

Supporting information

Ligand-Enabled, Iridium-Catalyzed *ortho*-Borylation of Fluoroarenes

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1. General information

1.1. Instrumentation

Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm silica gel containing a fluorescent indicator (Merck #1.05715 TLC Silica gel 60 F₂₅₄). The borylated fluoroarenes were developed on TLC plates visualized by UV irradiation, or by placing in an iodine chamber, or by staining with *p*-anisaldehyde in H₂SO₄. Preparative column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 40–50 μ m). Gel-permeation chromatography (GPC) was performed on Shimadzu LC-20A equipped with FP-2002 columns and using chloroform as an eluent.

¹H NMR and ¹³C{¹H} NMR spectra were recorded on a JEOL 500 spectrometer operating at 500 MHz for ¹H NMR and 126 MHz for ¹³C{¹H} NMR and were referenced to the residual proton resonances of the corresponding deuterated solvent: CDCl₃ (¹H: 7.26 ppm, ¹³C: 77.2 ppm), THF-*d*₈ (¹H: 3.58 ppm, ¹³C: 67.6 ppm). ¹⁹F NMR spectra were recorded on a JEOL 500 spectrometer operating at 471 MHz and were referenced to C₆F₆: –164.9 ppm. ¹¹B NMR spectra were recorded on a JEOL 500 spectrometer operating at 160 MHz and were referenced using the unified scale¹, the $\delta = 32.083974$. The multiplicity of signals is indicated using the following abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet and br = broad.

Gas chromatography (GC) analyses were performed at SHIMADZU GC-2025 equipped with a FID detector and a capillary column (HR-1, 0.25-mm i.d. x 25 m). Mass spectra (GC-MS) analysis were performed at SHIMADZU QP2010SE equipped with a capillary column (Rxi-5Sil MS, 0.25-mm i.d. x 30 m) (the temperature range was set from 50 to 300 °C, the spectra recording started after 3 min). High resolution mass spectra were taken at Bruker microTOF-Q III (APCI).

The melting points were determined using a Yanaco MP-500 apparatus and were uncorrected.

1.2. Materials

All reagents were purchased from commercial sources and used as received unless otherwise noted. Anhydrous THF, 1,4-dioxane (stabilizer-free), hexane, toluene and DCM were purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use.

THF-*d*₈ was distilled from Na/benzophenone mixture under atmosphere of argon and stored over MS 3Å in a glove box unless otherwise noted. A trace amount of deuterated benzene was detected in THF-*d*₈ after distillation (¹H NMR (500 MHz, THF-*d*₈), δ 7.30 (s); ¹³C{¹H} NMR (126 MHz, THF-*d*₈), δ 129.1 (t, *J* = 13.0 Hz)).

B₂Pin₂ was purchased from BLDpharm and recrystallized from hexane prior to use.



Figure S1. Distillation equipment for THF- d_8 .

1.3. General considerations

All the reactions using air- or moisture-sensitive compounds were carried out in a dry reaction vessel under an atmosphere of nitrogen or argon.

We recommend that the iridium-catalyzed borylation reactions to be conducted in a dry solvent, because we observed decrease in yield when wet solvent was used.

The ratio of isomers for isolated compounds was determined either by GC, ^{19}F NMR, or ^1H NMR, depending on which one is more convenient for a certain compound, and was almost identical to the isomer ratio in the crude material, unless otherwise noted.

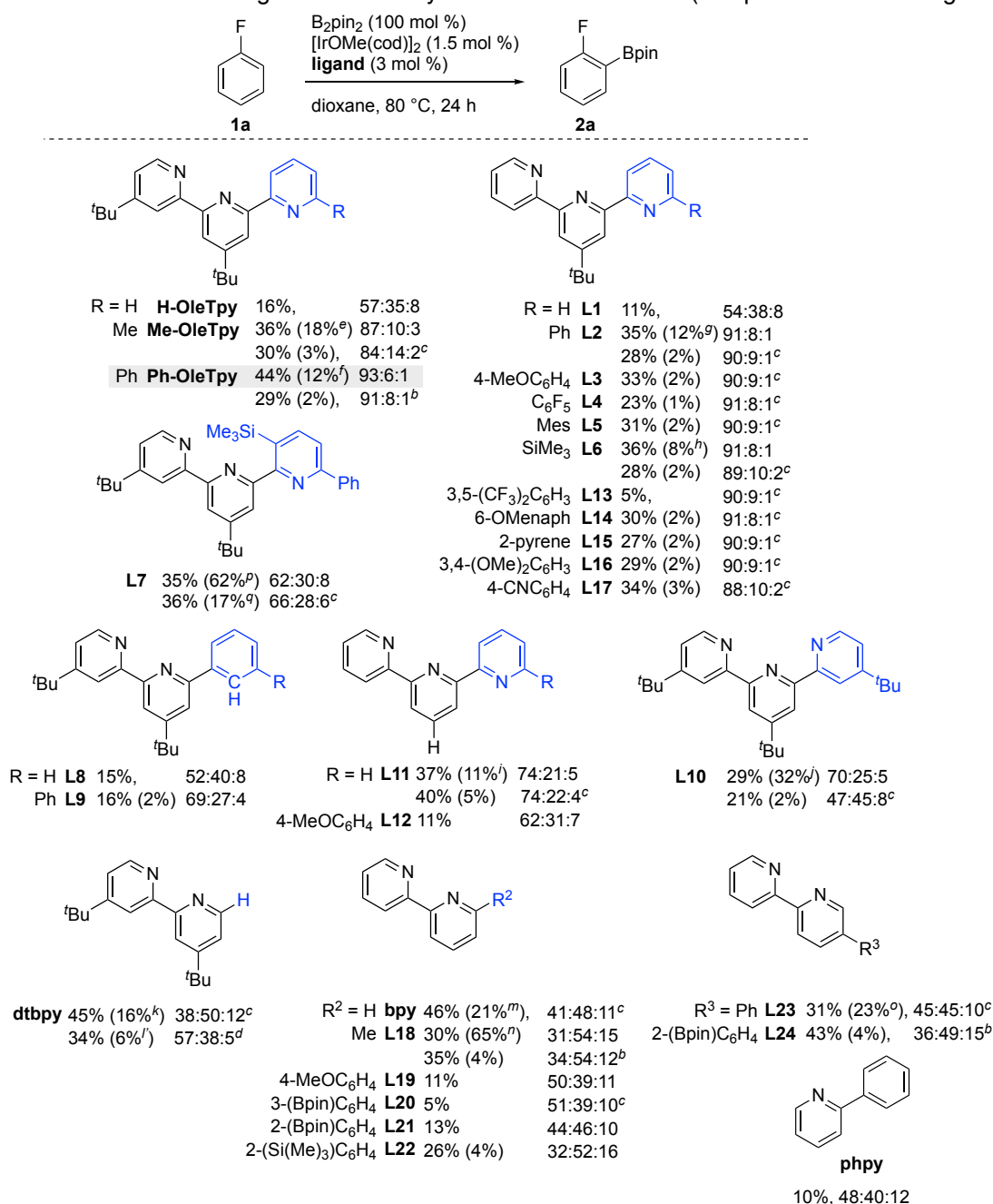
The NMR data are reported for the major isomer, except ^{19}F NMR data that are reported for both the major and minor isomers, if assigned. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The yield of borylated fluoroarenes is calculated based on the fluoroarene starting material.

2. Reaction development

2.1. Ligands screening

Scheme S1. Effect of the ligand on the borylation of fluorobenzene (comprehensive list of ligands).



^aReaction conditions: fluorobenzene (**1a**, 0.20 mmol), B_2pin_2 (100 mol %), $[IrOMe(cod)]_2$ (1.5 mol %), ligand (3 mol %) in dioxane (0.8 mol/L), 80 °C, 24 h. The yield and selectivity (reported as *ortho/meta/para*) were estimated by GC using tridecane or hexadecane as internal standard. The yield of the diborylated product is shown in parentheses. If the diborylated product is obtained in more than 5% the selectivity (2,6-/2,5-/2,4-/3,5-) is determined by GC and reported at the footnotes (e) to (q). ^b B_2pin_2 (50 mol%), dioxane (0.2 mol/L). ^cFluorobenzene (0.40 mmol), B_2pin_2 (50 mol%), $[IrOMe(cod)]_2$ (0.75 mol%), ligand (1.5 mol%) in dioxane (0.4 mol/L). ^dConditions at footnote (c) at 15 °C, 12 h. ^e25:68:6:<1. ^f38:50:12:<1. ^g32:62:6:<1. ^h32:62:6:<1. ⁱ19:70:8:3. ^j10:77:7:6. ^k7:50:19:24. ^l5:78:7:10. ^m4:58:17:21. ⁿ2:71:10:17. ^o5:57:19:19. ^p11:69:15:5. ^q12:70:13:5.

2.2. Conditions screening

Variation from the standard reaction conditions^a with the best ligand **Ph-OleTpy**:

^aStandard reaction conditions (Scheme S1): fluorobenzene **1a** (0.20 mmol), B₂pin₂ (100 mol %), [IrOMe(cod)]₂ (1.5 mol %), ligand (3 mol %) in dioxane (0.8 mol/L), 80 °C, 24 h. Yield was estimated by GC or ¹⁹F NMR.

Boron source

Entry	Boron source	Yield, mono (di), %	Ratio, o:m:p
Standard	B ₂ pin ₂ 100 mol%	44 (12)	93:6:1
1	B ₂ pin ₂ 50 mol%	28 (4)	90:9:1
2	HBpin 100 mol%	14 (1)	86:12:2
3	HBpin 200 mol%	20 (2)	87:11:2

Ir source

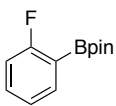
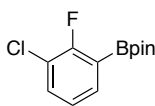
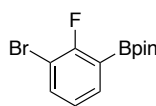
Entry	Ir source	Yield, mono (di), %	Ratio, o:m:p
Standard	[IrOMe(cod)] ₂	44 (12)	93:6:1
1	[IrCl(cod)] ₂	39 (17)	94:5:1
2	[IrCl(cod)] ₂	46 (19)	95:4:1

Solvent, concentration, time, reaction set up

Entry	Solvent	C (S), mol/L	t, h (if varied)	Reaction set up (if varied)	Yield, mono (di), %	Ratio, o:m:p
Standard	dioxane	0.8	24	mix all the solids, add dioxane at rt following by addition of substrate if liquid	44 (12)	93:6:1
1	THF	0.8	—	—	43 (9)	90:8:2
2	hexane	0.8	—	—	29 (6)	84:13:3
3	dioxane	0.5	—	—	38 (7)	93:6:1
4	dioxane	0.2	—	—	26 (2)	90:9:1
5	dioxane ^a	0.2	—	—	29 (2)	91:8:1
6	dioxane	0.8	44	—	49 (17) ^e	93:6:1
7	dioxane	0.8	—	premix [IrOMe(cod)] ₂ , B ₂ pin ₂ , Ph-OleTpy in dioxane at 80 °C for 105 min	33 (10)	89:9:2
8	dioxane	0.8	—	H₂O one drop^d	27 (4)	92:7:1
9	no solvent ^b	neat	—	—	74 (n.d.)	79:18:3
10	dioxane	0.4 ^c	—	no ligand	2 (n.d.)	37:47:15

^aB₂pin₂ (50 mol%). ^b**1a** (12 mmol, 1.1 mL). ^c**1a** (0.40 mmol), B₂pin₂ (50 mol%), [IrOMe(cod)]₂ (0.75 mol%), dioxane (0.4 mol/L), 14 h. ^ddrop was added by 50 μl syringe. ^e**1a** (0.60 mmol).

2.3. Control experiments with dtbpy ligand

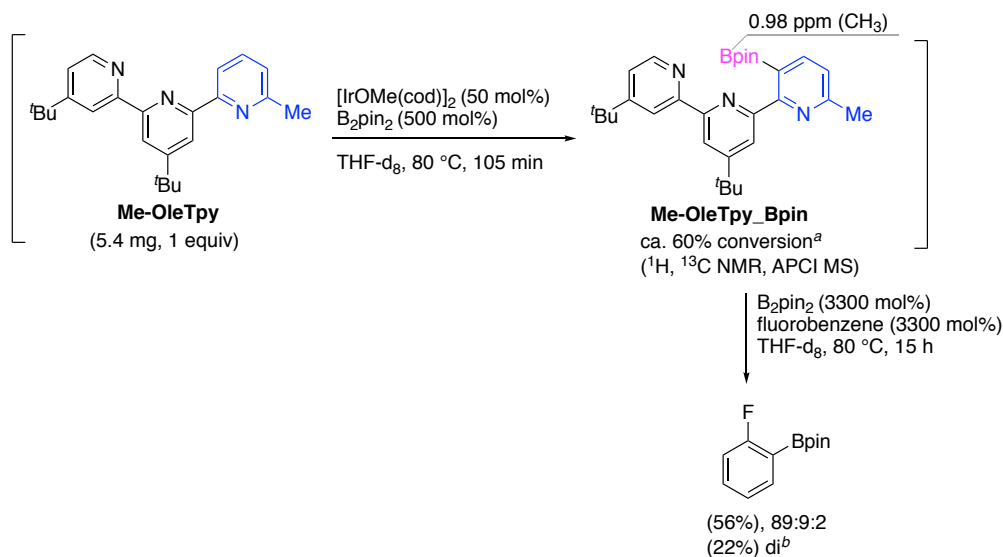
			
	2a	2b	2c
Ph-OleTpy	47% (49%), 93:6:1 16% (17%) di ^a	70% (84%), 97:3:<1	68% (81%), 94:5:1
dtbpy	(45%) + (16% di), 38:50:12 ^b (44%) + (17% di), 45:47:8 ^c (34%) + (6% di), 57:38:5 ^d	(48%) + (7% di), 38:37:25 ^e (20%) + (55% di) ^f , 8:72:21	(52%) + (6% di), 41:35:24 ^e (24%) + (55% di) ^f , 5:82:13

Reaction conditions: fluoroarene (**1**, 0.40 mmol), B₂pin₂ (100 mol %), [IrOMe(cod)]₂ (1.5 mol %), ligand (3 mol %) in dioxane (0.8 mol/L), 80 °C, 24 h. For **Ph-OleTpy** the yield of the isolated product (**2**) is reported; the yield in parentheses was determined by ¹⁹F NMR using trifluorotoluene as internal standard. For **dtbpy** the reported yield was estimated by GC using tridecane as internal standard. The isomer ratio is reported as *ortho/meta/para* for monoborylated fluoroarene and it was determined by GC or ¹⁹F NMR. Regioisomers of the diborylated product are reported as 2,6-/2,5-/2,4-/3,5- at footnotes (a) to (c). ^a**1a** (0.60 mmol), 44 h; 36:56:8:<1. ^bB₂pin₂ (50 mol%), [IrOMe(cod)]₂ (0.75 mol%), dtbpy (1.5 mol%) in dioxane (0.4 mol/L); 7:50:19:24. ^c**1a** (0.2 mmol), B₂pin₂ (50 mol%), dioxane (0.2 mol/L), 30 °C, 14 h; 5:70:10:15. ^dConditions at footnote (b), 15 °C, 12 h; 5:77:7:11. ^eConditions at footnote (c), 50 °C, 15 h; 3,5-isomer is the major diborylated product. ^ffluoroarene (0.20 mmol); 3,5-isomer is the major diborylated product.

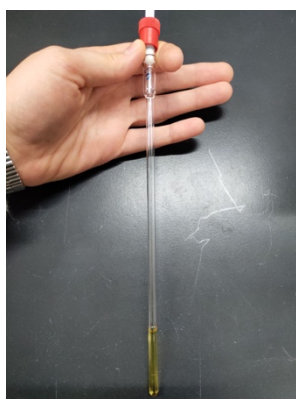
Figure S2. Comparison of regioselectivity of **Ph-OleTpy** vs **dtbpy** in the borylation of fluoroarenes **1a-1c**.

3. Mechanistic experiments

Scheme S2. NMR experiment in a gas-tight tube using **Me-OleTpy**.



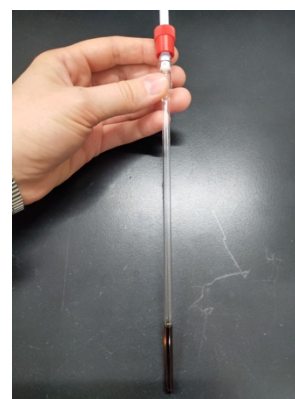
^aEstimated by ¹H NMR using mesitylene as internal standard. ^bConversion of fluorobenzene and isomer ratio were determined by ¹⁹F NMR.



After addition of THF- d_8 at rt



Heating



After heating at 80 °C for 105 min

Figure S3. Experiment in a gas-tight NMR tube.

Me-OleTpy (5.4 mg, 0.015 mmol), [IrOMe(cod)]₂ (5.0 mg, 0.0075 mmol) and B₂pin₂ (19 mg, 0.075 mmol) were placed into an oven dried (70 °C) gas-tight NMR tube and transferred into a glove box. THF- d_8 was added, the tube was sealed and taken out from the glove box. At this point, ¹H NMR indicated no changes to the ligand. The NMR tube was placed in an oil bath at 80 °C and left at this temperature for 105 min. At this point, the NMR was recorded and the borylated ligand was detected as a major species both by NMR and by mass spectrometry. After the NMR measurements, the NMR tube was transferred into a glove box, and B₂pin₂ (126 mg, 0.495 mmol) and fluorobenzene (0.046 mL, 0.495 mmol) were added. The tube was sealed, taken out from glove box and placed in an oil bath at 80 °C, where the reaction mixture was heated for 15 h. At this point, the conversion of fluorobenzene and the ratio were determined by ¹⁹F NMR. *Note 1:* The probe for mass spectroscopy was prepared inside a glove box. An aliquot was taken from the NMR tube, followed by dilution with dry THF containing BHT stabilizer. The vial was tightly closed and opened directly before injection of the sample into the mass spectrometer. *Note 2:* In order to estimate the conversion of **Me-OleTpy** to **Me-OleTpy-Bpin**, we repeated the experiment with mesitylene as internal standard. In this case, mesitylene was added inside the glove box directly to the NMR tube containing the solution of **Me-OleTpy**, [IrOMe(cod)]₂ and B₂pin₂ in THF- d_8 . This was defined as the 0 h point, and the sample was measured by ¹H NMR. After 3 h at 80 °C, the ¹H NMR spectrum was identical to the experiment without mesitylene, and the conversion of the ligand was estimated as ca. 60%. *Note 3:* The THF- d_8 was dried by storing over MS 3 Å. **Me-OleTpy:** ¹H NMR (500 MHz, THF- d_8) δ 8.70 (d, *J* = 2.0 Hz, 1H), 8.62 (d, *J* = 1.9 Hz, 1H), 8.60 (d, *J* = 1.9 Hz, 1H), 8.55 (d, *J* = 5.1 Hz, 1H), 8.46 (d, *J* = 7.7 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.37 (dd, *J* = 5.1, 2.0 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 2.61 (s, 3H), 1.45 (s, 9H), 1.42 (s, 9H). ¹³C{¹H} NMR (126 MHz, THF- d_8) δ 162.3 (C), 161.3 (C), 158.6 (C), 157.5 (C), 156.90 (C), 156.85 (C), 156.6 (C), 150.0 (CH), 137.8 (CH), 123.9 (CH), 121.6 (CH), 118.9 (CH), 118.7 (CH), 118.51 (CH), 118.47 (CH), 36.0 (C), 35.7 (C), 31.2 (3CH₃), 31.1 (3CH₃), 25.2 (CH₃)^a. **Me-OleTpy-Bpin:** ¹H NMR (500 MHz, THF- d_8) δ 8.53 (dd, *J* = 5.2, 0.8 Hz, 1H), 8.44 (d, *J* = 1.9 Hz, 1H), 8.36 (dd, *J* = 2.0, 0.8 Hz, 1H), 8.11 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 2.58 (s, 3H), 1.45 (s, 9H), 1.35 (s, 9H), 0.98 (s, 12H). ¹³C{¹H} NMR (126 MHz, THF- d_8) δ 163.3 (C), 161.6 (C), 161.0 (C), 159.9 (C), 159.0 (C), 158.2 (C), 157.2 (C), 150.0 (CH), 142.8 (CH), 122.1 (CH), 121.6 (CH), 120.1 (CH), 119.6 (CH), 119.1 (CH), 84.0 (4C)^b, 35.9

(C), 35.7 (C), 31.2 (3CH₃), 31.1 (3CH₃), 25.3 (4CH₃)^{a,b}; 24.8 (CH₃)^{a,b}. **MS, APCI, m/z**: calcd for C₃₀H₄₁BN₃O₂⁺, [M+H]⁺, 486.33. Found: 486.32.

^aSignal overlaps with signal of THF-*d*₈. The shift was determined by 2D experiments. ^bSignal overlaps with signals of boron derivatives present in the reaction mixture. The shift was determined by 2D experiments.

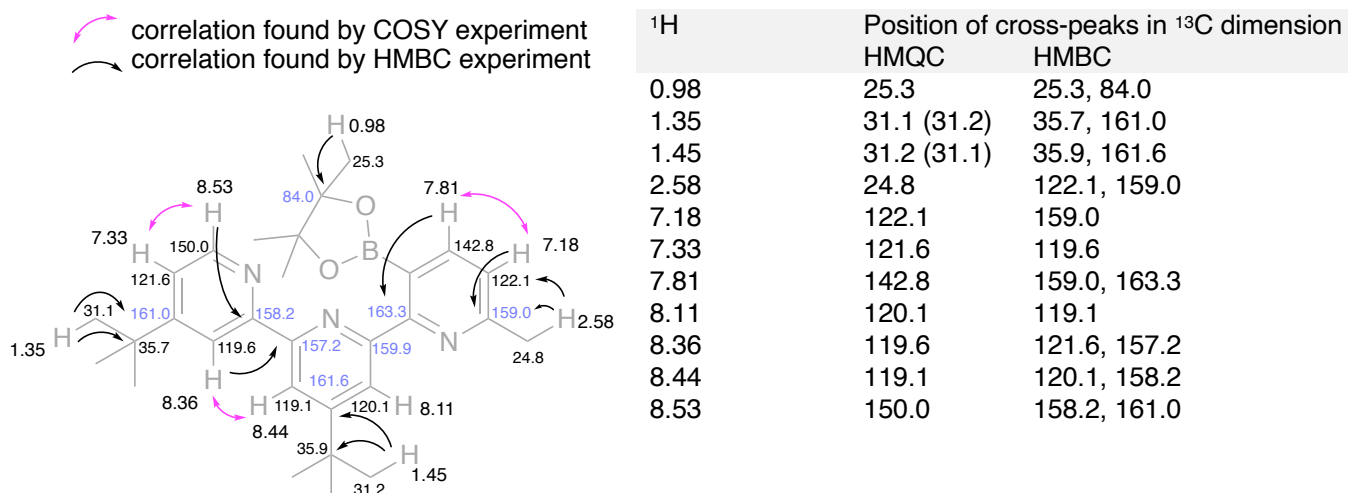


Figure S4. The NMR chemical shifts of **Me-OleTpy-Bpin** found by 2D experiments (COSY, HMQC, HMBC) and the selected correlations found by COSY and HMBC experiments (Solvent: THF-*d*₈).

Table S1. The list of heteronuclear correlations ¹H–¹³C, founded for compound **Me-OleTpy-Bpin** in HMQC and HMBC spectra (Solvent: THF-*d*₈).

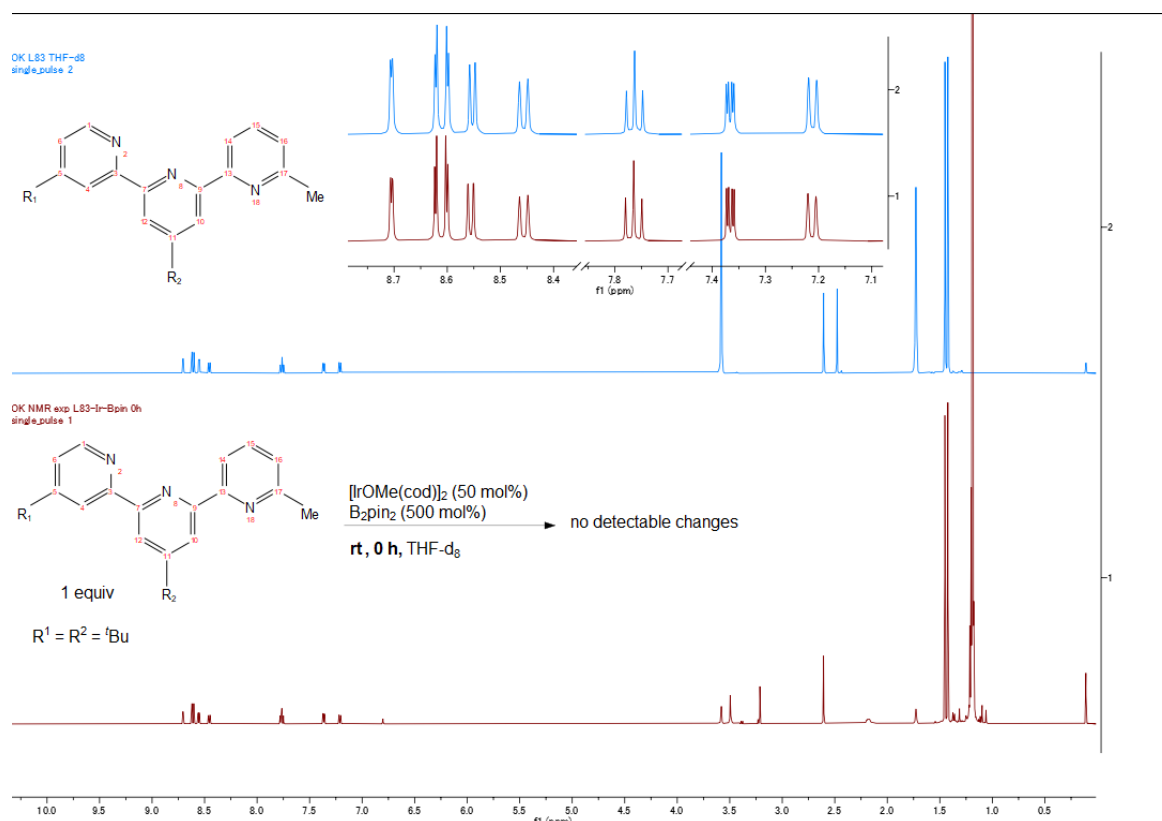


Figure S5. Comparison of the shifts in ¹H NMR of **Me-OleTpy** (top, blue) and **Me-OleTpy** after premixing with B_2pin_2 and $[\text{IrOMe}(\text{cod})]_2$ at rt (bottom, maroon).

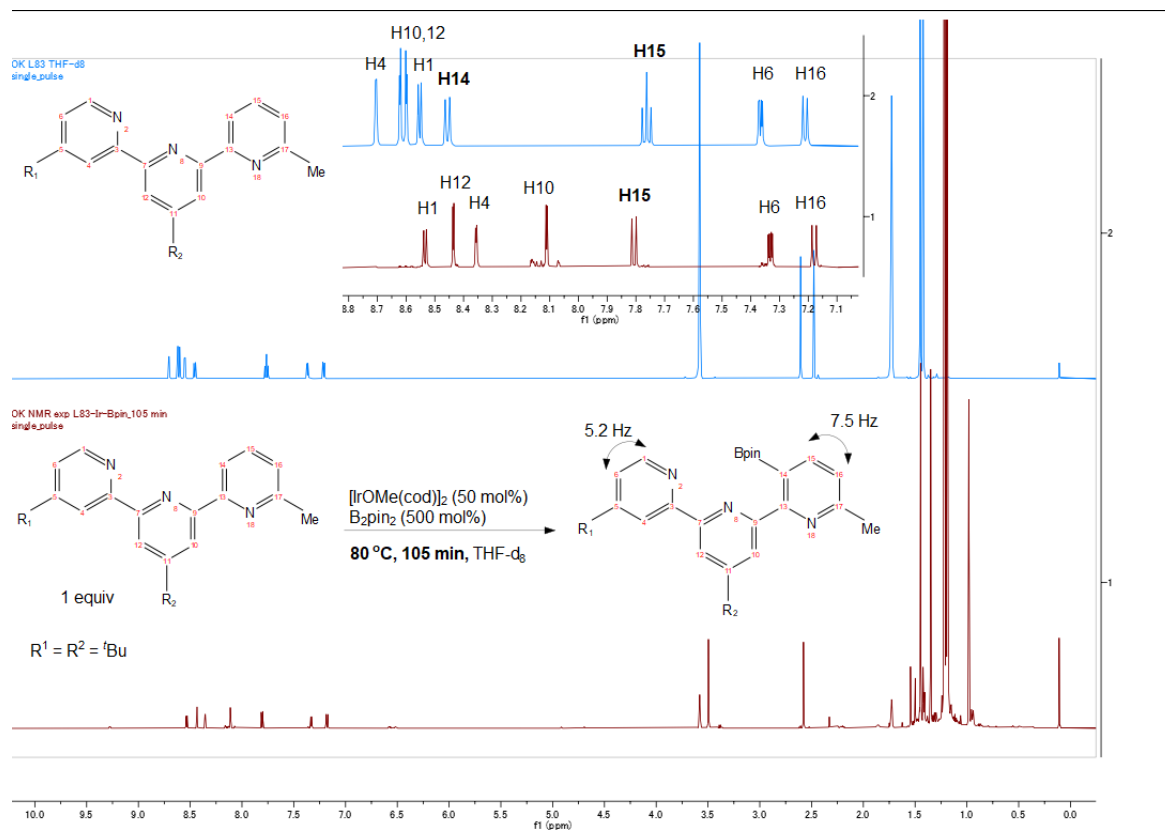


Figure S6. Comparison of the shifts in 1H NMR of **Me-OleTpy** (top, blue) and **Me-OleTpy_Bpin** after heating at 80 °C for 105 min (bottom, maroon).

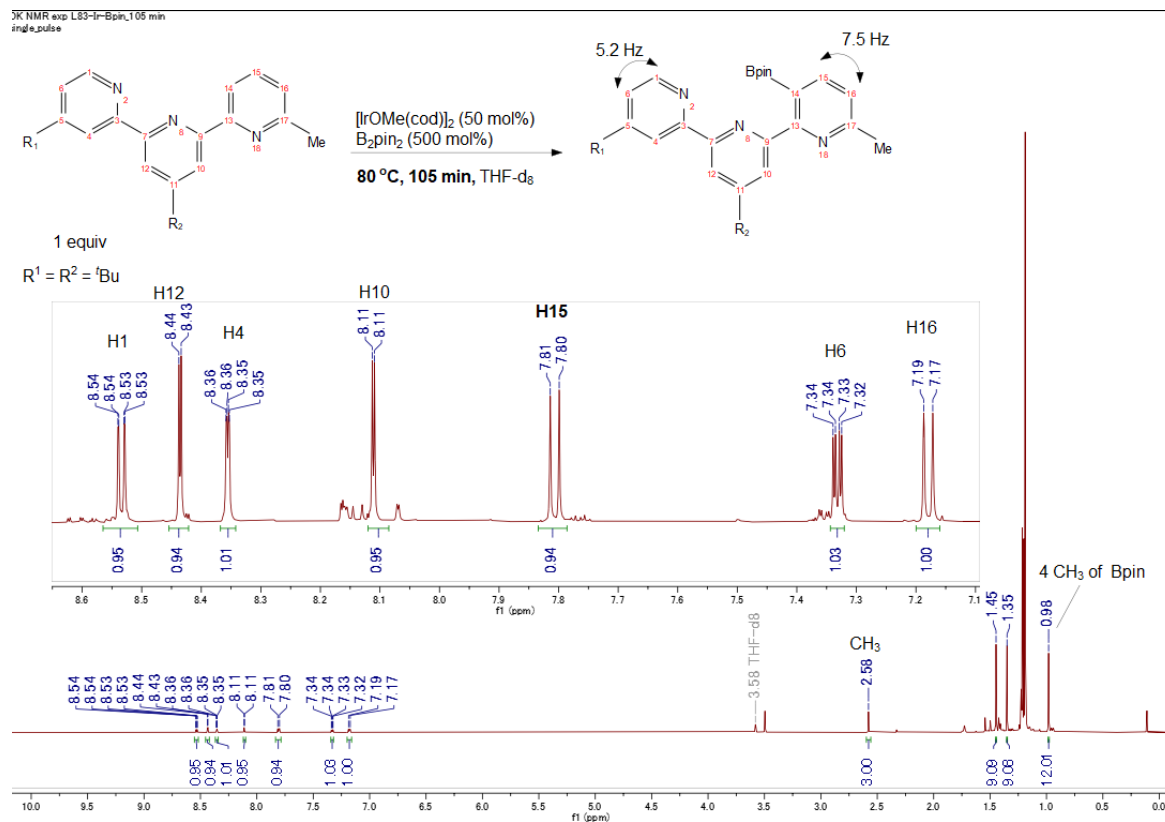


Figure S7. 1H NMR spectra of **Me-OleTpy_Bpin** (THF- d_8).

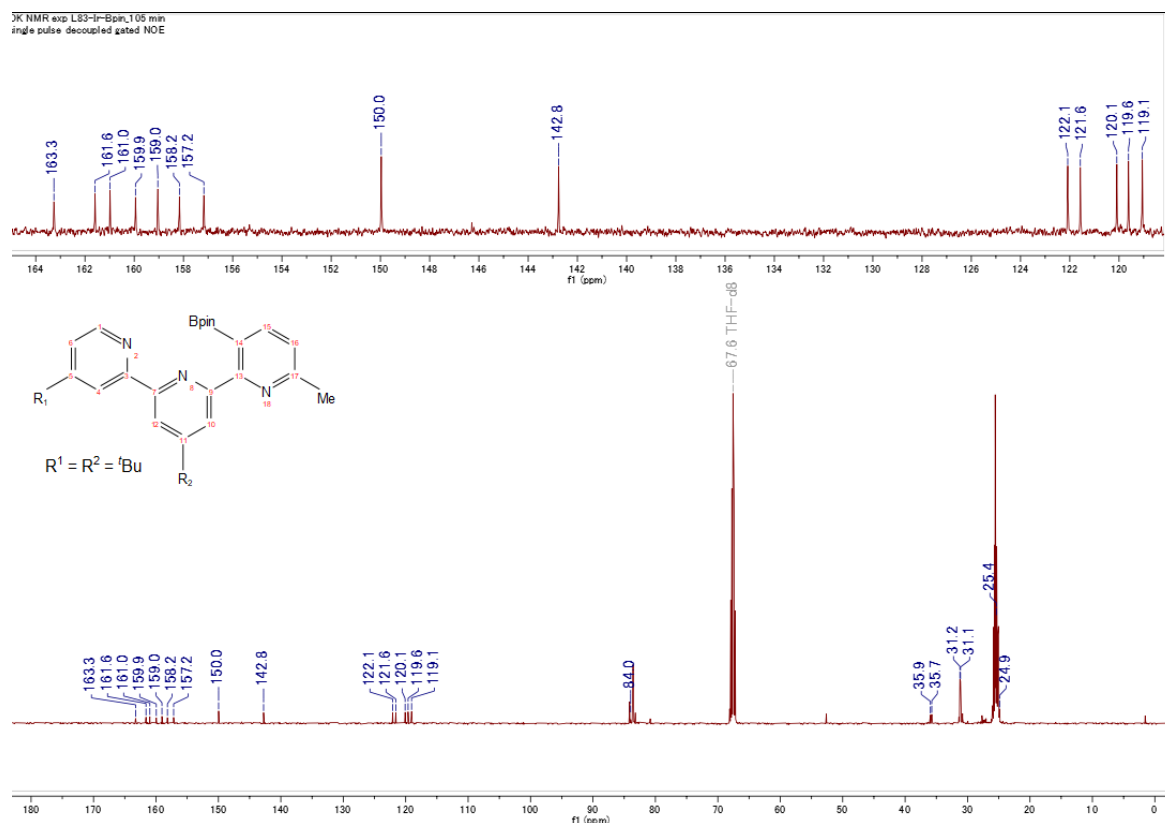
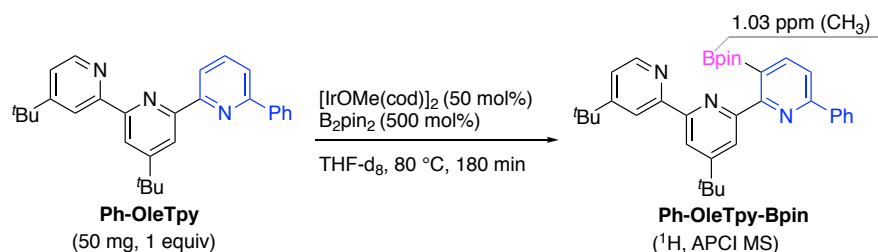


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of Me-OleTpy-Bpin (THF- d_8).

Borylation of Ph-OleTpy in a Schlenk tube

Scheme S3. Conversion of Ph-OleTpy to Ph-OleTpy-Bpin under the same conditions with the NMR experiment.

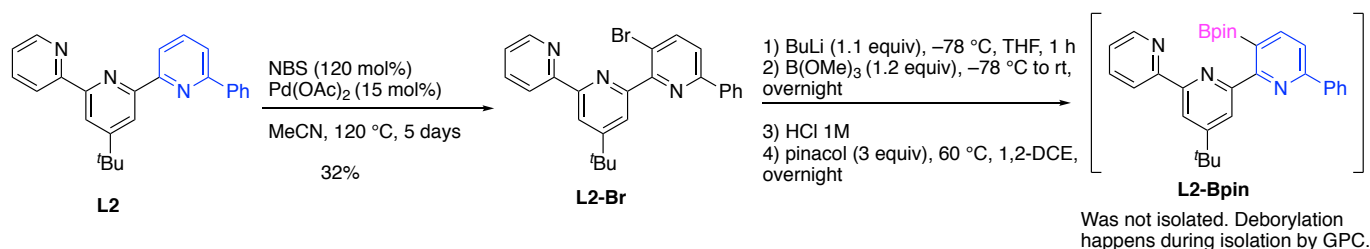


Ph-OleTpy (50 mg, 0.12 mmol), $[\text{IrOMe}(\text{cod})]_2$ (39 mg, 0.06 mmol) and B_2pin_2 (151 mg, 0.59 mmol) were placed into a Schlenk flask under an atmosphere of N_2 . Dry THF was added to the solids, the flask was sealed, and the reaction mixture was stirred at 80°C for 180 min. At this point, an aliquot was taken from the reaction mixture, the volatiles were removed under reduced pressure, CDCl_3 was added, and ^1H NMR was recorded to indicate the formation of the borylated ligand as the major species. ^1H NMR (500 MHz, Chloroform- d) δ 8.61 (d, $J = 5.3$ Hz, 1H), 8.25 – 8.31 (m, 3H), 8.11 – 8.18 (m, 2H), 8.05 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.48 – 7.53 (m, 2H), 7.41 – 7.46 (m, 1H), 7.30 (dd, $J = 5.3, 2.0$ Hz, 1H), 1.48 (s, 9H), 1.35 (s, 9H), 1.03 (s, 12H). **MS, APCI, m/z :** calcd for $\text{C}_{35}\text{H}_{43}\text{BN}_3\text{O}_2^+$, $[\text{M}+\text{H}]^+$, 548.34. Found: 548.34.

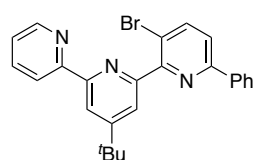
Attempt to synthesize 4'-(*tert*-butyl)-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':6',2''-terpyridine (L2-Bpin)

In order to prove the catalytic activity of borylated ligand, we tried to isolate the borylated ligand **L2-Bpin**. Although isolation of this compound failed because of fast protodeborylation, we compared the obtained ^1H NMR spectra of **L2-Bpin** (mixture with **L2**) with **Ph-OleTpy-Bpin** obtained *in situ* (Scheme S3) to further confirm the structure of the borylated ligand produced *in situ*.

Scheme S4. Synthesis of 4'-(*tert*-butyl)-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':6',2''-terpyridine (**L2-Bpin**).

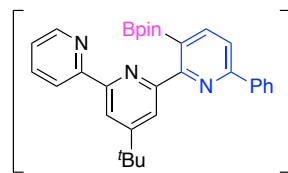


Synthesis of 3-bromo-4'-(*tert*-butyl)-6-phenyl-2,2':6',2''-terpyridine (**L2-Br**)



L2-Br was synthesized following the procedure adopted from the literature.² **L2** (250 mg, 0.68 mmol), *N*-bromosuccinimide (146 mg, 0.82 mmol) and $\text{Pd}(\text{OAc})_2$ (23 mg, 0.102 mmol) were suspended in MeCN (0.1 mol/L). The Schlenk flask was sealed with a screw cap and heated at 120 °C for 5 days. The reaction mixture was cooled down to rt, diluted with H_2O and extracted with EtOAc ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (96 mg, 0.22 mol, 32%) was obtained as a white solid after column chromatography: hexane to hexane–EtOAc 95:5. **L2** was recovered in 44% (109 mg, 0.30 mmol).

Synthesis of 4'-(*tert*-butyl)-6-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':6',2''-terpyridine (**L2-Bpin**)



To a solution of **L2-Br** (50 mg, 0.11 mmol) in THF (0.025 mol/L) BuLi (0.082 mL, 1.5 mol/L in hexane) was added dropwise via syringe at -78 °C resulting in a deep orange solution, which was stirred for 1 h. Then, $\text{B}(\text{OMe})_3$ (0.032 mL, 0.23 mmol, 0.932 g/mL) was added in one portion via syringe and stirring continued for another 5 min. The solution was allowed to warm slowly to rt overnight. At this point, 1M HCl was added and stirring continued for another 30 min. The aqueous layer was extracted with Et_2O ($\times 3$), then neutralized with aq. NaHCO_3 and extracted with DCM ($\times 2$). The organic layers were collected (separately the Et_2O extract and the DCM extract), washed with brine, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The residues were dried under reduced pressure, suspended in 1,2-dichloroethane, and pinacol (27 mg, 0.23 mmol) was added. The reaction mixture was heated overnight at 60 °C, then cooled down to rt and concentrated by rotary evaporation. ^1H NMR spectra indicated the presence of the mixture of **L2** and **L2-Bpin**. The ratio was found to be as follows: (from the DCM extract): **L2-Bpin/L2**, 75:25; (from the Et_2O extract): **L2-Bpin/L2**, 43:57. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.70 (ddd, $J = 4.8, 1.8, 1.0$ Hz, 1H), 8.49 (dt, $J = 8.0, 1.1$ Hz, 1H), 8.41 (d, $J = 1.8$ Hz, 1H), 8.39 (d, $J = 1.8$ Hz, 1H), 8.17 – 8.12 (m, 2H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.79 (dd,

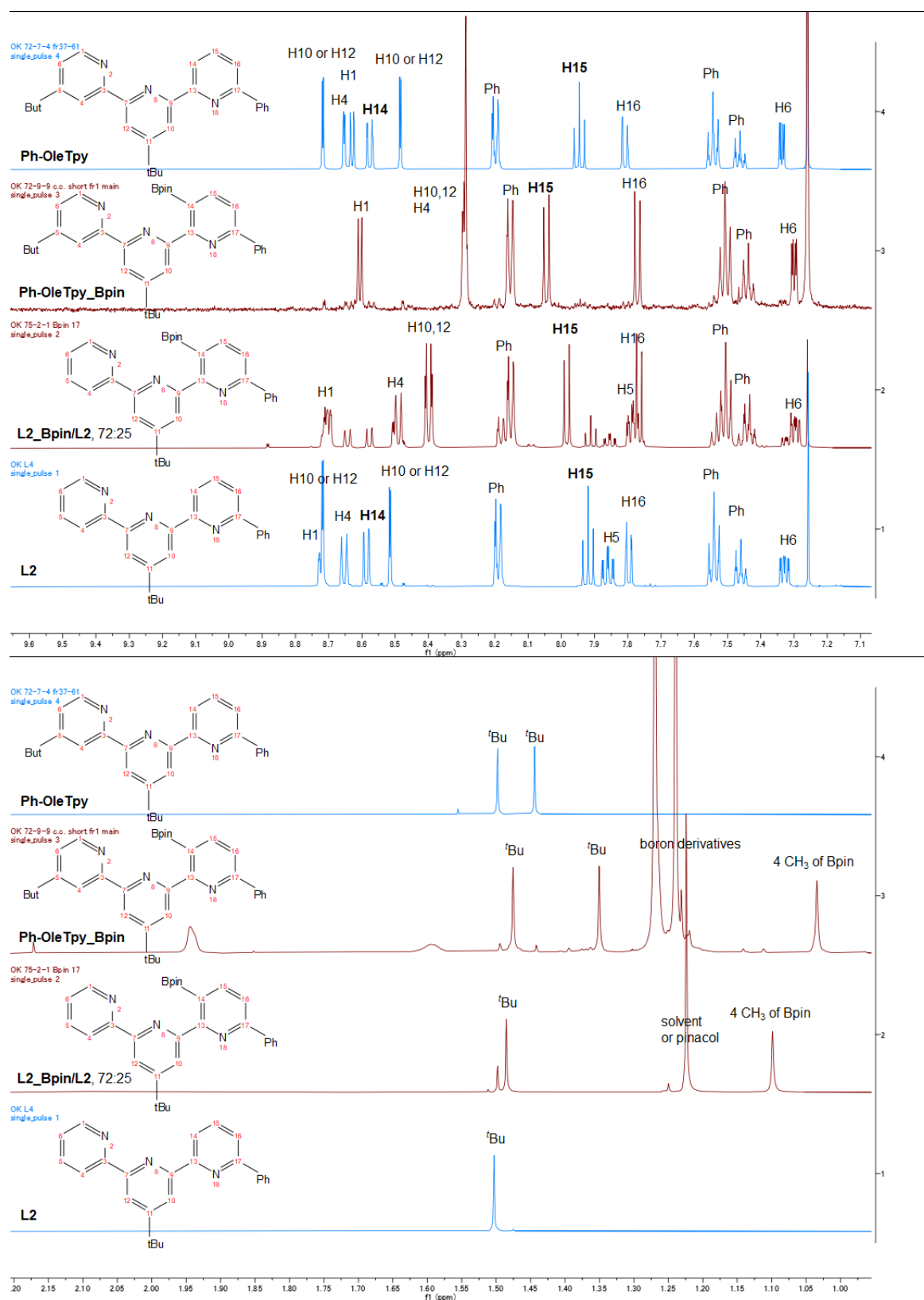
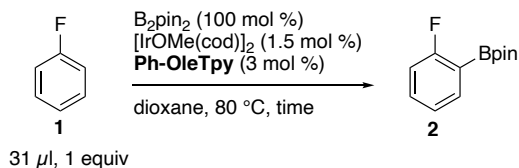


Figure S9. Comparison of the shifts in ^1H NMR of **Ph-OleTpy-Bpin** obtained by [Ir] catalysis (third spectrum) and **L2-Bpin** obtained from **L2-Br** (second spectrum). ^1H NMR spectra of **L2** and **Ph_OleTpy** are placed as the references (CDCl_3).

$J = 7.6, 1.8 \text{ Hz, 1H}$), $7.77 \text{ (d, } J = 7.7 \text{ Hz, 1H)}$, $7.50 \text{ (dd, } J = 8.3, 6.8 \text{ Hz, 2H)}$, $7.46 - 7.41 \text{ (m, 1H)}$, $7.30 \text{ (ddd, } J = 7.6, 4.8, 1.3 \text{ Hz, 1H)}$, 1.49 (s, 9H) , 1.10 (s, 12H) . The residues were combined and purification by GPC using chloroform as the eluent was attempted. However, **L2-Bpin** was protodeborylated and **L2** was recovered together with minor byproducts. The ^1H NMR spectrum with the ratio of isomers **L2-Bpin**/**L2** = 75:25 was used to make a comparison with **Ph-OleTpy-Bpin** obtained *in situ* (Scheme 3).

4. Reaction Profile



Reaction was performed in a gas-tight NMR tube

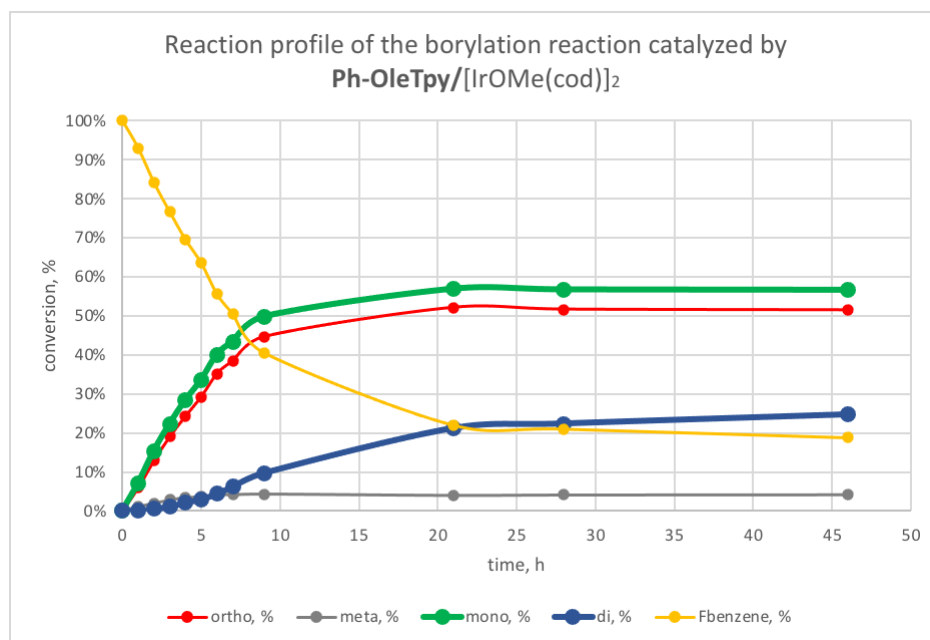


Figure S10. Kinetic profile of the borylation reaction catalyzed by **Ph-OleTpy**/[IrOMe(cod)]₂.

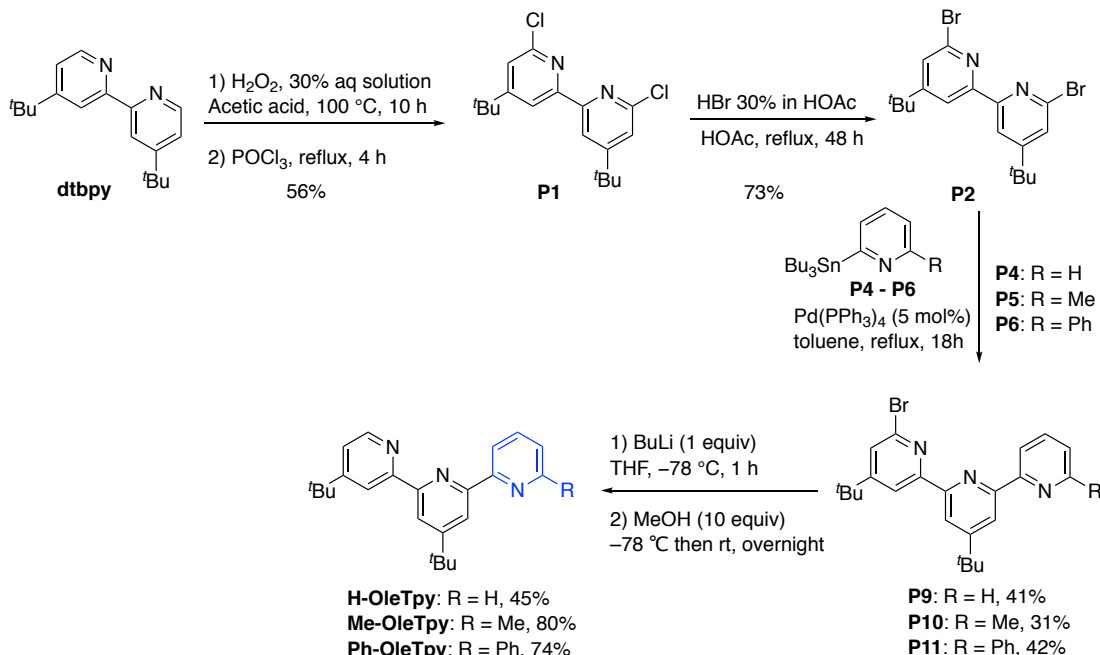
Ph-OleTpy (4.2 mg, 0.01 mmol), [IrOMe(cod)]₂ (3.3 mg, 0.005 mmol) and B₂pin₂ (84 mg, 0.33 mmol) were placed into an oven dried (70 °C) gas-tight NMR tube and transferred into a glove box. THF-*d*₈ (0.4 mL, 0.8 mol/L) was added to the solids, followed by addition of fluorobenzene (0.031 mL, 0.33 mmol). The tube was sealed and taken out from the glove box. At this point, the NMR was recorded as the zero point. The NMR tube was placed in an oil bath at 80 °C, and the NMR was recorded after: 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, 21 h, 28 h, 43 h. The data shown in Figure S10 were determined by the integration of the corresponding peaks in ^{19}F NMR spectra.

The reaction profile indicates that the *ortho*-isomer is dominant already after 1 h and remains the dominant species along the reaction course. The conversion is slowing down upon consumption of B₂pin₂ (at 9 h the dominant borylation species is HBpin): 0 h → 9 h, 60% conversion, 50% mono, 10% di; 9 h → 21 h, 18% conversion, 7% mono, 11% di

and remains almost unchanged in the presence of HBpin as solely borylation source (21 h → 43 h, 3% conversion, 0% mono, 3% di).

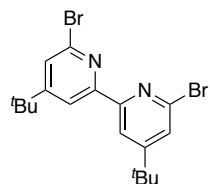
5. Synthesis and characterization data for ligands

Scheme S5. Synthesis of 4,4'-di-*tert*-butyl-6''-R-2,2':6',2''-terpyridines (**R-OleTpy**).

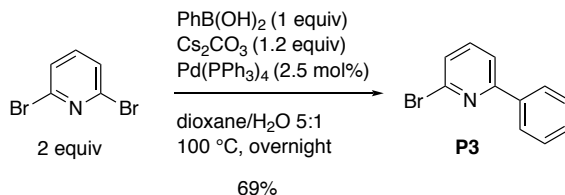


P1 was synthesized according to the procedure reported in the literature³ in 56% yield (3.18 g, 9.43 mmol) starting from dtbpy (4.5 mg, 1.68 mmol).

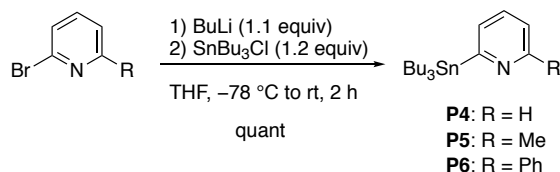
Synthesis of 6,6'-dibromo-4,4'-di-*tert*-butyl-2,2'-bipyridine (**P2**).



P2 was synthesized following the procedure adopted from the literature.⁴ In a two-necked flask equipped with a reflux condenser with CaCl_2 tube on a top and dropping funnel, **P1** (3.18 g, 9.43 mmol) was placed. AcOH (0.2 mol/L) was then added and the reaction mixture was heated to reflux. At this point, the dropwise addition of HBr (9 mL, 30% solution in AcOH) started. The reaction was monitored by GC and was run until completion (approximately 24 h). The reaction mixture was cooled down to rt, and then it was added portionwise to an aq. solution of K_2CO_3 . The amount of K_2CO_3 was adjusted to reach a basic pH. The precipitate was collected by filtration and washed with hexane. After drying under open air, 87% yield (3.51 mg, 8.24 mmol) of **P2** was obtained as a white-grey solid. Note: Additional amount of HBr has to be added if the reaction is not completed. Slow continuous addition of HBr solution is mandatory to achieve high conversion. $^1\text{H NMR}$ (500 MHz, Chloroform-d) δ 8.32 (d, J = 1.6 Hz, 2H), 7.46 (d, J = 1.6 Hz, 2H), 1.37 (s, 18H).

Scheme S6. Synthesis of 2-bromo-6-phenylpyridine (P3).

A solution of phenylboronic acid (1.03 g, 8.40 mmol), 2,6-dibromopyridine (4.0 g, 16.90 mmol) and Cs₂CO₃ (3.3 g, 10.1 mmol) in dioxane/H₂O 5/1 (40 mL/8 mL, 0.18 mol/L) was thoroughly degassed by bubbling N₂ gas. Pd(PPh₃)₄ (0.24 g, 0.21 mmol) was subsequently added to the reaction mixture under a N₂ flow. The Schlenk flask was sealed with a screw cap, placed in a 100 °C oil bath and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with H₂O, and extracted with EtOAc (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (1.33 g, 5.68 mmol, 69%) was obtained as a white solid after purification by GPC. The spectral data are in accordance with those reported in the literature.⁵ ¹H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 2H), 7.68 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.41 (dd, *J* = 7.8, 0.8 Hz, 1H).

Scheme S7. Synthesis of tributylstannyl derivatives (P4–P6).

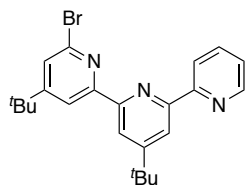
Compounds **P4–P6** were synthesized according to the procedure reported in the literature⁶ with some modifications. To a solution of 2-bromopyridine/ 2-bromo-6-methylpyridine/2-bromo-6-phenylpyridine **P3** (10 mmol) in THF (25 mL, 0.25 mol/L), BuLi (7.1 mL, 11 mmol, 1.57 M in hexane) was added at -78 °C and the resulting solution was stirred for 1 h. At this point, tributyltin chloride (3.9 g, 12 mmol) was added quickly and the mixture was allowed to warm slowly to rt and was stirred overnight. The reaction was diluted with water and extracted with Et₂O (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. Products were obtained quantitatively and used in the next step without any additional purification.

General procedure for the synthesis of 6-bromo-4,4'-di-*tert*-butyl-6''-R-2,2':6',2''-terpyridines (P9-P11).

To a suspension of 6,6'-dibromo-4,4'-di-*tert*-butyl-2,2'-bipyridine **P2** (100 mol%) in toluene (0.1 mol/L) 2-R-6-(tributylstannyl)pyridine **P4–P6** (100 mol%) was added. The mixture was thoroughly degassed by bubbling N₂ gas, followed by the addition of Pd(PPh₃)₄ (5 mol%). The Schlenk flask was sealed with a screw cap and the reaction mixture was refluxed overnight. Then the reaction mixture was diluted with water and was poured into a concentrated aq. solution of CsF (500 mol%). After 30 min stirring at rt, the biphasic mixture was filtered through Celite®. The aqueous phase was extracted with toluene (× 3). The organic layers were collected, dried over MgSO₄, filtered and

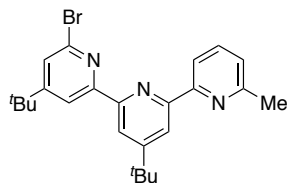
concentrated by rotary evaporation. Pure products were obtained in 31–42% yield after column chromatography or GPC.

6-Bromo-4,4'-di-*tert*-butyl-2,2':6',2''-terpyridine (P9)



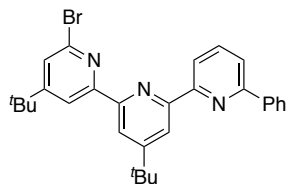
Starting from **P2** (250 mg, 0.59 mmol). The product (101 mg, 0.24 mmol, 41% yield) was obtained as a white solid after column chromatography: hexane to hexane/EtOAc (98:2 → 95:5). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.72 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.57 (d, *J* = 1.7 Hz, 1H), 8.56 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 8.42 (d, *J* = 1.8 Hz, 1H), 7.87 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.33 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 1.46 (s, 9H), 1.41 (s, 9H).

6-bromo-4,4'-di-*tert*-butyl-6''-methyl-2,2':6',2''-terpyridine (P10)



Starting from **P2** (300 mg, 0.70 mmol). The product (96 mg, 0.22 mmol, 31% yield) was obtained as a white solid after column chromatography: hexane to hexane–EtOAc (98:2 → 95:5). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 1.6 Hz, 1H), 8.52 (d, *J* = 1.8 Hz, 1H), 8.40 (d, *J* = 1.8 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 2.67 (s, 3H), 1.47 (s, 9H), 1.41 (s, 9H).

6-bromo-4,4'-di-*tert*-butyl-6''-phenyl-2,2':6',2''-terpyridine (P11)

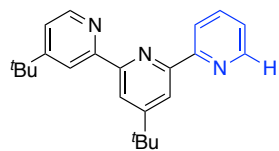


Starting from **P2** (643 mg, 1.51 mmol). The product (316 mg, 0.63 mmol, 42% yield) was obtained as a white solid after purification by GPC. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 1.8 Hz, 1H), 8.61 (d, *J* = 1.6 Hz, 1H), 8.53 (dd, *J* = 7.7, 1.0 Hz, 1H), 8.45 (d, *J* = 1.8 Hz, 1H), 8.17 – 8.21 (m, 2H), 7.94 (t, *J* = 7.8 Hz, 1H), 7.81 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.52 – 7.57 (m, 2H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.45 – 7.48 (m, 1H), 1.50 (s, 9H), 1.43 (s, 9H).

General procedure for the synthesis of 4,4'-di-*tert*-butyl-6''-R-2,2':6',2''-terpyridine (R-OleTpy).

To a solution of 6-bromo-4,4'-di-*tert*-butyl-6''-R-2,2':6',2''-terpyridine **P9–P11** (100 mol%) in THF (0.05 mol/L) at –78 °C, BuLi (110 mol%, 1.5 M in hexane) was added dropwise. The resulting solution was stirred for 40 min. Then, MeOH (1000 mol%) was added in one portion via syringe and stirring continued for another 15 min. The solution was allowed to warm slowly to rt overnight. The reaction was quenched with saturated H₂O, and the aqueous layer was extracted with EtOAc (× 3). The organic layers were collected, washed with brine, dried over MgSO₄, filtered and concentrated by rotary evaporation. Pure products were obtained in 45–80% yield after column chromatography or GPC.

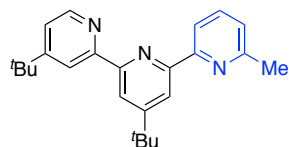
4,4'-di-*tert*-butyl-6''-phenyl-2,2':6',2''-terpyridine (H-OleTpy)



Starting from **P9** (101 mg, 0.24 mmol). The product (37 mg, 0.11 mmol, 45% yield) was obtained as a white solid (mp 111–112 °C) after column chromatography: hexane to hexane–EtOAc (95:5 → 9:1). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.72 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.65 – 8.59 (m, 3H), 8.50 (d, *J* = 1.8 Hz, 1H), 8.47 (d, *J* = 1.8 Hz, 1H), 7.87 (td,

$J = 7.7, 1.8$ Hz, 1H), 7.35 – 7.31 (m, 2H), 1.47 (s, 9H), 1.43 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 162.3 (C), 160.9 (C), 156.9 (C), 156.7 (C), 156.0 (C), 155.4 (C), 149.2 (CH), 149.2 (CH), 137.0 (CH), 123.7 (CH), 121.4 (CH), 120.9 (CH), 118.54 (CH), 118.45 (CH), 118.1 (CH), 35.5 (C), 35.1 (C), 30.9 (3CH₃), 30.8 (3CH₃). **HR-MS, APCI, m/z:** calcd for C₂₃H₂₈N₃⁺, [M+H]⁺, 346.2278. Found, 346.2292.

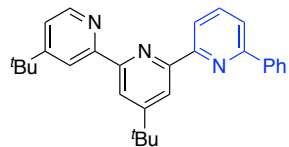
4,4'-di-*tert*-butyl-6''-methyl-2,2':6',2''-terpyridine (Me-OleTpy)



Starting from **P10** (96 mg, 0.22 mmol). The product (63 mg, 0.18 mmol, 80% yield) was obtained as a white solid (mp 154–156 °C) after GPC. ^1H NMR (500 MHz, Chloroform- d) δ 8.63 – 8.60 (m, 2H), 8.51 (d, $J = 1.9$ Hz, 1H), 8.45 (d, $J = 1.9$ Hz, 1H), 8.39 (d, $J = 7.8$ Hz, 1H), 7.75 (t, $J = 7.7$ Hz, 1H), 7.32 (dd, $J = 5.2, 2.0$ Hz, 1H), 7.19 (d, $J = 7.5$ Hz, 1H),

2.67 (s, 3H), 1.47 (s, 9H), 1.43 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 162.1 (C), 160.9 (C), 158.0 (C), 156.8 (C), 156.2 (C), 155.9 (C), 155.7 (C), 149.1 (CH), 137.1 (CH), 123.2 (CH), 120.9 (CH), 118.5 (CH), 118.4 (2CH), 118.0 (CH), 35.5 (C), 35.1 (C), 30.9 (3CH₃), 30.8 (3CH₃), 24.9 (CH₃). **HR-MS, APCI, m/z:** calcd for C₂₄H₂₉N₃⁺, [M]⁺, 359.2356. Found, 359.2349.

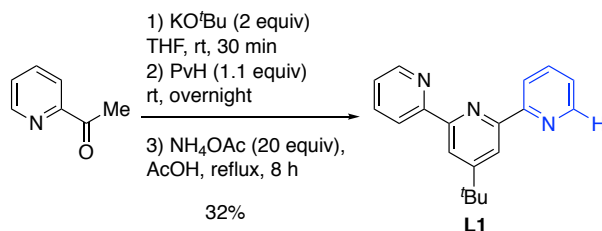
4,4'-di-*tert*-butyl-6''-phenyl-2,2':6',2''-terpyridine (Ph-OleTpy)



Starting from **P11** (310 mg, 0.62 mmol). The product (193 mg, 0.46 mmol, 74% yield) was obtained as a white solid (mp 145–146 °C) after column chromatography: hexane to hexane/EtOAc 95:5. ^1H NMR (500 MHz, Chloroform- d) δ 8.72 (d, $J = 1.9$ Hz, 1H), 8.65 (dd, $J = 2.0, 0.7$ Hz, 1H), 8.63 (dd, $J = 5.3, 0.8$ Hz, 1H), 8.58 (dd, $J = 7.8, 1.0$ Hz, 1H), 8.48 (d, $J = 1.8$ Hz, 1H), 8.22 – 8.17 (m, 2H), 7.95 (t, $J = 7.8$ Hz, 1H), 7.81 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.58 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.34 (dd, $J = 5.2, 2.0$ Hz, 1H), 1.50 (s, 9H), 1.44 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 162.1 (C), 160.9 (C), 156.8 (C), 156.44 (C), 156.42 (C), 155.9 (C), 155.6 (C), 149.2 (CH), 139.6 (C), 137.8 (CH), 129.1 (CH), 128.9 (2CH), 127.1 (2CH), 120.9 (CH), 120.3 (CH), 119.7 (CH), 118.5 (CH), 118.5 (CH), 118.2 (CH), 35.5 (C), 35.1 (C), 30.9 (3CH₃), 30.8 (3CH₃). **HR-MS, APCI, m/z:** calcd for C₂₉H₃₂N₃⁺, [M+H]⁺, 422.2591. Found, 422.2593.

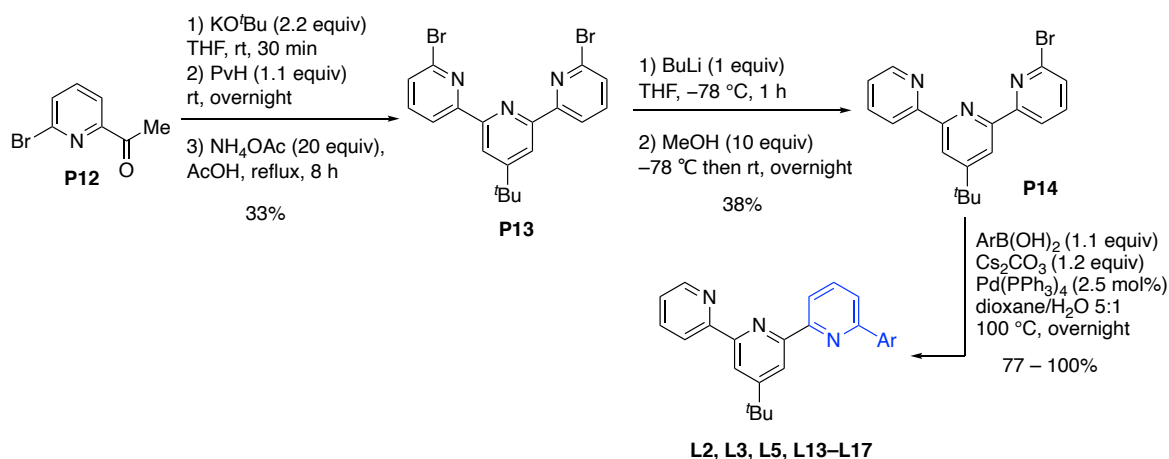
Scheme S8. Synthesis of 4'-(*tert*-butyl)-2,2':6',2''-terpyridine (**L1**).



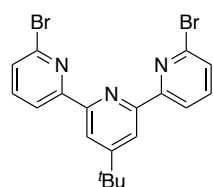
L1 was synthesized according to the procedure reported in the literature.⁷ 1-(Pyridin-2-yl)ethan-1-one (3.6 g, 0.03 mol) was added to a solution of KO^{*t*}Bu (3.3 g, 0.03 mol) in THF (150 ml, 0.2 mol/L), resulting in a pinkish suspension. After 30 min stirring at rt, pivalaldehyde (1.8 ml, 0.02 mol, 0.793 g/ml) was added and the deep-red mixture was stirred

overnight. Solid NH_4OAc (23 g, 0.3 mol) was dissolved in glacial HOAc (90 mL, 1.6 mol, 1.05 g/mL) and was added to the deep-red suspension; the resulting mixture was heated at 100 °C for 8 h. Solvents were removed by rotary evaporation and the pH of the residue was adjusted to neutral with K_2CO_3 . The aqueous layer was extracted with ether ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (1.39 g, 0.005 mol, 32%) was obtained as a whitish solid after column chromatography: hexane/ Et_2O 1:2 and subsequent recrystallization from hexane/ EtOAc 20:1. The spectral data are in accordance with those reported in the literature.⁷ **^1H NMR** (500 MHz, CHCl_3 - d) δ 8.72 (ddd, J = 4.8, 1.8, 0.9 Hz, 2H), 8.62 (dt, J = 7.9, 1.1 Hz, 2H), 8.50 (s, 2H), 7.85 (td, J = 7.7, 1.8 Hz, 2H), 7.33 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H), 1.47 (s, 9H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, CHCl_3 - d) δ 162.3 (C), 156.8 (2C), 155.5 (2C), 149.2 (2CH), 136.9 (2CH), 123.7 (2CH), 121.5 (2CH), 118.3 (2CH), 35.5 (C), 30.9 (3 CH_3).

Scheme S9. Synthesis of 4'-(*tert*-butyl)-6-aryl-2,2':6',2''-terpyridines (**L2**, **L3**, **L5**, **L13–L17**).



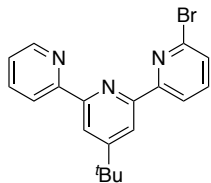
Synthesis of 6,6''-dibromo-4'-(*tert*-butyl)-2,2':6',2''-terpyridine (**P13**)



P13 was synthesized following the procedure adopted from the literature.⁷ 1-(6-Bromopyridin-2-yl)ethan-1-one **P12** (3.7 g, 0.019 mol) was added to a solution of KO^tBu (2.34 g, 0.021 mol) in THF (100 mL, 0.2 mol/L). The mixture turned bright orange. After 30 min stirring at rt, pivalaldehyde (1.1 mL, 0.01 mmol, 0.793 g/mL) was added and the mixture was stirred overnight.

Solid NH_4OAc (14.3 g, 0.19 mol) was dissolved in glacial HOAc (50 mL, 0.87 mol, 1.05 g/mL) with slight heating, and was added to the deep orange suspension; the resulting orange solution was refluxed for 8 h. Solvents were removed by rotary evaporation and the pH of the residue was adjusted to neutral with K_2CO_3 . The aqueous layer was extracted with EtOAc ($\times 3$), then DCM ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (1.37 g, 0.003 mol, 33%) was obtained as a whitish solid after trituration with hot hexane- EtOAc 5/1 and subsequent filtration of the suspension cooled down to rt. **^1H NMR** (500 MHz, CHCl_3 - d) δ 8.53 (dd, J = 7.7, 0.9 Hz, 2H), 8.46 (s, 2H), 7.69 (t, J = 7.8 Hz, 2H), 7.50 (dd, J = 7.8, 0.9 Hz, 2H), 1.47 (s, 9H).

Synthesis of 6-bromo-4'-(*tert*-butyl)-2,2':6',2''-terpyridine (P14)

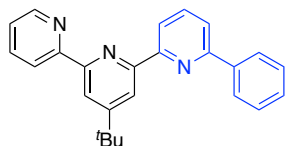


To a solution of 6,6''-dibromo-4'-(*tert*-butyl)-2,2':6',2''-terpyridine **P13** (2 g, 4.5 mmol) in THF (100 mL, 0.05 mol/L), BuLi (3.3 mL, 1.5 mol/L in hexane) was added dropwise via syringe over 10 min at -78°C , resulting in a deep-violet solution. The solution was stirred for 40 min, then MeOH (2 mL, 49 mmol, 0.791 g/mL) was added in one portion via syringe and stirring continued for another 15 min. The solution was allowed to warm slowly to 0°C , and then it was stirred in an ice bath overnight. Upon heating up solution changed color to a light yellow. The reaction was quenched with saturated NH_4Cl , and the aqueous layer was extracted with EtOAc ($\times 3$). The organic layers were collected, washed with brine, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (0.63 g, 1.7 mmol, 38%) was obtained as a yellowish solid after column chromatography: hexane–EtOAc (95:5). **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.71 (ddd, $J = 4.8, 1.8, 0.8$ Hz, 1H), 8.61 – 8.56 (m, 2H), 8.51 (d, $J = 1.8$ Hz, 1H), 8.45 (d, $J = 1.8$ Hz, 1H), 7.84 (td, $J = 7.7, 1.8$ Hz, 1H), 7.69 (t, $J = 7.8$ Hz, 1H), 7.50 (dd, $J = 7.8, 0.8$ Hz, 1H), 7.33 (ddd, $J = 7.4, 4.8, 1.2$ Hz, 1H), 1.47 (s, 9H).

General procedure for the synthesis of 4'-(*tert*-butyl)-6-aryl-2,2':6',2''-terpyridines

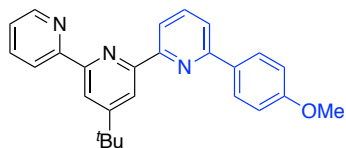
The procedure for the synthesis was adopted from the literature.⁸ A solution of 6-bromo-4'-(*tert*-butyl)-2,2':6',2''-terpyridine **P14** (50 mg, 0.14 mmol), the corresponding boronic acid (0.15 mmol) and Cs_2CO_3 (52 mg, 0.16 mmol) in dioxane/ H_2O 5/1 (2.5 mL/0.5 mL, 0.05 mol/L) was thoroughly degassed by bubbling N_2 gas. $\text{Pd}(\text{PPh}_3)_4$ (4 mg, 0.0035 mmol) was subsequently added to the reaction mixture under a N_2 flow. The Schlenk flask was sealed with a screw cap, placed in a 100°C oil bath and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with H_2O , and extracted with DCM ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. Pure products were obtained in 77–100% yield after column chromatography.

4'-(*tert*-butyl)-6-phenyl-2,2':6',2''-terpyridine (L2)



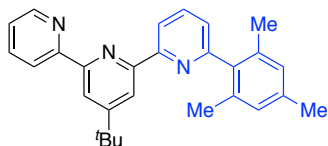
The product (47 mg, 0.13 mmol, 94% yield) was obtained as a white solid (mp 129°C) after column chromatography: hexane–EtOAc (9:1). **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.73 (dd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.72 (d, $J = 1.8$ Hz, 1H), 8.65 (dt, $J = 7.9, 1.2$ Hz, 1H), 8.59 (dd, $J = 7.8, 1.0$ Hz, 1H), 8.52 (d, $J = 1.8$ Hz, 1H), 8.21–8.16 (d, $J = 7.0$ Hz, 2H), 7.92 (t, $J = 7.8$ Hz, 1H), 7.86 (td, $J = 7.7, 1.8$ Hz, 1H), 7.80 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.59 – 7.51 (m, 2H), 7.49 – 7.43 (m, 1H), 7.33 (ddd, $J = 7.4, 4.8, 1.2$ Hz, 1H), 1.50 (s, 9H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform-*d*) δ 162.1 (C), 156.9 (C), 156.4 (2C), 155.7 (C), 155.4 (C), 149.2 (CH), 139.6 (C), 137.7 (CH), 137.0 (CH), 129.1 (CH), 128.9 (2CH), 127.1 (2CH), 123.7 (CH), 121.6 (CH), 120.3 (CH), 119.8 (CH), 118.4 (CH), 118.3 (CH), 35.5 (C), 30.9 (3CH₃). **HR-MS, APCI, m/z :** calcd for $\text{C}_{25}\text{H}_{24}\text{N}_3^+$, $[\text{M}+\text{H}]^+$, 366.1965. Found, 366.1958.

4'-(*tert*-butyl)-6-(4-methoxyphenyl)-2,2':6',2''-terpyridine (L3)



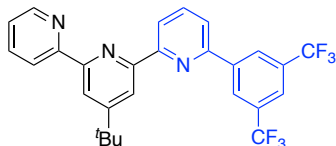
The product (54 mg, 0.14 mmol, 100% yield) was obtained as a white solid (mp 133–134 °C) after column chromatography: hexane–EtOAc (9:1). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.72 – 8.70 (m, 1H), 8.70 (d, *J* = 1.9 Hz, 1H), 8.66 – 8.63 (m, 1H), 8.51 (dd, *J* = 7.8, 0.7 Hz, 1H), 8.50 (d, *J* = 1.9 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.84 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.32 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H), 1.49 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.0 (C), 160.6 (C), 156.9 (C), 156.2 (C), 156.1 (C), 155.8 (C), 155.4 (C), 149.2 (CH), 137.6 (CH), 136.9 (CH), 132.2 (C), 128.3 (2CH), 123.7 (CH), 121.5 (CH), 119.5 (CH), 119.1 (CH), 118.3 (CH), 118.2 (CH), 114.3 (2CH), 55.5 (CH₃), 35.5 (C), 30.9 (3CH₃). **HR-MS, APCI, m/z**: calcd for C₂₆H₂₆N₃O⁺, [M+H]⁺, 396.2070. Found, 396.2081.

4'-(*tert*-butyl)-6-mesityl-2,2':6',2''-terpyridine (L5)



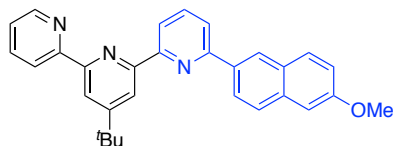
The product (50 mg, 0.12 mmol, 91% yield) was obtained as a white solid (mp 173–175 °C) after column chromatography: hexane–EtOAc (9:1 → 8:2). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.72 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.66 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.55 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.48 (d, *J* = 0.6 Hz, 2H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.33 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.00 (s, 2H), 2.37 (s, 3H), 2.15 (s, 6H), 1.42 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.2 (C), 159.1 (C), 156.9 (C), 156.6 (C), 155.9 (C), 155.3 (C), 149.2 (2C), 138.2 (C), 137.5 (C), 136.94 (CH), 136.87 (CH), 136.3 (CH), 128.6 (2CH), 124.9 (CH), 123.7 (CH), 121.5 (CH), 119.2 (CH), 118.7 (CH), 118.1 (CH), 35.5 (C), 30.9 (3CH₃), 21.3 (CH₃), 20.7 (2CH₃). **HR-MS, APCI, m/z**: calcd for C₂₈H₃₀N₃⁺, [M+H]⁺, 408.2434. Found, 408.2444.

6-(3,5-bis(trifluoromethyl)phenyl)-4'-(*tert*-butyl)-2,2':6',2''-terpyridine (L13)



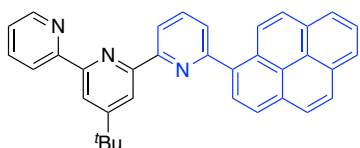
The product (66 mg, 0.13 mmol, 97% yield) was obtained as a white solid (mp 162–163 °C) after column chromatography: hexane–EtOAc (9:1 → 8:2). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.73 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.71 – 8.68 (m, 2H), 8.67 (br s, 2H), 8.64 (dt, *J* = 8.0, 1.0 Hz, 1H), 8.55 (d, *J* = 1.8 Hz, 1H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.90 – 7.84 (m, 2H), 7.35 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 1.50 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.4 (C), 156.9 (C), 156.7 (C), 155.7 (C), 154.9 (C), 153.0 (C), 149.3 (CH), 141.4 (C), 138.3 (CH), 137.0 (CH), 132.3 (C) (q, *J* = 33.4 Hz), 127.1 (2CH), 123.8 (CH), 123.6 (C) (q, *J* = 272.3 Hz), 122.7 – 122.5 (CH) (m), 121.5 (CH), 121.2 (CH), 120.2 (CH), 118.8 (CH), 118.4 (CH), 35.5 (2C), 30.8 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –66.1. **HR-MS, APCI, m/z**: calcd for C₂₇H₂₂F₆N₃⁺, [M+H]⁺, 502.1712. Found, 502.1716.

4'-(*tert*-butyl)-6-(6-methoxynaphthalen-2-yl)-2,2':6',2''-terpyridine (L14)



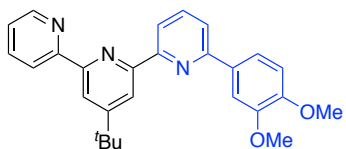
The product (55 mg, 0.12 mmol, 92% yield) was obtained as a white solid (mp 212–213 °C) after column chromatography: hexane–EtOAc (9:1 → 8:2). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 1.8 Hz, 1H), 8.73 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.67 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.60 – 8.56 (m, 2H), 8.53 (d, *J* = 1.8 Hz, 1H), 8.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.97 – 7.84 (m, 5H), 7.34 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 7.22 – 7.19 (m, 2H), 3.97 (s, 3H), 1.53 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.1 (C), 158.4 (C), 156.9 (C), 156.4 (2C), 155.8 (C), 155.4 (C), 149.2 (CH), 137.7 (CH), 137.0 (CH), 135.2 (C), 134.8 (C), 130.4 (CH), 129.1 (C), 127.4 (CH), 126.3 (CH), 125.3 (CH), 123.7 (CH), 121.6 (CH), 120.2 (CH), 119.6 (CH), 119.3 (CH), 118.4 (CH), 118.3 (CH), 105.8 (CH), 55.5 (CH₃), 35.5 (C), 30.9 (3CH₃). **HR-MS, APCI, m/z**: calcd for C₃₀H₂₈N₃O⁺, [M+H]⁺, 446.2227. Found, 446.2218.

4'-(*tert*-butyl)-6-(pyren-1-yl)-2,2':6',2''-terpyridine (L15)



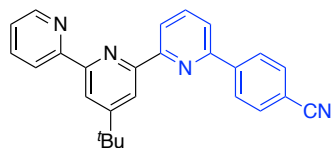
The product (66 mg, 0.14 mmol, 100% yield) was obtained as a light yellow solid (mp 175–177 °C) after column chromatography: hexane–EtOAc (8:2). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.76 – 8.69 (m, 5H), 8.53 (d, *J* = 1.8 Hz, 1H), 8.32 (s, 2H), 8.23 (td, *J* = 7.6, 1.2 Hz, 2H), 8.14 (s, 2H), 8.11 (d, *J* = 9.3 Hz, 1H), 8.05 (q, *J* = 7.8 Hz, 2H), 7.90 (td, *J* = 7.6, 1.8 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.35 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 1.44 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.3 (C), 158.8 (C), 156.9 (C), 156.5 (C), 155.7 (C), 155.5 (C), 149.2 (CH), 137.5 (CH), 137.0 (CH), 135.9 (C), 131.65 (C), 131.60 (C), 131.1 (C), 129.0 (C), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 126.2 (CH), 125.6 (CH), 125.5 (2CH), 125.4 (C), 125.2 (CH), 125.1 (C), 125.0 (CH), 123.7 (CH), 121.6 (CH), 119.5 (CH), 118.7 (CH), 118.3 (CH), 35.5 (C), 30.9 (3CH₃). **HR-MS, APCI, m/z**: calcd for C₃₅H₂₈N₃⁺, [M+H]⁺, 490.2278. Found, 490.2282.

4'-(*tert*-butyl)-6-(3,4-dimethoxyphenyl)-2,2':6',2''-terpyridine (L16)



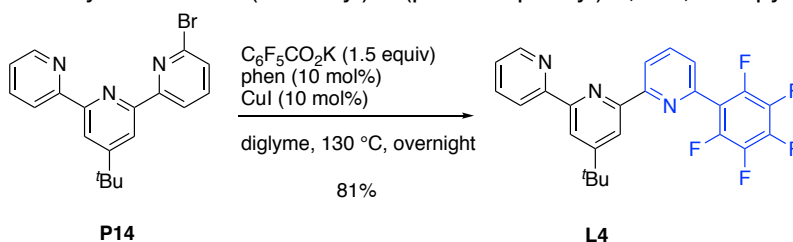
The product (54 mg, 0.13 mmol, 94% yield) was obtained as a white solid (mp 142–143 °C) after column chromatography: hexane–EtOAc (9:1 → 8:2). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 1.8 Hz, 1H), 8.72 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.65 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.53 (dd, *J* = 7.7, 0.9 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.69 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.33 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.06 (s, 3H), 3.98 (s, 3H), 1.49 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 161.9 (C), 156.9 (C), 156.0 (C), 155.8 (C), 155.7 (C), 155.4 (C), 150.2 (C), 149.4 (C), 149.2 (CH), 137.7 (CH), 136.9 (CH), 132.4 (C), 123.7 (CH), 121.6 (CH), 119.5 (CH), 119.4 (CH), 119.1 (CH), 118.3 (2CH), 111.2 (CH), 110.0 (CH), 56.1 (CH₃), 55.9 (CH₃), 35.4 (C), 30.8 (3CH₃). **HR-MS, APCI, m/z**: calcd for C₂₇H₂₈N₃O₂⁺, [M+H]⁺, 426.2176. Found, 426.2188.

4-(4'-(*tert*-butyl)-[2,2':6',2''-terpyridin]-6-yl)benzonitrile (L17)



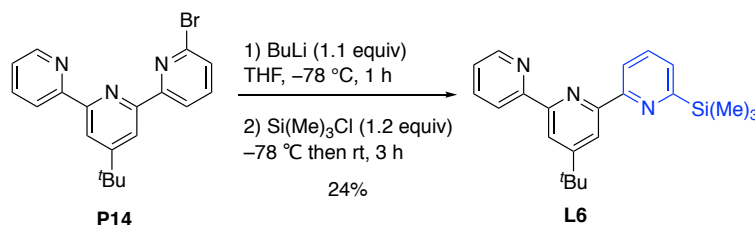
The product (41 mg, 0.10 mmol, 77% yield) was obtained as a white solid (mp 205 °C) after column chromatography: hexane–EtOAc (8:2). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.73 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H), 8.67 (dd, *J* = 7.8, 0.9 Hz, 1H), 8.65 (d, *J* = 1.9 Hz, 1H), 8.64 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 8.32 – 8.27 (m, 2H), 7.97 (t, *J* = 7.8 Hz, 1H), 7.87 (td, *J* = 7.7, 1.8 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.34 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 1.50 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.3 (C), 156.9 (C), 156.7 (C), 155.6 (C), 155.1 (C), 154.2 (C), 149.3 (CH), 143.7 (C), 138.1 (CH), 137.0 (CH), 132.8 (CH), 127.6 (2CH), 123.8 (2CH), 121.5 (CH), 121.1 (CH), 120.7 (CH), 119.1 (C), 118.6 (CH), 118.3 (CH), 112.5 (C), 35.5 (C), 30.9 (3CH₃). **HR-MS, APCI, m/z**: calcd for C₂₆H₂₃N₄⁺, [M+H]⁺, 391.1917. Found, 391.1925.

Scheme S10. Synthesis of 4'-(*tert*-butyl)-6-(perfluorophenyl)-2,2':6',2''-terpyridine (L4).



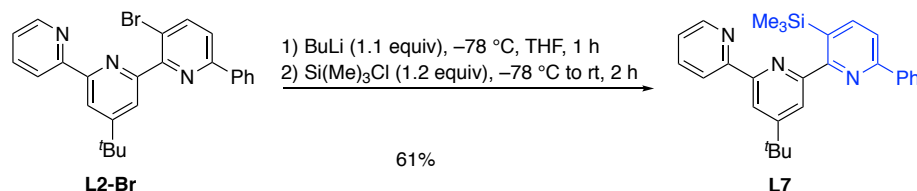
The synthetic procedure was adopted from the literature.⁹ CuI (2.6 mg, 0.014 mmol), phen (2.4 mg, 0.013 mmol), potassium 2,3,4,5,6-pentafluorobenzoate (51 mg, 0.20 mmol) and 6-bromo-4'-(*tert*-butyl)-2,2':6',2''-terpyridine (50 mg, 0.14 mmol) were placed in 10 mL Schlenk flask. The flask was evacuated and back filled with N₂ (× 3), then diglyme (1.4 mL, 0.1 mol/L) was added. The reaction vessel was sealed with a screw cap and stirred at 130 °C for 24 h. The reaction mixture was diluted with ethyl acetate and filtered through Celite ® to remove insoluble materials. The crude liquid was concentrated by rotary evaporation. Product (50 mg, 0.11 mmol, 81%) was obtained as a white solid (mp 179–180 °C) after column chromatography: hexane–EtOAc (9:1). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.72 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.69 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.63 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.52 (d, *J* = 1.8 Hz, 1H), 8.49 (d, *J* = 1.8 Hz, 1H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.34 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 1.46 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.4 (C), 157.4 (C), 156.7 (C), 155.6 (C), 154.8 (C), 149.3 (CH), 146.3 (C), 137.6 (CH), 137.0 (CH), 125.7 (CH), 123.8 (CH), 121.50 (CH), 121.46 (CH), 118.65 (CH), 118.63 (CH), 35.5 (C), 30.8 (3CH₃). Cq attached to F or next to F are not detected in ¹³C{¹H} NMR spectra due to coupling on the neighboring ¹⁹F. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –146.34 (d, *J* = 22.5 Hz), –157.45 (t, *J* = 22.3 Hz), –165.25 (t, *J* = 22.1 Hz). **HR-MS, APCI, m/z**: calcd for C₂₅H₁₉F₅N₃⁺, [M+H]⁺, 456.1494. Found, 456.1483.

Scheme S11. Synthesis of 4'-(*tert*-butyl)-6-(trimethylsilyl)-2,2':6',2''-terpyridine (L6).

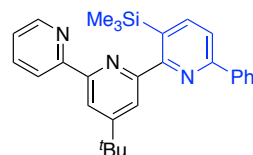


To a solution of 6-bromo-4'-(*tert*-butyl)-2,2':6',2''-terpyridine **P14** (187 mg, 0.51 mmol) in THF (5 mL, 0.1 mol/L), BuLi (0.37 mL, 1.5 mol/L in hexane) was added dropwise via syringe at -78°C , resulting in a deep-violet solution that was stirred for 1 h. Then, $\text{Si}(\text{Me})_3\text{Cl}$ (0.77 mL, 0.61 mmol, 0.856 g/mL) was added in one portion via syringe and stirring continued for another 5 min. The solution was allowed to warm slowly to rt and was stirred for 3 h. Upon heating, the color of the solution changed to orange. The reaction was quenched with H_2O , the aqueous layer was extracted with Et_2O ($\times 3$). The organic layers were collected, washed with brine, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (44 mg, 0.12 mmol, 24%) was obtained as a white solid (mp $77\text{--}79^{\circ}\text{C}$) after column chromatography: hexane to hexane– EtOAc (98:2 \rightarrow 95:5) and further separation of a byproduct by GPC. **^1H NMR** (500 MHz, CHCl_3 - d) δ 8.71 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.70 (d, $J = 1.9$ Hz, 1H), 8.63 (dt, $J = 8.0, 1.1$ Hz, 1H), 8.51 (dd, $J = 8.0, 1.2$ Hz, 1H), 8.47 (d, $J = 1.9$ Hz, 1H), 7.84 (td, $J = 7.7, 1.8$ Hz, 1H), 7.71 – 7.77 (m, 1H), 7.52 (dd, $J = 7.3, 1.2$ Hz, 1H), 7.31 (ddd, $J = 7.4, 4.8, 1.2$ Hz, 1H), 1.47 (s, 9H), 0.40 (s, 9H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, CHCl_3 - d) δ 167.6 (C), 161.9 (C), 157.0 (C), 156.15 (C), 156.14 (C), 155.3 (C), 149.2 (CH), 136.9 (CH), 134.8 (CH), 128.6 (CH), 123.6 (CH), 121.6 (CH), 120.2 (CH), 118.4 (CH), 118.0 (CH), 35.4 (C), 30.8 (3 CH_3), -1.6 (3 CH_3). **HR-MS, APCI, m/z** : calcd for $\text{C}_{22}\text{H}_{28}\text{N}_3\text{Si}^+$, $[\text{M}+\text{H}]^+$, 362.2047. Found, 362.2050.

Scheme S12. Synthesis of 4'-(*tert*-butyl)-6-phenyl-3-(trimethylsilyl)-2,2':6',2''-terpyridine (**L7**).

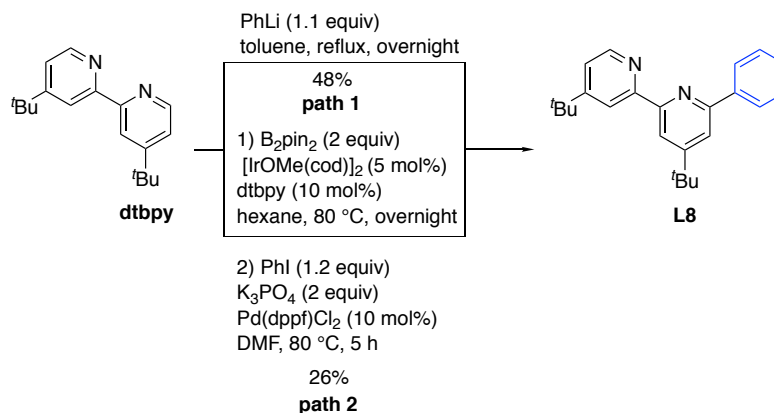


Synthesis of 4'-(*tert*-butyl)-6-phenyl-3-(trimethylsilyl)-2,2':6',2''-terpyridine (**L7**)



To a solution of 3-bromo-4'-(*tert*-butyl)-6-phenyl-2,2':6',2''-terpyridine **L2-Br** (Scheme S4) (34 mg, 0.08 mmol) in THF (3 mL, 0.025 mol/L), BuLi (0.06 mL, 1.5 mol/L in hexane) was added dropwise via syringe at -78°C resulting in an orange solution that was stirred for 1 h. Then, SiMe_3Cl (0.015 mL, 0.12 mmol, 0.856 g/mL) was added in one portion via syringe and stirring continued for another 5 min. The solution was allowed to warm slowly to rt and left stirring for 2 h. Upon heating up solution changed color to yellowish. The reaction was quenched with H_2O , the aqueous layer was extracted with Et_2O ($\times 3$). The organic layers were collected, washed with brine, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (20 mg, 0.05 mmol, 61%) was obtained as a white solid (mp $57\text{--}59^{\circ}\text{C}$) after GPC. **^1H NMR** (500 MHz, CHCl_3 - d) δ 8.72 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.48 (d, $J = 1.8$ Hz, 1H), 8.38 (dd, $J = 7.9, 1.0$ Hz, 1H), 8.15 – 8.10 (m, 2H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.89 (d, $J = 1.8$ Hz, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.77 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.30 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H), 1.47 (s, 9H), 0.05 (s, 9H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, CHCl_3 - d) δ 163.9 (C), 161.6 (C), 160.5 (C), 156.7 (C), 156.5 (C), 155.2 (C), 149.2 (CH), 144.5 (C), 139.5 (CH), 136.7 (CH), 132.4 (C), 129.1 (CH), 128.8 (2CH), 127.2 (2CH), 123.6 (CH), 122.3 (CH), 121.6 (CH), 118.8 (CH), 118.0 (CH), 35.4 (C), 30.9 (3 CH_3), 0.4 (3 CH_3). **HR-MS, APCI, m/z** : calcd for $\text{C}_{28}\text{H}_{32}\text{N}_3\text{Si}^+$, $[\text{M}+\text{H}]^+$, 438.2360. Found, 438.2339.

Scheme S13. Synthesis of 4,4'-di-*tert*-butyl-6-phenyl-2,2'-bipyridine (**L8**).

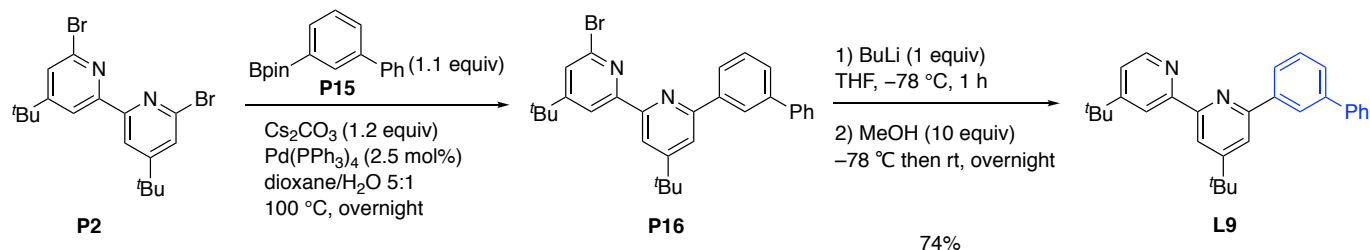


Path 1. The compound was synthesized according to the procedure reported in the literature.¹⁰ A solution of PhLi in Et₂O (14.5 ml, 1.23 mmol, 0.085 mol/L in Et₂O) was slowly added to a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridine (300 mg, 1.12 mmol) in toluene (6 ml, 0.2 mol/L), and the reaction mixture turned red immediately. The mixture was stirred at 110 °C overnight. During this time, the color changed to deep purple. The mixture was cooled down, filtered, and the solvent was removed upon rotary evaporation. Pure product (184 mg, 0.54 mmol, 48%) was obtained as a white solid after column chromatography: hexane–EtOAc (95:5). Note: phenyllithium was synthesized according to the procedure reported in the literature with some modifications.¹¹ Bromobenzene (1.4 ml, 13.2 mmol, 1.495 g/ml) was dissolved in hexane and cooled to –78 °C, followed by dropwise addition of BuLi (8.2 ml, 13.1 mmol, 1.6 mol/L in hexane) and allowed warm slowly to rt. After stirring for 48 h a white precipitate had formed and was isolated by filtration in the atmosphere of inert gas. The white solid was washed with hexane and dissolved in ether (50 mL). After titration of the obtained solution the concentration of phenyllithium was found to be 0.085M (4.3 mmol, 32%).

Path 2.

The compound was synthesized according to the procedure reported in the literature.¹² [IrOMe(cod)]₂ (42 mg, 0.063 mmol) and dtbpy (29 mg, 0.127 mmol) was dissolved in hexane (11 mL, 0.01 mol/L) and transferred to a solution of dtbpy (300 mg, 1.12 mmol) and B₂pin₂ (568 mg, 2.235 mmol) in hexane (19 mL, 0.06 mol/L) under an atmosphere of N₂. The Schlenk flask was sealed with a screw cap and heated at 80 °C overnight. The solvent was removed in vacuo, followed by addition of PhI (274 mg, 1.34 mmol), K₃PO₄ (475 mg, 2.24 mmol), Pd(dppf)Cl₂ dichloromethane adduct (92 mg, 0.11 mmol) and DMF (44 mL, 0.025 mol/L). The mixture was stirred for 5 h at 80 °C. The product was extracted with hexane (× 3), dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (99 mg, 0.29 mmol, 26%) was obtained as a white solid after column chromatography: hexane–EtOAc (95:5). The spectral data are in accordance with those reported in the literature.¹³ **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 2.0 Hz, 1H), 8.61 (dd, *J* = 5.2, 0.7 Hz, 1H), 8.39 (d, *J* = 1.7 Hz, 1H), 8.19 – 8.11 (m, 2H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.47 – 7.40 (m, 1H), 7.32 (dd, *J* = 5.2, 2.0 Hz, 1H), 1.44 (s, 9H), 1.41 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 161.8 (C), 160.9 (C), 156.9 (C), 156.6 (C), 156.4 (C), 149.1 (CH), 140.2 (C), 128.9 (CH), 128.8 (2CH), 127.2 (2CH), 120.9 (CH), 118.6 (CH), 117.6 (CH), 116.9 (CH), 35.4 (C), 35.1 (C), 30.9 (3CH₃), 30.8 (3CH₃).

Scheme S14. Synthesis of 6-([1,1'-biphenyl]-3-yl)-4,4'-di-*tert*-butyl-2,2'-bipyridine (**L9**).



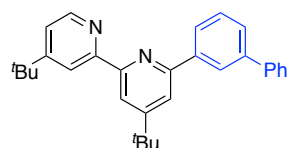
Synthesis of 2-([1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (P15**)**

The synthetic procedure was adopted from the literature.¹⁴ A mixture of 3-bromo-1,1'-biphenyl (200 mg, 0.86 mmol), bis(pinacolato)diboron (218 mg, 0.86 mmol), KOAc (250 mol%) and Pd(dppf)Cl₂ dichloromethane adduct (25 mg, 0.031) in dioxane (9 mL, 0.1 mol/L) was thoroughly degassed by bubbling a stream of N₂. The resulting solution was refluxed for 24 h. After cooling down to rt, the reaction was filtered through Celite ®. The filtrate was then diluted with water and extracted with EtOAc (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (158 mg, 0.564 mmol, 66%) was obtained as a white solid after column chromatography: hexane to hexane–EtOAc 95:5. The spectral data are in accordance with those reported in the literature.¹⁵ **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 1H), 7.79 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.69 (ddd, *J* = 7.7, 2.1, 1.3 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.48 – 7.40 (m, 3H), 7.37 – 7.31 (m, 1H), 1.36 (s, 12H).

Synthesis of 6-([1,1'-biphenyl]-3-yl)-6'-bromo-4,4'-di-*tert*-butyl-2,2'-bipyridine (P16**)**

The synthetic procedure was adopted from the literature.⁸ A suspension of 6,6'-dibromo-4,4'-di-*tert*-butyl-2,2'-bipyridine **P2** (170 mg, 0.399 mmol), 2-([1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **P15** (112 mg, 0.399 mmol) and Cs₂CO₃ (156 mg, 0.479 mmol) in dioxane/H₂O 5/1 (7 mL/1 mL, 0.05 mol/L) was thoroughly degassed by bubbling N₂ gas. Pd(PPh₃)₄ (12 mg, 0.010 mmol) was subsequently added to the reaction mixture under a N₂ flow. The Schlenk flask was sealed with a screw cap, placed in a 100 °C oil bath and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with H₂O, and extracted with EtOAc (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (32 mg, 0.064 mmol, 16%) was obtained as a white solid after GPC. Note: the material was partly lost due to mistake. **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.38 (t, *J* = 1.8 Hz, 1H), 8.37 (d, *J* = 1.7 Hz, 1H), 8.09 (ddd, *J* = 7.7, 1.8, 1.2 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.68 (ddd, *J* = 7.6, 1.8, 1.1 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.40 (dt, *J* = 7.4, 1.1 Hz, 1H), 1.45 (s, 9H), 1.40 (s, 9H).

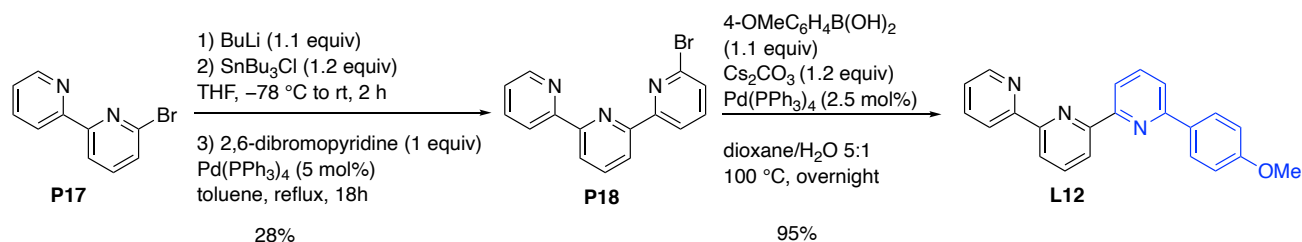
Synthesis of 6-([1,1'-biphenyl]-3-yl)-4,4'-di-*tert*-butyl-2,2'-bipyridine (L9**)**



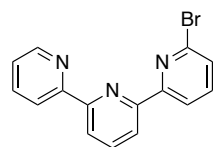
To a solution of 6-([1,1'-biphenyl]-3-yl)-6'-bromo-4,4'-di-*tert*-butyl-2,2'-bipyridine **P16** (32 mg, 0.064 mmol) in THF (3 mL, 0.025 mol/L) at –78 °C, BuLi (0.047 mL, 1.5 mol/L in hexane) was added dropwise via syringe, resulting in an orange solution that was stirred

for 1 h. Then, MeOH (0.026 mL, 0.64 mmol, 0.791 g/mL) was added in one portion via syringe and stirring continued for another 5 min. The solution was allowed to warm slowly to rt and was stirred for 1 h. Upon heating up, the color of the solution changed to light-green. The reaction was quenched with H₂O, and the aqueous layer was extracted with EtOAc (× 3). The organic layers were collected, washed with brine, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (20 mg, 0.048 mmol, 74%) was obtained as a white solid (mp 154–155 °C) after column chromatography: hexane to hexane–EtOAc (97:3 → 95:5). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 2.0, 0.7 Hz, 1H), 8.62 (dd, *J* = 5.2, 0.8 Hz, 1H), 8.42 (t, *J* = 1.8 Hz, 1H), 8.41 (d, *J* = 1.8 Hz, 1H), 8.12 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.81 (d, *J* = 1.7 Hz, 1H), 7.73 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.68 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.42 – 7.37 (m, 1H), 7.33 (dd, *J* = 5.2, 2.0 Hz, 1H), 1.46 (s, 9H), 1.42 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.0 (C), 161.0 (C), 156.8 (C), 156.4 (C), 156.3 (C), 149.1 (CH), 141.7 (C), 141.4 (C), 140.7 (C), 129.3 (CH), 129.0 (2CH), 127.7 (CH), 127.5 (CH), 127.4 (2CH), 126.3 (CH), 126.1 (CH), 121.0 (CH), 118.7 (CH), 117.6 (CH), 117.0 (CH), 35.4 (C), 35.1 (C), 30.9 (3CH₃), 30.7 (3CH₃). **HR-MS, APCI, m/z**: calcd for C₃₀H₃₃N₂⁺, [M+H]⁺, 421.2638. Found, 421.2634.

Scheme S15. Synthesis of 6-(4-methoxyphenyl)-2,2':6',2''-terpyridine (L12).



Synthesis of 6-bromo-2,2':6',2''-terpyridine (P18).



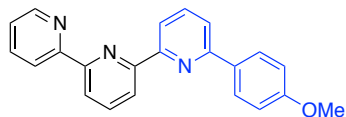
The synthetic procedure was adopted from the literature.⁶ To a solution of 6-bromo-2,2'-bipyridine **P17** (353 mg, 1.5 mmol) in THF (15 mL, 1.5 mol/L), BuLi (1.1 mL, 1.65 mmol, 1.5 M in hexane) was added at –78 °C, and the resulting solution was stirred for 1 h. Tributyltin chloride (586 mg, 1.80 mmol) was added quickly and the mixture was allowed to warm slowly to rt and

was stirred overnight. The reaction was diluted with water and extracted with Et₂O (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product was obtained quantitatively as a brown oil and used in the next step without any additional purification.

To a solution of 2,6-dibromopyridine (351 mg, 1.48 mmol) and Pd(PPh₃)₄ (87 mg, 0.07 mmol) in toluene (15 mL, 0.1 mol/L), 6-(tributylstannyl)-2,2'-bipyridine (660 mg, 1.48 mmol) was added. The mixture was thoroughly degassed by bubbling a N₂ gas, sealed with a screw cap and refluxed overnight. Then the reaction mixture was diluted with water and poured into a concentrated aq. solution of CsF (1.1 g, 7.4 mmol). After 30 min stirring at rt, the biphasic mixture was filtered through the plug of Celite®. The aqueous phase was extracted with toluene (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (128 mg, 0.41 mmol, 28%) was obtained as a white solid after column chromatography: hexane–EtOAc (95:5 → 9:1). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.71 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.59 (dd, *J* = 7.7, 0.8 Hz, 1H), 8.58 (dt, *J* = 7.9, 1.1 Hz, 1H),

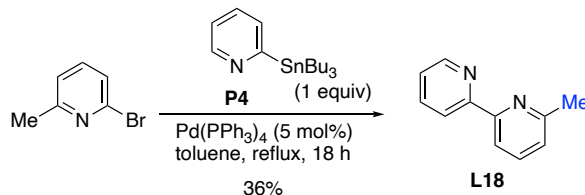
8.49 – 8.43 (m, 2H), 7.96 (t, $J = 7.8$ Hz, 1H), 7.86 (td, $J = 7.7, 1.8$ Hz, 1H), 7.71 (t, $J = 7.8$ Hz, 1H), 7.51 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.34 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H).

Synthesis of 6-(4-methoxyphenyl)-2,2':6',2''-terpyridine (**L12**)



The synthetic procedure was adopted from the literature.⁸ A solution of 6-bromo-2,2':6',2''-terpyridine **P18** (50 mg, 0.16 mmol), (4-methoxyphenyl)boronic acid (27 mg, 0.18 mmol) and Cs_2CO_3 (68 mg, 0.19 mmol) in dioxane/ H_2O 5/1 (2.5 ml/0.5 ml, 0.05 mol/L) was thoroughly degassed by bubbling N_2 gas. $\text{Pd}(\text{PPh}_3)_4$ (5 mg, 0.004 mmol) was subsequently added to the reaction mixture under N_2 . The Schlenk flask was sealed with a screw cap, placed into a 100 °C oil bath and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with H_2O , and extracted with DCM ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (52 mg, 0.15 mmol, 95% yield) was obtained as a white solid (mp 168–169 °C) after column chromatography: hexane–EtOAc (9:1). **^1H NMR** (500 MHz, Chloroform- d) δ 8.71 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.69 – 8.64 (m, 2H), 8.53 (dd, $J = 7.7, 0.9$ Hz, 1H), 8.46 (dd, $J = 7.8, 1.1$ Hz, 1H), 8.17 – 8.11 (m, 2H), 7.99 (t, $J = 7.8$ Hz, 1H), 7.89 (t, $J = 7.8$ Hz, 1H), 7.89 – 7.86 (m, 1H), 7.74 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.34 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H), 7.08 – 7.02 (m, 2H), 3.90 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform- d) δ 160.7 (C), 156.5 (C), 156.2 (C), 155.8 (2C), 155.4 (C), 149.3 (CH), 137.9 (CH), 137.7 (CH), 137.0 (CH), 132.2 (C), 128.4 (2CH), 123.9 (CH), 121.3 (CH), 121.1 (CH), 119.7 (CH), 118.8 (CH), 114.3 (CH), 55.5 (CH_3). **HR-MS, APCI, m/z** : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}^+$, $[\text{M}+\text{H}]^+$, 340.1445. Found, 340.1453.

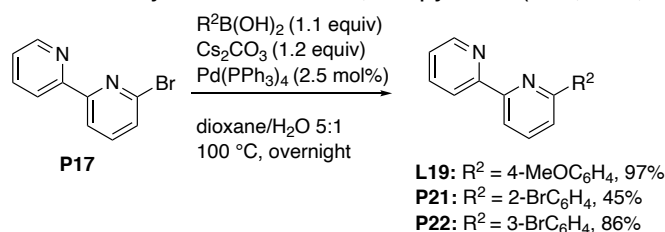
Scheme S16. Synthesis of 6-methyl-2,2'-bipyridine (**L18**).



To a solution of 2-bromo-6-methylpyridine (400 mg, 2.3 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (134 mg, 0.12 mmol) in toluene (12 mL, 0.2 mol/L), 2-(tributylstannyl)pyridine **P4** (847 mg, 2.30 mmol) was added. The mixture was thoroughly degassed by bubbling N_2 gas, sealed with a screw cap and refluxed overnight. Then the reaction mixture was diluted with water and poured into a concentrated aq. Solution of CsF (1.7 g, 11.50 mmol). After 30 min stirring at rt, the biphasic mixture was filtered through the plug of Celite®. The aqueous phase was extracted with toluene ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (138 mg, 0.82 mmol, 36%) was obtained as a colorless solid after column chromatography: hexane \rightarrow hexane–EtOAc (95:5 \rightarrow 9:1 \rightarrow 85:15) and keeping in a freezer (–30 °C) over weekend. The spectral data are in accordance with those reported in the literature.¹⁶ **^1H NMR** (500 MHz, Chloroform- d) δ 8.67 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.40 (dt, $J = 7.9, 1.1$ Hz, 1H), 8.16 (dt, $J = 7.9, 0.8$ Hz, 1H), 7.80 (td, $J = 7.7, 1.8$ Hz, 1H), 7.70 (t, $J = 7.7$ Hz, 1H), 7.29 (ddd, $J = 7.5, 4.8, 1.2$ Hz,

1H), 7.17 (d, $J = 7.6$ Hz, 1H), 2.64 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 158.1 (C), 156.7 (C), 155.7 (C), 149.3 (CH), 137.2 (CH), 137.0 (CH), 123.6 (CH), 123.4 (CH), 121.3 (CH), 118.2 (CH), 24.8 (CH₃).

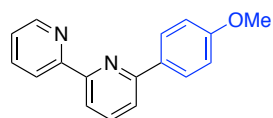
Scheme S17. Synthesis of 6-R²-2,2'-bipyridine (**L19**, **P21**, **P22**).



General procedure for the synthesis of 4,4'-di-*tert*-butyl-6''-R-2,2':6',2''-terpyridine (R-OleTpy).

The synthetic procedure was adopted from the literature.⁸ A solution of 6-bromo-2,2'-bipyridine (1 equiv) corresponding boronic acid (1.1 equiv) and Cs₂CO₃ (2 equiv) in dioxane/H₂O 5/1 (0.1 mol/L) was thoroughly degassed by bubbling N₂ gas. Pd(PPh₃)₄ (2.5 mol%) was subsequently added to the reaction mixture under N₂. The Schlenk flask was sealed with a screw cap, placed at 100 °C oil bath and left overnight. After cooling to room temperature, the reaction mixture was diluted with H₂O, and extracted with DCM (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. Pure products were obtained after column chromatography.

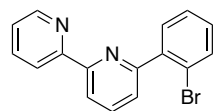
6-(4-methoxyphenyl)-2,2'-bipyridine (L19)



Starting from **P17** (117 mg, 0.5 mmol). The product (127 mg, 0.49 mmol, 97% yield) was obtained as a white solid after column chromatography: hexane–EtOAc (9:1). The spectral data are in accordance with those reported in the literature.¹⁷ ^1H NMR (500 MHz, Chloroform-

d) δ 8.69 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.63 (dt, $J = 8.0, 1.1$ Hz, 1H), 8.31 (dd, $J = 7.8, 1.0$ Hz, 1H), 8.17 – 8.09 (m, 2H), 7.85 (t, $J = 7.8$ Hz, 1H), 7.85 (td, $J = 7.7, 1.8$ Hz, 1H), 7.72 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.33 – 7.31 (m, 1H), 7.06 – 7.01 (m, 2H), 3.89 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 160.7 (C), 156.6 (C), 156.3 (C), 155.7 (C), 149.2 (CH), 137.8 (CH), 137.0 (CH), 132.2 (C), 128.4 (2CH), 123.8 (CH), 121.4 (CH), 119.7 (CH), 118.7 (CH), 114.2 (2CH), 55.5 (CH₃).

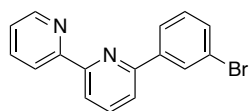
6-(2-bromophenyl)-2,2'-bipyridine (P21)



Starting from **P17** (200 mg, 0.85 mmol). The product (79 mg, 0.26 mmol, 30% yield) was obtained as a white solid after column chromatography: hexane–EtOAc (95:5). ^1H NMR (500 MHz, Chloroform- d) δ 8.69 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.52 (dt, $J = 8.0, 1.1$ Hz, 1H), 8.42 (dd, $J =$

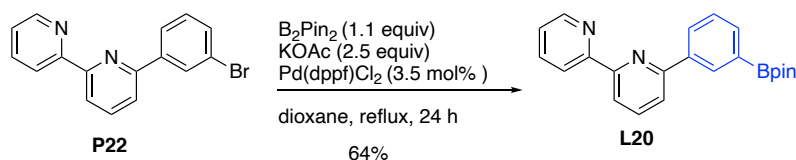
7.9, 1.0 Hz, 1H), 7.90 (t, $J = 7.8$ Hz, 1H), 7.81 (td, $J = 7.7, 1.8$ Hz, 1H), 7.71 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.68 – 7.57 (m, 2H), 7.44 (td, $J = 7.5, 1.2$ Hz, 1H), 7.31 (ddd, $J = 7.8, 4.9, 1.4$ Hz, 1H), 7.30 – 7.26 (m, 1H).

6-(3-bromophenyl)-2,2'-bipyridine (P22)



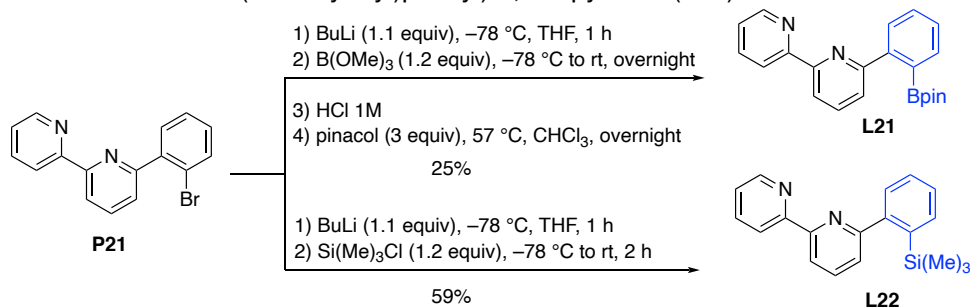
Starting from **P17** (117 mg, 0.50 mmol). The product (134 mg, 0.43 mmol, 86% yield) was obtained as a colorless oil after column chromatography: hexane–EtOAc (9:1). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.70 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 8.61 (dt, J = 8.0, 1.1 Hz, 1H), 8.40 (dd, J = 7.8, 0.9 Hz, 1H), 8.33 (t, J = 1.9 Hz, 1H), 8.04 (ddd, J = 7.8, 1.7, 1.0 Hz, 1H), 7.89 (t, J = 7.8 Hz, 1H), 7.86 (td, J = 7.8, 1.8 Hz, 1H), 7.74 (dd, J = 7.8, 1.0 Hz, 1H), 7.56 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.33 (ddd, J = 7.5, 4.8, 1.3 Hz, 1H).

Scheme S18. Synthesis of 6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine (L20).

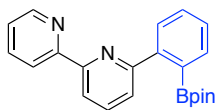


The synthetic procedure was adopted from the literature.¹⁴ A mixture of **P22** (136 mg, 0.44 mmol), bis(pinacolato)diboron (123 mg, 0.48 mmol), KOAc (108 mg, 1.10 mmol) and Pd(dppf)Cl₂ dichloromethane adduct (13 mg, 0.015 mmol) in dioxane (4.5 mL, 0.1 mol/L) was mixed and thoroughly degassed by bubbling a N₂ stream. The resulting solution was refluxed for 24 h. After cooling down to rt, the reaction mixture was passed through Celite ®. The filtrate was then diluted with water and extracted with EtOAc (× 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (99 mg, 0.28 mmol, 64% yield) was obtained as a viscous oil after column chromatography: hexane–EtOAc (95:5 → 85:15). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.69 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.66 (dt, J = 7.9, 1.1 Hz, 1H), 8.46 (t, J = 1.8 Hz, 1H), 8.39 – 8.34 (m, 2H), 7.94 – 7.75 (m, 4H), 7.55 – 7.51 (m, 1H), 7.33 (ddd, J = 7.4, 4.8, 1.2 Hz, 1H), 1.38 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 156.7 (C), 156.6 (C), 155.9 (C), 149.2 (CH), 138.9 (C), 137.8 (CH), 137.0 (CH), 135.6 (CH), 133.2 (CH), 130.3 (CH), 128.4 (CH), 123.8 (CH), 121.6 (CH), 120.7 (CH), 119.4 (CH), 84.1 (2C), 25.1 (4CH₃). **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 37.3. **HR-MS, APCI, m/z**: calcd for C₂₂H₁₈N₃O⁺, [M+H]⁺, 359.1925. Found, 359.1930.

Scheme S19. Synthesis of 6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine (L21) 6-(2-(trimethylsilyl)phenyl)-2,2'-bipyridine (L22).

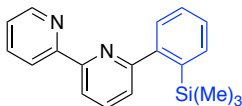


Synthesis of 6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine (L21).



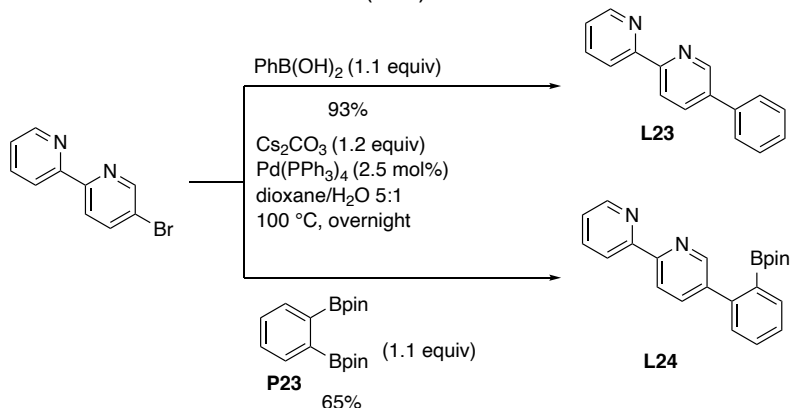
To a solution of **P21** (250 mg, 0.81 mmol) in THF (5 mL, 0.16 mol/L), BuLi (0.56 mL, 0.89 mmol, 1.59 mol/L in hexane) was added dropwise via syringe at $-78\text{ }^{\circ}\text{C}$, resulting in a dark-green solution that was stirred for 1 h. Then, B(OMe)_3 (0.108 mL, 0.97 mmol, 0.932 g/mL) was added in one portion via syringe and stirring continued for another 5 min. The solution was allowed to warm slowly to rt overnight, when its color changed to pale yellow. At this point 1M HCl aq. was added and stirring continued for another 30 min. The solution was neutralized with aq. NaHCO_3 and extracted with DCM ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The residues were triturated with hexane and the yellow solid was filtered off, resulting in 110 mg of crude material that was suspended in CHCl_3 (20 mL) followed by addition of pinacol (141 mg, 0.56 mmol). The reaction was heated overnight at $57\text{ }^{\circ}\text{C}$, then cooled down to rt and concentrated by rotary evaporation. The product (73 mg, 0.20 mmol, 25%) was obtained as an off-white solid (mp $120\text{--}122^{\circ}\text{C}$) after GPC. **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.69 – 8.66 (m, 1H), 8.59 – 8.55 (m, 1H), 8.36 (dd, $J = 7.9, 0.9\text{ Hz}$, 1H), 7.87 (t, $J = 7.8\text{ Hz}$, 1H), 7.78 (td, $J = 7.7, 1.8\text{ Hz}$, 1H), 7.72 (dd, $J = 7.3, 1.5\text{ Hz}$, 1H), 7.65 – 7.63 (m, 1H), 7.61 (dd, $J = 7.7, 1.0\text{ Hz}$, 1H), 7.49 (td, $J = 7.5, 1.4\text{ Hz}$, 1H), 7.42 (td, $J = 7.3, 1.2\text{ Hz}$, 1H), 7.29 (ddd, $J = 7.4, 4.8, 1.2\text{ Hz}$, 1H), 1.08 (s, 12H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform-*d*) δ 159.7 (C), 156.5 (C), 155.6 (C), 149.1 (CH), 145.9 (C), 137.4 (CH), 136.8 (CH), 134.0 (CH), 129.8 (CH), 128.2 (CH), 127.8 (CH), 123.8 (CH), 122.7 (CH), 122.3 (CH), 119.2 (CH), 83.8 (2C), 24.8 (4CH₃). **^{11}B NMR** (160 MHz, Chloroform-*d*) δ 37.4. **HR-MS, APCI, m/z** : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}^+$, $[\text{M}+\text{H}]^+$, 359.1925. Found, 359.1919.

Synthesis of 6-(2-(trimethylsilyl)phenyl)-2,2'-bipyridine (L22).



To a solution of **P21** (100 mg, 0.32 mmol) in THF (3 mL, 0.1 mol/L) BuLi (0.22 mL, 0.35 mmol, 1.59 mol/L in hexane) was added dropwise via syringe at $-78\text{ }^{\circ}\text{C}$ resulting in a dark green solution that kept stirring for 1 h. Then, $\text{Si(Me)}_3\text{Cl}$ (0.49 mL, 0.39 mmol, 0.856 g/mL) was added in one portion via syringe and stirring continued for another 5 min. Solution was allowed to warm slowly to rt overnight, when its color changed to yellow. The reaction was quenched with H_2O , the aqueous layer was extracted with Et_2O ($\times 3$). The organic layers were collected, washed with brine, dried over MgSO_4 , filtered and concentrated by rotary evaporation. The product (58 mg, 0.19 mmol, 59%) was obtained as a white solid (mp $114\text{--}116\text{ }^{\circ}\text{C}$) after GPC. **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.72 – 8.68 (m, 1H), 8.47 – 8.40 (m, 2H), 7.87 (t, $J = 7.8\text{ Hz}$, 1H), 7.81 – 7.75 (m, 1H), 7.71 (dd, $J = 7.6, 1.7\text{ Hz}$, 1H), 7.49 – 7.39 (m, 4H), 7.34 – 7.29 (m, 1H), 0.01 (s, 9H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform-*d*) δ 161.9 (C), 156.2 (C), 155.4 (C), 149.2 (CH), 148.0 (CH), 139.3 (C), 137.2 (C), 136.9 (CH), 135.2 (CH), 129.3 (CH), 128.8 (CH), 127.4 (CH), 124.1 (CH), 123.9 (CH), 121.8 (CH), 119.6 (CH), 0.6 (3CH₃). **HR-MS, APCI, m/z** : calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{Si}^+$, $[\text{M}+\text{H}]^+$, 305.1469. Found, 305.1474.

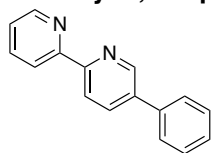
Scheme S20. Synthesis of 5-phenyl- (L23)/ 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine (L24).



General procedure for the synthesis of 5-phenyl- (L23)/ 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine (L24)

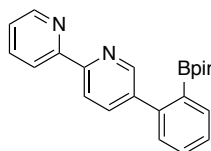
The synthetic procedure was adopted from the literature.⁸ A solution of 5-bromo-2,2'-bipyridine (1 equiv), the corresponding boronic acid (1.1 equiv) and Cs_2CO_3 (1.2 equiv) in dioxane/ H_2O 5/1 (0.1 mol/L) was thoroughly degassed by bubbling N_2 stream. $\text{Pd(PPh}_3)_4$ (2.5 mol%) was subsequently added to the reaction mixture under N_2 . The Schlenk flask was sealed with a screw cap, placed in a 100 °C oil bath and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with H_2O , and extracted with DCM ($\times 3$). The organic layers were collected, dried over MgSO_4 , filtered and concentrated by rotary evaporation. Pure products were obtained after column chromatography.

5-Phenyl-2,2'-bipyridine (L23)



Starting from 5-bromo-2,2'-bipyridine (100 mg, 0.43 mmol). The product (92 mg, 0.40 mmol, 93% yield) was obtained as an off-white solid after column chromatography: hexane–EtOAc (9:1). The spectral data are in accordance with those reported in the literature.¹⁸ **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.93 (dd, J = 2.3, 0.8 Hz, 1H), 8.71 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H), 8.48 (dd, J = 8.2, 0.8 Hz, 1H), 8.44 (dt, J = 8.0, 1.1 Hz, 1H), 8.03 (dd, J = 8.2, 2.3 Hz, 1H), 7.84 (td, J = 7.7, 1.8 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.40 (m, 1H), 7.32 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform-*d*) δ 156.1 (C), 155.1 (C), 149.4 (CH), 147.8 (CH), 137.8 (C), 137.1 (CH), 136.6 (C), 135.4 (CH), 129.3 (2CH), 128.3 (CH), 127.2 (2CH), 123.8 (CH), 121.2 (CH), 121.1 (CH).

5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine (L24)

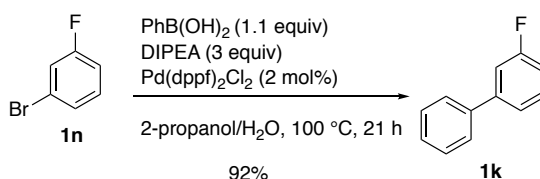


Starting from 5-bromo-2,2'-bipyridine (49 mg, 0.21 mmol). The product (49 mg, 0.14 mmol, 67% yield) was obtained as an off-white solid after column chromatography: hexane–EtOAc (9:1→8:2). The spectral data are in accordance with those reported in the literature.¹⁹ **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.71 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.69 (dd, J = 2.3, 0.8 Hz, 1H), 8.45 (dt, J = 8.0, 1.1 Hz, 1H), 8.41 (dd, J = 8.2, 0.8 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.52 (td, J = 7.5, 1.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.32 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 1.22 (s, 12H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform-*d*) δ 156.5 (C), 154.6 (C),

149.5 (CH), 149.3 (CH), 144.3 (C), 138.8 (CH), 137.6 (CH), 137.1 (CH), 135.6 (CH), 130.8 (CH), 129.5 (CH), 127.3 (CH), 123.7 (CH), 121.2 (CH), 120.0 (CH), 84.1 (2C), 24.8 (4CH₃). **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 37.1. Note: 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene **P23** was synthesized according to the procedure reported in the literature.²⁰

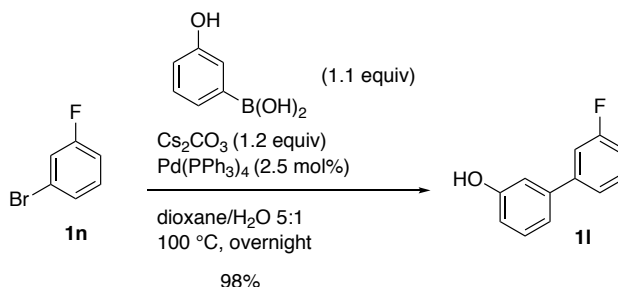
6. Synthesis and characterization data for substrates

Scheme S21. Synthesis of 3-fluoro-1,1'-biphenyl (**1k**).



This compound was synthesized according to the procedure reported in the literature.²¹ To a solution of phenylboronic acid (732 mg, 6.00 mmol) and Pd(dppf)Cl₂ dichloromethane adduct (8 mg, 0.100 mmol) in 2-propanol (5 mL) and H₂O (2.5 mL) was added 1-bromo-3-fluorobenzene (875 mg, 5.00 mmol) and diisopropylethylamine (2.61 mL, 15.00 mmol) at rt. After stirring for 21 h at 100 °C, the mixture was cooled down to rt, diluted with H₂O and extracted with EtOAc (\times 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (796 mg, 4.62 mmol, 92% yield) was obtained as a colorless solid after column chromatography: hexane to hexane–EtOAc (95:5). The spectral data are in accordance with those reported in the literature.²¹ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.48 – 7.35 (m, 5H), 7.33 – 7.27 (m, 1H), 7.10 – 6.98 (m, 1H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 163.3 (C) (d, J = 245.6 Hz), 143.7 (C) (d, J = 7.6 Hz), 140.1 (C), 130.4 (CH) (d, J = 8.4 Hz), 129.0 (2CH), 128.0 (CH), 127.3 (2CH), 122.9 (d, J = 2.9 Hz), 114.3 (CH), 114.1 (CH) (d, J = 2.4 Hz). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –116.4.

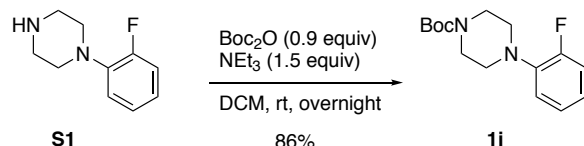
Scheme S22. Synthesis of 3'-fluoro-[1,1'-biphenyl]-3-ol (**1l**).



The synthetic procedure was adopted from the literature.⁸ A solution of 1-bromo-3-fluorobenzene (397 mg, 2.27 mmol), (3-hydroxyphenyl)boronic acid (328 mg, 2.38 mmol) and Cs₂CO₃ (887 mg, 2.72 mmol) in dioxane/H₂O 5/1 (25 ml/5 ml, 0.075 mol/L) was thoroughly degassed by bubbling N₂ gas. Pd(PPh₃)₄ (66 mg, 0.057 mmol) was subsequently added to the reaction mixture under N₂. The Schlenk flask was sealed with a screw cap, placed into a 100 °C oil bath and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with H₂O, and extracted with EtOAc (\times 3). The organic layers were collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (420 mg, 2.23 mmol, 98% yield) was obtained as a viscous colorless oil after column

chromatography: hexane to hexane–EtOAc (95:5→9:1). The spectral data are in accordance with those reported in the literature.²² **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 3H), 7.29 – 7.24 (m, 1H), 7.15 (ddd, J = 7.7, 1.8, 0.9 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.84 (ddd, J = 8.1, 2.6, 0.9 Hz, 1H), 4.82 (s, 1H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 163.3 (C) (d, J = 245.6 Hz), 156.0 (C), 143.1 (C) (d, J = 7.7 Hz), 141.8 (C) (d, 1.8 Hz), 130.4 (CH) (d, J = 8.4 Hz), 130.3 (CH), 122.9 (CH) (d, J = 2.9 Hz), 119.9 (CH), 114.9 (CH), 114.4 (CH) (d, 21.4 Hz), 114.2 (CH) (d, J = 52.2 Hz), 114.2 (CH) (d, 21.4 Hz). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –116.3.

Scheme S23. Synthesis of *tert*-butyl 4-(2-fluorophenyl)piperazine-1-carboxylate (**1i**).

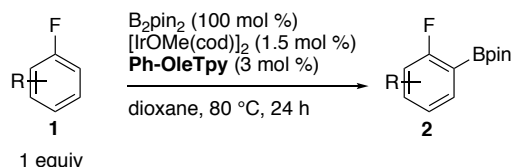


This compound was synthesized according to the procedure reported in the literature.²³ Boc₂O (220 mg, 1.01 mmol) was dissolved in DCM (6 mL, 0.2 mol/L) under N₂, and **S1** (200 mg, 1.11 mmol) was added. The mixture was cooled down to 0 °C, followed by dropwise addition of NEt₃ (0.23 mL, 1.67 mmol, 0.726 g/mL), and the resulting reaction mixture was stirred overnight, then poured into HCl 1M and extracted with DCM. The organic layer was washed with NaHCO₃ aq. and brine. The organic layer was collected, dried over MgSO₄, filtered and concentrated by rotary evaporation. The product (268 mg, 0.96 mmol, 86% yield) was obtained as a white solid after column chromatography: hexane–EtOAc (95:5). The spectral data are in accordance with those reported in the literature.²⁴ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.10 – 7.01 (m, 2H), 6.99 – 6.90 (m, 2H), 3.60 (t, J = 4.0 Hz, 4H), 3.02 (t, J = 4.0 Hz, 4H), 1.48 (s, 9H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 155.9 (C) (d, J = 246.0 Hz), 154.9 (C), 140.1 (C) (d, J = 8.5 Hz), 124.6 (CH) (d, J = 3.5 Hz), 123.0 (CH) (d, J = 7.9 Hz), 119.3 (CH) (d, J = 2.9 Hz), 116.3 (CH) (d, J = 20.7 Hz), 80.0 (C), 50.71 (CH₂), 50.68 (CH₂) 28.6 (3CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –126.1.

7. Synthesis and characterization data for *ortho*-to-F borylated arenes

7.1. Representative procedure

Scheme S24. Borylation of fluoroarenes (**1**) catalyzed by PhOle-Tpy/[IrOMe(cod)]₂.



[IrOMe(cod)]₂ (4 mg, 0.006 mmol, 3 mol% Ir), Ph-OleTpy (5.1 mg, 0.012 mmol, 3 mol% L) and B₂pin₂ (0.40 mmol, 102 mg) were placed into a Schlenk tube equipped with a stir bar under N₂. Dioxane was added (0.5 mL, C (fluoroarene) = 0.8 mol/L), followed by addition of the fluoroarene (0.40 mmol). The reaction vessel was sealed with a screw cap, and heated at 80 °C using a metal block. After stirring for 24 h, the reaction mixture was diluted with EtOAc, followed by addition of aq. NH₄Cl. An aliquot was taken from organic layer and passed through a plug of Florisil® with EtOAc. The resulting solution was analyzed by GC to estimate the yield and the ratio.

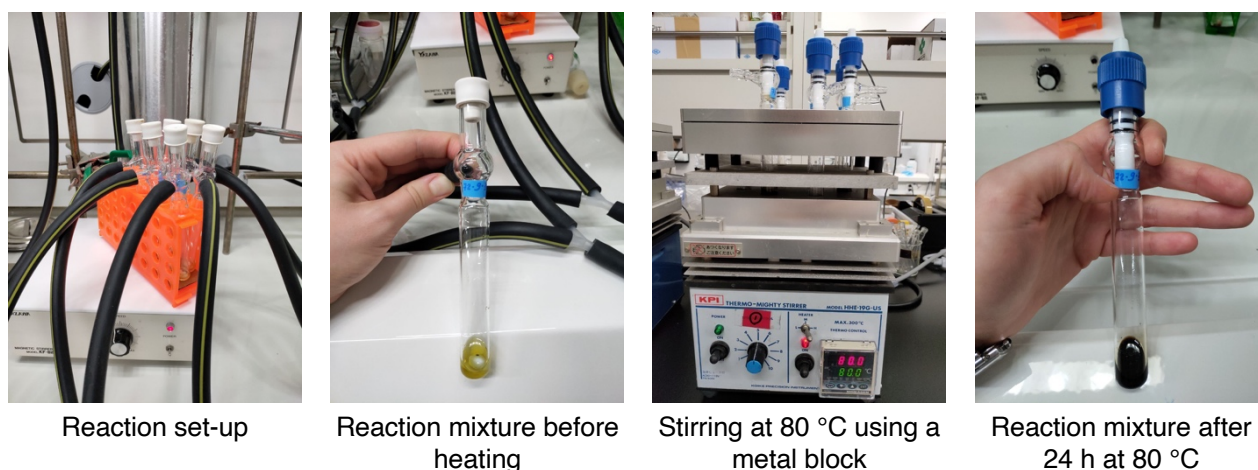
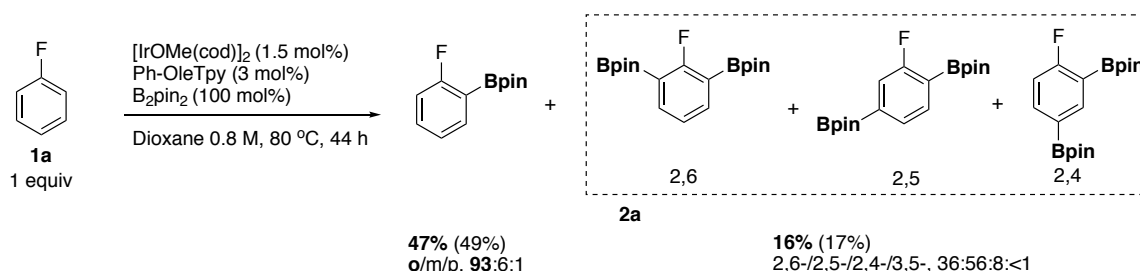


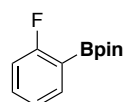
Figure S11. The iridium-catalyzed borylation reaction.

Selected compounds were isolated by the following procedure: the aqueous layer was extracted with EtOAc ($\times 3$ times), the organic extracts were passed through a plug of MgSO_4 and Florisil[®] and the resulting solution was combined with the aliquot taken for GC beforehand. The volatiles were evaporated. The resulting mixture was analyzed by ^{19}F NMR using trifluorotoluene as internal standard or by ^1H NMR using 1,1,2,2-tetrachloroethane as internal standard to determine the yield. Then the products were separated by GPC or by silica gel column chromatography. The details are specified for each substrate.

7.2. Characterization data



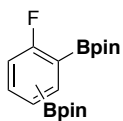
The reaction was conducted for 44 h on 0.60 mmol scale. Mono- and diborylated compounds were separated by GPC. The yield determined by ^{19}F NMR prior to isolation is 49% for mono- and 17% for diborylated product.



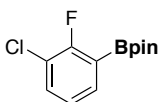
(2a): The compound was obtained as a mixture of o/m/p isomers and boron containing byproduct. In order to remove the traces of the byproduct column chromatography was performed. Elution system: gradient hexane to hexane/dichloromethane, 6:4. The compound was obtained as a colorless oil in 47% yield (62 mg, 0.28 mmol), o/m/p selectivity is **93:6:1**.²⁶ Note: the compound easily evaporates under reduced pressure.

The spectral data are in accordance with those reported in the literature.²⁵ ^1H NMR (500 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 1H), 7.46 – 7.40 (m, 1H), 7.17 – 7.10 (m, 1H), 7.05 – 6.99 (m, 1H), 1.36 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 167.3 (C) (d, J = 250.7 Hz), 137.0 (CH) (d, J = 7.9 Hz), 133.4 (CH) (d, J = 8.7 Hz), 123.7 (CH) (d, J = 3.3 Hz), 115.4 (CH) (d, J = 23.7 Hz), 84.0 (2C), 25.0 (4CH₃). ^{19}F NMR (471 MHz, Chloroform-*d*) δ ortho: –105.9; S34

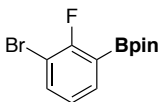
para: -111.6; meta -117.4. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.3. **GC-MS**, EI, *m/z* (retention time): ortho: [M⁺] 222, 207, 179, 160, 137, 123 (10.755); meta: [M⁺] 222, 207, 179, 165, 136, 123 (10.290); para: [M⁺] 222, 207, 179, 165, 136, 123 (10.185).



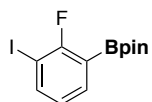
(2a): The compound was obtained as a mixture of 2,6-/2,5-/2,4-/3,5- isomers. Beige solid, 16% yield (33 mg, 0.09 mmol) 2,6-/2,5-/2,4-/3,5-, 36:56:8:<1.²⁶ The **¹H NMR** spectral data for 2,5-isomer is in accordance with those reported in the literature.²⁷ **2,6-isomer**: **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 7.2, 5.9 Hz, 2H), 7.13 (td, *J* = 7.2, 0.9 Hz, 1H), 1.33 (s, 12H); **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 171.7 (C) (d, *J* = 255.8 Hz), 140.2 (2CH) (d, *J* = 8.7 Hz), 123.4 (CH) (d, *J* = 3.4 Hz), 83.9 (2C), 25.0 (8CH₃). **2,5-isomer**: **¹H NMR** (500 MHz, Chloroform-*d*) δ : 7.72 (dd, *J* = 7.2, 5.8 Hz, 1H), 7.54 (dt, *J* = 7.2, 1.0 Hz, 1H), 7.44 (d, *J* = 9.6 Hz, 1H), 1.36 (s, 12H), 1.34 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 166.9 (C) (d, *J* = 251.2 Hz), 136.3 (CH) (d, *J* = 7.3 Hz), 129.7 (CH) (d, *J* = 3.3 Hz), 121.0 (CH) (d, *J* = 22.4 Hz), 84.3 (C), 84.1 (C), 25.0 (4CH₃), 24.96 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ 2,6-isomer: -95.0; 2,5-isomer: -107.4; 2,4-isomer: -101.3. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.3. **GC-MS**, EI, *m/z* (retention time): 2,6 and 2,5-isomers are overlapped: [M⁺] 348, 333, 287, 262 (19.155).



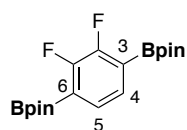
(2b): The compound was obtained as a mixture of o/m/p isomers after column chromatography: elution system is gradient of hexane to hexane/dichloromethane 1:1. Colorless oil, **70%** yield (71 mg, 0.28 mmol), o/m/p selectivity is **97:3**:<1.²⁶ The yield determined by **¹⁹F NMR** prior to isolation is 84% for mono- and 11% for diborylated product, o/m/p selectivity is 93:7:<1. The spectral data are in accordance with those reported in the literature.²⁸ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 1H), 7.51 – 7.45 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.2 (C) (d, *J* = 253.6 Hz), 135.0 (CH) (d, *J* = 7.3 Hz), 133.8 (CH), 124.6 (CH) (d, *J* = 4.1 Hz), 121.3 (C) (d, *J* = 19.8 Hz), 84.4 (2C), 24.9 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ ortho: -108.4; meta: -120.2. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.0 (br s). **GC-MS**, EI, *m/z* (retention time): ortho: [M⁺] 256, 241 (13.290); meta: 256, 241, 170, 157 (12.765).



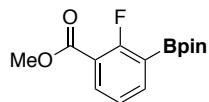
(2c): The compound was obtained as a mixture of o/m/p isomers after column chromatography: elution system is gradient of hexane to hexane/dichloromethane 1:1. White solid (after 1 night at -30 °C), **68%** yield (81 mg, 0.27 mmol), o/m/p selectivity is **94:5:1**.²⁹ The yield determined by **¹⁹F NMR** prior to isolation is 81% for mono- and 5% for diborylated product. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 163.0 (C) (d, *J* = 252.1 Hz), 136.8 (CH), 135.8 (CH) (d, *J* = 7.3 Hz), 125.0 (CH) (d, *J* = 4.0 Hz), 109.5 (C) (d, *J* = 23.4 Hz), 84.4 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ ortho: -99.9, meta: -112.0. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 34.9 (br s). **GC-MS**, EI, *m/z* (retention time): ortho: [M⁺] 300, 285, 238, 196 (14.440); meta: [M⁺] 300, 285, 214, 201 (13.985). **HR-MS, APCI, *m/z***: calcd for C₁₂H₁₆BBBrFO₂⁺, [M+H]⁺, 301.0405. Found, 301.0399.



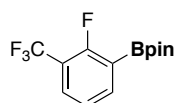
(**2d**): The yield and selectivity were determined by analyzing the crude reaction mixture: **18%** yield (25 mg, 0.07 mmol), o/m/p selectivity is **90:6:4**.²⁹ The compound was isolated for characterization purposes as a colorless oil by column chromatography: elution system is gradient of hexane to hexane/dichloromethane 1:1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.84 (ddd, J = 7.9, 6.2, 1.8 Hz, 1H), 7.69 (ddd, J = 7.3, 5.4, 1.7 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 165.5 (C) (d, J = 250.3 Hz), 142.7 (CH) (d, J = 2.3 Hz), 137.0 (CH) (d, J = 7.5 Hz), 125.5 (CH) (d, J = 3.6 Hz), 84.4 (2C), 82.0 (C) (d, J = 28.2 Hz), 26.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ ortho: -85.8, para: -92.4, meta: -98.4. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 34.9. **GC-MS**, EI, m/z (retention time): ortho: [M⁺] 348, 333, 286, 248 (14.440). **HR-MS, APCI, m/z**: calcd for C₁₂H₁₇BFIO₂⁺, [M+H]⁺, 349.0267. Found, 349.0279.



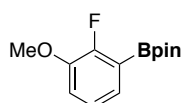
(**2e**): This reaction was performed with 150 mol% (0.60 mmol) of B₂pin₂. The compound was obtained as a mixture of 3,6-/3,5-isomers after GPC with chloroform as an eluent. White solid, **65%** yield (96 mg, 0.26 mmol), 3,6-/3,5- selectivity is **98:2**.²⁹ The yield estimated by GC prior to isolation is 68% for di- and 14% for monoborylated product. The spectral data are in accordance with those reported in the literature.³⁰ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.42 (s, 2H), 1.36 (s, 24H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 154.5 (C) (dd, J = 250.2, 15.3 Hz), 130.4 (CH) (t, J = 5.2 Hz), 84.4 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -133.2. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.1 (br s). **GC-MS**, EI, m/z (retention time): [M⁺] 366, 351, 323, 307, 262 (19.530). **HR-MS, APCI, m/z**: calcd for C₁₈H₂₇B₂F₂O₄⁺, [M+H]⁺, 367.2058. Found, 367.2055.



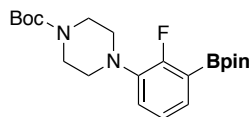
(**2f**): The compound was obtained as a 96:4 mixture of mono and diborylated products after column chromatography: elution system is gradient of hexane to hexane/EtOAc 9:1. Colorless oil, 67 mg total mass (63 mg of monoborylated product, 0.22 mmol, 56% yield), o/m/p selectivity is **65:33:2**.²⁹ The yield determined by ¹⁹F NMR prior to isolation is 75% for mono- and 7% for diborylated product, o/m/p selectivity is 60:36:4. For the *ortho*-isomer the spectral data are in accordance with those reported in the literature.³¹ *ortho*-isomer: **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.02 (dd, J = 7.5, 2.0 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 3.91 (s, 3H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 166.1 (C) (d, J = 264.3), 165.5 (C) (d, J = 3.2 Hz), 141.5 (CH) (d, J = 9.2 Hz), 135.5 (CH), 123.7 (CH) (d, J = 4.0 Hz), 118.7 (C) (d, J = 12.4 Hz), 84.4 (2C), 52.4 (CH₃), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -102.3. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 34.9. **GC-MS**, EI, m/z (retention time): 280, 266, 260, 249, 218, 181 (16.215). *meta*-isomer: **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.94 – 7.87 (m, 1H), 7.60 (dd, J = 7.7, 1.0 Hz, 1H), 7.54 (dd, J = 11.1, 1.0 Hz, 1H), 3.93 (s, 3H), 1.35 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 165.1 (C) (d, J = 3.8 Hz), 161.5 (C) (d, J = 259.1 Hz), 131.5 (CH), 130.0 (CH) (d, J = 3.4 Hz), 122.8 (CH) (d, J = 18.7 Hz), 120.8 (C), (d, J = 9.5 Hz), 84.6 (2C), 52.5 (CH₃), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -114.6. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 34.9. **GC-MS**, EI, m/z (retention time): [M⁺] 280, 265, 249, 237, 194, 181 (15.870).



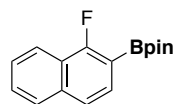
(2g): The compound was obtained as a 99:1 mixture of mono and diborylated products after column chromatography: elution system is gradient of hexane to hexane/dichloromethane 5:5. Colorless oil, 69 mg total mass (68 mg of monoborylated product, 0.23 mmol, 59% yield), o/m/p selectivity is **86:14:<1**.²⁹ The yield determined by ¹⁹F NMR prior to isolation is 88% for mono- and 10% for diborylated product. The spectral data are in accordance with those reported in the literature.³¹ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.96 – 7.88 (m, 1H), 7.72 – 7.66 (m, 1H), 7.26 – 7.21 (m, 1H), 1.37 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 164.2 (C) (d, *J* = 262.6 Hz), 140.9 (CH) (d, *J* = 8.7 Hz), 130.3 (CH) (d, *J* = 4.4 Hz), 123.7 (CH) (d, *J* = 4.0 Hz), 122.9 (C) (q, *J* = 272.8 Hz), 118.4 (C) (qd, *J* = 33.0, 14.8 Hz), 84.5 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ *ortho*: –64.7 (3F), –107.3 (1F), *meta*: –64.8 (3F), –119.3 (1F). **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 34.8 (br s). **GC-MS**, EI, *m/z* (retention time): *ortho*: [M⁺] 290, 275, 228, 191 (10.810); *meta*: 290, 275, 204, 191 (10.380).



(2h): The reaction was conducted for 67 h. The compound was obtained as a mixture of o/m/p isomers after column chromatography: elution system is gradient of hexane to hexane/dichloromethane 1:1 to dichloromethane. Colorless oil, **61%** yield (62 mg, 0.25 mmol), o/m/p selectivity is **98:1:1**.²⁹ The yield determined by ¹⁹F NMR prior to isolation is 73% for mono- and 6% for diborylated product. The spectral data are in accordance with those reported in the literature.³¹ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 1H), 7.07 – 7.05 (m, 2H), 3.87 (s, 3H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 157.0 (C) (d, *J* = 250.9 Hz), 147.7 (C) (d, *J* = 12.2 Hz), 127.6 (CH) (d, *J* = 7.3 Hz), 25.0 (4CH₃), 123.9 (CH) (d, *J* = 4.1 Hz), 117.1 (CH) (d, *J* = 2.3 Hz), 84.1 (2C), 56.7 (CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –128.4. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.1 (br s). **GC-MS**, EI, *m/z* (retention time): [M⁺] 252, 237, 192, 179, 167 (14.145).

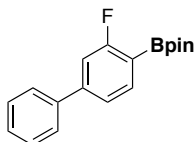


(2i): The reaction was conducted for 65 h on 0.20 mmol scale. The compound was obtained as a 95:5 mixture of mono and diborylated products after column chromatography: elution system is gradient of hexane to hexane/EtOAc 4:1. White solid, 50 mg total mass (46 mg of monoborylated product, 0.113 mmol, 57% yield), o/m/p selectivity is **84:13:3**.²⁶ The compound was collected in 3 fractions. The first one contained *meta* and *para* isomers as a dominant specie (7 mg total mass, o/m/p selectivity is 22:55:23) and the third *ortho* isomer (39 mg total mass, o/m/p selectivity is 95:5:<1). The yield determined by ¹⁹F NMR prior to isolation is 59% for mono- and 3% for diborylated product. Note: Compound is not stable under GC conditions. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.35 (ddd, *J* = 7.1, 4.9, 1.9 Hz, 1H), 7.09 – 7.05 (m, 1H), 7.02 (td, *J* = 8.0, 1.9 Hz, 1H), 3.56 (t, *J* = 5.1 Hz, 5H), 3.02 (t, *J* = 5.1 Hz, 5H), 1.48 (s, 9H), 1.35 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 160.3 (C) (d, *J* = 251.2 Hz), 154.9 (C), 139.9 (C) (d, *J* = 10.5 Hz), 129.6 (CH) (d, *J* = 8.2 Hz), 124.2 (CH) (d, *J* = 3.6 Hz), 122.6 (CH) (d, *J* = 3.4 Hz), 84.0 (C), 80.0 (C), 50.8 (CH₂), 50.7 (CH₂), 28.6 (3CH₃), 24.9 (4CH₃). **HR-MS, APCI, *m/z***: calcd for C₂₁H₃₃BFN₂O₄⁺, [M+H]⁺, 407.2512. Found, 407.2524.



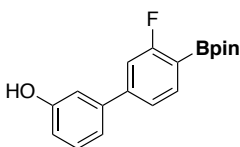
(2j): The compound was obtained as a mixture of o/m isomers after GPC. Yellowish oil, **65%** yield (71 mg, 0.26 mmol), o/m selectivity is **86:14**.²⁹ The yield determined by ¹⁹F NMR prior to isolation is 69% for mono- and 12% for diborylated product. **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.5

Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.72 (dd, $J = 8.2, 5.7$ Hz, 1H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.50 – 7.58 (m, 2H), 1.41 (s, 12H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform- d) δ 164.3 (C) (d, $J = 258.7$ Hz), 137.0 (C) (d, $J = 5.5$ Hz), 130.9 (CH) (d, $J = 8.9$ Hz), 128.1 (CH), 127.5 (CH) (d, $J = 3.2$ Hz), 126.3 (CH), 123.5 (C) (d, $J = 18.4$ Hz), 123.1 (CH) (d, $J = 4.1$ Hz), 121.6 (CH) (d, $J = 6.1$ Hz), 84.1 (2C), 25.0 (4CH₃). **^{19}F NMR** (471 MHz, Chloroform- d) δ ortho: –113.8; meta: –128.1. **^{11}B NMR** (160 MHz, Chloroform- d) δ 35.5 (br s). **GC-MS**, EI, m/z (retention time): ortho: [M⁺] 272, 257, 212, 187, 172 (17.535); meta: [M⁺] 272, 257, 186, 172 (17.175). **HR-MS, APCI, m/z** : calcd for C₁₆H₁₉BFO₂⁺, [M+H]⁺, 273.1451. Found, 273.1449.



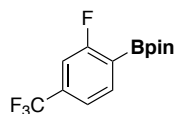
(2k): The compound was obtained as a mixture of o/m isomers after column chromatography with dichloromethane as an eluent and further separation of mono- and diborylated isomers by GPC. Yellowish oil, **48%** yield (57 mg, 0.19 mmol), o/m selectivity is **90:10**.²⁶ The yield determined by ^{19}F NMR prior to isolation is 66% for mono- and 3% for diborylated product. The spectral data are in

accordance with those reported in the literature.³³ **^1H NMR** (500 MHz, Chloroform- d) δ 7.80 (dd, $J = 7.7, 6.4$ Hz, 1H), 7.63 – 7.58 (m, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.28 (dd, $J = 10.7, 1.5$ Hz, 1H), 1.38 (s, 12H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform- d) δ 167.8 (C) (d, $J = 250.8$ Hz), 146.7 (C) (d, $J = 8.5$ Hz), 139.8 (C) (d, $J = 1.6$ Hz), 137.4 (CH) (d, $J = 8.7$ Hz), 129.0 (2CH), 128.3 (CH), 127.3 (2CH), 122.4 (CH) (d, $J = 2.8$ Hz), 113.9 (CH) (d, $J = 25.1$ Hz), 84.1 (2C), 25.0 (4CH₃). **^{19}F NMR** (471 MHz, Chloroform- d) δ ortho: –105.9; meta: –117.6. **^{11}B NMR** (160 MHz, Chloroform- d) δ 35.8 (br s). **GC-MS**, EI, m/z (retention time): ortho: [M⁺] 298, 283, 238, 213, 198 (19.565); meta: 298, 283, 212, 198 (18.830).

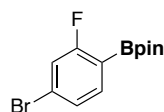


(2l): The reaction was conducted on 0.37 mmol scale. The substrate was premixed with HBpin (120 mol%) for 10 min at rt, dioxane as a solvent in the Schlenk flask under N₂ in order to protect the hydroxyl group *in situ*. Upon reaction, gas evolved. After 10 min, the other components (B₂pin₂, [IrOMe(cod)]₂, Ph-OleTpy) were added to the reaction mixture. The

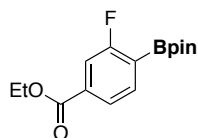
compound was obtained as a mixture of o/m isomers and boron containing byproducts, presumably 2-(cyclooct-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (Bpin)₂O after isolation by GPC. In order to remove the traces of the byproducts column chromatography was performed: elution system is gradient of hexane to hexane/EtOAc 8:2. The compound was obtained as a viscous white oil in **68%** yield (79 mg, 0.25 mmol), o/m selectivity is **93:7**.²⁶ The yield determined by ^{19}F NMR prior to isolation is 84% for mono- and <1% for diborylated product. **^1H NMR** (500 MHz, Chloroform- d) δ 7.78 (dd, $J = 7.7, 6.4$ Hz, 1H), 7.34 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.30 (t, $J = 7.9$ Hz, 1H), 7.22 (dd, $J = 10.6, 1.6$ Hz, 1H), 7.17 – 7.14 (m, 1H), 7.06 – 7.05 (m, 1H), 6.87 – 6.84 (m, 1H), 5.35 (s, 1H), 1.38 (s, 12H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform- d) δ 167.7 (C) (d, $J = 250.7$ Hz), 156.2 (C), 146.3 (C) (d, $J = 8.6$ Hz), 141.4 (C), 137.3 (CH) (d, $J = 8.7$ Hz), 130.3 (CH), 122.4 (CH) (d, $J = 2.8$ Hz), 119.7 (CH), 115.3 (CH), 114.2 (CH), 113.9 (CH) (d, $J = 25.2$ Hz), 84.2 (2C), 24.9 (4CH₃). **^{19}F NMR** (471 MHz, Chloroform- d) δ –117.4 (ortho), –105.8 (meta). **^{11}B NMR** (160 MHz, Chloroform- d) δ 35.0 (br s). **GC-MS**, EI, m/z (retention time): meta: [M⁺] 314, 299, 228, 214 (21.835); ortho: [M⁺] 314, 299, 254, 241, 229, 214 (22.535). **HR-MS, APCI, m/z** : calcd for C₁₈H₂₁BFO₃⁺, [M+H]⁺, 315.1562. Found, 315.1571.



(2m): The compound was obtained as a mixture of *o*/*m* isomers after GPC. Colorless oil, **61%** yield (71 mg, 0.24 mmol), *o*/*m* selectivity is **90:10**.²⁶ The yield determined by ¹⁹F NMR prior to isolation is 86% for monoborylated product. Diborylated product was not observed. The spectral data are in accordance with those reported in the literature.³³ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.6, 6.3 Hz, 1H), 7.40 (ddd, *J* = 7.6, 1.6, 0.8 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 1.37 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 166.9 (C) (d, *J* = 253.2 Hz), 137.8 (CH) (d, *J* = 8.4 Hz), 135.2 (C) (dq, *J* = 33.1, 8.2 Hz), 122.1 (C) (q, *J* = 273.9 Hz), 120.3 – 120.6 (CH) (m), 112.7 (CH) (dq, *J* = 27.5, 4.1 Hz), 84.6 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ *ortho*: –66.4 (CF₃), –103.8 (F); *meta*: –65.7 (CF₃), –115.4 (F). **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 34.9 (br s). **GC-MS**, EI, *m/z* (retention time): *ortho*: [M⁺] 290, 275, 231, 191 (10.084); *meta*: [M⁺] 290, 275, 204, 191 (9.500).

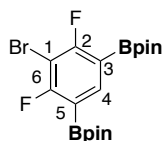


(2n): The compound was obtained as a mixture of *o*/*m* isomers after column chromatography: elution system is gradient of hexane to hexane/dichloromethane 1:1. Colorless oil, **58%** yield (70 mg, 0.23 mmol), *o*/*m* selectivity is **77:23**.²⁹ The compound was collected in 4 fractions. The first two contained *meta* isomer as a dominant specie and the other two *ortho*-isomer. The yield determined by ¹⁹F NMR prior to isolation is 82% for monoborylated product. Diborylated product was not observed. The spectral data are in accordance with those reported in the literature.³² *ortho*-isomer: **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 8.0, 6.4 Hz, 1H), 7.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.23 (dd, *J* = 8.8, 1.7 Hz, 1H), 1.35 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 167.0 (C) (d, *J* = 255.8 Hz), 137.9 (CH) (d, *J* = 8.9 Hz), 127.3 (CH) (d, *J* = 3.4 Hz), 126.6 (C) (d, *J* = 10.0 Hz), 119.2 (CH) (d, *J* = 27.2 Hz), 84.3 (2C), 24.9 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –103.5. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.0. **GC-MS**, EI, *m/z* (retention time): [M⁺] 300, 285, 241, 201 (13.965). *meta*-isomer: **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.41 (ddd, *J* = 8.5, 2.5, 0.8 Hz, 1H), 7.32 (ddd, *J* = 8.3, 2.5, 1.8 Hz, 1H), 1.34 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 162.4 (C) (d, *J* = 251.5 Hz), 133.4 (CH) (d, *J* = 3.1 Hz), 122.5 (C) (d, *J* = 8.5 Hz), 121.8 (CH) (d, *J* = 24.4 Hz), 119.9 (CH) (d, *J* = 19.1 Hz), 84.6 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ –114.8. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.2. **GC-MS**, EI, *m/z* (retention time): [M⁺] 300, 285, 214, 201 (13.450).



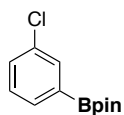
(2o): The compound was obtained as a mixture of *o*/*m* isomers after column chromatography: elution system is gradient of hexane to hexane/EtOAc 9:1. White solid (after 1 night at –30 °C), **80%** yield (94 mg, 0.32 mmol), *o*/*m* selectivity is **95:5**.²⁹ The yield determined by ¹⁹F NMR prior to isolation is 90% for monoborylated product. Diborylated product was not observed. The spectral data are in accordance with those reported in the literature.³³ **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.80 – 7.79 (m, 2H), 7.67 (dt, *J* = 9.7, 0.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.37 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-*d*) δ 167.0 (C) (d, *J* = 251.5 Hz), 166.0 (C) (d, *J* = 2.3 Hz), 137.0 (CH) (d, *J* = 8.1 Hz), 135.3 (C) (d, *J* = 8.3 Hz), 124.6 (CH) (d, *J* = 3.3 Hz), 116.3 (CH) (d, *J* = 26.0 Hz), 84.4 (2C), 61.6 (CH₂), 25.0 (4CH₃), 14.4 (CH₃). **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ *ortho*: –105.6; *meta*: –117.0. **¹¹B NMR** (160 MHz, Chloroform-*d*) δ 35.4 (br s). **GC-**

MS, EI, m/z (retention time): ortho: [M⁺] 294, 279, 249, 232, 224, 209, 190 (16.705); meta: [M⁺] 294, 279, 251, 223, 205, 195 (16.135)



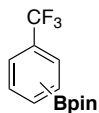
(2p): This reaction was performed with 200 mol% (0.80 mmol) of B₂pin₂. The compound was obtained solely as an 3,5-isomer after GPC with chloroform as an eluent. Beige solid, **76%** yield (136 mg, 0.31 mmol). The yield determined by ¹⁹F NMR prior to isolation is 80% for diborylated product.

Monoborylated product was not observed. **¹H NMR** (500 MHz, Chloroform-d) δ 8.05 (t, *J* = 7.0 Hz, 1H), 1.36 (s, 24H). **¹³C{¹H} NMR** (126 MHz, Chloroform-d) δ 166.4 (2C) (dd, *J* = 259.0, 5.4 Hz), 143.5 (CH) (t, *J* = 10.0 Hz), 84.4 (4C), 25.0 (8CH₃). **¹⁹F NMR** (471 MHz, Chloroform-d) δ -92.1. **¹¹B NMR** (160 MHz, Chloroform-d) δ 35.1 (br s). **GC-MS**, EI, m/z (retention time): [M⁺] 444, 429, 415, 385, 340 (21.295). **HR-MS, APCI, m/z**: calcd for C₁₈H₂₅B₂BrF₂O₄⁺, [M+H]⁺, 445.1163. Found, 445.1165.



(3): The reaction was conducted on 0.20 mmol scale. The yield and selectivity were determined by analyzing the crude reaction mixture: **41%** yield of monoborylated product (19 mg, 0.08 mmol) and **4%** of diborylated one (3 mg, 0.008 mmol)³⁴, m/p selectivity is **82:18**³⁵. The compound was isolated for

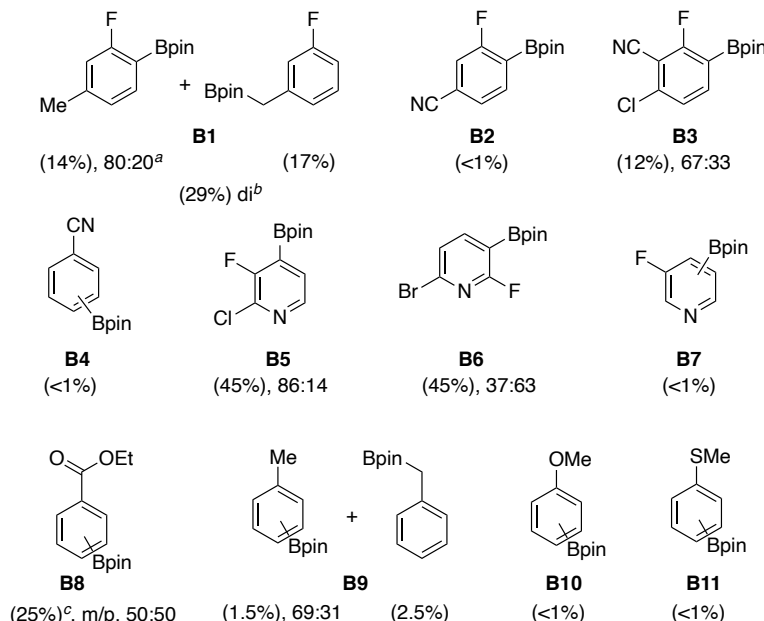
characterization purposes as a colorless oil: elution system is gradient of hexane to hexane/dichloromethane 1:1 to dichloromethane. meta-isomer: **¹H NMR** (500 MHz, Chloroform-d) δ 7.78 – 7.76 (m, 1H), 7.66 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.42 (ddd, *J* = 7.7, 2.3, 1.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 1.34 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-d) δ 134.7 (CH), 134.2 (C), 132.8 (CH), 131.4 (CH), 129.3 (CH), 84.3 (2C), 25.0 (4CH₃). **¹¹B NMR** (160 MHz, Chloroform-d) δ 34.8 (br s). **GC-MS**, EI, m/z (retention time): meta: [M⁺] 238, 223, 195, 181, 152, 139 (12.885); para: [M⁺] 238, 223, 152, 139 (12.835). The spectral data are in accordance with those reported in the literature.³⁶



(4): The yield and selectivity were determined by analyzing the crude reaction mixture: **58%** yield of monoborylated product (63 mg, 0.23 mmol) and **4%** of diborylated one (6 mg, 0.015 mmol)³⁴, m/p selectivity is 65:35²⁹ which corresponds to a statistical distribution of isomers. The compound was isolated for

characterization purposes as a colorless oil after column chromatography: elution system is gradient of hexane to hexane/ethyl acetate 9:1. The spectral data are in accordance with those reported in the literature.³⁷ meta-isomer: **¹H NMR** (500 MHz, Chloroform-d) δ 8.07 (s, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-d) δ 138.1 (CH), 133.0 (C) (q, *J* = 31.2 Hz), 131.5 (CH) (q, *J* = 3.9 Hz), 128.2 (CH), 127.9 (CH) (q, *J* = 3.2 Hz), 124.3 (C) (q, *J* = 272.5 Hz), 84.4 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-d) δ -65.8. **¹¹B NMR** (160 MHz, Chloroform-d) δ 35.8. **GC-MS**, EI, m/z (retention time): [M⁺] 272, 257, 229, 186, 173 (10.155). para-isomer: **¹H NMR** (500 MHz, Chloroform-d) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 1.36 (s, 12H). **¹³C{¹H} NMR** (126 MHz, Chloroform-d) δ 135.2 (2CH), 130.2 (C) (q, *J* = 32.1 Hz), 124.5 (2CH) (q, *J* = 3.2 Hz), 124.4 (C) (q, *J* = 271.3 Hz), 84.4 (2C), 25.0 (4CH₃). **¹⁹F NMR** (471 MHz, Chloroform-d) δ -66.2. **¹¹B NMR** (160 MHz, Chloroform-d) δ 35.8. **GC-MS**, EI, m/z (retention time): [M⁺] 272, 257, 229, 186, 173 (10.200).

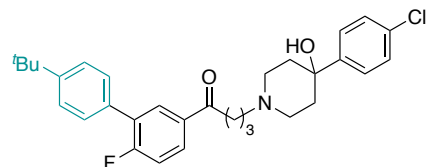
7.3. Other substrates



The yield and selectivity were determined by GC using tridecane as internal standard. ^aSelectivity was determined by ¹⁹F NMR. ^b26% is presumably the isomer borylated both at aromatic ring and benzylic site. ^cYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as internal standard.

Figure S12. Borylation of arenes catalyzed by **PhOle-Tpy**/[IrOMe(cod)]₂.

7.4. Late-stage functionalization of haloperidol



Haloperidol (75 mg, 0.20 mmol) was placed in a Schlenk tube, followed by addition of dioxane (0.4 mol/L). To the resulting suspension, HBpin (35 μ l, 0.24 mmol, 120 mol%) was added under N₂ in order to protect the hydroxyl group *in situ*. Upon reaction, gas evolved and a colorless solution formed. After 15

min, [IrOMe(cod)]₂ (2.0 mg, 0.003 mmol, 3 mol% Ir), Ph-OleTpy (2.5 mg, 0.006 mmol, 3 mol% L) and B₂pin₂ (0.2 mmol, 51 mg) were added under N₂. The vessel was sealed with a screw cap and the reaction mixture was heated at 80 °C using a metal block. After stirring for 24 h, an aliquot was sampled for NMR monitoring of haloperidol conversion. The aliquot was diluted with EtOAc, followed by addition of aq. NH₄Cl. The organic layer was separated and the volatiles were evaporated. The resulting solid was analyzed by ¹⁹F NMR: 30% haloperidol, 50% *ortho*-to-F monoborylated haloperidol, 12% diborylated haloperidol (presumably *ortho*, *ortho*-to-F), and 8% unidentified species were detected. MS, APCI, m/z: calcd for C₂₁H₂₄ClFNO₂⁺, [M+H]⁺ 376.15. Found, 376.15 (haloperidol); calcd for C₂₇H₃₅BClFNO₄⁺, [M+H]⁺, 502.23. Found, 502.23 (mono); calcd for C₃₃H₄₆B₂ClFNO₆⁺, [M+H]⁺, 628.32. Found, 628.32 (di). After the NMR analysis, the reaction mixture was concentrated in vacuo. A dioxane/H₂O 5/1 (0.1 mol/L) was degassed by N₂ bubbling in a separated flask and transferred to the Schlenk via a metal canula. At this point, Cs₂CO₃ (64 mg, 0.196 mmol), 4-^tBuC₆H₄Br (42 mg, 0.196 mmol) and Pd(PPh₃)₄ (5 mg, 0.004 mmol) were added, the Schlenk flask was sealed and heated at 100 °C using a metal block. After stirring for 14 h, the reaction was cooled down to rt, diluted with water and aq. NH₄Cl to adjust the pH to neutral and extracted with EtOAc (×3). The organic extracts were passed via plug of Florisil® and then dried over MgSO₄. The volatiles were evaporated and a 37% yield (38 mg,

0.075 mmol) of *ortho*-to-F arylated haloperidol was determined from ^1H NMR. The compound was obtained exclusively as *ortho*-to-F arylated isomer after column chromatography: elution system is EtOAc:MeOH:NH₄OH, 20:0.5:0.1.³⁸ White solid (mp 128–130 °C), 29% yield (29 mg, 0.057 mmol) after trituration with CH₃CN. An additional amount was eluted from the column as a mixture with haloperidol, 8 mg total mass (3 mg of product, 0.0065 mmol, 3% yield). Note: the amount of reactants required at the coupling step was calculated based on the estimated yield of borylated products. **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.12 (dd, J = 7.6, 2.3 Hz, 1H), 7.95 (ddd, J = 8.6, 4.7, 2.3 Hz, 1H), 7.54 – 7.47 (m, 4H), 7.38 – 7.34 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 (dd, J = 10.1, 8.6 Hz, 1H), 3.04 (t, J = 6.8 Hz, 2H), 2.86 (br s, 2H), 2.63 – 2.48 (m, 4H), 2.12 – 2.02 (m, 4H), 1.75 – 1.64 (m, 2H), 1.61 (br s, 1H), 1.37 (s, 9H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, Chloroform-*d*) δ 198.4 (C), 162.8 (C) (d, J = 255.9 Hz), 151.5 (C), 146.5 (C) 134.0 (C), 133.0 (C), 132.0 (C), 131.4 (CH) (d, J = 5.1 Hz), 129.4 (d, J = 14.0 Hz), 129.1 (CH) (d, J = 9.5 Hz), 128.8 (2CH) (d, J = 3.0 Hz), 128.6 (2CH), 126.2 (2CH), 125.8 (2CH), 116.6 (CH) (d, J = 23.5 Hz), 71.1 (C), 57.9 (CH₂), 49.4 (2CH₂), 38.1 (2CH₂), 36.3 (CH₂), 34.8 (C), 31.4 (3CH₃), 23.0 (CH₂). **HR-MS, APCI, m/z** : calcd for C₃₁H₃₆ClFNO₂⁺, [M+H]⁺, 508.2413. Found, 508.2409.

8. DFT Studies

All calculations were performed with the Gaussian 16 program package.³⁹ Structures were optimized using B3LYP-D3 and a basis set consisting of the Stuttgart–Dresden (SDD) basis set and effective core potential (ECP) for Ir and 6-31G(d,p) for the rest. Single point calculations were performed on the B3LYP-D3 geometries using M06 functional and a basis set consisting of the Stuttgart–Dresden (SDD) basis set and effective core potential (ECP) for Ir and 6-311+G(d,p) for the rest. To take into account the solvent effects, M06 calculations with the SMD method (1,4-dioxane as a solvent) as implemented in Gaussian 16 were performed. Each stationary point was adequately characterized by normal coordinate analysis (no imaginary frequencies for an equilibrium structure and one imaginary frequency for a transition structure) and thermal corrections were calculated under standard conditions (298.15 K, 1 atm).

The computational studies were performed using a simplified ligand model of **Me-OleTpy** and **L2** (Figure S13, S14, S15). The *N,N,N*-coordinated terpyridine Ir^{III}Bpin₃ complex (**D'**, 21.2 kcal/mol) undergoes rollover cyclometalation via **TS_{D'A'}** (33.3 kcal/mol) to afford the cyclometalated *N,N,C*-coordinated terpyridine Ir^{III}Bpin₂ (**A'**, 0.0 kcal/mol). Five isomeric structures are considered for the oxidative addition of fluorobenzene to **A'** (Figure S14), where **TS_{A'ortho}** (29.2 kcal/mol) and **TS_{A'meta2}** (30.3 kcal/mol) are the lowest energy transition states leading to ortho and meta borylated products, respectively, and thus ortho borylation is favored over meta borylation. These lowest energy transition states are described in Scheme 5b. The oxidative addition of B₂Pin₂ to **A'** via **TS_{A'C'}** (17.9 kcal/mol) affords *N,N,C*-coordinated terpyridine Ir^VBpin₄ (**C'**, 12.3 kcal/mol), which after C–B bond reductive elimination via **TS_{C'B'}** (14.2 kcal/mol) and **B'''** (0.6 kcal/mol, isomer of **B'**) affords **B'** (–4.4 kcal/mol) bearing a borylated terpyridine ligand and its isomer **B''** (–1.6 kcal/mol). The lowest ortho and meta transition states with **B''**, **TS_{B''ortho}** (29.3 kcal/mol) and **TS_{B''meta2}** (30.6 kcal/mol) are lower in energy and have more energy difference than those with **B'**, **TS_{B'ortho2}** (32.4 kcal/mol) and **TS_{B'meta2}** (32.5 kcal/mol). Therefore, the C–H oxidative addition with **B''** is more plausible. **B''** ($\Delta\Delta G(\text{meta-ortho})$: 1.3 kcal/mol) is as ortho selective as **A'** ($\Delta\Delta G(\text{meta-ortho})$: 1.1 kcal/mol).

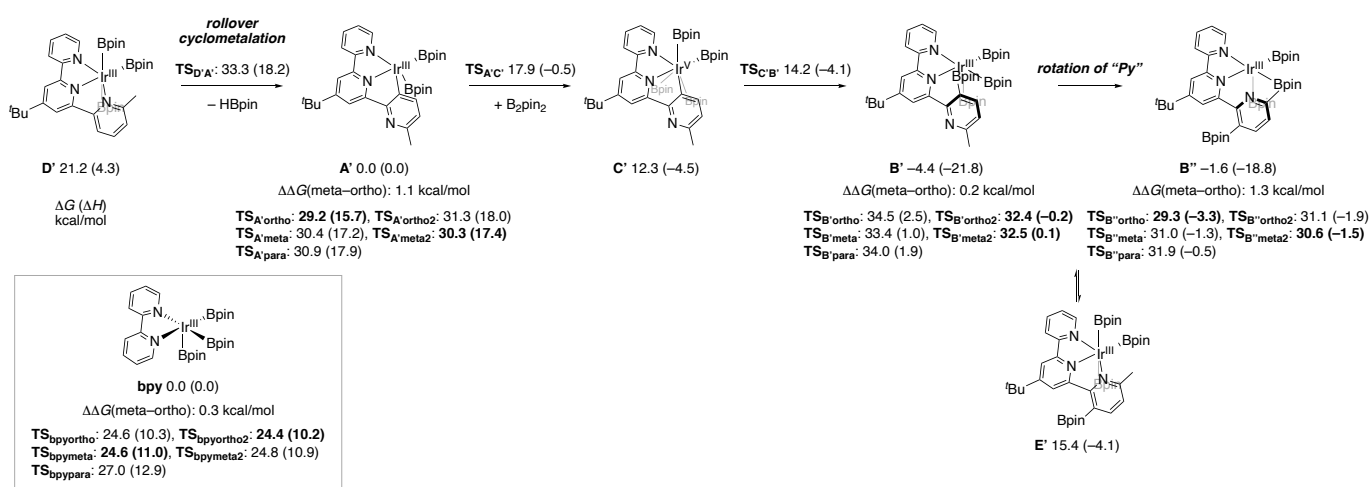


Figure S13. Gibbs free energies and enthalpies are given in kcal/mol, calculated at the M06/SDD:6-311+G(d,p)_{1,4-dioxane(SMD)}//B3LYP-D3/SDD:6-31G(d,p) level of theory.

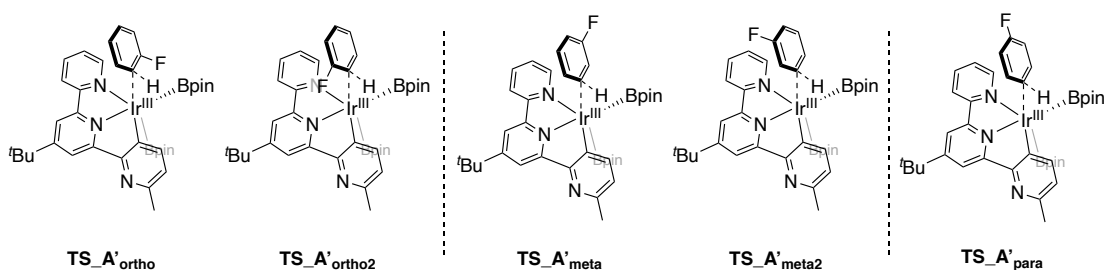


Figure S14. Five isomeric structures considered for C–H oxidative addition with Ir complexes.

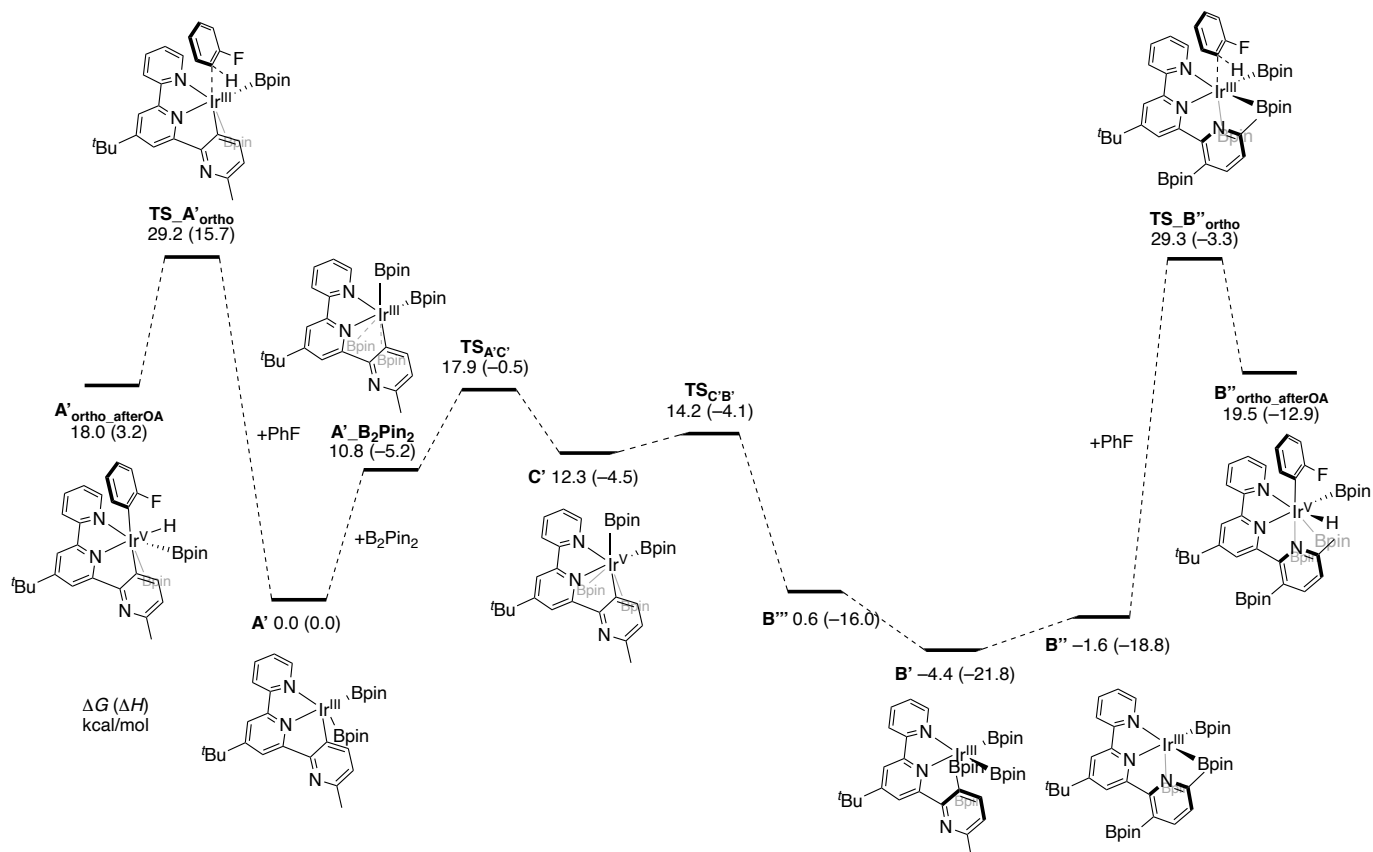


Figure S15. Energy profiles for the paths connecting complexes **A'**, **B'**, and **B''**, and the ortho C–H oxidative addition of fluorobenzene with **A'** and **B''**

Energies of Stationary Points

Table S2 Electronic Energies (E), Zero-point Energy Corrected Energies (E + ZPE), Electronic and Thermal Enthalpies (H), Gibbs Free Energies (G) of Stationary Points (in hartrees) Calculated at the M06/SDD:6-311+G(d,p)_{1,4}-dioxane(SMD)//B3LYP-D3/SDD:6-31G(d,p) level of theory.

	<i>E</i>	<i>E</i> +ZPE	<i>H</i>	<i>G</i>
B ₂ Pin ₂	-822.2520389	-821.8871869	-821.8666649	-821.9346429
HBpin	-411.7220137	-411.5306787	-411.5203577	-411.5636097
C ₆ H ₅ F	-331.363985	-331.271557	-331.26547	-331.300381
D'	-2276.421349	-2275.502529	-2275.449306	-2275.585534
TS _{D'A'}	-2276.393412	-2275.480899	-2275.427152	-2275.566298
A'_HBpin	-2276.432486	-2275.516774	-2275.462342	-2275.605035
A'	-1864.701957	-1863.979471	-1863.935792	-1864.055746
A'_B ₂ Pin ₂	-2686.965176	-2685.875241	-2685.810805	-2685.97323
TS _{A'C'}	-2686.956252	-2685.866945	-2685.803325	-2685.961848
C'	-2686.962922	-2685.874109	-2685.809692	-2685.970801
TS _{C'B'}	-2686.960753	-2685.872798	-2685.809008	-2685.967799
B'''	-2686.982646	-2685.892379	-2685.827975	-2685.989475
B'	-2686.99185	-2685.901364	-2685.837165	-2685.997356
B''	-2686.987052	-2685.896725	-2685.832452	-2685.992928
E'	-2686.963561	-2685.872305	-2685.809016	-2685.96578
TS _{A'ortho}	-2196.038164	-2195.226121	-2195.176209	-2195.30959
A'_ortho_afterOA	-2196.060754	-2195.245926	-2195.196137	-2195.327517
TS _{A'ortho2}	-2196.034496	-2195.222611	-2195.172638	-2195.306303
A'_ortho2_afterOA	-2196.05508	-2195.240318	-2195.190496	-2195.322204
TS _{A'meta}	-2196.035905	-2195.223838	-2195.173921	-2195.307676
A'_meta_afterOA	-2196.056095	-2195.241354	-2195.191535	-2195.323304
TS _{A'meta2}	-2196.035522	-2195.223551	-2195.173599	-2195.307774
A'_meta2_afterOA	-2196.056237	-2195.241506	-2195.191684	-2195.323526
TS _{A'para}	-2196.03466	-2195.222654	-2195.1727	-2195.306907
A'_para_afterOA	-2196.05437	-2195.23974	-2195.189869	-2195.322034
TS _{B'ortho}	-3018.314753	-3017.134384	-3017.063977	-3017.235831
B'_ortho_afterOA	-3018.346226	-3017.163634	-3017.093152	-3017.265299
TS _{B'ortho2}	-3018.319448	-3017.138517	-3017.068318	-3017.239214
B'_ortho2_afterOA	-3018.340116	-3017.158001	-3017.087451	-3017.259953
TS _{B'meta}	-3018.317536	-3017.136731	-3017.066401	-3017.237589
B'_meta_afterOA	-3018.339964	-3017.155663	-3017.085685	-3017.255763
TS _{B'meta2}	-3018.318914	-3017.13808	-3017.067788	-3017.238931
B'_meta2_afterOA	-3018.343524	-3017.160979	-3017.090459	-3017.262903
TS _{B'para}	-3018.316092	-3017.135325	-3017.064963	-3017.236551
B'_para_afterOA	-3018.338464	-3017.154253	-3017.08421	-3017.255171
TS _{B''ortho}	-3018.324264	-3017.14329	-3017.073214	-3017.244027
B''_ortho_afterOA	-3018.341952	-3017.158669	-3017.088542	-3017.259625
TS _{B''ortho2}	-3018.322569	-3017.140995	-3017.070993	-3017.241289
B''_ortho2_afterOA	-3018.329905	-3017.14655	-3017.076388	-3017.246582
TS _{B''meta}	-3018.321616	-3017.140173	-3017.070012	-3017.241434
B''_meta_afterOA	-3018.325994	-3017.14279	-3017.072453	-3017.243685
TS _{B''meta2}	-3018.321834	-3017.140501	-3017.070349	-3017.242024
B''_meta2_afterOA	-3018.326335	-3017.143066	-3017.072732	-3017.244141
TS _{B''para}	-3018.320199	-3017.138771	-3017.068646	-3017.23993
B''_para_afterOA	-3018.324246	-3017.140846	-3017.070551	-3017.241532
bpylrBpin ₃	-1832.97974	-1832.27205	-1832.229149	-1832.347168
TS _{bpyortho}	-2164.32439	-2163.527224	-2163.478167	-2163.608407
bpyortho_afterOA	-2164.345941	-2163.546201	-2163.49725	-2163.625952
TS _{bpyortho2}	-2164.324577	-2163.527377	-2163.47831	-2163.608738
bpyortho2_afterOA	-2164.349832	-2163.550397	-2163.501306	-2163.630365
TS _{bpymeta}	-2164.323393	-2163.526172	-2163.477059	-2163.608303
bpymeta_afterOA	-2164.346007	-2163.546638	-2163.497487	-2163.627086
TS _{bpymeta2}	-2164.323597	-2163.526274	-2163.477203	-2163.608027
bpymeta2_afterOA	-2164.345857	-2163.54635	-2163.497257	-2163.626507
TS _{bpypara}	-2164.320527	-2163.523144	-2163.47409	-2163.604517
bpypara_afterOA	-2164.341468	-2163.541781	-2163.492697	-2163.62179

9. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR charts of ligands

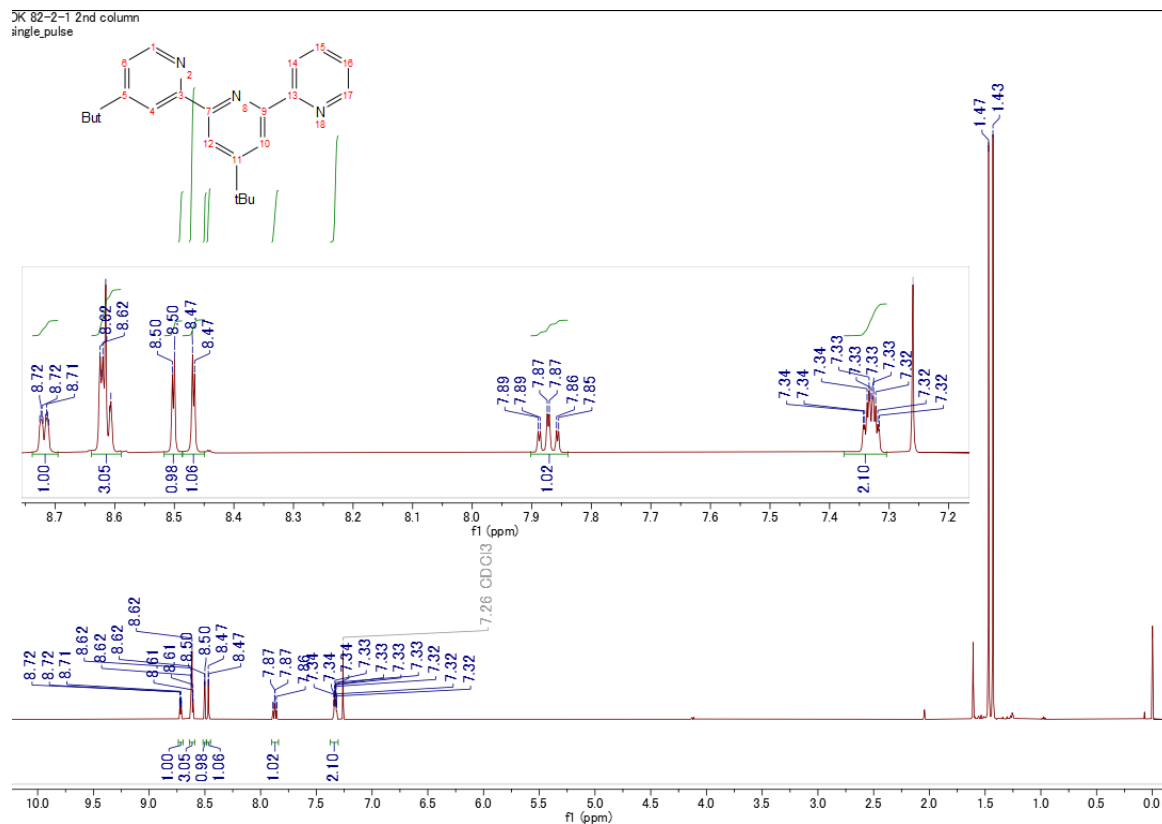


Figure S16. ^1H NMR spectra (CDCl_3) of H-OleTpy.

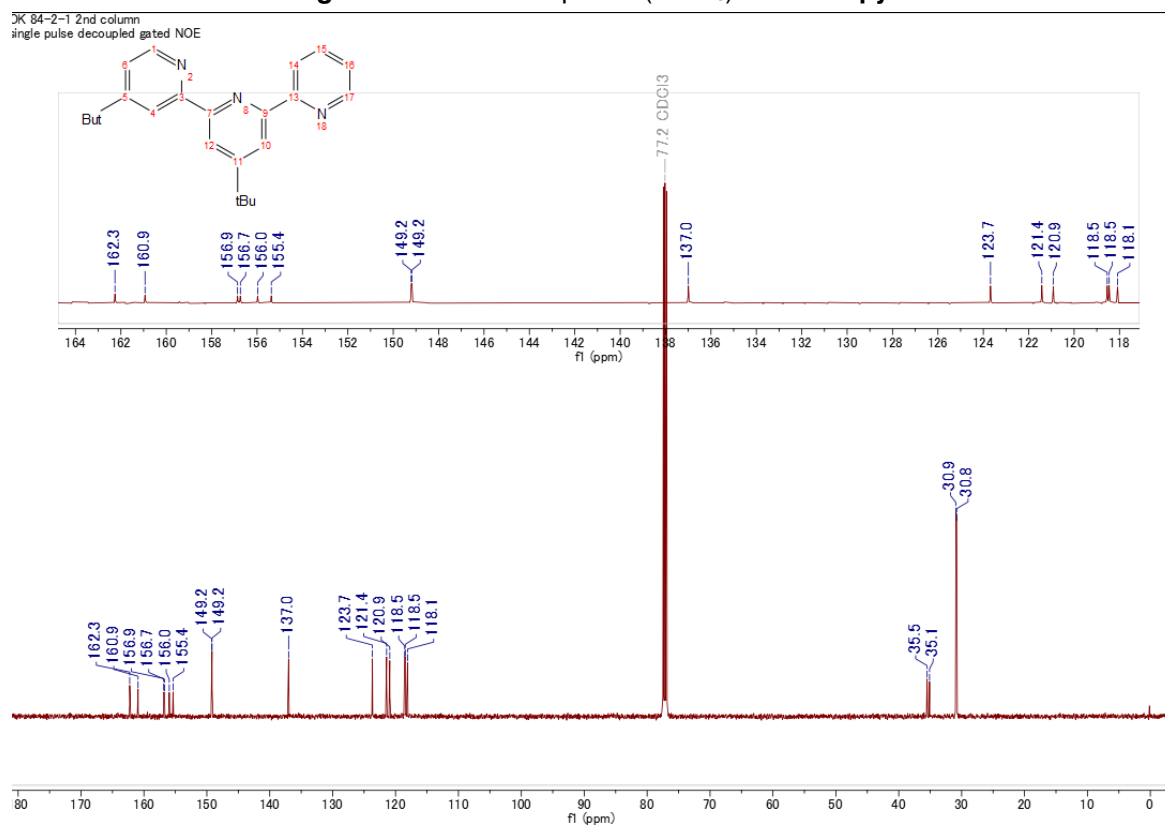


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of H-OleTpy.

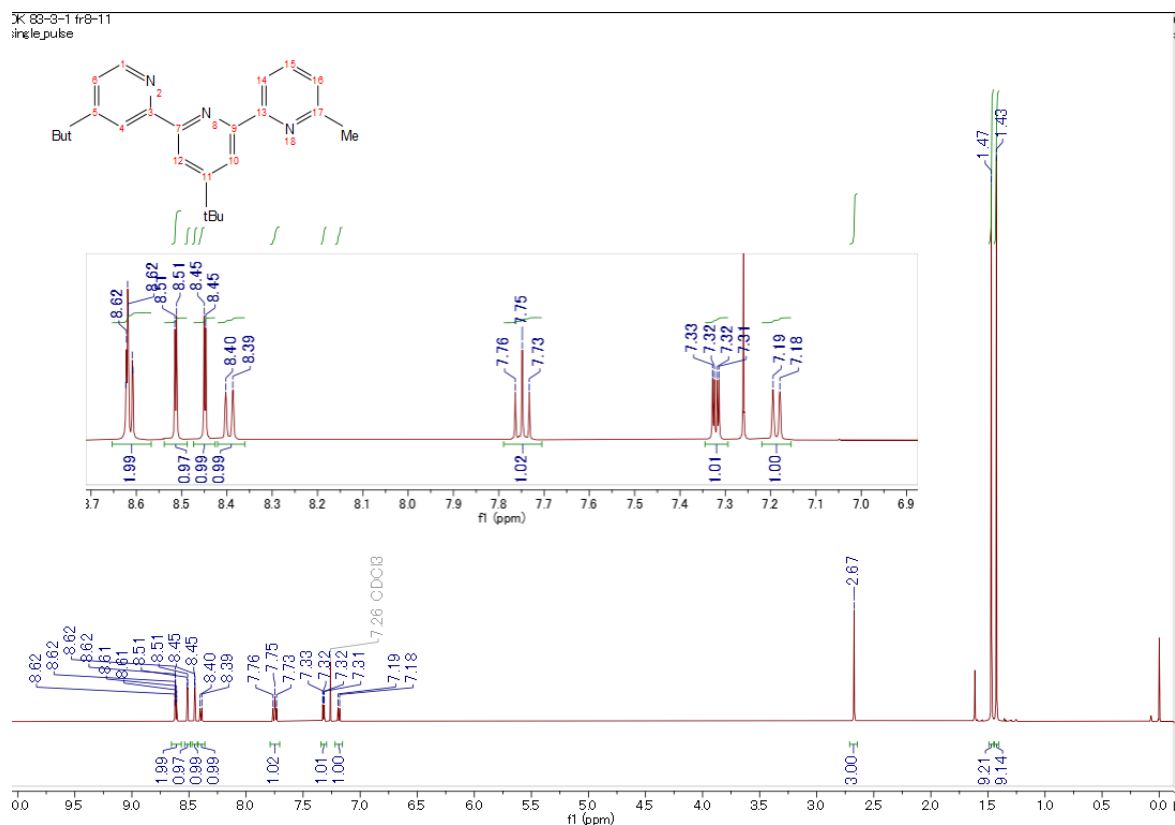


Figure S18. ¹H NMR spectra (CDCl₃) of Me-OleTpy.

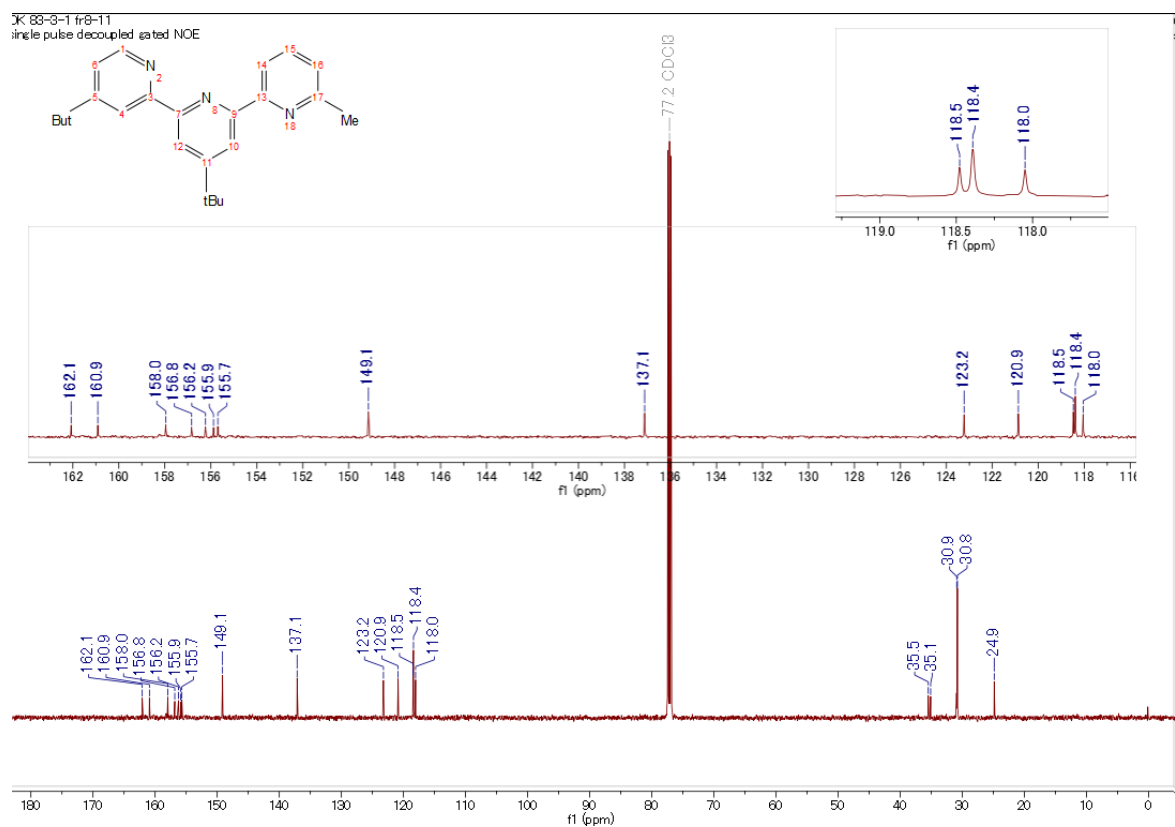


Figure S19. ¹³C{¹H} NMR spectra (CDCl₃) of Me-OleTpy.

JK 72-7-4 f-37-61
single_pulse

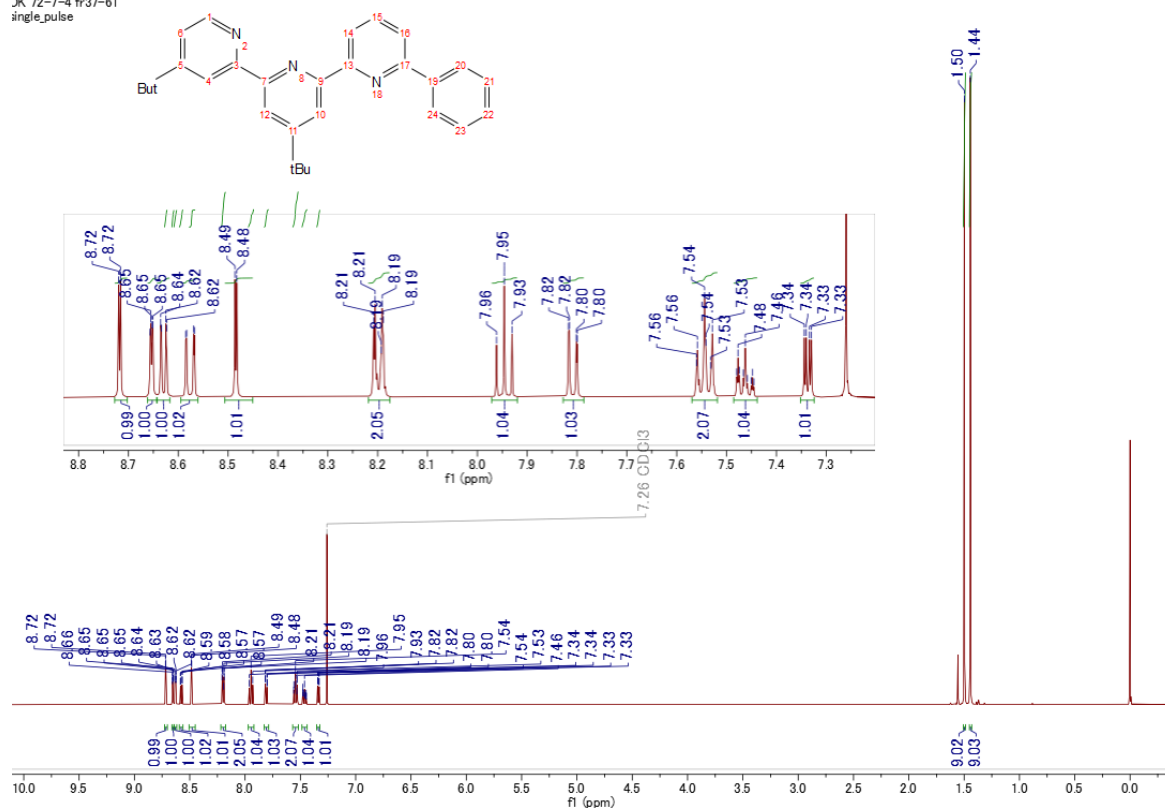


Figure S20. ¹H NMR spectra (CDCl₃) of Ph-OleTpy.

JK 72-7-1 column
single_pulse decoupled gated NOE

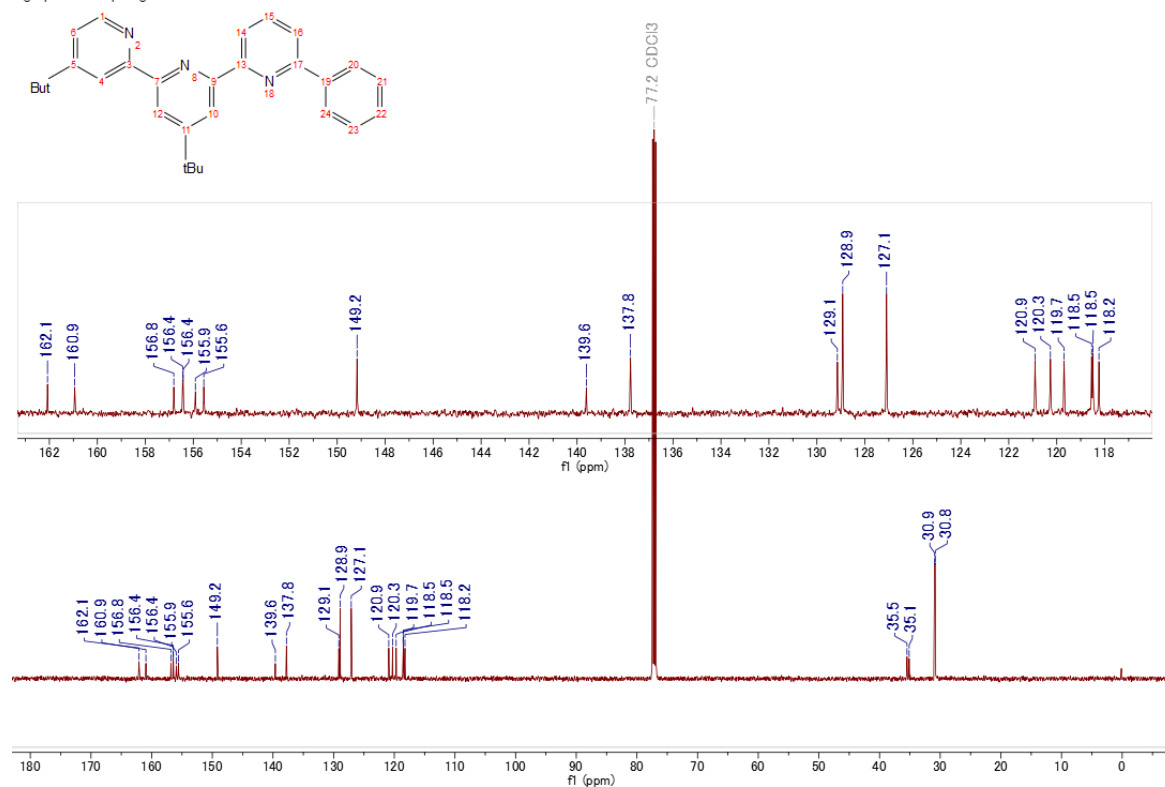


Figure S21. ¹³C{¹H} NMR spectra (CDCl₃) of Ph-OleTpy.

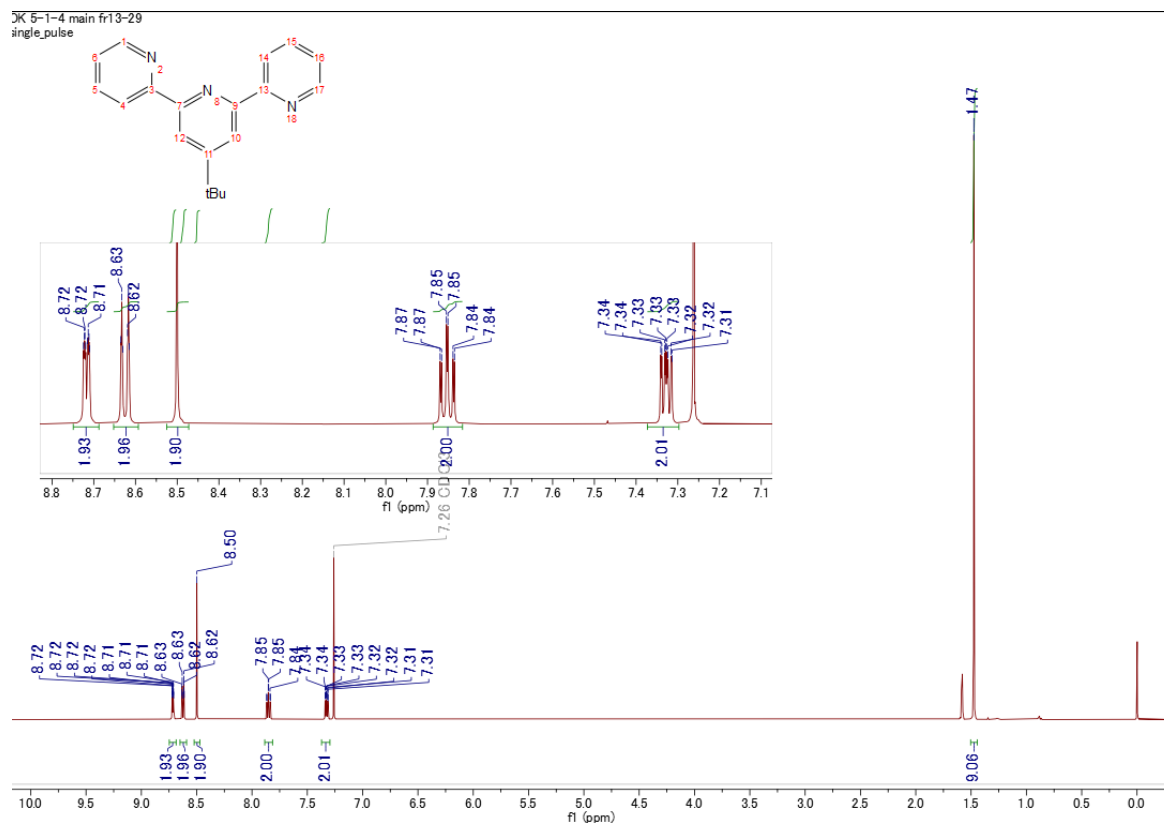


Figure S22. ¹H NMR spectra (CDCl₃) of L1.

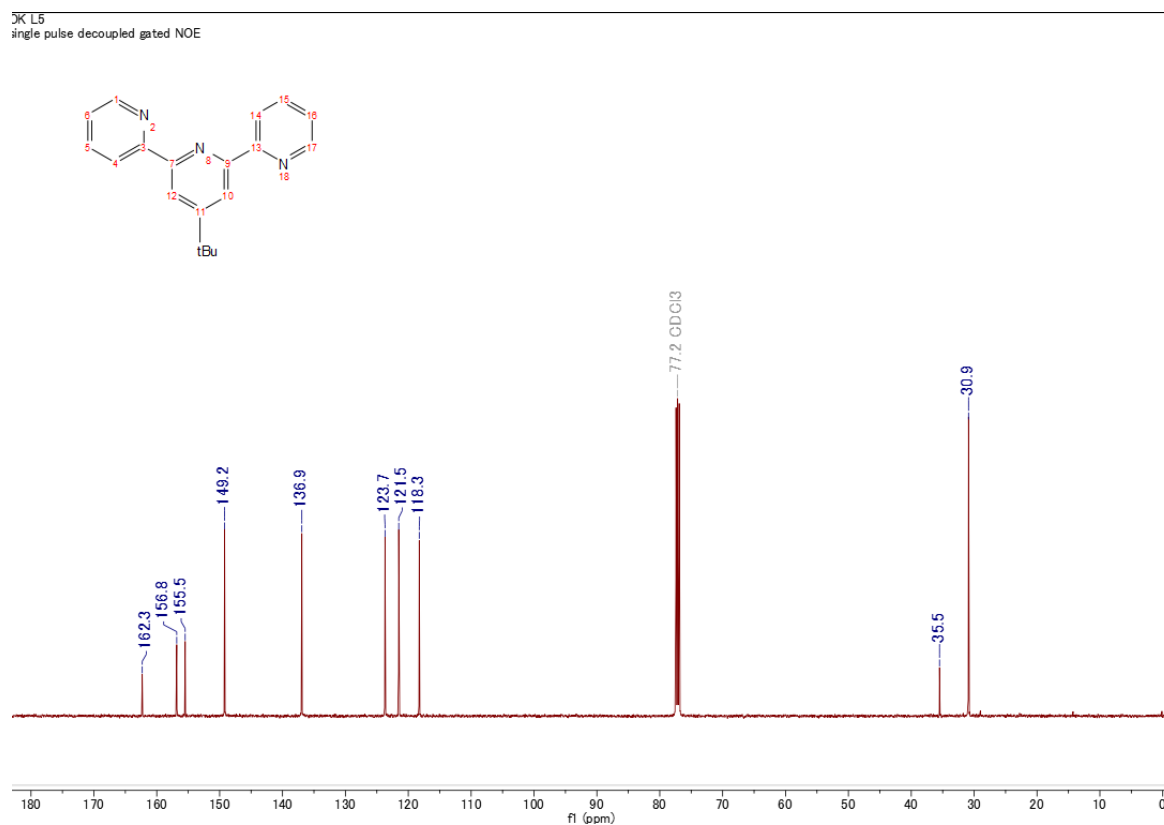


Figure S23. ¹³C{¹H} NMR spectra (CDCl₃) of L1.

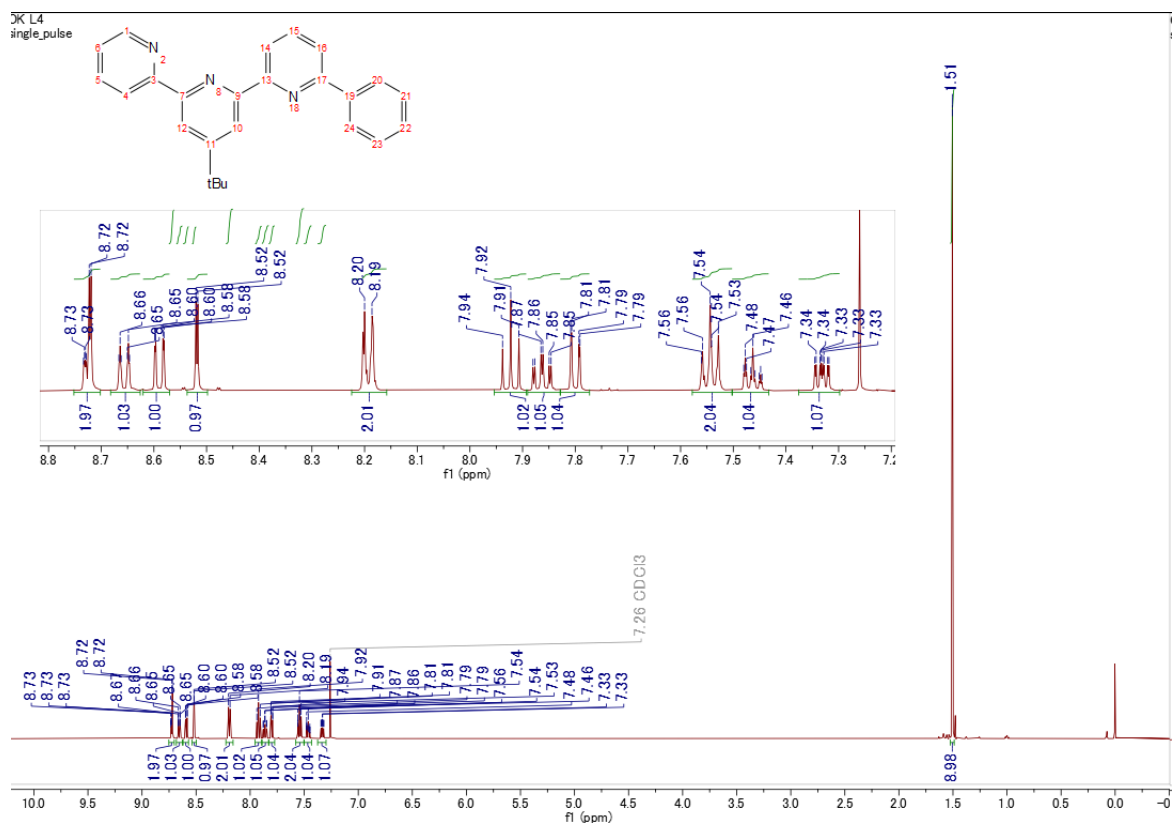


Figure S24. ¹H NMR spectra (CDCl₃) of L2.

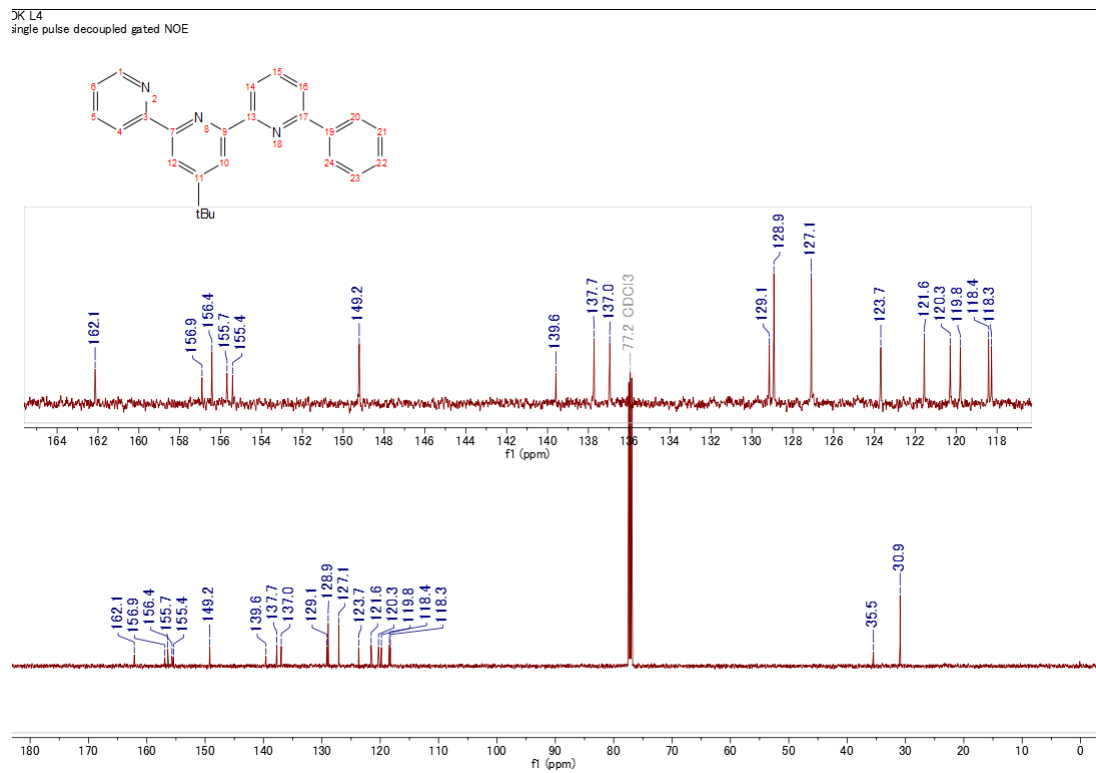


Figure S25. ¹³C{¹H} NMR spectra (CDCl₃) of L2.

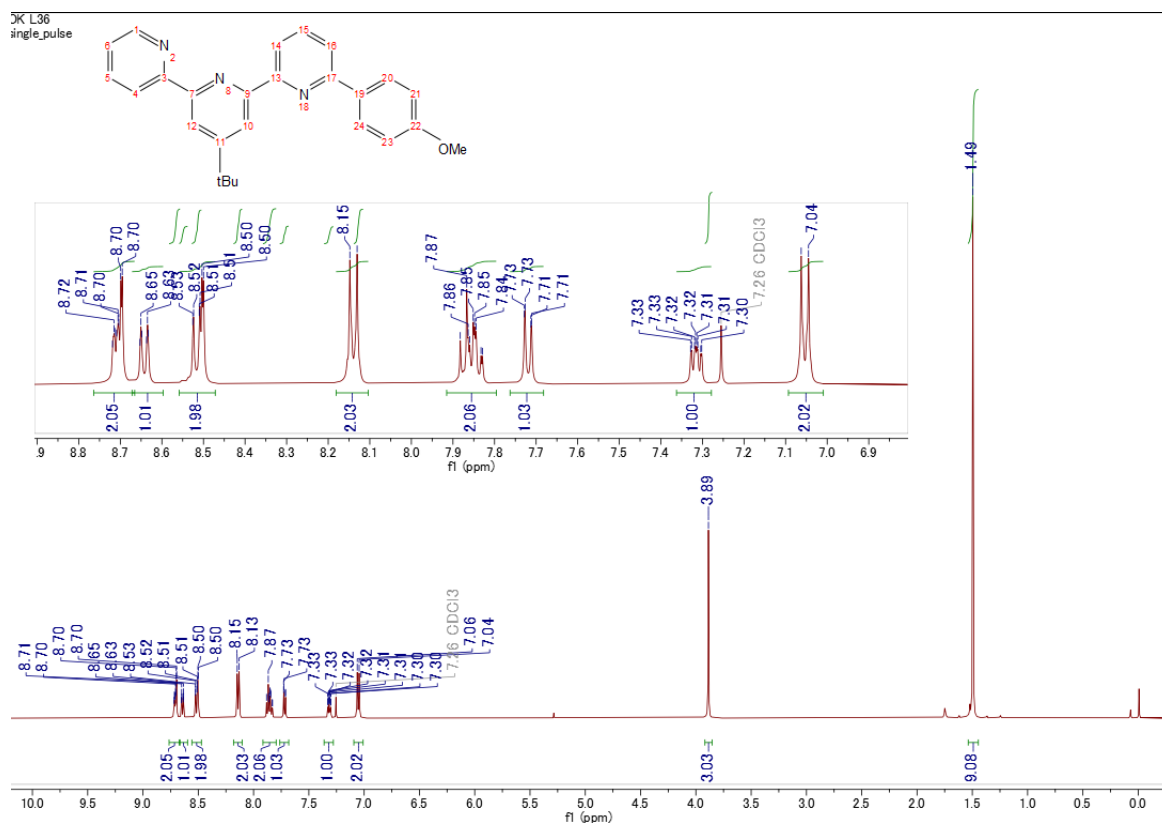


Figure S26. ¹H NMR spectra (CDCl₃) of L3.

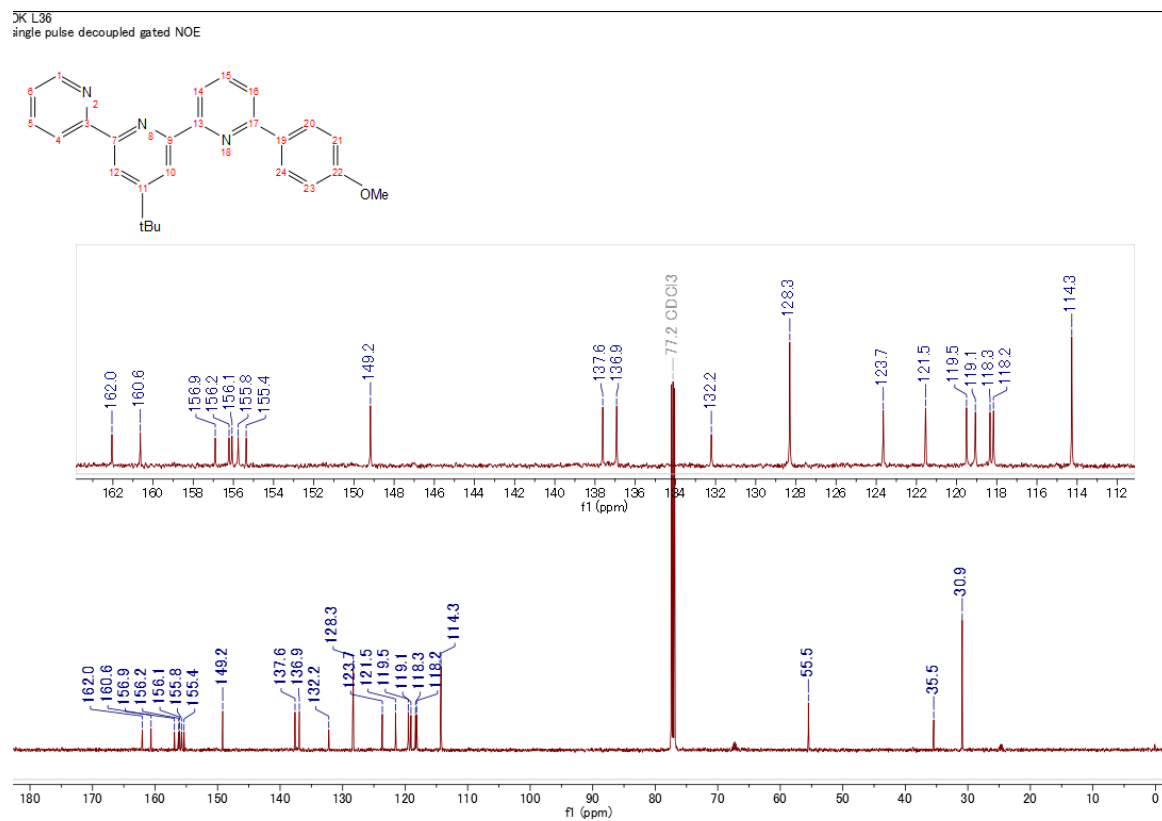


Figure S27. ¹³C{¹H} NMR spectra (CDCl₃) of L3.

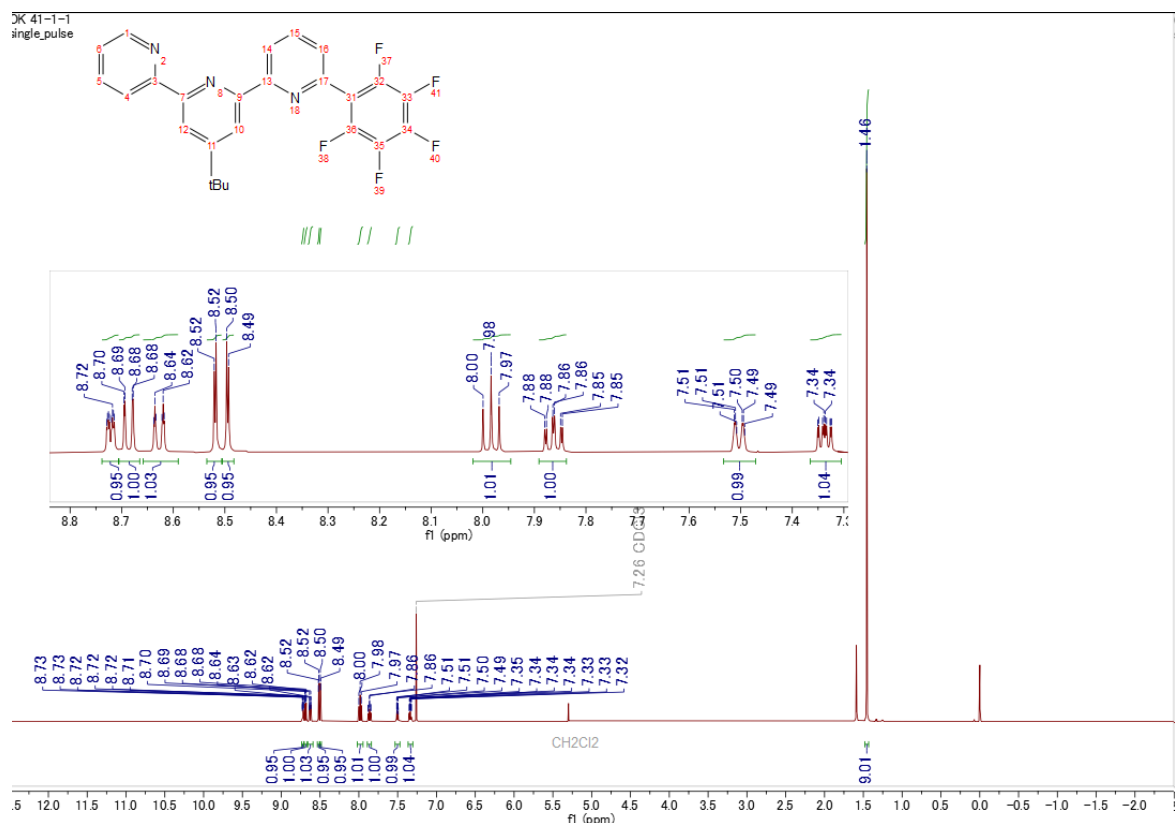


Figure S28. ¹H NMR spectra (CDCl₃) of L4.

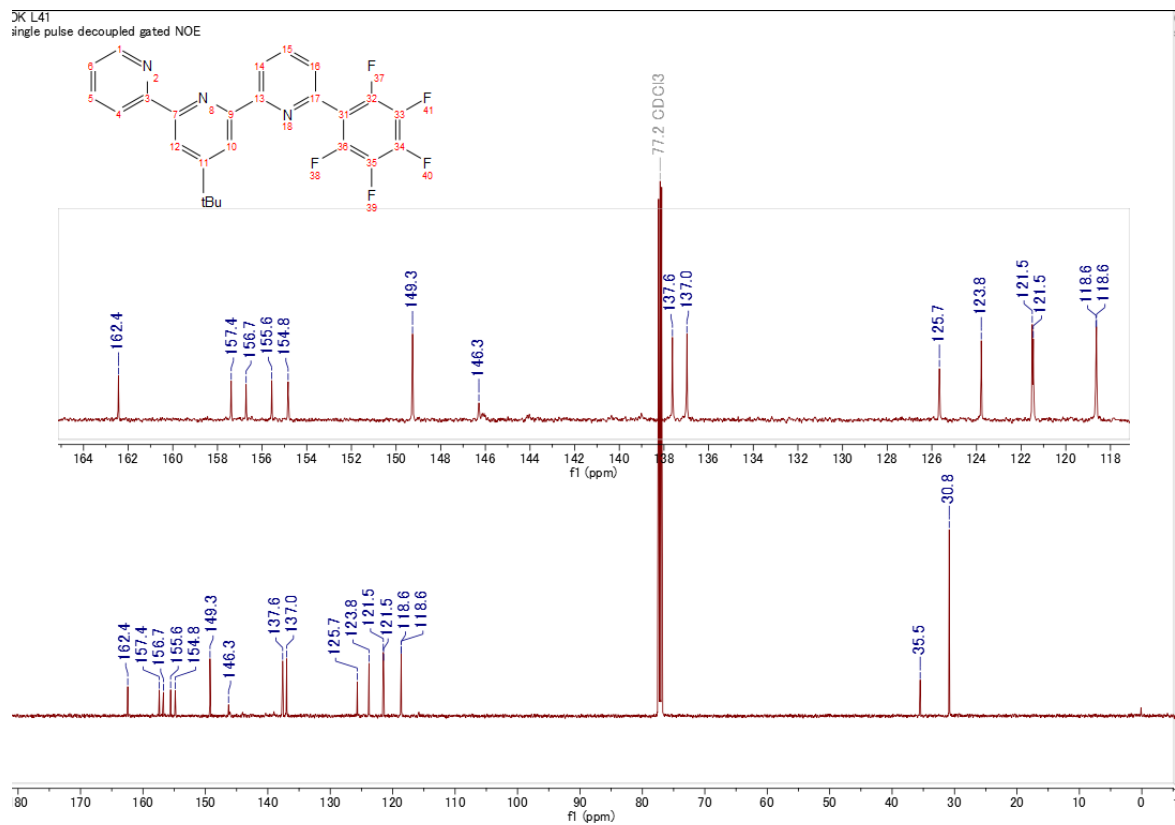


Figure S29. ¹³C{¹H} NMR spectra (CDCl₃) of L4.

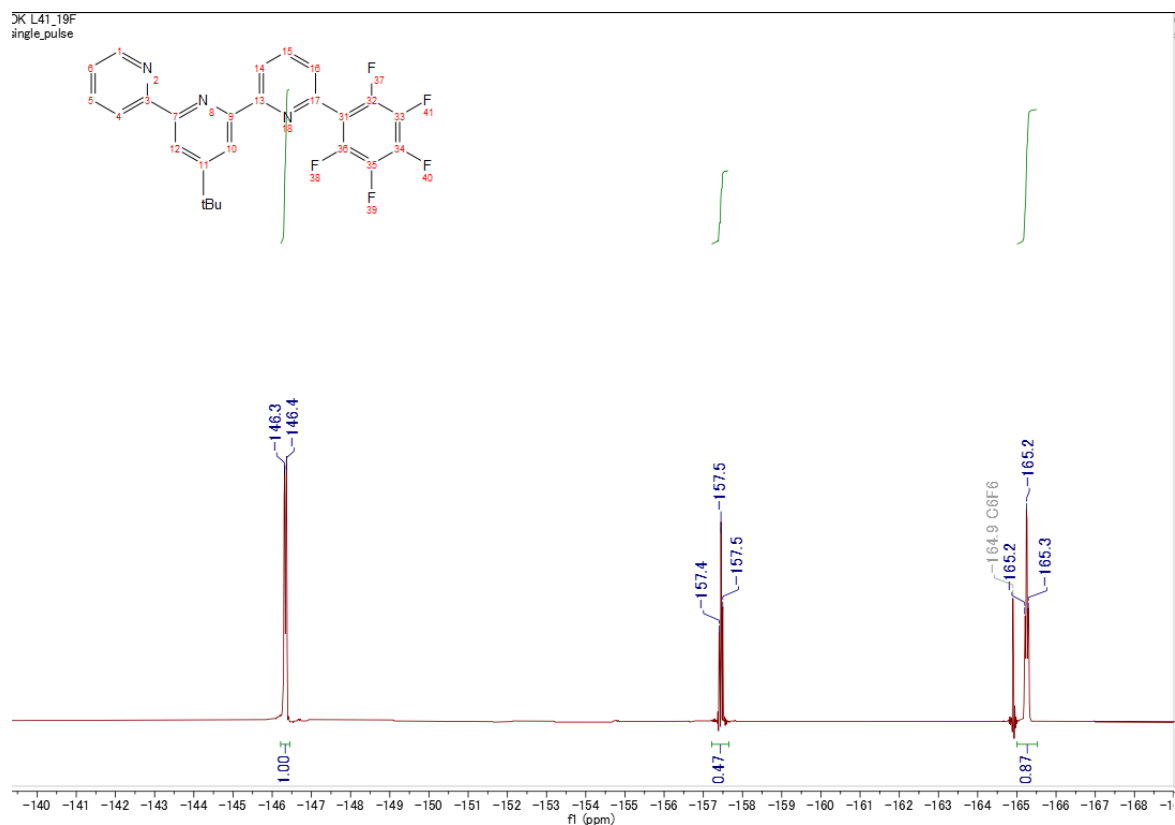


Figure S30. ¹⁹F NMR spectra (CDCl₃) of L4.

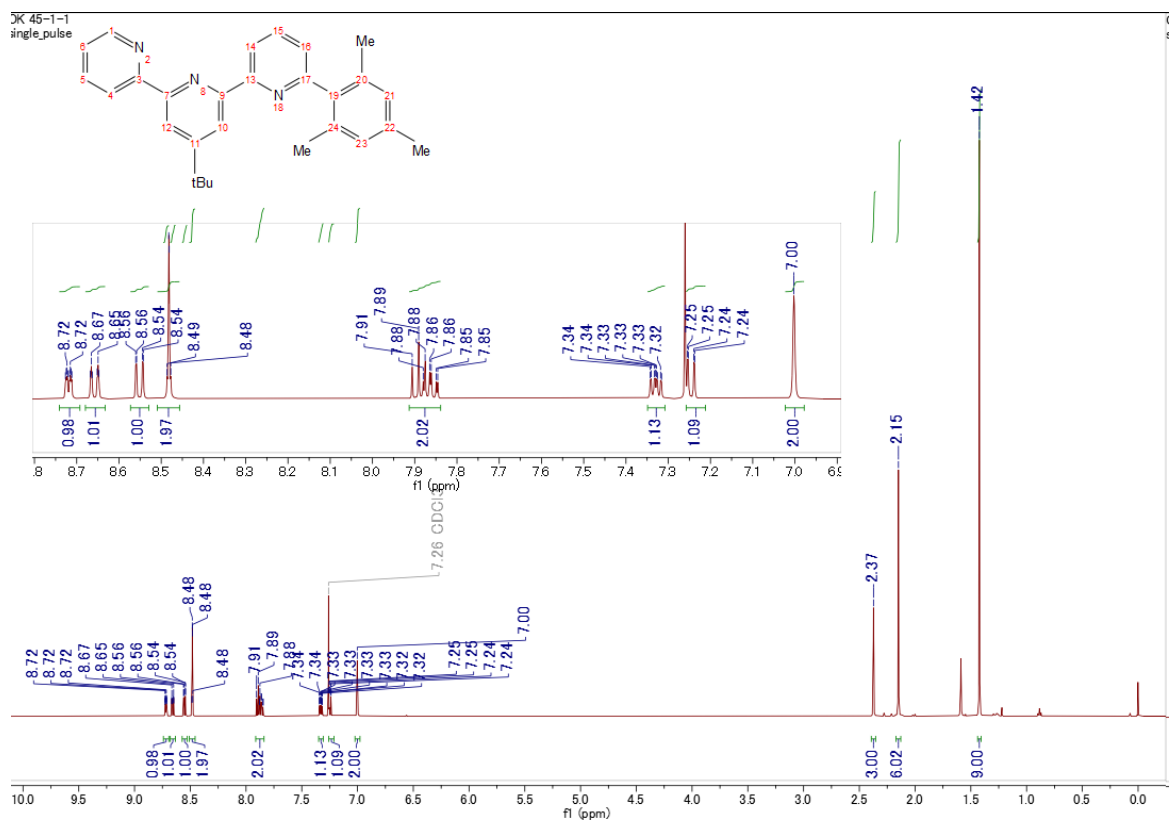


Figure S31. ¹H NMR spectra (CDCl₃) of L5.

JK L45
single pulse decoupled gated NOE

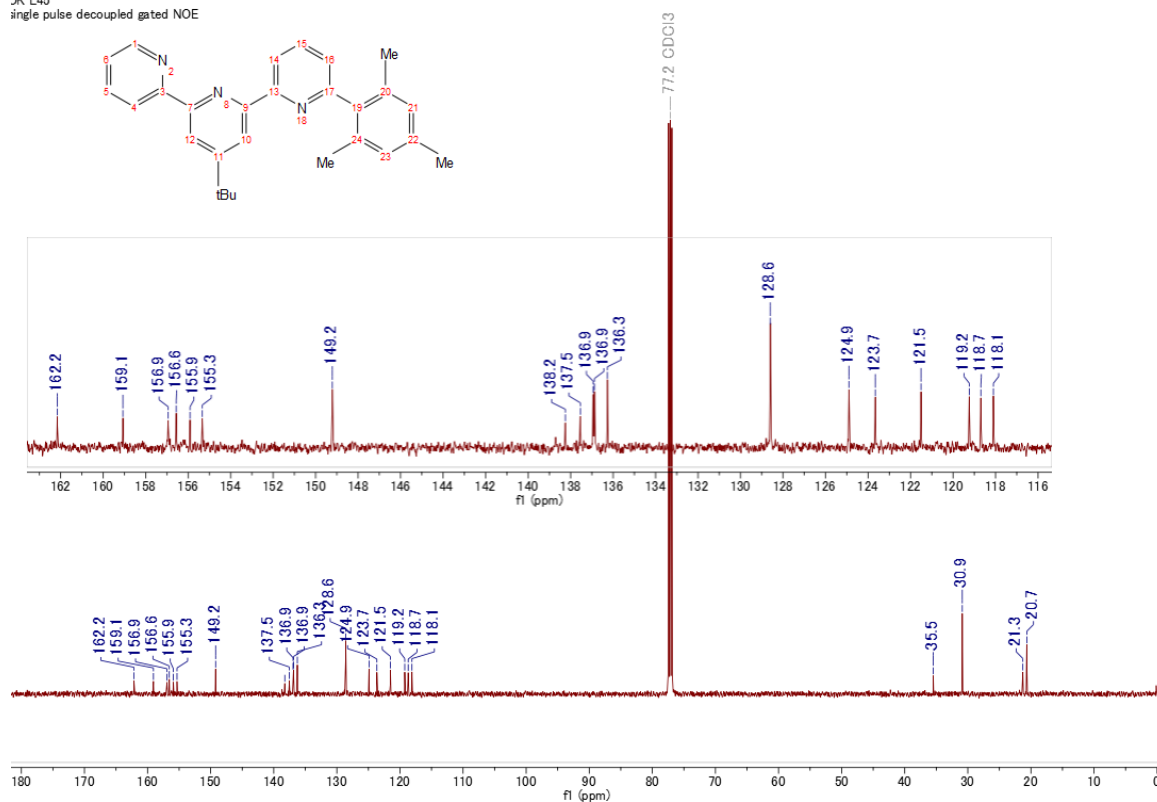


Figure S32. ¹³C{¹H} NMR spectra (CDCl₃) of L5.

JK L80 GPC5
single pulse

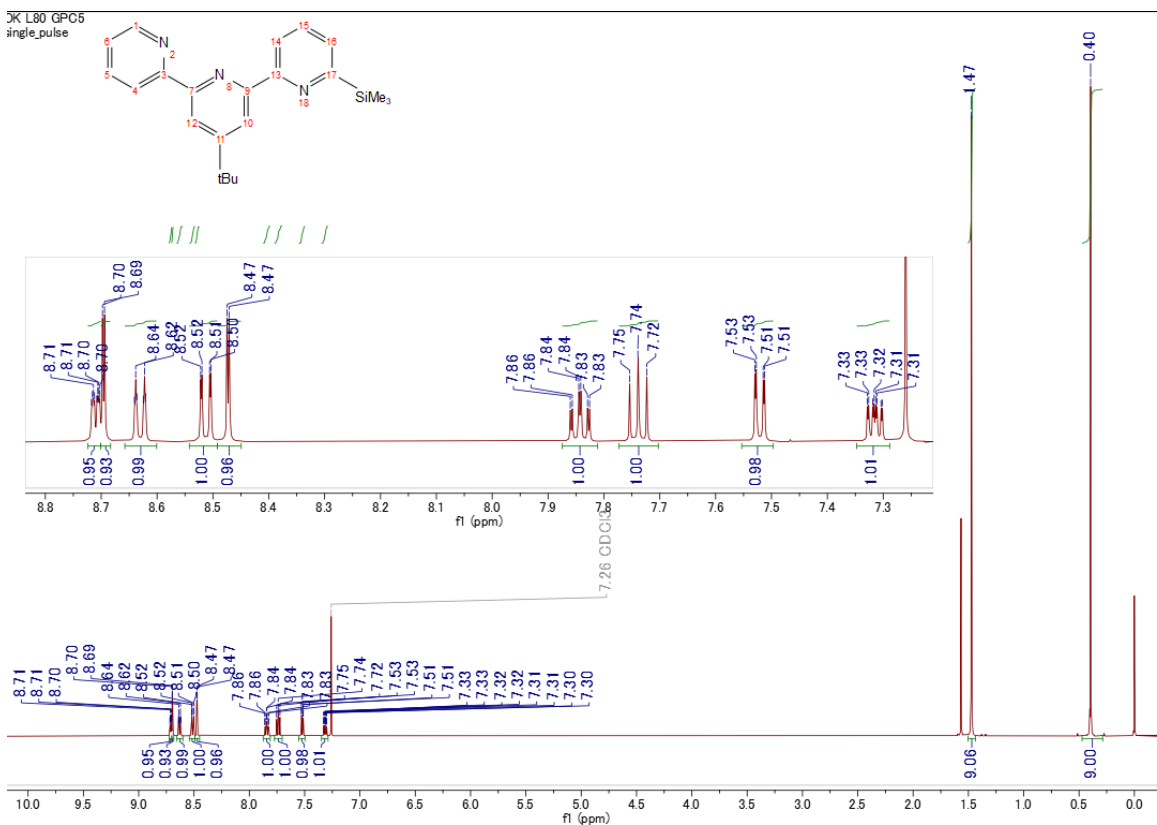


Figure S33. ¹H NMR spectra (CDCl₃) of L6.

JK L80 GPC5
single pulse decoupled gated NOE

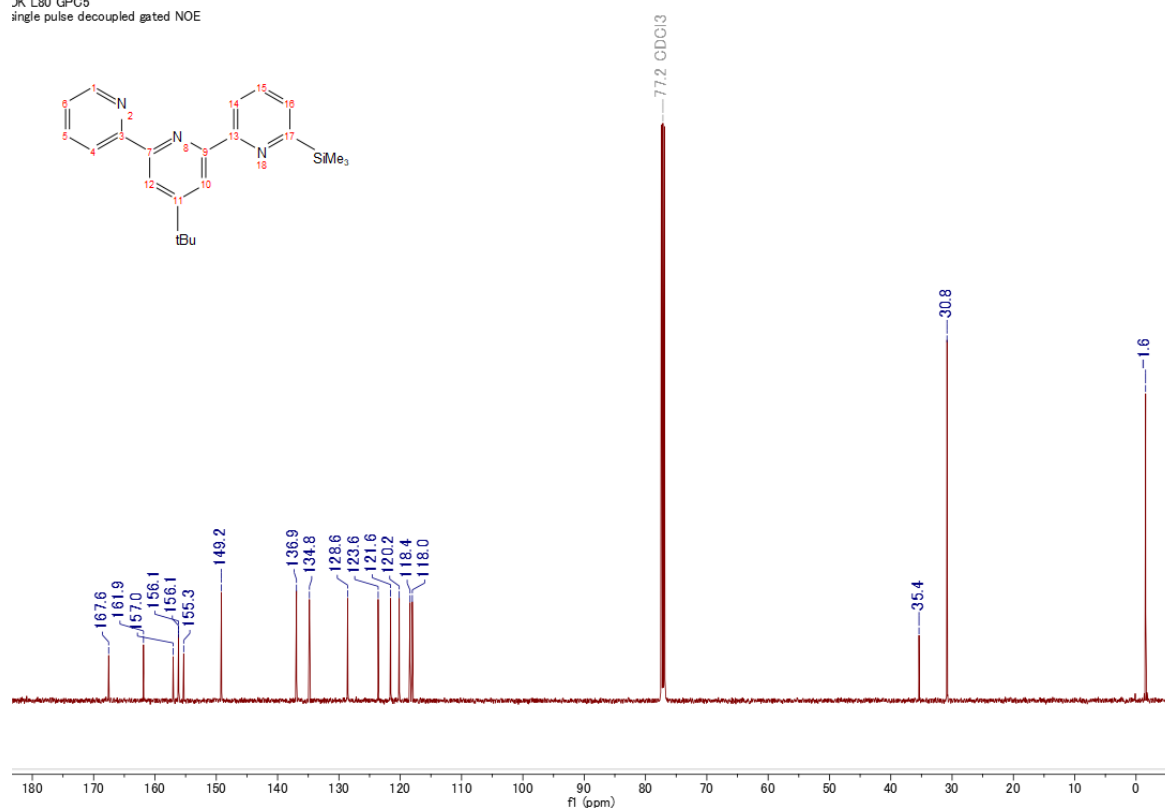


Figure S34. ¹³C{¹H} NMR spectra (CDCl₃) of L6.

JK 30-1-1
single_pulse

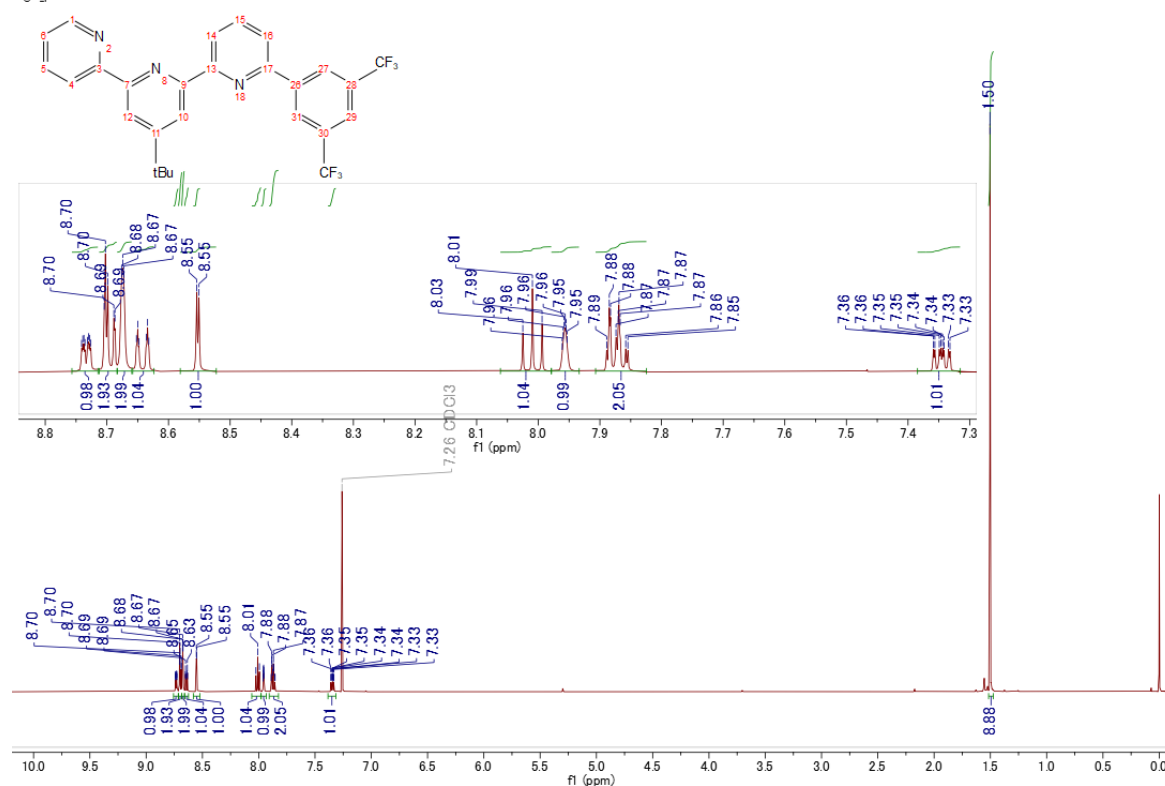


Figure S35. ¹H NMR spectra (CDCl₃) of L13.

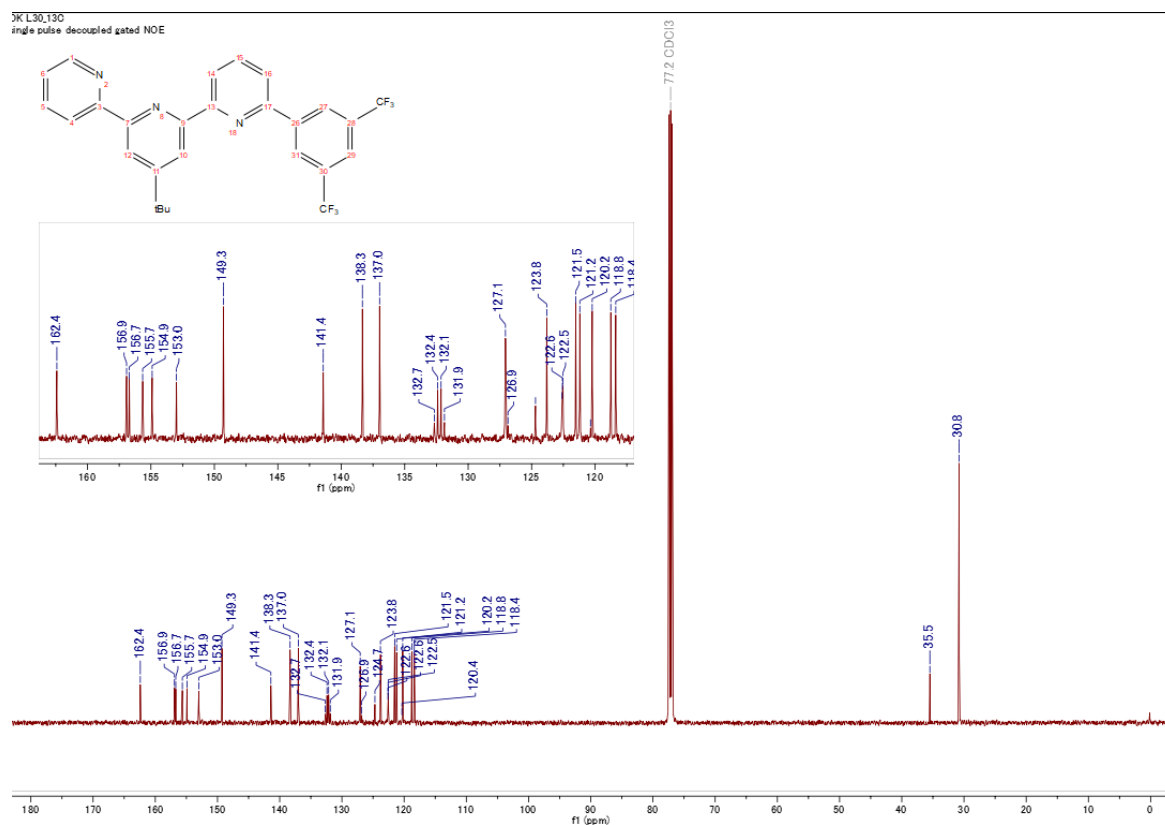


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of L13.

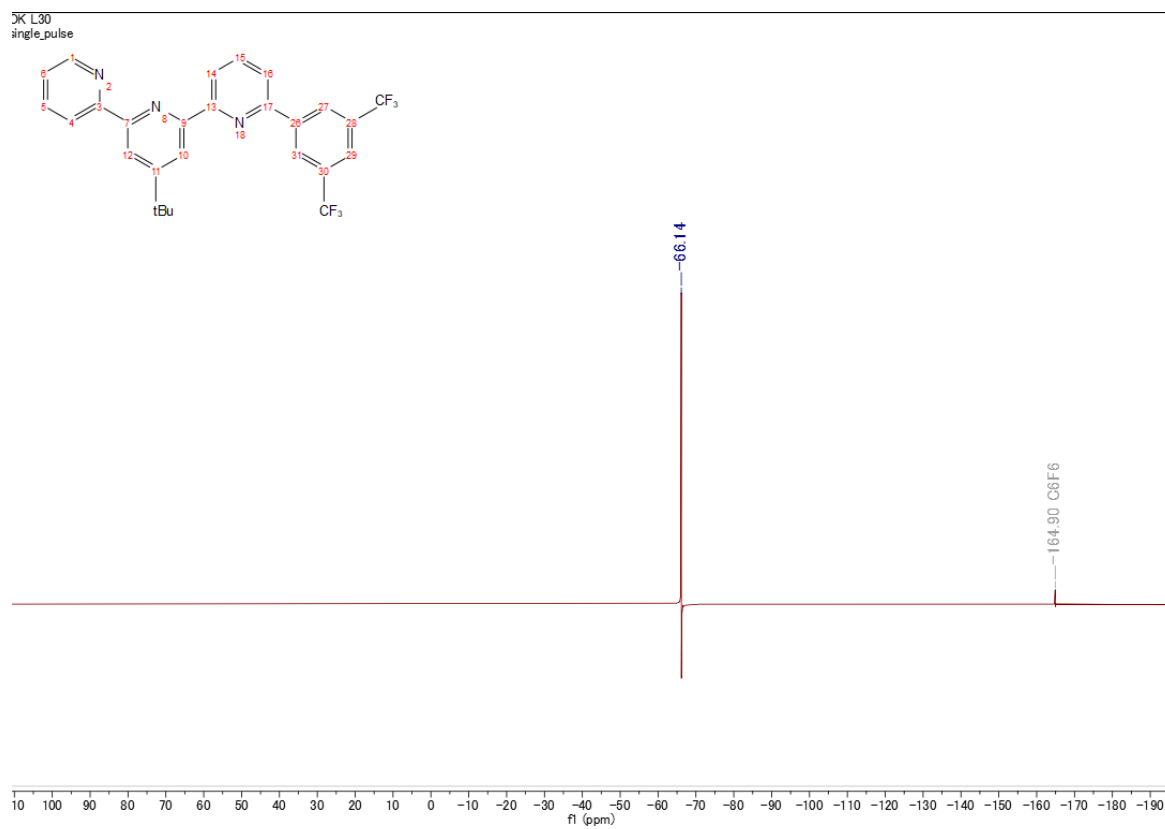


Figure S37. ^{19}F NMR spectra (CDCl_3) of L13.

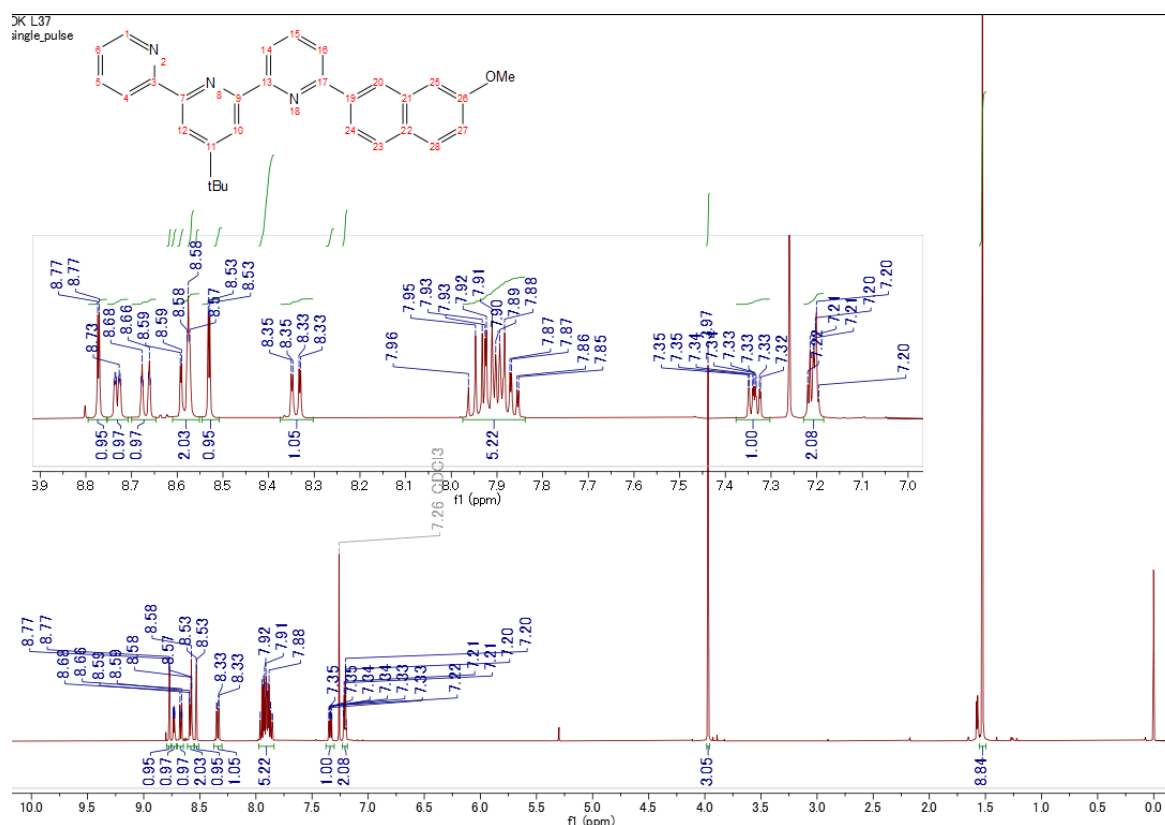


Figure S38. ¹H NMR spectra (CDCl₃) of L14.

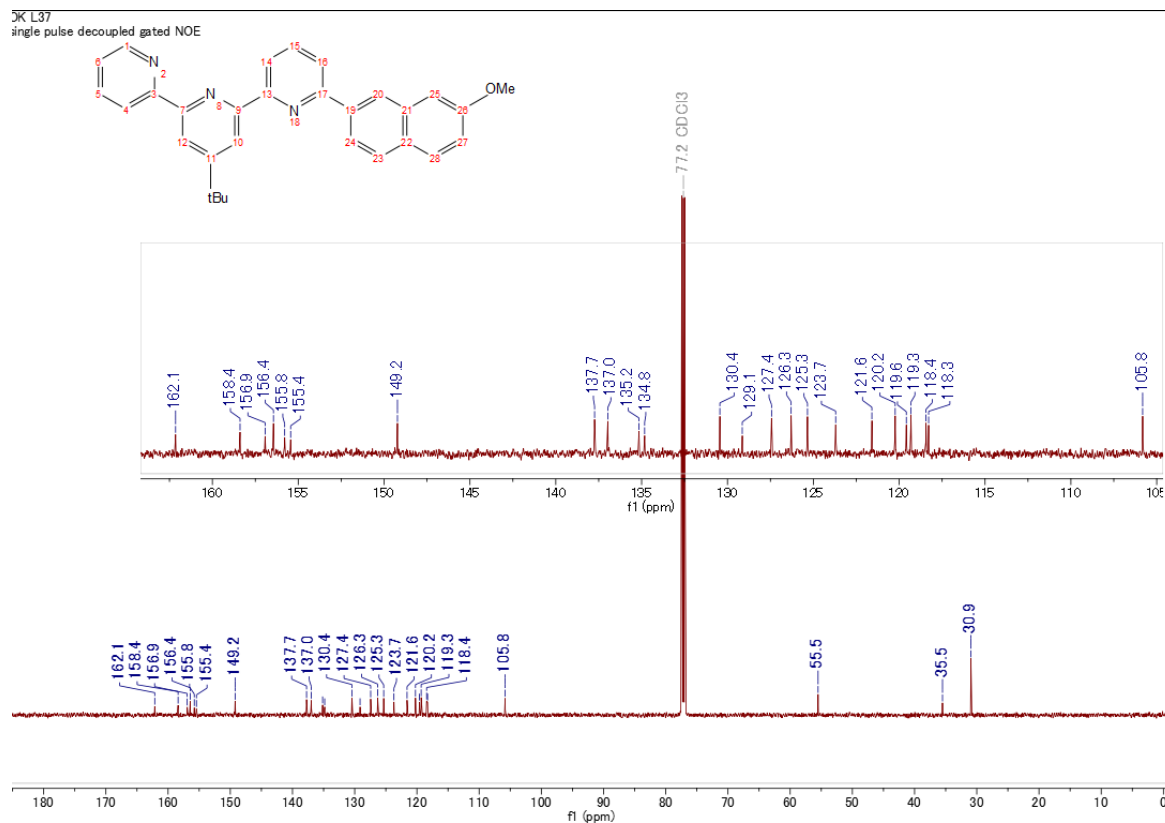


Figure S39. ¹³C{¹H} NMR spectra (CDCl₃) of L14.

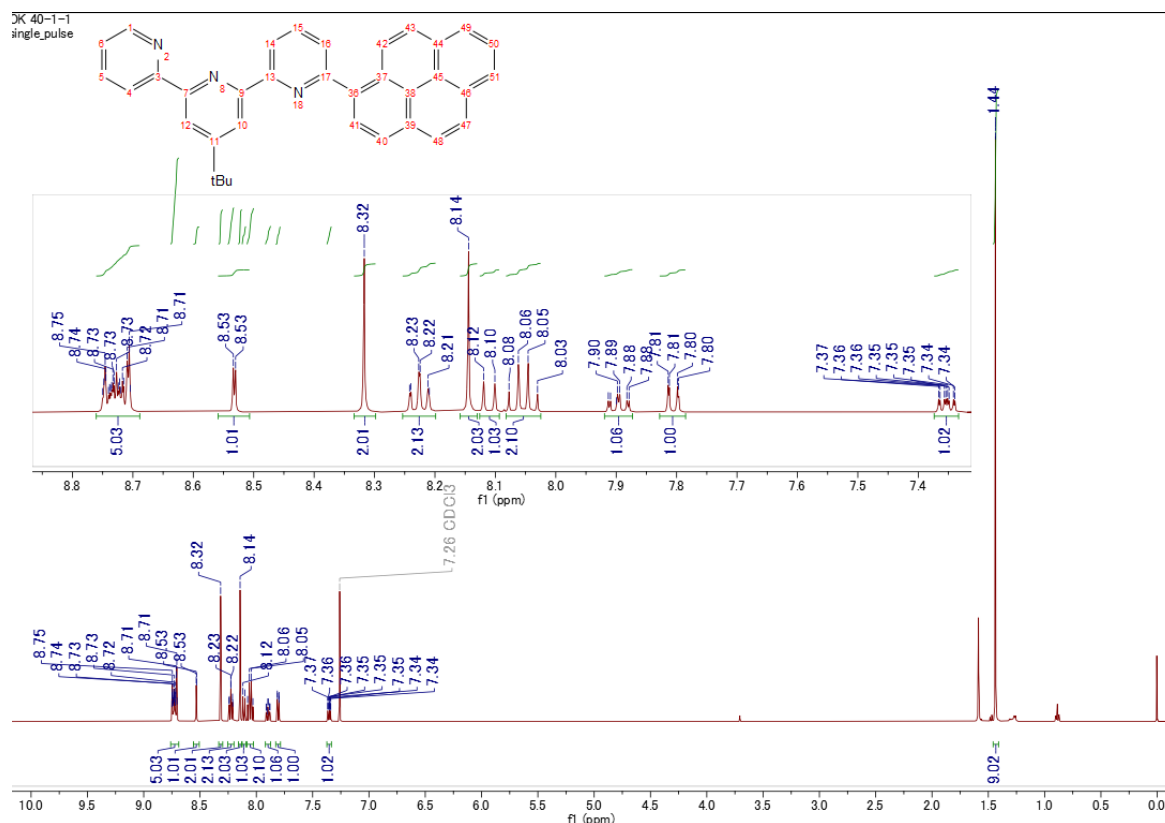


Figure S40. ^1H NMR spectra (CDCl_3) of L15.

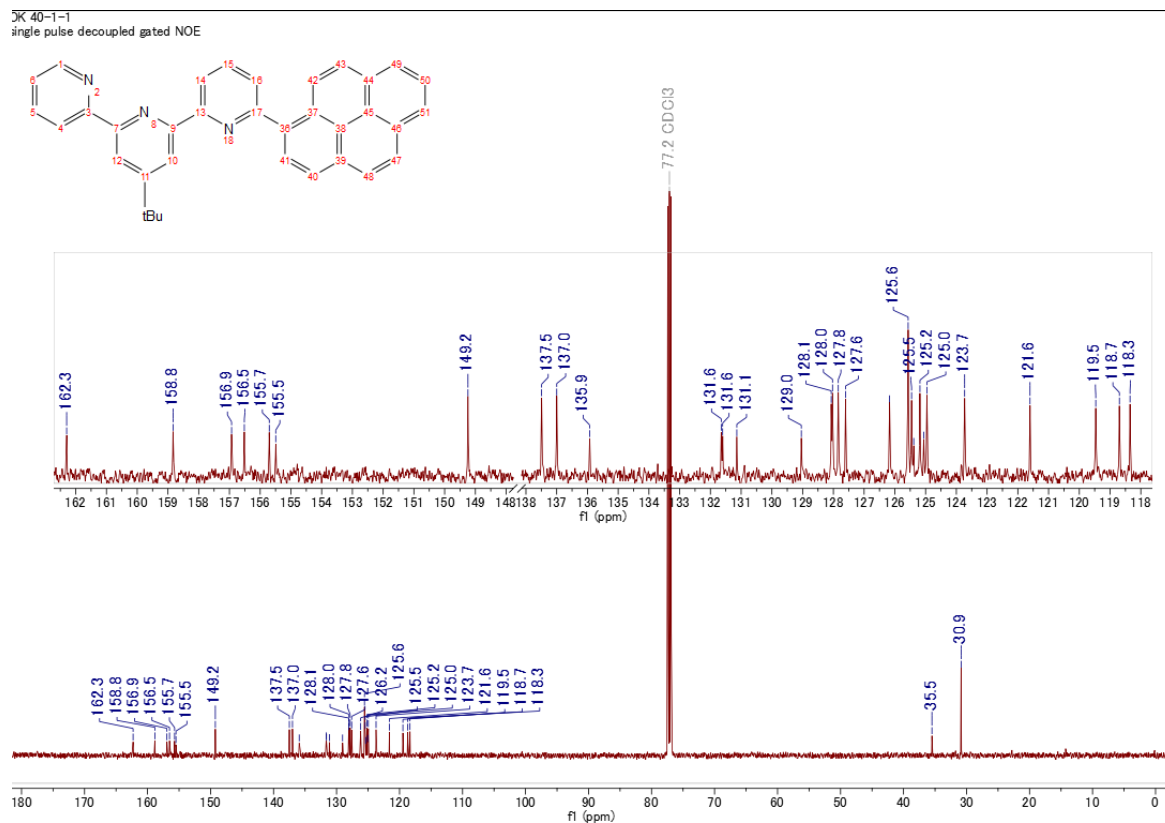


Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of L15.

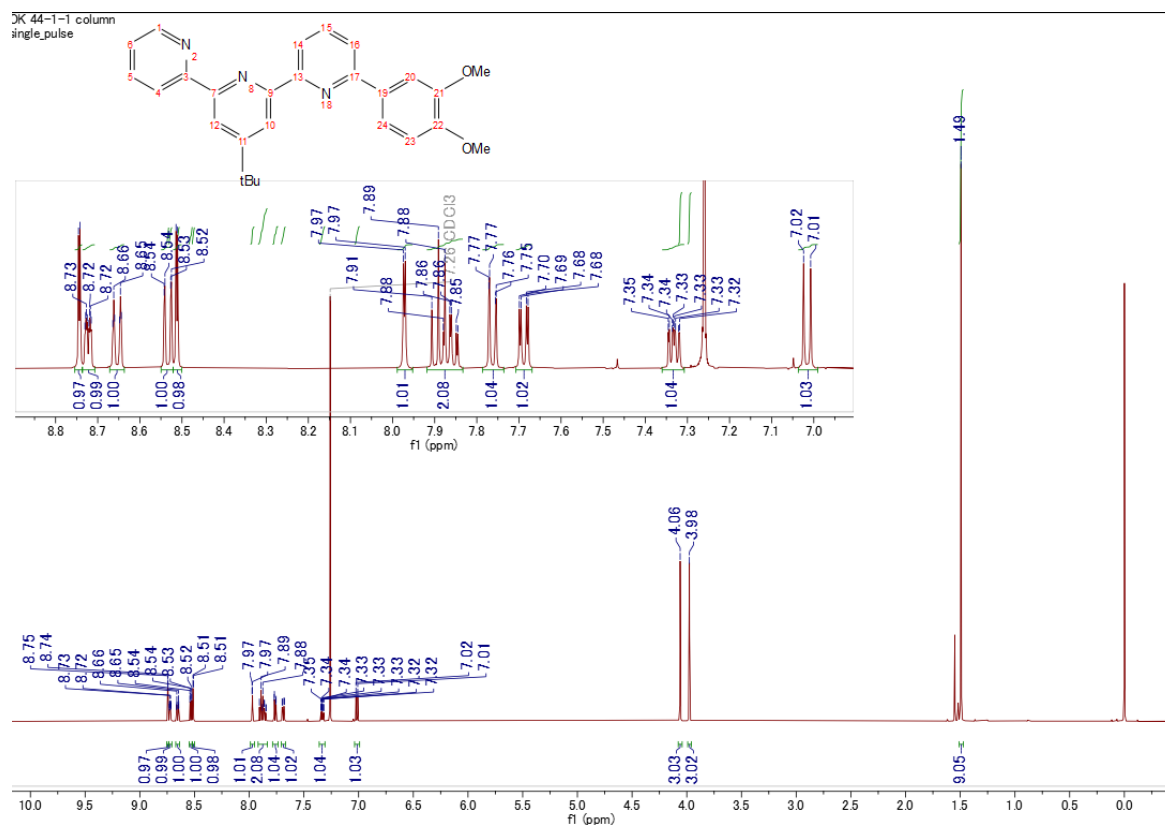


Figure S42. ¹H NMR spectra (CDCl₃) of L16.

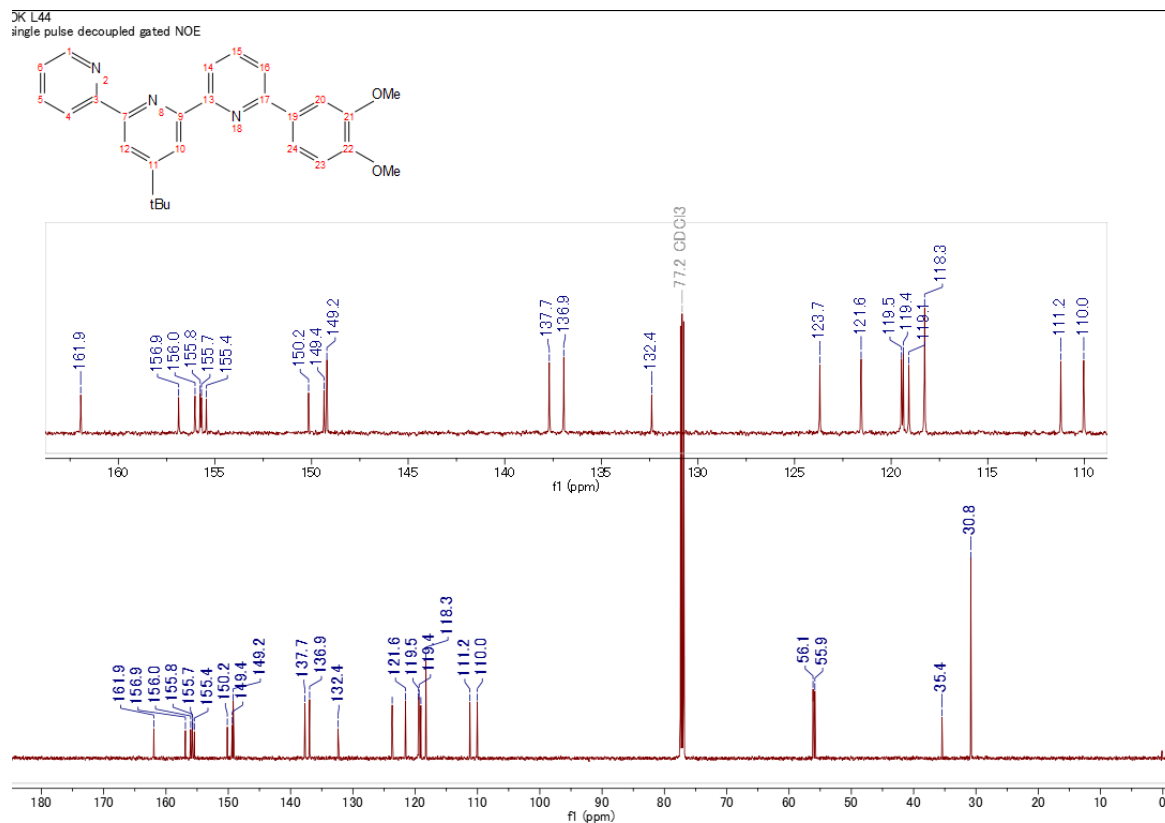


Figure S43. ¹³C{¹H} NMR spectra (CDCl₃) of L16.

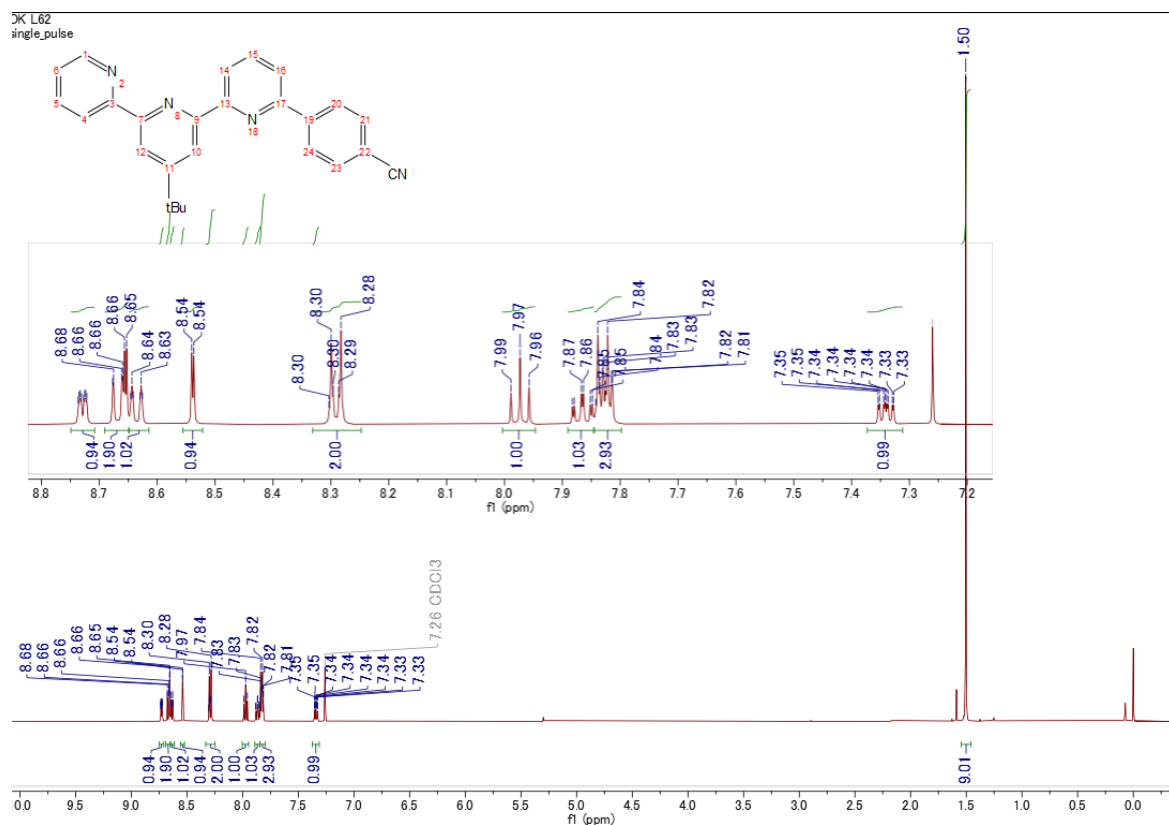


Figure S44. ¹H NMR spectra (CDCl₃) of L17.

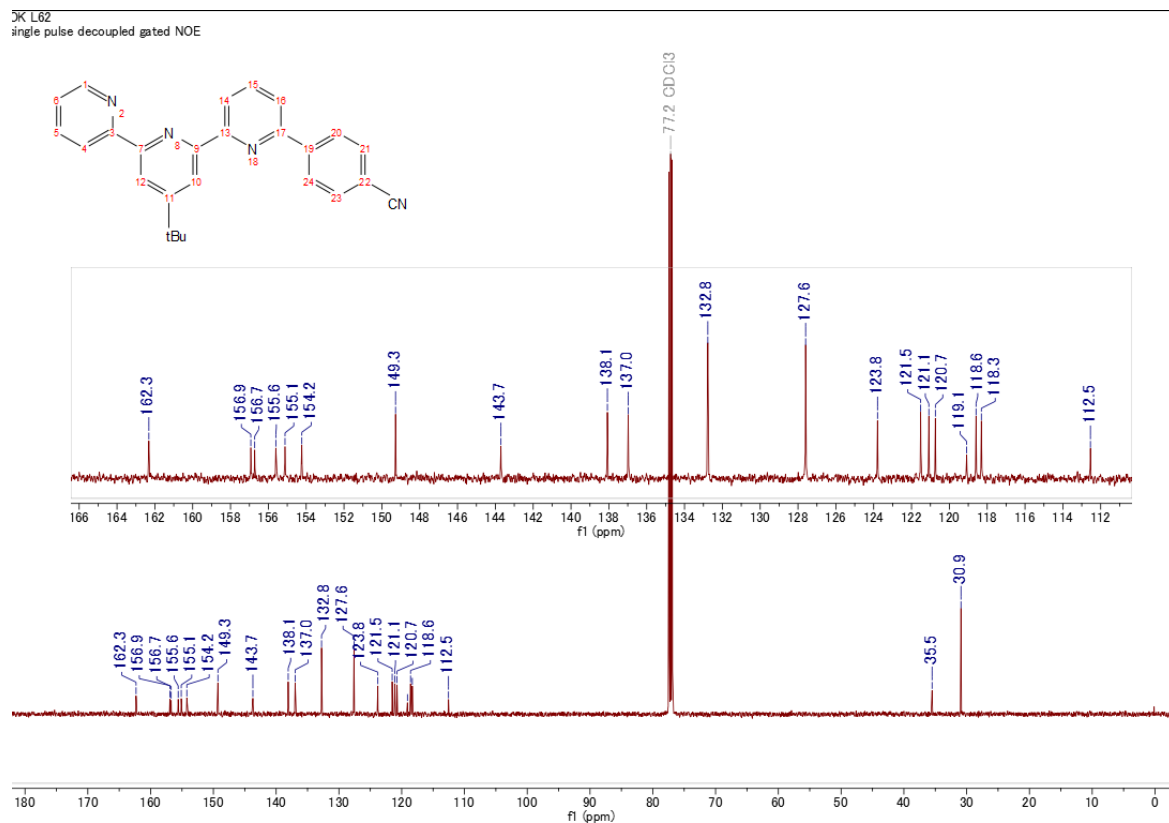


Figure S45. ¹³C{¹H} NMR spectra (CDCl₃) of L17.

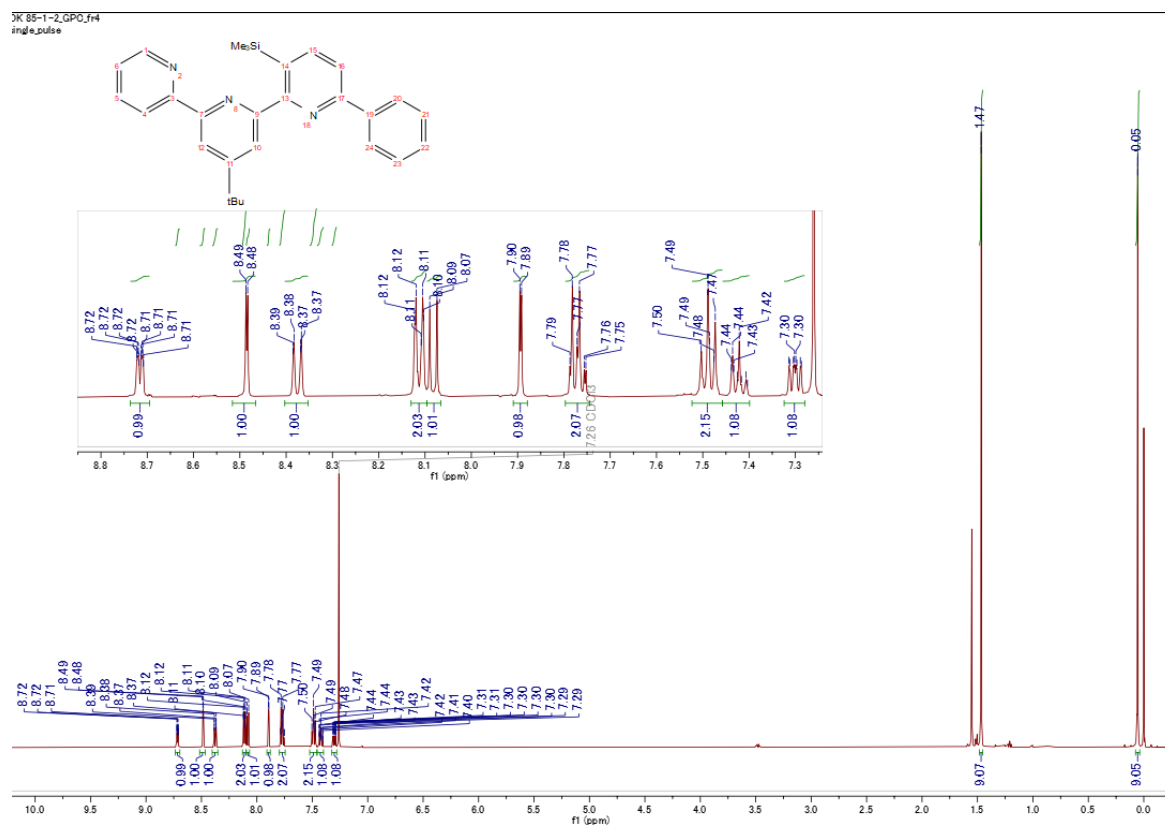


Figure S46. ¹H NMR spectra (CDCl₃) of L7.

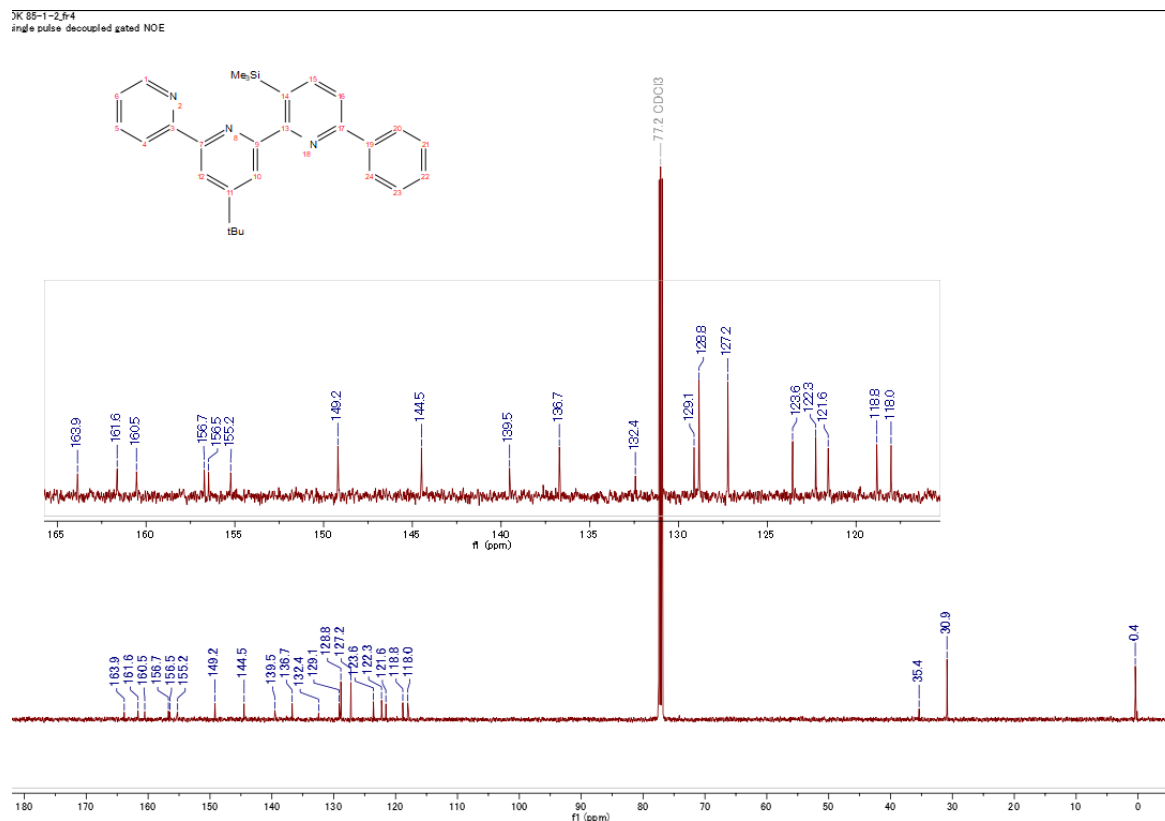


Figure S47. ¹³C{¹H} NMR spectra (CDCl₃) of L7.

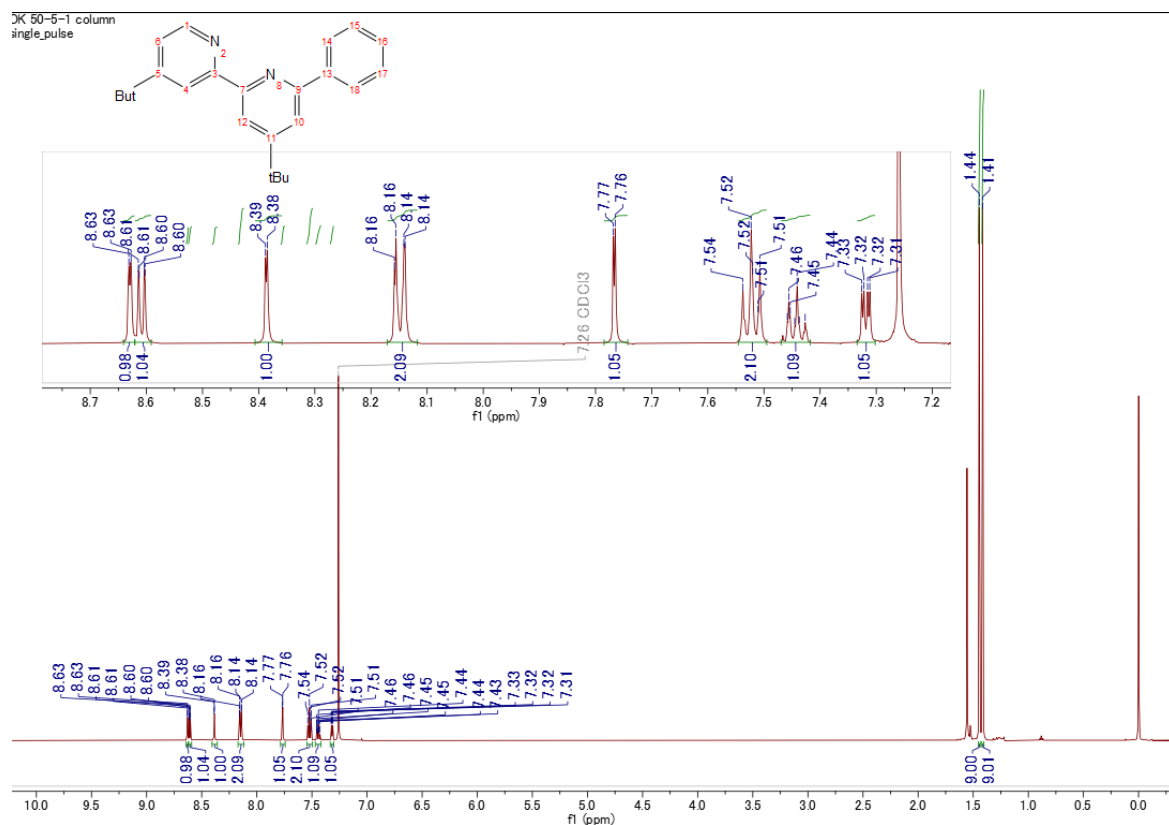


Figure S48. ¹H NMR spectra (CDCl₃) of L8.

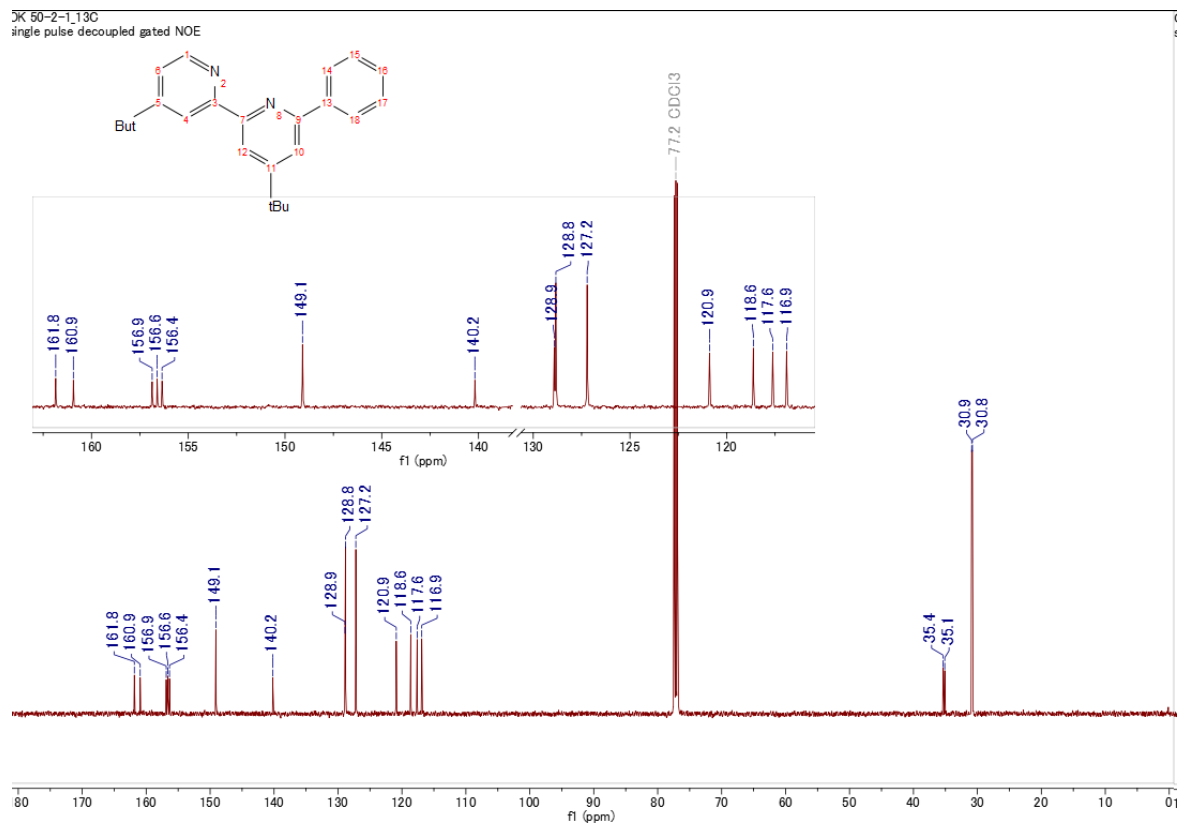


Figure S49. ¹³C{¹H} NMR spectra (CDCl₃) of L8.

JK 81-3-1 6-20-26
single_pulse

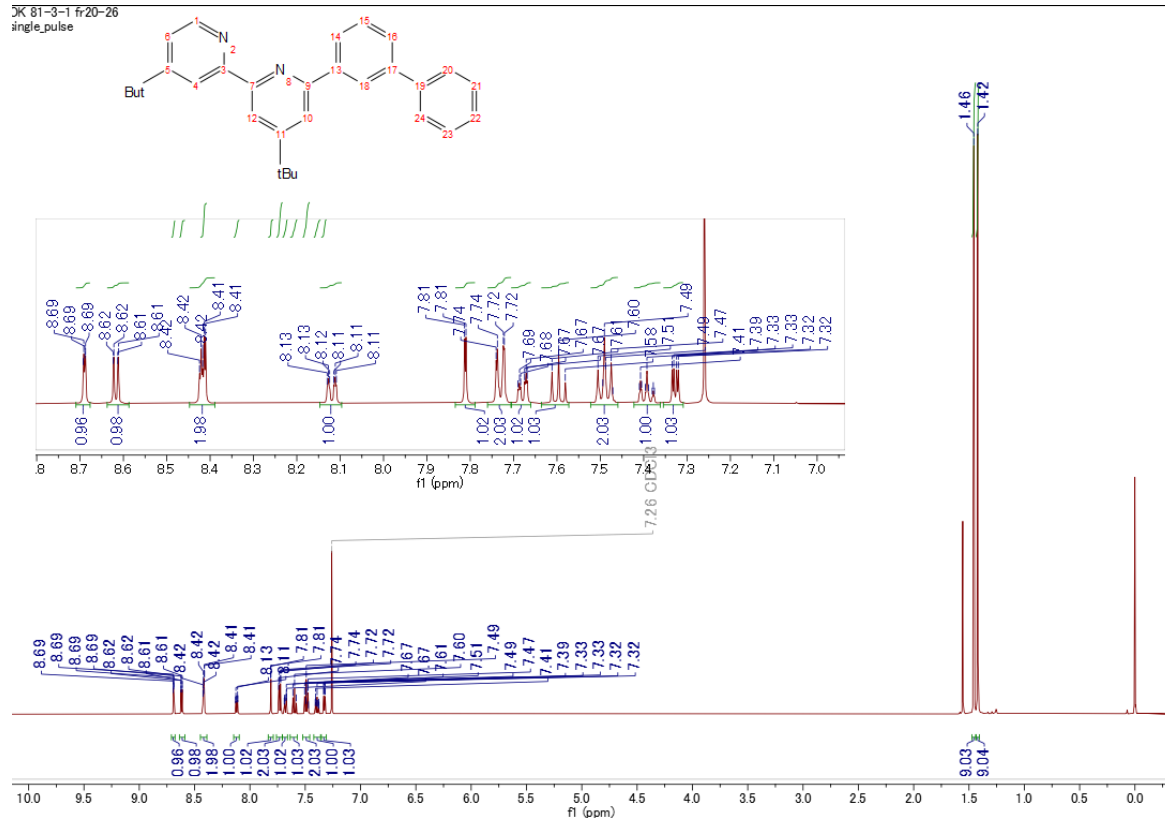


Figure S50. ¹H NMR spectra (CDCl₃) of L9.

JK 81-3-1 6-20-26
single_pulse decoupled gated NOE

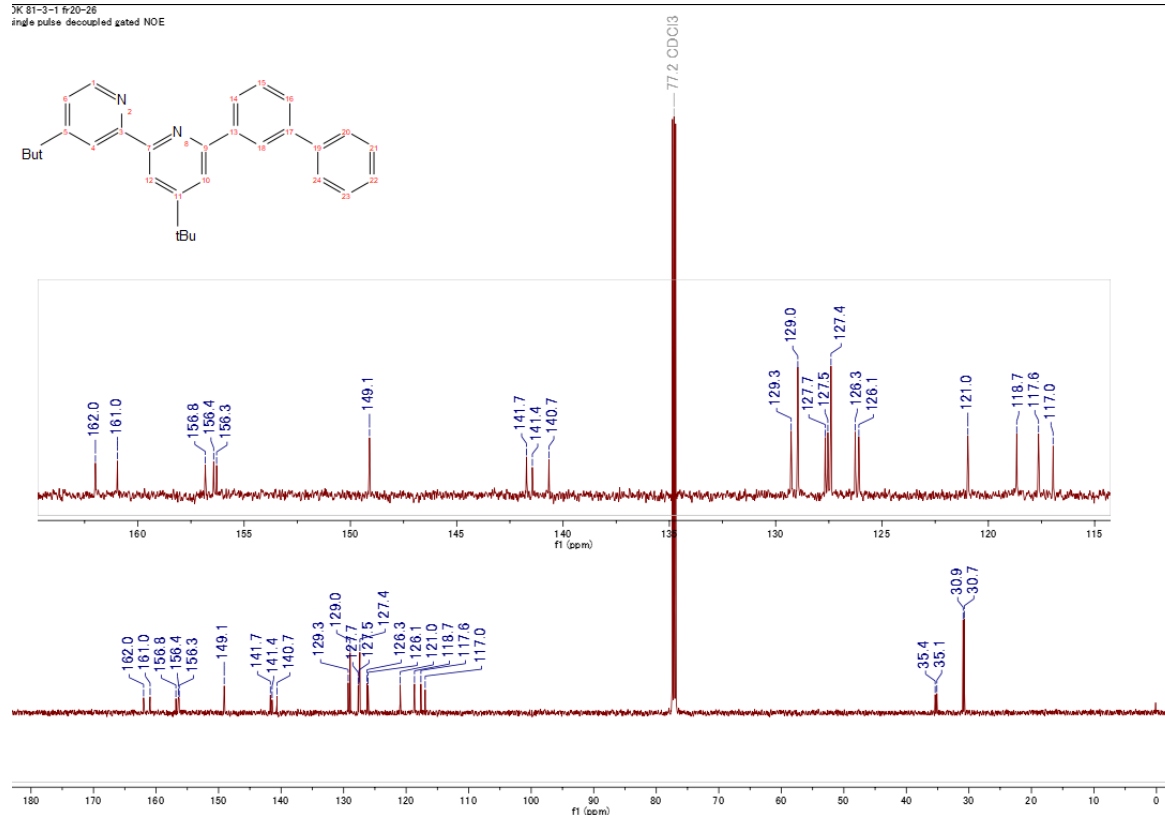
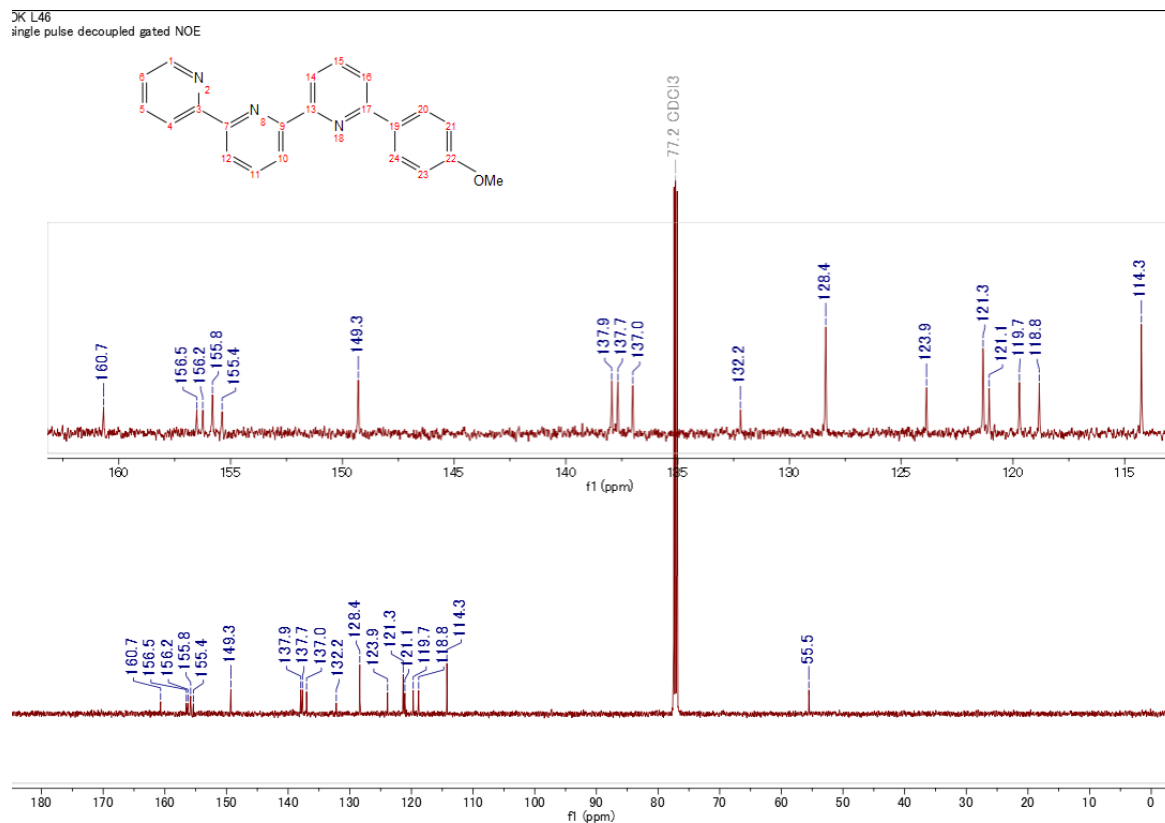
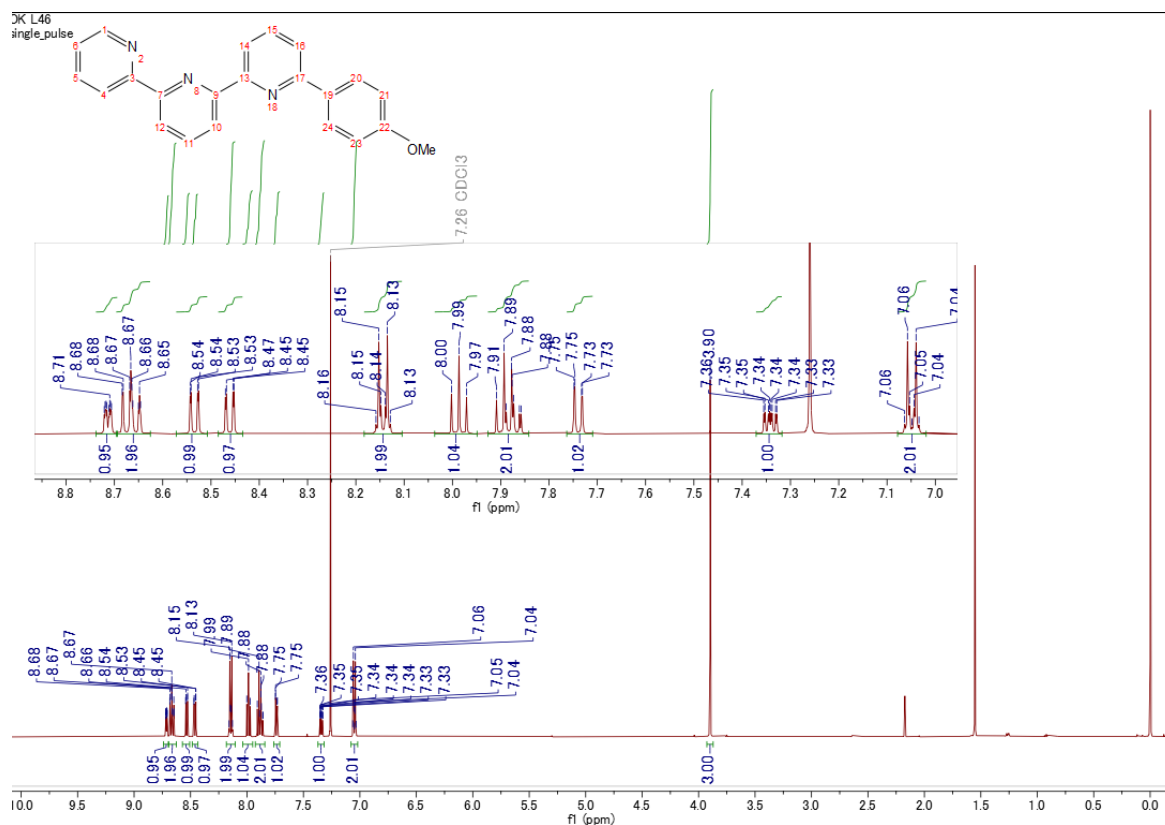


Figure S51. ¹³C{¹H} NMR spectra (CDCl₃) of L9.



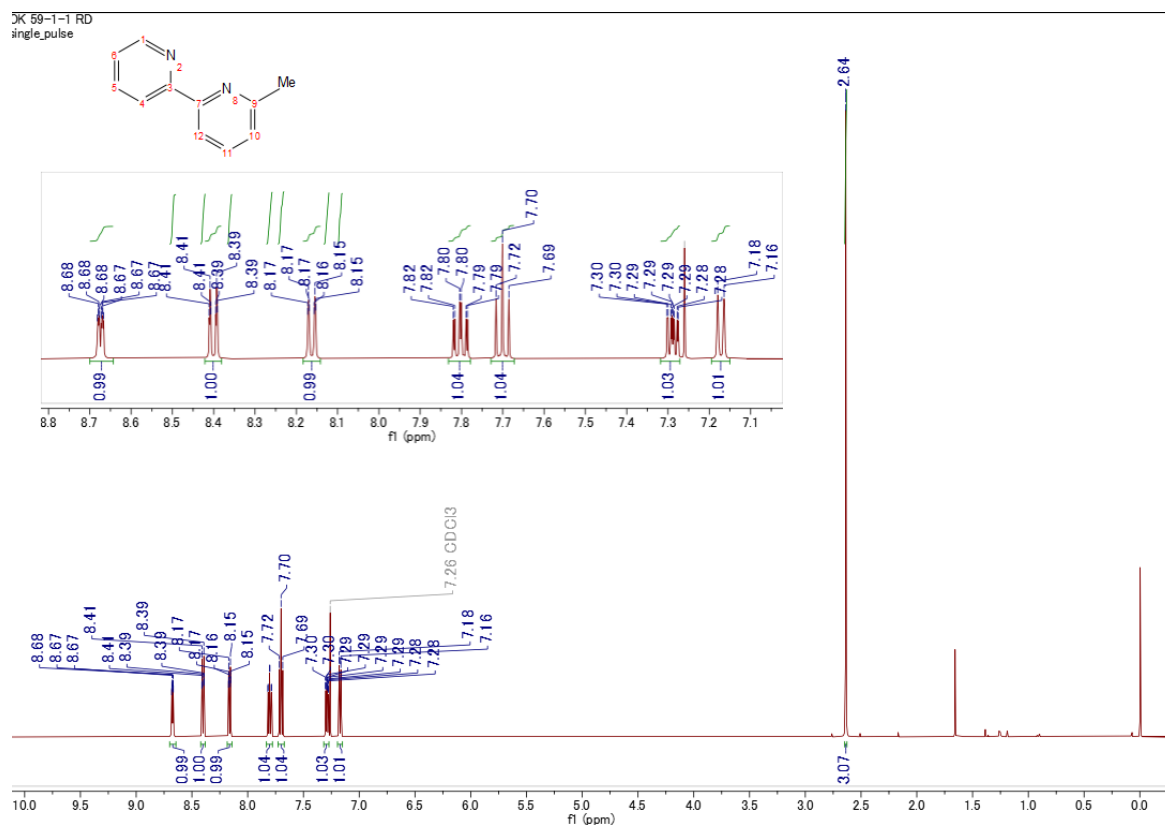


Figure S54. ¹H NMR spectra (CDCl₃) of L18.

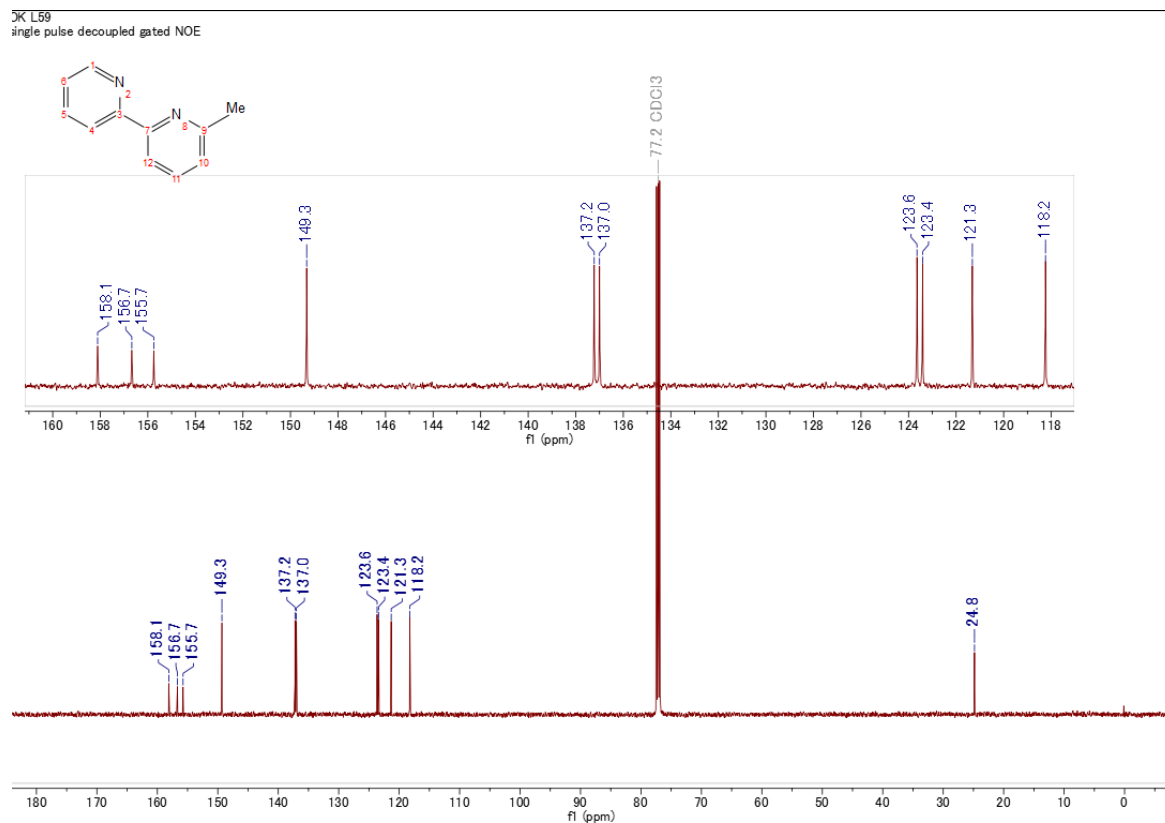


Figure S55. ¹³C{¹H} NMR spectra (CDCl₃) of L18.

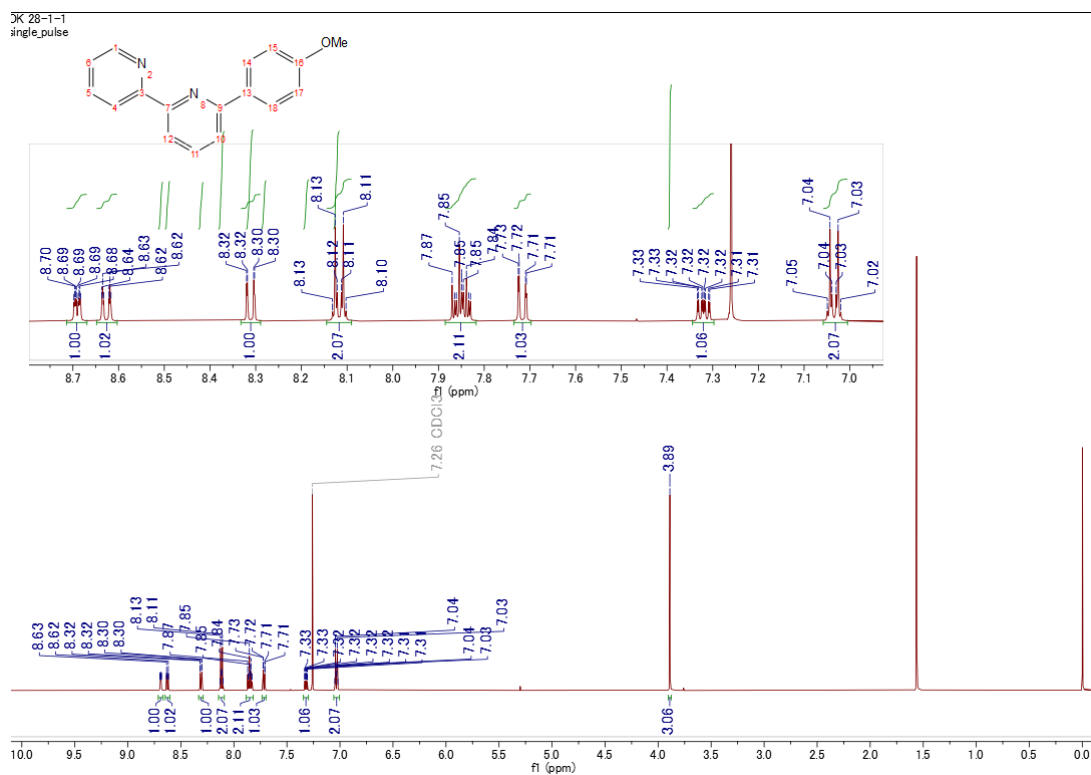


Figure S56. ¹H NMR spectra (CDCl₃) of L19.

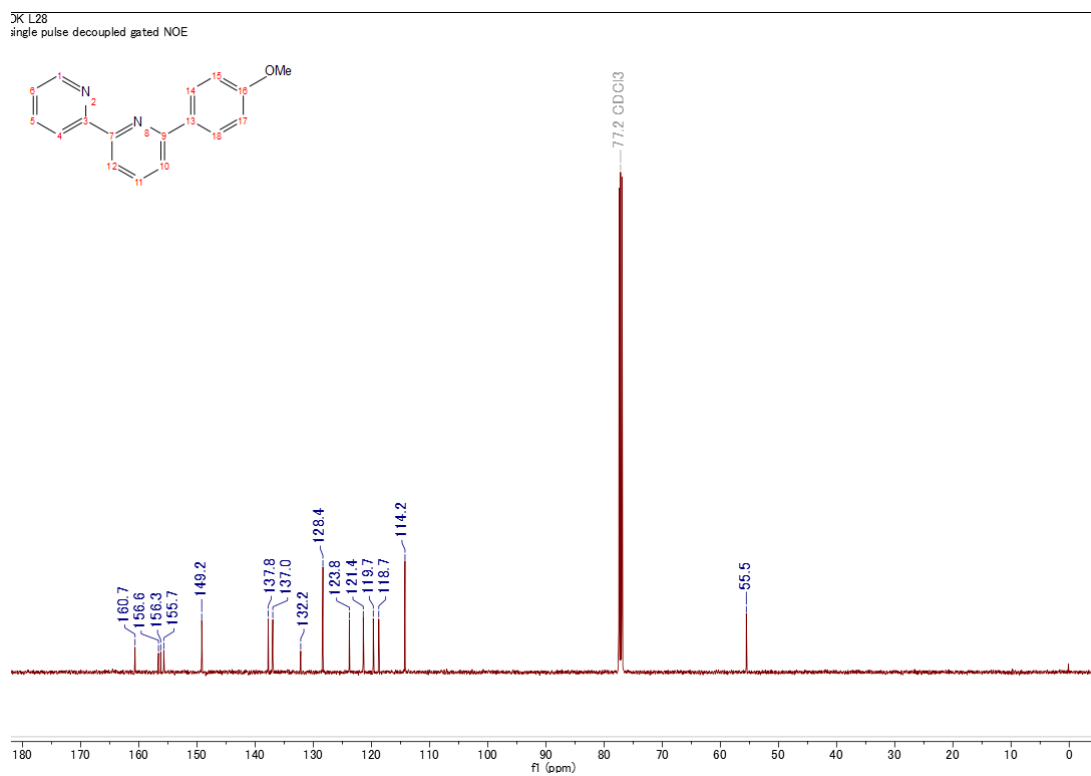


Figure S57. ¹³C{¹H} NMR spectra (CDCl₃) of L19.

JK 59-2-1 column
single_pulse

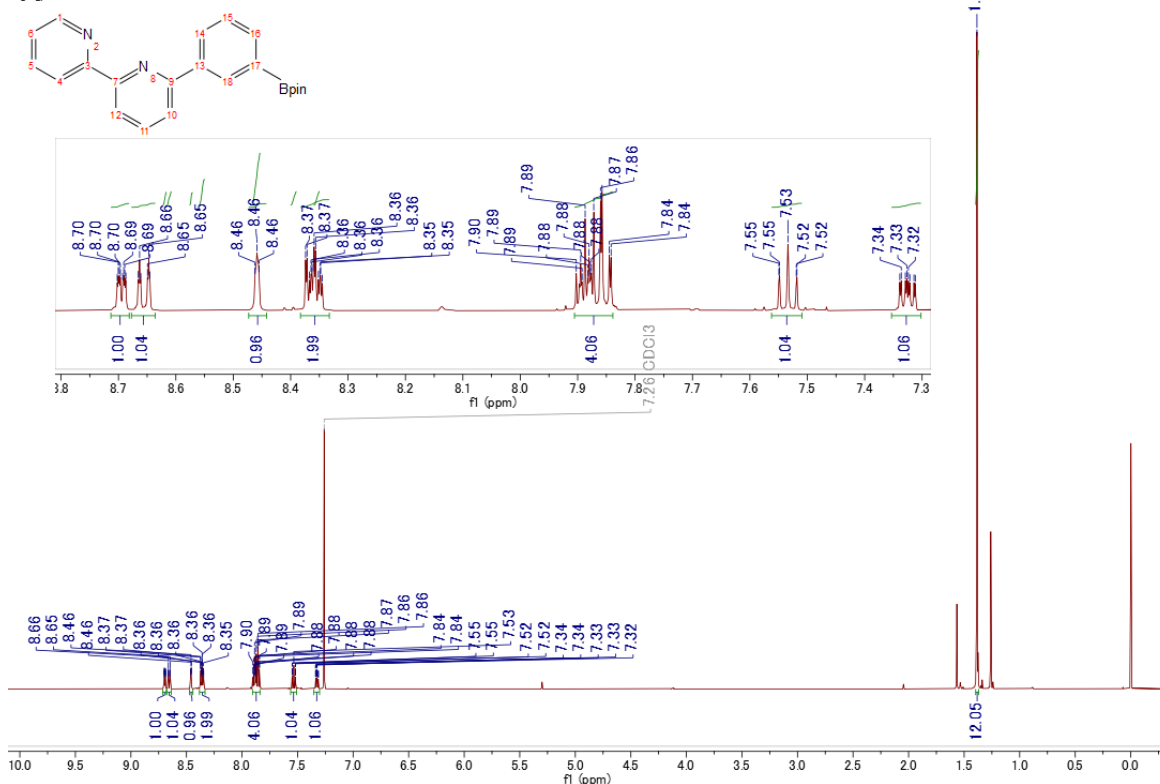


Figure S58. ^1H NMR spectra (CDCl_3) of L20.

JK L29
single pulse decoupled gated NOE

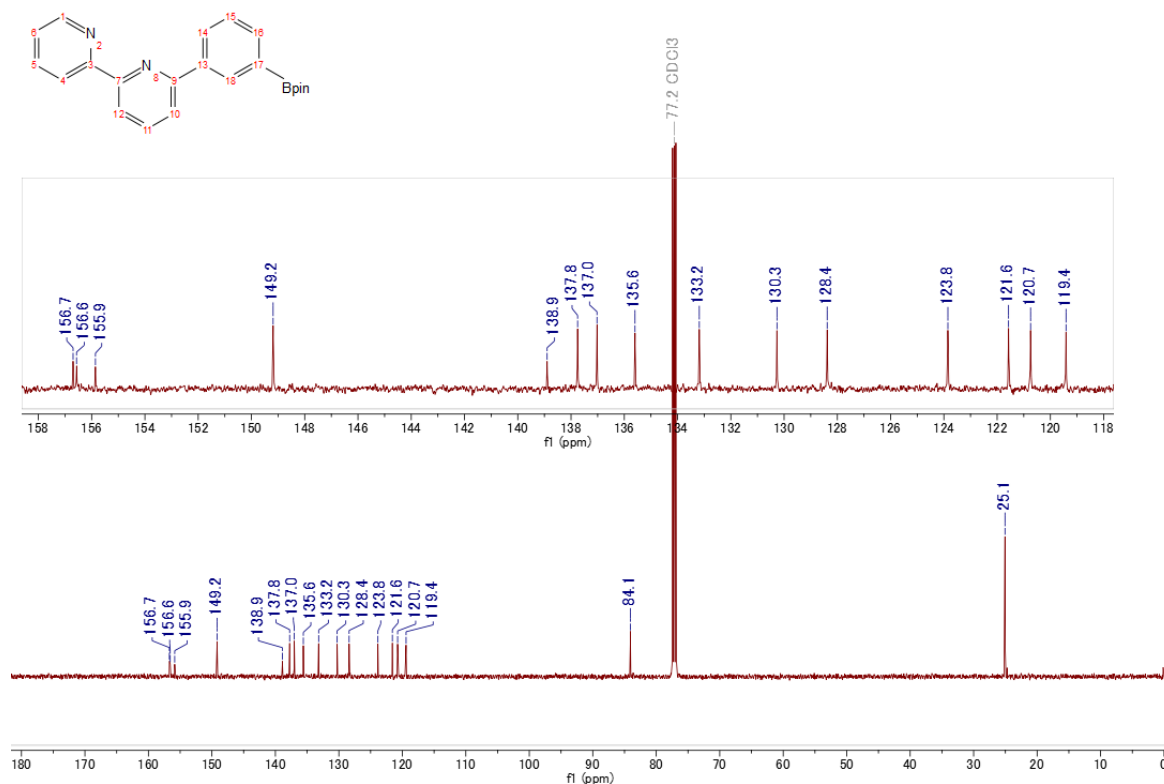


Figure S59. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of L20.

JK 64-7-1 GPC
single_pulse

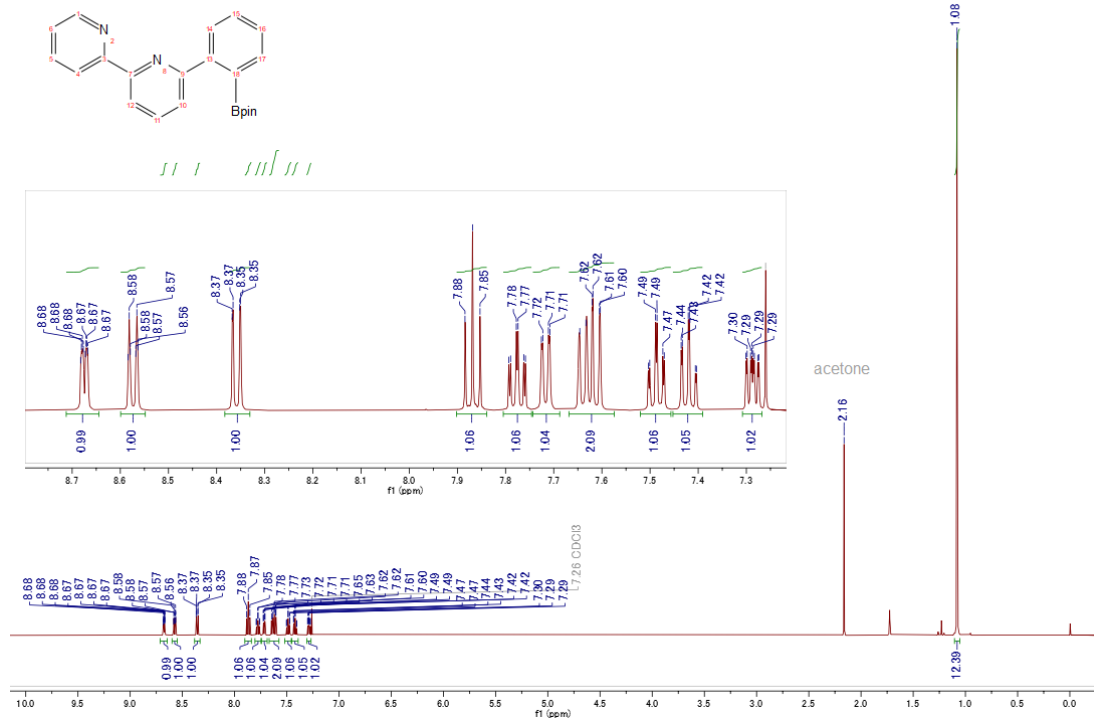


Figure S60. ¹H NMR spectra (CDCl₃) of L21.

JK 64-7-1 GPC
single_pulse decoupled gated NOE

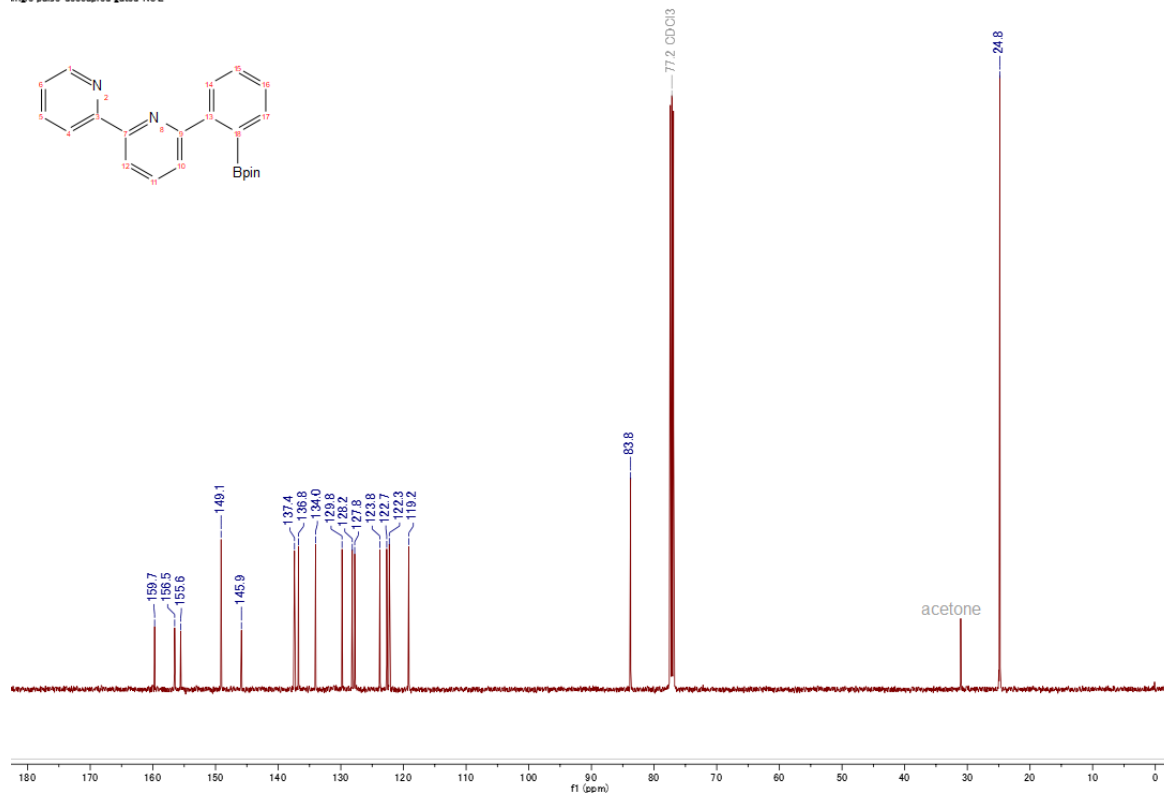
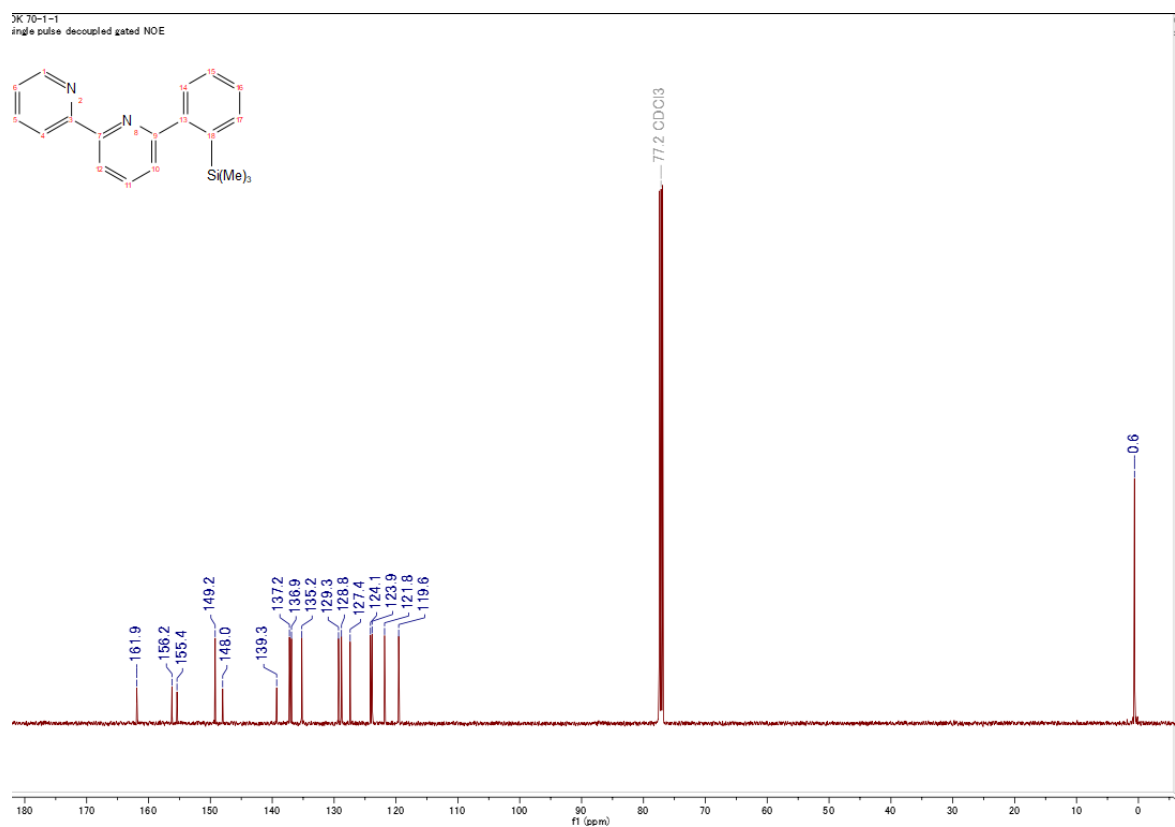
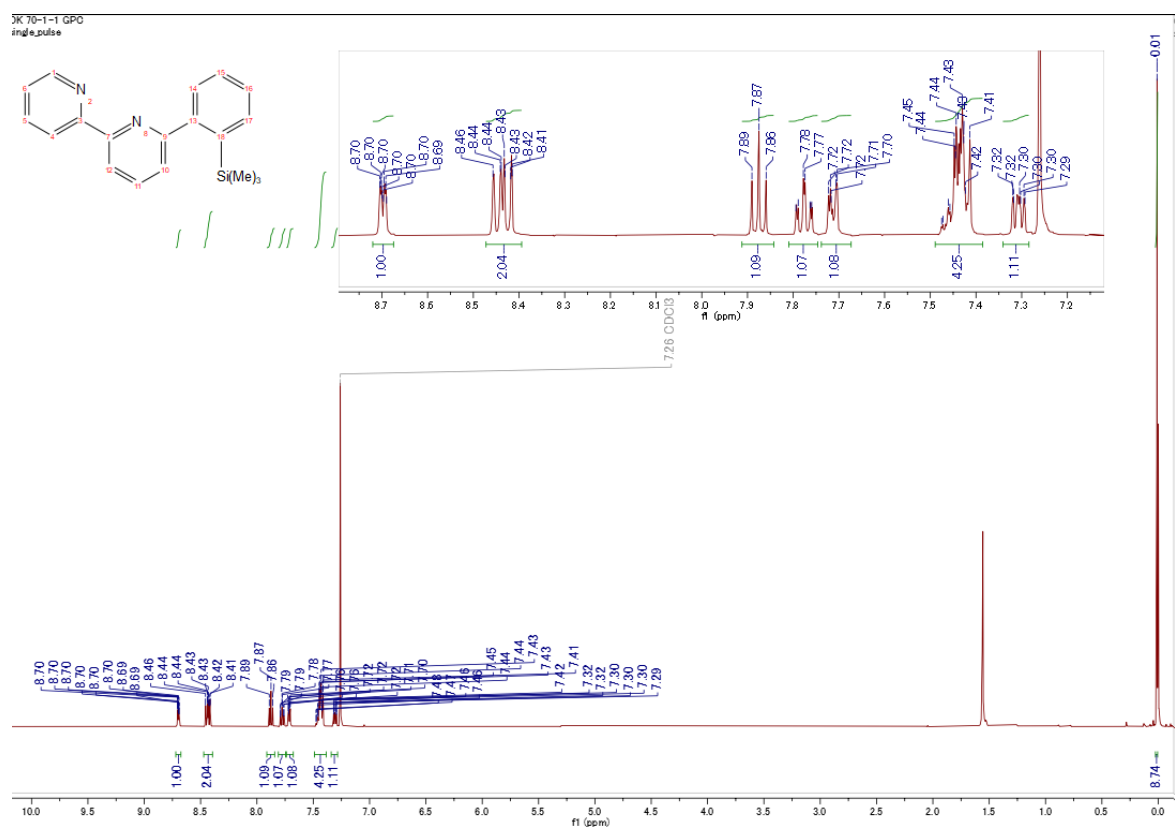


Figure S61. ¹³C{¹H} NMR spectra (CDCl₃) of L21.



JK L63
single_pulse

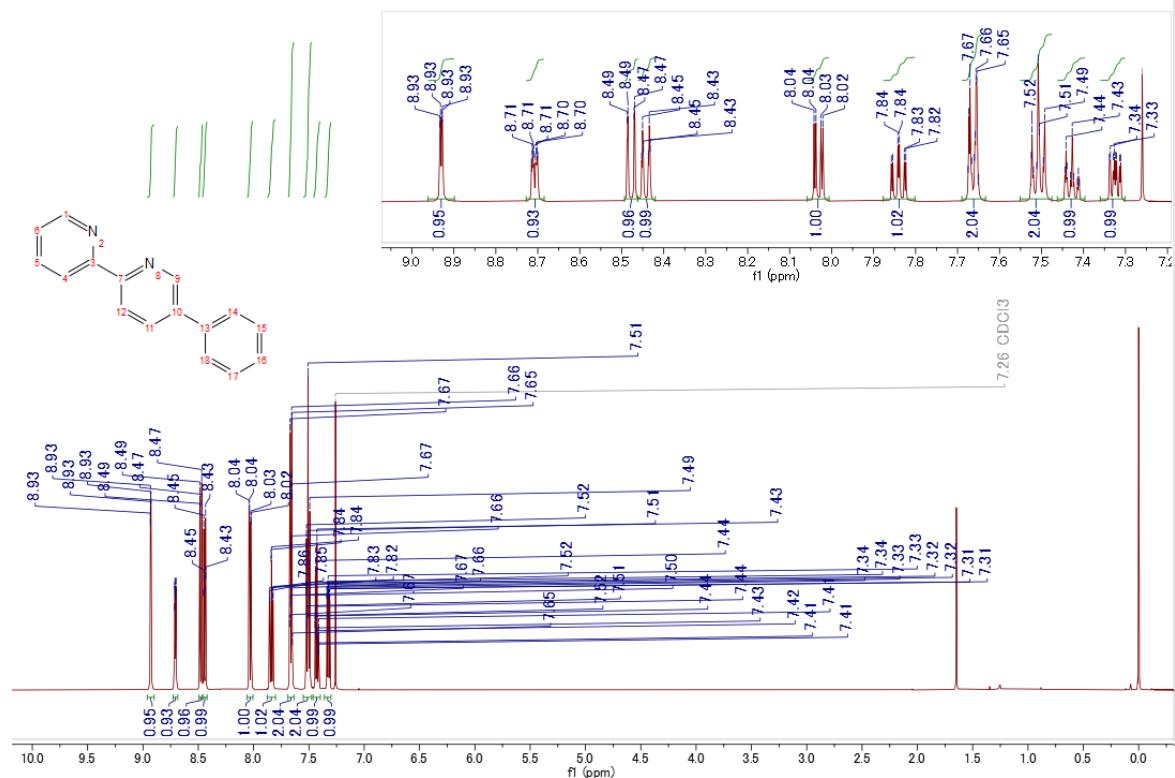


Figure S64. ^1H NMR spectra (CDCl₃) of L23.

JK L63
single pulse decoupled gated NOE

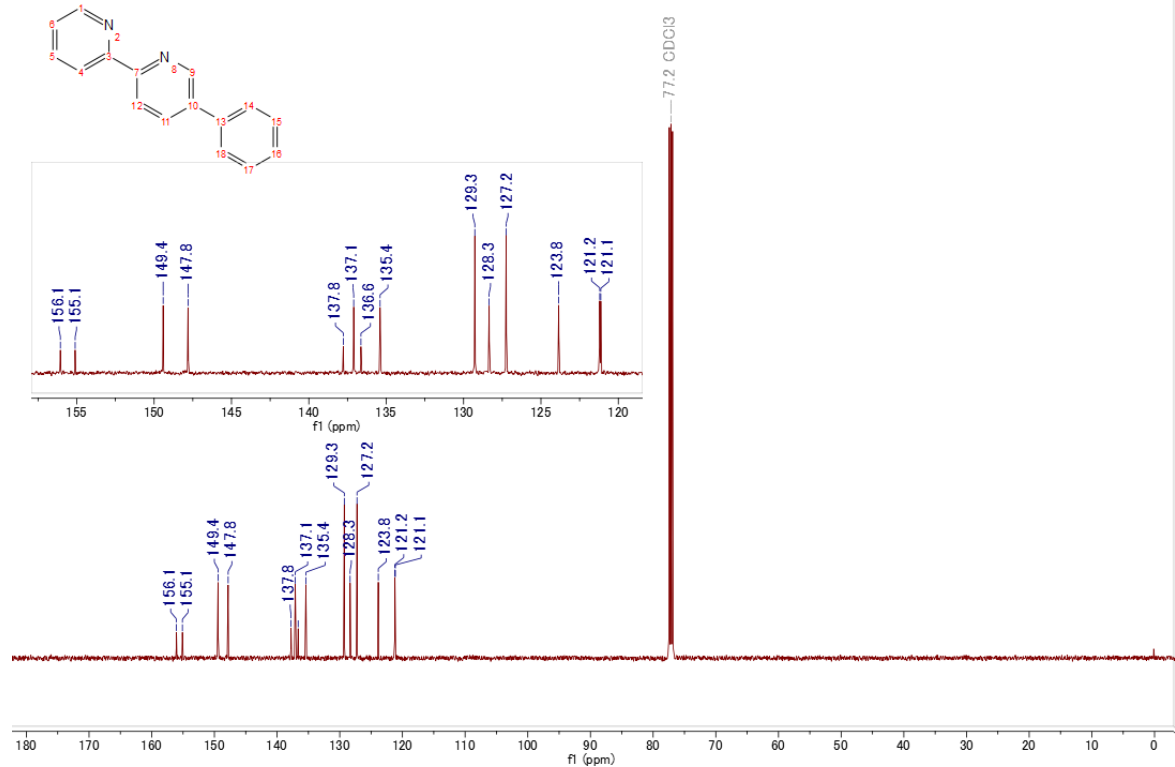
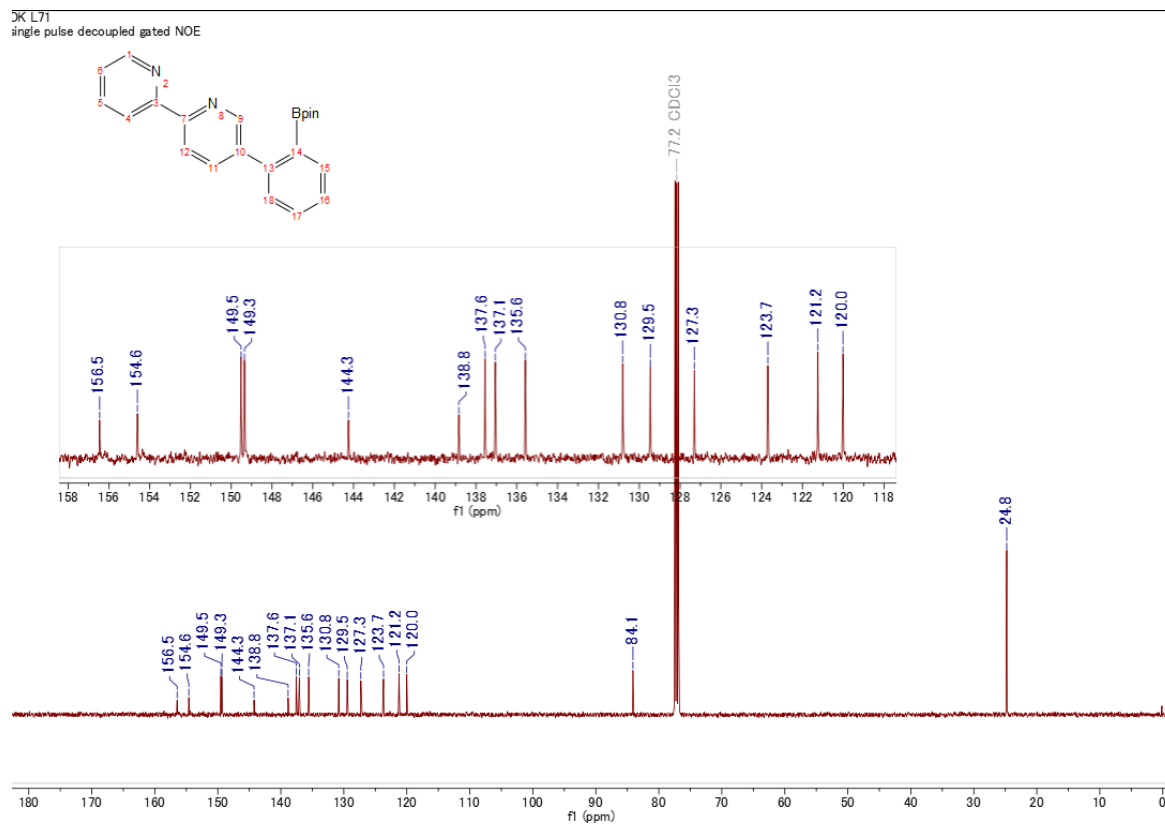
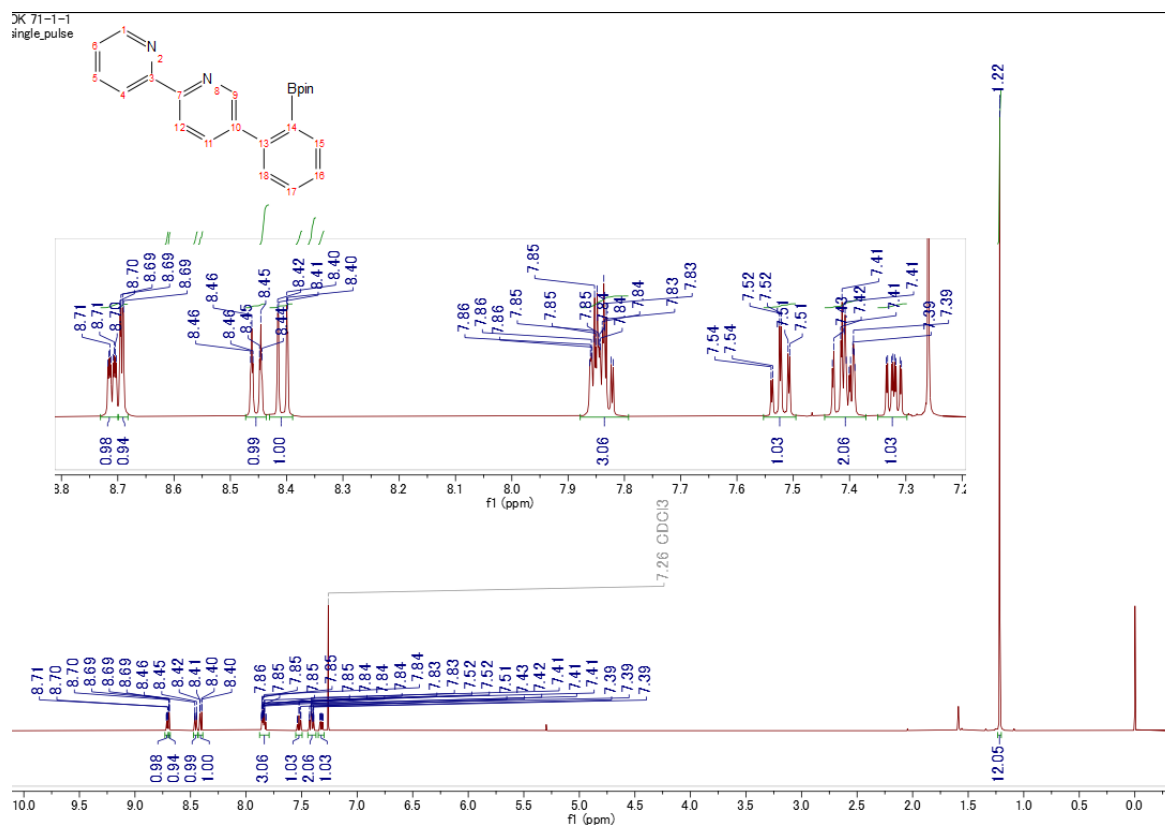


Figure S65. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl₃) of L23.



10. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR charts of *ortho*-to-F borylated arenes

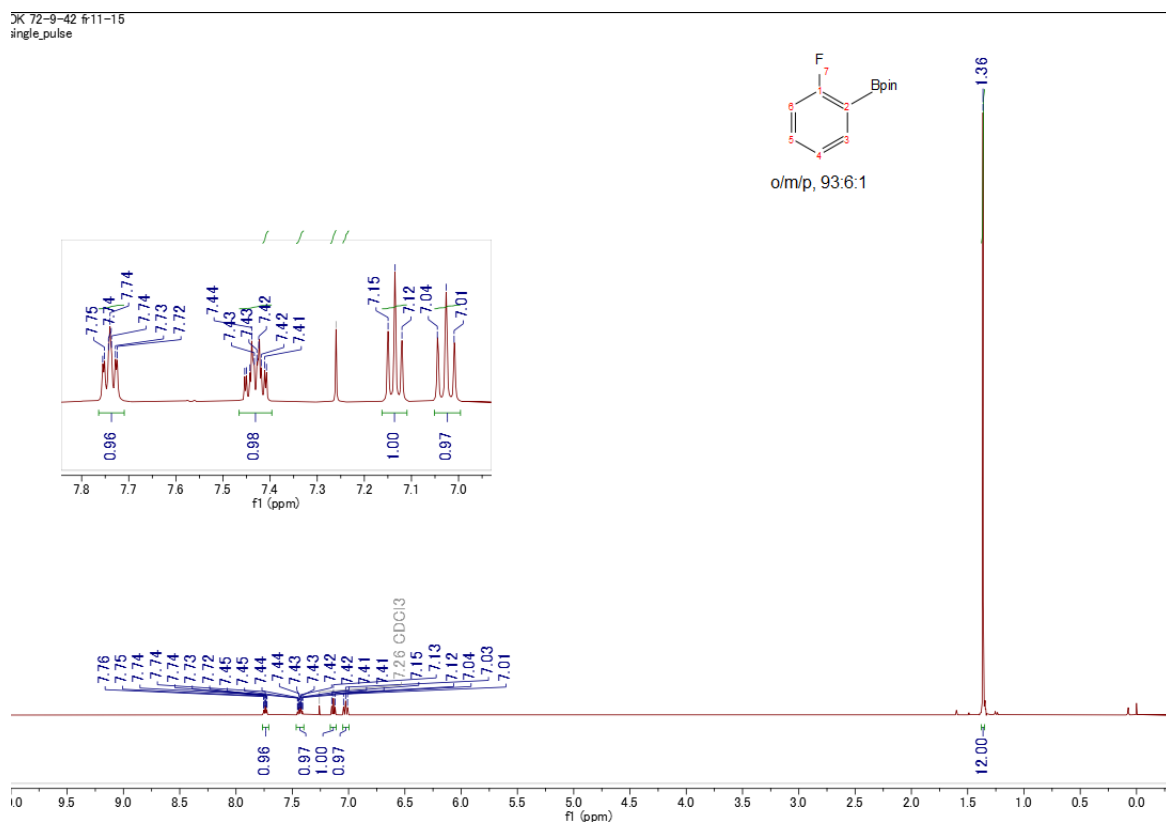


Figure S68. ^1H NMR spectra (CDCl_3) of **2a**.

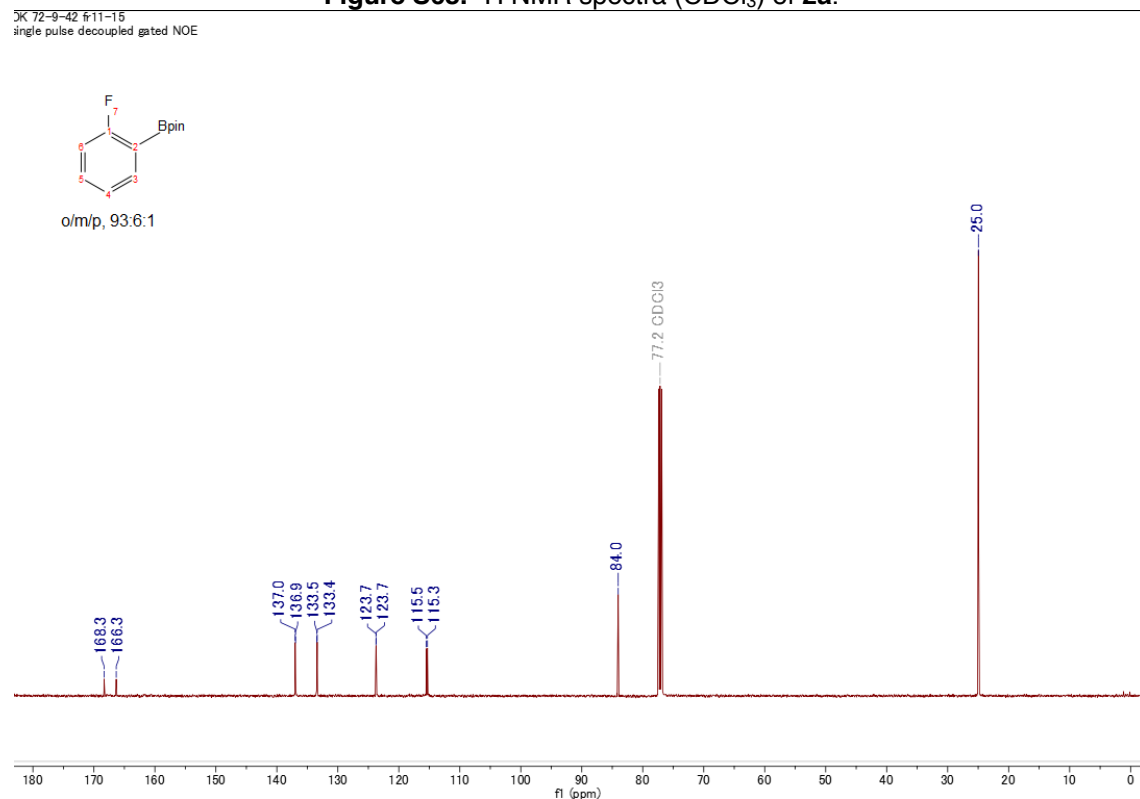
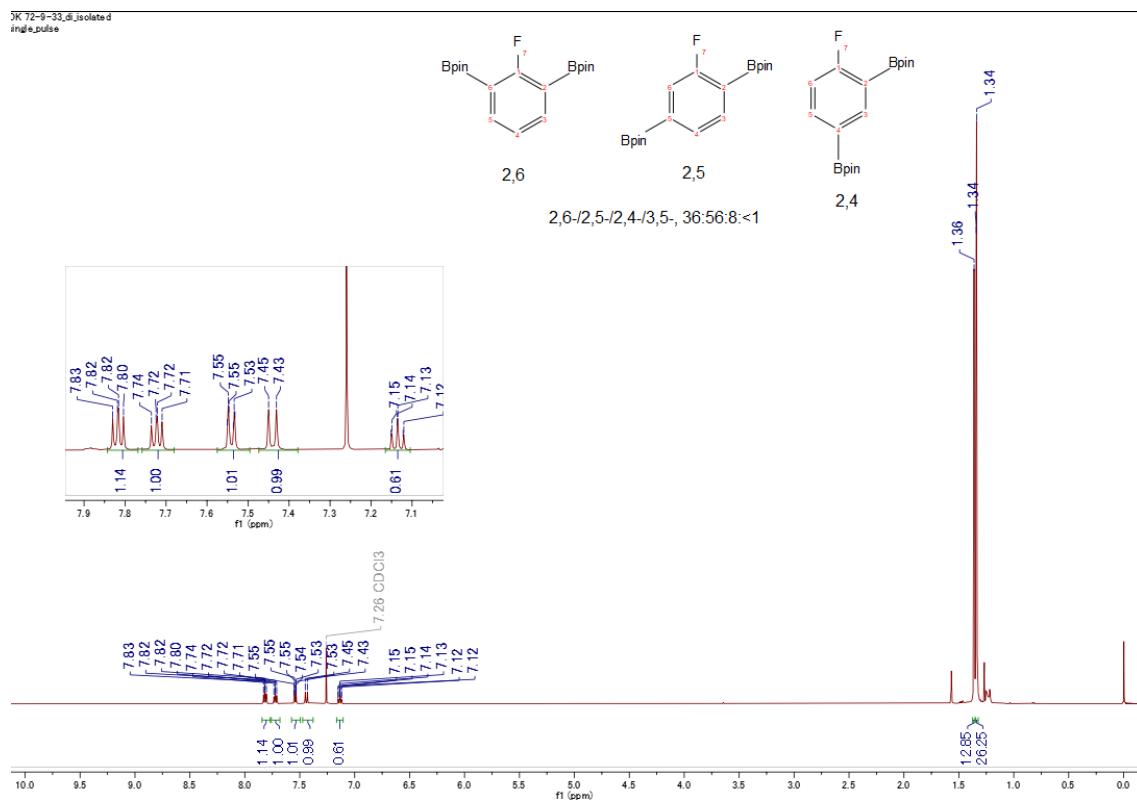
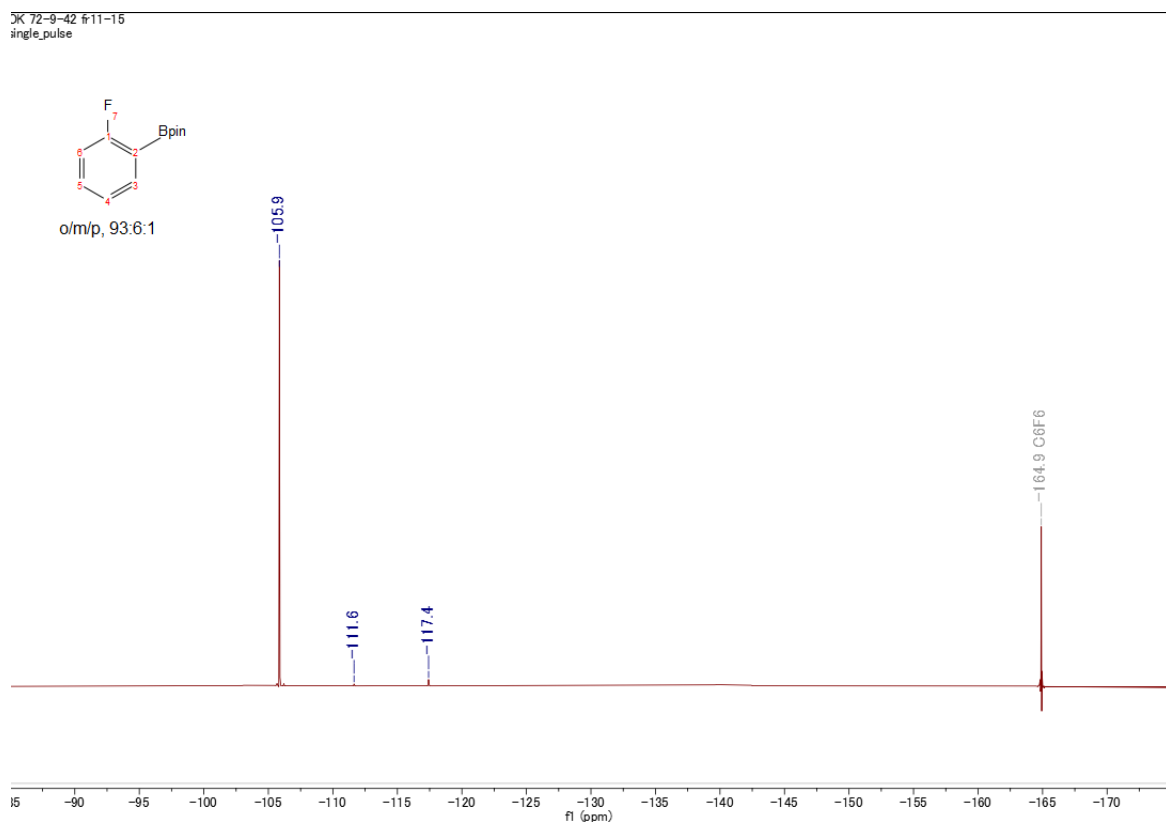


Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **2a**.



JK 72-9-33_d_high 0
single pulse decoupled gated NOE

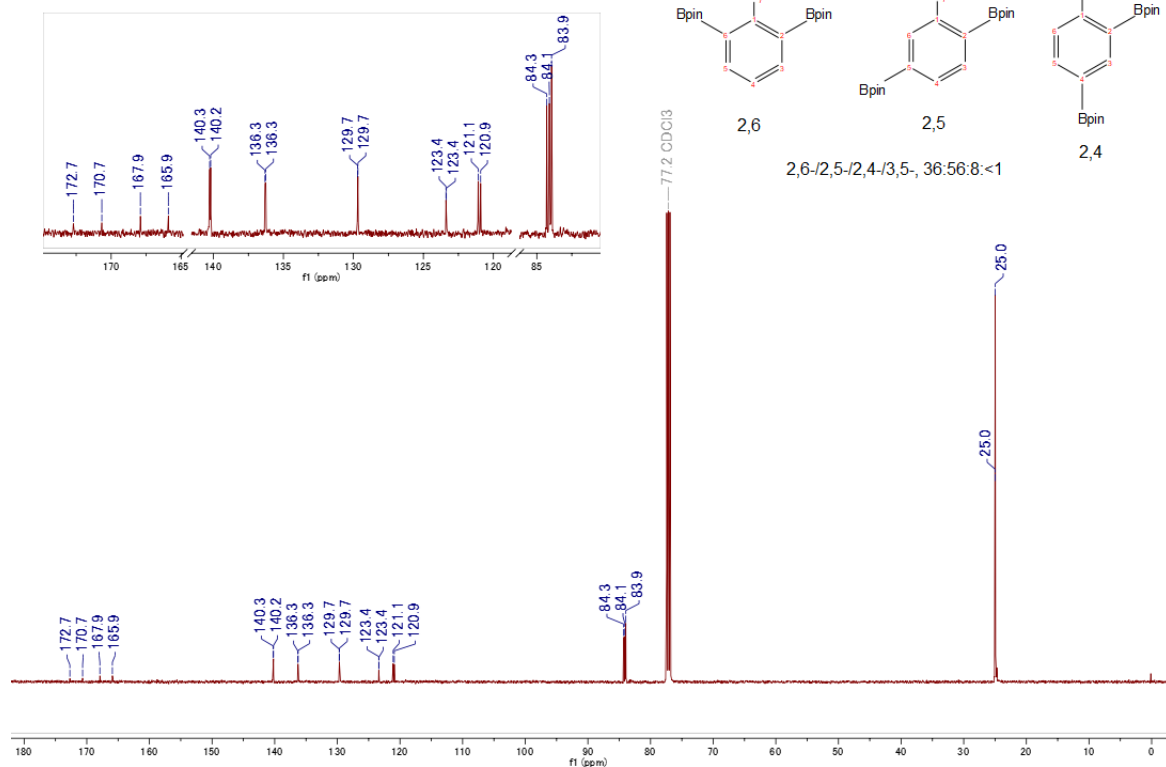


Figure S72. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **2a**.

JK 72-9-33_d_isolated
single_pulse

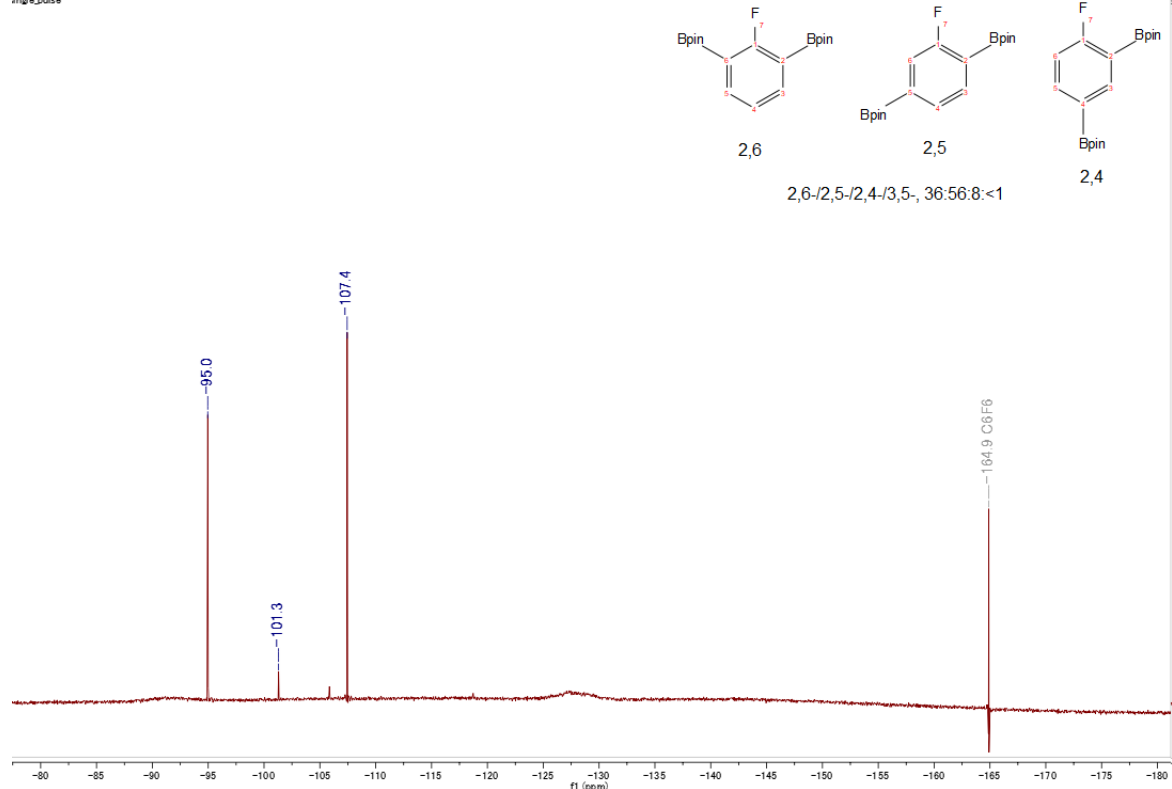


Figure S73. ^{19}F NMR spectra (CDCl_3) of **2a**.

JK 72-9-5 fr5-19 high C
single_pulse

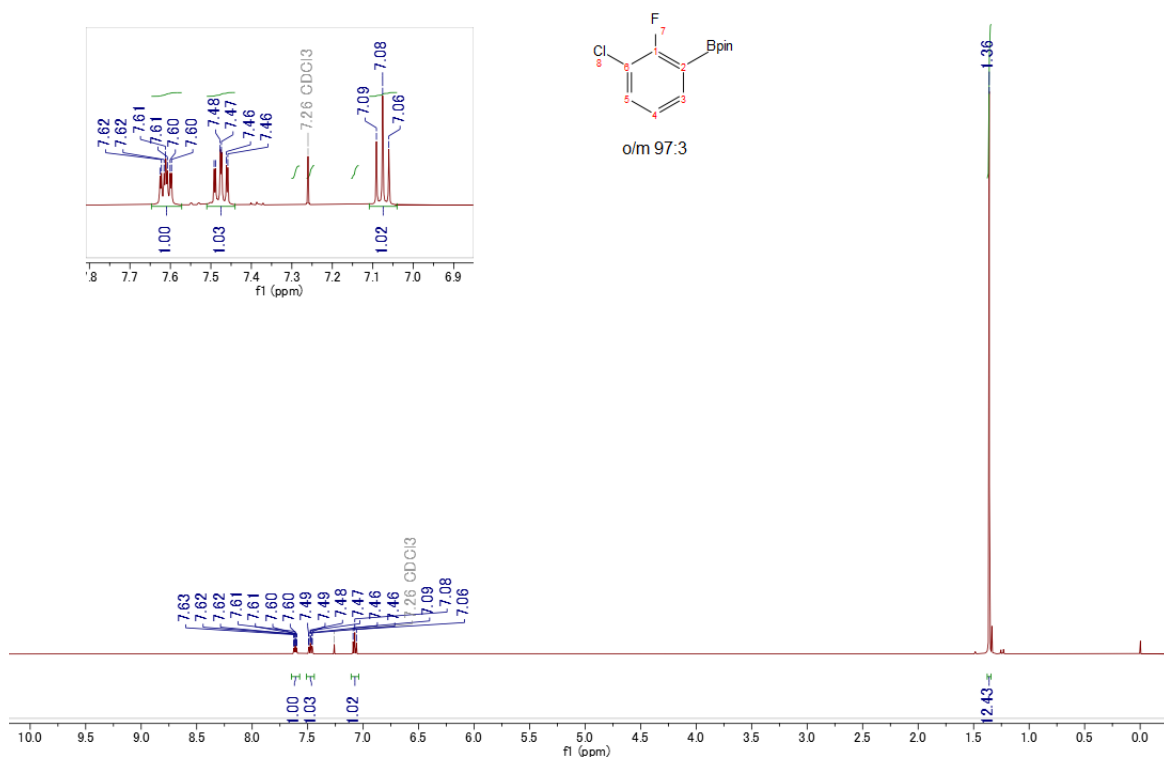


Figure S74. ¹H NMR spectra (CDCl₃) of 2b.

JK 72-9-5 fr5-19 high C
single_pulse decoupled gated NOE

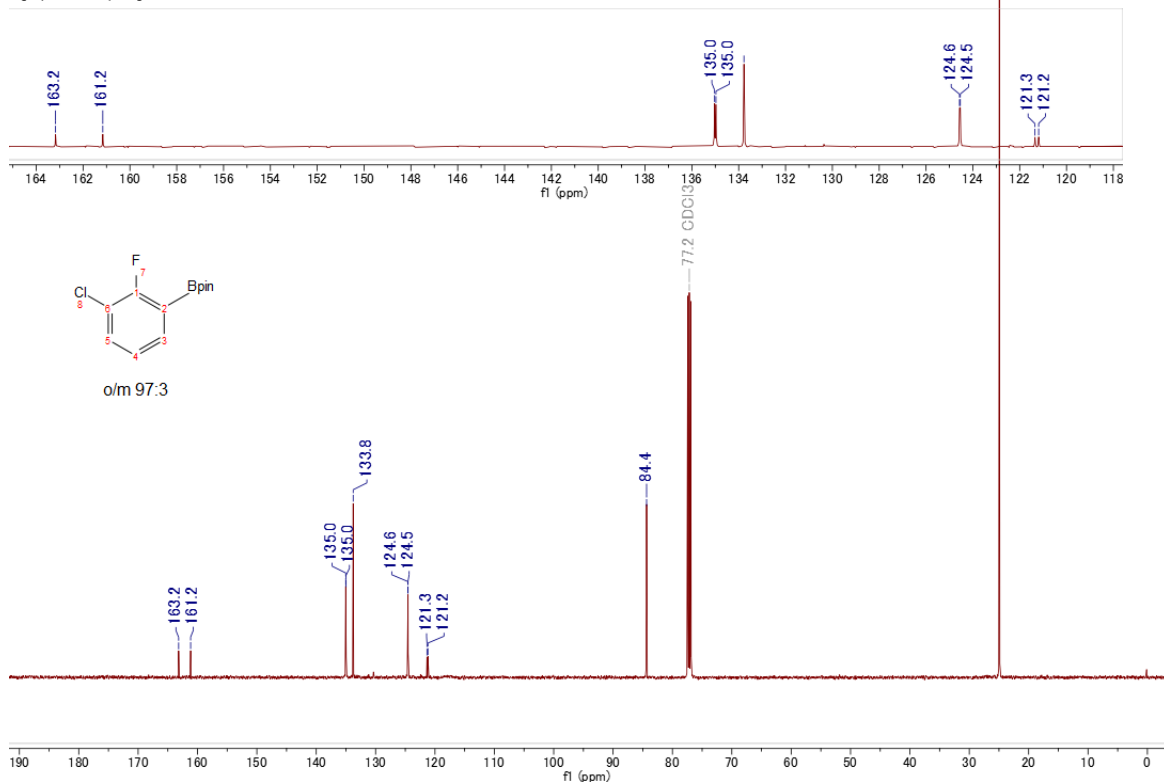


Figure S75. ¹³C{¹H} NMR spectra (CDCl₃) of 2b.

JK 72-9-5 fr5-19 19F
single_pulse

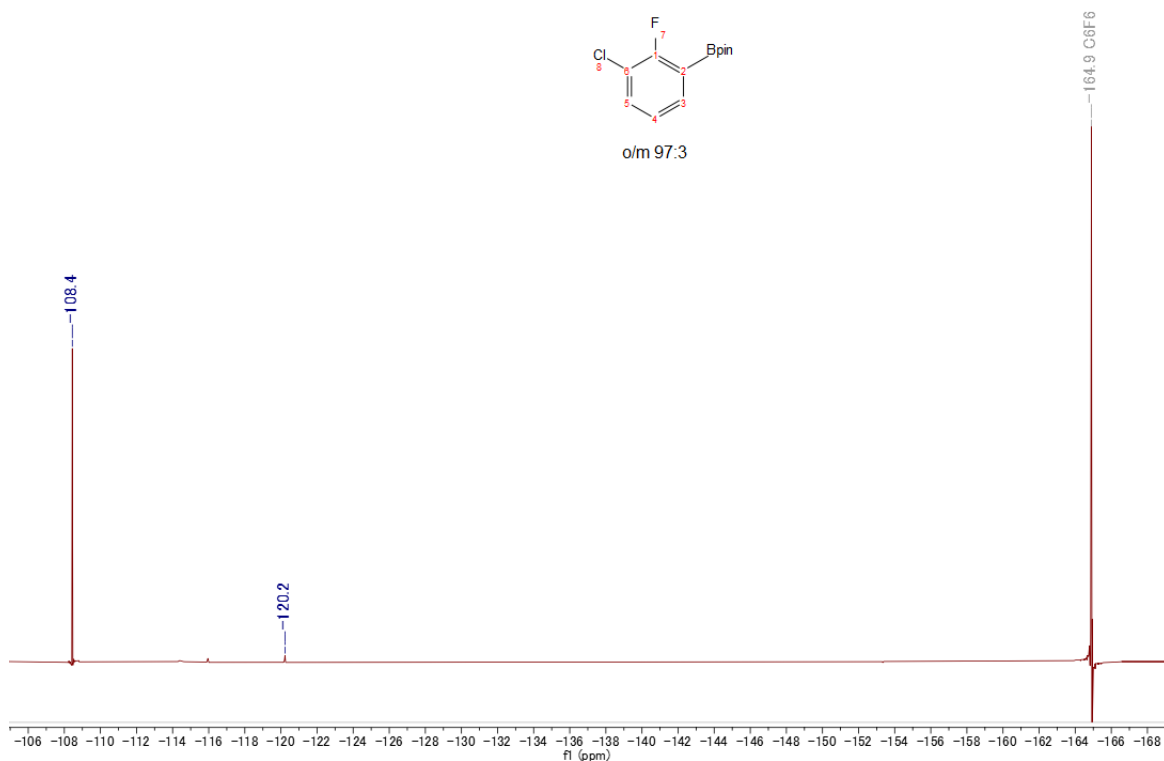


Figure S76. ^{19}F NMR spectra (CDCl_3) of 2b.

JK 72-9-6 isolation fr7-37
single_pulse

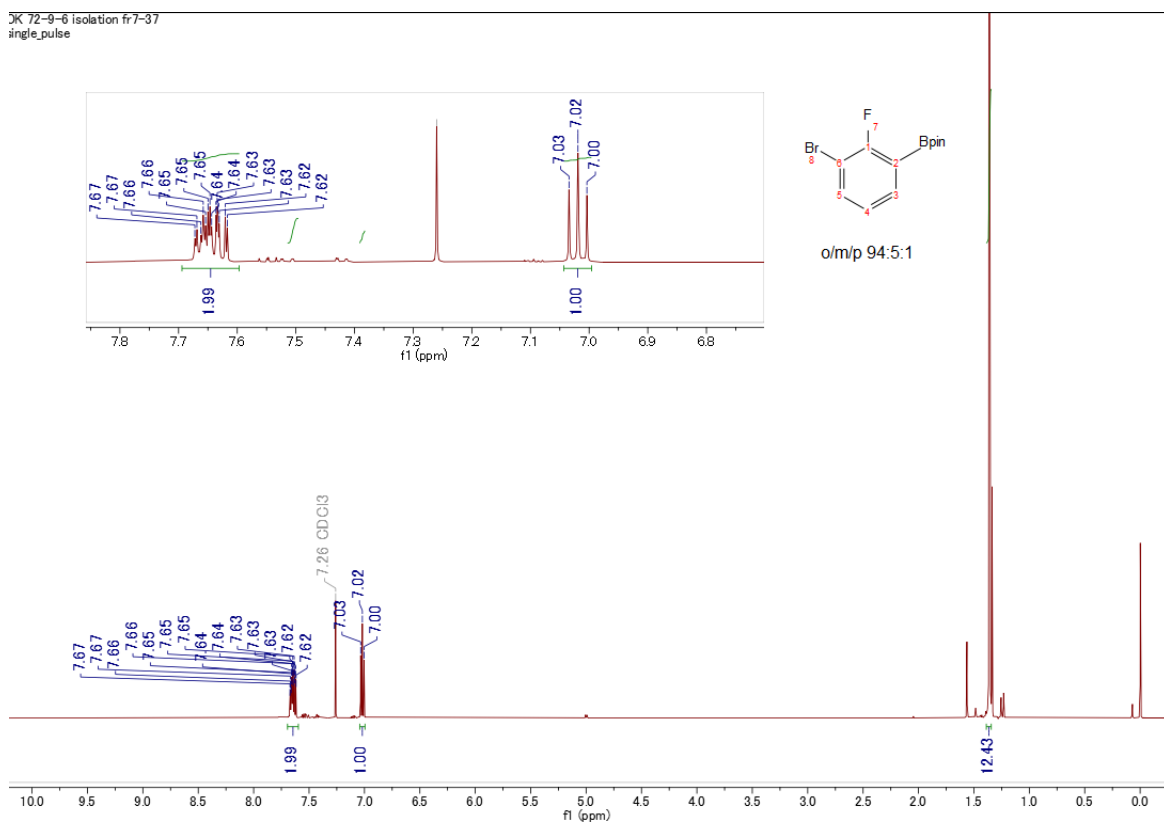
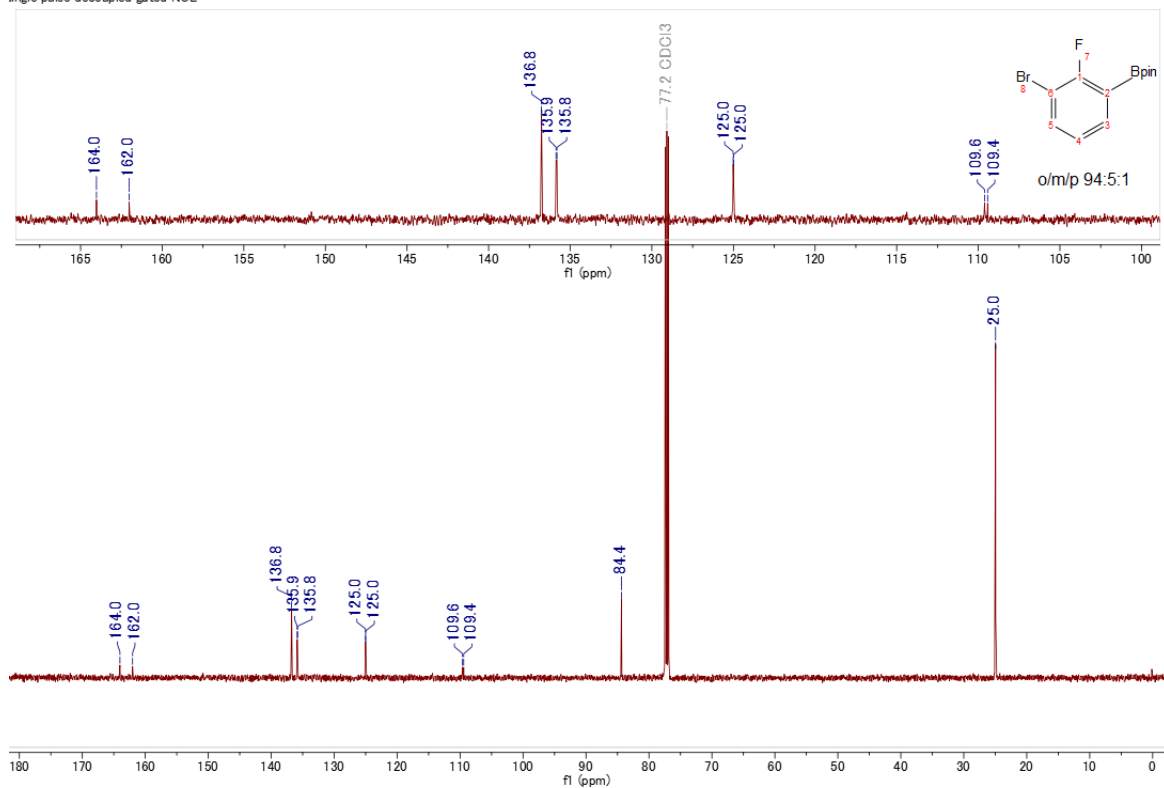
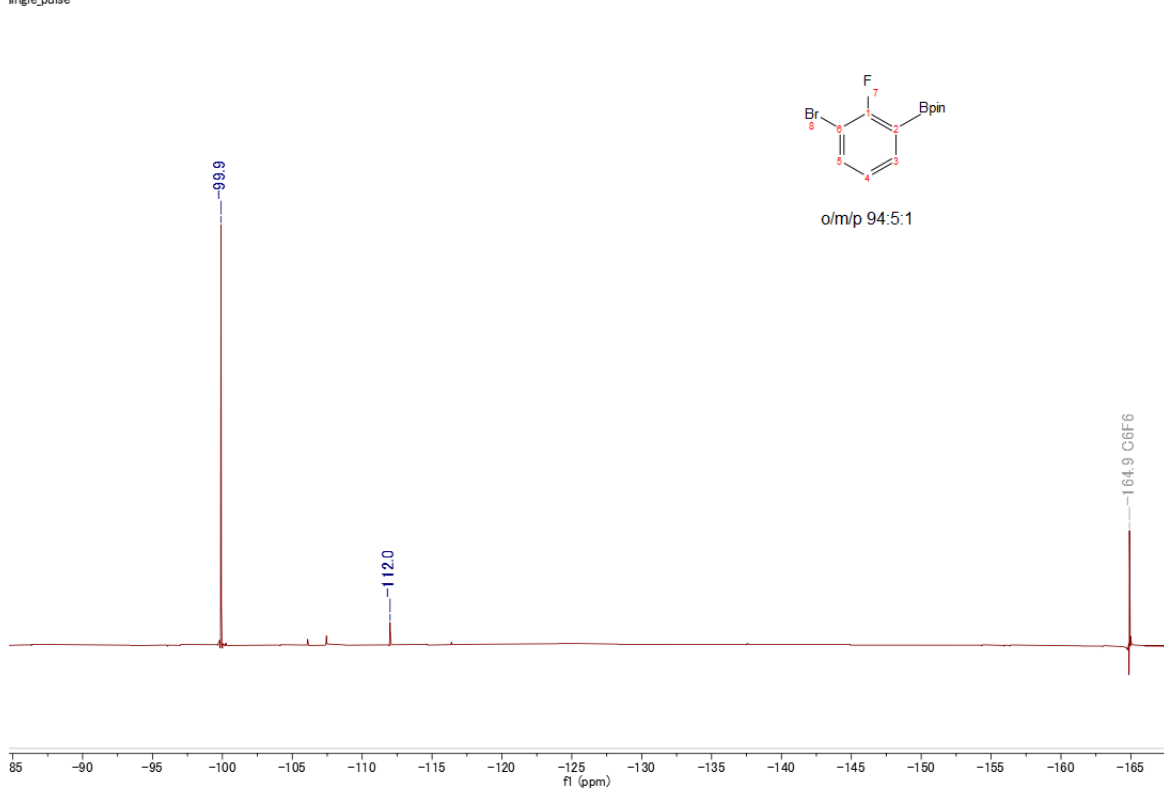


Figure S77. ^1H NMR spectra (CDCl_3) of 2c.

JK 72-9-6 isolation fr 7-37
single pulse decoupled gated NOE



JK 72-9-6 isolation fr 7-37
single_pulse



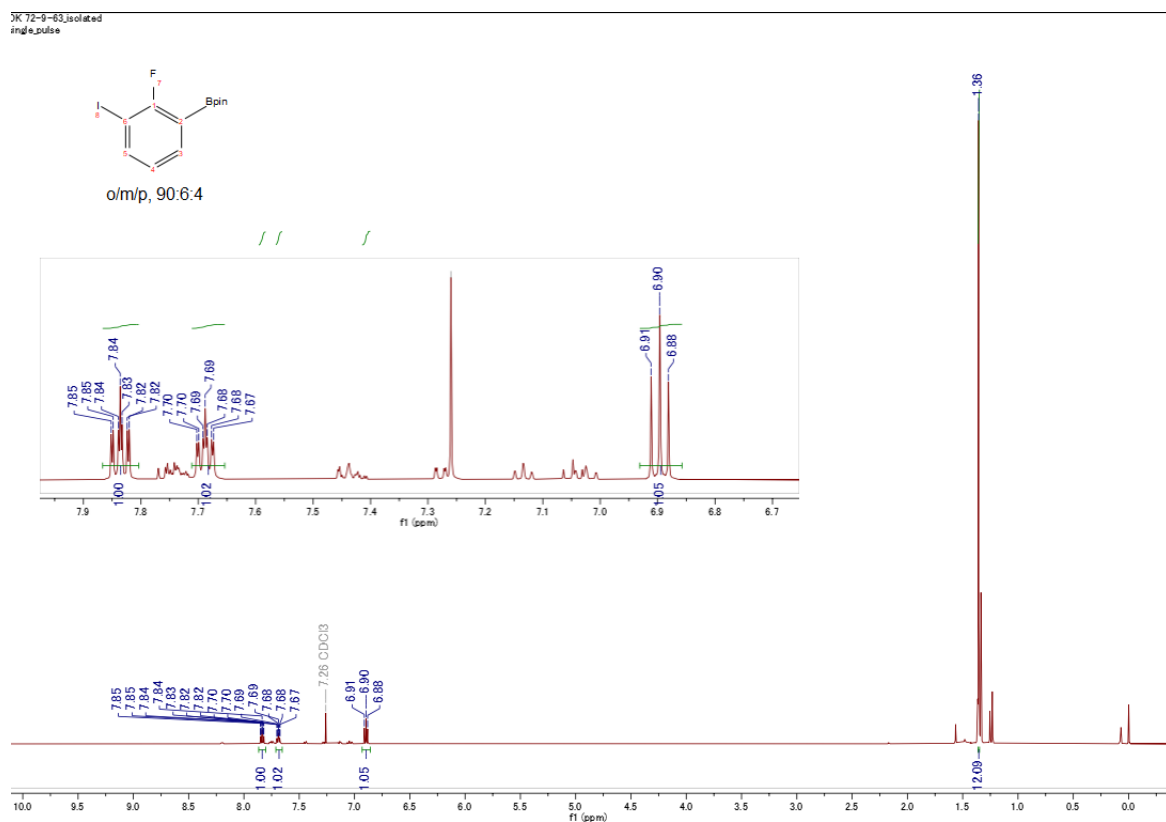


Figure S80. ¹H NMR spectra (CDCl₃) of 2d.

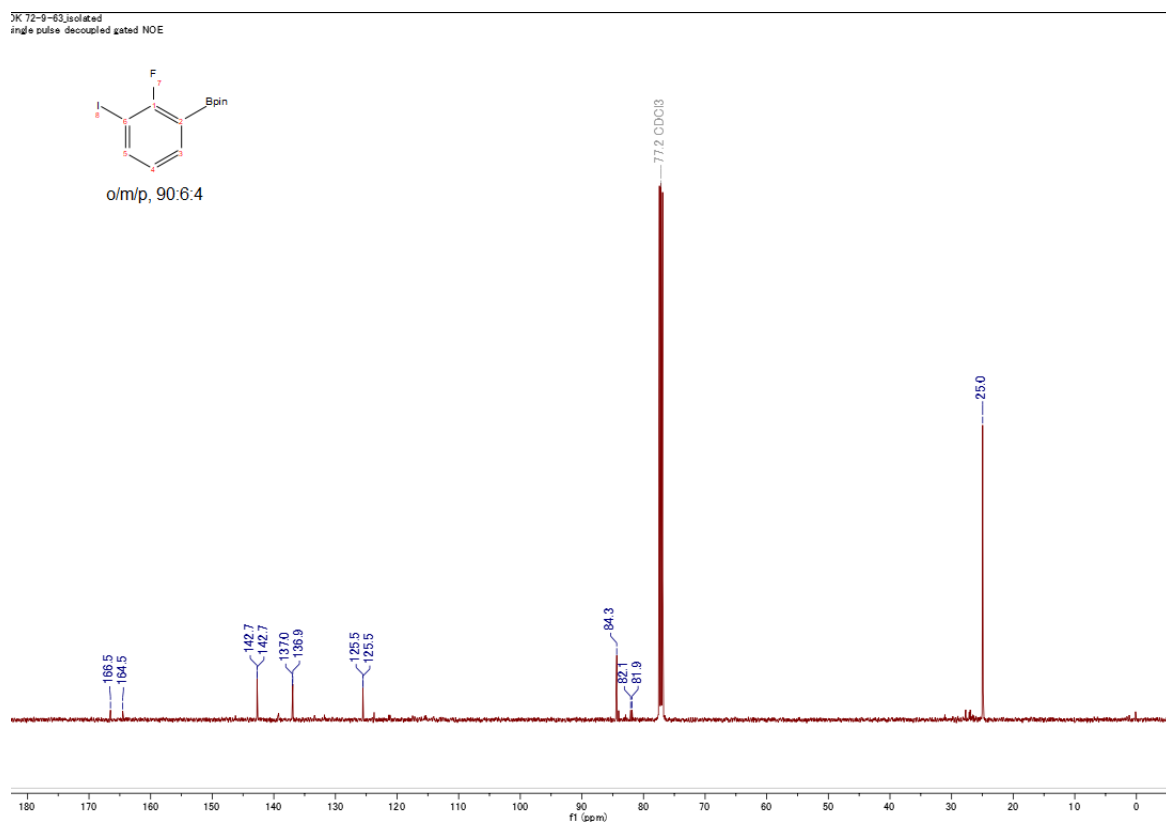


Figure S81. ¹³C{¹H} NMR spectra (CDCl₃) of 2d.

JK 72-9-63_isolated
angle_pulse

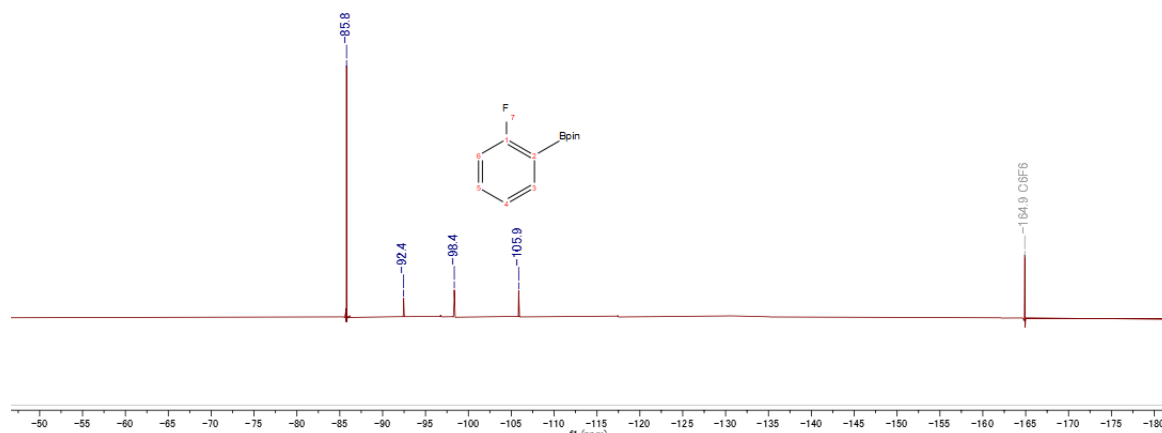
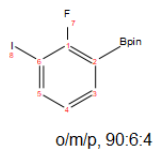


Figure S82. ¹⁹F NMR spectra (CDCl₃) of **2d**.

JK 72-9-28_isolated high 0
angle_pulse

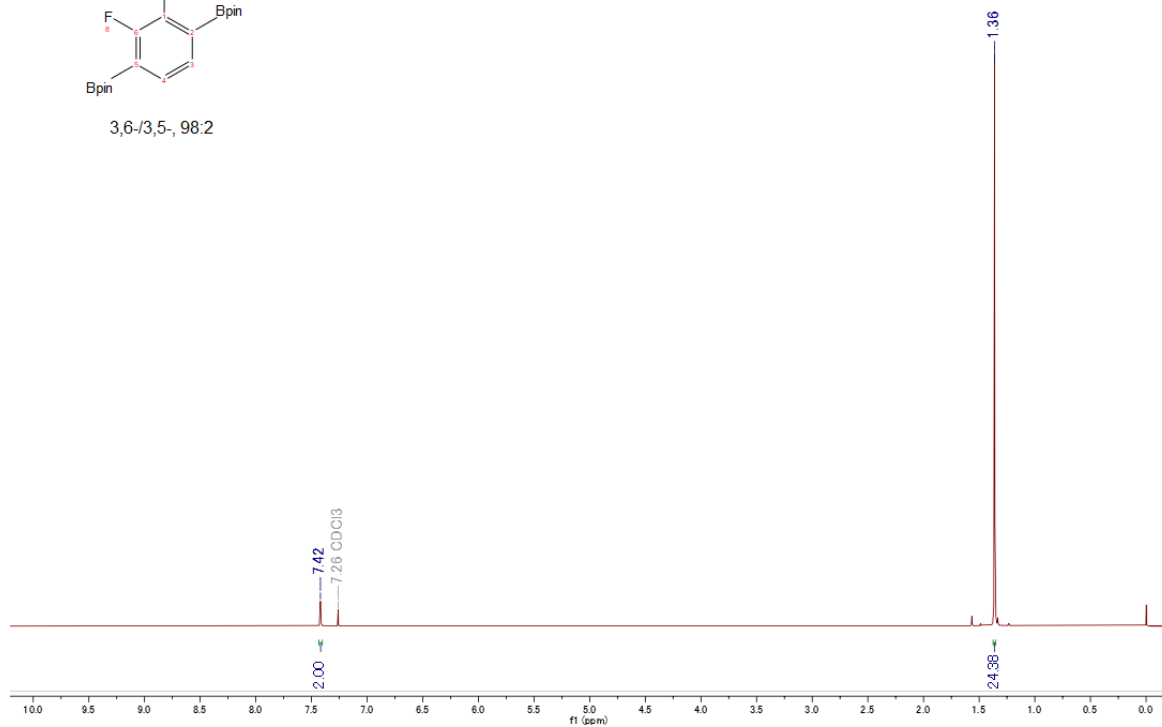
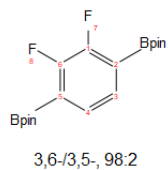


Figure S83. ¹H NMR spectra (CDCl₃) of **2e**.

JK 72-9-28, isolated high O
single pulse decoupled gated NOE

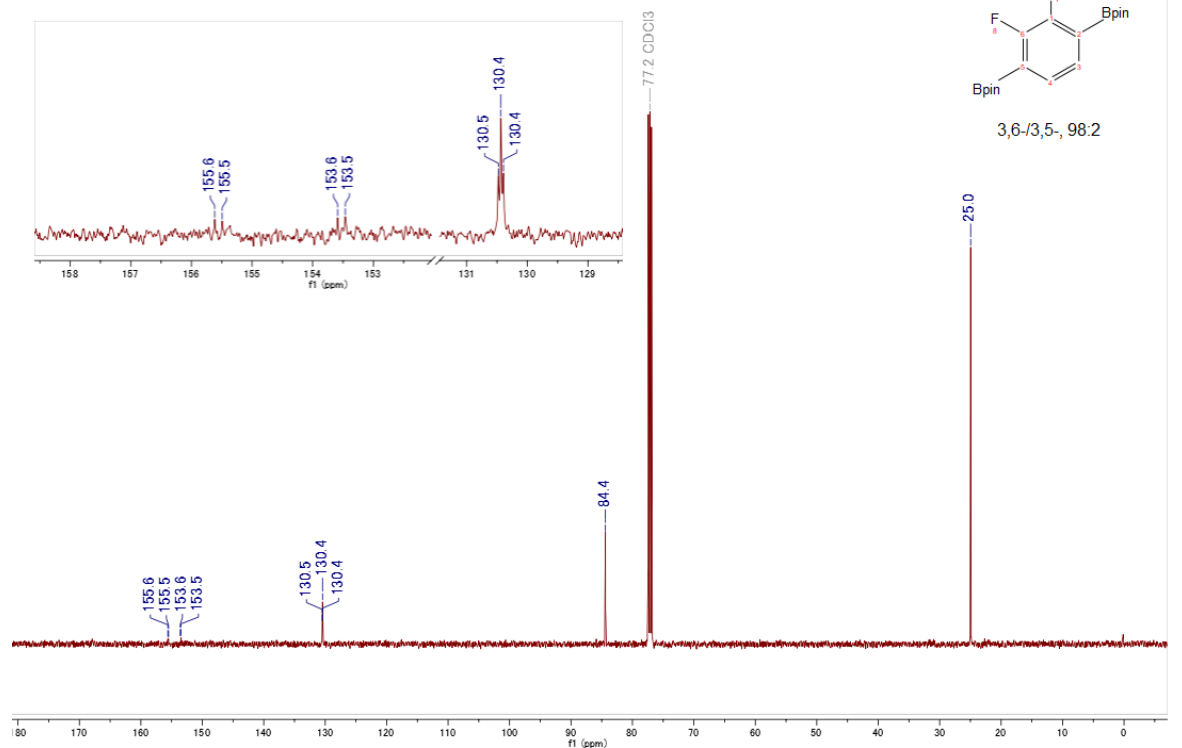


Figure S84. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **2e**.

JK 72-9-28, isolated high O
single pulse

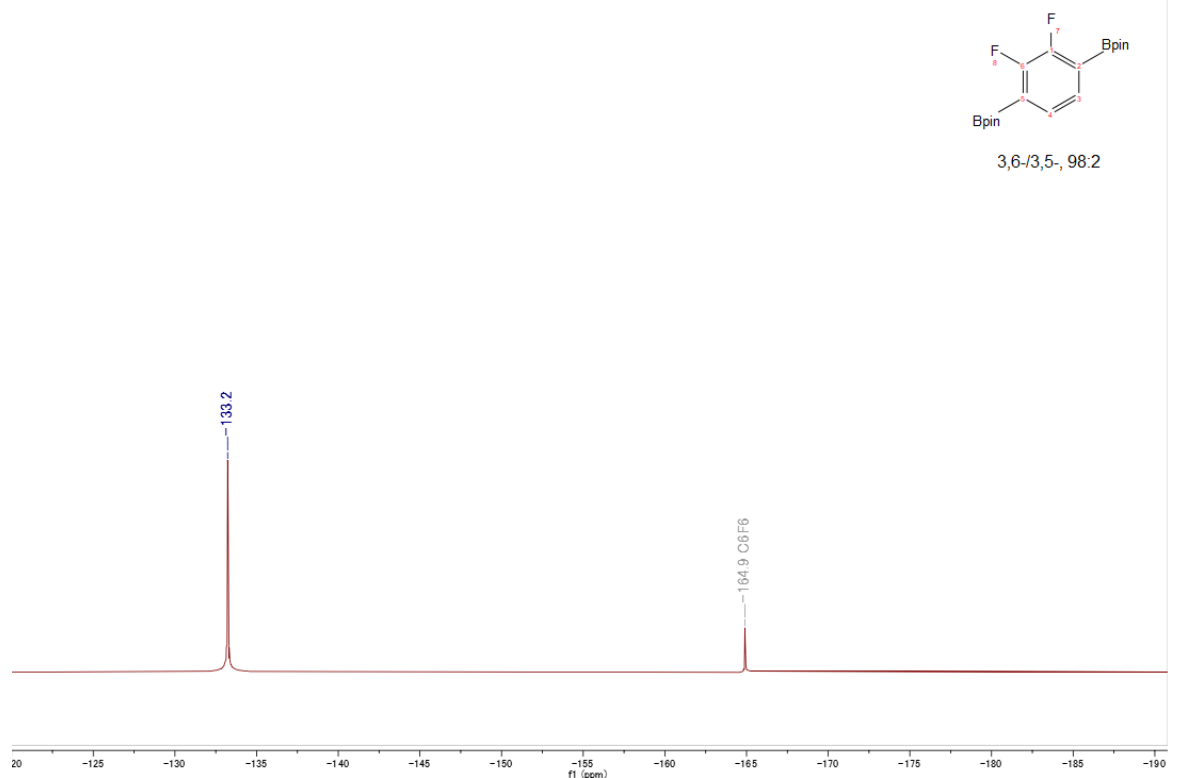


Figure S85. ^{19}F NMR spectra (CDCl_3) of **2e**.

JK 72-9-64_isol
single_pulse

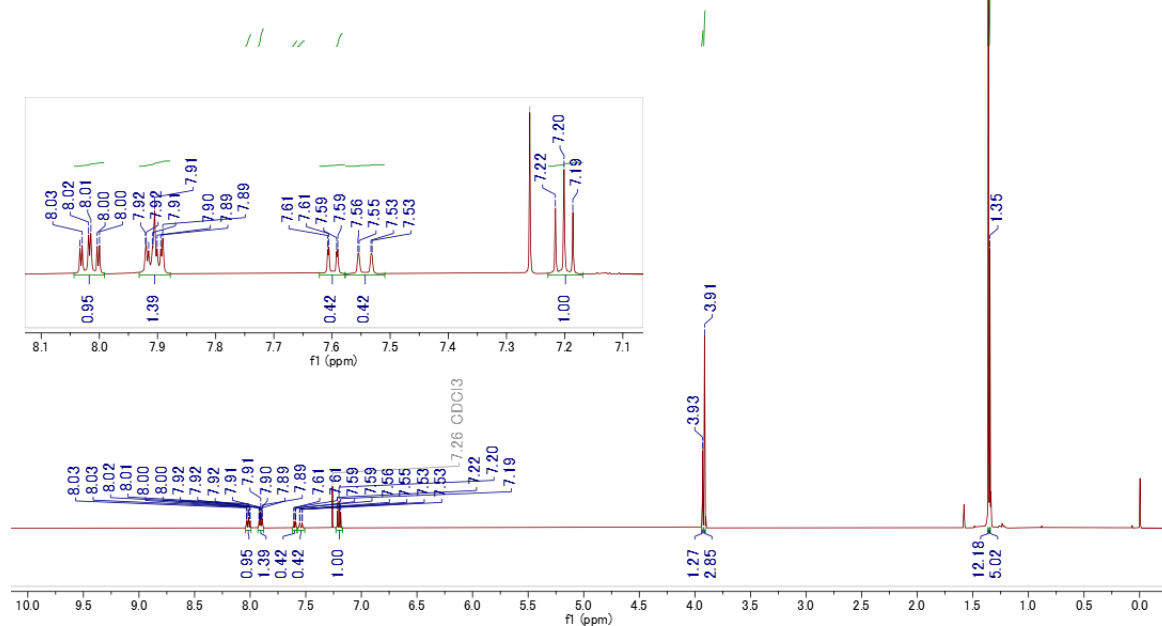
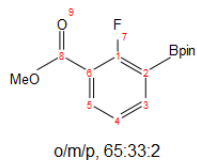


Figure S86. ^1H NMR spectra (CDCl_3) of **2f**.

JK 72-9-64_isol
single_pulse decoupled gated NOE

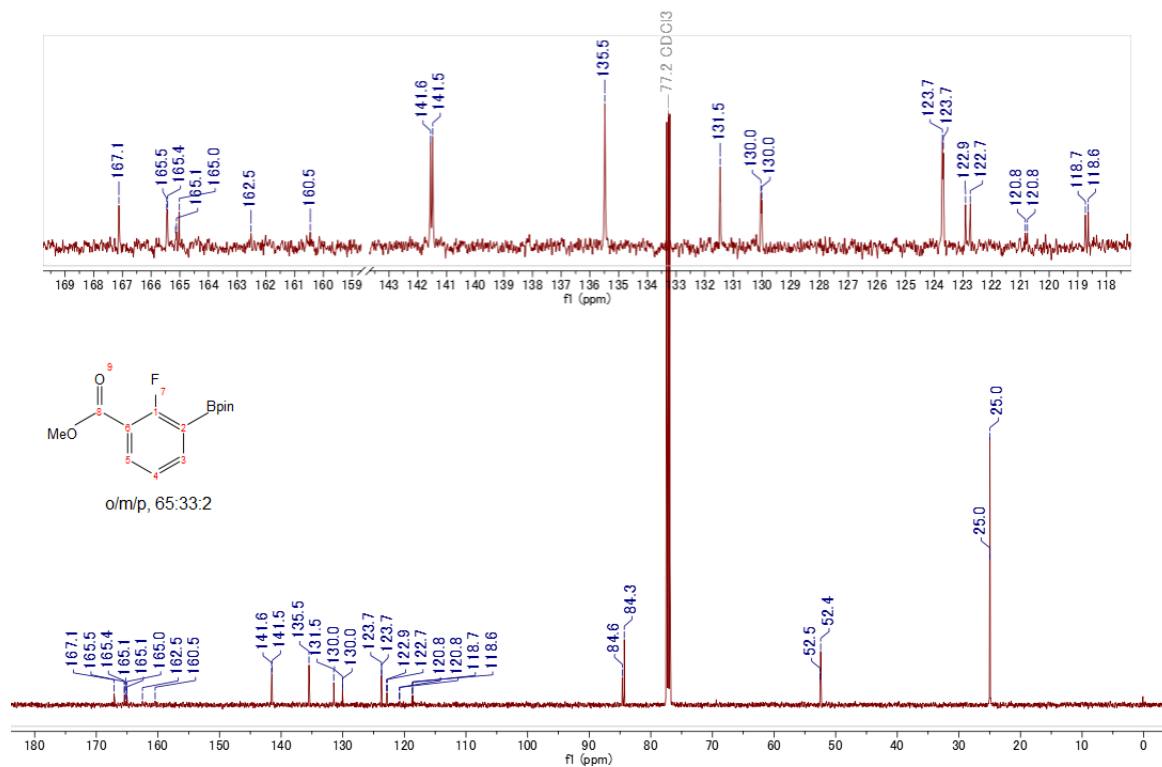
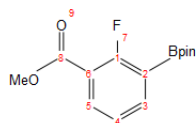


Figure S87. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **2f**.

JK 72-9-64_isolated_19F
single_pulse



o/m/p, 65.33:2

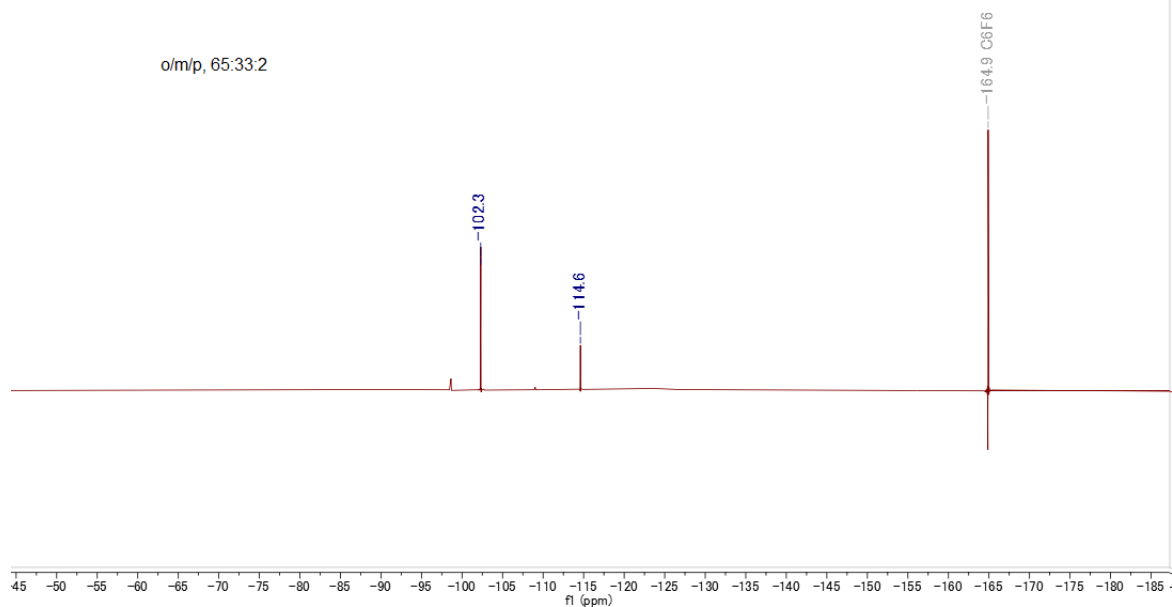
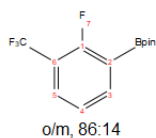


Figure S88. ^{19}F NMR spectra (CDCl_3) of **2f**.

JK 72-9-78_isolated_f14-10
single_pulse



o/m, 86:14

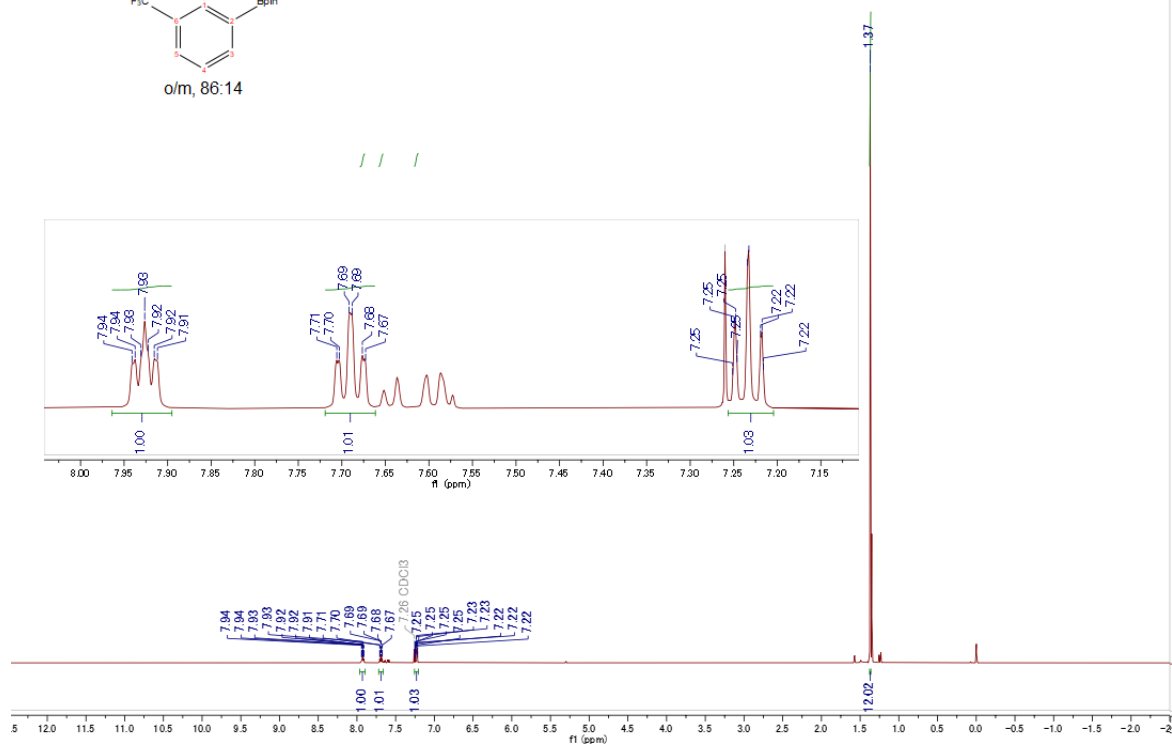


Figure S89. ^1H NMR spectra (CDCl_3) of **2g**.

JK 72-9-69_isolated.f14-10
single_pulse decoupled gated NOE

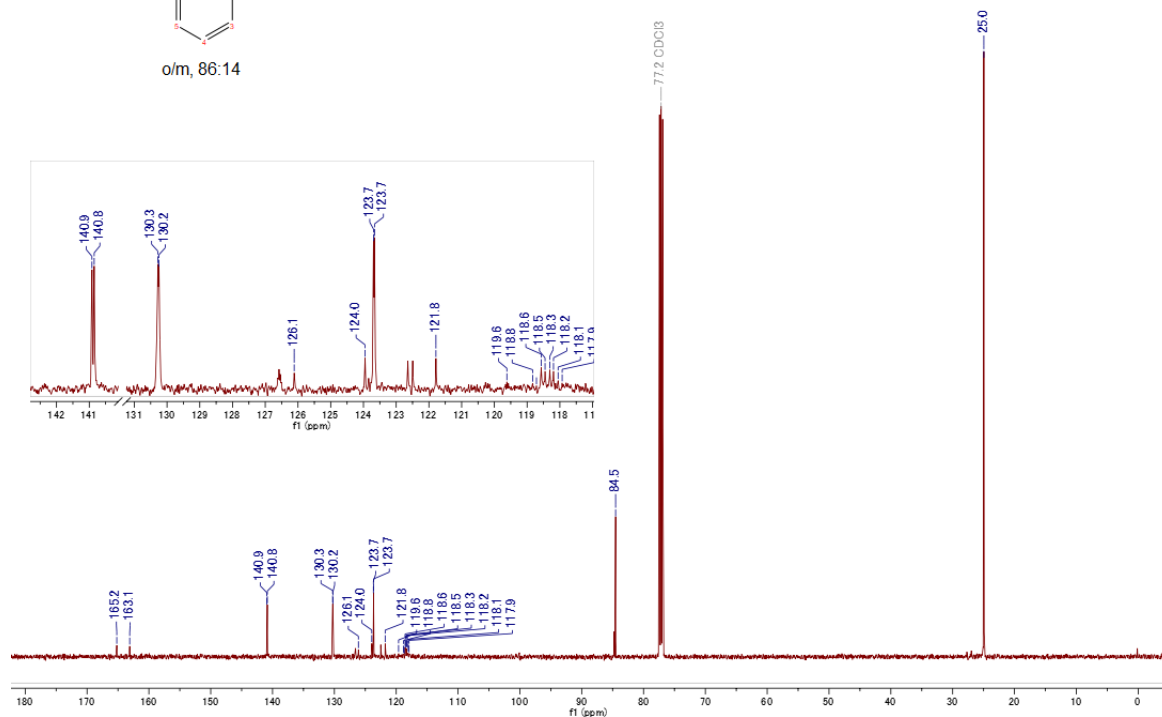
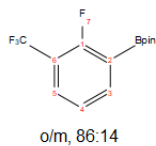


Figure S90. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **2g**.

JK 72-9-69_isolated.f14-10
single_pulse

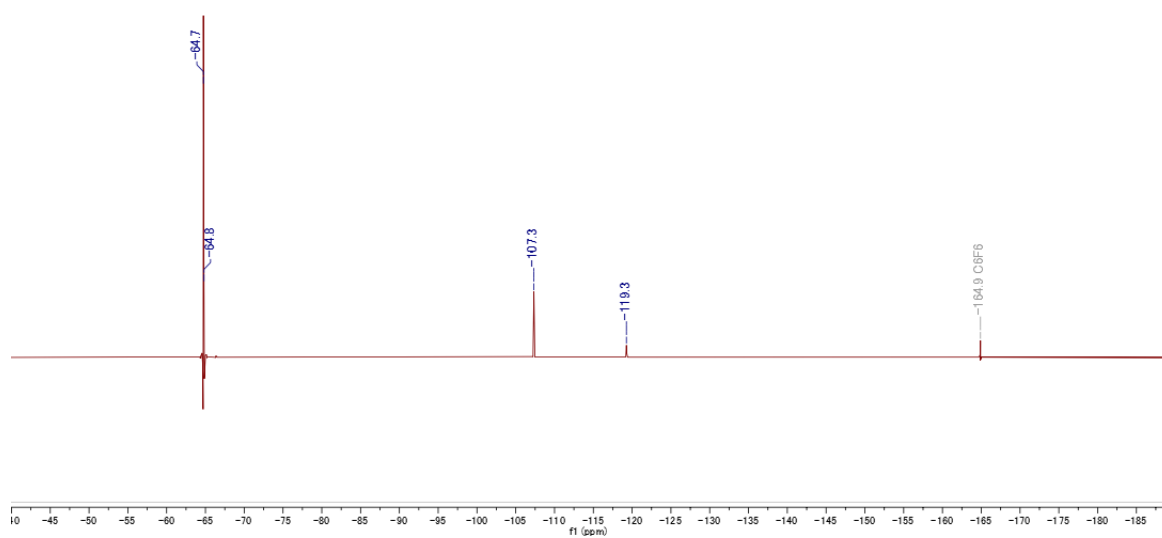
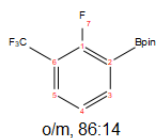


Figure S91. ^{19}F NMR spectra (CDCl_3) of **2g**.

JK 72-9-27 f#28-32
single_pulse

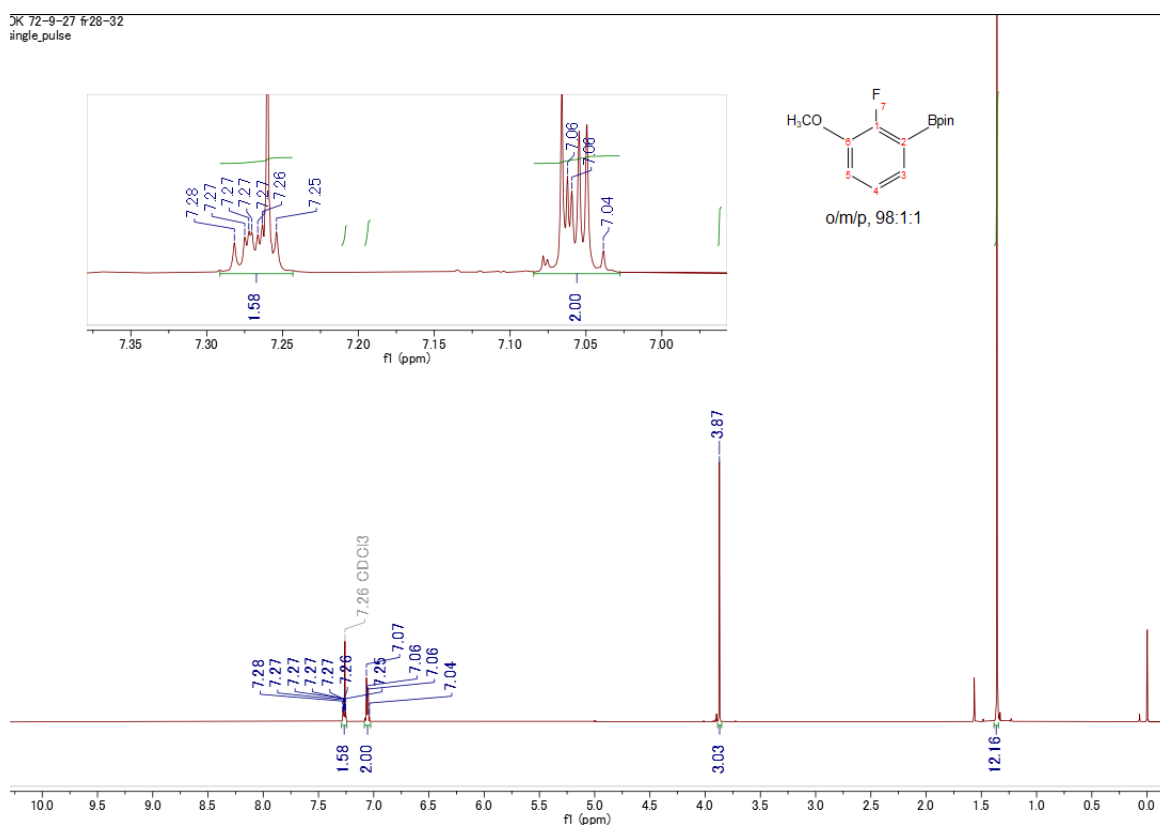


Figure S92. ^1H NMR spectra (CDCl_3) of 2h.

JK 72-9-27 f#28-32
single_pulse decoupled gated NOE

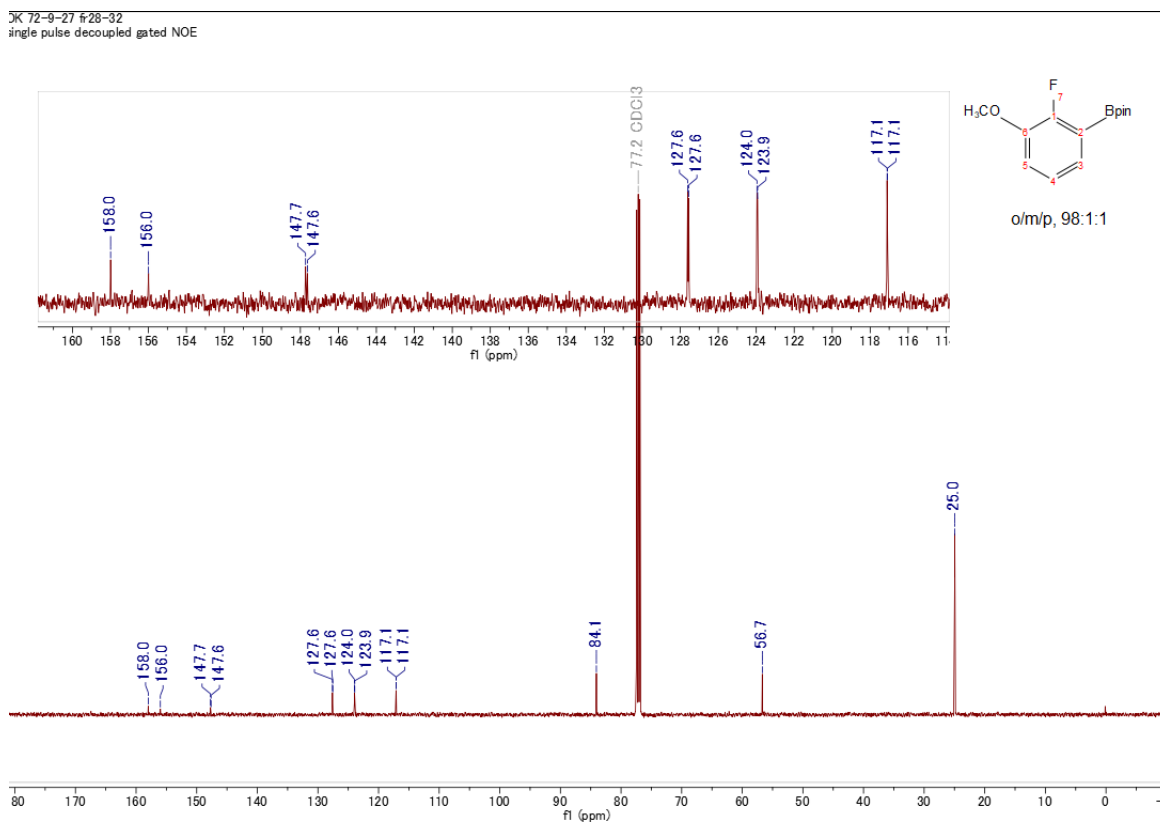


Figure S93. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of 2h.

JK 72-9-27 f28-32 1
single_pulse

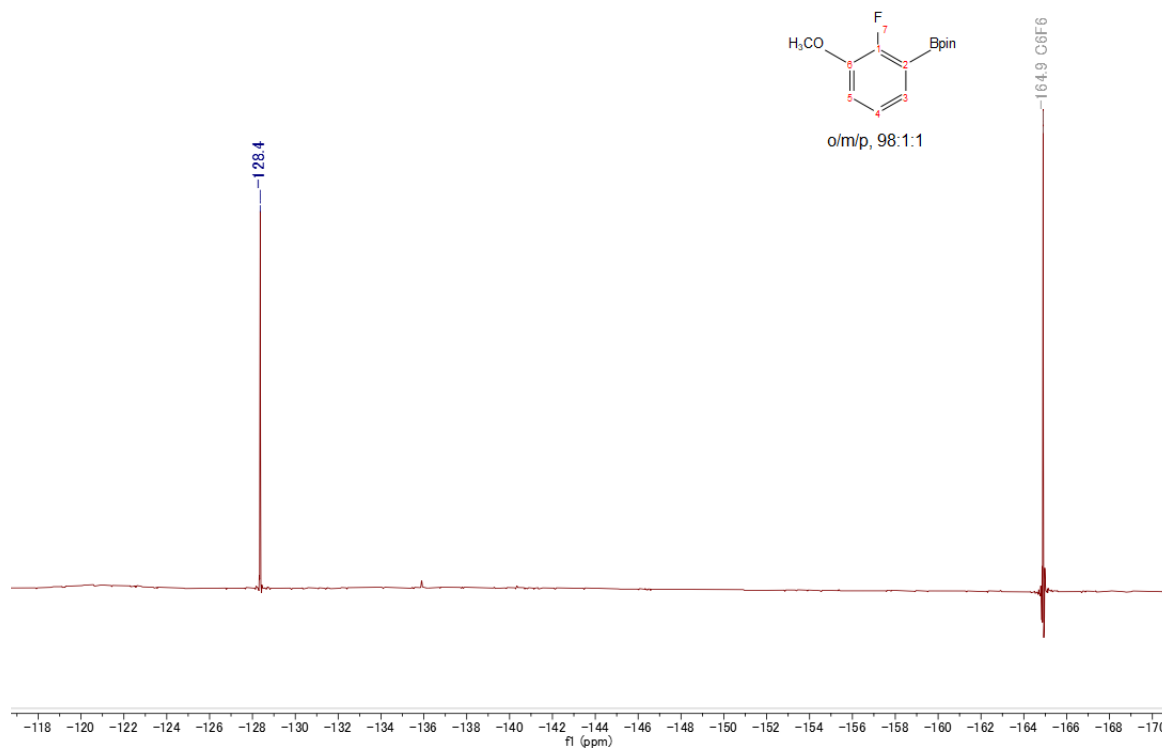


Figure S94. ¹⁹F NMR spectra (CDCl₃) of **2h**.

JK 72-9-79 isolated
single_pulse

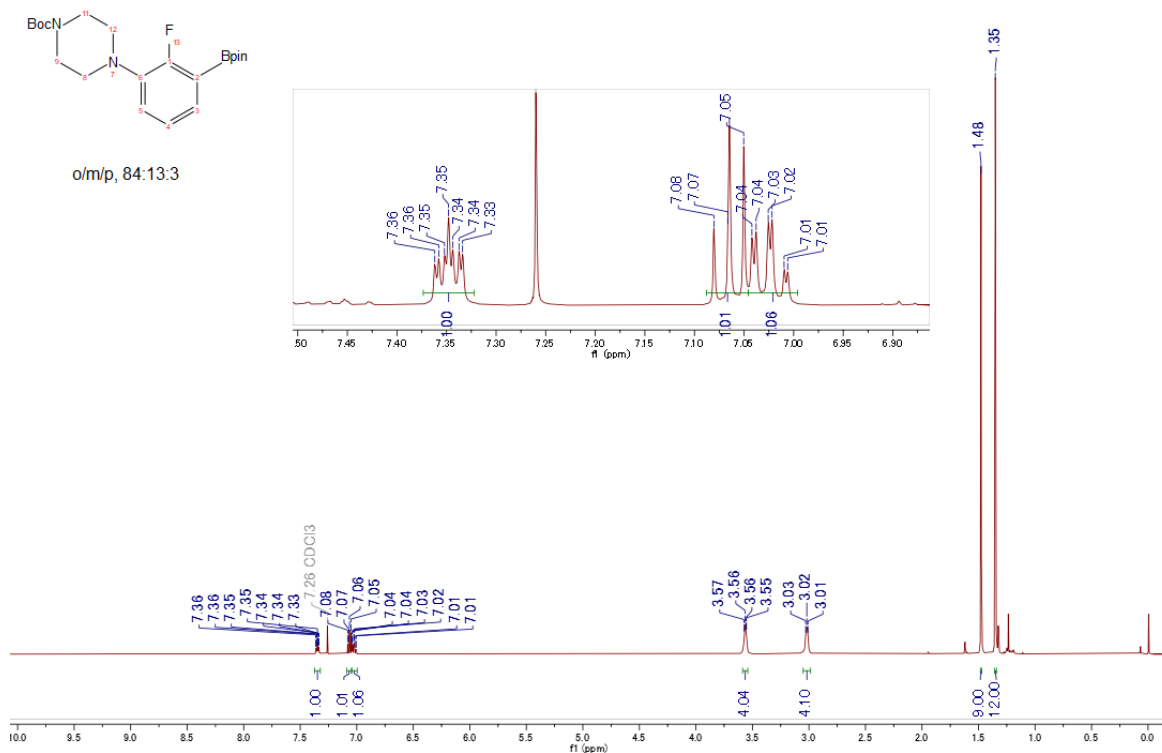
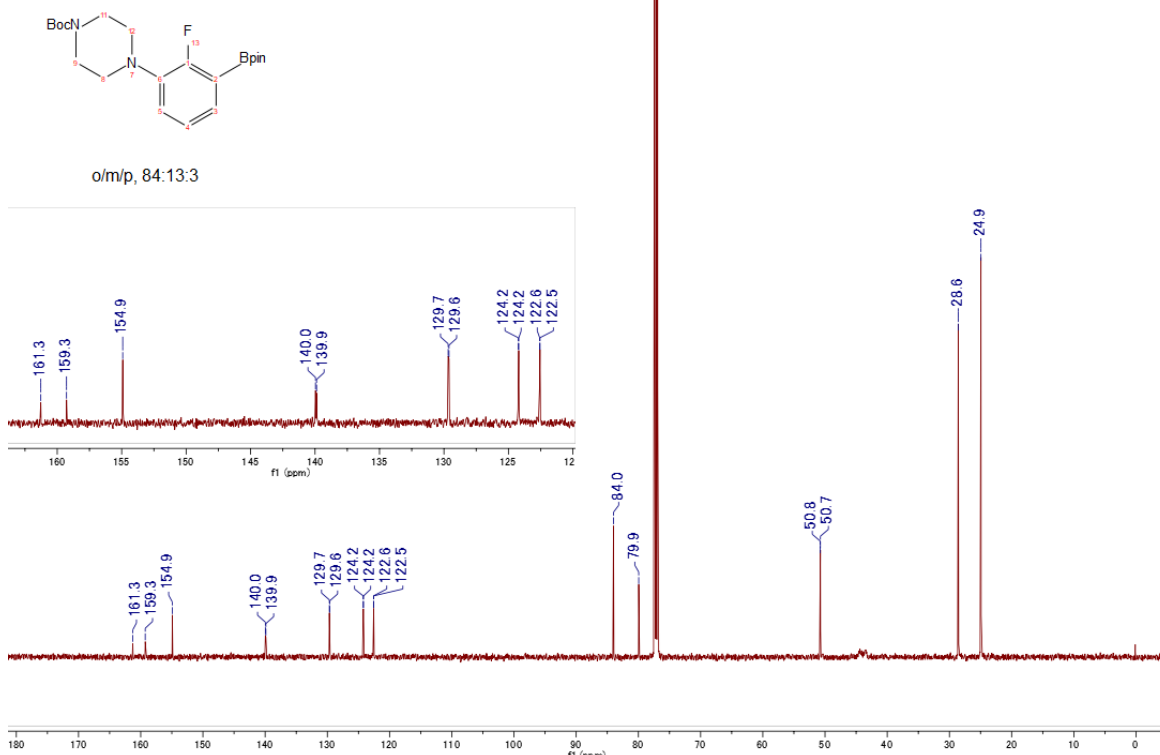
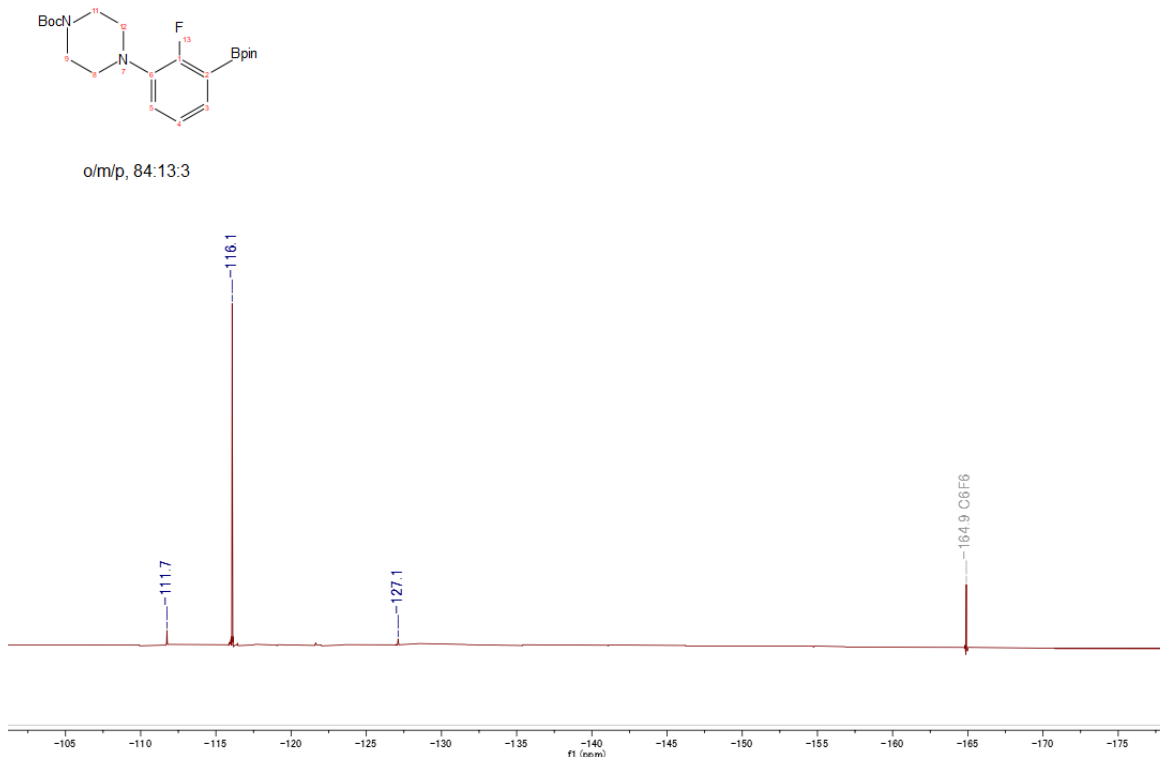


Figure S95. ¹H NMR spectra (CDCl₃) of **2i**.

JK 72-9-79 isolated
single pulse decoupled gated NOE



JK 72-9-79 isolated
single pulse



JK 72-9-11_isolated_highC
single_pulse

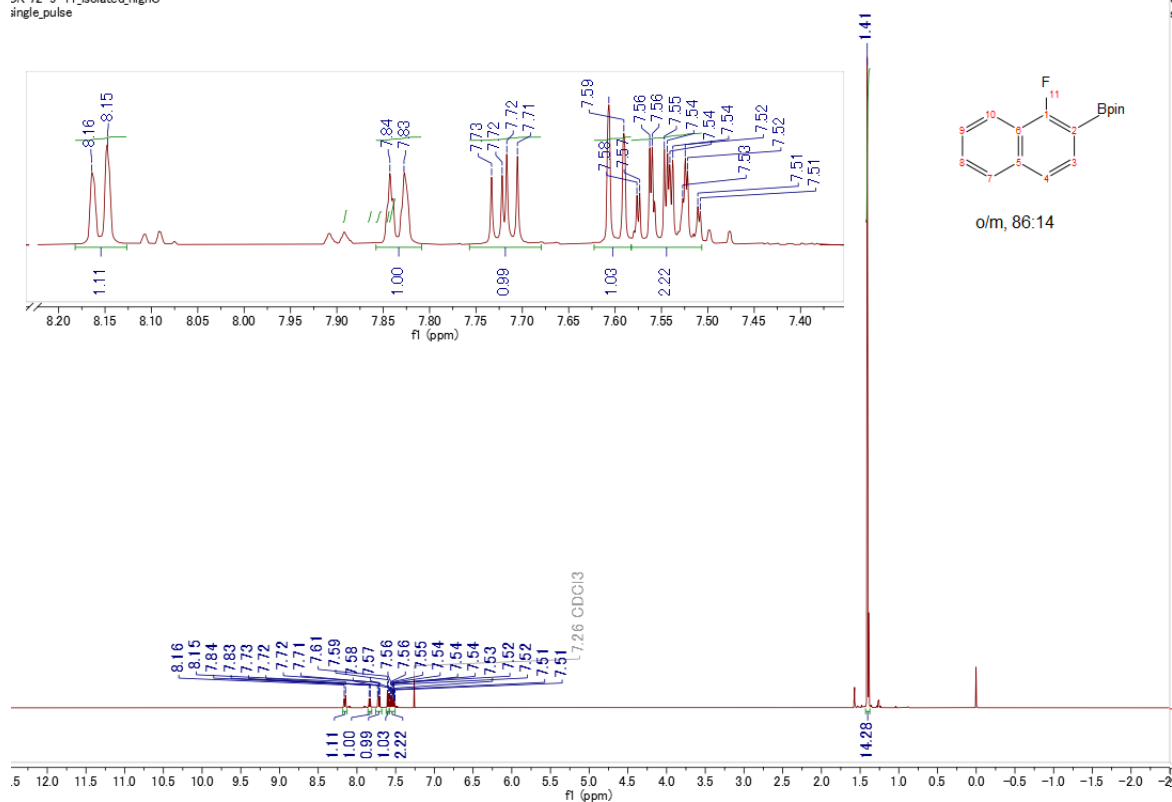


Figure S98. ¹H NMR spectra (CDCl₃) of 2j.

JK 72-9-11_isolated_highC
single_pulse decoupled gated NOE

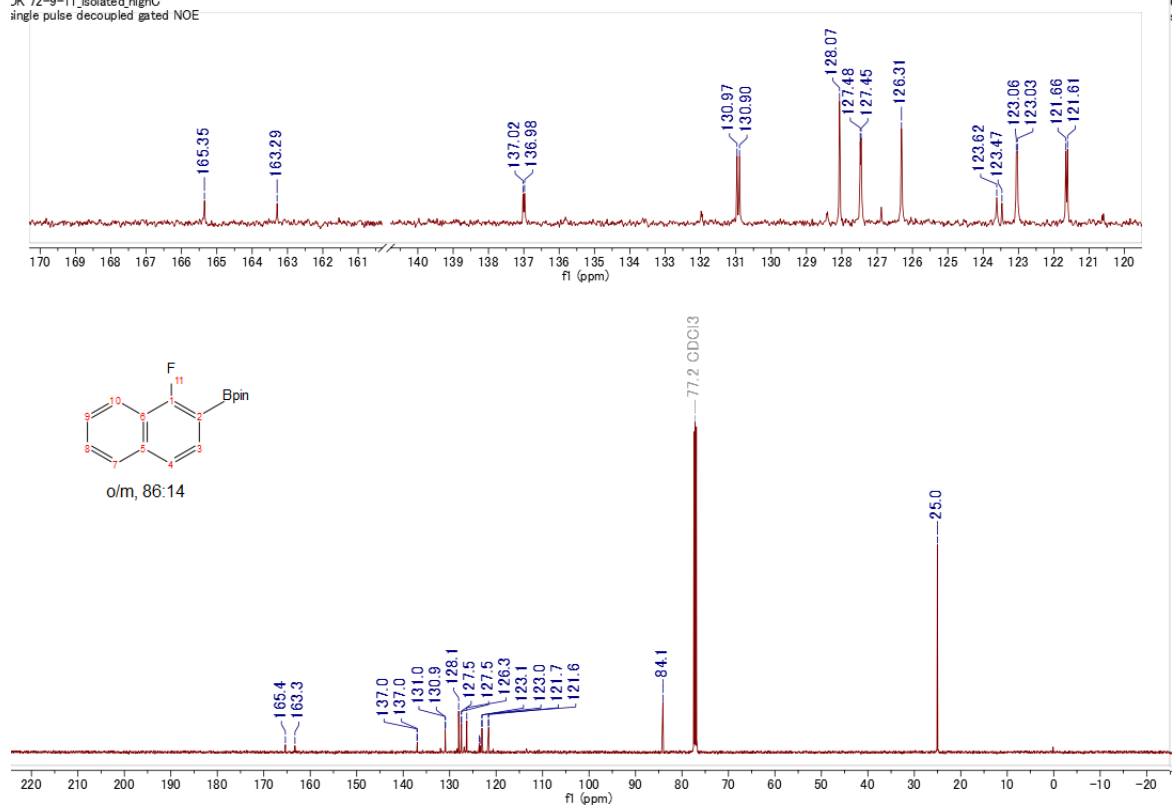
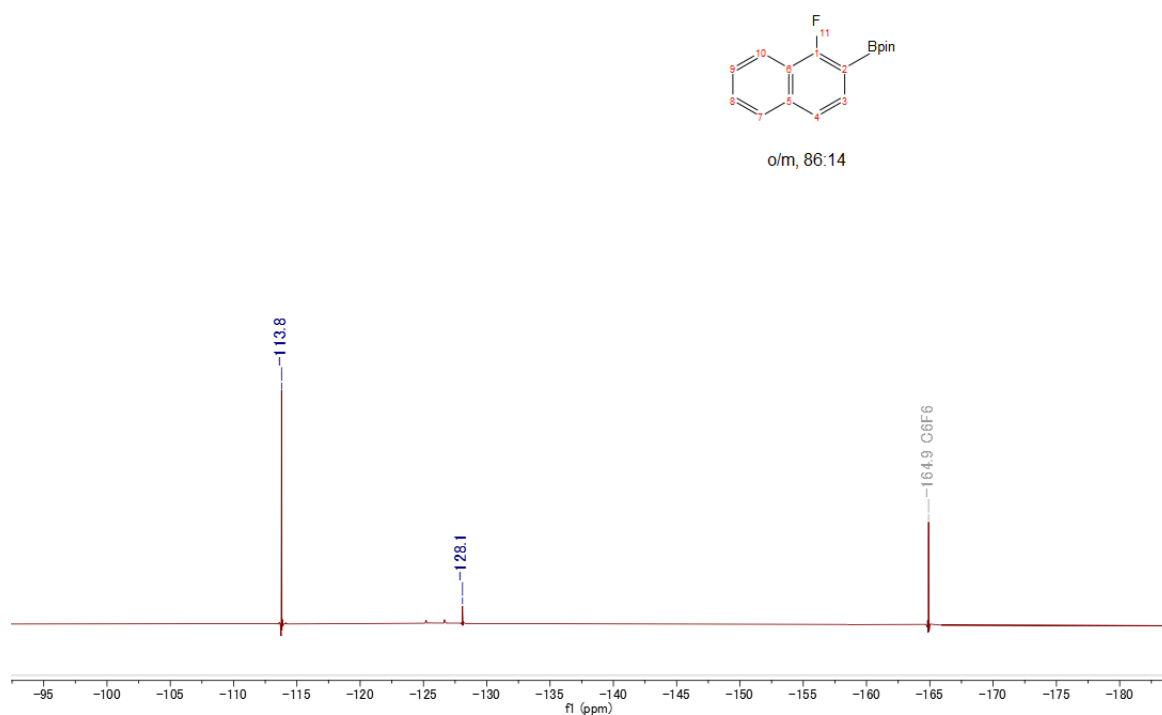
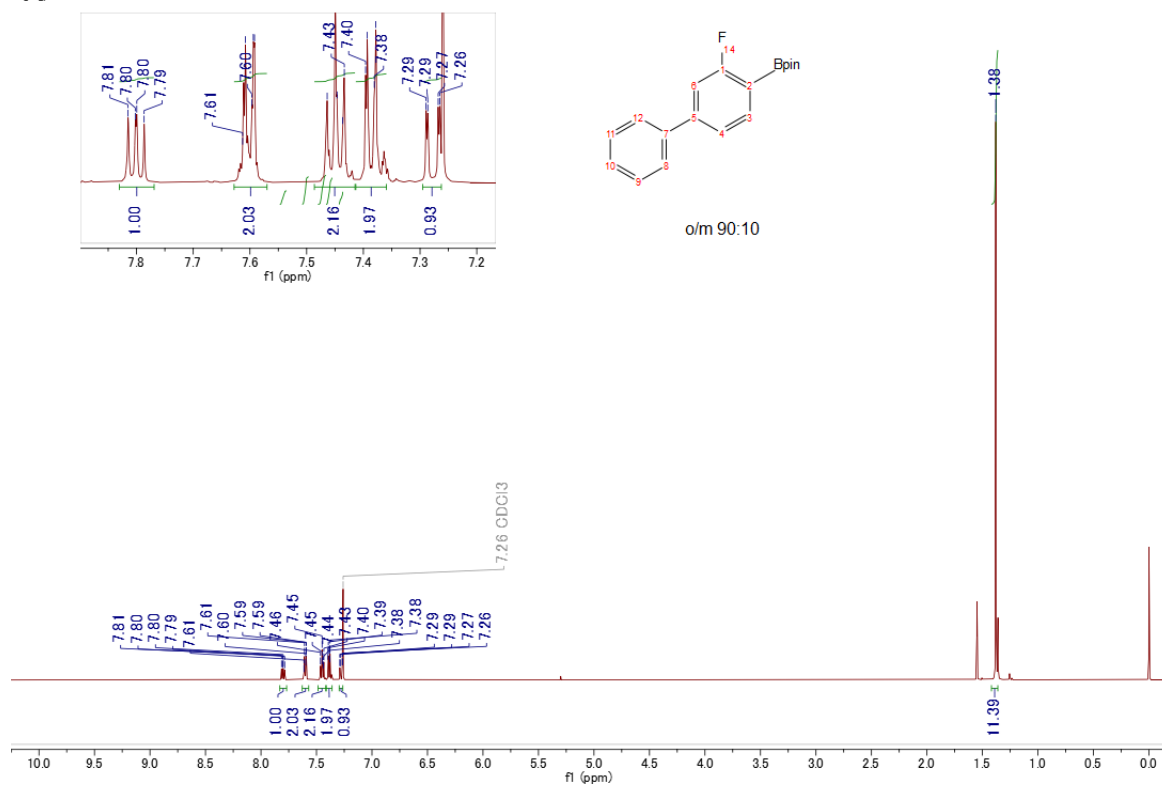


Figure S99. ¹³C{¹H} NMR spectra (CDCl₃) of 2j.

JK 72-9-11_isolated_highC
single_pulse



JK 72-9-4 GPC fr.4,5
single_pulse



OK 72-9-4 isolated, 13C
single pulse decoupled gated NOE

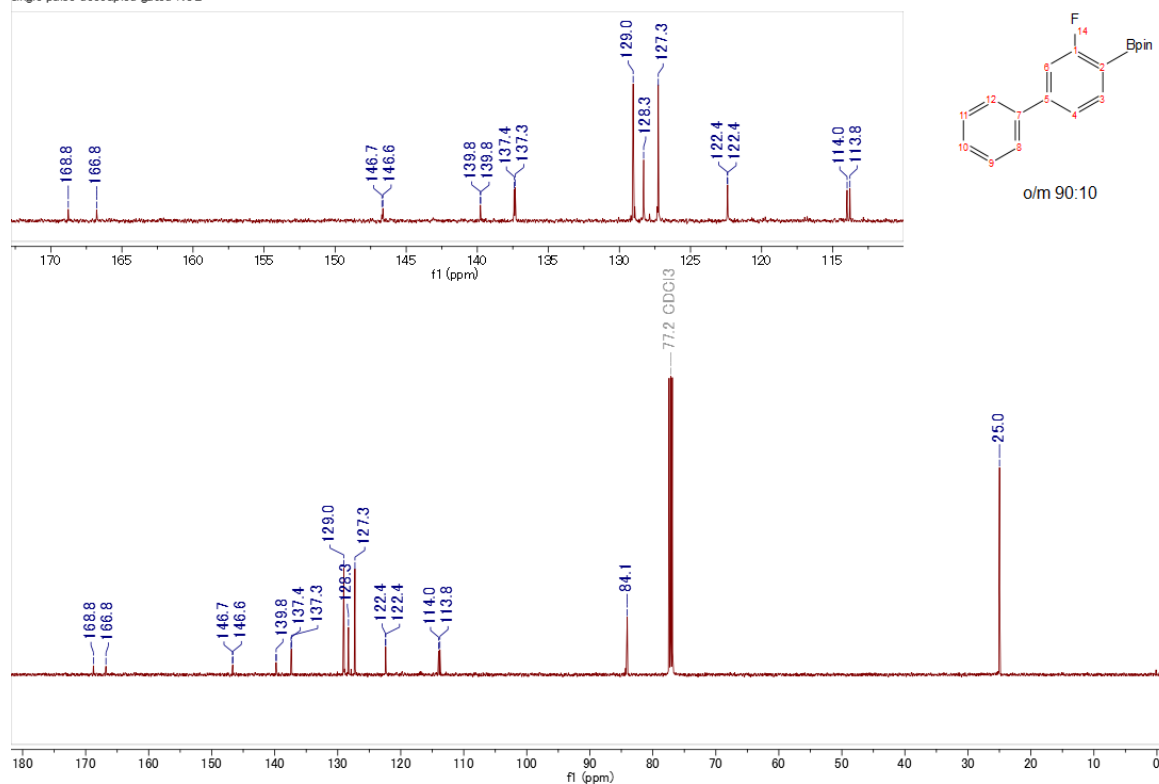


Figure S102. ¹³C{¹H} NMR spectra (CDCl₃) of 2k.

OK 72-9-4 GPC fr.4,5
single pulse

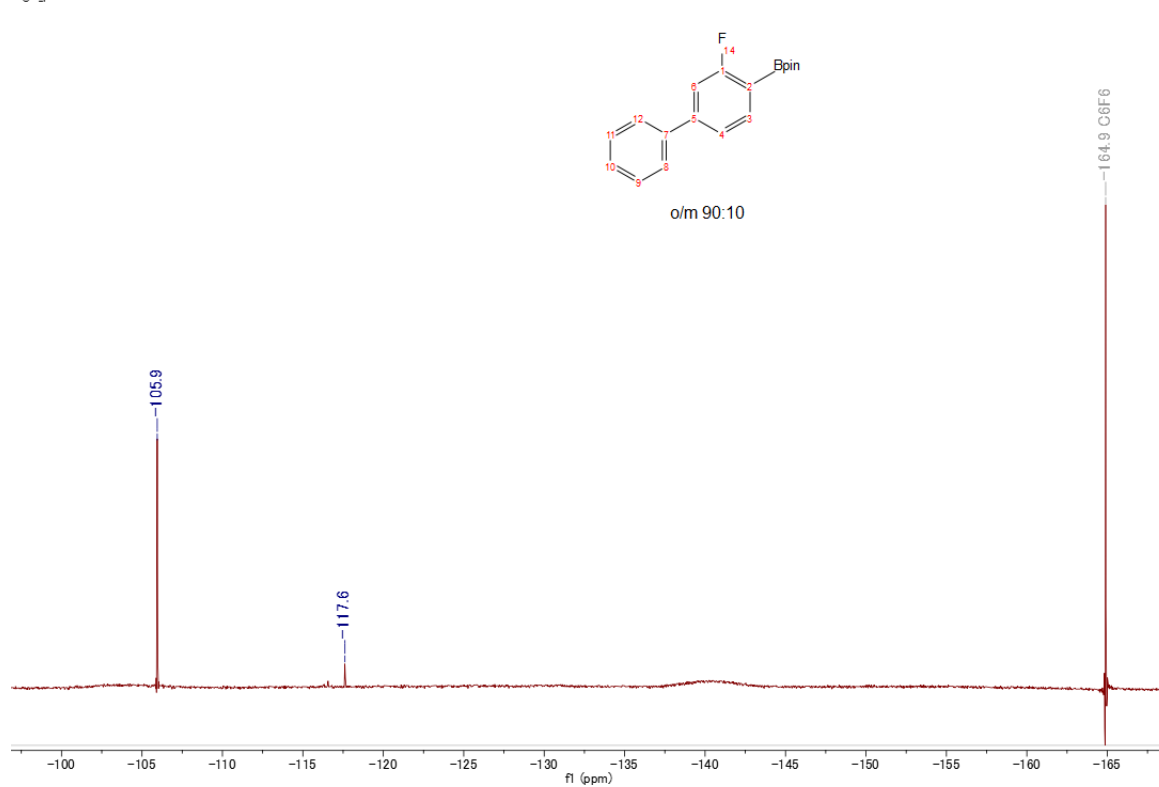


Figure S103. ¹⁹F NMR spectra (CDCl₃) of 2k.

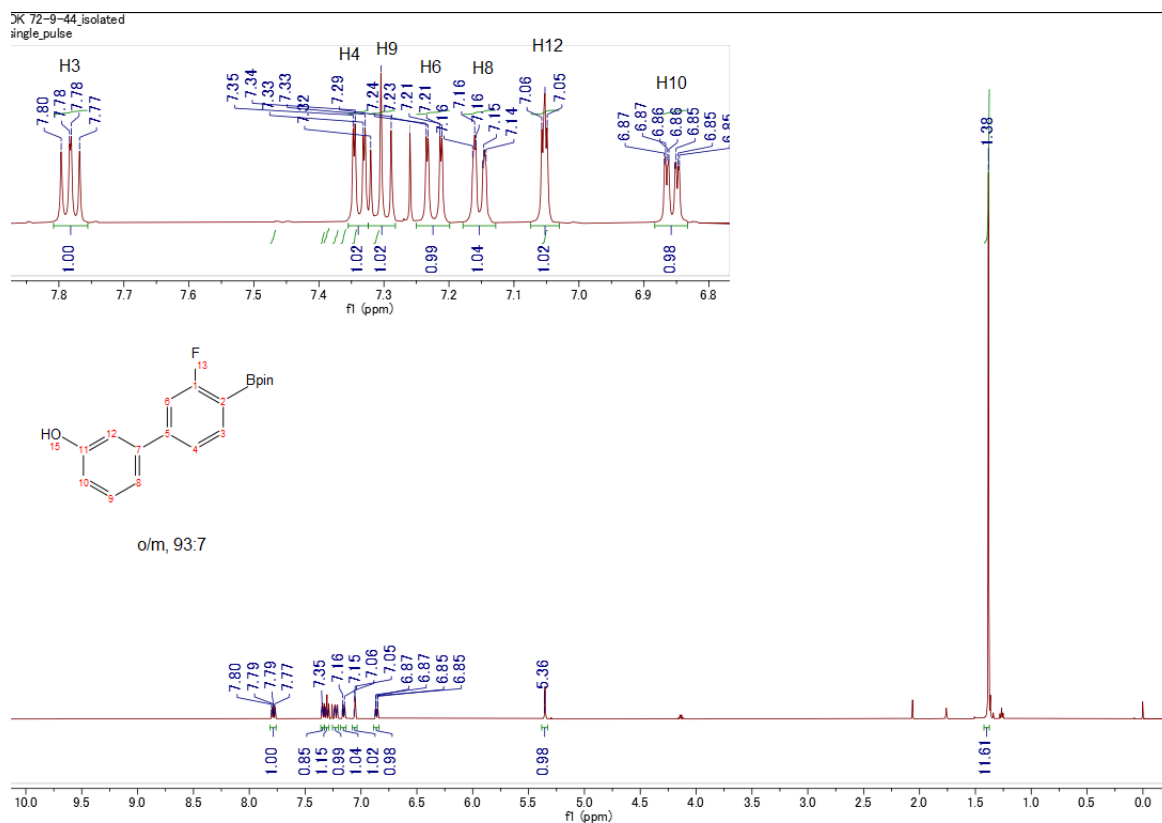


Figure S104. ¹H NMR spectra (CDCl₃) of 2I.

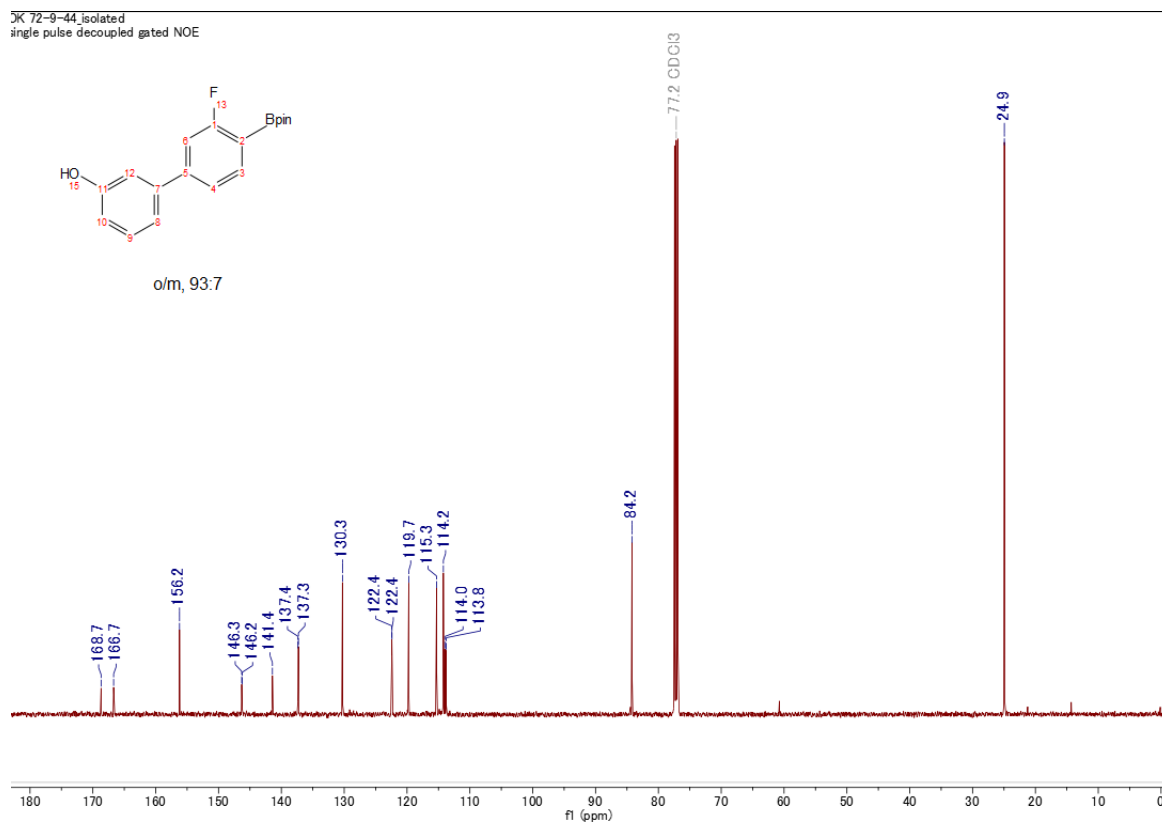


Figure S105. ¹³C NMR spectra (CDCl₃) of 2I.

JK 72-9-44_isolated_19F
angle_pulse

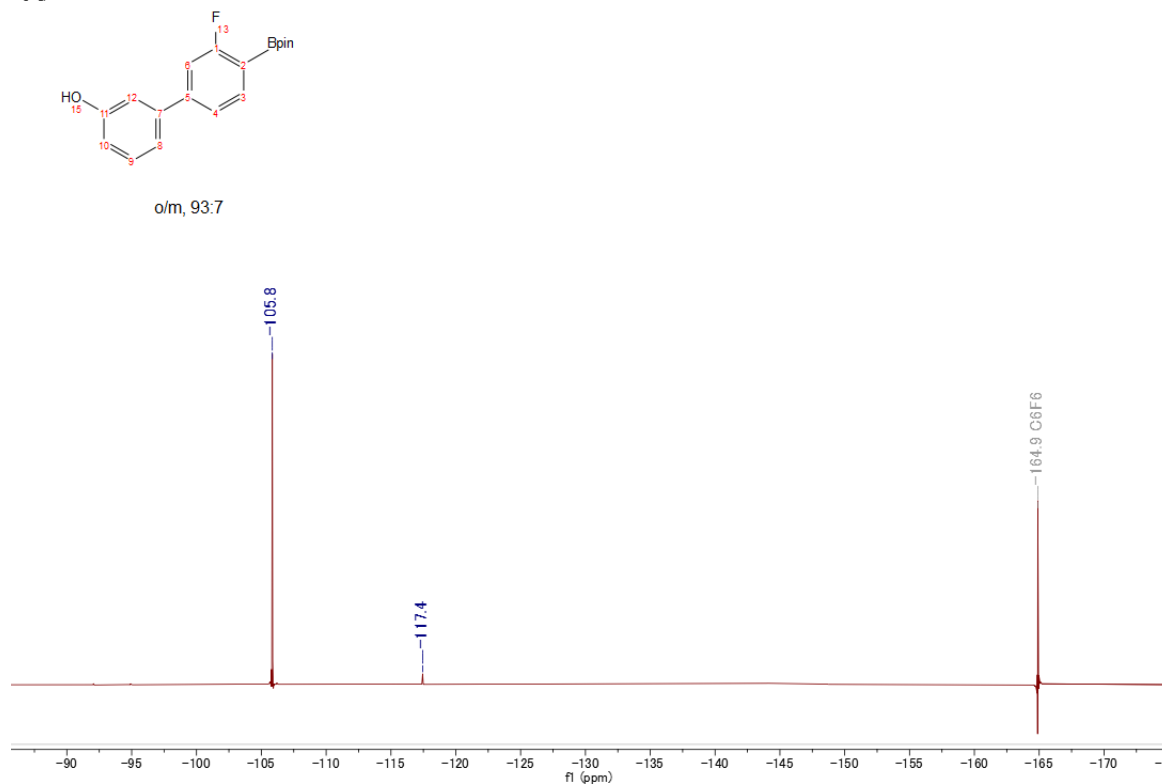


Figure S106. ^{19}F NMR spectra (CDCl_3) of 2l.

JK 72-9-13_isolated
angle_pulse

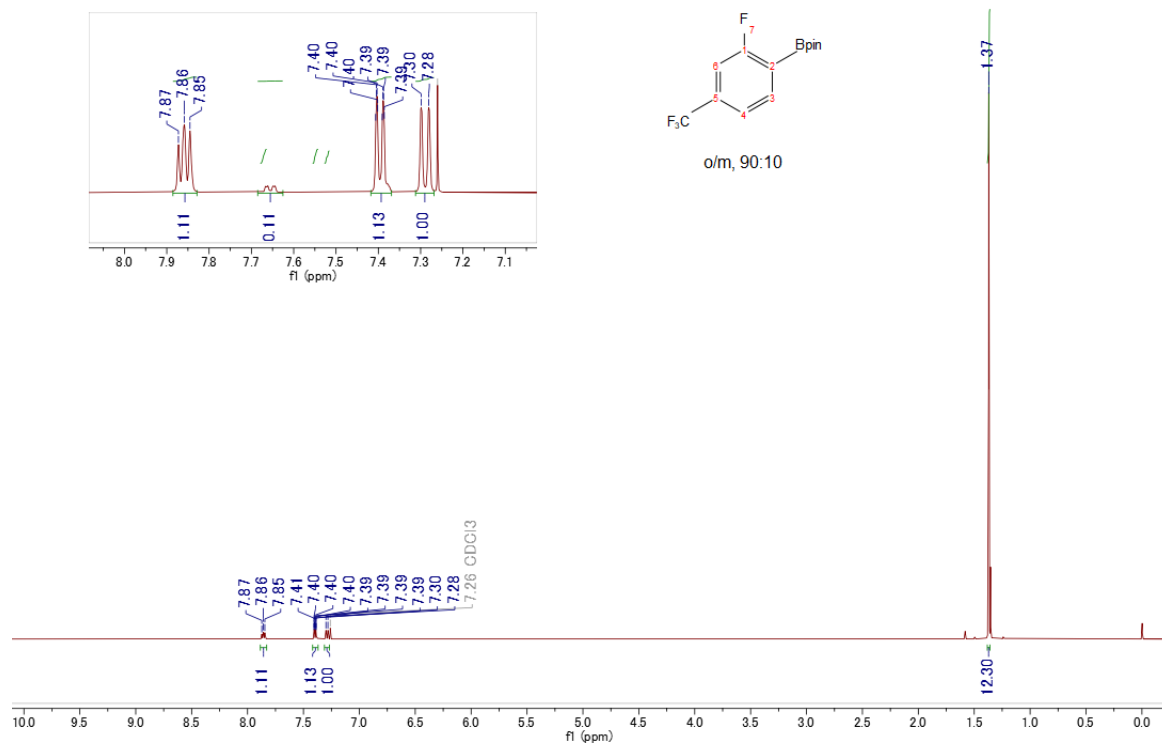


Figure S107. ^1H NMR spectra (CDCl_3) of 2m.

JK 72-9-13_isolated
single pulse decoupled gated NOE

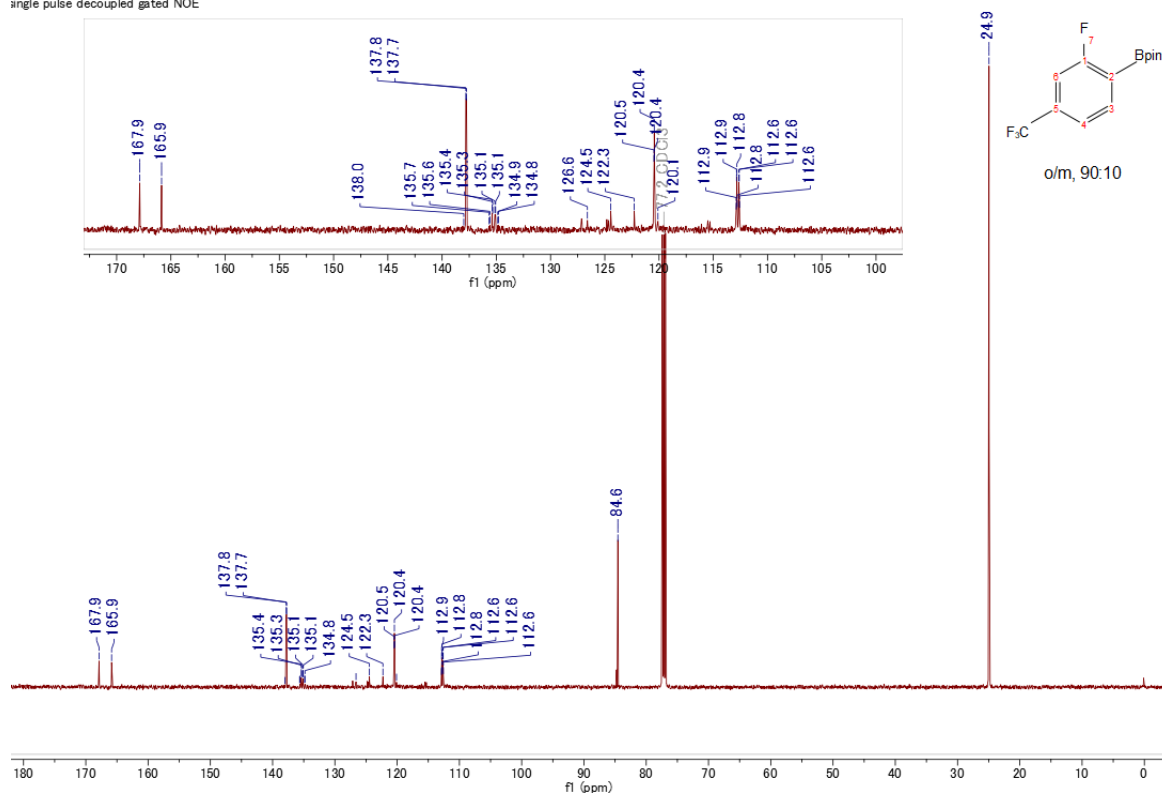


Figure S108. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of 2m.

JK 72-9-13_isolated
single_pulse

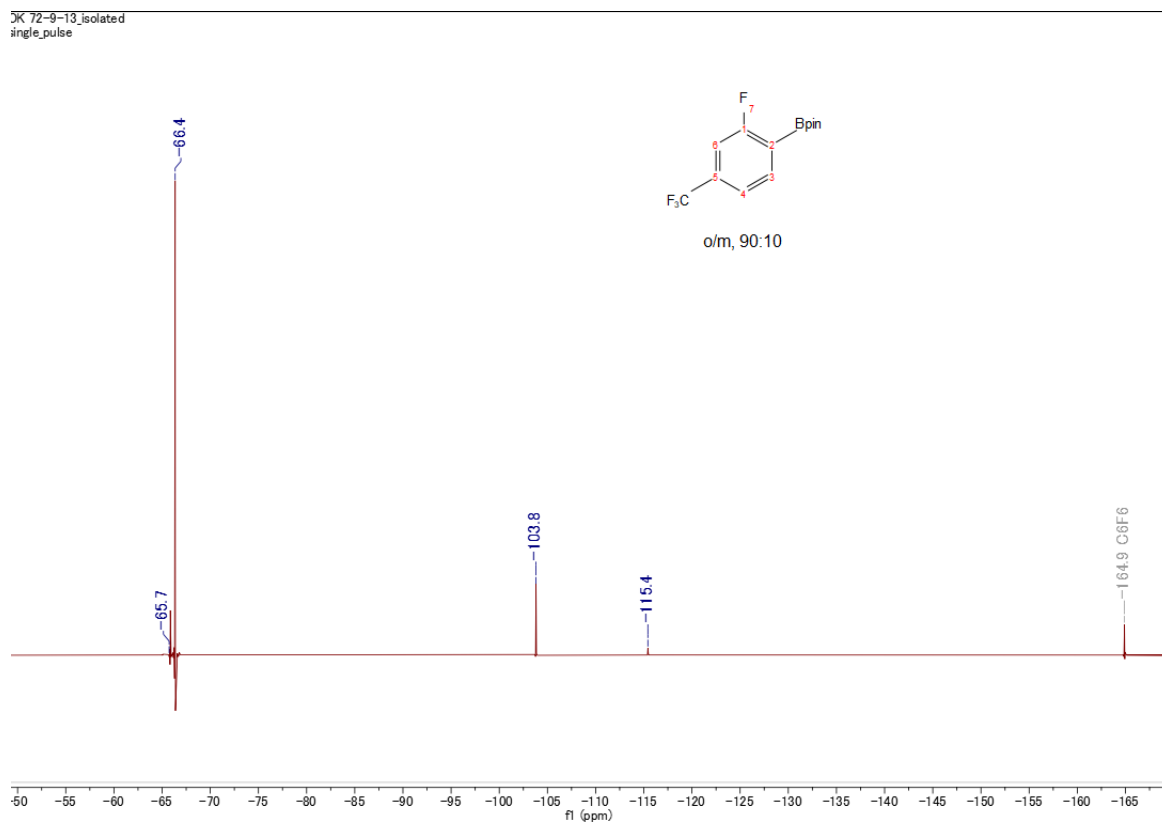


Figure S109. ^{19}F NMR spectra (CDCl_3) of 2m.

JK 72-9-48,5/2
single_pulse

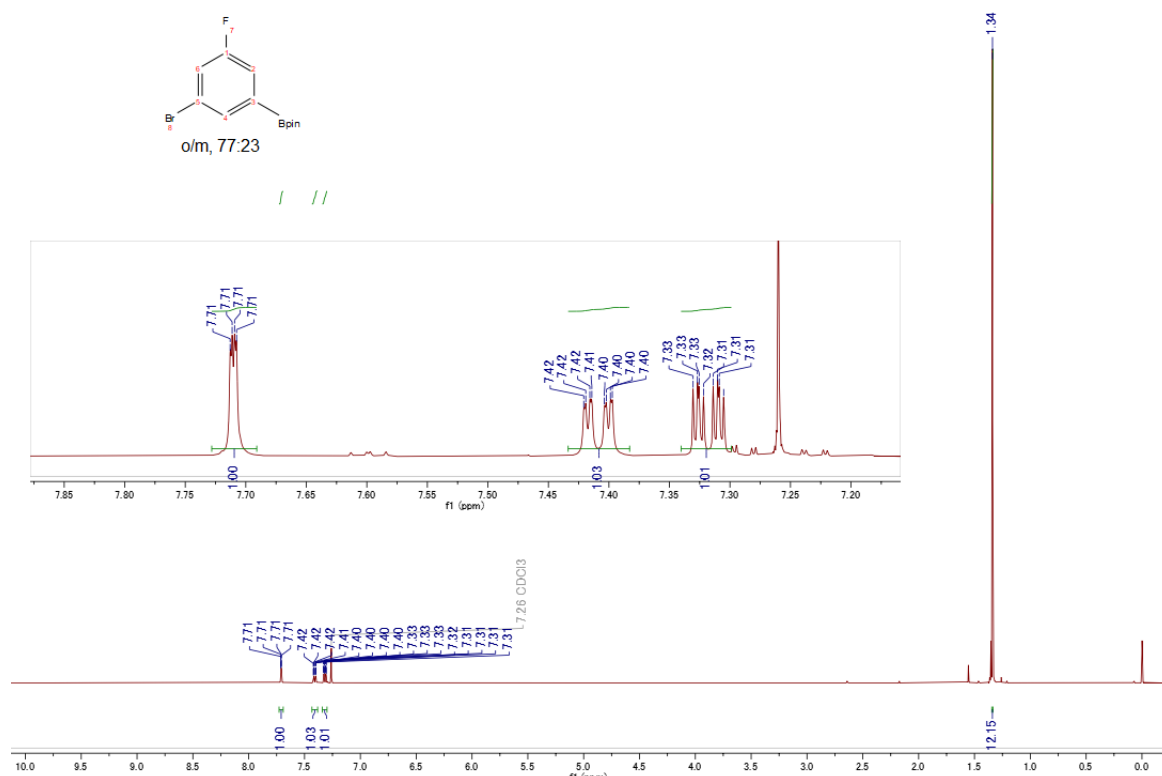


Figure S110. ¹H NMR spectra (CDCl₃) of **2n** (fractions with *meta*-isomer is the major one).

JK 72-9-48,5/2
single_pulse decoupled gated NOE

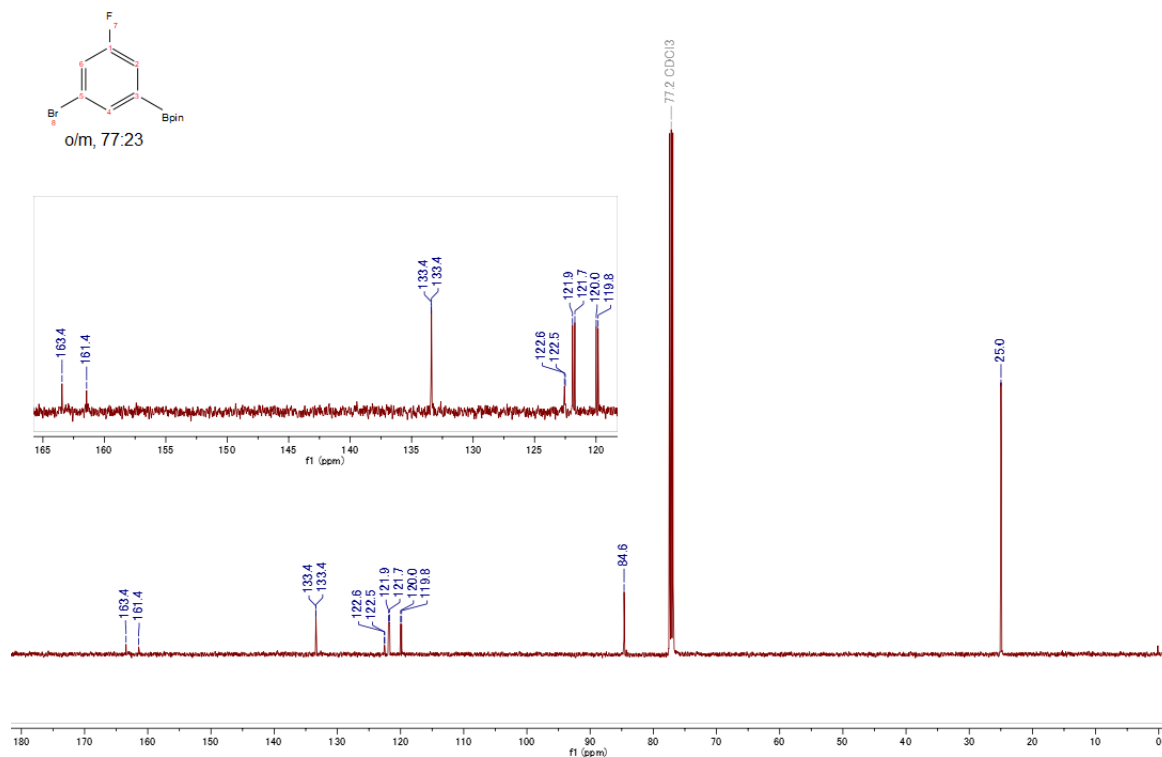


Figure S111. ¹³C{¹H} NMR spectra (CDCl₃) of **2n** (fractions with *meta*-isomer the major one).

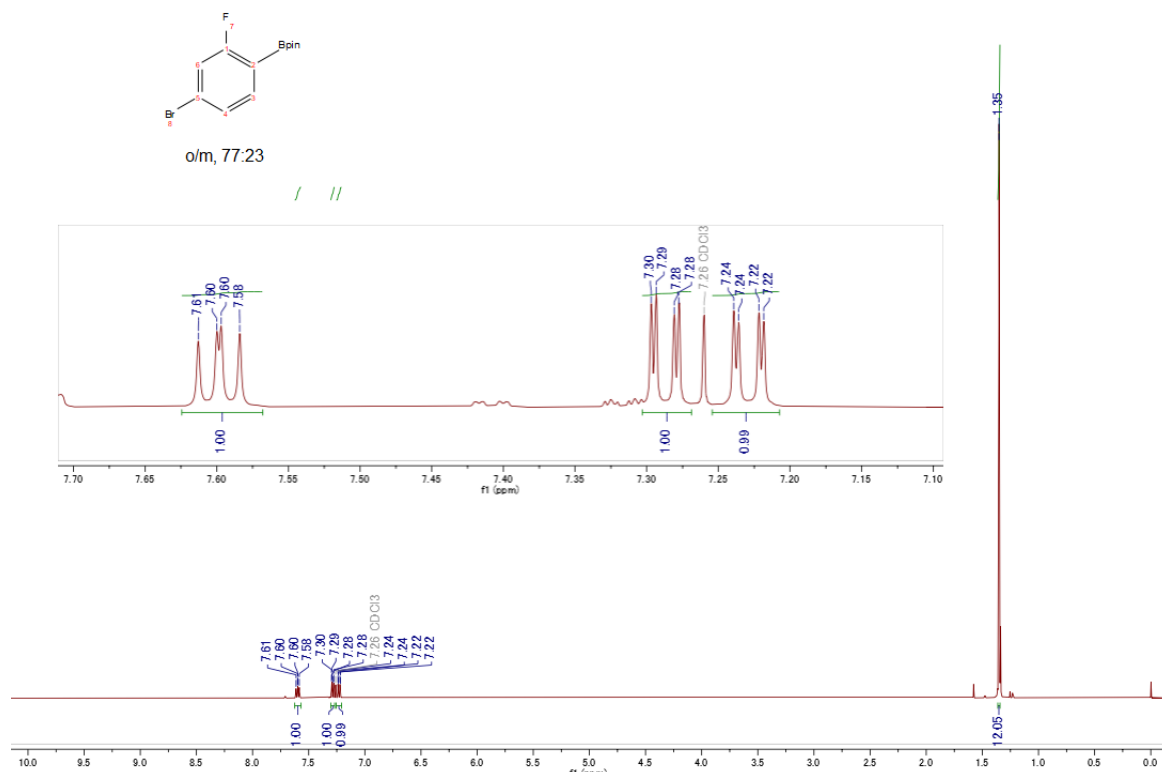


Figure S112. ¹H NMR spectra (CDCl₃) of **2n** (fractions with *ortho*-isomer the major one).

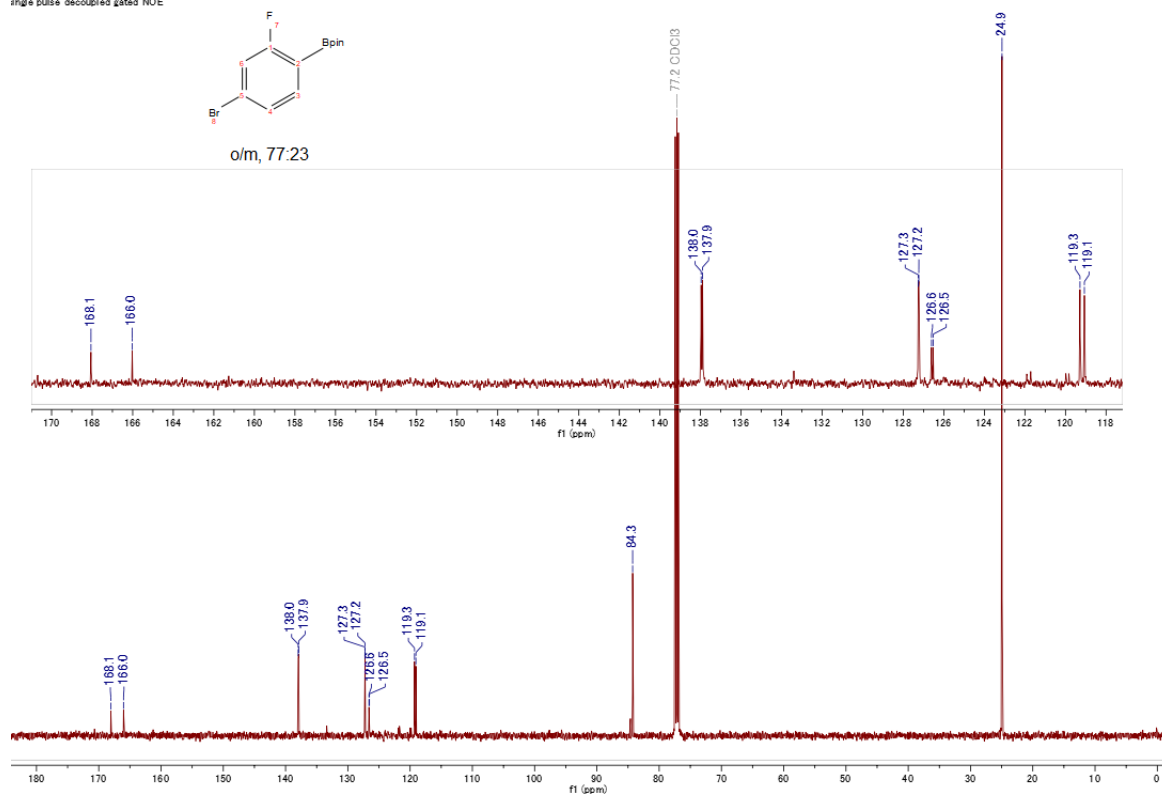


Figure S113. ¹³C{¹H} NMR spectra (CDCl₃) of **2n** (fractions with *ortho*-isomer the major one).

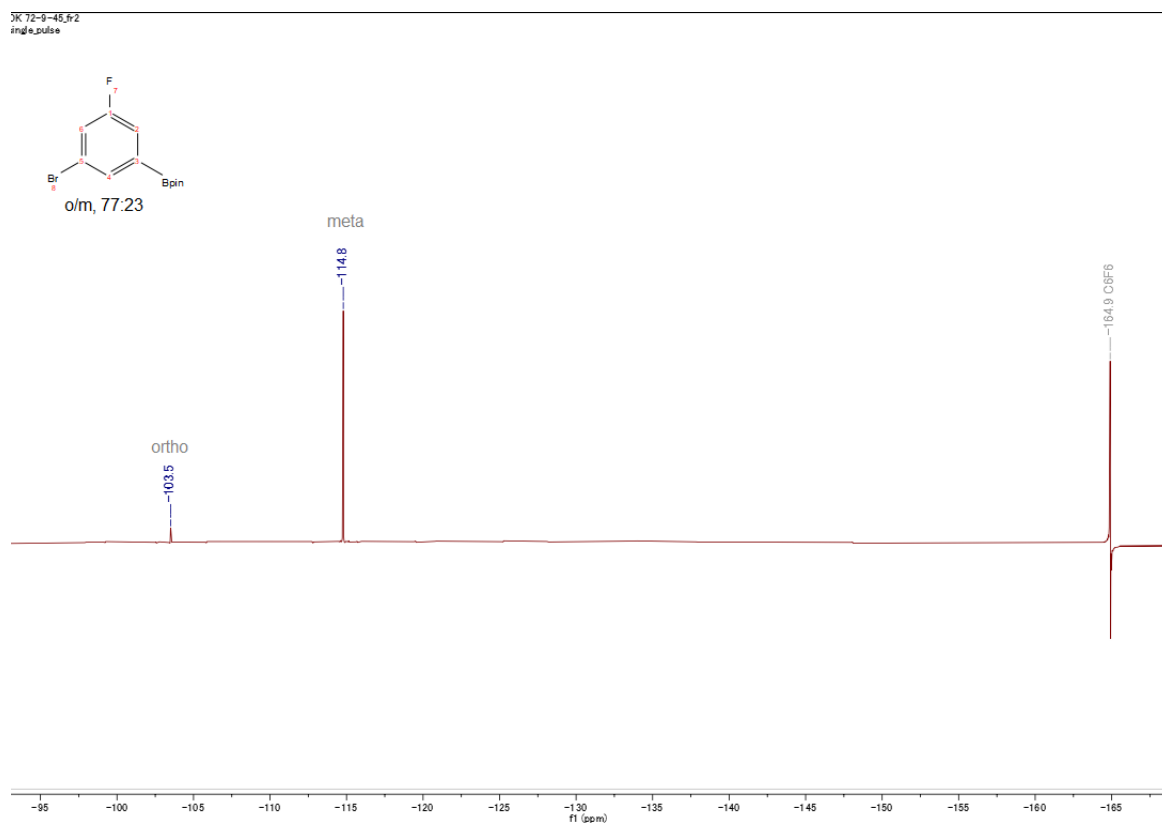


Figure S114. ¹⁹F NMR spectra (CDCl₃) of **2n** (fractions with *meta*-isomer the major one).

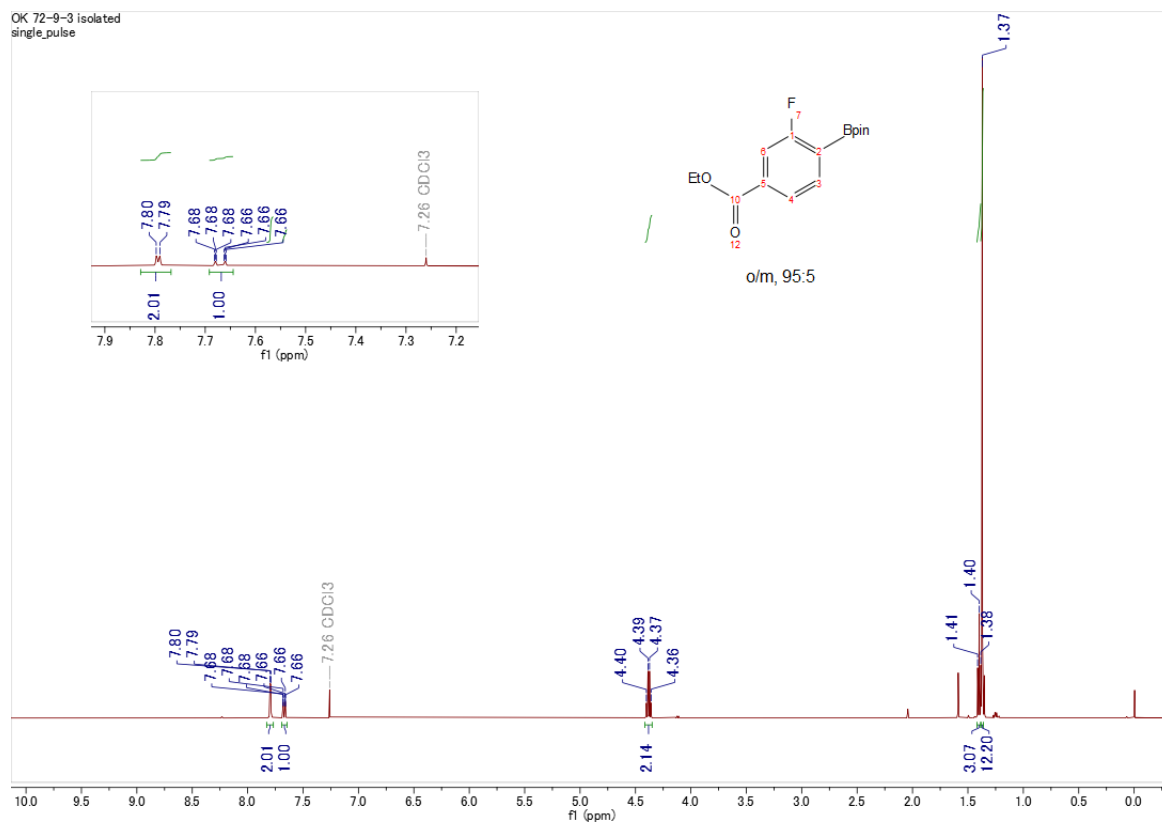


Figure S115. ¹H NMR spectra (CDCl₃) of **2o**.

OK 72-9-3 isolated
single pulse decoupled gated NOE

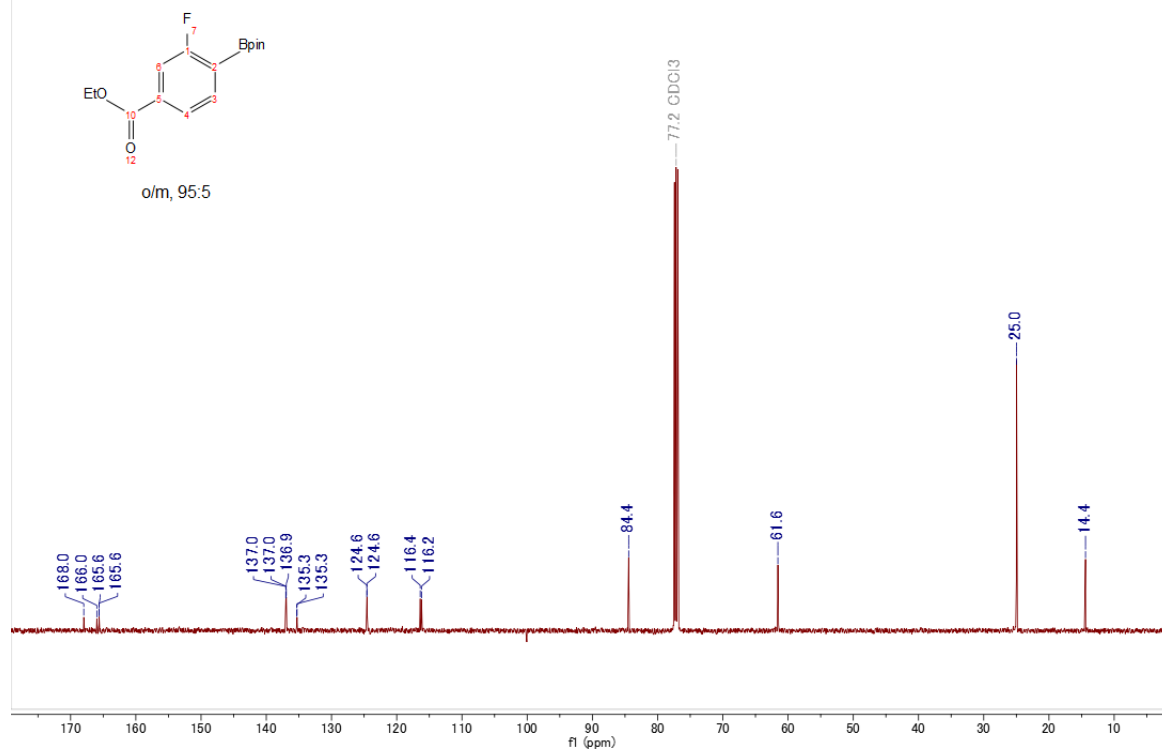


Figure S116. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl₃) of **2o**.

OK 72-9-3 isolated
single pulse

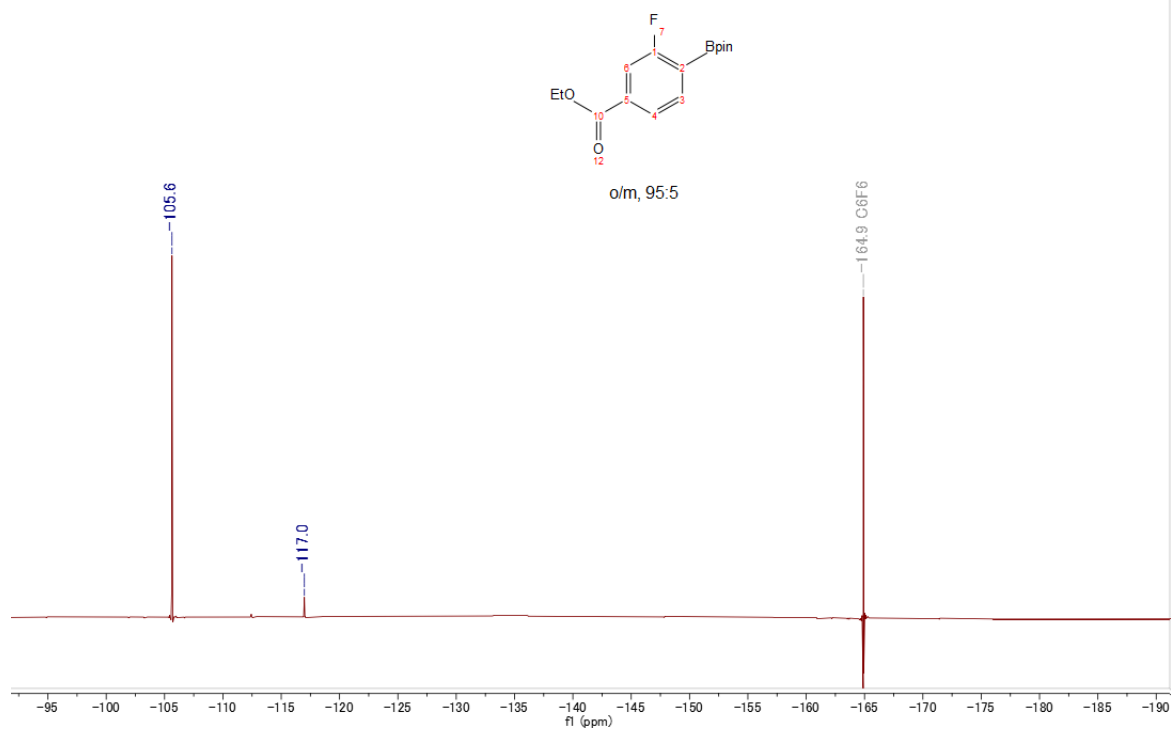


Figure S117. ^{19}F NMR spectra (CDCl₃) of **2o**.

JK 72-9-43_isolated
single_pulse

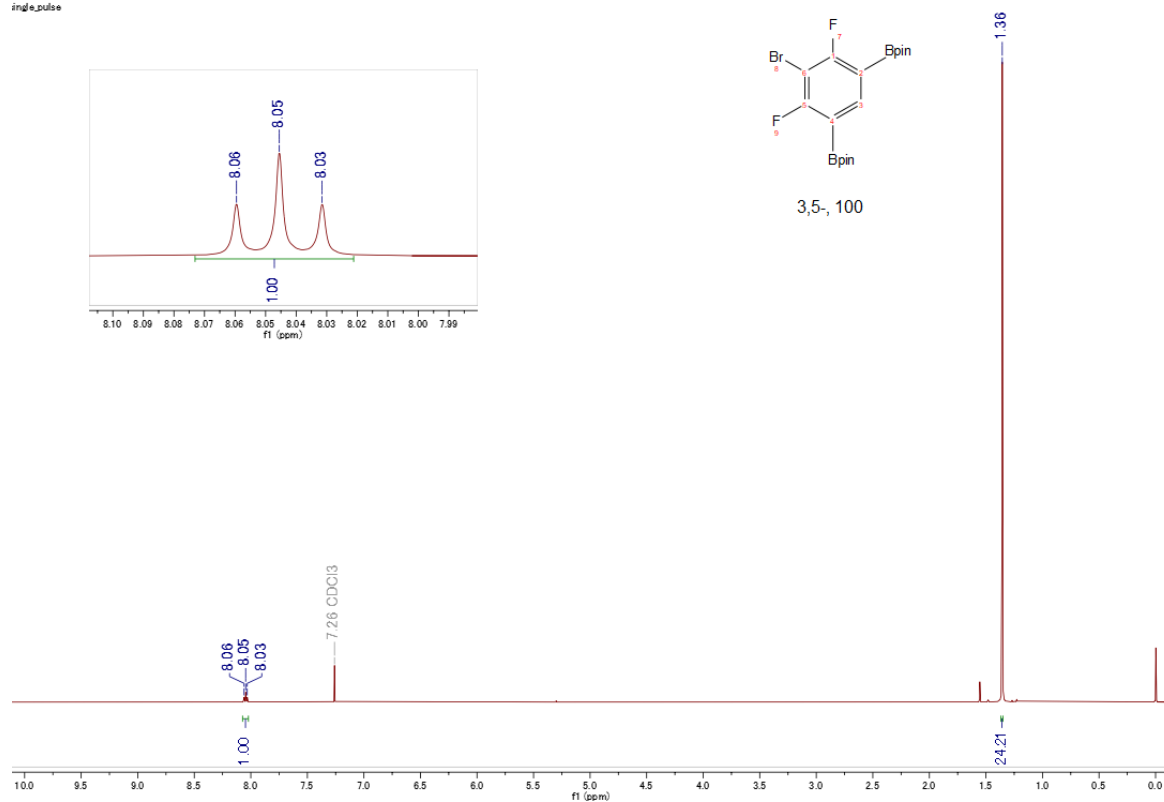


Figure S118. ¹H NMR spectra (CDCl₃) of **2p**.

JK 72-9-43_isolated
single_pulse decoupled gated NOE

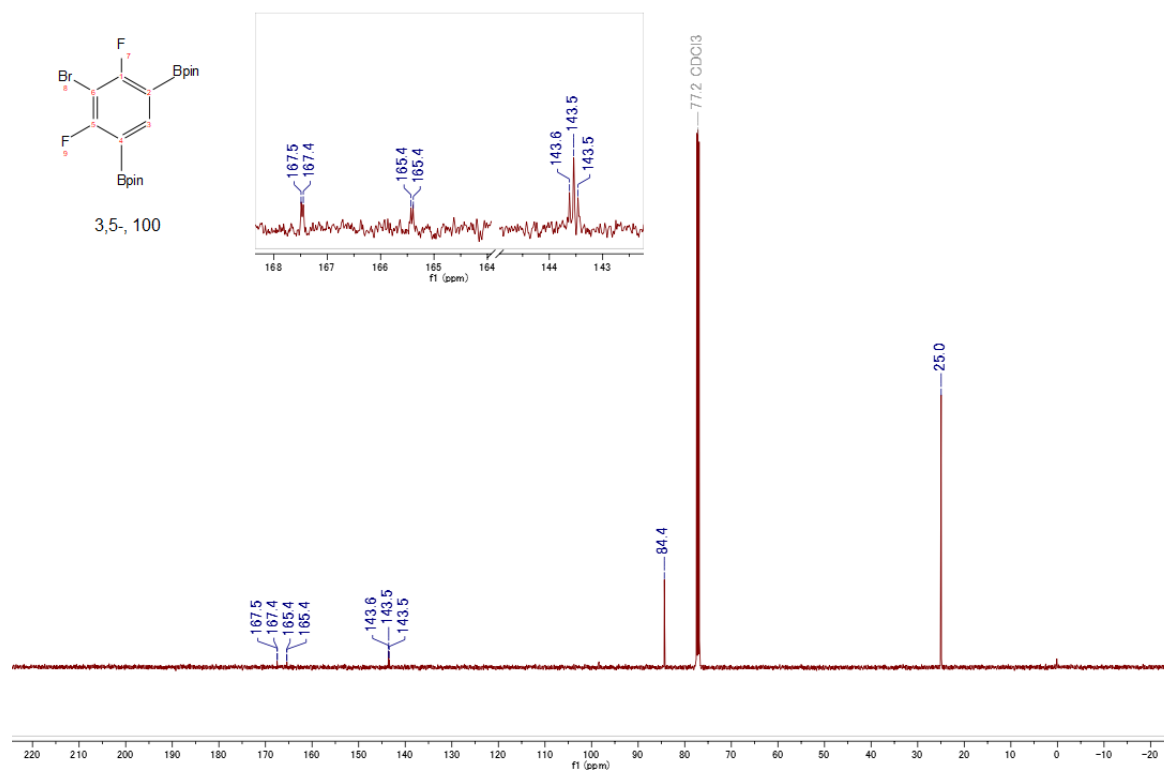
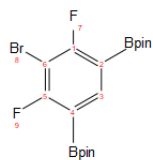


Figure S119. ¹³C{¹H} NMR spectra (CDCl₃) of **2p**.

JK 72-9-43 isolated
single_pulse



3,5-, 100

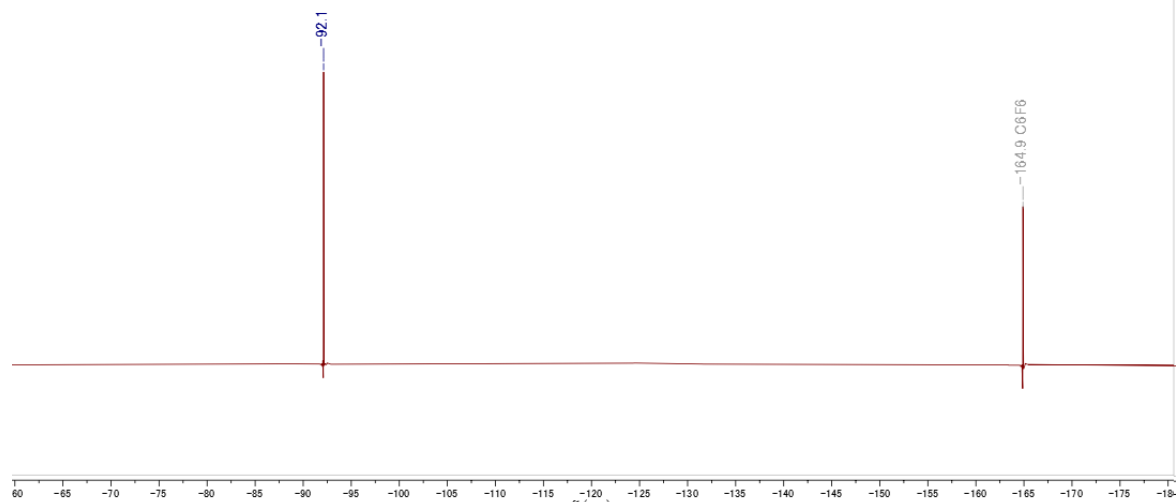


Figure S120. ^{19}F NMR spectra (CDCl_3) of **2p**.

JK 72-9-26 #5,6
single_pulse

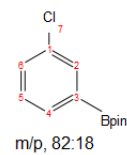
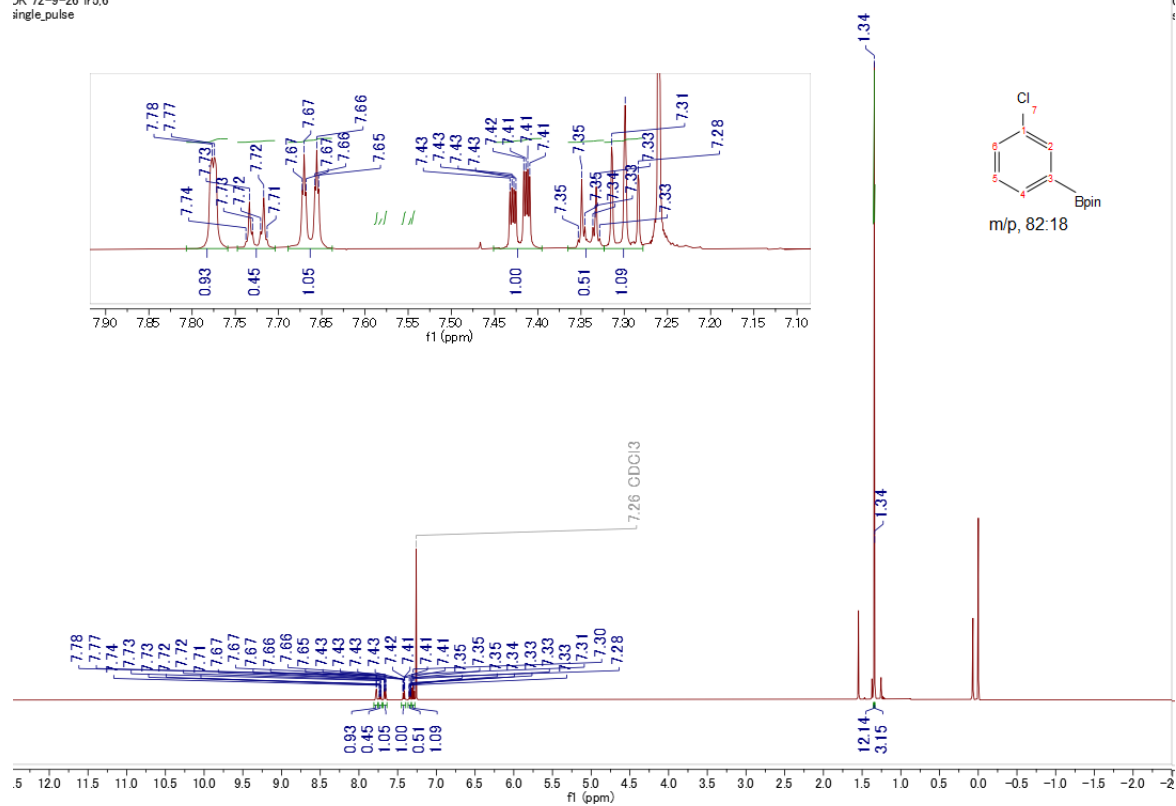


Figure S121. ^1H NMR spectra (CDCl_3) of **3**.

JK 72-9-26 f15.6
single pulse decoupled gated NOE

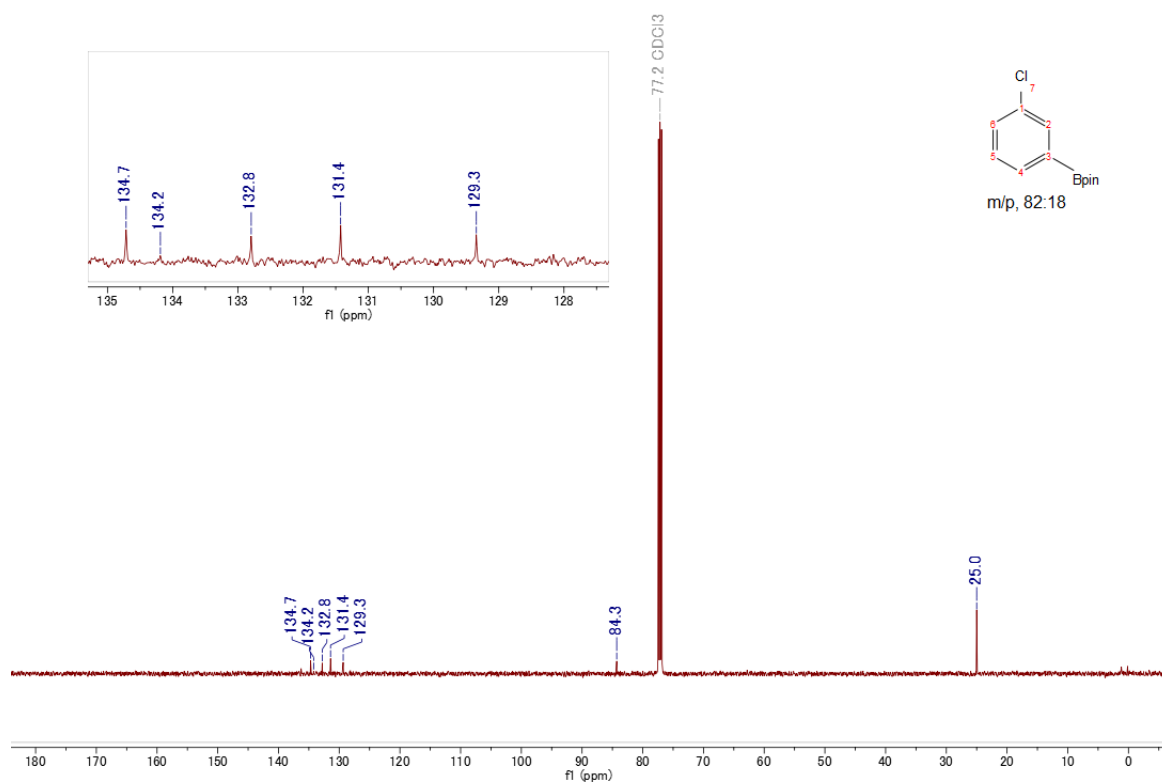


Figure S122. ¹³C{¹H} NMR spectra (CDCl₃) of **3**.

JK 72-9-65 f12-18
single pulse

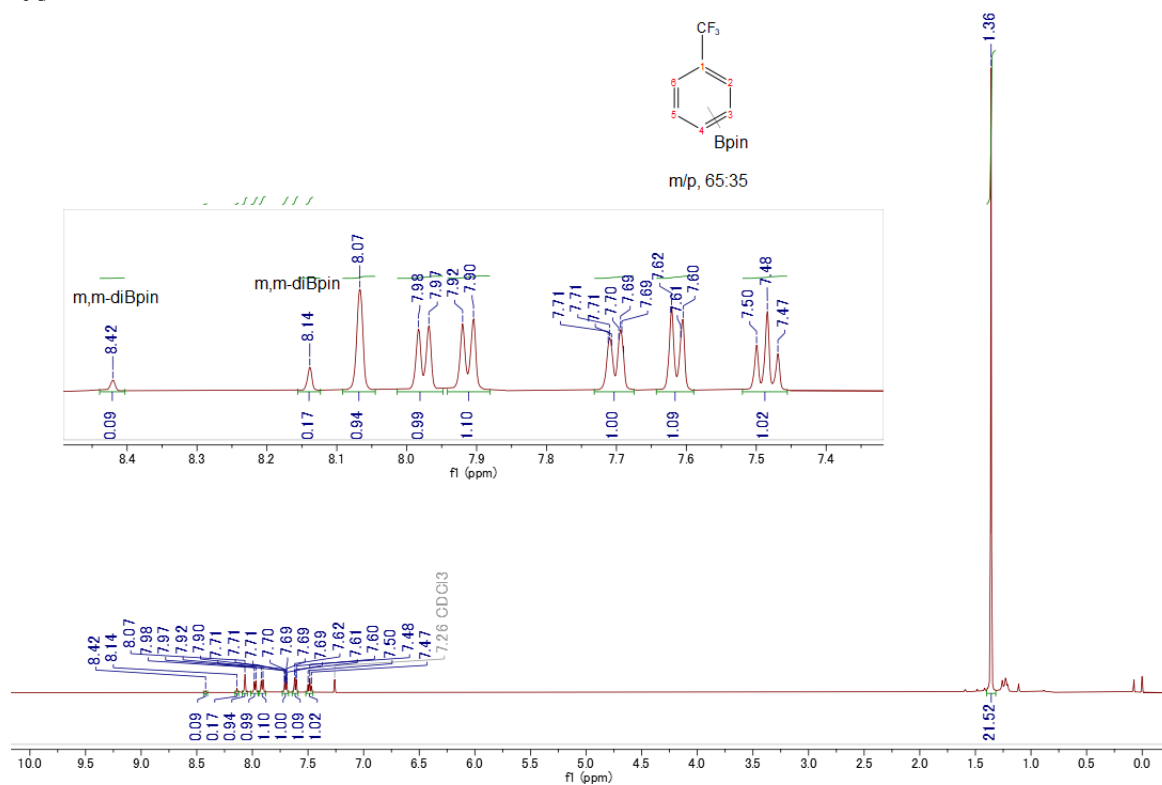


Figure S123. ¹H NMR spectra (CDCl₃) of **4**.

JK 72-9-65_isol
single pulse decoupled gated NOE

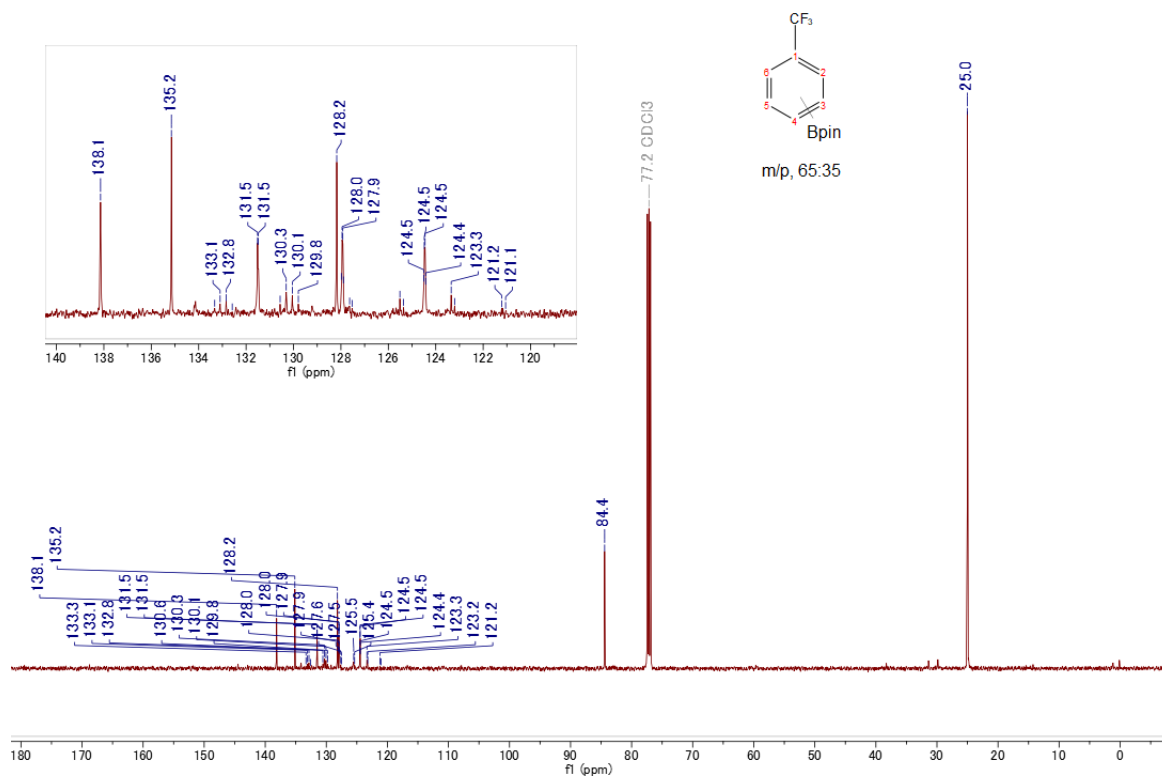


Figure S124. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **4**.

JK 72-9-65_isol
single_pulse

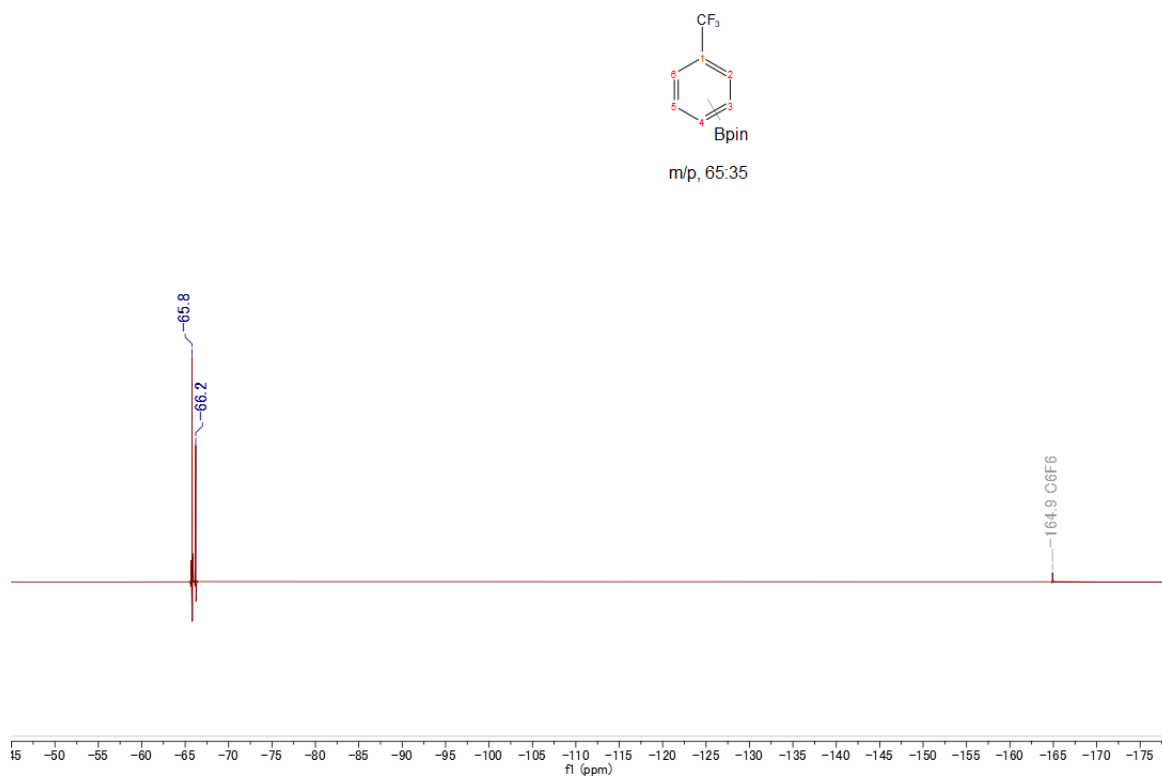


Figure S125. ^{19}F NMR spectra (CDCl_3) of **4**.

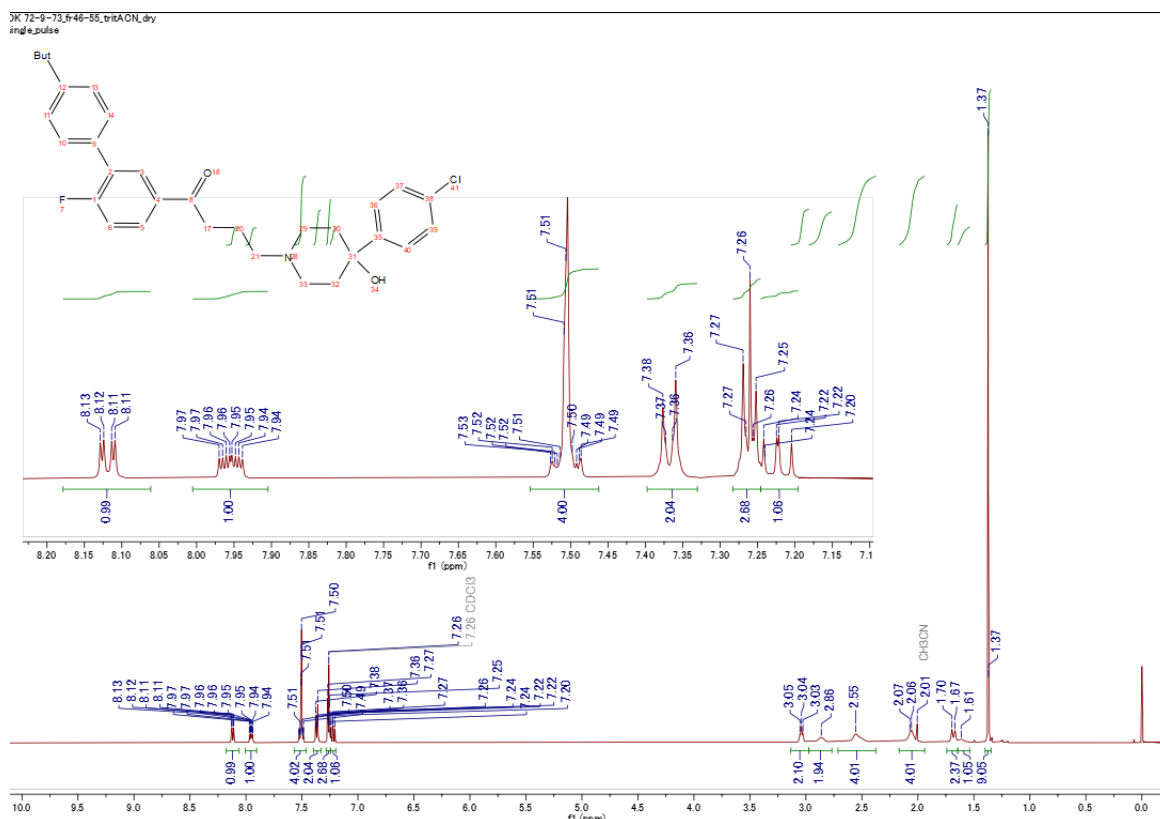


Figure S126. ¹H NMR spectra (CDCl₃) of haloperidol derivative.

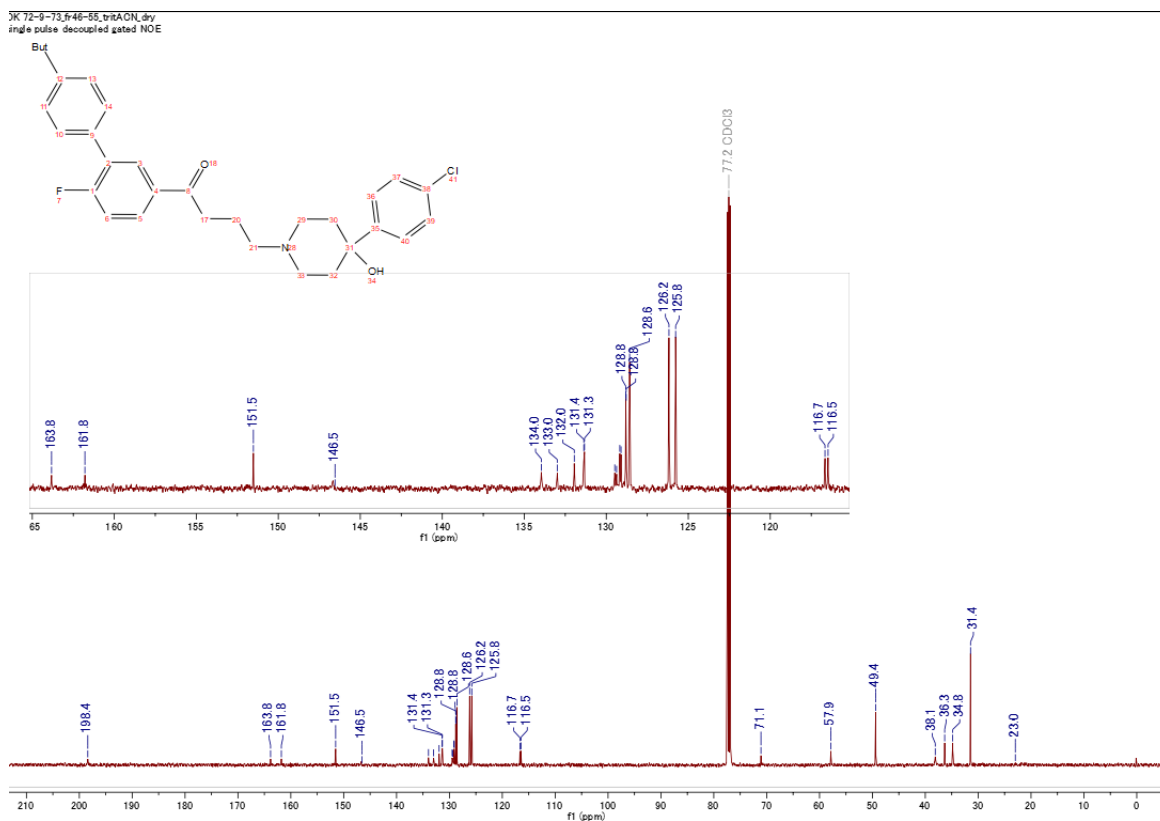


Figure S127. ¹³C{¹H} NMR spectra (CDCl₃) of haloperidol derivative.

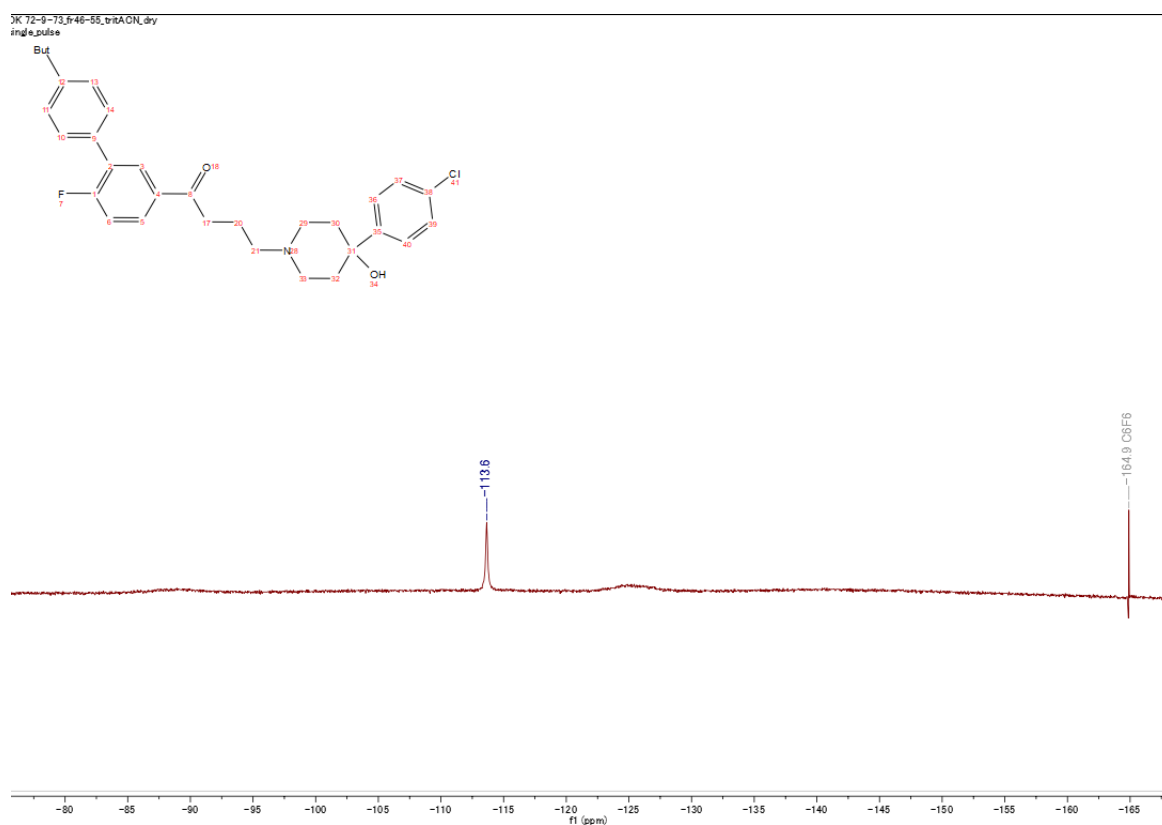


Figure S128. ^{19}F NMR spectra (CDCl₃) of haloperidol derivative.

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