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Selective Lithiation of 4-(1*H*-1-Pyrrolyl)pyridine. Access to New Electron-Releasing Ligands

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The first lithiation of 4-(1*H*-1-pyrrolyl)pyridine has been realized. The use of BuLi-containing lithium aggregates induced the selective pyridine ring functionalization by taking advantage of the electron-donor effect of the pyrrole nucleus. Opportune substituents were introduced α to the pyridine nitrogen leading to new electron-enriched pyridylphosphine, bipyridine, and terpyridine ligands.

Introduction

N-Arylpyrroles are important compounds displaying a broad spectrum of applications as agrochemicals,[1] pharmaceuticals,[2] and transition-metal ligands.[3] The versatility of the pyrrole moiety has allowed a number of selective functionalization reactions since this electron-rich ring can be easily α-substituted by direct electrophilic substitution.[4] Hydrogen−lithium exchange has also been studied. Using BuLi−TMEDA chelate or BuLi−*t*-BuOK (LICKOR) superbase, the clean α lithiation of the pyrrole ring was obtained under thermodynamic control via a dilithiated species (Scheme 1).[5] The monosubstitution of the aromatic ring was only observed in the presence of a directing group (e.g., F or CF_3)[5,6]

4-(1*H*-1-Pyrrolyl)pyridine **1** also displays interesting applications as an electron-releasing ligand.[7] Indeed, the electronic density of the pyrrole nucleus at the 4 position is easily transferred to the pyridine ring as illustrated by charge calculations on the nitrogen atoms (Figure 1).[8]

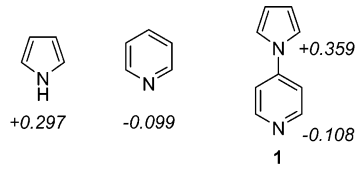
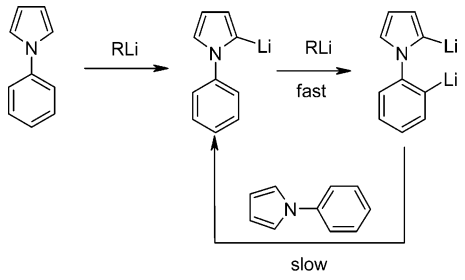
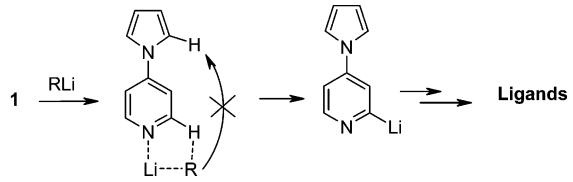


FIGURE 1. Charge calculations in pyrrole, pyridine, and **1**.

SCHEME 1. Formation of Mono- and Dilithiated Intermediates from Phenylpyrrole



SCHEME 2. Expected Selective Lithium Chelation by Pyridine Nitrogen



We thought that this polarization could be useful to enhance lithium complexation by pyridine nitrogen and perform selective α-lithiation of the pyridine ring. To our knowledge, the metalation of such substrates has not been reported yet, and a success could open the way to a new range of polyheterocyclic ligands bearing the electron-releasing pyrrole moiety (Scheme 2).

Results and Discussion

Compound **1** was first reacted with typical lithiating agents under the best conditions reported in the literature, and the reaction media were subsequently quenched with MeSSMe as electrophile (Scheme 3).

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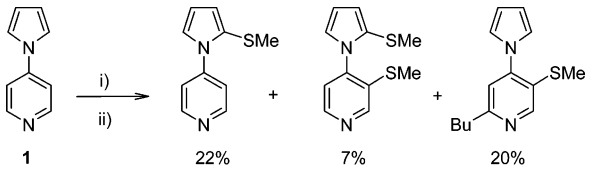
SCHEME 3. Lithiation of 1 with BuLi-*t*-BuOK[a]



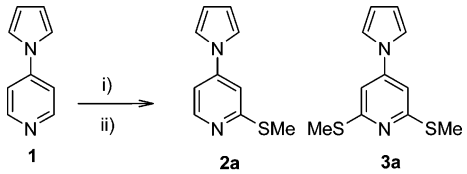
[a] Key: (i) BuLi−*t*-BuOK (1 equiv), THF, −78 °C, 1 h; (ii) MeSSMe (1.5 equiv) THF, −78 °C.

Reaction with *n*-BuLi, *t*-BuLi, and *n*-BuLi−TMEDA only resulted in nucleophilic addition on the pyridine ring[9] while **1** was fully recovered after reaction with LDA or LTMP. On the other hand, reaction with LICKOR led to metalation α to the pyrrole nitrogen and at C-3 of the pyridine ring in agreement with the selectivity observed with phenylpyrrole.[5] Nucleophilic addition product was also present in a notable amount in the mixture.

This indicated the absence of metal chelation by pyridine nitrogen with the LICKOR superbase under the conditions used. So, a less nucleophilic and more chelating base was necessary, and we investigated the metalation with the BuLi−$Me_2N(CH_2)_2OLi$ reagent (BuLi−LiDMAE) developed in our laboratory.[10] The metalation was carried out under various conditions in hexane or toluene known to favor aggregate formation,[10a] and lithiated species were quenched with MeSSMe in THF[11] (Table 1). As shown, all experiments led to pyridine ring lithiation with full retention of the pyrrole nucleus. Metalation conducted at 0 °C led to a notable amount (15%) of the disubstituted product **3a**. All attempts to optimize the preparation of **3a** using this one-pot procedure remained unsuccessful. On the other hand**,** the selective formation of **2a** was easily achieved by lowering the temperature to −78 °C. The yield was notably improved (90% isolated) when hexane was replaced by toluene. This could be explained by the better solubility of **1** in the latter solvent allowing further extent of the metalation.

The best conditions determined in Table 1 were then used to investigate the introduction of substituents at C-2 with special focus on potentially reactive heterocycles for further functionalization reactions or new ligands. First attempts resulted only in sluggish reactions giving the target compounds in low yields (typically 15%). Since THF used in the quenching step could be a source of protonation of lithiated **1**, we performed the same experiments in THF-d_8. The same yields were obtained without any deuterium incorporation in **1** indicating the absence of protonation by THF. Then we performed a deuteration experiment with MeOD omitting THF as cosolvent. Under these conditions, **1** led to **2b** with a deuterium content >98%. Thus, the role of THF could be a strong coordination of lithitated species avoiding complete quenching by electrophiles. Condensations were then realized in toluene, and we were pleased to obtain the halogenated and tin products **2c**−**e** and the new N,P ligand **2f** in fair to good yields (Scheme 4). The reason for the different behavior of MeSSMe in THF remains, however, unclear.

TABLE 1. Lithiation of 1 with BuLi−LiDMAE[a]

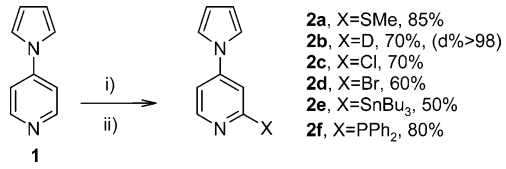


Key: i) BuLi-LiDMAE, solvent, T°C, 1h. ii) MeSSMe THF, -78 °C, 1h

entry	base (equiv)	solvent A	*T* (°C)	**2a**[b] (%)	**3a**[b] (%)
1[d]	2	hexane	0	64	15
2[d]	2	hexane	−40	78	2
3[d]	3	hexane	−40	84	1
4	4	hexane	−40	99	1
5[d]	3	hexane	−78	80	
6	3	toluene	−78	>99 (90)[c]	

[a] Reactions performed on 10 mmol of **1**. [b] Product ratio determined by GC. [c] Isolated yield in parentheses. [d] The remaining part was unreacted **1**.

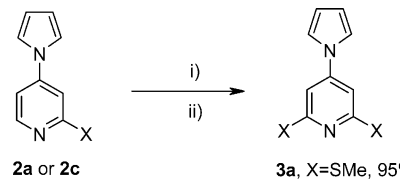
SCHEME 4. Preparation of C-2-Substituted Derivatives of 1[a]



[a] Key: (i) BuLi−LiDMAE (3 equiv), toluene, −78 °C, 1 h; (ii) MeSSME or MeOD or C_2Cl_6 or CBr_4 or $ClSnBu_3$ or $ClPPh_2$ (3.5 equiv), toluene, −78 °C, 1 h.

The previous obtention of a disubstituted derivative **3a** in small amounts in our first experiments (Table 1) prompted us to examine the preparation of some 2,6-disubstituted derivatives using an iterative lithiation of **2a** and **2c** bearing base tolerant substituents (Scheme 5).[10] Using this procedure, the expected products **3a** and **3c** were obtained in good overall yields (from **1**).

SCHEME 5. Preparation of 2,6-Disubstituted Derivatives of 1[a]



[a] Key: (i) BuLi−LiDMAE (3 equiv), toluene −78 °C, 1 h; (ii) MeSSMe or C_2Cl_6, toluene, −78 °C, 1 h.

(8) Mulliken charges obtained by calculation in MOPAC using the PM3 semiempirical method.

(9) 2-Butyl-4-(1*H*-1-pyrrolyl)pyridine and 2-*tert*-butyl-4-(1*H*-1-pyrrolyl)pyridine were obtained in 15 and 18% yield after reaction of **1** with *n*-BuLi and *t*-BuLi, respectively. The remaining part was unreacted **1**.

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(11) From our own experience, MeSSMe is a good trapping agent for pyridyllithiums. THF was assumed to ensure good trapping of lithio intermediates by disruption of aggregates.

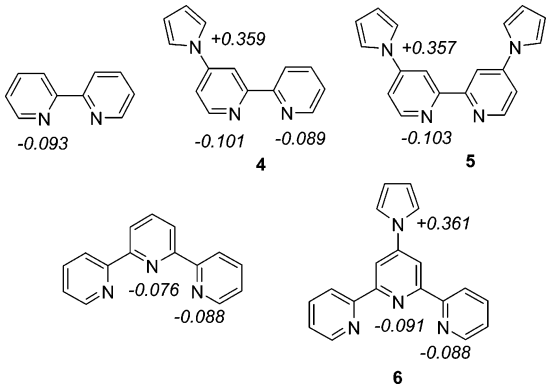
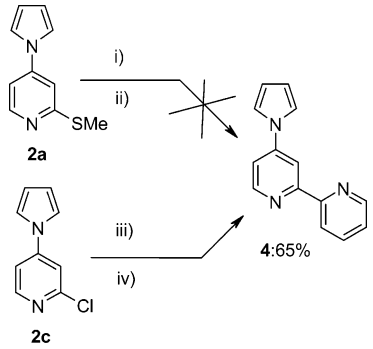


FIGURE 2. Effect of pyrrole on electronegativity of pyridine nitrogen in ligands **4**−**6**.

SCHEME 6. Preparation of Ligand 4[a]



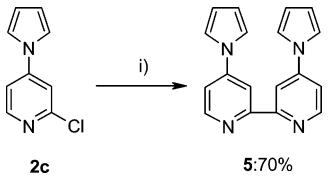
[a] Key: (i) MMPP (0.5 equiv), MeOH, 0 °C, 1 h; (ii) 2-PyLi or 2-PyMgBr (1.1 equiv), THF, −78 °C, 1 h; (iii) 2-PySnBu$_3$ (1.1 equiv), PdCl$_2$(PPh$_3$)$_2$ (5%), PPh$_3$ (10%), xylene, reflux, 24 h.

The availability of reactive precursors allowed us to envision the preparation of new electron-releasing ligands via organometallic coupling reactions. We focused our investigations on bipyridines and terpyridine **4**−**6** in which the pyridine nitrogen atom is electronically enriched by the pyrrole nucleus as indicated by charge calculations (Figure 2).[8]

The preparation of **4** was first examined from **2a** by coupling the corresponding pyridyl sulfoxides with pyridyllithium or pyridylmagnesium chloride as described by Uenishi and co-workers.[12] So, **2a** was first oxidized in 80% yield with MMPP in methanol and subsequently reacted with 2-pyridyllithium or 2-pyridylmagnesium bromide. Unfortunately, the reaction did not produce any coupling product but only an untractable mixture (Scheme 6). Then, we turned to the Stille coupling[13] of chloro derivative **2c** with 2-tributylstannylpyridine, and **4** was obtained in 65% yield under unoptimized conditions. Cross-coupling using the bromo derivative **2d** did not allow us to improve this yield indicating that oxidative addition of palladium into the C-halogen bond was not the limiting step.

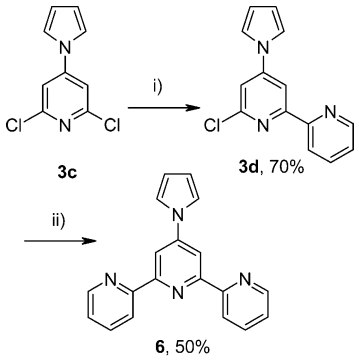
The symmetrical ligand **5** was next prepared by homocoupling of **2a** under nickel catalysis. Two different systems were tested, the NiCl$_2$/PPh$_3$/Zn[14] and *t*-BuONa/NiCRA/PPh$_3$.[15] The reaction proceeded smoothly giving **5** in similar yields of (70%) with both catalysts (Scheme 7)

SCHEME 7. Preparation of Ligand 5[a]



[a] Key: (i) NiCl$_2$, 6H$_2$O (1.1 equiv), PPh$_3$ (4.4 equiv), Zn (1.1 equiv), DMF, 50 °C, 1.5 h or *t*-BuONa−NiCRA−PPh$_3$ (4.2.1.4), DME, 65 °C, 2 h.

SCHEME 8. Preparation of 6 via the Two-Step Procedure[a]



[a] Key: (i) 2-PySnBu$_3$ (2.2 equiv), PdCl$_2$(PPh$_3$)$_2$ (10%), PPh$_3$ (20%), xylene, reflux, 24 h; (ii) 2-PySnBu$_3$ (1.1 equiv), PdCl$_2$(PPh$_3$)$_2$ (10%), PPh$_3$ (20%), xylene, reflux, 24 h.

The preparation of tpy **6** was first attempted from **3c** using a one-pot Stille coupling procedure. Unfortunately, the reaction remained stopped at the monochlorinated bipyridine **3d** obtained in 70% yield, the remaining part being unreacted **3c**. The reason for the inhibition of the second coupling could be explained by a strong in situ chelation of palladium species by formed chlorobipyridine **3d**. Such a limitation was already observed during our previous works on 4-DMAP.[10f] Thus, we opted for sequential coupling from **3d** which was coupled in acceptable yield giving **6** in 50% yield after crystallization in ether (Scheme 8).

In summary, we have performed the first pyridine ring lithiation of 4-(1*H*-1-pyrrolyl)pyridine using the BuLi−LiDMAE reagent while other reagents led only to nucleophilic addition or not selective sluggish metalations. The electron-donor effect of the pyrrole nucleus was assumed to enhance lithium aggregates chelation by pyridine nitrogen leading to selective C-2 lithiation. Introduction of opportune mono- or disubstitution led to preparation of new bpy an tpy ligands in good yields. Work is now in progress to involve these new ligands in organometallic reactions.

Experimental Section

General Methods. All solvents were distilled and stored on sodium wire before use. 2-Dimethylaminoethanol was distilled under nitrogen and stored on molecular sieves. 4-(1*H*-

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(13) For a book on the Stille coupling reaction, see: Farina, V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; John Wiley and Sons: New York, 1998.

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1-Pyrrolyl)pyridine **1** was prepared from 4-aminopyridine and 2,5-dimethoxytetrahydrofuran in boiling acetic acid according to a published procedure.[16] *n*-BuLi was used as a commercial 1.6 M solution in hexanes. All other reagents were commercially available and used as such. ^{1}H and ^{13}C were obtained in $CDCl_3$ (unless otherwise stated) on a Bruker DRX400 instrument at 400 and, 100 MHz, respectively. GC experiments were performed on a Shimadzu chromatograph fitted with a 15 m capillary column. GC/MS (EI) were obtained on HP5971 spectrometer.

General Procedure for Monolithiation of 4-(1*H*-Pyrrol-1-yl)pyridine 1 and Derivatives. To a solution of 2-dimethylaminoethanol (DMAE) (3.2 mL, 32 mmol) in 25 mL of anhydrous toluene cooled at −5 °C was added dropwise *n*-BuLi (40 mL of a 1.6 M solution in hexanes, 64.2 mmol). The temperature must be kept below 0 °C. After 0.5 h, the reaction mixture was cooled at −78 °C, and a solution of the substrate (10.7 mmol) in 20 mL of anhydrous toluene was added dropwise. After 1.5 h of stirring at −78 °C, the appropriate electrophile (typically 37.5 mmol) was added dropwise in 25 mL of toluene to the orange solution. After 1 h, the medium was allowed to warm at room temperature and hydrolyzed at 0 °C with 40 mL of water. After extraction with ether and washing with water, the combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was then purified by column chromatography on silica gel with hexanes−ethyl acetate mixtures as eluents.

2-(Methylsulfanyl)-4-(1*H*-pyrrol-1-yl)pyridine, 2a. Obtained by condensation with MeSSMe (3.37 mL, 37.5 mmol) in 25 mL of anhydrous THF. Column chromatography with hexane/AcOEt (40/60) **2a** as a brown solid (1.83 g, 90%). ^{1}H NMR: δ_H 2,59 (s, 3H), 6.37 (t, J = 2 Hz, 2H), 6.96 (m, 2H), 6.99 (m, 2H), 8.40 (dt, J = 6 Hz, 1H). ^{13}C NMR: δ_C 13.8, 110.2, 111.0, 112.6, 113.4, 118.8, 51.0 ppm. MS (EI) *m/z*: 190 (M^+, 100), 175 (1), 156 (2), 143 (36), 130 (1.5), 117 (21), 105 (6), 90 (12), 78 (8), 63 (9), 51 (11). Anal. Calcd: C, 63.13; H, 5.30; N, 14.72. Found: C, 62.92; H, 5.17; N, 14.59.

2-^{2}H-4-(1*H*-pyrrol-1-yl)pyridine, 2b. Obtained by condensation with neat MeOD (2.15 mL, 0.05 mol). ^{1}H NMR: δ_H 6.40 (t, J = 2 Hz, 2H), 7.20 (m, 2H), 7.30 (m, 2H), 8.60 (m, 1H). Deuterium content >98%.

2-Chloro-4-(1*H*-pyrrol-1-yl)pyridine, 2c. Obtained by condensation with C_2Cl_6 (8.88 g, 37.5 mmol) in 40 mL of anhydrous toluene. Purification on column chromatography by a first elution with hexane followed by second elution with hexane/AcOEt (40/60) (1.79 g, 70%). ^{1}H NMR: δ_H 6.41 (t, J = 2 Hz, 2H), 7.17 (t, J = 2 Hz, 2H), 7.22 (m, J = 2 Hz, 1H), 7.32 (d, J = 2 Hz, 1H), 8.35 (d, J = 6 Hz, 1H). ^{13}C NMR: δ_C 112.7, 113.4, 113.8, 118.8, 151.3 ppm. MS (EI) *m/z*: 180 (M + 2, 32), 178 (M^+, 100), 152 (7), 143 (21), 116 (31), 89 (17), 63 (11), 51 (23). Anal. Calcd: C, 60.52; H, 3.95; N, 15.68. Found: C, 60.92; H, 4.08; N, 15.39.

2-Bromo-4-(1*H*-pyrrol-1-yl)pyridine, 2d. Obtained by condensation with CBr_4 (12.4 g, 37.5 mmol) in 40 mL of anhydrous toluene. Column chromatography with hexane/AcOEt (80/20) yielded **2d** (1.49 g, 60%). ^{1}H NMR: δ_H 6.41 (t, J = 2 Hz, 2H), 7.17 (t, J = 2 Hz, 2H), 7.25 (dd, J = 2, 6 Hz, 1H), 7.49 (d, J = 2 Hz, 1H), 8.34 (d, J = 6 Hz, 1H). ^{13}C NMR: δ_C 113.4, 117.6, 118.8, 152.5. MS (EI) *m/z*: 224 (M + 2, 98), 222 (M^+, 100), 143 (65), 116 (74), 89 (24), 63 (15), 51 (28). Anal. Calcd: C, 48.46; H, 3.16; N, 12.56. Found: C, 48.65; H, 3.08; N, 12.49.

4-Pyrrol-1-yl-2-tributylstannylpyridine, 2e. Obtained by condensation with $ClSnBu_3$ (1.2 g, 37.5 mmol) in 40 mL of anhydrous toluene. After removal of unreacted **1** by column chromatography with hexane/AcOEt (80/20) and Kugelrorh distillation (200 °C, 6 mbars), **2e** was obtained in pure form as a colorless oil (2.32 g, 50%). ^{1}H NMR: δ_H 0.89 (t, J = 7 Hz, 9H), 1.16 (t, J = 5 Hz, 6H), 1.37 (sext, J = 5 Hz, 6H), 1.60 (qt, J = 7 Hz, 6H), 6.38 (t, J = 2 Hz, 2H), 7.10 (t, J = 2 Hz, 2H), 7.18 (dd, J = 6, 2 Hz, 1H), 7.42 (d, J = 2 Hz, 1H), 8.70 (dd, J = 6, 2 Hz, 1H). ^{13}C NMR: δ_C 9.9, 13.7, 27.6, 29.0, 112.1, 118.5, 121.9, 144.5, 151.6, 176.9. Anal. Calcd: C, 58.22; H, 7.91; N, 6.47. Found: C, 57.82; H, 7.72; N, 6.15.

2-Diphenylphosphanyl-4-(1*H*-pyrrol-1-yl)pyridine, 2f. Obtained by condensation with $ClPPh_2$ (8.26 g, 37.5 mmol) in 40 mL of anhydrous toluene. Column chromatography with hexane/AcOEt (80/20) yielded **2e** as a white solid (2.8 g, 80%). ^{1}H NMR: δ_H 6.30 (t, J = 2 Hz, 2H), 6.98 (t, J = 2 Hz, 2H), 7.06 (m, 1H), 7.13 (dd, J = 4, 2 Hz, 1H), 7.39 (m, 10H), 8.66 (d, J = 6 Hz, 1H). ^{13}C NMR: δ_C 111.8, 112.3, 117.2, 117.6, 118.2, 128.8, 128.9, 129.4, 134.1, 134.5, 135.7, 135.9, 151.6, 151.8. Anal. Calcd: C, 76.82, H, 5.22; N, 8.53. Found: C, 77.18; H, 5.30; N, 8.51.

2,6-Bis(methylsulfanyl)-4-(1*H*-pyrrol-1-yl)pyridine, 3a. Obtained by metalation of **2a** and condensation with DMDS (3.37 mL, 37.5 mmol) in 25 mL of anhydrous THF. Eluent hexane/AcOEt (40/60) (2,40 g, 95%). ^{1}H NMR: δ_H 2.60 (s, 6H), 6.34 (t, J = 2 Hz, 2H), 6.87 (s, 2H), 7.10 (t, J = 2 Hz, 2H). ^{13}C NMR: δ_C 13.5, 105.5, 112.2, 118.7, 161.1. MS (EI) *m/z*: 236 (M^+, 100), 202 (16), 175 (5), 156 (9), 142 (11), 116 (4), 108 (11), 82 (8), 63 (15), 51 (5). Anal. Calcd: C, 55.90; H, 5.12; N, 11.85. Found: C, 55.85; H, 5.18; N, 12.19.

2,6-Dichloro-4-(1*H*-pyrrol-1-yl)pyridine, 3c. Obtained by metalation of **2c** and condensation with C_2Cl_6 (8.88 g, 37.5 mmol) in 25 mL of anhydrous toluene. Eluent hexane/AcOEt (10/90) (1.96 g, 86%). ^{1}H NMR: δ_H 6.43 (t, J = 2 Hz, 2H), 7.14 (t, J = 2 Hz, 2H), 7.26 (s, 2H). ^{13}C NMR: δ_C 112.5, 113.4, 119.3. MS (EI) *m/z*: 214 (M + 2, 66), 212 (M^+, 100), 177 (13), 142 (27), 114 (15), 88 (5), 63 (12), 51 (16). Anal. Calcd: C, 50.74; H, 2.84; N, 13.15. Found: C, 50.94; H, 3.16; N, 12.87.

General Procedure for Stille Couplings. A mixture of the appropriate pyridyl halide **2c**, **3c,** or **3d** (3 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and PPh_3 (79 mg, 0.3 mmol) in 6 mL of degassed xylene was refluxed under nitrogen for 5 min. A solution of 2-tributylstannylpyridine (1.21 g, 3.3 mmol) in 5 mL of xylene was then added gradually (2 h). After 12 h of stirring under reflux, the mixture was cooled and filtered over a pad of Celite and washed with CH_2Cl_2. The organic layer was then evaporated and purified by column chromatography exept for tpy **6** which was precipated from ether.

2,2′-Pyridinyl-4-(1*H*-pyrrol-1-yl)pyridine, 4. Obtained by Stille coupling of **2c** (380 mg, 3 mmol) with 2-tributylstannylpyridine (1.21 g, 3.3 mmol). Column chromatography with elution gradient from hexane/AcOEt (40/60) to AcOEt yielded **4** as a yellow gummy solid (431 mg, 65%). ^{1}H NMR: δ_H 6.41 (t, J = 2 Hz, 2H), 7.29 (m, 2H), 7.34 (t, J = 2 Hz, 2H), 7.82 (m, 1H), 8.46 (m, 2H), 8.65 (m, 2H). ^{13}C NMR: δ_C 111.0, 112.6, 113.7, 118.9, 121.7, 121.5, 124.2, 124.6, 137.4, 149.6, 151.0. MS (EI) *m/z*: 221 (M^+, 100), 194 (25), 168 (11), 142 (2), 128 (6), 110 (5), 89 (4), 63 (4), 51 (29). Anal. Calcd: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.96; H, 5.08; N, 18.39.

2-Chloro-6-(2-pyridinyl)-4-(1*H*-pyrrol-1-yl)pyridine, 3d. Obtained by Stille coupling of **3c** (1.9 g, 9 mmol) and 2-tributylstannylpyridine (4.5 g, 9.9 mmol). Column chromatography with hexane/AcOEt (40/60) as eluent yielded **3c** as a brown solid (1.6 g, 70%). ^{1}H NMR: δ_H 6.41 (t, J = 2 Hz, 2H), 7.25−7.34 (m, 4H), 7.82 (t, J = 8 Hz, 1H), 8.43 (m, 2H), 8.68 (d, J = 2 Hz, 1H). ^{13}C NMR: δ_C 109.4, 112.9, 113.2, 118.9, 121.9, 124.9, 137.3, 149.4. Anal. Calcd: C, 65.76; H, 3.94; N, 16.43. Found: C, 65.91; H, 3.58; N, 16.39.

2,6-Bis(2′-pyridinyl)-4-(1*H*-pyrrol-1-yl)pyridine, 6. Obtained by Stille coupling of **3c** (1.16 g, 4.5 mmol) and 2-tributylstannylpyridine (2.25 g, 4,95 mmol). After filtration on Celite and evaporation of solvents, the residue was crystallized from diethyl ether yielding **6** as a gray powder (600 mg, 50%). ^{1}H NMR: δ_H 6.46 (m, 2H), 7.37 (m, 2H), 7.51 (m, 2H), 7.83 (m, 2H), 8.53 (m, 2H), 8.66 (m, 4H). ^{13}C NMR: δ_C 110.8, 112.4,

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119.3, 121.8, 124.6, 137.4, 149.6. Anal. Calcd: C, 76.49; H, 4.73; N, 18.78. Found: C, 76.36; H, 5.02; N, 18.56.

2,2′-Bis(4-(1*H*-pyrrol-1-yl)pyridinyl), 5. Two alternative pathways were used to prepare liganded Ni^0 reagents:

(i) To a solution of $NiCl_2 \cdot 6H_2O$ (600 mg, 2.5 mmol) and PPh_3 (2.65 g, 10 mmol) in DMF (15 mL) at 50 °C was added zinc powder (167 mg, 2.5 mmol) under nitrogen.

(ii) To a suspension of $Ni(OAc)_2$ (440 mg, 2.5 mmol), NaH (550 mg, 10 mmol), and PPh_3 (2.65 g, 10 mmol) in anhydrous THF (20 mL) at 65 °C was added a solution of *tert*-butyl alcohol (360 mg, 5 mmol) in THF (5 mL).

After 1 h under stirring, **2c** (427 mg, 2.4 mmol) was added to the reagent and the temperature was maintained for 2 h. The mixture was then treated with ammonia and extracted with chloroform. After drying over $MgSO_4$ and evaporation, the crude product was purified by column chromatography using a gradient from hexane/AcOEt (40/60) to AcOEt. With both the reagents **5** was obtained as a white solid (480 mg 70%). ^{1}H NMR: δ_H 6.42 (t, J = 2 Hz, 4H), 7.32 (d, J = 2 Hz, 4H), 7.35 (t, J = 2 Hz, 2H), 8,52 (d, J = 6 Hz, 2H), 8.65 (d, J = 6 Hz, 2H). ^{13}C NMR: δ_C 111.2, 112.7, 114.0, 119.0, 151.0. Anal. Calcd: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.48; H, 4.85; N, 19.14.

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