Exploitation of differential reactivity of the carbon–chlorine bonds in 1,3-dichloroisoquinoline. Routes to new *N*,*N*-chelate ligands and 1,3-disubstituted isoquinolines

Alan Ford, Ekkehard Sinn and Simon Woodward*

School of Chemistry, University of Hull, Kingston-upon-Hull HU6 7RX, UK

Under $Pd(PPh_3)_4$ catalysis, coupling of arylboronic acids to the 1-position of 1,3-dichloroisoquinoline takes place, leading exclusively to 1-aryl-3-chloroisoquinolines. This regiochemistry is demonstrated by the crystal structure of 3-chloro-1-(8-methoxy-1-naphthyl)isoquinoline. The 3-chloro group may be modified by nickel-catalysed reaction with Grignard reagents or direct nucleophilic displacement with $LiSCH_2Ph$. Attempted lithiation of the 3-position is not successful (either deprotonation or complex reactivity results). Under zinc reduction in the presence of $NiCl_2$–PPh_3 and NaI, the 1-aryl-3-chloroisoquinolines furnish 3,3′-biisoquinolines in good yield.

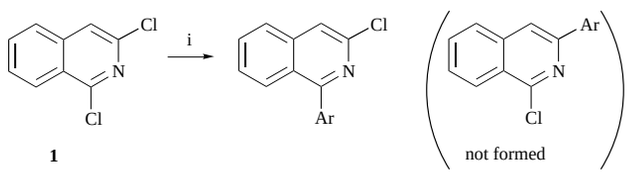
Introduction

N,*N*-Chelates, especially 2,2′-bipyridyl (bpy) and its analogues, are ubiquitous ligands as additives and modifiers in organic reactions mediated by transition metals.[1] For example, although the combination of $RuCl_3$–$NaIO_4$ is normally a powerful system for the cleavage of C=C bonds,[2] in the presence of bpy the nature of the oxidant is moderated and useful epoxidation chemistry results.[3,4] We are interested in the preparation of new bpy-analogues for use in a wide range of transition metal promoted chemistry, including related ruthenium-catalysed oxidations.[5,6] This paper addresses the synthesis of new *N*,*N*-chelates based on isoquinolines, whereby the steric and electronic environment about a coordinated transition metal can be easily perturbed by simple substitutions to the basic core structure. Such approaches are useful as they allow the 'tuning' of rates and selectivities of metal catalysts when optimising the efficiency of individual catalytic systems. In addition a number of different approaches to the synthesis of 1,3-diarylisoquinolines have been developed.

Results and discussion

1,3-Selective cross-coupling reactions

Simple canonical structure arguments indicate that the 1-chloro substituent of 1,3-dichloroisoquinoline[7–9] should be significantly more reactive than its 3-position counterpart. This differential reactivity may be exploited in palladium-catalysed cross-coupling of 1,3-dichloroisoquinoline with arylboronic acids (Suzuki reactions). Regiochemistry in palladium-catalysed reactions of polyhalo substrates is determined at the moment of oxidative addition. We reasoned that the rate of oxidative addition of the isoquinoline's benzylic 1-chloro group would greatly exceed that of the 3-chloro group, leading to high regioselectivity regardless of the steric requirements of the nucleophilic coupling partner. When 1,3-dichloroisoquinoline **1** reacts with phenylboronic acid only the 1-substituted product **2** is formed, none of the 3-substituted regioisomer is isolated from the reaction mixture (Scheme 1). Optimal conditions for this reaction are attained if 3 equiv. of CsF promoter are used.[10] In these cases the reactions are faster and cleaner than those with other bases [5–6 h with CsF *vs*. overnight with Na_2CO_3 or $Ba(OH)_2$]. Under fluoride promotion even the highly hindered 8-methoxy-1-naphthylboronic acid couples in good yield (80%). It is noteworthy that a reasonable barrier to racemisation is expected in atropisomeric **8**, whereas 1-naphthyl-



1

2 Ar = Ph
3 Ar = 4-C_6H_4Me
4 Ar = 2-C_6H_4Me
5 Ar = 2-$C_6H_4(OMe)$
6 Ar = 1-(2-$C_{10}H_6OMe$)
7 Ar = 1-$C_{10}H_7$
8 Ar = 1-(8-$C_{10}H_6OMe$)

Scheme 1 *Reagents and conditions:* i, $ArB(OH)_2$, CsF, $Pd(PPh_3)_4$ (3 mol%), DME, 6 h

isoquinoline racemises freely.[11] This 1,3-isoquinoline coupling selectivity appears not to have been demonstrated before. Selective mono-coupling reactions normally rely on the presence of C–I/C–Br or C–Br/C–OSO_3CF_3 bonds for differential reactivity.[12] Molecules similar to **2–8** are known but in these cases there are no regiochemical issues to be addressed.[13,14] Two reports of rate differences in the oxidative addition of polyhalogenoheterocycles have appeared very recently during the course of our studies. Reactions at the 6-position of 2,6-dichloropurines with organotin or organozinc reagents under catalysis by $[Pd(PPh_3)_2]$ sources are known.[15] 2,4-Dichloroquinazoline is electronically different at the 2- and 4-positions; the 4-position is more electrophilic. Under $Pd(PPh_3)_4$ catalysis, AlR_3 (R = Me, Bu^i) couples first to the benzylic 4-position in refluxing THF or 1,2-dichloroethane. Subsequent addition of more AlR_3 results in coupling to the 2-position.[16]

The regiochemistry of the isoquinoline in Scheme 1 is confirmed by a number of techniques. Complete assignment of the isoquinoline protons of all compounds is possible at 600 MHz. In particular, the 2D NOESY spectrum of **3** shows a clear cross-peak for the *o*-tolyl proton signal and that due to H-C(8) on the isoquinoline. Degradation of **6** by stoichiometric amounts of $PdCl_2$–$NaBH_4$ results in material with ^{1}H NMR spectra identical to the known 1-(2-methoxynaphthyl)isoquinoline.[13] In the case of **8** the atom connectivity was further confirmed by the results of a crystallographic study (Fig. 1). Although all the arylboronic acids tried were successful, there is one limitation on this selective coupling strategy: vinylboronic acids do not participate in the reactions, as $Me_2C{=}CHB(OH)_2$ fails to couple with **1** when the coupling is promoted with

Na_2CO_3. Analogous reactions using CsF have not been carried out.

Disubstituted isoquinolines

Despite their simple constitution, 1,3-disubstituted isoquinolines are not always easily prepared by traditional methods. Often several steps are required to reach the desired target. Several modifications of the new 1-aryl-3-chloroisoquinolines are possible leading to efficient syntheses of new 1,3-disubstituted species. This chemistry is summarised in Scheme 2. The 3-chloro substituent is resistant to transmetallation with BuLi or Bu^{t}Li; only deprotonation at H-C(4) results. This may be achieved cleanly with LiNPr$^i_2$ at 0 °C, or with BuLi·TMEDA or lithium 2,2,6,6-tetramethylpiperidine at −78 °C in THF. Deuteriation of the resulting anion leads to **9** or **10**. Partial transmetallation of the 3-chloro group may be effected in some cases with $LiC_{10}H_8$, followed by a proton quench. For example, rapid addition of **8** to 2.5 equiv. of $LiC_{10}H_8$ at −70 °C yields some **11**, after D_2O quench. However, this reaction is not synthetically useful as variable quantities of uncharacterised reduction products are also formed; use of electrophiles other than H^+ led only to **11**.

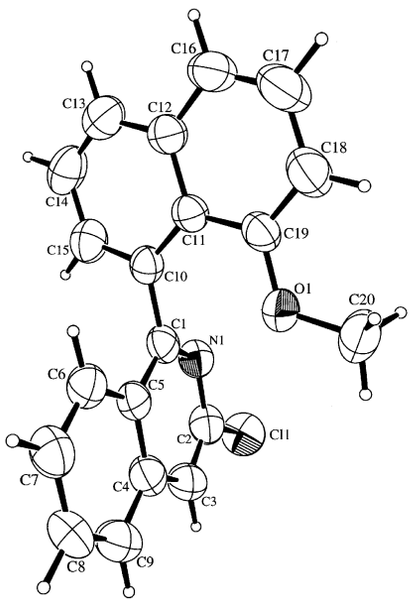
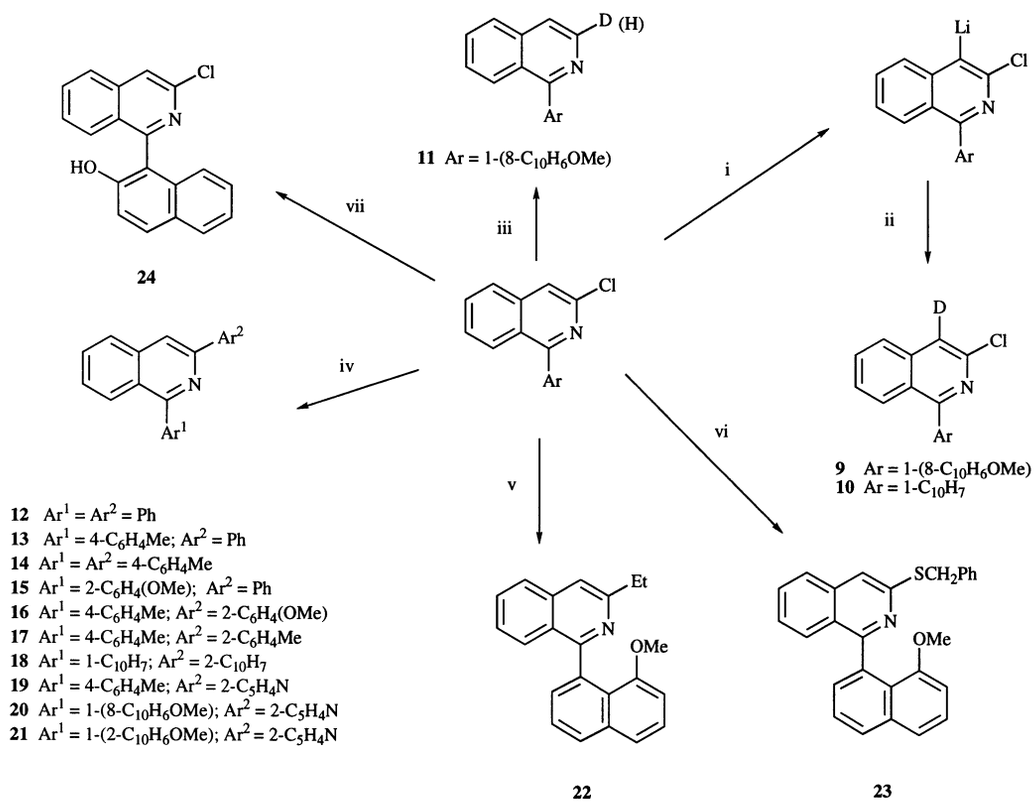


Fig. 1 An ORTEP view of one of the two identical **8** molecules in the unit cell. Selected bond distances: Cl(1)–C(2) 1.742(4), N(1)–C(1) 1.318(5), N(1)–C(2) 1.343(4), O(1)–C(19) 1.367 Å; dihedral angle: N(1)–C(1)–C(10)–C(11) 94.8°

Reaction of the 1-aryl-3-chloroisoquinolines with Grignard reagents at room temperature affords entry to the mixed isoquinolines **12–15**. These reactions are best carried out using catalysis with 10 mol% $NiCl_2$(dppf) [dppf = 1,1′-bis(diphenylphosphino)ferrocene], as far higher reaction rates are attained than with other chelate phosphine nickel catalysts. For example, compound **12** is isolated in 78% within 1 h using $NiCl_2$(dppf), while 70 h are required for equivalent preparations of **13–14** using $NiCl_2$(dppp) [dppf = 1,3-bis(diphenylphosphino)propane] (84 and 75% yield respectively). As an alternative to nickel catalysis, $Pd(PPh_3)_4$ (5 mol%) may be used to promote a second $ArB(OH)_2$ coupling, as in the synthesis of **16–18**. Forcing conditions are necessary as the 3-chloro substituent is only reactive in DMF at 100 °C. The heterocyclic systems **19** (61%), **20** (94%) and **21** (80%) are accessible *via* Stille-type coupling with 2-(Me_3Sn)C_5H_4N. These reactions are rather sluggish and a rather large catalyst loading [$Pd(PPh_3)_4$, 28 mol%] at elevated temperature is required. Competitive product binding to the catalyst necessitates these conditions. In a final catalytic reaction with organoborates it proved possible to introduce an ethyl substituent at the 3-position. Under $NiCl_2$(dppf) catalysis, in the presence of excess zinc dust, reaction of **8** with Li[BEt_3(O-Pr^i)] led to smooth formation of **22** in 70% yield. This efficient



Scheme 2 *Reagents and conditions:* i, LiNPr$^i_2$, THF, 0 °C; or LiTMP, THF, 0 °C; or BuLi·TMEDA, THF, −78 °C; ii, D_2O; iii, $LiC_{10}H_8$, THF, −70 °C, then D_2O or H_2O; iv, Ar^2MgBr, $NiCl_2$(dppf) (5 mol%), THF 0 °C to room temp., 1 h; or $Ar^2B(OH)_2$, Cs_2CO_3, $Pd(PPh_3)_4$ (5 mol%), DMF, 100 °C, 18 h; or 2-(Me_3Sn)C_5H_5N, $Pd(PPh_3)_4$ (28 mol%), DMF, 100 °C, 18 h; v, $LiBEt_3$(OPr^i), $NiCl_2$(dppf) (6.5 mol%), THF, reflux, 3 h; vi, $LiSCH_2Ph$, DMF, 120 °C, 6 h; vii, BBr_3, CH_2Cl_2, −78 °C to room temp., 18 h

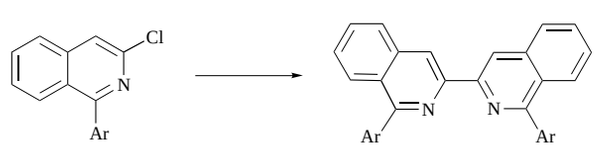
transfer of the ethyl functionality is of note as reductive elimination of the Ni(Et)(Ar)(dppf) intermediate must be rapid to avoid competing β-hydride elimination. Similar effects have been noted by Miyaura *et al.*[17]

In the absence of catalytic activation, the 3-chloro function is rather reluctant to participate in nucleophilic substitution reactions. Reaction of **8** with $LiSCH_2Ph$ is only achieved in DMF at high temperatures (120 °C). Under these conditions the desired product **23** is attained but some dealkylation of the methoxyether occurs as a low yield competing side reaction. The isolation of **23** allows an estimation of the barrier to rotation about the atropisomeric 1,1′-axis. At room temperature in $CDCl_3$ or [$^2H_8$]toluene the ^1H NMR spectrum of **23** shows a typical AB pattern for the diastereotopic benzyl protons. The appearance of the spectrum is identical in the temperature range −20 to +100° C. The signals do not broaden or coalesce and only a slight reduction in the chemical shift difference between the AB-pair is observed. Based on the unchanging nature of the spectrum, compound **23** must have an appreciable barrier to rotation ($\Delta G^{\ddagger} > 100$ kJ mol^{-1}) and similar barriers are likely in the related 8-methoxynaphthyl compounds **8** and **22**. The 8-methoxy function significantly increases the barrier to racemisation, as this value for 1-naphthylisoquinoline is 78.3 kJ mol^{-1} at 298 K.[11] To assess the effect of the 8-methoxy group on the rotational barriers in **8**, **22** and **23** a simple model of the transition state was investigated using the atomic coordinates of **8**. Rotation about the 1,1′-bond indicates that *anti* transition states (*i.e.* those in structures **22–23**) constitute the lowest energy pathway to racemisation for these compounds.[18] Simple Chem 3D modelling using the coordinates of **8** indicates that as the dihedral angle falls from 90 to 72° the separation of the isoquinoline nitrogen and the 8-OMe ether oxygen falls to 2.71 Å; the sum of the N,O van der Waals radii. At a dihedral angle of 0° the N–O distance is only 1.76 Å corresponding to about two thirds of the sum of N,O van der Waals radii. It is likely that these strong interactions lead to significant barriers to 1,1′-rotation.

For those compounds possessing methoxyether functionality, deliberate dealkylation can be effected by use of BBr_3. For example, reaction of **6** with BBr_3 at −78 °C followed by warming to room temperature yields the substituted naphthol **24** in reasonable yield (78%).

Colon reactions

Compounds **2–8** also engage in nickel-catalysed reductive dimerisations (zinc-based Colon reactions[19,20]) to furnish the 3,3′-biisoquinolines **25–31** (69–88%, Scheme 3). These reactions allowed us to improve the procedure for the preparation of 2,2′-bipyridyl-type compounds. Investigation of the primary literature reveals that the isolated yields reported by many different groups for the Colon procedure span a wide range of yields (*ca.* 30–90%) even for very similar molecules. Analysis of the crude reaction mixture containing **25** by FAB mass spectrometry revealed the presence of insoluble $ZnCl_2$(**25**) as the major product in addition to smaller amounts of **25**. Given that stoichiometric amounts of $ZnCl_2$ are produced in zinc-promoted pyridyl dimerisations, loss of product as insoluble zinc complexes is not unexpected. We find that reproducibly high yields of free ligand are attained if aqueous Na_3PO_4 or 6 M HCl is added to the reaction mixture prior to work-up to remove the $ZnCl_2$.



2 Ar = Ph
3 Ar = 4-C_6H_4Me
4 Ar = 2-C_6H_4Me
5 Ar = 2-C_6H_4(OMe)
6 Ar = 1-(2-$C_{10}H_6$OMe)
7 Ar = 1-$C_{10}H_7$
8 Ar = 1-(8-$C_{10}H_6$OMe)

25 Ar = Ph
26 Ar = 4-C_6H_4Me
27 Ar = 2-C_6H_4Me
28 Ar = 2-C_6H_4(OMe)
29 Ar = 1-(2-$C_{10}H_6$OMe)
30 Ar = 1-$C_{10}H_7$
31 Ar = 1-(8-$C_{10}H_6$OMe)

Scheme 3 *Reagents and conditions:* i, NaI, Zn, $NiCl_2$ (10 mol%), PPh_3 (30 mol%), THF, reflux, 3 h

In conclusion we have demonstrated that by exploiting the differential reactivity of the two carbon–chlorine bonds in 1,3-dichloroisoquinoline, a wide range of novel isoquinolines and *N*,*N*-chelate ligands are easily accessible. The metal complexes and use of these ligands in various transition metal mediated reactions is currently being explored.

Experimental

All reactions involving air sensitive reagents were carried out under argon or nitrogen atmospheres using standard Schlenk techniques. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium–benzophenone immediately prior to use. Toluene and acetonitrile were distilled from calcium hydride, dimethylformamide (DMF) was dried over 4 Å molecular sieves. $POCl_3$ was distilled before use. All other reagents were used as supplied. The light petroleum used had bp 40–60 °C. Flash chromatography was carried out on activated silica gel (Rhône-Poulenc Sorbsil C60 40/60H) or alumina (BDH, Brockmann Grade I). Thin layer chromatography (TLC) analyses used Merck Kieselgel 60 $HF_{254+366}$ plates. Infrared spectra were recorded using a Perkin-Elmer 983G instrument. Proton NMR spectra (270 MHz) and ^{13}C NMR spectra (67.8 MHz) were recorded on a JEOL-270 spectrometer at ambient temperature in $CDCl_3$. High field proton NMR spectra were obtained on a Bruker VXR600S (600 MHz). For all NMR spectra tetramethylsilane was used as the internal standard; *J* values are given in Hz. Finnigan 1020 (electron impact ionisation, EI) and VG-ZAB (EI and fast atom bombardment ionisation, FAB) machines were employed for mass spectrometry studies. The arylboronic acids (except 8-methoxy-1-naphthylboronic acid) and 2-(Me_3Sn)C_5H_4N[21] used were literature compounds. General routes to 1,3-dichloroisoquinoline were employed.[7–9]

8-Methoxy-1-naphthylboronic acid

A solution of Bu^{t}Li (1.7 M in pentane; 50 cm^3, 0.085 mol) was added dropwise to 1-methoxynaphthalene (12.18 g, 11.2 cm^3, 0.077 mol) in cyclohexane (50 cm^3) and the mixture was stirred at room temperature for 24 h. The resulting pale orange–brown suspension was added slowly, using a wide-bore cannula, to a stirred solution of $B(OMe)_3$ (16 g, 17.5 cm^3, 0.154 mmol) in THF (100 cm^3), keeping the temperature below −60 °C. The reaction mixture was allowed to warm to room temperature overnight, then quenched with 10% HCl and stirred under argon for 1 h. The mixture was extracted with Et_2O and the combined extracts dried over $MgSO_4$. Removal of the solvents furnished the crude product which was washed with hexane to give a fine white powder (6.2 g, 40%); mp 134–136 °C; ν_{max}(KBr disc)/cm^{-1} 3390br s (OH), 3045w, 2940w (CH), 1611m, 1500s, 1462m (CC), 1348br s (BO), 1250s (CO), 819s, 773s, 759m (CH); δ_H[270 MHz, $(CD_3)_2SO$] 7.77 (dd, 1 H, *J* 8.06 and 1.22, Ar-H), 7.6 [br s, 2 H, $B(OH)_2$], 7.48–7.32 (m, 4 H, Ar-H), 6.93 (dd, 1 H, *J* 7.08 and 1.47, Ar-H), 3.89 (s, 3 H, OCH_3); δ_C[68 MHz, $(CD_3)_2SO$] 155.7, 133.5, 127.8, 126.8, 126.4, 125.8, 125.7, 120.3, 104.5, 55.5. This material was used as obtained.

Representative preparation of the 1-aryl-3-chloroisoquinolines: 3-chloro-1-phenylisoquinoline 2

A mixture of 1,3-dichloroisoquinoline **1** (0.99 g, 5 mmol) and $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) in DME (25 cm^3) was warmed to form a yellow solution. Phenylboronic acid (0.67 g, 5.5 mmol) and CsF (1.75 g, 11 mmol) were added and the mixture heated

under reflux for 6 h. Water and Et_2O were added, the organic layer separated and the aqueous layer extracted twice with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to yield the crude product which was purified by dry flash chromatography (1:4 CH_2Cl_2–light petroleum changing to neat CH_2Cl_2). Yield 1.08 g (90%); mp 81–82 °C (Found: C, 75.0; H, 4.2; N, 5.8. Calc. for $C_{15}H_{10}ClN$: C, 75.1; H, 4.2; N, 5.8%); ν_{max}(KBr disc)/cm^{-1} 3050w, 3030w (CH), 1610m (CN), 1565m, 1540s, 1485m (CC), 855s, 760s, 700s (CH); δ_H(600 MHz, $CDCl_3$) 8.09 (m, 1 H, H-8), 7.81 (d with unresolved splitting, $J_{5,6}$ 8.4, 1 H, H-5), 7.71 (apparent d, 1 H, $J_{4,5}$ 1.0, H-4), 7.71–7.68 (m, 3 H, H-2′, H-6′ and H-6), 7.52–7.49 (m, 4 H, Ar-H); δ_C(68 MHz, $CDCl_3$) 161.5, 144.8, 139.0, 138.2, 130.9, 130.1, 129.1, 128.5, 127.9, 127.4, 126.3, 125.5, 118.9; *m/z* (EI) 239, 241 (M^+).

3-Chloro-1-(4-tolyl)isoquinoline 3. The same procedure was used as for the preparation of compound **2**. Yield 87%; mp 116–117 °C (Found: C, 75.6; H, 4.7; N, 5.5. Calc. for $C_{16}H_{12}ClN$: C, 75.7; H, 4.8; N, 5.5%); ν_{max}(KBr disc)/cm^{-1} 3060w, 2920w (CH), 1610m (CN), 1570m, 1540s, 1482m (CC), 860s, 835s (CH); δ_H(600 MHz, $CDCl_3$) 8.11 (m, 1 H, H-8), 7.79 (m, 1 H, H-5), 7.68 (s, 1 H, H-4), 7.67 (m, 1 H, H-6), 7.60–7.58 (m, 2 H, H-3′ and H-5′), 7.51 (ddd, 1 H, *J* 8.6, 6.8 and 1.1, H-7), 7.34–7.32 (m, 2 H, H-2′ and H-6′), 2.45 (s, 3 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 161.6, 144.8, 139.1, 139.0, 135.4, 130.8, 130.1, 129.1, 128.0, 127.2, 126.3, 125.6, 118.6, 21.4; *m/z* (EI) 253, 255 (M^+).

3-Chloro-1-(2-tolyl)isoquinoline 4. The same procedure was used as for the preparation of compound **2**. Yield 67%; mp 43–44 °C (Found: C, 75.7; H, 5.0; N, 5.4. Calc. for $C_{16}H_{12}ClN$: C, 75.7; H, 4.8; N, 5.5%); ν_{max}(KBr disc)/cm^{-1} 3060w, 2920w (CH), 1613m (CN), 1572m, 1545s, 1480m (CC), 855s, 730s (CH); δ_H(600 MHz, $CDCl_3$) 7.81 (m, 1 H, H-5), 7.74 (apparent d, 1 H, *J* 0.75, H-4), 7.69 (ddd, 1 H, *J* 8.1, 6.7 and 1.2, H-6), 7.63 (m, 1 H, H-8), 7.46 (ddd, 1 H, *J* 8.1, 6.8 and 1.2, H-7), 7.4–7.3 (m, 4 H, Ar-H), 2.08 (s, 3 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 162.3, 144.7, 138.5, 137.7, 136.5, 131.1, 130.4, 129.7, 128.9, 127.6, 127.4, 126.2, 125.7, 119.0, 19.9; *m/z* (EI) 253, 255 (M^+).

1-(2-Methoxyphenyl)-3-chloroisoquinoline 5. The same procedure was used as for the preparation of compound **2**. Yield 65%; mp 96–96.5 °C (Found: C, 70.9; H, 4.4; N, 5.1. Calc. for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.5; N, 5.2%); ν_{max}(KBr disc)/cm^{-1} 3060w, 2940w (CH), 1615m (CN), 1600m, 1580m, 1540m, 1480s (CC), 1242s (CO), 855s, 745s (CH); δ_H(600 MHz, $CDCl_3$) 7.78 (m, 1 H, H-5), 7.72 (apparent d, 1 H, *J* 0.86, H-4), 7.68 (m, 1 H, H-8), 7.66 (ddd, 1 H, *J* 8.1, 6.7 and 1.2, H-6), 7.48–7.44 (m, 2 H, H-5′ and H-7), 7.38 (dd with unresolved splitting, 1 H, *J* 7.4 and 1.75, H-3′), 7.10 (ddd, 1 H, *J* 8.4, 7.4 and 1.0, H-4′), 7.03 (dd, 1 H, *J* 8.3 and 1.0, H-6′), 3.69 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 160.0, 157.1, 144.8, 138.2, 131.3, 130.8, 130.5, 128.2, 127.5, 127.0, 126.7, 126.0, 120.9, 119.2, 111.2, 55.6; *m/z* (EI) 269, 271 (M^+).

3-Chloro-1-(2-methoxy-1-naphthyl)isoquinoline 6. The same procedure was used as for the preparation of compound **2**. Yield 85%; mp 159–160 °C; ν_{max}(KBr disc)/cm^{-1} 3060w, 2950w (CH), 1615m (CN), 1590m, 1575m, 1540m, 1505m (CC), 1260s, 1245s (CO), 810m, 750s (CH); δ_H(600 MHz, $CDCl_3$) 8.01 (apparent dd, 1 H, $J_{4',3'}$ 9.1 and $J_{4',5'}$ 0.6, H-4′), 7.85 (d with unresolved splitting, 1 H, $J_{5',6'}$ 8.1, H-5′), 7.84 (d with unresolved splitting, 1 H, $J_{5,6}$ 8.2, H-5), 7.81 (s, 1 H, H-4), 7.67 (ddd, 1 H, $J_{6,5}$ 8.2, $J_{6,7}$ 6.7 and $J_{6,8}$ 1.2, H-6), 7.48 (m, 1 H, H-8), 7.41 (d, 1 H, $J_{3',4'}$ 9.1, H-3′), 7.32 (ddd, 1 H, $J_{7,8}$ 8.5, $J_{7,6}$ 6.7 and $J_{7,5}$ 1.1, H-7), 7.37 (ddd, 1 H, $J_{6',5'}$ 8.1, $J_{6',7'}$ 6.7 and $J_{6',8'}$ 1.1, H-6′), 7.26 (ddd, 1 H, $J_{7',8'}$ 8.4, $J_{7',6'}$ 6.7 and $J_{7',5'}$ 1.4, H-7′), 7.03 (m, 1 H, H-8′), 3.12 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 159.2, 155.0, 145.2, 138.4, 133.7, 131.1, 131.0, 129.1, 128.0, 127.8, 127.4, 127.1, 126.2, 125.0, 123.9, 120.7, 119.3, 113.4, 56.6; *m/z* (EI) 319, 321 (M^+) [Found (HRMS): 319.0764. $C_{20}H_{14}ClNO$ requires 319.0764].

3-Chloro-1-(1-naphthyl)isoquinoline 7. The same procedure was used as for the preparation of compound **2**. Yield 69%; mp 113–114 °C (Found: C, 78.4; H, 4.1; N, 4.8. Calc. for $C_{19}H_{12}ClN$: C, 78.8; H, 4.2; N, 4.8%); ν_{max}(KBr disc)/cm^{-1} 3050w (CH), 1613m (CN), 1570m, 1545s, 1485m (CC), 870s, 855s, 775s (CH); δ_H(600 MHz, $CDCl_3$) 8.00–7.99 (m, 1 H, H-4′), 7.93 (d with unresolved splitting, 1 H, $J_{5',6'}$ 8.1, H-5′), 7.86–7.84 (m, 1 H, H-5), 7.83 (apparent d, 1 H, *J* 0.98, H-4), 7.69 (ddd, 1 H, $J_{6,5}$ 8.3, $J_{6,7}$ 6.8 and $J_{6,8}$ 1.1, H-6), 7.60 (dd, 1 H, $J_{3',4'}$ 8.1 and $J_{3',2'}$ 6.9, H-3′), 7.59–7.57 (m, 1 H, H-8), 7.57 (dd, 1 H, $J_{2',3'}$ 6.9 and $J_{2',4'}$ 1.5, H-2′), 7.48 (ddd, 1 H, $J_{6',5'}$ 8.1, $J_{6',7'}$ 6.5 and $J_{6',8'}$ 1.4, H-6′), 7.38 (ddd, 1 H, $J_{7,8}$ 8.5, $J_{7,6}$ 6.8 and $J_{7,5}$ 1.2, H-7), 7.38–7.36 (m, 1 H, H-8′), 7.34 (ddd, 1 H, $J_{7',8'}$ 8.5, $J_{7',6'}$ 6.5 and $J_{7',5'}$ 1.3, H-7′); δ_C(68 MHz, $CDCl_3$) 161.3, 144.9, 138.5, 135.6, 133.7, 132.1, 131.2, 129.3, 128.3, 128.1, 127.9, 127.4, 127.2, 126.6, 126.2, 126.1, 125.8, 125.2, 119.4; *m/z* (EI) 289, 291 (M^+).

3-Chloro-1-(8-methoxy-1-naphthyl)isoquinoline 8. The same procedure was used as for the preparation of compound **2**. Yield 80%; mp 144 °C (Found: C, 74.9; H, 4.4; N, 4.4. Calc. for $C_{20}H_{14}ClNO$: C, 75.1; H, 4.4; N, 4.4%); ν_{max}(KBr disc)/cm^{-1} 3060w, 2940w (CH), 1610m (CN), 1573m, 1545m, 1460m (CC), 1257s (CO), 853m, 820s, 760m (CH); δ_H(600 MHz, $CDCl_3$) 7.94 (dd, 1 H, $J_{4',3'}$ 8.2 and $J_{4',2'}$ 1.3, H-4′), 7.79 (d with unresolved splitting, 1 H, $J_{5,6}$ 8.3, H-5), 7.72 (apparent d, 1 H, *J* 0.8, H-4), 7.62 (ddd, 1 H, $J_{6,5}$ 8.3, $J_{6,7}$ 6.7 and $J_{6,8}$ 1.2, H-6), 7.56 (dd, 1 H, $J_{3',4'}$ 8.2 and $J_{3',2'}$ 7.0, H-3′), 7.54 (dd, 1 H, $J_{5',6'}$ 8.2 and $J_{5',7'}$ 0.9, H-5′), 7.42 (dd, 1 H, $J_{2',3'}$ 7.0 and $J_{2',4'}$ 1.3, H-2′), 7.42–7.39 (m, 2 H, H-8 and H-6′), 7.31 (ddd, 1 H, $J_{7,8}$ 8.1, $J_{7,6}$ 6.7 and $J_{7,5}$ 1.2, H-7), 6.88 (dd, 1 H, $J_{7',6'}$ 7.1 and $J_{7',5'}$ 0.9, H-7′), 3.12 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 165.2, 155.7, 143.9, 137.3, 135.3, 134.0, 130.5, 129.0, 128.3, 127.8, 127.3, 126.7, 126.4, 125.7, 125.6, 124.2, 121.2, 117.9, 106.4, 55.5; *m/z* (EI) 319, 321 (M^+).

Lithiation of 3-chloro-1-(1-naphthyl)isoquinoline 7 and D_2O quench

A solution of BuLi (1.6 M in hexanes; 800 mm^3 0.125 mmol) was added dropwise to 2,2,6,6-tetramethylpiperidine (17 mg, 21 mm^3, 0.125 mmol) in THF (2.5 cm^3) at 0 °C. The mixture was stirred for 5 min then a solution of the 3-chloro-1-(1-naphthyl)-isoquinoline **7** (28 mg, 0.11 mmol) in THF (2.5 cm^3) was added dropwise. The mixture was stirred for 15 min then quenched with D_2O. After the reaction had reached room temperature, the solvents were removed *in vacuo* and CH_2Cl_2 added. The solution was dried over $MgSO_4$ and evaporated to give the crude product, the ^{1}H NMR spectrum of which was identical to the starting material, save for the absence of the 4-isoquinoline signal. All other data were in accord with the formation of **10**.

Lithiation using lithium naphthalenide: radical anion reduction of 8

A solution of 3-chloro-1-(8-methoxy-1-naphthyl)isoquinoline **8** (50 mg, 0.156 mmol) in THF (2.5 cm^3) was cooled to −72 °C (CO_2–EtOH) and stirred while a solution of $LiC_{10}H_8$ (0.23 M in THF; 2.4 cm^3, 0.546 mmol) was added rapidly. The mixture was stirred at −72 °C for 5 min then quenched with H_2O (0.1 cm^3). After warming to room temperature, the solvent was evaporated and CH_2Cl_2 added. The solution was dried ($MgSO_4$) and concentrated to give the crude product which was washed two or three times with pentane; δ_H(270 MHz, $CDCl_3$) 8.56 (d, 1 H, *J* 5.5, H-3), 7.95 (dd, 1 H, *J* 8.5 and 1.5, H-4′), 7.90–7.86 (m, 1 H, H-5), 7.64 (d with unresolved splitting, 1 H, *J* 5.5, H-4), 7.66–7.54 (m, 3 H, Ar-H), 7.46–7.40 (m, 3 H, Ar-H), 7.34 (ddd, 1 H, *J* 8.0, 6.5 and 1.3, H-7), 6.69 (dd, 1 H, *J* 7.8 and 1.0, H-7′), 3.10 (s, 3 H, OCH_3). When the reaction was carried out as above and quenched with D_2O the intensities of the H-3 and H-4′ signals were in the ratio 0.28:1, indicating 60% deuterium incorporation.

Representative preparation of 1,3-diarylisoquinolines *via* $NiCl_2$-(dppf) catalysed Grignard coupling of 1,3-diphenylisoquinoline 12

A mixture of $NiCl_2$ (6.5 mg, 0.05 mmol) and dppf (28 mg, 0.05 mmol) in THF (5 cm^3) was warmed to give a dark green solution. Solid 3-chloro-1-phenylisoquinoline **2** (240 mg, 1.00 mmol) was added and the mixture cooled to 0 °C then treated dropwise with a solution of PhMgBr (3.0 M in Et_2O; 0.4 cm^3, 1.2 mmol). The mixture was stirred at 0 °C for 30 min then at room temperature for 30 min. Water and Et_2O were added, the organic layer separated and the aqueous layer extracted twice with Et_2O. The combined organic extracts were washed with water and brine, dried over $MgSO_4$ and concentrated. Flash chromatography (SiO_2, 2:3 CH_2Cl_2–light petroleum) gave 1,3-diphenylisoquinoline as a colourless oil which solidified slowly. Yield 219 mg (78%); mp 71–73 °C; ν_{max}(KBr disc)/cm^{-1} 3045w (CH), 1615m (CN), 1585w, 1552m, 1490m (CC), 770s, 765s, 690s, 682s (CH); δ_H(270 MHz, $CDCl_3$) 8.22 (m, 2 H, 3-phenyl H-2 and H-6), 8.13 (m, 1 H, H-8), 8.08 (s, 1 H, H-4), 7.94 (m, 1 H, H-5), 7.82 (m, 2 H, 1-phenyl H-2 and H-6), 7.68 (ddd, 1 H, *J* 1.2, 6.8 and 8.2, H-6), 7.60–7.48 (m, 6 H, Ar-H), 7.40 (m, 1 H, 3-phenyl H-4); δ_C(68 MHz, $CDCl_3$) 160.4, 150.2, 139.9, 139.6, 137.9, 130.3, 130.1, 128.7, 128.6, 128.5, 128.3, 127.6, 127.5, 127.1, 126.9, 125.8, 115.8; *m/z* (EI) 281 (M^+) [Found (HRMS): 281.1204. $C_{21}H_{15}N$ requires 281.1204].

3-Phenyl-1-(4-tolyl)isoquinoline 13. The same procedure was used as for the preparation of compound **12**. Yield 84%; mp 56–57 °C; ν_{max}(KBr disc)/cm^{-1} 3050w, 2910w (CH), 1615m (CN), 1585w, 1550m, 1490m (CC), 825s, 770s, 685s (CH); δ_H(270 MHz, $CDCl_3$) 8.22 (m, 2 H, phenyl H-2 and H-6), 8.15 (m, 1 H, H-8), 8.05 (apparent d, 1 H, *J* 0.97, H-4), 7.92 (m, 1 H, H-5), 7.72 (m, 2 H, tolyl H-3 and H-5), 7.67 (ddd, 1 H, *J* 1.23, 6.84 and 8.18, H-6), 7.50 (m, 1 H, H-7), 7.48 (m, 2 H, phenyl H-3 and H-5), 7.39 (m, 1 H, phenyl H-4), 7.36 (m, 2 H, tolyl H-2 and H-6), 2.48 (s, 3 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 160.4, 150.2, 139.7, 138.5, 137.9, 137.1, 130.2, 130.0, 129.0, 128.7, 128.5, 127.7, 127.5, 127.1, 126.8, 125.9, 115.5, 21.4; *m/z* (EI) 295 (M^+) [Found (HRMS): 295.1361. $C_{22}H_{17}N$ requires 295.1361].

1,3-Di(4-tolyl)isoquinoline 14. The same procedure was used as for the preparation of compound **12**. Yield 73%; mp 89–90 °C; ν_{max}(KBr disc)/cm^{-1} 3050w, 2920w (CH), 1615m (CN), 1605m, 1580m, 1550s, 1520m (CC), 825br s (CH); δ_H(600 MHz, $CDCl_3$) 8.14–8.12 (m, 1 H, H-8), 8.12–8.10 (m, 2 H, 3-tolyl H-3 and H-5), 8.02 (s, 1 H, H-4), 7.91–7.89 (m, 1 H, H-5), 7.72–7.69 (m, 2 H, 1-tolyl H-3 and H-5), 7.65 (ddd, 1 H, *J* 8.1, 6.6 and 1.1, H-6), 7.47 (ddd, 1 H, *J* 8.1, 6.8 and 1.1, H-7), 7.37–7.35 (m, 2 H, 1-tolyl H-2 and H-6), 7.30–7.28 (m, 2 H, 3-tolyl H-2 and H-6), 2.47 (s, 3 H, 1-tolyl CH_3), 2.41 (s, 3 H, 3-tolyl CH_3); δ_C(68 MHz, $CDCl_3$) 153.9, 143.7, 132.0, 131.9, 131.5, 130.7, 130.4, 123.7, 123.5, 123.0, 122.5, 121.2, 120.9, 120.5, 120.2, 119.3, 108.5, 15.0, 14.9; *m/z* (EI) 309 (M^+) [Found (HRMS): 309.1517. $C_{23}H_{19}N$ requires 309.1517].

1-(2-Methoxyphenyl)-3-phenylisoquinoline 15. The same procedure was used as for the preparation of compound **12**. Yield 58%; mp 113–114 °C; ν_{max}(KBr disc)/cm^{-1} 3050w, 2922w (CH), 1612m (CN), 1592m, 1574m, 1557s (CC), 1242 (CO), 758s, 695s (CH); δ_H(270 MHz, $CDCl_3$) 8.18–8.14 (m, 2 H, phenyl H-2 and H-6), 8.06 (s, 1 H, H-4), 7.91–7.89 (m, 1 H, H-5), 7.71–7.69 (m, 1 H, H-8), 7.64 (ddd, 1 H, *J* 8.1, 6.8 and 1.2, H-6), 7.53–7.36 (m, 6 H, Ar-H), 7.18–7.12 [m, 1 H, 2-C_6H_4(OMe) H-4], 7.09–7.05 [m, 1 H, 2-C_6H_4(OMe) H-6], 3.71 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 159.1, 157.5, 150.6, 139.9, 137.0, 131.6, 130.0, 129.95, 128.7, 128.3, 128.0, 127.25, 127.2, 126.6, 120.9, 116.2, 111.2, 55.6; *m/z* (EI) 311 (M^+) [Found (HRMS): 311.1310. $C_{22}H_{17}NO$ requires 311.1310].

Representative preparation of 1,3-diarylisoquinolines *via* catalytic Suzuki coupling of 3-(2-methoxyphenyl)-1-(4-tolyl)-isoquinoline 16

A mixture of 3-chloro-1-(4-tolyl)isoquinoline **3** (253 mg, 1 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in degassed DMF (5 cm^3) was warmed to give a bright yellow solution. Solid 2-methoxyphenylboronic acid (1.1 mmol) and Cs_2CO_3 (488.7 mg, 1.5 mmol) were added and the mixture was heated at 100 °C (18 h). Water and Et_2O were added to the cooled mixture, the organic phase separated and the aqueous layer extracted twice with Et_2O. The combined organic layers were washed with 1 M HCl and brine and then dried over Mg_4SO and concentrated. The residue was purified by flash chromatography (SiO_2, 3:2 light petroleum–CH_2Cl_2) to yield 3-(2-methoxyphenyl)-1-(4-tolyl)isoquinoline **16** as a white solid, 200 mg (61%); mp 130–131 °C; ν_{max}(KBr disc)/cm^{-1} 3045w, 2943w (CH), 1612m (CN), 1597w, 1566m, 1549m (CC), 1240 (CO), 825m, 756s (CH); δ_H(270 MHz, $CDCl_3$) 8.24 (s, 1 H, H-4), 8.12 (dd, 1 H, $J_{8,7}$ 8.5 and $J_{8,6}$ 1.0, H-8), 8.07 [dd, 1 H, $J_{3',4'}$ 7.6 and $J_{3',5'}$ 1.9, 2-C_6H_4(OMe) H-3], 7.91–7.88 (m, 1 H, H-5), 7.70–7.67 (m, 2 H, tolyl H-3 and H-5), 7.65 (ddd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 6.8 and $J_{6,8}$ 1.2, H-6), 7.49 (ddd, 1 H, $J_{7,8}$ 8.5, $J_{7,6}$ 6.8 and $J_{7,5}$ 1.4, H-7), 7.38–7.32 [m, 3 H, tolyl H-2 and H-6, 2-C_6H_4(OMe) H-5], 7.10 [dt, 1 H, $J_{4',3'} \approx J_{4',5'} \approx 7.6$ and $J_{4',6'}$ 1.2, 2-C_6H_4(OMe) H-4], 7.05–7.02 [m, 1 H, 2-C_6H_4(OMe) H-6], 3.93 (s, 3 H, OCH_3), 2.46 (s, 3 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 160.1, 157.3, 148.1, 138.3, 137.2, 137.2, 131.8, 130.1, 129.7, 129.3, 129.0, 127.6, 127.5, 126.7, 125.5, 121.1, 120.4, 111.5, 55.8, 21.4; *m/z* (EI) 325 (M^+) [Found (HRMS): 325.1467. $C_{23}H_{19}NO$ requires 325.1467].

1-(4-Tolyl)-3-(2-tolyl)isoquinoline 17. The same procedure was used as for the preparation of compound **16**. Yield 77%; mp 109–110 °C; ν_{max}(KBr disc)/cm^{-1} 3050w, 3022w (CH), 1610m (CN), 1583w, 1549m, 1490m (CC), 802s, 799s, 762s (CH); δ_H(270 MHz, $CDCl_3$) 8.19–8.15 (m, 1 H, H-8), 7.92–7.88 (m, 1 H, H-5), 7.73 (s, 1 H, H-4), 7.69 (ddd, 1 H, *J* 8.2, 6.7 and 1.2, H-6), 7.68–7.64 (m, 2 H, *p*-tolyl H-3 and H-5), 7.59–7.54 (m, 1 H, Ar-H), 7.53 (ddd, 1 H, *J* 8.2, 6.7 and 1.5, H-7), 7.36–7.32 (m, 2 H, *p*-tolyl H-2 and H-6), 7.32–7.26 (m, 3 H, Ar-H), 2.49 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3); δ_C(68 MHz, $CDCl_3$) 160.0, 153.0, 138.4, 137.5, 136.4, 130.8, 130.2, 130.1, 129.0, 128.0, 127.7, 127.2, 126.9, 125.9, 125.3, 119.3, 21.4, 20.8; *m/z* (EI) 309 (M^+) [Found (HRMS): 309.1517. $C_{23}H_{19}N$ requires 309.171 75].

1-(1-Naphthyl)-3-(2-naphthyl)isoquinoline 18. The same procedure was used as for the preparation of compound **16**. Yield 68%; mp 174–175 °C; ν_{max}(KBr disc)/cm^{-1} 3043w (CH), 1612w (CN), 1580w, 1557s, 1501w (CC), 812s, 808s, 775s, 747s (CH); δ_H(270 MHz, $CDCl_3$) 8.71 (s with unresolved splitting, 1 H, Ar-H), 8.33–8.29 (m, 2 H, Ar-H), 8.05–7.92 (m, 5 H, Ar-H), 7.88–7.83 (m, 1 H, Ar-H), 7.72–7.48 (m, 8 H, Ar-H), 7.41–7.32 (m, 2 H, Ar-H); δ_C(68 MHz, $CDCl_3$) 160.4, 150.4, 137.5, 137.3, 137.0, 133.8, 133.7, 133.5, 132.5, 130.4, 128.9, 128.8, 128.4, 128.3, 128.0, 127.9, 127.7, 127.5, 127.4, 127.0, 126.6, 126.3, 126.3, 126.2, 126.0, 125.3, 125.0, 116.5; *m/z* (EI) 381 (M^+) [Found (HRMS): 381.1518. $C_{29}H_{19}N$ requires 381.1518].

Representative preparation of 1,3-diarylisoquinolines *via* catalytic Stille coupling of 1-(4-tolyl)-3-(2-pyridyl)isoquinoline 19

A mixture of 3-chloro-1-(4-tolyl)isoquinoline **3** (127 mg, 0.5 mmol), 2-pyridyltrimethylstannane (145 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (192 mg, 0.167 mmol) in DMF (5 cm^3) was heated at 100 °C for 18 h. Water and Et_2O were added, the organic phase separated and the aqueous phase extracted twice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography (SiO_2, 1:4 EtOAc–light petroleum) to yield 1-(4-tolyl)-3-(2-pyridyl)isoquinoline **19** as a white solid (90 mg, 61%); mp 109–110 °C (Found: C, 84.8; H, 5.4; N, 9.5. Calc. for $C_{21}H_{16}N_2$: C, 85.1; H, 5.4; N, 9.45%); ν_{max}(KBr disc)/cm^{-1} 3050w, 2920w (CH), 1610m, 1575s (CN), 1555m, 1490m, 1470s (CC), 825s, 788s, 740s (CH); δ_H(270 MHz, $CDCl_3$) 8.77 (s, 1 H, H-4), 8.73 (ddd, 1 H, $J_{6',5'}$ 4.7, $J_{6',4'}$ 1.7 and $J_{6',3'}$ 1.0, pyridyl

H-6), 8.64 (ddd, 1 H, $J_{3',4'}$ 8.1 and $J_{3',5'} \approx J_{3',6'} \approx 1.0$, pyridyl H-3), 8.16 (dd, 1 H, $J_{8,7}$ 8.4 and $J_{8,6}$ 1.1, H-8), 8.03–8.00 (m, 1 H, H-5), 7.81 (ddd, 1 H, $J_{4',3'}$ 8.1, $J_{4',5'}$ 7.5 and $J_{4',6'}$ 1.8, pyridyl H-4), 7.73–7.70 (m, 2 H, tolyl H-3 and H-5), 7.68 (ddd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 6.9 and $J_{6,8}$ 1.1, H-6), 7.53 (ddd, 1 H, $J_{7,8}$ 8.4, $J_{7,6}$ 6.9 and $J_{7,5}$ 1.5, H-7), 7.39–7.36 (m, 2 H, tolyl H-2 and H-6), 7.29 (ddd, 1 H, $J_{5',4'}$ 7.4, $J_{5',6'}$ 4.7 and $J_{5',3'}$ 1.1, H-5), 2.48 (s, 3 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 160.1, 156.7, 149.2, 148.8, 138.6, 137.8, 137.0, 136.9, 130.2, 130.0, 129.0, 128.3, 127.6, 127.4, 126.8, 123.3, 121.6, 116.6, 21.2; *m*/*z* (EI) 296 (M^+).

1-(8-Methoxy-1-naphthyl)-3-(2-pyridyl)isoquinoline 20. The same procedure was used for the preparation of compound **19**. Yield 94%; mp 186–188 °C; ν_{max}(KBr disc)/cm^{-1} 3050w, 2930w (CH), 1610m, 1575s (CN), 1560s, 1450m, 1460m (CC), 1260s (CO), 825s, 795m, 690m (CO); δ_H(600 MHz, $CDCl_3$) 8.77 (apparent d, 1 H, *J* 0.6, H-4), 8.73 (ddd, 1 H, $J_{6'',5''}$ 4.8, $J_{6'',4''}$ 1.8 and $J_{6'',3''}$ 0.9, pyridyl H-6), 8.53 (ddd, 1 H, $J_{3'',4''}$ 8.0 and $J_{3'',5''} \approx J_{3'',6''} \approx 1.0$, pyridyl H-3), 8.00 (apparent d, 1 H, *J* 8.2, H-5), 7.97 (dd, 1 H, $J_{4',3'}$ 8.2 and $J_{4',2'}$ 1.3, naphthyl H-4), 7.75 (ddd, 1 H, $J_{4'',3''}$ 8.0, $J_{4'',5''}$ 7.4 and $J_{4'',6''}$ 1.8, pyridyl H-4), 7.62 (dd, 1 H, $J_{3',4'}$ 8.2 and $J_{3',2'}$ 6.9, naphthyl H-3), 7.61 (ddd, 1 H, $J_{6,5}$ 8.1, $J_{6,7}$ 6.7 and $J_{6,8}$ 1.2, H-6), 7.57 (dd, 1 H, $J_{5',6'}$ 8.3 and $J_{5',7'}$ 1.0, naphthyl H-5), 7.53 (dd, 1 H, $J_{2',3'}$ 6.9, $J_{2',4'}$ 1.3, naphthyl H-2), 7.41 (apparent t, 1 H, *J* 7.8, naphthyl H-6), 7.39–7.37 (m, 1 H, H-8), 7.31 (ddd, 1 H, $J_{7,8}$ 8.0, $J_{7,6}$ 6.7 and $J_{7,5}$ 1.2, H-7), 7.27 (ddd, 1 H, $J_{5'',4''}$ 7.4, $J_{5'',6''}$ 4.8 and $J_{5'',3''}$ 1.2, pyridyl H-5), 6.68 (apparent d, 1 H, *J* 7.1, naphthyl H-7), 3.03 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 163.9, 157.1, 156.1, 149.2, 148.1, 136.9, 136.0, 135.9, 135.3, 129.6, 128.6, 128.4, 127.6, 127.4, 126.9, 126.3, 125.8, 124.6, 123.1, 121.9, 121.2, 116.3, 106.4, 55.4; *m*/*z* (EI) 362 (M^+) [Found (HRMS): 362.1419. $C_{25}H_{18}N_2O$ requires 362.1419].

1-(2-Methoxy-1-naphthyl)-3-(2-pyridyl)isoquinoline 21. The same procedure was used as for the preparation of compound **19**. Yield 80%; mp 155–156 °C (Found: C, 69.8; H, 4.4; N, 6.2. Calc. for $C_{25}H_{18}N_2O{\cdot}CH_2Cl_2$: C, 69.8; H, 4.5; N, 6.3%); ν_{max}(KBr disc)/cm^{-1} 3050w, 2930w (CH), 1615m (CN), 1590m, 1575s, 1557m (CC), 1212s, 1198s (CO), 807m, 795m, 690s (CH); δ_H(270 MHz, $CDCl_3$) 8.88 (s, 1 H, H-4), 8.74 (ddd, 1 H, $J_{6'',5''}$ 4.9, $J_{6'',4''}$ 1.9 and $J_{6'',3''}$ 1.0, pyridyl H-6), 8.50 (ddd, 1 H, $J_{3'',4''}$ 7.0 and $J_{3'',5''} \approx J_{3'',6''}$ 1.0, pyridyl H-3), 8.07–8.02 (m, 2 H, naphthyl H-4 and H-5), 7.90–7.87 (m, 1 H, H-5), 7.76–7.70 (m, 1 H, pyridyl H-4), 7.69–7.63 (ddd, $J_{6,5}$ 8.1, $J_{6,7}$ 6.6 and $J_{6,8}$ 1.21 H, H-6), 7.51–7.16 (m, 7 H, Ar-H), 3.78 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 157.7, 156.9, 154.9, 149.5, 149.2, 137.1, 136.9, 134.0, 130.4, 130.2, 129.3, 128.9, 128.1, 128.0, 127.5, 127.4, 126.8, 125.1, 123.8, 123.2, 122.5, 122.0, 117.3, 113.9, 56.8; *m*/*z* (EI) 362 (M^+).

3-Ethyl-(8-methoxy-1-naphthyl)isoquinoline 22

A mixture of $NiCl_2$(dppf) (21 mg, 0.031 mmol) and Zn (31 mg, 0.47 mmol) in THF (2.5 cm^3) was warmed at 50 °C for 30 min to give a pale yellow–green solution and then 3-chloro-1-(8-methoxy-1-naphthyl)isoquinoline **8** (100 mg, 0.313 mmol) was added. Super-Hydride® $LiBHEt_3$ (1.0 M in THF; 0.5 cm^3, 0.5 mmol) was added to Pr^iOH (30 mg, 38 mm^3, 1 mmol) and when evolution of gas had ceased, the solution was added *via* cannula to the catalyst–substrate mix. The mixture was heated under reflux for 3 h, filtered and evaporated. The residue was purified by flash chromatography (SiO_2, 4:1 light petroleum–Et_2O) to afford 3-ethyl-(8-methoxy-1-naphthyl)isoquinoline as a white solid (69 mg, 70%); mp 114–115 °C (Found: C, 84.0; H, 6.15; N, 4.4. Calc. for $C_{22}H_{19}NO$: C, 84.3; H, 6.1; N, 4.4%); ν_{max}(KBr)/cm^{-1} 3045w, 2960w, 2922w (CH), 1613m (CN), 1578m, 1553s, 1501w (CC), 1260s (CO), 820s, 767s; δ_H(270 MHz, $CDCl_3$) 7.93 (dd, 1 H, *J* 8.1 and 1.2, H-4′), 7.82–7.77 (m, 1 H, H-5), 7.60–7.52 (m, 3 H, Ar-H), 7.48 (s, 1 H, H-4), 7.45–7.33 (m, 3 H, Ar-H), 7.24 (ddd, 1 H, *J* 8.1, 6.6 and 1.2, H-7), 6.60–6.66 (m, 1 H, H-7′), 3.08 (s, 3 H, OCH_3), 3.03 (q, 2 H, *J* 7.5, CH_2CH_3), 1.41 (t, 3 H, *J* 7.5, CH_2CH_3); δ_C(68 MHz, $CDCl_3$) 163.8, 156.2, 155.4, 136.2, 135.7, 135.5, 129.4, 128.5, 128.2, 127.5, 126.9, 126.2, 126.0, 125.7, 125.5, 121.1, 115.4, 106.3, 55.5, 31.3, 14.6; *m*/*z* (EI) 313 (M^+).

3-(Benzylthio)-1-(8-methoxy-1-naphthyl)isoquinoline 23

A solution of Super-Hydride® (1.0 M $LiBHEt_3$ in THF; 1.0 cm^3, 1.0 mmol) was added slowly to dibenzyl disulfide (123 mg, 0.50 mmol). When gas evolution had ceased, the solvent was removed *in vacuo* and 3-chloro-1-(8-methoxy-1-naphthyl)-isoquinoline **8** and DMF (5 cm^3) were added. The mixture was heated for 6 h at 120 °C then cooled and diluted with Et_2O and 1 M HCl. Sufficient CH_2Cl_2 was added to just dissolve the dark solid, the organic layer was separated and the aqueous phase extracted with Et_2O. The combined organic extracts were washed with 1 M HCl (×5), water (×2), then brine (×2) and dried over $MgSO_4$. The solution was evaporated and the residue purified by flash chromatography (SiO_2, 4:1 light petroleum–Et_2O) to afford 246 mg (60%) of product; mp 127–129 °C; ν_{max}(KBr)/cm^{-1} 3052w, 2930w (CH), 1612m (CN), 1572m, 1547m, 1502m (CC), 1259s (CO), 821s, 771s, 762s, 750s (CH); δ_H(270 MHz, $CDCl_3$) 7.92 (dd, 1 H, *J* 8.3, 1.2, Ar-H), 7.69–7.64 (m, 1 H, Ar-H), 7.61–7.48 (m, 4 H, Ar-H), 7.44–7.41 (m, 2 H, Ar-H), 7.39–7.30 (m, 3 H, Ar-H), 7.23–7.17 (m, 4 H, Ar-H), 6.72–6.68 (m, 1 H, Ar-H), 4.52–4.36 (m, 2 H, CH_2), 3.04 (s, 3 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 164.2, 160.0, 149.4, 138.8, 136.1, 135.3, 132.4, 132.2, 129.9, 129.0, 128.6, 128.3, 128.2, 127.6, 126.8, 126.6, 126.3, 125.7, 125.5, 124.4, 121.1, 116.9, 106.2, 55.4, 35.8; *m*/*z* (EI) 407 (M^+) [Found (HRMS): 407.1344. $C_{27}H_{21}NOS$ requires 407.1344].

3-Chloro-1-(2-hydroxy-1-naphthyl)isoquinoline 24

A solution of 3-chloro-1-(2-methoxy-1-naphthyl)isoquinoline **6** (1.00 g, 3.13 mmol) in CH_2Cl_2 (10 cm^3) was cooled to −78 °C and treated dropwise with BBr_3 (1.6 g, 0.6 cm^3, 6.3 mmol). The mixture was allowed to warm to room temperature overnight, then quenched with H_2O and made basic with concentrated ammonia. The organic layer was separated and the aqueous layer extracted twice with CH_2Cl_2. The combined organic extracts were washed with water and brine, then passed through a short plug of SiO_2 and evaporated to afford the crude product which was washed with a little Et_2O. Yield 0.75 g (78%); mp 212–215 °C; ν_{max}(KBr disc)/cm^{-1} 3100br s (OH), 3062s (CH), 1613m (CN), 1575m, 1547m, 1503m (CC), 1340s (OH), 1261s (CO), 871s, 818m, 742s (CH); δ_H(270 MHz, $CDCl_3$) 7.93–7.90 (m, 1 H, Ar-H), 7.88–7.83 (m, 3 H, Ar-H), 7.73 (ddd, 1 H, *J* 8.3, 6.7 and 1.2, Ar-H), 7.59–7.55 (m, 1 H, Ar-H), 7.39 (ddd, 1 H, *J* 8.2, 6.7 and 1.4, Ar-H), 7.35–7.22 (m, 3 H, Ar-H), 7.12–7.08 (m, 1 H, Ar-H); δ_C(68 MHz, $CDCl_3$) 159.0, 152.8, 144.0, 138.1, 133.4, 131.4, 130.4, 128.0, 127.95, 127.7, 127.1, 127.05, 126.8, 126.5, 123.5, 122.8, 119.2, 116.8; *m*/*z* (EI) 305, 307 (M^+) [Found (HRMS): 305.0590. $C_{19}H_{12}ClNO$ requires 305.0607].

Representative Colon reaction: preparation of 1,1′-diphenyl-3,3′-biisoquinoline 25

A mixture of $NiCl_2$ (13 mg, 0.10 mmol), PPh_3 (80 mg, 0.30 mmol), Zn dust (100 mg, 1.5 mmol) and NaI (150 mg, 1.0 mmol) in THF (5 cm^3) was warmed to 50 °C for 30 min, resulting in a blood-red solution. To this was added a solution of 3-chloro-1-phenylisoquinoline **2** (239 mg, 1.00 mmol) in THF (2.5 cm^3) and the mixture heated for a further 3 h. The mixture was quenched with 6 M HCl, made basic with concentrated ammonia solution, filtered and extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. Column chromatography (activity II Al_2O_3, 3:2 light petroleum–CH_2Cl_2) afforded 1,1′-diphenyl-3,3′-biisoquinoline **25** as a white solid (190 mg, 93%); mp 280 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3050w (CH), 1612m (CN), 1560m, 1550m, 1480w (CC), 760m, 750s, 695m (CH); δ_H(270 MHz, $CDCl_3$) 9.00 (s, 2 H, H-4), 8.15 (m, 2 H, H-8), 8.04–8.01 (m, 2 H, H-5), 7.91–7.87 (m, 4 H, phenyl H-2 and H-6), 7.68 (ddd, 2 H, *J* 8.1, 6.8 and 1.0, H-6), 7.61–7.59 (m, 4 H,

phenyl H-3 and H-5), 7.64–7.58 (m, 2 H, phenyl H-4), 7.52 (ddd, 2 H, *J* 8.3, 6.8 and 1.2, H-7); δ_C(68 MHz, $CDCl_3$) 160.2, 149.3, 140.1, 137.9, 130.3, 130.0, 128.7, 128.4, 128.3, 127.6, 127.2, 126.7, 117.1; *m*/*z* (EI) 408 (M^+) [Found (HRMS): 408.1626. $C_{30}H_{20}N_2$ requires 408.1626].

1,1′-Di(4-tolyl)-3,3′-biisoquinoline 26. The same procedure was used as for the preparation of compound **25**. Yield 73%; mp 220 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3050w, 2920w (CH), 1612s (CN), 1565m, 1550m, 1480m (CC), 820s, 750s (CH); δ_H(270 MHz, $CDCl_3$) 8.99 (s, 2 H, H-4), 8.15 (m, 2 H, H-8), 8.03–8.00 (m, 2 H, H-5), 7.8–7.77 (m, 4 H, tolyl H-3 and H-5), 7.67 (ddd, 2 H, *J* 8.1, 6.8 and 1.0, H-6), 7.51 (ddd, 2 H, *J* 8.3, 6.8 and 1.2, H-7), 7.43–7.41 (m, 4 H, tolyl H-2 and H-6), 2.51 (s, 6 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 160.2, 149.2, 138.6, 137.9, 137.2, 130.3, 129.9, 129.1, 128.2, 127.7, 127.0, 126.7, 116.9, 21.5; *m*/*z* (EI) 436 (M^+) [Found (HRMS): 436.1939. $C_{32}H_{24}N_2$ requires 436.1939].

1,1′-Di(2-tolyl)-3,3′-biisoquinoline 27. The same procedure was used as for the preparation of compound **25**. Yield 75%; mp 200 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3060w, 2950w (CH), 1610m (CN), 1560br m, 1480w (CC), 750s, 730s (CH); δ_H(600 MHz, $CDCl_3$) 8.94 (s, 2 H, H-4), 7.98 (d with unresolved splitting, 2 H, *J* 8.2, H-5), 7.66 (m, 2 H, H-8), 7.64 (ddd, 2 H, *J* 8.0, 6.7 and 1.2, H-6), 7.48–7.38 (m, 10 H, Ar-H), 2.21 (s, 3 H, Ar-CH_3), 2.20 (s, 3 H, Ar-CH_3); δ_C(68 MHz, $CDCl_3$) 160.9, 149.4, 139.5, 137.4, 136.8, 130.5, 130.0, 129.9, 128.5, 128.1, 127.5, 127.4, 127.1, 125.6, 117.2, 20.1; *m*/*z* (EI) 436 (M^+) [Found (HRMS): 436.1939. $C_{32}H_{24}N_2$ requires 436.1939].

1,1′-Bis(2-methoxyphenyl)-3,3′-biisoquinoline 28. The same procedure was used as for the preparation of compound **25**. Yield 81%; mp 290 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3060w, 2930w (CH), 1615m (CN), 1597m, 1575m, 1562m (CC), 1240s (CO), 756s, 752s (CH); δ_H(270 MHz, $CDCl_3$) 8.96 (s, 2 H, H-4), 7.98–7.93 (m, 2 H, H-8), 7.71–7.66 (m, 2 H, H-5), 7.65–7.58 (m, 2 H, H-6), 7.56–7.49 (m, 4 H, H-3′ and H-5′), 7.43 (m, 2 H, H-7), 7.20 (t with unresolved splitting, *J* 7.5, 2 H, H-4′), 7.11 (m, 2 H, H-6′), 3.54 (s, 6 H, OCH_3); δ_C(68 MHz, $CDCl_3$) 158.6, 157.6, 149.8, 137.1, 131.7, 130.0, 129.8, 129.5, 127.9, 127.6, 126.6, 120.9, 117.5, 111.4, 55.6; *m*/*z* (EI) 468 (M^+) [Found (HRMS): 468.1838. $C_{32}H_{24}N_2O_2$ requires 468.1838].

1,1′-Bis(2-methoxy-1-naphthyl)-3,3′-biisoquinoline 29. The same procedure was used as for the preparation of compound **25**. Yield 73%; mp 280 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3060w, 2939w (CH), 1615m (CN), 1590m, 1560m, 1505m (CC), 1265s, 1250s (CO), 815s, 750s (CH); δ_H(270 MHz) 8.99 (br s, 2 H, Ar-H), 8.79–8.11 (m, 2 H, Ar-H), 7.96–7.91 (m, 2 H, Ar-H), 7.62–7.55 (m, 2 H, Ar-H), 7.54–7.49 (m, 2 H, Ar-H), 7.50–7.43 (m, 4 H, Ar-H), 7.41–7.27 (m, 8 H, Ar-H), 3.83 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3); δ_C[68 MHz, $CDCl_3$–$(CD_3)_2SO$] 161.0, 157.4, 154.7, 149.8, 136.9, 133.8, 130.2, 129.8, 129.0, 128.4, 127.8, 127.0, 126.8, 126.5, 124.9, 123.5, 117.3, 113.9, 56.5; *m*/*z* (EI) 568 (M^+) [Found (HRMS): 568.2150. $C_{40}H_{28}N_2O_2$ requires 568.2151].

1,1′-Di(1-naphthyl)-3,3′-biisoquinoline 30. The same procedure was used as for the preparation of compound **25**. Yield 82%; mp 270 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3050w (CH), 1612m (CN), 1552m, 1483m (CC), 802m, 792s, 773s, 750s (CH); δ_H(270 MHz, $CDCl_3$) 9.08 (s, 2 H, H-4), 8.09–8.06 (m, 2 H, Ar-H), 8.03–7.99 (m, 2 H, Ar-H), 7.99–7.95 (m, 2 H, Ar-H), 7.76–7.33 (m, 16 H, Ar-H); *m*/*z* (EI) 508 (M^+) [Found (HRMS): 509.1939. $C_{38}H_{24}N_2$ requires 508.1939].

1,1′-Bis(8-methoxy-1-naphthyl)-3,3′-biisoquinoline 31. The same procedure was used as for the preparation of compound **25**. Yield 64%; mp 320 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3050w, 2960w (CH), 1610m (CN), 1580m, 1560m, 1500m (CC), 1255s (CO), 820s, 765s, 755s (CH); δ_H(270 MHz) 8.86 (s, 2 H, H-4), 8.03 (dd, 2 H, *J* 8.3 and 1.5, H-4′), 7.96–7.92 (m, 2 H, H-8), 7.70–7.54 (m, 8 H, Ar-H), 7.45 (2 H, t, *J* 7.8, Ar-H), 7.39–7.25 (m, 4 H, Ar-H), 6.74 (m, 2 H, H-7′), 3.06 (s, 6 H, OCH_3); δ_C(68 MHz) 163.8, 156.1, 148.8, 136.1, 135.9, 135.2, 129.25, 128.6, 128.4, 127.5, 127.2, 127.1, 126.2, 125.8, 124.6, 121.1, 121.0, 116.5, 106.2, 55.2; *m*/*z* (EI) 568 (M^+) [Found (HRMS): 568.2150. $C_{40}H_{28}N_2O_2$ requires 568.2151].

Crystallographic data for 3-chloro-1-(8-methoxy-1-naphthyl)-isoquinoline 8

Crystals were grown by slow diffusion of hexane into a dichloromethane solution of **8** and were mounted on a glass fibre for the analysis.

Crystal data. The crystal was a colourless plate of approximate dimensions 0.40 × 0.60 × 0.50 mm, $C_{20}H_{14}ClNO$, M_w = 319.8, triclinic, space group $P\bar{1}$, a = 11.814(5), b = 14.227(5), c = 11.704(4) Å, α = 90.62(3), β = 115.91(3), γ = 112.56(3)°, V = 1596(3) $Å^3$, Z = 4, D_c = 1.33 g cm^{-3}, μ(Mo-Kα) = 2.40 cm^{-1}, F(000) = 664.

Data collection and processing. All measurements were made as previously described[22] using a Rigaku AFC6S diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections (2θ ranges 16.2–28.7° for cell parameters and orientation matrix determination; *ca.* 2–57.1° for full data collection). Data were collected at 25 °C using the ω–2θ scan technique. Scans of range (1.68 + 0.30 tan θ)° were made at a speed of 8.0° min^{-1} (in omega). Stationary background counts were recorded on each side of the reflection.

Of the 8506 reflections collected, 7427 were unique (R_{int} = 0.038); equivalent reflections were averaged. Of these, 2637 reflections had [$F_o^2 > 3\sigma(F_o^2)$], where $\sigma(F_o^2)$ was estimated from the counting statistics.[22,23] Lorentz-polarisation and absorption corrections were applied (transmision factors 0.71, −1.20). The intensitites of three standard reflections measured after every 150 reflections showed no greater fluctuations than expected from Poisson statistics.

Structure solution and refinement. The structure was solved by direct methods.[24] The non-hydrogen atoms were refined either anisotropically or isotropically. Full-matrix least-squares refinement was carried out using the TEXRAY programme set, as previously described.[22] The unweighted and weighted agreement factors converged at R = 0.046 and R_w = 0.046 respectively. The standard deviation of an observation of unit weight was 1.95. The weighting scheme was based on counting statistics and included a factor (p = 0.02) to downweight intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *vs.* $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. While the first molecule in the unit cell is well behaved, molecule 2 demonstrates slight thermal flexing about the 1,1′-binaphthyl bond. Attempts to model this disorder with partial atom fragments produced poorer agreement.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/88.

Acknowledgements

We are grateful to the EPSRC for access to their Ultra High Field NMR (Dr Ian H. Sadler, University of Edinburgh) and FAB Mass spectrometry (Dr J. A. Ballantine, University of Wales) services and for a project studentship (A. F.). We thank Johnson Matthey for a generous loan of $PdCl_2$ and Professor Brian E. Mann (University of Sheffield) and Dr John M. Brown (University of Oxford) for much advice and help.

References

1 A. Togni and L. M. Venanzi, *Agnew. Chem., Int. Ed. Engl.*, 1994, **33**, 497.

2 P. H. J. Carlson, T. Katsuki, V. S. Martin and K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936.
3 A. J. Bailey, W. P. Griffith, A. J. P. White and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1833.
4 C. Eskernazi, G. Balavoine, F. Meunier and H. Rivière, *J. Chem. Soc., Chem. Commun.*, 1985, 111.
5 A. Ford, E. Sinn and S. Woodward, *J. Organomet. Chem.*, 1995, **493**, 215.
6 S. Bennet, S. M. Brown, G. Conole, M. Kessler, S. Rowling, E. Sinn and S. Woodward, *J. Chem. Soc., Dalton Trans.*, 1995, 367.
7 M. M. Robison, *J. Am. Chem. Soc.*, 1958, **80**, 5481.
8 G. Simchen, *Agnew. Chem., Int. Ed. Engl.*, 1966, **5**, 663.
9 G. Simchen and W. Krämer, *Chem. Ber.*, 1969, **102**, 3666.
10 S. W. Wright, D. L. Hageman and L. D. McClure, *J. Org. Chem.*, 1994, **59**, 6095.
11 J. R. Pedersen, *Acta Chem. Scand., Ser. A*, 1974, **28**, 213.
12 M. Hird, G. W. Gray and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1991, **206**, 187.
13 N. W. Alcock, J. M. Brown and D. I. Humes, *Tetrahedron: Asymmetry*, 1993, **4**, 743.
14 J.-M. Valk, T. D. W. Claridge and J. M. Brown, *Tetrahedron: Asymmetry*, 1995, **6**, 2597.
15 L.-L. Gundersen, G. Langli and F. Rise, *Tetrahedron Lett.*, 1995, **36**, 1945.
16 I. Mangalagiu, T. Beneche and K. Undheim, *Tetrahedron Lett.*, 1996, **37**, 1309.
17 N. Miyaura, T. Ishiyama, H. Sasaki, M. Ishikawa, M. Satoh and A. Suzuki, *J. Am. Chem. Soc.*, 1989, **111**, 314.
18 M. Kranz, T. Clark and P. Von Rague, *J. Org. Chem.*, 1993, **58**, 3317.
19 I. Colon and D. R. Kelsey, *J. Org. Chem.*, 1986, **51**, 2627.
20 M. Iyoda, H. Otsuka, K. Sato, N. Nisato and M. Oda, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 80.
21 Y. Yamamoto and A. Yanagi, *Chem. Pharm. Bull.*, 1982, **30**, 1731.
22 J. R. Blackhouse, H. M. Lowe, E. Sinn, S. Suzuki and S. Woodward, *J. Chem. Soc., Dalton Trans.*, 1995, 1489.
23 P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.
24 C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.

Paper 6/05827B
Received 21*st August* 1996
Accepted 6*th November* 1996