Supporting Information

Copper-Catalyzed *ipso*-Borylation of Fluoroarenes

Takashi Niwa,* Hidenori Ochiai, and Takamitsu Hosoya*

Chemical Biology Team, Division of Bio-Function Dynamic Imaging,
RIKEN Center for Life Science Technologies
6-7-3 Minatojima-minamimachi, Chuo-ku, Kobe 650-0047, Japan

*takashi.niwa@riken.jp, *takamitsu.hosoya@riken.jp

Contents

Instrumentation and chemicals

All reactions were performed under argon atmosphere unless otherwise indicated. All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk techniques or in a MIWA DBO-1KH-NYWS glovebox under an atmosphere of argon. Unless otherwise noted, copper-catalyzed *ipso*-borylation reactions were conducted in a 4 mL (15 × 45 mm) screw-thread clear vial (Thermo Scientific, Cat. No. C4015-1) with a cap assembled with a septum (Thermo Scientific, Cat. No. C4015-75A).

Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck, Merck Silica Gel 60 F_{254}). Preparative TLC (PTLC) was carried out using precoated silica-gel plates (for 0.50 mm, 1.0 mm and 2.0 mm: Merck, Merck Silica Gel 60 F_{254}). Column chromatography was conducted by hand using silica-gel (SiliCycle Inc., SiliaFlash) or on a YAMAZEN Automated Flash Chromatography System that consists of AI-580 and Parallel Frac FR-360 with silica-gel-packed column (Biotage Zip cartridge or Yamazen Universal Column Premium). Recycling preparative high performance liquid chromatography (HPLC) was performed by LC-908-C60 system (Japan Analytical Industry Co., Ltd.) or by LC-Forte/R system (YMC Co., Ltd.) with high-resolution gel permeation chromatography (GPC) column (Japan Analytical Industry Co., Ltd., JAIGEL-1H or YMC Co., Ltd., YMC-GPC T2000).

Gas chromatography (GC) analysis was carried out on a Shimadzu GC-2014 using an INERT CAP 1 (30 m, 0.32 mm I.D., 0.25 μm df) column and helium as the carrier gas.

Melting points (mp) were measured with an OptiMelt automated melting point apparatus (Stanford Research Systems, Inc.) and were uncorrected.

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (373 MHz), and ^{11}B NMR (127 MHz) spectra were obtained from measurements at room temperature on a JEOL 400SS spectrometer. Chloroform-d_1 ($CDCl_3$) containing 0.05% tetramethylsilane (TMS) (99.8%D, Cambridge Isotope Laboratories, Inc.) was used as a solvent for NMR measurements. Chemical shifts (δ) are given in parts per million (ppm) downfield from a signal of TMS in $CDCl_3$ (δ 0.00 ppm for ^{1}H NMR) or $CDCl_3$ (δ 77.0 ppm for ^{13}C NMR) as an internal standard, or trifluoromethylbenzene (δ –62.6 ppm for ^{19}F NMR, Tokyo Chemical Industry Co., Ltd.) or $BF_3{\cdot}OEt_2$ (δ 0.0 ppm for ^{11}B NMR, Tokyo Chemical Industry Co., Ltd.) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, sep, m, and br signify singlet, doublet, triplet, septet, multiplet, and broad, respectively.

IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with a MIRacl™A single reflection horizontal ATR unit (PIKE Technologies, Inc.) with the absorption bands given in cm^{-1}.

High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700V or JMS-T100LC under positive electrospray ionization (ESI^+) conditions or electron ionization (EI^+) conditions at Molecular Characterization, Collaboration Promotion Unit, RIKEN, or a Thermo Fisher Scientific Exactive^{TM} Plus Orbitrap mass spectrometer under positive electrospray ionization (ESI^+) conditions.

Microwave irradiation reactions were conducted using Biotage Japan Ltd. Initiator+ Eight apparatus in a 2–5 mL microwave vial (Cat. No. 351521).

UV-visible absorbance spectra were measured with a Shimadzu UV-1800 spectrophotometer at 22 °C (room temperature).

EPR spectra were measured with a JES-PX1060 spectrometer at Materials Characterization Central Laboratory, Waseda University.

1,3-Bis(2,6-diisopropylphenyl)imidazole-2-ylidene(chloro)silver (IPrAgCl),[S1] chloro(tricyclohexylphosphine)copper(I) dimer ($[CuCl(PCy_3)]_2$),[S2] chlorobis(tricyclohexylphosphine)copper(I) ($CuCl(PCy_3)_2$),[S2] 4-fluorobiphenyl (**1a**),[S3] 4-fluoro-4′-methylbiphenyl (**1b**),[S3] 4-*tert*-butyl-4′-fluorobiphenyl (**1c**),[S3] 4-fluoro-4′-methoxybiphenyl (**1d**),[S3] 4-fluoro-4′-phenoxybiphenyl (**1e**),[S3] 4-fluoro-4′-(*N*-morpholinyl)biphenyl (**1f**),[S3] 2-fluorobiphenyl (**1j**),[S3] 4-fluorophenyl methoxymethyl ether (**1o**),[S3] 1-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**1q**),[S4] *N*-(4-fluorophenyl)pyrrole (**1t**),[S3] and 1-(4-fluorophenyl)-1H-pyrazole (**1u**)[S3] were prepared according to the reported methods.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Bis(pinacolato)diboron (**2a**, $(Bpin)_2$) and bis(neopentyl glycolato)diboron (**2b**) were purchased from Frontier Scientific Inc.

Toluene (deoxygenated), benzene (super dehydrated), cyclopentyl methyl ether (CPME, super dehydrated), 1,4-dioxane (super dehydrated), *N*,*N*-dimethylformamide (DMF, deoxygenated), acetone (dehydrated), acetonitrile (MeCN, super dehydrated), and methanol (deoxygenated) were purchased from Wako Pure Chemical Industries, Ltd.

Tricyclohexylphosphine (PCy_3), di(1-adamantyl)-*n*-butylphosphine ($Ad_2P(n\text{-Bu})$), and tri(*tert*-butyl)phosphine ($P(t\text{-Bu})_3$) were purchased from Strem Chemicals, Inc.

Tetrakis(acetonitrile)copper(I) hexafluorophosphate ($CuPF_6(MeCN)_4$), copper(II) acetate ($Cu(OAc)_2$), tri(*o*-tolyl)phosphine ($P(o\text{-tol})_3$), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos), 2-dicyclohexylphosphino-2′-dimethylaminobiphenyl (Davephos), 1,2-bis(diphenylphosphino)benzene (dppbz), rubidium fluoride (RbF), potassium fluoride (KF, spray-dried), sodium fluoride (NaF), cesium pivalate (CsOPiv), potassium phosphate (K_3PO_4), 4-fluorophenyl phenyl

ether (**1n**), 1,3,4-trifluorobenzene (**1ac**), 9,10-dihydroanthracene (DHA), 4-fluorophenylboronic acid, and [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) chloride dichloromethane adduct were purchased from Sigma–Aldrich Japan Inc.

Copper(I) acetate (CuOAc), copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$), tricyclopentylphosphine ($P(c\text{-}C_5H_9)_3$), 1,1′-bis(diphenylphosphino)ferrocene (dppf), sodium *tert*-butoxide (NaO*t*-Bu), tetrabutylammonium fluoride (TBAF, 1.0 M in THF solution), tetrabutylammonium difluorotriphenylsilicate (TBAT), cesium bis(trifluoromethanesulfonyl)imide ($CsNTf_2$), *p*-bromofluorobenzene, *p*-fluoroiodobenzene, 1-fluoronaphthalene (**1h**), fluorobenzene (**1k**), 4-fluorotoluene (**1l**), 4-fluoro-*N*,*N*-dimethylaniline (**1p**), 2-fluorotoluene (**1r**), 3-(4-fluorophenyl)-1-isopropylindole (**1v**), blonanserin (**1w**), 1,3-difluorobenzene (**1y**), 1,2-difluorobenzene (**1z**), 1,3,5-trifluorobenzene (**1ab**), phenyl *p*-toluenesulfonate, phenyl trifluoromethanesulfonate, trifluoromethylbenzene, 1,4-bis(trifluoromethyl)benzene, 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO), Galvinoxyl free radical, 1,4-difluorobenzene (**1q′**), *tert*-butyl 4-bromobenzoate, phenylboronic acid, 1-bromo-3-fluorobenzene, 3-fluorobenzoyl chloride, 5-bromo-2-fluorobenzaldehyde (**S1**), sodium borohydride, and allylmagnesium bromide (0.7 M solution in Et_2O) were purchased from Tokyo Chemical Industry Co., Ltd.

Chlorobenzene (**4**), bromobenzene, ethyl acetate (EtOAc), ammonium chloride, *n*-dodecane, copper(I) chloride (CuCl), copper(I) bromide (CuBr), copper(I) iodide (CuI), copper(II) chloride ($CuCl_2$), copper(II) bromide ($CuBr_2$), triphenylphosphine (PPh_3), cesium fluoride (CsF), lithium fluoride (LiF), potassium *tert*-butoxide (KO*t*-Bu), cesium carbonate (Cs_2CO_3), potassium carbonate (K_2CO_3), anisole, naphthalene, pyrene, 2,6-di-*tert*-butyl-4-methylphenol (BHT), diisopropylethylamine, 2-propanol, sodium sulfate (Na_2SO_4), *n*-hexane, hydrochloric acid (35% aqueous), diethyl ether (Et_2O), *N*-bromosuccinimide, palladium(II) acetate, barium hydroxide octahydrate ($Ba(OH)_2{\cdot}8H_2O$), acetic acid (AcOH), and toluene (non-deoxygenated, 99% (GC)) were purchased from Nacalai Tesque, Inc.

Copper(II) fluoride (CuF_2) and 4-fluoroanisole (**1m**) were purchased from Alfa Aesar.

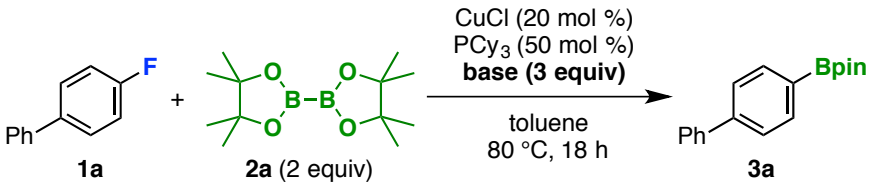
Optimization study of copper-catalyzed *ipso*-borylation of 1a

General procedure for optimization study of *ipso*-borylation of fluoroarenes 1

To a capped vial were added a fluoroarene **1** (0.200 mmol, 1 equiv), copper source, a ligand, bis(pinacolato)diboron (**2a**, $(Bpin)_2$, 102 mg, 0.402 mmol, 2 equiv), a base, and a solvent (1.0 mL) in a glovebox filled with argon gas, and the solution was stirred for the time indicated in the table at 80 °C. The reaction vial was cooled to room temperature and taken out from the glovebox. To the reaction mixture was added EtOAc (0.8 mL) saturated aqueous ammonium chloride (0.8 mL), followed by *n*-dodecane (22.7 μL, 0.100 mmol) as an internal standard. After stirring the mixture vigorously, GC analysis was conducted using a portion of the resulting organic phase.

GC conditions for analyses of the borylated product **3a**: Constant linear column flow was adjusted to 30 cm/sec. Temperatures of the injector and the detector were held at 300 °C and 330 °C, respectively, and the GC oven temperature program was set as follows: initially held at 75 °C for 2 min, heated to 300 °C at the rate of 16 °C/min, and held at 300 °C for 2 min. Retention times: *n*-dodecane (7.4 min, internal standard), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (14.7 min, **3a**).

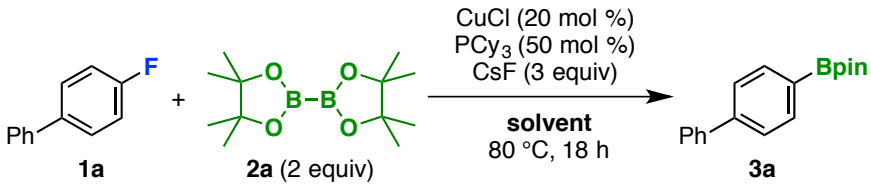
Table S1. Optimization of base



entry	**base**	yield (%)[a]
1	CsF	>99
2	RbF	0
2	KF	0
3	NaF	0
4	LiF	0
5	Cs_2CO_3	0
6	CsOPiv	1
7	KO*t*-Bu	0
8	NaO*t*-Bu	0
9	K_2CO_3	0
10	K_3PO_4	0
11	TBAF in THF (1 M)	0
12	TBAT	<4
13[b]	KF + $CsNTf_2$	0
14[b]	TBAT + $CsNTf_2$	6

[a]Determined by GC analysis. [b]3 equiv of both reagents were used.

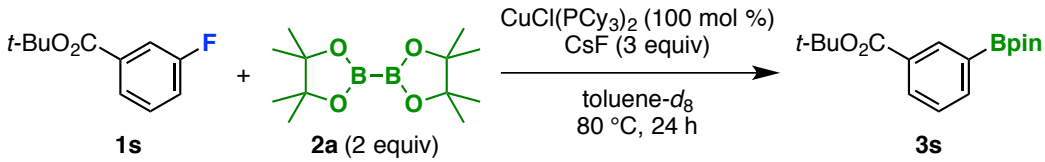
Table S2. Optimization of solvent



entry	**solvent**	yield (%)[a]
1	toluene (deoxygenated)	>99
2	benzene	81
3	CPME	86
4	1,4-dioxane	47
5	acetone	0
6	DMF	<1
7	MeCN	0
8	methanol	0

[a]Determined by GC analysis.

Table S3. Attempts for *ipso*-borylation of electron-deficient fluoroarene 1s



entry	**Change from standard conditions**	yield (%)[a]
1	none	32
2	Using 20 mol % of Cu complex	0
3	Using toluene	0
4	Using benzene	<15
5	Using CPME	<1

[a]Isolated yields.

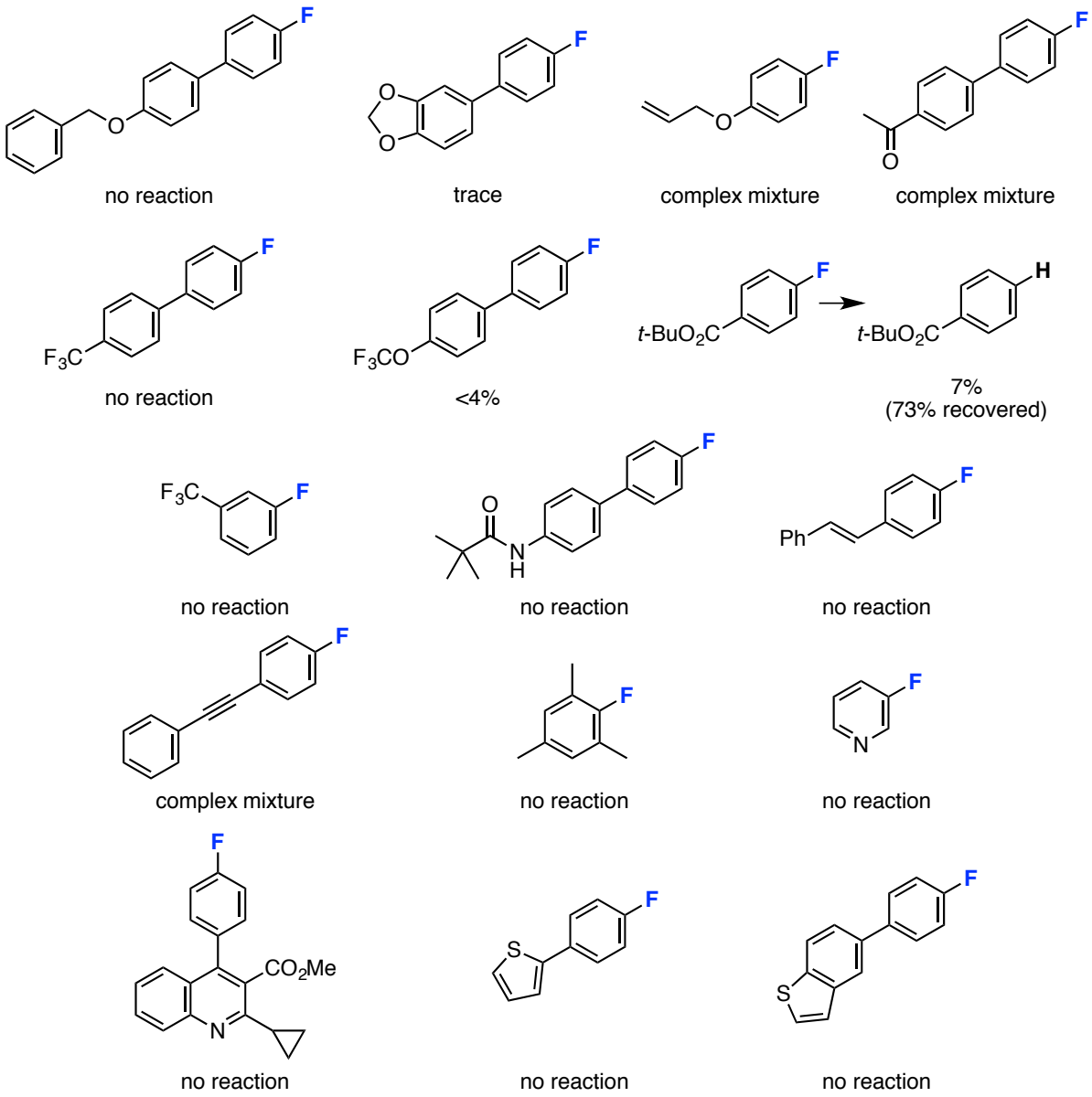
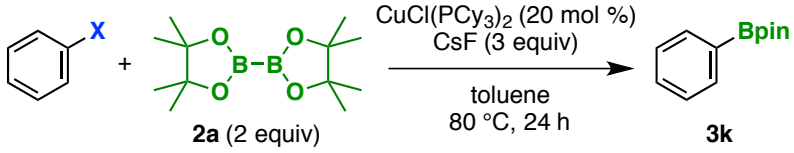


Figure S1. Examples of unsuccessful substrates for the *ipso*-borylation. Isolated yields are shown.

Table S4. *ipso*-borylation of other electrophilic (pseudo)halobenzenes



entry	**X**	yield (%)[a]
1	Cl (**4**)	11
2	Br	53
3	OTs	0
4	OTf	0

[a]Determined by GC analysis.

GC conditions for analyses of the borylated product **3k**: Constant linear column flow was adjusted to 30 cm/sec. Temperatures of both the injector and the detector were held at 250 °C, and the GC oven temperature program was set as follows: initially held at 50 °C for 2 min, heated to 200 °C at the rate of 16 °C/min, and held at 200 °C for 9 min. Retention times: *n*-dodecane (8.8 min, internal standard), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (10.1 min, **3k**).

Scheme S1. Attempts of defluoroborylation of fluoroarenes bearing a bromo or an iodo group

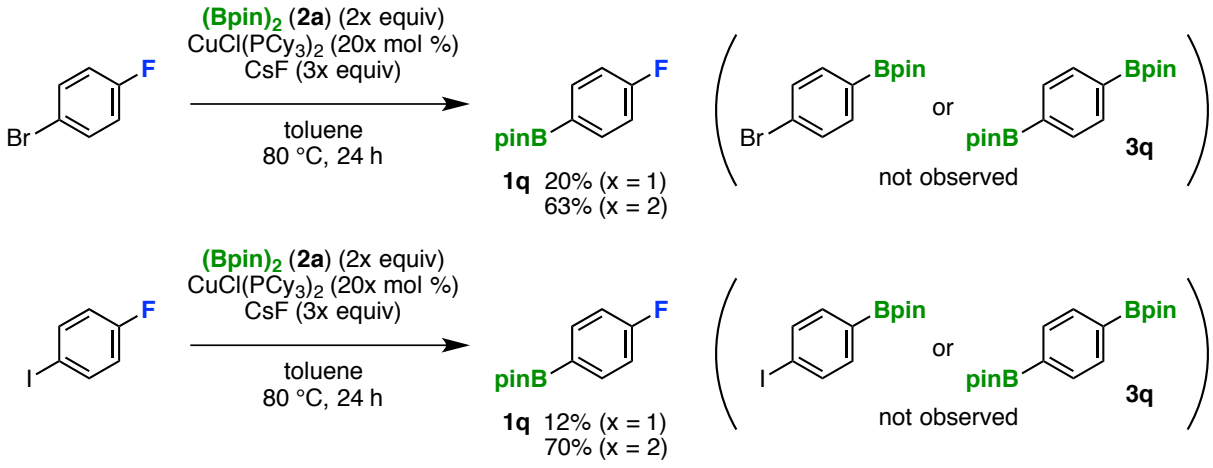
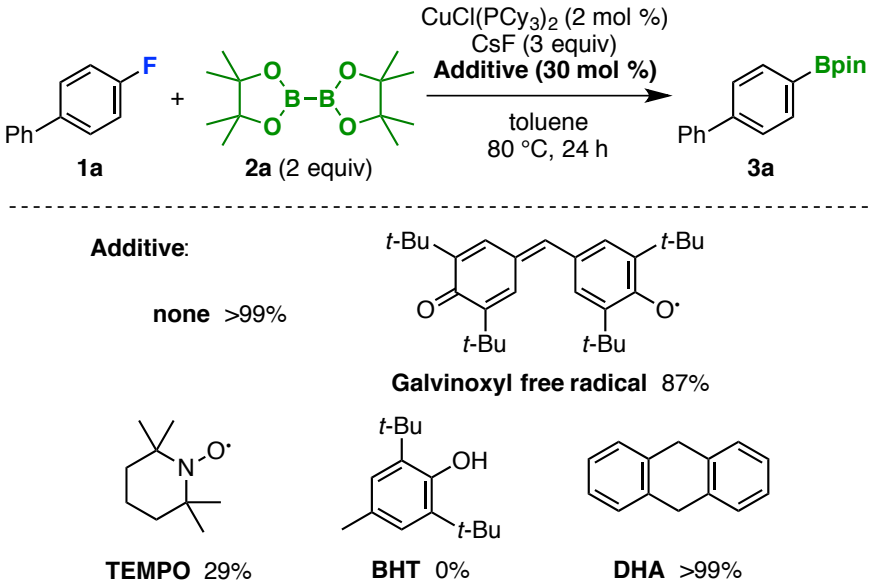


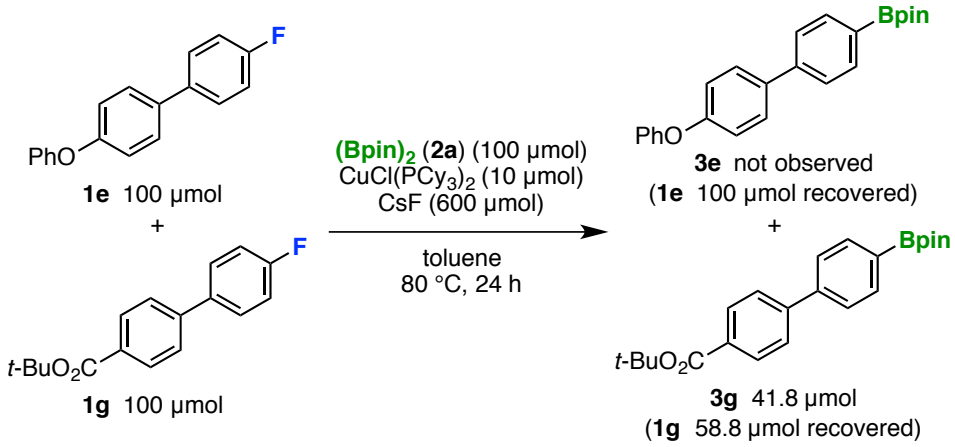
Table S5. *ipso*-Borylation of 1a in the presence of radical scavengers[a]



[a]Determined by GC analysis.

As shown in Table S5, Galvinoxyl free radical and DHA did not inhibit the defluoroborylation of **1a**, indicating the involvement of a free radical species in this reaction is unlikely. Decrease of the yield of **3a** by the addition of TEMPO or BHT can be explained by deactivation of the catalyst by these reagents via oxidation of the copper center or protonation of the borylcopper species.

Competition experiment using electron-rich and electron-deficient fluoroarenes (Scheme 6)



To a capped vial were added **1e** (26.4 mg, 100 μmol), **1g** (27.2 mg, 100 μmol), bis(tricyclohexylphosphine)copper chloride (6.6 mg, 10 μmol), bis(pinacolato)diboron (**2a**, $(Bpin)_2$, 25.4 mg, 100 μmol), cesium fluoride (stored in the glovebox, 90.6 mg, 600 μmol), and toluene (deoxygenated, 1.0 mL) in a glovebox filled with argon gas. After stirring for 30 sec at room temperature, the mixture was heated at 80 ºC with stirring for 24 h. After cooling to room temperature, the reaction vial was taken out from the glovebox and to the mixture was added saturated aqueous ammonium chloride (ca. 2 mL) and extracted with EtOAc (ca. 3 mL × 3). The combined organic extract was dried over Na_2SO_4 and, after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by PTLC (*n*-hexane/EtOAc = 5/1) to give **3g** (15.9 mg, 41.8 μmol) and recovered **1e** (26.5 mg, 100 μmol) and **1g** (16.0 mg, 58.8 μmol).

UV-visible absorption analyses of reaction mixtures (Figure 1)

To a capped vial were added bis(tricyclohexylphosphine)copper chloride (33.0 mg, 50.0 μmol, 1 equiv), bis(pinacolato)diboron (**2a**, $(Bpin)_2$, 50.7 mg, 200 μmol, 4.0 equiv), cesium fluoride (stored in the glovebox, 45.6 mg, 300 μmol, 6.0 equiv), any of the additives (4-fluorobiphenyl (**1a**), 1,4-bis(trifluoromethyl)benzene, TEMPO, or none; 50.0 μmol, 1.0 equiv), and toluene (deoxygenated, 1.0 mL) in a glovebox filled with argon gas. After stirring for 30 sec at room temperature, the mixture was heated at 80 ºC with stirring for 3 h. After cooling to room temperature, the mixture was diluted with deoxygenated toluene (2 mL). The suspension was filtered through a pad of cotton. A portion of the filtrate (60 μL) was diluted with toluene (940 μL) to prepare a sample (1.0 mM for copper complex), which was transferred into an Optima fluorescence quartz cell (No. 30007, chamber volume = 1.0 mL, 10 mm light path) and capped with PTFE stopper and parafilm®.

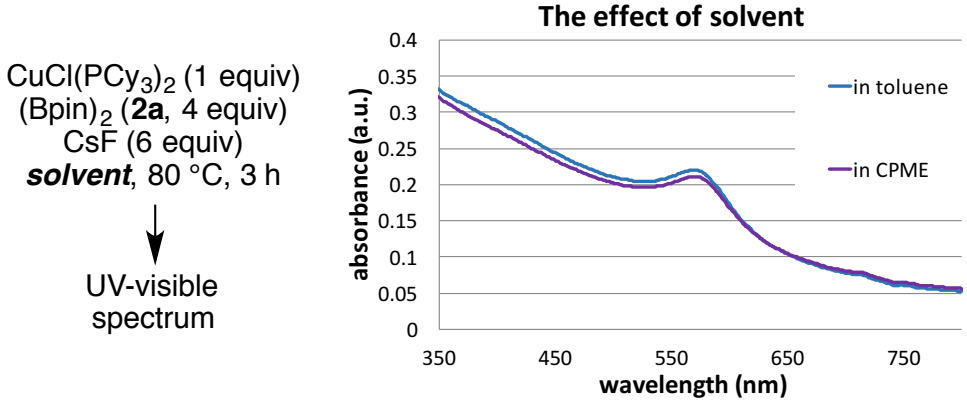


Figure S2. UV-Visible absorption spectra of a mixture of $CuCl(PCy_3)_2$, $(Bpin)_2$ (**2a**), and CsF in toluene or CPME.

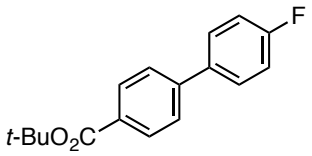
EPR analysis of a reaction mixture

To a capped vial were added 4-fluorobiphenyl (**1a**) (8.5 mg, 50 μmol, 1.0 equiv), bis(tricyclohexylphosphine)copper chloride (33.0 mg, 50.0 μmol, 1 equiv), bis(pinacolato)diboron (**2a**, $(Bpin)_2$, 50.7 mg, 200 μmol, 4.0 equiv), and cesium fluoride (45.6 mg, 300 μmol, 6.0 equiv). After replacing the air in the flask with argon, to the flask was added toluene (deoxygenated, 1.0 mL) using a syringe. After stirring for 30 sec at room temperature, the mixture was heated at 80 ºC with stirring for 3 h to afford a dark red suspension. After cooling to room temperature, the mixture was diluted with deoxygenated toluene (1 mL). A part of the suspension (ca. 0.7 mL) was transferred into a Shigemi quartz ESR tube and capped with PTFE stopper and parafilm®. The sample was frozen at –196 °C using a glass Dewar vessel and EPR analysis was conducted at the same temperature.

EPR analyses of several samples, of which the combination of reagents and additives differed, were conducted similarly.

Synthetic procedure and characterization data

***tert*-Butyl 4-(4′-fluorobiphenyl)carboxylate (1g)**



A solution of 4-fluorophenylboronic acid (504 mg, 3.60 mmol, 1.2 equiv), *tert*-butyl 4-bromobenzoate (771 mg, 3.00 mmol, 1 equiv), diisopropylethylamine (1.57 mL, 9.01 mmol, 3.0 equiv) and [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) chloride dichloromethane adduct (50.0 mg, 61.2 μmol, 0.020 equiv) in 2-propanol (2.5 mL) and water (0.5 mL) was heated at 120 °C for 30 min under microwave irradiation. After cooling to room temperature, the reaction mixture was diluted with EtOAc (ca. 10 mL) and water (ca. 5 mL), and the mixture was then extracted with EtOAc (ca. 10 mL × 3). The combined organic extract was washed with brine (5 mL), dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residual was purified by passing through a short pad of silica gel (*n*-hexane/ethyl acetate = 10/1) to give **1g** (673 mg, 2.47 mmol, 82.4%) as a white solid;

TLC R_f = 0.50 (*n*-hexane/ethyl acetate = 9/1);

mp 92–93 ºC;

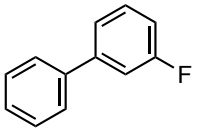
^{1}H NMR ($CDCl_3$) δ 1.62 (s, 9H), 7.11–7.18 (AA′BB′, 2H), 7.56–7.59 (m, 4H), 8.03–8.06 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 28.2 (3C), 81.1 (1C), 115.8 (d, $^2J_{C–F}$ = 23.0 Hz, 2C), 126.7 (2C), 128.9 (d, $^3J_{C–F}$ = 7.7 Hz, 2C), 130.0 (2C), 130.8 (1C), 136.3 (d, $^4J_{C–F}$ = 2.8 Hz, 1C), 144.1 (1C), 162.8 (d, $^1J_{C–F}$ = 247.9 Hz, 1C), 165.6 (1C);

^{19}F NMR ($CDCl_3$) δ –114.3;

The chemical shifts were consistent with those reported in the literature.[S5]

3-Fluorobiphenyl (1i)



To a solution of phenylboronic acid (732 mg, 6.00 mmol, 1.2 equiv) and [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) chloride dichloromethane adduct (81.7 mg, 0.100 mmol, 0.020 equiv) in 2-propanol (5 mL) and water (2.5 mL) were added 1-bromo-3-fluoro-benzene (875 mg, 5.00 mmol, 1 equiv) and diisopropylethylamine (2.61 mL, 15.0 mmol, 3.0 equiv) at room temperature. After stirring for 21 h at 100 ˚C, the mixture was cooled down to room

temperature, added water (ca. 5 mL), and then extracted with EtOAc (ca. 10 mL × 3). The combined organic extract was washed with brine (ca. 5 mL), dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residual was purified by passing through a short pad of silica gel (*n*-hexane/ethyl acetate = 10/1) to give **1i** (823 mg, 4.78 mmol, 95.6%) as a white solid;

TLC R_f = 0.68 (*n*-hexane/ethyl acetate = 10/1);

mp 28–30 ºC;

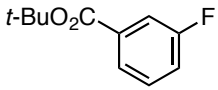
^{1}H NMR ($CDCl_3$) δ 7.01–7.07 (m, 1H), 7.27–7.31 (m, 1H), 7.35–7.41 (m, 3H), 7.43–7.47 (AA′BB′C, 2H), 7.56–7.59 (m, 2H);

^{13}C NMR ($CDCl_3$) δ 114.0 (d, $^2J_{C–F}$ = 20.0 Hz, 1C + 1C, two signals overlapped), 122.7 (d, $^4J_{C–F}$ = 2.8 Hz, 1C), 127.1 (2C), 127.8 (1C), 128.8 (2C), 130.2 (d, $^3J_{C–F}$ = 8.7 Hz, 1C), 139.9 (d, $^4J_{C–F}$ = 1.9 Hz, 1C), 143.5 (d, $^3J_{C–F}$ = 7.7 Hz, 1C), 163.2 (d, $^1J_{C–F}$ = 246.1 Hz, 1C);

^{19}F NMR ($CDCl_3$) δ –113.1;

The chemical shifts were consistent with those reported in the literature.[S6]

***tert*-Butyl 3-fluorobenzoate (1s)**



To a solution of potassium *tert*-butoxide (1.12 g, 9.98 mmol, 1 equiv) in THF (20 mL) was added 3-fluorobenzoyl chloride (1.26 mL, 10.5 mmol, 1.05 equiv) at 0 °C. After warming to room temperature, the reaction mixture was stirred for 1.5 h at the same temperature. To the mixture was added aqueous potassium carbonate (ca. 2 M, ca. 20 mL) at 0 °C. The mixture was stirred for 10 min at room temperature and extracted with Et_2O (ca. 20 mL × 3). The combined organic extract was washed with aqueous potassium carbonate (ca. 2 M, ca. 10 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1) to give **1s** (1.41 g, 4.64 mmol, 46.4%) as a colorless oil;

TLC R_f = 0.55 (*n*-hexane/ethyl acetate = 9/1);

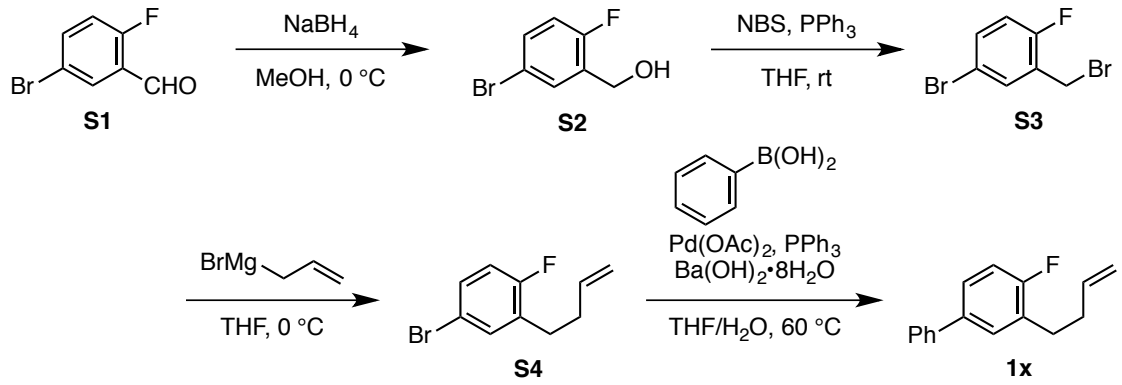
^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9H), 7.2 (dddd, $J_{H–F}$ = 7.9 Hz, $J_{H–H}$ = 7.9, 2.8, 1.2 Hz, 1H), 7.39 (ddd, $J_{H–F}$ = 5.5 Hz, $J_{H–H}$ = 7.9, 7.9 Hz, 1H), 7.66 (ddd, $J_{H–F}$ = 9.5 Hz, $J_{H–H}$ = 2.8, 1.2 Hz, 1H), 7.78 (ddd, $J_{H–H}$ = 7.9, 1.2, 1.2 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 28.1 (3C), 81.6 (1C), 116.3 (d, $^2J_{C–F}$ = 22.9 Hz, 1C), 119.4 (d, $^2J_{C–F}$ = 21.0 Hz, 1C), 125.1 (d, $^4J_{C–F}$ = 2.9 Hz, 1C), 129.7 (d, $^3J_{C–F}$ = 7.7 Hz, 1C), 134.2 (d, $^3J_{C–F}$ = 7.7 Hz, 1C), 162.5 (d, $^1J_{C–F}$ = 246.0 Hz, 1C), 164.5 (1C);

^{19}F NMR ($CDCl_3$) δ –112.8;

The chemical shifts were consistent with those reported in the literature.[S7]

3-(3-Butenyl)-4-fluorobiphenyl (1x)



To a solution of 5-bromo-2-fluorobenzaldehyde (**S1**, 4.11 g, 20.2 mmol, 1 equiv) in methanol (50 mL) was added sodium borohydride (1.06 g, 28.0 mmol, 1.4 equiv) at 0 °C. After warming to room temperature, the reaction mixture was stirred for 1 h at the same temperature. To the mixture was added aqueous hydrochloric acid (ca. 1 M, ca. 30 mL) at 0 °C. The mixture was stirred for 10 min at room temperature and extracted with EtOAc (ca. 20 mL × 3). The combined organic extract was washed with brine (ca. 10 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to give a crude mixture that contained 1-bromo-4-fluoro-3-(hydroxymethyl)benzene (**S2**), which was used for the next step without further purification.

To a solution of the crude mixture in THF (40 mL) were added triphenylphosphine (5.51 g, 21.0 mmol, 1.0 equiv) and *N*-bromosuccinimide (3.63 g, 20.4 mmol, 1.0 equiv) sequentially at 0 °C. After stirring the mixture for 45 min at room temperature, to this was added saturated aqueous sodium thiosulfate (ca. 10 mL) and diluted with Et_2O (60 mL) at 0 °C and stirred for 10 min. After warming to room temperature and filtration through a pad of Celite©, the filtrate was concentrated under reduced pressure. Then the filtrate was concentrated under reduced pressure to give a crude mixture that contained 1-bromo-3-(bromomethyl)-4-fluorobenzene (**S3**), which was used for the next step without further purification.

To a solution of the crude mixture in THF (30 mL) was dropwisely added allylmagnesium bromide (0.7 M solution in Et_2O, 42.9 mL, 30.0 mmol, 1.5 equiv) at 0 °C. After warming to room temperature, the reaction mixture was stirred for 30 min at the same temperature. To this was added saturated aqueous ammonium chloride (ca. 10 mL) at 0 °C. After warming to room temperature, the mixture was extracted with Et_2O (ca. 10 mL × 3). The combined organic extract was washed with brine (ca. 10 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to give a crude mixture that contained 1-bromo-3-(3-butenyl)-4-fluorobenzene (**S4**), which was used for the next step without further purification.

To a solution of the crude mixture in THF (100 mL) and water (20 mL) added phenylboronic acid (2.93 g, 24.0 mmol, 1.2 equiv), palladium(II) acetate (44.9 mg, 0.200 mmol, 0.01 equiv), triphenylphosphine (210 mg, 0.801 mmol, 0.04 equiv), and barium hydroxide octahydrate (12.6 g, 39.9 mmol, 2.0 equiv) at room temperature. After stirring for 16 h with heating at 60 °C, the reaction mixture was cooled to room temperature, and filtered through a pad of Celite©. The filtrate was concentrated under reduced pressure and extracted with EtOAc (ca. 15 mL × 3). The combined organic extract was washed with brine (ca. 15 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 20/1) to give **1x** (2.86 g, 12.6 mmol, 62.6% from 5-bromo-2-fluorobenzaldehyde) as a colorless oil;

TLC R_f = 0.55 (*n*-hexane);

^{1}H NMR ($CDCl_3$) δ 2.41 (tddd, J = 7.1, 6.7, 1.5, 0.8 Hz, 2H), 2.80 (t, J = 7.1 Hz, 2H), 5.00 (ddt, J = 10.0, 2.4, 0.8 Hz, 1H), 5.06 (ddt, J = 17.0, 2.4, 1.5 Hz, 1H), 5.88 (ddt, J = 17.0, 10.0, 6.7 Hz, 1H), 7.07 (dd, $J_{H–F}$ = 9.5 Hz, $J_{H–H}$ = 8.3 Hz, 1H), 7.31–7.45 (m, 5H), 7.52–7.55 (m, 2H);

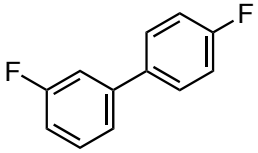
^{13}C NMR ($CDCl_3$) δ 28.7 (1C), 34.2 (1C), 115.3 (1C), 115.4 (d, $^2J_{C–F}$ = 22.9 Hz, 1C), 126.2 (d, $^3J_{C–F}$ = 8.6 Hz, 1C), 127.0 (2C), 127.1 (1C), 128.7 (2C), 128.8 (d, $^2J_{C–F}$ = 14.3 Hz, 1C), 129.4 (d, $^3J_{C–F}$ = 4.8 Hz, 1C), 137.1 (d, $^4J_{C–F}$ = 3.8 Hz, 1C), 137.7 (1C), 140.5 (1C), 160.8 (d, $^1J_{C–F}$ = 245.1 Hz, 1C);

^{19}F NMR ($CDCl_3$) δ –121.1;

IR (ZnSe, cm^{-1}) 756, 1173, 1271, 1300, 1445;

HRMS (ESI^+) *m*/*z* 249.1058 (249.1050 calcd for $C_{16}H_{15}FNa^+$, $[M+Na]^+$).

3,4′-Difluorobiphenyl (1aa)



A solution of 4-fluorophenylboronic acid (336 mg, 2.40 mmol, 1.2 equiv), [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) chloride dichloromethane adduct (32.7 mg, 40.0 μmol, 0.02 equiv) 1-bromo-3-fluorobenzene (350 mg, 2.00 mmol, 1 equiv), and diisopropylethylamine (1.08 mL, 6.20 mmol, 3.1 equiv) in 2-propanol (3 mL) and water (0.5 mL) was stirred at 120 °C for 30 min under microwave irradiation. After cooling to room temperature, this mixture was diluted with Et_2O (5 mL) and water (5 mL), and then was extracted with Et_2O (ca. 3 mL × 3). The combined organic extract was washed with brine (ca. 5 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane) to give **1aa** (366 mg, 1.92 mmol, 96.2%) as a colorless oil;

TLC R_f = 0.62 (*n*-hexane/EtOAc = 9/1);
^{1}H NMR ($CDCl_3$) δ 7.01–7.06 (m, 1H), 7.11–7.17 (m, 2H), 7.22–7.27 (m, 1H), 7.30–7.33 (m, 1H), 7.37–7.42 (m, 1H), 7.51–7.56 (m, 2H);
^{13}C NMR ($CDCl_3$) δ 113.9 (d, $^2J_{C–F}$ = 21.9 Hz, 1C), 114.0 (d, $^2J_{C–F}$ = 21.0 Hz, 1C), 115.7 (d, $^2J_{C–F}$ = 22.0 Hz, 2C), 122.6 (d, $^4J_{C–F}$ = 2.9 Hz, 1C), 128.7 (d, $^3J_{C–F}$ = 8.6 Hz, 2C), 130.3 (d, $^3J_{C–F}$ = 7.7 Hz, 1C), 136.0 (1C), 142.4 (d, $^3J_{C–F}$ = 8.6 Hz, 1C), 162.7 (d, $^1J_{C–F}$ = 247.0 Hz, 1C), 163.2 (d, $^1J_{C–F}$ = 245.1 Hz, 1C);
^{19}F NMR ($CDCl_3$) δ –114.6, –112.7;
IR (ZnSe, cm^{-1}) 690, 781, 835, 880, 1184, 1229, 1485, 1516, 1581, 1598, 1614;
HRMS (ESI$^+$) *m*/*z* 191.0662 (191.0667 calcd for $C_{12}H_9F_2^+$, $[M+H]^+$).

General procedure for copper-catalyzed *ipso*-borylation of fluoroarenes

To a capped vial were added fluoroarene **1** (0.200 mmol, 1 equiv), bis(pinacolato)diboron (102 mg, 0.402 mmol, 2.0 equiv), bis(tricyclohexylphosphine)copper chloride (6.6 mg, 10 μmol, 0.05 equiv), cesium fluoride (stored in the glovebox, 91.0 mg, 0.600 mmol, 3.0 equiv) and toluene (deoxygenated, 1.0 mL) in a glovebox filled with argon gas. After stirring for 30 sec at room temperature, the mixture was heated at 80 ºC with stirring for 24 h. After cooling to room temperature and taken out from the glovebox, to the mixture was added saturated aqueous ammonium chloride (ca. 2 mL) and extracted with EtOAc (ca. 3 mL × 3). The combined organic extract was dried over Na_2SO_4 and, after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by PTLC or silica-gel column chromatography to give arylboronic acid pinacol ester **3**.

Copper-catalyzed defluoroborylation of 3 mmol of 1a using CuCl and PCy_3 (Table 1, entry 13)

To a one-necked 20 mL round bottom flask were added 4-fluorobiphenyl (**1a**, 511 mg, 2.97 mmol, 1 equiv), bis(pinacolato)diboron (1.52 g, 5.99 mmol, 2.0 equiv), copper(I) chloride (14.9 mg, 0.151 mmol, 0.051 equiv), tricyclohexylphosphine (126 mg, 0.449 mmol, 0.15 equiv), cesium fluoride (stored in the glovebox, 1.37 g, 9.02 mmol, 3.0 equiv) and toluene (deoxygenated, 10 mL) in a glovebox filled with argon gas. The flask was capped with a glass stopper, taken out from the glovebox, and stirred the mixture at 80 ºC (oil bath temperature) with stirring for 24 h. After cooling to room temperature, to the mixture was added saturated aqueous ammonium chloride (ca. 5 mL). After stirring mixture for 15 min at room temperature, this mixture was extracted with EtOAc (ca. 10 mL × 3). The combined organic extract was dried over Na_2SO_4 and, after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column

chromatography (*n*-hexane/EtOAc = 100/1) to give **3a** (797 mg, 2.84 mmol, 95.8%) as a colorless solid.

Copper-catalyzed defluoroborylation of 3 mmol of 1a (Table 2, entry 5)

To a one-necked 20 mL round bottom flask were added 4-fluorobiphenyl (**1a**, 511 mg, 2.97 mmol, 1 equiv), bis(pinacolato)diboron (1.52 g, 5.99 mmol, 2.0 equiv), bis(tricyclohexyl-phosphine)copper chloride (99.0 mg, 0.150 mmol, 0.05 equiv), cesium fluoride (stored in the glovebox, 1.37 g, 9.02 mmol, 3.0 equiv), and toluene (deoxygenated, 10 mL) in a glovebox filled with argon gas. The flask was capped with a glass stopper, taken out from the glovebox, and stirred the mixture at 80 ºC (oil bath temperature) with stirring for 24 h. After cooling to room temperature, to the mixture was added saturated aqueous ammonium chloride (ca. 5 mL). After stirring mixture for 15 min at room temperature, this mixture was extracted with EtOAc (ca. 10 mL × 3). The combined organic extract was dried over Na_2SO_4 and, after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 100/1) to give **3a** (811 mg, 2.89 mmol, 97.5%) as a colorless solid.

Copper-catalyzed defluoroborylation of 50 mmol of 1a (Table 2, entry 5)

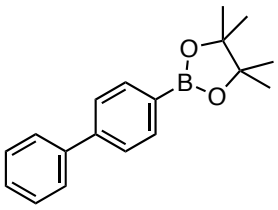
Under air atmosphere, to a one-necked 500 mL round bottom flask equipper with a stopcock were added 4-fluorobiphenyl (**1a**, 8.51 g, 49.4 mmol, 1 equiv), bis(pinacolato)diboron (25.4 g, 100 mmol, 2.0 equiv), bis(tricyclohexylphosphine)copper chloride (1.65 g, 2.50 mmol, 0.05 equiv), and cesium fluoride (stored outside the glovebox, 22.8 g, 150 mmol, 3.0 equiv). After replacing air in the flask with argon, to the flask was added toluene (non-deoxygenated, 250 mL) by using a syringe. The mixture was heated at 80 ºC (oil bath temperature) with stirring for 24 h. After cooling to room temperature, to the mixture was slowly added saturated aqueous ammonium chloride (ca. 30 mL) at 0 °C. During the addition, gas generation was observed. After stirring for 15 min at room temperature, this mixture was concentrated into ca. 30 mL volume under reduced pressure, and then extracted with EtOAc (ca. 30 mL × 3). The combined organic extract was dried over Na_2SO_4 and, after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc/AcOH = 50/2/1) to give **3a** (12.9 g, 46.0 mmol, 93.2%) as a colorless solid.

Copper-catalyzed multi-*ipso*-borylation of polyfluoroarenes (Table 4)

To a capped vial were added polyfluoroarene **1** (1 equiv, ***n***: the number of fluorine atoms in the substrates, 1 equiv), bis(pinacolato)diboron (2.0 × ***n*** equiv), bis(tricyclohexylphosphine)copper chloride (0.05 × ***n*** equiv), cesium fluoride (3.0 × ***n*** equiv) and toluene (deoxygenated, 1.0 mL) in a

glovebox filled with argon gas. After stirring for 30 sec at room temperature, the mixture was heated at 80 ºC with stirring for 24 h. After cooling to room temperature, to the mixture was added saturated aqueous ammonium chloride (ca. 2 mL) and extracted with EtOAc (ca. 3 mL × 3). The combined organic extract was dried over Na_2SO_4 and, after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give multiborylated benzene **3**.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3a)



Yields: 94.8% (Table 1, entry 13, 797 mg, 2.84 mmol), 86.0% (Table 2, entry 1, 48.2 mg, 0.172 mmol), 93.7% (Table 2, entry 5, 52.5 mg, 0.187 mmol) for 0.2 mmol scale; 96.5% (Table 2, entry 5, 811 mg, 2.89 mmol) for 3 mmol scale; 92.1% (Table 2, entry 5, 12.9 g, 46.0 mmol) for 50 mmol scale;

Colorless solid (mp 111–112 °C);

Eluent for PTLC purification for 0.2 mmol scale: *n*-hexane/EtOAc = 10/1;

Eluent for silica-gel column chromatography in large-scale reactions: see experimental procedures;

TLC R_f = 0.52 (*n*-hexane/EtOAc = 10/1);

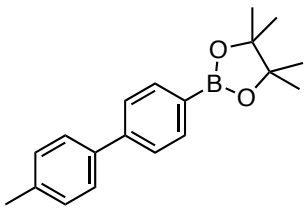
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 7.35 (tt, J = 7.4, 1.3 Hz, 1H), 7.42–7.46 (m, 2H), 7.60–7.63 (m, 4H), 7.89 (d, J = 8.3 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.8 (2C), 126.4 (2C), 127.2 (2C), 127.5 (1C), 128.7 (2C), 135.2 (2C), 141.0 (1C), 143.9 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.5;

The chemical shifts were consistent with those reported in the literature.[S8]

4-Methyl-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3b)



Yield: 89.7% (52.8 mg, 0.180 mmol);

Colorless solid (mp 112–114 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 20/1;

TLC R_f = 0.72 (*n*-hexane/EtOAc = 10/1);

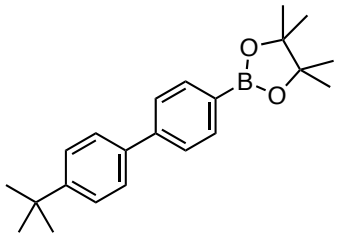
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 2.40 (s, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 21.1 (1C), 24.9 (4C), 83.8 (2C), 126.2 (2C), 127.0 (2C), 129.5 (2C), 135.2 (2C), 137.4 (1C), 138.1 (1C), 143.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.2;

The chemical shifts were consistent with those reported in the literature.[S3]

4-*tert*-Butyl-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3c)



Yield: 77.2% (51.9 mg, 0.154 mmol);

Colorless solid (mp 158–161 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.48 (*n*-hexane/EtOAc = 10/1);

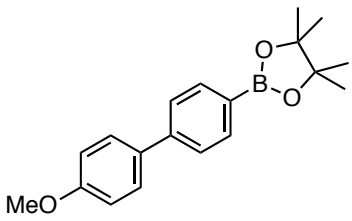
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H + 9H, two signals overlapped), 7.47 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 31.3 (3C), 34.6 (1C), 83.8 (2C), 125.7 (2C), 126.3 (2C), 126.8 (2C), 135.2 (2C), 138.1 (1C), 143.7 (1C), 150.6 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.6;

The chemical shifts were consistent with those reported in the literature.[S3]

4-Methoxy-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3d)



Yields: 80.9% (using 5 mol % of Cu catalyst, 50.2 mg, 0.162 mmol), 90.7% (using 20 mol % of Cu

catalyst, 56.3 mg, 0.182 mmol);

Colorless solid (mp 147–148 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.32 (*n*-hexane/EtOAc = 10/1);

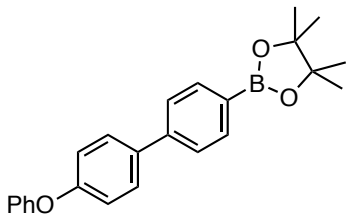
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 3.84 (s, 3H), 6.95–6.99 (AA′BB′, 2H), 7.54–7.58 (m, 4H), 7.85–7.87 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 55.3 (1C), 83.7 (2C), 114.2 (2C), 125.9 (2C), 128.2 (2C), 133.4 (1C), 135.2 (2C), 143.4 (1C), 159.4 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.3;

The chemical shifts were consistent with those reported in the literature.[S3]

4-Phenoxy-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3e)



Yield: 95.8% (71.3 mg, 0.192 mmol);

Colorless solid (mp 155–156 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.24 (*n*-hexane/EtOAc = 20/1);

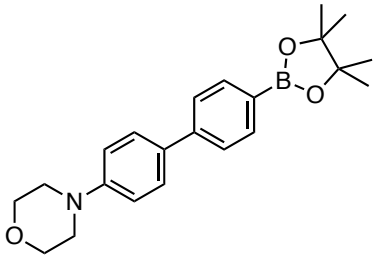
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 7.05–7.09 (m, 4H), 7.10–7.15 (AA′BB′C, 1H), 7.33–7.38 (AA′BB′, 2H), 7.56–7.60 (m, 4H), 7.87–7.89 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.8 (2C), 119.0 (2C + 2C), 123.4 (1C), 126.2 (2C), 128.5 (2C), 129.8 (2C), 135.3 (2C), 136.0 (1C), 143.2 (1C), 157.0 (1C), 157.1 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.6;

The chemical shifts were consistent with those reported in the literature.[S3]

4-(*N*-Morpholinyl)-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3f)



Yield: 95.7% (69.9 mg, 0.191 mmol);

Colorless solid (mp 212–213 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 3/1;

TLC R_f = 0.68 (*n*-hexane/EtOAc = 2/1);

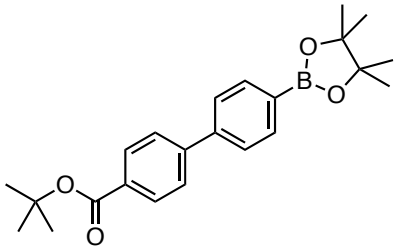
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 3.20–3.22 (AA′BB′, 4H), 3.87–3.89 (AA′BB′, 4H), 6.96–6.99 (AA′BB′, 2H), 7.54–7.59 (m, 4H), 7.84–7.86 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 49.1 (2C), 66.9 (2C), 83.7 (2C), 115.7 (2C), 125.7 (2C), 127.9 (2C), 132.3 (1C), 135.2 (2C), 143.4 (1C), 150.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.8;

The chemical shifts were consistent with those reported in the literature.[S3]

***tert*-Butyl 4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenylcarboxylate (3g)**



Yield: 53.5% (using 5 mol % of Cu catalyst, 40.7 mg, 0.107 mmol), 61.5% (using 20 mol % of Cu catalyst, 46.8 mg, 0.123 mmol);

Colorless solid (mp 137–138 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.32 (*n*-hexane/EtOAc = 10/1);

^{1}H NMR ($CDCl_3$) δ 1.37 (s, 12H), 1.62 (s, 9H), 7.61–7.64 (AA′BB′, 2H), 7.64–7.67 (AA′BB′, 2H), 7.89–7.91 (AA′BB′, 2H), 8.04–8.07 (AA′BB′, 2H);

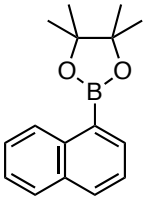
^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 28.2 (3C), 81.0 (1C), 83.9 (2C), 126.5 (2C), 127.0 (2C), 129.9 (2C), 131.0 (1C), 135.3 (2C), 142.8 (1C), 144.9 (1C), 165.6 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.5;

IR (ZnSe, cm^{-1}) 773, 1091, 1143, 1294, 1357, 1606, 1712;

HRMS (EI^+) *m/z* 380.2161 (380.2159 calcd for $C_{23}H_{29}BO_4^+$, $[M]^+$).

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (3h)



Yield: 63.4% (32.2 mg, 0.127 mmol);

Colorless solid (mp 57–58 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 20/1;

TLC R_f = 0.72 (*n*-hexane/EtOAc = 10/1);

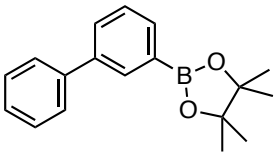
^{1}H NMR ($CDCl_3$) δ 1.43 (s, 12H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.51–7.55 (m, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 6.8 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.7 (2C), 124.9 (1C), 125.5 (1C), 126.3 (1C), 128.3 (1C), 128.4 (1C), 131.6 (1C), 133.2 (1C), 135.6 (1C), 136.9 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.5;

The chemical shifts were consistent with those reported in the literature.[S8]

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3i)



Yield: 75.1% (42.1 mg, 0.150 mmol);

Colorless solid (mp 79–80 °C);

Eluent for PTLC separation: *n*-hexane/EtOAc = 20/1;

TLC R_f = 0.52 (*n*-hexane/EtOAc = 20/1);

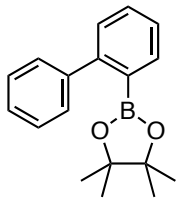
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 7.33 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.41–7.47 (m, 3H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 8.05 (s, 1H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.9 (2C), 127.2 (1C + 2C), 128.2 (1C), 128.6 (2C), 130.0 (1C), 133.5 (1C), 133.6 (1C), 140.5 (1C), 141.1 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.0;

The chemical shifts were consistent with those reported in the literature.[S9]

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3j)



Yield: 76.7% (43.0 mg, 0.154 mmol);

Colorless solid (mp 80–82 °C);

Eluent for PTLC separation: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.62 (*n*-hexane/EtOAc = 10/1);

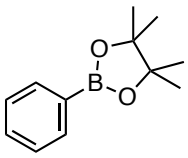
^{1}H NMR ($CDCl_3$) δ 1.20 (s, 12H), 7.30–7.46 (m, 8H), 7.71 (d, J = 7.3 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 24.6 (4C), 83.7 (2C), 126.2 (1C), 126.8 (1C), 127.7 (2C), 128.9 (1C), 129.1 (2C), 130.0 (1C), 134.4 (1C), 143.2 (1C), 147.5 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.1;

The chemical shifts were consistent with those reported in the literature.[S8]

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3k)



Yield: 70.8% (28.9 mg, 0.142 mmol);

Colorless oil;

Eluent for PTLC purification: *n*-hexane/EtOAc/AcOH = 20/1/0.1;

TLC R_f = 0.49 (*n*-hexane/EtOAc = 10/1);

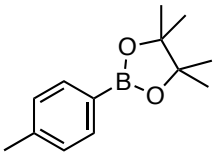
^{1}H NMR ($CDCl_3$) δ 1.35 (s, 12H), 7.35–7.39 (m, 2H), 7.46 (tt, J = 7.5, 1.1 Hz, 1H), 7.81 (dd, J = 8.3, 1.1 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 83.7 (2C), 127.7 (2C), 131.2 (1C), 134.7 (2C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.1;

The chemical shifts were consistent with those reported in the literature.[S8]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (3l)



Yield: 53.9% (23.5 mg, 0.108 mmol);

Colorless solid (mp 53–54 °C);

Eluent for PTLC separation: *n*-hexane/EtOAc = 20/1;

TLC R_f = 0.43 (*n*-hexane/EtOAc = 20/1);

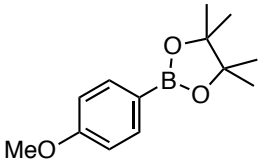
^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 2.36 (s, 3H), 7.18 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 21.7 (1C), 24.8 (4C), 83.6 (2C), 128.5 (2C), 134.8 (2C), 141.4 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.3;

The chemical shifts were consistent with those reported in the literature.[S8]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (3m)



Yields: 41.6% (using 5 mol % of Cu catalyst, 19.5 mg, 83.3 μmol), 70.7% (using 60 mol % of Cu catalyst, 33.1 mg, 0.141 mmol);

Colorless oil;

Eluent for PTLC purification: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.46 (*n*-hexane/EtOAc = 10/1);

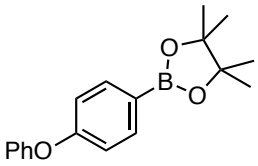
^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 3.83 (s, 3H), 6.88–6.91 (AA′BB′, 2H), 7.74–7.76 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 55.1 (1C), 83.5 (2C), 113.3 (2C), 136.5 (2C), 162.1 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.0;

The chemical shifts were consistent with those reported in the literature.[S8]

Phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl ether (3n)



Yield: 69.4% (41.1 mg, 0.139 mmol);

Colorless oil;

Eluent for PTLC purification: *n*-hexane/EtOAc = 4/1;

TLC R_f = 0.48 (*n*-hexane/EtOAc = 4/1);

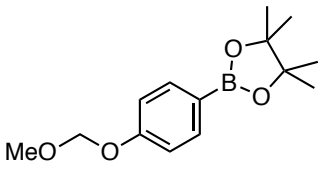
^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 6.97–6.99 (AA′BB′, 2H), 7.02–7.04 (AA′BB′C, 2H), 7.13 (t, J = 7.9 Hz, 1H), 7.33–7.37 (AA′BB′C, 2H), 7.77–7.79 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 83.7 (2C), 117.6 (2C), 119.4 (2C), 123.6 (1C), 129.7 (2C), 136.6 (2C), 156.5 (1C), 160.1 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.6;

The chemical shifts were consistent with those reported in the literature.[S10]

1-Methoxymethoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3o)



Yield: 35.8% (18.9 mg, 71.6 μmol);

Colorless oil;

Eluent for PTLC purification: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.39 (*n*-hexane/EtOAc = 10/1);

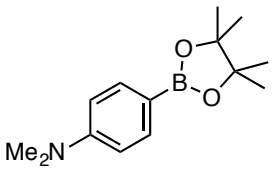
^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 3.47 (s, 3H), 5.20 (s, 2H), 7.01–7.04 (AA′BB′, 2H), 7.73–7.77 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 56.0 (1C), 83.6 (2C), 94.0 (1C), 115.4 (2C), 136.5 (2C), 159.7 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.6;

The chemical shifts were consistent with those reported in the literature.[S3]

***N*,*N*-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3p)**



Yield: 20.8% (10.3 mg, 41.7 μmol);

Colorless solid (mp 119–120 °C);

Eluent for PTLC separation: *n*-hexane/EtOAc = 5/1;

TLC R_f = 0.35 (*n*-hexane/EtOAc = 10/1);

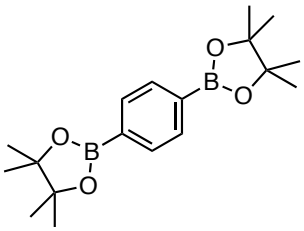
^{1}H NMR ($CDCl_3$) δ 1.32 (s, 12H), 2.98 (s, 6H), 6.67–6.70 (AA′BB′, 2H), 7.67–7.70 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 40.1 (2C), 83.1 (2C), 111.2 (2C), 136.1 (2C), 152.5 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.4;

The chemical shifts were consistent with those reported in the literature.[S3]

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3q)



Yields: 83.3% (Table 3, 55.0 mg, 0.167 mmol) from **1q**, 80.6% (Table 4, 26.6 mg, 80.6 μmol) from 0.1 mmol of 1,4-difluorobenzene (**1q′**) with 0.4 mmol of **2a**, 59.2% (Table 4, 39.1 mg, 0.119 mmol) from 0.2 mmol of **1q′** with 0.4 mmol of **2a**;

Colorless solid (mp 191–193 °C);

Eluent for silica-gel column chromatography: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.50 (*n*-hexane/EtOAc = 9/1);

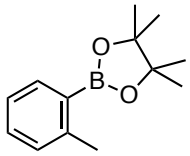
^{1}H NMR ($CDCl_3$) δ 1.35 (s, 24H), 7.80 (s, 4H);

^{13}C NMR ($CDCl_3$) δ 24.8 (8C), 83.8 (4C), 133.9 (4C) (the signals for the carbons that are attached to the boron atoms were not observed);

^{11}B NMR ($CDCl_3$) δ 30.7;

The chemical shifts were consistent with those reported in the literature.[S8]

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (3r)



Yield: 79.3% (34.6 mg, 0.159 mmol);

Colorless oil;

Eluent for PTLC separation: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.55 (*n*-hexane/EtOAc = 10/1);

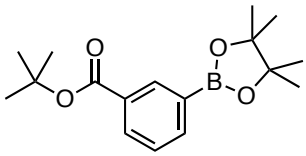
^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 2.54 (s, 3H), 7.14–7.18 (m, 2H), 7.31 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H), 7.76 (dd, *J* = 7.5, 1.6 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 22.2 (1C), 24.9 (4C), 83.4 (2C), 124.7 (1C), 129.8 (1C), 130.8 (1C), 135.8 (1C), 144.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.7;

The chemical shifts were consistent with those reported in the literature.[S3]

***tert*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3s)**



Yield: 31.7% (19.3 mg, 63.4 μmol);

Colorless solid (mp 48–50 °C);

Eluent for PTLC purification: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.46 (*n*-hexane/EtOAc = 9/1);

^{1}H NMR ($CDCl_3$) δ 1.35 (s, 12H), 1.60 (s, 9H), 7.42 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 8.40 (s, 1H);

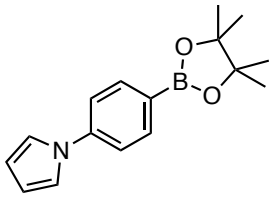
^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 28.2 (3C), 81.0 (1C), 84.0 (2C), 127.6 (1C), 131.4 (1C), 132.1 (1C), 135.6 (1C), 138.6 (1C), 165.9 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.8;

IR (ZnSe, cm^{-1}) 700, 1144, 1287, 1362, 1714, 2978;

HRMS (ESI^+) *m/z* 327.1730 (327.1738 calcd for $C_{17}H_{25}BNaO_4^+$, $[M+Na]^+$).

***N*-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrole (3t)**



Yield: 81.9% (44.1 mg, 0.164 mmol);

Colorless solid (mp 87–88 °C);

Eluent for PTLC separation: *n*-hexane/EtOAc = 5/1;

TLC R_f = 0.70 (*n*-hexane/EtOAc = 5/1);

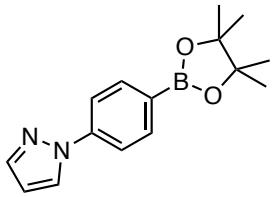
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 6.36 (dd, *J* = 2.3, 2.3 Hz, 2H), 7.14 (dd, *J* = 2.3, 2.3 Hz, 2H), 7.38–7.41 (AA′BB′, 2H), 7.84–7.87 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.9 (2C), 110.7 (2C), 119.1 (2C), 119.2 (2C), 136.2 (2C), 142.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.8;

The chemical shifts were consistent with those reported in the literature.[S3]

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1*H*-pyrazole (3u)



Yield: 79.2% (42.8 mg, 0.158 mmol);

Colorless solid (mp 71–72 °C);

Eluent for PTLC separation: *n*-hexane/EtOAc = 3/1;

TLC R_f = 0.18 (*n*-hexane/EtOAc = 5/1);

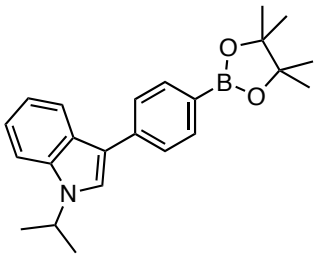
^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H), 6.48 (dd, *J* = 2.4, 1.7 Hz, 1H), 7.70–7.74 (AA′BB′, 2H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.88–7.91 (AA′BB′, 2H), 7.98 (dd, *J* = 2.4, 0.7 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.9 (2C), 107.8 (1C), 118.0 (2C), 126.7 (1C), 136.1 (2C), 141.3 (1C), 142.2 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.3;

The chemical shifts were consistent with those reported in the literature.[S3]

1-Isopropyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)indole (3v)



Yield: 96.0% (69.4 mg, 0.192 mmol);

Yellow oil;

Eluent for PTLC separation: *n*-hexane/EtOAc = 10/1;

TLC R_f = 0.29 (*n*-hexane/EtOAc = 10/1);

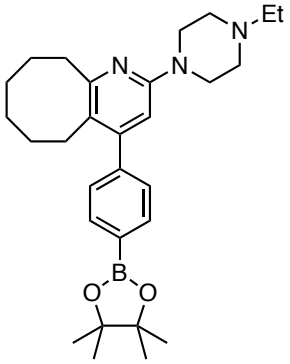
^{1}H NMR ($CDCl_3$) δ 1.37 (s, 12H), 1.57 (d, *J* = 6.8 Hz, 6H), 4.71 (sep, *J* = 6.8 Hz, 1H), 7.18 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H), 7.26 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.68–7.70 (AA′BB′, 2H), 7.87–7.89 (AA′BB′, 2H), 7.97 (d, *J* = 7.5 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 22.8 (2C), 24.9 (4C), 47.1 (1C), 83.6 (2C), 109.8 (1C), 116.7 (1C), 120.0 (2C), 121.8 (1C), 121.9 (1C), 126.1 (1C), 126.4 (2C), 135.2 (2C), 136.4 (1C), 138.9 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.1;

The chemical shifts were consistent with those reported in the literature.[S3]

Defluoroborylated blonanserin 3w



Yield: 87.1% (41.4 mg, 87.1 μmol) from 0.1 mmol of **1w**;

Colorless oil;

PTLC purification (CH_2Cl_2/MeOH = 9/1) followed by GPC purification ($CHCl_3$);

TLC R_f = 0.48 (CH_2Cl_2/MeOH = 9/1);

^{1}H NMR ($CDCl_3$) δ 1.15 (t, *J* = 7.1 Hz, 3H), 1.36 (s, 12H), 1.36–1.43 (m, 6H), 1.78 (br s, 2H), 2.51 (br s, 2H), 2.56–2.58 (m, 6H), 2.89 (t, *J* = 5.9 Hz, 2H), 3.55 (br s, 4H), 6.31 (s, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 11.8 (1C), 24.9 (4C), 25.8 (1C), 26.5 (1C + 1C, two signals overlapped), 30.6

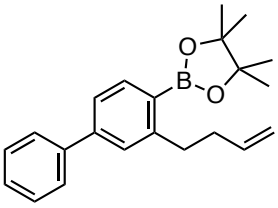
(1C), 31.5 (1C), 35.5 (1C), 45.4 (2C), 52.4 (1C), 52.6 (2C), 83.8 (2C), 105.7 (1C), 122.9 (1C), 127.9 (2C), 134.4 (2C), 144.4 (1C), 151.3 (1C), 157.2 (1C), 159.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.9;

IR (ZnSe, cm^{-1}) 754, 1144, 1360, 1395, 1589, 2920, 2980;

HRMS (ESI^+) *m*/*z* 476.3448 (476.3443 calcd for $C_{29}H_{43}BO_2N_3^+$, $[M+H]^+$).

3-(3-Butenyl)-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3x)



Yield: 62.5% (41.8 mg, 0.125 mmol);

Colorless oil;

Eluent for PTLC purification: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.64 (*n*-hexane/EtOAc = 9/1);

^{1}H NMR ($CDCl_3$) δ 1.35 (s, 12H), 2.36 (dt, *J* = 8.3, 7.9 Hz, 2H), 3.04 (t, *J* = 7.9 Hz, 2H), 4.97 (dd, *J* = 9.9, 0.8 Hz, 1H), 5.05 (dd, *J* = 17.0, 0.8 Hz, 1H), 5.92 (ddt, *J* = 17.0, 9.9, 8.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.41–7.45 (m, 4H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.86 (t, *J* = 8.3 Hz, 1H);

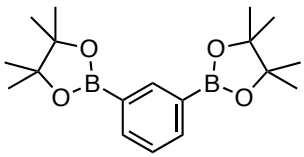
^{13}C NMR ($CDCl_3$) δ 24.8 (4C), 35.6 (1C), 37.5 (1C), 83.4 (2C), 114.4 (1C), 123.8 (1C), 127.2 (2C), 127.4 (1C), 128.1 (1C), 128.7 (2C), 136.7 (1C), 138.7 (1C), 141.1 (1C), 143.4 (1C), 149.6 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.2;

IR (ZnSe, cm^{-1}) 860, 1146, 1350, 1608, 2978;

HRMS (ESI^+) *m*/*z* 335.2166 (335.2177 calcd for $C_{22}H_{28}BO_2^+$, $[M+H]^+$).

1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3y)



Yield: 84.2% (27.8 mg, 84.2 μmol) from 0.1 mmol of **1y**;

Colorless solid (mp 131–133 °C);

Eluent for silica-gel column chromatography: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.72 (*n*-hexane/EtOAc = 4/1);

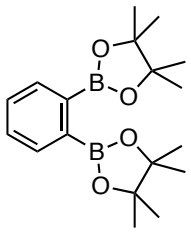
^{1}H NMR ($CDCl_3$) δ 1.34 (s, 24H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.90 (d, *J* = 7.1 Hz, 2H), 8.28 (s, 1H);

^{13}C NMR ($CDCl_3$) δ 24.9 (8C), 83.7 (4C), 127.0 (1C), 137.6 (2C), 141.2 (1C) (the signals for the carbons that are attached to the boron atoms were not observed);

^{11}B NMR ($CDCl_3$) δ 29.9;

The chemical shifts were consistent with those reported in the literature.[S11]

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3z)



Yield: 91.5% (60.4 mg, 0.183 mmol) from 0.2 mmol of **1z**;

Colorless solid (mp 89–91 °C);

Eluent for silica-gel column chromatography: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.60 (*n*-hexane/EtOAc = 4/1);

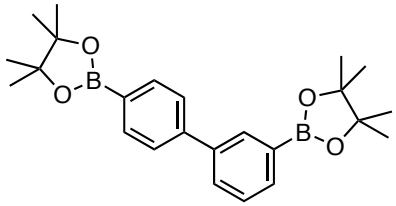
^{1}H NMR ($CDCl_3$) δ 1.37 (s, 24H), 7.35–7.39 (AA′BB′, 2H), 7.63–7.67 (AA′BB′, 2H);

^{13}C NMR ($CDCl_3$) δ 24.9 (8C), 83.9 (4C), 129.1 (2C), 133.4 (2C) (the signals for the carbons that are attached to the boron atoms were not observed);

^{11}B NMR ($CDCl_3$) δ 30.5;

The chemical shifts were consistent with those reported in the literature.[S12]

3,4′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (3aa)



Yield: 70.0% (56.9 mg, 0.140 mmol) from 0.2 mmol of **1aa**;

Colorless solid (mp 158–160 °C);

Eluent for silica-gel column chromatography: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.55 (*n*-hexane/EtOAc = 5/1);

^{1}H NMR ($CDCl_3$) δ 1.36 (s, 12H + 12H, two signals overlapped), 7.45 (dd, J = 7.5, 7.5 Hz, 1H), 7.65 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 7.5 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.87 (d, J = 7.9 Hz, 2H), 8.07 (s, 1H);

^{13}C NMR ($CDCl_3$) δ 24.8 (4C + 4C, two signals overlapped), 83.7 (2C), 83.9 (2C), 126.5 (2C), 128.2 (1C), 130.1 (1C), 133.4 (1C), 134.0 (1C), 135.1 (2C), 140.3 (1C), 143.7 (1C) (the signals for

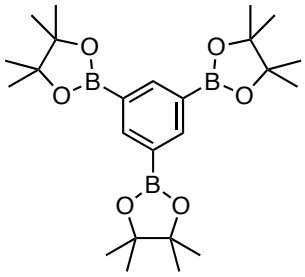
the carbons that are attached to the boron atoms were not observed);

^{11}B NMR ($CDCl_3$) δ 29.8 (1B + 1B, two signals overlapped);

IR (ZnSe, cm^{-1}) 1094, 1144, 1267, 1317, 1358, 1609, 2980;

HRMS (ESI^+) *m*/*z* 407.2550 (407.2559 calcd for $C_{24}H_{33}B_2O_4^+$, $[M+H]^+$).

1,3,5-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3ab)



Yield: 86.5% (27.6 mg, 60.5 μmol) from 70 μmol of **1ab**;

Colorless solid (mp 270–272 °C);

Eluent for silica-gel column chromatography: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.70 (*n*-hexane/EtOAc = 4/1);

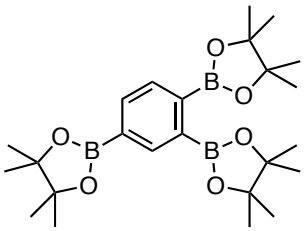
^{1}H NMR ($CDCl_3$) δ 1.33 (s, 36H), 8.37 (s, 3H);

^{13}C NMR ($CDCl_3$) δ 24.9 (12C), 83.7 (6C), 127.3 (br s, 3C), 144.1 (3C);

^{11}B NMR ($CDCl_3$) δ 30.0 (3B);

The chemical shifts were consistent with those reported in the literature.[S13]

1,2,4-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3ac)



Yield: 73.0% (23.3 mg, 51.1 μmol) from 70 μmol of **1ac**;

Colorless solid (mp 175–179 °C);

Eluent for silica-gel column chromatography: *n*-hexane/EtOAc = 9/1;

TLC R_f = 0.62 (*n*-hexane/EtOAc = 4/1);

^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 1.36 (s, 12H + 12H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 1H), 8.08 (s, 1H);

^{13}C NMR ($CDCl_3$) δ 24.85 (4C), 24.88 (4C), 24.94 (4C), 83.7 (2C), 83.8 (2C), 83.9 (2C), 132.5 (1C), 135.4 (1C), 139.5 (1C) (the signals for the carbons that are attached to the boron atoms were

not observed);

^{11}B NMR ($CDCl_3$) δ 29.7, 30.8 (either peak would indicate two signals overlapped);

The chemical shifts were consistent with those reported in the literature.[S14]

References for Supporting Information

S1 Yu, X.-Y.; Patrick, B. O.; James, B. R. *Organometallics* **2006**, *25*, 2359–2363.

S2 Bowmaker, G. A.; Boyd, S. E.; Hanna, J. V.; Hart, R. D.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Darton Trans.* **2002**, 2722–2730.

S3 Niwa, T.; Ochiai, H.; Watanabe, Y.; Hosoya, T. *J. Am. Chem. Soc.* **2015**, *137*, 14313–14318.

S4 Fier, P. S.; Luo, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 2552–2559.

S5 Denmark, S. E.; Smith, R. C.; Chang, W.-T. T.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 3104–3118.

S6 Hartmann, C. E.; Nolan, S. P.; Cazin, C. S. J. *Organometallics* **2009**, *28*, 2915–2919.

S7 Li, X.; Zou, D.; Zhu, H.; Wang, Y.; Li, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 1836–1839.

S8 Uetake, Y.; Niwa, T.; Hosoya, T. *Org. Lett.* **2016**, *18*, 2758–2761.

S9 Bheeter, C. B.; Chowdhury, A. D.; Adam, R.; Jackstell, R.; Beller, M. *Org. Biomol. Chem.* **2015**, *13*, 10336–10340.

S10 Dzhevakov, P. B.; Topchiy, M. A.; Zharkova, D. A.; Morozov, O. S.; Asachenko, A. F.; Nechaev, M. S. *Adv. Synth. Catal.* **2016**, *358*, 977–983.

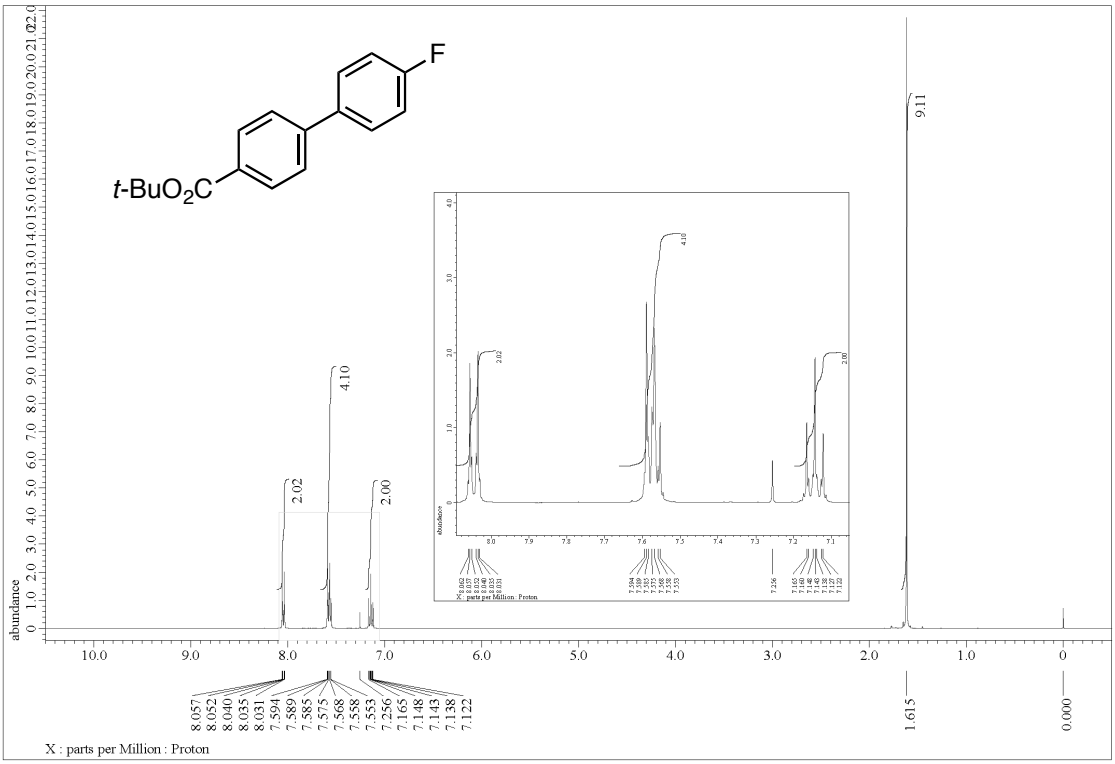
S11 Han, F. S.; Higuchi, M.; Kurth, D. G. *Org. Lett.* **2007**, *9*, 559–562.

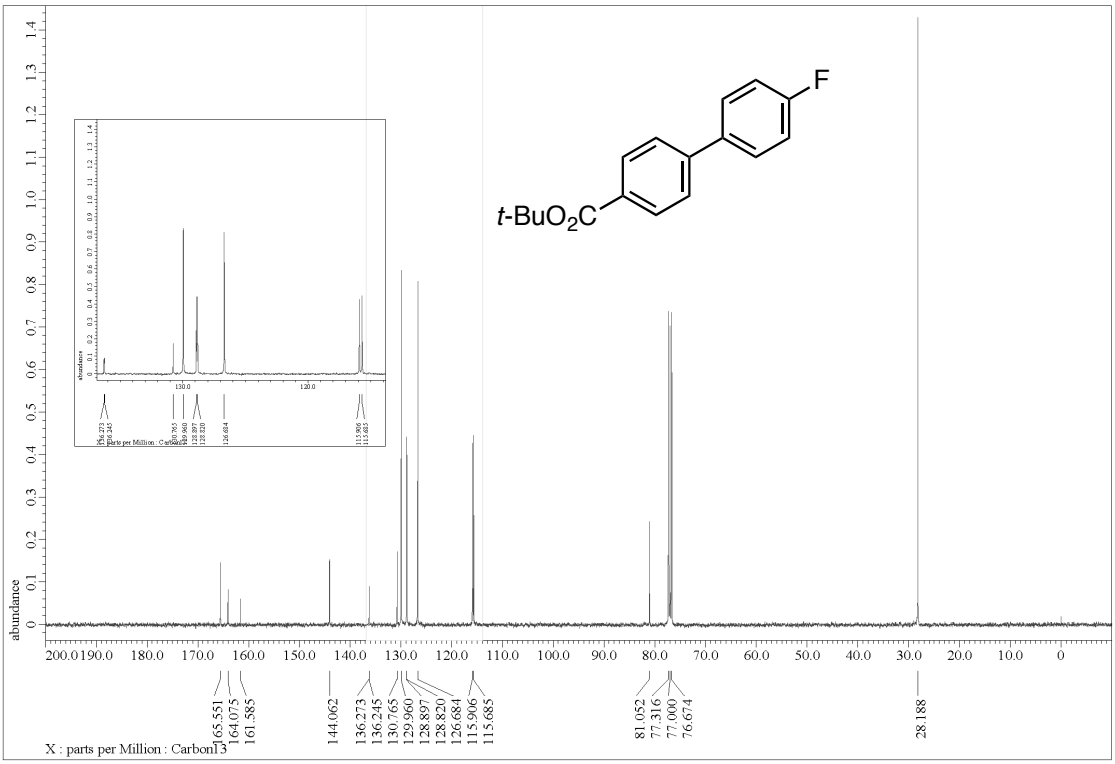
S12 Seven, Ö.; Qu, Z.-W.; Zhu, H.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Chem. Eur. J.* **2012**, *18*, 11284–11295.

S13 Mfuh, A. M.; Nguyen, V. T.; Chhetri, B.; Burch, J. E.; Doyle, J. D.; Nesterov, V. N.; Arman, H. D.; Larionov, O. V. *J. Am. Chem. Soc.* **2016**, *138*, 2985–2988.

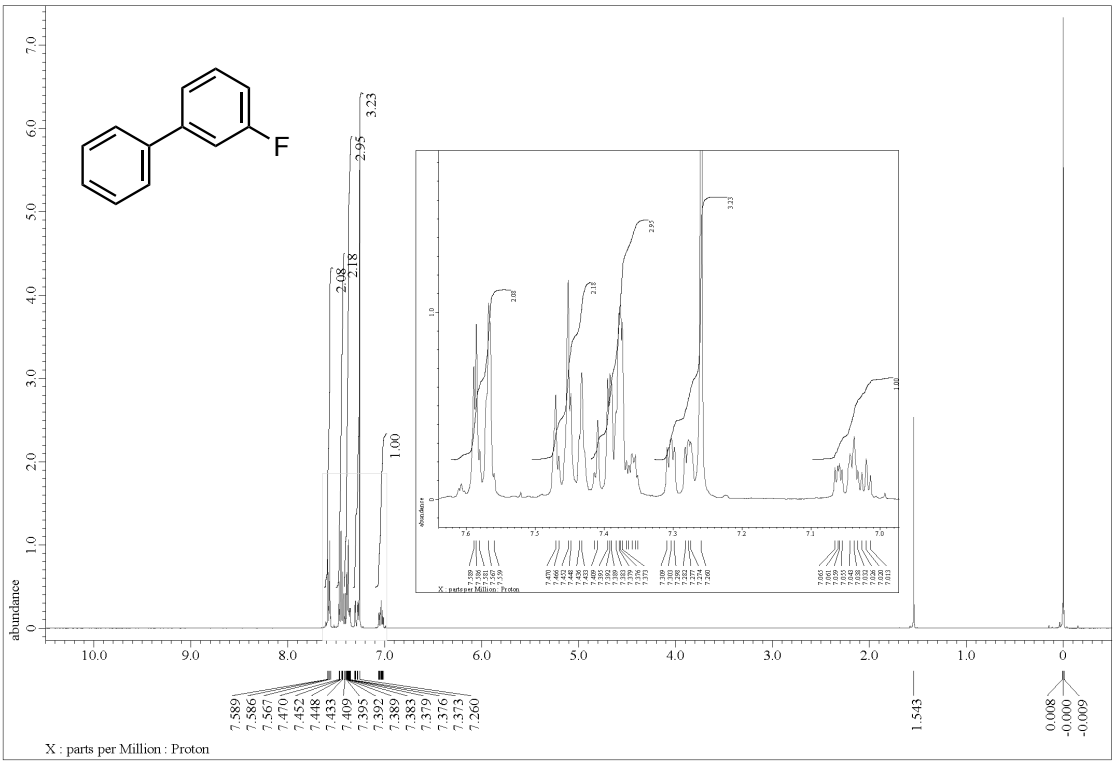
S14 Durka, K.; Luliński, S.; Smętek, J.; Dąbrowski, M.; Serwatowski, J.; Woźniak, K. *Eur. J. Org. Chem.* **2013**, 3023–3032.

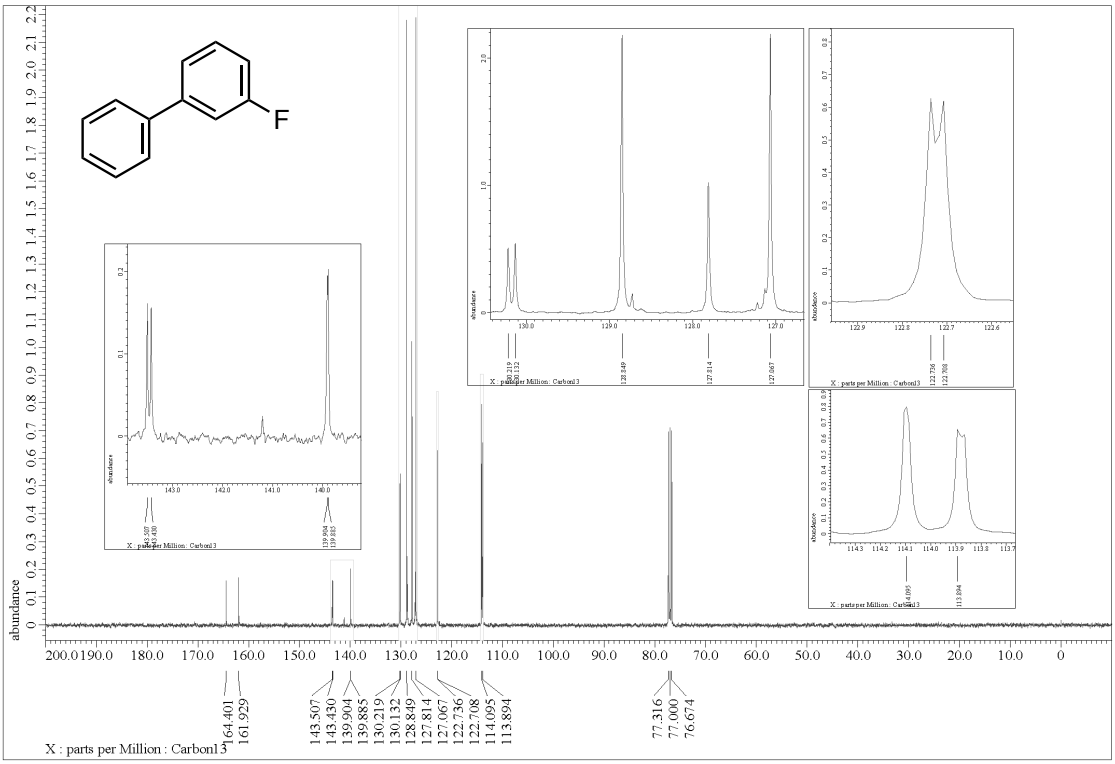
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1g** ($CDCl_3$)



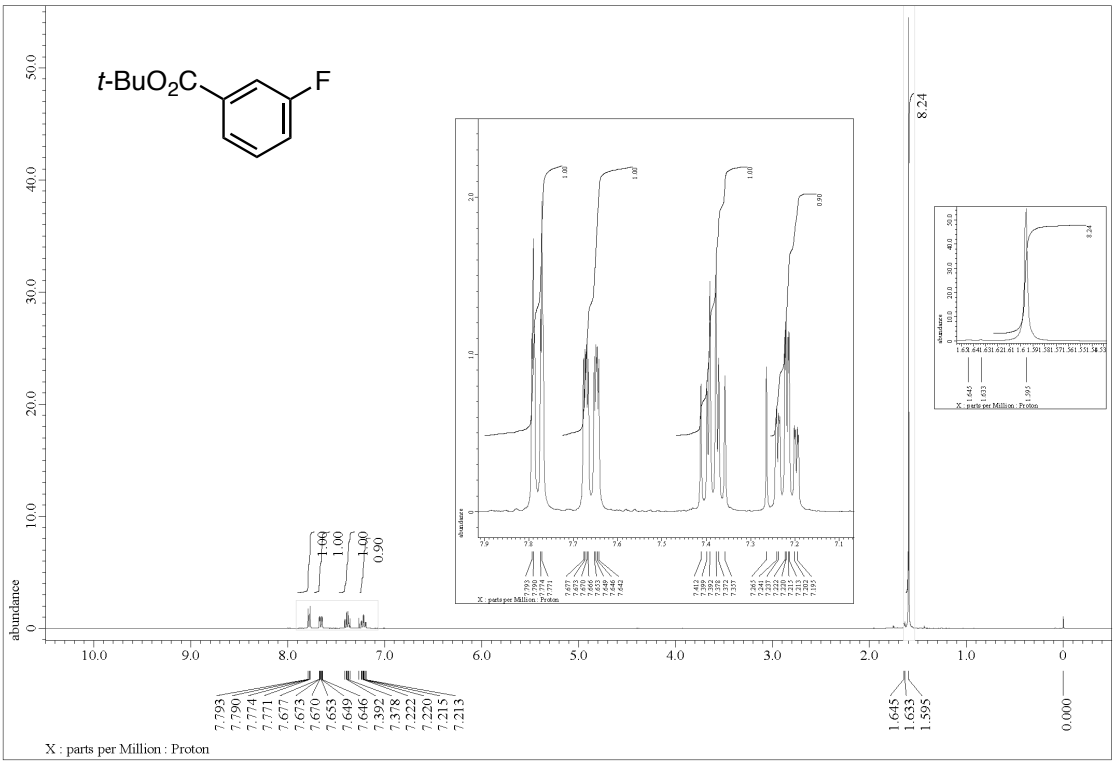


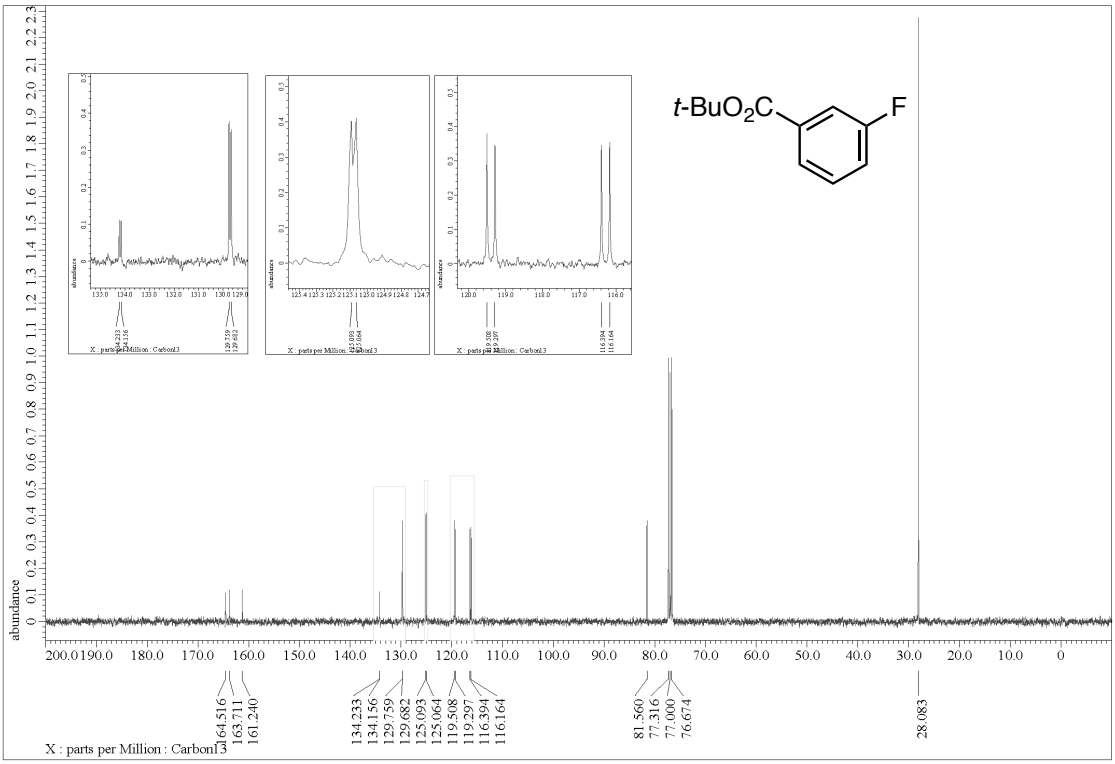
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1i** ($CDCl_3$)



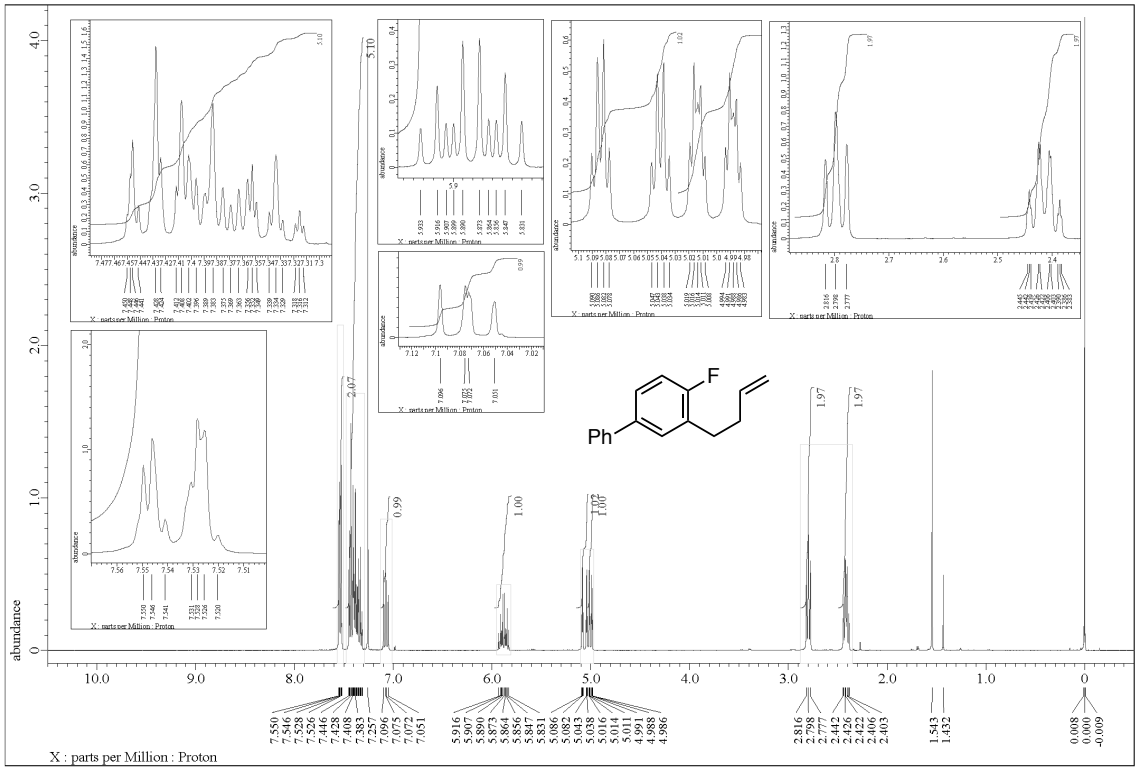


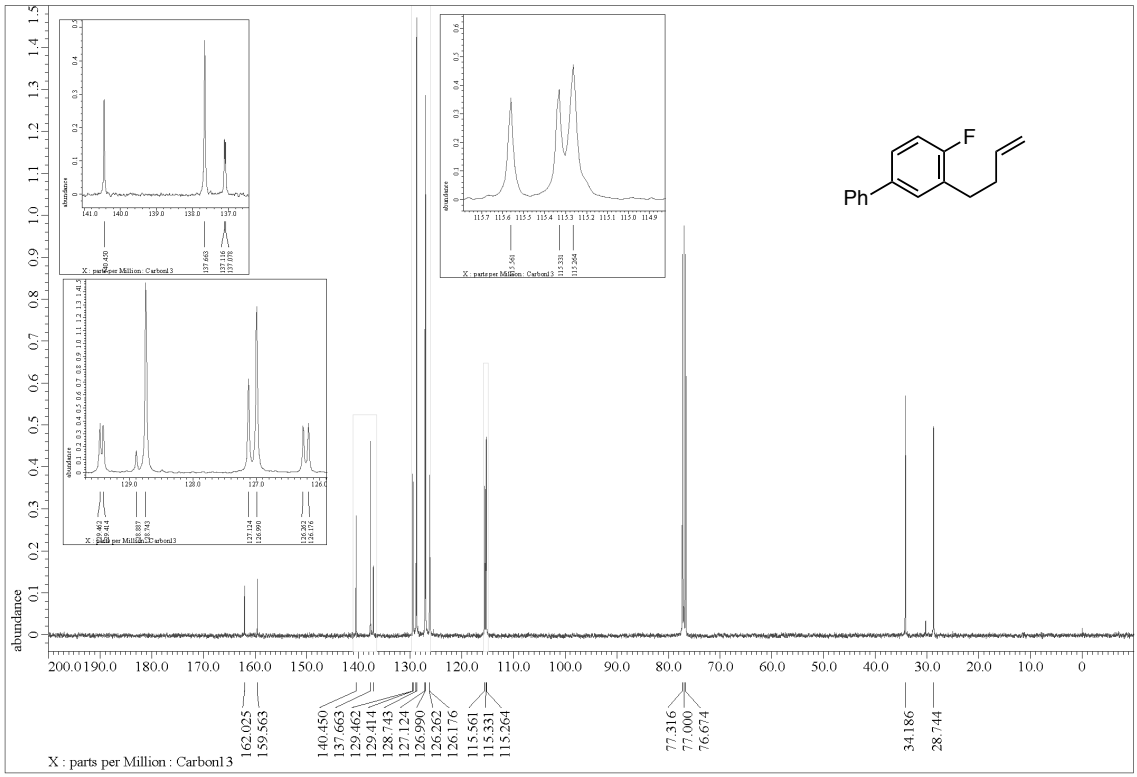
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1s** ($CDCl_3$)



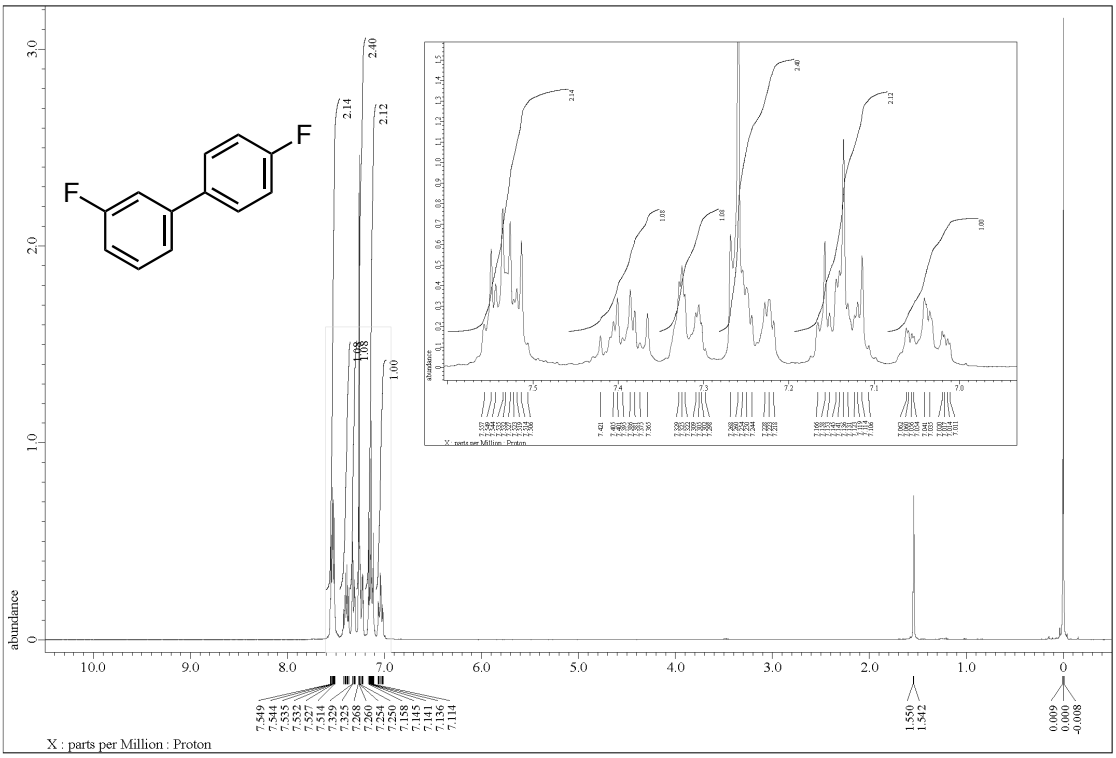


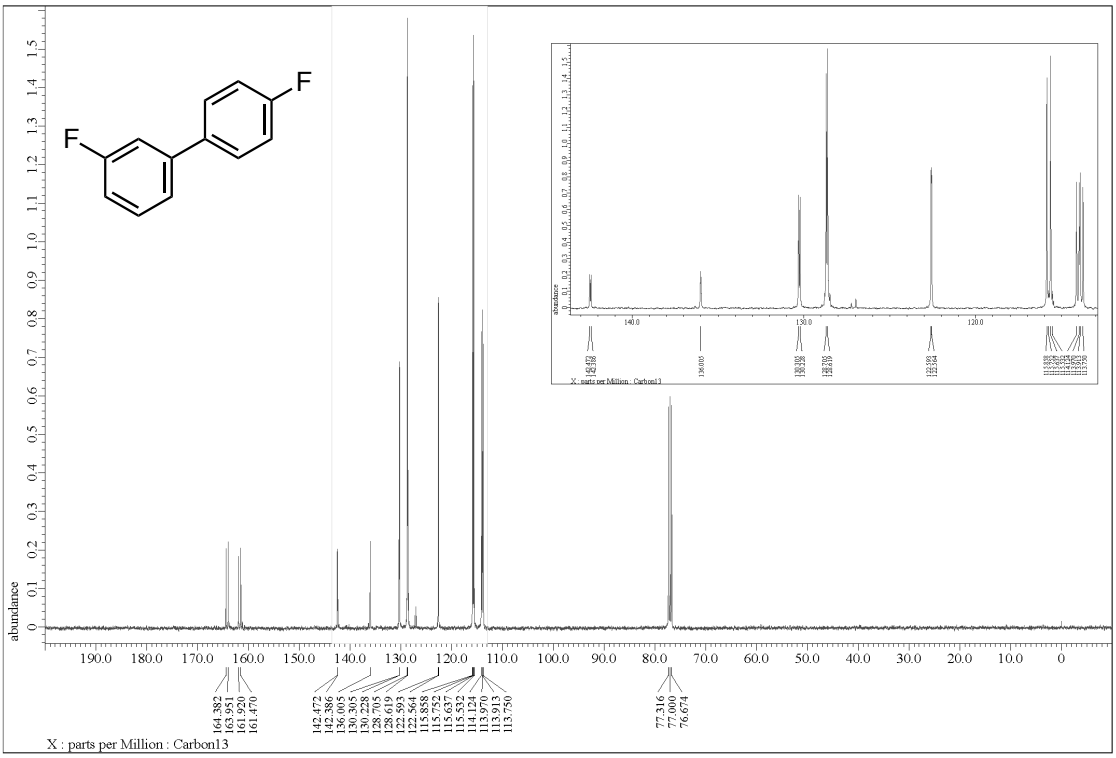
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1x** ($CDCl_3$)



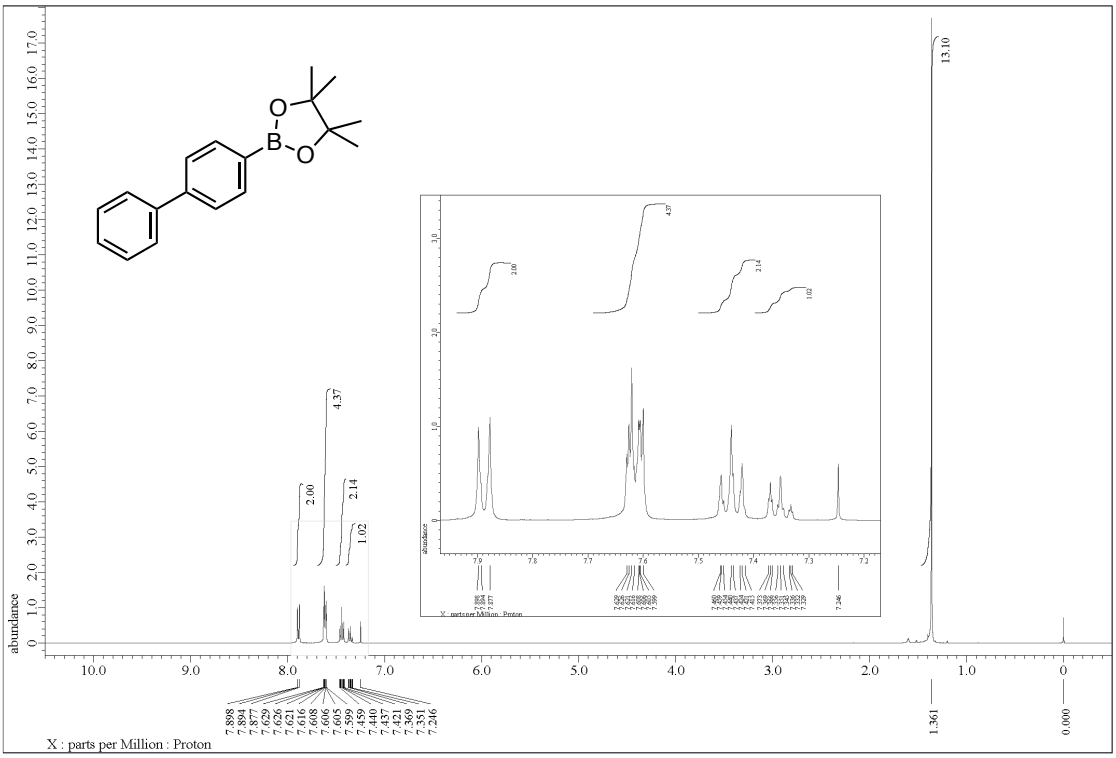


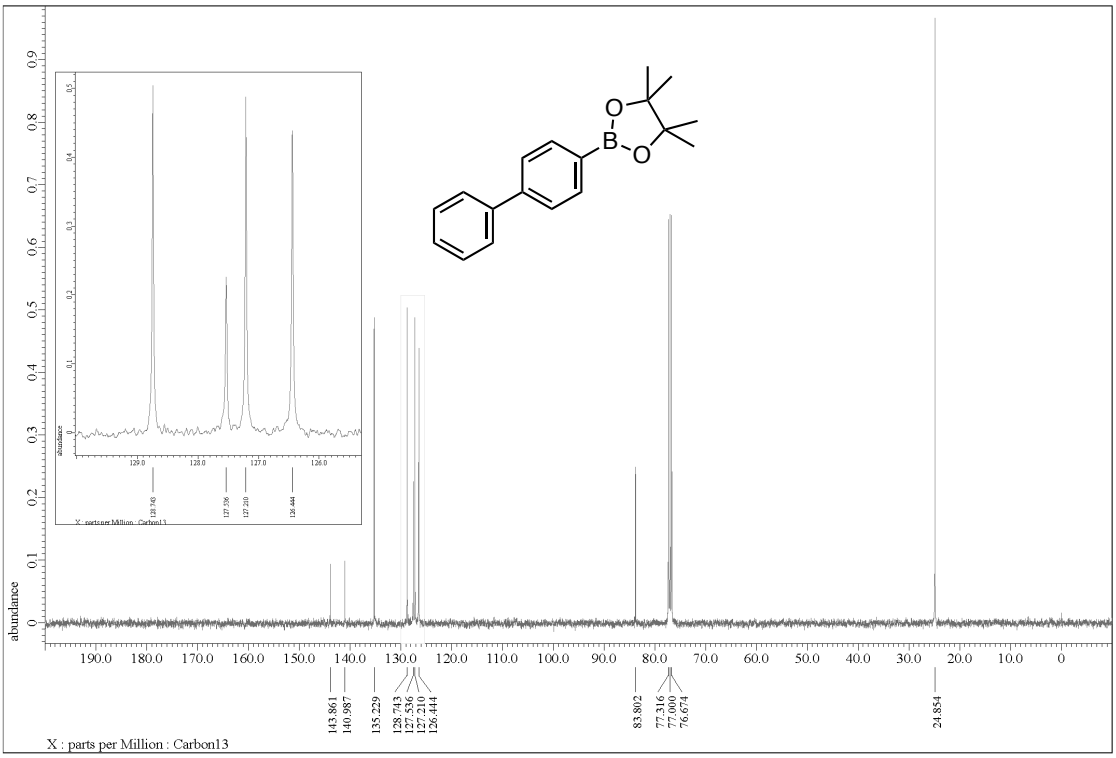
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **1aa** ($CDCl_3$)



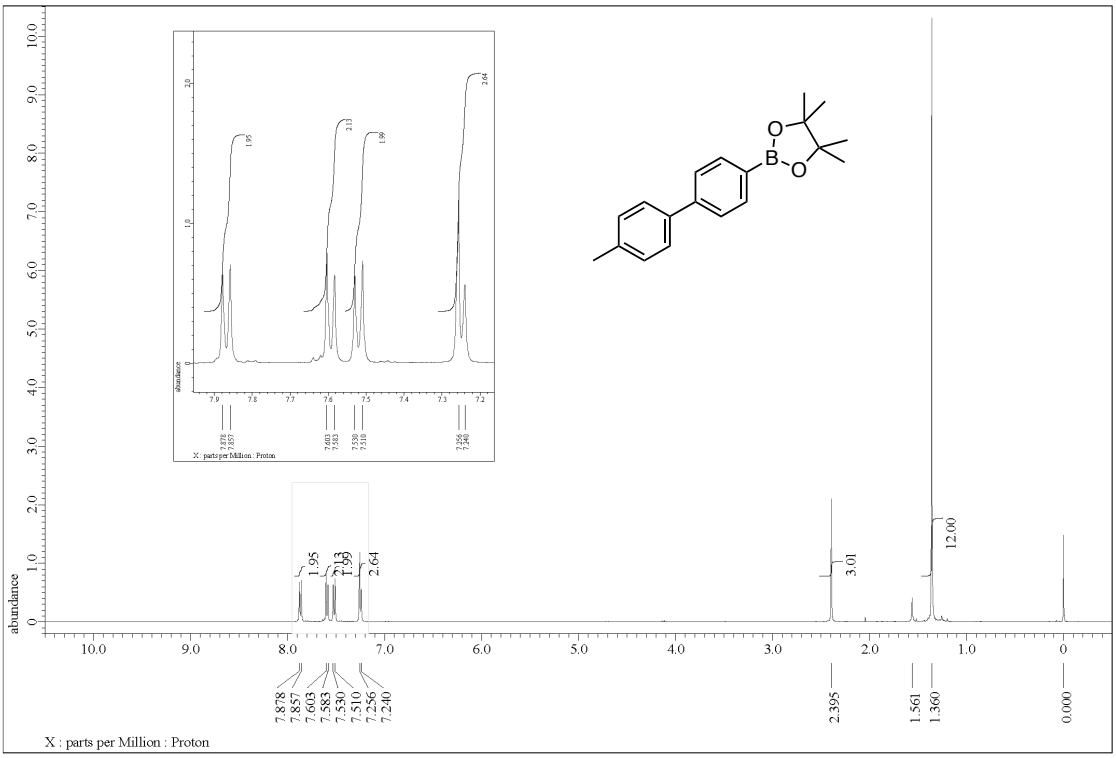


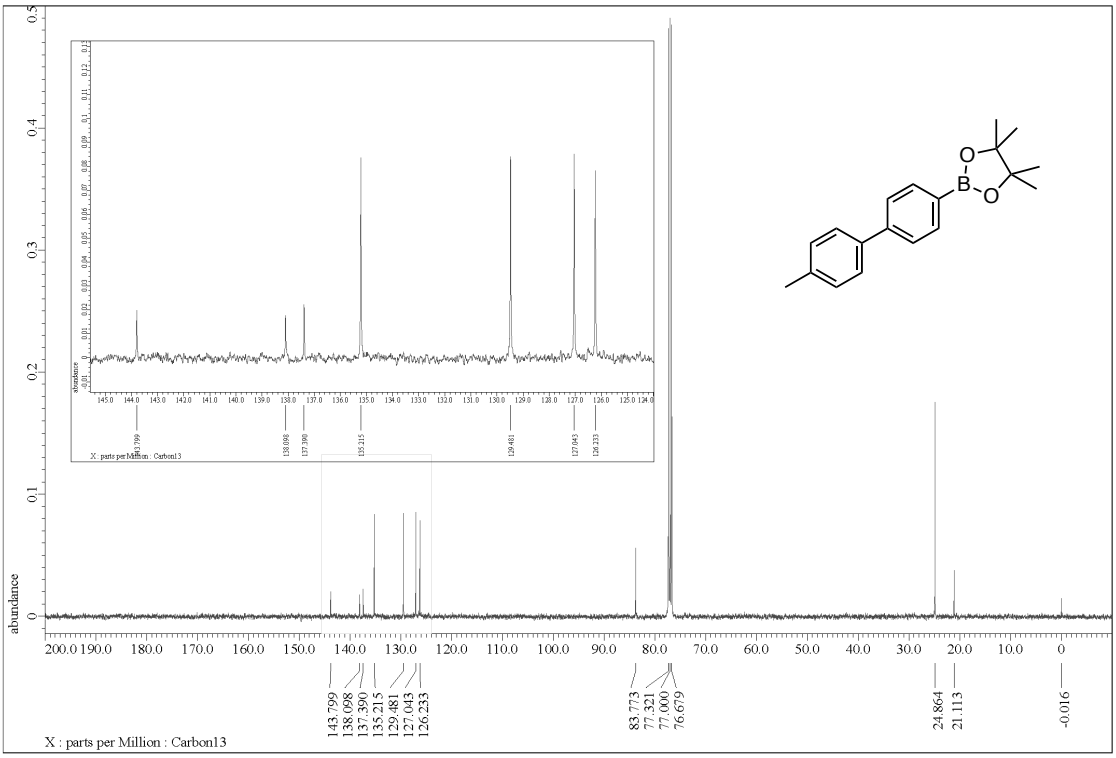
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3a** ($CDCl_3$)



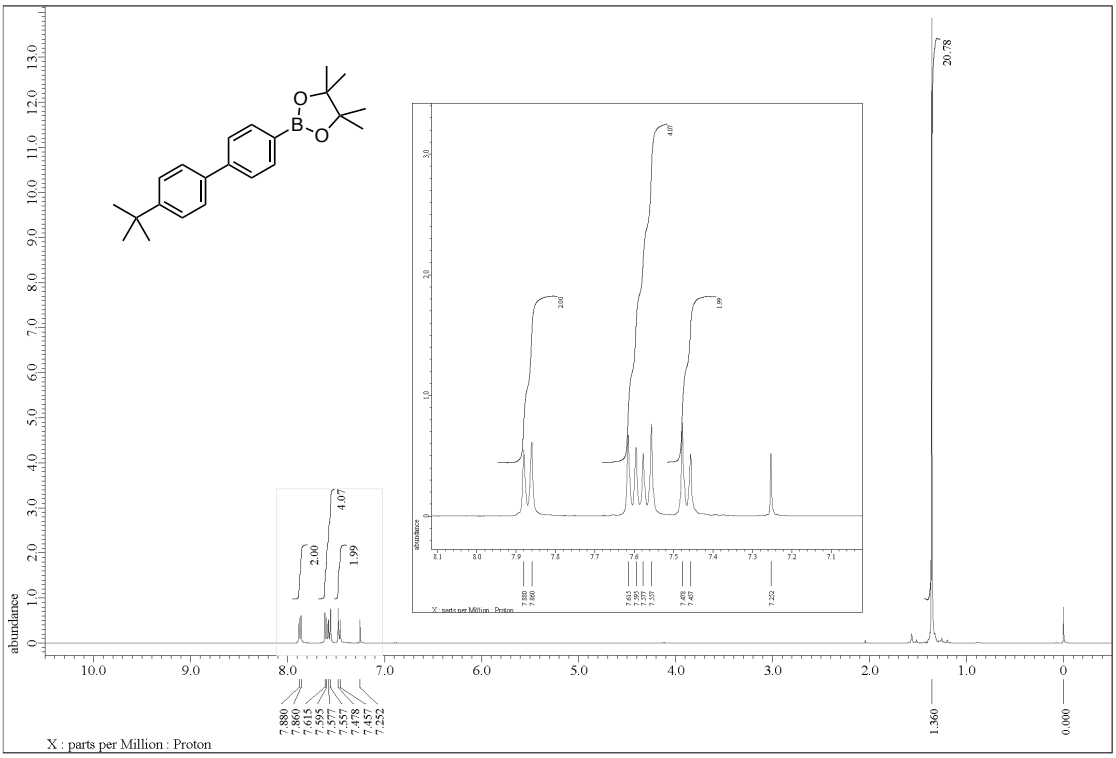


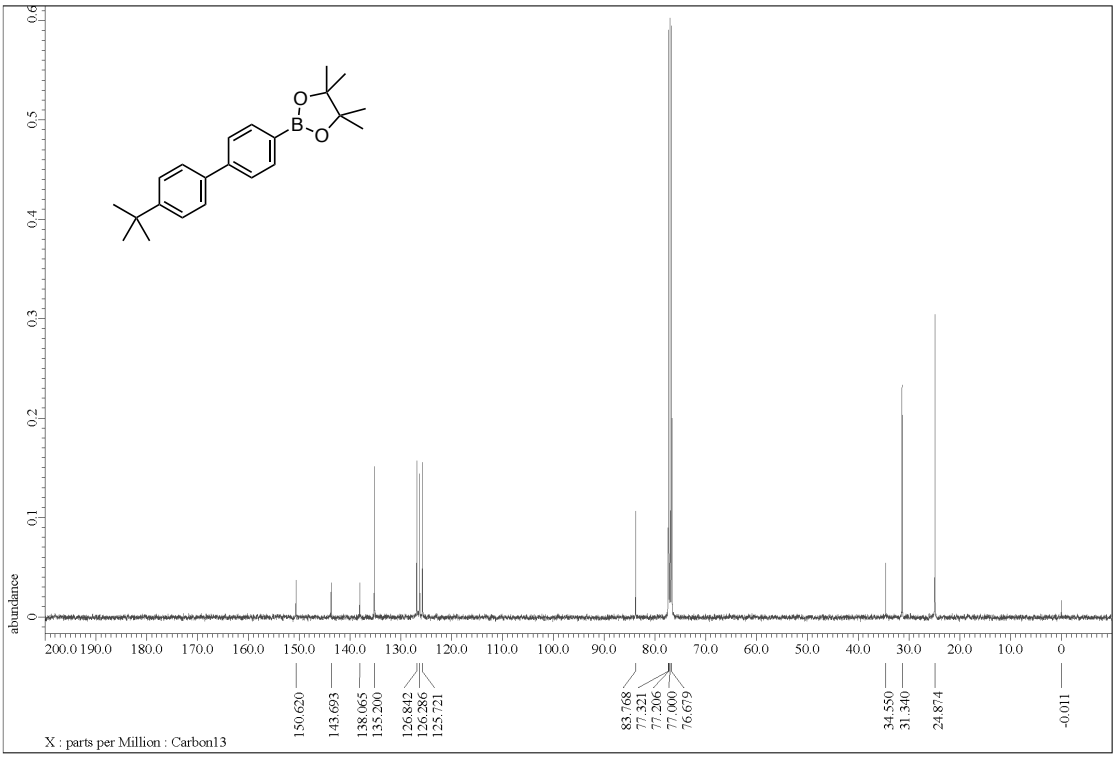
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3b** ($CDCl_3$)



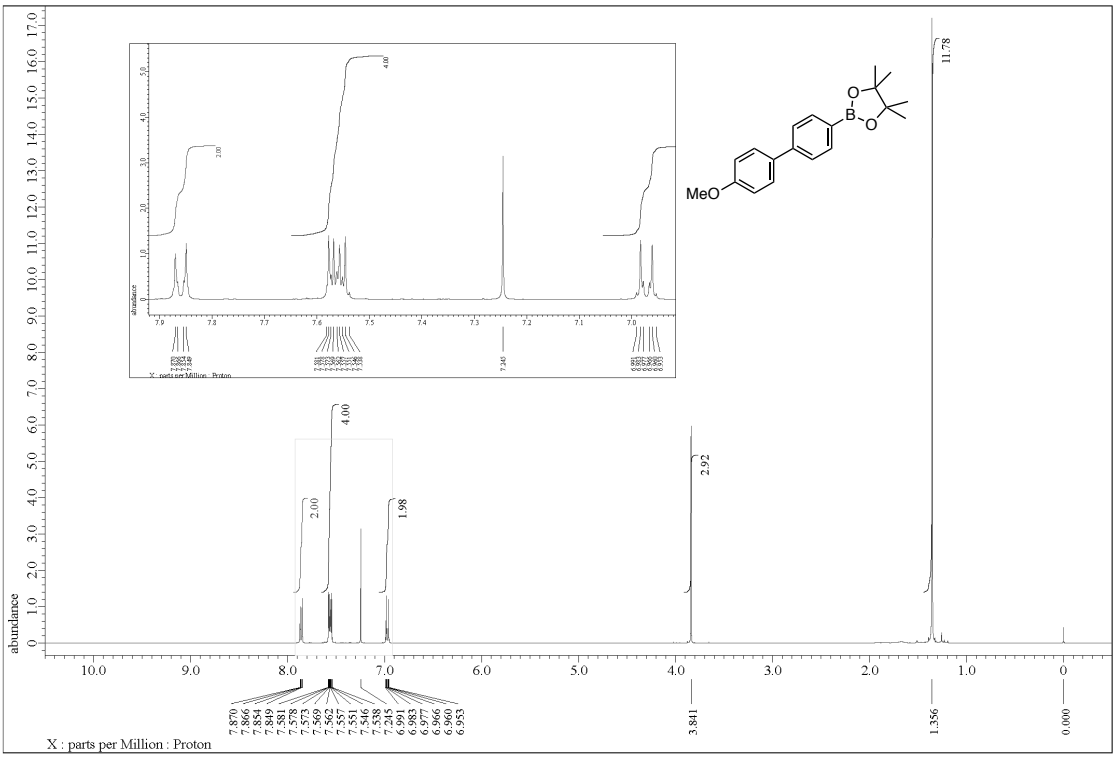


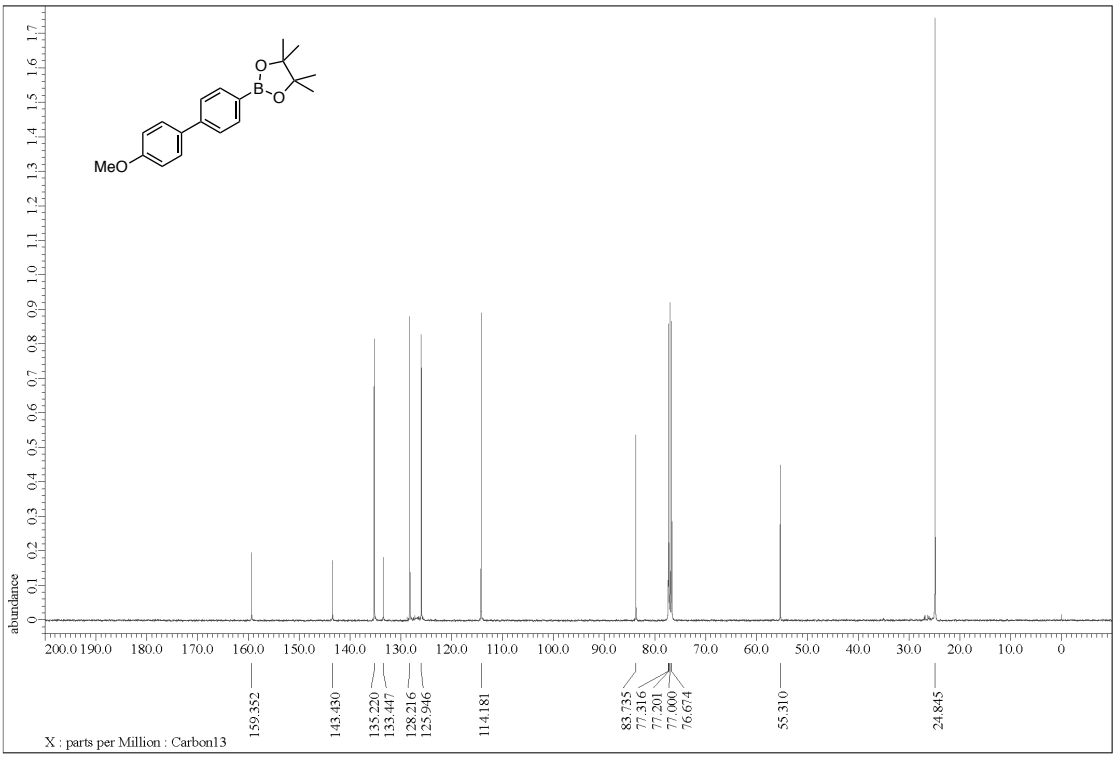
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3c** ($CDCl_3$)



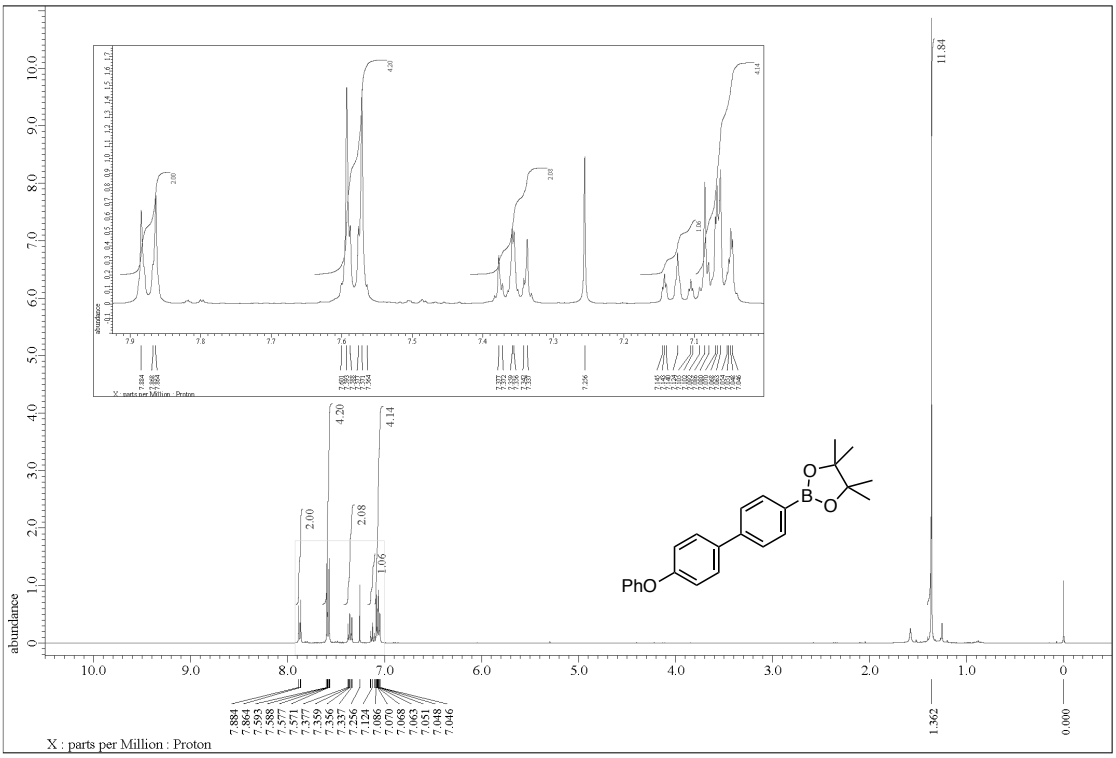


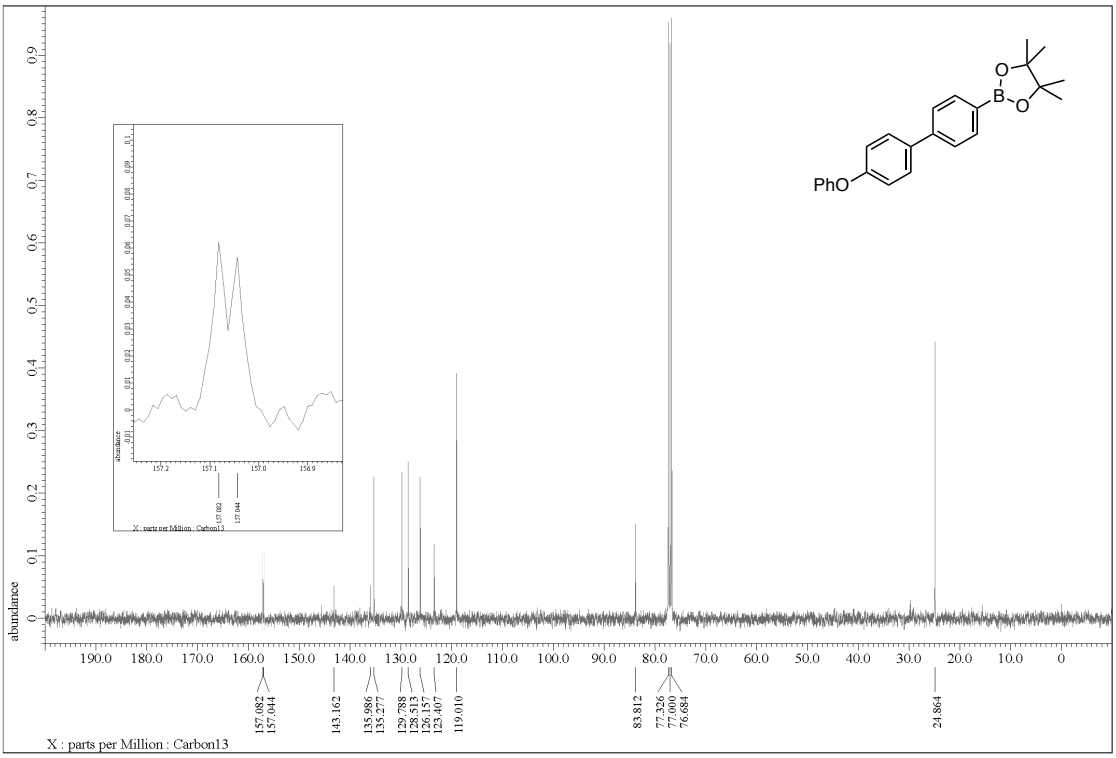
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3d** ($CDCl_3$)



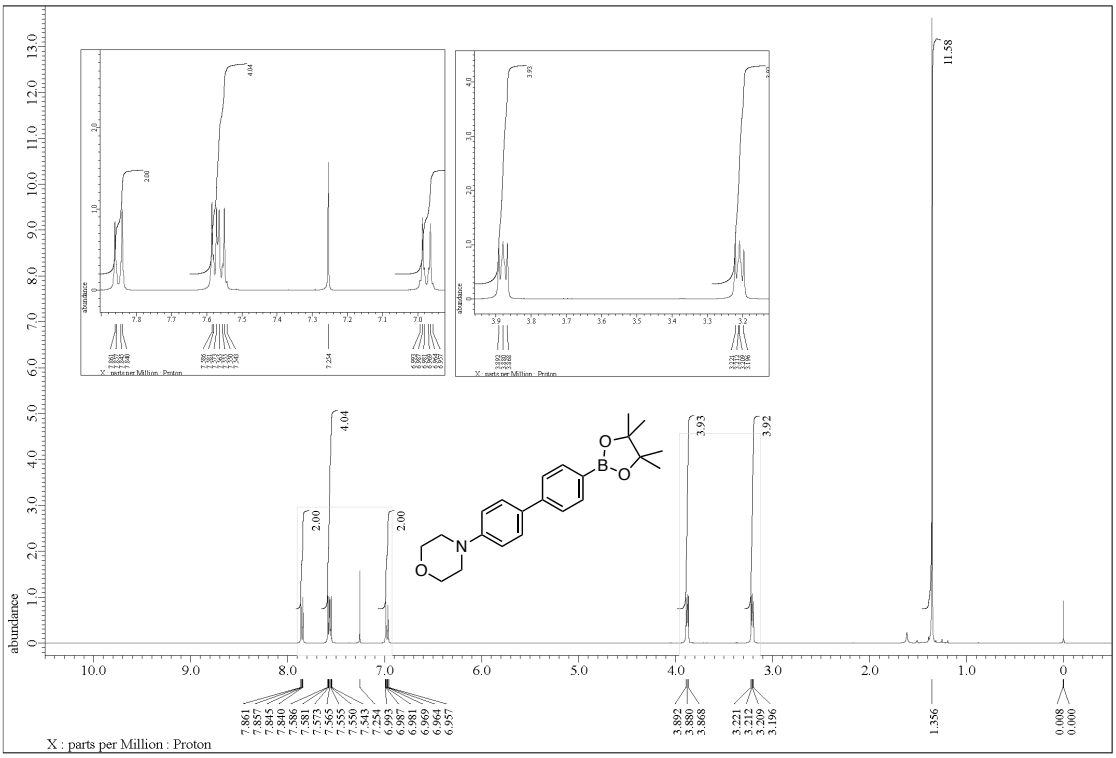


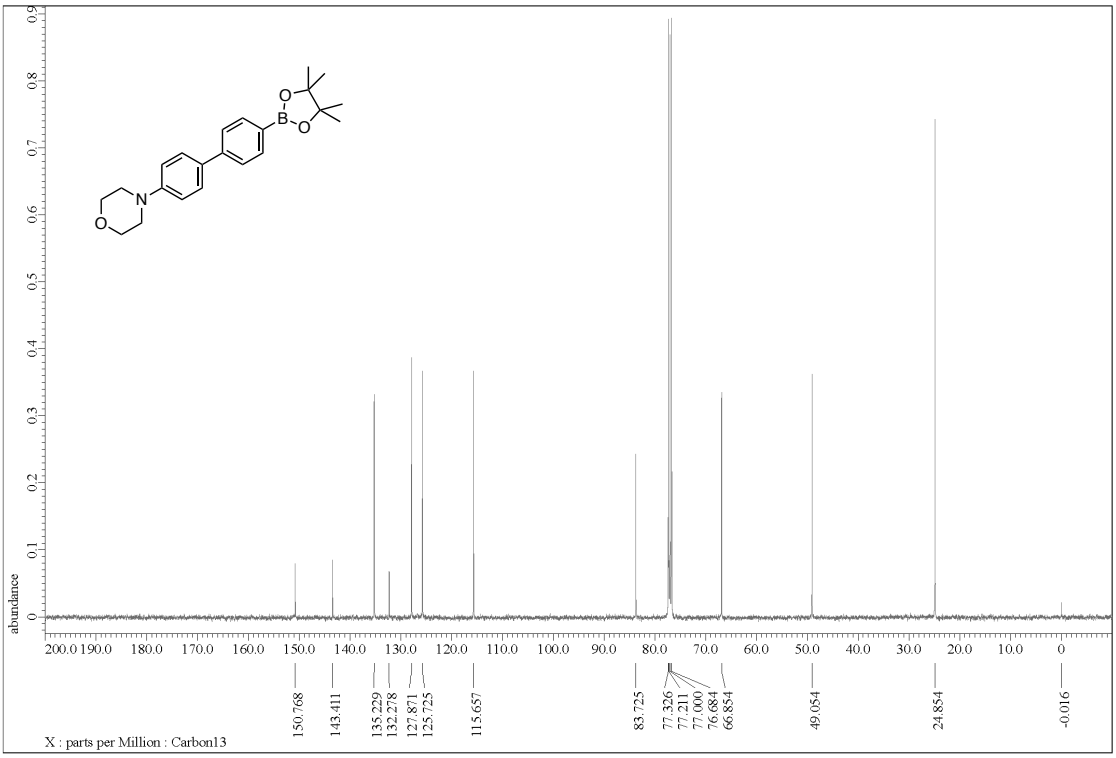
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3e** ($CDCl_3$)



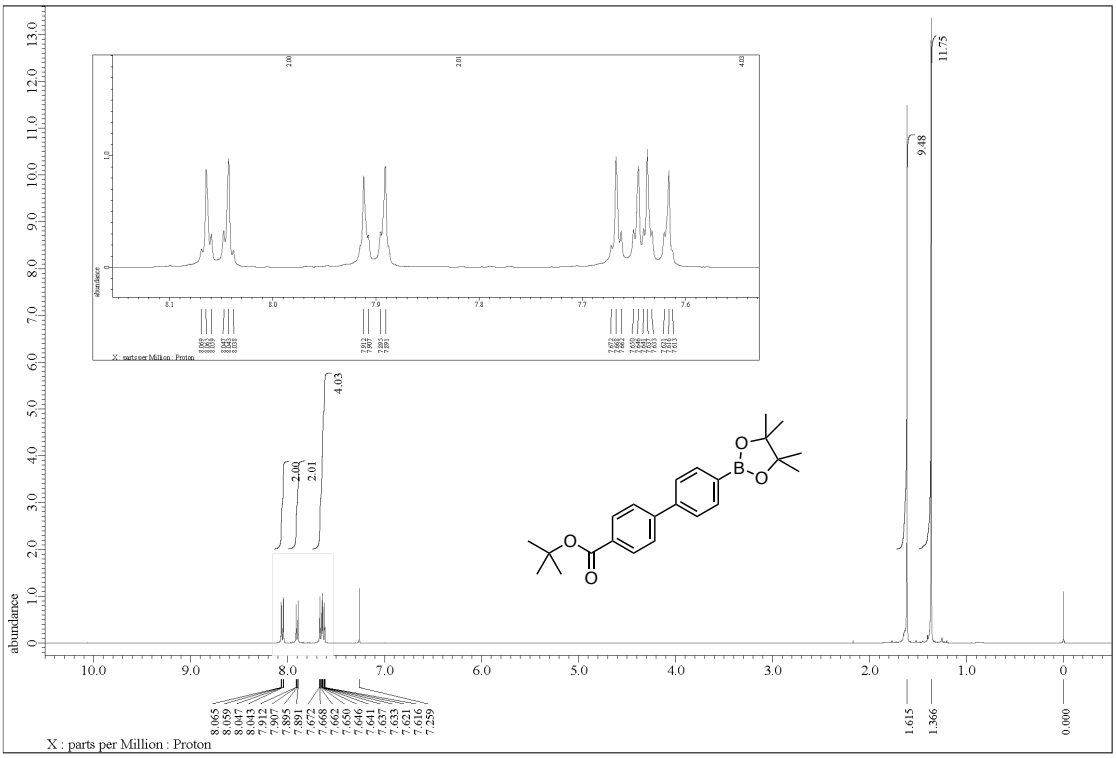


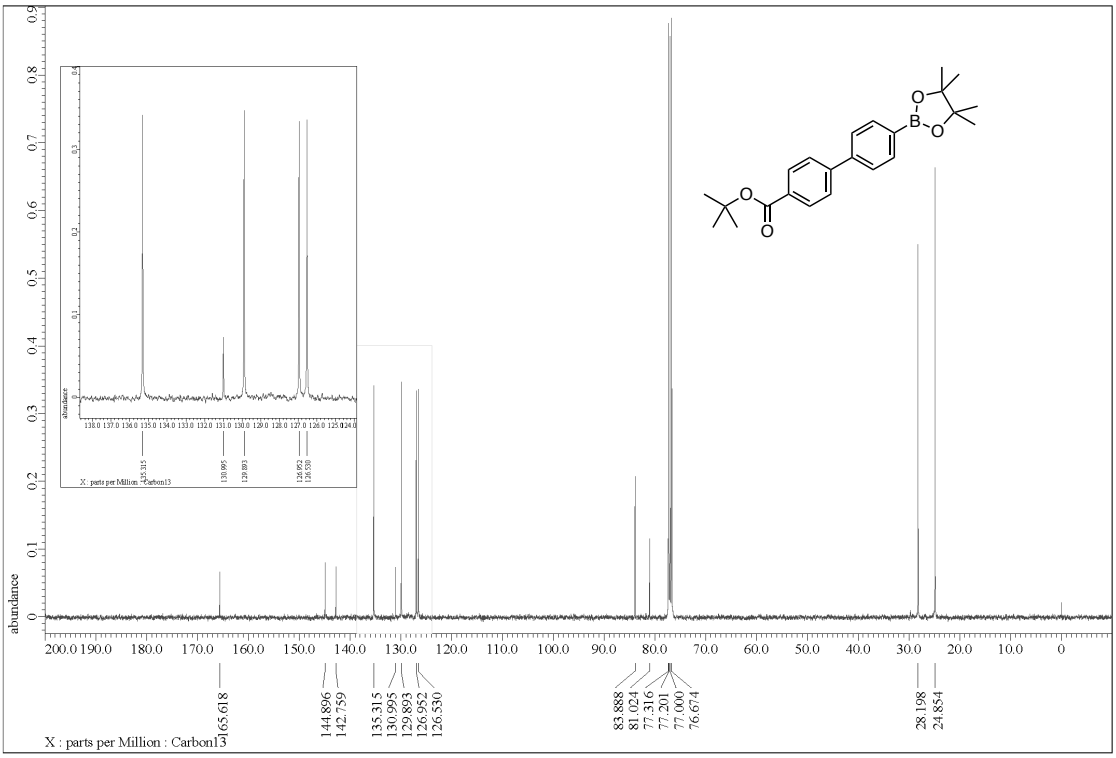
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3f** ($CDCl_3$)



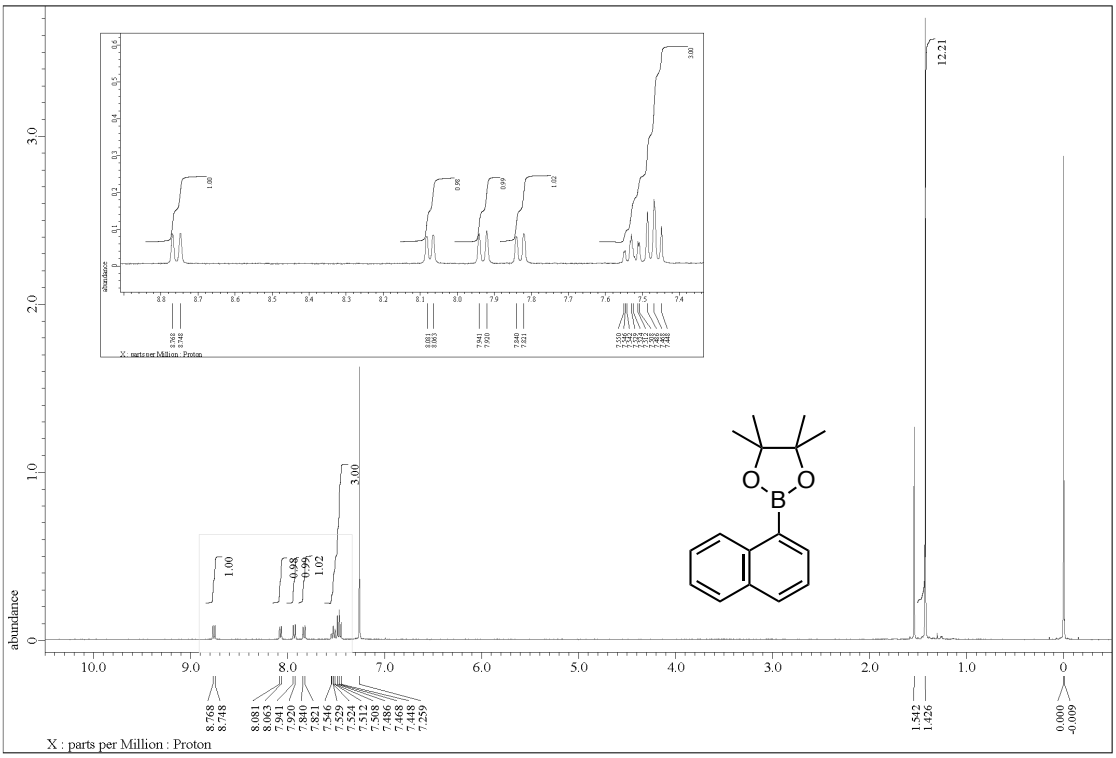


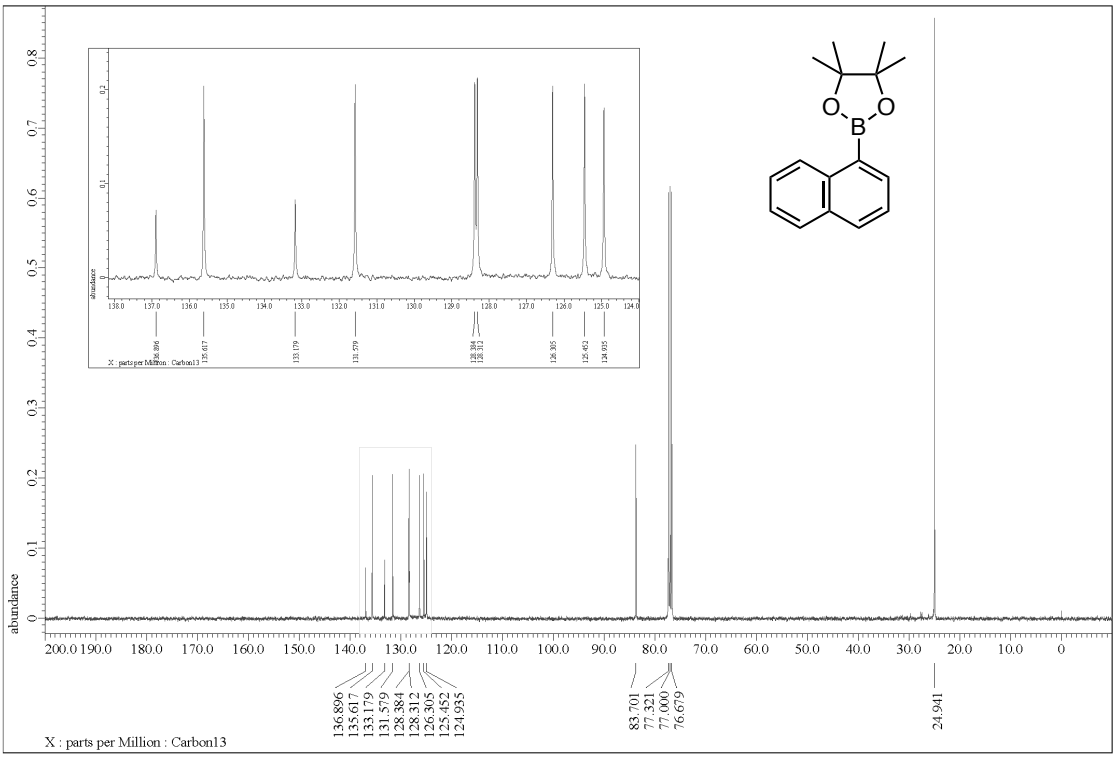
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3g** ($CDCl_3$)



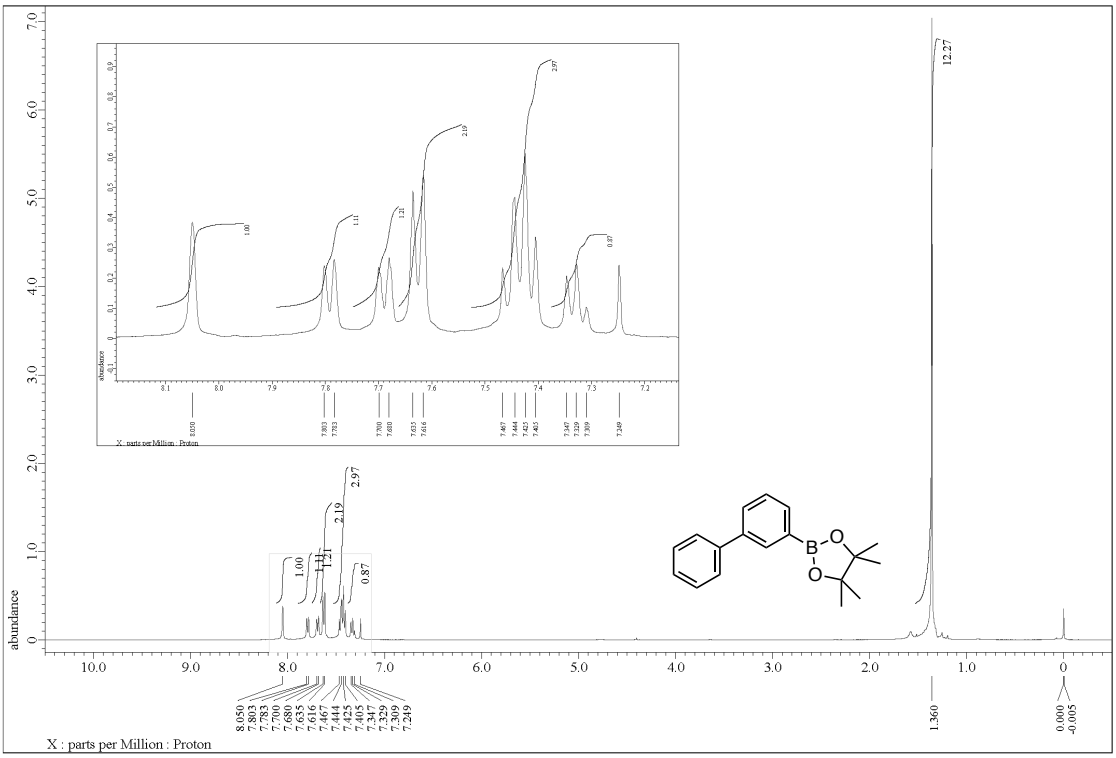


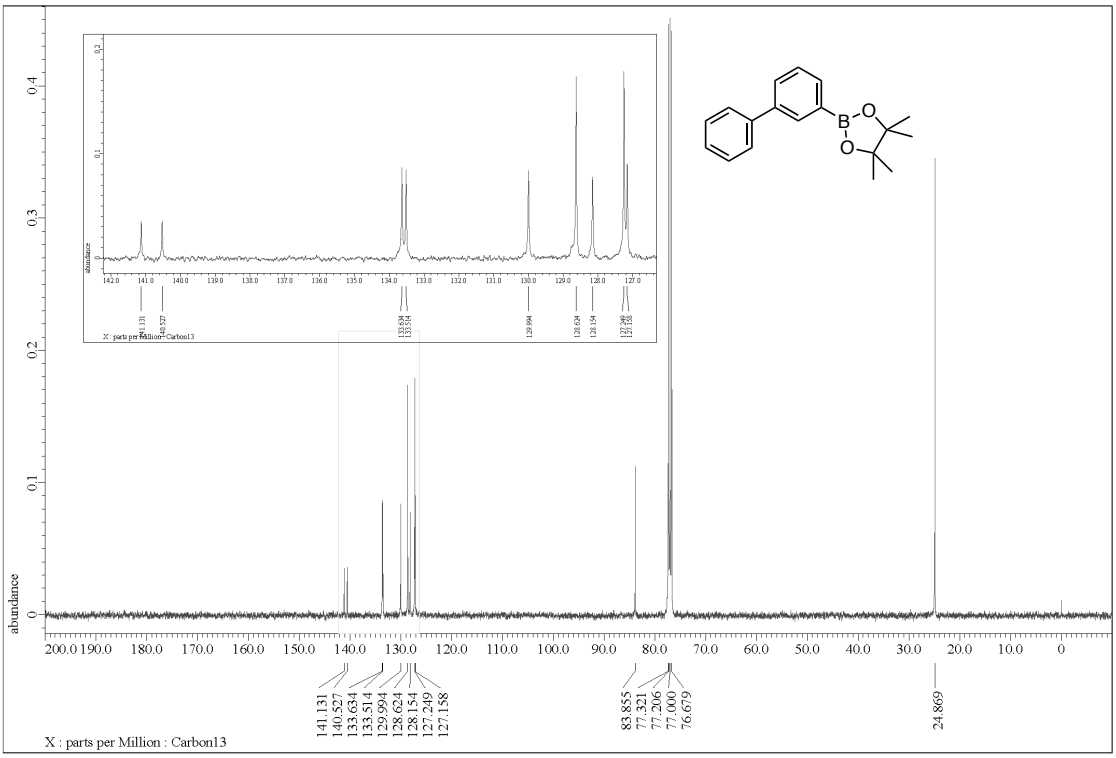
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3h** ($CDCl_3$)



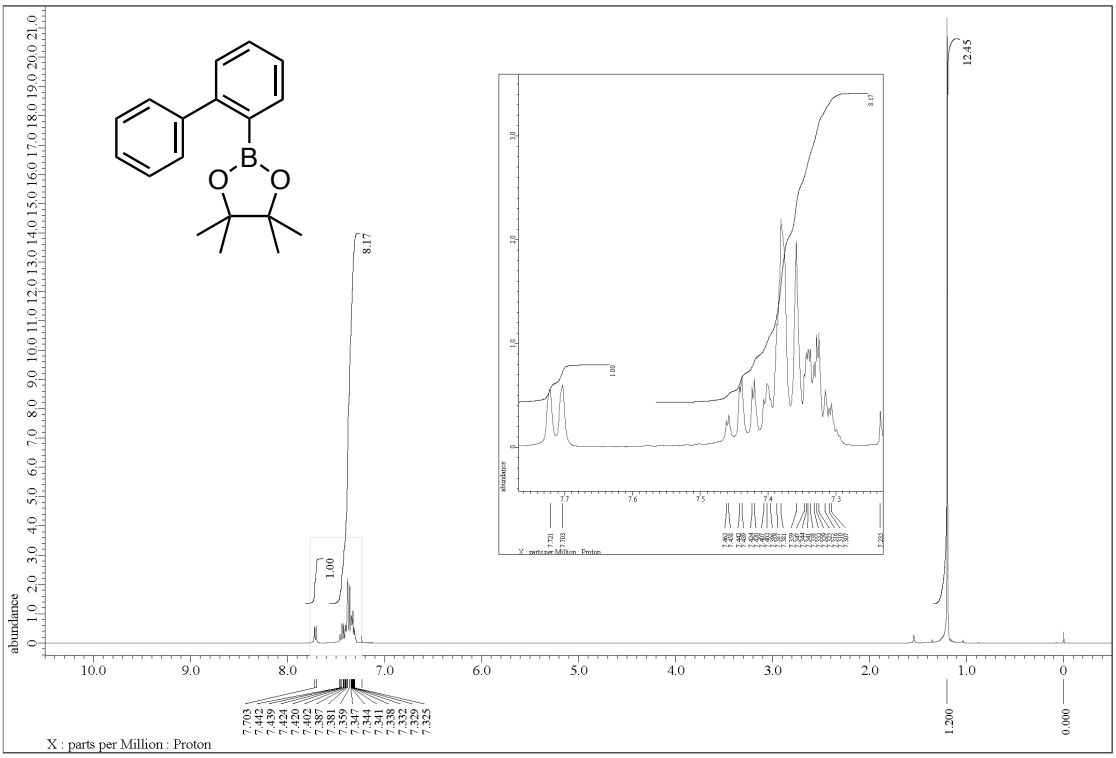


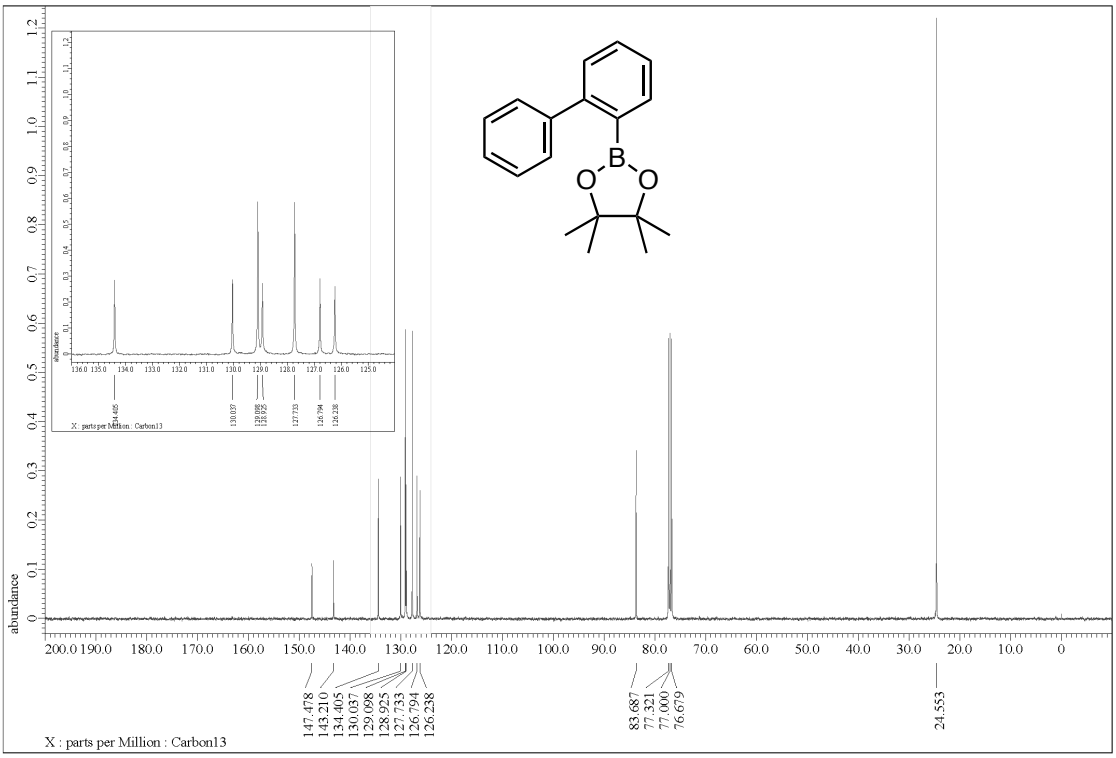
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3i** ($CDCl_3$)



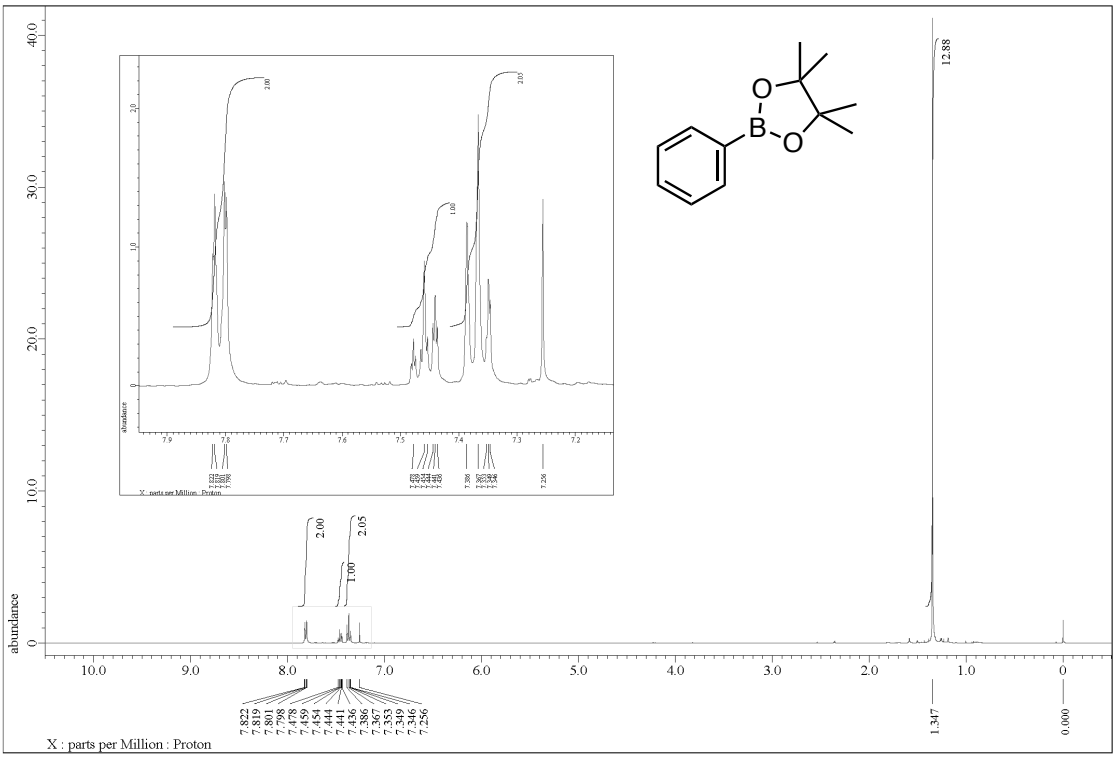


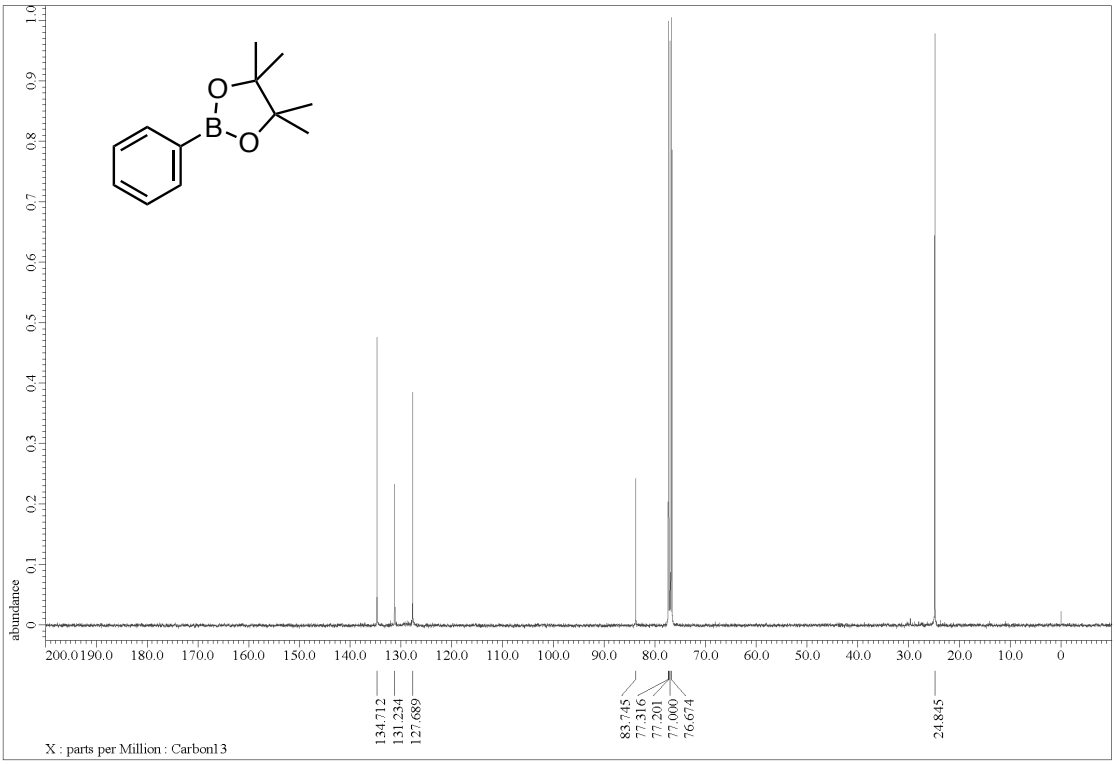
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3j** ($CDCl_3$)



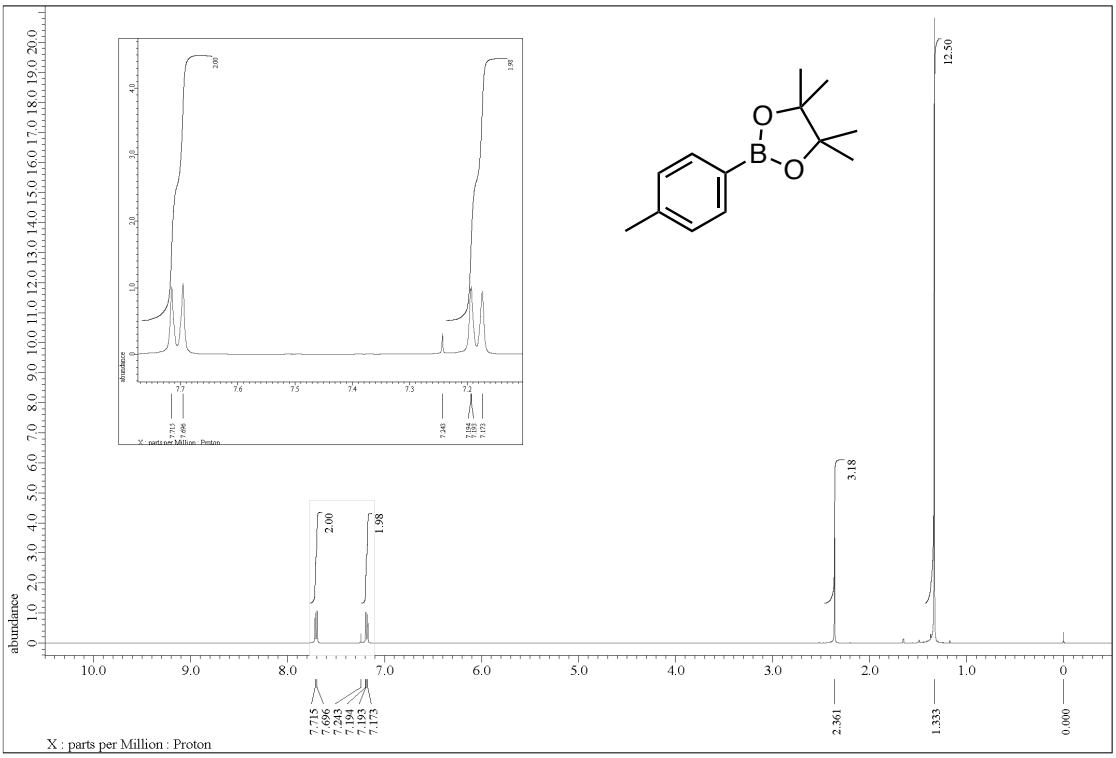


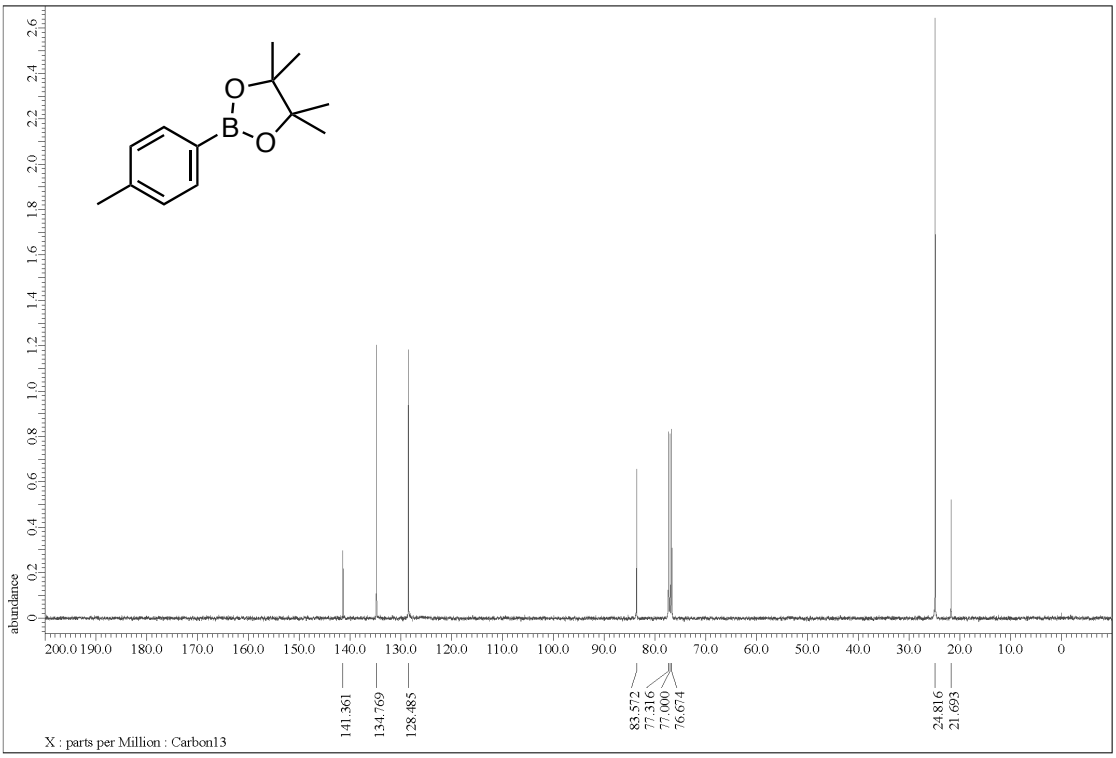
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3k** ($CDCl_3$)



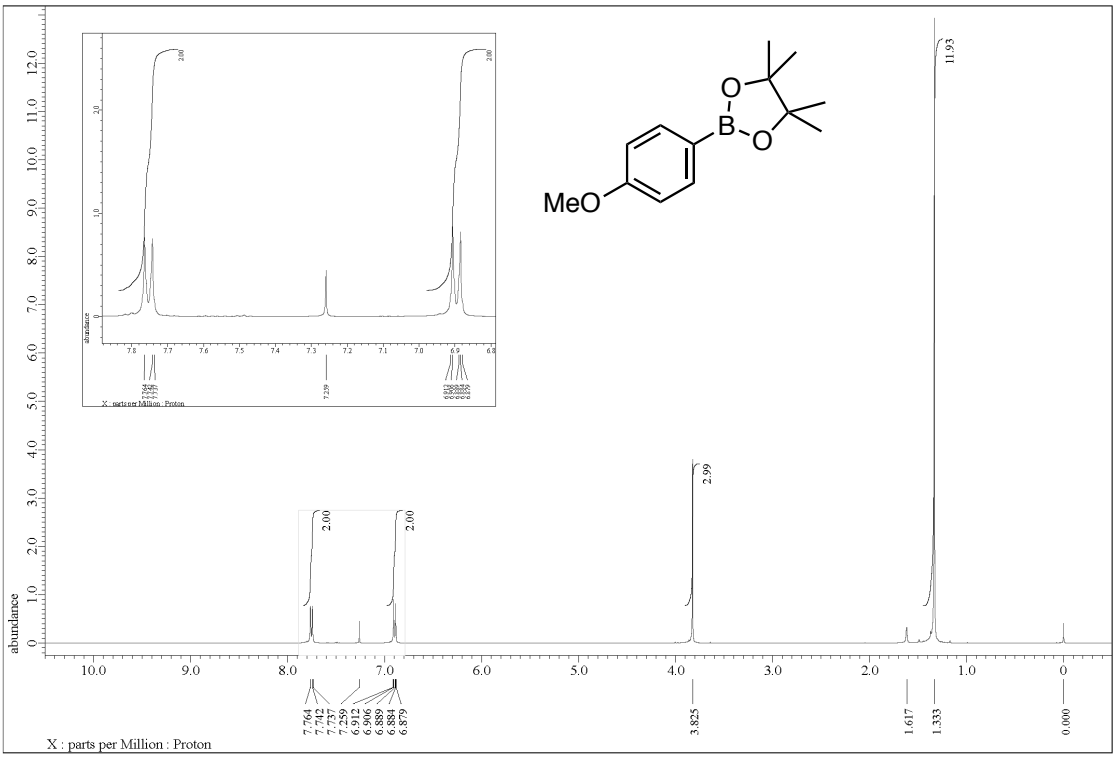


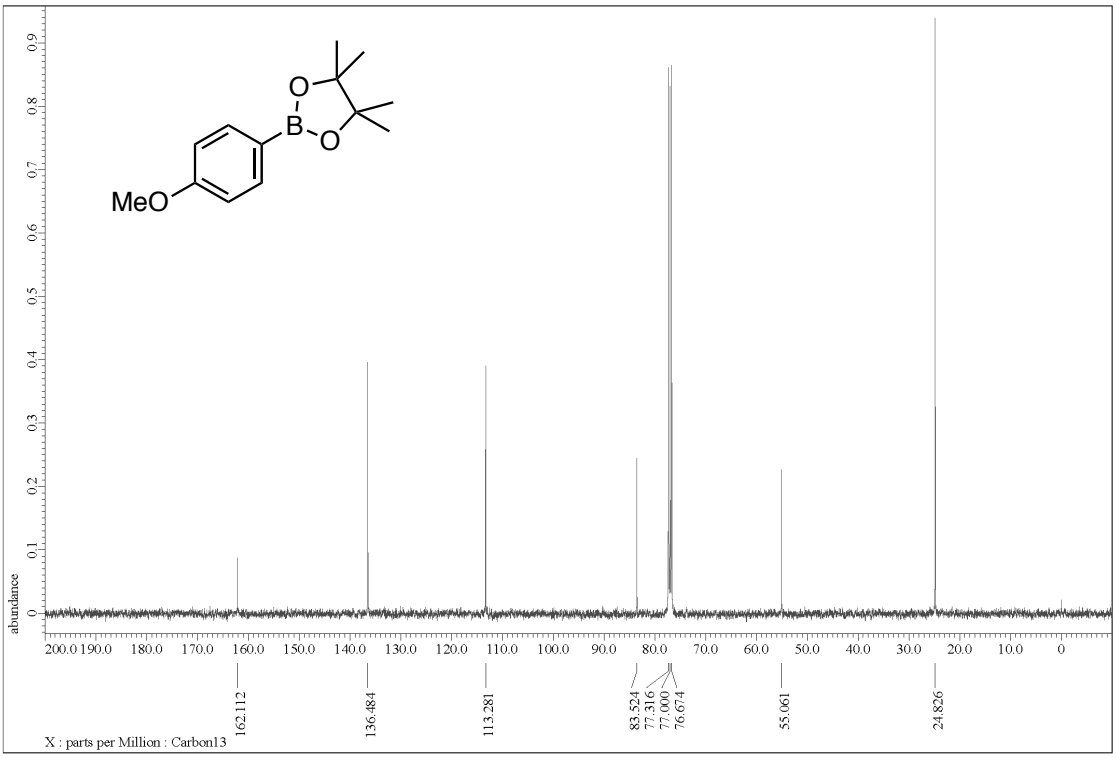
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3l** ($CDCl_3$)



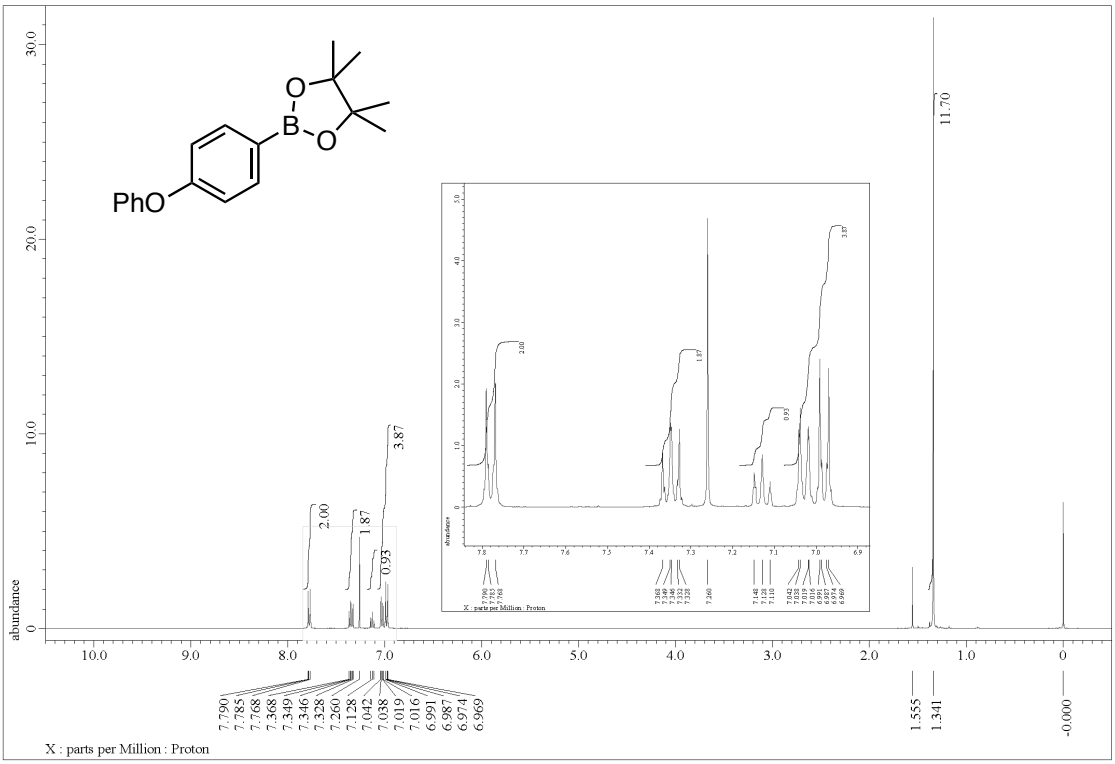


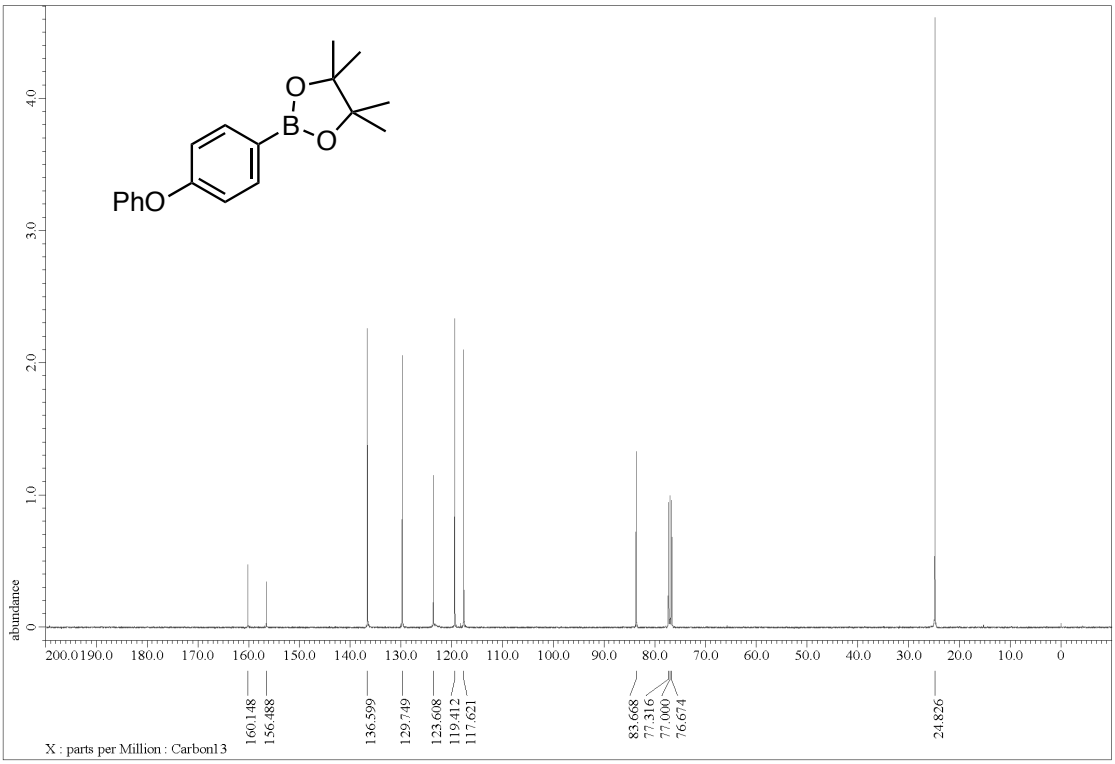
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3m** ($CDCl_3$)



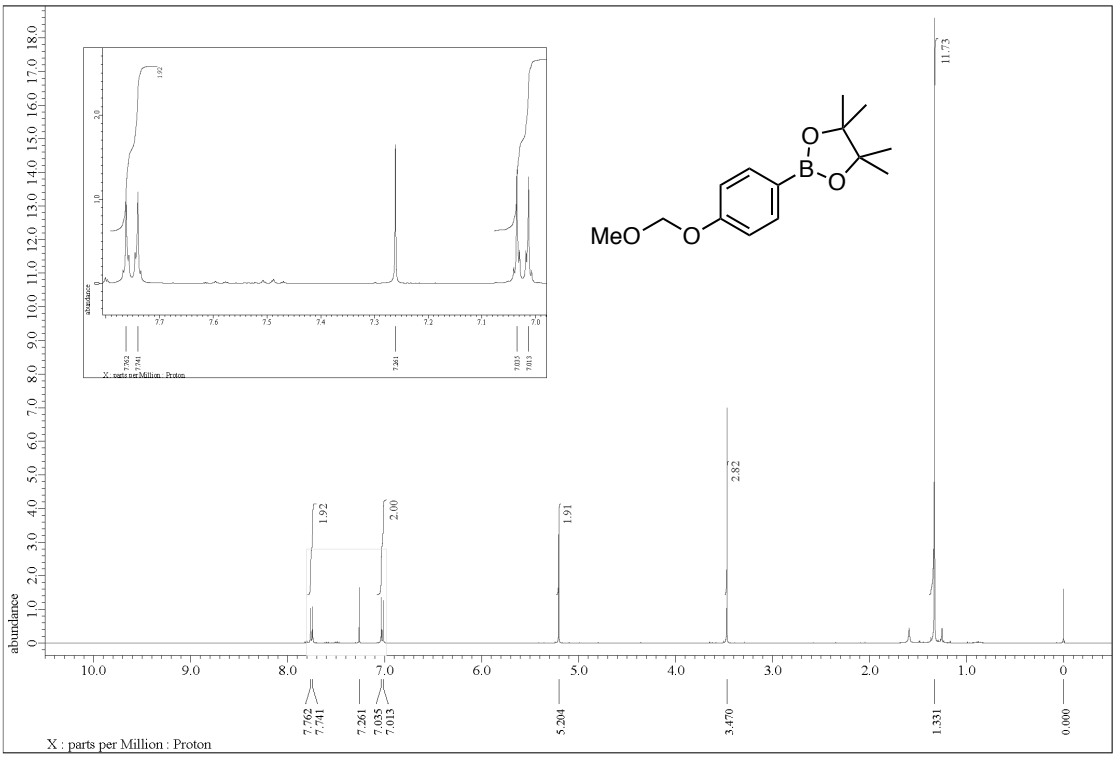


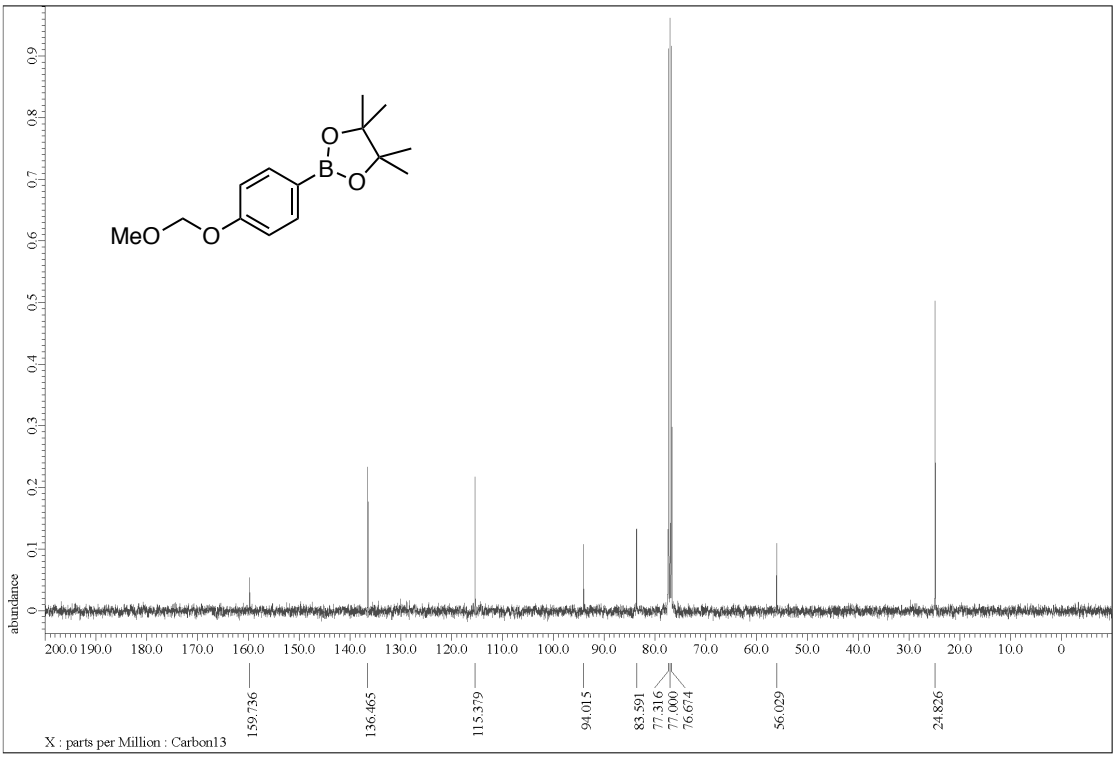
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3n** ($CDCl_3$)



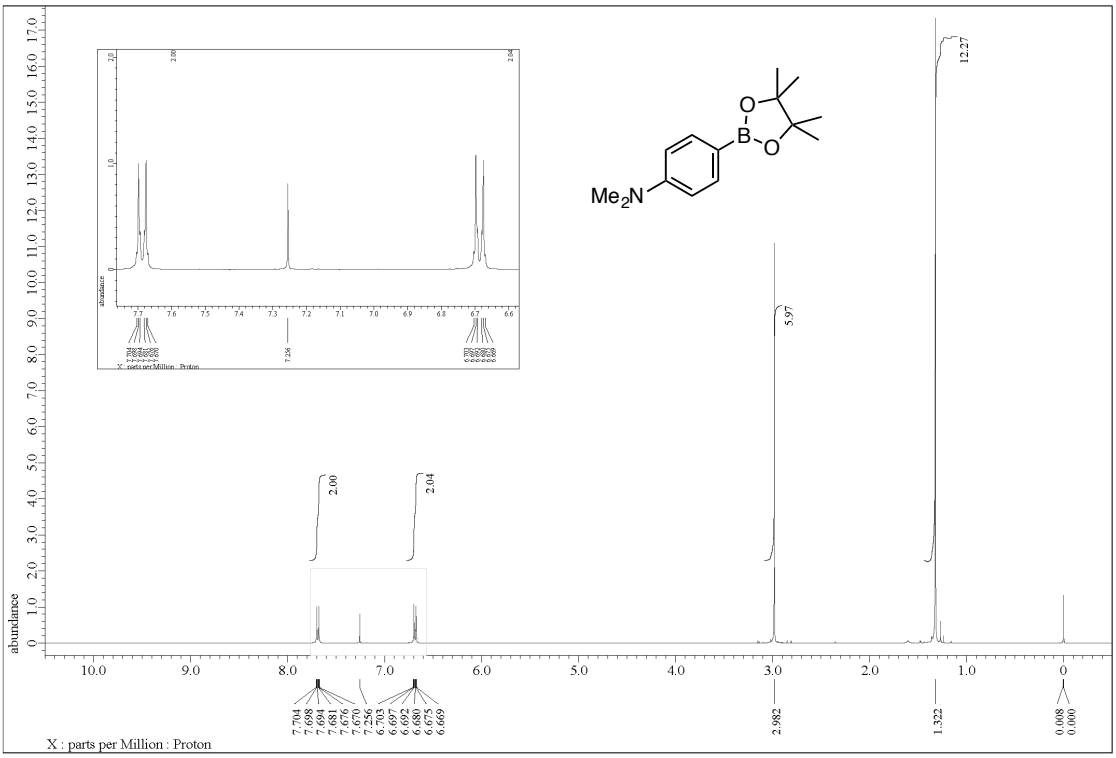


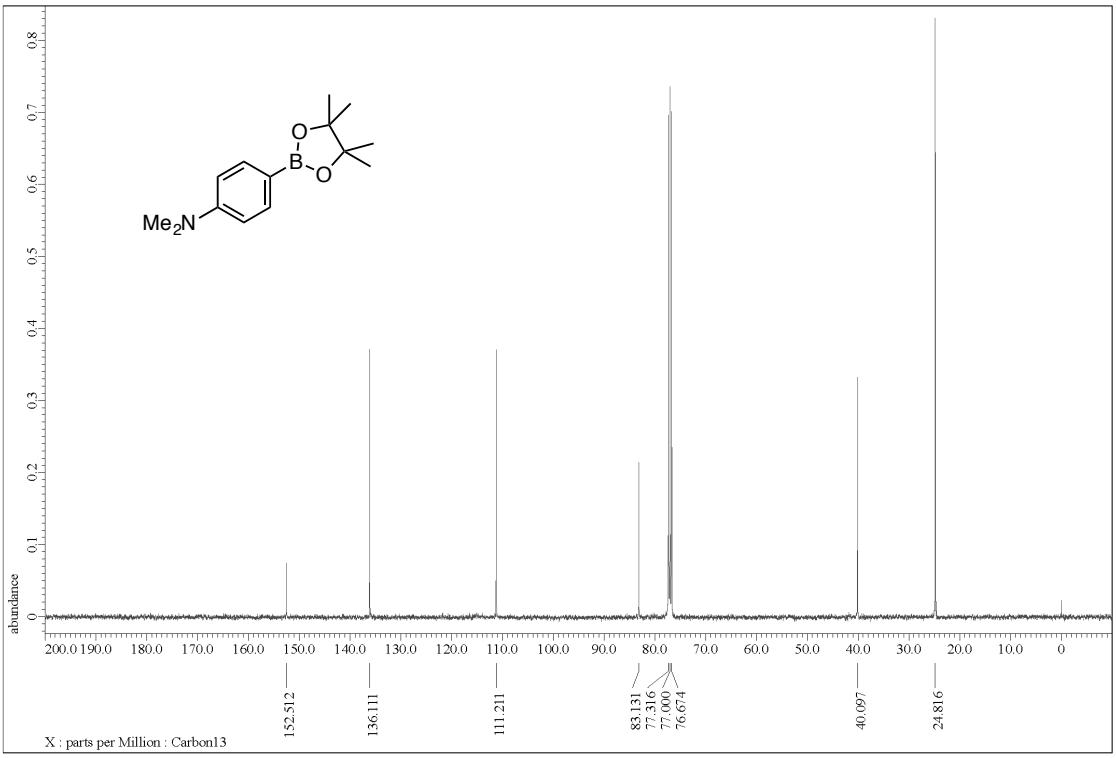
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3o** ($CDCl_3$)



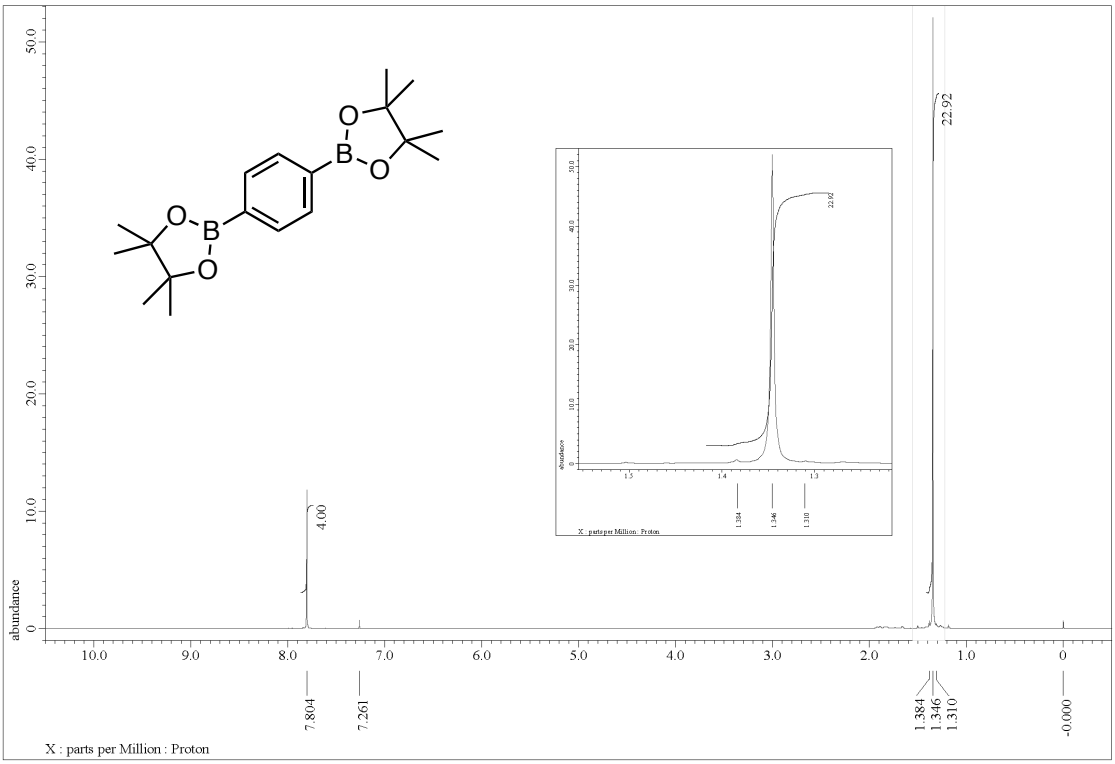


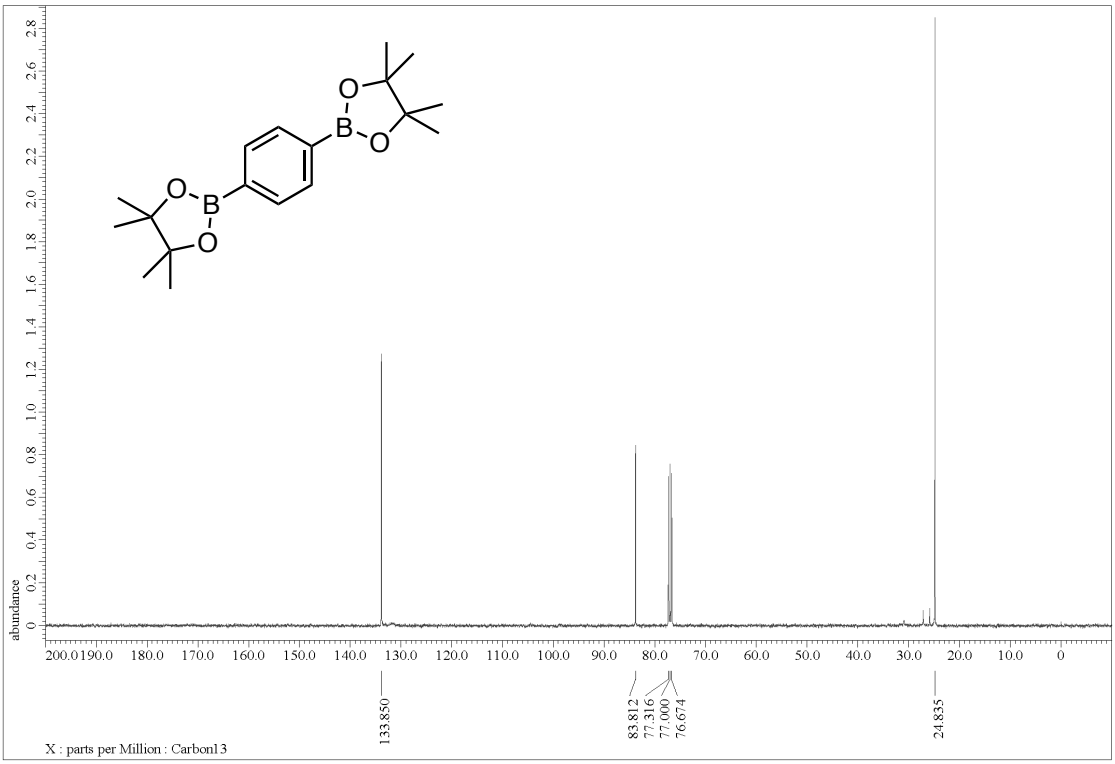
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3p** ($CDCl_3$)



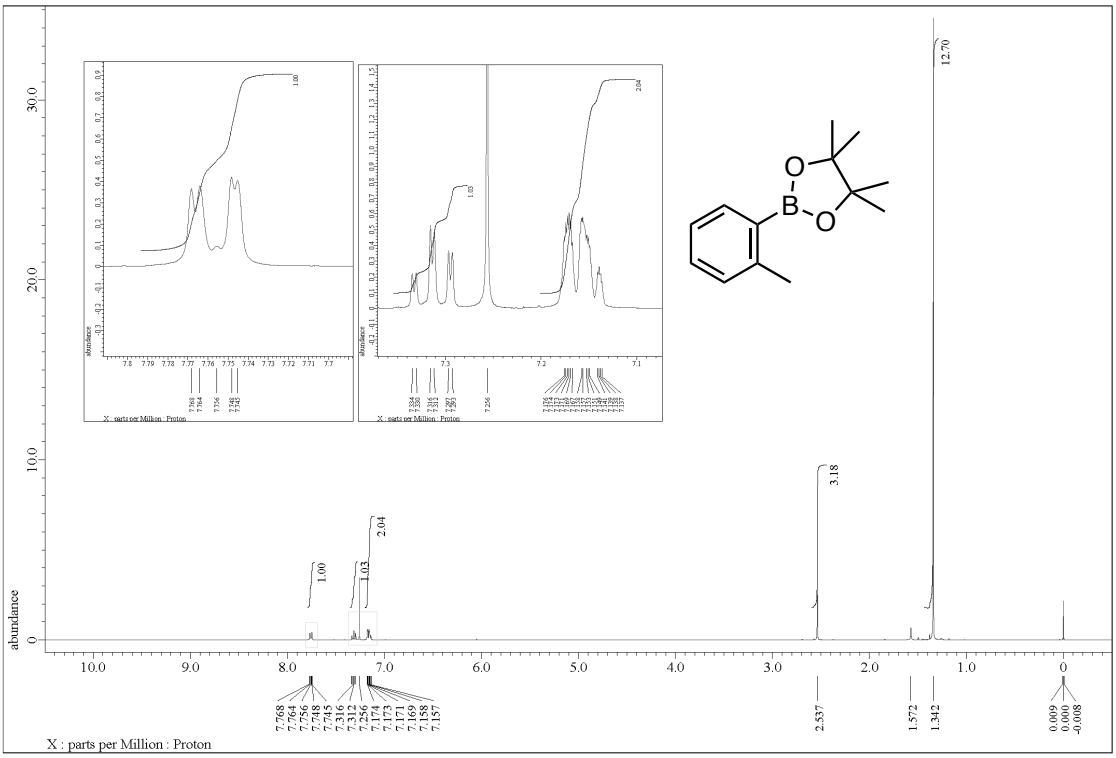


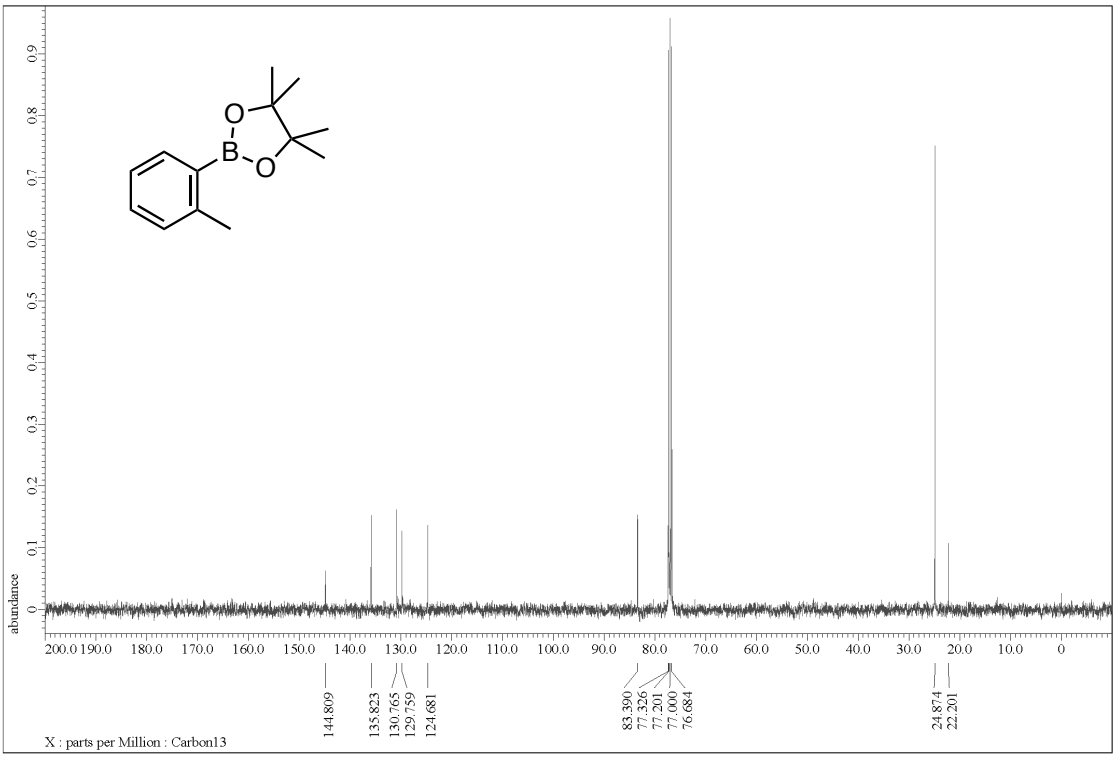
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3q** ($CDCl_3$)



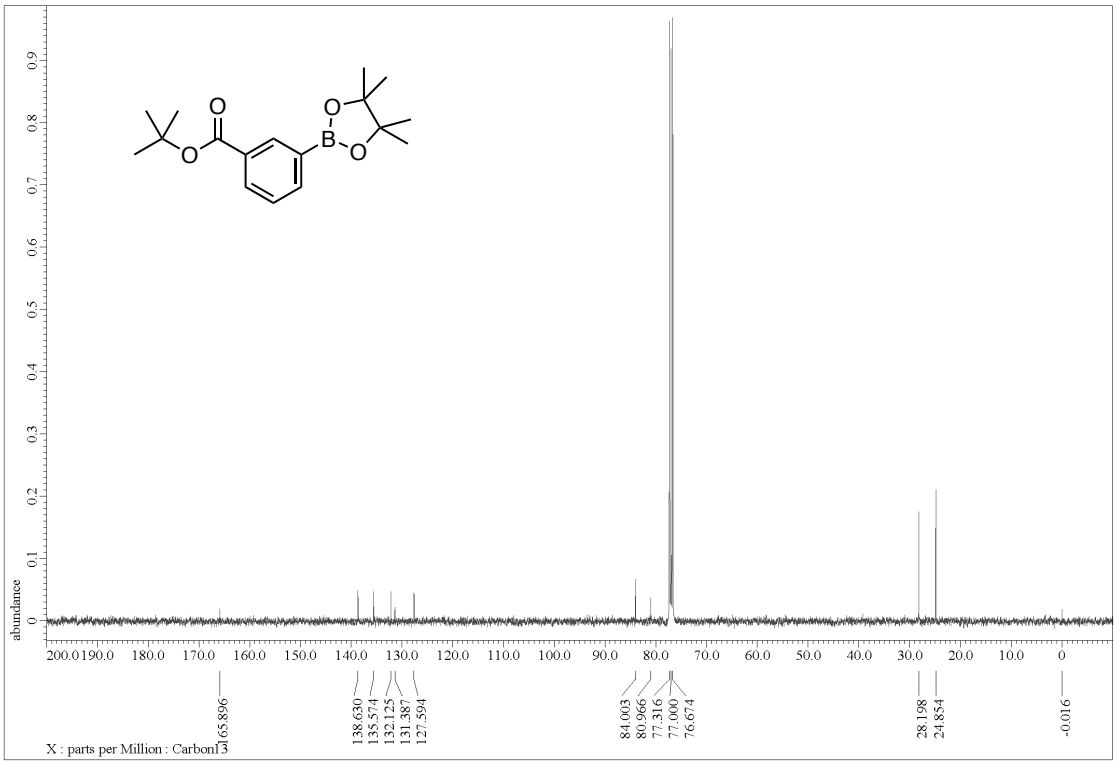


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3r** ($CDCl_3$)

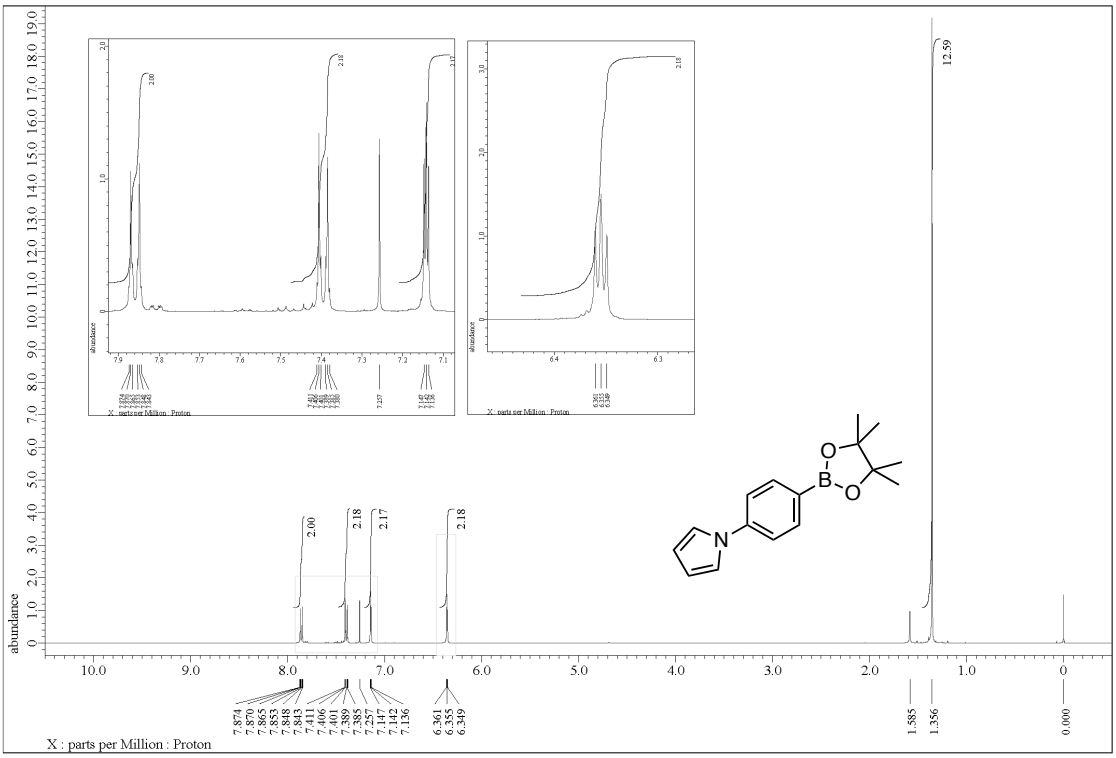


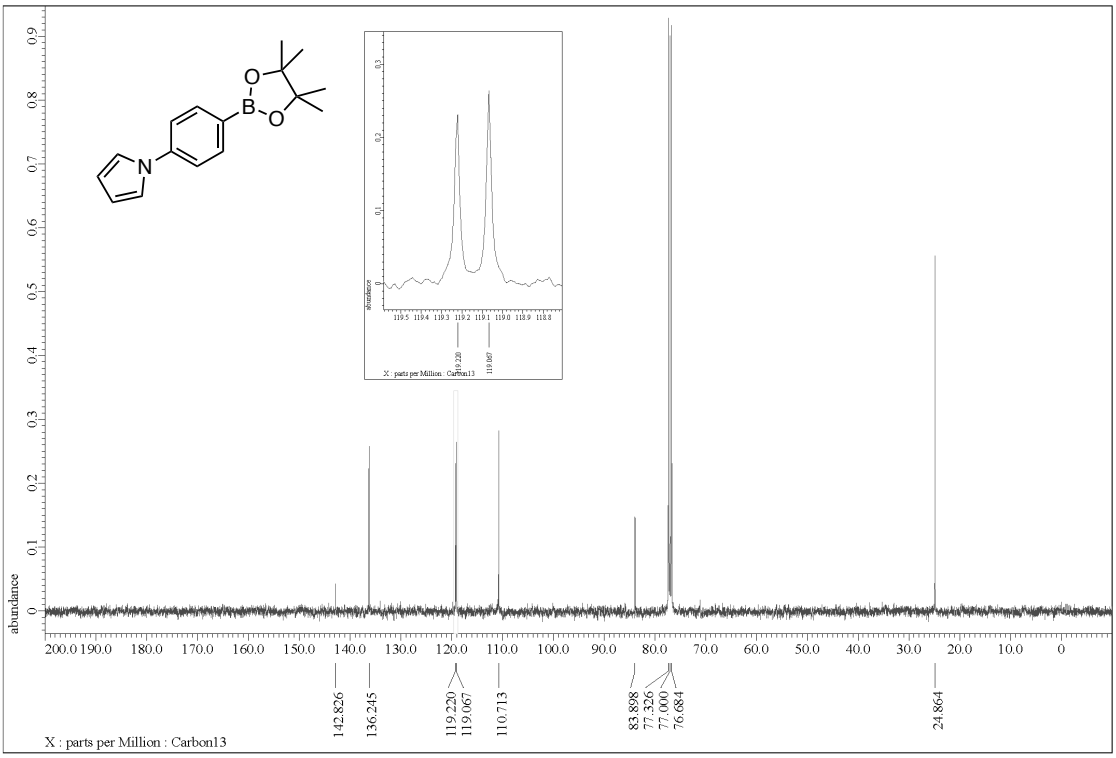


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3s** ($CDCl_3$)

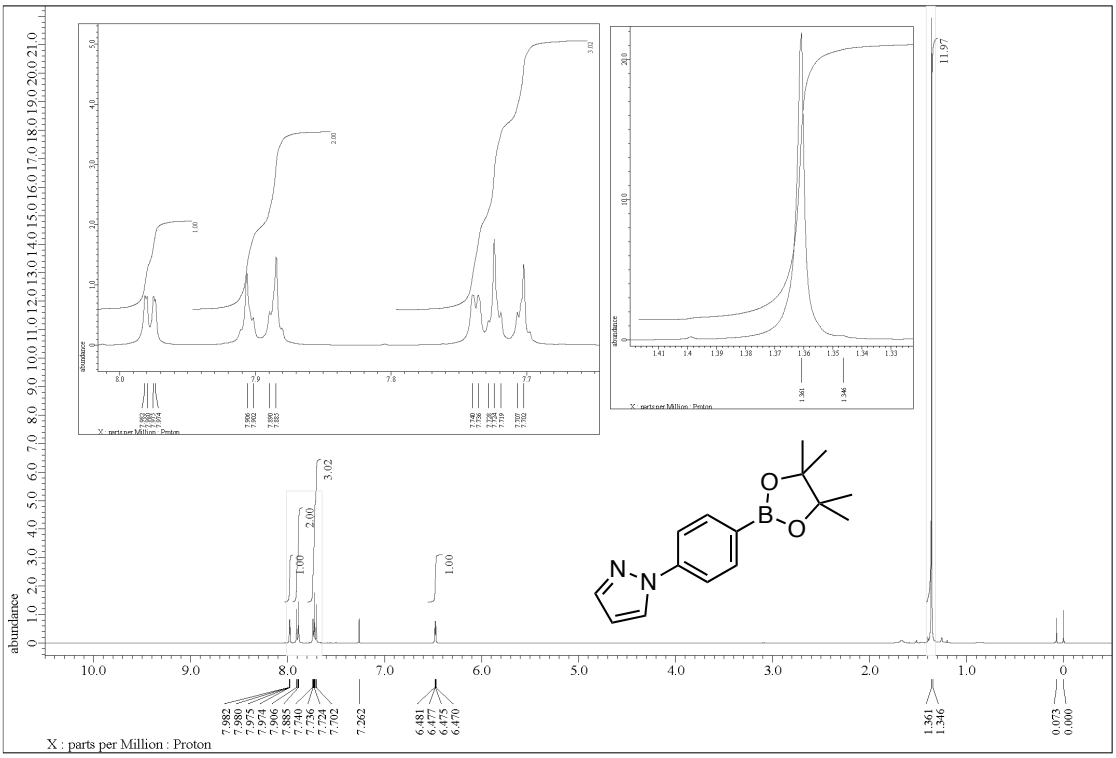


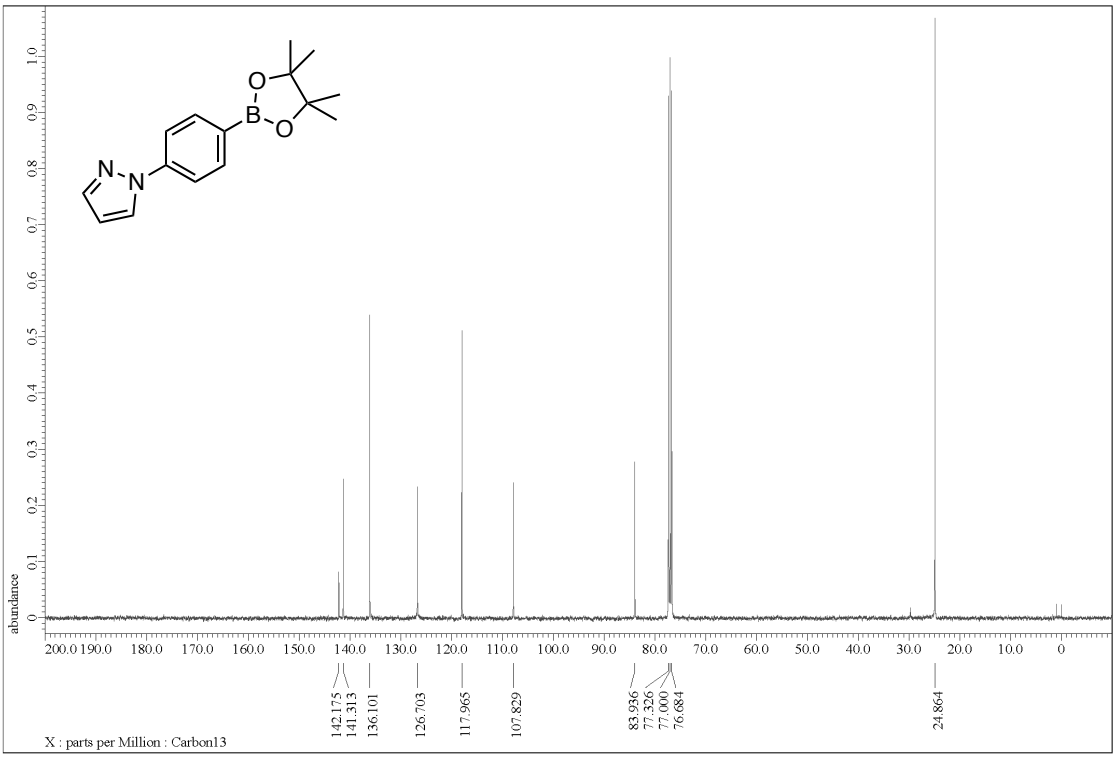
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3t** ($CDCl_3$)



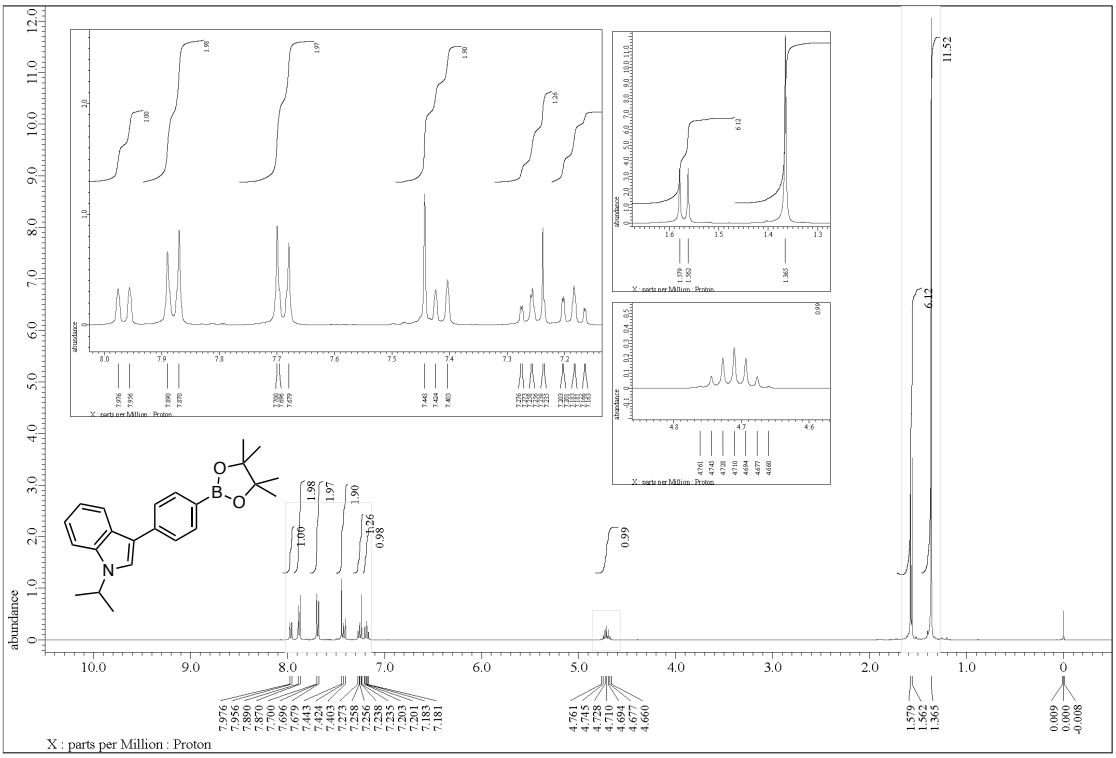


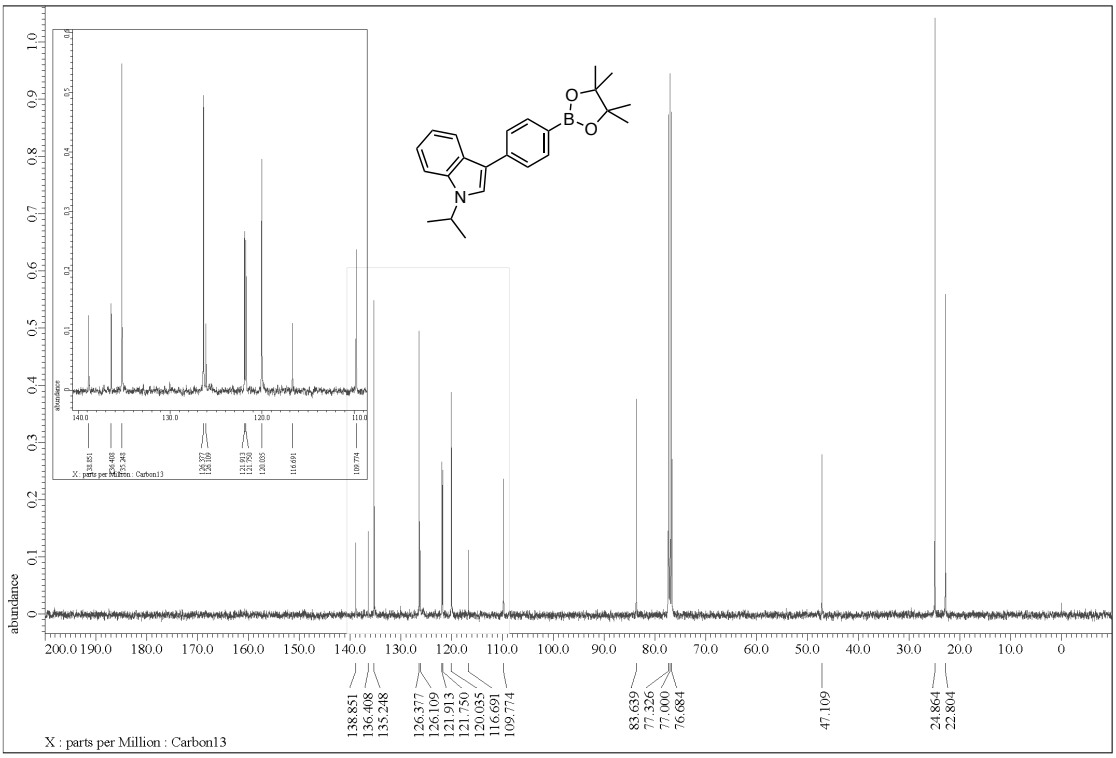
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3u** ($CDCl_3$)



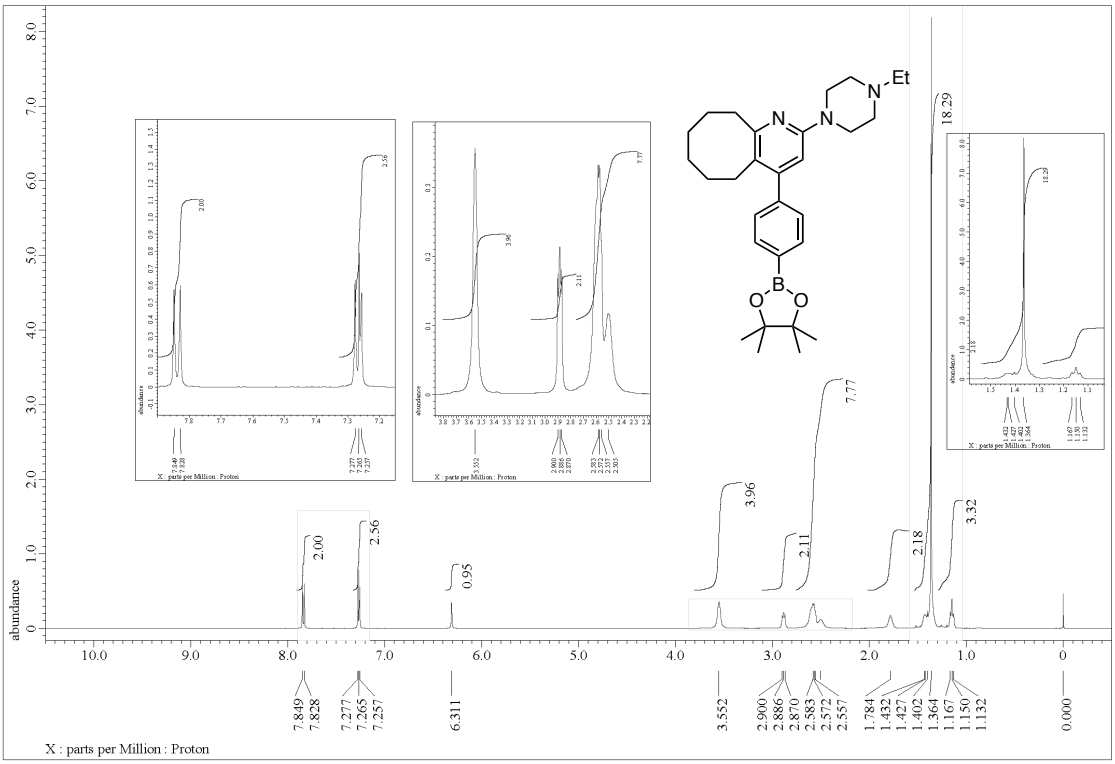


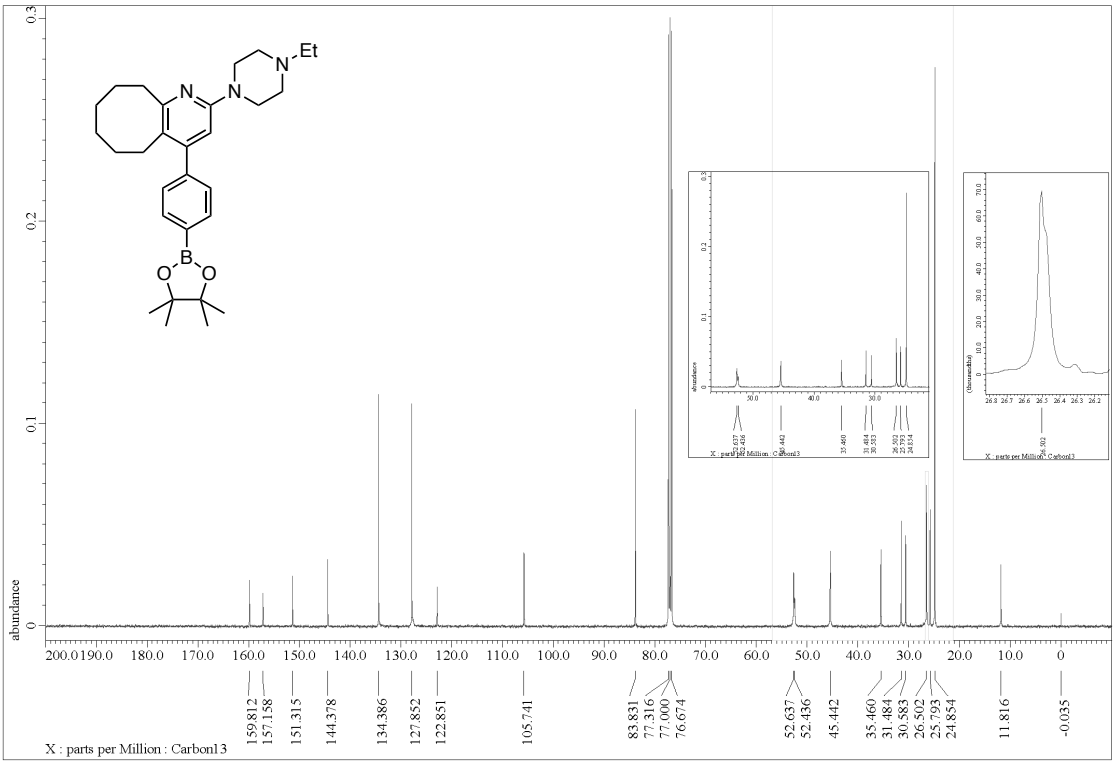
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3v** ($CDCl_3$)



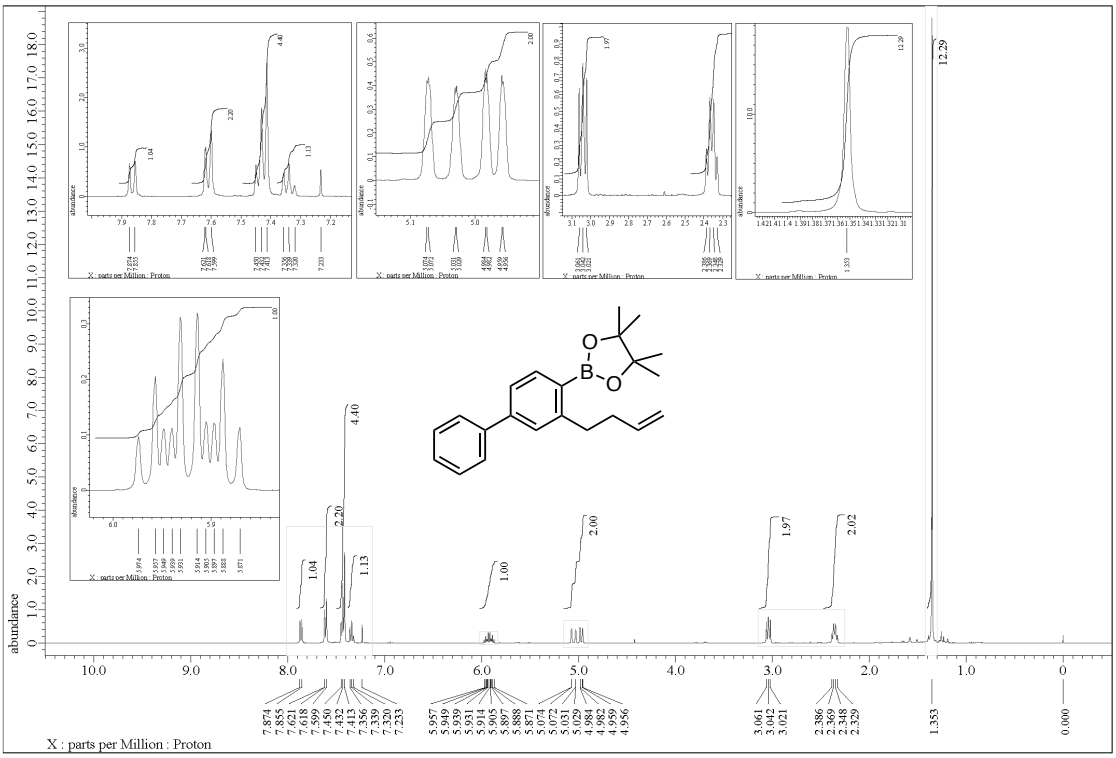


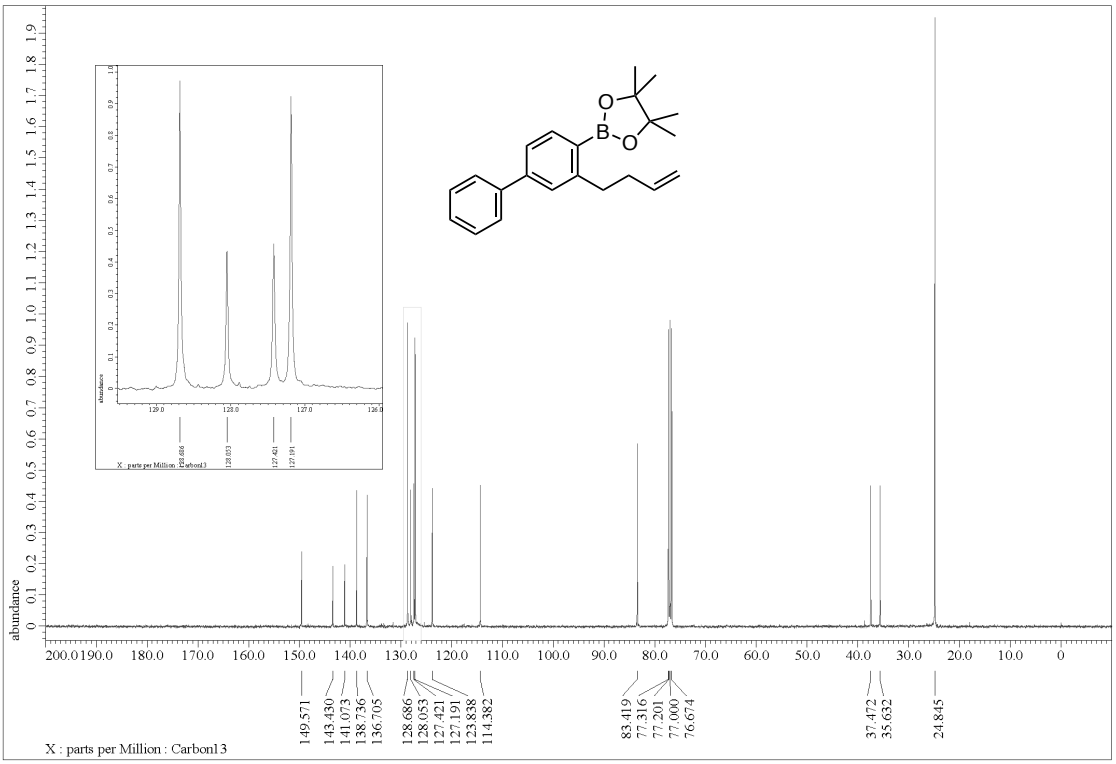
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3w** ($CDCl_3$)



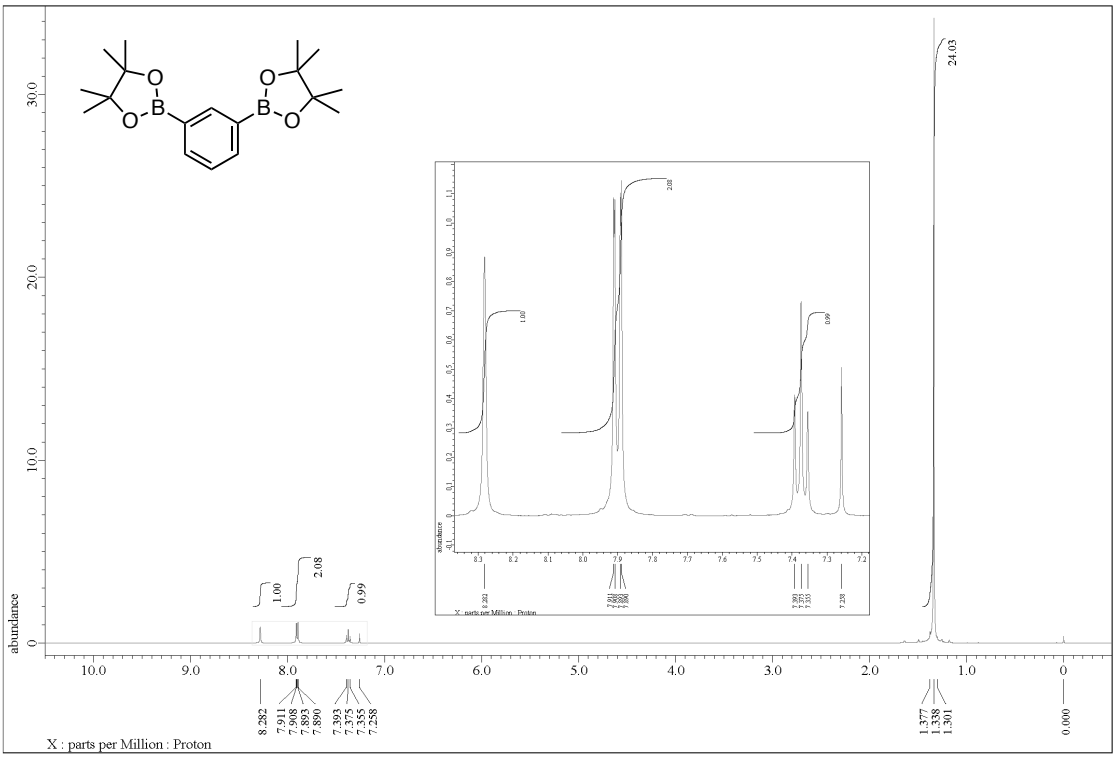


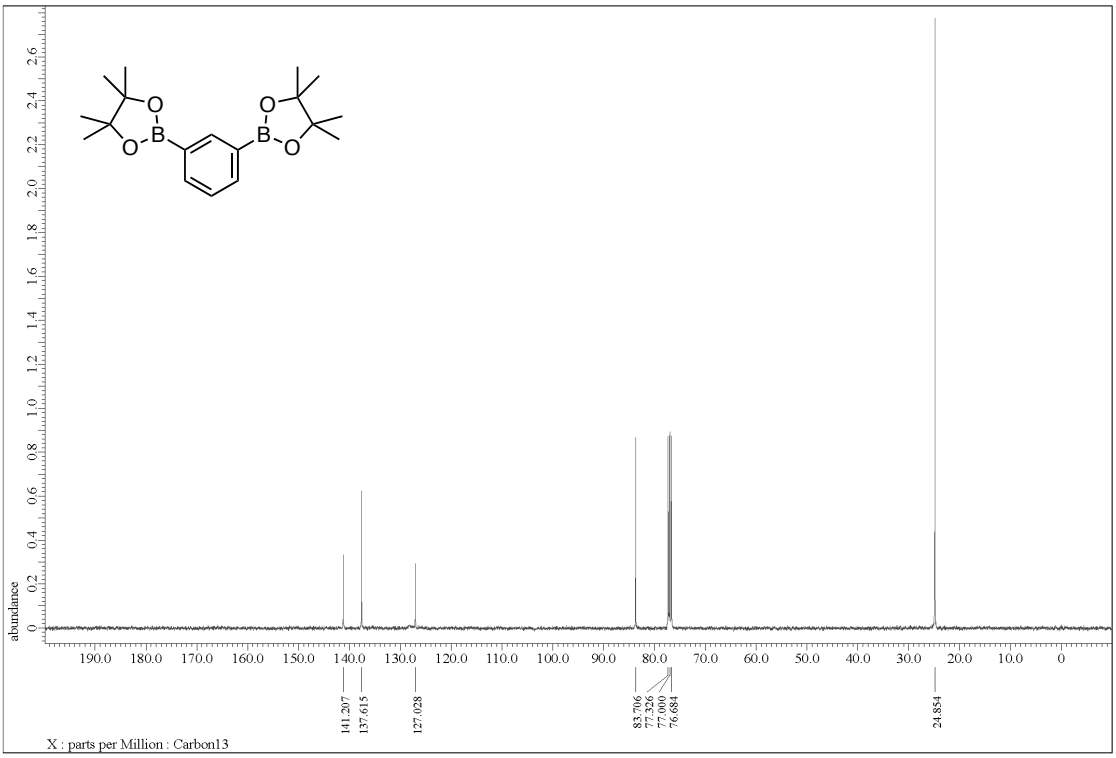
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3x** ($CDCl_3$)



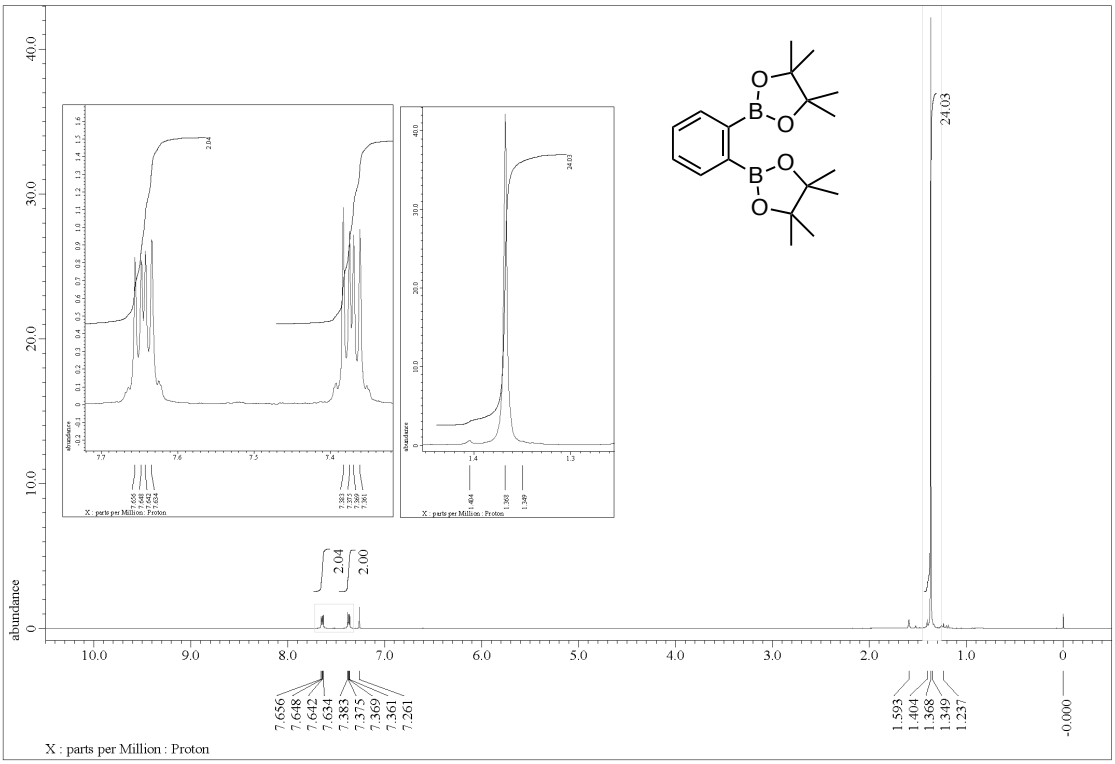


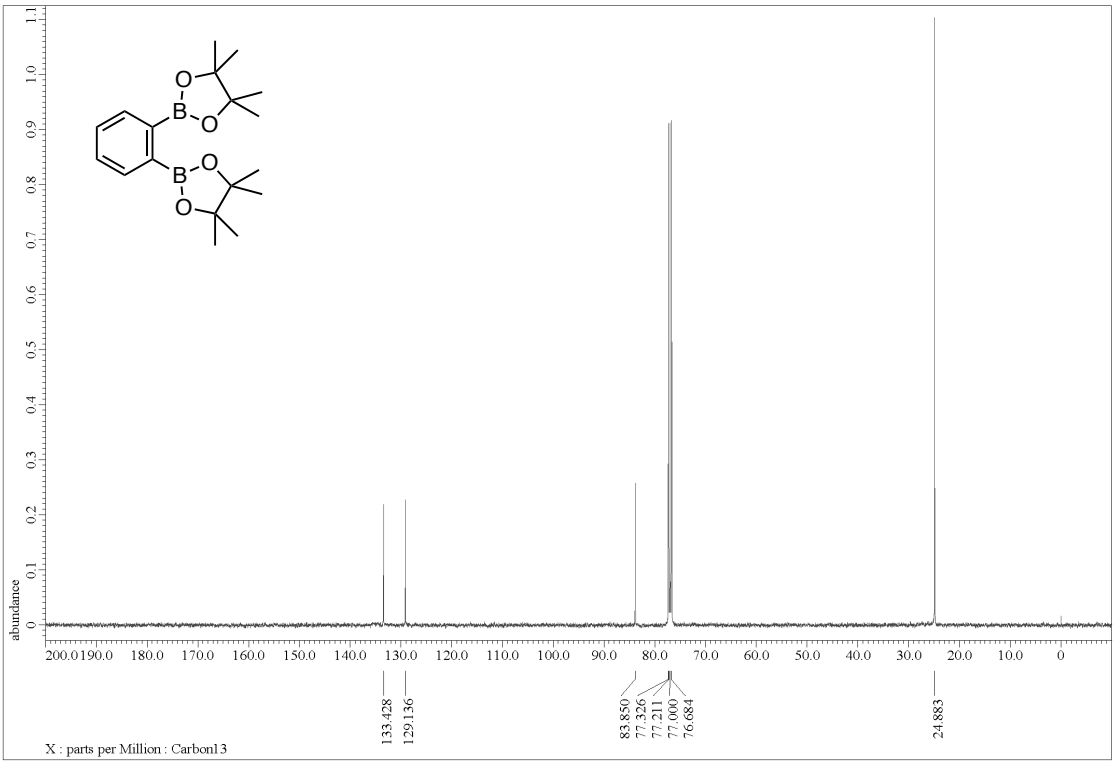
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3y** ($CDCl_3$)



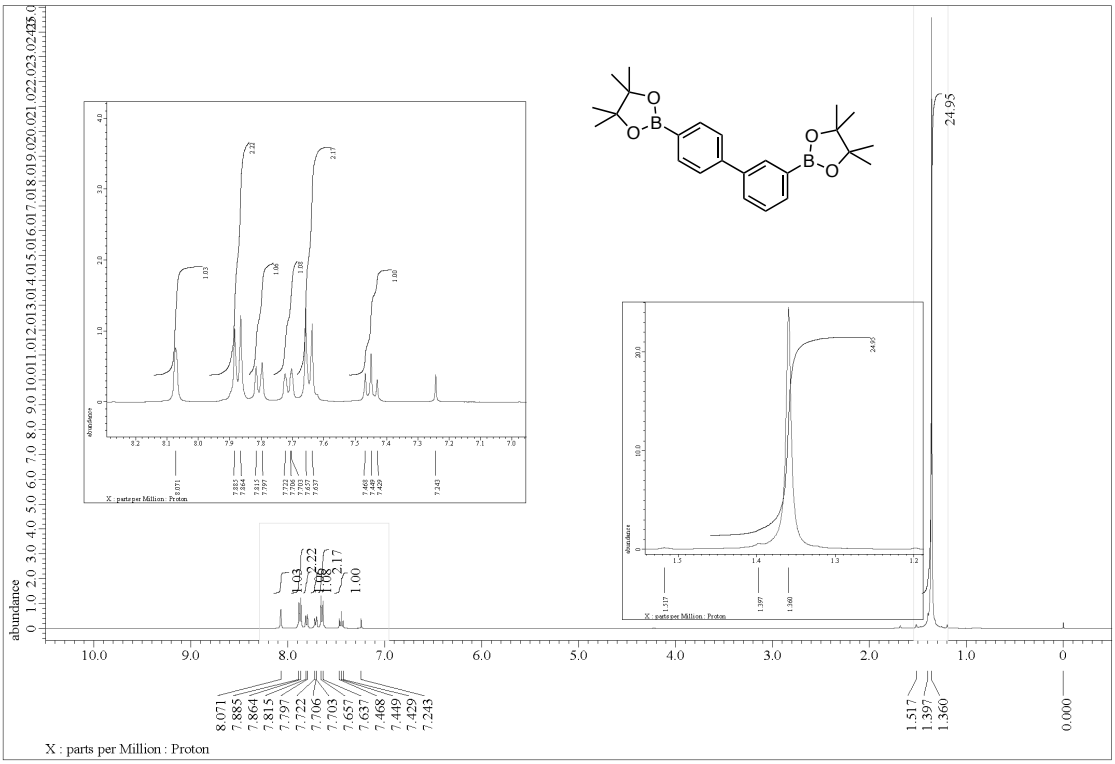


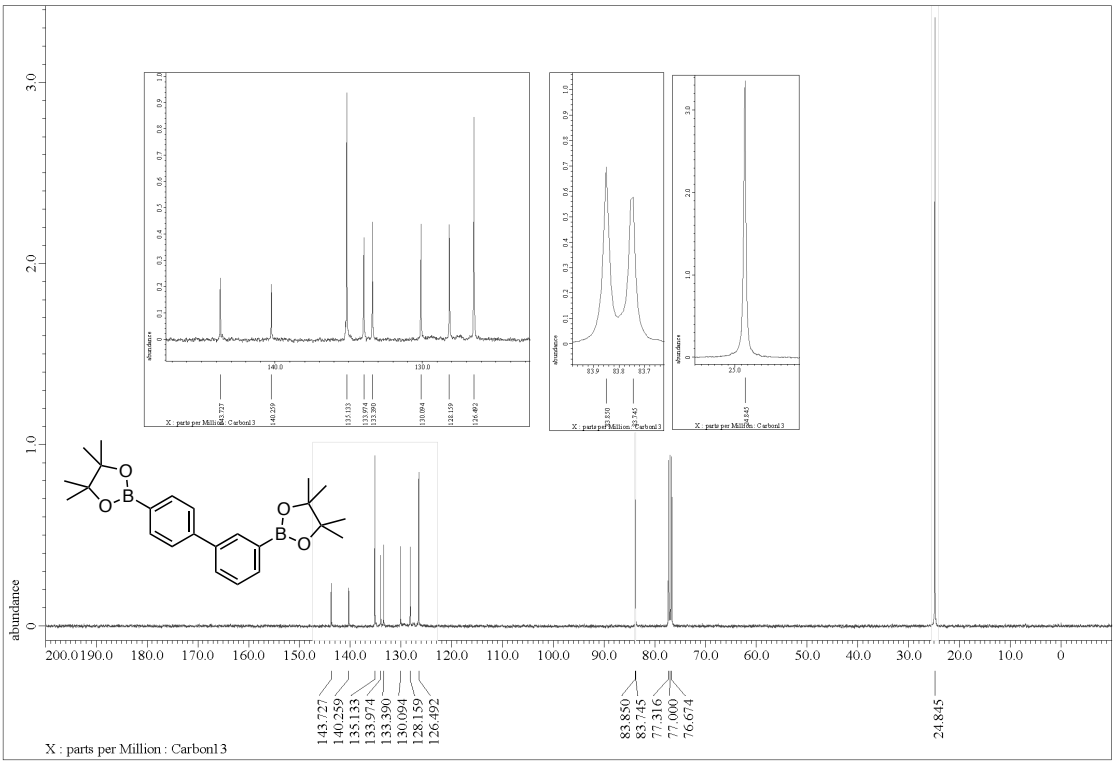
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3z** ($CDCl_3$)



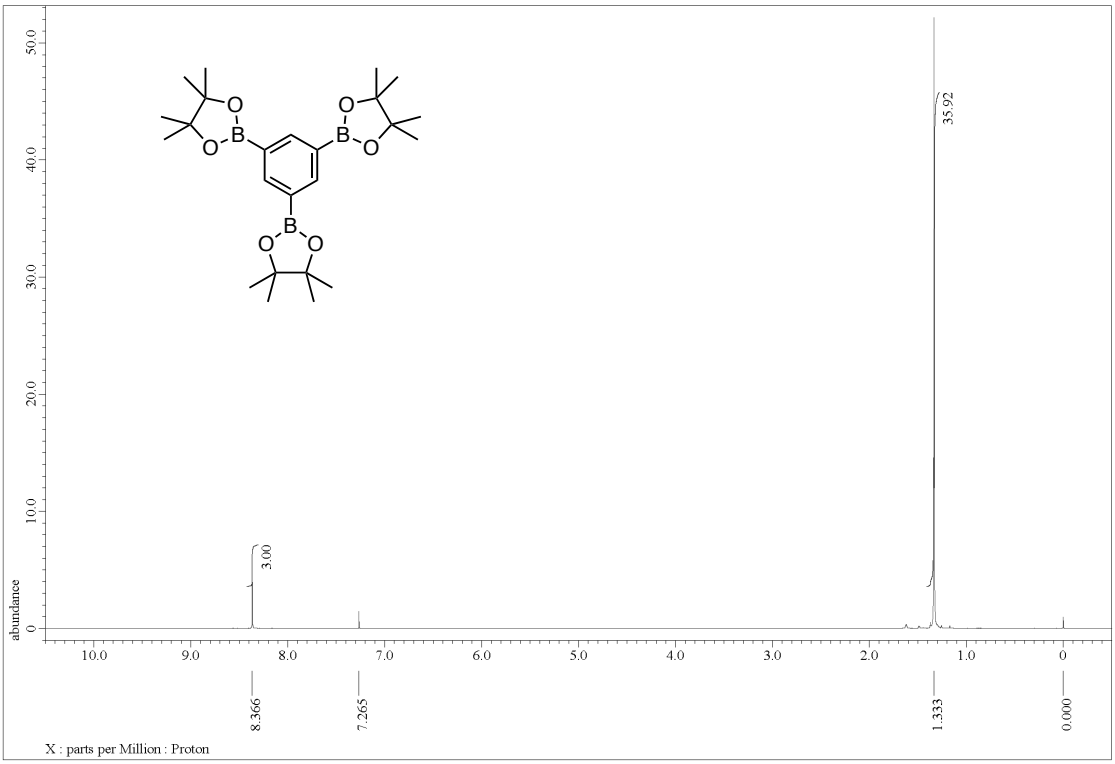


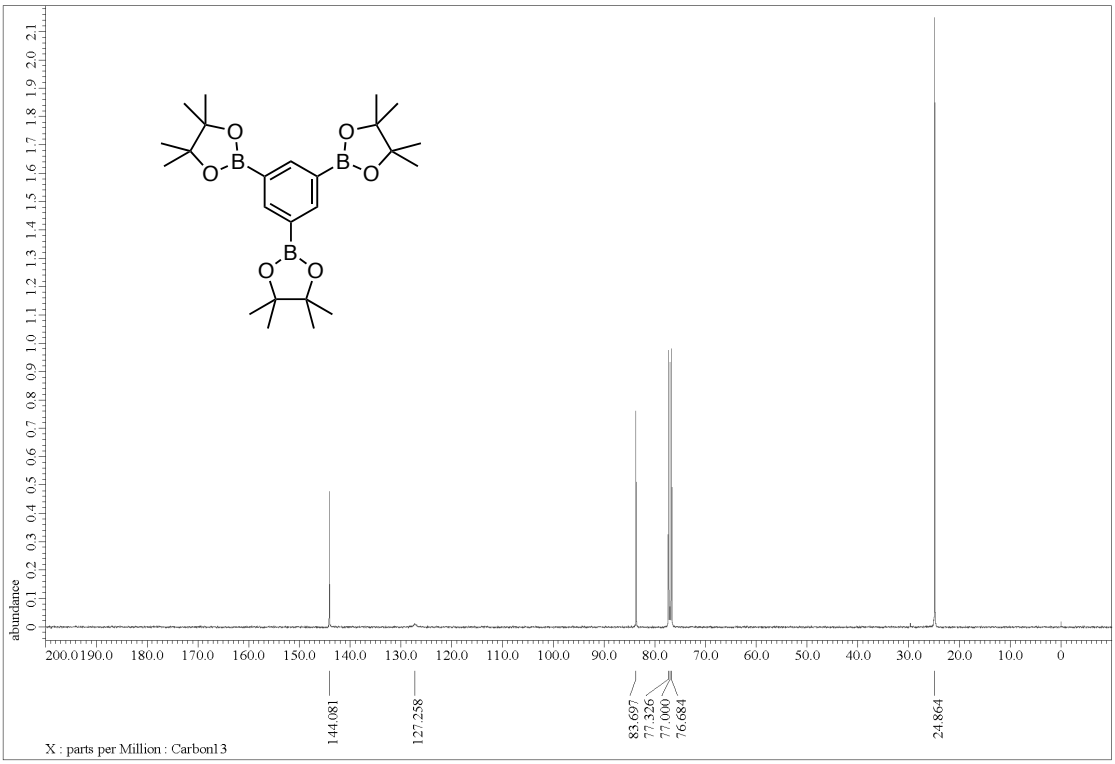
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3aa** ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3ab** ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **3ac** ($CDCl_3$)