Supplementary Information

Transition-metal-free, one-pot synthesis of Benzoxaboroles from *o*-bromobenzaldehydes *via* visible-light-promoted borylation

Table of Contents:

1. General information

Column chromatography was generally performed on silica gel (200-300 mesh) using EtOAc-Petroleum 1:5 as the eluent and reactions were monitored by thin layer chromatography visualize the course of the reactions. Other chemicals were purchased from Beijing Ouhe chemical Co. Ltd and used received without further purification. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or d_6-DMSO on a Bruker DRX-400 spectrometer operating at 400 MHz and 151 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, $CDCl_3$= 7.26 ppm, d_6-DMSO= 2.50 ppm. for ^{13}C NMR: $CDCl_3$= 77.00 ppm, d_6-DMSO= 39.95 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d =doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet and br = broad.

2. Setup for photocatalytic reactions

The reaction setup is depicted in **Figure S1.** 3W LED blue lights are available for purchase. During the first experiment the temperature was monitored inside the Schlenk tube and did not exceed the room temperature.

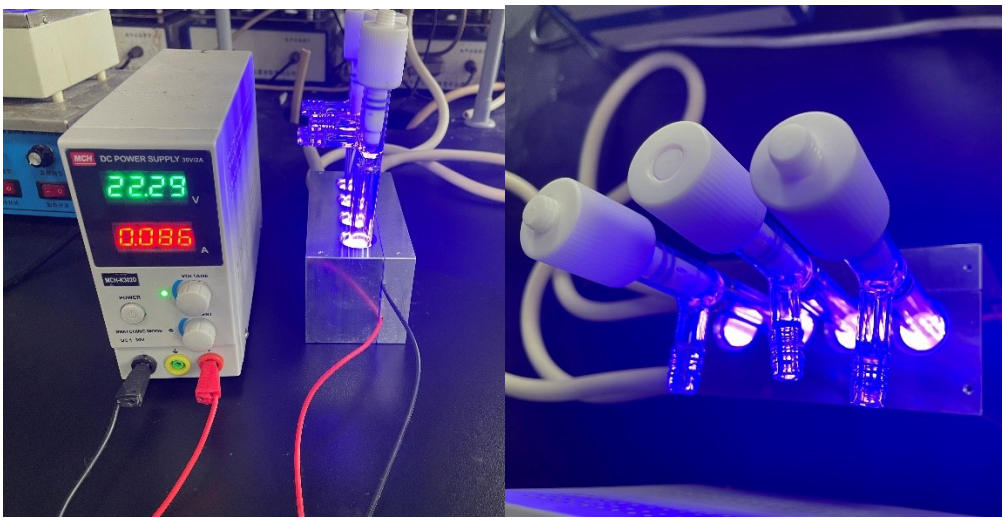
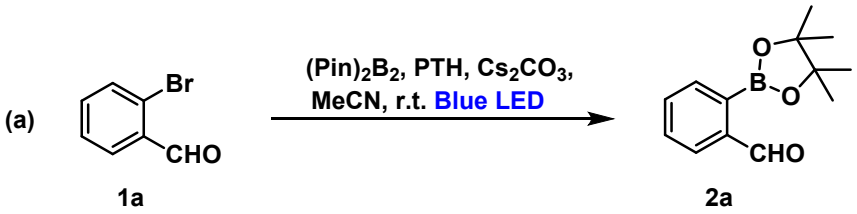
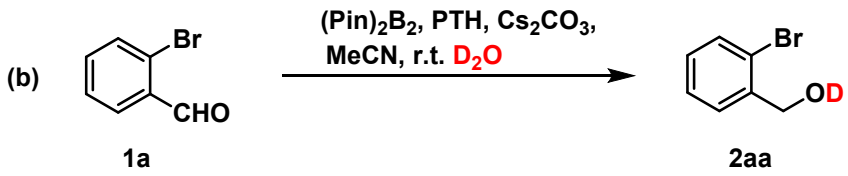


Figure S1. LED reaction setup

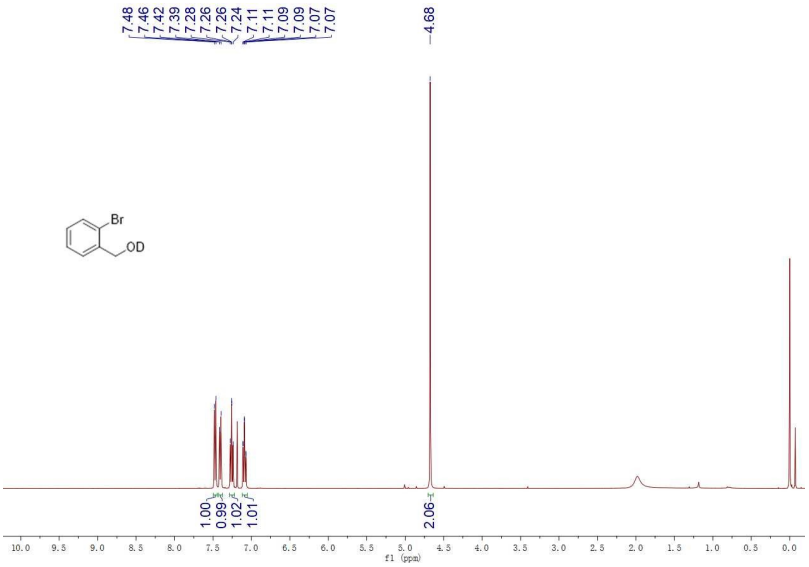
3. Investigation of Mechanism



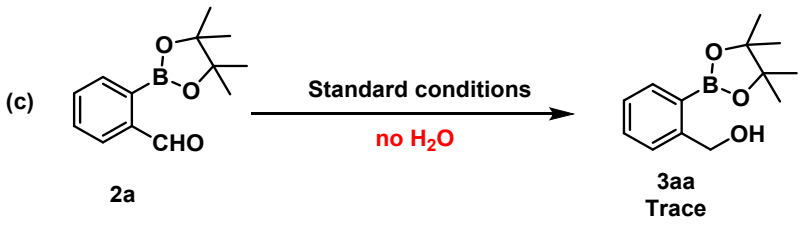
The mixture of 2-bromobenzaldehyde (1a, 0.25 mmol), $(Pin)_2B_2$ (1 mmol, 4 equiv.), PTH (10 mol %), Cs_2CO_3 (0.5 mmol, 2 equiv.) in MeCN (3 mL) was stirred and irradiated with an 3W blue LED at room temperature for 16 h. After the reaction completed (monitored by TLC), Then water (2 mL) was added and the mixture was extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the intermediate products 2a.



The mixture of 2-bromobenzaldehyde (1a, 0.25 mmol), $(Pin)_2B_2$ (1 mmol, 4 equiv.), PTH (10 mol %), Cs_2CO_3 (0.5 mmol, 2 equiv.) in MeCN (2 mL) and D_2O was stirred and irradiated with an 3W blue LED at room temperature for 12 h. After the reaction completed (monitored by TLC), the mixture was extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the products 2aa.



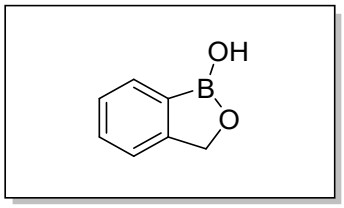
^{1}H-NMR spectrum of 2aa



Through the control reaction (a), we obtained the intermediate products 2a with standard conditions. The mixture of 2-bromobenzaldehyde (1a, 0.25 mmol), $(Pin)_2B_2$ (1 mmol, 4 equiv.), PTH (10 mol %), Cs_2CO_3 (0.5 mmol, 2 equiv.) in MeCN (3 mL) was stirred and irradiated with an 3W blue LED at room temperature for 16 h. After the reaction completed (monitored by TLC), only traces amount of 3aa can be detected without H_2O.

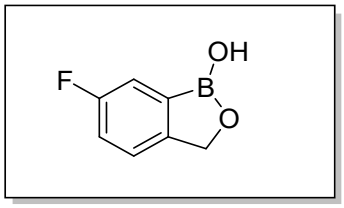
4. Analytical data of the products

Benzo[c][1,2]oxaborol-1(3H)-ol (3a)[1]:



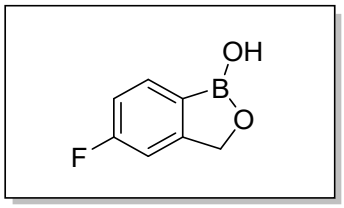
Yield: 55%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ7.83 (d, 1H, Ph-H), 7.53 (m, 1H, Ph-H), 7.42 – 7.38 (m, 2H, Ph-H), 5.18 (s, 2H, CH_2).^{13}C NMR (151 MHz, $CDCl_3$) δ 153.44 (Ph), 153.42 (Ph), 131.12 (Ph), 130.67 (Ph), 127.27 (Ph), 121.11 (Ph), 71.31 (CH_2).

6-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (3b)[1]:



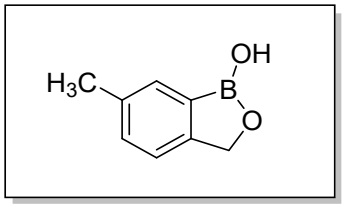
Yield: 53%. White solid.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 - 7.44 (m, 1H, Ph-H), 7.10 (t, *J* = 8.2 Hz, 1H, Ph-H), 6.87 (d, *J* = 8.8 Hz, 1H, Ph-H), 4.28 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.72 (d, *J* = 248.4Hz, Ph), 140.87 (d, *J* = 7.6Hz, Ph), 134.48 (Ph), 131.69 (d, *J* = 8.3Hz, Ph), 116.32 (d, *J* = 21.5Hz, Ph), 115.34 (d, *J* = 20.9Hz, Ph), 61.70 (CH_2).

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



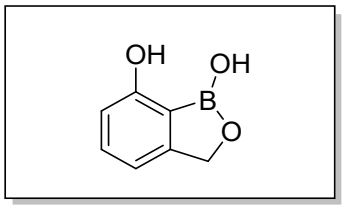
Yield: 55%. White solid.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H, Ph-H), 7.39 (m, 1H, Ph-H), 7.10 – 7.05 (m, 1H, Ph-H), 5.15 (d, 2H, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.77 (d, *J* = 396.8Hz, Ph), 130.88 (d, *J* = 75.1Hz, Ph), 127.27 (Ph), 121.11 (Ph), 115.23 (d, *J* =22.1Hz, Ph), 108.33 (d, *J* = 22.3Hz, Ph), 71.04 (d, *J* = 81.6Hz, CH_2).

6-methylbenzo[c][1,2]oxaborol-1(3H)-ol (3d)[2]:



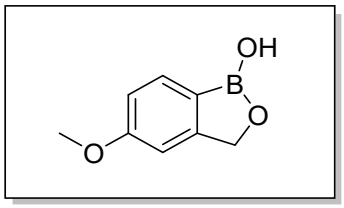
Yield: 68%. White solid.^{1}H NMR (300 MHz, DMSO-d_6) δ 7.42 (d, J = 7.8 Hz, 1H, Ph-H), 7.16 (d, J = 7.7 Hz, 1H, Ph-H), 6.84 (s, 1H, Ph-H), 4.15 – 4.05 (m, 2H, CH_2), 2.29 (s, 3H, CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 142.57 (Ph), 138.70 (Ph), 129.61 (Ph), 119.12 (Ph), 113.28 (Ph), 112.25 (Ph), 55.24 (CH_2),24.84 (CH_3).

Benzo[c][1,2]oxaborole-1,7(3H)-diol (3e)[2]:



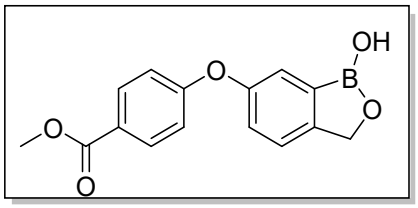
Yield: 56%. White solid.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, J = 7.8 Hz, 1H, Ph-H), 6.90 (d, J = 8.8 Hz, 2H, Ph-H), 6.80 – 6.78 (m, 1H, Ph-H), 4.66 (s, 2H, CH_2).^{13}C NMR (151 MHz, $CDCl_3$) δ 156.12 (Ph), 142.48 (Ph), 129.83 (Ph), 119.02 (Ph), 114.74 (Ph), 113.87 (Ph), 65.07 (CH_2).

5-methoxybenzo[c][1,2]oxaborol-1(3H)-ol (3f)[1]:



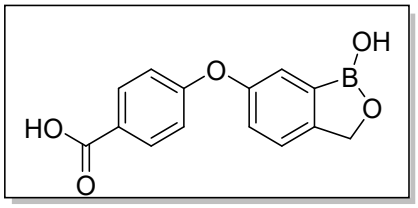
Yield: 63%. White solid.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (m, 2H, Ph-H), 6.88 (m, 1H, Ph-H), 4.36 – 4.29 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 159.16 (Ph), 140.46 (Ph), 131.82 (Ph), 131.20 (Ph), 114.19 (Ph), 113.28 (Ph), 62.97 (CH_2), 55.33 (CH_3).

Methyl 4-((1-hydroxy-1,3-dihydrobenzo[c][1,2]oxaborol-6-yl)oxy)benzoate (3g)[3]:



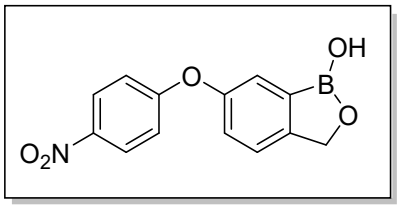
Yield: 54%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.30 (s, 1H, OH), 7.97 (d, J = 8.7 Hz, 2H, Ph-H), 7.55 -7.42 (m, 2H, Ph-H), 7.27 (dd, J = 8.2, 2.2 Hz, 1H, Ph-H), 7.05 (d, J = 8.7 Hz, 2H, Ph-H), 5.01 (s, 2H, CH_2), 3.83 (s, 3H, CH_3). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.13 (Ph), 162.22 (Ph), 154.54 (Ph), 150.57 (Ph), 132.02 (Ph), 124.29 (Ph), 123.85 (Ph), 123.56 (Ph), 121.99 (Ph), 117.58 (Ph), 70.19 (CH_2), 52.46 (CH_3).

4-((1-hydroxy-1,3-dihydrobenzo[c][1,2]oxaborol-6-yl)oxy)benzoic acid (3h)[3]:



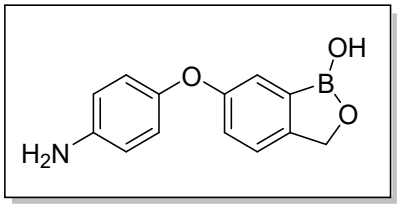
Yield: 54%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.95 (dd, *J* = 5.4, 3.2 Hz, 2H, Ph-H), 7.50 (d, *J* = 8.2 Hz, 1H, Ph-H), 7.42 (s, 1H, Ph-H), 7.27 (d, *J* = 8.2 Hz, 1H, Ph-H), 7.04 (d, *J* = 8.7 Hz, 2H, Ph-H), 5.01 (s, 2H, CH_2). ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.21 (Ph), 161.80 (Ph), 154.89 (Ph), 150.37 (Ph), 132.14 (Ph), 125.63 (Ph), 123.84 (Ph), 123.45 (Ph), 121.44 (Ph), 117.66 (Ph), 70.21 (CH_2).

6-(4-nitrophenoxy)benzo[c][1,2]oxaborol-1(3H)-ol (3i)[4]:



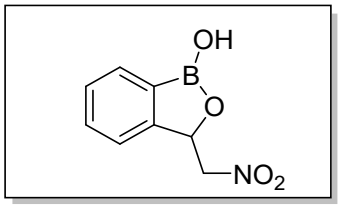
Yield: 17%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.30 (s, 1H, OH), 8.35 – 8.15 (m, 2H, Ph-H), 7.60 – 7.43 (m, 2H, Ph-H), 7.32 (dd, *J* = 8.2, 2.1 Hz, 1H, Ph-H), 7.21 – 7.07 (m, 2H, Ph-H), 5.03 (s, 2H, CH_2). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.67 (Ph), 154.00 (Ph), 151.19 (Ph), 142.64 (Ph), 126.64 (Ph), 124.10 (Ph), 123.80 (Ph), 122.11 (Ph), 117.78 (Ph), 70.25 (CH_2).

6-(4-aminophenoxy)benzo[c][1,2]oxaborol-1(3H)-ol (3j)[4]:



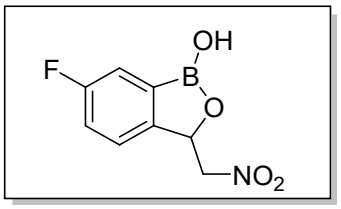
Yield: 37%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.12 – 9.10 (m, 1H, OH), 7.45 – 7.25 (m, 1H, Ph-H), 7.24 – 7.00 (m, 2H, Ph-H), 6.88 – 6.56 (m, 4H, Ph-H), 5.00 – 4.88 (m, 4H, NH_2,CH_2). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.81 (Ph), 147.58 (Ph), 146.40 (Ph), 145.85 (Ph), 123.04 (Ph), 121.35 (Ph), 120.71 (Ph), 117.46 (Ph), 115.41 (Ph), 70.03 (CH_2).

3-(nitromethyl)benzo[c][1,2]oxaborol-1(3H)-ol (4a)[5]:



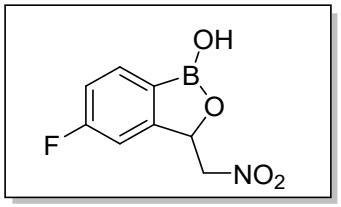
Yield: 48%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.94 (s, 1H, OH), 7.03-7.01 (m, 2H, Ph-H), 6.96-6.92 (m, H, Ph-H), 6.85-6.77 (m, 1H, Ph-H), 5.34-5.28 (m, 1H, CH), 487 (m,2H, CH_2),.^{13}C NMR (151 MHz, $CDCl_3$) δ 142.02 (Ph), 139.79 (Ph), 130.69 (Ph), 130.05 (Ph), 128.99 (Ph), 128.00 (Ph), 68.93 (CH), 63.97 (CH_2).

4-chloro-3-(nitromethyl)benzo[c][1,2]oxaborol-1(3H)-ol (4b):



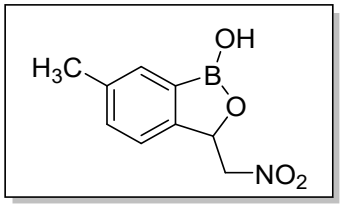
Yield: 42%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.21-7.16 (m, 1H, Ph-H), 7.03-7.00 (m, 1H, Ph-H), 6.95-6.93 (m, 1H, Ph-H), 5.95-5.55 (m, 1H, CH), 4.79-4.74 (m, 1H, CH_2), 4.42-4,32 (m, 1H, CH_2).^{13}C NMR (151 MHz, $CDCl_3$) δ 162.65 (Ph), 141.48 (Ph), 134.61 (Ph), 126.83 (Ph), 116.62 (Ph), 115.66 (Ph), 70.78 (CH), 67.92 (CH_2). HRMS (ESI) m/z calcd for $C_8H_7BFNO_4$ $[M+H]^+$: 212.0452, found 212.0455.

5-fluoro-3-(nitromethyl)benzo[c][1,2]oxaborol-1(3H)-ol (4c):



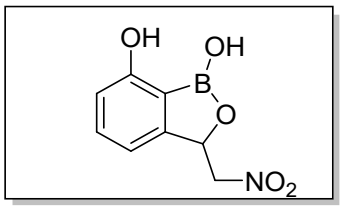
Yield: 46%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ7.51-7.49 (m, 2H, Ph-H), 7.46-7.34 (m, 1H, Ph-H), 5.26-5.23 (m, 1H, CH), 4.78-4.76 (m, 1H, CH_2), 4.66-4.64 (m, 1H, CH_2).^{13}C NMR (151 MHz, DMSO-d_6) δ 162.45 (d, J = 250.2Hz, Ph), 141.04 (d, J = 9.0Hz, Ph), 131.59 (Ph), 130.63 (Ph), 115.52 (d, J = 8.3Hz, Ph), 112.51 (d, J = 8.3Hz, Ph), 70.53 (CH), 66.79 (d, J = 80.3Hz, CH_2). HRMS (ESI) m/z calcd for $C_8H_7BFNO_4$ $[M+H]^+$: 212.0452, found 212.0457.

6-methyl-3-(nitromethyl)benzo[c][1,2]oxaborol-1(3H)-ol (4d):



Yield: 49%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.21-7.16 (m, 1H, Ph-H), 7.02 (m, 1H, Ph-H), 6.94 (m, 1H, Ph-H), 5.59-5.55 (m, 1H, CH), 4.79-4.74 (m, 1H, CH_2) , 4.42-4.32 (m, 1H, CH_2), 1.77 (s, 3H, Ph-CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 159.87 (Ph), 158.46 (Ph), 132.46 (Ph), 131.03 (Ph), 117.80 (Ph), 114.95 (Ph), 75.11 (CH), 55.56 (CH_2), 24.82 (CH_3). HRMS (ESI) m/z calcd for $C_9H_{10}BNO_4$ $[M+H]^+$: 208.0703, found 208.0700.

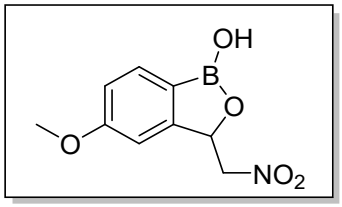
3-(nitromethyl)benzo[c][1,2]oxaborole-1,7(3H)-diol (4e):



Yield: 48%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H, OH), 7.47 (s, 1H, Ph-H), 7.37 (s, 1H, Ph-H), 7.15 (s, 1H, Ph-H), 5.09 (m, 1H, CH), 4.68 (m, 1H, CH_2), 4.34 (m, 1H, CH_2).^{13}C NMR (151 MHz, $CDCl_3$) δ 156.37 (Ph), 137.91 (Ph), 130.38

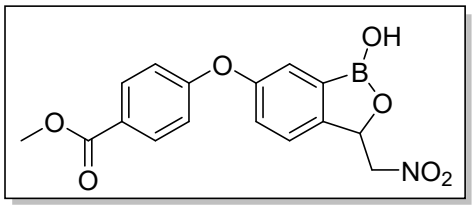
(Ph), 123.37 (Ph), 121.93 (Ph), 114.75 (Ph), 70.18 (CH), 58.06 (CH_2). HRMS (ESI) m/z calcd for $C_8H_8BNO_5$ $[M+H]^+$: 210.0496, found 210.0498.

5-methoxy-3-(nitromethyl)benzo[c][1,2]oxaborol-1(3H)-ol (4f):



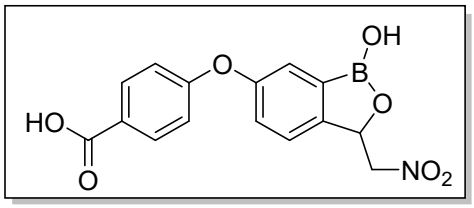
Yield: 43%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ8.87 – 8.83 (m, 1H, Ph-H), 8.28-8.23 (d, J = 7.5 Hz, 1H, Ph-H), 7.77-7.74 (d, J = 7.9 Hz, 1H, Ph-H), 5.72 (m, 1H, CH), 5.13 (m, 1H, CH_2), 4.79 – 4.71 (m, 1H, CH_2), 1.77 (s, 3H, CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 157.78 (Ph), 137.55 (Ph), 131.69 (Ph), 130.40 (Ph), 117.13 (Ph), 114.28 (Ph), 70.04 (CH), 67.10 (CH_2),54.85 (OCH_3). HRMS (ESI) m/z calcd for $C_9H_{10}BNO_5$ $[M+H]^+$: 224.0653, found 224.0657.

Methyl-4-((1-hydroxy-3-(nitromethyl)-1,3-dihydrobenzo[c][1,2]oxaborol-6-yl)oxy)benzoate (4g):



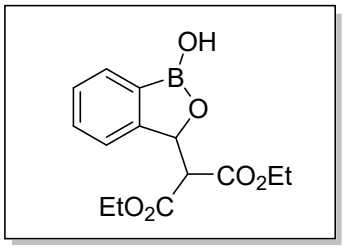
Yield: 40%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.96 -7.91 (m, 3H, Ph-H), 7.17 - 7.08 (m, 2H, Ph-H), 7.03 - 6.94 (m, 2H, Ph-H), 5.24 - 5.21 (m, 1H, CH), 4.81-4.75 (m, 1H, CH_2), 4.27 – 4.19 (m, 1H, CH_2), 3.82 (s, 3H, CH_3). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.68 (Ph), 161.25 (Ph), 161.03 (Ph), 136.97 (Ph), 134.46 (Ph), 132.60 (Ph), 129.72 (Ph), 128.09 (Ph), 127.19 (Ph), 115.41 (Ph), 114.91 (Ph), 70.46 (CH), 66.86 (CH_2), 57.60 (CH_3). HRMS (ESI) m/z calcd for $C_{16}H_{14}BNO_7$ $[M+H]^+$: 344.0863, found 344.0860.

4-((1-hydroxy-3-(nitromethyl)-1,3-dihydrobenzo[c][1,2]oxaborol-6-yl)oxy)benzoic acid (4h):



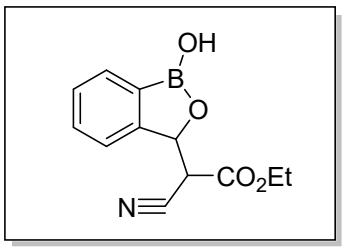
Yield: 43%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.83 (s, 1H, COOH), 9.52(s, 1H, OH), 7.97 – 7.95 (m, 2H, Ph-H), 7.65 – 7.64 (m, 1H, Ph-H), 7.39 – 7.33 (m, 2H, Ph-H), 7.05 – 7.03 (m, 2H, Ph-H), 5.98 – 5.73 (m, 1H, CH), 5.50 – 5.35 (m, 1H, CH_2), 4.74 – 4.61 (m, 1H, CH_2). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.19 (COOH), 161.71 (Ph), 151.86 (Ph), 148.79 (Ph), 135.46 (Ph), 130.51 (Ph), 128.17 (Ph), 126.34 (Ph), 125.89 (Ph), 118.46 (Ph), 115.62 (Ph), 75.75 (CH), 70.44 (CH_2). HRMS (ESI) m/z calcd for $C_{15}H_{12}BNO_7$ $[M+H]^+$: 330.0707, found 330.0711.

Diethyl 2-(1-hydroxy-1,3-dihydrobenzo[c][1,2]oxaborol-3-yl)malonate (4i)[6]:



Yield: 26%. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.57 (s, 1H, OH), 7.68 – 7.52 (m, 2H, Ph-H), 7.45-7.40 (m, 2H, Ph-H), 4.99 (s, 1H, CH), 4.37 (m, 2H, CH_2), 4.24 (m, 2H, CH_2), 3.39 (s, 1H, CH), 1.42 (m, 6H, CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.35 (CO), 169.49 (CO), 135.48 (Ph), 133.01 (Ph), 130.75 (Ph), 128.19 (Ph),127.92 (Ph), 125.00 (Ph), 72.25 (CH), 62.49 (CH_2), 61.32 (CH_2), 41.20 (CH), 14.05 (CH_3).

Ethyl-2-cyano-2-(1-hydroxy-1,3-dihydrobenzo[c][1,2]oxaborol-3-yl)acetate (4j)[6]:



Yield: 31%. White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.78 (m, 1H, Ph-H), 7.60 (m, 1H, Ph-H), 7.48 (m, 1H, Ph-H), 7.31 (m, 1H, Ph-H),5.13 (s, 1H, CH), 4.04 (m, 1H, CH_2), 3.17 (m, 1H, CH), 1.07 (m, 3H, CH_3).^{13}C NMR (300 MHz, DMSO-d_6) δ 164.17 (CO), 141.190 (Ph), 135.62 (Ph), 131.43 (Ph), 128.89 (Ph), 128.26 (Ph), 124.30 (Ph), 117.19 (CN), 74.04 (CH), 65.77 (CH_2), 45.29 (CH), 15.34 (CH_3).

5. References

1. S. J. Baker, Y.-K. Zhang, T. Akama, A. Lau, H. Zhou, V. Hernandez, W. Mao, M. R. K. Alley, V. Sanders and J. J. Plattner, *J Med Chem*, 2006, **49**, 4447-4450.
2. J. F. Cairns and H. R. Snyder, *J Org Chem*, 1964, **29**, 2810-2812.
3. Y. K. Zhang, J. J. Plattner, E. E. Easom, R. T. Jacobs, D. Guo, V. Sanders, Y. R. Freund, B. Campo, P. J. Rosenthal, W. Bu, F. J. Gamo, L. M. Sanz, M. Ge, L. Li, J. Ding and Y. Yang, *J Med Chem*, 2015, **58**, 5344-5354.
4. T. Akama, C. Dong, C. Virtucio, D. Sullivan, Y. Zhou, Y. K. Zhang, F. Rock, Y. Freund, L. Liu, W. Bu, A. Wu, X. Q. Fan and K. Jarnagin, *J Pharmacol Exp Ther*, 2013, **347**, 615-625.
5. A. B. Shapiro, N. Gao, L. Hajec and D. C. McKinney, *Anal Biochem*, 2012, **431**, 48-53.
6. J. Sravan Kumar, M. A. Alam, S. Gurrapu, G. Nelson, M. Williams, M. A. Corsello, J. L. Johnson, S. C. Jonnalagadda and V. R. Mereddy, *J Heterocyclic Chem*, 2013, **50**, 814-820.

6. Spectrum

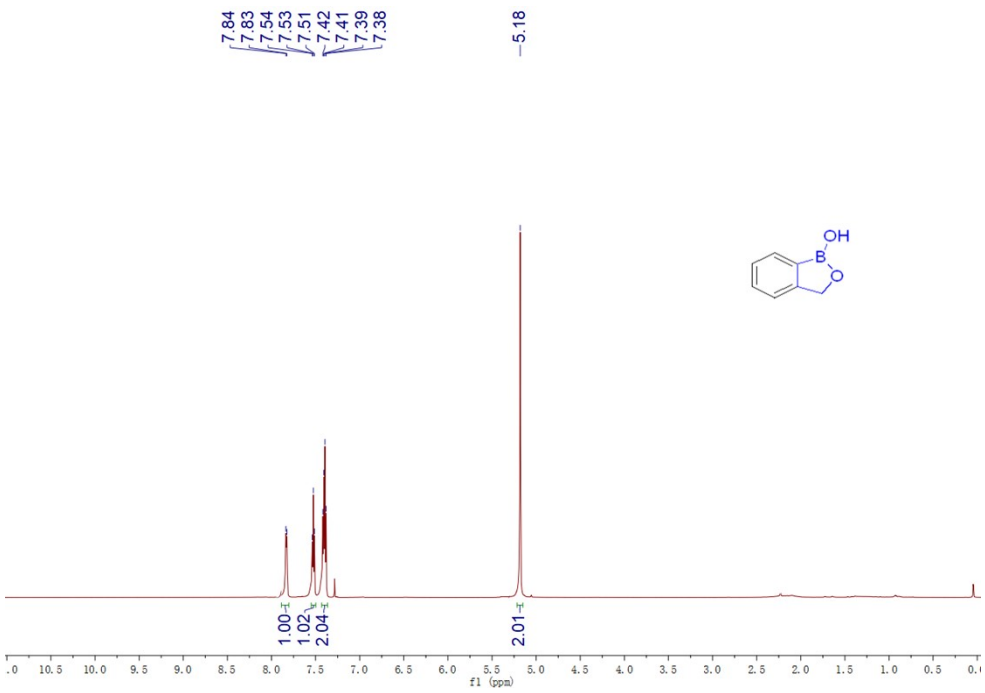


Figure S2. ^{1}H-NMR spectrum of 3a

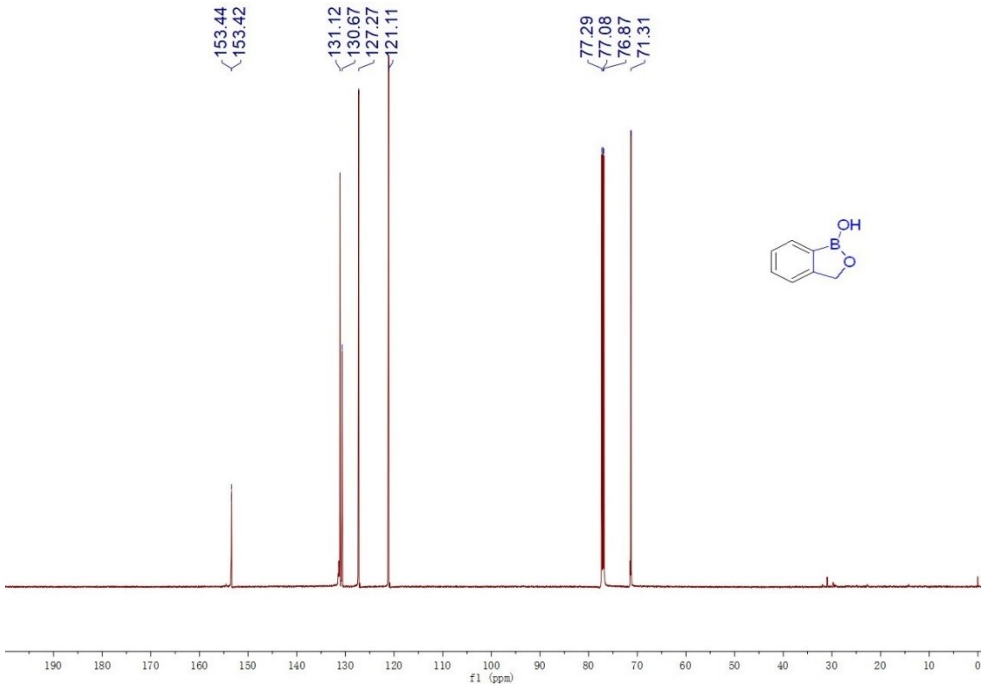


Figure S3. ^{13}C-NMR spectrum of 3a

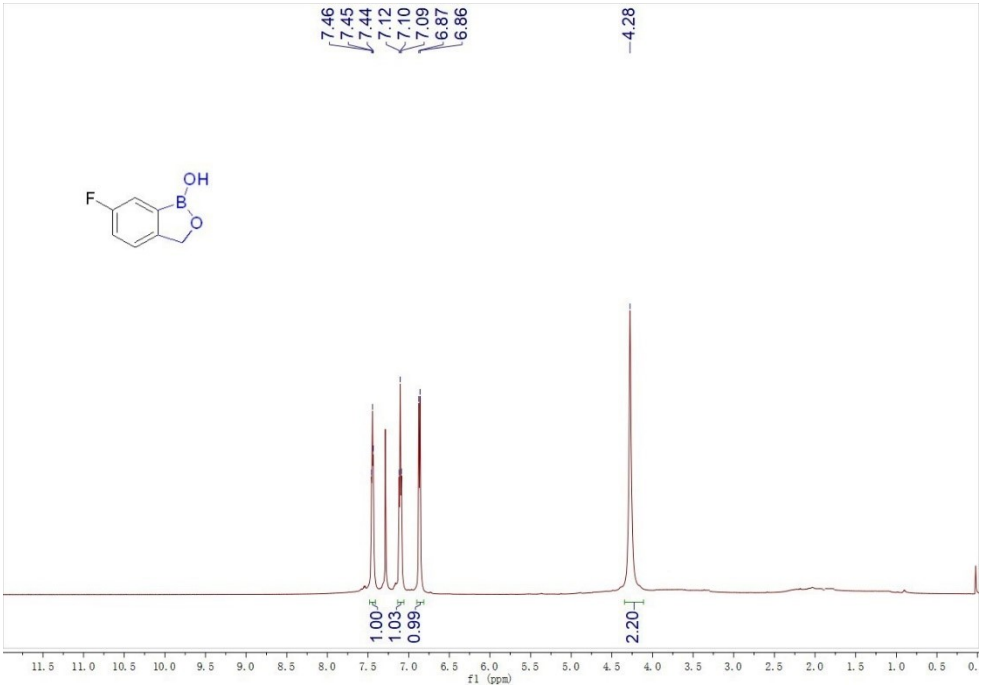


Figure S4. ^{1}H-NMR spectrum of 3b

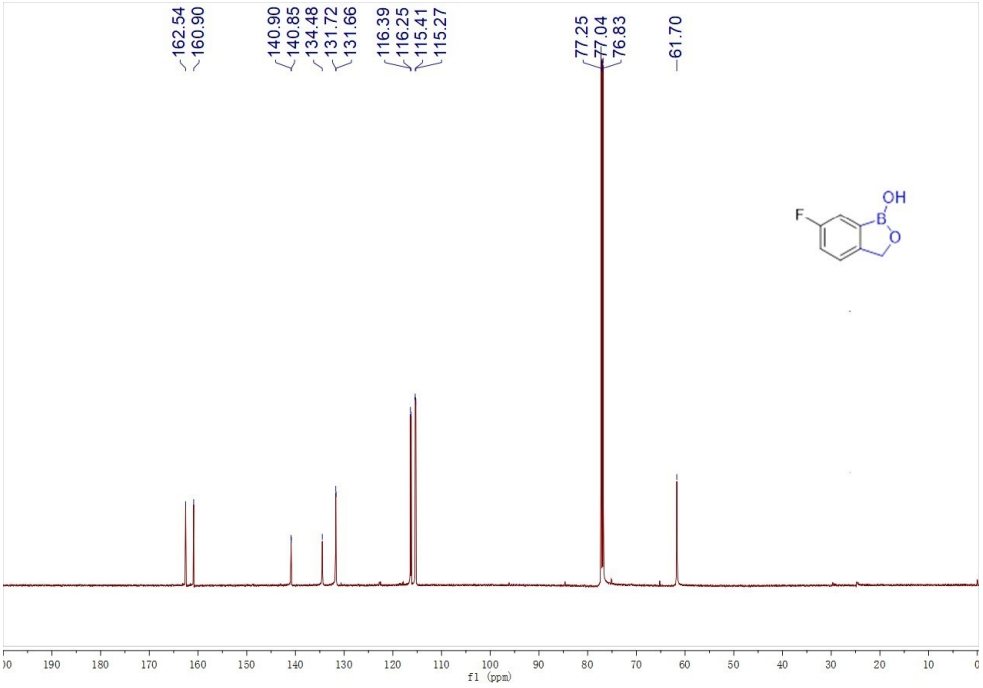


Figure S5. ^{13}C-NMR spectrum of 3b

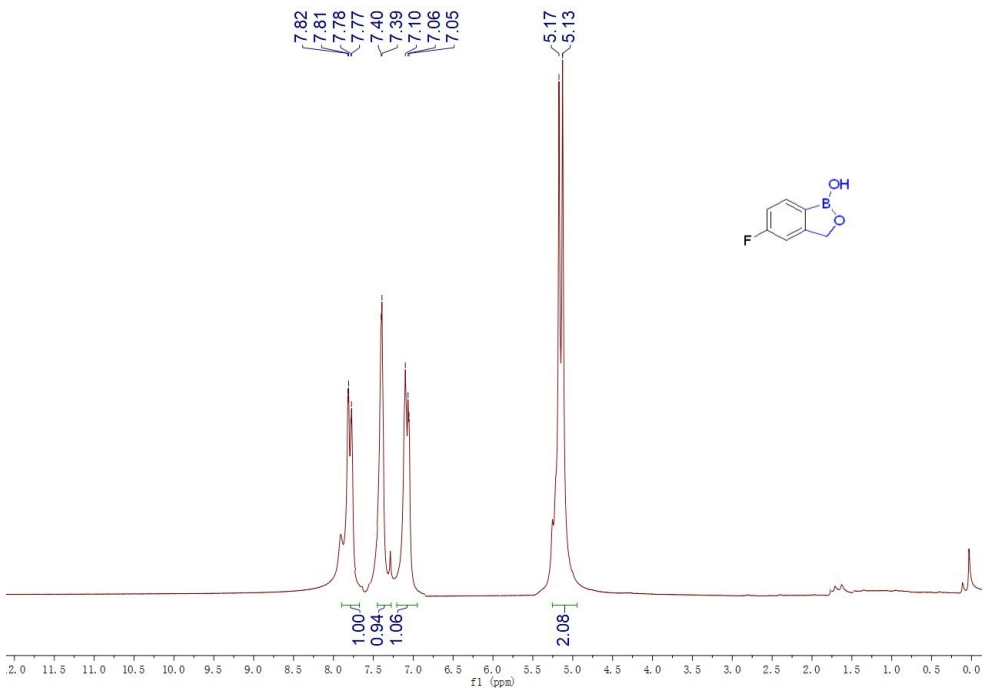


Figure S6. ^{1}H-NMR spectrum of 3c

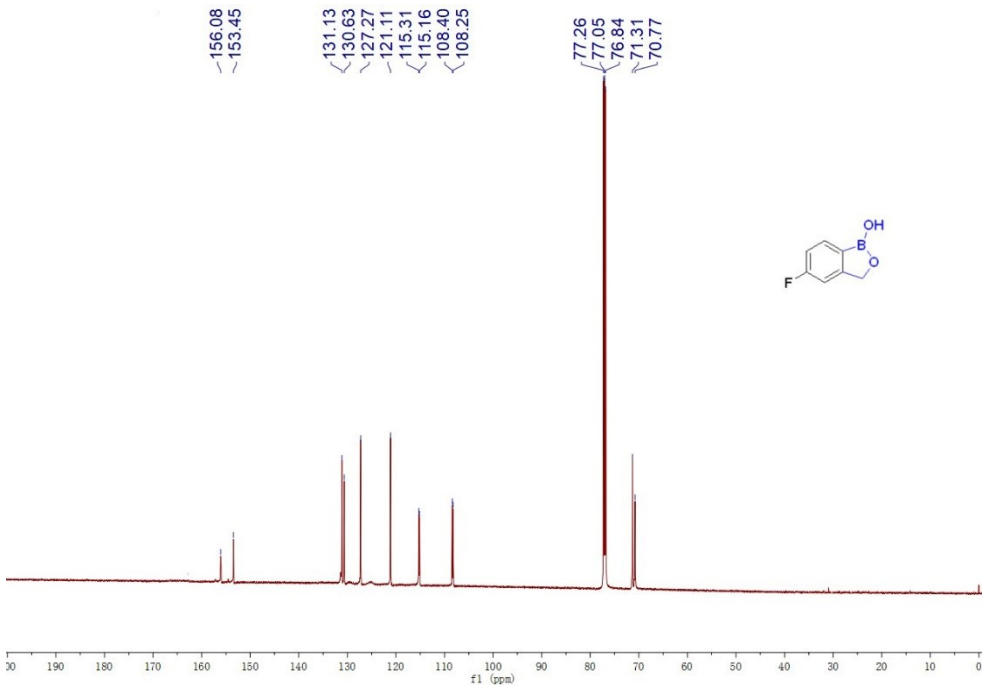


Figure S7. ^{13}C-NMR spectrum of 3c

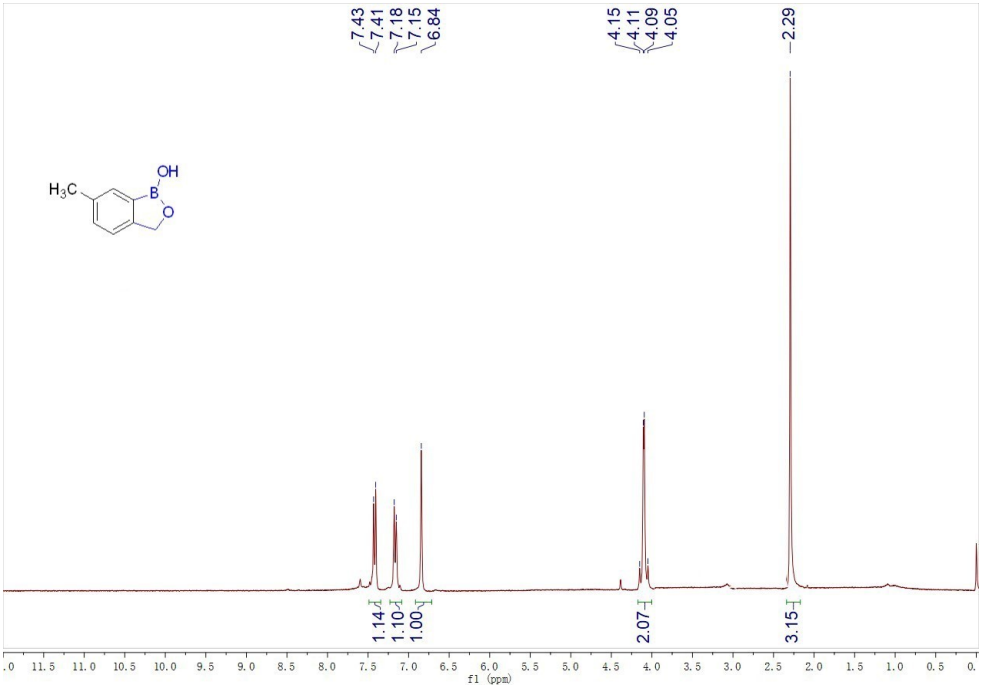


Figure S8. ^{1}H-NMR spectrum of 3d

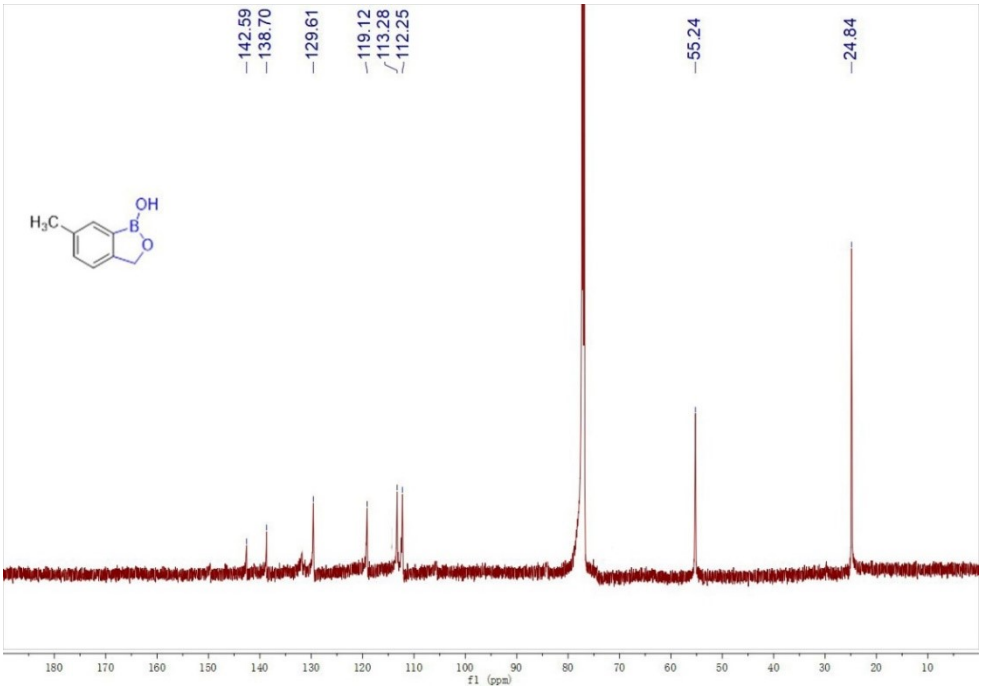


Figure S9. ^{13}C-NMR spectrum of 3d

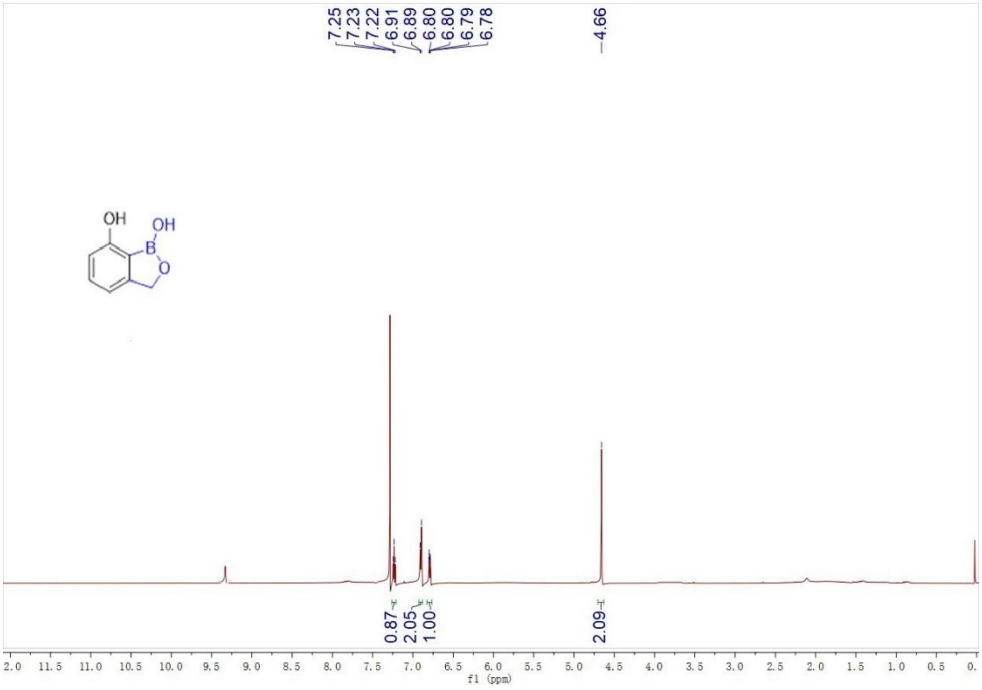


Figure S10. ^{1}H-NMR spectrum of 3e

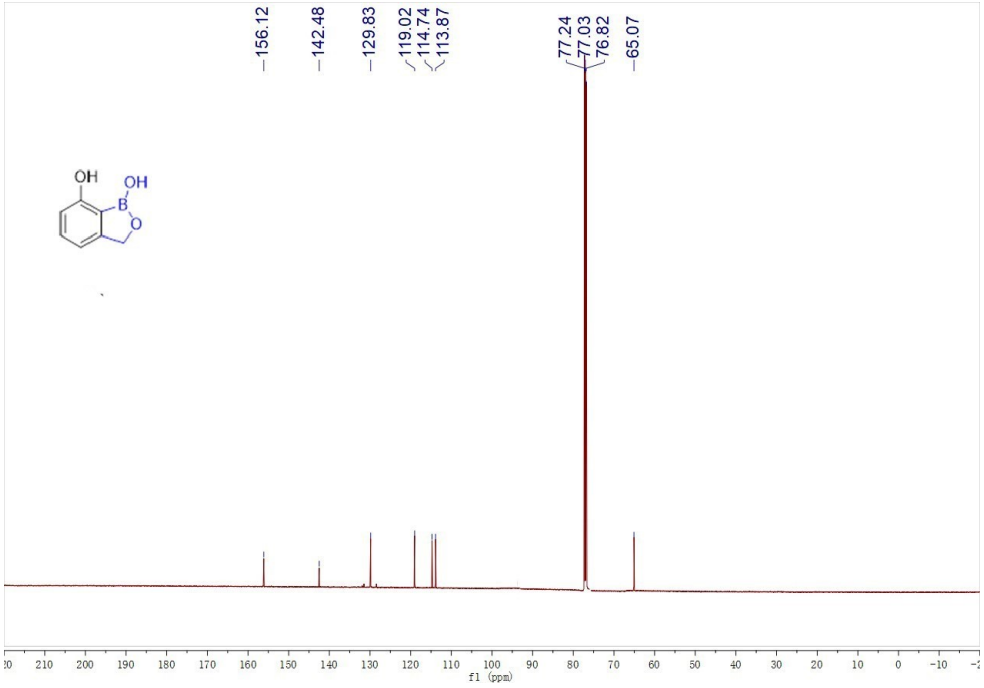


Figure S11. ^{13}C-NMR spectrum of 3e

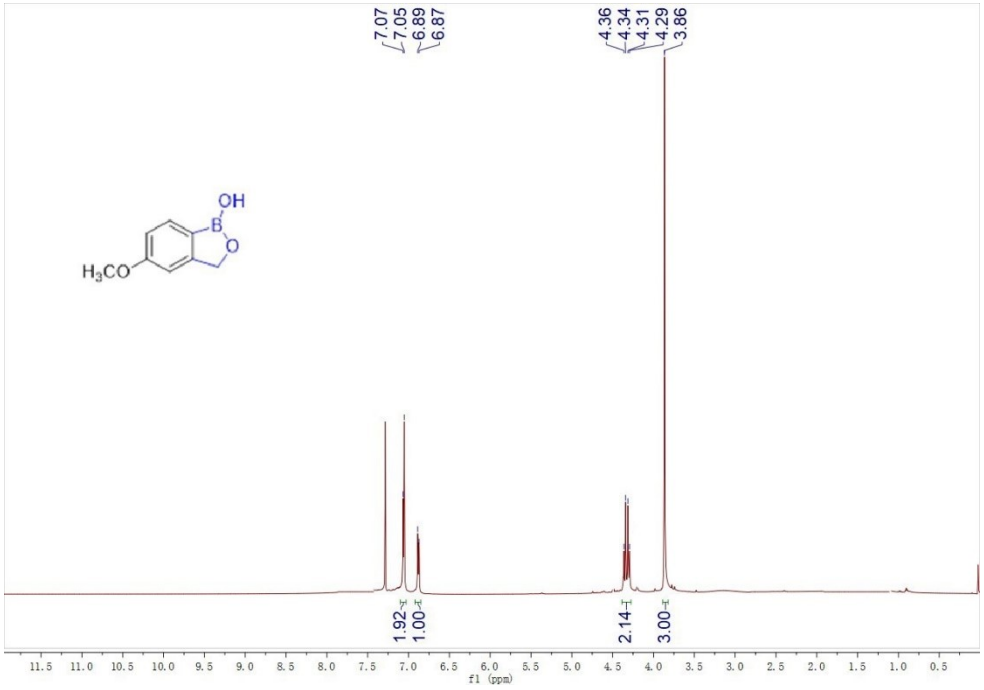


Figure S12. ^{1}H-NMR spectrum of 3f

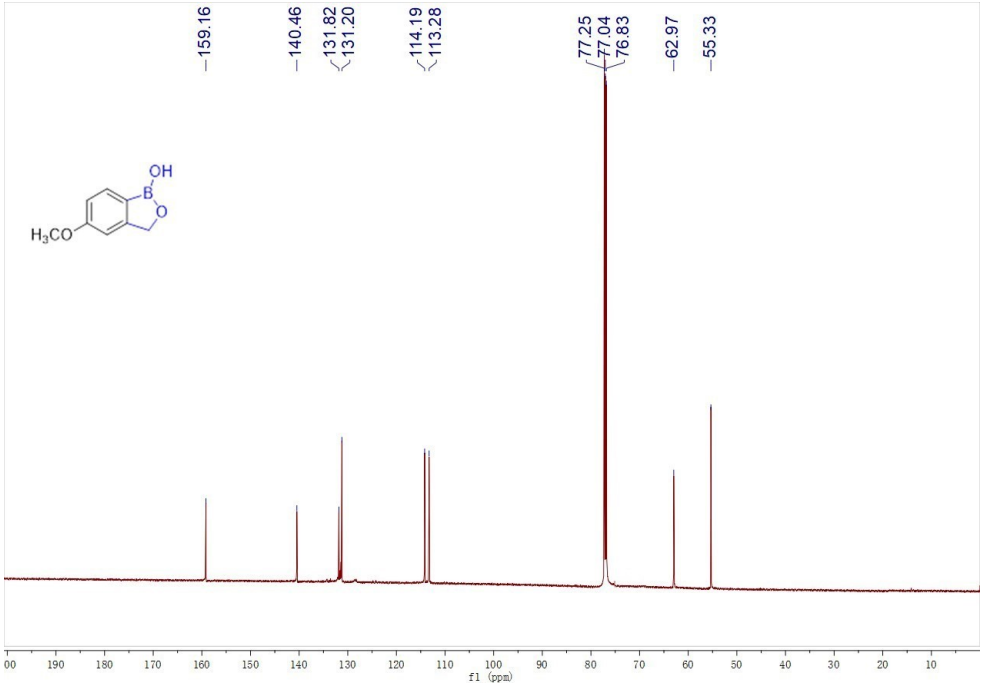


Figure S13. ^{13}C-NMR spectrum of 3f

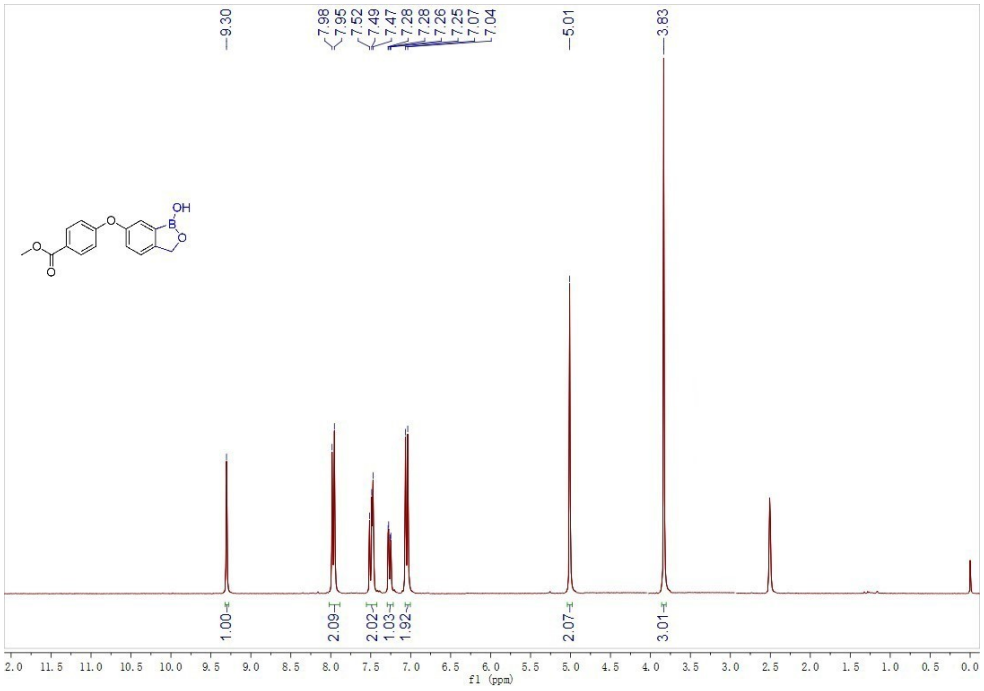


Figure S14. ^{1}H-NMR spectrum of 3g

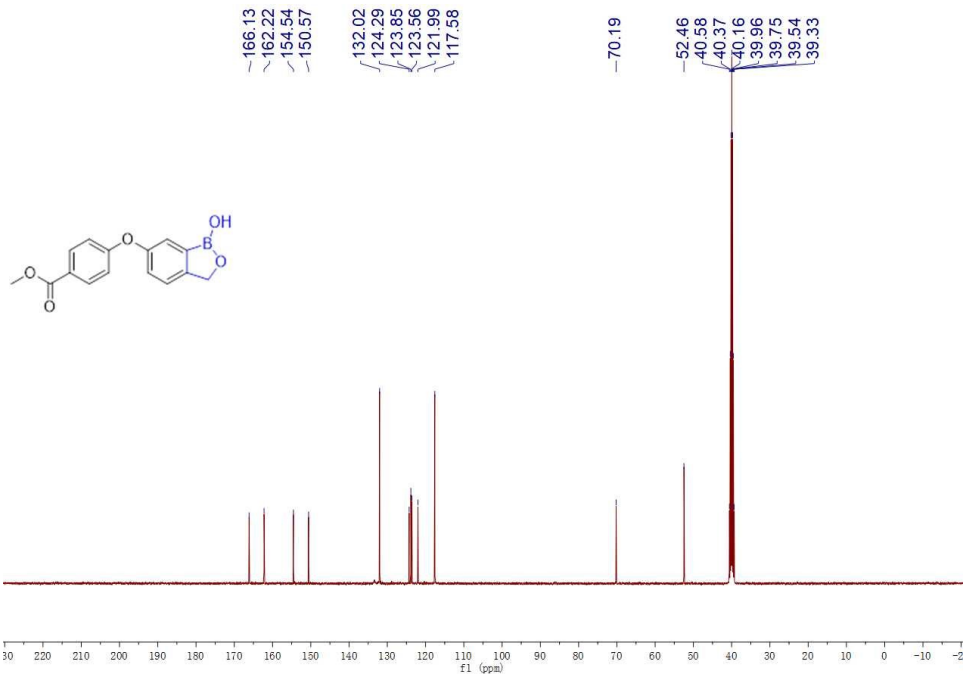


Figure S15. ^{13}C-NMR spectrum of 3g

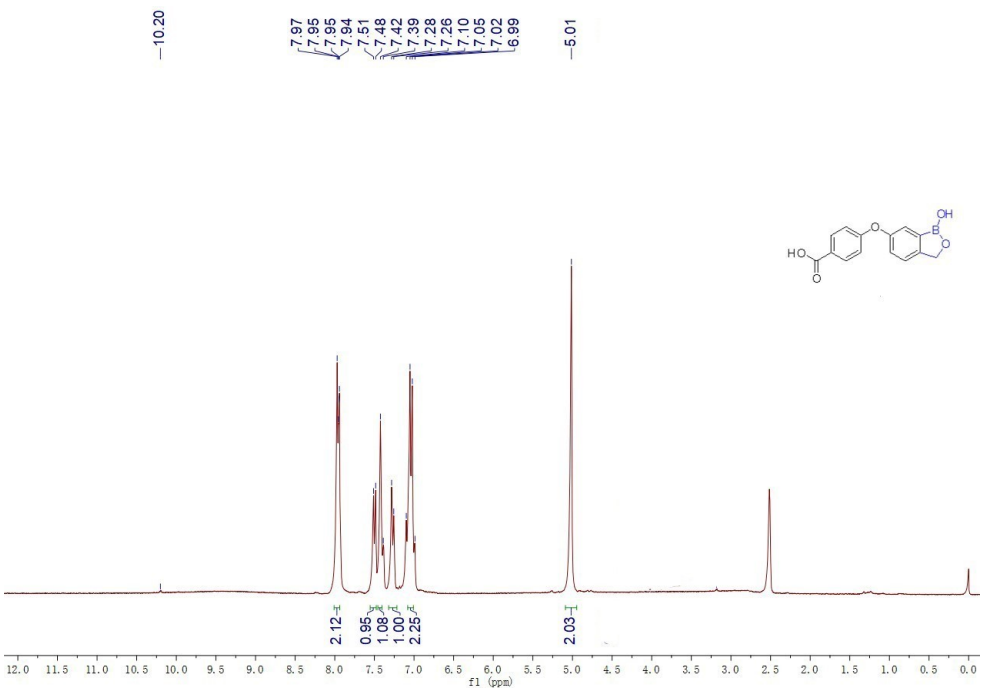


Figure S16. ^{1}H-NMR spectrum of 3h

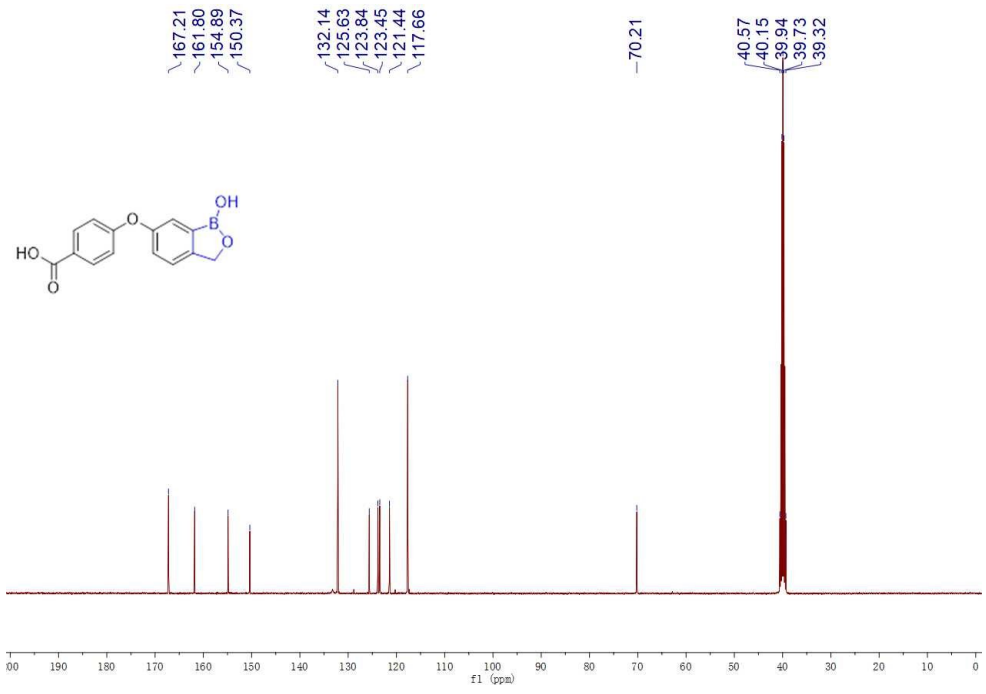


Figure S17. ^{13}C-NMR spectrum of 3h

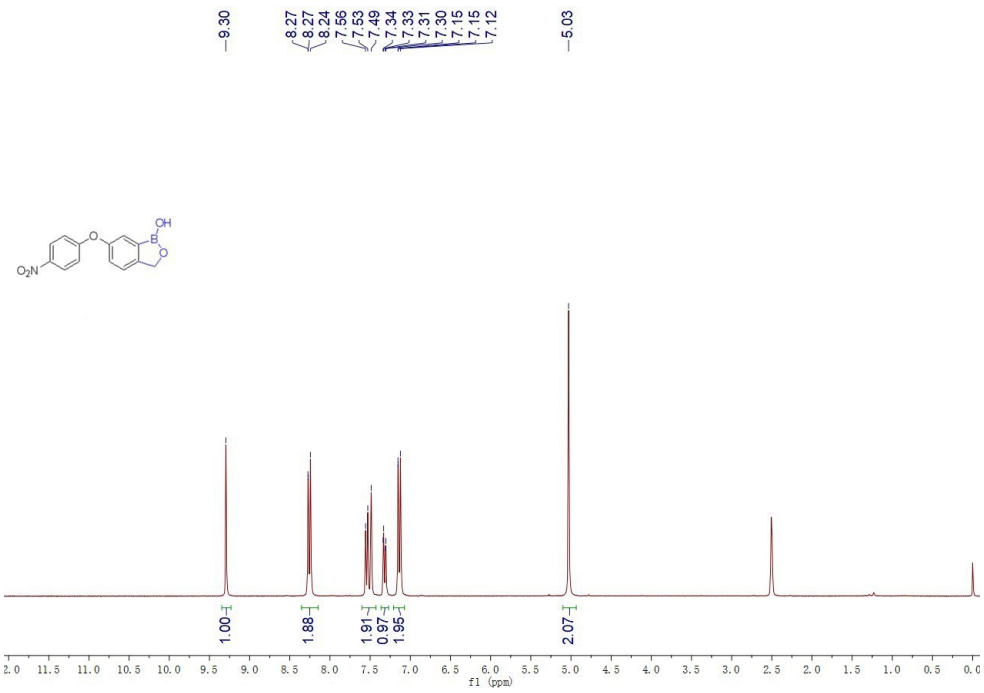


Figure S18. ^{1}H-NMR spectrum of 3i

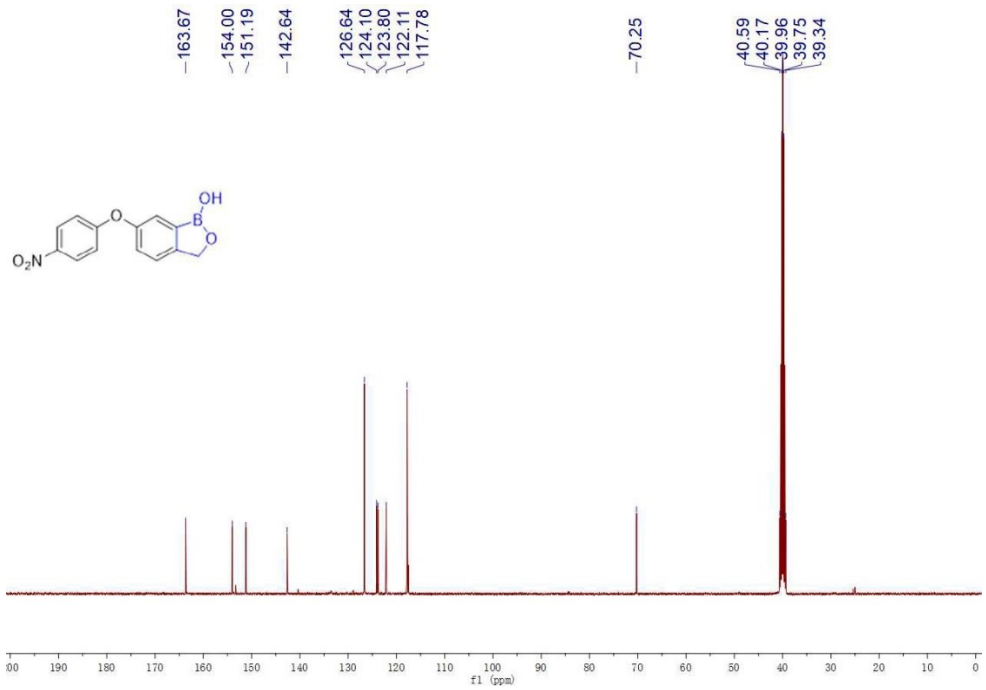


Figure S19. ^{13}C-NMR spectrum of 3i

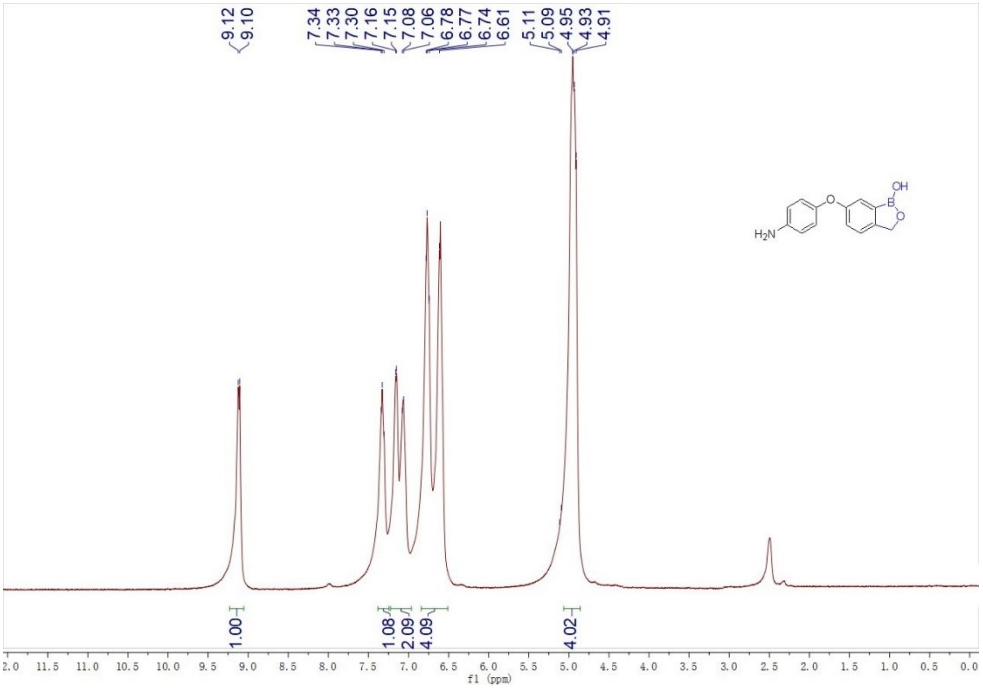


Figure S20. ^{1}H-NMR spectrum of 3j

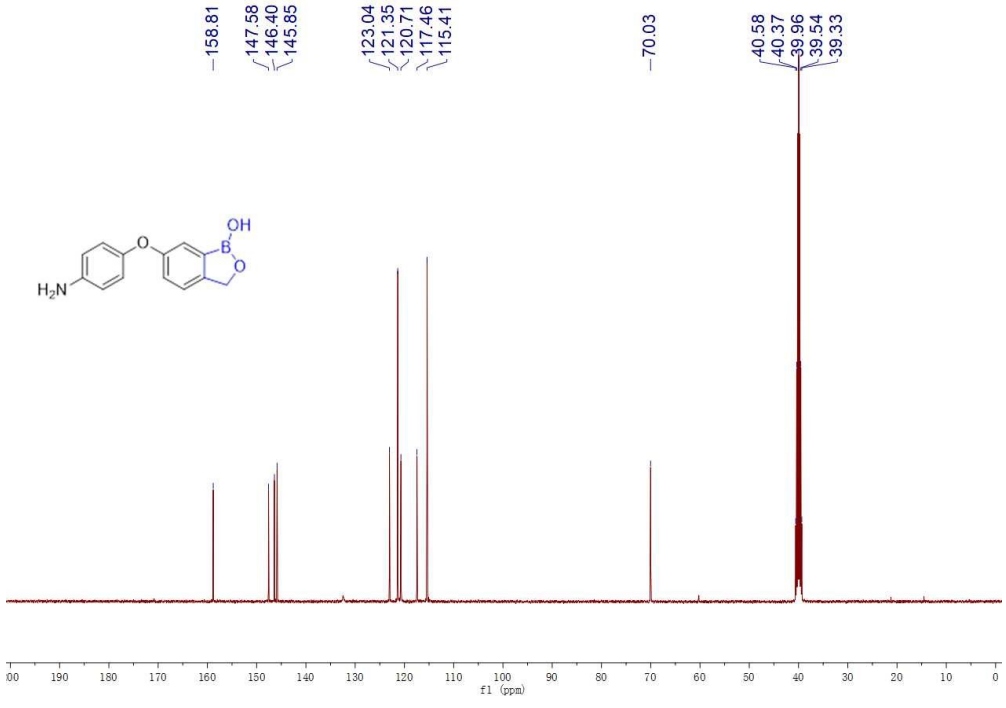


Figure S21. ^{13}C-NMR spectrum of 3j

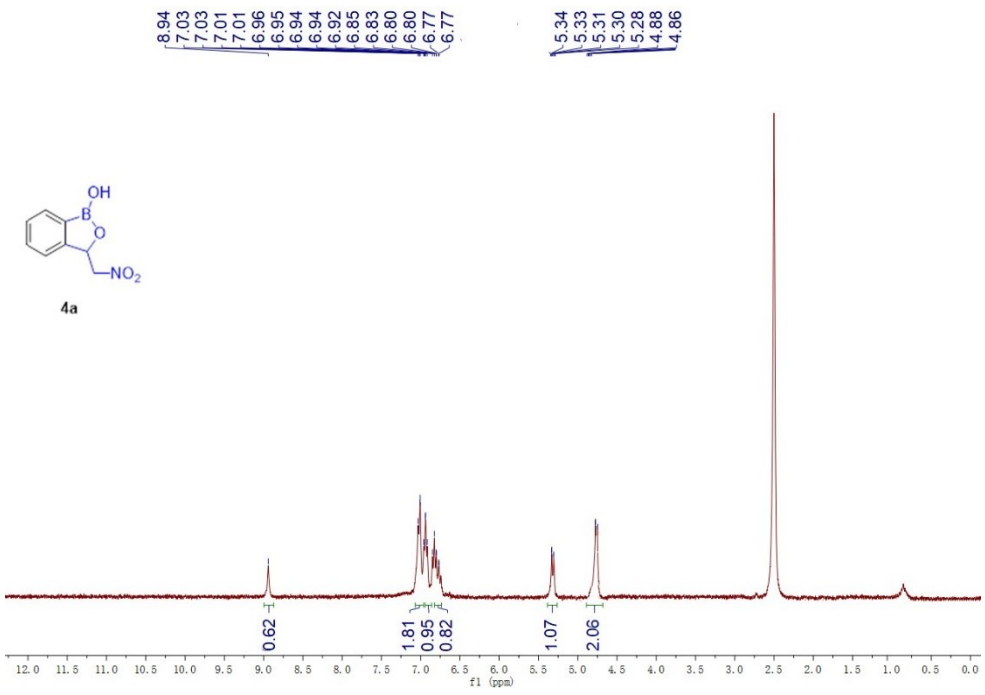


Figure S22. ^{1}H-NMR spectrum of 4a

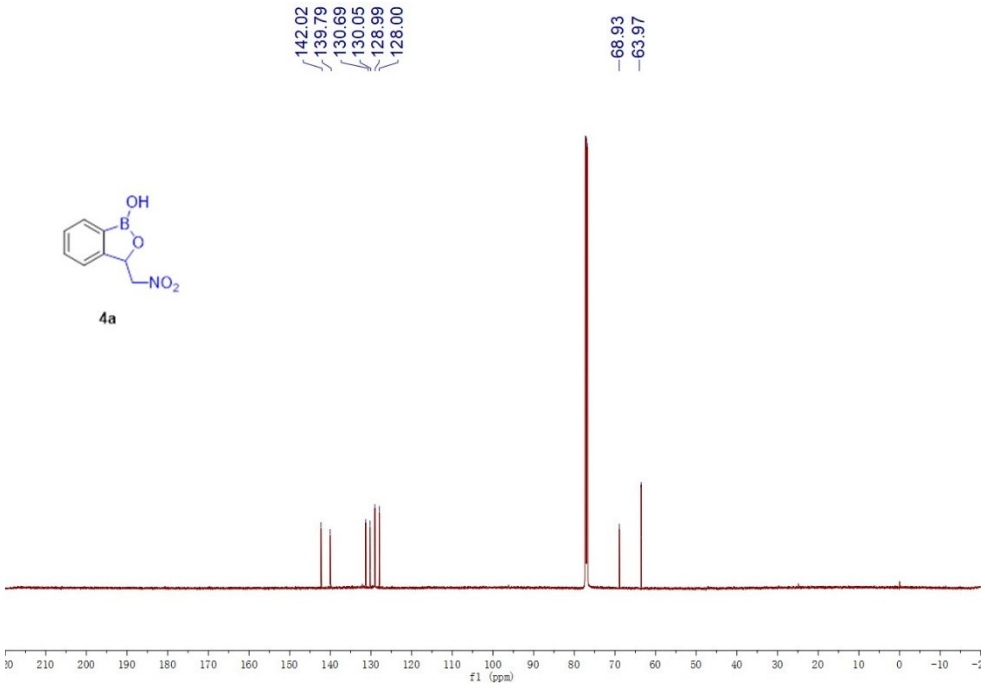


Figure S23. ^{13}C-NMR spectrum of 4a

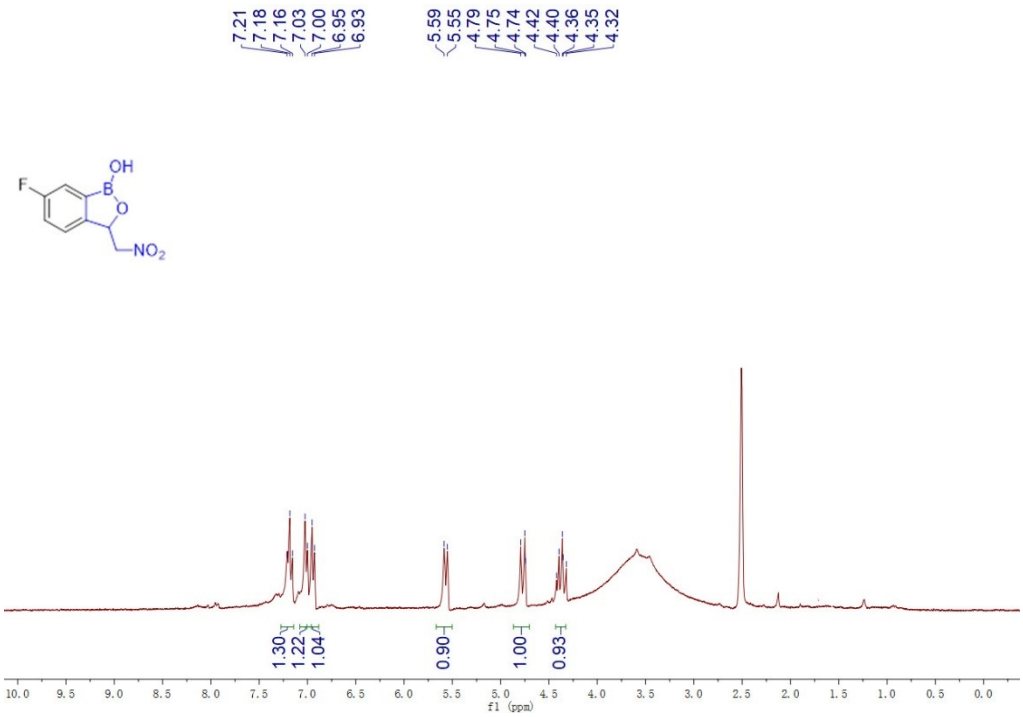


Figure S24. ^{1}H-NMR spectrum of 4b

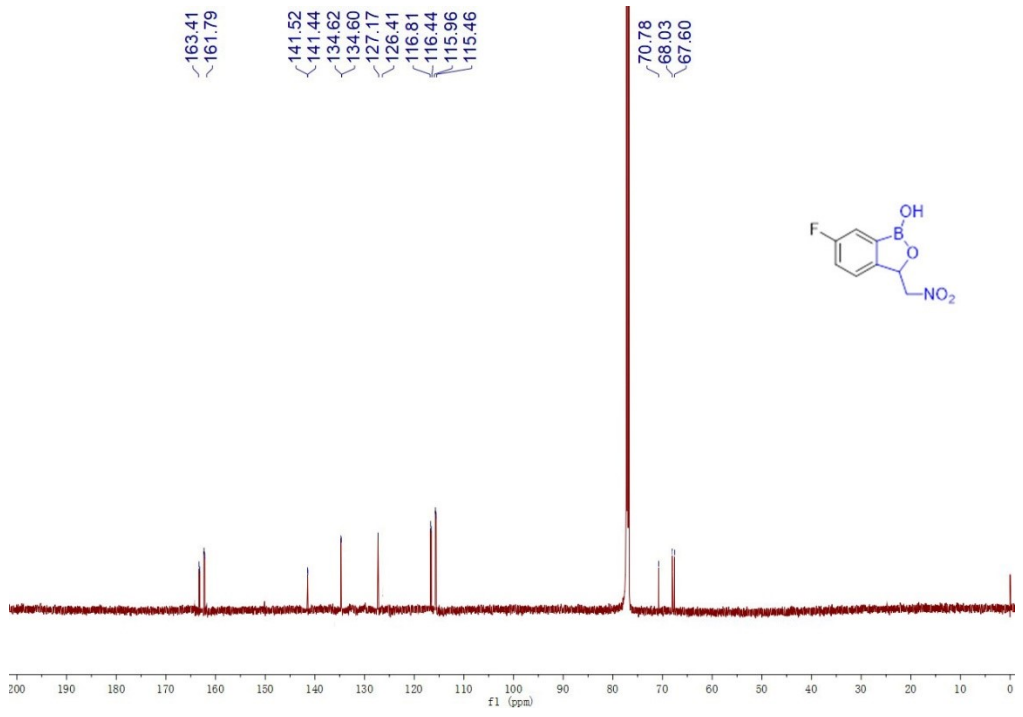


Figure S25. ^{13}C-NMR spectrum of 4b

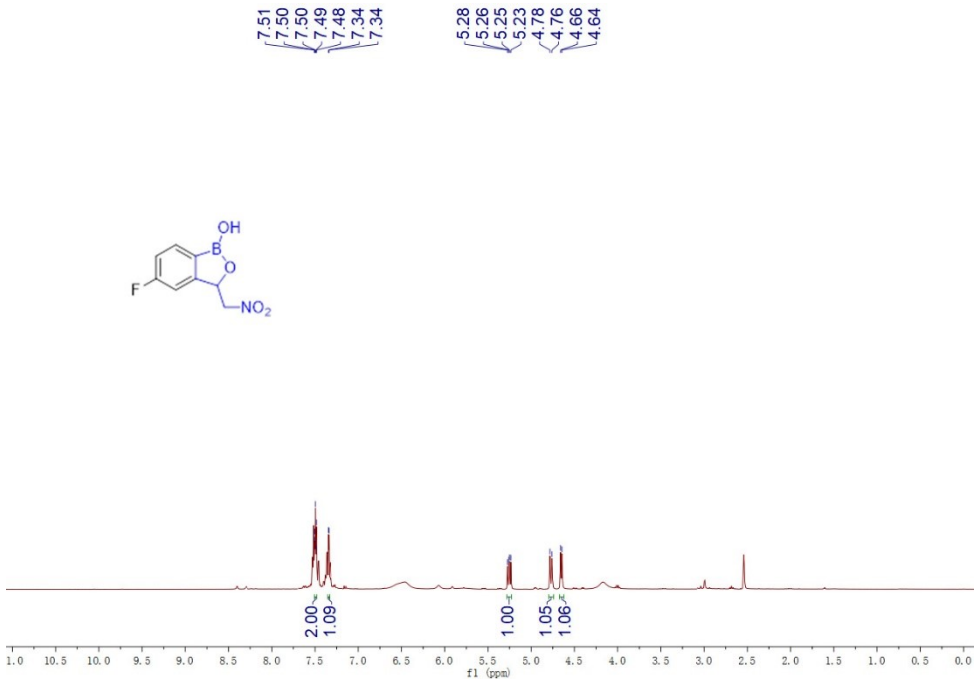


Figure S26. ^{1}H-NMR spectrum of 4c

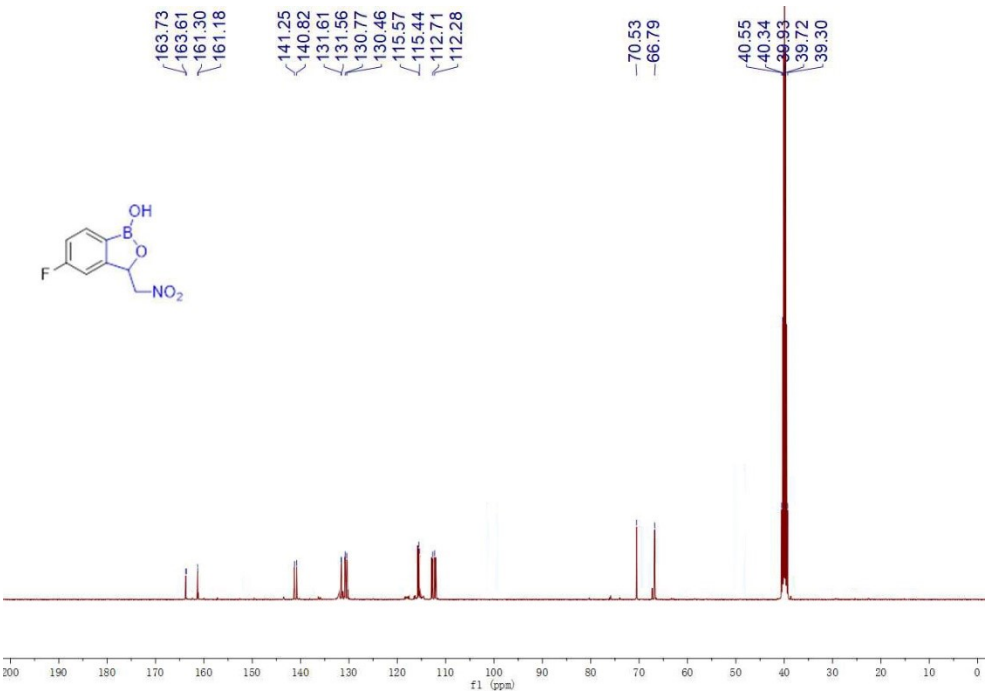


Figure S27. ^{13}C-NMR spectrum of 4c

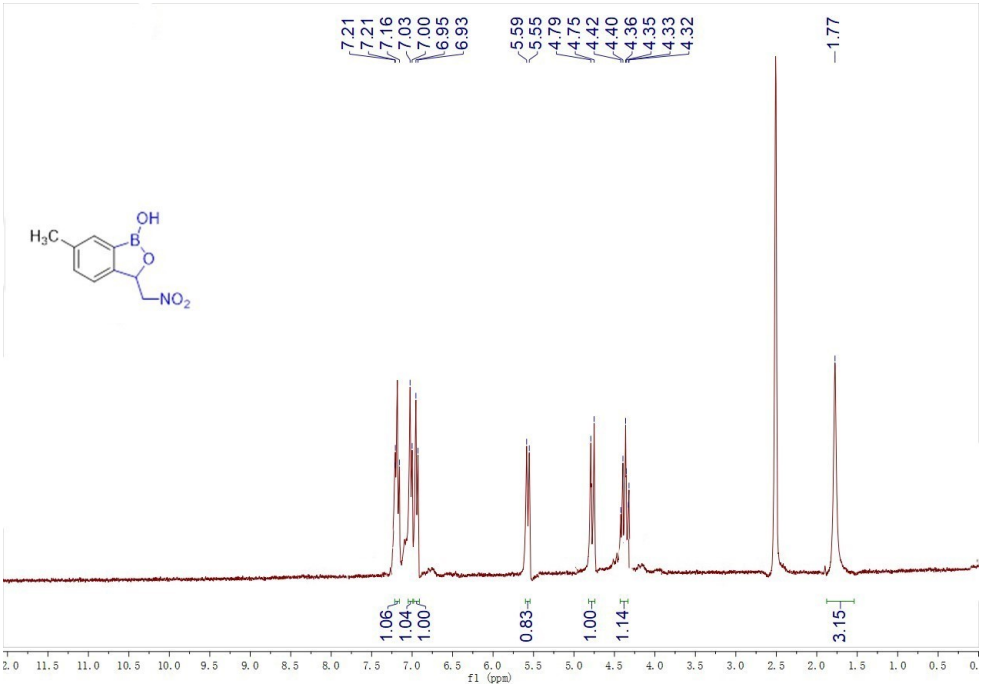


Figure S28. ^{1}H-NMR spectrum of 4d

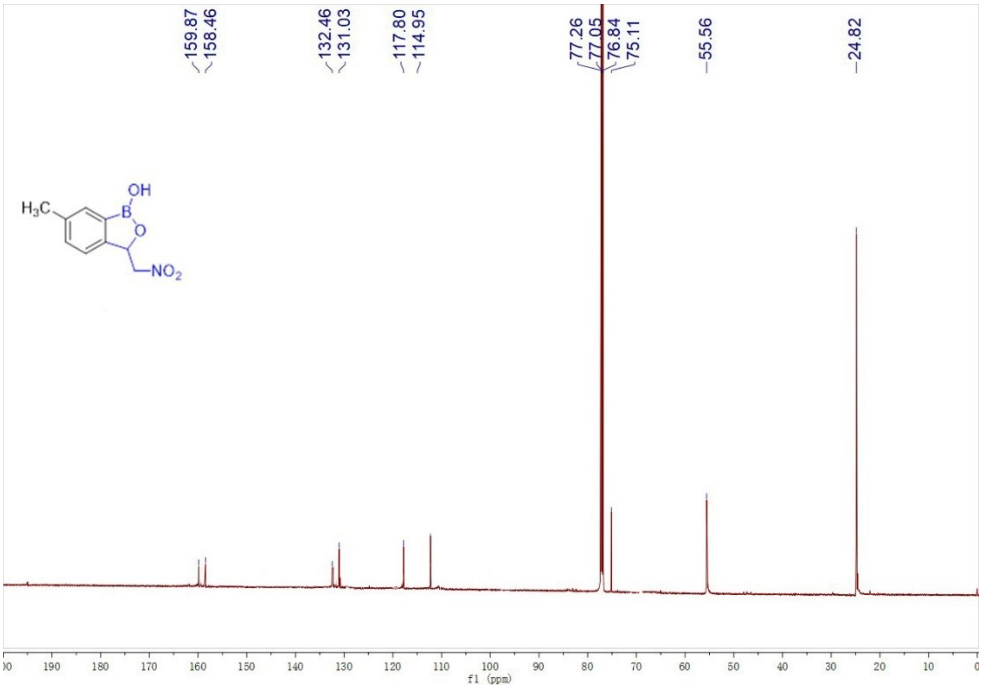


Figure S29. ^{13}C-NMR spectrum of 4d

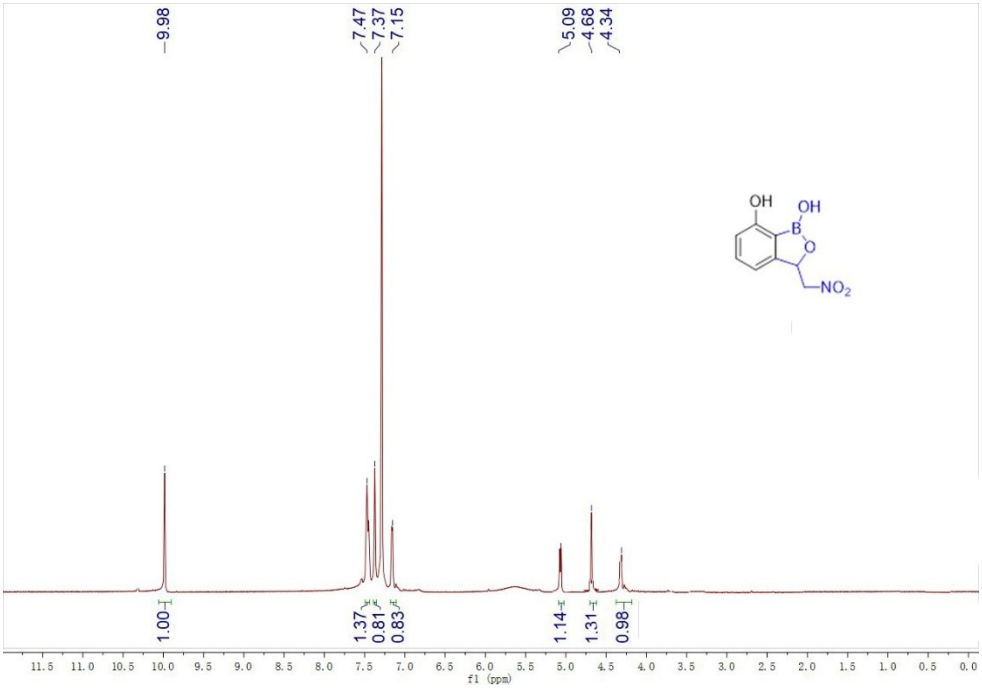


Figure S30. ^{1}H-NMR spectrum of 4e

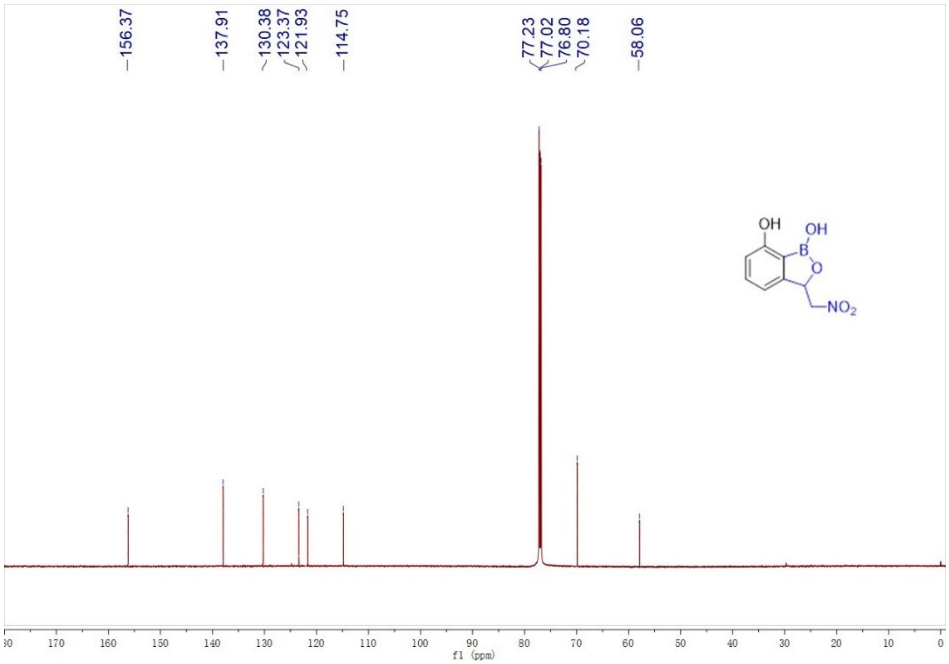


Figure S31. ^{13}C-NMR spectrum of 4e

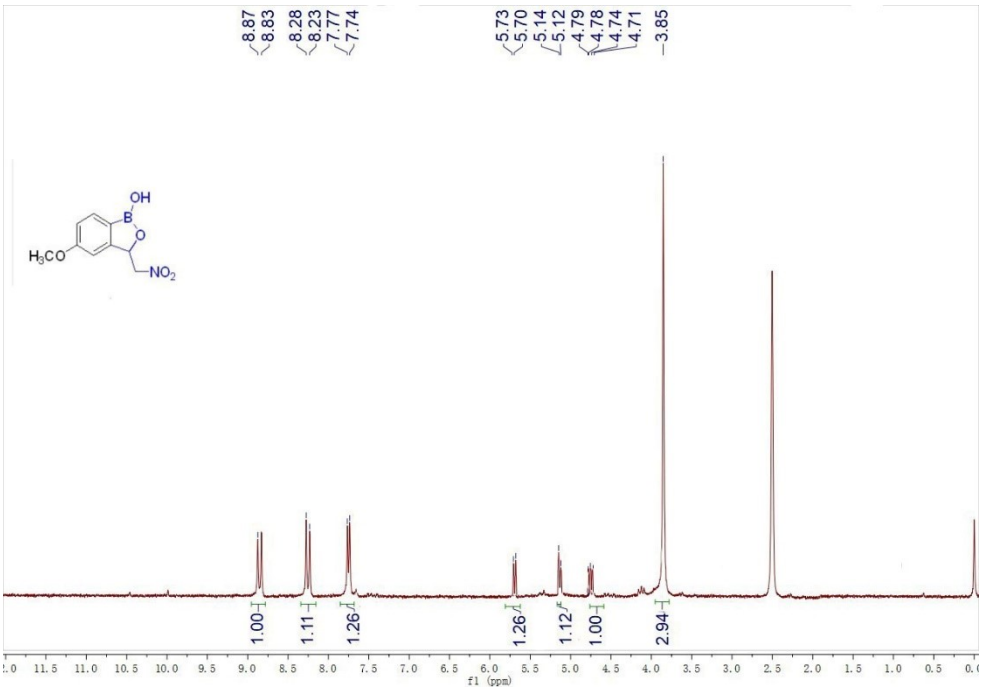


Figure S32. ^{1}H-NMR spectrum of 4f

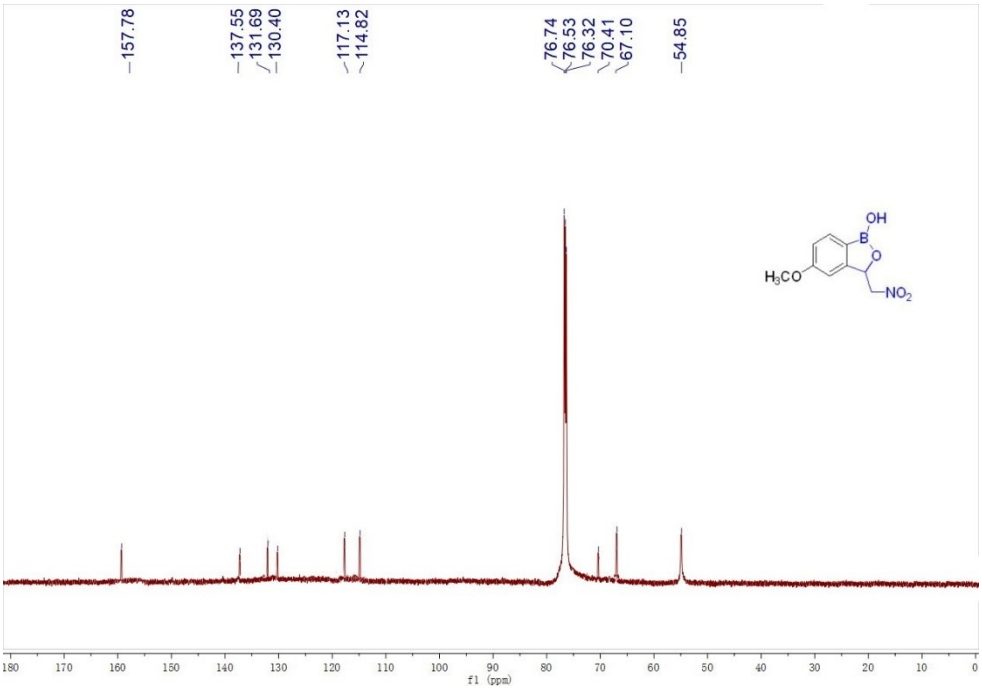


Figure S33. ^{13}C-NMR spectrum of 4f

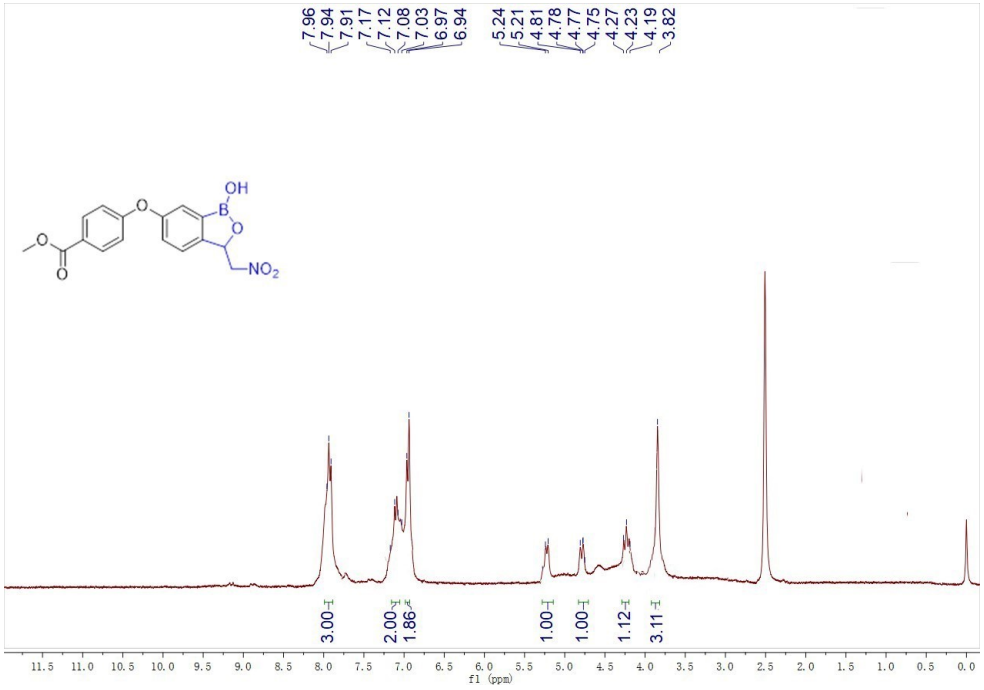


Figure S34. ^{1}H-NMR spectrum of 4g

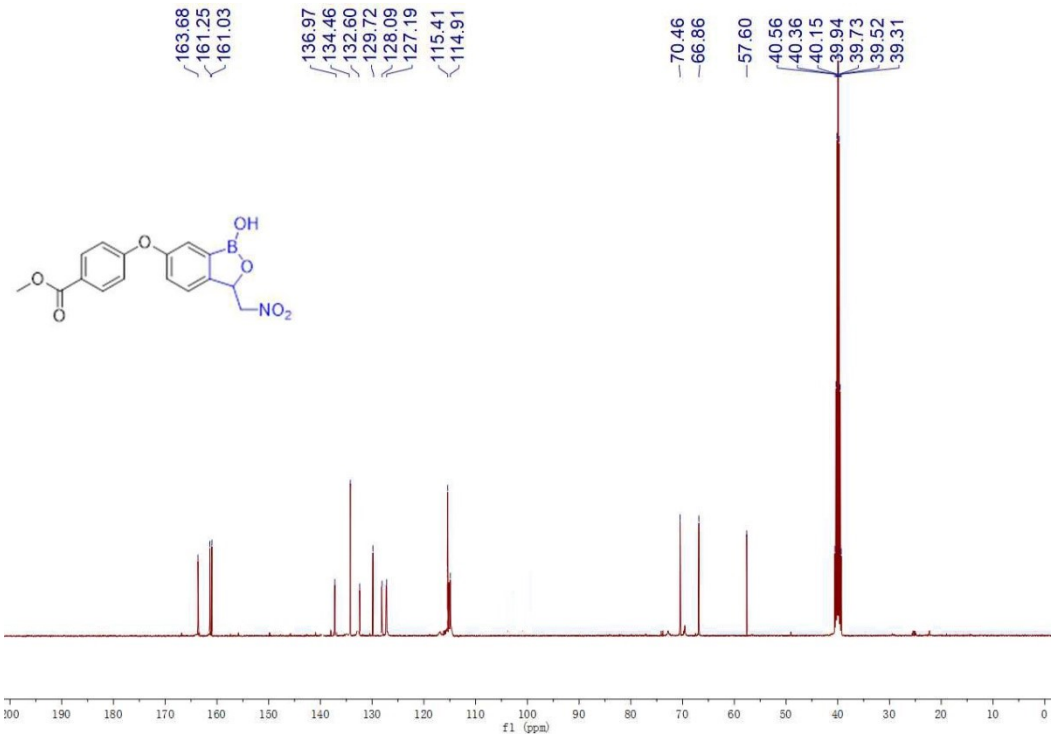


Figure S35. ^{13}C-NMR spectrum of 4g

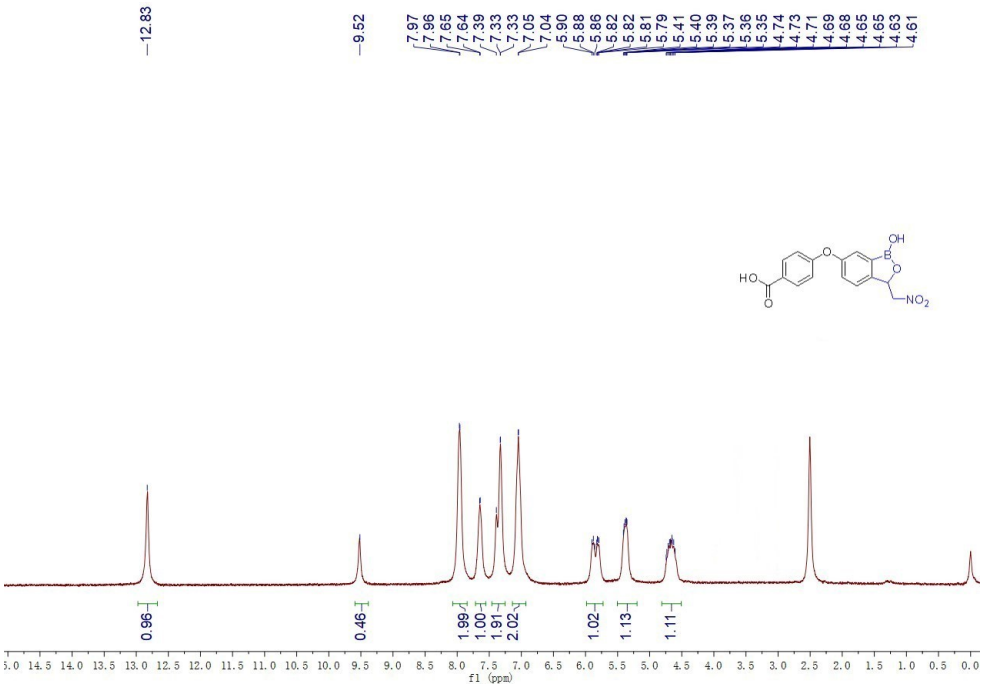


Figure S36. ^{1}H-NMR spectrum of 4h

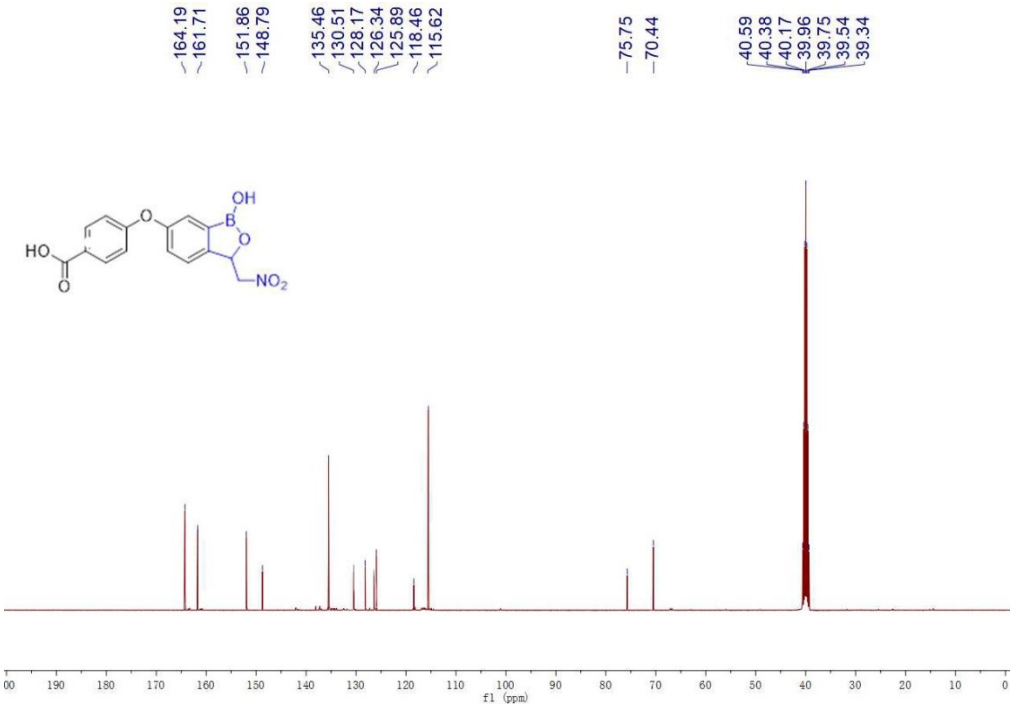


Figure S37. ^{13}C-NMR spectrum of 4h

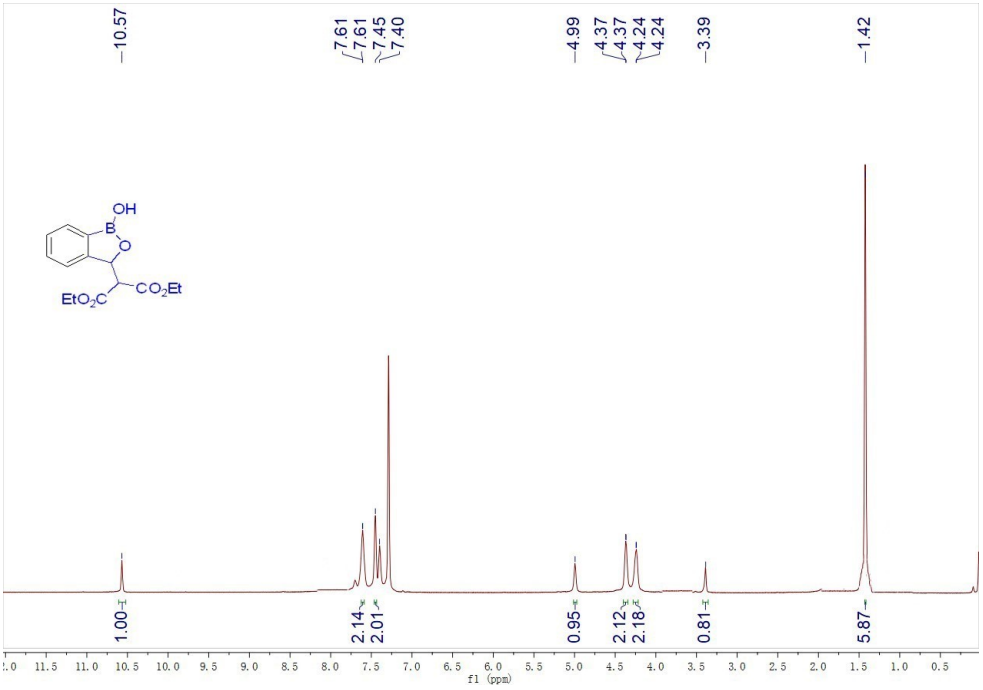


Figure S38. ^{1}H-NMR spectrum of 4i

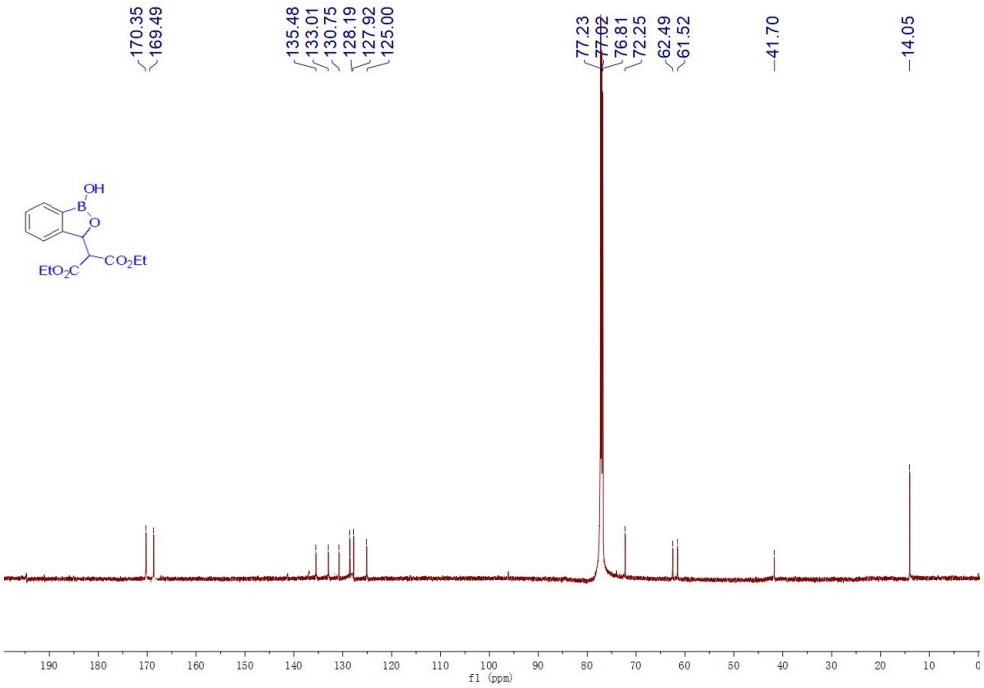


Figure S39. ^{13}C-NMR spectrum of 4i

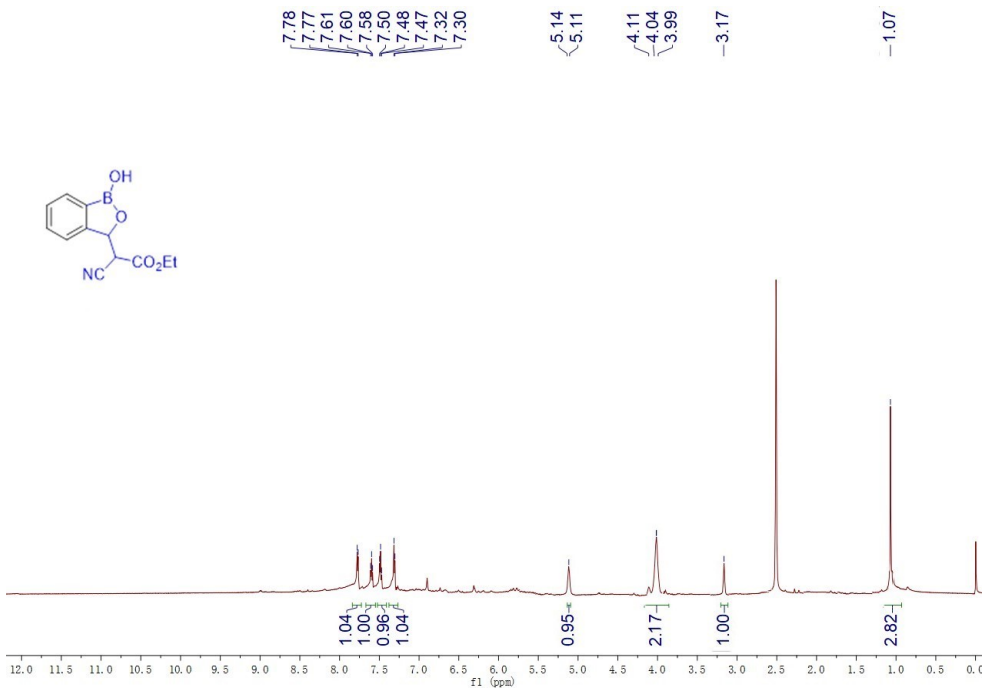


Figure S40. ^{1}H-NMR spectrum of 4j

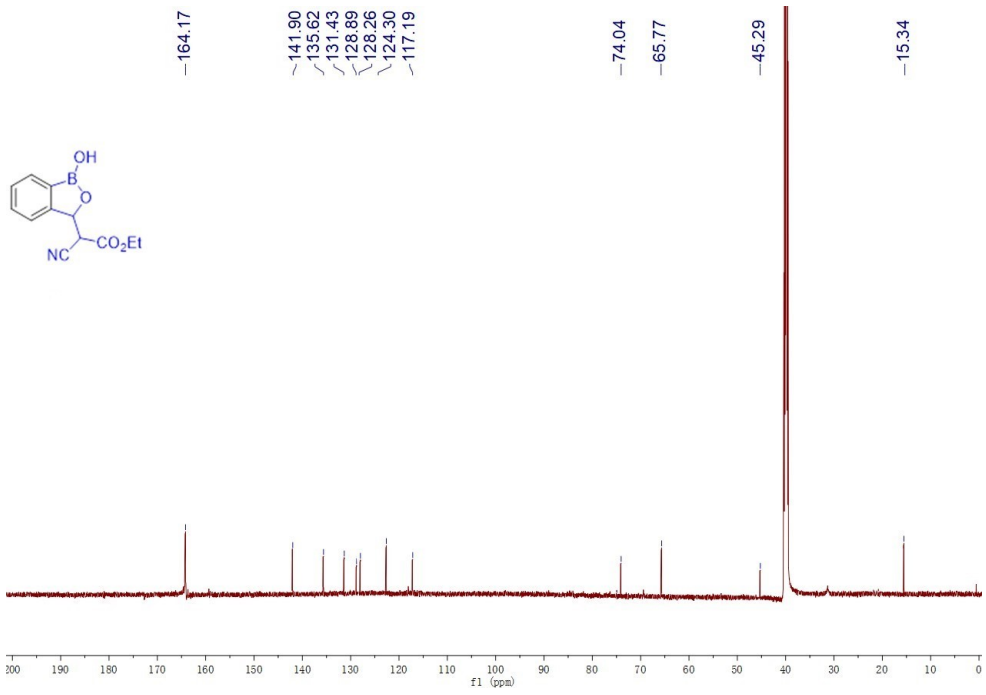


Figure S41. ^{13}C-NMR spectrum of 4j