Supporting Information

for

Nitrogen-boron coordination versus OH…N hydrogen bonding in pyridoxaboroles – aza analogues of benzoxaboroles

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1. NMR spectra of new compounds

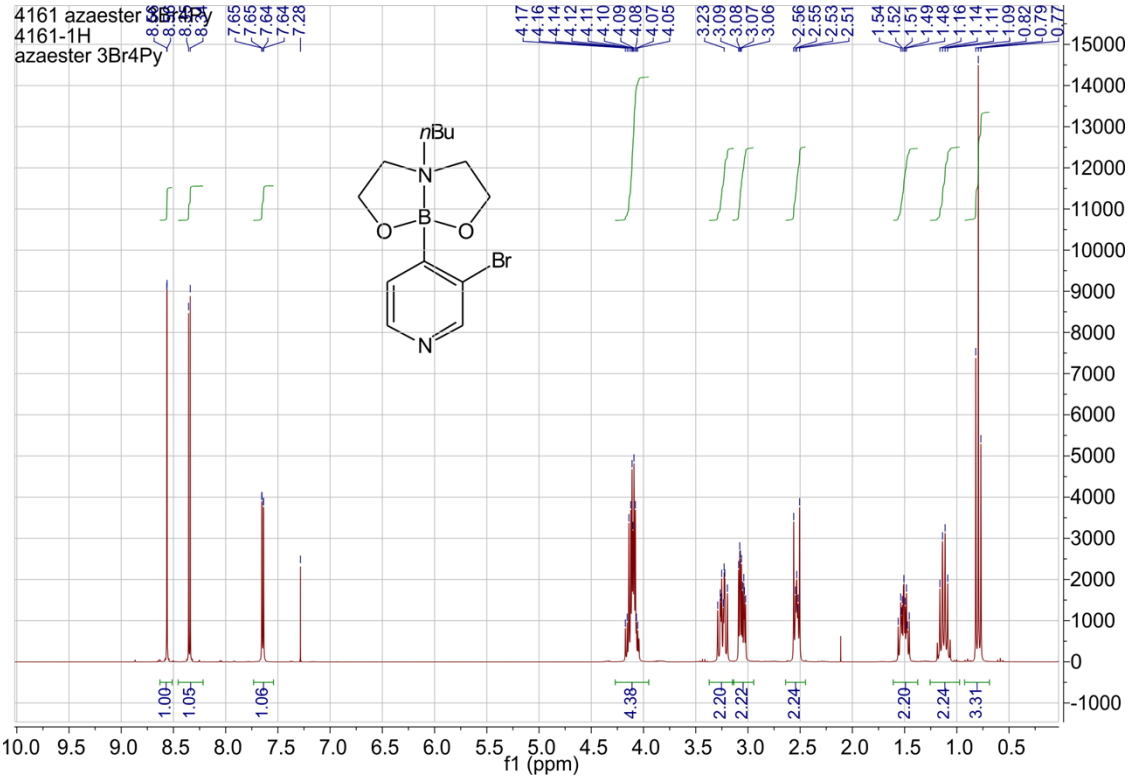

Figure S1. ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$ solution).

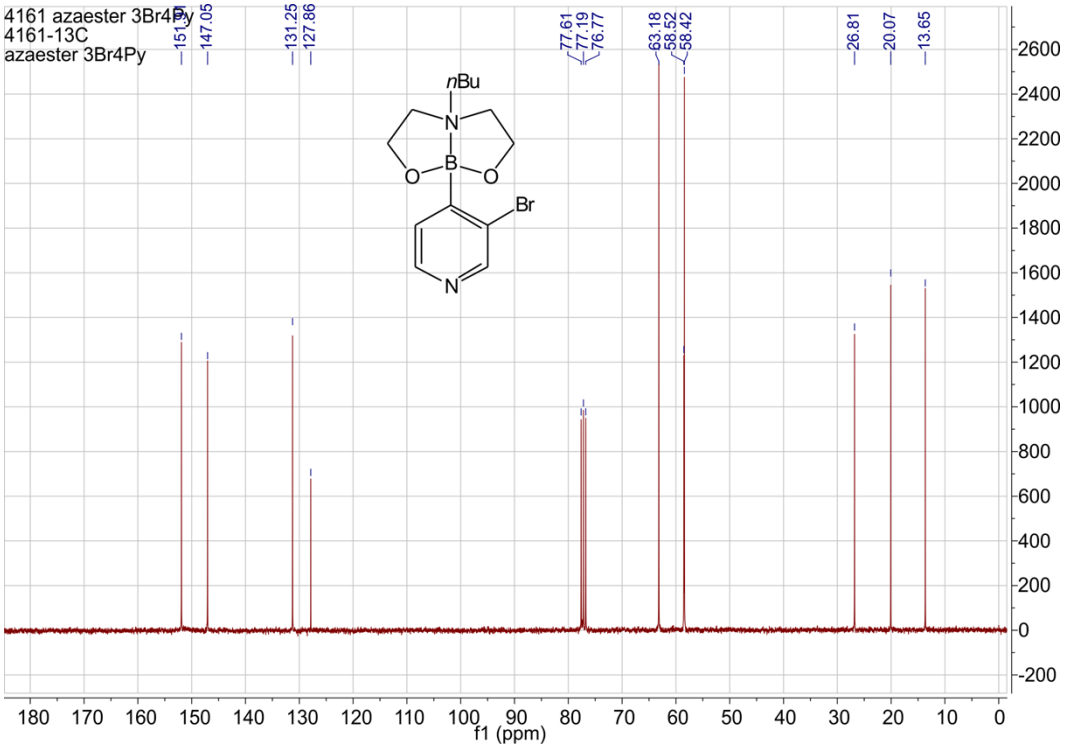

Figure S2. ^{13}C NMR spectrum of compound **2** (100.6 MHz, $CDCl_3$ solution).

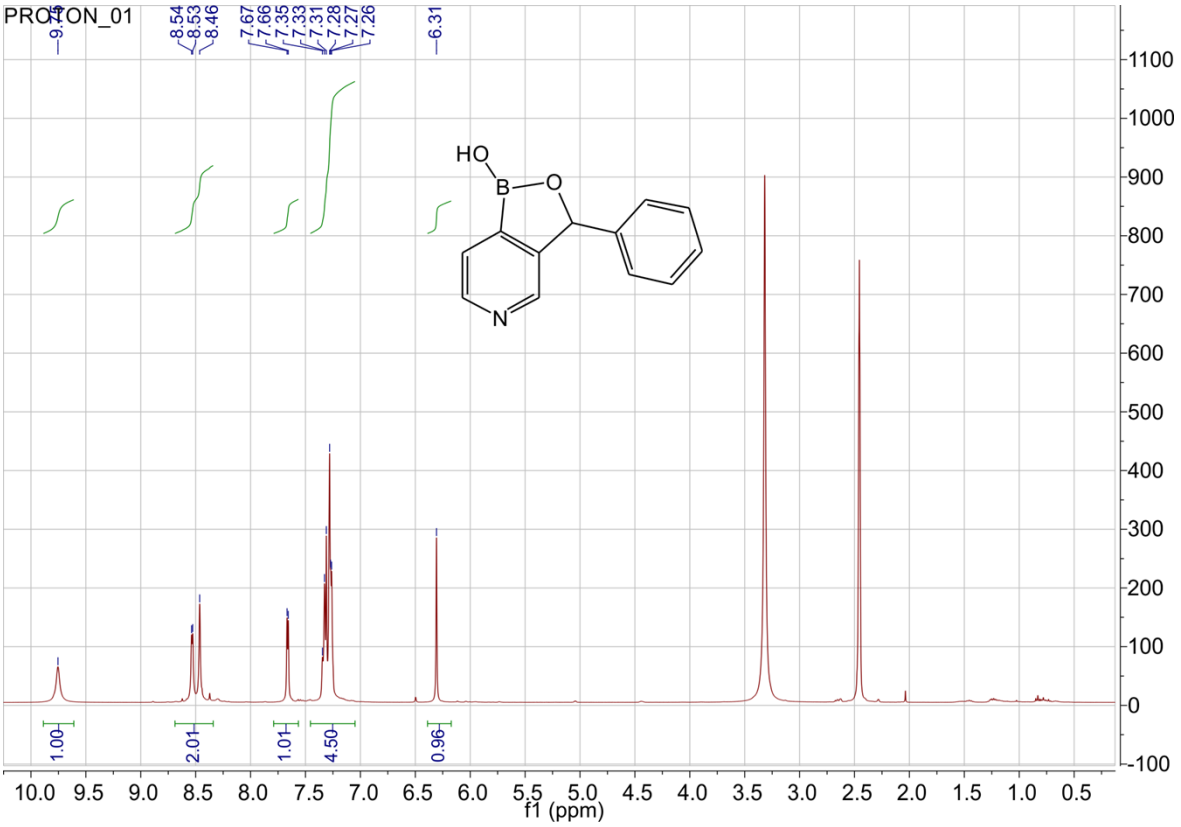

Figure S3. ^{1}H NMR spectrum of compound **3a** (400 MHz, DMSO-d_6 solution).

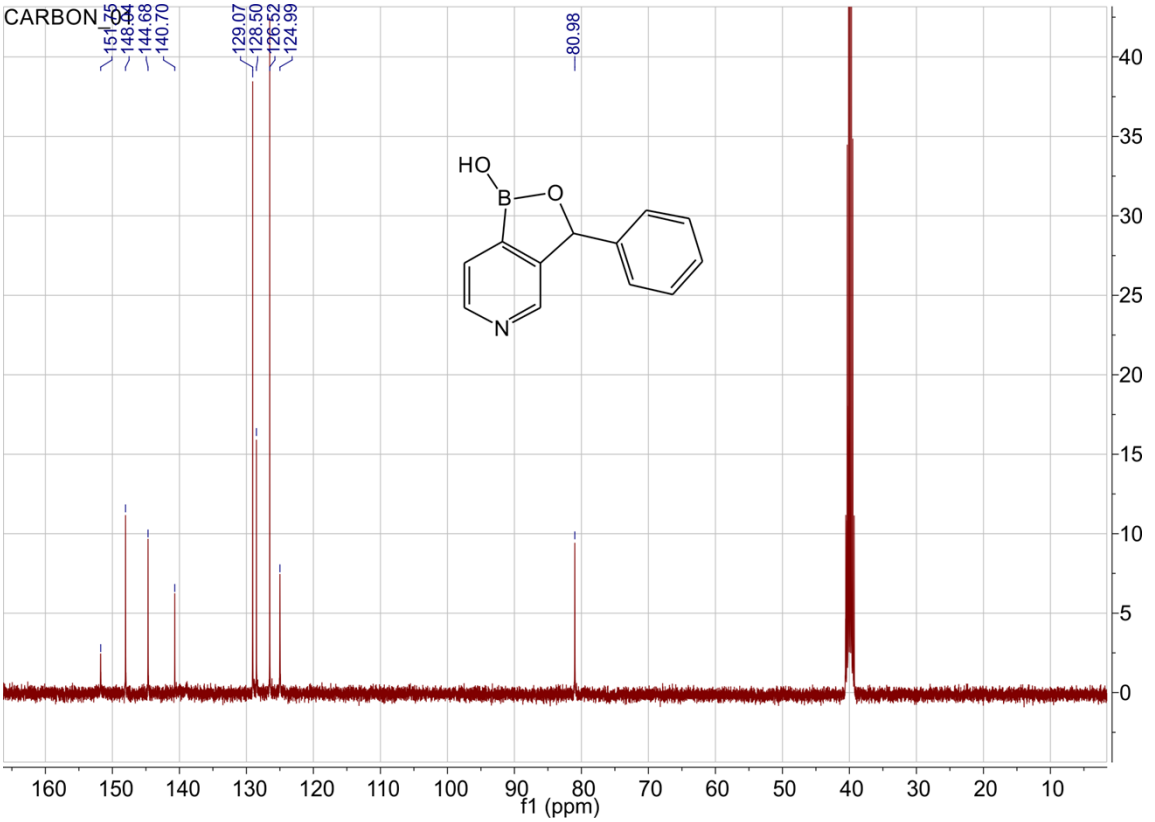

Figure S4. ^{13}C NMR spectrum of compound **3a** (100.6 MHz, DMSO-d_6 solution).

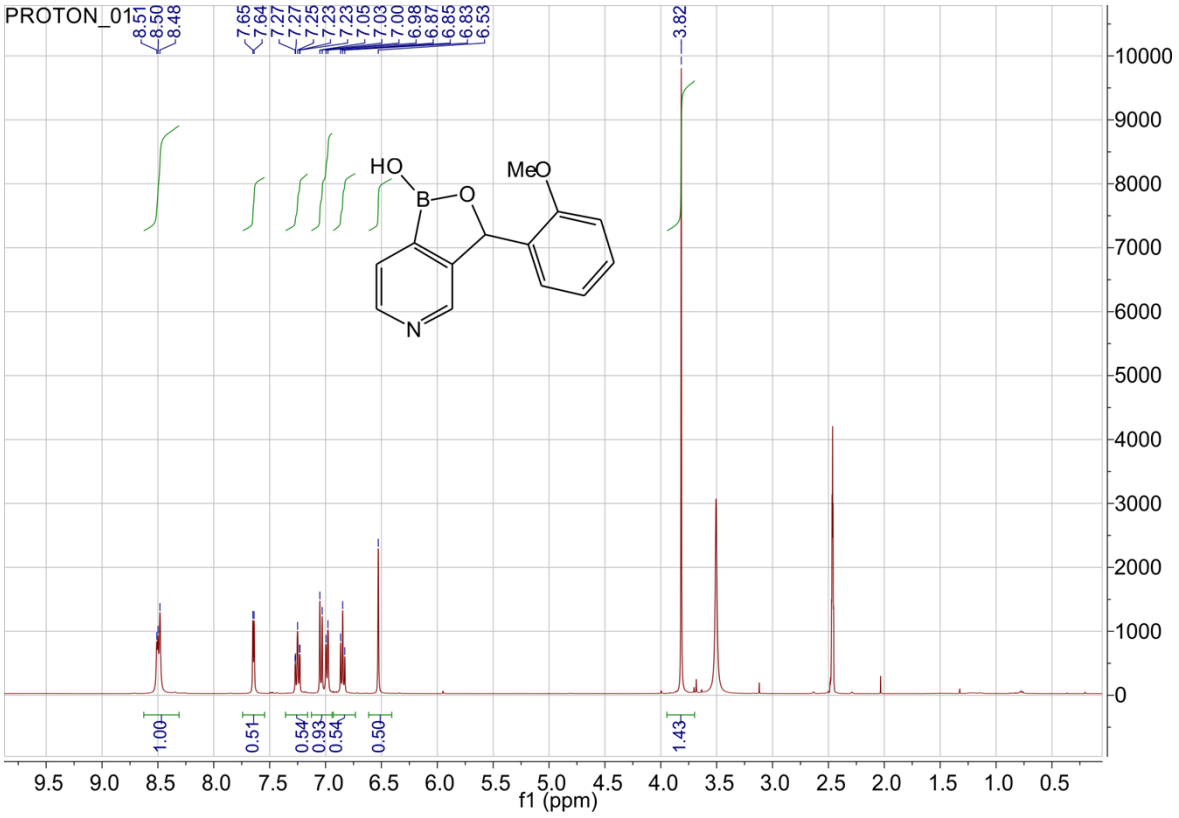

Figure S5. [1]H NMR spectrum of compound **3b** (400 MHz, DMSO-d_6 solution).

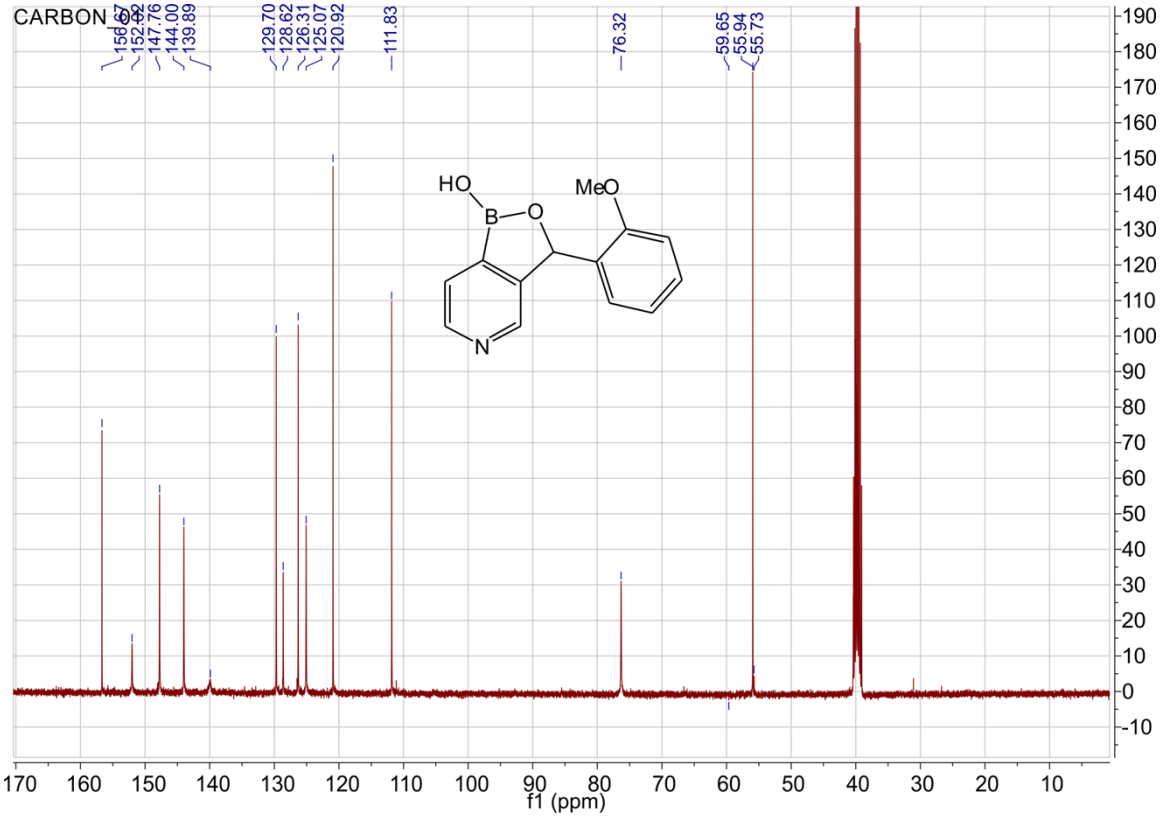

Figure S6. [13]C NMR spectrum of compound **3b** (100.6 MHz, DMSO-d_6 solution).

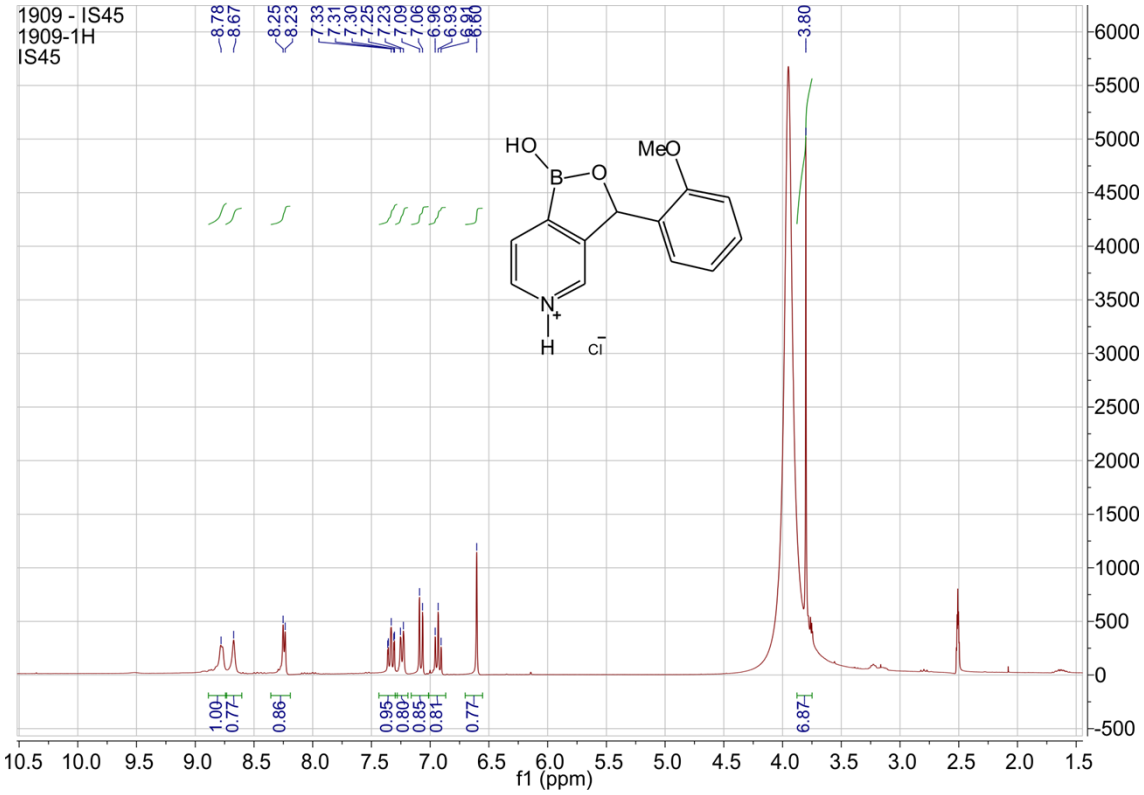

Figure S7. ^{1}H NMR spectrum of compound **[3b-H]Cl** (300 MHz, DMSO-d_6 solution).

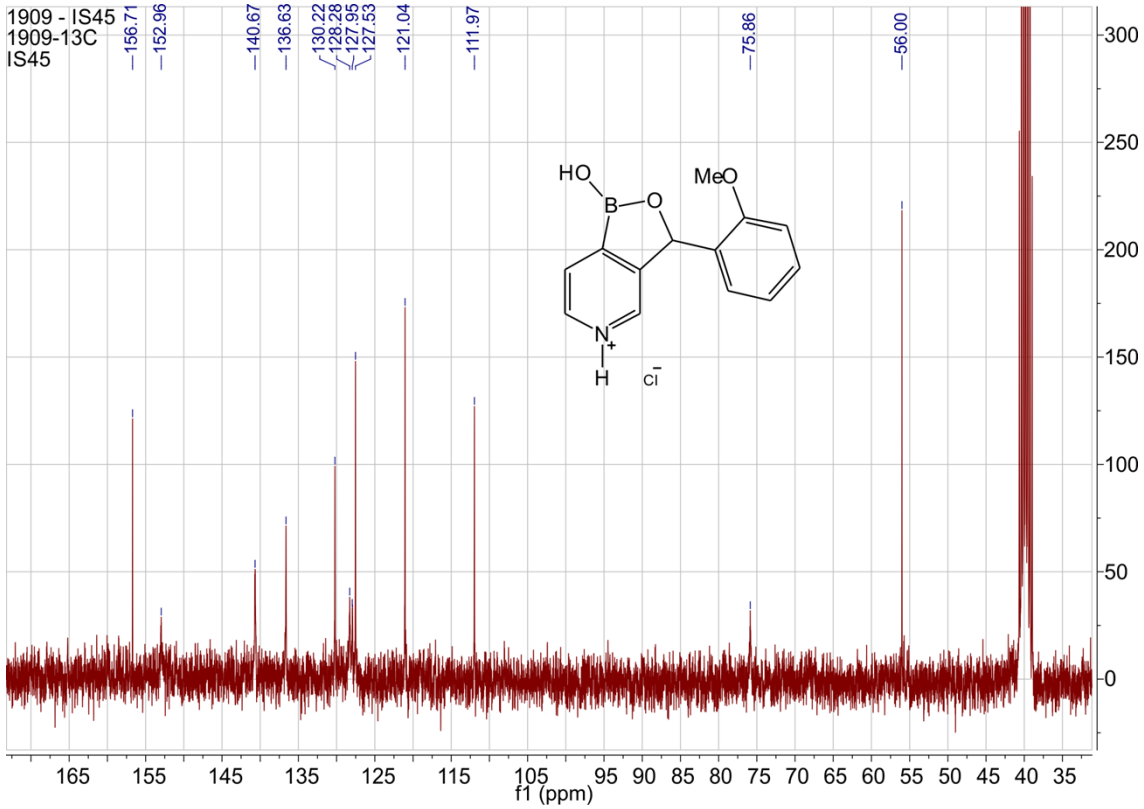

Figure S8. ^{13}C NMR spectrum of compound **[3b-H]Cl** (75.5 MHz, DMSO-d_6 solution).

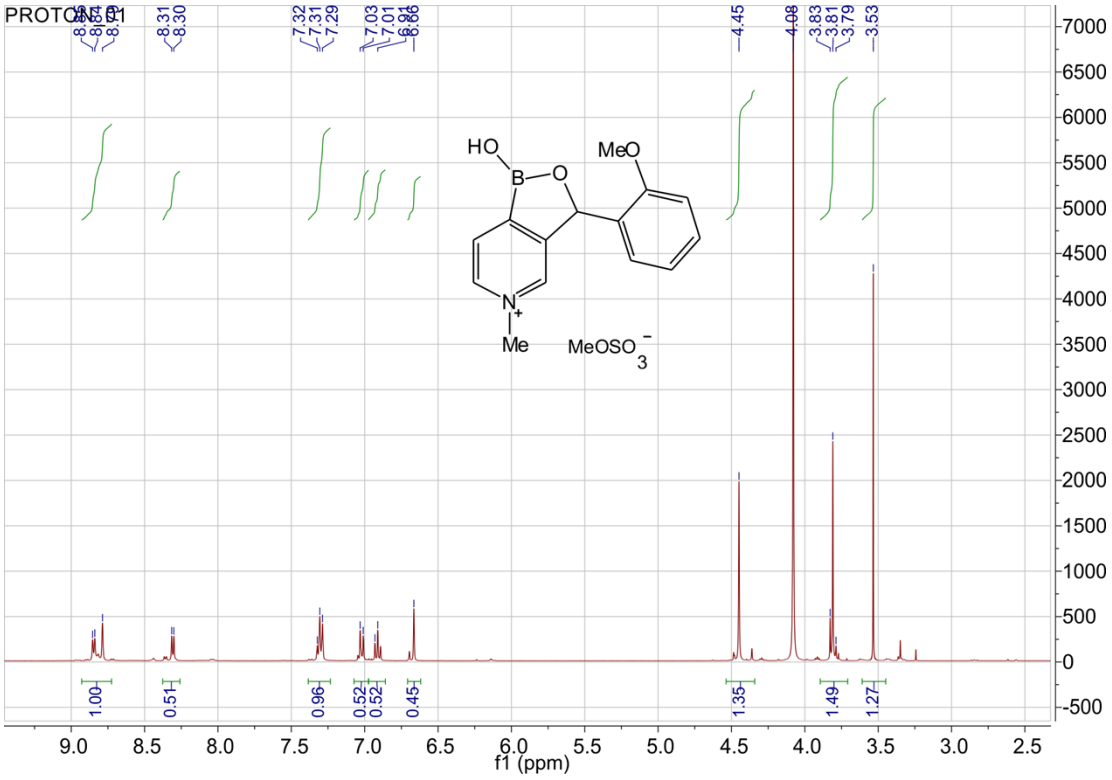

Figure S9. ^{1}H NMR spectrum of compound **[3b-Me]MeOSO$_3$** (400 MHz, DMSO-d_6 solution).

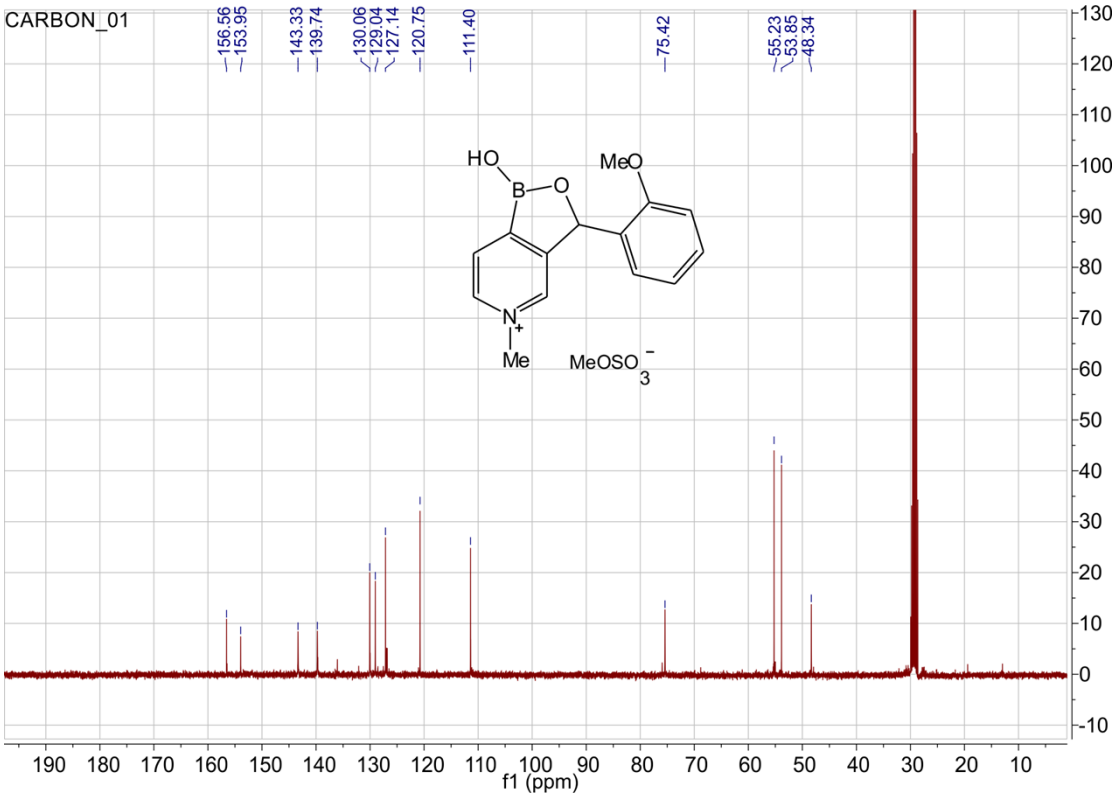

Figure S10. ^{13}C NMR spectrum of compound **[3b-Me]MeOSO$_3$** (100.6 MHz, DMSO-d_6 solution).

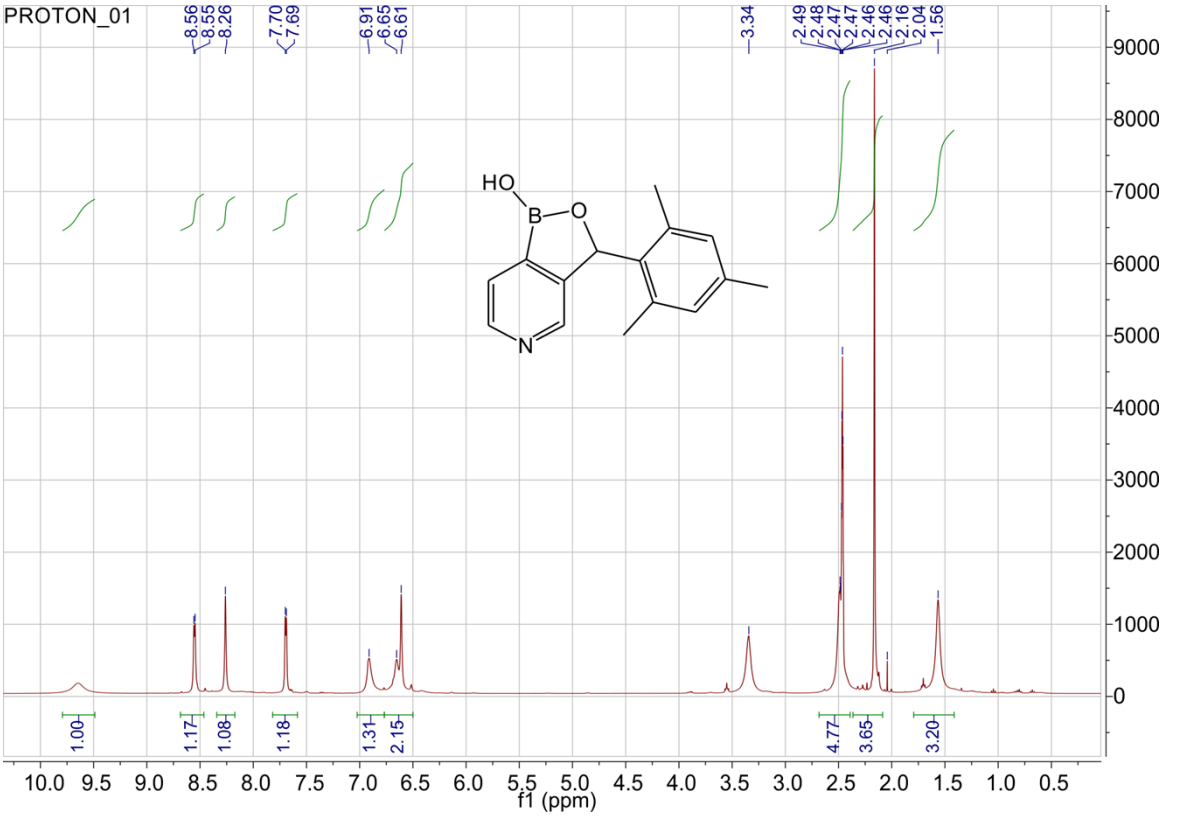

Figure S11. ^{1}H NMR spectrum of compound **3c** (300 MHz, DMSO-d_6 solution).

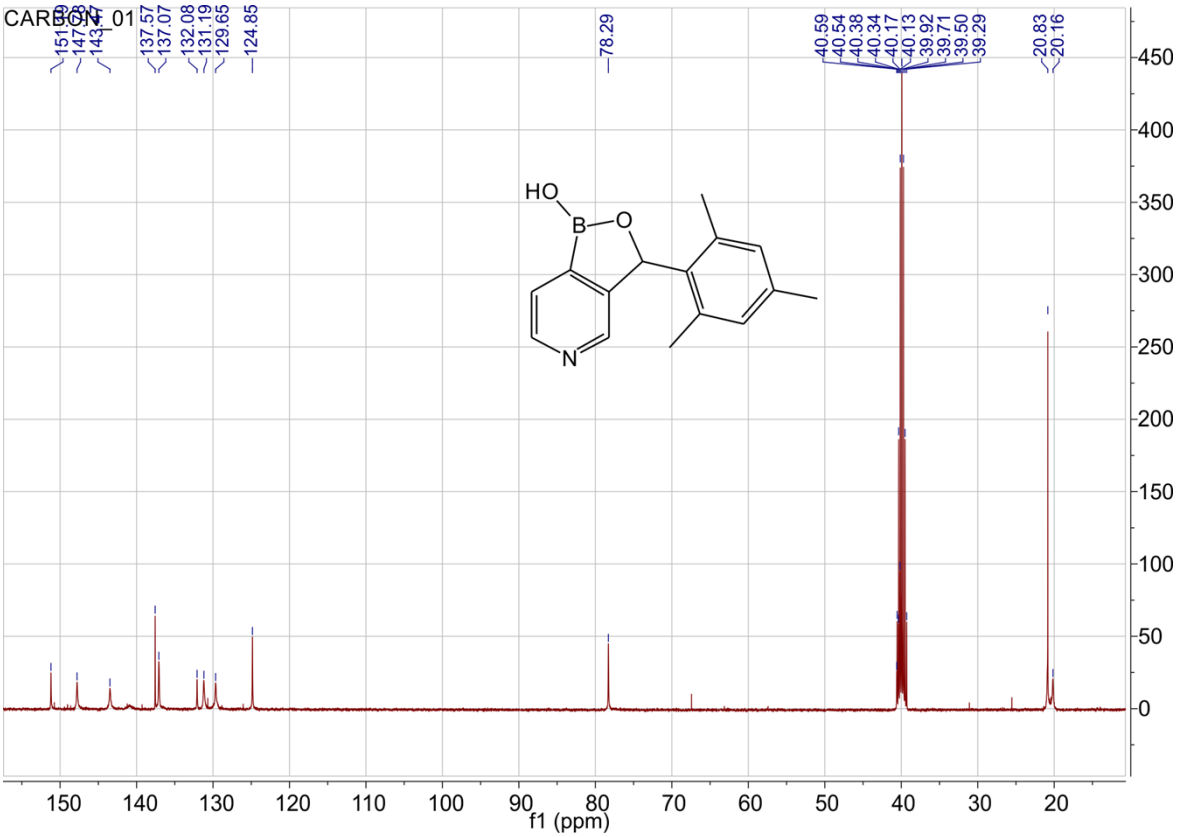

Figure S12. ^{13}C NMR spectrum of compound **3c** (100.6 MHz, DMSO-d_6 solution).

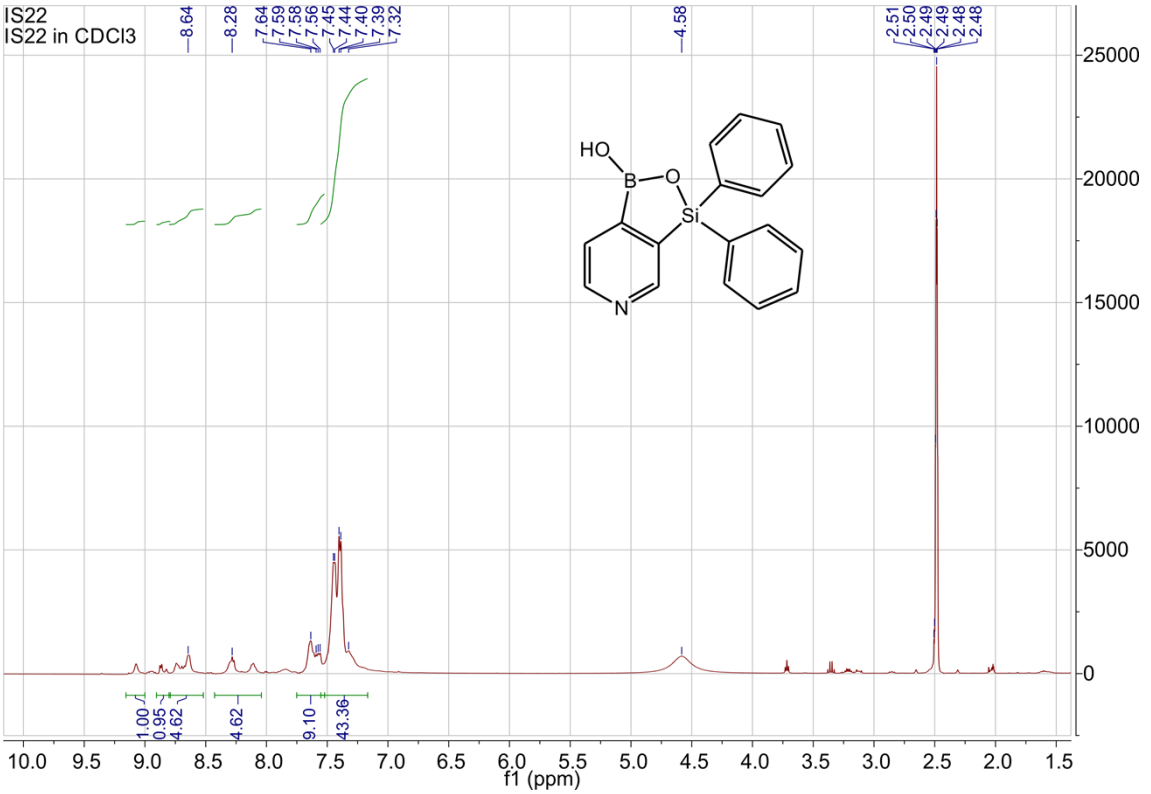

Figure S13. ^{1}H NMR spectrum of compound **4** (300 MHz, DMSO-d_6 solution).

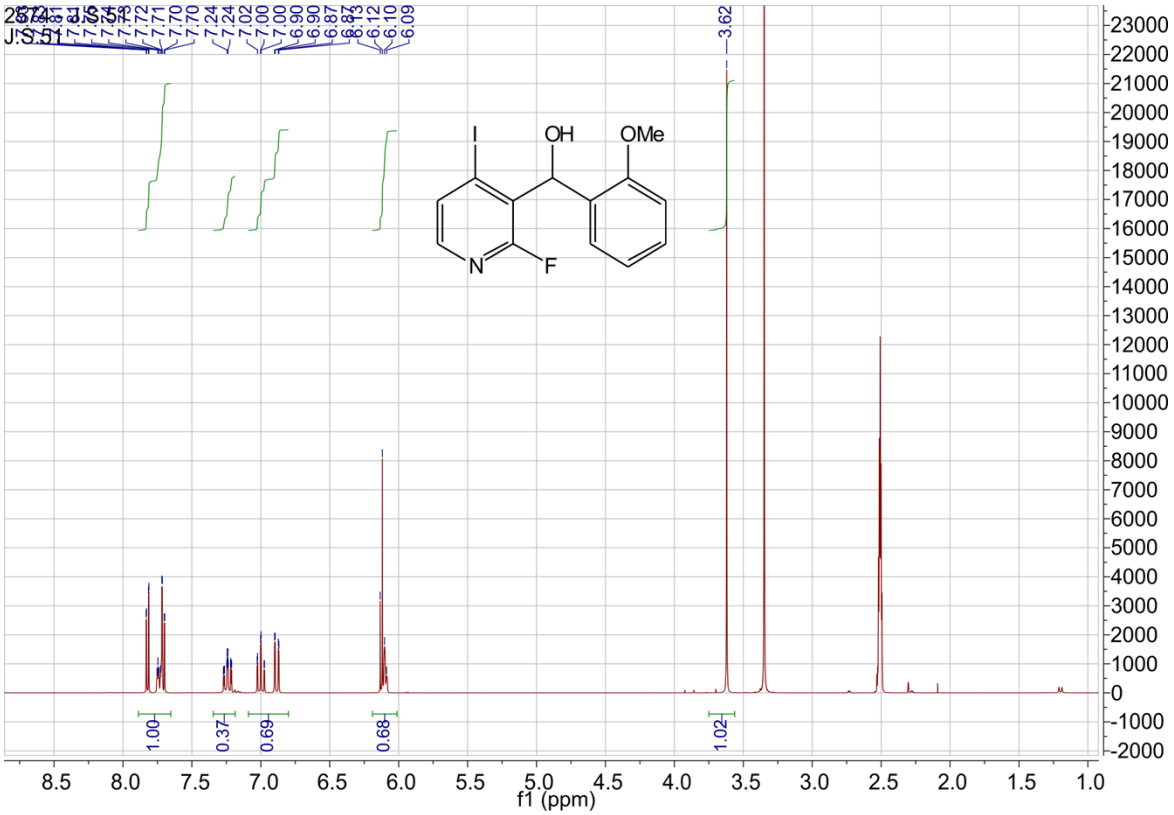

Figure S14. ^{1}H NMR spectrum of compound **5a** (300 MHz, DMSO-d_6 solution).

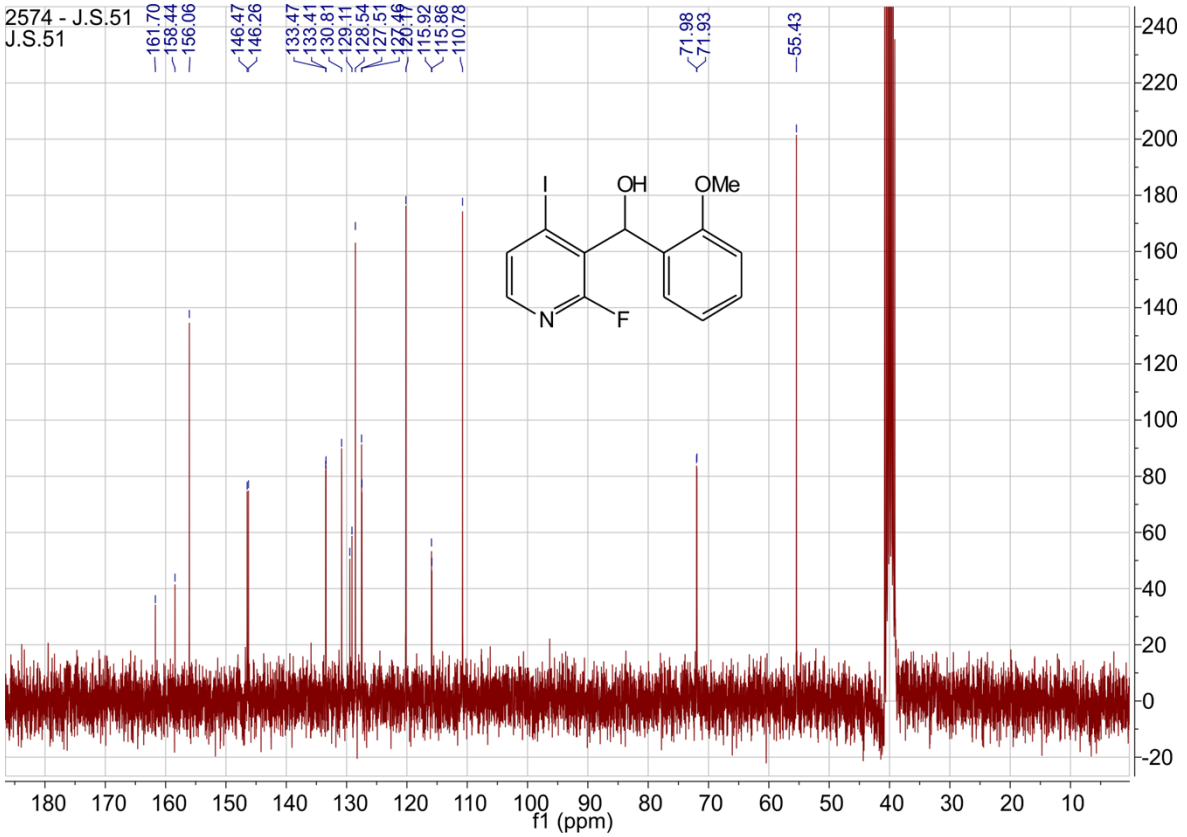

Figure S15. ^{13}C NMR spectrum of compound **5a** (75.5 MHz, DMSO-d_6 solution).

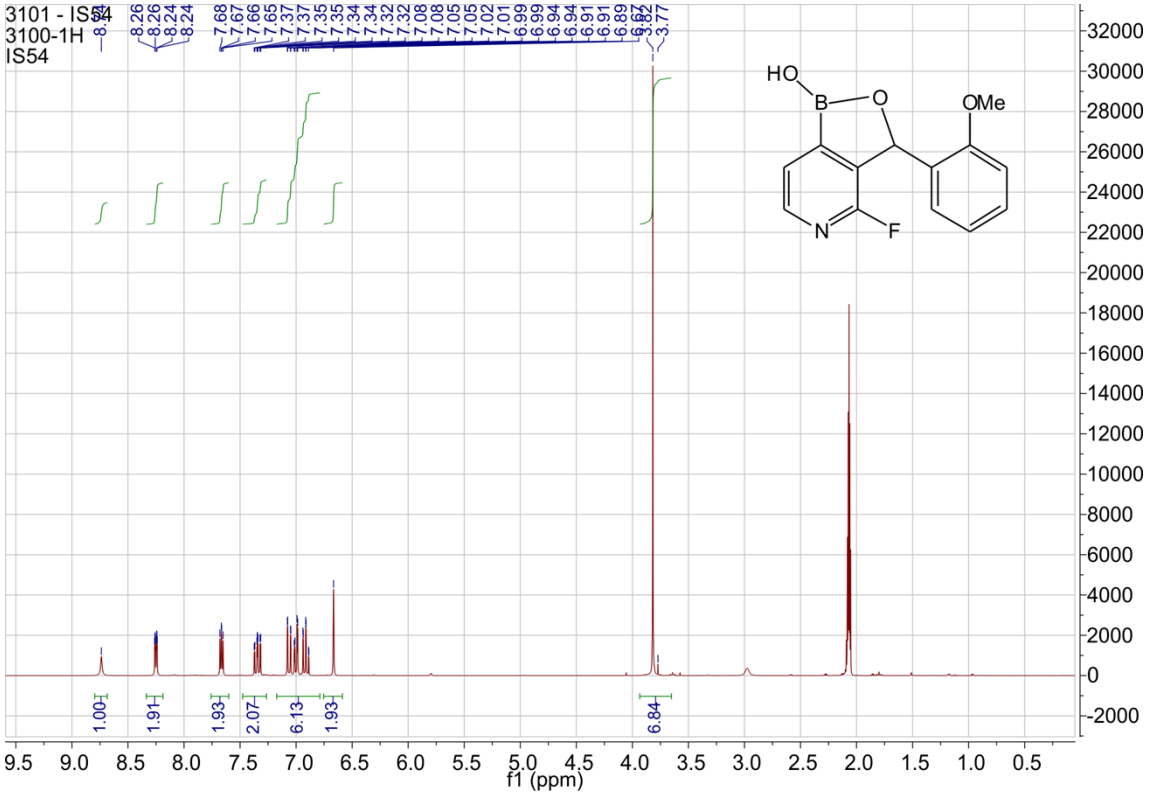

Figure S16. ^{1}H NMR spectrum of compound **5b** (400 MHz, acetone-d_6 solution).

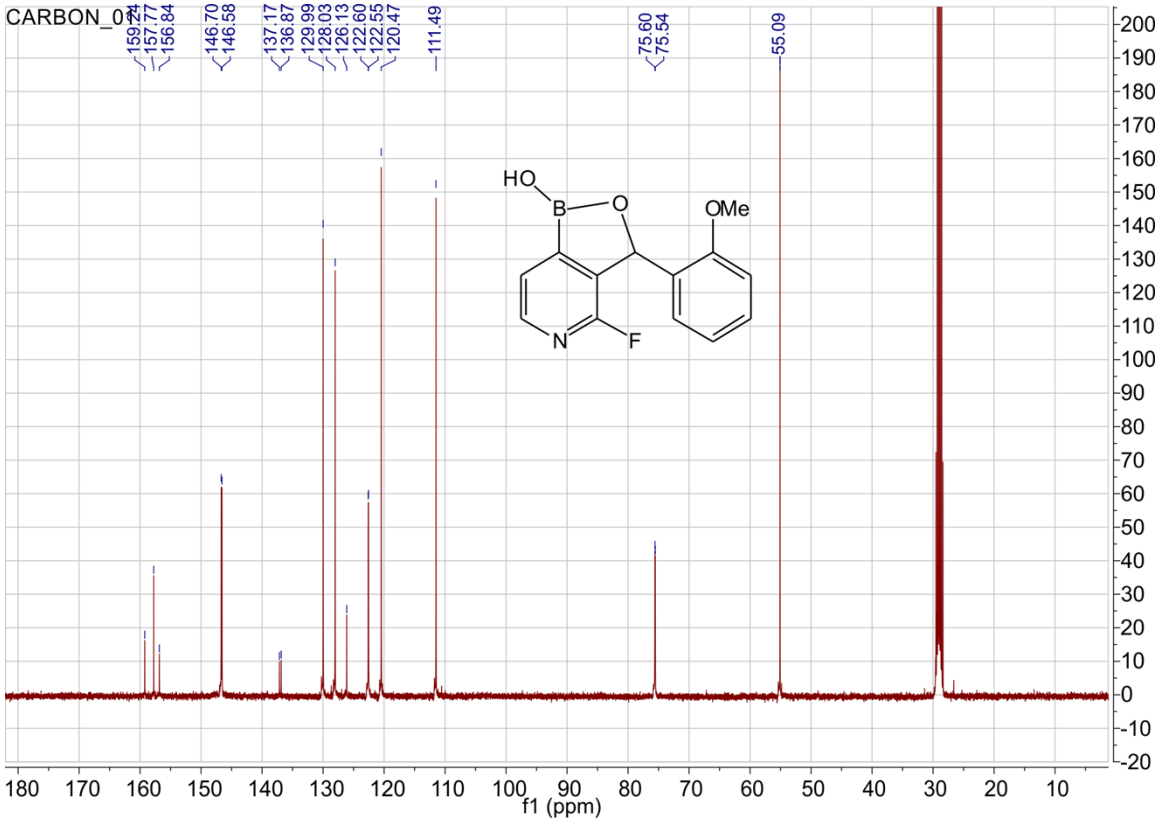

Figure S17. ^{13}C NMR spectrum of compound **5b** (75.5 MHz, acetone-d_6 solution).

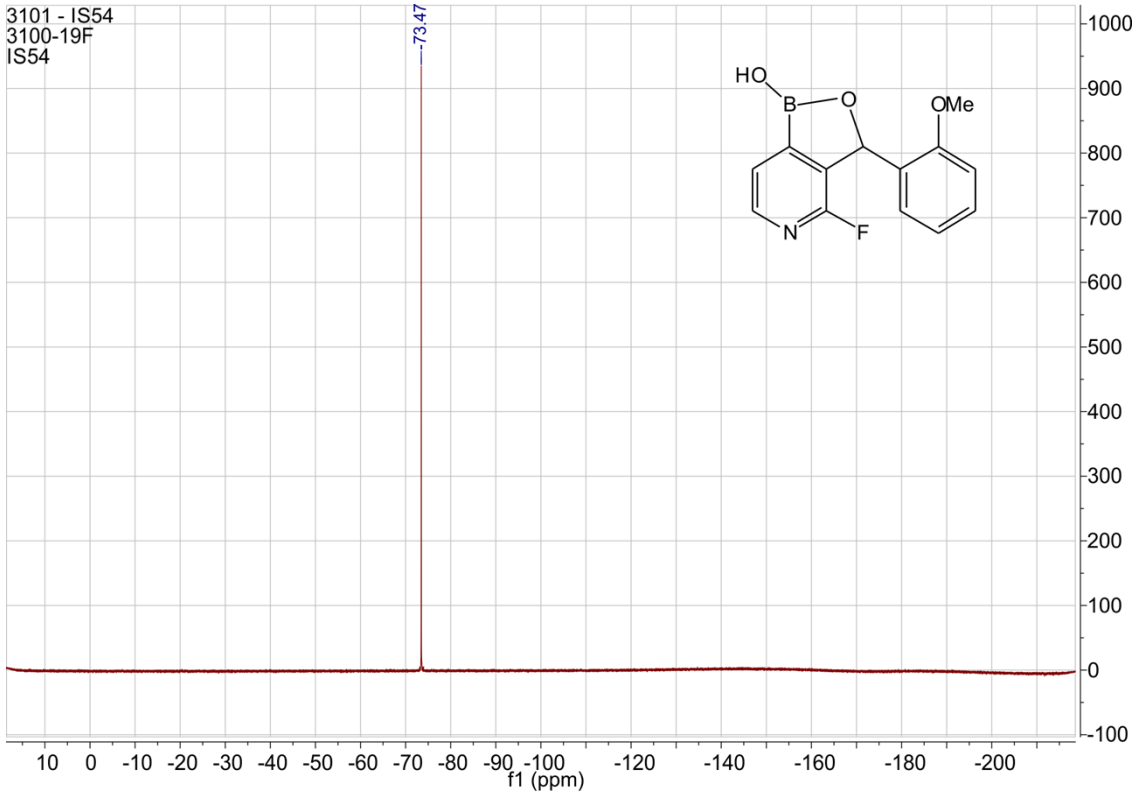

Figure S18. ^{19}F NMR spectrum of compound **5b** (282 MHz, acetone-d_6 solution).

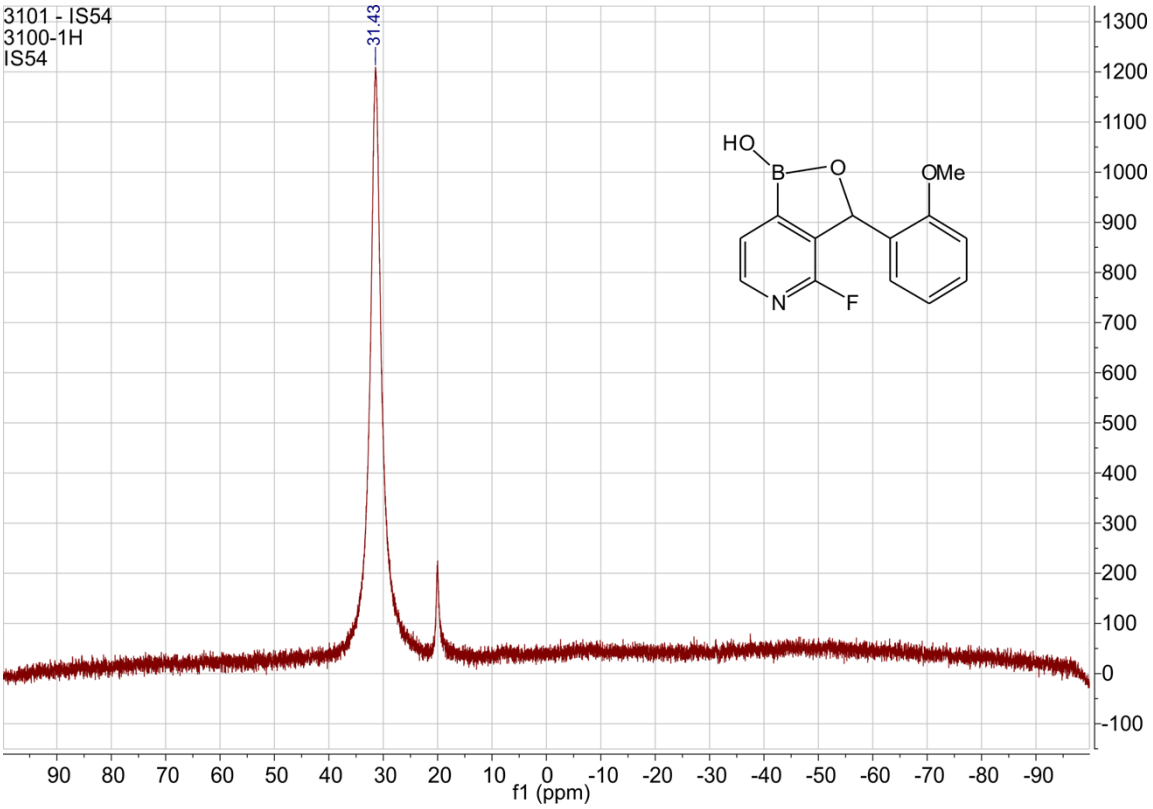

Figure S19. ^{11}B NMR spectrum of compound **5b** (96.2 MHz, acetone-d_6 solution).

2. The pK_a measurements

General: The pK_a values of compounds under studies (**3a-3c**, **[3b-H]Cl, [3b-Me]MeOSO$_3$, 6b**) were measured in water/methanol by the titration with 0.1 M NaOH. The pK_a values were estimated as equal to pH values for corresponding half-equivalence points. The titration curves of all measured compounds are typical of weak acids. Due to the use of dilute solutions in all measurements, it was generally assumed that $K_c \approx K_a$.

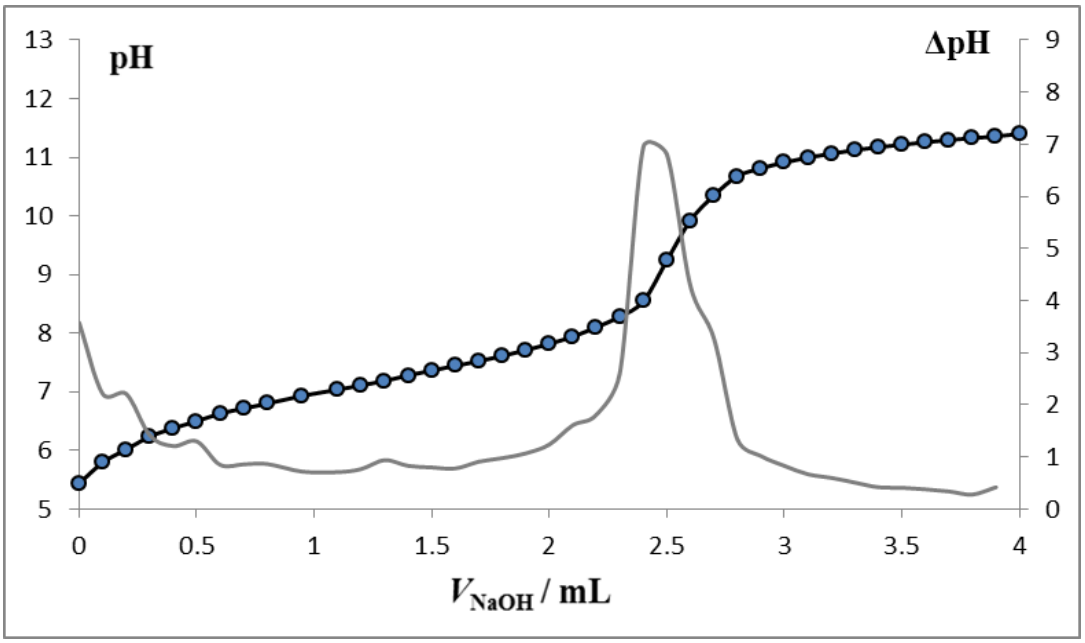

Figure S20. Titration curve of **3a** in water/methanol 1:1 solutions with 0.1 M NaOH.

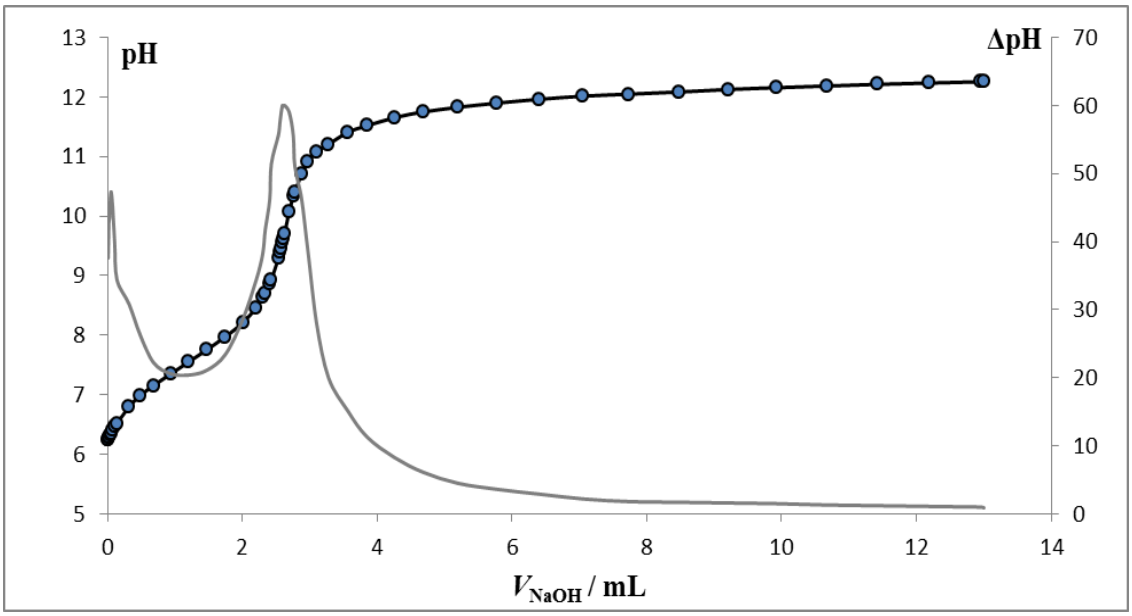

Figure S21. Titration curve of **3b** in water/methanol 1:1 solutions with 0.1 M NaOH.

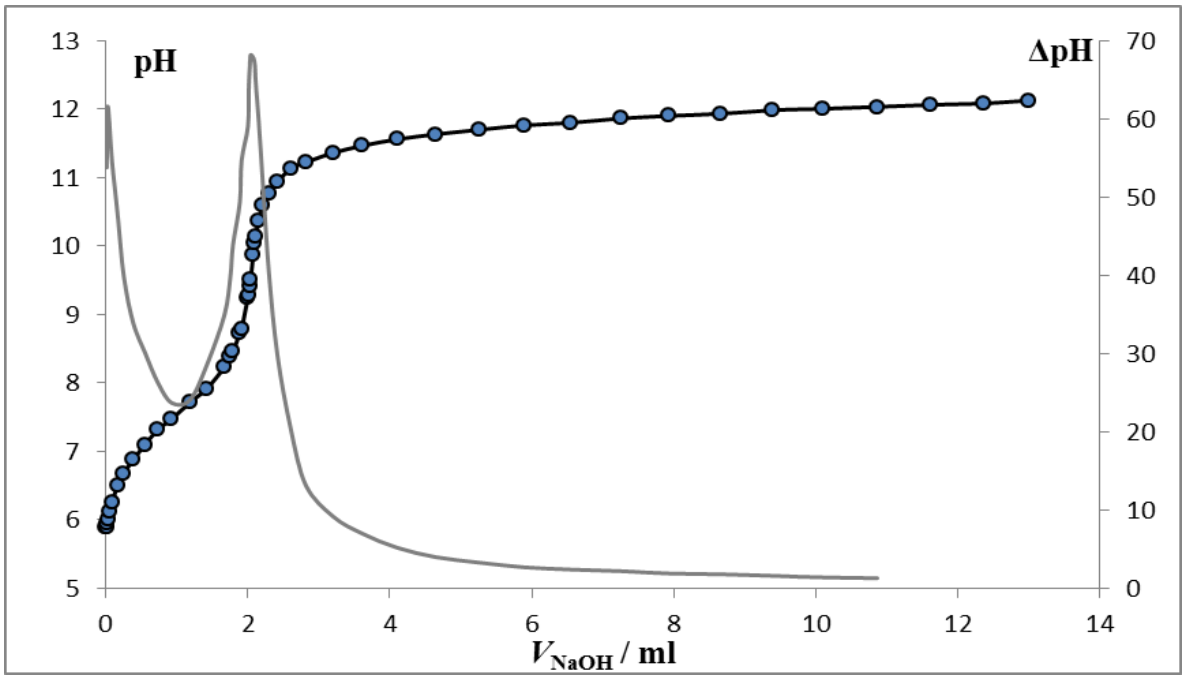

Figure S22. Titration curve of **3c** in water/methanol 1:1 solutions with 0.1 M NaOH.

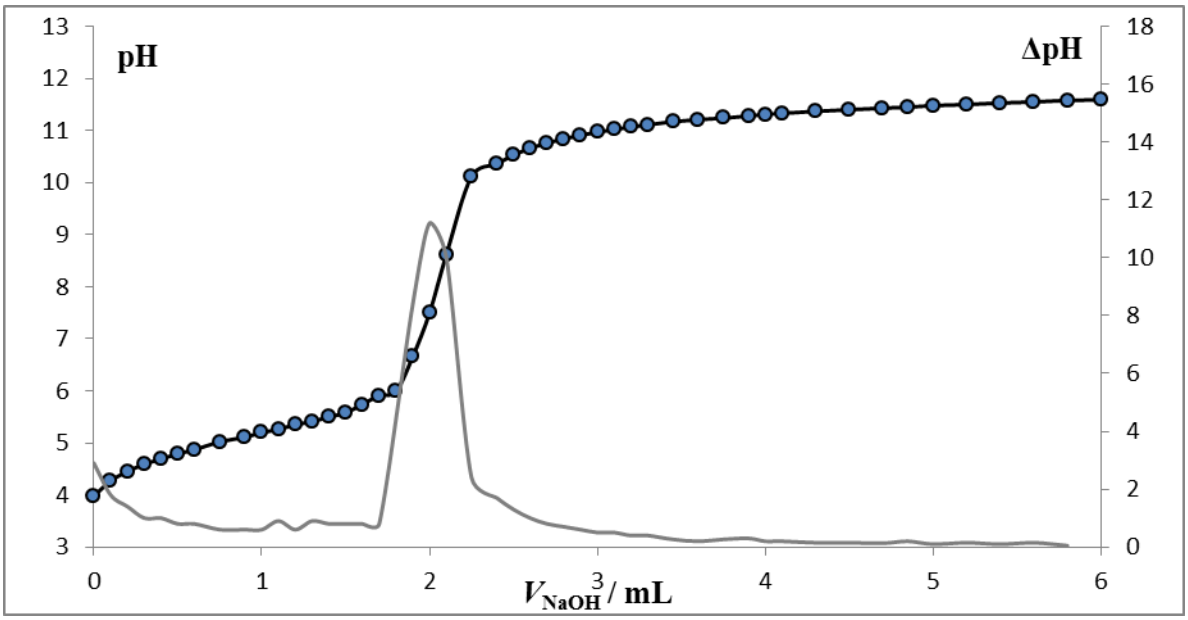

Figure S23. Titration curve of **6b** in water/methanol 1:1 solutions with 0.1 M NaOH.

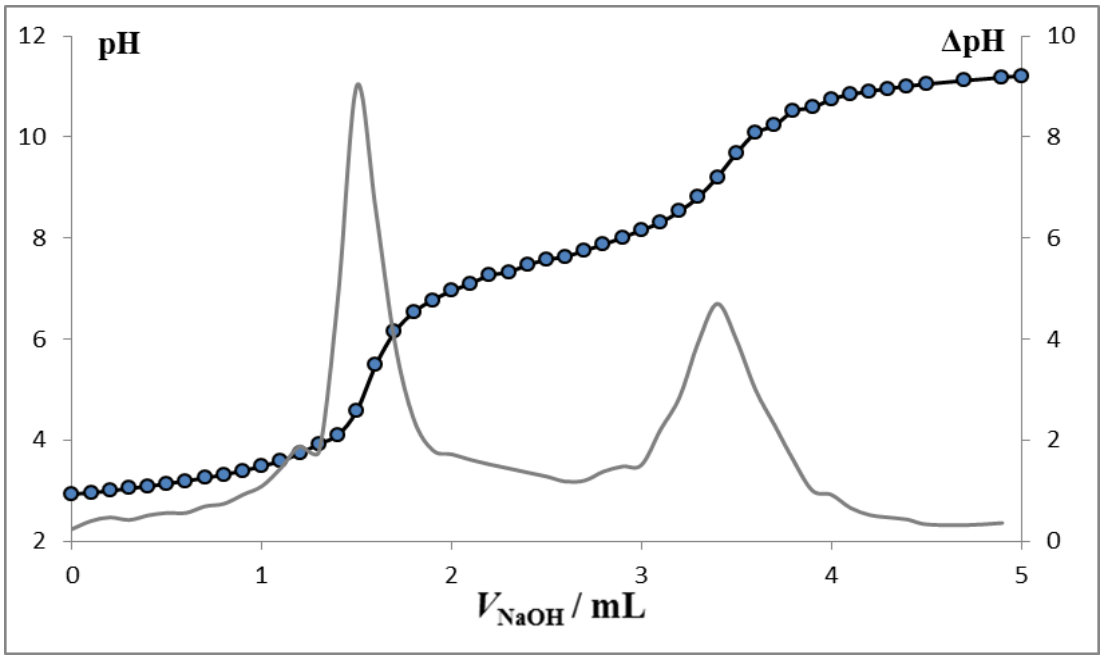

Figure S24. Titration curve of **[3b-H]Cl** in water/methanol 1:1 solutions with 0.1 M NaOH.

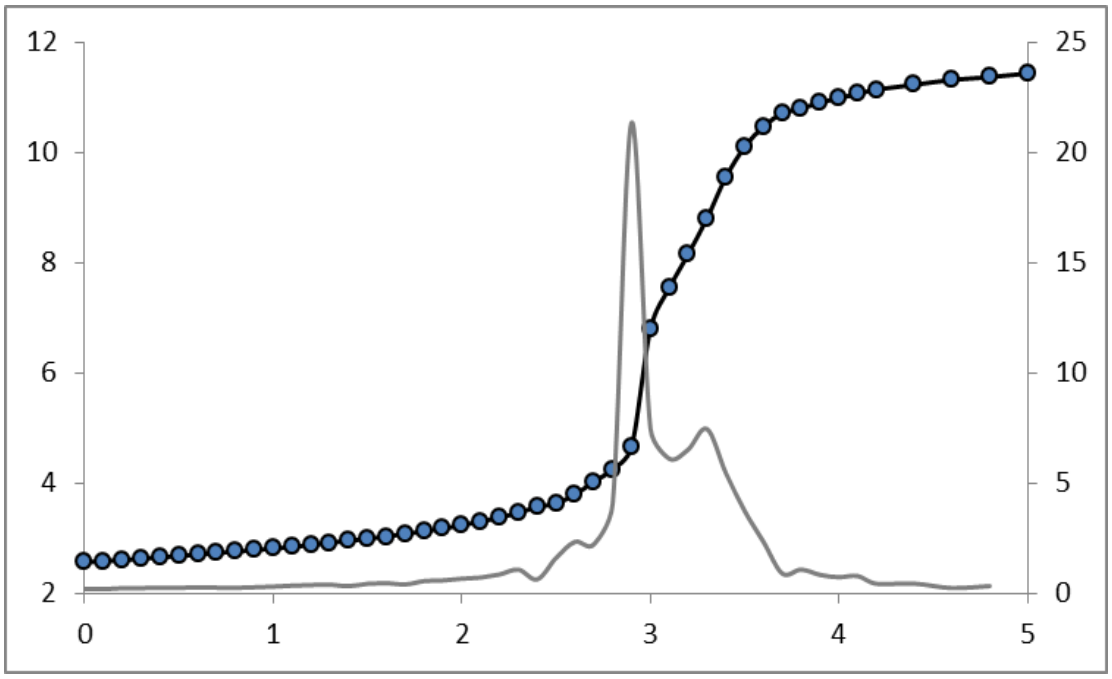

Figure S25. Titration curve of **[3b-Me]MeOSO$_3$** in water/methanol 1:1 solutions with 0.1 M NaOH.

Thermal analysis

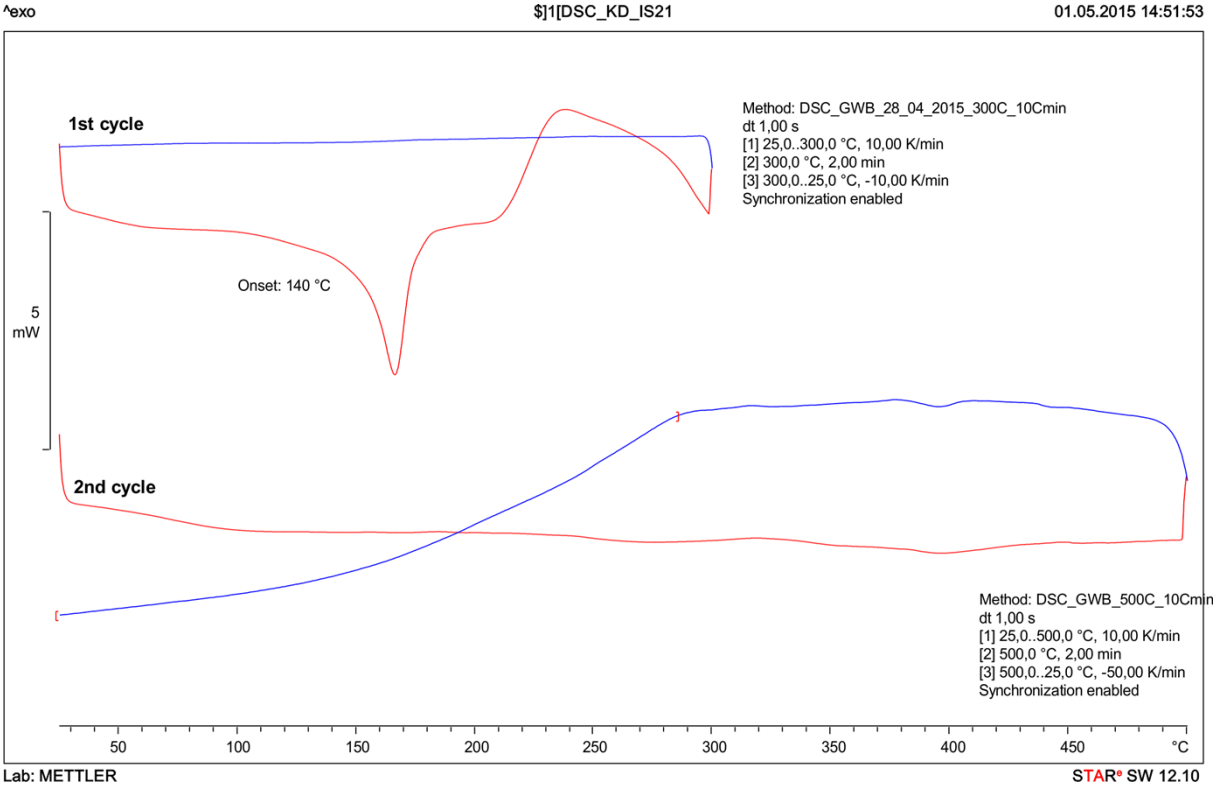

Figure S26. DSC curve of **3a**.

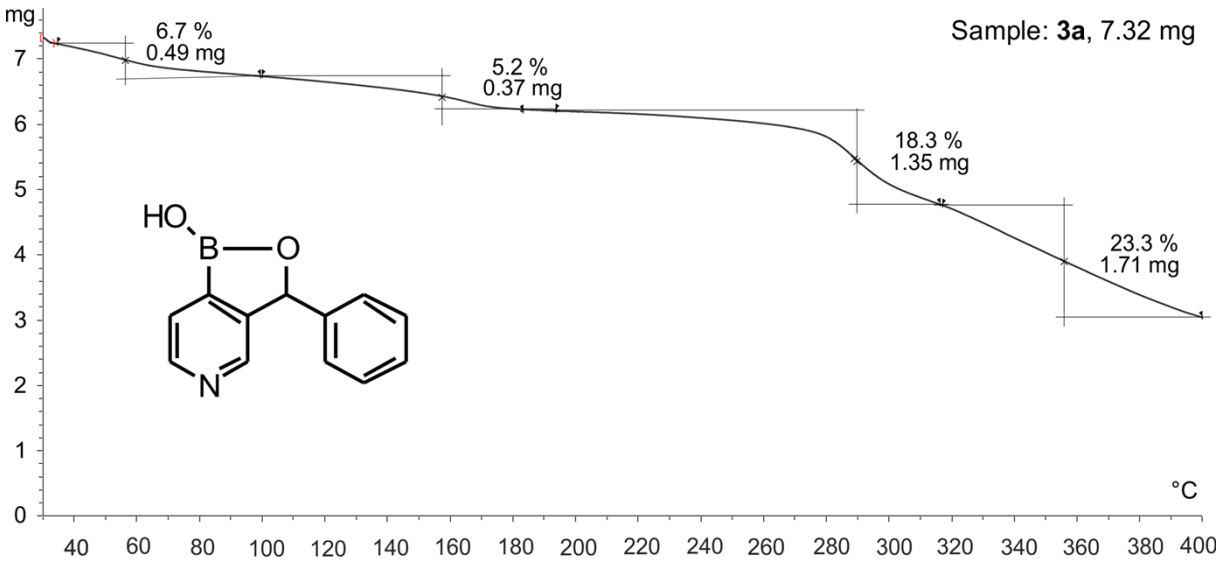

Figure S27. TGA curve of **3a**.

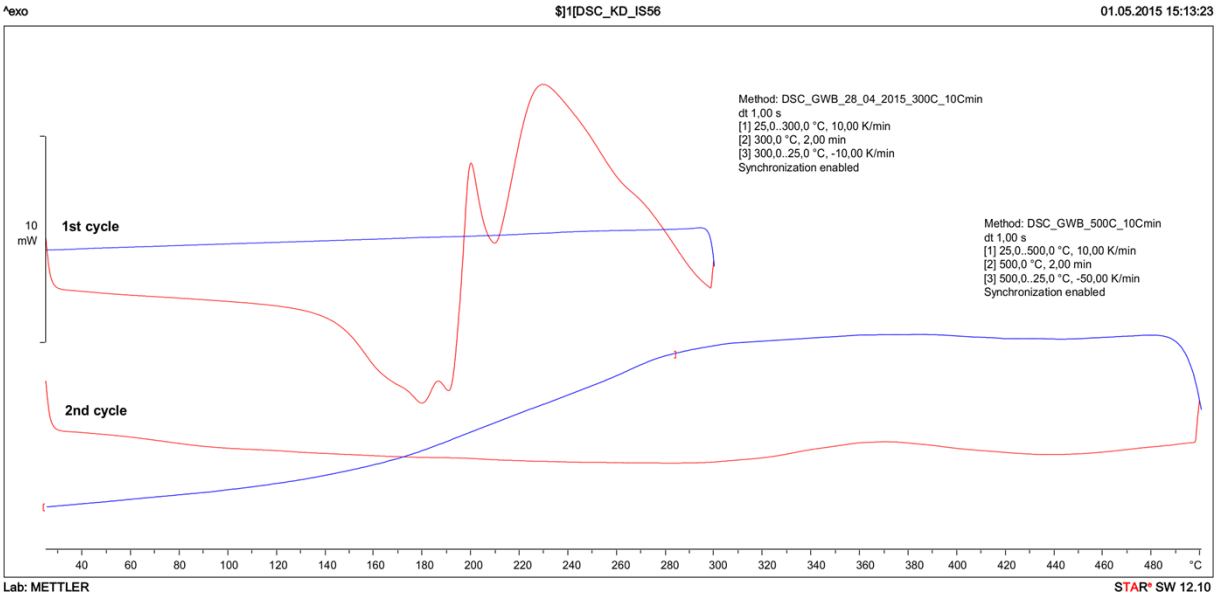

Figure S28. DSC curve of **3b**.

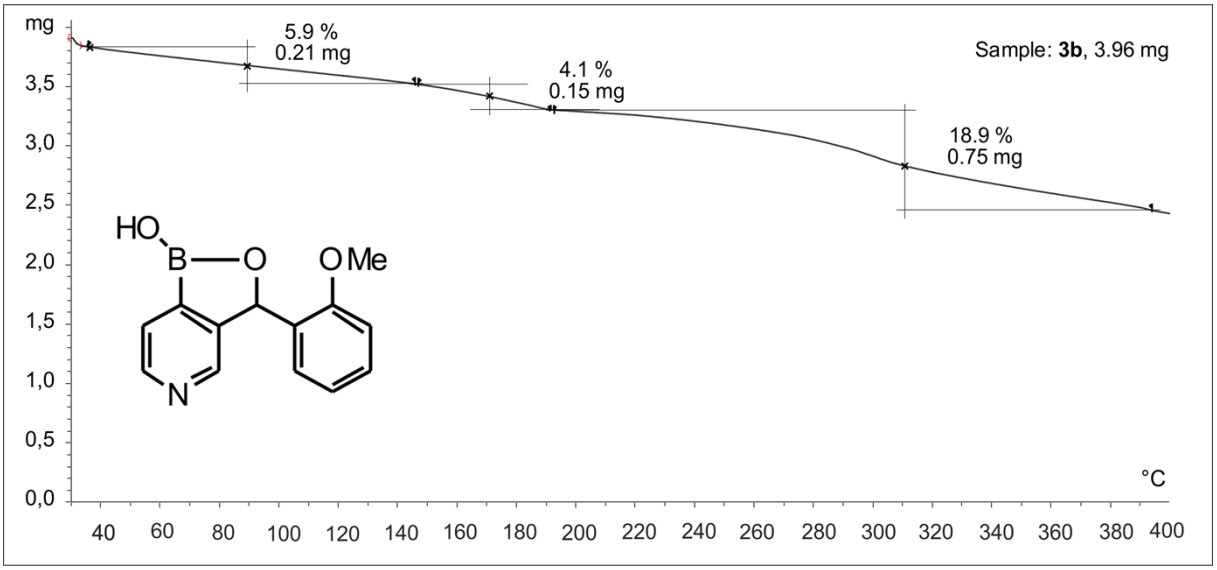

Figure S29. TGA curve of **3b**.

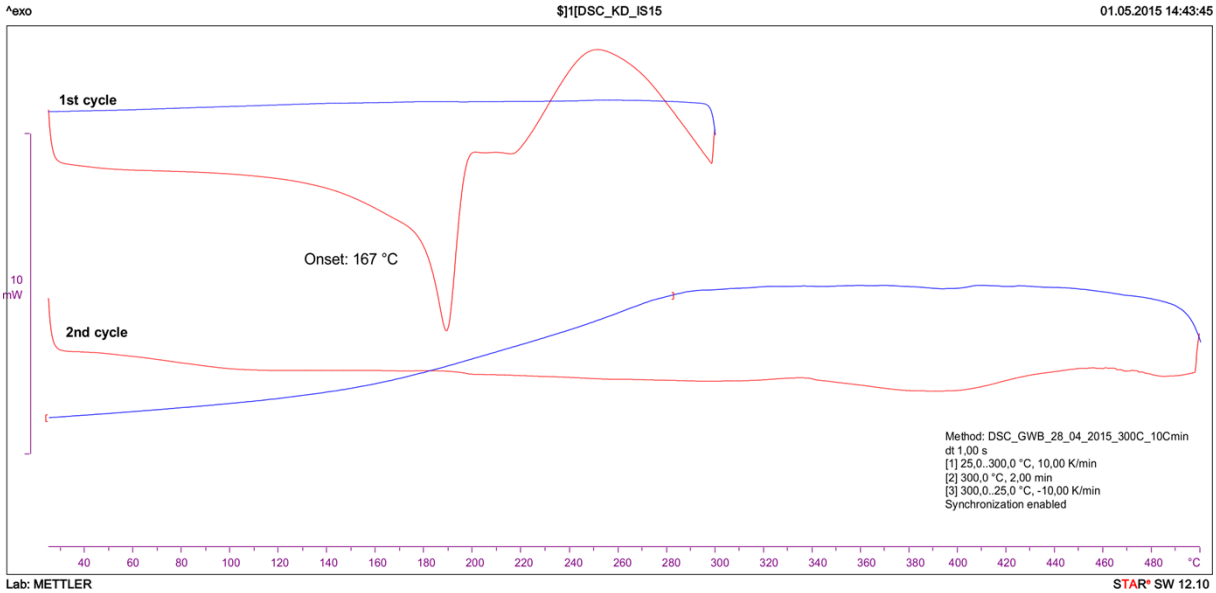

Figure S30. DSC curve of **3c**.

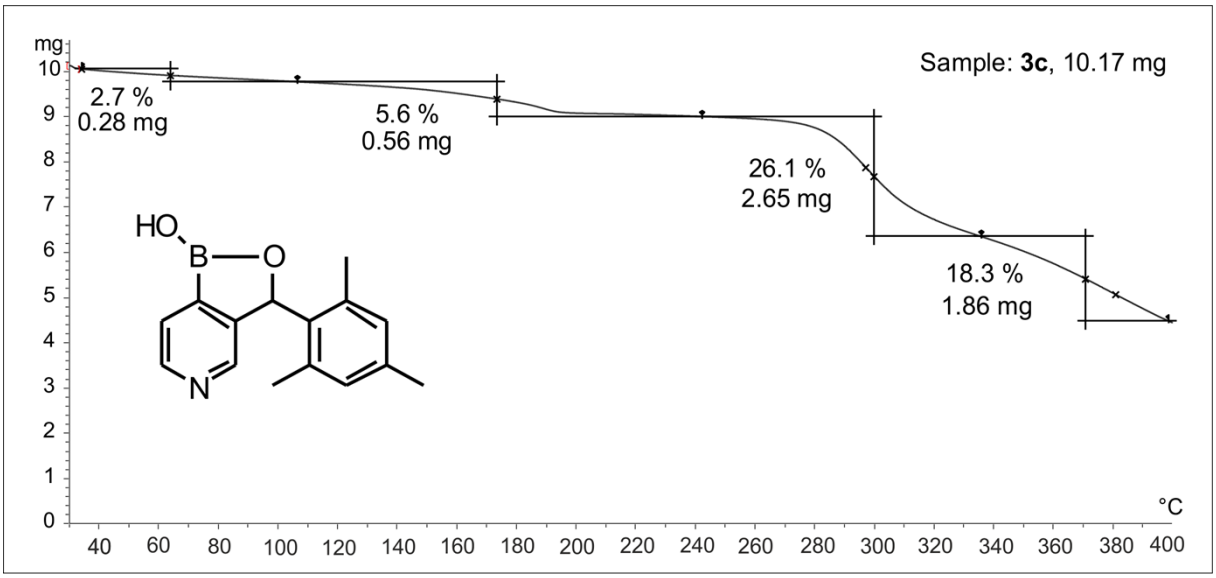

Figure S31. TGA curve of **3c**.

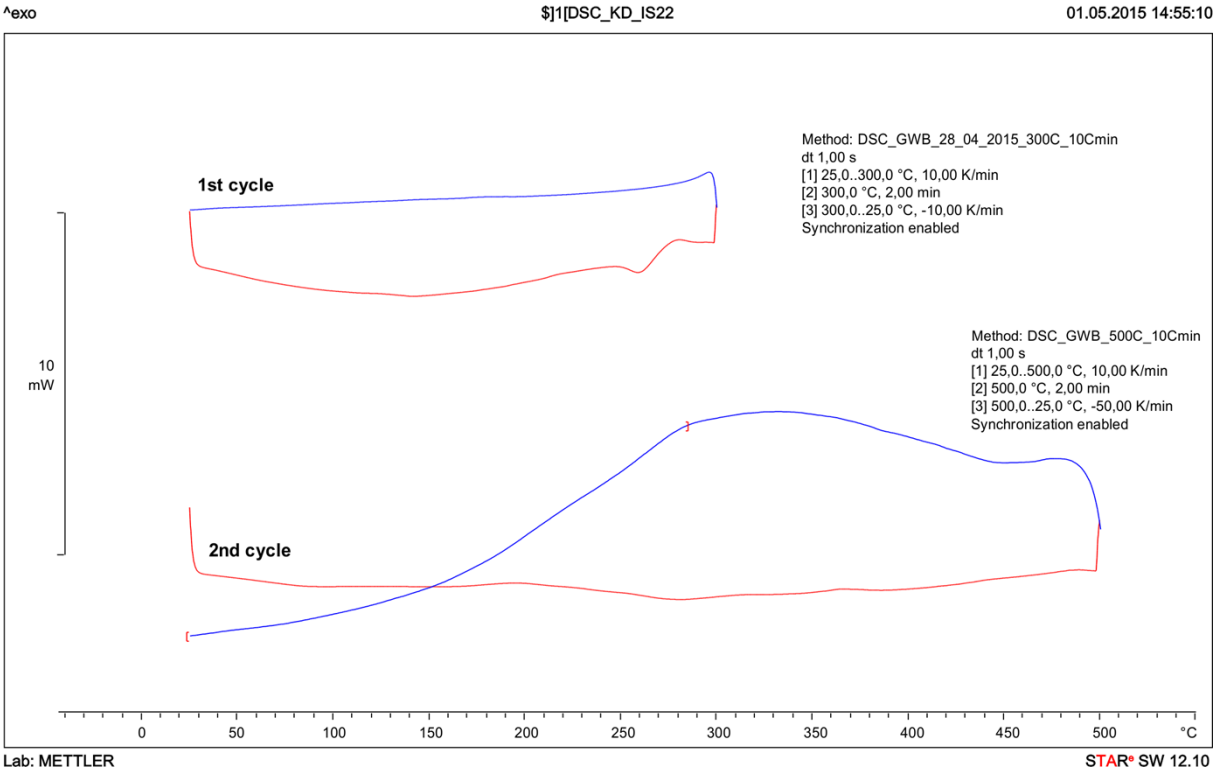

Figure S32. DSC curve of **4**.

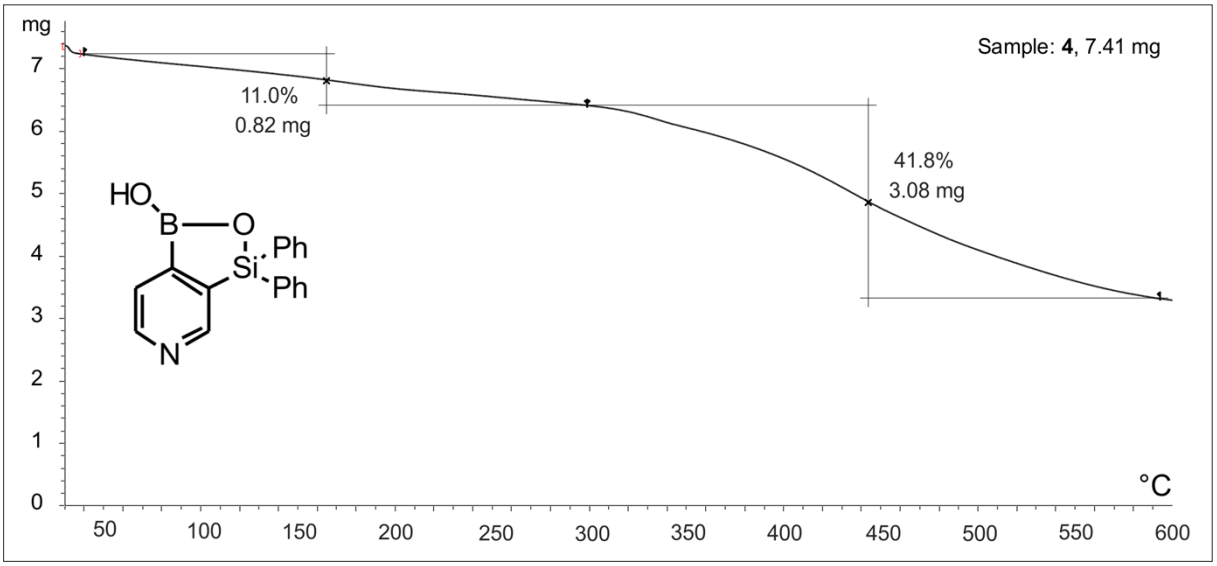

Figure S33. TGA curve of **4**.

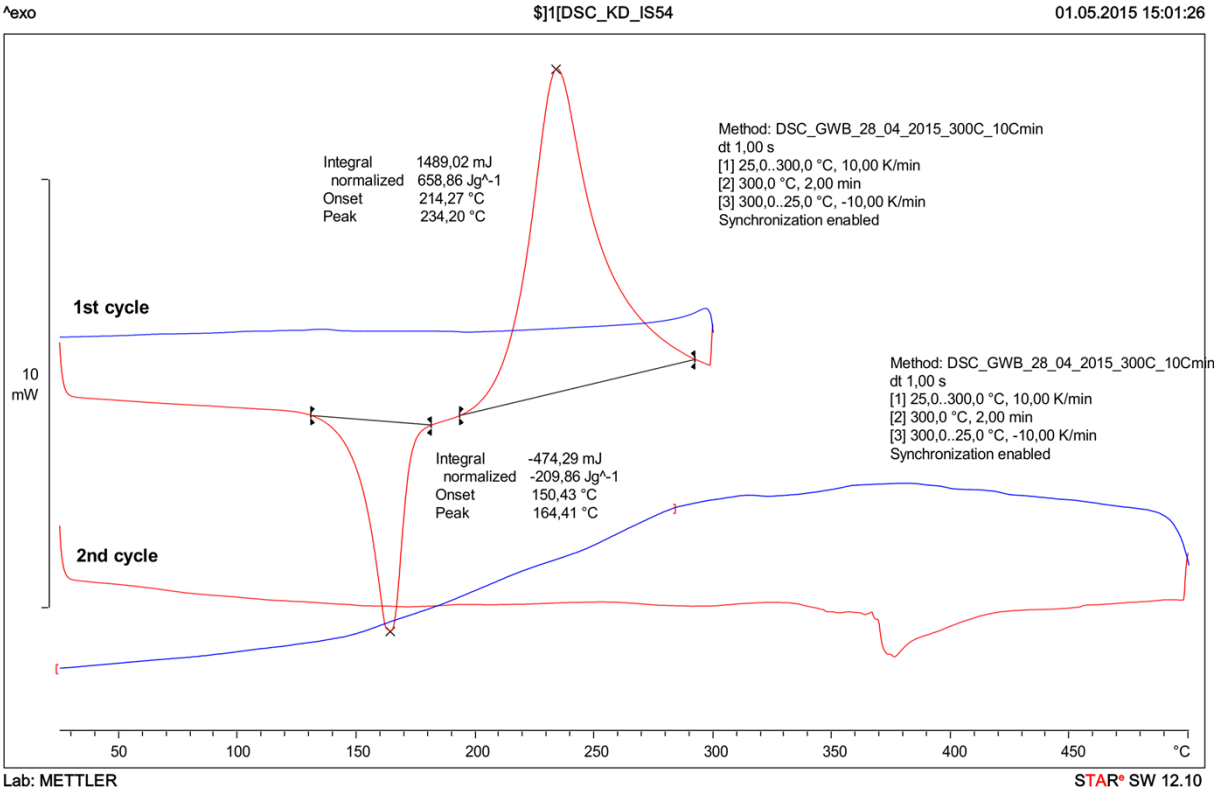

Figure S34. DSC curve of **5b**.

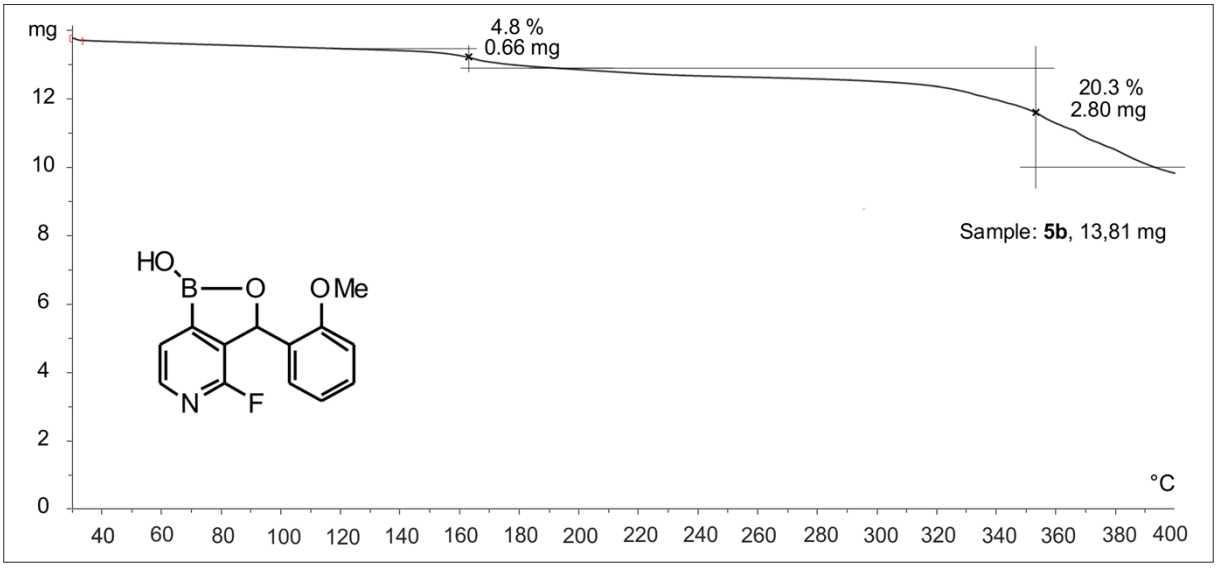

Figure S35. TGA curve of **5b**.