Supporting Information

Diversity-oriented synthesis enables the rapid development of quinoxaline-based bis-boron fluorophores: photophysical properties and sensing applications

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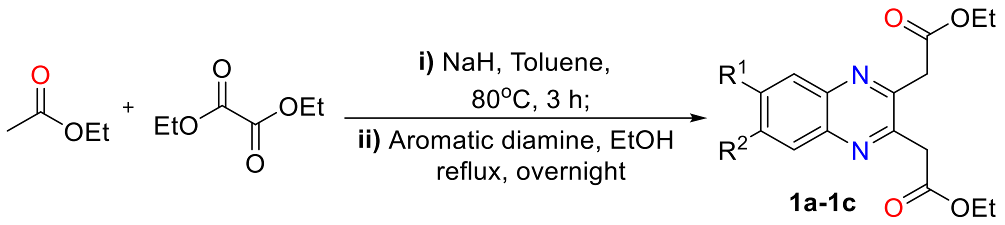
I. General information

Unless specified otherwise, all solvents and reactants were purchased from commercial companies, and all reactions were carried out under N_2 atmosphere. A Bruker 400 AVANCE III HD spectrometer was operating at 400 MHz, 101 MHz, 376 MHz, and 128 MHz for ^{1}H, ^{13}C, ^{19}F and ^{11}B acquisitions, respectively. ^{1}H NMR spectra were recorded by using tetramethylsilane (TMS, 0 ppm) as an internal standard in $CDCl_3$. ^{13}C NMR spectra were recorded by using residual non-deuterated solvents as an internal standard in $CDCl_3$ (δ =77.16 ppm) or d_6-DMSO (δ =39.52 ppm). ^{19}F NMR and ^{11}B NMR spectra are unreferenced. High resolution mass spectrums (HRMS) were recorded on an Agilent Q-TOF 6540 mass spectrometer using electrospray ionization. Photoluminescence (PL) spectra, absolute quantum yields, and fluorescence lifetime were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer and FLS 980 fluorescence spectrophotometer (Edinburgh Instruments Ltd, UK) with a calibrated integrating sphere system. The X-ray diffraction data were collected on an Agilent Xcalibur Eos diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-2θ scan mode. The thermal gravimetric analysis (TGA) measurements were performed on a TA instruments Q500 from room temperature to 600 ℃ at a rate of 5°C/min under nitrogen atmosphere. Crystallographic data for **3b**, **3c**, and **3k** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre. (Deposition number: **3b** 2329222, **3c** 2329220, and **3k** 2329221). DFT calculations were conducted on Gaussian 09 program at the B3LYP-D3(BJ)/6-31G(d) basis sets.

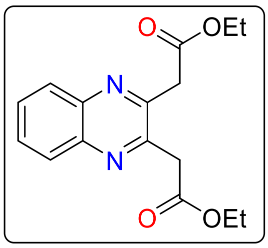
II. Experimental procedure and characterization data

II-1. General procedure for quinoxaline-based ligands[1]



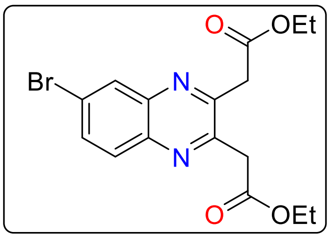
To a 500 mL round-bottom flask equipped with a stir bar was charged with diethyl oxalate (20 mmol, 1.0 equiv.), ethyl acetate (60.0 mmol, 3.0 equiv.) and toluene (60 mL), and then NaH (50.0 mmol, 2.5 equiv., 60% in mineral oil) was added slowly into the mixture at 0 ℃ in an ice bath. The reaction mixture was heated at 80 ℃ for 3 hours. After the completion of the reaction, the reaction was quenched with water (2 mL) and then extracted with ethyl acetate (3 × 50 mL), and adjust pH to 5 with 1 mol/L hydrochloric acid, then washed with brine (3 × 20 mL). The combined organic layer was dried by Na_2SO_4 and concentrated under reduced pressure. The crude products were used for next step without any further purification. The crude product (1.2 equiv.) and corresponding aromatic diamine (5 mmol, 1.0 equiv.) was refluxed in anhydrous EtOH overnight. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 10:1) to give the products (**1a-1c**).

Diethyl 2,2'-(quinoxaline-2,3-diyl)diacetate (1a)



Yellow solid, 4.24 g, 70% yield (PE: EA = 10:1 as the eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 6.3, 3.5 Hz, 2H), 7.73 (dd, J = 6.4, 3.4 Hz, 2H), 4.22 (q, J = 7.2 Hz, 4H), 4.15 (s, 4H), 1.27 (t, J = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.56, 149.75, 141.35, 129.90, 128.85, 61.51, 42.15, 14.19.
HRMS (ESI) calcd for $C_{16}H_{19}N_2O_4^+$ $[M+H]^+$ = 303.1339, found 303.1343.

Diethyl 2,2'-(6-bromoquinoxaline-2,3-diyl)diacetate (1b)



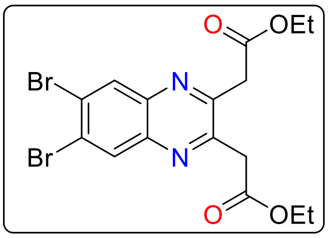
Yellow solid, 5.03g, 65% yield (PE: EA = 8:1 as the eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.81 (dd, *J* = 8.9, 2.2 Hz, 1H), δ 4.21 (q, *J* = 7.1 Hz, 4H), 4.12 (d, *J* = 3.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 3H, CH_3 in Et), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3 in Et).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.39, 150.84, 150.21, 141.96, 140.15, 133.53, 131.29, 130.26, 123.90, 61.68, 42.16, 14.25.

HRMS (ESI) calcd for $C_{16}H_{18}BrN_2O_4^+$ $[M+H]^+$ = 381.0444, found 381.0452.

Diethyl 2,2'-(6,7-dibromoquinoxaline-2,3-diyl)diacetate (1c)



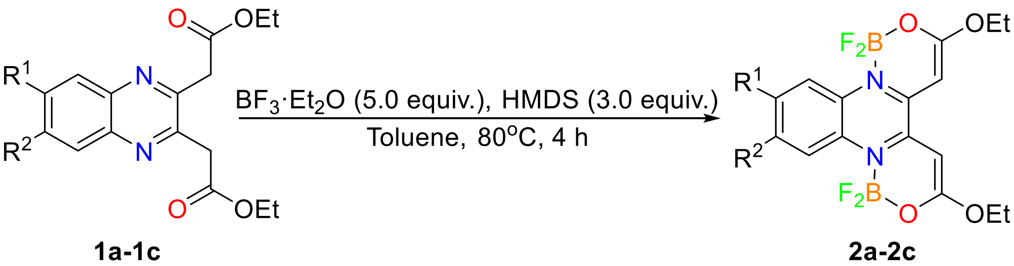
Brown solid, 4.97 g, 54% yield (PE: EA = 8:1 as the eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 4H), 4.11 (s, 4H), 1.28 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.20, 151.26, 140.62, 133.06, 126.60, 61.77, 42.17, 14.27.

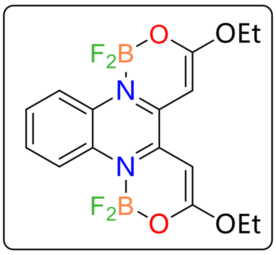
HRMS (ESI) calcd for $C_{16}H_{16}Br_2N_2O_4^+$ $[M+H]^+$ = 458.9550, found 458.9552.

II-2. General procedure for quinoxaline-based bis-boron complexes[2]



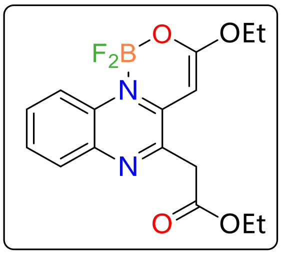
To **1a-1c** (5 mmol) in toluene was added HMDS (3.0 equiv.), and the mixture was stirred for 10 minutes before boron trifluoride etherate (5.0 equiv.) was added via syringe. The reaction mixture was stirring at 80°C for 4 hours. After cooling down to room temperature, the reaction mixture was extracted with dichloromethane (30 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (PE/DCM = 1/1, v/v) followed by recrystallization from hexane.

3,6-Diethoxy-1,1,8,8-tetrafluoro-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (2a)



Orange solid, 1.65 g, 83% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dq, *J* = 6.8, 3.3 Hz, 2H), 7.36 (dt, *J* = 6.6, 3.6 Hz, 2H), 5.47 (s, 2H), 4.55 (q, *J* = 7.1 Hz, 4H), 1.47 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, DMSO) δ 169.97, 150.12, 127.69, 126.61, 120.15, 76.73, 65.93, 14.06.
^{19}F NMR (376 MHz, $CDCl_3$) δ -127.38 (d, *J* = 26.6 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ 2.16.
HRMS (ESI) calcd for $C_{16}H_{17}B_2F_4N_2O_4^+$ $[M+H]^+$ = 399.1305, found 399.1311.

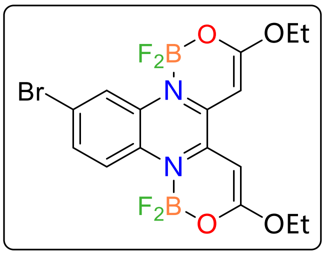
Ethyl 2-(3-ethoxy-1,1-difluoro-1H-1λ^4,11λ^4-[1,3,2]oxazaborinino[3,4-*a*]quinoxalin-5-yl)acetate (2a-mono)



Green-yellow solid, 150.6 mg, 86% yield. (NEt_3 as the base at 25 °C in DCM for 0.5 mmol scale).

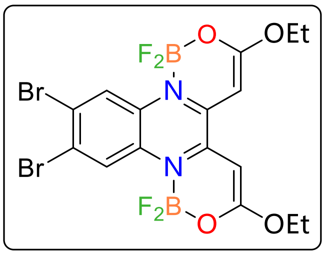
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.64 (ddd, *J* = 8.7, 7.1, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 5.25 (s, 1H), 4.49 (t, *J* = 7.1 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58, 168.57, 149.51, 148.21, 137.48, 131.61, 130.79, 129.79, 126.56, 120.38, 74.55, 64.79, 61.75, 42.54, 14.35, 14.14.
^{19}F NMR (376 MHz, $CDCl_3$) δ -127.96 (dd, *J* = 33.3, 13.2 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ 2.24 (t, *J* = 17.5 Hz).
HRMS (ESI) calcd for $C_{16}H_{18}BF_2N_2O_4^+$ $[M+H]^+$ = 351.1322, found 351.1330.

11-Bromo-3,6-diethoxy-1,1,8,8-tetrafluoro-1,8-dihydro-1λ⁴,8λ⁴,9λ⁴,14λ⁴-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (2b)



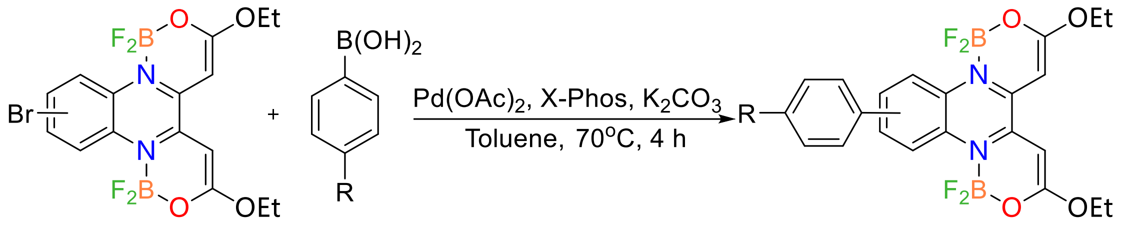
Brown solid, 1.83 g, 77% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (q, *J* = 2.2 Hz, 1H), 7.98 (dt, *J* = 9.2, 2.6 Hz, 1H), 7.44 (dd, *J* = 9.2, 2.1 Hz, 1H), δ 5.46 (d, *J* = 5.9 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.45 (t, *J* = 7.1, 3H, CH_3 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.66, 170.49, 149.58, 149.25, 130.01, 129.19, 127.25, 123.52, 123.44, 123.36, 122.23, 122.15, 122.07, 120.47, 65.91, 65.79, 14.36.
^{19}F NMR (376 MHz, $CDCl_3$) δ -127.50, -127.57, -127.63.
^{11}B NMR (128 MHz, $CDCl_3$) δ 2.01.
HRMS (ESI) calcd for $C_{16}H_{16}B_2BrF_4N_2O_4^+$ $[M+H]^+$ = 477.0410, found 477.0427.

11,12-Dibromo-3,6-diethoxy-1,1,8,8-tetrafluoro-1,8-dihydro-1λ⁴,8λ⁴,9λ⁴,14λ⁴-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (2c)



Brown solid, 1.78 g, 64% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 2H), 5.50 (s, 2H), 4.55 (q, *J* = 7.1 Hz, 4H), 1.45 (t, *J* = 7.1 Hz, 6H).
*We attempted to use $CDCl_3$, *d*$_6$-DMSO, and CD_3CN as deuterated solvents. However, due to the poor solubility, the ^{13}C and ^{11}B NMR of **2c** were not obtained.
^{19}F NMR (376 MHz, $CDCl_3$) δ -127.77 – -127.95 (m).
HRMS (ESI) calcd for $C_{16}H_{15}B_2Br_2F_4N_2O_4^+$ $[M+H]^+$ = 554.9515, found 554.9531.

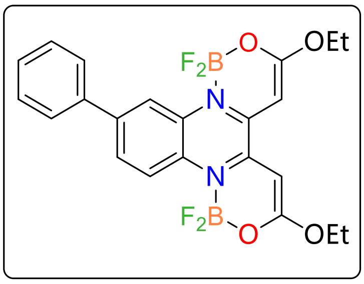
II-3. General procedure for Suzuki-Miyaura coupling of bis-boron complexes[3]



2b or **2c** **3a-3e, 4a-4c**

An oven-dried Schlenk tube was charged with compound **2b** or **2c** (0.5 mmol), arylboronic acid (2.0 equiv.), $Pd(OAc)_2$ (0.05 equiv.), X-Phos (0.2 equiv.), and K_2CO_3 (3.0 equiv.). The reaction vessel was evacuated and backfilled with nitrogen, 1 mL of toluene was then added via syringe. The reaction mixture was stirring at 70°C for 4 hours. After cooling to room temperature, the crude product was purified by silica gel flash chromatography (PE /DCM = 2:1) to afford the target product.

3,6-diethoxy-1,1,8,8-tetrafluoro-11-phenyl-1,8-dihydro-1λ4,8λ4,9λ4,14λ4-bis([1,3,2]oxazaborinino)[3,4-a:4',3'-c]quinoxaline (3a)



Orange solid, 203.8 mg, 86% yield. (PE/DCM = 2: 1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.5 Hz, 1H), 8.22 (dt, *J* = 9.0, 2.9 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.63 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.47 (td, *J* = 7.2, 6.3, 1.3 Hz, 2H), 7.42 – 7.37 (m, 1H), 5.47 (d, *J* = 2.1 Hz, 2H), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.47 (t, *J* = 7.1 Hz, 6H).

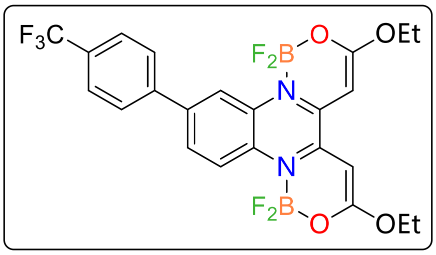
^{13}C NMR (101 MHz, $CDCl_3$) δ170.32, 170.20, 149.56, 149.07, 139.95, 139.62, 129.10, 128.10, 127.37, 126.06, 121.33, 121.26, 121.26, 121.19, 119.03, 76.42, 76.29, 65.57, 14.40.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.20 (d, *J* = 28.6 Hz), -127.50 (d, *J* = 28.8 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.18.

HRMS (ESI) calcd for $C_{22}H_{21}B_2F_4N_2O_4^+$ $[M+H]^+$ = 475.1618, found 475.1634.

3,6-diethoxy-1,1,8,8-tetrafluoro-11-(4-(trifluoromethyl)phenyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3b)



Green solid, 238.5 mg, 88% yield. (PE/DCM = 2:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.5 Hz, 1H), 8.22 (dt, *J* = 9.0, 2.8 Hz, 1H), 7.74 (q, *J* = 8.4 Hz, 4H), 7.60 (dd, *J* = 8.9, 1.9 Hz, 1H), 5.50 (s, 2H), 4.56 (q, *J* = 7.1 Hz, 4H), 1.48 (t, *J* = 7.1 Hz, 6H).

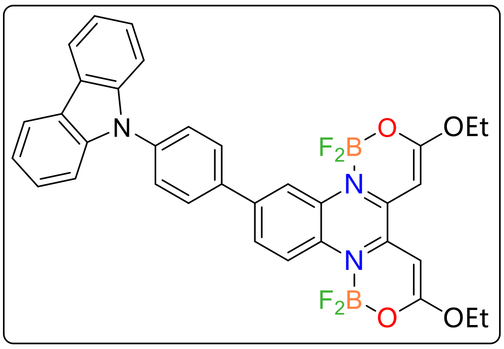
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.46, 149.65, 149.28, 143.12, 138.18, 128.71, 128.18, 127.64, 125.96 (q, *J* = 271.8 Hz), 125.88 (q, *J* = 32.3 Hz), 121.36 (q, *J* = 3.4 Hz), 119.25, 76.70, 65.73, 14.37.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49, -127.35 (dd, *J* = 89.3, 29.4 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.12.

HRMS (ESI) calcd for $C_{23}H_{20}B_2F_7N_2O_4^+$ $[M+H]^+$ = 543.1492, found 543.1512.

11-(4-(9H-carbazol-9-yl)phenyl)-3,6-diethoxy-1,1,8,8-tetrafluoro-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3c)



Yellow solid, 204.5 mg, 64% yield. (PE/DCM = 1: 1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.46 (m, 1H), 8.27 (d, *J* = 8.9 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 8.2 Hz, 3H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.30 (t, *J* = 7.0 Hz, 2H), 5.51 (d, *J* = 2.0 Hz, 2H), 4.55 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.54 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.49 (t, *J* = 7.1 Hz, 6H).

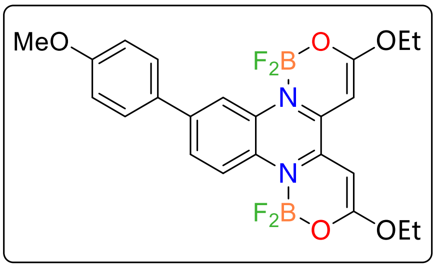
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.65, 148.88, 148.39, 140.13, 138.17, 137.88, 136.90, 128.02, 127.12, 126.83, 125.39, 125.16, 122.84, 120.69, 119.67, 119.41, 109.26, 75.82, 75.72, 64.86, 13.62.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.10, -127.43.

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.30.

HRMS (ESI) calcd for $C_{34}H_{28}B_2F_4N_3O_4^+$ $[M+H]^+$ = 640.2197, found 640.2211.

3,6-diethoxy-1,1,8,8-tetrafluoro-11-(4-methoxyphenyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3d)



Red solid, 161.3 mg, 81% yield. (PE/DCM = 2:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.5 Hz, 1H), 8.11 (dt, *J* = 9.1, 2.9 Hz, 1H), 7.58 – 7.47 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.40 (d, *J* = 4.5 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.45 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 3.79 (s, 3H), 1.37 (t, *J* = 7.1, 3H, CH_3 in Et), 1.37 (t, *J* = 7.1, 3H, CH_3 in Et).

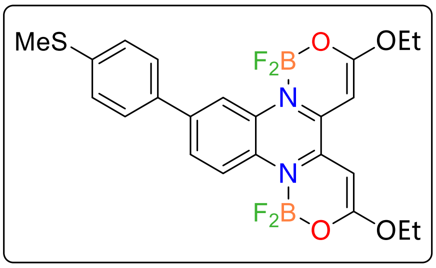
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.27, 170.08, 159.87, 149.54, 148.88, 139.65, 135.27, 132.10, 128.48, 127.24, 125.74, 121.23, 118.42, 114.57, 76.36, 76.10, 65.52, 55.54, 14.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.21 (d, *J* = 25.8 Hz), -127.54 (d, *J* = 24.0 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.19.

HRMS (ESI) calcd for $C_{23}H_{24}B_2F_4N_2O_5^+$ $[M+H]^+$ = 505.1724, found 505.1746.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11-(4-(methylthio)phenyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3e)



Red solid, 184.6 mg, 71% yield. (PE/DCM = 2:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.47 (d, *J* = 2.6 Hz, 2H), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.51 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 2.53 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 6H).

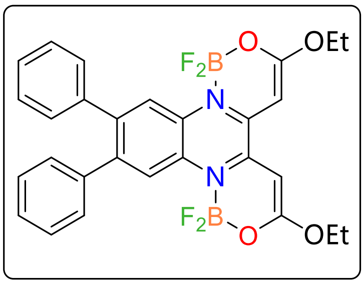
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 170.17, 149.55, 148.98, 139.22, 138.84, 136.25, 128.77, 127.63, 127.03, 125.69, 121.30, 118.55, 76.44, 76.28, 65.58, 65.52, 15.89, 14.41, 14.38.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.18 (d, *J* = 22.4 Hz), -127.49 (d, *J* = 23.2 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.19.

HRMS (ESI) calcd for $C_{23}H_{24}B_2F_4N_2O_4S^+$ $[M+H]^+$ = 521.1495, found 521.1496.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11,12-diphenyl-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (4a)



Orange solid, 209.0 mg, 76% yield. (PE/DCM = 2:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, *J* = 2.8 Hz, 2H), 7.27 – 7.22 (m, 6H), 7.19 (dd, *J* = 6.8, 3.1 Hz, 4H), 5.48 (s, 2H), 4.51 (q, *J* = 7.1 Hz, 4H), 1.43 (t, *J* = 7.1 Hz, 6H).

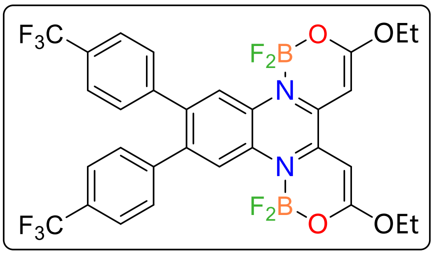
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.17, 149.16, 140.12, 139.71, 129.95, 128.05, 127.49, 127.07, 122.35 (t, *J* = 7.2 Hz), 76.32, 65.44, 14.25.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.40, -127.47.

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.17.

HRMS (ESI) calcd for $C_{28}H_{26}BF_2N_2O_4^+$ $[M+H]^+$ = 551.1931, found 551.1933.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11,12-bis(4-(trifluoromethyl)phenyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (4b)



Green-yellow solid, 281.3 mg, 82% yield. (PE/DCM = 2: 1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 5.54 (s, 2H), 4.55 (d, *J* = 7.1 Hz, 4H), 1.46 (t, *J* = 7.1 Hz, 6H).

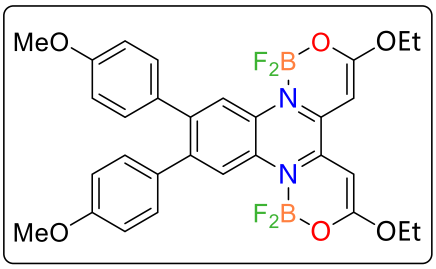
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.64, 149.55, 143.41, 137.86, 132.17, 130.31, 129.82 (q, *J* = 32.2 Hz), 125.43 (q, *J* = 3.7 Hz), 124.18 (q, *J* = 272.2 Hz), 122.76, 122.69, 65.89, 14.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51, -127.45 (d, *J* = 19.3 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.16.

HRMS (ESI) calcd for $C_{30}H_{23}B_2F_{10}N_2O_4^+$ $[M+H]^+$ = 687.1679, found 687.1684.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11,12-bis(4-methoxyphenyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (4c)



Red solid, 225.8 mg, 74% yield. (PE/DCM = 2: 1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (t, *J* = 2.5 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 4H), 6.70 (d, *J* = 8.6 Hz, 4H), 5.36 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 4H), 3.69 (s, 6H), 1.31 (t, *J* = 7.1 Hz, 6H).

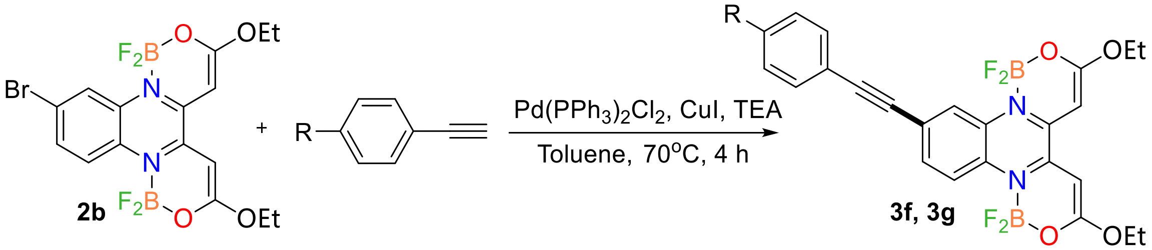
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.11, 158.85, 149.05, 139.34, 132.75, 131.09, 127.37, 122.19, 113.66, 76.21, 65.44, 55.29, 14.29.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.33, -127.38.

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.16.

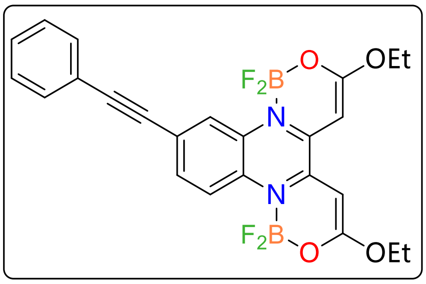
HRMS (ESI) calcd for $C_{30}H_{30}B_2F_4N_2O_6^+$ $[M+H]^+$ = 611.2142, found 611.2141.

II-4. General procedure for Sonogashira coupling of bis-boron complexes[4]



Under N_2 atmosphere, compound **2b** (0.5 mmol), phenylacetylene (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (0.05 equiv.), and CuI (0.1 equiv.) were dissolved in triethylamine (1 mL) and toluene (1 ml), the flask was vacuumed and back-filled with N_2 for several times. The solution was stirred at 70°C for 4 hours. The solvent then was removed under reduced pressure and the crude product was purified by column chromatography (PE:DCM =2:1 as the eluent) to afford the target product.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11-(phenylethynyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3f)



Orange solid, 169.3 mg, 68% yield. (PE/DCM = 1:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.2 Hz, 1H), 8.09 (d, *J* = 8.9 Hz, 2H), 7.57 (dd, *J* = 6.5, 3.2 Hz, 3H), 7.47 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.40 – 7.32 (m, 5H), 5.47 (d, *J* = 2.3 Hz, 2H), 4.53 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et).

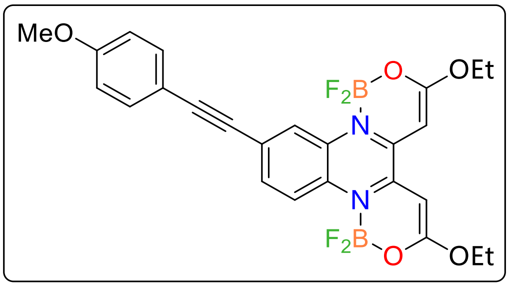
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.44, 149.57, 149.16, 131.91, 130.12, 128.70, 128.50, 128.21, 128.09, 123.59 (t, *J* = 7.1 Hz), 122.98, 122.19, 120.93 (t, *J* = 6.9 Hz), 91.43, 88.76, 76.68, 65.73, 14.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.39 (d, *J* = 26.6 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.10.

HRMS (ESI) calcd for $C_{24}H_{21}B_2F_4N_2O_4^+$ $[M+H]^+$ = 499.1618, found 499.1636.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11-((4-methoxyphenyl)ethynyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3g)



Orange solid, 186.9 mg, 73% yield. (PE/DCM = 1:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (q, *J* = 2.3 Hz, 1H), 8.11 (dt, *J* = 9.0, 2.8 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.46 (dd, *J* = 8.9, 1.7 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.47 (s, 2H), 4.53 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et).

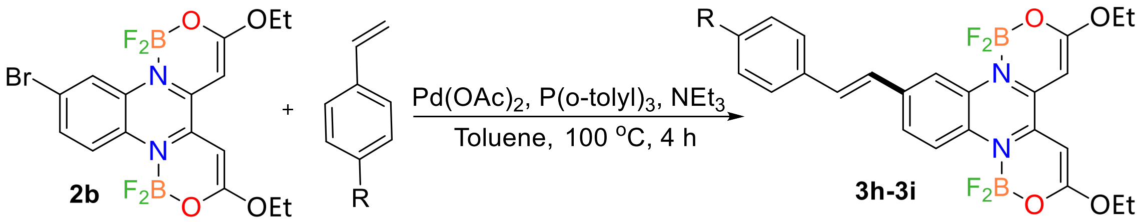
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.39, 170.31, 159.99, 149.54, 149.04, 133.37, 129.95, 128.22, 127.85, 123.29, 122.54, 120.85, 115.03, 114.16, 91.59, 87.59, 76.66, 76.60, 65.67, 55.42, 14.33.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.37 (q, *J* = 23.1, 20.4 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.09.

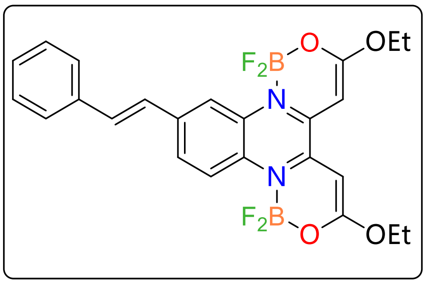
HRMS (ESI) calcd for $C_{25}H_{23}B_2F_4N_2O_5^+$ [M+H]$^+$ = 529.1724, found 529.1727.

II-5. General procedure for Heck coupling of bis-boron complexes[5]



A Schlenk tube was charged with **2b** (0.5 mmol), styrene (1.5 equiv.), $Pd(OAc)_2$ (0.05 equiv.), P(*o*-tolyl)$_3$ (0.1 equiv.), toluene (1 mL) and triethylamine (1 mL). The flask was degassed and purged with nitrogen for three times. The mixture was heated at 100 ℃ for 4 hours. After cooling to room temperature, the crude product was purified by silica gel flash chromatography (PE/DCM = 1:1) to afford the target product.

(*E*)-3,6-Diethoxy-1,1,8,8-tetrafluoro-11-styryl-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3h)



Red solid, 185.0 mg, 74% yield. (PE/DCM = 1:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.13 (d, *J* = 8.9 Hz, 1H), 7.54 (t, *J* = 8.2 Hz, 3H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.17 – 7.12 (m, 2H), 5.43 (d, *J* = 4.7 Hz, 2H), 5.29 (s, 1H), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.51 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et), 1.43 (t, *J* = 7.1, 3H, CH_3 in Et).

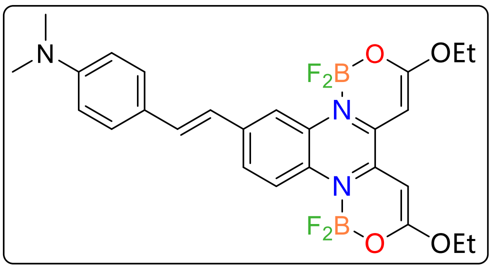
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.23, 170.04, 149.49, 148.70, 136.97, 136.39, 130.61, 128.84, 128.73, 128.15, 127.44, 126.91, 124.80, δ 121.17 (t, *J* = 8.1 Hz), 118.92, 76.37, 76.22, 65.54, 14.40.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.14 (d, *J* = 21.7 Hz), -127.46 (d, *J* = 22.3 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.13.

HRMS (ESI) calcd for $C_{24}H_{23}B_2F_4N_2O_4^+$ $[M+H]^+$ = 501.1775, found 501,1789.

(*E*)-4-(2-(3,6-Diethoxy-1,1,8,8-tetrafluoro-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxalin-11-yl)vinyl)-N,N-dimethylaniline (3i)



Black-gray solid, 187.4 mg, 69% yield. (PE/DCM = 1:1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.4 Hz, 1H), 8.03 (dt, *J* = 9.1, 2.9 Hz, 1H), 7.48 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.05 (d, *J* = 16.2 Hz, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 5.37 (d, *J* = 7.3 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.43 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.38 (t, *J* = 7.1, 3H, CH_3 in Et), 1.36 (t, *J* = 7.1, 3H, CH_3 in Et).

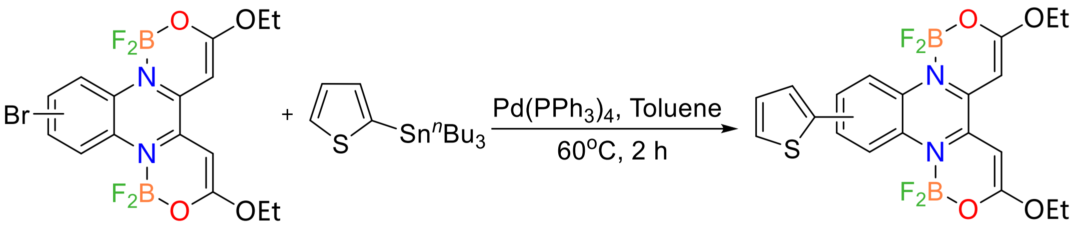
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.13, 169.81, 150.06, 149.44, 148.35, 137.47, 130.86, 128.87, 128.15, 127.28, 126.01, 124.61, 123.33, 121.10, 118.13, 112.86, 76.20, 75.88, 65.45, 65.35, 40.87, 14.43.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.21 (d, *J* = 24.5 Hz), -127.59 (d, *J* = 21.7 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.16.

HRMS (ESI) calcd for $C_{26}H_{28}B_2F_4N_3O_4^+$ $[M+H]^+$ = 544.2197, found 544.2191.

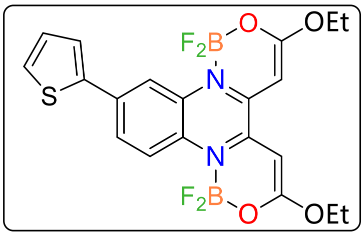
II-6. General procedure for Stille coupling of bis-boron complexes[6]



2b or **2c** **3j** or **4d**

An oven-dried Schlenk tube was charged with **2b/2c** (0.5 mmol) and $Pd(PPh_3)_4$ (0.05 equiv.) under nitrogen. After adding the dry toluene (3 mL) and tributyl(thiophen-2-yl)stannane (1.3 equiv.) via syringe, the mixture was kept stirring at 60°C for 2 hours. After cooling to room temperature, water was added, and the crude mixture was extracted with DCM (10 mL). The organic layers were combined, washed with brine and dried over magnesium sulfate. The solvents were removed under vacuum and the residue was chromatographed on a silica gel column (PE/DCM = 2:1) to afford the target product.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11-(thiophen-2-yl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3j)



Deep-red solid, 240.0 mg, 84% yield. (PE/DCM = 2: 1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.3 Hz, 1H), 8.14 (dt, *J* = 9.0, 2.8 Hz, 1H), 7.59 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.42 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.33 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.46 (d, *J* = 4.9 Hz, 2H), 4.52 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.51 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.44 (t, *J* = 7.1, 3H, CH_3 in Et), 1.43 (t, *J* = 7.1, 3H, CH_3 in Et).

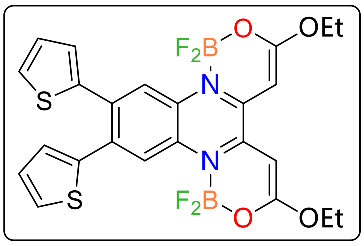
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.25, 170.02, 149.48, 148.72, 142.78, 133.20, 128.67, 128.30, 127.49, 125.96, 124.79, 124.39, 121.27, 121.19, 117.25, 76.44, 76.17, 65.41, 14.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.35 (d, *J* = 26.1 Hz), -127.53 (d, *J* = 26.2 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.20 (d, *J* = 17.6 Hz).

HRMS (ESI) calcd for $C_{20}H_{19}B_2F_4N_2O_4S^+$ $[M+H]^+$ = 481.1182, found 481.1198.

3,6-Diethoxy-1,1,8,8-tetrafluoro-11,12-di(thiophen-2-yl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (4d)



Deep-red solid, 281.1 mg, 81% yield. (PE/DCM = 2: 1 as eluent)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.34 (dd, *J* = 4.6, 1.7 Hz, 2H), 7.04 – 6.99 (m, 4H), 5.52 (s, 2H), 4.55 (q, *J* = 7.1 Hz, 4H), 1.47 (t, *J* = 7.1 Hz, 6H).

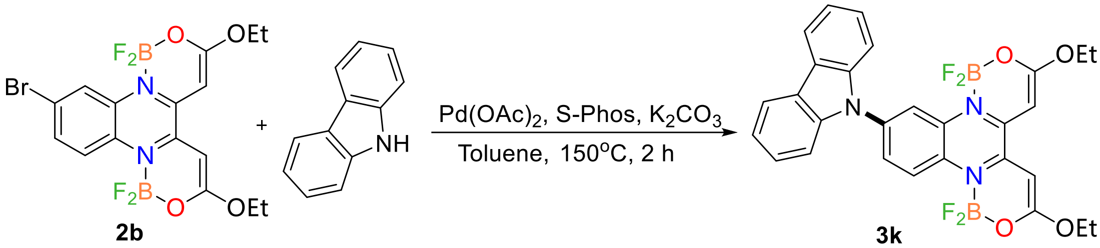
^{13}C NMR (101 MHz, $CDCl_3$) 170.32, 149.21, 141.25, 132.72, 127.97, 127.55, 127.03, 126.85, 122.50 (t, *J* = 7.4 Hz), 65.58, 14.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.59, -127.65.

^{11}B NMR (128 MHz, $CDCl_3$) δ 2.12.

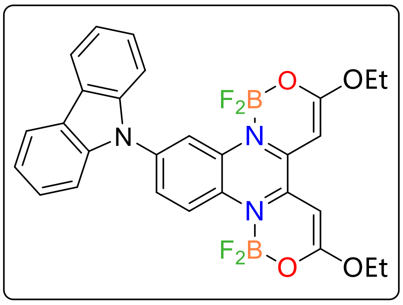
HRMS (ESI) calcd for $C_{24}H_{22}B_2F_4N_2O_4S_2^+$ $[M+H]^+$ = 563.1059, found 563.1055.

II-7. General procedure for Buchwald-Hartwig amination of bis-boron complexes[7]



An oven-dried Schlenk tube was charged with **2b** (0.5 mmol), 9*H*-carbozole (1.2 equiv.), $Pd(OAc)_2$ (0.05 equiv.), S-Phos (0.1 equiv.), and *t*-BuOK (3.0 equiv.). The reaction vessel was evacuated and backfilled again with nitrogen for three times before toluene (1 mL) was added via syringe. The reaction mixture was kept stirring at 150°C for 2 hours. After cooling to room temperature, the crude product was purified by silica gel flash chromatography (PE/DCM = 1:1 as eluent) to afford **3k** (281.6 mg, 62% yield) as a purple solid.

11-(9*H*-Carbazol-9-yl)-3,6-diethoxy-1,1,8,8-tetrafluoro-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3k)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.5 Hz, 1H), 8.27 (dt, *J* = 9.2, 2.6 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 2H), 7.54 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 5.44 (d, *J* = 4.8 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 4.43 (q, *J* = 7.1 Hz, 2H, CH_2 in Et), 1.38 (t, *J* = 7.1, 3H, CH_3 in Et), 1.36 (t, *J* = 7.1, 3H, CH_3 in Et).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.62, 170.39, 149.63, 149.17, 140.39, 136.33, 129.33, 126.84, 126.41, 124.94, 123.90, 122.25, 120.63, 120.47, 118.47, 110.00, 76.56, 65.83, 65.75, 14.40, 14.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -127.46 (dd, *J* = 54.4, 29.1 Hz).

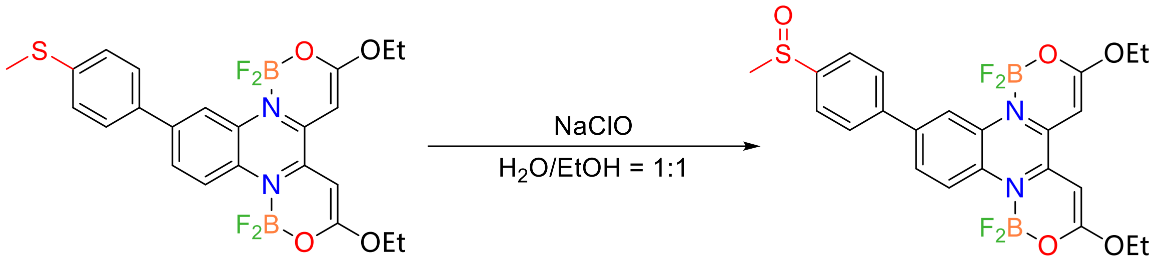
^{11}B NMR (128 MHz, $CDCl_3$) δ 2.18.

HRMS (ESI) calcd for $C_{28}H_{24}B_2F_4N_3O_4^+$ $[M+H]^+$ = 564.1884, found 564.1871.

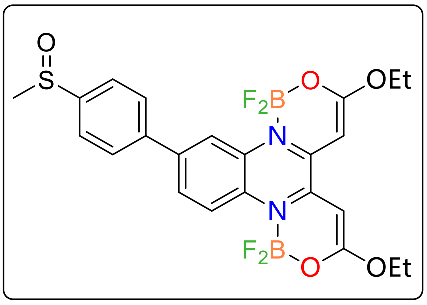
II-8. Preparation of ROS and RNS

The stock solution of ClO^- (2.0 mM) was prepared by diluting a NaClO aqueous solution (1.4 mol/L), and the concentration was determined from absorption at λ = 292 nm (ε = 350 M^{-1} cm^{-1}). Hydrogen peroxide (H_2O_2) was prepared by diluting a 30% H_2O_2 solution, and the final concentration of H_2O_2 was 100 μM. *tert*-Butyl hydroperoxide (TBHP, 100 μM) was prepared in degassed deionized water. Hydroxyl radical (•OH) was generated *in situ* by a Fenton reaction: $FeCl_2$ (100 μM) was added to 10 equiv. of H_2O_2, and the concentration of •OH was estimated from the concentration of Fe (II). Nitric oxide (NO) was generated from SNP (Sodium Nitroferricyanide (III) Dihydrate), which was added into degassed deionized water under N_2 and stirred for 30 min. Singlet oxygen ($^1O_2$) was prepared by adding $NaMoO_4$ to a solution of H_2O_2 in PBS solution (pH 7.4, 10.0 mM).

II-9. Preparation of 3e-SO from 3e and NaClO

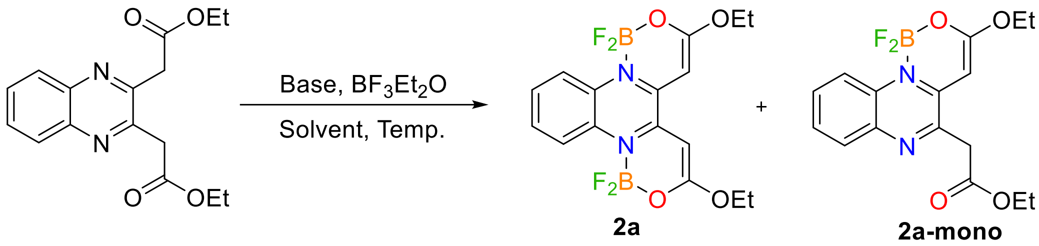


3,6-Diethoxy-1,1,8,8-tetrafluoro-11-(4-(methylsulfinyl)phenyl)-1,8-dihydro-1λ^4,8λ^4,9λ^4,14λ^4-bis([1,3,2]oxazaborinino)[3,4-*a*:4',3'-*c*]quinoxaline (3e-SO)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.62 (m 4H), 7.52 (d, *J* = 8.4 Hz, 1H), 5.43 (s, 2H), 4.46 (q, *J* = 7.2 Hz, 4H), 2.70 (s, 3H), 1.38 (t, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.40, 149.63, 149.23, 145.38, 142.52, 138.27, 128.70, 128.26, 128.13, 125.86, 124.30, 121.47, 119.25, 76.69, 65.71, 44.23, 14.37.
^{19}F NMR (376 MHz, $CDCl_3$) δ -127.22 (d, *J* = 25.6 Hz), -127.47 (d, *J* = 24.4 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ 2.20.
HRMS (ESI) calcd for $C_{23}H_{24}B_2F_4N_2O_5S^+$ $[M+H]^+$ = 537.1444, found 537.1449.

Table S1. Optimization of boron coordinated reactions.[a]



Entry	Solvent	Base	Temp.	Result
1	DCM	NEt_3	25°C	**2-mono**, 86% yield
2	Toluene	NEt_3	80°C	**2,** 77% yield
3	Toluene	HMDS	80°C	**2,** 83% yield
4	Toluene	HMDS	110°C	**2,** 78% yield

[a] Reaction conditions: Base (3 equiv.), $BF_3 \cdot Et_2O$ (5 equiv.) in solvent for 4 hours.

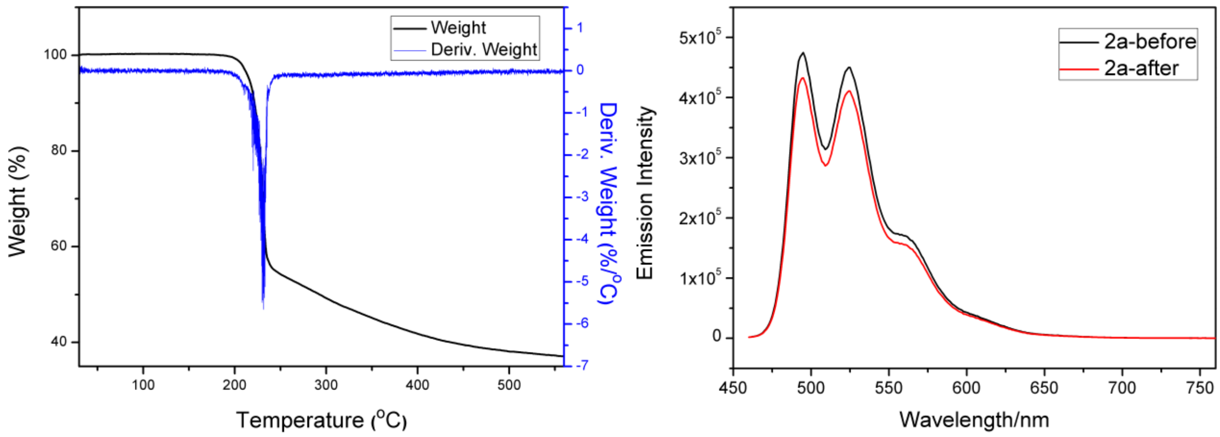


Fig. S1 TGA curves and derivative weight of **2a** (left) and photostability of **2a** under continuous irradiation with a 500W Xe lamp over 20 minutes (right).

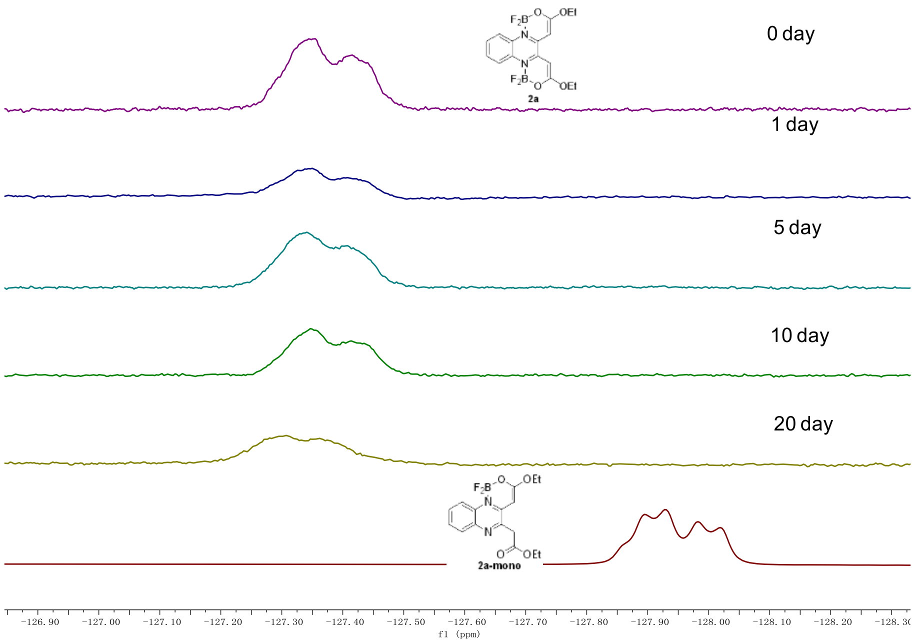
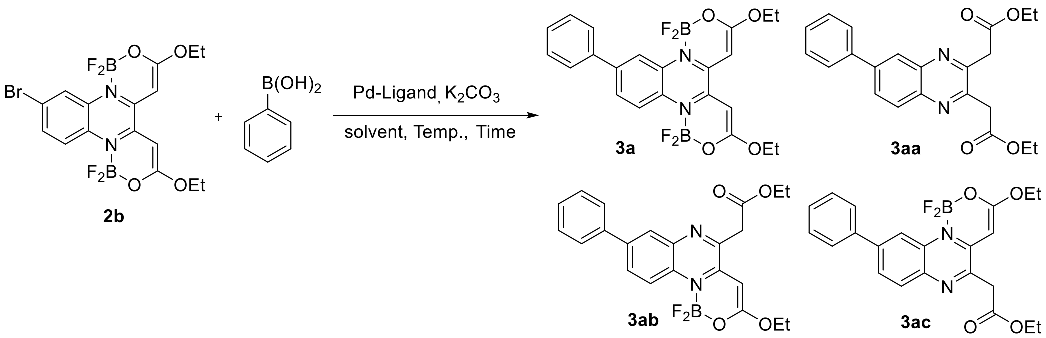


Fig. S2 [19]F NMR of **2a** in $CDCl_3$ for different times compared with **2a-mono**. Notice: **2a-mono** is unstable in solution and has deteriorated in $CDCl_3$ for 12 hours.

Table S2 Optimization of Suzuki-Coupling reactions.[a]



Entry	Pd catalyst/ligand	Solvent	Temp.	Yield (%)
1	$Pd(PPh_3)Cl_2$	Dioxane:H_2O	100°C	**3aa,** 75%
2	$Pd(PPh_3)Cl_2$	Dioxane:H_2O	70°C	**3aa**, 82%
3	$Pd(PPh_3)Cl_2$	THF	70°C	**3ab+3ac**, 45%
4	$Pd(PPh_3)Cl_2$	THF	50°C	**3ab+3ac**, 73%
5	$Pd(OAc)_2$/XPhos	Toluene	r.t.	**3a**, 66%
6	$Pd(OAc)_2$/XPhos	Toluene	70°C	**3a** 73% & **(3ab+3ac)** 18%
7	$Pd(OAc)_2$/XPhos	Toluene	70°C	**3a**, 86%

[a] **2b** (0.3 mmol), phenylboronic acid (2.0 equiv.), Pd catalyst (5 mol%), ligand (10 mol%), K_2CO_3 (3.0 equiv.), solvent (1 mL), 10 h.

III. Crystallographic and structural refinement data

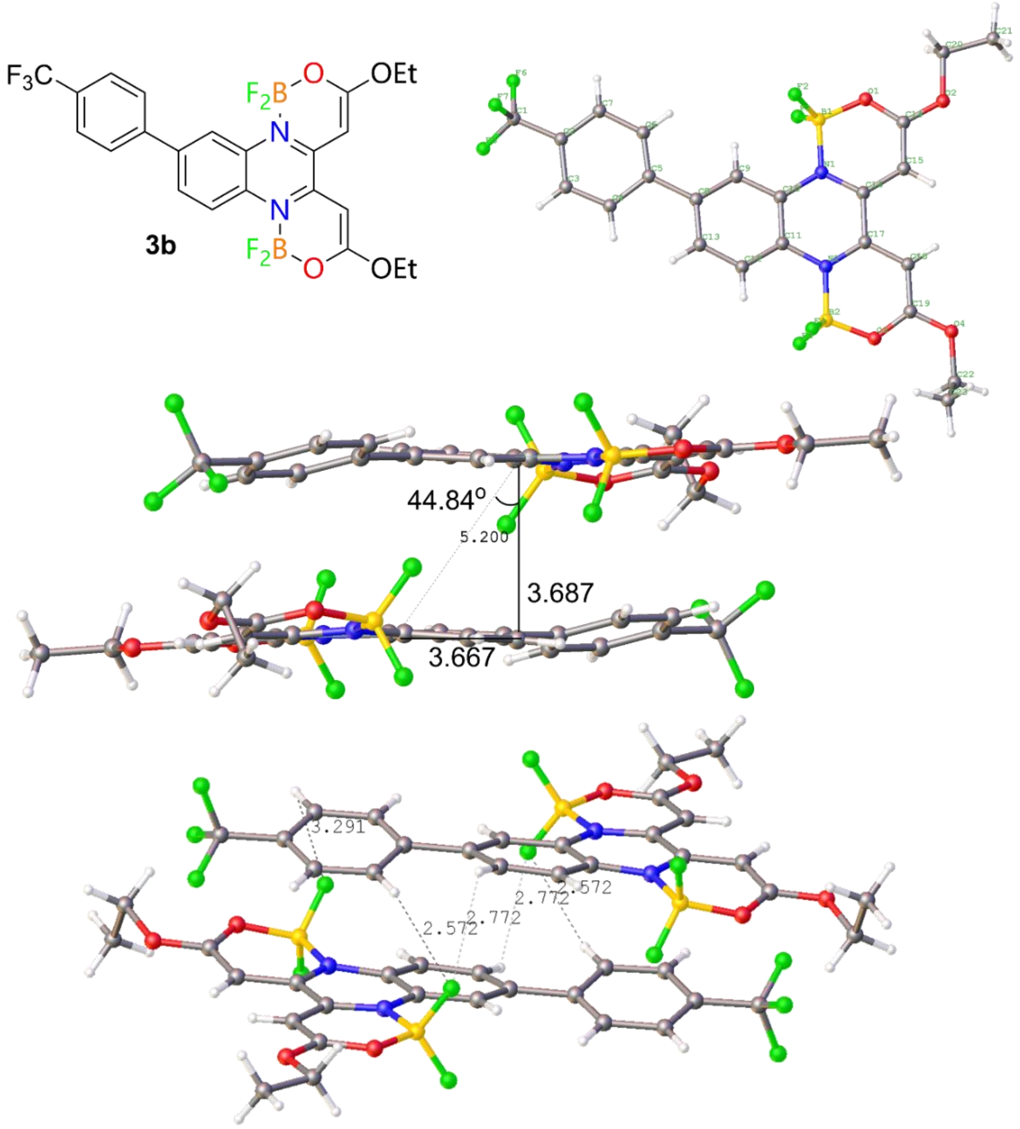


Fig. S3 Crystal-packing pattern of **3b** between the adjacent interlayered crystals from side view. Interlayer distance is 3.687 Å and the corresponding slip angel of 44.84° for coplanar inclined arrangements of its transition dipole. H, light gray; C, gray; N, blue; O, red; F, green; B, yellow.

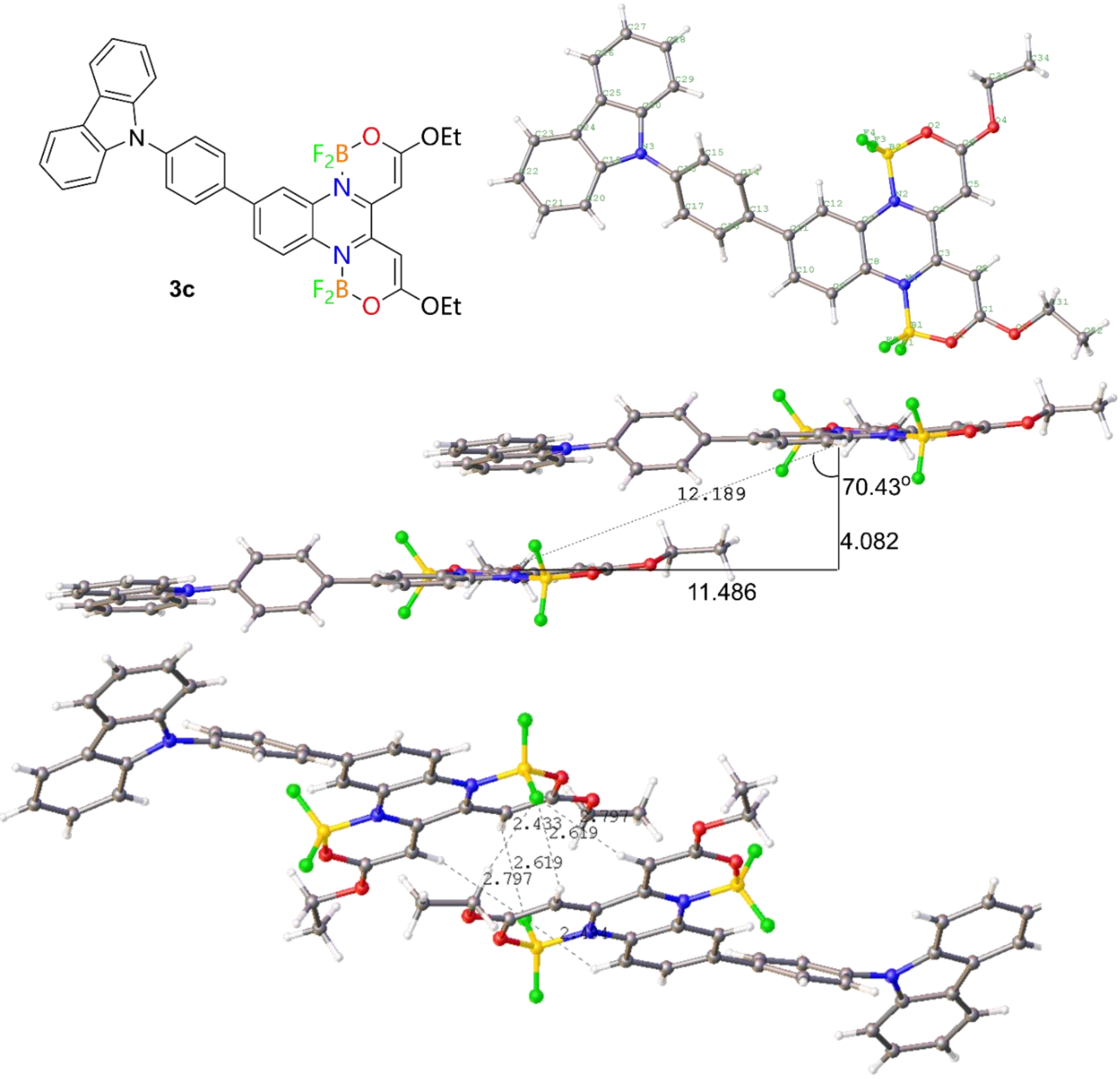


Fig. S4 Crystal-packing pattern of **3c** between the adjacent interlayered crystals from side view. Interlayer distance is 4.082 Å and the corresponding slip angel of 70.43° for coplanar inclined arrangements of its transition dipole. H, light gray; C, gray; N, blue; O, red; F, green; B, yellow.

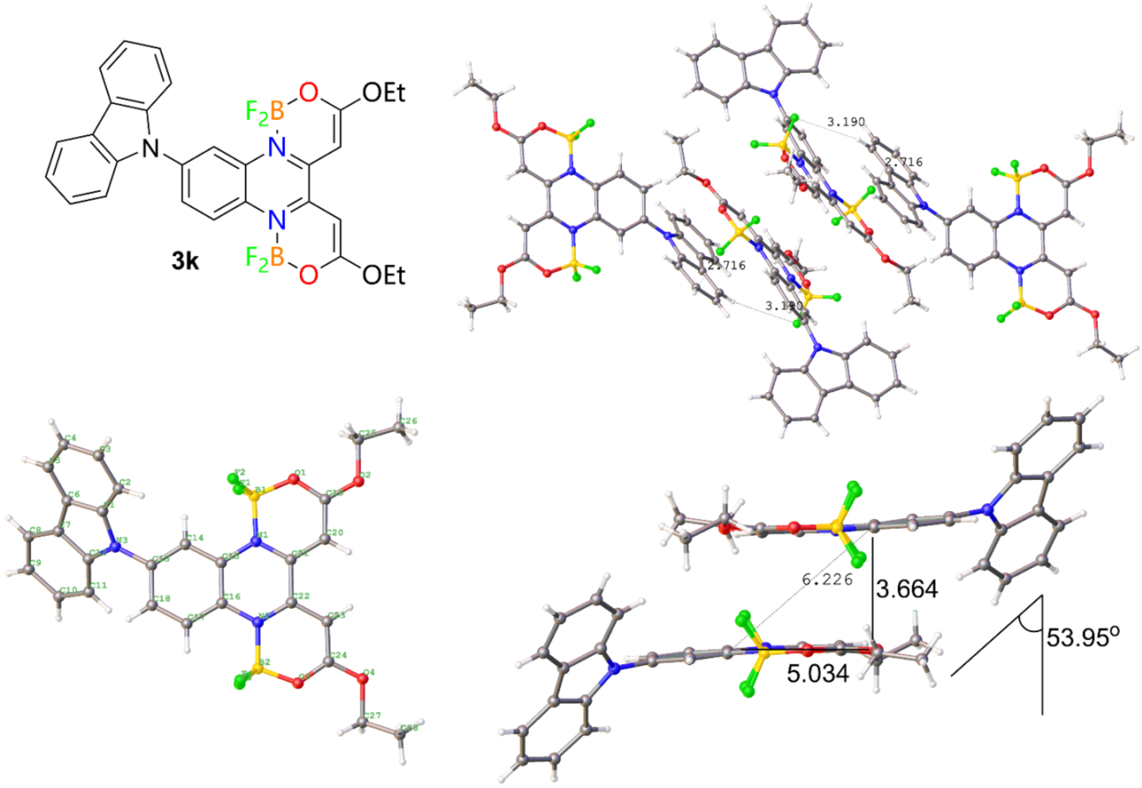


Fig. S5 Crystal-packing pattern of **3k** between the adjacent interlayered crystals from side view. Interlayer distance is 3.664 Å and the corresponding slip angel of 53.95° for coplanar inclined arrangements of its transition dipole. H, light gray; C, gray; N, blue; O, red; F, green; B, yellow.

Table S3 Crystal data and structure refinements for **3b** obtained from crystallography.

Identification code	**3b**
CCDC No.	2329222
Empirical formula	$C_{23}H_{19}B_2F_7N_2O_4$
Formula weight	542.02
Temperature/K	118.25(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.7996(5)
b/Å	27.3747(14)
c/Å	9.3692(5)
α/°	90.00
β/°	92.549(5)
γ/°	90.00
Volume/Å^3	2254.7(2)
Z	4
ρ_{calc}g/cm^3	1.597
μ/mm^{-1}	0.145
F(000)	1104.0
Crystal size/mm^3	0.35 × 0.26 × 0.14
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.24 to 52
Index ranges	-10 ≤ h ≤ 10, -33 ≤ k ≤ 30, -11 ≤ l ≤ 8
Reflections collected	9269
Independent reflections	4304 [R_{int} = 0.0409, R_{sigma} = 0.0659]
Data/restraints/parameters	4304/12/345
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1332
Final R indexes [all data]	R_1 = 0.0876, wR_2 = 0.1483
Largest diff. peak/hole / e Å^{-3}	0.99/-0.28

Table S4 Crystal data and structure refinements for **3c** obtained from crystallography.

Compound	**3c**
CCDC No.	2329220
Empirical formula	$C_{34}H_{27}B_2F_4N_3O_4$
Formula weight	724.185
Temperature/K	115(4)
Crystal system	triclinic
Space group	P-1
a/Å	11.4676(7)
b/Å	12.1893(8)
c/Å	13.0225(8)
α/°	102.544(5)
β/°	105.810(5)
γ/°	104.715(5)
Volume/Å^3	1611.8(2)
Z	2
ρ_{calc}g/cm^3	1.492
μ/mm^{-1}	0.271
F(000)	745.0
Crystal size/mm^3	0.4 × 0.36 × 0.21
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.16 to 52
Index ranges	$-15 \leq h \leq 14$, $-15 \leq k \leq 15$, $-17 \leq l \leq 16$
Reflections collected	13055
Independent reflections	6201 [R_{int} = 0.0351, R_{sigma} = 0.0601]
Data/restraints/parameters	6201/0/453
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0584, wR_2 = 0.1255
Final R indexes [all data]	R_1 = 0.0778, wR_2 = 0.1412
Largest diff. peak/hole / e Å^{-3}	1.38/-1.27

Table S5 Crystal data and structure refinements for **3k** obtained from crystallography.

Identification code	**3k**
CCDC No.	2329221
Empirical formula	$C_{28}H_{23}B_2F_4N_3O_4$
Formula weight	563.11
Temperature/K	118.15(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.4139(5)
b/Å	11.676(2)
c/Å	19.1275(8)
α/°	90.00
β/°	94.138(4)
γ/°	90.00
Volume/Å^3	2542.5(5)
Z	4
ρ_{calc}g/cm^3	1.471
μ/mm^{-1}	0.117
F(000)	1160.0
Crystal size/mm^3	0.35 × 0.33 × 0.33
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.4 to 52
Index ranges	$-12 \leq h \leq 13$, $-13 \leq k \leq 11$, $-17 \leq l \leq 23$
Reflections collected	10584
Independent reflections	4850 [R_{int} = 0.0370, R_{sigma} = 0.0607]
Data/restraints/parameters	4850/0/374
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.0945
Final R indexes [all data]	R_1 = 0.0728, wR_2 = 0.1087
Largest diff. peak/hole / e Å^{-3}	0.20/-0.26

Table S6 Selected bond lengths [Å] and dihedral angles [deg] of **3b**, **3c** and **3k** obtained from crystallography.

Details \ Compounds	**3b**	**3c**	**3k**
O1-B1 distance[Å]	1.476(4)	1.465(4)	1.483(3)
N1-B1 distance[Å]	1.583(4)	1.580(3)	1.580(3)
O3-B2 distance[Å]	1.488(4)	1.483(3)	1.469(3)
N2-B2 distance[Å]	1.576(4)	1.585(3)	1.587(3)
C(X)-C(Y) distance[Å]	C14-C15 1.385(4)	C1-C2 1.374(4)	C19-C20 1.379(3)
	C15-C16 1.381(4)	C2-C3 1.398(4)	C20-C21 1.380(3)
	C17-C18 1.400(4)	C4-C5 1.387(4)	C22-C23 1.390(3)
	C18-C19 1.372(5)	C5-C6 1.390(3)	C23-C24 1.378(3)
C(X)-O(Y) distance[Å]	O1-C14 1.287(4)	O1-C1 1.294(3)	O1-C19 1.289(2)
	O3-C19 1.290(4)	O2-C6 1.285(3)	O3-C24 1.290(3)
slip angles [deg]	44.84	70.40	53.95

IV. Photophysical properties of quinoxaline-based bis-boron complexes

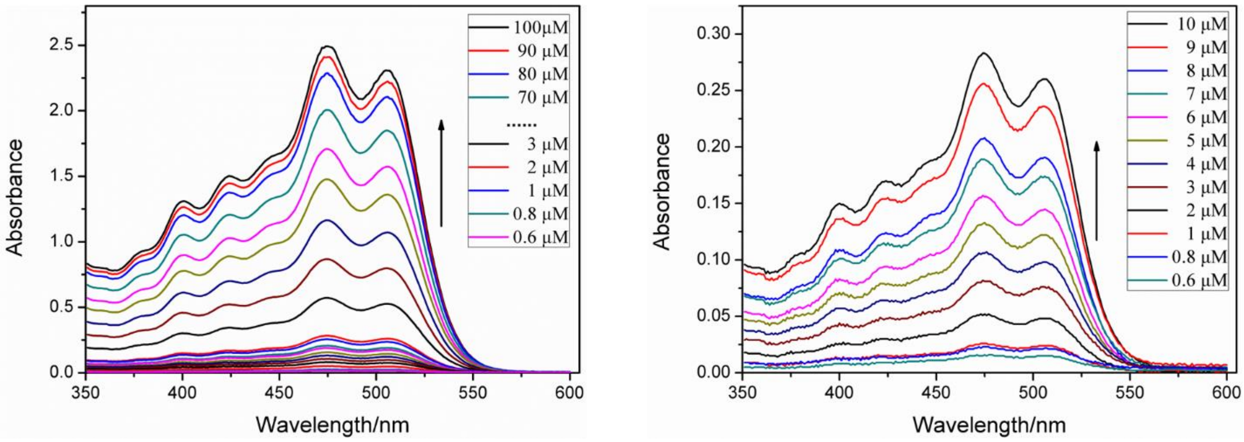


Fig. S6 Concentration-dependent UV-vis absorption of **3e** in CH_2Cl_2 at room temperature.

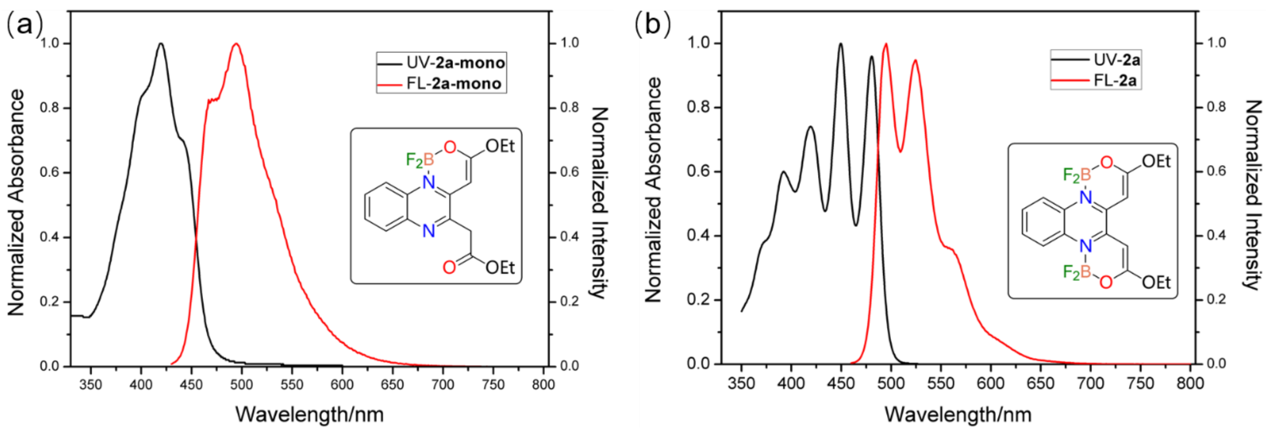


Fig. S7 Normalized absorption and emission spectra of **2a** & **2a-mono** in DCM.

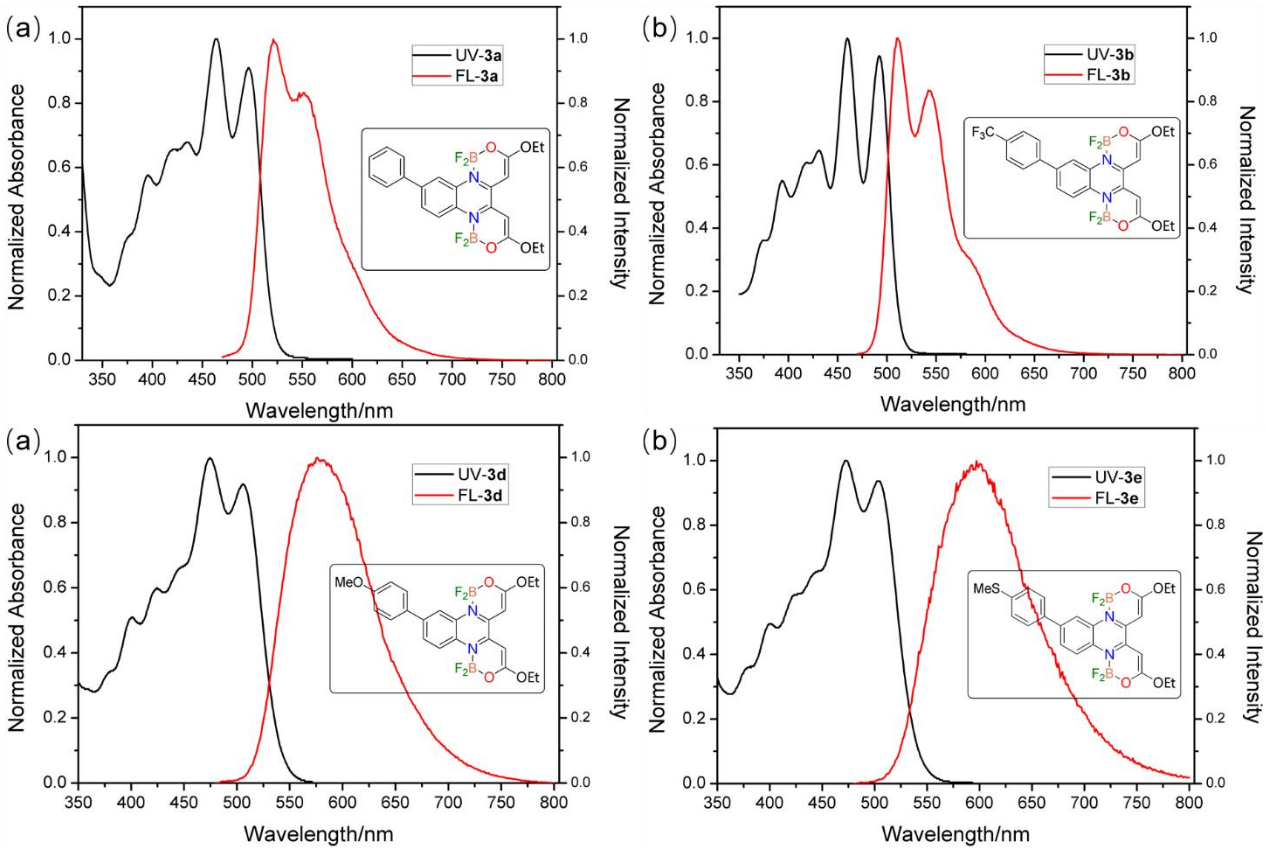


Fig. S8 Normalized absorption and emission spectra of **3a-3b** & **3d-3e** in DCM.

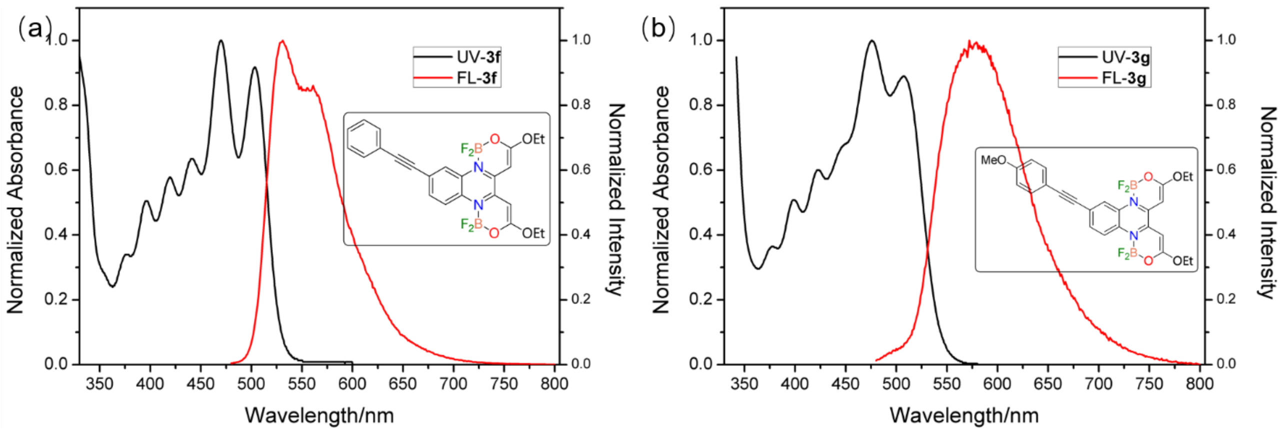


Fig. S9 Normalized absorption and emission spectra of **3f-3g** in DCM.

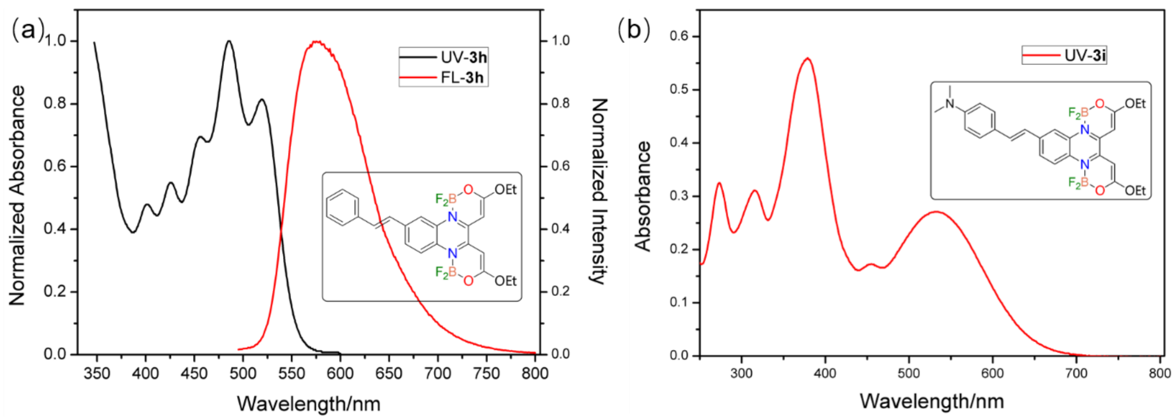


Fig. S10 Normalized absorption and emission spectra of **3h** in DCM and **3i** in toluene.

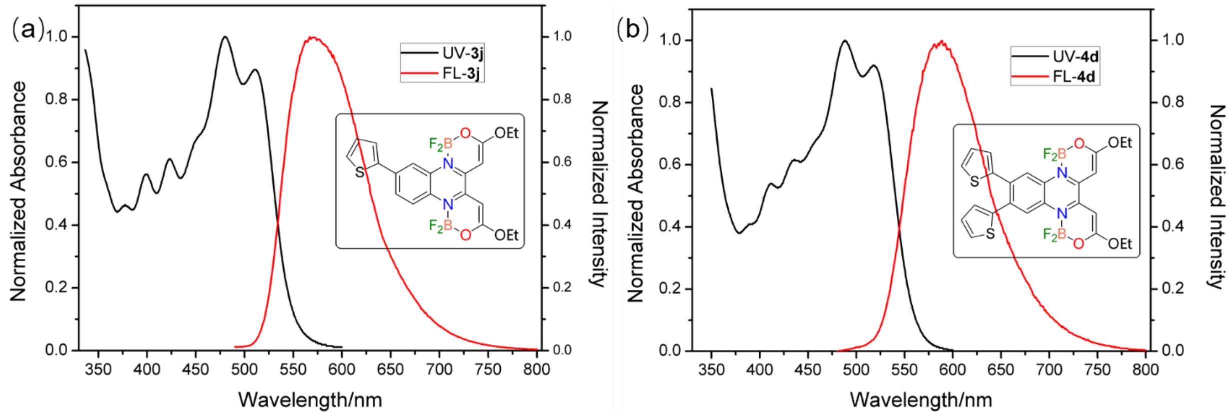


Fig. S11 Normalized absorption and emission spectra of **3j** & **4d** in DCM.

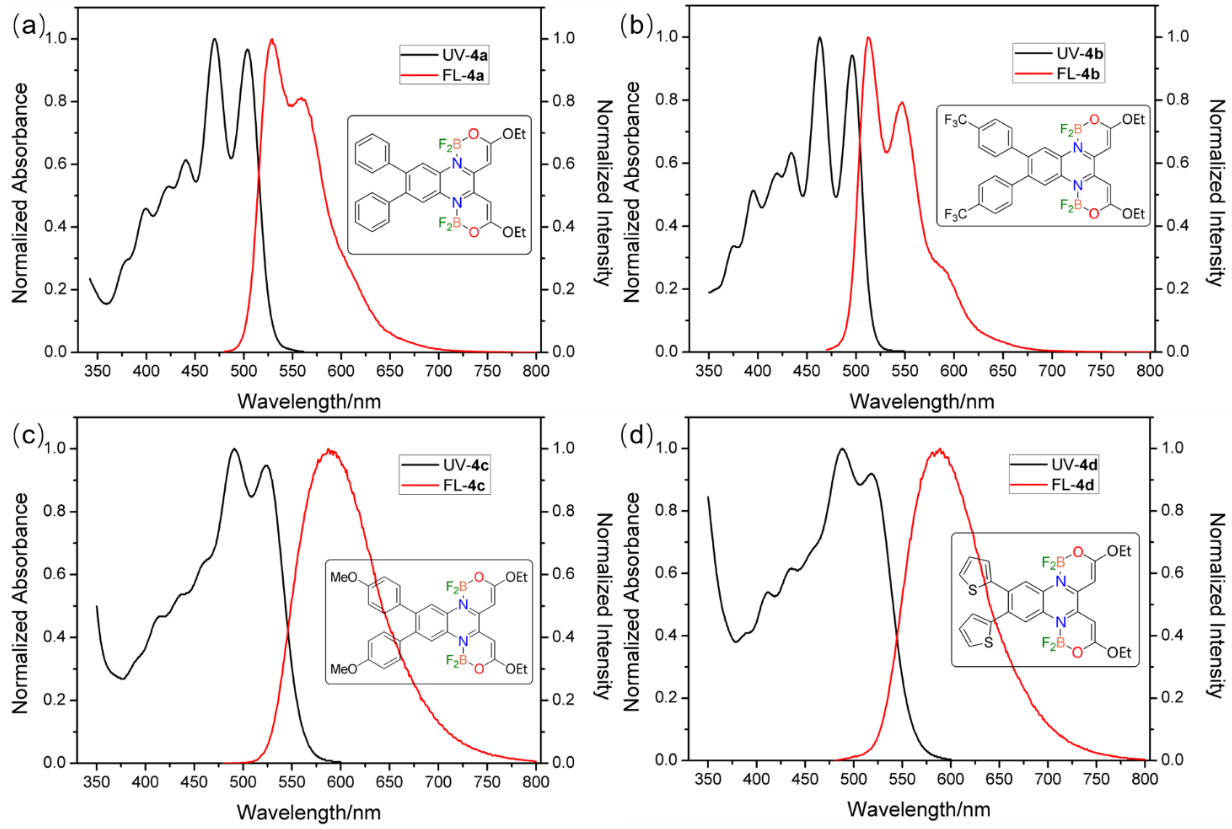


Fig. S12 Normalized absorption and emission spectra of **4a-4d** in DCM.

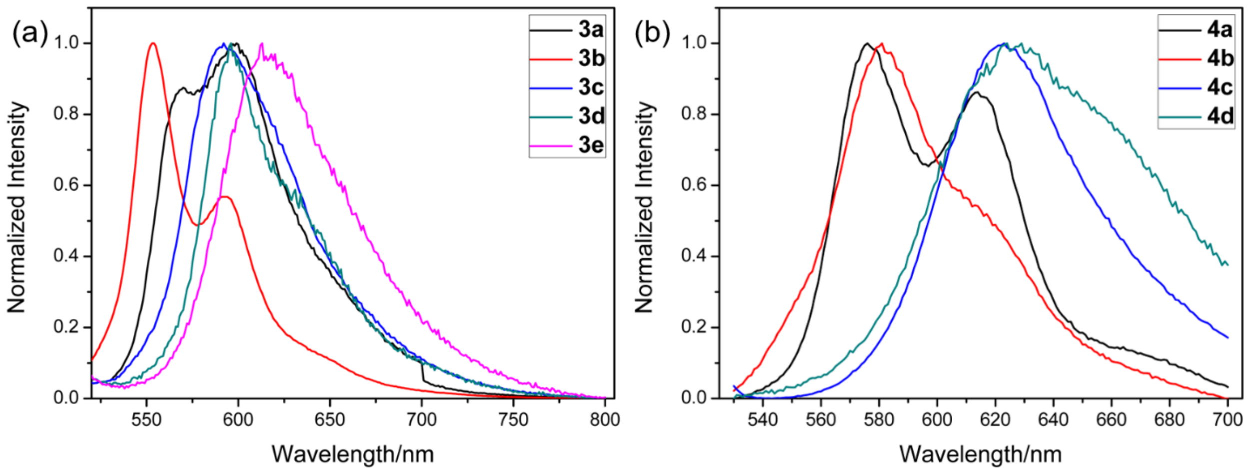


Fig. S13 Normalized emission spectra of **3a-3e** (a) and **4a-4d** (b) in powder state.

Table S7. Photophysical properties of selected compounds **3a-3e** and **4a-4d** in dichloromethane and solid powder.

Entry	Dichloromethane [a]				Powder	
	λ_{abs}^{max}/nm (log ε_{max}) [b]	λ_{em}^{max} /nm [b]	Stokes shift [c]/nm	Φ_f [d,e] /%	λ_{em} (nm)	Φ_f [e] (%)
3a	465 (4.63), 496 (4.61)	521, 552	56	61	570, 599	26
3b	460 (4.54), 493 (4.51)	510, 542	50	48	553, 593	32
3c	473 (4.32), 506 (4.28)	561	88	79	592	41
3d	475 (4.52), 506 (4.48)	578	103	88	596	36
3e	472 (4.59), 503 (4.53)	600	128	81	613	33
4a	470 (4.21), 504 (4.49)	528, 569	58	52	576, 614	37
4b	462 (4.43), 495 (4.41)	512, 547	50	48	581	40
4c	483 (4.44), 515 (4.42)	590	107	91	623	38
4d	480 (4.40), 509 (4.35)	586	106	79	624	43

[a] The spectra were recorded in CH_2Cl_2 (c = 1.0 $\times 10^{-5}$ M) at room temperature. [b] Data correspond to the strongest absorption/emission peaks. [c] Energy gap between the absorption and emission maxima in CH_2Cl_2 solution. [d] In toluene. [e] Absolute quantum yield determined by a calibrated integrating sphere system.

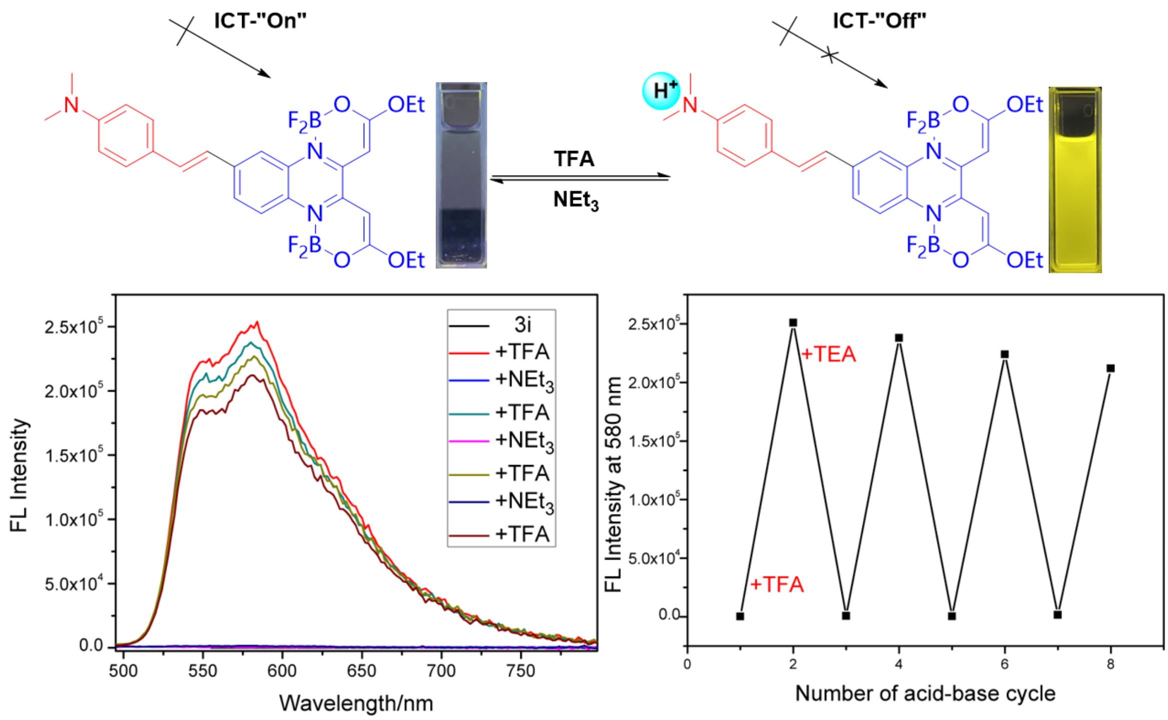


Fig. S14 (a) Mechanism of **3i** as a "turn-on" pH sensor. (b) Emission spectra of initial, TFA and NEt_3 additive of **3i**. (c) Reversible switching of the emission of **3i** by the TFA-NEt_3 additive cycle. Insets: photos of **3i** in DCM irradiated at 365 nm.

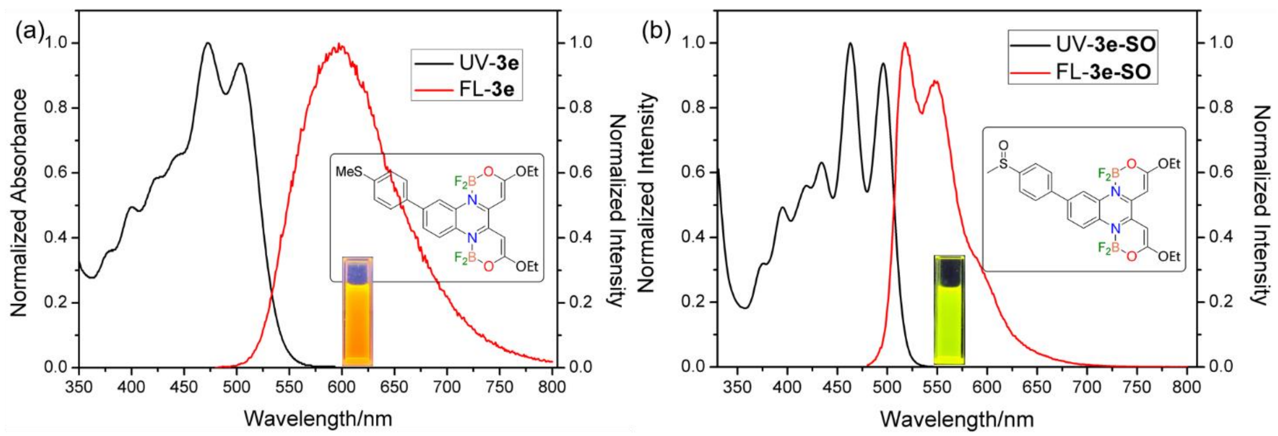


Fig. S15 Normalized absorption and emission spectra of **3e** (left) and **3e-SO** (right) in DCM. Insets: photos of **3e** and **3e-SO** in DCM irradiated at 365 nm.

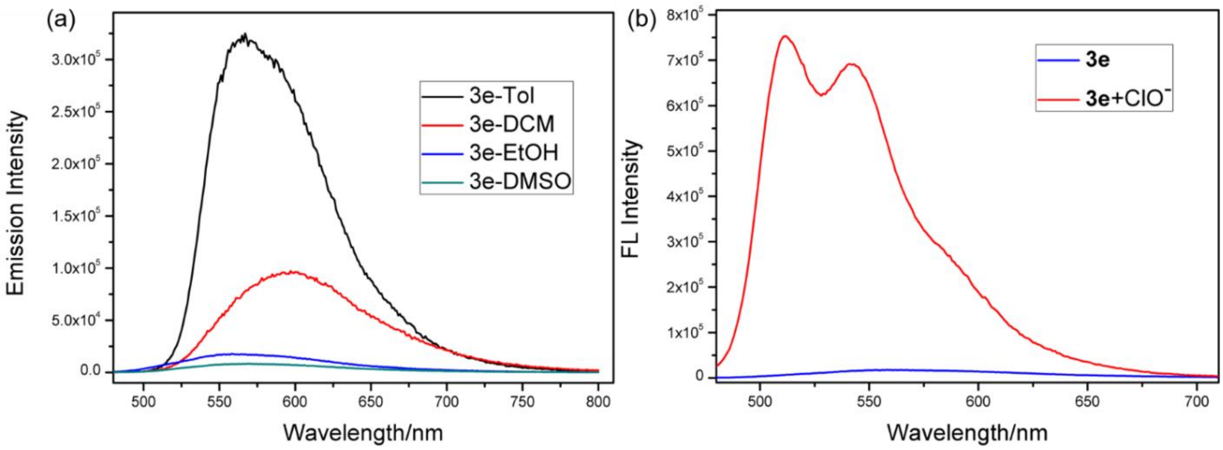


Fig. S16 (a) Emission intensity of **3e** in different solvents and (b) Emission of **3e** compared with ClO^- additive in EtOH. (Concertation: 1×10^{-5} mol/L)

V. Electrochemical studies

The redox potentials of **2a** and **3a-3c** were measured by cyclic voltammetry in dichloromethane containing tetrabutylammonium hexafluorophosphate $[(n\text{-Bu})_4N][PF_6]$ (0.1 M) as a supporting electrolyte, purged with argon prior to conduct the experiments. All compounds exhibited one or two reversible oxidations and reductions. The redox potentials as well as the experimental HOMO and LUMO energy levels determined by the first oxidation and reduction potentials.

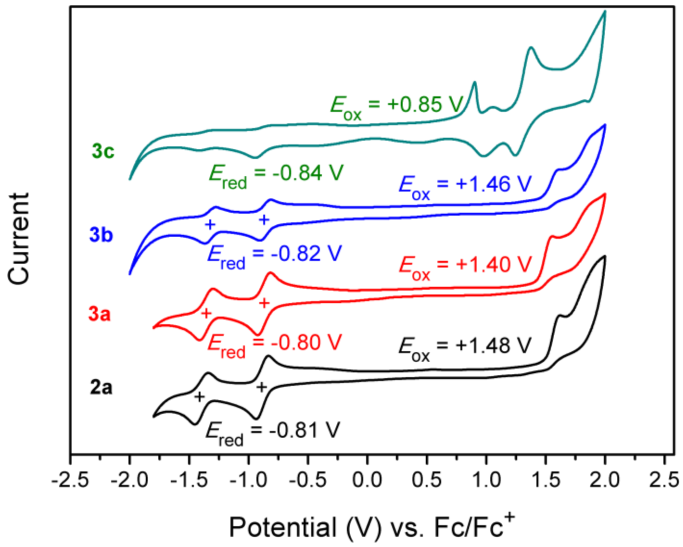


Fig. S17 Cyclic voltammograms of **2a** and **3a-3c** in CH_2Cl_2 (1 mM), measured with $[(n\text{-Bu})_4N][PF_6]$ as a supporting electrolyte at a scan rate of 100 mV·s^{-1}.

Table S8 Electrochemical data of complexes **2a** and **3a-c**.[a]

Compounds	$E_{\text{ox onset}}$ **(V)**	$E_{\text{red onset}}$ **(V)**	E_{HOMO} **(eV)**	E_{LUMO} **(eV)**
2a	1.48	-0.81	-5.82	-3.45
3a	1.40	-0.80	-5.74	-3.54
3b	1.46	-0.82	-5.80	-3.52
3c	0.85	-0.84	-5.19	-3.49

[a] Potentials are given against ferrocene/ferrocenium (Fc/Fc$^+$).

VI. DFT calculations

All calculations were performed using the B3LYP-D3(BJ)/6-31G(d) level of theory with the Polarizable Continuum Model (PCM) solvent model for dichloromethane, utilizing the Gaussian 09 software package. Ground state geometries were optimized using the Berny Optimization Algorithm, and Time-Dependent Density Functional Theory (TD-DFT) calculations were carried out based on the optimized ground state geometries to obtain excited state properties. The corresponding command lines are "opt=calcfc b3lyp/6-31G(d) em=gd3bj scrf=(solvent=Dichloromethane)" for ground state optimization, and "td=(50-50, nstates=3) b3lyp/6-31G(d) em=gd3bj scrf=(solvent=Dichloromethane)" for TDDFT calculations.

Table S9 Frontier orbital energy calculated by B3LYP-D3(BJ)/6-31G(d) based on optimized ground state geometries.

Compounds	Energy (eV)			
	HOMO-1	HOMO	LUMO	LUMO+1
2a	-6.38499	-5.8669	-2.72107	-1.19782
3a	-6.34581	-5.8171	-2.81114	-1.394
3b	-6.53683	-5.99071	-2.93005	-1.60244
3c	-5.90608	-5.42881	-2.83182	-1.45768

Table S10 Selected excited state energies (eV) and oscillator strengths calculated by TD-B3LYP-D3(BJ)/6-31G(d).

Compounds	Electronic Transitions [a]	Energy (eV)	Wavelength (nm)	f [b]	CI [c]	Composition
2a	S0→S1	2.8184	439.9	0.3482	0.10763	HOMO-1→LUMO+1
					0.70069	HOMO→LUMO
	S0→S2	3.1624	392.0	0.0773	0.70373	HOMO-1→LUMO
	S0→S3	3.9014	317.8	0.0000	0.56067	HOMO-2→LUMO
					0.42758	HOMO→LUMO+1
3a	S0→S1	2.6491	468.0	0.4905	0.10254	HOMO-1→LUMO
					0.69504	HOMO→LUMO
	S0→S2	3.0456	407.1	0.0580	0.70088	HOMO-1→LUMO
	S0→S3	3.6736	337.5	0.0264	0.11995	HOMO-4→LUMO
					0.67618	HOMO-3→LUMO
					0.11544	HOMO-2→LUMO+1

3b	S0→S1	2.6999	459.2	0.5313	0.69526	HOMO→LUMO
	S0→S2	3.1035	399.5	0.0507	0.70178	HOMO-1→LUMO
	S0→S3	3.757	330.0	0.0065	0.20009	HOMO-4→LUMO
					0.61005	HOMO-2→LUMO
					0.26927	HOMO→LUMO+1
3c	S0→S1	2.2962	539.9	0.1944	0.70549	HOMO→LUMO
	S0→S2	2.7634	448.7	0.4212	0.70106	HOMO-2→LUMO
	S0→S3	2.8255	438.8	0.0000	0.70682	HOMO-1→LUMO

[a] Only presented with selected low-lying states. [b] Oscillator strength. [c] Configuration interaction coefficients, shown in absolute values.

Optimized geometries in Angstrom:

2a

SCF energy = -1479.3180001 Hartree

C	-0.69785500	-4.51462500	0.05513900
C	-1.39251100	-3.31833200	0.10294800
C	-0.70476000	-2.09155000	0.04317600
C	0.70478000	-2.09154300	-0.04335300
C	1.39254200	-3.31831600	-0.10319600
C	0.69789900	-4.51461600	-0.05541000
H	-1.24485000	-5.45069700	0.10159500
H	-2.46754000	-3.32964900	0.19123700
H	2.46756300	-3.32961100	-0.19157300
H	1.24490000	-5.45068200	-0.10191900
C	0.73936500	0.30011700	-0.00311800
C	-0.73936300	0.30010900	0.00307400
N	-1.39958400	-0.87382200	0.05152300
N	1.39959200	-0.87380900	-0.05160900
B	-2.98739800	-0.92201900	0.05410200
B	2.98740200	-0.92199700	-0.05390100
C	1.43160500	1.51525300	0.04359200
H	0.92888300	2.46306900	0.11414000
C	-1.43161100	1.51524700	-0.04356900
H	-0.92889400	2.46306900	-0.11408100

C	-2.82023300	1.53099600	-0.01341200
C	2.82022900	1.53101700	0.01340400
O	3.54357100	0.46277800	-0.05751500
O	-3.54357000	0.46274500	0.05743300
F	3.43194000	-1.54804200	-1.20148300
F	3.42721800	-1.55184000	1.09241300
F	-3.42744000	-1.55210000	-1.09199000
F	-3.43171500	-1.54774700	1.20192600
O	3.43924900	2.69488000	0.05262100
O	-3.43927100	2.69485900	-0.05265000
C	4.89829700	2.71019200	0.02922600
H	5.26146300	2.12779500	0.87955300
H	5.23167700	2.22735400	-0.89268500
C	5.32220400	4.16092000	0.10363000
H	4.96488800	4.62524900	1.02759700
H	6.41508200	4.21787800	0.08728400
H	4.93310700	4.72584500	-0.74871000
C	-4.89832000	2.71016300	-0.02923100
H	-5.23167100	2.22749300	0.89277800
H	-5.26151000	2.12761000	-0.87944000
C	-5.32224200	4.16087300	-0.10388900
H	-6.41511900	4.21782700	-0.08747600
H	-4.93308800	4.72596900	0.74831200
H	-4.96499500	4.62502300	-1.02797400

3a

SCF energy = -1710.4013158 Hartree

C	5.64628100	-1.59109100	-0.59623500
C	7.01357100	-1.32923900	-0.66281100
C	7.52435200	-0.12816100	-0.16632000
C	6.65622400	0.80920000	0.39792300
C	5.28923100	0.54781100	0.46542000
O	-0.43784500	3.40418400	-0.07188800
C	-1.68719100	3.08387400	0.00502400

C	-2.14063600	1.77079500	0.04410900
O	-2.81910800	-3.25698600	0.16424300
C	-3.58629500	-2.22837200	-0.01012000
C	-1.22913000	0.71053300	-0.00041700
C	-3.10151000	-0.93110000	-0.08742000
C	-1.72234600	-0.68215100	0.02172400
C	4.76261900	-0.65621100	-0.03220000
N	-0.84307300	-1.68979100	0.14632100
N	0.09918800	0.93795100	-0.05370600
C	2.39069800	0.10708100	-0.08926600
C	1.00966000	-0.12481000	-0.00217100
C	0.53399800	-1.44394200	0.15731000
C	1.46423400	-2.49140100	0.29343600
C	2.82047100	-2.23673000	0.24060400
C	3.30973900	-0.93050700	0.03682500
B	-1.33839300	-3.20535000	0.17886700
F	-0.90746300	-3.80080000	1.34885300
F	-0.86096800	-3.85129300	-0.94396800
B	0.68101800	2.41680000	-0.05387200
F	1.43110200	2.62518800	-1.19485300
F	1.41259500	2.61791300	1.09830200
O	-2.57393700	4.05886600	0.04101800
C	-3.32043400	6.32634600	0.06368400
C	-2.09665800	5.43807500	0.00852200
O	-4.86131000	-2.56910200	-0.08865300
C	-7.21356200	-2.23754400	-0.30389700
C	-5.87081800	-1.53997800	-0.25964300
H	5.25699900	-2.51698900	-1.00866500
H	7.67960600	-2.06127900	-1.11045500
H	8.58993000	0.07538400	-0.21783900
H	7.04479700	1.74265700	0.79480900
H	4.62495100	1.27092200	0.92896000
H	-3.20101500	1.61578400	0.13536000
H	-3.78717600	-0.12153700	-0.25153700

H	2.74705900	1.10499100	-0.28831300
H	1.11839800	-3.49984100	0.45915900
H	3.51528100	-3.05797700	0.37871500
H	-3.00538700	7.37425300	0.04077500
H	-3.97523700	6.14266700	-0.79332400
H	-3.88656900	6.15489700	0.98405800
H	-1.43332500	5.59147000	0.86324400
H	-1.52204900	5.58029400	-0.90993500
H	-8.00434300	-1.49209700	-0.43265000
H	-7.25813500	-2.94008000	-1.14109900
H	-7.39781300	-2.78335600	0.62594800
H	-5.80285800	-0.84324100	0.58175900
H	-5.66382900	-1.00092400	-1.18950500

3b

SCF energy = -2047.442935 Hartree

C	-4.28089700	0.57513500	-0.55240500
C	-5.64645000	0.83300500	-0.50453600
C	-6.51674200	-0.12067800	0.02905000
C	-6.01449000	-1.33016600	0.51513100
C	-4.64756500	-1.58246400	0.46698900
O	1.41518000	3.44730800	0.09783500
C	2.66995300	3.14358300	0.00605600
C	3.12689000	1.83359500	-0.04767800
O	3.83676400	-3.19077800	-0.15138400
C	4.59288800	-2.16011500	0.05134000
C	2.21701900	0.76444400	-0.00438100
C	4.09776600	-0.86512300	0.12448700
C	2.72128900	-0.62414300	-0.01859000
C	-3.75813100	-0.63452000	-0.06488600
N	1.85040800	-1.63730900	-0.16656900
N	0.89198400	0.98176000	0.04090700
C	-1.39452200	0.14010100	0.03950900
C	-0.01147000	-0.08496000	-0.02949000

C	0.47393300	-1.39944500	-0.19907800
C	-0.44815200	-2.45018300	-0.36540300
C	-1.80599100	-2.20291600	-0.32892900
C	-2.30358800	-0.90149300	-0.11462900
B	2.35580300	-3.15085100	-0.19115300
F	1.95004800	-3.74783300	-1.36852200
F	1.86265200	-3.79804400	0.92311100
B	0.30625300	2.46588100	0.03929300
F	-0.40112200	2.66027800	-1.12995300
F	-0.47804700	2.65124900	1.16198500
O	3.44043600	4.21645200	-0.01623200
C	5.47823000	5.45657500	-0.06281800
C	4.88303000	4.06512800	-0.08700900
O	5.86682800	-2.49261600	0.16053400
C	8.21128500	-2.14942200	0.43688800
C	6.86628600	-1.45889300	0.36372800
C	-7.98279200	0.17824700	0.13618200
F	-8.29162100	0.76970300	1.31766400
F	-8.73788300	-0.94151200	0.05708300
F	-8.40383100	1.01777100	-0.83714000
H	-3.61513600	1.30847700	-0.99542800
H	-6.03654000	1.76645400	-0.89509700
H	-6.68885600	-2.07049000	0.93152600
H	-4.26558900	-2.51568600	0.86755400
H	4.17862900	1.64789600	-0.15687000
H	4.77360300	-0.05385500	0.31908500
H	-1.75693400	1.13422000	0.24620900
H	-0.09411100	-3.45400000	-0.54144000
H	-2.49412800	-3.02556100	-0.48972200
H	6.56881900	5.38365500	-0.11655300
H	5.12650800	6.04385600	-0.91590300
H	5.20932500	5.97770300	0.86048700
H	5.21173300	3.46757500	0.76922400
H	5.13094800	3.53487800	-1.01197900

H	8.99414800	-1.40053900	0.59155800
H	8.23839400	-2.85793200	1.26972800
H	8.42233500	-2.68698400	-0.49200800
H	6.81486900	-0.75715500	-0.47465400
H	6.63287800	-0.92800200	1.29196500

3c

SCF energy = -2226.7342516 Hartree

F	-1.22025000	2.62824900	0.88979300
F	-3.74404800	-3.76824700	1.27196200
F	-1.28353600	2.40569100	-1.39132700
F	-3.83073000	-3.90409700	-1.01577200
O	-5.19566400	4.09052200	-0.37818600
O	-3.08166800	3.36788000	-0.27280900
O	-5.70074100	-3.19630100	0.15017400
O	-7.71432000	-2.41509900	0.35371900
N	6.14194700	-0.17290800	0.05042400
N	-2.63428700	0.89273200	-0.06431500
N	-3.67124400	-1.70589900	0.00500100
C	1.96630200	-0.86168100	-0.01680500
C	-2.28707200	-1.51314900	-0.05030600
C	-3.97079900	0.71124800	-0.06179300
C	-0.37360500	-0.01380100	0.00435100
H	0.02084000	0.98529700	0.09657100
C	-1.39618000	-2.60234100	-0.09362100
H	-1.77922000	-3.60946400	-0.14638600
C	-6.42906800	-2.12912900	0.23651200
C	-5.89763600	-0.84814400	0.19363700
H	-6.55345600	-0.00354800	0.28745200
C	3.89411600	0.49428000	-0.62618700
H	4.31208600	1.35431700	-1.13815000
C	-4.34339800	3.09012100	-0.27667700
C	8.16970400	0.85736500	0.34048900
C	4.20794500	-1.53544600	0.65139800

H	4.86379300	-2.21911900	1.17960800
C	-1.76308900	-0.20291800	-0.03268400
C	-4.66820300	5.44712600	-0.49205000
H	-4.06354600	5.65436200	0.39423800
H	-4.02343200	5.49098300	-1.37317900
C	2.52208100	0.27041100	-0.63660300
H	1.87578100	0.96476700	-1.16418400
C	2.83614700	-1.76247400	0.61933700
H	2.43303200	-2.62996200	1.13209600
C	-4.51255100	-0.65948000	0.04921000
C	7.13174500	-1.09130800	-0.31850300
C	-4.84453100	1.79752400	-0.17550500
H	-5.91251900	1.67767400	-0.21643200
C	4.74608500	-0.40564200	0.02478600
C	0.50596600	-1.09182000	-0.03209900
C	6.19508500	2.19526400	0.93768200
H	5.12117200	2.30294700	1.04105700
C	-0.03105700	-2.39365200	-0.09097200
H	0.63179100	-3.24969800	-0.15565000
C	-8.68651800	-1.34002100	0.43715000
H	-8.45885800	-0.73351300	1.31936000
H	-8.59578800	-0.71835700	-0.45912200
C	9.01435800	1.91286400	0.70144000
H	10.09237500	1.80525800	0.61967900
C	9.43467400	-2.50503000	-0.95527500
H	10.32348900	-3.07634700	-1.20560200
C	8.16551300	-3.08499000	-1.12863400
H	8.08868200	-4.09684900	-1.51584000
C	7.05843400	3.23096700	1.29108600
H	6.64075400	4.15964200	1.66896700
C	-5.85961500	6.37290700	-0.60450400
H	-6.45627100	6.13629000	-1.49052500
H	-6.49764600	6.29864400	0.28118800
H	-5.50569600	7.40498300	-0.69071500

C	8.40438900	-0.48450800	-0.15236300
B	-4.21968200	-3.19974500	0.10717000
C	-10.05317100	-1.98323800	0.53729900
H	-10.25797200	-2.59774600	-0.34412500
H	-10.12210400	-2.61132900	1.43014800
H	-10.81648200	-1.20166500	0.60177000
C	8.45312800	3.09743400	1.17164100
H	9.09680500	3.92523700	1.45356600
B	-2.00007500	2.34221500	-0.21409600
C	6.99850600	-2.38912600	-0.81729100
H	6.02316500	-2.83993200	-0.96245200
C	6.76345100	1.01532900	0.45237200
C	9.56035600	-1.20502300	-0.47203000
H	10.54036800	-0.75260300	-0.34849100

VI. Reference

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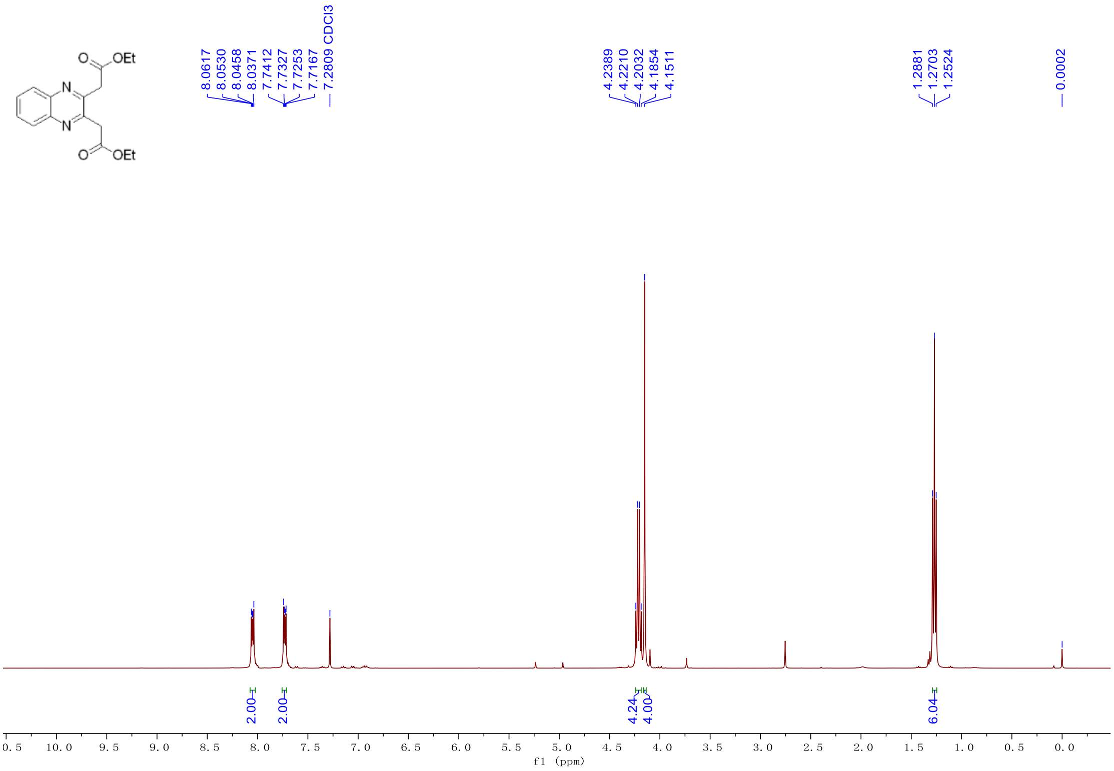
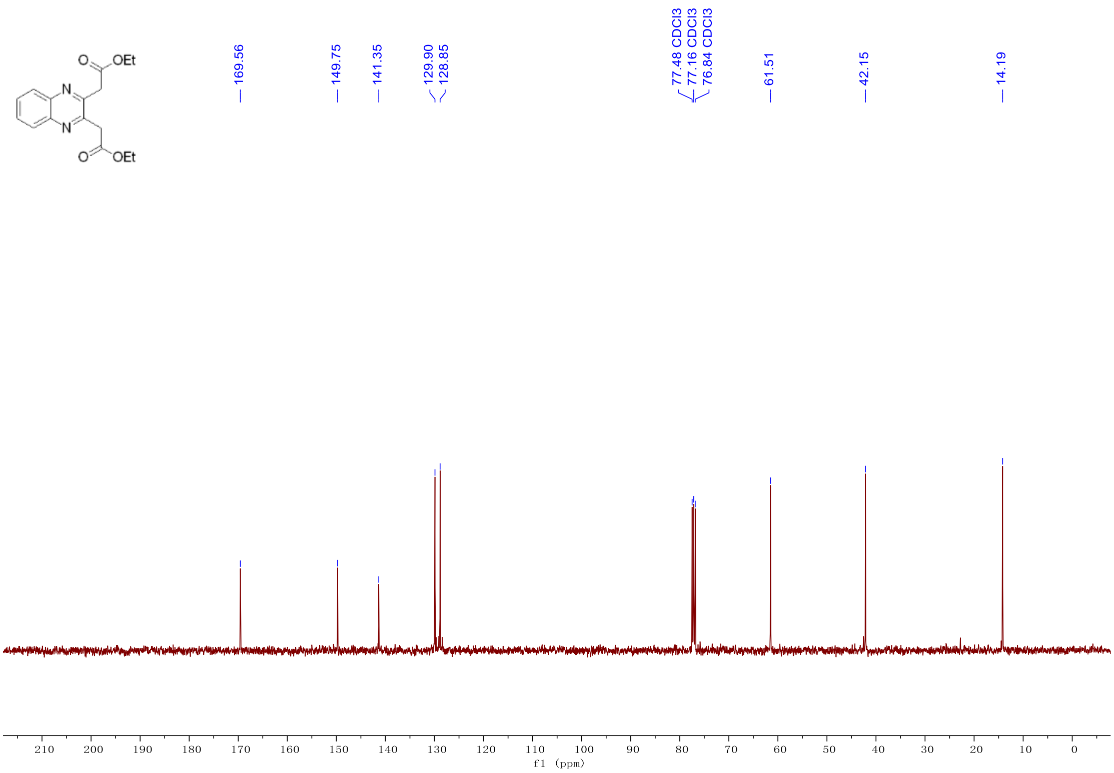
VII. NMR spectra

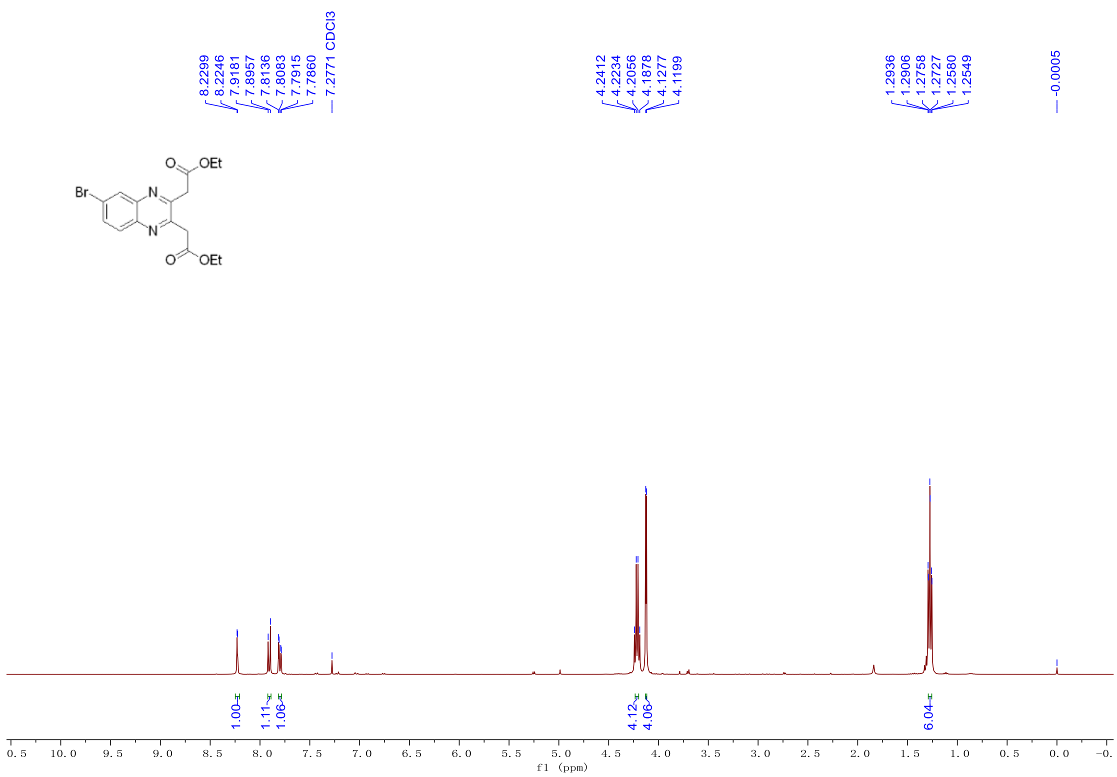
^{1}H NMR of **1a** (400 MHz, $CDCl_3$)



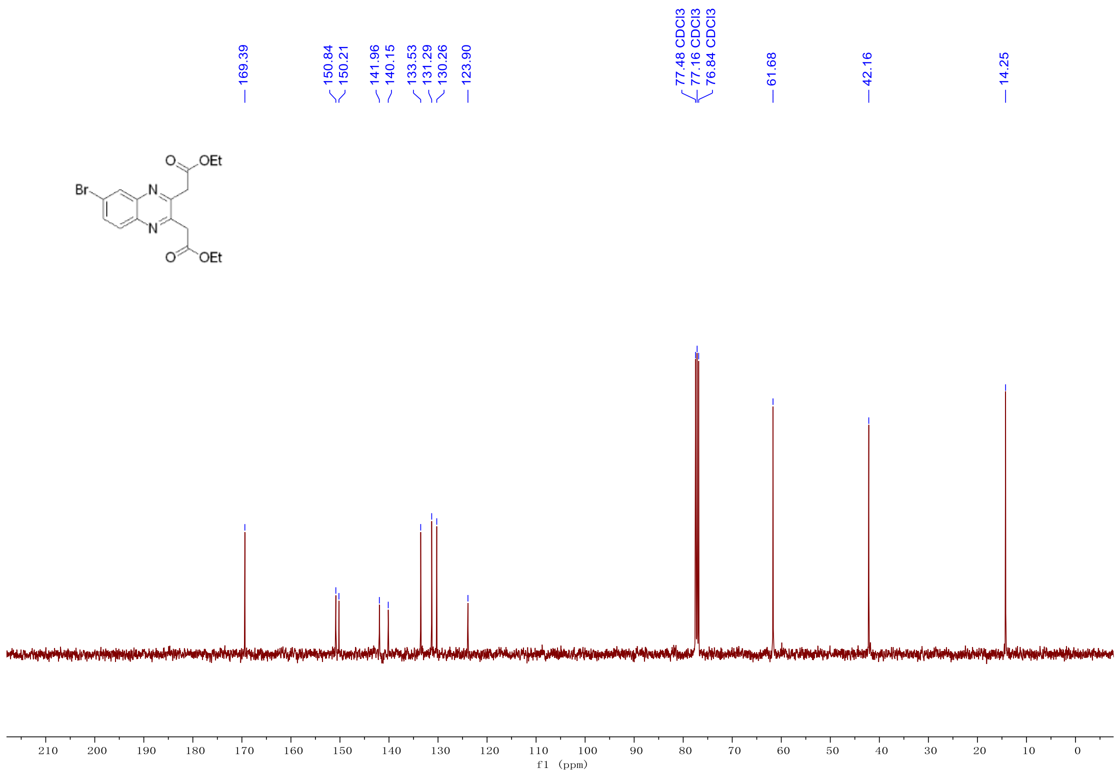
^{13}C NMR of **1a** (101 MHz, $CDCl_3$)



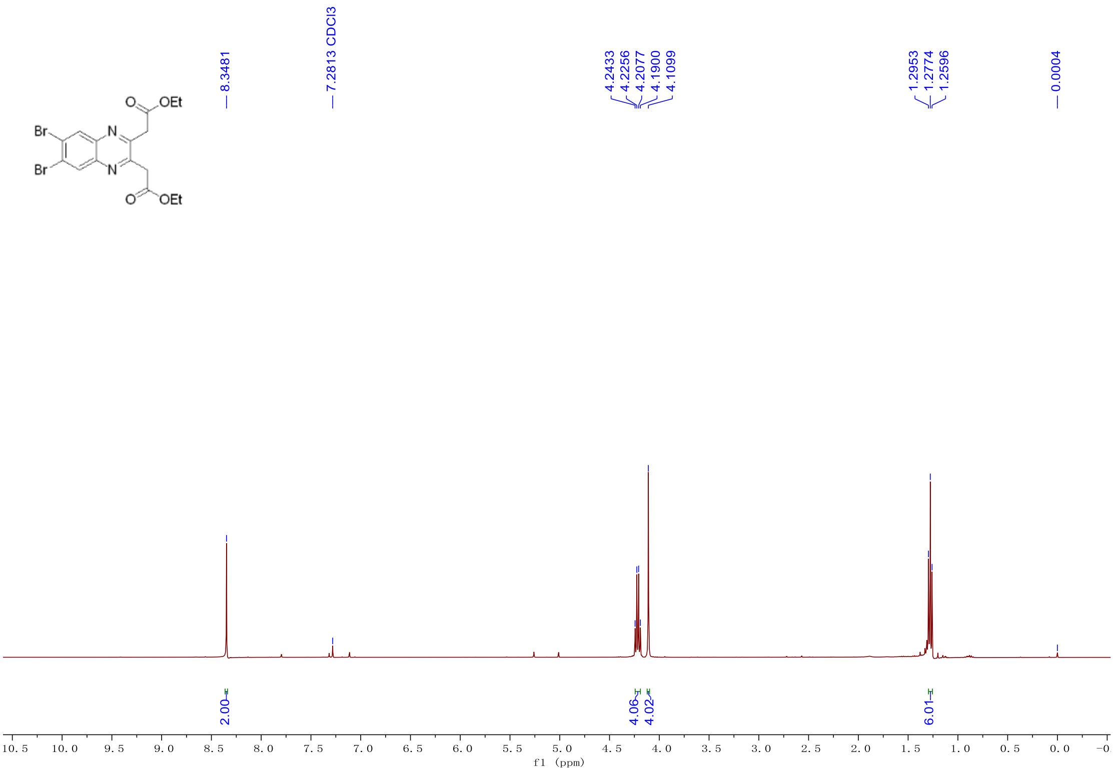
[1]H NMR of **1b** (400 MHz, $CDCl_3$)



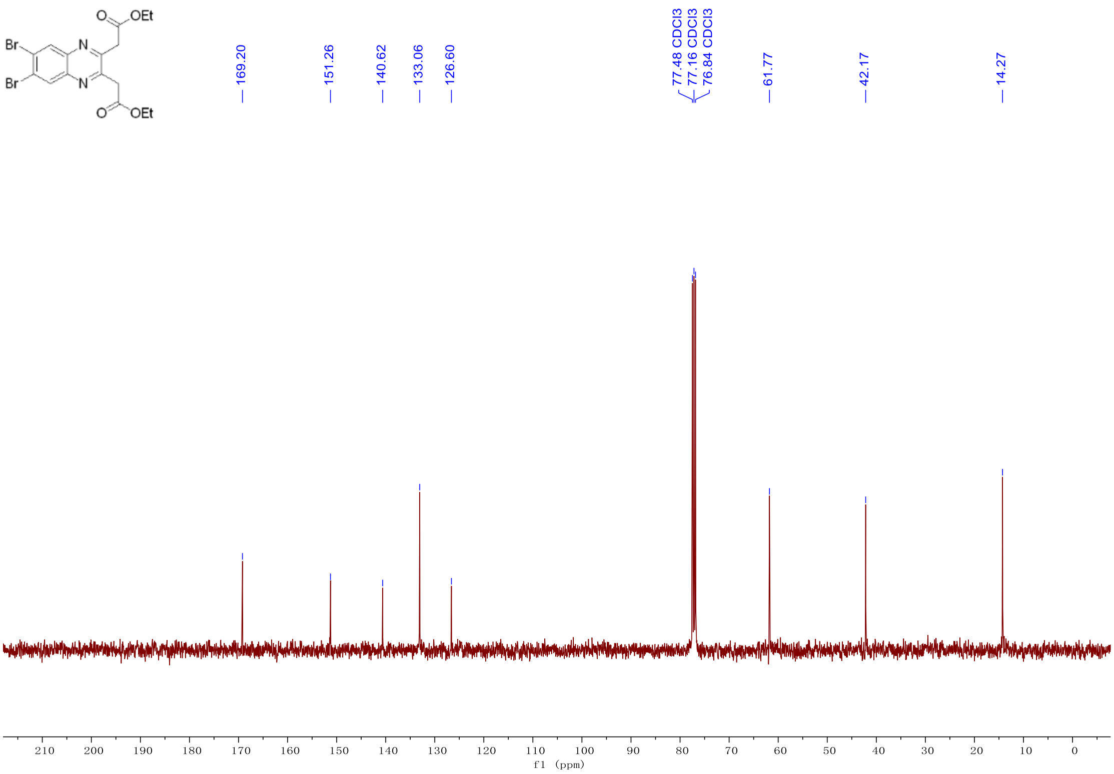
[13]C NMR of **1b** (101 MHz, $CDCl_3$)



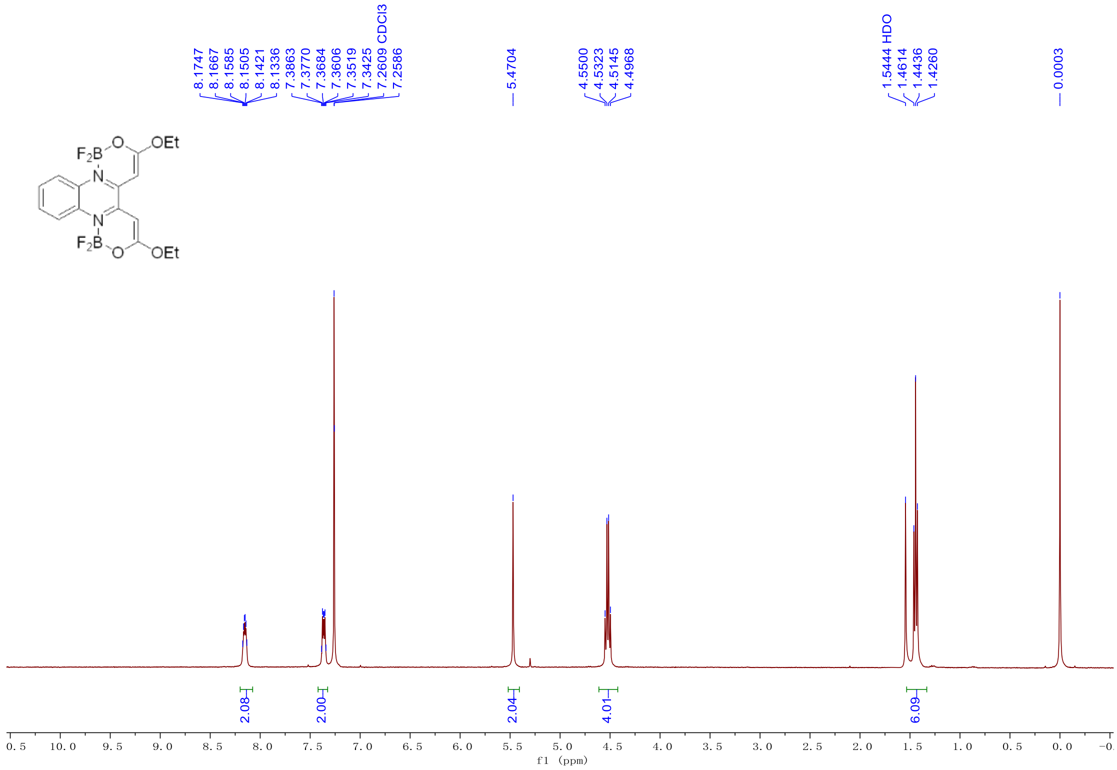
^{1}H NMR of **1c** (400 MHz, $CDCl_3$)



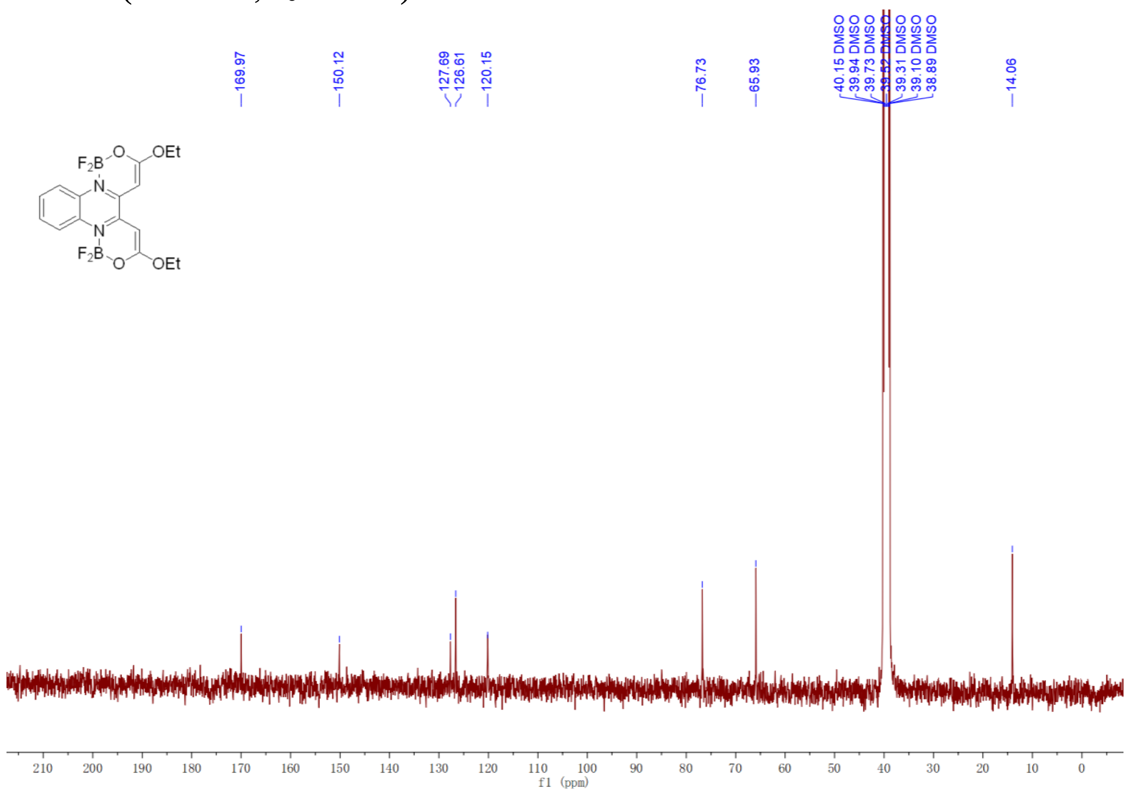
^{13}C NMR of **1c** (101 MHz, $CDCl_3$)



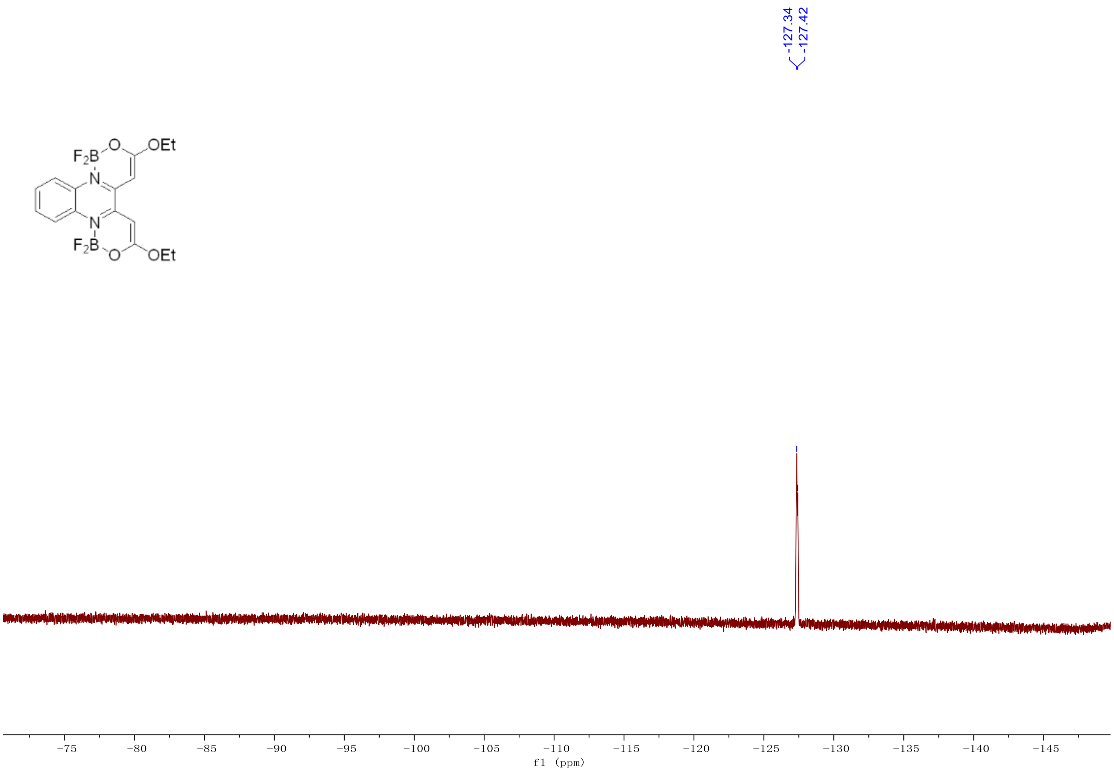
^{1}H NMR of **2a** (400 MHz, $CDCl_3$)



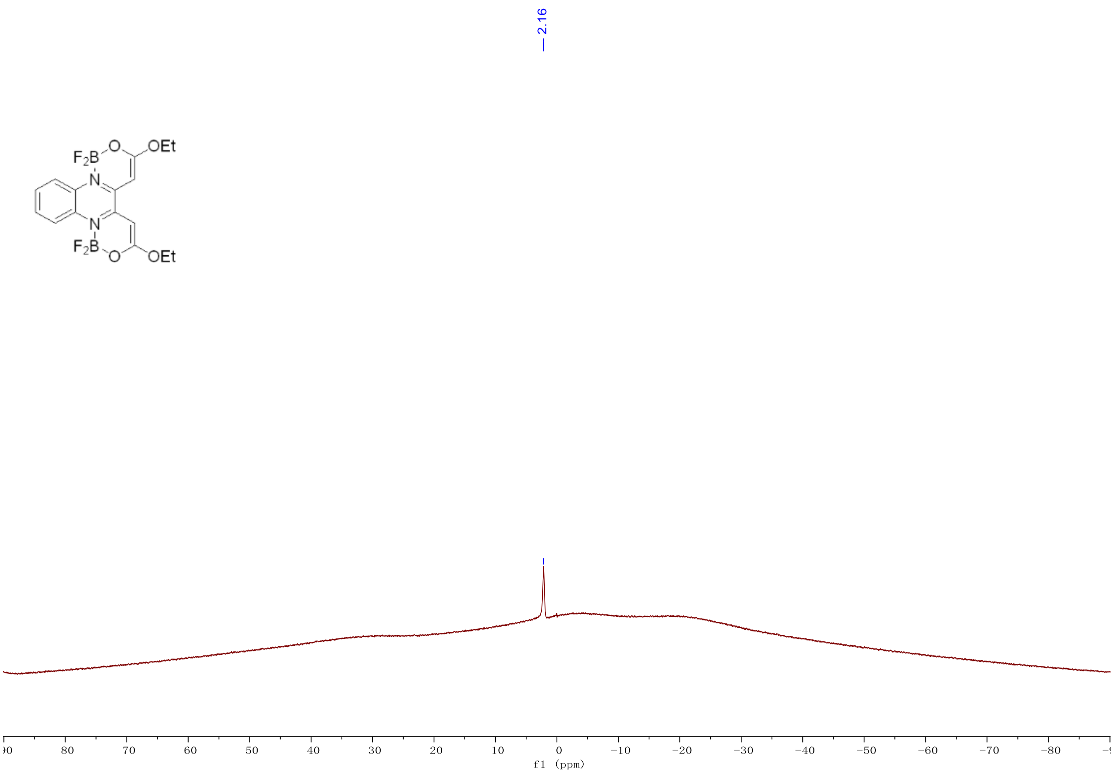
^{13}C NMR of **2a** (101 MHz, d_6-DMSO)



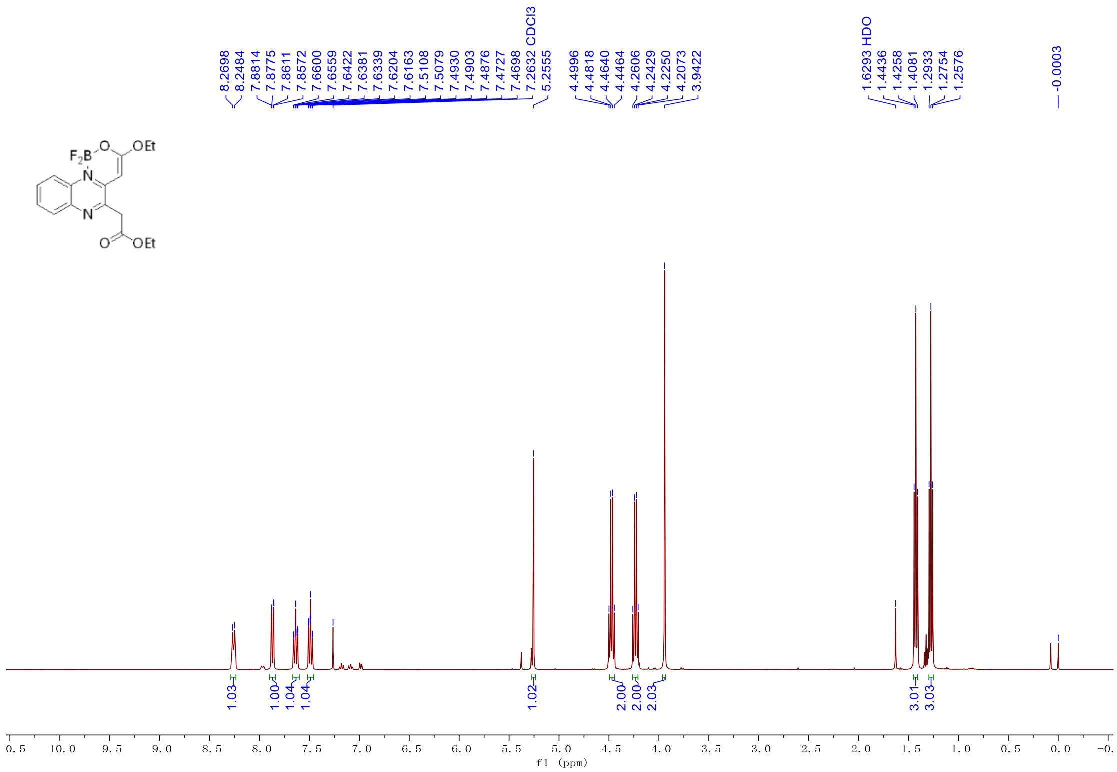
^{19}F NMR of **2a** (376 MHz, $CDCl_3$)



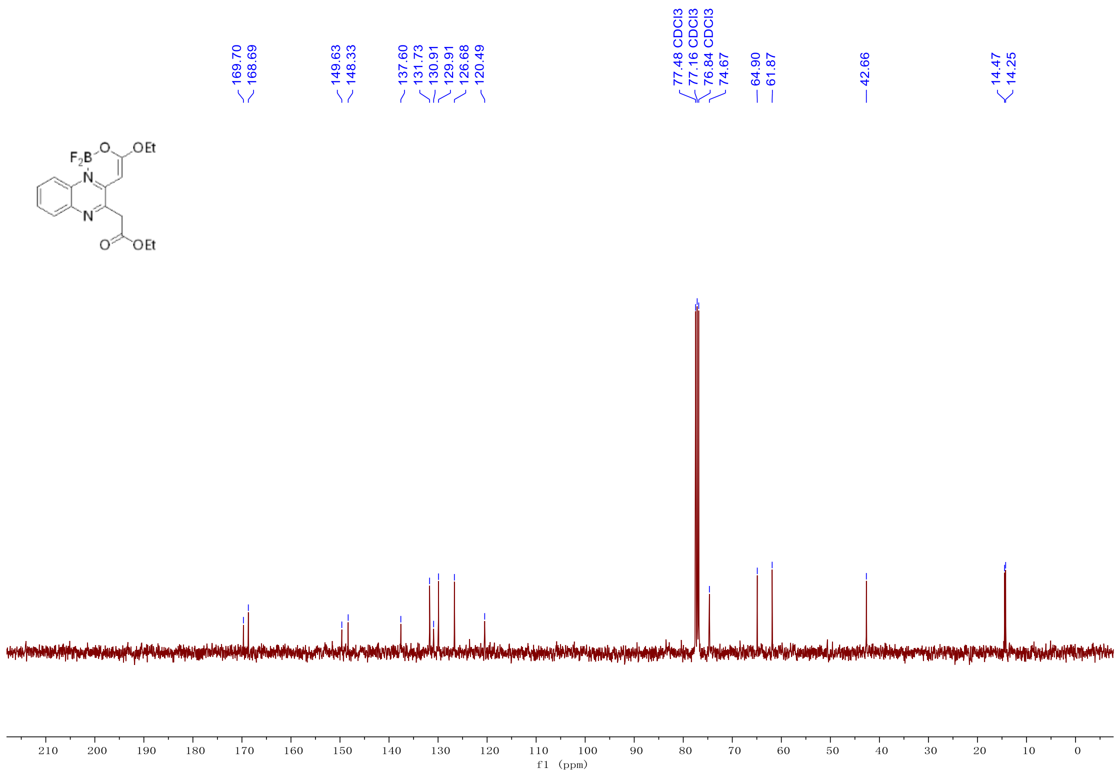
^{11}B NMR of **2a** (128 MHz, $CDCl_3$)



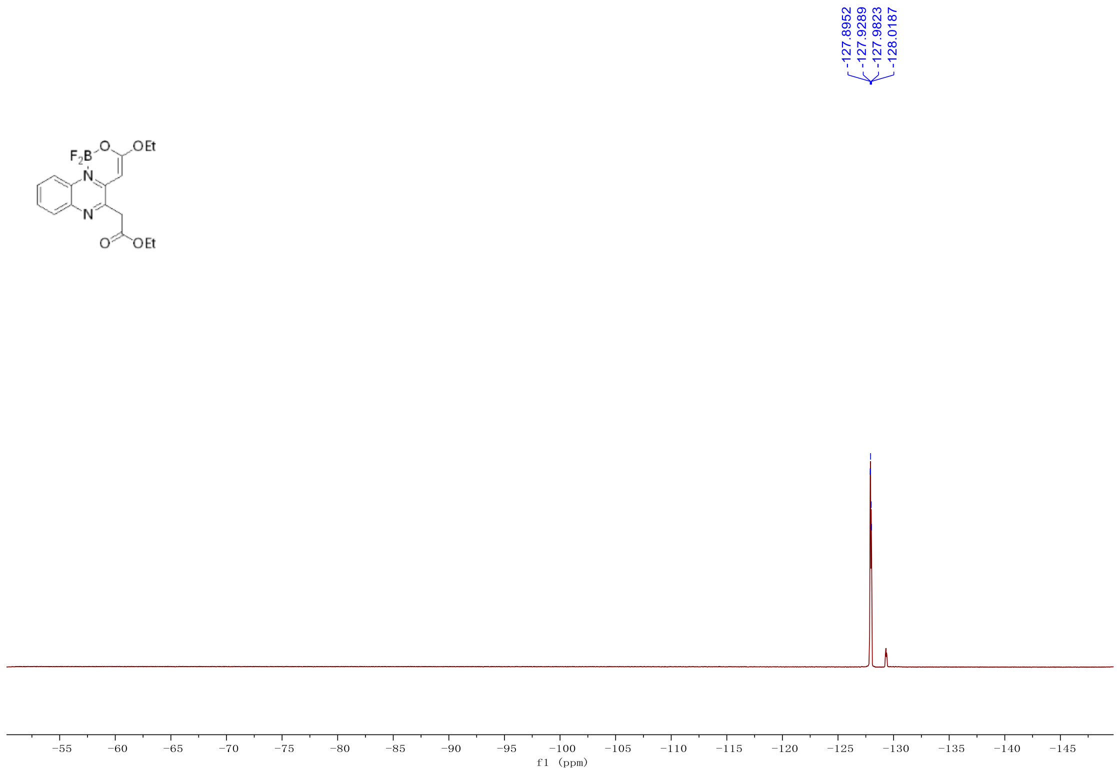
^{1}H NMR of **2a-mono** (400 MHz, $CDCl_3$)



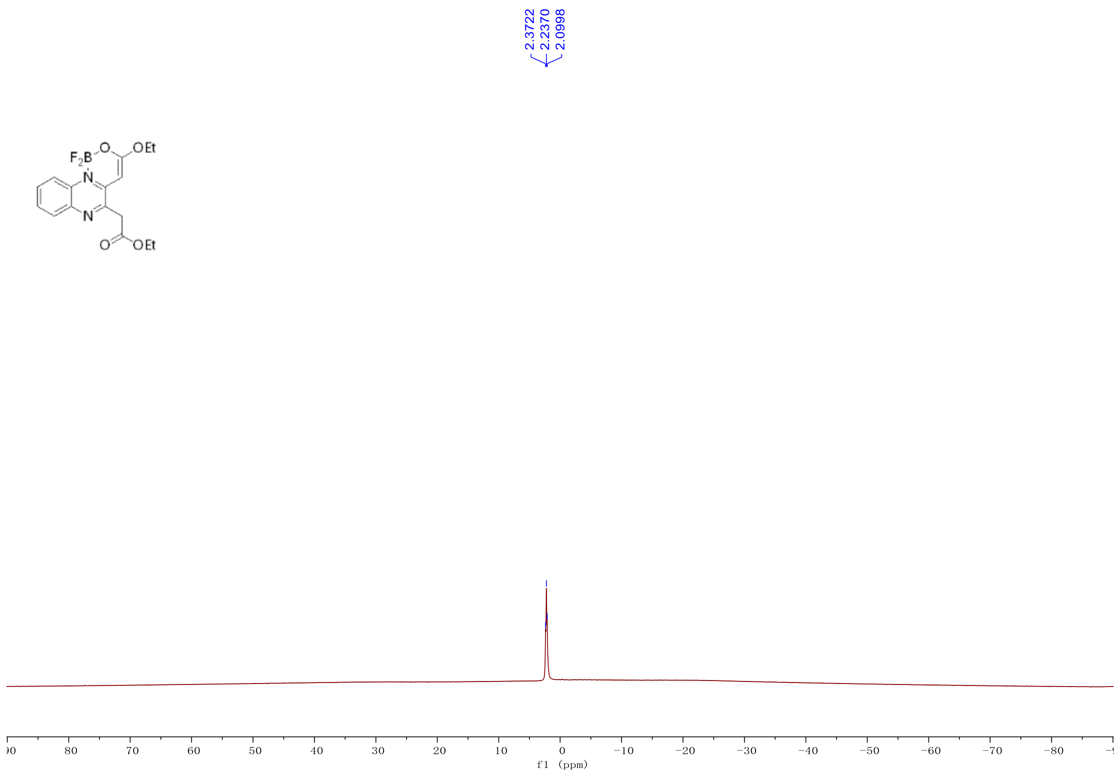
^{13}C NMR of **2a-mono** (101 MHz, $CDCl_3$)



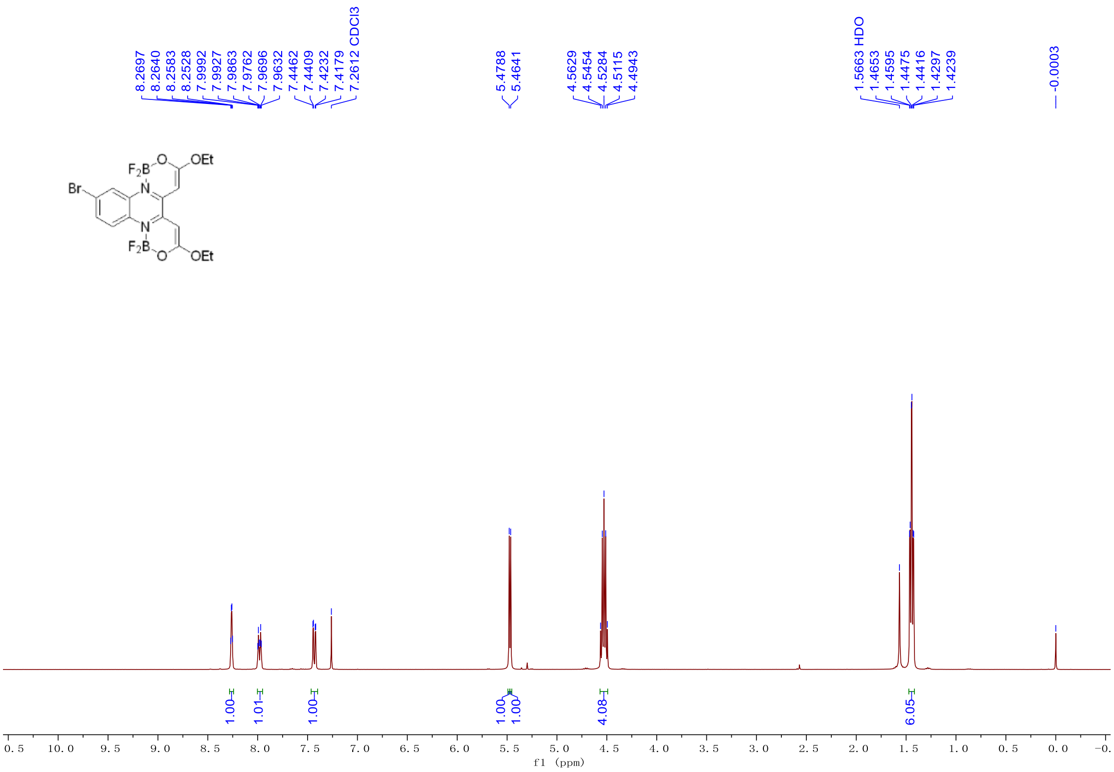
^{19}F NMR of **2a-mono** (376 MHz, $CDCl_3$)



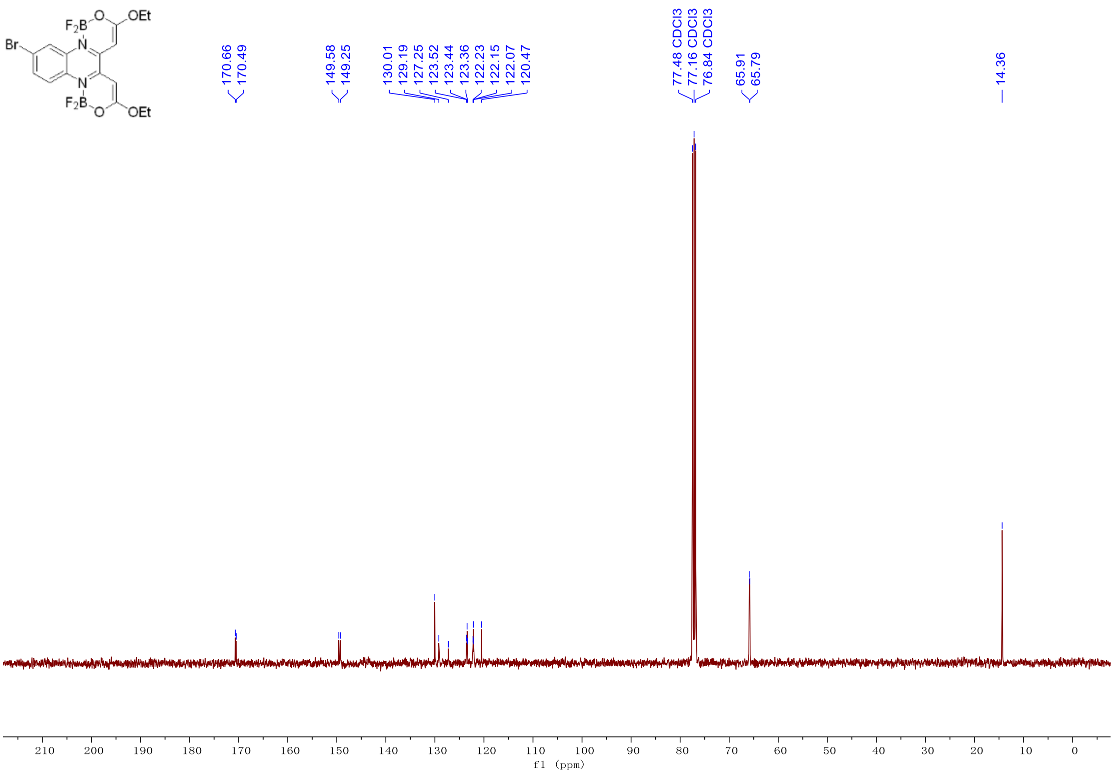
^{11}B NMR of **2a-mono** (128 MHz, $CDCl_3$)



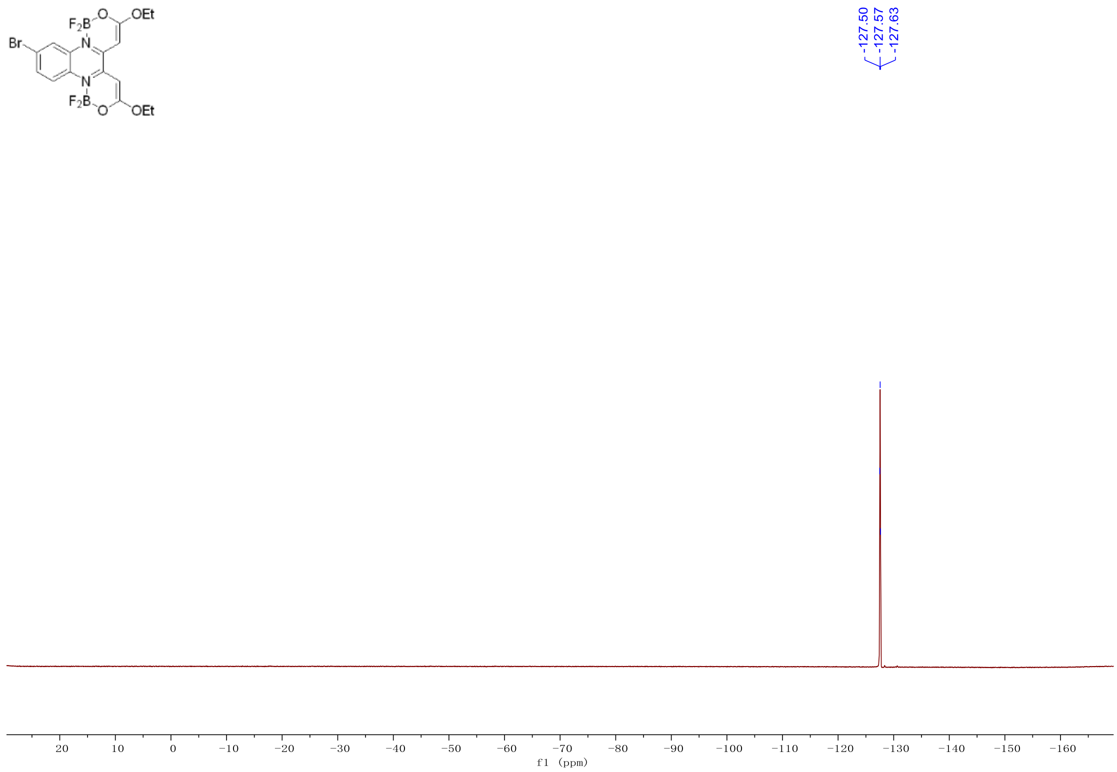
^{1}H NMR of **2b** (400 MHz, $CDCl_3$)



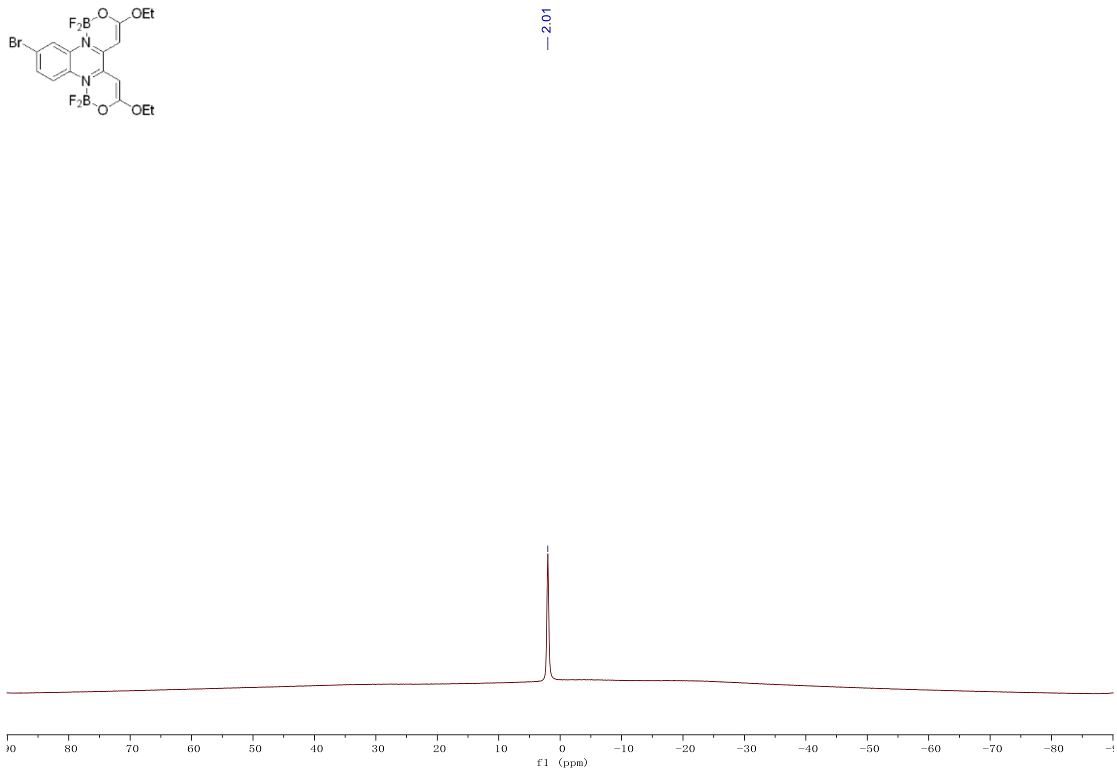
^{13}C NMR of **2b** (101 MHz, $CDCl_3$)



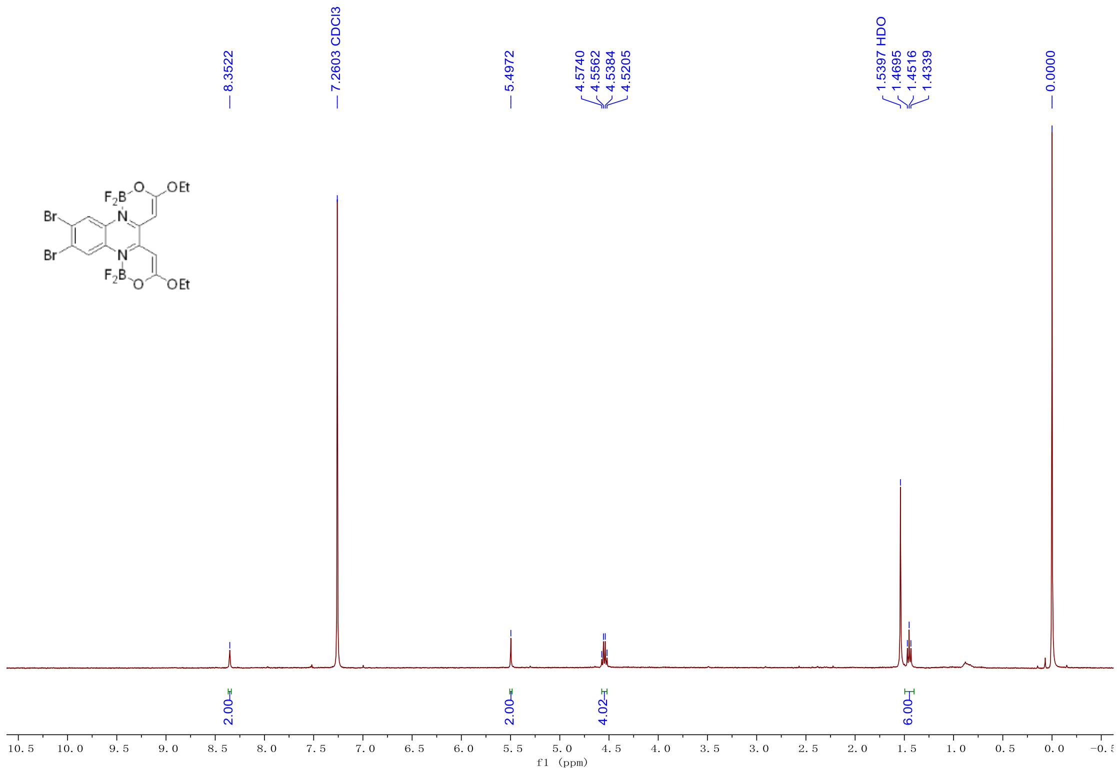
^{19}F NMR of **2b**



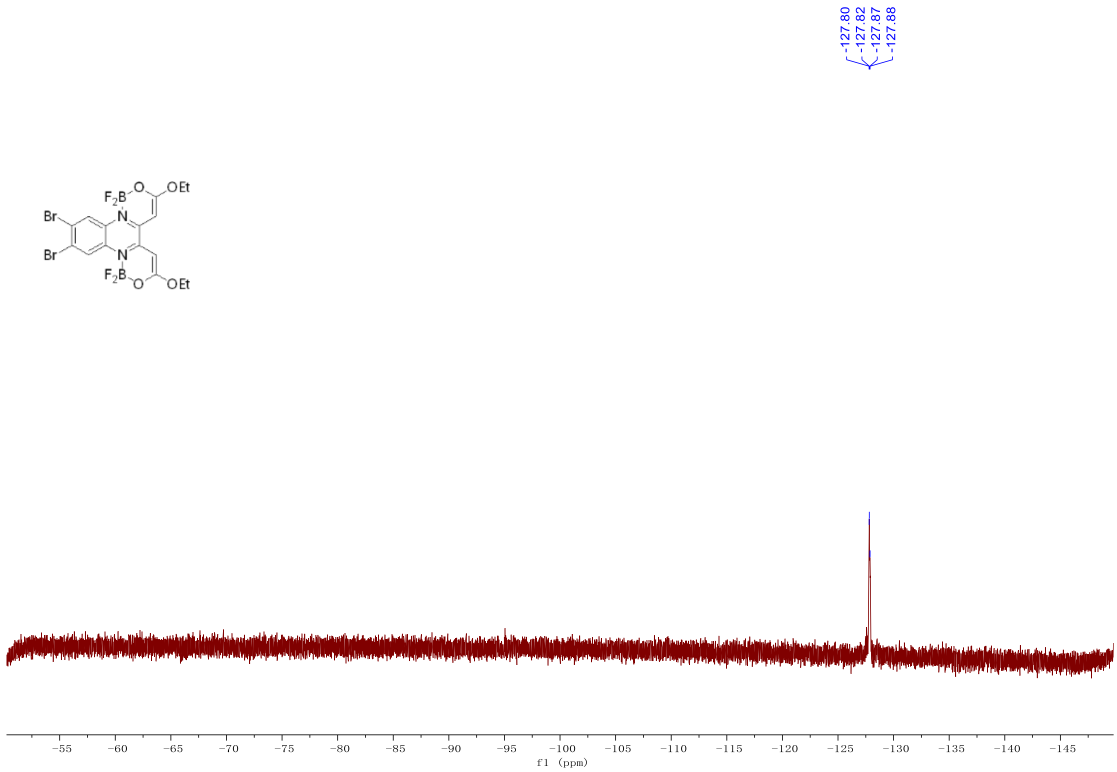
^{11}B NMR of **2b** (128 MHz, $CDCl_3$)



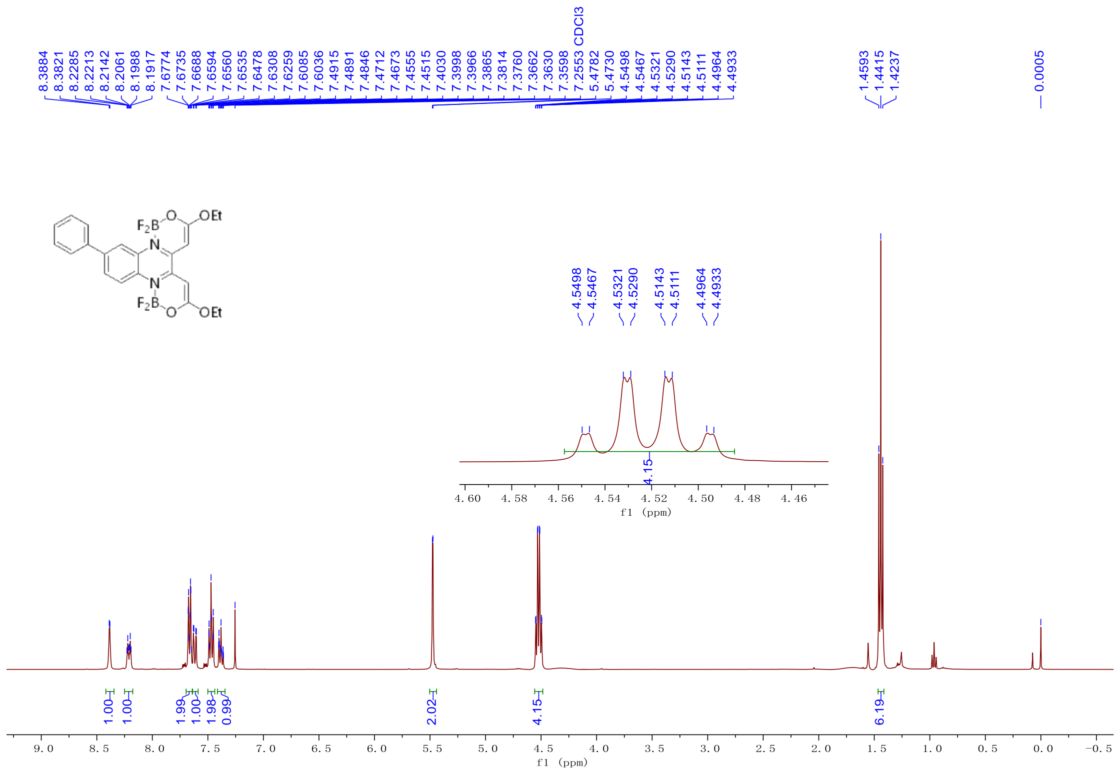
^{1}H NMR of **2c** (400 MHz, $CDCl_3$)



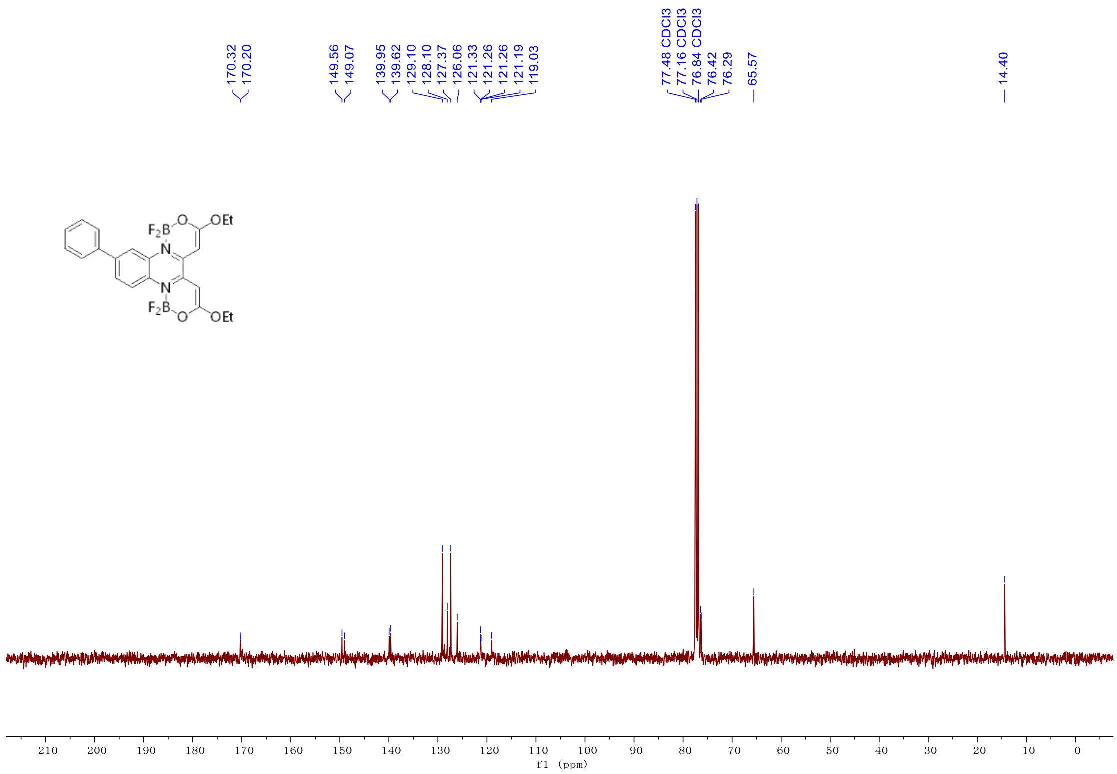
^{19}F NMR of **2c** (376 MHz, $CDCl_3$)



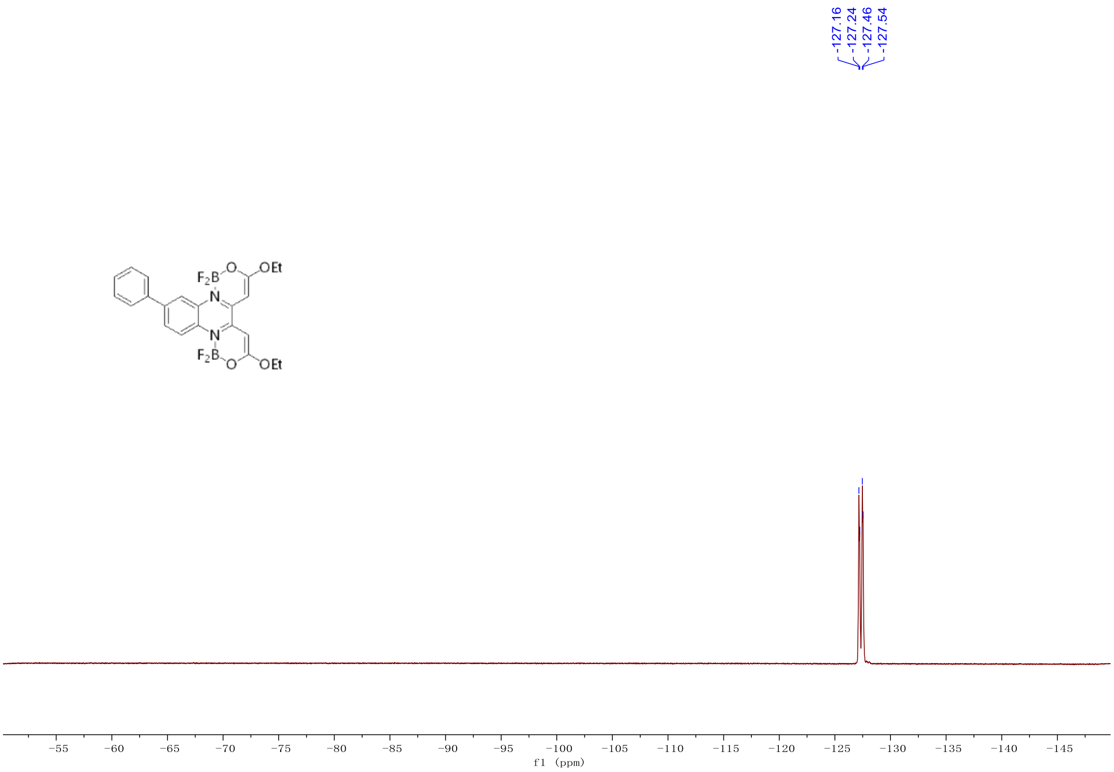
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



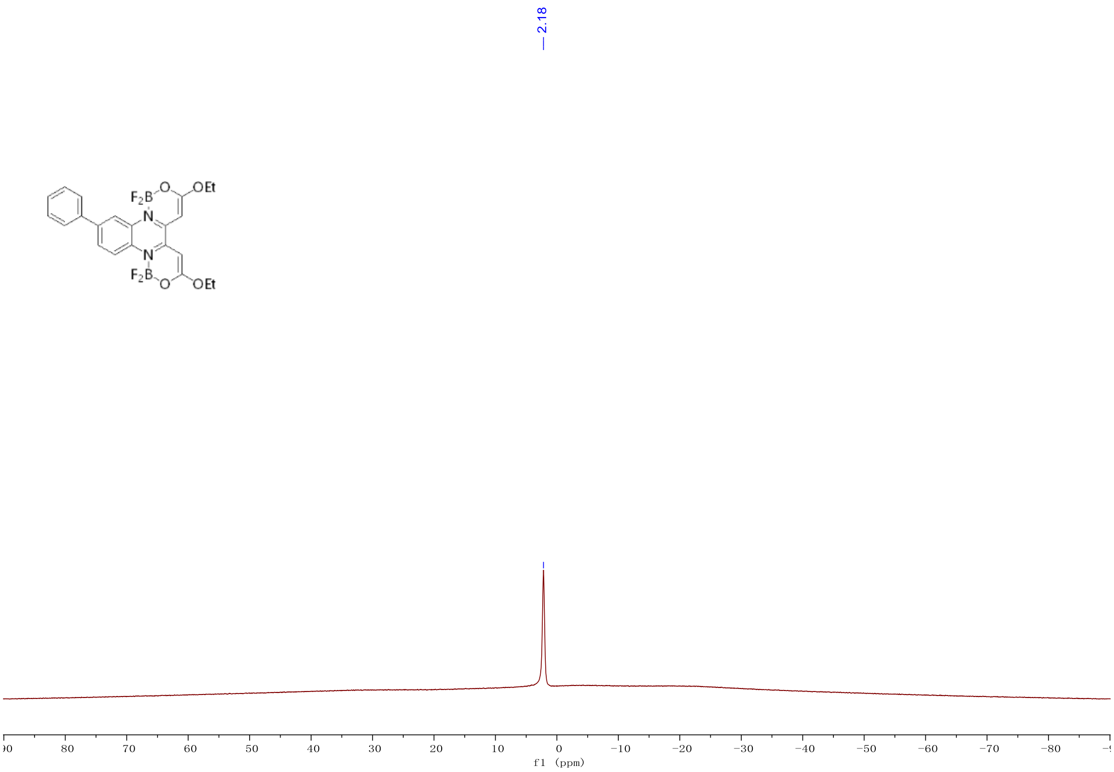
^{13}C NMR of **3a** (101 MHz, $CDCl_3$)



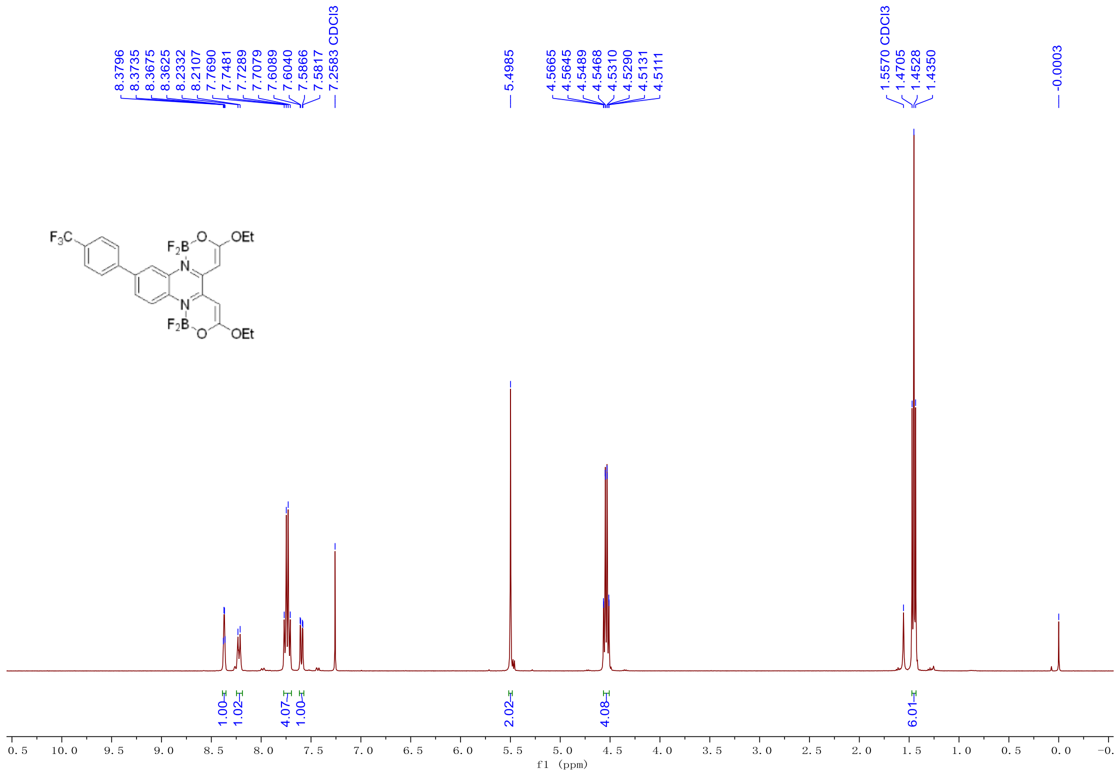
^{19}F NMR of **3a** (376 MHz, $CDCl_3$)



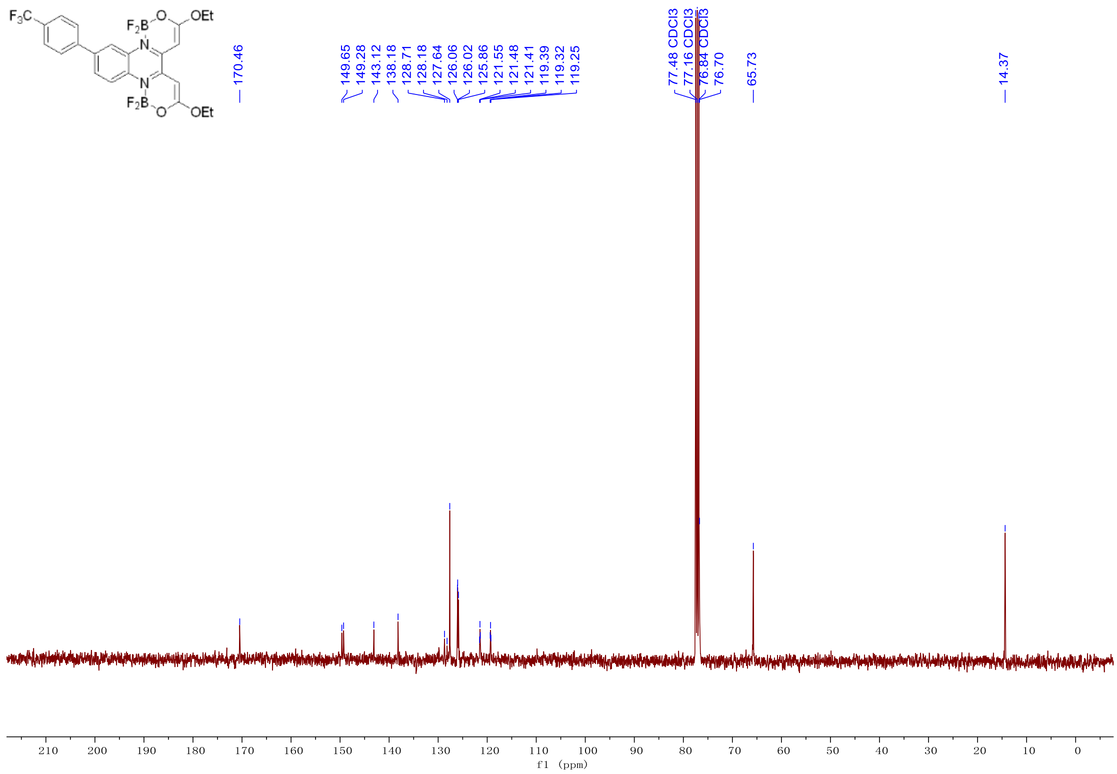
^{11}B NMR of **3a** (128 MHz, $CDCl_3$)



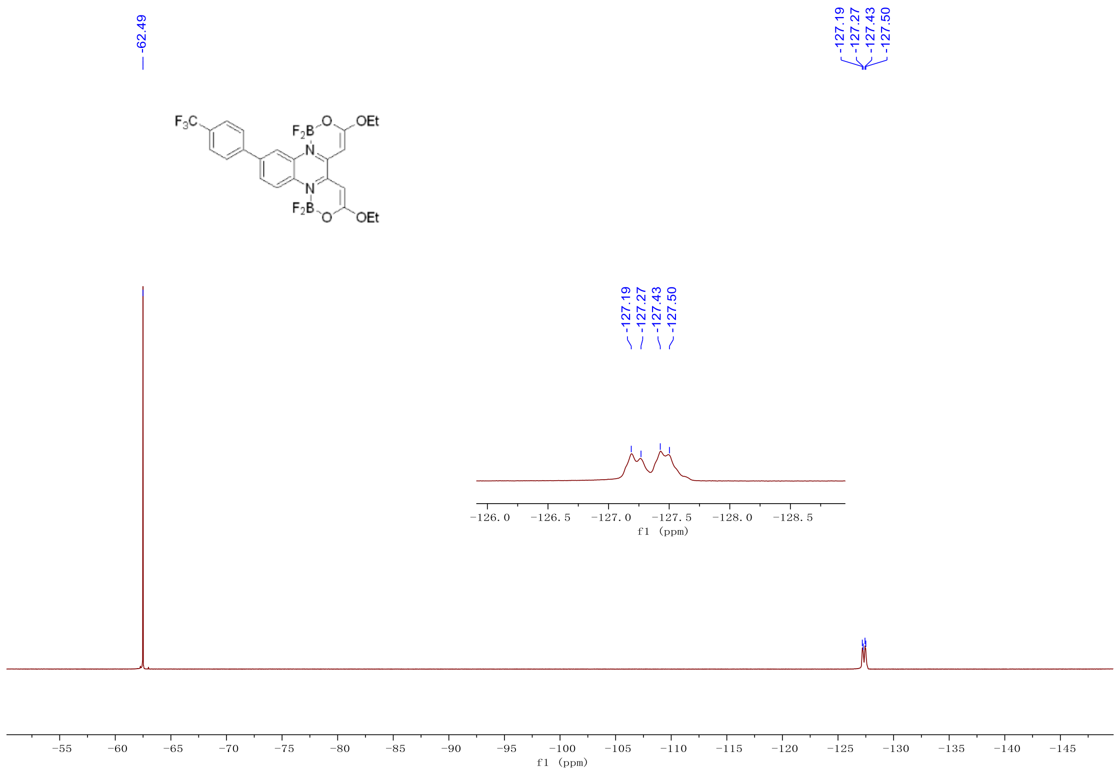
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



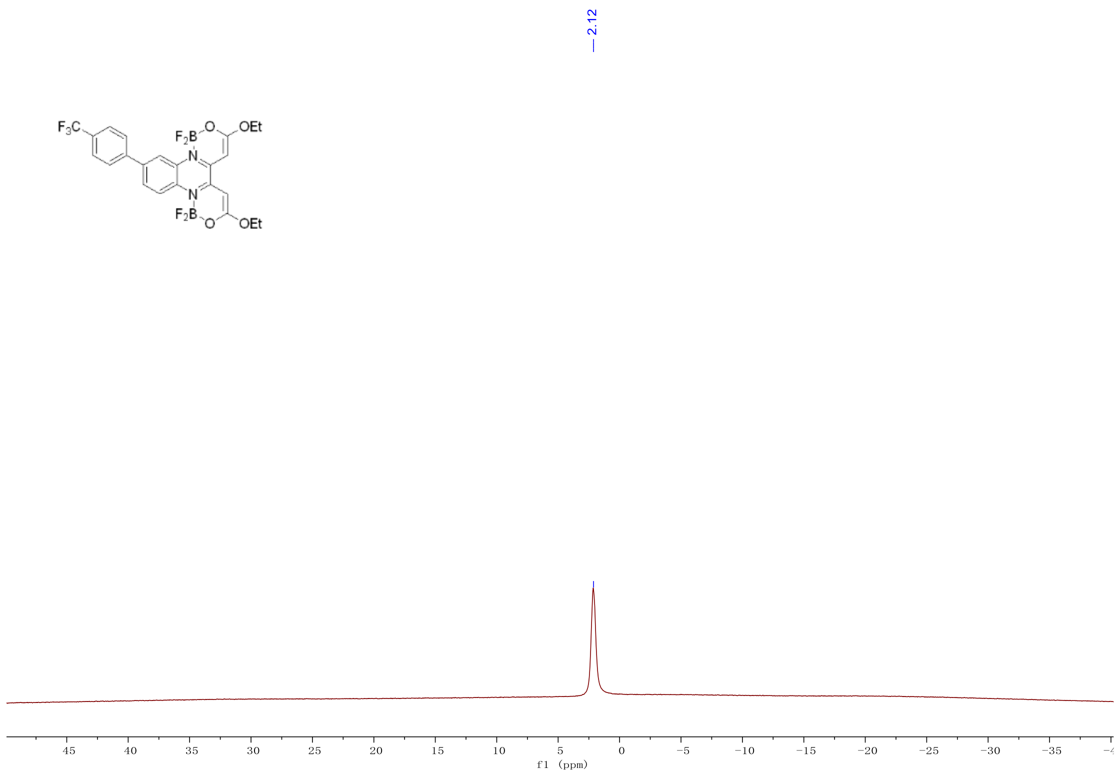
^{13}C NMR of **3b** (101 MHz, $CDCl_3$)



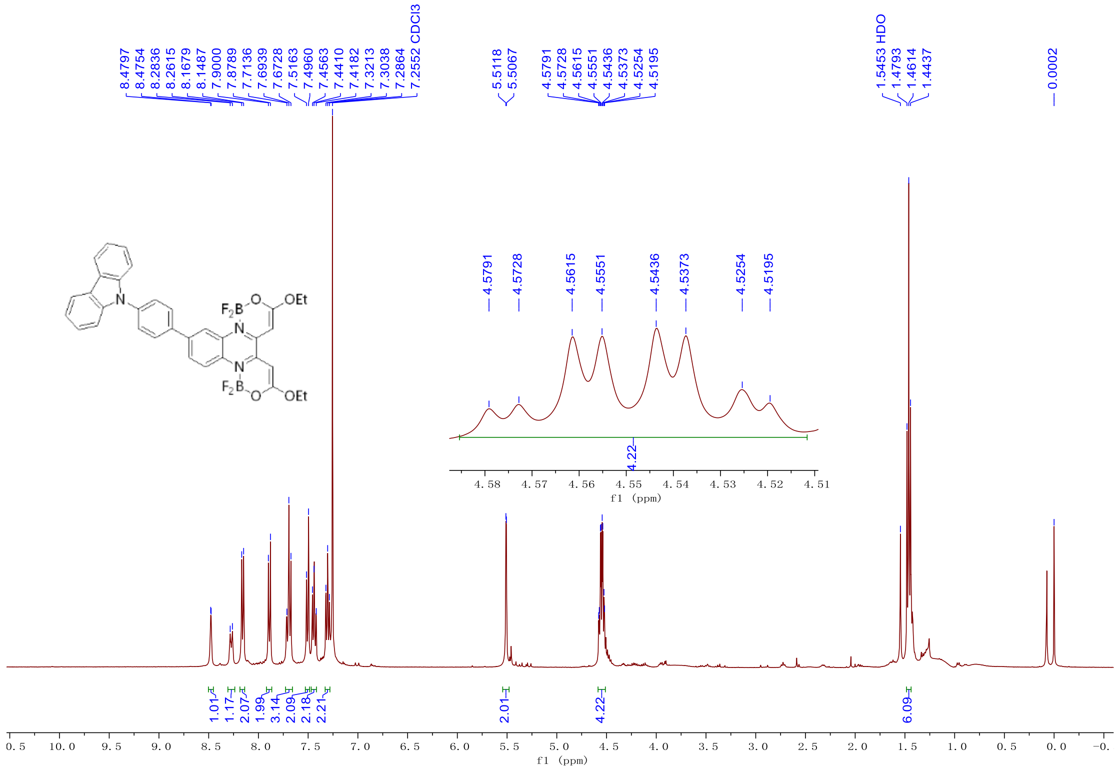
^{19}F NMR of **3b** (376 MHz, $CDCl_3$)



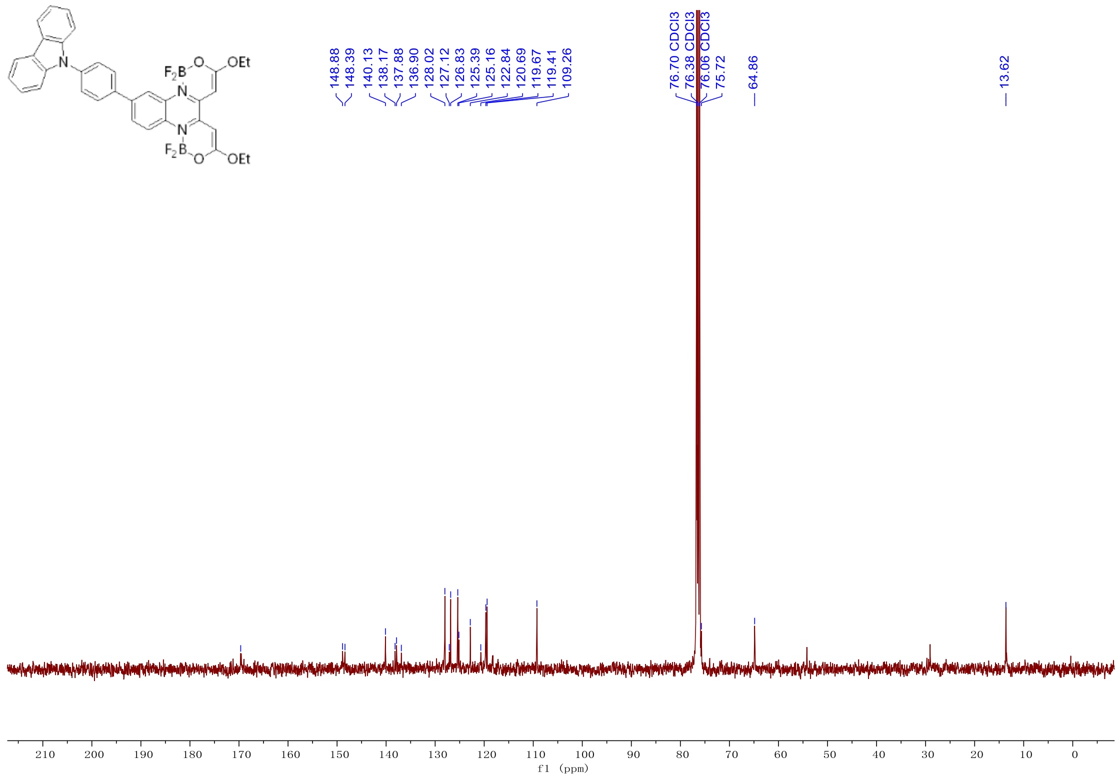
^{11}B NMR of **3b** (128 MHz, $CDCl_3$)



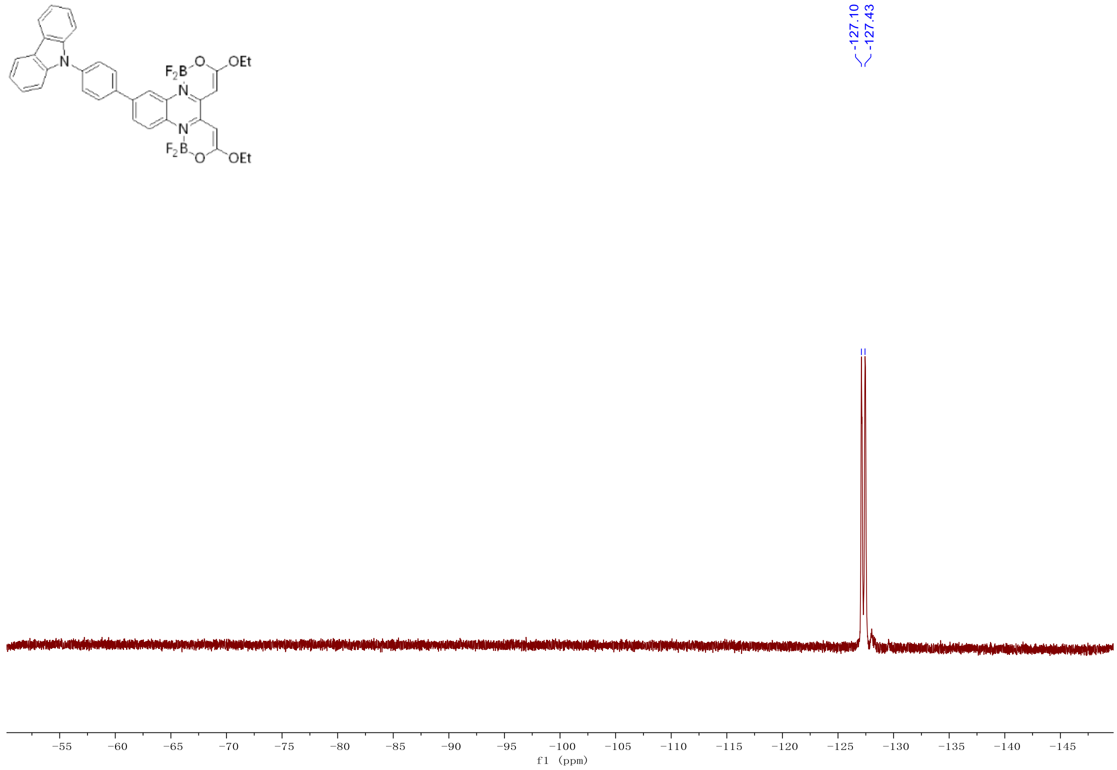
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



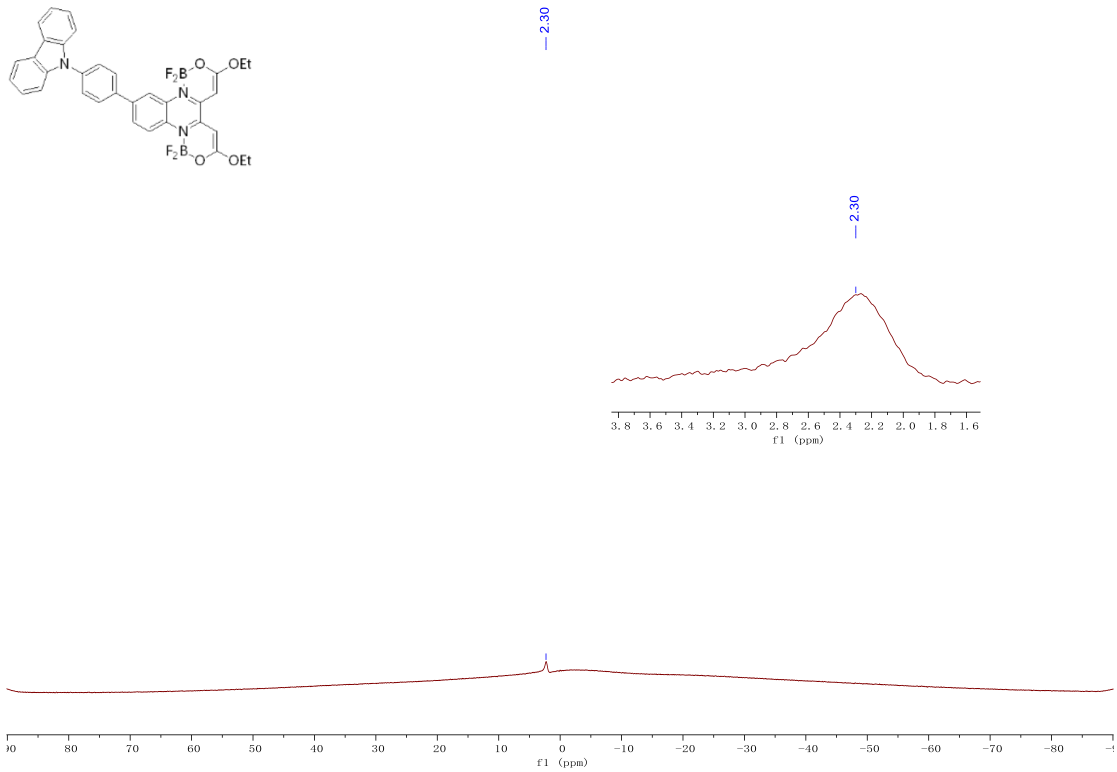
^{13}C NMR of **3c** (101 MHz, $CDCl_3$)



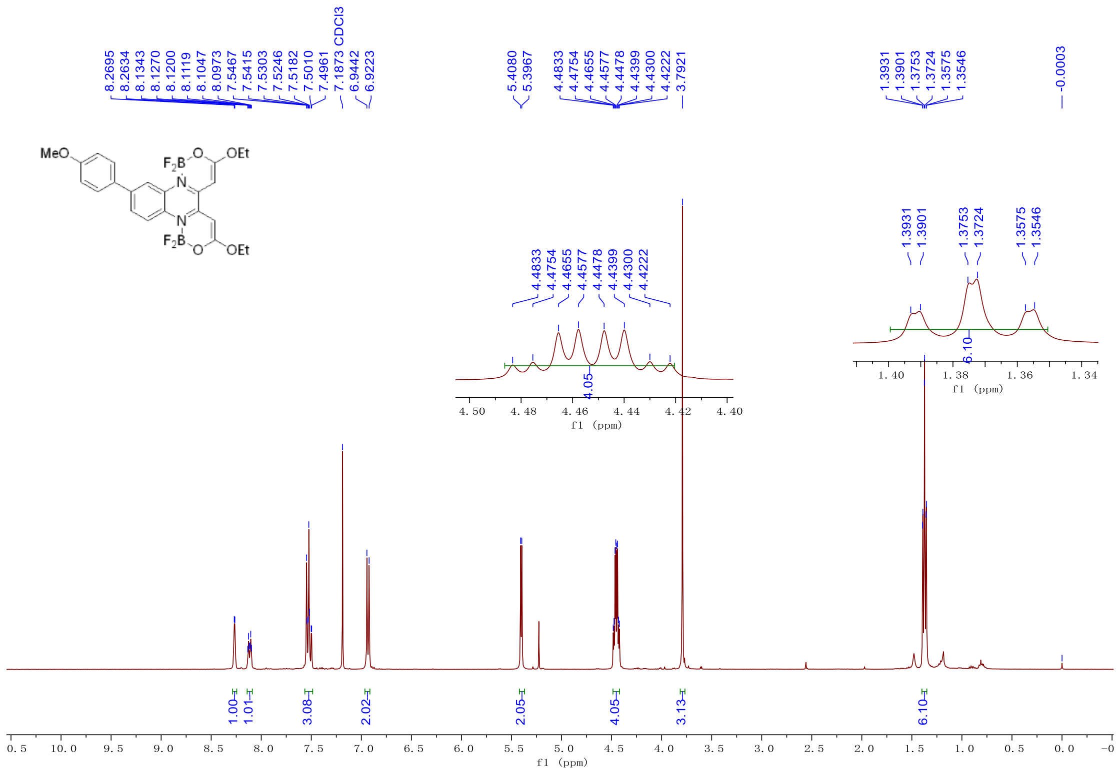
[19]F NMR of **3c** (376 MHz, $CDCl_3$)



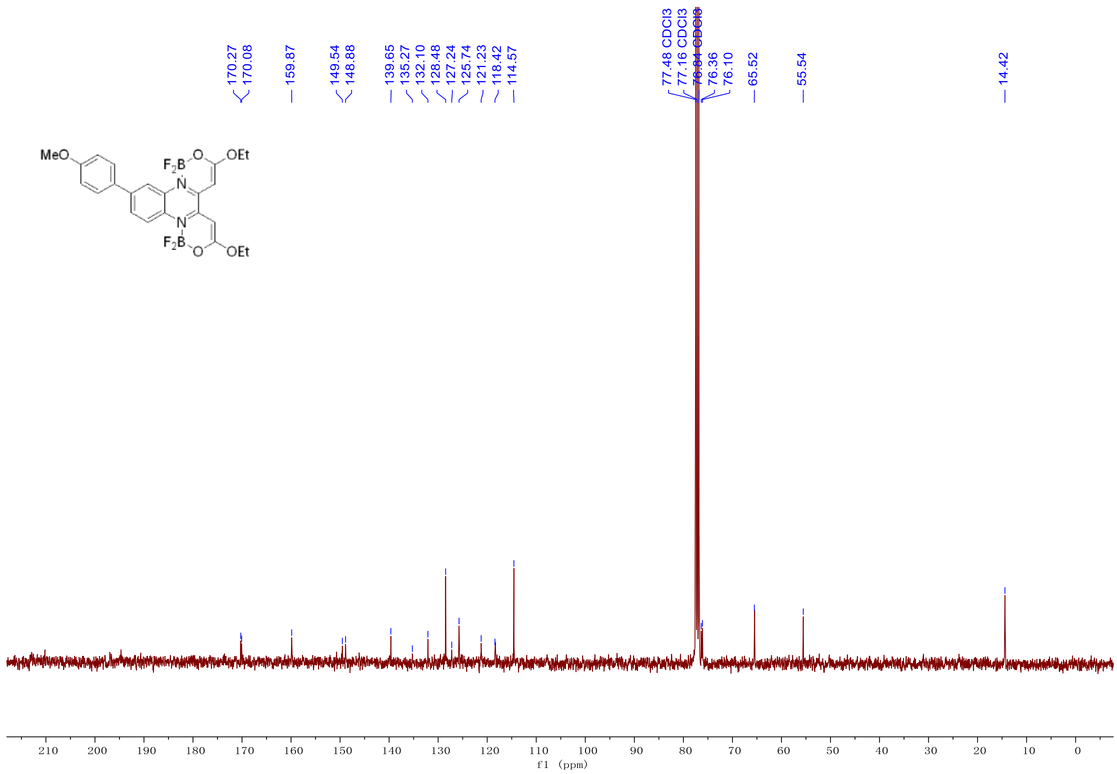
[11]B NMR of **3c** (128 MHz, $CDCl_3$)



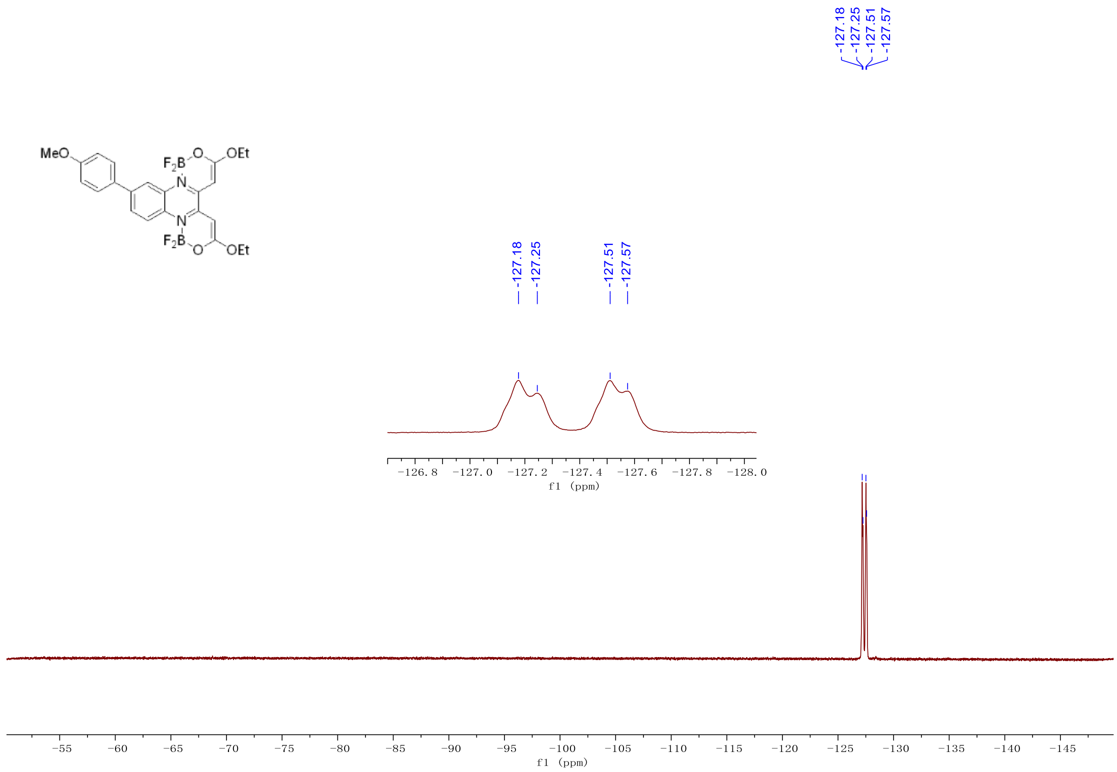
[1]H NMR of **3d** (400 MHz, $CDCl_3$)



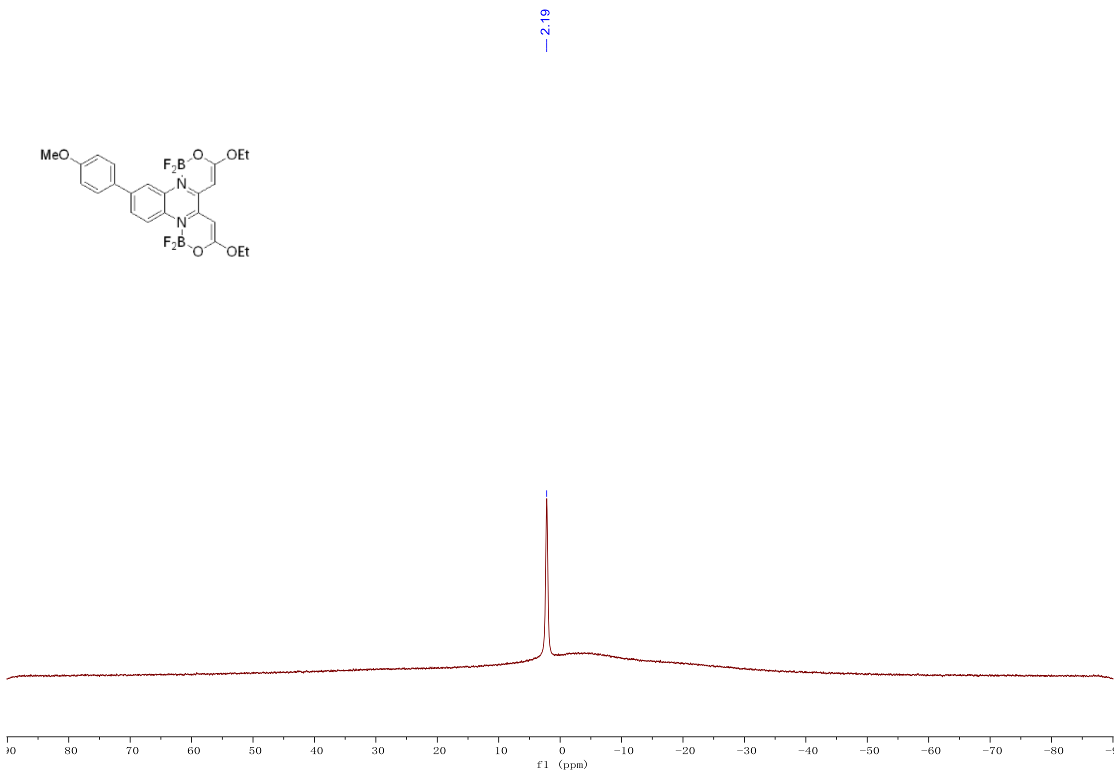
[13]C NMR of **3d** (101 MHz, $CDCl_3$)



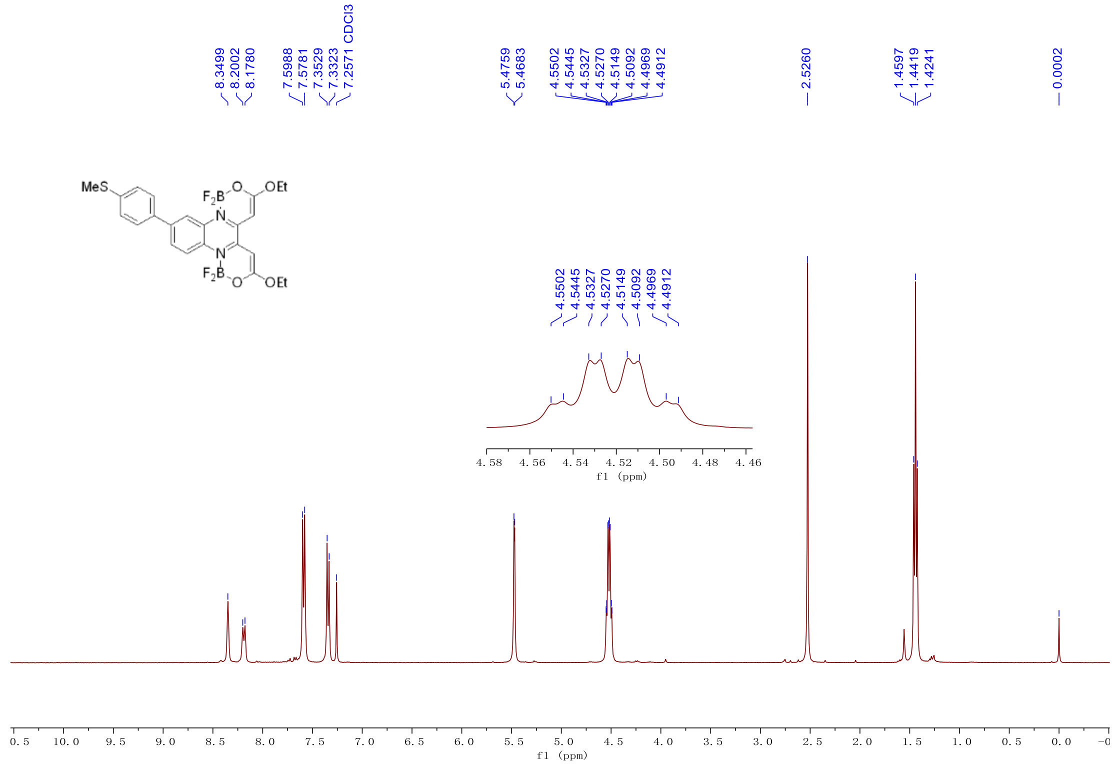
^{19}F NMR of **3d** (376 MHz, $CDCl_3$)



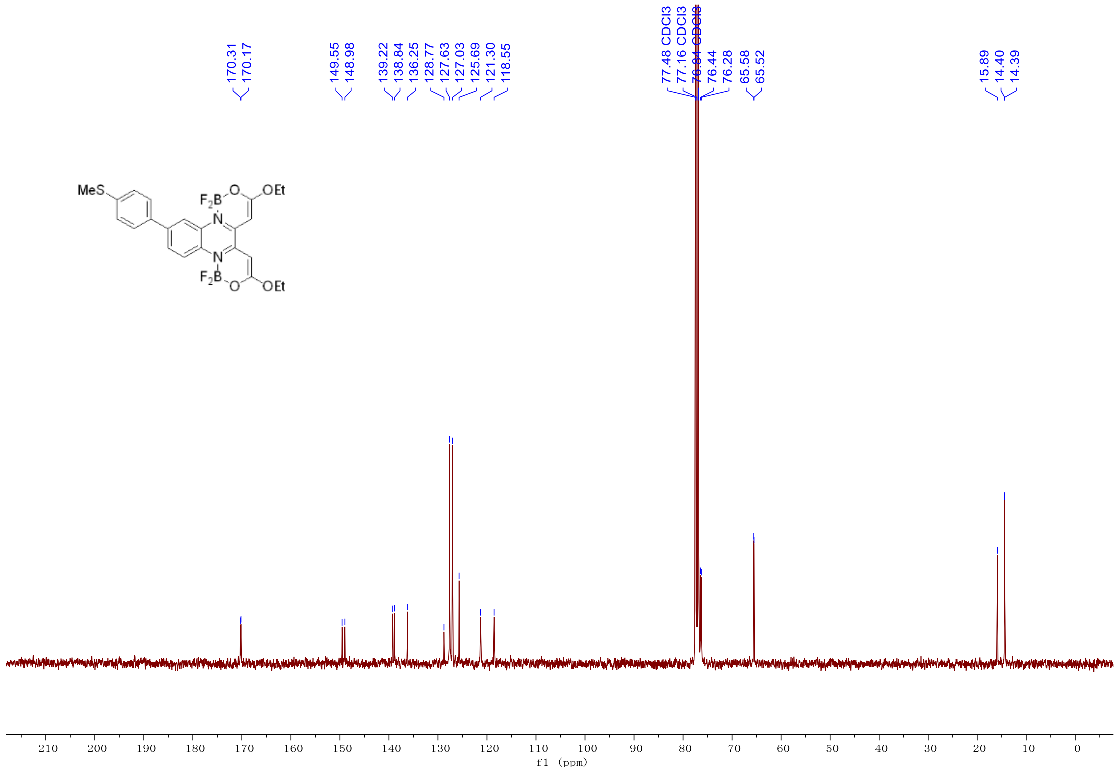
^{11}B NMR of **3d** (128 MHz, $CDCl_3$)



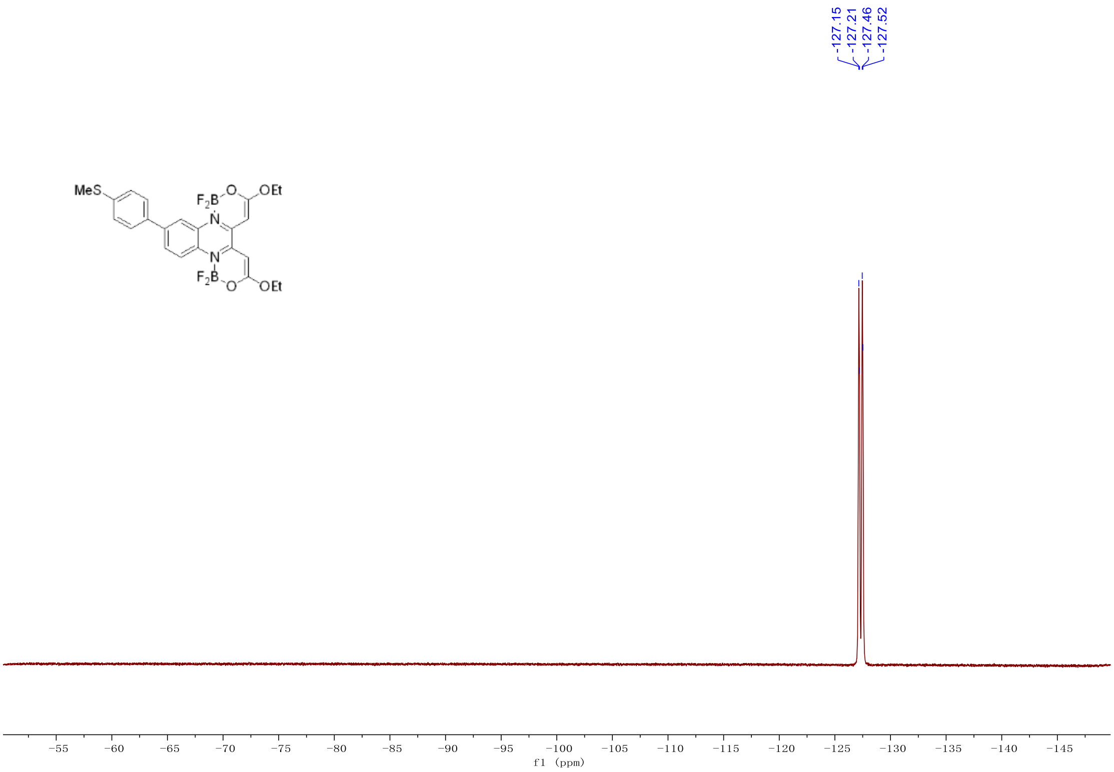
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



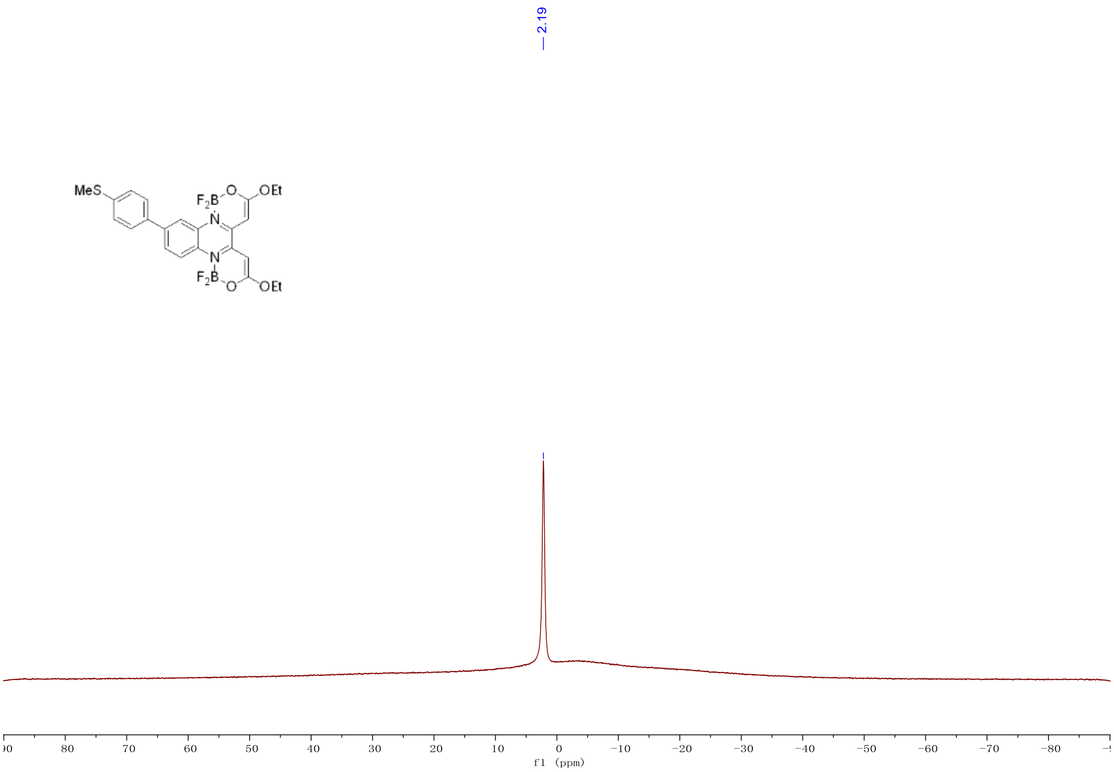
^{13}C NMR of **3e** (101 MHz, $CDCl_3$)



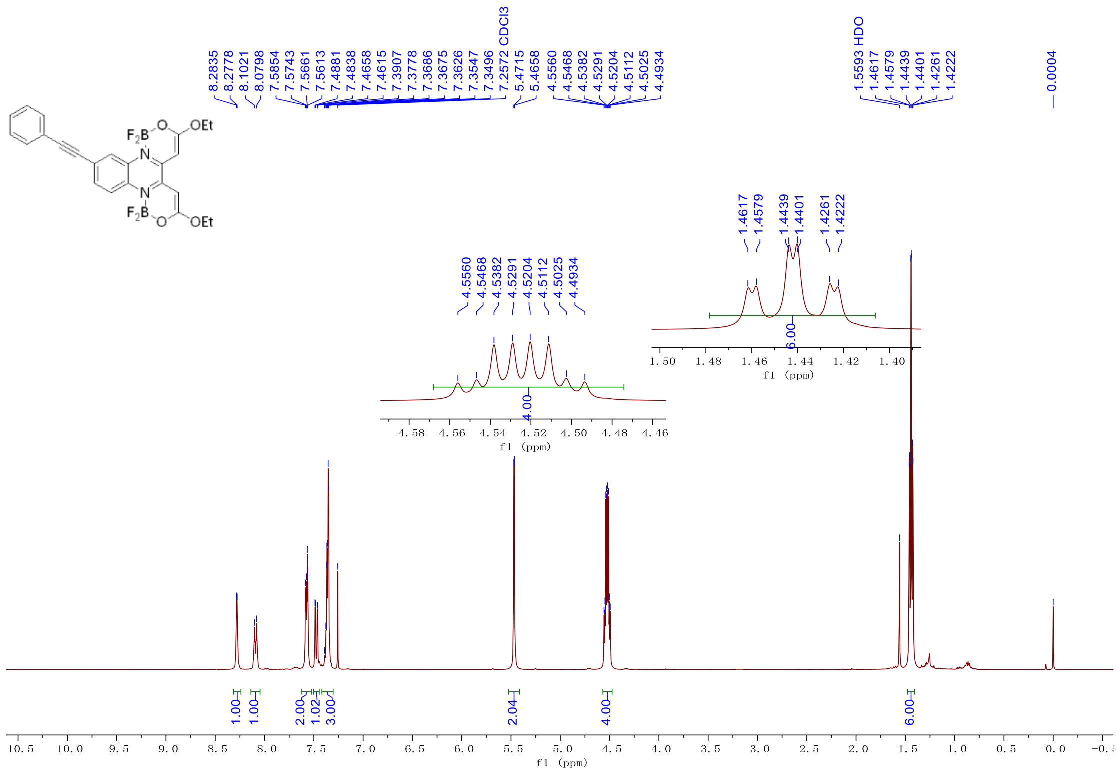
^{19}F NMR of **3e** (376 MHz, $CDCl_3$)



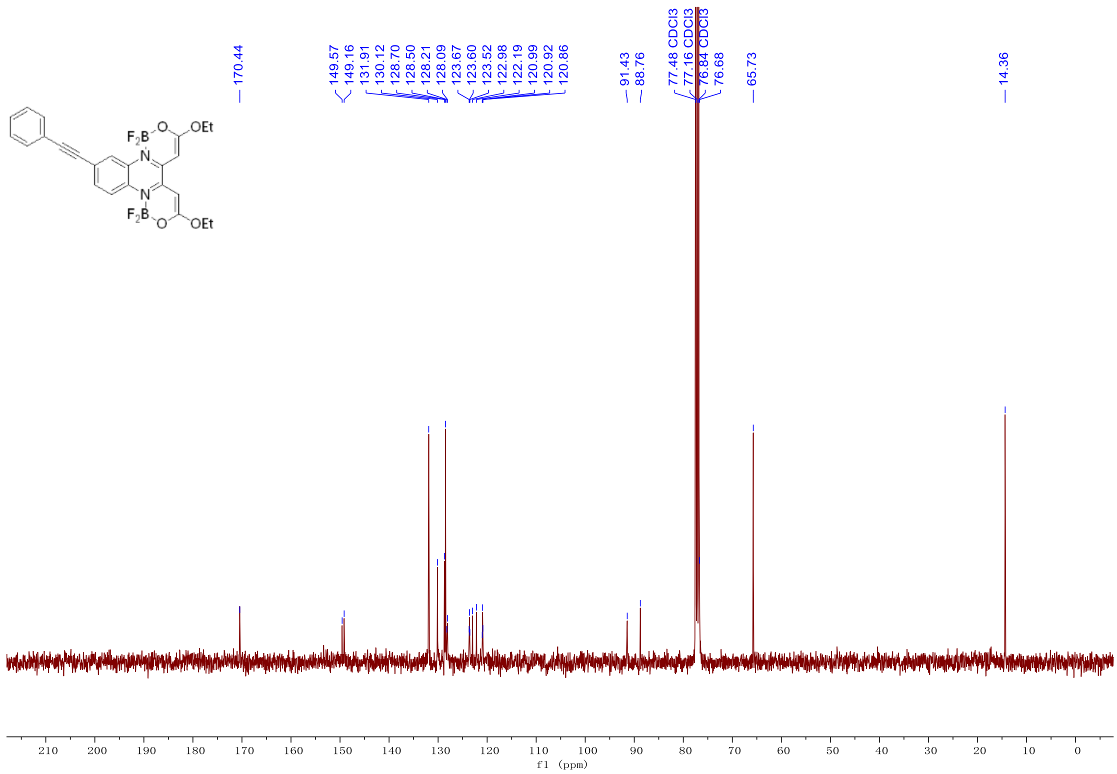
^{11}B NMR of **3e** (128 MHz, $CDCl_3$)



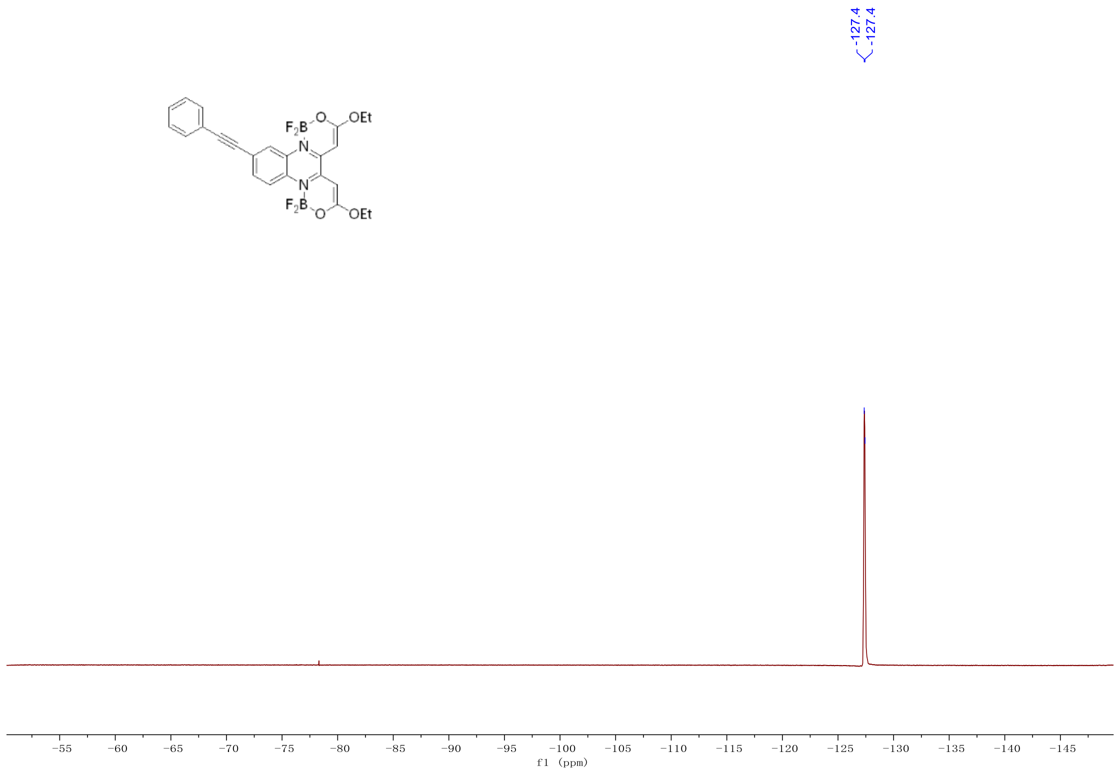
[1]H NMR of **3f** (400 MHz, $CDCl_3$)



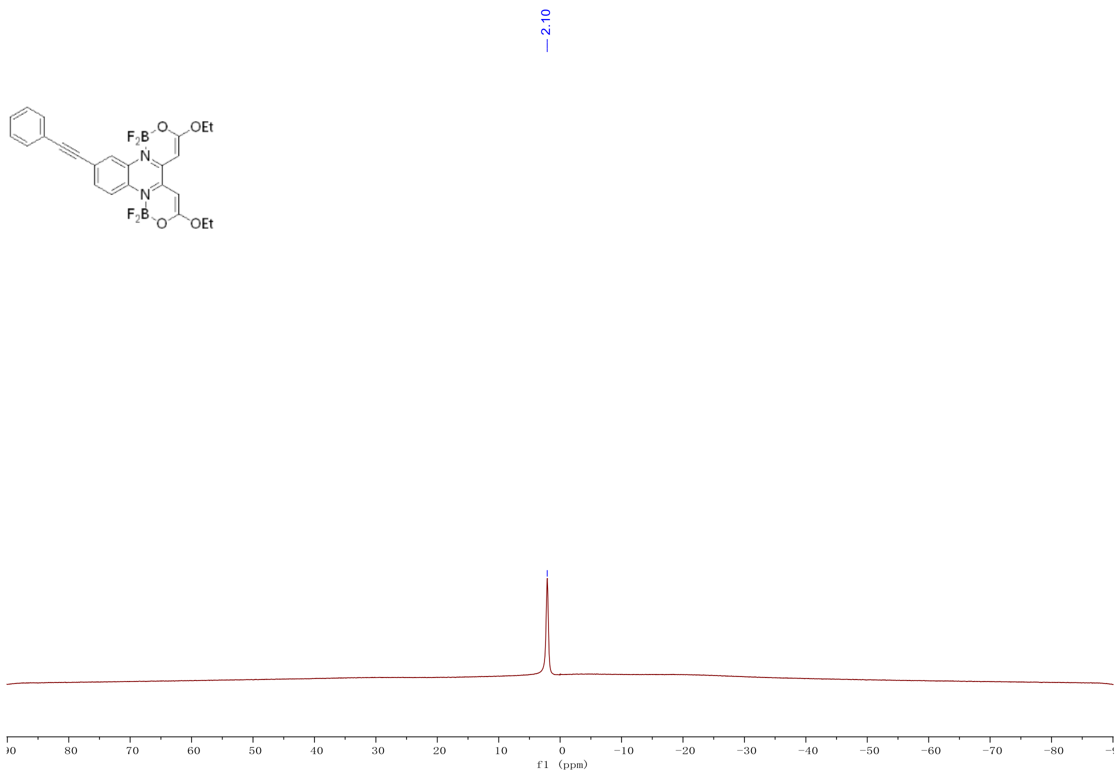
[13]C NMR of **3f** (101 MHz, $CDCl_3$)



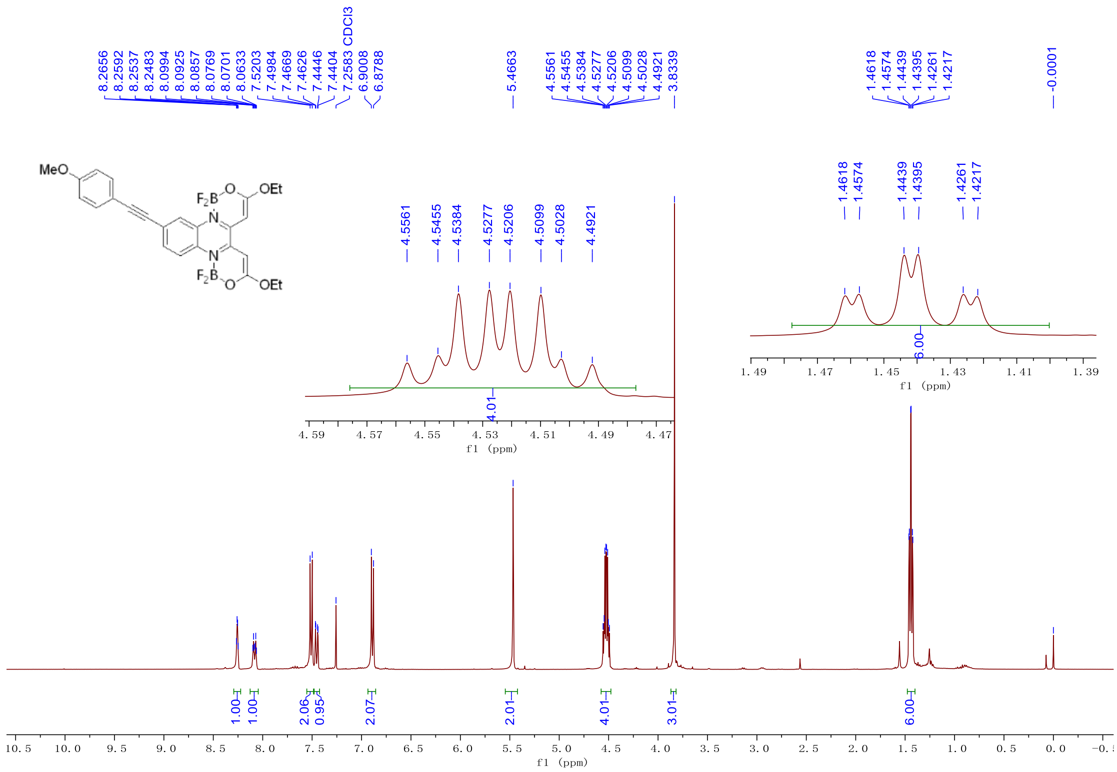
^{19}F NMR of **3f** (376 MHz, $CDCl_3$)



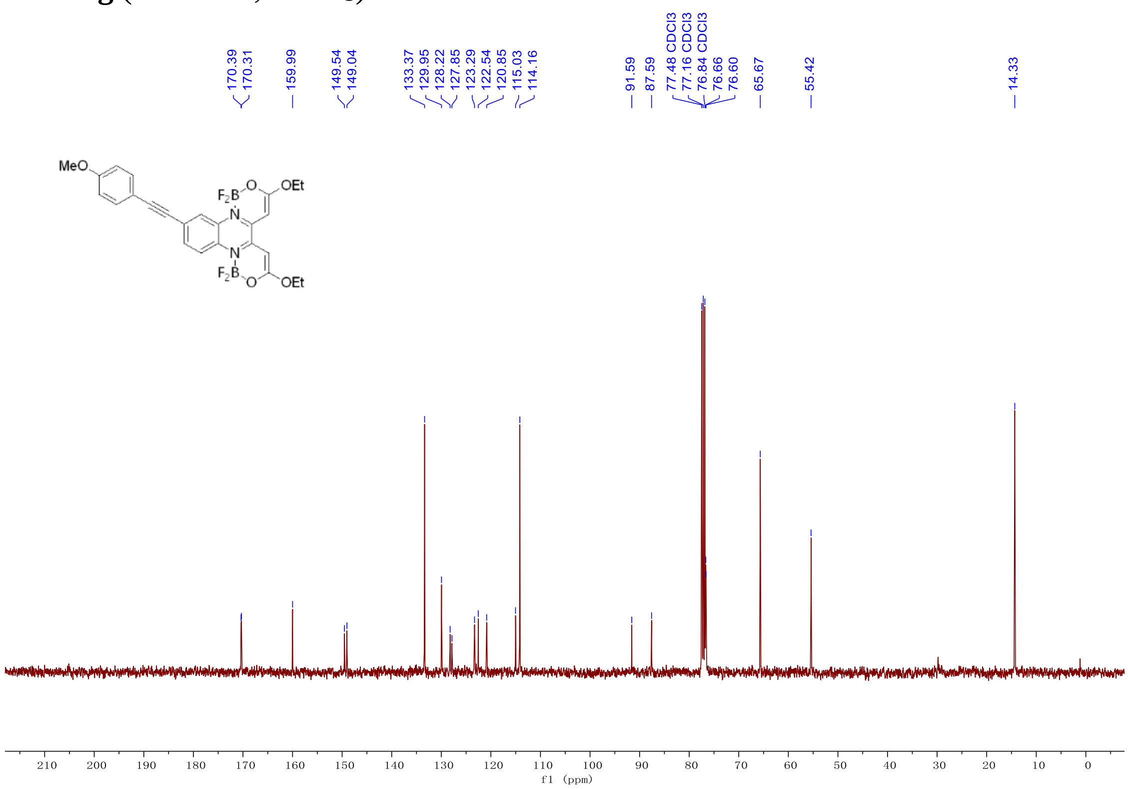
^{11}B NMR of **3f** (128 MHz, $CDCl_3$)



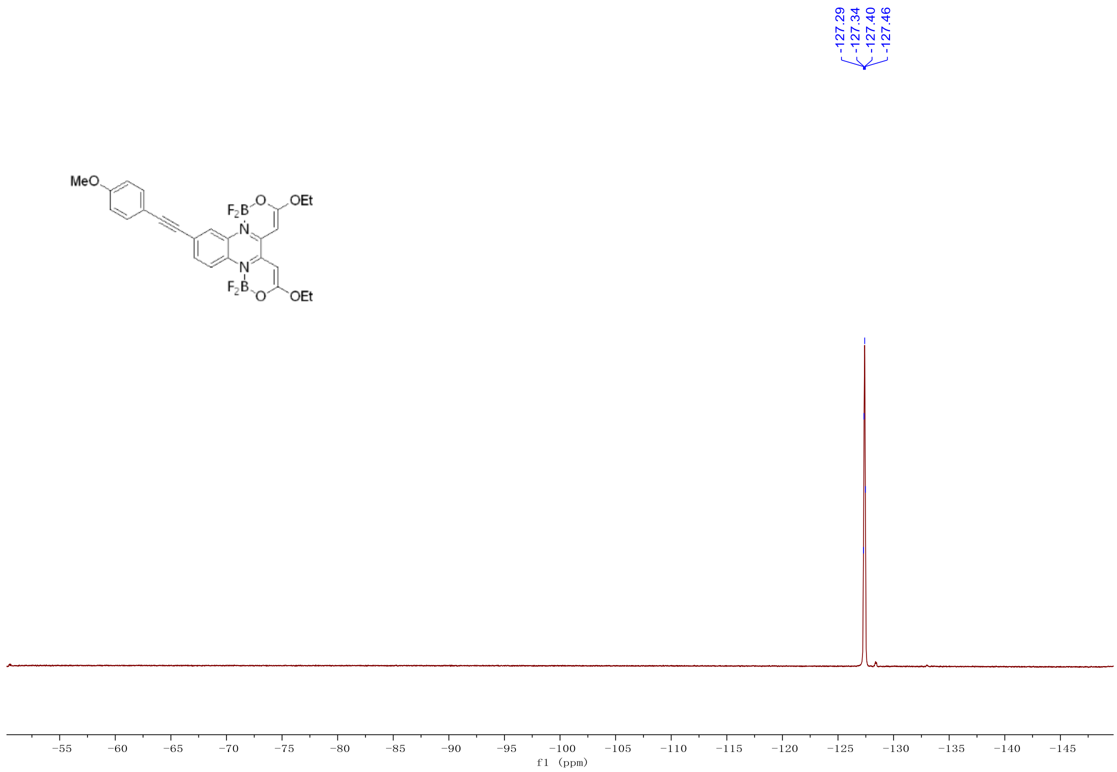
^{1}H NMR of **3g** (400 MHz, $CDCl_3$)



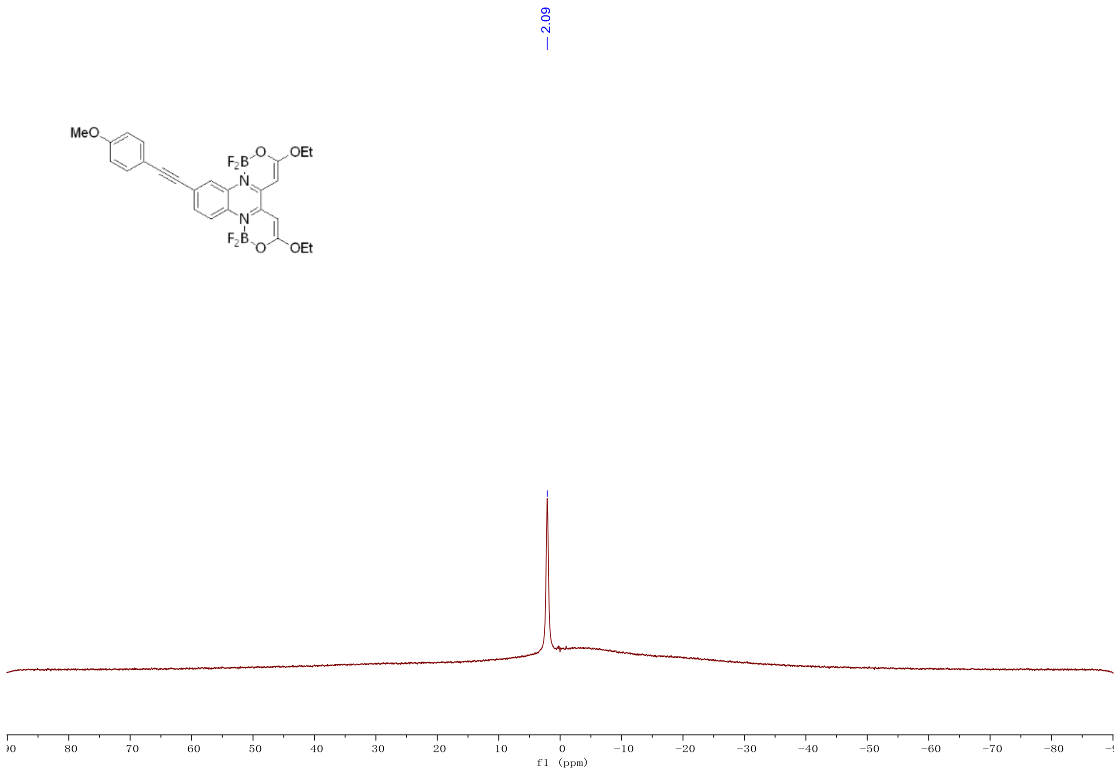
^{13}C NMR of **3g** (101 MHz, $CDCl_3$)



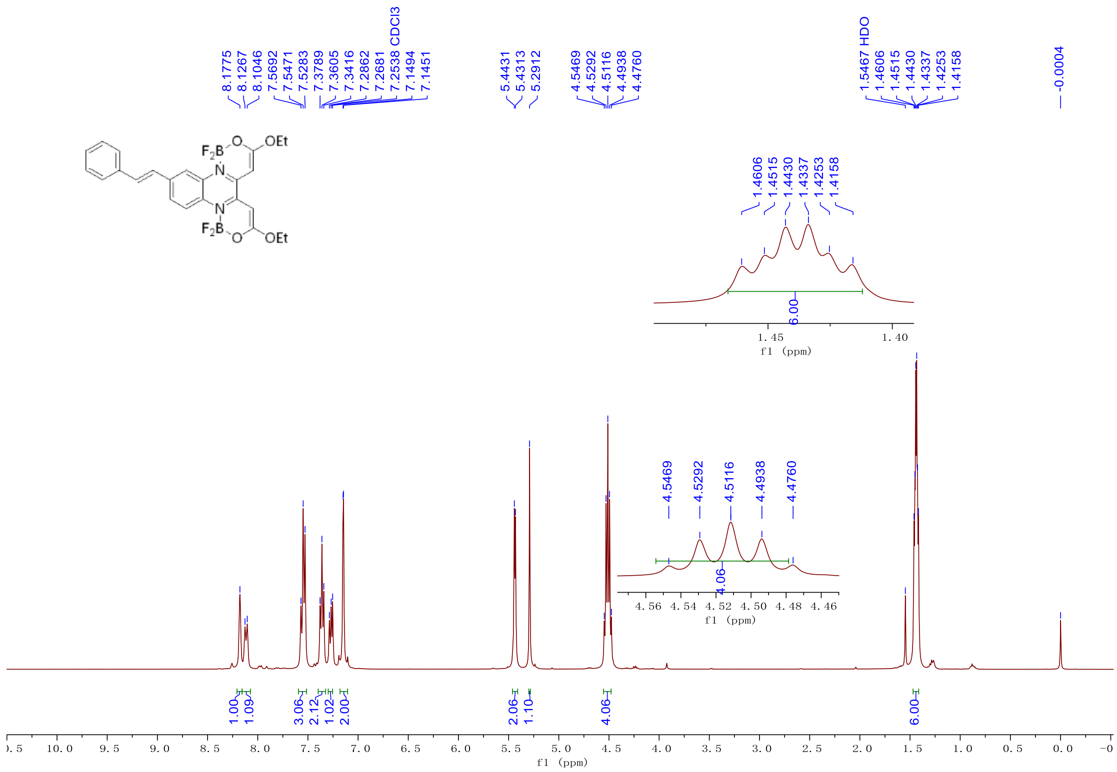
^{19}F NMR of **3g** (376 MHz, $CDCl_3$)



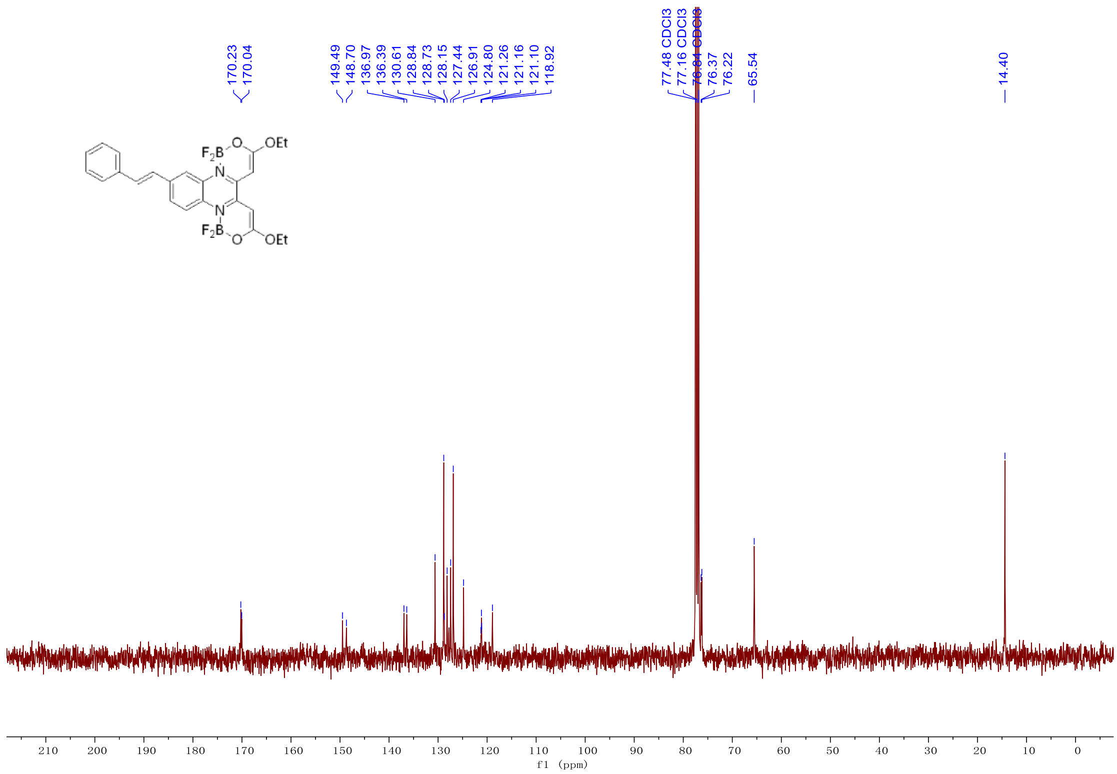
^{11}B NMR of **3g** (128 MHz, $CDCl_3$)



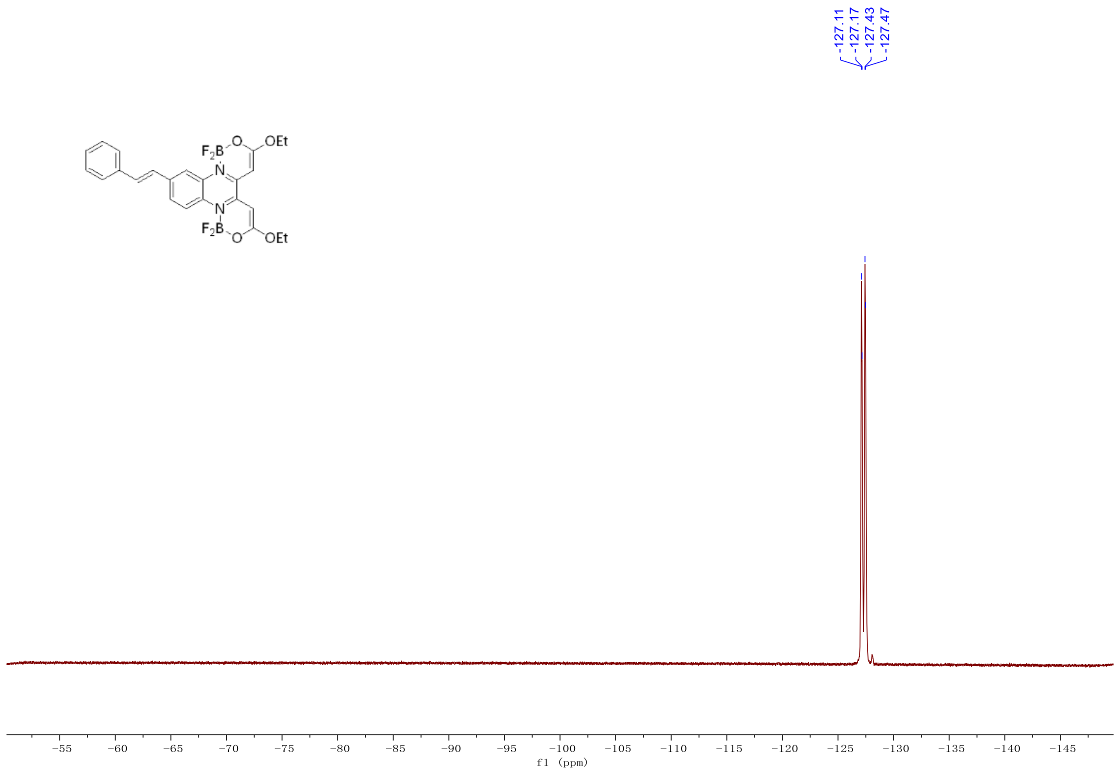
[1]H NMR of **3h** (400 MHz, $CDCl_3$)



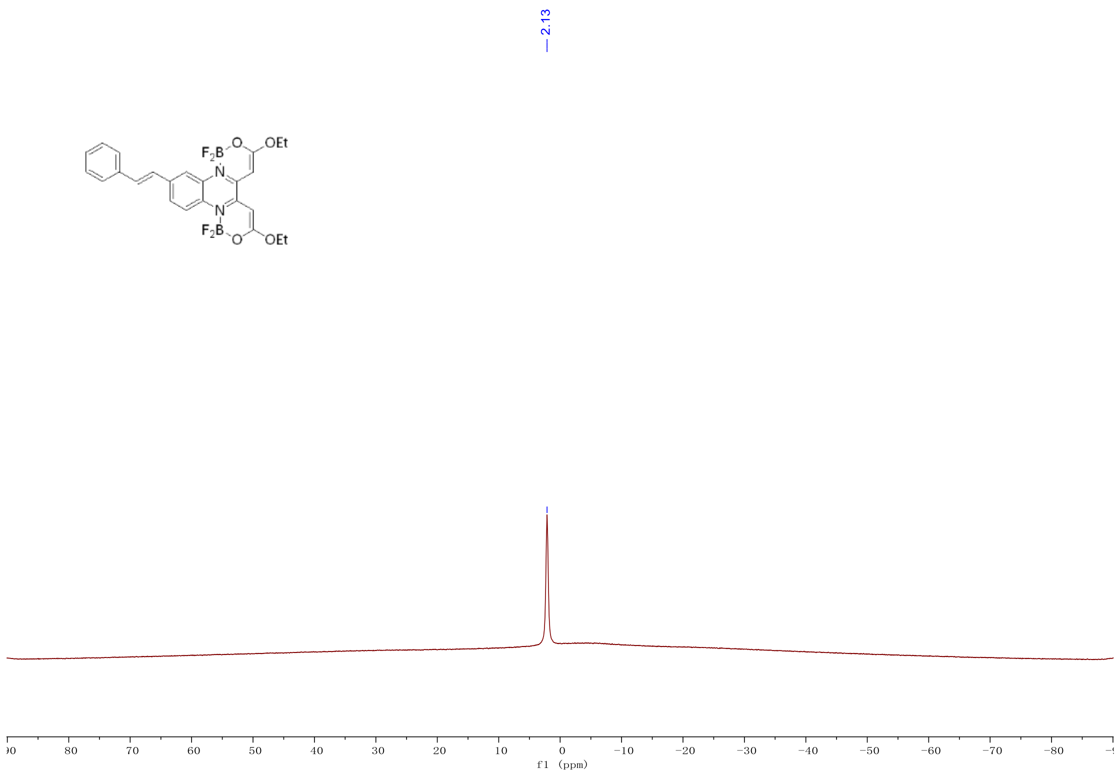
[13]C NMR of **3h** (101 MHz, $CDCl_3$)



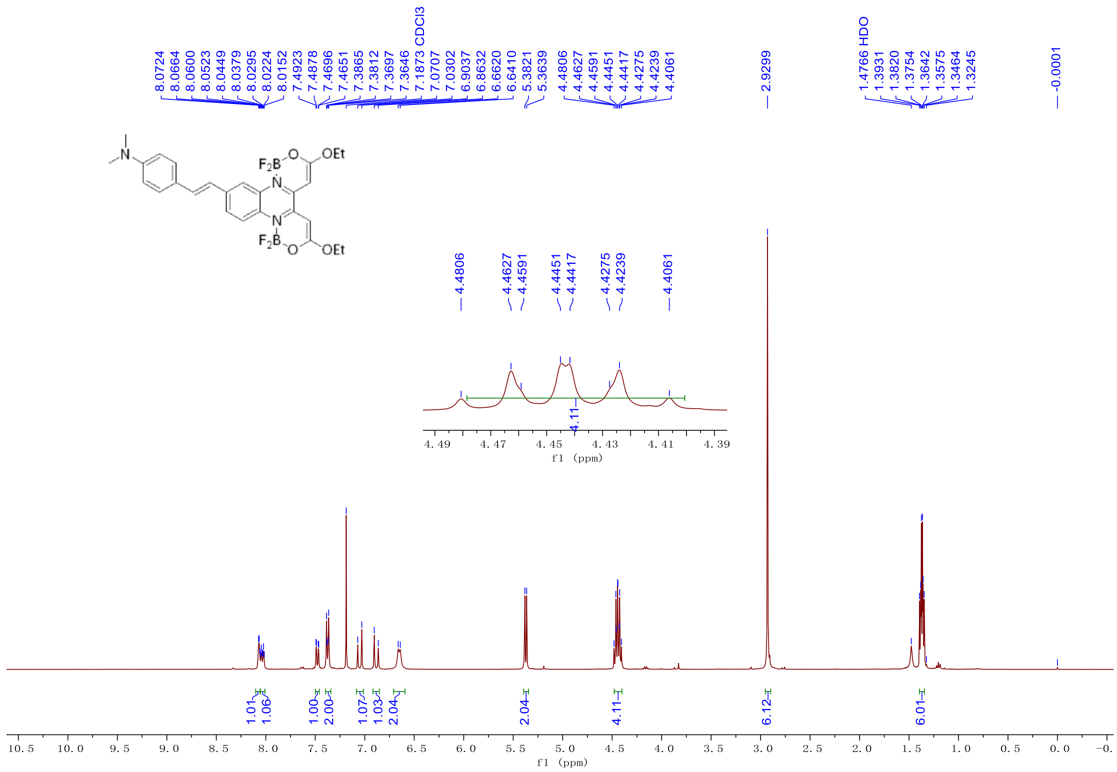
^{19}F NMR of **3h** (376 MHz, $CDCl_3$)



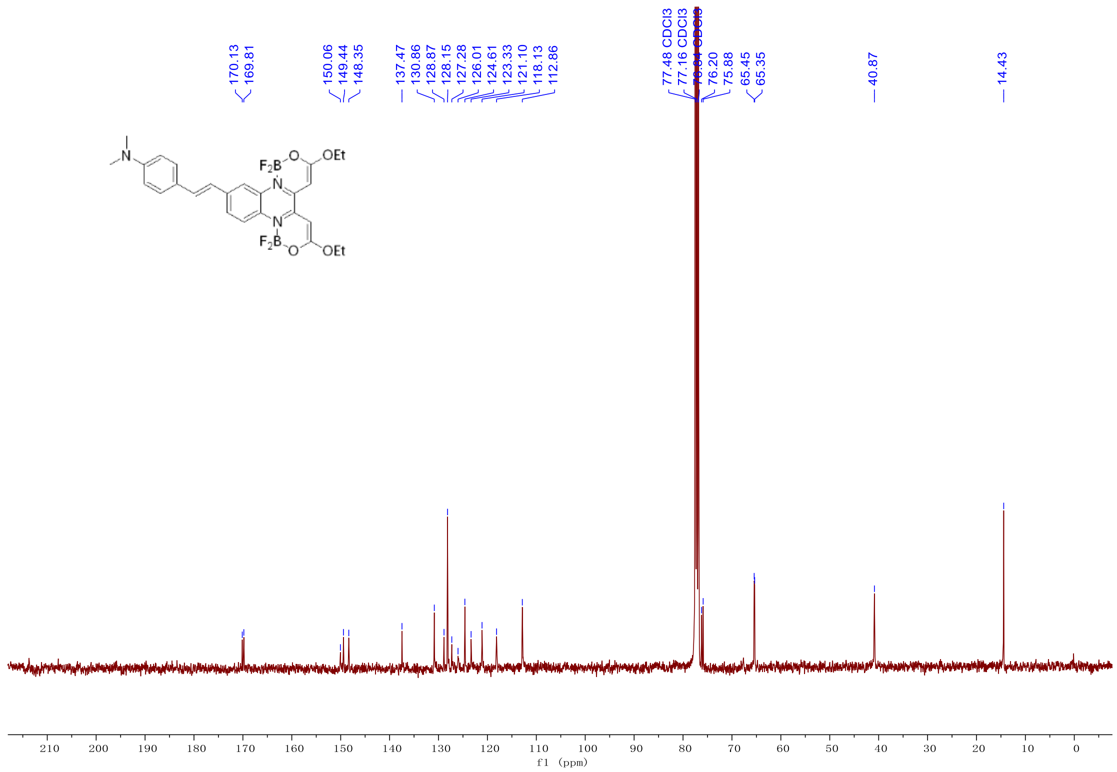
^{11}B NMR of **3h** (128 MHz, $CDCl_3$)



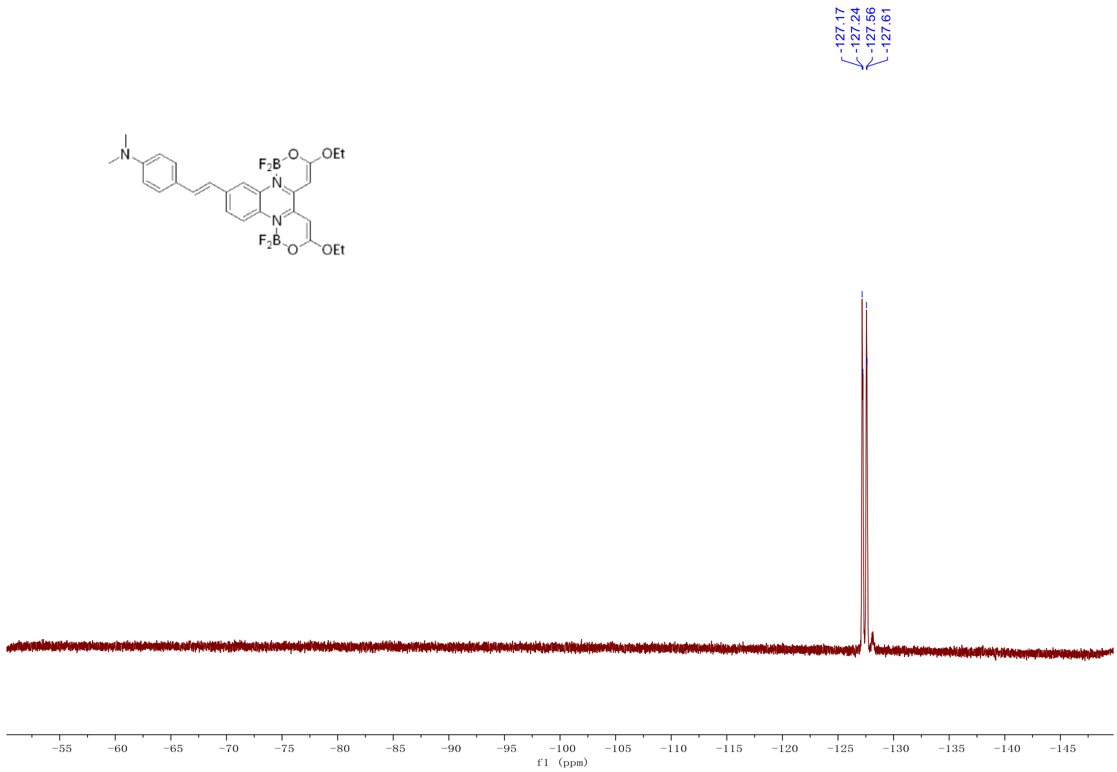
[1]H NMR of **3i** (400 MHz, $CDCl_3$)



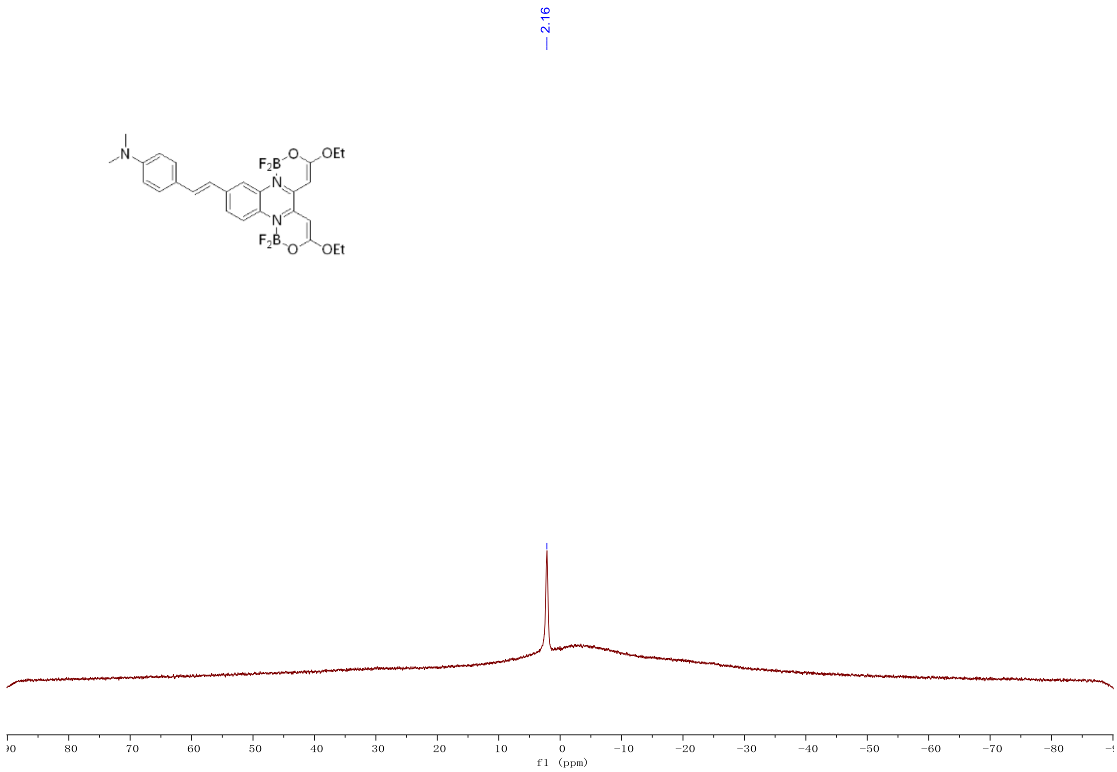
[13]C NMR of **3i** (101 MHz, $CDCl_3$)



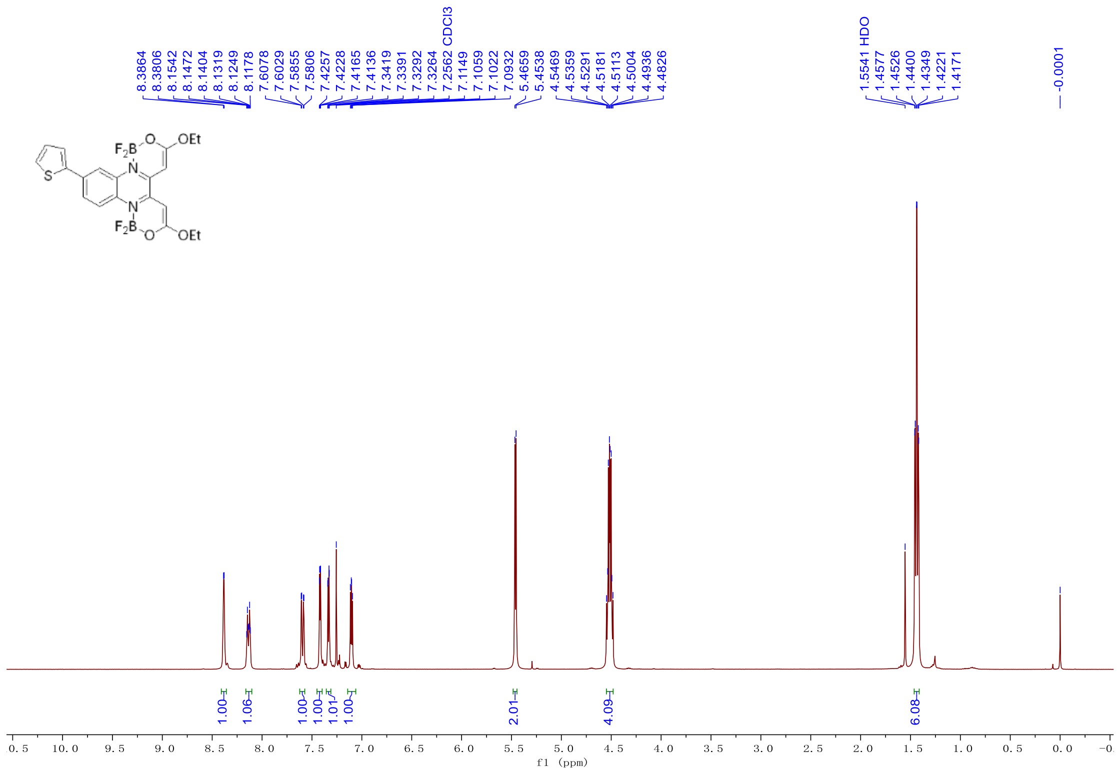
^{19}F NMR of **3i** (376 MHz, $CDCl_3$)



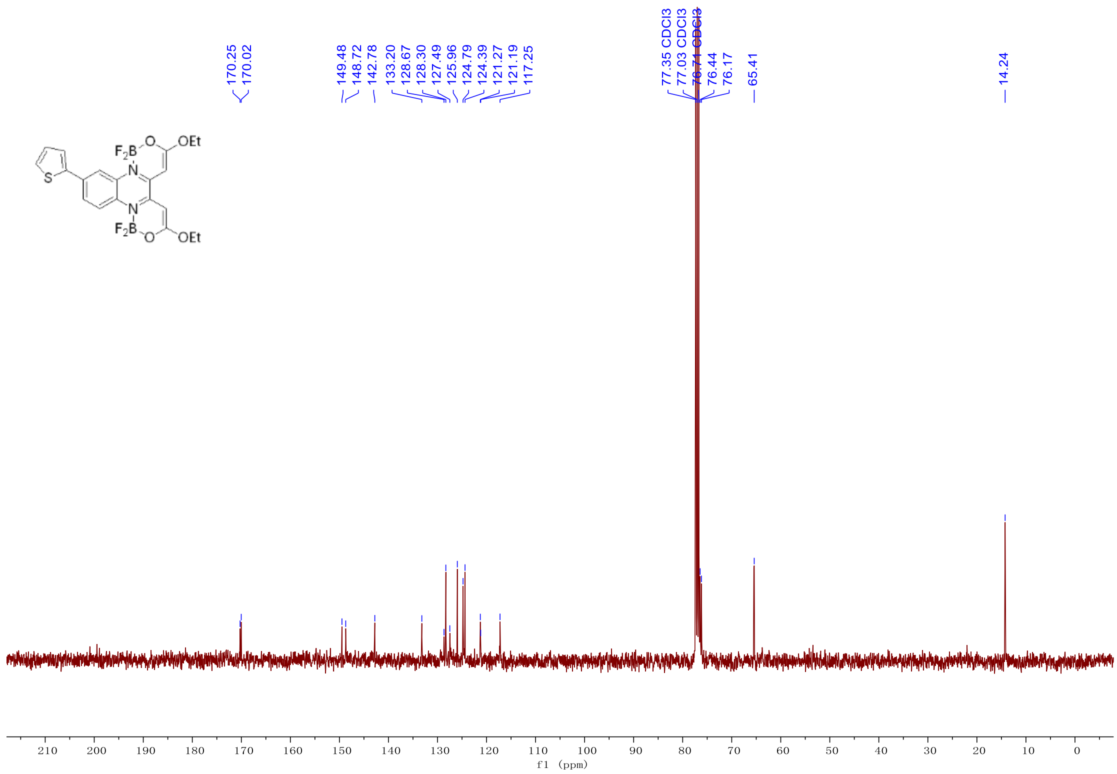
^{11}B NMR of **3i** (128 MHz, $CDCl_3$)



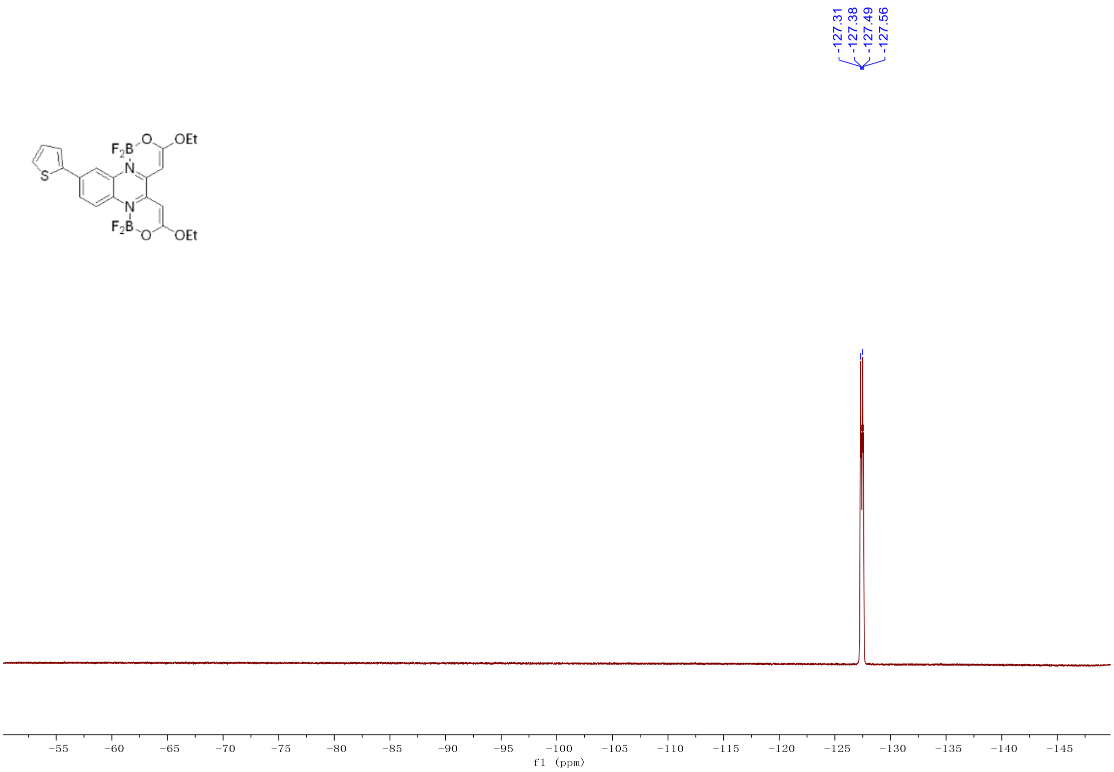
^{1}H NMR of **3j** (400 MHz, $CDCl_3$)



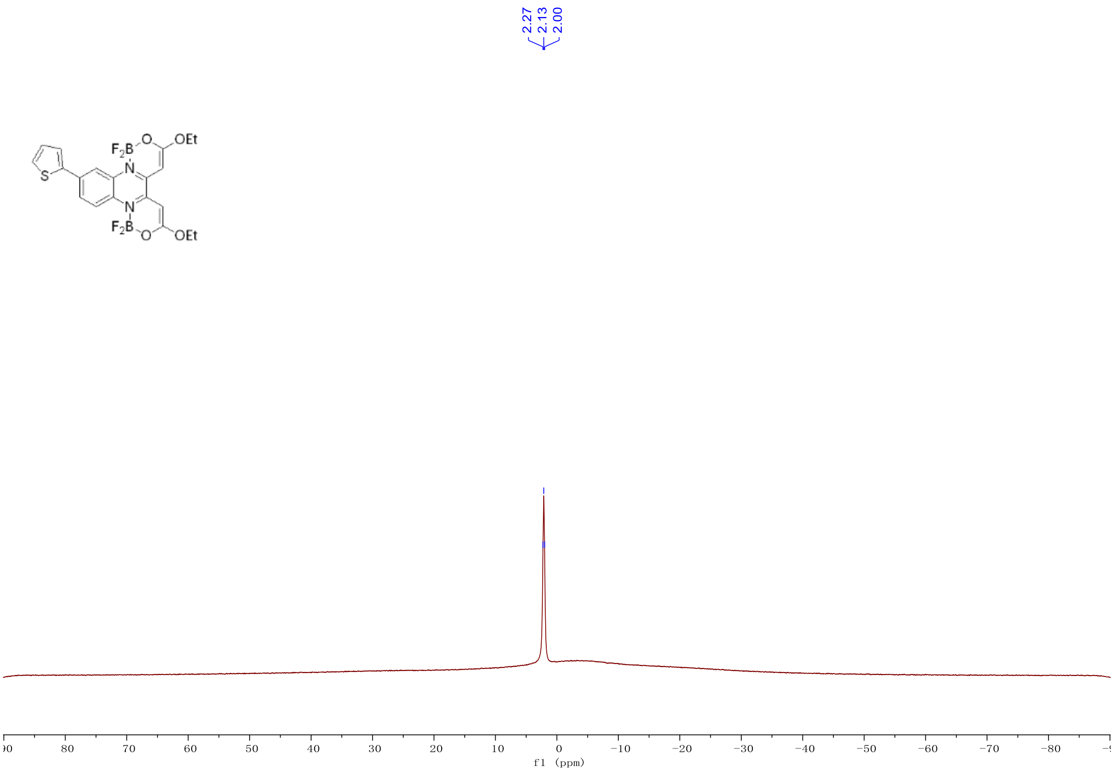
^{13}C NMR of **3j** (101 MHz, $CDCl_3$)



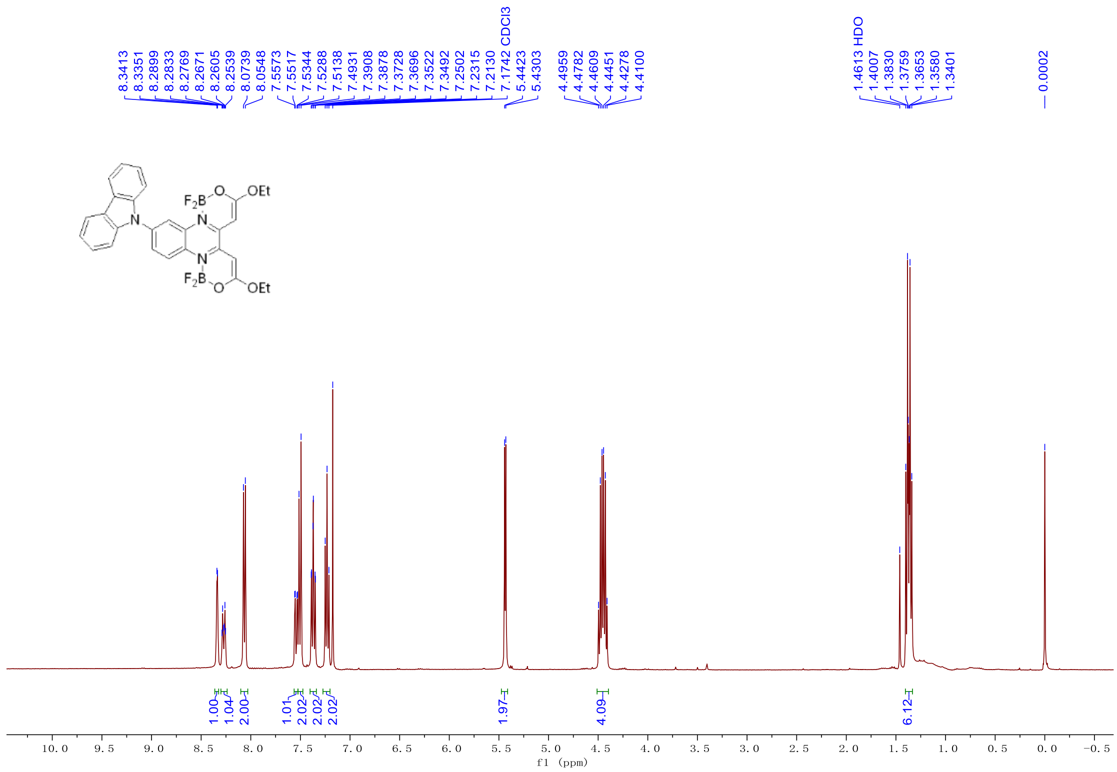
^{19}F NMR of **3j** (376 MHz, $CDCl_3$)



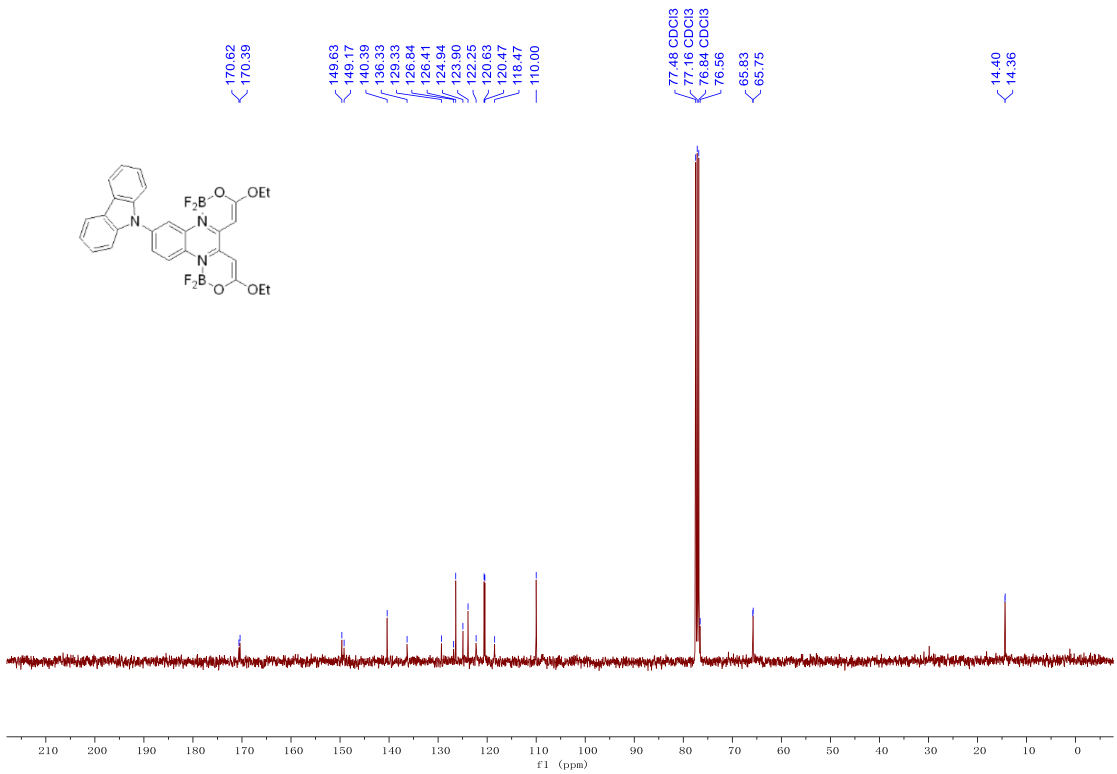
^{11}B NMR of **3j** (128 MHz, $CDCl_3$)



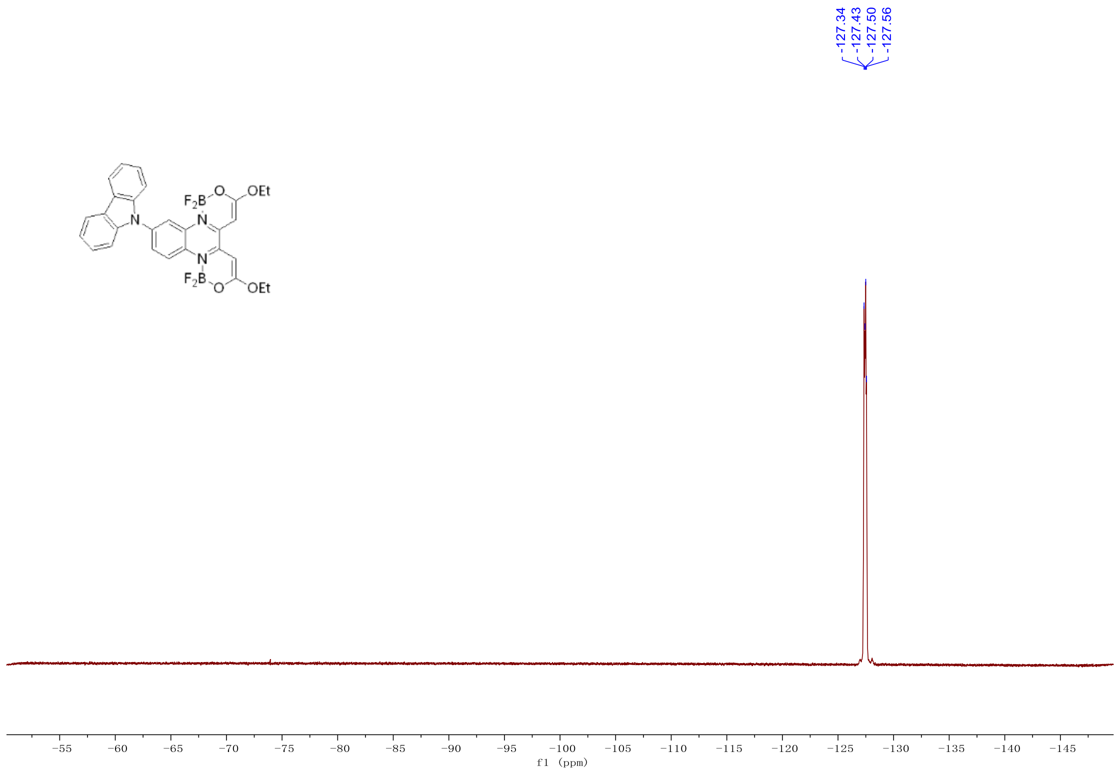
[1]H NMR of **3k** (400 MHz, $CDCl_3$)



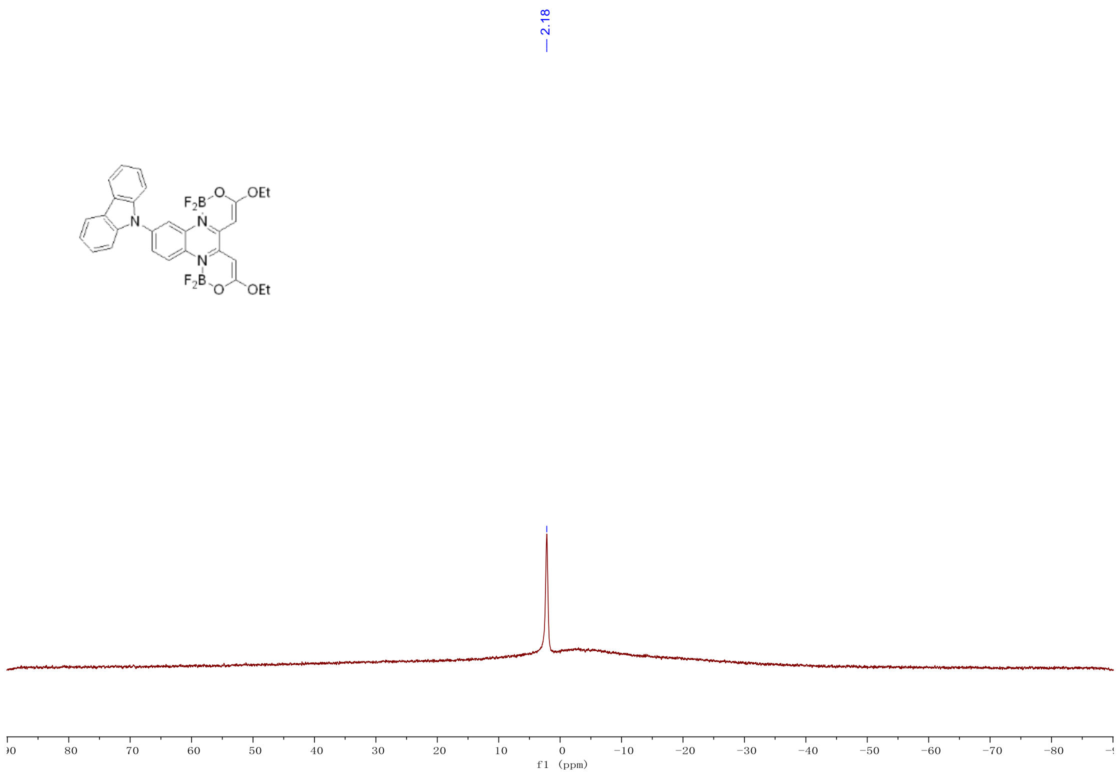
[13]C NMR of **3k** (101 MHz, $CDCl_3$)



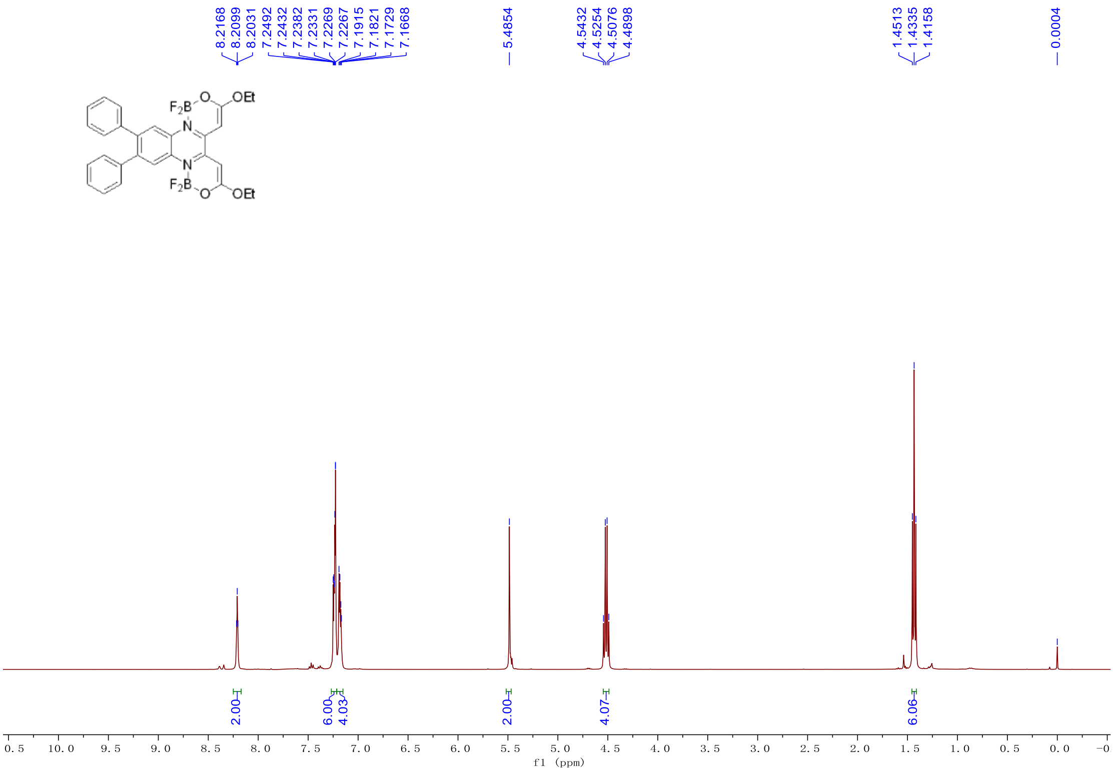
^{19}F NMR of **3k** (376 MHz, $CDCl_3$)



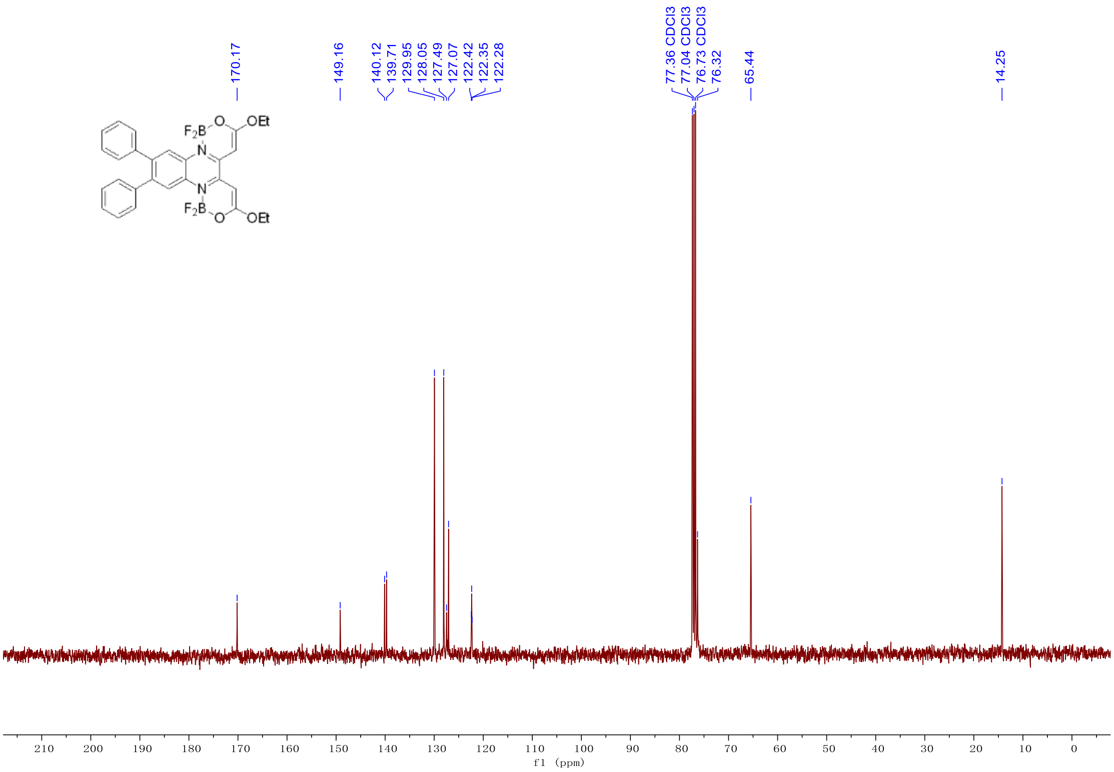
^{11}B NMR of **3k** (128 MHz, $CDCl_3$)



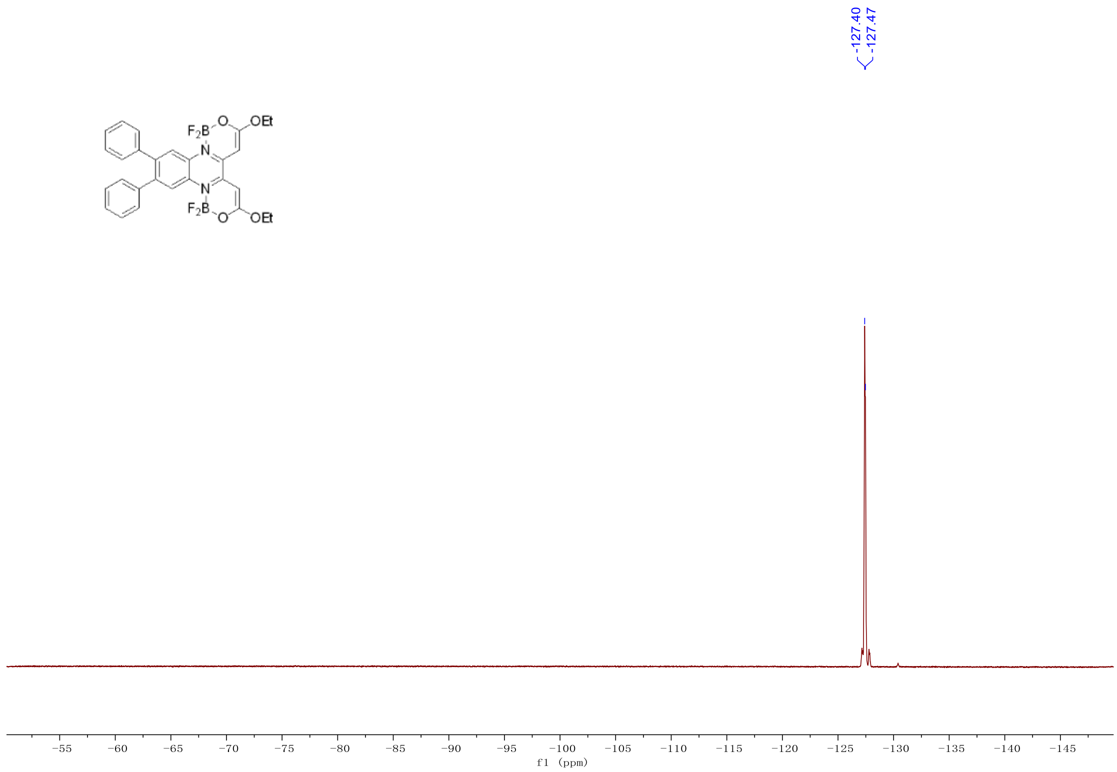
^{1}H NMR of **4a** (400 MHz, $CDCl_3$)



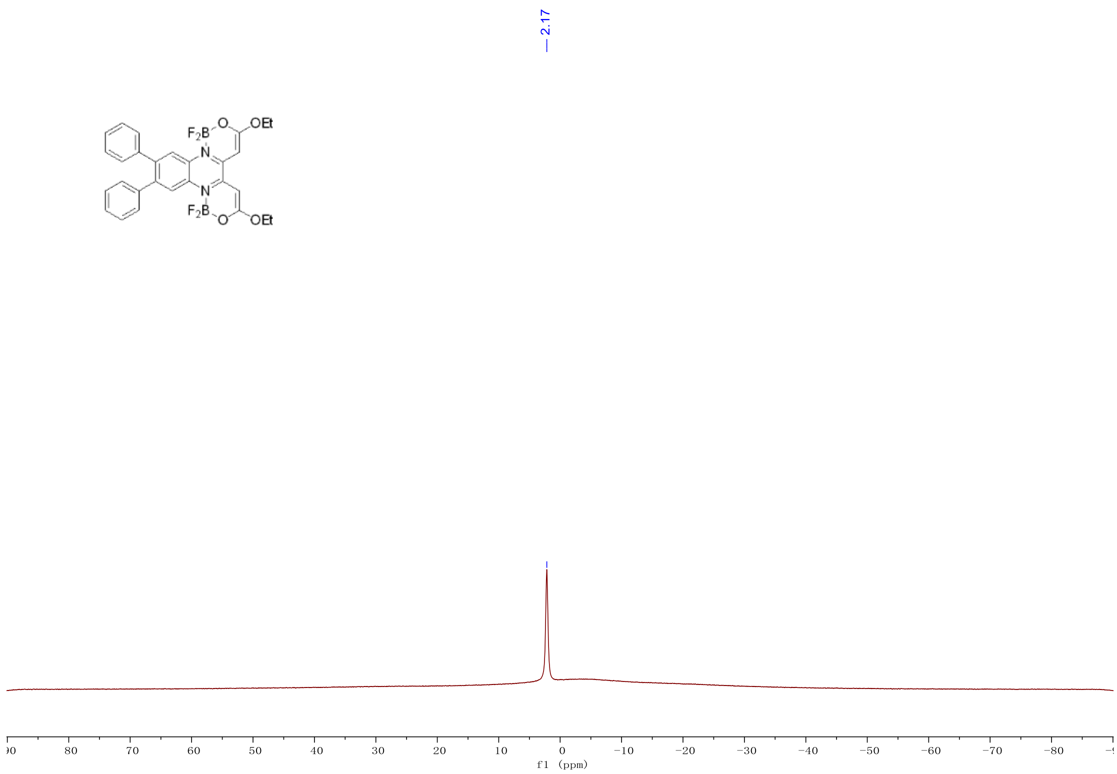
^{13}C NMR of **4a** (101 MHz, $CDCl_3$)



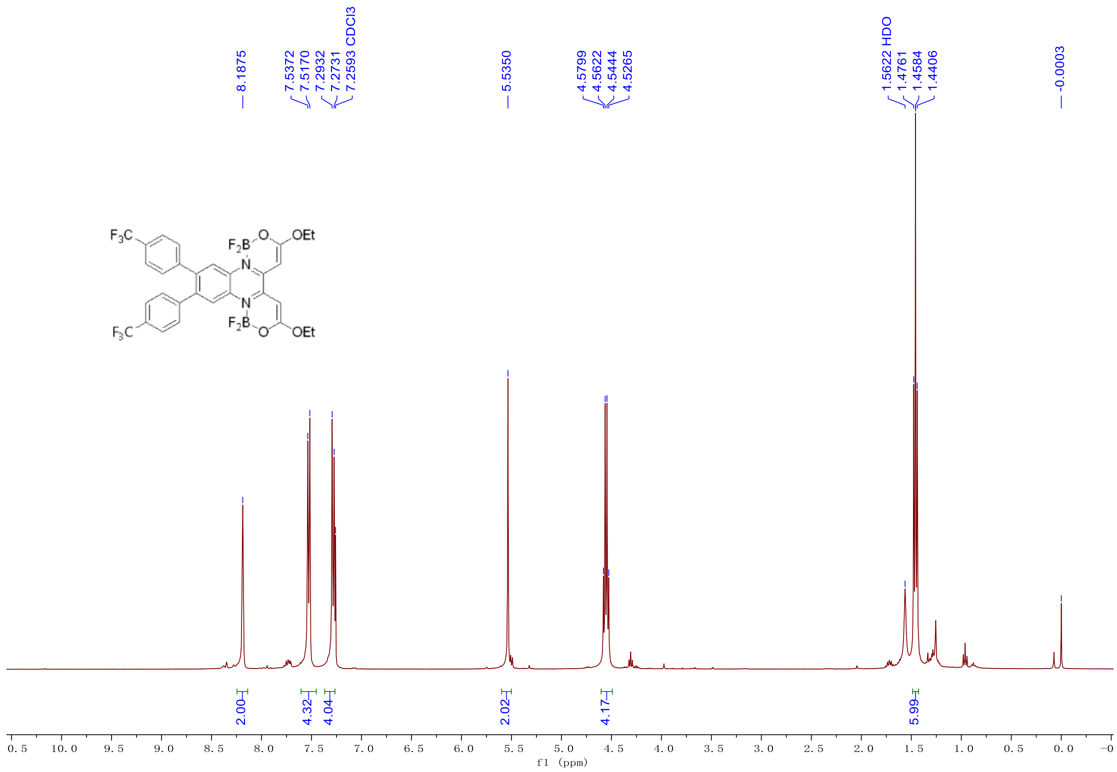
^{19}F NMR of **4a** (376 MHz, $CDCl_3$)



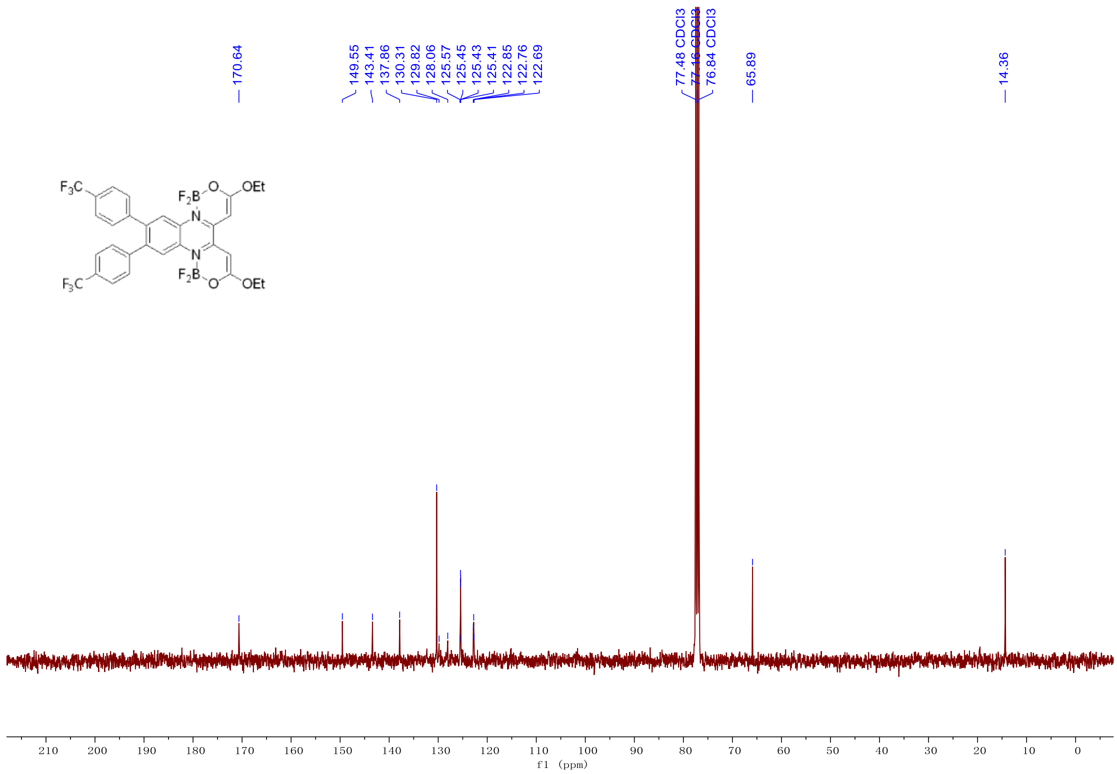
^{11}B NMR of **4a** (128 MHz, $CDCl_3$)



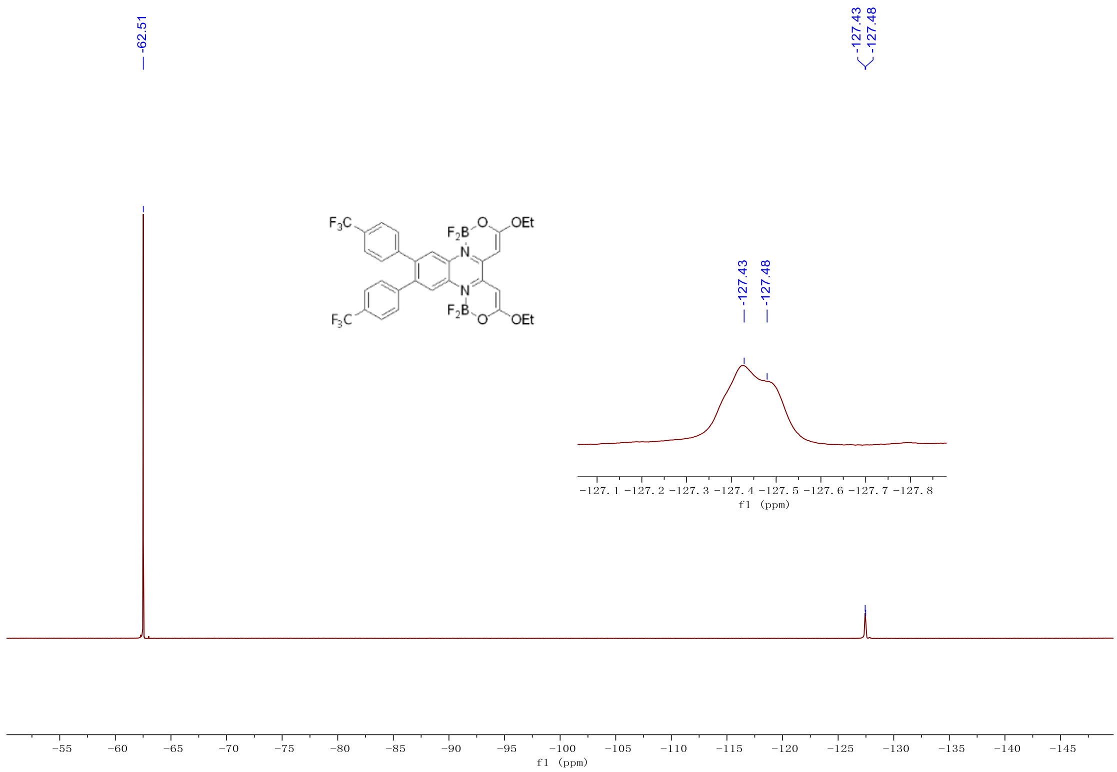
[1]H NMR of **4b** (400 MHz, $CDCl_3$)



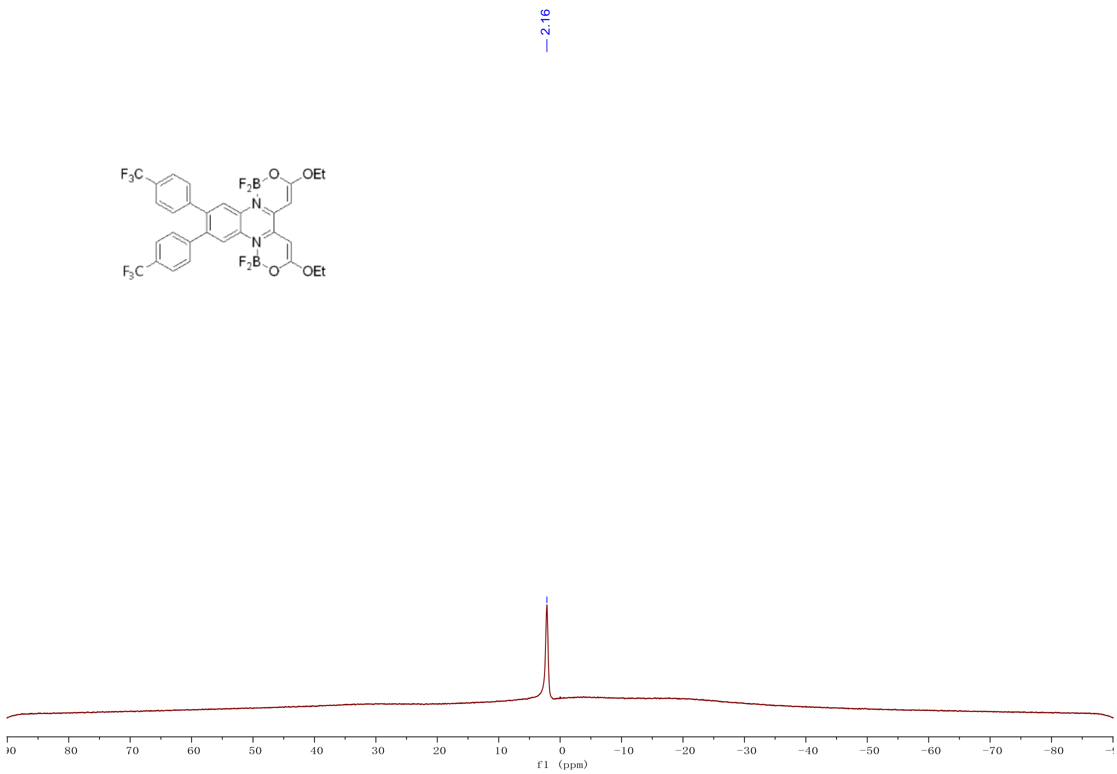
[13]C NMR of **4b** (101 MHz, $CDCl_3$)



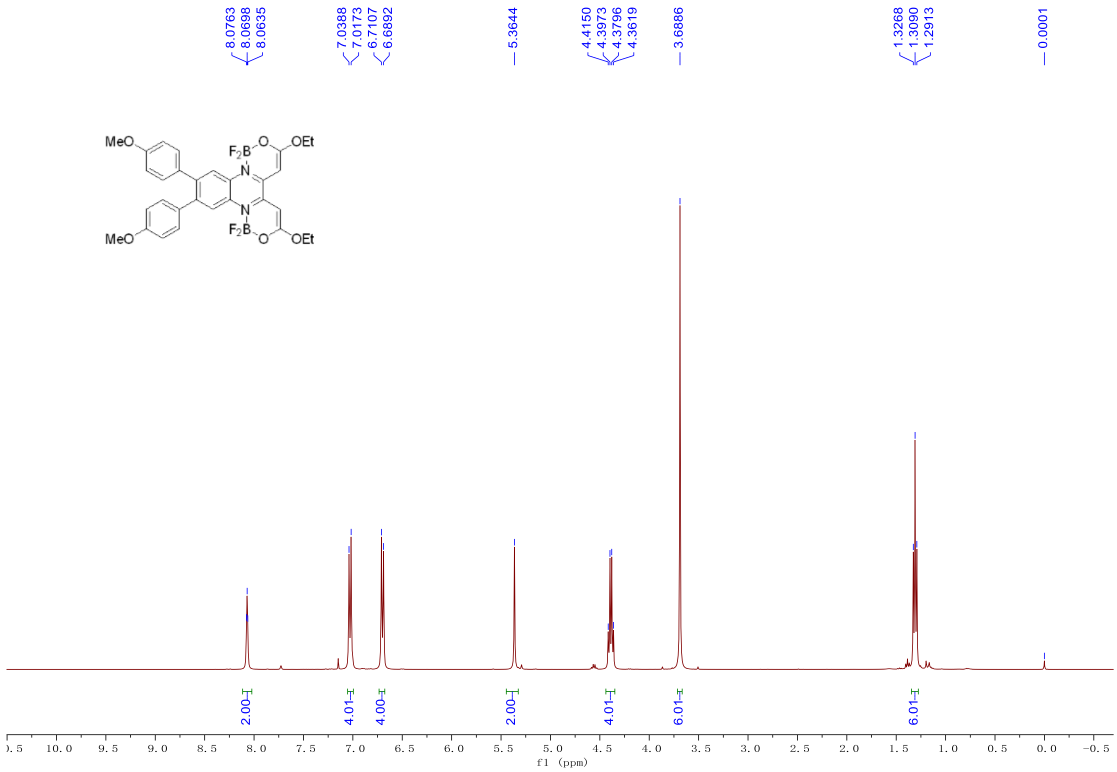
^{19}F NMR of **4b** (376 MHz, $CDCl_3$)



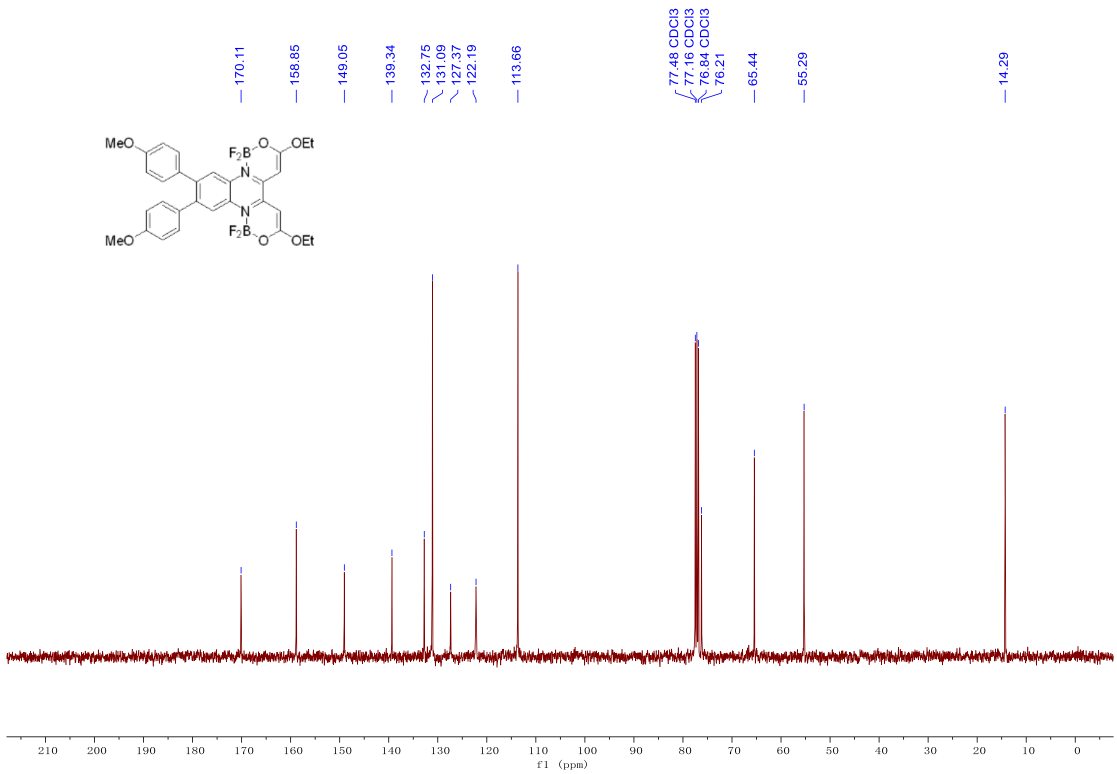
^{11}B NMR of **4b** (128 MHz, $CDCl_3$)



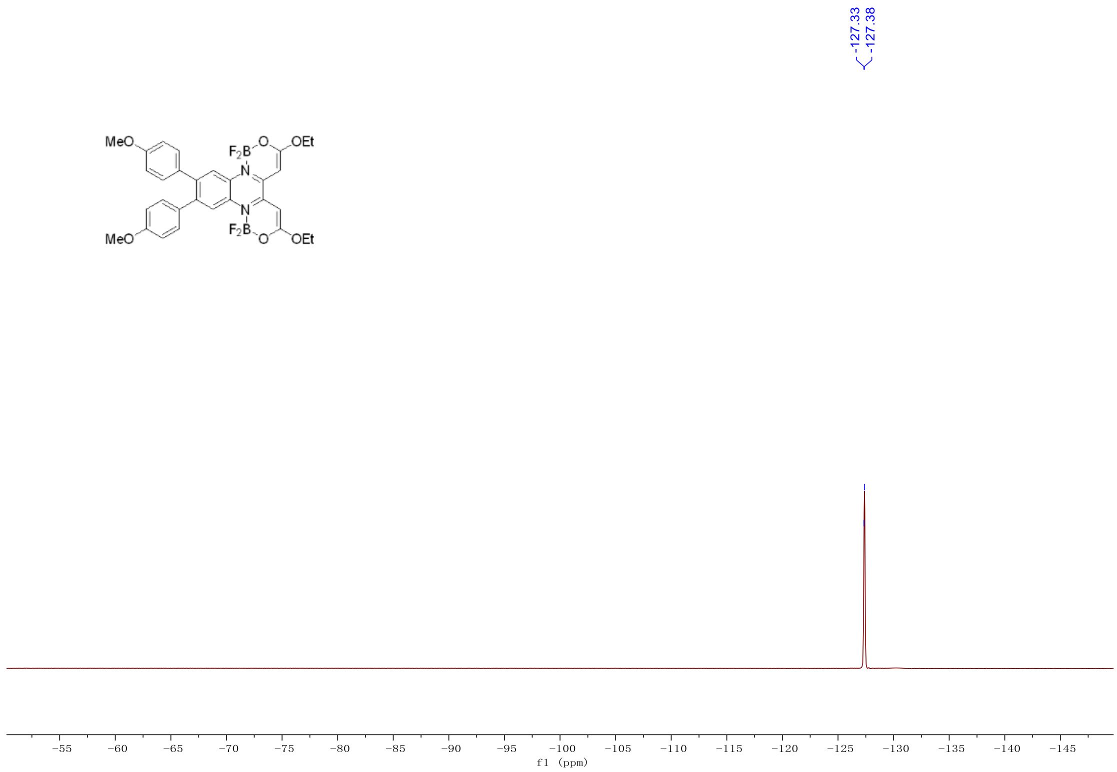
^{1}H NMR of **4c** (400 MHz, $CDCl_3$)



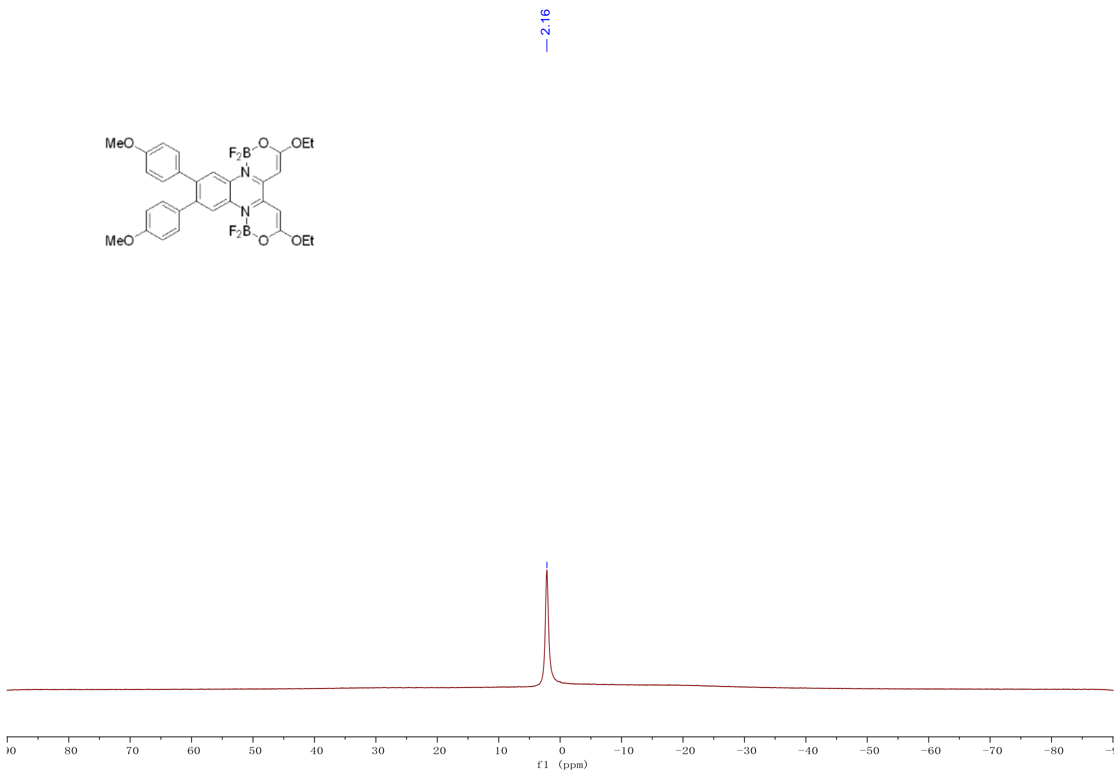
^{13}C NMR of **4c** (101 MHz, $CDCl_3$)



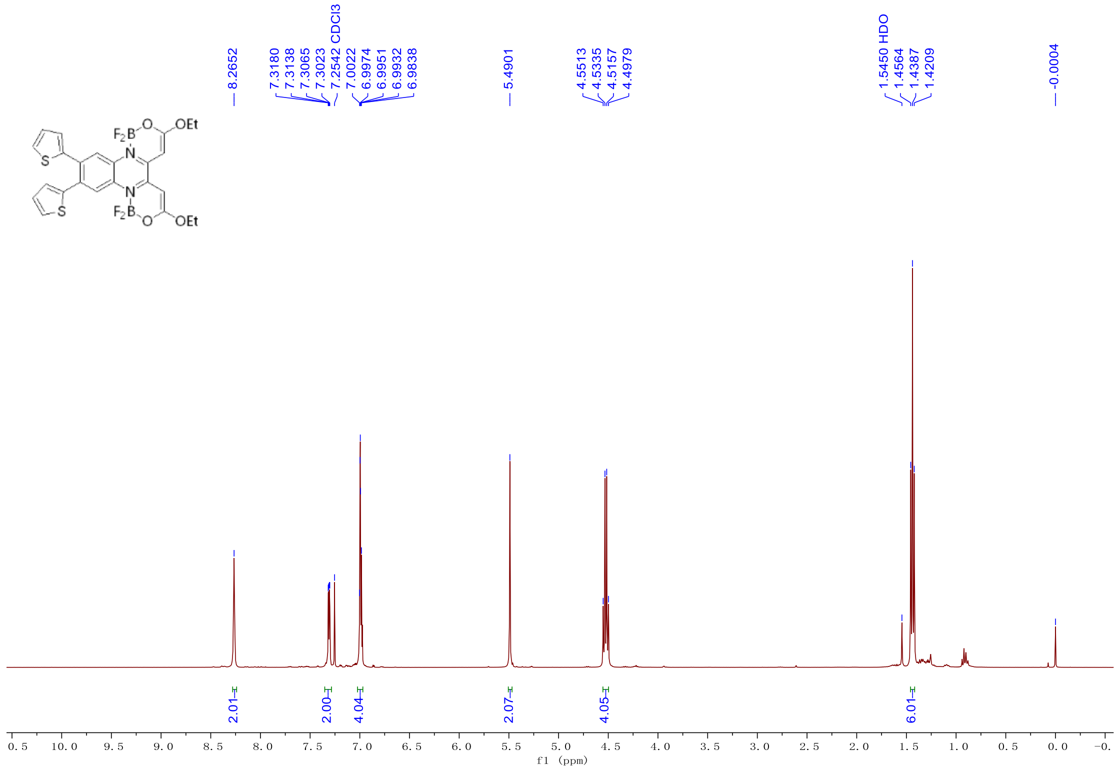
^{19}F NMR of **4c** (376 MHz, $CDCl_3$)



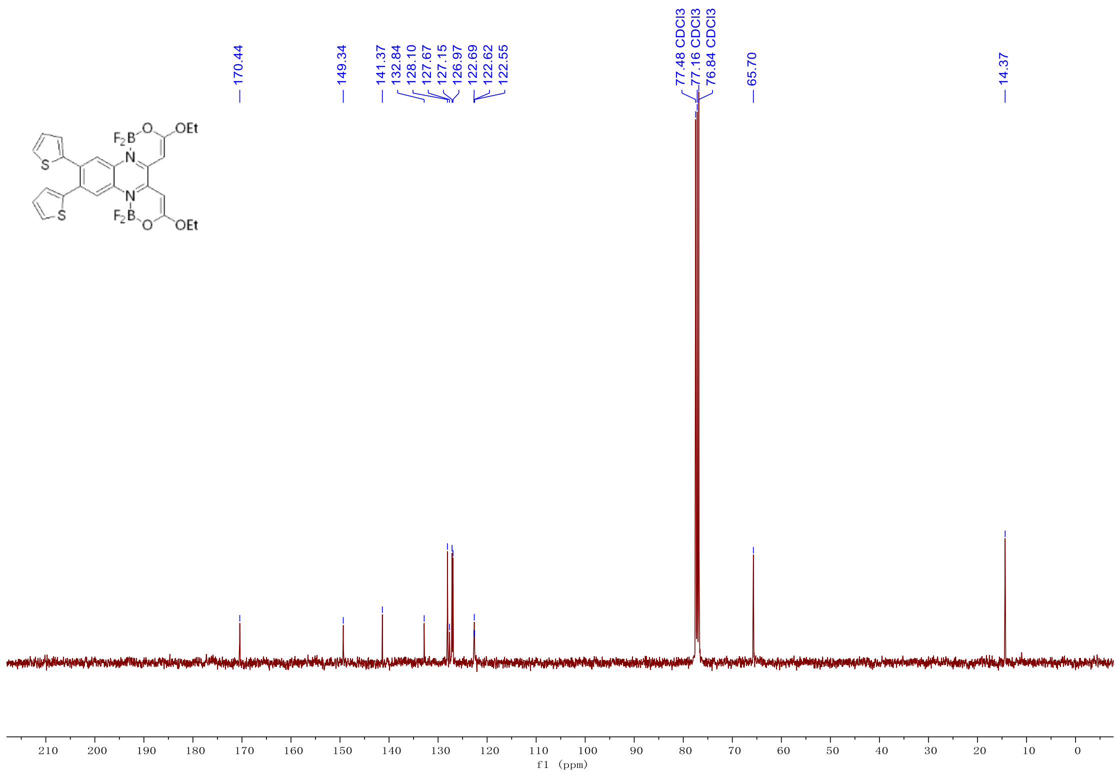
^{11}B NMR of **4c** (128 MHz, $CDCl_3$)



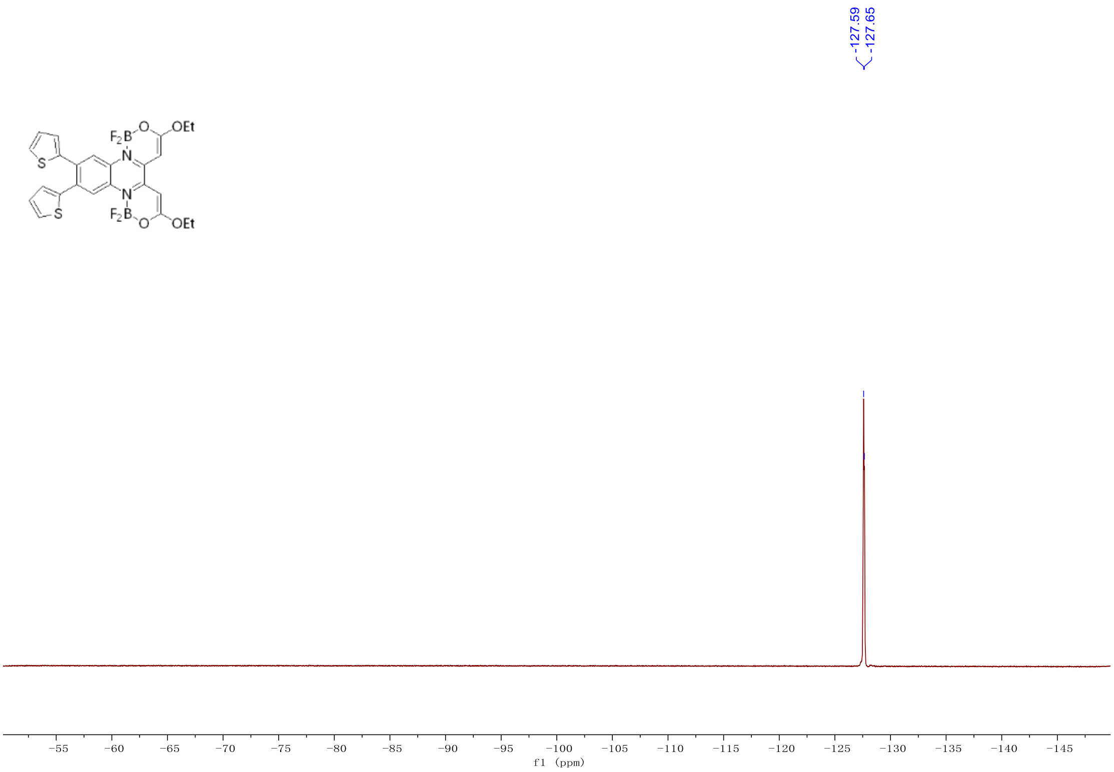
^{1}H NMR of **4d** (400 MHz, $CDCl_3$)



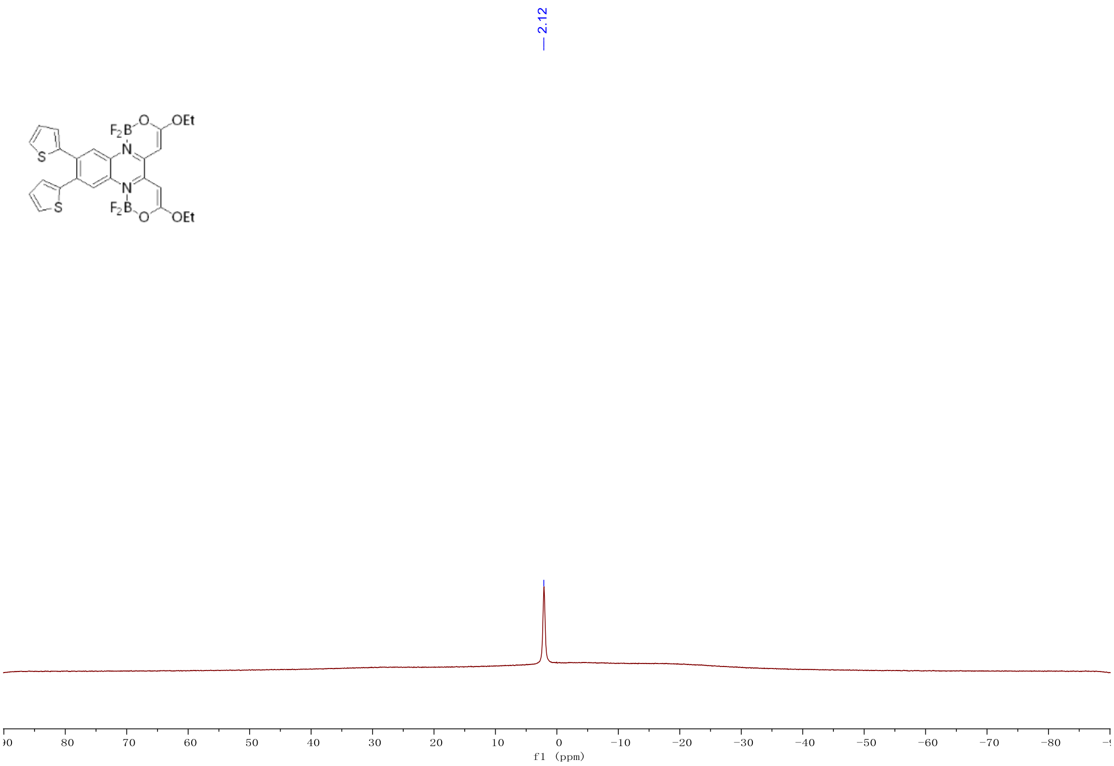
^{13}C NMR of **4d** (101 MHz, $CDCl_3$)



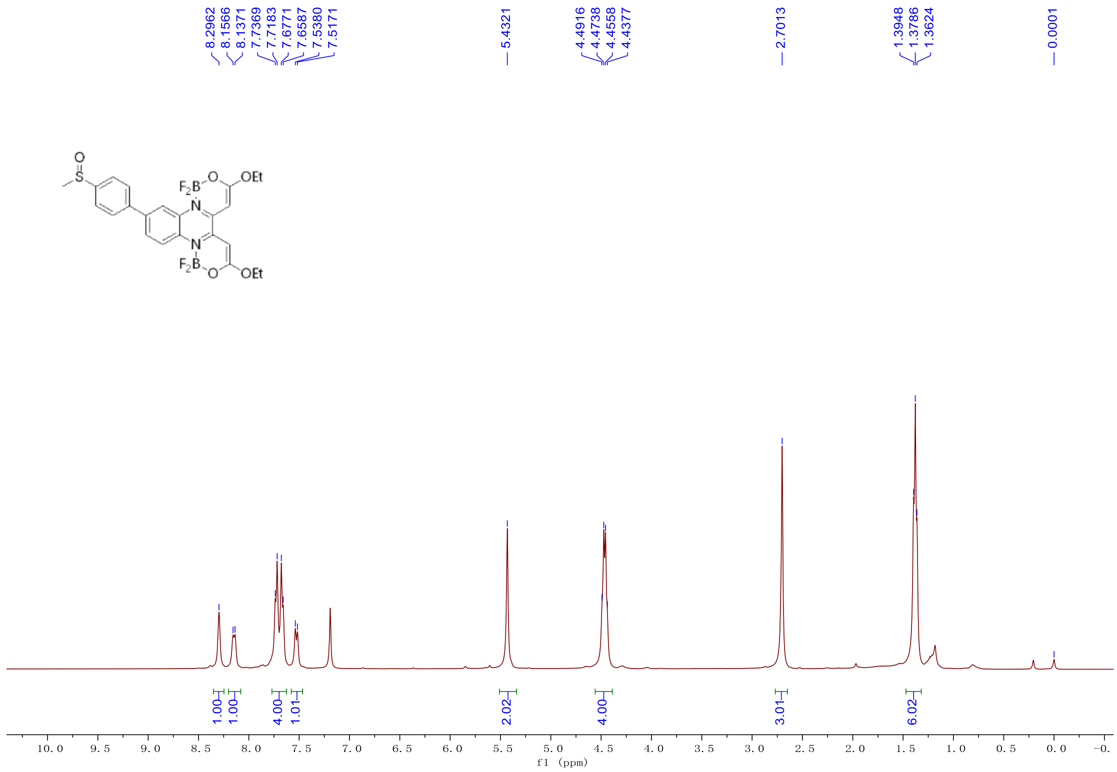
^{19}F NMR of **4d** (376 MHz, $CDCl_3$)



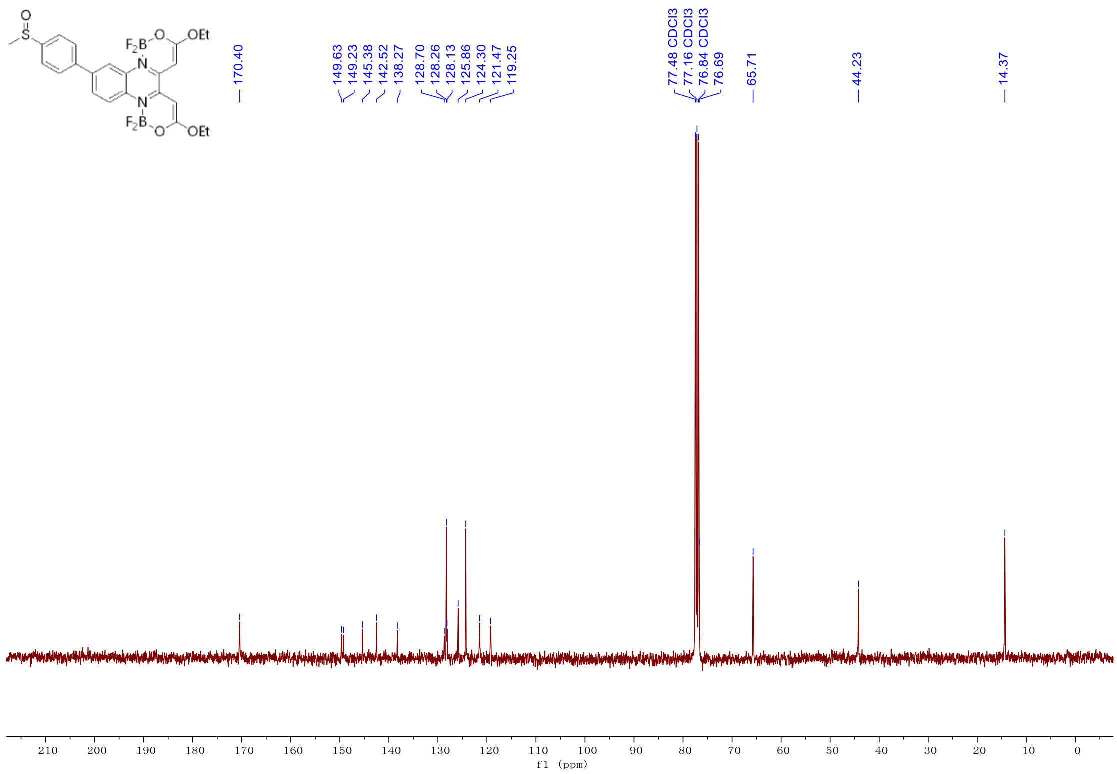
^{11}B NMR of **4d** (128 MHz, $CDCl_3$)



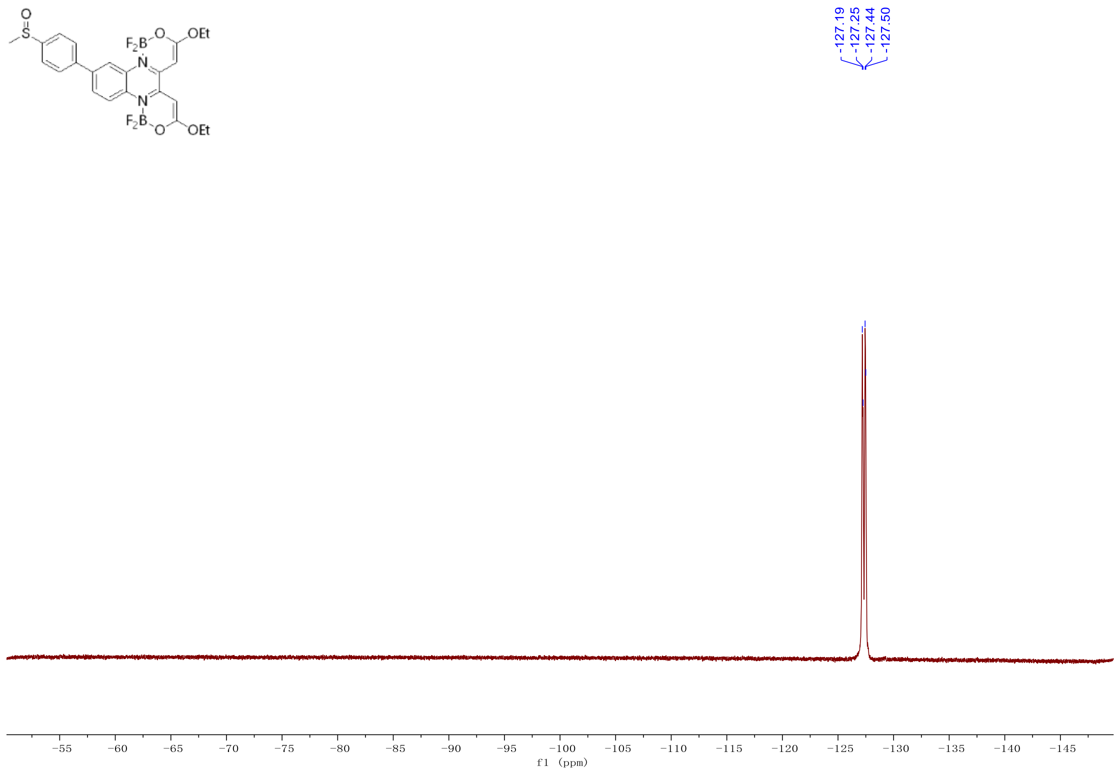
^{1}H NMR of **3e-SO** (400 MHz, $CDCl_3$)



^{13}C NMR of **3e-SO** (101 MHz, $CDCl_3$)



^{19}F NMR of **3e-SO** (376 MHz, $CDCl_3$)



^{11}B NMR of **3e-SO** (128 MHz, $CDCl_3$)