Supporting Information

Room temperature nickel-catalyzed borylation/cyclization synthesis of benzoxaboroles and benzodiazaborines

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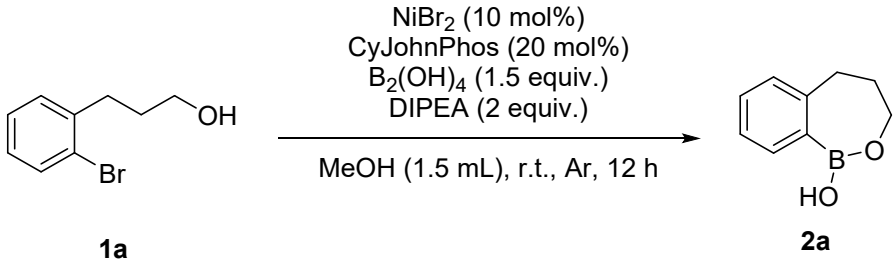
1. General Information

Chemicals were purchased from Shanghai Haohong Scientific Co., Ltd and used without further purification unless otherwise mentioned. All commercially available reagents and solvents were used without further purification unless otherwise stated. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 Ultra Shield spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F, and 128 MHz for ^{11}B) in DMSO-d_6 and Chloroform-*d*. Data are reported as follows: chemical shifts (δ) reported in parts per million (ppm), multiplicity, coupling constants (*J*) reported in Hertz (Hz), and integration. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized under ultraviolet light. Liquid chromatography was performed on Agilent 2060. High-resolution mass spectra (HR-MS) were recorded under electron impact (EI-TOF) (70 eV) condition using a Micro Mass GCT CA 055 instrument.

2. Experimental Procedures

2.1 Representative Procedures for Substrates 2a-2g

4,5-dihydrobenzo[*c*][1,2]oxaborepin-1(3*H*)-ol (2a)[1]

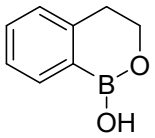


1a **2a**

3-(2-Bromo-phenyl)-propan-1-ol (**1a**, 0.5 mmol, 107.5 mg), $NiBr_2$ (0.05 mmol, 10.9 mg), CyJohnPhos (0.1 mmol, 35.0 mg), $B_2(OH)_4$ (0.75 mmol, 67.2 mg) and DIPEA (1 mmol, 129.2 mg) were added in a reaction tube with MeOH (1.5 mL), and the mixture was stirred at room temperature for 12 h under argon atmosphere. The reaction was extracted with saturated NaCl (aq) and ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Petroleum ether/ ethyl acetate (9:1) to afford 4,5-dihydrobenzo[*c*][1,2]oxaborepin-1(3*H*)-ol **2a** as a colorless oil (70.5 mg; 87% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (s, 1H), 7.52 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.32 (td, *J* = 7.4, 1.5 Hz, 1H), 7.22 – 7.15 (m, 2H), 3.74 (t, *J* = 6.0 Hz, 2H), 2.77 (t, *J* = 6.9 Hz, 2H), 1.93 (p, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.69, 133.91, 130.53, 128.41, 125.82, 62.77, 32.06, 30.20. ^{11}B NMR (128 MHz, DMSO-d_6) δ 30.37. HRMS (EI$^+$) calcd for $C_9H_{11}BO_2$ (M^+) 162.0847; found, 162.0855.

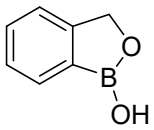
Analytical Data for Other Substrates:

3,4-dihydro-1*H*-benzo[*c*][1,2]oxaborinin-1-ol (2b)[1]



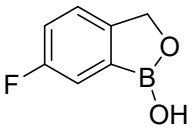
Petroleum ether/ acetone (3:1). White solid (62.1 mg; 84% yield). M.p.: 60.9-62.3°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.43 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.18 (m, 2H), 4.07 (t, *J* = 5.9 Hz, 2H), 2.86 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.28, 133.33, 131.39, 127.21, 126.34, 63.64, 32.43. HRMS (EI$^+$) calcd for $C_8H_9BO_2$ (M^+) 148.0690; found, 148.0698.

benzo[*c*][1,2]oxaborol-1(3*H*)-ol (2c)[1]



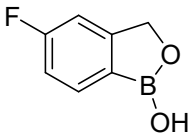
Petroleum ether/ ethyl acetate (9:1). White solid (51.6 mg; 77% yield). M.p.: 99.4-100.7°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 4.99 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.35, 130.97, 130.95, 127.27, 121.80, 70.41. HRMS (EI$^+$) calcd for $C_7H_7BO_2$ (M^+) 134.0534; found, 134.0538.

6-fluorobenzo[*c*][1,2]oxaborol-1(3*H*)-ol (2d)[2]



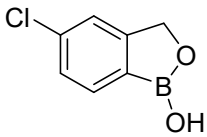
Petroleum ether/ ethyl acetate (9:1). White solid (54.7 mg; 72% yield). M.p.: 122.0-123.2°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 7.48-7.42 (m, 2H), 7.34-7.28 (m, 1H), 4.97 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.18 (d, J = 242.1 Hz), 150.03 (d, J = 1.3 Hz), 123.91 (d, J = 8.1 Hz), 118.51 (d, J = 23.4 Hz), 116.41 (d, J = 20.2 Hz), 70.16. ^{19}F NMR (376 MHz, DMSO-d_6) δ -110.35 (td, J = 9.6, 5.6 Hz). HRMS (EI$^+$) calcd for $C_7H_6FBO_2$ (M^+) 152.0439; found, 152.0444.

5-fluorobenzo[*c*][1,2]oxaborol-1(3*H*)-ol (2e)[2]



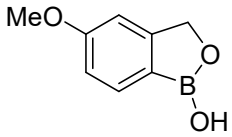
Petroleum ether/ ethyl acetate (9:1). White solid (53.2 mg; 70% yield). M.p.: 129.4-130.6°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 1H), 7.77 (dd, J = 8.1, 5.8 Hz, 1H), 7.26 (dd, J = 9.5, 2.2 Hz, 1H), 7.18 (ddd, J = 10.2, 8.0, 2.3 Hz, 1H), 4.98 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.73 (d, J = 247.3 Hz), 157.28 (d, J = 8.9 Hz), 133.15 (d, J = 9.4 Hz), 115.00 (d, J = 22.0 Hz), 108.98 (d, J = 22.2 Hz), 70.05 (d, J = 2.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -116.74 (td, J = 8.8, 4.4 Hz). HRMS (EI$^+$) calcd for $C_7H_6FBO_2$ (M^+) 152.0439; found, 152.0446.

5-chlorobenzo[*c*][1,2]oxaborol-1(3*H*)-ol (2f)[2]



Petroleum ether/ ethyl acetate (9:1). White solid (53.0 mg; 63% yield). M.p.: 144.6-145.9°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 1.8 Hz, 1H), 7.39 (dd, J = 7.8, 1.8 Hz, 1H), 4.98 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.60, 136.17, 132.75, 127.59, 122.15, 70.02. HRMS (EI$^+$) calcd for $C_7H_6B^{35}ClO_2$ (M^+) 168.0144; found, 168.0151; $C_7H_6B^{37}ClO_2$ (M^+) 170.0114; found, 170.0123.

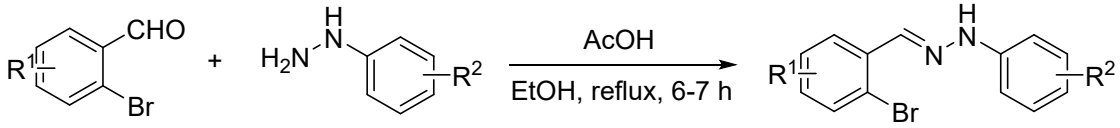
5-methoxybenzo[*c*][1,2]oxaborol-1(3*H*)-ol (2g)[2]



Petroleum ether/ ethyl acetate (9:1). White solid (71.3 mg; 87% yield). M.p.: 114.3-115.5°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 2.0 Hz, 1H), 6.91 (dd, J = 8.1, 2.2 Hz, 1H), 4.93 (s, 2H),

3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.25, 156.91, 132.19, 114.80, 106.25, 70.18, 55.63. HRMS (EI$^+$) calcd for $C_8H_9BO_3$ (M^+) 164.0639; found, 164.0647.

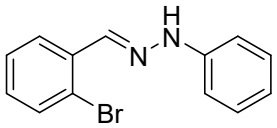
2.2 Synthesis of the Starting Material Hydrazones 3



3

Substrate obtained according to literature method[3]: In a solution of 2-bromobenzaldehyde or several substituted-2-bromobenzaldehyde derivatives (1.0 mmol), aryl-hydrazine (1.0 mmol) and a trace of acetic acid were refluxed in ethanol (8-10 mL) for approximately 6-7 h at 80 °C in an oil bath. The solvent was evaporated under vacuum. Then, the residue was chromatographed on silica gel to afford hydrazones **3**. As a representative example, compound **3a** was synthesized as described above while its substituted analogues were obtained following the same general methodology.

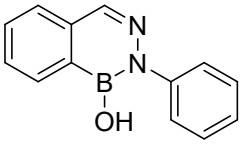
3a:



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.01 (s, 1H), 7.51 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.15 – 7.06 (m, 3H), 6.95 – 6.85 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.35, 135.87, 134.19, 133.02, 129.50, 129.43, 127.57, 127.04, 122.73, 120.54, 112.93. MS (GC-MS): m/z 274.0, 276.0 (M^+).

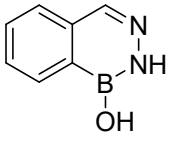
2.3 Representative Procedures for Substrates 4a-4r

2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4a)[4]



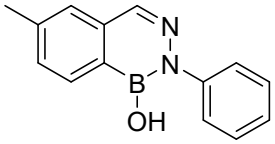
3-(2-Bromo-phenyl)-propan-1-ol (**3a**, 0.5 mmol, 137.6 mg), $NiBr_2$ (0.05 mmol, 10.9 mg), CyJohnPhos (0.1 mmol, 35.0 mg), $B_2(OH)_4$ (0.75 mmol, 67.2 mg) and DIPEA (1 mmol, 129.2 mg) were added in a reaction tube with MeOH (1.5 mL), and the mixture was stirred at room temperature for 24 h under argon atmosphere. The reaction was extracted with saturated NaCl (aq) and ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Petroleum ether/ ethyl acetate (3:1) to afford 2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol **4a** as a pale yellow solid (83.3 mg; 75% yield). M.p.: 133.8-135.3°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (s, 1H), 8.39 (d, *J* = 7.6 Hz, 1H), 8.19 (s, 1H), 7.82 – 7.74 (m, 2H), 7.65 (td, *J* = 7.3, 1.4 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.44 – 7.38 (m, 2H), 7.24 – 7.19 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.83, 139.66, 135.50, 132.17, 131.97, 129.52, 128.66, 127.49, 125.38, 125.08. ^{11}B NMR (128 MHz, DMSO-d_6) δ 27.55. HRMS (EI$^+$) calcd for $C_{13}H_{11}BN_2O$ (M^+) 222.0959; found, 222.0966.

benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4b)[5]



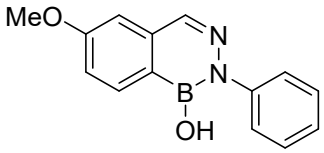
Petroleum ether/ ethyl acetate (3:1). Yellow solid (62.8 mg; 86% yield). M.p.: 235.0-236.5°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.19 (d, J = 7.9 Hz, 1H), 8.17 (s, 1H), 7.99 (s, 1H), 7.73 – 7.68 (m, 2H), 7.58 (ddd, J = 8.1, 5.7, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.03, 136.26, 131.40, 131.39, 128.75, 127.16. HRMS (EI$^+$) calcd for $C_7H_7BN_2O$ (M^+) 146.0646; found, 146.0654.

6-methyl-2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4c)



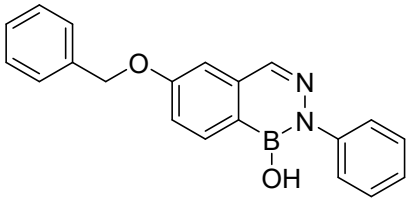
Petroleum ether/ ethyl acetate (5:1). Yellow solid (83.8 mg; 71% yield). M.p.: 137.1-138.2°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 1H), 8.29 (d, J = 7.7 Hz, 1H), 8.13 (s, 1H), 7.61 (s, 1H), 7.59 – 7.55 (m, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.24 – 7.19 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.86, 141.73, 139.60, 135.78, 132.24, 130.84, 128.62, 127.27, 125.25, 124.97, 21.86. HRMS (EI$^+$) calcd for $C_{14}H_{13}BN_2O$ (M^+) 236.1115; found, 236.1124.

6-methoxy-2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4d)[6]



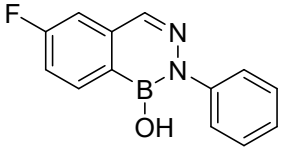
Petroleum ether/ ethyl acetate (5:1). Yellow solid (93.3 mg; 74% yield). M.p.: 137.6-139.0°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.16 (s, 1H), 7.62 – 7.59 (m, 2H), 7.41 (t, J = 7.9 Hz, 2H), 7.33 (d, J = 2.4 Hz, 1H), 7.27 (dd, J = 8.4, 2.4 Hz, 1H), 7.22 (dt, J = 14.7, 1.2 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.22, 146.89, 139.43, 137.59, 134.07, 128.60, 125.19, 124.93, 118.37, 109.32, 55.76. ^{11}B NMR (128 MHz, DMSO-d_6) δ 27.59. HRMS (EI$^+$) calcd for $C_{14}H_{13}BN_2O2$ (M^+) 252.1065; found, 252.1073.

6-(benzyloxy)-2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4e)



Petroleum ether/ ethyl acetate (5:1). Pale yellow solid (111.6 mg; 68% yield). M.p.: 170.7-171.3°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.13 (s, 1H), 7.59 – 7.55 (m, 2H), 7.53 – 7.49 (m, 2H), 7.45 – 7.41 (m, 3H), 7.41 – 7.35 (m, 3H), 7.33 (dd, J = 8.5, 2.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 5.25 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.30, 146.84, 139.37, 137.53, 137.16, 134.15, 129.01, 128.62, 128.52, 128.42, 125.23, 124.92, 118.85, 110.48, 69.85. HRMS (EI$^+$) calcd for $C_{20}H_{17}BN_2O_2$ (M^+) 328.1378; found, 328.1380.

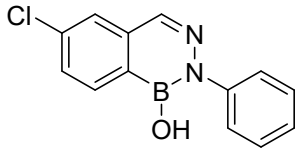
6-fluoro-2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4f)



Petroleum ether/ ethyl acetate (5:1). Brown solid (99.6 mg; 83% yield). M.p.: 206.6-208.1°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 8.53 – 8.42 (m, 1H), 8.20 (s, 1H), 7.66 (dd, J = 9.8, 2.2 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.44 – 7.39 (m, 2H), 7.24 (t, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.53 (d, J = 249.5 Hz), 146.59, 138.64 (d, J = 4.0 Hz), 137.73 (d, J = 8.1 Hz), 135.53 (d, J = 9.1 Hz), 128.70, 125.56, 125.11, 117.79 (d, J = 22.2 Hz), 112.57 (d, J = 20.2

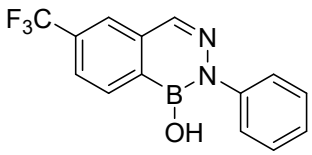
Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -108.01 (td, J = 9.7, 6.2 Hz). HRMS (EI$^+$) calcd for $C_{13}H_{10}BFN_2O$ (M^+) 240.0865; found, 240.0872.

6-chloro-2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4g)



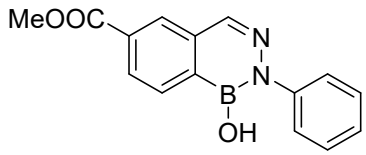
Petroleum ether/ ethyl acetate (5:1). Pale yellow solid (96.2 mg; 75% yield). M.p.: 146.4-147.6°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 8.43 (d, J = 8.2 Hz, 1H), 8.21 (s, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.72 (dd, J = 8.2, 2.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.45 – 7.39 (m, 2H), 7.29 – 7.19 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.55, 138.38, 136.99, 136.82, 134.53, 129.58, 128.69, 126.75, 125.59, 125.09. HRMS (EI$^+$) calcd for $C_{13}H_{10}B^{35}ClN_2O$ (M^+) 256.0569; found, 256.0579; $C_{13}H_{10}B^{37}ClN_2O$ (M^+) 258.0540; found, 258.0549.

2-phenyl-6-(trifluoromethyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4h)



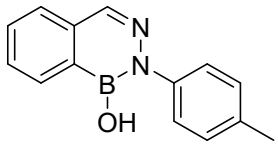
Petroleum ether/ ethyl acetate (5:1). Brown solid (110.2 mg; 76% yield). M.p.: 143.9-145.3°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.37 (s, 1H), 8.28 (s, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.27 – 7.23 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.42, 138.89, 135.44, 133.63, 131.93 (q, J = 32.0 Hz), 128.71, 125.73, 125.12, 124.52 (q, J = 273.9 Hz), 124.48 (q, J = 4.1 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.30. HRMS (EI$^+$) calcd for $C_{14}H_{10}BF_3N_2O$ (M^+) 290.0833; found, 290.0835.

methyl 1-hydroxy-2-phenyl-1,2-dihydrobenzo[*d*][1,2,3]diazaborinine-6-carboxylate (4i)



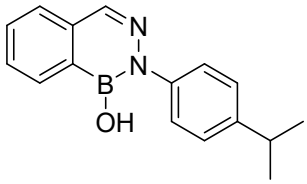
Petroleum ether/ ethyl acetate (5:1). Yellow solid (107.8 mg; 77% yield). M.p.: 138.6-139.9°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 8.43 (d, J = 8.2 Hz, 1H), 8.21 (s, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.72 (dd, J = 8.2, 2.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.45 – 7.39 (m, 2H), 7.29 – 7.19 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.45, 146.56, 139.45, 135.45, 132.92, 132.62, 128.85, 128.72, 128.66, 125.65, 125.12, 52.96. HRMS (EI$^+$) calcd for $C_{15}H_{13}BN_2O_3$ (M^+) 280.1014; found, 280.1022.

2-(*p*-tolyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4k)



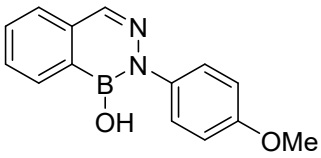
Petroleum ether/ ethyl acetate (10:1). Pale yellow solid (89.7 mg; 76% yield). M.p.: 146.1-147.6°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (s, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.18 (s, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.66 (td, J = 7.2, 1.5 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.38, 139.39, 135.51, 134.36, 132.23, 131.86, 129.40, 129.11, 127.41, 124.93, 21.04. HRMS (EI$^+$) calcd for $C_{14}H_{13}BN_2O$ (M^+) 236.1115; found, 236.1124.

2-(4-isopropylphenyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4l)



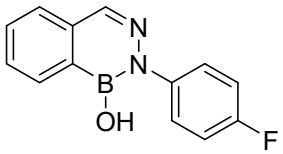
Petroleum ether/ ethyl acetate (10:1). Pale yellow solid (99.1 mg; 75% yield). M.p.: 149.6-151.0°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.40 (d, J = 7.6 Hz, 1H), 8.18 (s, 1H), 7.79 (dd, J = 13.1, 7.5 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.41, 144.63, 139.41, 135.49, 132.11, 131.86, 129.41, 127.42, 126.43, 124.96, 33.48, 24.51. HRMS (EI$^+$) calcd for $C_{16}H_{17}BN_2O$ (M^+) 264.1428; found, 264.1436.

2-(4-methoxyphenyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4m)



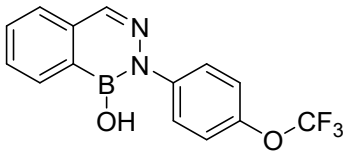
Petroleum ether/ ethyl acetate (3:1). Yellow solid (102.1 mg; 81% yield). M.p.: 150.0-151.5°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 1H), 8.42 (d, J = 7.3 Hz, 1H), 8.17 (s, 1H), 7.83 – 7.74 (m, 2H), 7.66 (td, J = 7.3, 1.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.00 – 6.95 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.11, 139.96, 139.17, 135.51, 132.16, 131.78, 129.34, 127.38, 126.24, 113.82, 55.74. HRMS (EI$^+$) calcd for $C_{14}H_{13}BN_2O_2$ (M^+) 252.1065; found, 252.1072.

2-(4-fluorophenyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4n)



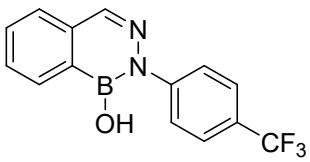
Petroleum ether/ ethyl acetate (4:1). Yellow solid (106.8 mg; 89% yield). M.p.: 212.6-214.0°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 1H), 8.41 (d, J = 7.6 Hz, 1H), 8.20 (s, 1H), 7.85 – 7.75 (m, 2H), 7.68 (td, J = 7.6, 1.4 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.28 – 7.20 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.99 (d, J = 241.4 Hz), 143.15 (d, J = 3.0 Hz), 139.69, 135.48, 132.15, 131.98, 129.57, 127.54, 126.73 (d, J = 8.0 Hz), 115.24 (d, J = 23.2 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.44 (tt, J = 8.7, 4.3 Hz). HRMS (EI$^+$) calcd for $C_{13}H_{10}BFN_2O$ (M^+) 240.0865; found, 240.0873.

2-(4-(trifluoromethoxy)phenyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4o)



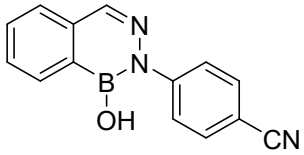
Petroleum ether/ ethyl acetate (4:1). Yellow solid (125.5 mg; 82% yield). M.p.: 136.3-137.5°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 8.42 (d, J = 7.6 Hz, 1H), 8.23 (s, 1H), 7.85 – 7.77 (m, 2H), 7.75 – 7.71 (m, 2H), 7.69 (td, J = 7.3, 1.5 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.92, 145.63 (q, J = 1.3 Hz), 140.16, 135.44, 132.26, 132.14, 129.73, 127.65, 126.30, 121.42, 120.70 (q, J = 257.2 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.88. HRMS (EI$^+$) calcd for $C_{14}H_{10}BF_3N_2O_2$ (M^+) 306.0782; found, 306.0784.

2-(4-(trifluoromethyl)phenyl)benzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol (4p)[7]



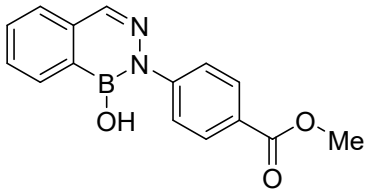
Petroleum ether/ ethyl acetate (4:1). Pale purple solid (134.9 mg; 93% yield). M.p.: 157.5-159.8°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.39 (s, 1H), 8.46 (d, J = 7.1 Hz, 1H), 8.27 (s, 1H), 7.90 (d, J = 8.5 Hz, 2H), 7.86 – 7.76 (m, 4H), 7.70 (td, J = 7.3, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.29, 140.65, 135.33, 132.37, 132.25, 129.85, 127.70, 125.80 (q, J = 3.9 Hz), 125.29 (q, J = 31.6 Hz), 124.97 (q, J = 272.5 Hz), 124.79. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.38. HRMS (EI$^+$) calcd for $C_{14}H_{10}BF_3N_2O$ (M^+) 290.0833; found, 290.0840.

4-(1-hydroxybenzo[*d*][1,2,3]diazaborinin-2(1*H*)-yl)benzonitrile (4q)[7]



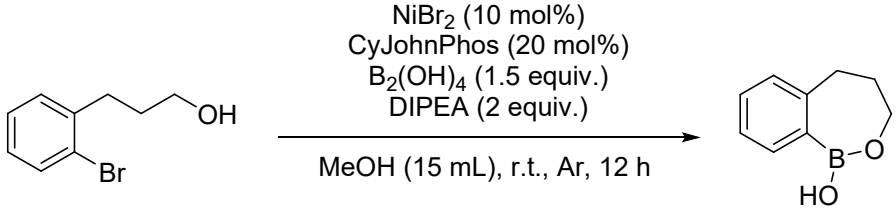
Petroleum ether/ ethyl acetate (3:1). Orange solid (125.5 mg; 91% yield). M.p.: 237.1-238.6°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H), 8.45 (d, J = 7.6 Hz, 1H), 8.29 (s, 1H), 7.93 – 7.84 (m, 5H), 7.81 (td, J = 7.3, 1.3 Hz, 1H), 7.71 (td, J = 7.3, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.92, 141.03, 135.27, 133.00, 132.43, 132.39, 130.00, 127.81, 124.77, 119.63, 107.08. HRMS (EI$^+$) calcd for $C_{14}H_{10}BN_3O$ (M^+) 247.0911; found, 247.0914.

methyl 4-(1-hydroxybenzo[*d*][1,2,3]diazaborinin-2(1*H*)-yl)benzoate (4r)



Petroleum ether/ ethyl acetate (4:1). Yellow solid (131.6 mg; 94% yield). M.p.: 154.5-156.8°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.39 (s, 1H), 8.46 (d, J = 7.1 Hz, 1H), 8.27 (s, 1H), 8.04 – 7.99 (m, 2H), 7.86 – 7.78 (m, 4H), 7.70 (td, J = 7.3, 1.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.74, 151.33, 140.84, 135.53, 132.61, 132.48, 130.15, 127.91, 126.12, 124.43, 52.72. ^{11}B NMR (128 MHz, DMSO-d_6) δ 27.49. HRMS (EI$^+$) calcd for $C_{15}H_{13}BN_2O_3$ (M^+) 280.1014; found, 280.1016.

2.4 Gram-Scale Amplification Experiments

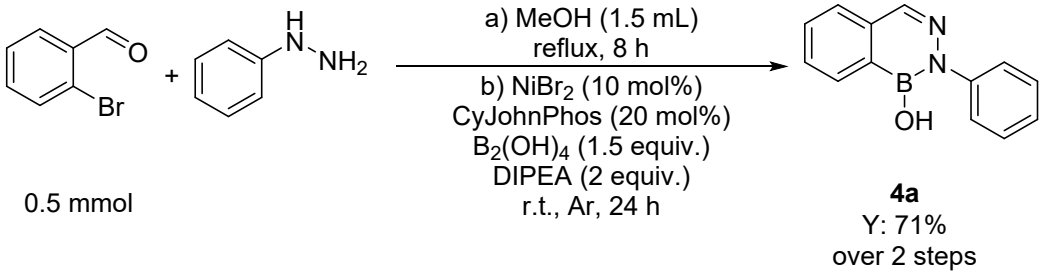


1a
5 mmol
1.075 g

2a
0.729 g
Y: 90%

3-(2-Bromo-phenyl)-propan-1-ol (**1a**, 5 mmol, 1.075 g), $NiBr_2$ (0.5 mmol, 109.3 mg), CyJohnPhos (1 mmol, 350.5 mg), $B_2(OH)_4$ (7.5 mmol, 672.4 mg) and DIPEA (10 mmol, 1292.4 mg) were added in a reaction tube with MeOH (15 mL), and the mixture was stirred at room temperature for 12 h under argon atmosphere. The reaction was extracted with saturated NaCl (aq) and ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Petroleum ether/ ethyl acetate (9:1) to afford 4,5-dihydrobenzo[*c*][1,2]oxaborepin-1(3*H*)-ol **2a** as a colorless oil (729.0 mg; 90% yield).

2.5 One-pot Two-step Procedure



A solution of 2-bromobenzaldehyde (0.5 mmol) and aryl-hydrazine (0.5 mmol) were refluxed in methanol (1.5 mL) for 8 h. Then $NiBr_2$ (0.05 mmol, 10.9 mg), CyJohnPhos (0.1 mmol, 35.0 mg), $B_2(OH)_4$ (0.75 mmol, 67.2 mg) and DIPEA (1 mmol, 129.2 mg) were added in the reaction tube, and the mixture was stirred at room temperature for 24 h under argon atmosphere. The reaction was extracted with saturated NaCl (aq) and ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Petroleum ether/ ethyl acetate (3:1) to afford 2-phenylbenzo[*d*][1,2,3]diazaborinin-1(2*H*)-ol **4a** as a pale yellow solid (78.8 mg; 71% yield).

3. References

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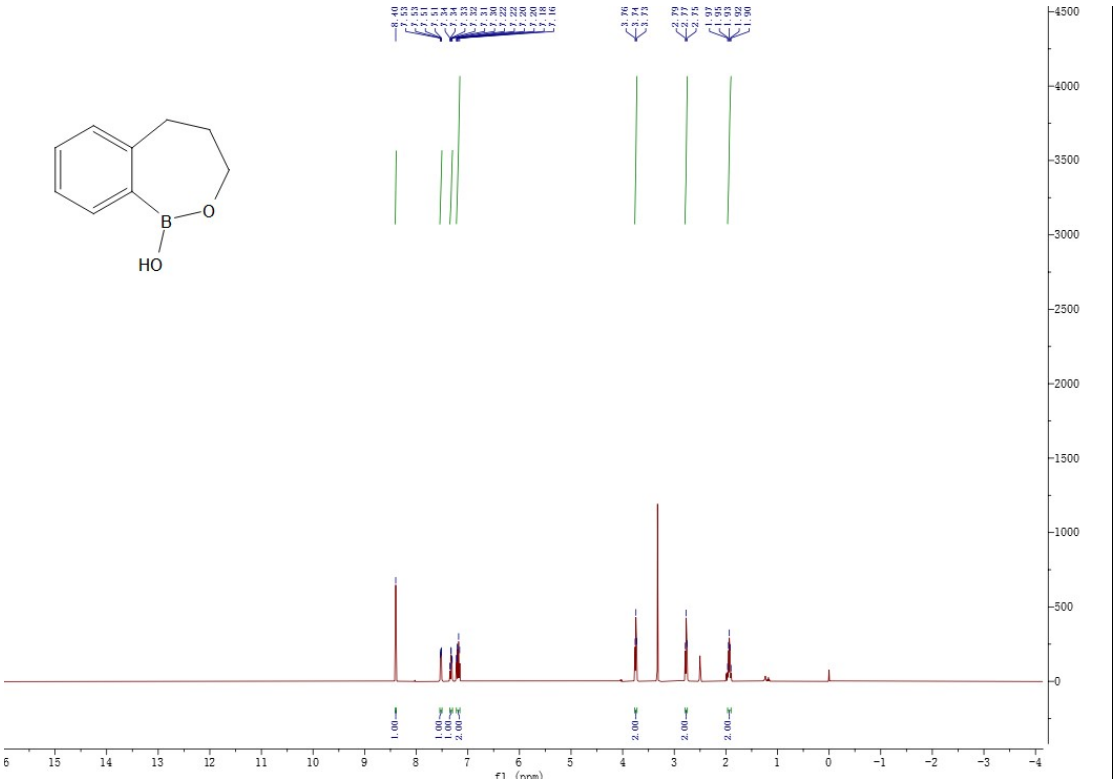
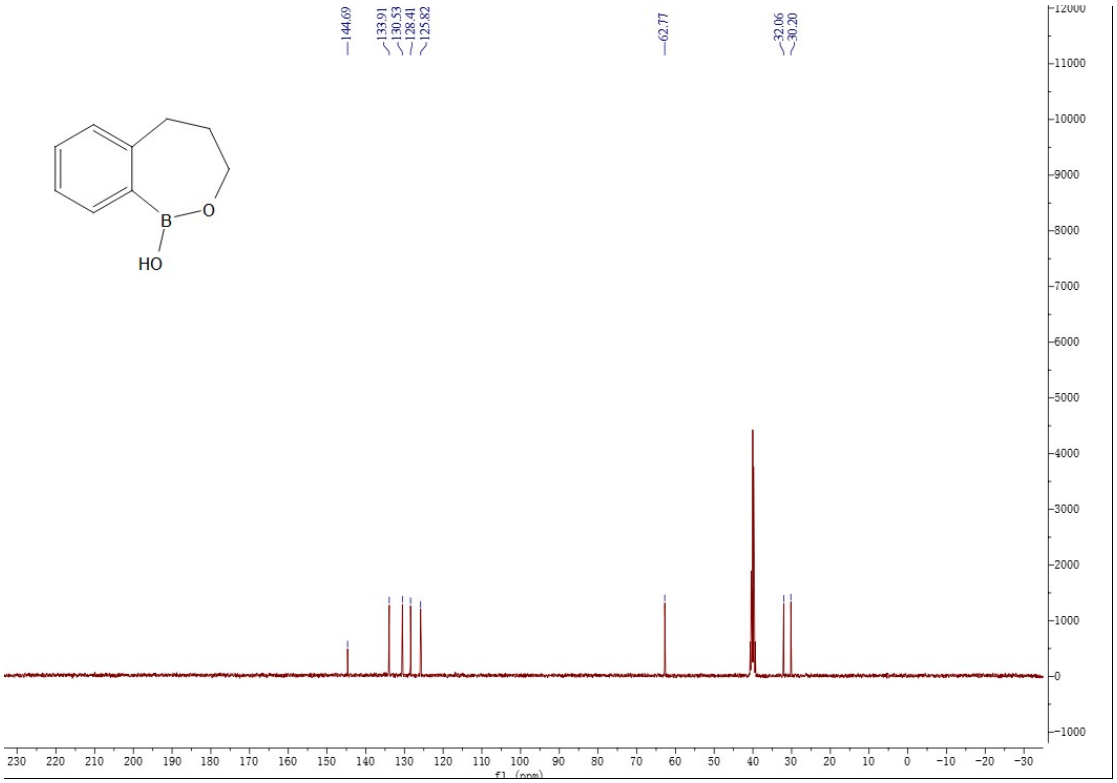
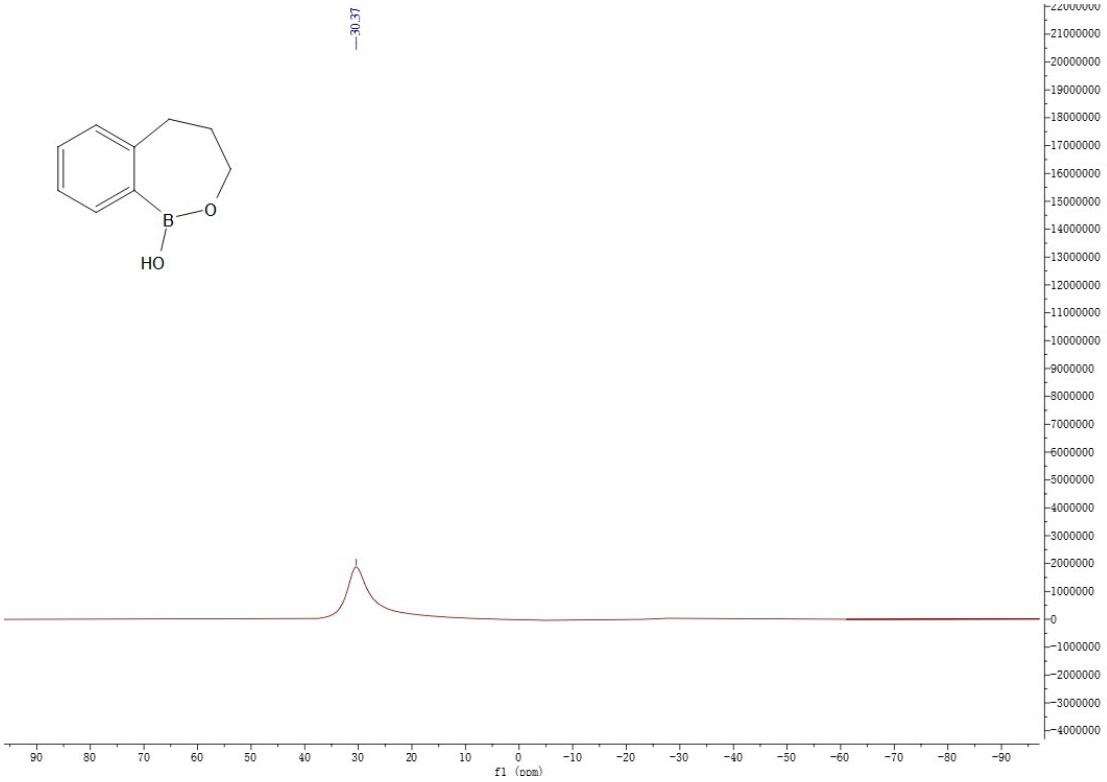
7. S. H. Kim, L. Steere, Y. K. Zhang, C. McGregor, C. Hahne, Y. S. Zhou, C. L. Liu, Y. Cai, H. B. Zhou, X. F. Chen, E. Puumala, D. Duncan, G. D. Wright, T. Liu, L. Whitesell and L. E. Cowen, Inhibiting C-4 Methyl Sterol Oxidase with Novel Diazaborines to Target Fungal Plant Pathogens, *ACS Chem. Biol.*, 2022, **17**, 1343-1350.

4. NMR Spectrums



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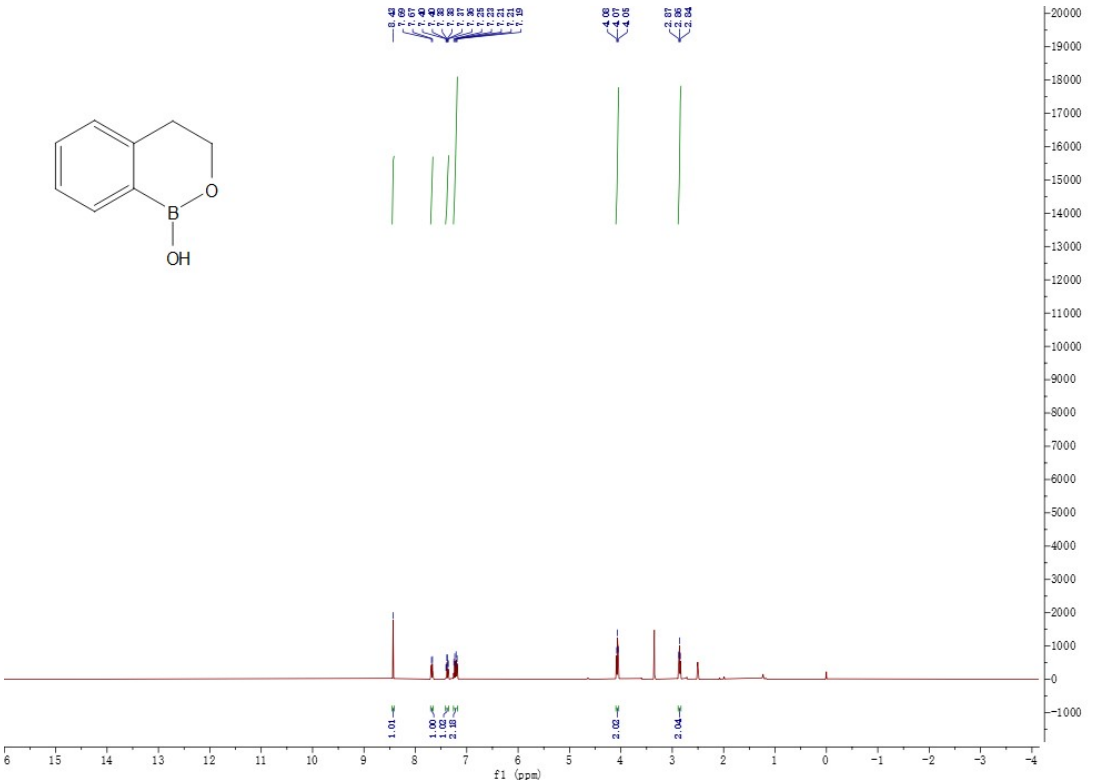
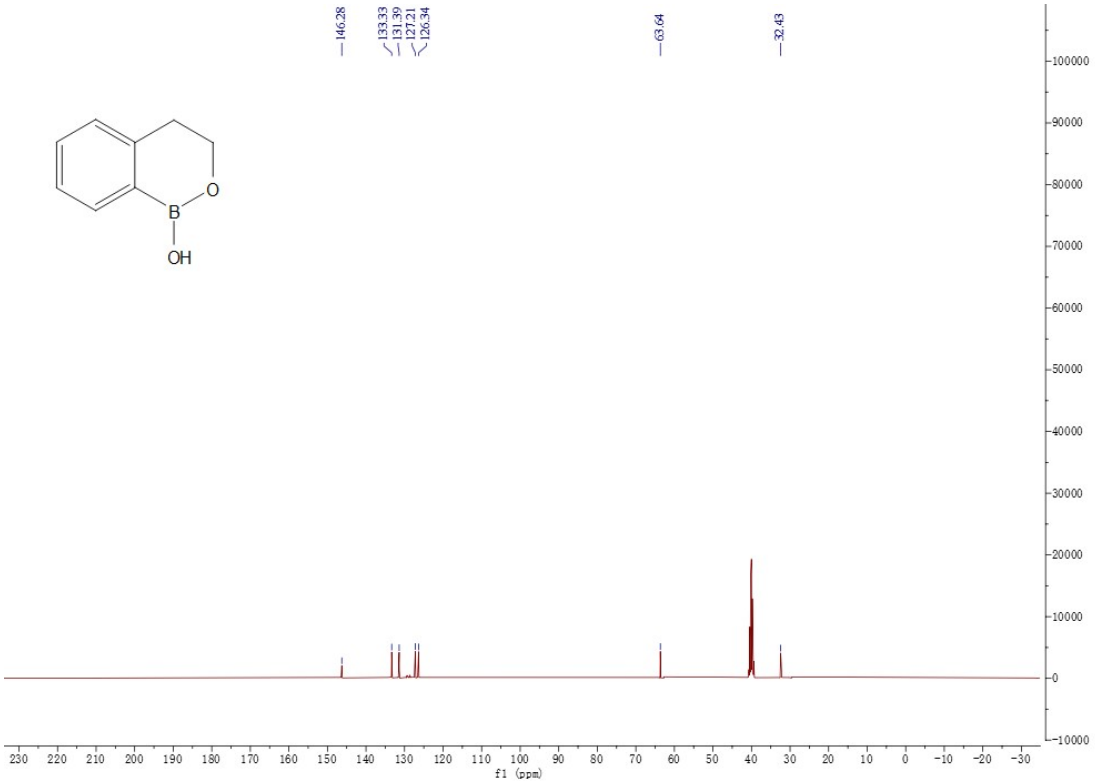
B
O
HO
f1 (ppm)


B
O
OH
f1 (ppm)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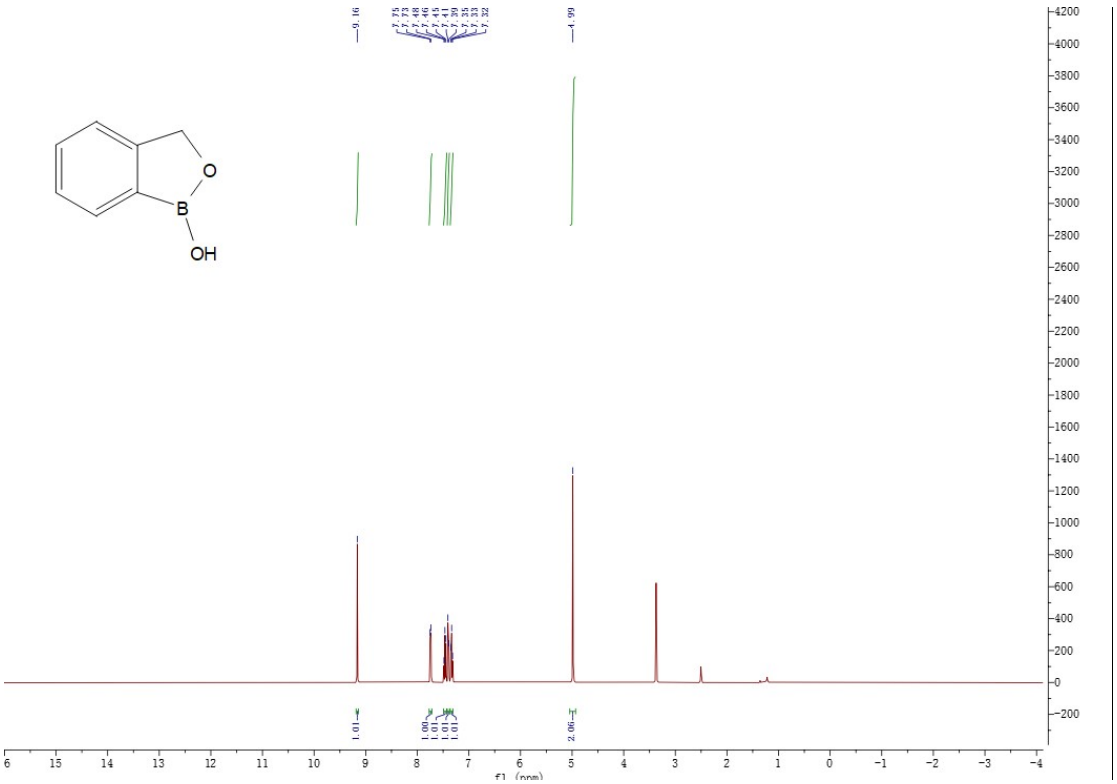
B
OH
f1 (ppm)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B
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1.00
1.01
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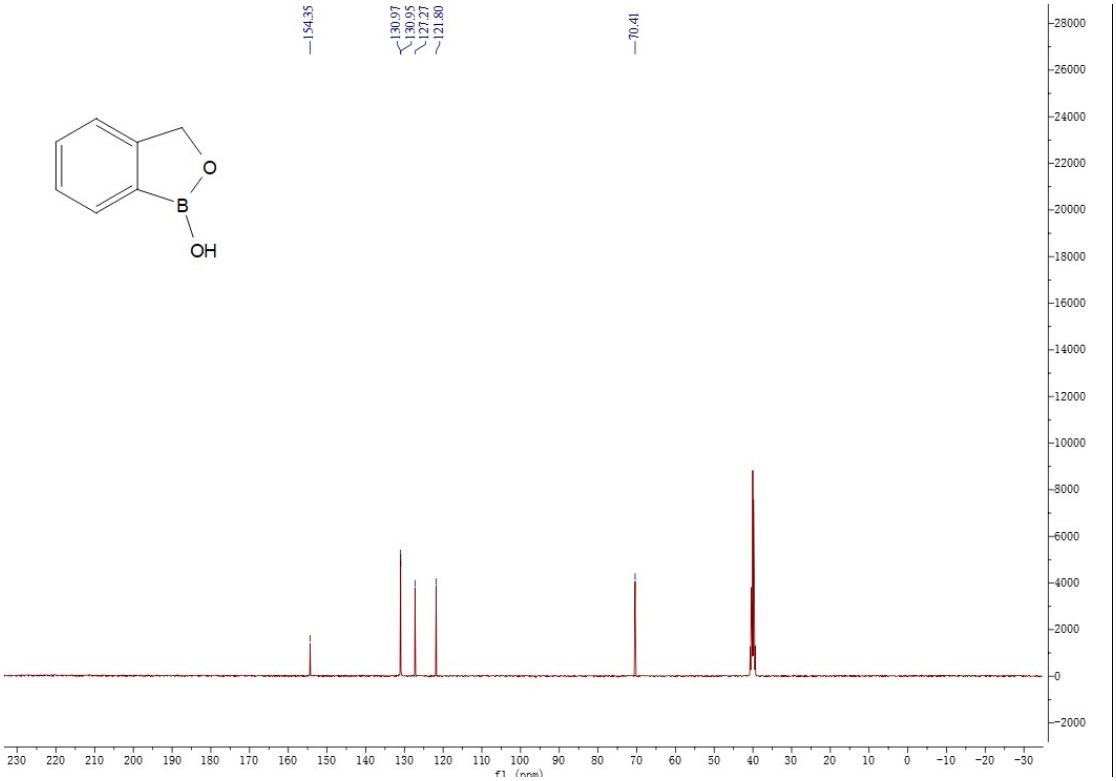
2.06
f1 (ppm)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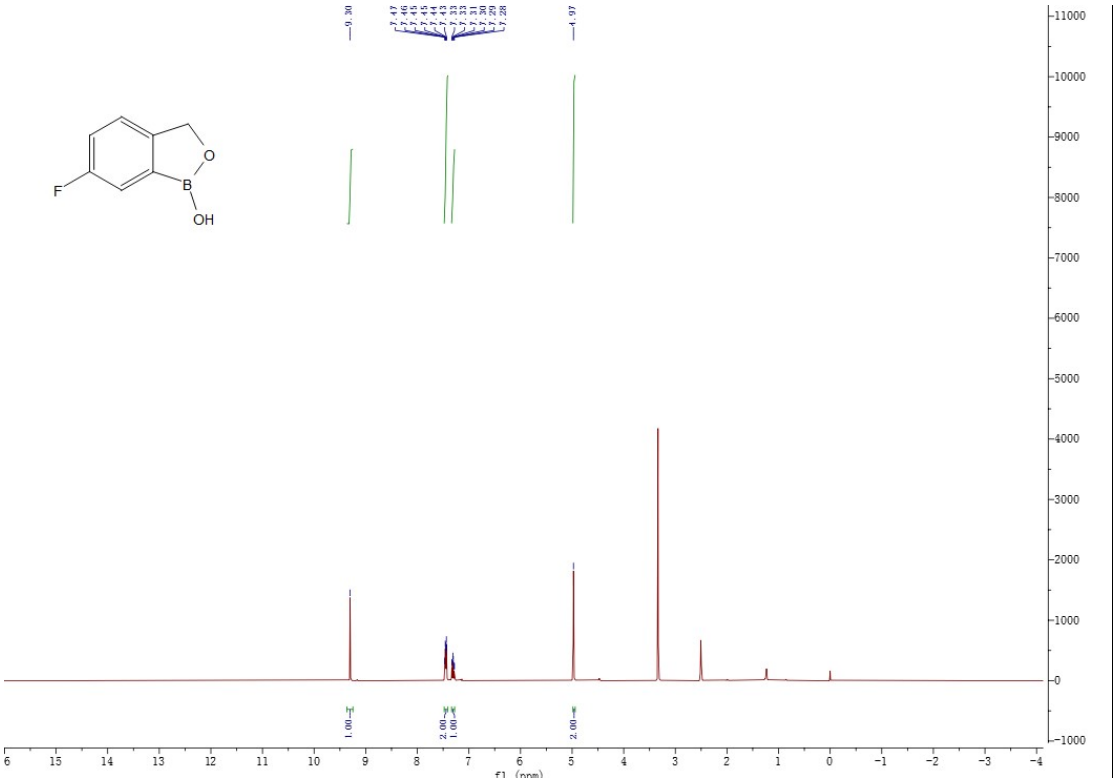
OH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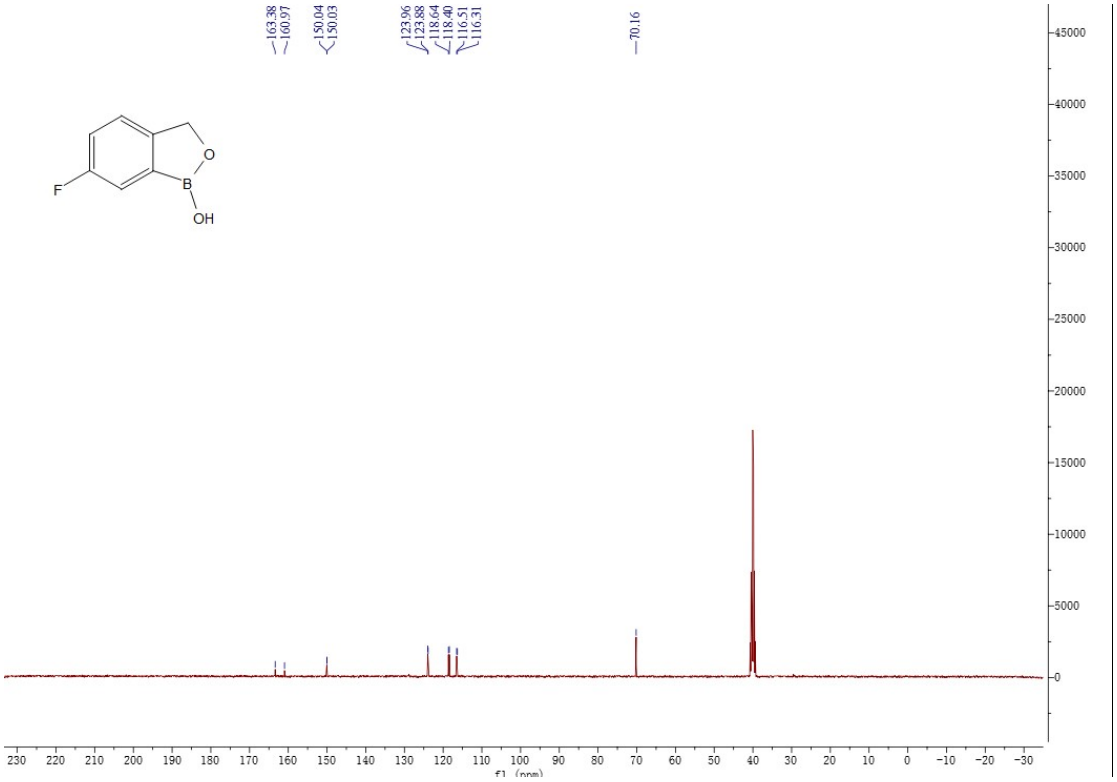
B
OH
F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150.03
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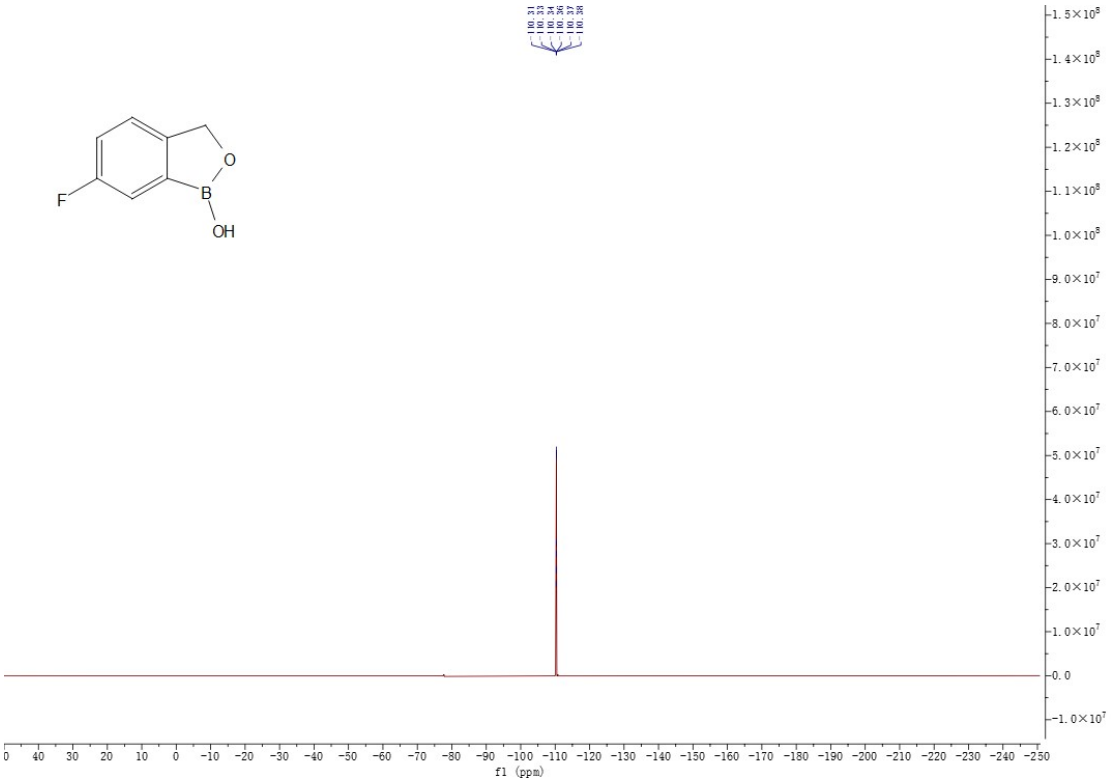
70.16
F
O
B
OH
f1 (ppm)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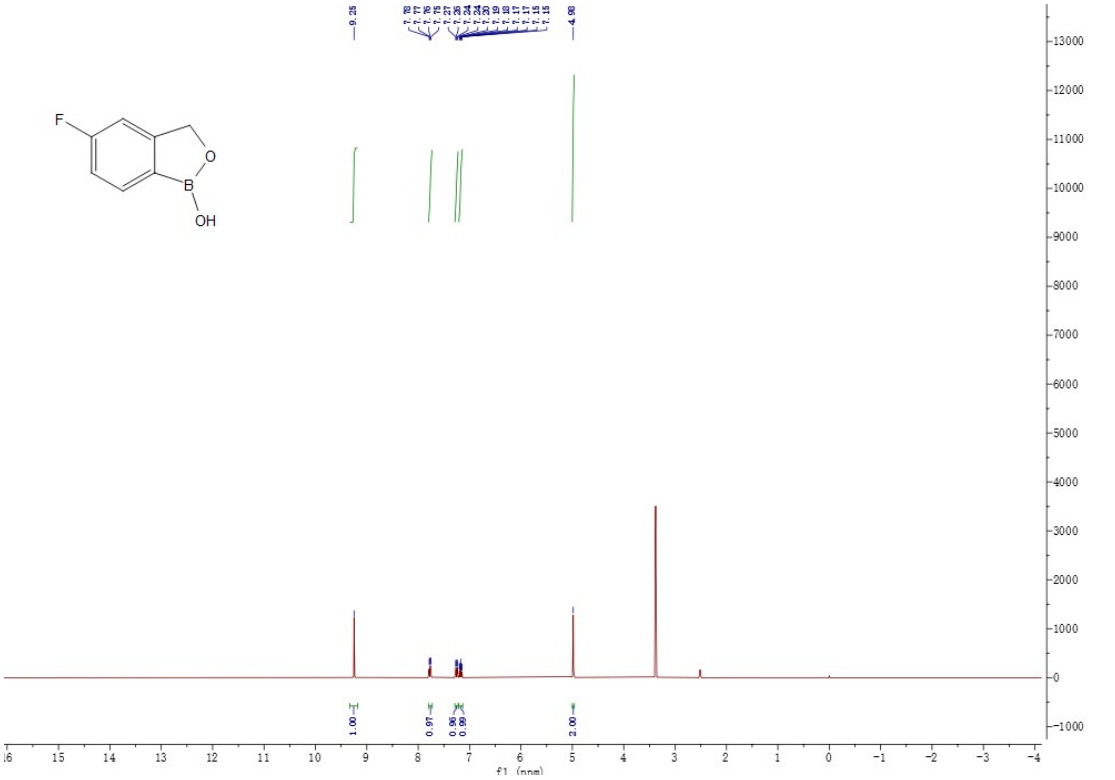
O
B
OH
f1 (ppm)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O
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7.19
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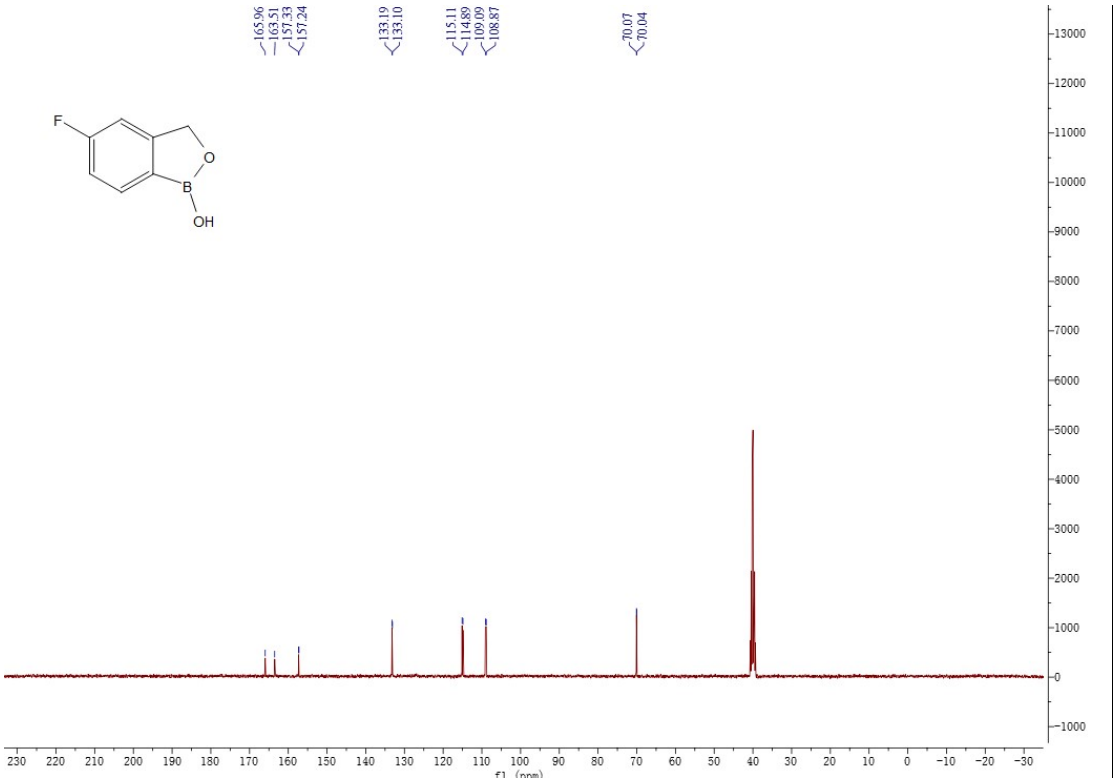
f1 (ppm)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O
B
OH
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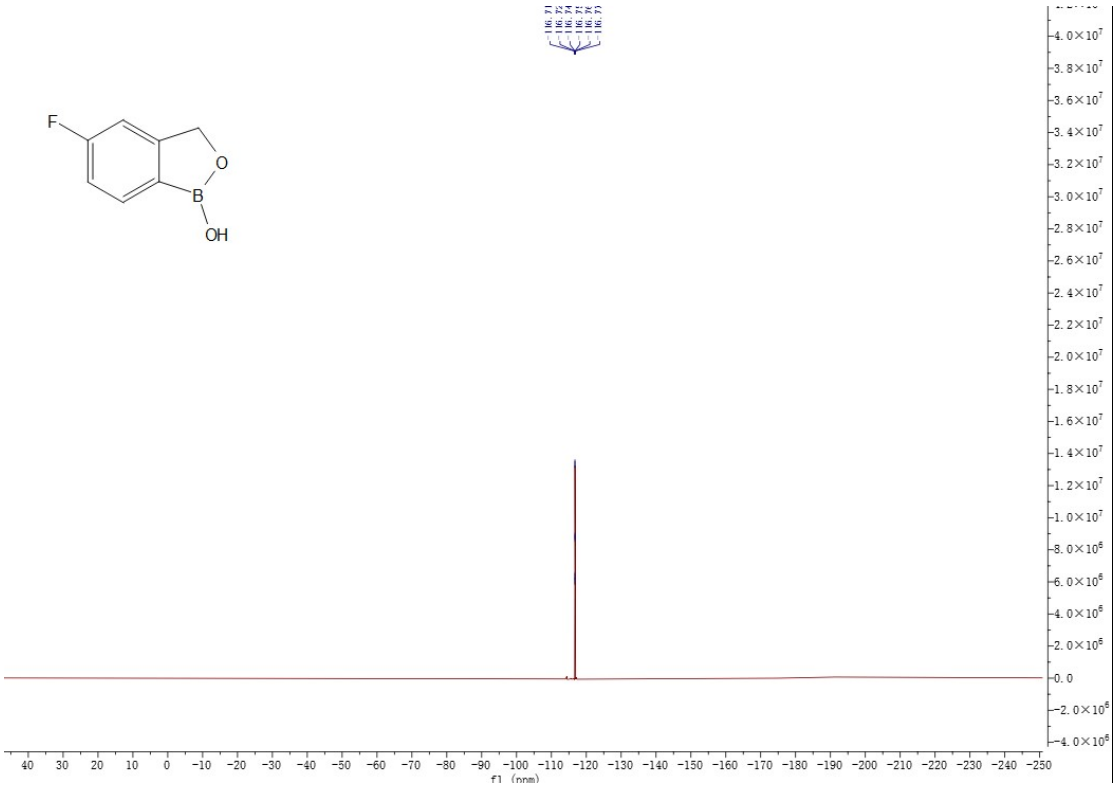
f1 (ppm)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O
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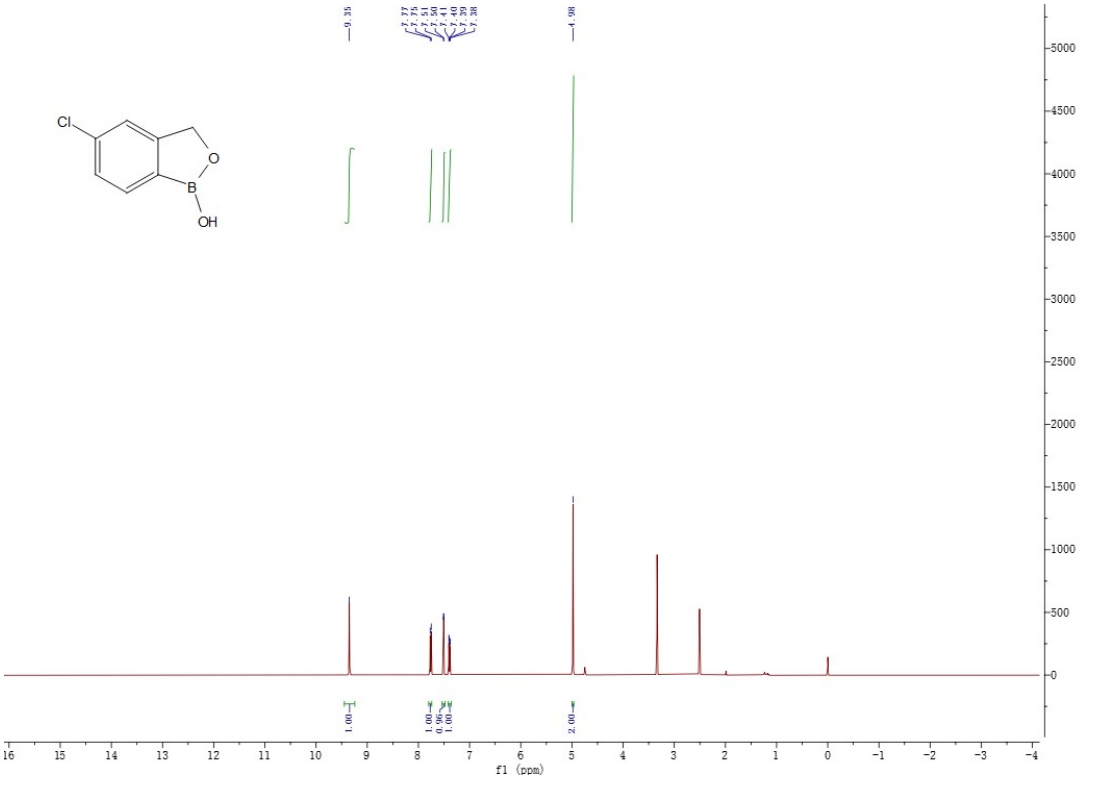
Cl
O
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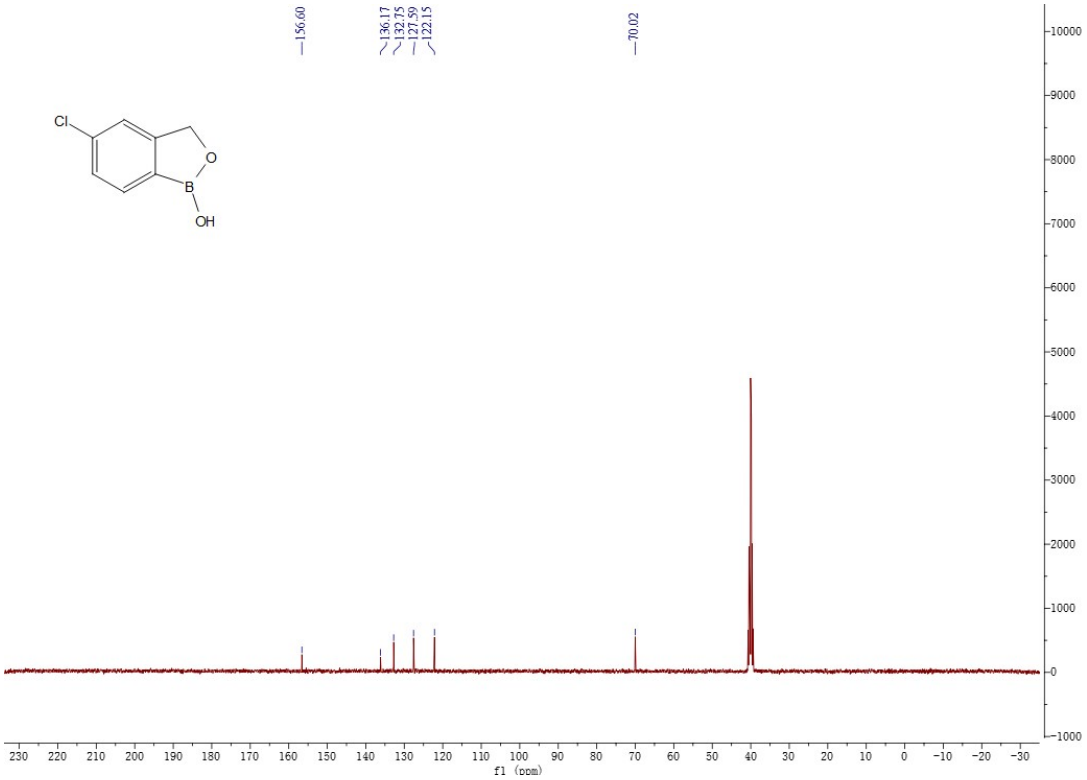
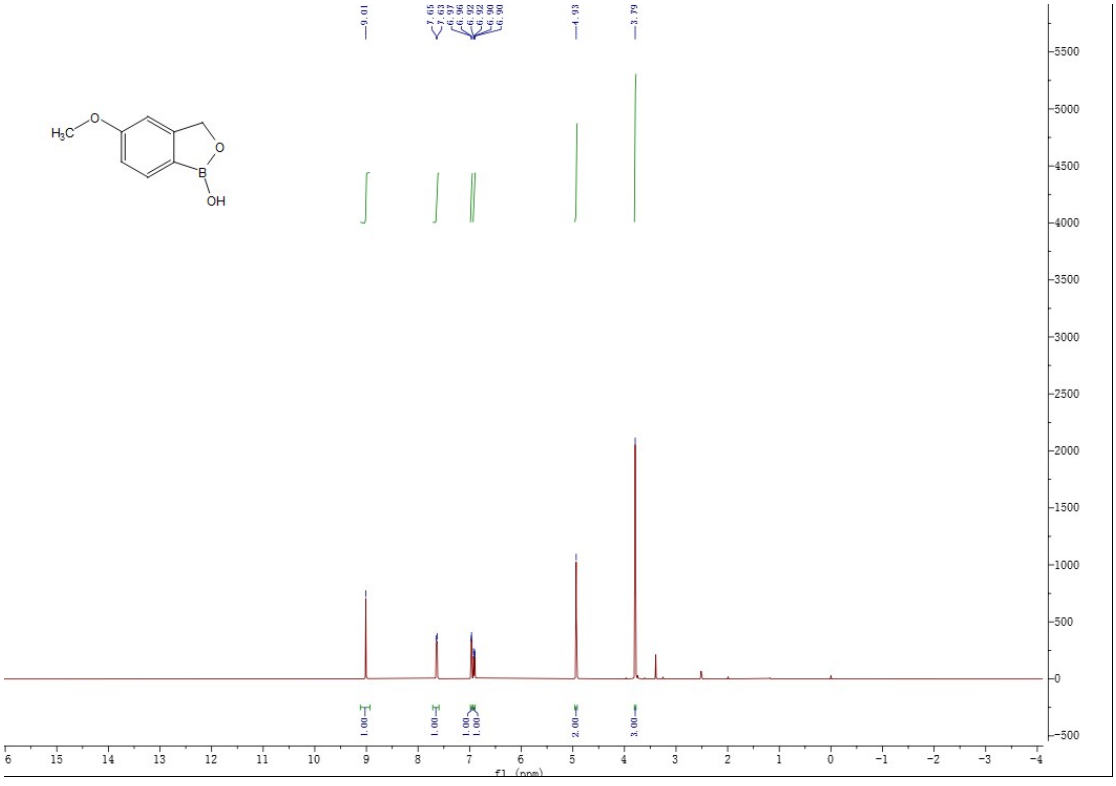
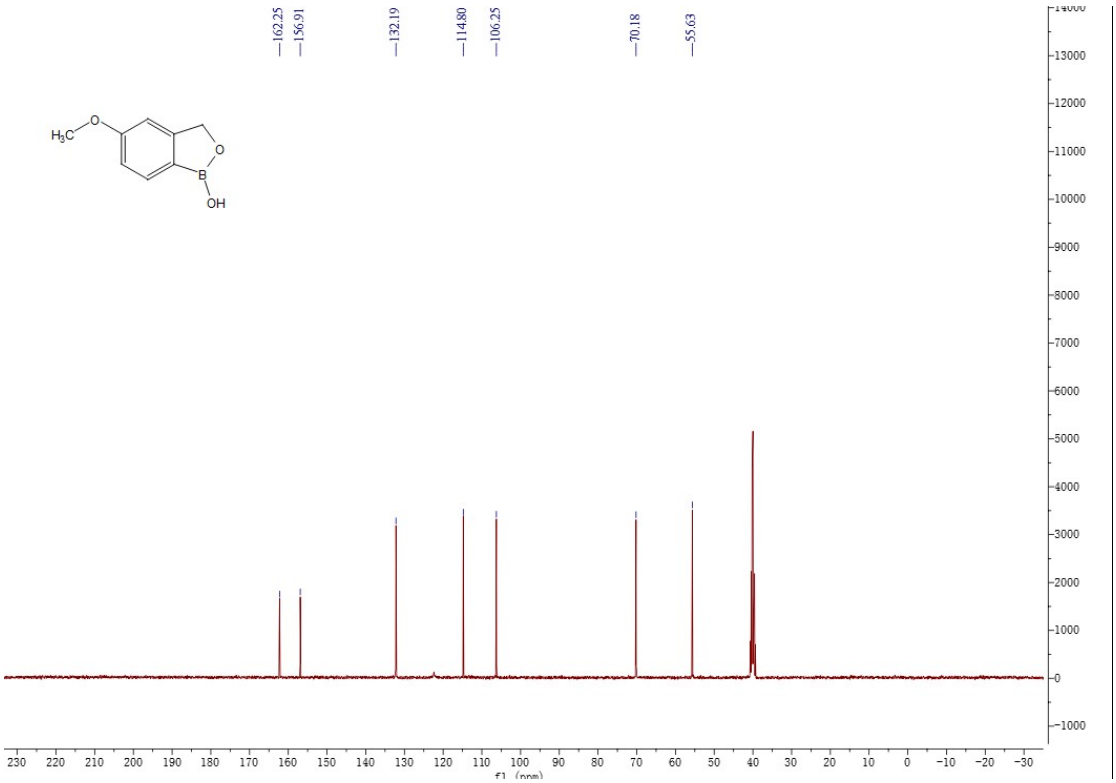
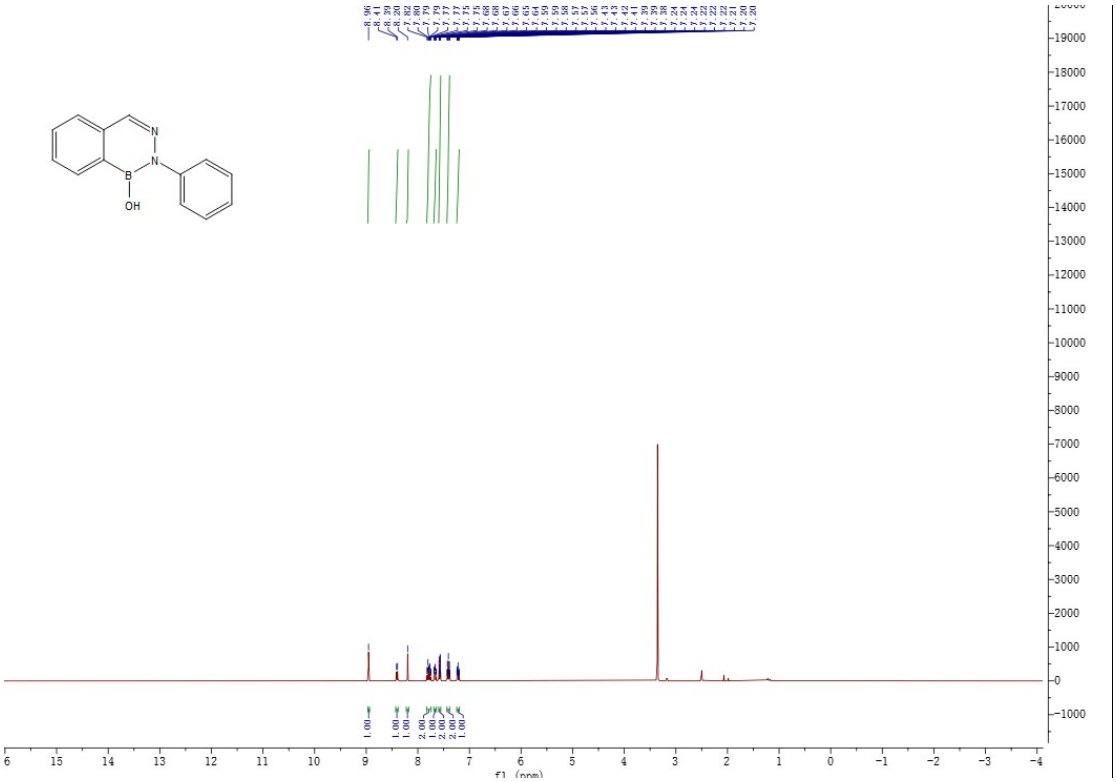
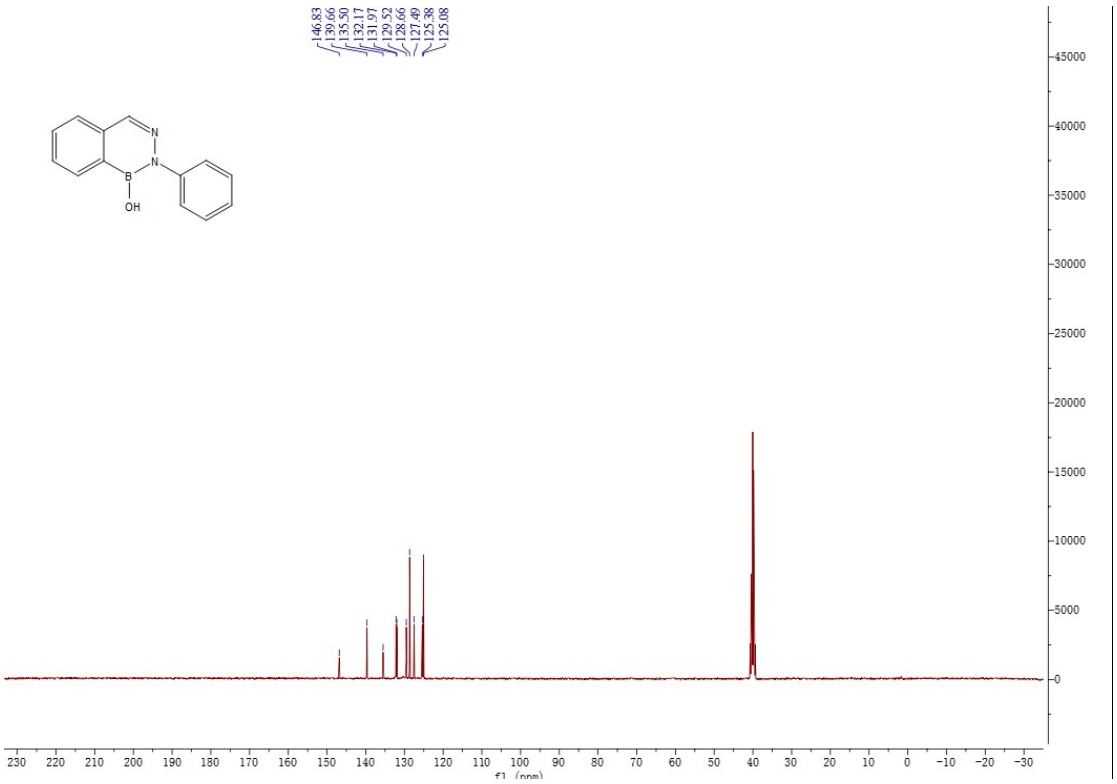
7.77
7.75
7.51
7.50
7.41
7.40
7.39
7.38
4.98
1.00
1.00
0.96
1.00
2.00
f1 (ppm)

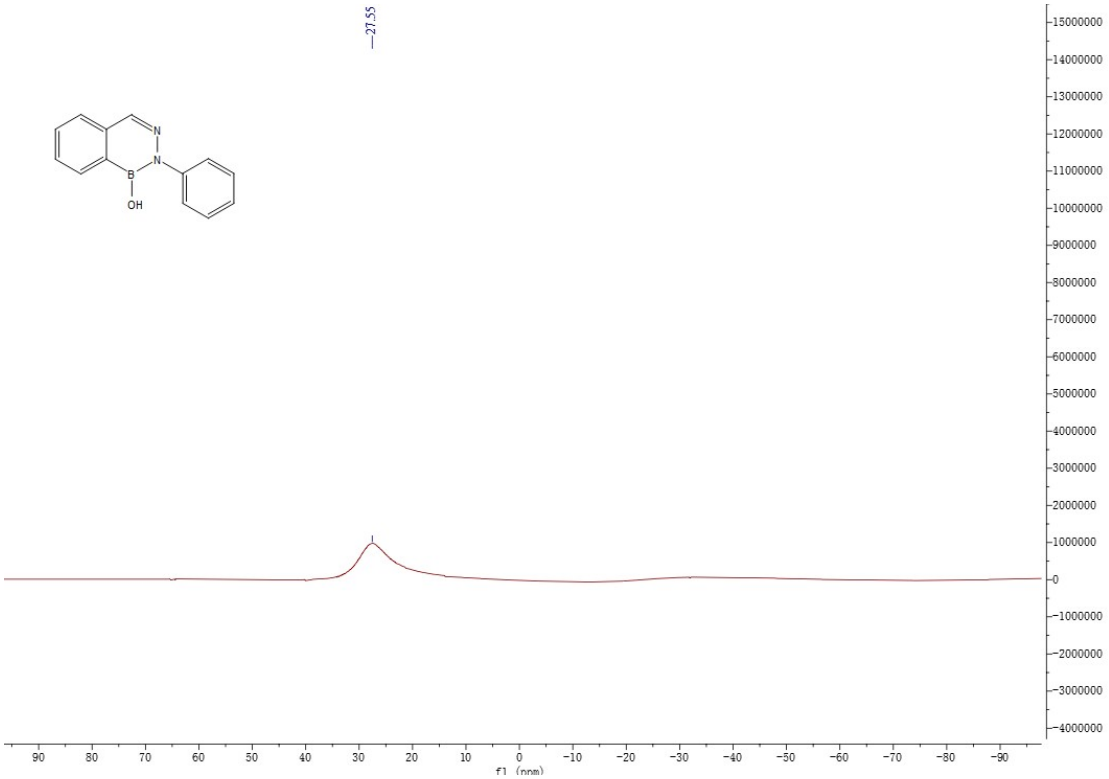

156.60
136.17
132.75
127.59
122.15
70.02
Cl
O
B
OH
f1 (ppm)

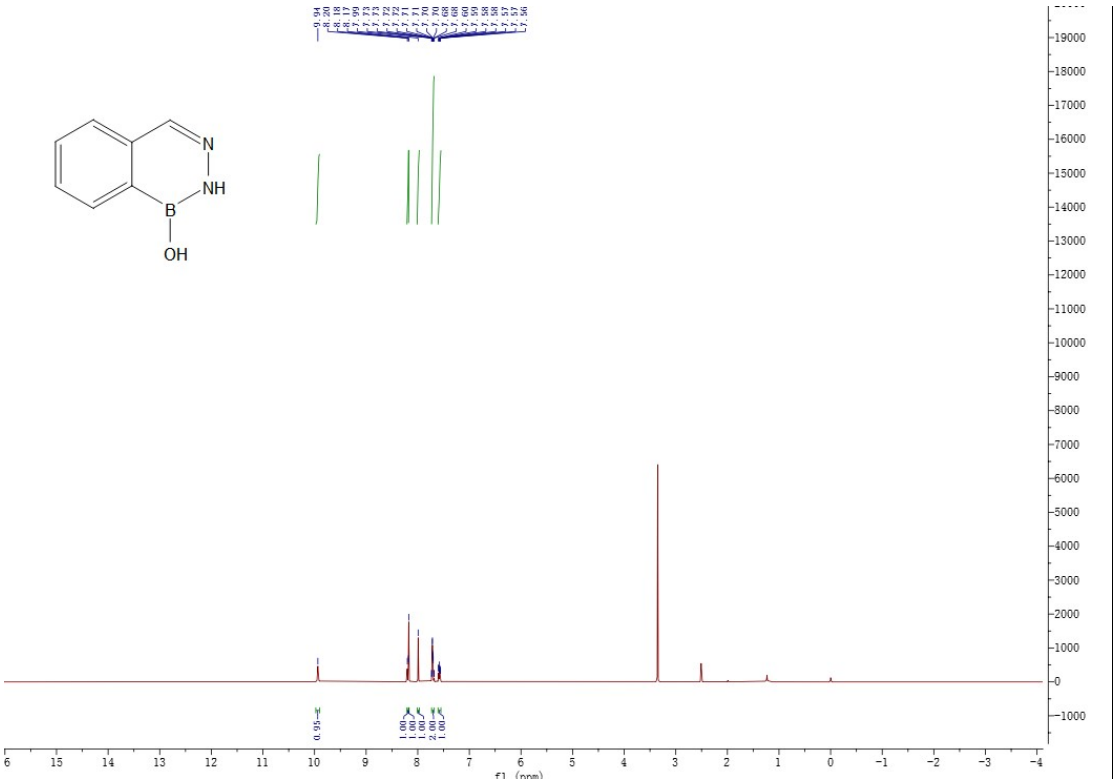

9.01
7.65
7.63
6.97
6.96
6.92
6.90
6.90
4.93
3.79
H3C
O
O
B
OH
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

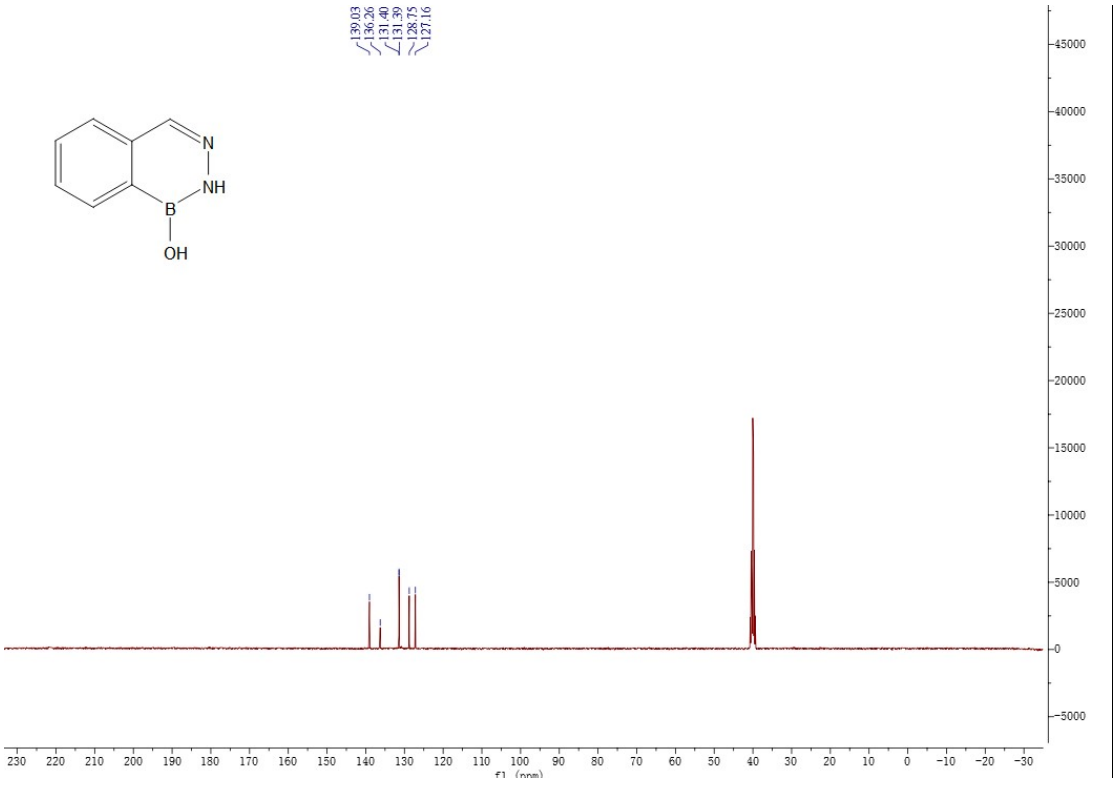

162.25
156.91
132.19
114.80
106.25
70.18
55.63
H3C
O
O
B
OH
f1 (ppm)

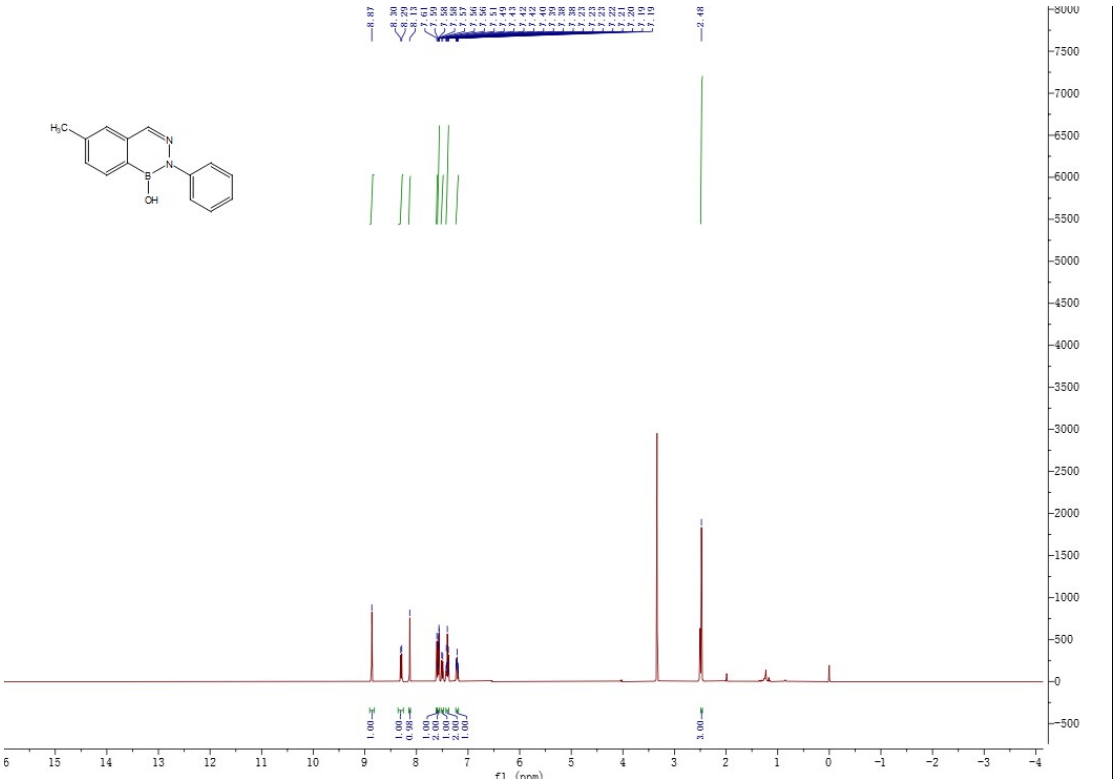

N
N
B
OH
f1 (ppm)

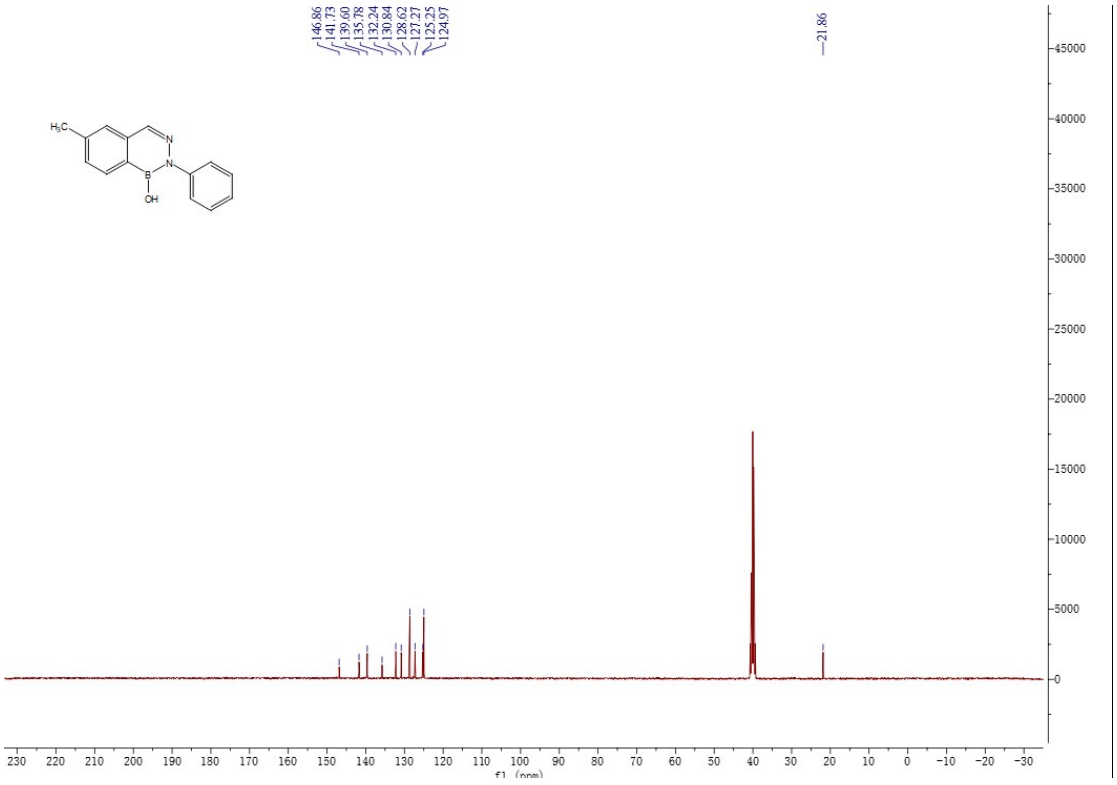

146.83
139.66
135.50
132.17
131.97
129.52
128.66
127.49
125.38
125.08
N
N
B
OH
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

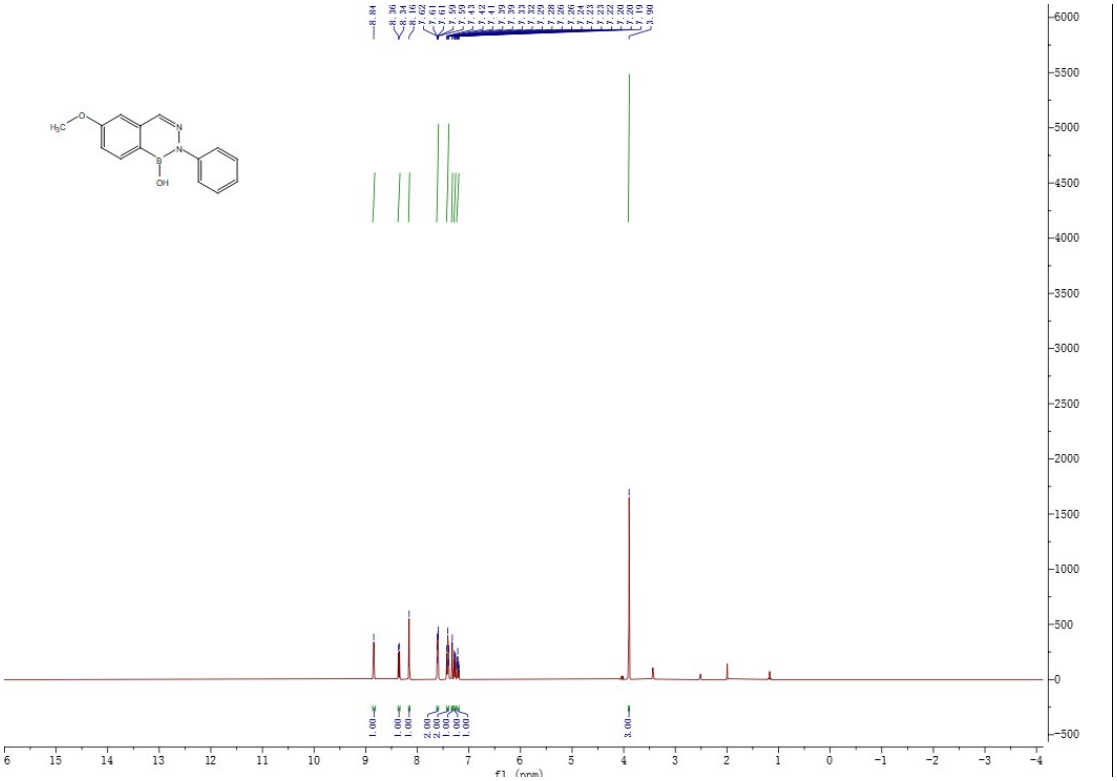

27.55
N
N
B
OH
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
-2000000
-3000000
-4000000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

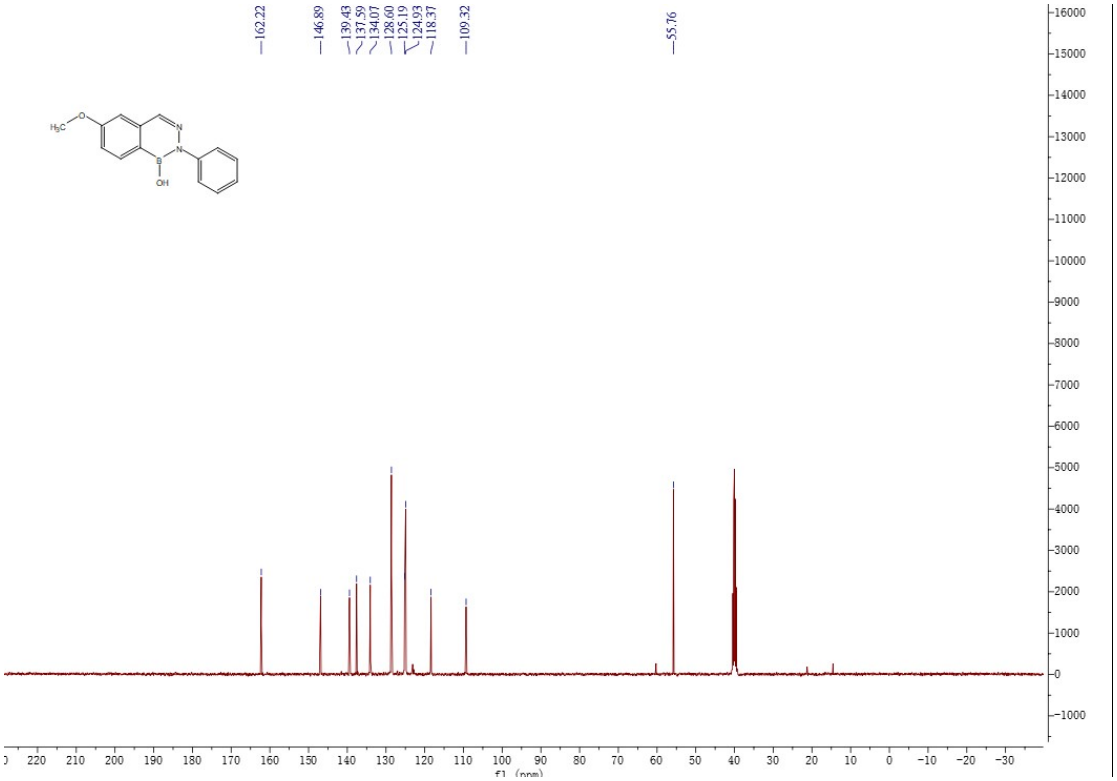

N
NH
B
OH

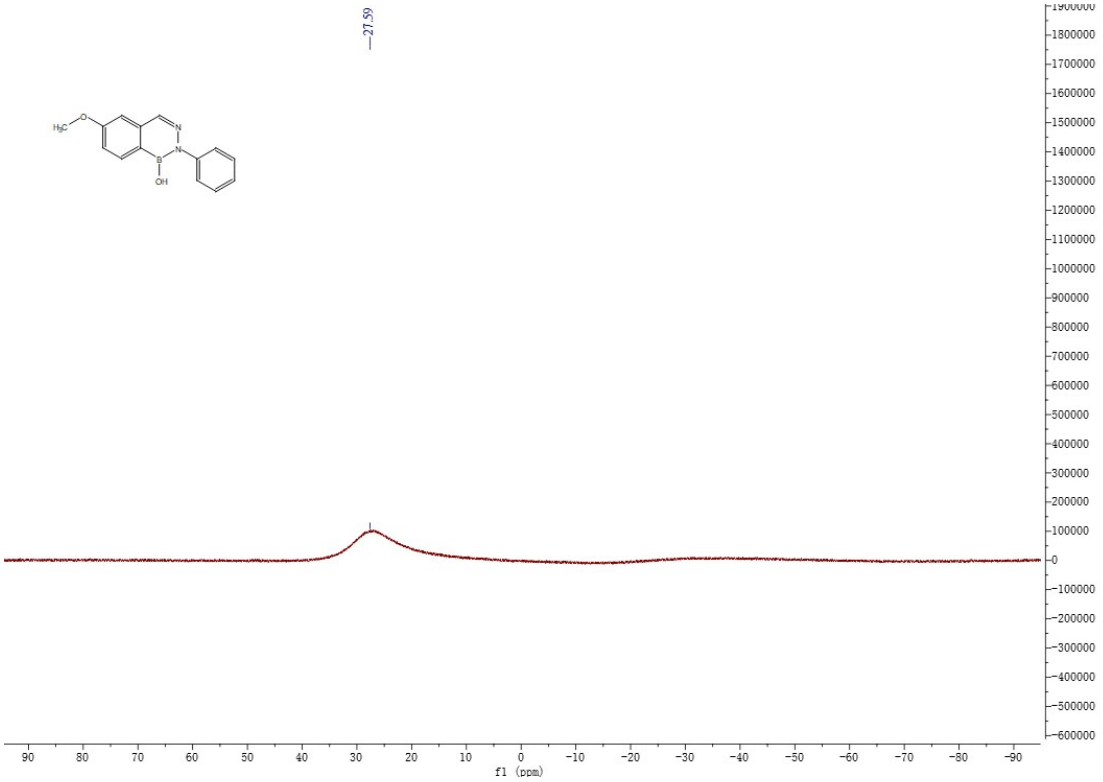

N
NH
B
OH

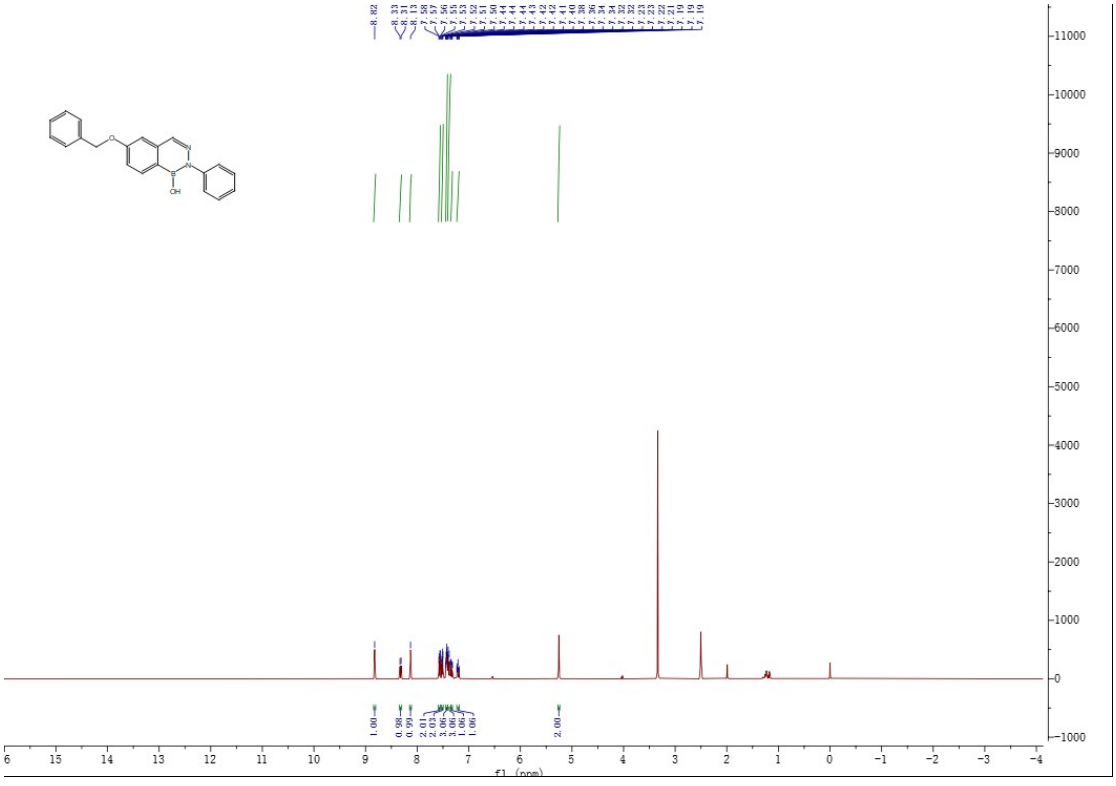

8.87
8.30
8.29
8.13
7.61
7.59
7.58
7.57
7.56
7.51
7.49
7.43
7.42
7.41
7.40
7.39
7.38
7.23
7.23
7.22
7.21
7.20
7.19
2.48
H3C
N
N
B
OH
1.00
1.00
0.98
1.00
2.00
2.00
2.00
1.00
3.00
f1 (ppm)

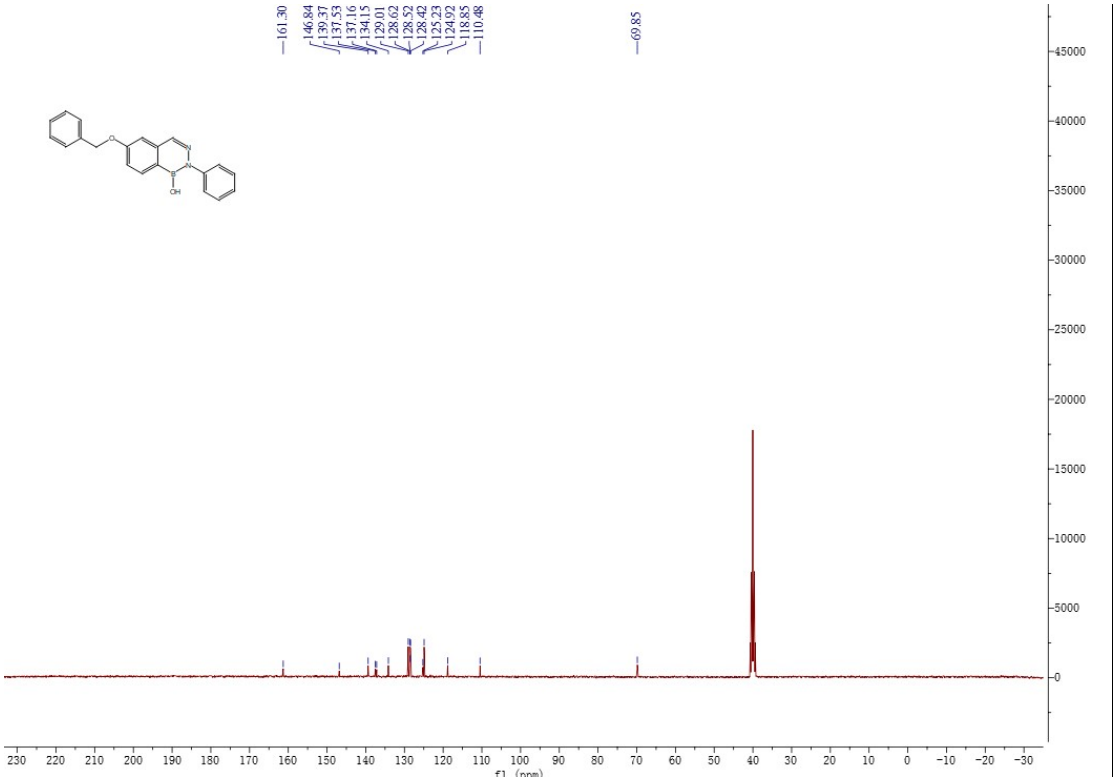

146.86
141.73
139.60
135.78
132.24
130.84
128.62
127.27
125.25
124.97
21.86
H3C
N
N
B
OH
f1 (ppm)

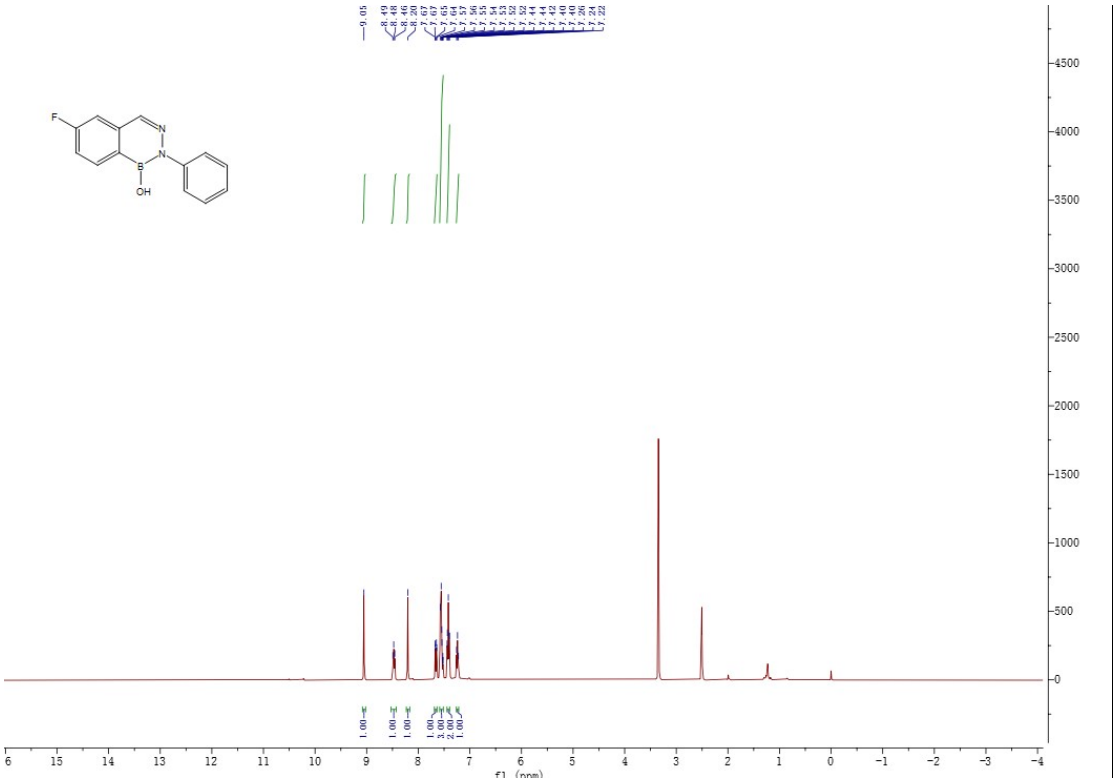





27.59
f1 (ppm)


8.82
8.33
8.31
8.13
7.58
7.56
7.55
7.53
7.52
7.51
7.50
7.47
7.44
7.43
7.42
7.41
7.40
7.38
7.36
7.34
7.32
7.32
7.23
7.22
7.22
7.21
7.19
7.19
1.00
0.98
0.99
2.03
3.06
3.06
1.06
2.00
f1 (ppm)


161.30
146.84
139.37
137.53
137.16
134.15
129.01
128.62
128.52
128.42
125.23
124.92
118.85
110.48
69.85
O
N
N
B
OH


9.05
8.49
8.48
8.46
8.20
7.67
7.66
7.65
7.64
7.53
7.56
7.55
7.54
7.53
7.52
7.52
7.44
7.44
7.42
7.40
7.40
7.26
7.24
7.22
F
N
N
B
OH
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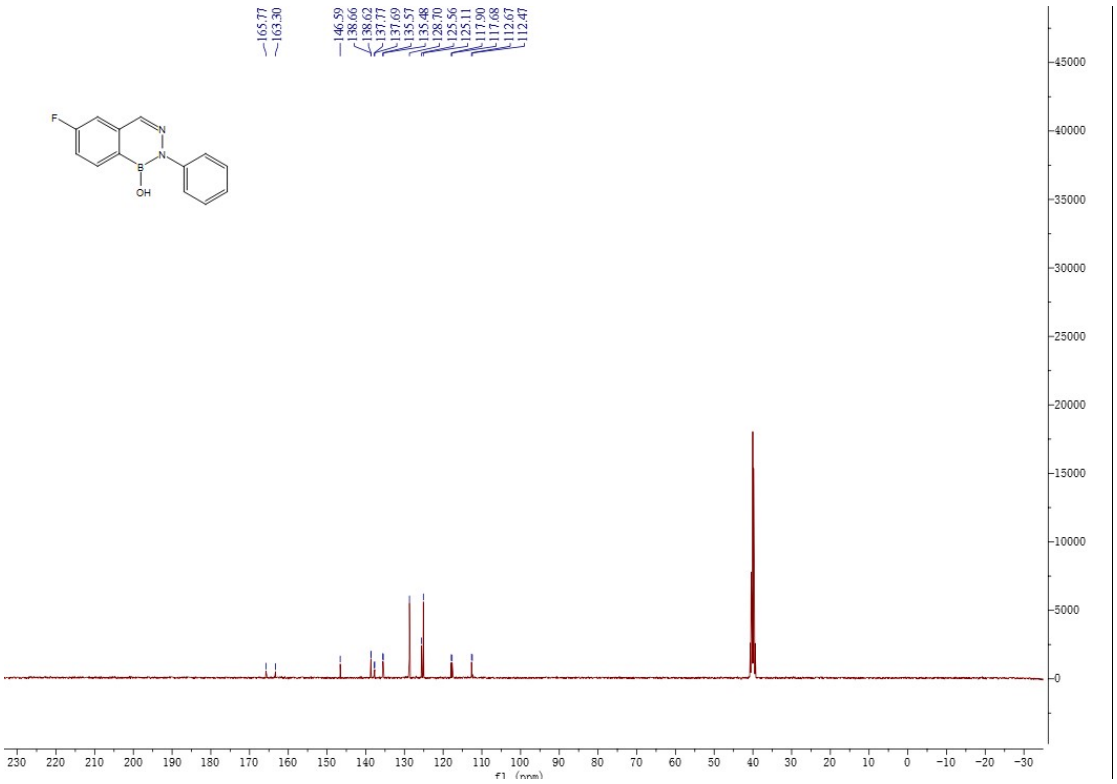
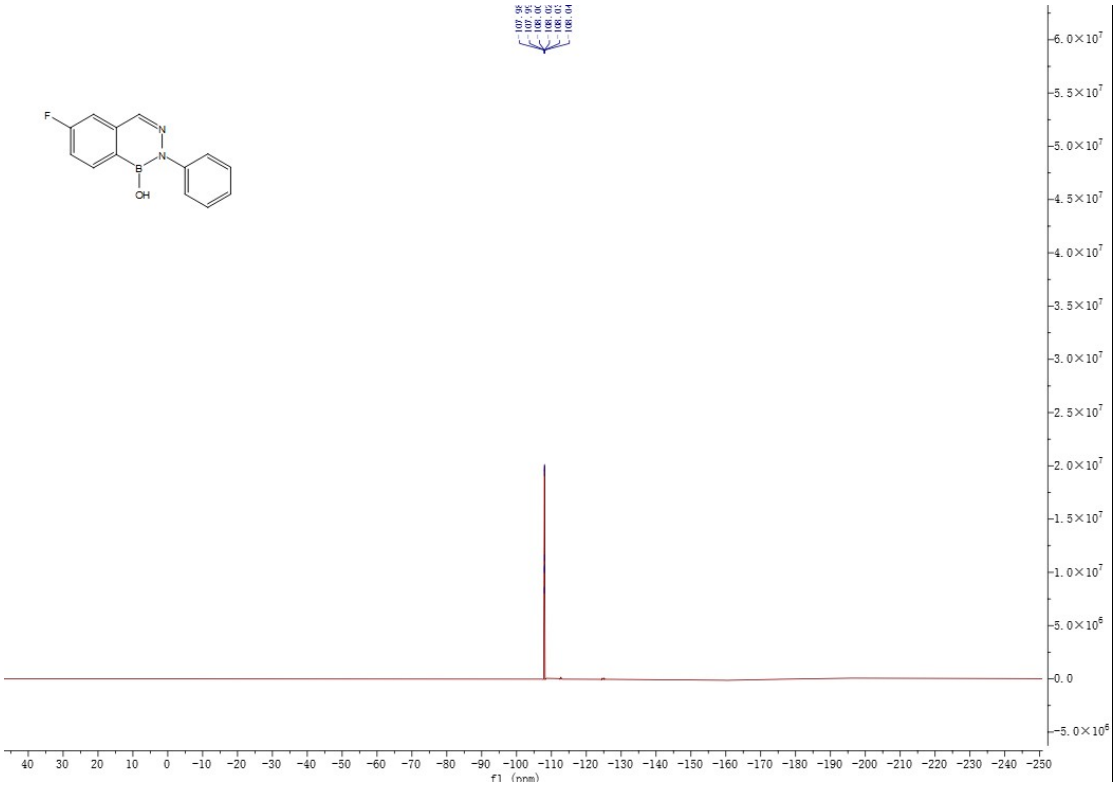
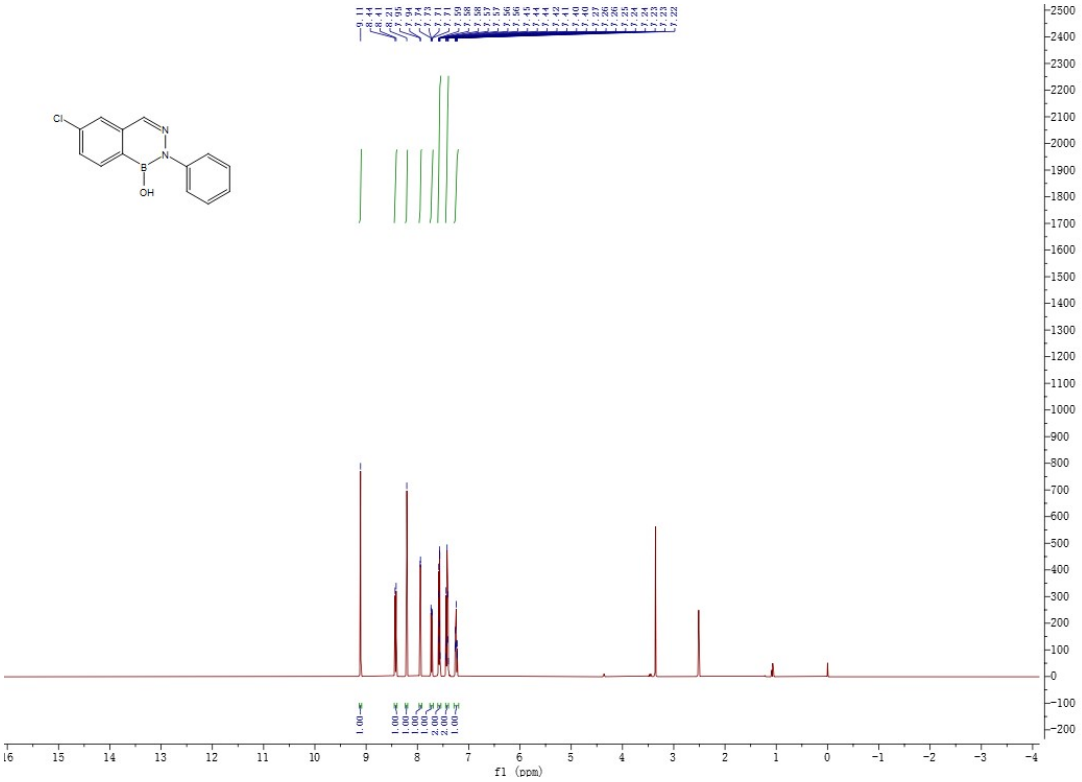
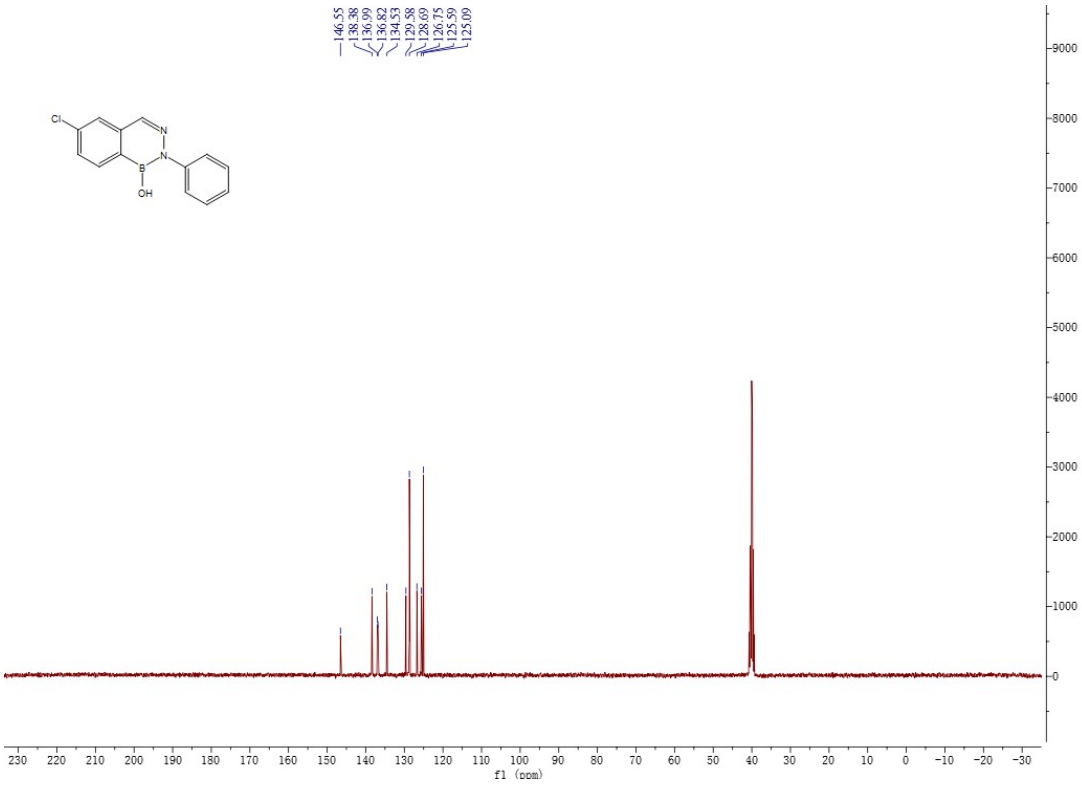
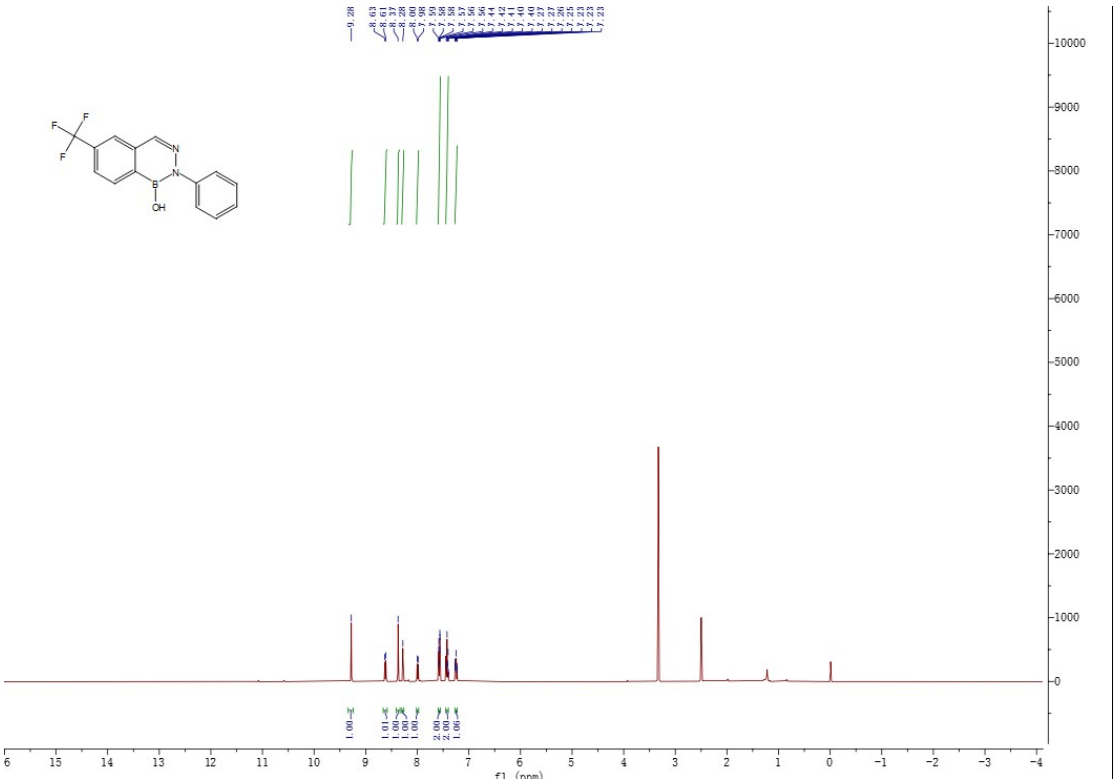
1.00
1.00
3.00
3.00
2.00
1.00

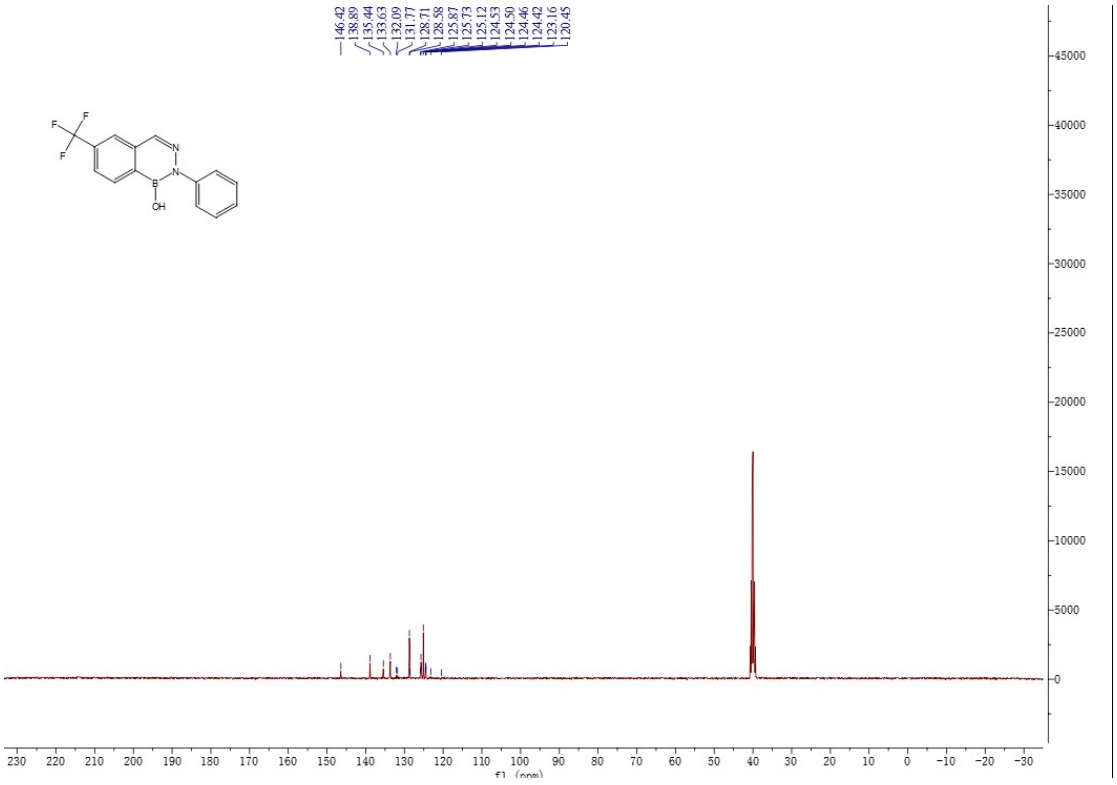

165.77
163.30
146.59
138.66
138.62
137.77
137.69
135.57
135.48
128.70
125.56
125.11
117.90
117.68
112.67
112.47
F
N
N
B
OH
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

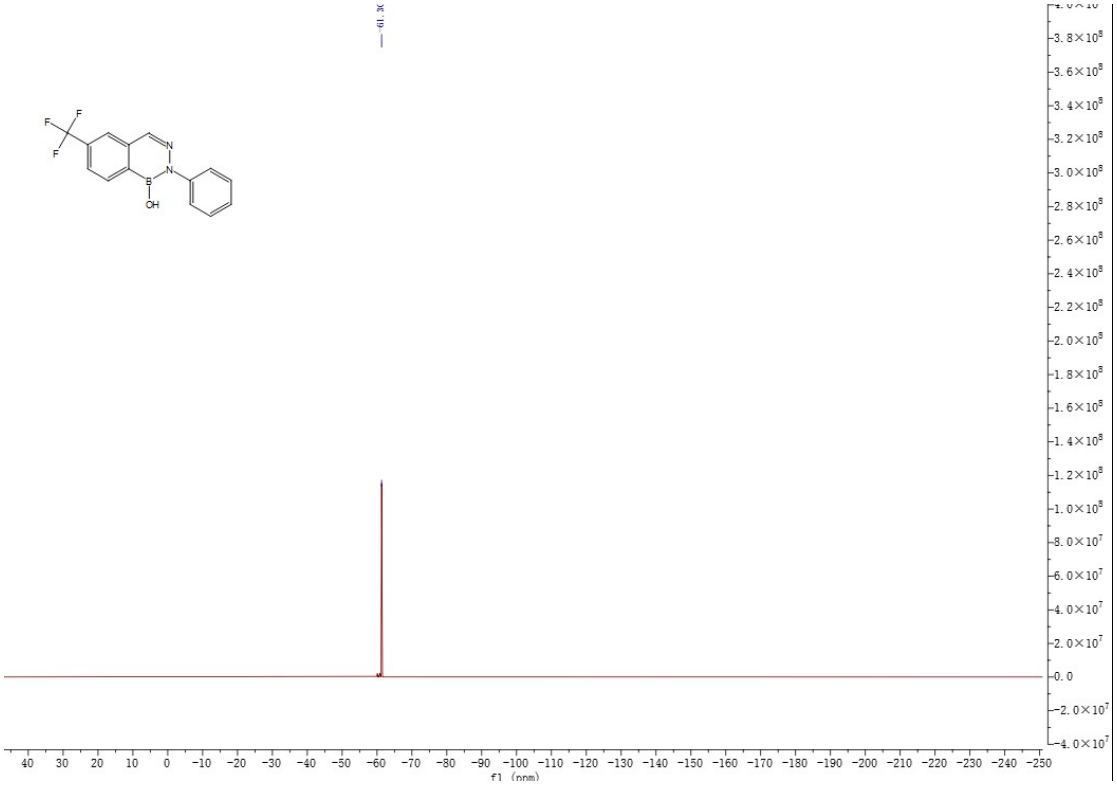

107.98
107.96
108.06
108.03
108.01
108.04
F
N
N
B
OH
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

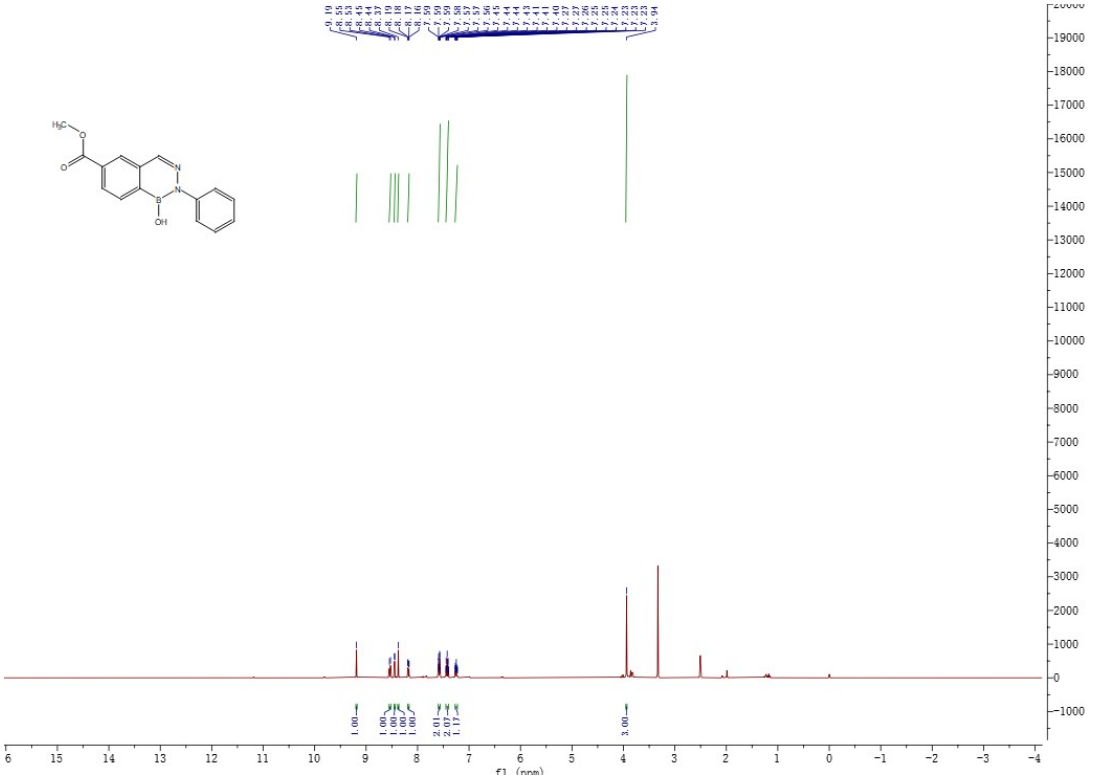

9.11
8.44
8.21
7.95
7.94
7.73
7.71
7.59
7.58
7.57
7.57
7.56
7.56
7.45
7.44
7.44
7.42
7.41
7.40
7.40
7.27
7.26
7.25
7.24
7.24
7.23
7.22
Cl
N
N
B
OH
1.00
1.00
1.00
1.00
2.00
1.00
f1 (ppm)

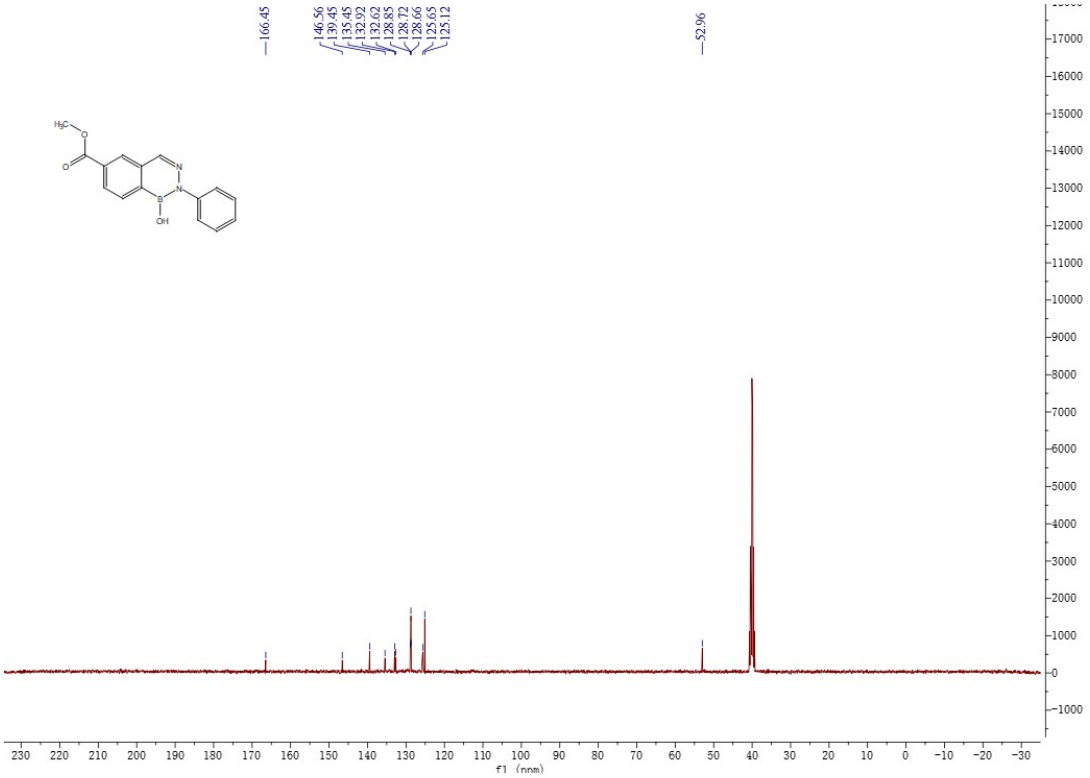

146.55
138.38
136.99
136.82
134.53
129.58
128.69
126.75
125.59
125.09
Cl
N
N
B
OH
f1 (ppm)

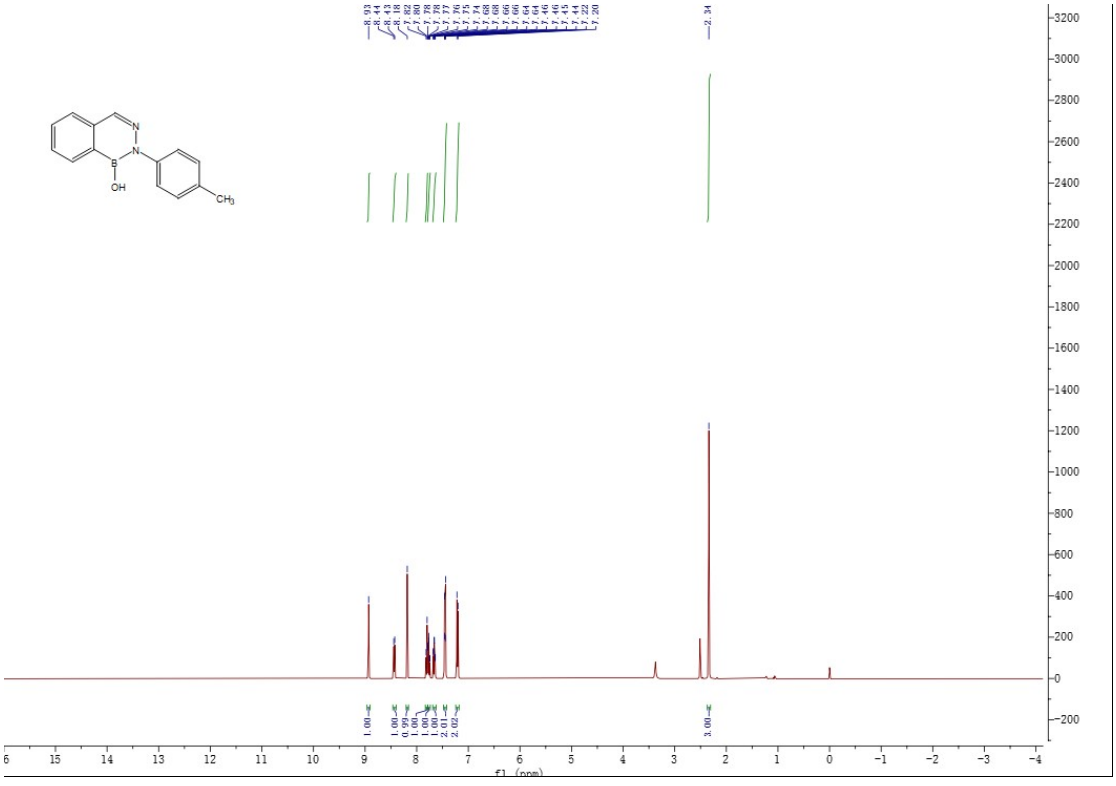

9.28
8.63
8.61
8.31
8.28
8.00
7.98
7.59
7.58
7.57
7.56
7.44
7.42
7.41
7.40
7.27
7.26
7.25
7.23
7.23
7.23
F
F
F
N
N
B
OH
1.00
1.01
1.00
1.00
2.00
2.00
1.06
f1 (ppm)

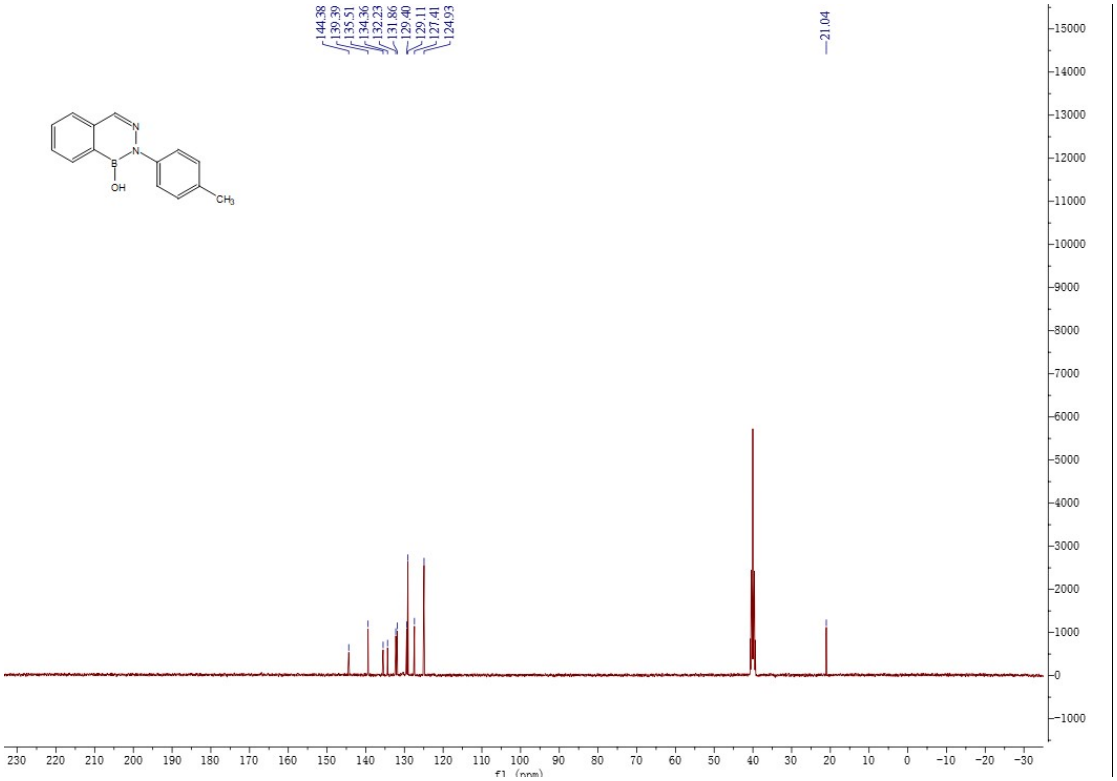

146.42
138.89
135.44
133.63
132.09
131.77
128.71
128.58
125.87
125.73
125.12
124.53
124.50
124.46
124.42
123.16
120.45
F
F
F
N
N
B
OH
f1 (ppm)

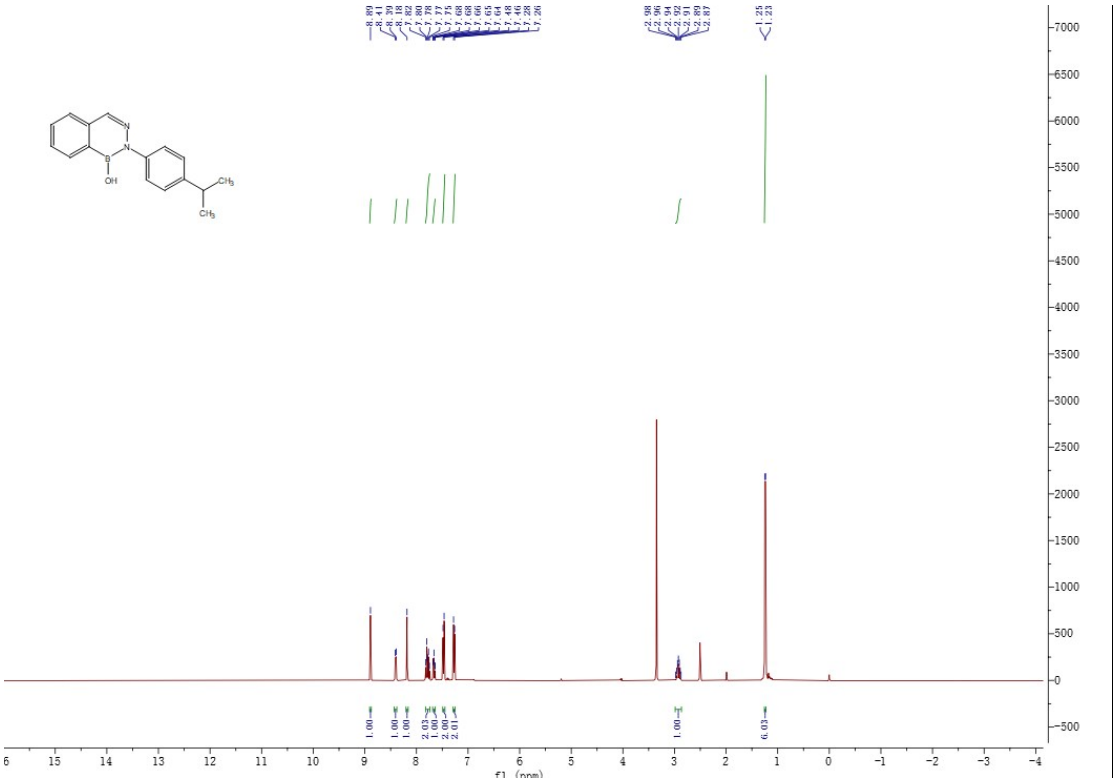

F
F
F
N
N
B
OH
f1 (ppm)

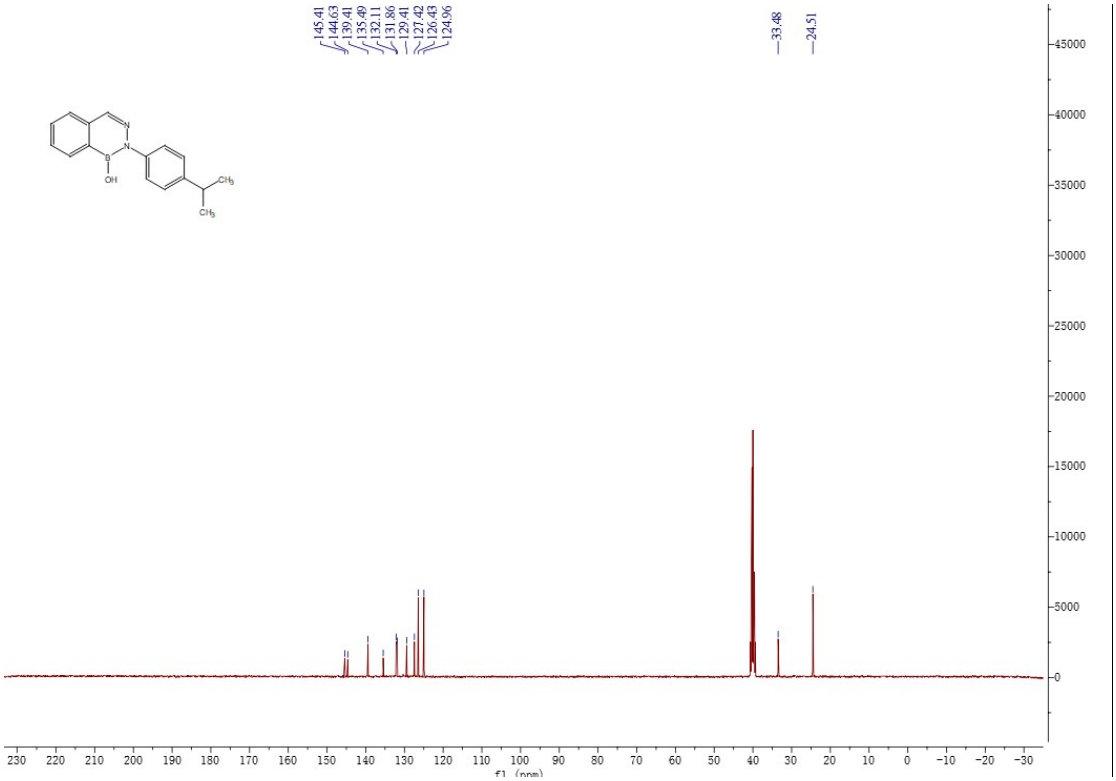

H3C
O
O
N
N
B
OH
f1 (ppm)

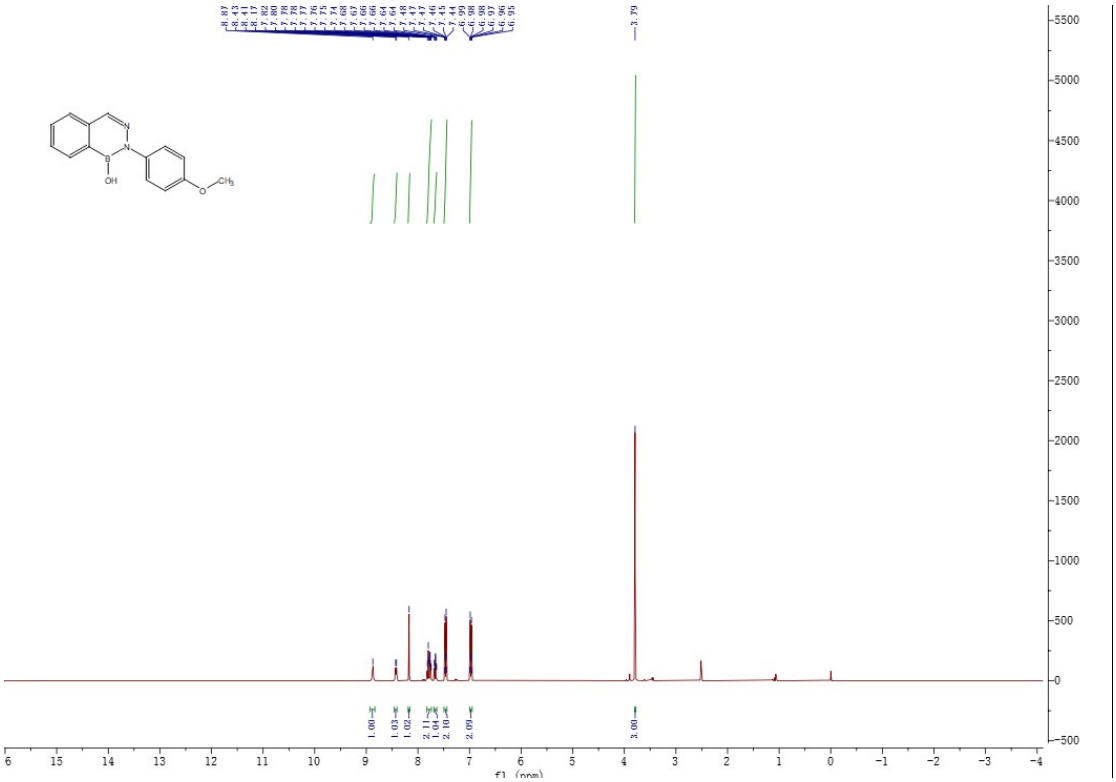

166.45
146.56
139.45
135.45
132.92
132.62
128.85
128.72
128.66
125.65
125.12
52.96
f1 (ppm)

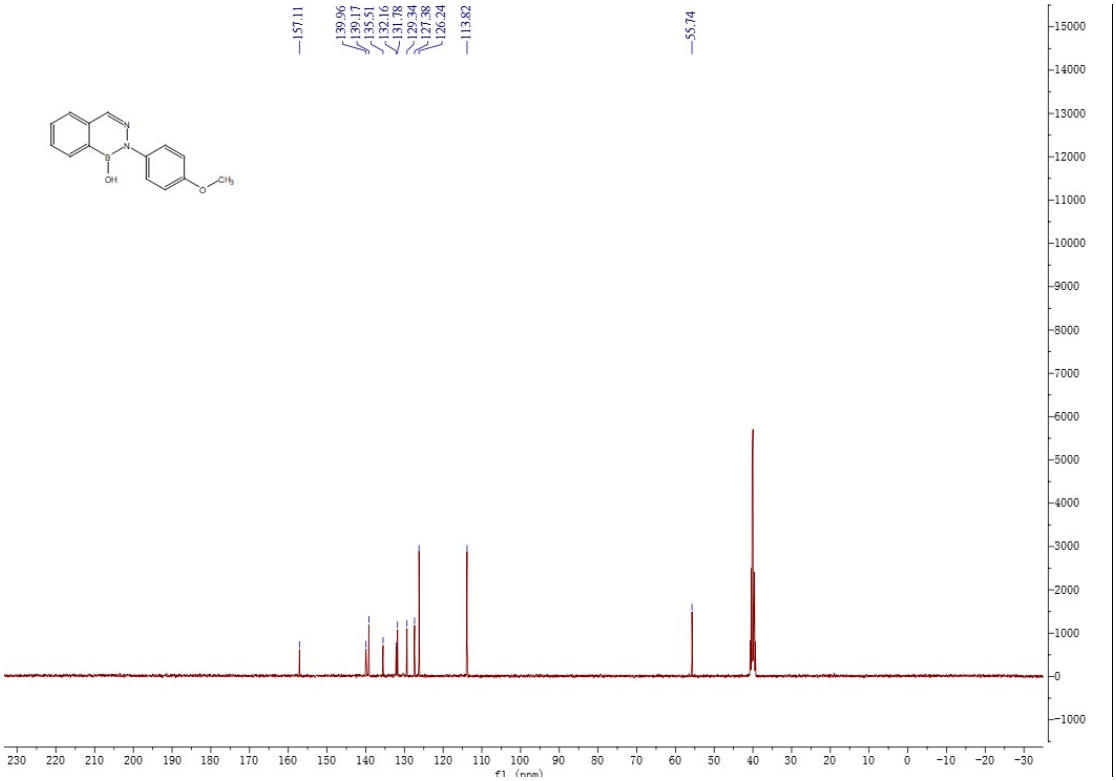

2.34
f1 (ppm)

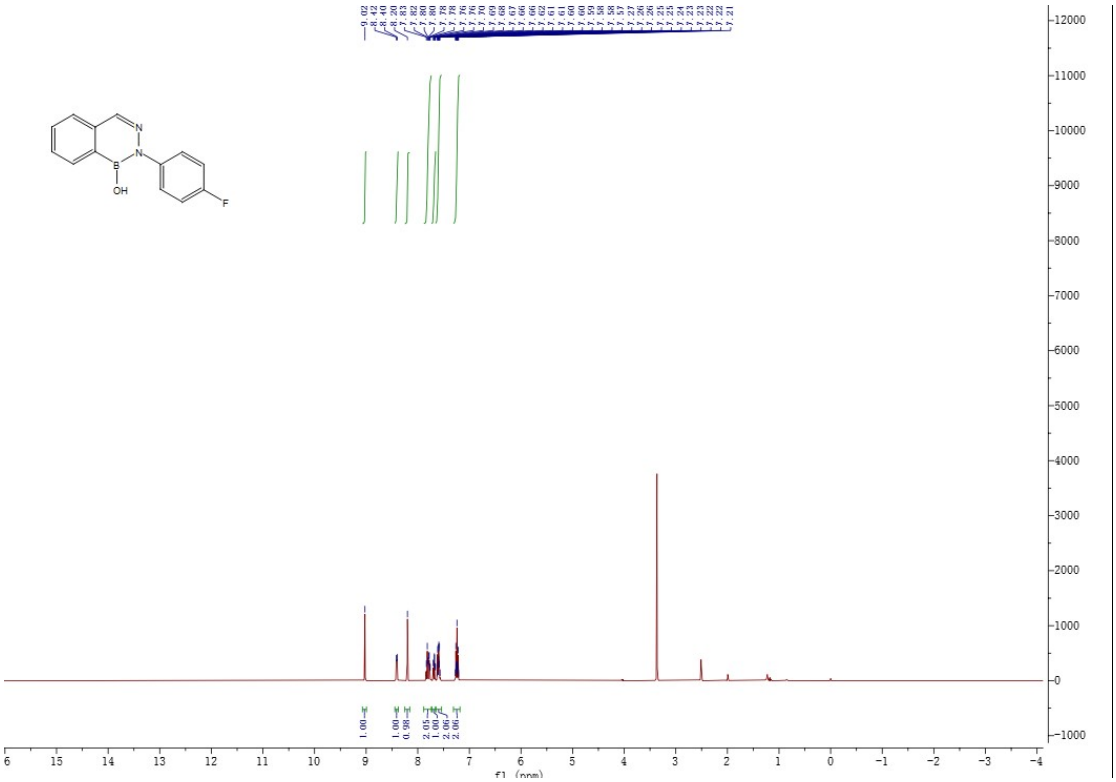

144.38
139.39
135.51
134.36
132.23
131.86
129.40
129.11
127.41
124.93
21.04
OH
CH3

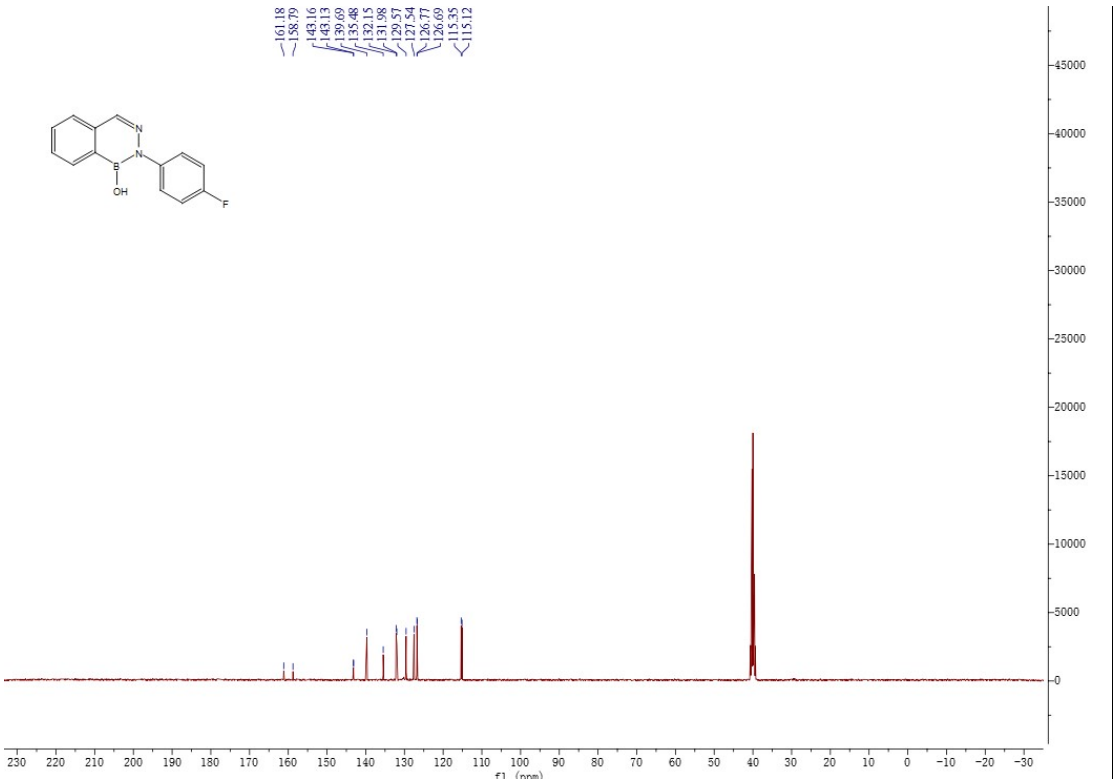

8.89
8.41
8.30
8.18
7.82
7.80
7.78
7.77
7.75
7.68
7.66
7.65
7.64
7.48
7.46
7.28
7.26
2.98
2.96
2.94
2.92
2.91
2.89
2.87
1.25
1.23
OH
CH3
CH3

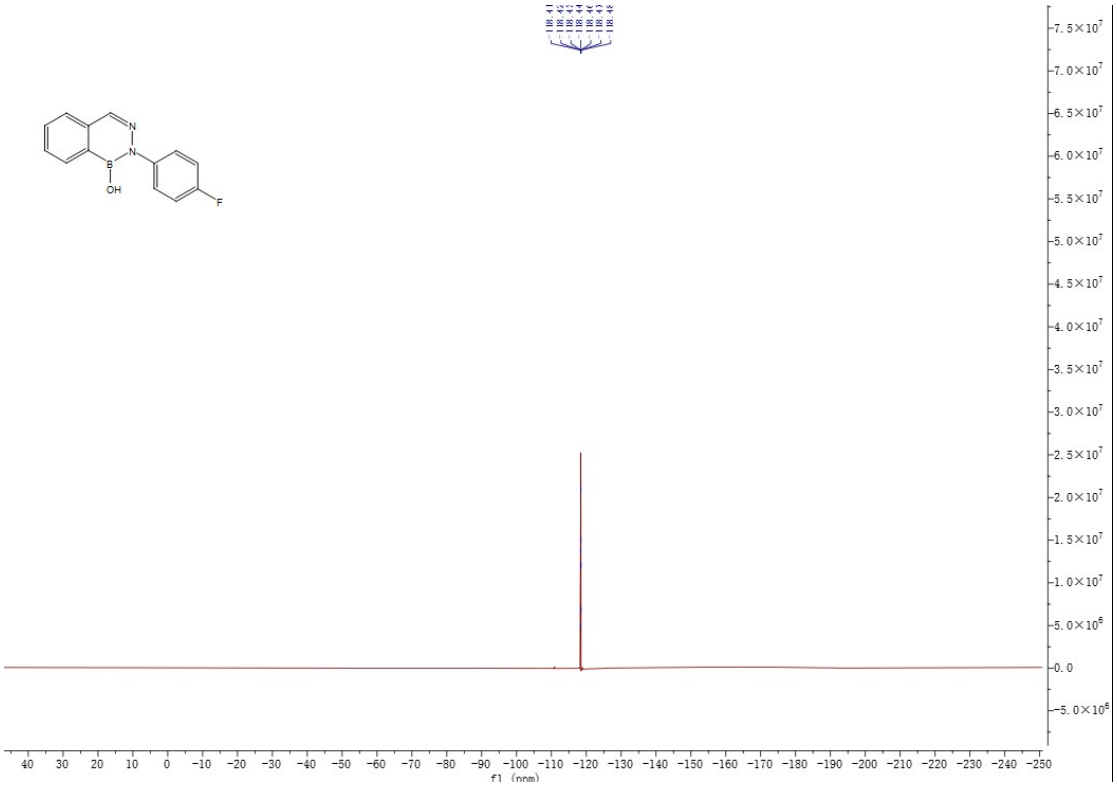

145.41
144.63
130.41
135.49
132.11
131.86
129.41
127.42
126.43
124.96
33.48
24.51
f1 (ppm)

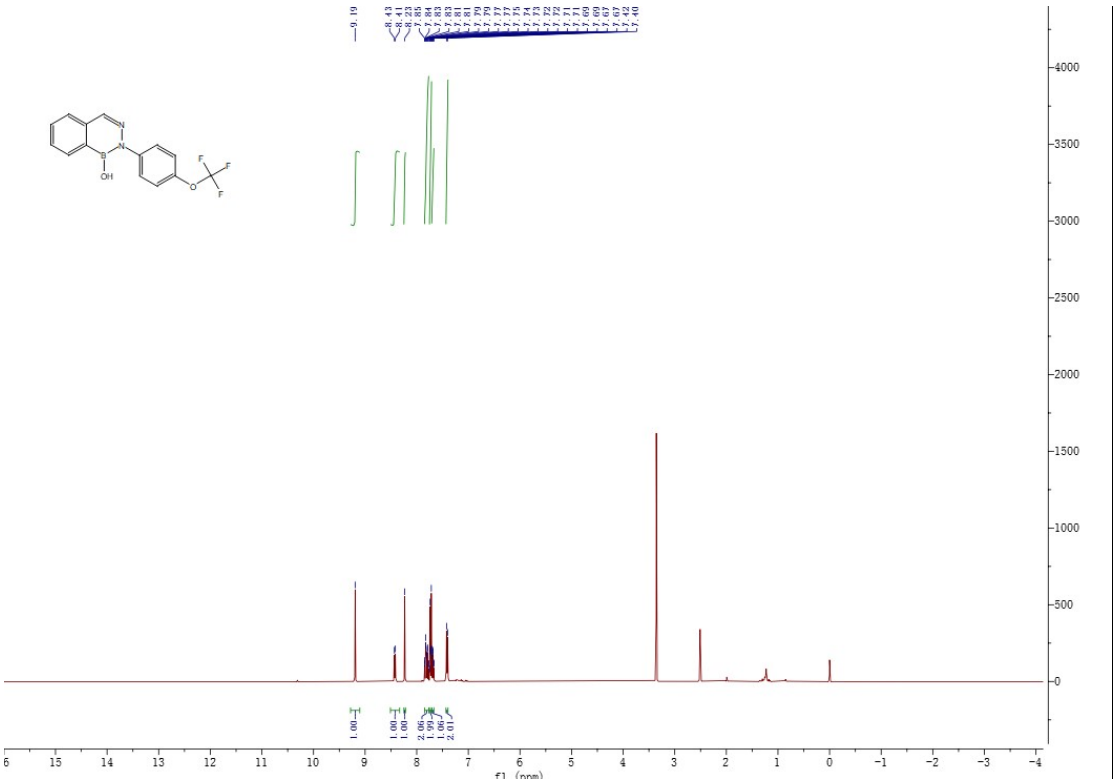

3.79
1.00
1.03
1.02
2.11
2.04
2.10
2.09
3.00
f1 (ppm)

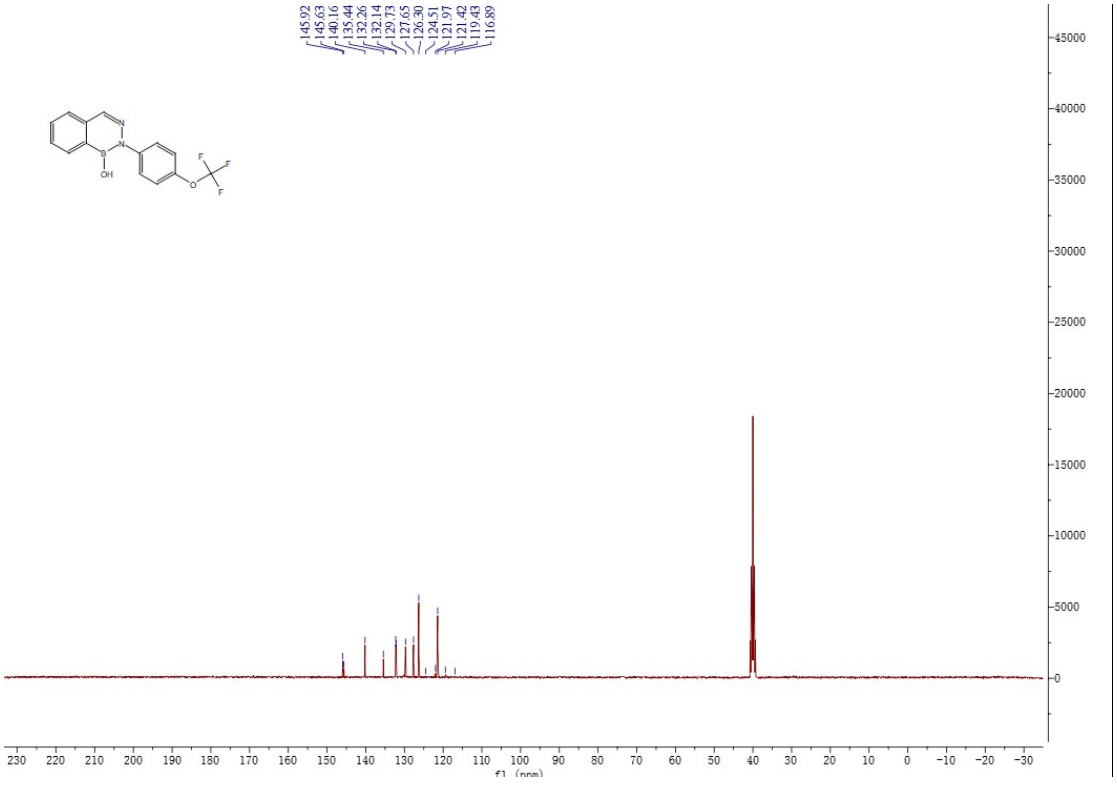

157.11
139.96
139.17
135.51
132.16
131.78
129.34
127.38
126.24
113.82
55.74
OH
O
CH3
f1 (ppm)

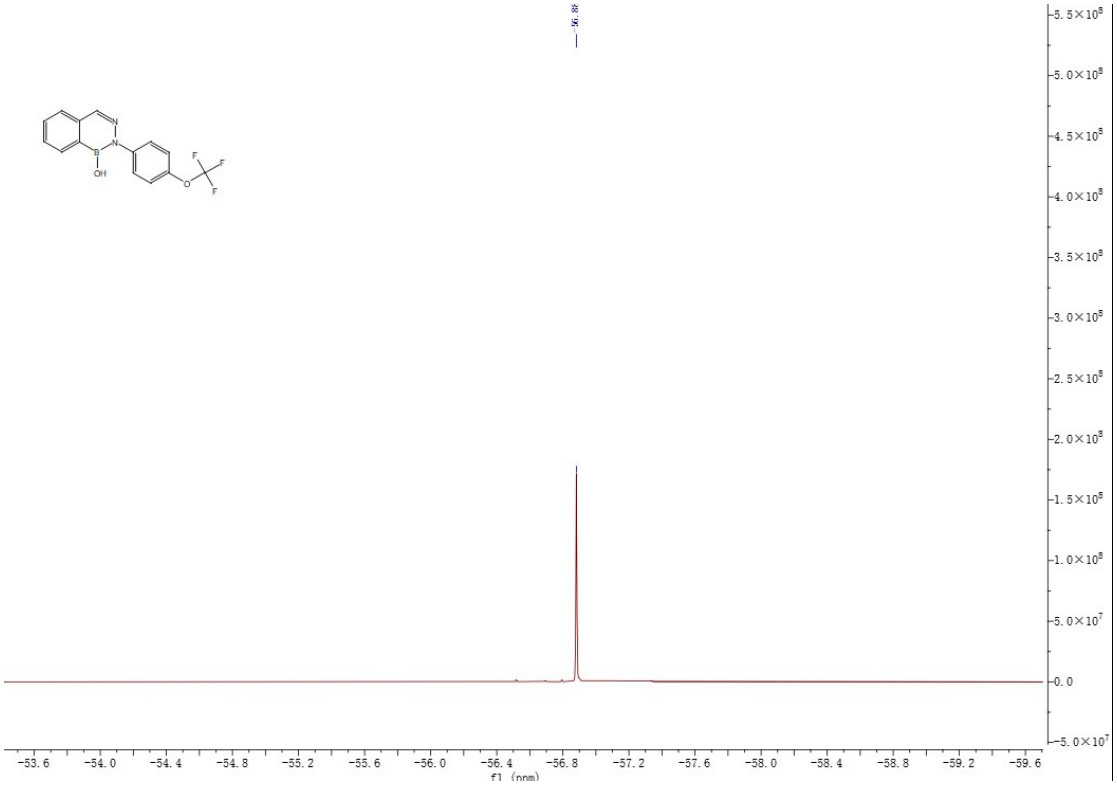

9.02
8.42
8.40
8.39
8.38
7.82
7.80
7.78
7.78
7.76
7.76
7.70
7.68
7.68
7.67
7.66
7.66
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.27
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.21
1.00
1.00
0.98
2.03
2.00
2.06
2.06
OH
F
f1 (ppm)

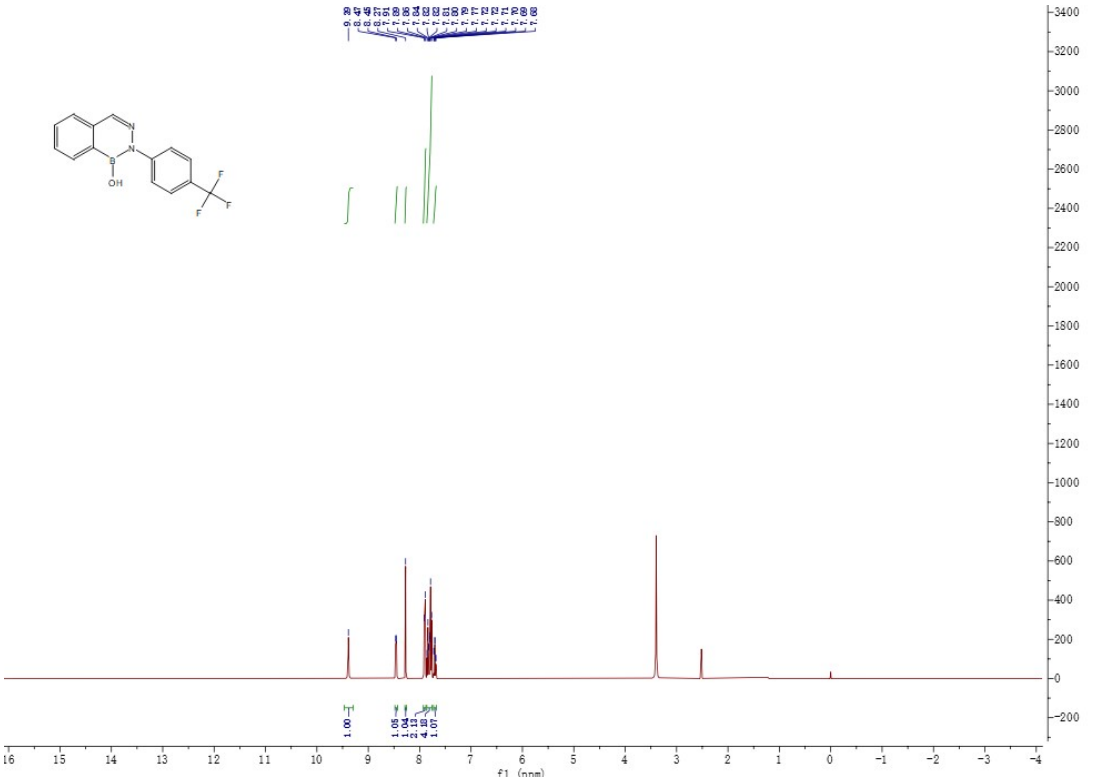

161.18
158.79
143.16
143.13
139.69
135.48
132.15
131.98
129.57
127.54
126.77
126.69
115.35
115.12
N
N
B
OH
F
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


18.41
18.42
18.43
18.44
18.45
18.46
18.47
18.48
N
N
B
OH
F
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)


9.19
8.43
8.41
7.85
7.84
7.83
7.81
7.79
7.77
7.75
7.74
7.73
7.72
7.71
7.69
7.67
7.66
7.42
7.40
1.00
1.00
1.00
2.06
1.99
1.06
2.01
f1 (ppm)


145.92
145.63
140.16
135.44
132.26
132.14
129.73
127.65
126.30
124.51
121.97
121.42
119.43
116.89
f1 (ppm)


-56.88
5.5×10^8
5.0×10^8
4.5×10^8
4.0×10^8
3.5×10^8
3.0×10^8
2.5×10^8
2.0×10^8
1.5×10^8
1.0×10^8
5.0×10^7
0.0
-5.0×10^7
-53.6 -54.0 -54.4 -54.8 -55.2 -55.6 -56.0 -56.4 -56.8 -57.2 -57.6 -58.0 -58.4 -58.8 -59.2 -59.6
f1 (ppm)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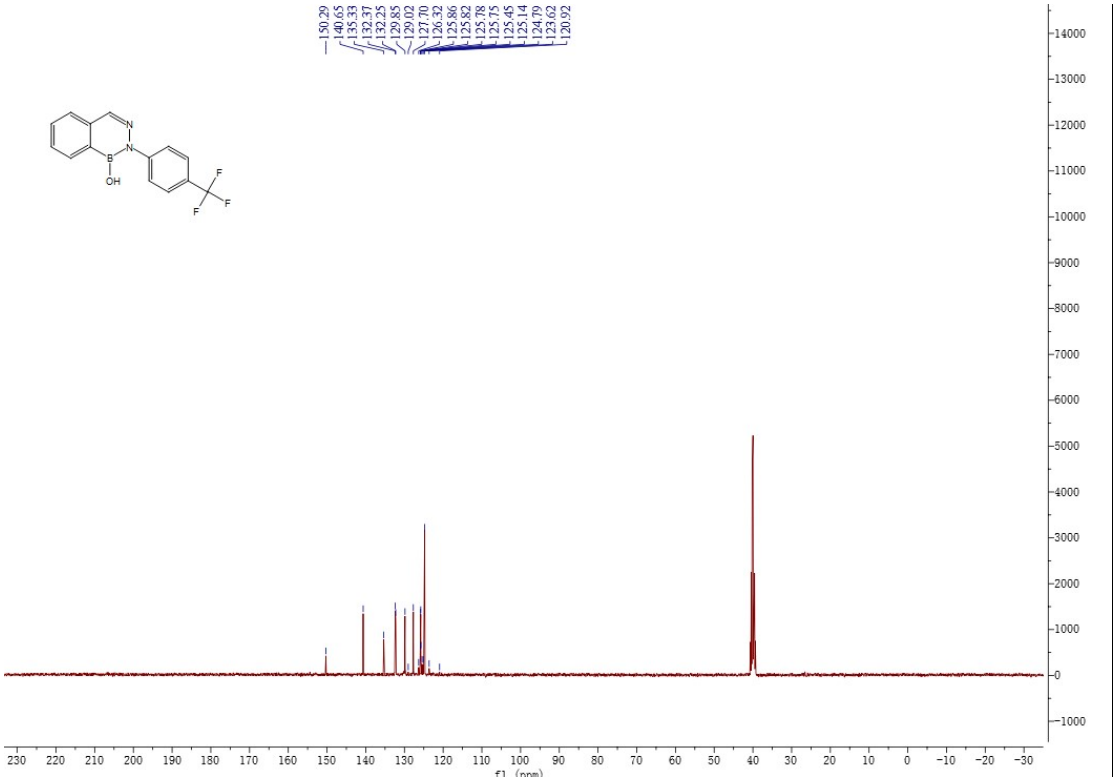
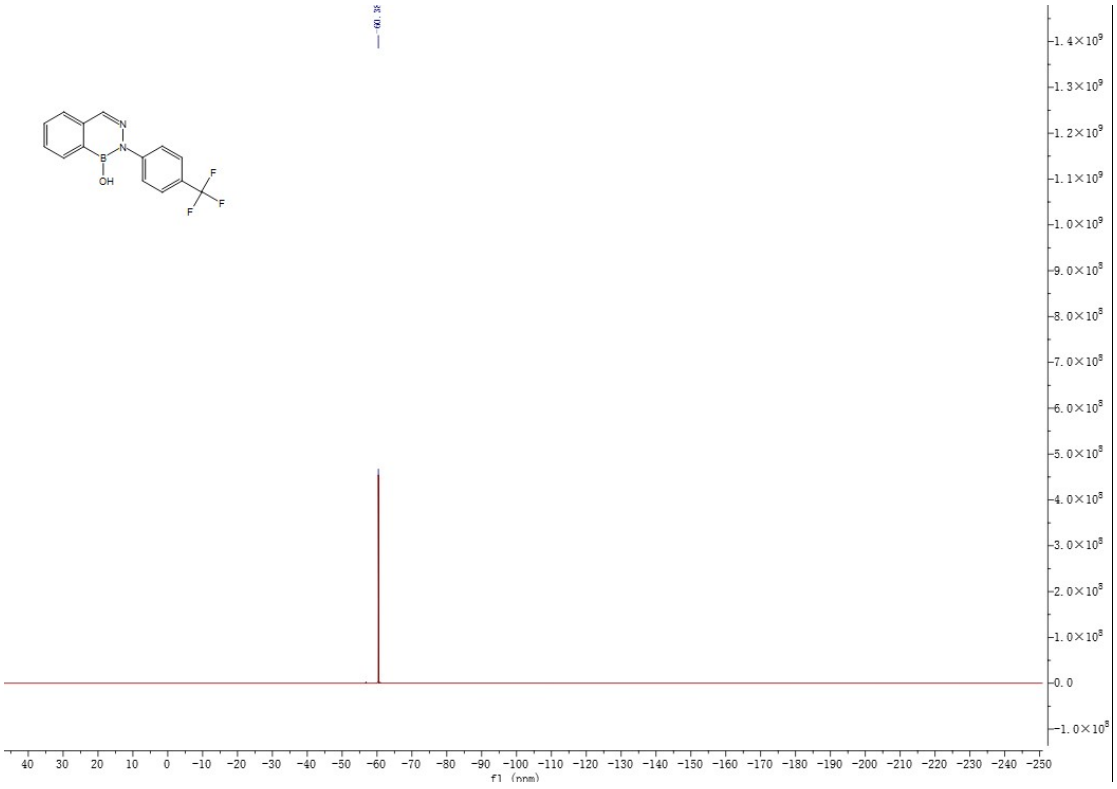
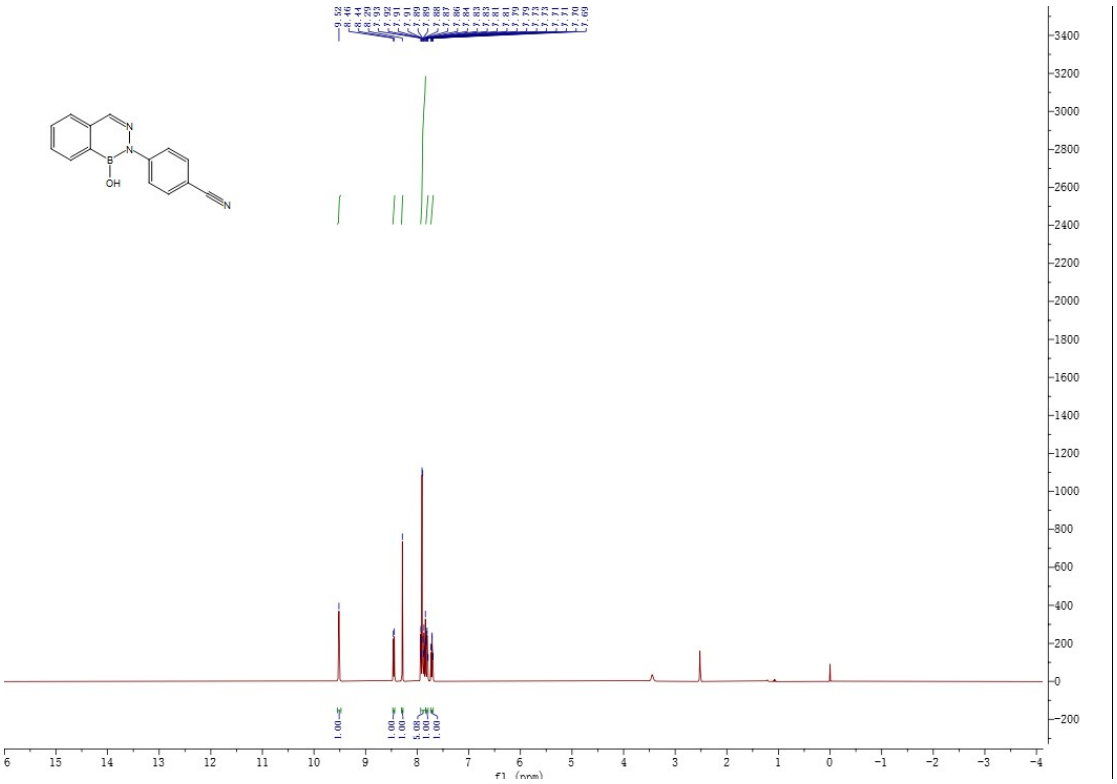
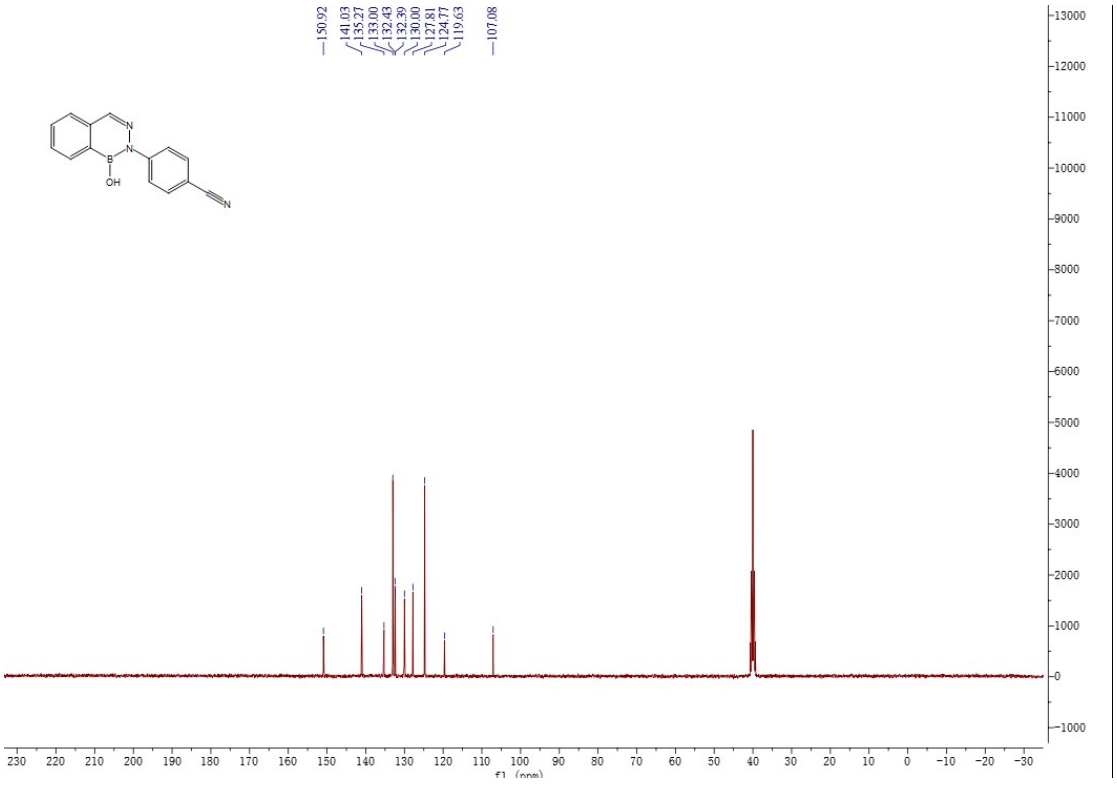
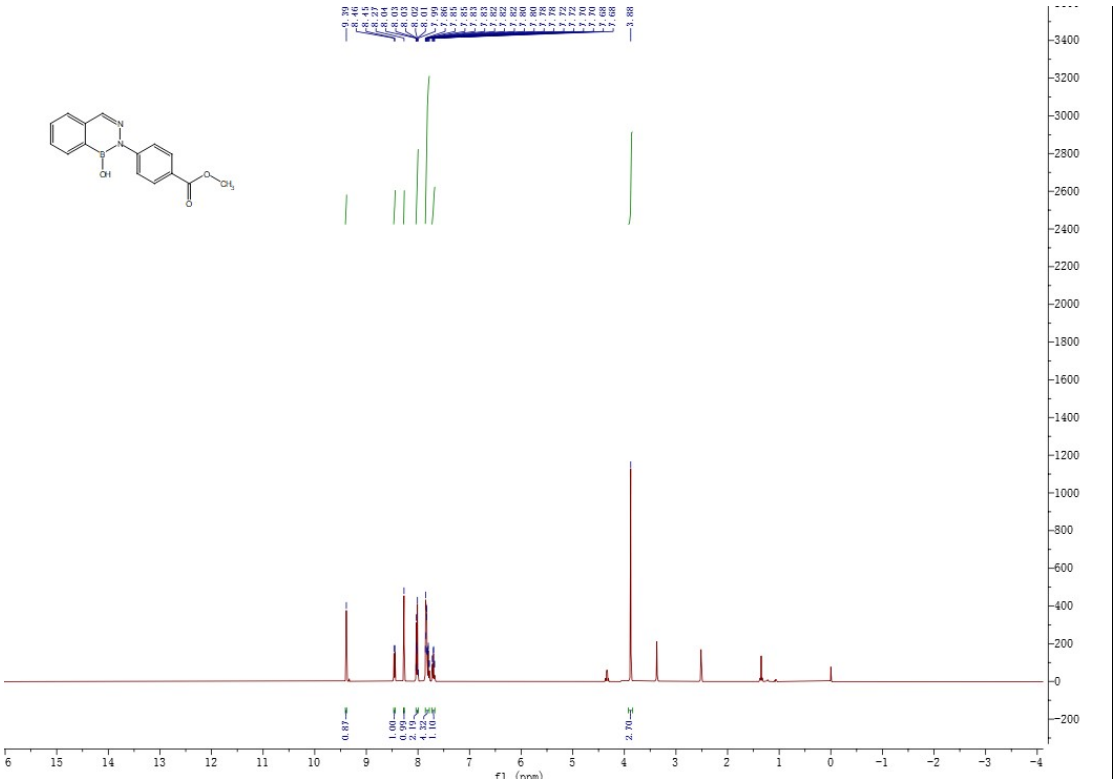
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

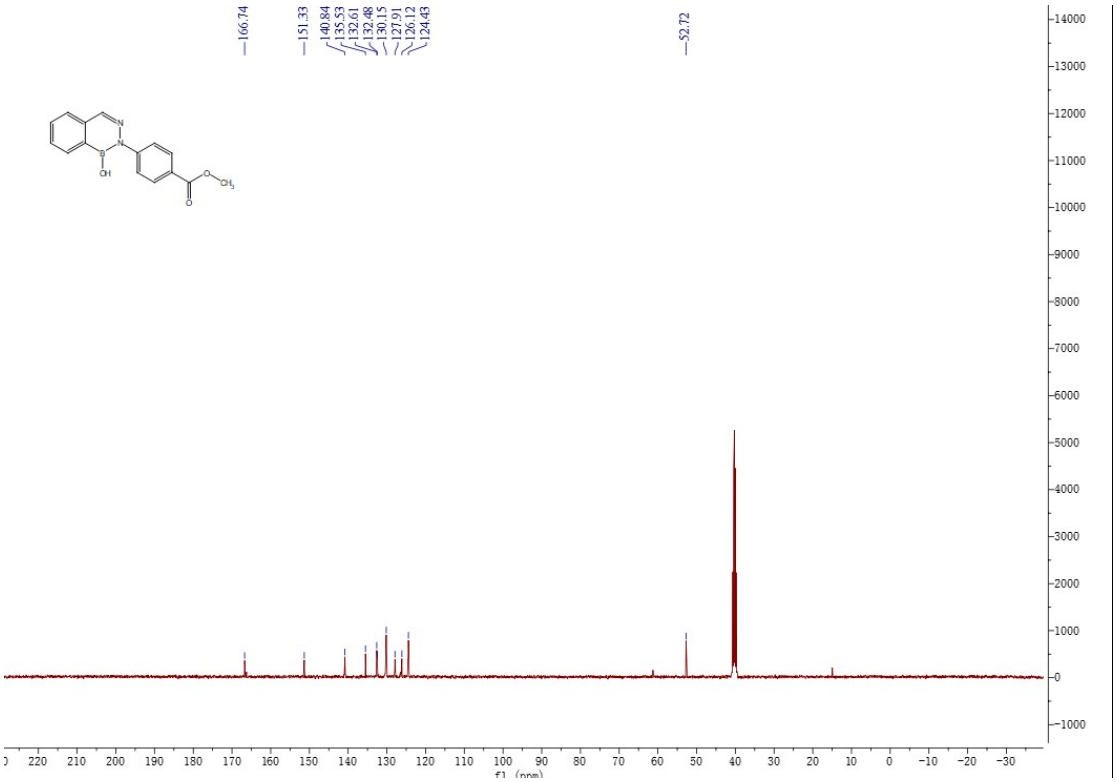

150.29
140.65
135.33
132.37
132.25
129.85
129.02
127.70
126.32
125.86
125.82
125.78
125.75
125.45
125.14
124.79
123.62
120.92
B
OH
N
N
F
F
F

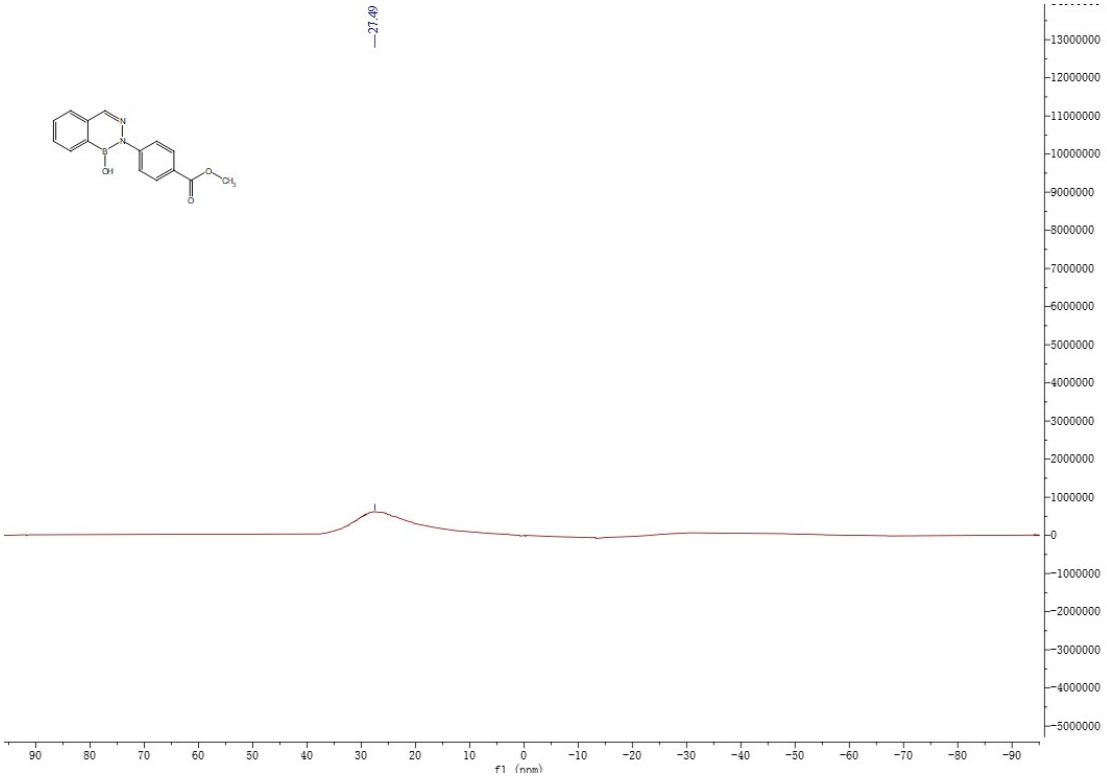

B
OH
N
N
F
F
F










27.49
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12000000
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4000000
3000000
2000000
1000000
0
-1000000
-2000000
-3000000
-4000000
-5000000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)