Supporting Information

Palladium-Catalyzed Three-Component Coupling of Benzynes, Benzylic/Allylic Bromides and 1,1-Bis[(pinacolato)boryl]methane

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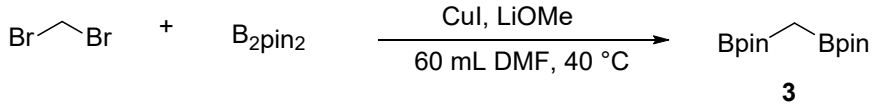
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1. General

All reactions were performed under nitrogen atmosphere in an oven-dried reaction tube. Solvents were distilled under nitrogen atmosphere prior to use. Toluene, dioxane, and THF were dried over Na with benzophenoneketyl intermediate as indicator. MeCN were dried over CaH_2. The boiling point of petroleum ether is between 60 and 70 °C. Unless otherwise noted, commercially available reagents were used as received. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. ^{1}H NMR spectra were recorded on Bruker ARX 400 (400 MHz); ^{13}C NMR spectra were recorded on Bruker ARX 400 (101 MHz). The data for NMR spectra were reported as follows: chemical shifts (δ) were reported in ppm using tetramethylsilane as internal standard when using $CDCl_3$ as solvent, and coupling constants (J) were in Hertz (Hz). IR spectra were recorded on Nicolet 5MX−S infrared spectrometer and were reported in terms of frequency of absorption (cm^{-1}). HRMS were obtained on Bruker APEX IV FTMS. PE: petroleum ether; EA: ethyl acetate.

2. General procedures

2.1. Synthesis of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methane 3

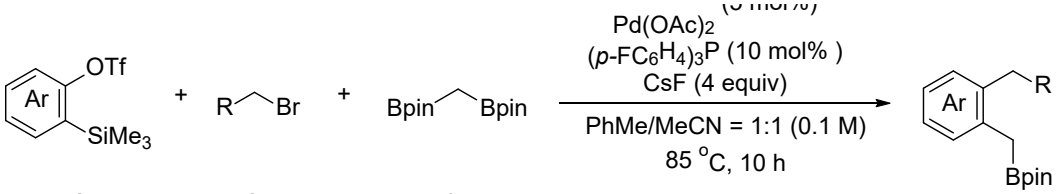


3

According to the literature procedures [1], an oven-dried 250 mL round-bottom flask with magnetic stir bar was charged with CuI (0.95 g, 0.5 mmol), LiOMe (4.75 g, 125 mmol) and $B_2(pin)_2$ (27.9 g, 110 mmol, 2.2 equiv). The flask was sealed with a rubber stopper, evacuated and refilled with nitrogen for three times, followed by the addition of DMF (60

mL). After which, dibromomethane (3.5 mL, 50.0 mmol) was added slowly *via* syringe at room temperature (*note*: be careful of intense heat release!). The reaction mixture was stirred at 40 °C for 12 h. Upon completion, 20 mL diethyl ether was added and the mixture was stirred to make the salt precipitate. The slurry was filtered through a silica gel plug, rinsed with diethyl ether. The filtrate was added 25 mL H_2O and extracted with diethyl ether (25 mL × 2). The combined organic phases were washed with brine (30 mL), dried with Na_2SO_4, then concentrated *in vacuo*. The crude product was purified by silica gel column chromatography to afford the pure product (PE:EA = 10:1, purified twice if necessary). The desired product **3** was obtained as a white solid (8.27 g, 63%).

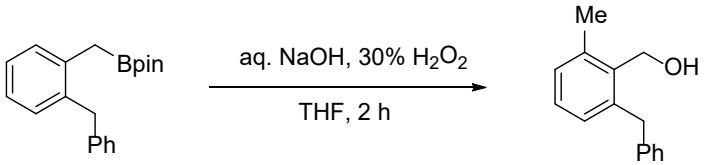
2.2. Experimental procedure for the three-component coupling reaction



1 2 equiv | **2** 1.4 equiv | **3a** 0.3 mmol | **4a-w**

An oven-dried 10 mL Schlenk flask with magnetic stir bar was charged with *gem*-diboronates **3** (0.3 mmol), $Pd(OAc)_2$ (5 mol%) and tris(*p*-fluorophenyl)phosphine (10 mol%). The flask was sealed with a rubber stopper, evacuated and filled with nitrogen for three times, followed by the addition of toluene (1.5 mL), MeCN (1.5 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2 equiv) and bromide (1.4 equiv). The reaction mixture was stirred at 85 °C for 10 h. Upon completion, the mixture was cooled to room temperature and filtered through a short plug of silica gel, rinsed with ethyl acetate. The filtrate was evaporated by rotary evaporation and the crude product was purified by silica gel column chromatography to afford the pure product (PE : EA = 10 : 1).

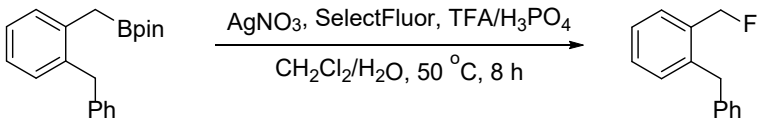
2.3. Experimental procedure for the oxidation reaction of 4a



4a | **5**

According to the literature procedures [2], a 5 mL round-bottom flask with magnetic stir bar was charged with 3 M NaOH solution (0.35 mL), 30% aqueous H_2O_2 (0.2 mL) and THF (2 mL). After cooled to 0 °C, **4a** (0.2 mmol) was dropwise added. The reaction mixture was stirred at room temperature for 2 hours during which white solids were observed to precipitate. Upon completion, 10 mL H_2O was added and extracted with diethyl ether (10 mL × 3). The combined organic phases were washed with brine (10 mL), dried with Na_2SO_4, and then concentrated *in vacuo*. The crude product was purified by thin layer chromatography to afford the pure product **5** (PE : EA = 5 : 1).

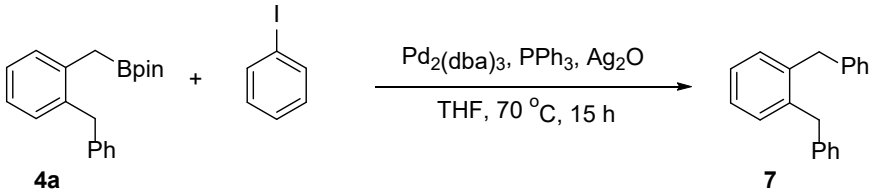
2.4. Experimental procedure for the fluorination of 4a



4a | **6**

According to the literature procedures [3], an oven-dried 10 mL Schlenk flask with magnetic stir bar was charged with $AgNO_3$ (6.8 mg, 0.04 mmol) and SelectFluor (212 mg, 0.6 mmol). The reaction vessel was evacuated and filled with nitrogen for three times. Then dichloromethane (0.6 mL), TFA (0.4 mL), H_3PO_4 (0.1 mL) and water (0.9 mL) were added successively at rt. The reaction mixture was then stirred at 50 °C for 8 h. The resulting mixture was extracted with CH_2Cl_2 (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4. After concentrating *in vacuo*, crude product was purified by thin layer chromatography to afford the pure product **6** (PE : EA = 10 : 1).

2.5. Experimental procedure for the cross-coupling of 4a

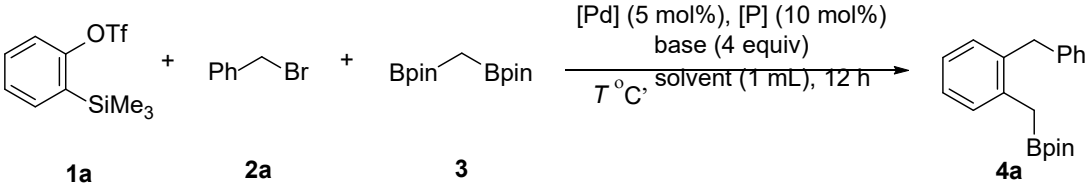


4a **7**

According to the literature procedures [4], an oven-dried 10 mL Schlenk flask with magnetic stir bar was charged with $Pd_2(dba)_3$ (7.4 mg, 20 mol% Pd), PPh_3 (52.4 mg, 10 mol%) and Ag_2O (46.3 mg, 1 equiv). The flask was sealed with a rubber stopper, evacuated and filled with nitrogen for three times, followed by the addition of THF (2 mL), iodobenzene (22.3 μL, 1 equiv) and **4a** (0.3 mmol). The reaction mixture was stirred at 70 °C for 15 h. Upon completion, the mixture was cooled to room temperature and filtered through a short plug of silica gel, rinsed with ethyl acetate. The filtrate was concentrated *in vacuo*, and then purified by thin layer chromatography to afford the pure product **7** (PE : EA = 10 : 1).

3. Reaction optimization

Table S1. Reaction optimization for the coupling reaction using DCE as the solvent.



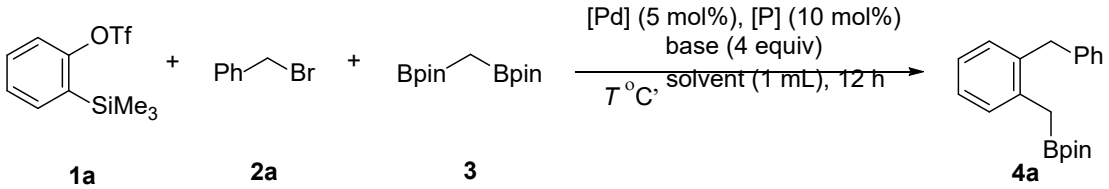
1a 2 equiv **2a** 1 equiv **3** 0.1 mmol **4a**

Entry	*T* (°C)	Solvent	[Pd] (5 mol%)	[P] (10 mol%)	Yield (%)[a]
1	80	MeCN	$PdCl_2$	dppe	6
2	80	PhMe	$PdCl_2$	dppe	13
3	80	THF	$PdCl_2$	dppe	25
5	80	Dioxane	$PdCl_2$	dppe	19
6	80	DCE	$PdCl_2$	dppe	34
7	80	DCE/MeCN = 1:1	$PdCl_2$	dppe	31
8	80	DCE/PhMe = 1:1	$PdCl_2$	dppe	2
9	80	DCE/THF = 1:1	$PdCl_2$	dppe	32
9	80	DCE/Dioxane = 1:1	$PdCl_2$	dppe	12
10	70	DCE	$PdCl_2$	dppe	10
11	60	DCE	$PdCl_2$	dppe	7
12	90	DCE	$PdCl_2$	dppe	40
13	100	DCE	$PdCl_2$	dppe	40

14	90	DCE	$Pd(OAc)_2$	dppe	31
15	90	DCE	$Pd(PPh_3)_2Cl$	dppe	32
16	90	DCE	$Pd(PhCN)_2Cl_2$	dppe	30
17	90	DCE	$Pd_2(dba)_3$	dppe	38
18	90	DCE	$Pd(PPh_3)_2(OAc)_2$	dppe	27
19	90	DCE	$PdCl_2$	PPh_3	34
20	90	DCE	$PdCl_2$	$P(2\text{-furyl})_3$	0
21	90	DCE	$PdCl_2$	dppp	39
22	90	DCE	$PdCl_2$	dppbz	8
23	90	DCE	$PdCl_2$	xantphos	34
24	90	DCE (0.05 M)	$PdCl_2$	dppe	36

[a] Yields were determined by ^1H NMR spectroscopy analysis of crude reaction mixture using CH_2Br_2 as an internal standard.

Table S2. Reaction optimization for the coupling reaction using PhMe/MeCN as the solvents.

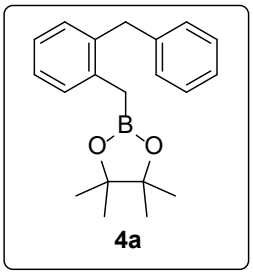


1a 2 equiv + **2a** 1 equiv + **3** 0.1 mmol → **4a**

Entry	*T* (°C)	Solvent	[Pd] (5 mol%)	[P] (10 mol%)	Yield (%)[a]
1	60	MeCN	$Pd(PPh_3)_2Cl_2$	dppe	6
2	60	PhMe	$Pd(PPh_3)_2Cl_2$	dppe	13
3	60	PhMe/MeCN = 1:1	$Pd(PPh_3)_2Cl_2$	dppe	45
4	70	PhMe/MeCN = 1:1	$Pd(PPh_3)_2Cl_2$	dppe	48
5	80	PhMe/MeCN = 1:1	$Pd(PPh_3)_2Cl_2$	dppe	51
6	85	PhMe/MeCN = 1:1	$Pd(PPh_3)_2Cl_2$	dppe	56
7	90	PhMe/MeCN = 1:1	$Pd(PPh_3)_2Cl_2$	dppe	52
8	90	PhMe/MeCN = 1:1	$PdCl_2$	dppe	47
9	85	PhMe/MeCN = 1:1	$Pd(MeCN)_2Cl_2$	dppe	56
10	85	PhMe/MeCN = 1:1	$Pd(MeCN)_2Cl_2$	dppe	51
11	85	PhMe/MeCN = 1:1	$Pd_2(dba)_3$	dppe	39
12	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	dppe	61
13	85	PhMe/MeCN = 1:1	$Pd(PPh_3)_2(OAc)_2$	dppe	46
14	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	dppp	53
15	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	dppbz	16
16	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(Ph_2P_2)CH_2$	49
17	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	PPh_3	65
18	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(p\text{-}MeOC_6H_4)_3P$	61
19	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(p\text{-}FC_6H_4)_3P$	69
20	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(p\text{-}ClC_6H_4)_3P$	67
21	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(p\text{-}CF_3C_6H_4)_3P$	64
22	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(3,5\text{-}(CF_3)_2C_6H_3)_3P$	48
23	85	PhMe/MeCN = 1:1	$Pd(OAc)_2$	$(C_6F_5)_3P$	26

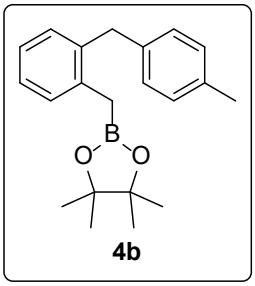
[a] Yields were determined by ^1H NMR spectroscopy analysis of crude reaction mixture using CH_2Br_2 as an internal standard.

4. H NMR, ^{13}C NMR, ^{11}B NMR, IR, and HRMS data of compounds



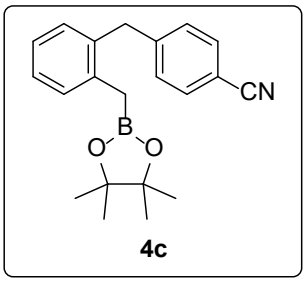
4a

2-(2-benzylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a colorless oil (isolated yield 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.1 Hz, 2H), 7.17 (dd, J = 7.5, 2.0 Hz, 2H), 7.16 – 7.12 (m, 3H), 7.08 (ddd, J = 14.5, 6.5, 1.7 Hz, 1H), 7.01 (dd, J = 7.5, 1.6 Hz, 1H), 3.99 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 138.4, 137.6, 130.0, 129.9, 129.0, 128.3, 126.3, 125.8, 125.2, 83.4, 39.3, 24.7; IR (film): 1743, 1379, 1331, 1244, 1144 cm^{-1}; HRMS (EI): calculated for $C_{20}H_{29}NBO_2$ ($[M+NH_4]^+$): m/z = 326.2291, found: 326.2286.



4b

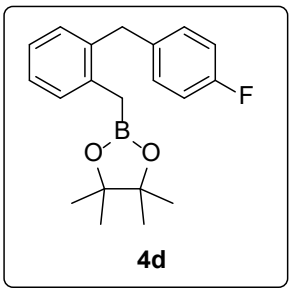
4,4,5,5-tetramethyl-2-(2-(4-methylbenzyl)benzyl)-1,3,2-dioxaborolane (4b). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a colorless oil (isolated yield 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 7.5, 1.7 Hz, 1H), 7.11 (td, J = 7.3, 1.6 Hz, 1H), 7.09 – 6.97 (m, 6H), 3.95 (s, 2H), 2.30 (s, 3H), 2.24 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.5, 135.2, 130.0, 129.8, 129.0, 128.8, 126.2, 125.2, 83.3, 38.9, 24.7, 21.0; HRMS (EI): calculated for $C_{21}H_{28}BO_2$ ($[M+H]^+$): m/z = 323.2182, found: 323.2173.



4c

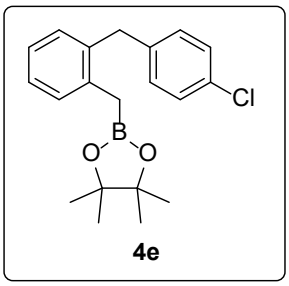
4-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzyl)benzonitrile (4c). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.20 – 7.14 (m, 2H), 7.11 (td, J = 7.2, 2.1 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 4.05 (s, 2H), 2.18 (s, 2H), 1.19 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 137.6, 136.7, 132.1, 130.3, 130.1, 129.6, 128.84, 127.0, 125.5, 109.7, 83.5, 39.4, 24.8, 24.7; IR (film):

1670, 1649, 1618, 1539, 1457, 1147 cm^{-1}; HRMS (EI): calculated for $C_{21}H_{28}BN_2O_2$ ($[M+NH_4]^+$): *m*/*z* = 351.2244, found: 351.2237.



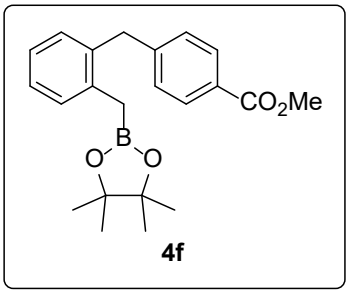
4d

2-(2-(4-fluorobenzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (ddd, *J* = 14.7, 6.7, 1.8 Hz, 2H), 7.08 (ddd, *J* = 7.8, 5.2, 2.2 Hz, 3H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.91 (m, 2H), 3.96 (s, 2H), 2.22 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 160.1, 138.2, 137.6, 136.3, 136.3, 130.3, 130.2, 130.2, 129.9, 126.5, 125.3, 115.2, 115.0, 83.4, 38.5, 24.8; IR (film): 1738, 1508, 1383, 1371, 1337, 1238, 1223, 1146 cm^{-1}; HRMS (EI): calculated for $C_{20}H_{28}BFNO_2$ ($[M+NH_4]^+$): *m*/*z* = 344.2197, found: 344.2193.



4e

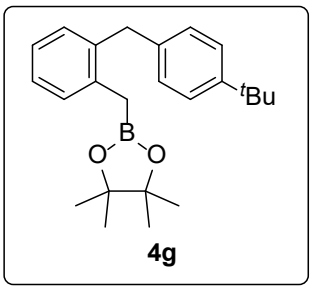
2-(2-(4-chlorobenzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.03 (m, 7H), 6.99 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.95 (s, 2H), 2.21 (s, 2H), 1.20 (d, *J* = 8.5 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 137.9, 137.6, 131.6, 130.3, 130.2, 130.0, 129.4, 128.4, 128.2, 126.6, 125.4, 83.4, 38.7, 24.8, 24.7; HRMS (EI): calculated for $C_{20}H_{25}BClO_2$ ($[M+H]^+$): m/z = 343.1636, found: 343.1632.



4f

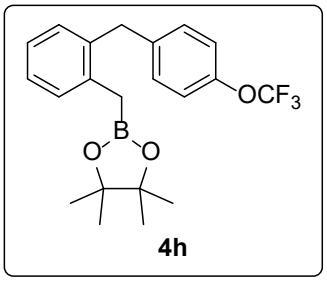
methyl 4-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzyl)benzoate (4f). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.17 (dd, *J* = 5.1, 1.7 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.09 (td, *J* = 7.3, 1.8 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.05 (s, 2H), 3.89 (s, 3H), 2.22 (s, 2H), 1.19 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 146.3, 137.6, 137.5, 130.2, 130.0, 129.7, 129.0,

127.8, 126.7, 126.6, 125.4, 83.4, 52.0, 39.3, 24.7; IR (film): 1745, 1734, 1723, 1374, 1280, 1241 cm^{-1}; HRMS (EI): calculated for $C_{22}H_{28}BO_4$ ([M+H]$^+$): *m*/*z* = 367.2081, found: 367.2067.



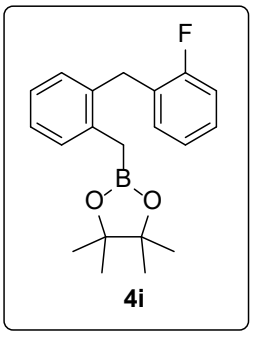
4g

2-(2-(4-(tert-butyl)benzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.15 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.09 – 7.02 (m, 4H), 3.96 (s, 2H), 2.25 (s, 2H), 1.29 (s, 9H), 1.19 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 138.5, 137.6, 137.5, 130.0, 128.5, 126.3, 125.2, 83.3, 38.8, 34.3, 31.4, 24.7; IR (film): 1541, 1373, 1349, 1332, 1146 cm^{-1}; HRMS (EI): calculated for $C_{24}H_{37}BNO_2$ ([M+NH_4]$^+$): *m*/*z* = 382.2917, found: 382.2912.



4h

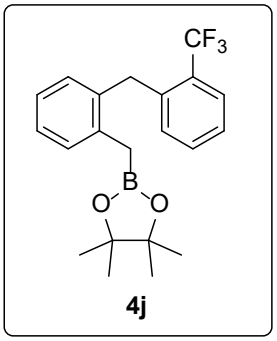
4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethoxy)benzyl)benzyl)-1,3,2-dioxaborolane (4h). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 3H), 7.13 (s, 2H), 7.12 – 7.08 (m, 3H), 7.01 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.99 (s, 2H), 2.22 (s, 2H), 1.19 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 139.5, 137.7, 137.6, 130.2, 130.1, 130.0, 126.7, 125.4, 120.9, 83.4, 38.6, 24.7; IR (film): 1745, 1508, 1382, 1373, 1348, 1331, 1263, 1224, 1164, 1544 cm^{-1}; HRMS (EI): calculated for $C_{21}H_{28}BF_3NO_3$ ([M+NH_4]$^+$): *m*/*z* = 410.2114, found: 410.2109.



4i

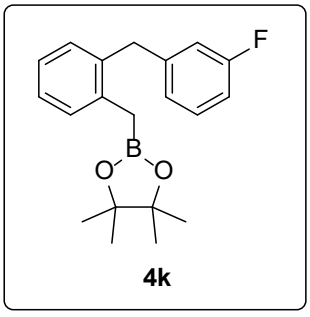
2-(2-(2-fluorobenzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 7.14 (td, *J* = 7.3, 1.6 Hz, 1H), 7.09 (td, *J* = 7.3, 1.8 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.79 (m, 2H), 3.99 (s, 2H), 2.22 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

164.2, 161.8, 143.4, 143.4, 137.6, 137.6, 130.2, 130.0, 129.6, 129.6, 126.6, 125.4, 124.6, 124.5, 115.9, 115.6, 112.8, 112.6, 83.4, 39.0, 39.0, 24.7; IR (film): 1738, 1491, 1376, 1345, 1243, 1147 cm^{-1}; HRMS (EI): calculated for $C_{20}H_{28}BFNO_2$ ($[M+NH_4]^+$): *m*/*z* = 344.2197, found: 344.2192.



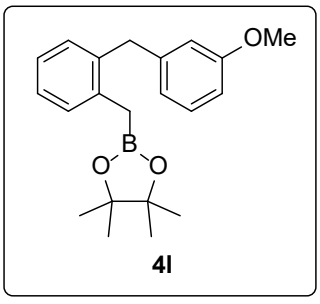
4j

4,4,5,5-tetramethyl-2-(2-(2-(trifluoromethyl)benzyl)benzyl)-1,3,2-dioxaborolane (4j). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.09 (td, *J* = 7.4, 1.9 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 4.19 (s, 2H), 2.20 (s, 2H), 1.19 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 137.9, 137.1, 131.8, 130.8, 130.2, 130.0, 126.6, 126.0, 125.8, 125.4, 83.4, 35.3, 24.7; IR (film): 1748, 1346, 1332, 1315, 1169, 1150 cm^{-1}; HRMS (EI): calculated for $C_{21}H_{28}BF_3NO_2$ ($[M+NH_4]^+$): *m*/*z* = 394.2165, found: 394.2162.



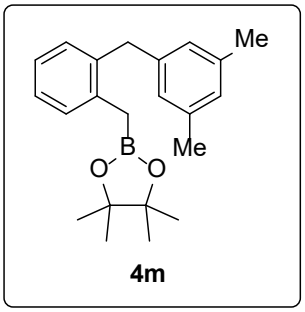
4k

2-(2-(3-fluorobenzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dt, *J* = 18.7, 6.9 Hz, 4H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 11.2 Hz, 1H), 7.01 – 6.96 (m, 3H), 4.00 (s, 2H), 2.26 (s, 2H), 1.21 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.0, 130.9, 130.8, 130.0, 129.6, 127.6, 127.6, 126.5, 125.3, 124.0, 123.9, 115.1, 114.9, 83.4, 83.3, 31.9, 31.9, 24.8, 24.7; IR (film): 1742, 1615, 1587, 1380, 1488, 1346, 1331, 1248, 1144, cm^{-1}; HRMS (EI): calculated for $C_{20}H_{28}BFNO_2$ ($[M+NH_4]^+$): *m*/*z* = 344.2197, found: 344.2194.



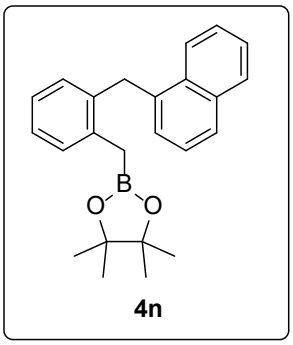
4l

2-(2-(3-methoxybenzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.9 Hz, 2H), 7.12 (td, J = 7.3, 1.7 Hz, 1H), 7.07 (td, J = 7.3, 1.8 Hz, 1H), 7.01 (dd, J = 7.5, 1.6 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.69 (s, 1H), 3.97 (s, 2H), 3.75 (s, 3H), 2.25 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 142.3, 138.2, 137.6, 130.0, 129.9, 129.2, 126.4, 125.2, 121.4, 114.8, 111.1, 83.4, 55.1, 39.3, 24.7; IR (film): 1740, 1603, 1491, 1374, 1332, 1144, 1051 cm^{-1}; HRMS (EI): calculated for $C_{21}H_{31}BNO_3$ ([M+NH_4]$^+$): m/z = 356.2397, found: 356.2392.



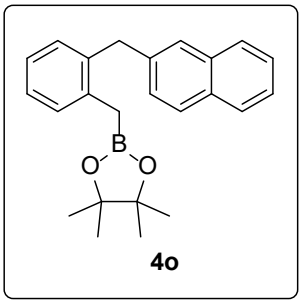
4m

2-(2-(3,5-dimethylbenzyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4m). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 7.5, 1.7 Hz, 1H), 7.12 (td, J = 7.3, 1.7 Hz, 1H), 7.07 (td, J = 7.3, 1.8 Hz, 1H), 7.00 (dd, J = 7.5, 1.6 Hz, 1H), 6.82 (s, 1H), 6.76 (s, 2H), 3.91 (s, 2H), 2.27 (s, 2H), 2.25 (s, 6H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.7, 137.7, 137.5, 129.9, 127.5, 126.8, 126.2, 125.2, 83.3, 39.1, 24.7, 21.3; IR (film): 1740, 1601, 1377, 1346, 1329, 1146, 1241 cm^{-1}; HRMS (EI): calculated for $C_{22}H_{33}BNO_2$ ([M+NH_4]$^+$): m/z = 354.2604, found: 354.2598.



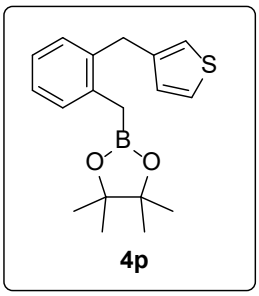
4n

4,4,5,5-tetramethyl-2-(2-(naphthalen-1-ylmethyl)benzyl)-1,3,2-dioxaborolane (4n). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.53 – 7.35 (m, 4H), 7.22 (dd, J = 7.6, 1.4 Hz, 1H), 7.17 (d, J = 7.0 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.96 (td, J = 7.5, 1.4 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 4.42 (s, 2H), 2.37 (s, 2H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.5, 136.3, 129.7, 129.1, 128.5, 127.1, 126.9, 126.2, 125.8, 125.6, 125.5, 125.3, 124.6, 83.5, 36.5, 24.8; IR (film): 1751, 1657, 1647, 1539, 1462, 1383, 1332 cm^{-1}; HRMS (EI): calculated for $C_{24}H_{31}BNO_2$ ([M+NH_4]$^+$): m/z = 376.2448, found: 376.2444.



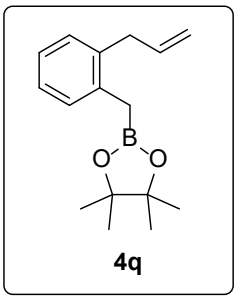
4o

4,4,5,5-tetramethyl-2-(2-(naphthalen-2-ylmethyl)benzyl)-1,3,2-dioxaborolane (4o). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 3H), 7.55 (s, 1H), 7.41 (td, *J* = 7.4, 6.7, 3.7 Hz, 2H), 7.31 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.15 (td, *J* = 7.3, 1.8 Hz, 1H), 7.09 (td, *J* = 7.2, 1.6 Hz, 1H), 7.05 (dd, *J* = 7.6, 1.8 Hz, 1H), 4.15 (s, 2H), 2.29 (s, 2H), 1.17 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.2, 137.7, 133.6, 132.0, 130.1, 127.8, 127.8, 127.6, 127.5, 127.1, 126.4, 125.8, 125.3, 125.2, 83.4, 39.5, 24.7; IR (film): 1742, 1373, 1331, 1237, 1143 cm^{-1}; HRMS (EI): calculated for $C_{24}H_{28}BO_2$ ([M+H]$^+$): m/z = 359.2182, found: 359.2177.



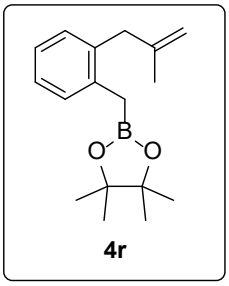
4p

4,4,5,5-tetramethyl-2-(2-(thiophen-3-ylmethyl)benzyl)-1,3,2-dioxaborolane (4p). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.14 (m, 1H), 7.13 – 7.08 (m, 3H), 5.96 (ddt, *J* = 16.8, 10.1, 6.4 Hz, 1H), 5.07 – 4.98 (m, 2H), 3.38 (d, *J* = 6.4 Hz, 2H), 2.28 (s, 2H), 1.22 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.3, 136.9, 129.9, 129.2, 126.3, 125.3, 115.7, 83.4, 37.7, 24.7; IR (film): 1743, 1383, 1332, 1248, 1144, 1047 cm^{-1}; HRMS (EI): calculated for $C_{18}H_{24}BO_2S$ ([M+H]$^+$): *m*/*z* = 315.15890, found: 315.1584.



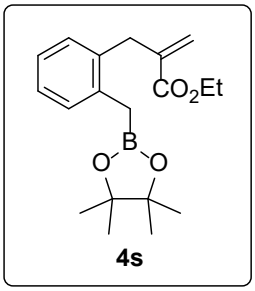
4q

2-(2-allylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4q). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 52% for bromide and 46% for iodide); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.14 (m, 1H), 7.13 – 7.08 (m, 3H), 5.96 (ddt, *J* = 16.8, 10.1, 6.4 Hz, 1H), 5.07 – 4.98 (m, 2H), 3.38 (d, *J* = 6.4 Hz, 2H), 2.28 (s, 2H), 1.22 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.3, 136.9, 129.9, 129.2, 126.2, 125.3, 115.7, 83.4, 37.7, 24.7; IR (film):1749, 1376, 1344, 1047 cm^{-1}; HRMS (EI): calculated for $C_{16}H_{24}BO_2$ ([M+H]$^+$): *m*/*z* = 259.1869, found: 259.1862.



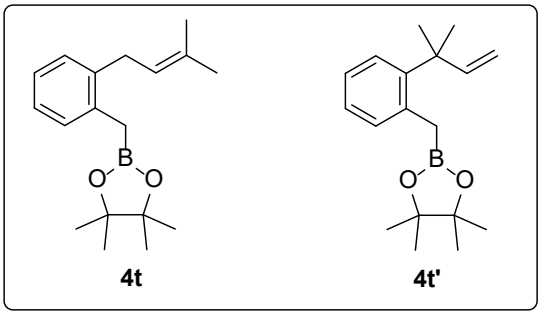
4r

4,4,5,5-tetramethyl-2-(2-(2-methylallyl)benzyl)-1,3,2-dioxaborolane (4r). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 43%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.07 (m, 5H), 4.80 (s, 1H), 4.56 (s, 1H), 3.31 (s, 2H), 2.26 (s, 2H), 1.72 (s, 3H), 1.22 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 129.9, 129.7, 126.2, 125.1, 111.9, 83.3, 45.8, 41.9, 24.7, 22.7; IR (film): 1751, 1734, 1376, 1329, 1244, 1047 cm^{-1}; HRMS (EI): calculated for $C_{17}H_{26}BO_2$ ([M+H]$^+$): m/z = 273.2026, found: 273.2017.



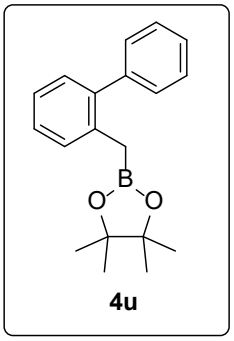
4s

ethyl 2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzyl)acrylate (4s). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 7.2, 1.6 Hz, 1H), 7.15 (dd, J = 6.6, 2.1 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.08 – 7.05 (m, 1H), 6.20 (q, J = 1.5 Hz, 1H), 5.18 (q, J = 1.7 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.62 (t, J = 1.6 Hz, 2H), 2.22 (s, 2H), 1.29 (t, J = 7.2 Hz, 3H), 1.22 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 139.5, 137.8, 136.1, 130.1, 130.1, 126.6, 125.8, 125.3, 83.4, 60.7, 35.3, 24.7, 14.2; IR (film): 1744, 1735, 1718, 1376, 1240 cm^{-1}; HRMS (EI): calculated for $C_{19}H_{28}BO_4$ ([M+H]$^+$): m/z = 331.2081, found: 331.2069.



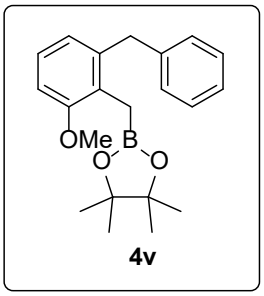
4t **4t'**

4,4,5,5-tetramethyl-2-(2-(3-methylbut-2-en-1-yl)benzyl)-1,3,2-dioxaborolane (4t) and 4,4,5,5-tetramethyl-2-(2-(2-methylbut-3-en-2-yl)benzyl)-1,3,2-dioxaborolane (4t'). The title compounds were prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 30% in total); Isomers could be detected in the ^{1}H NMR and ^{13}C NMR.



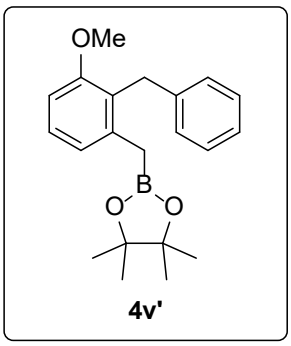
4u

[2-([1,1'-biphenyl]-2-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4u). The title compound was prepared via the *general procedure II*. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 81%, m.p. = 81-85 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.16 (m, 11H), 2.28 (s, 2H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 141.6, 136.5, 130.1, 130.0, 129.5, 128.0, 127.2, 126.6, 125.1, 83.3, 24.7; IR (film): 1570, 1420, 1332, 1155, 1115 cm^{-1}.



4v

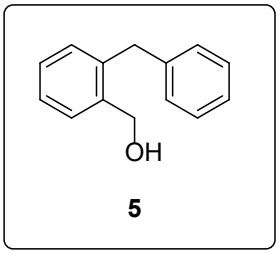
2-(2-benzyl-6-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4v). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 16%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.2 Hz, 2H), 7.14 (d, J = 7.9 Hz, 3H), 7.07 (t, J = 7.9 Hz, 1H), 6.73 (dd, J = 7.9, 4.6 Hz, 2H), 4.00 (s, 2H), 3.80 (s, 3H), 2.15 (s, 2H), 1.17 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 139.2, 128.8, 128.2, 125.7, 125.4, 122.7, 108.0, 82.9, 55.3, 39.7, 24.67; IR (film): 1746, 1734, 1459, 1261, 1374, 1346, 1261, 1252, 1146, 1050 cm^{-1}; HRMS (EI): calculated for $C_{21}H_{28}BO_3$ ([M+H]$^+$): m/z = 339.2132, found: 339.2123.



4v'

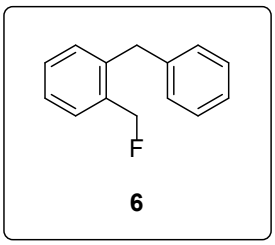
2-(2-benzyl-3-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4v'). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 13%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 6.9 Hz, 2H), 7.11 (d, J = 7.4 Hz, 4H), 6.81 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 4.06 (s, 2H), 3.76 (s, 3H), 2.22 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 140.9, 128.2, 128.0, 126.9,

126.8, 125.3, 122.6, 107.6, 83.3, 55.5, 31.7, 24.7; IR (film): 1749, 1473, 1376, 1246, 1149 cm^{-1}; HRMS (EI): calculated for $C_{21}H_{28}BO_3$ ([M+H]$^+$): *m*/*z* = 339.2132, found: 339.2125.



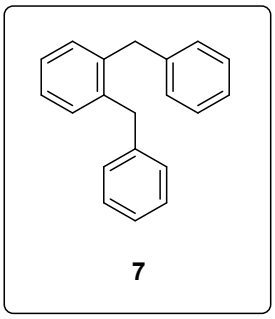
5

(2-benzylphenyl)methanol (5). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.4, 3.6 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.18 (ddt, *J* = 9.1, 5.6, 2.6 Hz, 2H), 7.14 – 7.09 (m, 2H), 4.62 (s, 2H), 4.07 (s, 2H), 1.56 (s, 1H); The data was consistent with the previous report.



6

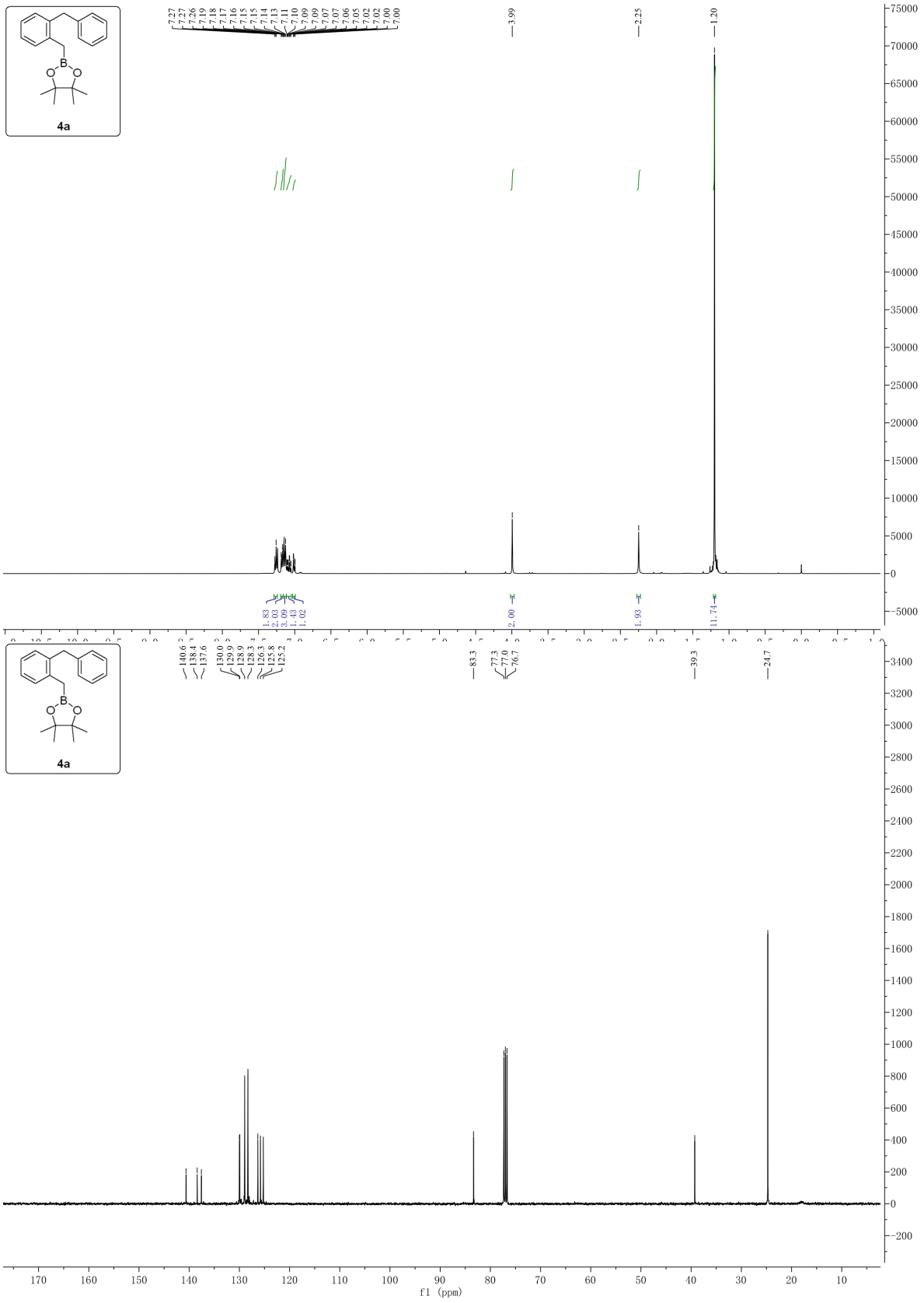
1-benzyl-2-(fluoromethyl)benzene (6). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 7.3, 1.8 Hz, 1H), 7.35 – 7.24 (m, 4H), 7.24 – 7.16 (m, 2H), 7.16 – 7.10 (m, 2H), 5.37 (d, *J* = 47.8 Hz, 2H), 4.08 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.6, 130.6, 129.2, 129.2, 129.1, 129.0, 128.8, 128.5, 126.7, 126.2, 83.8, 82.1, 38.3 cm^{-1}.

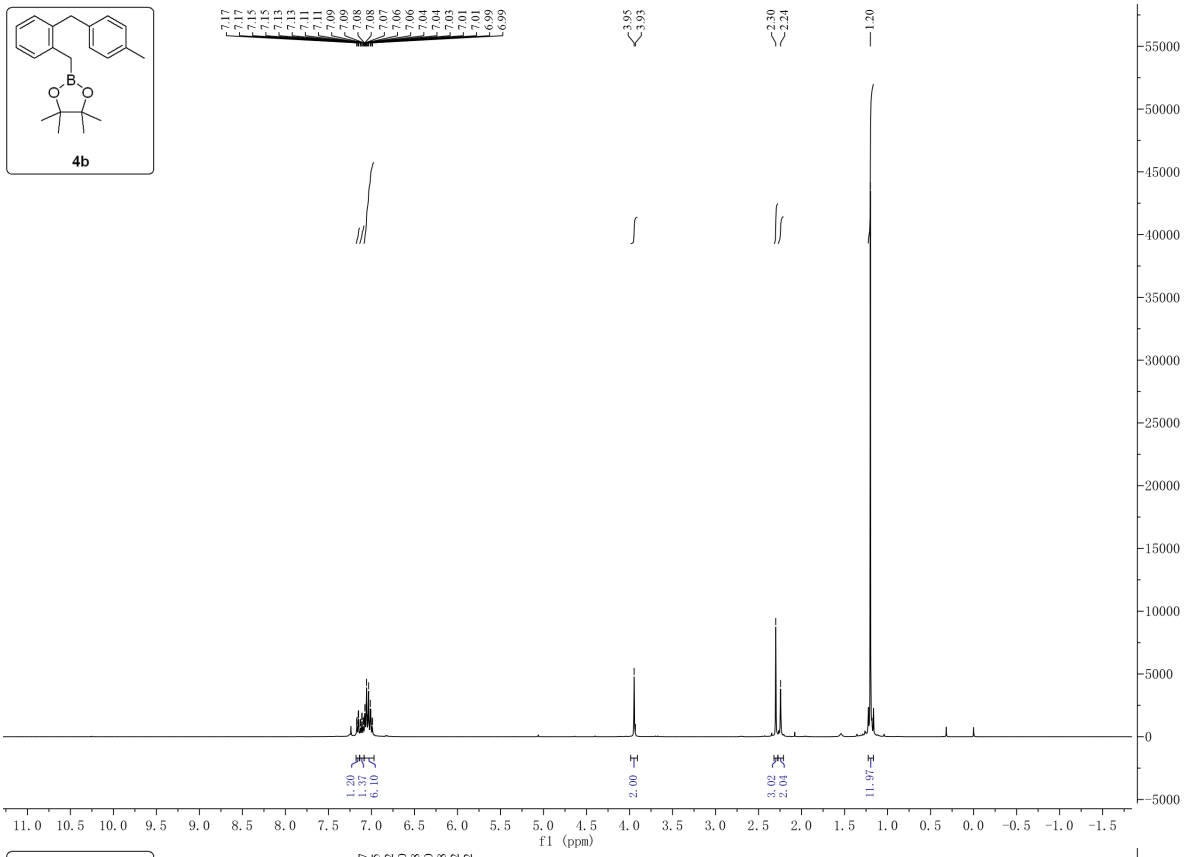


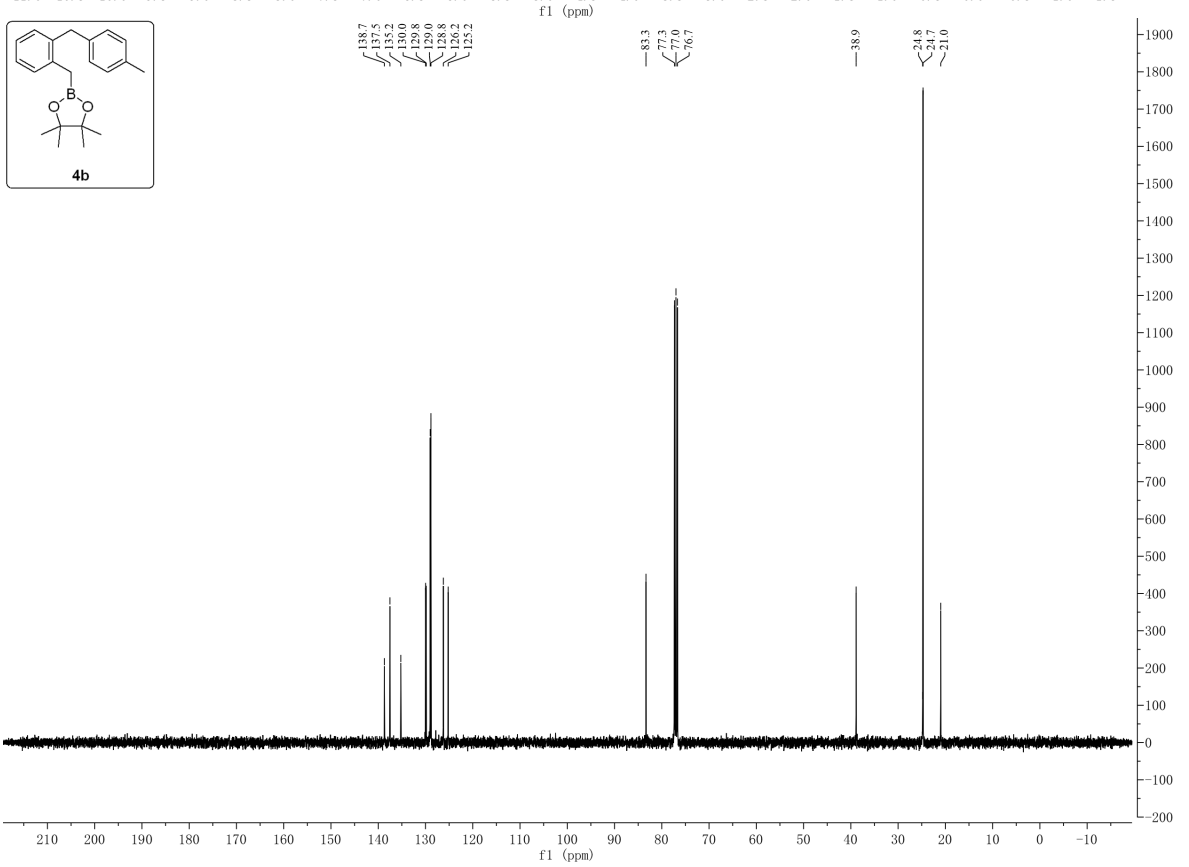
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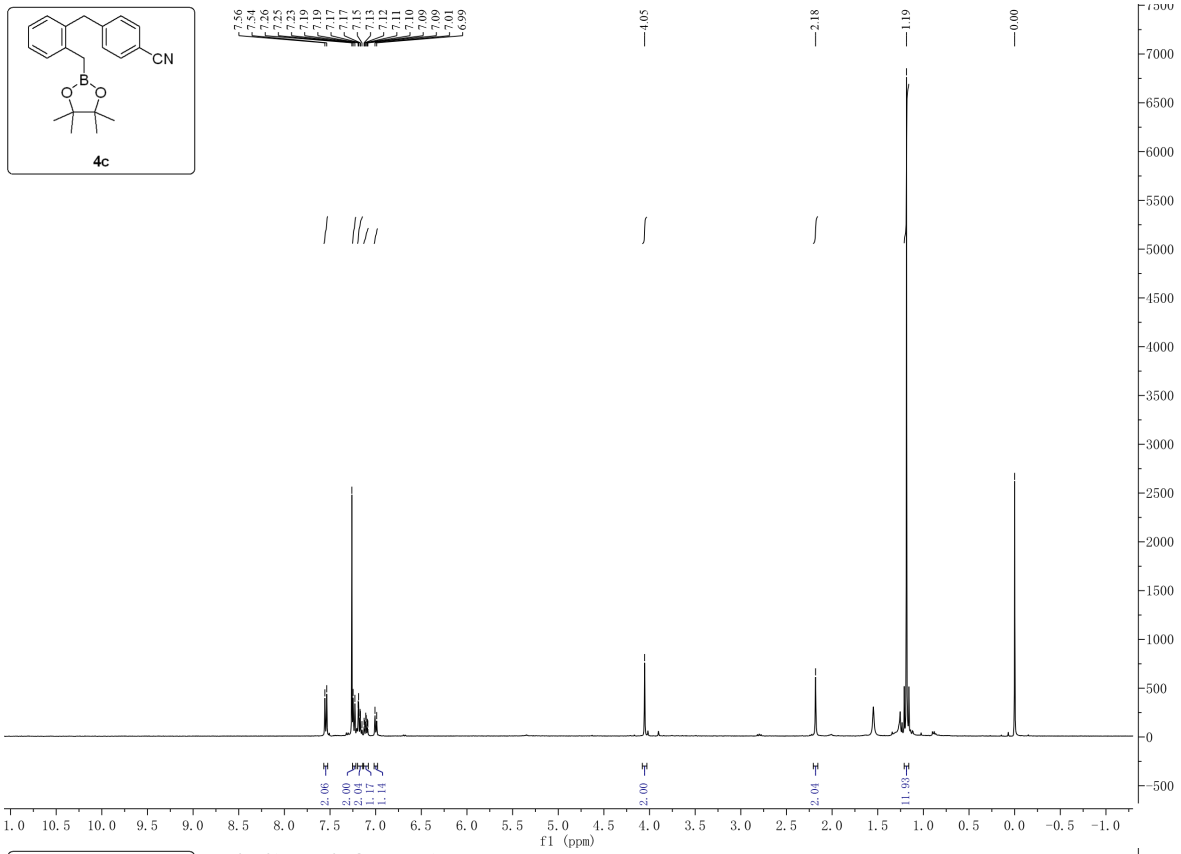
1,2-dibenzylbenzene (7). The title compound was prepared via the general procedure. After purification by silica gel column chromatography using PE:EA = 10:1 as eluting solvent, the product was isolated as a white solid (isolated yield 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 8.0, 6.6 Hz, 4H), 7.13 – 7.06 (m, 4H), 7.04 (dd, *J* = 5.5, 3.6 Hz, 2H), 7.01 – 6.96 (m, 4H), 3.86 (s, 4H); The data was consistent with the previous report.

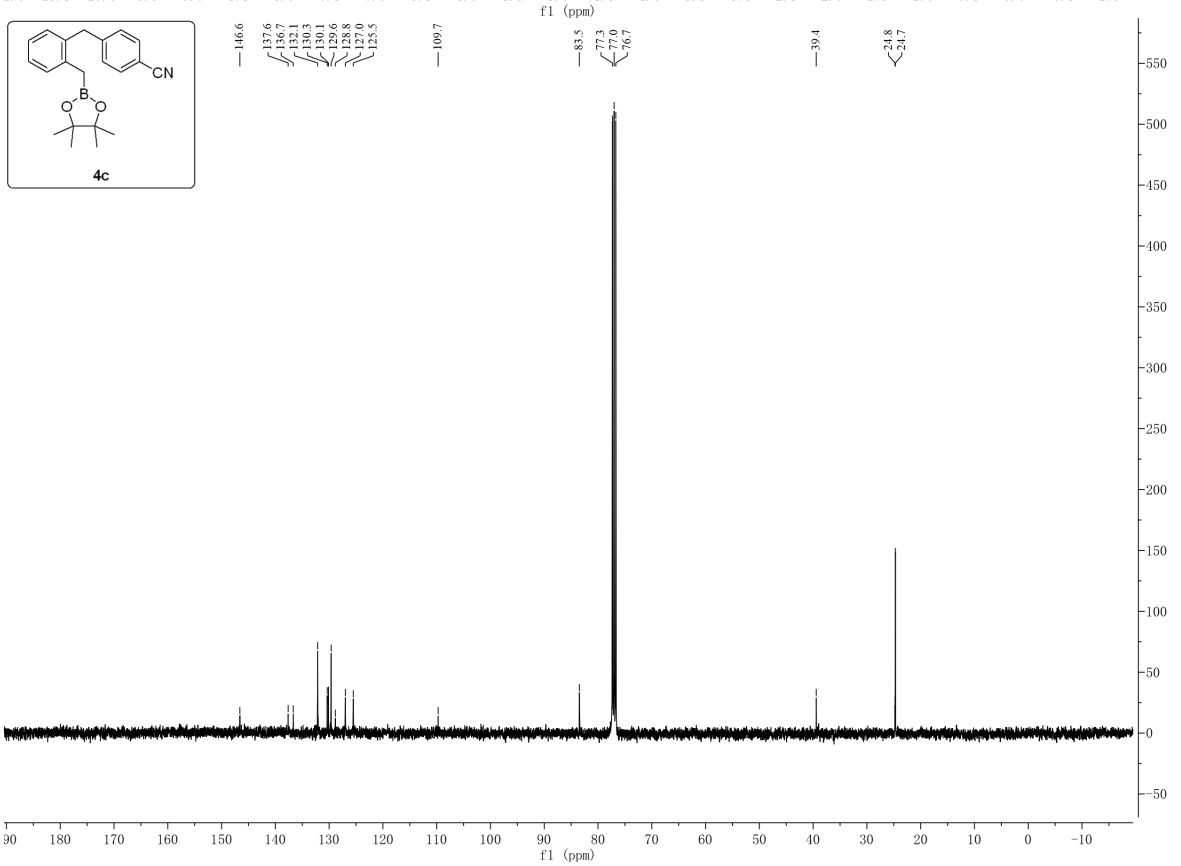
5. H NMR and ^{13}C NMR spectra of the products

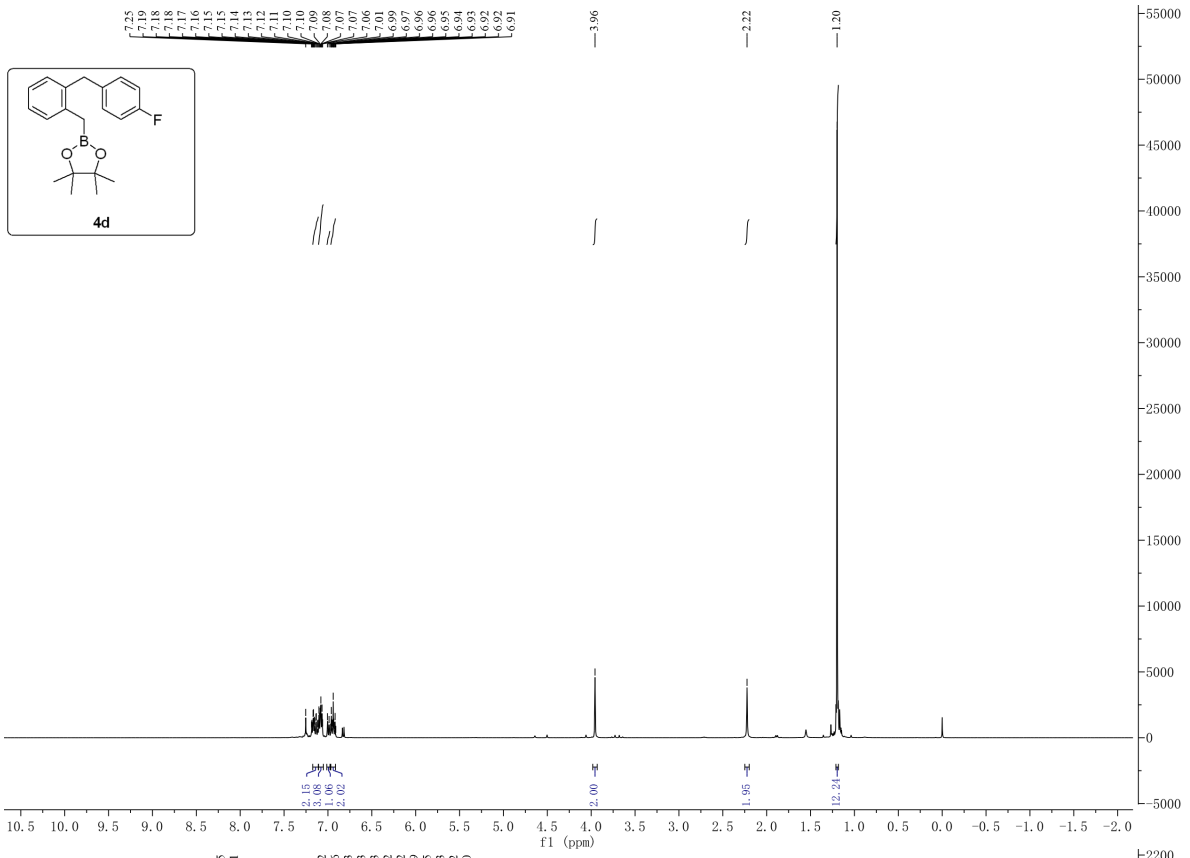

4a
7.27
7.26
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.11
7.10
7.09
7.07
7.06
7.05
7.02
7.00
3.99
2.25
1.20
1.83
2.03
3.09
1.43
1.02
2.00
1.93
11.74
4a
140.6
138.4
137.6
130.0
129.9
128.9
128.3
126.3
125.8
125.2
83.3
77.3
77.0
76.7
39.3
24.7
f1 (ppm)

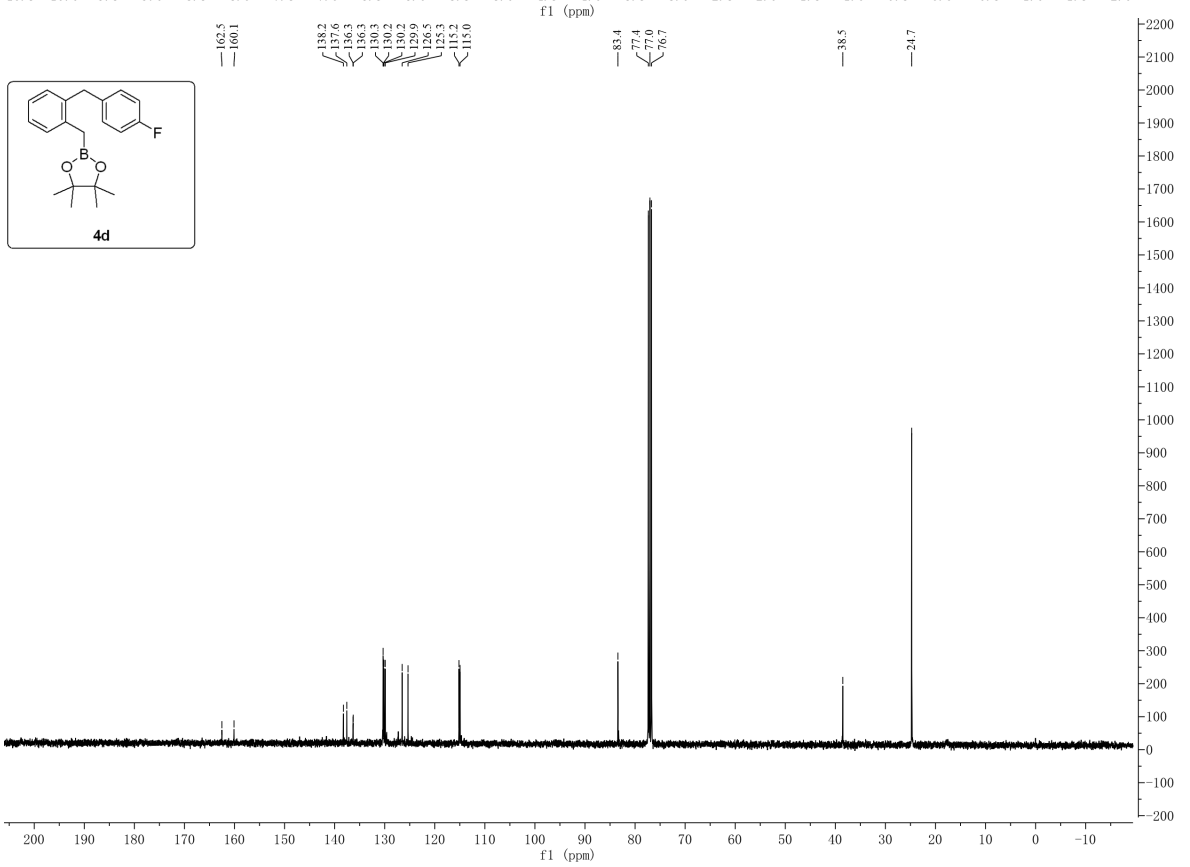

4b
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7.17
7.15
7.15
7.13
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7.11
7.11
7.09
7.09
7.08
7.08
7.07
7.06
7.06
7.04
7.04
7.03
7.01
7.01
6.99
6.99
3.95
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3.02
2.04
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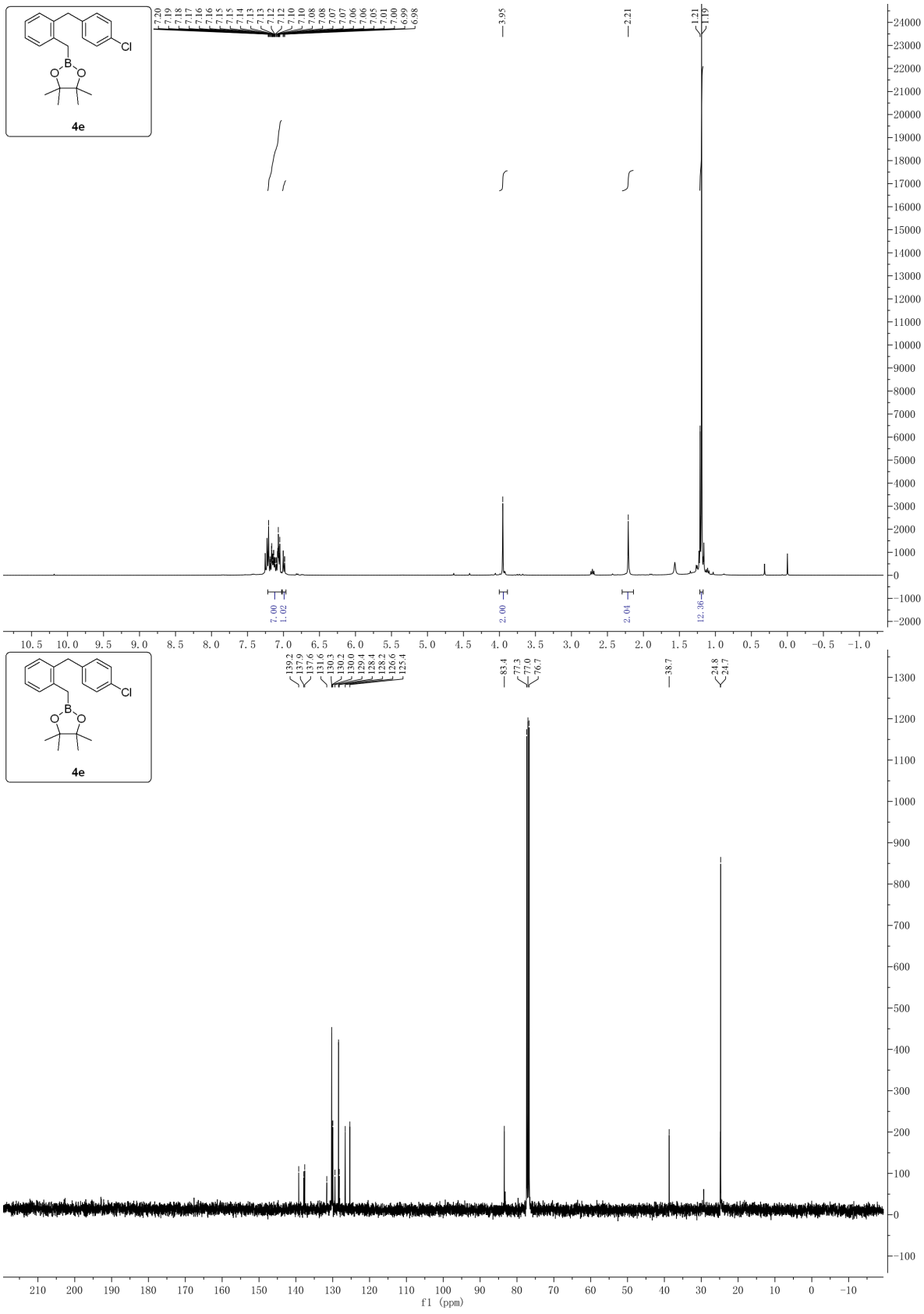

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137.5
135.2
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129.8
129.0
128.8
126.2
125.2
83.3
77.3
77.0
76.7
38.9
24.8
24.7
21.0
f1 (ppm)


CN
B
O
O
4c
7.56
7.54
7.26
7.25
7.23
7.19
7.17
7.17
7.15
7.13
7.12
7.11
7.10
7.09
7.09
7.01
6.99
4.05
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2.06
2.00
2.04
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1.14
2.00
2.04
11.93
f1 (ppm)

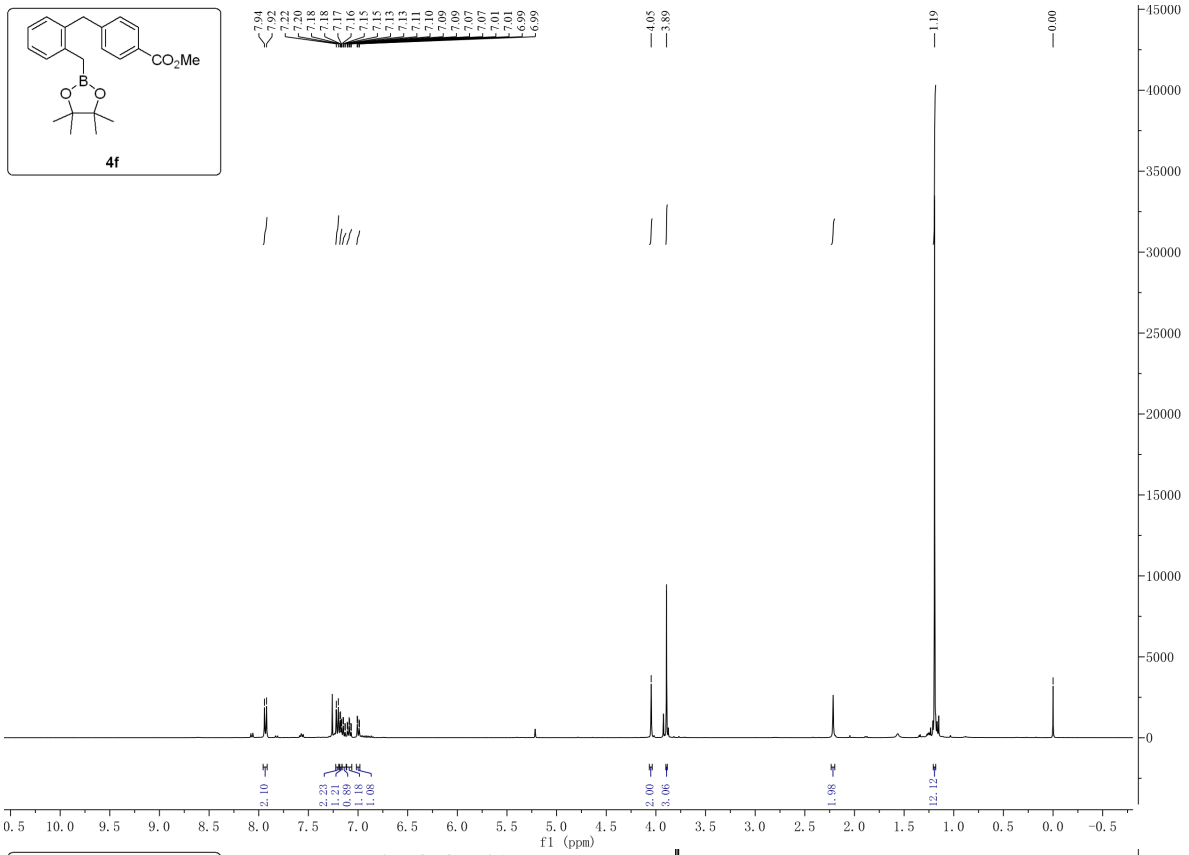

CN
B
O
O
4c
146.6
137.6
136.7
132.1
130.3
130.1
129.6
128.8
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125.5
109.7
83.5
77.3
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76.7
39.4
24.8
24.7
f1 (ppm)

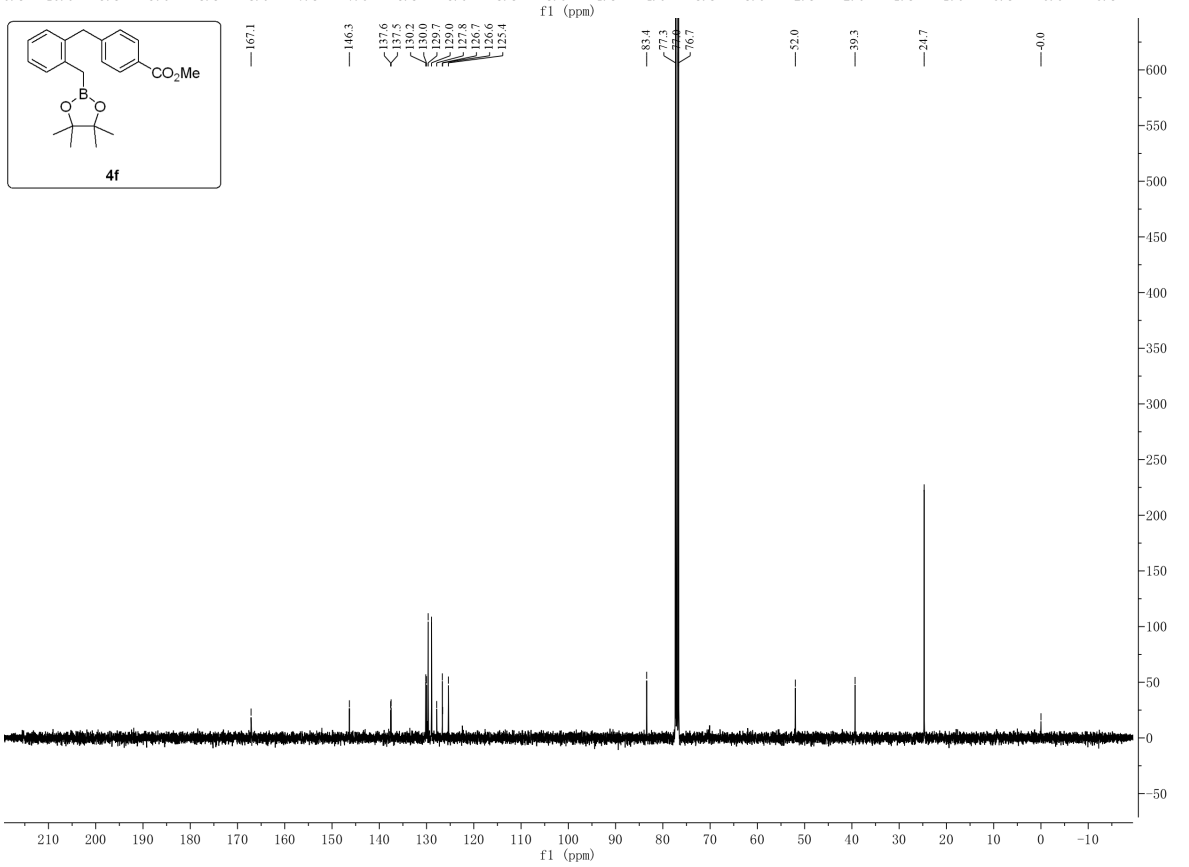

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6.99
6.97
6.96
6.96
6.95
6.94
6.93
6.92
6.92
6.91
3.96
2.22
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B
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O
4d
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2.08
1.06
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2.00
1.95
12.24
f1 (ppm)

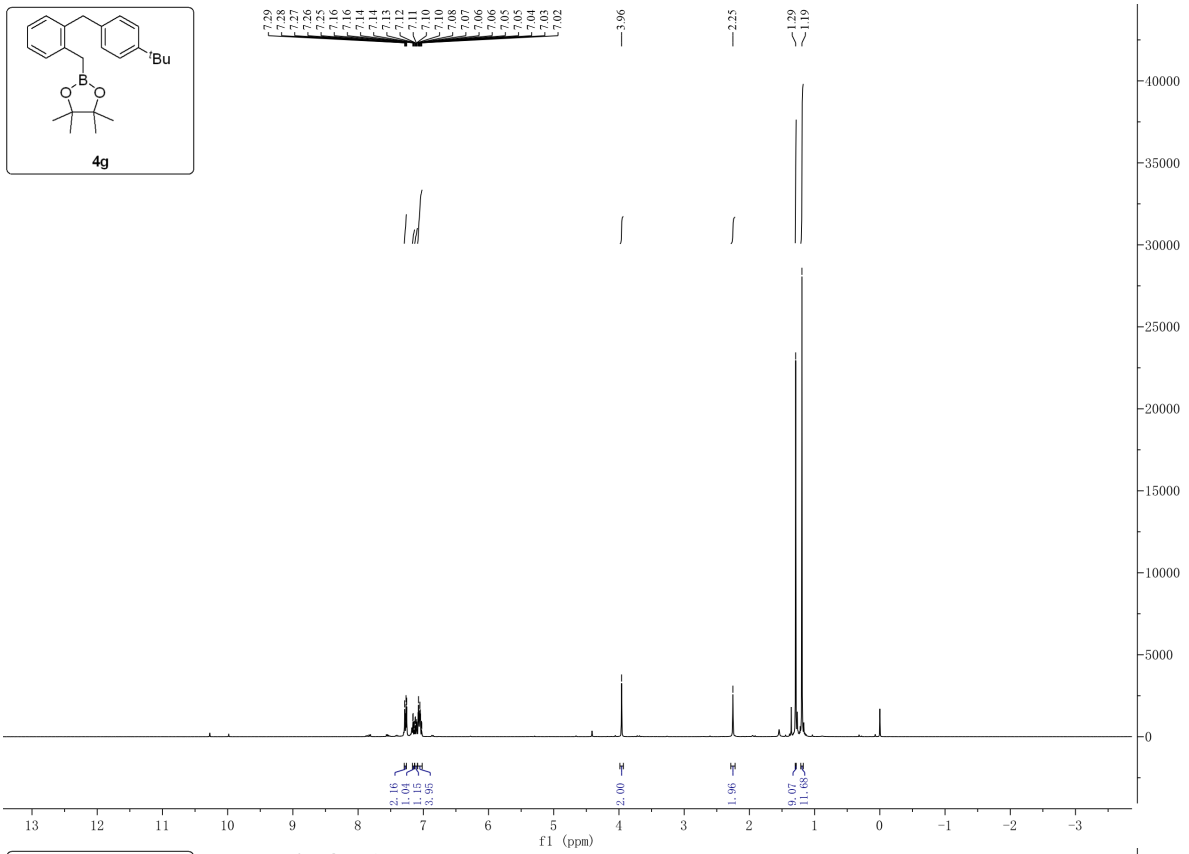

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138.2
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136.3
136.3
130.3
130.2
129.9
126.5
125.3
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77.4
77.0
76.7
38.5
24.7
F
B
O
O
4d
f1 (ppm)

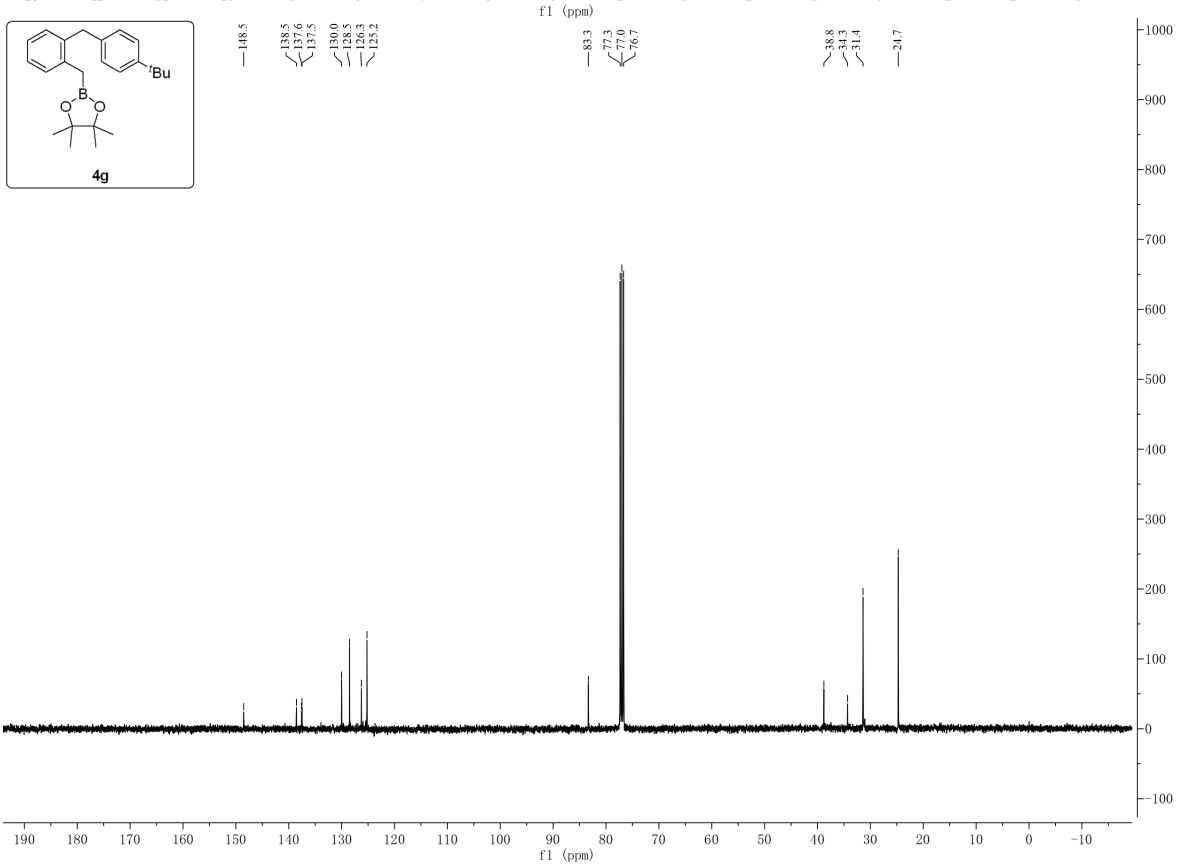

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7.13
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7.08
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7.07
7.07
7.06
7.06
7.05
7.01
7.00
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1.19
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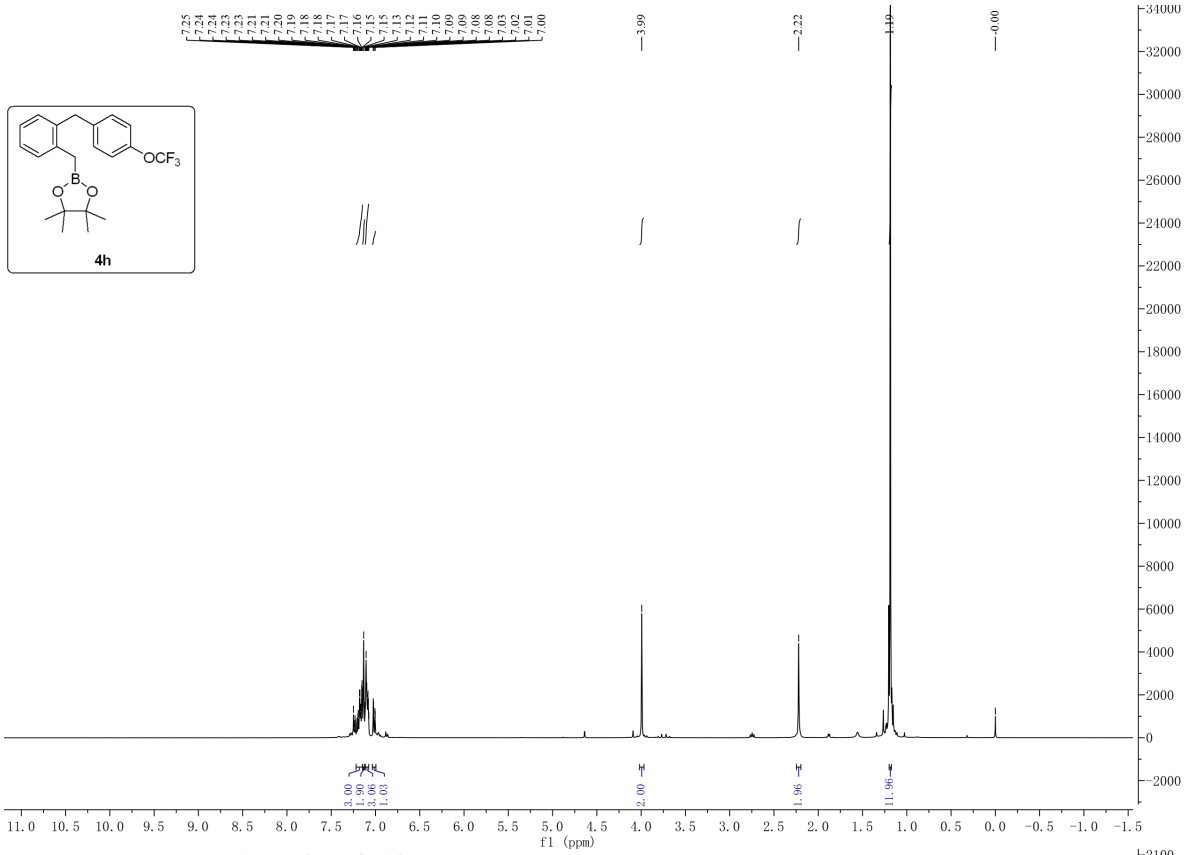
4e
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137.9
137.6
131.6
130.3
130.2
130.0
129.4
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125.4
83.4
77.3
77.0
76.7
38.7
24.8
24.7
f1 (ppm)

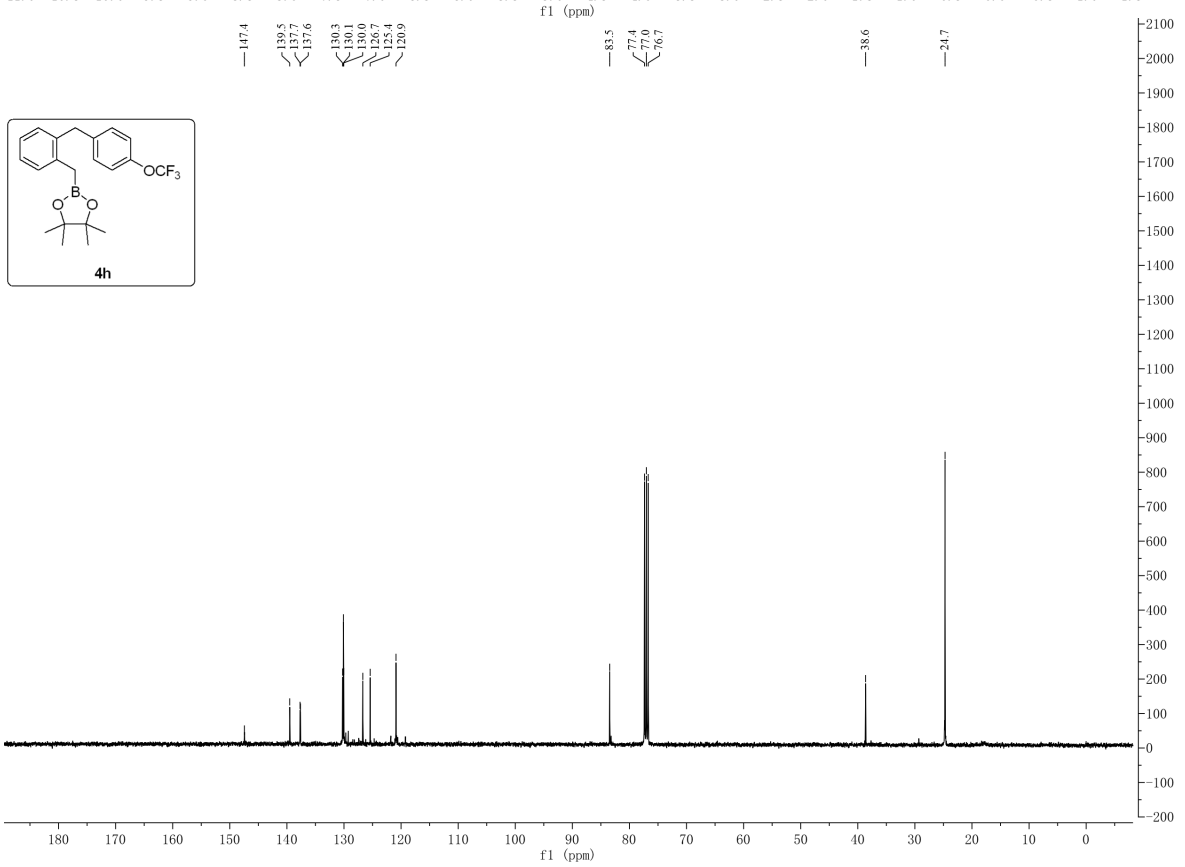

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7.01
7.01
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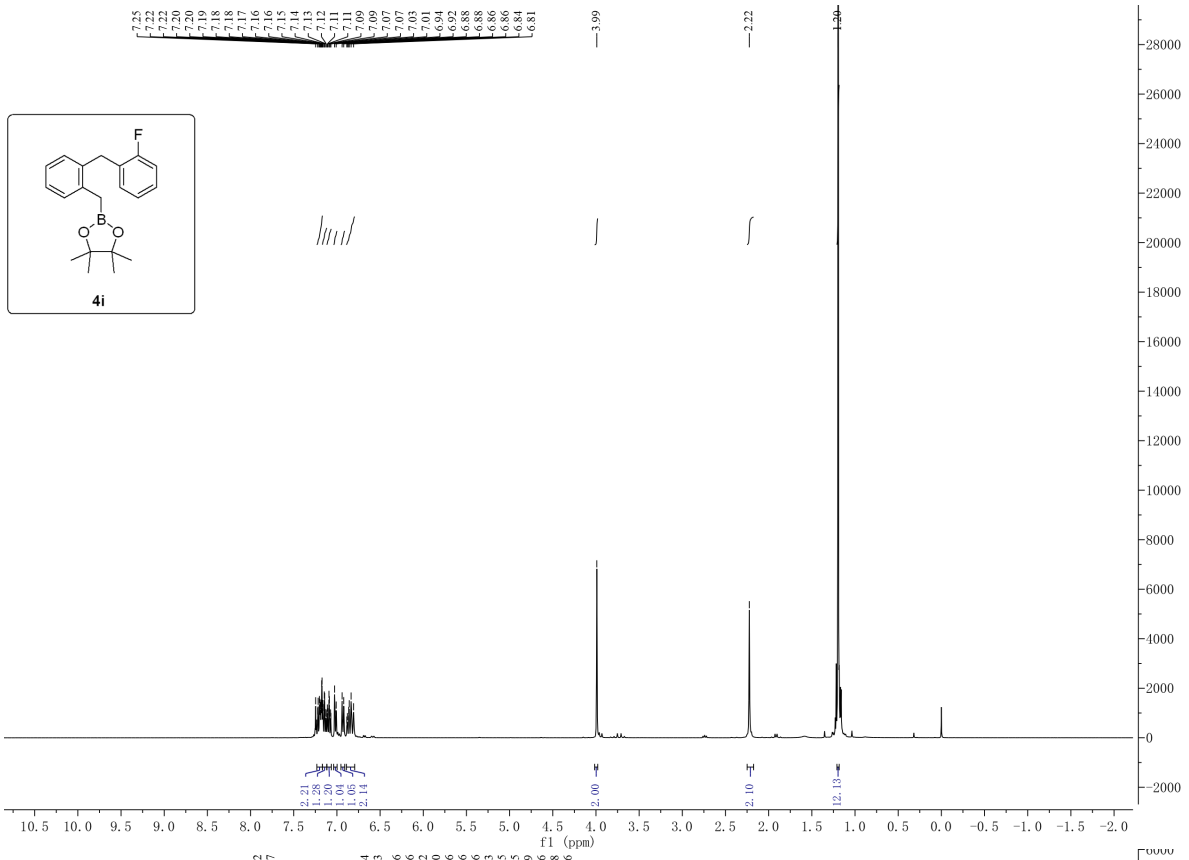

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127.8
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76.7
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f1 (ppm)

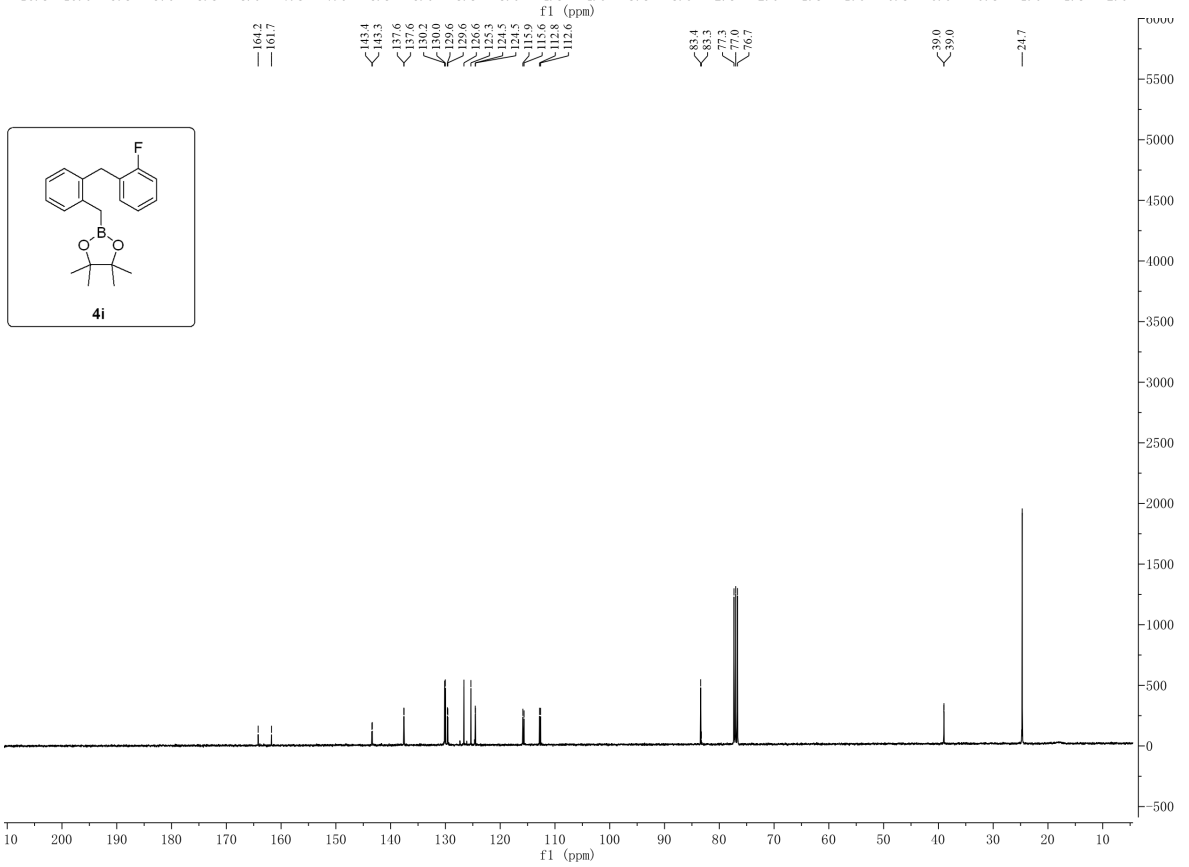

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7.10
7.08
7.07
7.06
7.06
7.05
7.05
7.04
7.03
7.02
3.96
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1.04
1.15
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9.07
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f1 (ppm)

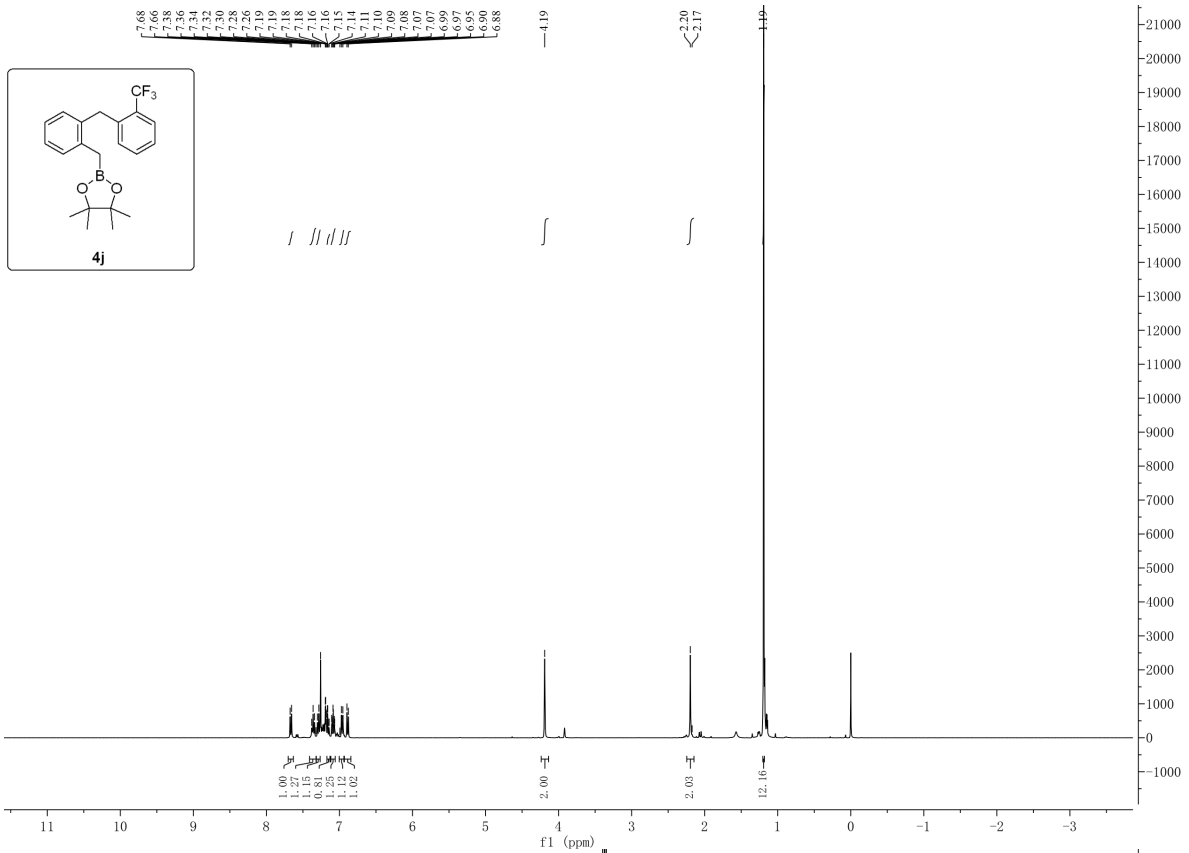

4g
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137.6
137.5
130.0
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126.3
125.2
83.3
77.3
77.0
76.7
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31.4
24.7
f1 (ppm)

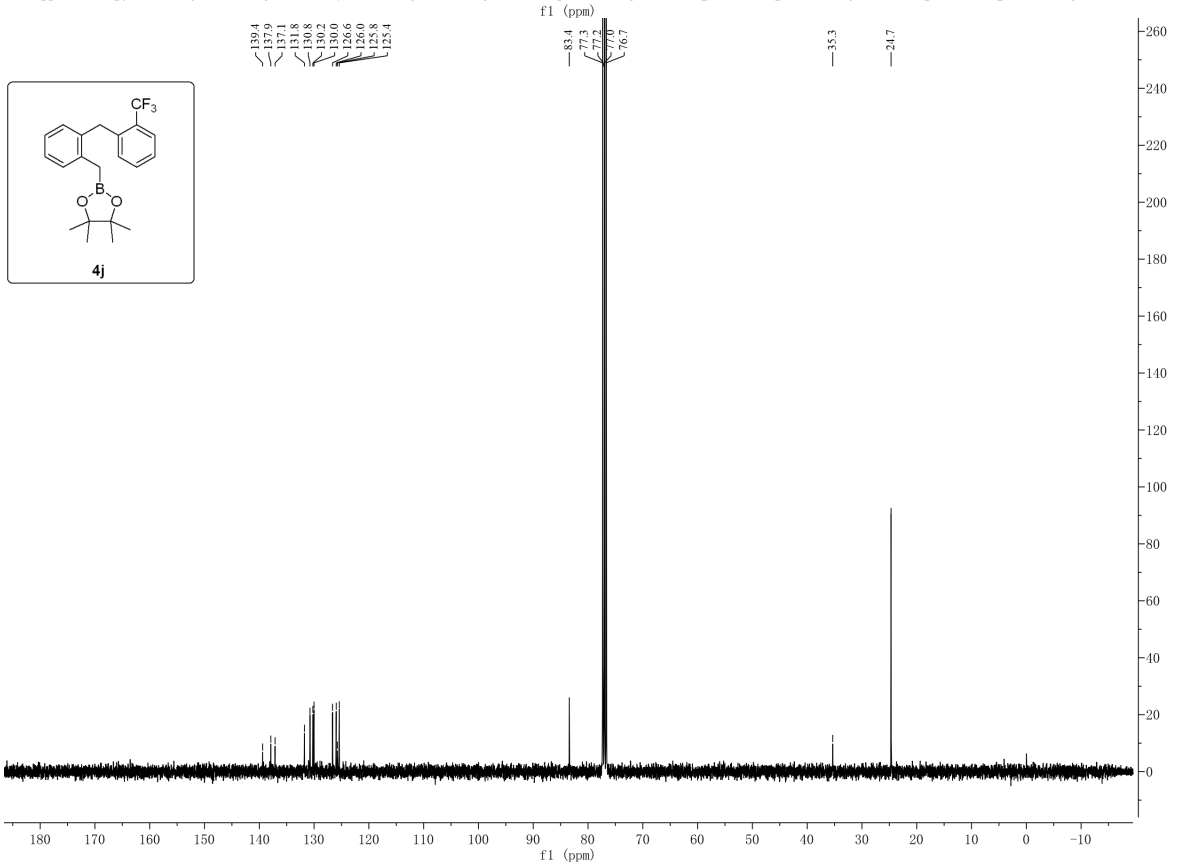

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7.16
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7.13
7.12
7.11
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7.09
7.09
7.08
7.08
7.05
7.02
7.01
7.00
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O
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2.00
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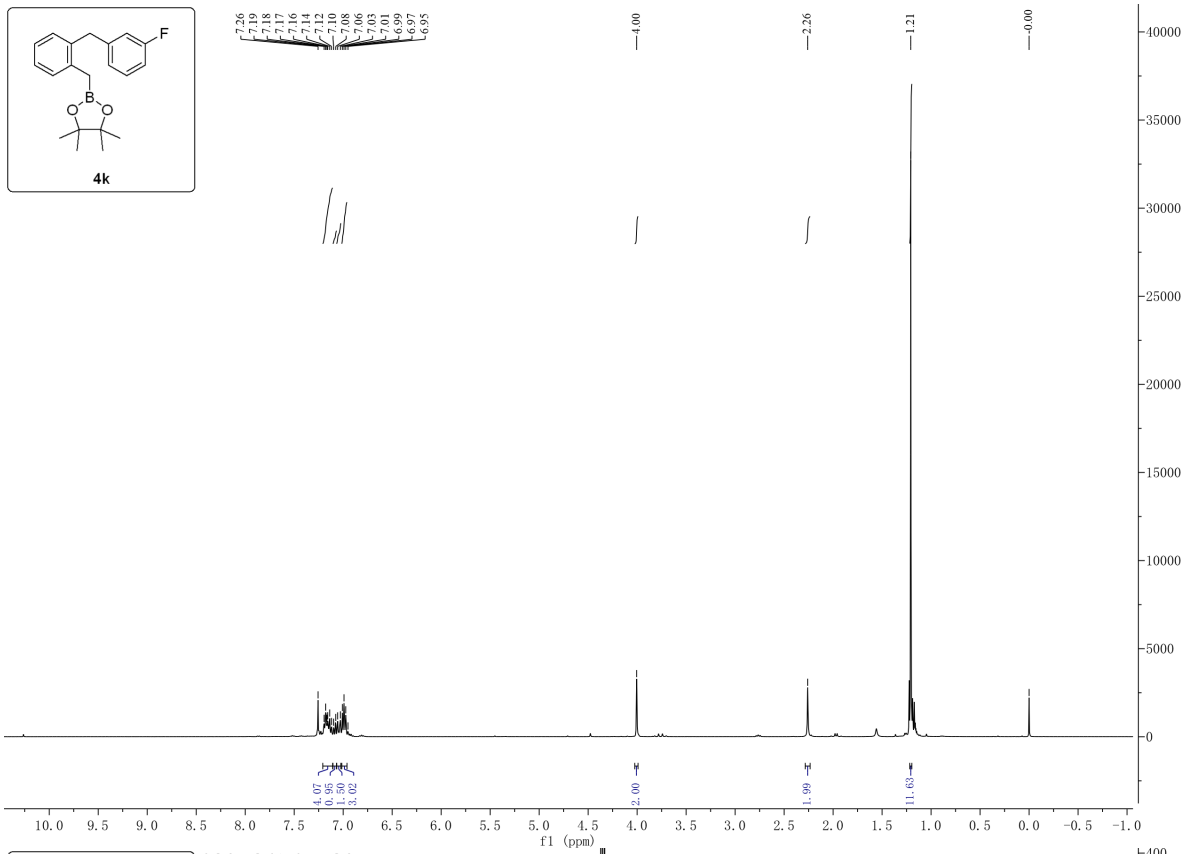

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76.7
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OCF3
B
O
O
4h
f1 (ppm)

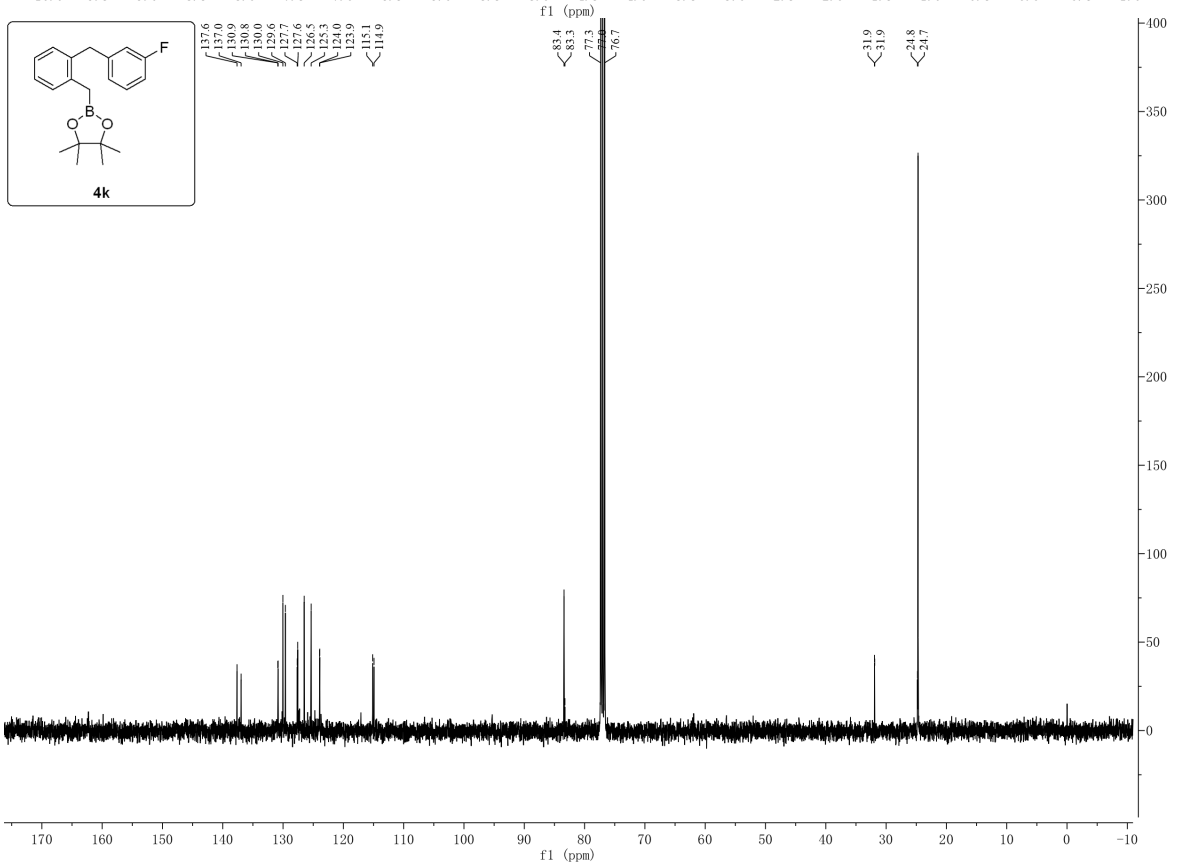

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7.11
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7.03
7.01
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6.92
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6.88
6.86
6.86
6.84
6.81
3.99
2.22
1.20
F
B
O
O
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1.05
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2.00
2.10
12.13
f1 (ppm)

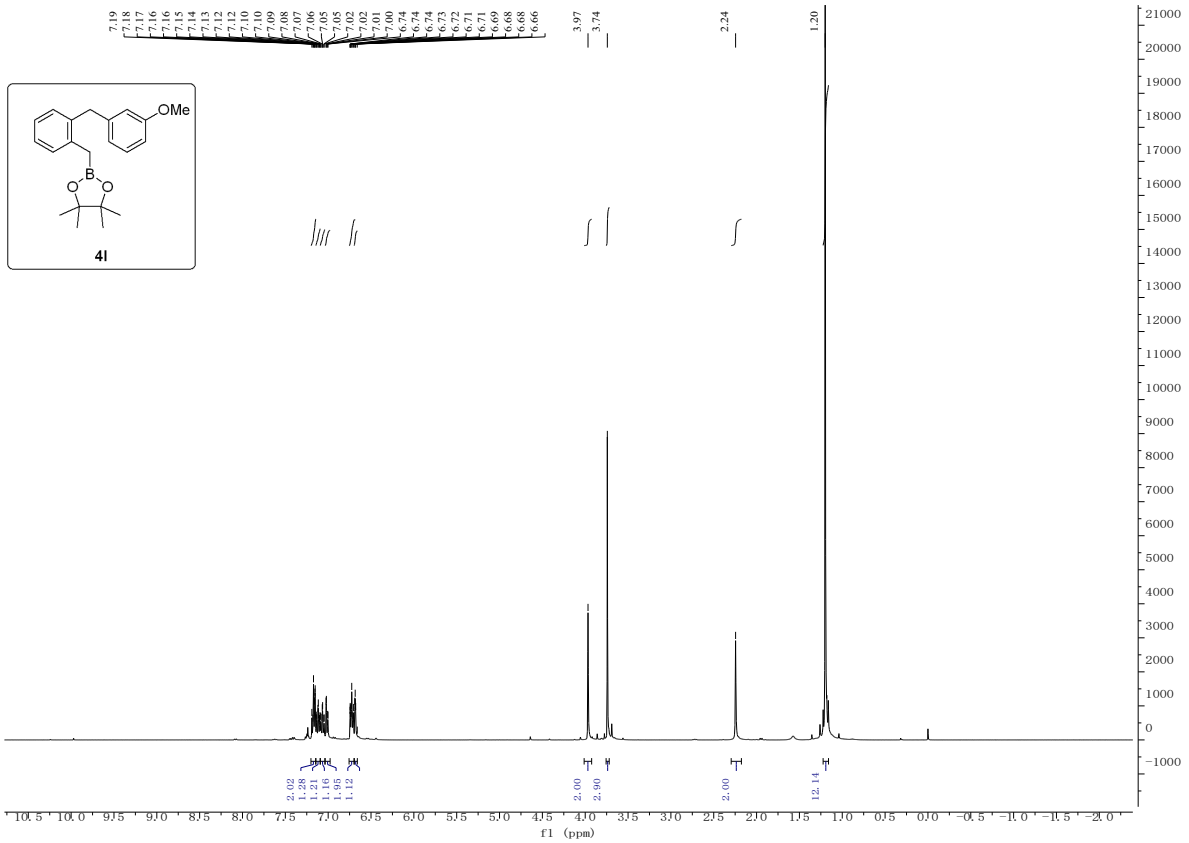

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124.5
124.5
115.9
115.6
112.8
112.6
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83.3
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77.0
76.7
39.0
39.0
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F
B
O
O
4i
f1 (ppm)

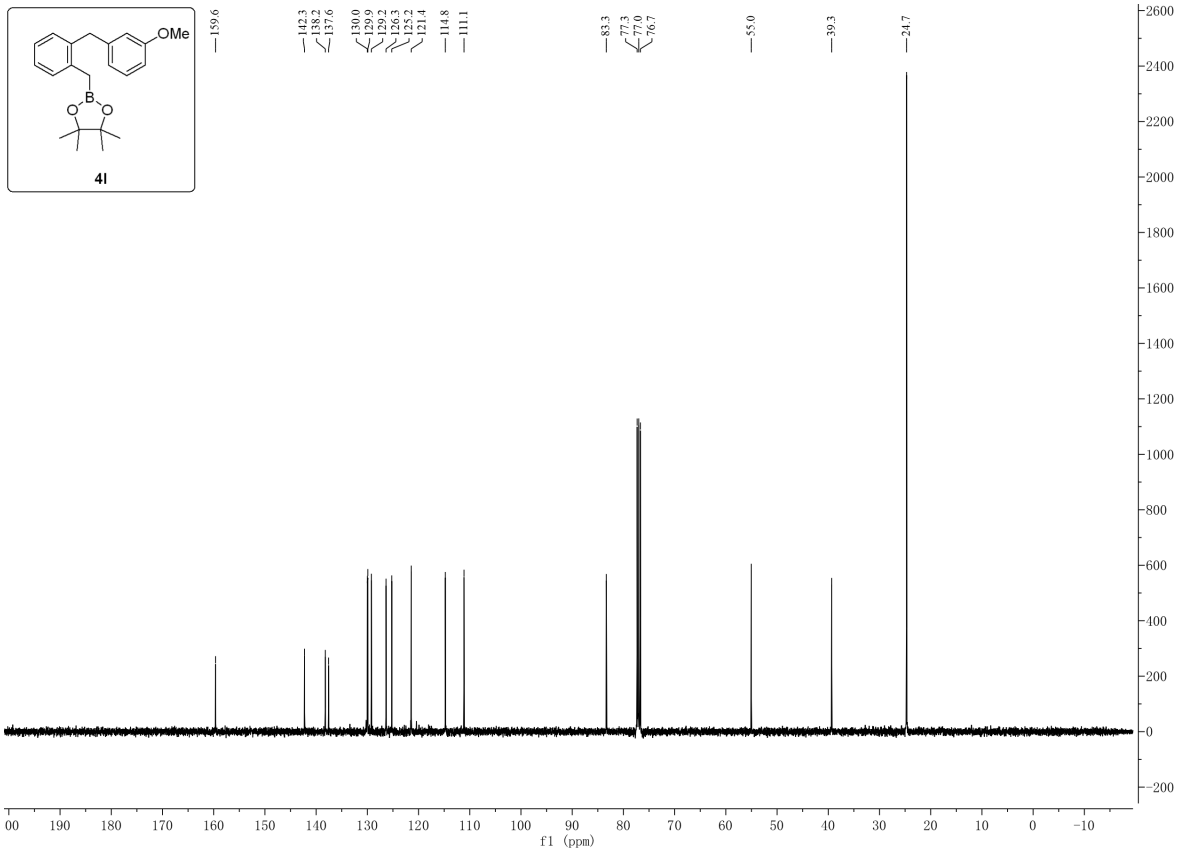

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7.16
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7.15
7.14
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7.07
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6.90
6.88
4.19
2.20
2.17
1.10
CF3
B
O
O
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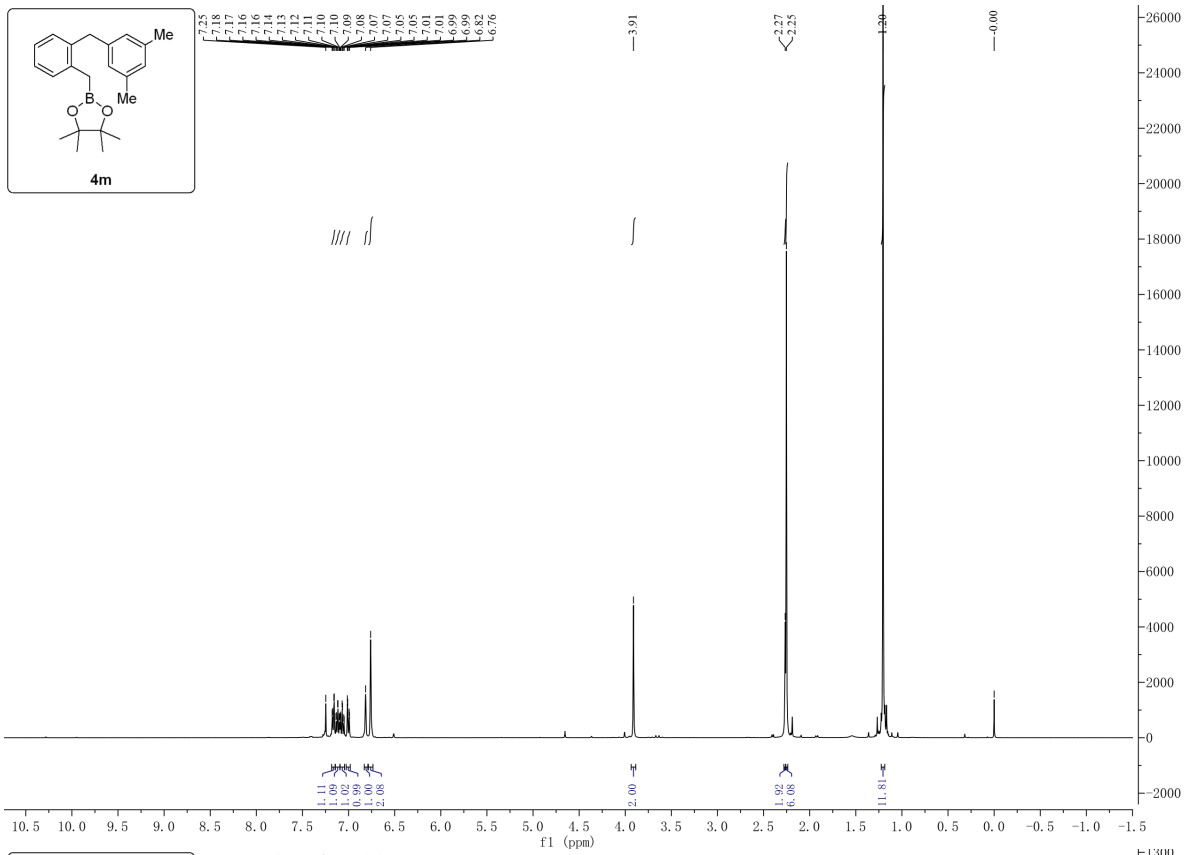

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131.8
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130.0
126.6
126.0
125.8
125.4
83.4
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77.2
77.0
76.7
35.3
24.7
CF3
B
O
O
4j
f1 (ppm)

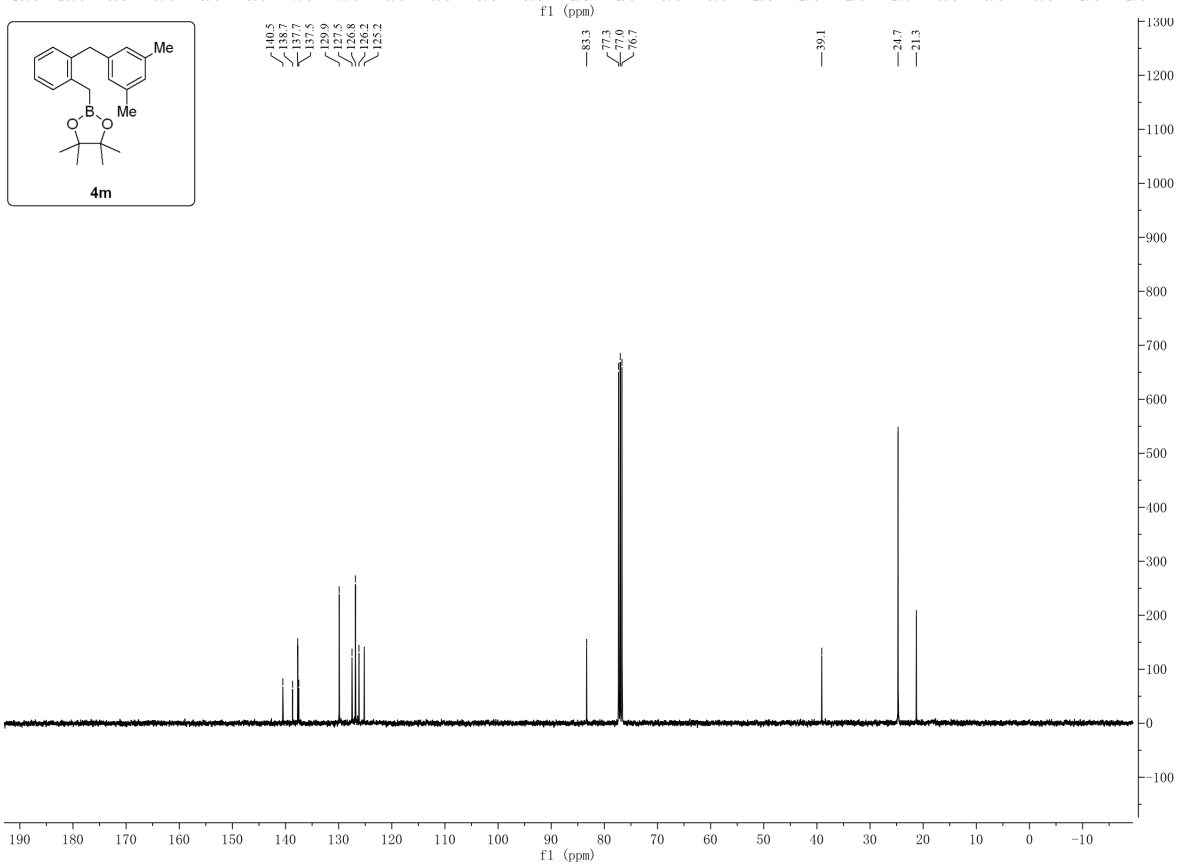

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7.16
7.14
7.12
7.10
7.08
7.06
7.03
7.01
6.99
6.97
6.95
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2.00
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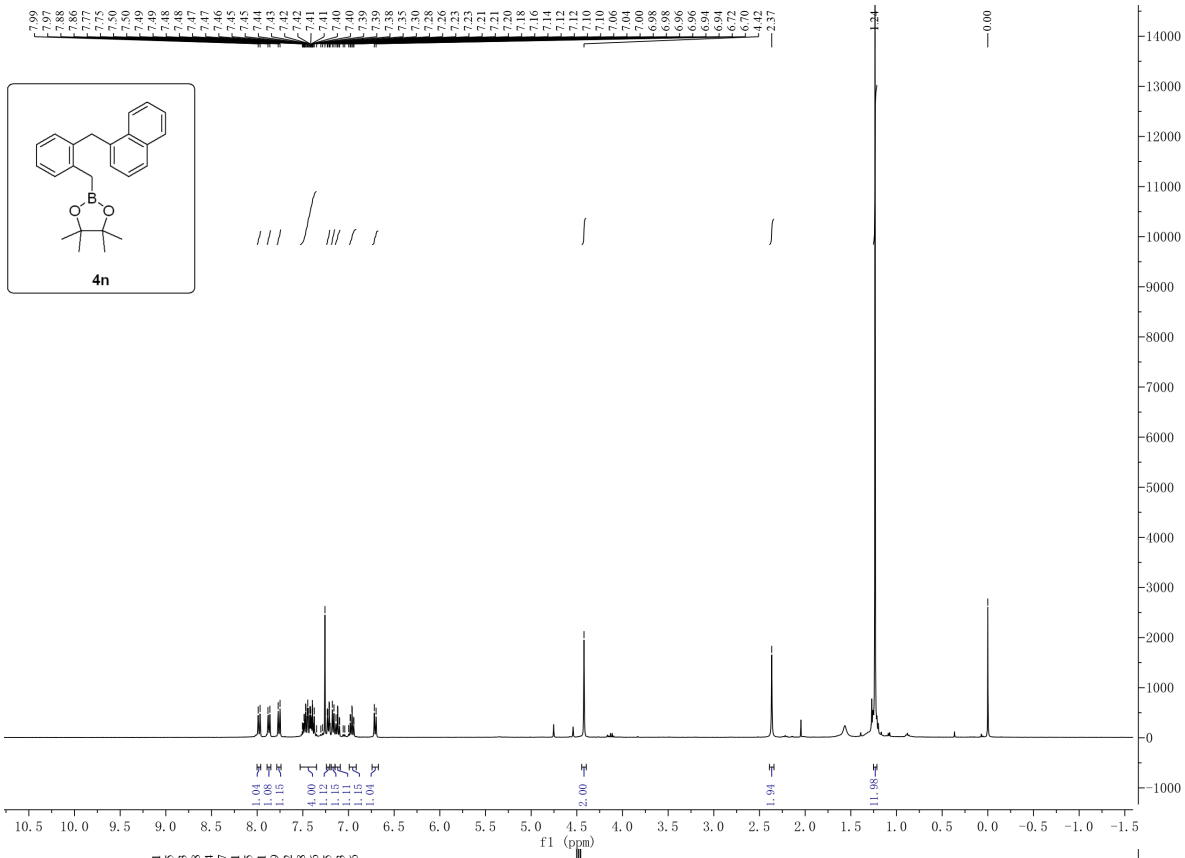

4k
137.6
137.0
130.9
130.8
130.0
129.6
127.7
127.6
126.5
125.3
124.0
123.9
115.1
114.9
83.4
83.3
77.3
77.0
76.7
31.9
31.9
24.8
24.7
f1 (ppm)

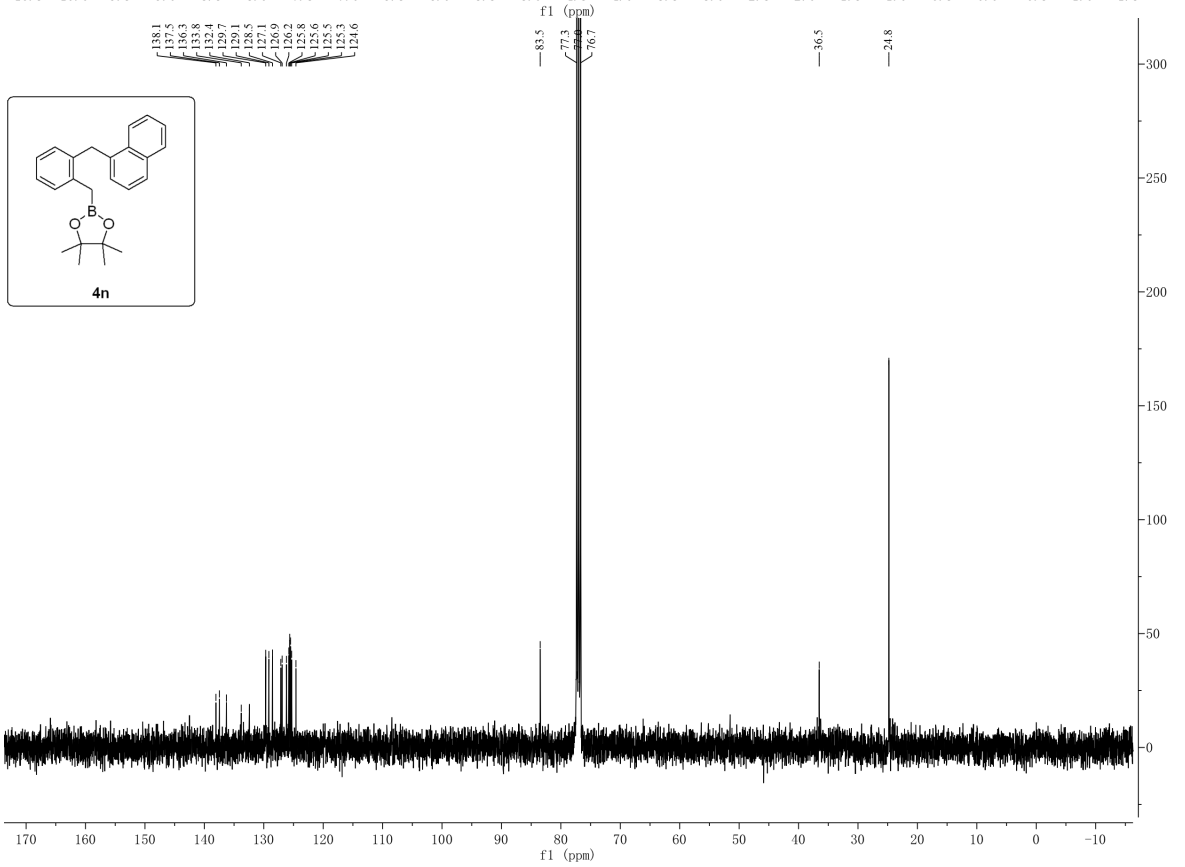

OMe
B
O
O
4l
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.13
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7.12
7.10
7.10
7.09
7.08
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7.06
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6.74
6.73
6.72
6.71
6.71
6.69
6.68
6.68
6.66
3.97
3.74
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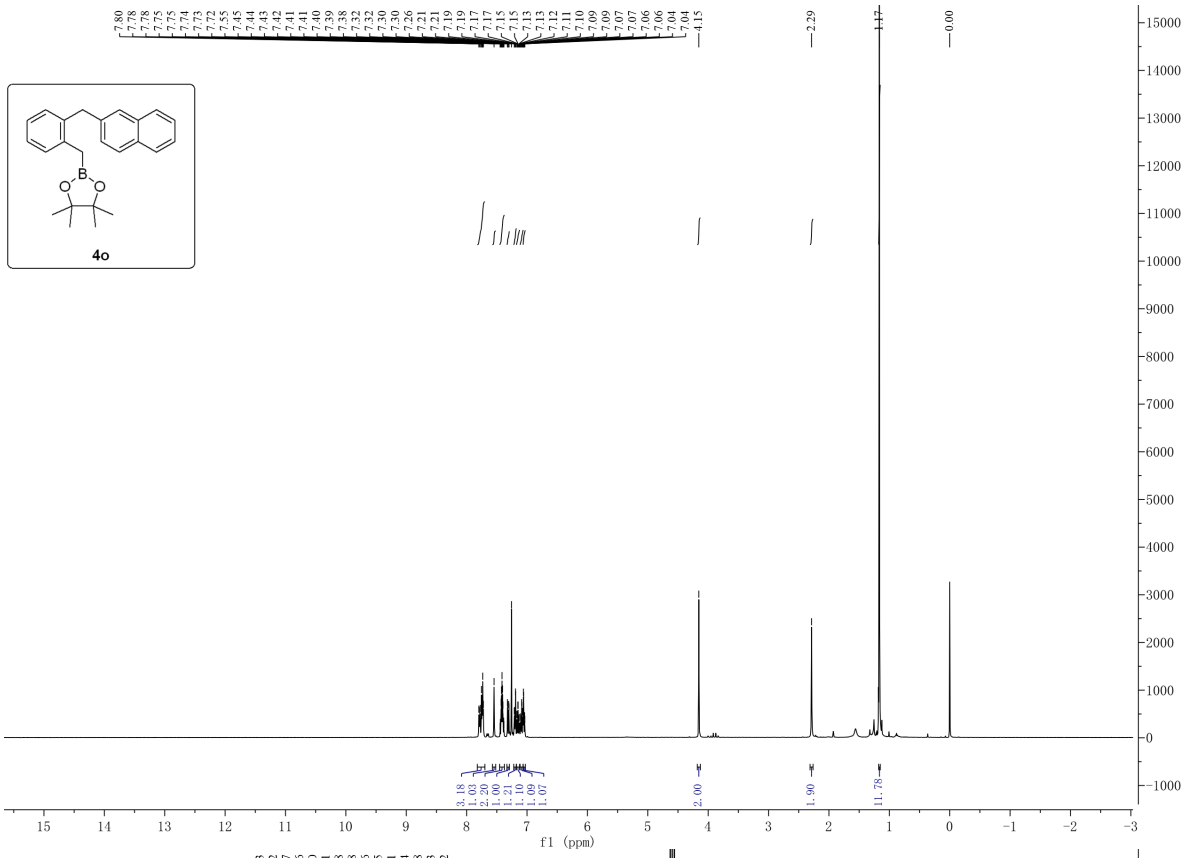

OMe
B
O
O
4l
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138.2
137.6
130.0
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129.2
126.3
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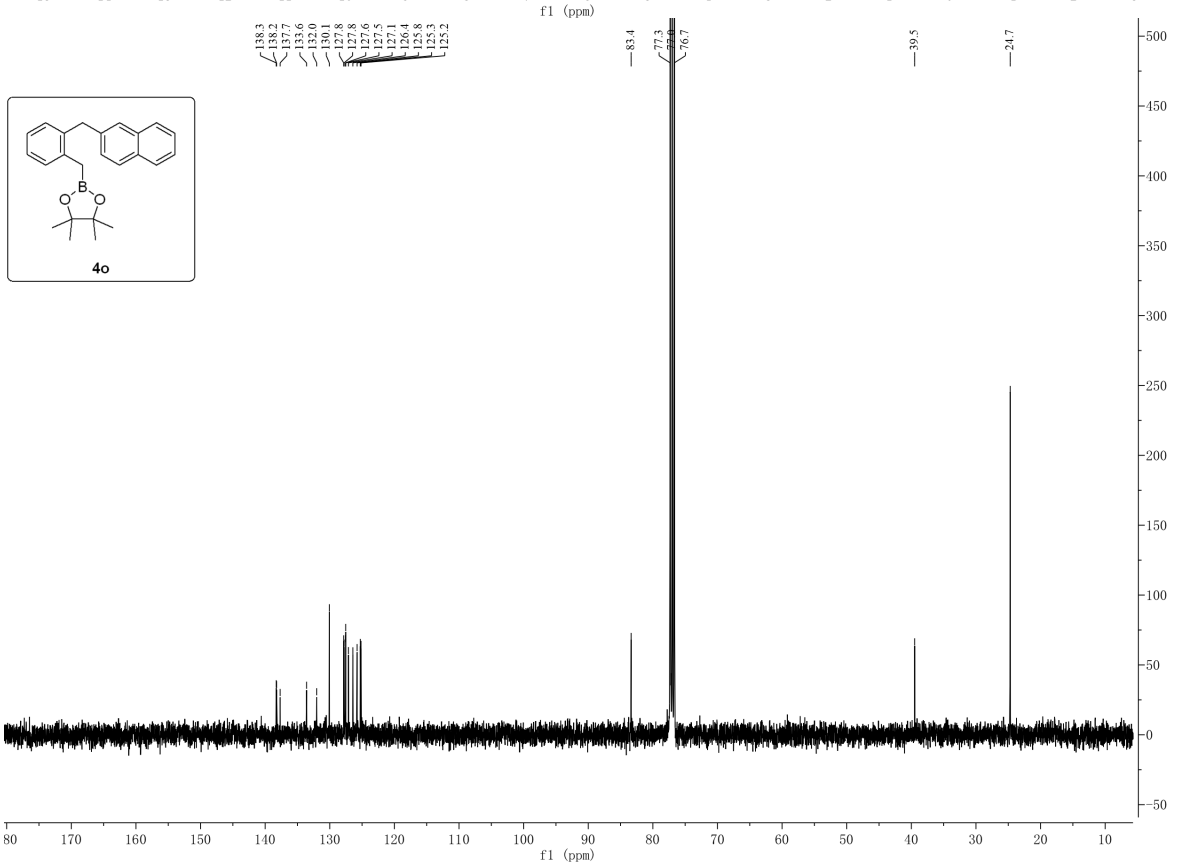

Me
Me
B
O
O
4m
7.25
7.18
7.17
7.16
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7.14
7.13
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7.11
7.10
7.10
7.09
7.08
7.07
7.07
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7.01
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6.82
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1.09
1.02
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1.00
2.08
2.00
1.92
6.08
11.81
f1 (ppm)

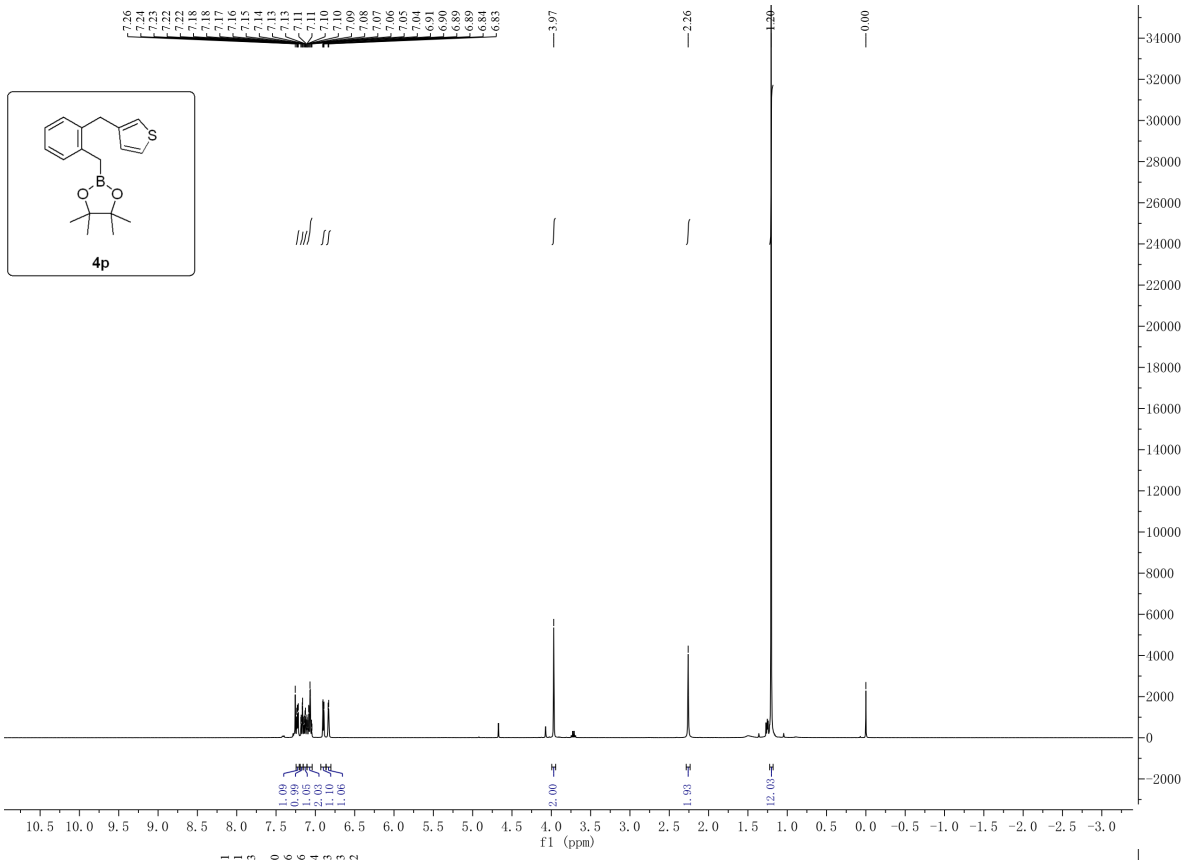

Me
Me
B
O
O
4m
140.5
138.7
137.7
137.5
129.9
127.5
126.8
126.2
125.2
83.3
77.3
77.0
76.7
39.1
24.7
21.3
f1 (ppm)

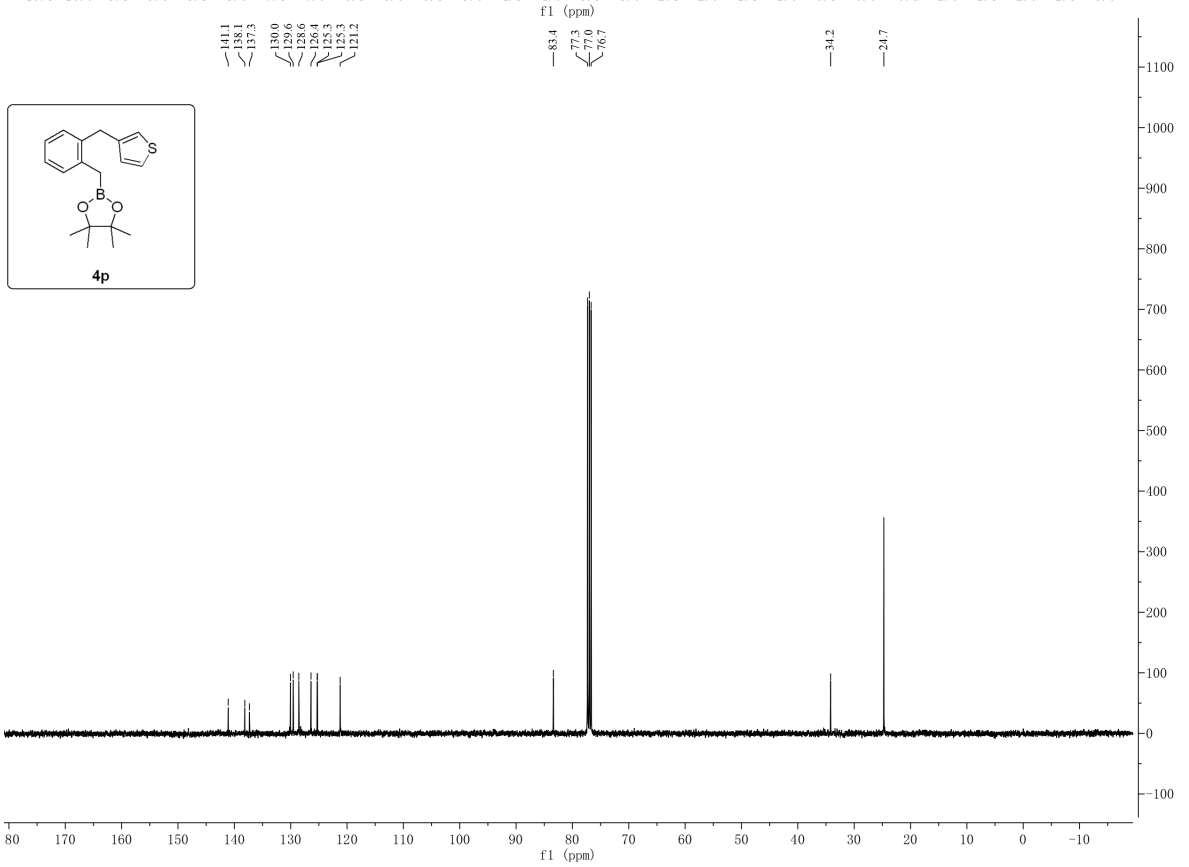

4n
f1 (ppm)

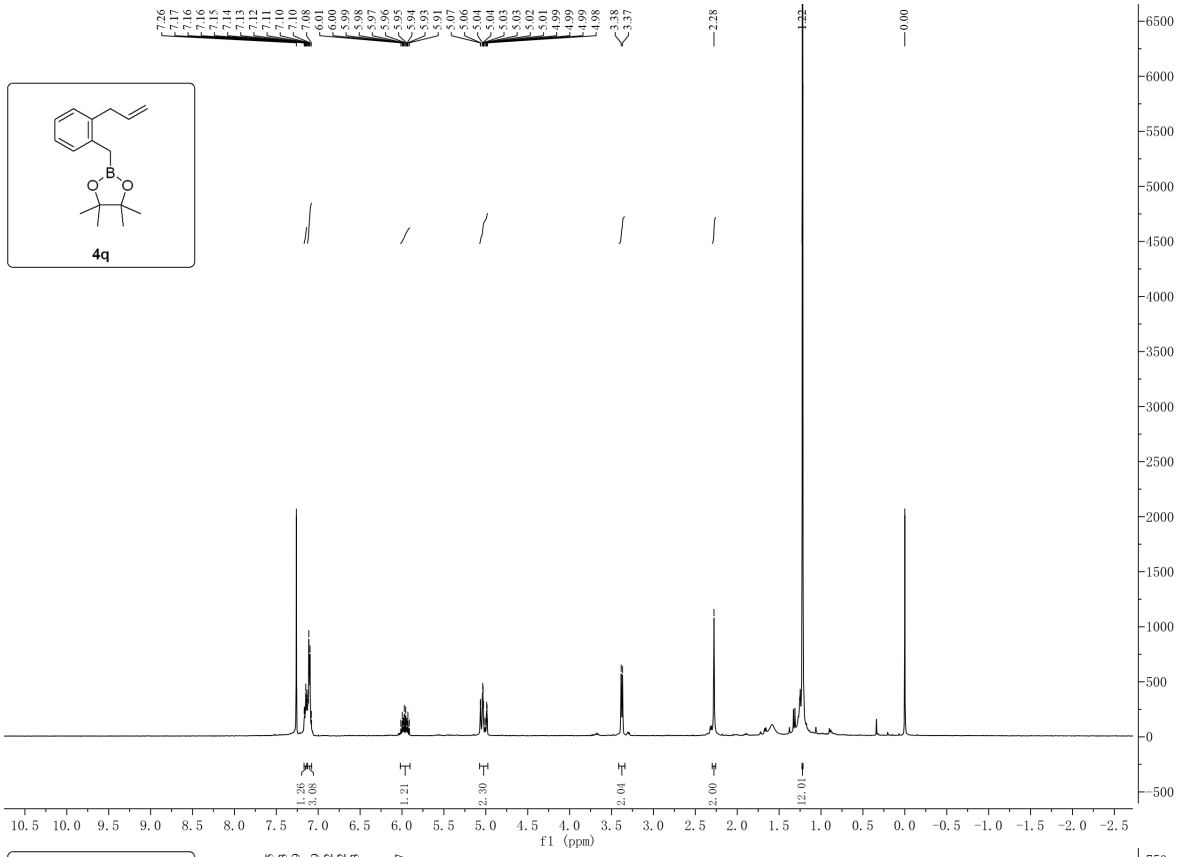

4n
f1 (ppm)

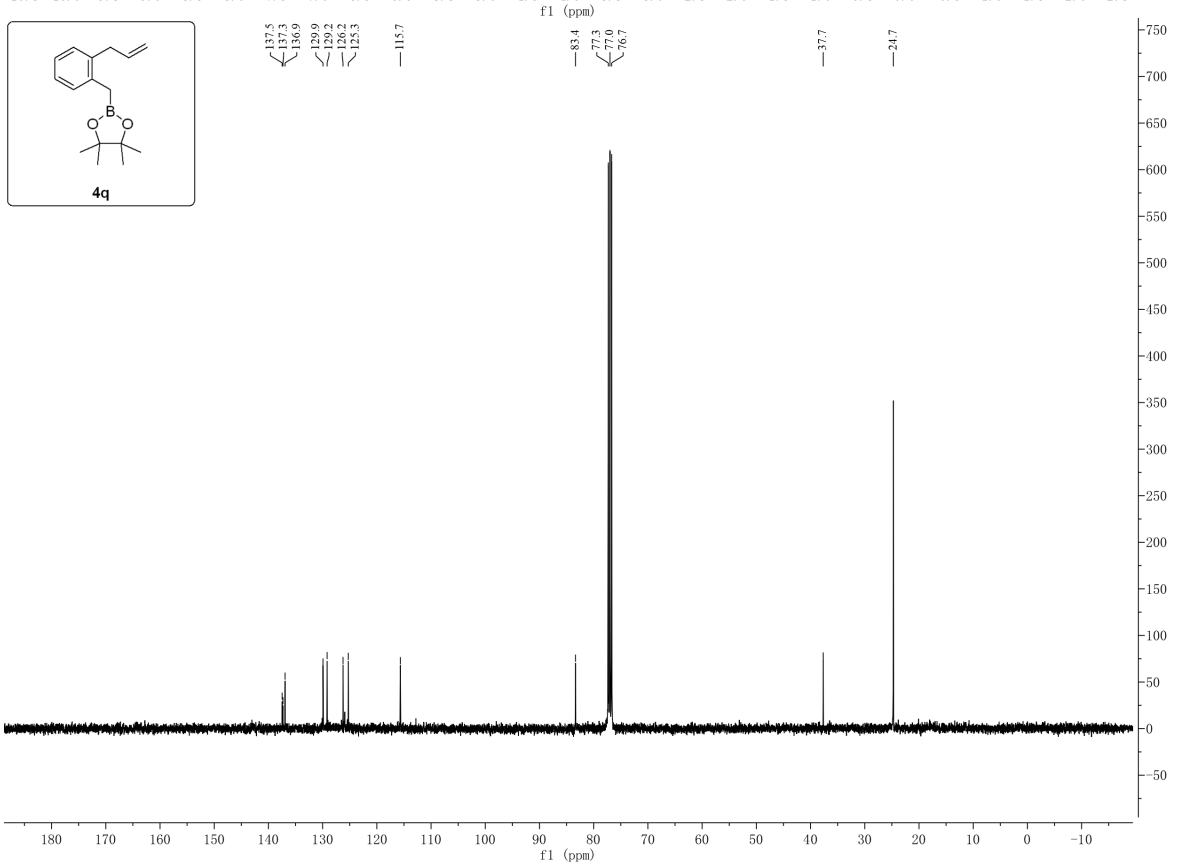

7.80
7.78
7.78
7.78
7.75
7.75
7.75
7.74
7.73
7.72
7.55
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.32
7.32
7.30
7.30
7.26
7.21
7.21
7.19
7.19
7.17
7.17
7.15
7.15
7.13
7.13
7.12
7.11
7.10
7.09
7.09
7.07
7.07
7.06
7.06
7.04
7.04
4.15
2.29
1.17
0.00
4o
3.18
1.03
2.20
1.00
1.21
1.10
1.09
1.07
2.00
1.90
11.78
f1 (ppm)

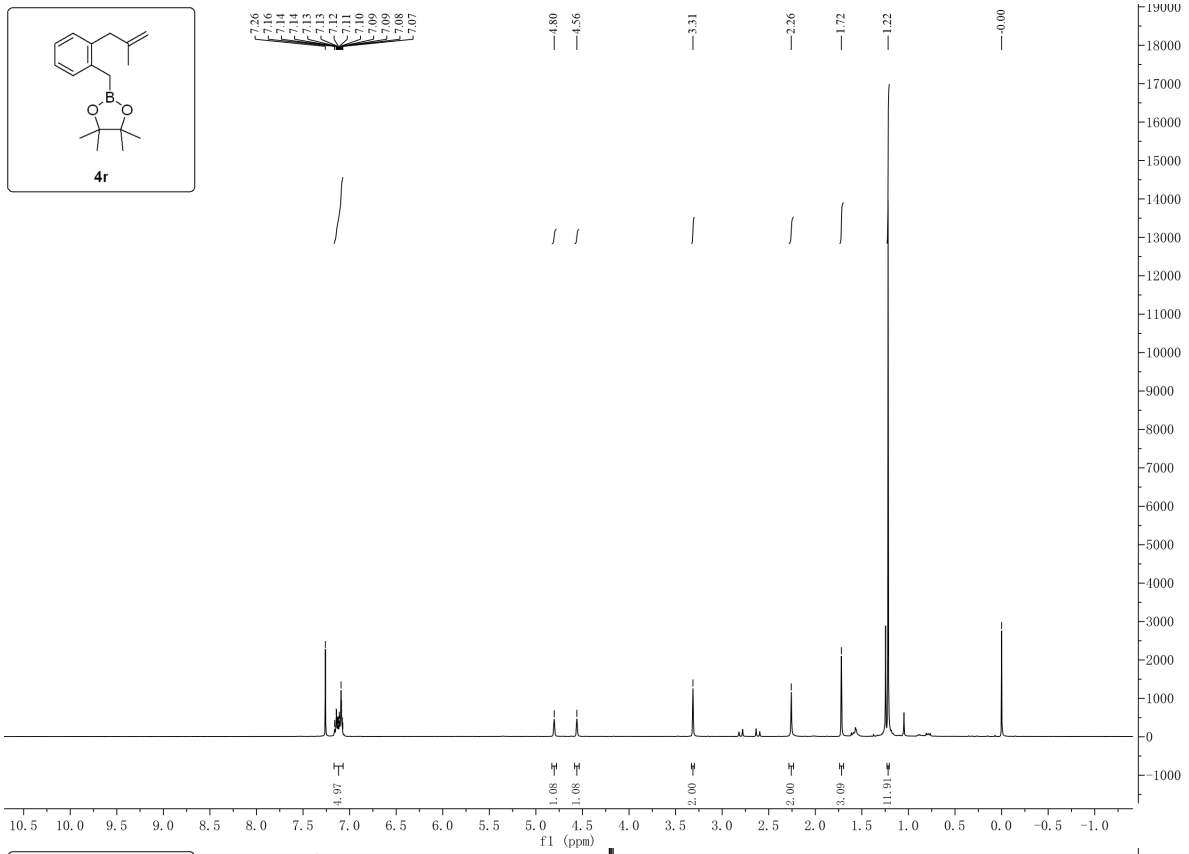

138.3
138.2
137.7
133.6
132.0
130.1
127.8
127.8
127.6
127.5
127.1
126.4
125.8
125.3
125.2
83.4
77.3
77.0
76.7
39.5
24.7
4o
f1 (ppm)

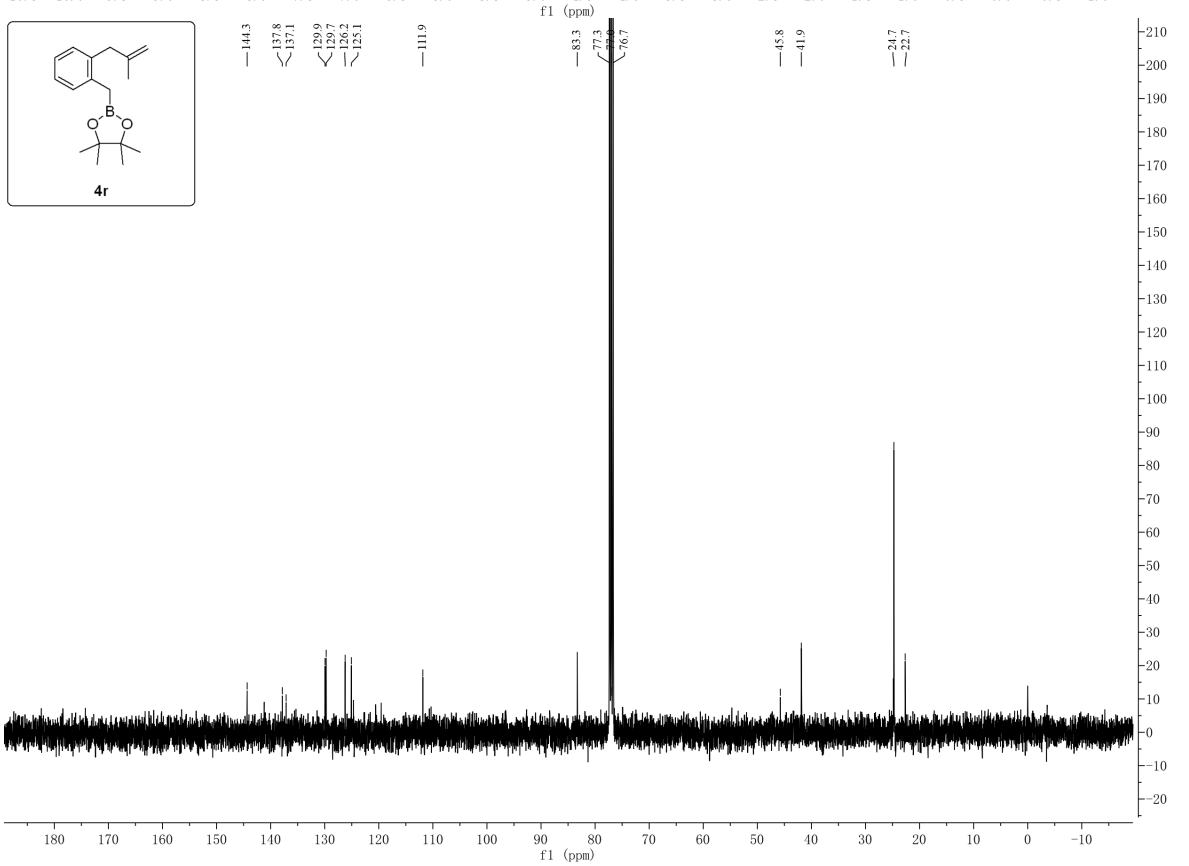

7.26
7.24
7.23
7.22
7.22
7.18
7.18
7.17
7.16
7.15
7.14
7.13
7.13
7.11
7.11
7.10
7.10
7.09
7.08
7.07
7.06
7.05
7.04
6.91
6.90
6.89
6.89
6.84
6.83
3.97
2.26
1.20
0.00
4p
1.09
0.99
1.05
2.03
2.10
1.06
2.00
1.93
12.03
f1 (ppm)

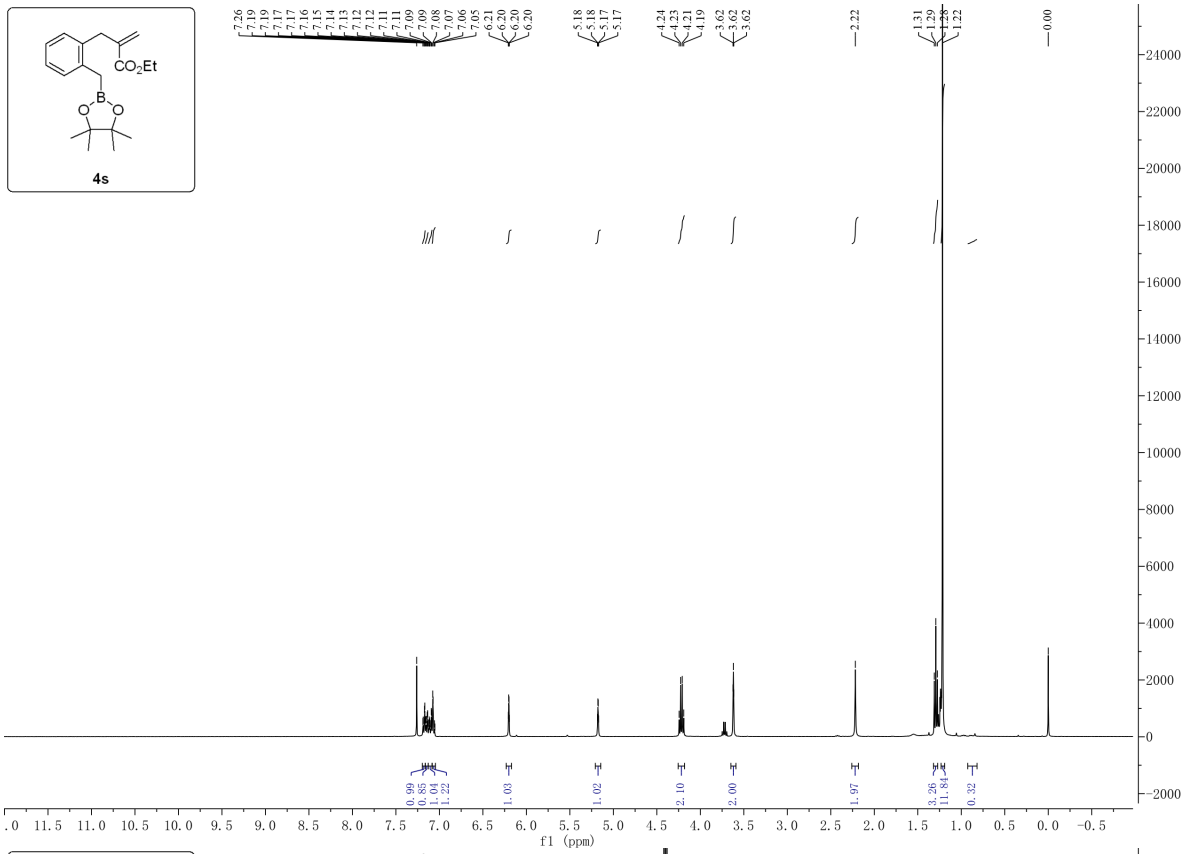

141.1
138.1
137.3
130.0
129.6
128.6
126.4
125.3
125.3
121.2
83.4
77.3
77.0
76.7
34.2
24.7
4p
f1 (ppm)

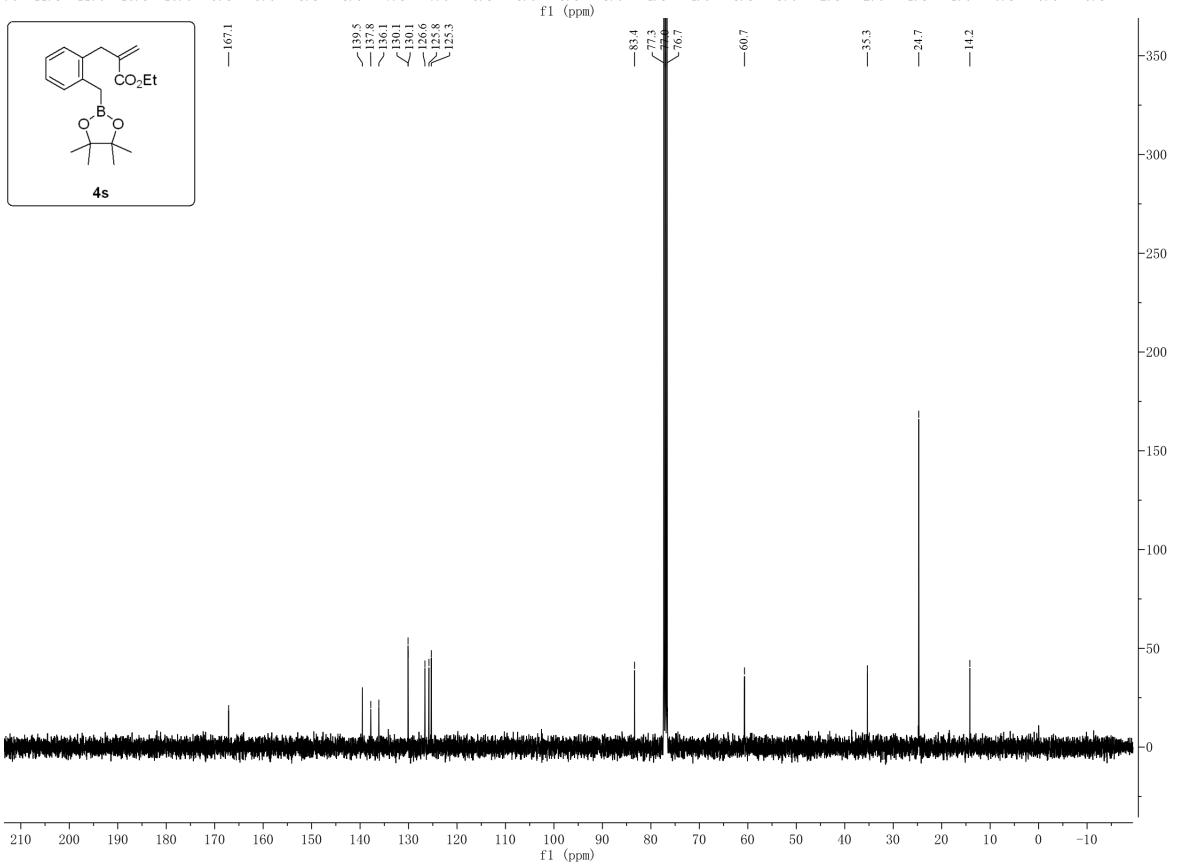

4q
f1 (ppm)

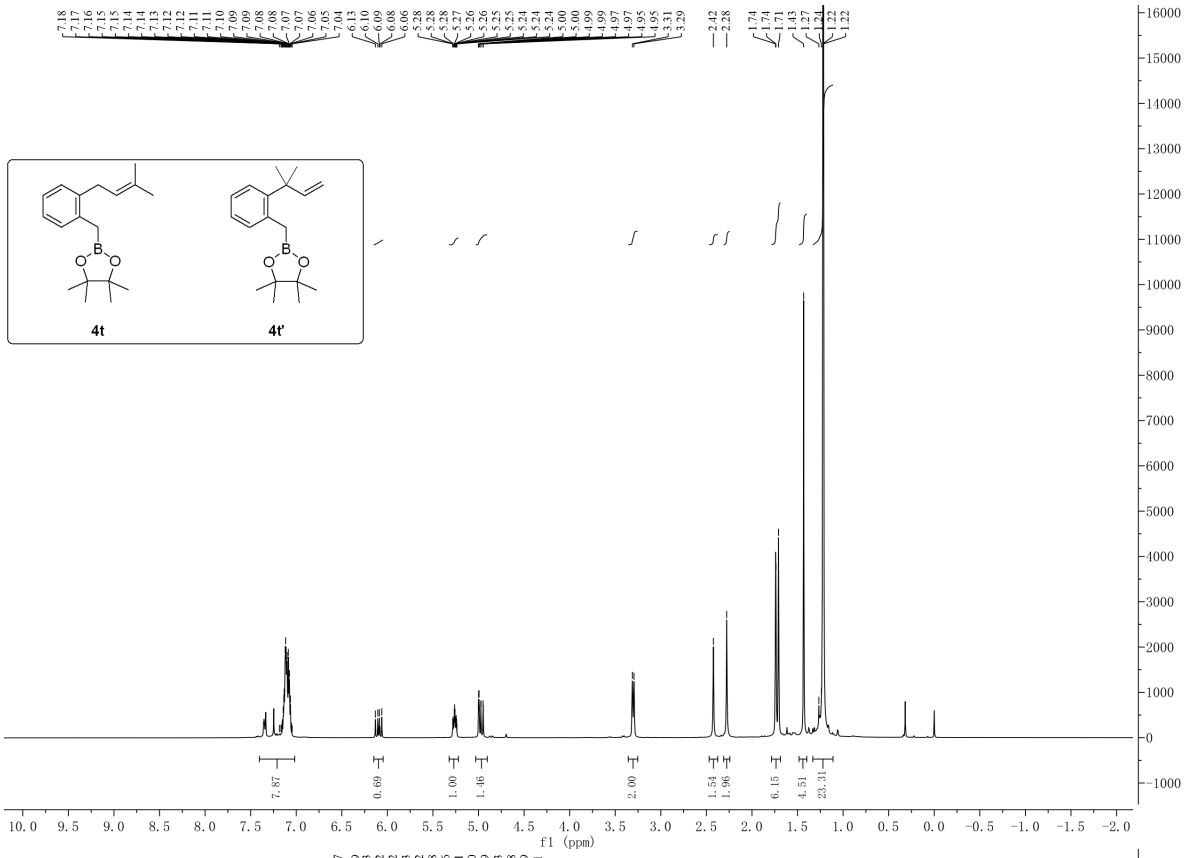

4q
f1 (ppm)

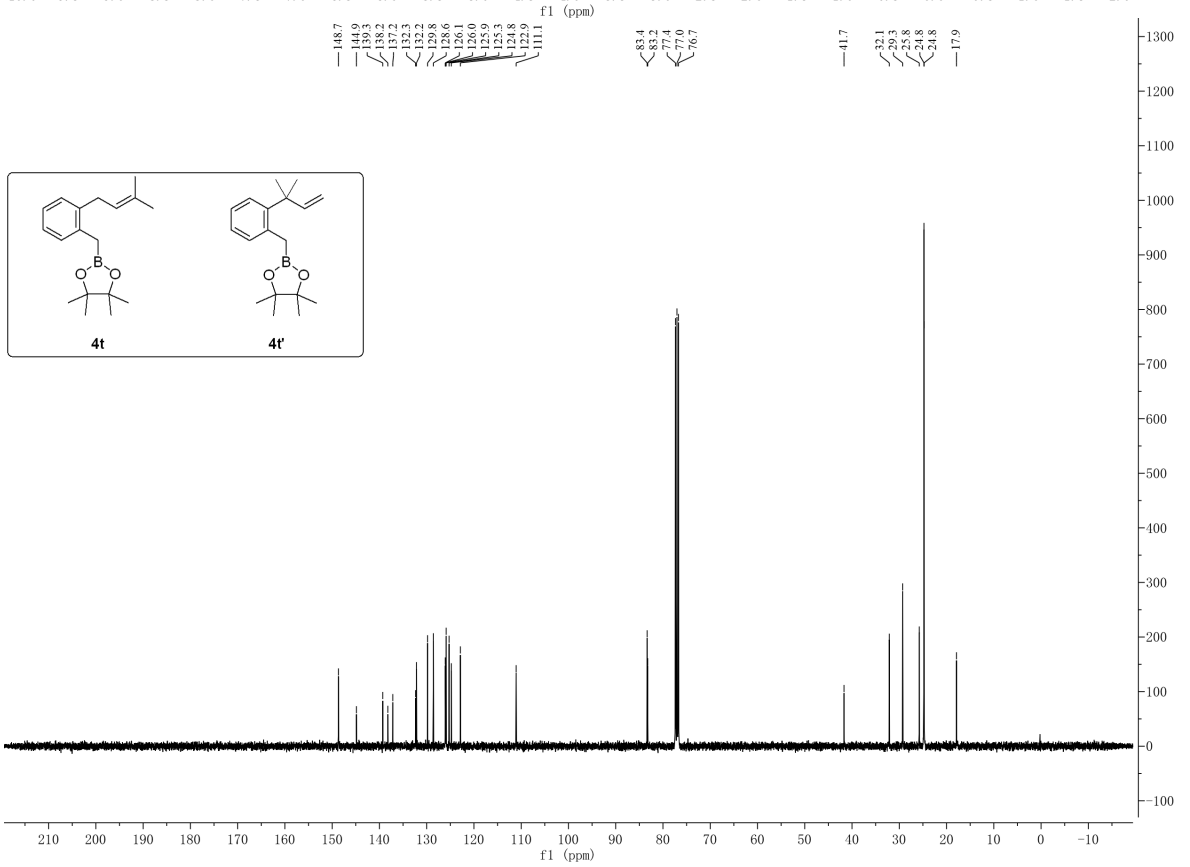

4r
7.26
7.16
7.14
7.14
7.13
7.13
7.12
7.11
7.10
7.09
7.09
7.08
7.07
4.80
4.56
3.31
2.26
1.72
1.22
0.00
4.97
1.08
1.08
2.00
2.00
3.09
11.91
f1 (ppm)

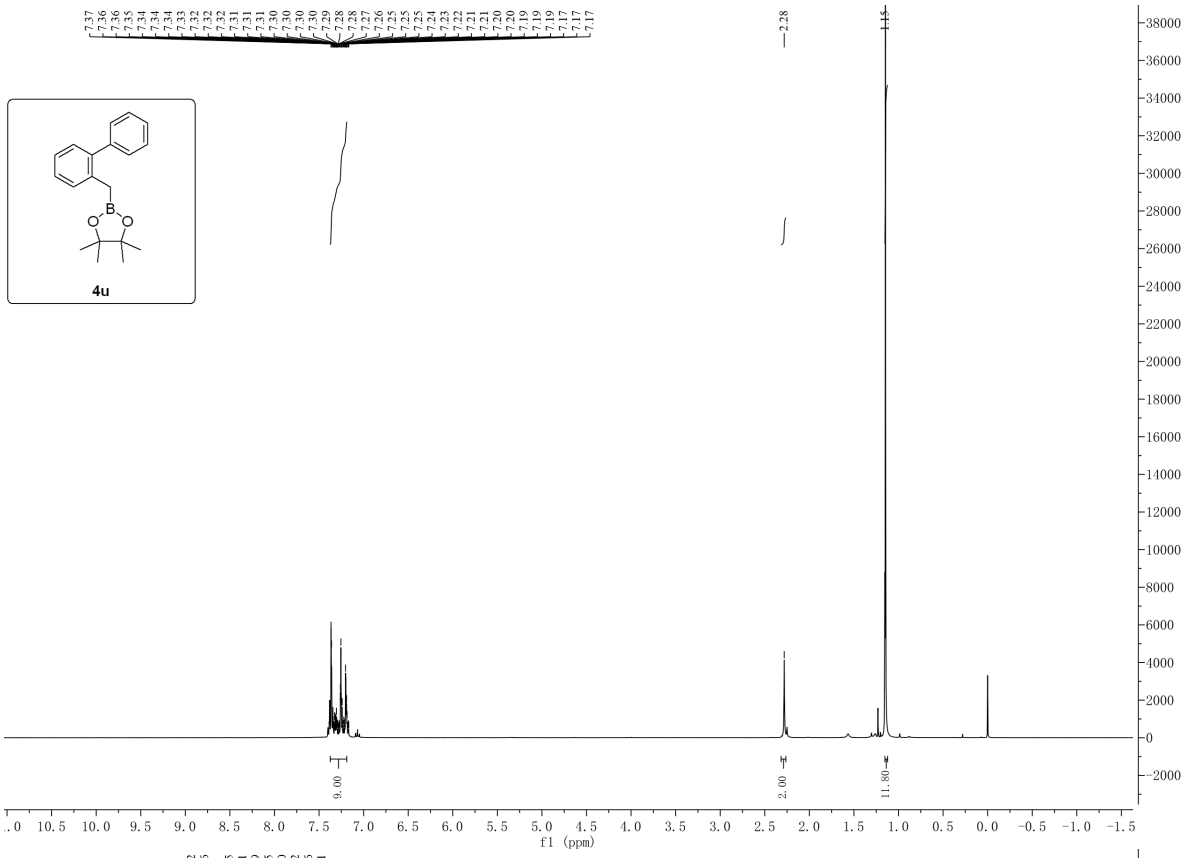

4r
144.3
137.8
137.1
129.9
129.7
126.2
125.1
111.9
83.3
77.3
77.0
76.7
45.8
41.9
24.7
22.7
f1 (ppm)

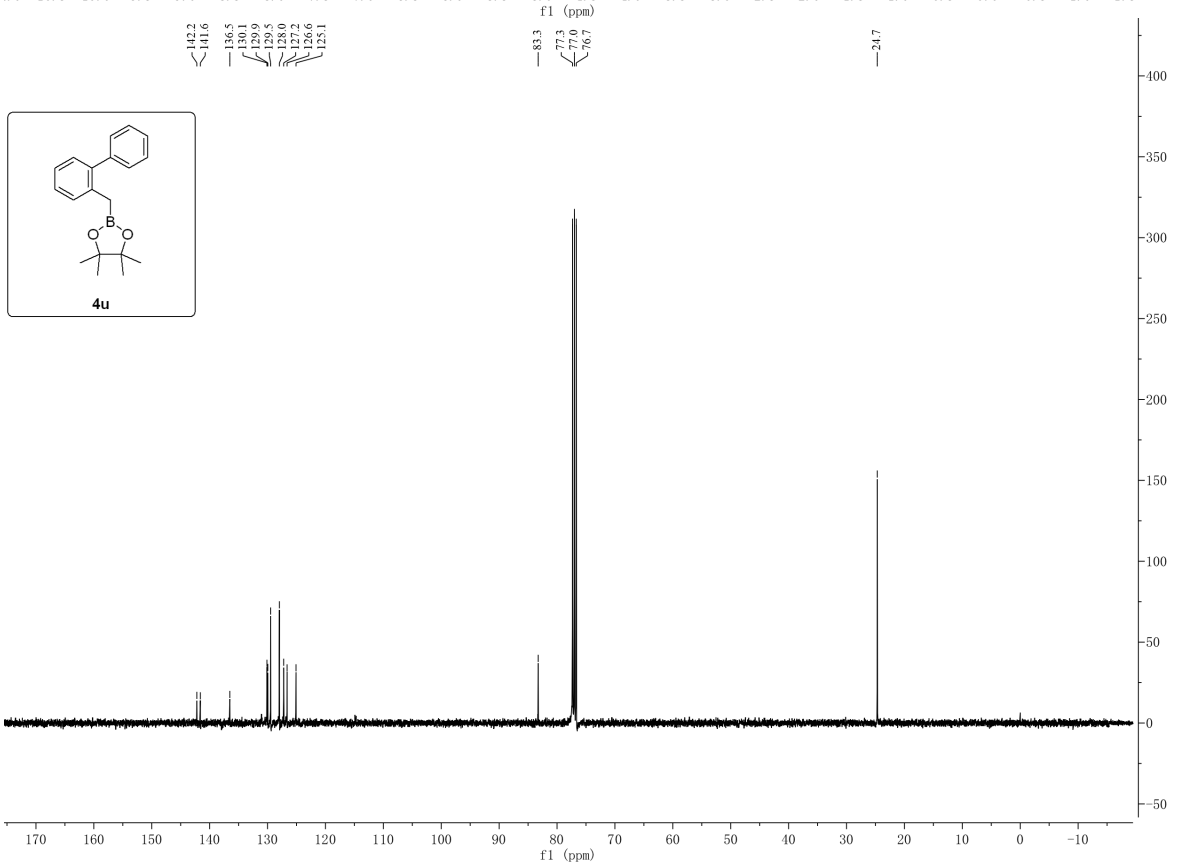

4s
7.26
7.19
7.19
7.17
7.17
7.16
7.15
7.14
7.13
7.12
7.12
7.11
7.11
7.09
7.09
7.08
7.07
7.06
7.05
6.21
6.20
6.20
6.20
5.18
5.18
5.17
5.17
4.24
4.23
4.21
4.19
3.62
3.62
3.62
2.22
1.31
1.29
1.28
1.22
0.00
0.99
0.85
1.04
1.22
1.03
1.02
2.10
2.00
1.97
3.26
11.84
0.32
f1 (ppm)

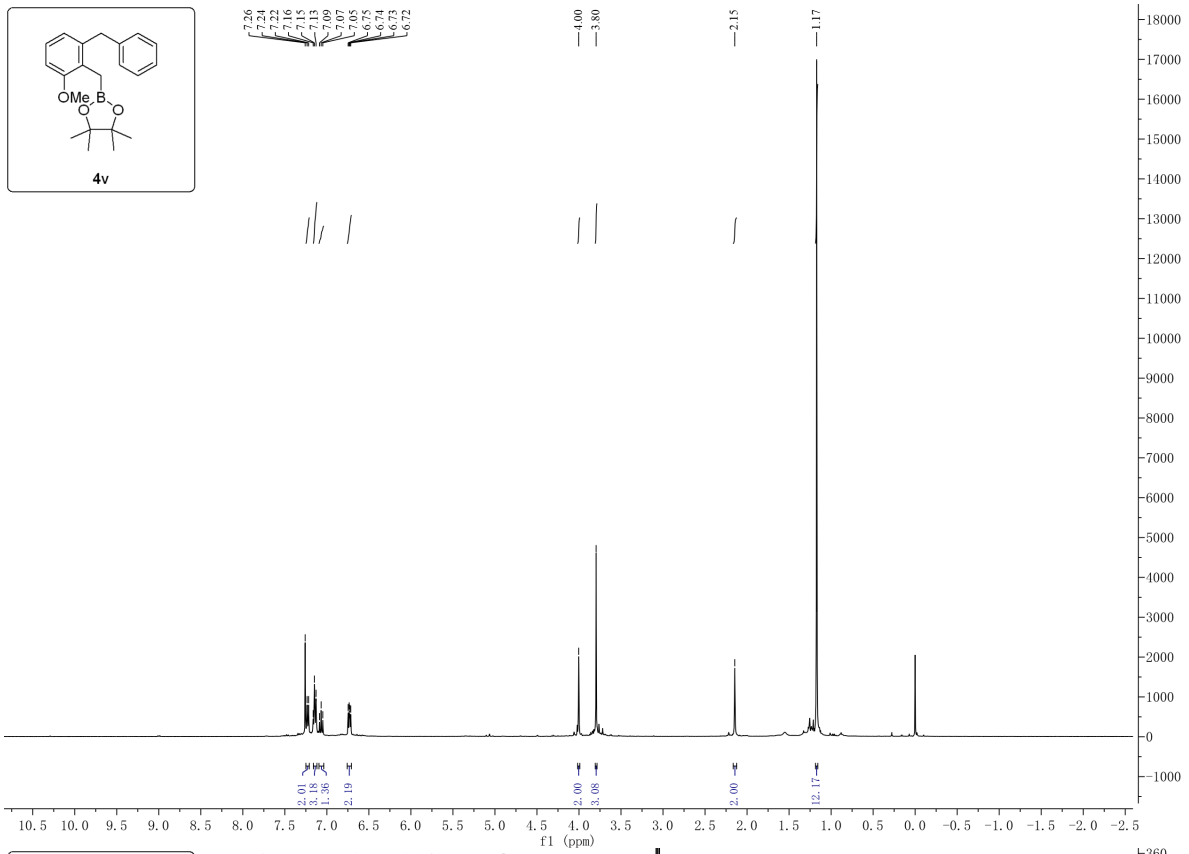

4s
167.1
139.5
137.8
136.1
130.1
130.1
126.6
125.8
125.3
83.4
77.3
77.0
76.7
60.7
35.3
24.7
14.2
f1 (ppm)

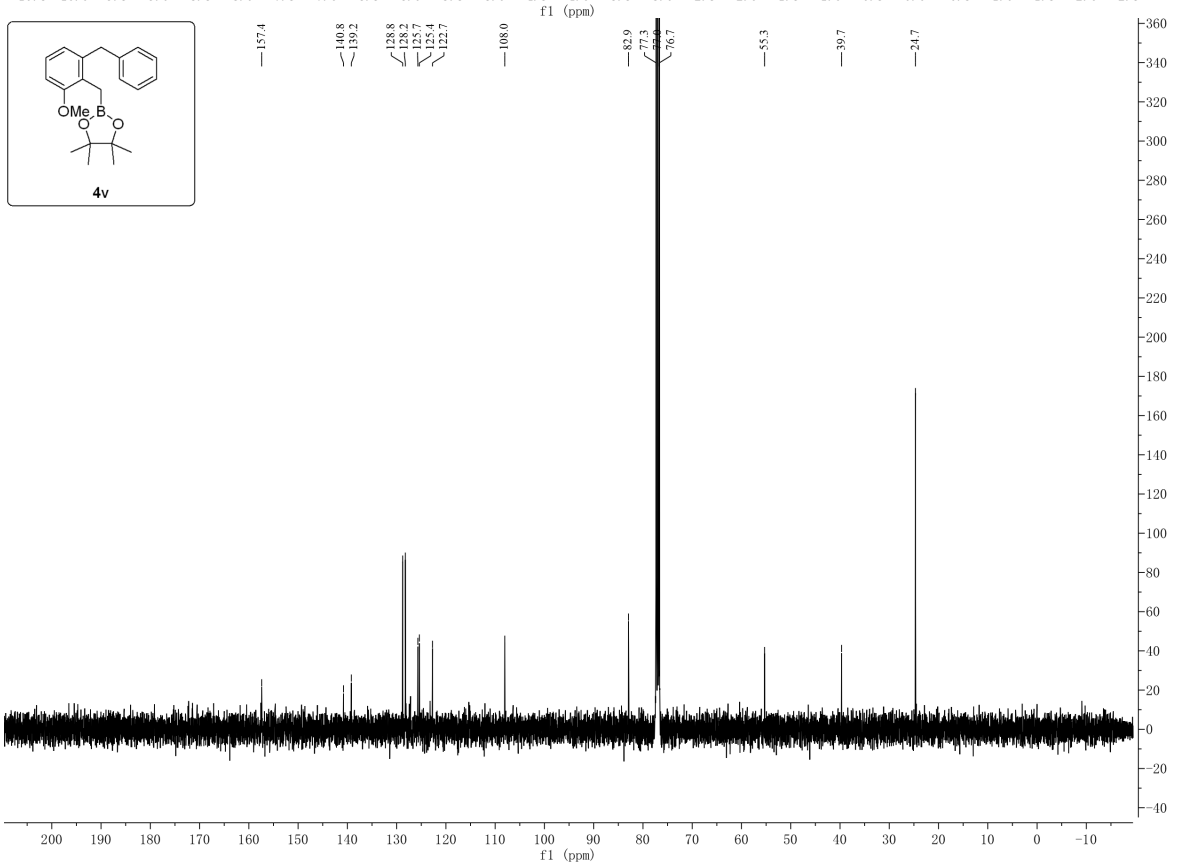

4t
4t'
f1 (ppm)

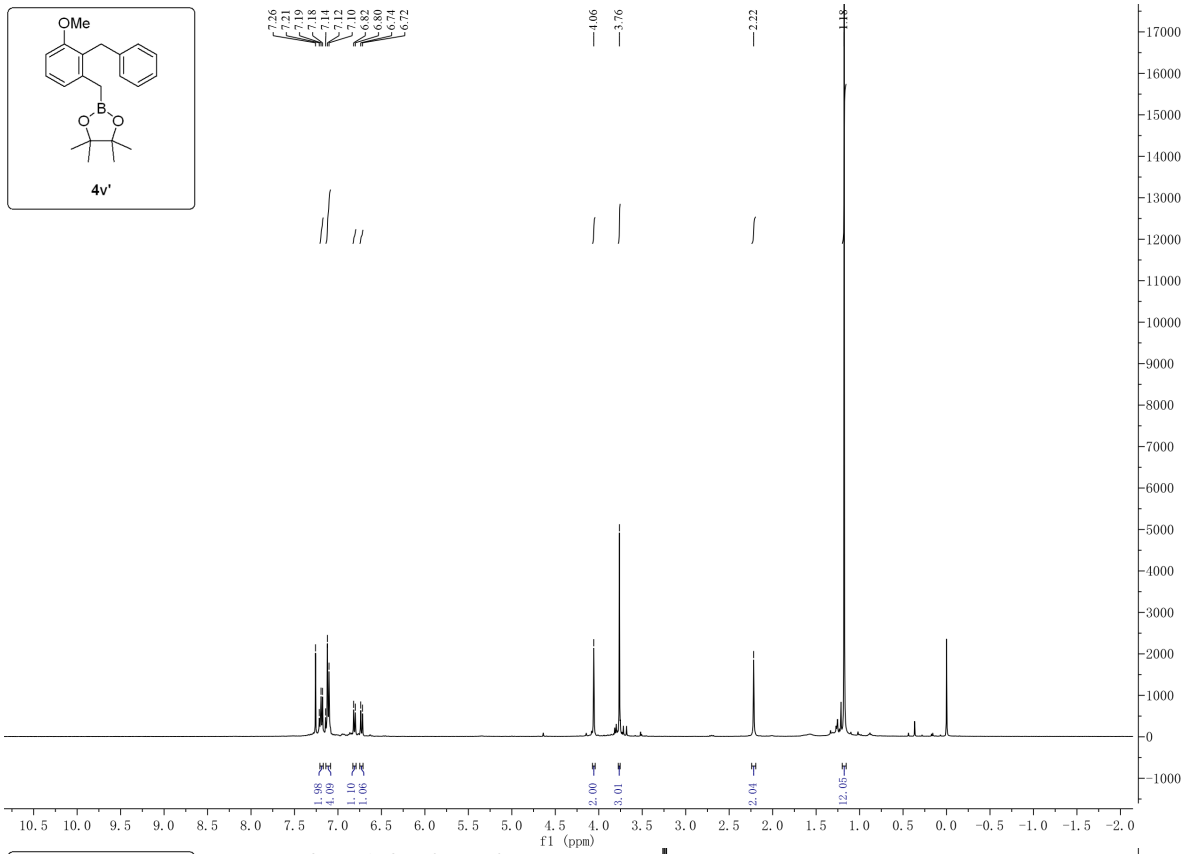

4t
4t'
f1 (ppm)

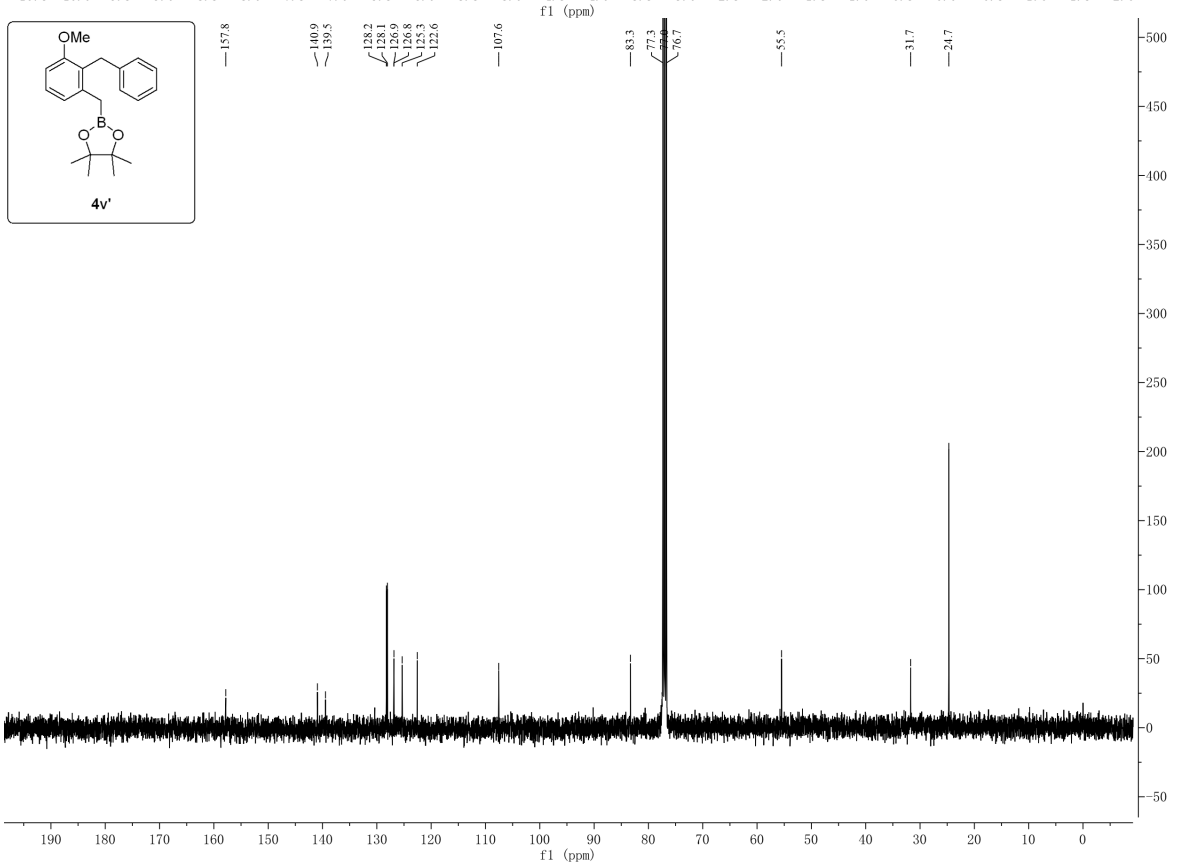

4u
f1 (ppm)

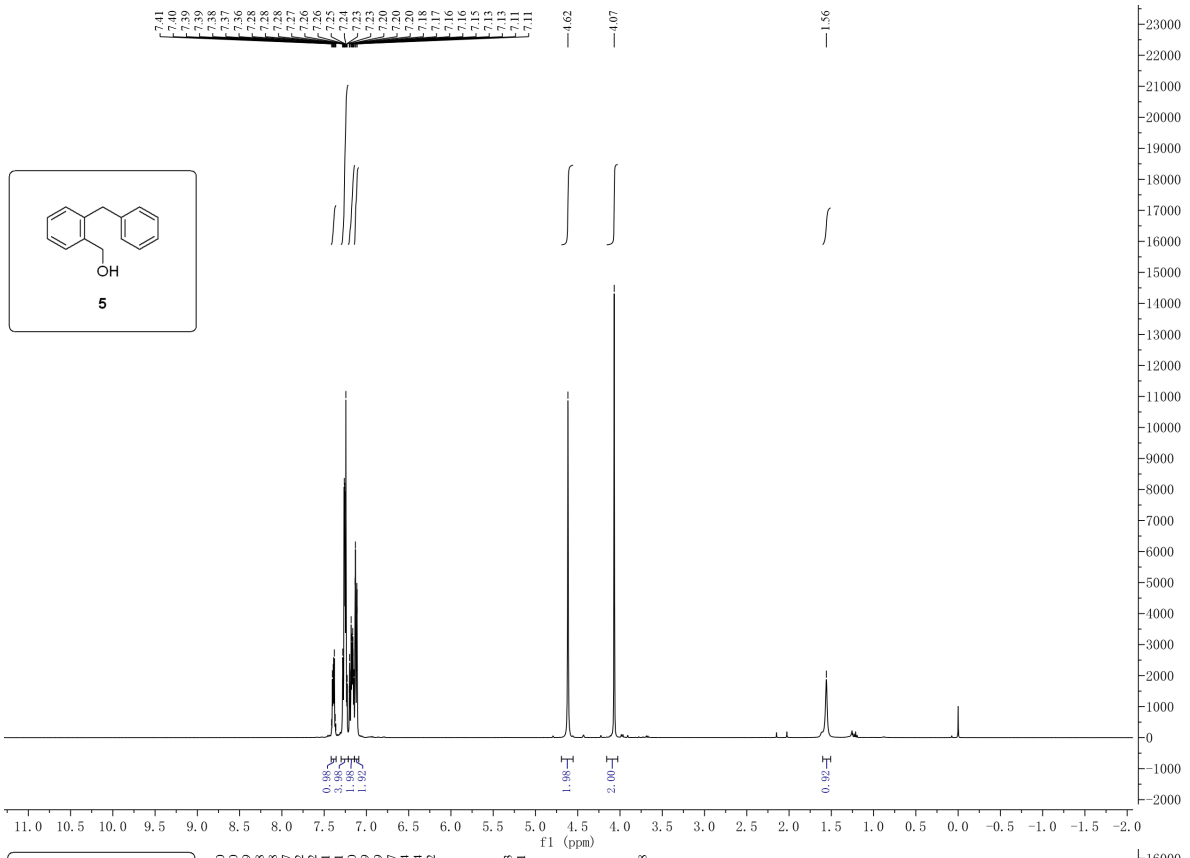

4u
f1 (ppm)

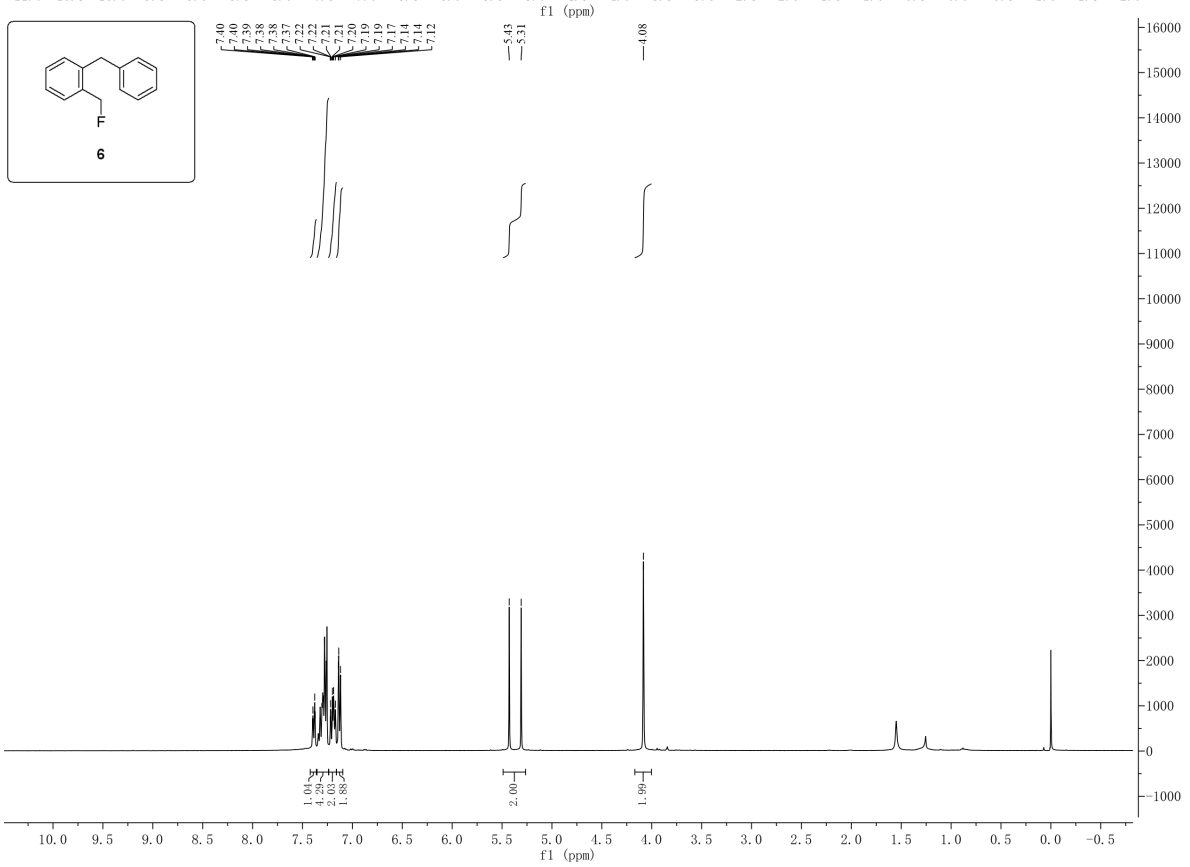

4v
7.26
7.24
7.22
7.16
7.15
7.13
7.09
7.07
7.05
6.75
6.74
6.73
6.72
4.00
3.80
2.15
1.17
2.01
3.18
1.36
2.19
2.00
3.08
2.00
12.17
f1 (ppm)

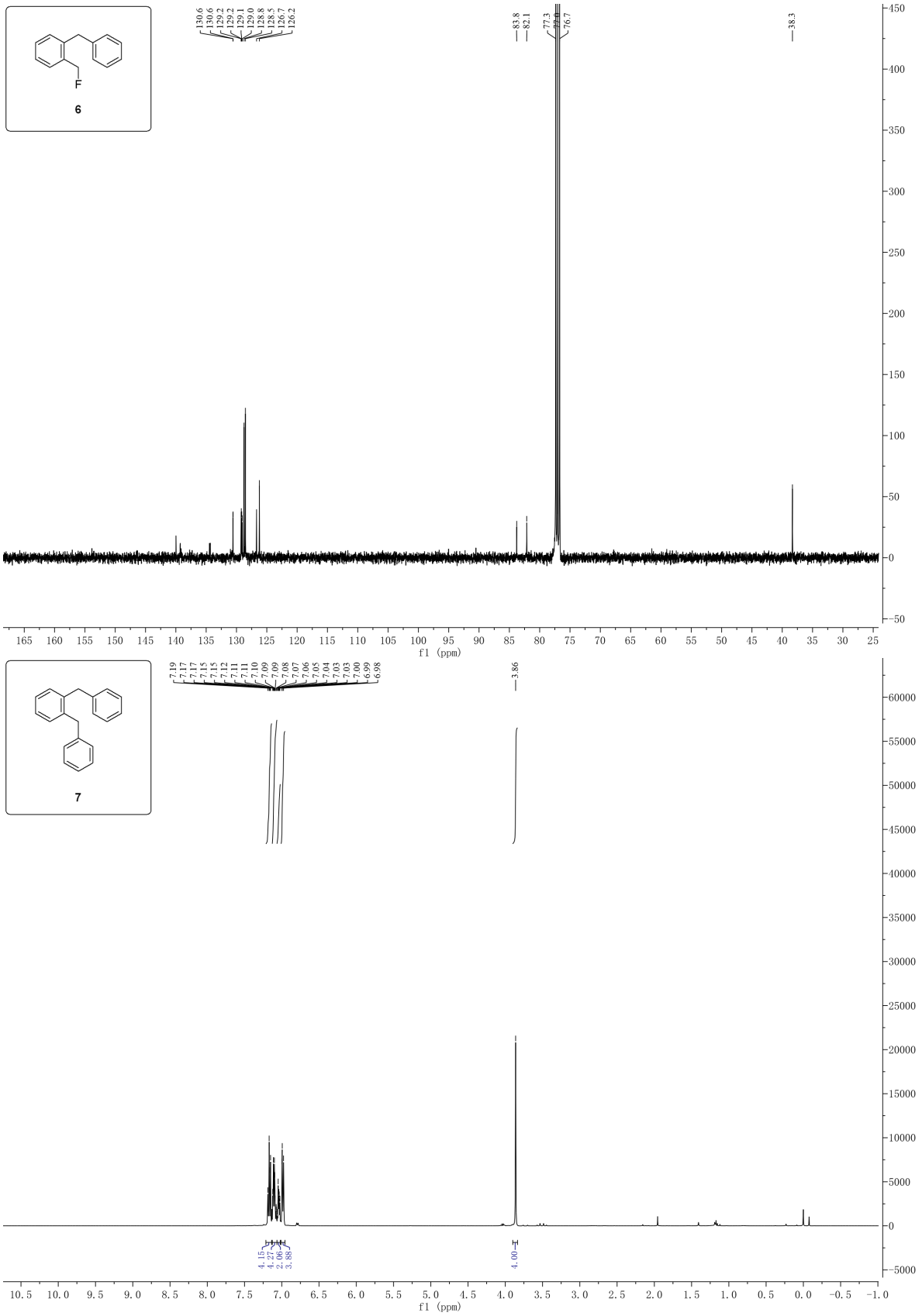

4v
157.4
140.8
139.2
128.8
128.2
125.7
125.4
122.7
108.0
82.9
77.3
77.0
76.7
55.3
39.7
24.7
f1 (ppm)


OMe
B
O
O
4v'
7.26
7.21
7.19
7.18
7.14
7.12
7.10
6.82
6.80
6.74
6.72
4.06
3.76
2.22
1.18
1.98
4.09
1.10
1.06
2.00
3.01
2.04
12.05
f1 (ppm)


OMe
B
O
O
4v'
157.8
140.9
139.5
128.2
128.1
126.9
126.8
125.3
122.6
107.6
83.3
77.3
77.0
76.7
55.5
31.7
24.7
f1 (ppm)


OH
5
f1 (ppm)


F
6
f1 (ppm)



References

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3. Li, Z.; Song, L.; Li, C. Silver-catalyzed radical aminofluorination of unactivated alkenes in aqueous media. *J. Am. Chem. Soc.* **2013**, *135*, 4640−4643.
4. Crudden, C.; Ziebenhaus, C.; Rygus, J.; Ghozati, K.; Unsworth, P.; Nambo, M.; Voth, S.; Hutchinson, M.; Laberge, V.; Maekawa, Y.; Imao, D. Iterative protecting group-free cross-coupling leading to chiral multiply arylated structures. *Nat. Commun.* **2016**, *7*, 11065−11072.