

Supporting Information

**Cobalt-Catalyzed C(sp²)-H Borylation with an Air-Stable, Readily
Prepared Terpyridine Cobalt(II) Bis(acetate) Precatalyst**

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I. Additional Spectroscopic Data

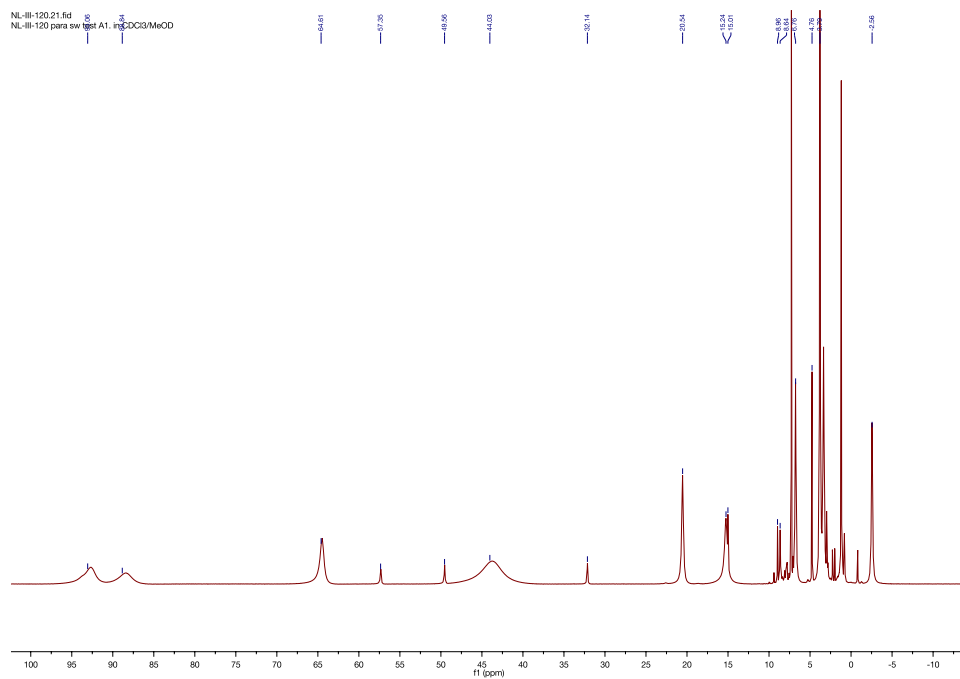


Figure S1. CDCl₃ ¹H NMR spectrum of (^{4r}Tpy)Co(OAc)₂ at 23 °C.

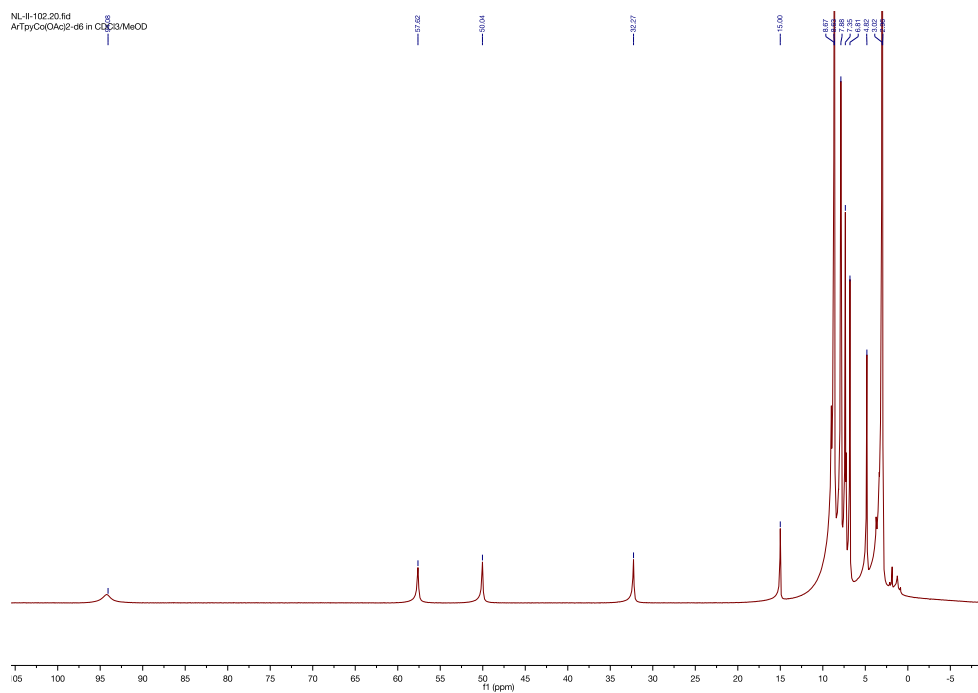
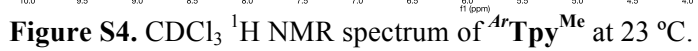
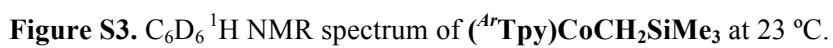


Figure S2. CDCl₃ ¹H NMR spectrum of (^{4r}Tpy)Co(OAc)₂-d₆ at 23 °C.



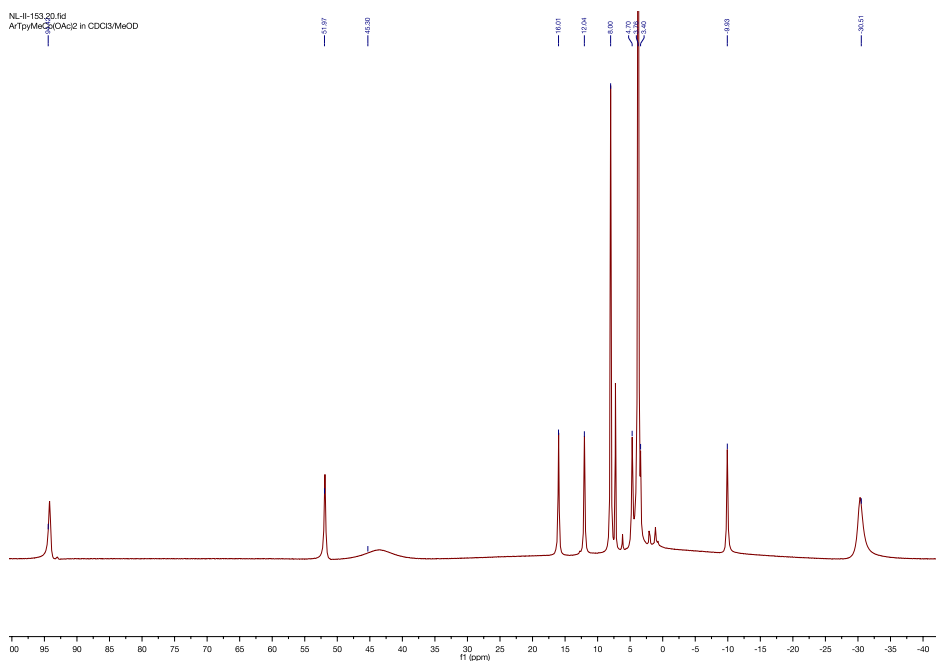


Figure S5. CDCl_3 ^1H NMR spectrum of $(^{\text{Ar}}\text{Tpy}^{\text{Me}})\text{Co}(\text{OAc})_2$ at 23 °C.

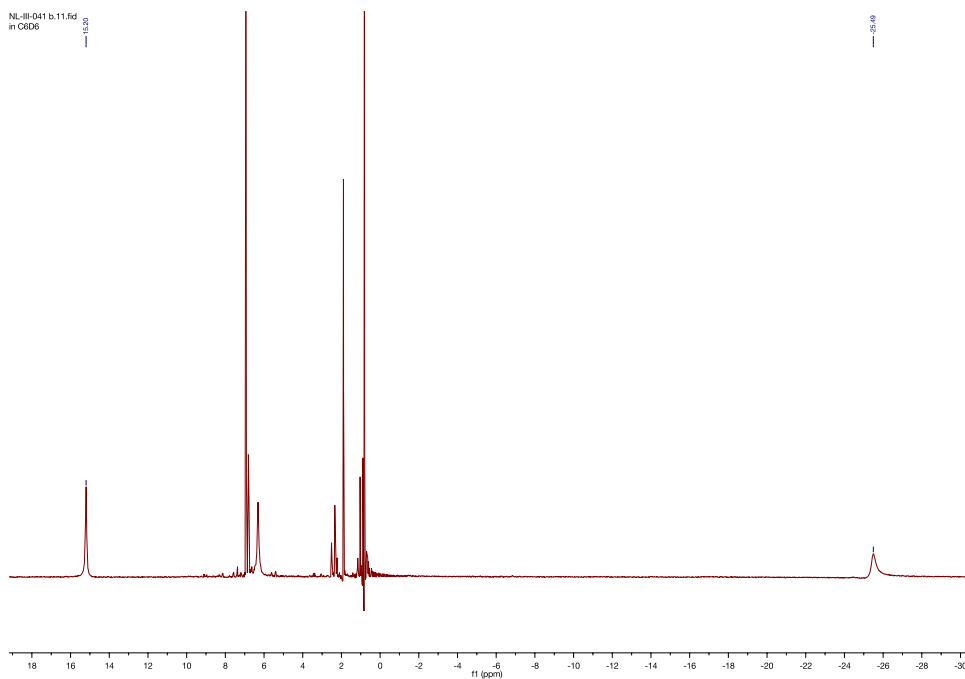
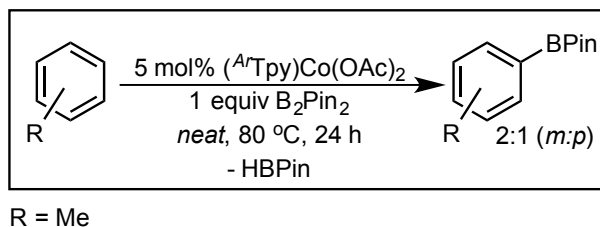


Figure S6. C_6D_6 ^1H NMR spectrum of $\text{Co}[\text{PinB}(\text{OAc})_2]_2$ at 23 °C. Peaks at 6-8 ppm correspond to free $^{\text{Ar}}\text{Tpy}^{\text{Me}}$ ligand. Peaks at 0-2 ppm correspond to residual solvent.

Table S1. Reaction conditions: toluene (5.7 mmol), B₂Pin₂ (0.38 mmol), catalyst (0.019 mmol, 5 mol%), 80 °C. Percent yields based on GC-FID using cyclooctane as an internal standard.



<i>Alkoxide</i>	<i>% yield</i>
10 mol% LiOMe	80
100 mol% LiOMe	90
100 mol% NaOAc	53
100 mol% KO ^t Bu	75
100 mol% NaO ^t Bu	69

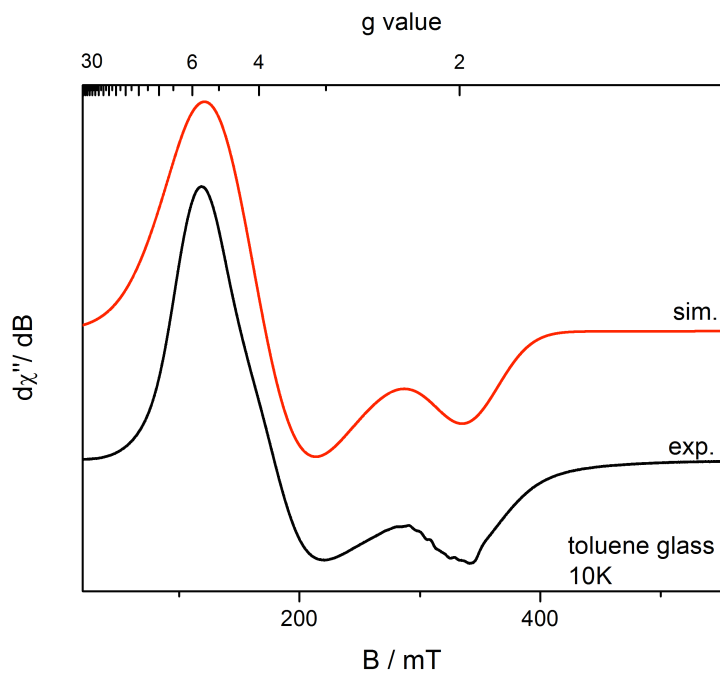


Figure S7. X-band EPR spectrum of (^{Ar}Tpy)Co(OAc)₂ recorded in toluene glass at 10K. Microwave frequency = 9.378 GHz, power = 0.63 mW, modulation amplitude = 1 mT/100 kHz.; Spectroscopic parameters; g_z = 5.66, g_y = 5.59, g_x = 1.99, H_{strain} = (100, 10, 10), g_{strain} = (1.71, 1.30, 0.37).

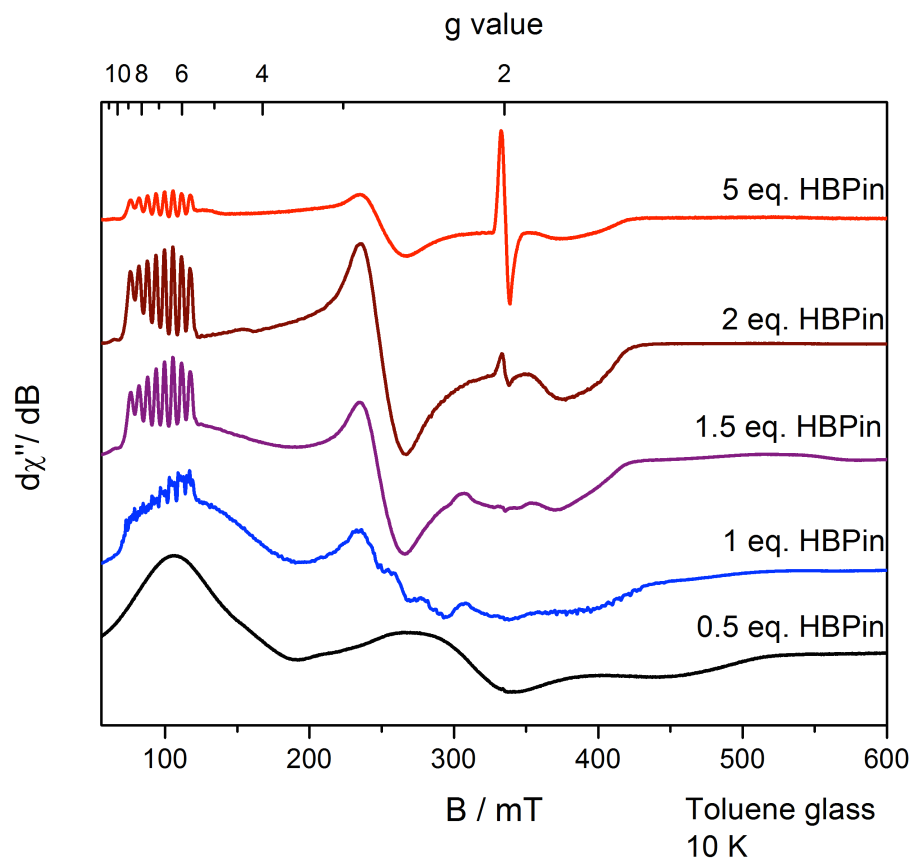


Figure S8. X-band EPR spectrum of (^{Ar}Tpy)Co(OAc) $_2$ plus x equivalents of HBPin recorded in toluene glass at 10K. Microwave frequency = 9.380 GHz, power = 2.0 mW, modulation amplitude = 1 mT/100 kHz.

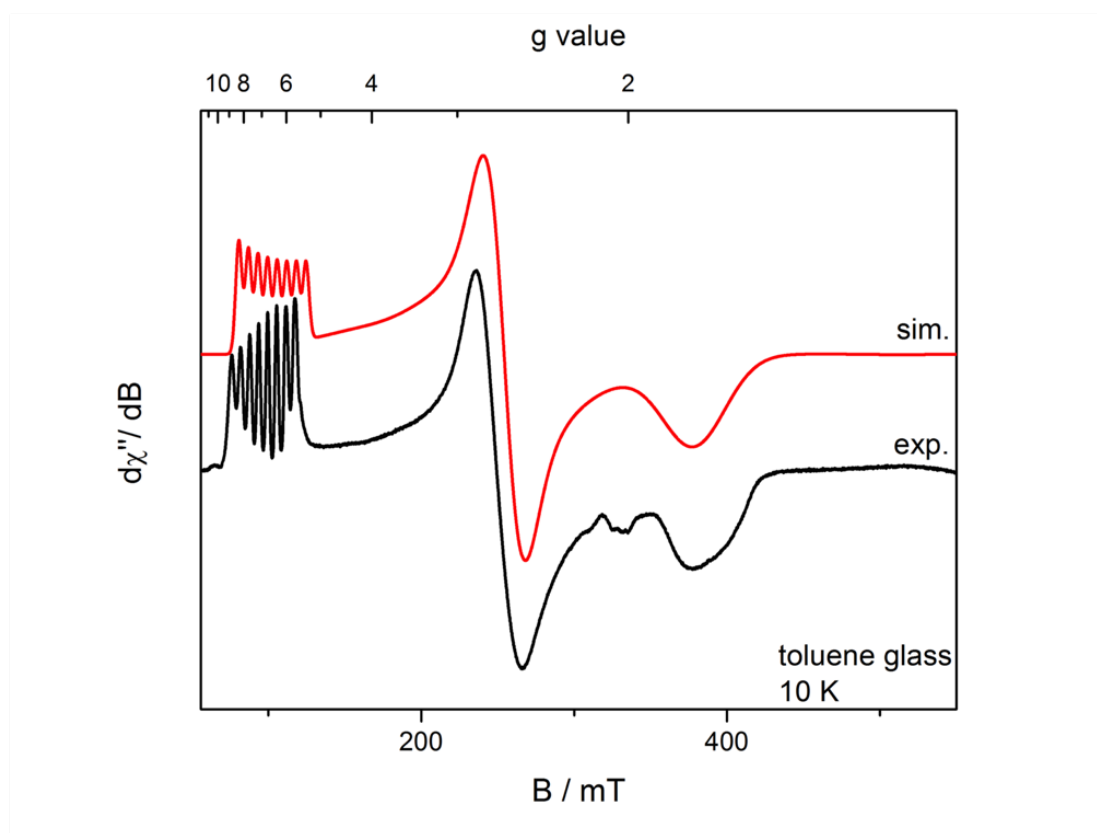
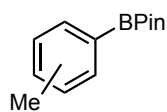


Figure S9. X-band EPR spectrum of $\text{Co}[\text{PinB}(\text{OAc})_2]$ generated from addition of 2 equivalents HBPIn to $(^{\text{Ar}}\text{Tpy}^{\text{Me}})\text{Co}(\text{OAc})_2$ in toluene at room temperature. Spectra collected at 10 K in toluene glass. Microwave frequency = 9.380 GHz, power = 2.0 mW, modulation amplitude = 1 mT/100 kHz. Simulation parameters for complex A: $g_z = 1.99$, $g_y = 2.66$, $g_x = 2.04$, $g_{\text{strain}} = (0.19, 0.01, 0.17)$, $A_z = 225$ MHz, $A_y = 1$ MHz, $A_x = 1$ MHz, $A_{\text{strain}} = (58, 0, 0)$.

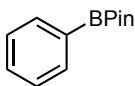
II. Characterization Data for Borylation Products



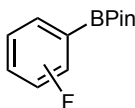
(1a): A mixture of isomers was isolated as an off-white solid (0.061 g, 80%)

following removal of excess solvent under reduced pressure, redissolving in CDCl_3 , and filtration of the crude reaction mixture through a plug of silica in a Pasteur pipette. The *meta*:*para* ratio was determined to be 70:30 by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform- d , 23 °C): δ 137.12, 135.34, 132.05, 131.78, 127.69, 83.14,

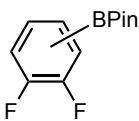
24.07, 21.27 (*meta*); δ 141.55, 134.81, 128.51, 83.77, 24.84, 21.73 (*para*). The ^1H NMR and ^{13}C NMR spectrum agree with previously reported data.¹



(1b): The excess solvent was removed under reduced pressure. The crude reaction mixture was dissolved in CDCl_3 , passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification. The compound was isolated as a white solid (0.060 g, 84% yield) upon removal of solvent in vacuo. ^1H NMR (chloroform-*d*, 23 °C): δ 7.82 (d, $\Delta\nu_{1/2} = 7.31$ Hz, 2H), 7.45 – 7.36 (m, 3H), 1.35 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 134.87, 131.39, 127.84, 83.91, 25.02. ^1H and ^{13}C NMR data agree with previously reported data.²

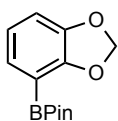


(1c): The excess solvent was removed under reduced pressure. The crude reaction mixture was dissolved in CDCl_3 , passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification. The mixture of isomers were isolated as a white solid (0.055 g, 65% yield) upon removal of solvent in vacuo. The ^1H NMR was not assigned since the proton resonances of the *meta* and *para* isomers overlap with each other. The *ortho*: *meta* ratio was determined to be 80:20 by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 168.17, 166.18, 137.02, 136.79, 133.32, 133.25, 123.58, 123.50, 115.34 115.15, 84.12, 24.50 (*ortho*).; δ 163.46, 161.50, 131.26, 130.30, 129.50, 129.44, 121.03, 120.88, 118.25, 118.09, 83.91, 24.84 (*meta*). ^{13}C NMR data agree with previously reported data.³

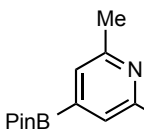


(1d): The crude reaction mixture was exposed to air to quench the catalyst and filtered through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification. NMR yield of the crude mixture was determined by

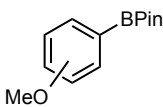
^{19}F NMR using fluorobenzene as an external standard (70% yield). The ^1H NMR was not assigned since the proton resonances of the 3- and 4- borylated isomers overlap with each other. The 3:4 ratio was determined to be 70:30 by integration of the characteristic peaks in the ^{19}F NMR spectrum. A trace amount of *ortho* borylated fluorobenzene was observed in the ^{19}F NMR, likely due to defluorination-borylation. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 154.5, 150.4, 131.1, 124.0, 120.78, 119.27, 117.83, 117.21, 83.72, 25.12 (3); δ 153.65, 153.57, 151.98, 151.90, 151.18, 151.10, 149.53, 149.45, 131.53, 123.96, 123.82, 116.84, 116.41, 84.19, 25.42. (4). ^{13}C NMR data agree with previously reported data.^{4,5}



(1e): The crude reaction mixture was exposed to air to quench the catalyst and filtered through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification. NMR yield of the crude mixture was determined using cyclooctane as an external standard (90% yield). ^1H NMR (chloroform-*d*, 23 °C): δ 7.21 (dd, $J = 7.31$ Hz, $J = 1.5$ Hz, 1H), 6.92 (dd, $J = 7.31$ Hz, $J = 1.1$ Hz 1H), 6.82 (t, $J = 7.31$ Hz, 1H), 6.02 (s, 2H), 1.36 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 152.54, 146.87, 127.82, 121.06, 111.16, 100.72, 83.91, 24.80. ^1H and ^{13}C NMR data agree with previously reported data.⁶

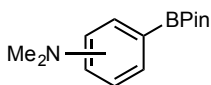


(1f): The compound was isolated (0.029 g, 32% yield) upon removal of solvent in vacuo. ^1H NMR (chloroform-*d*, 23 °C): δ 7.31 (s, 2H), 2.52 (s, 6H), 1.35 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 156.92, 125.16, 84.25, 24.74. ^1H and ^{13}C NMR data agree with previously reported data.⁷

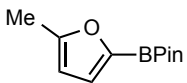


(1g): The crude reaction mixture was exposed to air to quench the catalyst and filtered through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR

spectroscopy without additional purification. NMR yield of the crude mixture was determined using cyclooctane as an external standard (60% yield). The ^1H NMR was not assigned since the proton resonances of the *meta* and *para* isomers overlap with each other. The *meta: para* ratio was determined to be 75:25 by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 159.20, 129.06, 128.61, 118.48, 117.42, 83.39, 54.46, 24.41 (*meta*).; δ 161.85, 136.54, 113.46, 83.39, 54.46, 24.41 (*para*). δ 164.19, 136.87, 132.54, 120.21, 110.06, 82.26, 59.91, 24.63 (*ortho*). ^{13}C NMR data agree with previously reported data.^{8,9,10}



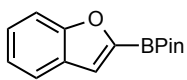
(1h): The crude reaction mixture was exposed to air to quench the catalyst and filtered through a plug of silica gel in a Pasteur pipette and then analyzed by ^1H and ^{13}C NMR spectroscopy without additional purification. NMR yield of the crude mixture was determined using cyclooctane as an external standard (67%yield). The ^1H NMR was not assigned since the proton resonances of the *meta*, *para* and *ortho* isomers overlap with each other. The *meta: para: ortho* ratio was determined to be 75:25:trace by integration of the characteristic peaks in the quantitative ^{13}C NMR spectrum. $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 150.0, 128.94, 127.19, 118.65, 117.94, 83.18, 55.10, 24.54 (*meta*).; δ 159.01, 136.51, 113.3, 83.85, 55.26.1, 24.86 (*para*). ^{13}C NMR data agree with previously reported data.^{11,12}



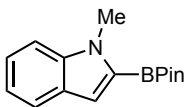
(1i): A 0.01 M solution of (Ar Tpy)Co(OAc)₂ in 2-methylfuran was prepared. To a 10 mL reaction vial, 0.36 mL of the 0.01 M solution of (Ar Tpy)Co(OAc)₂ (0.003 mmol catalyst) was added. The vial was also charged with a magnetic stir bar and 0.014 g (0.359 mmol) of LiOMe, and 0.091 g (0.359 mmol) of B₂Pin₂. The resulting mixture was heated in an oil bath at 80 °C for 36 hours. The crude reaction mixture was dissolved in hexane and the resulting solution was passed through a plug of silica gel in a Pasteur pipette to remove the catalyst. The title

compound was isolated as a colorless oil (0.074 g, 98% yield) upon removal of solvent in vacuo.

^1H NMR (chloroform-*d*, 23 °C): δ 6.94 (d, $\Delta\nu_{1/2}$ = 3.07 Hz, 1H), 5.99 (d, $\Delta\nu_{1/2}$ = 3.07 Hz, 1H), 2.30 (s, 3H), 1.29 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 157.58, 124.80, 106.87, 83.90, 24.66, 13.83. ^1H and ^{13}C NMR data agree with previously reported data.¹³



(1j): Isolated as a white solid (0.081 g, 88%). ^1H NMR (chloroform-*d*, 23 °C): δ 7.63 (d, $\Delta\nu_{1/2}$ = 7.91 Hz, 1H), 7.57 (d, $\Delta\nu_{1/2}$ = 7.90 Hz, 1H), 7.40 (s, 1H), 7.34 (ddd, $\Delta\nu_{1/2}$ = 8.4, 7.2, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 1.39 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 157.54, 127.49, 125.95, 122.73, 121.90, 119.56, 111.99, 84.71, 24.81. ^1H and ^{13}C NMR data agree with previously reported data.¹⁴



(1k): Isolated as a white solid (0.058 g, 60%). ^1H NMR (chloroform-*d*, 23 °C): δ 7.64 (d, $\Delta\nu_{1/2}$ = 8.05 Hz, 1H), 7.07 – 7.36 (m, 5H), 3.98 (s, 3H), 1.37 (s, 12H). $\{^1\text{H}\}^{13}\text{C}$ NMR (chloroform-*d*, 23 °C): δ 140.14, 127.84, 123.17, 121.60, 119.29, 114.24, 109.69, 83.70, 32.25, 24.86. ^1H and ^{13}C NMR data agree with previously reported data.¹⁵

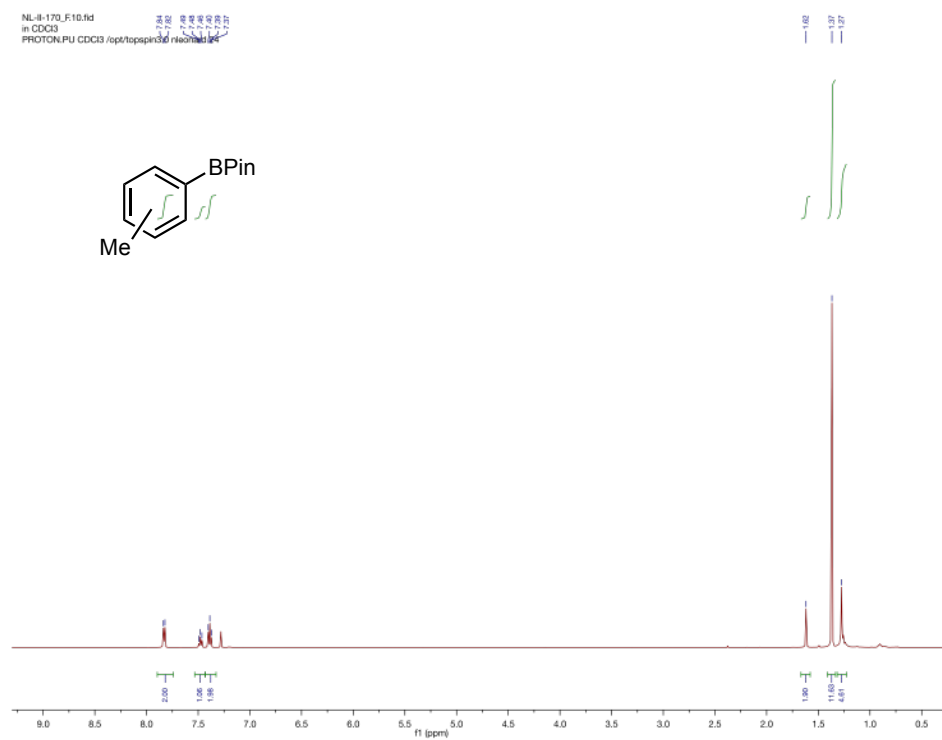


Figure S10. ¹H NMR spectrum of **1a** in CDCl₃ at 23 °C.

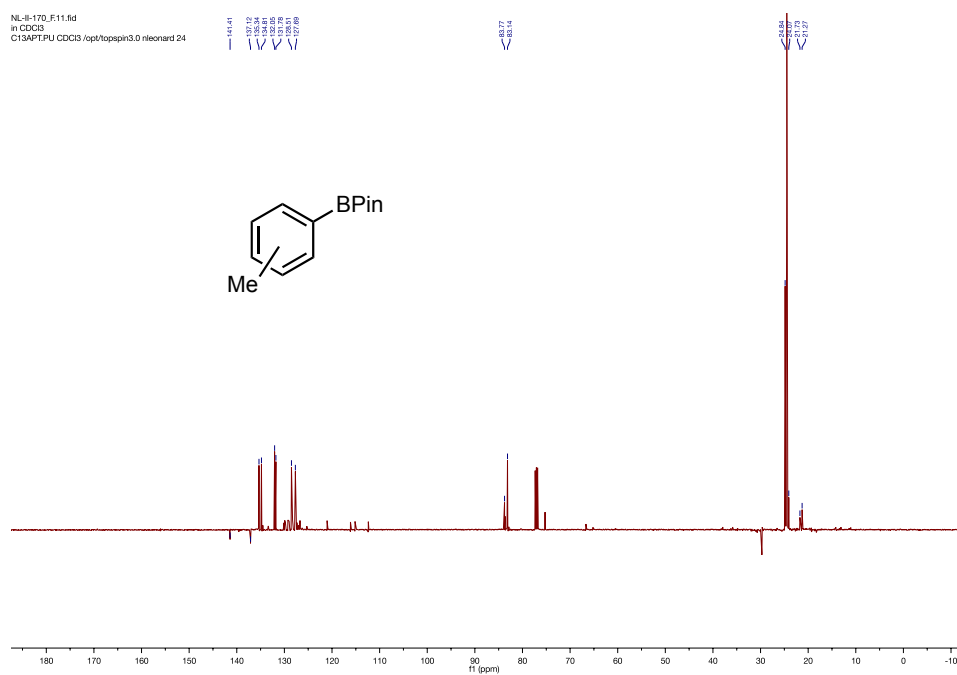
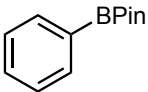


Figure S11. ¹³C NMR spectrum of **1a** in CDCl₃ at 23 °C.



c1ccccc1BPin
 NL-1170_E11.fid
 in CDCl3
 C13APT.PU CDCl3 /ap01sp010.0 nlsdard 43

134.47
 131.59
 127.46
 83.91
 76.00
 25.08

S13

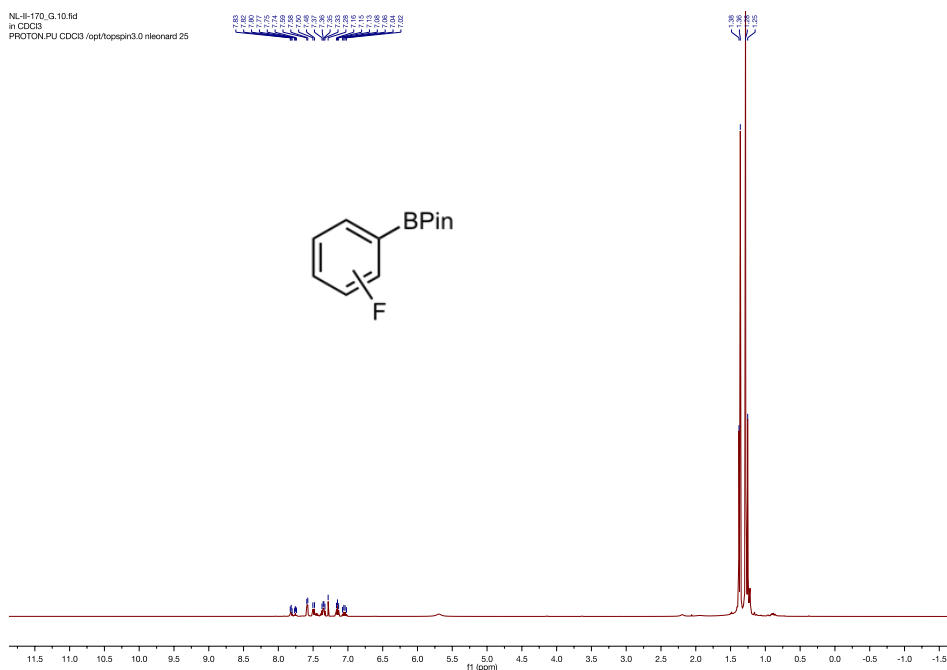


Figure S14. ¹H NMR spectrum of **1c** in CDCl₃ at 23 °C.

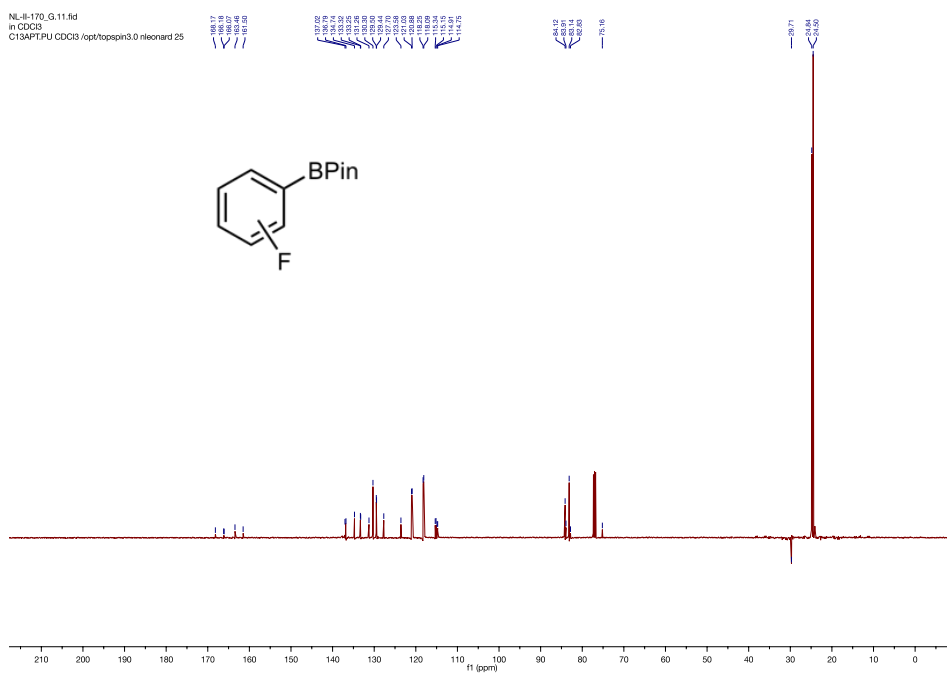
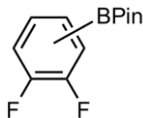


Figure S15. ¹³C NMR spectrum of **1c** in CDCl₃ at 23 °C.



Fc1ccccc1F

S15

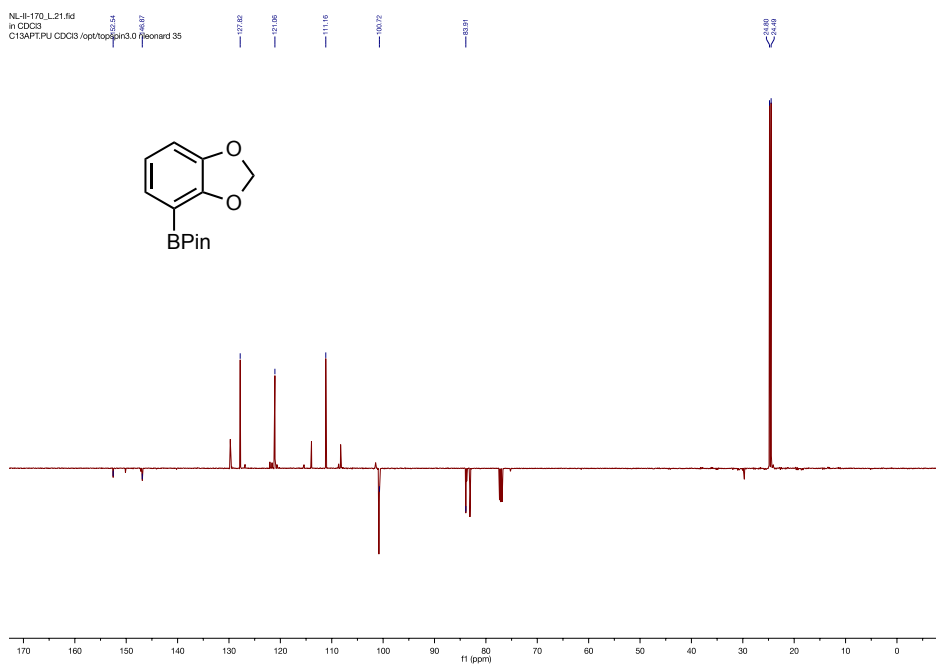


Figure S18. ^{13}C NMR spectrum of crude reaction mixture of **1e** in CDCl_3 at 23 °C.

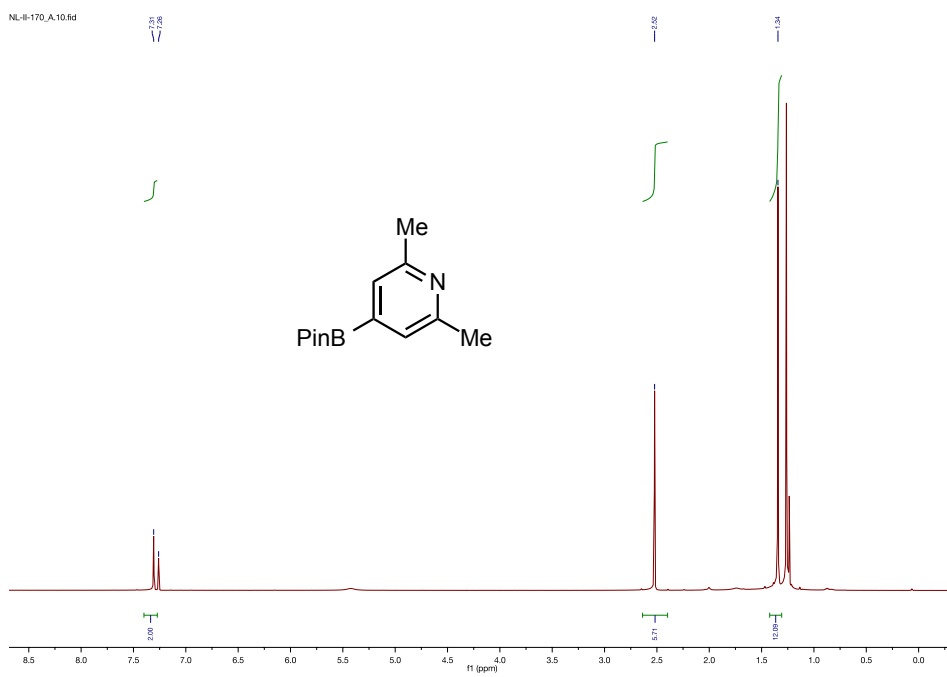


Figure S19. ^1H NMR spectrum of **1f** in CDCl_3 at 23 °C.

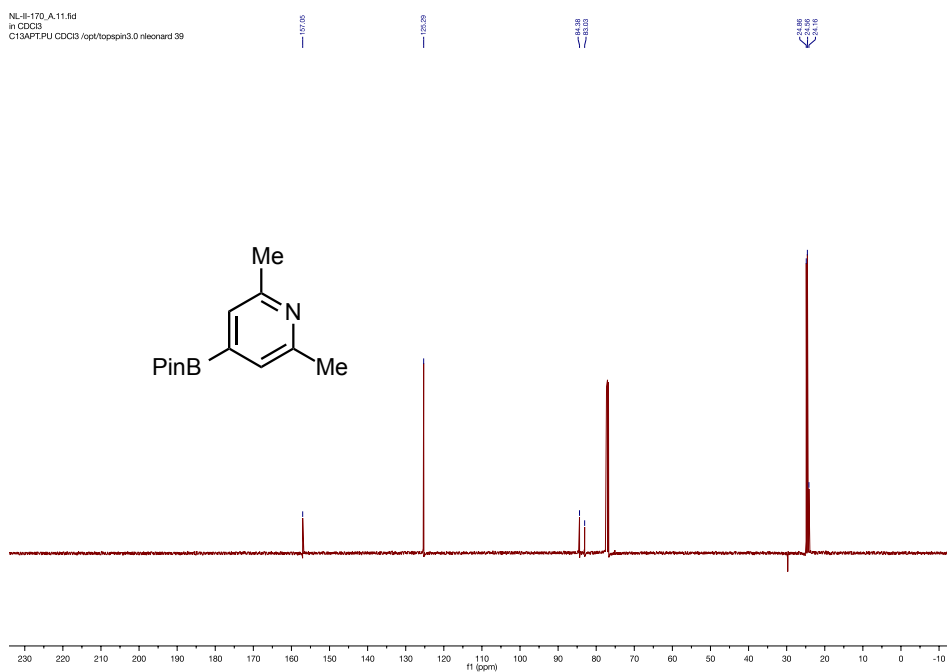


Figure S20. ¹³C NMR spectrum of **1f** in CDCl₃ at 23 °C.

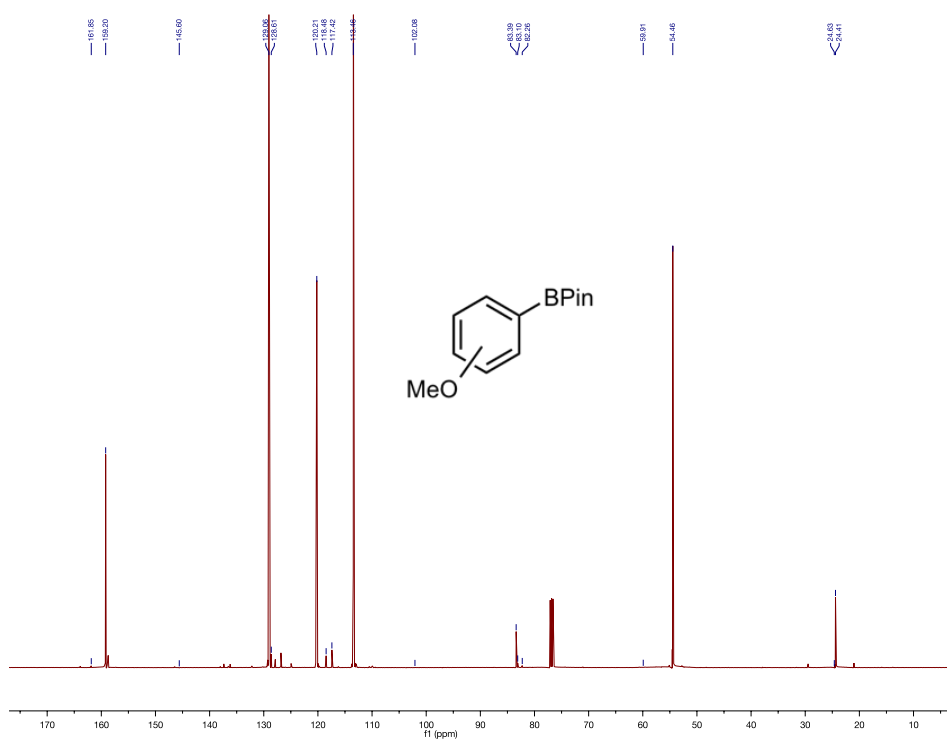


Figure S21. ¹³C NMR spectrum of crude reaction mixture of **1g** in CDCl₃ at 23 °C.

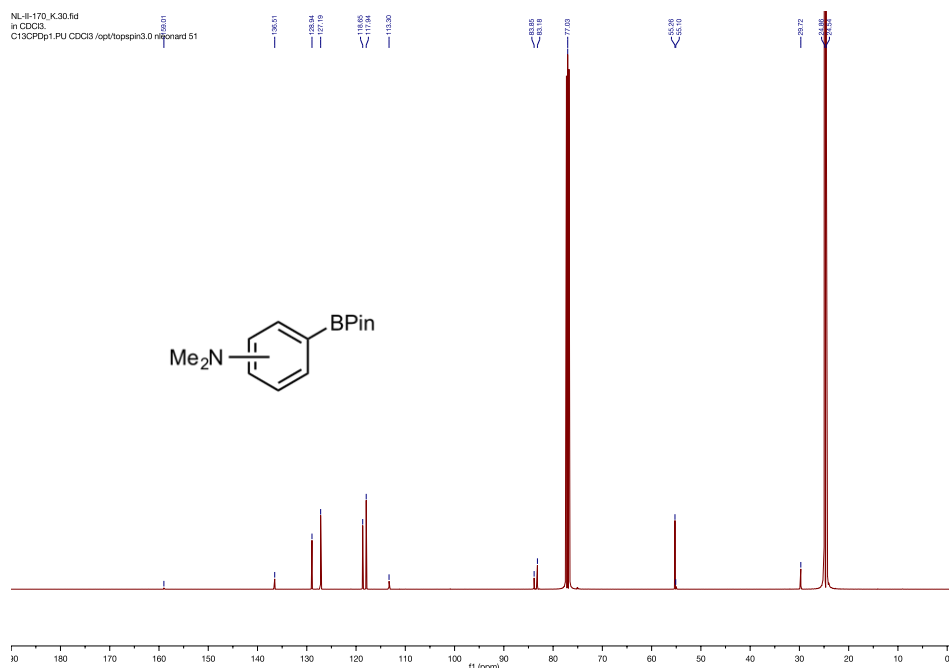


Figure S22. ¹³C NMR spectrum of crude reaction mixture of **1h** in CDCl₃ at 23 °C.

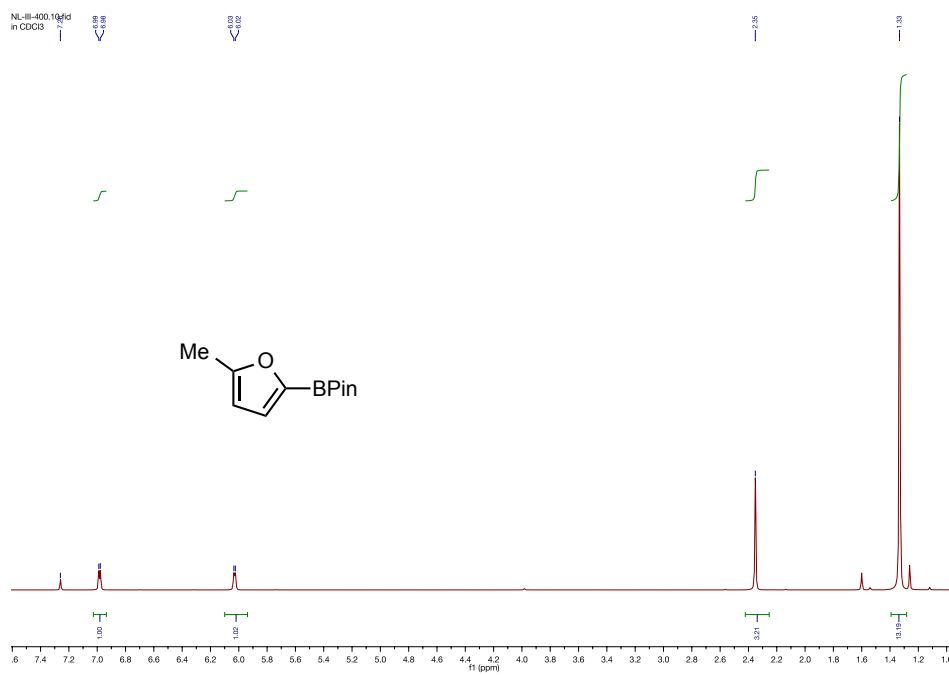
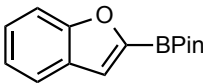


Figure S23. ¹H NMR spectrum of **1i** CDCl₃ at 23 °C.



¹H NMR spectrum (400 MHz, CDCl₃) of compound 10. The chemical structure of 1-methyl-2-(4,4,5,5-tetramethyl-1,3-dioxol-2-yl)indole is shown above the spectrum. The spectrum displays peaks in the aromatic region (6.8-7.5 ppm) and a singlet for the methyl group (3.9 ppm). Integration values are provided below the baseline.

Chemical Shift (ppm)	Integration
7.45 (d)	1.00
7.35 (d)	1.00
7.25 (m)	0.94
7.15 (m)	1.10
3.90 (s)	3.04

Figure S27. ^1H NMR spectrum of **1k** in CDCl_3 at 23 $^\circ\text{C}$.

III. References

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