Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iridium-catalyzed *meta*-selective C-H borylation of phenol derivatives

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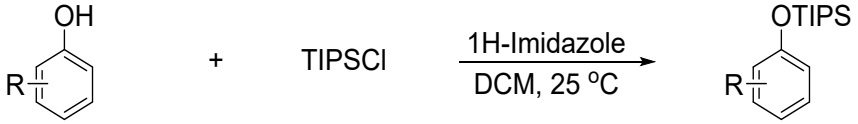
1. General information

Analytic methods. All reactions were carried out at inert atmosphere using reaction tubes and were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV-light at 254 nm and 365 nm. Flash column chromatography was performed using Yantai Yinlong flash silica gel (200-300 mesh). Melting points were recorded on an Electrothermal digital melting point apparatus. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Data for ^{19}F NMR are reported in terms of chemical shift (δ, ppm). HRMS spectra were obtained by using BRUKER micrOTOF-Q III instrument with ESI source or EI source. The crystal was measured by using Agilent or Bruker instrument. IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}).

General preparation for chemicals. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. An oil bath was used for reactions requiring heating. Temperatures quoted are external.

2. Synthesis of the starting materials

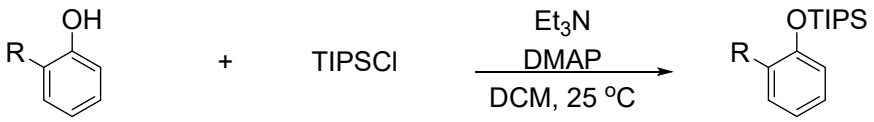
2.1. General procedure for the preparation of 1a-1d, 1h-1r, 1t-1w, 1y-1ao



General procedure to protect the phenol substrates： In a clean, oven dried 50 mL round bottom flask containing magnetic stir-bar, phenol (5.0 mmol), imidazole (2.5 equiv, 12.5 mmol) were added DCM

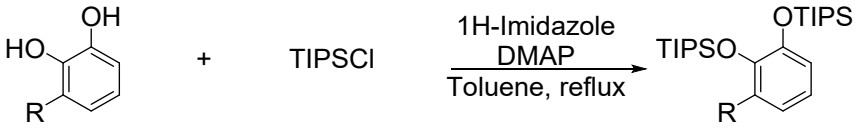
(20 mL). Then drop TIPSCl (1.2 equiv, 5.5 mmol) at 0 °C. This reaction flask was placed in a preheated oil bath at 25 °C to stir vigorously for 12 h. After TLC analysis had shown complete conversion of the starting materials, 1M NaOH (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed in vacuo. The resulting residue was purified by column chromatography (pe.ether / EtOAc = 50 / 1) on silica gel to give the product **1a-1d, 1h-1r, 1t-1w, 1y-1ao**. These compound **1a**[2], **1b**[4], **1c**[3], **1d**[5], **1i**[3], **1j**[3], **1k**[1],**1l**[3], **1m**[8], **1p-1q**[3], **1y**[3], **1ab**[3] have been reported.

2.2. General procedure for the preparation of 1e-1g, 4a and 5a.



General procedure to protect the phenol substrates： In a clean, oven dried 50 mL round bottom flask containing magnetic stir-bar, phenol (5.0 mmol), DMAP (10 mol%, 0.5mmol), Et_3N (2.5 equiv, 12.5 mmol) were added DCM (20 mL). Then drop TIPSCl (1.2 equiv, 5.5 mmol) at 0 °C. This reaction flask was placed in a preheated oil bath at 25 °C to stir vigorously for 12 h. After TLC analysis had shown complete conversion of the starting materials, 1M NaOH (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed in vacuo. The resulting residue was purified by column chromatography (pe.ether / EtOAc = 20 / 1) on silica gel to give the product **1e-1g, 4a and 5a**. These compound **1e**[6], **4a**[7] have been reported.

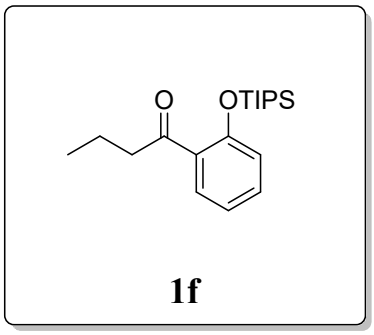
2.3. General procedure for the preparation of 1s and 1x.



General procedure to protect the phenol substrates： In a clean, oven dried 50 mL round bottom flask containing magnetic stir-bar, phenol (5.0 mmol), DMAP (10 mol%, 0.5mmol), imidazole (2.5 equiv, 12.5 mmol) were added Toluene (20 ml). Then drop TIPSCl (1.2 equiv, 5.5 mmol) at 0 °C. This reaction flask

was placed in a preheated oil bath at 120 °C to stir vigorously for 18 h. After TLC analysis had shown complete conversion of the starting materials, 1M NaOH (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The resulting residue was purified by column chromatography (pe.ether / EtOAc = 50 / 1) on silica gel to give the product **1s and 1x**.

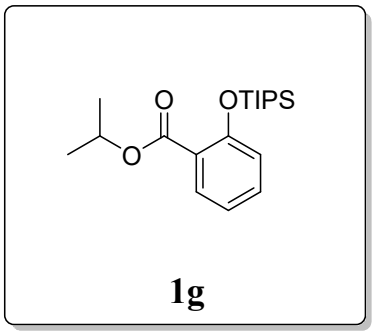
1-(2-((triisopropylsilyl)oxy)phenyl)butan-1-one (1f)



1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.7, 1.8 Hz, 1H), 7.31-7.27 (m, 1H), 6.95 (t, J = 7.0 Hz, 1H), 6.85 (dd, J = 8.2, 0.7 Hz, 1H), 3.02-2.93 (m, 2H), 1.74-1.64 (m, 2H), 1.38-1.28 (m, 3H), 1.11 (d, J = 7.4 Hz, 19H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 204.2, 154.6, 132.3, 131.5, 129.8, 121.0, 119.5, 77.5, 77.2, 76.8, 45.6, 18.0, 17.8, 13.9, 13.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{33}O_2Si^+$, m/z: 321.2244, found: 321.2240.

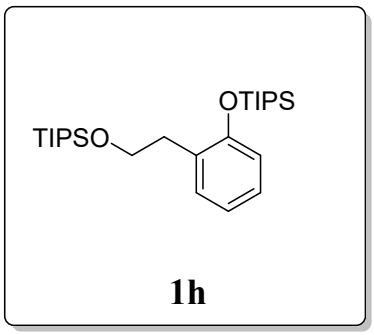
isopropyl 2-((triisopropylsilyl)oxy)benzoate (1g)



1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.7, 1.8 Hz, 1H), 7.33-7.27 (m, 1H), 6.96-6.89 (m, 1H), 6.87 (dd, J = 8.3, 0.6 Hz, 1H), 5.21 (m, 1H), 1.36- 1.29 (m, 9H), 1.12 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.3, 155.4, 132.5, 131.1, 123.9, 120.4, 120.3, 77.5, 77.2, 76.8, 68.1, 22.1, 18.1, 17.9, 13.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{33}O_3Si^+$, m/z: 337.2193, found: 337.2192.

Triisopropyl(2-(2-((triisopropylsilyl)oxy)ethyl)phenoxy)silane (1h)

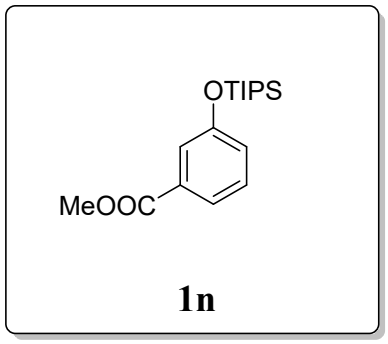


1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.4 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 3.92 (t, J = 7.1 Hz, 2H), 2.95 (t, J = 6.9 Hz, 2H), 1.41-1.29 (m, 3H), 1.16 (d, J = 8.0 Hz, 18H), 1.07 (d, J = 4.9 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 131.5, 129.3, 127.2,

120.6, 118.0, 77.5, 77.2, 76.8, 63.5, 34.7, 18.3, 18.2, 13.3, 12.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{51}O_2Si_2^+$, m/z: 451.3422, found: 451.3417.

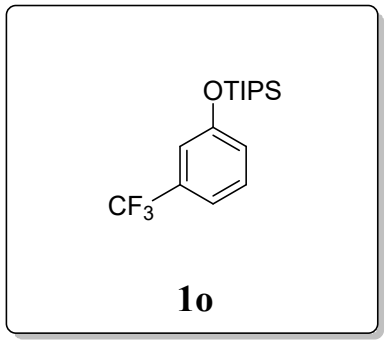
methyl 3-((triisopropylsilyl)oxy)benzoate (1n)



1n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.54 (dd, J = 2.6, 1.6 Hz, 1H), 7.28 (t, J = 7.9 Hz, 1H), 7.09-7.05 (m, 1H), 3.90 (s, 3H), 1.31 – 1.23 (m, 3H), 1.11 (d, J = 7.5 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.1, 156.2, 131.6, 129.4, 124.7, 122.4, 120.9, 52.2, 18.0, 12.7. **HRMS (E**SI) calcd for $[M+H]^+$ $C_{17}H_{29}O_3Si^+$, m/z: 309.1880, found: 309.1885.

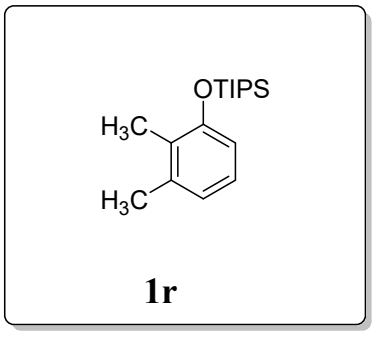
triisopropyl(3-(trifluoromethyl)phenoxy)silane (1o)



1o

^{1}H NMR (**400 MHz, $CDCl_3$**) δ 7.33 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (s, 1H), 7.06 (dd, *J* = 8.2, 2.5 Hz, 1H), 1.35 – 1.24 (m, 3H), 1.13 (d, *J* = 7.5 Hz, 19H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.5, 132.0 (q, *J* = 32.2 Hz), 130.0, 124.1 (q, *J* = 272.3 Hz), 123.3, 117.8 (q, *J* = 3.8 Hz), 116.9 (q, *J* = 3.7 Hz), 17.9, 12.7. **^{19}F NMR** (377 MHz, **$CDCl_3$**) δ -62.76. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{16}H_{26}F_3OSi^+$, m/z: 319.1700, found: 319.1705.

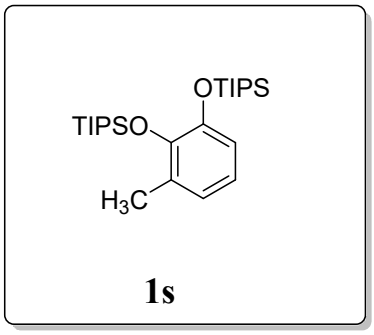
(2,3-dimethylphenoxy)triisopropylsilane (1r)



1r

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, J = 7.8 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H), 1.42-1.33 (m, 3H), 1.19 (d, J = 7.3 Hz, 19H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.2, 138.2, 127.1, 125.6, 122.5, 115.8, 77.5, 77.2, 76.8, 20.5, 18.2, 13.3, 12.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{17}H_{31}OSi^+$, m/z: 279.2139, found: 279.2136.

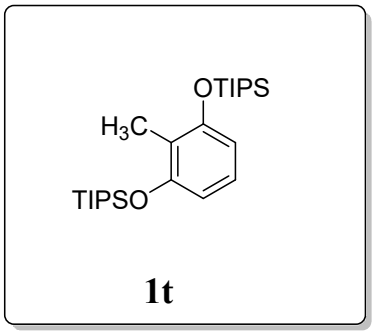
((3-methyl-1,2-phenylene)bis(oxy))bis(triisopropylsilane) (1s)



1s

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72-6.62 (m, 3H), 2.26 (s, 3H), 1.41-1.27 (m, 6H), 1.12 (t, J = 7.4 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.3, 145.8, 130.5, 123.2, 120.5, 117.5, 77.5, 77.2, 76.8, 18.2, 18.2, 17.9, 14.4, 13.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{49}O_2Si_2^+$, m/z: 437.3266, found: 437.3265.

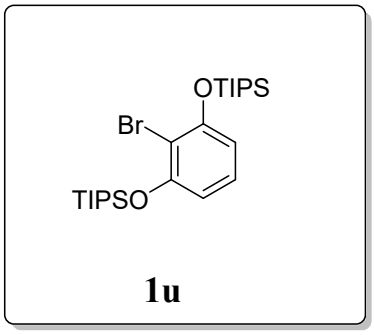
((2-methyl-1,3-phenylene)bis(oxy))bis(triisopropylsilane) (1t)



1t

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (t, J = 8.1 Hz, 1H), 6.44 (d, J = 8.1 Hz, 2H), 2.16 (s, 3H), 1.33-1.23 (m, 6H), 1.11 (d, J = 7.5 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.4, 125.4, 119.6, 111.5, 77.5, 77.2, 76.8, 18.2, 13.2, 10.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{25}H_{49}O_2Si_2^+$, m/z: 437.3266, found: 437.3270.

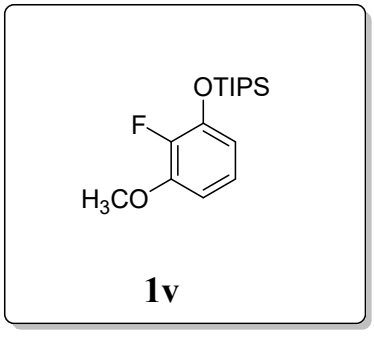
((2-bromo-1,3-phenylene)bis(oxy))bis(triisopropylsilane) (1u)



1u

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (t, J = 8.2 Hz, 1H), 6.54 (d, J = 8.2 Hz, 2H), 1.40-1.23 (m, 6H), 1.13 (d, J = 7.4 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5, 126.2, 117.6, 112.8, 77.5, 77.2, 76.8, 18.1, 13.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{46}BrO_2Si_2^+$, m/z: 501.2214, found: 501.2219.

(2-fluoro-3-methoxyphenoxy)triisopropylsilane (1v)

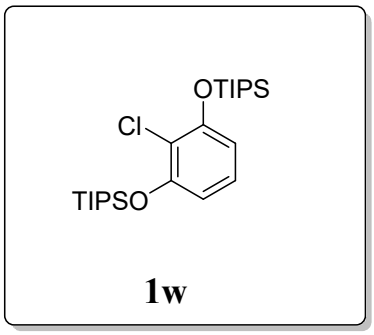


1v

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89-6.84 (m, 1H), 6.57 (q, J = 7.5 Hz, 2H), 3.86 (s, 3H), 1.34-1.23 (m, 3H), 1.12 (d, J = 7.7

Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.1 (d, $J_{C\text{-}F}$ = 9.1 Hz), 145.8, 144.9 (d, $J_{C\text{-}F}$ = 9.9 Hz), 143.4, 122.9 (d, $J_{C\text{-}F}$ = 5.4 Hz), 114.2, 105.8, 56.4, 17.9, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -155.01. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{16}H_{28}FO_2Si^+$, m/z: 299.1837, found: 299.1835.

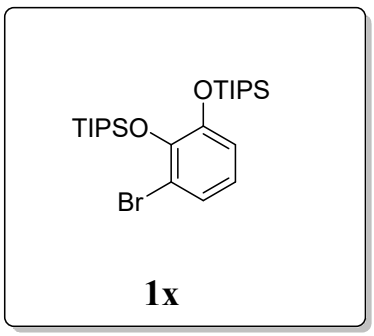
((2-chloro-1,3-phenylene)bis(oxy))bis(triisopropylsilane) (1w)



1w

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (t, J = 8.2 Hz, 1H), 6.54 (d, J = 8.2 Hz, 2H), 1.40-1.23 (m, 6H), 1.13 (d, J = 7.4 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5, 126.2, 117.6, 112.8, 77.5, 77.2, 76.8, 18.1, 13.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{46}ClO_2Si_2^+$, m/z: 457.2719, found: 457.2716.

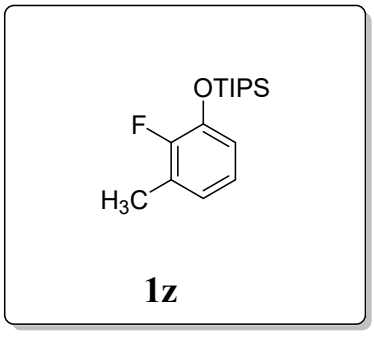
((3-bromo-1,2-phenylene)bis(oxy))bis(triisopropylsilane) (1x)



1x

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, J = 8.0, 1.5 Hz, 1H), 6.79 (dd, J = 8.1, 1.5 Hz, 1H), 6.63 (t, J = 8.1 Hz, 1H), 1.52-1.41 (m, 3H), 1.37-1.28 (m, 3H), 1.12 (d, J = 7.6 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.7, 145.5, 125.5, 121.5, 118.8, 117.1, 77.48, 77.2, 76.8, 18.2, 18.1, 14.4, 13.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{46}BrO_2Si_2^+$, m/z: 501.2214, found: 501.2217.

(2-fluoro-3-methylphenoxy)triisopropylsilane (1z)

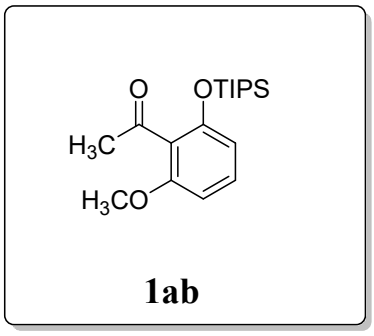


1z

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dd, J = 11.8, 4.5 Hz, 1H), 6.82-6.78 (m, 1H), 6.77-6.72 (m, 1H), 2.29 (d, J = 2.2 Hz, 3H), 1.35-1.26 (m, 3H), 1.15 (d, J = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.2, 151.8, 143.9 (d, $J_{C\text{-}F}$ = 12.6 Hz), 126.1 (d, $J_{C\text{-}F}$ = 15.2 Hz), 123.3 (t, $J_{C\text{-}F}$ = 4.2 Hz), 119.2 (d, $J_{C\text{-}F}$ = 1.4

Hz), 18.0, 14.7 (d, $J_{C\text{-}F}$ = 4.5 Hz), 12.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -136.70. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{16}H_{28}FOSi^+$, m/z: 283.1888, found: 283.1886.

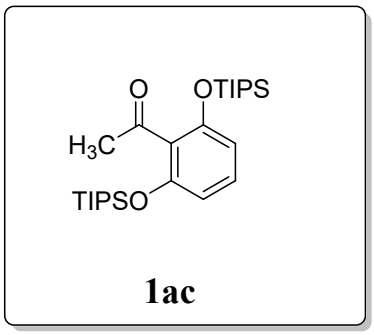
1-(2-methoxy-6-((triisopropylsilyl)oxy)phenyl)ethan-1-one (1ab)



1ab

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 8.3 Hz, 1H), 6.45 (dd, J = 13.3, 8.3 Hz, 2H), 3.74 (s, 3H), 2.44 (s, 3H), 1.30-1.20 (m, 3H), 1.06 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.9, 156.8, 152.9, 129.9, 123.2, 111.6, 103.6, 77.5, 77.2, 76.8, 55.7, 32.4, 18.0, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{31}O_3Si^+$, m/z: 323.2037, found: 323.2039.

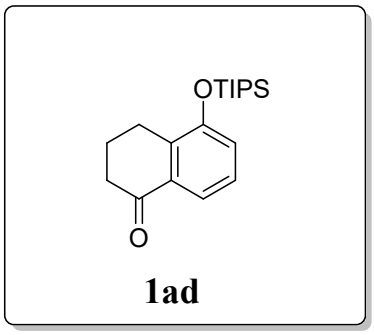
1-(2,6-bis((triisopropylsilyl)oxy)phenyl)ethan-1-one (1ac)



1ac

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, J = 8.2 Hz, 1H), 6.42 (d, J = 8.3 Hz, 2H), 2.45 (s, 3H), 1.30-1.20 (m, 6H), 1.07 (d, J = 7.5 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.9, 153.0, 129.4, 126.1, 111.6, 77.5, 77.2, 76.8, 32.6, 18.1, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{26}H_{49}O_3Si_2^+$, m/z: 465.3215, found: 465.3210.

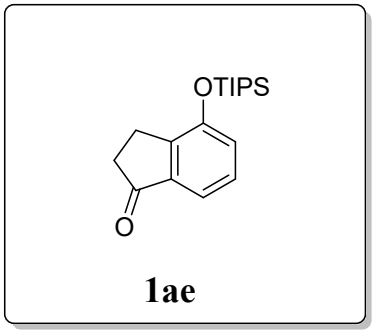
5-((triisopropylsilyl)oxy)-3,4-dihydronaphthalen-1(2H)-one (1ad)



1ad

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.8, 0.8 Hz, 1H), 7.13 (t, J = 7.9 Hz, 1H), 6.97 (dd, J = 8.0, 1.1 Hz, 1H), 2.92 (t, J = 6.1 Hz, 2H), 2.63-2.56 (m, 2H), 2.14-2.04 (m, 2H), 1.35-1.24 (m, 3H), 1.11 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.7, 153.5, 135.3, 134.1, 126.5, 122.5, 119.5, 77.5, 77.2, 76.8, 38.8, 23.7, 22.6, 18.1, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{31}O_2Si^+$, m/z: 319.2088, found: 319.2084.

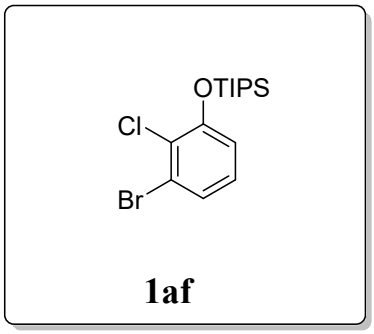
4-((triisopropylsilyl)oxy)-2,3-dihydro-1H-inden-1-one (1ae)



1ae

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.8, 0.8 Hz, 1H), 7.13 (t, J = 7.9 Hz, 1H), 6.97 (dd, J = 8.0, 1.1 Hz, 1H), 2.92 (t, J = 6.1 Hz, 2H), 2.63-2.56 (m, 2H), 2.14-2.04 (m, 2H), 1.35-1.24 (m, 3H), 1.11 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.7, 153.5, 135.3, 134.1, 126.5, 122.5, 119.5, 77.5, 77.2, 76.8, 38.8, 23.7, 22.6, 18.1, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{29}O_2Si^+$, m/z: 305.1931, found: 305.1934.

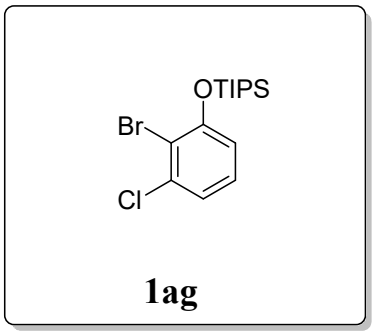
(3-bromo-2-chlorophenoxy)triisopropylsilane (1af)



1af

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.0, 1.4 Hz, 1H), 6.97 (t, J = 8.1 Hz, 1H), 6.86 (dd, J = 8.2, 1.4 Hz, 1H), 1.37-1.26 (m, 3H), 1.13 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.4, 127.6, 126.5, 125.8, 123.8, 118.6, 77.5, 77.2, 76.8, 18.0, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}BrClOSi^+$, m/z: 363.0541, found: 363.0545.

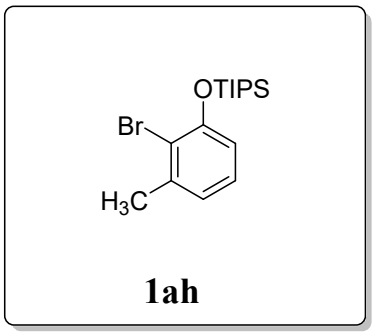
(2-bromo-3-chlorophenoxy)triisopropylsilane (1ag)



1ag

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.02 (m, 2H), 6.79 (dd, J = 7.6, 2.0 Hz, 1H), 1.39-1.29 (m, 3H), 1.14 (d, J = 7.5 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.7, 135.8, 128.0, 122.6, 117.4, 116.3, 77.5, 77.2, 76.8, 18.1, 13.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}BrClOSi^+$, m/z: 363.0541, found: 363.0544.

(2-bromo-3-methylphenoxy)triisopropylsilane (1ah)

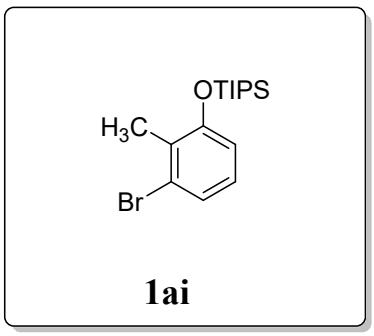


1ah

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 2.43 (s, 3H), 1.41-1.31 (m, 3H), 1.17 (d, J = 7.5 Hz, 18H). **^{13}C NMR (100 MHz,**

$CDCl_3$) δ 153.2, 139.9, 127.2, 123.0, 117.9, 116.8, 77.5, 77.2, 76.8, 23.8, 18.2, 13.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{16}H_{28}BrOSi^+$, m/z: 343.1087, found: 343.1089.

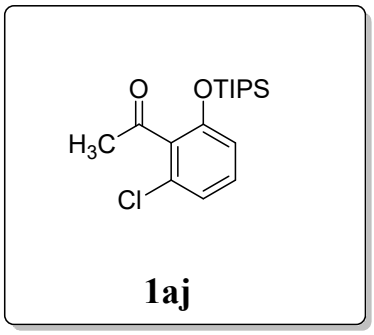
(3-bromo-2-methylphenoxy)triisopropylsilane (1ai)



1ai

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 7.5 Hz, 1H), 6.91 (t, J = 8.1 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 2.38 (s, 3H), 1.37-1.28 (m, 3H), 1.14 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 129.1, 127.0, 126.0, 125.0, 117.1, 77.5, 77.2, 76.8, 18.2, 16.8, 13.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{16}H_{28}BrOSi^+$, m/z: 343.1087, found: 343.1082.

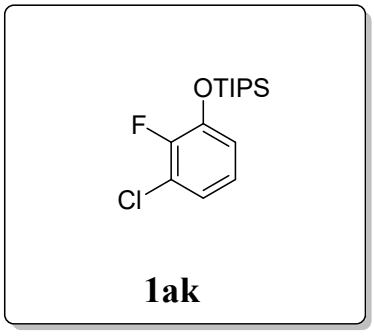
1-(2-chloro-6-((triisopropylsilyl)oxy)phenyl)ethan-1-one (1aj)



1aj

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, J = 8.2 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 2.49 (s, 3H), 1.33-1.21 (m, 3H), 1.07 (d, J = 7.5 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 201.5, 153.0, 133.1, 130.0, 129.8, 121.9, 117.0, 77.5, 77.2, 76.8, 31.9, 18.0, 12.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{17}H_{28}ClO_2Si^+$, m/z: 327.1542, found: 327.1536.

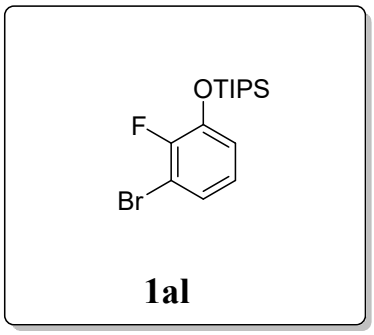
(3-chloro-2-fluorophenoxy)triisopropylsilane (1ak)



1ak

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.94 (m, 1H), 6.92-6.82 (m, 2H), 1.35-1.24 (m, 3H), 1.12 (d, J = 7.5 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.8, 149.4, 145.3 (d, $J_{C\text{-}F}$ = 11.8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 5.1 Hz), 122.5, 122.0 (d, $J_{C\text{-}F}$ = 15.8 Hz), 120.2, 17.9, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -133.54. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}ClFOSi^+$, m/z: 303.1342, found: 303.1340.

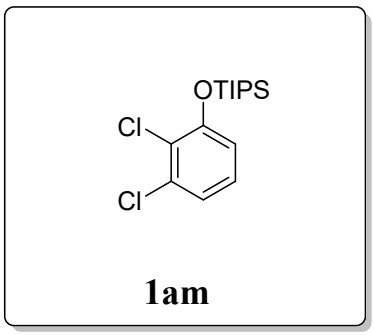
(3-bromo-2-fluorophenoxy)triisopropylsilane (1al)



1al

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.08 (m, 1H), 6.92-6.82 (m, 2H), 1.34-1.24 (m, 3H), 1.12 (d, J = 7.3 Hz, 19H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.7, 150.3, 145.1 (d, $J_{C\text{-}F}$ = 12.9 Hz), 125.2, 124.6 (d, $J_{C\text{-}F}$ = 4.8 Hz), 120.9 (d, $J_{C\text{-}F}$ = 1.4 Hz), 110.0 (d, $J_{C\text{-}F}$ = 18.9 Hz), 17.9, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -125.00. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}BrFOSi^+$, m/z: 347.0837, found: 347.0833.

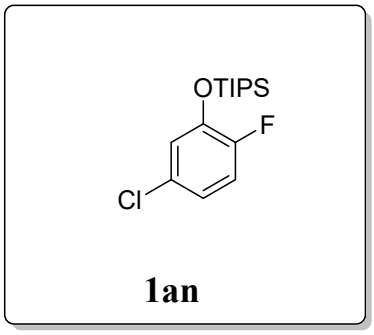
(2,3-dichlorophenoxy)triisopropylsilane (1am)



1am

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.00 (m, 2H), 6.83 (dd, *J* = 6.9, 2.7 Hz, 1H), 1.37-1.28 (m, 3H), 1.14 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.6, 133.9, 127.1, 124.7, 122.6, 118.1, 77.5, 77.2, 76.8, 18.0, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}Cl_2OSi^+$, m/z: 319.1046, found: 319.1039.

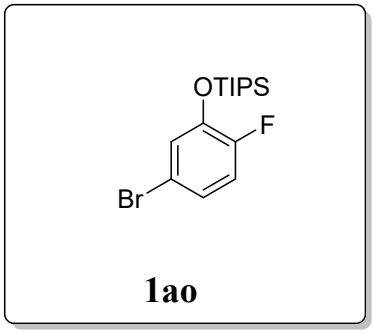
(5-chloro-2-fluorophenoxy)triisopropylsilane (1an)



1an

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.94 (m, 2H), 6.88-6.83 (m, 1H), 1.35 -1.25 (m, 3H), 1.13 (d, J = 7.7 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 151.9, 144.7 (d, $J_{C\text{-}F}$ = 13.4 Hz), 128.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 122.2 (d, $J_{C\text{-}F}$ = 1.7 Hz), 121.5 (d, $J_{C\text{-}F}$ = 6.8 Hz), 117.2, 117.0, 17.9, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -134.16. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}ClFOSi^+$, m/z: 303.1342, found: 303.1333.

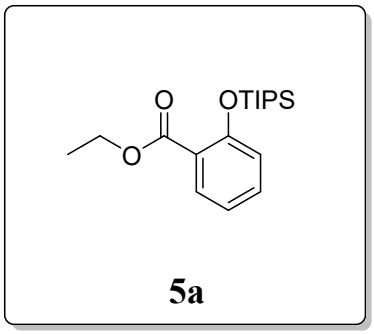
(5-bromo-2-fluorophenoxy)triisopropylsilane (1ao)



1ao

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, J = 7.6, 2.4 Hz, 1H), 7.02-6.98 (m, 1H), 6.92 (dd, J = 10.3, 8.7 Hz, 1H), 1.34-1.23 (m, 3H), 1.12 (d, J = 7.6 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.8, 152.3, 145.0 (d, $J_{C\text{-}F}$ = 13.2 Hz), 125.1 (d, $J_{C\text{-}F}$ = 1.9 Hz), 124.4 (d, $J_{C\text{-}F}$ = 6.7 Hz), 117.8, 117.6, 116.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 17.9, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -133.57. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{25}BrFOSi^+$, m/z: 347.0837, found: 347.0833.

ethyl 2-((triisopropylsilyl)oxy)benzoate (5a)



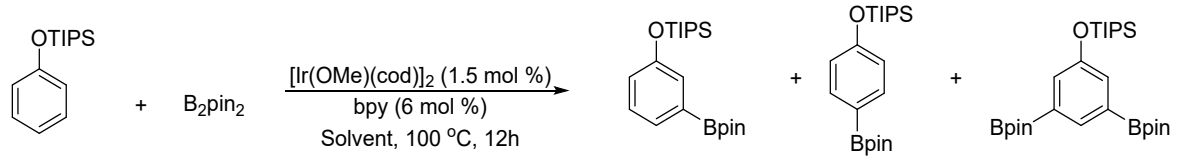
5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.8, 1.8 Hz, 1H), 7.33-7.29 (m, 1H), 6.95-6.91 (m, 1H), 6.87 (dd, J = 8.3, 0.8 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.39-1.27 (m, 6H), 1.11 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.0, 155.4, 132.7, 131.3, 123.4, 120.5, 120.3, 77.5, 77.2, 76.8, 60.8, 18.0, 14.5, 13.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{31}O_3Si^+$, m/z: 323.2037, found: 323.2030.

3. Reactions of 1a and 2a under different conditions

3.1 Screening of unsubstituted substrates

Table S-1: Screening of Solvent

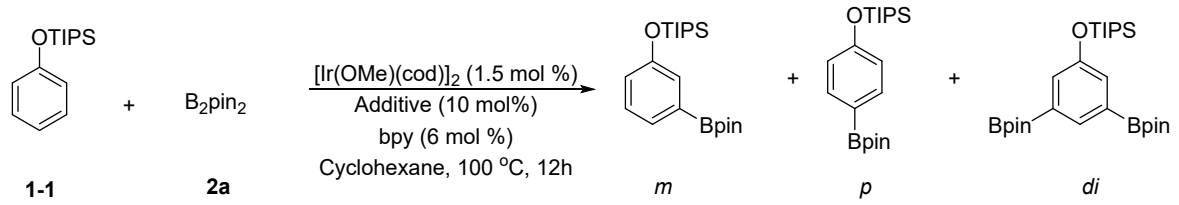


1-1 **2a** *m* *p* *di*

Entry [a]	Solvent	Yield (%) [b]	*m / p / di*
1	DCE	N.R.	-
2	1,4-Dioxane	N.R.	-
3	MTBE	N.R.	-
4	Toluene	N.R.	-
5	**Cyclohexane**	**51**	6 / 1 / 0.35
6	hexane	45	5 / 1 / 0.36
7	THF	77	3.2 / 1/ 1.4

[a]Reaction conditions: **1-1** (0.2 mmol), **2a** (0.24 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), bpy (6 mol%), **Solvent** (0.5 mL) at 100℃ for 12 h in a sealed tube, isolated yield after chromatography.

Table S-2: Screening of Additive

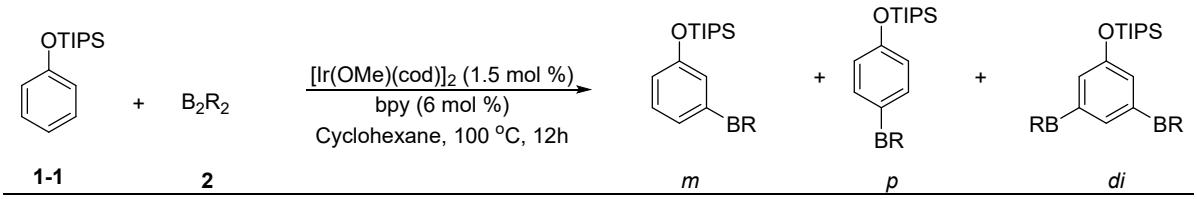


1-1 **2a** *m* *p* *di*

Entry [a]	Additve	Yield (%)	*m / p / di*
1	**None**	**51**	**6 / 1 / 0.35**
2	1-Ad-OH	64	4.4/1/0.6
3	$Fe(OAc)_2$	66	4.2/1/0.8
4	$AlCl_3$	N.R.	-
5	$FeCl_3$	trace	-
6	$Fe_3(CO)_{12}$	94	2 / 1 / 3.6
7	$Cu(OAc)_2$	N.R.	-

[a]Reaction conditions: **1-1** (0.2 mmol), **2a** (0.15 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), bpy (6 mol%), **Solvent** (0.5 mL) at 100℃ for 12 h in a sealed tube, isolated yield after chromatography.

Table S-3:**Screening of B-Source**

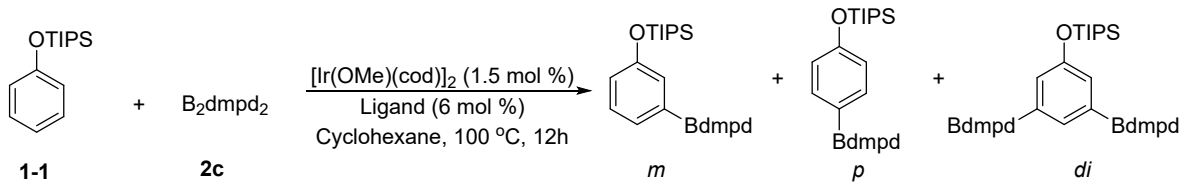


1-1 **2** *m* *p* *di*

2a, B_2Pin_2	2b, B_2hex_2	2c, B_2dmpd_2	2d, B_2nep_2
51%, m / p / di=6:1:0.35	58%, m / p / di=7.4:1:0.3	81%, m / p / di=7:1:0.8	N.R

[a]Reaction conditions: **1-1** (0.2 mmol), **2** (0.24 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), bpy (6 mol%), Cyclohexane (0.5 mL) at 100℃ for 12 h in a sealed tube, isolated yield after chromatography.

Table S-4 : **Screening of Ligand**



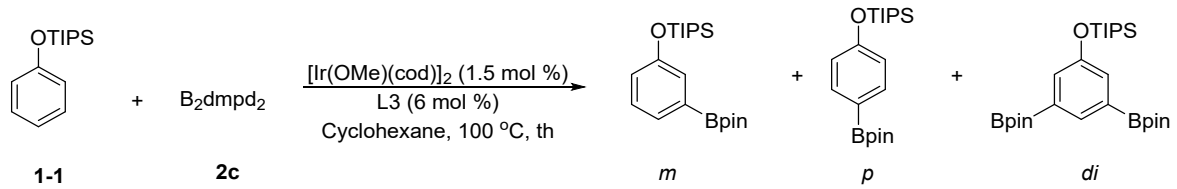
1-1 **2c** *m* *p* *di*

L_1, bpy	**L_2**, dtbpy	**L_3**, Phen	**L_4**, Me_4Phen
81%, *m/p/di*=7:1:0.8	80%, *m/p/di*=6.2:1:0.8	95%, *m/p/di*=10.7:1:2.2	99%, *m/p/di*=2.4:1:1.4

L_5, 2,9-Me_2Phen	**L_6**, trace	**L_7**, BINAP	**L_8**, DPEPhOS
64%, *m/p/di*=5.4:1:0.8		N.R	N.R

[a]Reaction conditions: **1-1** (0.2 mmol), **2c** (0.24 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), Ligand (6 mol%), Cyclohexane (0.5 mL) at 100℃ for 12 h in a sealed tube, isolated yield after chromatography.

Table S-5 : **Screening of reaction time**

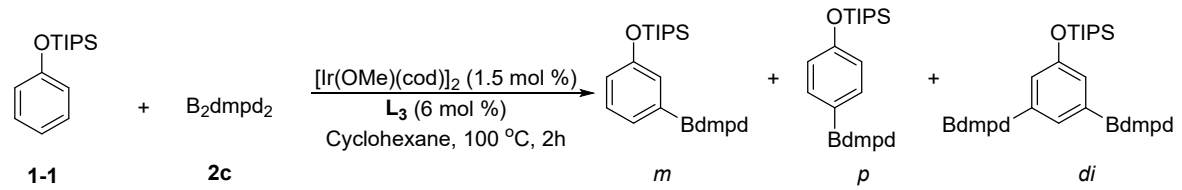


1-1 **2c** *m* *p* *di*

Entry [a]	**t/h**	**Yield (%)**	***m / p / di***
1	18	99	10.1:1:3.0
2	12	95	10.7:1:2.2
3	8	95	10.2:1:1.5
4	5	94	10.4:1:1
5	**2**	**94**	**10.8:1:0.5**
6	1	80	11.2:1:0.2
7	0.5	51	10.0:1:0.2

[a]Reaction conditions: **1-1** (0.2 mmol), **2c** (0.24 mmol), $[Ir(OMe)(cod)]_2$ (5 mol%), $\mathbf{L_3}$ (6 mol%), Cyclohexane (0.5 ml) at 100℃ for **t** h in a sealed tube, isolated yield after chromatography.

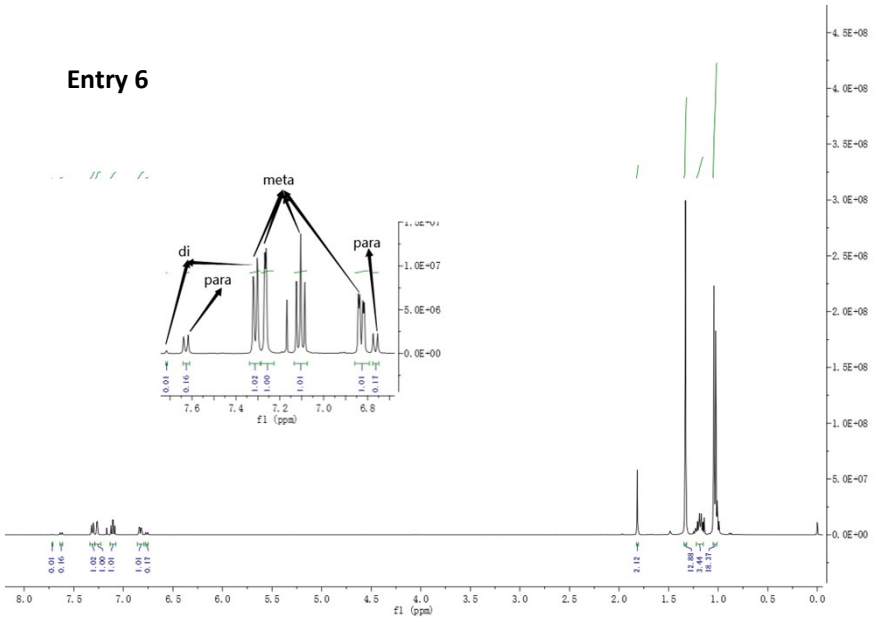
Table S-6 : **Screening of raw-material ratio**



1-1 **2c** *m* *p* *di*

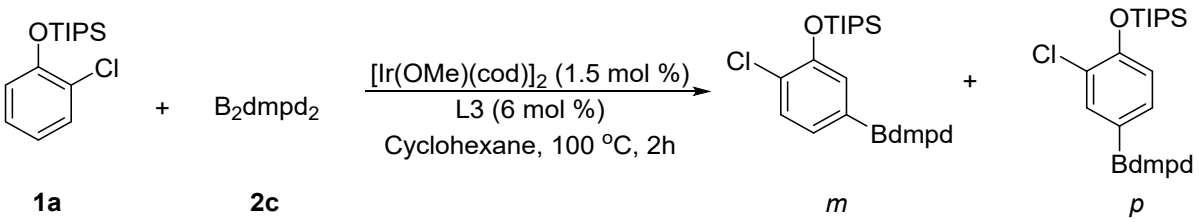
Entry [a]	1a:2c	Yield (%)	*m / p / di*
1	1:1.5	68	10.1:1:3.6
2	1:1.2	94	10.8:1:0.5
3	1:1.0	87	10.2:1:1.6
4	1.2:1	85	10.1:1:0.7
5	1.5:1	86	10.3:1:0.6
6	**2.0:1**	**73**	**11.5:1:0.1**
7	2.5:1	68	11.3:1:0.1

[a]Reaction conditions: **1-1**(0.2 mmol), **2c** (**x** mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), $\mathbf{L_3}$ (6 mol%), Cyclohexane (0.5 ml) at 100℃ for 12 h in a sealed tube, isolated yield after chromatography.



3.2 Screening of substituted substrates

Table S-7 : **Screening of raw-material ratio**

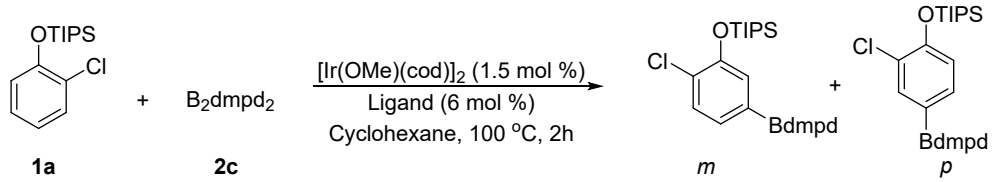


1a **2c** *m* *p*

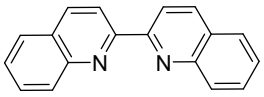
Entry [a]	1a:2c	Yield (%)	*m* / *p*
1	1.2:1	90	5.1:1
2	**1.5:1**	**93**	**6.2:1**
3	2.0:1	89	6.0:1
4	2.5:1	88	5.6:1

[a]Reaction conditions: **1a** (0.2 mmol), **2c** (**x** mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), $\mathbf{L_3}$ (6 mol%), Cyclohexane (0.5 ml) at 100℃ for 12 h in a sealed tube, isolated yield after chromatography.

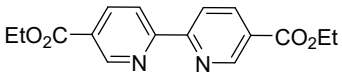
Table S-8 : Screening of Ligand



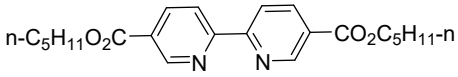
1a **2c** *m* *p*



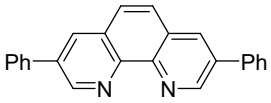
L_9, trace



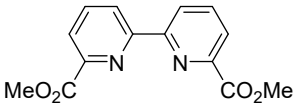
L_{10}
82%, *m/p*=1.8:1



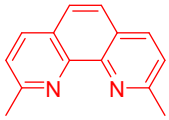
L_{11}
56%, *m/p*=2.0:1



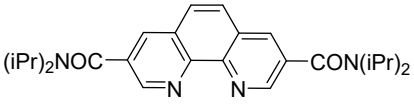
L_{12}, 3,8-Ph_2Phen
98%, *m/p*=3.6:1



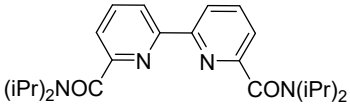
L_{13}
85%, *m/p*=2.2:1



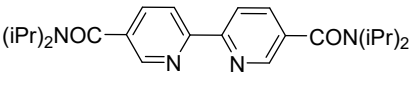
L_5, Me_2Phen
47%, *m/p*=7.1:1



L_{14}
90%, *m/p*=1:2



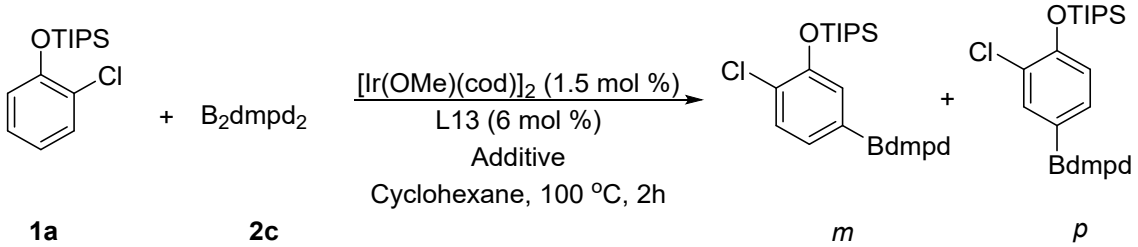
L_{15}, N.R



L_{16}
99%, *m/p*=2.3:1

[a]Reaction conditions: **1a** (0.3 mmol), **2c** (0.2 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), **Ligand** (6 mol%), Cyclohexane (0.5 ml) at 100℃ for 2 h in a sealed tube, isolated yield after chromatography.

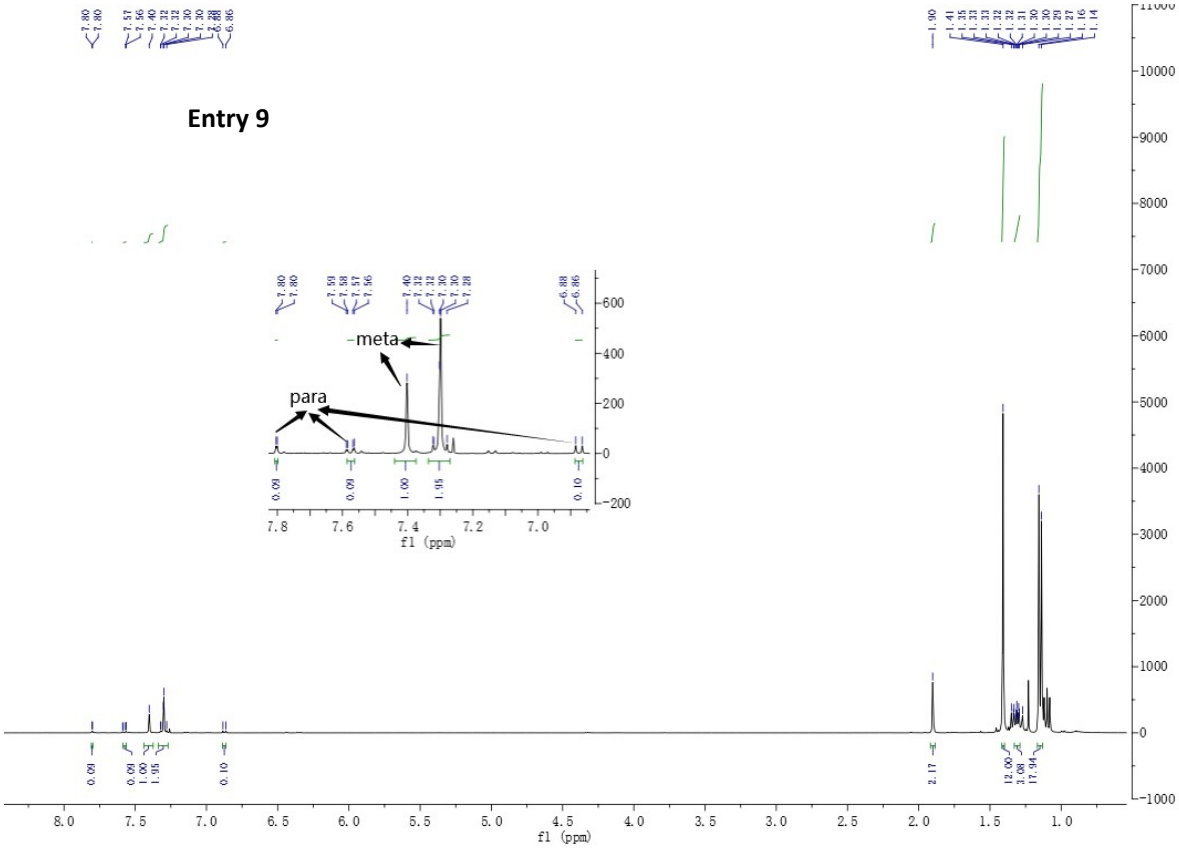
Table SS-3 : **Screening of Additive**



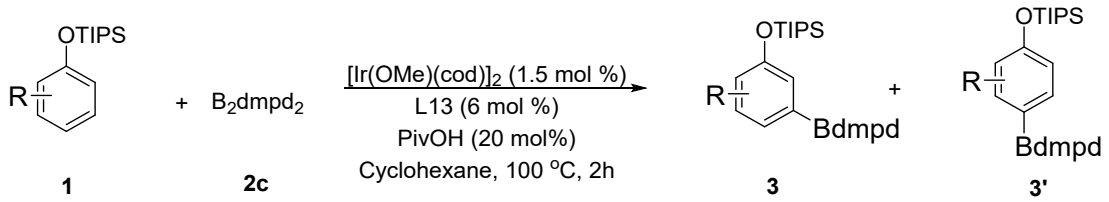
1a **2c** *m* *p*

Entry [a]	Additive	Yield (%)	*m / p*
1	$Fe(OAc)_2$ (10 mol%)	trace	-
2	$Cu(OTf)_2$ (10 mol%)	N.R	-
3	PivOH (10 mol%)	91	9.6:1
4	1-Ad-OH (10 mol%)	86	9.1:1
5	HOAc (10 mol%)	85	9.0:1
6	BNDHP (10 mol%)	81	9.0:1
7	TFA (10 mol%)	N.R.	-
9	**PivOH (20 mol%)**	**88**	**11:1**
10	PivOH (30 mol%)	77	10.6:1
11	PivOH (50 mol%)	63	10.2:1
12	PivOH (100 mol%)	59	9.1:1

[a]Reaction conditions: **1a** (0.3 mmol), **2c** (0.2 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), $\mathbf{L_{13}}$ (6 mol%), **Additive,** Cyclohexane (0.5 ml) at 100℃ for 2 h in a sealed tube, isolated yield after chromatography.



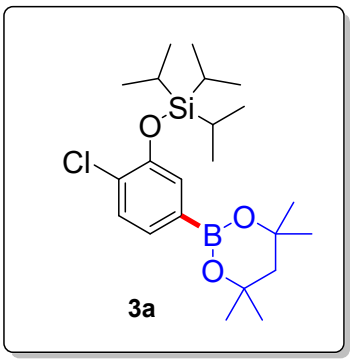
4. Preparation of 3a-3j, 3an-3ao.



1 **2c** **3** **3'**

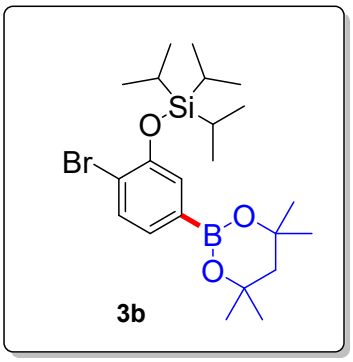
To a 10 mL reaction tube was sequentially added $\mathbf{L_{13}}$ (6 mol%, 2.5 mg), $[Ir(OMe)(cod)]_2$ (1.5 mol%, 2.0 mg), PivOH(20 mol%, 4.1 mg), **1** (0.3 mmol, 1.5 equiv), Bis(2,4-dimethylpentane-2,4-glycolato)diboron **2c** (0.2 mmol, 56.4 mg, 1.0 equiv) and Cyclohexane (0.5 ml) in golvebox. The reaction mixture was stirred at 100 °C for 2 hours. After the reaction mixture cooled down, ethyl acetate was added to dilute the reaction mixture. Then the reaction mixture was filtered through a plug of celite. The solution was concentrated by rotary evaporation under reduced pressure. After this, the mixture was purified by column chromatography (pe.ether/EtOAc = 50 : 1-10 : 1) to afford the product.

(2-chloro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropylsilane (3a)



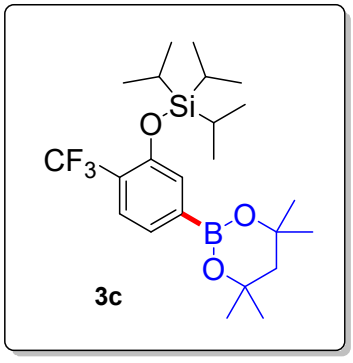
According to the general procedure, **3ac** was obtained in 88% yield (74.8 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, J = 1.5 Hz, 1H)*, 7.59 – 7.56 (m, 1H)*, 7.40 (s, 1H), 7.34 – 7.27 (m, 2H), 6.87 (d, J = 8.1 Hz, 1H)*, 1.90 (s, 2H), 1.41 (s, 12H), 1.33-1.29 (m, 3H), 1.15 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.1, 132.5, 127.1, 124.9, 117.4, 77.4, 77.0, 76.7, 70.9, 48.8, 31.8, 31.8, 18.0, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{38}BClO_3Si^+$, m/z: 424.2372, found: 424.2383.

(2-bromo-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropylsilane (3b)



According to the general procedure, **3ae** was obtained in 81% yield (76.0 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, J = 1.5 Hz, 1H)*, 7.62 (dd, J = 8.0, 1.6 Hz, 1H)*, 7.48 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 1.3 Hz, 1H), 7.23 (dd, J = 7.8, 1.4 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H)*, 1.90 (s, 2H), 1.41 (s, 12H), 1.36 – 1.31 (m, 3H), 1.16 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.1, 132.5, 127.1, 124.9, 117.4, 70.9, 48.8, 31.8, 18.0, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{38}BBrO_3Si^+$, m/z: 468.1867, found: 468.1853.

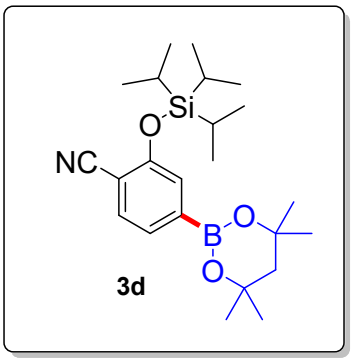
triisopropyl(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-(trifluoromethyl)-phenoxy)silane (3c)



According to the general procedure, **3ah** was obtained in 97% yield (88.9 mg). White solid, **m.p. =** 37-39 °C.. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (s, 1H)*, 7.87 (d, J = 7.9 Hz, 1H)*, 7.50 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 10.3 Hz, 2H), 6.88 (d, J = 8.2 Hz, 1H)*, 1.93 (s, 2H), 1.43 (s, 12H), 1.40 – 1.31 (m, 3H), 1.15 (d, J

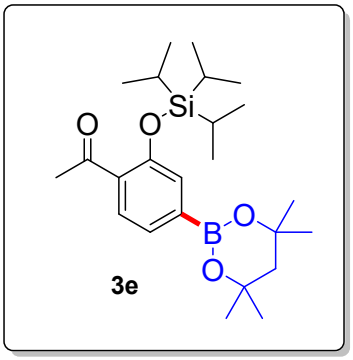
= 7.5 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5 (q, J_{C-F} = 1.0 Hz), 126.0 (q, J_{C-F} = 5.0 Hz), 125.0, 124.8, 124.1 (q, J_{C-F}=271.0 Hz), 121.6 (q, J_{C-F} = 30.0 Hz), 71.1, 48.8, 31.7, 17.9, 12.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.2. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{38}BF_3O_3Si^+$, m/z: 458.2635, found: 458.2629.

4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)benzonitrile (3d)



According to the general procedure, **3ai** was obtained in 83% yield (69.0 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, J = 1.6 Hz, 1H)*, 7.87 (dd, J = 8.4, 1.7 Hz, 1H)*, 7.46 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 3.5 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H)*, 1.92 (s, 2H), 1.41 (s, 12H), 1.38-1.31 (m, 3H), 1.15 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.5, 132.4, 125.9, 124.4, 117.5, 105.7, 71.3, 48.8, 31.7, 17.9, 12.7. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{38}BNO_3Si^+$, m/z: 415.2714, found: 415.2701.

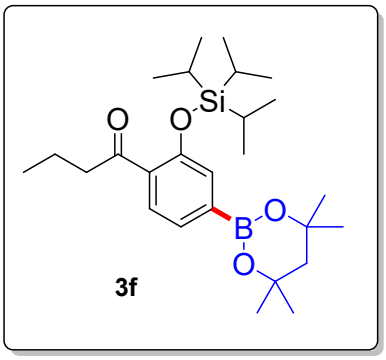
1-(4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)phenyl)-ethan-1-one (3e)



According to the general procedure, **3ai** was obtained in 81% yield (70.1 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (d, J = 1.7 Hz, 1H)*, 7.90 (d, J = 8.2 Hz, 1H)*, 7.56 (d, J = 7.8 Hz, 1H), 7.38 (dd, J = 3.8, 3.1 Hz, 2H), 6.82 (d, J = 8.2 Hz, 1H)*, 2.63 (s, 3H), 1.91 (s, 2H), 1.41 (s, 12H), 1.38-1.31 (m, 3H), 1.13 (d, J = 7.4 Hz, 18H).

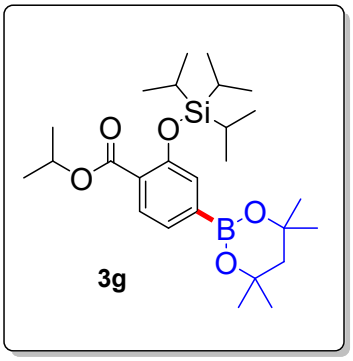
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 154.4, 131.7, 128.9, 125.8, 125.1, 71.1, 48.8, 31.8, 31.5, 18.0, 13.1. **HRMS (EI)** calcd for $[M]^+$ $C_{24}H_{41}BO_4Si^+$, m/z: 432.2867, found: 432.2852.

1-(4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)phenyl)-butan-1-one (3f)



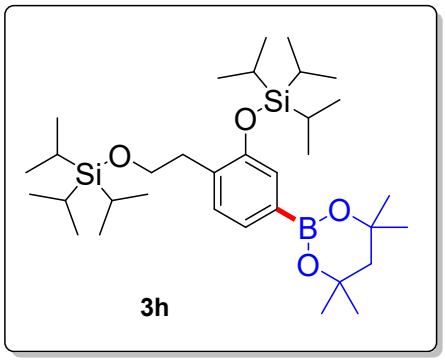
According to the general procedure, **3aj** was obtained in 79% yield (72.8 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 1.7 Hz, 1H)*, 7.77 (dd, *J* = 8.2, 1.8 Hz, 1H)*, 7.48 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.78 (dd, *J* = 8.2, 1.0 Hz, 1H)*, 2.99 (t, *J* = 7.4 Hz, 2H), 1.91 (s, 2H), 1.72 – 1.66 (m, 2H), 1.40 (s, 12H), 1.37 – 1.30 (m, 3H), 1.13 (d, *J* = 7.4 Hz, 18H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 204.6, 153.7, 132.2, 128.6, 125.9, 125.0, 71.0, 48.8, 45.6, 31.8, 18.0, 17.8, 13.8, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{26}H_{45}BO_4Si^+$, m/z: 460.3180, found: 460.3171.

Isopropyl-4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)-benzoate (3g)



According to the general procedure, **3ak** was obtained in 76% yield (72.4 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, J = 1.7 Hz, 1H)*, 7.77 (dd, J = 8.2, 1.7 Hz, 1H)*, 7.59 (d, J = 7.6 Hz, 1H), 7.37 (s, 1H), 7.34 (dd, J = 7.6, 0.8 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H)*, 5.21 (m, J = 6.3 Hz, 1H), 1.90 (s, 2H), 1.89 (s, 1H), 1.40 (s, 12H), 1.35–1.29 (m, 9H), 1.13 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.6, 154.3, 129.9, 125.7, 125.3, 124.7, 71.0, 67.8, 48.8, 31.8, 22.0, 18.0, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{26}H_{45}BO_5Si^+$, m/z: 476.3129, found: 476.3118.

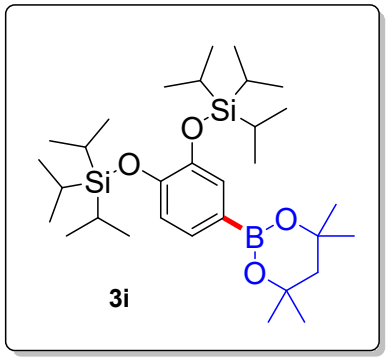
triisopropyl(4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)-phenethoxy)silane (3h)



3h

According to the general procedure, **3af** was obtained in 88% yield (104.0 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (s, 1H)*, 7.58 (d, J = 8.0 Hz, 1H)*, 7.33 (d, J = 4.5 Hz, 2H), 7.16 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H)*, 3.87 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.4 Hz, 2H), 1.90 (s, 2H), 1.41 (s, 12H), 1.37-1.31 (m, 3H), 1.15 (d, J = 7.4 Hz, 18H), 1.13 – 1.09 (m, 3H), 1.06 (d, J = 4.2 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5, 131.1, 130.4, 125.9, 123.4, 70.6, 63.5, 48.9, 34.8, 31.8, 18.2, 18.1, 12.9, 12.1, 1.1. **HRMS (EI)** calcd for $[M]^+$ $C33H63BO4Si2^+$, m/z: 590.4358, found: 590.4350.

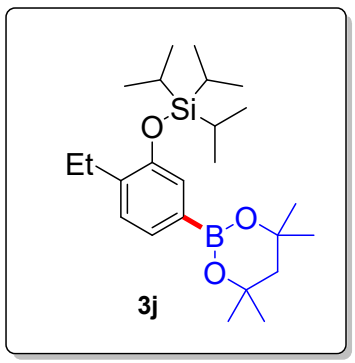
((4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1,2-phenylene)bis(oxy))bis(triiso-propylsilane) (3i)



3i

According to the general procedure, **3ag** was obtained in 70% yield (78.8 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (d, J = 1.5 Hz, 1H), 7.24 (dd, J = 7.9, 1.5 Hz, 1H), 6.94 (dd, J = 8.0, 1.6 Hz, 1H)*, 6.86 (s, 1H)*, 6.79 (d, J = 7.9 Hz, 1H), 6.75 (dd, J = 8.4, 1.6 Hz, 1H)*, 1.88 (s, 2H), 1.39 (s, 12H), 1.33 – 1.27 (m, 6H), 1.12 (t, J = 7.7 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.0, 146.1, 126.6, 125.7, 119.2, 70.5, 48.9, 31.9, 18.1, 18.0, 13.2, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C31H59BO4Si2^+$, m/z: 562.4045, found: 562.4039.

(2-ethyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropylsilane (3j)

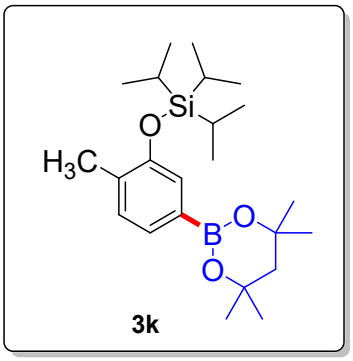


3j

According to the general procedure, **3ab** was obtained in 61% yield (51.1 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (s, 1H)*, 7.57 (dd, *J* = 8.0, 1.7 Hz, 1H)*, 7.34 (d, *J* = 7.3 Hz, 1H), 7.31 (s, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.0

Hz, 1H)*, 2.67 (q, J = 7.5 Hz, 2H), 1.90 (s, 2H), 1.41 (s, 12H), 1.36-1.29 (m, 3H), 1.20 (t, J = 7.5 Hz, 3H), 1.15 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.1, 136.5, 128.5, 126.1, 123.3, 70.6, 48.9, 31.8, 23.9, 18.1, 14.3, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{24}H_{43}BO_3Si^+$, m/z: 418.3075, found: 418.3071.

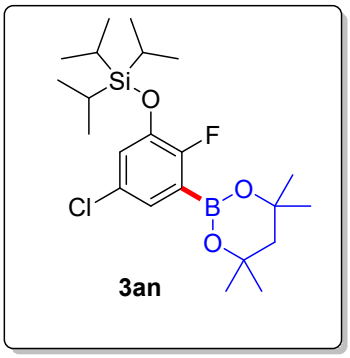
triisopropyl(2-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)silane (3k)



3k

According to the general procedure, **3aa** was obtained in 83% yield (67.1 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (s, 1H)*, 7.56 (d, J = 8.0 Hz, 1H)*, 7.31-7.29 (t, J = 3.2 Hz, 2H), 7.10 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H)*, 2.26 (s, 3H), 1.90 (s, 2H), 1.41 (s, 12H), 1.35 – 1.29 (m, 3H), 1.14 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.6, 130.7, 130.1, 126.0, 123.4, 70.6, 48.9, 31.9, 18.1, 17.1, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{41}BO_3Si^+$, m/z: 404.2918, found: 404.2916.

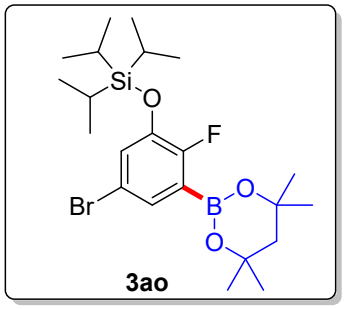
(5-chloro-2-fluoro-3-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)tri-isopropylsilane (3an)



3an

According to the general procedure, **3by** was obtained in 92% yield (81.5 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.18 (dd, J = 4.0, 2.7 Hz, 1H), 6.92 (dd, J = 7.2, 2.7 Hz, 1H), 1.93 (s, 2H), 1.43 (s, 12H), 1.30-1.26 (m, 3H), 1.11 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.0, 155.5, 144.6 (d, $J_{C\text{-}F}$ = 15.7 Hz), 127.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 126.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 123.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 71.7, 49.1, 31.9, 18.0, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -126.65. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BClFO_3Si^+$, m/z: 442.2278, found: 442.2273.

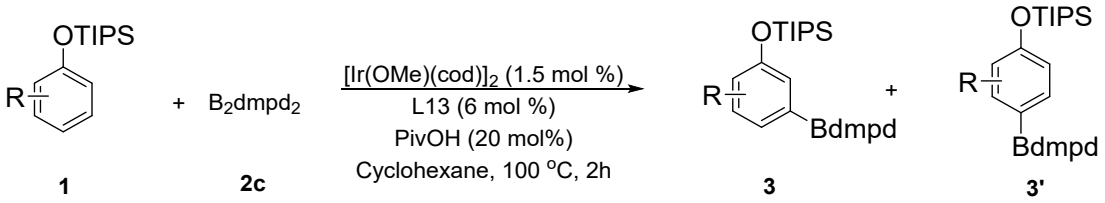
(5-bromo-2-fluoro-3-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)tri-isopropylsilane (3ao)



3ao

According to the general procedure, **3bz** was obtained in 87% yield (84.8 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (dd, *J* = 4.1, 2.6 Hz, 1H), 7.06 (dd, *J* = 7.3, 2.5 Hz, 1H), 1.92 (s, 2H), 1.43 (s, 12H), 1.30-1.26 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.5, 156.0, 144.8 (d, $J_{C\text{-}F}$ = 15.6 Hz), 129.7 (d, $J_{C\text{-}F}$ = 7.4 Hz), 126.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 115.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 77.5, 77.2, 76.8, 71.7, 49.1, 31.9, 18.0, 12.8. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -126.07. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BBrFO_3Si^+$, m/z: 486.1772, found: 486.1771.

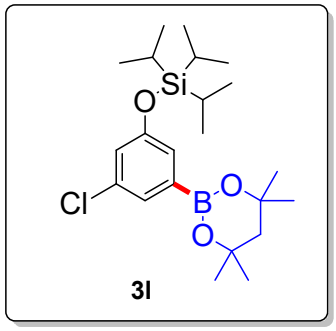
5. Preparation of substrate 3l-3am



1 **2c** **3** **3'**

To a 10 mL reaction tube was sequentially added $\mathbf{L_{13}}$ (6 mol%, 2.5 mg), $[Ir(OMe)(cod)]_2$ (1.5 mol%, 2.0 mg), PivOH(20 mol%, 4.1 mg), **1** (0.2 mmol, 1.0 equiv), Bis(2,4-dimethylpentane-2,4-glycolato)diboron **2c** (0.3 mmol, 84.6 mg, 1.5 equiv) and Cyclohexane (0.5 ml) . The reaction mixture was stirred at 100 °C for 2 hours. After the reaction mixture cooled down, ethyl acetate was added to dilute the reaction mixture. Then the reaction mixture was filtered through a plug of celite. The solution was concentrated by rotary evaporation under reduced pressure. After this, the mixture was purified by column chromatography (pe.ether/EtOAc = 50 : 1) to afford the product.

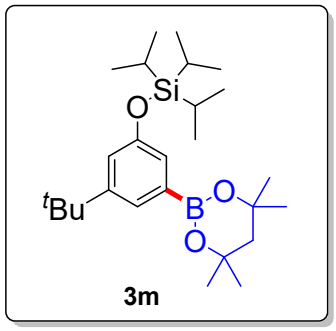
(3-chloro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropyl-silane (3l)



3l

According to the general procedure, **3am** was obtained in 99% yield (84.1 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, J = 1.2 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 6.91 (t, J = 2.1 Hz, 1H), 1.90 (s, 2H), 1.42 (s, 12H), 1.30-1.24 (m, 3H), 1.12 (d, J = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.3, 133.9, 126.3, 123.4, 121.8, 71.2, 49.0, 31.9, 18.1, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{38}BClO_3Si^+$, m/z: 424.2372, found: 424.2380.

(3-(tert-butyl)-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)tri-isopropyl-silane (3m)

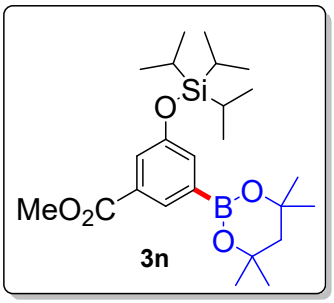


3m

According to the general procedure, **3an** was obtained in 41% yield (36.6 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (d, J = 0.8 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 6.97 (t, J = 2.1 Hz, 1H), 1.90 (s, 2H), 1.42 (s, 12H), 1.32 (s, 9H), 1.29-1.24 (m,

3H), 1.13 (d, J = 7.2 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.3, 151.6, 123.0, 122.4, 119.4, 70.8, 49.1, 34.7, 32.0, 31.6, 18.2, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{26}H_{47}BO_3Si^+$, m/z: 446.3388, found: 446.3379.

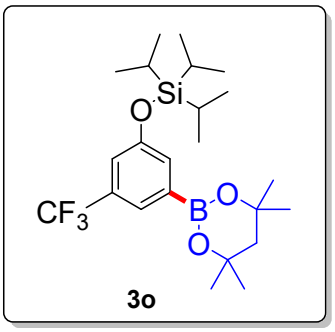
methyl 3-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-5-((triisopropylsilyl)oxy)-benzoate (3n)



3n

According to the general procedure, **3ao** was obtained in 89% yield (79.8 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (s, 1H), 7.57-7.54 (m, 1H), 7.52 (d, J = 2.5 Hz, 1H), 3.90 (s, 3H), 1.90 (s, 2H), 1.42 (s, 12H), 1.29-1.23 (m, 3H), 1.11 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.6, 155.6, 130.6, 129.9, 127.6, 122.3, 71.1, 52.1, 49.0, 31.9, 18.1, 12.7. **HRMS (EI)** calcd for $[M]^+$ $C_{24}H_{41}BO_5Si^+$, m/z: 448.2816, found: 448.2811.

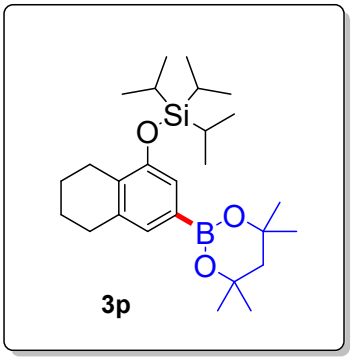
triisopropyl(3-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-5-(trifluoromethyl)-phenoxy)silane (3o)



3o

According to the general procedure, **3ap** was obtained in 93% yield (85.3 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (s, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.14 (s, 1H), 1.93 (s, 2H), 1.44 (s, 12H), 1.31-1.24 (m, 3H), 1.14 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.7, 131.0 (q, $J_{C\text{-}F}$ = 31.7 Hz), 128.5, 124.5(q, $J_{C\text{-}F}$ = 270.8 Hz), 122.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 118.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 71.3, 49.1, 31.9, 18.1, 12.8. **^{19}F NMR (377 MHz, CDCl3)** δ -62.20. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{38}BF_3O_3Si^+$, m/z: 458.2635, found: 458.2629.

triisopropyl((3-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-5,6,7,8-tetrahydro-naphthalen-1-yl)oxy)silane (3p)

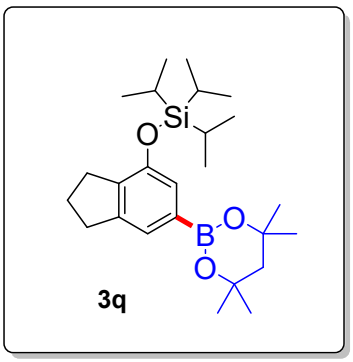


3p

According to the general procedure, **3bc** was obtained in 78% yield (69.3 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ

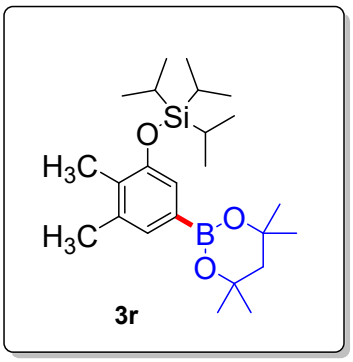
7.15 (s, 1H), 7.13 (s, 1H), 2.77 (t, J = 5.9 Hz, 2H), 2.72 (t, J = 6.2 Hz, 2H), 1.90 (s, 2H), 1.83 – 1.71 (m, 4H), 1.41 (s, 12H), 1.34 – 1.30 (m, 3H), 1.15 (d, J = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.2, 137.7, 130.2, 126.8, 120.0, 70.5, 48.9, 31.8, 29.8, 24.3, 23.2, 23.1, 18.2, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{26}H_{45}BO_3Si^+$, m/z: 444.3231, found: 444.3224.

triisopropyl((6-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2,3-dihydro-1H-inden-4-yl)oxy)silane (3q)



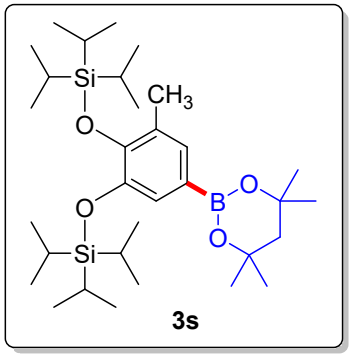
According to the general procedure, **3bd** was obtained in 75% yield (64.6 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 (s, 1H), 7.05 (s, 1H), 2.81 (q, *J* = 7.5 Hz, 4H), 2.00 – 1.90 (m, 2H), 1.80 (s, 2H), 1.31 (s, 12H), 1.22 – 1.18 (m, 3H), 1.04 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.8, 145.6, 136.6, 122.2, 121.7, 70.6, 48.9, 33.2, 31.9, 30.1, 25.0, 18.1, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{25}H_{43}BO_3Si^+$, m/z: 430.3075, found: 430.3080.

(2,3-dimethyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropylsilane (3r)



According to the general procedure, **3bg** was obtained in 56% yield (46.9 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 (s, 1H), 7.18 (s, 1H), 2.27 (s, 3H), 2.19 (s, 3H), 1.89 (s, 2H), 1.41 (s, 12H), 1.34 – 1.30 (m, 3H), 1.14 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.4, 137.0, 129.2, 127.5, 121.2, 70.6, 48.9, 31.8, 20.2, 18.1, 12.9, 12.7. **HRMS (EI)** calcd for $[M]^+$ $C_{24}H_{43}BO_3Si^+$, m/z: 418.3075, found: 418.3083.

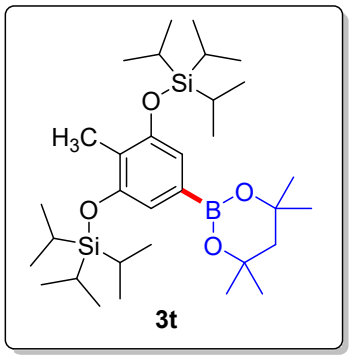
((3-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1,2-phenylene)bis(oxy))bis(triisopropylsilane) (3s)



3s

According to the general procedure, 3bs was obtained in 94% yield (105.0 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 (d, J = 1.1 Hz, 1H), 7.16 (s, 1H), 2.25 (s, 3H), 1.89 (s, 2H), 1.40 (s, 12H), 1.37-1.20 (m, 6H), 1.12 (dd, J = 12.7, 7.5 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.7, 146.4, 129.4, 128.8, 123.4, 77.5, 77.2, 76.8, 70.6, 49.0, 32.0, 18.3, 18.2, 17.8, 14.4, 13.5. **HRMS (EI)** calcd for $[M]^+$ $C_{32}H_{61}BO_4Si_2^+$, m/z: 353.1416, found: 353.1421.

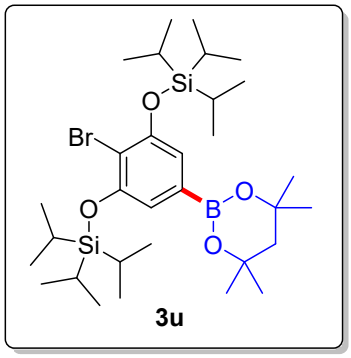
((2-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1,3-phenylene)bis(oxy)) bis(triisopropylsilane) (3t)



3t

According to the general procedure, **3bp** was obtained in 62% yield (71.5 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.94 (s, 2H), 2.18 (s, 3H), 1.89 (s, 2H), 1.39 (s, 12H), 1.35-1.29 (m, 6H), 1.13 (d, J = 7.3 Hz, 36H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 121.6, 116.6, 77.5, 77.2, 76.8, 70.6, 48.9, 32.0, 18.2, 13.0, 10.5. **HRMS (EI)** calcd for $[M]^+$ $C_{32}H_{61}BO_4Si_2^+$, m/z: 576.4201, found: 576.4118.

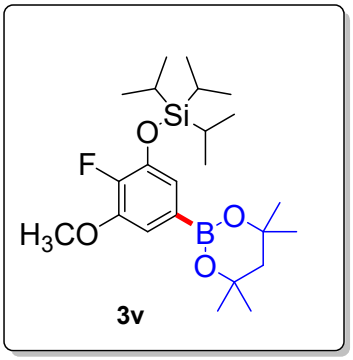
((2-bromo-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1,3-phenylene)bis(oxy))bis (triisopropylsilane) (3u)



3u

According to the general procedure, **3br** was obtained in 94% yield (120.6 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.98 (s, 2H), 1.89 (s, 2H), 1.39 (s, 12H), 1.35-1.29 (m, 6H), 1.15 (d, *J* = 7.4 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.7, 117.3, 110.9, 77.5, 77.2, 76.8, 70.9, 48.9, 31.9, 18.2, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{31}H_{58}BBrO_4Si_2^+$, m/z: 640.3150, found: 640.3152.

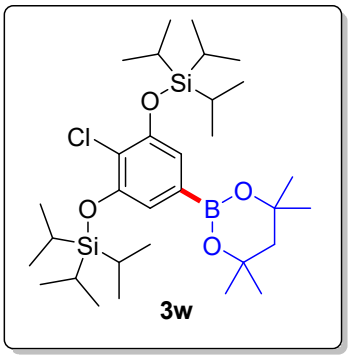
(2-fluoro-3-methoxy-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triiso-propylsilane (3v)



3v

According to the general procedure, **3bl** was obtained in 92% yield (80.7 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 1.90 (s, 2H), 1.41 (s, 12H), 1.35-1.27 (m, 3H), 1.12 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.1 (d, J_{C-F} = 8.5 Hz), 147.3, 144.8, 143.9 (d, J_{C-F} = 9.5 Hz), 119.8, 110.6, 70.9, 56.4, 48.9, 31.8, 17.8, 12.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -152.0. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{40}BFO_4Si^+$, m/z: 438.2773, found: 438.2767.

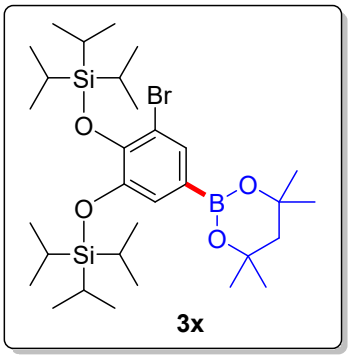
((2-chloro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1,3-phenylene)bis(oxy))bis (triisopropylsilane) (3w)



3w

According to the general procedure, **3bq** was obtained in 94% yield (112.3 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.02 (s, 2H), 1.89 (s, 2H), 1.40 (s, 12H), 1.35-1.29 (m, 6H), 1.15 (d, J = 7.3 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.6, 119.3, 117.8, 77.5, 77.2, 76.8, 70.9, 48.9, 31.9, 18.1, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{31}H_{58}BClO_4Si_2^+$, m/z: 596.3655, found: 596.3650.

((3-bromo-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1,2-phenylene)bis(oxy))bis (triisopropylsilane) (3x)

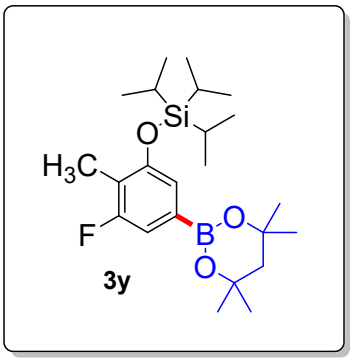


3x

According to the general procedure, **3bt** was obtained in 71% yield (91.1 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, J = 1.3 Hz, 1H), 7.29 (d, J = 1.3 Hz, 1H), 1.88 (s, 2H), 1.50-1.43 (m, 3H), 1.39 (s, 12H), 1.35-1.26 (m, 3H), 1.12 (dd, J

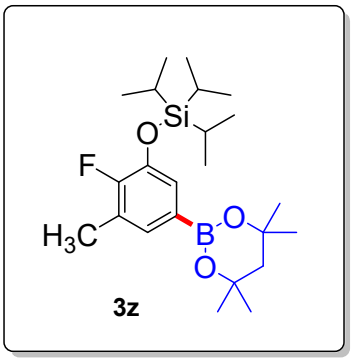
= 7.5, 4.4 Hz, 36H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.7, 146.9, 130.9, 124.4, 116.6, 77.5, 77.2, 76.8, 71.0, 48.9, 31.9, 18.3, 18.2, 14.4, 13.5. **HRMS (EI)** calcd for $[M]^+$ $C_{31}H_{58}BBrO_4Si_2^+$, m/z: 640.3150, found: 640.3158.

(3-fluoro-2-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triiso-propylsilane (3y)



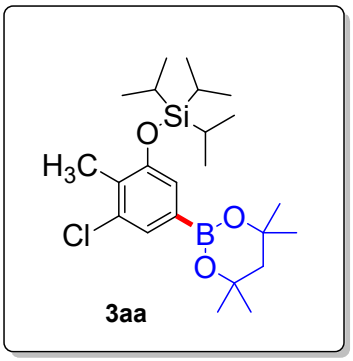
According to the general procedure, **3bb** was obtained in 73% yield (61.7 mg). COlorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.10 (s, 1H), 7.07 (d, J = 9.5 Hz, 1H), 2.17 (d, J = 1.8 Hz, 3H), 1.92 (s, 1H)*, 1.90 (s, 2H), 1.43 (s, 1H)*, 1.40 (s, 12H), 1.37 – 1.21 (m, 3H), 1.13 (d, J = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.0, 160.6, 154.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 118.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 118.0 (d, $J_{C\text{-}F}$ = 18.2 Hz), 112.1 (d, $J_{C\text{-}F}$ = 20.9 Hz), 70.8, 48.8, 31.8, 18.0, 12.8, 8.7 (d, $J_{C\text{-}F}$ = 4.9 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -117.5*, -117.6. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{40}BFO_3Si^+$, m/z: 422.2824, found: 422.2821.

(2-fluoro-3-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triiso-propylsilane (3z)



According to the general procedure, **3bk** was obtained in 79% yield (66.7 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 7.0 Hz, 1H), 2.26 (d, J = 1.8 Hz, 3H), 1.90 (s, 2H), 1.41 (s, 12H), 1.34 – 1.29 (m, 3H), 1.13 (d, J = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.7, 153.2, 142.9 (d, $J_{C\text{-}F}$ = 12.0 Hz), 128.8 (d, $J_{C\text{-}F}$ = 4.2 Hz), 124.8 (d, $J_{C\text{-}F}$ = 14.6 Hz), 124.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 70.8, 48.9, 31.8, 17.9, 14.5 (d, $J_{C\text{-}F}$ = 4.5 Hz), 12.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -134.1. **HRMS (EI)** calcd for $[M]^+$ C23H40BFO3Si$^+$, m/z: 422.2824, found: 422.2821.

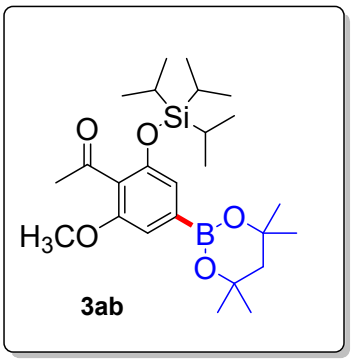
(3-chloro-2-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triiso-propylsilane (3aa)



3aa

According to the general procedure, **3ba** was obtained in 85% yield (74.6 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (s, 1H), 7.20 (s, 1H), 2.32 (s, 3H), 1.90 (s, 2H), 1.40 (s, 12H), 1.37 – 1.25 (m, 6H), 1.13 (d, J = 7.3 Hz, 18H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4, 134.7, 128.9, 126.6, 121.6, 70.9, 48.8, 31.8, 18.0, 13.8, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{40}BClO_3Si^+$, m/z: 438.2528, found: 438.2520.

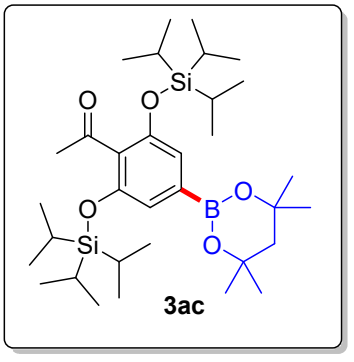
1-(2-methoxy-4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-6-((triisopropylsilyl)oxy)-phenyl)ethan-1-one (3ab)



3ab

According to the general procedure, **3bm** was obtained in 84% yield (77.7 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.00 (s, 1H), 6.93 (s, 1H), 3.82 (s, 3H), 2.45 (s, 3H), 1.90 (s, 2H), 1.40 (s, 12H), 1.30 – 1.24 (m, 3H), 1.09 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 203.2, 156.1, 152.0, 124.6, 117.2, 108.1, 71.0, 55.8, 48.8, 32.3, 31.8, 18.0, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{25}H_{43}BO_5Si^+$, m/z: 462.2973, found: 462.2971.

1-(4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2,6-bis((triisopropylsilyl)oxy)phenyl) ethan-1-one (3ac)

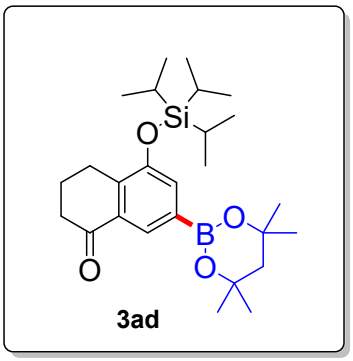


3ac

According to the general procedure, 3bo was obtained in 90% yield (108.8 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl3)** δ 6.91 (s, 2H), 2.44 (s, 3H), 1.89 (s, 2H), 1.38 (s, 12H), 1.31-1.21 (m, 6H), 1.09 (d, J = 7.4 Hz, 36H). **^{13}C NMR (100 MHz, CDCl3)** δ 203.1, 152.0, 127.1, 116.5, 70.8, 48.7, 32.3, 31.7, 18.0, 12.7.

HRMS (EI) calcd for [M]+ $C_{33}H_{61}BO_5Si_2^+$, m/z: 604.4151, found: 604.4144.

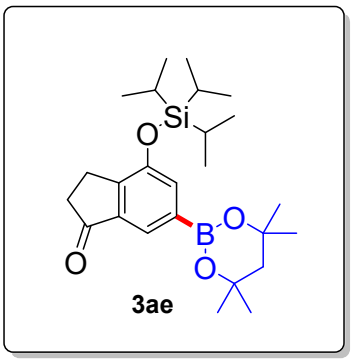
7-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-5-((triisopropylsilyl)oxy)-3,4-dihydronaphthalen-1(2H)-one (3ad)



3ad

According to the general procedure **B**, **3be** was obtained in 71% yield (65.1 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (s, 1H), 7.48 (s, 1H), 2.93 (t, *J* = 6.1 Hz, 2H), 2.64 – 2.59 (m, 2H), 2.12 – 2.03 (m, 2H), 1.89 (s, 2H), 1.39 (s, 12H), 1.34 – 1.28 (m, 3H), 1.13 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.3, 152.7, 137.0, 133.3, 127.8, 125.0, 70.9, 48.9, 39.0, 31.8, 23.9, 22.6, 18.1, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{26}H_{43}BO_4Si^+$, m/z: 458.3024, found: 458.3016.

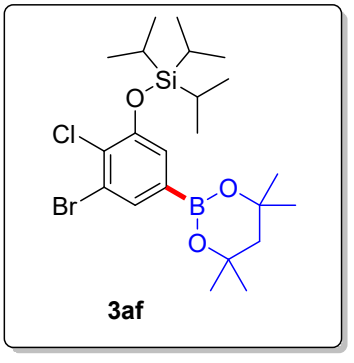
6-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-4-((triisopropylsilyl)oxy)-2,3-dihydro-1H-inden-1-one (3ae)



3ae

According to the general procedure, **3ea** was obtained in 49% yield (43.6 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (s, 1H), 7.51 (s, 1H), 3.09-3.02 (m, 2H), 2.69-2.64 (m, 2H), 1.91 (s, 2H), 1.40 (s, 12H), 1.32-1.28 (m, 3H), 1.13 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.8, 153.0, 147.7, 138.3, 128.7, 121.8, 71.0, 48.8, 36.4, 31.8, 23.1, 18.0, 12.7. **HRMS (EI)** calcd for $[M]^+$ $C_{25}H_{41}BO_4Si^+$, m/z: 444.2867, found: 444.2861.

(3-bromo-2-chloro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropyl-silane (3af)

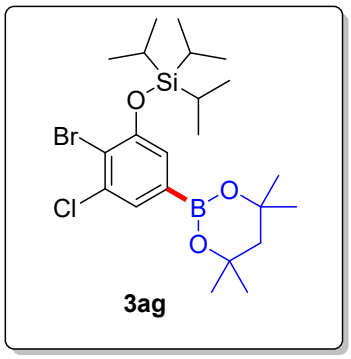


3af

According to the general procedure, **3bu** was obtained in 85% yield (85.6 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ

7.62 (d, J = 1.2 Hz, 1H), 7.32 (d, J = 1.2 Hz, 1H), 1.90 (s, 2H), 1.40 (s, 12H), 1.34-1.29 (m, 3H), 1.14 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.6, 130.7, 127.9, 123.8, 123.1, 77.5, 77.2, 76.8, 71.3, 48.9, 31.9, 18.1, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BBrClO_3Si^+$, m/z: 502.1477, found: 502.1473.

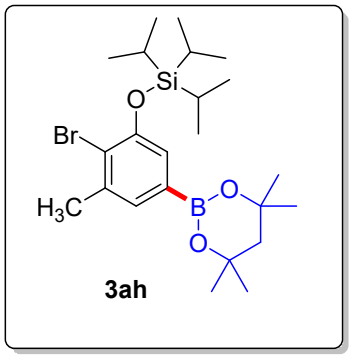
(2-bromo-3-chloro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropyl-silane (3ag)



3ag

According to the general procedure, **3bu** was obtained in 98% yield (98.7 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (d, J = 0.4 Hz, 1H), 7.25 (s, 1H), 1.90 (s, 2H), 1.41 (s, 12H), 1.36-1.30 (m, 3H), 1.15 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 135.0, 127.4, 122.6, 118.0, 77.5, 77.2, 76.8, 71.3, 48.9, 31.9, 18.1, 12.9. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BBrClO_3Si^+$, m/z: 502.1477, found: 502.1474.

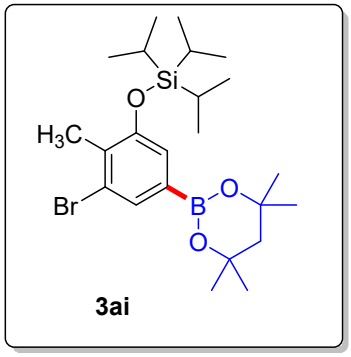
(2-bromo-3-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)tri-isopropylsilane (3ah)



3ah

According to the general procedure, **3bw** was obtained in 82% yield (79.3 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (s, 1H), 7.22 (s, 1H), 2.42 (s, 3H), 1.90 (s, 2H), 1.41 (s, 12H), 1.35-1.31 (m, 3H), 1.16 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.4, 138.7, 128.0, 122.1, 120.2, 77.5, 77.2, 76.8, 71.0, 49.0, 31.9, 23.6, 18.2, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{40}BBrO_3Si^+$, m/z: 482.2023, found: 482.2021.

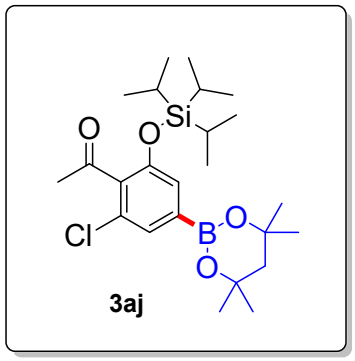
(3-bromo-2-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)tri-isopropylsilane (3ai)



3ai

According to the general procedure, **3bx** was obtained in 80% yield (77.4 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (s, 1H), 7.23 (s, 1H), 2.36 (s, 3H), 1.90 (s, 2H), 1.40 (s, 12H), 1.33-1.28 (m, 3H), 1.13 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 130.8, 130.0, 125.7, 122.4, 77.5, 77.2, 76.8, 71.0, 49.0, 31.9, 18.2, 16.9, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{40}BBrO_3Si^+$, m/z: 482.2023, found: 482.2026.

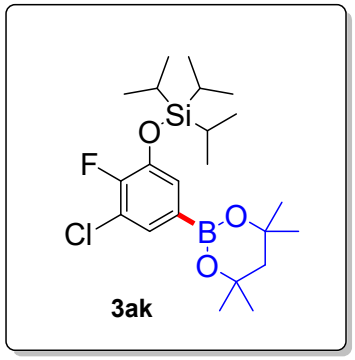
1-(2-chloro-4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-6-((triisopropylsilyl)oxy)-phenyl)ethan-1-one (3aj)



3aj

According to the general procedure, **3bn** was obtained in 97% yield (90.6 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (s, 1H), 7.22 (s, 1H), 2.49 (s, 3H), 1.90 (s, 2H), 1.40 (s, 12H), 1.33-1.26 (m, 3H), 1.09 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 201.8, 152.1, 134.1, 128.8, 126.7, 122.1, 71.2, 48.8, 31.7, 31.7, 17.9, 12.7. **HRMS (EI)** calcd for $[M]^+$ $C_{24}H_{40}BClO_4Si^+$, m/z: 466.2477, found: 466.2472.

(3-chloro-2-fluoro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triiso-propylsilane (3ak)

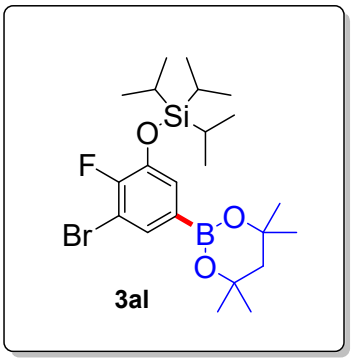


3ak

According to the general procedure, **3bi** was obtained in 99% yield (87.7 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 6.7, 1.4 Hz, 1H), 7.32 (dd, *J* = 8.2, 1.4 Hz, 1H), 1.92 (s, 2H), 1.43 (s, 12H), 1.33-1.29 (m, 3H), 1.14 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.9, 150.4, 144.2 (d, $J_{C\text{-}F}$ = 11.5 Hz), 127.7, 125.3, 71.2, 48.9, 31.7, 17.8, 12.7. **^{19}F**

NMR (377 MHz, $CDCl_3$) δ -131.28. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BClFO_3Si^+$, m/z: 442.2278, found: 442.2274.

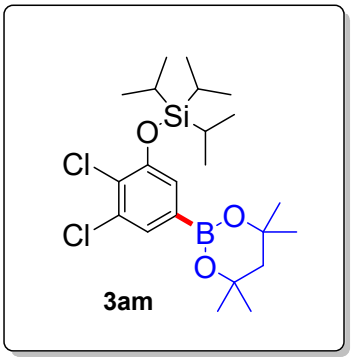
(3-bromo-2-fluoro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triiso-propylsilane (3al)



3al

According to the general procedure, **3bj** was obtained in 99% yield (96.5 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (dd, *J* = 6.3, 1.4 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.4 Hz, 1H), 1.90 (s, 2H), 1.41 (s, 12H), 1.33-1.27 (m, 3H), 1.12 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.7, 151.3, 144.1 (d, $J_{C\text{-}F}$ = 12.3 Hz), 130.5, 126.1 (d, $J_{C\text{-}F}$ = 1.9 Hz), 109.2 (d, $J_{C\text{-}F}$ = 18.2 Hz), 71.2, 48.8, 31.7, 17.8, 12.7. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -122.80. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BBrFO_3Si^+$, m/z: 486.1772, found: 486.1771.

(2,3-dichloro-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)triisopropylsilane (3am)

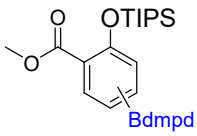


3am

According to the general procedure, **3bh** was obtained in 92% yield (84.5 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 0.8 Hz, 1H), 7.28 (s, 1H), 1.90 (s, 2H), 1.40 (s, 12H), 1.34-1.28 (m, 3H), 1.14 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.6, 132.9, 127.4, 126.0, 123.0, 71.2, 48.8, 31.7, 17.9, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{22}H_{37}BCl_2O_3Si^+$, m/z: 458.1982, found: 458.1974.

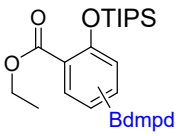
6. Application

a)The borylation of drug molecules:



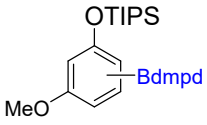
4, 72%, m/p>20:1

from Methyl Salicylate



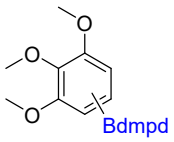
5, 89%, m/p>20:1

from Ethyl Salicylate



6, 99%, m/p>20:1

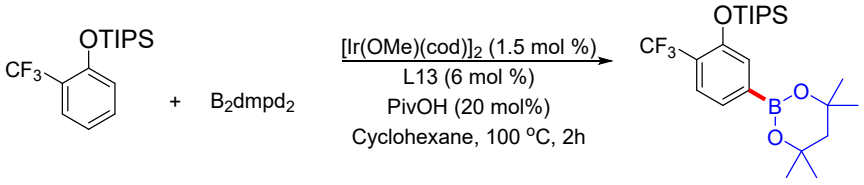
from Resorcinol



7,92%, m/p>20:1

from Pyrogallol

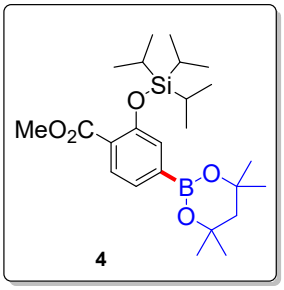
b) Gram scale reaction:



(**1ah**, 3.75 mmol) **2c** (2.5 mmol) **3ah**, 94%, 1.08g

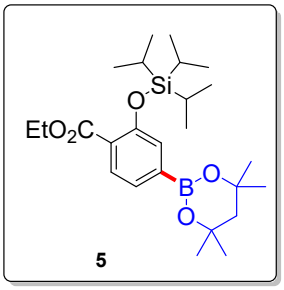
General Procedure for **4, 5, 6, 7** as above procedure **4**.

methyl 4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)benzoate (4)



According to the general procedure **3** , **3aa** was obtained in 72% yield (64.6 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 7.3 Hz, 2H), 3.85 (s, 3H), 1.90 (s, 2H), 1.41 (s, 12H), 1.34 -1.28 (m, 3H), 1.13 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.0, 154.7, 130.5, 125.9, 125.5, 123.7, 77.5, 77.2, 76.8, 71.1, 51.8, 48.9, 31.9, 18.1, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{24}H_{41}BO_5Si^+$, m/z: 448.2816, found: 448.2811.

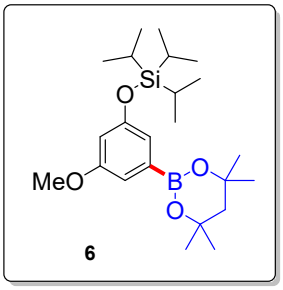
ethyl 4-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-2-((triisopropylsilyl)oxy)benzoate (5)



According to the general procedure **3** , **5** was obtained in 89% yield (82.3 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, J =

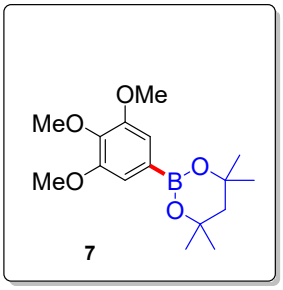
7.8 Hz, 1H)*, 7.67 (d, J = 7.6 Hz, 1H), 7.47 (s, 1H)*, 7.39 (dd, J = 9.1, 1.4 Hz, 2H), 7.33 (d, J = 7.0 Hz, 1H)*, 4.43 (q, J = 7.1 Hz, 1H)*, 4.36 (q, J = 7.1 Hz, 2H), 1.93 (s, 2H), 1.91 (s, 1H)*, 1.43 (s, 12H), 1.41-1.31 (m, 6H), 1.16 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.4, 154.5, 130.2, 125.8, 125.4, 124.3, 71.1, 60.7, 48.9, 31.9, 18.1, 14.5, 13.0. **HRMS (EI)** calcd for $[M]^+$ $C_{25}H_{43}BO_5Si^+$, m/z: 462.2973, found: 462.2964.

triisopropyl(3-methoxy-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)silane (6)



According to the general procedure **4** , **6** was obtained in 99% yield (83.3 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.99 (d, J = 2.2 Hz, 1H), 6.98 (d, J = 2.3 Hz, 1H), 6.51 (t, J = 2.3 Hz, 1H), 3.81 (s, 3H), 1.90 (s, 2H), 1.42 (s, 12H), 1.31-1.27 (m, 3H), 1.13 (d, J = 7.3 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.2, 156.6, 118.0, 110.9, 108.4, 70.9, 55.4, 49.0, 31.9, 18.1, 12.8. **HRMS (EI)** calcd for $[M]^+$ $C_{23}H_{41}BO_4Si^+$, m/z: 420.2867, found: 420.2860.

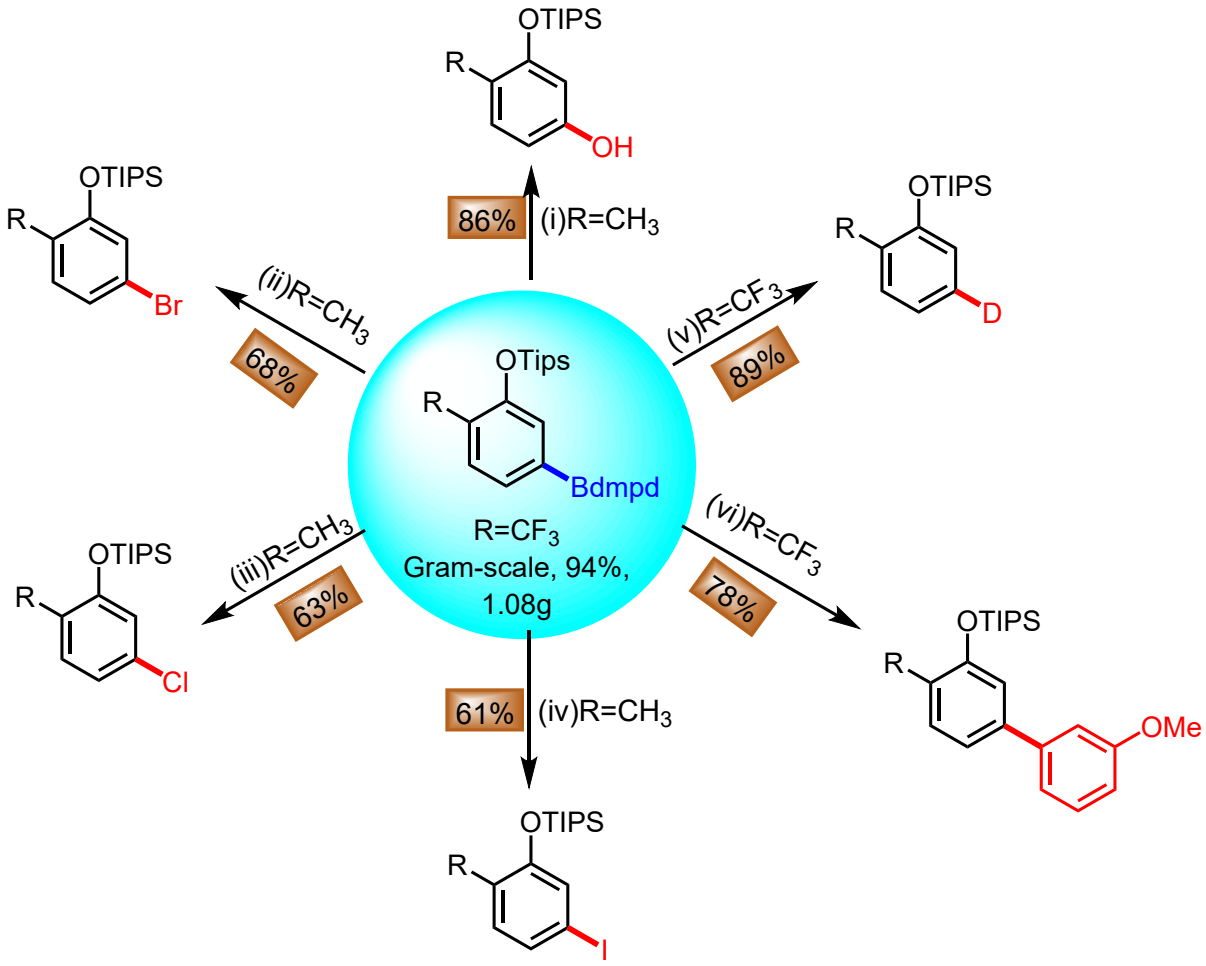
triisopropyl(3-methoxy-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)phenoxy)silane (7)



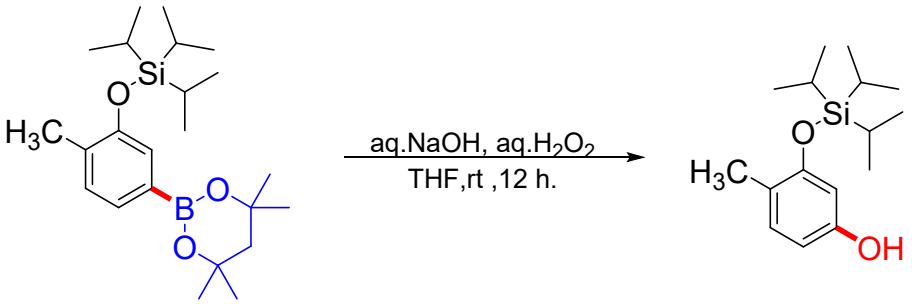
According to the general procedure **4** , **6** was obtained in 99% yield (83.3 mg). Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (s, 2H), 3.91 (s, 6H), 3.86 (s, 3H), 1.90 (s, 2H), 1.42 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.8, 140.3, 110.5, 71.03, 60.8, 56.2, 49.1, 31.9. **HRMS (EI)** calcd for $[M]^+$ $C_{16}H_{25}BO_5^+$, m/z: 308.1795, found: 308.1792.

Gram-scale synthesis of 3ah: To a 25 mL round bottom flask was sequentially added L13 (6 mol%, 31.3 mg), $[Ir(OMe)(cod)]_2$ (1.5 mol%, 25.0 mg), PivOH(20 mol%, 51.3 mg), **1ah** (3.75 mmol, 1.5 equiv), Bis(2,4-dimethylpentane-2,4-glycolato)diboron **2c** (2.5 mmol, 715 mg, 1.0 equiv) and Cyclohexane (8 ml) . The reaction mixture was stirred at 100 °C for 4 hours. After the reaction mixture cooled down, ethyl acetate was added to dilute the reaction mixture. Then

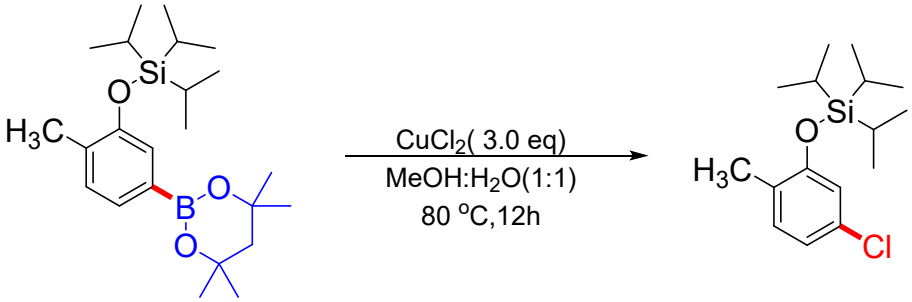
the reaction mixture was filtered through a plug of celite. The solution was concentrated by rotary evaporation under reduced pressure. After this, the mixture was purified by column chromatography (pe.ether/EtOAc = 50 : 1) to afford the product **3ah** (1.08g, 94%).



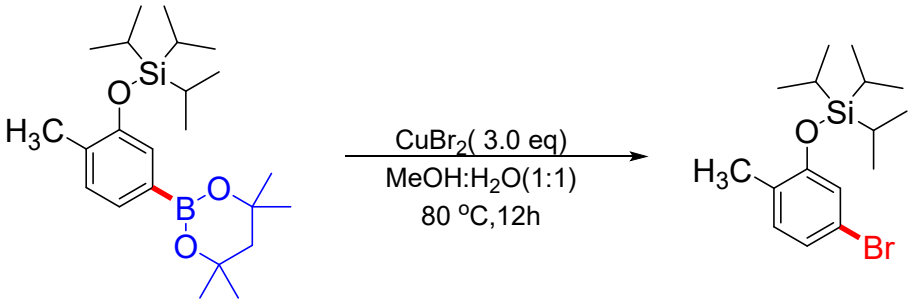
7. Useful Synthetic Transformations



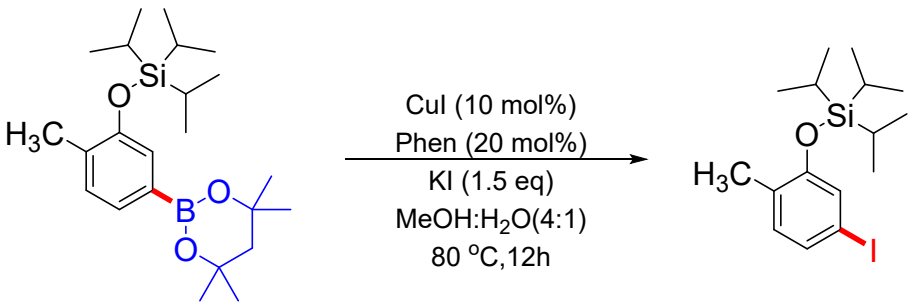
To a stirred solution of **3ab** (0.2 mmol, 1.0 eq) in THF (2 mL), NaOH (aq., 2M, 2ml) and H_2O_2(30 wt%, 2ml) was added. After this, the mixture was stirred for 12 h at room temperature. Monitor the progress of the reaction by TLC. When the reaction is complete, dilute the reaction mixture with water, extract the reaction mixture with EtOAc(3×5ml). The combine organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification with silica gel (pe.ether/EtOAc = 3:1) gave 48.2 mg (86%) of the product **8a** as colorless oil.



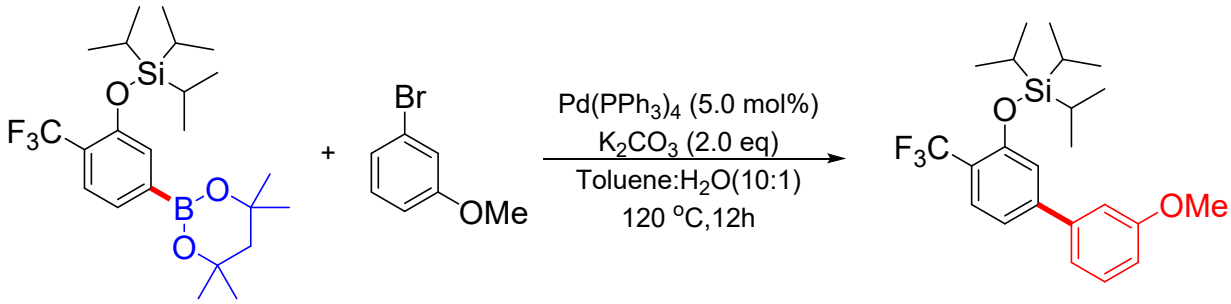
In a 10.0 mL reaction tube was charged with **3ab** (0.2 mmol, 1.0 eq), $CuCl_2$ (80.7 mg, 3.0 equiv.), MeOH (2.0 mL) and H_2O (2.0 mL). The reaction vial was capped with a teflon pressure cap and the reaction mixture was stirred at 80 °C for 12 h. After 12 h, the reaction mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (5 mL×3). The combine organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of crude mass with silica gel (pe.ether/EtOAc = 100:1) gave 40.7 mg (68%) of the product (**8b**) as colourless liquid.



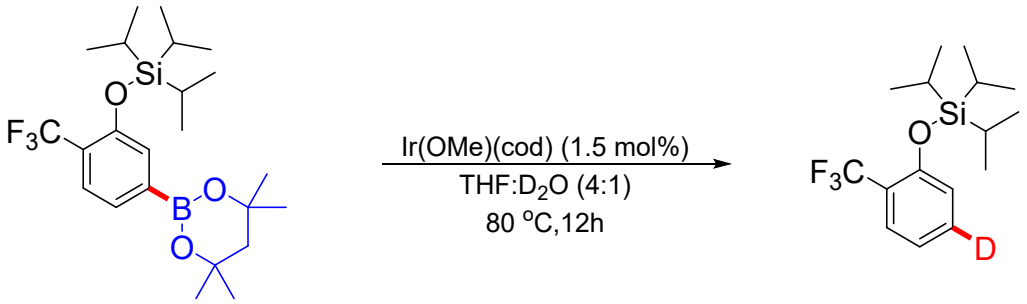
In a 10.0 mL reaction tube was charged with **3ab** (0.2 mmol, 1.0 eq), $CuBr_2$ (134.0 mg, 3.0 equiv.), MeOH (2.0 mL) and H_2O (2.0 mL). The reaction vial was capped with a teflon pressure cap and the reaction mixture was stirred at 80 °C for 12 h. After 12 h, the reaction mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (5 mL×3). The combine organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification of crude mass with silica gel (pe.ether/EtOAc = 100:1) gave 43.3 mg (63%) of the product (**8c**) as colourless liquid.



In a 15 mL pressure tube, CuI (3.80 mg, 10 mol%), phen (7.2 mg, 20.0 mol%) , KI (49.8 mg, 1.5 eq), **3ab** (0.2 mmol, 1.0 eq) were dissolved in MeOH:H_2O (2 mL:0.5 mL) under air. The reaction mixture was then stirred at 80 °C for 12 h. The reaction mixture was then cooled to room temperature and all solvent evaporated. Next it was extracted with EtOAc (10 ml×3). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (pe.ether/EtOAc = 100:1) to give **8d** (47.6 mg, 61%) as colourless liquid.

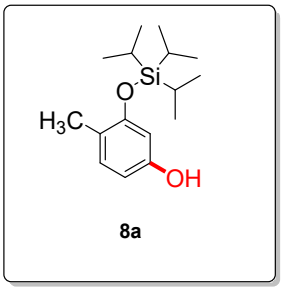


To a degassed 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer under an argon atmosphere were added **3ah** (0.2 mmol, 1.0 eq), $Pd(PPh_3)_4$ (11.6 mg, 5 mol%), K_2CO_3 (55.2 mg, 2.0 equiv.) and 3-Bromoanisole (44.9 mg, 1.2 eq). The system was degassed well and the toluene:H_2O (10:1, 2.75ml)was added into the flask. Then the reaction mixture heated at 120 °C. After 12 h, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3×10 mL) and dried over Na_2SO_4. Solvent evaporated under reduced pressure and chromatographic separation with silica gel (pe.ether/EtOAc = 20:1) gave 66.2 mg of **8e** (78%) as colourless liquid.



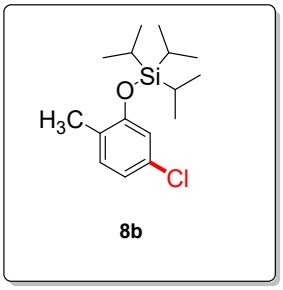
In an argon filled glove box, a 5.0 mL reaction tube was charged with $[Ir(OMe)(cod)]_2$ (2.0 mg, 1.5 mol%), **3ah** (0.2mmol, 1.0 eq) and dry THF (2.0 mL). The reaction vial was sealed and brought out of the glove box and charged with D_2O (0.5 mL). The reaction vial was resealed and heated at 80 °C for 12 h. The reaction mixture was then cooled to room temperature and extracted with Et_2O (20 mL x 3). The combine organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Chromatographic purification with silica gel (pe.ether/EtOAc = 100:1) gave 56.9 mg (89%) of

the product **8f** as colourless liquid.



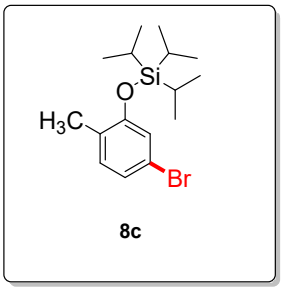
8a

Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.95 (d, J = 8.0 Hz, 1H), 6.41-6.24 (m, 2H), 5.10 (s, 1H), 2.16 (s, 3H), 1.34-1.24 (m, 3H), 1.12 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.3, 154.4, 131.2, 121.1, 107.6, 106.1, 18.3, 16.5, 13.2. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{16}H_{28}NaO_2Si^+$, m/z: 303.1751, found: 303.1745.



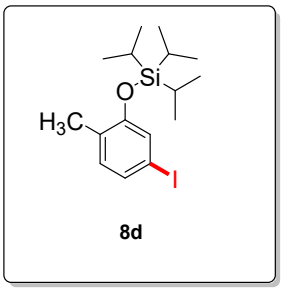
8b

Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (d, J = 8.0 Hz, 1H), 6.90-6.85 (m, 1H), 6.84 (s, 1H), 2.25 (s, 3H), 1.42-1.31 (m, 3H), 1.18 (d, J = 7.6 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 131.5, 131.5, 127.2, 120.9, 118.4, 18.1, 16.7, 13.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{16}H_{27}ClNaOSi^+$, m/z: 321.1412, found: 321.1409.



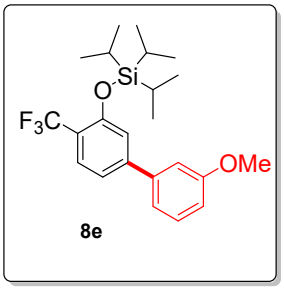
8c

Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.01 (d, J = 1.2 Hz, 2H), 6.98 (s, 1H), 2.23 (s, 3H), 1.39-1.31 (m, 3H), 1.17 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.2, 131.9, 127.7, 123.8, 121.2, 119.1, 18.1, 16.7, 13.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{16}H_{27}BrNaOSi^+$, m/z: 365.0907, found: 365.0898.



8d

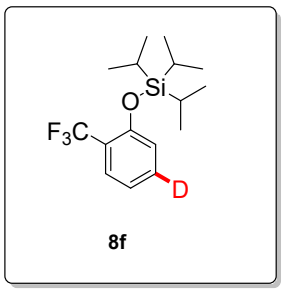
Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (dd, J = 7.9, 1.4 Hz, 1H), 7.10 (d, J = 1.4 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 2.18 (s, 3H), 1.31-1.25 (m, 3H), 1.11 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.3, 132.4, 129.9, 128.6, 127.1, 90.0, 18.1, 16.9, 13.1. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{16}H_{27}INaOSi^+$, m/z: 413.0768, found: 413.0763.



8e

Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, J = 8.1 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 10.7 Hz,

2H), 7.10-7.05 (m, 1H), 6.96 (dd, J = 8.2, 2.1 Hz, 1H), 3.88 (s, 3H), 1.44-1.33 (m, 3H), 1.17 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.2, 154.8, 146.1, 141.5, 130.2, 128.2(C-F, J_{C-F} = 270.6 Hz), 127.7 (q, J_{C-F} = 5.1 Hz), 125.5(C-F, J_{C-F} = 270.6 Hz), 122.8(C-F, J_{C-F} = 270.6 Hz), 120.0(C-F, J_{C-F} = 270.6 Hz), 119.7, 118.9, 118.1, 113.6, 113.1, 55.4, 18.0, 13.2. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -61.87. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{23}H_{31}F_3NaO_2Si^+$, m/z: 447.1938, found: 447.1931.



8f

Colorless Oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.91 (s, 1H), 1.39-1.30 (m, 3H), 1.13 (d, J = 7.4 Hz, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.6 (d, J = 1.7 Hz), 128.3 (C-F, J_{C-F} = 270.6 Hz), 126.1 (q, J_{C-F} = 5.0 Hz), 125.6 (C-F, J_{C-F} = 270.6 Hz), 125.2, 124.9, 122.9 (C-F, J_{C-F} = 270.6 Hz), 122.2, 121.9, 121.6, 121.3, 120.19 (C-F, J_{C-F} = 270.6 Hz), 71.3, 48.9, 31.9, 18.0, 13.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.21. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{16}H_{24}DF_3NaOSi^+$, m/z: 342.1582, found: 342.1580.

8. References

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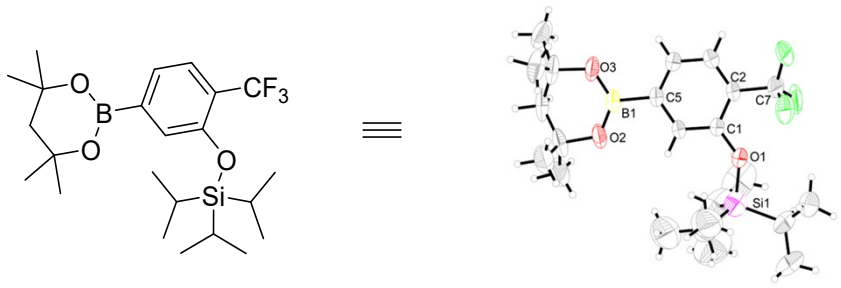
9. Crystal data and structure refinement for 3ah

t system (dichloromethane and hexane)，the solution was evaporated at room temperature for about one week, sing crystals were formed.



3ah CCDC 2205174

The thermal ellipsoid was drawn at the 50% probability level.

Bond precision: C-C = 0.0050 A Wavelength=0.71073

Cell: a=11.691(4) b=9.567(4) c=12.612(5)
alpha=90 beta=104.951(10) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1362.9(9)	1363.0(9)
Space group	P 21/m	P 1 21/m 1
Hall group	-P 2yb	-P 2yb
Moiety formula	C23 H38 B F3 O3 Si	0.5(C46 H76 B2 F6 O6 Si2)
Sum formula	C23 H38 B F3 O3 Si	C23 H38 B F3 O3 Si
Mr	458.43	458.43
Dx,g cm-3	1.117	1.117
Z	2	2
Mu (mm-1)	0.126	0.126
F000	492.0	492.0
F000'	492.43	
h,k,lmax	15,12,16	15,12,16
Nref	3354	3313
Tmin,Tmax	0.927,0.951	0.674,0.746
Tmin'	0.927	

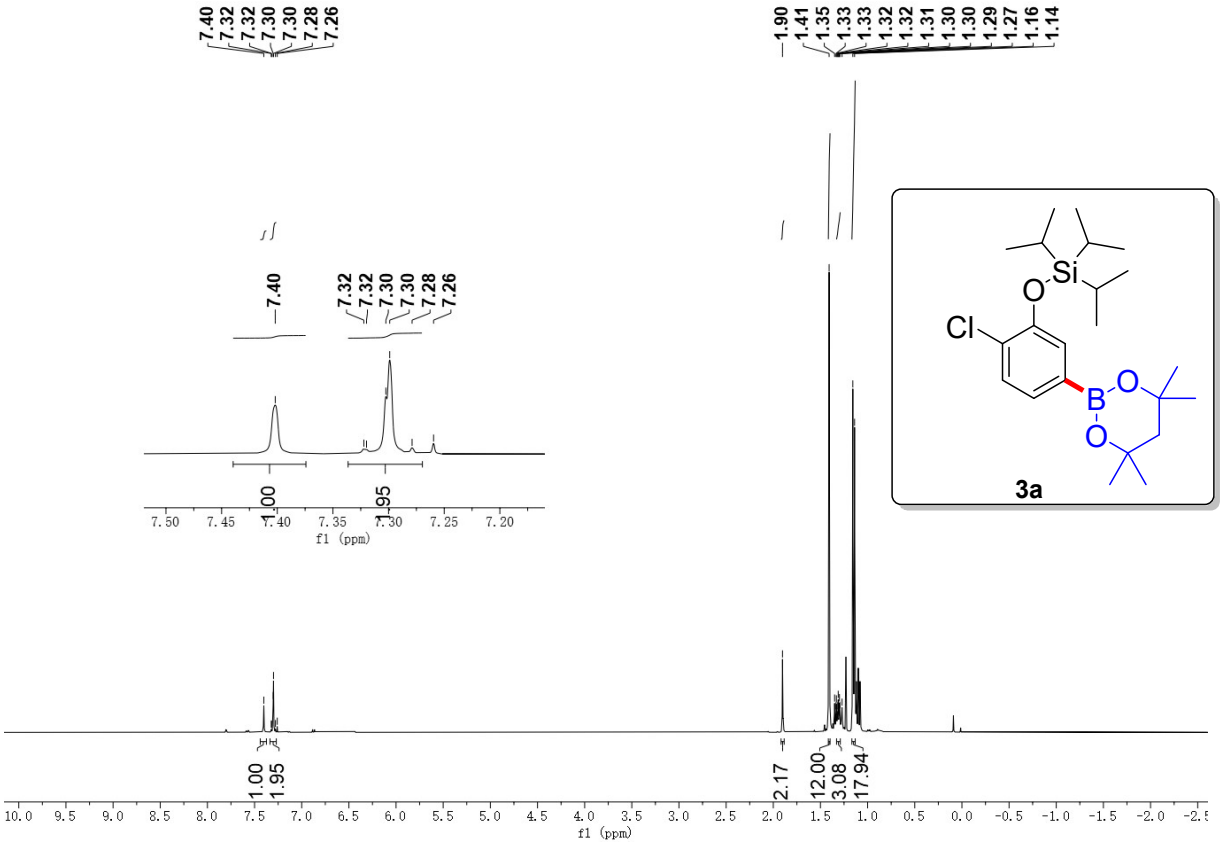
Correction method= # Reported T Limits: Tmin=0.674 Tmax=0.746
AbsCorr = MULTI-SCAN

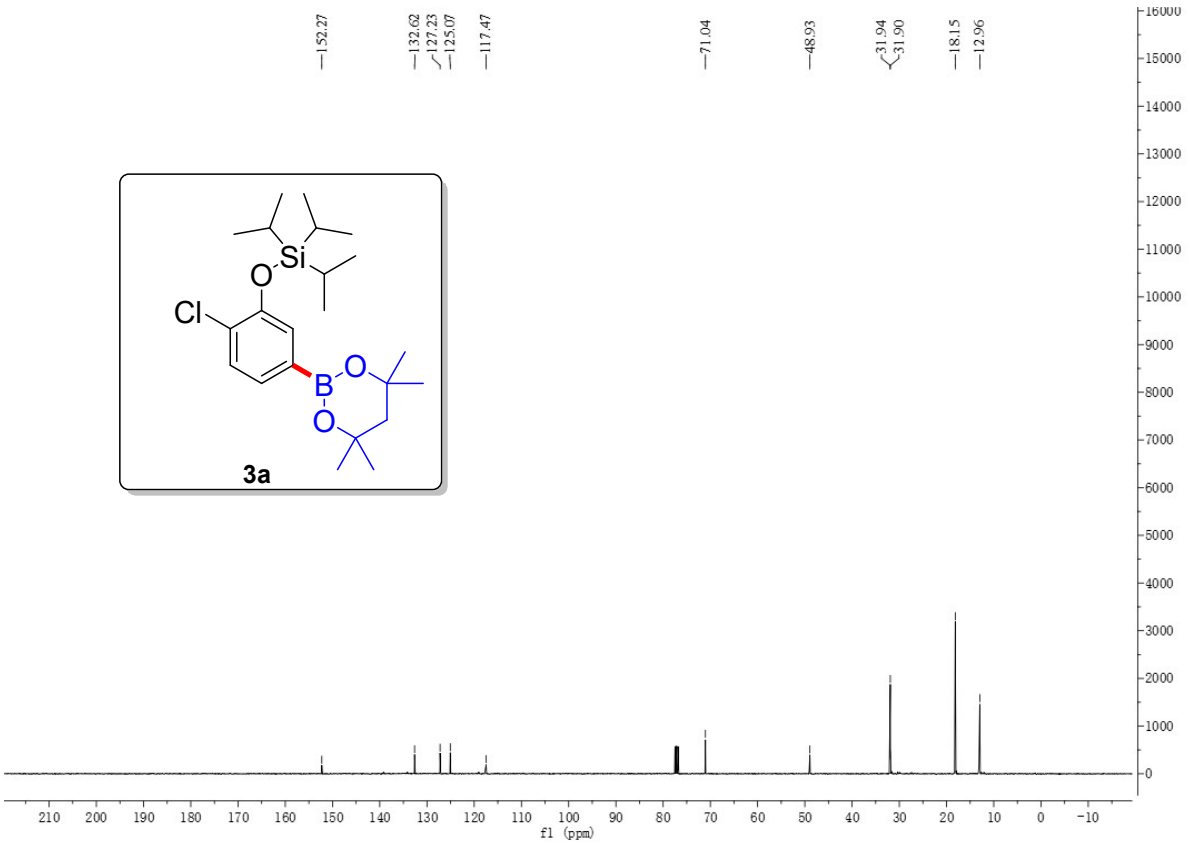
Data completeness= 0.988 Theta(max)= 27.594

R(reflections)= 0.0800(1674) wR2(reflections)= 0.2780(3313)

S = 1.026 Npar= 264

10. ^{1}H, ^{13}C and ^{19}F NMR spectra of new substrates and all product




152.27
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31.94
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Si
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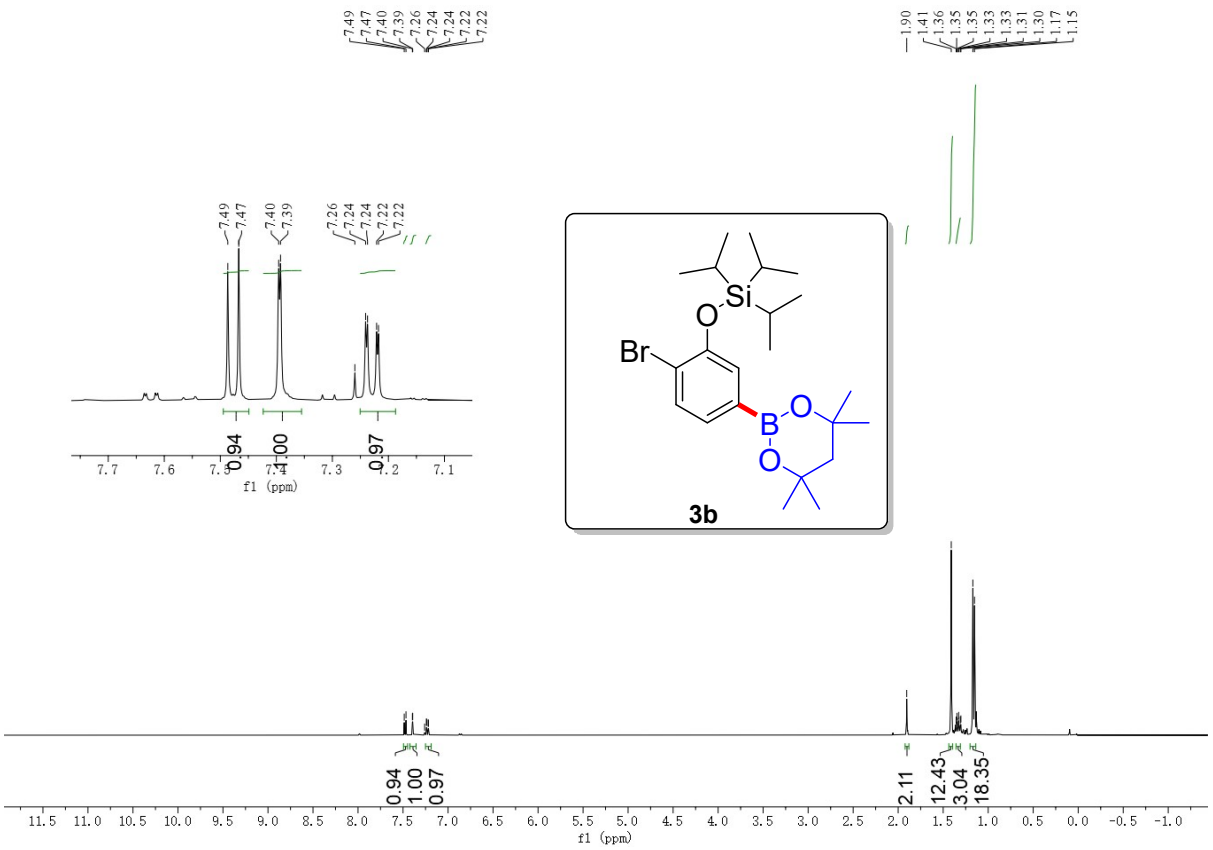
Cl
B
O
O
3a
f1 (ppm)


7.49
7.47
7.40
7.39
7.26
7.24
7.24
7.22
7.22
1.90
1.41
1.36
1.35
1.35
1.33
1.33
1.31
1.30
1.17
1.15
0.94
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2.11
12.43
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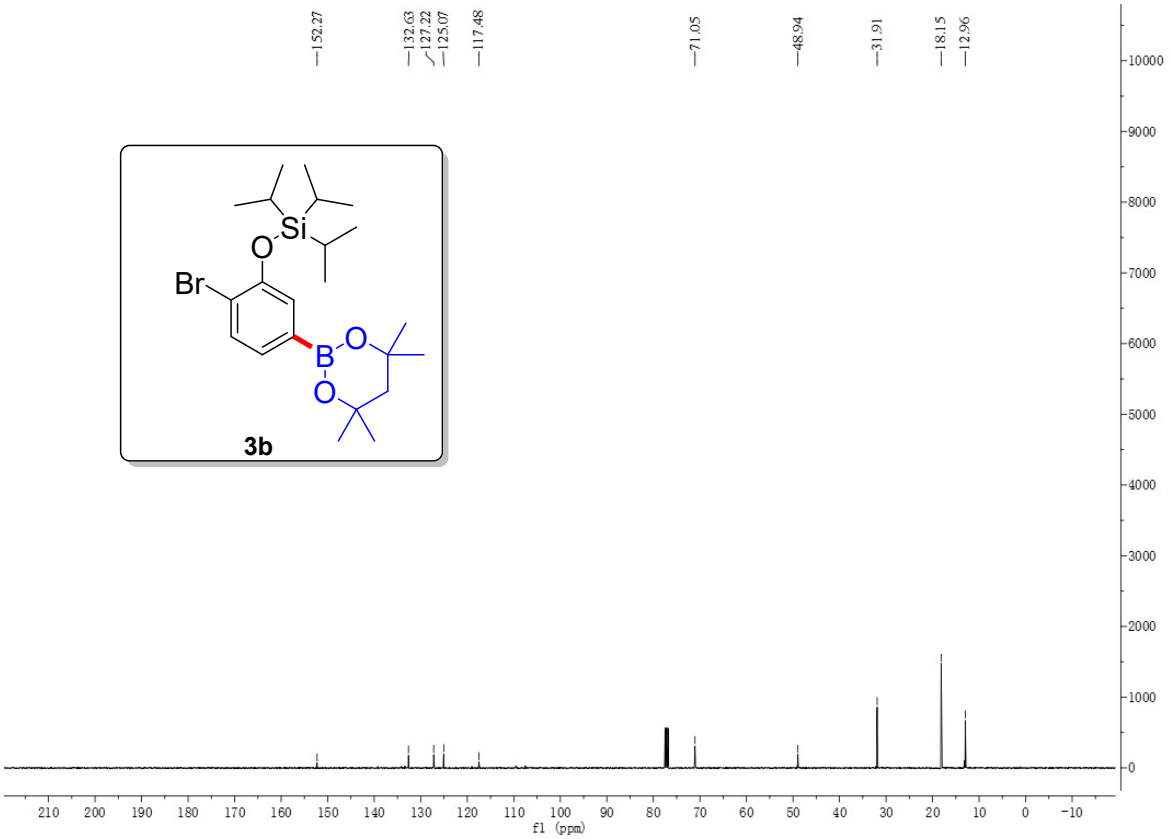
18.35
Si
O
Br
B
O
O
3b
f1 (ppm)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125.07
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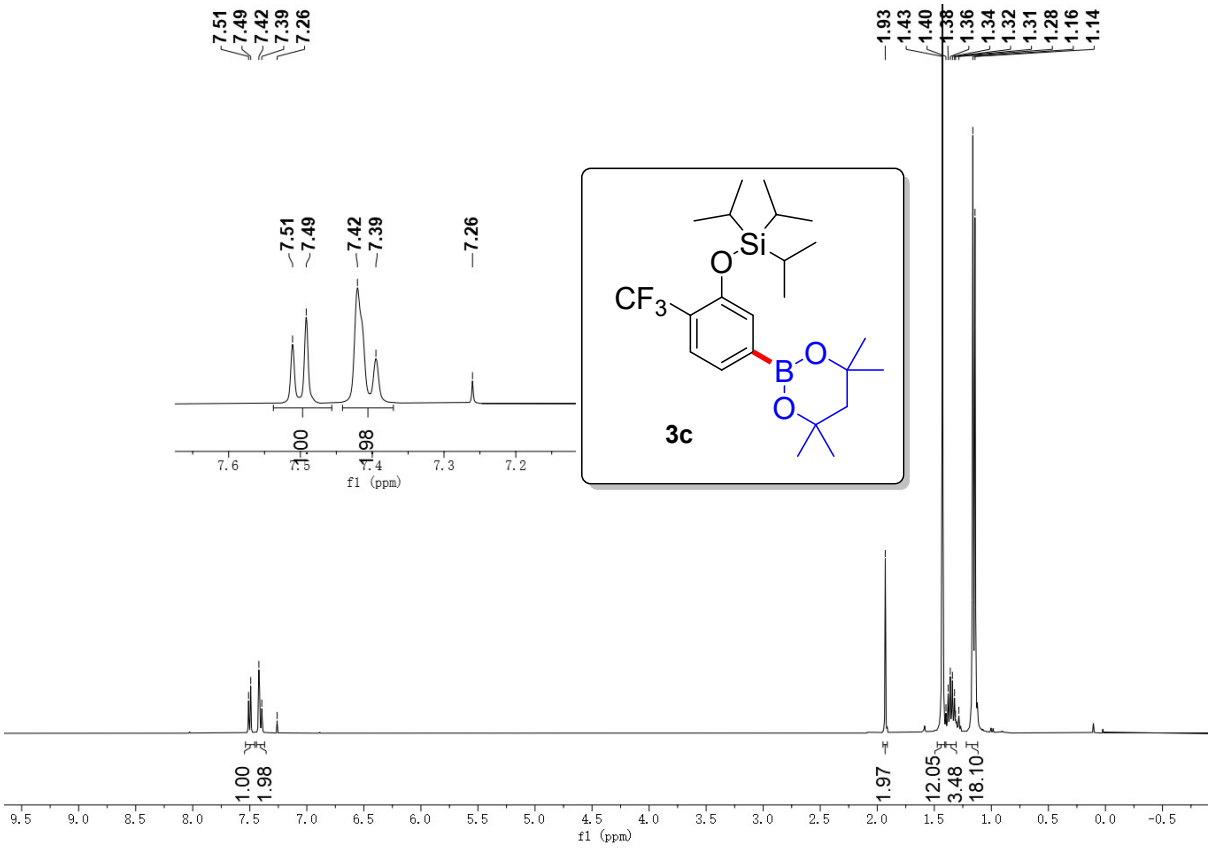
71.05
48.94
31.91
18.15
12.96
Si
O
Br
B
O
O
3b
f1 (ppm)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7.49
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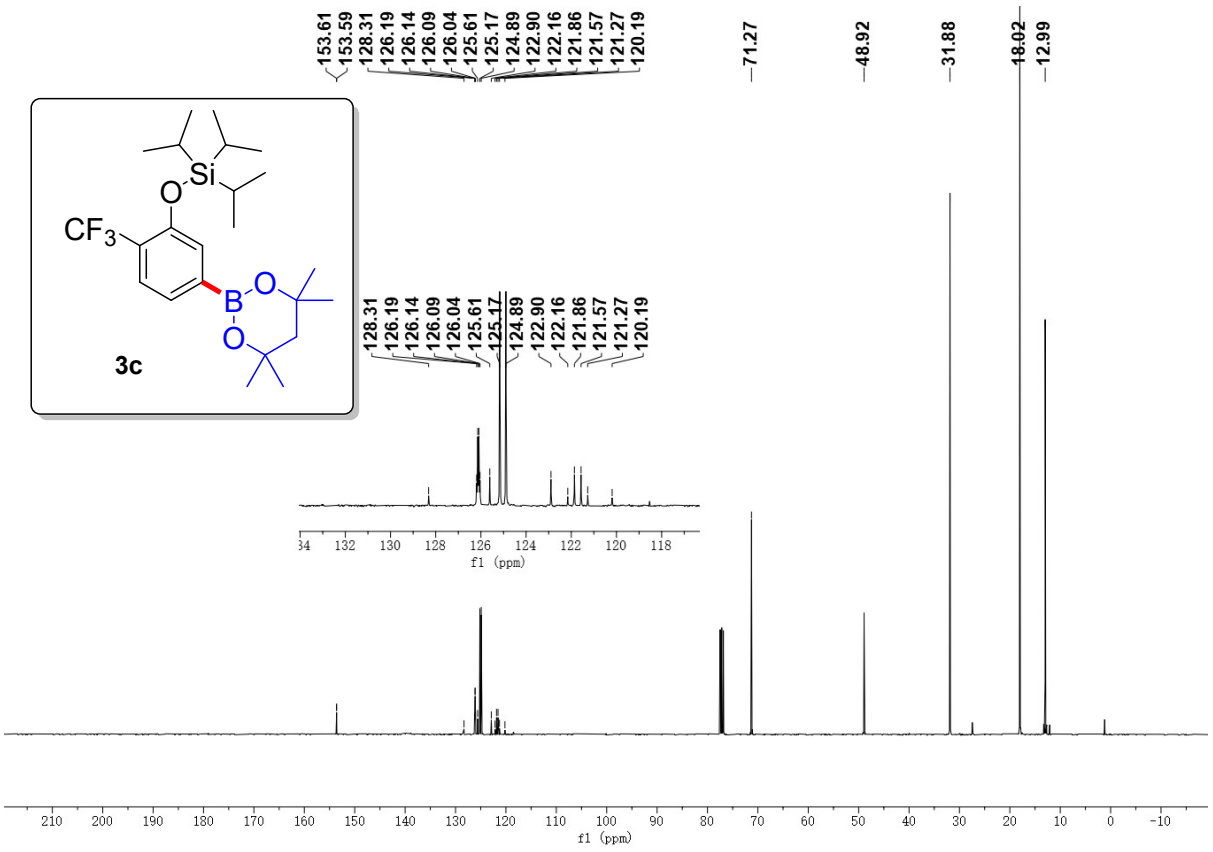
1.36
1.34
1.32
1.31
1.28
1.16
1.14
Si
O
CF3
B
O
O
3c
1.00
1.98
1.97
12.05
3.48
18.10
f1 (ppm)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126.04
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122.90
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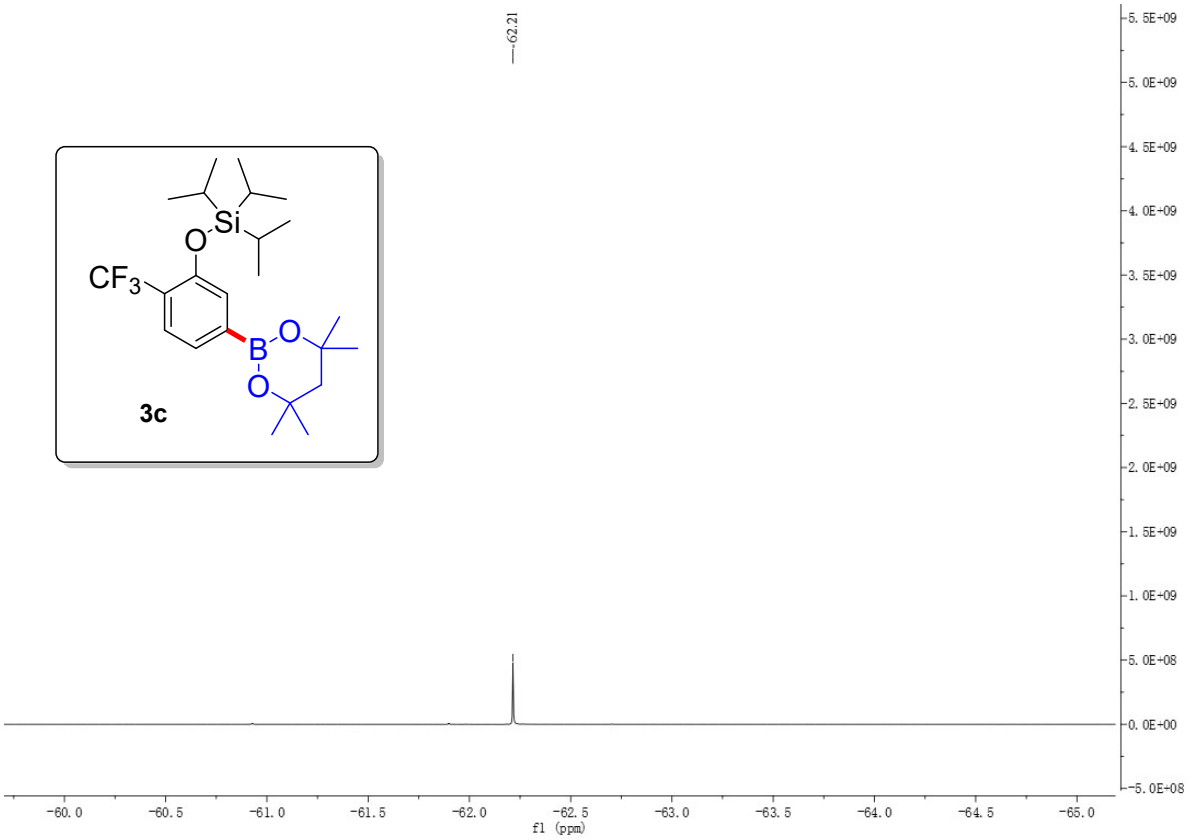
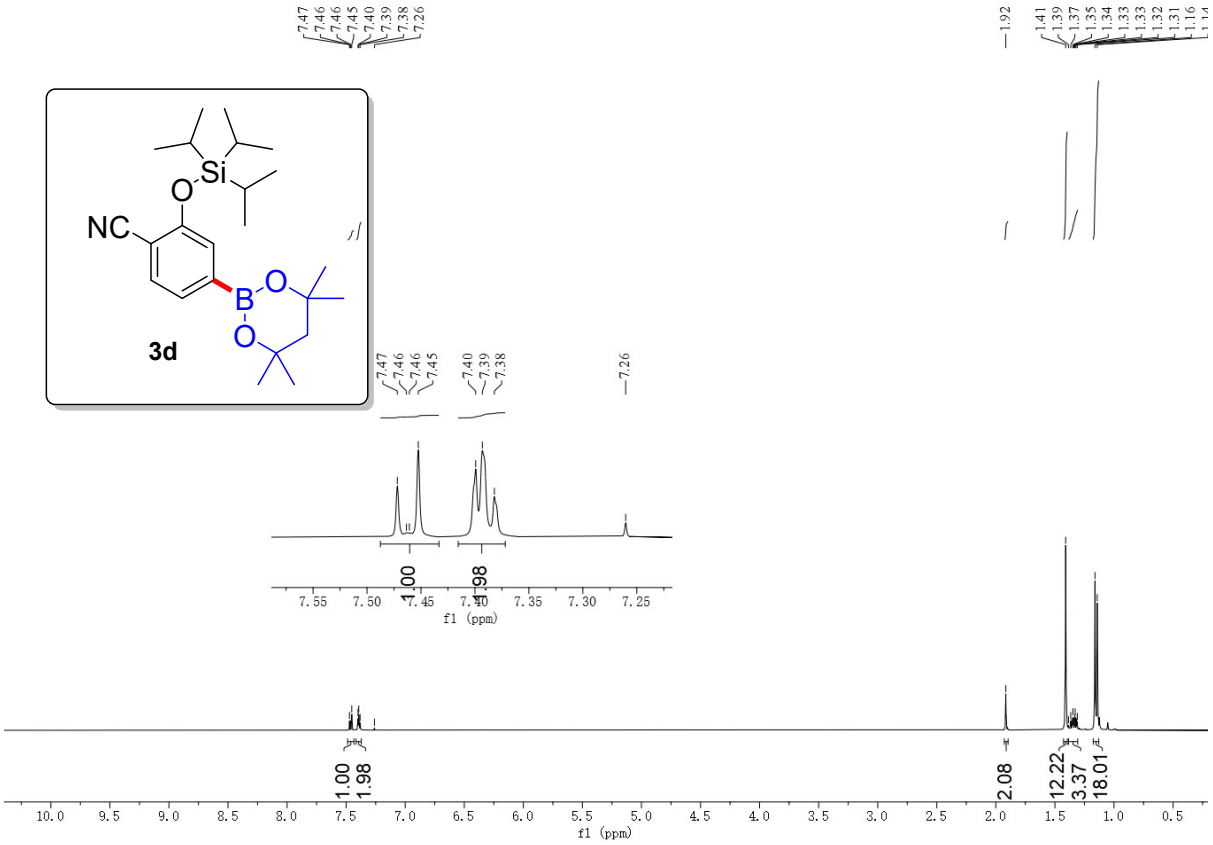
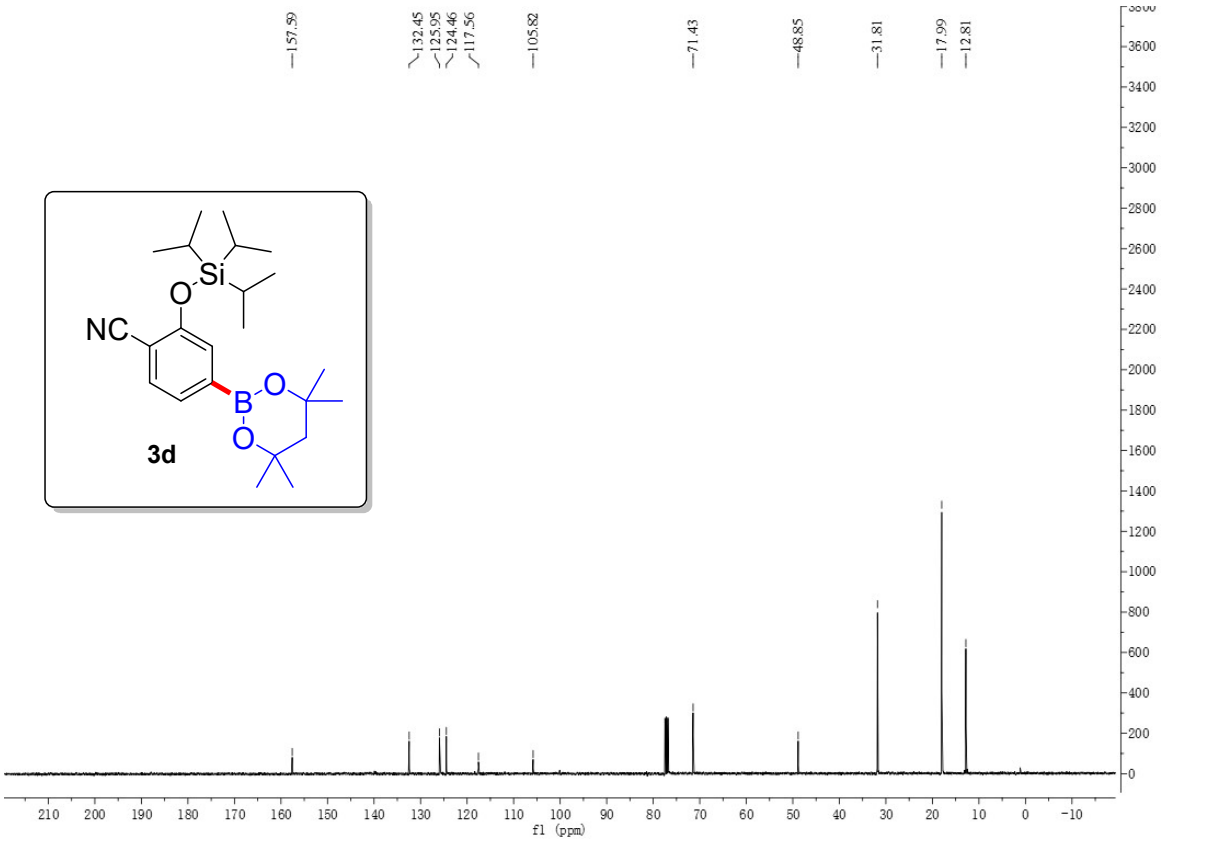
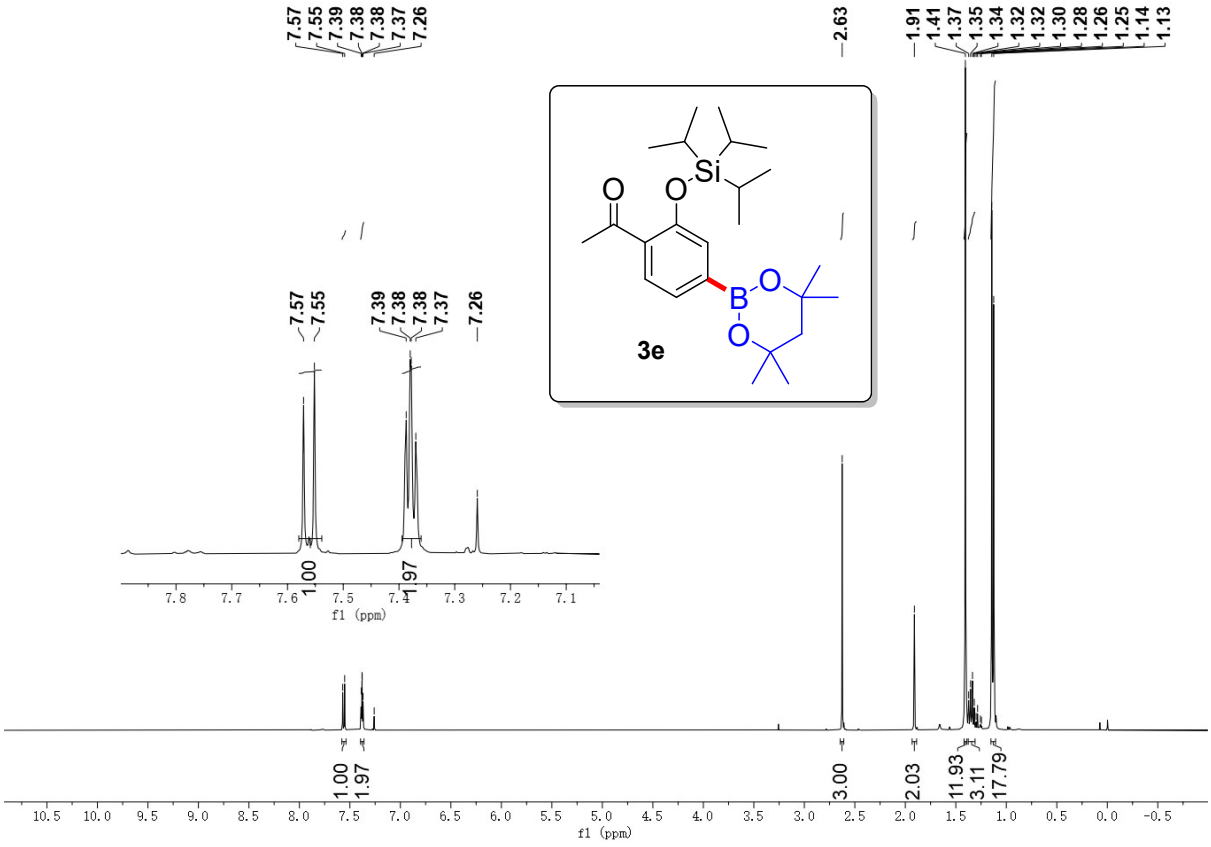
121.27
120.19
71.27
48.92
31.88
18.02
12.99
3c
f1 (ppm)


62.21
3c
f1 (ppm)


3d
NC
Si
O
B
O
O
f1 (ppm)


3d
NC
Si
O
B
O
O
f1 (ppm)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7.55
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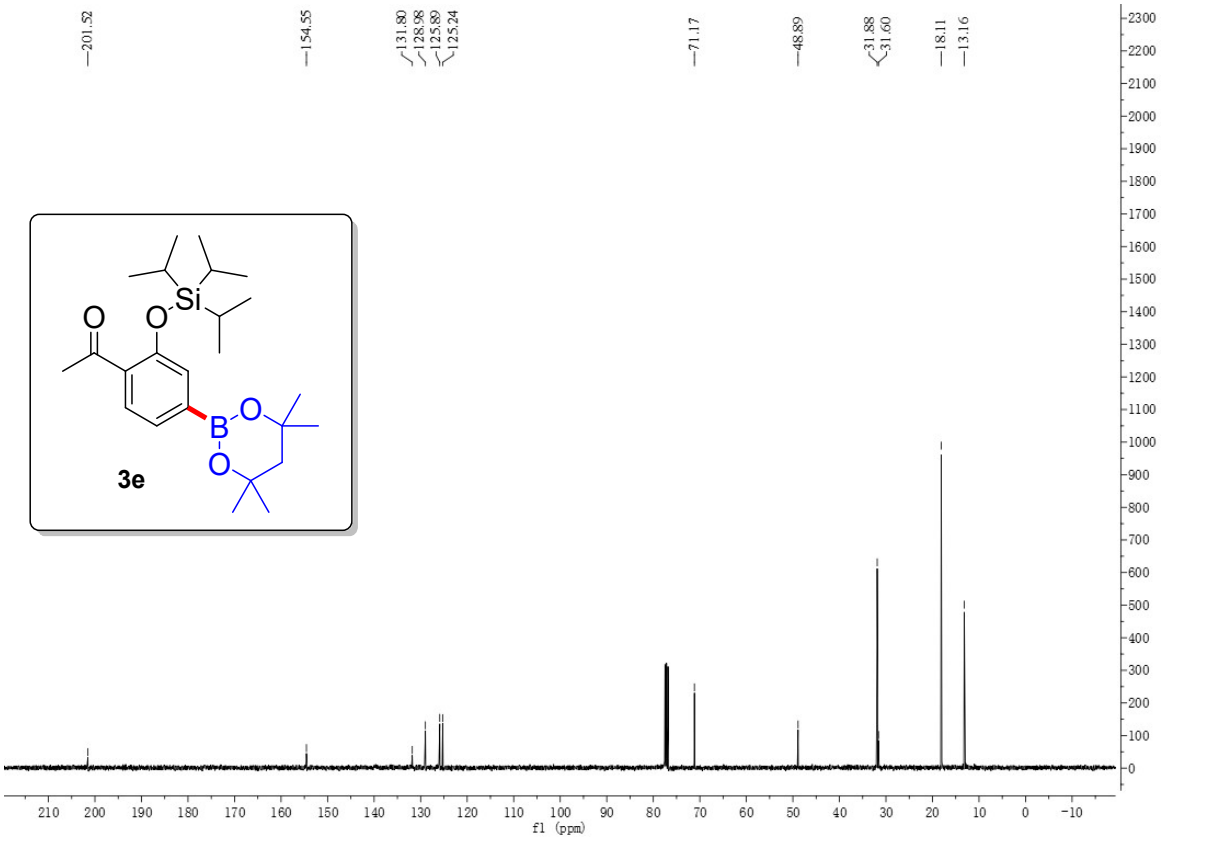
7.38
7.38
7.37
7.26
2.63
1.91
1.41
1.37
1.35
1.34
1.32
1.32
1.30
1.28
1.26
1.25
1.14
1.13
3e
1.00
1.97
3.00
2.03
11.93
3.11
17.79
f1 (ppm)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154.55
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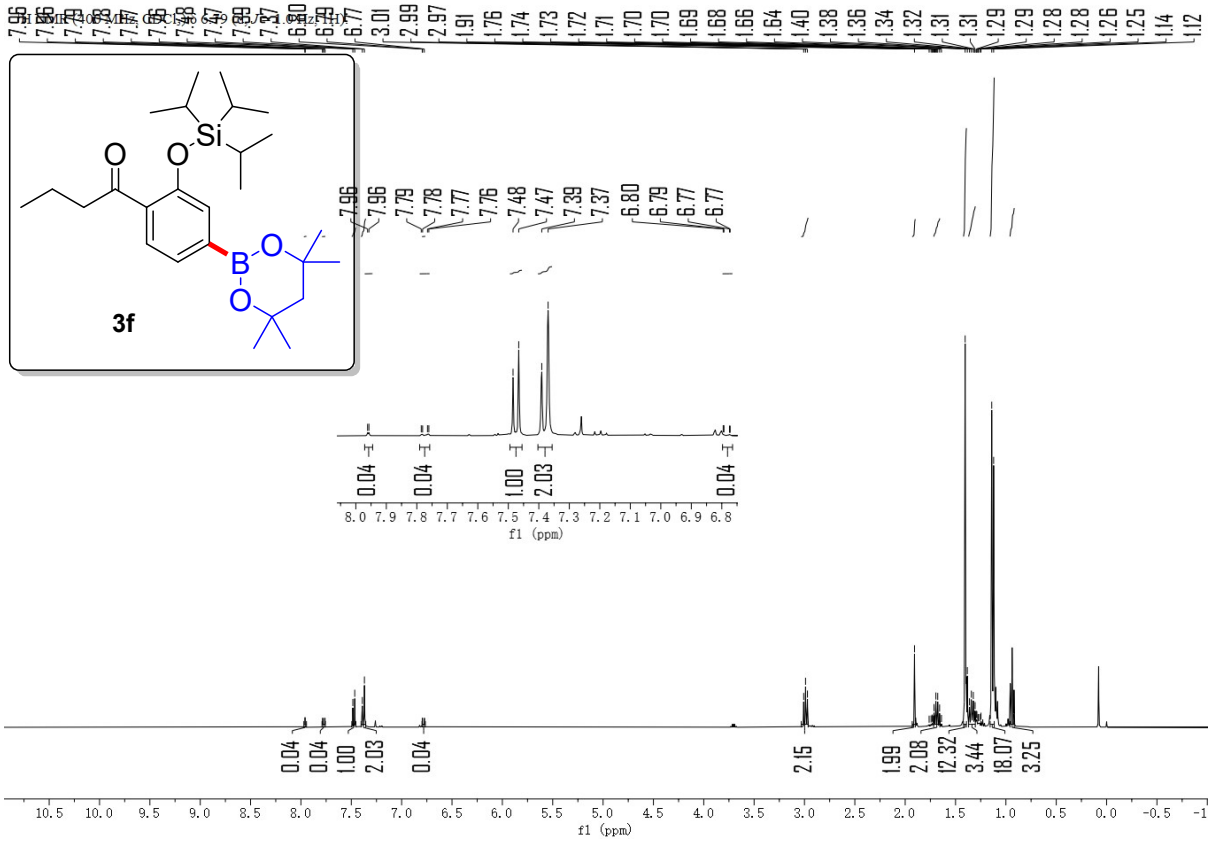
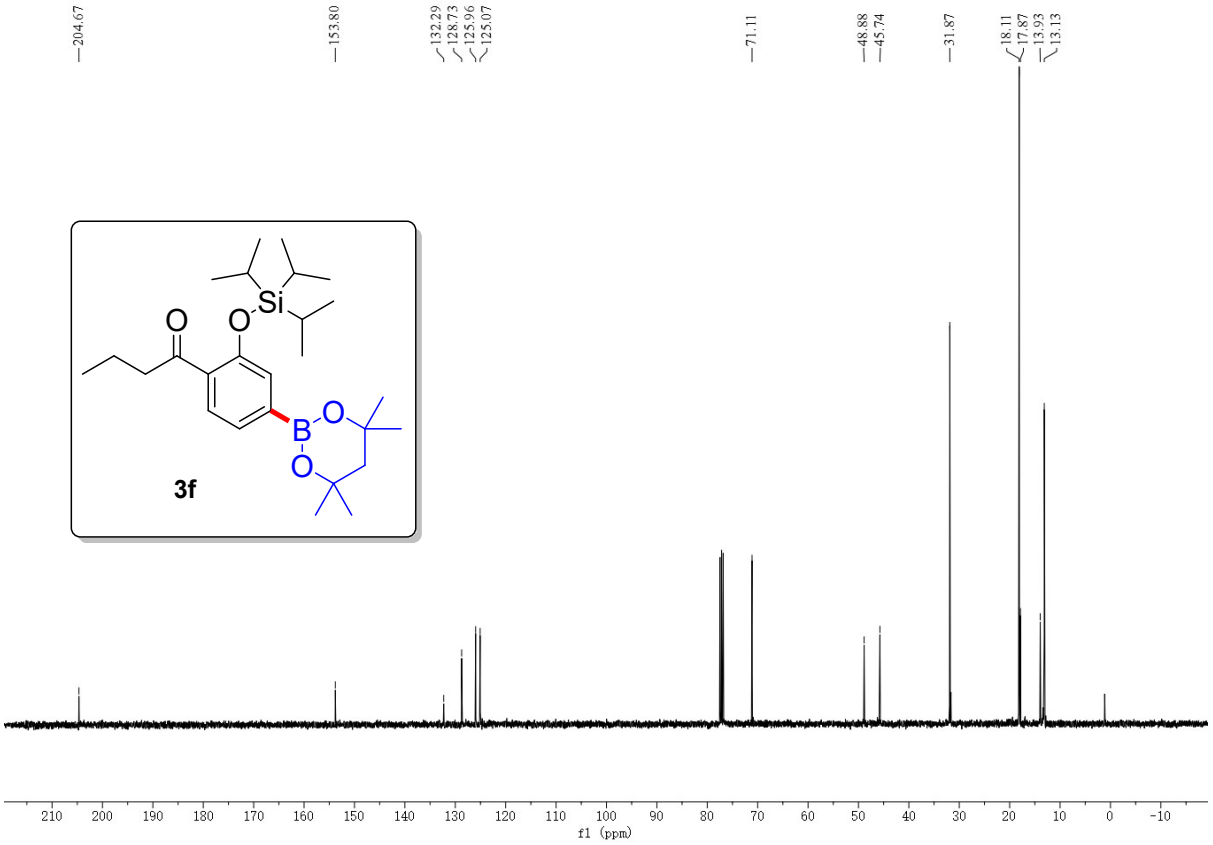
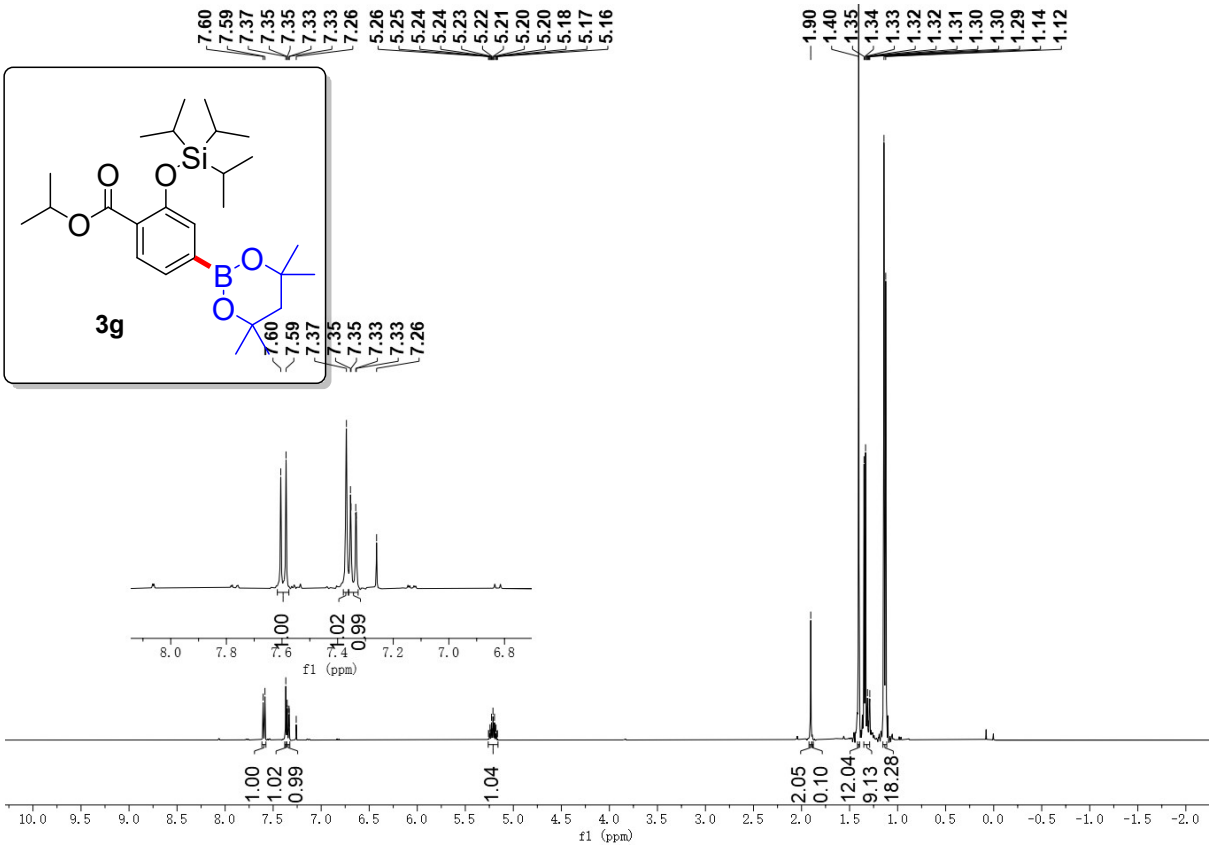
31.88
31.60
18.11
13.16
3e
f1 (ppm)


3f
f1 (ppm)


3f
f1 (ppm)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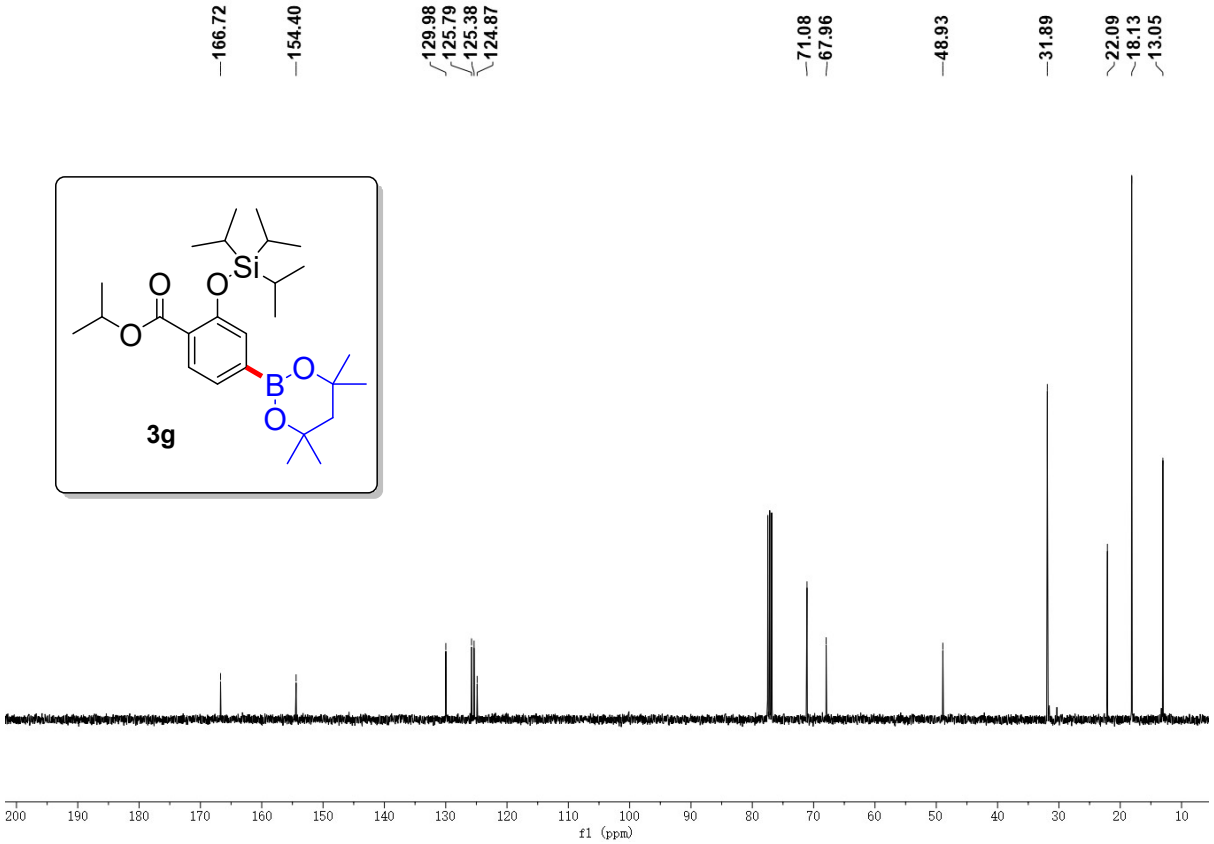
7.35
7.33
7.33
7.26
5.26
5.25
5.24
5.24
5.23
5.22
5.21
5.20
5.20
5.18
5.17
5.16
1.90
1.40
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.30
1.29
1.14
1.12
3g
1.00
1.02
0.99
1.04
2.05
0.10
12.04
9.13
18.28
f1 (ppm)


166.72
154.40
129.98
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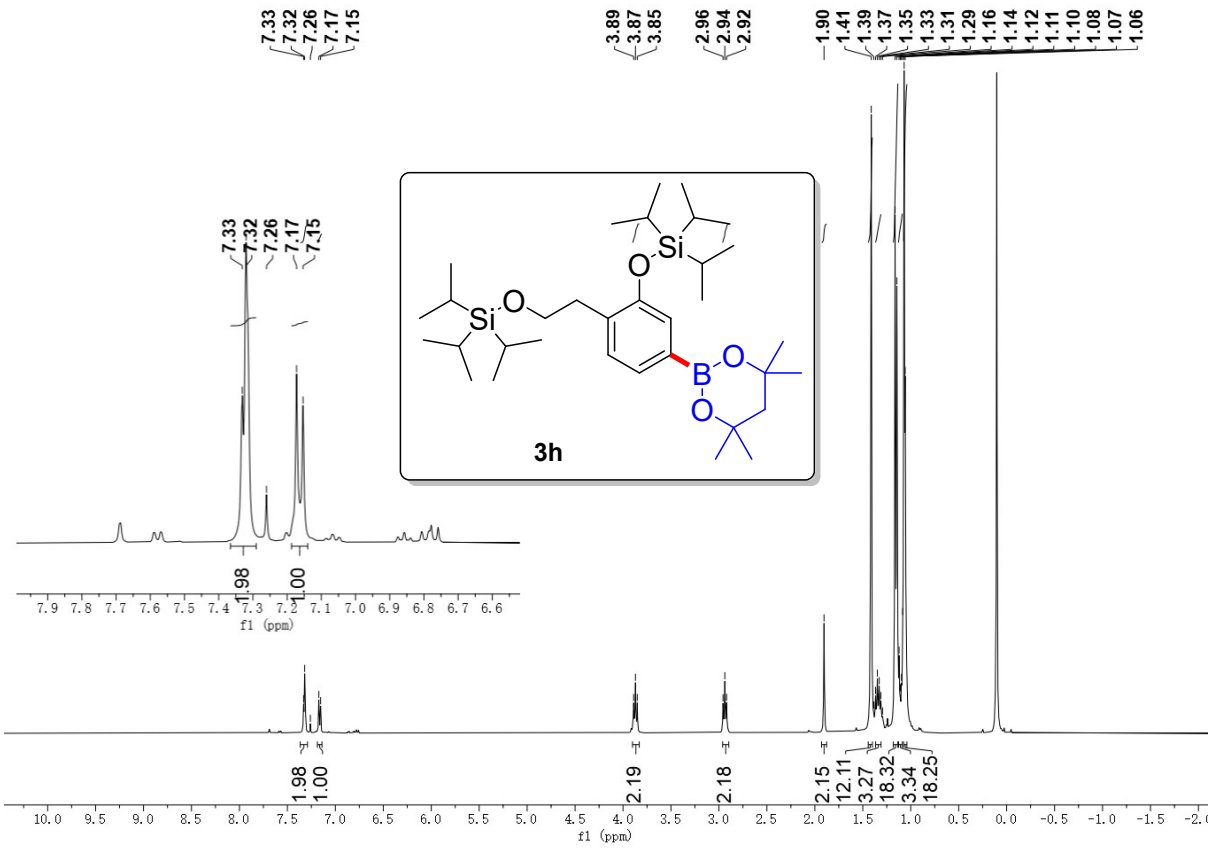
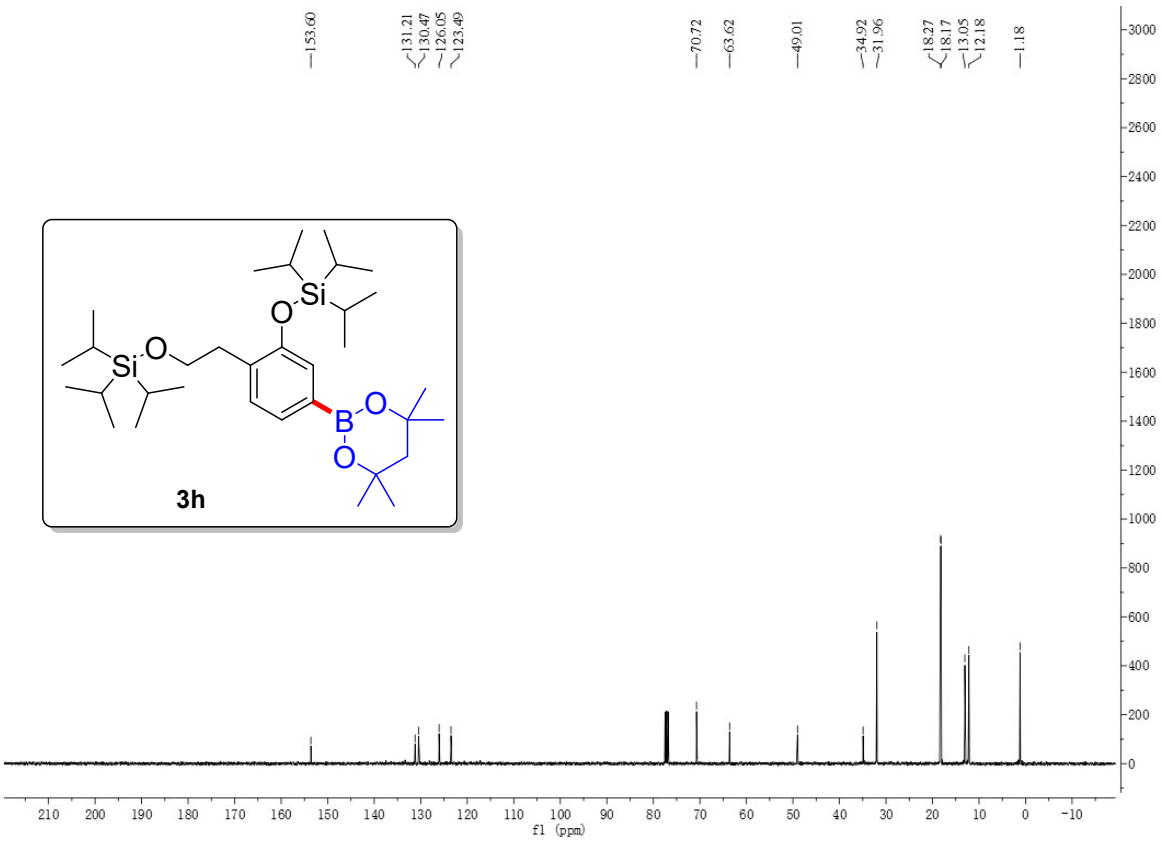
125.38
124.87
71.08
67.96
48.93
31.89
22.09
18.13
13.05
3g
f1 (ppm)


7.33
7.32
7.26
7.17
7.15
3.89
3.87
3.85
2.96
2.94
2.92
1.90
1.41
1.39
1.37
1.35
1.33
1.31
1.29
1.16
1.14
1.12
1.11
1.10
1.08
1.07
1.06
3h
1.98
1.00
2.19
2.18
2.15
12.11
3.27
18.32
3.34
18.25
f1 (ppm)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131.21
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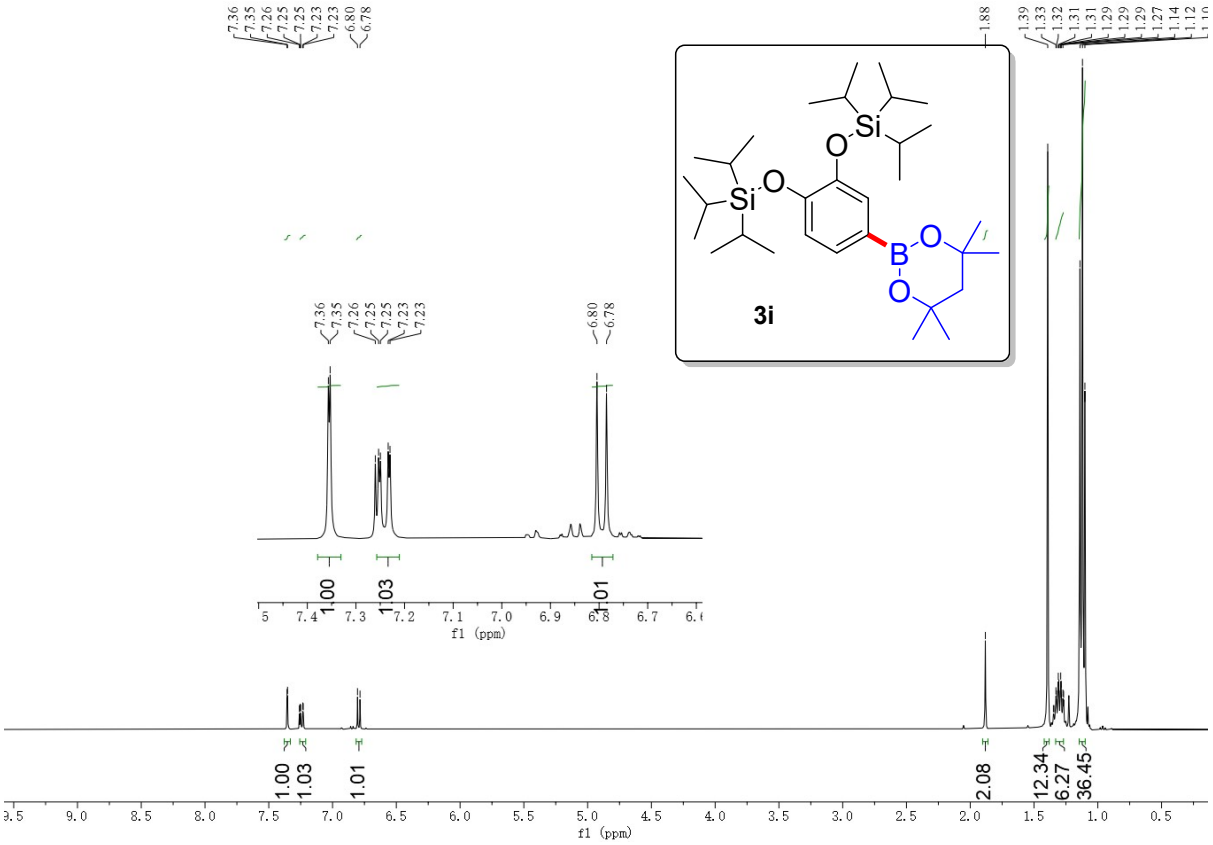
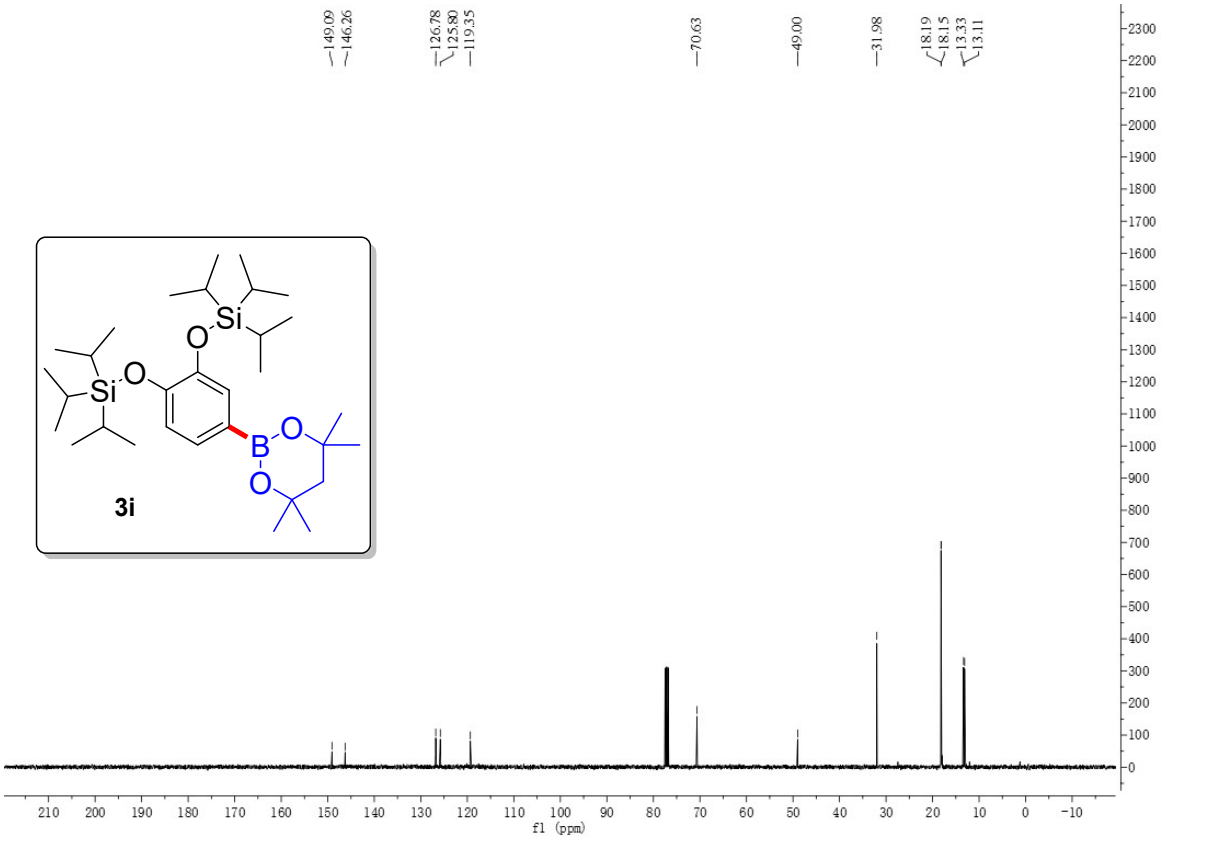
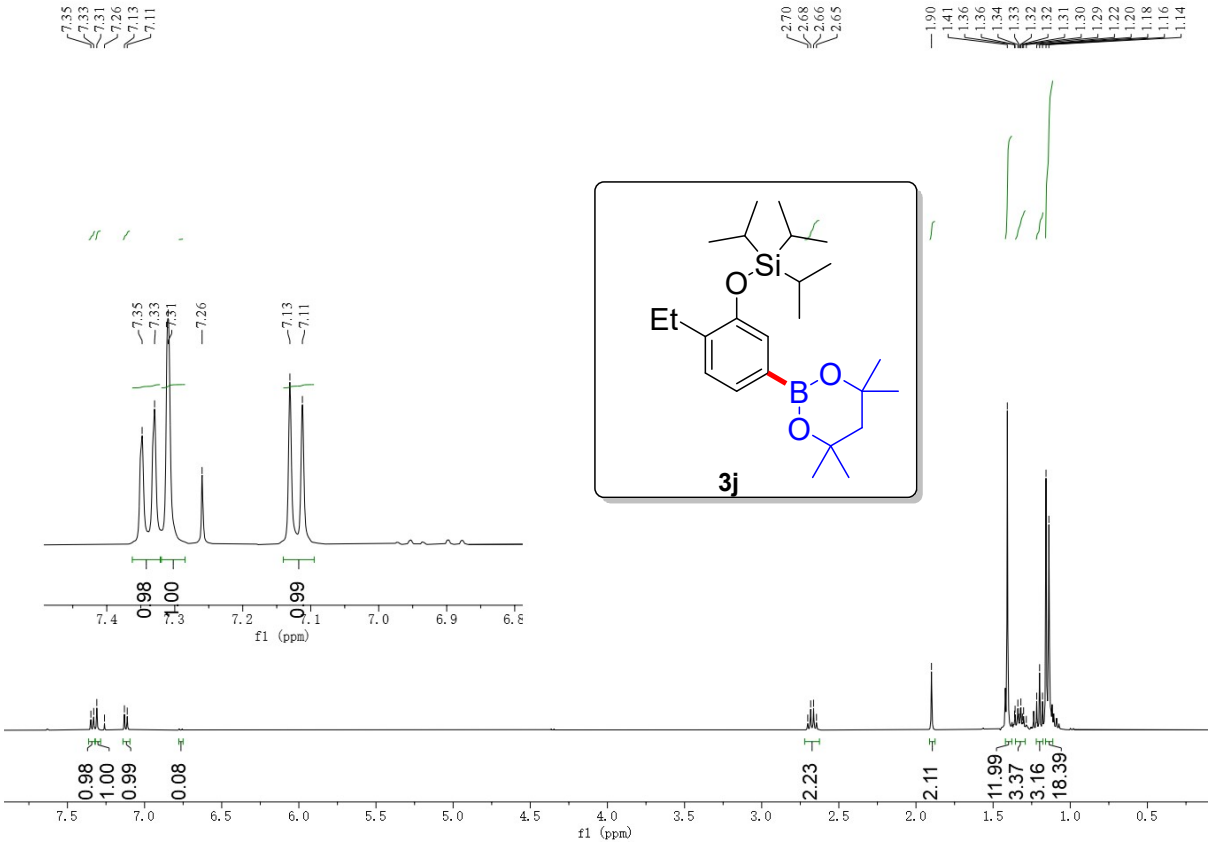
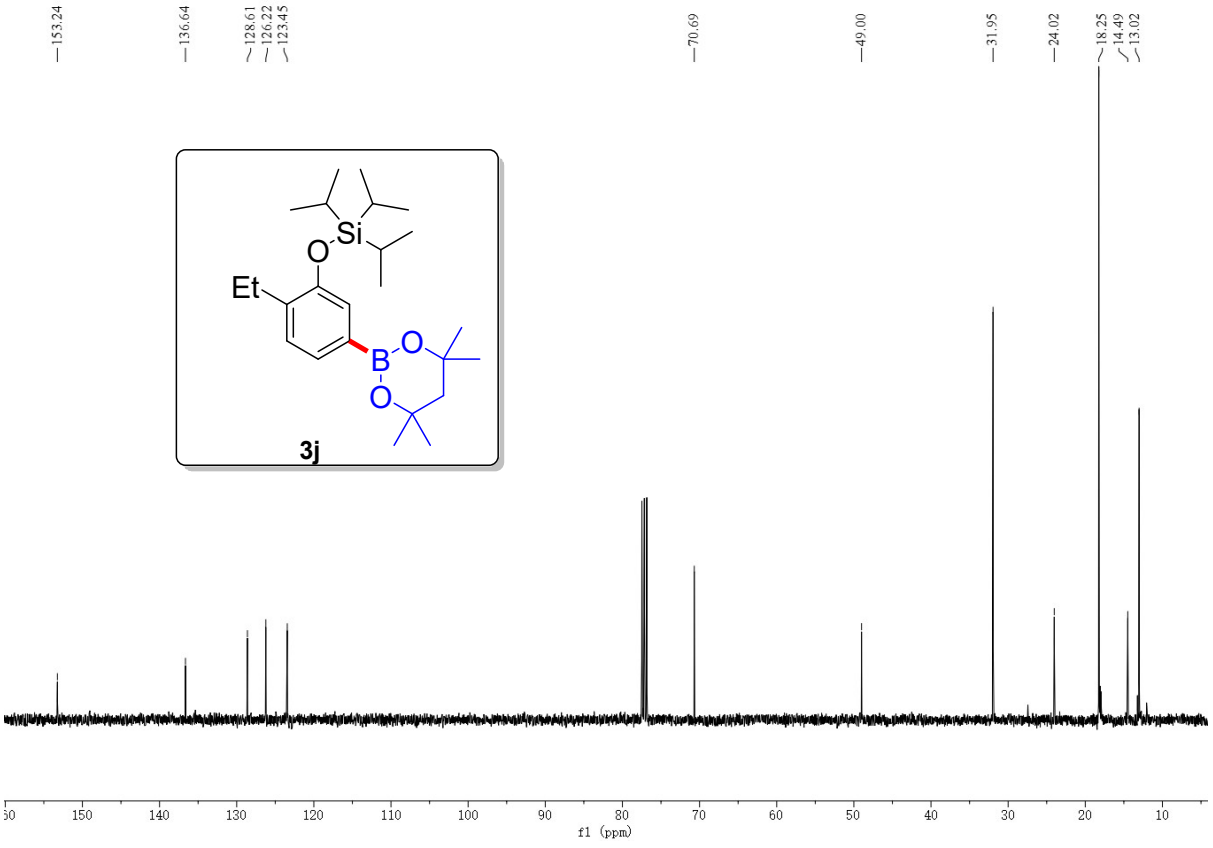
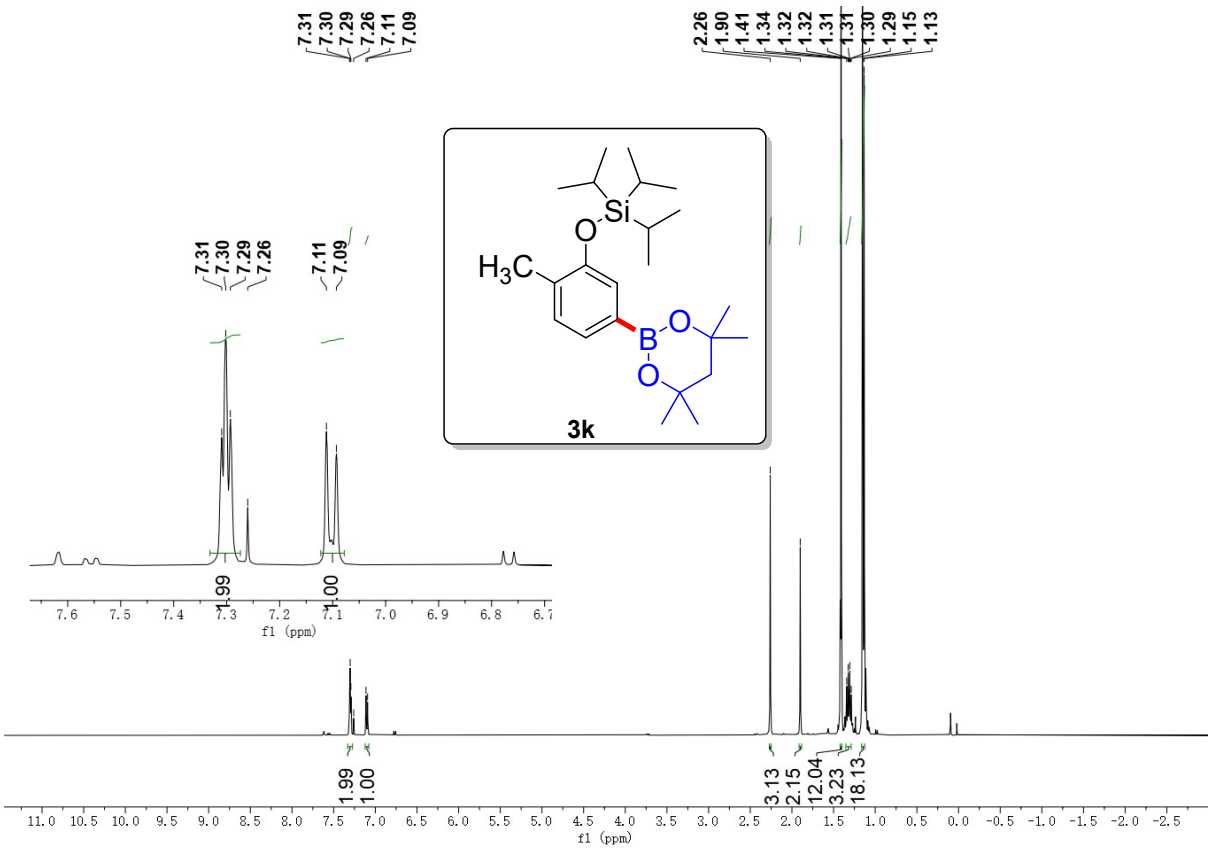
126.05
123.49
70.72
63.62
49.01
34.92
31.96
18.27
18.17
13.05
12.18
1.18
3h
f1 (ppm)


3i
f1 (ppm)


3i
f1 (ppm)


3j
f1 (ppm)


3j
f1 (ppm)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7.30
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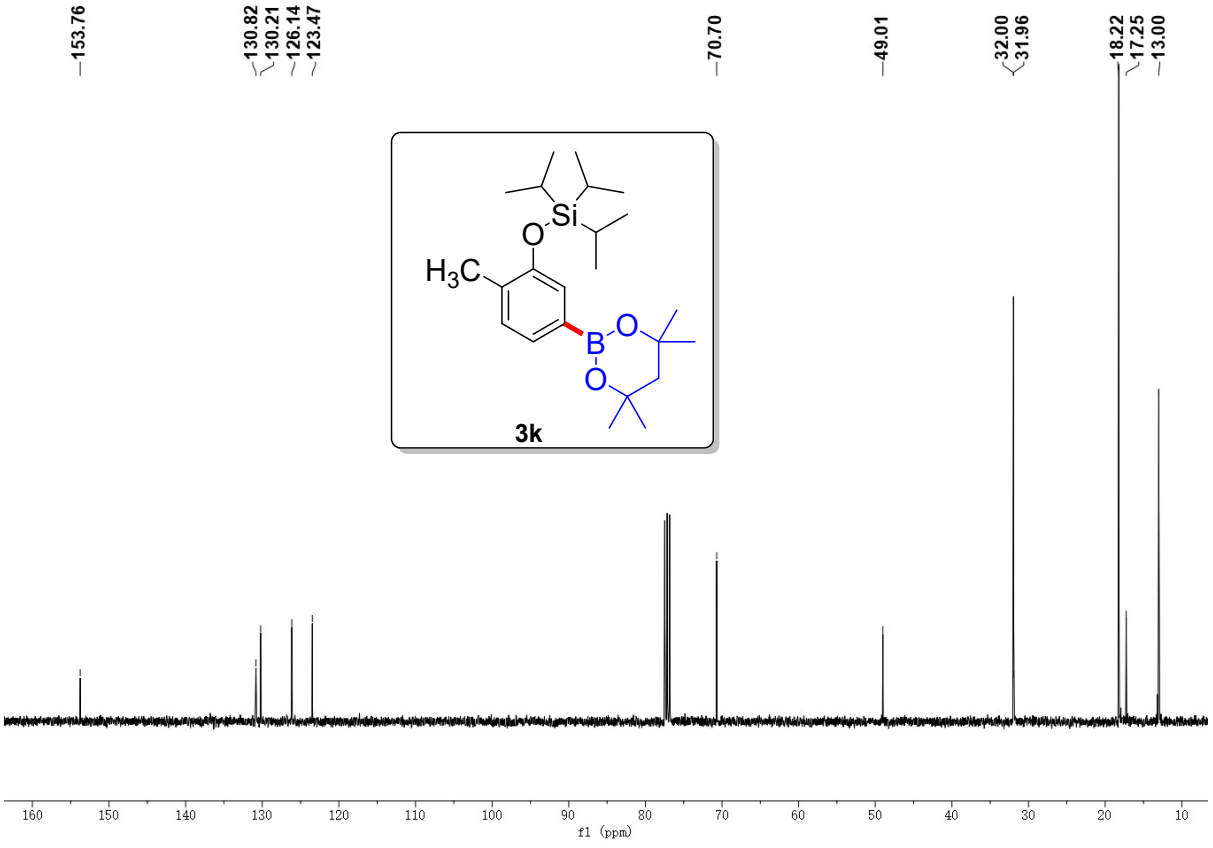
7.26
7.11
7.09
2.26
1.90
1.41
1.34
1.32
1.32
1.31
1.31
1.30
1.29
1.15
1.13
Si
O
H3C
B
O
O
3k
1.99
1.00
3.13
2.15
12.04
3.23
18.13
f1 (ppm)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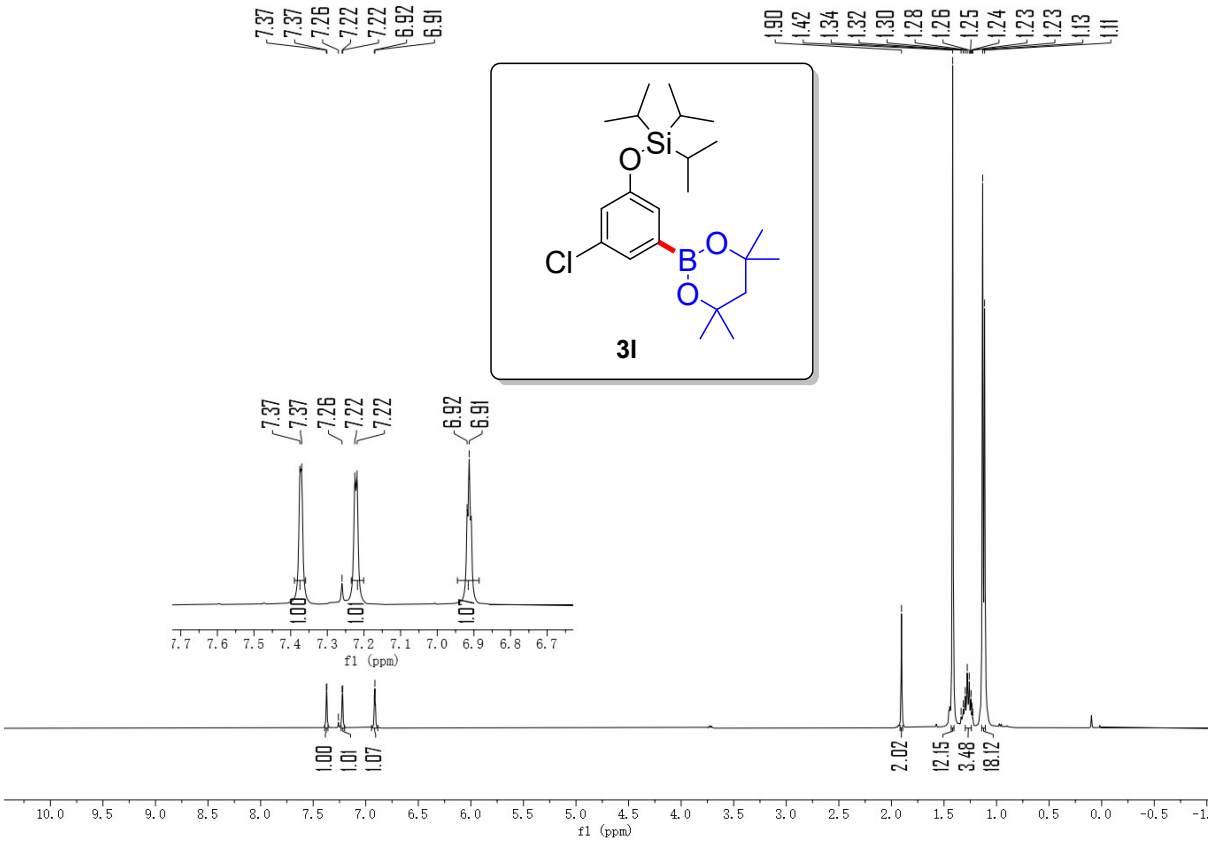
123.47
70.70
49.01
32.00
31.96
18.22
17.25
13.00
Si
O
H3C
B
O
O
3k
f1 (ppm)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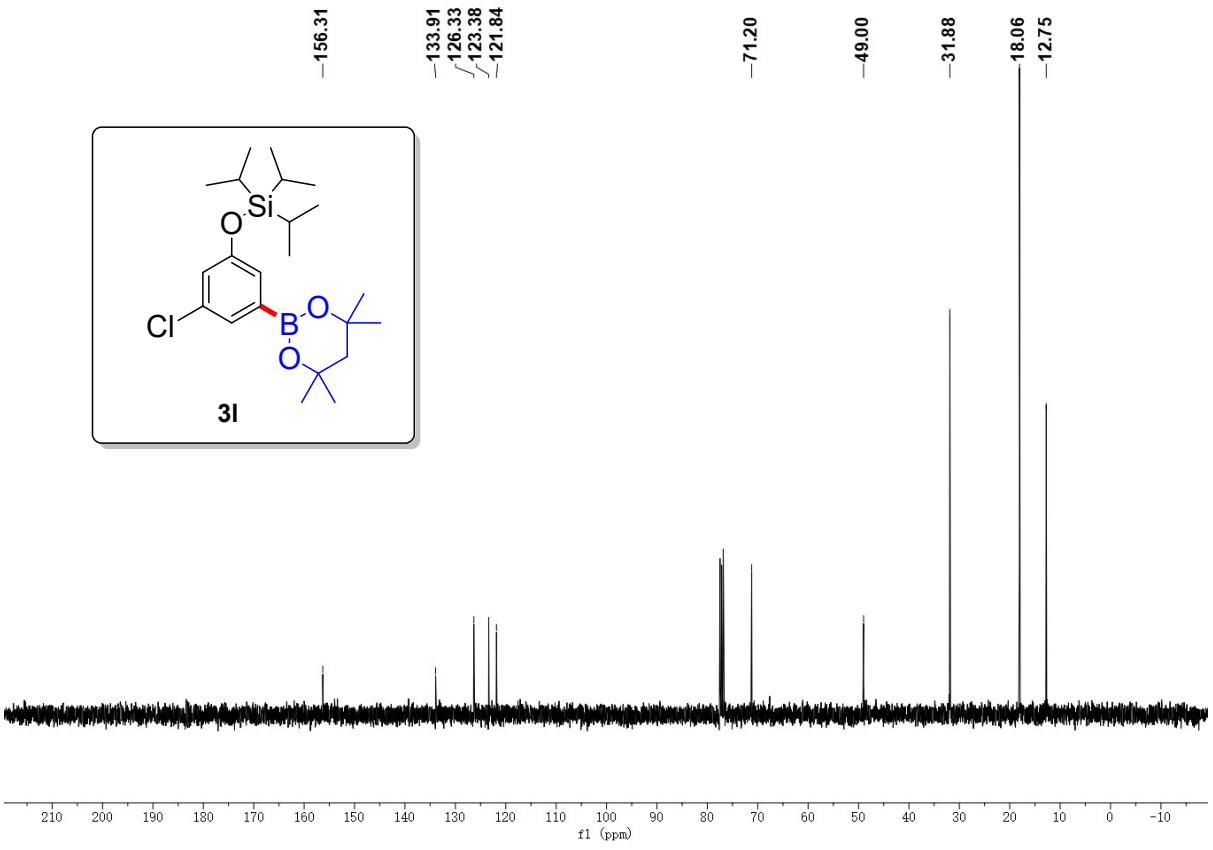
7.37
7.26
7.22
7.22
6.92
6.91
1.90
1.42
1.34
1.32
1.30
1.28
1.26
1.25
1.24
1.23
1.23
1.13
1.11
Si
O
Cl
B
O
O
3l
1.00
1.01
1.07
2.02
12.15
3.48
18.12
f1 (ppm)


156.31
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123.38
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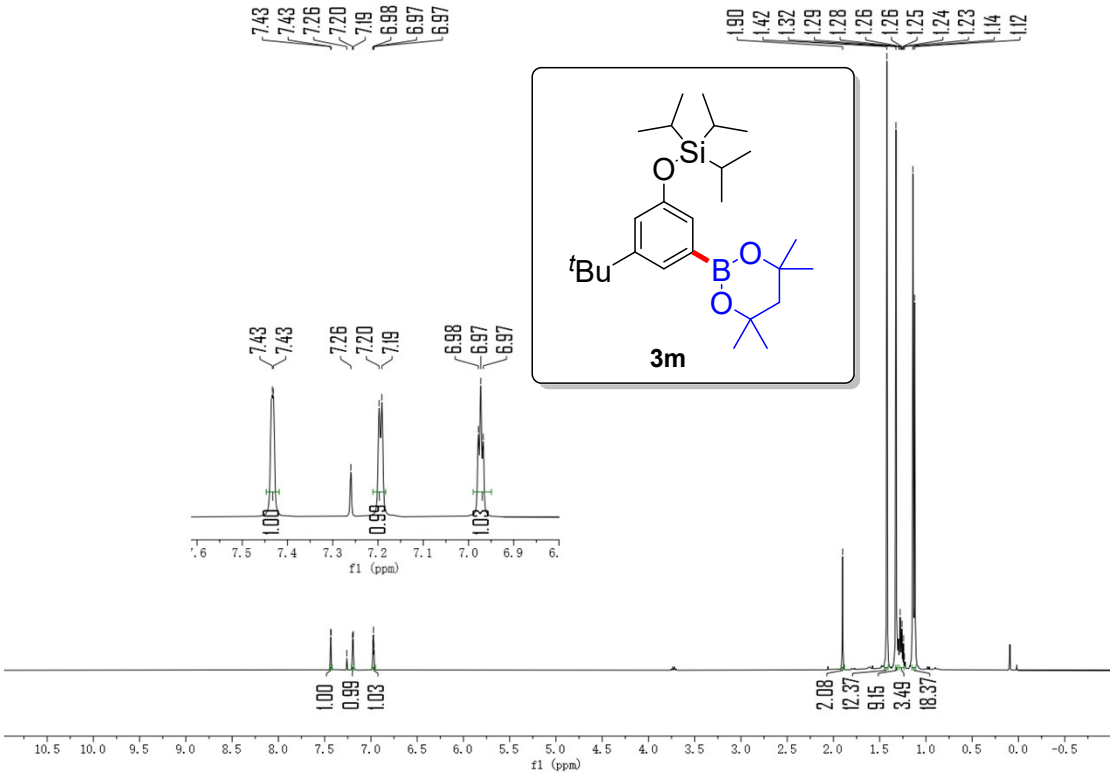
18.06
12.75
Si
O
Cl
B
O
O
3l
f1 (ppm)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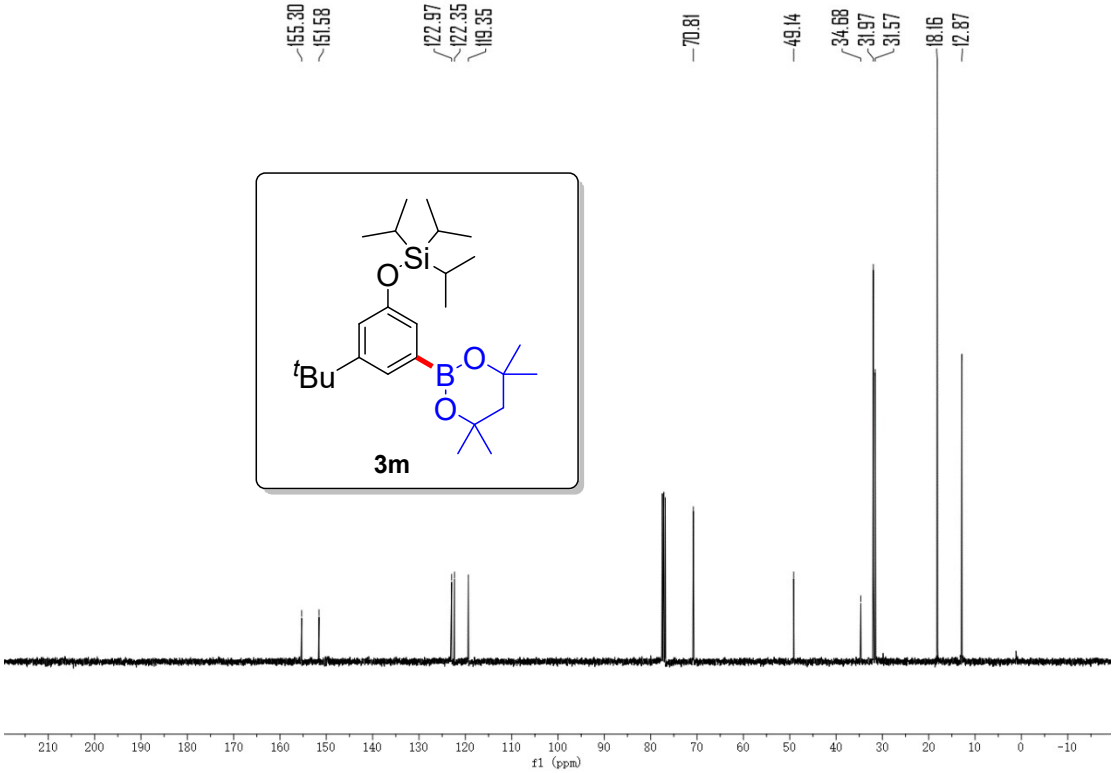
7.43
7.26
7.20
7.19
6.98
6.97
6.97
1.90
1.42
1.32
1.29
1.28
1.26
1.26
1.25
1.24
1.23
1.14
1.12
Si
O
tBu
B
O
O
3m
1.00
0.99
1.03
2.08
12.37
9.15
3.49
18.37
f1 (ppm)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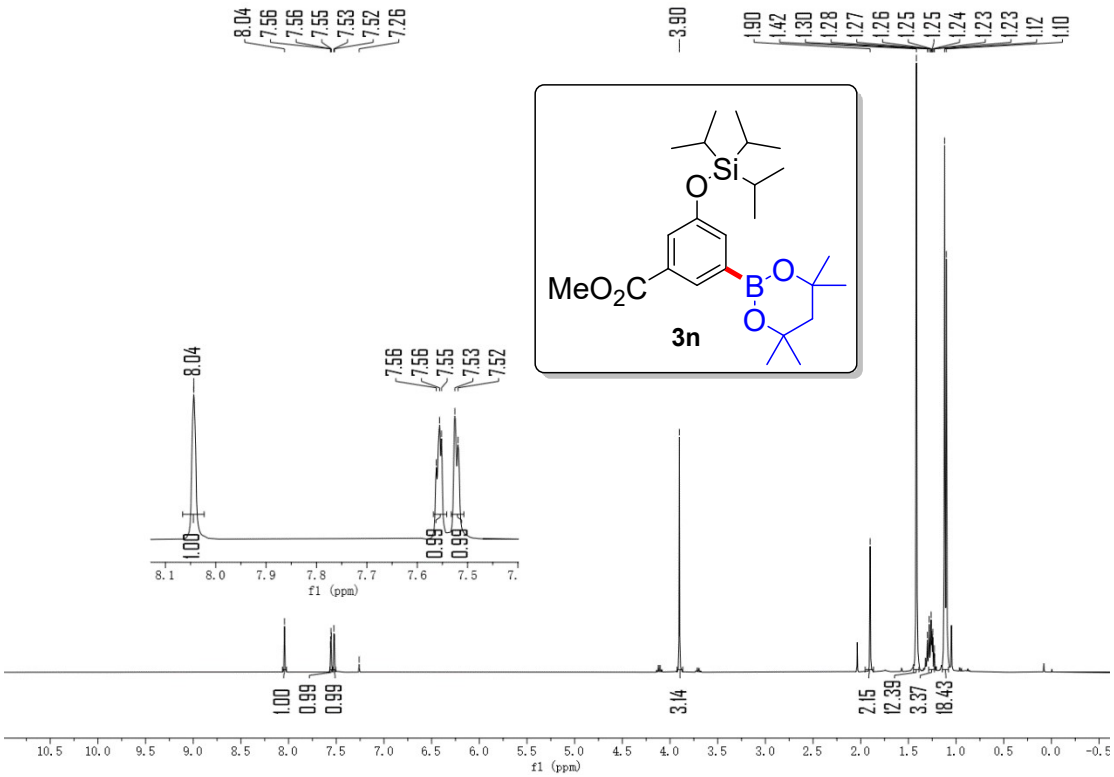
O
tBu
B
O
O
3m
f1 (ppm)


8.04
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7.56
7.55
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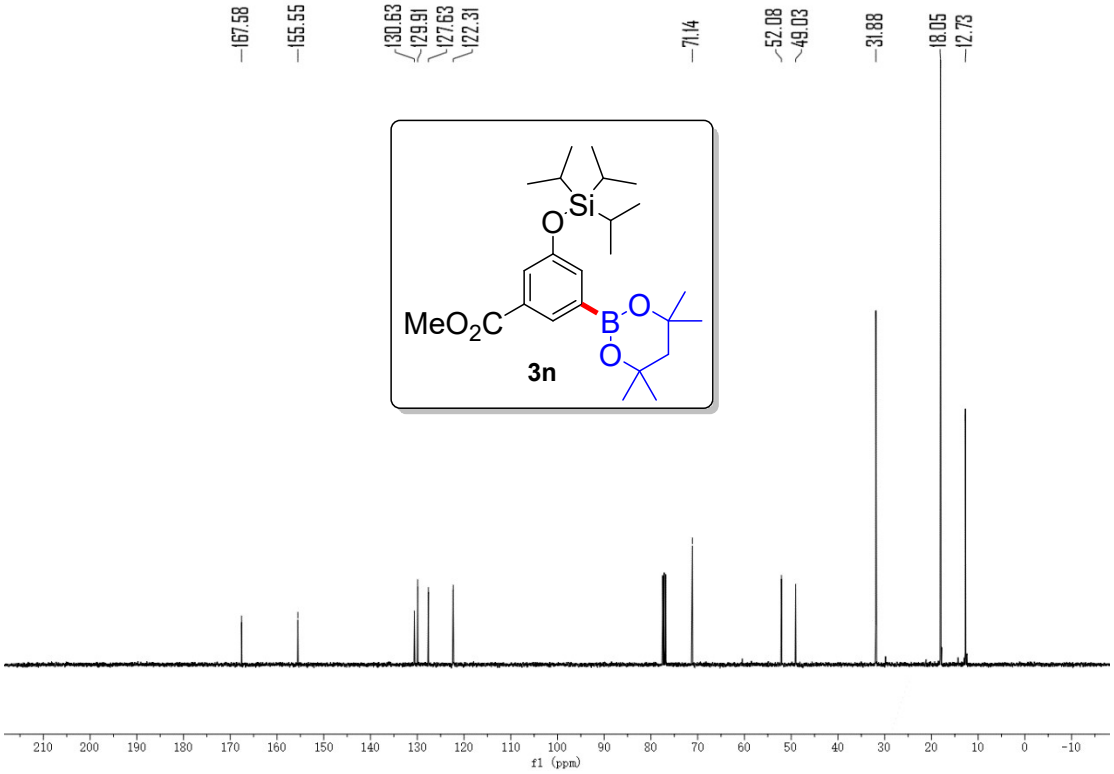
7.52
7.26
3.90
1.90
1.42
1.30
1.28
1.27
1.26
1.25
1.25
1.24
1.23
1.23
1.12
1.10
MeO2C
3n
1.00
0.99
0.99
3.14
2.15
12.39
3.37
18.43
f1 (ppm)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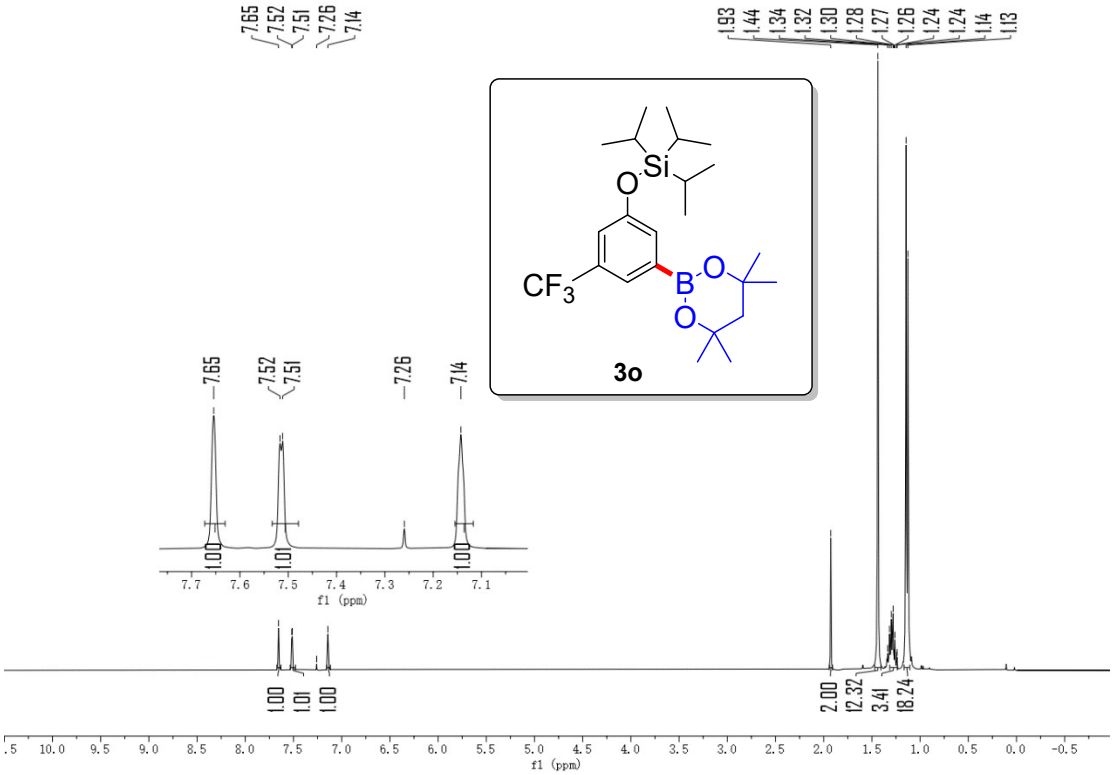
31.88
18.05
12.73
MeO2C
3n
f1 (ppm)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7.26
7.14
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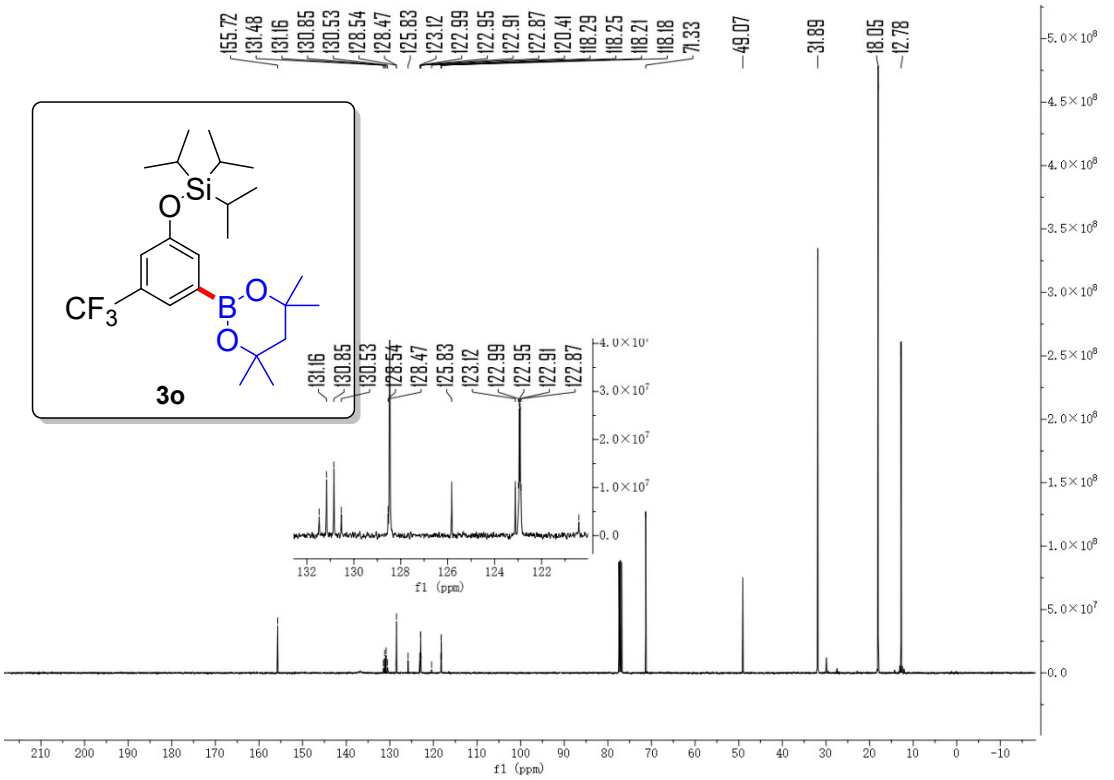
1.44
1.34
1.32
1.30
1.28
1.27
1.26
1.24
1.24
1.14
1.13
Si
O
CF3
B
O
O
3o
1.00
1.01
1.00
2.00
12.32
3.41
18.24
f1 (ppm)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128.54
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125.83
123.12
122.99
122.95
122.91
122.87
120.41
118.29
118.25
118.21
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49.07
31.89
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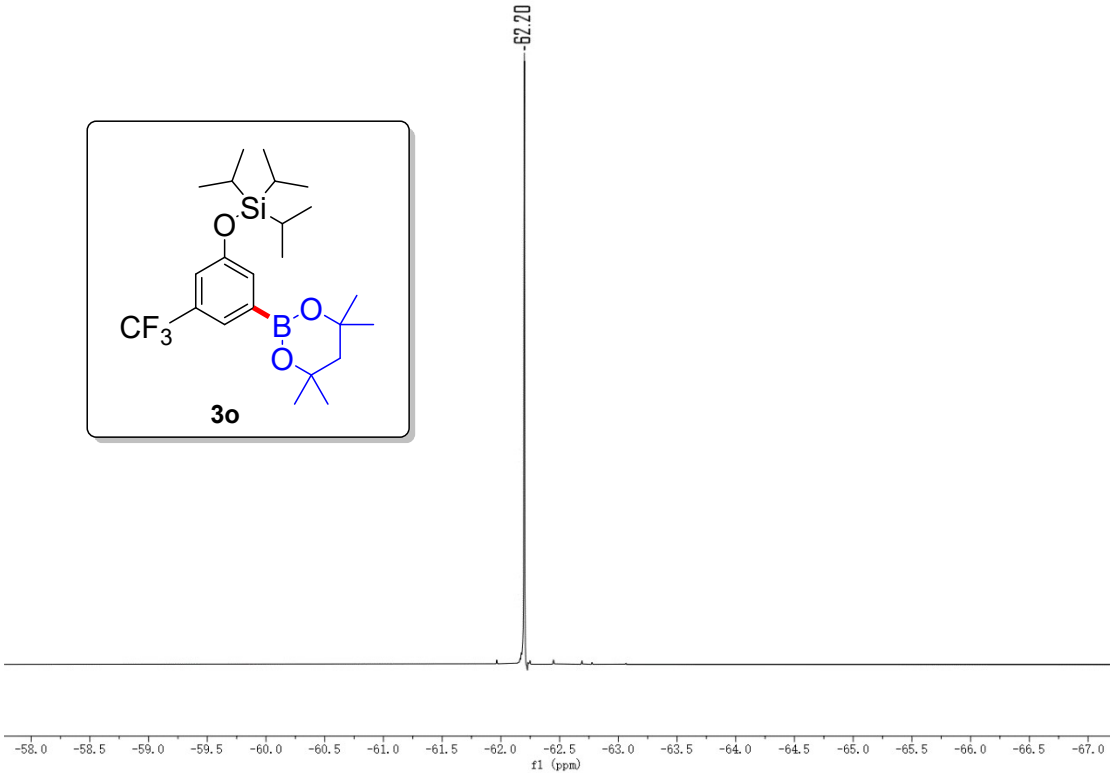
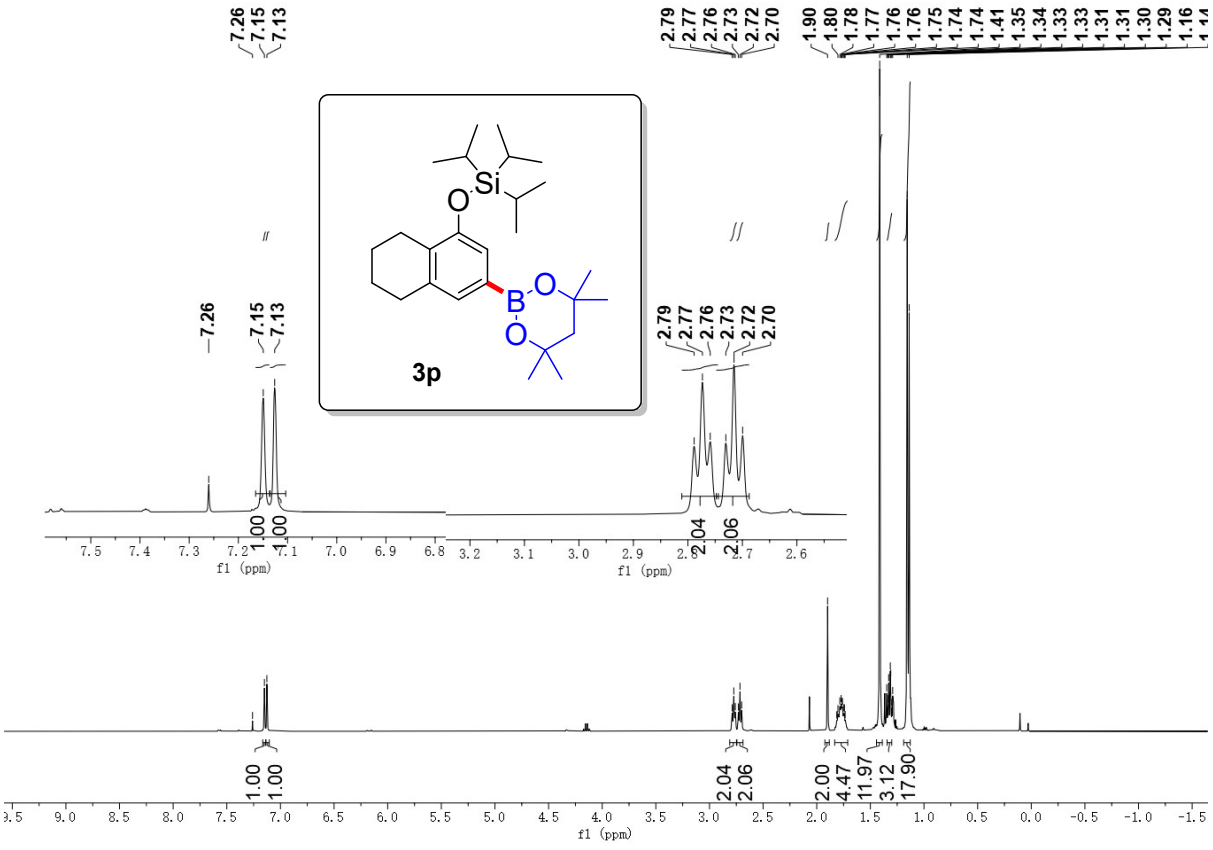
12.78
Si
O
CF3
B
O
O
3o
f1 (ppm)


-62.20
3o
-58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0
f1 (ppm)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7.13
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2.76
2.73
2.72
2.70
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1.80
1.78
1.77
1.76
1.76
1.75
1.74
1.74
1.41
1.35
1.34
1.33
1.33
1.31
1.31
1.30
1.29
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3p
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1.00
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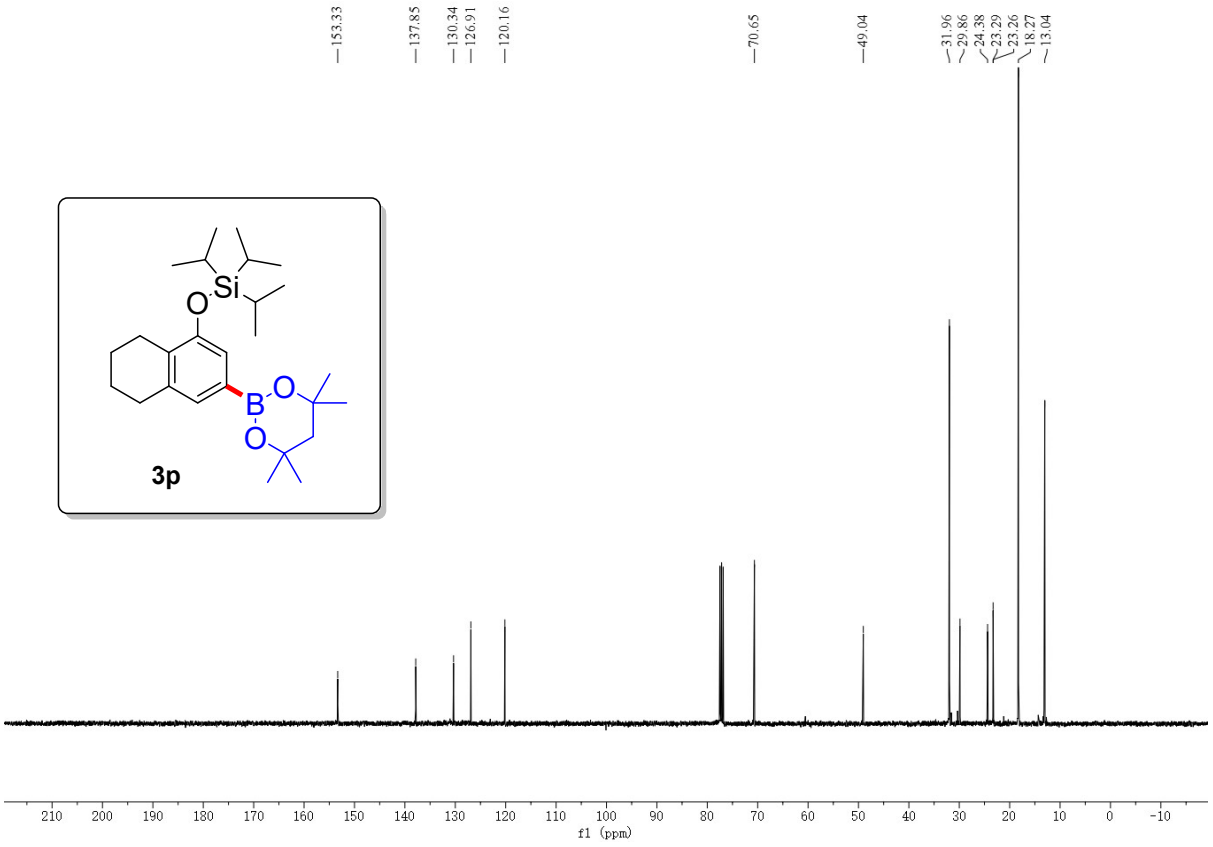
2.06
2.00
4.47
11.97
3.12
17.90
f1 (ppm)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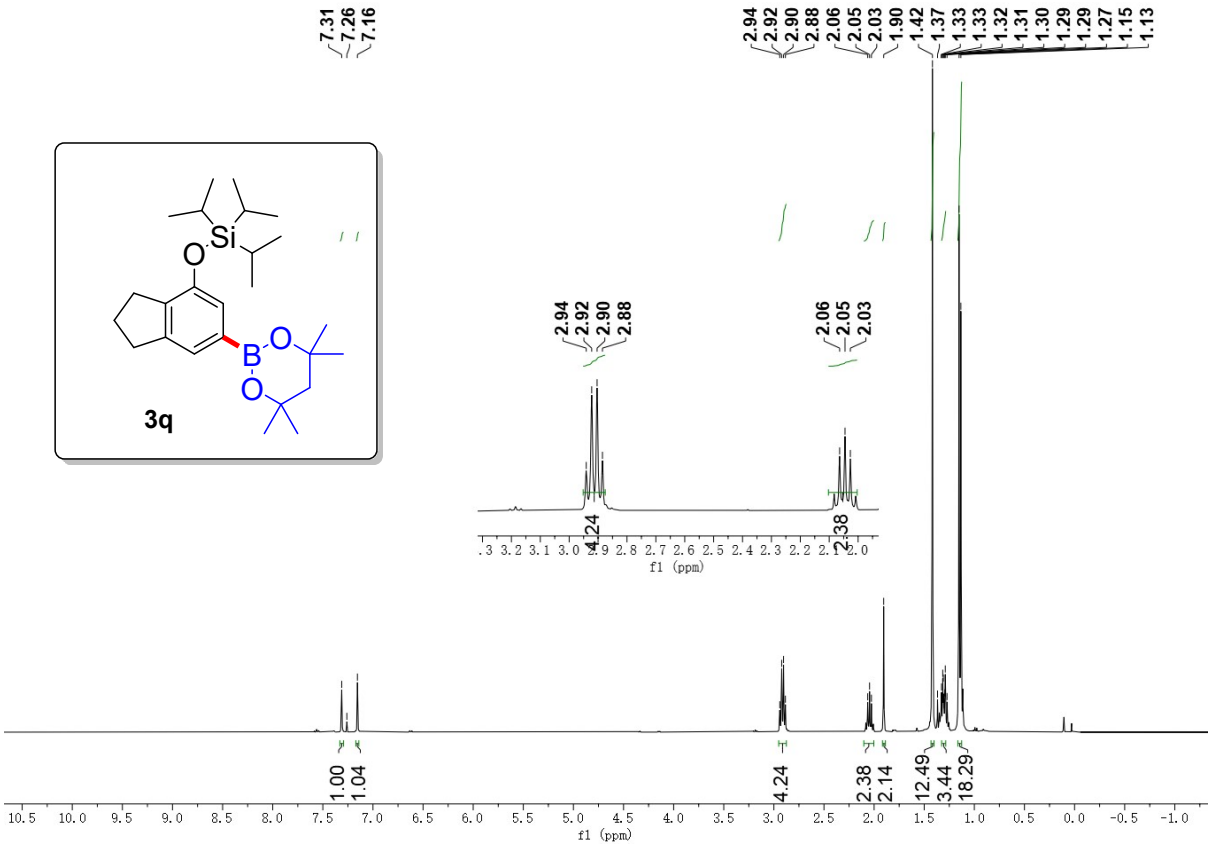
29.86
24.38
23.29
23.26
18.27
13.04
3p
f1 (ppm)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7.26
7.16
2.94
2.92
2.90
2.88
2.06
2.05
2.03
1.90
1.42
1.37
1.33
1.33
1.32
1.31
1.30
1.29
1.29
1.27
1.15
1.13
3q
4.24
2.38
f1 (ppm)
1.00
1.04
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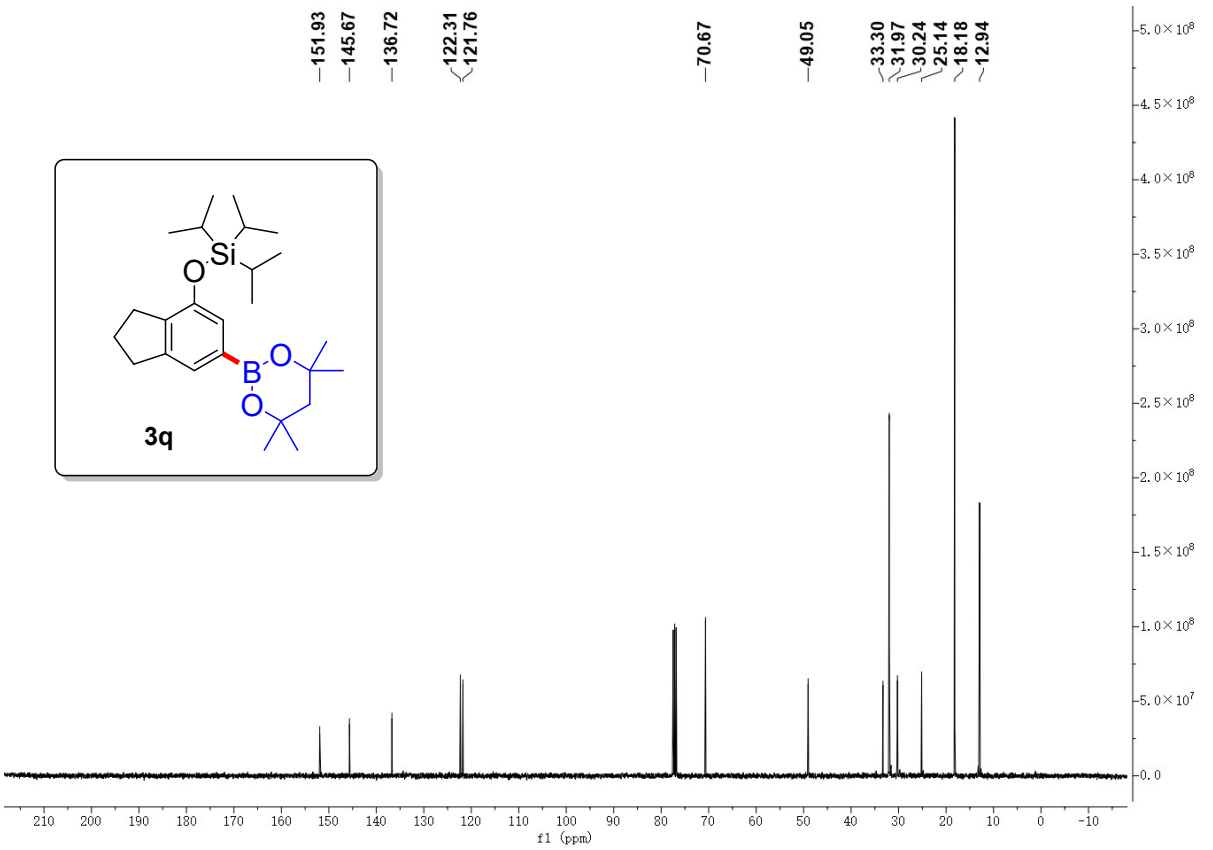
2.14
12.49
3.44
18.29
f1 (ppm)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145.67
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121.76
70.67
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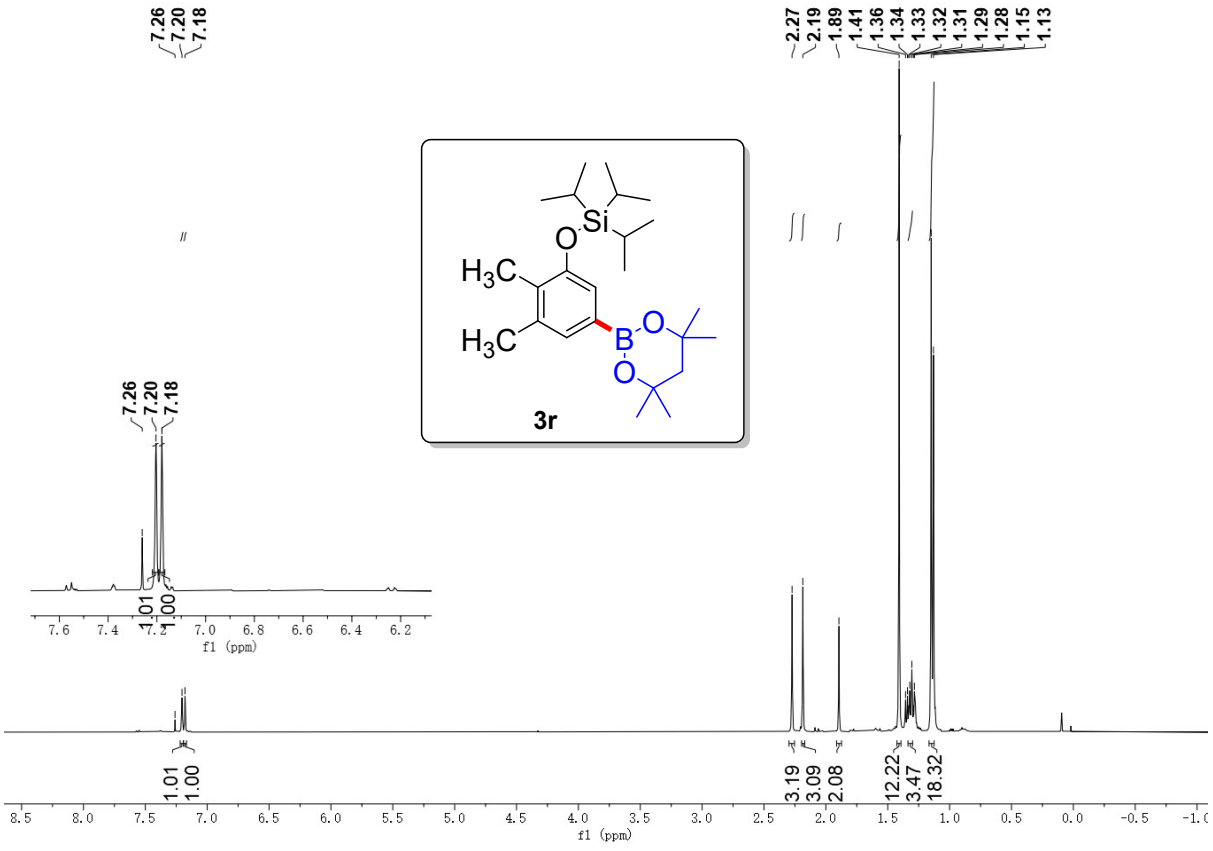
31.97
30.24
25.14
18.18
12.94
Si
O
B
O
O
3q
f1 (ppm)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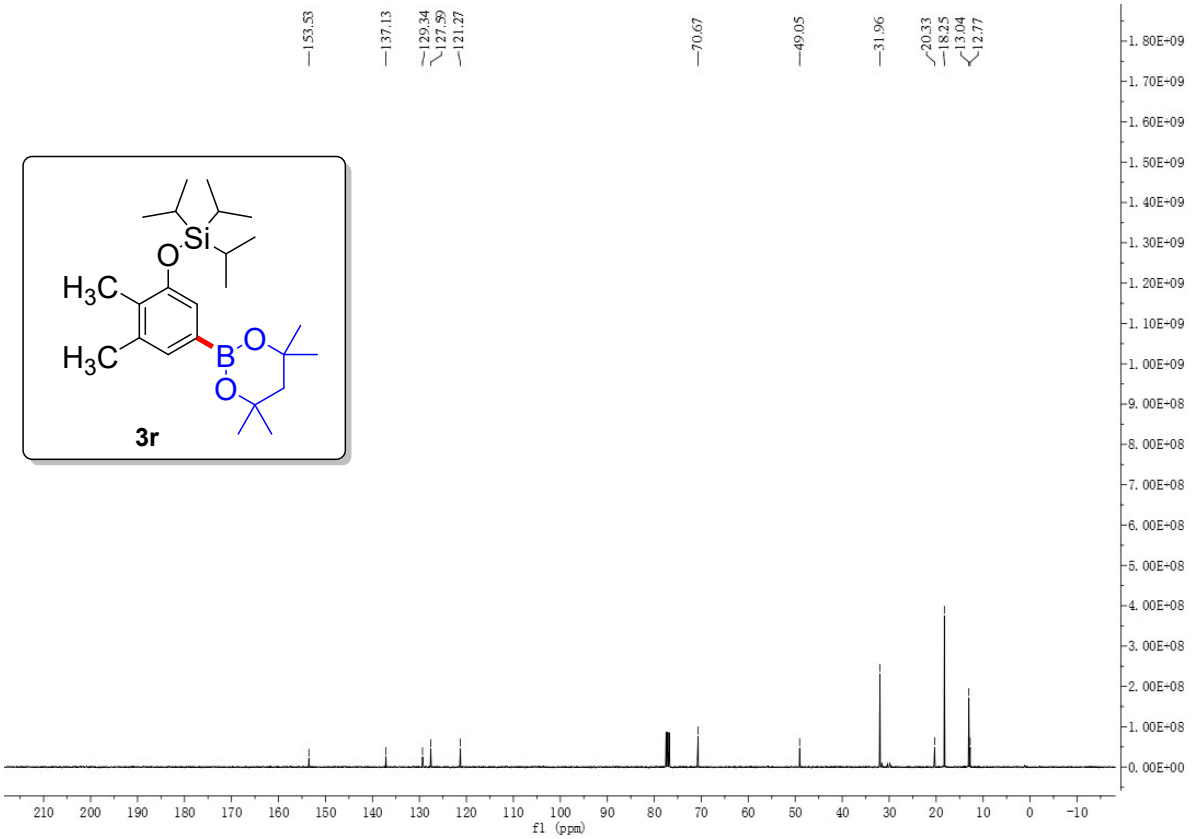
1.89
1.41
1.36
1.34
1.33
1.32
1.31
1.29
1.28
1.15
1.13
Si
O
H3C
H3C
B
O
O
3r
1.01
1.00
3.19
3.09
2.08
12.22
3.47
18.32
f1 (ppm)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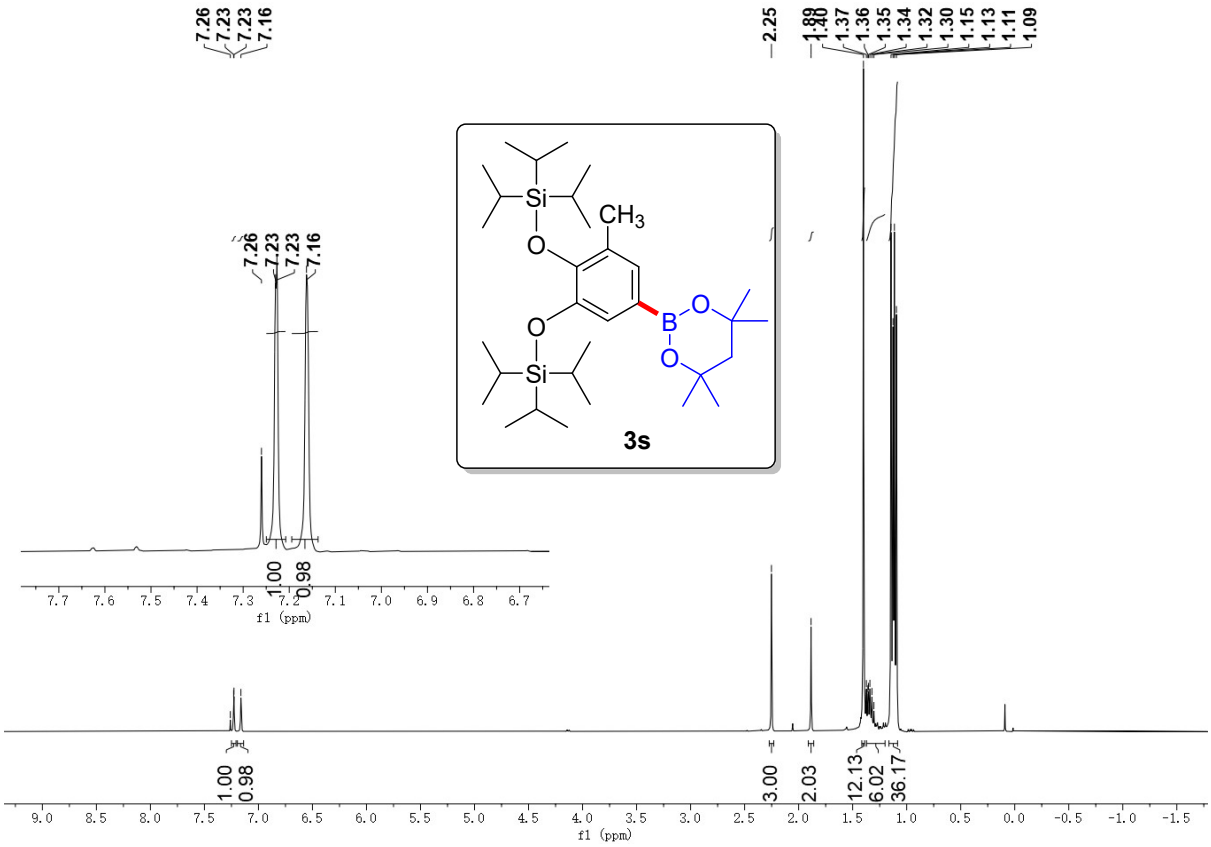
127.59
121.27
70.67
49.05
31.96
20.33
18.25
13.04
12.77
3r
f1 (ppm)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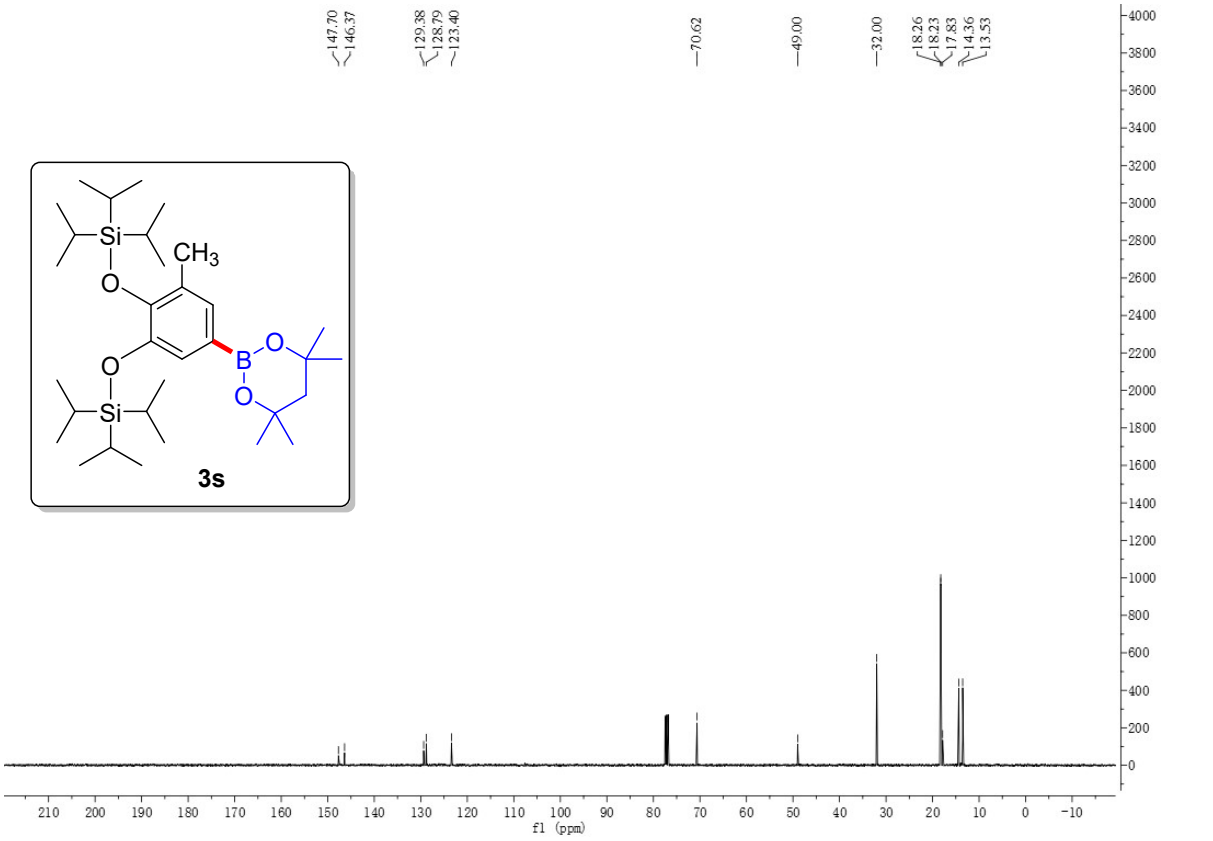
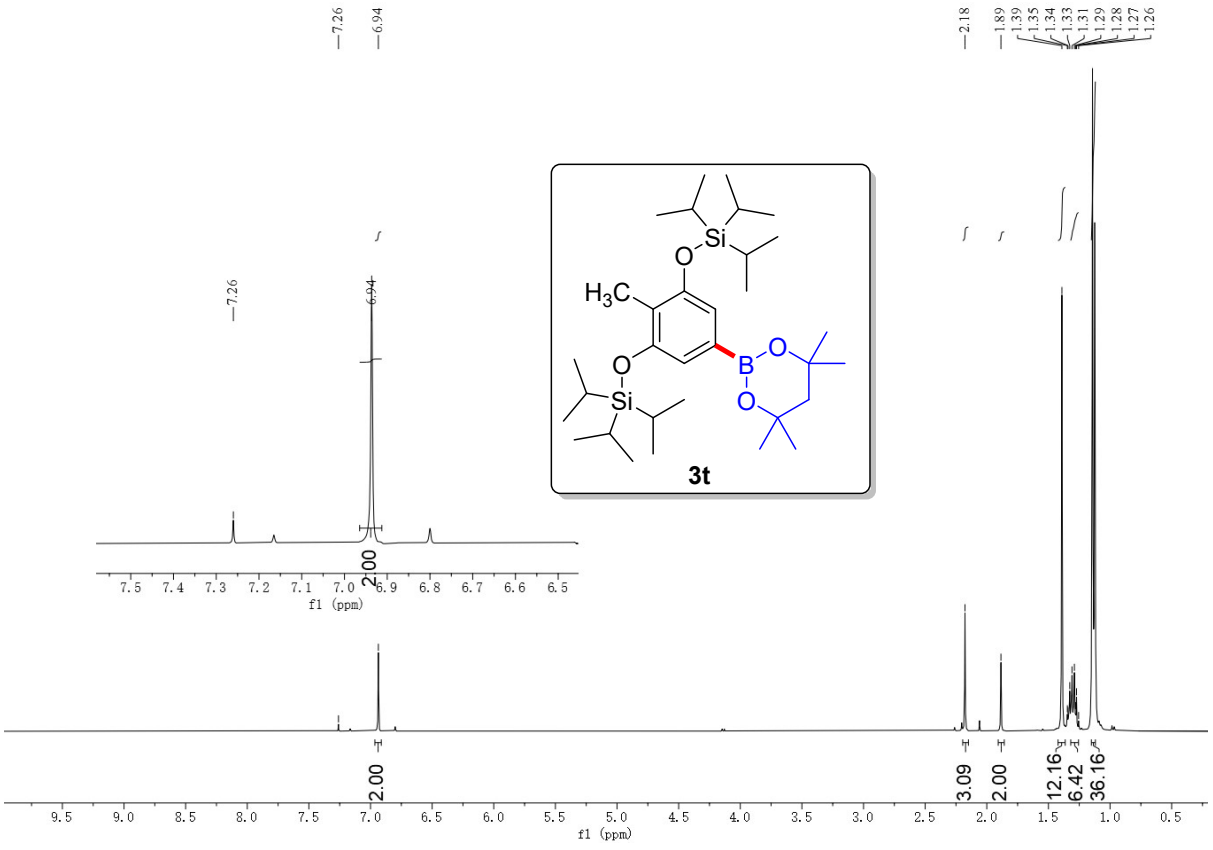
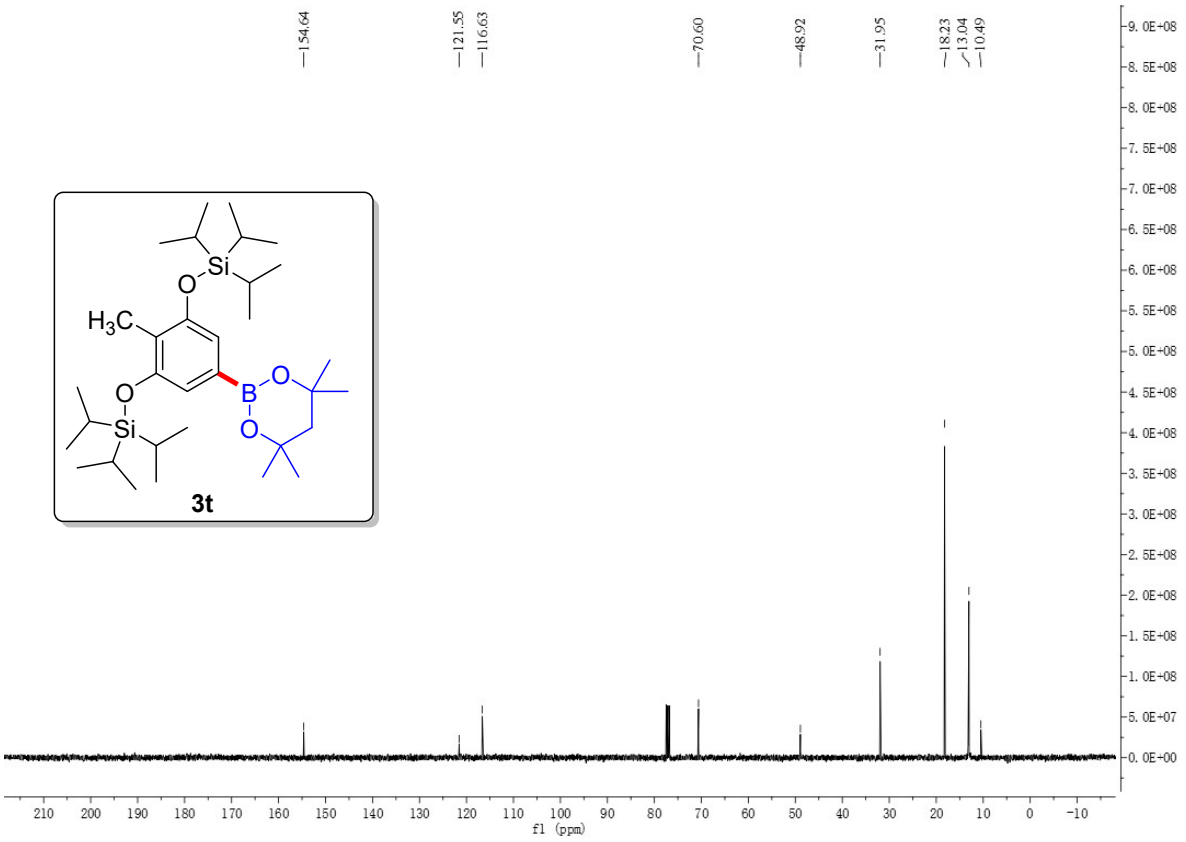
7.23
7.23
7.16
2.25
1.38
1.37
1.36
1.35
1.34
1.32
1.30
1.15
1.13
1.11
1.09
3s
1.00
0.98
3.00
2.03
12.13
6.02
36.17
f1 (ppm)


147.70
146.37
129.38
128.79
123.40
70.62
49.00
32.00
18.26
18.23
17.83
14.36
13.53
Si
CH3
O
O
Si
B
O
O
3s
f1 (ppm)


7.26
6.94
2.18
1.89
1.39
1.35
1.34
1.33
1.31
1.29
1.28
1.27
1.26
Si
O
H3C
O
Si
B
O
O
3t
2.00
3.09
2.00
12.16
6.42
36.16
f1 (ppm)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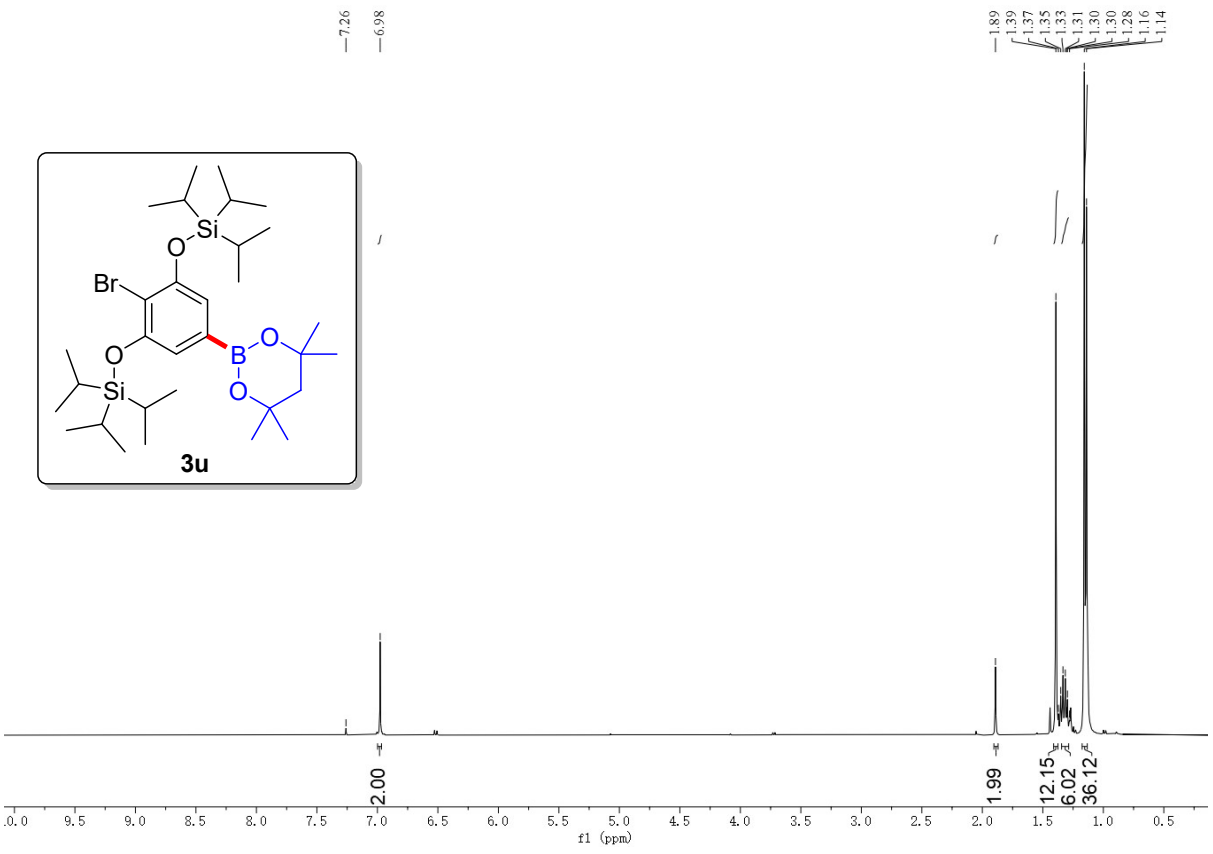
116.63
70.60
48.92
31.95
18.23
13.04
10.49
3t
f1 (ppm)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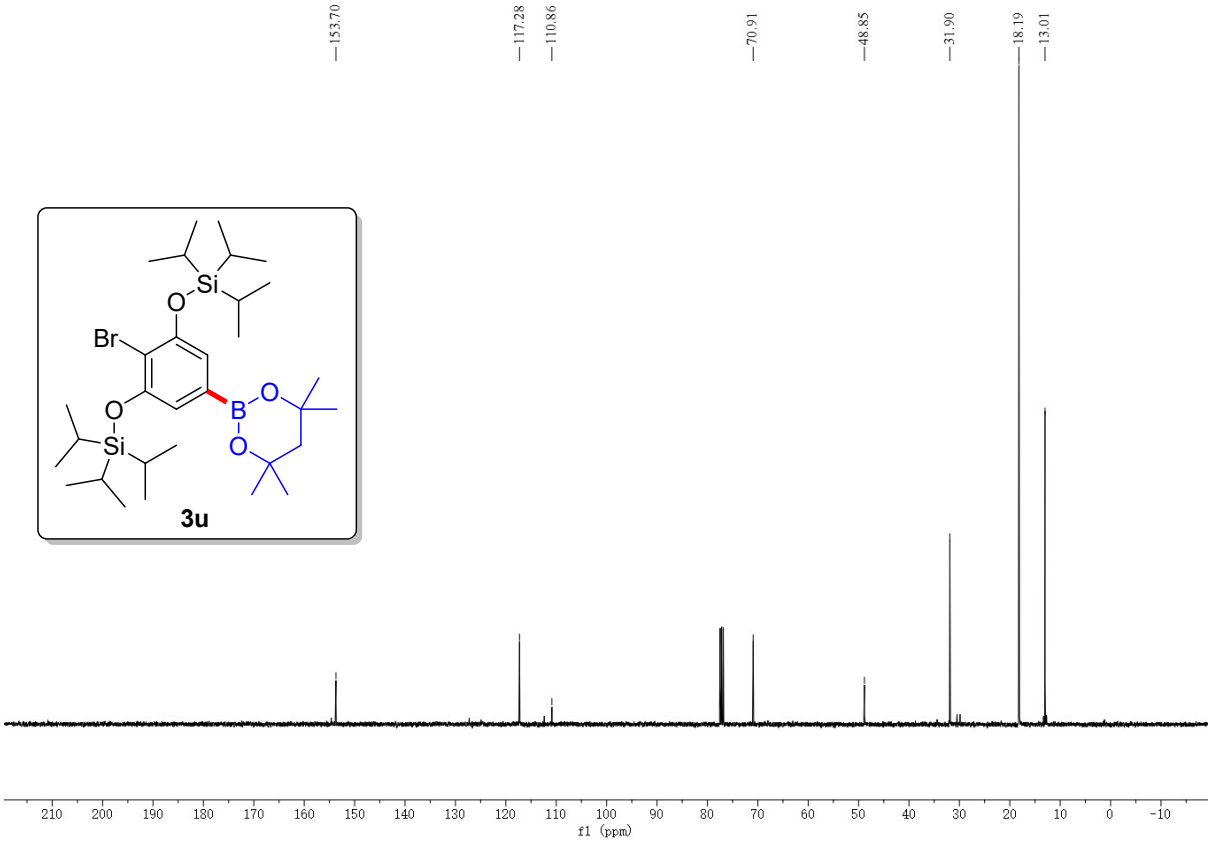
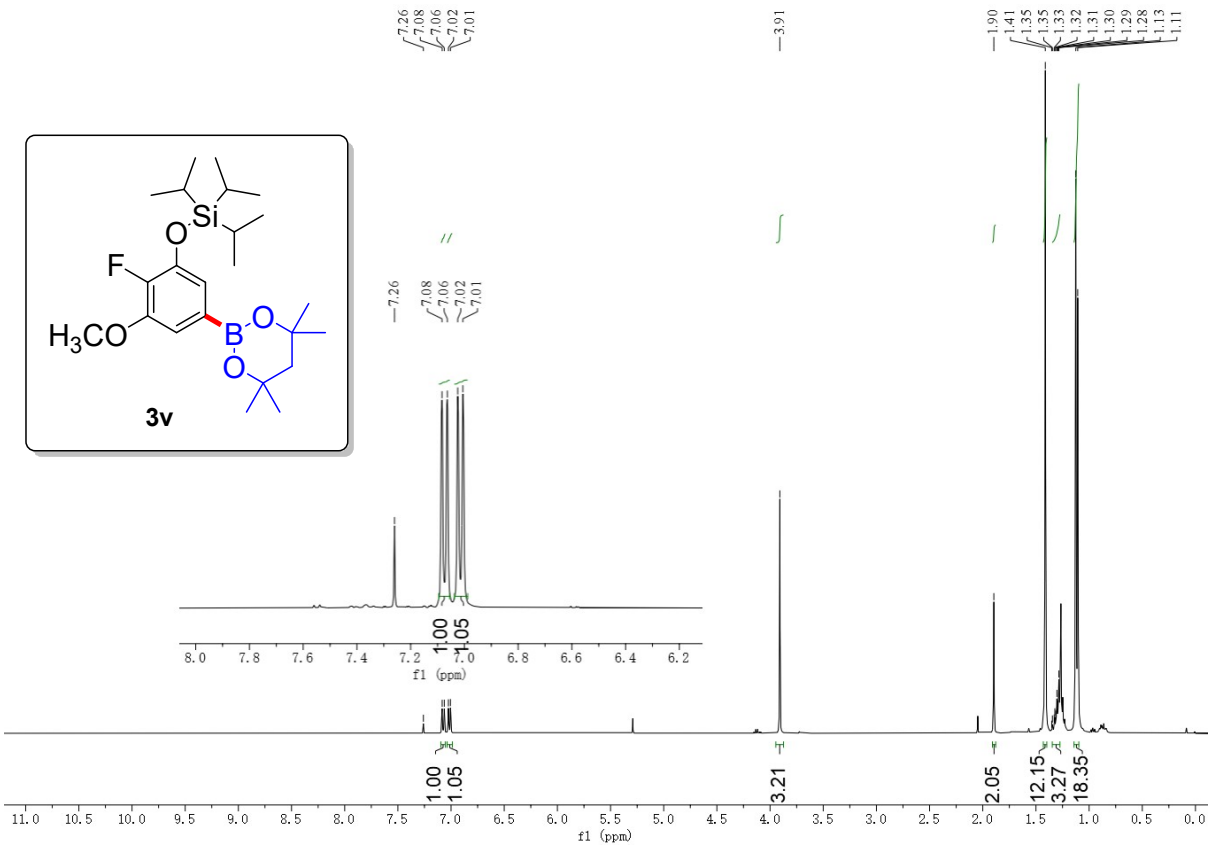
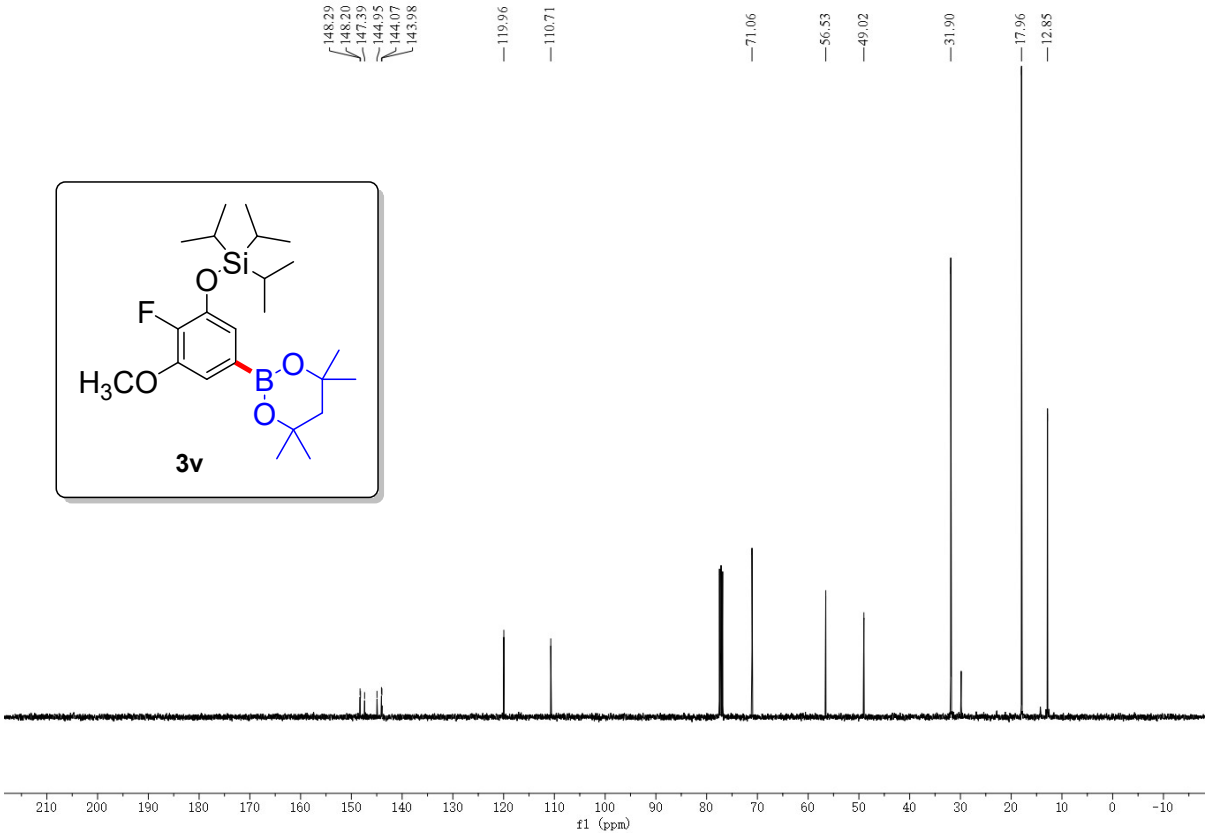
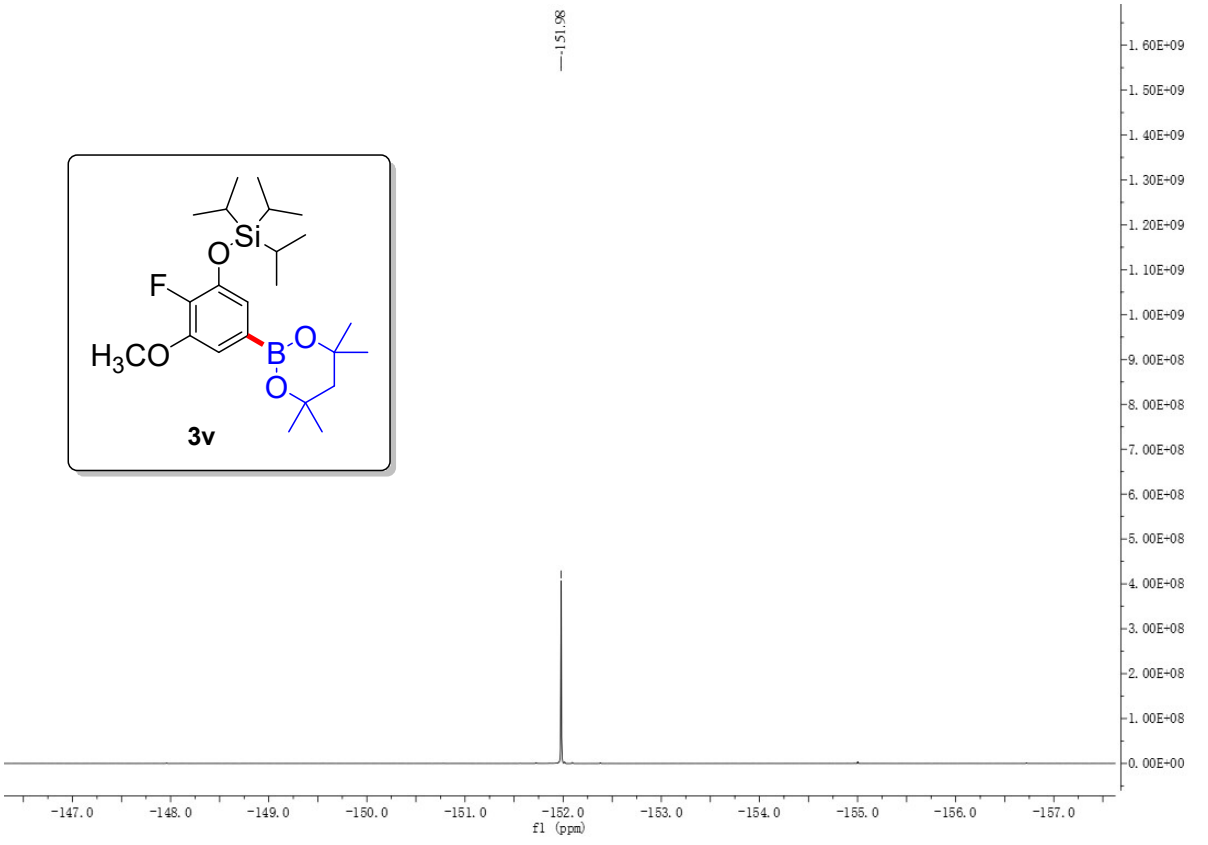
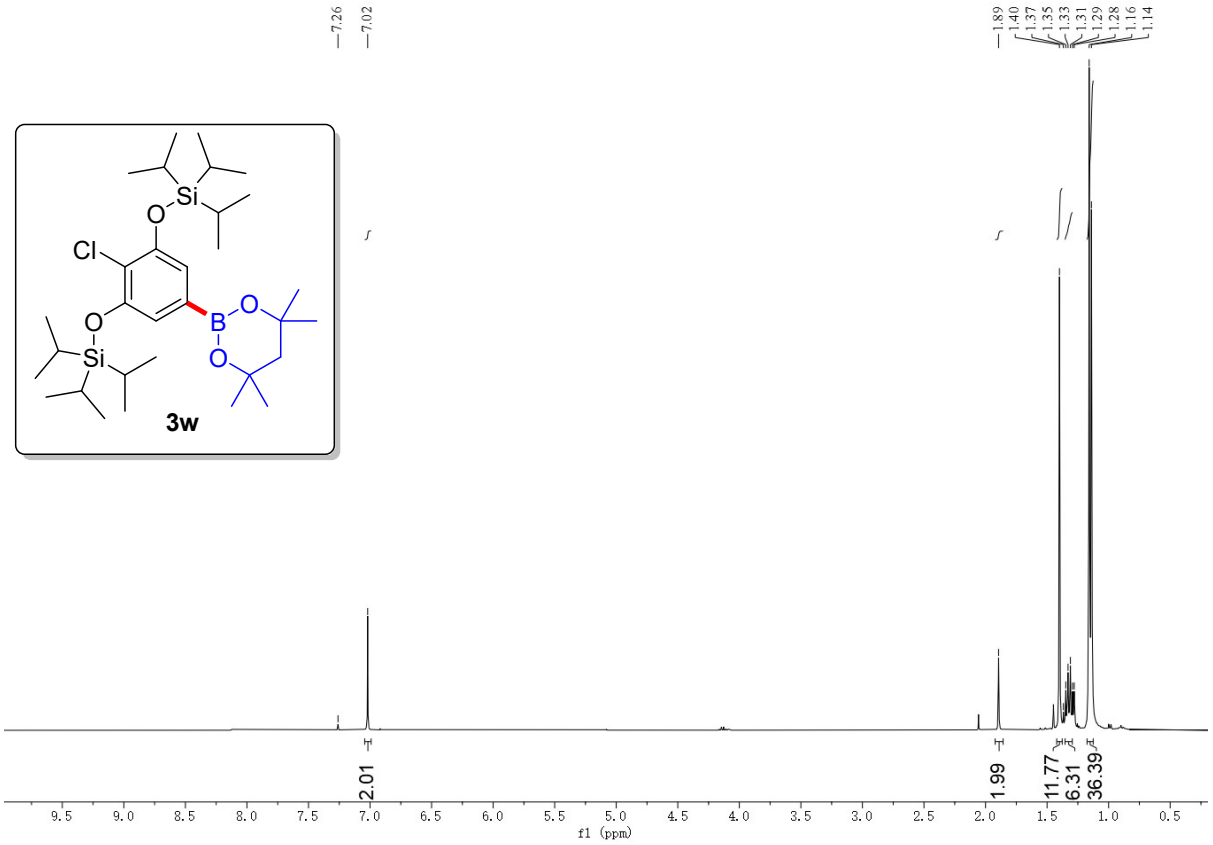
6.98
1.89
1.39
1.37
1.35
1.33
1.31
1.30
1.30
1.28
1.16
1.14
3u
2.00
1.99
12.15
6.02
36.12
f1 (ppm)

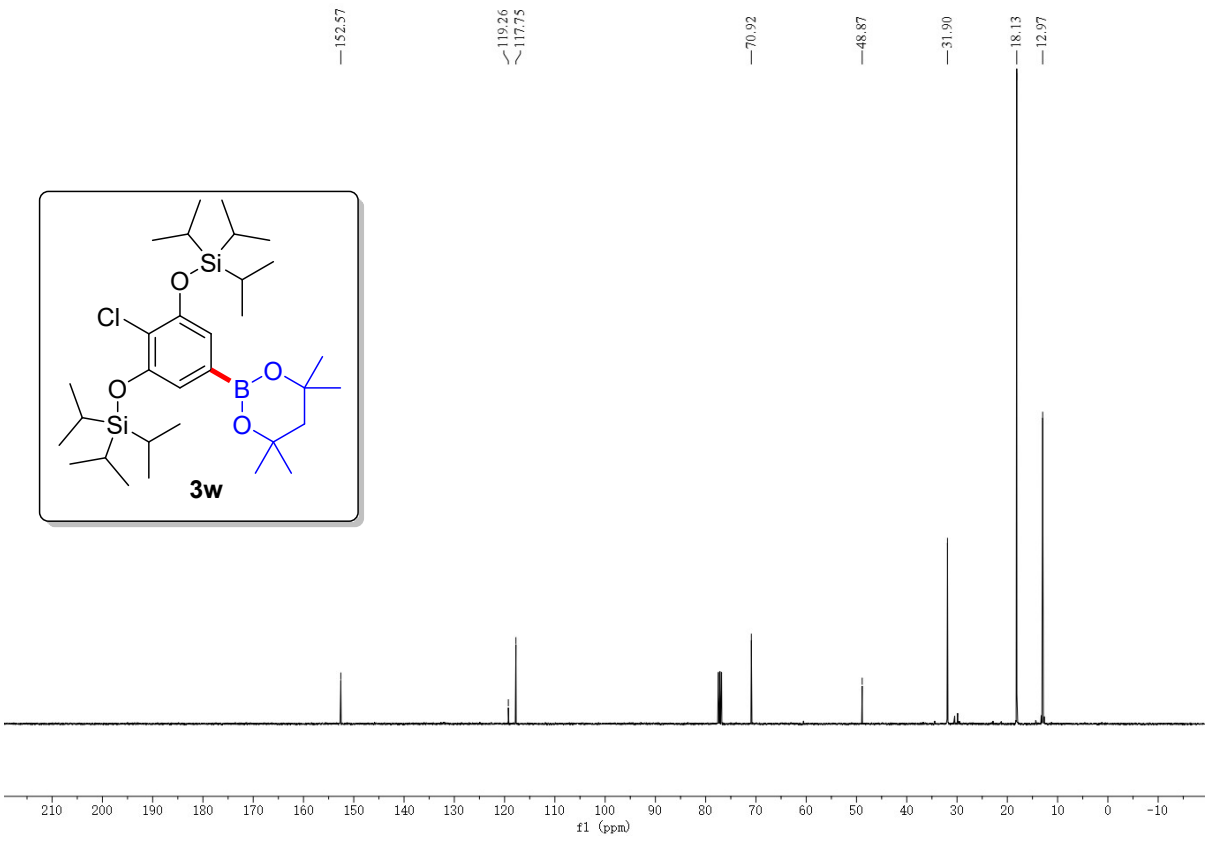

153.70
117.28
110.86
70.91
48.85
31.90
18.19
13.01
Si
O
Br
O
Si
B
O
O
3u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

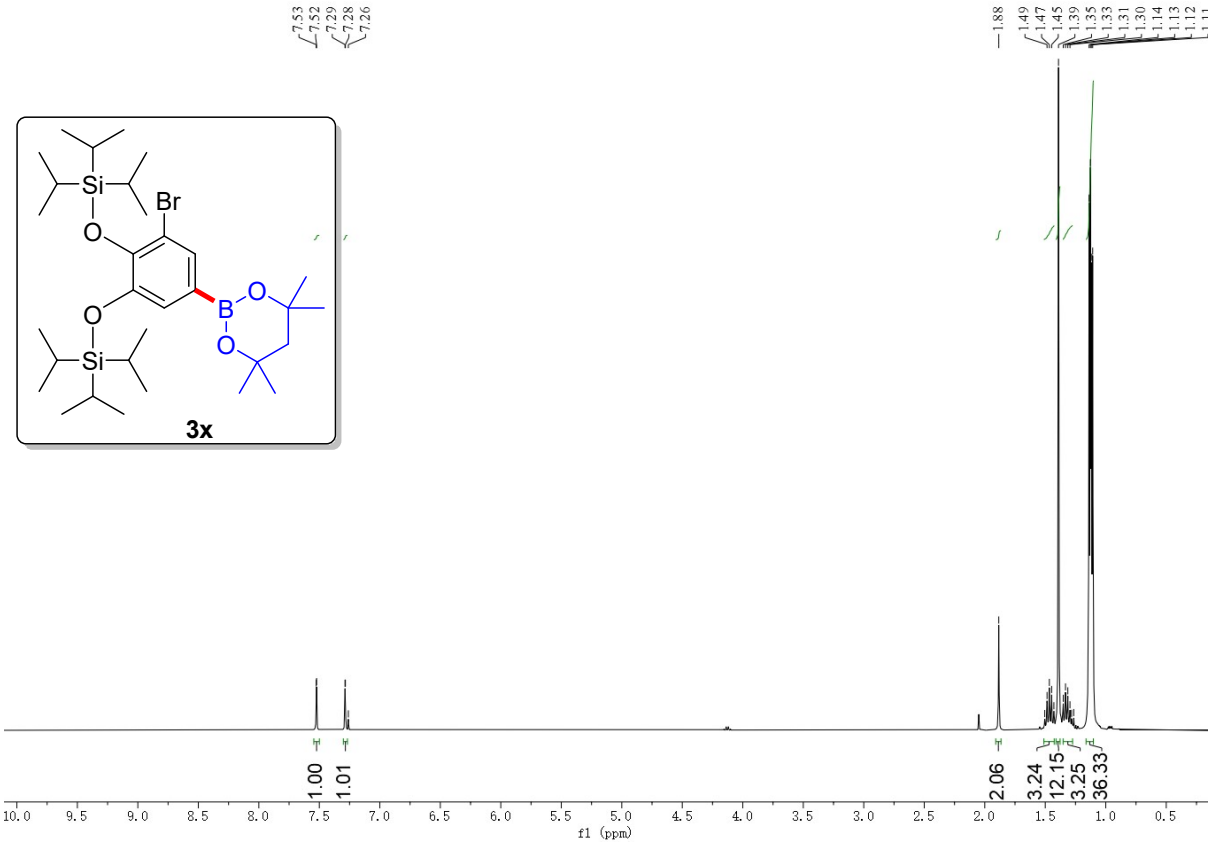

7.26
7.08
7.06
7.02
7.01
3.91
1.90
1.41
1.35
1.33
1.32
1.31
1.30
1.29
1.28
1.13
1.11
Si
O
F
H3CO
B
O
O
3v
1.00
1.05
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
1.00
1.05
3.21
2.05
12.15
3.27
18.35
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

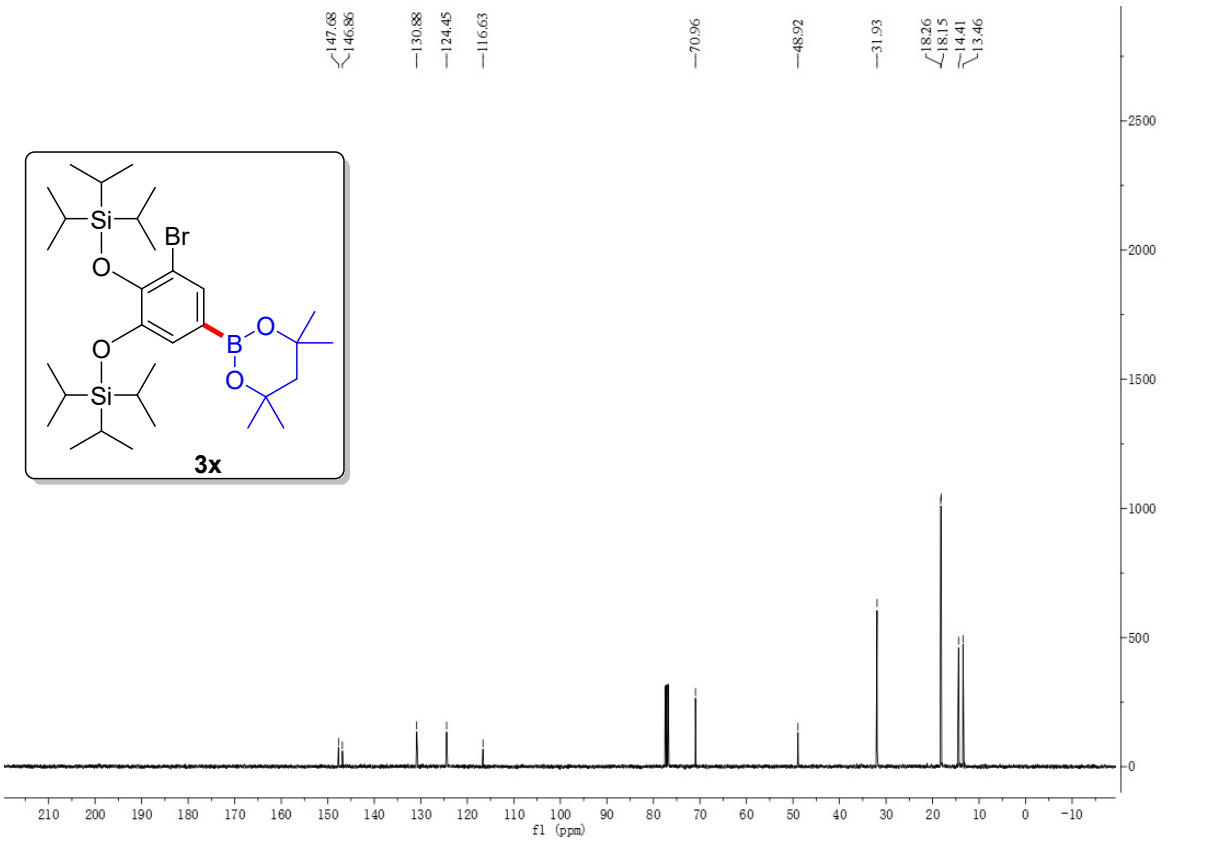

148.29
148.20
147.39
144.95
144.07
143.98
119.96
110.71
71.06
56.53
49.02
31.90
17.96
12.85
O
Si
F
H3CO
B
O
O
3v
f1 (ppm)

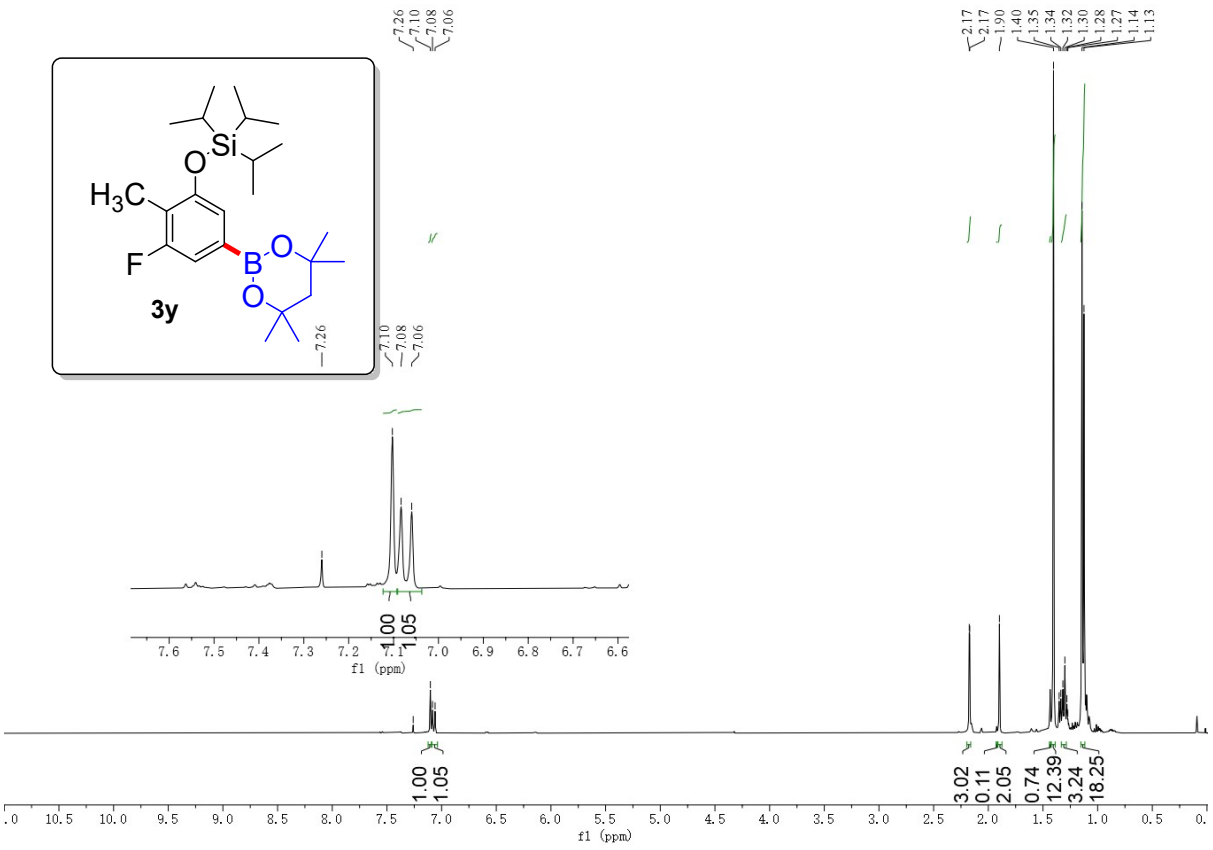

151.98
O
Si
F
H3CO
B
O
O
3v
f1 (ppm)

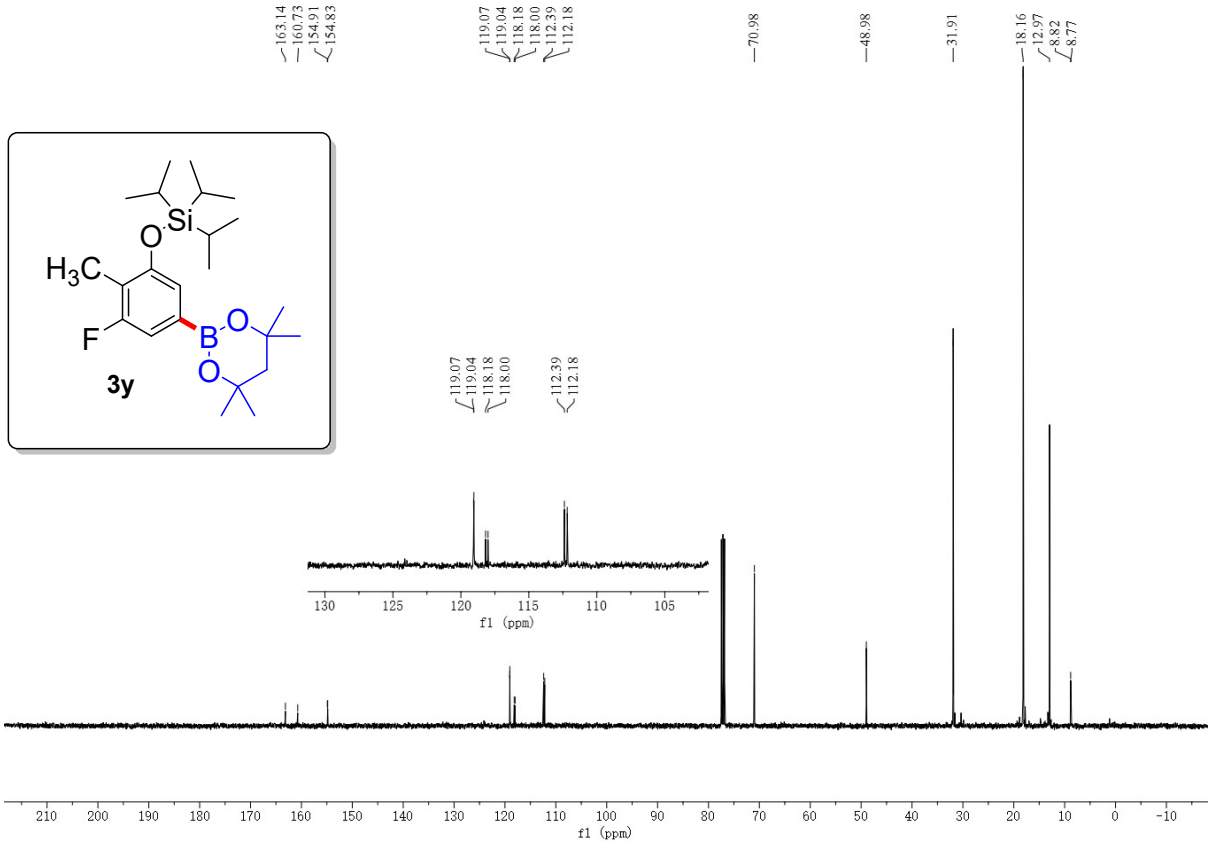

7.26
7.02
1.89
1.40
1.37
1.35
1.33
1.31
1.29
1.28
1.16
1.14
Cl
O
Si
B
O
3w
2.01
1.99
11.77
6.31
36.39
f1 (ppm)

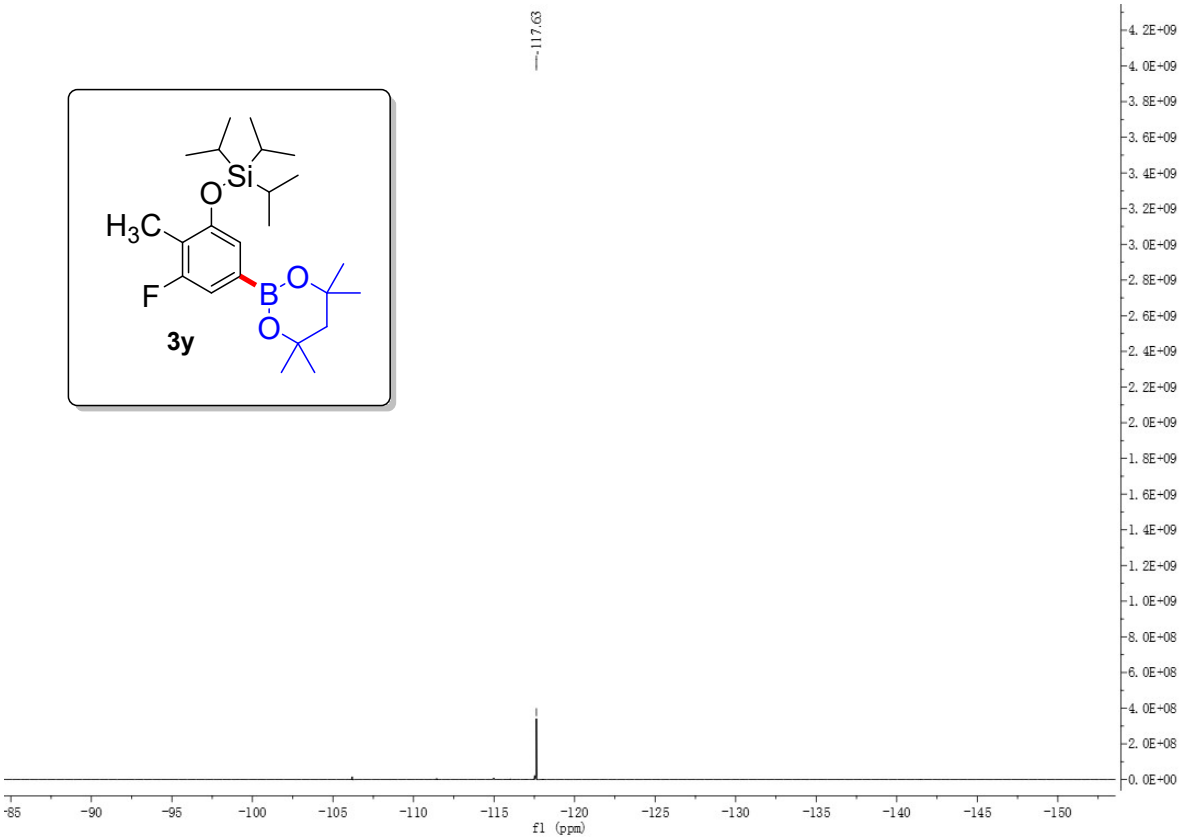

152.57
119.26
117.75
70.92
48.87
31.90
18.13
12.97
Cl
O
Si
B
O
3w
f1 (ppm)

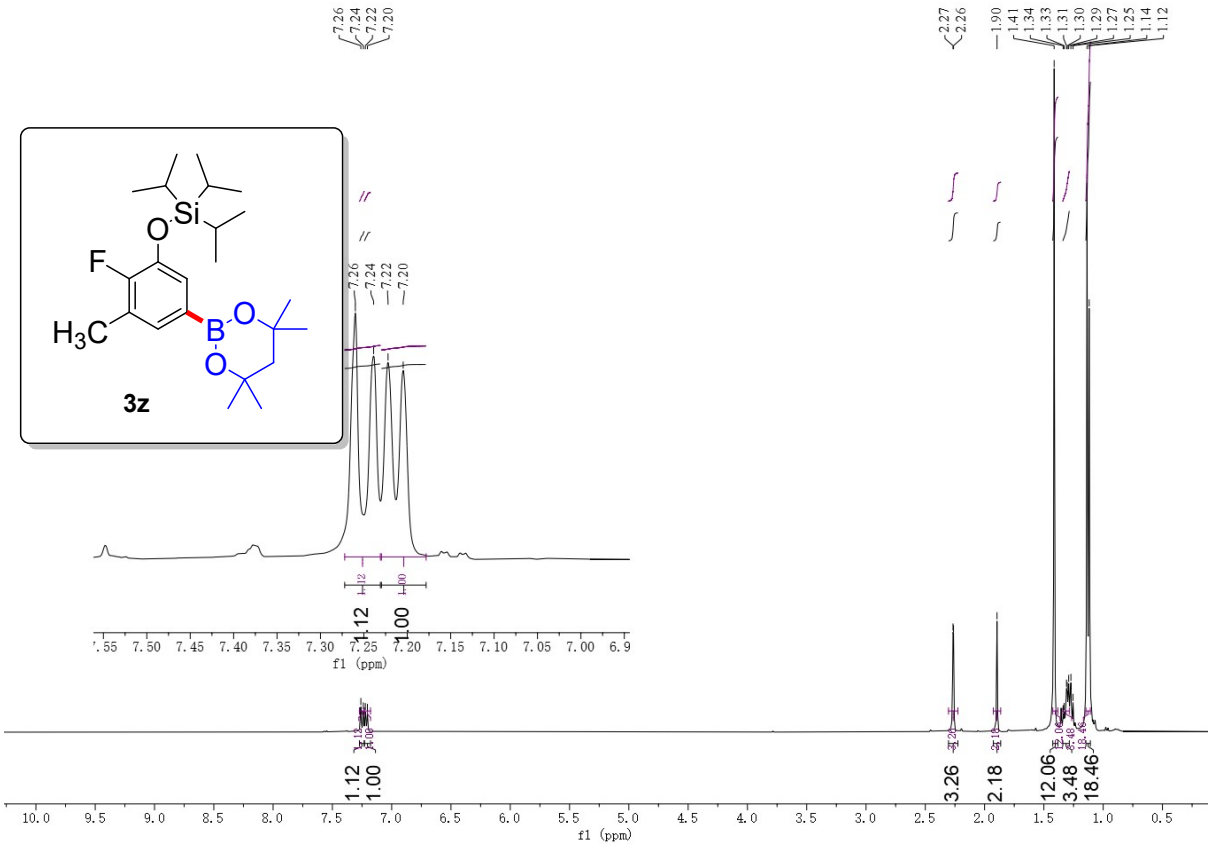

7.53
7.52
7.29
7.28
7.26
1.88
1.49
1.47
1.45
1.39
1.35
1.33
1.31
1.30
1.14
1.13
1.12
Si
Br
O
O
B
O
O
Si
3x
1.00
1.01
2.06
3.24
12.15
3.25
36.33
f1 (ppm)

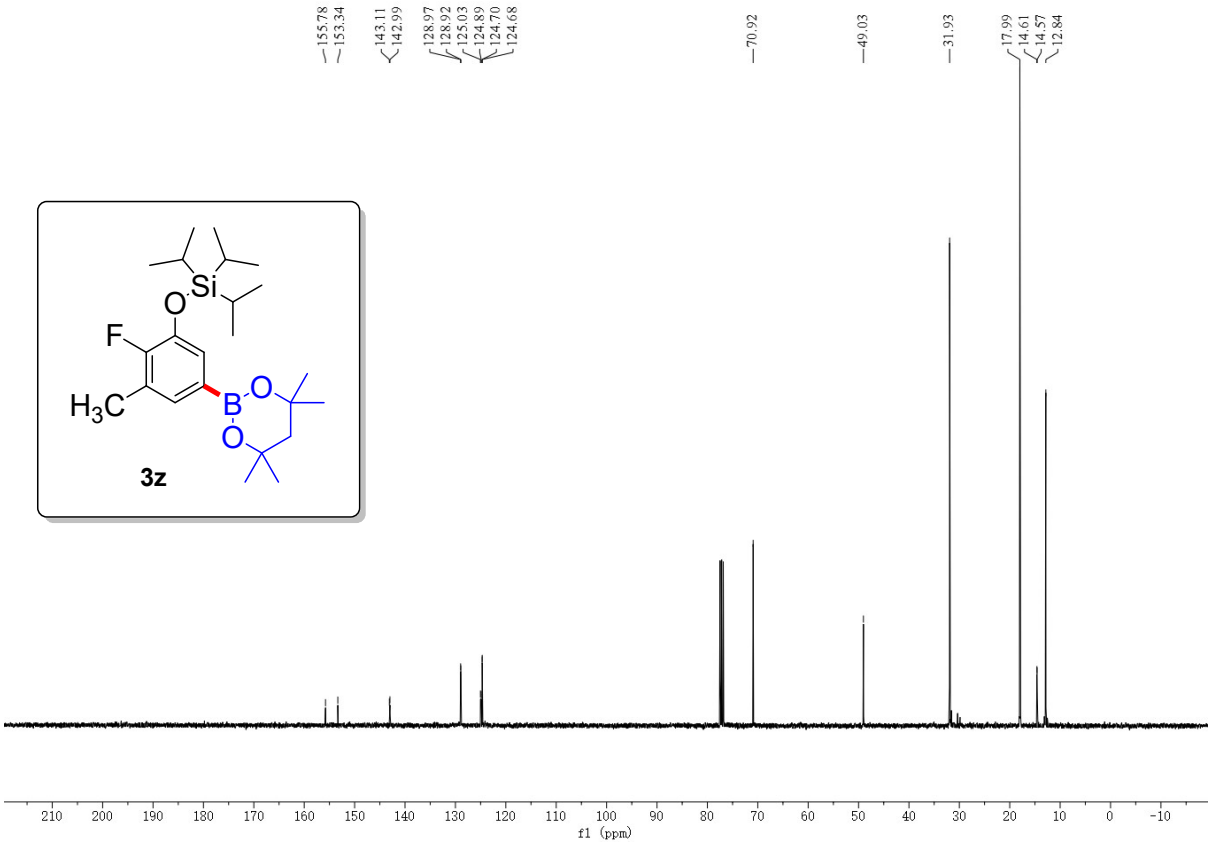

147.68
146.86
130.88
124.45
116.63
70.96
48.92
31.93
18.26
18.15
14.41
13.46
Si
Br
O
O
B
O
O
Si
3x
2500
2000
1500
1000
500
0
f1 (ppm)

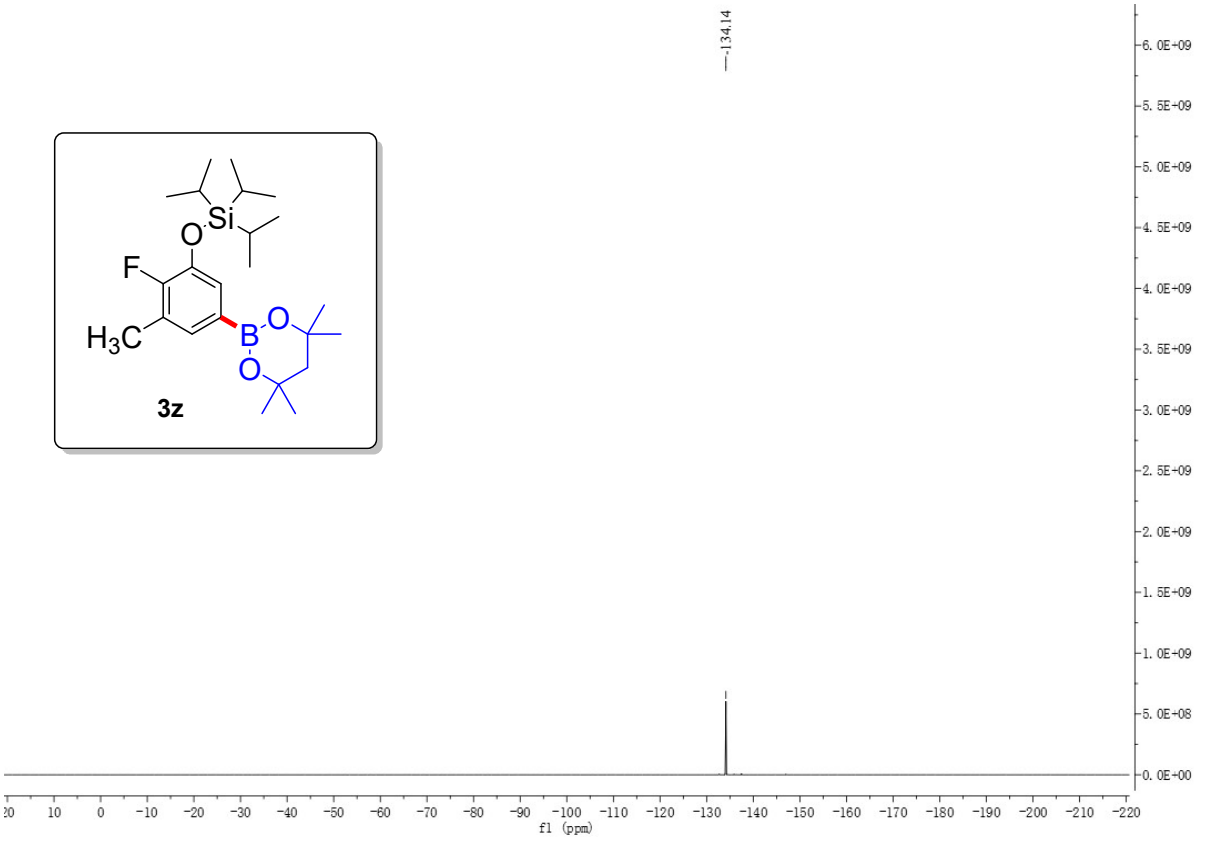

3y
f1 (ppm)

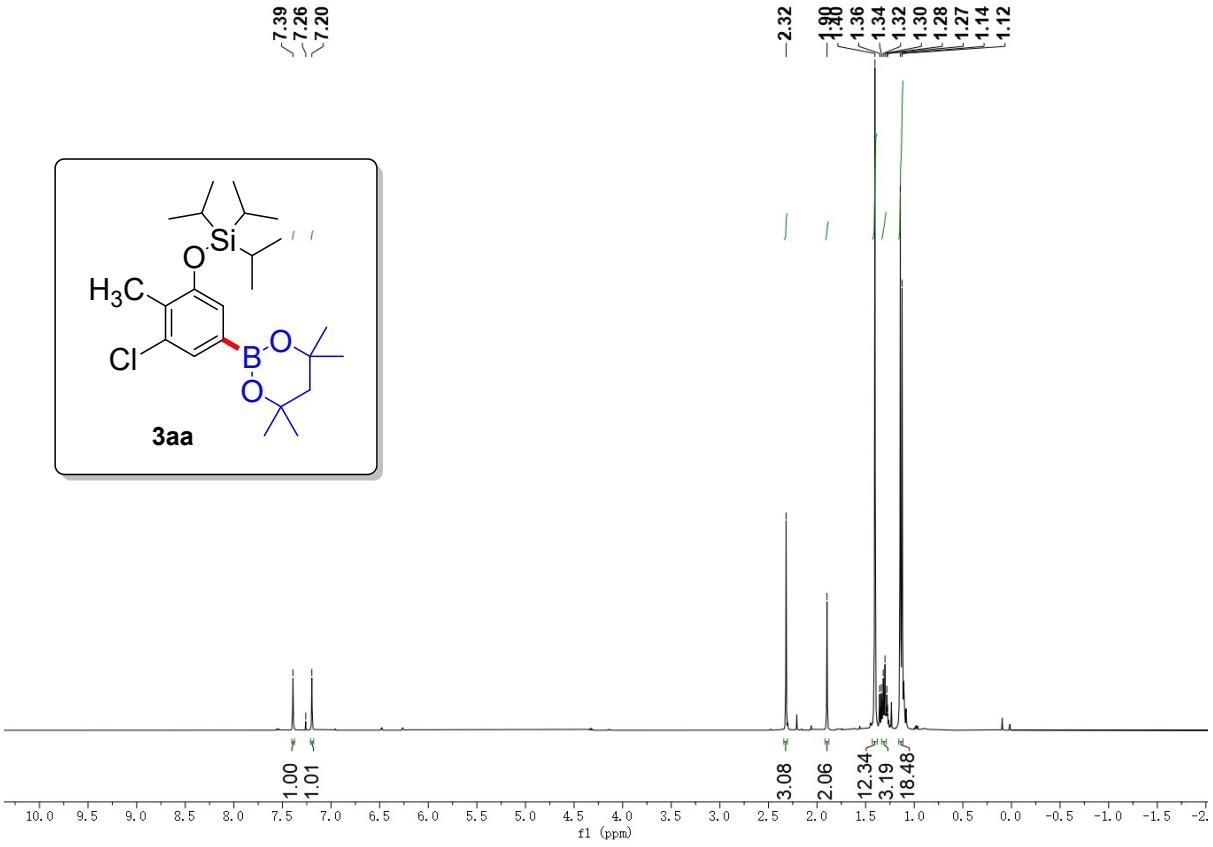

3y
f1 (ppm)

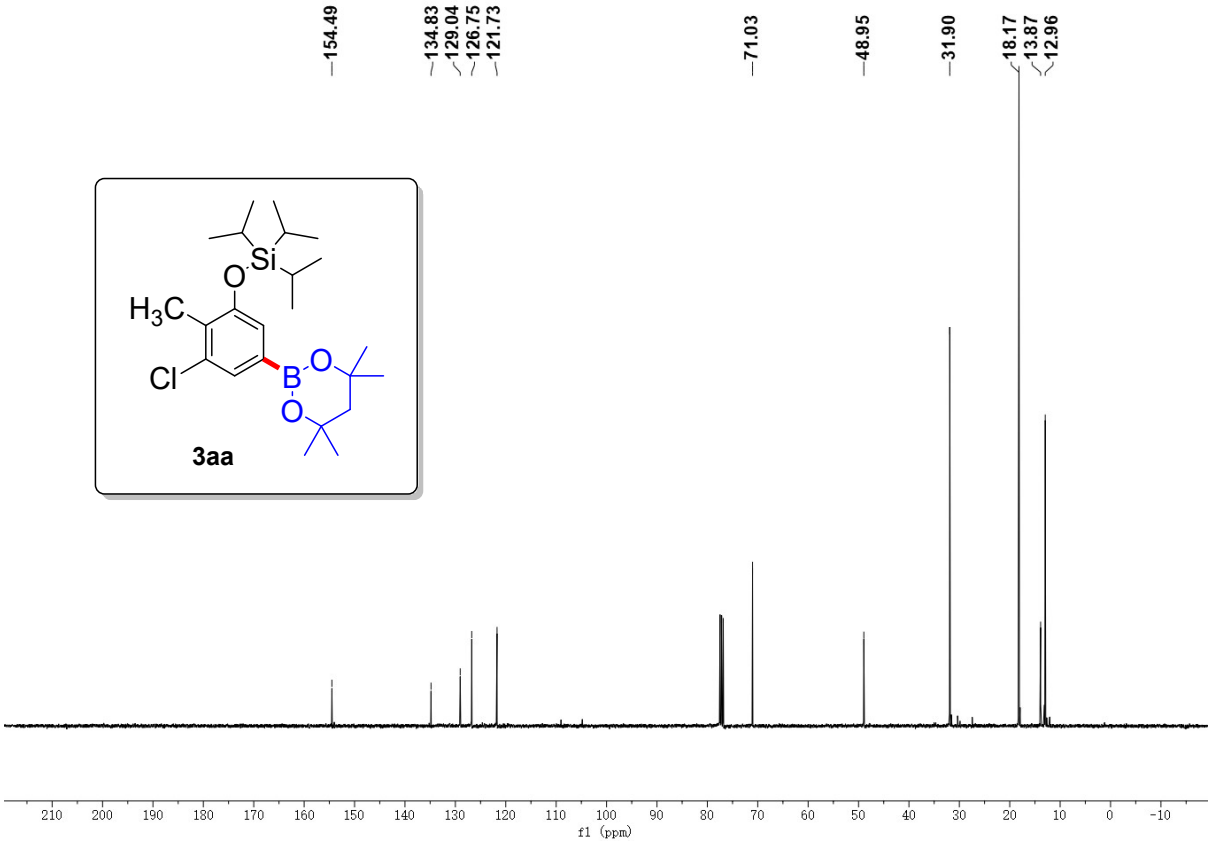

3y
117.63
f1 (ppm)

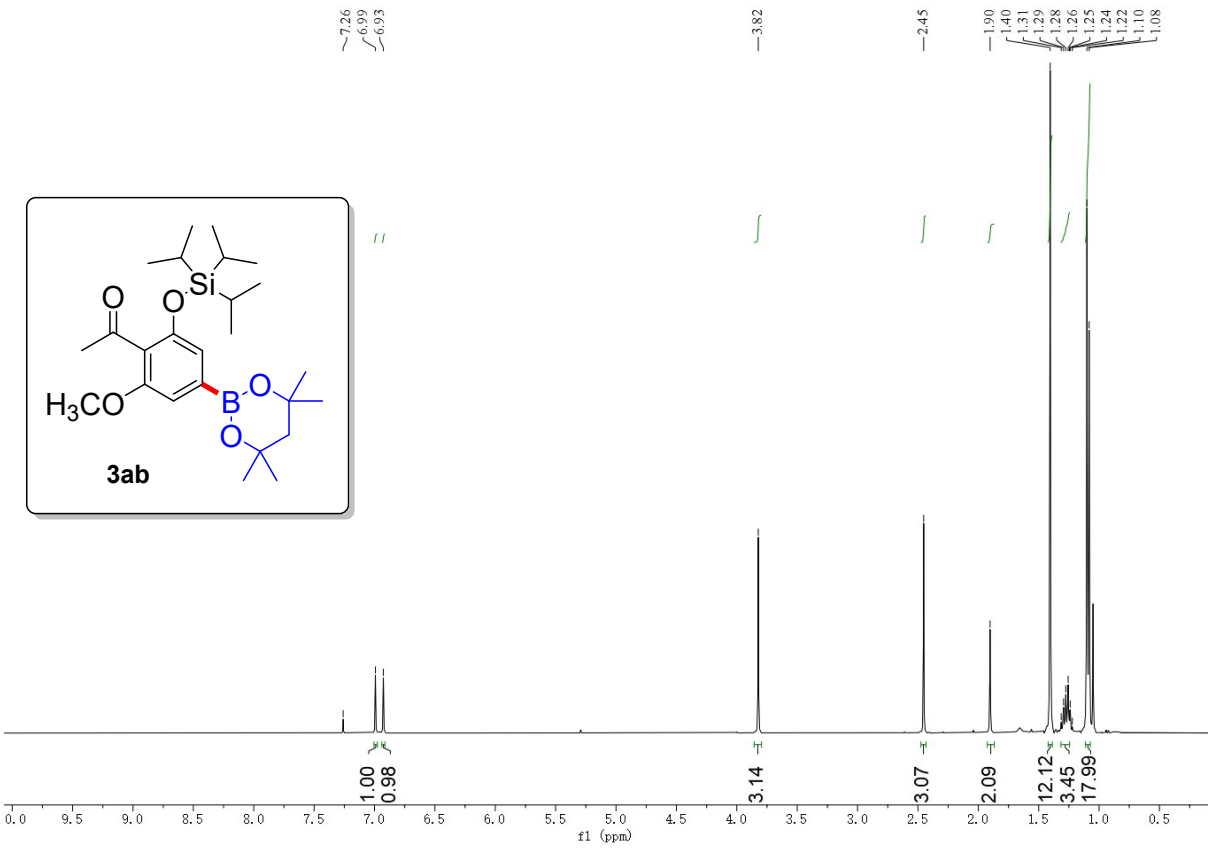

3z
7.26
7.24
7.22
7.20
1.12
1.00
2.27
2.26
1.90
1.41
1.34
1.33
1.31
1.30
1.29
1.27
1.25
1.14
1.12
3.26
2.18
12.06
3.48
18.46
f1 (ppm)


155.78
153.34
143.11
142.99
128.97
128.92
125.03
124.89
124.70
124.68
70.92
49.03
31.93
17.99
14.61
14.57
12.84
Si
O
F
H3C
B
O
O
3z
f1 (ppm)


134.14
Si
O
F
H3C
B
O
O
3z
f1 (ppm)


7.39
7.26
7.20
2.32
1.40
1.36
1.34
1.32
1.30
1.28
1.27
1.14
1.12
Si
O
H3C
Cl
B
O
O
3aa
1.00
1.01
3.08
2.06
12.34
3.19
18.48
f1 (ppm)


154.49
134.83
129.04
126.75
121.73
71.03
48.95
31.90
18.17
13.87
12.96
Si
O
H3C
Cl
B
O
O
3aa
f1 (ppm)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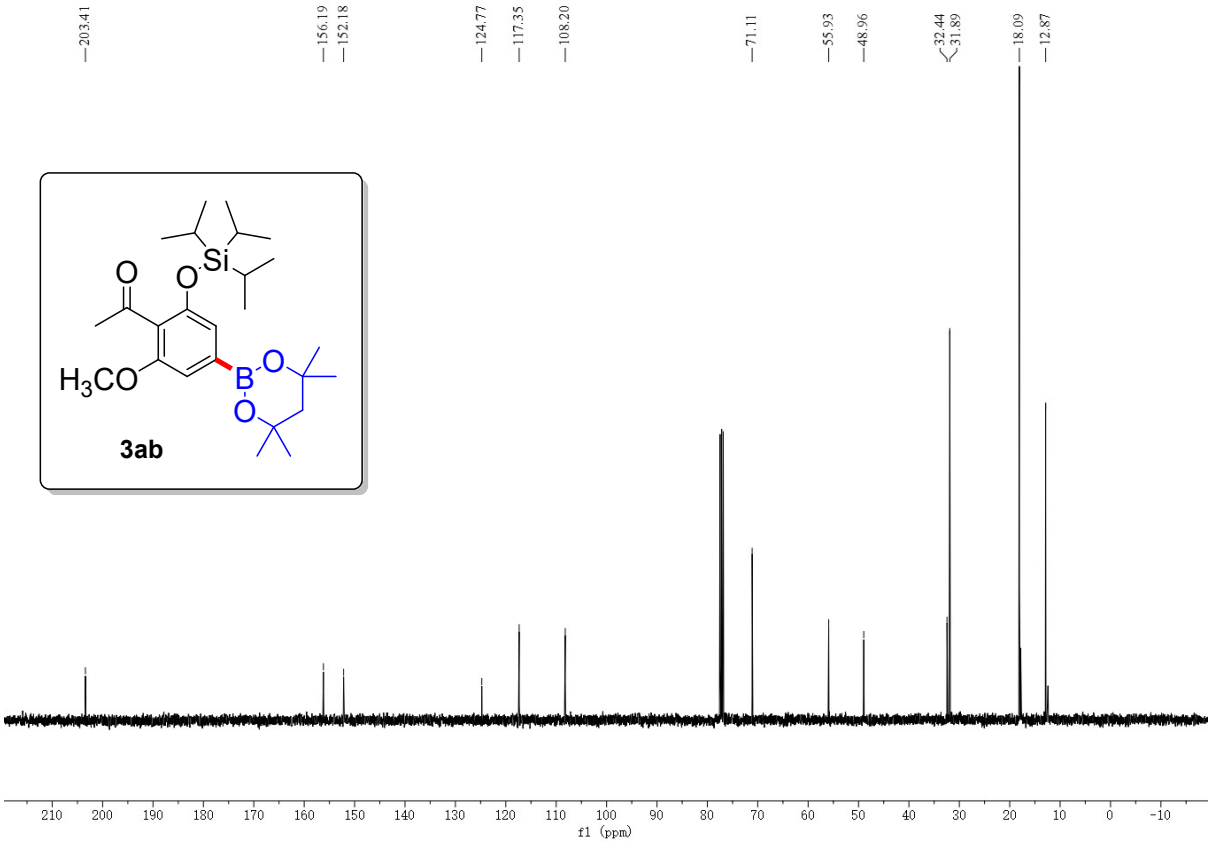
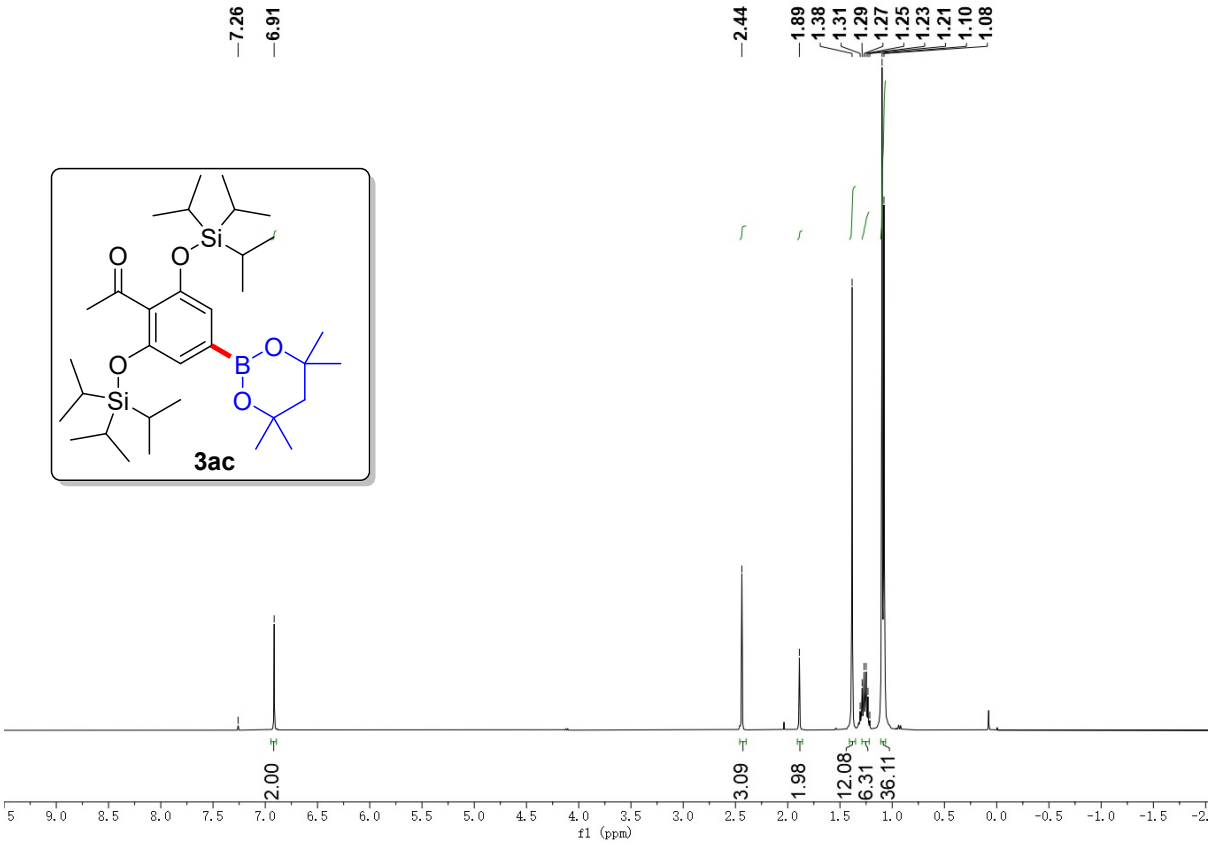
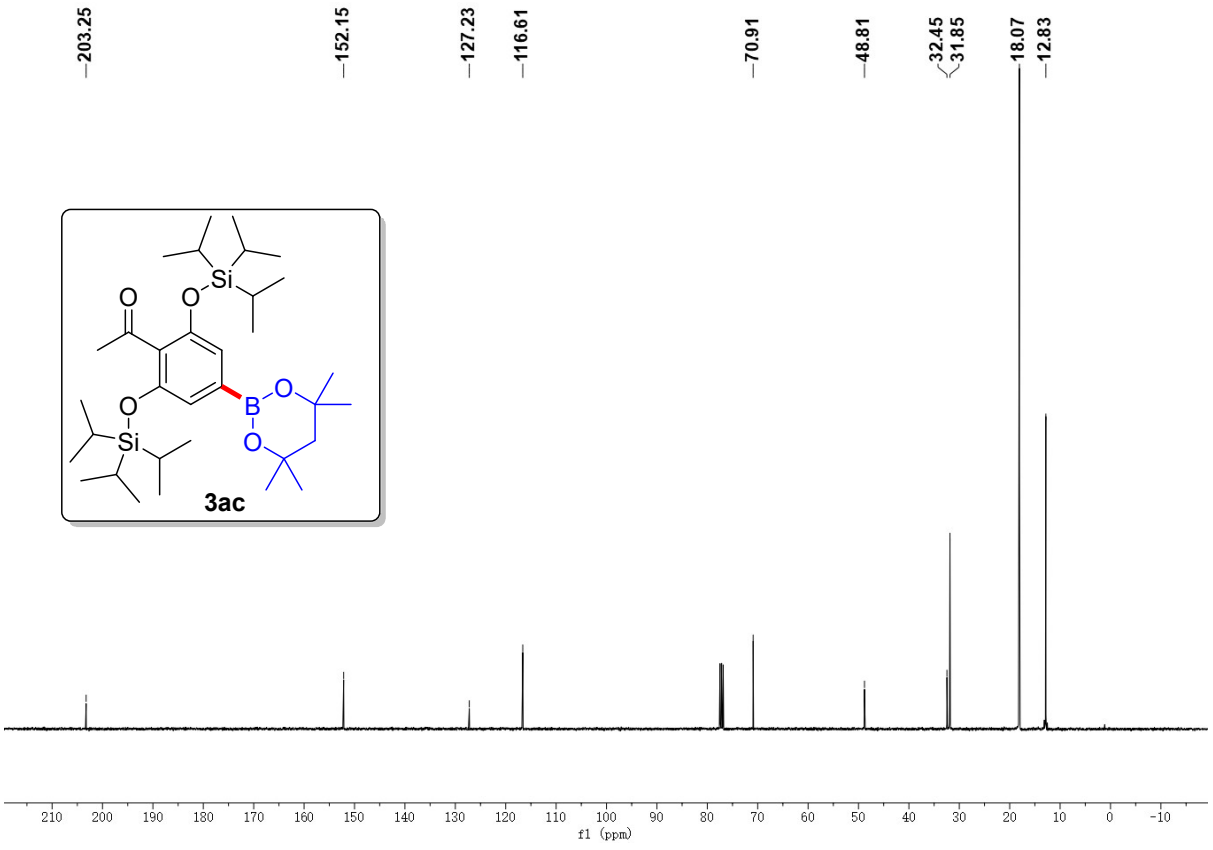
6.99
6.93
3.82
2.45
1.90
1.40
1.31
1.29
1.28
1.26
1.25
1.24
1.22
1.10
1.08
O
O
Si
H3CO
B
O
O
3ab
1.00
0.98
3.14
3.07
2.09
12.12
3.45
17.99
f1 (ppm)


203.41
156.19
152.18
124.77
117.35
108.20
71.11
55.93
48.96
32.44
31.89
18.09
12.87
O
O
Si
H3CO
B
O
O
3ab
f1 (ppm)


7.26
6.91
2.44
1.89
1.38
1.31
1.29
1.27
1.25
1.23
1.21
1.10
1.08
3ac
2.00
3.09
1.98
12.08
6.31
36.11
f1 (ppm)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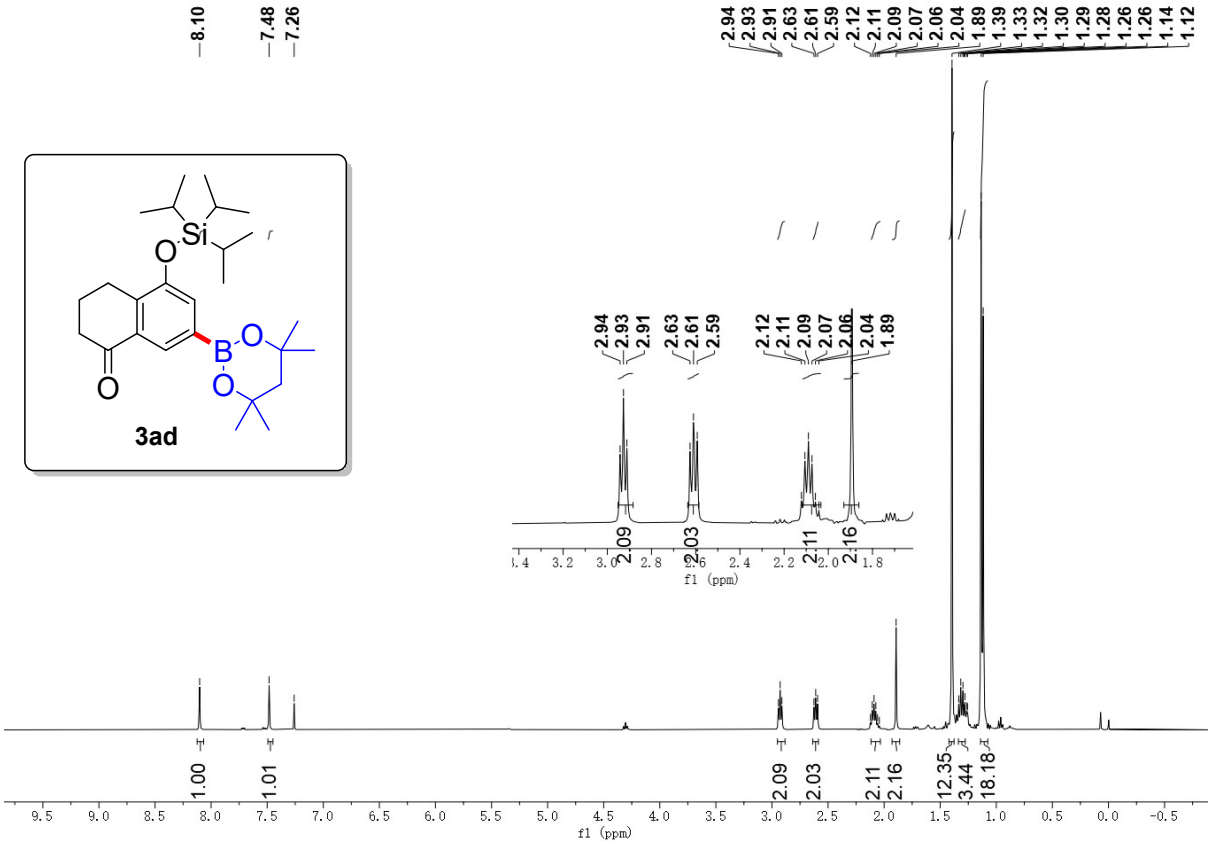
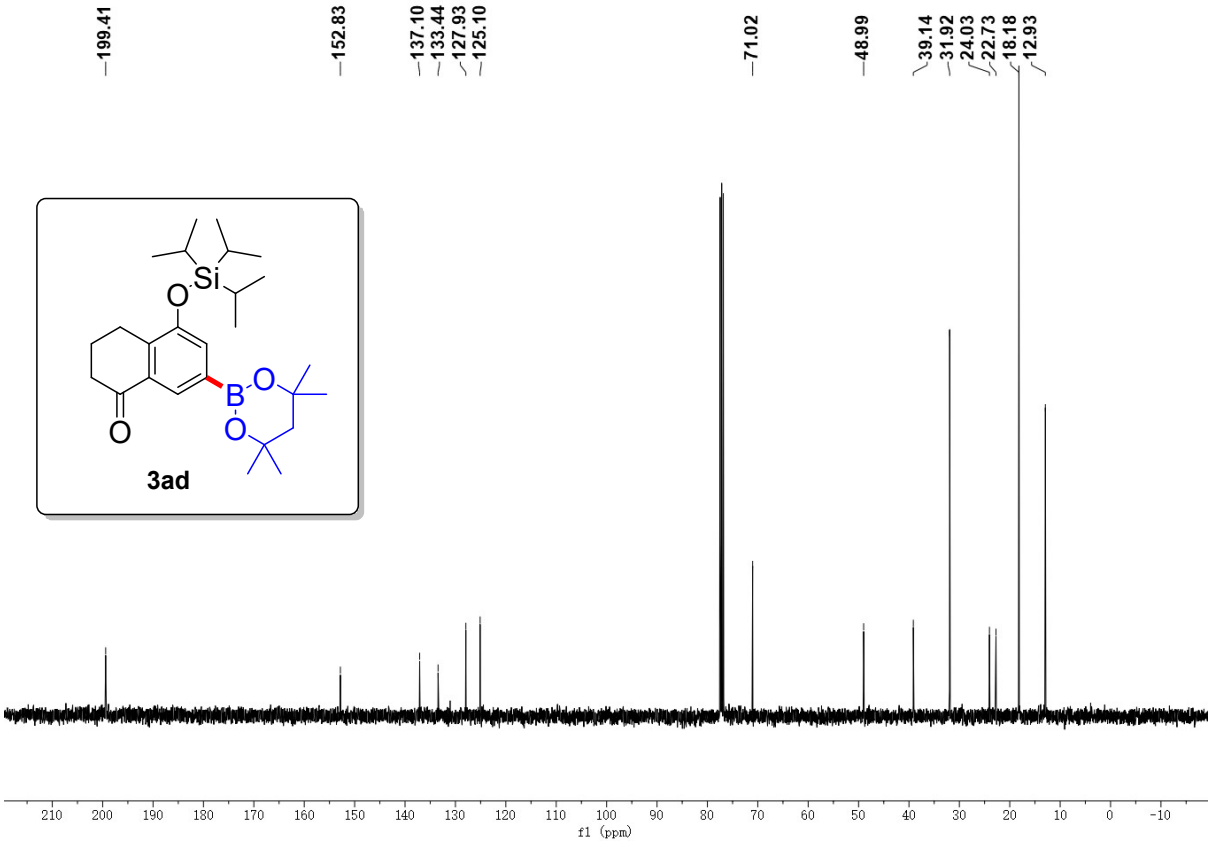
116.61
70.91
48.81
32.45
31.85
18.07
12.83
3ac
f1 (ppm)


8.10
7.48
7.26
2.94
2.93
2.91
2.63
2.61
2.59
2.12
2.11
2.09
2.07
2.06
2.04
1.89
1.39
1.33
1.32
1.30
1.29
1.28
1.26
1.26
1.14
1.12
3ad
f1 (ppm)
1.00
1.01
2.09
2.03
2.11
2.16
12.35
3.44
18.18


199.41
152.83
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133.44
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125.10
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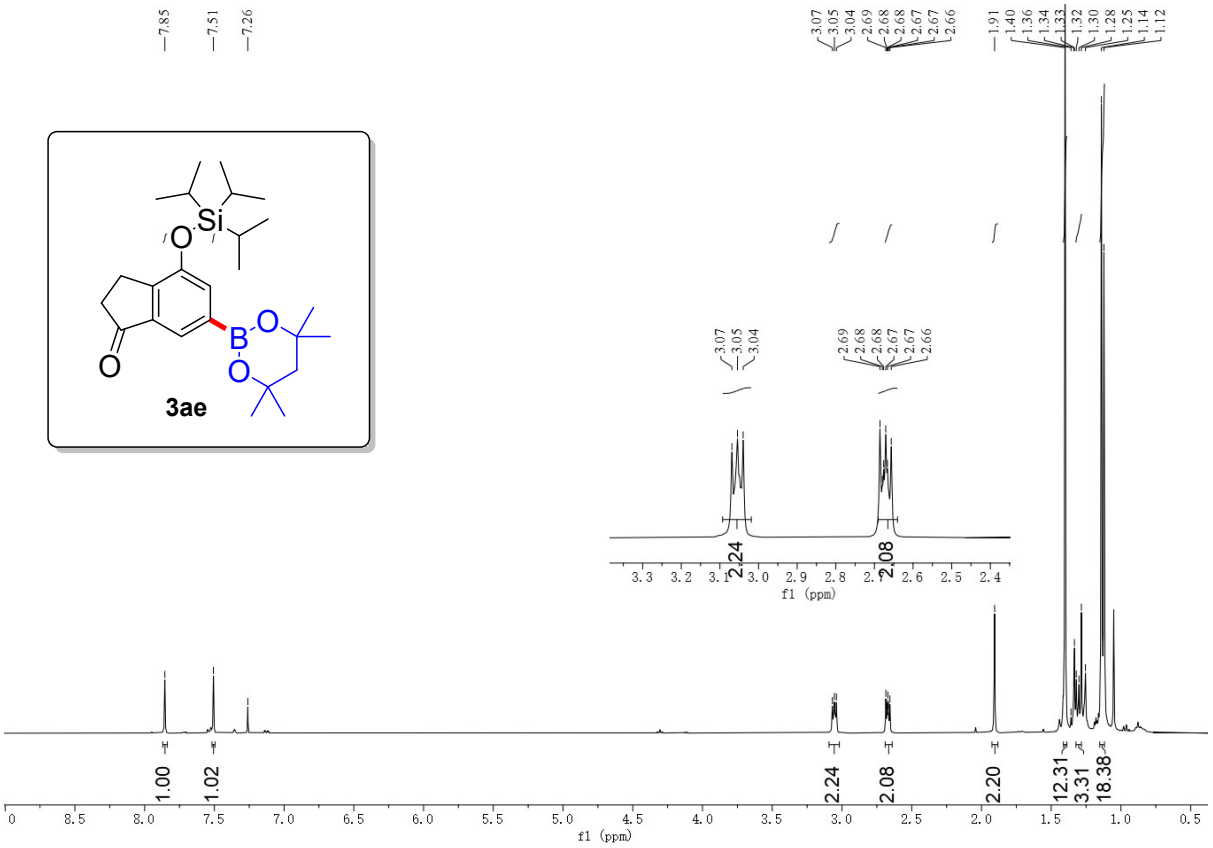
48.99
39.14
31.92
24.03
22.73
18.18
12.93
3ad
f1 (ppm)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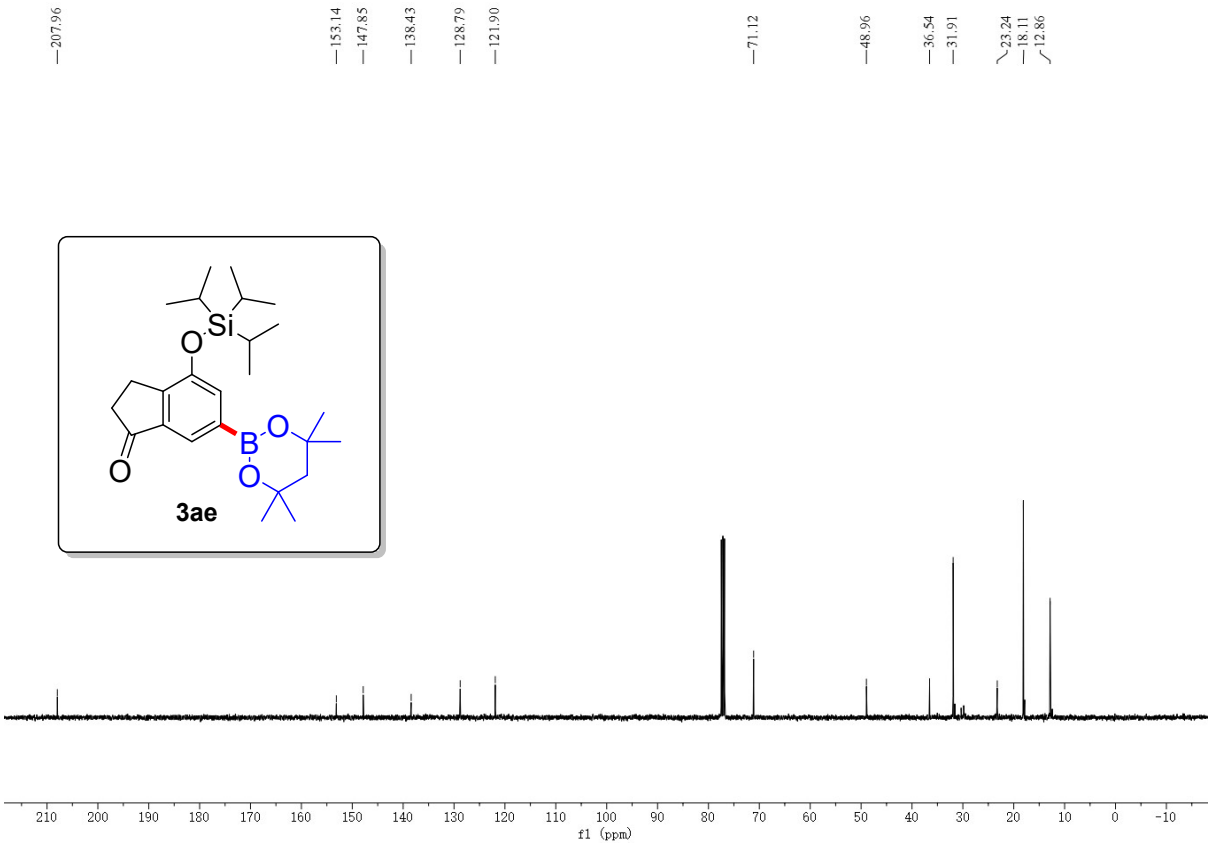
7.51
7.26
3.07
3.05
3.04
2.69
2.68
2.68
2.67
2.67
2.66
1.91
1.40
1.36
1.34
1.33
1.32
1.30
1.28
1.25
1.14
1.12
Si
O
B
O
O
O
3ae
2.24
2.08
f1 (ppm)
1.00
1.02
2.24
2.08
2.20
12.31
3.31
18.38
f1 (ppm)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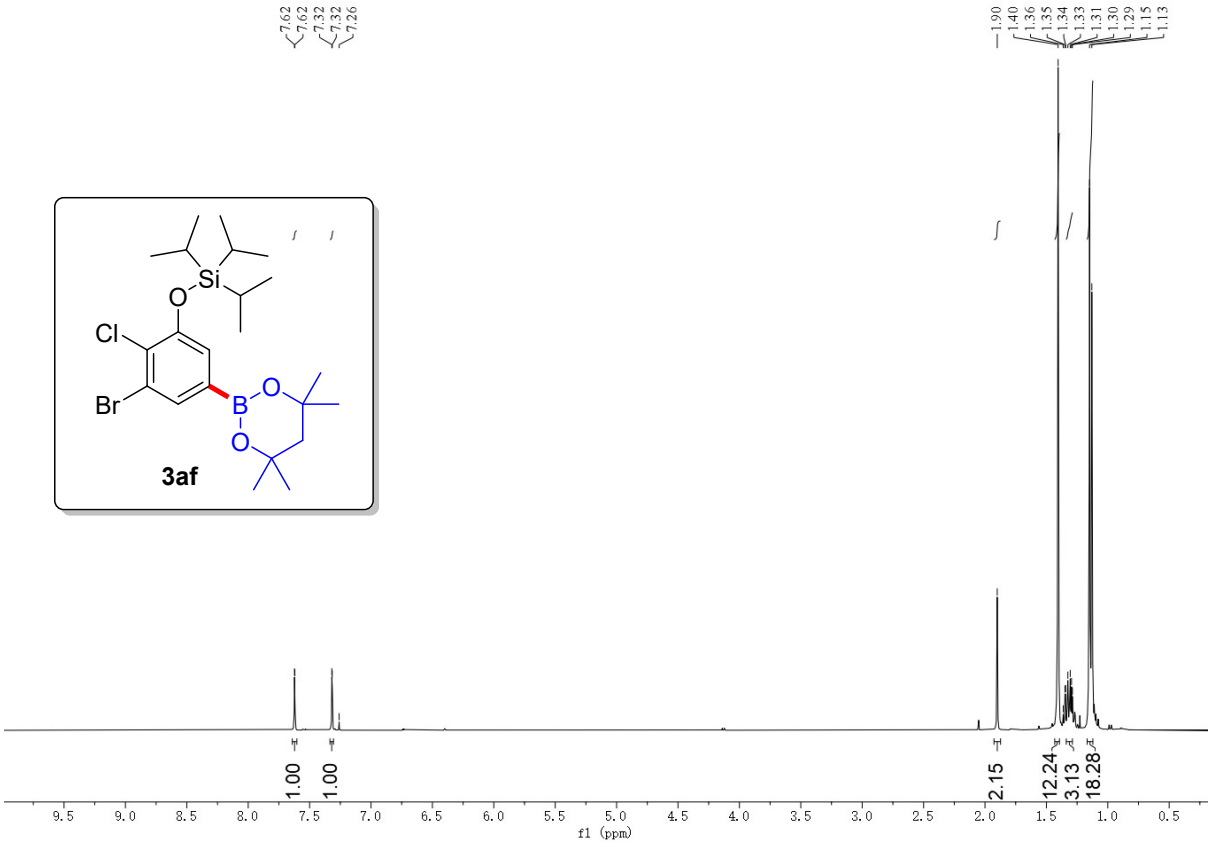
138.43
128.79
121.90
71.12
48.96
36.54
31.91
23.24
18.11
12.86
Si
O
B
O
O
O
3ae
f1 (ppm)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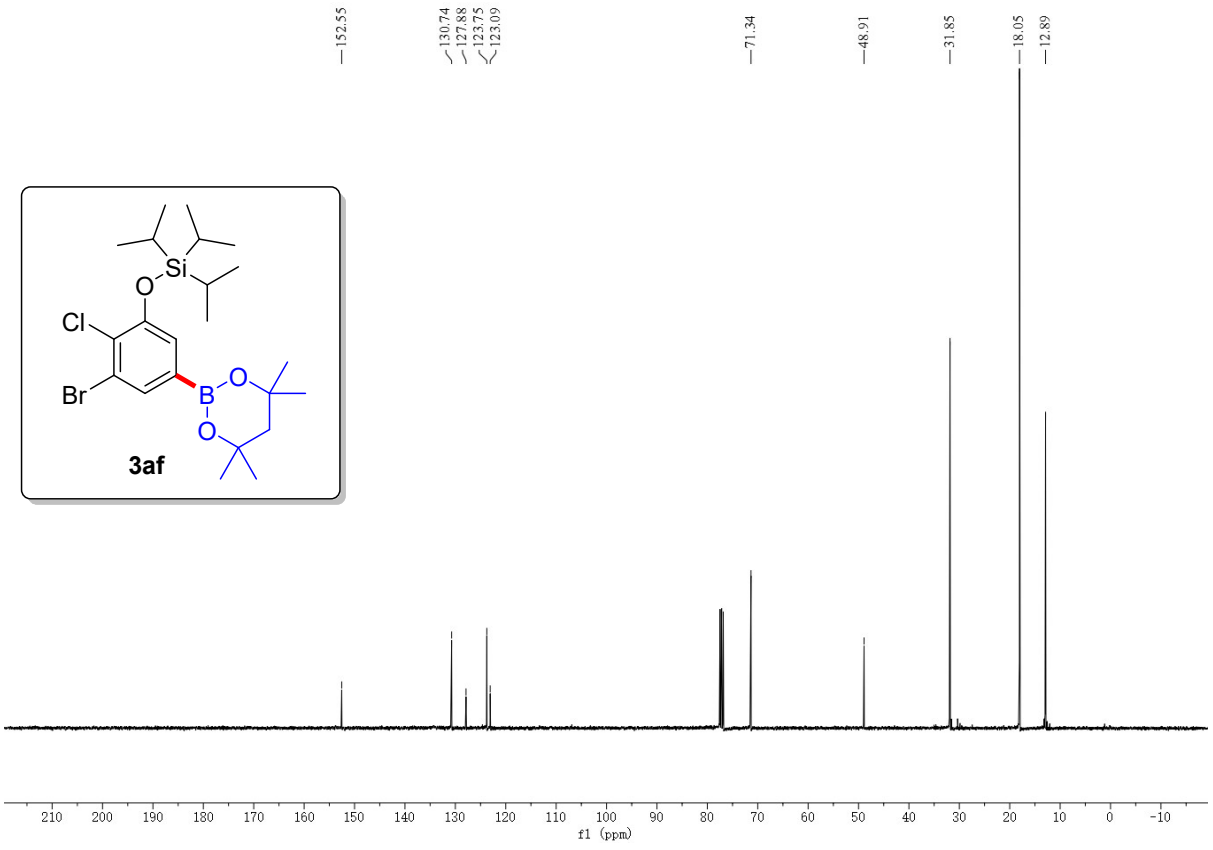
7.62
7.32
7.32
7.26
1.90
1.40
1.36
1.35
1.34
1.33
1.31
1.30
1.29
1.15
1.13
Si
O
Cl
Br
B
O
O
3af
1.00
1.00
2.15
12.24
3.13
18.28
f1 (ppm)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130.74
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123.75
123.09
71.34
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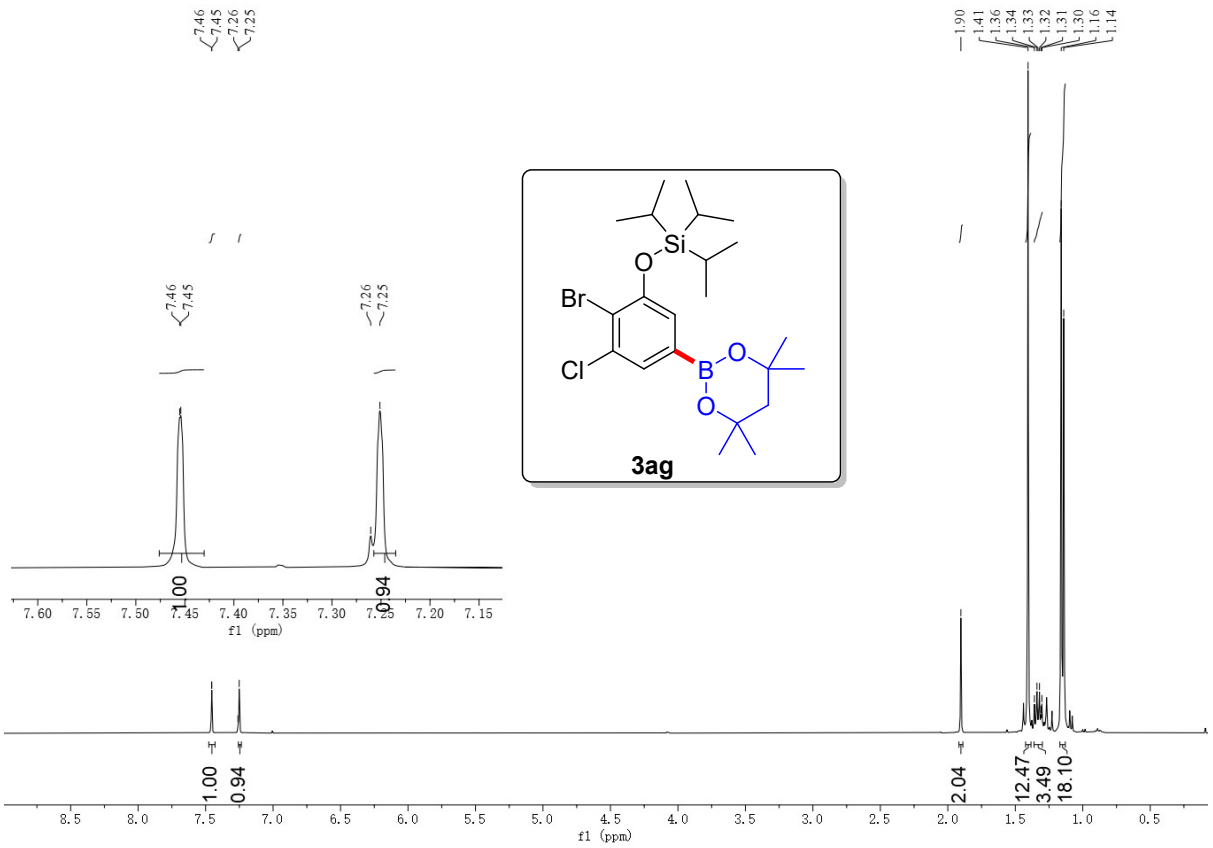
31.85
18.05
12.89
Si
O
Cl
Br
B
O
O
3af
f1 (ppm)


7.46
7.45
7.26
7.25
1.90
1.41
1.36
1.34
1.33
1.32
1.31
1.30
1.16
1.14
Br
Cl
Si
O
B
O
O
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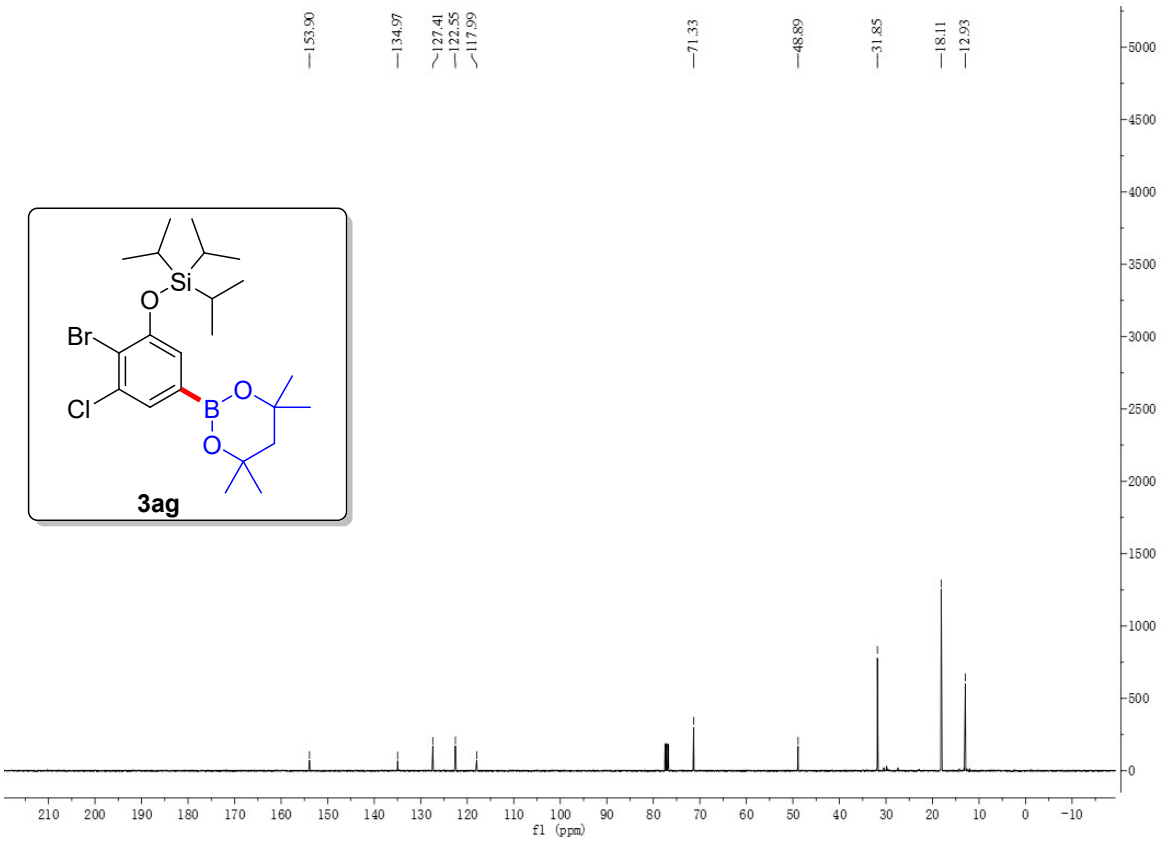
1.00
0.94
2.04
12.47
3.49
18.10
f1 (ppm)


153.90
134.97
127.41
122.55
117.99
71.33
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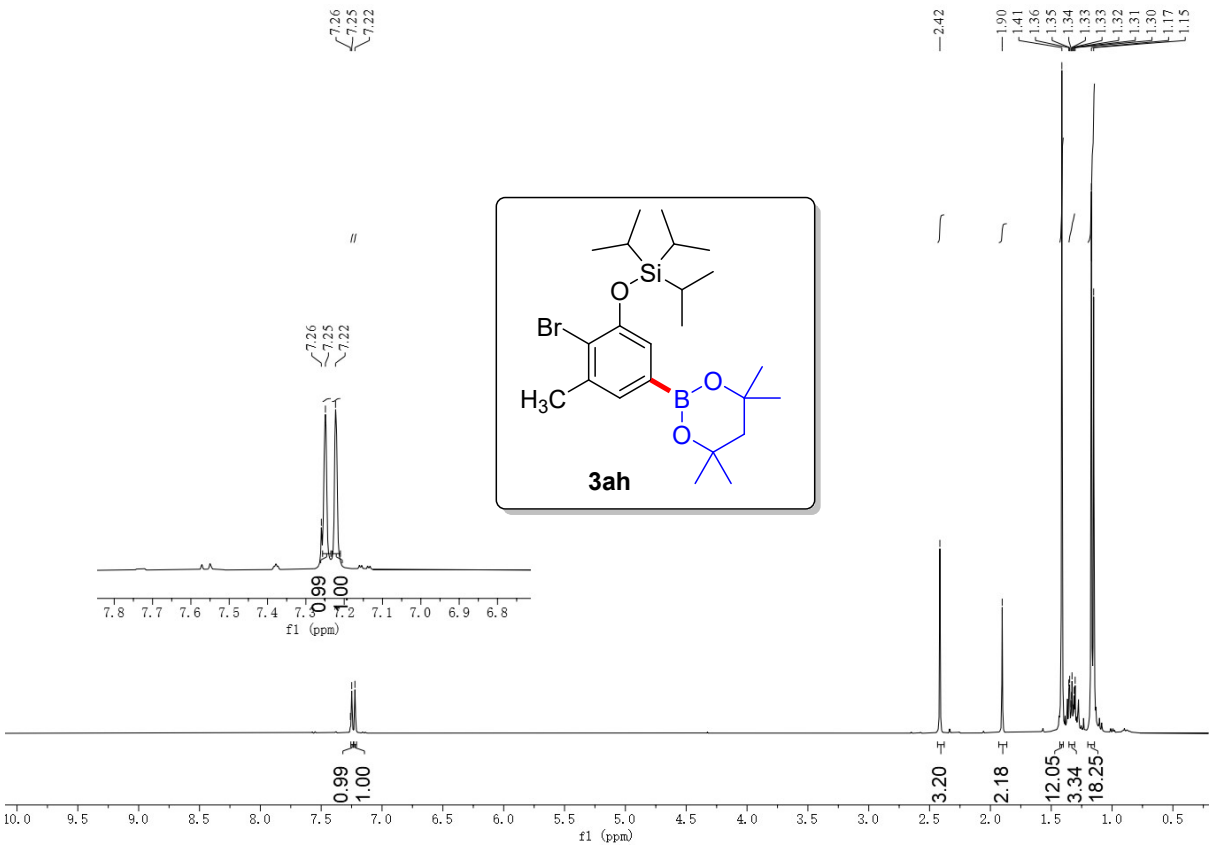
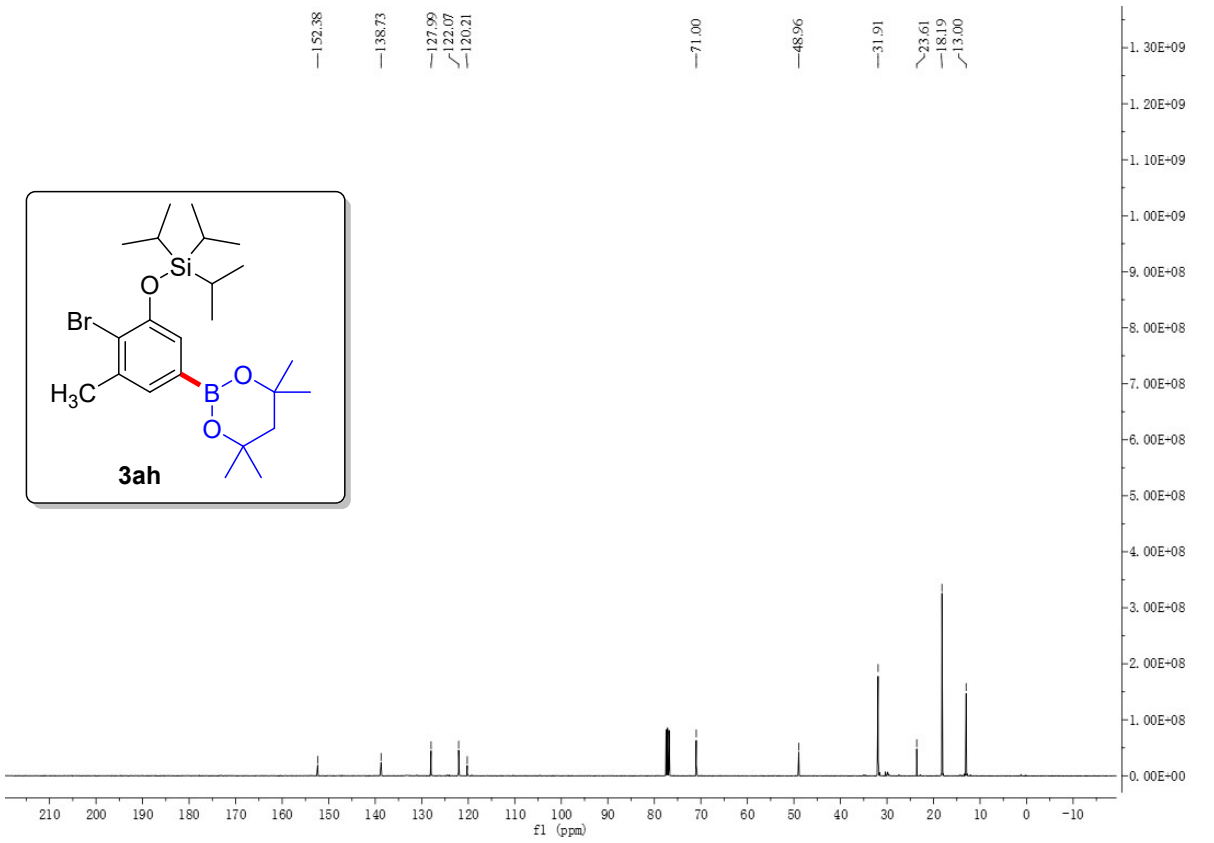
31.85
18.11
12.93
Br
Cl
Si
O
B
O
O
3ag
f1 (ppm)


7.26
7.25
7.22
2.42
1.90
1.41
1.36
1.35
1.34
1.33
1.33
1.32
1.31
1.30
1.17
1.15
Br
O
Si
H3C
B
O
O
3ah
0.99
1.00
f1 (ppm)
3.20
2.18
12.05
3.34
18.25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127.99
122.07
120.21
71.00
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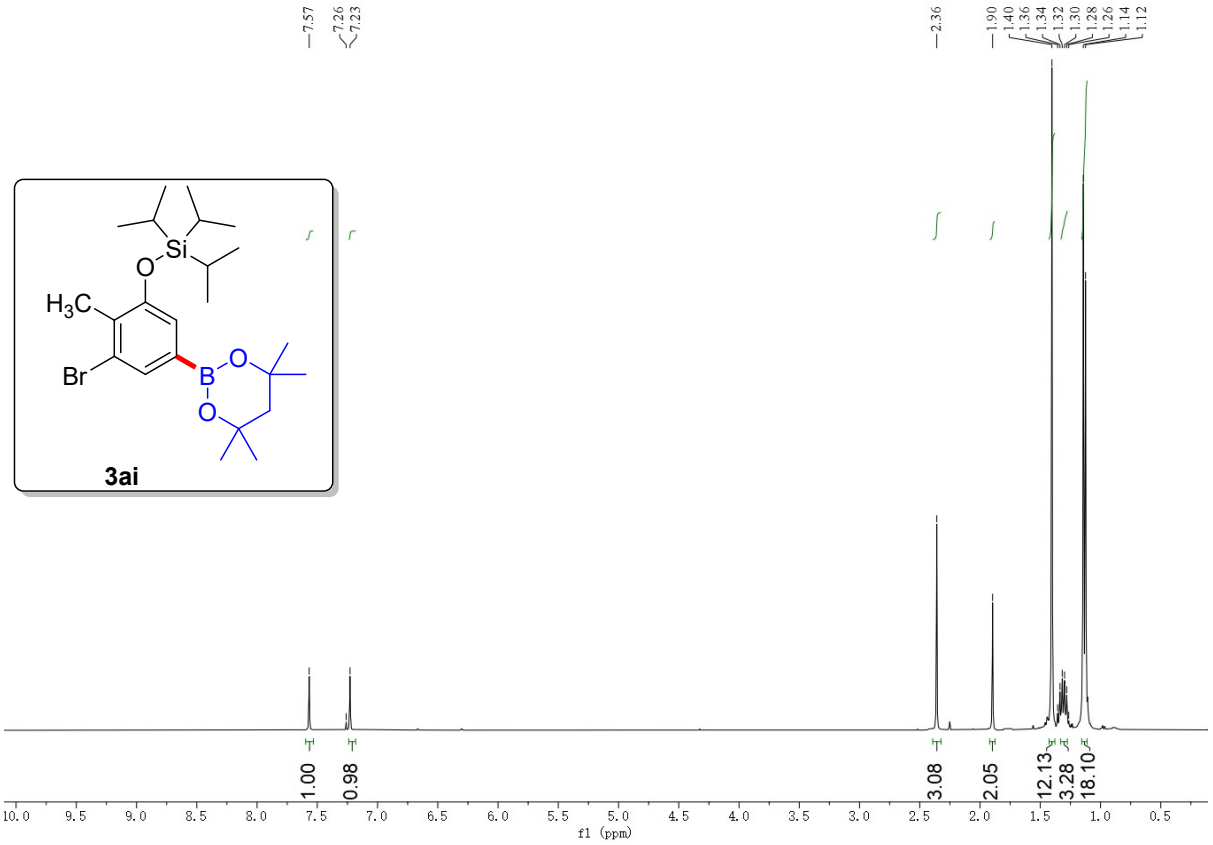
31.91
23.61
18.19
13.00
Br
O
Si
H3C
B
O
O
3ah
f1 (ppm)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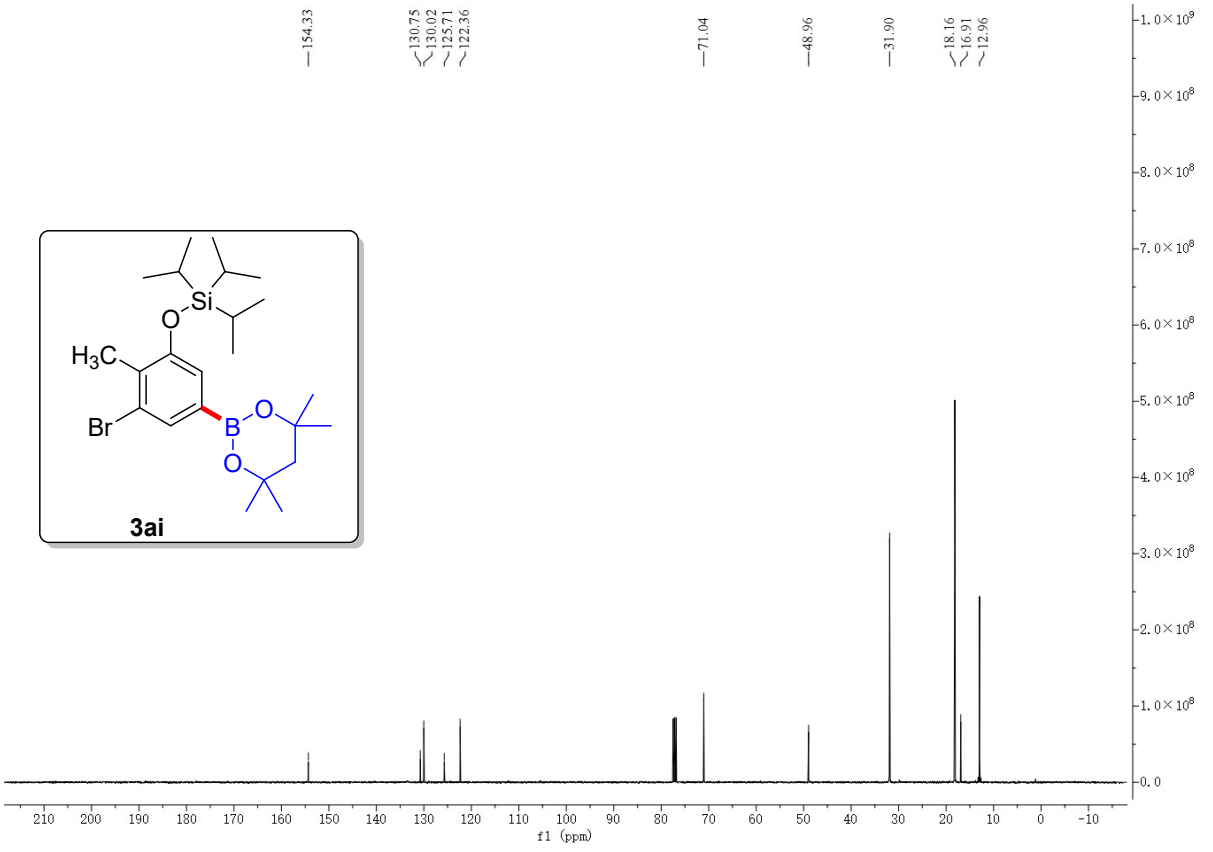
7.26
7.23
2.36
1.90
1.40
1.36
1.34
1.32
1.30
1.28
1.26
1.14
1.12
Si
O
H3C
Br
B
O
O
3ai
1.00
0.98
3.08
2.05
12.13
3.28
18.10
f1 (ppm)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130.75
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125.71
122.36
71.04
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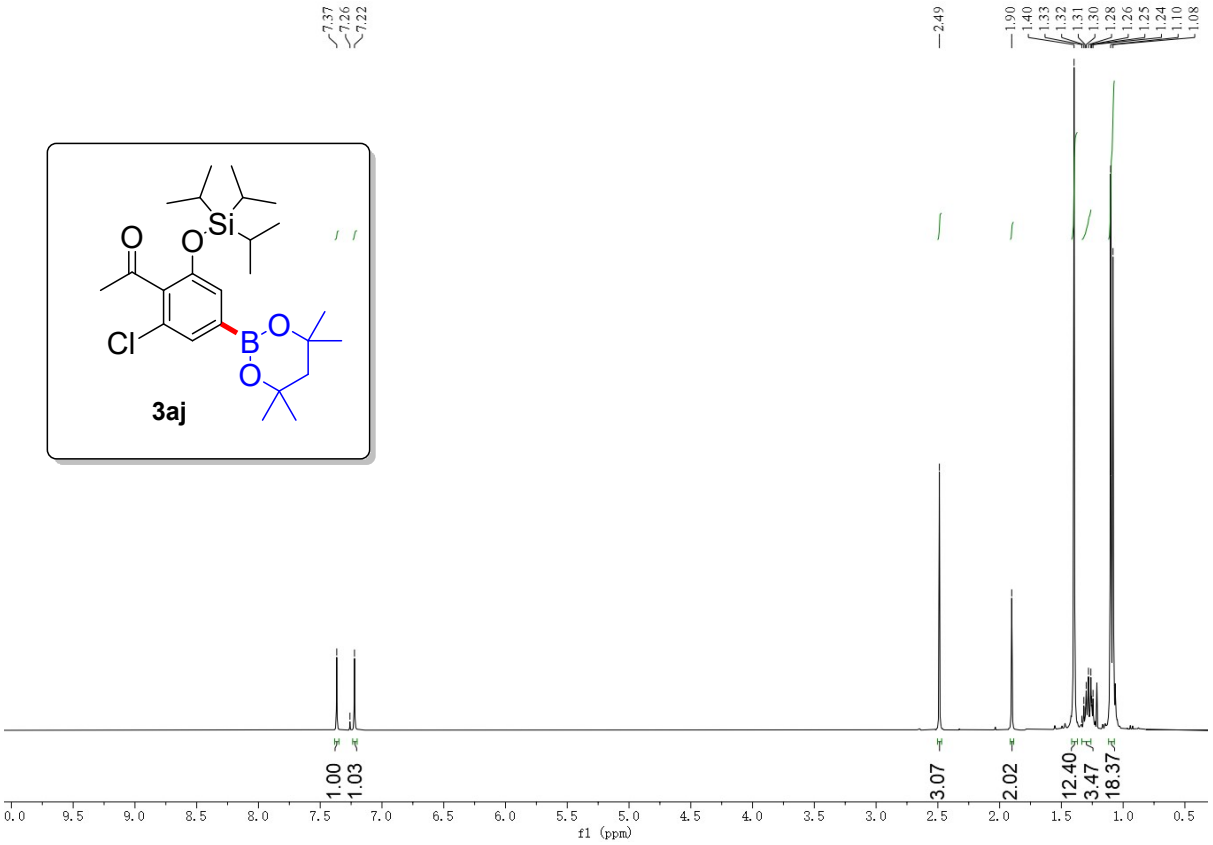
31.90
18.16
16.91
12.96
Si
O
H3C
Br
B
O
O
3ai
f1 (ppm)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7.26
7.22
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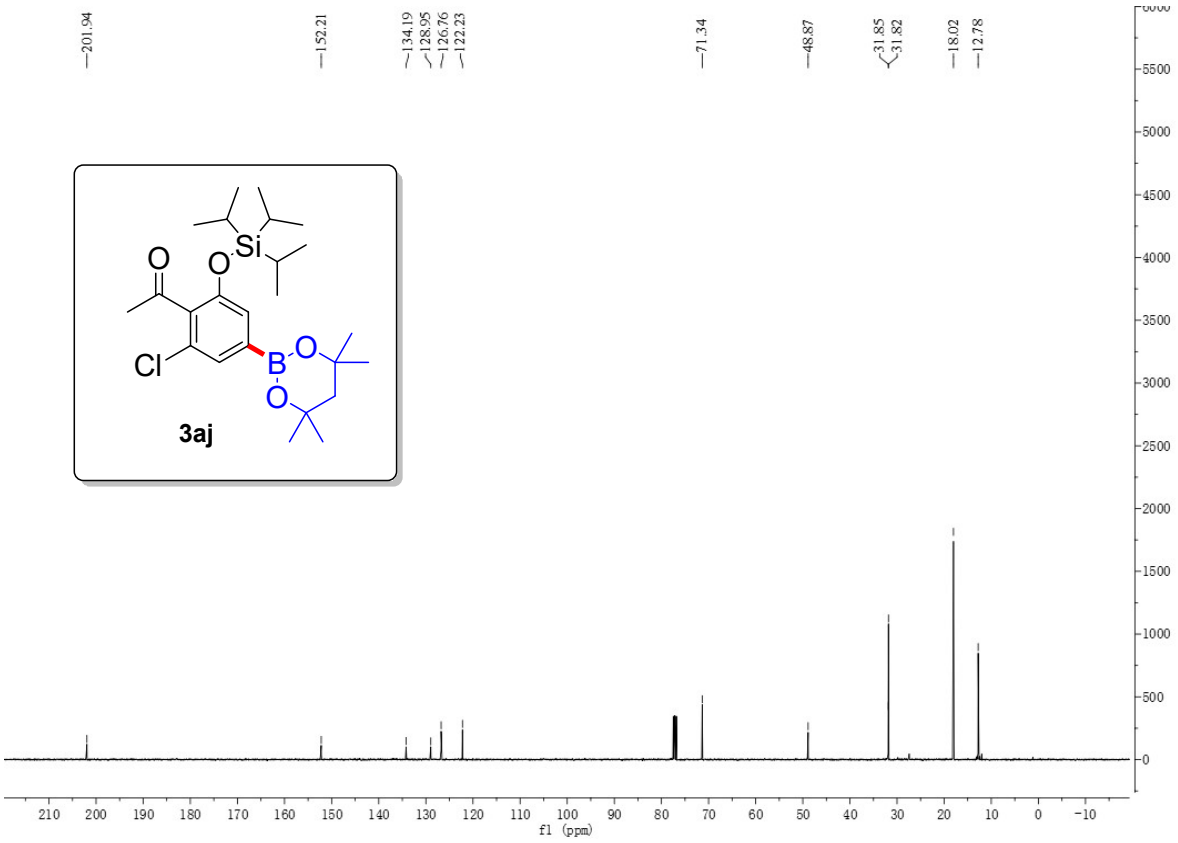
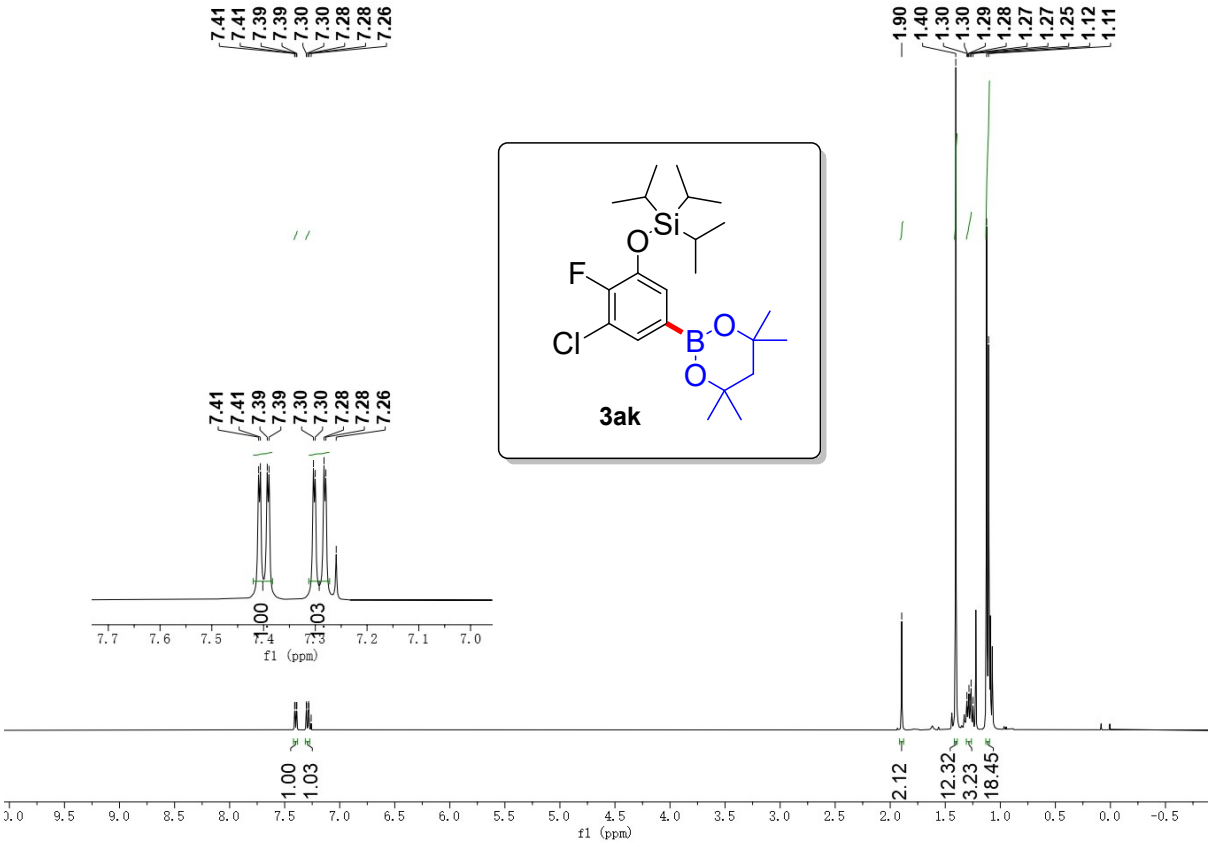
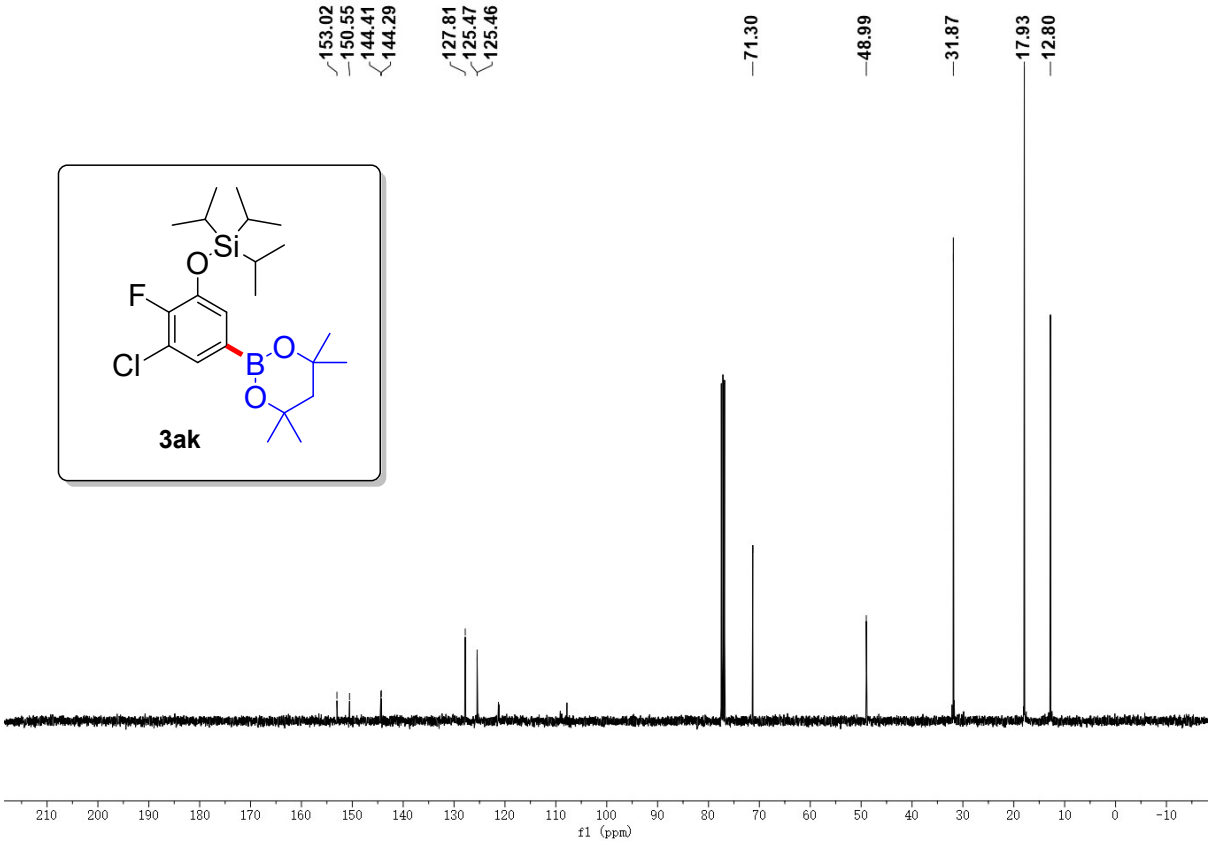
1.40
1.33
1.32
1.31
1.30
1.28
1.26
1.25
1.24
1.10
1.08
Si
O
O
Cl
B
O
O
3aj
1.00
1.03
3.07
2.02
12.40
3.47
18.37
f1 (ppm)


201.94
152.21
134.19
128.95
126.76
122.23
71.34
48.87
31.85
31.82
18.02
12.78
Si
O
O
Cl
B
O
O
3aj
f1 (ppm)


7.41
7.41
7.39
7.39
7.30
7.30
7.28
7.28
7.26
1.90
1.40
1.30
1.30
1.29
1.28
1.27
1.27
1.25
1.12
1.11
Si
O
F
Cl
B
O
O
3ak
1.00
1.03
2.12
12.32
3.23
18.45
f1 (ppm)


153.02
150.55
144.41
144.29
127.81
125.47
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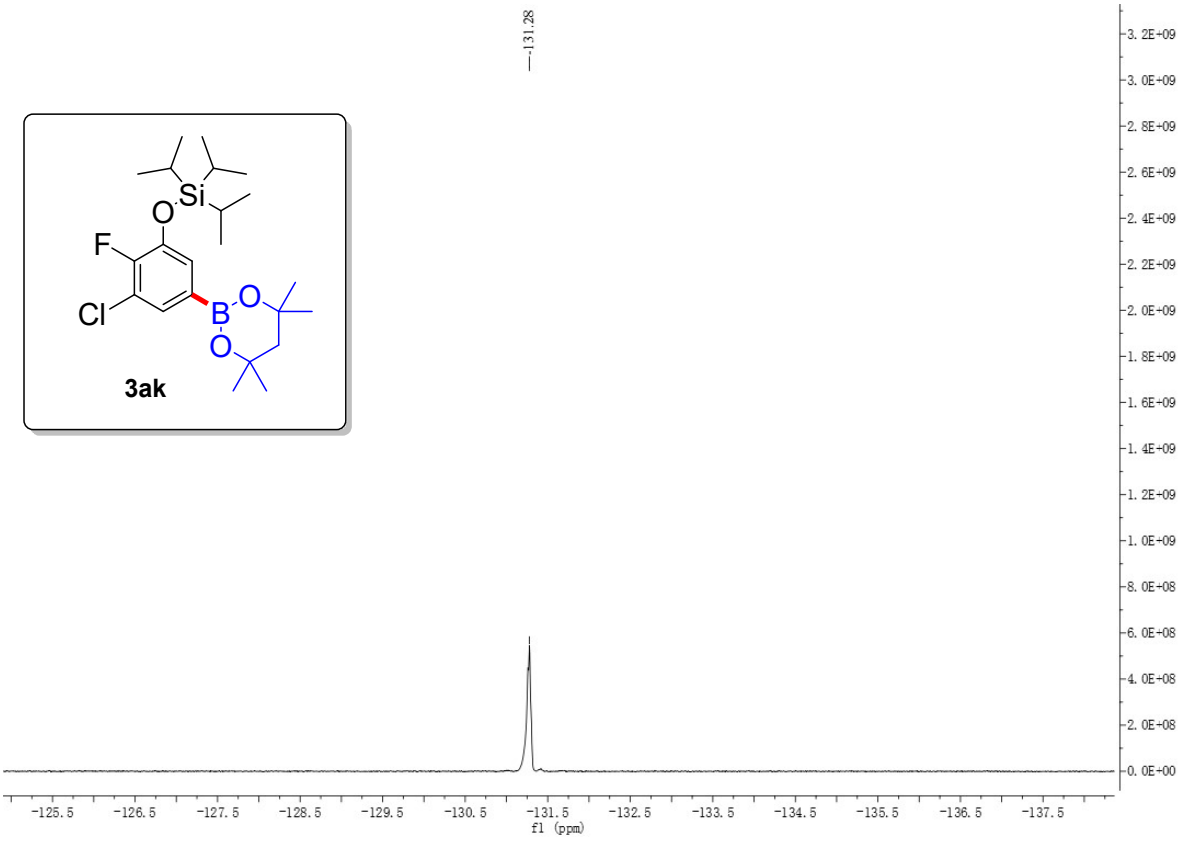
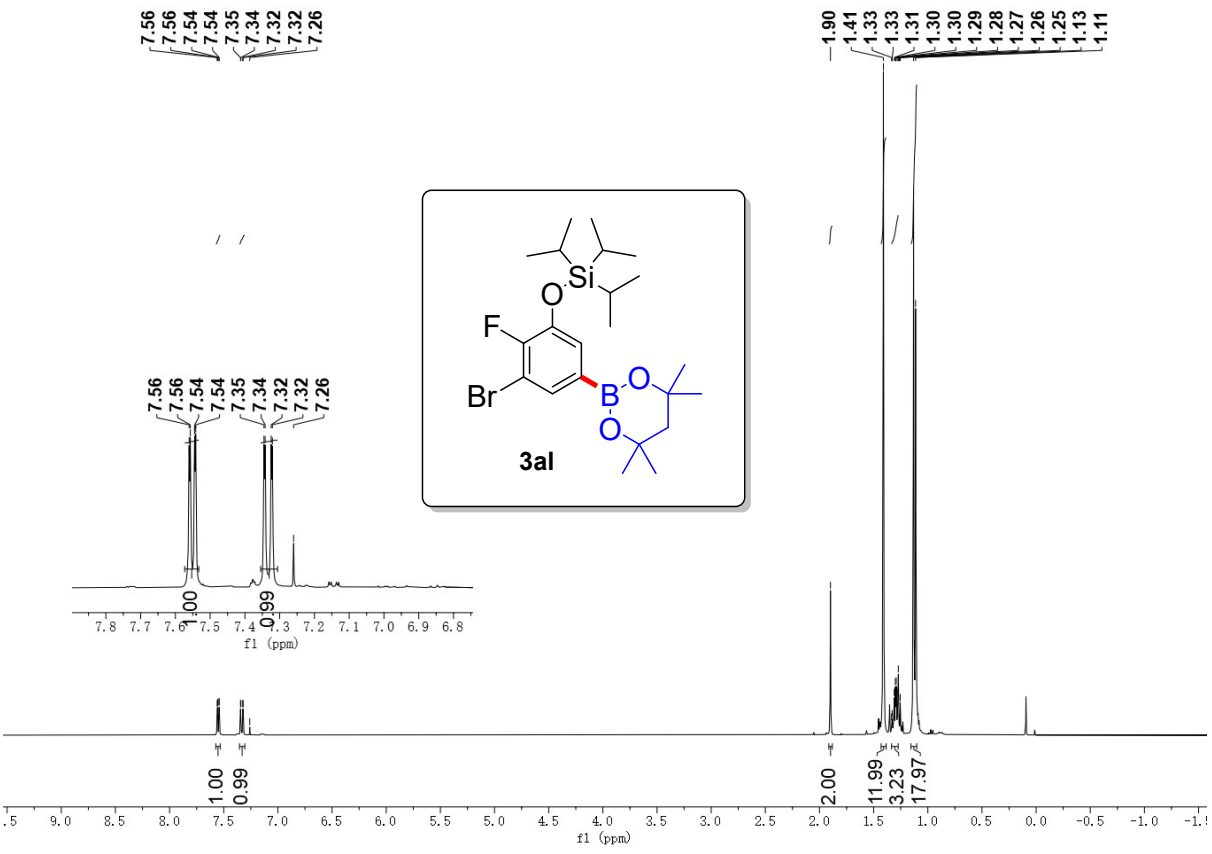
71.30
48.99
31.87
17.93
12.80
Si
O
F
Cl
B
O
O
3ak
f1 (ppm)


Si
O
F
Cl
B
O
O
3ak
-131.28
f1 (ppm)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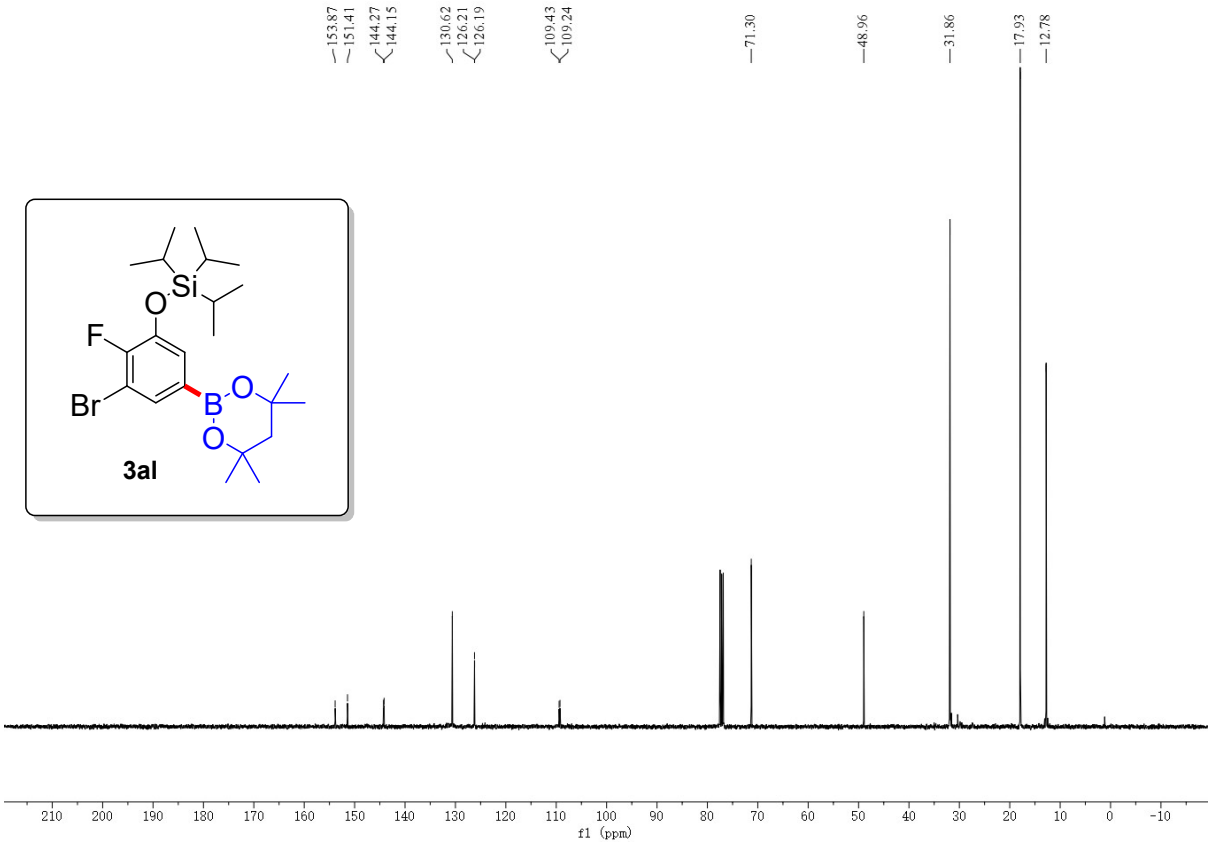
7.56
7.54
7.54
7.35
7.34
7.32
7.32
7.26
1.90
1.41
1.33
1.33
1.31
1.30
1.30
1.29
1.28
1.27
1.26
1.25
1.13
1.11
Si
O
F
Br
B
O
O
3al
1.00
0.99
2.00
11.99
3.23
17.97
f1 (ppm)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151.41
144.27
144.15
130.62
126.21
126.19
109.43
109.24
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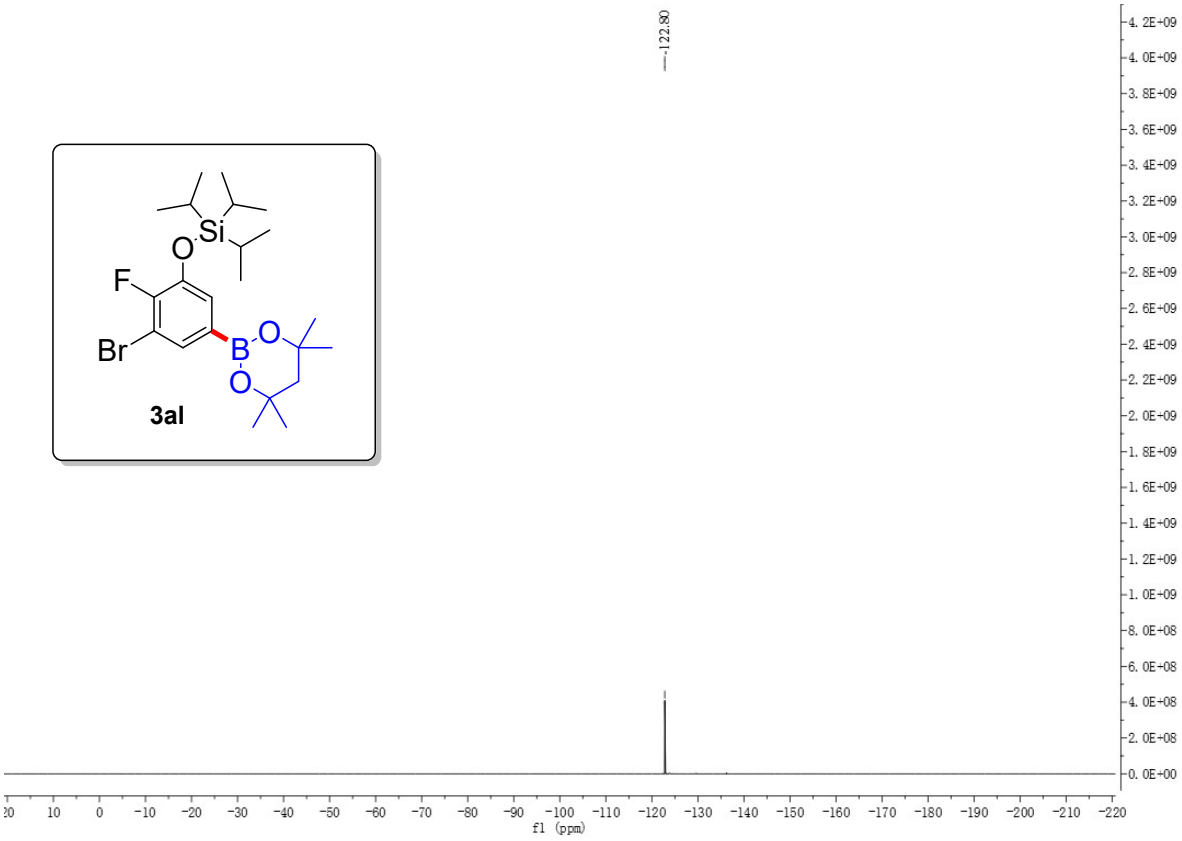
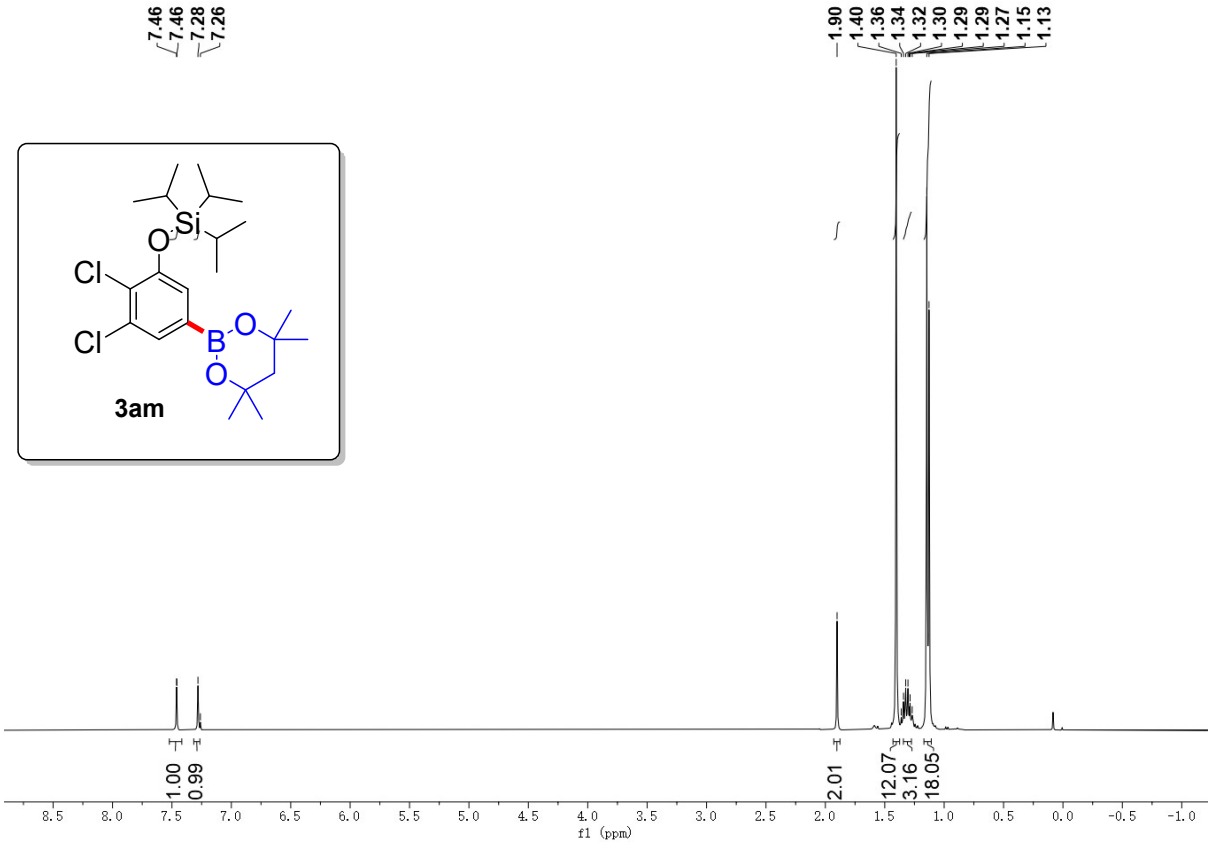
48.96
31.86
17.93
12.78
Si
O
F
Br
B
O
O
3al
f1 (ppm)


122.80
Si
O
F
Br
B
O
O
3al
f1 (ppm)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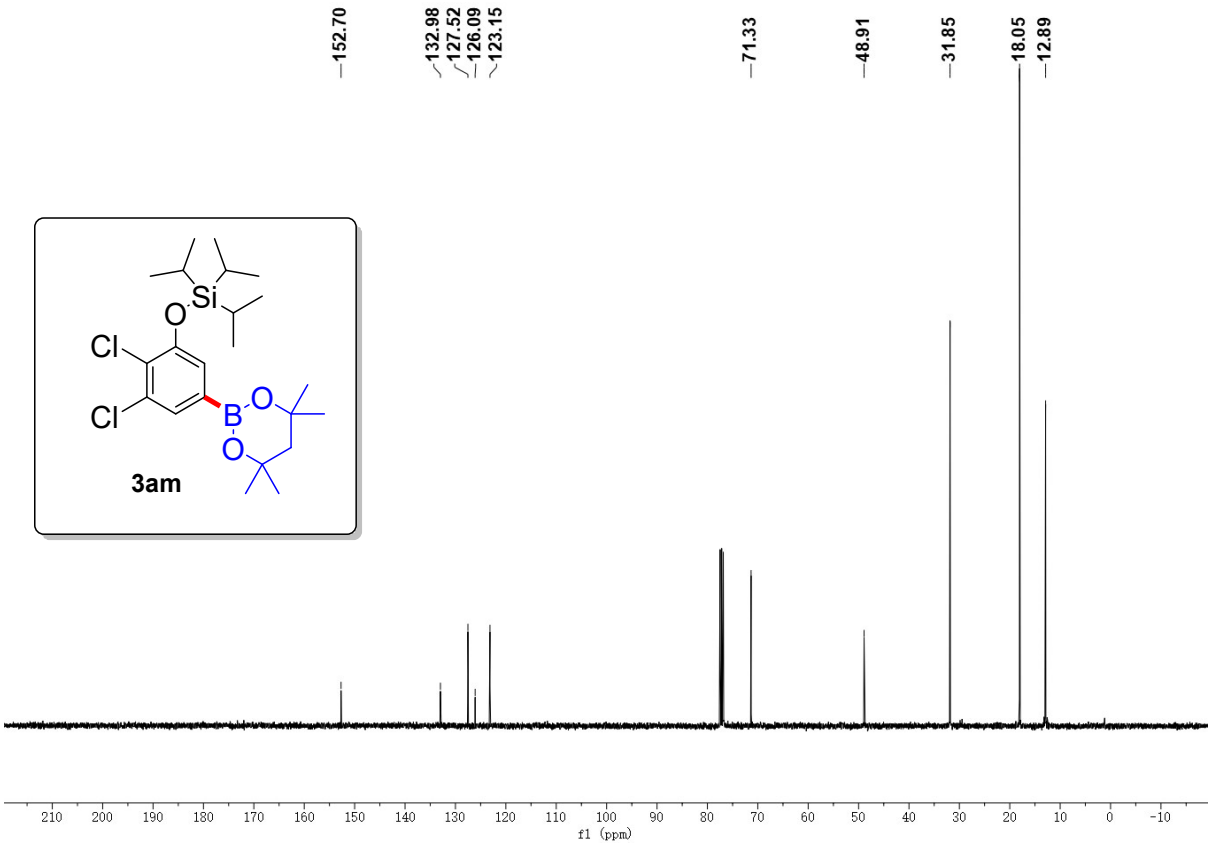
7.46
7.28
7.26
1.90
1.40
1.36
1.34
1.32
1.30
1.29
1.29
1.27
1.15
1.13
Si
O
Cl
Cl
B
O
O
3am
1.00
0.99
2.01
12.07
3.16
18.05
f1 (ppm)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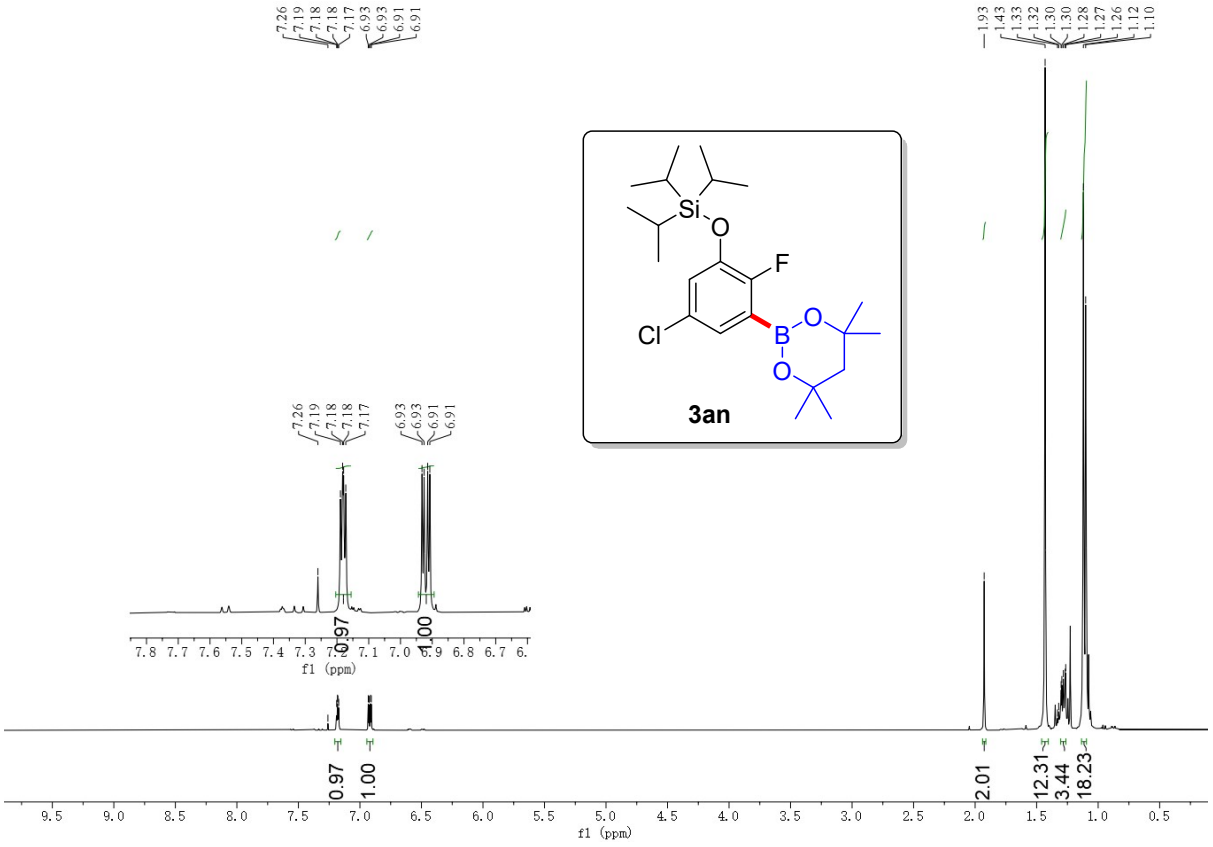
132.98
127.52
126.09
123.15
71.33
48.91
31.85
18.05
12.89
Si
O
Cl
Cl
B
O
O
3am
f1 (ppm)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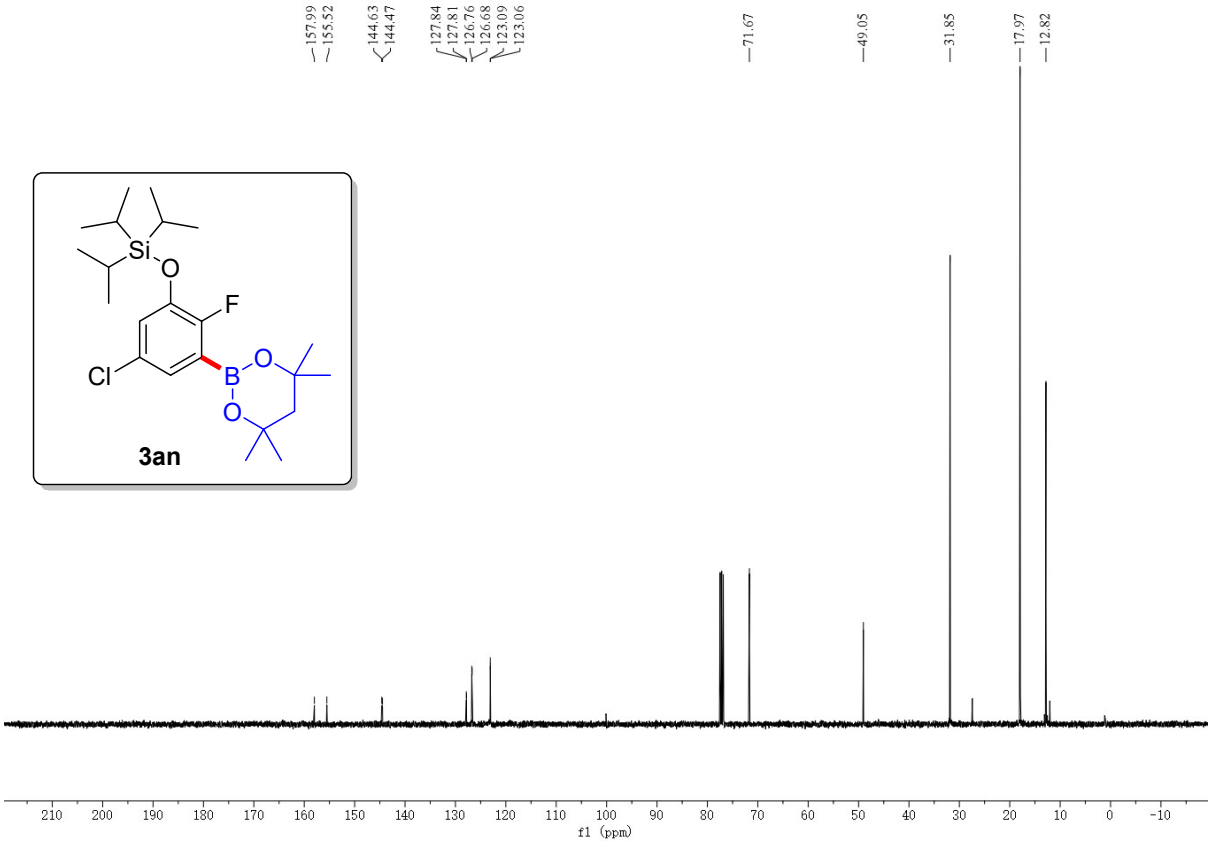
7.19
7.18
7.18
7.17
6.93
6.93
6.91
6.91
1.93
1.43
1.33
1.32
1.30
1.30
1.28
1.27
1.26
1.12
1.10
Si
O
F
Cl
B
O
O
3an
0.97
1.00
2.01
12.31
3.44
18.23
f1 (ppm)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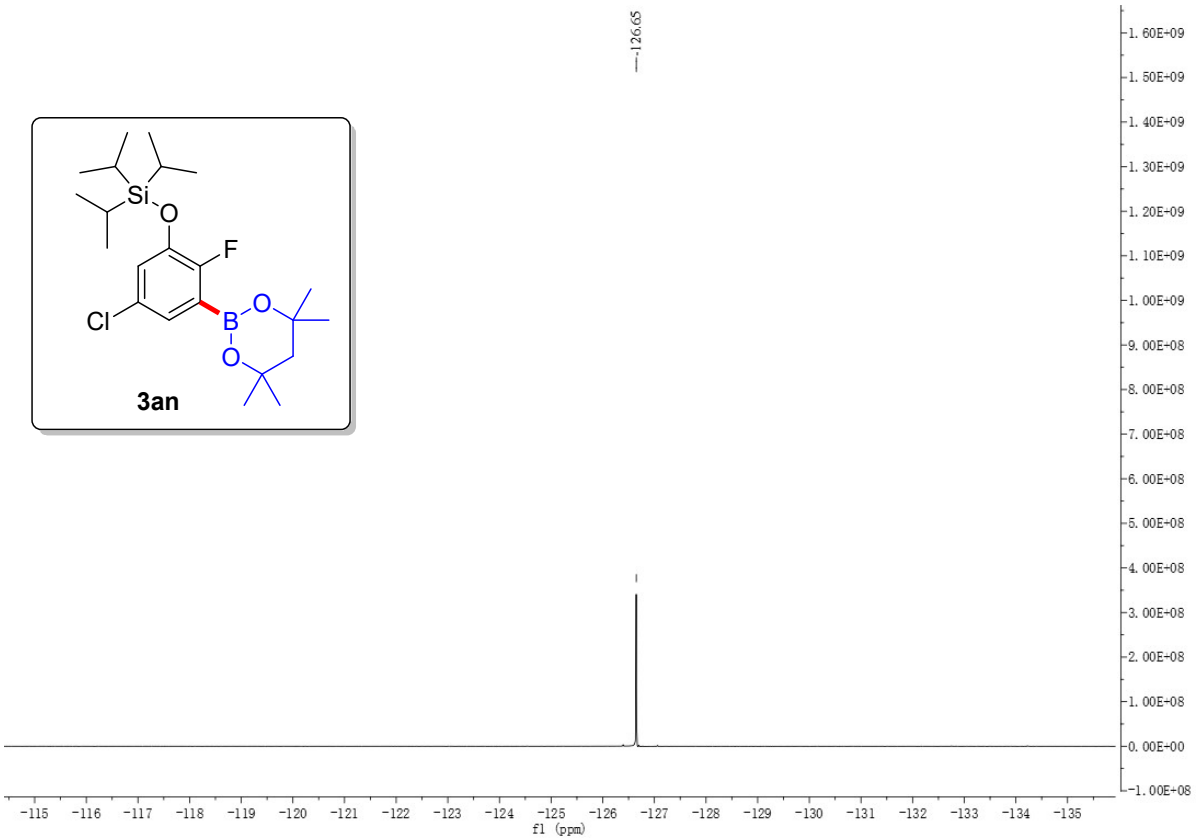
144.63
144.47
127.84
127.81
126.76
126.68
123.09
123.06
71.67
49.05
31.85
17.97
12.82
Si
O
F
Cl
B
O
O
3an
f1 (ppm)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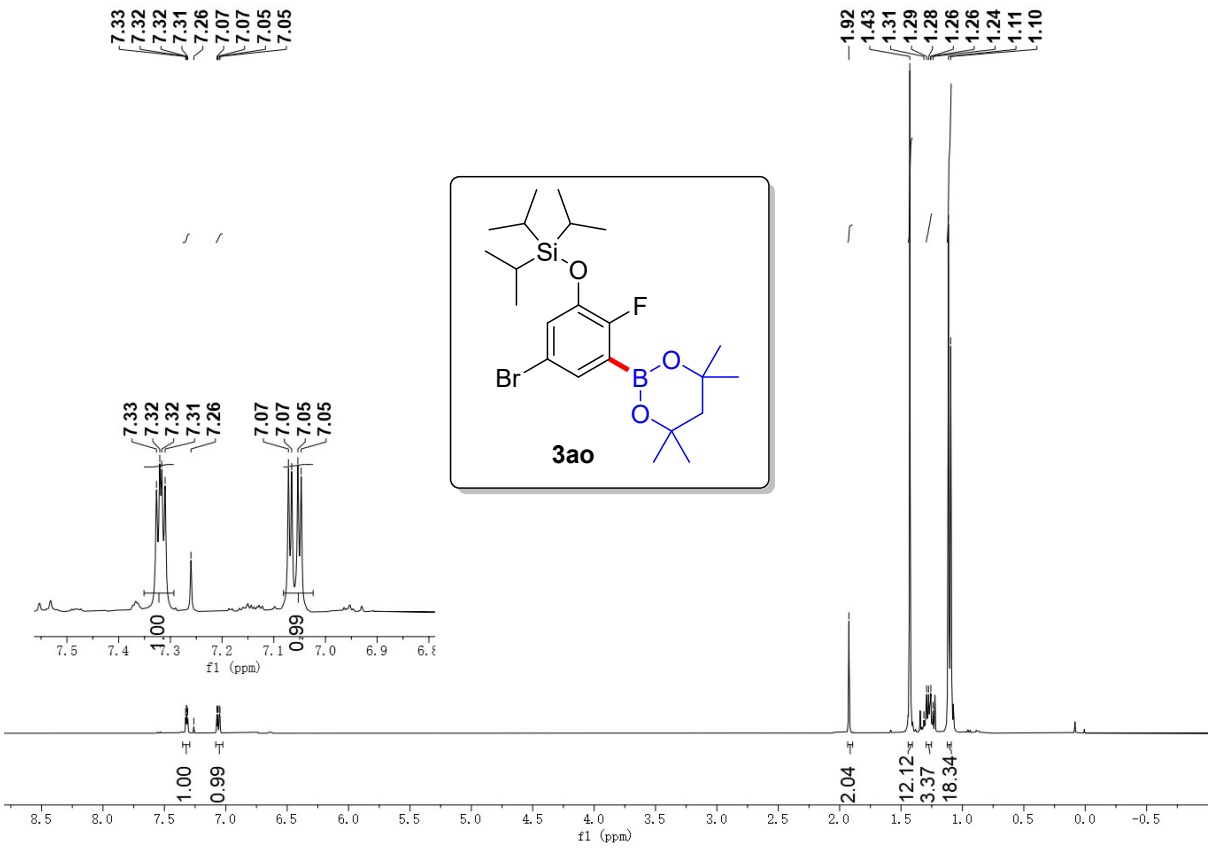
Si
O
F
Cl
B
O
O
3an
f1 (ppm)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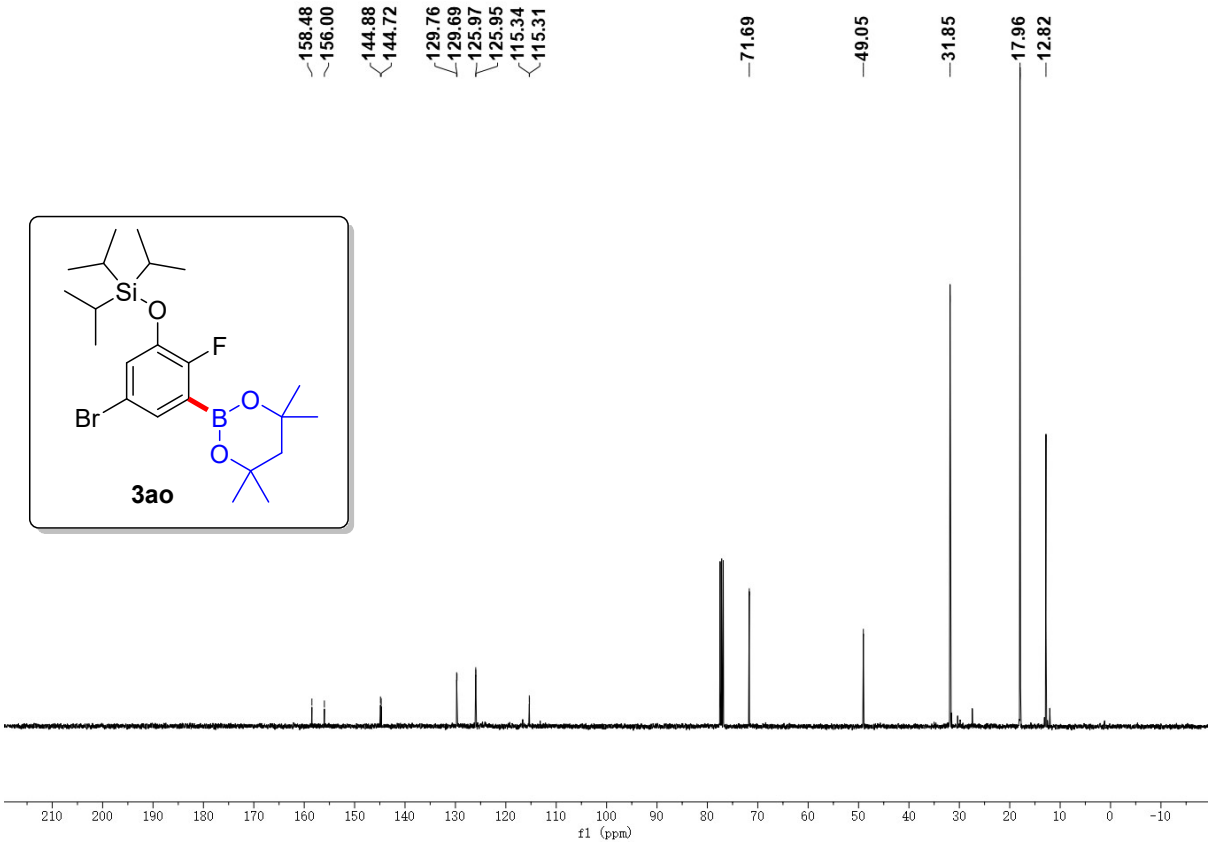
7.32
7.32
7.31
7.26
7.07
7.07
7.05
7.05
1.92
1.43
1.31
1.29
1.28
1.26
1.26
1.24
1.11
1.10
Si
O
F
Br
B
O
O
3ao
1.00
0.99
2.04
12.12
3.37
18.34
f1 (ppm)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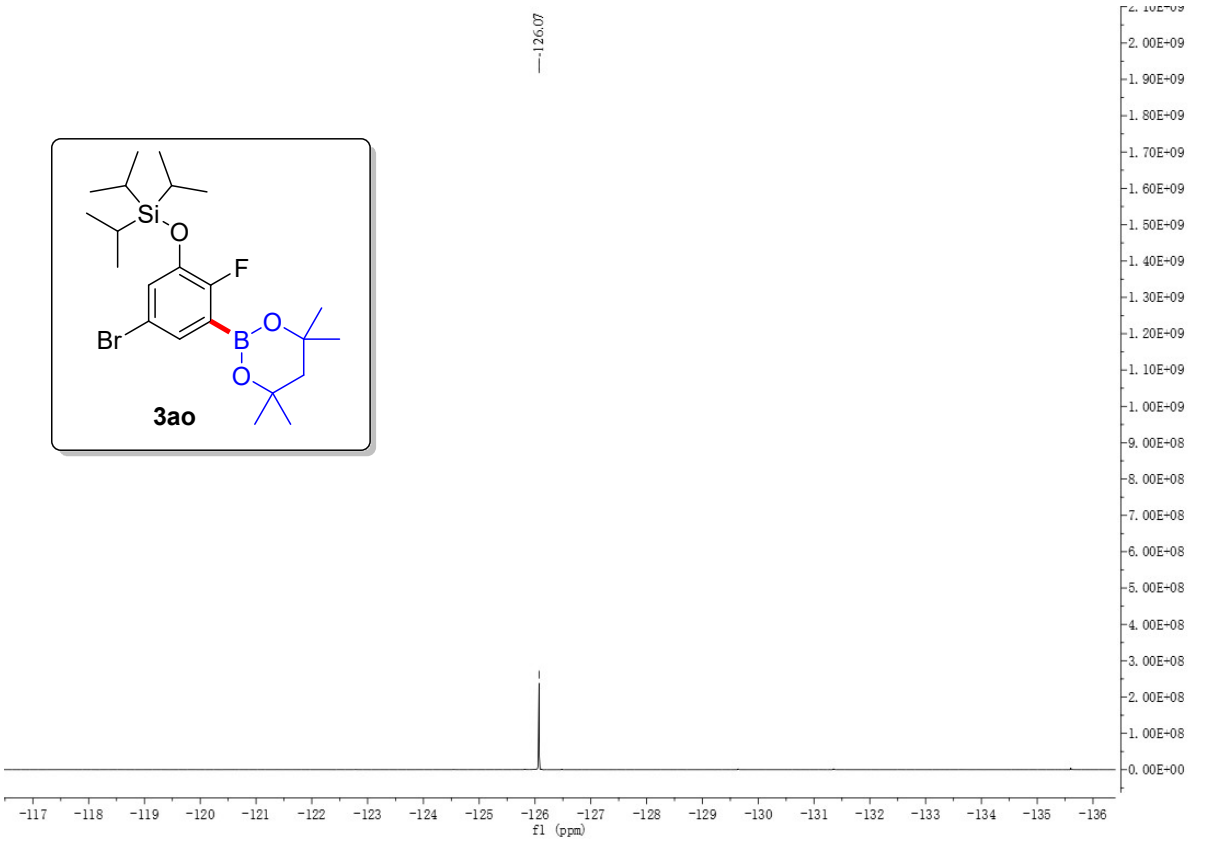
156.00
144.88
144.72
129.76
129.69
125.97
125.95
115.34
115.31
71.69
49.05
31.85
17.96
12.82
Si
O
F
Br
B
O
O
3ao
f1 (ppm)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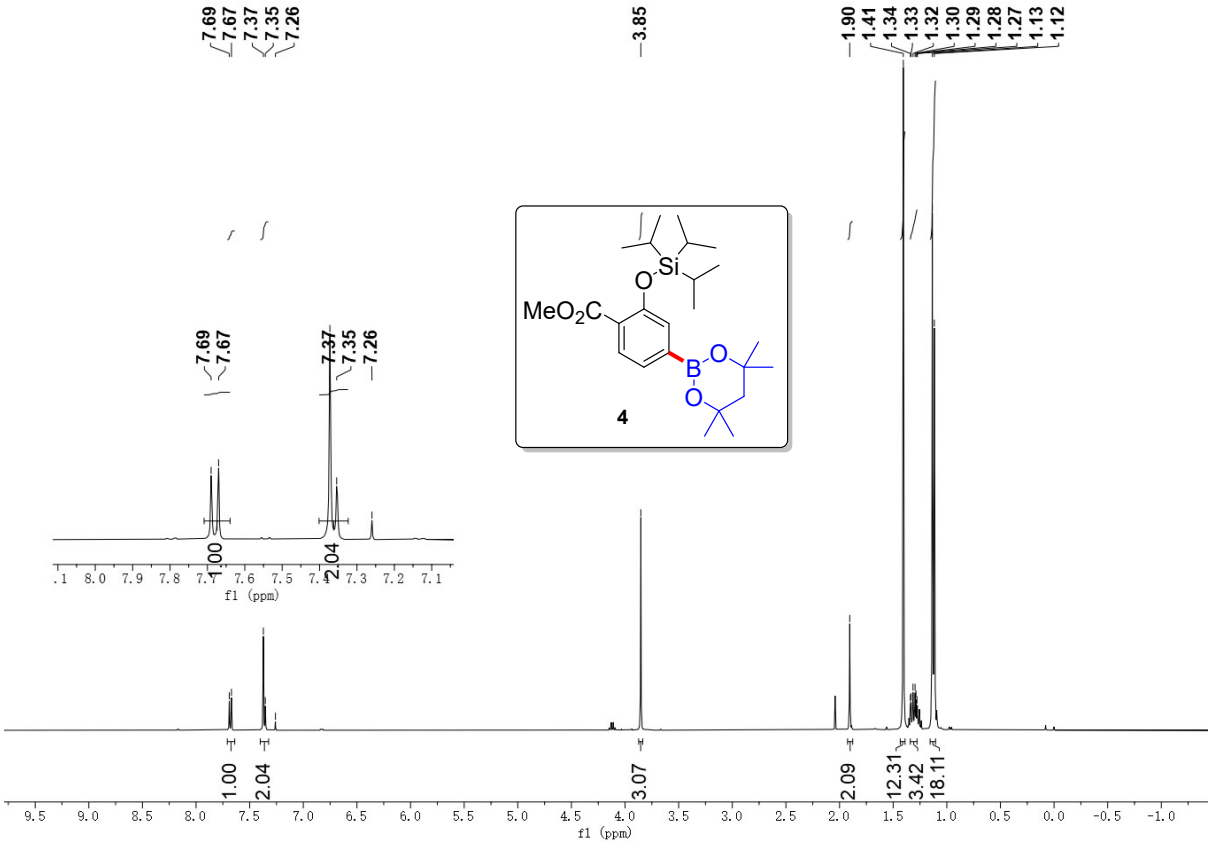
Si
O
F
Br
B
O
O
3ao
f1 (ppm)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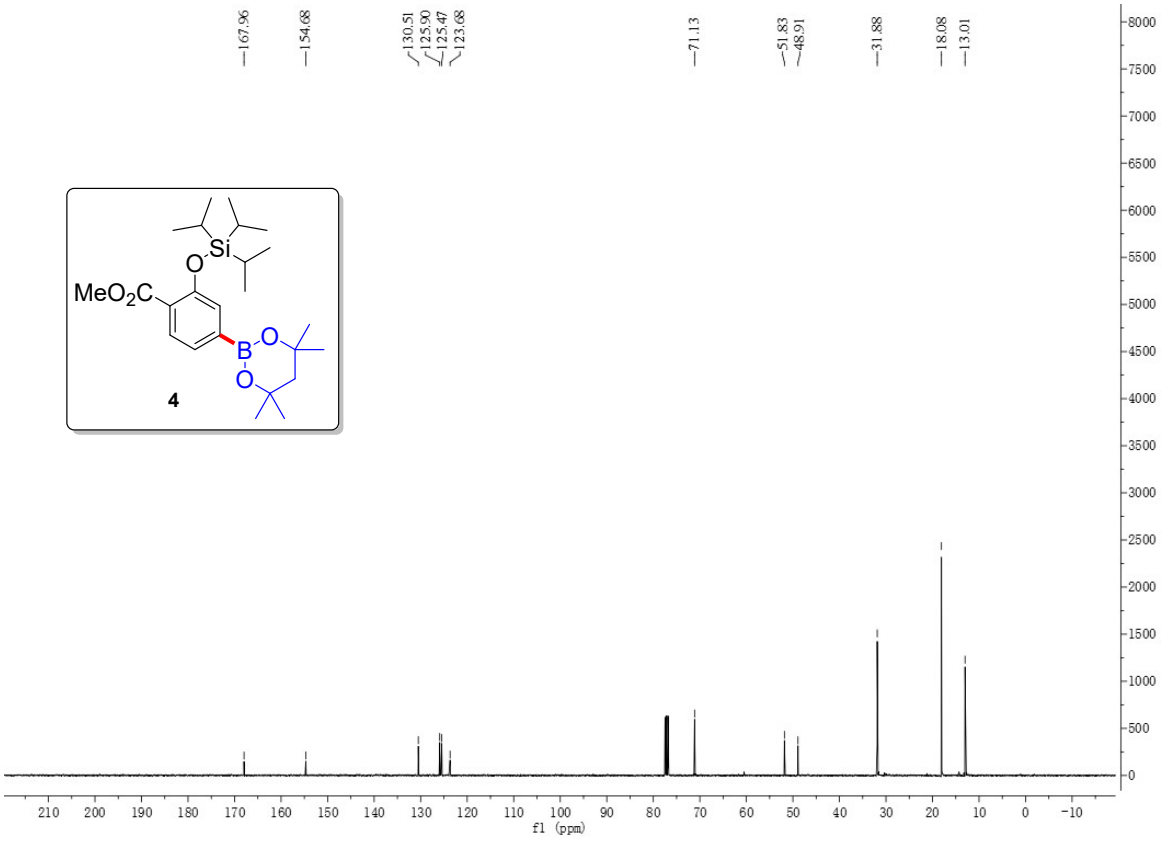
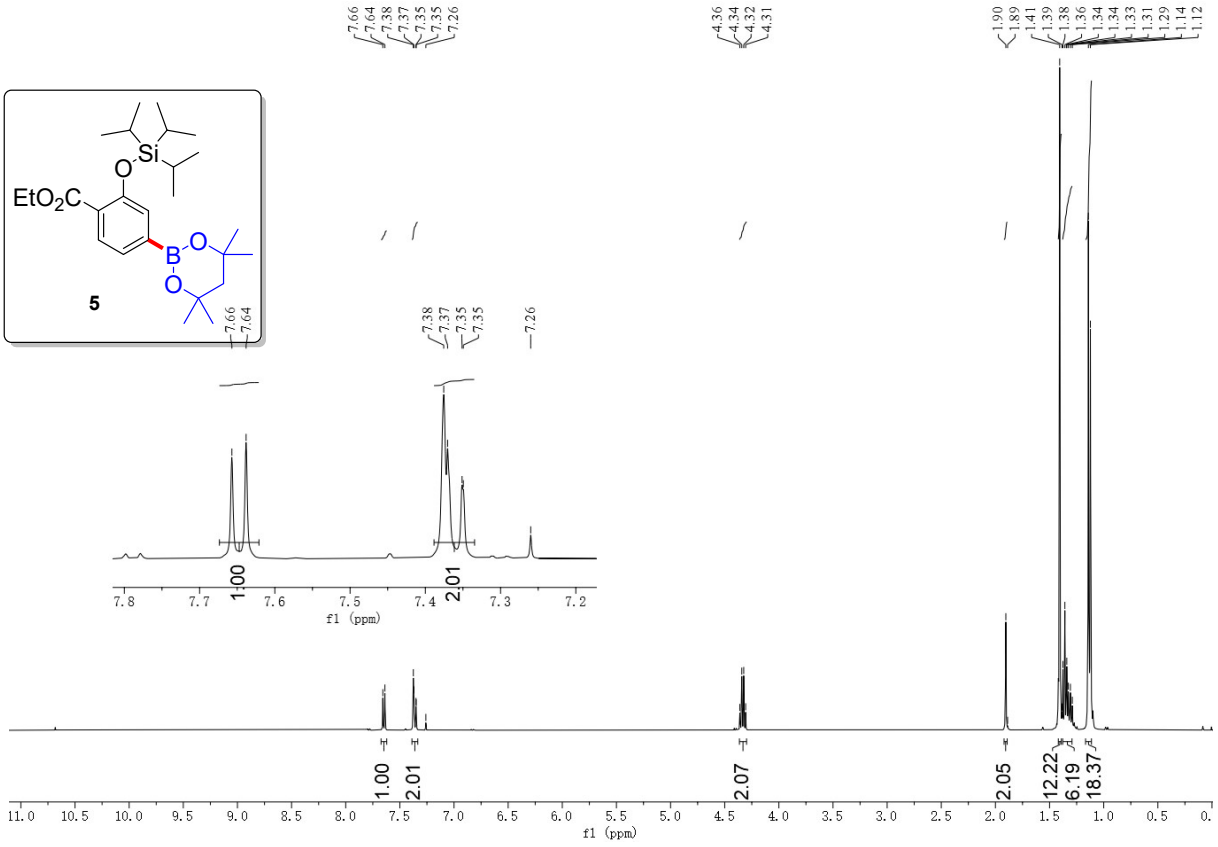
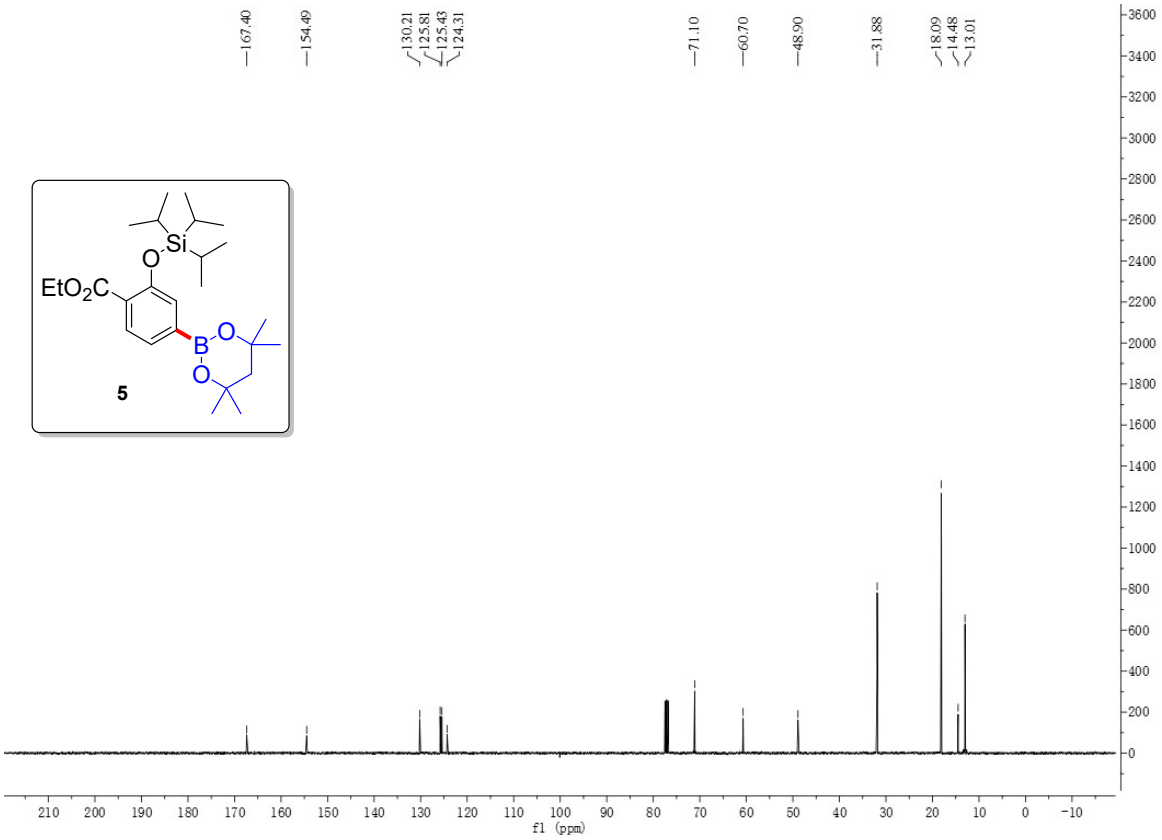
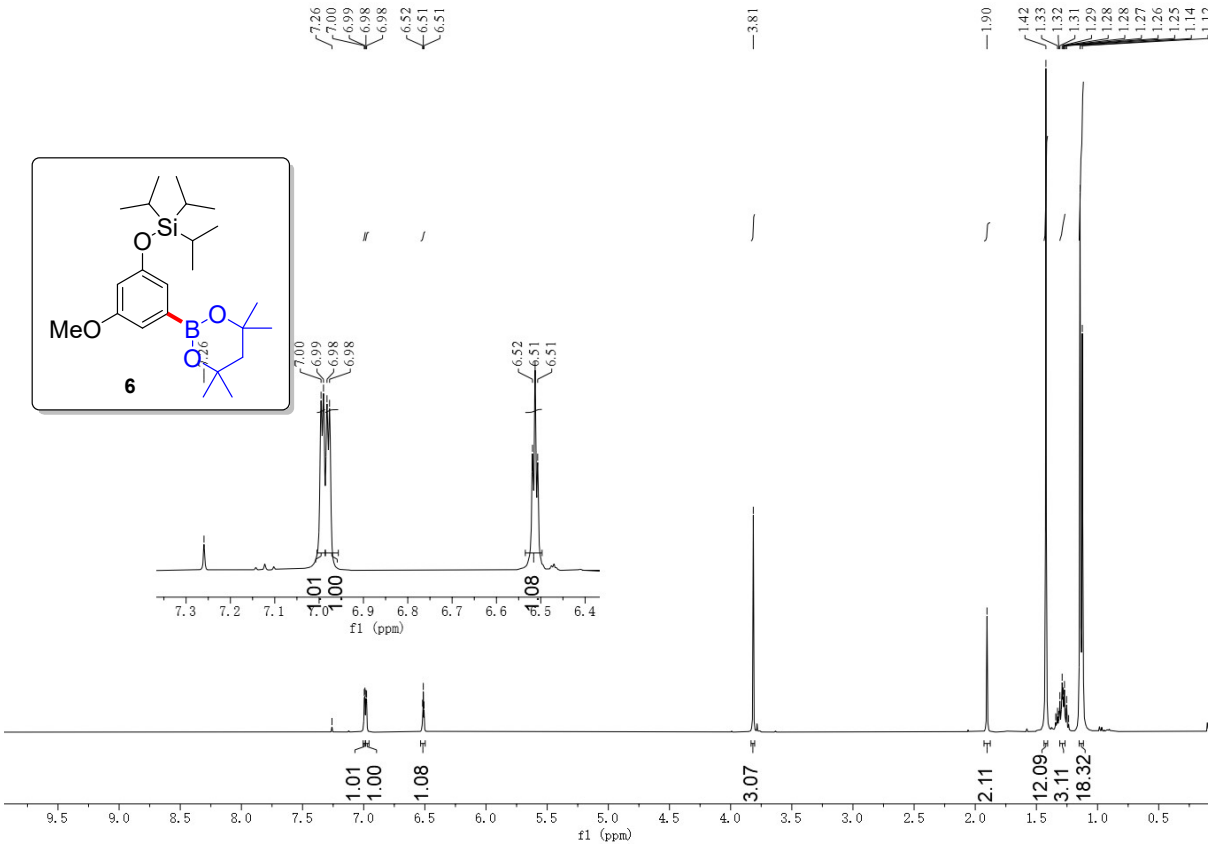
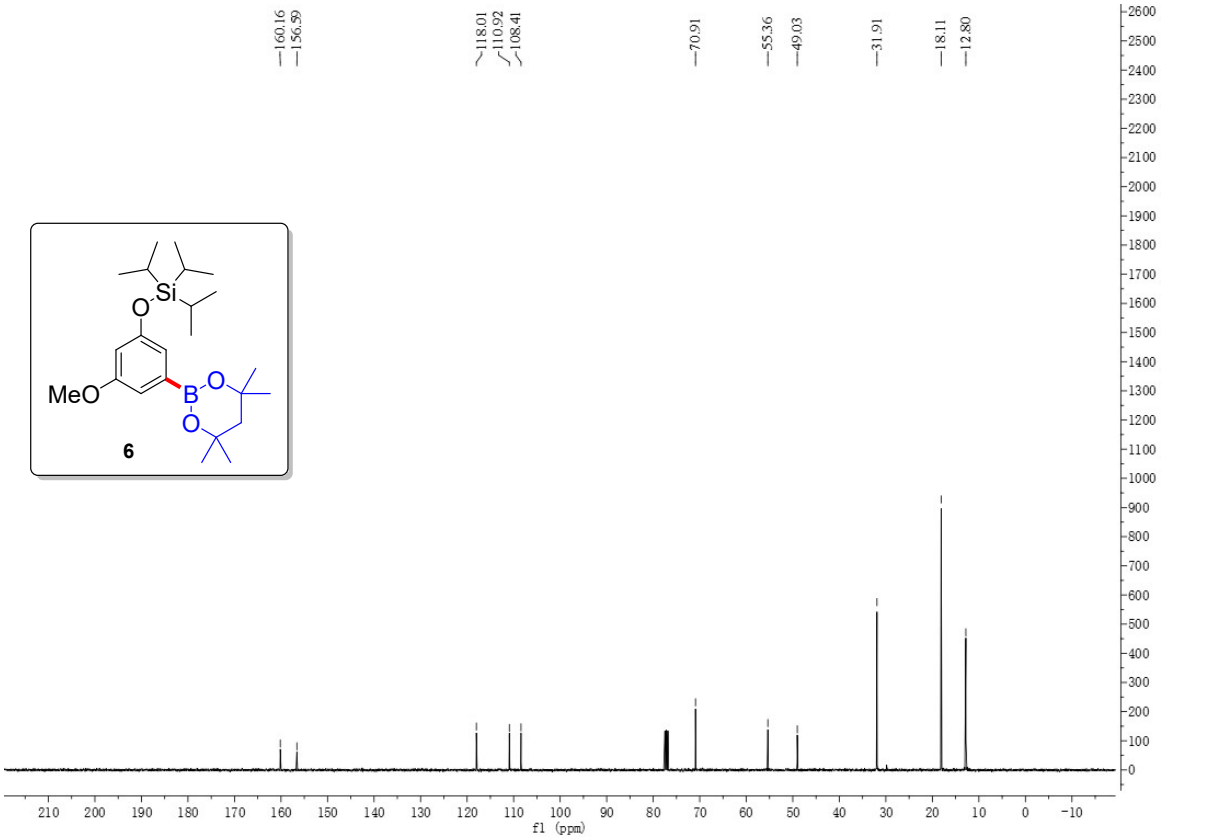
7.67
7.37
7.35
7.26
3.85
1.90
1.41
1.34
1.33
1.32
1.30
1.29
1.28
1.27
1.13
1.12
MeO2C
Si
O
B
O
O
4
1.00
2.04
3.07
2.09
12.31
3.42
18.11
f1 (ppm)

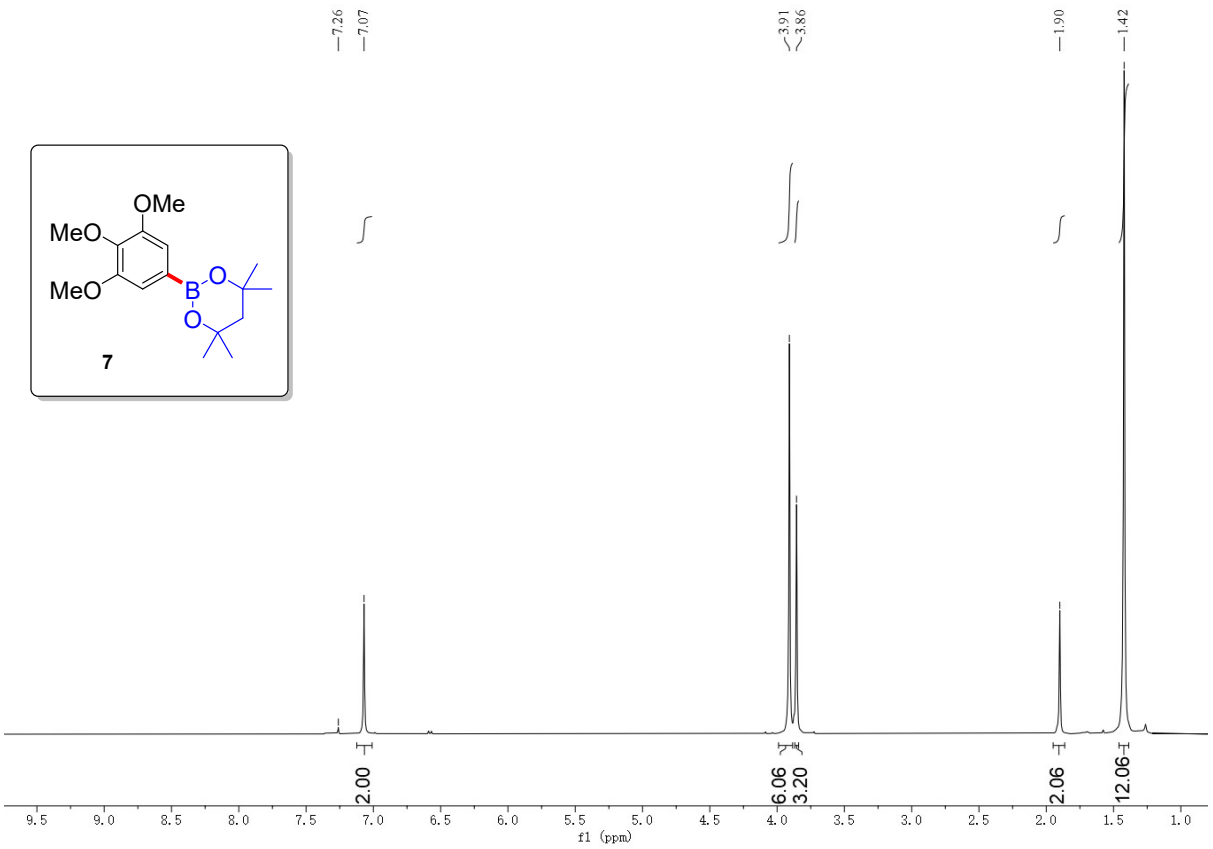

167.96
154.68
130.51
125.90
125.47
123.68
71.13
51.83
48.91
31.88
18.08
13.01
MeO2C
Si
O
B
O
O
4
f1 (ppm)

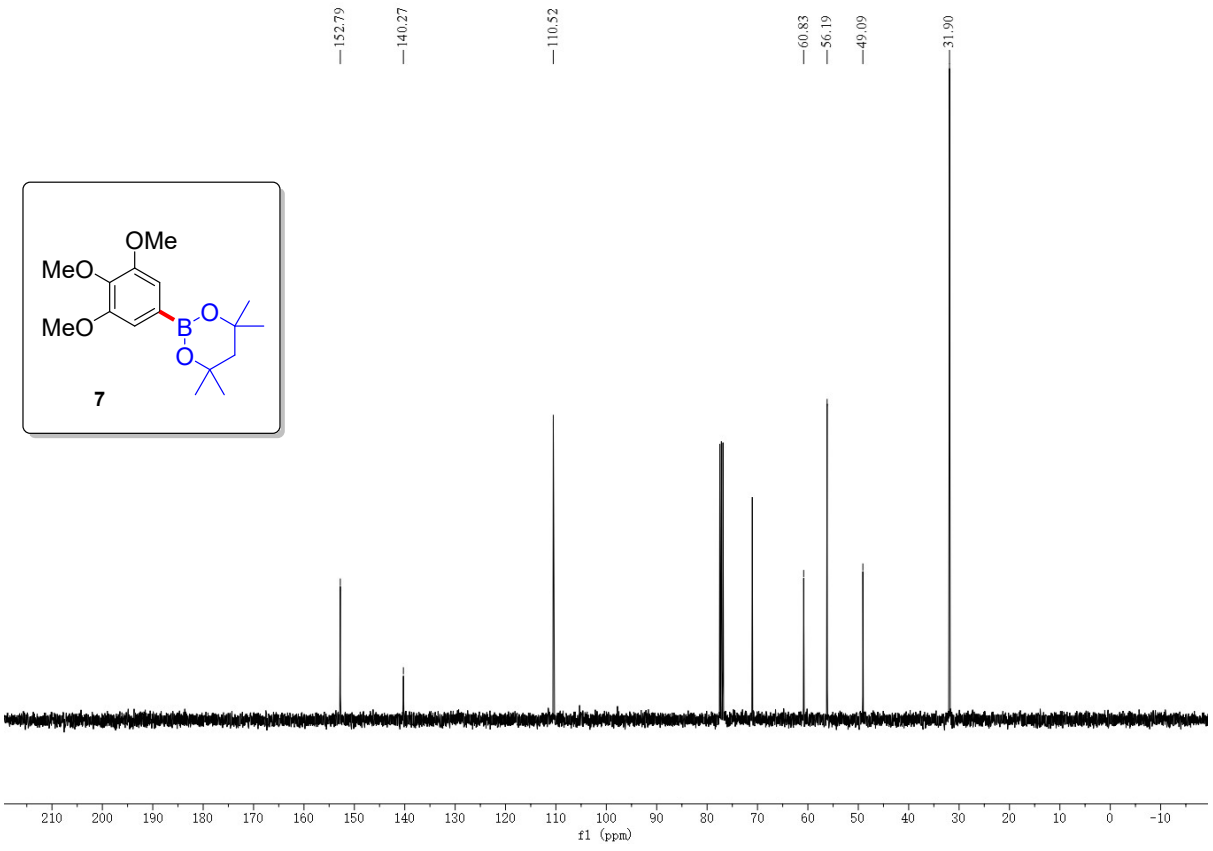

EtO2C
Si
O
B
O
O
5
7.66
7.64
7.38
7.37
7.35
7.35
7.26
4.36
4.34
4.32
4.31
1.90
1.89
1.41
1.39
1.38
1.36
1.34
1.34
1.33
1.31
1.29
1.14
1.12
1.00
2.01
2.07
2.05
12.22
6.19
18.37
f1 (ppm)

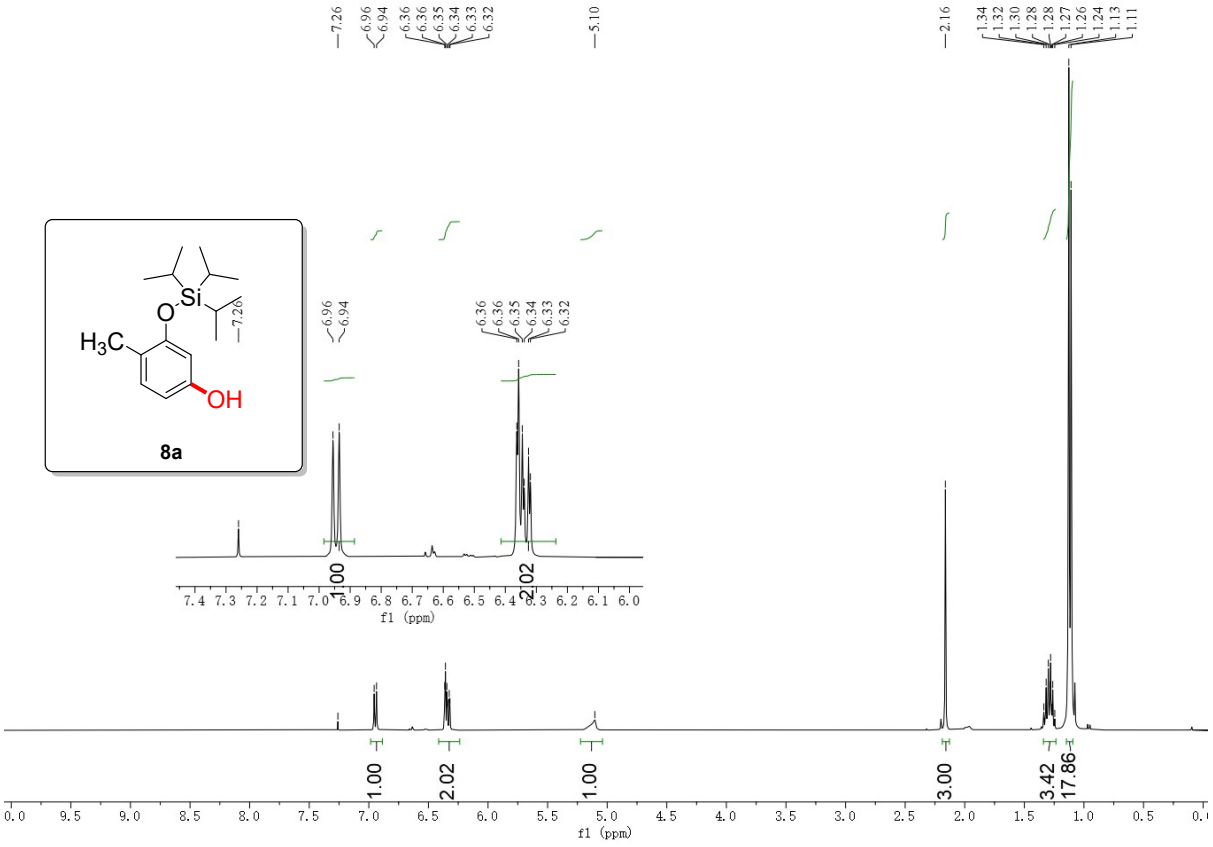

EtO2C
Si
O
B
O
O
5
167.40
154.49
130.21
125.81
125.43
124.31
71.10
60.70
48.90
31.88
18.09
14.48
13.01
f1 (ppm)

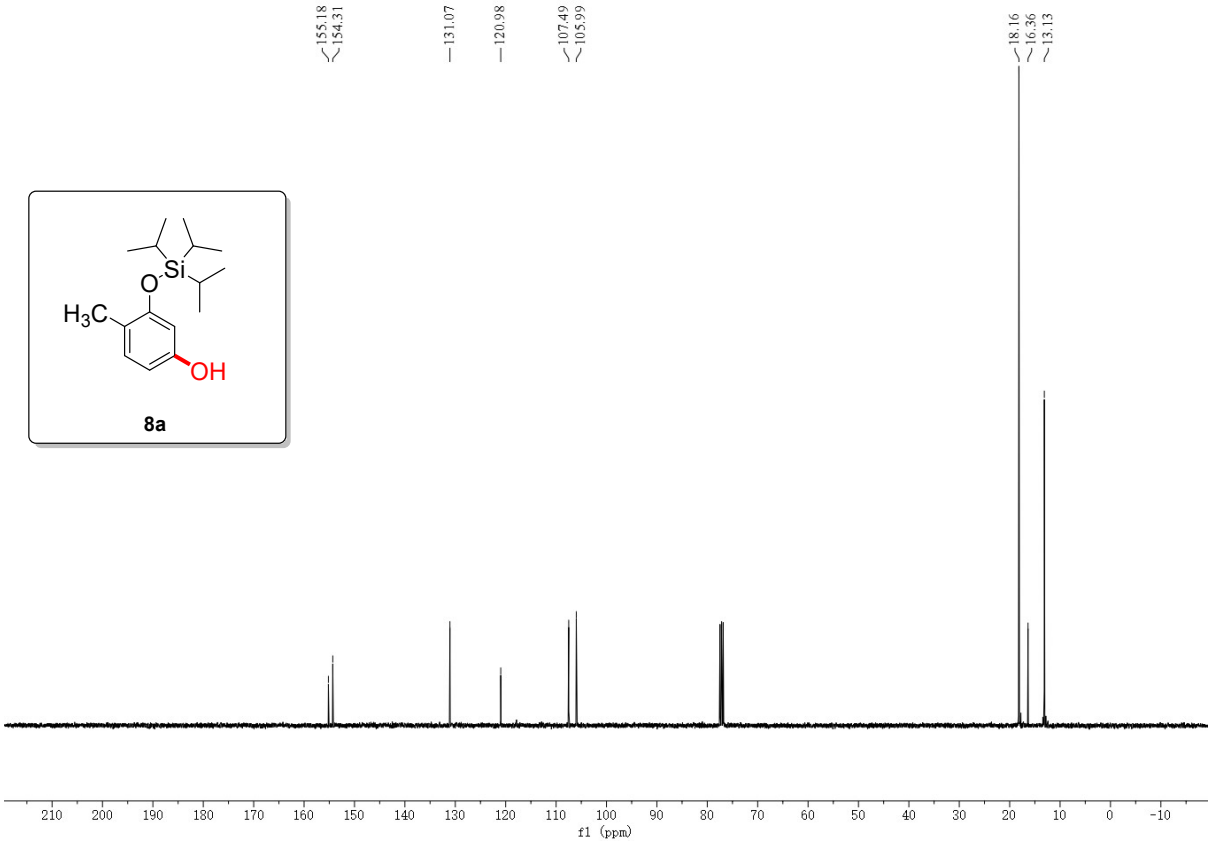

6
f1 (ppm)


6
f1 (ppm)


7.26
7.07
3.91
3.86
1.90
1.42
OMe
MeO
MeO
B
O
O
7
2.00
6.06
3.20
2.06
12.06
f1 (ppm)


152.79
140.27
110.52
60.83
56.19
49.09
31.90
OMe
MeO
MeO
B
O
O
7
f1 (ppm)


7.26
6.96
6.94
6.36
6.35
6.34
6.33
6.32
5.10
2.16
1.34
1.32
1.30
1.28
1.27
1.26
1.24
1.13
1.11
Si
O
H3C
OH
8a
1.00
2.02
1.00
3.00
3.42
17.86
f1 (ppm)


155.18
154.31
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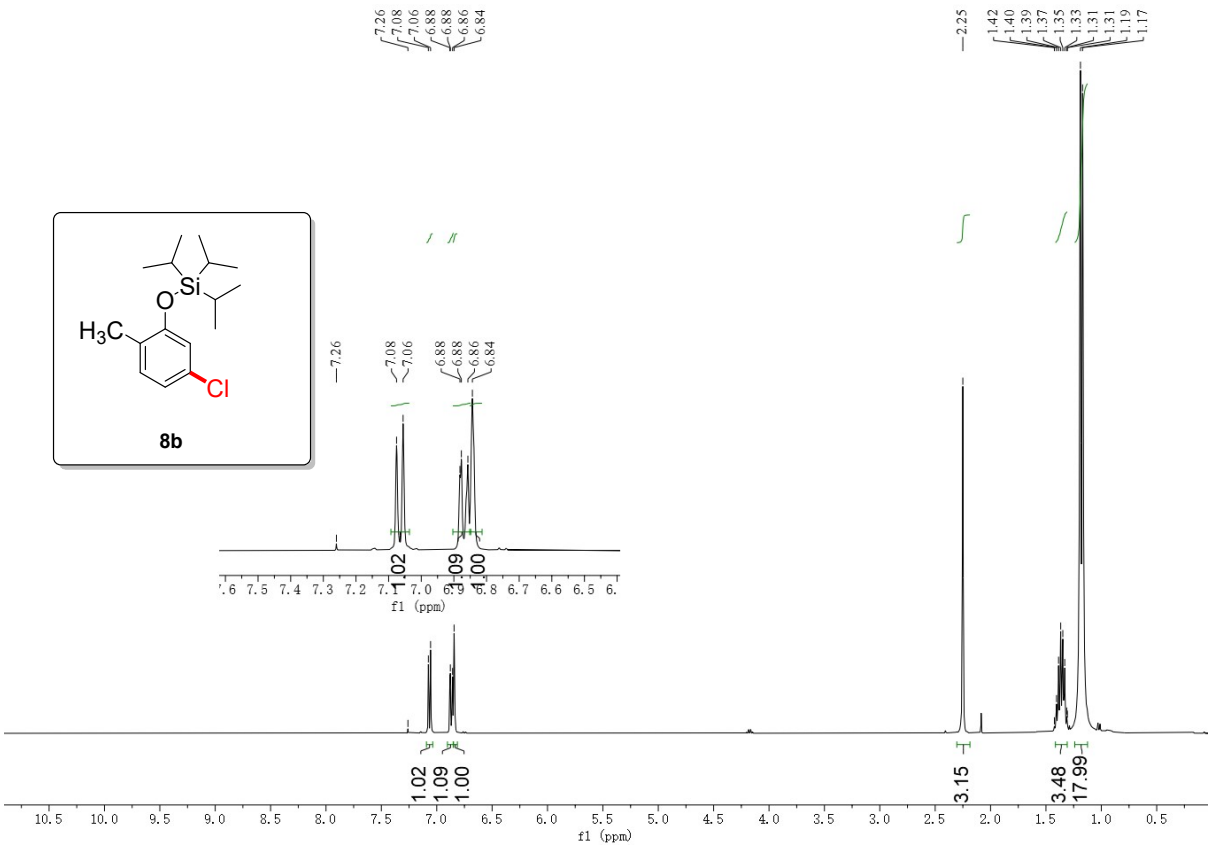
120.98
107.49
105.99
18.16
16.36
13.13
Si
O
H3C
OH
8a
f1 (ppm)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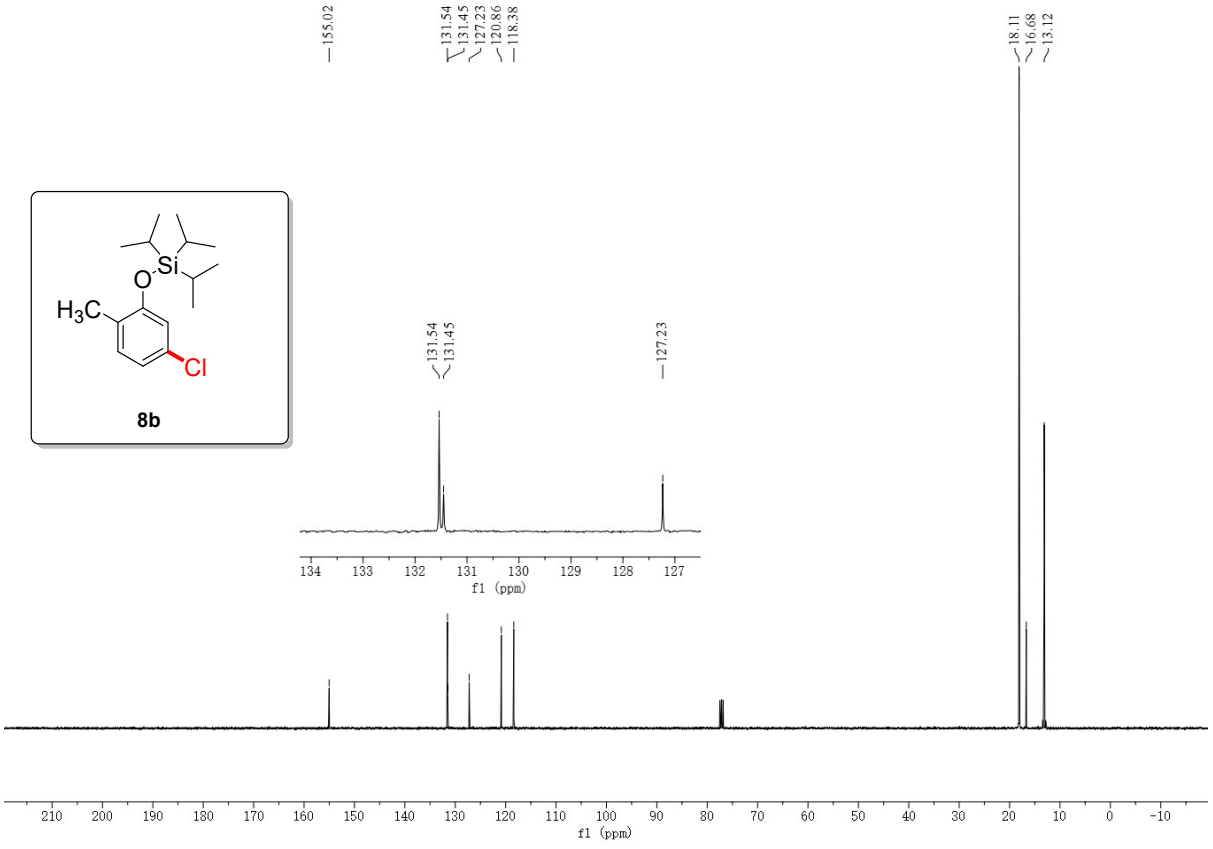
7.08
7.06
6.88
6.88
6.86
6.84
2.25
1.42
1.40
1.39
1.37
1.35
1.33
1.31
1.31
1.19
1.17
Si
O
H3C
Cl
8b
1.02
1.09
1.00
3.15
3.48
17.99
f1 (ppm)


155.02
131.54
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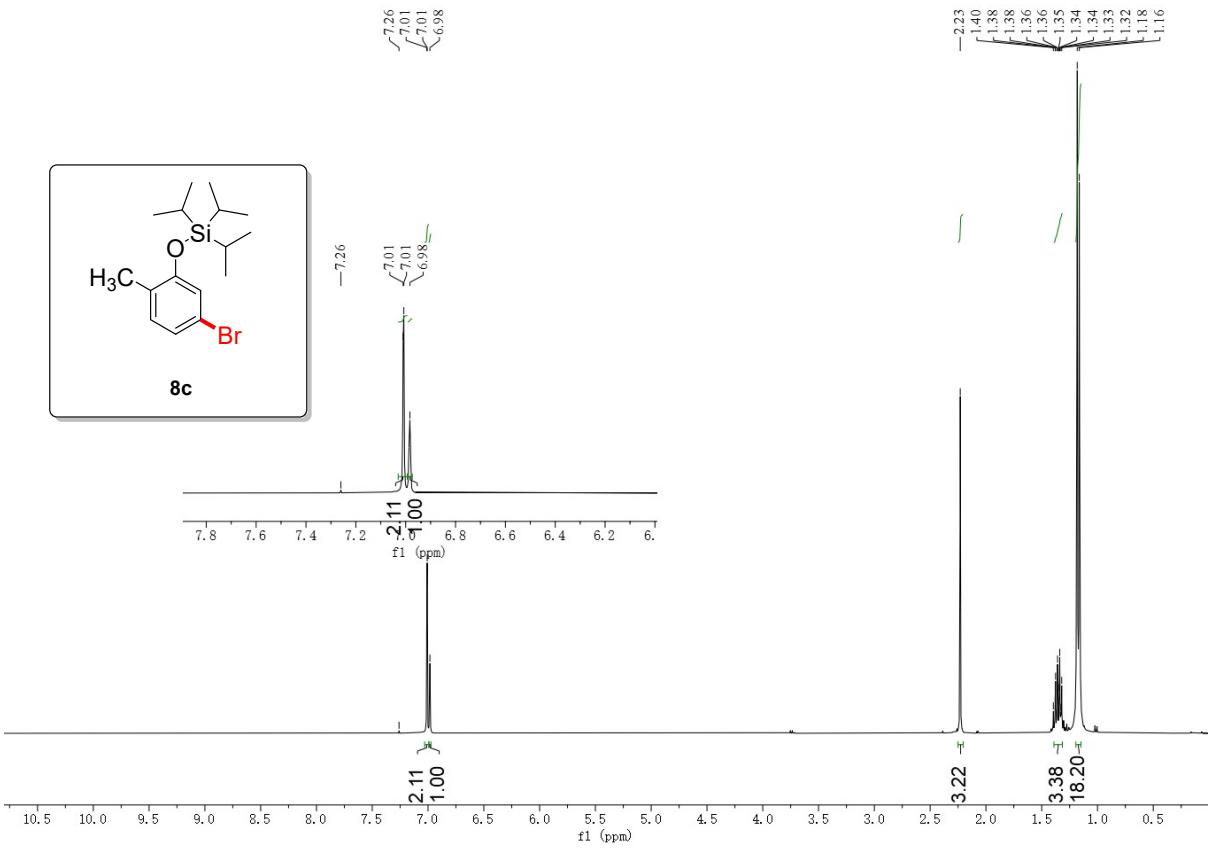
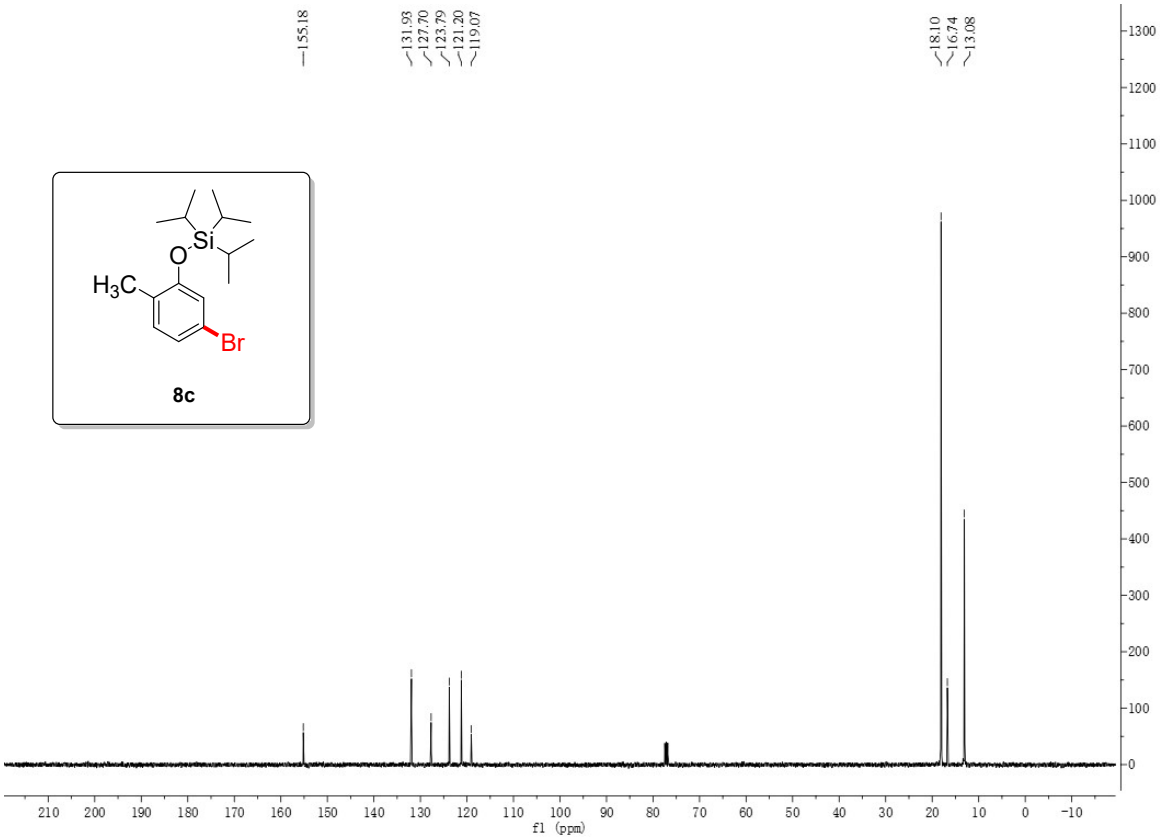
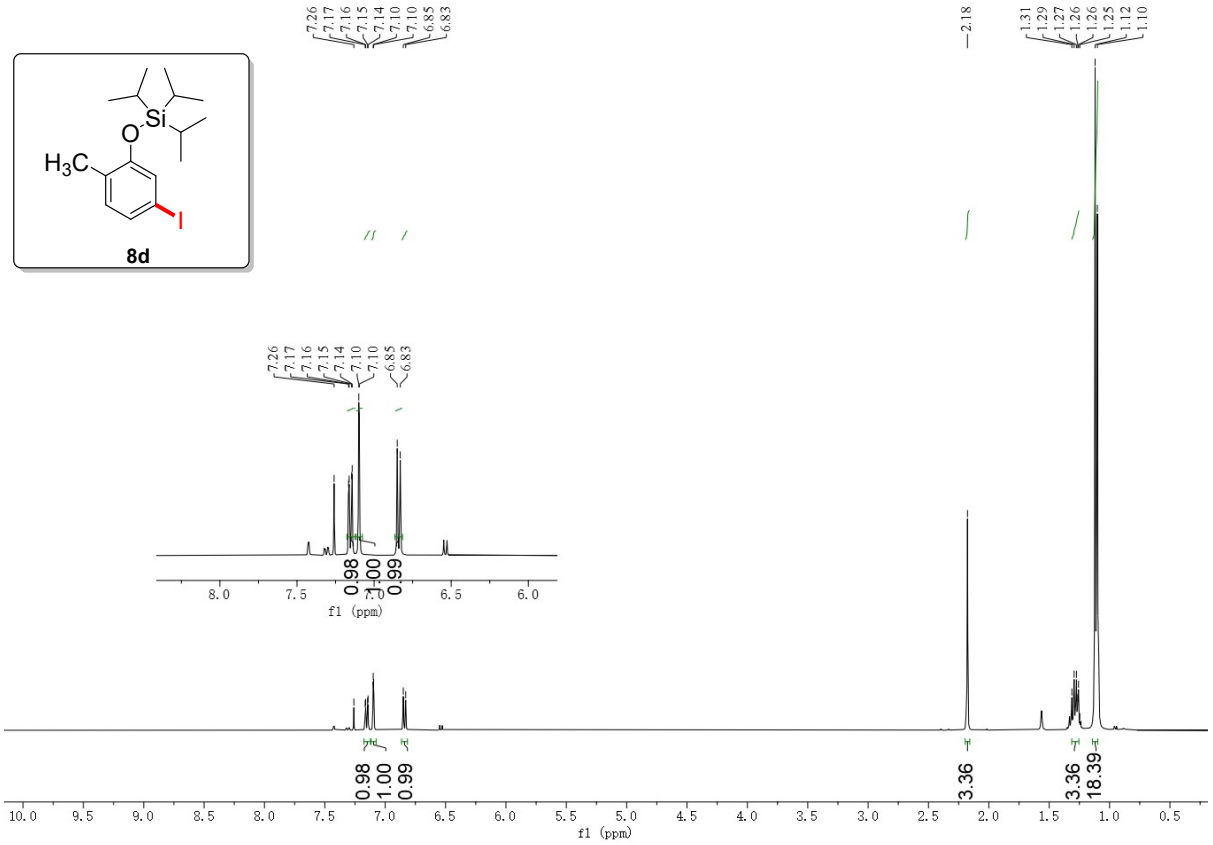
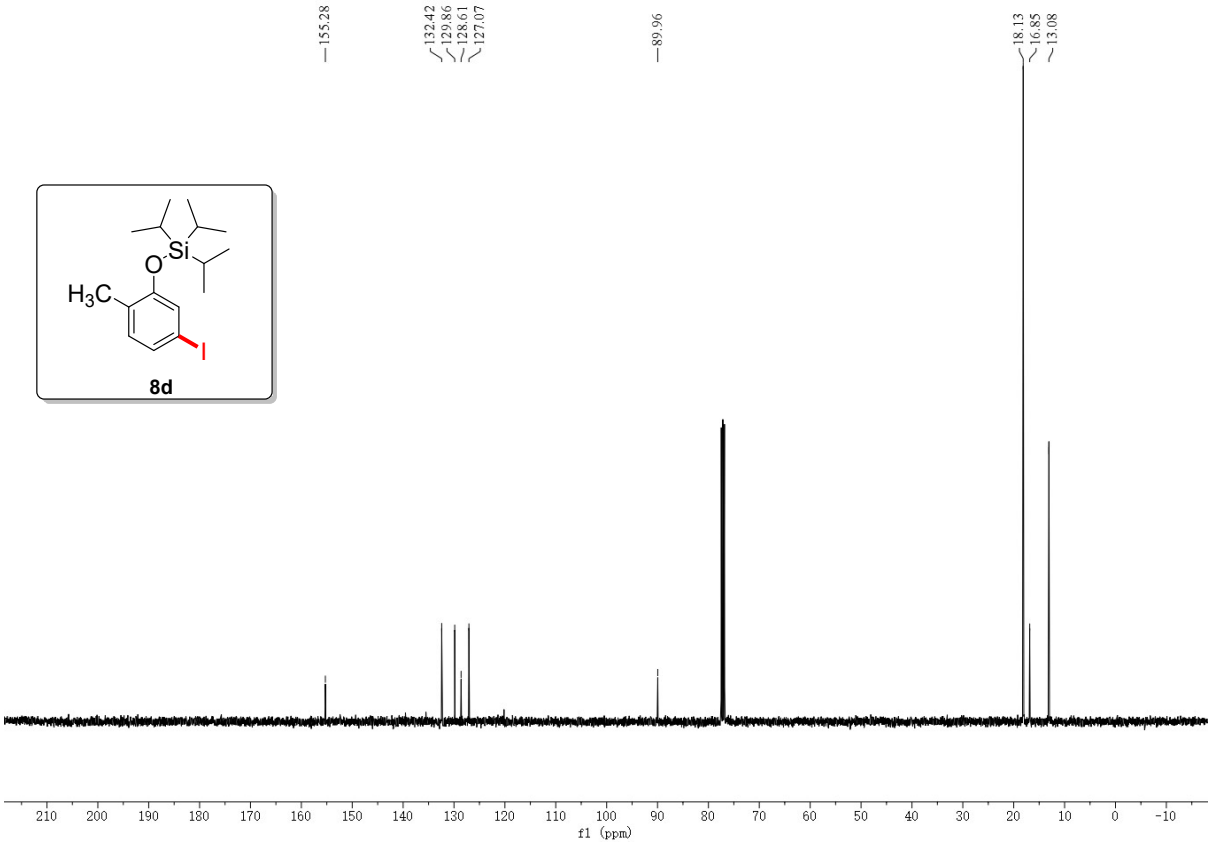
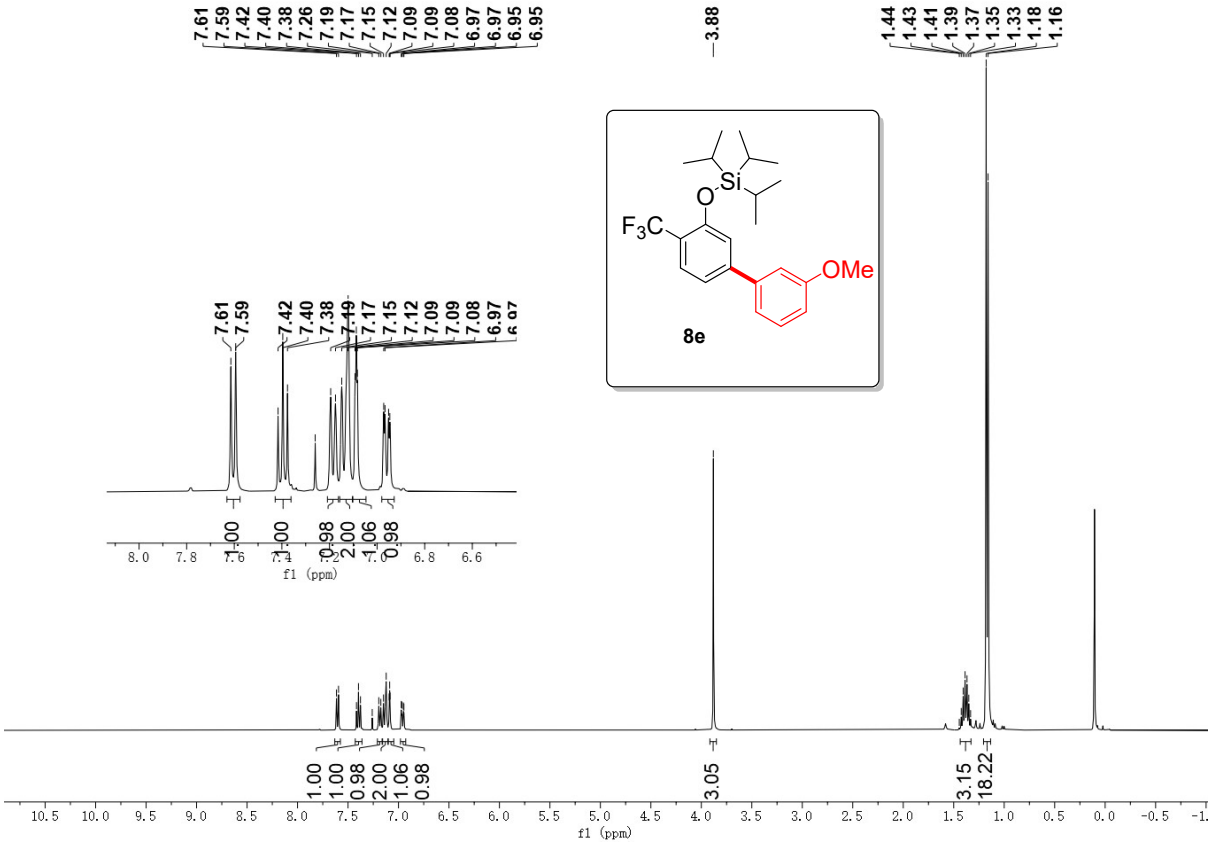
120.86
118.38
18.11
16.68
13.12
Si
O
H3C
Cl
8b
f1 (ppm)

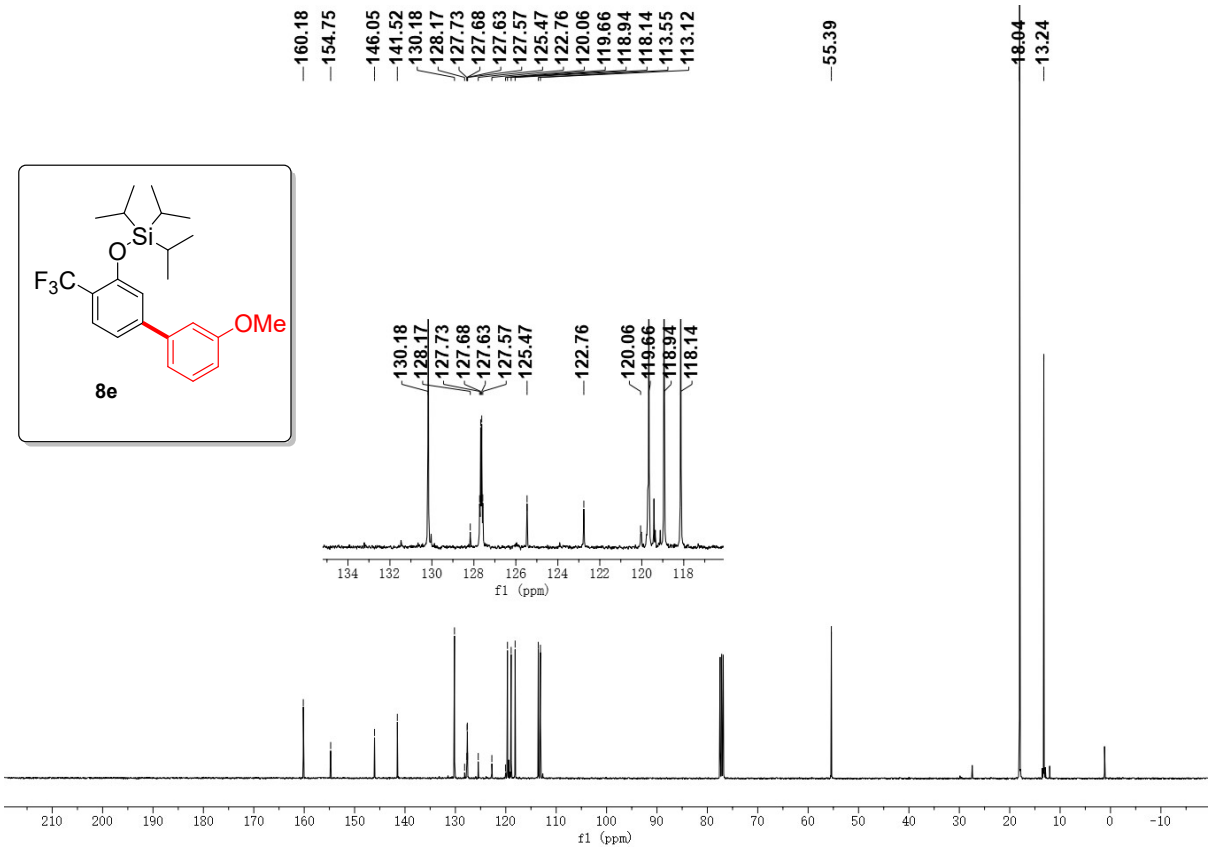

7.26
7.01
7.01
6.98
2.23
1.40
1.38
1.38
1.36
1.36
1.35
1.34
1.34
1.33
1.32
1.18
1.16
Si
O
H3C
Br
8c
2.11
1.00
3.22
3.38
18.20
f1 (ppm)

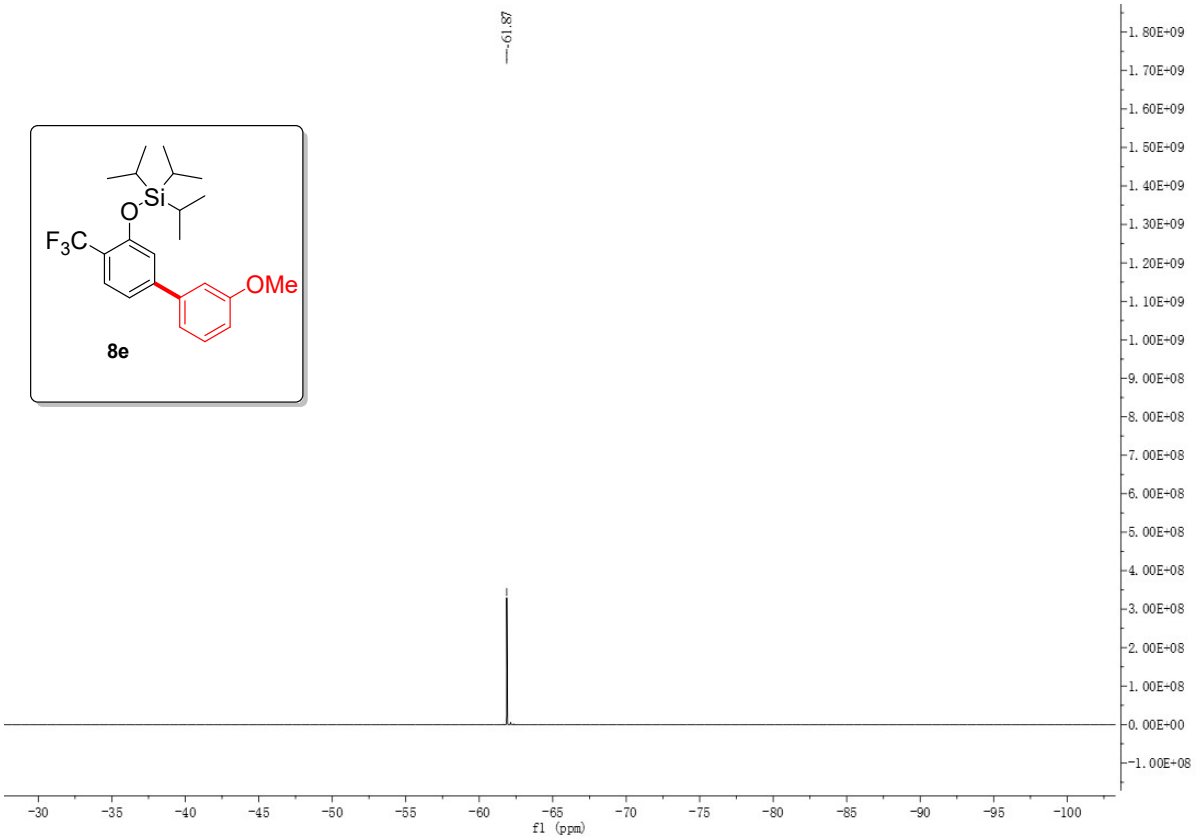

155.18
131.93
127.70
123.79
121.20
119.07
18.10
16.74
13.08
Si
O
H3C
Br
8c
f1 (ppm)

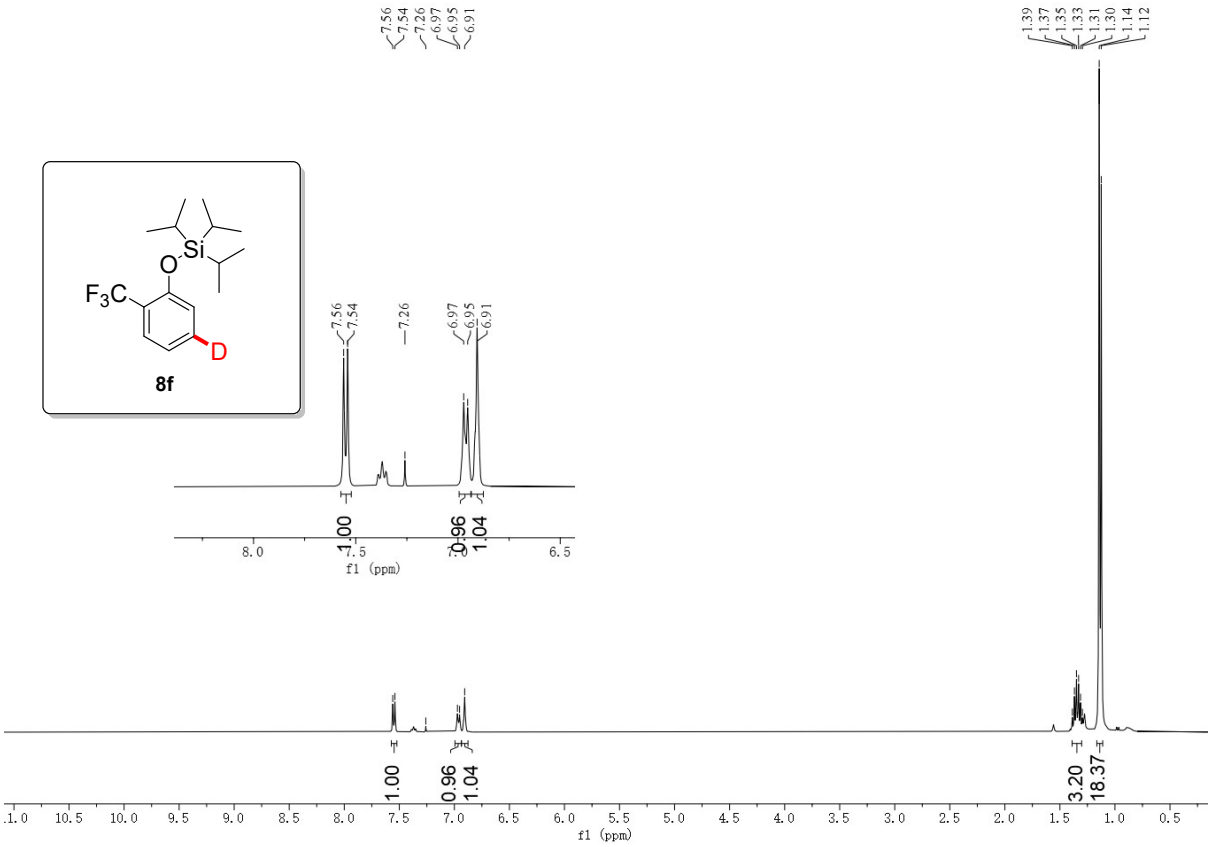

8d
7.26
7.17
7.16
7.15
7.14
7.10
7.10
6.85
6.83
2.18
1.31
1.29
1.27
1.26
1.26
1.25
1.12
1.10
0.98
1.00
0.99
3.36
3.36
18.39
f1 (ppm)

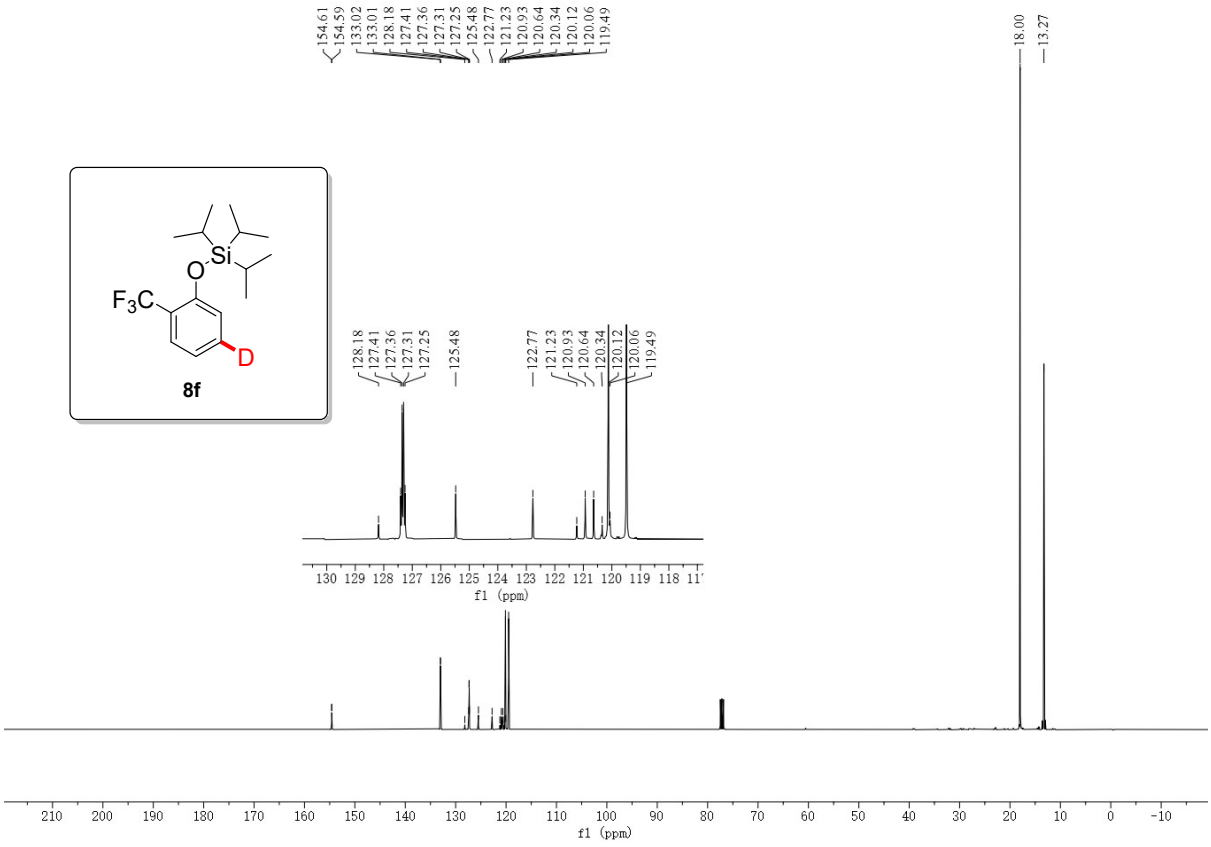

8d
155.28
132.42
129.86
128.61
127.07
89.96
18.13
16.85
13.08
f1 (ppm)

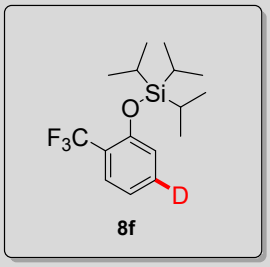

7.61
7.59
7.42
7.40
7.38
7.26
7.19
7.17
7.15
7.12
7.09
7.09
7.08
6.97
6.95
6.95
3.88
1.44
1.43
1.41
1.39
1.37
1.35
1.33
1.18
1.16
Si
O
F3C
OMe
8e
1.00
1.00
0.98
2.00
1.06
0.98
3.05
3.15
18.22
f1 (ppm)


160.18
154.75
146.05
141.52
130.18
128.17
127.73
127.68
127.63
127.57
125.47
122.76
120.06
119.66
118.94
118.14
113.55
113.12
55.39
18.04
13.24
Si
O
F3C
OMe
8e
f1 (ppm)


-61.87
F3C
O
Si
OMe
8e
f1 (ppm)


7.56
7.54
7.26
6.97
6.95
6.91
1.39
1.37
1.35
1.33
1.31
1.30
1.14
1.12
F3C
O
Si
D
8f
1.00
0.96
1.04
3.20
18.37
f1 (ppm)


154.61
154.59
133.02
133.01
128.18
127.41
127.36
127.31
127.25
125.48
122.77
121.23
120.93
120.64
120.34
120.12
120.06
119.49
18.00
13.27
Si
O
F3C
D
8f
f1 (ppm)
f1 (ppm)


Si
O
F3C
D
8f