

Supporting Information

Highly Selective Directed Arylation Reactions *via* Back-to-Back Dehydrogenative C–H Borylation/Arylation Reactions

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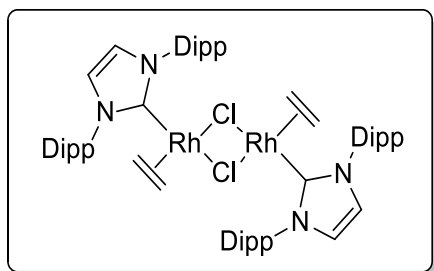
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General Experimental Information

Unless otherwise specified, all manipulations were carried out under an atmosphere of dry argon in oven-dried glassware, or under a nitrogen atmosphere in a glovebox (M. Braun) with oxygen and water levels ≤ 2 ppm. All solvents were distilled from either CaH_2 or Na, deoxygenated with a minimum of three freeze-pump-thaw cycles and stored under N_2 over molecular sieves ($4\text{\AA}$) prior to use. Pinacolborane was purchased from Sigma Aldrich and purified by short path distillation and stored at $-30\text{ }^\circ\text{C}$ under a nitrogen atmosphere. 2-Phenylpyridine was purchased from Sigma Aldrich, distilled from CaH_2 and stored at $-30\text{ }^\circ\text{C}$ under a nitrogen atmosphere. 2-Phenylpyridines (**4a–n**) were synthesized according to literature procedures.^{1,2} $[\text{Rh}(\text{IPr})(\text{C}_2\text{H}_4)\text{Cl}]_2$ (**1**) was prepared according to our previously reported synthesis³ and stored at $-30\text{ }^\circ\text{C}$ under a nitrogen atmosphere. Addition of water for the arylation reactions was accomplished by bubbling Ar through distilled water for a minimum of 30 minutes and adding the water to the reaction mixture with a μL glass syringe. RhCl_3 and $\text{Pd}_2(\text{dba})_3$ were generously donated by Johnson Matthey and used without further purification. NMR spectra were recorded on a Bruker Avance 400 or 500 MHz (^1H) where indicated. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard (CDCl_3 , δ 7.26 ppm; CD_2Cl_2 , δ 5.32 ppm; C_6D_6 , δ 7.16 ppm). Boron NMR spectra (^{11}B) were recorded at 128 MHz and 160 MHz and referenced to an external standard ($\text{BF}_3\cdot\text{OEt}$, δ 0 ppm). Purification of C–H borylation products was achieved by column chromatography using a stationary phase of Aluminum oxide purchased from Sigma Aldrich (activated, basic, Brockmann Grade I, $58\text{ }\text{\AA}$ porosity, pH 9.0–10.0) and eluted with reagent grade hexanes and ethyl acetate (EtOAc). Purification of the arylated products was achieved on column chromatography using flash grade silica gel (Silicycle, $50\text{ }\mu\text{m}$ particle size, $60\text{ }\text{\AA}$ porosity) and eluted with reagent grade mixtures of hexanes/EtOAc or DCM/MeOH. Elemental analyses were performed using a Thermo Scientific Flash 2000 CHNS Elemental Analyzer. High-resolution mass spectrometry (HRMS) was performed using a Micromass GCT (GC–Time of Flight Mass Spectrometer). X-ray data collection was performed on a Bruker SMART APEX II X-ray diffractometer.

Synthesis of $[\text{Rh}(\text{IPr})(\text{C}_2\text{H}_4)\text{Cl}]_2$ (**1**)³



In a nitrogen-filled glovebox, a 4 dram vial equipped with a stir bar was charged with $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (30 mg, 0.08 mmol), which was taken up in THF (6 mL). *N,N'*-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (60 mg, 0.16 mmol) in THF (6 mL) and added drop-wise, and the solution was stirred for 3 hours at room temperature. The reaction was then filtered through a plug of Celite and the THF was removed *in vacuo*. The residue was tritiated with hexanes to afford 87 mg of an orange-yellow powder (87 mg, 98% yield). Complex **1** was stored as a powder at -30°C under nitrogen. Spectral data are consistent with that which we have previously reported.¹

Synthesis of $[\text{Rh}(\text{IPr})(2\text{-Ph-Pyr})\text{HCl}]$ (**3a**)

In a nitrogen-filled glovebox, 2-phenyl pyridine (4.2 mg, 0.027 mmol) in C_6D_6 (2.0 mL) was added to a solution of **1** (15 mg, 0.013 mmol) in C_6D_6 (2.0 mL) and the mixture was allowed to stir for 3 days. The formation of a new rhodium hydride complex was confirmed by ^1H NMR (500 MHz, C_6D_6) which displayed the characteristic doublet -24.5 ppm, $^1J_{\text{Rh-H}} = 48.9$ Hz.

Synthesis of $[\text{Rh}(\text{IPr})(2,2'\text{-Biquinoline})\text{HCl}]$ (**3b**)

In a nitrogen-filled glovebox, 2,2'-biquinoline (7 mg, 0.026 mmol) in C_6D_6 (2.0 mL) was added to a solution of **1** (15 mg, 0.013 mmol) in C_6D_6 (2.0 mL) and the solution was allowed to stir at RT for 10 days which resulted in an intractable mixture according to ^1H NMR. The C_6D_6 was evaporated. A co-crystal of compounds **3b** and **3c** in a ratio of 3:2 respectively was obtained by a slow diffusion of hexanes into a concentrated THF solution of the mixture.

Optimization of C–H Borylation on Phenyl Pyridine

General Optimization Procedure

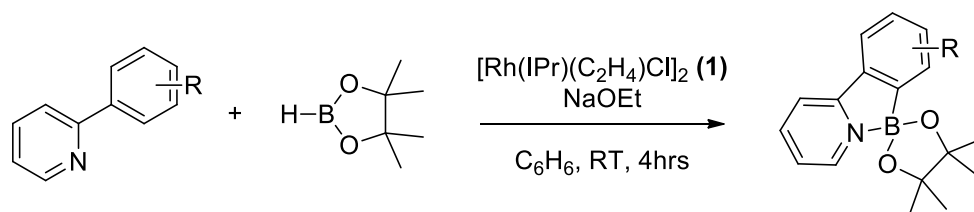
To an oven-dried round bottom flask containing a stir bar, base was added followed by substrate (0.13 mmol), pinacolborane and **1** in the indicated solvent at the indicated concentration. The mixture was vigorously stirred for the indicated time at room temperature. The solution was filtered through celite, and the solvent was removed under reduced pressure. Yields were determined by ¹H NMR using 1,4, dimethoxybenzene as an internal standard.

Table S1 Optimization of C-H Borylation

Entry	Base (eq.)	Catalyst	Mol %	HBPIn (eq.)	Solvent	% Yield ^a
1	-	1	1	1.5	C ₆ H ₆	ND
2	KO ^t Bu (0.5)	1	1	1.5	C ₆ H ₆	32
3	KO ^t Bu (0.25)	1	1	1.5	C ₆ H ₆	70
4 ^b	KO ^t Bu (0.25)	1	1	1.5	C ₆ H ₆	70
5 ^c	KO ^t Bu (0.25)	1	1	1.5	C ₆ H ₆	69
6	KO ^t Bu (0.12)	1	1	1.5	C ₆ H ₆	72
7	NaOMe (0.25)	1	1	1.5	C ₆ H ₆	32
8	NaOEt (0.25)	1	1	1.5	C ₆ H ₆	84
9	Cs ₂ CO ₃ (0.25)	1	1	1.5	C ₆ H ₆	28
10 ^b	Cs ₂ CO ₃ (0.25)	1	1	1.5	C ₆ H ₆	62
11	K ₃ PO ₄ (0.25)	1	1	1.5	C ₆ H ₆	8
12	K ₂ CO ₃ (0.25)	1	1	1.5	C ₆ H ₆	0
13	NaOEt (0.25)	1	1	1.5	THF	25
14	NaOEt (0.25)	1	1	1.5	Toluene	73
15	NaOEt (0.25)	1	1	1.5	CF ₃ C ₆ H ₅ ,	82
16	NaOEt (0.25)	1	1	2.0	C ₆ H ₆	91
17	NaOEt (0.25)	1	1	3.0	C ₆ H ₆	81
18	NaOEt (0.25)	1	2	2.0	C ₆ H ₆	91
19	NaOEt (0.25)	1	0.5	2.0	C ₆ H ₆	30
20	NaOEt (0.25)	[Rh(COD)(IPr)Cl]	2	2.0	C ₆ H ₆	ND

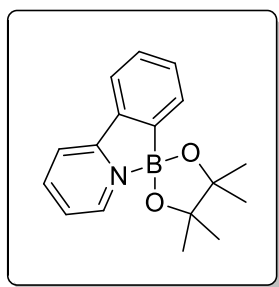
^a NMR yield using 1,4 dimethoxy benzene as an internal standard, average of 2 runs ^b 8 hours ^c at 0.05 M

General Procedure for C–H Borylation of 2–Phenylpyridines (5a–5n)



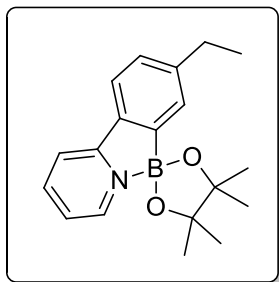
To an oven-dried round bottom flask equipped with a stir bar, NaOEt (8.5 mg, 0.125 mmol) was added. Substrate (0.5 mmol) and **1** (5.55 mg, 0.005 mmol, 1%) were taken up in 4 mL of benzene and added to the round bottom flask. Pinacolborane (128 mg, 1 mmol) was taken up in 0.6 mL of benzene then added to the stirring mixture and the reaction was vigorously stirred for 4 hours. After the elapsed time, the flask was removed from the glovebox and the contents loaded directly onto an alumina column (eluted with ethyl acetate/hexanes mixtures). The organic fractions were then collected and concentrated *in vacuo*. Occasionally, traces of pinacol are present in the ^1H NMR spectra of compounds **5a–5k**.

2–(2–Boronic acid pinacolate ester)–phenylpyridine (5a):



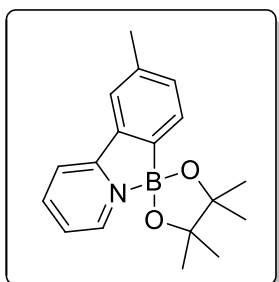
Synthesized according to the general procedure and purified by column chromatography eluting with a 7:3 EtOAc/Hexanes mixture to afford a yellow powder (114 mg, 81% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.66 (d, J = 5.5 Hz, 1H), 7.95, (td, J = 7.8, 1.5 Hz, 1H) 7.79 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.41 (td, J = 7.3, 0.9 Hz, 1H), 7.35 (dd, J = 9.5, 3.4 Hz, 1H), 7.29 (td, J = 7.5, 1.1 Hz, 1H), 1.43 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.67, 143.33, 141.92, 137.25, 131.57 (2 Carbons as determined by HSQC), 127.93, 122.79, 121.32, 117.54, 80.33, 27.14 ($C-B$ bond not observed). ^{11}B NMR (128 MHz, CDCl_3): δ 13.3. HRMS(EI) calculated for $\text{C}_{17}\text{H}_{20}\text{BNO}_2$: 281.1587. Found: 281.1599. (EA) Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{BNO}_2$: C, 72.62; H, 7.17; N, 4.98. Found: C, 72.12; H, 6.93; N, 5.27.

2-(4-Ethyl-2-boronic acid pinacolate ester)-phenylpyridine (5b):



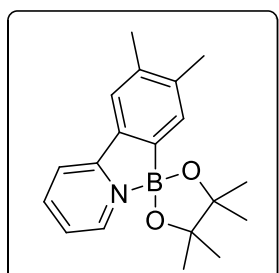
Synthesized according to the general procedure and eluted with 7:3 EtOAc/Hexanes mixture to afford an off-white powder (130 mg, 84% yield). Single crystals suitable for X-ray crystallography were obtained by evaporation of a diluted pentane solution. ^1H NMR (500 MHz, CDCl_3): δ 8.62 (d, $J = 4.1$ Hz, 1H), 7.90 (t, $J = 7.0$ Hz, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 7.5$ Hz, 1H), 7.52 (s, 1H), 7.30–7.28 (m, 1H), 7.12 (d, $J = 7.1$ Hz, 1H), 2.68 (br q, $J = 7.3$ Hz, 2H), 1.43 (s, 12H), 1.25 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 156.87, 147.97, 143.21, 141.77, 135.05, 131.27, 127.58, 122.24, 121.36, 117.25, 80.27, 29.45, 27.15, 15.64 (C-B bond not observed). ^{11}B NMR (160 MHz, CDCl_3): δ 13.3. HRMS (EI) calculated for $\text{C}_{19}\text{H}_{24}\text{BNO}_2$: 309.1900. Found: 309.1904. (EA) Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{BNO}_2$: C, 73.80; H, 7.82; N, 4.53. Found: C, 73.34; H, 8.05; N, 4.24.

2-(2-Boronic acid pinacolate ester-5-methyl)phenylpyridine (5c):



Synthesized according to the general procedure and eluted with 7:3 EtOAc/Hexanes mixture to afford an off-white powder (122 mg, 83% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 5.1$ Hz, 1H), 7.89 (t, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.59 (d, $J = 7.3$ Hz, 1H), 7.44 (s, 1H), 7.29 (t, $J = 6.3$ Hz, 1H), 7.21 (d, $J = 7.2$ Hz, 1H), 2.35 (s, 3H), 1.41 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.72, 143.24, 141.68, 137.55, 137.39, 132.43, 131.36, 122.55, 121.90, 117.37, 80.20, 26.98, 21.43 (C-B bond not observed). ^{11}B NMR (128 MHz, CDCl_3): δ 13.7. HRMS (EI) calculated for $\text{C}_{18}\text{H}_{22}\text{BNO}_2$: 295.1744. Found: 295.1747. (EA) Attempts to obtain elemental analyses with acceptable carbon content were unsuccessful, while hydrogen and nitrogen content are in the acceptable range. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{BNO}_2$: C, 73.24; H, 7.51; N, 4.75. Found: C, 73.88; H, 7.98; N, 4.57.

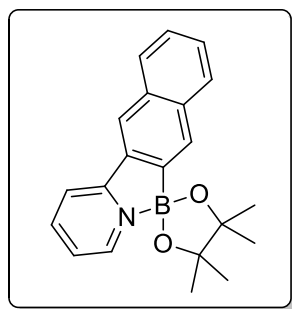
2-(2-Boronic acid pinacolate ester-4,5-dimethyl)phenylpyridine (5f):



Synthesized according to the general procedure and eluted with 7:3 EtOAc/Hexanes mixture to afford an off-white powder (119 mg, 77%

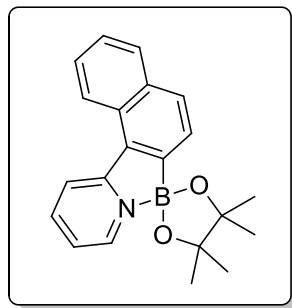
yield). **¹H NMR** (500 MHz, CDCl₃): δ 8.61 (d, *J* = 5.2 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.46 (s, 1H), 7.41 (s, 1H), 7.27 (t, *J* = 6.4 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 1.43 (s, 12H). **¹³C NMR** (125 MHz, CDCl₃): δ 156.94, 143.20, 141.58, 140.37, 136.06, 135.42, 132.89, 122.48, 122.06, 117.10, 80.17, 27.04, 20.34, 20.06 (*C–B* bond not observed). **¹¹B NMR** (160 MHz, CDCl₃): δ 13.9. **HRMS (EI)** calculated for C₁₉H₂₄BNO₂: 309.1900. Found: 309.1913. **(EA)** Anal. Calcd for C₁₉H₂₄BNO₂: C, 73.80; H, 7.82; N, 4.53. Found: C, 74.19; H, 7.99; N, 4.57.

2-(3-Boronic acid pinacolate ester)naphthalene-2-yl-pyridine (5i):



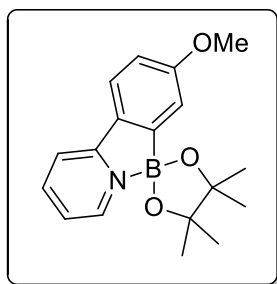
Synthesized according to the general procedure and eluted with 4:1 EtOAc/Hexanes mixture to afford a white powder (131 mg, 79% yield). **¹H NMR** (500 MHz, CD₂Cl₂): δ 8.72 (d, *J* = 5.2 Hz, 1H), 8.21 (s, 1H), 8.13 (s, 1H), 7.99–7.94 (m, 2H), 7.91 (t, *J* = 9.1 Hz, 2H), 7.53 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 5.4 Hz, 1H), 1.49 (s, 12H). **¹³C NMR** (125 MHz, CD₂Cl₂): δ 156.06, 143.53, 141.98, 136.24, 136.07, 133.67, 130.99, 128.95, 128.71, 127.28, 126.17, 123.70, 121.59, 118.79, 80.65, 27.29 (*C–B* bond not observed). **¹¹B NMR** (128 MHz, CD₂Cl₂): δ 13.4. **HRMS (EI)** calculated for C₂₁H₂₂BNO₂: 331.1744. Found: 331.1747. **(EA)** Anal. Calcd for C₂₁H₂₂BNO₂: C, 76.15; H, 6.69; N, 4.23. Found: C, 76.53; H, 6.95; N, 4.21.

2-(2-Boronic acid pinacolate ester)naphthalene-1-yl-pyridine (5j):



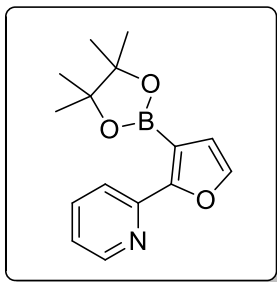
Synthesized according to the general procedure and eluted with 3:2 Hexanes/EtOAc mixture to afford a yellow powder (96 mg, 58% yield). **¹H NMR** (500 MHz, CDCl₃): δ 8.76 (d, *J* = 5.0 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.91–7.88 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.4, 1H), 1.43 (s, 12H). **¹³C NMR** (125 MHz, CDCl₃): δ 157.66, 144.35, 141.56, 134.71, 133.73, 131.63, 129.78, 129.71, 128.52, 127.14, 125.27, 122.92, 121.90, 121.79, 80.77, 27.22 (*C–B* bond not observed). **¹¹B NMR** (128 MHz, CDCl₃): δ 14.3. **HRMS (EI)** calculated for C₂₁H₂₂BNO₂: 331.1744. Found: 331.1747. **(EA)** Anal. Calcd for C₂₁H₂₂BNO₂: C, 76.15; H, 6.69; N, 4.23. Found: C, 76.33; H, 6.84; N, 4.44.

2-(1-Boronic acid pinacolate ester-4-methoxy)phenylpyridine (5k):



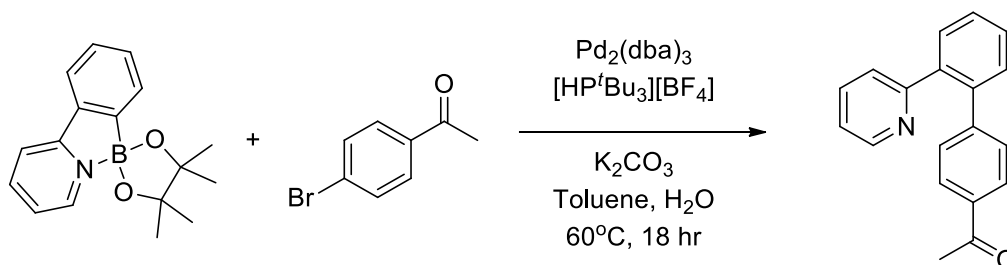
Synthesized according to the general procedure and eluted with 7:3 EtOAc/Hexanes mixture to afford an off-white powder (126 mg, 81% yield). **¹H NMR** (500 MHz, CDCl₃): δ 8.57 (d, *J* = 5.2 Hz, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.26–7.22 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 1.41 (s, 12H). **¹³C NMR** (125 MHz, CDCl₃): δ 162.79, 156.67, 142.97, 141.92, 130.04, 122.83, 121.46, 116.76, 116.37, 113.82, 80.21, 55.38, 27.17 (*C–B* bond not observed). **¹¹B NMR** (128 MHz, CDCl₃): δ 12.7. **HRMS (EI)** calculated for C₁₈H₂₂BNO₃: 311.1693. Found: 311.1696. **(EA)** Attempts to obtain elemental analyses with acceptable carbon content were unsuccessful, while hydrogen and nitrogen content are in the acceptable range. Anal. Calcd for C₁₈H₂₂BNO₃: C, 69.47; H, 7.13; N, 4.50. Found: C, 69.02; H, 7.09; N, 4.50.

2-(3-Boronic acid pinacolate ester-furan-2-yl)pyridine (5n):



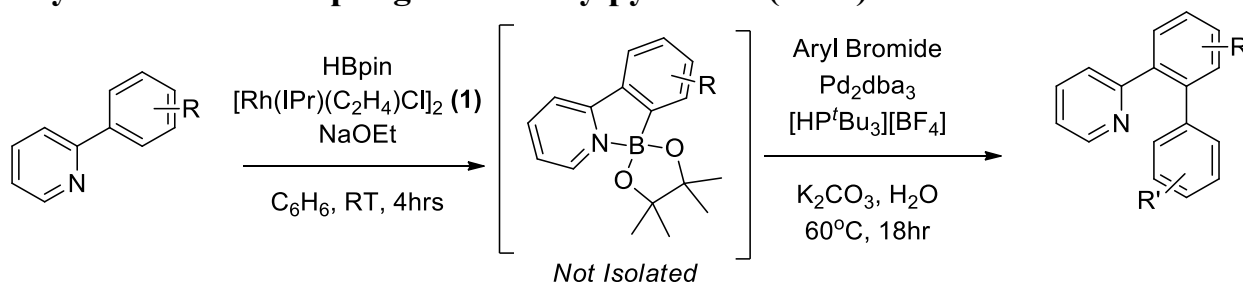
Synthesized according to the general procedure. ¹H NMR indicated near quantitative conversion of the starting material 2-(furan-yl)pyridine to the product **5n**, however the final product was not able to be isolated on the alumina column and complete decomposition was observed by ¹¹B and ¹H NMR upon attempted purification. Characterization of the crude reaction mixture: **¹H NMR** (400 MHz, C₆D₆): δ 8.45 (d, *J* = 4.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.16 (peak overlaps with C₆D₆ solvent, presence confirmed by 2-D COSY NMR), 7.10 (t, *J* = 6.9 Hz, 1H), 6.70 (d, *J* = 1.6 Hz, 1H), 6.58–6.54 (m, 1H), 1.23 (s, 12H). **¹³C NMR** (100 MHz, C₆D₆): δ 158.18, 149.71, 149.24, 142.94, 136.43, 122.31, 121.01, 116.37, 82.88, 24.95, 24.67 (*C–B* bond not observed). **¹¹B NMR** (128 MHz, C₆D₆): δ 30.7. **HRMS (EI)** calculated for C₁₅H₁₈BNO₃: 271.1380. Found: 271.1391.

Suzuki–Miyaura Cross–Coupling of Isolated 2-Phenylpyridine (6a)⁴



In an oven-dried 50 mL round bottom flask equipped with a stir bar, borylated 2-phenylpyridine (**5a**) (110 mg, 0.39 mmol) 4-bromoacetophenone (92.7 mg, 0.47 mmol), K_2CO_3 (161.5 mg, 1.17 mmol), $[HP^tBu_3][BF_4]$ (11.3 mg, 0.039 mmol) and $Pd_2(dba)_3$ (9 mg, 0.0098 mmol) were mixed in 4 mL of toluene. The flask was sealed with a rubber septum and removed from the glovebox. Degassed H_2O (21 μL , 1.17 mmol) was added via syringe. The reaction vessel was placed in an oil bath at 60 °C and allowed to stir for 18 hours. Afterwards, the mixture was allowed to cool to room temperature and the crude mixture filtered through Celite with EtOAc. The filtrate was concentrated and isolated by column chromatography (4:1 Hexanes/EtOAc) to afford a yellow solid (87 mg, 82% yield). 1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 4.3 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.73–7.71 (m, 1H), 7.51 (dd, J = 8.7, 5.3 Hz, 2H), 7.47–7.42 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.15–7.12 (m, 1H), 6.95 (d, J = 7.8 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.91, 158.97, 149.65, 146.55, 139.73, 139.57, 135.62, 135.43, 130.74, 130.40, 129.97, 128.75, 128.42, 128.25, 125.29, 121.70, 26.70. HRMS (EI) calculated for $C_{19}H_{15}NO$: 273.1154. Found: 273.1165.

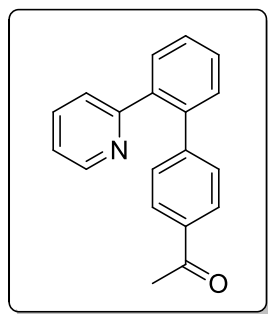
General Arylation Procedure for the one-pot C–H Borylation and Suzuki–Miyaura Cross–Coupling of 2–Phenylpyridines (**6a–h**)



To an oven dried 50 mL round bottom flask equipped with a stir bar, NaOEt (8.5 mg, 0.125 mmol) was added. In separate vials, **1** (5.55 mg, 0.005 mmol, 1 mol%) and phenyl pyridine (0.5 mmol) were each taken up in 2 mL of benzene each and sequentially added to the round bottom flask. HBpin (128 mg, 1 mmol) was taken up in 0.6 mL of benzene and added to the stirring

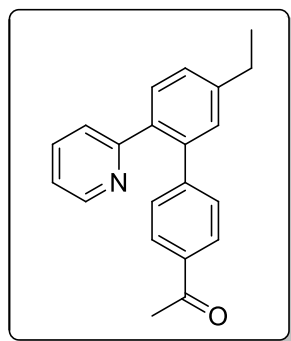
solution (total reaction volume = 4.6 mL, 0.11 M concentration). The flask was sealed with a septum and vigorously stirred in the glovebox for 4 hours. After this time, aryl bromide (0.55 mmol, 1.1 eq), K₂CO₃ (207 mg, 1.5 mmol), [HP^tBu₃][BF₄] (14.5 mg, 0.05 mmol, 10 mol%) and Pd₂(dba)₃ (11.5 mg, 0.0125 mmol, 2.5 mol%) were added to the reaction mixture. The flask was sealed with a rubber septum and removed from the glove box. Degassed H₂O (27 μL, 1.5 mmol) was added through the septum via syringe. The reaction flask was placed in an oil bath at 60 °C and allowed to stir for 18 hours. Afterwards, the mixture was allowed to cool to room temperature and filtered through Celite in EtOAc. The filtrate was concentrated and the product isolated by column chromatography on silica gel. Occasionally, traces of pinacol are present in the ¹H NMR spectra of compounds **6a-6h**.

Synthesis of 2-(2-(4-acetylphenyl))phenylpyridine (**6a**)



Synthesized according to the general arylation procedure using 2-phenylpyridine (78 mg, 0.5 mmol) and 4-bromoacetophenone (109 mg, 0.55 mmol). Isolated eluting with a 4:1 Hexanes/EtOAc solvent mixture to afford an off-white solid (93 mg, 68% yield). Spectral data are consistent with those reported above.

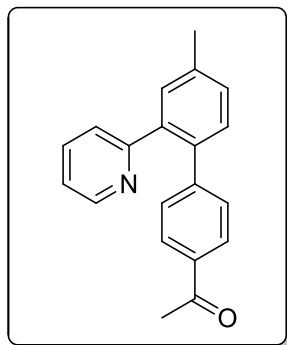
Synthesis of 2-(2-(4-acetylphenyl)-4-ethylphenyl)pyridine (**6b**)



Synthesized according to the general arylation procedure using 2-(4-ethylphenyl)pyridine (92 mg, 0.5 mmol) and 4-bromoacetophenone (109 mg, 0.55 mmol). The product was isolated by column chromatography eluting with a 98:2 CH₂Cl₂/MeOH solvent mixture to afford a yellow oil (100 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 4.7 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.42 (td, *J* = 7.7, 1.5 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.28–7.26 (m, 3H), 7.12 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 2.59 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H), trace hexanes observed at 1.27 ppm. ¹³C NMR (100 MHz, CDCl₃): δ 198.01, 159.08, 149.63, 146.93, 145.05, 139.57, 137.25, 135.60, 135.45, 130.85,

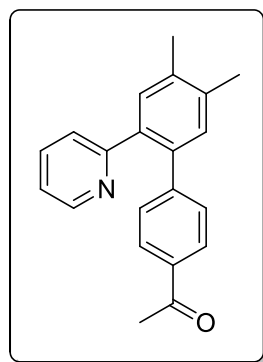
130.04, 130.01, 128.27, 128.05, 125.33, 121.53, 28.78, 26.73, 15.65. **HRMS (EI)** calculated for $C_{21}H_{19}NO$: 301.1467. Found: 301.1455.

Synthesis of 2-(2-(4-acetylphenyl)-5-methylphenyl)pyridine (6c)



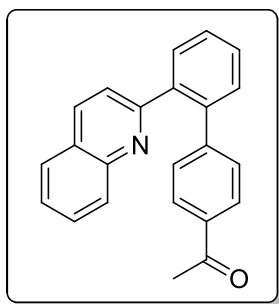
Synthesized according to the general arylation procedure using 2-(3-methylphenyl)pyridine (85 mg, 0.5 mmol) and 4-bromoacetophenone (109 mg, 0.55 mmol). The product was isolated by column chromatography eluting with a 4:1 Hexanes/EtOAc solvent mixture to afford an off-white solid (62 mg, 44% yield). **1H NMR** (400 MHz, $CDCl_3$): δ 8.62 (d, J = 4.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.40 (td, J = 7.7, 1.7 Hz, 1H), 7.34–7.29 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.13–7.10 (m, 1H), 6.89 (d, J = 7.9 Hz, 1H), 2.57 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.95, 159.15, 149.68, 146.60, 139.56, 138.40, 136.80, 135.58, 135.34, 131.41, 130.42, 130.01, 129.54, 128.26, 125.41, 121.67, 26.70, 21.25. **HRMS (EI)** calculated for $C_{20}H_{17}NO$: 287.1310. Found: 287.1319.

Synthesis of 2-(2-(4-acetylphenyl)-4,5-dimethylphenyl)pyridine (6d)



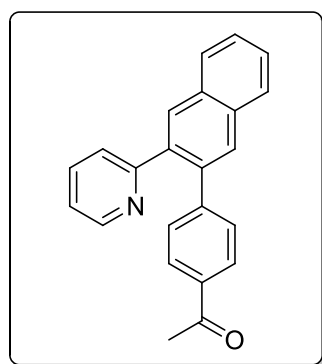
Synthesized according to the general arylation procedure using 2-(3,4-dimethylphenyl)pyridine (92 mg, 0.5 mmol) and 4-bromoacetophenone (109 mg, 0.55 mmol). The product was isolated by column chromatography eluting with a 3:1 Hexanes/EtOAc solvent mixture to afford an off-white solid (82 mg, 54% yield). **1H NMR** (400 MHz, $CDCl_3$): δ 8.61 (d, J = 4.5 Hz, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.49 (s, 1H), 7.37 (t, J = 8.4 Hz, 1H), 7.24 (s, 1H), 7.22 (d, J = 5.9 Hz, 2H), 7.10–7.07 (m, 1H), 6.86 (d, J = 7.9 Hz, 1H), 2.56 (s, 3H), 2.36 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.93, 159.04, 149.61, 146.69, 137.32, 137.18, 137.03, 137.01, 135.48, 135.27, 131.94, 131.69, 129.97, 128.22, 125.38, 121.44, 26.66, 19.62, 19.51. **HRMS (EI)** calculated for $C_{21}H_{19}NO$: 301.1467. Found: 301.1459.

Synthesis of 2-(2-(4-acetylphenyl)phenyl)quinolone (6e)



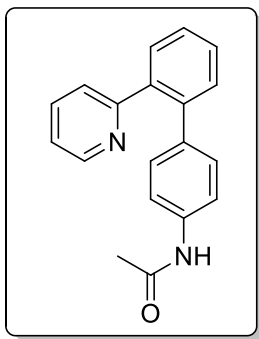
Synthesized according to the general arylation procedure using 2-phenylquinoline (103 mg, 0.5 mmol) and 4-bromoacetophenone (109 mg, 0.55 mmol). The product was isolated by column chromatography eluting with a 4:1 Hexanes/EtOAc solvent mixture to afford a yellow solid (81 mg, 50% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.87–7.83 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.76–7.71 (m, 2H), 7.57–7.52 (m, 3H), 7.51–7.48 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 2.54 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 197.92, 159.49, 148.35, 146.37, 140.08, 139.76, 135.62, 135.33, 131.15, 130.46, 130.13, 129.71 (2 carbons as determined by HSQC), 129.13, 128.69, 128.36, 127.64, 126.75, 126.67, 123.42, 26.70. **HRMS (EI)** calculated for C₂₃H₁₇NO: 323.1310. Found: 323.1299.

Synthesis of 2-(3-(4-acetylphenyl)naphthalen-2-yl)pyridine (6f)



Synthesized according to the general arylation procedure using 2-(2-naphthyl)pyridine (2 mg, 0.5 mmol) and 4-bromoacetophenone (109 mg, 0.55 mmol). The product was isolated by column chromatography eluting with a 3:1 Hexanes/EtOAc solvent mixture to afford a yellow solid (95 mg, 59% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.63 (d, *J* = 4.3 Hz, 1H), 8.19 (s, 1H), 7.95–7.89 (m, 3H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.55–7.53 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.16–7.13 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 2.59 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 197.95, 158.94, 149.68, 146.61, 137.72, 137.58, 135.68, 135.47, 133.21, 133.03, 130.46, 130.08, 129.86, 128.36, 128.28, 127.97, 127.13, 126.93, 125.42, 121.76, 26.72. **HRMS (EI)** calculated for C₂₃H₁₇NO: 323.1310. Found: 323.1322.

Synthesis of 2-(2-(2-acetanilide)phenyl)pyridine (6g)

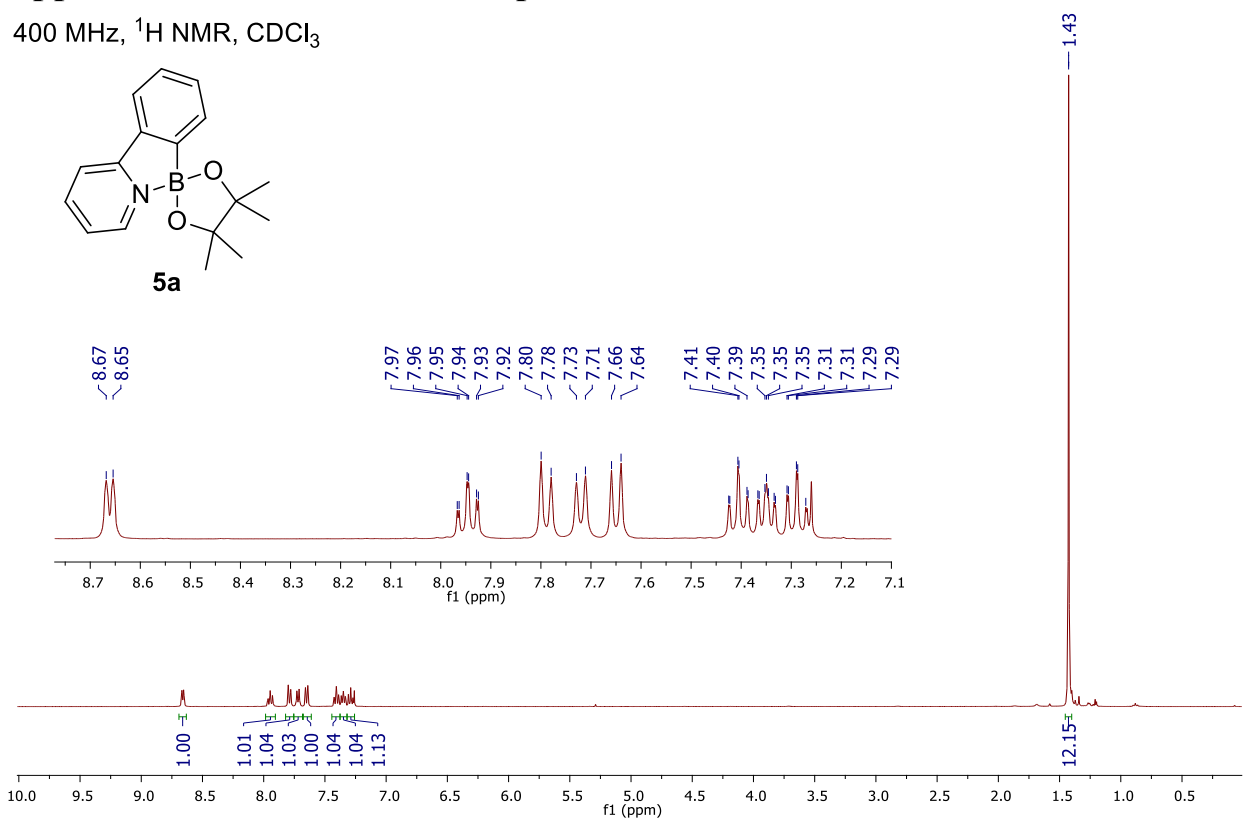


Synthesized according to the general arylation procedure using 2-phenylpyridine (78 mg, 0.5 mmol, 1 eq) and 4-bromoacetanilide (118 mg, 0.55 mmol, 1.1 eq). The product was isolated by column chromatography eluting with a 3:1 EtOAc/Hexanes solvent mixture to afford an off-white solid (66 mg, 46% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.72 (d, J = 5.1 Hz, 1H), 8.04 (d, J = 7.3 Hz, 2H), 7.90 (s, 1H), 7.67 (s, 4H), 7.50 (t, J = 7.3 Hz, 2H), 7.45–7.41 (m, 3H), 2.21 (s, 3H).

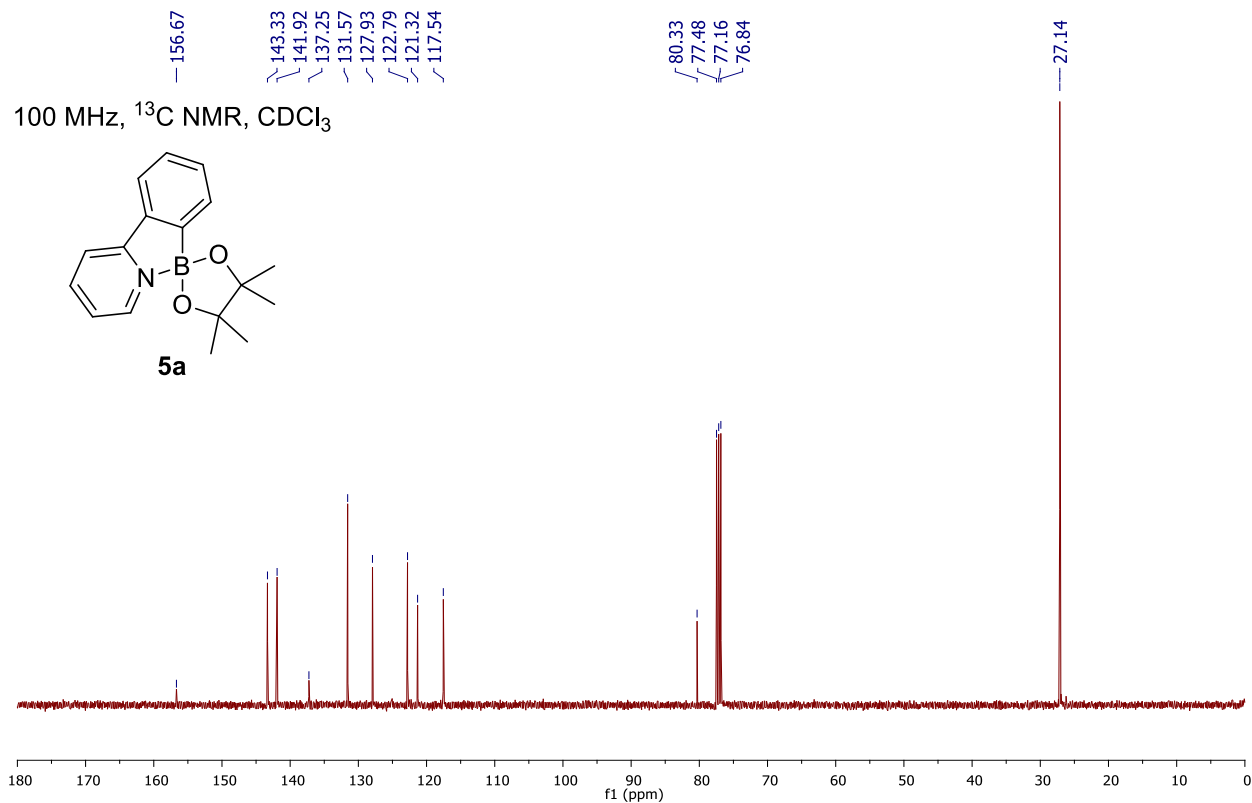
¹³C NMR (100 MHz, CDCl₃): δ 168.49, 158.34, 150.27, 148.62, 139.68, 139.00, 134.32, 129.19, 128.93, 127.87, 127.20, 120.52, 120.33, 119.98, 118.49, 24.83. **HRMS (EI)** calculated for C₁₉H₁₆N₂O: 288.1263.

Appendix I: ^1H and ^{13}C NMR Spectra

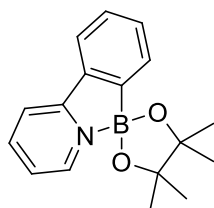
400 MHz, ^1H NMR, CDCl_3



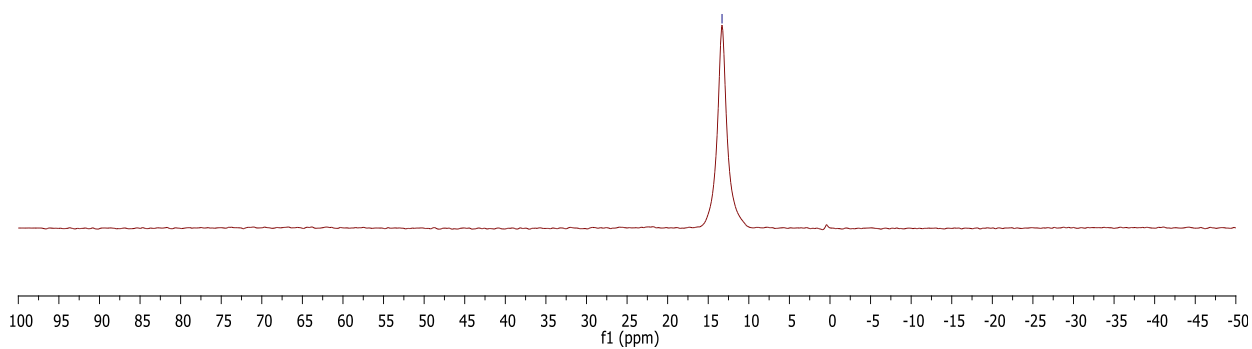
100 MHz, ^{13}C NMR, CDCl_3



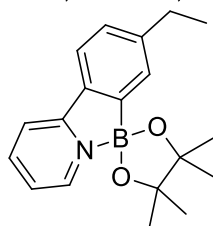
125 MHz, ^{11}B NMR, CDCl_3



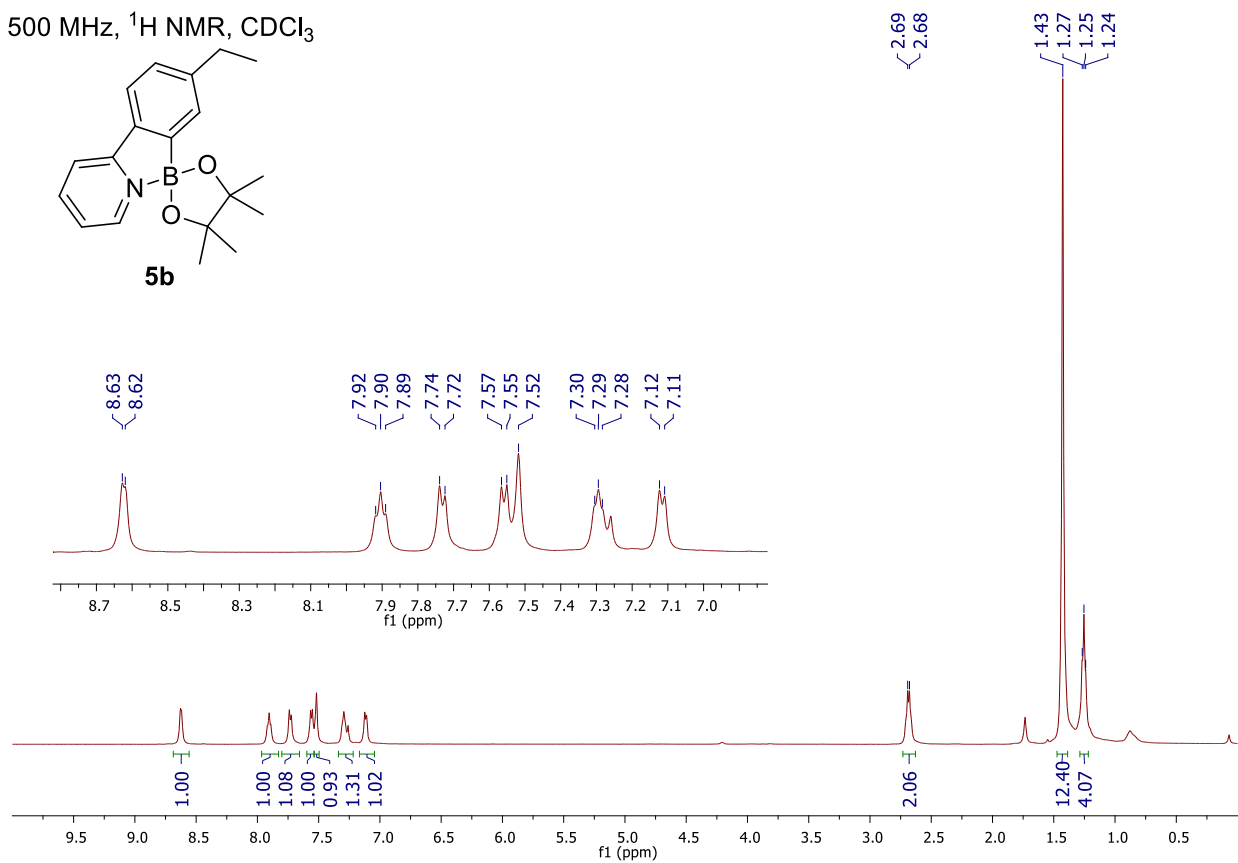
5a

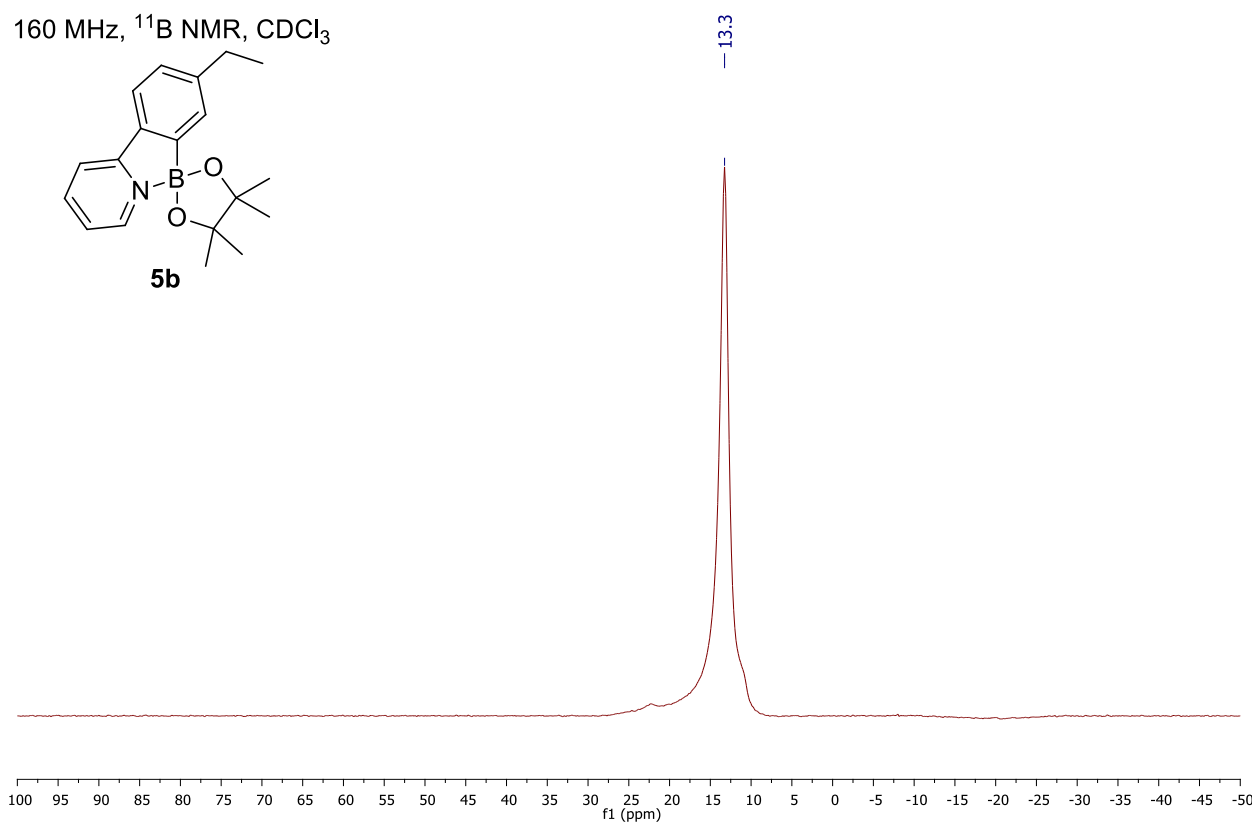
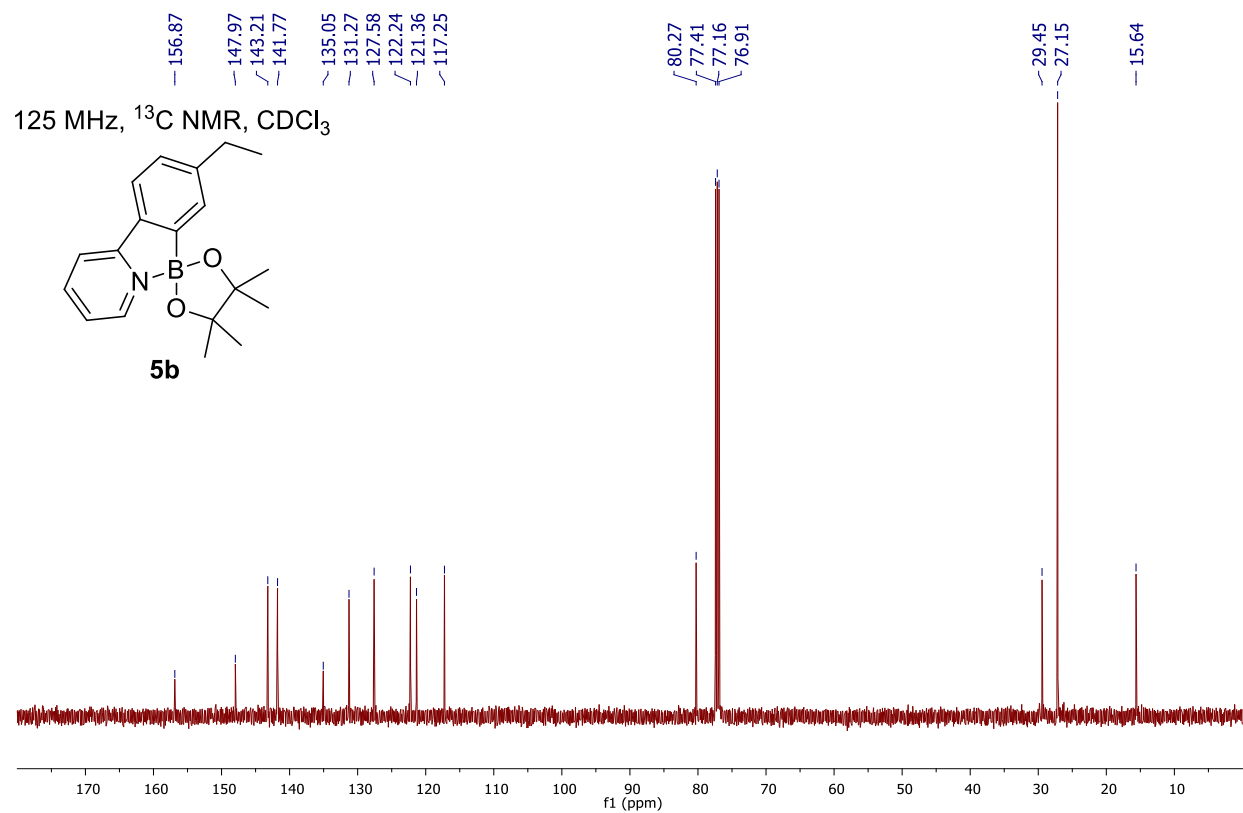


500 MHz, ^1H NMR, CDCl_3

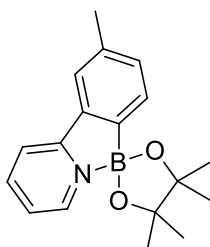


5b

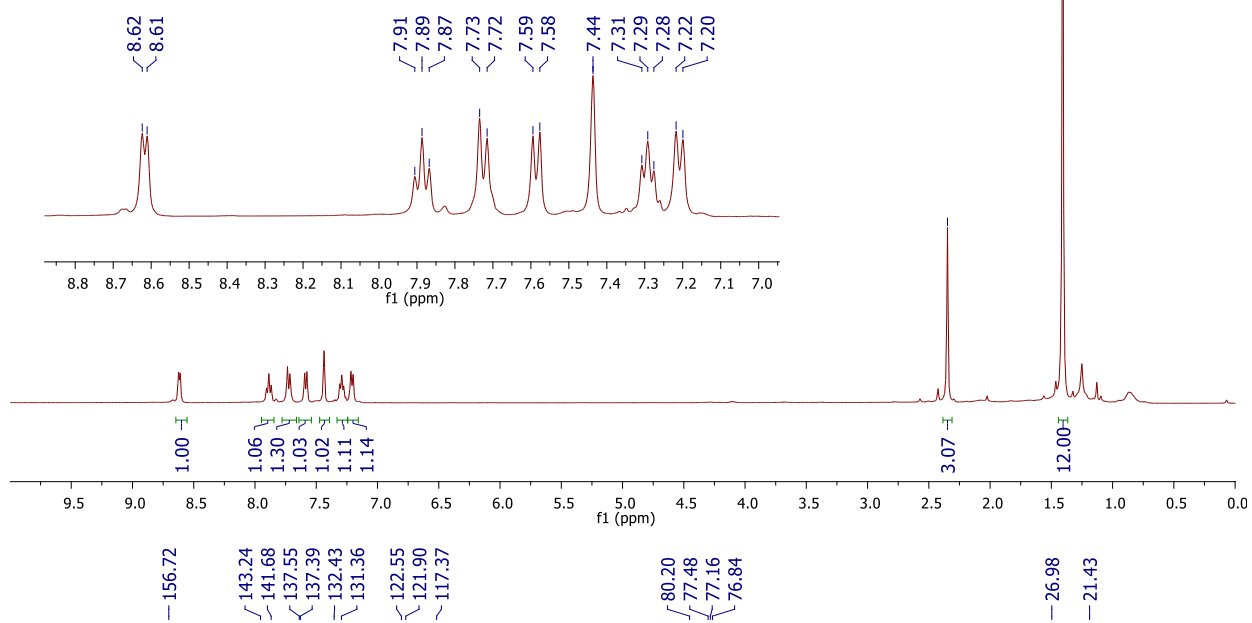




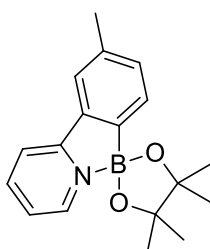
400 MHz, ^1H NMR, CDCl_3



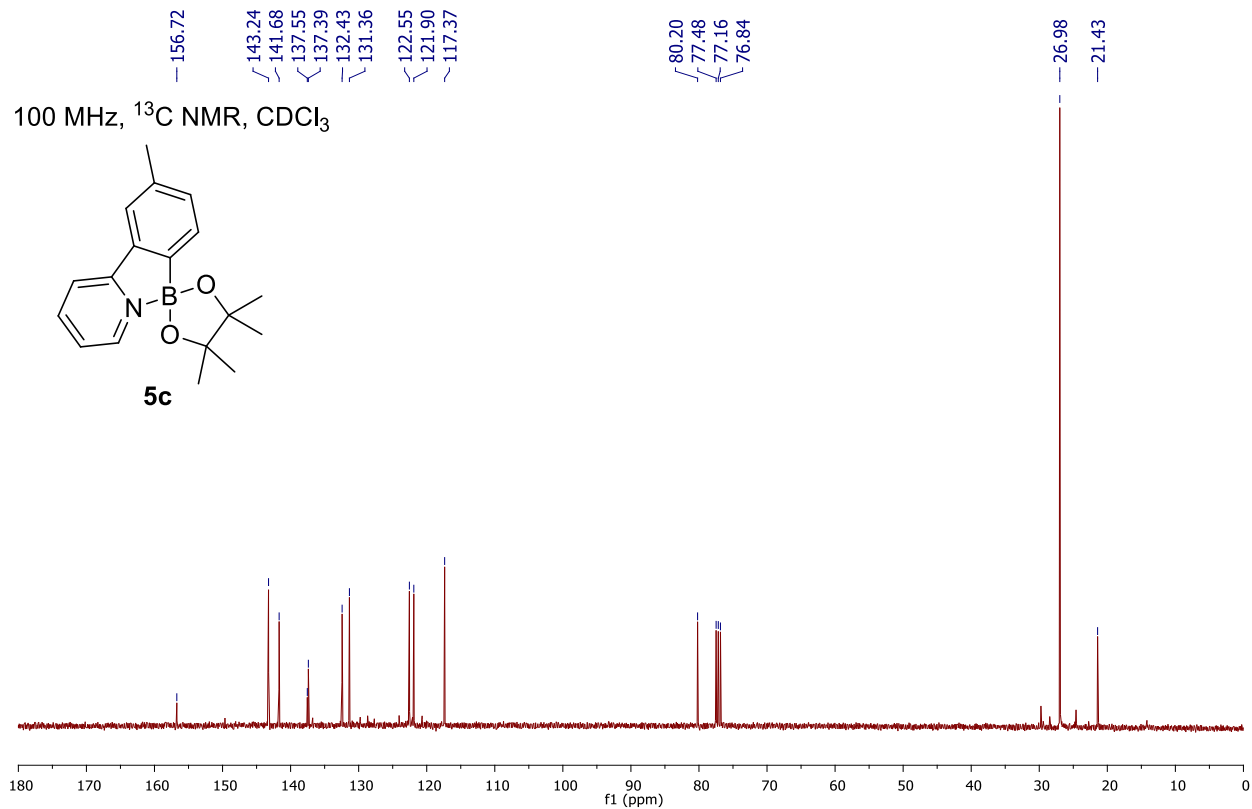
5c



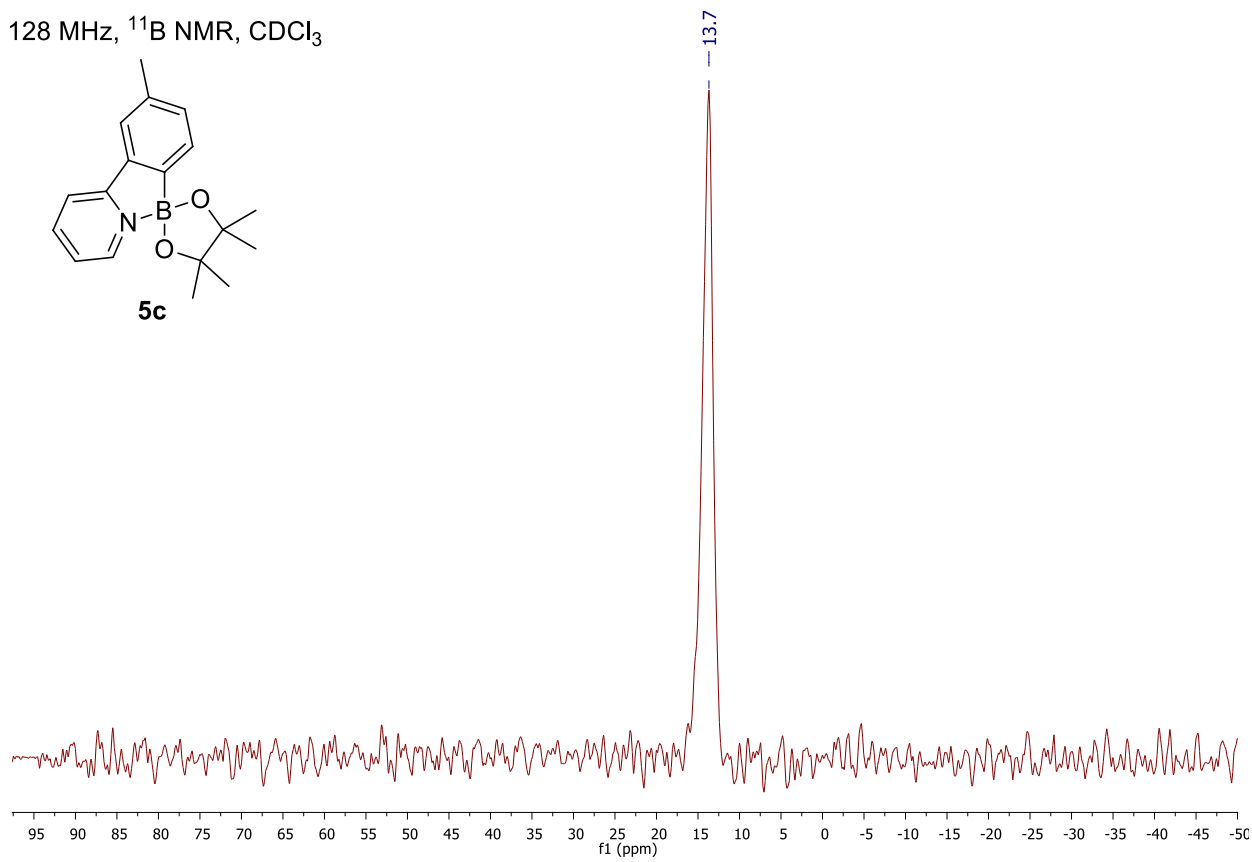
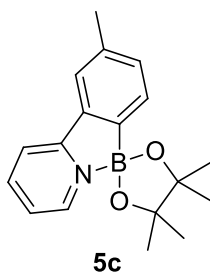
100 MHz, ^{13}C NMR, CDCl_3



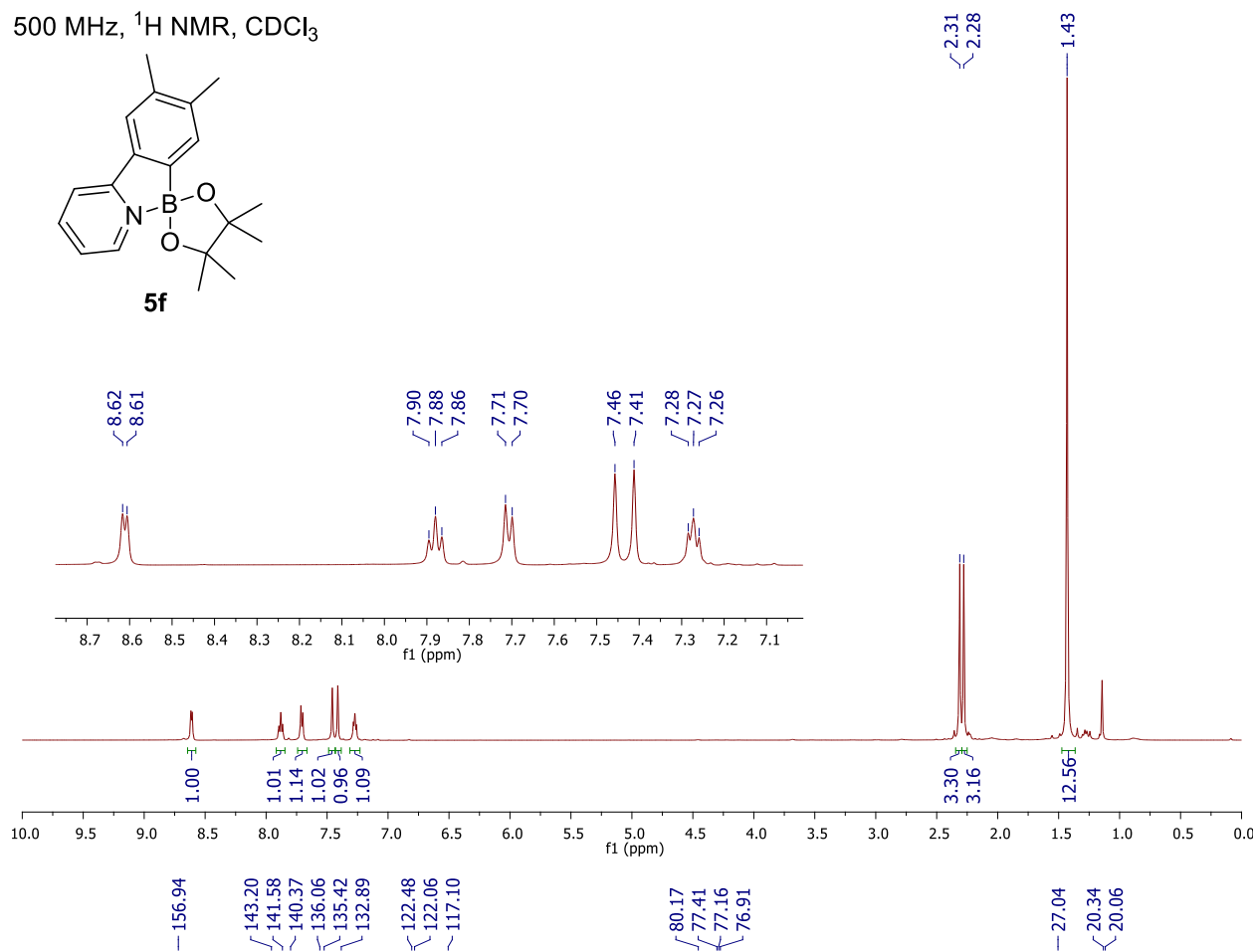
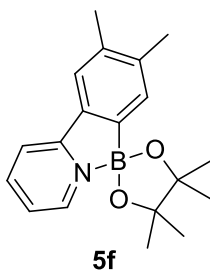
5c



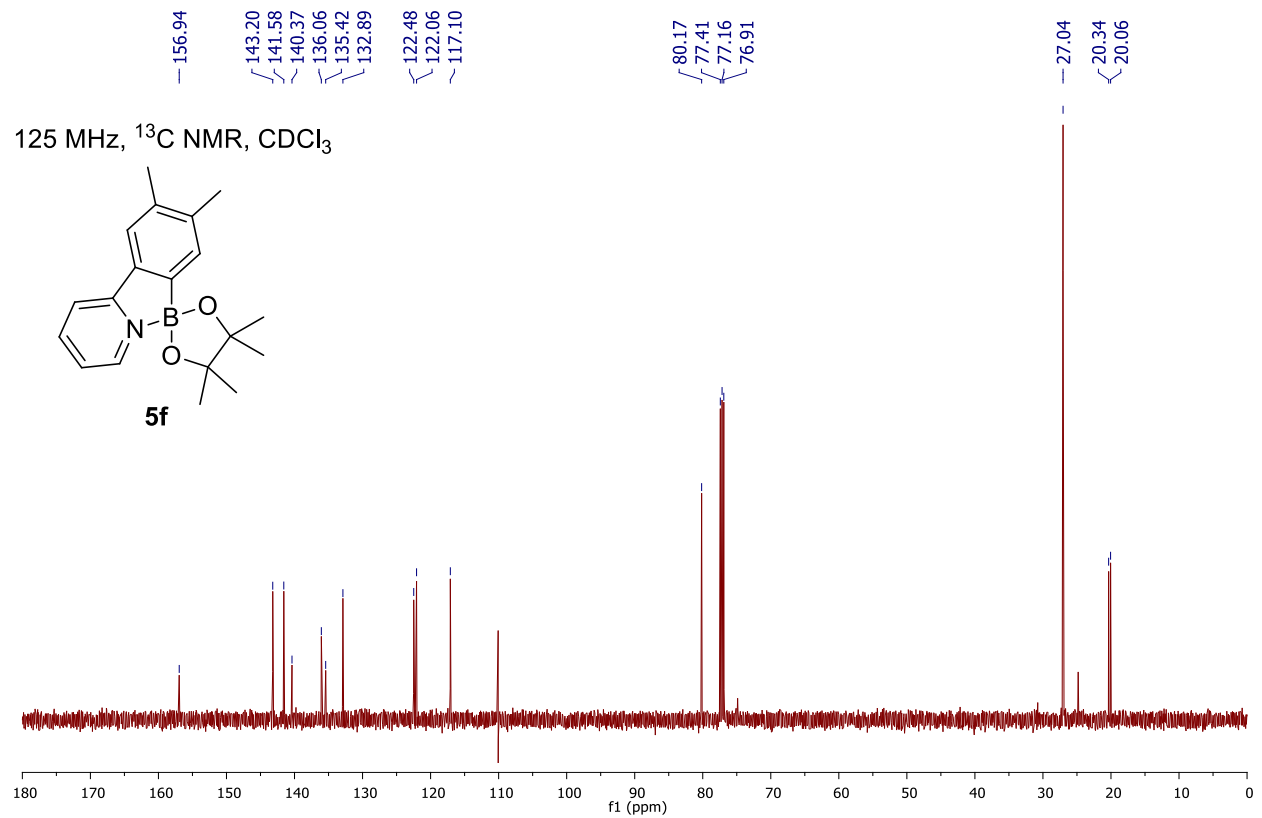
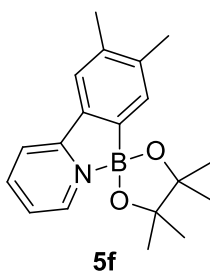
128 MHz, ^{11}B NMR, CDCl_3



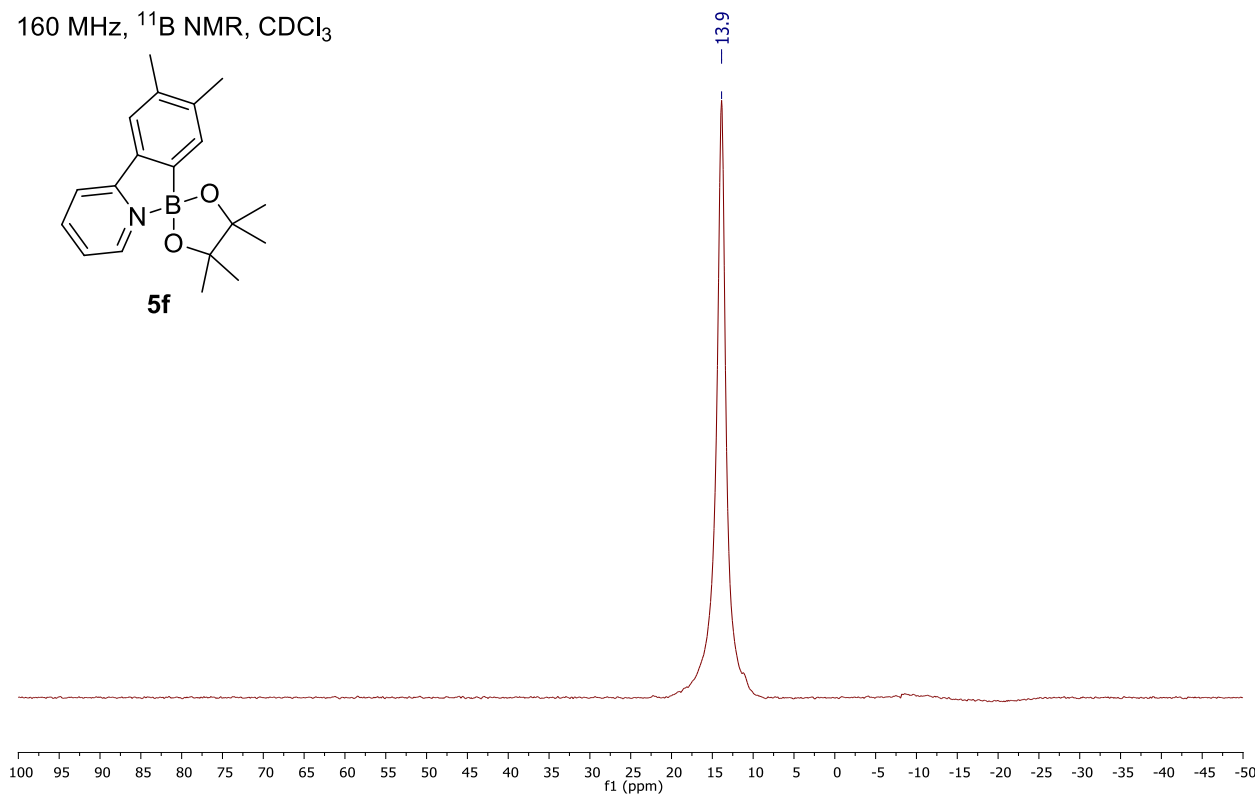
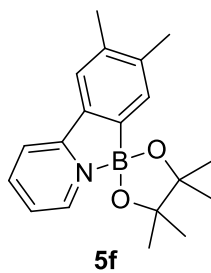
500 MHz, ^1H NMR, CDCl_3



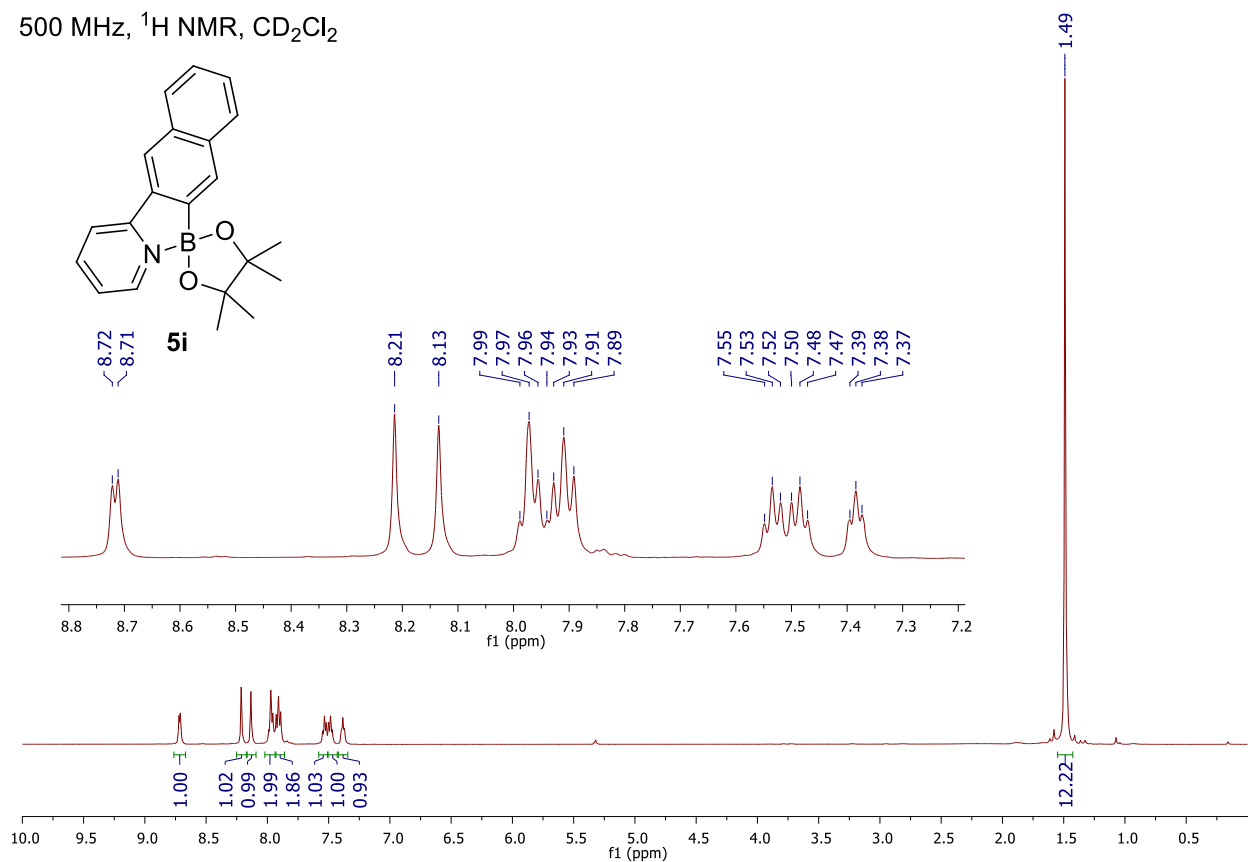
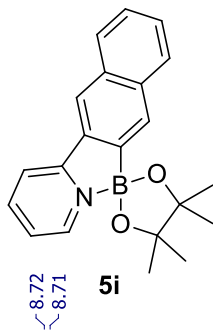
125 MHz, ^{13}C NMR, CDCl_3

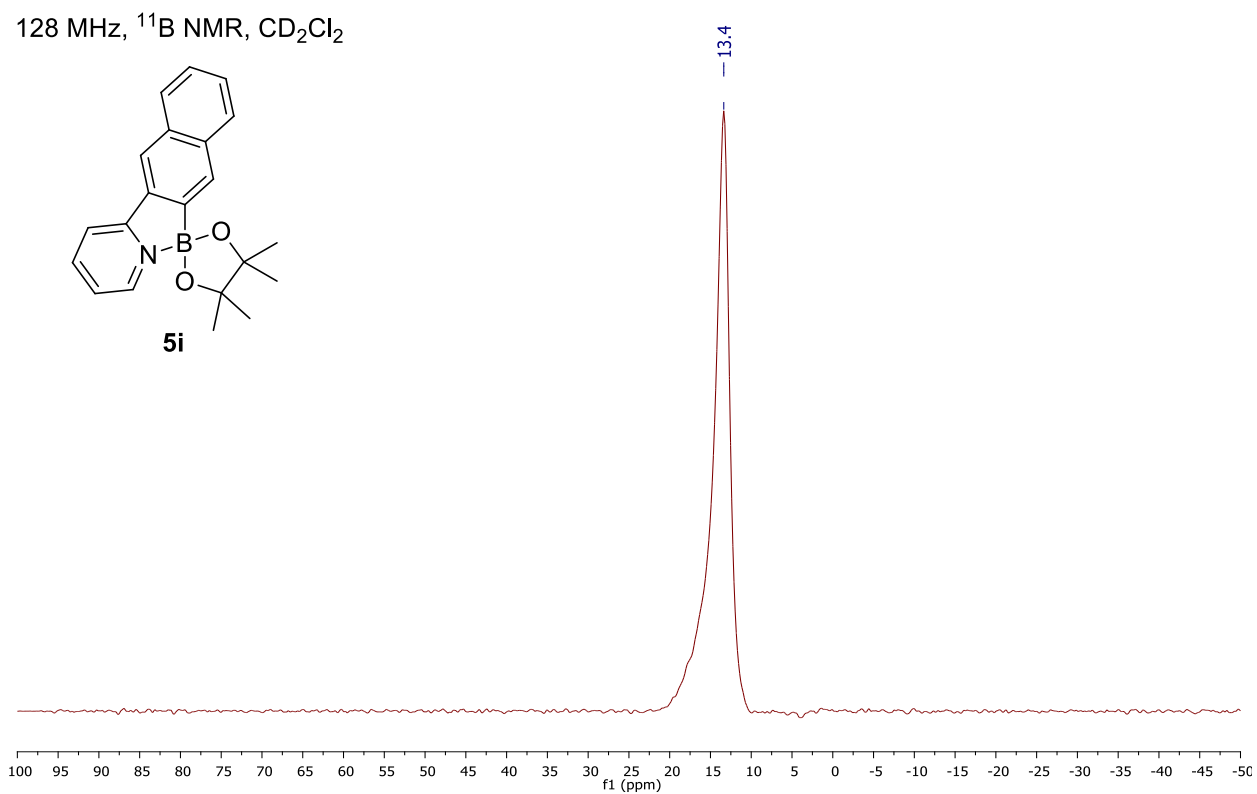
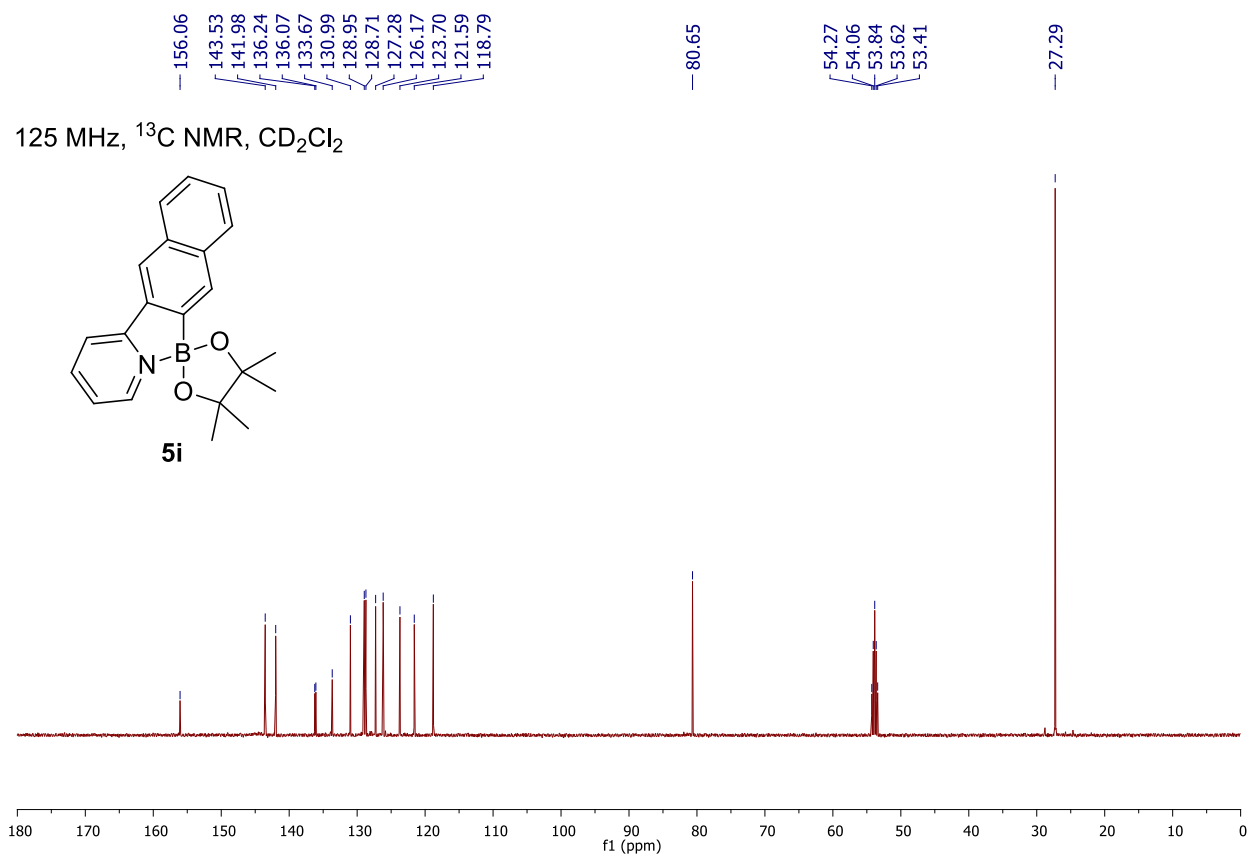


160 MHz, ^{11}B NMR, CDCl_3

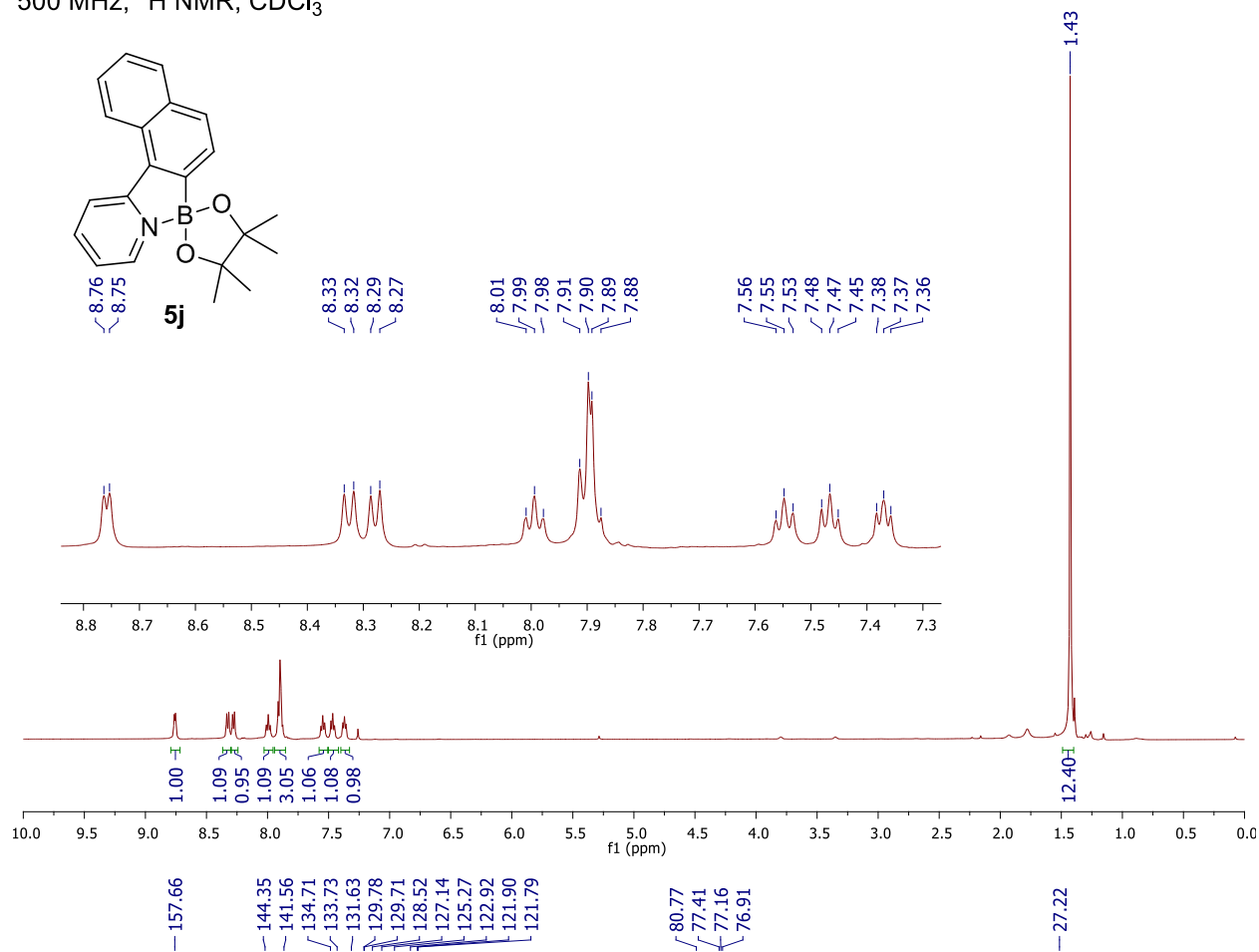


500 MHz, ^1H NMR, CD_2Cl_2

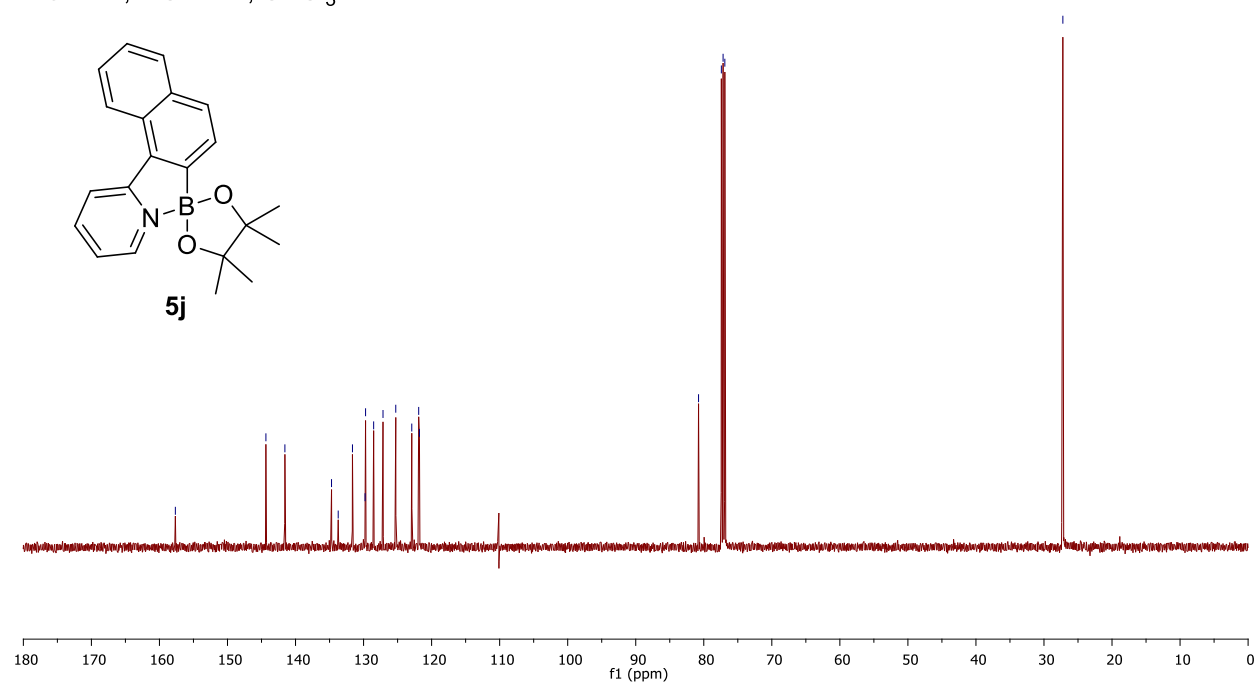




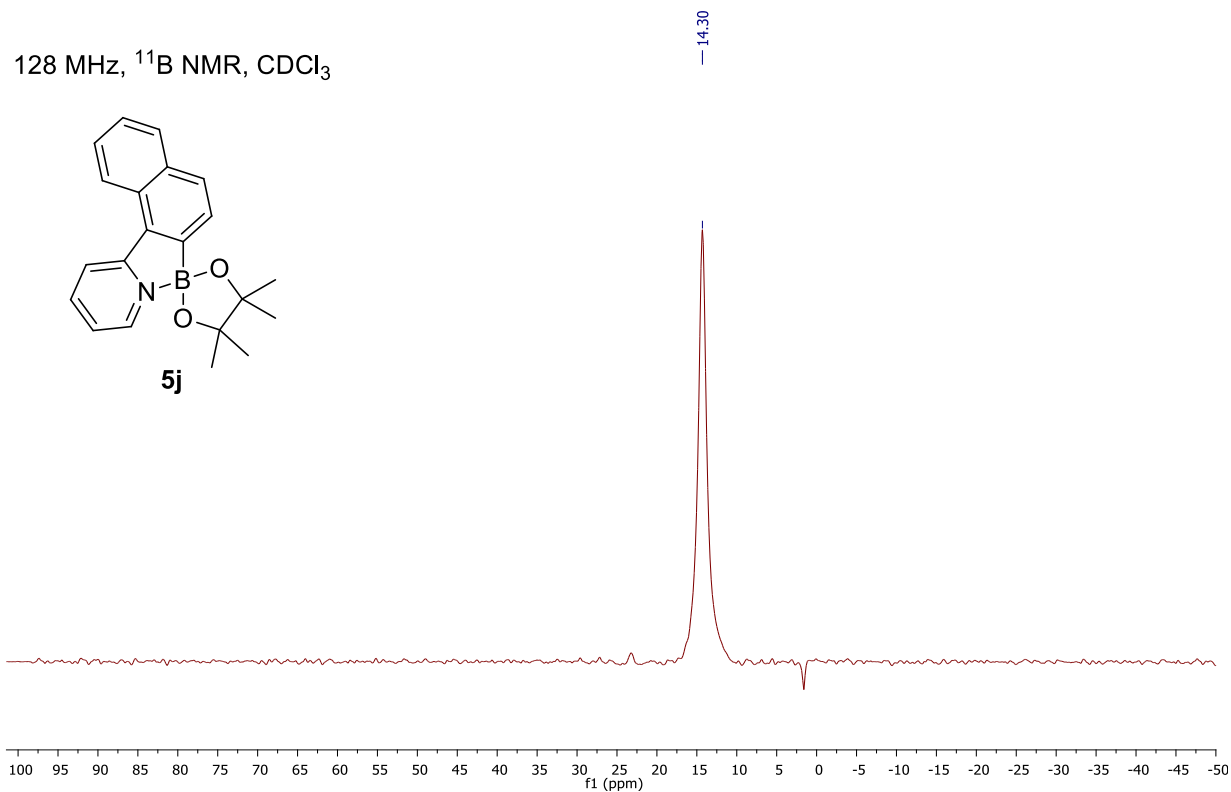
500 MHz, ^1H NMR, CDCl_3



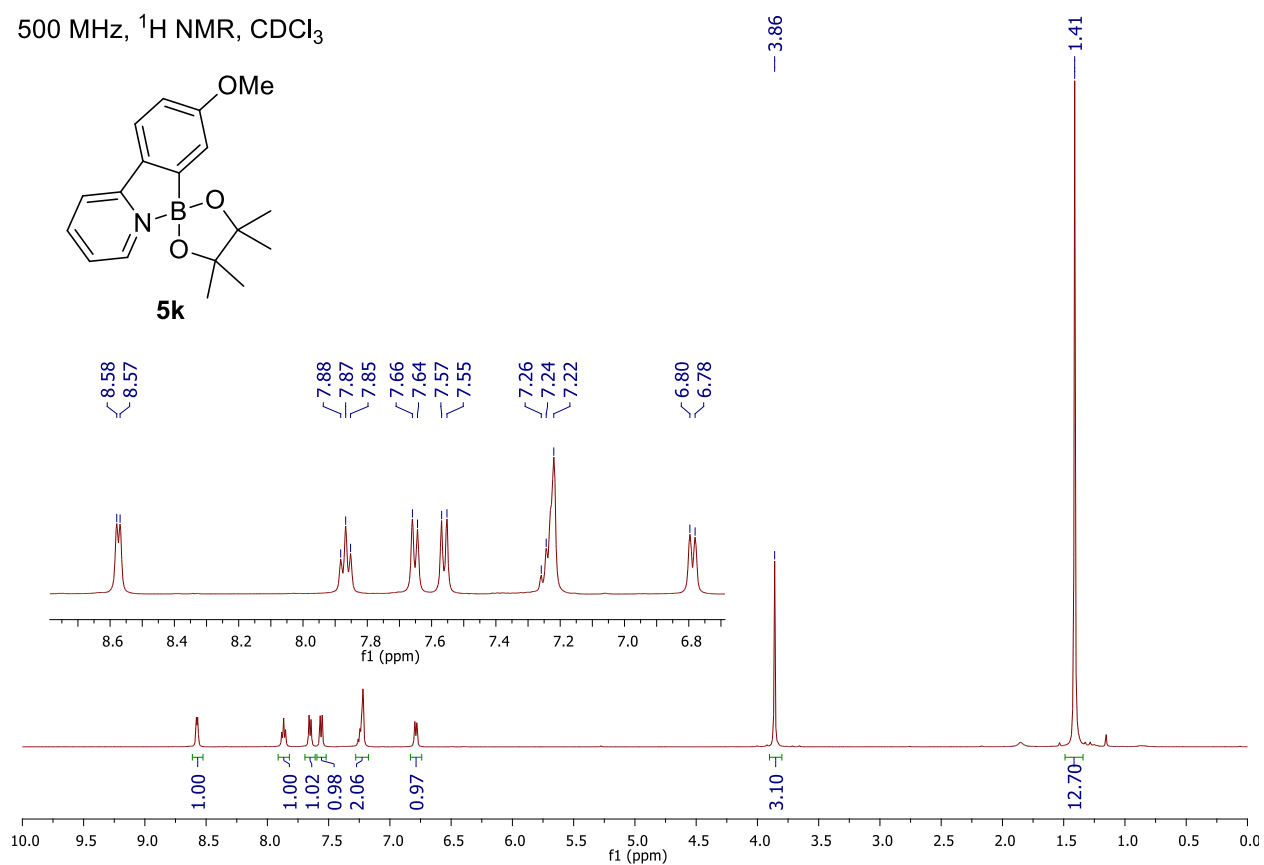
125 MHz, ^{13}C NMR, CDCl_3

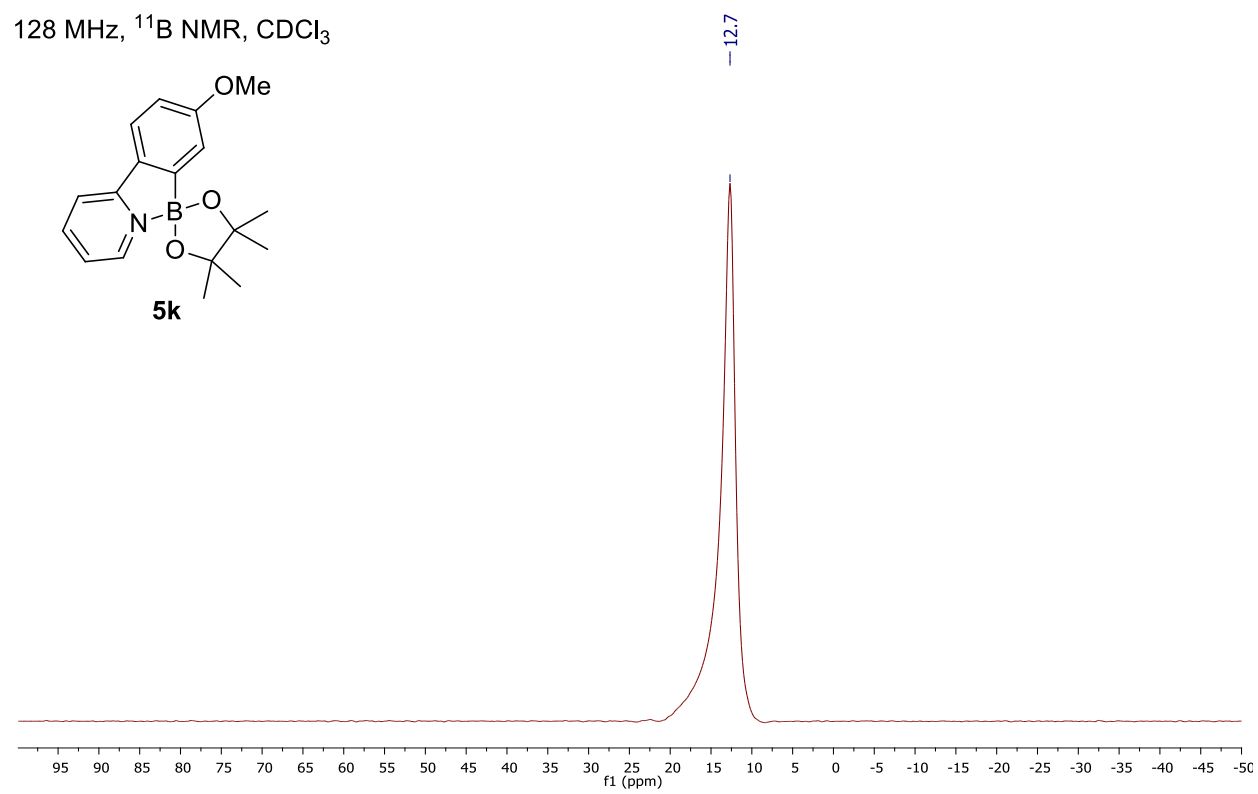
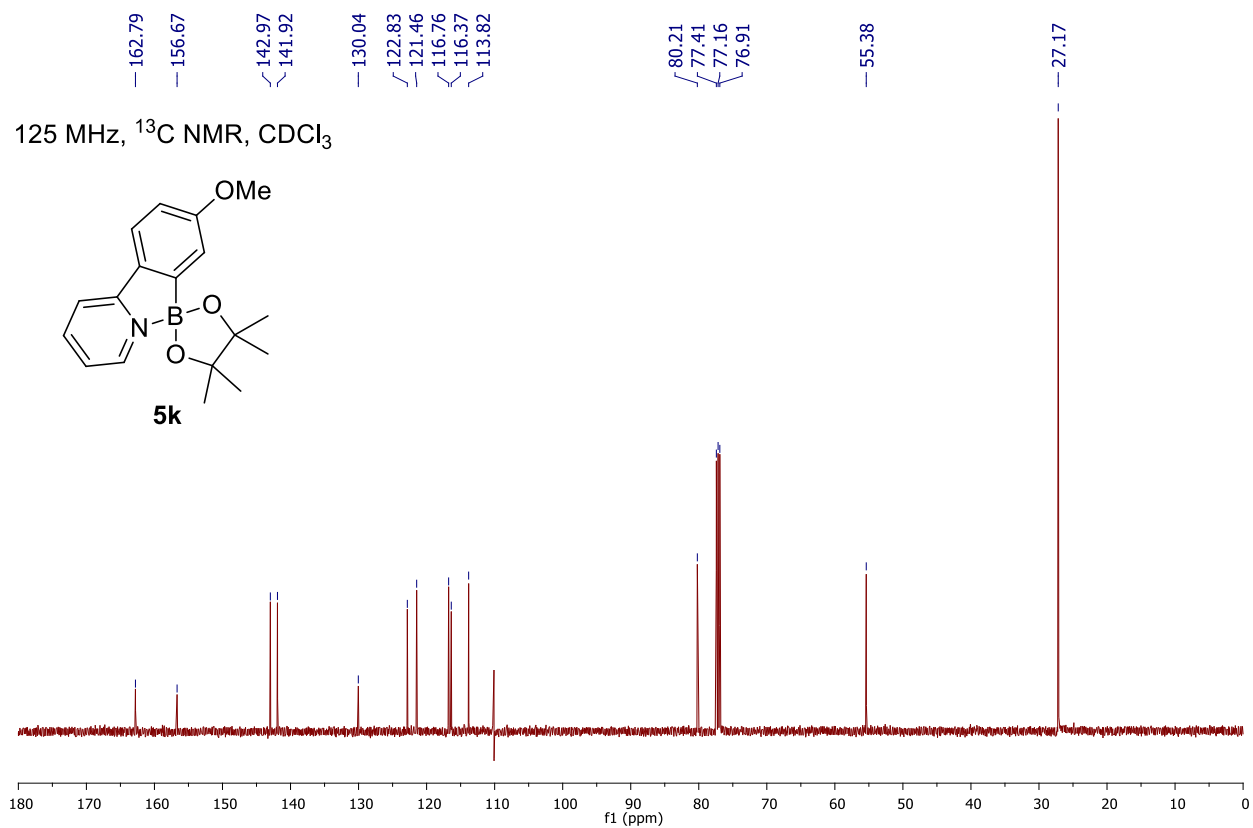


128 MHz, ^{11}B NMR, CDCl_3

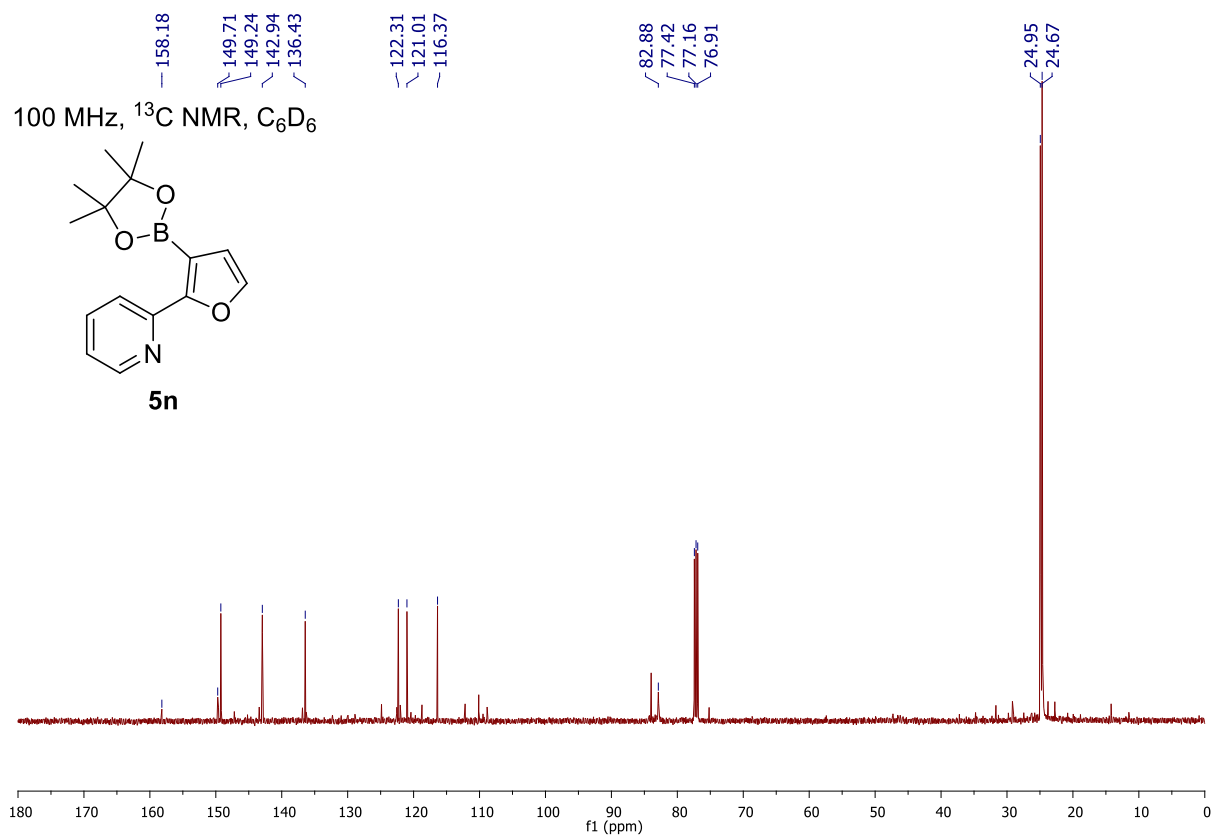
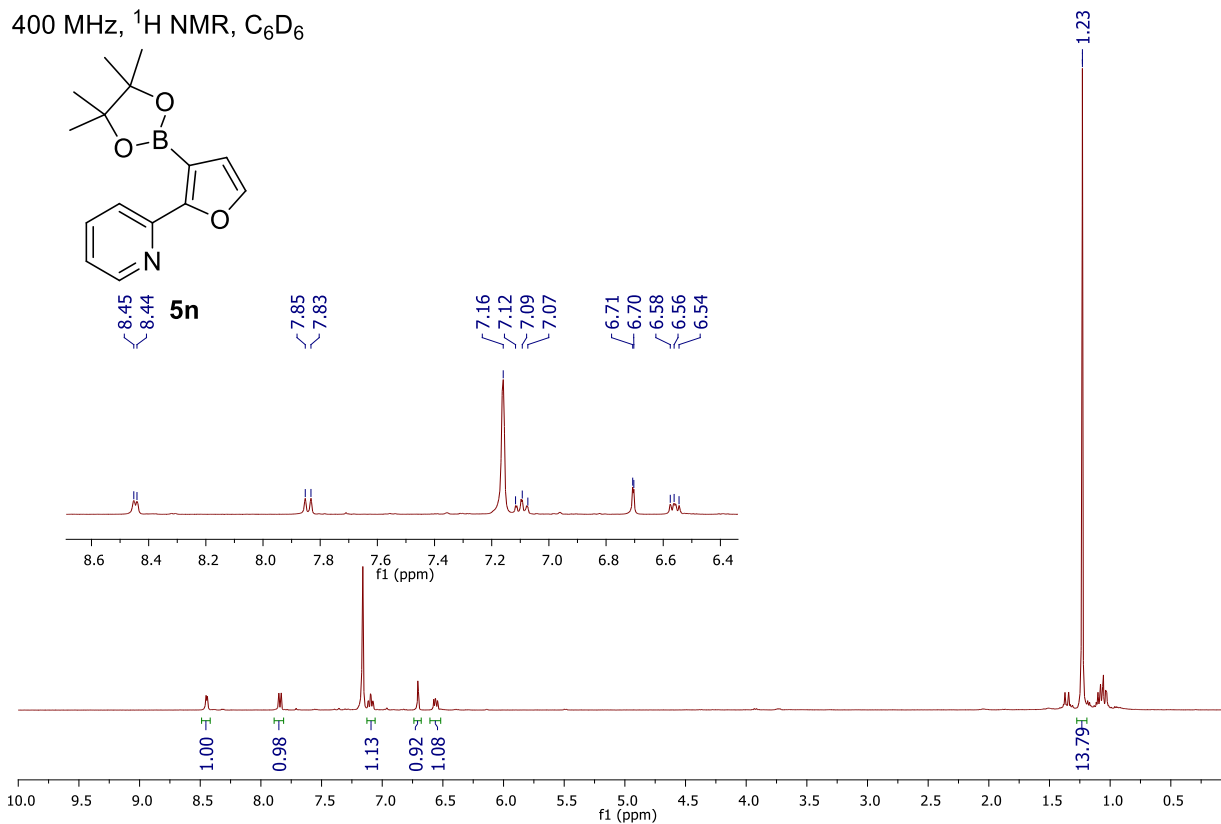


500 MHz, ^1H NMR, CDCl_3

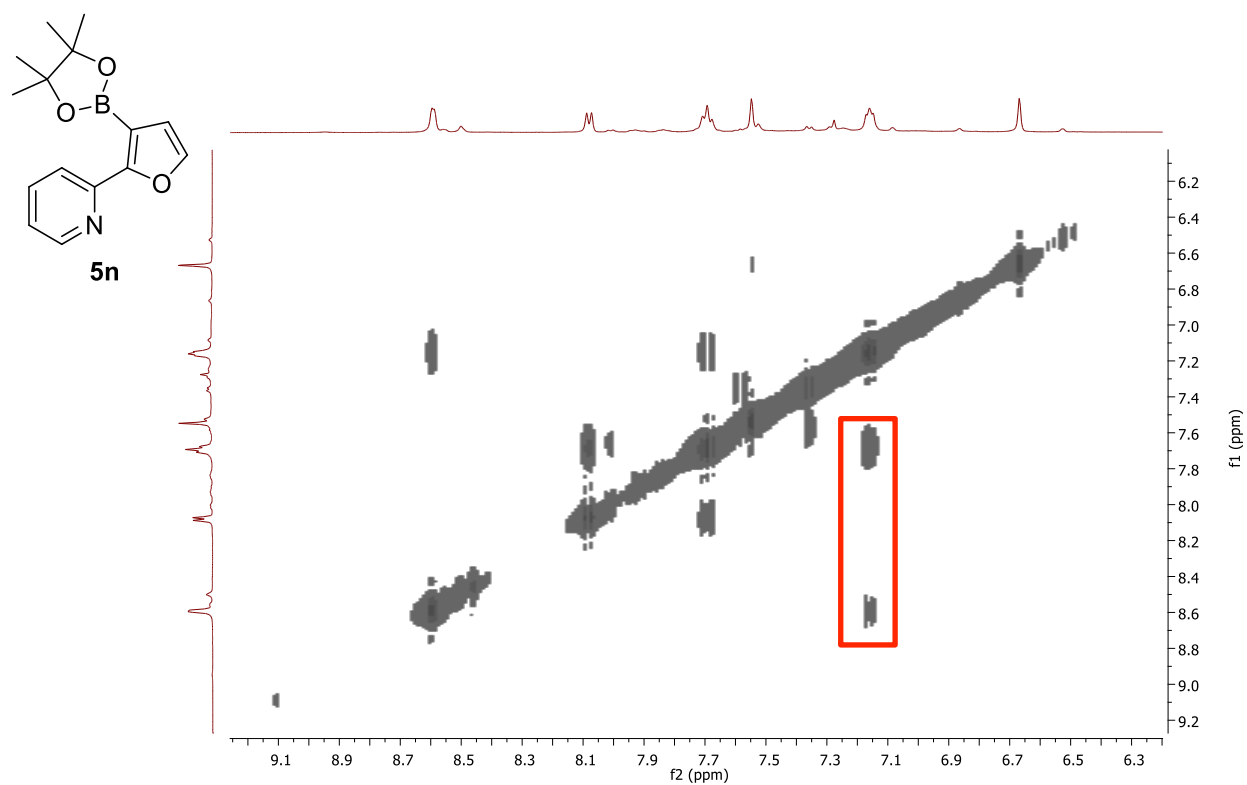
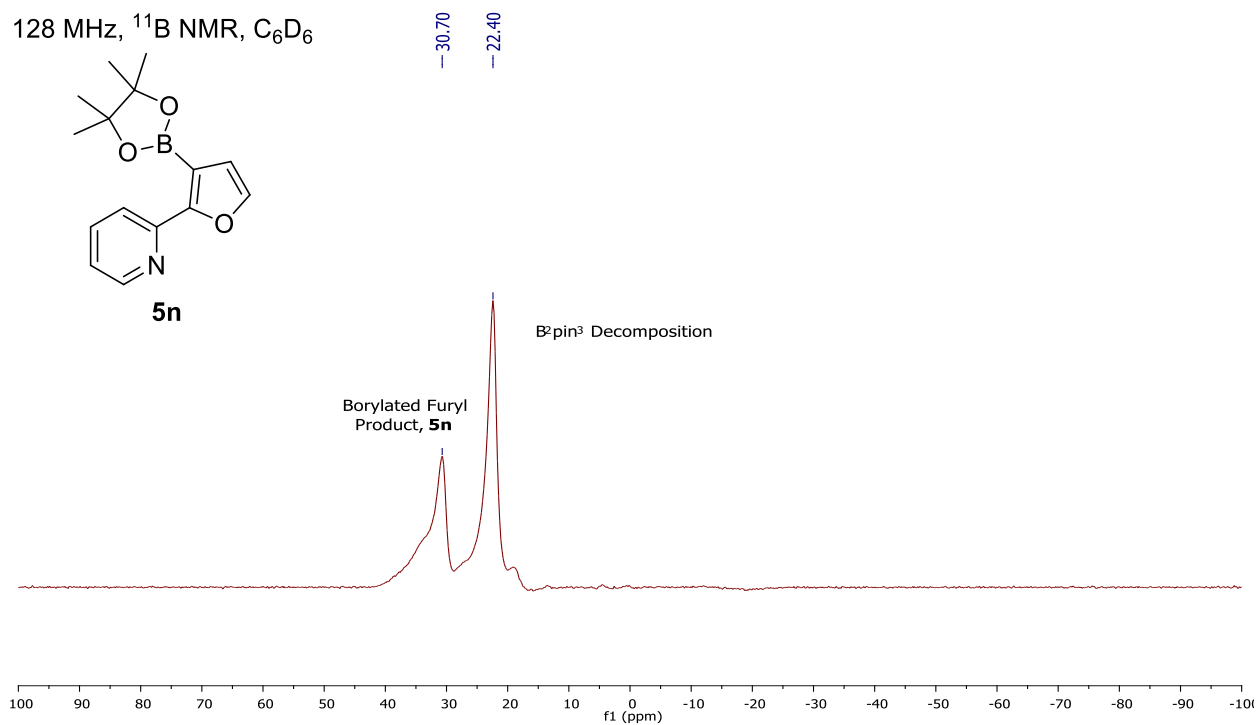
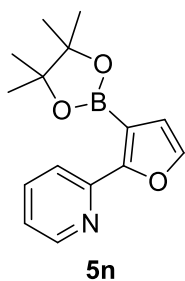




400 MHz, ^1H NMR, C_6D_6

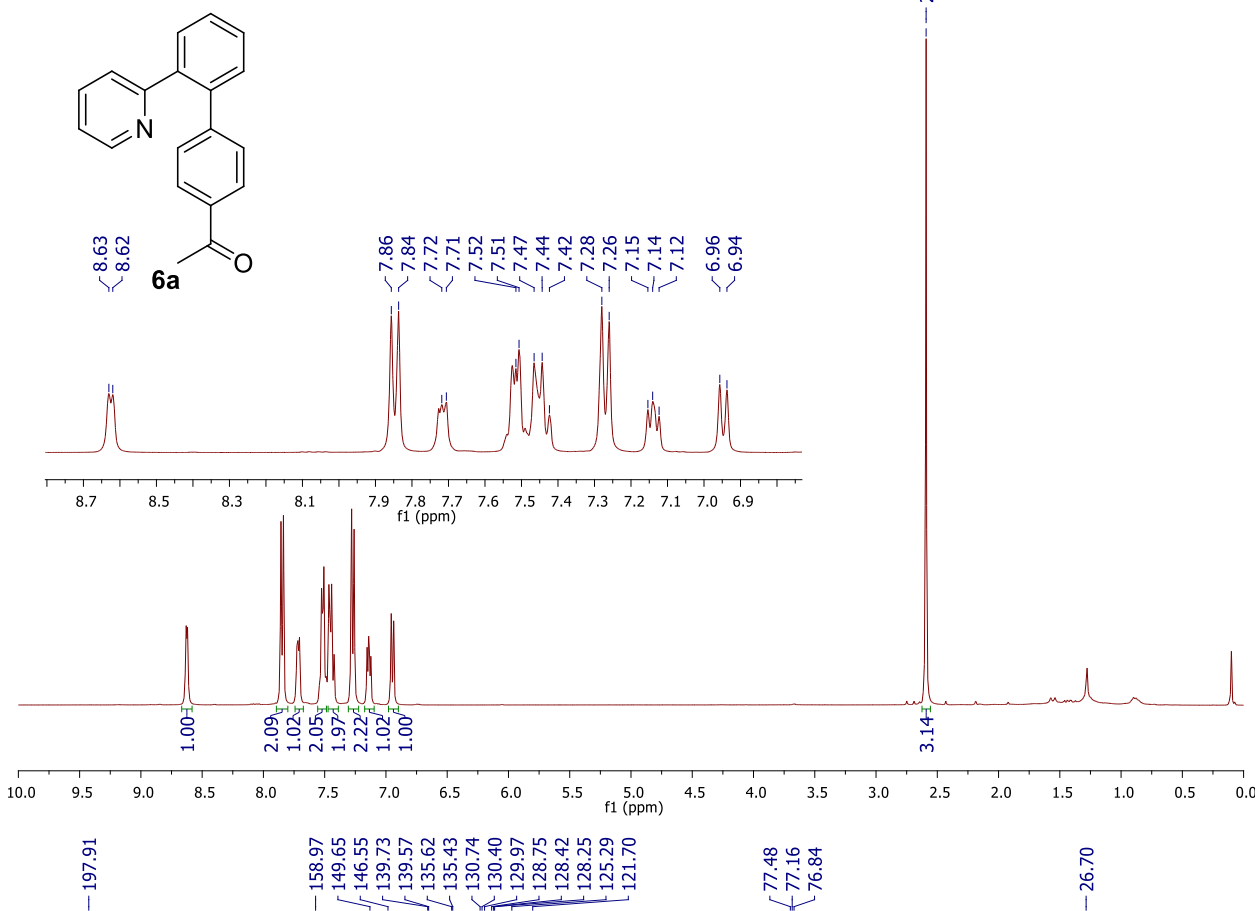


128 MHz, ^{11}B NMR, C_6D_6

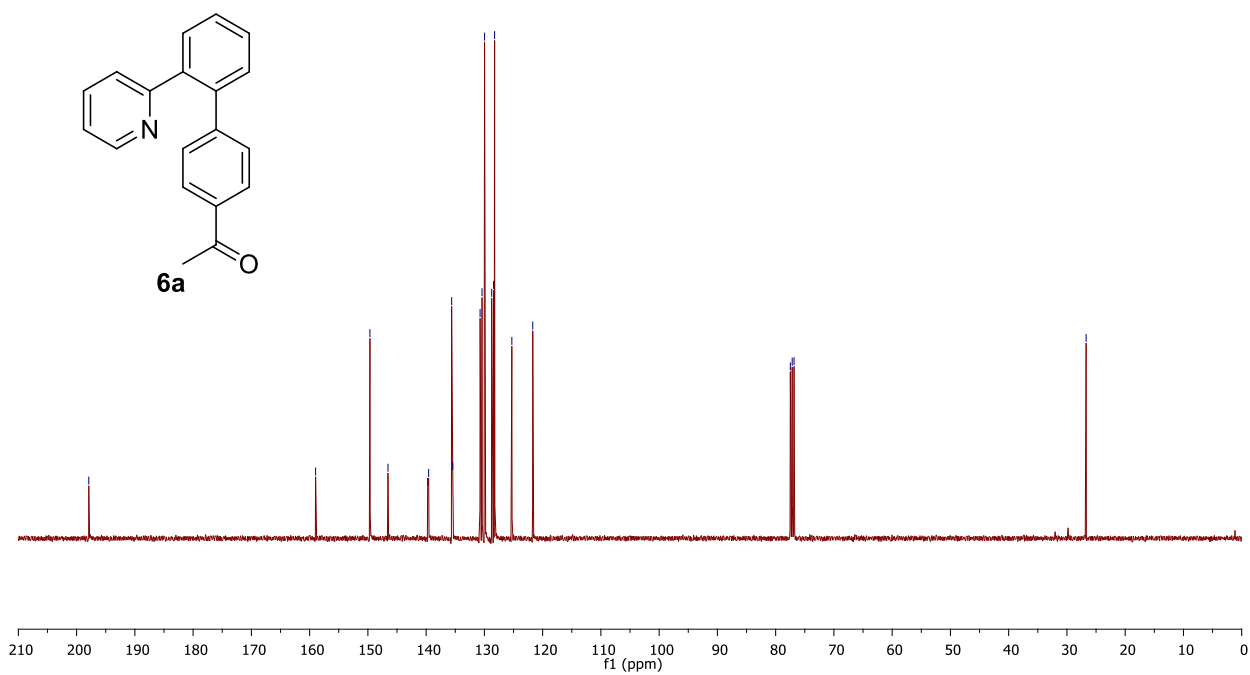


COSY of 2-(3-boronic acid pinacolate ester-furan-2-yl)pyridine derivative. The box highlights the presence of the proton at C5 on the furyl ring which was hidden as a result of the solvent.

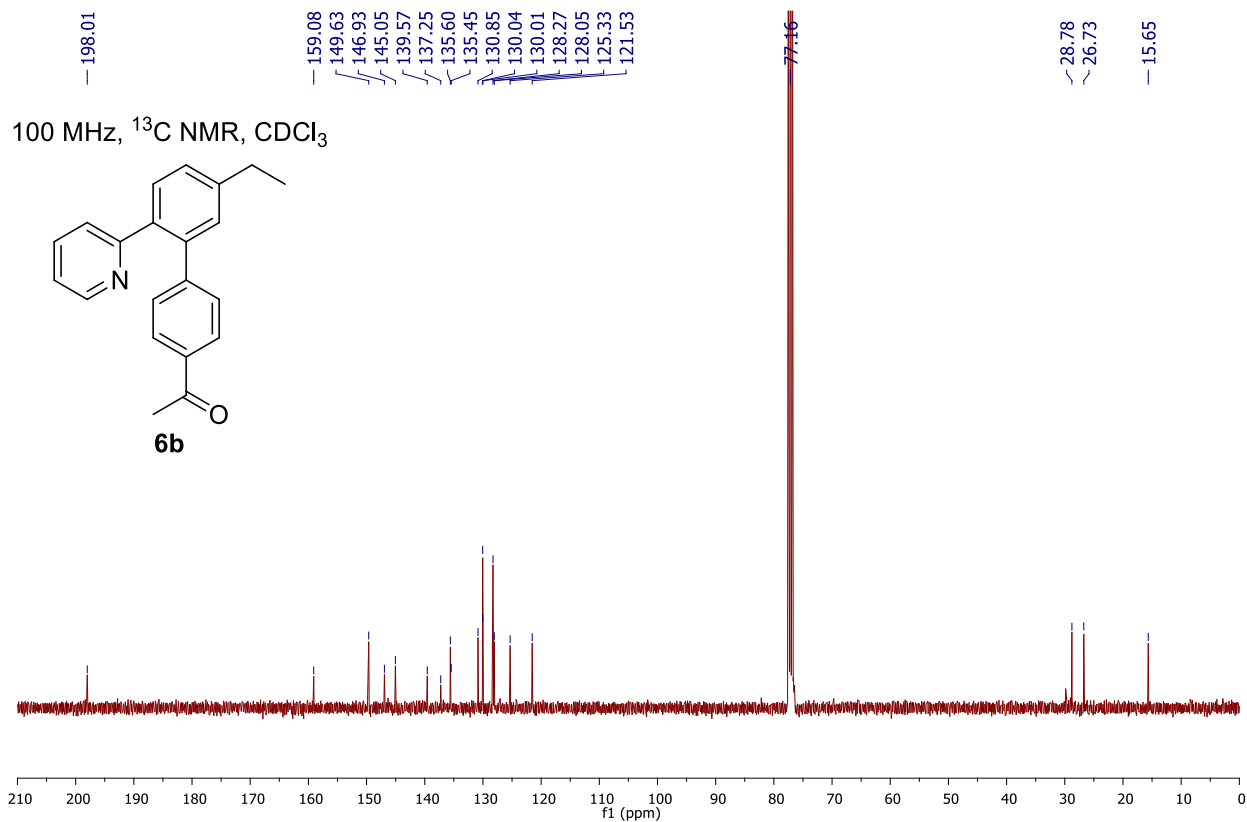
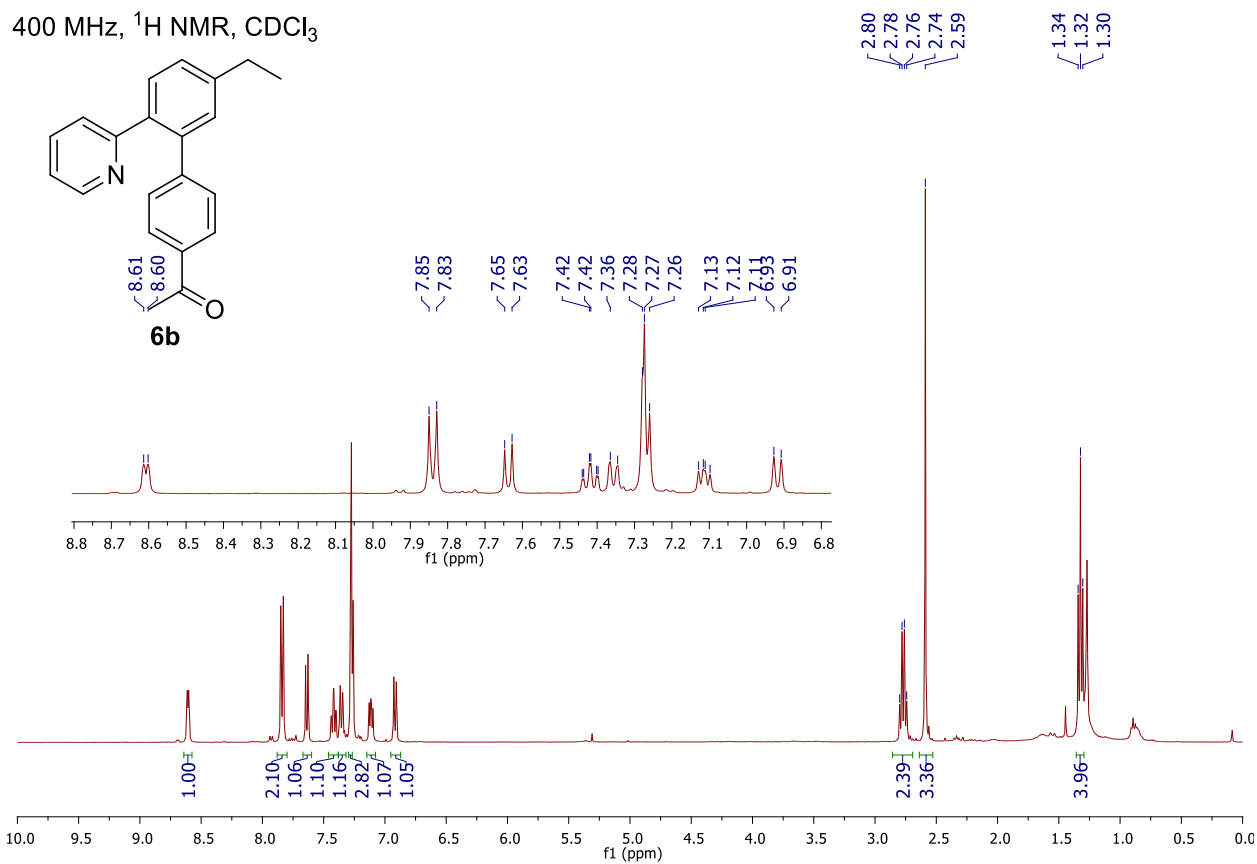
400 MHz, ^1H NMR, CDCl_3



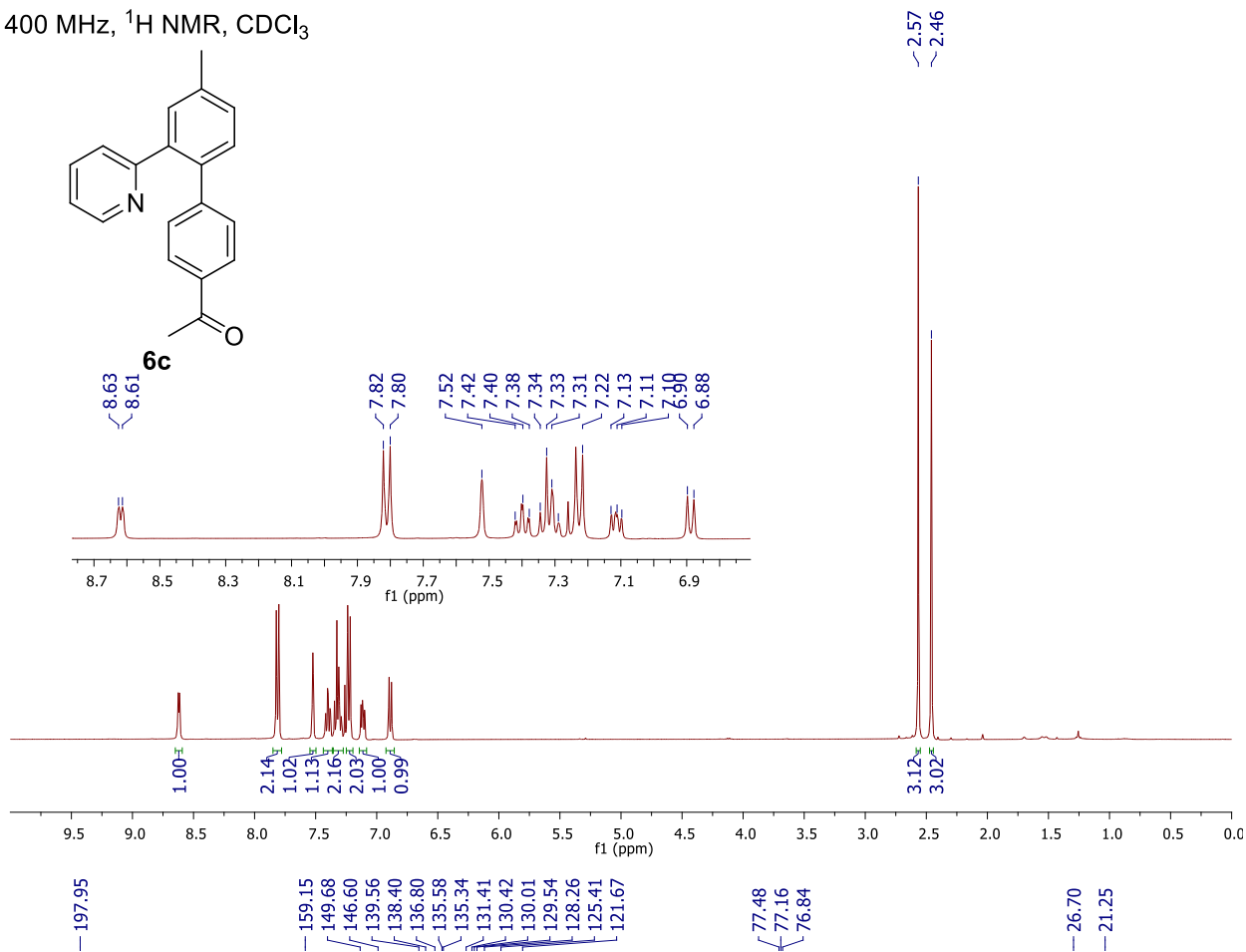
100 MHz, ^{13}C NMR, CDCl_3



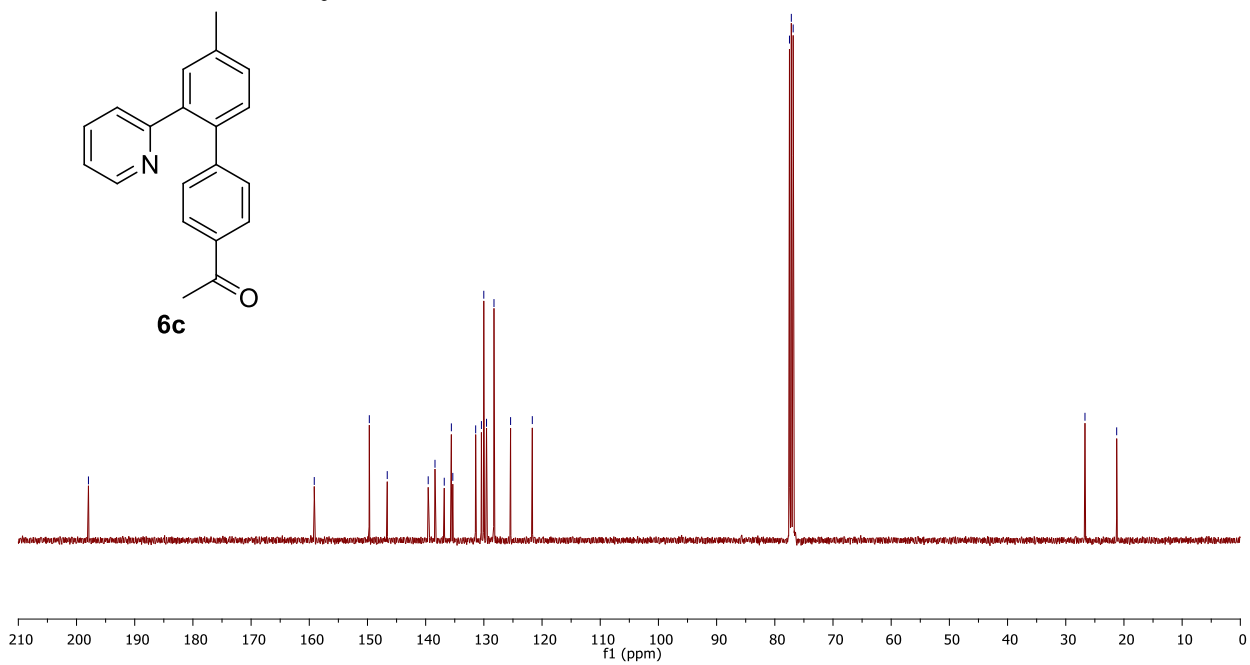
400 MHz, ^1H NMR, CDCl_3



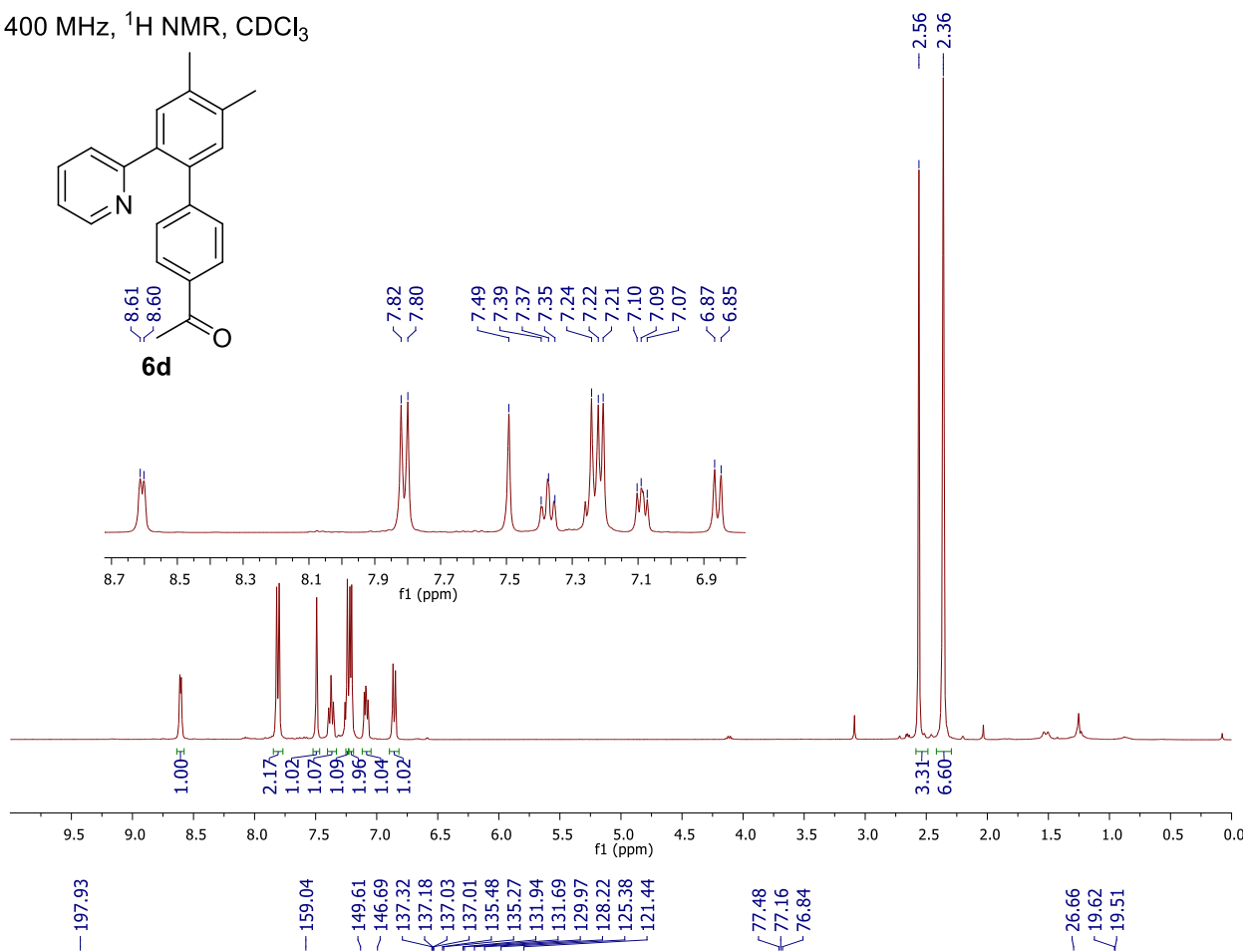
400 MHz, ^1H NMR, CDCl_3



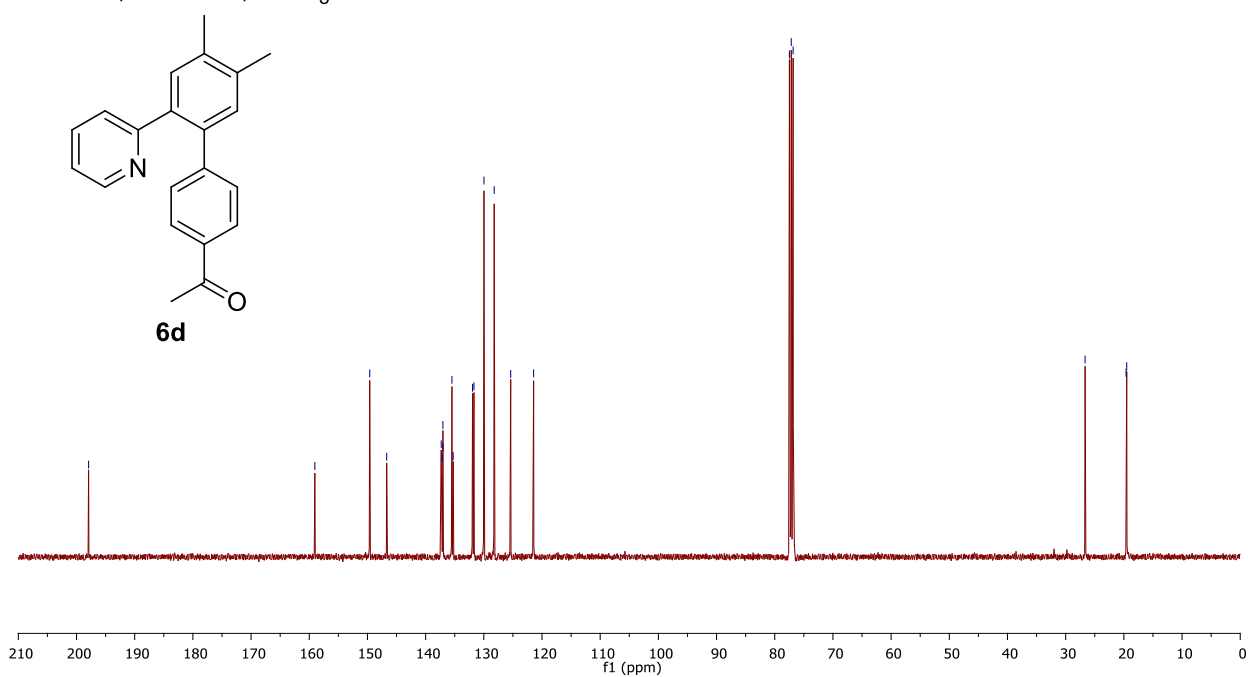
100 MHz, ^{13}C NMR, CDCl_3



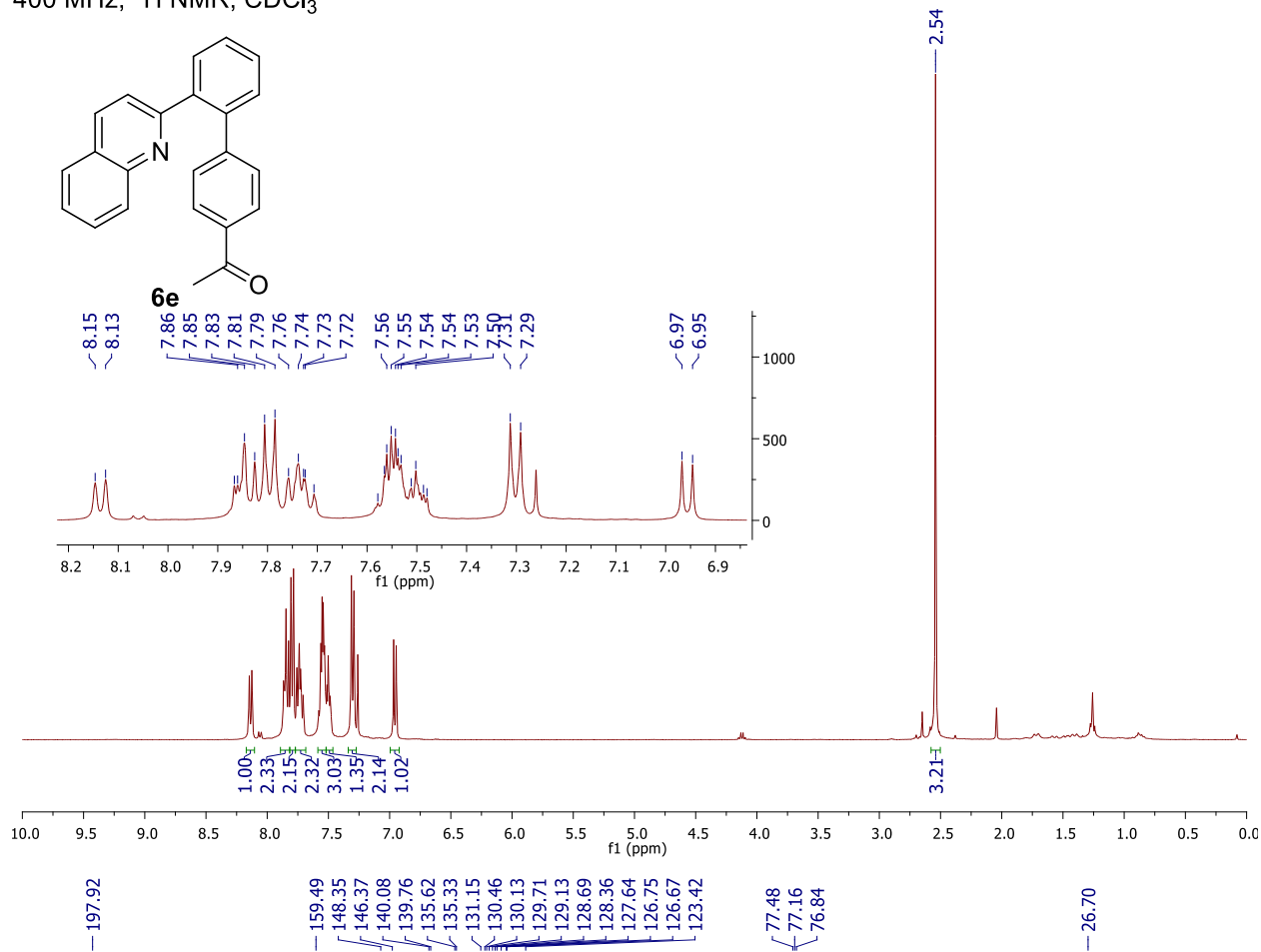
400 MHz, ^1H NMR, CDCl_3



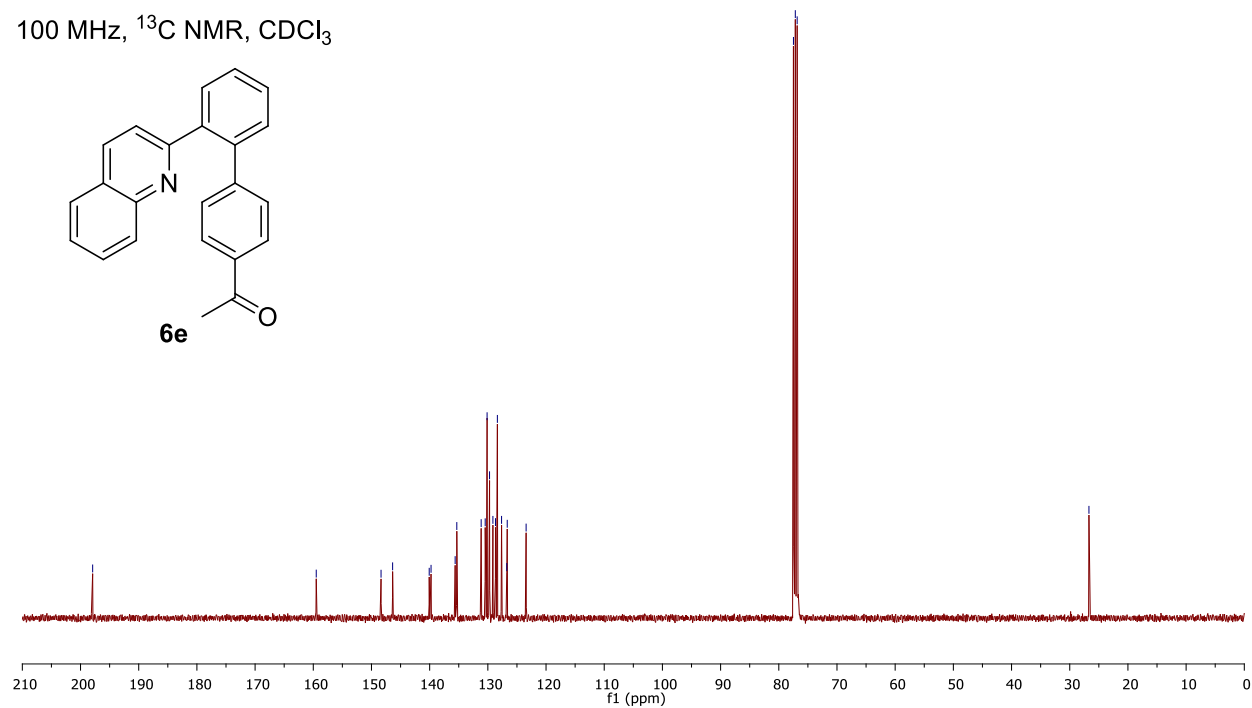
100 MHz, ^{13}C NMR, CDCl_3



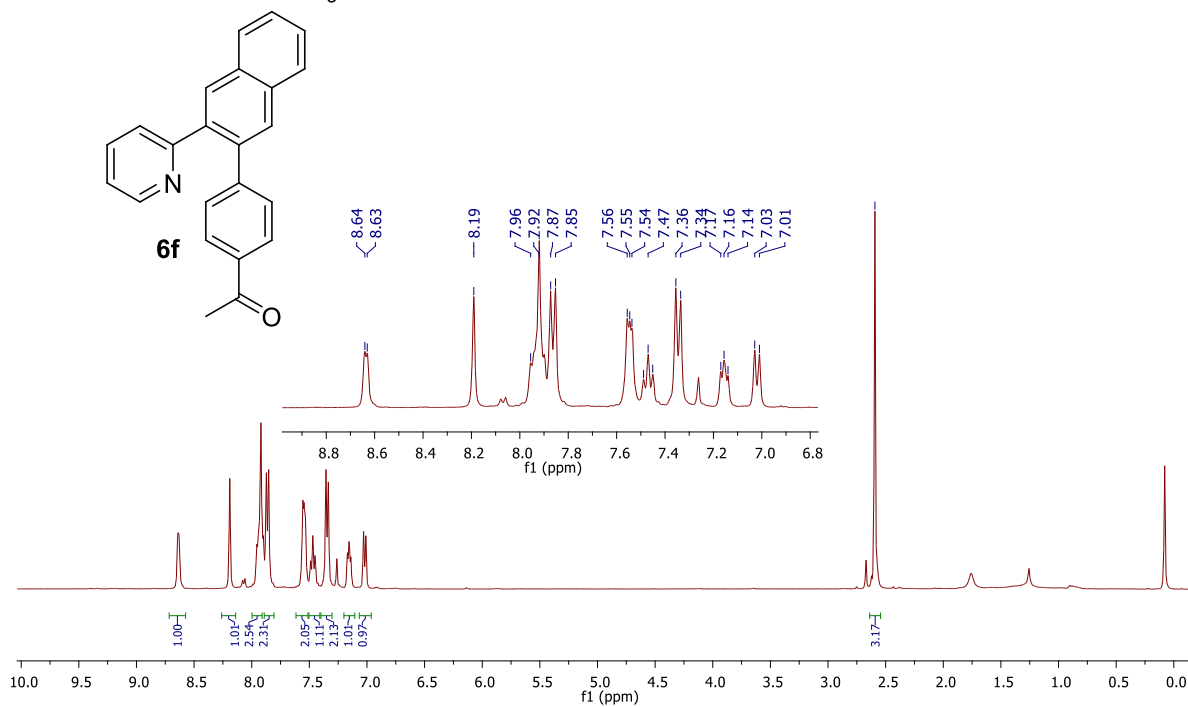
400 MHz, ^1H NMR, CDCl_3



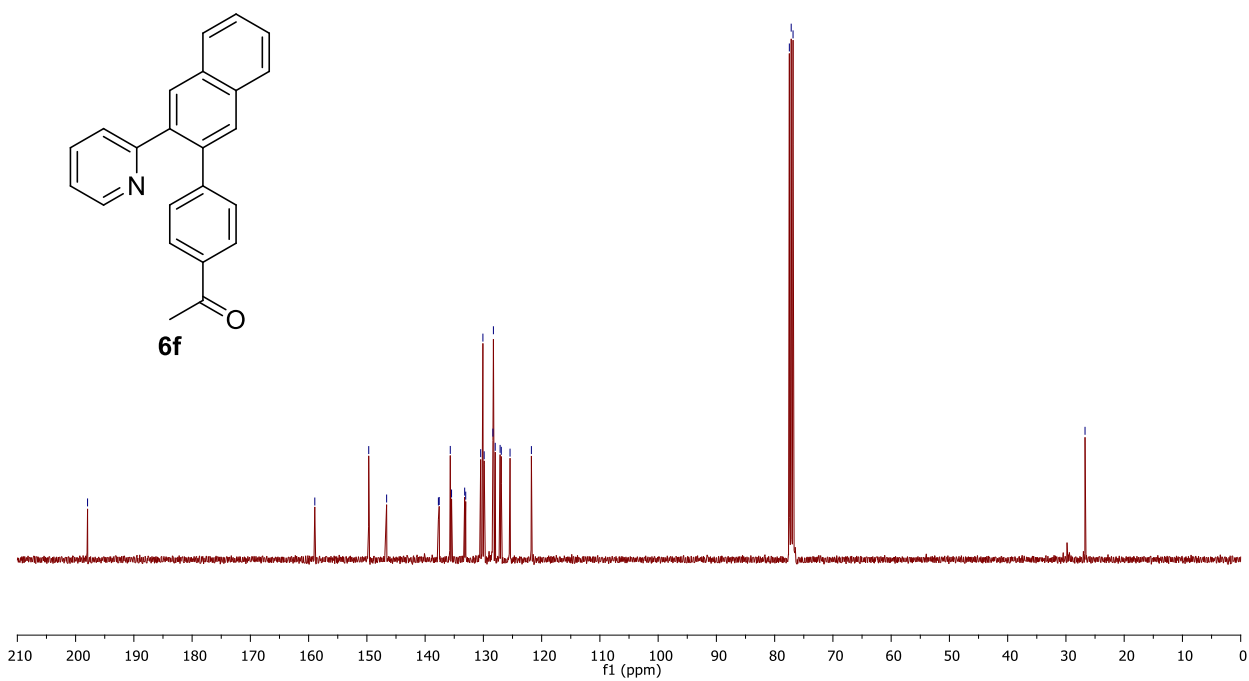
100 MHz, ^{13}C NMR, CDCl_3



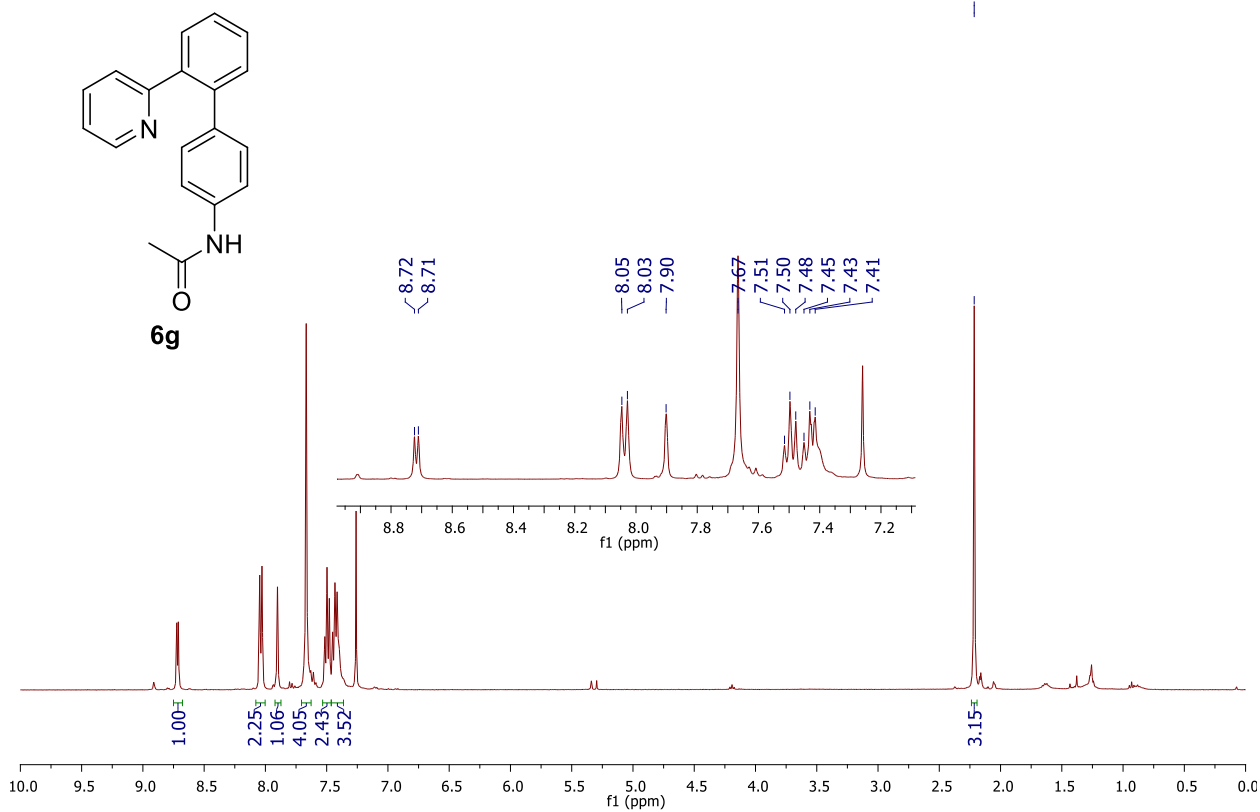
400 MHz, ^1H NMR, CDCl_3



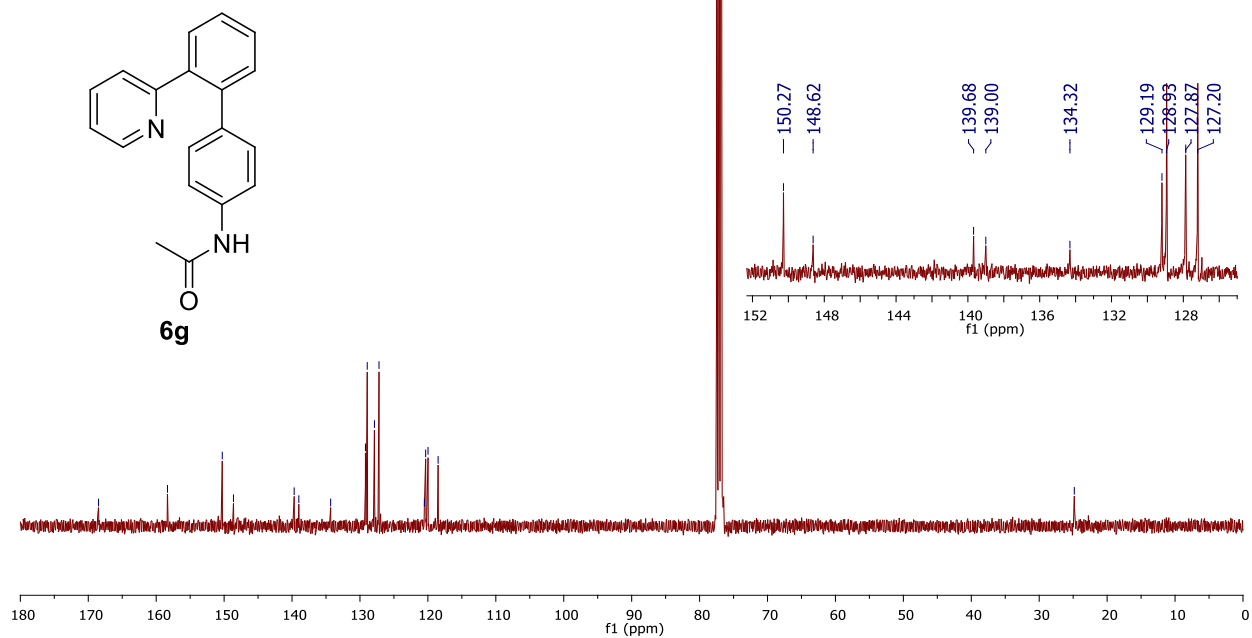
100 MHz, ^{13}C NMR, CDCl_3



400 MHz, ^1H NMR, CDCl_3



100 MHz, ^{13}C NMR, CDCl_3

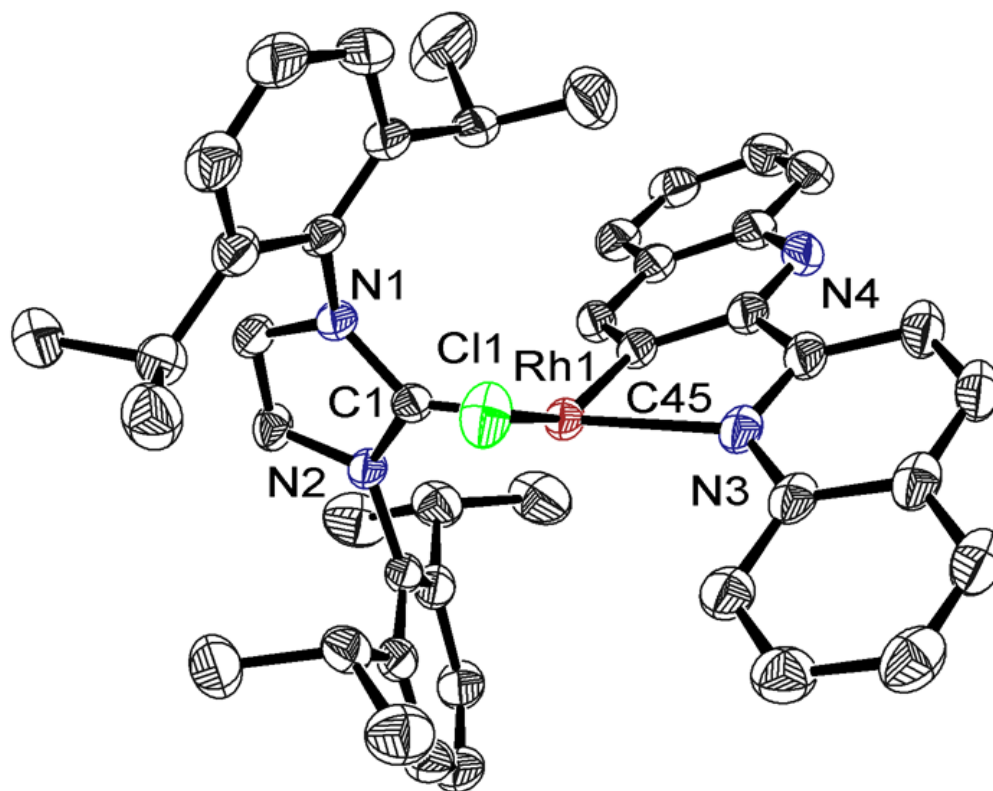


Appendix II: Crystallographic Refinement Data

Figure S1. Molecular Structure of **3b/3c** (Displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are omitted for clarity.)

i) molecule 1 (**3b**) (60%)

a)



ii) molecule 2 (**3c**) (40%)

a)

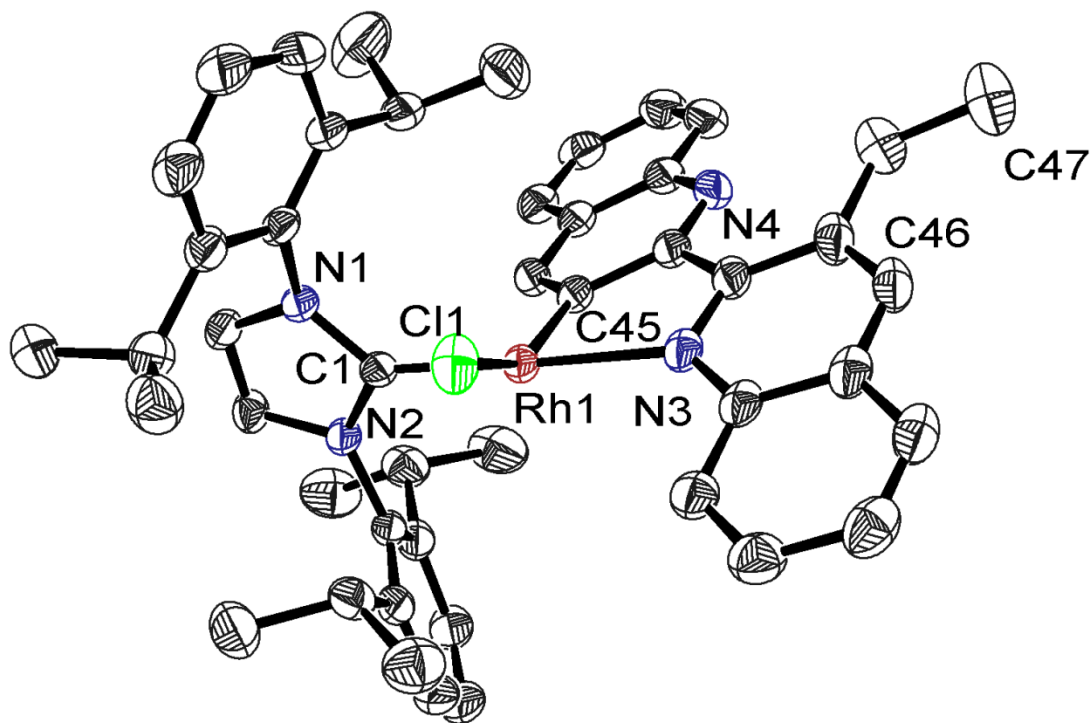


Table S2. Crystal data and structure refinement for **3b/3c**

Identification code	cc117a	
Empirical formula	C _{49.20} H _{55.80} Cl N ₄ Rh	
Formula weight	841.54	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.5336(10) Å	α = 61.6840(10)°.
	b = 13.3530(10) Å	β = 87.1810(10)°.
	c = 15.0479(12) Å	γ = 79.8940(10)°.
Volume	2181.0(3) Å ³	
Z	2	
Density (calculated)	1.281 Mg/m ³	

Absorption coefficient	0.490 mm ⁻¹
F(000)	882
Crystal size	0.30 x 0.20 x 0.08 mm ³
Theta range for data collection	1.76 to 26.00°.
Index ranges	-15<=h<=15, -16<=k<=16, -18<=l<=18
Reflections collected	21252
Independent reflections	8484 [R(int) = 0.0234]
Completeness to theta = 26.00°	98.8 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9618 and 0.8668
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8484 / 5 / 508
Goodness-of-fit on F ²	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1075
R indices (all data)	R1 = 0.0468, wR2 = 0.1134
Largest diff. peak and hole	1.816 and -0.501 e.Å ⁻³

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	1937(1)	1696(1)	7074(1)	26(1)
Cl(1)	2604(1)	1692(1)	8556(1)	41(1)
N(1)	4326(2)	1752(2)	6388(2)	27(1)
N(2)	3306(2)	3177(2)	5372(2)	28(1)
N(3)	508(2)	1040(2)	7840(2)	32(1)
N(4)	751(2)	-675(2)	6489(2)	36(1)
C(1)	3268(2)	2244(2)	6265(2)	25(1)
C(2)	4983(2)	2339(2)	5579(2)	31(1)
C(3)	4353(2)	3233(3)	4952(2)	32(1)
C(4)	4822(2)	898(2)	7314(2)	29(1)
C(5)	4804(2)	-235(3)	7571(2)	34(1)
C(6)	5368(3)	-1005(3)	8432(3)	46(1)
C(7)	5912(3)	-650(3)	8983(3)	51(1)
C(8)	5906(3)	473(3)	8711(3)	44(1)
C(9)	5368(2)	1276(3)	7870(2)	34(1)
C(10)	4199(2)	-642(3)	6992(3)	39(1)
C(11)	3384(3)	-1392(4)	7685(4)	67(1)
C(12)	4953(4)	-1247(5)	6441(4)	78(2)
C(13)	5402(3)	2513(3)	7589(2)	37(1)
C(14)	6520(3)	2837(3)	7142(3)	48(1)
C(15)	5093(3)	2824(3)	8486(3)	52(1)
C(16)	2433(2)	4095(2)	4945(2)	30(1)
C(17)	2045(2)	4763(2)	5470(2)	34(1)
C(18)	1239(3)	5669(3)	5016(3)	41(1)
C(19)	874(3)	5913(3)	4078(3)	46(1)
C(20)	1287(3)	5266(3)	3566(3)	43(1)
C(21)	2075(2)	4328(3)	3993(2)	36(1)
C(22)	2526(3)	4599(3)	6439(2)	37(1)
C(23)	1708(3)	4930(3)	7153(3)	54(1)
C(24)	3486(3)	5256(3)	6182(3)	53(1)
C(25)	2507(3)	3657(3)	3382(3)	43(1)

C(26)	3165(4)	4342(3)	2439(3)	61(1)
C(27)	1586(4)	3237(3)	3091(3)	66(1)
C(28)	-157(2)	1352(3)	8516(2)	33(1)
C(29)	-63(3)	2348(3)	8595(2)	39(1)
C(30)	-761(3)	2690(3)	9225(3)	46(1)
C(31)	-1553(3)	2036(3)	9832(3)	48(1)
C(32)	-1646(3)	1066(3)	9787(2)	42(1)
C(33)	-961(2)	700(3)	9112(2)	36(1)
C(34)	-1059(2)	-268(3)	8996(2)	40(1)
C(35)	-442(2)	-552(3)	8283(2)	39(1)
C(36)	319(2)	171(3)	7676(2)	33(1)
C(37)	937(2)	82(2)	6788(2)	32(1)
C(38)	1243(2)	-662(3)	5609(2)	37(1)
C(39)	1038(3)	-1454(3)	5261(3)	45(1)
C(40)	1480(3)	-1429(3)	4357(3)	48(1)
C(41)	2146(3)	-642(3)	3764(3)	42(1)
C(42)	2374(2)	130(3)	4076(3)	38(1)
C(43)	1926(2)	134(2)	5011(2)	33(1)
C(44)	2134(2)	905(2)	5379(2)	32(1)
C(45)	1668(2)	895(2)	6272(2)	29(1)
C(46)	-538(5)	-1676(5)	8244(5)	51(2)
C(47A)	-1290(7)	-2478(7)	9059(7)	62(2)
C(47B)	395(18)	-2650(20)	8400(20)	62(2)
C(48)	4529(15)	-4643(17)	9766(16)	285(8)
C(49)	3474(14)	-5024(15)	9640(13)	255(7)
C(50)	2739(16)	-5890(20)	9949(17)	225(9)
C(51)	1573(19)	-5360(20)	9965(19)	132(8)

Table S4. Bond lengths [Å] and angles [°] **3b**.

Rh(1)-C(45)	2.027(3)
Rh(1)-C(1)	2.045(3)
Rh(1)-N(3)	2.166(2)
Rh(1)-Cl(1)	2.4170(8)
N(1)-C(1)	1.352(3)
N(1)-C(4)	1.399(3)
N(1)-C(2)	1.414(4)
N(2)-C(1)	1.337(3)
N(2)-C(16)	1.401(3)
N(2)-C(3)	1.428(4)
N(3)-C(36)	1.356(4)
N(3)-C(28)	1.449(4)
N(4)-C(37)	1.342(4)
N(4)-C(38)	1.428(4)
C(2)-C(3)	1.269(4)
C(2)-H(2A)	0.9500
C(3)-H(3A)	0.9500
C(4)-C(5)	1.376(4)
C(4)-C(9)	1.415(4)
C(5)-C(6)	1.344(4)
C(5)-C(10)	1.513(4)
C(6)-C(7)	1.385(5)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.353(5)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.322(4)
C(8)-H(8A)	0.9500
C(9)-C(13)	1.507(4)
C(10)-C(11)	1.549(5)
C(10)-C(12)	1.587(5)
C(10)-H(10A)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.564(5)
C(13)-C(15)	1.603(5)
C(13)-H(13A)	1.0000
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(21)	1.393(4)
C(16)-C(17)	1.461(4)
C(17)-C(18)	1.344(4)
C(17)-C(22)	1.509(5)
C(18)-C(19)	1.372(5)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.430(5)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.350(4)
C(20)-H(20A)	0.9500
C(21)-C(25)	1.582(5)
C(22)-C(24)	1.539(5)
C(22)-C(23)	1.607(5)
C(22)-H(22A)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(27)	1.533(5)
C(25)-C(26)	1.564(5)
C(25)-H(25A)	1.0000
C(26)-H(26A)	0.9800

C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.415(5)
C(28)-C(33)	1.434(4)
C(29)-C(30)	1.436(5)
C(29)-H(29A)	0.9500
C(30)-C(31)	1.429(5)
C(30)-H(30A)	0.9500
C(31)-C(32)	1.355(5)
C(31)-H(31A)	0.9500
C(32)-C(33)	1.498(5)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.410(5)
C(34)-C(35)	1.447(5)
C(34)-H(34A)	0.9500
C(35)-C(36)	1.442(4)
C(35)-C(46)	1.555(7)
C(36)-C(37)	1.555(4)
C(37)-C(45)	1.449(4)
C(38)-C(43)	1.417(4)
C(38)-C(39)	1.446(5)
C(39)-C(40)	1.431(5)
C(39)-H(39A)	0.9500
C(40)-C(41)	1.394(5)
C(40)-H(40A)	0.9500
C(41)-C(42)	1.394(5)
C(41)-H(41A)	0.9500
C(42)-C(43)	1.491(5)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.444(4)
C(44)-C(45)	1.434(4)
C(44)-H(44A)	0.9500
C(46)-C(47B)	1.519(18)

C(46)-C(47A)	1.591(9)
C(46)-H(46A)	1.0000
C(47A)-H(47A)	0.9800
C(47A)-H(47B)	0.9800
C(47A)-H(47C)	0.9800
C(47B)-H(47D)	0.9800
C(47B)-H(47E)	0.9800
C(47B)-H(47F)	0.9800
C(48)-C(48)#1	1.36(3)
C(48)-C(49)	1.549(15)
C(49)-C(50)	1.490(16)
C(50)-C(51)	1.514(17)
C(45)-Rh(1)-C(1)	91.56(11)
C(45)-Rh(1)-N(3)	82.90(11)
C(1)-Rh(1)-N(3)	174.47(10)
C(45)-Rh(1)-Cl(1)	152.33(8)
C(1)-Rh(1)-Cl(1)	93.59(8)
N(3)-Rh(1)-Cl(1)	91.37(7)
C(1)-N(1)-C(4)	124.0(2)
C(1)-N(1)-C(2)	115.2(2)
C(4)-N(1)-C(2)	119.1(2)
C(1)-N(2)-C(16)	123.0(2)
C(1)-N(2)-C(3)	114.2(2)
C(16)-N(2)-C(3)	122.3(2)
C(36)-N(3)-C(28)	120.4(2)
C(36)-N(3)-Rh(1)	110.61(19)
C(28)-N(3)-Rh(1)	128.8(2)
C(37)-N(4)-C(38)	119.9(3)
N(2)-C(1)-N(1)	98.9(2)
N(2)-C(1)-Rh(1)	128.40(19)
N(1)-C(1)-Rh(1)	132.4(2)
C(3)-C(2)-N(1)	105.1(2)
C(3)-C(2)-H(2A)	127.4
N(1)-C(2)-H(2A)	127.4
C(2)-C(3)-N(2)	106.5(3)

C(2)-C(3)-H(3A)	126.8
N(2)-C(3)-H(3A)	126.8
C(5)-C(4)-N(1)	117.5(3)
C(5)-C(4)-C(9)	125.7(3)
N(1)-C(4)-C(9)	116.6(3)
C(6)-C(5)-C(4)	113.9(3)
C(6)-C(5)-C(10)	120.2(3)
C(4)-C(5)-C(10)	125.8(3)
C(5)-C(6)-C(7)	121.2(3)
C(5)-C(6)-H(6A)	119.4
C(7)-C(6)-H(6A)	119.4
C(8)-C(7)-C(6)	123.3(3)
C(8)-C(7)-H(7A)	118.4
C(6)-C(7)-H(7A)	118.4
C(9)-C(8)-C(7)	118.7(3)
C(9)-C(8)-H(8A)	120.7
C(7)-C(8)-H(8A)	120.7
C(8)-C(9)-C(4)	117.3(3)
C(8)-C(9)-C(13)	116.7(3)
C(4)-C(9)-C(13)	126.0(3)
C(5)-C(10)-C(11)	109.7(3)
C(5)-C(10)-C(12)	114.6(3)
C(11)-C(10)-C(12)	112.9(3)
C(5)-C(10)-H(10A)	106.3
C(11)-C(10)-H(10A)	106.3
C(12)-C(10)-H(10A)	106.3
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5

H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(9)-C(13)-C(14)	110.5(3)
C(9)-C(13)-C(15)	113.8(3)
C(14)-C(13)-C(15)	112.2(3)
C(9)-C(13)-H(13A)	106.6
C(14)-C(13)-H(13A)	106.6
C(15)-C(13)-H(13A)	106.6
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(21)-C(16)-N(2)	114.2(3)
C(21)-C(16)-C(17)	126.3(3)
N(2)-C(16)-C(17)	119.3(3)
C(18)-C(17)-C(16)	117.7(3)
C(18)-C(17)-C(22)	116.0(3)
C(16)-C(17)-C(22)	126.1(3)
C(17)-C(18)-C(19)	116.9(3)
C(17)-C(18)-H(18A)	121.6
C(19)-C(18)-H(18A)	121.6
C(18)-C(19)-C(20)	124.5(3)
C(18)-C(19)-H(19A)	117.8
C(20)-C(19)-H(19A)	117.8
C(21)-C(20)-C(19)	121.4(3)
C(21)-C(20)-H(20A)	119.3
C(19)-C(20)-H(20A)	119.3
C(20)-C(21)-C(16)	113.2(3)

C(20)-C(21)-C(25)	119.0(3)
C(16)-C(21)-C(25)	127.8(3)
C(17)-C(22)-C(24)	108.5(3)
C(17)-C(22)-C(23)	116.7(3)
C(24)-C(22)-C(23)	110.8(3)
C(17)-C(22)-H(22A)	106.8
C(24)-C(22)-H(22A)	106.8
C(23)-C(22)-H(22A)	106.8
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(27)-C(25)-C(26)	111.0(3)
C(27)-C(25)-C(21)	111.2(3)
C(26)-C(25)-C(21)	114.3(3)
C(27)-C(25)-H(25A)	106.6
C(26)-C(25)-H(25A)	106.6
C(21)-C(25)-H(25A)	106.6
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5

H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(29)-C(28)-C(33)	116.5(3)
C(29)-C(28)-N(3)	121.0(3)
C(33)-C(28)-N(3)	122.4(3)
C(28)-C(29)-C(30)	121.0(3)
C(28)-C(29)-H(29A)	119.5
C(30)-C(29)-H(29A)	119.5
C(31)-C(30)-C(29)	122.8(3)
C(31)-C(30)-H(30A)	118.6
C(29)-C(30)-H(30A)	118.6
C(32)-C(31)-C(30)	117.5(3)
C(32)-C(31)-H(31A)	121.3
C(30)-C(31)-H(31A)	121.3
C(31)-C(32)-C(33)	121.5(3)
C(31)-C(32)-H(32A)	119.3
C(33)-C(32)-H(32A)	119.3
C(34)-C(33)-C(28)	115.3(3)
C(34)-C(33)-C(32)	124.0(3)
C(28)-C(33)-C(32)	120.7(3)
C(33)-C(34)-C(35)	122.8(3)
C(33)-C(34)-H(34A)	118.6
C(35)-C(34)-H(34A)	118.6
C(36)-C(35)-C(34)	118.8(3)
C(36)-C(35)-C(46)	121.0(3)
C(34)-C(35)-C(46)	119.9(3)
N(3)-C(36)-C(35)	119.6(3)
N(3)-C(36)-C(37)	114.9(2)
C(35)-C(36)-C(37)	125.4(3)
N(4)-C(37)-C(45)	122.4(3)
N(4)-C(37)-C(36)	120.9(3)
C(45)-C(37)-C(36)	116.6(3)
C(43)-C(38)-N(4)	122.9(3)
C(43)-C(38)-C(39)	116.1(3)
N(4)-C(38)-C(39)	121.0(3)
C(40)-C(39)-C(38)	122.4(3)

C(40)-C(39)-H(39A)	118.8
C(38)-C(39)-H(39A)	118.8
C(41)-C(40)-C(39)	121.6(3)
C(41)-C(40)-H(40A)	119.2
C(39)-C(40)-H(40A)	119.2
C(42)-C(41)-C(40)	118.0(3)
C(42)-C(41)-H(41A)	121.0
C(40)-C(41)-H(41A)	121.0
C(41)-C(42)-C(43)	122.0(3)
C(41)-C(42)-H(42A)	119.0
C(43)-C(42)-H(42A)	119.0
C(38)-C(43)-C(44)	115.3(3)
C(38)-C(43)-C(42)	119.9(3)
C(44)-C(43)-C(42)	124.8(3)
C(45)-C(44)-C(43)	122.9(3)
C(45)-C(44)-H(44A)	118.5
C(43)-C(44)-H(44A)	118.5
C(44)-C(45)-C(37)	116.5(3)
C(44)-C(45)-Rh(1)	132.4(2)
C(37)-C(45)-Rh(1)	110.8(2)
C(47B)-C(46)-C(35)	125.5(11)
C(47B)-C(46)-C(47A)	95.8(11)
C(35)-C(46)-C(47A)	115.7(5)
C(47B)-C(46)-H(46A)	106.1
C(35)-C(46)-H(46A)	106.1
C(47A)-C(46)-H(46A)	106.1
C(46)-C(47A)-H(47A)	109.5
C(46)-C(47A)-H(47B)	109.5
H(47A)-C(47A)-H(47B)	109.5
C(46)-C(47A)-H(47C)	109.5
H(47A)-C(47A)-H(47C)	109.5
H(47B)-C(47A)-H(47C)	109.5
C(46)-C(47B)-H(47D)	109.5
C(46)-C(47B)-H(47E)	109.5
H(47D)-C(47B)-H(47E)	109.5
C(46)-C(47B)-H(47F)	109.5

H(47D)-C(47B)-H(47F)	109.5
H(47E)-C(47B)-H(47F)	109.5
C(48)#1-C(48)-C(49)	126(2)
C(50)-C(49)-C(48)	152.0(19)
C(49)-C(50)-C(51)	111(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y-1,-z+2

Table S5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	22(1)	24(1)	26(1)	-5(1)	-1(1)	-4(1)
Cl(1)	36(1)	53(1)	30(1)	-14(1)	0(1)	-13(1)
N(1)	24(1)	24(1)	27(1)	-7(1)	-4(1)	-2(1)
N(2)	22(1)	24(1)	27(1)	-4(1)	-2(1)	-4(1)
N(3)	22(1)	31(1)	26(1)	-1(1)	-3(1)	-2(1)
N(4)	30(1)	28(1)	42(2)	-7(1)	-5(1)	-6(1)
C(1)	25(1)	22(1)	25(1)	-8(1)	-4(1)	-2(1)
C(2)	22(1)	32(2)	32(2)	-12(1)	0(1)	-3(1)
C(3)	26(1)	34(2)	28(1)	-8(1)	2(1)	-9(1)
C(4)	21(1)	29(1)	28(1)	-8(1)	-4(1)	0(1)
C(5)	27(1)	28(1)	36(2)	-8(1)	-5(1)	0(1)
C(6)	44(2)	30(2)	46(2)	-4(2)	-12(2)	-1(1)
C(7)	44(2)	45(2)	40(2)	-1(2)	-18(2)	0(2)
C(8)	37(2)	51(2)	37(2)	-16(2)	-12(1)	-5(2)
C(9)	28(1)	35(2)	33(2)	-12(1)	-2(1)	-4(1)
C(10)	32(2)	28(2)	51(2)	-14(1)	-11(1)	0(1)
C(11)	54(2)	48(2)	73(3)	-1(2)	-22(2)	-18(2)
C(12)	53(2)	95(4)	119(4)	-81(4)	-14(3)	3(2)
C(13)	36(2)	36(2)	40(2)	-18(1)	-4(1)	-5(1)
C(14)	43(2)	44(2)	60(2)	-25(2)	5(2)	-15(2)
C(15)	53(2)	54(2)	57(2)	-32(2)	3(2)	-15(2)
C(16)	23(1)	21(1)	34(2)	-2(1)	-2(1)	-4(1)
C(17)	27(1)	23(1)	38(2)	-4(1)	3(1)	-7(1)
C(18)	35(2)	27(2)	49(2)	-9(1)	4(1)	-2(1)
C(19)	33(2)	30(2)	53(2)	-3(2)	-8(2)	2(1)
C(20)	36(2)	33(2)	40(2)	-2(1)	-11(1)	-3(1)
C(21)	29(2)	29(2)	34(2)	-2(1)	-4(1)	-6(1)
C(22)	40(2)	27(1)	39(2)	-12(1)	0(1)	-7(1)
C(23)	59(2)	50(2)	49(2)	-22(2)	5(2)	-4(2)
C(24)	51(2)	48(2)	59(2)	-21(2)	-1(2)	-18(2)
C(25)	50(2)	34(2)	36(2)	-9(1)	-10(2)	-5(1)

C(26)	83(3)	50(2)	38(2)	-12(2)	5(2)	-7(2)
C(27)	76(3)	46(2)	67(3)	-18(2)	-38(2)	-2(2)
C(28)	24(1)	35(2)	26(1)	-4(1)	-6(1)	0(1)
C(29)	34(2)	34(2)	34(2)	-6(1)	0(1)	-2(1)
C(30)	46(2)	38(2)	42(2)	-13(2)	0(2)	0(2)
C(31)	39(2)	57(2)	36(2)	-17(2)	4(1)	0(2)
C(32)	29(2)	53(2)	32(2)	-10(2)	1(1)	-7(1)
C(33)	25(1)	42(2)	25(1)	-2(1)	-5(1)	-3(1)
C(34)	28(2)	44(2)	32(2)	-2(1)	-3(1)	-12(1)
C(35)	29(2)	44(2)	34(2)	-7(1)	-2(1)	-12(1)
C(36)	24(1)	31(2)	32(2)	-5(1)	-6(1)	-5(1)
C(37)	24(1)	27(1)	33(2)	-4(1)	-5(1)	-2(1)
C(38)	29(2)	28(2)	43(2)	-10(1)	-9(1)	-1(1)
C(39)	42(2)	31(2)	60(2)	-18(2)	-7(2)	-6(1)
C(40)	47(2)	36(2)	62(2)	-26(2)	-9(2)	-2(2)
C(41)	39(2)	39(2)	45(2)	-21(2)	-10(1)	5(1)
C(42)	33(2)	36(2)	43(2)	-18(1)	-5(1)	-1(1)
C(43)	25(1)	29(1)	38(2)	-12(1)	-8(1)	0(1)
C(44)	27(1)	27(1)	34(2)	-8(1)	-3(1)	-6(1)
C(45)	22(1)	26(1)	32(2)	-8(1)	-6(1)	-2(1)
C(46)	53(4)	50(3)	50(4)	-21(3)	6(3)	-19(3)
C(47A)	60(5)	79(6)	51(5)	-28(5)	12(4)	-36(5)
C(47B)	60(5)	79(6)	51(5)	-28(5)	12(4)	-36(5)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **3b**.

	x	y	z	U(eq)
H(2A)	5734	2114	5518	37
H(3A)	4542	3822	4326	38
H(6A)	5394	-1807	8667	55
H(7A)	6309	-1224	9582	62
H(8A)	6281	680	9116	52
H(10A)	3756	65	6447	47
H(11A)	2928	-970	7989	101
H(11B)	3782	-2114	8219	101
H(11C)	2926	-1567	7284	101
H(12A)	5392	-702	5956	117
H(12B)	4501	-1482	6084	117
H(12C)	5432	-1928	6944	117
H(13A)	4841	3003	7033	45
H(14A)	6648	2694	6561	72
H(14B)	7099	2366	7659	72
H(14C)	6513	3656	6924	72
H(15A)	4368	2656	8713	77
H(15B)	5098	3646	8243	77
H(15C)	5623	2361	9052	77
H(18A)	935	6120	5330	50
H(19A)	310	6556	3746	56
H(20A)	999	5500	2911	52
H(22A)	2835	3759	6842	44
H(23A)	1056	4589	7231	81
H(23B)	1505	5772	6845	81
H(23C)	2064	4632	7817	81
H(24A)	4009	4988	5802	79
H(24B)	3839	5114	6807	79
H(24C)	3221	6086	5772	79
H(25A)	3018	2951	3852	52

H(26A)	3371	3890	2082	92
H(26B)	3819	4485	2659	92
H(26C)	2715	5081	1986	92
H(27A)	1197	2796	3696	99
H(27B)	1888	2743	2792	99
H(27C)	1083	3904	2601	99
H(29A)	470	2797	8227	46
H(30A)	-694	3381	9238	55
H(31A)	-1998	2273	10252	57
H(32A)	-2157	606	10193	50
H(34A)	-1551	-754	9403	48
H(39A)	594	-2010	5646	54
H(40A)	1316	-1963	4157	57
H(41A)	2434	-631	3164	50
H(42A)	2830	669	3682	46
H(44A)	2601	1443	5014	38
H(46A)	-884	-1422	7569	61
H(47A)	-2051	-2172	8828	92
H(47B)	-1180	-2494	9705	92
H(47C)	-1100	-3264	9144	92
H(47D)	1059	-2490	8594	92
H(47E)	503	-2697	7774	92
H(47F)	227	-3379	8939	92

Table S7. Torsion angles [°] for **3b**.

C(45)-Rh(1)-N(3)-C(36)	18.39(19)
C(1)-Rh(1)-N(3)-C(36)	19.4(10)
Cl(1)-Rh(1)-N(3)-C(36)	-134.46(18)
C(45)-Rh(1)-N(3)-C(28)	-166.5(2)
C(1)-Rh(1)-N(3)-C(28)	-165.6(9)
Cl(1)-Rh(1)-N(3)-C(28)	40.6(2)
C(16)-N(2)-C(1)-N(1)	-170.5(3)
C(3)-N(2)-C(1)-N(1)	1.5(3)
C(16)-N(2)-C(1)-Rh(1)	15.6(4)
C(3)-N(2)-C(1)-Rh(1)	-172.3(2)
C(4)-N(1)-C(1)-N(2)	162.8(3)
C(2)-N(1)-C(1)-N(2)	-2.3(3)
C(4)-N(1)-C(1)-Rh(1)	-23.7(4)
C(2)-N(1)-C(1)-Rh(1)	171.2(2)
C(45)-Rh(1)-C(1)-N(2)	83.9(3)
N(3)-Rh(1)-C(1)-N(2)	83.0(10)
Cl(1)-Rh(1)-C(1)-N(2)	-123.3(2)
C(45)-Rh(1)-C(1)-N(1)	-87.9(3)
N(3)-Rh(1)-C(1)-N(1)	-88.8(10)
Cl(1)-Rh(1)-C(1)-N(1)	64.9(3)
C(1)-N(1)-C(2)-C(3)	2.3(3)
C(4)-N(1)-C(2)-C(3)	-163.6(3)
N(1)-C(2)-C(3)-N(2)	-1.1(3)
C(1)-N(2)-C(3)-C(2)	-0.3(4)
C(16)-N(2)-C(3)-C(2)	171.8(3)
C(1)-N(1)-C(4)-C(5)	89.1(3)
C(2)-N(1)-C(4)-C(5)	-106.4(3)
C(1)-N(1)-C(4)-C(9)	-95.4(3)
C(2)-N(1)-C(4)-C(9)	69.1(3)
N(1)-C(4)-C(5)-C(6)	175.1(3)
C(9)-C(4)-C(5)-C(6)	0.1(5)
N(1)-C(4)-C(5)-C(10)	-6.5(4)
C(9)-C(4)-C(5)-C(10)	178.4(3)
C(4)-C(5)-C(6)-C(7)	-0.4(5)

C(10)-C(5)-C(6)-C(7)	-178.9(3)
C(5)-C(6)-C(7)-C(8)	0.9(6)
C(6)-C(7)-C(8)-C(9)	-1.0(6)
C(7)-C(8)-C(9)-C(4)	0.6(5)
C(7)-C(8)-C(9)-C(13)	-178.9(3)
C(5)-C(4)-C(9)-C(8)	-0.2(5)
N(1)-C(4)-C(9)-C(8)	-175.3(3)
C(5)-C(4)-C(9)-C(13)	179.3(3)
N(1)-C(4)-C(9)-C(13)	4.2(4)
C(6)-C(5)-C(10)-C(11)	57.1(4)
C(4)-C(5)-C(10)-C(11)	-121.2(3)
C(6)-C(5)-C(10)-C(12)	-71.2(5)
C(4)-C(5)-C(10)-C(12)	110.5(4)
C(8)-C(9)-C(13)-C(14)	76.3(4)
C(4)-C(9)-C(13)-C(14)	-103.1(3)
C(8)-C(9)-C(13)-C(15)	-51.0(4)
C(4)-C(9)-C(13)-C(15)	129.6(3)
C(1)-N(2)-C(16)-C(21)	-122.4(3)
C(3)-N(2)-C(16)-C(21)	66.2(3)
C(1)-N(2)-C(16)-C(17)	62.4(4)
C(3)-N(2)-C(16)-C(17)	-109.0(3)
C(21)-C(16)-C(17)-C(18)	2.5(4)
N(2)-C(16)-C(17)-C(18)	177.0(3)
C(21)-C(16)-C(17)-C(22)	-171.9(3)
N(2)-C(16)-C(17)-C(22)	2.7(4)
C(16)-C(17)-C(18)-C(19)	-2.2(4)
C(22)-C(17)-C(18)-C(19)	172.7(3)
C(17)-C(18)-C(19)-C(20)	0.6(5)
C(18)-C(19)-C(20)-C(21)	1.2(5)
C(19)-C(20)-C(21)-C(16)	-1.1(4)
C(19)-C(20)-C(21)-C(25)	-179.2(3)
N(2)-C(16)-C(21)-C(20)	-175.5(3)
C(17)-C(16)-C(21)-C(20)	-0.7(4)
N(2)-C(16)-C(21)-C(25)	2.4(4)
C(17)-C(16)-C(21)-C(25)	177.2(3)
C(18)-C(17)-C(22)-C(24)	-90.9(3)

C(16)-C(17)-C(22)-C(24)	83.5(4)
C(18)-C(17)-C(22)-C(23)	35.0(4)
C(16)-C(17)-C(22)-C(23)	-150.6(3)
C(20)-C(21)-C(25)-C(27)	-57.9(4)
C(16)-C(21)-C(25)-C(27)	124.2(3)
C(20)-C(21)-C(25)-C(26)	68.8(4)
C(16)-C(21)-C(25)-C(26)	-109.1(4)
C(36)-N(3)-C(28)-C(29)	-171.8(3)
Rh(1)-N(3)-C(28)-C(29)	13.6(4)
C(36)-N(3)-C(28)-C(33)	6.3(4)
Rh(1)-N(3)-C(28)-C(33)	-168.37(19)
C(33)-C(28)-C(29)-C(30)	-1.4(4)
N(3)-C(28)-C(29)-C(30)	176.7(3)
C(28)-C(29)-C(30)-C(31)	2.5(5)
C(29)-C(30)-C(31)-C(32)	-1.1(5)
C(30)-C(31)-C(32)-C(33)	-1.2(5)
C(29)-C(28)-C(33)-C(34)	178.2(3)
N(3)-C(28)-C(33)-C(34)	0.1(4)
C(29)-C(28)-C(33)-C(32)	-0.8(4)
N(3)-C(28)-C(33)-C(32)	-178.9(2)
C(31)-C(32)-C(33)-C(34)	-176.7(3)
C(31)-C(32)-C(33)-C(28)	2.2(4)
C(28)-C(33)-C(34)-C(35)	-3.6(4)
C(32)-C(33)-C(34)-C(35)	175.3(3)
C(33)-C(34)-C(35)-C(36)	1.1(4)
C(33)-C(34)-C(35)-C(46)	176.2(4)
C(28)-N(3)-C(36)-C(35)	-8.9(4)
Rh(1)-N(3)-C(36)-C(35)	166.7(2)
C(28)-N(3)-C(36)-C(37)	168.8(2)
Rh(1)-N(3)-C(36)-C(37)	-15.7(3)
C(34)-C(35)-C(36)-N(3)	5.4(4)
C(46)-C(35)-C(36)-N(3)	-169.6(4)
C(34)-C(35)-C(36)-C(37)	-172.0(3)
C(46)-C(35)-C(36)-C(37)	13.0(5)
C(38)-N(4)-C(37)-C(45)	-2.9(4)
C(38)-N(4)-C(37)-C(36)	173.6(2)

N(3)-C(36)-C(37)-N(4)	-174.2(2)
C(35)-C(36)-C(37)-N(4)	3.3(4)
N(3)-C(36)-C(37)-C(45)	2.5(3)
C(35)-C(36)-C(37)-C(45)	180.0(3)
C(37)-N(4)-C(38)-C(43)	-0.7(4)
C(37)-N(4)-C(38)-C(39)	-178.8(3)
C(43)-C(38)-C(39)-C(40)	-1.0(5)
N(4)-C(38)-C(39)-C(40)	177.2(3)
C(38)-C(39)-C(40)-C(41)	0.6(5)
C(39)-C(40)-C(41)-C(42)	0.1(5)
C(40)-C(41)-C(42)-C(43)	-0.3(5)
N(4)-C(38)-C(43)-C(44)	2.8(4)
C(39)-C(38)-C(43)-C(44)	-179.1(3)
N(4)-C(38)-C(43)-C(42)	-177.4(3)
C(39)-C(38)-C(43)-C(42)	0.8(4)
C(41)-C(42)-C(43)-C(38)	-0.1(4)
C(41)-C(42)-C(43)-C(44)	179.7(3)
C(38)-C(43)-C(44)-C(45)	-1.4(4)
C(42)-C(43)-C(44)-C(45)	178.7(3)
C(43)-C(44)-C(45)-C(37)	-1.7(4)
C(43)-C(44)-C(45)-Rh(1)	171.0(2)
N(4)-C(37)-C(45)-C(44)	4.0(4)
C(36)-C(37)-C(45)-C(44)	-172.6(2)
N(4)-C(37)-C(45)-Rh(1)	-170.3(2)
C(36)-C(37)-C(45)-Rh(1)	13.1(3)
C(1)-Rh(1)-C(45)-C(44)	-9.4(3)
N(3)-Rh(1)-C(45)-C(44)	170.5(3)
Cl(1)-Rh(1)-C(45)-C(44)	-110.2(3)
C(1)-Rh(1)-C(45)-C(37)	163.69(19)
N(3)-Rh(1)-C(45)-C(37)	-16.40(18)
Cl(1)-Rh(1)-C(45)-C(37)	62.9(3)
C(36)-C(35)-C(46)-C(47B)	53.3(14)
C(34)-C(35)-C(46)-C(47B)	-121.7(14)
C(36)-C(35)-C(46)-C(47A)	172.0(5)
C(34)-C(35)-C(46)-C(47A)	-3.0(7)
C(48)#1-C(48)-C(49)-C(50)	23(6)

C(48)-C(49)-C(50)-C(51)

135(4)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y-1, -z+2$

Figure S2. Molecular ellipsoid plot for **5b**.

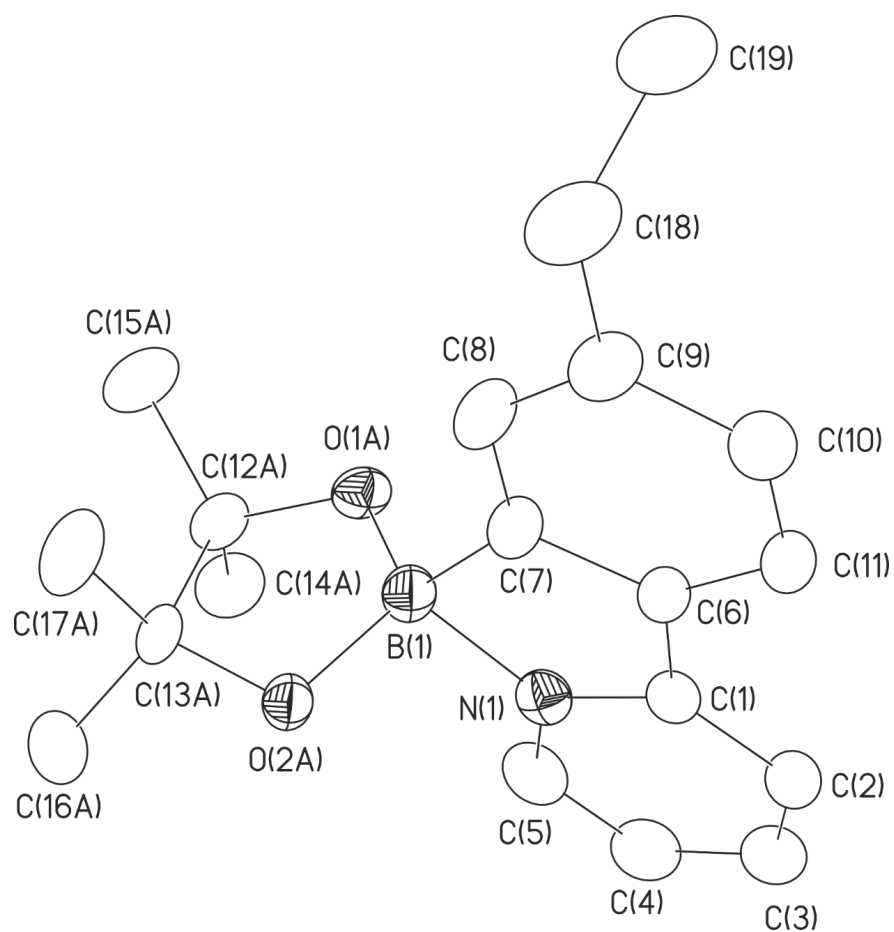


Table S8. Crystal Data and Structure Refinement for **5b**.

Identification code	ccoz_200a
Empirical formula	C ₁₈ H ₂₄ B ₁ N ₁ O ₂
Formula weight	309.20
Crystal Color, Habit	colourless, block-like
Crystal dimensions (mm)	0.324 × 0.258 × 0.188
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> [14]
Unit cell parameters ^a	
<i>a</i> (Å)	10.0448(9)
<i>b</i> (Å)	13.1778(10)
<i>c</i> (Å)	13.6491(12)
<i>α</i> (°)	90
<i>β</i> (°)	96.075(2)
<i>γ</i> (°)	90
<i>V</i> (Å ³)	1796.6(3)
<i>Z</i> ^b	4
<i>F</i> (000)	664
Density (ρ _{calcd})	1.143 Mg/m ³
Absorption coefficient (μ)	0.072 mm ⁻¹
Diffractometer	Bruker-AXS Smart Apex II diffractometer ^c
Radiation	monochromated Mo K _α
Wavelength (Mo K _α)	0.71073 Å
Temperature	-93(2) °C [180(2) K]
Scan type	ω-and φ-scans (0.5°/frame, 15 s exposure/frame, 3 sets)
Theta range for data collection	2.559 to 25.681°
Completeness to theta = 25.242°	99.9%
Reflections collected ^d	12196
Index ranges	-12 ≤ <i>h</i> ≤ 12, -16 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 16
Independent reflections [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)] ^e	3403 [<i>R</i> _{int} = 0.0318] ^f
Observed reflections [<i>F</i> _o ² > 2σ(<i>F</i> _o ²)] ^g	2475
Absorption correction method	multi-scan [SADABS] ^k
Anomalous Dispersion	For all non-hydrogen atoms
Structure solution method	Direct methods (SIR-2004) ^h

Refinement method	Full-matrix least-squares on F^2 (SHELXL-2013) ⁱ
Function Minimized	$\Sigma w(F_o ^2 - kF_c ^2)^2$ (k : overall scale factor)
Weighing scheme, w $w = [\sigma(F_o^2) + (a P)^2 + (b P)]^{-1}$	$w = [\sigma(F_o^2) + (0.0476 P)^2 + (0.2010 P)]^{-1}$
P -factor	$[\text{Max}(F_o^2, 0) + 2 F_c^2]/3$
Data / restraints / parameters	3403 $[F_o^2 \geq -3\sigma(F_o^2)]$ / 0 / 278
Reflection (observed)/parameter ratio	9:1
Reflection (data)/parameter ratio	12:1
Goodness-of-fit ^j on F^2 $\text{Goof} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ n : number of reflections, p : number of parameters	1.039
Final R indices $R_1 = [\Sigma F_o - F_c]/[\Sigma F_o]$ for $[F_o^2 > 2\sigma(F_o^2)]^i$ $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ [all data]	0.0391 0.1066
Max. Shift/Error in Final Cycle	0.000
Largest difference peak and hole	0.124 and -0.167 e ⁻ /Å ³
Transmission factor (min)	0.7119 [SADABS] ^k
Transmission factor (max)	0.7457 [SADABS] ^k

Table S9. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and site occupancy factors for **5b**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)	s.o.f.
N(1)	8791(1)	229(1)	3095(1)	42(1)	
C(1)	10052(1)	159(1)	3550(1)	39(1)	
C(2)	10885(2)	-629(1)	3328(1)	48(1)	
C(3)	10422(2)	-1336(1)	2633(1)	58(1)	
C(4)	9140(2)	-1256(1)	2167(1)	60(1)	
C(5)	8345(2)	-468(1)	2419(1)	55(1)	
C(6)	10331(1)	1007(1)	4242(1)	38(1)	
C(7)	9220(1)	1642(1)	4247(1)	41(1)	
C(8)	9371(2)	2492(1)	4863(1)	49(1)	
C(9)	10557(2)	2698(1)	5450(1)	49(1)	
C(10)	11626(2)	2025(1)	5430(1)	48(1)	
C(11)	11525(1)	1173(1)	4836(1)	43(1)	
O(1A)	7460(17)	1844(11)	2726(13)	45(1)	0.718
O(2A)	6790(2)	731(1)	3867(1)	43(1)	0.718
C(12A)	6033(2)	1832(2)	2566(2)	50(1)	0.718
C(13A)	5669(8)	1308(5)	3557(4)	46(1)	0.718
C(14A)	5594(2)	1207(2)	1645(2)	67(1)	0.718
C(15A)	5553(3)	2924(2)	2392(2)	77(1)	0.718
C(16A)	4425(4)	644(5)	3409(4)	75(1)	0.718
C(17A)	5459(3)	2108(2)	4343(2)	75(1)	0.718
O(1B)	7330(50)	1950(30)	2770(30)	45(1)	0.282
O(2B)	6949(5)	1050(3)	4239(3)	36(1)	0.282
C(12B)	5986(5)	2216(4)	3072(4)	45(1)	0.282
C(13B)	5570(20)	1451(15)	3762(14)	46(1)	0.282
C(14B)	6128(6)	3259(3)	3573(4)	53(1)	0.282
C(15B)	5045(7)	2332(7)	2141(5)	72(2)	0.282
C(16B)	4924(10)	460(9)	3252(9)	64(3)	0.282
C(17B)	4815(7)	1722(5)	4604(5)	58(2)	0.282

C(18)	10710(2)	3630(1)	6099(1)	69(1)
C(19)	11596(2)	4434(1)	5706(2)	81(1)
B(1)	7953(2)	1222(1)	3525(1)	44(1)

Table S10. Interatomic Distances [Å] for **5b**.

N(1)-C(5)	1.3442(18)		
N(1)-C(1)	1.3535(17)		
N(1)-B(1)	1.694(2)		
C(1)-C(2)	1.3864(19)		
C(1)-C(6)	1.4710(18)		
C(2)-C(3)	1.376(2)		
C(3)-C(4)	1.378(2)		
C(4)-C(5)	1.377(2)		
C(6)-C(11)	1.3911(18)		
C(6)-C(7)	1.3955(18)		
C(7)-C(8)	1.3991(19)		
C(7)-B(1)	1.623(2)		
C(8)-C(9)	1.391(2)		
C(9)-C(10)	1.395(2)		
C(9)-C(18)	1.513(2)		
C(10)-C(11)	1.3824(19)		
O(1A)-B(1)	1.412(16)	C(13B)-C(17B)	1.488(16)
O(2A)-B(1)	1.455(3)	C(18)-C(19)	1.517(3)
O(1A)-C(12A)	1.427(17)		
O(2A)-C(13A)	1.387(8)		
C(12A)-C(15A)	1.528(3)		
C(12A)-C(13A)	1.595(7)		
C(12A)-C(14A)	1.529(3)		
C(13A)-C(16A)	1.521(10)		
C(13A)-C(17A)	1.535(5)		
O(1B)-B(1)	1.49(4)		
O(2B)-B(1)	1.493(5)		
O(1B)-C(12B)	1.49(4)		
O(2B)-C(13B)	1.56(2)		
C(12B)-C(13B)	1.47(2)		
C(12B)-C(14B)	1.535(8)		
C(12B)-C(15B)	1.510(8)		
C(13B)-C(16B)	1.59(2)		

NOTE:

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S11. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5b**.

The anisotropic displacement factor exponent takes the form:

$$[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N(1)	46(1)	50(1)	32(1)	6(1)	7(1)	-1(1)
C(1)	43(1)	43(1)	34(1)	6(1)	14(1)	0(1)
C(2)	49(1)	48(1)	51(1)	0(1)	21(1)	3(1)
C(3)	71(1)	51(1)	56(1)	-7(1)	27(1)	-2(1)
C(4)	81(1)	60(1)	43(1)	-11(1)	19(1)	-9(1)
C(5)	61(1)	70(1)	36(1)	1(1)	5(1)	-13(1)
C(6)	39(1)	42(1)	33(1)	6(1)	11(1)	5(1)
C(7)	46(1)	50(1)	30(1)	8(1)	10(1)	12(1)
C(8)	58(1)	53(1)	36(1)	5(1)	9(1)	20(1)
C(9)	66(1)	50(1)	33(1)	1(1)	5(1)	8(1)
C(10)	51(1)	54(1)	39(1)	4(1)	0(1)	0(1)
C(11)	39(1)	48(1)	42(1)	7(1)	8(1)	6(1)
O(1A)	50(3)	42(3)	41(2)	11(2)	-4(2)	2(2)
O(2A)	40(1)	47(1)	44(1)	9(1)	10(1)	7(1)
C(12A)	50(1)	46(1)	51(1)	5(1)	-8(1)	11(1)
C(13A)	39(2)	42(2)	60(3)	-8(2)	10(2)	13(1)
C(14A)	72(2)	68(2)	55(1)	-1(1)	-18(1)	2(1)
C(15A)	81(2)	55(2)	88(2)	9(2)	-22(2)	20(1)
C(16A)	50(3)	79(3)	98(3)	-3(2)	14(2)	-3(2)
C(17A)	76(2)	83(2)	66(2)	-9(2)	16(2)	33(2)

O(1B)	50(3)	42(3)	41(2)	11(2)	-4(2)	2(2)
O(2B)	35(2)	36(2)	36(3)	1(2)	-1(2)	1(2)
C(12B)	38(3)	51(3)	44(3)	-2(3)	-3(3)	10(2)
C(13B)	39(2)	42(2)	60(3)	-8(2)	10(2)	13(1)
C(14B)	50(3)	34(2)	76(4)	2(2)	5(3)	1(2)
C(15B)	62(4)	92(5)	55(4)	28(4)	-15(3)	-3(4)
C(16B)	70(8)	62(5)	58(5)	2(4)	-6(5)	-20(6)
C(17B)	46(4)	73(4)	58(4)	-2(3)	16(3)	6(3)
C(18)	102(2)	61(1)	44(1)	-7(1)	2(1)	13(1)
C(19)	104(2)	58(1)	77(1)	-14(1)	-7(1)	5(1)
B(1)	43(1)	50(1)	40(1)	14(1)	7(1)	7(1)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5b**.

Atom	x	y	z	U(eq)	s.o.f.
H(2)	11767	-680	3653	58	
H(3)	10984	-1879	2475	70	
H(4)	8812	-1736	1681	72	
H(5)	7456	-414	2107	66	
H(8)	8637	2944	4880	58	
H(10)	12439	2154	5833	58	
H(11)	12252	712	4832	51	
H(14A)	5780	487	1781	100	0.718
H(14B)	6087	1431	1102	100	0.718
H(14C)	4631	1300	1462	100	0.718
H(15A)	4575	2948	2368	115	0.718
H(15B)	5826	3169	1765	115	0.718
H(15C)	5951	3356	2930	115	0.718
H(16A)	4246	352	4042	113	0.718
H(16B)	4569	97	2946	113	0.718
H(16C)	3658	1056	3144	113	0.718
H(17A)	5379	1771	4974	112	0.718

H(17B)	4639	2491	4143	112	0.718
H(17C)	6225	2572	4414	112	0.718
H(14D)	5239	3519	3674	80	0.282
H(14E)	6566	3730	3153	80	0.282
H(14F)	6669	3194	4210	80	0.282
H(15D)	4147	2498	2311	107	0.282
H(15E)	5013	1695	1768	107	0.282
H(15F)	5365	2878	1738	107	0.282
H(16D)	4985	-99	3729	97	0.282
H(16E)	5405	276	2689	97	0.282
H(16F)	3982	590	3024	97	0.282
H(17D)	4575	1101	4941	87	0.282
H(17E)	3998	2089	4359	87	0.282
H(17F)	5372	2153	5067	87	0.282
H(18A)	11097	3428	6767	83	
H(18B)	9814	3924	6154	83	
H(19A)	11664	5018	6152	121	
H(19B)	11207	4651	5050	121	
H(19C)	12490	4151	5660	121	

Table S13. Selected torsion angles [°] for **5b**.

C(5)-N(1)-C(1)-C(2)	-0.33(18)
B(1)-N(1)-C(1)-C(2)	177.50(11)
C(5)-N(1)-C(1)-C(6)	178.93(11)
B(1)-N(1)-C(1)-C(6)	-3.23(13)
N(1)-C(1)-C(2)-C(3)	0.58(19)
C(6)-C(1)-C(2)-C(3)	-178.54(12)
C(1)-C(2)-C(3)-C(4)	-0.1(2)
C(2)-C(3)-C(4)-C(5)	-0.6(2)
C(1)-N(1)-C(5)-C(4)	-0.4(2)
B(1)-N(1)-C(5)-C(4)	-177.84(12)
C(3)-C(4)-C(5)-N(1)	0.9(2)
N(1)-C(1)-C(6)-C(11)	179.80(12)
C(2)-C(1)-C(6)-C(11)	-1.0(2)
N(1)-C(1)-C(6)-C(7)	0.63(14)
C(2)-C(1)-C(6)-C(7)	179.82(13)
C(11)-C(6)-C(7)-C(8)	2.15(18)
C(1)-C(6)-C(7)-C(8)	-178.65(11)
C(11)-C(6)-C(7)-B(1)	-176.84(11)
C(1)-C(6)-C(7)-B(1)	2.36(14)
C(6)-C(7)-C(8)-C(9)	-0.55(19)
B(1)-C(7)-C(8)-C(9)	178.19(13)
C(7)-C(8)-C(9)-C(10)	-0.8(2)
C(7)-C(8)-C(9)-C(18)	178.99(13)
C(8)-C(9)-C(10)-C(11)	0.6(2)
C(18)-C(9)-C(10)-C(11)	-179.16(13)
C(9)-C(10)-C(11)-C(6)	0.9(2)
C(7)-C(6)-C(11)-C(10)	-2.34(19)
C(1)-C(6)-C(11)-C(10)	178.59(12)
B(1)-O(1A)-C(12A)-C(15A)	135.7(7)
B(1)-O(1A)-C(12A)-C(14A)	-106.2(9)
B(1)-O(1A)-C(12A)-C(13A)	13.2(10)
B(1)-O(2A)-C(13A)-C(16A)	151.2(3)
B(1)-O(2A)-C(13A)-C(17A)	-89.5(5)

B(1)-O(2A)-C(13A)-C(12A)	29.1(4)
O(1A)-C(12A)-C(13A)-O(2A)	-25.7(7)
C(15A)-C(12A)-C(13A)-O(2A)	-142.3(3)
C(14A)-C(12A)-C(13A)-O(2A)	90.9(4)
O(1A)-C(12A)-C(13A)-C(16A)	-146.2(7)
C(15A)-C(12A)-C(13A)-C(16A)	97.3(4)
C(14A)-C(12A)-C(13A)-C(16A)	-29.5(5)
O(1A)-C(12A)-C(13A)-C(17A)	91.7(7)
C(15A)-C(12A)-C(13A)-C(17A)	-24.9(6)
C(14A)-C(12A)-C(13A)-C(17A)	-151.7(4)
B(1)-O(1B)-C(12B)-C(13B)	-19(3)
B(1)-O(1B)-C(12B)-C(15B)	-144(2)
B(1)-O(1B)-C(12B)-C(14B)	101(2)
O(1B)-C(12B)-C(13B)-C(17B)	144(2)
C(15B)-C(12B)-C(13B)-C(17B)	-95.9(17)
C(14B)-C(12B)-C(13B)-C(17B)	26(2)
O(1B)-C(12B)-C(13B)-O(2B)	27(2)
C(15B)-C(12B)-C(13B)-O(2B)	147.5(8)
C(14B)-C(12B)-C(13B)-O(2B)	-90.7(8)
O(1B)-C(12B)-C(13B)-C(16B)	-82(2)
C(15B)-C(12B)-C(13B)-C(16B)	38.3(15)
C(14B)-C(12B)-C(13B)-C(16B)	160.1(10)
B(1)-O(2B)-C(13B)-C(12B)	-25.5(10)
B(1)-O(2B)-C(13B)-C(17B)	-153.8(10)
B(1)-O(2B)-C(13B)-C(16B)	93.0(11)
C(8)-C(9)-C(18)-C(19)	-106.98(18)
C(10)-C(9)-C(18)-C(19)	72.78(18)
C(12A)-O(1A)-B(1)-O(2A)	3.4(10)
C(12A)-O(1A)-B(1)-C(7)	-140.5(7)
C(12A)-O(1A)-B(1)-N(1)	113.1(8)
C(13A)-O(2A)-B(1)-O(1A)	-21.6(6)
C(13A)-O(2A)-B(1)-C(7)	119.2(3)
C(13A)-O(2A)-B(1)-N(1)	-136.0(2)
C(13B)-O(2B)-B(1)-O(1B)	14.7(19)
C(13B)-O(2B)-B(1)-C(7)	137.1(8)

C(13B)-O(2B)-B(1)-N(1)	-120.3(8)
C(12B)-O(1B)-B(1)-O(2B)	2(3)
C(12B)-O(1B)-B(1)-C(7)	-110(2)
C(12B)-O(1B)-B(1)-N(1)	139.1(17)
C(6)-C(7)-B(1)-O(1A)	-118.2(6)
C(8)-C(7)-B(1)-O(1A)	63.0(7)
C(6)-C(7)-B(1)-O(2A)	104.92(17)
C(8)-C(7)-B(1)-O(2A)	-73.9(2)
C(6)-C(7)-B(1)-O(2B)	118.6(2)
C(8)-C(7)-B(1)-O(2B)	-60.2(3)
C(6)-C(7)-B(1)-O(1B)	-126.4(17)
C(8)-C(7)-B(1)-O(1B)	54.9(17)
C(6)-C(7)-B(1)-N(1)	-3.65(12)
C(8)-C(7)-B(1)-N(1)	177.56(13)
C(5)-N(1)-B(1)-O(1A)	-57.1(8)
C(1)-N(1)-B(1)-O(1A)	125.3(8)
C(5)-N(1)-B(1)-O(2A)	55.13(17)
C(1)-N(1)-B(1)-O(2A)	-122.47(13)
C(5)-N(1)-B(1)-O(2B)	75.5(3)
C(1)-N(1)-B(1)-O(2B)	-102.1(2)
C(5)-N(1)-B(1)-O(1B)	-55(2)
C(1)-N(1)-B(1)-O(1B)	127(2)
C(5)-N(1)-B(1)-C(7)	-178.31(12)
C(1)-N(1)-B(1)-C(7)	4.10(12)

NOTE:

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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