Electronic Supplementary Information

for

Nickel-catalysed decarbonylative borylation of aroyl fluorides

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1. General

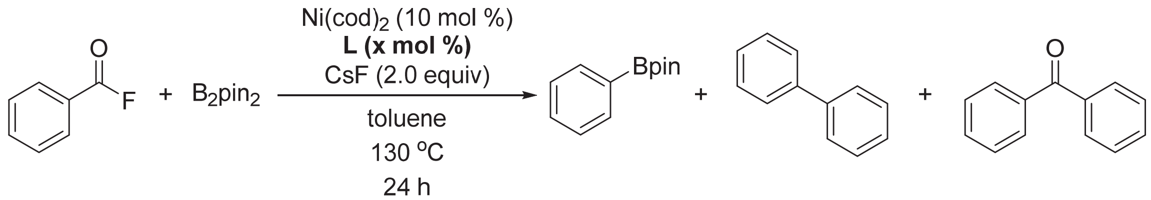
Unless otherwise noted, all the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 ºC) and heated under reduced pressure prior to use. Solvents were employed as eluents for all other routine operation, as well as dehydrated solvent were purchased from commercial suppliers and employed without any further purification. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40-100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^{1}H, ^{13}C{1H} and ^{19}F{1H}) were recorded on Varian INOVA-600 (600 MHz), Mercury-400 (400 MHz), or 300-NMR ASW (300 MHz) spectrometers. Chemical shifts (*δ*) are in parts per million relative to $CDCl_3$ at 7.26 ppm for ^{1}H and at 77.16 ppm for ^{13}C{^{1}H}. The ^{19}F{^{1}H} NMR spectra were measured by using CCl_3F ($\delta = 0.00$ ppm) as an external standard. The NMR yields were determined using dibromomethane as an internal standard. The GC yields were determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. HRMS analyses were obtained by using a double focusing magnetic sector mass spectrometer (JEOL JMS-700 MStation). Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzoyl fluoride (**1a**) (purity > 98%) was purchased from TCI. Bis(pinacolato)diboron (**2a**) (purity > 99%) was obtained from Sigma-Aldrich Co. Bis(1,5-cyclooctadiene)nickel was purchased from Merck. Triphenylphosphine, *n*-octane and potassium fluoride (purity > 95%) were obtained from Nacalai Tesque. *n*-Dodecane and sodium chloride (purity > 99%) were purchased from Kanto Chemical Co. Aroyl fluorides **1b-1w** were prepared according to the literatures[1-2] and showed the identical spectra reported.

2. Optimization of Reaction Conditions

Table S1. Screening of Ligands

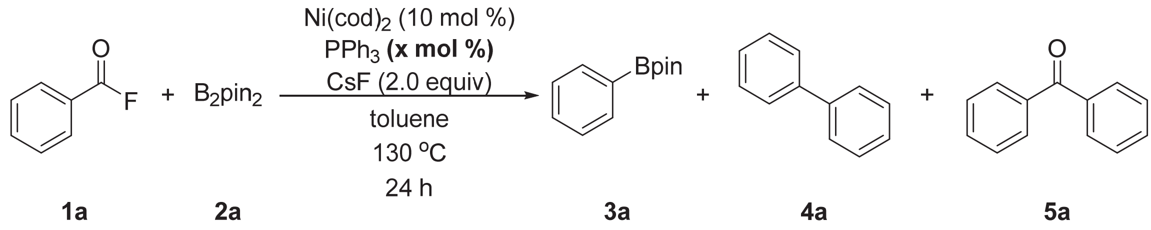


1a **2a** **3a** **4a** **5a**

entry[a]	**ligand (x mol %)**	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	DPPE (10)	0	157	0	0	1
2	DPPP (10)	0	104	3	0	6
3	DPPF (10)	0	103	3	0	0
4	DCyPE (10)	0	111	1	0	0
5	DPEphos (10)	0	90	5	0	5
6	Xantphos (10)	0	106	1	0	0
7	Triphos (10)	0	98	1	0	0
8	PEt_3 (20)	0	76	5	0	6
9	P^tBu_3 (20)	0	156	1	0	3
10	P^nBu_3 (20)	0	88	16	0	0
11	PPh_3 (20)	0	137	14	0	<1
12	P(*p*-tol)$_3$ (20)	0	136	12	0	0
13	$P(C_6F_5)_3$ (20)	4	146	0	0	2
14	PCy_3 (20)	0	68	8	0	0
15	Ruphos (20)	0	146	3	0	0
16[c]	IPr·HCl (20)	0	43	2	0	0
17	$^nBu_3P$ (30)	4	56	13	0	0
18	PPh_2(*o*-tol) (30)	0	122	16	14	2
19	PPh_2Py (30)	0	77	4	0	0
20	PPh_2Cy (30)	0	86	12	0	0
21	$PPh_2(NMe_2C_6H_4)$ (30)	0	76	6	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), Ni(cod)$_2$ (0.02 mmol) and CsF (0.4 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard. [c]NaO^{t}Bu (20 mol %) was added.

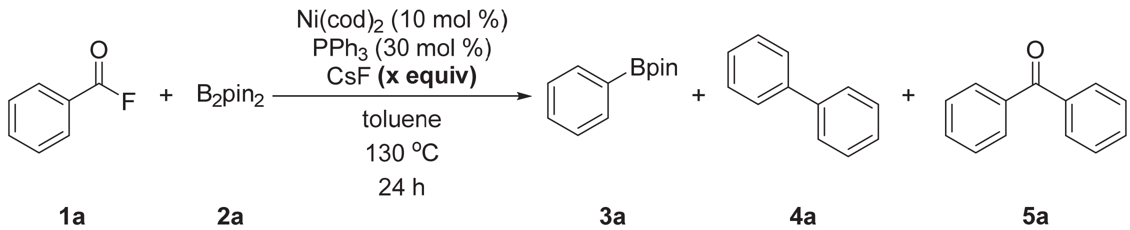
Table S2. Screening of the Amount of PPh_3



entry[a]	PPh_3 (**x mol %**)	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	PPh_3 (10)	0	139	3	0	0
2	PPh_3 (20)	0	137	14	0	<1
3	PPh_3 (30)	0	81	23	0	0
4	PPh_3 (40)	0	86	6	0	0
5	PPh_3 (50)	0	87	6	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol) and CsF (0.4 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

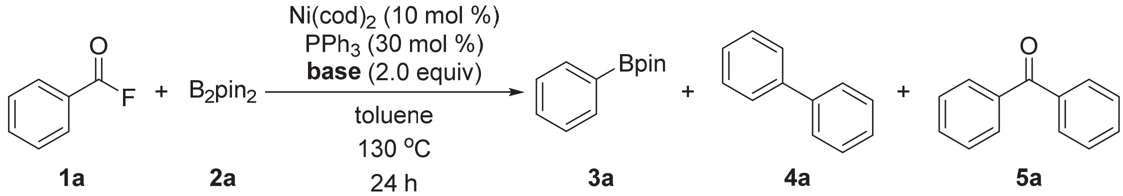
Table S3. Screening of the Amount of CsF



entry[a]	CsF (**x equiv**)	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	1.0	0	105	17	<1	0
2	2.0	0	81	23	0	0
3	3.0	0	104	6	1	0
4	4.0	0	48	4	2	0
5	6.0	0	103	4	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol) and PPh_3 (0.06 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

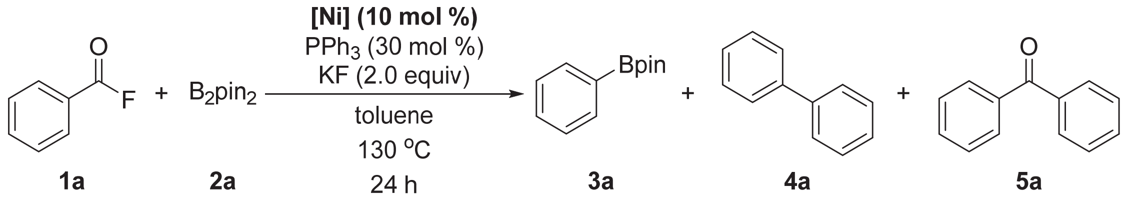
Table S4. Screening of the Bases



entry[a]	**base**	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	LiO^{t}Bu	0	72	4	3	0
2	NaO^{t}Bu	0	116	2	3	0
3	KO^{t}Bu	0	122	<1	5	0
4	Li_2CO_3	0	130	7	4	1
5	Na_2CO_3	0	103	5	4	0
6	K_2CO_3	0	113	6	5	0
7	Cs_2CO_3	0	1	8	4	0
8	K_3PO_4	0	92	4	0	0
9	KOH	0	140	5	1	0
10	KOAc	0	81	4	0	0
11[c]	$LiOCH_3$	10	106	3	0	0
12	PivONa	1	22	3	0	0
13	KPF_6	3	97	10	0	0
14	NaF	30	129	27	1	0
15	KF	0	103	33	4	0
16	CsF	0	81	23	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol) and PPh_3 (0.06 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

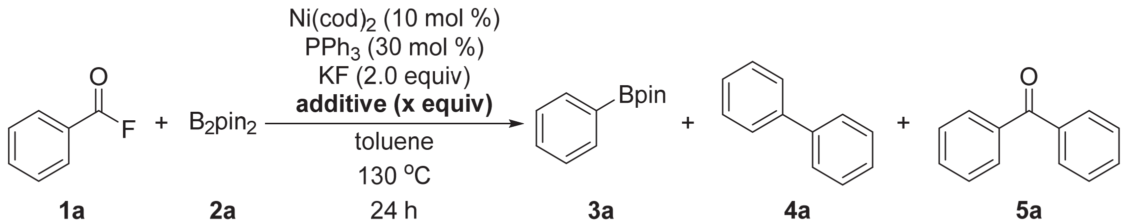
Table S5. Screening of the Catalysts



entry[a]	[Ni]	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	Ni(cod)$_2$	0	103	33	4	0
2	NiCl$_2$	0	91	32	0	0
3	NiBr$_2$	0	111	14	0	0
4	Ni(acac)$_2$	0	89	12	0	0
5	Ni(OAc)$_2$·4H$_2$O	0	102	4	0	0

[a]**1a** (0.2 mmol), B$_2$pin$_2$ (0.4 mmol), PPh$_3$ (0.06) KF (0.4 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

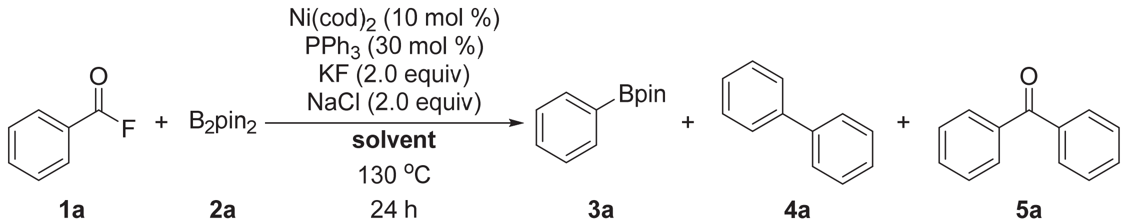
Table S6. Screening of the Additives



entry[a]	additive (x equiv)	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	-	0	103	33	4	0
2	NaCl (1.0)	0	105	54	0	0
3	NaCl (2.0)	0	117	58	0	0

[a]**1a** (0.2 mmol), B$_2$pin$_2$ (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), PPh$_3$ (0.06 mmol) and KF (0.4 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

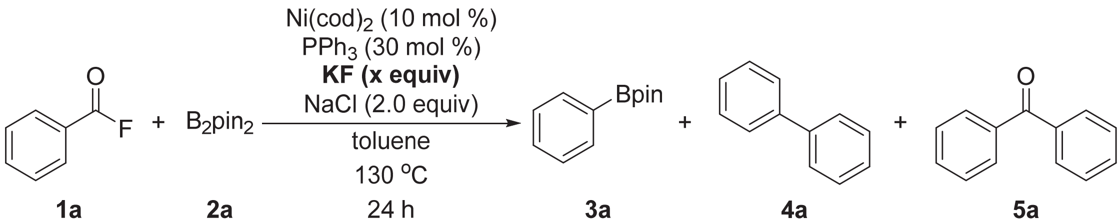
Table S7. Screening of the Solvents



entry[a]	solvent	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	toluene	0	117	58	0	0
2	DMSO	0	130	18	0	0
3	DMF	0	128	10	0	0
4	1,4-Dioxane	0	112	36	0	0
5	hexane	0	136	18	0	0
6	DCE	69	197	<1	0	0
7	octane	0	119	39	0	0
8	NMP	0	119	5	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol), KF (0.4 mmol) and NaCl (0.4 mmol) in solvent (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

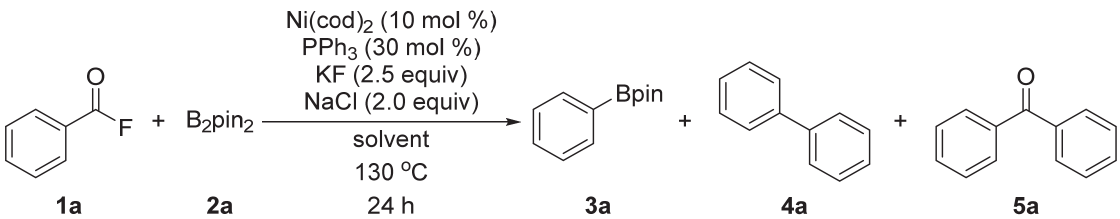
Table S8. Screening of the Amount of KF



entry[a]	**KF (x equiv)**	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	1.0	22	126	32	0	0
2	1.5	5	119	34	0	0
3	2.0	0	117	58	0	0
4	2.5	0	125	61	0	0
5	3.0	43	127	41	0	0
6	3.5	25	127	43	0	0
7	4.0	30	119	53	0	0
8	5.0	42	138	31	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol) and NaCl (0.4 mmol) in toluene (1.0 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

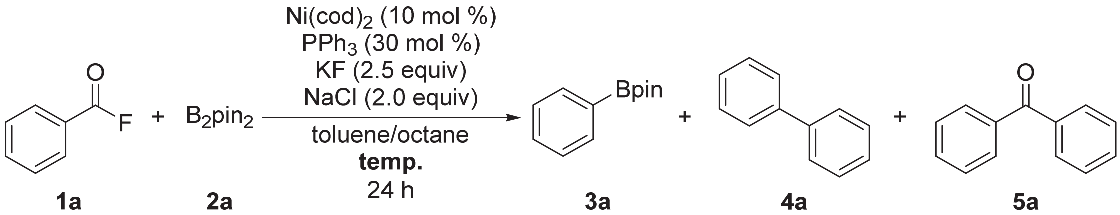
Table S9. Screening of the Binary Solvent System



entry[a]	**solvent**	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	toluene	0	125	61	0	0
2	toluene:octane = 1:1	0	110	47	0	0
3	toluene:octane = 2:1	0	90	80	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol), KF (0.5 mmol) and NaCl (0.4 mmol) in solvent (1 mL) at 130 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

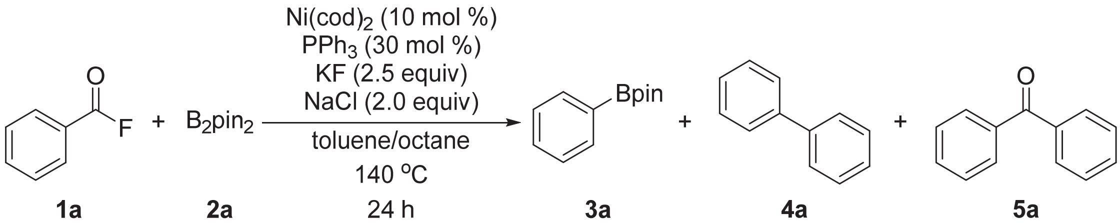
Table S10. Screening of Temperatures



entry[a]	temp. (ºC)	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	130	0	90	80	0	0
2	140	0	88	85 (83)[c]	0	0
3	150	0	77	83	0	0

[a]**1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol), KF (0.5 mmol) and NaCl (0.4 mmol) in toluene/octane (v/v = 2/1) for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard. [c]Isolated yield.

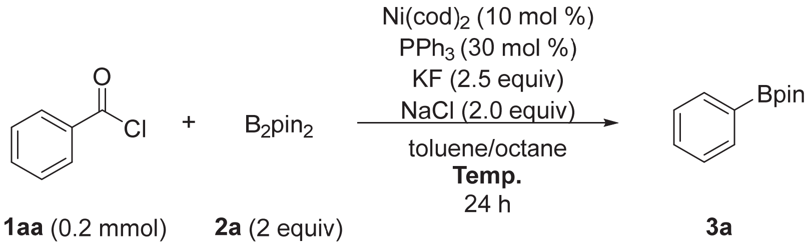
Table S11. Screening of the Amount of B_2pin_2



entry[a]	**B_2pin_2 (x equiv)**	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	1	60	67	21	0	0
2	1.2	7	42	52	0	0
3	1.5	24	69	51	0	0
4	2	0	88	85	0	0

[a]**1a** (0.2 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol), KF (0.5 mmol) and NaCl (0.4 mmol) in toluene/octane (v/v = 2/1) at140 ºC for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

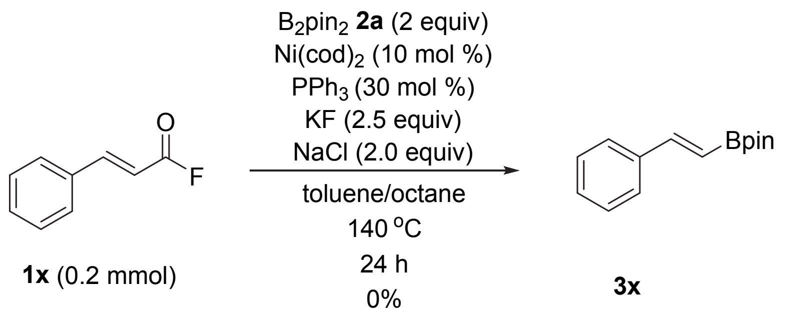
Table S12. The Reactions of Benzoyl Chloride (1aa) as the Coupling Partner in Ni-catalyzed Decarbonylative Borylation

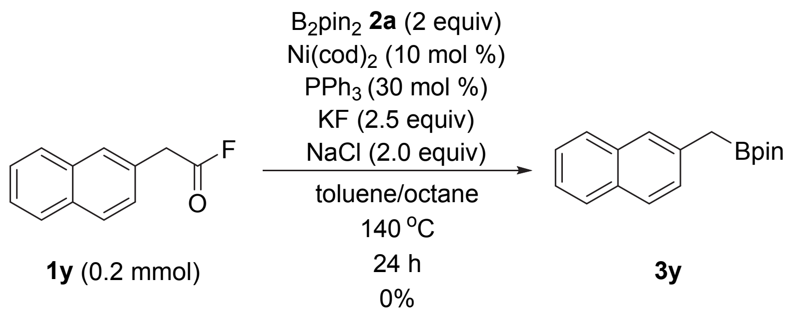


entry[a]	**Temp.** (ºC)	**1aa** (%)[b]	**2a** (%)[b]	**3a** (%)[b]
1	rt.	90	191	0
2	50	95	190	0
3	80	84	188	0

[a]**1aa** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol), KF (0.5 mmol) and NaCl (0.4 mmol) in toluene/octane (v/v = 2/1) for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

Vinyl and Benzylboronates in Ni-Catalyzed Decarbonylative Borylation

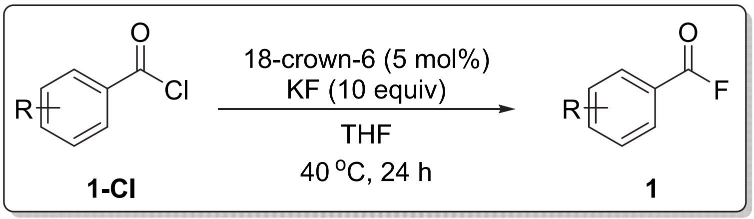




[a]**1** (0.2 mmol), B_2pin_2 (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.06 mmol), KF (0.5 mmol) and NaCl (0.4 mmol) in toluene/octane (v/v = 2/1) at 140 ºC for 24 h.

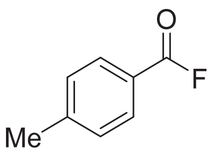
3. Synthesis of Aroyl Fluorides

3.1 Representative Procedure for the Synthesis of Aroyl Fluorides from Acid Chlorides[1]



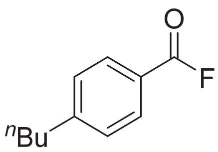
To a 50 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added aroyl chlorides **1-Cl** (4.0 mmol), 18-crown-6 (52.9 mg, 0.2 mmol, 5 mol %), KF (2.32 g, 40 mmol, 10 equiv), and THF (20 mL). After the reaction was stirred at 40 ºC for 24 h, the insoluble inorganic solid (KF or KCl) was filtered, and the volatiles were concentrated using a rotary evaporator. The crude product was purified by bulb-to-bulb distillation to afford the corresponding aroyl fluorides **1** in 20-89% yields.

4-Methylbenzoyl fluoride (1b)[3]



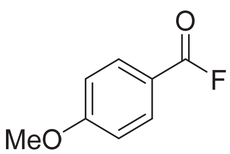
Colorless oil, yield: 46% (254.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.28-7.21 (m, 2H), 7.83-7.89 (m, 2H); ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ 17.42.

4-Butylbenzoyl fluoride (1c)[4]



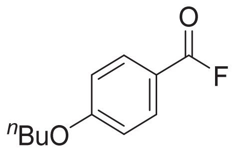
Colorless oil, yield: 84% (605.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 3H), 1.36 (h, J = 7.4 Hz, 2H), 1.60-1.65 (m, 2H), 2.69-2.72 (m, 2H), 7.31-7.34 (m, 2H), 7.92-7.97 (m, 2H); ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ 17.41.

4-Methoxybenzoyl fluoride (1d)[5,6]



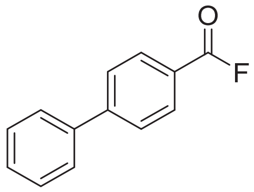
Colorless oil, yield: 50% (308.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.98 (dd, J = 9.0, 1.4 Hz, 2H), 7.96-8.02 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 15.94.

4-Butoxybenzoyl fluoride (1e)[4]



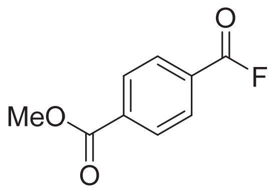
Colorless oil, yield: 87% (682.8 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3H), 1.47-1.54 (m, 2H), 1.77-1.82 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 6.93-6.99 (m, 2H), 7.94-7.99 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 15.75.

[1,1'-Biphenyl]-4-carbonyl fluoride (1g)[7]



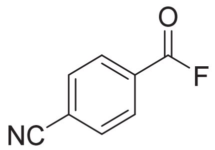
White solid, yield: 68% (544.6 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.52 (m, 3H), 7.62-7.66 (m, 2H), 7.73-7.76 (m, 2H), 8.10-8.14 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 18.11.

Methyl 4-(fluorocarbonyl)benzoate (1i)[8]



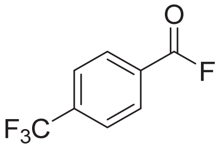
White solid, yield: 60% (437.2 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 8.10-8.14 (m, 2H), 8.16-8.21 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 20.06.

4-Cyanobenzoyl fluoride (1k)[3]



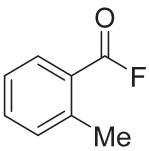
White solid, yield: 80% (477.2 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 7.78-7.82 (m, 2H), 8.21-8.24 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 20.20.

4-(Trifluoromethyl)benzoyl fluoride (1l)[9]



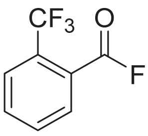
Colorless oil, yield: 58% (445.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.85 (m, 2H), 8.19 (d, J = 8.2 Hz, 2H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -63.53, 19.95.

2-Methylbenzoyl fluoride (1n)[3]



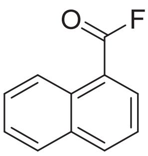
Colorless oil, yield: 44% (243.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (d, J = 1.9 Hz, 3H), 7.29-7.37 (m, 2H), 7.55 (td, J = 7.5, 1.5 Hz, 1H), 7.96-8.02 (m, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 29.15.

2-(Trifluoromethyl)benzoyl fluoride (1p)[10]



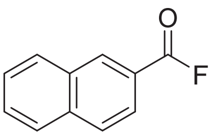
Colorless oil, yield: 50% (384.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.82 (m, 2H), 7.89 (ddt, J = 7.8, 1.4, 0.7 Hz, 1H), 8.04-8.10 (m, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -60.50, 36.21.

1-Naphthoyl fluoride (1q)[6]



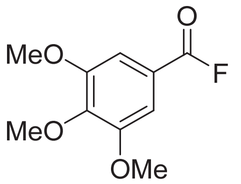
White solid, yield: 89% (620.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.65 (m, 2H), 7.72 (ddd, J = 8.6, 6.9, 1.4 Hz, 1H), 7.95 (ddd, J = 8.2, 1.5, 0.7 Hz, 1H), 8.19 (dt, J = 8.3, 1.2 Hz, 1H), 8.36 (dd, J = 7.4, 1.3 Hz, 1H), 9.02 (dt, J = 8.7, 1.0 Hz, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 18.05.

Methyl 2-naphthoate (1r)[7]



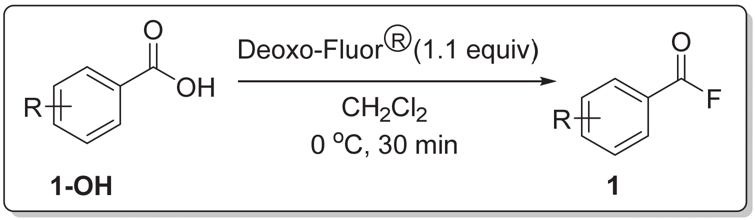
White solid, yield: 60% (418.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.65 (m, 1H), 7.67-7.71 (m, 1H), 7.90-8.03 (m, 4H), 8.65 (s, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 18.04.

3,4,5-Trimethoxybenzoyl fluoride (1u)[3]



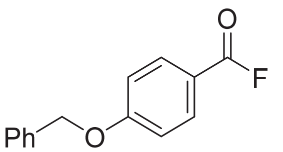
White solid, yield: 72% (616.6 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 6H), 3.95 (s, 3H), 7.28 (s, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ 16.59.

3.2 Representative Procedure for the Synthesis of Aroyl Fluorides from Carboxylic Acids[2]



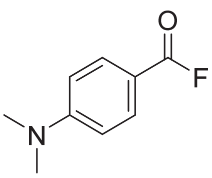
To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added carboxylic acids **1-OH** (3.0 mmol) and CH_2Cl_2 (15 mL). After the mixture was stirred at 0 ºC, Deoxo-Fluor® reagent (1.1 equiv, 608 μL, 3.3 mmol) was slowly added to the reaction mixture. After the reaction mixture was stirred at 0 ºC for 30 min, the solution was slowly poured into saturated $NaHCO_3$, and after CO_2 evolution ceased it was extracted into CH_2Cl_2 (3 × 15 mL), and dried over $MgSO_4$. The crude product was purified by flash chromatography (Hexane:Et_2O = 10:1) to afford the corresponding aroyl fluorides **1** in 22-89% yields.

4-(Benzyloxy)benzoyl fluoride (1f)



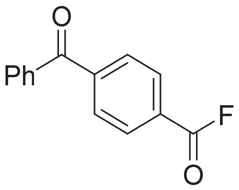
White solid, yield: 28% (193.4 mg), melting point: 105-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (s, 2H), 7.03-7.08 (m, 2H), 7.34-7.46 (m, 5H), 7.97-8.02 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 70.5, 115.4, 117.2 (d, J = 61.2 Hz), 127.6, 128.6, 128.9, 133.9 (d, J = 4.52 Hz), 135.8, 157.4 (d, J = 339.93 Hz), 164.4; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 16.08. FT-IR (neat, cm^{-1}): 640 (s), 688 (m), 740 (m), 842 (s), 1024 (s), 1174 (m), 1213 (s), 1244 (s), 1313 (s), 1384 (s), 1454 (s), 1508 (s), 1579 (s), 1602 (s), 1759 (s), 2945 (s). Anal. Calcd for $C_{14}H_{11}FO_2$: C, 73.03; H, 4.82%. Found: C, 72.99; H, 4.68%.

4-(Dimethylamino)benzoyl fluoride (1h)[11]



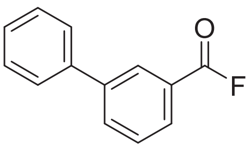
White solid, yield: 22% (110.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 6H), 6.64-6.68 (m, 2H), 7.84-7.89 (m, 2H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 12.32.

4-Benzoylbenzoyl fluoride (1j)



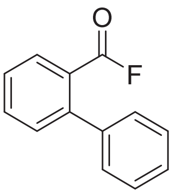
White solid, yield: 47% (321.8 mg), melting point: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.55 (m, 2H), 7.62-7.68 (m, 1H), 7.78-7.83 (m, 2H), 7.90-7.92 (m, 2H), 8.16-8.20 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 127.9 (d, J = 61.7 Hz), 128.8, 130.3, 130.3, 131.5 (d, J = 3.5 Hz), 133.5, 136.5, 143.6, 156.7 (d, J = 345.6 Hz), 195.6; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 19.95. FT-IR (neat, cm^{-1}): 692 (s), 702 (s), 869 (s), 929 (s), 1001 (s), 1026 (s), 1406 (s), 1448 (s), 1651 (s), 1805 (m). HRMS (FAB$^+$): Calcd for $C_{14}H_9FO_2$: 228.0587. Found: 228.0568.

[1,1'-Biphenyl]-3-carbonyl fluoride (1m)[4]



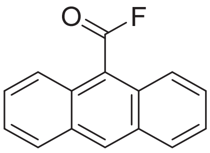
White solid, yield: 68% (408.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.44 (m, 1H), 7.47-7.52 (m, 2H), 7.59-7.64 (m, 3H), 7.90-7.94 (m, 1H), 8.02-8.04 (m, 1H), 8.27 (t, J = 1.8 Hz, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 18.62.

[1,1'-Biphenyl]-2-carbonyl fluoride (1o)[12]



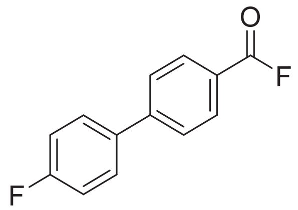
Colorless oil, yield: 50% (300.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.35 (m, 2H), 7.41-7.53 (m, 5H), 7.68 (td, J = 7.6, 1.4 Hz, 1H), 8.04 (dd, J = 7.9, 1.4 Hz, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 34.91.

Anthracene-9-carbonyl fluoride (1s)[4]



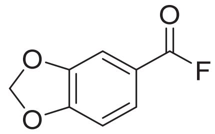
Yellow solid, yield: 57% (383.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55-7.57 (m, 2H), 7.65-7.68 (m, 2H), 8.08 (d, J = 8.4 Hz, 2H), 8.31-8.33 (m, 2H), 8.68 (s, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ 59.61.

4'-Fluoro-[1,1'-biphenyl]-4-carbonyl fluoride (1t)[7]



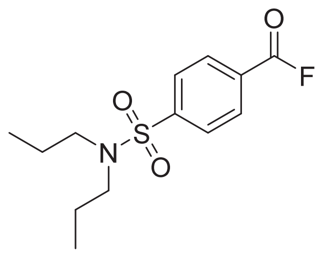
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.23 (m, 2H), 7.58-7.64 (m, 2H), 7.68-7.72 (m, 2H), 8.09-8.14 (m, 2H); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ −113.02, 18.16.

Benzo[d][1,3]dioxole-5-carbonyl fluoride (1v)



White solid, yield: 68% (343.0 mg), melting point: 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (s, 2H), 6.88-6.93 (m, 1H), 7.40-7.43 (m, 1H), 7.67 (dd, J = 8.2, 1.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 102.5, 108.7, 110.8 (d, J = 4.1 Hz), 118.5 (d, J = 62.3 Hz), 128.4 (d, J = 4.0 Hz), 148.4, 153.9, 157.0 (d, J = 341.0 Hz); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ 16.42. FT-IR (neat, cm^{-1}): 717 (s), 744 (s), 894 (m), 925 (s), 1020 (m), 1265 (m), 1448 (s), 1506 (m), 1797 (s), 2922 (s). Anal. Calcd for $C_8H_5FO_3$: C, 57.15; H, 3.00%. Found: C, 57.14; H, 2.74%.

4-(*N,N*-Dipropylsulfamoyl)benzoyl fluoride (1w)

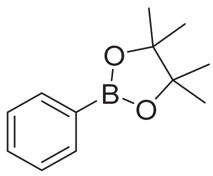


White solid, yield: 31% (267.2 mg), melting point: 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 7.4 Hz, 6H), 1.50-1.60 (m, 4H), 3.09-3.15 (m, 4H), 7.96 (d, J = 8.5 Hz, 2H), 8.18 (d, J = 8.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 11.3, 22.1, 50.0, 127.7, 128.2 (d, J = 62.6 Hz), 132.2 (d, J = 3.4 Hz), 146.8, 156.2 (d, J = 345.4 Hz); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ 20.21. FT-IR (neat, cm^{-1}): 682 (s),734 (s), 997 (s), 1024 (m), 1087 (s), 1161 (s), 1240 (m), 1346 (s), 1807 (s), 1824 (s), 2875 (s), 2935 (s), 2974 (s). Anal. Calcd for $C_{13}H_{18}FNO_3S$: C, 54.34; H, 6.31; N, 4.87%. Found: C, 54.58; H, 6.43; N, 4.82%.

4. Ni-Catalyzed Decarbonylative Borylation of Aroyl Fluorides

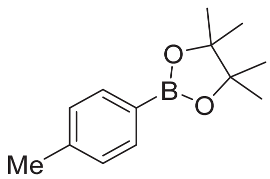
An oven dried Schlenk tube containing a stirring bar was charged with Ni(cod)$_2$ (5.5 mg, 0.02 mmol, 10 mol %), PPh_3 (15.7 mg, 0.06 mmol, 30.0 mol %), toluene (0.66 mL), octane (0.33 mL) and stirring for 30 s at room temperature. Next, aroyl fluoride (0.2 mmol, 24.8 mg), KF (30.6 mg, 0.5 mmol, 2.5 equiv.), bis(pinacolato)diboron (**2a**) (101.6 mg, 0.4 mmol, 2.0 equiv), and NaCl (23.4 mg, 0.4 mmol, 2 equiv) were added. The mixture was heated at 140 ºC with stirring for 24 h. After cooling to room temperature, to the mixture was added saturated aqueous ammonium chloride (ca. 3 mL) and extracted with EtOAc (ca. 3 mL × 3). The combined organic extract was dried over Na_2SO_4, and then filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the corresponding final product **3**.

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3a)[13]



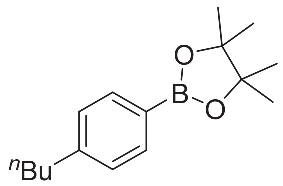
Colorless oil, yield: 83% (33.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 12H), 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1H), 7.81 (dd, J = 8.0, 1.4 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.0, 83.9, 127.8, 131.4, 134.9. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.91.

4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (3b)[14]



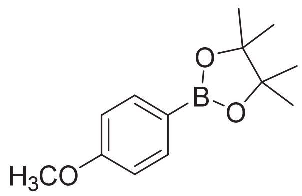
Colorless solid, yield: 65% (28.4 mg), melting point: 53-54 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 12H), 2.37 (s, 3H), 7.17-7.21 (m, 2H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 21.9, 25.0, 83.7, 128.6, 134.9, 141.5. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.93.

2-(4-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)[13]



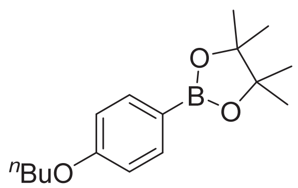
Colorless oil, yield: 82% (42.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3H), 1.34 (s, 14H), 1.58-1.64 (m, 2H), 2.61-2.65 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 14.1, 22.5, 25.0, 33.6, 36.0, 83.7, 128.0, 134.9, 146.5. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.97.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)[15]



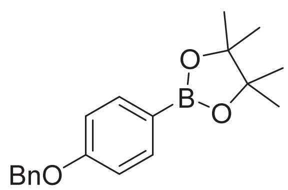
Colorless oil, yield: 60% (28.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 12H), 3.83 (s, 3H), 6.90 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.0, 55.2, 83.7, 113.4, 136.6, 162.3. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.83.

2-(4-Butoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)[16]



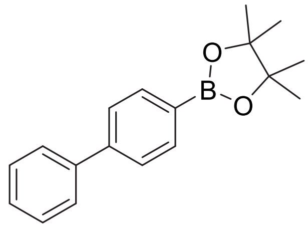
Colorless oil, yield: 68% (37.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3H), 1.33 (s, 12H), 1.46-1.52 (m, 2H), 1.74-1.79 (m, 2H), 3.99 (t, J = 6.5 Hz, 2H), 6.87-6.91 (m, 2H), 7.71-7.77 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 14.0, 19.4, 25.0, 31.4, 67. 6, 83.6, 114.0, 136.6, 161.9. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.83.

2-(4-(Benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)[15]



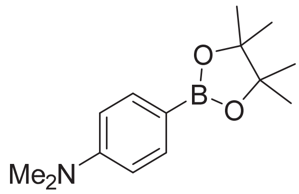
White solid, yield: 50% (31.0 mg), melting point: 85-86 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.33 (s, 12H), 5.10 (s, 2H), 6.96-6.99 (m, 2H), 7.30-7.34 (m, 1H), 7.38 (dd, J = 8.5, 6.7 Hz, 2H), 7.43 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 25.0, 69.8, 83.7, 114.3, 127.6, 128.1, 128.7, 136.7, 136.9, 161.4. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$) δ 30.80.

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)[15]



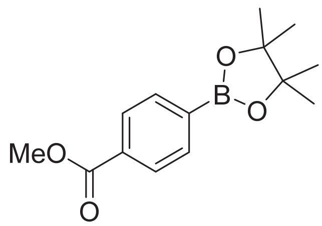
Colorless solid, yield: 87% (48.7 mg), melting point: 118-119 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 12H), 7.34-7.38 (m, 1H), 7.42-7.48 (m, 2H), 7.59-7.65 (m, 4H), 7.89 (d, J = 8.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 25.0, 84.0, 126.6, 127.4, 127.7, 128.9, 135.4, 141.2, 144.0. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$) δ 30.99.

***N,N*-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3h)**[15]



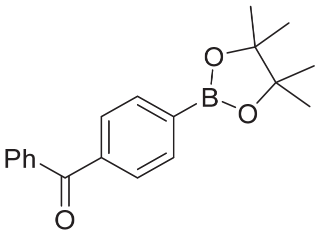
White solid, yield: 60% (29.7 mg), melting point: 114-116 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.33 (s, 12H), 2.99 (s, 6H), 6.70 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 25.0, 40.3, 83.3, 111.4, 136.3, 152.6. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$) δ 30.79.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3i)[15]



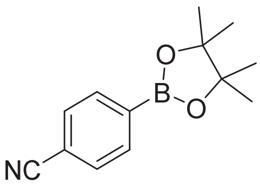
White solid, yield: 64% (33.6 mg), melting point: 79-81 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 12H), 3.90 (s, 3H), 7.86 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 25.0, 52.2, 84.3, 128.7, 132.4, 134.8, 167.2. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$) δ 30.70.

Phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (3j)[14]



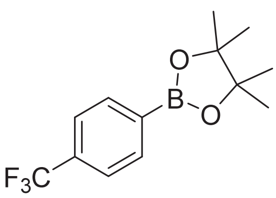
White solid, yield: 71% (43.8 mg), melting point: 110-111 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 12H), 7.48 (dd, J = 8.1, 7.3 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.76-7.81 (m, 4H), 7.90-7.93 (m, 2H) $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 25.0, 84.3, 128.4, 129.2, 130.3, 132.7, 134.7, 137.6, 139.9, 197.1. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$) δ 30.66.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (3k)[15]



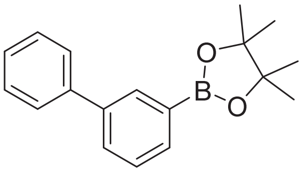
White solid, yield: 45% (20.6 mg), melting point: 100-101 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 1.35 (s, 12H), 7.64 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 24.8, 84.4, 114.5, 118.8, 131.1, 135.1. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$) δ 30.42.

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3l)[14]



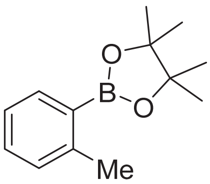
Colorless solid, yield: 56% (30.5 mg), melting point: 76-77 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 1.36 (s, 12H), 7.61 (d, J = 7.4 Hz, 2H), 7.92 (d, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 25.0, 84.4, 124.3 (q, J = 271.8 Hz), 124.5 (d, J = 3.7 Hz), 133.0 (q, J = 32.2 Hz), 135.2. (The signal for the carbon that is attached to the boron atom was not observed); $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$) δ 30.56.

2-([1,1'-Biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)[14]



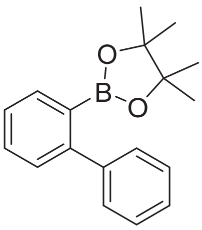
Colorless solid, yield: 60% (33.6 mg), melting point: 84-85 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 12H), 7.33-7.36 (m, 1H), 7.43-7.48 (m, 3H), 7.63-7.66 (m, 2H), 7.70-7.72 (m, 1H), 7.81-7.82 (m, 1H), 8.07 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.0, 84.0, 127.3, 127.4, 128.3, 128.8, 130.1, 133.7, 133.8, 140.7, 141.3. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 31.00.

4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (3n)[15]



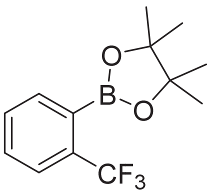
Colorless oil, yield: 38% (16.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.36 (s, 12H), 2.55 (s, 3H), 7.15-7.19 (m, 2H), 7.33 (td, J = 7.5, 1.5 Hz, 1H), 7.78 (dd, J = 7.5, 1.5 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 22.3, 25.0, 83.4, 124.8, 129.9, 130.9, 136.0, 144.9. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 31.33.

2-([1,1'-Biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)[14]



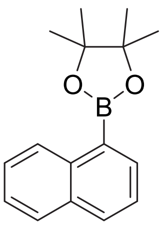
Colorless solid, yield: 78% (43.7 mg), melting point: 81-82 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.22 (s, 12H), 7.32-7.42 (m, 7H), 7.44-7.47 (m, 1H), 7.71-7.74 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 24.7, 83.9, 126.4, 127.0, 127.9, 129.1, 129.3, 130.2, 134.6, 143.4, 147.6. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 31.73.

4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3p)[15]



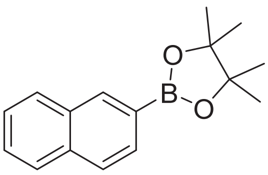
Colorless oil, yield: 49% (26.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 12H), 7.48-7.52 (m, 2H), 7.65-7.67 (m, 1H), 7.71-7.74 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 24.8, 84.6, 124.6 (q, J = 271.8), 125.4 (d, J = 5.0 Hz), 130.1, 130.8, 133.9 (q, J = 31.4 Hz), 134.8. (The signal for the carbon that is attached to the boron atom was not observed); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -59.70; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 31.17.

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (3q)[14]



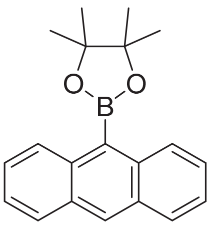
White solid, yield: 82% (41.7 mg), melting point: 54-55 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.43 (s, 12H), 7.46-7.48 (m, 2H), 7.53-7.55 (m, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.82-7.85 (m, 1H), 8.08 (d, J = 6.8 Hz, 1H), 8.75-8.79 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.1, 83.9, 125.1, 125.6, 126.5, 128.46, 128.54, 131.7, 133.3, 135.8, 137.1. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 31.52.

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (3r)[15]



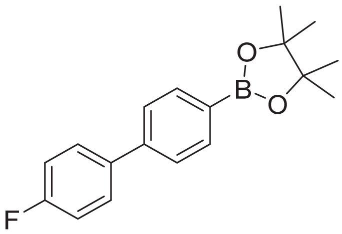
White solid, yield: 68% (34.6 mg), melting point: 62-63 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.40 (s, 12H), 7.47-7.53 (m, 2H), 7.83-7.87 (m, 3H), 7.89-7.91 (m, 1H), 8.39 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.1, 84.1, 125.9, 127.09, 127.10, 127.8, 128.8, 130.5, 132.9, 135.1, 136.4. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 31.14.

2-(Anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)[17]



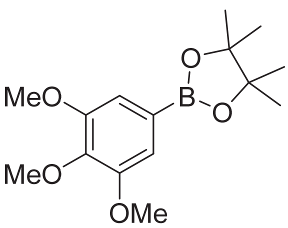
Yellow solid, yield: 55% (33.5 mg), melting point: 134-135 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.59 (s, 12H), 7.45 (dd, J = 7.8, 6.5 Hz, 2H), 7.49 (dd, J = 8.7, 6.5 Hz, 2H), 8.00 (dd, J = 8.4, 1.5 Hz, 2H), 8.44-8.49 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.3, 84.5, 125.0, 125.9, 128.4, 128.9, 129.6, 131.3, 136.0. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 32.96.

2-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)[18]



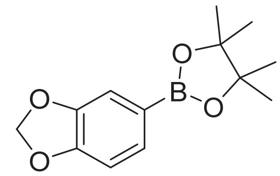
White solid, yield: 71% (42.5 mg), melting point: 115-116 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (s, 12H), 7.11-7.15 (m, 2H), 7.55-7.59 (m, 4H), 7.87-7.90 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.0, 84.0, 115.8 (d, J = 21.4 Hz), 126.4, 128.9 (d, J = 8.1 Hz), 135.4, 137.2 (d, J = 3.3 Hz), 143.0, 162.8 (d, J = 246.8 Hz). (The signal for the carbon that is attached to the boron atom was not observed); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -115.31; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.85.

4,4,5,5-Tetramethyl-2-(3,4,5-trimethoxyphenyl)-1,3,2-dioxaborolane (3u)[19]



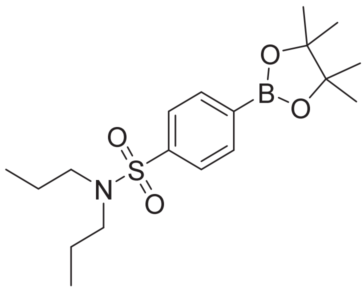
Colorless solid, yield: 50% (29.4 mg), melting point: 105-106 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (s, 12H), 3.87 (s, 3H), 3.90 (s, 6H), 7.03 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.0, 56.3, 60.9, 84.0, 111.4, 140.9, 153.0. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.64.

2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3v)[14]



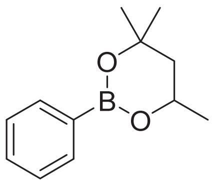
Colorless oil, yield: 75% (37.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.33 (s, 12H), 5.95 (s, 2H), 6.83 (d, J = 7.7 Hz, 1H), 7.24 (d, J = 1.1 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 25.0, 83.8, 100.9, 108.4, 114.1, 129.8, 147.3, 150.3. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.57.

***N,N*-Dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (3w)**[15]



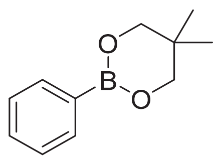
White solid, yield: 74% (54.4 mg), melting point: 149-150 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.85 (t, J = 7.4 Hz, 6H), 1.35 (s, 12H), 1.48-1.57 (m, 4H), 3.02-3.09 (m, 4H), 7.78 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 11.3, 22.1, 25.0, 50.1, 84.5, 126.1, 135.3, 142.5. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 30.43.

4,4,6-Trimethyl-2-phenyl-1,3,2-dioxaborinane (4b)[20]



Colorless oil, yield: 54% (22.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.40-1.45 (m, 9H), 1.64 (dd, J = 13.8, 11.5 Hz, 1H), 1.90 (dd, J = 13.8, 3.0 Hz, 1H), 4.39 (ddq, J = 12.3, 6.2, 3.1 Hz, 1H), 7.38-7.42 (m, 2H), 7.44-7.48 (m, 1H), 7.90 (dd, J = 8.1, 1.5 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 23.3, 28.3, 31.4, 46.1, 65.0, 71.0, 127.5, 130.4, 133.9. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 26.80.

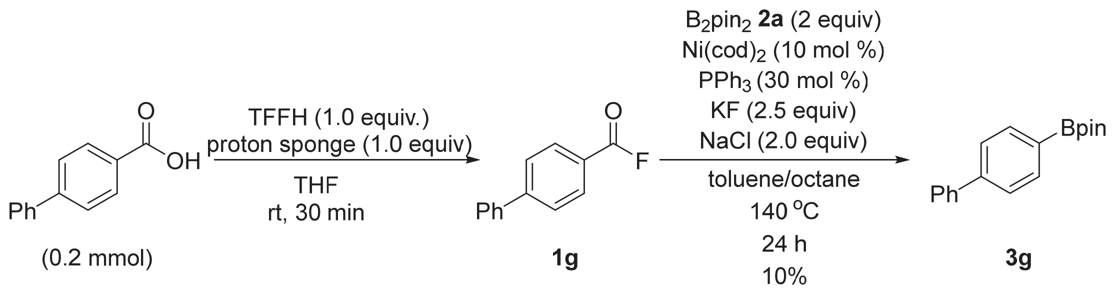
5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (4c)[21]



Colorless oil, yield: 55% (20.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.03 (s, 6H), 3.78 (s, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.41-7.46 (m, 1H), 7.82 (d, J = 7.9 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 22.1, 32.0, 72.5, 127.7, 130.8, 134.0. (The signal for the carbon that is attached to the boron atom was not observed); ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ 26.84.

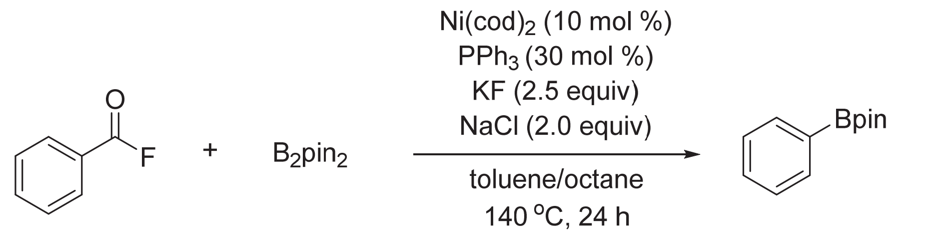
One-pot Synthesis from Carboxylic Acid without Isolation of Aroyl Fluorides.

To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added [1,1'-biphenyl]-4-carboxylic acid (39.6 mg, 0.2 mmol) and TFFH (52.8 mg, 0.2 mmol, 1.0 equiv), proton sponge (42.9 mg, 0.2 mmol, 1.0 equiv), and THF (0.4 mL). After the reaction mixture was stirred at room temperature for 15 to 30 min, a pre-mixed solution of $Ni(cod)_2$ (5.5 mg, 0.02 mmol, 10 mol %), PPh_3 (15.7 mg, 0.06 mmol, 30 mol %) in toluene (0.66 mL) and octane (0.33 mL) was added. Then, KF (30.6 mg, 0.5 mmol, 2.5 equiv), bis(pinacolato)diboron (**2a**) (101.6 mg, 0.6 mmol, 2.0 equiv), and NaCl (23.4 mg, 0.6 mmol, 2.0 equiv) were added. The mixture was heated at 140 ºC with stirring for 24 h. After the reaction, *n*-dodecane was added as an internal standard and stirring the mixture vigorously. Take a portion of the mixture, diluted by Et_2O (2 mL), GC analysis was measured to evident the formation of **3g** in 10%.



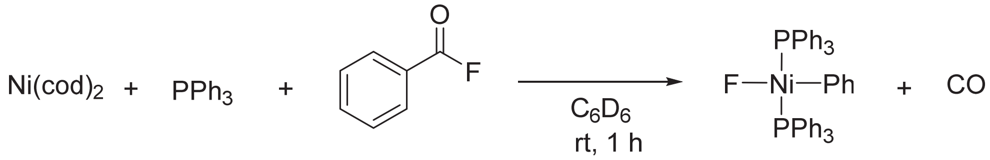
Gram-scale Experiment

An oven-dried two necked flask (100 mL) containing a stirring bar was charged with $Ni(cod)_2$ (275 mg, 1.0 mmol, 10 mol %), PPh_3 (785 mg, 3.0 mmol, 30 mol %), toluene (33 mL), octane (16.5 mL) and stirring for 1 min at room temperature. Then, benzoyl fluoride (**1a**) (10 mmol, 1.07 mL), KF (1.53 g, 25 mmol, 2.5 equiv), bis(pinacolato)diboron (**2a**) (5.08 g, 20 mmol, 2.0 equiv), and NaCl (1.17 g, 20 mmol, 2.0 equiv) were added. The mixture was heated at 140 ºC with stirring for 24 h. After cooling to room temperature, to the mixture were added saturated aqueous ammonium chloride (ca. 50 mL) and extracted with EtOAc (ca. 50 mL × 3), successively. The combined organic extracts were dried over Na_2SO_4, and then filtrated. The filtrate was concentrated under reduced pressure to give the residue, which was purified by column chromatography on silica gel to afford **3a** (1.19 g, 58%).

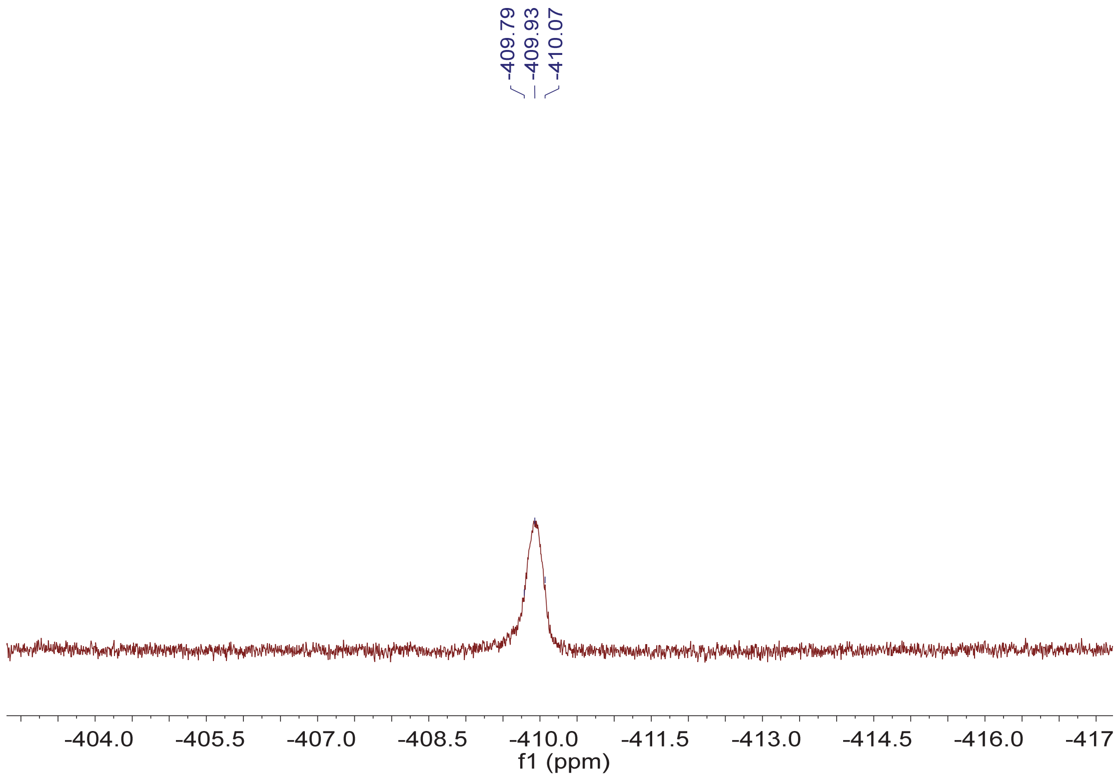


1a (10 mmol) **2a** (2 equiv) **3a,** 58% (1.19 g)

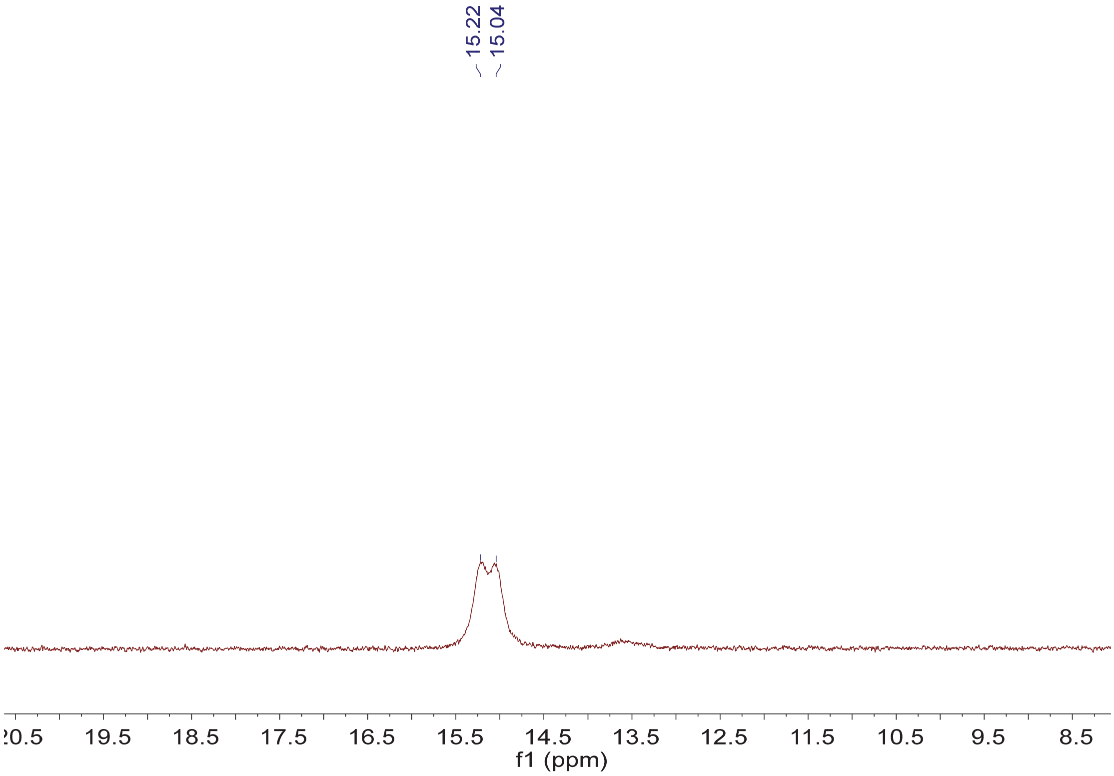
5. Elucidation of the Isolation of Oxidative Adduct



An oven dried Schlenk tube containing a stirring bar was charged with $Ni(cod)_2$ (13.7 mg, 0.03 mmol,), PPh_3 (26.2 mg, 0.1 mmol), C_6D_6 (0.66 mL) and stirring for 30 seconds at room temperature. The resulting dark red solution was transferred to an NMR tube. Then, benzoyl fluoride (660 μL, 0.03 mmol) was added, the solution rapidly changed from a dark red to a bright orange. After 5 min, the $^{19}F\{^1H\}$ NMR was measured.

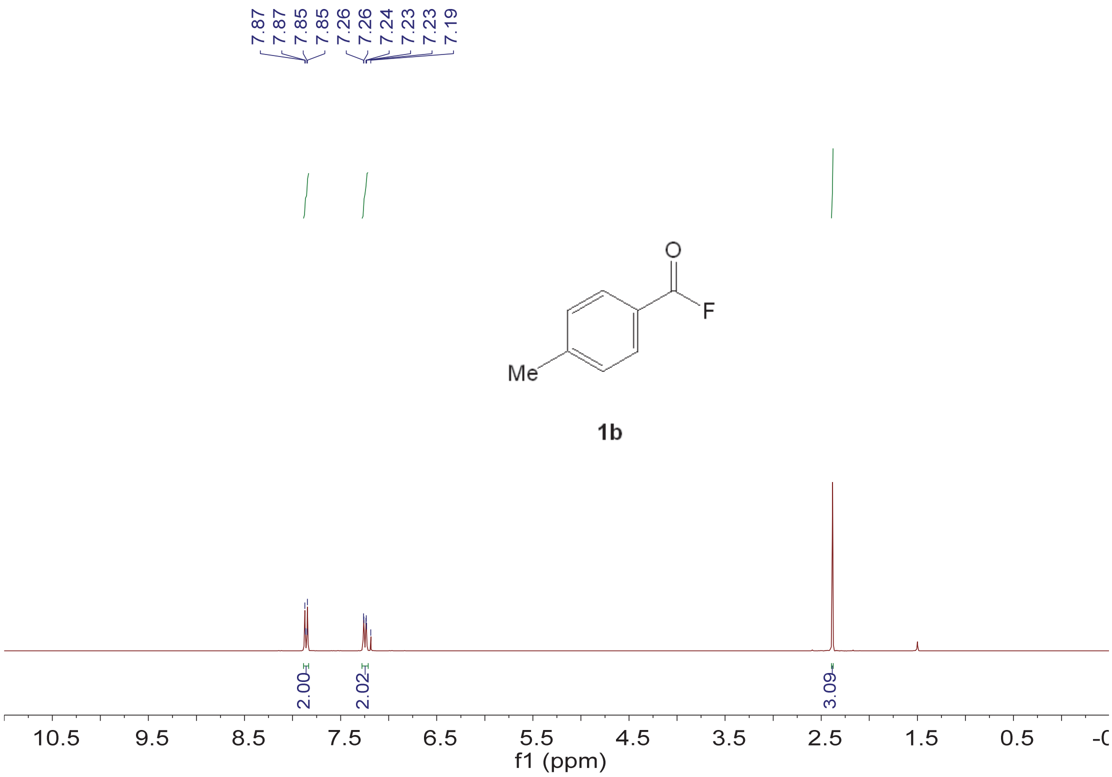


$^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6) spectrum of the reaction mixture (C_6D_6, rt, 1 h).

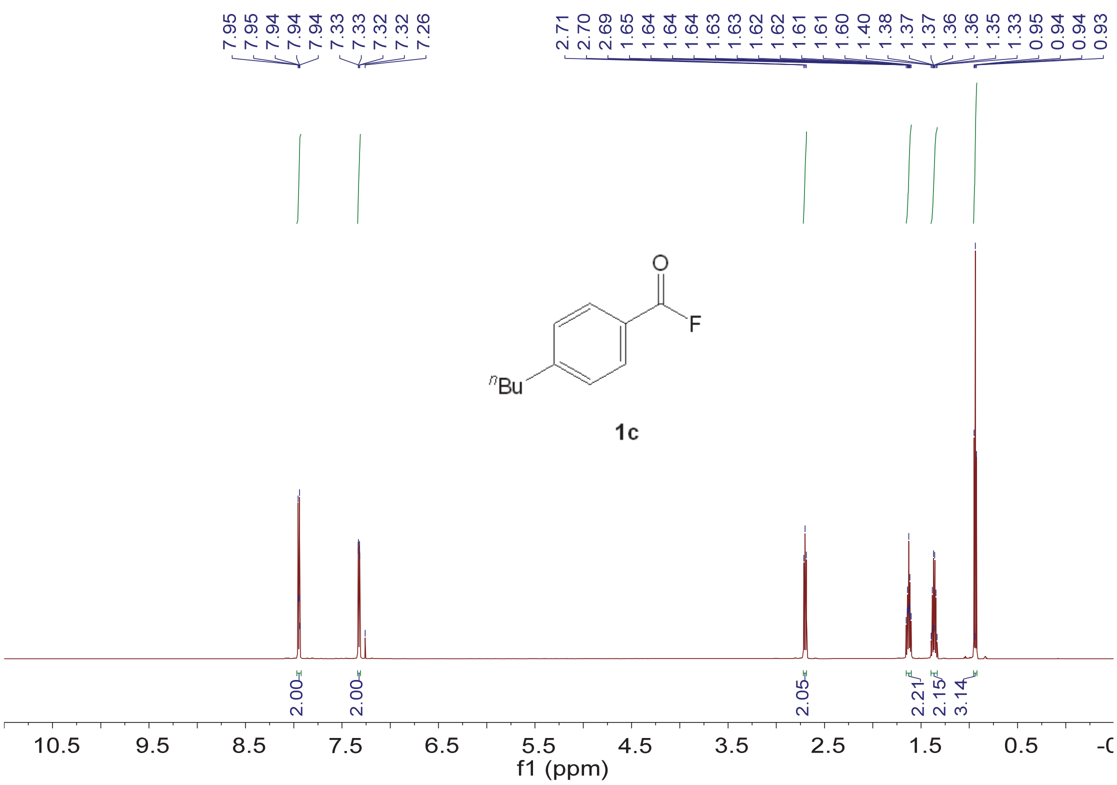


$^{31}P\{^{1}H\}$ NMR (243 MHz) spectrum of the reaction mixture (C_6D_6, rt, 1 h).

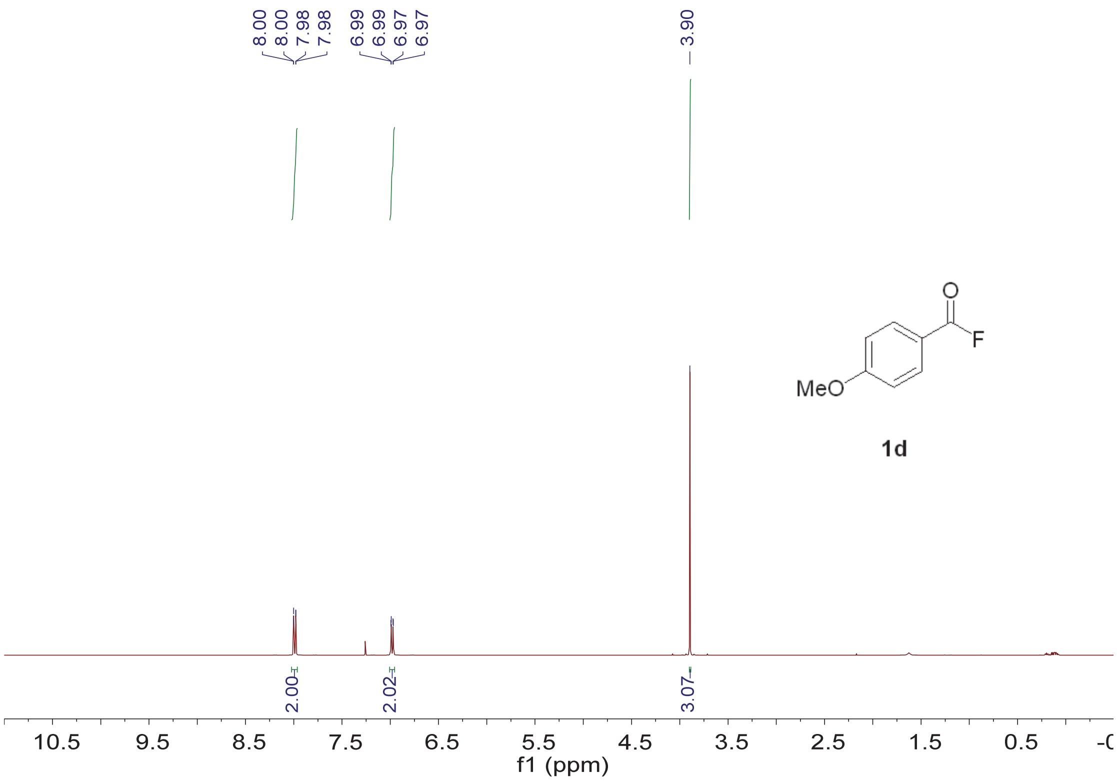
5. Copies of NMR Charts



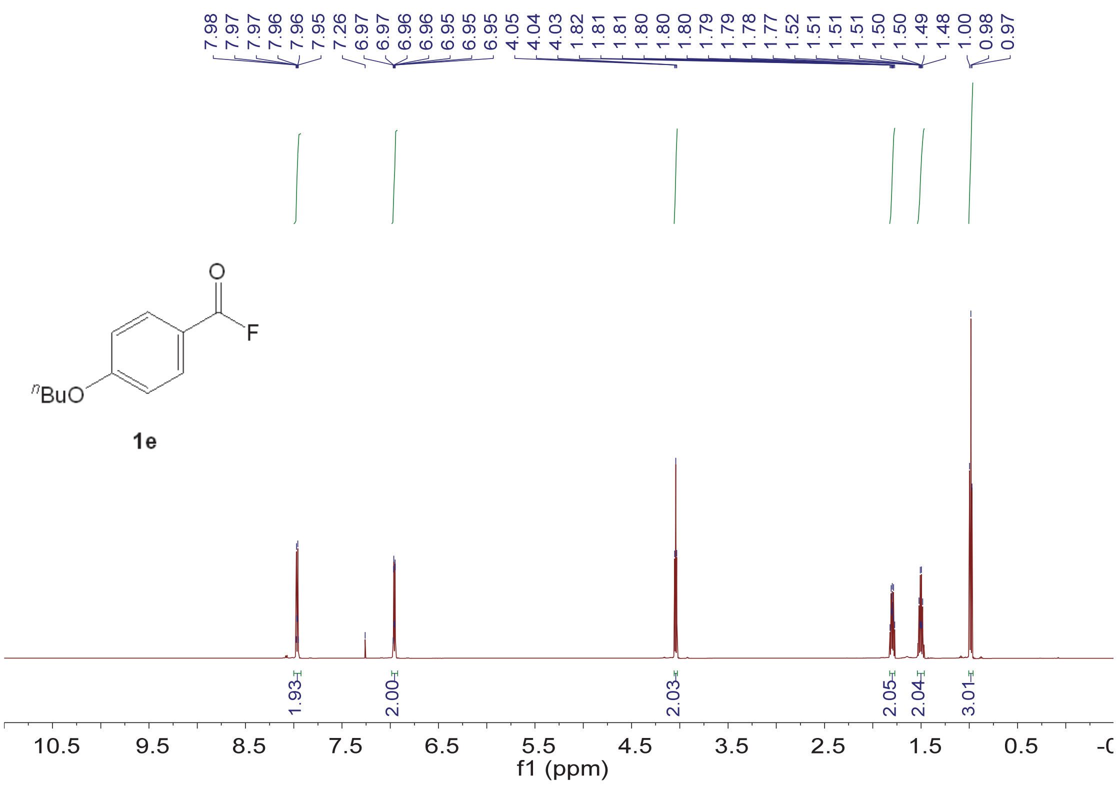
^{1}H NMR (300 MHz) spectrum of **1b** ($CDCl_3$, rt).



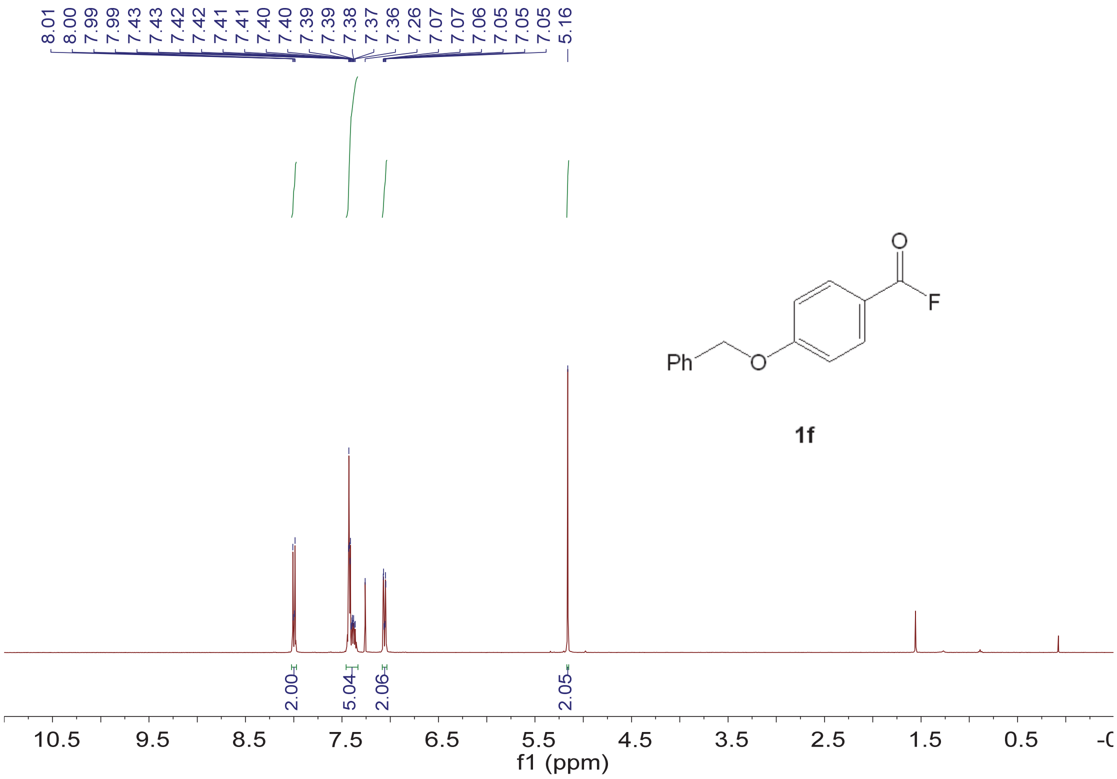
^{1}H NMR (600 MHz) spectrum of **1c** ($CDCl_3$, rt).



^{1}H NMR (400 MHz) spectrum of **1d** ($CDCl_3$, rt).



^{1}H NMR (600 MHz) spectrum of **1e** ($CDCl_3$, rt).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5.16
Ph
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5.04
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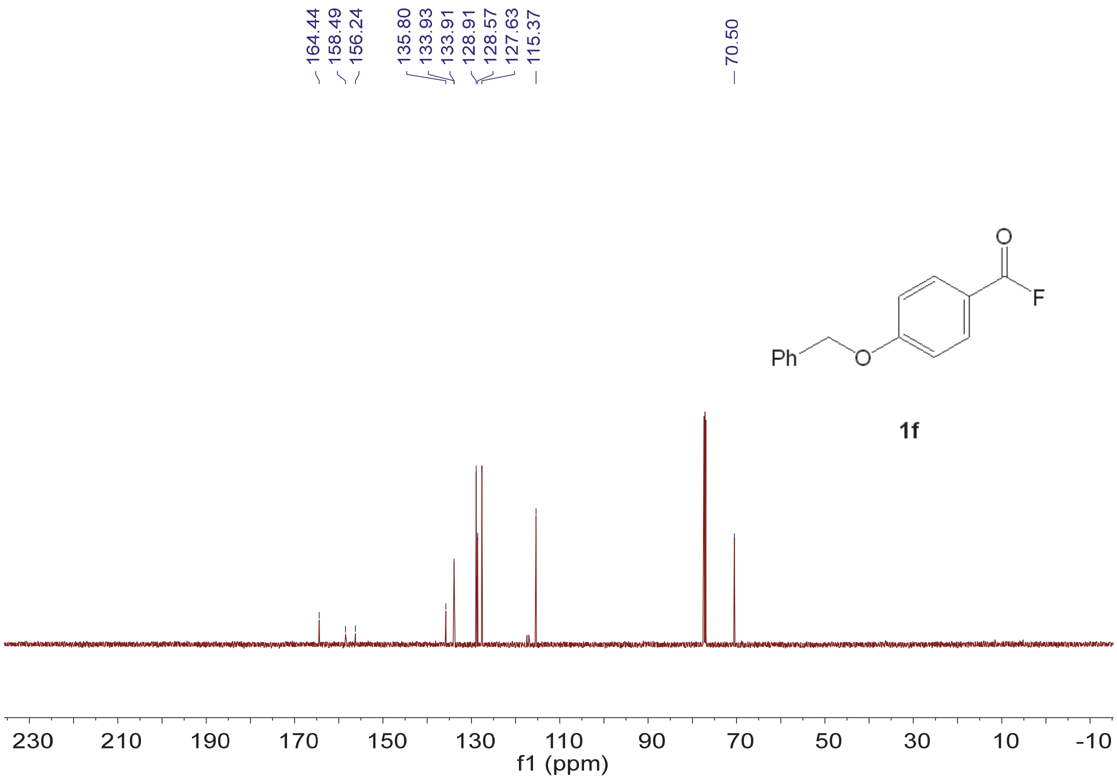
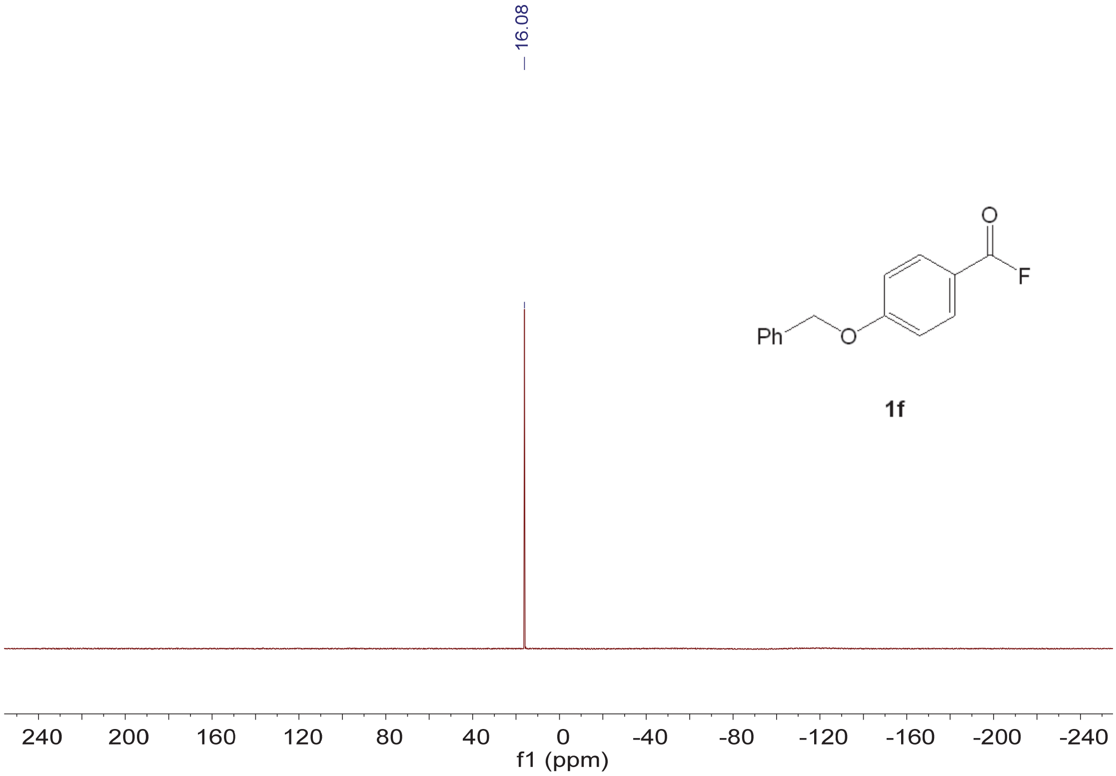
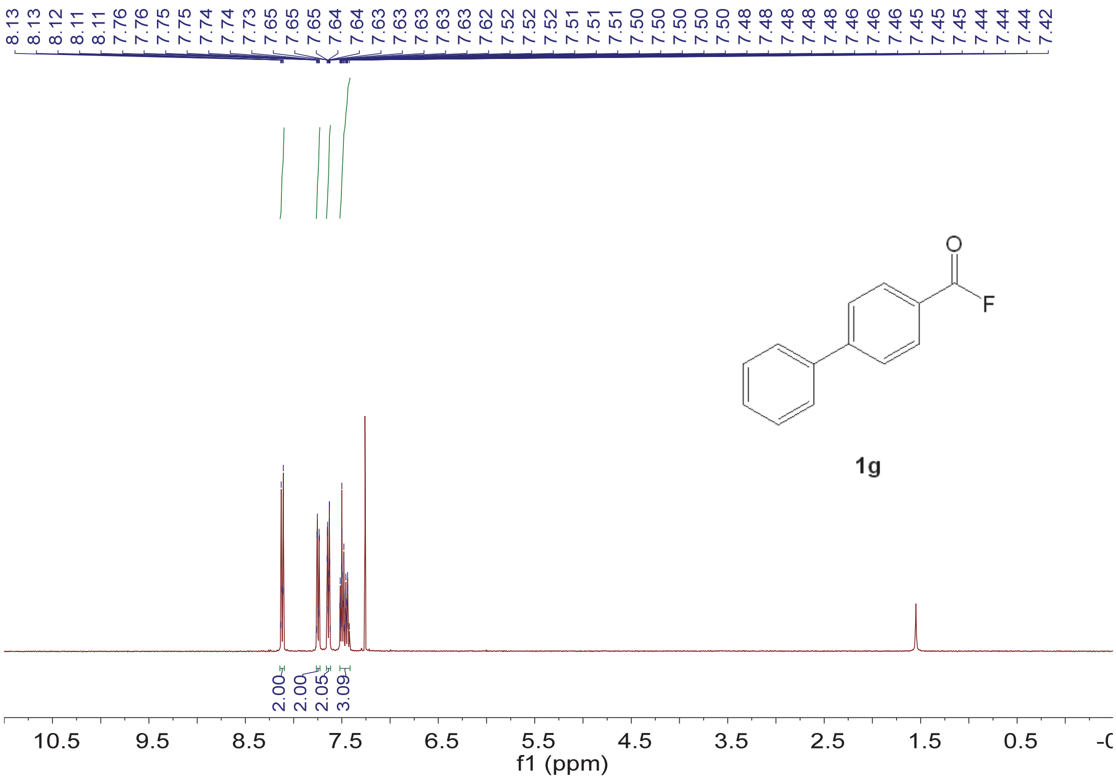
2.5
1.5
0.5
f1 (ppm)

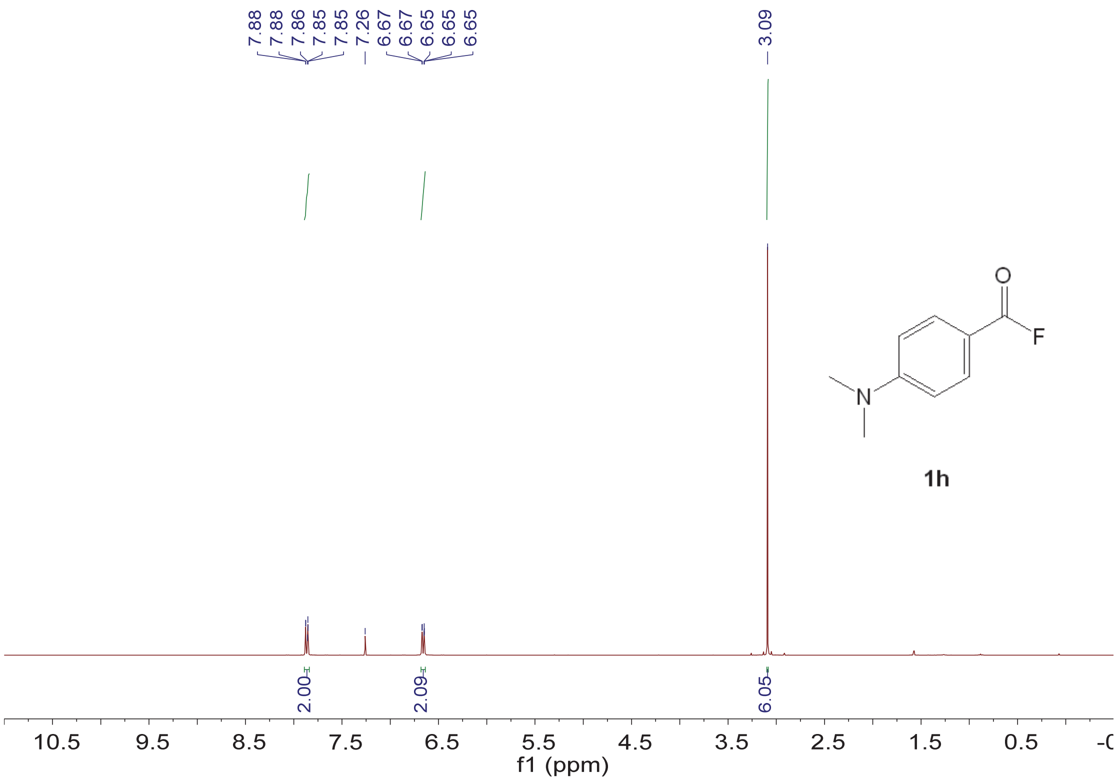

164.44
158.49
156.24
135.80
133.93
133.91
128.91
128.57
127.63
115.37
70.50
Ph
O
O
F
1f
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



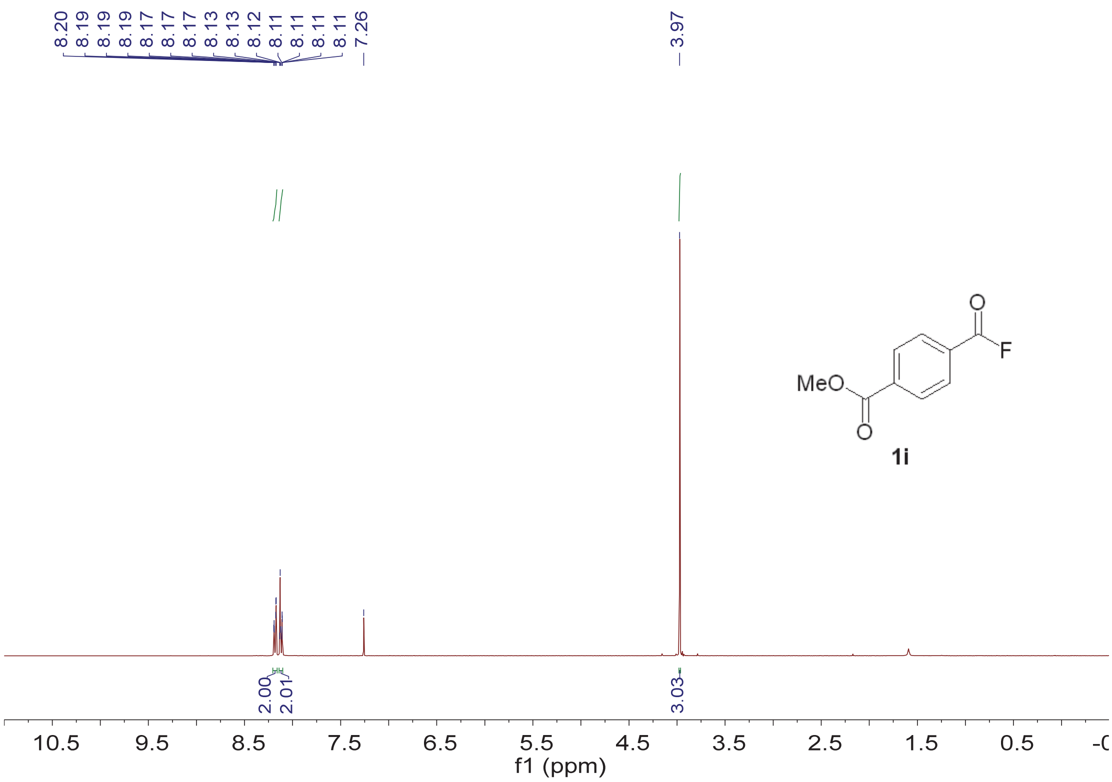
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **1f** ($CDCl_3$, rt).



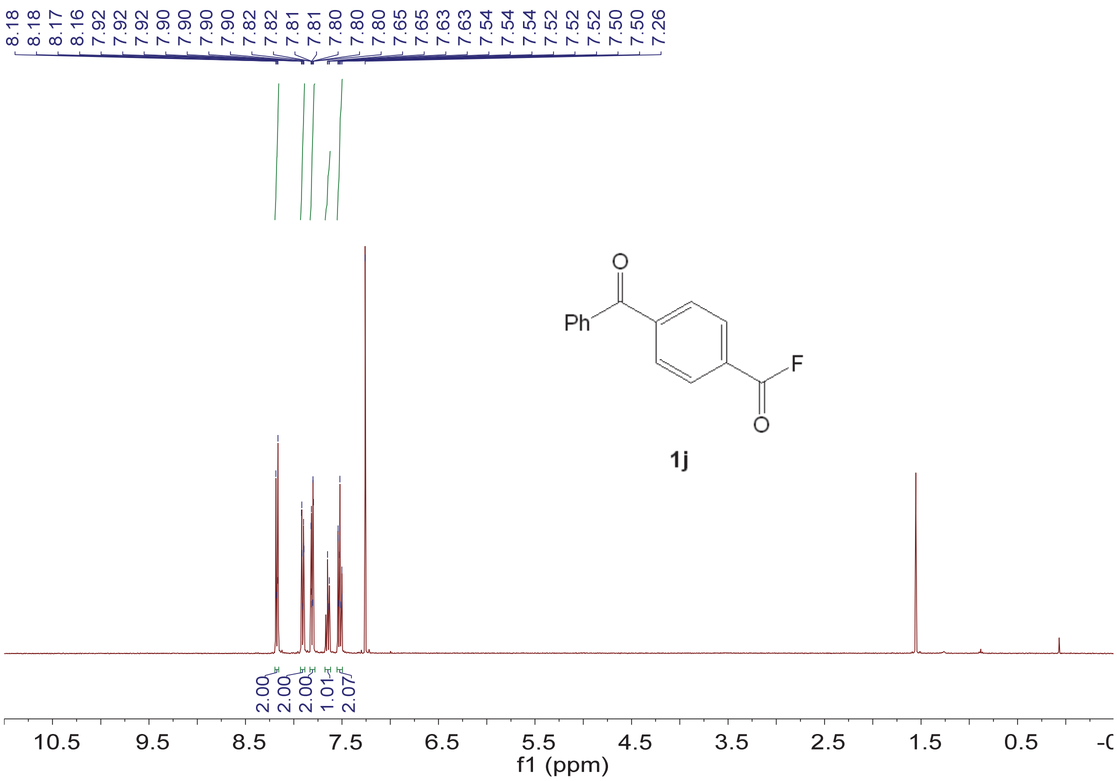
^{1}H NMR (400 MHz) spectrum of **1g** ($CDCl_3$, rt).

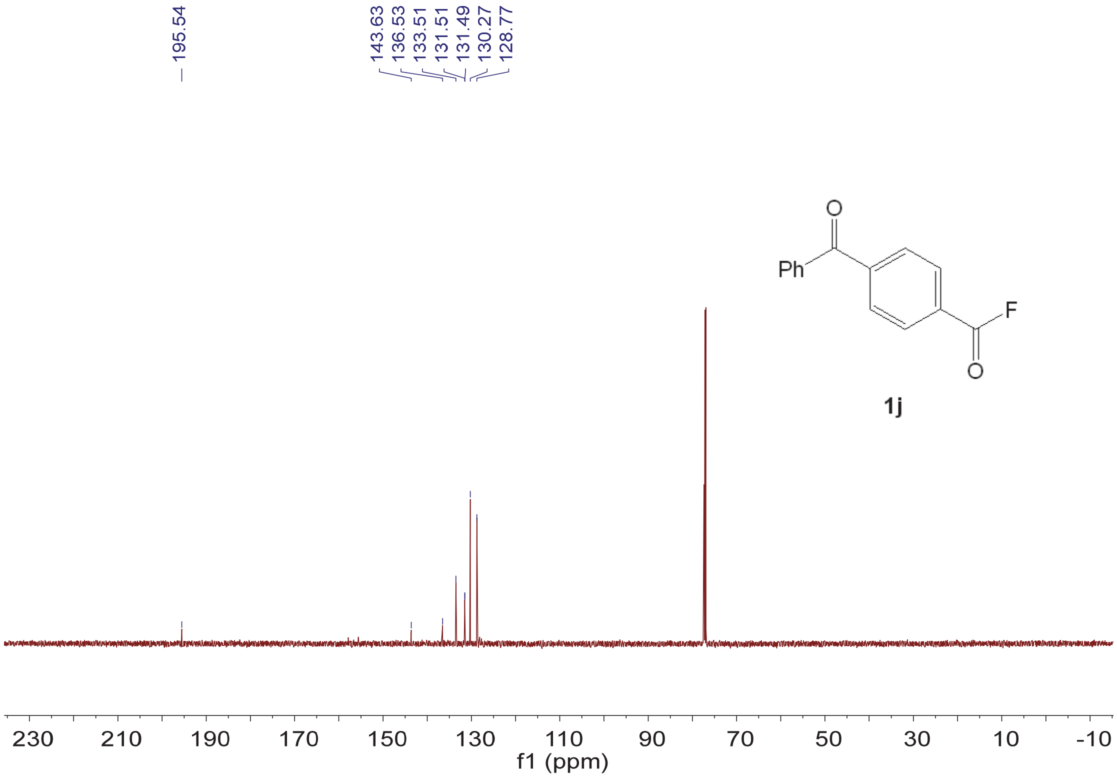


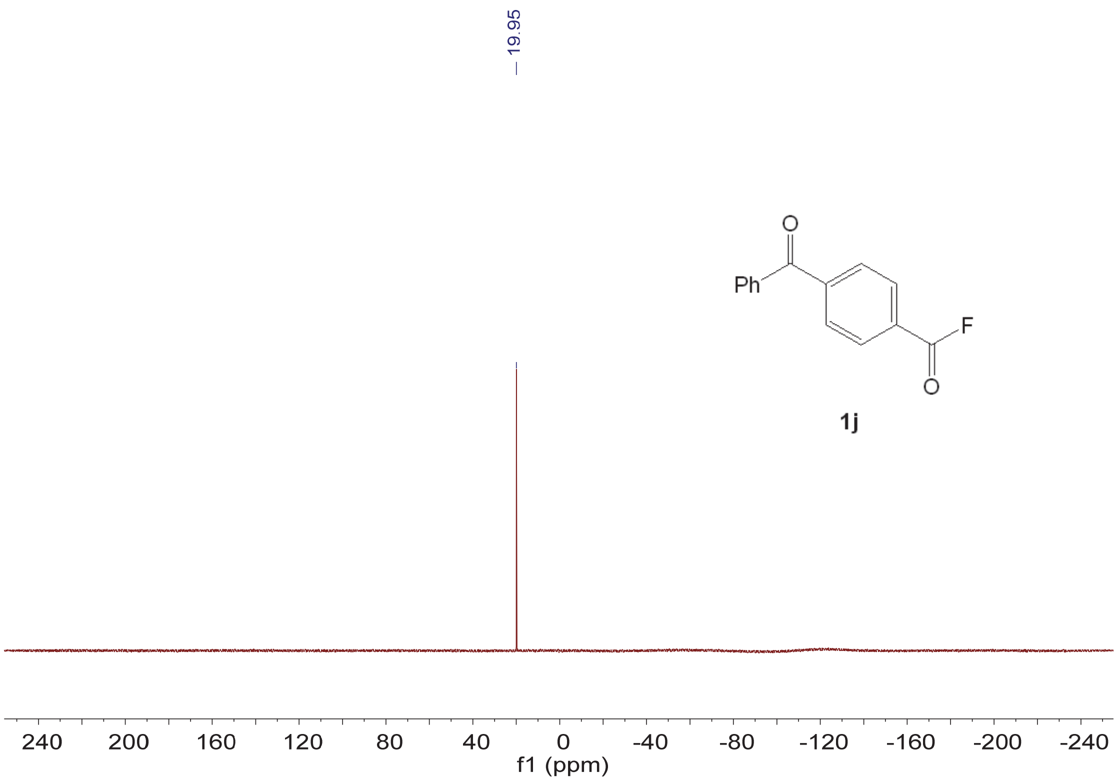
[1]H NMR (400 MHz) spectrum of **1h** ($CDCl_3$, rt).



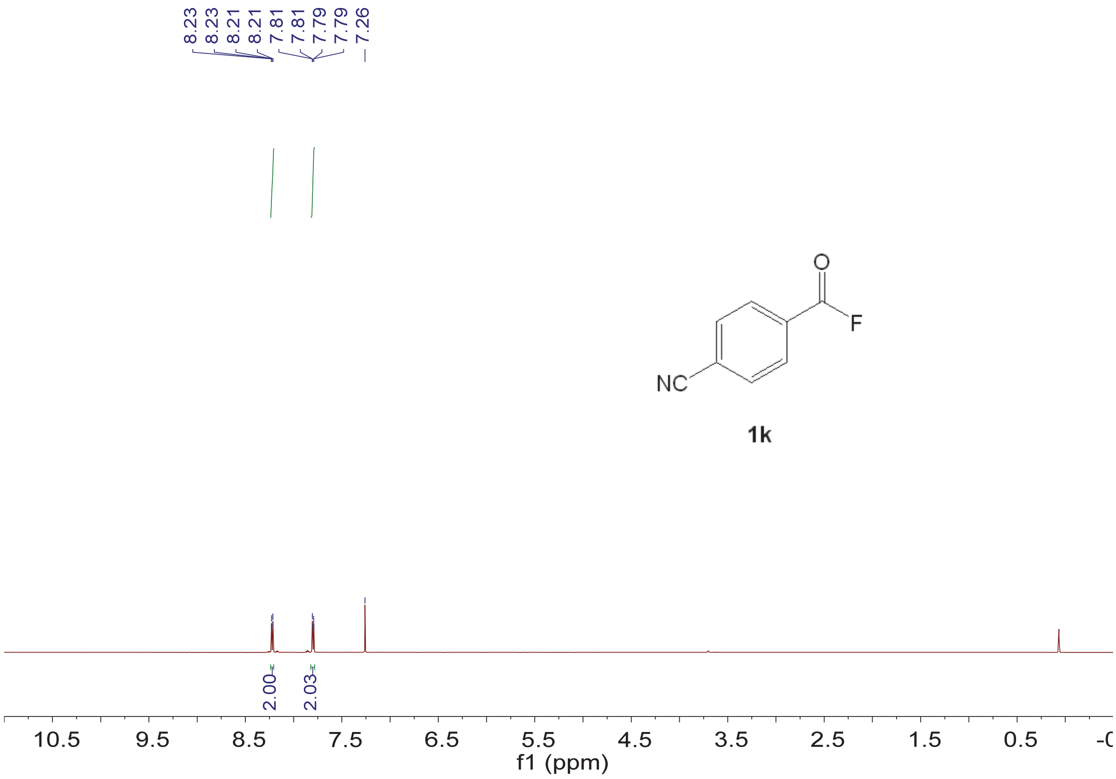
[1]H NMR (400 MHz) spectrum of **1i** ($CDCl_3$, rt).


8.18
8.18
8.17
8.16
7.92
7.92
7.92
7.90
7.90
7.90
7.90
7.82
7.82
7.81
7.81
7.80
7.80
7.65
7.65
7.63
7.63
7.54
7.54
7.54
7.52
7.52
7.52
7.50
7.50
7.26
Ph
O
F
O
1j
2.00
2.00
2.00
1.01
2.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

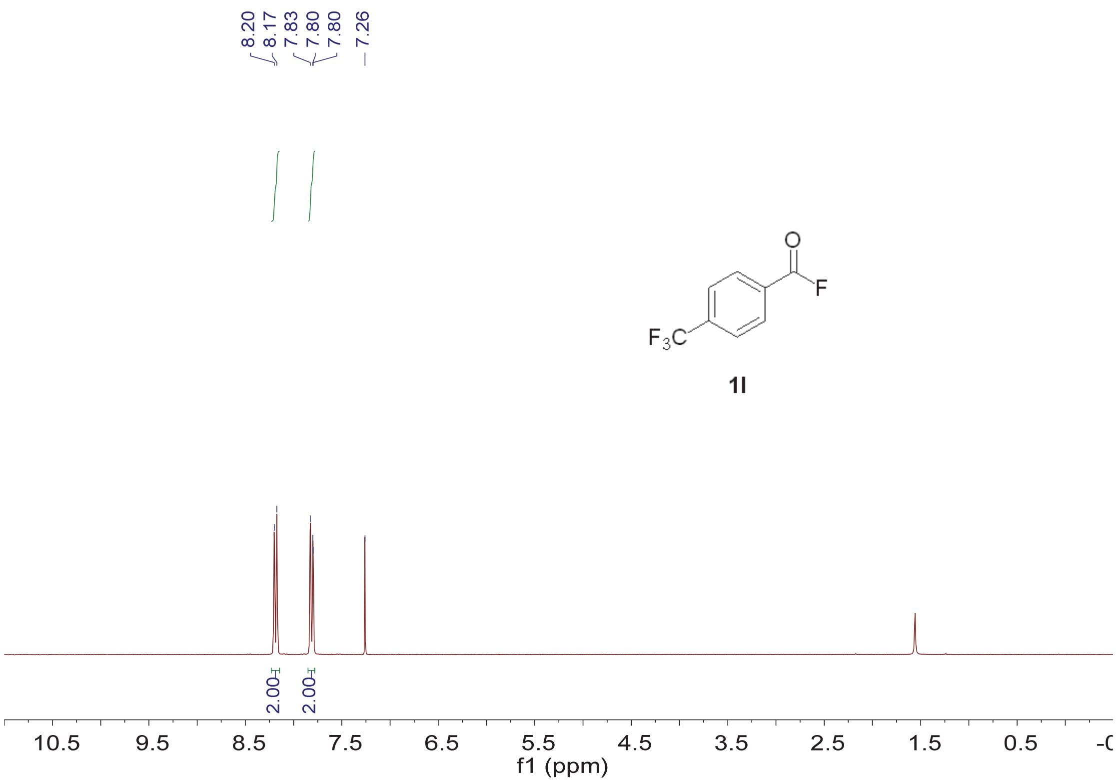

195.54
143.63
136.53
133.51
131.51
131.49
130.27
128.77
Ph
O
F
O
1j
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



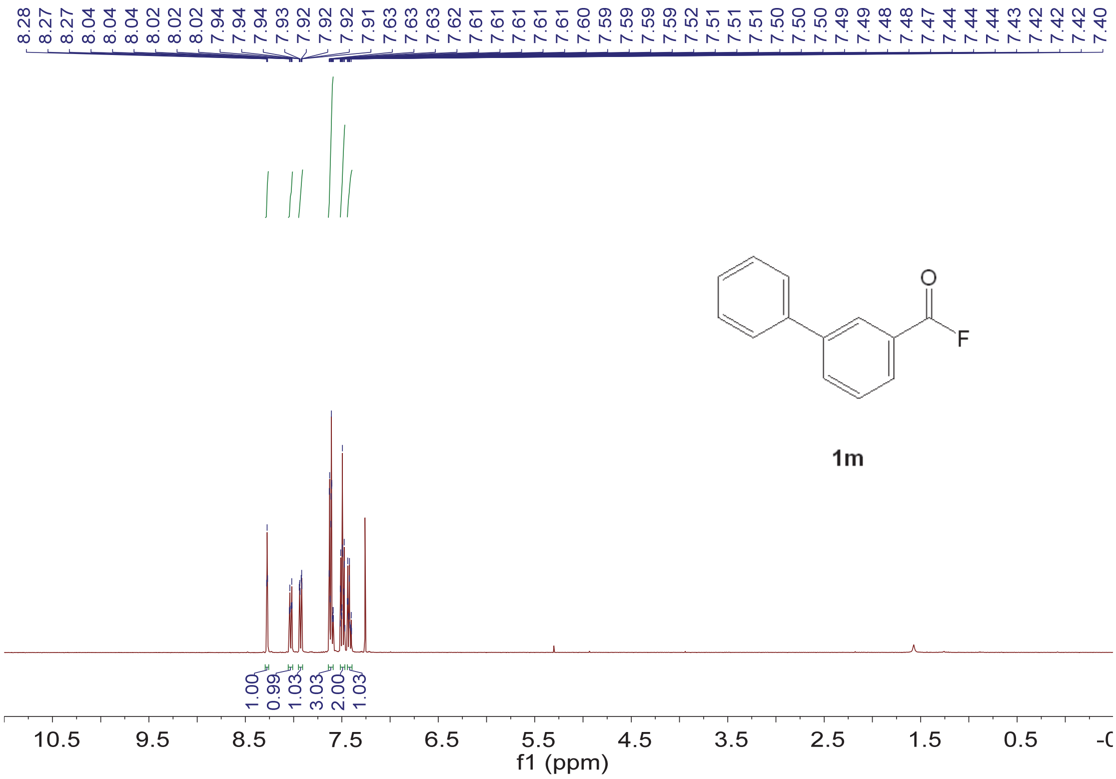
[1]H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{19}F\{^{1}H\}$ NMR (376 MHz) spectra of **1j** ($CDCl_3$, rt).



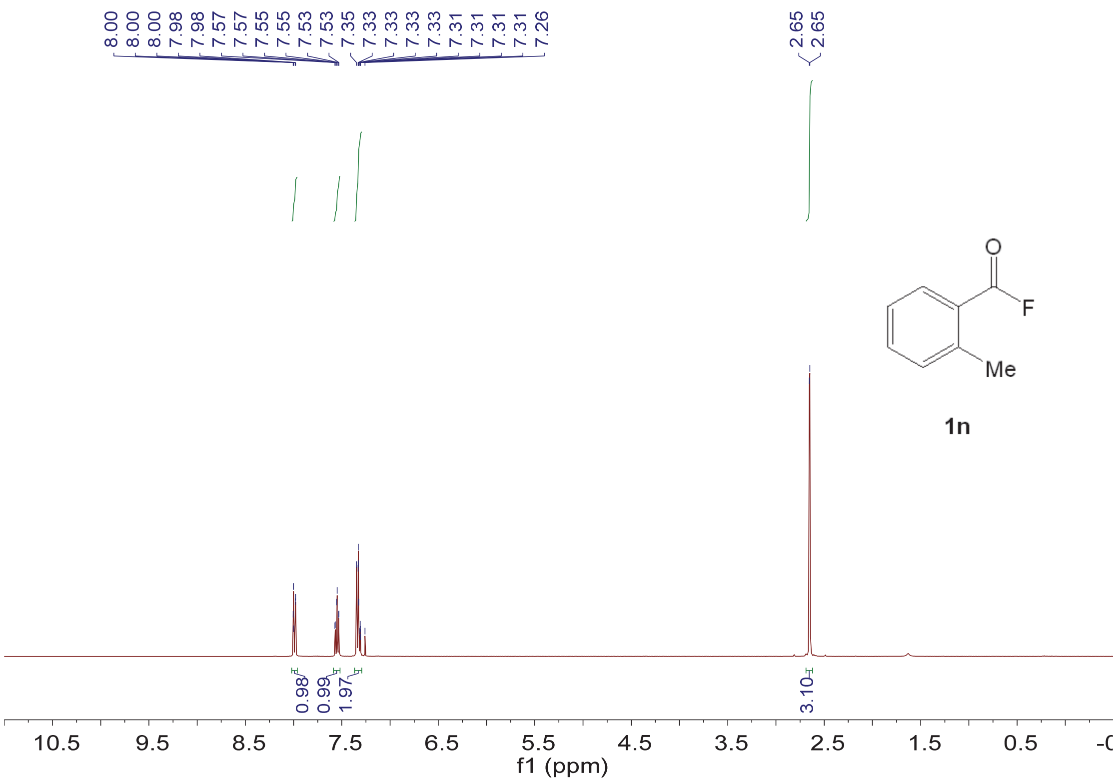
^{1}H NMR (600 MHz) spectrum of **1k** ($CDCl_3$, rt).



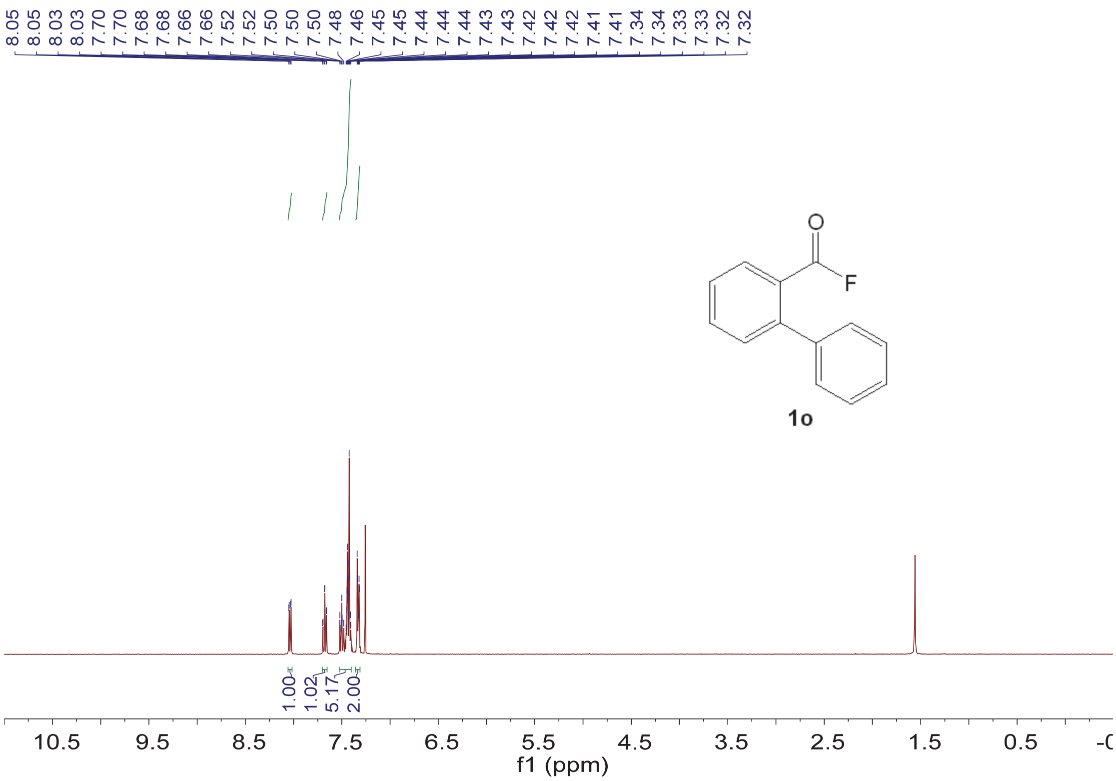
^{1}H NMR (300 MHz) spectrum of **1l** ($CDCl_3$, rt).



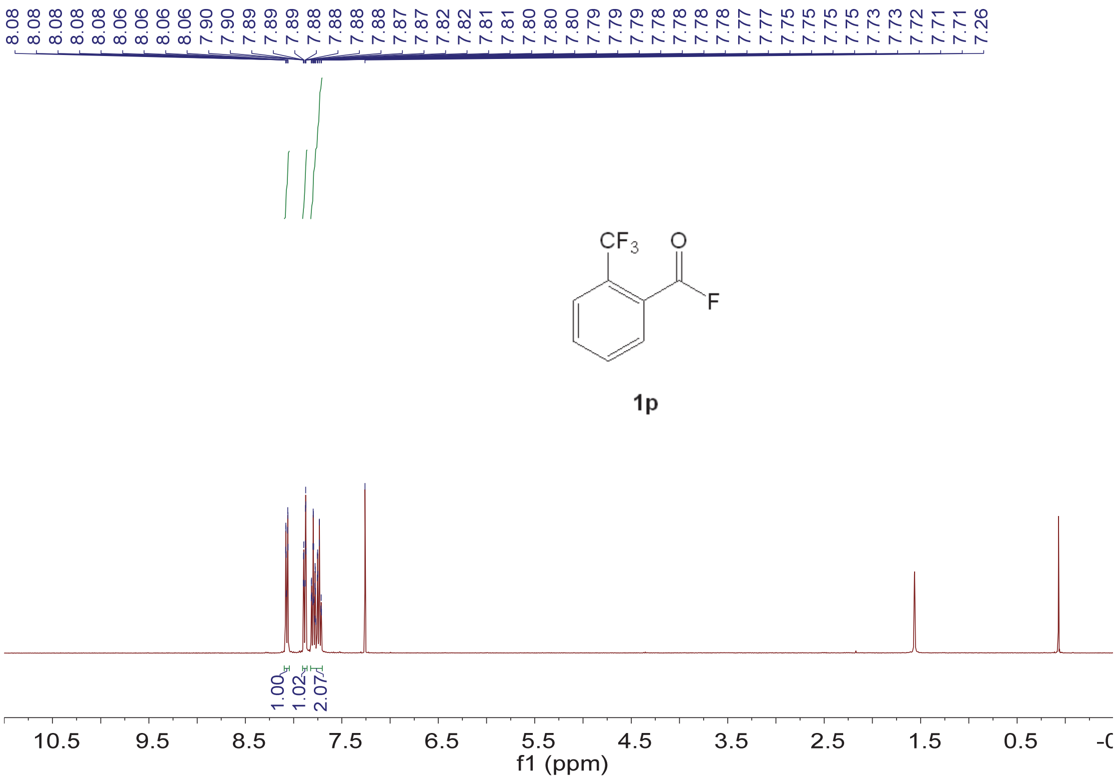
^{1}H NMR (400 MHz) spectrum of **1m** ($CDCl_3$, rt).



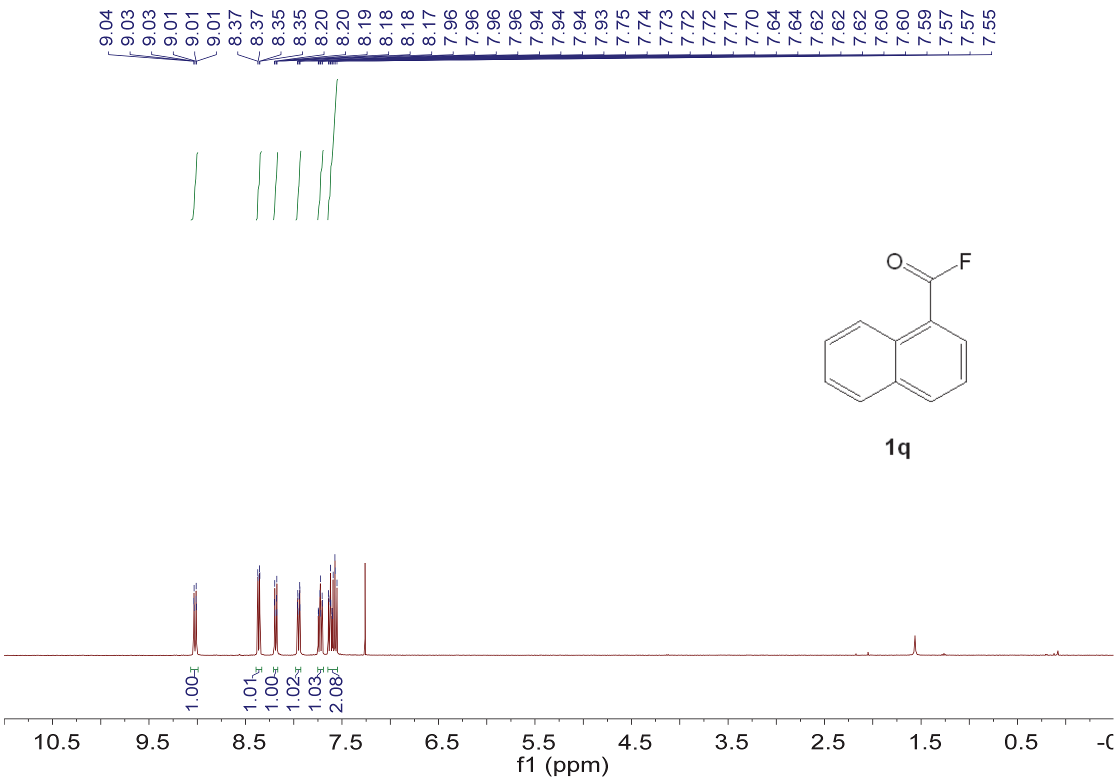
^{1}H NMR (400 MHz) spectrum of **1n** ($CDCl_3$, rt).



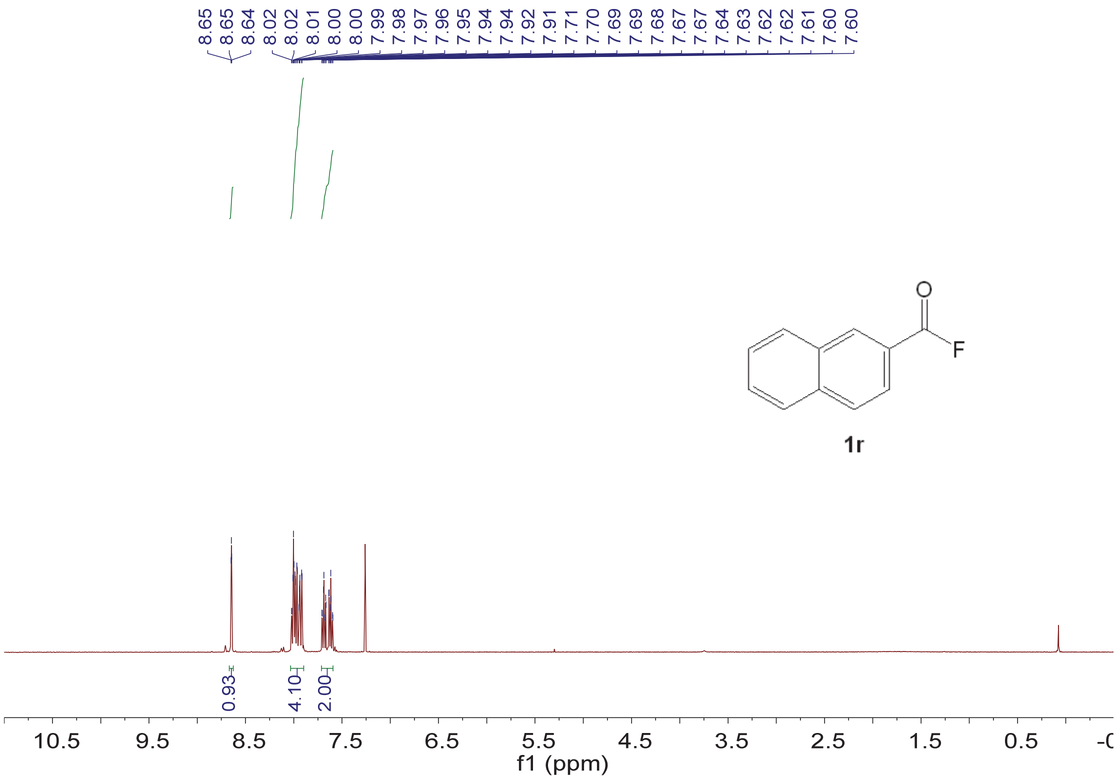
^{1}H NMR (400 MHz) spectrum of **1o** ($CDCl_3$, rt).



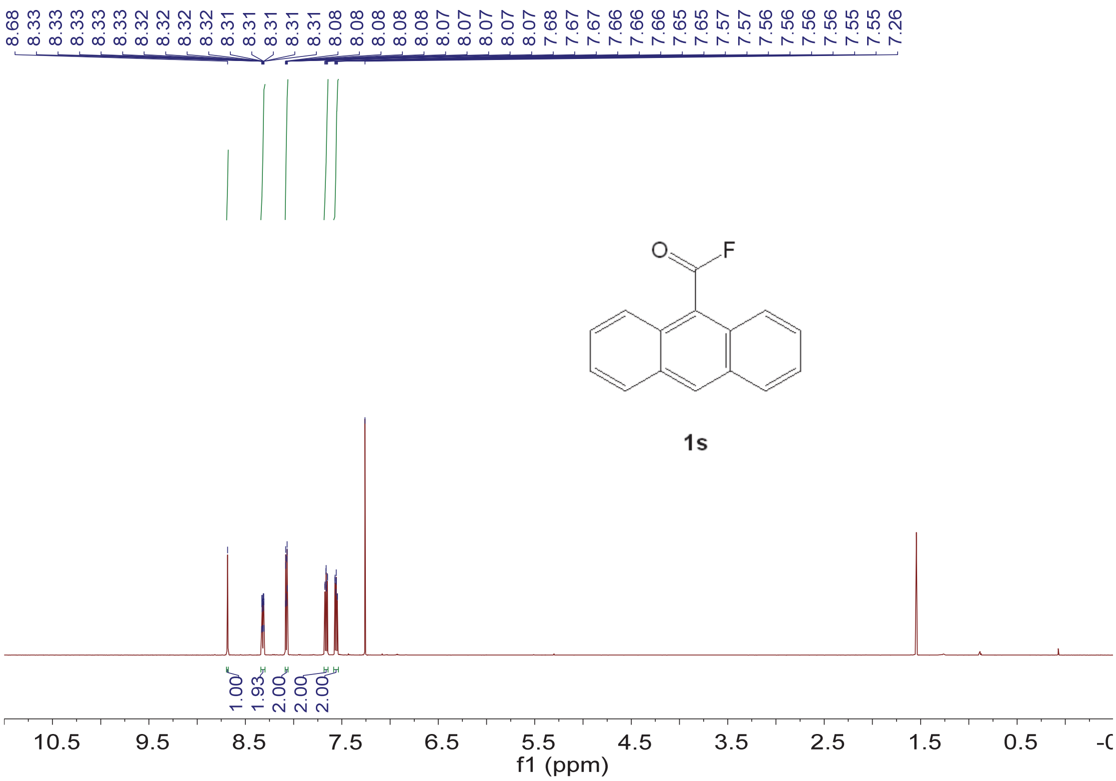
^{1}H NMR (400 MHz) spectrum of **1p** ($CDCl_3$, rt).



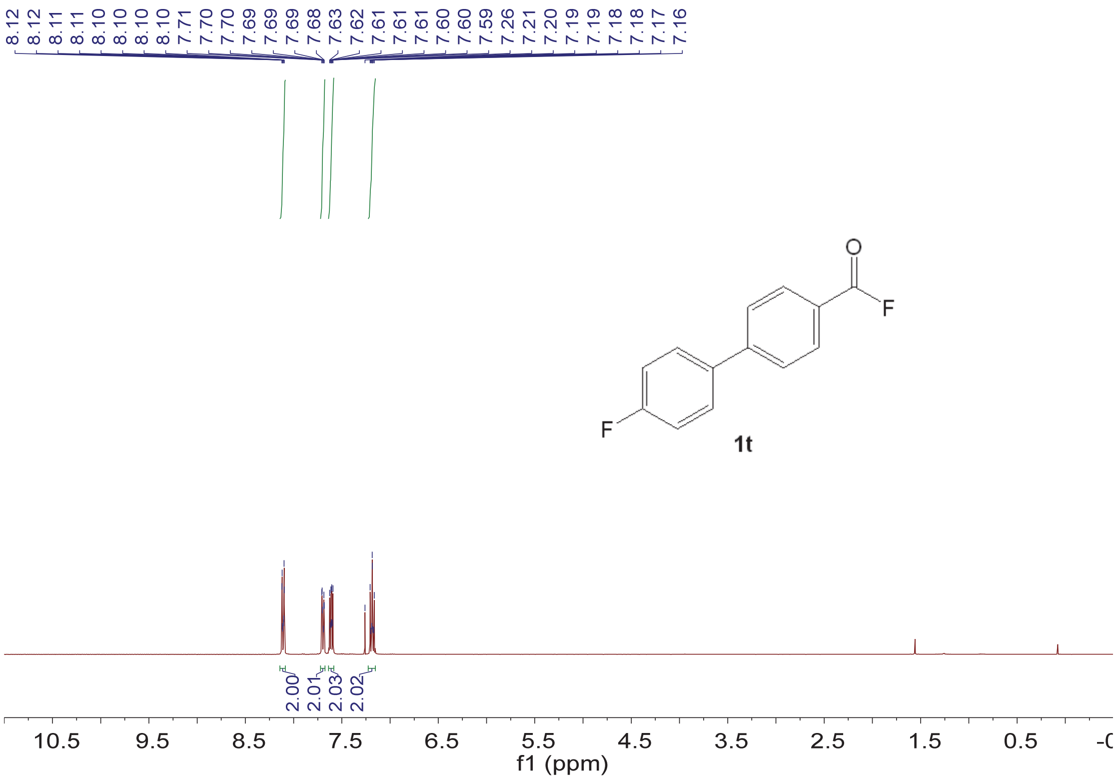
[1]H NMR (400 MHz) spectrum of **1q** ($CDCl_3$, rt).



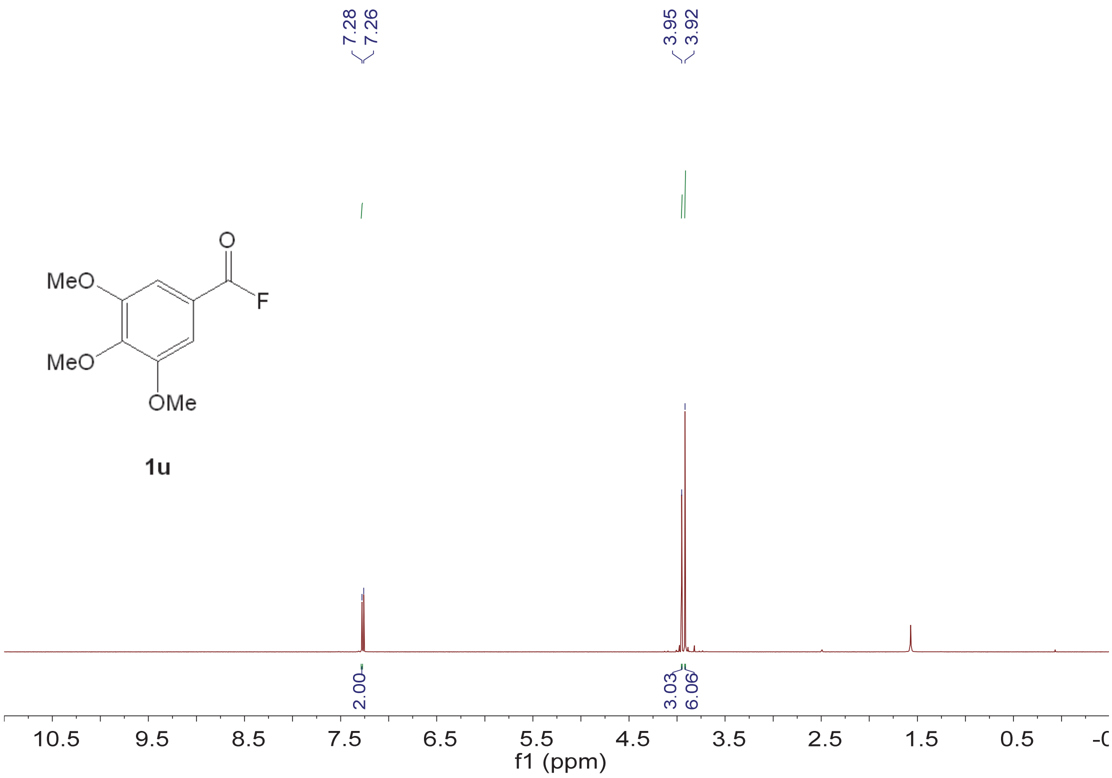
[1]H NMR (400 MHz) spectrum of **1r** ($CDCl_3$, rt).



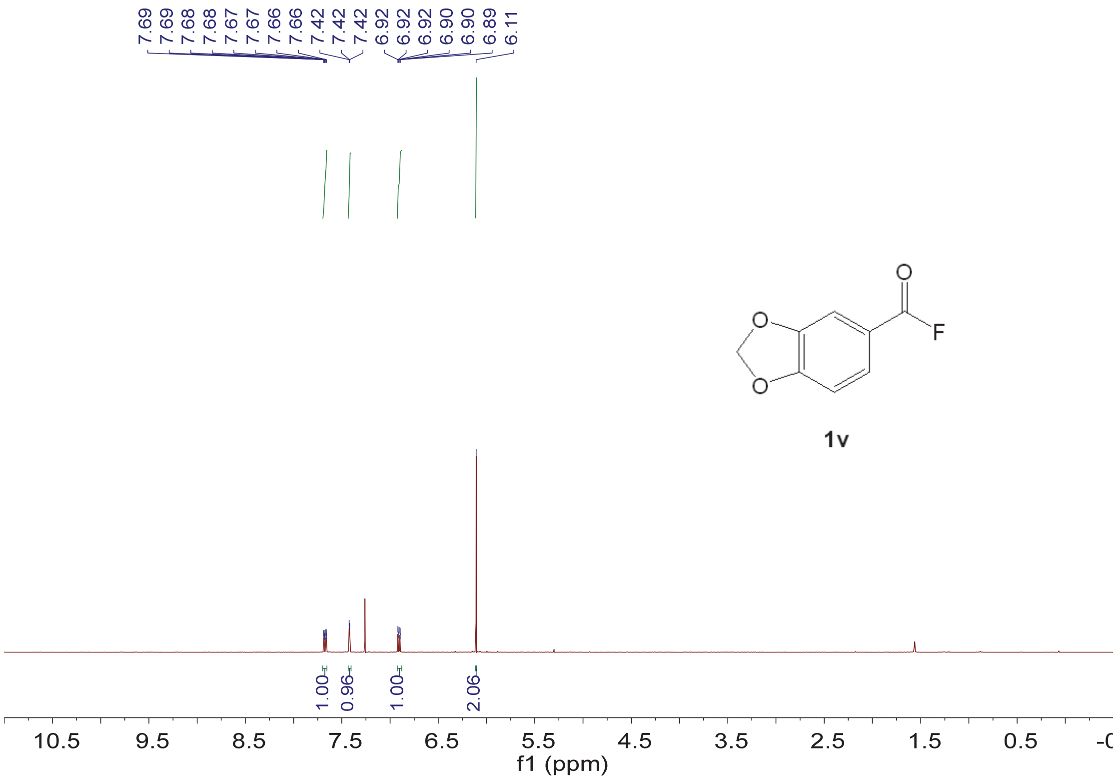
^{1}H NMR (600 MHz) spectrum of **1s** ($CDCl_3$, rt).

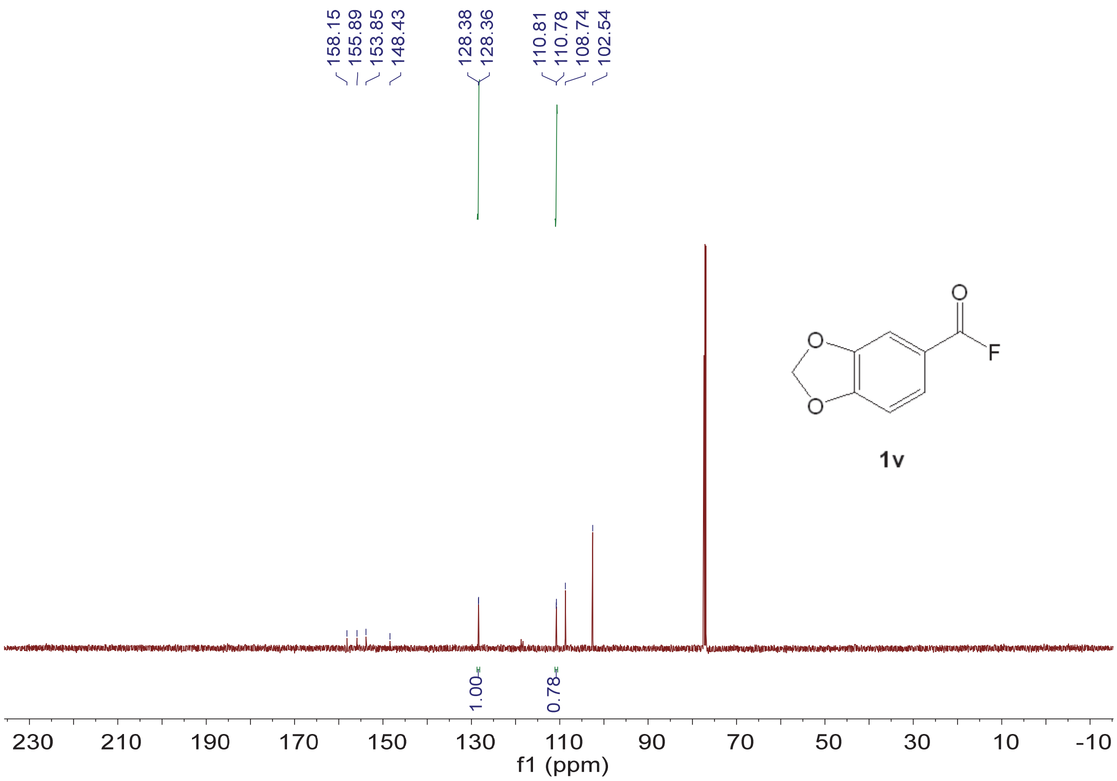


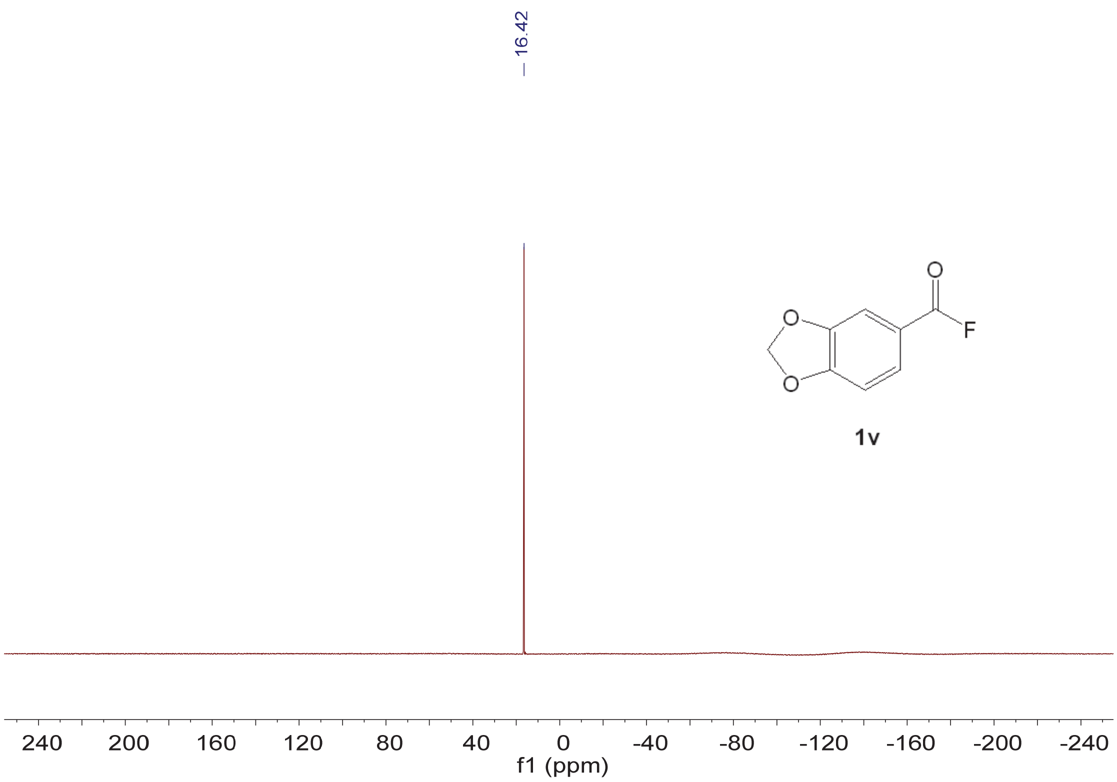
^{1}H NMR (400 MHz) spectrum of **1t** ($CDCl_3$, rt).



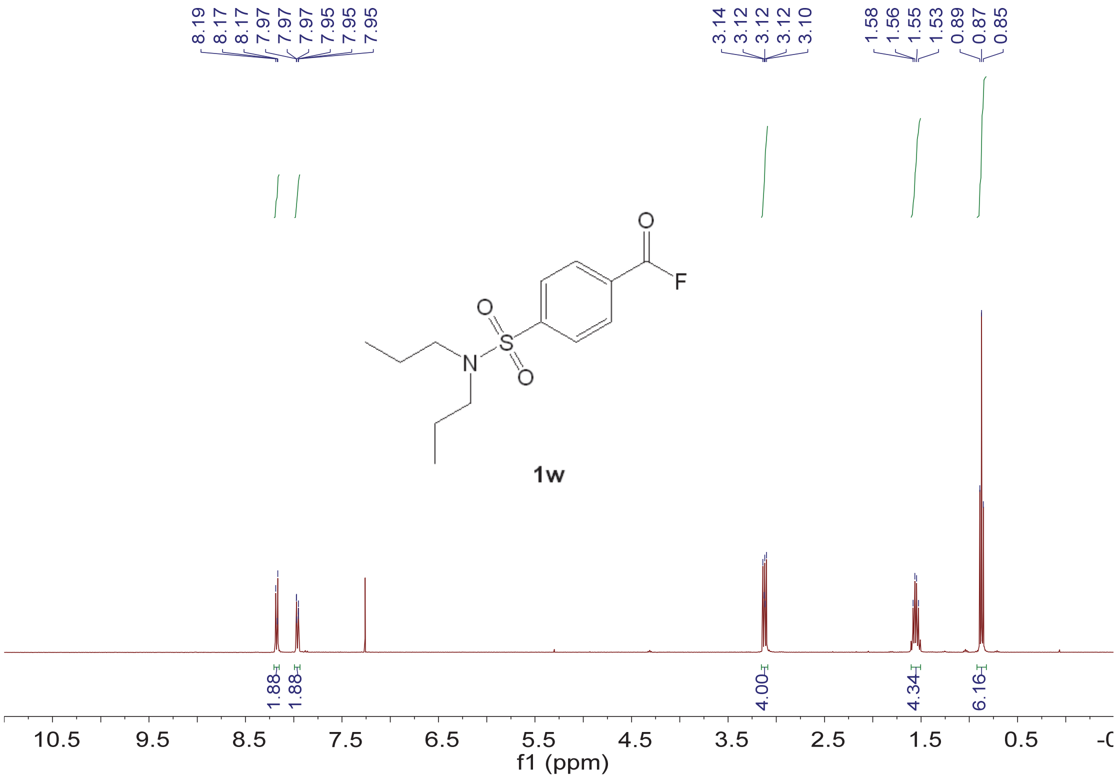
[1]H NMR (400 MHz) spectrum of **1u** ($CDCl_3$, rt).



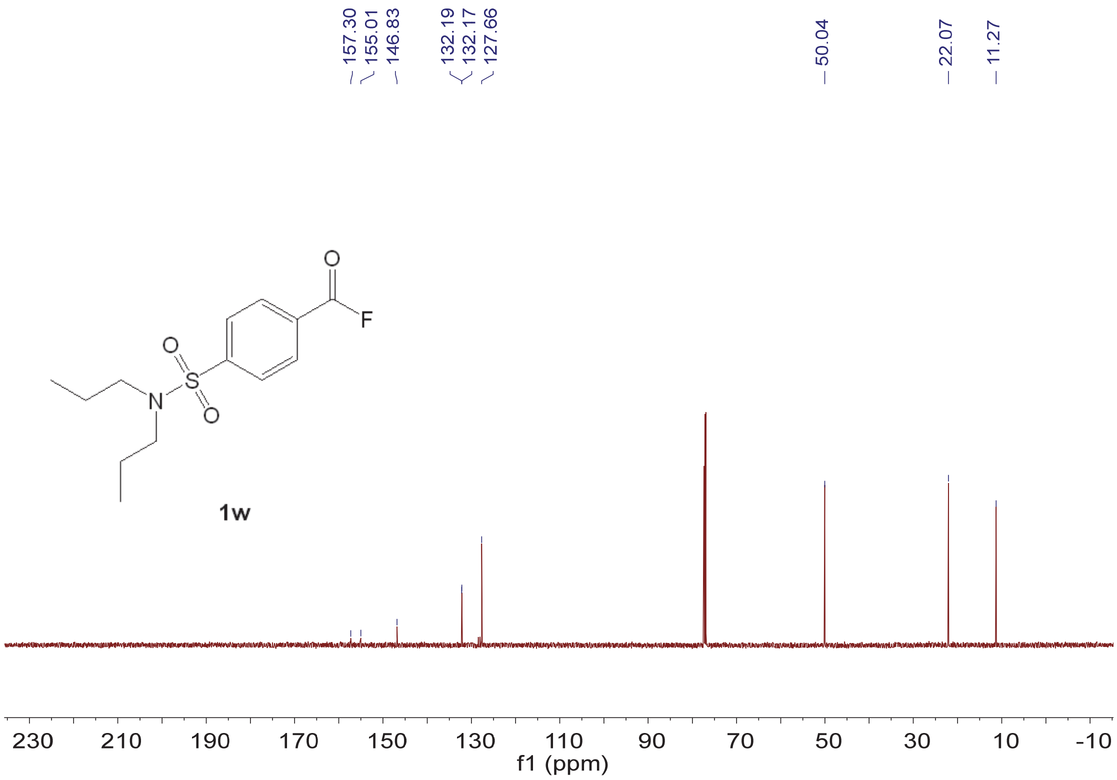




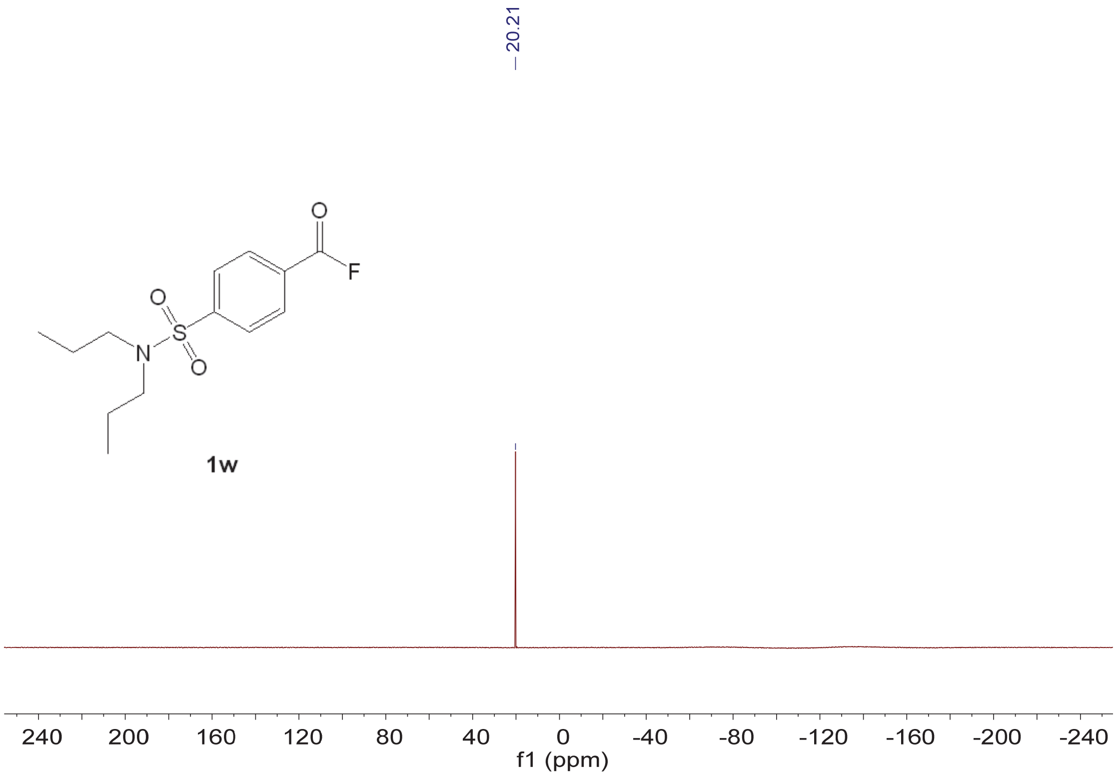
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **1v** ($CDCl_3$, rt).



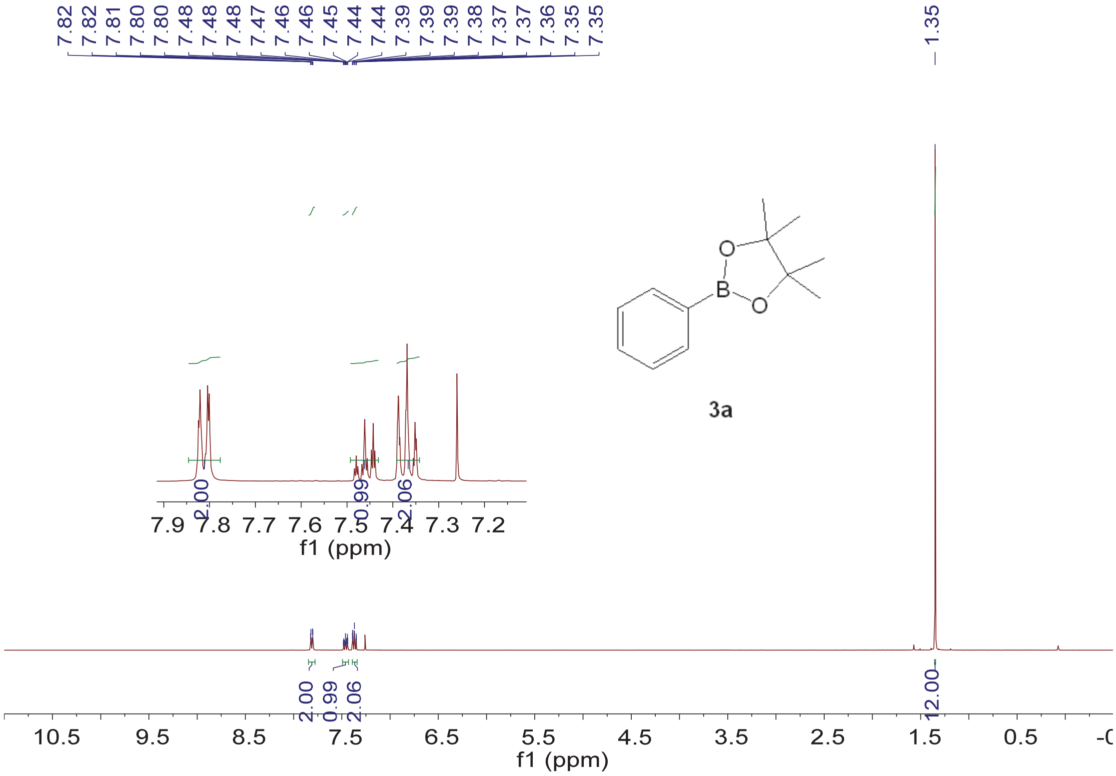
8.19
8.17
8.17
7.97
7.97
7.97
7.95
7.95
7.95
3.14
3.12
3.12
3.12
3.10
1.58
1.56
1.55
1.53
0.89
0.87
0.85
1w
1.88
1.88
4.00
4.34
6.16
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

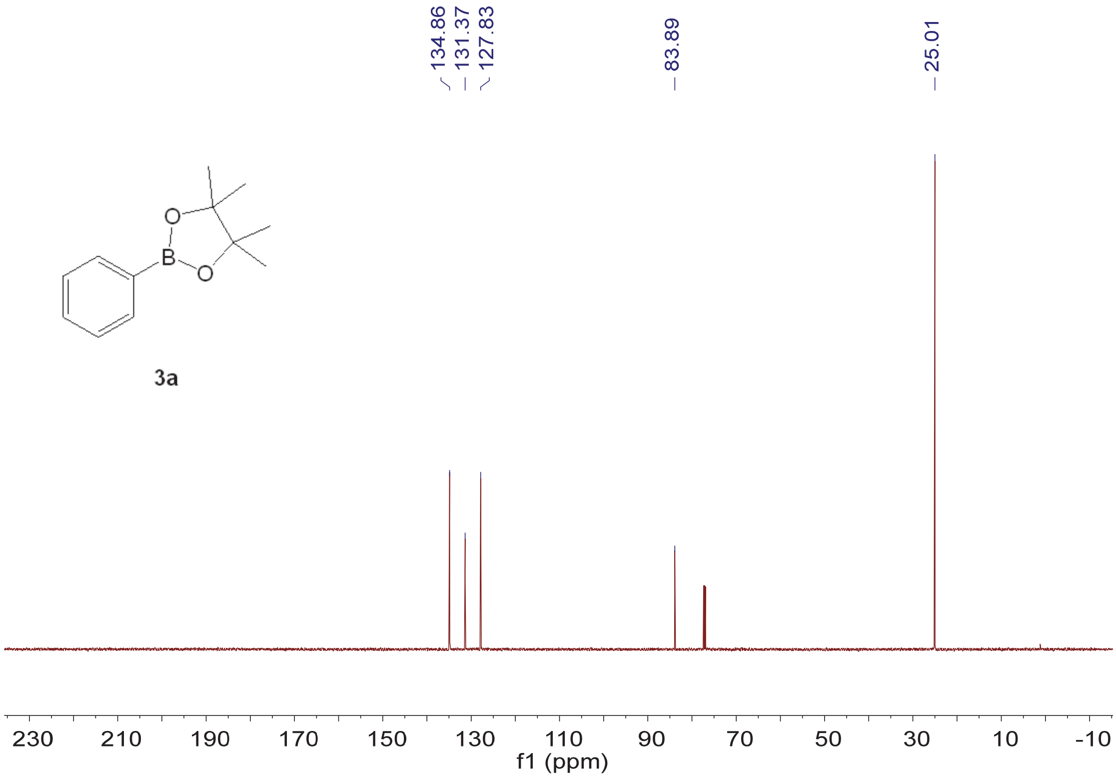


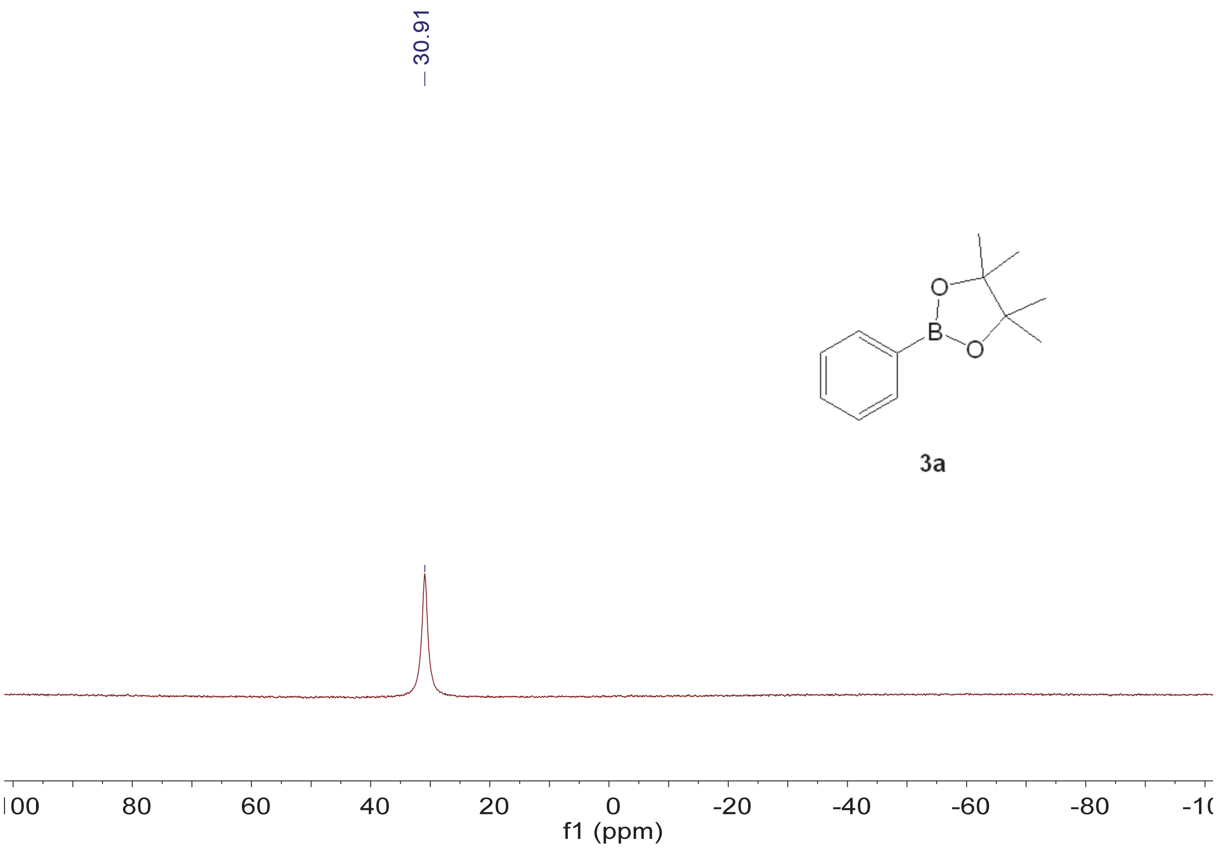
157.30
155.01
146.83
132.19
132.17
127.66
50.04
22.07
11.27
1w
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



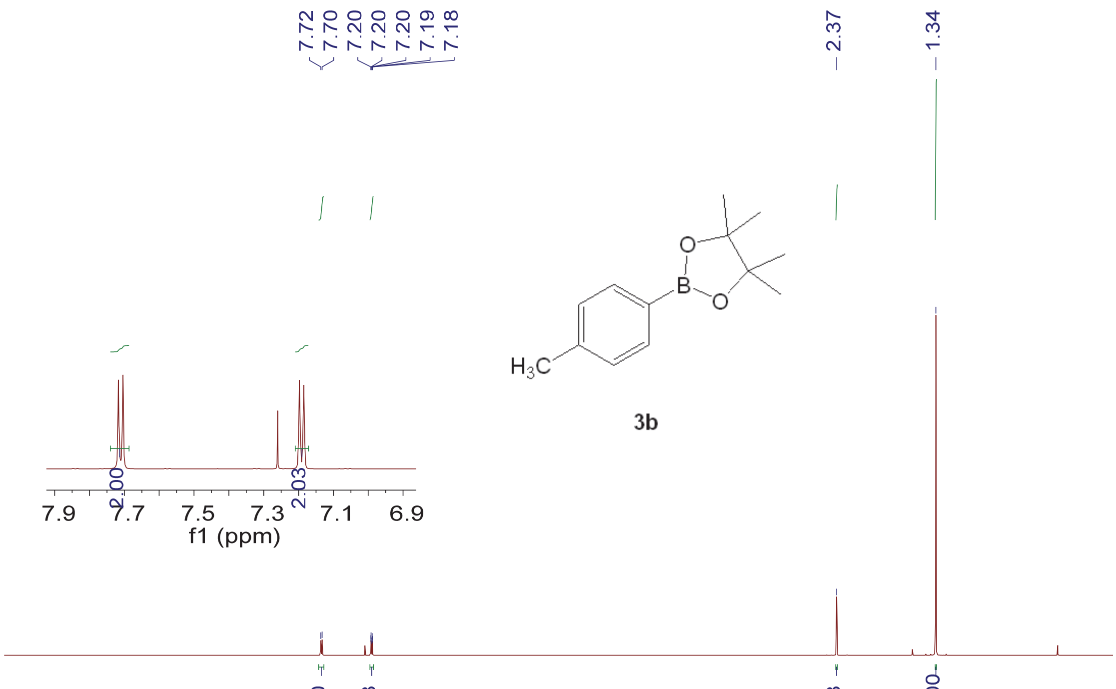
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **1w** ($CDCl_3$, rt).

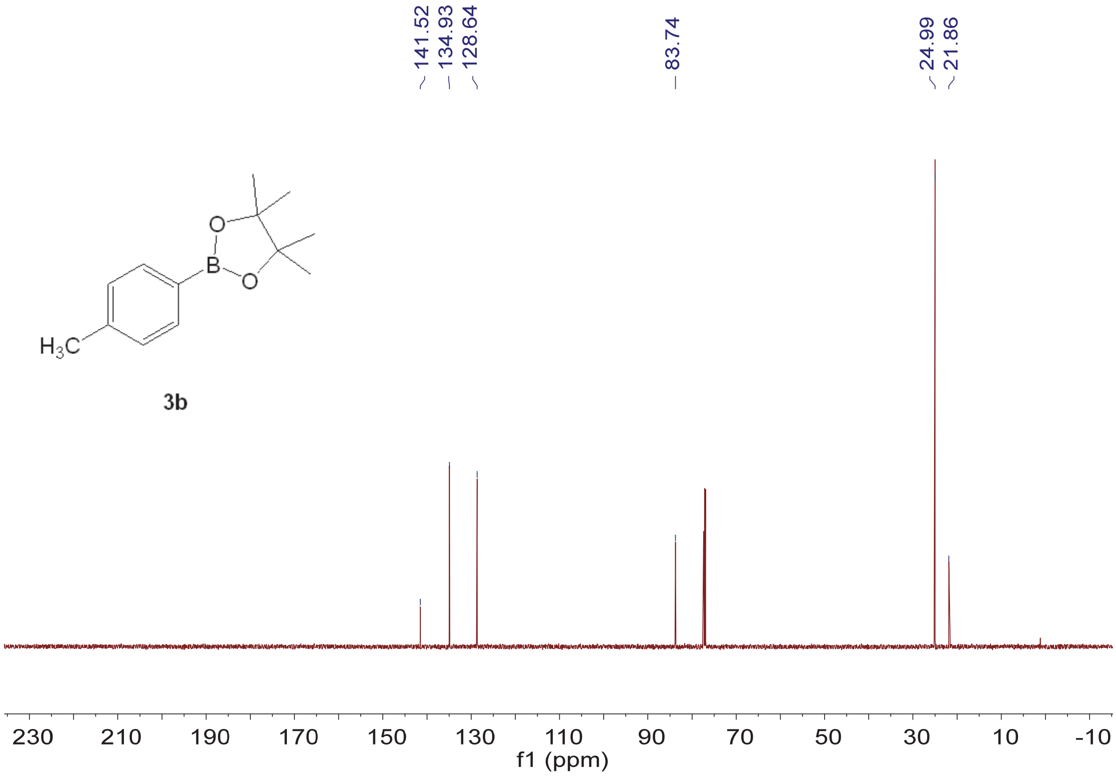

7.82 7.82 7.81 7.80 7.80 7.48 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.39 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.35
1.35
3a
2.00 0.99 2.06
12.00
f1 (ppm)

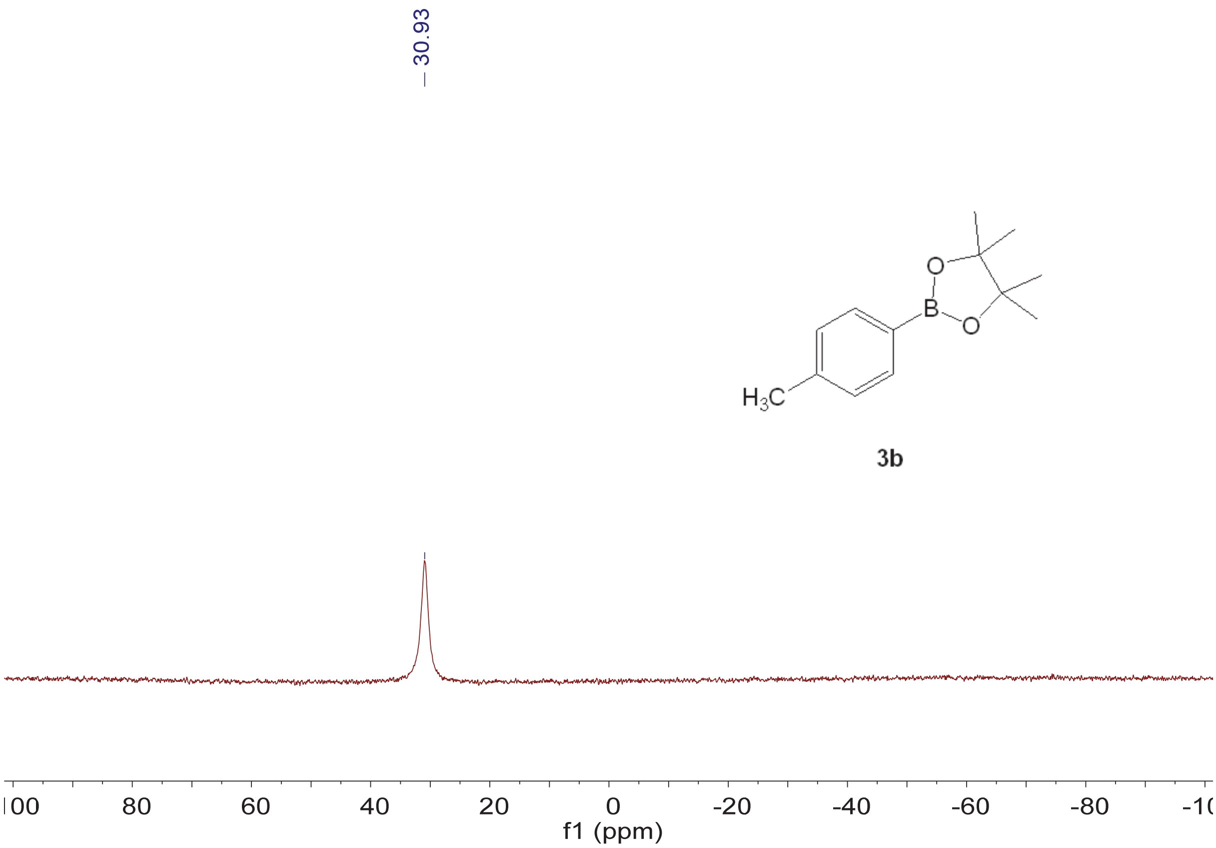

134.86 131.37 127.83
83.89
25.01
3a
f1 (ppm)



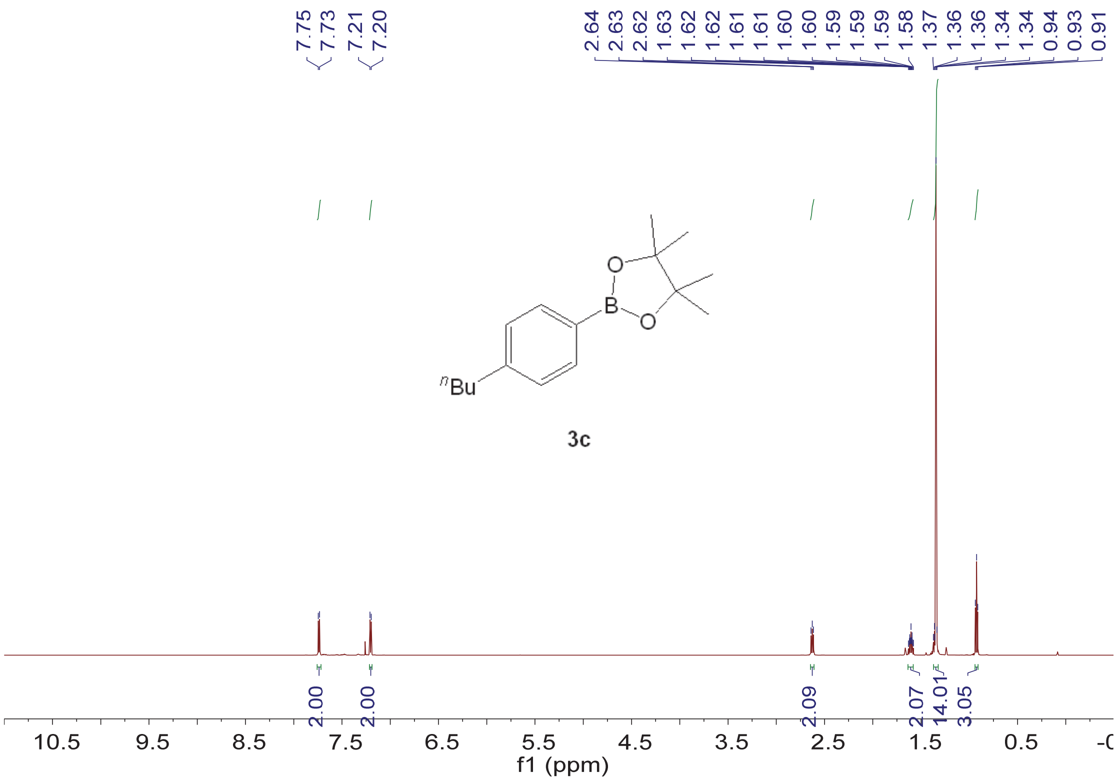
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3a** ($CDCl_3$, rt).



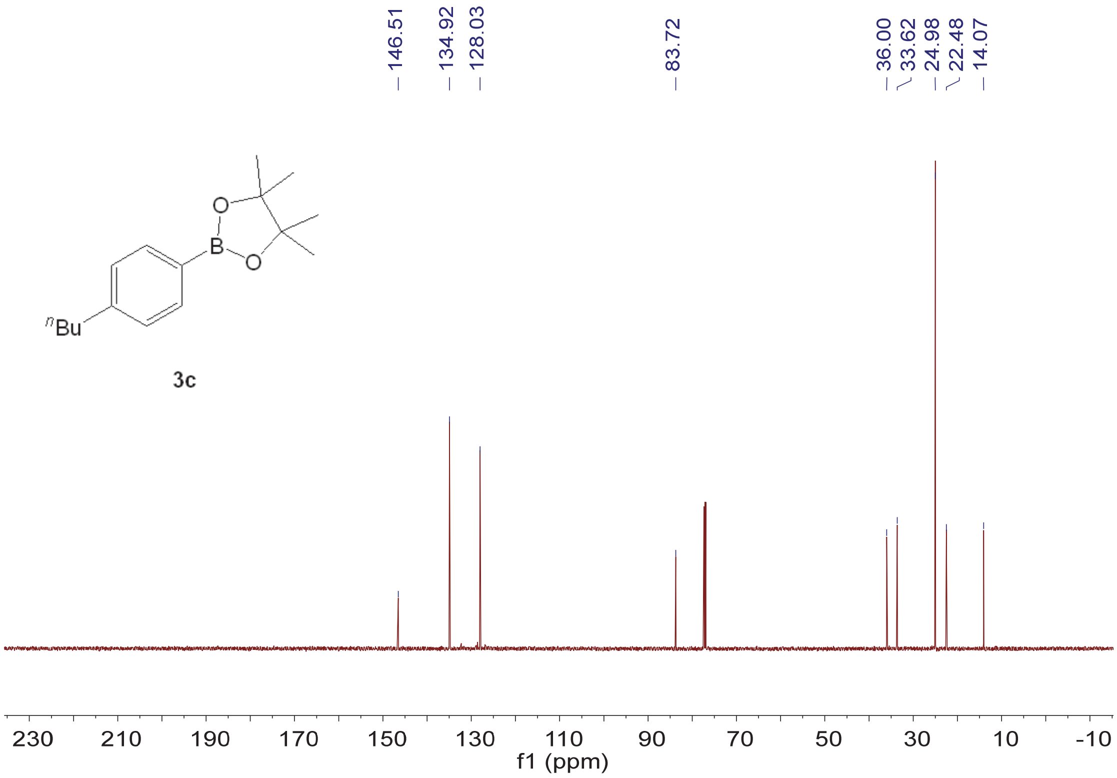




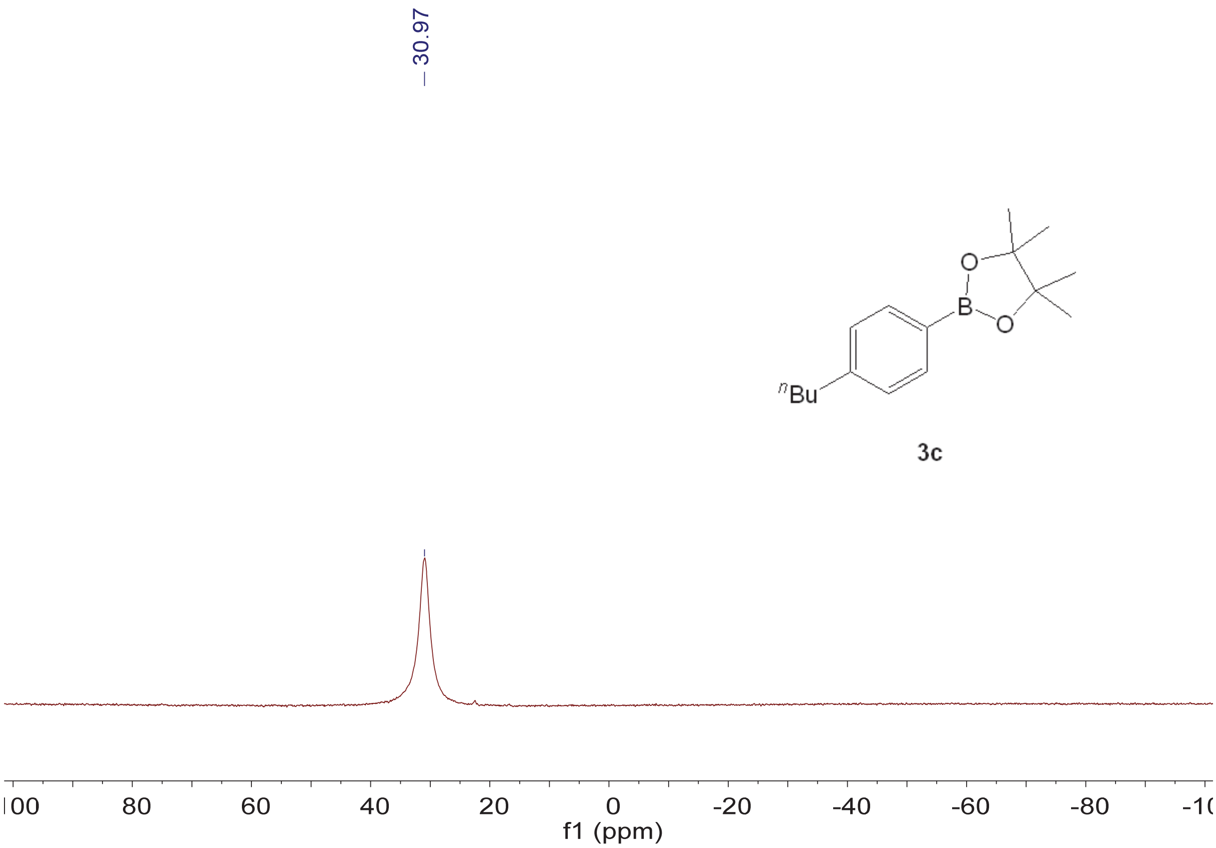
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3b** ($CDCl_3$, rt).



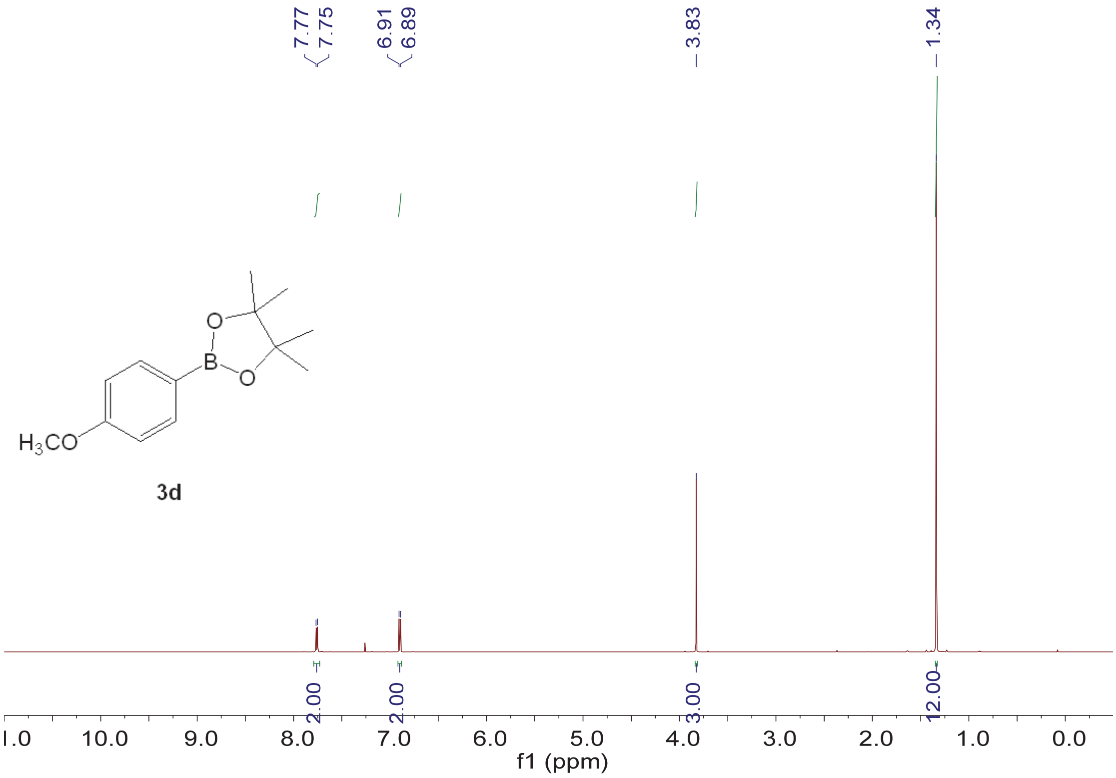
3c

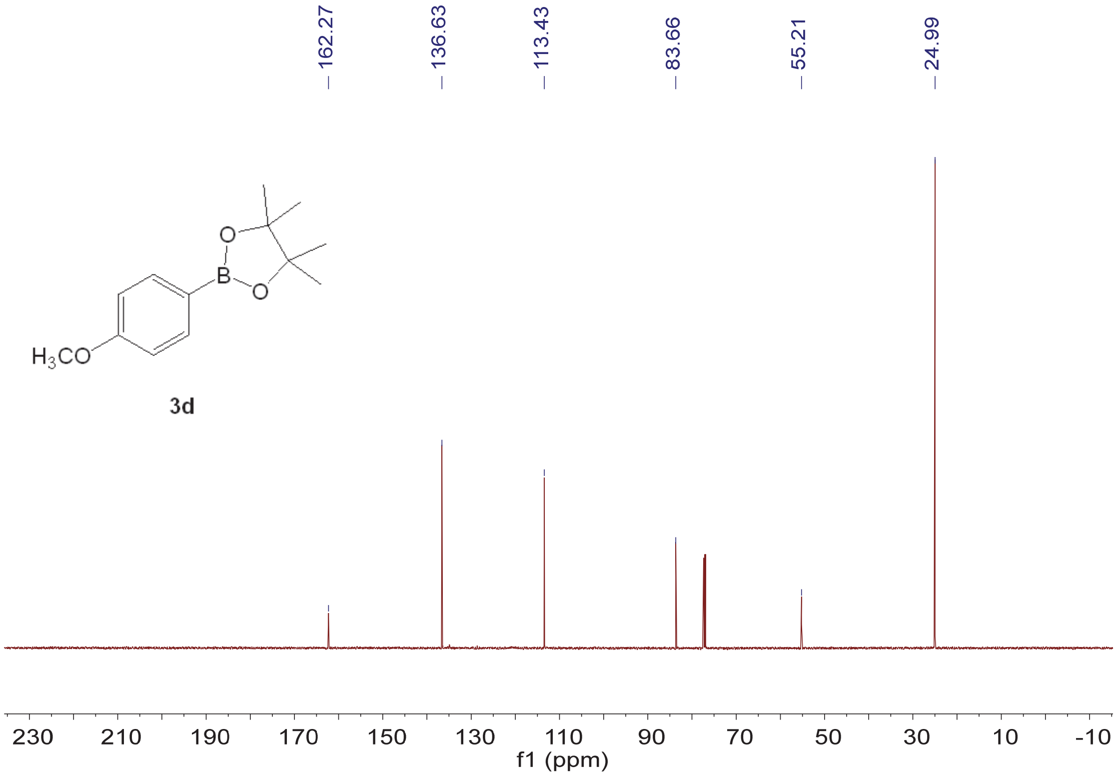


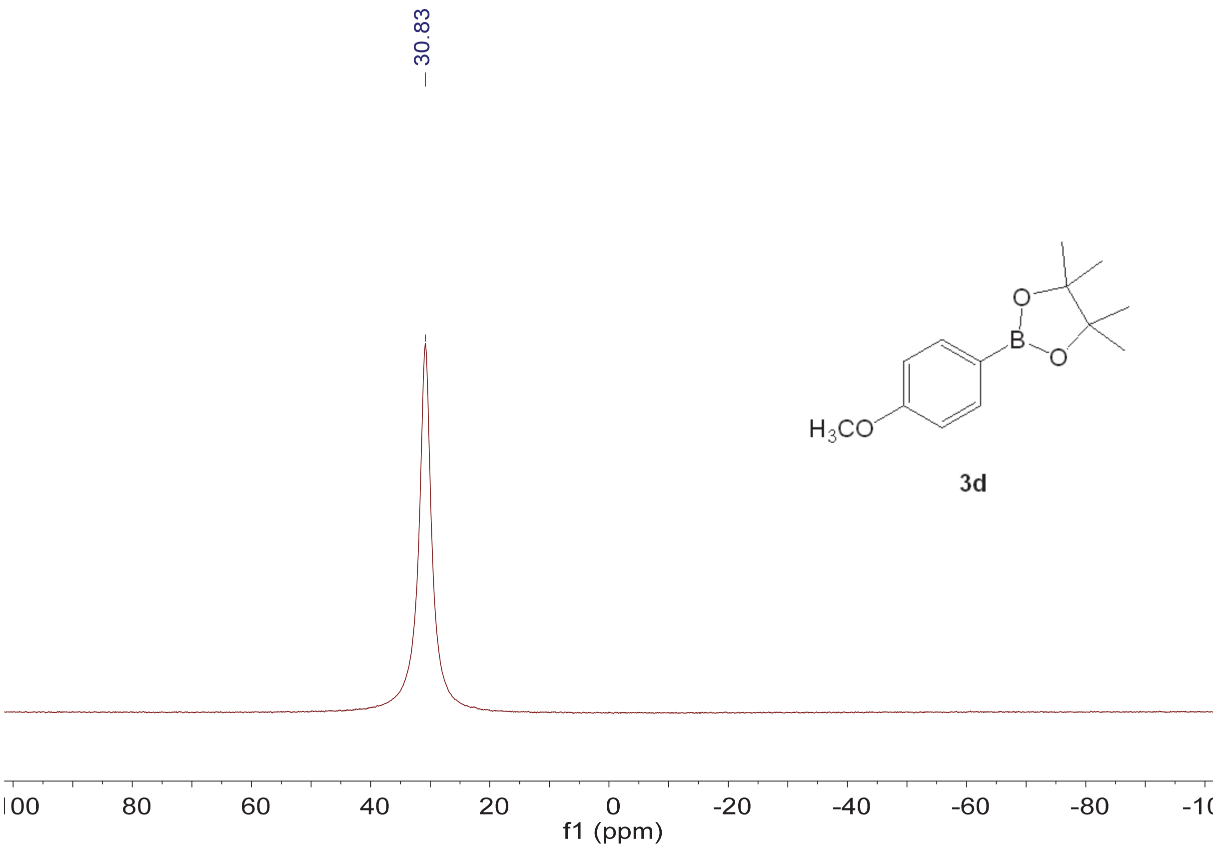
3c



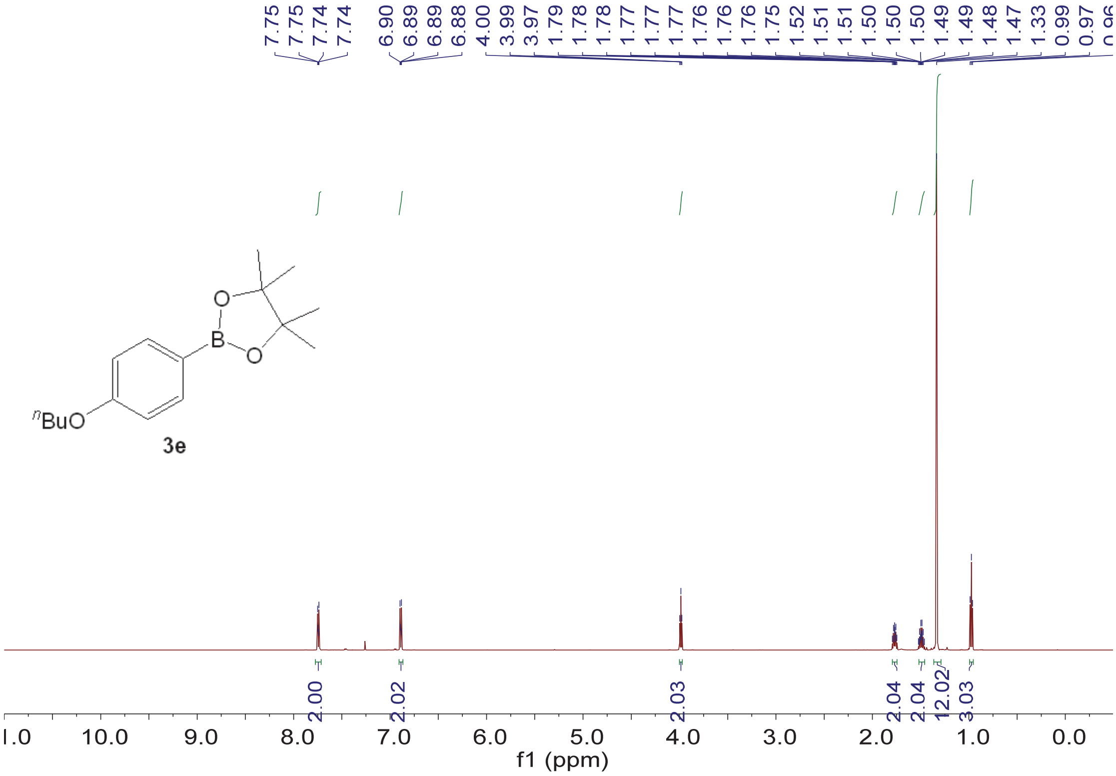
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3c** ($CDCl_3$, rt).







^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3d** ($CDCl_3$, rt).


7.75
7.75
7.74
7.74
6.90
6.89
6.89
6.88
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3.99
3.97
1.79
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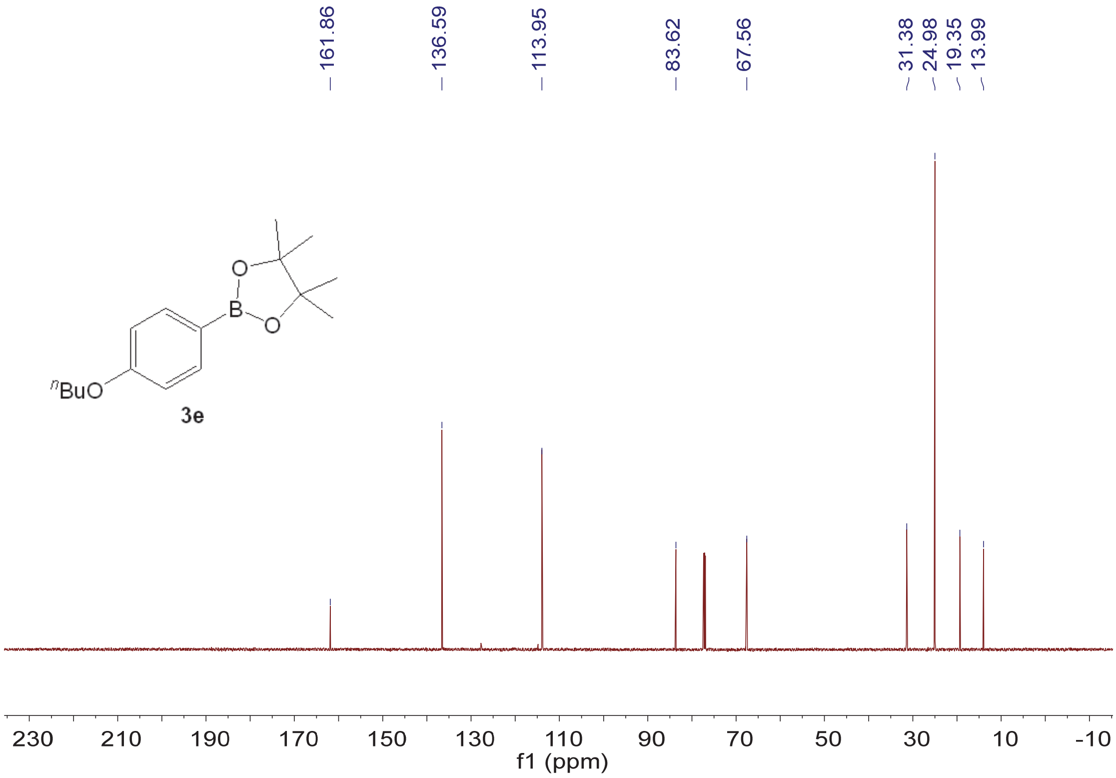
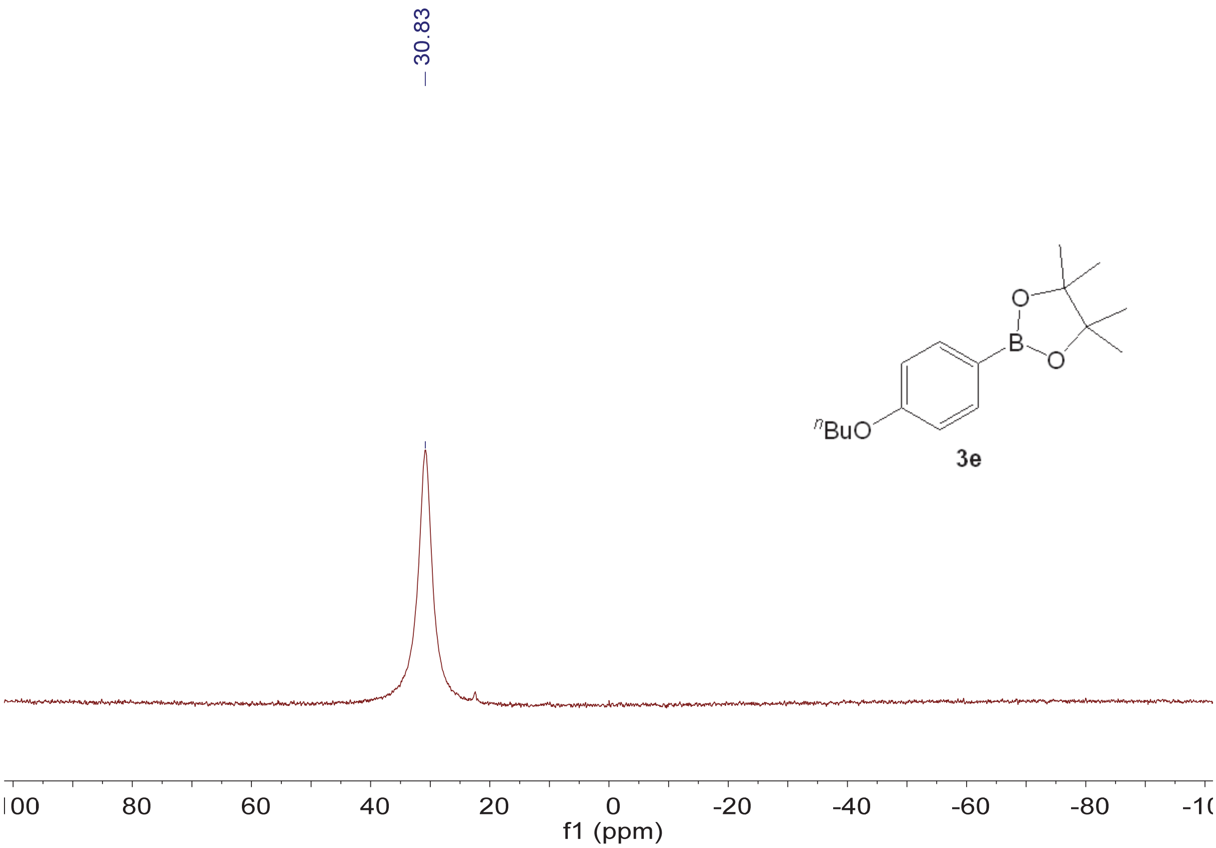
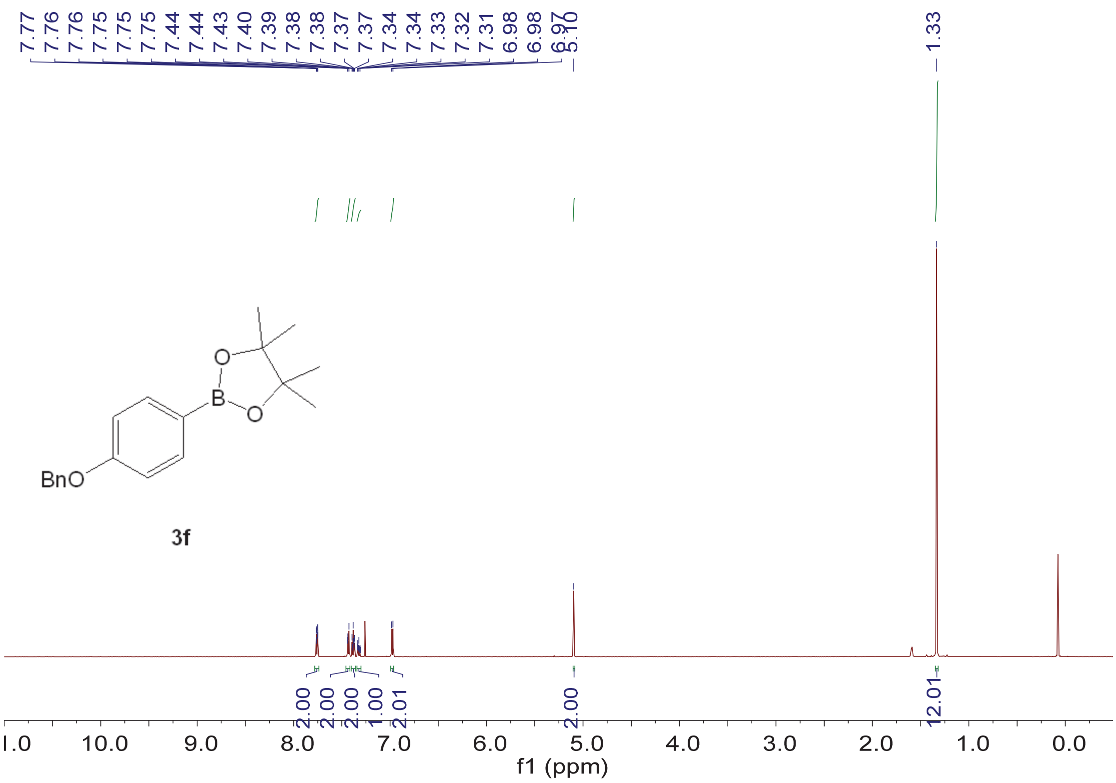
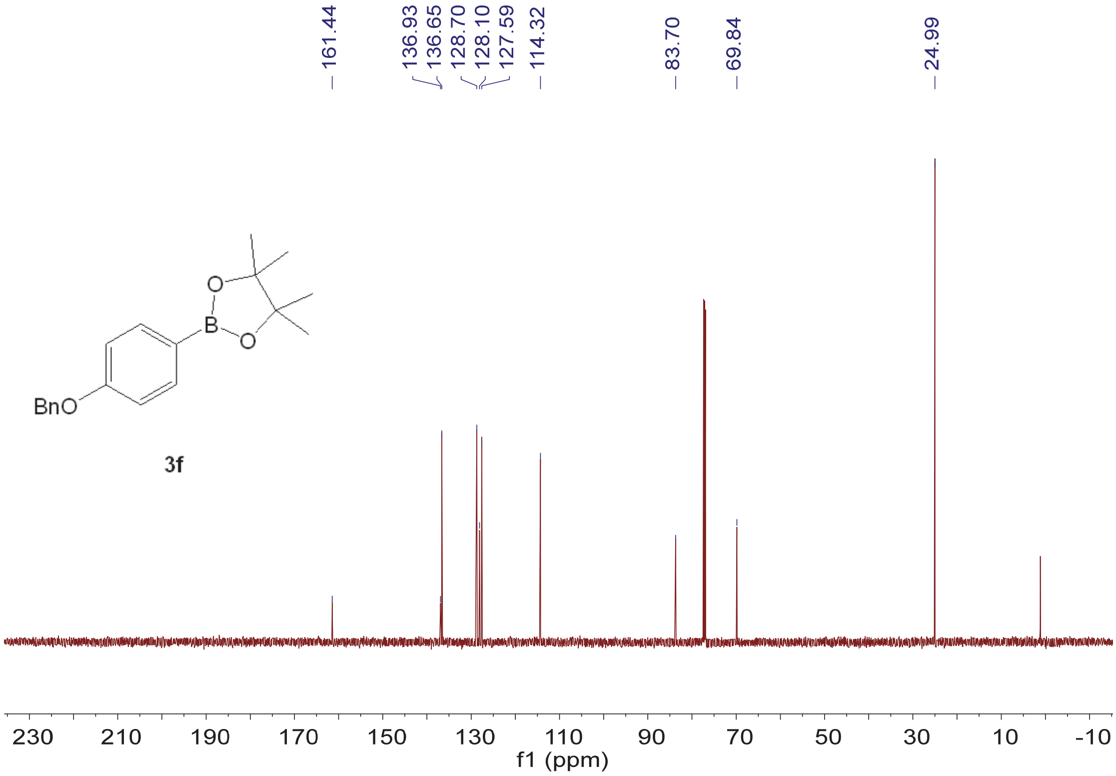
1.78
1.77
1.77
1.77
1.76
1.76
1.76
1.75
1.52
1.51
1.51
1.50
1.50
1.50
1.49
1.49
1.48
1.47
1.33
0.99
0.97
ⁿBuO
3e
2.00
2.02
2.03
2.04
2.04
12.02
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

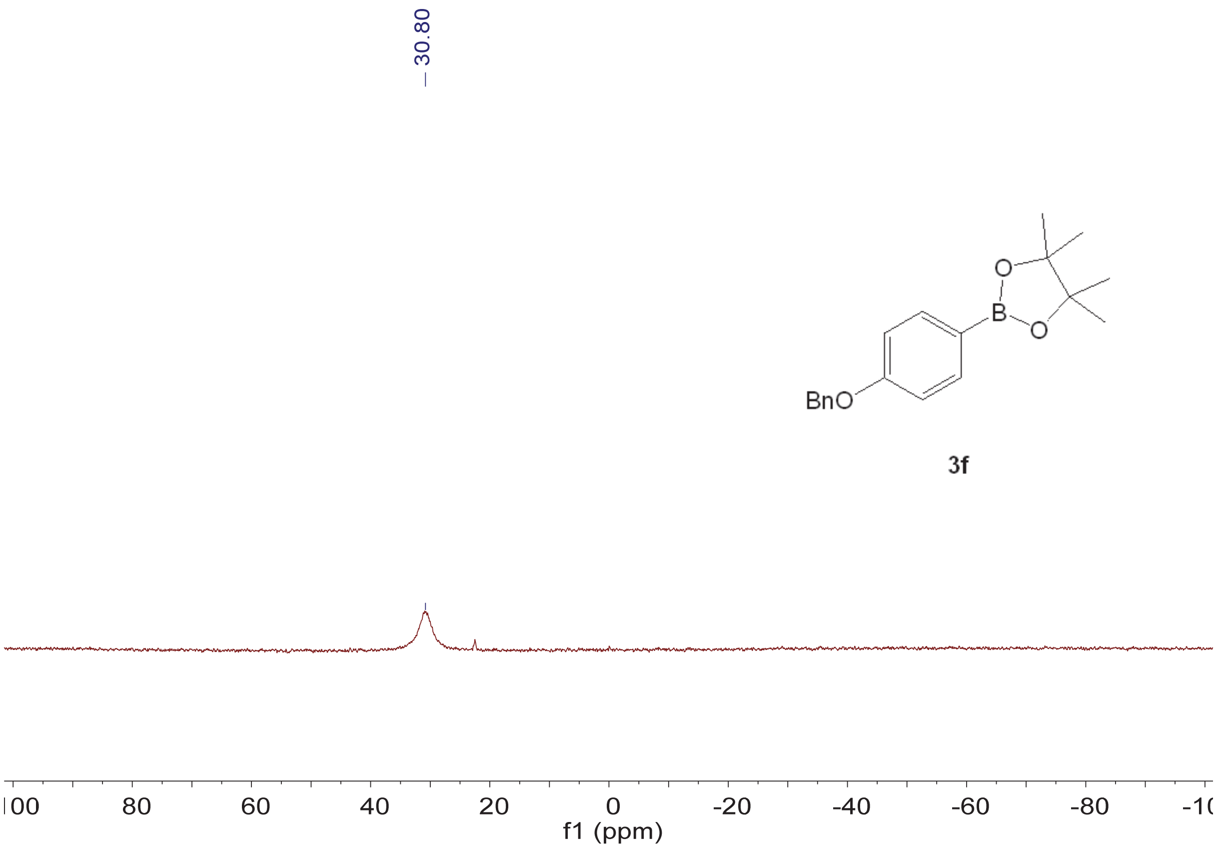

161.86
136.59
113.95
83.62
67.56
31.38
24.98
19.35
13.99
ⁿBuO
3e
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



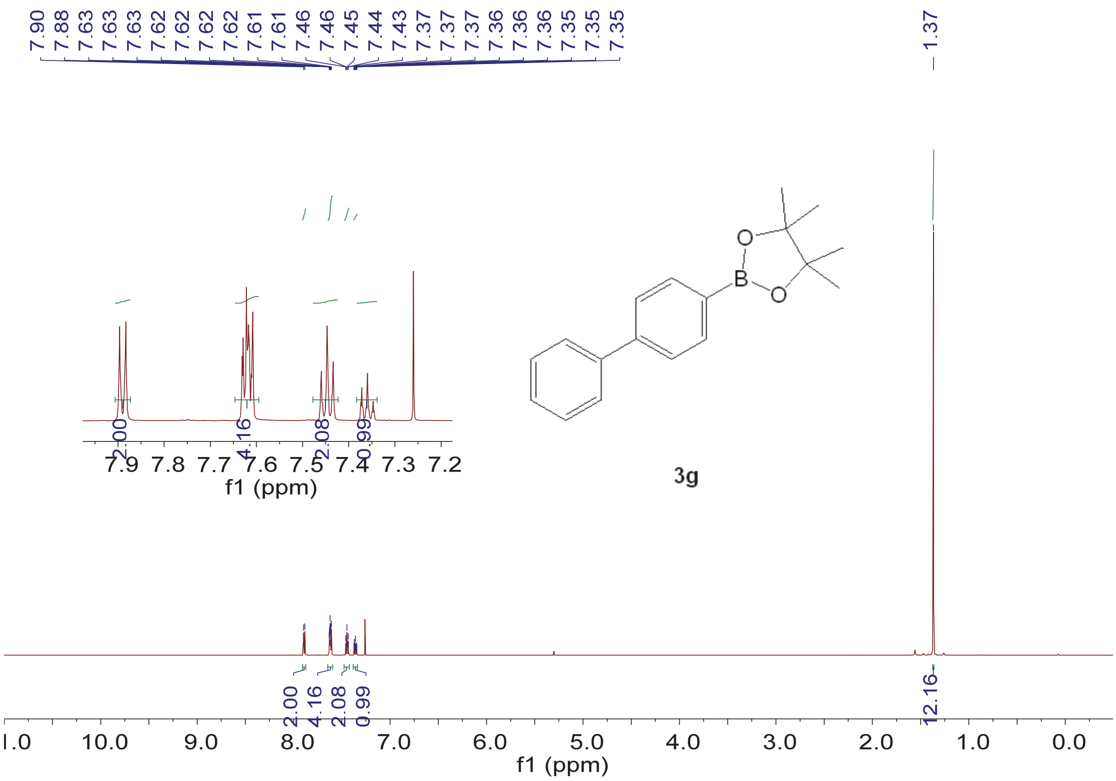
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3e** ($CDCl_3$, rt).







^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3f** ($CDCl_3$, rt).


7.90
7.88
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7.63
7.63
7.62
7.62
7.62
7.62
7.61
7.61
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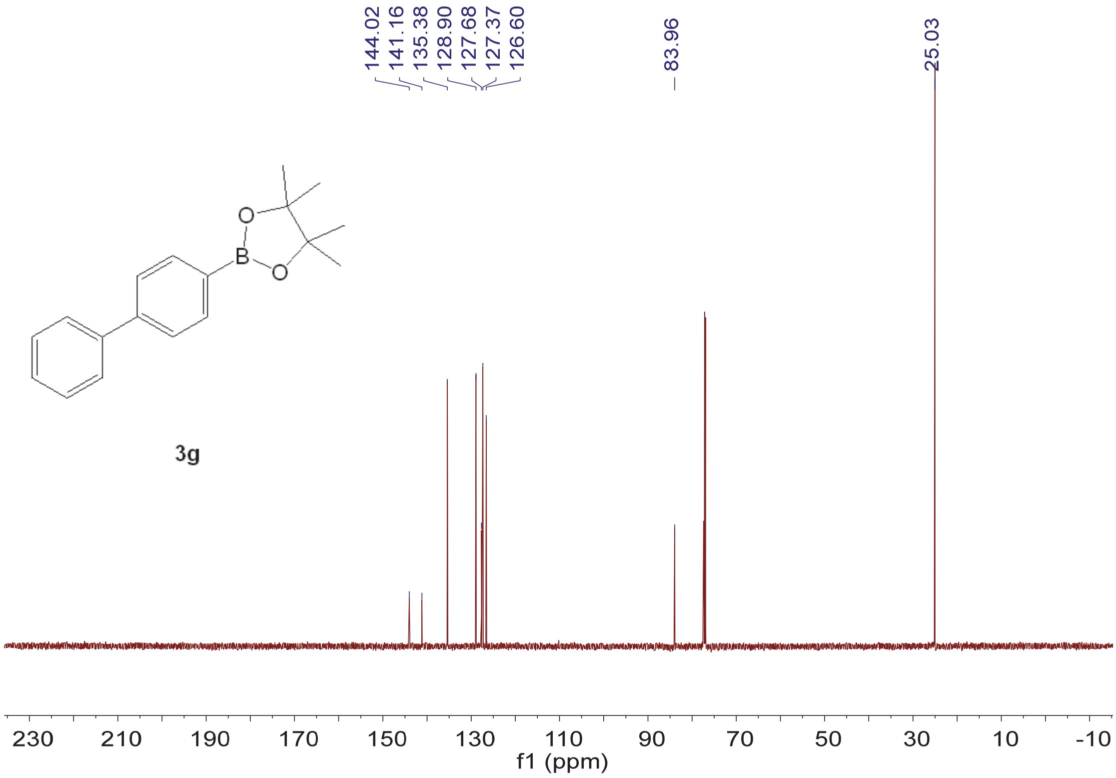
7.45
7.44
7.43
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
1.37
2.00
4.16
2.08
0.99
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
O
B
O
3g
12.16
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


144.02
141.16
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128.90
127.68
127.37
126.60
83.96
25.03
O
B
O
3g
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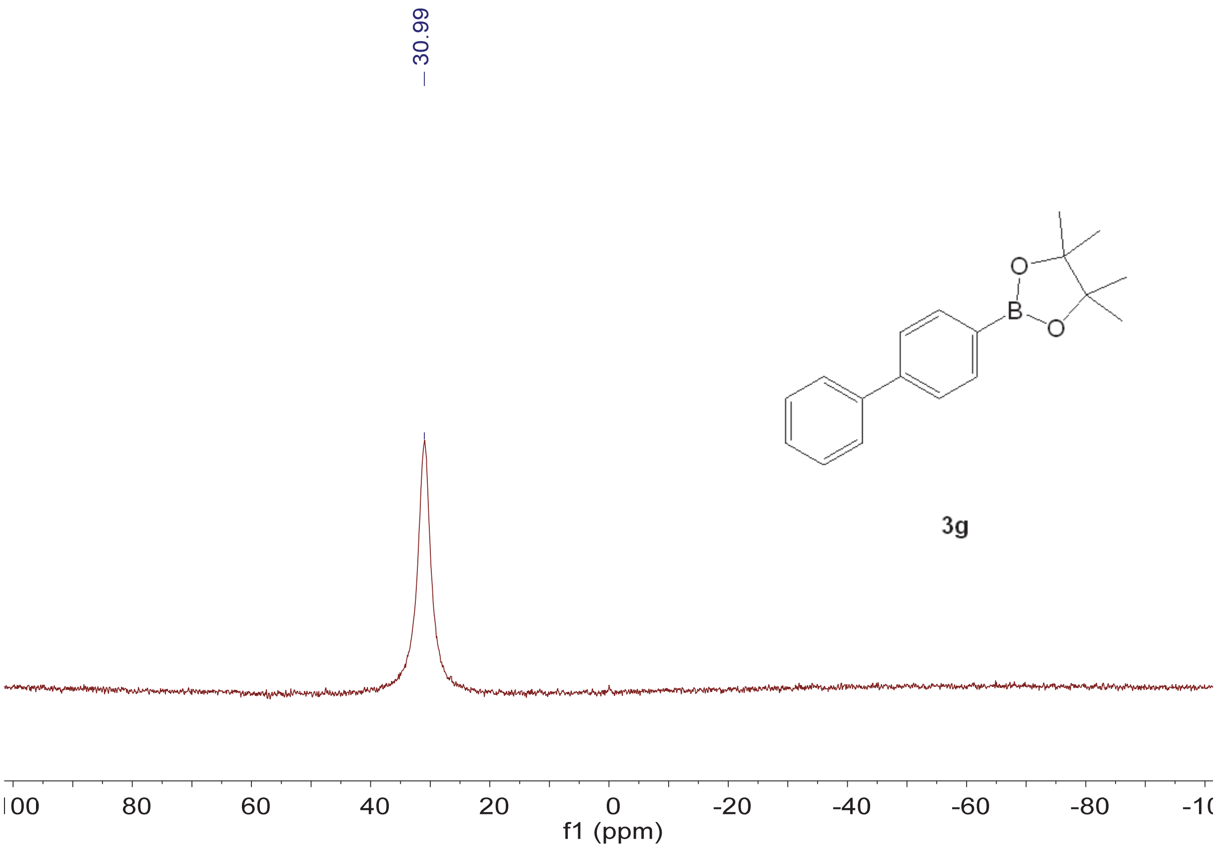
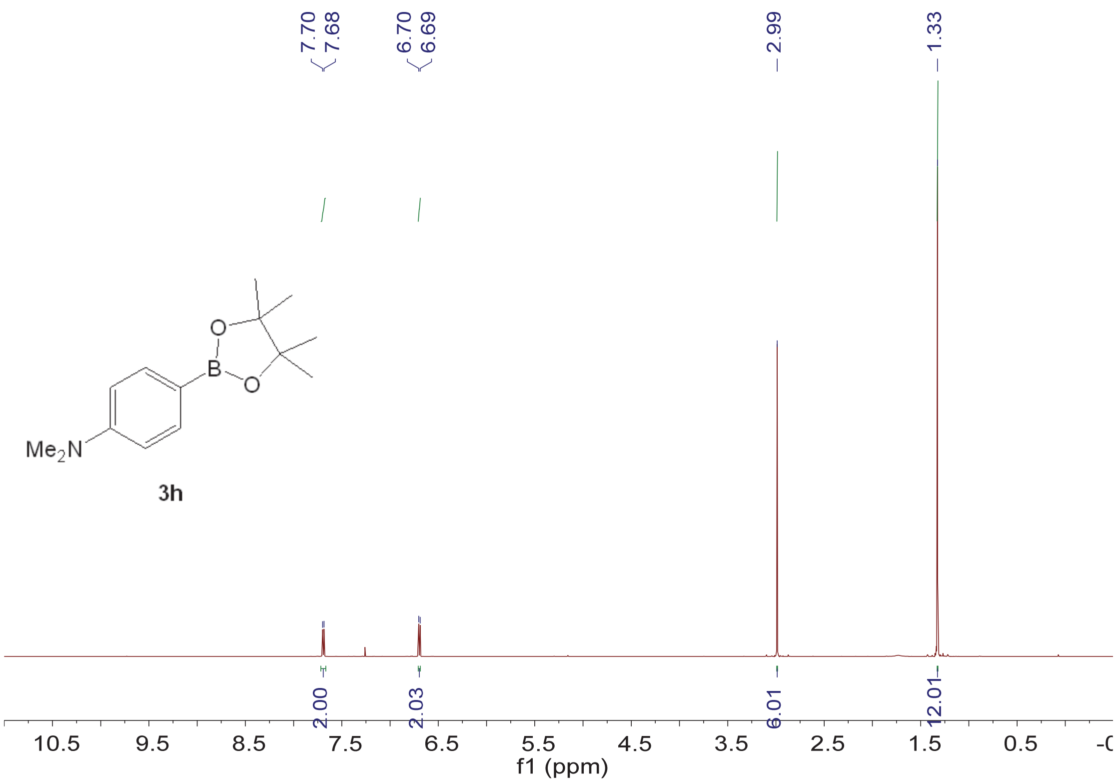
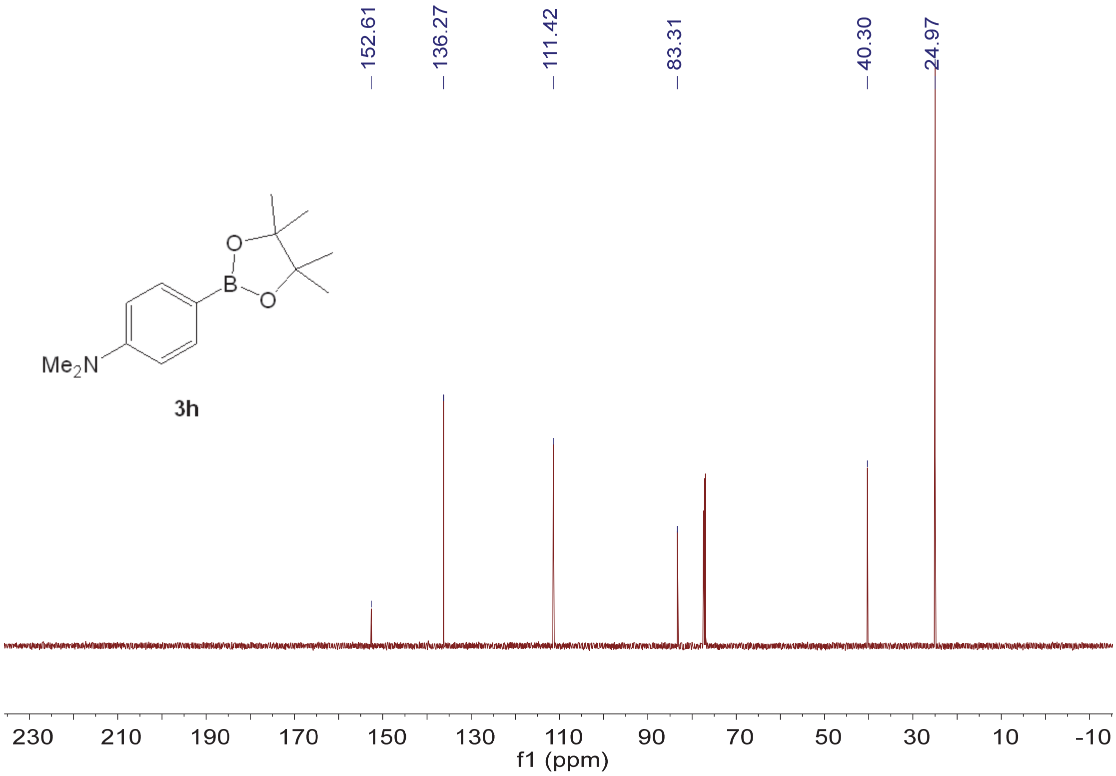
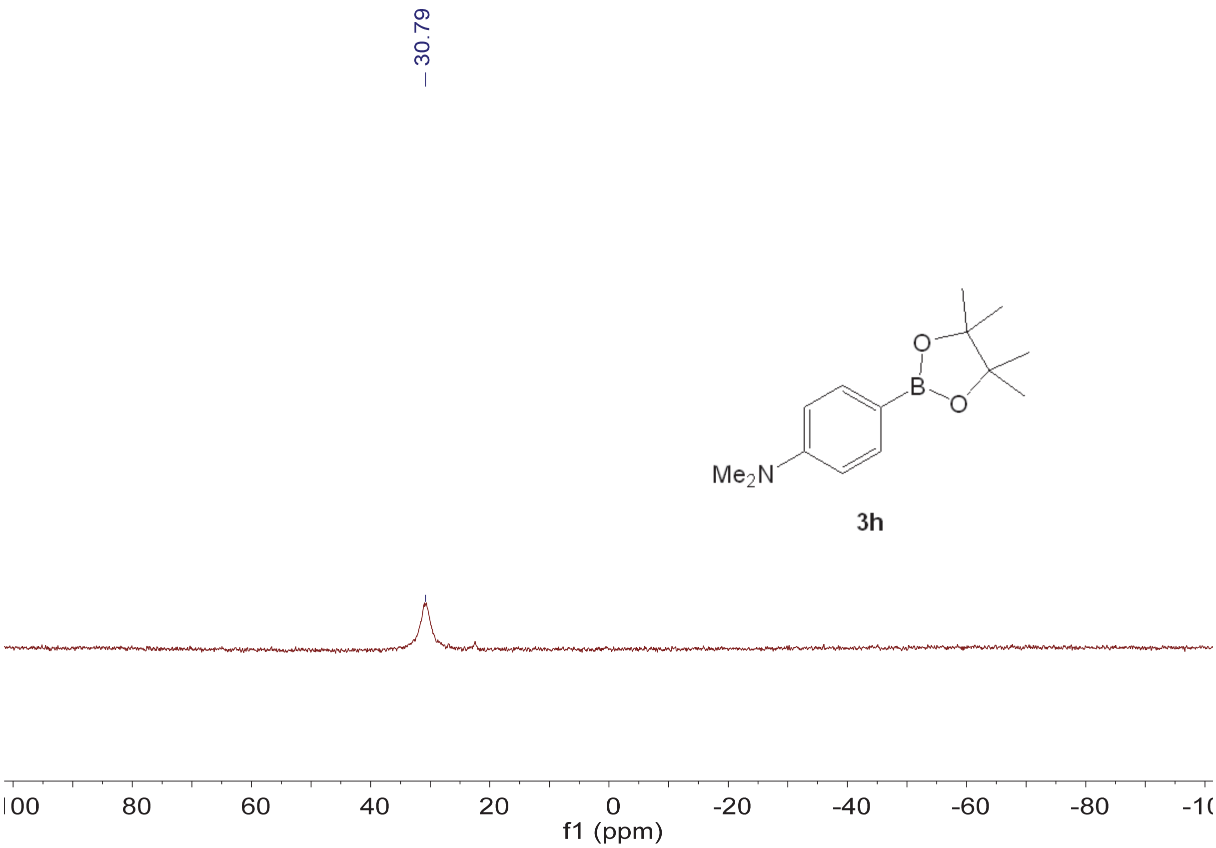
f1 (ppm)



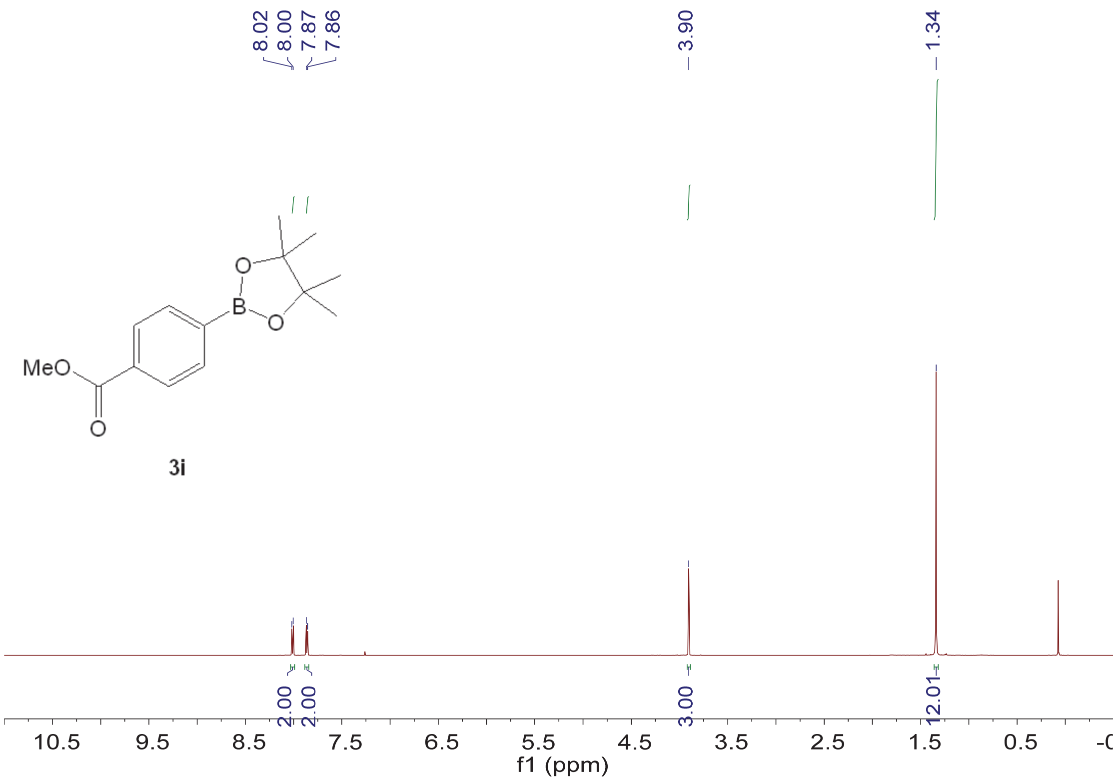
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3g** ($CDCl_3$, rt).

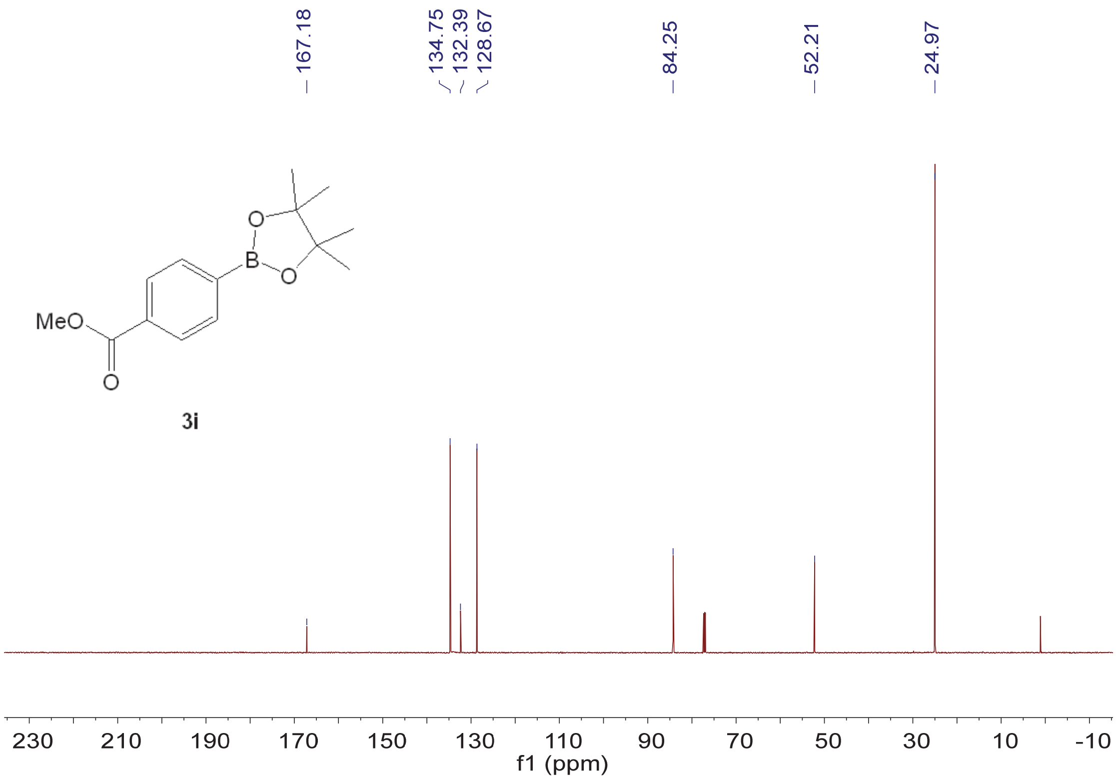


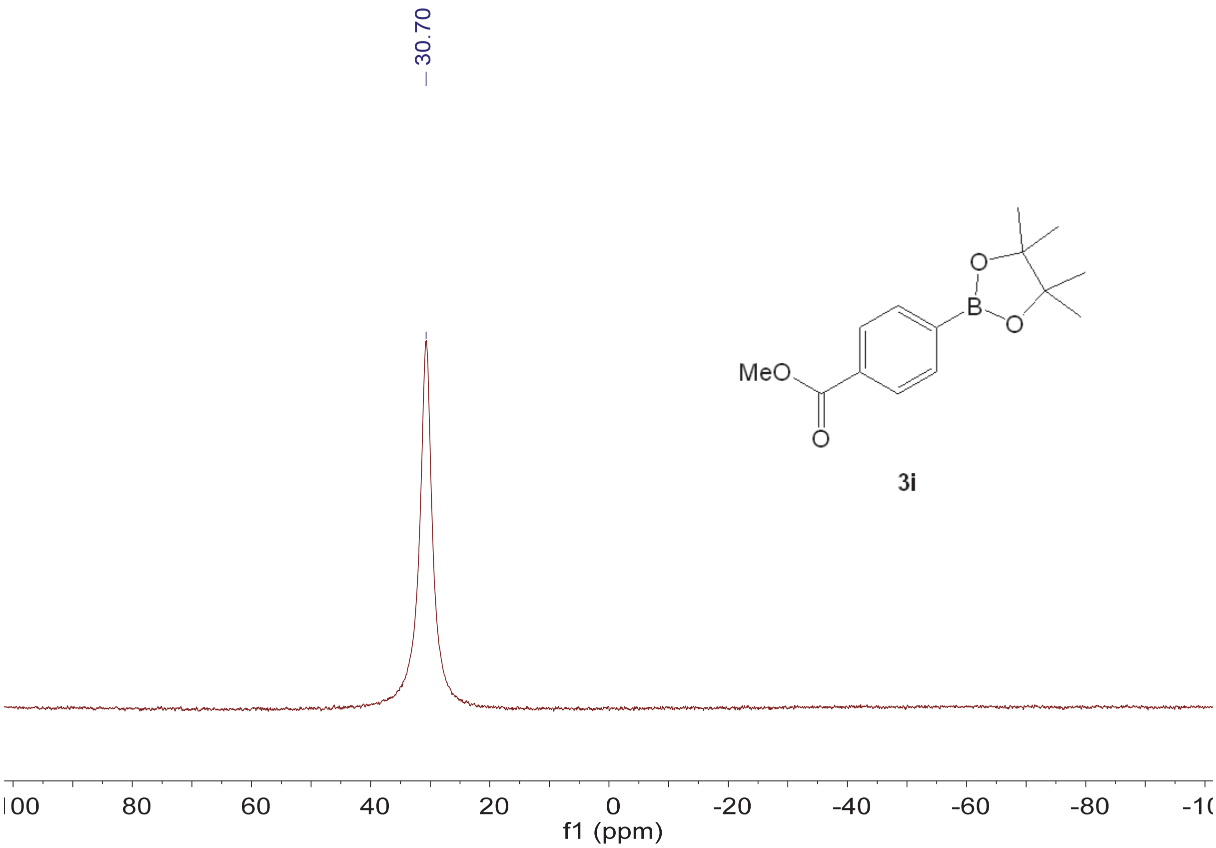




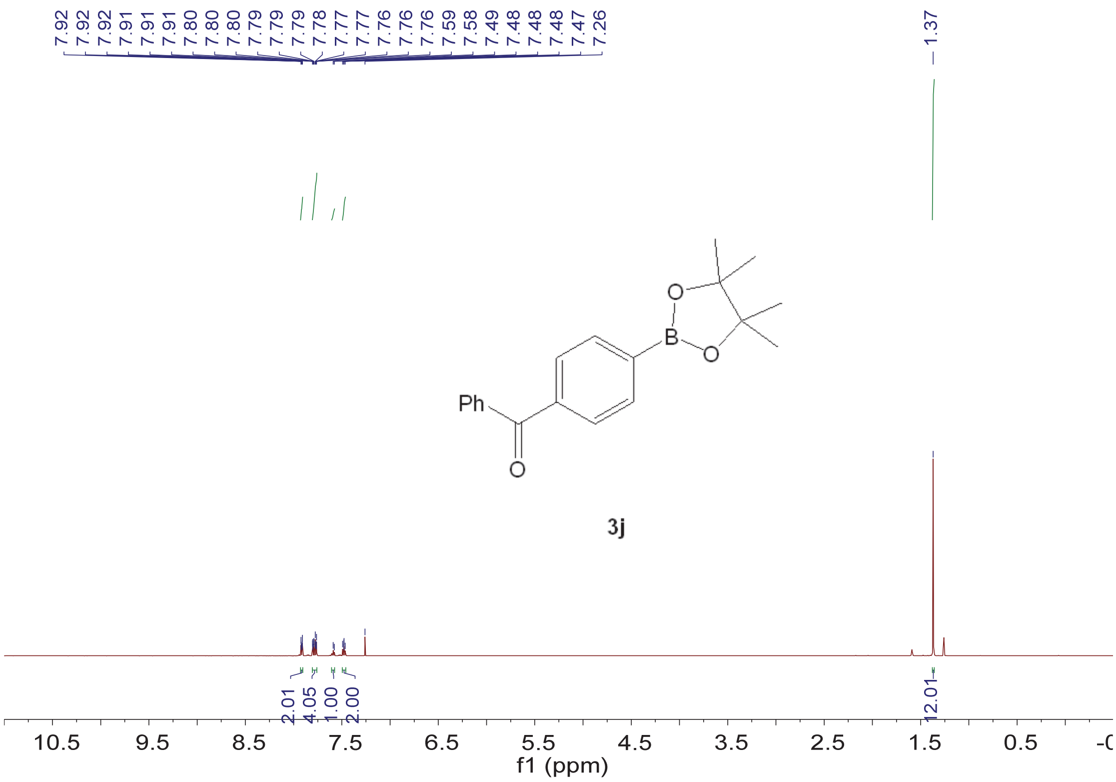
[1]H NMR (600 MHz), [13]C{[1]H} NMR (151 MHz) and [11]B{[1]H} NMR (192 MHz) spectra of **3h** ($CDCl_3$, rt).

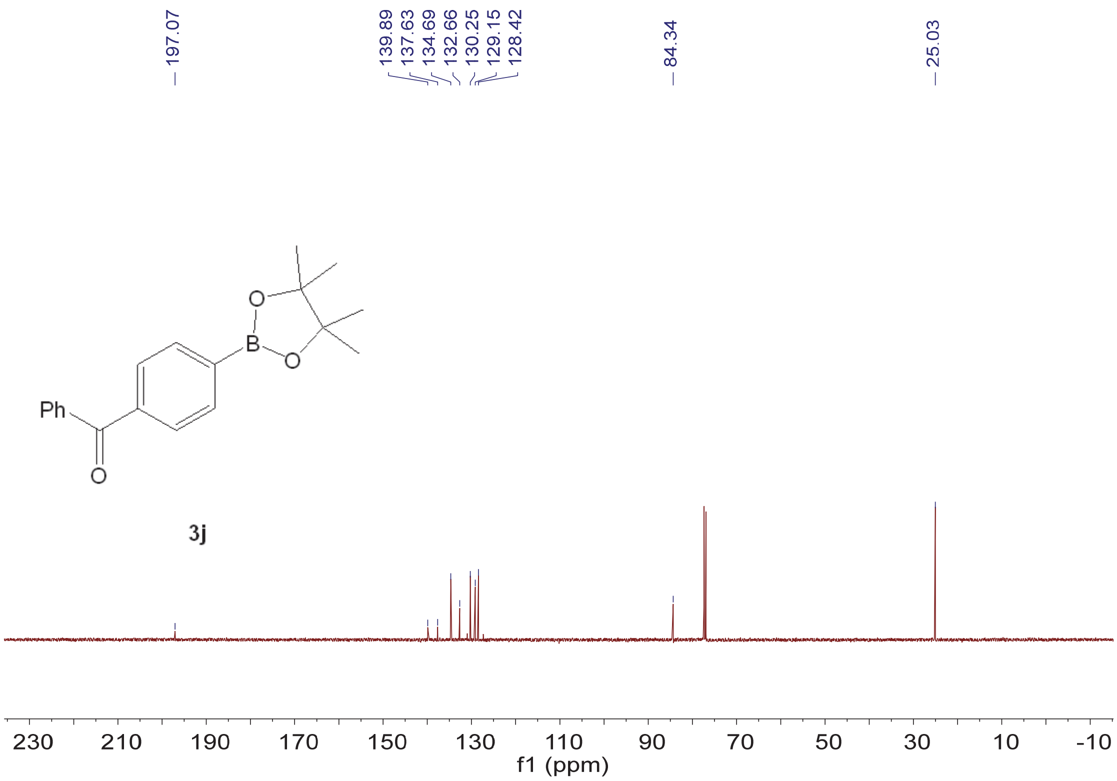

8.02
8.00
7.87
7.86
3.90
1.34
MeO
B
O
O
O
3i
2.00
2.00
3.00
12.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

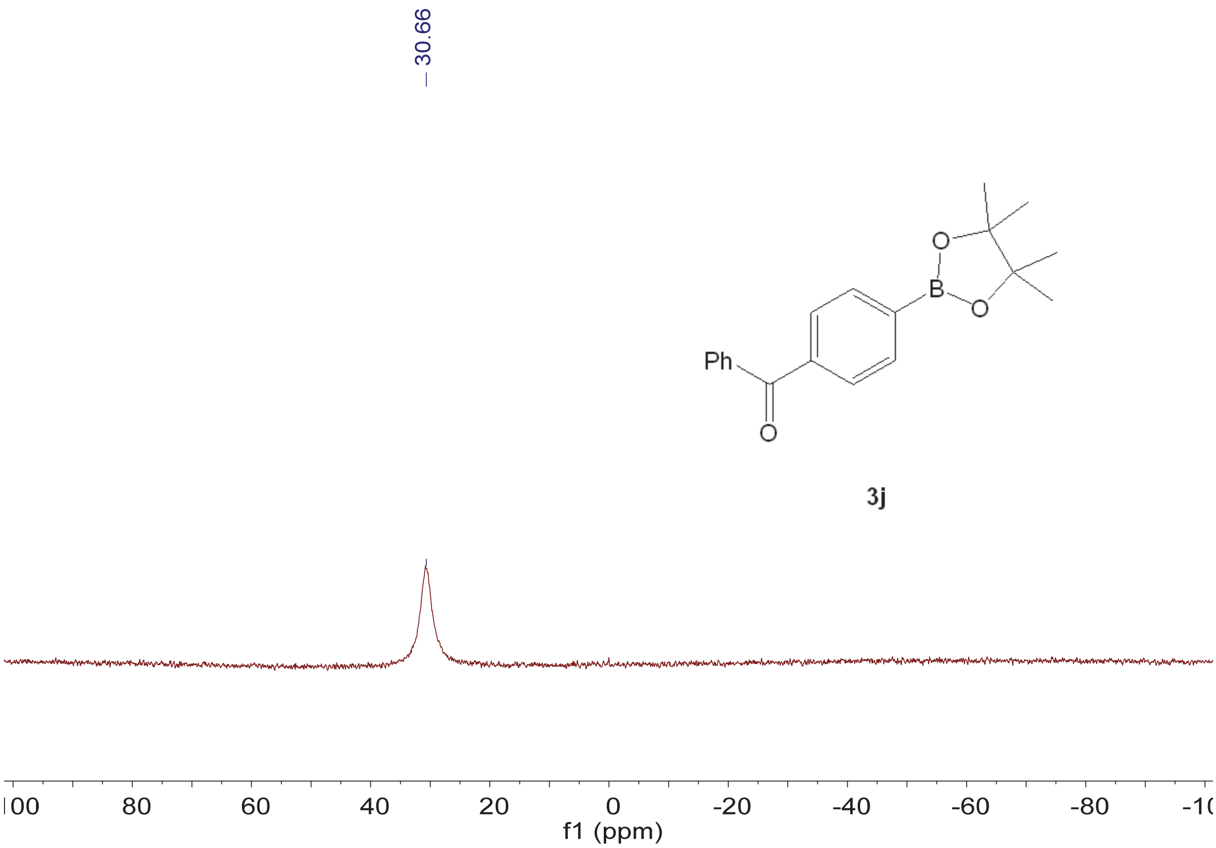

167.18
134.75
132.39
128.67
84.25
52.21
24.97
MeO
B
O
O
O
3i
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



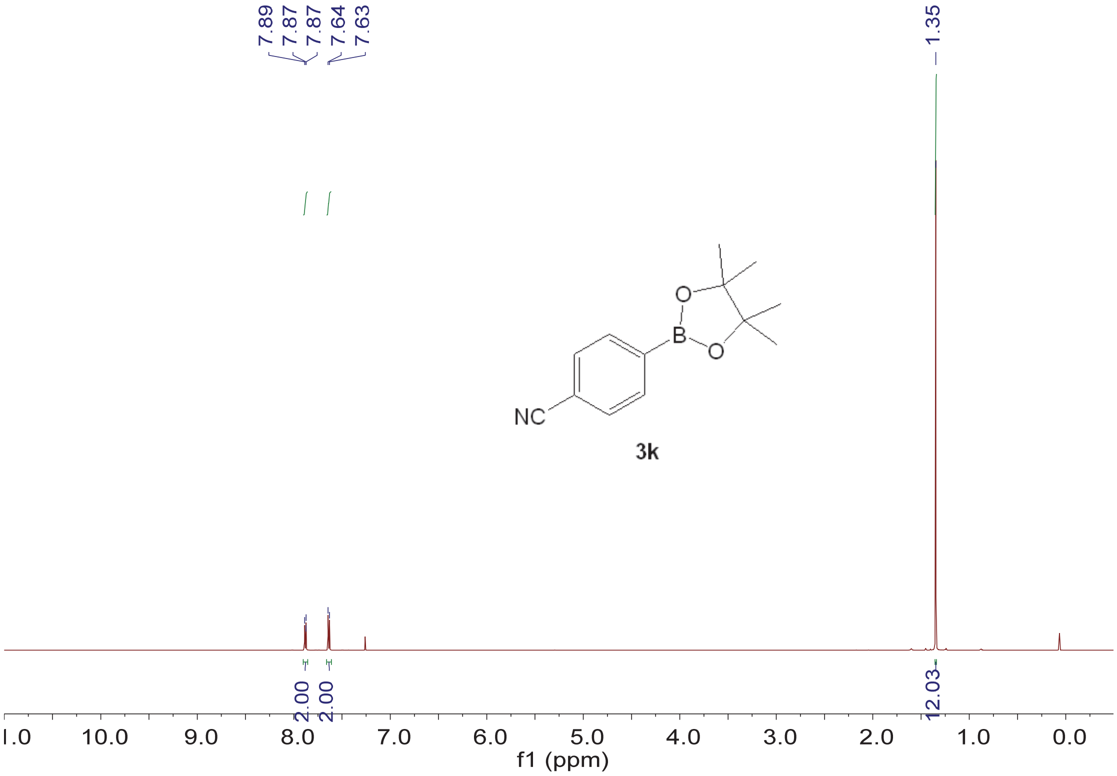
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3i** ($CDCl_3$, rt).

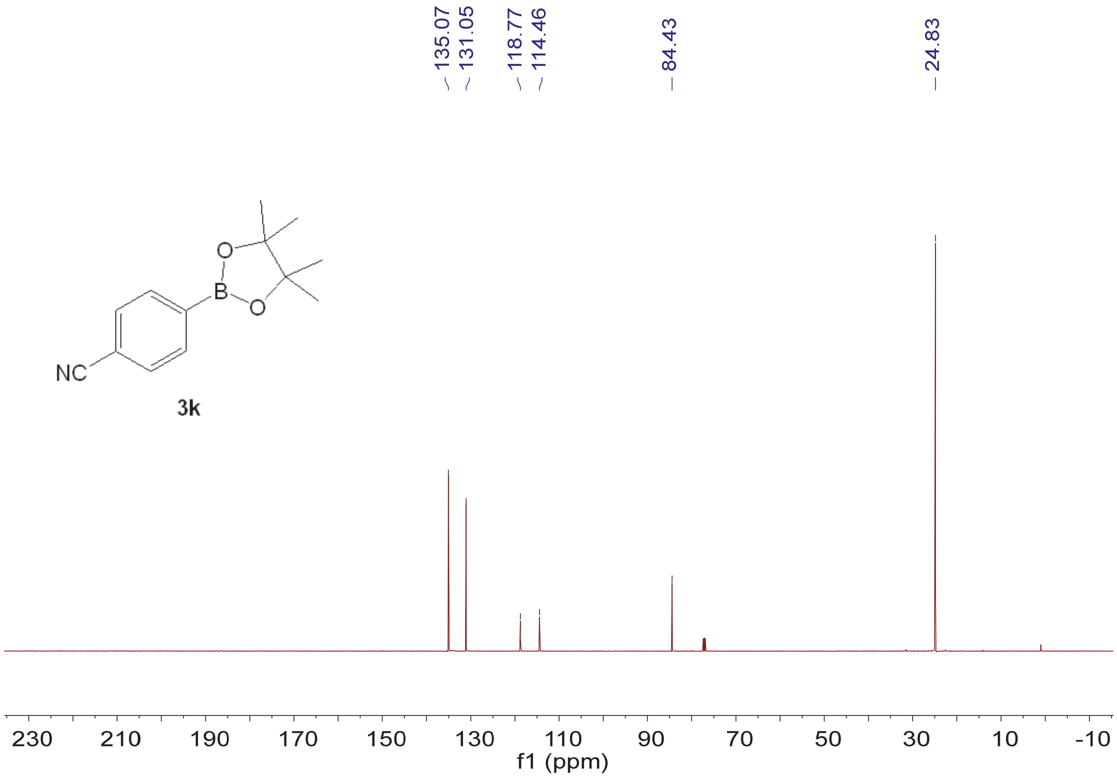






^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3j** ($CDCl_3$, rt).


7.89
7.87
7.87
7.64
7.63
1.35
NC
3k
2.00
2.00
12.03
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


135.07
131.05
118.77
114.46
84.43
24.83
NC
3k
230
210
190
170
150
130
110
90
70
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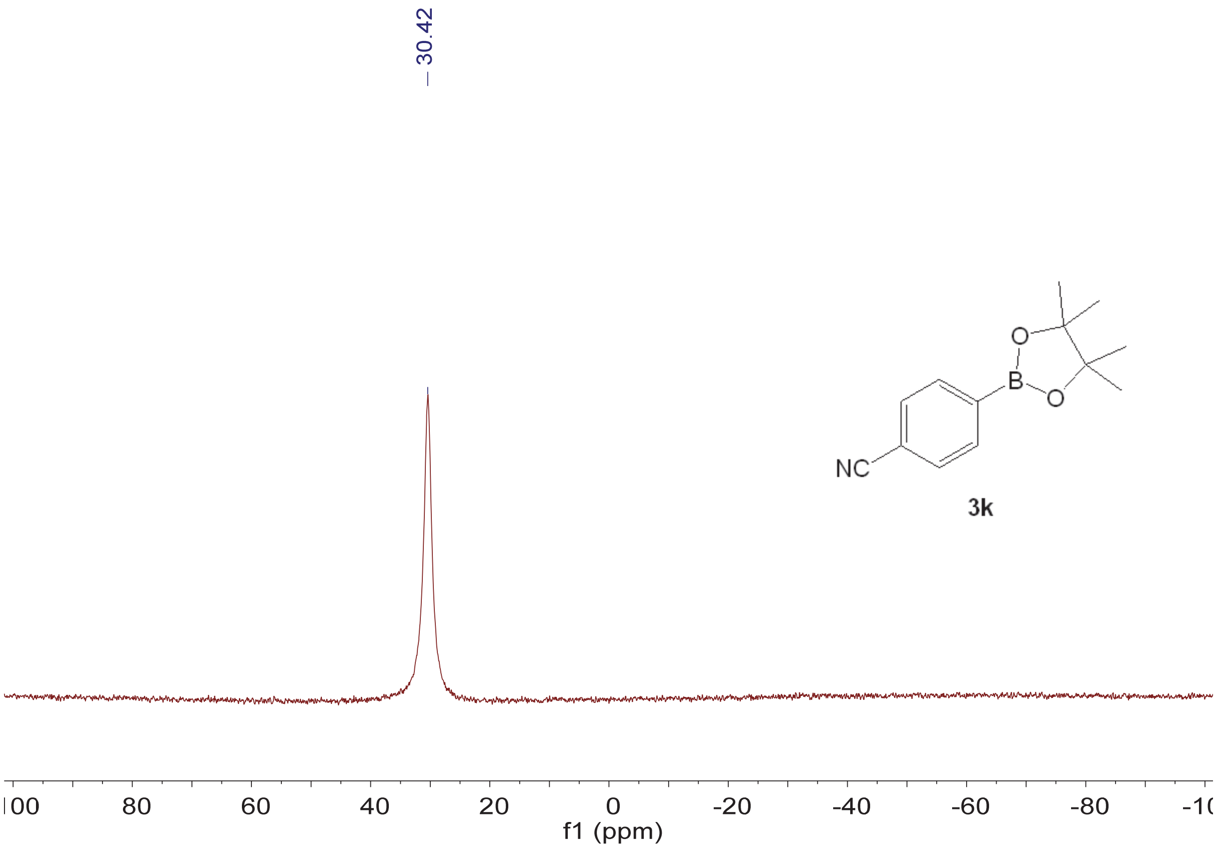
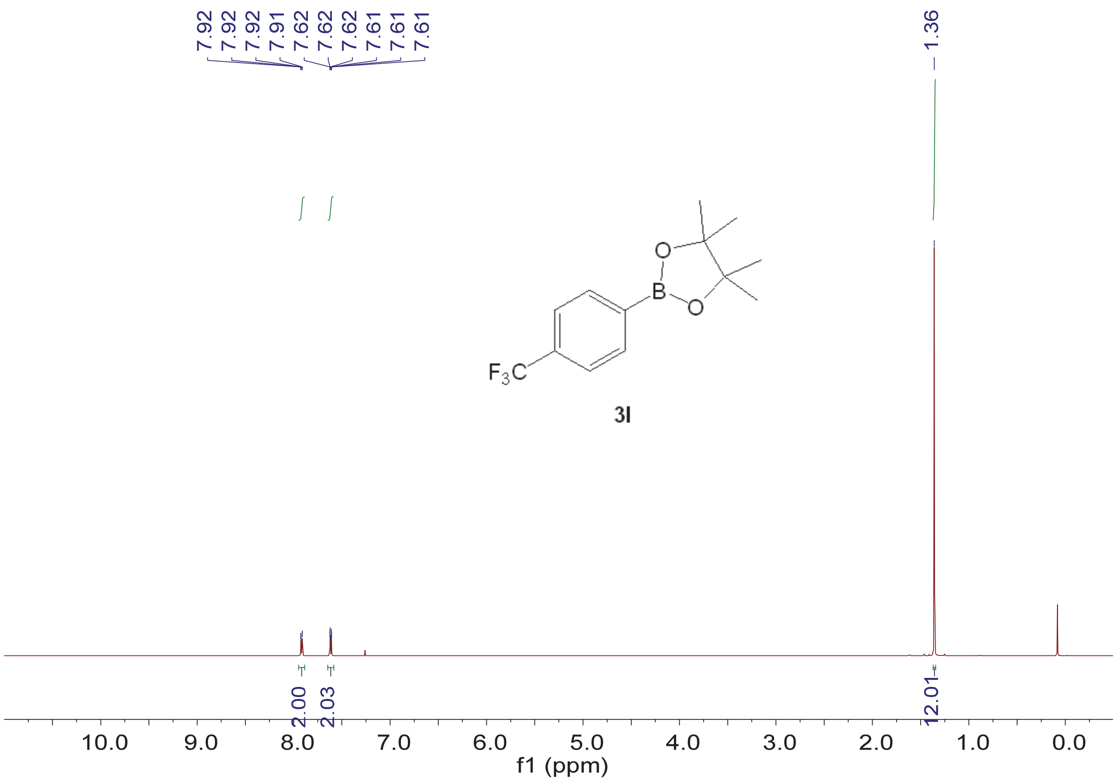
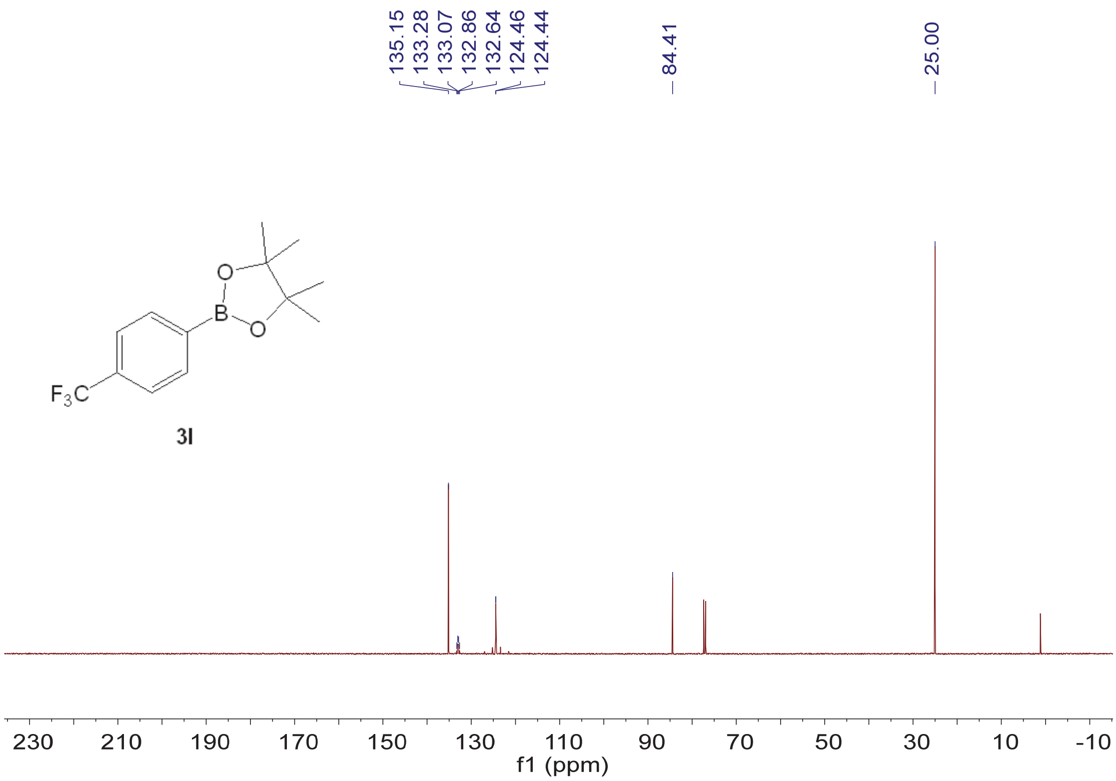
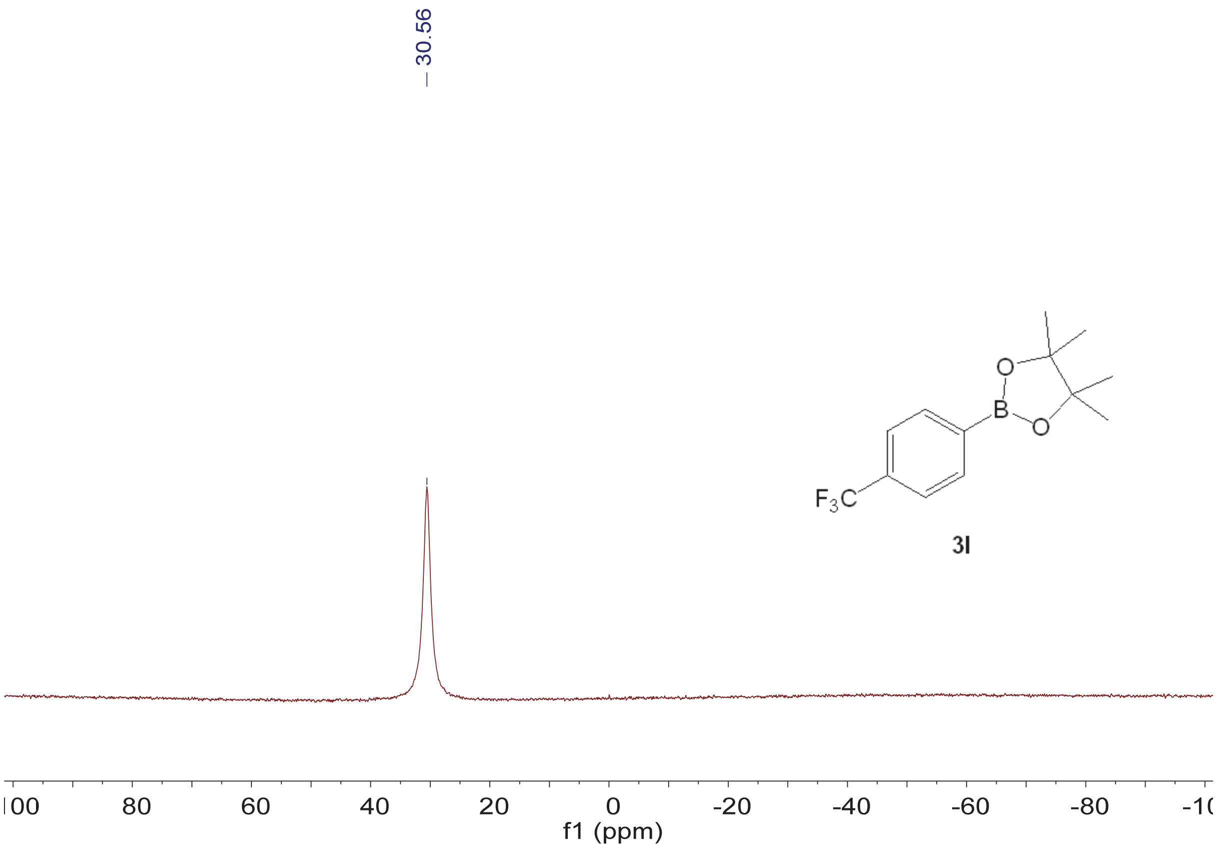
30
10
-10
f1 (ppm)



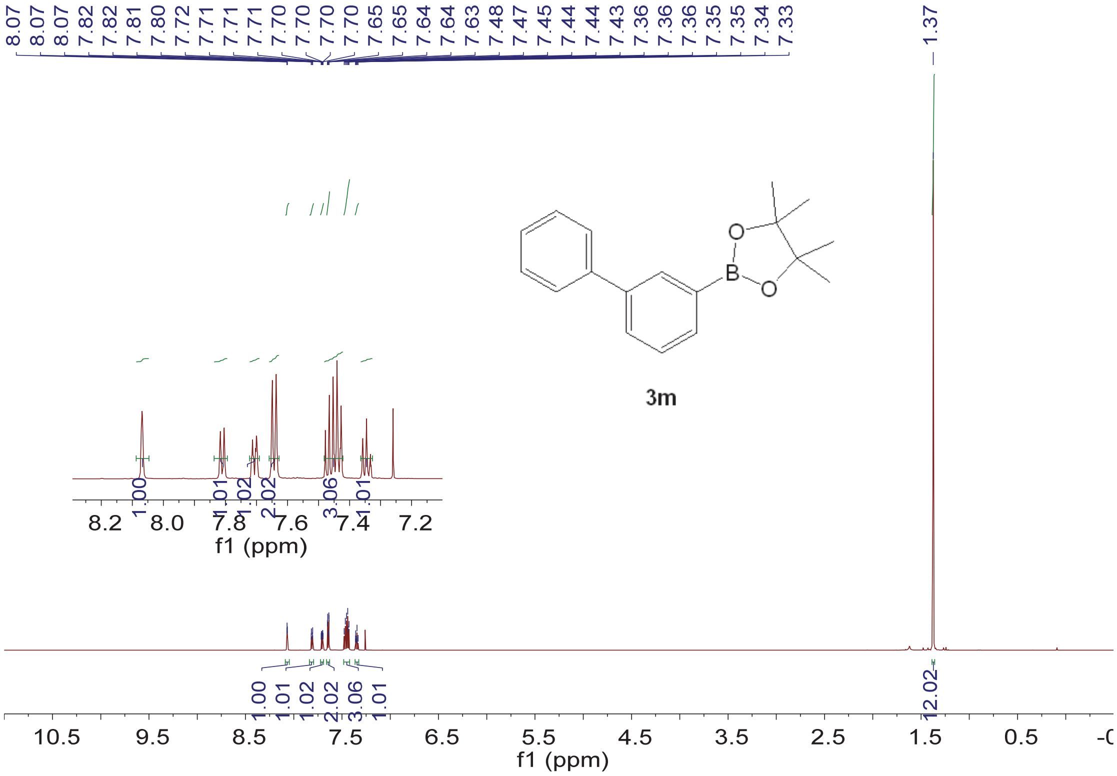
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3k** ($CDCl_3$, rt).







^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3l** ($CDCl_3$, rt).


8.07
8.07
8.07
7.82
7.82
7.81
7.80
7.72
7.71
7.71
7.71
7.70
7.70
7.70
7.70
7.65
7.65
7.64
7.64
7.63
7.48
7.47
7.45
7.44
7.44
7.43
7.36
7.36
7.36
7.35
7.35
7.34
7.33
1.37
3m
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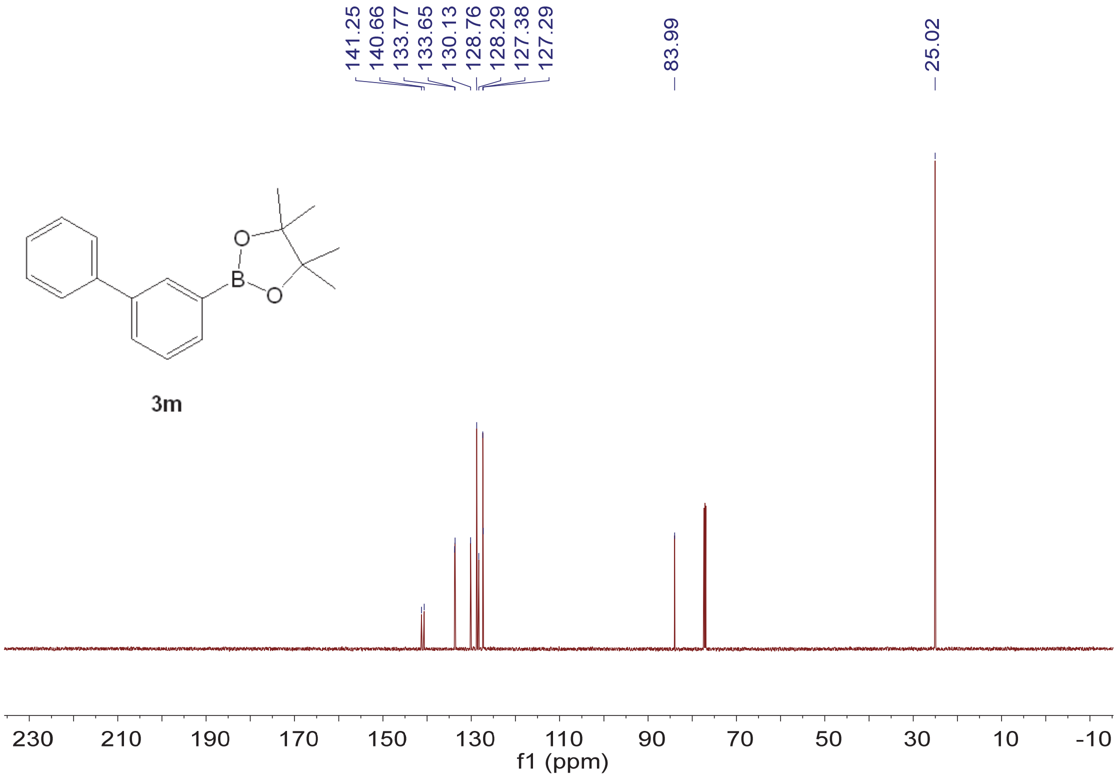
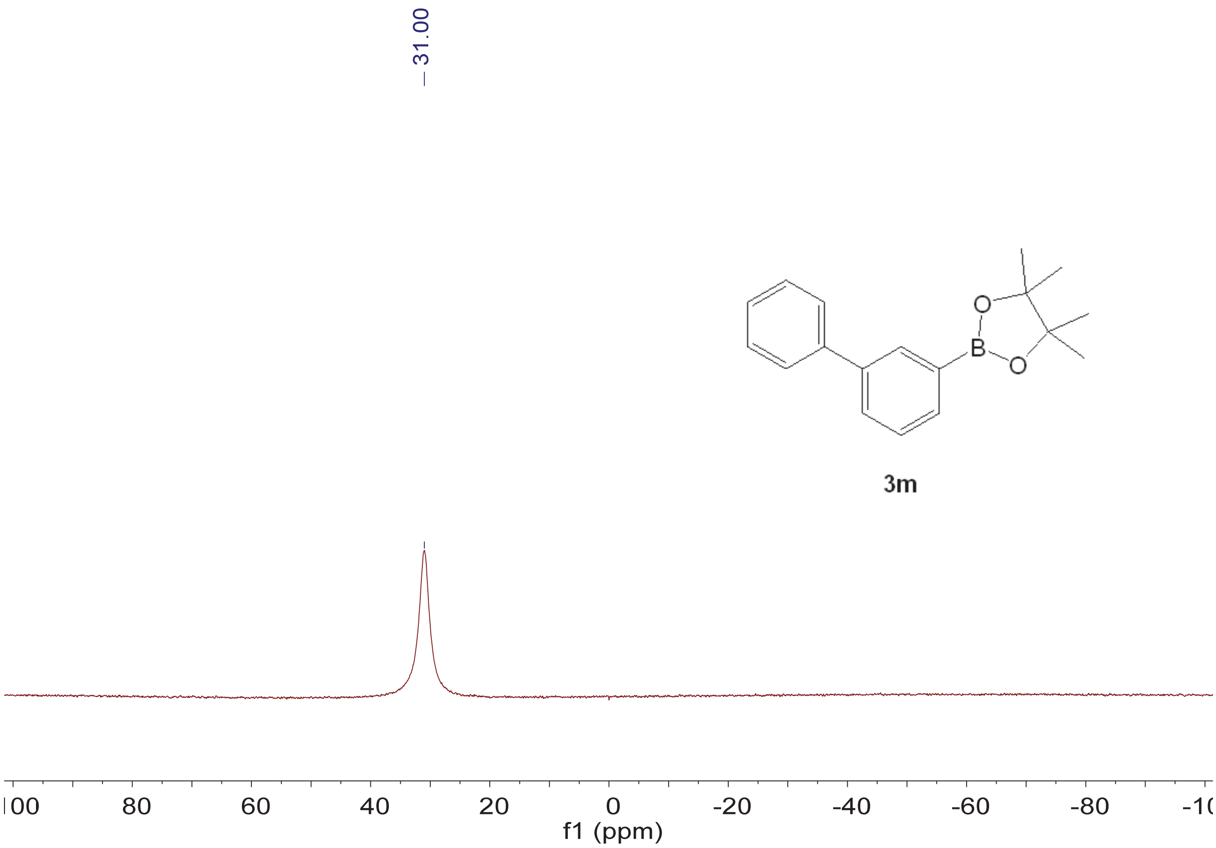
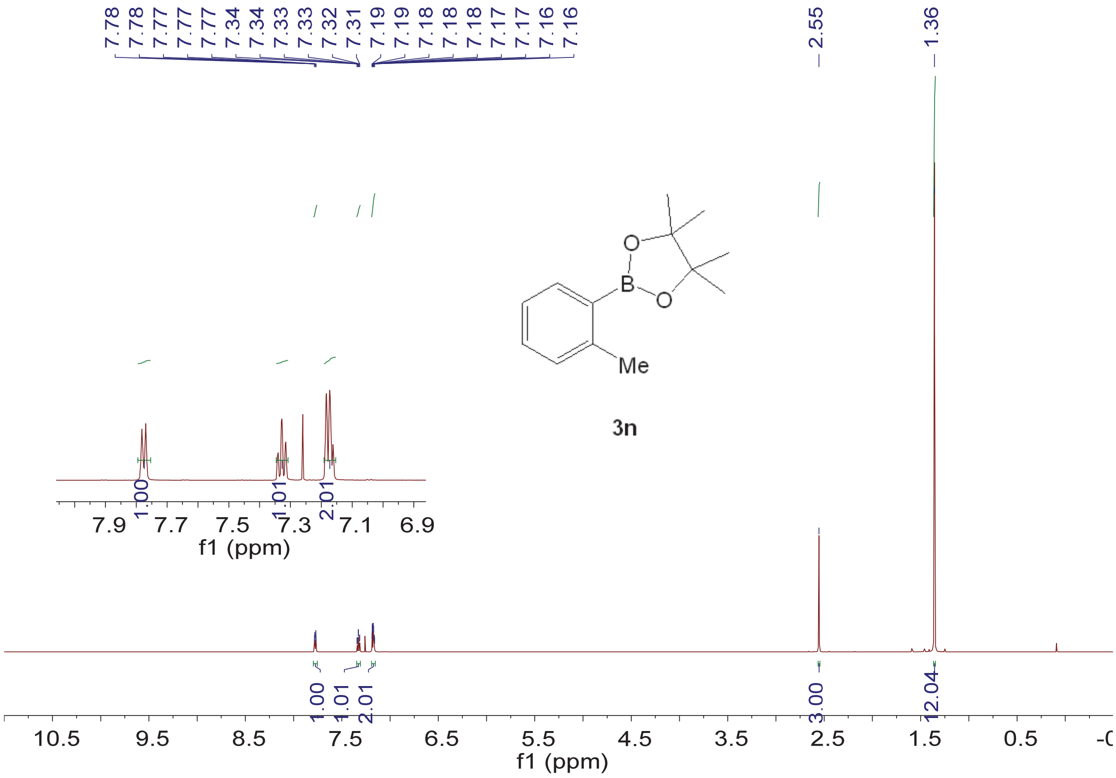
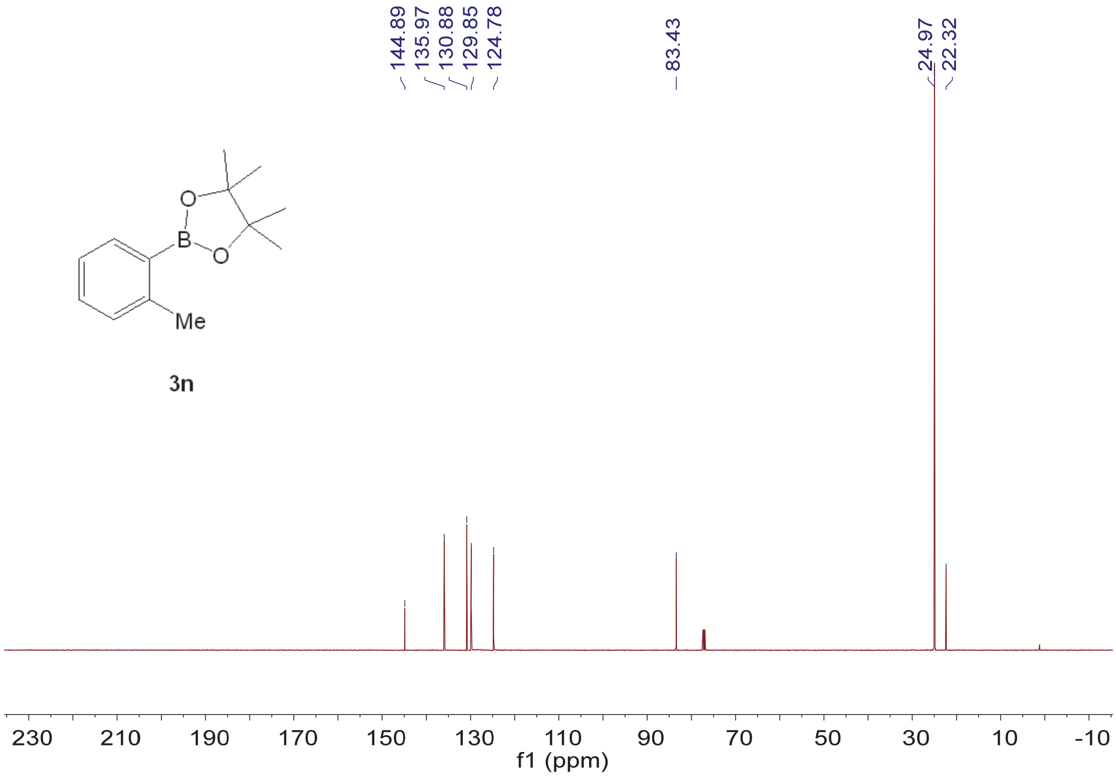
1.01
1.02
2.02
3.06
1.01
12.02
f1 (ppm)


141.25
140.66
133.77
133.65
130.13
128.76
128.29
127.38
127.29
83.99
25.02
3m
f1 (ppm)

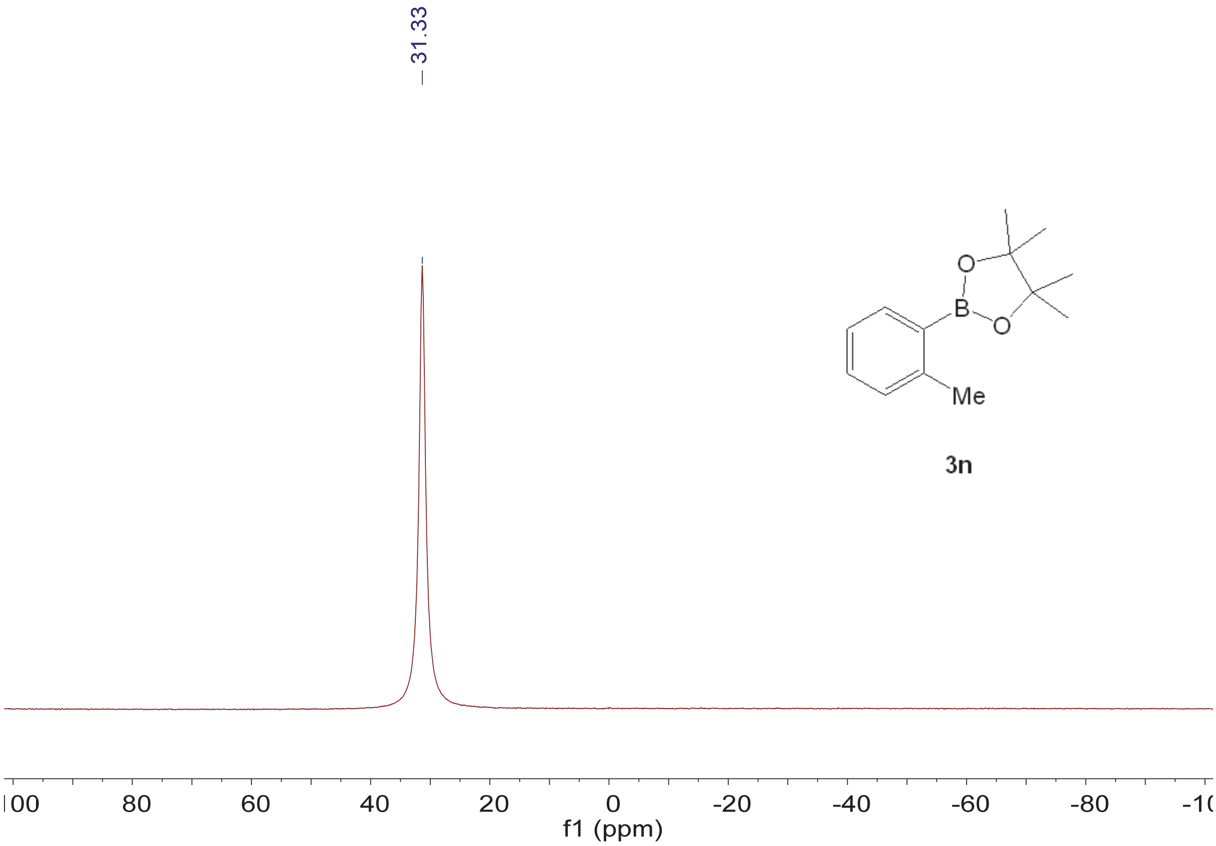


[1]H NMR (600 MHz), [13]C{[1]H} NMR (151 MHz) and [11]B{[1]H} NMR (192 MHz) spectra of **3m** ($CDCl_3$, rt).



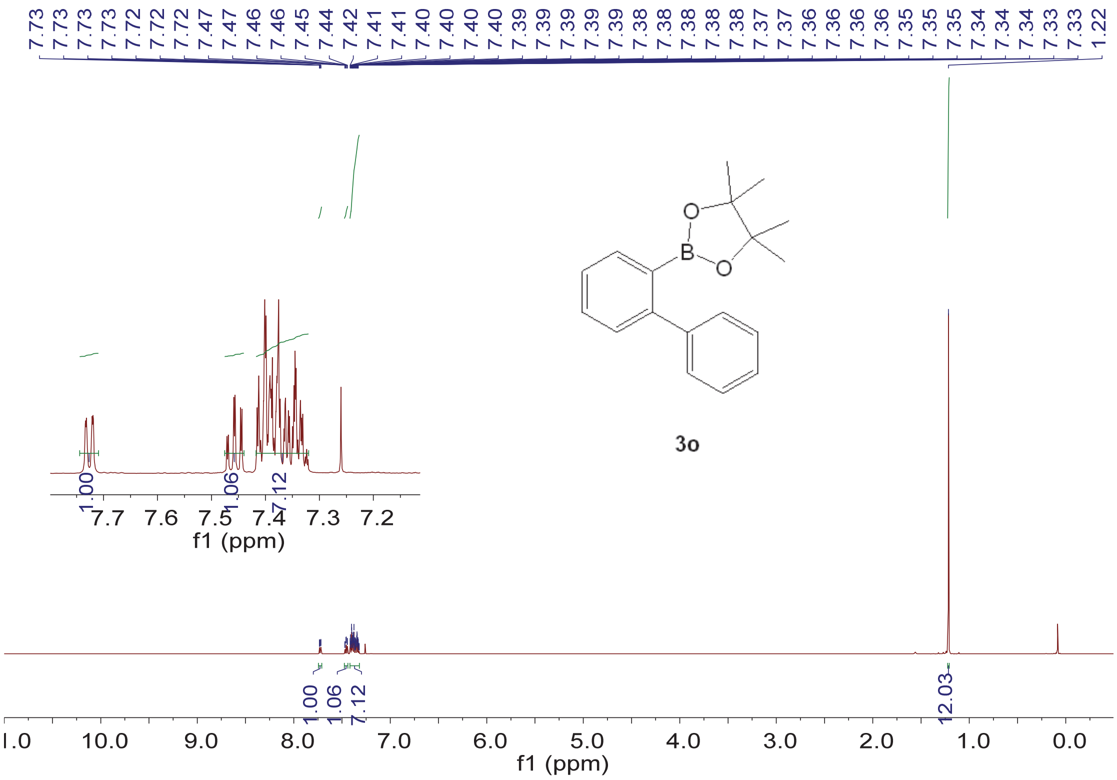

144.89
135.97
130.88
129.85
124.78
83.43
24.97
22.32
230 210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

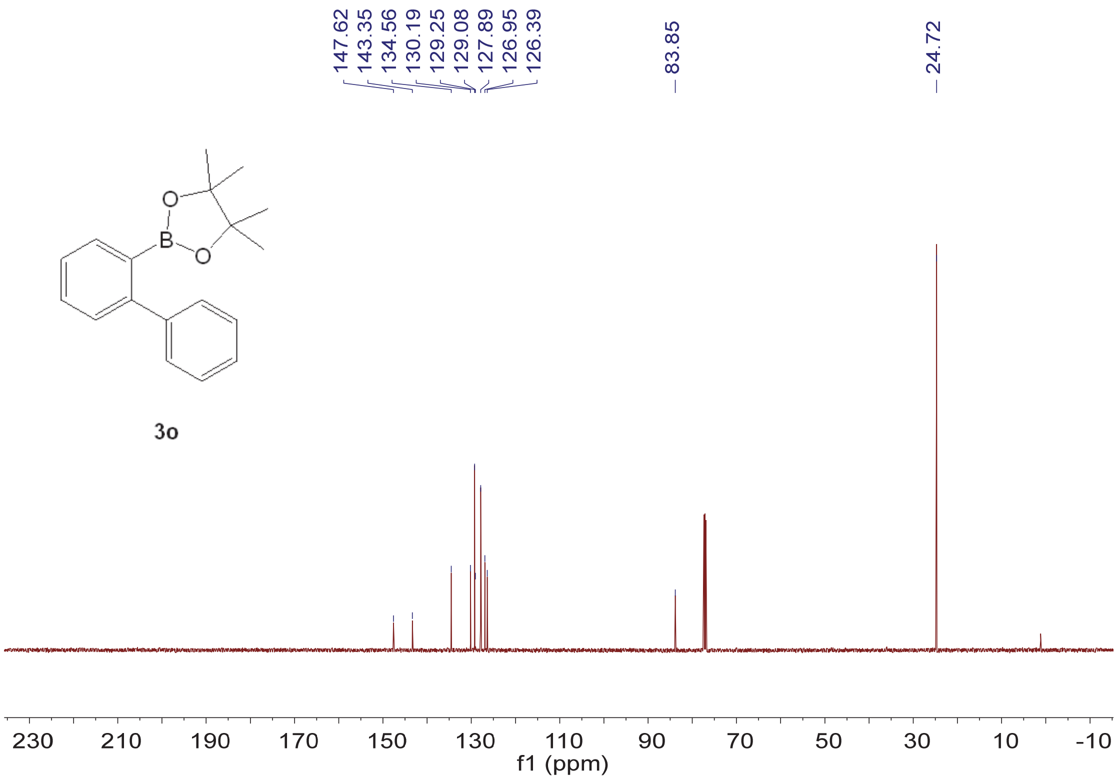
3n

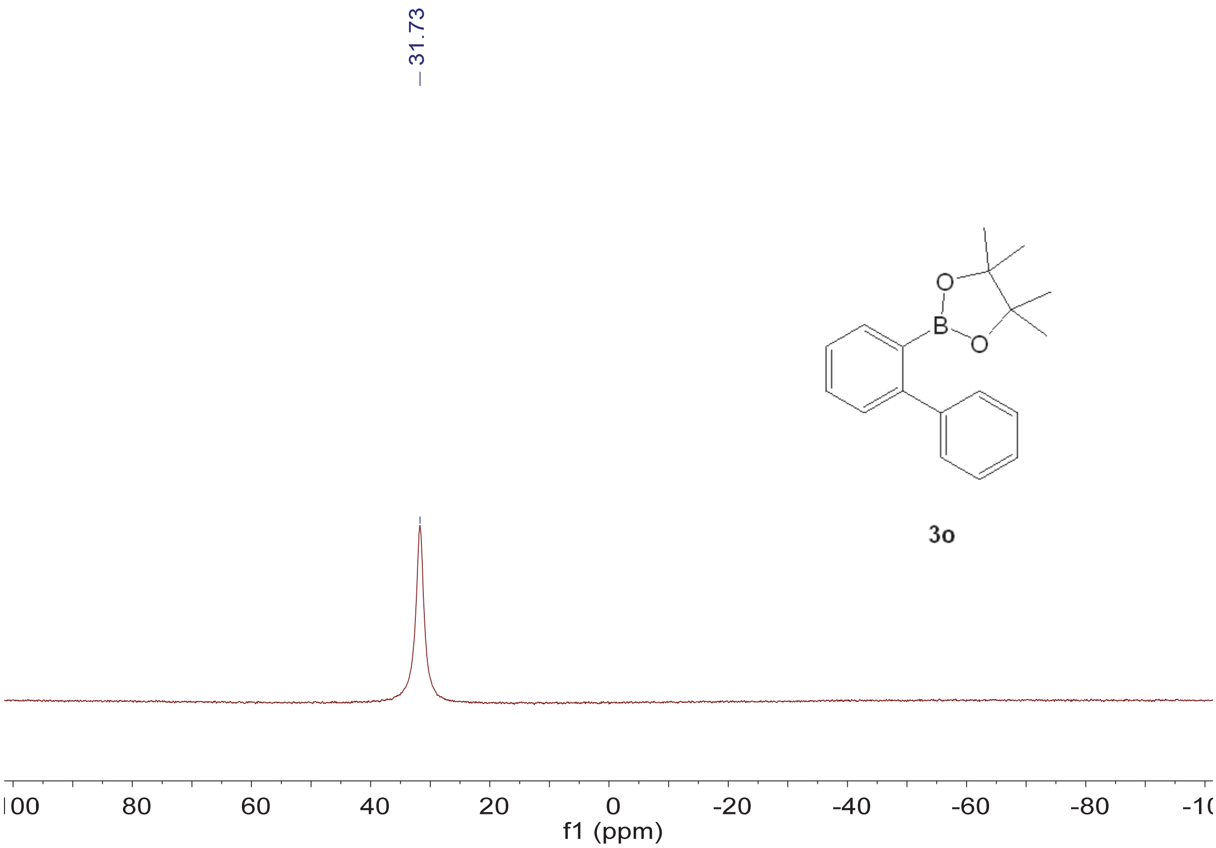

31.33
100 80 60 40 20 0 -20 -40 -60 -80 -100
f1 (ppm)

3n

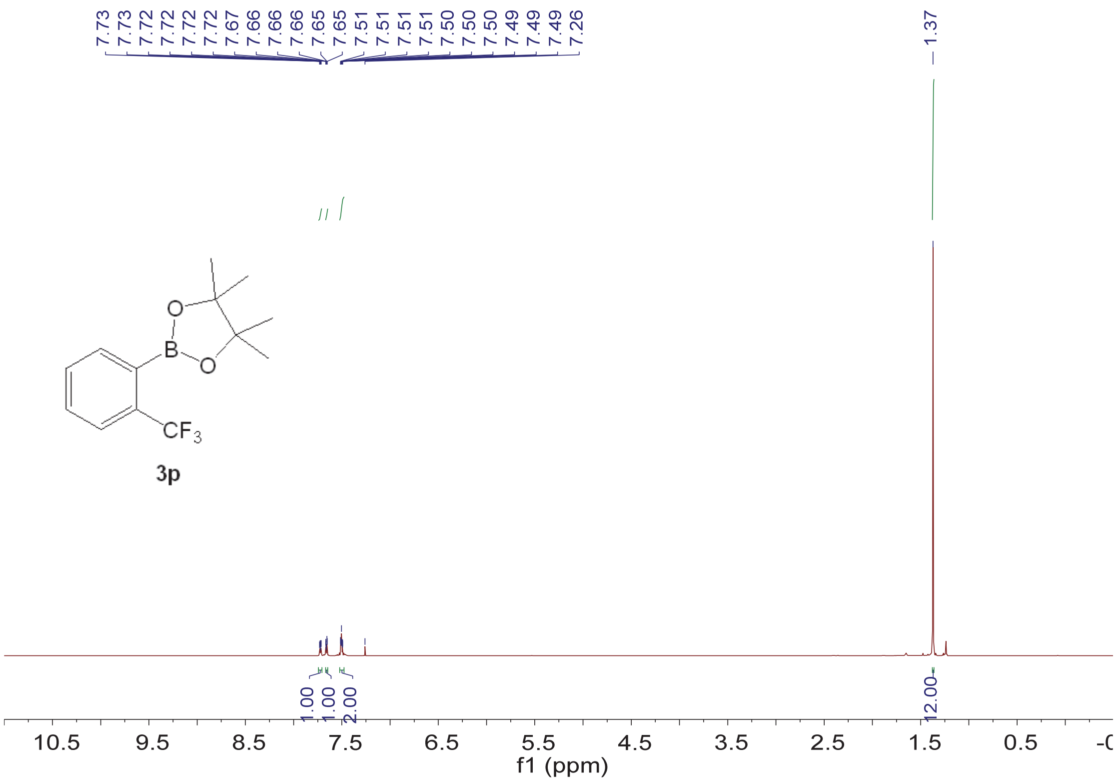
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3n** ($CDCl_3$, rt).

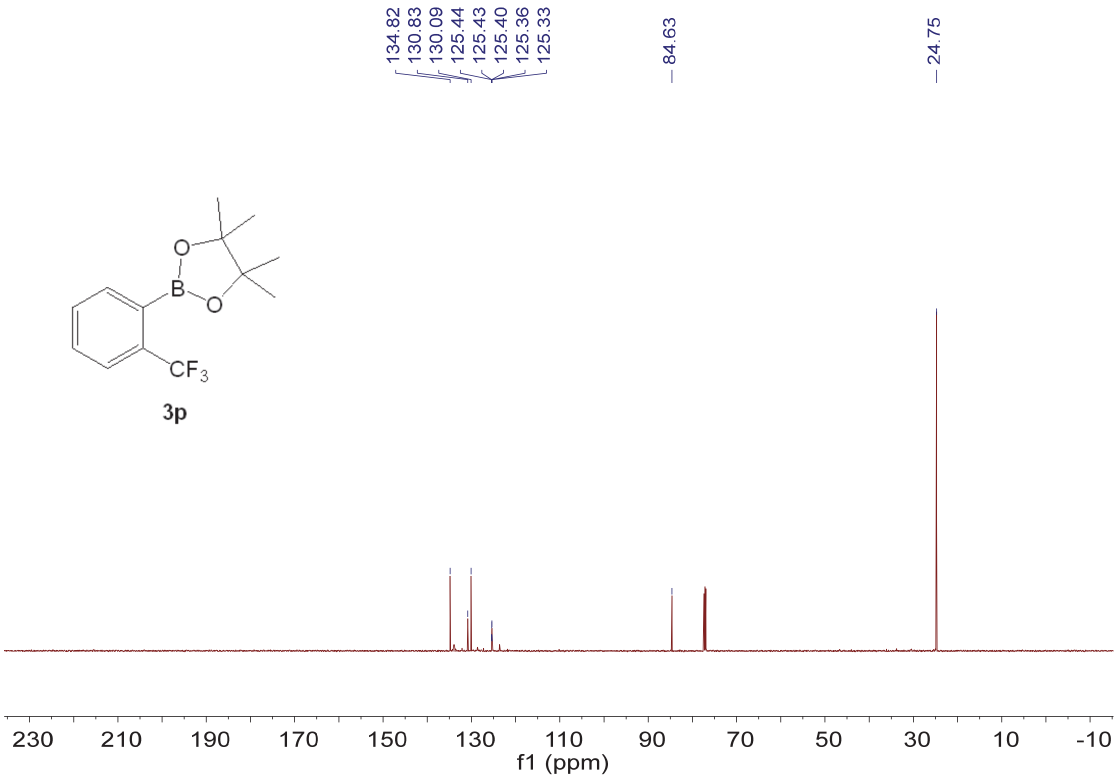


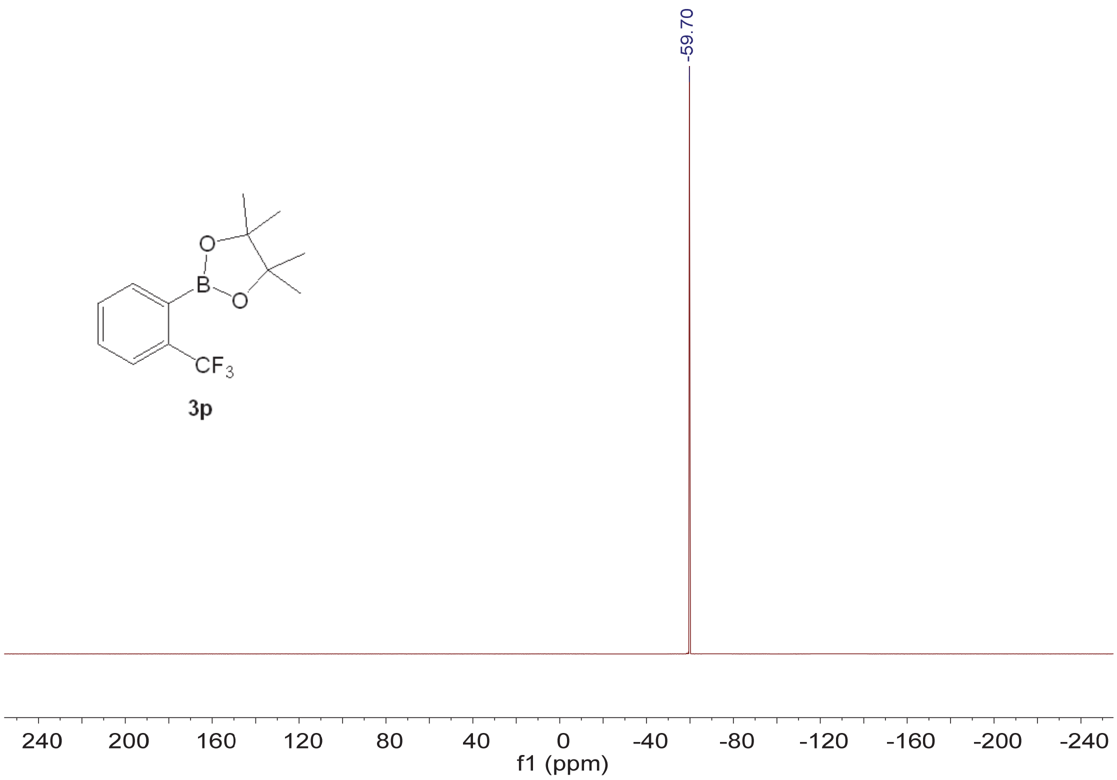


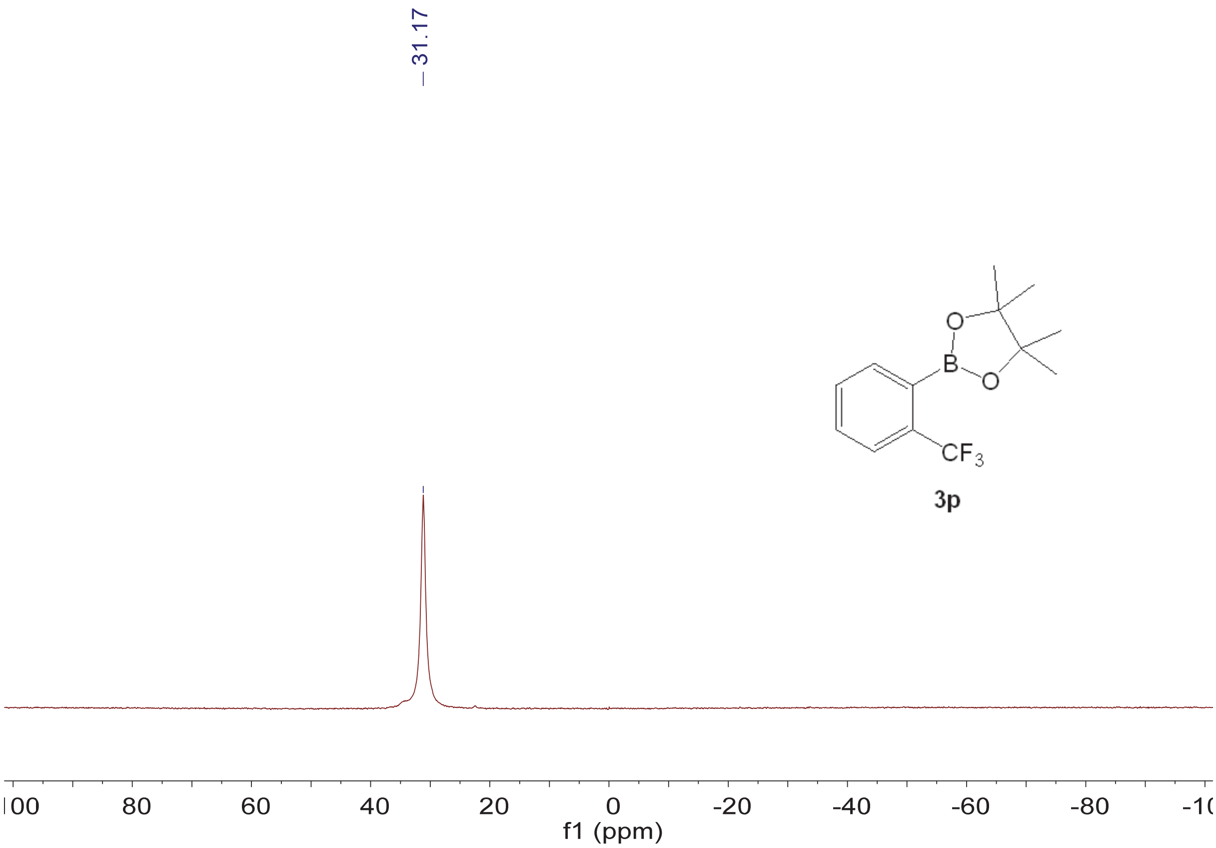


^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3o** ($CDCl_3$, rt).

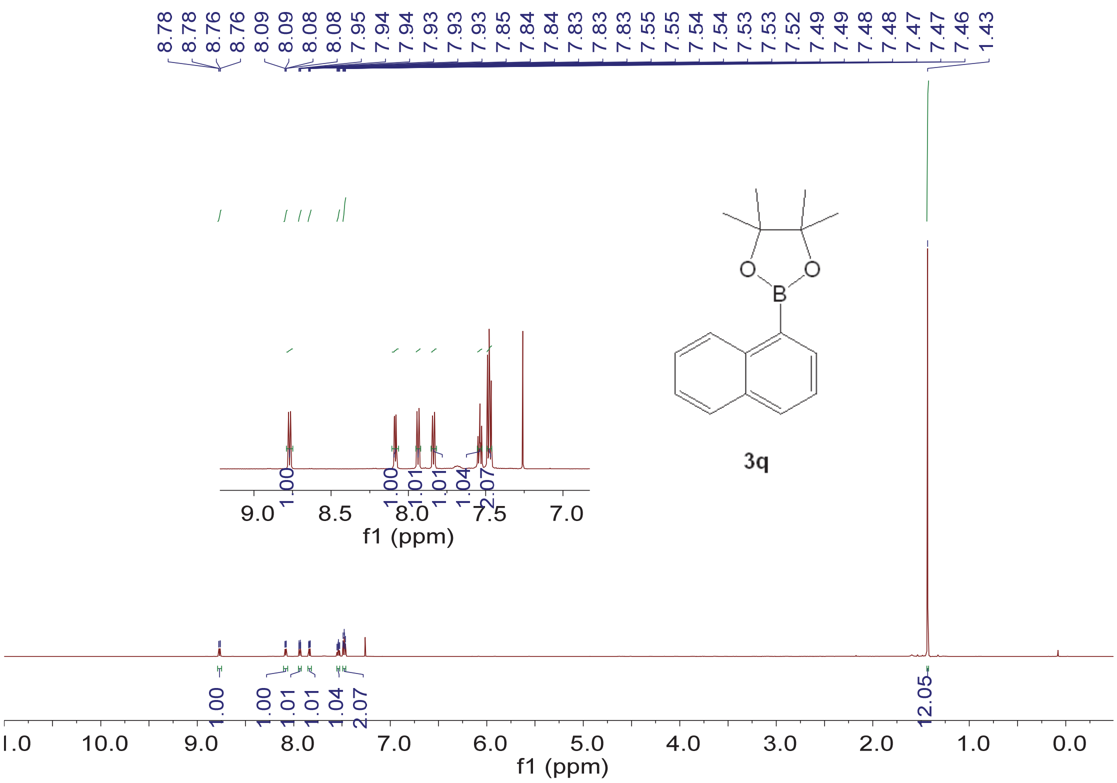


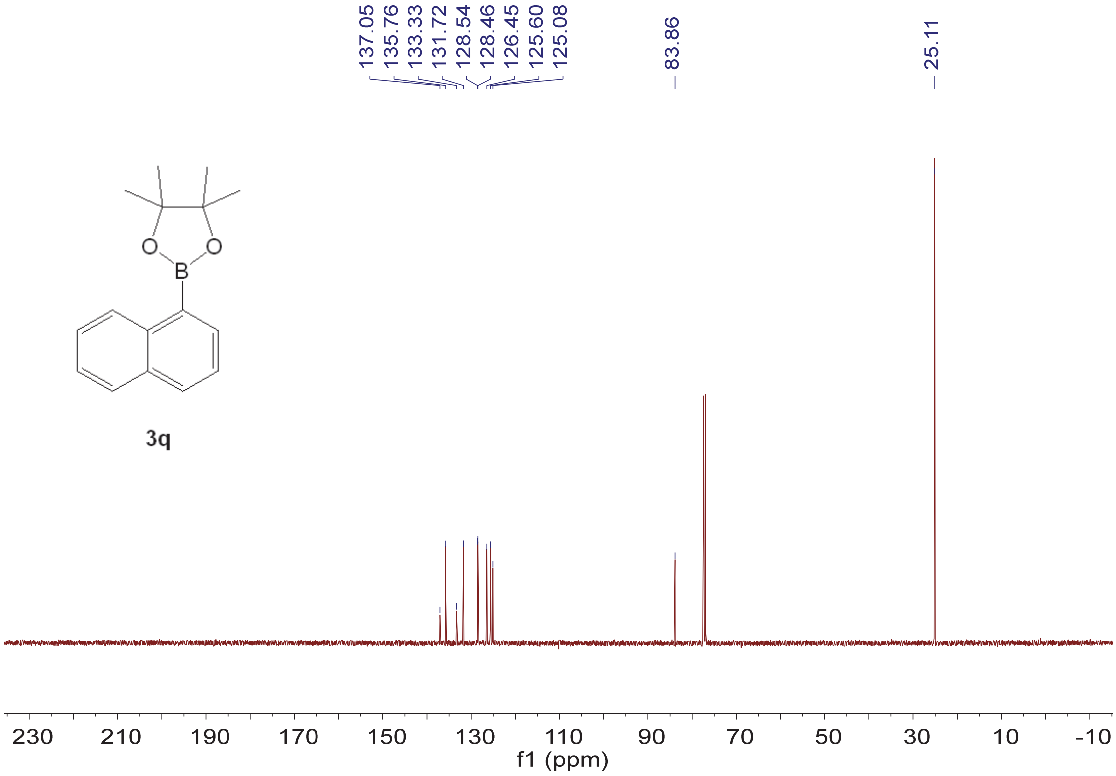

134.82
130.83
130.09
125.44
125.43
125.40
125.36
125.33
84.63
24.75
O
B
O
CF3
3p
230 210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

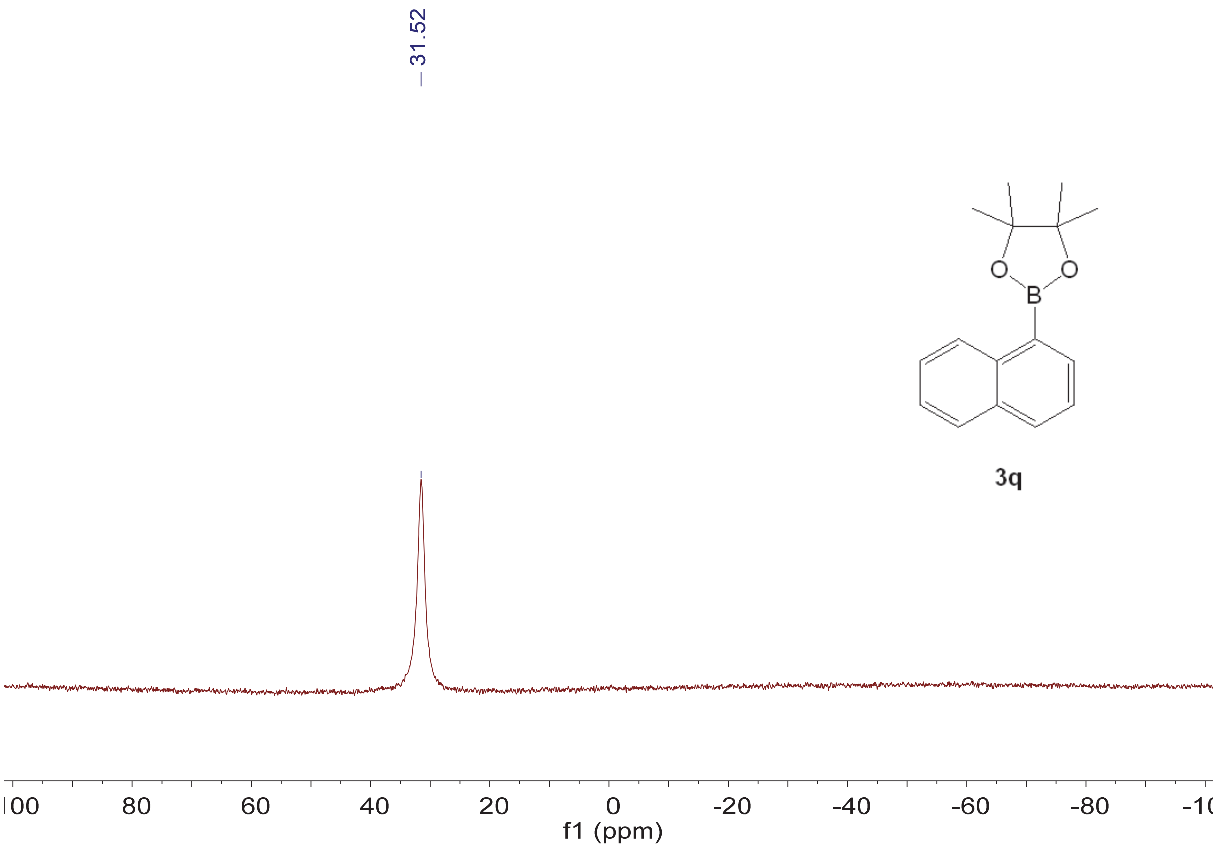

-59.70
O
B
O
CF3
3p
240 200 160 120 80 40 0 -40 -80 -120 -160 -200 -240
f1 (ppm)



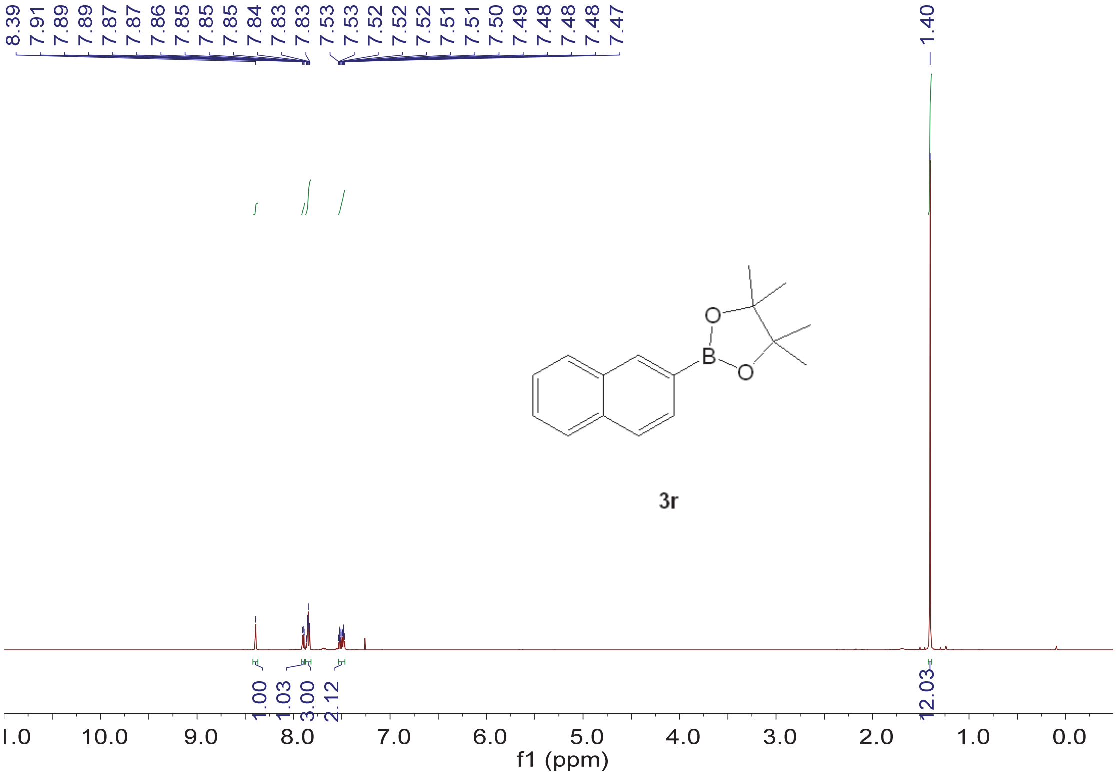
[1]H NMR (600 MHz), [13]C{[1]H} NMR (151 MHz), [19]F{[1]H} NMR (376 MHz) and [11]B{[1]H} NMR (192 MHz) spectra of **3p** ($CDCl_3$, rt).







^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3q** ($CDCl_3$, rt).


8.39
7.91
7.89
7.89
7.87
7.87
7.86
7.85
7.85
7.85
7.84
7.83
7.83
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.48
7.47
1.40
3r
1.00
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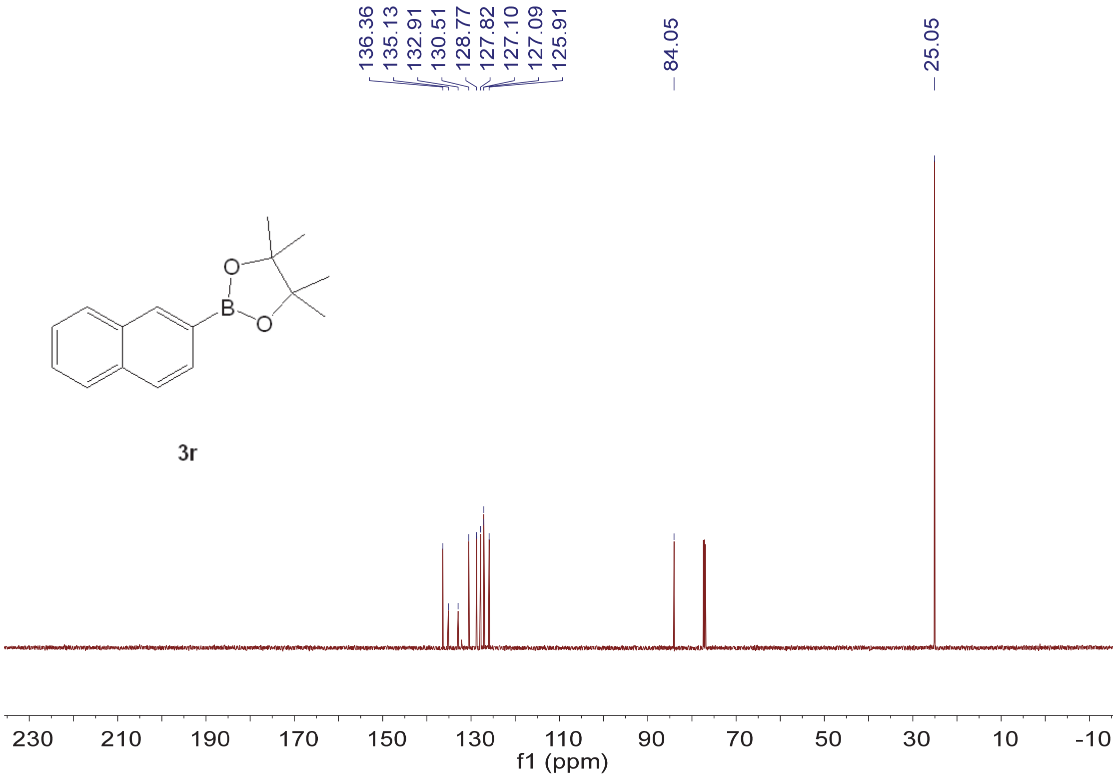
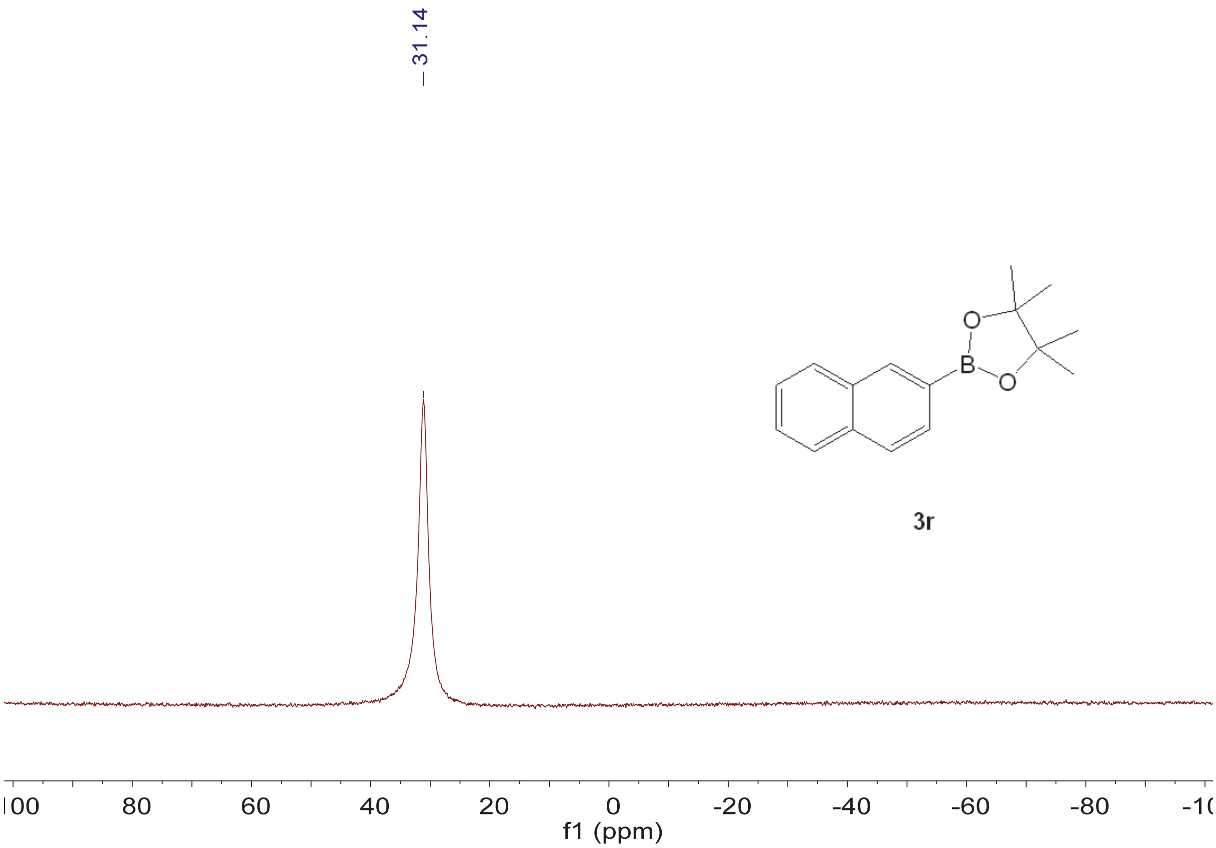
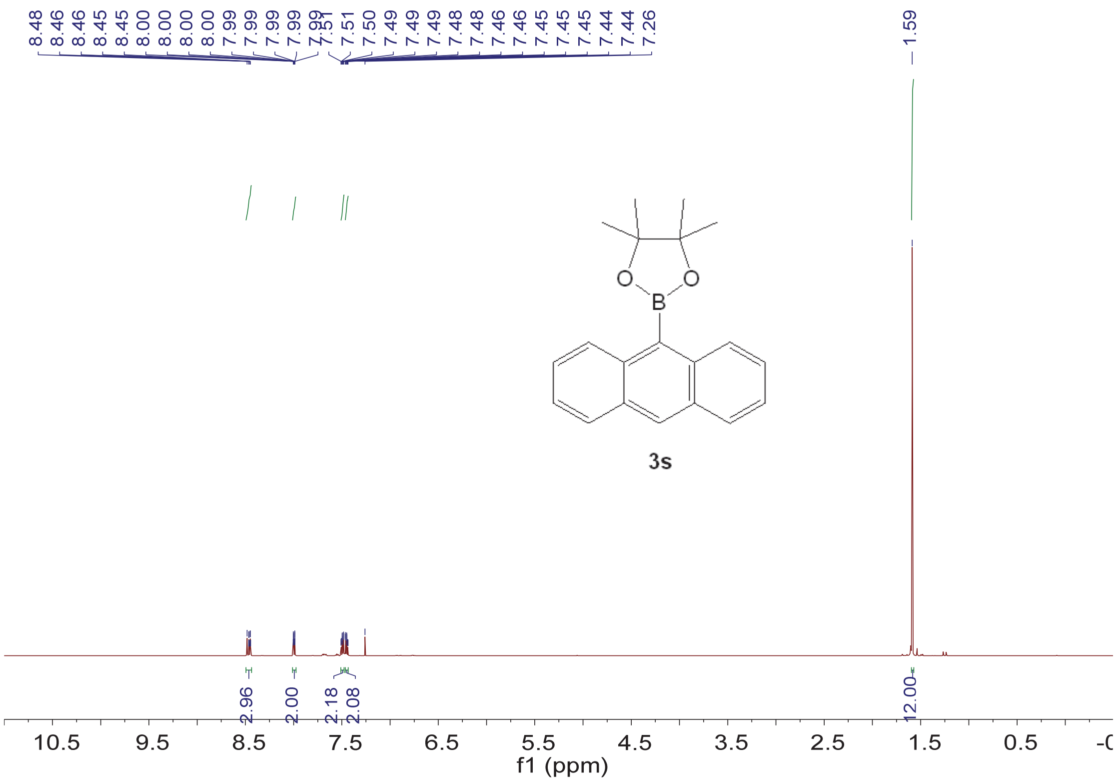
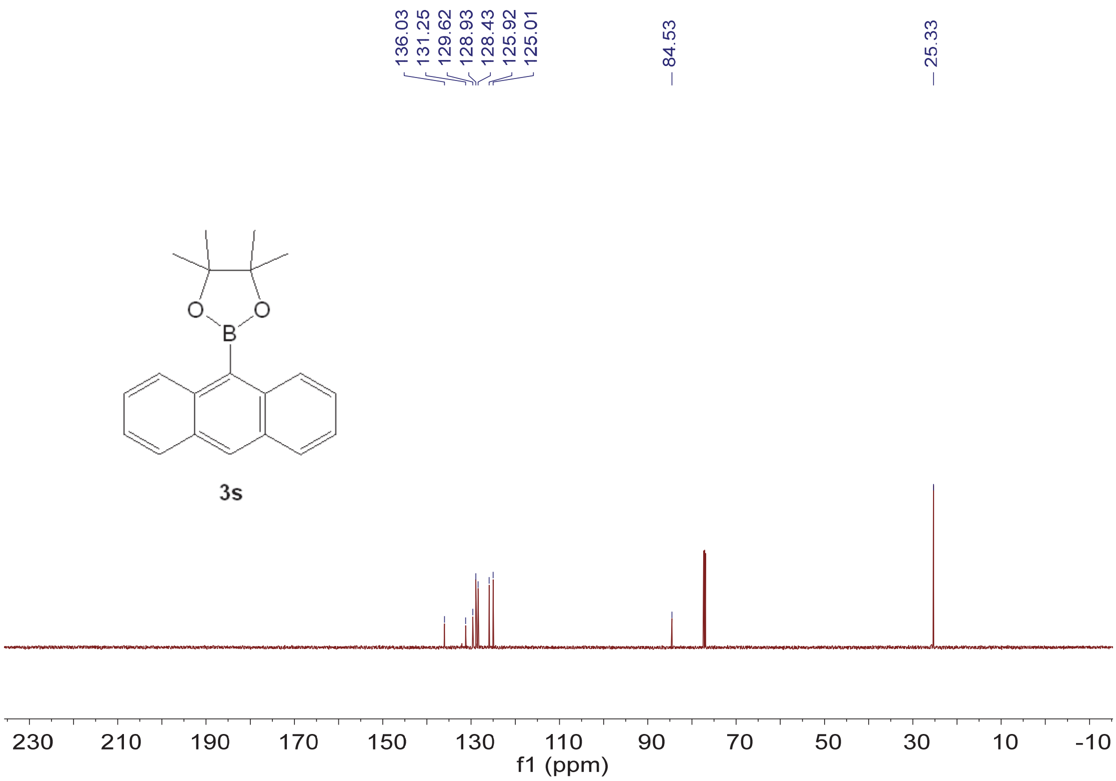
2.12
12.03
f1 (ppm)

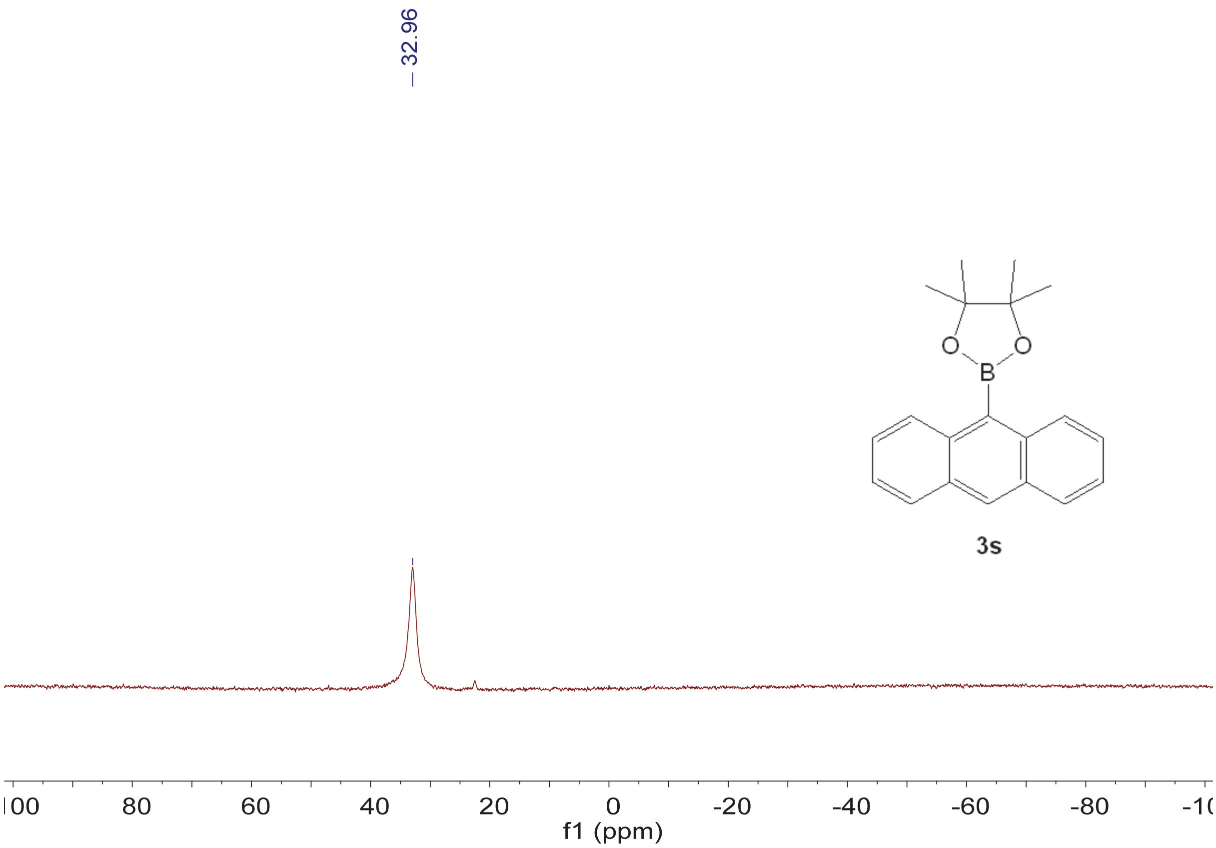

136.36
135.13
132.91
130.51
128.77
127.82
127.10
127.09
125.91
84.05
25.05
3r
f1 (ppm)



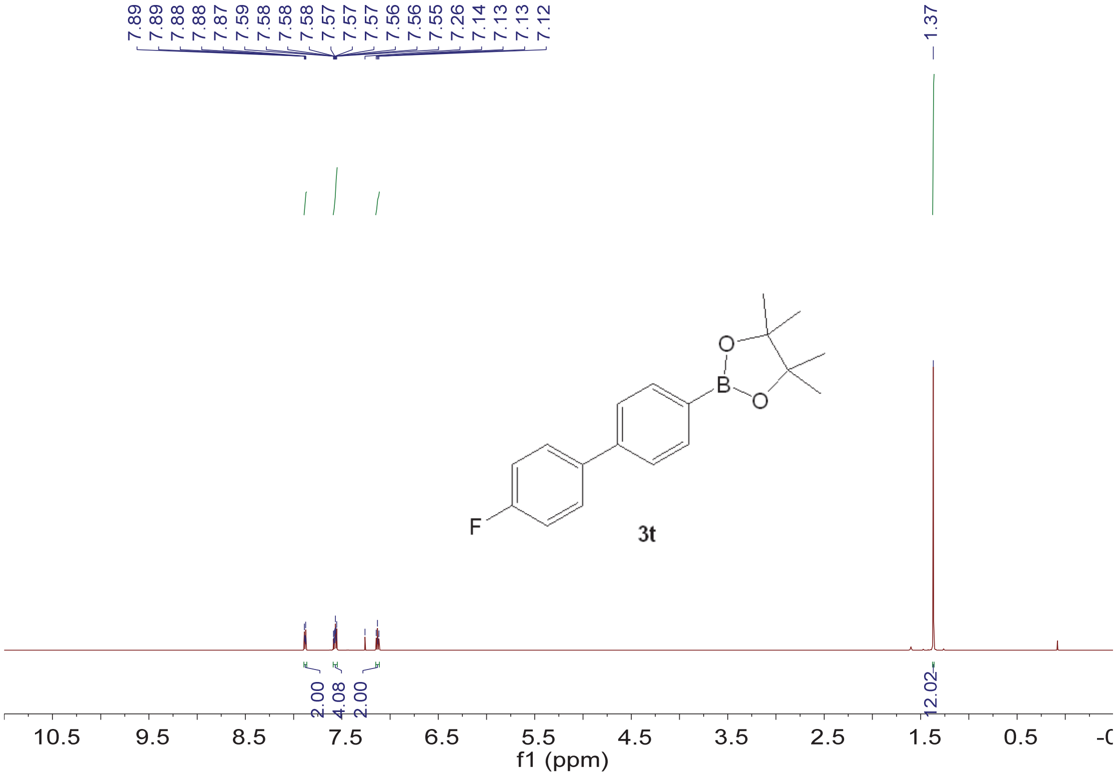
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3r** ($CDCl_3$, rt).

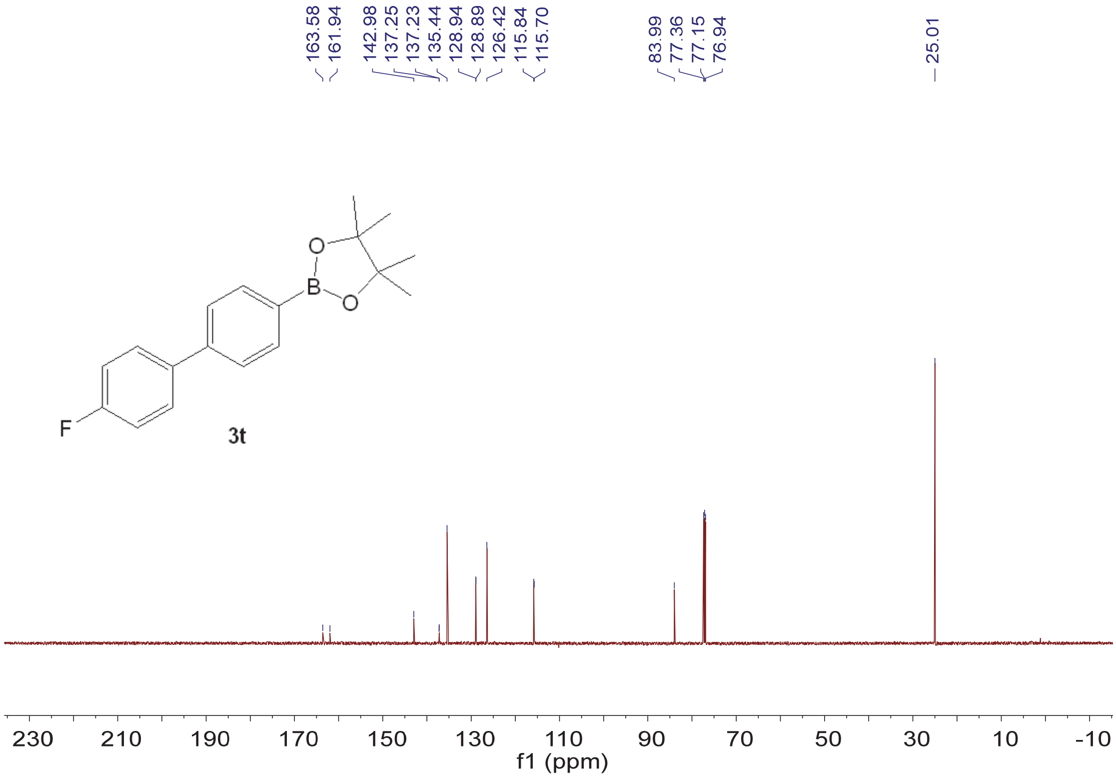


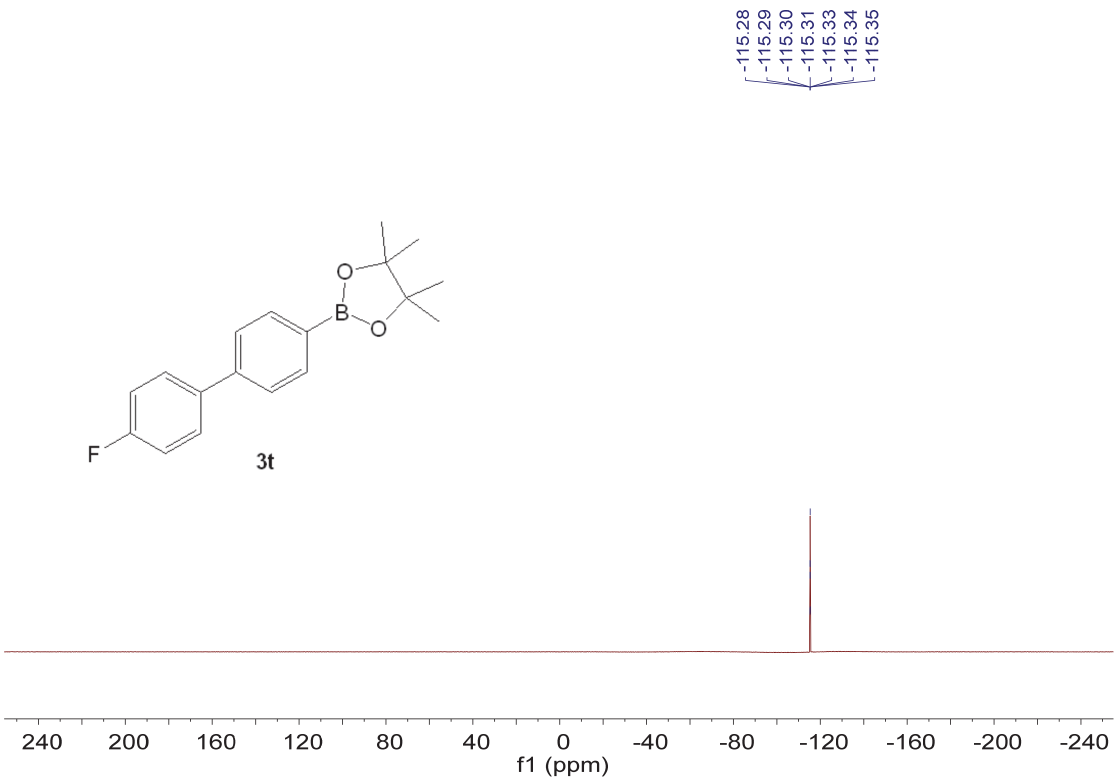


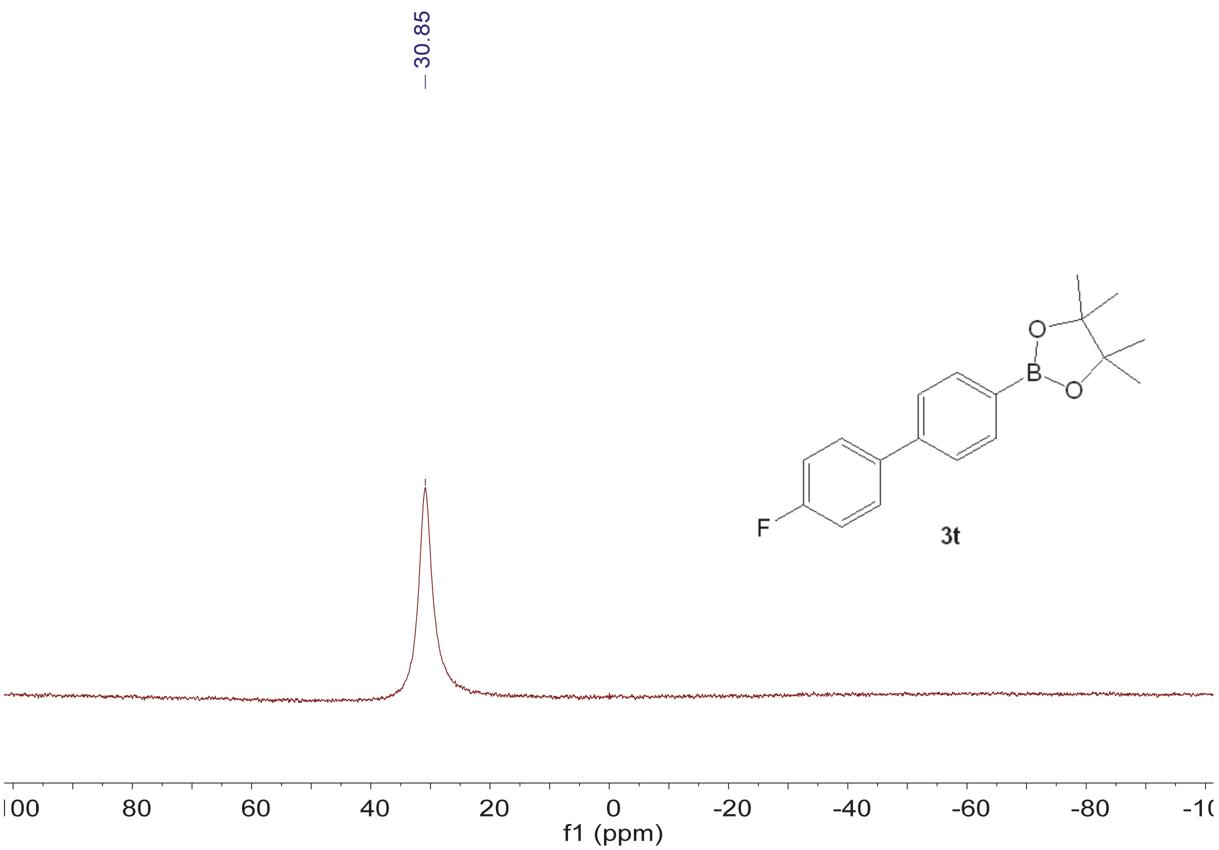


^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **3s** ($CDCl_3$, rt).

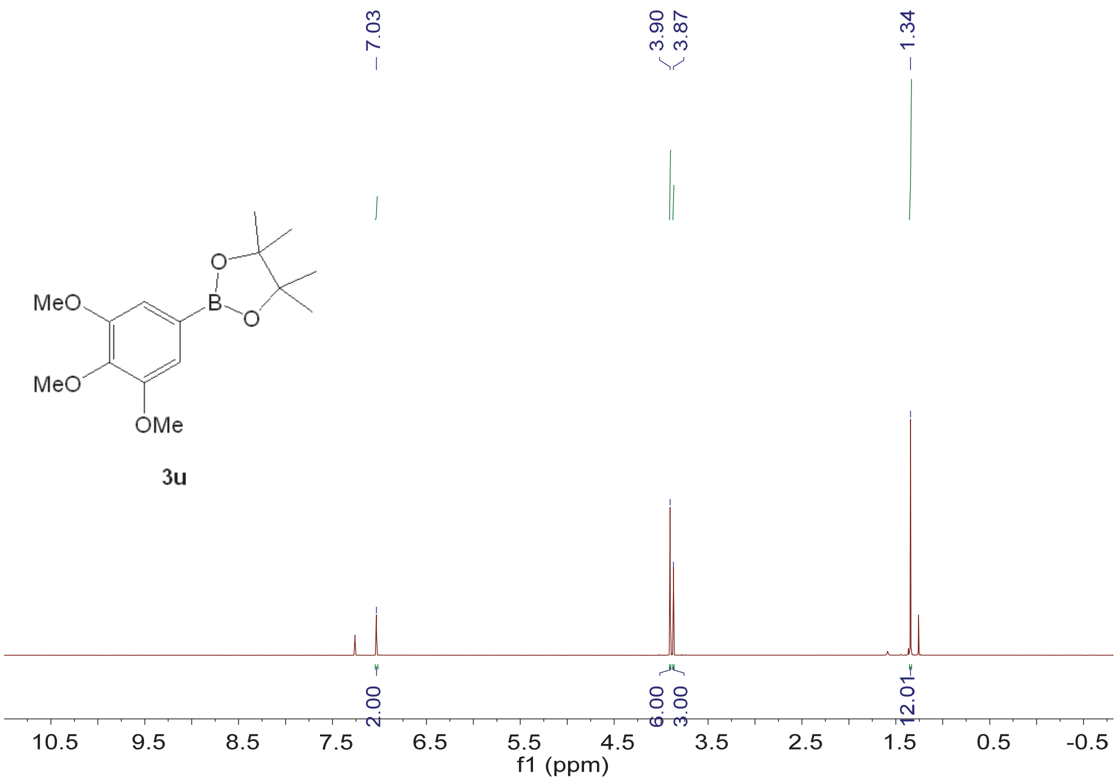

7.89 7.89 7.88 7.88 7.87 7.59 7.58 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.55 7.26 7.14 7.13 7.13 7.12
1.37
3t
2.00 4.08 2.00
12.02
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


163.58 161.94 142.98 137.25 137.23 135.44 128.94 128.89 126.42 115.84 115.70
83.99 77.36 77.15 76.94
25.01
3t
230 210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

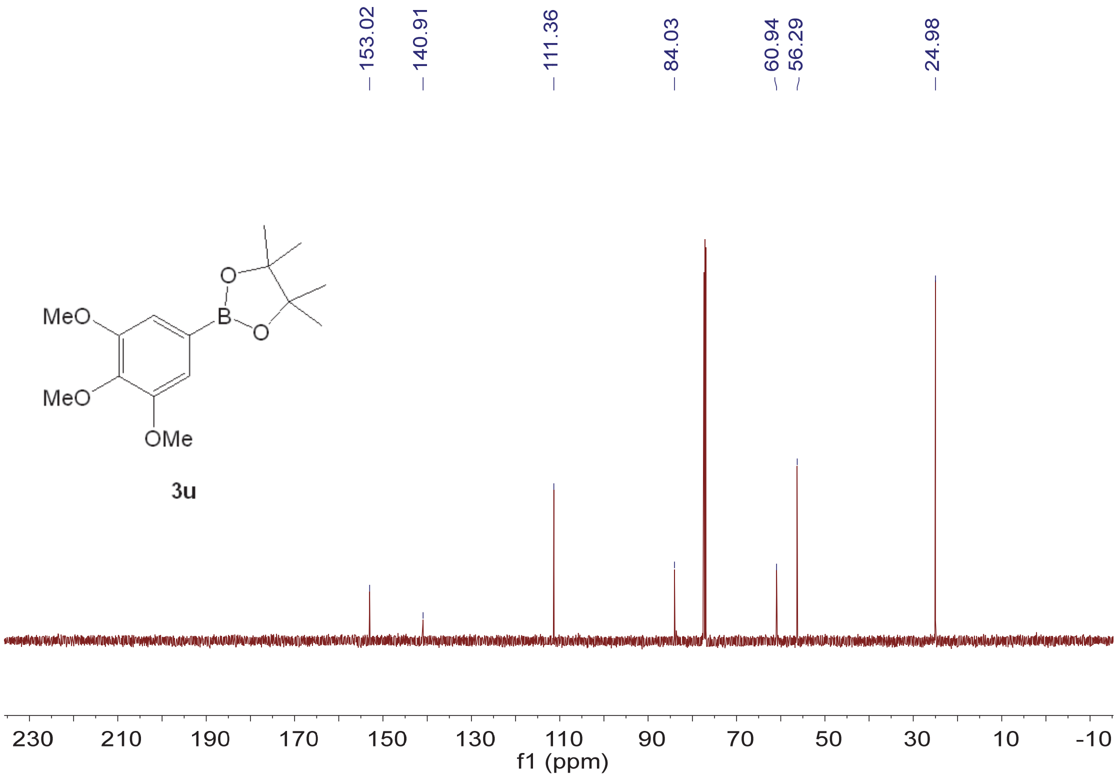




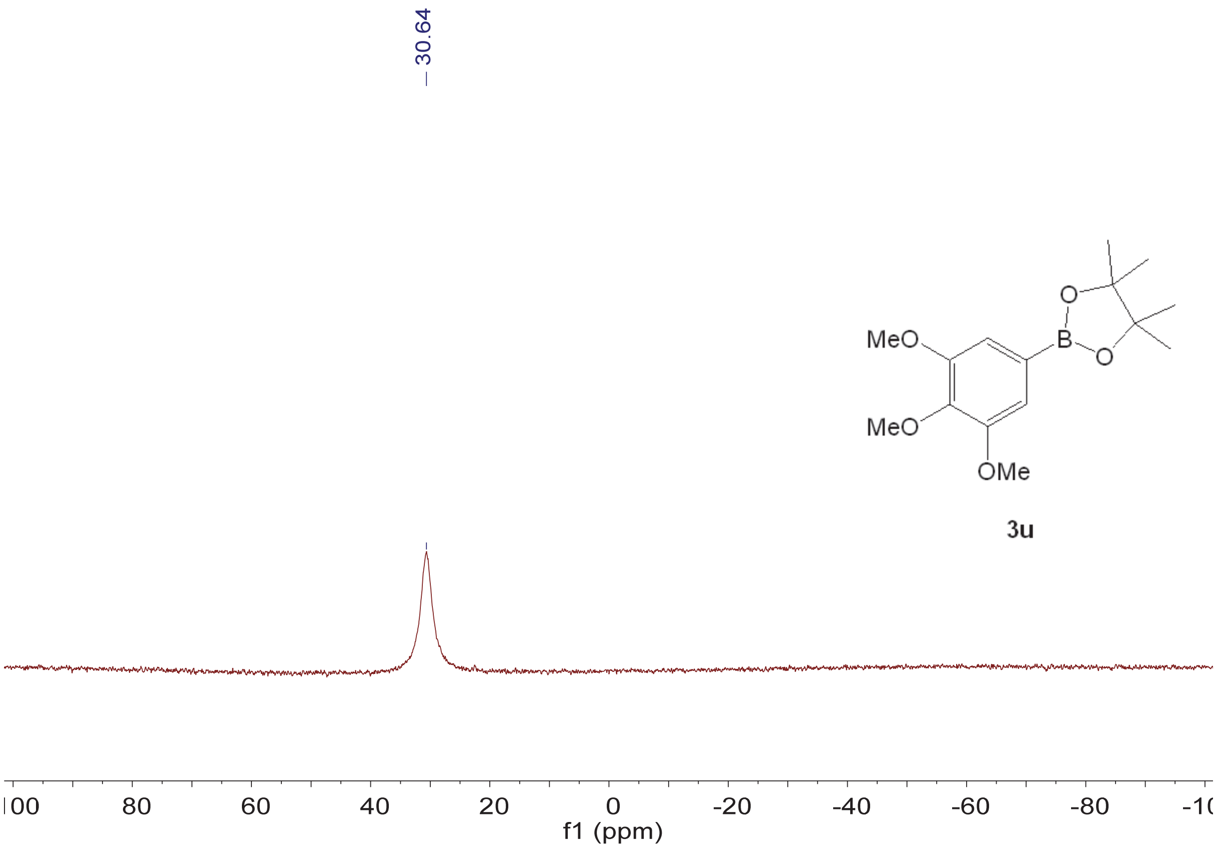
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz), $^{19}F\{^{1}H\}$ NMR (376 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3t** ($CDCl_3$, rt).



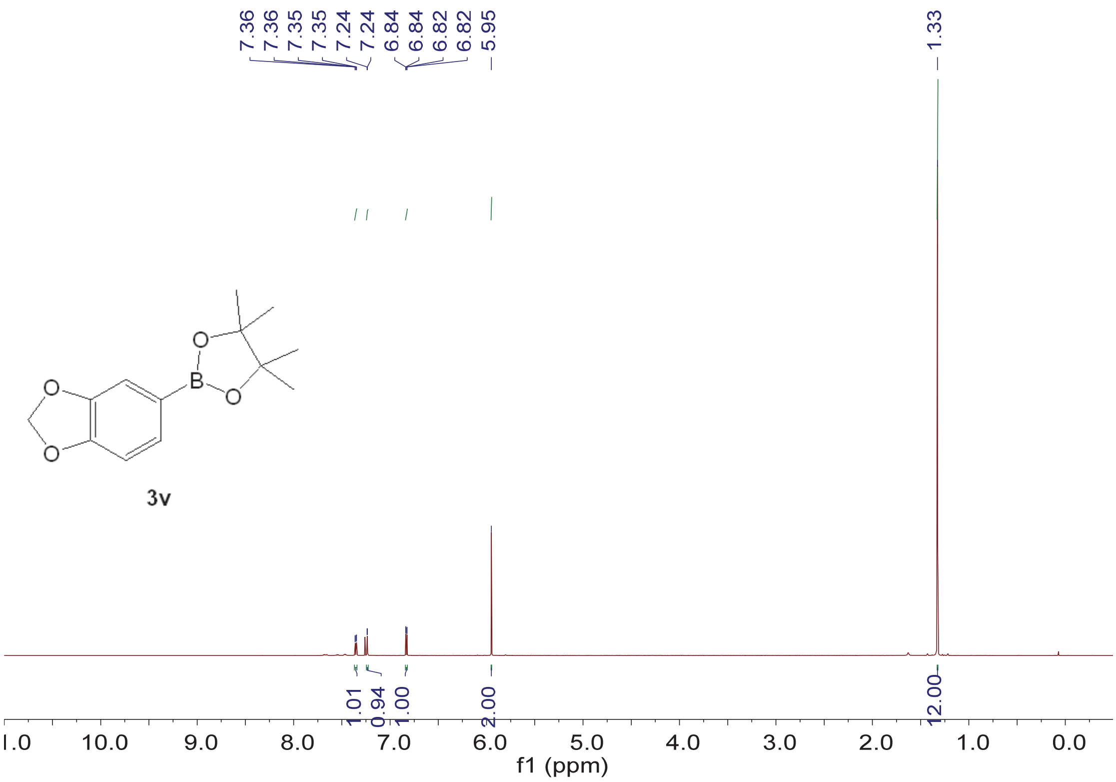
7.03
3.90
3.87
1.34
MeO
MeO
OMe
B
O
O
3u
2.00
6.00
3.00
12.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

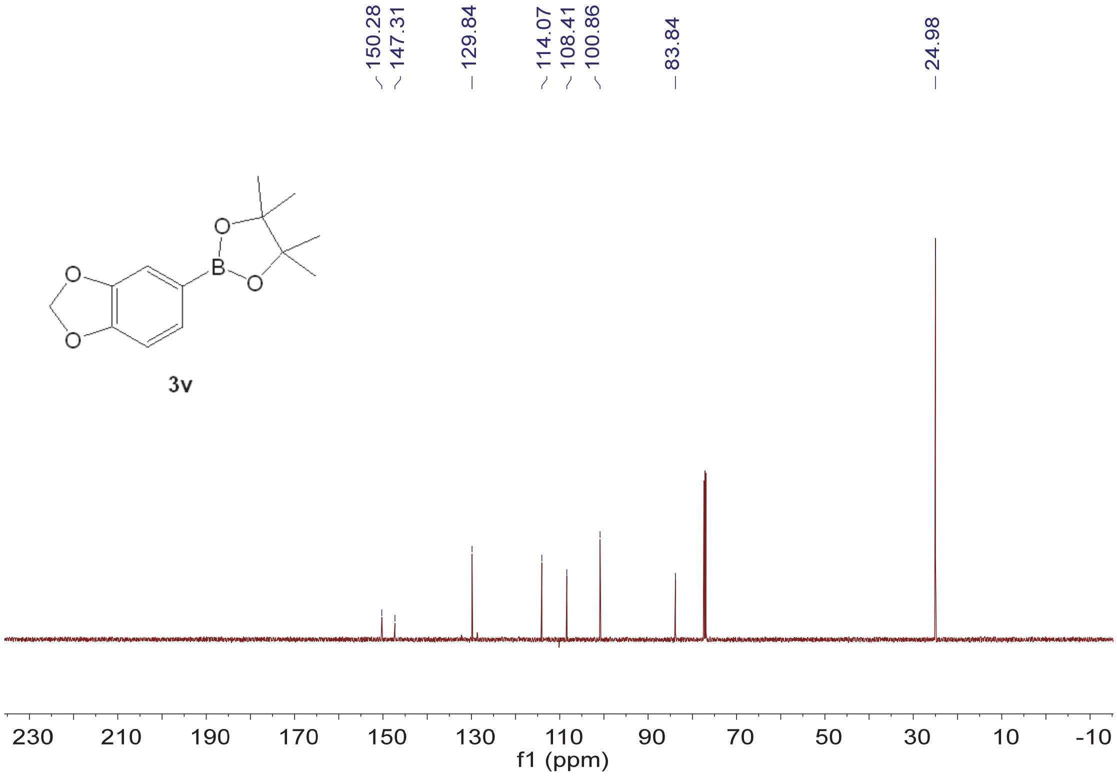


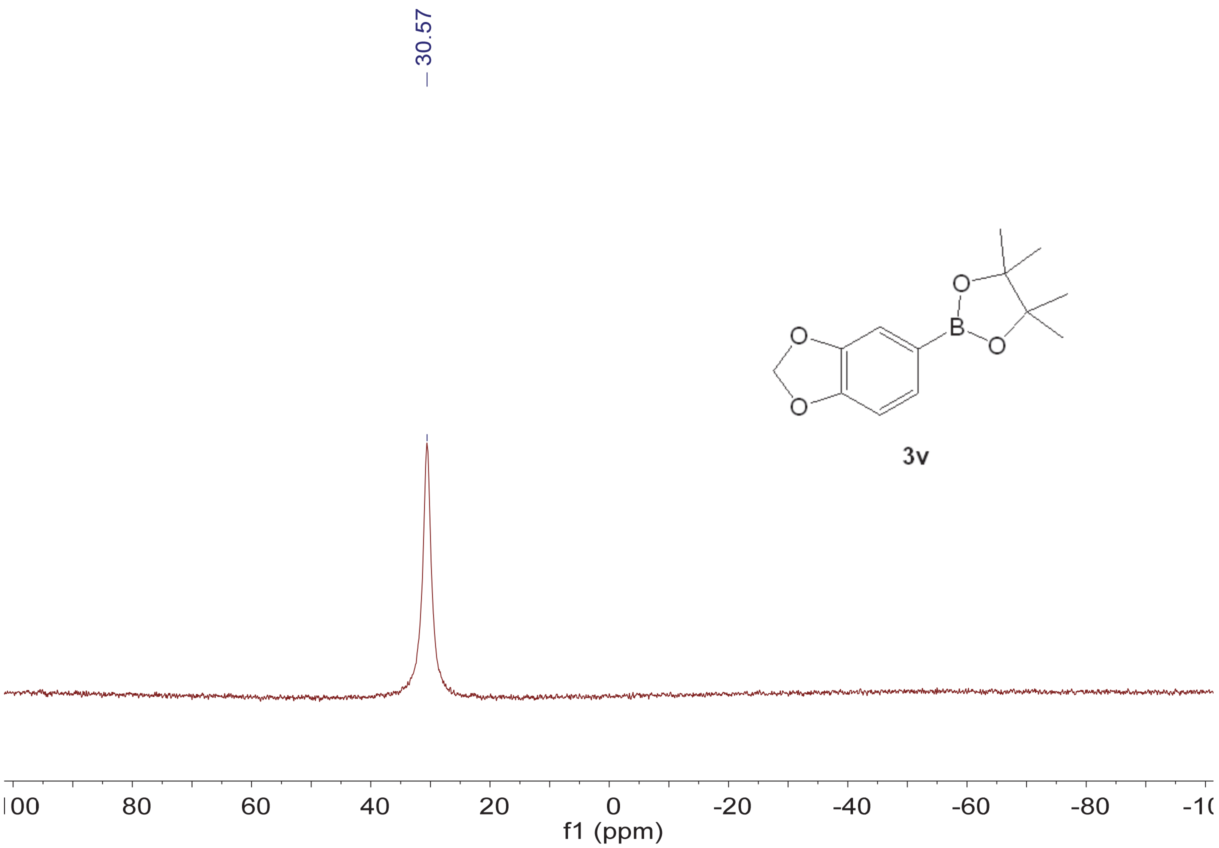
153.02
140.91
111.36
84.03
60.94
56.29
24.98
MeO
MeO
OMe
B
O
O
3u
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)



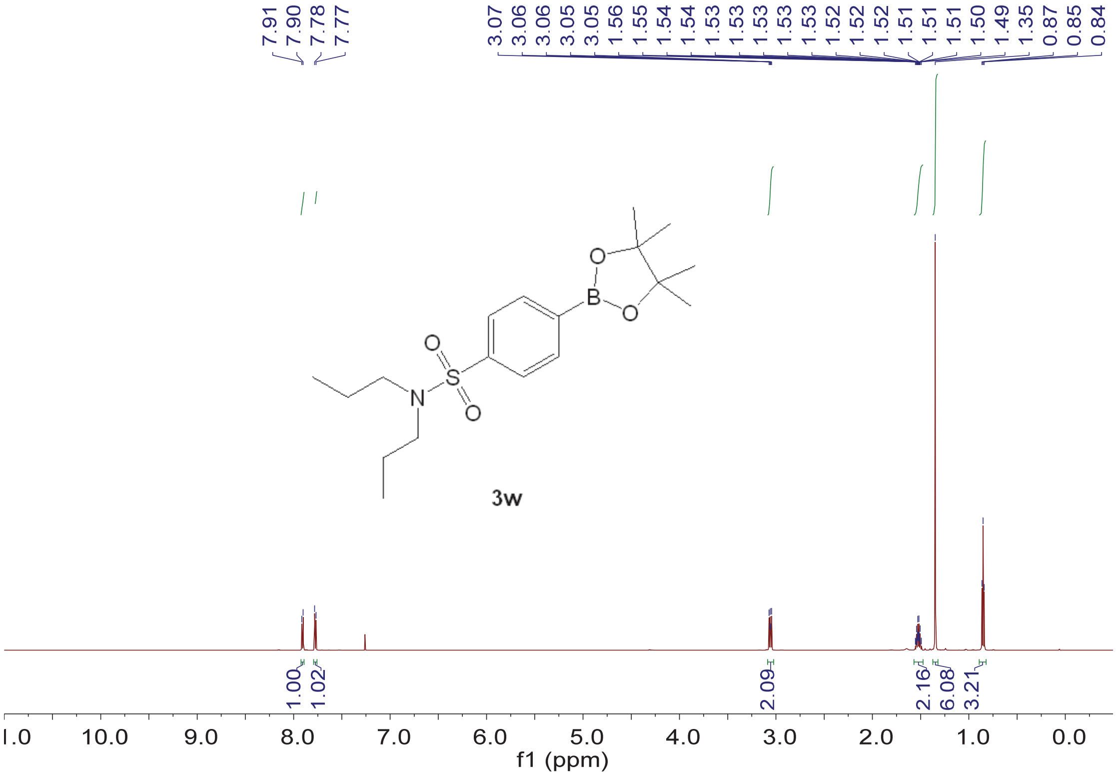
^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3u** ($CDCl_3$, rt).

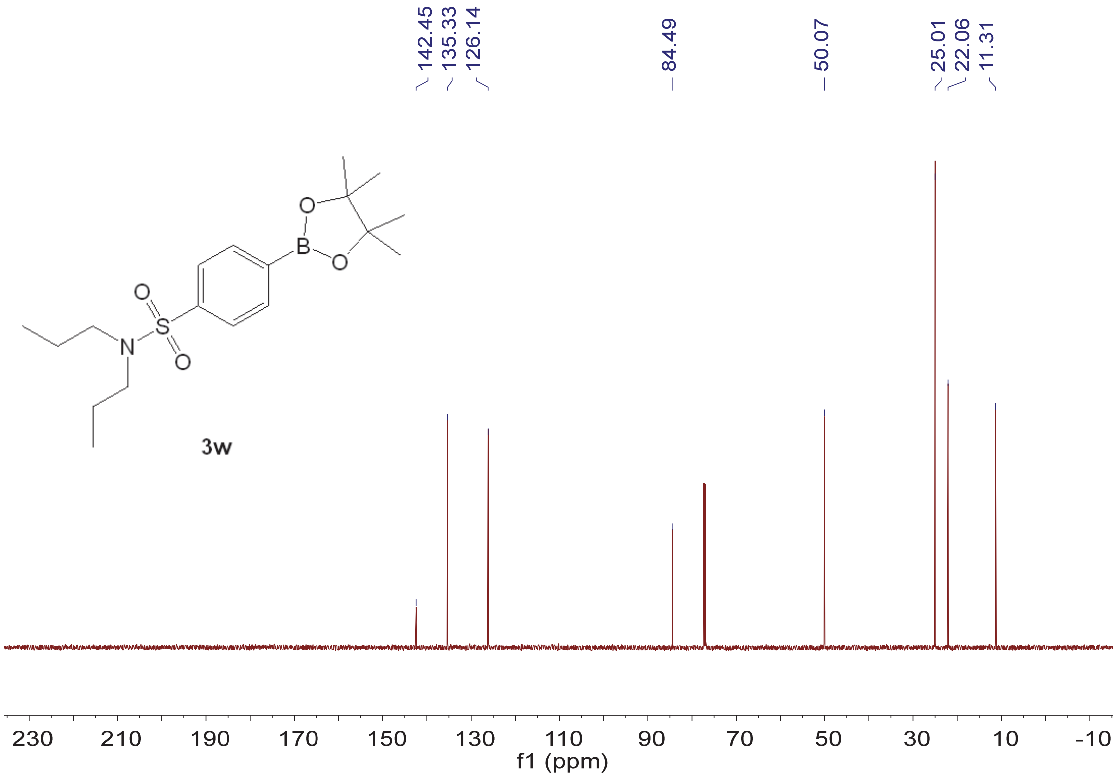


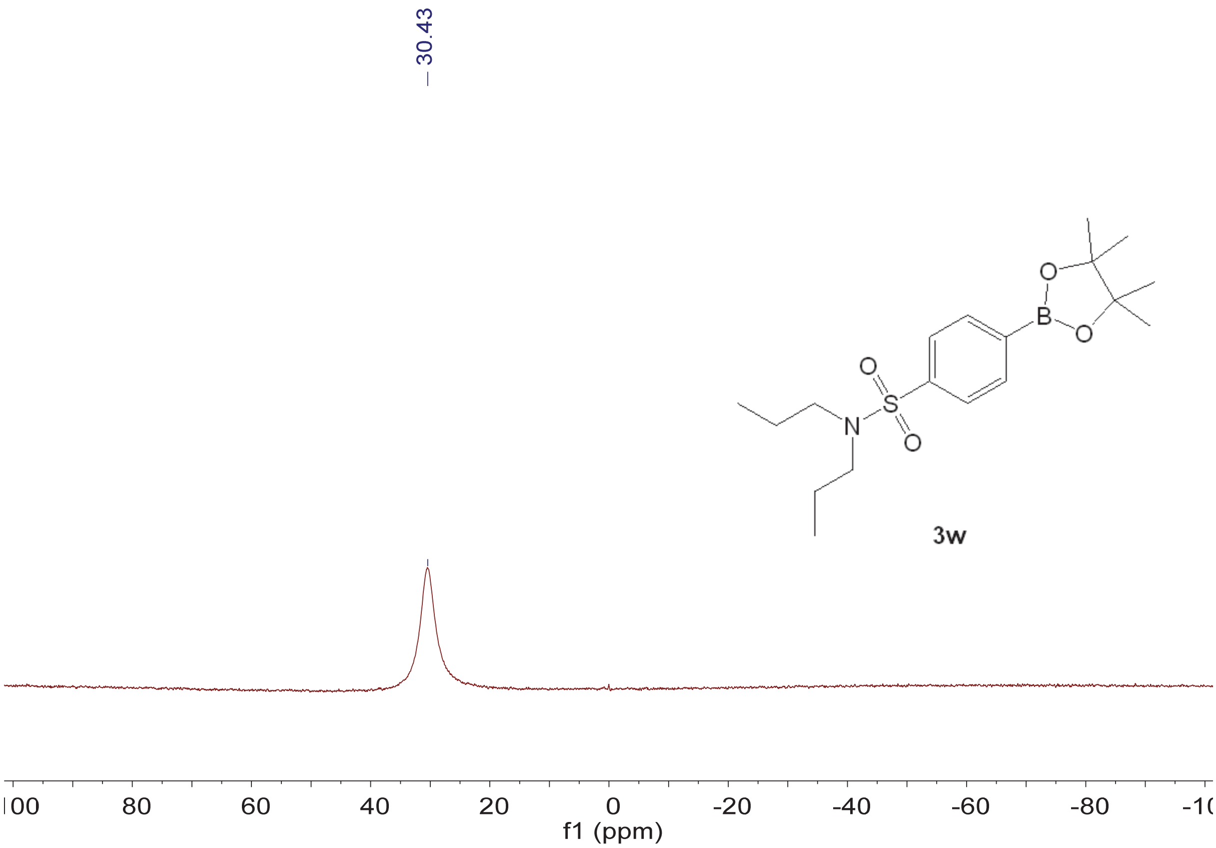




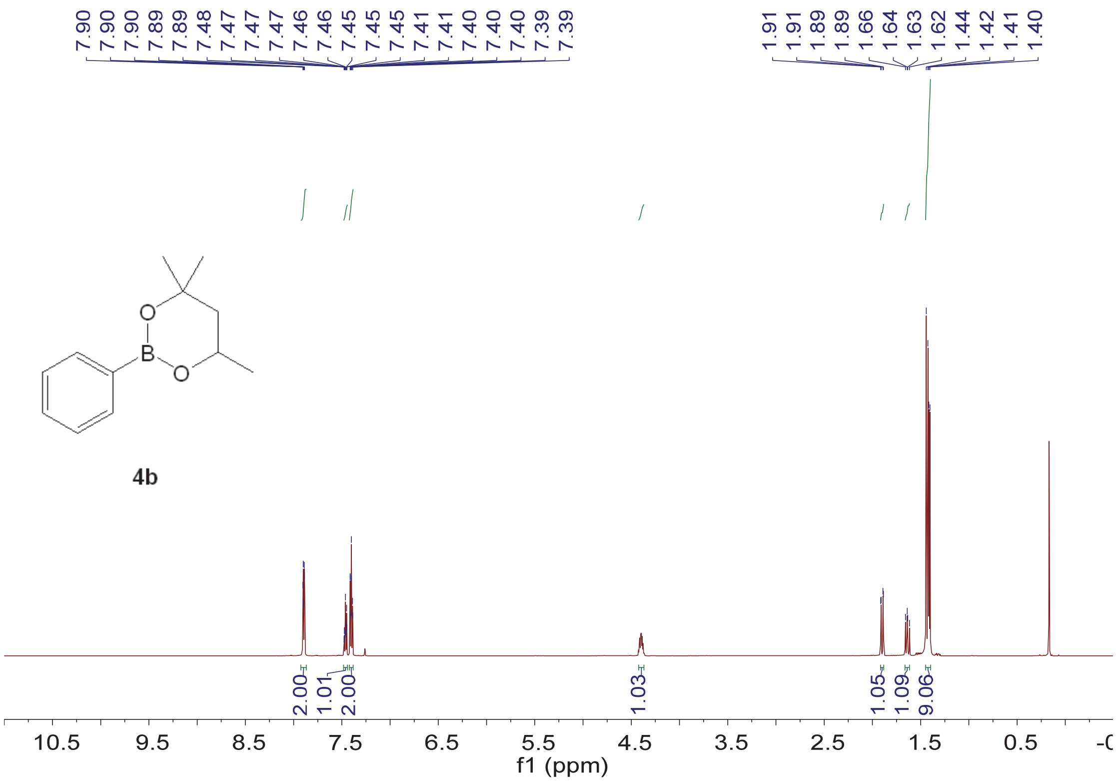
[1]H NMR (600 MHz), [13]C{[1]H} NMR (151 MHz) and [11]B{[1]H} NMR (192 MHz) spectra of **3v** ($CDCl_3$, rt).

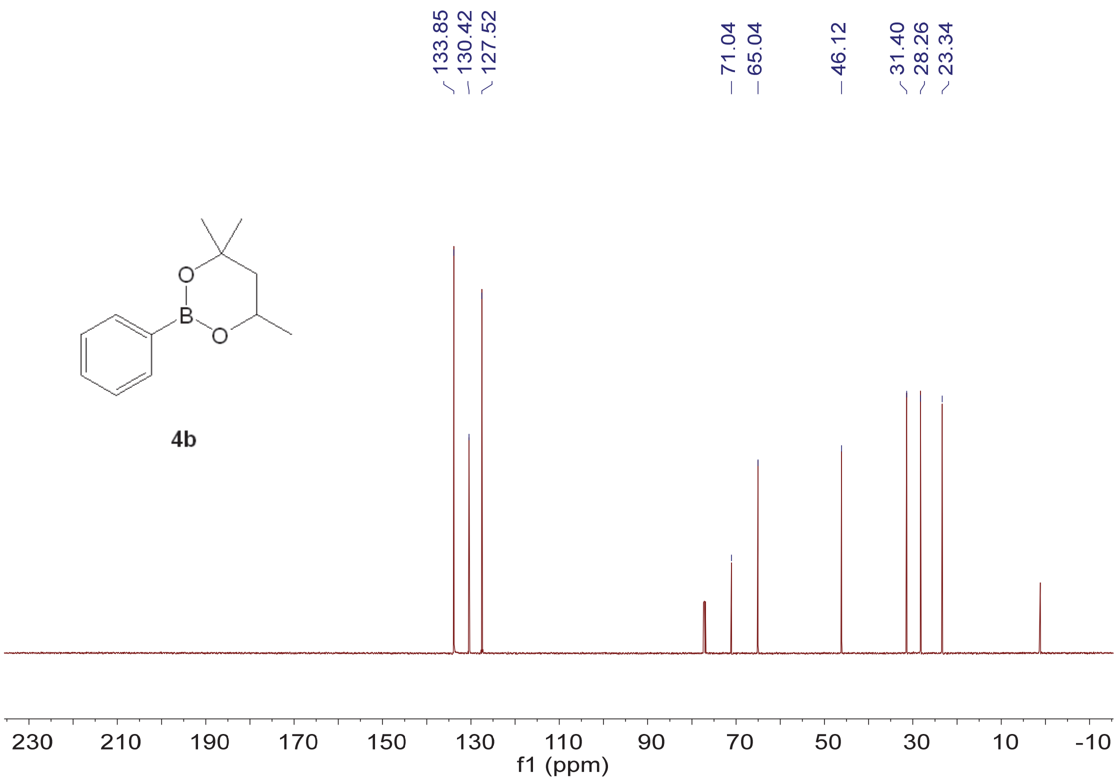

7.91
7.90
7.78
7.77
3.07
3.06
3.06
3.05
3.05
1.56
1.55
1.54
1.54
1.53
1.53
1.53
1.53
1.53
1.52
1.52
1.52
1.51
1.51
1.51
1.50
1.49
1.35
0.87
0.85
0.84
3w
1.00
1.02
2.09
2.16
6.08
3.21
f1 (ppm)

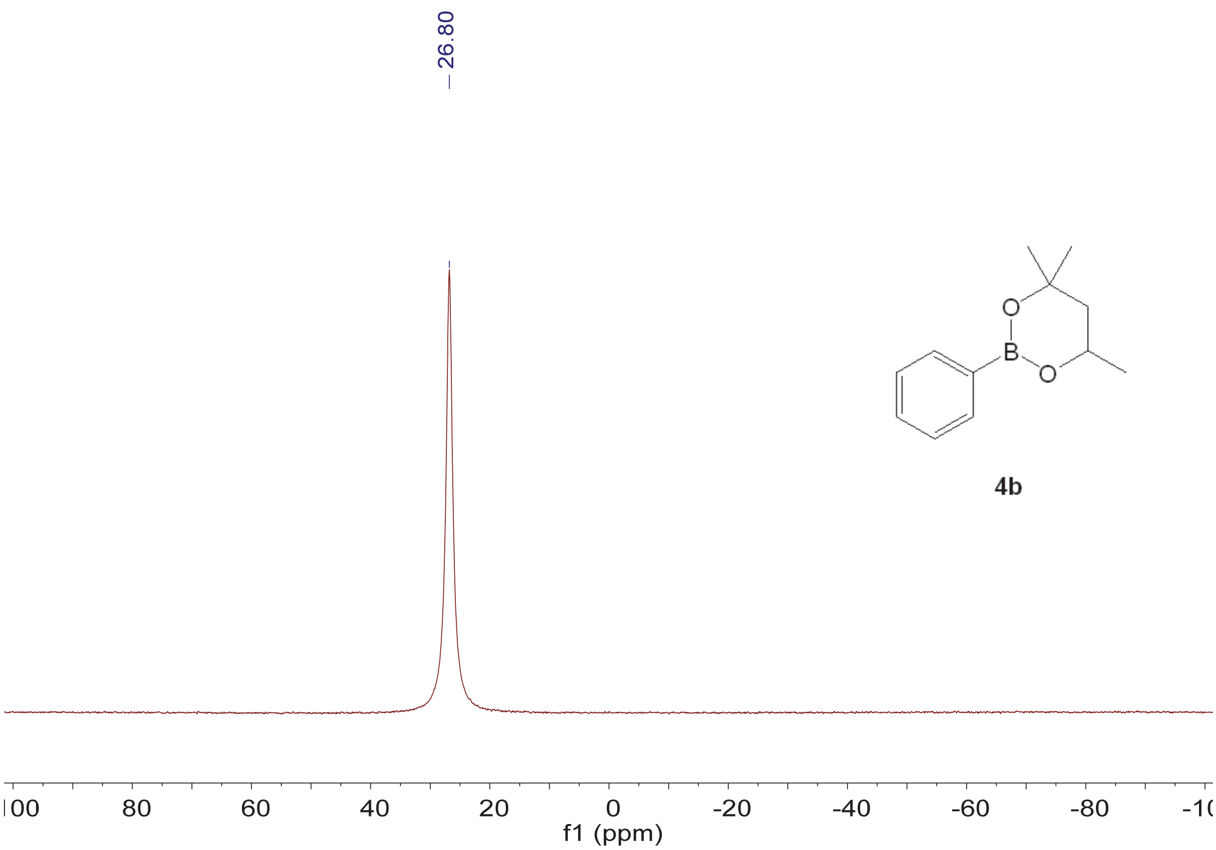

142.45
135.33
126.14
84.49
50.07
25.01
22.06
11.31
3w
f1 (ppm)



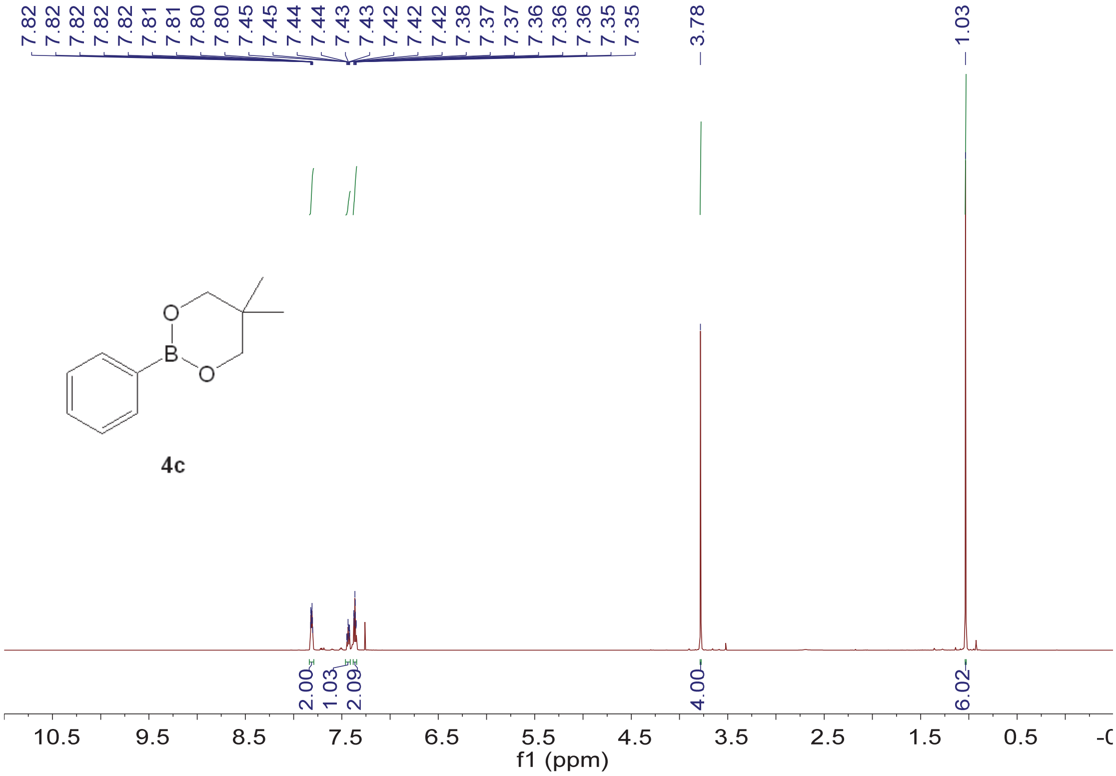
[1]H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (151 MHz) and $^{11}B\{^{1}H\}$ NMR (192 MHz) spectra of **3w** ($CDCl_3$, rt).

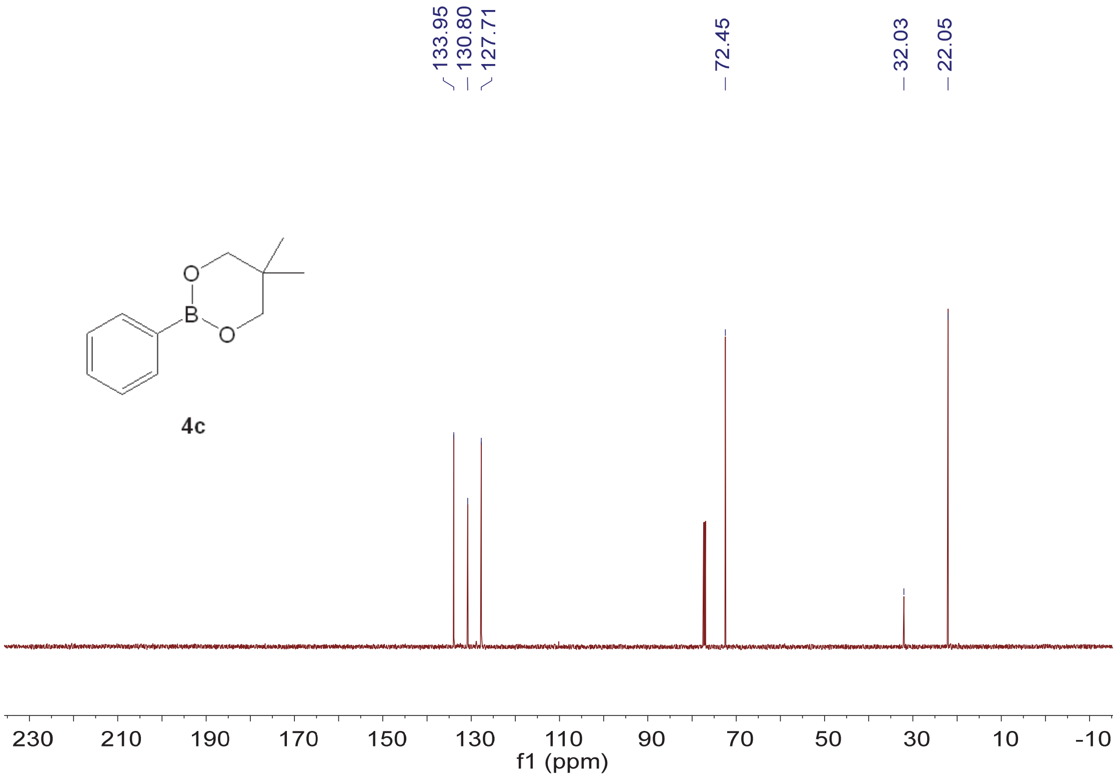


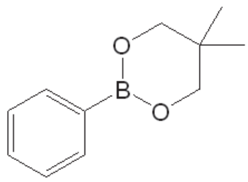




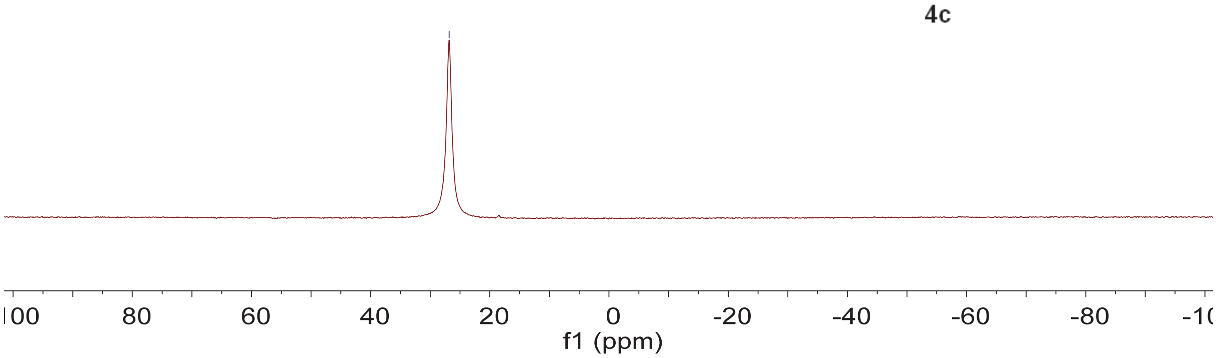
[1]H NMR (600 MHz), [13]C{[1]H} NMR (151 MHz) and [11]B{[1]H} NMR (192 MHz) spectra of **4b** ($CDCl_3$, rt).


7.82 7.82 7.82 7.82 7.82 7.81 7.81 7.80 7.80 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35
3.78
1.03
4c
2.00
1.03
2.09
4.00
6.02
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


133.95
130.80
127.71
72.45
32.03
22.05
4c
230 210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)



4c



^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{11}B{^{1}H} NMR (192 MHz) spectra of **4c** ($CDCl_3$, rt).

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