Practical Syntheses of *N*-Hexylcarbazol-2-yl- and -3-yl-boronic Acids, Their Cross-Coupled Products and a Derived Tris-cyclometalated (Pyridin-2-yl)carbazole Iridium(III) Complex

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Abstract: The syntheses of *N*-hexylcarbazol-2-yl- and -3-yl-boronic acids (**1** and **2**) are described on a ca. 7 g scale, starting from commercially available 2,5-dibromonitrobenzene (**4**) and carbazole (**11**), respectively. Compounds **1** and **2** underwent efficient palladium-catalyzed cross-coupling reactions under Suzuki–Miyaura conditions to yield products **17**, **18** and **20**. Compound **18** reacted with $IrCl_3$ to give the tris-cyclometalated (pyridin-2-yl)carbazole iridium(III) complex **21**, the X-ray crystal structure of which is reported.

Key words: carbazole, boronic acid, fluorene, cross-coupling reaction, cyclometalating ligands, iridium complex

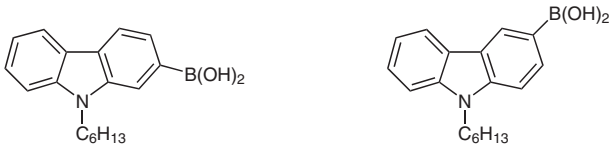

Figure 1 *N*-Hexylcarbazol-2-yl- and -3-yl-boronic acids (**1** and **2**).

Functionalized carbazoles are of considerable interest as bioactive compounds that display a broad spectrum of pharmacological properties.[1] Many condensed ring systems are known, and some derivatives with pendant aryl or heteroaryl derivatives have been investigated. For example, hyellazole (2-phenyl-3-methyl-4-methoxycarbazole) has been widely studied,[1] and pyrazolyl and quinolyl derivatives have been reported very recently.[2] Carbazole derivatives bearing aryl and heteroaryl substituents are very important in organic materials chemistry due to their high stability, processability and the hole-transporting properties of the carbazole unit.[3] For example, they are key building blocks for photorefractive materials,[4] liquid crystals,[5] field effect transistors,[6] and light-emitting polymers.[7] Carbazole-2,7-diboronic acid (or diboronate ester) has been used for the synthesis of symmetrical 2,7-diarylcarbazole derivatives.[3,8] We now report the efficient syntheses of *N*-hexylcarbazol-2-yl- and -3-yl-boronic acids (**1** and **2**) (Figure 1) and establish that they undergo clean Suzuki–Miyaura cross-coupling reactions to yield products **17**, **18** and **20**, which are ligands for cyclometalation studies.

The first step in our route to carbazol-2-yl-boronic acid (**1**) (Scheme 1) was Suzuki–Miyaura coupling[9] of phenylboronic acid (**3**) with 2,5-dibromonitrobenzene (**4**) (both of which are commercially available) in the presence of catalytic $Pd(PPh_3)_4$. Under a variety of conditions, product mixtures were obtained. Longer reaction times (e.g. 22 h) favored formation of compound **6** (ca. 50% yield) arising from a two-fold reaction. Optimized conditions (5.5 h at 90 °C) gave a mixture of the desired product **5** (77%), **6** (8%) and unreacted **4** (15%). This mixture was heated in triethylphosphine under Cadogan's reductive cyclization conditions[10] to afford 2-bromocarbazole (**7**) (57% yield based on **5**) contaminated with 2-phenylcarbazole (**8**) (6%) which was derived from **6**.

2-Bromocarbazole (**7**) has been synthesized by Percec et al.[11] in two steps (13% overall yield) starting from 2-nitrobiphenyl, which was converted into 4-bromo-2′-nitrobiphenyl followed by ring-closure. Our cross-coupling strategy provided a considerably higher overall yield of **7** (36%) and the by-product **8** was readily removed at the next stage. Thus the mixture of **7** and **8** was subjected to a standard alkylation reaction[12] with hexyl bromide; chromatography cleanly separated *N*-hexyl-2-bromocarbazole (**9**) (99% based on **7**) from *N*-hexyl-2-phenylcarbazole (**10**). Compound **9** was hydroxyborolylated[12] by lithiation with *n*-BuLi, addition of triisopropylborate and then hydrolysis with HCl, to give the boronic acid **1** in 83% yield (Scheme 1).

For the synthesis of carbazol-3-ylboronic acid (**2**), the key intermediate was 3-bromocarbazole (**12**), which has been obtained previously by treatment of carbazole (**11**) with bromine in pyridine.[11,13] In our hands carbazole (**11**) was not soluble in pyridine, and we prepared **12** by a modification of the procedure of Smith et al.,[14] replacing trimethyltin chloride with the less toxic trimethylsilyl chloride. Lithiation of carbazole (**11**) with *n*-BuLi, followed by silylation and bromination gave mixtures of **11**, **12** and **13** in a ratio of 4:5:1, respectively, after chromatography (by ^1H NMR data). Recrystallization removed **13** to give a mixture of **11** and **12** in a 2:3 ratio. This enabled us to complete the synthesis of boronic acid **2** successfully, in 13% overall yield from **11**.

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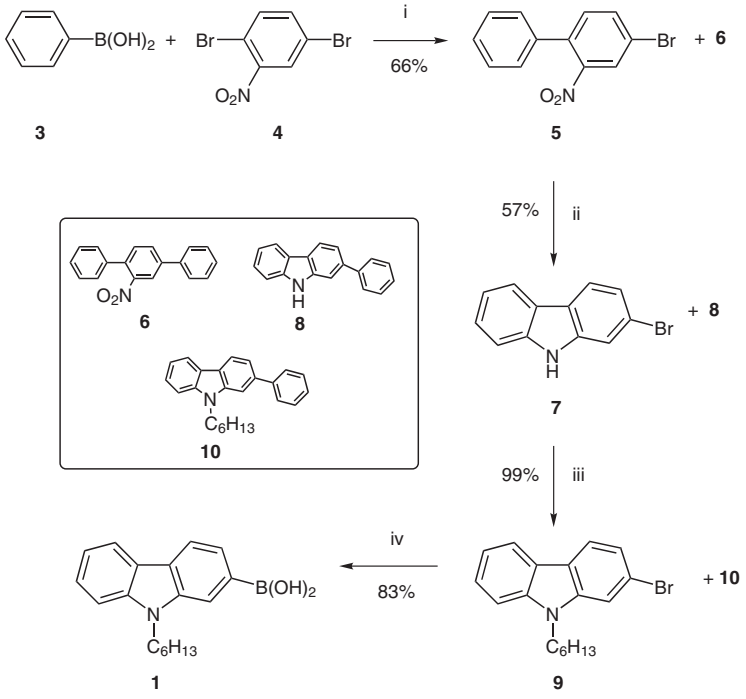
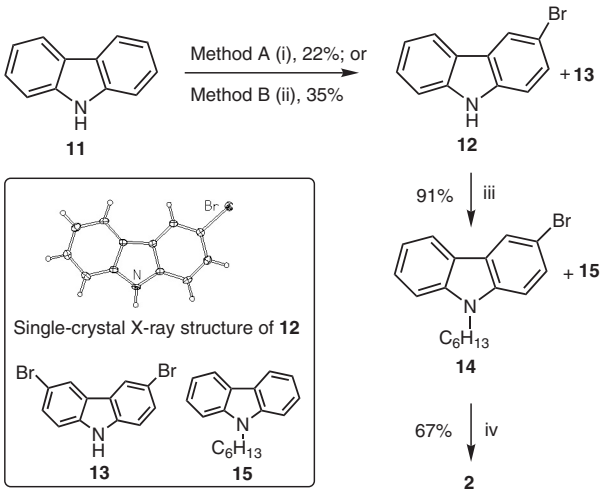


Scheme 1 *Reagents and conditions*: (i) $Pd(PPh_3)_4$ (3% equiv), aq 2 M Na_2CO_3 (3 equiv), toluene, 90 °C, 5.5 h; (ii) $(EtO)_3P$, reflux, 10 h; (iii) *t*-BuOK (1.2 equiv), DMF, 20 °C, 2 h; 1-bromohexane (1.5 equiv), 130 °C, 65 h; (iv) *n*-BuLi (1.2 equiv), THF, –78 °C, 2 h; $(i\text{-PrO})_3B$ (3.0 equiv), –78 to 20 °C, 16 h; concd HCl, 20 °C, 2 h.

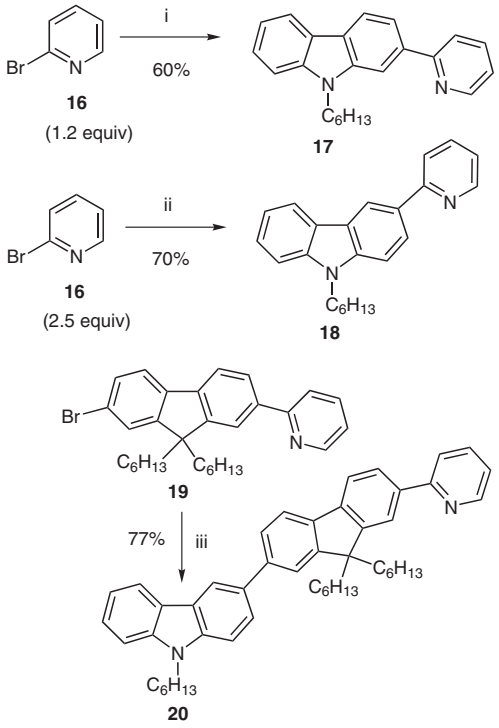
However, we have found that bromine in dimethylformamide at room temperature (conditions which have not been reported previously) is the best way to prepare **12** from **11** (Scheme 2), and is preferable to all other procedures.[15] Upon simple filtration, compound **12** was thereby obtained in >90% yield, contaminated with ca. 10% of unreacted **11** and on some occasions with ca. 2% of 3,6-dibromocarbazole (**13**). Recrystallization from chloroform lowered the yield of **12** (35%) and removed the traces of **13**. The single-crystal X-ray structure of **12** was obtained (Scheme 2, inset). The mixture of **11** and **12** was alkylated, as above, to give a mixture of **14** and **15** (ca. 9:1 ratio; 91% yield of **14**, based on **12**). Hydroxyborolylation of **14**, as above, gave *N*-hexylcarbazol-3-ylboronic acid (**2**) in 67% yield, after easy separation from **15**. A borolane derivative of **2**, namely 2-(9-hexylcarbazol-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, has been reported recently,[16] without any experimental details. The routes in Schemes 1 and 2 have reproducibly provided pure products **1** and **2** on ca. 7 g scales, with straightforward purification steps.

To confirm the suitability of reagents **1** and **2** for cross-coupling reactions, 2-bromopyridine (**16**) and 2-(7-bromo-9,9-dihexylfluoren-2-yl)pyridine (**19**)[17] were chosen as the halogenated partners. Standard Suzuki–Miyaura conditions [either $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ as catalyst, toluene, Na_2CO_3 (aq 2 M), 90 °C, 21–54 h] gave **17**, **18** and **20** (60%, 70% and 77% yields, respectively; Scheme 3). Shorter reaction times gave lower yields of products.

Compounds **17**, **18** and **20** are new ligands for cyclometalated complexes for use in electrophosphorescent devices. To illustrate their ability to form metal complexes, following a modified literature method,[18] an excess of **18** was treated with iridium(III) chloride under microwave irradiation. The triply cyclometalated iridium(III) complex **21** was obtained in 14% yield (Scheme 4). This complex represents a rare example of a triply cyclometalated iridium(III) complex in which a carbazole unit is directly



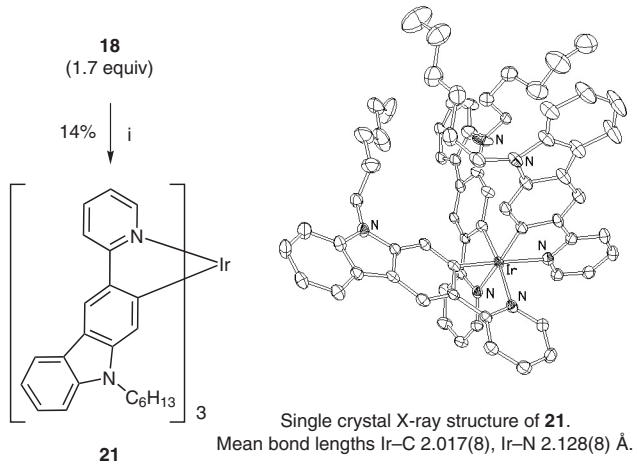
Scheme 2 *Reagents and conditions*: (i) *n*-BuLi (1.0 equiv), –78 °C, 15 min; Me_3SiCl (1.0 equiv), 20 °C, 3 h; Br_2 (1.0 equiv), –78 °C, 1 h; 20 °C, 2 h (ii) Br_2 (1.1 equiv), DMF, 0–20 °C, 1–27 h; (iii) *t*-BuOK (1.2 equiv), DMF, 20 °C, 1 h; 1-bromohexane (1.5 equiv) 130 °C, 65 h; (iv) *n*-BuLi (1.2 equiv), THF, –78 °C, 1 h; $(i\text{-PrO})_3B$ (3.0 equiv), –78 to 20 °C, 22 h; concd HCl (5.0 equiv), 20 °C, 2 h.



Scheme 3 *Reagents and conditions*: (i) boronic acid **1,** $Pd(PPh_3)_2Cl_2$ (4% equiv), aq 2 M Na_2CO_3 (4 equiv), toluene, 90 °C, 21 h; (ii) boronic acid **2**, $Pd(PPh_3)_2Cl_2$ (6% equiv), aq 2 M Na_2CO_3 (10 equiv), toluene, 90 °C, 40 h; (iii) boronic acid **2** (1.5 equiv), $Pd(PPh_3)_4$ (7% equiv), aq 2 M Na_2CO_3 (17 equiv), toluene, 90 °C, 54 h.

bonded to the metal core.[19] By analogy, we anticipate that other ligands of this family will form similar cyclometalated complexes.

The structure of **21** was confirmed by a single-crystal X-ray diffraction study of the solvate **21**·$2CH_2Cl_2$·$0.5Me_2CO$ (Scheme 4, H atoms and minor positions of the disordered *n*-hexyl groups are omitted). The iridium atom has *fac*-octahedral coordination with the three 9-hexyl-3-(pyridin-2-yl)carbazole ligands, whose pyridinyl-carbazole moieties are nearly planar (and mutually perpendicular), while the *n*-hexyl chains and solvent molecules are intensely disordered. The crystals instantly lost solvent and decomposed if taken out of the mother liquor. In the same experiment, unsolvated and air-stable crystals of **21** were also formed. Remarkably, the crystal lattice and the packing of the molecules are essentially the same as in the solvate, but loose packing without solvent resulted in even stronger disorder of the *n*-hexyl chains and librational disorder of the entire molecules as well. A *facial* structure of complex **21** is also supported by the NMR data.



Scheme 4 *Reagents and conditions*: (i) $IrCl_3$, Na_2CO_3 (2 equiv), ethylene glycol–H_2O, 220 °C, microwave (220 W), 30 min.

In summary, efficient and inexpensive routes have been developed for the synthesis of the carbazolyl-boronic acids **1** and **2**, which are versatile reagents for the construction of new aryl- and heteroaryl-carbazole derivatives. In addition, we have established that pyridinyl-carbazole ligand **18** bonds directly through the carbazole unit to form *facial* tris-cyclometalated iridium(III) complexes which will be studied as electrophosphorescent dopants in organic light emitting devices (OLEDs). Iridium(III) complexes of ligands **17** and **20** and the photophysical properties of this family of compounds will be described in a forthcoming paper.

All reactions were performed under argon, which was dried by passage through a column of P_2O_5. All reagents were of standard reagent grade and purchased from Aldrich, Lancaster and Fluorochem and used as supplied. THF was dried and distilled prior to use over potassium or sodium metal. All other solvents were used without prior purification. Petroleum ether used had bp 40–60 °C. Column chromatography was carried out on silica gel (40–60 μm). ^{1}H NMR spectra were recorded on a Varian Unity 300 at 300 MHz, a Varian VXR 400s at 400 MHz or a Varian Inova 500 spectrometer at 500 MHz using deuteriated solvent as the lock and tetramethylsilane as the internal reference. ^{13}C NMR spectra were recorded using broadband decoupling on the above spectrometers at 75, 100 and 125 MHz, respectively. Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionization mode as indicated. Electrospray high-resolution mass spectra were obtained on a Micromass LCT (TOF). Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyzer. Melting points were recorded on a Stuart Scientific SMP3 apparatus and are uncorrected.

4-Bromo-2-nitrobiphenyl (5)[20]

Phenylboronic acid (**3**; 10.0 g, 82.0 mmol), 2,5-dibromonitrobenzene (**4**; 23.1 g, 82.3 mmol) and $Pd(PPh_3)_4$ (2.8 g, 2.5 mmol) were dissolved in a mixture of toluene (250 mL) and aq 2 M Na_2CO_3 (124 mL). The degassed mixture was heated at 90 °C for 5.5 h, cooled to 20 °C and then diluted with distilled H_2O. The organic phase was separated and the organic products were extracted into CH_2Cl_2 (4×50 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give a dark brown liquid. Distillation under high vacuum (72 °C/3×10^{-2} mm Hg) gave an inseparable mixture of **4**, **5** and **6** as a light-orange semi-solid (19.2 g). The ^{1}H NMR analyses indicated that 77% of the mixture was compound **5** (14.8 g, 66%). The mixture was used in the next step without further purification.

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, 1 H, *J* = 2.0 Hz, H-3), 7.75 (dd, 1 H, *J* = 8.2, 2.0 Hz, H-5), 7.45–7.41 (m, 3 H), 7.33 (d, 1 H, *J* = 8.2 Hz, H-6), 7.31–7.27 (m, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 136.5, 135.6, 135.5, 133.5, 131.8, 129.5, 129.1, 128.8, 128.0, 127.3, 124.2, 121.6.

MS (EI): *m*/*z* (%) = 280 (5, [M$^+$]), 279 (40, [M$^+$]), 278 (8, [M$^+$]), 277 (36, [M$^+$]), 153 (31), 152 (100), 151 (72), 150 (42).

HRMS (EI$^+$): *m*/*z* calcd for $C_{12}H_8BrNO_2$: 276.9738; found: 276.9733.

2-Bromocarbazole (7)

The above mixture of **4**, **5** and **6** [19.2 g, ≡ **5** (14.8 g, 53.1 mmol)] and $(EtO)_3P$ (61.8 g, 371.9 mmol) was refluxed for 10 h. Excess $(EtO)_3P$ was distilled off under vacuum (72–76 °C/9 mm Hg). The remaining residue was diluted with a 1:1 mixture of MeOH and distilled H_2O to give a precipitate which was filtered off and washed several times with a 1:1 mixture of MeOH–H_2O, and with petroleum ether. Column chromatography (petroleum ether and CH_2Cl_2) gave a mixture of **7** and **8** as a white amorphous solid (8.0 g). ^{1}H NMR analyses indicated that 94% of the mixture was product **7** (7.5 g, 57% based on **5**); R_f 0.38 (petroleum ether–CH_2Cl_2, 1:1). The ^{1}H, ^{13}C NMR and MS data were in agreement with the literature data.[11] The mixture was used in the next step without further purification.

2-Bromo-9-hexylcarbazole (9)

Solid *t*-BuOK (4.2 g, 37.4 mmol) was added to a solution of the above product mixture of **7** and **8** [8.0 g, ≡ **7** (7.5 g, 31.2 mmol)] in anhyd DMF (150 mL). The mixture was stirred for 2 h at 20 °C, and then 1-bromohexane (7.7 g, 46.8 mmol) was added, followed by heating at 130 °C for 65 h. The solvent and excess 1-bromohexane were removed under vacuum (40 °C/9 mm Hg) to leave a light brown liquid, which was diluted with H_2O, and the organic products were extracted into CH_2Cl_2 (4 × 50 mL). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a light brown liquid. Chromatographic purification by eluting with a mixture of hexane and CH_2Cl_2 (9:1) gave **9** (10.3 g, 99% based on **7**) as a clear oil; R_f 0.39 (petroleum ether–CH_2Cl_2, 8:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, 1 H, *J* = 7.9 Hz, H-5), 7.94 (d, 1 H, *J* = 8.3 Hz, H-4), 7.55 (d, 1 H, *J* = 1.6 Hz, H-1), 7.50 (t, 1 H, *J* = 7.7 Hz, H-7), 7.40 (d, 1 H, *J* = 8.2 Hz, H-8), 7.34 (dd, 1 H, *J* = 8.2, 1.6 Hz, H-3), 7.26 (t, 1 H, *J* = 7.9 Hz, H-6), 4.23 (t, 2 H, *J* = 7.4 Hz, NCH_2), 1.85 (p, 2 H, *J* = 7.4 Hz, NCH_2CH_2), 1.45–1.25 (m, 6 H, $CH_2CH_2CH_2$), 0.90 (t, 3 H, *J* = 6.9 Hz, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.3, 140.6, 126.0, 122.4, 121.9, 121.8, 121.5, 120.3, 119.3, 119.2, 111.8, 108.9, 43.2, 31.6, 28.8, 26.9, 22.6, 14.0.

MS (EI): *m*/*z* (%) = 332 (16, [M$^+$]), 331 (83, [M$^+$]), 330 (18, [M$^+$]), 329 (86, [M$^+$]), 261 (15), 260 (97), 259 (17), 258 (100).

HRMS (EI$^+$): *m*/*z* calcd for $C_{18}H_{20}BrN$: 329.0779; found: 329.0779.

9-Hexylcarbazol-2-ylboronic Acid (1)

n-BuLi (1.6 M in hexanes, 23.3 mL, 37.3 mmol) was added dropwise to a solution of 2-bromo-9-hexylcarbazole (**9**; 10.3 g, 31.1 mmol) in anhyd THF (150 mL) at –78 °C. The light-green mixture was stirred at –78 °C for 2 h, then $(i\text{-PrO})_3B$ (17.5 g, 93.2 mmol) was added and the mixture was stirred for 16 h while allowing the temperature to rise to 20 °C. Conc. HCl (13.2 mL) was added and stirring was continued for 2 h to give a clear light-brown solution which was neutralized (pH 7) with aq 2 M Na_2CO_3 (85 mL) and then concentrated under reduced pressure to give a precipitate. The precipitate was washed several times with H_2O and petroleum ether, respectively, to give compound **1** (7.6 g, 83%) as a white solid, mp 179–181 °C. The C, H, N analysis was obtained upon converting **1** into its boroxine derivative by heating at 70 °C for 2 days.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, H-1), 8.29 (d, 1 H, *J* = 7.6 Hz, H-4), 8.22 (d, 1 H, *J* = 7.6 Hz, H-5), 8.21 (d, 1 H, *J* = 7.9 Hz, H-3), 7.55 (t, 1 H, *J* = 7.7 Hz, H-7), 7.48 (d, 1 H, *J* = 8.3 Hz, H-8), 7.29 (t, 1 H, *J* = 7.6 Hz, H-6), 4.47 (t, 2 H, *J* = 7.3 Hz, NCH_2), 2.02 (p, 2 H, *J* = 7.6 Hz, NCH_2CH_2), 1.60–1.25 (m, 6 H, $CH_2CH_2CH_2$), 0.91 (t, 3 H, *J* = 7.4 Hz, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.5, 140.4, 127.6, 126.8, 126.7, 125.9, 122.8, 121.3, 120.1, 119.1, 116.3, 109.3, 43.4, 31.9, 29.4, 27.4, 22.9, 14.3.

Anal. Calcd for $C_{54}H_{60}B_3N_3O_3$: C, 78.0; H, 7.3; N, 5.1. Found: C, 77.8; H, 7.2; N, 5.0.

3-Bromocarbazole (12)

Method A: A solution of *n*-BuLi (2.5 M in hexanes, 2.4 mL, 6.0 mmol) was added to a solution of carbazole (**11**; 1.0 g, 6.0 mmol) in THF (50 mL) at –78 °C. The mixture was stirred for 15 min both at –78 °C and at 20 °C, then cooled to –78 °C and chlorotrimethylsilane (650 mg, 6.0 mmol) was added. The mixture was stirred at 20 °C for 3 h, cooled to –78 °C and Br_2 (956 mg, 6.0 mmol) was added. The mixture was stirred at –78 °C for 1 h, at 20 °C for 2 h and then quenched with distilled H_2O. After removal of solvents, the solid residue was washed with aq 2 M $NaHCO_3$ (3 × 50 mL), distilled H_2O (3 × 50 mL) and hexane (4 × 100 mL) to give a light-brown solid. Column chromatography (petroleum ether and CH_2Cl_2) gave a mixture of **11**, **12** and **13** (1.1 g) in a ratio of 4:5:1, respectively (by ^{1}H NMR data). After removal of **13** by recrystallization from $CHCl_3$, a mixture of **11** and **12** was obtained as a white-floppy solid. ^{1}H NMR established that 60% of this mixture was compound **12** (0.32 g, 22%); R_f 0.37 (petroleum ether–CH_2Cl_2, 1:1). This mixture was used in the next step without further purification. The ^{1}H, ^{13}C NMR and MS data for **12** were in agreement with the literature data.[13c,14]

Method B: Br_2 (30.8 g, 192.5 mmol) was added to a solution of carbazole (**11**; 29.3 g, 175.0 mmol) in DMF (150 mL) at 0 °C and the mixture stirred for 21 h, while gradually warming to 20 °C. The mixture was quenched with aq 15% $Na_2S_2O_3$ solution and then diluted with distilled H_2O until the products precipitated. The solid was washed with distilled H_2O (4 × 100 mL) and hexane (4 × 100 mL). Recrystallization from $CHCl_3$ gave mixtures of **11** and **12** (16.1 g) as a white solid, 93% of which was the desired compound **12** (15.0 g, 35%) based on ^{1}H NMR data. This mixture was used in the next step without further purification. The ^{1}H NMR data were in agreement with the literature.[13c,14] Compound **12** was characterized by single crystal X-ray structural analysis.

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Crystal Data[21]

$C_{12}H_8BrN$, *M* = 246.10, monoclinic, space group $P2_1/c$ (No. 14), *T* = 120 K, *a* = 20.312(3), *b* = 5.8017(8), *c* = 7.805(1) Å, β = 91.75(1)°, *V* = 919.3(2) Å^3, *Z* = 4, μ = 4.42 mm^{-1}, *R* = 0.037 on 1985 unique data with $I>2\sigma(I)$.

3-Bromo-9-hexylcarbazole (14)

Solid *t*-BuOK (1.8 g, 15.6 mmol) was added to a solution of a mixture of **11** and **12** [3.2 g, ≡ **12** (2.9 g, 11.8 mmol)] in anhyd DMF (60 mL). The mixture was stirred for 1 h at 20 °C and then 1-bromohexane (3.2 g, 19.7 mmol) was added. The mixture was heated at 130 °C for 65 h, cooled to 20 °C and quenched with distilled H_2O. Upon evaporation, the residue was diluted with H_2O and the organic products were extracted into CH_2Cl_2 (4 × 40 mL). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a light-brown liquid. This was chromatographed, eluting with a mixture of hexane and CH_2Cl_2 (9:1) to give mixtures of **14** and **15** (4.0.g) as a clear oil. ^{1}H NMR data indicated that 90% of the mixture was compound **14** (3.6 g, 91% based on **12**); R_f 0.42 (petroleum ether–CH_2Cl_2, 8:2). This mixture was used in the next step without further purification.

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^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (s, 1 H, H-4), 8.07 (d, 1 H, *J* = 7.8 Hz, H-5), 7.56 (dd, 1 H, *J* = 8.6, 1.6 Hz, H-2), 7.52 (t, 1 H, *J* = 7.8 Hz, H-7), 7.43 (d, 1 H, *J* = 8.3 Hz, H-8), 7.29 (d, 1 H, *J* = 8.6 Hz, H-1), 7.28 (t, 1 H, *J* = 7.8 Hz, H-6), 4.27 (t, 2 H, *J* = 7.4 Hz, NCH_2), 1.87 (p, 2 H, *J* = 7.4 Hz, NCH_2CH_2), 1.46–1.27 (m, 6 H, $CH_2CH_2CH_2$), 0.90 (t, 3 H, *J* = 7.0 Hz, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.0, 139.3, 128.5, 126.6, 124.8, 123.3, 122.1, 120.8, 119.4, 111.8, 110.4, 109.2, 43.5, 31.8, 29.1, 27.2, 22.8, 14.3.

MS (EI): *m*/*z* (%) = 332 (12, [M$^+$]), 331 (56, [M$^+$]), 330 (12, [M$^+$]), 329 (56, [M$^+$]), 261 (20), 260 (98), 259 (20), 258 (100).

HRMS (EI$^+$): *m*/*z* calcd for $C_{18}H_{20}BrN$: 329.0779; found: 329.0779.

9-Hexylcarbazol-3-ylboronic Acid (2)

n-BuLi (2.5 M in hexanes, 5.2 mL, 12.9 mmol) was added dropwise to a mixture of **14** and **15** [4.0 g, ≡ **14** (3.6 g, 10.8 mmol)] in anhyd THF (100 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h and then (*i*-PrO)$_3$B (6.1 g, 32.3 mmol) was added. The mixture was stirred for 22 h, while gradually warming to 20 °C. Conc. HCl (4.3 mL) was added and stirring continued for 2 h to give a clear blue solution, which was neutralized (pH 7) with aq 2M Na_2CO_3. The organic phase was separated and the organic products were extracted into CH_2Cl_2 (4 × 30 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give a light-blue solid which was chromatographed (petroleum ether–EtOAc, 1:1) and then recrystallized from EtOAc to afford **2** (2.1 g, 67% based on **14**) as a white solid; mp 182–184 °C. C, H and N analyses were obtained upon converting **2** into its boroxine derivative by heating at 70 °C for 2 days; R_f 0.53 (petroleum ether–EtOAc, 1:1).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.55 (s, 1 H, H-4), 7.99 (d, 1 H, *J* = 7.8 Hz, H-5), 7.87 (dd, 1 H, *J* = 8.2, 1.6 Hz, H-2), 7.58 [s, 1 H, B(OH)$_2$], 7.41–7.25 (m, 3 H), 7.12 (m, 1 H, H-6), 4.22 (t, 2 H, *J* = 7.4 Hz, NCH_2), 1.76 (p, 2 H, *J* = 7.5 Hz, NCH_2CH_2), 1.38–1.09 (m, 6 H, $CH_2CH_2CH_2$), 0.76 (t, 3 H, *J* = 7.1 Hz, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7, 141.0, 133.4, 129.1, 126.1, 123.6, 123.1, 121.0, 120.6, 119.7, 109.2, 108.5, 43.5, 31.9, 29.3, 27.4, 22.9, 14.4.

Anal. Calcd for $C_{54}H_{60}B_3N_3O_3$: C, 78.0; H, 7.3; N, 5.1. Found: C, 78.1; H, 7.4; N, 5.1.

9-Hexyl-2-(pyridin-2-yl)carbazole (17)

Compound **1** (1.5 g, 5.1 mmol), 2-bromopyridine (**16**; 1.0 g, 6.1 mmol) and $Pd(PPh_3)_2Cl_2$ (143 mg, 0.2 mmol) were dissolved in a mixture of toluene (20 mL) and aq 2 M Na_2CO_3 (10 mL, 20 mmol). The mixture was degassed several times, then heated at 90 °C for 21 h, cooled to 20 °C and then diluted with distilled H_2O. The organic phase was separated and the organic products were extracted into CH_2Cl_2 (4 × 30 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give a light-orange liquid, which was chromatographed, eluting with a mixture of petroleum ether and CH_2Cl_2. This was followed by a Kugelrohr distillation (110 °C/6 × 10^{-2} mm Hg) to remove traces of **16**, giving compound **17** (1.0 g, 60%) as a pale orange liquid; R_f 0.36 (CH_2Cl_2). (Reaction time 8 h gave **17** in 9% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.77 (d, 1 H, *J* = 4.5 Hz, pyridyl H-6), 8.18 (d, 1 H, *J* = 8.2 Hz, H-4), 8.16 (d, 1 H, *J* = 0.9 Hz, H-1), 8.14 (d, 1 H, *J* = 7.6 Hz, H-5), 7.89 (d, 1 H, *J* = 8.2 Hz, pyridyl H-3), 7.83 (dd, 1 H, *J* = 8.2, 1.6 Hz, H-3), 7.80 (t, 1 H, *J* = 7.8, 1.9 Hz, pyridyl H-4), 7.50 (dt, 1 H, *J* = 7.0, 1.2 Hz, H-7), 7.44 (d, 1 H, *J* = 8.2 Hz, H-8), 7.28–7.24 (m, 2 H, H-6 and pyridyl H-5), 4.40 (t, 2 H, *J* = 7.4 Hz, NCH_2), 1.93 (p, 2 H, *J* = 7.4 Hz, NCH_2CH_2), 1.44 (p, 2 H, *J* = 7.4 Hz, $NCH_2CH_2CH_2$), 1.39–1.23 (m, 4 H, CH_2CH_2), 0.88 (t, 3 H, *J* = 7.2 Hz, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5, 149.9, 141.5, 141.2, 137.2, 137.1, 126.2, 123.8, 122.8, 122.1, 121.3, 120.9, 120.7, 119.2, 118.1, 109.1, 107.6, 43.4, 31.9, 29.3, 27.2, 22.8, 14.3.

MS (EI$^+$): *m*/*z* (%) = 328 (72, [M$^+$]), 257 (100), 244 (26), 129 (30).

HRMS (EI$^+$): *m*/*z* calcd for $C_{23}H_{24}N_2$: 328.1940; found: 328.1944.

9-Hexyl-3-(pyridin-2-yl)carbazole (18)

Compound **2** (1.9 g, 6.3 mmol), 2-bromopyridine **16** (2.5 g, 15.8 mmol) and $Pd(PPh_3)_2Cl_2$ (0.3 g, 0.4 mmol) were dissolved in a mixture of toluene (64 mL) and aq 2 M Na_2CO_3 (32 mL, 64 mmol). The mixture was degassed several times, heated at 90 °C for 40 h, then cooled to 20 °C and diluted with distilled H_2O. The organic products were extracted with EtOAc (4 × 30 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give a dark-brown solid, which was chromatographed, eluting with a mixture of petroleum ether and EtOAc (4:1). This was followed by Kugelrohr distillation (110 °C/6 × 10^{-2} mm Hg) to remove traces of **16**, giving compound **18** (1.5 g, 70%) as a pale orange oil; R_f 0.24 (CH_2Cl_2). (Reaction time of 8 h gave **18** in 13% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.89 (1 H, s), 8.82 (1 H, d, *J* = 3.9 Hz), 8.29 (1 H, d, *J* = 7.5 Hz), 8.20 (1 H, d, *J* = 8.7 Hz), 7.88 (1 H, d, *J* = 6.0 Hz), 7.76 (1 H, m), 7.58–7.46 (3 H, m), 7.35 (1 H, m), 7.23 (1 H, m), 4.29 (t, 2 H, *J* = 7.4 Hz, NCH_2), 1.89 (p, 2 H, *J* = 6.8 Hz, NCH_2CH_2), 1.49–1.22 (m, 6 H, $CH_2CH_2CH_2$), 0.92 (t, 3 H, *J* = 7.6 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 149.7, 141.3, 141.2, 136.9, 130.5, 126.0, 125.0, 123.5, 123.4, 121.3, 120.4, 119.32, 119.29, 109.1, 109.0, 43.3, 31.8, 29.1, 27.2, 22.8, 14.3.

MS (EI$^+$): *m*/*z* (%) = 328 (76, [M$^+$]), 257 (100), 243 (25).

HRMS (EI$^+$): *m*/*z* calcd for $C_{23}H_{24}N_2$: 328.1940; found: 328.1938.

Anal. Calcd for $C_{23}H_{24}N_2$: C, 84.1; H, 7.4; N, 8.5. Found: C, 83.9; H, 7.4; N, 8.2.

3-[9,9-Dihexyl-7-(pyridine-2-yl)fluoren-2-yl]-9-hexylcarbazole (20)

A mixture of **2** (1.0 g, 3.5 mmol), **19** (1.2 g, 2.4 mmol) and $Pd(PPh_3)_4$ (195 mg, 0.17 mmol) dissolved in toluene (40 mL) and aq 2 M Na_2CO_3 (20 mL, 40 mmol) was heated at 90 °C for 54 h. Work-up as described for **18** gave a black liquid. Chromatographic purification by eluting with a mixture of petroleum ether and CH_2Cl_2 removed a fast-running impurity, then gave a foamy white solid which contained a minor impurity with a similar R_f value. Further purification, both by Kugelrohr distillation (140 °C/0.02 mm Hg) and by column chromatography (petroleum ether–EtOAc, 95:5), afforded **20** (1.22 g, 77%) as a glassy solid; mp 53–54 °C; R_f 0.23 (petroleum ether–EtOAc, 9:1).

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.69 (d, 1 H, *J* = 4.7 Hz, pyridyl H-6), 8.55 (s, 1 H), 8.28 (s, 1 H, carbazolyl H-4), 8.23 (d, 1 H, *J* = 7.9 Hz), 8.16 (d, 1 H, *J* = 7.9 Hz, carbazolyl H-5), 8.02 (d, 1 H, *J* = 7.9 Hz), 7.96–7.90 (m, 3 H), 7.89–7.83 (m, 2 H), 7.80 (d, 1 H, *J* = 7.9 Hz), 7.68 (d, 1 H, *J* = 8.4 Hz), 7.59 (d, 1 H, *J* = 8.2 Hz), 7.48 (t, 1 H, *J* = 7.5 Hz, carbazolyl H-7), 7.31 (t, 1 H, *J* = 4.7 Hz, pyridyl H-5), 7.23 (t, 1 H, *J* = 7.5 Hz, carbazolyl H-6), 4.47 (t, 2 H, *J* = 7.2 Hz, NCH_2), 2.30–2.15 (m, 4 H), 1.91 (p, 2 H, *J* = 7.5 Hz, NCH_2CH_2), 1.42 (p, 2 H, *J* = 7.6 Hz), 1.38–1.23 (m, 4 H, CH_2CH_2), 1.16–0.98 (m, 12 H), 0.84 (t, 3 H, *J* = 7.2 Hz, CH_3), 0.80–0.69 (m, 4 H), 0.71 (t, 6 H, *J* = 7.1 Hz, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.0, 152.3, 151.9, 149.7, 142.5, 141.7, 141.2, 140.2, 139.3, 137.8, 137.2, 132.9, 126.4, 126.2, 126.1, 125.6, 123.6, 123.2, 122.1, 121.9, 121.5, 121.0, 120.7, 120.5, 120.1, 119.1, 109.2, 109.1, 55.7, 43.5, 40.8, 31.9, 31.8, 30.0, 29.3, 27.3, 24.1, 22.9, 22.8, 14.3.

Anal. Calcd for $C_{48}H_{56}N_2$: C, 87.22; H, 8.54; N, 4.24. Found: C, 87.24; H, 8.51; N, 4.45.

MS (EI): *m*/*z* (%) = 663 (20, [M$^+$]), 662 (66, [M$^+$]), 661 (100, [M$^+$]), 660 (44, [M$^+$]).

***fac*-Tris[9-Hexyl-3-(pyridin-2-yl)carbazole]iridium(III) (21)**

$IrCl_3$ (42.9 mg, 0.12 mmol), 9-hexyl-3-(pyridin-2-yl)carbazole (**18**; 200 mg, 0.61 mmol), and Na_2CO_3 (26 mg, 0.24 mmol) in a mixture of ethylene glycol (4 mL) and distilled H_2O (1 mL) were placed in a reaction vessel and blanketed with argon. The mixture was heated to 220 °C by microwave irradiation (Personal Chemistry, Emrys Optimizer, Microwave reactor, 200 W) for 30 min. The mixture was diluted with H_2O (10 mL) and the organic products were extracted with EtOAc (3 × 15 mL). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude product. The crude product was purified by chromatography by eluting with a mixture of *n*-hexane and EtOAc (8:2) to afford **21** (20 mg, 14%) as a bright yellow solid; R_f 0.48 (petroleum ether–CH_2Cl_2, 1:1). A pure and a solvated form of **21**, grown from a mixture of CH_2Cl_2 and acetone, was characterized by single crystal X-ray structural analysis.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.63 (s, 3 H), 8.26 (d, 3 H, *J* = 8.0 Hz), 8.06 (d, 3 H, *J* = 8.0 Hz), 7.81 (dd, 3 H, *J* = 5.5 Hz), 7.73 (td, 3 H, *J* = 8.5 Hz), 7.26 (m, 6 H), 7.06 (t, 3 H, *J* = 7.0 Hz), 6.98 (t, 3 H, *J* = 4.5 Hz), 6.91 (s, 3 H), 3.76 (m, 6 H), 1.43 (m, 6 H), 0.89 (m, 18 H), 0.63 (m, 9 H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 168.1, 161.9, 148.2, 147.5, 144.4, 140.9, 137.5, 137.0, 125.4, 124.6, 121.8, 119.5, 119.2, 117.8, 117.1, 116.3, 109.2, 43.2, 32.0, 29.2, 27.4, 23.0, 14.2.

MS (MALDI-TOF): *m*/*z* calcd for $C_{69}H_{69}IrN_6$ (M$^+$) 1174.5; found: 1774.4.

Anal. Calcd for $C_{69}H_{69}IrN_6$: C, 70.6; H, 5.9; N, 7.2. Found: C, 70.5; H, 6.1; N, 6.9.

Crystal Data[22]

21

$C_{69}H_{69}IrN_6$, *M* = 1174.50, triclinic, space group *P*–1 (No. 2), *T* = 120 K, *a* = 13.031(2), *b* = 20.049(2), *c* = 23.621(3) Å, α = 82.45(1), β = 78.17(1), γ = 72.15(1)°, *V* = 5734(1) Å^3, *Z* = 4, μ = 2.38 mm^{-1}, *R* = 0.082 on 10322 unique data with *I*>2 σ(*I*).

21·2CH_2Cl_2·0.5Me_2CO

M = 1373.39, triclinic, space group *P*–1 (No. 2), *T* = 120 K, *a* = 15.331(2), *b* = 19.532(3), *c* = 23.946(3) Å, α = 82.57(1), β = 77.56(1), γ = 69.72(1)°, *V* = 6557(1) Å^3, *Z* = 4, μ = 2.25 mm^{-1}, *R* = 0.053 on 22361 unique data with *I*>2σ(*I*).

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