Regioselective alkylation of 2-phenylpyridines with terminal alkenes *via* C–H bond activation by a rhodium catalyst

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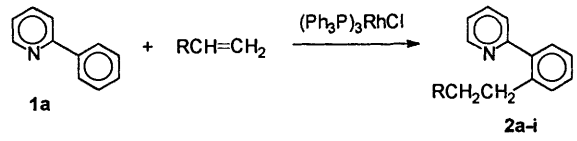
2-Phenylpyridine 1a reacts with various terminal alkenes in the presence of a rhodium(I) complex catalyst to give the corresponding mono *ortho*-alkylated products 2a–i and doubly alkylated products 3a–b (9:1). The same reaction using 3-methyl-2-phenylpyridine 1b gives the mono alkylated products 2j–n exclusively under the same reaction conditions due to steric hindrance between the methyl group of the pyridine and the alkyl group of 2j–n.

There is currently great interest in transition metal mediated C–H bond activations.[1] One goal is to develop new routes for selective C–C bond formation. Although there are numerous cases of stoichiometric C–H bond activations, catalytic functionalizations by C–H bond activation are still a relatively rare phenomenon.[2] Cyclometallation is well known as a good method for intramolecular activation of C–H bonds in transition metal complexes,[3] and very recently, ruthenium-catalysed, highly regioselective *ortho* alkylation of acetophenones with terminal alkenes was reported by Murai *et al.*[4] 2-Substituted pyridines are good substrates for cyclometallation,[5] as the *ortho* aromatic C–H bond of the phenyl ring in 2-phenylpyridine is easily cleaved by transition metal complexes,[3] and the selective functionalization of 2-phenylpyridines has been studied by many organic chemists.[6] We have found that 2-phenylpyridines react with alkenes in the presence of a rhodium(I) complex as a catalyst to give the anti-Markownikoff *ortho* alkylated products. Here we report the regioselective alkylation of the phenyl ring of 2-phenylpyridines with various alkenes. Some preliminary results of this work have already been communicated.[7]

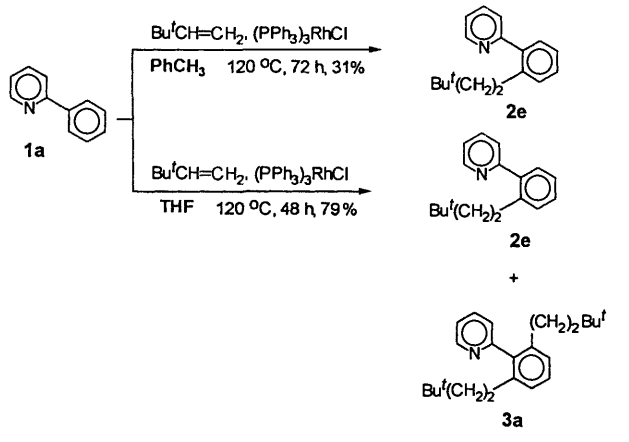
Results and discussion

2-Phenylpyridine **1a** was chosen for alkylation *via* sp^2 C–H bond activation by a Rh^I catalyst. 2-Phenylpyridine **1a** was reacted with pent-1-ene (5 equiv.) in toluene at 120 °C for 19 h in the presence of Wilkinson's complex as a catalyst (10 mol%) to give trace amounts of the alkylated product **2a** (Scheme 1). The alkylated product was identified by the $-CH_2CH_2-$



Scheme 1

signals (δ 2.67–2.71) in ^1H NMR spectrum of the reaction mixture. When this reaction was prolonged for 6 days, the reaction gave the alkylated product **2a** in 26% yield after purification by column chromatography. In order to learn the pathway of the alkylation, **1a** was reacted with pent-1-ene in [$^2H_8$]toluene at 120 °C in the presence of Wilkinson's complex. The reaction mixture was checked by ^1H NMR spectroscopy from time to time. During the reaction pent-1-ene was observed to be isomerized to pent-2-ene completely in 4 h, and the alkylated product **2a** could not be found. To determine whether **2a** is produced from pent-1-ene or pent-2-ene under the same conditions, pent-2-ene was applied to this alkylation. The reaction gave the same alkylated product **2a** as that obtained from pent-1-ene. Even though 30 mol% of Wilkinson's complex was used, the yield did not increase significantly (36% in pent-1-ene). When methyl vinyl ketone, an alkene containing a carbonyl group, was used, the reaction gave only 9% of the alkylated product **2d** after 4 days. In the case of vinyl acetate, the alkylated product was not detected, probably due to poor reactivity of the intermediate formed by chelation between the carbonyl group and the Rh catalyst.[8] The isomerization of the alkene competed with the alkylation reaction between the alkene and **1a**. 3,3-Dimethylbut-1-ene is not isomerized under the same conditions. Thus, 2-phenylpyridine **1a** reacted with 3,3-dimethylbut-1-ene in toluene as solvent at 120 °C for 72 h to give 31% of the desired alkylated product **2e** after column chromatographic isolation (Scheme 2). To determine the effects



Scheme 2

of the solvent, THF was used instead of toluene. After 24 h, the reaction gave 53% of the alkylated product **2e** together with a trace amount of the doubly alkylated product **3a**. When the reaction time was prolonged to 48 h, the yield of the alkylated product increased to 79%. The reaction in THF increased the yields dramatically and reduced the reaction time. When 1 equiv. of triphenylphosphine (based on **1a**) was used, a trace amount of **2e** was obtained, indicating that excess of ligand might retard alkylation.

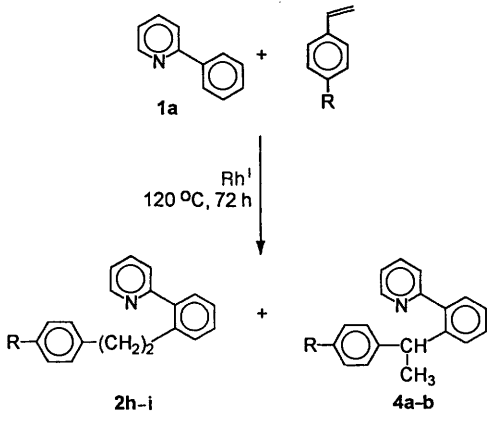
Table 1 The results of the alkylation of 2-phenylpyridine **1a** by $(Ph_3P)_3RhCl$

Run	Alkene	Product	Solvent	T/°C	t/h	Yield (%)
1	Pent-1-ene	**2a**	Toluene	125	144	26
2[a]	Pent-1-ene	**2a**	Toluene	120	72	36
3	Pent-2-ene	**2a**	Toluene	120	120	25
4	Non-1-ene	**2c**	Toluene	125	144	19
5	Methyl vinyl ketone	**2d**	Toluene	120	96	9
6	$CH_3CO_2CH{=}CH_2$		Toluene	120	96	No reaction
7	$Bu^tCH{=}CH_2$	**2e**	Toluene	120	72	31[b]
8	$Bu^tCH{=}CH_2$	**2e**	THF	120	48	79[c]
9[d]	$Bu^tCH{=}CH_2$	**2e**	THF	120	48	Trace
10	Hex-1-ene	**2b**	THF	120	72	70[e]
11	$Me_3SiCH{=}CH_2$	**2f**	THF	120	72	12
12	Styrene	**2h**	THF	120	72	43[f]
13	*p*-Methylstyrene	**2i**	THF	120	72	36[g]

[a] 30 mol% of $(Ph_3P)_3RhCl$ was used. [b] A trace amount of the doubly alkylated product was detected. [c] The doubly alkylated product was isolated (4%). [d] 1 equiv. of PPh_3 was used. [e] The doubly alkylated product was isolated (1.5%). [f] The ratio of Markownikoff product (**4a**) to anti-Markownikoff product (**2h**) was 8:92. [g] The ratio of Markownikoff product (**4b**) to anti-Markownikoff product (**2i**) was 3:97.

The results of alkylation are listed in Table 1. In the case of the linear alk-1-enes, such as hex-1-ene, the reaction mixture gave 70% yield of the desired product **2b** after 72 h. Vinyltrimethylsilane gave a low yield (12%) of the alkylated product **2f**.

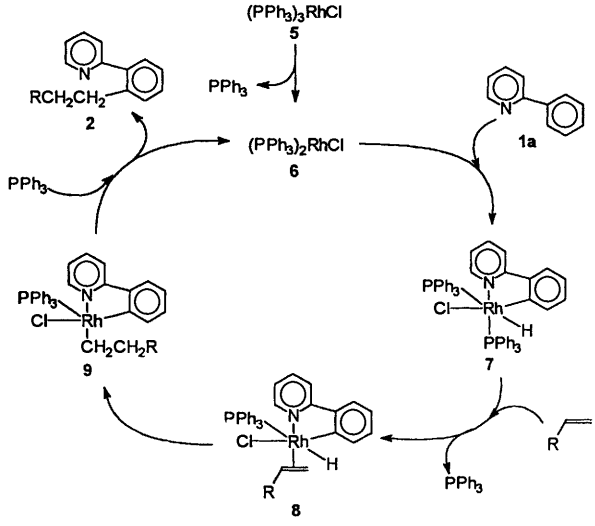
The reaction of 2-phenylpyridine **1a** with styrene or *p*-methylstyrene in THF at 120 °C for 72 h in the presence of Wilkinson's complex as a catalyst gave the corresponding alkylated products **2h–i** and **4a–b** in 43% (**2h** + **4a**) or 36% (**2i** + **4b**) yields, respectively (Scheme 3). Exceptionally, these



Scheme 3

reactions resulted in the Markownikoff product **4** as a minor product. Formation of the branched product **4** is probably due to the stability of the 2-alkylrhodium species shown.[9]

A possible mechanism for this reaction can be postulated from the above results (see Scheme 4). The reaction appears to be initiated *via* formation of the highly reactive rhodium complex $(PPh_3)_2RhCl$ **6** by one ligand liberation, and **6** reacts with **1a** to form the rhodium(III) hydride complex **7** by cleavage of an aromatic C–H bond at the *ortho* position of the phenyl ring in **1a**. The insertion of a hydride from **8** into the coordinated alkene may form anti-Markownikoff hydrometallated complex intermediate **9**. The intermediate complex **9** converts to the alkylated product **2** and **6** by reaction with an external ligand. The alkylated product **2** may further couple with an alkene to give the doubly alkylated product.



Scheme 4 A possible mechanism for *ortho* position alkylation by C–H bond activation

As another ligand in the rhodium catalyst, tricyclohexylphosphine was introduced instead of triphenylphosphine. The desired catalyst, tris(tricyclohexylphosphine)rhodium(I) chloride could be obtained *in situ* from the ligand exchange of chlorobis(cyclooctene)rhodium dimer by tricyclohexylphosphine.[10] The results obtained in this catalytic system are listed in Table 2. 2-Phenylpyridine **1a** was reacted with 3,3-dimethylbut-1-ene in THF at 100 °C for 22 h in the presence of chlorobis(cyclooctene)rhodium dimer (5 mol%), $[(C_8H_{14})_2RhCl]_2$ and tricyclohexylphosphine (3 equiv. of Rh) to give the alkylated products **2e** and **3a** in 98% yield: 20 turnovers was the maximum achieved. The new catalytic system gave high yields with a short reaction time at lower reaction temperature. Linear aliphatic alk-1-enes such as pent-1-ene, hex-1-ene, oct-1-ene and non-1-ene were reexamined. In the case of pent-1-ene, the reaction afforded a high yield (63%) of the desired alkylated product **2a**, as shown in run 2. Yet, in the cases of other alkenes, the alkylated products were obtained in low yields (25–35%).

3-Methyl-2-phenylpyridine, **1b** containing a methyl group at the 3-position of the pyridine ring, was examined for this alkylation. The results are listed in Table 3. Treatment of **1b** with 3,3-dimethylbut-1-ene in THF at 110 °C for 21 h in the presence of rhodium catalyst (10 mol%) made *in situ* from $[(C_8H_{14})_2RhCl]_2$ and tricyclohexylphosphine gave the mono alkylated product **2j** exclusively in 99% yield (Scheme 5). The doubly alkylated product could not be detected, probably due to interference in the formation of the rhodium–hydride

Table 2 The results of the alkylation of **1a** by $[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$ as a catalyst[a]

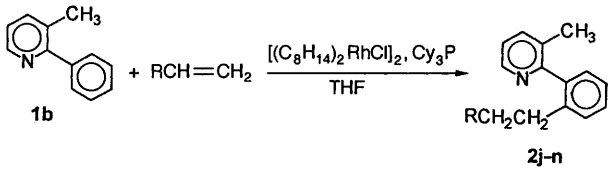
Run	Alkene	Product	T/°C	t/h	Yield (%)	Mono:doubly
1	$Bu^tCH{=}CH_2$	**2e**	100	22	98	92:8
2	Pent-1-ene	**2a**	100	96	63	94:6
3	Hex-1-ene	**2b**	120	144	35	100:0
4	Oct-1-ene	**2g**	120	144	33	100:0
5	Non-1-ene	**2c**	140	72	25	100:0

[a] 5 mol% of $[(C_8H_{14})_2RhCl]_2$ + 6 Cy_3P was used.

Table 3 The results of the alkylation of 3-methyl-2-phenylpyridine **1b**[a]

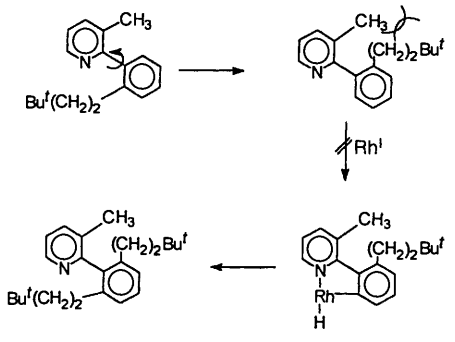
Run	Alkene	Product	Catalyst	T/°C	t/h	Yield (%)[b]
1	$Bu^tCH{=}CH_2$	**2j**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	105–110	21	99
2	Pent-1-ene	**2k**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	110	72	68
3	Hex-1-ene	**2l**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	110	48	54
4	$(EtO)_3SiCH{=}CH_2$	**2m**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	110	38	67
5[c]	$(EtO)_3SiCH{=}CH_2$	**2m**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	120	5	96
6[d]	$(MeO)_3SiCH{=}CH_2$	**2n**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	125	5	97
7[e]	$Bu^tCH{=}CH_2$	**2j**	$[(C_8H_{14})_2RhCl]_2$ + $6Cy_3P$	120	12	58
8	$Bu^tCH{=}CH_2$	**2j**	$[(C_8H_{14})_2RhCl]_2$	110	20	Trace

[a] **1b**:alkene:catalyst (based on Rh) = 1:5:0.1, solvent THF. [b] Isolated yield based on **1b**. [c] **1b**:alkene:catalyst = 1:5:0.15. [d] **1b**:alkene:catalyst = 1:5:0.20. [e] **1b**:alkene:catalyst = 1:5:0.05.



Scheme 5

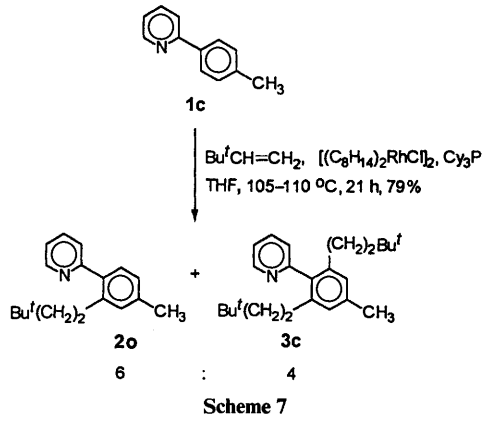
complex with the mono alkylated product by the steric hindrance of the methyl group in the pyridine ring and the alkyl in the phenyl group (Scheme 6).



Scheme 6

Linear 1-alkyl alkenes such as pent-1-ene and hex-1-ene gave moderate yields of the corresponding alkylated products (**2k** and **2l**), respectively (anti-Markownikoff products only). Conjugated alkenes such as isoprene gave trace amounts of the alkylated product, probably due to the stability of the η^3-complex formed from the reaction of the conjugated alkene and the hydride of the hydrido metal complex. In the case of vinylsilanes, triethoxyvinylsilane reacted with **1b** in the presence of 10 mol% (based on Rh) of catalyst to give the alkylated product **2m** in 67% yield after 38 h. When 15 mol% of rhodium catalyst was used, the reaction time was reduced to 4.5 h and the isolated yield increased to 96% (run 5). Trimethoxyvinylsilane showed similar reactivity (97%). In order to reduce the amount of rhodium catalyst, the use of 5 mol% of catalyst was investigated. Under these conditions 3,3-dimethylbut-1-ene was alkylated to **2j** in 58% yield. This result shows that more than 10 mol% of the catalyst must be used to increase the yields.

To compare the ligand effects, when $[(C_8H_{14})_2RhCl]_2$ was used, the reaction gave a trace amount of **2j**, as shown in run 8, which showed that the phosphine ligand is essential for the alkylation. Finally, 2-(*p*-tolyl)pyridine **1c** was examined as a candidate for alkylation. The substrate **1c** reacted with 3,3-dimethylbut-1-ene in THF at 105–110 °C for 21 h in the presence of the Rh^I complex to give the mono alkylated product **2o** and doubly alkylated product **3c** in 79% after chromatographic isolation (**2o**:**3c** = 6:4) (Scheme 7). Unlike **1a**, the



Scheme 7

ratio of the doubly alkylated product **3c** increased, probably due to the electronic effect of the methyl group in the phenyl ring.

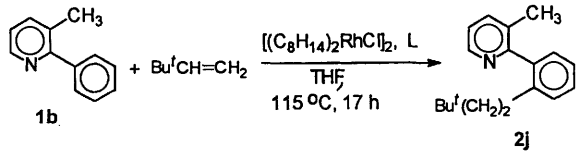
In order to compare the effects of phosphorus(III) ligands in the alkylation of 2-phenylpyridines, 3-methyl-2-phenylpyridine **1b** was chosen. Generally, the steric and electronic properties of phosphorus(III) ligands can be parameterized into steric and electronic components by Tolman's cone angle and the pK_a of phosphorus(III) ligands, respectively.[11] The substrate **1b** reacted with 3,3-dimethylbut-1-ene in the presence of $[(C_8H_{14})_2RhCl]_2$ and various phosphorus(III) ligands such as trimethylphosphine, tricyclohexylphosphine, triphenylphosphine, tributylphosphine, triethylphosphite, triphenylphosphite and tri(*p*-tolyl)phosphine in THF at 115 °C for 17 h (Scheme 8). The results obtained are listed in Table 4.

In the case of $(EtO)_3P$ having the smallest cone angle (109°), the alkylation gave the lowest yield (4%). Cy_3P, having the largest cone angle (170°), gave the highest conversion yield (92%). Interestingly, the conversion yield of **1b** increased as the

Table 4 The results of alkylation of **1b** by various phosphorus(III) ligands[a]

Run	Phosphine ligand	pK_a	Cone angle/°	GC yield (%)
1	$(EtO)_3P$	3.31	109	4
2	Me_3P	8.65	118	21
3	$(PhO)_3P$	−2.00	128	6
4	Bu_3P	8.43	132	40
5	$(p\text{-Tolyl})_3P$	3.84	145	70
6	Ph_3P	2.73	145	80
7	Cy_3P	9.70	170	92

[a] **1b**:$[(C_8H_{14})_2RhCl]_2$:L:$Bu^tCH{=}CH_2$ = 1:0.05:0.3:5; 115 °C, 17 h, THF.



Scheme 8

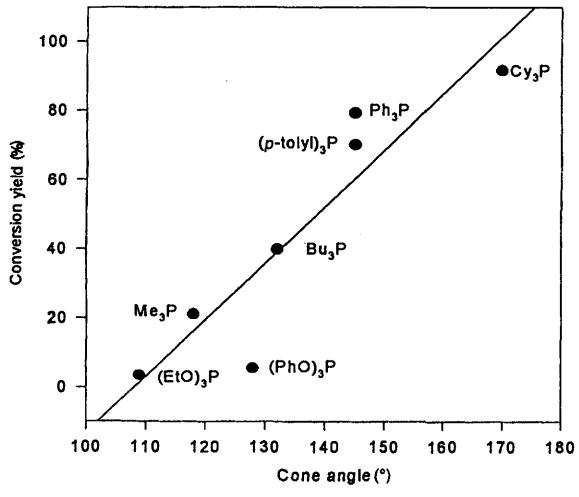


Fig. 1 Effects of the cone angle of phosphorus(III) ligands in alkylations of **1b**

cone angle increased, as shown in Fig. 1. On the other hand, pK_a of phosphorus(III) ligands has no correlation with alkylations of **1b**.

These results show that alkylation of 2-phenylpyridines with alkenes *via* aromatic C–H bond activation depends to a greater extent on the steric factor (cone angle) of phosphorus(III) ligands than on the electronic factor.

In conclusion, this work shows the first regioselective alkylation of 2-phenylpyridines with terminal alkenes: 2-Phenylpyridine **1a** reacted with terminal alkenes in the presence of a rhodium(I) complex catalyst to give the mono *ortho*-alkylated products **2a–i** and doubly alkylated products **3a–b** (>9:1). The same reaction of 3-methyl-2-phenylpyridine **1b** gave the mono alkylated products **2j–n** exclusively under the same reaction conditions due to the steric hindrance between the methyl group of pyridine and the alkyl group of **2**. As the catalyst ligand, tricyclohexylphosphine was found to be more effective than triphenylphosphine. This alkylation reaction appears to depend more on the steric nature of phosphorus(III) ligands than the electronic nature.

Experimental

^1H NMR Spectra were recorded on Bruker AC-300F (300 MHz) and Bruker AC-200 (200 MHz) spectrometers. The chemical shifts (δ) are reported in ppm relative to internal tetramethylsilane in $CDCl_3$; J values are given in Hz. ^{13}C NMR Spectra were recorded on Bruker AC-300F (75 MHz) and Bruker AC-200 (50.3 MHz) spectrometers. Infrared spectra were run on a Nicolet magna 550 FT-IR spectrophotometer. 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 (TLC) was performed on a glass plate (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-phenylpyridines

Method A. A screw-capped pressure vial was charged with $(Ph_3P)_3RhCl$ (10 mol%, 0.064 mmol) dissolved in THF (3 cm^3), and **1a** (100 mg, 0.64 mmol) and alkene (5 equiv., 3.2 mmol) were added. The reaction mixture was heated at 110–120 °C for 48–144 h with stirring. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography on silica gel (EtOAc–hexane, 1:10).

Method B. A screw-capped pressure vial was charged with chlorobis(cyclooctene)rhodium(I) dimer (23.1 mg, 5 mol%) and tricyclohexylphosphine (54.2 mg, 30 mol%) dissolved in THF (3 cm^3), and **1a** (100 mg, 0.64 mmol) and alkene (5 equiv., 3.2 mmol) were added. The reaction mixture was heated at 100–140 °C for 22–144 h with stirring. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography on silica gel.

2-(2-Pentylphenyl)pyridine 2a. δ_H(200 MHz; $CDCl_3$) 8.66–8.67 (1 H, m, 6-H), 7.68–7.80 (1 H, m, 4-H), 7.20–7.40 (6 H, m, 3,5-H and 3′,4′,5′ and 6′-H), 2.71 (1 H, d, J 7.68), 2.67 (1 H, d, J 6.03), 1.25–1.60 [2 H, m, $CH_3(CH_2)_2CH_2$], 1.0–1.25 (4 H, m, $CH_3CH_2CH_2$), 0.79 (3 H, t, J 6.4, CH_3); δ_C(50.3 MHz; $CDCl_3$) 160.34 (C-2 in py), 149.09 (C-6 in py), 140.75 (C-1 in Ph), 140.32 (C-2 in Ph), 135.99 (C-4 in py), 129.66 (C-4,5 in Ph), 128.20 (C-6 in Ph), 125.67 (C-3 in Ph), 124.04 (C-3 in py), 121.52 (C-5 in py), 32.87 (C-1 in pentyl), 31.61 (C-2 in pentyl), 30.89 (C-3 in pentyl), 22.26 (C-4 in pentyl), 13.88 (CH_3); m/z 225 (M^+, 24%), 196 (M^+ − ethyl, 4.9), 182 (M^+ − propyl, 100), 168 (M^+ − butyl, 19), 167 (54.0), 154 (7.8), 91 (95.5); ν_{max}(NaCl)/cm^{-1} 3060w, 2960w, 2930s, 2860s, 1586s, 1562s, 1470m, 1425s, 1025s, 990w, 795w, 750vs (Found: C, 85.19; H, 8.52; N, 6.09. $C_{16}H_{19}N$ requires C, 85.29; H, 8.49; N, 6.22%).

2-(2-Hexylphenyl)pyridine 2b. δ_H(200 MHz; $CDCl_3$) 8.60–8.70 (1 H, m, 6-H in py), 7.72 (1 H, dt, J 1.81, 7.68, 4-H in py), 7.00–7.39 (6 H, m, Ar-H in Ph and py), 2.69 (2 H, t, J 7.64), 1.30–1.50 (2 H, m), 1.16 (6 H, br s), 0.81 (3 H, t, J 6.21); δ_C(50.3 MHz; $CDCl_3$) 160.34, 149.05, 140.76, 140.31, 135.97, 129.66, 129.64, 128.20, 125.65, 124.04, 121.50, 32.89, 31.43, 31.15, 29.04, 22.41, 13.95; m/z 239 (M^+, 10%), 196 (M^+ − propyl, 2), 182 (M^+ − butyl, 39), 168 (M^+ − pentyl, 8), 86 (68.8), 84 (100); ν_{max}(NaCl)/cm^{-1} 3060w, 3010w, 2960m, 2935s, 2860m, 1590m, 1565m, 1470m, 1460m, 1445m, 1425m, 1355w, 1030w, 995w, 800m, 755vs (Found: C, 85.20; H, 8.89; N, 5.95. $C_{17}H_{21}N$ requires C, 85.31; H, 8.84; N, 5.85%).

2-(2-Nonylphenyl)pyridine 2c. δ_H(200 MHz; $CDCl_3$) 8.66–8.70 (1 H, m, 6-H), 7.68–7.73 (1 H, m, 4-H), 7.20–7.40 (6 H, m, 3,5-H and 3′,4′,5′ and 6′-H), 2.71 (1 H, d, J 7.65), 2.67 (1 H, d, J 5.85), 1.38–1.48 (2 H, m), 1.0–1.38 (12 H, br s), 0.87 (3 H, t, J 6.7); δ_C(50.3 MHz; $CDCl_3$) 160.35, 149.10, 140.78, 140.33, 136.00, 129.87, 128.22, 125.67, 124.06, 121.53, 32.91, 31.85, 31.23, 29.40, 29.25, 22.64, 14.08; m/z 281 (M^+, 3.8%), 182 (100), 167 (57.6); ν_{max}(NaCl)/cm^{-1} 3060w, 3010w, 2960w, 2930vs, 2860s, 1586s, 1562m, 1490w, 1470s, 1440m, 1425s, 1150w, 1025s, 992w, 796w, 750s, 725w (Found: C, 85.10; H, 9.86; N, 5.01. $C_{20}H_{27}N$ requires C, 85.36; H, 9.66; N, 4.98%).

2-[2-(3-Oxobutyl)phenyl]pyridine 2d. δ_H(200 MHz; $CDCl_3$) 8.60–8.70 (1 H, m, 6-H), 7.70–7.85 (1 H, m, 4-H), 7.19–7.43 (6 H, m, 3,5-H and 3′,4′,5′ and 6′-H), 2.97 (1 H, d, J 9.58), 2.94 (1 H, d, J 8.25), 2.60–2.73 (2 H, t), 2.05 (3 H, s); δ_C(50.3 MHz; $CDCl_3$)

158.96, 149.04, 140.31, 139.07, 136.40, 129.87, 129.77, 128.50, 126.26, 123.97, 121.80, 45.39, 29.78, 27.44; *m/z* 225 (M^+, 1%), 183 (10.2), 182 ($M^+ - COCH_3$, 59.4), 168 ($M^+ - CH_2COCH_3$, 6.1), 167 (40.3), 154 ($M^+ - CH_2CH_2COCH_3$, 2.8), 84 (100); ν_{max}(NaCl)/cm^{-1} 3050w, 3000w, 2930m, 1708s (CO), 1670m, 1580s, 1465m, 1440m, 1420s, 1350s, 1220w, 1160w, 755s.

2-(2-Hexylphenyl)pyridine 2e. δ_H(200 MHz; $CDCl_3$) 8.67 (1 H, d, *J* 4.9, 6-H), 7.70 (1 H, t, *J* 7.5, 4-H), 7.39–7.70 (6 H, m, 3,5-H and 3′,4′,5′,6′-H), 2.60–2.71 (2 H, m), 1.28–1.38 (2 H, m), 0.76 (9 H, s); δ_C(50.3 MHz; $CDCl_3$) 160.19, 148.95, 141.38, 140.21, 135.95, 129.77, 129.59, 128.25, 125.58, 124.00, 121.50, 46.14 (CH_2), 30.38 (C in Bu^t), 29.01 (CH_3 in Bu^t), 28.37 (CH_2); *m/z* 239 (M^+, 8.0%), 182 ($M^+ - Bu^t$, 100), 167 (36.2), 84 (76.5); ν_{max}(film, NaCl)/cm^{-1} 3060w, 3002w, 2950vs, 2900m, 2880m, 1582s, 1560m, 1468s, 1440m, 1422s, 1360m, 1245w, 1150w, 1090w, 1020m, 990w, 795w, 750s (Found: C, 85.42; H, 8.93; N, 5.65. $C_{17}H_{21}N$ requires C, 85.31; H, 8.84; N, 5.85%).

2-[2-(2-Trimethylsilylethyl)phenyl]pyridine 2f. δ_H(200 MHz; $CDCl_3$) 8.60–8.75 (1 H, m, 6-H), 7.73 (1 H, t, *J* 7.7, 3-H), 7.20–7.40 (6 H, m, 3,5-H and 3′,4′,5′,6′-H), 2.64–2.74 (2 H, m, CH_2), 0.64–0.74 (2 H, m, CH_2), −0.13 (9 H, s, Me_3Si); δ_C(50.3 MHz, $CDCl_3$) 160.30, 149.09, 143.54, 139.76, 136.03, 129.70, 129.19, 128.39, 125.57, 124.06, 121.54, 27.29 (CH_2), 19.19 (CH_2), −1.99 [$Si(CH_3)$]; *m/z* 255 (M^+, 20%), 240 ($M^+ - CH_3$, 11), 183 ($M^+ - SiMe_3$, 14), 182 (100), 167 (28.5); ν_{max}(NaCl)/cm^{-1} 3050m, 3000m, 2950s, 2890m, 1665w, 1583s, 1555m, 1485w, 1468s, 1438m, 1422s, 1245s, 1198w, 1175w, 1145w, 1115w, 1095w, 1022m, 988m, 910m, 860s, 840s, 795m, 750vs, 720w, 690m, 635w, 620m.

2-(2-Octylphenyl)pyridine 2g. δ_H(200 MHz; $CDCl_3$) 8.66–8.70 (1 H, m, 6-H in py), 7.72 (1 H, dt, *J* 1.8, 7.64, 4-H in py), 7.20–7.40 (6 H, m, Ar-H), 2.69 (2 H, t, *J* 7.67), 1.25–1.60 (2 H, m), 1.17 (10 H, br s), 0.85 (3 H, t, *J* 6.4); δ_C(50.3 MHz; $CDCl_3$) 160.35, 149.06, 140.77, 140.30, 135.98, 129.67, 129.65, 128.21, 125.66, 124.05, 121.51, 32.91, 31.79, 31.20, 29.39, 29.19, 29.08, 22.59, 14.03; *m/z* 267 (M^+, 17%), 238 (M^+ − ethyl, 5), 224 (M^+ − propyl, 4), 196 (M^+ − pentyl, 5), 182 (M^+ − hexyl, 100), 84 (10); ν_{max}(NaCl)/cm^{-1} 3060w, 3010w, 2960m, 2930vs, 2860m, 1590s, 1560m, 1495w, 1470s, 1445m, 1427m, 1160w, 1025w, 995w, 800m, 755s (Found: C, 85.18; H, 9.57; N, 5.25. $C_{19}H_{25}N$ requires C, 85.34; H, 9.42; N, 5.24%).

2-[2-(2-Phenethyl)phenyl]pyridine 2h. δ_H(200 MHz; $CDCl_3$) 8.60–8.75 (1 H, m, 6-H), 7.69 (1 H, t, *J* 7.7, 4-H), 6.97–7.36 (11 H, m, Ph, 3,5-H and 3′,4′,5′,6′-H), 2.97–3.10 (2 H, m, CH_2), 2.70–2.81 (2 H, m, CH_2); δ_C(50.3 MHz; $CDCl_3$) 160.14, 149.00, 141.95, 140.38, 139.72, 136.15, 129.85, 129.72, 128.25, 128.15, 126.03, 125.66, 123.94, 121.62, 37.76 (CH_2), 35.33 (CH_2); *m/z* 259 (M^+, 38%), 258 (M^+ − 1, 55), 182 (M^+ − Ph, 4), 168 ($M^+ - CH_2Ph$, 58), 167 (100); ν_{max}(NaCl)/cm^{-1} 3060m, 3030m, 2930m, 2860w, 1605m, 1587s, 1560m, 1495m, 1470s, 1455m, 1443m, 1427s, 1150w, 1095w, 1027m, 995m, 800m, 755vs, 705s (Found: C, 87.92; H, 6.71; N, 5.37. $C_{19}H_{17}N$ requires C, 87.99; H, 6.61; N, 5.40%).

2-{2-[2-(*p*-Tolyl)ethyl]phenyl}pyridine 2i. δ_H(200 MHz; $CDCl_3$) 8.60–8.75 (1 H, m, 6-H), 7.72 (1 H, t, *J* 7.7, 4-H), 7.19–7.37 (6 H, m, 3,5-H and 3′,4′,5′,6′-H), 6.87–7.04 (4 H, m, tolyl), 2.90–3.03 (2 H, m, CH_2), 2.68–2.77 (2 H, m, CH_2), 2.28 (3 H, s, *p*-Me); δ_C(50.3 MHz; $CDCl_3$) 160.22, 149.07, 140.43, 139.87, 138.96, 136.16, 135.13, 129.76, 128.89, 128.74, 128.35, 128.16, 127.43, 126.04, 124.01, 121.67, 37.35 (CH_2), 35.49 (CH_2), 20.96 (CH_3 in tolyl); *m/z* 273 (M^+, 61%), 180 (19), 167 (100), 155 (20), 86 (22), 84 (35); ν_{max}(NaCl)/cm^{-1} 3050m, 3020m, 2930s, 2860m, 1587s, 1565m, 1515s, 1495w, 1470s, 1445m, 1425s, 1155w, 1115w, 1045w, 1030m, 995w, 810m, 800m, 755vs (Found: C, 87.97; H, 6.73; N, 5.45. $C_{20}H_{19}N$ requires C, 87.87; H, 7.01; N, 5.12%).

3-Methyl-2-(3,3-dimethylbutylphenyl)pyridine 2j. δ_H(300 MHz; $CDCl_3$) 8.48–8.51 (1 H, m, 6-H in py), 7.56 (1 H, d, 4-H in py), 7.13–7.31 (5 H, aromatic H), 2.23–2.52 (2 H, br s), 2.11 (3 H, s, 3-CH_3), 1.05–1.46 (2 H, br s), 0.68 (9 H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 159.39, 146.35, 141.03, 139.64, 137.48, 131.40, 129.33, 128.55, 127.89, 125.44, 122.01, 45.48 (CH_2), 30.13 (C in Bu^t), 28.80 (CH_3 in Bu^t), 28.28 (CH_2), 19.18 (CH_3 in py); *m/z* 253 (M^+, 6%), 238 ($M^+ - CH_3$, 9), 196 ($M^+ - Bu^t$, 100), 181 (27); ν_{max}(NaCl)/cm^{-1} 3057w, 3015w, 2954vs, 2905m, 2866m, 1594m, 1571m, 1490w, 1473m, 1449m, 1426m, 1393w, 1364m, 1247w, 1119w, 1023m, 791m, 756s, 733w, 627w (Found: C, 85.07; H, 9.23; N, 5.67. $C_{18}H_{23}N$ requires C, 85.32; H, 9.15; N, 5.53%).

3-Methyl-2-(2-pentylphenyl)pyridine 2k. δ_H(300 MHz; $CDCl_3$) 8.48–8.51 (1 H, m, 6-H in py), 7.56 (1 H, dd, *J* 0.74, 7.46, 4-H in py), 7.12–7.32 (5 H, aromatic H), 2.40 (2 H, br s), 2.10 (3 H, s, 3-CH_3), 1.40 (2 H, t, *J* 7.03), 1.11–1.16 (4 H, m), 0.77 (3 H, t, *J* 6.52, CH_3); δ_C(75 MHz; $CDCl_3$) 159.47, 146.37, 140.30, 139.70, 137.48, 131.37, 129.15, 128.52, 127.77, 125.47, 121.97, 32.71, 31.40, 30.16, 22.13, 19.12 (CH_3 in py), 13.77; *m/z* 239 (M^+, 12%), 224 ($M^+ - CH_3$, 53), 210 (M^+ − ethyl, 9), 196 (M^+ − propyl, 100), 182 (M^+ − butyl, 26), 168 (19); ν_{max}(NaCl)/cm^{-1} 3057w, 3015w, 2955s, 2927s, 2859s, 1587m, 1571m, 1490w, 1448s, 1428s, 1380w, 1182w, 1119w, 1065w, 1024m, 791s, 756s, 627m (Found: C, 84.97; H, 9.27; N, 5.74. $C_{17}H_{21}N$ requires C, 85.31; H, 8.84; N, 5.85%).

3-Methyl-2-(2-hexylphenyl)pyridine 2l. δ_H(300 MHz; $CDCl_3$) 8.50 (1 H, d, *J* 5.05, 6-H in py), 7.56 (1 H, dd, *J* 0.70, 7.52, 4-H in py), 7.12–7.34 (5 H, aromatic H), 2.39 (2 H, br s), 2.10 (3 H, s, 3-CH_3), 1.39 (2 H, t, *J* 7.13), 1.05–1.26 (6 H, m), 0.79 (3 H, t, *J* 6.57, CH_3); δ_C(75 MHz; $CDCl_3$) 159.52, 146.42, 140.39, 139.75, 137.52, 131.42, 129.19, 128.57, 127.82, 125.51, 122.00, 32.78, 31.34, 30.47, 28.92, 22.33, 19.16 (CH_3 in py), 13.95; *m/z* 253 (M^+, 13%), 238 ($M^+ - CH_3$, 63), 210 (M^+ − propyl, 9), 196 (M^+ − butyl, 100), 182 (M^+ − pentyl, 26); ν_{max}(NaCl)/cm^{-1} 3057w, 3015w, 2955s, 2927s, 2857s, 1589m, 1573m, 1560m, 1490w, 1457s, 1446s, 1423s, 1381w, 1116w, 1024m, 791s, 754s, 627m (Found: C, 85.22; H, 9.30; N, 5.48. $C_{18}H_{23}N$ requires C, 85.32; H, 9.15; N, 5.53%).

3-Methyl-2-(2-triethoxysilylethyl)pyridine 2m. δ_H(300 MHz; $CDCl_3$) 8.49 (1 H, d, *J* 4.95, 6-H in py), 7.57 (1 H, d, *J* 7.83, 4-H in py), 7.10–7.37 (5 H, aromatic H), 3.65 [6 H, q, *J* 7.02, $SiO(CH_2CH_3)_3$], 2.50 (2 H, br s, $PhCH_2CH_2Si$), 2.11 (3 H, s, 3-CH_3), 1.12 [9 H, t, *J* 7.02, $SiO(CH_2CH_3)_3$], 0.81 (2 H, br s, $PhCH_2CH_2Si$); δ_C(75 MHz; $CDCl_3$) 159.36, 146.38, 142.28, 139.15, 137.72, 131.64, 128.60, 128.16, 125.64, 122.10, 58.11 (CH_2O), 26.05 (CH_2), 19.19 (CH_3 in py), 18.13 (CH_3 in ethoxy), 12.04 (CH_2Si); *m/z* 359 (M^+, 35%), 344 ($M^+ - CH_3$, 77), 314 (M^+ − OEt, 12), 196 [$M^+ - Si(OEt)_3 + 1$, 100], 181 (29), 79 (18); ν_{max}(NaCl)/cm^{-1} 3058w, 2974s, 2927s, 2890s, 1584w, 1568w, 1490w, 1444m, 1424m, 1390m, 1365w, 1295w, 1185m, 1166s, 1103s, 1079s, 1024m, 994w, 959s, 839w, 820m, 791s, 759s, 627w (Found: C, 66.43; H, 8.46; N, 3.93. $C_{20}H_{29}NO_3Si$ requires C, 66.81; H, 8.13; N, 3.90%).

3-Methyl-2-(2-trimethoxysilylethyl)pyridine 2n. δ_H(300 MHz; $CDCl_3$) 8.50 (1 H, d, *J* 5.03, 6-H in py), 7.58 (1 H, d, *J* 7.31, 4-H in py), 7.14–7.34 (5 H, H in Ar and 5-H in py), 3.40 [9 H, s, $Si(OCH_3)_3$], 2.51 (2 H, br s, α-CH_2 to Ph), 2.11 (3 H, s, 3-CH_3 in py), 0.83 (2 H, br s, $SiCH_2$); δ_C(75 MHz; $CDCl_3$) 159.27, 146.35, 141.94, 139.19, 137.56, 131.42, 128.57, 128.03, 125.61, 122.00, 50.10 (CH_3O), 25.78 (CH_2), 19.08 (CH_3 in py), 10.69 (CH_2Si); *m/z* 317 (M^+, 31%), 302 ($M^+ - CH_3$, 84), 196 ($M^+ - Si(OMe)_3$, 100), 181 (43), 121 [$Si(OMe)_3^+$, 15], 91 (26); ν_{max}(NaCl)/cm^{-1} 3050w, 2942s, 2840s, 1775w, 1584w, 1573w, 1490w, 1448m, 1424m, 1192s, 1086s, 1023w, 995w, 906w, 875w, 843m, 826s, 791s, 760s, 627w.

2-(2-Hexyl-4-methylphenyl)pyridine 2o. δ_H(300 MHz; $CDCl_3$) 8.64–8.67 (1 H, m, 6-H in py), 7.70 (1 H, d, 6′-H), 7.69 (1 H, dt, *J* 7.68, 1.79, 4-H in py), 7.35 (1 H, d, *J* 7.82, 3-H in py), 7.16–7.24 (1 H, m, 5-H in py), 7.09 (1 H, s, 3′-H), 7.06 (1 H, d, *J* 7.70, 5′-H), 2.61–2.68 (2 H, m, CH_2CH_2Ph), 2.36 (3 H, s, 4′-Me), 1.29–1.36 (2 H, m, CH_2CH_2Ph), 0.77 (9 H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 160.20, 148.91, 141.20, 137.89, 137.40, 135.89, 130.53, 129.59, 126.34, 124.01, 121.31, 46.22, 30.40, 29.01, 28.29, 21.13

(CH_3 in tolyl); *m/z* 253 (M^+, 10%), 238 ($M^+ - CH_3$, 7), 196 ($M^+ - Bu^t$, 100), 181 (27); ν_{max}(NaCl)/cm^{-1} 3053w, 3008w, 2953s, 2906m, 2865m, 1617m, 1587s, 1564w, 1467s, 1427s, 1364m, 1252w, 1150w, 1026w, 993w, 884w, 823w, 790m, 748m, 722w, 628w (Found: C, 85.10; H, 9.44; N, 5.46. $C_{18}H_{23}N$ requires C, 85.32; H, 9.15; N, 5.53%).

2-(2,6-Dihexylphenyl)pyridine 3a. δ_H(200 MHz; $CDCl_3$) 8.71 (1 H, d, *J* 4.7, 6-H in py), 7.71 (1 H, t, *J* 7.64, 4-H in py), 7.40–7.52 (1 H, m, 3-H in py), 7.20–7.31 (3 H, m, H in Ph), 7.09 (1 H, d, *J* 7.14, 5-H in py), 2.28 (4 H, t, *J* 9.5, α-CH_2 to Ph), 1.21–1.37 (4 H, m, α-CH_2 to Ph), 0.67 (18 H, s, Bu^t); δ_C(50.3 MHz, $CDCl_3$) 159.49, 149.21, 141.36, 135.63, 128.10, 126.62, 125.15, 121.59, 46.04, 30.25, 28.91; *m/z* 323 (M^+, 8.5%), 266 ($M^+ - Bu^t$, 100), 252 ($M^+ - CH_2Bu^t$, 2.9), 57 (4.3); ν_{max}(NaCl)/cm^{-1} 3040w, 2940m, 2885m, 2850m, 1572m, 1550w, 1450w, 1420w, 1355m, 1235m, 1110w, 1015w, 980w, 755m (Found: C, 85.07; H, 10.50; N, 4.43. $C_{23}H_{33}N$ requires C, 85.39; H, 10.28; N, 4.33%).

2-(2,6-Dipentylphenyl)pyridine 3b. δ_H(200 MHz; $CDCl_3$) 8.60–8.70 (1 H, m, 6-H in py), 7.73 (1 H, dt, *J* 1.81, 7.68, 4-H in py), 7.21–7.29 (3 H, m, Ar-H in Ph), 7.11 (2 H, d, *J* 6.95, 3,5-H in py), 2.29 (4 H, t, *J* 7.92), 1.30–1.50 (4 H, m), 1.02–1.25 (8 H, m), 0.77 (6 H, t, *J* 6.46); δ_C(50.3 MHz; $CDCl_3$) 159.74, 149.28, 140.75, 140.31, 135.65, 127.91, 126.49, 125.00, 121.54, 33.52, 31.73, 30.75, 22.25, 13.87; *m/z* 295 (M^+, 21%), 266 (M^+ – ethyl, 4), 252 (M^+ – propyl, 59), 238 (M^+ – butyl, 7), 180 (11), 86 (66), 84 (100); ν_{max}(NaCl)/cm^{-1} 3070w, 2960m, 2935vs, 2870m, 1670w, 1600w, 1585m, 1565w, 1480w, 1465m, 1425w, 1030w, 795w, 755m.

2-(2,6-Dihexyl-4-methylphenyl)pyridine 3c. δ_H(300 MHz; $CDCl_3$) 8.67–8.71 (1 H, m, 6-H in py), 7.70, (1 H, dt, *J* 7.70, 1.81, 4-H in py), 7.26 (1 H, d, *J* 7.84, 3-H in py), 7.18–7.24 (1 H, m, 5-H in py), 6.91 (2 H, s, 3′-H and 5′-H), 2.33 (3 H, s, 4′-Me), 2.21–2.28 (4 H, m), 1.32 (2 H, t), 1.23 (2 H, t), 0.66 (18 H, s, Bu^t); δ_C(75 MHz; $CDCl_3$) 159.55, 149.17, 141.20, 137.50, 137.01, 135.53, 127.36, 125.30, 121.43, 46.07, 30.22, 28.88, 28.80, 21.17; *m/z* 337 (M^+, 8%), 322 ($M^+ - CH_3$, 7), 280 ($M^+ - Bu^t$, 100), 84 (14); ν_{max}(NaCl)/cm^{-1} 3044w, 3007w, 2954vs, 2905s, 2867s, 1611m, 1586s, 1563m, 1463s, 1426m, 1392w, 1364s, 1246m, 1025w, 989w, 856s, 795w, 754w, 723w, 626w (Found: C, 85.35; H, 10.60; N, 4.05. $C_{24}H_{35}N$ requires C, 85.40; H, 10.45; N, 4.15%).

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References

1 B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154; A. A. Bengali, B. A. Arndtsen, P. M. Burger, R. H. Schultz, B. H. Weiller, K. R. Kyle, C. B. Moore and R. G. Bergman, *Pure Appl. Chem.*, 1995, **67**, 281; W. D. Jones and F. J. Feher, *Acc. Chem. Res.*, 1989, **22**, 91; T. C. Flood and J. A. Statler, *Organometallics*, 1984, **3**, 1795; G. W. Parshall, *Chem. Tech.*, 1984, 628; G. W. Parshall, *Acc. Chem. Res.*, 1975, **8**, 113.

2 B. M. Trost, K. Imi and I. W. Davies, *J. Am. Chem. Soc.*, 1995, **117**, 5371; N. A. Williams, Y. Uchimaru and M. Tanaka, *J. Chem. Soc., Chem. Commum.*, 1995, 1129; F. Kakiuchi, Y. Tanaka, T. Sato, N. Chatani and S. Murai, *Chem. Lett.*, 1995, 679; F. Kakiuchi, Y. Yamamoto, N. Chatani and S. Murai, *Chem. Lett.*, 1995, 681; G. C. Hsu, W. P. Kosar and W. D. Jones, *Organometallics*, 1994, **13**, 385; S. Rodewald and R. F. Jordan, *J. Am. Chem. Soc.*, 1994, **116**, 4491; H. Guo and W. P. Weber, *Polym. Bull.*, 1994, **32**, 525; H. Guo, M. A. Tapsak and W. P. Weber, *Polym. Bull.*, 1994, **33**, 417; G. Halbritter, F. Knoch, A. Wolski and H. Kish, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1603; Y. Uchimaru, A. M. M. E. Sayed and M. Tanaka, *Organometallics*, 1993, **12**, 2065; M. Ishikawa, A. Naka and J. Ohshita, *Organometallics*, 1993, **12**, 4987; M. Ishikawa, S. Okazaki, A. Naka and H. Sakamoto, *Organometallics*, 1992, **11**, 4235; E. J. Moore, W. R. Pretzer, T. J. O'Connell, J. Harris, L. LaBounty, L. Chou and S. S. Grimmer, *J. Am. Chem. Soc.*, 1992, **114**, 5888; T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada and M. Tanaka, *J. Am. Chem. Soc.*, 1990, **112**, 7221; R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, 1989, **111**, 778; A. J. Kunin and R. Eisenberg, *Organometallics*, 1988, 7, 2124; T. B. Marder, C. D. Roe and D. Milstein, *Organometallics*, 1988, **7**, 1451; E. M. Gordon and R. Eisenberg, *J. Mol. Catal.*, 1988, **45**, 57; T. Sakakura and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1987, 758; M. J. Burk and R. H. Crabtree, *J. Am. Chem. Soc.*, 1987, **109**, 8025; L. N. Lewis and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 2728; W. D. Jones and W. P. Kosar, *J. Am. Chem. Soc.*, 1986, **108**, 5640; D. Baudry, M. Ephritikhine, H. Felkin and S. J. Holmes-Smith, *Organometallics*, 1983, **2**, 161.

3 A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403; G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451; E. C. Constable, *Polyhedron*, 1984, **3**, 1037; M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73.

4 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, 1993, **366**, 529; S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Pure Appl. Chem.*, 1994, **66**, 1257; F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 62; M. Sonoda, F. Kakiuchi, N. Chatani and S. Murai, *J. Organomet. Chem.*, 1995, **504**, 151.

5 K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson and R. J. Watts, *Inorg. Chem.*, 1991, **30**, 1685 and references cited therein.

6 H. B. Degussa, *Aldrichimica Acta*, 1981, **14**, 13.

7 Y.-G. Lim, Y. H. Kim and J.-B. Kang, *J. Chem. Soc., Chem. Commun.*, 1994, 2267.

8 E. Hauptman, M. Brookhart, P. J. Fagan and J. C. Calabrese, *Organometallics*, 1994, **13**, 774.

9 A. Onopchenko, E. T. Sabourin and D. L. Beach, *J. Org. Chem.*, 1983, **48**, 5101; A. van Rooy, E. Orij, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Organometallics*, 1995, **14**, 34.

10 R. C. Larock, K. Oertle and G. F. Potter, *J. Am. Chem. Soc.*, 1980, **102**, 190.

11 P. B. Dias, M. E. Minas de Piedade and J. A. M. Simoes, *Coord. Chem. Rev.*, 1994, **135/136**, 737; C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313; M. M. Rahman, H.-Y. Liu, K. Eriks, A. Prock and W. P. Giering, *Organometallics*, 1989, **8**, 1; R. J. Angelici, *Acc. Chem. Res.*, 1995, **28**, 51.

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