Synthesis of aryl-substituted 2-pyridyl-1,10-phenanthrolines; a series of oriented terpyridine analogues†‡

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A 3 × 3 matrix of manisyl (4-methoxy-2,6-dimethylphenyl) substituted pyridyl-1,10-phenanthrolines has been synthesized by utilizing a general palladium catalyzed cross-coupling procedure. The directionality of these terdentate ligands will generate chiral octahedral ML_2 complexes, potentially useful for the metal templated synthesis of topologically chiral structures.

Introduction

The terdentate 2,2′:6′,2″-terpyridine (terpy) has been used extensively for the formation of octahedral transition metal complexes,[1] and a wealth of symmetrical derivatives have been prepared,[2] including bridged[3] and chiral examples.[4] Only a limited number of unsymmetrical analogues are known,[5] of which 2-(pyrid-2-yl)-1,10-phenanthroline (pherpy) presents a unique juxtaposition of the 1,10-phenanthroline (phen) backbone upon a terpyridine (Fig. 1). The extra double bond of the pherpy differentiates the left and right side and, when schematically represented, provides the pherpy with an orientation that the terpyridine lacks (Fig. 1b). As such, pyridyl-phenanthrolines are useful building blocks for oriented topological isomers *via* octahedral transition metal templates. However, the limited synthetic access to functionalized derivatives, in addition to the poor solubility of the parent heterocycle,[6] restrict the study of this family of compounds.

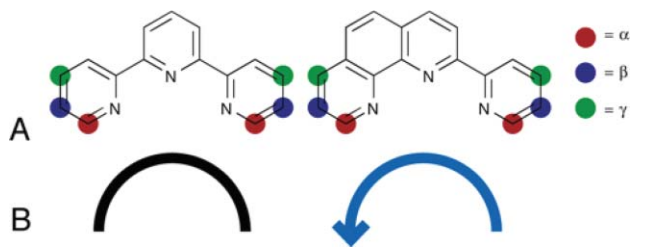

Fig. 1 Chemical (a) and schematic (b) representations of terpy and pherpy with the α- (red), β- (green), and γ- (blue) positions highlighted.

Early syntheses of these compounds utilized aryl lithium reagents[7] or condensation methods[8] and are limited in generality. Recently, a modular synthesis of polypyridine ligands *via* palladium catalyzed cross coupling was introduced.[9] Assuming the generality of this modular approach, it leads one to a retrosynthetic strategy where the array of pherpy derivatives arises from the combinatorial coupling of a common set of building blocks (Fig. 2). Systematic variation of the substitution pattern not only facilitates the investigation and fine tuning of the electronic properties of the ligands, but also enables one to specify the spatial orientation of the resulting metal complexes and allows elaboration of octahedral *endo*- and *exo*-topic metallosupramolecular structures.[10]

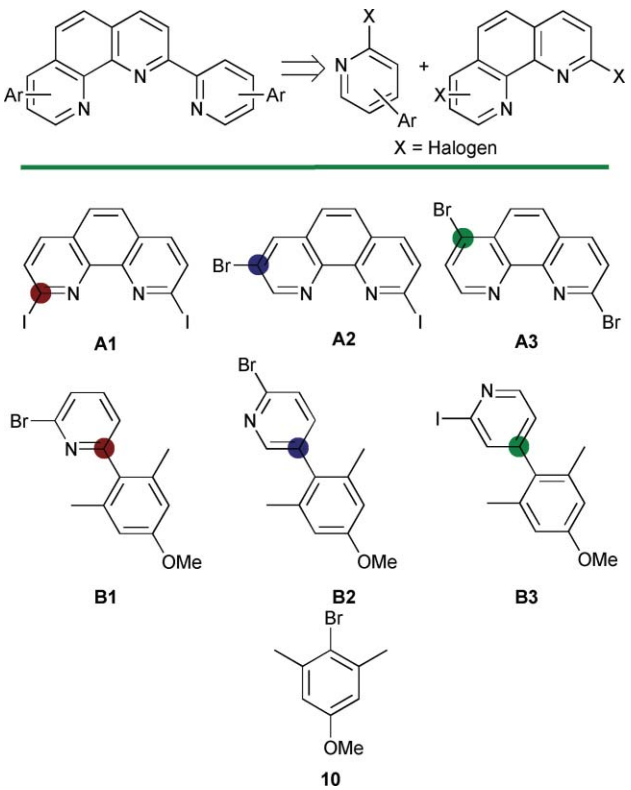

Fig. 2 Retrosynthesis and common building blocks.

Focusing on the positions α (red), β (green), and γ (blue), relative to the nitrogens reveals that dihalo-phenanthrolines **A1–A3**, aryl pyridines **B1–B3**, and aryl halide **10**[11] (Fig. 2) suffice to synthesize a 3 × 3 matrix of pyridyl-phenanthrolines (Fig. 3).

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† Dedicated to Professor Andrew B. Holmes on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: 2D-NMR data for complex **15** and crystallographic data and .cif files for compounds **1** and **4**. See DOI: 10.1039/b804106g

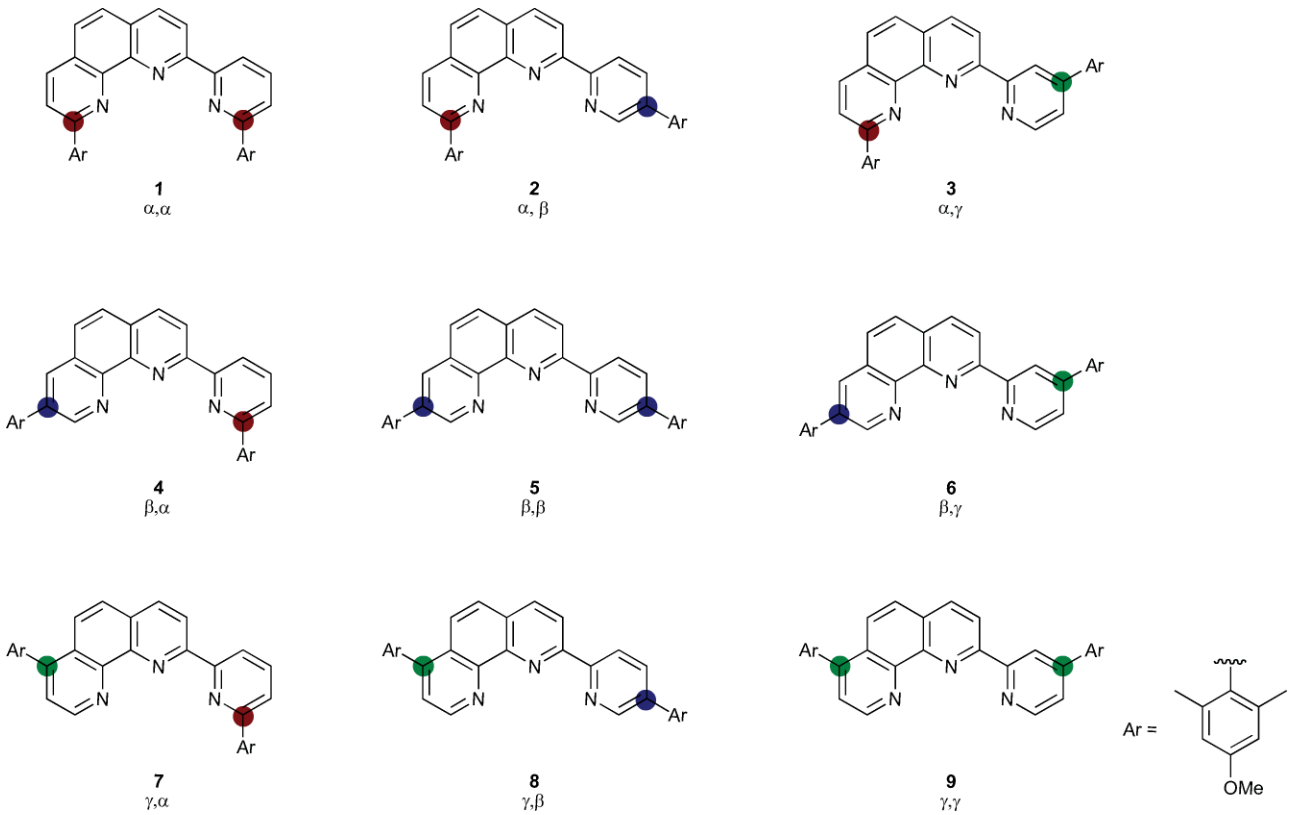
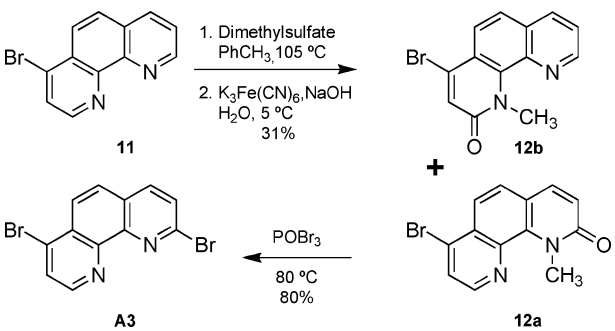


Fig. 3 Manisyl pyridyl-phenanthrolines.

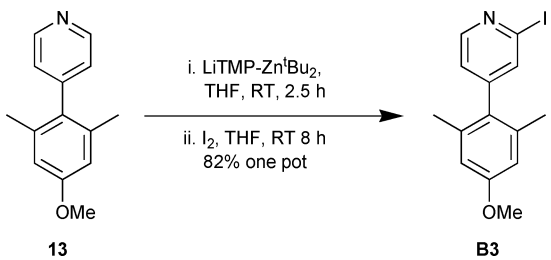
Results and discussion

Diiodo-phenanthroline **A1** and 3-bromo-9-iodo-phenanthroline **A2** were prepared according to literature procedures.[12] The previously unknown 2,7-dibromo-phenanthroline **A3** was prepared by methylation of 4-bromo-phenanthroline **11**[13] with dimethylsulfate, giving a 2 : 1 mixture of phenanthrolinium salt regioisomers. Subsequent oxidation of the mixture gave the desired **12a** and its regioisomer **12b** (Scheme 1).[14] After chromatographic separation, treatment of **12a** with phosphoryl bromide gave 2,7-dibromo-phenanthroline **A3**.



Scheme 1 Synthesis of 2,7-dibromophenanthroline.

Aryl pyridines **B1** and **B2** were also prepared according to literature procedures.[9] 2-Iodo-4-manisyl pyridine **B3** was made from 4-manisylpyridine **13**[9] *via* directed ortho metalation using lithium di-*tert*-butyltetramethyl-piperidinozincate (LiTMP-Zn^{t}Bu$_2$)[15] as the base (Scheme 2).



Scheme 2 Synthesis of 2-iodo-4-manisylpyridine.

The Negishi cross-coupling protocol[16] was chosen because the resulting terdentate ligands can precipitate from the reaction mixture after complexing the residual zinc chloride, thereby reducing catalyst poisoning and simplifying purification.[9] Manisylpyridines **B1–B3** were converted into the organozinc reagents and coupled to the appropriate dihalo-phenanthroline to produce the corresponding halo-pyridyl-phenanthrolines **C1–C6** (Scheme 3) in good yields (Table 1).

Lower yields of **C7–C9** were obtained due to unselective reactivity of the bromines in **A3**. Coupling of **A3** with **B1** or **B3** results in a regioisomeric mixture of mono-coupled products from which the desired halo-pherpy precipitated as the zinc salt. Coupling of **A3** and **B2** gives only the di-coupled product in THF; in DME, a 2 : 1 mixture of mono and dicoupled material was obtained and separated by chromatography.

The submission of halo-pherpys **C2** and **C4** to Negishi conditions cleanly gave products in good yields (Scheme 4 and Table 2), whereas **C1** and **C5** gave mixtures of product and starting

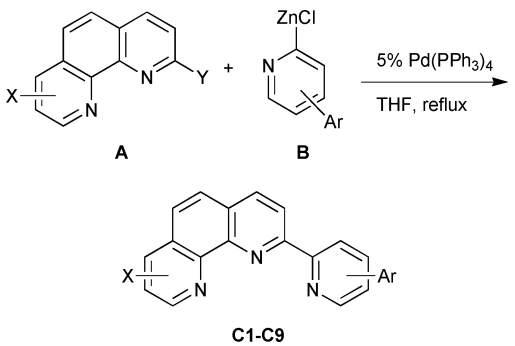
Table 1 Negishi couplings of halo-pherpys

Halo-pyr	Halo-phen	Product	Yield (%)
B1	**A1**	**C1**	52
B2	**A1**	**C2**	74
B3	**A1**	**C3**	26
B1	**A2**	**C4**	86
B2	**A2**	**C5**	60
B3	**A2**	**C6**	52
B1	**A3**	**C7**	18
B2	**A3**	**C8**	18
B3	**A3**	**C9**	20[a]

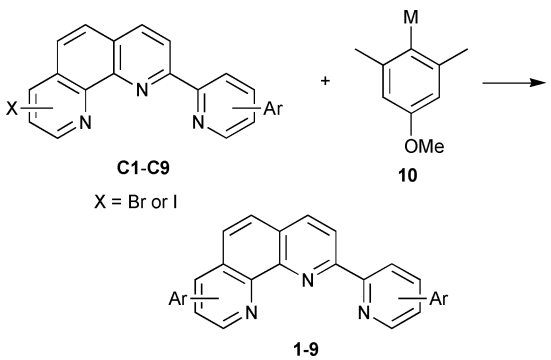
[a] DME.

Table 2 Pd-catalyzed couplings of halo-pherpys

Halo-pherpy	Method	Product	Yield (%)
C1	**A**	**1**	40
C2	**A**	**2**	74
C3	**B**	**3**	74
C4	**A**	**4**	79
C5	**B**	**5**	65
C6	**B**	**6**	90
C7	**B**	**7**	84
C8	**A**	**8**	12
C9	**B**	**9**	84



Scheme 3 Negishi couplings of halo-pherpys.



Scheme 4 Palladium catalyzed couplings of pherpys. *Reaction conditions:* Method (A) M = ZnCl, 5% $Pd(PPh_3)_4$, THF, reflux. Method (B) M = $B(OH)_2$, $Ba(OH)_2$, 5–10% $Pd(PPh_3)_4$, DME–H_2O, 90 °C.

material. Negishi reactions of **C7** and **C8** did not couple and only starting material was recovered. The halo-pherpys also contain the terdentate binding unit and can precipitate from the reaction mixture as the zinc salt, thereby preventing the reaction from reaching completion.

In order to avoid precipitation of the zinc complex, the Suzuki–Miyaura cross-coupling procedure[17] was investigated. Halo-pyridyl-phenanthrolines **C2**–**C4**, **C6**, **C7**, and **C9** gave the desired manisyl-pyridyl-phenanthrolines in good yields (Scheme 4 and Table 2).

The crystal structures of representative pyridyl-phenanthrolines **1** and **4** were determined (Fig. 4).[18] The phenanthroline core is nearly planar, with torsion angles of 6.25(7)° and 3.62(11)° between rings **A** and **B** of **1** and **4**, respectively. The manisyl substituents of **4** adopt an orthogonal conformation relative to the adjacent pyridyl plane, 88.22 ° (11) and 86.05 ° (11), effectively minimizing orbital overlap. In **1**, however, the manisyl group in the pyridyl α-position approaches orthogonality (82.29(8)°), but the manisyl group α- to the phenanthroline nitrogen atom deviates significantly from orthogonality (60.30(7)°) and orbital overlap increases. The free pyridyl ring **C** adopts a transoid conformation (with torsion angles of 22.62(7)° and 10.07(11)° relative to the phenanthroline core (rings **A** and **B**) of **1** and **4**, respectively. Upon terdentate metal coordination, the *cis* conformation will be adopted and the geometry of the ligand will alter significantly.

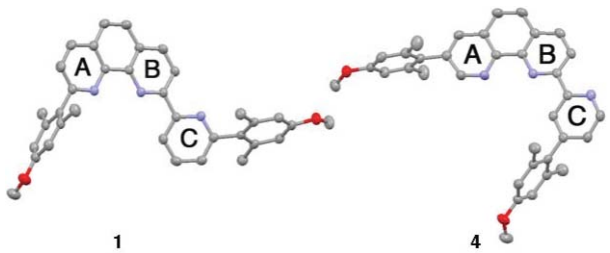


Fig. 4 Views of the molecular structures of **1** and **4**. Thermal ellipsoids at 50% probability level.

With pyridyl-phenanthrolines now in hand, the effects of structural variation on the photophysical properties were examined. It is known that the emissive properties of aryl substituted 2,2′-bipyridines and terpyridines depend on the nature[19] and location[9] of the substituent. The electronic and photophysical properties of polypyridyl metal complexes also depend on those of the ligand,[20] and yet the fluorescent properties of terpy and its derivatives have been much less studied.[9,19–21]

The UV–Vis absorption spectra of **1–9** in acetonitrile are similar, with intense broad π–π* transitions around ~290 nm and 310 nm and a weak π–π* transition at 350 nm (representative spectra are shown in Fig. 5, see ESI for complete spectra‡). The emission spectra are broad and structureless with a large Stokes shift (~130nm) (Fig. 5 and Table 3), strongly indicative of a charge-transfer excited (CT*) state.[23] The sharper bands at 360 and 375 nm in the spectra of **4**, **7**, **8**, and **9** resemble the emission of 1,10-phenanthroline[24] and are likely from a similar locally excited (LE*) state.

Pyridyl-phenanthrolines with the manisyl groups in the β-position relative to the nitrogen atom on the pyridine ring, **2**, **5**, and **8**, have high quantum yields ($0.41 < \Phi_f < 0.62$) (Table 3), whereas substitution in the α or γ position displays low quantum yields ($0.03 < \Phi_f < 0.18$). Conversely, the location of the manisyl group on the phenanthroline core has only a minor effect on

Table 3 Photophysical data of pyridyl-phenanthrolines in acetonitrile

	λ_{max}abs/nm	ε_{max}/M^{-1} cm^{-1}	λ_{max}em/nm	Φ_f[a]
1	293	31 800	424	0.175
2	296	33 300	435	0.408
3	291	14 900	428	0.083
4	294	45 800	375	0.070
5	297	39 200	438	0.623
6	294	38 600	375	0.070
7	287	36 700	372	0.026
8	291	29 700	443	0.607
9	288	37 900	372	0.038

[a] Relative to 9,10-DPA.[25]

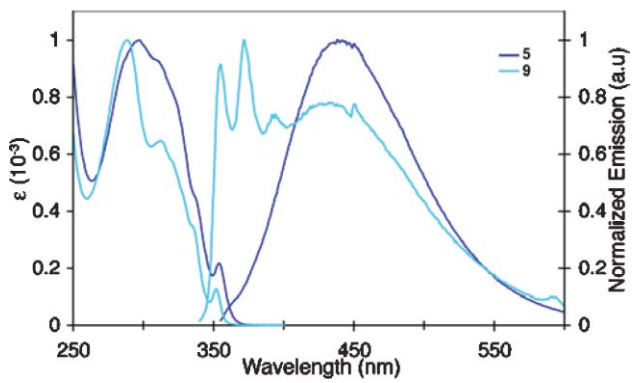
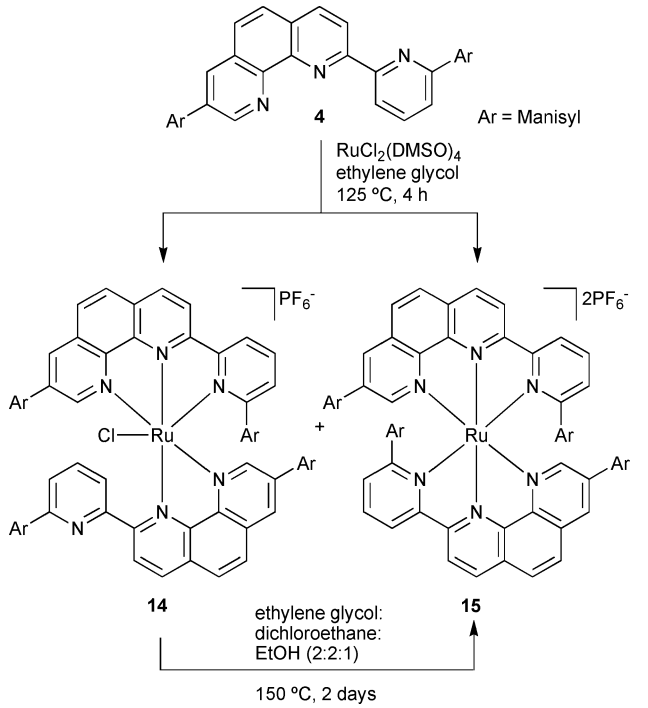


Fig. 5 Combined normalized absorption and emission spectra of representative manisyl-pyridyl-phenanthrolines **2** and **5** in ACN.[22]

the quantum yield. The relationship between the CT* quantum yield and manisyl regiochemistry indicates that manisyl acts as the donor and the pyridyl-phenanthroline as the acceptor. Given that the *ortho*-methyl groups hold the manisyl groups in an orthogonal position, reducing orbital overlap, a twisted intramolecular charge (TICT) state is plausible.[26] Similar to previous manisyl substituted terpys and bipys,[9] one can infer that the base fluorophore is again a 4-manisyl-2,2′-bipyridine.

As homoleptic ML_2 complexes of 6- and 6,6″-aryl substituted terpyridines are rare,[6a,7,27] due to steric reasons,[28] the partially hindered pyridyl-phenanthroline **4** was chosen as the model ligand. Reaction of **4** with $RuCl_2(DMSO)_4$ in ethylene glycol for four hours gave a 2 : 1 mixture of the partially reacted complex **14** and final product **15** (Scheme 5). As expected, the ^{1}H-NMR spectrum of **14** is very complex due to the many possible constitutional, atropo- and stereo-isomers. No further attempts were made to characterize the mixture of stereoisomers and after heating for two days the mixture cleanly converted to **15**.

The ^{1}H-NMR resonances of pyridyl-phenanthroline **4** shift upon binding to ruthenium.[29] The complex is C_2-symmetric and the manisyl protons are now diastereotopic and split into two sets of signals. Titration of racemic **15** with the D_3-symmetric chiral shift reagent [n-Bu_3NH][Δ-TRISPHAT][30] results in diastereomeric ion pairs distinguishable by ^{1}H-NMR (Fig. 6). Protons **e** and **b** are the most sensitive to the presence of TRISPHAT and proton **e** clearly resolves at one equivalent of anion and sharpens with additional anion equivalents. Only after two equivalents are protons **b** of the two diastereomers fully resolved. Proton **d** approaches clean separation with excess anion whereas the



Scheme 5 Synthesis of racemic pyridyl-phenanthroline ruthenium complex **13**.

resolutions of protons **j** and **l** are reduced after two equivalents. Protons **b**–**f** are located on the manisyl pyridine section of the ligand and are affected to the greatest extent indicating that significant diastereomeric ion pair interactions occur at this site.

Conclusions

The syntheses of the pyridyl-phenanthrolines reported here demonstrate a general method based on palladium-catalyzed cross-coupling. The combination of readily accessible heterocyclic building blocks is a simple strategy that allows a systematic variation of new and useful substitution patterns for unsymmetrical oligopyridines. Incorporation of manisyl groups as aryl substituents enables further structural elaboration, grants enhanced solubility and intriguing photophysical properties. The chiral nature of the ruthenium complex **15** was confirmed by ^{1}H-NMR and by titration with the chiral shift reagent Δ-TRISPHAT. The clear enantiodifferentiation by Δ-TRISPHAT indicates that strong ion pairing with the enantiopure D_3-symmetric anion can distinguish between the C_2-symmetric cations. Attempts to resolve pyridyl-phenanthroline complexes are currently under investigation. In conclusion, pyridyl-phenanthrolines are versatile starting points for the formation of chiral *mer,mer*-octahedral ML_2 complexes and the subsequent metal templated syntheses of topologically interesting molecules.[31]

Experimental

^{1}H- and ^{13}C NMR spectra were recorded on Varian (Mercury 300/400 mHz and Unity 500 mHz) and Bruker (600 mHz) spectrometers and were referenced to residual $CHCl_3$ (^{1}H-NMR: 7.26 ppm; and ^{13}C-NMR 77.00 ppm), CD_3CN (^{1}H-NMR: 1.94 ppm and ^{13}C-NMR: 1.39 ppm), or CD_2Cl_2 (^{1}H-NMR:

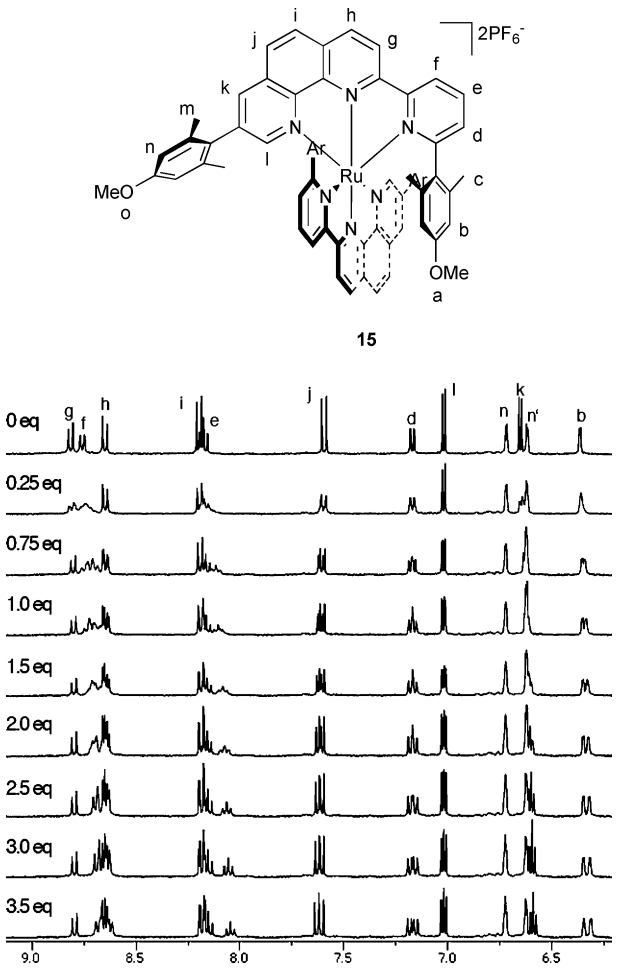


Fig. 6 Section of the ^{1}H NMR spectra of racemic **15** in CD_2Cl_2 upon titration with [n-Bu_3NH][Λ-TRISPHAT].

5.31 ppm and ^{13}C-NMR: 54.00 ppm). High-resolution mass spectral (HRMS) analyses were performed by the University of California, Riverside mass spectrometry facility in EI mode.

All experiments were carried out under argon in freshly distilled anhydrous solvents unless otherwise noted. Commercial chemicals were used as supplied from Aldrich or Acros Chemical Co. Column chromatography was performed on neutral aluminium oxide (Brockmann III) and silica gel (230–425 mesh). Melting points are uncorrected and recorded on a Mel-Temp Laboratory Device. All X-ray measurements were made on a *Nonius KappaCCD* area-detector diffractometer using graphite-monochromated Mo *K*a radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Data reduction was performed with *HKL Denzo* and *Scalepack*.[32] All calculations were performed using the *SHELXL97* program.[33] 2,9-Diiodo-1,10-phenanthroline, 2-iodo-8-bromo-1,10-phenanthroline,[12] 1*H*-1,10-phenanthrolin-4-one,[13a] 4-(4-methoxy-2,6-dimethylphenyl)pyridine, 2-bromo-5-(4-methoxy-2,6-dimethylphenyl)pyridine, 2-bromo-6-(4-methoxy-2,6-dimethylphenyl)pyridine,[9] and dichlorotetrakis(dimethyl sulfoxide)ruthenium(II)[34] were all prepared according to literature procedures. [n-Bu_3NH][Δ-TRISPHAT] was graciously provided by Richard Frantz from the Lacour group in Geneva.

4-Bromo-1,10-phenanthroline

1*H*-1,10-Phenanthrolin-4-one (5.00 g, 25.50 mmol) was placed in a dry 100 mL round-bottom flask under argon. Phosphorous oxybromide (18.00 g, 63.80 mmol) was added and the neat mixture was placed in a hot oil bath at 105 °C and stirred overnight. The solution was cooled to room temperature and quenched with aqueous ammonium hydroxide until strongly basic. The brown precipitate was filtered and washed with water. The solid was dissolved in warm chloroform, and washed three times with water. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a white solid (5.21 g, 79%, yield). Mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.21 (1H, dd, J = 4.4, 1.6 Hz), 8.94 (1H, d, J = 4.4 Hz), 8.28 (1H, dd, J = 8.0, 1.6 Hz), 8.21 (1H, d, J = 9.2 Hz), 7.92 (1H, d, J = 4.4 Hz), 7.89 (1H, d, J = 9.2 Hz), 7.67 (1H, dd, J = 8.0, 4.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.75, 149.72, 147.09, 145.65, 136.14, 134.02, 128.58, 128.16, 127.73, 127.11, 124.87, 123.60; HRMS *m*/*z*: calc. for $C_{12}H_7BrN_2$: 257.979259: found 257.978540.

7-Bromo-1-methyl-1*H*-1,10-phenanthrolin-2-one (12a) and 4-bromo-1-methyl-1*H*-1,10-phenanthrolin-2-one (12b). 4-Bromo-1,10-phenanthroline (3.43 g, 12.50 mmol) was dissolved in toluene (30 mL) and heated to reflux. Dimethyl sulfate (1.55 mL, 16.30 mmol) was dissolved in toluene (12 mL) and slowly added over 30 min. After an additional 1 h at reflux, the excess toluene was decanted. The residual tan solid was rinsed three times with toluene and dried under hi-vacuum overnight. The phenanthrolinium salt was dissolved in cold water (45 mL) and slowly added dropwise into a solution of $K_3Fe(CN)_6$ (10.28 g, 31.30 mmol) in water (35 mL) at 0 °C. Simultaneously, NaOH (11.35 g, 284 mmol) in water (40 mL) was also added dropwise into the reaction flask. The mixture was stirred for 1 h at 0 °C and warmed to room temperature, affording a yellow solution with a green suspension. The precipitate was filtered and washed with water. The green solid was dissolved in methylene chloride, and washed three times with water. The organic layer was separated, dried with magnesium sulfate, filtered, and after evaporation, placed under hi-vacuum overnight to give a mixture of **12a**, **12b**, and starting material **11** (5 : 2 : 1) as a green solid. Column chromatography on neutral alumina with methylene chloride gave two products; **12a** (1.301 g, 36%), and **12b** (0.493 g, 13%) as white solids. **12a**: mp 176–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.70 (1H, d, J = 4.8 Hz), 8.03 (1H, d, J = 9.0 Hz), 7.82 (1H, d, J = 4.5 Hz), 7.81 (1H, d, J = 9.3 Hz), 7.68 (1H, d, J = 8.7 Hz), 6.95 (1H, d, J = 9.3 Hz), 4.42 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 164.26, 146.27, 140.87, 138.78, 138.08, 133.84, 129.44, 127.92, 126.07, 123.17, 121.07, 120.97, 38.34; HRMS *m*/*z*: calc. for: $C_{13}H_9BrN_2O$: 287.98983 found 287.98950. **12b**: mp 180–183 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.98 (1H, dd, J = 4.2, 1.8 Hz), 8.22 (1H, dd, J = 8.1, 1.5 Hz), 8.11 (1H, d, J = 8.1 Hz), 7.64 (1H, d, J = 9.0 Hz), 7.55 (1H, dd, J = 8.1, 3.9 Hz), 7.35 (1H, s), 4.42 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 162.45, 147.35, 139.77, 138.15, 135.94, 135.77, 130.28, 125.77, 125.56, 125.65, 122.42, 119.52, 38.62; HRMS *m*/*z*: calc. for: $C_{13}H_9BrN_2O$: 287.98983 found 287.98913.

2,7-Dibromo-1,10-phenanthroline

7-Bromo-1-methyl-1*H*-1,10-phenanthrolin-2-one (0.76 g, 2.63 mmol) was placed in a dry 50 mL round-bottom flask under argon.

Phosphorous oxybromide (1.95 g, 6.57 mmol) was added and the mixture placed in a hot oil bath at 105 °C and stirred overnight. The solution was cooled to room temperature and quenched with aqueous ammonium hydroxide until strongly basic. The brown precipitate was filtered and washed with water. The solid was dissolved in warm chloroform, and washed three times with water. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a brown solid (0.790 g, 90%). Column chromatography on neutral alumina with chloroform: hexanes (7 : 3 to 1 : 0) as eluant gave a white solid (0.450 g, 50%). Mp 218–221 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.99 (1H, d, $J = 4.8$ Hz), 8.27 (1H, d, $J = 9.0$ Hz), 8.12 (1H, d, $J = 8.4$ Hz), 7.94 (1H, d, $J = 4.5$ Hz) 7.89 (1H, d, $J = 9.0$), 7.83 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 150.15, 146.09, 145.85, 142.98, 138.07, 133.98, 128.51, 128.42, 127.42, 126.97, 125.45, 125.45; HRMS m/z: calc. for [M$^+$] $C_{12}H_6Br_2N_2$: 335.889770 found 335.889380.

2-Iodo-4-(4-methoxy-2,6-dimethylphenyl)-pyridine

Using Schlenk techniques, 2,2,6,6-tetramethylpiperidine (TMP) (6.62 g, 46.94 mmol) was added to THF (125 mL) and cooled to −78 °C. n-BuLi (20.98 mL of a 2.35 M sol in hexanes, 49.30 mmol) was added dropwise and the solution stirred for 30 min at 0 °C. A THF solution (100 mL) of di-*tert*-butylzinc at 0 °C prepared from $ZnCl_2$ (6.70 g, 49.30 mmol) and t-BuLi (57.99 mL of a 1.7 M sol in pentane, 98.57 mmol) was cannulated into the LiTMP solution at −78 °C. The solution was warmed to room temperature and stirred for 45 min. 4-Manisyl pyridine (5.00 g, 23.47 mmol) was dissolved in THF and cannulated into the solution of LiTMP-Zn^{t}Bu$_2$. After stirring at room temperature for 2.5 h, a solution of iodine (59.61 g, 235 mmol) in THF (250 mL) was slowly added dropwise and stirred overnight. The solvent was removed on a rotary evaporator and the reaction quenched with aqueous sodium thiosulfate. The mixture was extracted with methylene chloride and washed with aqueous sodium thiosulfate and water. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to afford a brown solid. Recrystallization from hot hexanes gave off-white crystals (6.52 g, 82%). Physical and spectral data matched literature. Mp = 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.41 (1H, d, $J = 4.8$ Hz), 7.57 (1H, d, $J = 2.0$ Hz), 7.09 (1H, dd, $J = 4.8$, 2.0 Hz), 6.65 (2H, s), 3.82 (3H, s), 2.02 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.95, 151.22, 150.44, 136.46, 135.86, 129.87, 124.56, 118.41, 112.91, 55.20, 21.05.

4-Methoxy-2,6-dimethylphenylboronic acid

A solution of bromo-manisyl (0.50 g, 2.33 mmol) in THF (50 mL) was cooled to −78 °C and n-BuLi (1.02 mL of a 2.5M sol in hexanes, 2.56 mmol) was added slowly *via* syringe. The resulting white solution was stirred for 20 min at −78 °C before trimethoxy borate (0.42 g, 4.08 mmol) was added dropwise. The clear solution was stirred overnight at room temperature. The reaction was quenched and hydrolyzed with 10% hydrochloric acid (1 mL) and water (1 mL) and stirred for 6 h at room temperature. The solution was diluted with diethyl ether and washed with water. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to give a white solid (0.305 g, 73%). Mp 110–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.55 (2H, s), 4.57 (2H, bs), 3.77 (3H, s), 2.37 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 160.13, 141.56, 112.17, 109.98, 55.00, 22.39; HRMS m/z: calc. for [M$^+$] $C_9H_{13}BO_3$: 180.095775 found 180.095428.

General procedure for Negishi cross-couplings

A THF solution of pyridyl halide (1.05 molar equiv. at 1 M) was cooled to −78 °C and n-BuLi (1.1 molar equiv. of a 2.5 M sol in hexanes) was added and stirred for 5 min. To this was cannulated a THF solution of $ZnCl_2$ (1.1 molar equiv. at 1 M). The solution was stirred, allowed to warm to room temperature, and then cannulated into a THF solution of halo-phenanthroline or pyridyl phenanthroline (1.0 molar equiv. at 0.5 M) and $Pd(PPh_3)_4$ (0.05 molar equiv.). The resulting solution was heated at reflux overnight. After cooling to room temperature, any precipitate was filtered and washed with cold THF before drying. The precipitate was dissolved in chloroform and extracted with a saturated aqueous EDTA solution basified with sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated. The crude was then purified on silica or an alumina oxide plug as indicated for each compound.

General procedure for Suzuki–Miyaura cross-couplings

Manisylboronic acid **10** (1.5 molar equiv.), halo pyridyl-phenanthroline (1.0 molar equiv.), $Pd(PPh_3)_4$ (0.05 molar equiv.), and $Ba(OH)_2{\cdot}8H_2O$ (2.0 molar equiv.) were placed in a 10 mL round bottom flask. After the addition of DME–water (6 : 1), the flask was placed in an oil bath at 90 °C and stirred overnight. The gray precipitate was filtered and discarded, and the filtrate was diluted in chloroform and extracted with a saturated aqueous EDTA solution basified with sodium bicarbonate. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated. Residual Ph_3PO was removed by trituration with diethyl ether and purification on silica or alumina oxide for each compound as indicated.

9-Iodo-2-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C1). Prepared using general Negishi coupling procedures. White film (0.135 g, 52%). Mp 130–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.90 (1H, d, $J = 8.0$ Hz), 8.82 (1H, d, $J = 8.4$ Hz), 8.30 (1H, d, $J = 8.4$ Hz), 8.01 (1H, d, $J = 8.4$ Hz), 7.99 (1H, t, $J = 7.6$ Hz), 7.86 (1H, d, $J = 8.4$ Hz), 7.84 (1H, d, $J = 8.4$ Hz), 7.74 (1H, d, $J = 8.4$ Hz), 7.32 (1H, d, $J = 7.6$ Hz), 6.72 (2H, s), 3.85 (3H, s), 2.14 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.70, 158.69, 156.93, 155.71, 147.41, 144.27, 137.46, 137.09, 136.94, 136.69, 134.08, 133.48, 128.71, 127.92, 127.19, 125.94, 125.57, 121.72, 120.48, 119.25, 112.96, 55.26, 20.92; HRMS(DEI) m/z: calc. for [M$^+$] $C_{26}H_{20}IN_3O$: 517.06511: found 517.064292.

9-Iodo-2-[5-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C2). Prepared using general Negishi coupling procedures. White film (0.288 g, 74%). Mp 227–230 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.04 (1H, d, $J = 7.5$ Hz), 8.87 (1H, d, $J = 8.4$ Hz), 8.55 (1H, d, $J = 1.5$ Hz), 8.41 (1H, d, $J = 8.4$ Hz), 8.04 (1H, d, $J = 8.1$ Hz), 7.91 (1H, d, $J = 9.3$ Hz), 7.88 (1H, d, $J = 8.4$ Hz), 7.79 (1H, d, $J = 8.7$ Hz), 7.77 (1H, dd, $J = 7.8$ Hz, 2.0 Hz), 6.74 (2H, s), 3.85 (3H, s), 2.10 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.72, 156.36, 154.14, 149.68, 147.34, 144.34, 138.50, 137.72, 137.13, 136.93, 136.90, 134.13, 130.24, 128.68, 127.95, 127.14,

126.03, 122.40, 120.99, 119.27, 112.86, 55.23, 21.38; HRMS *m/z*: calc. for $[M]^+$ $C_{26}H_{20}IN_3O$: 517.065114: found 517.066198.

9-Iodo-2-[4-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C3). Prepared using general Negishi coupling procedures. Trituration with cold methylene chloride gave a white solid (0.092 g, 26%). Mp 271–274 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.89 (1H, d, $J = 8.4$ Hz), 8.78 (1H, d, $J = 4.8$ Hz), 8.71 (1H, s), 8.39 (1H, d, $J = 8.4$ Hz), 7.99 (1H, d, $J = 8.8$ Hz), 7.88 (1H, d, $J = 8.8$ Hz), 7.84 (1H, d, $J = 8.4$ Hz), 7.76 (1H, d, $J = 8.8$ Hz), 7.21 (1H, dd, $J = 4.8$ Hz, 2.0 Hz), 6.71 (2H, s), 3.85 (3H, s), 2.13 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.97, 157.06, 156.39, 150.70, 149.243, 147.65, 144.67, 137.05, 137.00, 136.95, 134.32, 132.04, 128.97, 128.15, 127.32, 126.23, 125.95, 123.84, 121.69, 119.26, 113.06, 55.13, 21.12; HRMS(DEI) *m/z*: calc. for $[M - H^+]$ $C_{26}H_{19}IN_3O$: 516.057289: found 516.058552.

8-Bromo-2-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C4). Prepared using general Negishi coupling procedures. Off-white solid (0.419 g, 86%). Mp 174–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.24 (1H, d, $J = 3.0$ Hz), 8.83 (1H, d, $J = 8.0$ Hz), 8.80 (1H, d, $J = 8.0$ Hz), 8.43 (1H, d, $J = 2.0$ Hz), 8.32 (1H, d, $J = 8.0$ Hz), 7.97 (1H, t, $J = 8.0$ Hz), 7.88 (1H, d, $J = 9.0$ Hz), 7.73 (1H, d, $J = 9.0$ Hz), 7.32 (1H, d, $J = 1.0$ Hz), 6.72 (2H, s), 3.85 (3H, s), 2.14 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.79, 158.70, 157.04, 155.78, 150.99, 145.25, 144.42, 137.42, 137.07, 136.75, 136.75, 133.42, 129.88, 128.53, 127.89, 125.50, 125.36, 121.73, 120.52, 119.58, 112.94, 55.25, 20.91; HRMS(DEI) *m/z*: calc. for $[M - 1^+]$ $C_{26}H_{19}N_3O$: 468.071149; found: 468.070224.

8-Bromo-2-[5-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C5). Prepared using general Negishi coupling procedures. Off-white solid (0.401 g, 60%). ^{1}H NMR, ^{13}C NMR, and mass spectrum matched literature.[13] Mp 114–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.20 (1H, d, $J = 2.5$ Hz), 8.95 (1H, d, $J = 8.0$ Hz), 8.81 (1H, d, $J = 8.0$ Hz), 8.53 (1H, d, $J = 2.0$ Hz), 8.39 (1H, d, $J = 2.5$ Hz), 8.37 (1H, d, $J = 8.0$ Hz), 7.86 (1H, d, $J = 8.0$ Hz), 7.72 (1H, dd, $J = 8.0$, 2.0 Hz), 7.70 (1H, d, $J = 8.0$ Hz), 6.70 (2H, s), 3.82 (3H, s), 2.06 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.72, 156.50, 154.21, 151.01, 149.75, 145.32, 144.36, 138.48, 137.69, 137.41, 137.07, 136.94, 130.18, 129.91, 128.50, 127.84, 125.44, 122.41, 121.02, 119.63, 112.86, 55.23, 21.37.

8-Bromo-2-[4-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C6). Prepared using general Negishi coupling procedures. White solid (0.132 g, 52%). Mp 224–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.15 (1H, d, $J = 2.4$ Hz), 8.90 (1H, d, $J = 8.4$ Hz), 8.79 (1H, d, $J = 4.8$ Hz), 8.74 (1H, s), 8.41 (1H, d, $J = 2.4$ Hz), 8.40 (1H, d, $J = 8.8$ Hz), 7.88 (1H, d, $J = 8.8$ Hz), 7.72 (1H, d, $J = 8.8$ Hz), 7.20 (1H, dd, $J = 5.2$, 1.2 Hz), 6.72 (2H, s), 3.85 (3H, s), 2.10 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.67, 156.62, 156.12, 150.85, 150.40, 149.10, 145.32, 144.37, 137.34, 136.84, 136.74, 131.79, 129.88, 128.59, 127.82, 125.66, 125.47, 123.44, 121.31, 119.57, 112.81, 55.21, 21.28; HRMS(DEI) *m/z*: calc. for $[M - H^+]$ $C_{26}H_{19}BrN_3O$: 468.071149: found 468.071740.

7-Bromo-2-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C7). Prepared using general Negishi coupling procedures. Column chromatography on neutral alumina with methylene chloride–hexanes (2 : 1 then 1 : 0) as eluant gave a white solid (0.052 g, 18%). Mp decomposes >330 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.00 (1H, d, $J = 4.4$ Hz), 8.85 (1H, d, $J = 8.4$ Hz), 8.82 (1H, d, $J = 8.4$ Hz), 8.35 (1H, d, $J = 8.4$ Hz), 8.24 (1H, d, $J = 9.2$ Hz), 7.98 (1H, t, $J = 8.0$ Hz), 7.94 (1H, d, $J = 9.2$ Hz), 7.31 (1H, dd, $J = 7.6$, 1.0 Hz), 6.72 (2H, s), 3.85 (3H, s), 2.14 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.79, 158.70, 157.17, 155.76, 149.60, 147.22, 145.07, 137.43, 137.06, 136.75, 134.07, 133.42, 128.56, 128.36, 126.96, 126.86, 125.53, 124.81, 122.00, 120.57, 112.94, 55.25, 20.90; HRMS *m/z*: calc. for $[M - H]^+$ $C_{26}H_{19}BrN_3O$: 468.071149: found 468.073072.

7-Bromo-2-[5-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C8). Prepared using general Negishi coupling procedures substituting DME for THF. Column chromatography on neutral alumina with methylene chloride as eluant followed by radial chromatography on silica with chloroform–methanol (1 : 0 then 97 : 3) gave a white solid (0.065 g, 18%). Mp 240–242 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.00 (1H, d, $J = 4.4$ Hz), 9.00 (1H, d, $J = 9.2$ Hz), 8.85 (1H, d, $J = 8.4$ Hz), 8.55 (1H, d, $J = 2.0$ Hz), 8.43 (1H, d, $J = 8.4$ Hz), 8.24 (1H, d, $J = 9.2$ Hz), 7.96 (1H, d, $J = 9.2$ Hz), 7.94 (1H, d, $J = 4.4$ Hz), 7.74 (1H, dd, $J = 8.0$ Hz, 2.0 Hz), 6.72 (2H, s), 3.84 (3H, s), 2.08 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.79, 156.68, 154.24, 149.78, 149.63, 147.23, 145.20, 138.47, 137.70, 137.12, 136.92, 134.06, 130.23, 128.54, 128.43, 127.70, 126.91, 124.90, 122.46, 121.32, 112.91, 55.25, 21.35; HRMS(DEI) *m/z*: calc. for $[M^+]$ $C_{26}H_{20}BrN_3O$: 469.078974; found 469.080195.

7-Bromo-2-[4-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (C9). Prepared using general Negishi coupling procedures. Column chromatography on neutral alumina with methylene chloride as eluant gave a white solid (0.059 g, 20%). Mp 255–257 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.91 (1H, d, $J = 4.8$ Hz), 8.90 (1H, d, $J = 8.4$ Hz), 8.80 (1H, d, $J = 4.8$ Hz), 8.74 (1H, d, $J = 0.8$ Hz), 8.43 (1H, d, $J = 8.4$ Hz), 8.24 (1H, d, $J = 8.8$ Hz), 7.95 (1H, d, $J = 9.2$ Hz), 7.91 (1H, d, $J = 4.8$ Hz), 7.21 (1H, dd, $J = 4.8$ Hz, 1.6 Hz), 6.72 (2H, s), 3.85 (3H, s), 2.10 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.67, 156.81, 156.14, 150.48, 149.55, 149.49, 149.15, 147.21, 145.18, 136.88, 136.80, 134.01, 131.83, 128.64, 127.70, 126.88, 125.71, 124.96, 123.52, 121.66, 112.80, 55.25, 21.31; HRMS(DEI) *m/z*: calc. for $[M - 1^+]$ $C_{26}H_{19}BrN_3O$ 468.071149; found 468.069385.

2-(4-Methoxy-2,6-dimethyl-phenyl)-9-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (1). Prepared using general Negishi coupling procedures. Column chromatography on silica with methylene chloride–methanol (97 : 3) as eluant gave a white film (0.470 g, 40%). Mp 201–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.83 (1H, dd, $J = 8.0$, 0.8 Hz), 8.77 (1H, d, $J = 8.4$ Hz), 8.31 (1H, d, $J = 8.0$ Hz), 8.29 (1H, d, $J = 8.4$ Hz), 7.92 (1H, t, $J = 7.6$ Hz), 7.84 (2H, s), 7.61 (1H, d, $J = 8.4$ Hz), 7.25 (1H, dd, $J = 7.6$, 0.8 Hz), 6.77 (2H, s), 6.71 (2H, s), 3.88 (3H, s), 3.84 (3H, s), 2.29 (6H, s), 2.13 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 159.36, 158.78, 158.64, 158.45, 156.38, 156.22, 145.89, 145.66, 137.97, 137.44, 136.98, 136.47, 135.62, 133.57, 133.53, 128.69, 126.93, 126.29, 126.09, 125.19, 125.12, 121.11, 120.53, 113.07, 112.92, 55.22, 55.22, 21.41, 20.90; HRMS(DEI) *m/z*: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.231953.

2-(4-Methoxy-2,6-dimethyl-phenyl)-9-[5-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (2). Prepared using

general Negishi coupling procedures. Column chromatography on neutral alumina with methylene chloride–hexanes (1 : 1 then 1 : 0) as eluant gave a white film (0.130 g, 74%). Mp 125–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.92 (1H, d, $J = 8.1$ Hz), 8.81 (1H, d, $J = 8.4$ Hz), 8.51 (1H, d, $J = 1.8$ Hz), 8.41 (1H, d, $J = 8.7$ Hz), 8.29 (1H, d, $J = 8.4$ Hz), 7.86 (2H), 7.69 (1H, dd, $J = 8.1$, 2.1 Hz), 7.62 (1H, d, $J = 8.4$ Hz), 6.75 (2H, s), 6.72 (2H, s), 3.86 (3H, s), 3.84 (3H, s), 2.31 (6H, s), 2.07 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 159.41, 158.75, 158.66, 155.77, 154.72, 149.49, 145.87, 145.81, 138.38, 138.01, 137.75, 136.69, 135.523, 133.54, 130.38, 128.68, 126.95, 126.43, 126.02, 125.25, 125.25, 122.46, 120.32, 113.09, 112.82, 55.22, 55.22, 21.49, 21.27; HRMS(DEI) m/z: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.232151.

2-(4-Methoxy-2,6-dimethyl-phenyl)-9-[4-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (3). Prepared using general Suzuki–Miyaura coupling procedures. Residual Ph_3PO was removed by trituration with diethyl ether and column chromatography on neutral alumina with methylene chloride as eluant gave a white film (0.028 g, 74%). Mp 258–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.79 (1H, d, $J = 8.4$ Hz), 8.76 (1H, d, $J = 4.8$ Hz), 8.66 (1H, d, $J = 0.8$ Hz), 8.39 (1H, d, $J = 8.4$ Hz), 8.27 (1H, d, $J = 8.0$ Hz), 7.84 (2H, s), 7.58 (1H, d, $J = 8.0$ Hz), 7.16 (1H, dd, $J = 4.8$, 1.6 Hz), 6.69 (2H, s), 6.68 (2H, s), 3.85 (3H, s), 3.84 (3H, s), 2.23 (6H, s), 2.09 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 159.35, 158.72, 158.57, 156.45, 155.96, 150.02, 150.02, 148.87, 145.84, 138.01, 136.81, 136.63, 135.46, 133.29, 131.86, 128.74, 126.92, 126.47, 126.00, 125.50, 125.30, 124.00, 120.70, 113.16, 112.85, 55.21, 55.17, 21.42, 21.25; HRMS(DEI) m/z: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.232834

8-(4-Methoxy-2,6-dimethyl-phenyl)-2-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (4). Prepared using general Negishi coupling procedures. Column chromatography on neutral alumina with methylene chloride–hexanes (2 : 1 then 3 : 1) as eluant gave a white film (0.176 g, 79%). Mp 223–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.08 (1H, d, $J = 2.4$ Hz), 8.92 (1H, dd, $J = 7.6$, 0.8 Hz), 8.80 (1H, d, $J = 8.4$ Hz), 8.34 (1H, d, $J = 8.4$ Hz), 8.07 (1H, d, $J = 2.4$ Hz), 7.97 (1H, t, $J = 8.0$ Hz) 7.86 (1H, d, $J = 8.8$ Hz), 7.81 (1H, d, $J = 8.8$ Hz), 7.30 (1H, dd, $J = 7.6$, 0.8 Hz), 6.76 (2H, s), 6.72 (2H, s), 3.86 (3H, s), 3.84 (3H, s), 2.15 (6H, s), 2.07 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.86, 158.65, 158.63, 156.67, 155.92, 151.75, 145.42, 144.72, 137.83, 137.39, 136.90, 136.65, 136.36, 135.76, 133.49, 130.06, 128.59, 128.49, 126.62, 126.49, 125.33, 121.24, 120.49, 112.90, 112.90, 55.22, 55.19, 21.42, 20.86; HRMS(DEI) m/z: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.2323842

8-(4-Methoxy-2,6-dimethyl-phenyl)-9-[5-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (5). Prepared using general Suzuki–Miyaura coupling procedures. Residual Ph_3PO was removed by column chromatography on neutral alumina with methylene chloride–hexanes (2 : 1) as eluant gave a white film (0.042 g, 65%). ^{1}H NMR, ^{13}C NMR, and mass spectrum matched literature.[13] Mp 132–135 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.08 (1H, d, $J = 2.0$ Hz), 9.07 (1H, d, $J = 8.0$ Hz), 8.87 (1H, d, $J = 8.5$ Hz), 8.57 (1H, d, $J = 2.0$ Hz), 8.44 (1H, d, $J = 8.5$ Hz), 8.09 (1H, d, $J = 2.0$ Hz), 7.91 (1H, d, $J = 9.0$ Hz), 7.84 (1H, d, $J = 9.0$ Hz), 7.75 (1H, dd, $J = 8.0$, 2.0 Hz), 6.77 (2H, s), 6.74 (2H, s), 3.87 (3H, s), 3.85 (3H, s), 2.10 (6H, s), 2.08 (6H, s). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.19, 159.01, 156.46, 154.68, 152.11, 149.91, 145.80, 144.95, 138.61, 138.08, 137.92, 137.14, 137.11, 136.63, 136.07, 130.47, 130.24, 128.86, 128.71, 126.82, 126.80, 122.61, 120.74, 113.05, 112.99, 55.19, 55.16, 21.27, 21.18.

8-(4-Methoxy-2,6-dimethyl-phenyl)-9-[4-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (6). Prepared using general Suzuki–Miyaura coupling procedures. Residual Ph_3PO was removed by trituration with diethyl ether and column chromatography on neutral alumina with methylene chloride as eluant gave a white film (0.064 g, 90%). Mp 228–230 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.98 (1H, d, $J = 2.4$ Hz), 8.90 (1H, d, $J = 8.4$ Hz), 8.80 (1H, d, $J = 4.8$ Hz), 8.79 (1H, s), 8.43 (1H, d, $J = 8.4$ Hz), 8.05 (1H, d, $J = 2.0$ Hz), 7.89 (1H, d, $J = 8.8$ Hz), 7.82 (1H, d, $J = 8.4$ Hz), 7.20 (1H, d, $J = 8$,4 Hz), 6.74 (2H, s), 6.70 (2H, s), 3.85 (3H, s), 3.84 (3H, s), 2.10 (6H, s), 2.04 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.85, 158.59, 156.33, 156.28, 151.64, 150.47, 149.05, 145.51, 144.69, 137.85, 136.85, 136.74, 136.45, 135.82, 131.84, 130.01, 128.68, 128.64, 126.68, 126.66, 125.56, 123.37, 120.98, 112.86, 112.70, 55.23, 55.19, 21.42, 21.29; HRMS(DEI) m/z: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.232201.

7-(4-Methoxy-2,6-dimethyl-phenyl)-9-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (7). Prepared using general Suzuki–Miyaura coupling procedures. Column chromatography on neutral alumina with methylene chloride as eluant gave a white film (0.047 g, 84%). Mp 257–260 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.29 (1H, d, $J = 4.5$ Hz), 8.90 (1H, d, $J = 7.5$ Hz), 8.77 (1H, d, $J = 8.5$ Hz), 8.30 (1H, d, $J = 8.0$ Hz), 7.98 (1H, t, $J = 8.0$ Hz), 7.71 (1H, d, $J = 9.5$ Hz), 7.46 (1H, d, $J = 4.5$ Hz), 7.41 (1H, d, $J = 9.0$ Hz), 7.30 (1H, d, $J = 7.5$ Hz), 6.78 (2H, s), 6.72 (2H, s) 3.89 (3H, s), 3.85 (3H, s), 2.15 (6H, s), 1.93 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.04, 158.66, 158.65, 156.65, 156.09, 150.08, 147.85, 146.60, 145.77, 137.43, 137.34, 136.99, 136.55, 136.55, 133.51, 129.38, 128.46, 126.43, 125.31, 123.99, 123.84, 121.43, 120.57, 112.93, 112.86, 55.25, 55.23, 20.91, 20.78; HRMS(DEI) m/z: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.233015.

7-(4-Methoxy-2,6-dimethyl-phenyl)-2-[5-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (8). Prepared using general Negishi coupling procedures. Column chromatography on silica with methylene chloride–methanol (97 : 3) as eluant gave a white film. Residual Ph_3PO was removed by trituration with ethyl ether to give a white solid (0.011 g, 12%). Mp 300–301 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.28 (1H, d, $J = 4.2$ Hz), 9.05 (1H, d, $J = 7.8$ Hz), 8.82 (1H, d, $J = 8.4$ Hz), 8.56 (1H, d, $J = 2.1$ Hz), 8.39 (1H, d, $J = 8.7$ Hz), 7.76 (1H, dd, $J = 8.1$, 2.1 Hz), 7.74 (1H, d, $J = 9.0$ Hz), 7.46 (1H, d, $J = 4.5$ Hz), 7.43 (1H, d, $J = 9.3$ Hz), 6.78 (2H, s), 6.73 (2H, s) 3.89 (3H, s), 3.85 (3H, s), 2.15 (6H, s), 1.92 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.11, 158.77, 156.15, 154.57, 150.16, 149.72, 147.99, 145.92, 138.50, 137.80, 137.40, 136.94, 136.83, 130.33, 129.39, 128.52, 128.22, 126.47, 126.47, 124.11, 124.01, 122.50, 120.77, 112.89, 112.89, 55.26, 55.26, 21.38, 20.78; HRMS(DEI) m/z: calc. for $[M^+]$ $C_{35}H_{31}N_3O_2$: 525.241628; found: 525.240412.

7-(4-Methoxy-2,6-dimethyl-phenyl)-9-[4-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline (9). Prepared using general Suzuki–Miyaura coupling procedures. Column

chromatography on neutral alumina with methylene chloride as eluant gave a white film (0.052 g, 84%). Mp 213–217 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.20 (1H, d, $J = 4.5$ Hz), 8.90 (1H, d, $J = 9.0$ Hz), 8.84 (1H, s), 8.80 (1H, d, $J = 5.0$ Hz), 8.37 (1H, d, $J = 8.0$ Hz), 7.72 (1H, d, $J = 8.5$ Hz), 7.43 (1H, d, $J = 4.5$ Hz), 7.41 (1H, d, $J = 9.0$ Hz), 7.20 (1H, dd, $J = 4.5$, 1.5 Hz), 6.77 (2H, s), 6.73 (2H, s), 3.88 (3H, s), 3.86 (3H, s), 2.12 (6H, s), 1.89 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.26, 158.84, 156.56, 156.39, 150.61, 150.15, 149.23, 148.06, 146.71, 145.98, 137.47, 136.94, 136.86, 132.07, 129.49, 128.72, 128.28, 126.55, 125.66, 124.12, 124.11, 123.51, 121.11, 112.95, 112.84, 55.19, 55,17, 21.16, 20.58; HRMS(DEI) m/z: calc. for $[M - H^+]$ $C_{35}H_{30}N_3O_2$: 524.233803; found: 524.232151.

Ru[8-(4-methoxy-2,6-dimethyl-phenyl)-2-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline]$_2$Cl-PF$_6$ (14) and Ru[8-(4-methoxy-2,6-dimethyl-phenyl)-2-[6-(4-methoxy-2,6-dimethylphenyl)-pyridin-2-yl]-1,10-phenanthroline]$_2$-PF$_6$ (15). An ethylene glycol solution (5 mL) of ligand **4** (0.038 g, 7.24×10^{-5} moles) and $RuCl_2(DMSO)_4$ (0.018 g, 3.62×10^{-5} moles) was heated at 125 °C for 4 h. The solution was cooled to room temperature and a saturated aqueous solution of potassium hexafluorophosphate was added to induce precipitation. The dark reddish-brown precipitate was filtered over celite and washed with water and diethyl ether. The precipitate was dissolved in methylene chloride and dried over magnesium sulfate, filtered, and evaporated to afford a red-brown crystalline solid (0.041 g). Column chromatography on silica gel with ACN–H_2O–sat. aq. KPF_6 (100 : 0:0; 97 : 3 : 0.3; 95 : 5 : 0.5) as eluant gave **14** as a red-brown solid (0.009 g, 20%) (ESI-MS: m/z for $[M]^+$ calc. 1187.3, found 1187.4) and **15** as a red crystalline solid (0.05 g, 10%). Complex **14** was not characterized but dissolved in a solution of ethylene glycol–dichloroethane–ethanol (1 : 1 : 0.5 mL) and heated to 150 °C for 2 days. After precipitation with aq. KPF_6, only compound **15** (0.006 g, 60%) was isolated (0.011 g, 21% over 2 steps). Mp >350 °C; ^{1}H NMR (600 MHz, CD_3CN, δ): 8.78 (2H, d, $J = 9.0$ Hz), 8.75 (2H, dd, $J = 8.4$, 1.2 Hz), 8.68 (2H, d, $J = 8.4$ Hz), 8.25 (2H, d, $J = 9.0$ Hz), 8.16 (2H, t, $J = 7.8$ Hz), 7.56 (2H, d, $J = 9.0$, Hz), 7.22 (2H, dd, $J = 7.80$, 1.2 Hz), 6.93 (2H, d, $J = 5.4$ Hz), 6.79 (2H, d, $J = 2.4$ Hz), 6.68 (2H, d, $J = 2.4$ Hz), 6.62 (2H, d, $J = 6.0$ Hz), 6.39 (2H, d, $J = 2.4$ Hz), 5.39 (2H, d, $J = 1.8$ Hz), 3.78 (6H, s), 3.77 (6H, s), 1.87 (6H, s), 1.27 (6H, s), 1.22 (6H, s), 0.18 (6H, s); ^{13}C NMR (150 MHz, CD_3CN, δ): 167.70, 161.15, 161.07, 160.35, 157.18, 153.60, 150.90, 149.91, 147.20, 140.52, 138.45, 138.19, 137.81, 137.27, 133.96, 131.69, 131.25, 131.06, 130.66, 129.30, 128.82, 127.68, 127.44, 125.54, 123.80, 114.28, 114.19, 114.08, 112.18, 55.97, 55.83, 21.05, 20.80, 19.95, 19.07; ESI-MS: m/z for $[M]^{2+}$ calc. 576.2, found 575.4; m/z for $[M + PF_6^-]^+$ calc. 1297.3, found 1297.2.

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