8), 117 (23) and 106 (8); ν_{max}(NaCl)/cm^{-1} 3013w, 2957s, 2925s, 2872m, 2855s, 1586s, 1563m, 1468s, 1431m, 1373w, 1153w, 1049w, 998w, 787m, 748m and 626w.

2-(Dodec-2-enyl)pyridine 4a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.40; δ_H(300 MHz; $CDCl_3$) 8.54 (1H, d, *J* 4.9, 6-H in Py), 7.59 (1H, dt, *J* 8.0, 2.0, 4-H in Py), 7.38 (1H, d, *J* 8.1, 3-H in Py), 7.07 (1H, dd, *J* 7.4, 4.9, 5-H in Py), 6.38 (1H, t, *J* 7.2, =CH), 2.25 (2H, q, *J* 7.2, =CHCH_2), 2.09 (3H, s, =CCH_3), 1.47 (2H, q, *J* 7.1, =CHCH$_2$CH_2), 1.27 [12H, br s, $(CH_2)_6$] and 0.84–0.91 (3H, m, CH_3); δ_C(75 MHz; $CDCl_3$) 160.06, 148.63, 136.04, 134.21, 132.04, 121.09, 119.45, 31.83, 29.52, 29.43, 29.32, 29.27, 28.99, 28.81, 22.60, 14.14 and 14.03; *m*/*z* 245 (M^+, 19%), 244 ($M^+ - 1$, 7), 230 ($M^+ - CH_3$, 7), 216 ($M^+ - CH_2CH_3$, 6), 202 [$M^+ - (CH_2)_2CH_3$, 6], 188 [$M^+ - (CH_2)_3CH_3$, 8], 174 [$M^+ - (CH_2)_4CH_3$, 11], 160 [$M^+ - (CH_2)_5CH_3$, 13], 147 (15), 146 [$M^+ - (CH_2)_6CH_3$, 100], 144 (10), 133 (30), 132 [$M^+ - (CH_2)_7CH_3$, 62], 131 (22), 130 (22), 120 (13), 118 [$M^+ - (CH_2)_8CH_3$, 17], 117 (42), 107 (12) and 106 (15); ν_{max}(NaCl)/cm^{-1} 3082w, 3049w, 2988m, 2955s, 2925vs, 2854s, 1646w, 1585s, 1564m, 1467s, 1431s, 1378m, 1281w, 1153w, 1099w, 1071w, 1046w, 990w, 776s, 742m, 722w and 613w (Found: C, 82.90; H, 11.10; N, 6.00. $C_{17}H_{27}N$ requires C, 83.20; H, 11.09; N, 5.71%).

2-(Undec-2-enyl)pyridine 5a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.38; δ_H(300 MHz; $CDCl_3$) 8.55 (1H, d, *J* 4.4, 6-H in Py), 7.59 (1H, t, *J* 7.5, 4-H in Py), 7.38 (1H, d, *J* 8.3, 3-H in Py), 7.08 (1H, dd, *J* 7.5, 4.7, 5-H in Py), 6.39 (1H, t, *J* 7.9, =CH), 2.26 (2H, q, *J* 7.3, =CHCH_2), 2.10 (3H, s, =CCH_3), 1.47 (2H, q, *J* 7.0, =CHCH$_2$CH_2), 1.27 [10H, br s, $(CH_2)_5$] and 0.85–0.91 (3H, m, CH_3); δ_C(75 MHz; $CDCl_3$) 160.08, 148.64, 136.06, 134.22, 132.07, 121.11, 119.47, 31.84, 29.44, 29.33, 29.24, 28.82, 22.61, 14.16 and 14.03; *m*/*z* 231 (M^+, 17%), 230 ($M^+ - 1$, 7), 216 ($M^+ - CH_3$, 8), 202 ($M^+ - CH_2CH_3$, 6), 188 [$M^+ - (CH_2)_2CH_3$, 8], 174 [$M^+ - (CH_2)_3CH_3$, 11], 160 [$M^+ - (CH_2)_4CH_3$, 14], 147 (14), 146 [$M^+ - (CH_2)_5CH_3$, 100], 144 (10), 133 (31), 132 [$M^+ - (CH_2)_6CH_3$, 66], 131 (25), 130 (25), 120 (16), 118 [$M^+ - (CH_2)_7CH_3$, 19], 117 (49), 107 (12) and 106 (14); ν_{max}(NaCl)/cm^{-1} 3082w, 3049w, 2998m, 2955s, 2925vs, 2854s, 1646w, 1585s, 1564m, 1467s, 1431s, 1378m, 1281w, 1153w, 1099w, 1071w, 1046w, 990w, 776s, 742m, 722w and 613w (Found: C, 82.90; H, 11.08; N, 6.02. $C_{16}H_{25}N$ requires C, 83.06; H, 10.89; N, 6.05%).

2-(5-Trimethylsilylpent-2-enyl)pyridine 6a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.48; δ_H(300 MHz; $CDCl_3$) 8.51 (1H, d, *J* 4.7, 6-H in Py), 7.55 (1H, t, *J* 8.5, 4-H in Py), 7.34 (1H, d, *J* 8.1, 3-H in Py), 7.02–7.09 (1H, m, 5-H in Py), 6.35 (1H, t, *J* 7.6, =CH), 1.83–1.89 (2H, m, =CHCH_2), 2.06 (3H, s, =CCH_3), 0.51–0.57 (2H, m, =CHCH$_2$CH_2) and −0.01 [9H, s, Si(CH_3)$_3$]; *m*/*z* 219 (M^+, 21%), 218 ($M^+ - 1$, 9), 204 ($M^+ - CH_3$, 13), 176 (11), 147 (12), 146 ($M^+ - SiMe_3$, 98), 144 (10), 132 (21), 131 (20), 130 (15), 118 (6), 117 (18), 92 (12), 74 (9), 73 ($SiMe_3^+$, 100) and 51 (10); ν_{max}(NaCl)/cm^{-1} 2953s, 2922m, 2897m, 1644w (*E*), 1585s, 1564m, 1467s, 1431s, 1379w, 1248s, 1174w, 1046w, 990w, 920w, 860s, 836s, 777s, 746s and 692m.

2-{2-[2,2-Bis(trimethylsilyl)ethyl]prop-2-enyl}pyridine 10. δ_H(300 MHz; $CDCl_3$) 8.56–8.60 (1H, m, 6-H in Py), 7.61 (1H, t, *J* 7.6, 4-H in Py), 7.07–7.13 (2H, 3,5-H in Py), 2.09–2.18 (4H, =CCH_2), 1.97 (3H, s, =CCH_3), 0.67–0.73 (4H, =CHCH$_2$CH_2) and 0.46 [18H, s, Si$(CH_3)_3$]; δ_C(75 MHz; $CDCl_3$) 163.15, 149.15, 142.28, 135.82, 128.87, 123.20, 120.81, 25.32, 24.88, 18.81, 15.49, 13.38 and −1.86; *m*/*z* 319 (M^+, 7%), 304 ($M^+ - CH_3$, 6), 246 ($M^+ - SiMe_3$, 14), 232 ($M^+ - CH_2SiMe_3$, 5), 218 ($M^+ - CH_2CH_2SiMe_3$, 14), 158 (4), 144 (9), 92 (10), 74 (10), 73 ($SiMe_3^+$, 100) and 59 (9); ν_{max}(NaCl)/cm^{-1} 2954s, 2897m, 2875m, 1586s, 1562m, 1468s, 1428m, 1372w, 1248s, 1173w, 1148w, 1095w, 1076w, 1045w, 990w, 912w, 861s, 837s, 789m, 748s and 691m.

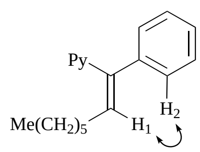
2-(5-Ferrocenylpent-2-enyl)pyridine 7a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.35; δ_H(300 MHz; $CDCl_3$) 8.56 (1H, d, *J* 4.9, 6-H in Py), 7.61 (1H, t, *J* 7.5, 4-H in Py), 7.38 (1H, d, *J* 8.1, 3-H in Py), 7.08–7.14 (1H, m, 5-H in Py), 6.40–6.45 (1H, m, =CH), 4.0–4.16 (9H, Fc), 2.43–2.56 [4H, m, =CH(CH_2)$_2$] and 2.09 (3H, s, =CCH_3); δ_C(75 MHz; $CDCl_3$) 159.92, 148.84, 148.71, 136.20, 131.23, 121.31, 119.58, 68.44, 68.03, 67.15, 30.41, 29.29 and 14.28; *m*/*z* 331 (M^+, 43), 266 (M^+ − Fc, 100), 199 ($FcCH_2^+$, 60), 121 (77), 85 (36), 83 (60) and 56 (42); ν_{max}(NaCl)/cm^{-1} 3090m, 3049w, 2997w, 2922m, 2853w, 1644w (*E*), 1584s, 1564m, 1467s, 1431s, 1380w, 1281w, 1154w, 1105s, 1042m, 1024w, 1001m, 818s, 777s and 744m (Found: C, 72.30; H, 6.27; N, 4.27. $C_{20}H_{21}NFe$ requires C, 72.52; H, 6.39; N, 4.23%).

2-(5-Phenoxypent-2-enyl)pyridine 8a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.26; δ_H(300 MHz; $CDCl_3$) 8.52–8.55 (1H, m, 6-H in Py), 7.61 (1H, t, *J* 7.5, 4-H in Py), 7.37 (1H, d, *J* 7.9, 3-H in Py), 6.81–7.29 (6H, 5-H in Py and H in Ph), 6.40 (1H, t, *J* 7.4, =CH), 3.98 (2H, t, *J* 6.3, PhOCH_2), 2.45 (2H, q, *J* 7.3, =CCH_2), 2.10 (3H, s, =CCH_3) and 1.95 (2H, quintet, *J* 6.9, =CH$_2$CH_2); δ_C(75 MHz; $CDCl_3$) 159.76, 158.88, 148.47, 136.42, 135.05, 130.85, 129.30, 121.45, 120.44, 119.80, 114.40, 66.89, 28.79, 25.17 and 14.27; *m*/*z* 253 (M^+, 26%), 176 [$M^+ - (CH_2)_3O$, 1.4], 160 (M^+ − OPh, 34), 158 (8), 147 (12), 146 ($M^+ - CH_2OPh$, 100), 144 (31), 133 (37), 132 [$M^+ - (CH_2)_2OPh$, 51], 131 (41), 130 (47), 120 (25), 118 [$M^+ - (CH_2)_3OPh$, 14], 117 (51), 94 ($PhOH^+$, 5), 93 (PhO^+, 7), 78 (Py^+, 12), 77 (Ph^+, 20), 65 (16) and 51 (10); ν_{max}(NaCl)/cm^{-1} 3060w, 3044w, 2999w, 2942m, 2871w, 1646w (*E*), 1590s, 1586s, 1564m, 1497s, 1470s, 1432s, 1385w, 1302w, 1270w, 1245s (C–O–C), 1172m, 1154w, 1080w, 1038s, 883w, 814w, 776s, 754s, 692s and 511w; **8b** (*Z* isomer); R_F (EtOAc–hexane, 1 : 10) 0.21; δ_H(300 MHz; $CDCl_3$) 8.56–8.60 (1H, m, 6-H in Py), 7.60 (1H, t, *J* 7.7, 4-H in Py), 6.81–7.30 (7H, 3,5-H in Py and H in Ph), 5.66 (1H, t, *J* 7.5, =CH), 3.91 (2H, t, *J* 6.4, PhOCH_2), 2.28 (2H, q, *J* 7.5, =CCH_2), 2.12 (3H, s, =CCH_3) and 1.85 (2H, quintet, *J* 6.9, =CH$_2$CH_2); δ_C(75 MHz; $CDCl_3$) 159.87, 158.91, 149.20, 136.26, 135.85, 129.34, 129.16, 123.11, 121.44, 120.45, 114.43, 66.98, 29.43, 25.50 and 23.85; *m*/*z* 253 (M^+, 10%), 160 (M^+ − OPh, 11), 147 (12), 146 ($M^+ - CH_2OPh$, 100), 144 (11), 133 (52), 132 [$M^+ - (CH_2)_2OPh$, 23], 131 (33), 130 (30), 118 [$M^+ - (CH_2)_3OPh$, 8], 117 (24), 94 ($PhOH^+$, 4), 93 (PhO^+, 5), 78 (Py^+, 11), 77 (Ph^+, 19), 65 (14) and 51 (14); ν_{max}(NaCl)/cm^{-1} 3060w, 3040w, 2940w, 2922w, 2871w, 1600s, 1586s, 1562w, 1497s, 1469s, 1431m, 1245s (C–O–C), 1038m, 752s and 692m.

1-Phenyl-1-pyridylhept-1-ene 16a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.39; δ_H(300 MHz; $CDCl_3$) 8.56–8.60 (1H, m, 6-H in Py), 7.47 (1H, dt, *J* 7.7, 1.8, 4-H in Py), 7.18–7.43 (5H, m, H in Ph), 7.04 (1H, dd, *J* 7.5, 7.7, 5-H in Py), 6.92 (1H, t, *J* 7.7, CH=), 6.86 (1H, d, *J* 7.7, 3H in Py), 2.10 (2H, q, *J* 7.8, $=CCH_2$), 1.31–1.55 (2H, m, CH_2CH_2C=), 1.24–1.30 (4H, m, $CH_3CH_2CH_2$) and 0.85 (3H, t, *J* 6.7, CH_3); δ_C(75 MHz; $CDCl_3$) 158.59, 149.02, 140.42, 139.00, 136.07, 133.91, 129.87, 128.29, 126.96, 121.90, 121.35, 31.49, 29.56, 29.19, 22.41 and 13.89; *m*/*z* 252 (M^+ + 1, 7%), 251 (M^+, 36), 250 (M^+ − 1, 5), 222 (4), 209 (18), 208 (100), 194 (21), 193 (32), 192 (11), 180 (13), 167 (18), 93 (8), 92 (22), 91 (39) and 51 (8); ν_{max}(NaCl)/cm^{-1} 3078m, 3054m, 3024m, 3001m, 2956s, 2925vs, 2854s, 1632w, 1583s, 1565m, 1493w, 1464s, 1428s, 1366w, 1264w, 1151w, 1095w, 1072w, 1049w, 1027w, 993w, 928w, 882w, 781s, 743m and 703s (Found: C, 86.20; H, 8.47; N, 5.33. $C_{18}H_{21}N$ requires C, 86.01; H, 8.42; N, 5.57%); **16b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.29; δ_H(300 MHz; $CDCl_3$) 8.66–8.69 (1H, m, 6-H in Py), 7.68 (1H, t, *J* 7.6, 4-H in Py), 7.17–7.27 (7H, m, 3,5-H in Py and H in Ph), 6.19 (1H, t, *J* 7.5, CH=), 2.15 (2H, q, *J* 7, $=CCH_2$), 1.43–1.49 (2H, m, CH_2CH_2C=), 1.23–1.30 (4H, m, $CH_3CH_2CH_2$) and 0.86 (3H, t, *J* 6.5, CH_3); δ_C(75 MHz; $CDCl_3$) 159.20, 149.52, 141.74, 140.94, 135.94, 132.60, 128.13, 127.15, 126.89, 125.03, 121.66, 31.45, 29.50, 29.39, 22.44 and 13.96; *m*/*z* 252 (M^+ + 1, 8%), 251 (M^+, 33), 209 (17), 208 (100), 194 (15), 193 (30), 192 (9), 180 (9), 168 (5), 167 (16), 117 (6), 115 (5), 93 (8), 92 (33), 91 (58), 65 (9) and 51 (10); ν_{max}(NaCl)/cm^{-1} 3078w, 3056m, 3022m, 2956s, 2925vs, 2854s, 1631w, 1584m, 1562m, 1492m, 1467m, 1428m, 1369w, 1149w, 1047w, 993w, 825w, 794m, 754m and 698m.

1-Phenyl-1-pyridyloct-1-ene 17a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.41; δ_H(300 MHz; $CDCl_3$) 8.57–8.60 (1H, m, 6-H in Py), 7.45 (1H, t, *J* 7.5, 4-H in Py), 7.06–7.40 (6H, m, 3-H in Py and ArH), 6.91 (1H, t, *J* 7.7, =CH), 6.86 (1H, d, *J* 8.0, 5-H in Py), 2.10 [2H, q, *J* 7.4, $CH_2CH_2(CH_2)_3CH_3$], 1.47 [2H, quintet, *J* 7.3, $CH_2CH_2(CH_2)_3CH_3$], 1.19–1.32 [6H, m, $CH_2(CH_2)_3CH_3$] and 0.85 (3H, t, *J* 7.0, CH_3); δ_C(75 MHz; $CDCl_3$) 158.65, 149.06, 140.46, 139.05, 136.12, 133.96, 129.92, 128.33, 126.99, 121.95, 121.39, 31.63, 29.64, 29.52, 29.03, 22.53 and 14.02; *m*/*z* 266 (M^+ + 1, 7%), 265 (M^+, 31), 264 (M^+ − 1, 5), 222 [M^+ − $(CH_2)_2CH_3$, 4], 209 (17), 208 [M^+ − $(CH_2)_3CH_3$, 100], 194 [M^+ − $(CH_2)_4CH_3$, 23], 193 (32), 192 (11), 180 [M^+ − $(CH_2)_5CH_3$, 13], 167 (18), 84 (11) and 78 (6); ν_{max}(NaCl)/cm^{-1} 3078m, 3054m, 3024m, 3001m, 2955s, 2925vs, 2854s, 1632w, 1583s, 1564m, 1493w, 1465s, 1428s, 1366w, 1269w, 1151w, 1072w, 1051w, 1027w, 993w, 907w, 782s, 744m and 703s; **17b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.32; δ_H(300 MHz; $CDCl_3$) 8.68 (1H, d, *J* 6.0, 6-H in Py), 7.68 (1H, t, *J* 7.7, 4-H in Py), 7.17–7.27 (7H, m, 3,5-H in Py and ArH), 6.18 (1H, t, *J* 7.6, =CH), 2.16 [2H, q, *J* 7.5, $CH_2CH_2(CH_2)_3CH_3$], 1.45 [2H, quintet, *J* 7.3, $CH_2CH_2(CH_2)_3CH_3$], 1.20–1.32 [6H, m, $CH_2(CH_2)_3CH$] and 0.86 (3H, t, *J* 7.1, CH_3); δ_C(75 MHz; $CDCl_3$) 159.21, 149.53, 141.76, 140.94, 135.95, 132.62, 128.15, 127.17, 126.90, 125.05, 121.67, 31.63, 29.68, 29.54, 28.93, 22.54 and 14.04; *m*/*z* 266 (M^+ + 1, 7%), 265 (M^+, 30), 222 [M^+ − $(CH_2)_2CH_3$, 4], 209 (17), 208 [M^+ − $(CH_2)_3CH_3$, 100], 194 [M^+ − $(CH_2)_4CH_3$, 18], 193 (30), 192 (10), 180 [M^+ − $(CH_2)_5CH_3$, 9], 167 (16), 93 (10), 86 (41), 84 (69), 78 (10) and 51 (11); ν_{max}(NaCl)/cm^{-1} 3078w, 3056w, 3022w, 2956m, 2925s, 2854m, 1631w, 1584m, 1562w, 1493w, 1467m, 1428m, 1369w, 1149w, 1049w, 993w, 892w, 793w, 753m and 697m (Found: C, 85.94; H, 8.80; N, 5.05. $C_{19}H_{23}N$ requires C, 85.99; H, 8.74; N, 5.28%).

NOESY spectra of **17a** *and* **17b**.—The NOESY spectrum of the **17b** isomer showed strong correlativity for the vinylic proton (H1) and phenyl ring protons (H2); **17a** failed to indicate such correlativity.



17b

1-Phenyl-1-pyridyl-5,5-dimethylhex-1-ene 18a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.40; δ_H(300 MHz; $CDCl_3$) 8.56–8.59 (1H, m, 6-H in Py), 7.49 (1H, t, *J* 7.7, 4-H in Py), 7.06–7.43 (7H, ArH), 6.88 (1H, t, *J* 7.8, =CH), 2.02–2.16 (2H, m, CH_2C=), 1.33–1.41 (2H, m, CH_2Bu^t) and 0.83 (9H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 158.70, 149.11, 141.78, 140.20, 136.13, 134.51, 129.88, 128.35, 127.07, 121.95, 121.41, 43.82, 29.17, 29.06 and 25.12; *m*/*z* 265 (M^+, 11%), 264 (M^+ − 1, 2), 209 (16), 208 (100), 194 (16), 193 (21), 180 (6), 167 (10), 86 (6) and 84 (10); ν_{max}(NaCl)/cm^{-1} (GC-IRD) 3069m, 2962vs, 1585s, 1469s, 1372m, 1244w, 1153w, 1035w, 922w and 779m; **18b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.31; δ_H(300 MHz; $CDCl_3$) 8.66–8.70 (1H, m, 6-H in Py), 7.69 (1H, t, *J* 7.7, 4-H in Py), 7.18–7.30 (7H, ArH), 6.18 (1H, t, *J* 7.7, =CH), 2.07–2.16 (2H, m, CH_2C=), 1.33–1.40 (2H, m, CH_2Bu^t) and 0.82 (9H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 158.72, 149.55, 141.76, 140.66, 135.94, 133.12, 128.16, 127.15, 126.88, 124.96, 121.71, 43.89, 30.44, 29.20 and 25.11; *m*/*z* 265 (M^+, 9%), 209 (17), 208 (100), 194 (12), 193 (22), 167 (10), 86 (12) and 84 (19); ν_{max}(NaCl)/cm^{-1} 3057w, 3021w, 2954s, 2905m, 2864m, 1631w, 1585s, 1563m, 1494m, 1469s, 1444m, 1427m, 1392w, 1364m, 1245w, 1148w, 1074w, 1048w, 1029w, 991w, 914w, 867w, 797w, 748s and 698s.

1-Phenyl-1-pyridyl-2,2-bis(3,3-dimethylbutyl)ethylene 19. δ_H(300 MHz; $CDCl_3$) 8.56–8.59 (1H, m, 6-H in Py), 7.03–7.43 (8H, ArH), 2.04–2.12 (4H, m, CH_2C=), 1.31–1.41 (4H, m, CH_2Bu^t) and 0.76 (18H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 161.43, 149.04, 143.43, 141.86, 135.75, 129.36, 128.13, 127.97, 126.31, 124.32, 120.91, 42.80, 42.74, 29.14, 29.03, 27.66 and 27.31; *m*/*z* 349 (M^+, 21%), 334 (8), 293 (25), 292 (100), 220 (11), 207 (14), 206 (15), 193 (8), 84 (10) and 57 (10); ν_{max}(NaCl)/cm^{-1} (GC-IRD) 3068m, 2961vs, 1584m, 1472m, 1372m, 1245w, 1149w and 1043w.

1-Phenyl-1-pyridyldec-1-ene 20a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.43; δ_H(300 MHz; $CDCl_3$) 8.57–8.60 (1H, m, 6-H in Py), 7.45 (1H, t, *J* 7.5, 4-H in Py), 7.04–7.41 (6H, m, 3-H in Py and ArH), 6.91 (1H, t, *J* 7.7, =CH), 6.86 (1H, d, *J* 8.0, 5-H in Py), 2.10 [2H, q, *J* 7.4, $CH_2CH_2(CH_2)_5CH_3$], 1.47 [2H, quintet, *J* 7.2, $CH_2CH_2(CH_2)_5CH_3$], 1.22–1.30 [10H, m, $CH_2(CH_2)_5CH_3$] and 0.86 (3H, t, *J* 7.0, CH_3); δ_C(75 MHz; $CDCl_3$) 158.66, 149.07, 140.45, 139.05, 136.13, 133.98, 129.93, 128.33, 126.99, 121.96, 121.40, 31.83, 29.64, 29.54, 29.38, 29.37, 29.17, 22.61 and 14.05; *m*/*z* 294 (M^+ + 1, 5%), 293 (M^+, 23), 278 (M^+ − CH_3, 1), 264 (M^+ − CH_2CH_3, 2), 222 [M^+ − $(CH_2)_4CH_3$, 4], 209 (18), 208 [M^+ − $(CH_2)_5CH_3$, 100], 194 [M^+ − $(CH_2)_6CH_3$, 22], 193 (30), 180 [M^+ − $(CH_2)_7CH_3$, 12], 167 (17), 93 (7), 86 (21) and 84 (31); ν_{max}(NaCl)/cm^{-1} 3078m, 3055m, 3024m, 3001m, 2956s, 2925vs, 2853s, 1632w, 1583s, 1565m, 1493w, 1464s, 1429s, 1367w, 1267w, 1151w, 1093w, 1072w, 1051w, 1027w, 993w, 782s, 744m and 702s; **20b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.35; δ_H(300 MHz; $CDCl_3$) 8.66–8.69 (1H, m, 6-H in Py), 7.68 (1H, t, *J* 7.7, 4-H in Py), 7.17–7.29 (7H, m, 3,5-H in Py and ArH), 6.18 (1H, t, *J* 7.5, =CH), 2.15 [2H, q, *J* 7.4, $CH_2CH_2(CH_2)_5CH_3$], 1.45 [2H, quintet, *J* 7.6, $CH_2(CH_2)_5CH_3$], 1.23–1.32 [10H, m, $CH_2(CH_2)_5CH_3$] and 0.87 (3H, t, *J* 7.1, CH_3); δ_C(75 MHz; $CDCl_3$) 159.22, 149.54, 141.77, 140.95, 135.95, 132.64, 128.15, 127.18, 126.90, 125.06, 121.67, 31.85, 29.71, 29.66, 29.54, 29.38, 29.19, 22.63 and 14.07; *m*/*z* 294 (M^+ + 1, 6%), 293 (M^+, 27), 250 [M^+ − $(CH_2)_2CH_3$, 2], 222 [M^+ − $(CH_2)_4CH_3$, 4], 209 (17), 208 [M^+ − $(CH_2)_5CH_3$, 100], 194 [M^+ − $(CH_2)_6CH_3$, 17], 193 (28), 180 [M^+ − $(CH_2)_7CH_3$, 9], 167 (17), 88 (9), 86 (52) and 84 (88); ν_{max}(NaCl)/cm^{-1} 3078m, 3056m, 3023m, 3001m, 2924vs, 2853s, 1631w, 1584m, 1563m, 1493m, 1466m, 1429m, 1368w, 1150w, 1049w, 993w, 789w, 753m and 699m (Found: C, 85.78; H, 9.51; N, 4.71. $C_{21}H_{27}N$ requires C, 85.95; H, 9.27; N, 4.77%).

1-Phenyl-1-pyridyldodec-1-ene 21a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.47; δ_H(300 MHz; $CDCl_3$) 8.57–8.60 (1H, m, 6-H in Py), 7.48 (1H, dt, *J* 7.6, 1.8, 4-H in Py), 7.05–7.44 (6H, ArH and 5-H in Py), 6.92 (1H, t, *J* 7.7, =CH), 6.86 (1H, d, *J* 8.0, 3-H in Py), 2.10 (2H, q, *J* 7.4, =CHCH_2), 1.47 (2H, quintet, *J* 7.6, =CHCH_2CH_2), 1.23 [14H, br s, $(CH_2)_7$] and 0.88 (3H, t, *J* 6.5, CH_3); δ_C(75 MHz; $CDCl_3$) 158.60, 149.07, 140.41, 139.12, 133.95, 129.91, 128.33, 126.99, 121.96, 121.39, 31.85, 29.63, 29.53, 29.42, 29.36, 29.29, 22.64 and 14.08; *m/z* 322 (M^+ + 1, 9%), 321 (M^+, 37), 320 (M^+ − 1, 7), 278 [$M^+ - (CH_2)_2CH_3$, 3], 264 [$M^+ - (CH_2)_3CH_3$, 3], 222 [$M^+ - (CH_2)_6CH_3$, 3], 209 (17), 208 [$M^+ - (CH_2)_7CH_3$, 100], 194 [$M^+ - (CH_2)_8CH_3$, 23], 193 (28), 180 (12), 168 (7) and 167 (14); ν_{max}(NaCl)/cm^{-1} 3083w, 3057w, 3026w, 3000w, 2955s, 2925s, 2854s, 1583s, 1565w, 1495w, 1462s, 1442w, 1428s, 1154w, 1071w, 782m, 743w and 702s; **21b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.37; δ_H(300 MHz; $CDCl_3$) 8.66–8.70 (1H, m, 6-H in Py), 7.69 (1H, t, *J* 7.7, 1.9, 4-H in Py), 7.18–7.29 (7H, ArH and 3,5-H in Py), 6.18 (1H, t, *J* 7.6, =CH), 2.15 (2H, q, *J* 7.4, =CHCH_2), 1.41–1.47 (2H, m, =CHCH_2CH_2), 1.23 [14H, s, $(CH_2)_7$] and 0.87 (3H, t, *J* 6.5, CH_3); *m/z* 322 (M^+ + 1, 8%), 321 (M^+, 34), 320 (M^+ − 1, 6), 209 (19), 208 [$M^+ - (CH_2)_7CH_3$, 100], 194 [$M^+ - (CH_2)_8CH_3$, 17], 193 (28), 180 (9) and 167 (15); ν_{max}(NaCl)/cm^{-1} 2925s, 2854s, 1666m, 1586m, 1568w, 1493w, 1467m, 1446m, 1432m, 1319w, 1302w, 1150w, 913m, 746s and 697s (Found: C, 85.78; H, 10.01; N, 4.11. $C_{23}H_{31}N$ requires C, 85.92; H, 9.72; N, 4.36%).

1-Phenyl-1-pyridyl-2-[2-(*p*-tolyl)ethyl]ethylene 22a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.27; δ_H(300 MHz; $CDCl_3$) 8.57–8.61 (1H, m, 6-H in Py), 7.48 (1H, t, *J* 7.7, 4-H in Py), 6.96–7.37 (10H, m, 3-H in Py and ArH), 6.94 (1H, t, *J* 7.6, =CH), 6.85 (1H, d, *J* 8.0, 5-H in Py), 2.74 (2H, t, *J* 7.8, =CHCH_2CH_2Ph), 2.40 (2H, q, *J* 7.7, CH_2CH_2Ph) and 2.29 (3H, s, CH_3); δ_C(75 MHz; $CDCl_3$) 158.50, 149.10, 141.18, 138.78, 138.64, 136.17, 135.20, 132.66, 129.90, 128.92, 128.46, 128.37, 127.10, 122.05, 121.55, 35.39, 31.84 and 20.95; *m/z* 300 (M^+ + 1, 12%), 299 (M^+, 50), 298 (M^+ − 1, 7), 208 ($M^+ - PhCH_3$, 8), 195 (18), 194 ($M^+ - CH_2PhCH_3$, 100), 193 (30), 192 (15), 168 (10), 167 (16) and 131 (12); ν_{max}(NaCl)/cm^{-1} 3051m, 3021m, 2921m, 2856w, 1679w, 1631w, 1583s, 1562m, 1513m, 1492w, 1465s, 1428s, 1364w, 1268w, 1152w, 1113w, 1072w, 1025w, 810m, 782s, 746m and 703s; **22b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.14; δ_H(300 MHz; $CDCl_3$) 8.65–8.68 (1H, m, 6-H in Py), 7.63 (1H, t, *J* 7.7, 4-H in Py), 7.02–7.36 (11H, m, 3-H in Py and ArH), 6.20 (1H, t, *J* 7.5, =CH), 2.74 (2H, t, *J* 7.7, =CHCH_2CH_2Ph), 2.46 (2H, q, *J* 7.7, CH_2CH_2Ph) and 2.33 (3H, s, CH_3); δ_C(75 MHz; $CDCl_3$) 158.94, 149.49, 141.55, 138.52, 135.99, 135.25, 131.28, 128.94, 128.38, 128.32, 128.15, 127.03, 124.95, 121.76, 117.68, 35.46, 31.61 and 20.97; *m/z* 300 (M^+ + 1, 18%), 299 (M^+, 59), 195 (18), 194 ($M^+ - CH_2C_6H_4CH_3$, 100), 193 (42), 192 (21), 182 (19), 168 (21), 167 (26) and 131 (34); ν_{max}(NaCl)/cm^{-1} 3052m, 3021m, 2922m, 2857w, 1669m, 1584s, 1563m, 1513m, 1492m, 1469m, 1430s, 1304w, 1281w, 1244w, 1152w, 1114w, 1047w, 994w, 937w, 807m, 748s, 698s and 650w.

1-Phenyl-1-pyridyl-4-triethoxysilylbut-1-ene 23a. (*E* isomer) R_F (EtOAc–hexane, 1 : 10) 0.27; δ_H(300 MHz; $CDCl_3$) 8.57–8.59 (1H, m, 6-H in Py), 7.49 (1H, dt, *J* 7.8, 1.8, 4-H in Py), 7.06–7.42 (6H, ArH and 5-H in Py), 6.92 (1H, t, *J* 7.7, =CH), 6.88 (1H, d, *J* 8.2, 3-H in Py), 3.74 [6H, q, *J* 7.1, Si(OCH_2CH_3)], 2.16–2.26 (2H, m, =CHCH_2), 1.15 [9H, t, *J* 7.1, Si(OCH_2CH_3)] and 0.78–0.85 (2H, m, =CHCH_2CH_2Si); δ_C(75 MHz; $CDCl_3$) 158.60, 149.10, 139.65, 138.74, 136.12, 135.62, 129.87, 128.35, 127.04, 122.01, 121.44, 58.25, 22.84, 18.17 and 10.54; *m/z* 372 (M^+ + 1, 29%), 371 (M^+, 100), 370 (M^+ − 1, 16), 326 (8), 209 (18), 208 [$M^+ - Si(OEt)_3$, 96], 206 (18), 194 [$M^+ - CH_2Si(OEt)_3$, 22], 193 (21), 167 (11), 163 [$Si(OEt)_3^+$, 14] and 119 (16); ν_{max}(NaCl)/cm^{-1} 3083w, 3060w, 3026w, 2974s, 2925m, 2887m, 1583s, 1500w, 1470m, 1447m, 1429m, 1390s, 1364w, 1297w, 1188m, 1166s, 1103s, 1079s, 1028w, 990w, 959s, 786s, 774s, 704s and 620w; **23b** (*Z* isomer) R_F (EtOAc–hexane, 1 : 10) 0.17; δ_H(300 MHz; $CDCl_3$) 8.65–8.69 (1H, m, 6-H in Py), 7.68 (1H, dt, *J* 7.6, 1.8, 4-H in Py), 7.17–7.30 (7H, ArH and 3,5-H in Py), 6.24 (1H, t, *J* 7.5, =CH), 3.77 [6H, q, *J* 7.0, Si(OCH_2CH_3)], 2.23–2.33 (2H, m, =CHCH_2), 1.17 [9H, t, *J* 7.0, Si(OCH_2CH_3)] and 0.79–0.85 (2H, m, =CHCH_2CH_2Si); δ_C(75 MHz; $CDCl_3$) 158.98, 149.46, 141.57, 139.96, 135.94, 134.32, 128.09, 127.15, 126.87, 125.04, 121.66, 58.25, 22.86, 18.17 and 10.65; *m/z* 372 (M^+ + 1, 26%), 371 (M^+, 93), 370 (M^+ − 1, 15), 326 (13), 209 (19), 208 [$M^+ - Si(OEt)_3$, 100], 206 (20), 194 [$M^+ - CH_2Si(OEt)_3$, 18], 193 (26), 167 (12), 163 [$Si(OEt)_3^+$, 12] and 119 (15); ν_{max}(NaCl)/cm^{-1} 3080w, 3060w, 2974s, 2925m, 2886m, 1587m, 1564w, 1495m, 1471m, 1444m, 1429m, 1390m, 1365w, 1294w, 1166m, 1103s, 1079s, 992w, 959s, 791s, 759s, 699m and 634w (Found: C, 67.63; H, 8.06; N, 3.67. $C_{21}H_{29}NO_3Si$ requires C, 67.89; H, 7.87; N, 3.77%).

2-Methyl-6-(hept-1-enyl)pyridine 25a. (*trans* isomer) R_F (EtOAc–hexane, 1 : 10) 0.41; δ_H(200 MHz; $CDCl_3$) 7.48 (1H, t, *J* 7.7, 4-H in Py), 7.09 (1H, d, *J* 7.7, 3-H in Py), 6.95 (1H, d, *J* 7.5, 5-H in Py), 6.69 (1H, dt, *J* 15.7, 6.7, C*H*=CHPy), 6.47 (1H, d, *J* 15.8, CH=C*H*Py), 2.53 (3H, s, CH_3 in Py), 2.25 (2H, q, *J* 6.6, =CHCH_2), 1.25–1.60 [6H, m, $(CH_2)_3CH_3$] and 0.89 (3H, t, *J* 5.7, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.86, 155.75, 136.74, 135.59, 129.84, 121.12, 117.69, 32.80, 31.44, 28.61, 24.36, 22.51 and 13.99; *m/z* 189 (M^+, 23%), 174 (17), 160 (20), 147 (19), 146 (100), 144 (9), 133 (19), 132 (58), 131 (37), 130 (18), 120 (13), 119 (14), 118 (9), 117 (26), 107 (24), 93 (10), 77 (8) and 65 (13); ν_{max}(NaCl)/cm^{-1} 3060w, 2950s, 2920s, 2850s, 1650w, 1575s, 1445s, 1370w, 1155w, 970m and 770m; **25b** (*cis* isomer) R_F (EtOAc–hexane, 1 : 10) 0.29; δ_H(200 MHz; $CDCl_3$) 7.51 (1H, t, *J* 7.7, 4-H in Py), 7.05 (1H, d, *J* 7.7, 3-H in Py), 6.95 (1H, d, *J* 7.7, 5-H in Py), 6.45 (1H, d, *J* 11.8, PyC*H*=), 5.86 (1H, dt, *J* 11.8, 7.4, =C*H*CH$_2$), 2.54 (3H, s, CH_3 in Py), 2.46–2.59 [2H, m, C$H_2$$(CH_2)_3CH_3$], 1.23–1.51 [6H, m, CH_2(CH_2)$_3$$CH_3$] and 0.88 (3H, t, *J* 6.8, CH_2CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.7, 156.10, 136.98, 136.09, 128.70, 120.62 (2C), 31.59, 29.37, 28.77, 24.52, 22.49 and 13.98; *m/z* 189 (M^+, 14%), 160 (10), 147 (14), 146 (100), 144 (8), 132 (11), 131 (34), 130 (12), 117 (8) and 65 (10); ν_{max}(NaCl)/cm^{-1} 3060w, 3005m, 2960s, 2920s, 2860s, 2850s, 1640w, 1580s, 1570s, 1452s, 1370w, 1195w, 1156w, 1090w, 810s, 750w and 720w (Found: C, 82.42; H, 10.02; N, 7.54. $C_{31}H_{19}N$ requires C, 82.48; H, 10.12; N, 7.40%).

2-Methyl-6-(oct-1-enyl)pyridine 26a. (*trans* isomer) R_F (EtOAc–hexane, 1 : 10) 0.50; δ_H(200 MHz; $CDCl_3$) 7.46 (1H, t, *J* 7.7, 4-H in Py), 7.06 (1H, d, *J* 7.7, 3-H in Py), 6.93 (1H, d, *J* 7.6, 5-H in Py), 6.69 (1H, dt, *J* 15.7, 6.9, C*H*=CHPy), 6.46 (1H, d, *J* 15.8, CH=C*H*Py), 2.52 (3H, s, CH_3 in Py), 2.24 (2H, q, *J* 6.9, =CHCH_2), 1.10–1.54 [8H, m, (CH_2)$_4$$CH_3$] and 0.89 (3H, t, *J* 5.7, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.84, 155.72, 136.41, 135.58, 130.19, 120.95, 117.59, 32.80, 31.70, 29.64, 28.92, 24.54, 22.56 and 14.02; *m/z* 203 (M^+, 17%), 174 (24), 160 (19), 147 (20), 146 (100), 144 (11), 133 (24), 132 (64), 131 (38), 130 (17), 120 (22), 119 (19), 117 (30), 107 (29), 77 (11) and 65 (18); ν_{max}(NaCl)/cm^{-1} 3060w, 2950s, 2920s, 2850s, 1645w, 1580s, 1570s, 1445s, 1370w, 1152w, 970m and 770m; **26b** (*cis* isomer) R_F (EtOAc–hexane, 1 : 10) 0.41; δ_H(200 MHz; $CDCl_3$) 7.50 (1H, t, *J* 7.7, 4-H in Py), 7.04 (1H, d, *J* 7.7, 3-H in Py), 6.94 (1H, d, *J* 7.7, 5-H in Py), 6.42 (1H, d, *J* 11.9, PyCH=), 5.85 (1H, t, *J* 11.9, =C*H*CH$_2$), 2.53 (3H, s, CH_3 in Py), 2.47–2.58 [2H, m, C$H_2$$(CH_2)_4CH_3$], 1.28–1.50 [8H, m, CH_2(CH_2)$_4$$CH_3$] and 0.87 [3H, t, *J* 6.6, $CH_2(CH_2)_4$CH_3]; δ_C(50.3 MHz; $CDCl_3$) 157.74, 156.16, 136.85, 135.97, 128.81, 120.59, 120.48, 31.68, 29.65, 29.00, 28.78, 24.56, 22.56 and 13.99; *m/z* 203 (M^+, 8%), 160 (10), 147 (14), 146 (100), 144 (8), 132 (12), 131 (30), 130 (11), 120 (7), 117 (8), 107 (11) and 65 (11); ν_{max}(NaCl)/cm^{-1} 3060w, 3005m, 2960s, 2920s, 2850s, 1640w, 1580s, 1570s, 1450s, 1370w, 1195w, 1156w, 1090w, 810s, 745w and 720w (Found: C, 82.62; H, 10.30; N, 7.07. $C_{14}H_{21}N$ requires C, 82.70; H, 10.41; N, 6.89%).

2-Methyl-6-(dec-1-enyl)pyridine 27a. (*trans* isomer) R_F (EtOAc–hexane, 1 : 10) 0.53; δ_H(200 MHz; $CDCl_3$) 7.48 (1H, t, *J* 7.8, 4-H in Py), 7.07 (1H, d, *J* 7.7, 3-H in Py), 6.94 (1H, d, *J* 7.7, 5-H in Py), 6.69 (1H, dt, *J* 15.8, 6.8, =C*H*CH$_2$), 6.46 (1H, d, J 15.8, PyCH=), 2.53 (3H, s, CH_3 in Py), 2.25 [2H, q, J 7.0, $CH_2(CH_2)_6CH_3$], 1.27–1.53 [12H, m, $CH_2(CH_2)_6CH_3$] and 0.88 (3H, t, J 6.6, CH_2CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.90, 155.75, 136.45, 135.65, 130.21, 120.98, 117.62, 32.83, 31.87, 29.46, 29.26, 28.97, 24.57, 22.64 and 14.06; *m/z* 231 (M^+, 16%), 216 (8), 202 (11), 188 (16), 174 (26), 160 (16), 147 (25), 146 (100), 144 (12), 134 (9), 133 (32), 132 (58), 131 (33), 130 (17), 120 (23), 119 (15), 117 (24), 107 (42) and 65 (9); ν_{max}(NaCl)/cm^{-1} 2950m, 2920s, 2850s, 1650w, 1570m, 1445s, 1370w, 1156w, 970w, 770w and 720w (Found: C, 82.91; H, 10.76; N, 6.33. $C_{16}H_{25}N$ requires C, 83.06; H, 10.89; N, 6.05%); **27b** (*cis* isomer) R_F (EtOAc–hexane, 1:10) 0.50; δ_H(200 MHz; $CDCl_3$) 7.49 (1H, t, J 7.6, 4-H in Py), 7.03 (1H, d, J 7.6, 3-H in Py), 6.93 (1H, d, J 7.6, 5-H in Py), 6.44 (1H, d, J 11.8, CH=C*H*Py), 5.85 (1H, dt, J 11.8, 7.1, C*H*=CHPy), 2.53 (3H, s, CH_3 in Py), 2.45–2.60 (2H, q, =CHC*H*$_2$), 1.12–1.50 [12H, m, $(CH_2)_6CH_3$] and 0.87 (3H, t, J 5.7, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.72, 156.12, 136.83, 135.96, 128.79, 120.57, 120.47, 31.82, 29.67, 29.42, 29.33, 29.22, 28.76, 24.57, 22.60 and 14.02; *m/z* 231 (M^+, 8%), 160 (9), 147 (16), 146 (100), 132 (13), 131 (25) and 107 (17); ν_{max}(NaCl)/cm^{-1} 3060w, 3005m, 2950s, 2920s, 2850s, 1640w, 1580s, 1570s, 1450s, 1370w, 1195w, 1155w, 1090w, 810s, 745w and 720w.

2-Methyl-6-(undec-1-enyl)pyridine 28a. (*trans* isomer) R_F (EtOAc–hexane, 1:10) 0.50; δ_H(200 MHz; $CDCl_3$) 7.46 (1H, t, J 7.7, 4-H in Py), 7.06 (1H, d, J 7.7, 3-H in Py), 6.93 (1H, d, J 7.6, 5-H in Py), 6.69 (1H, dt, J 15.7, 6.9, C*H*=CHPy), 6.46 (1H, d, J 15.8, CH=C*H*Py), 2.52 (3H, s, CH_3 in Py), 2.24 (2H, q, J 6.9, =CHC*H*$_2$), 1.2–1.55 [14H, m, $(CH_2)_7CH_3$] and 0.8 (3H, t, J 5.7, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.84, 155.72, 136.39, 135.58, 130.19, 120.92, 117.57, 32.79, 31.85, 29.49, 29.26, 28.95, 24.54, 22.61 and 14.01; *m/z* 245 (M^+, 12%), 174 (24), 160 (20), 147 (22), 146 (100), 144 (13), 133 (36), 132 (62), 131 (34), 130 (19), 120 (24), 119 (21), 118 (13), 117 (26), 107 (55), 93 (13) and 65 (15); ν_{max}(NaCl)/cm^{-1} 3060w, 3005w, 2960s, 2920s, 2850s, 1650w, 1570s, 1445s, 1370w, 1195w, 1156w, 1090w, 970m, 810w, 770w, 740w and 690w (Found: C, 83.04; H, 11.00; N, 5.96. $C_{17}H_{27}N$ requires C, 83.20; H, 11.09; N, 5.71%); **28b** (*cis* isomer) R_F (EtOAc–hexane, 1:10) 0.38; δ_H(200 MHz; $CDCl_3$) 7.51 (1H, t, J 7.7, 4-H in Py), 7.05 (1H, d, J 7.7, 3-H in Py), 6.96 (1H, d, J 7.7, 5-H in Py), 6.44 (1H, d, J 11.8, CH=C*H*Py), 5.86 (1H, dt, J 11.8, 7.3, C*H*=CHPy), 2.54 (3H, s, CH_3 in Py), 2.45–2.60 (2H, =CHC*H*$_2$), 1.02–1.60 [14H, m, $(CH_2)_7CH_3$] and 0.87 (3H, t, J 6.2, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.77, 156.13, 136.89, 136.03, 128.81, 120.61, 120.53, 31.87, 29.70, 29.55, 29.48, 29.35, 29.30, 28.78, 24.59, 22.64 and 14.02; *m/z* 245 (M^+, 11%), 230 ($M^+ - CH_3$, 2), 216 ($M^+ - CH_2CH_3$, 5), 202 [$M^+ - (CH_2)_2CH_3$, 5], 188 [$M^+ - (CH_2)_3CH_3$, 4], 174 [$M^+ - (CH_2)_4CH_3$, 5], 160 [$M^+ - (CH_2)_5CH_3$, 9], 147 (17), 146 [$M^+ - (CH_2)_6CH_3$, 100], 132 [$M^+ - (CH_2)_7CH_3$, 13] and 107 (16); ν_{max}(NaCl)/cm^{-1} 3060w, 3010m, 2950s, 2920s, 2850s, 1640w, 1580s, 1570s, 1455s, 1370w, 1200w, 1155w, 1090w, 810s, 745w and 720w.

2-Methyl-6-(tetradec-1-enyl)pyridine 29a. (*trans* isomer) R_F (EtOAc–hexane, 1:10) 0.50; δ_H(200 MHz; $CDCl_3$) 7.46 (1H, t, J 7.7, 4-H in Py), 7.06 (1H, d, J 7.7, 3-H in Py), 6.93 (1H, d, J 7.6, 5-H in Py), 6.69 [1H, dt, J 15.7, 6.9, C*H*=CHPy], 6.46 (1H, d, J 15.7, CH=C*H*Py), 2.53 (3H, s, CH_3 in Py), 2.24 (2H, q, J 7.1, =CHC*H*$_2$), 1.10–1.53 [20H, m, $(CH_2)_{10}CH_3$] and 0.88 (3H, t, J 5.8, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.86, 155.75, 136.41, 135.61, 130.22, 120.95, 117.60, 32.82, 31.90, 29.63, 29.50, 29.31, 28.97, 24.57, 22.66 and 14.07; *m/z* 287 (M^+, 14%), 244 (7), 230 (9), 216 (12), 202 (11), 188 (14), 174 (32), 160 (20), 158 (6), 147 (19), 146 (100), 144 (14), 134 (9), 133 (42), 132 (61), 131 (28), 130 (14), 120 (24), 119 (17), 117 (22) and 107 (61); ν_{max}(NaCl)/cm^{-1} 3060w, 2950s, 2920s, 2850s, 1650w, 1570s, 1450w, 1370w, 1156w, 1090w, 970m, 810w, 770m, 740w, 720w and 690w (Found: C, 83.75; H, 11.70; N, 4.53. $C_{20}H_{33}N$ requires C, 83.56; H, 11.57; N, 4.87%).

2-Methyl-6-(hexadec-1-enyl)pyridine 30a. (*trans* isomer) R_F (EtOAc–hexane, 1:10) 0.56; δ_H(200 MHz; $CDCl_3$) 7.46 (1H, t, J 7.7, 4-H in Py), 7.06 (1H, d, J 7.7, 3-H in Py), 6.93 (1H, d, J 7.6, 5-H in Py), 6.69 (1H, dt, J 15.7, 6.9, C*H*=CHPy), 6.46 (1H, d, J 15.8, CH=C*H*Py), 2.53 (3H, s, CH_3 in Py), 2.24 (2H, q, J 7.1, =CHC*H*$_2$), 1.15–1.53 [24H, m, $(CH_2)_{12}CH_3$] and 0.88 (3H, t, J 5.7, CH_3); δ_C(50.3 MHz; $CDCl_3$) 157.86, 155.75, 136.42, 135.62, 130.22, 120.96, 117.61, 32.82, 31.91, 29.66, 29.51, 29.32, 28.98, 24.57, 22.66 and 14.08; *m/z* 315 (M^+, 23%), 216 (11), 202 (13), 188 (16), 174 (32), 160 (22), 147 (18), 146 (100), 144 (12), 133 (36), 132 (42), 131 (25), 130 (9), 120 (25), 118 (16), 116 (18) and 107 (49); ν_{max}(NaCl)/cm^{-1} 3060w, 2950s, 2920s, 2850s, 1650w, 1570s, 1450s, 1370w, 1155w, 1090w, 970m, 810w, 770m and 720w (Found: C, 83.51; H, 12.00; N, 4.47. $C_{22}H_{37}N$ requires C, 83.74; H, 11.82; N, 4.44%).

2-Methyl-6-(5,5-dimethylhex-1-enyl)pyridine 31a,b. δ_H(200 MHz; $CDCl_3$) 7.48 (1H, q, J 7.74, 4-H in Py), 6.90–7.09 (2H, m, 3,5-H in Py), 6.70 (dt, J 15.7, 6.64, *trans* isomer), 6.36–6.52 (dd, J 11.7, 15.1), 5.85 (dt, J 11.77, 7.53, *cis* isomer), 2.52 (3H, s, C*H*$_3$Py), 2.15–2.30 (m) and 2.50–2.65 (m) (2H, C*H*$_2$CH$_2$Bu^t), 1.25–1.45 (m, 2H, C*H*$_2$Bu^t) and 0.92 (9H, s, Bu^t); δ_C(50.3 MHz; $CDCl_3$) *cis* (*c*) and *trans* (*t*) mixture 157.73, 156.17, 137.54 (*c*), 136.42 (*t*), 136.26 (*t*), 136.02 (*c*), 129.77, 128.29 (*c*), 120.93 (*t*), 120.58 (*c*), 120.48 (*c*), 117.54 (*t*), 43.74, 43.24, 30.49, 30.32, 29.28, 28.08, 24.58 and 24.27; *m/z* (*cis* isomer) 203 (M^+, 5%), 188 ($M^+ - 15$, 7), 147 (10), 146 ($M^+ - Bu^t$, 100), 144 (5), 132 ($M^+ - CH_2Bu^t$, 7), 131 (20); *m/z* (*trans* isomer) 203 (M^+, 22.6%), 188 ($M^+ - 15$, 33), 147 (14), 146 ($M^+ - Bu^t$, 100), 144 (9), 133 (8), 132 ($M^+ - CH_2Bu^t$, 39), 131 (23), 130 (13), 120 (9), 119 (9), 117 (16), 107 (15), 92 (16), 91 (23), 65 (13) and 57 (14); ν_{max}(NaCl)/cm^{-1} (mixture) 3070w, 3020w, 2960vs, 2910s, 2870s, 1715w, 1585s, 1460s, 1370m, 1250w, 1202w, 1165w, 1100w, 1000w, 980w, 820m, 790w, 755w; (GC–IRD, *cis* isomer) 3021w, 2961vs, 1644w, 1578s, 1460m, 1376w, 1203w, 1094w, 814m; (GC–IRD, *trans* isomer) 3067m, 2962vs, 1655w, 1579s, 1456s, 1373w, 1243w, 1156w, 1086w, 972m and 773m.

Dimers of **24A** δ_H(300 MHz; $CDCl_3$) 6.90–7.52 (6H, ArH in Py), 6.63 (1H, t, J 7.4, =C*H*CH$_2$), 3.77 (2H, d, J 7.36, =CHC*H*$_2$), 2.53 (6H, s, two CH_3 in Py), 2.19 (3H, s, PyCC*H*=); *m/z* 239 (16, $M^+ + 1$), 238 (88, M^+), 237 (43, $M^+ - 1$), 224 (16), 223 (92.2, $M^+ - CH_3$), 222 (14), 221 (11), 147 (11), 146 (100), 145 (20), 144 (32), 132 (13), 131 (33), 130 (21), 120 (25), 119 (15), 118 (25), 107 (21), 94 (19), 84 (10) and 65 (18). **B** δ_H(300 MHz; $CDCl_3$) 6.90–7.52 (6H, ArH in Py), 6.96 (1H, dd, J 15.8, 7.0, =C*H*CHCH$_3$), 6.56 (1H, d, J 15.8, PyC*H*=), 3.83 (1H, quintet, J 7.0, =CHC*H*CH$_3$), 2.51–2.52 (6H, two CH_3 in Py) and 1.52 (3H, d, J 7.0, =CHCHC*H*$_3$); *m/z* 238 (42%, M^+), 237 (19, $M^+ - 1$), 223 (100, $M^+ - CH_3$), 146 (79), 131 (22), 120 (17), 107 (9), 94 (8), 84 (7) and 65 (12).

2-(Oct-1-enyl)pyridine 33.[17] δ_H(200 MHz; $CDCl_3$) 8.50–8.61 (1H), 7.50–7.67 (1H, m), 7.24 (1H), 7.0–7.14 (1H, m), 6.74 (*trans*, dt, J 15.5, 6.8), 6.42–6.52 (1H, m), 5.88 (*cis*, dt, J 11.8, 7.0), 2.56 (*cis*, q, J 6.4, CH_2), 2.25 (*trans*, q, J 6.8, CH_2), 1.22–1.51 (8H, m) and 0.90 (3H, m); δ_C(50.3 MHz; $CDCl_3$) 156.9, 156.2, 149.4, 149.2, 137.4, 136.3, 136.1, 135.8, 129.9, 128.5, 126.0, 123.7, 121.4, 121.0, 120.9, 32.8, 31.7, 29.7, 29.0, 28.9, 28.8, 22.6 and 14.0; *m/z* (*trans* isomer) 189 (M^+, 14%), 160 (23), 146 (19), 133 (18), 132 (100), 130 (12), 119 (20), 118 (55), 117 (49), 106 (22), 105 (15), 93 (26), 79 (8), 78 (10); (*cis* isomer) 189 (M^+, 12%), 160 (5), 146 (11), 133 (13), 132 (100), 130 (9), 117 (34) and 93 (9); ν_{max}(NaCl)/cm^{-1} (mix) 3050w, 3005w, 2950s, 2920s, 2860s, 2850s, 1640m, 1580s, 1565m, 1465s, 1430m, 1405w, 1148m, 1090w, 1047w, 990w, 970m, 805w and 740m.

2-(Hept-1-enyl)pyridine 34.[17] δ_H(200 MHz; $CDCl_3$) 8.51–8.61 (1H), 7.59 (1H, t, J 7.3), 7.24 (1H, d, J 8.0), 7.04–7.11 (1H, m), 6.74 (*trans*, dt, J 15.6, 7.9), 6.47 (1H), 5.88 (*cis*, dt, J 11.8, 7.2), 2.56 (*cis*, q, J 7.6, CH_2), 2.26 (*trans*, q, J 7.4, CH_2), 1.22–1.55 (6H, m) and 0.90 (3H, m); δ_C(50.3 MHz; $CDCl_3$) 156.9, 149.4, 149.2, 137.4, 136.3, 136.1, 135.8, 129.9, 128.5, 123.7, 121.4, 121.0, 120.9, 32.8, 31.5, 31.4, 29.4, 28.8, 28.7, 22.5 and 14.0; *m/z* (*trans* isomer) 175 (M^+, 14%), 146 (11), 133 (14), 132 (100), 130 (11), 118 (17), 117 (44), 93 (8) and 78 (7); ν_{max}(NaCl)/cm^{-1}

(mix) 3050w, 3010m, 2950s, 2920s, 2860s, 2850s, 1640m, 1580s, 1565m, 1465s, 1430m, 1405w, 1148m, 1090w, 1047w, 990w, 970w, 805m and 740m.

2-(Undec-1-enyl)pyridine 35.[17] δ_H(200 MHz; $CDCl_3$) 8.50–8.60 (1H), 7.53–7.61 (1H, m), 7.22 (1H, d, *J* 7.8), 6.90–7.14 (1H, m), 6.74 (*trans*, dt, *J* 15.7, 7.9), 6.42–6.51 (1H), 5.87 (*cis*, dt, *J* 11.6, 7.2), 2.56 (*cis*, q, *J* 7.2, CH_2), 2.25 (*trans*, q, *J* 7.1, CH_2), 1.19–1.51 (14H, m) and 0.88 (3H, t, *J* 5.4); δ_C(50.3 MHz; $CDCl_3$) 156.9, 156.2, 149.4, 149.2, 137.4, 136.3, 136.1, 135.8, 130.0, 128.9, 128.5, 126.0, 123.7, 121.4, 121.0, 120.8, 32.8, 31.9, 31.6, 29.7, 29.5, 29.3, 29.0, 28.8, 22.6 and 14.0; *m*/*z* 231 (M^+, 10%), 202 (9), 188 (12), 174 (15), 160 (23), 146 (19), 133 (19), 132 (100), 130 (15), 119 (26), 118 (59), 117 (48), 106 (28), 105 (16), 93 (43) and 91 (9); ν_{max}(NaCl)/cm^{-1} 3080w, 3000w, 2920s, 2850s, 1650w, 1582s, 1560m, 1465s, 1427m, 1145w, 970m and 740m.

2-[2-(3′,3′-Dimethylbutyl)cyclohex-1-enyl]pyridine 37. δ_H(300 MHz; $CDCl_3$) 8.58 (1H, d, *J* 4.9, 6-H in Py), 7.61 (1H, t, *J* 7.5, 4-H in Py), 7.13 (1H, t, *J* 7.5, 5-H in Py), 7.10 (1H, d, *J* 4.6, 3-H in Py), 2.34 (2H, br s, 6′-CH_2), 2.11 (2H, br s, 3′-CH_2), 1.81–1.87 (2H, m, β-CH_2 to Bu^t), 1.70–1.73 (4H, m, 4′, 5′-CH_2), 1.22–1.28 (2H, m, α-CH_2 to Bu^t), 0.72 (9H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 162.26, 149.08, 136.47, 135.73, 132.13, 124.24, 120.93, 42.65, 30.29, 29.29, 29.13, 28.99, 23.11 and 22.93; *m*/*z* 243 (M^+, 9%), 228 ($M^+ - 15$, 4), 187 (15), 186 ($M^+ - Bu^t$, 100), 172 (8), 158 (6), 144 (7), 143 (6) and 130 (5); ν_{max}(NaCl)/cm^{-1} 2951vs, 2933vs, 2862s, 2862s, 2834m, 1585s, 1562m, 1466s, 1448w, 1428m, 1364m, 1247w, 782m and 747m.

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