Supporting Information for

Selective, ambient-temperature C-4 deuteration of pyrazole derivatives by D_2O

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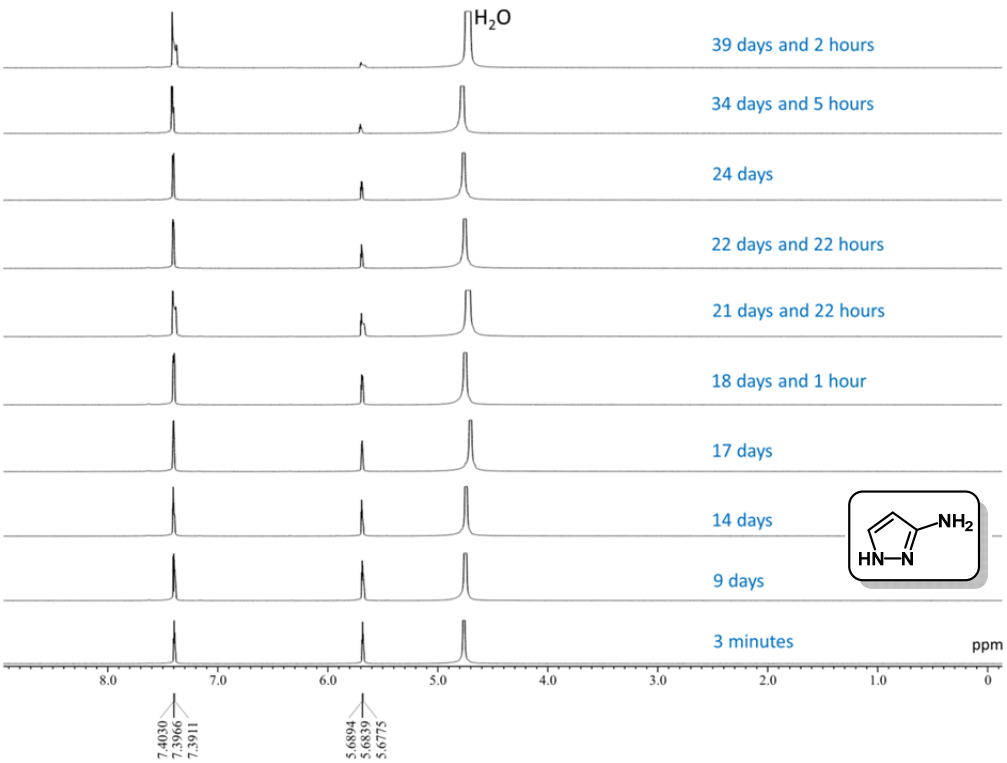

Figure S1. ^{1}H NMR monitoring of the deuteration of **1** in D_2O in the absence of catalyst at 25 °C.

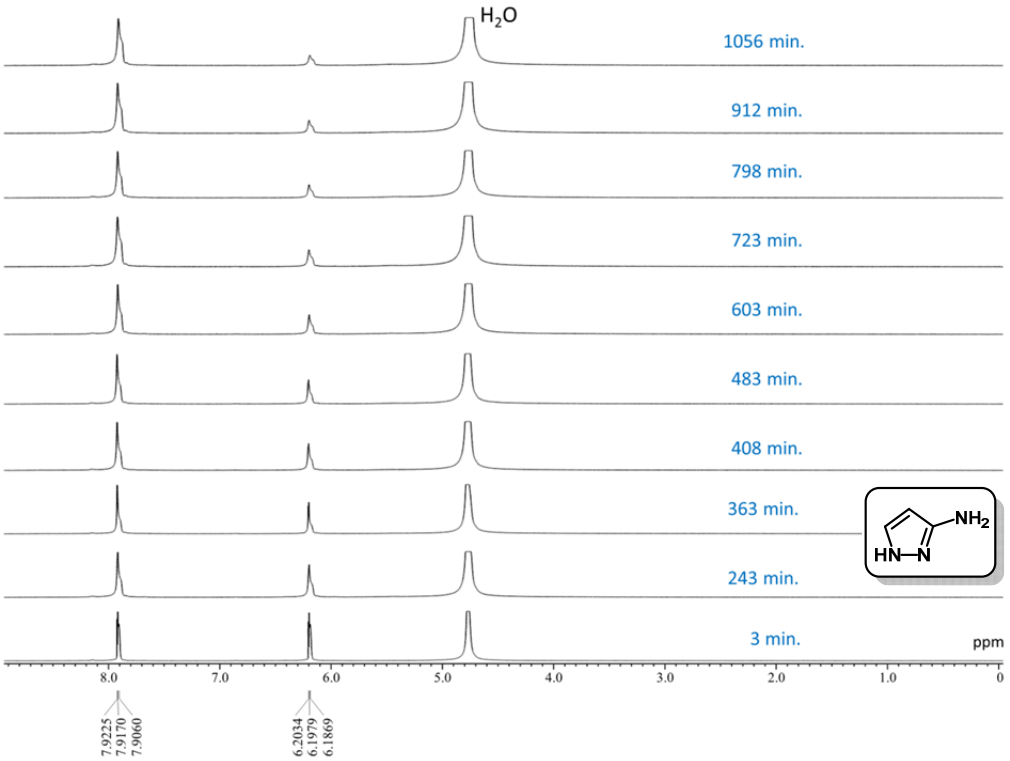

Figure S2. ^{1}H NMR monitoring of the deuteration of **1** in D_2O in the absence of catalyst at 70 °C.

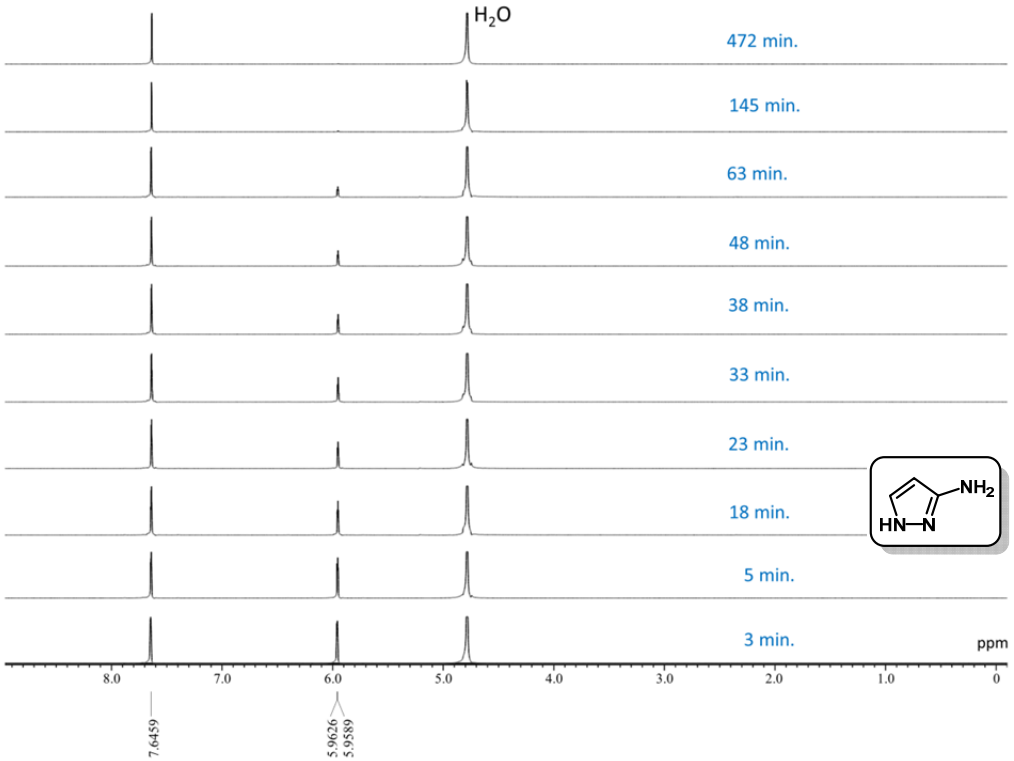

Figure S3. ^{1}H NMR monitoring of the deuteration of **1** in D_2O with 100 mol % DCl at 25 °C.

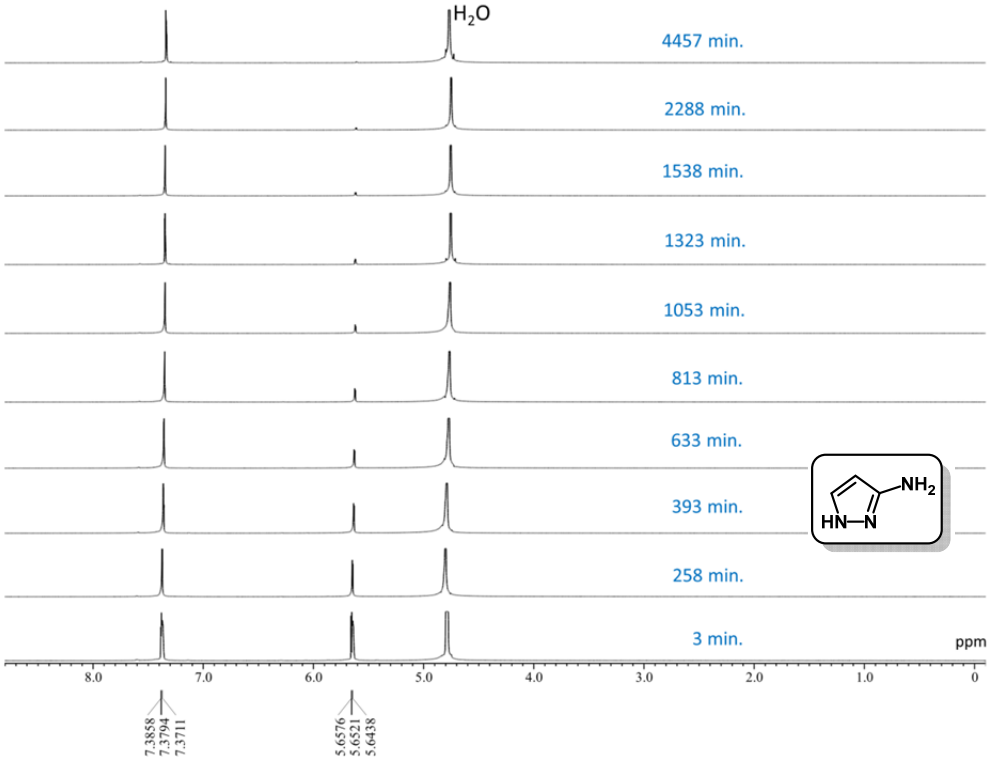

Figure S4. ^{1}H NMR monitoring of the deuteration of **1** in D_2O with 100 mol % NaOD at 25 °C.

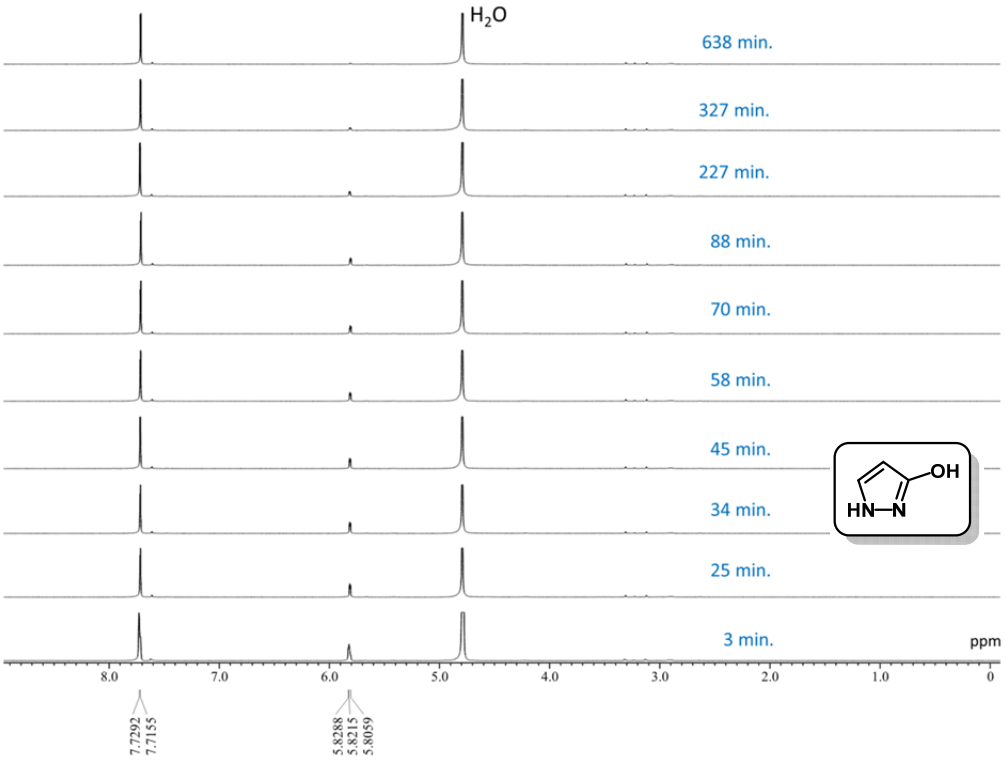

Figure S5. ^{1}H NMR monitoring of the deuteration of **2** in D_2O with 100 mol % DCl at 25 °C.

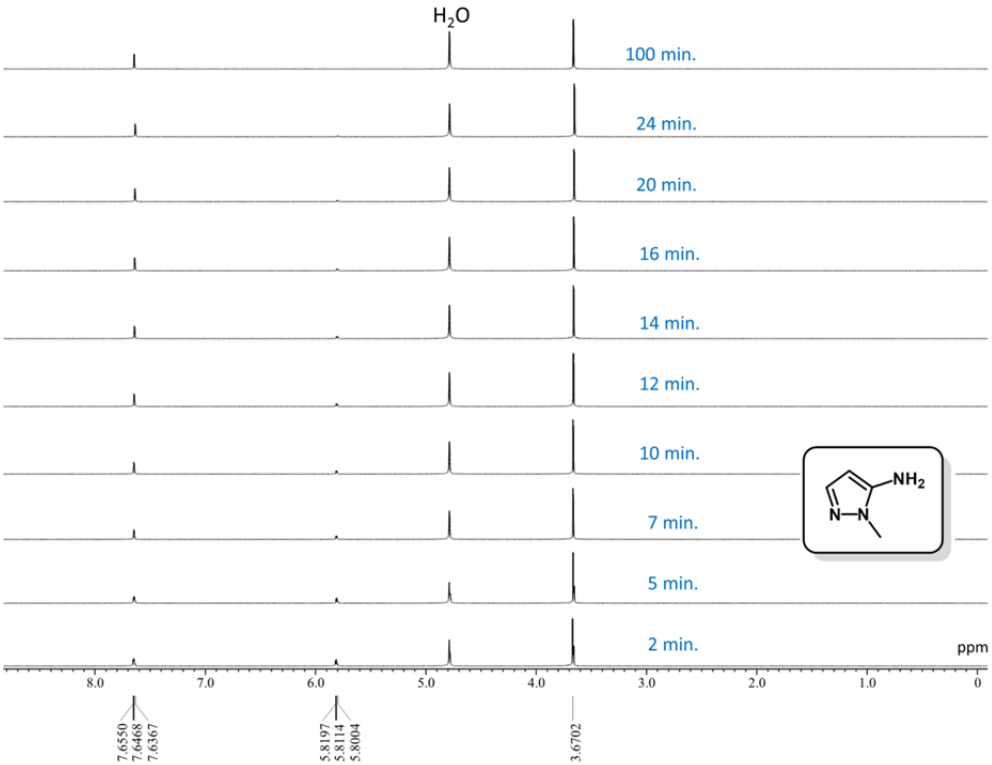

Figure S6. ^{1}H NMR monitoring of the deuteration of **3** in D_2O with 100 mol % DCl at 25 °C.

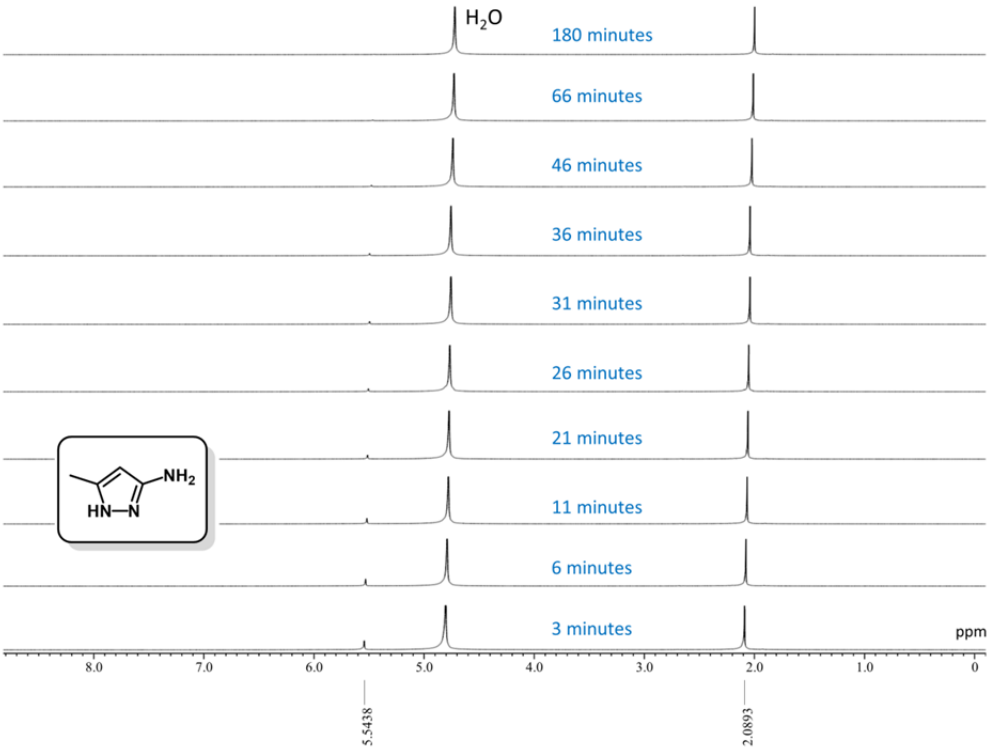

Figure S7. ^{1}H NMR monitoring of the deuteration of **4** in D_2O with 100 mol % DCl at 25 °C.

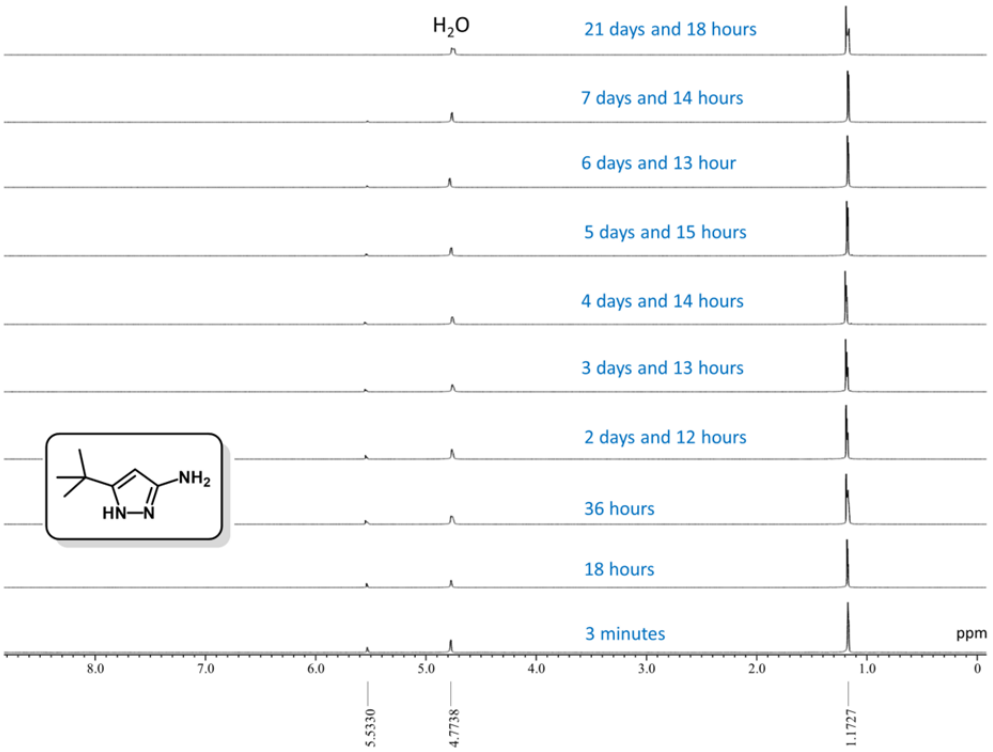

Figure S8. ^{1}H NMR monitoring of the deuteration of **6** in D_2O in the absence of catalyst at 25 °C.

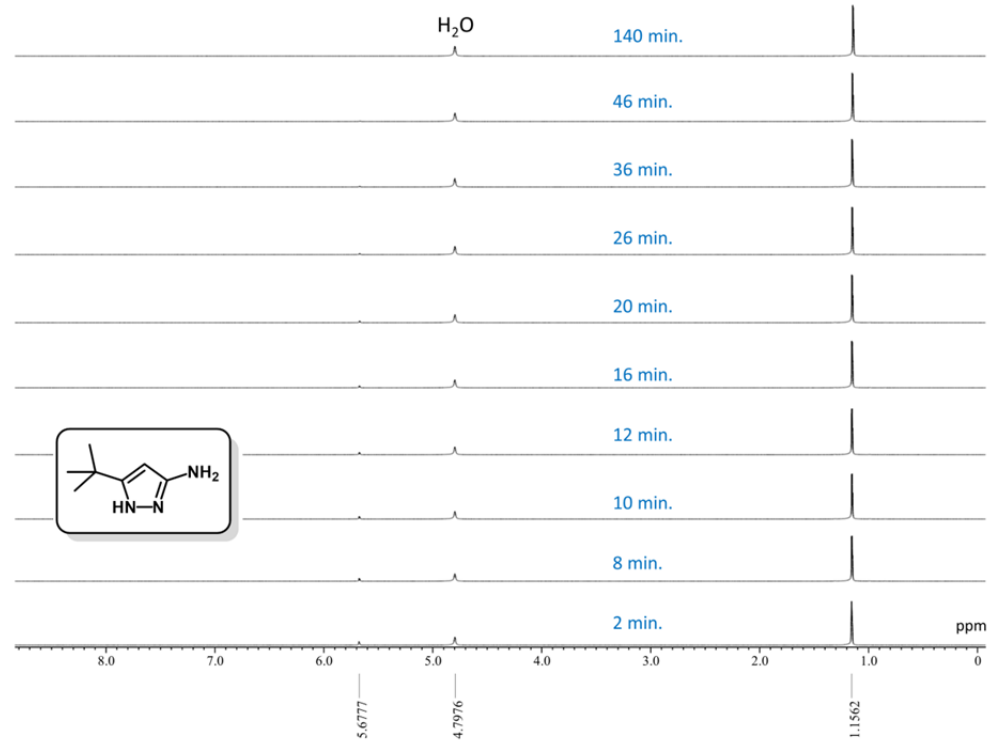

Figure S9. ^{1}H NMR monitoring of the deuteration of **6** in D_2O with 100 mol % DCl at 25 °C.

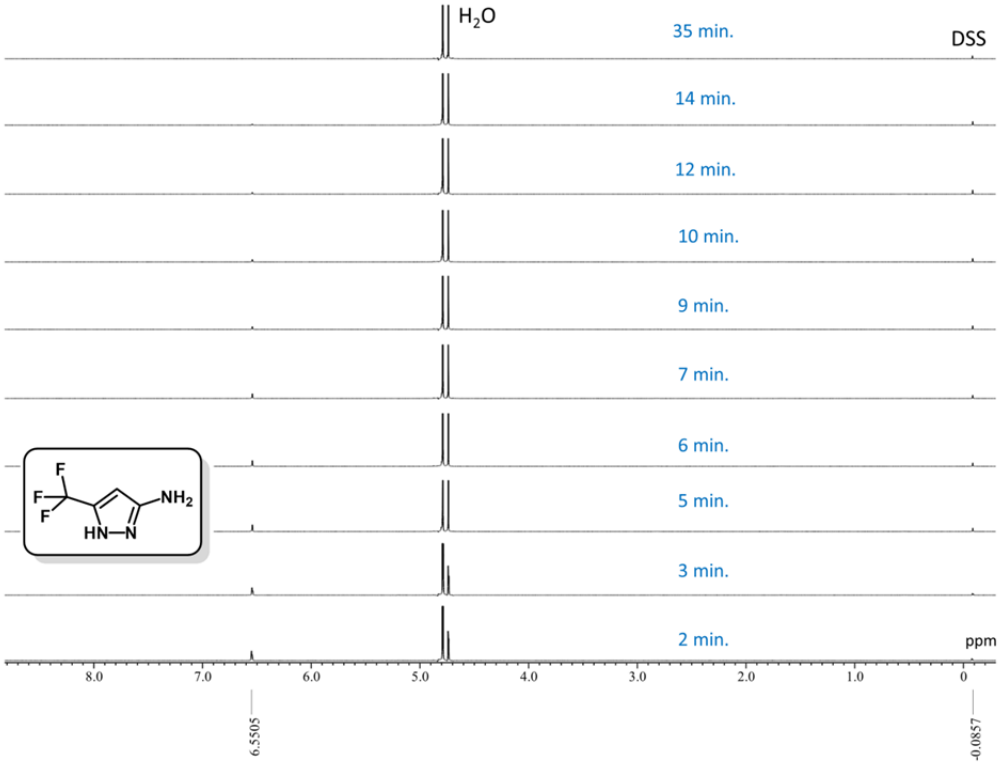

Figure S10. ^{1}H NMR monitoring of the deuteration of **7** in D_2O with 100 mol % DCl at 25 °C (with DSS sodium salt as reference in a coaxial tube).

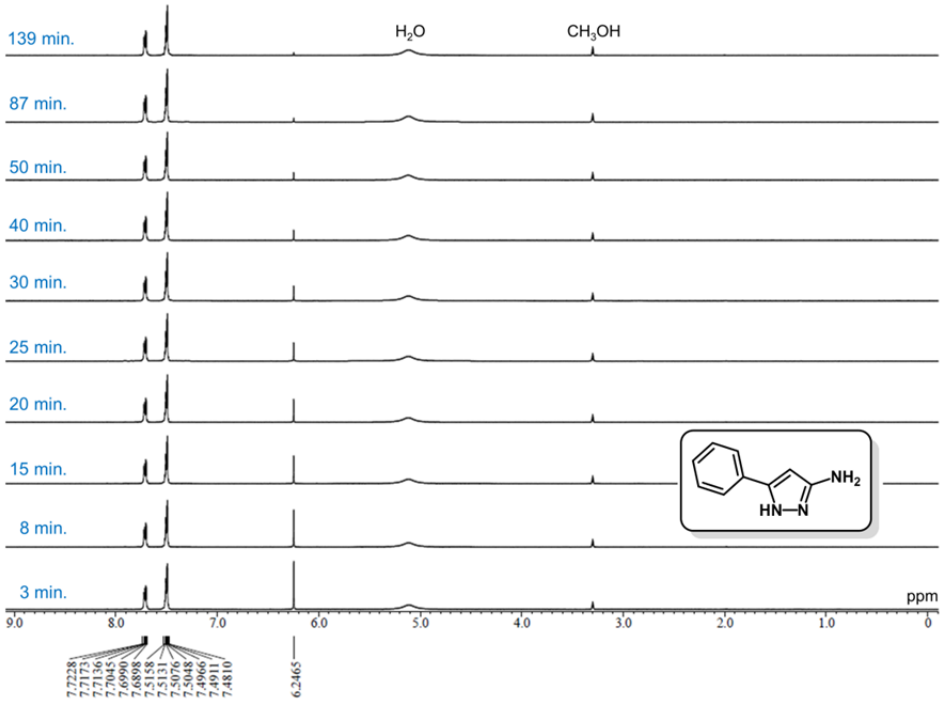

Figure S11. ^{1}H NMR monitoring of the deuteration of **8** in CD_3OD with 100 mol % DCl at 25 °C.

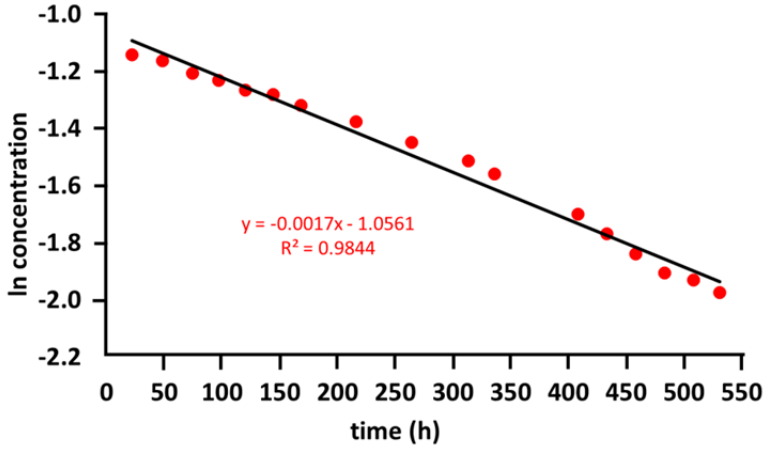

Figure S12. Deuteration of **1** in D_2O in the absence of catalyst at 25 °C.

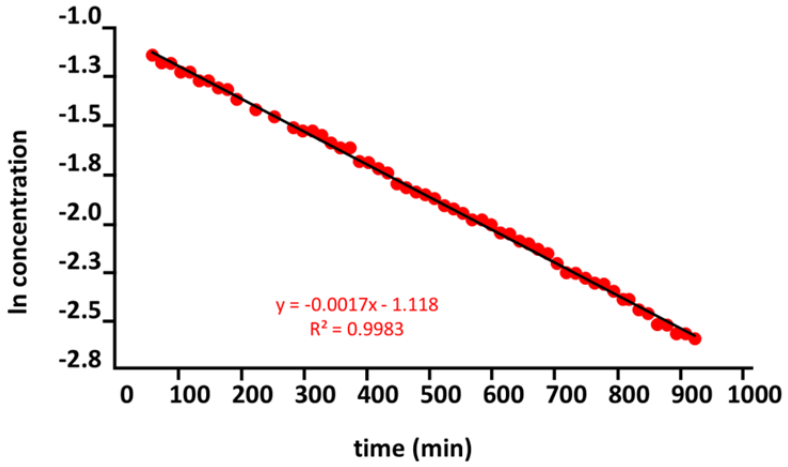

Figure S13. Deuteration of **1** in D_2O in the absence of catalyst at 70 °C.

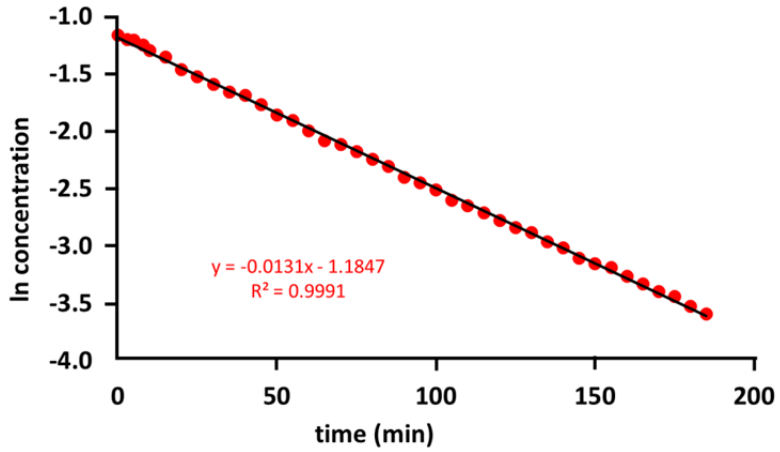

Figure S14. Deuteration of **1** in D_2O with 10 mol % DCl at 25 °C.

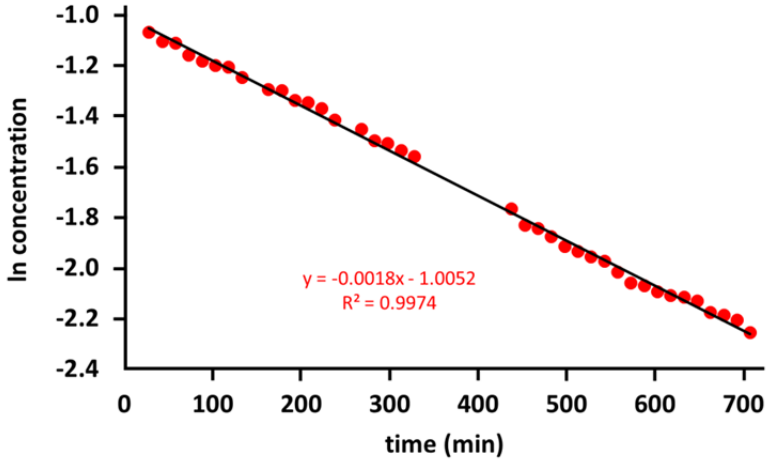

Figure S15. Deuteration of **1** in D_2O with 1 mol % DCl at 25 °C.

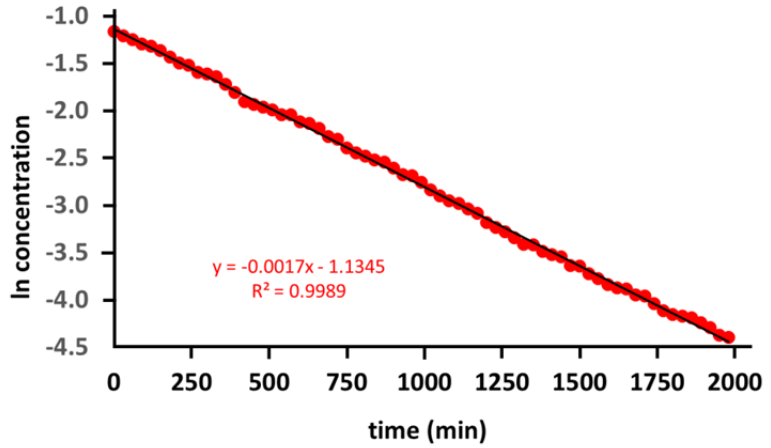

Figure S16. Deuteration of **1** in D_2O with 100 mol % NaOD at 25 °C.

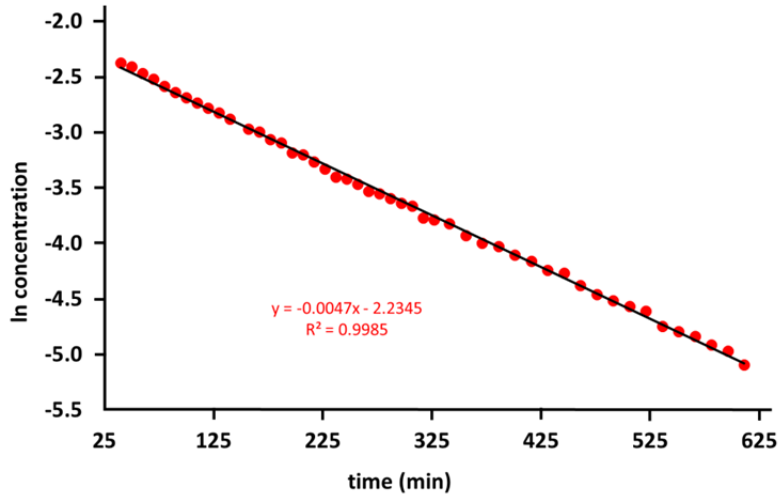

Figure S17. Deuteration of **2** in D_2O with 100 mol % DCl at 25 °C.

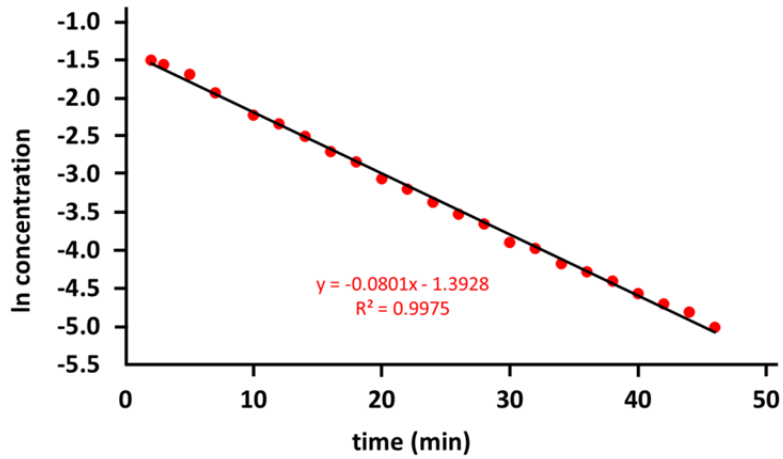

Figure S18. Deuteration of **3** in D_2O with 100 mol % DCl at 25 °C.

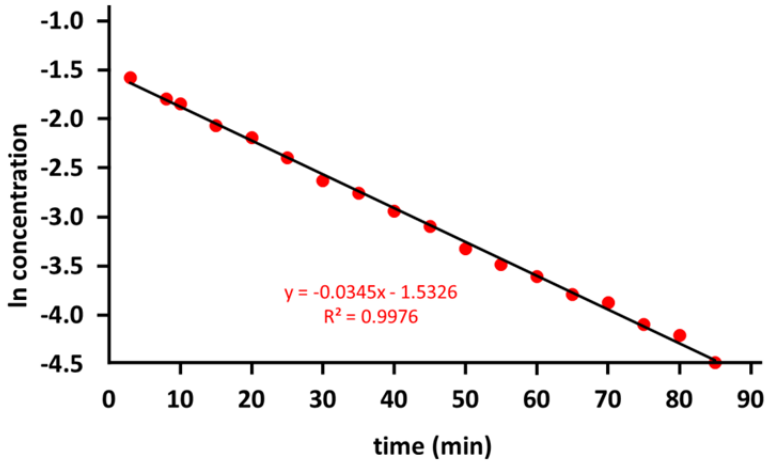

Figure S19. Deuteration of **4** in D_2O with 100 mol % DCl at 25 °C.

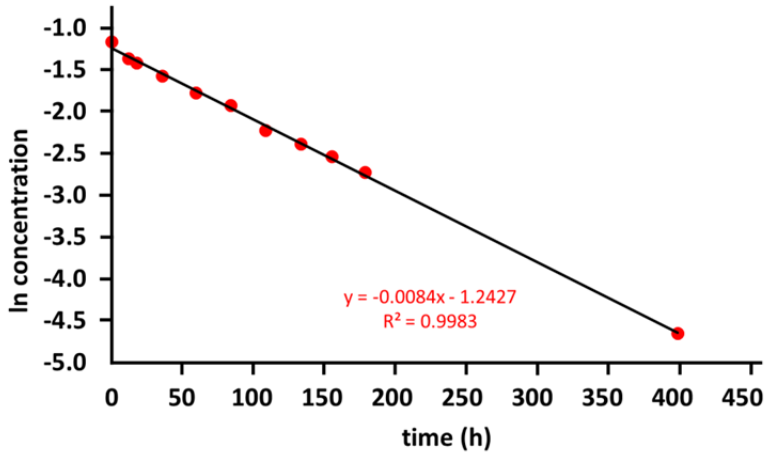

Figure S20. Deuteration of **6** in D_2O in the absence of catalyst at 25 °C.

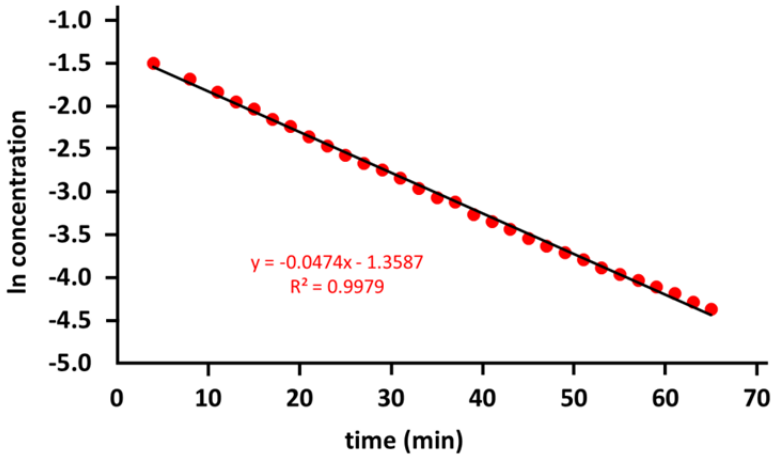

Figure S21. Deuteration of **6** in D_2O with 100 mol % DCl at 25 °C.

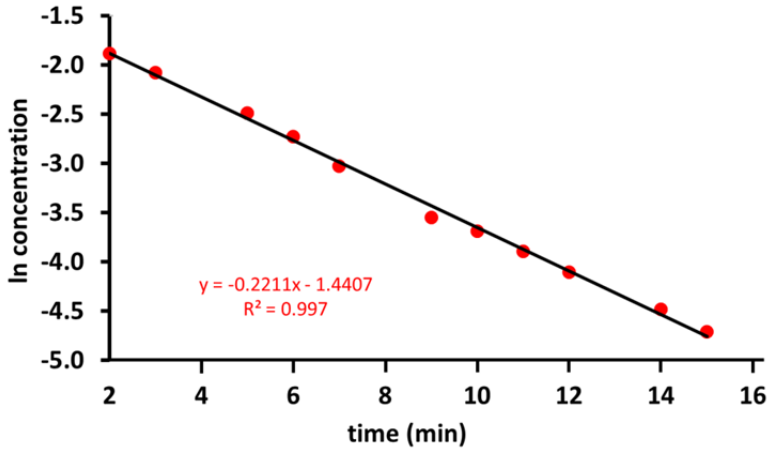

Figure S22. Deuteration of **7** in D_2O with 100 mol % DCl at 25 °C (with DSS sodium salt as reference in a coaxial NMR tube).

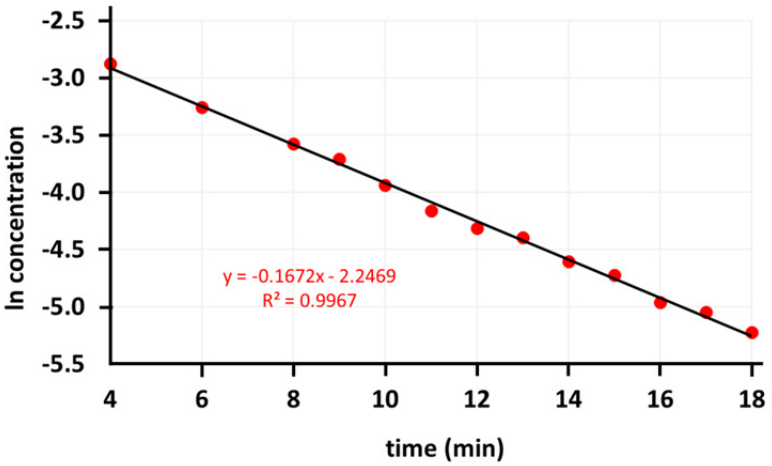

Figure S23. Deuteration of **7** in D_2O (containing dissolved DSS sodium salt as reference) with 100 mol % DCl at 25 °C.

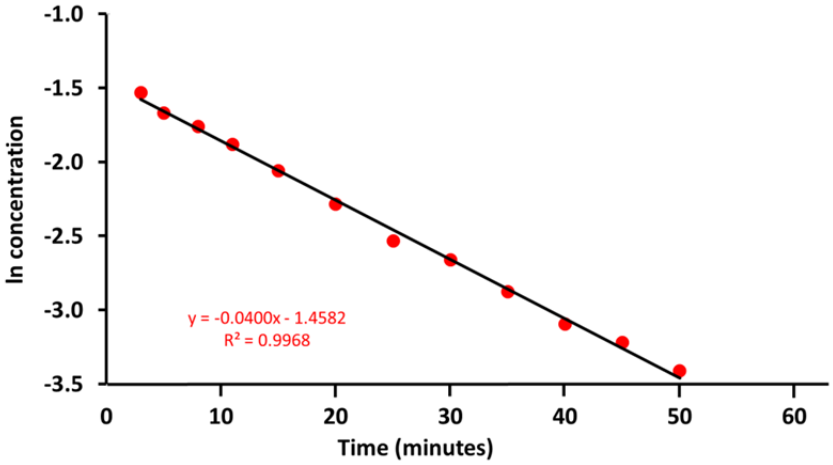

Figure S24. Deuteration of **8** in CD_3OD with 100 mol % DCl at 25 °C.

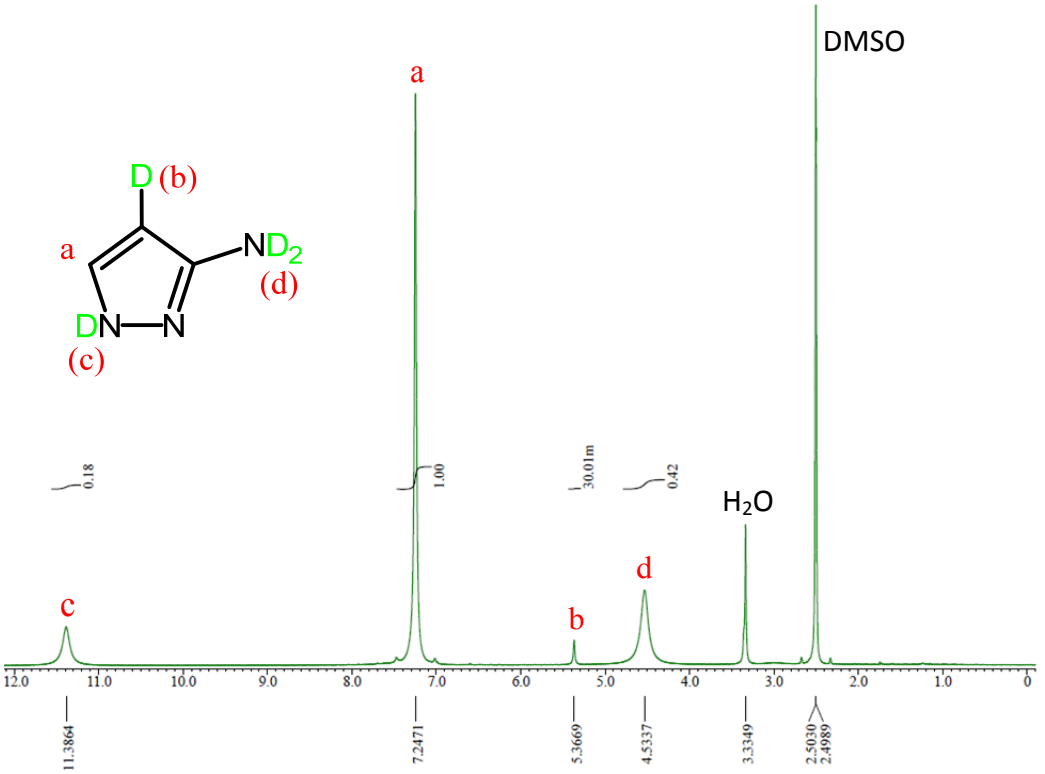

Figure S25. ^{1}H NMR spectrum of partially protiated 3(5)-aminopyrazole-d_4 (obtained from **1)** in wet DMSO-d_6.

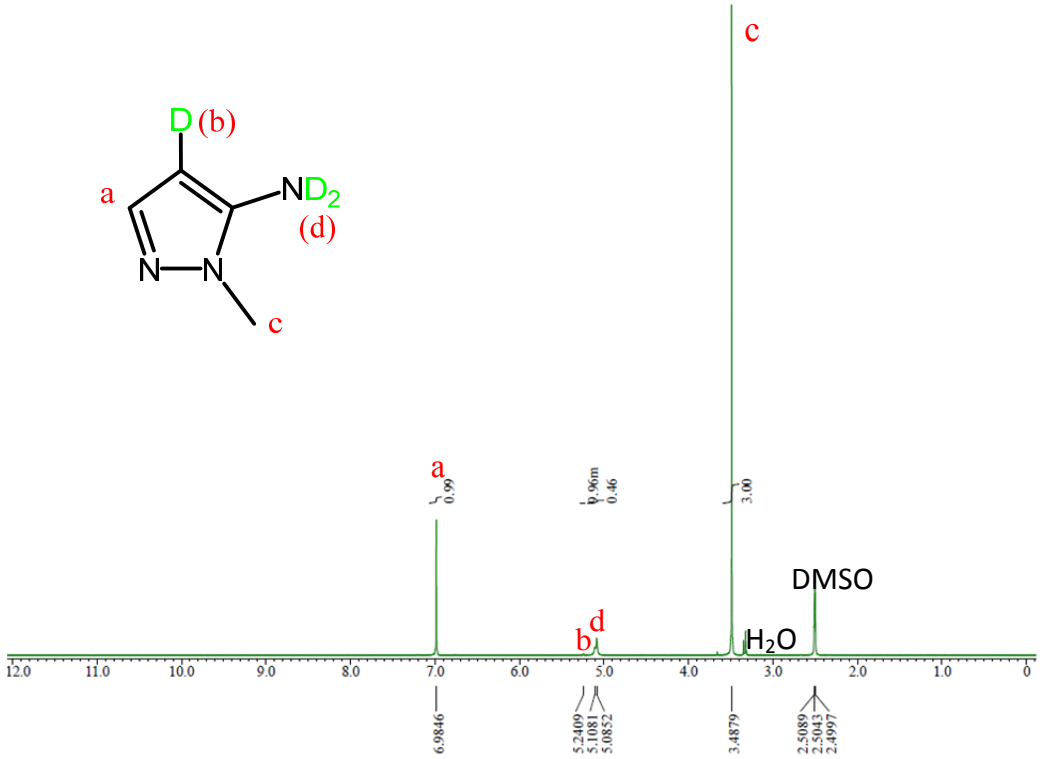

Figure S26. ^{1}H NMR spectrum of partially protiated 5-amino-1-methylpyrazole-d_3 (obtained from **3**) in wet DMSO-d_6.

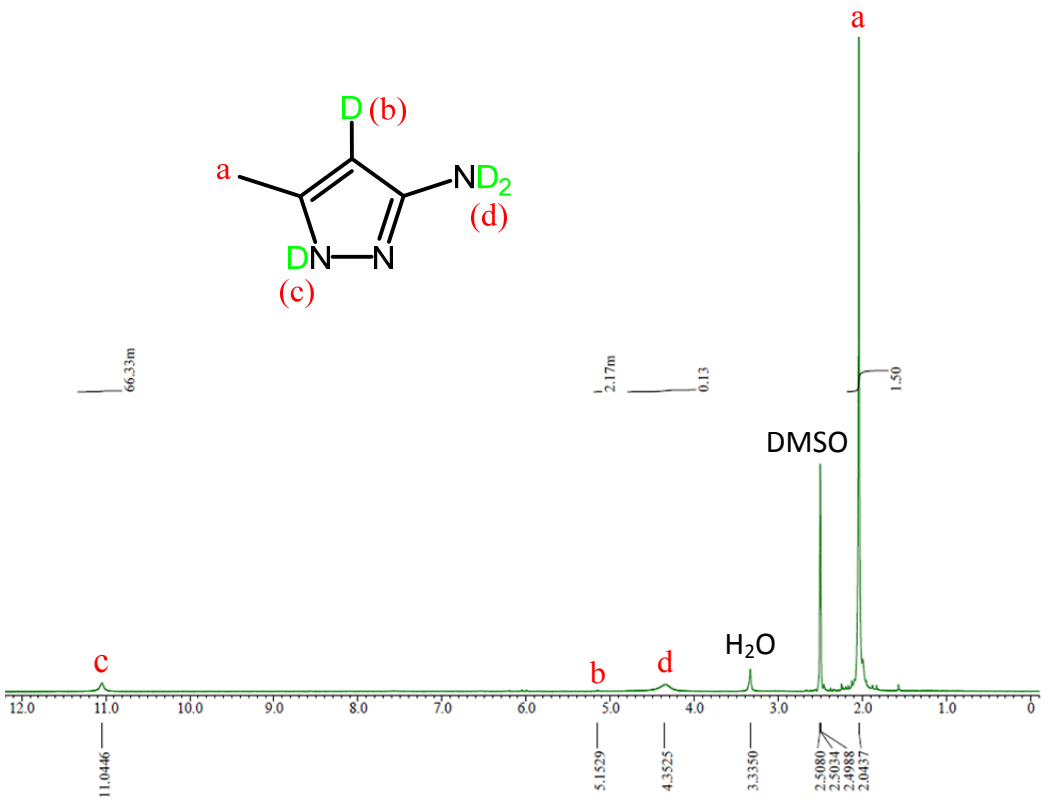

Figure S27. ^{1}H NMR spectrum of partially protiated 3(5)-amino-5(3)-methylpyrazole-d_4 (obtained from **4**) in wet DMSO-d_6.

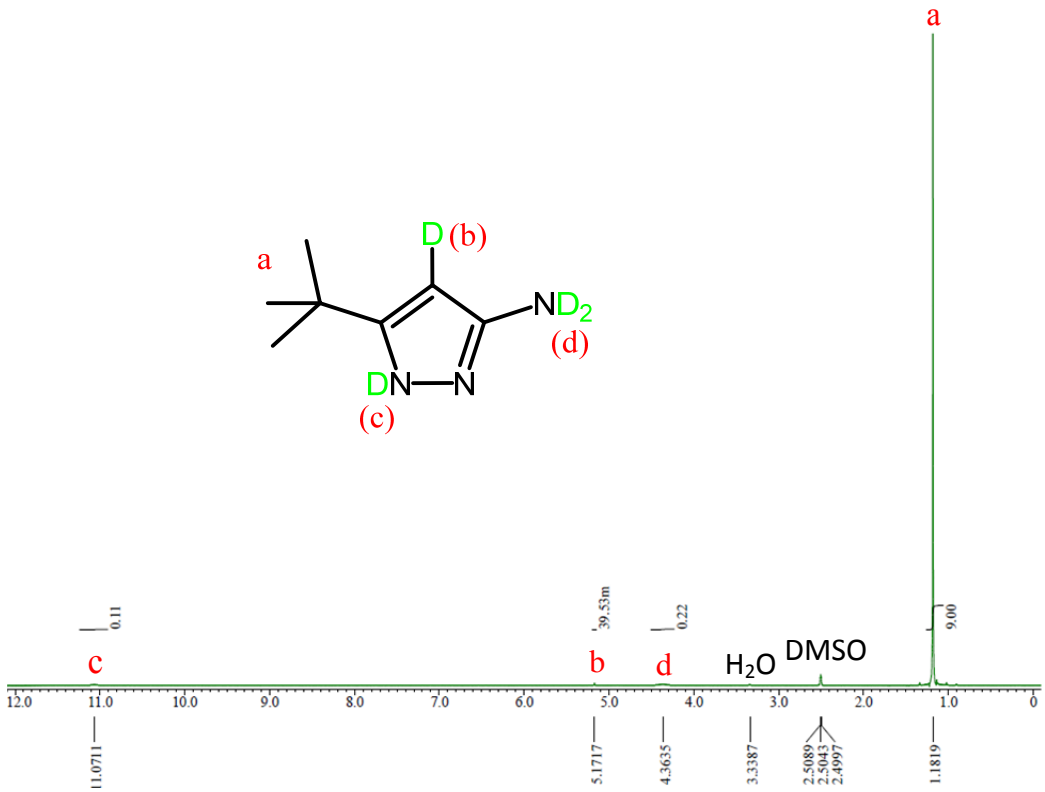

Figure S28. ^{1}H NMR spectrum of partially protiated 3(5)-amino-5(3)-*tert*-butylpyrazole-d_4 (obtained from **6**) in wet DMSO-d_6.

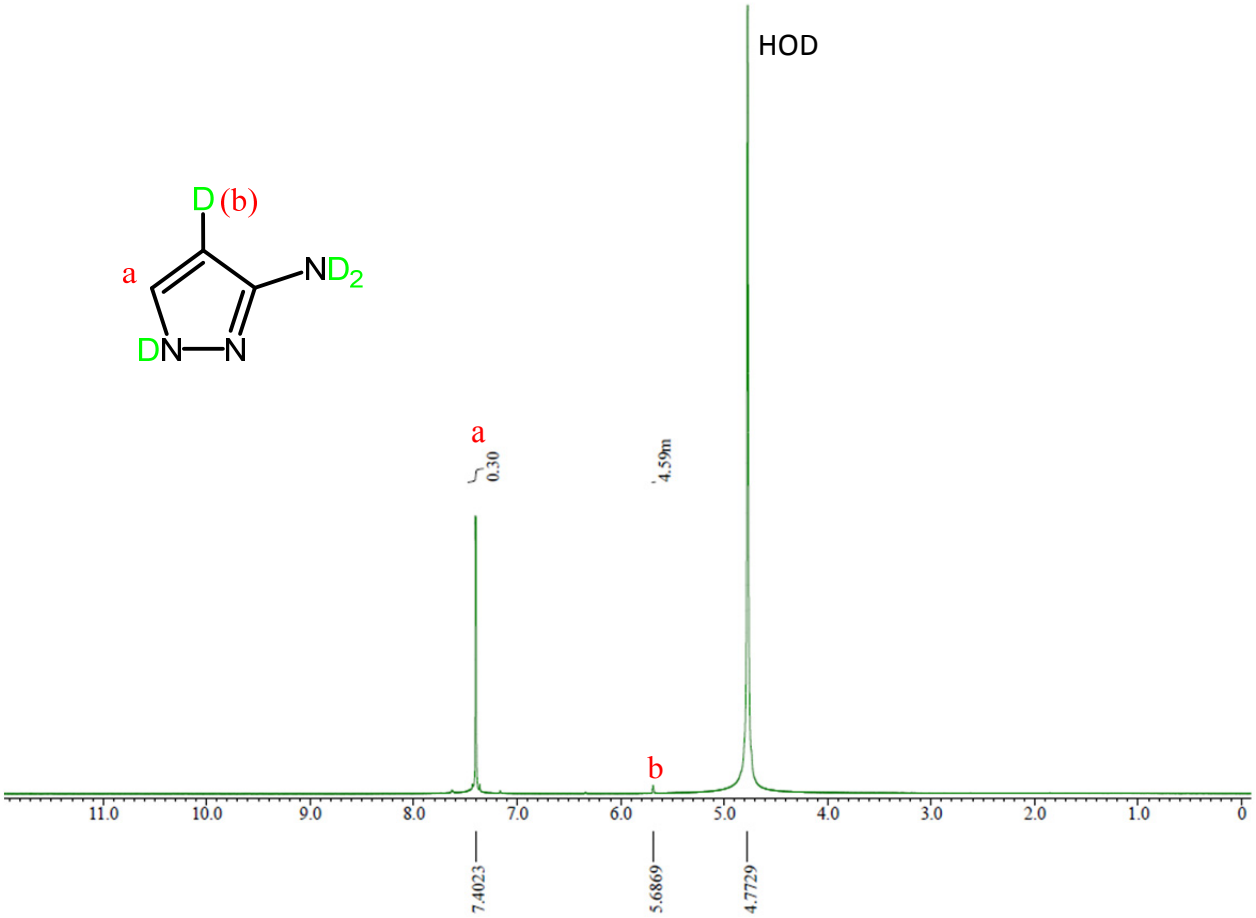

Figure S29. ^{1}H NMR spectrum of 3(5)-aminopyrazole-d_4 in D_2O.

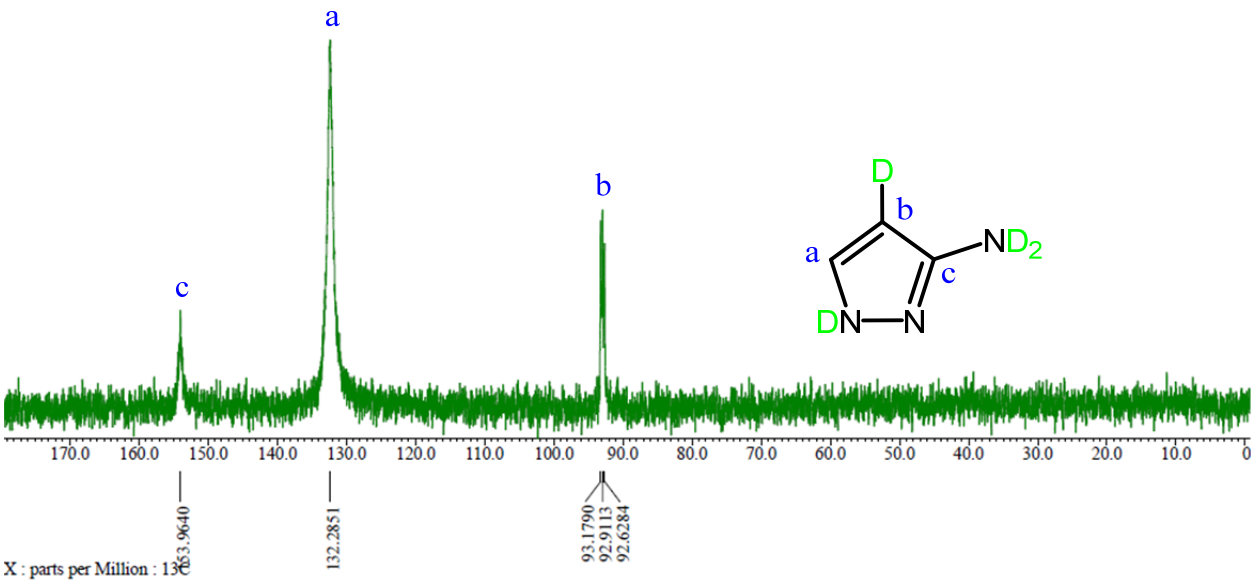

Figure S30. ^{13}C NMR spectrum of 3(5)-aminopyrazole-d_4 in D_2O.

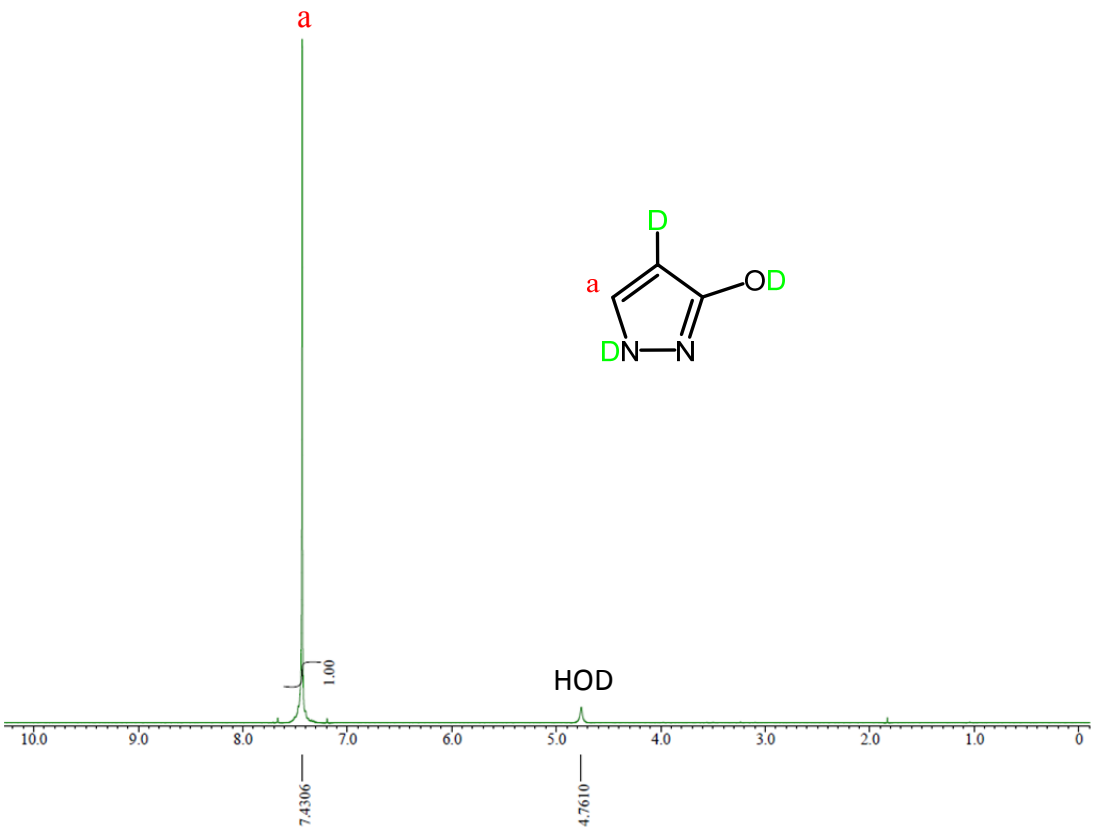

Figure S31. ^{1}H NMR spectrum of 3(5)-hydroxypyrazole-d_3 in D_2O.

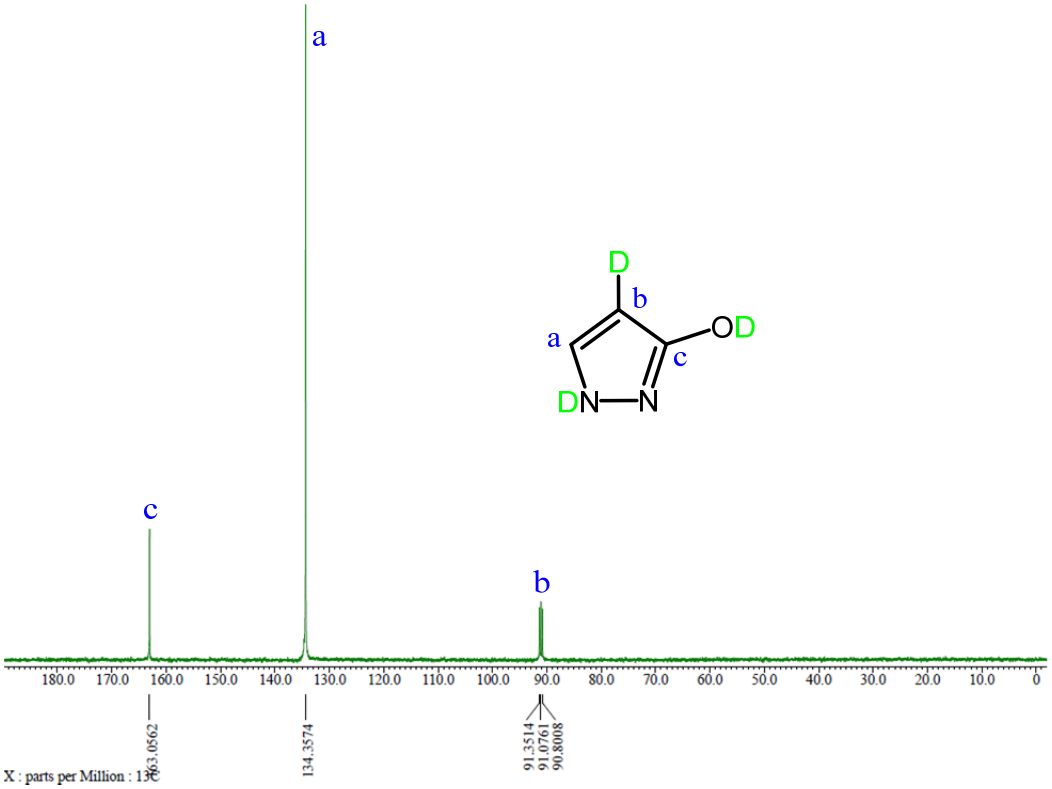

Figure S32. ^{13}C NMR spectrum of 3(5)-hydroxypyrazole-d_3 in D_2O.

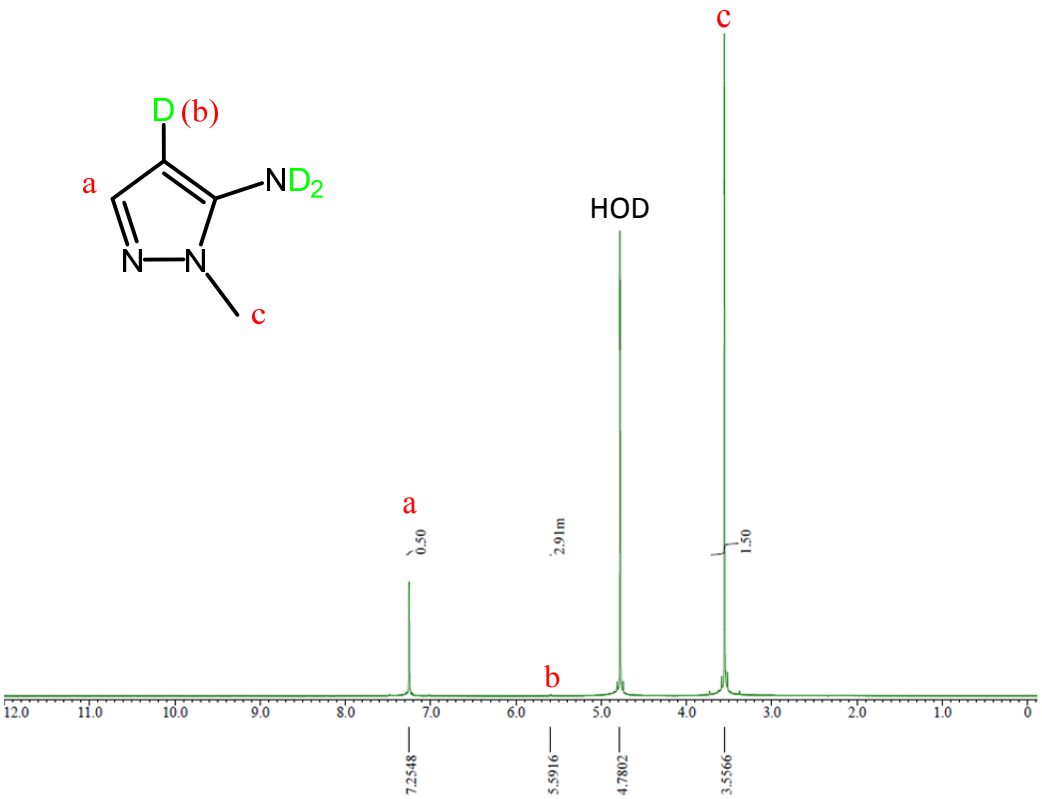

Figure S33. ^{1}H NMR spectrum of 5-amino-1-methylpyrazole-d_3 in D_2O.

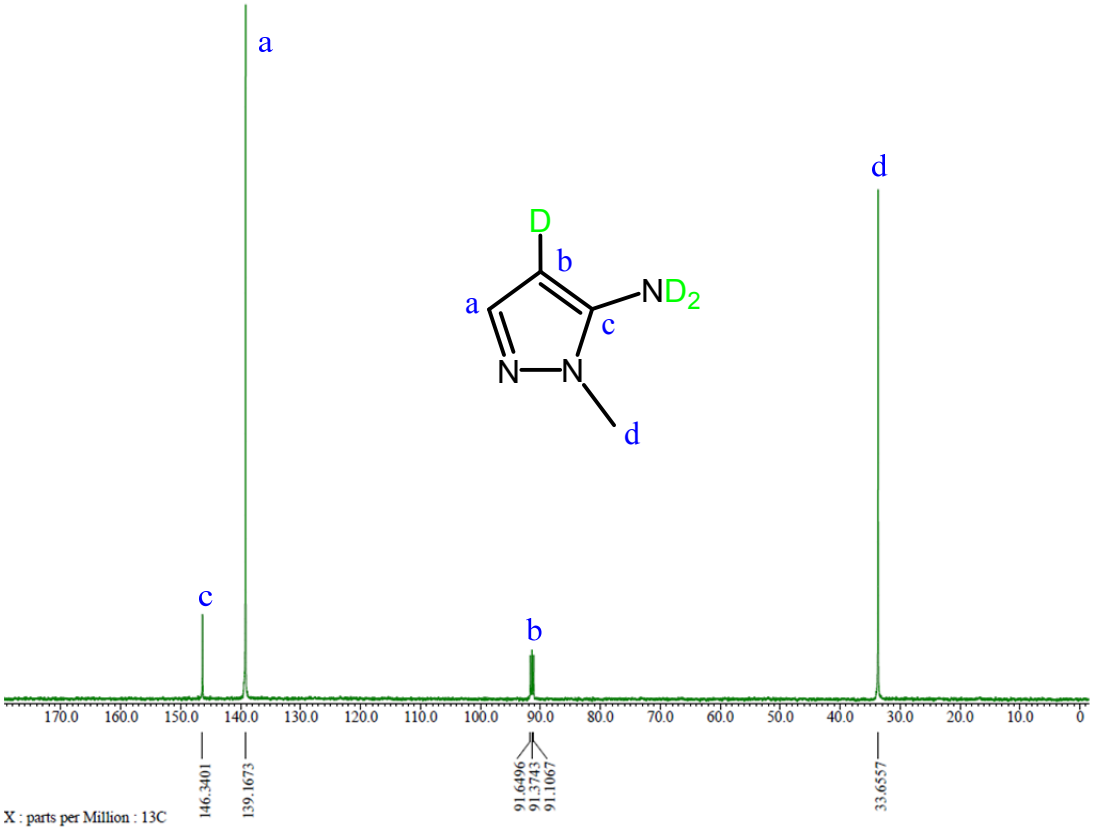

Figure S34. ^{13}C NMR spectrum of 5-amino-1-methylpyrazole-d_3 in D_2O.

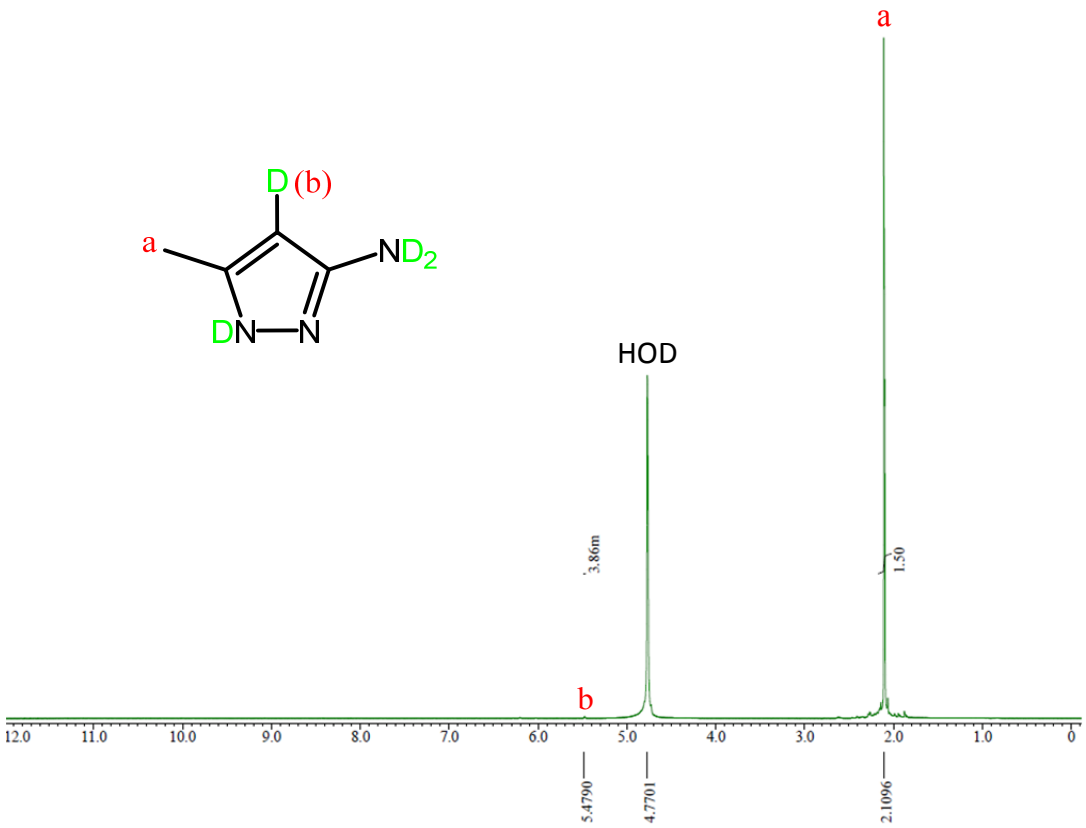

Figure S35. ^{1}H NMR spectrum of 3(5)-amino-5(3)-methylpyrazole-d_4 in D_2O.

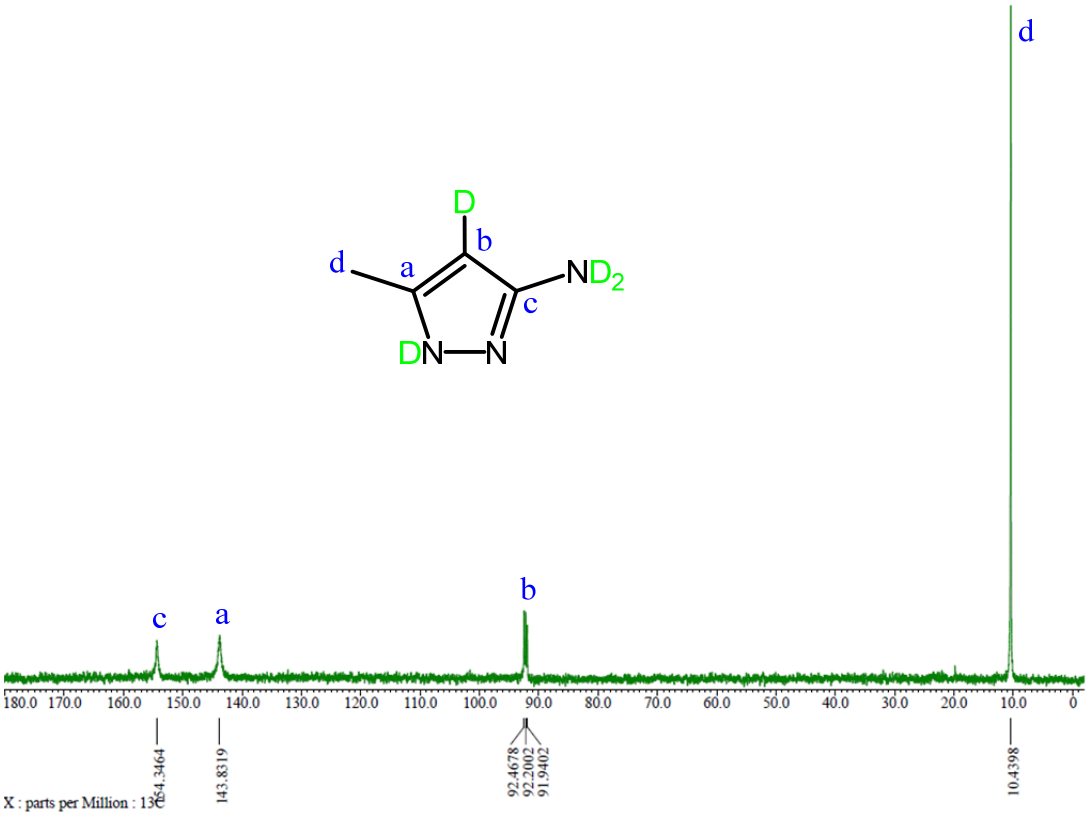

Figure S36. ^{13}C NMR spectrum of 3(5)-amino-5(3)-methylpyrazole-d_4 in D_2O.

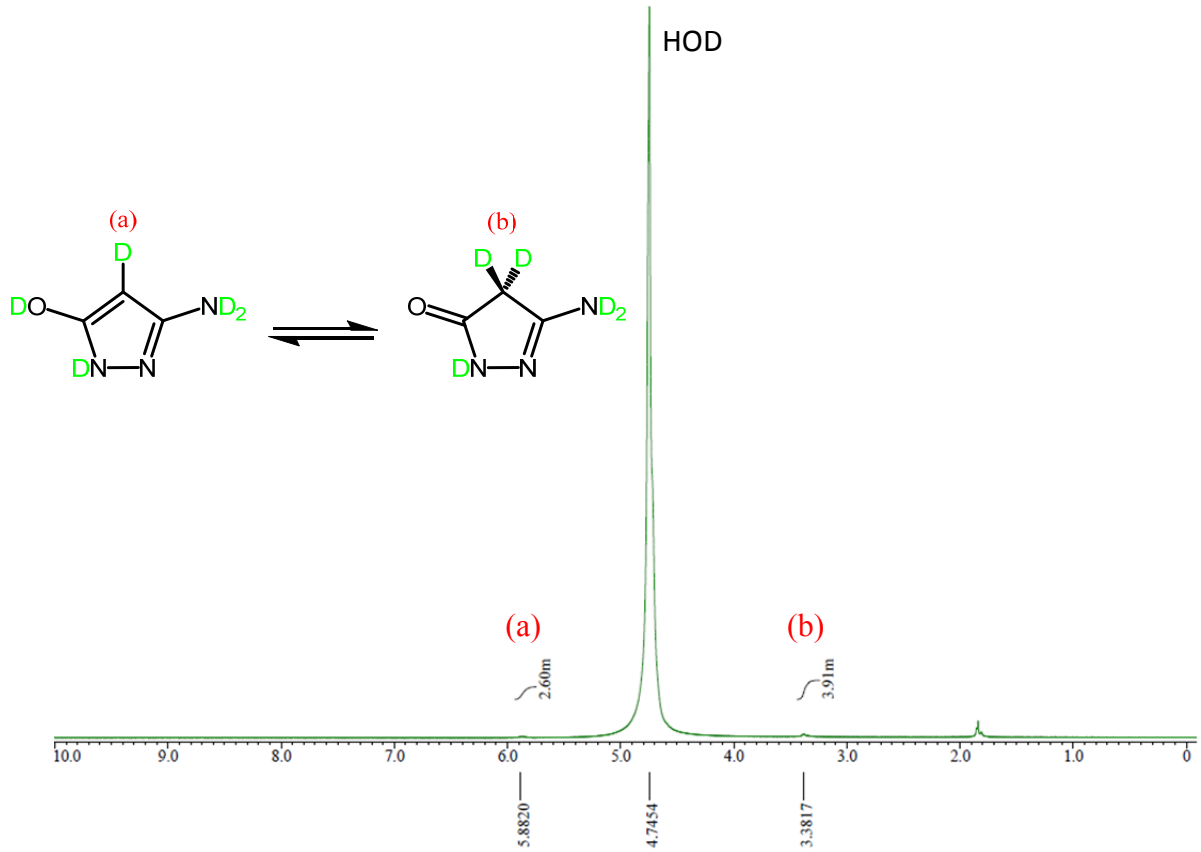

Figure S37. ^{1}H NMR spectrum of 3(5)-amino-5(3)-hydroxypyrazole-d_5 in D_2O.

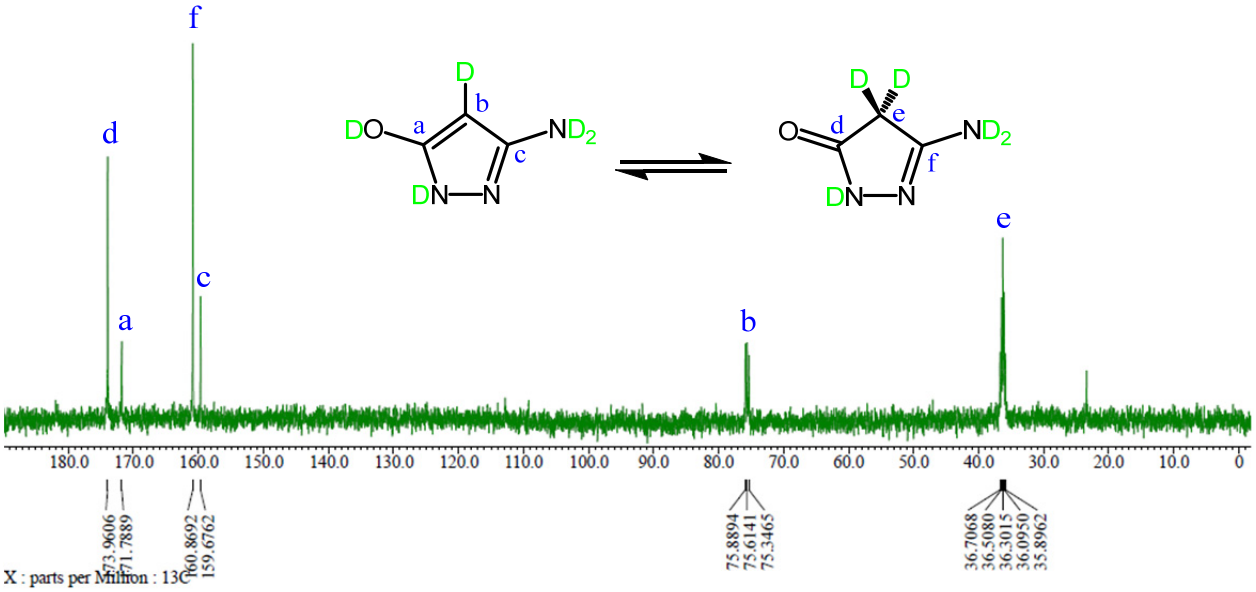

Figure S38. ^{13}C NMR spectrum of 3(5)-amino-5(3)-hydroxypyrazole-d_5 in D_2O.

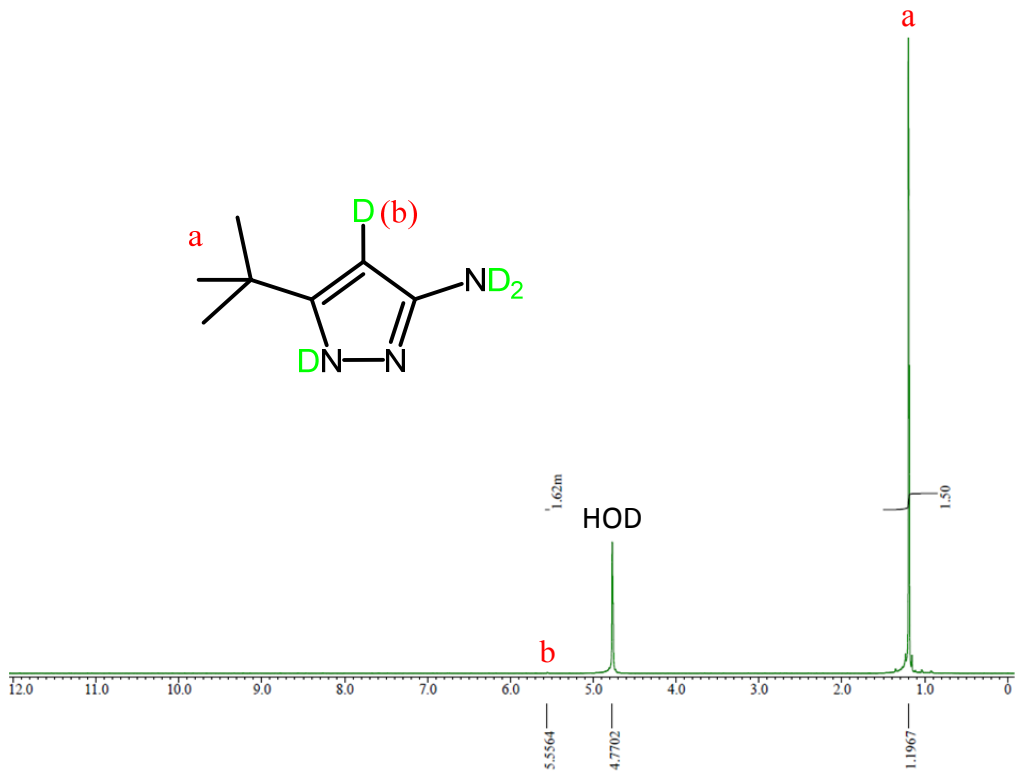

Figure S39. ^{1}H NMR spectrum of 3(5)-amino-5(3)-*tert*-butylpyrazole-d_4 in D_2O.

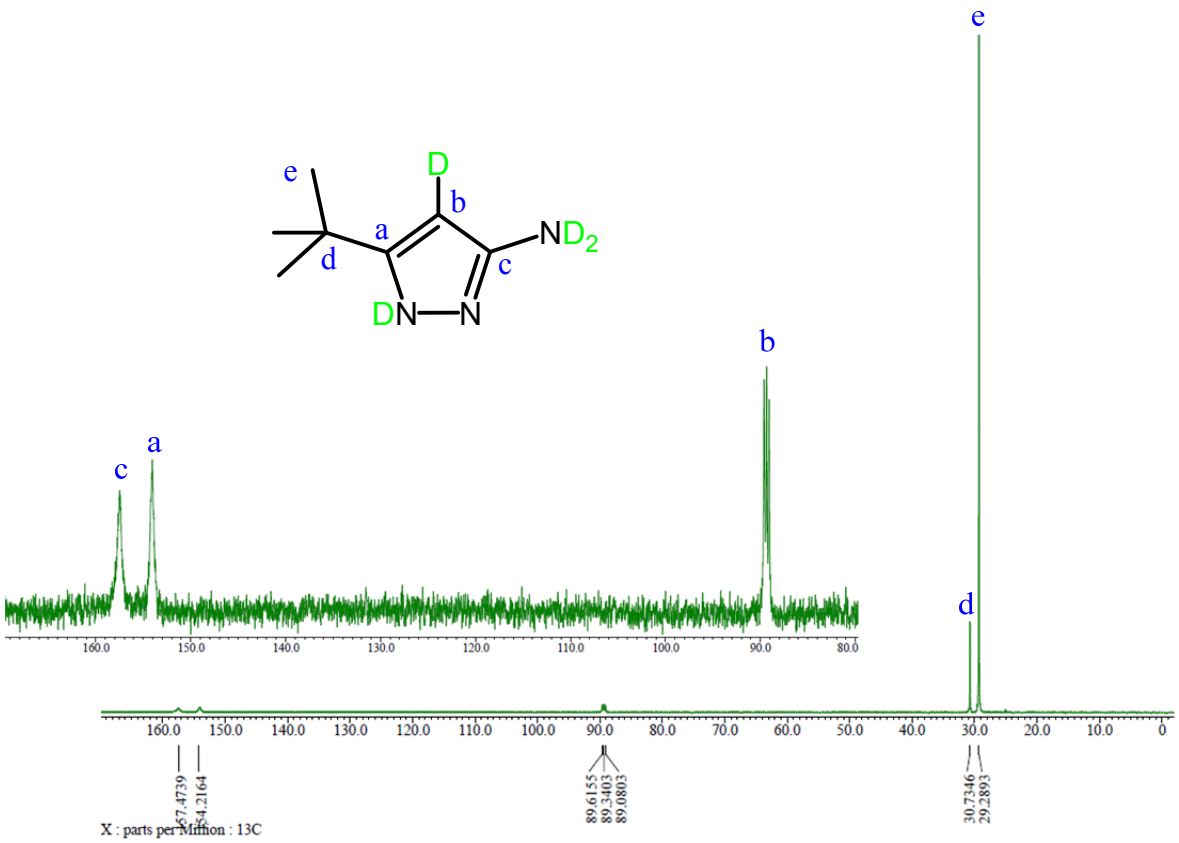

Figure S40. ^{13}C NMR spectrum of 3(5)-amino-5(3)-*tert*-butylpyrazole-d_4 in D_2O.

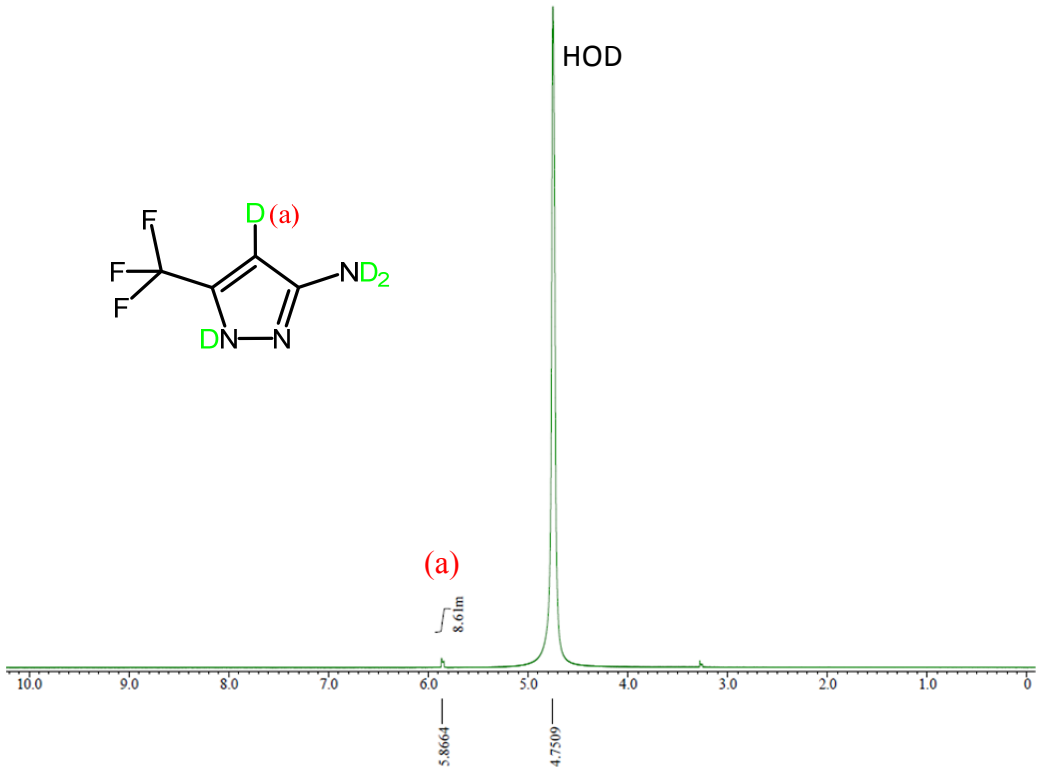

Figure S41. ^{1}H NMR spectrum of 3(5)-amino-5(3)-trifluoromethylpyrazole-d_4 in D_2O.

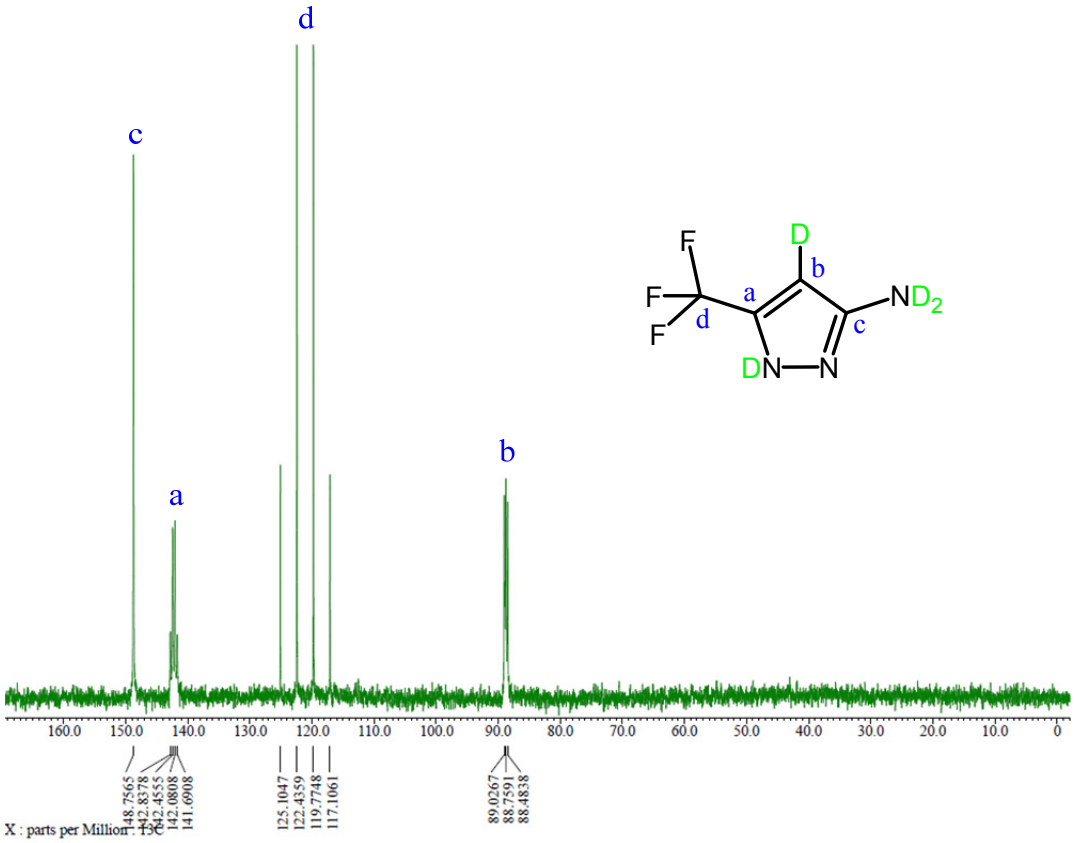

Figure S42. ^{13}C NMR spectrum of 3(5)-amino-5(3)-trifluoromethylpyrazole-d_4 in D_2O.

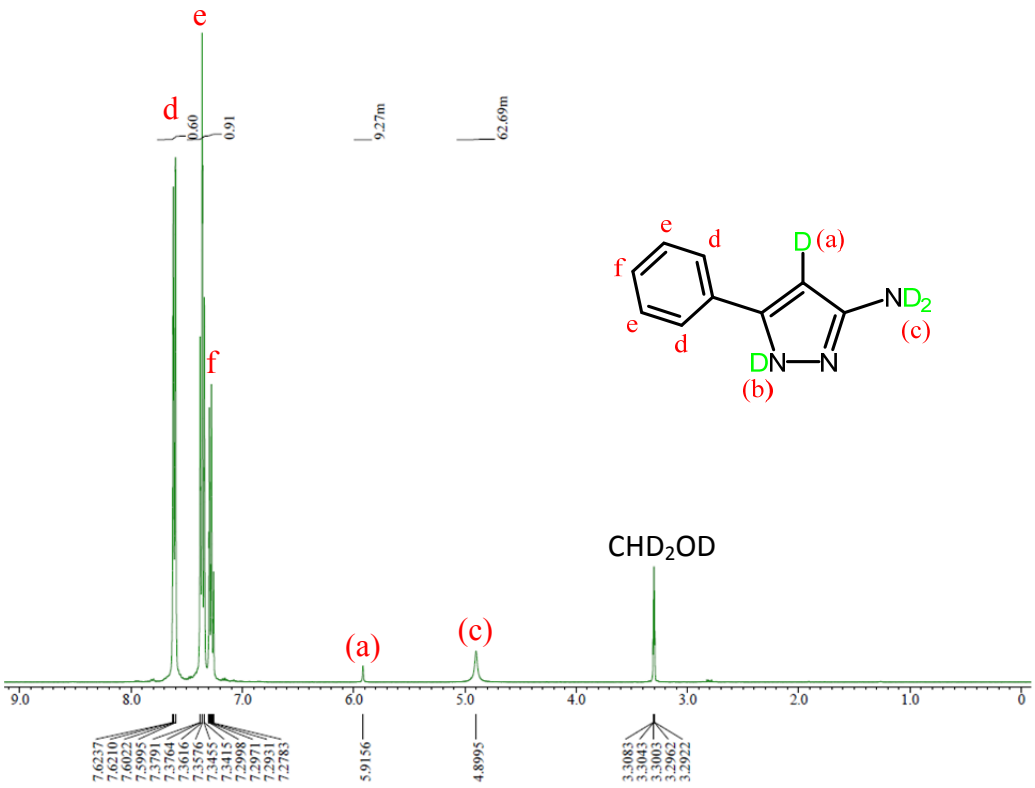

Figure S43. ^{1}H NMR spectrum of 3(5)-amino-5(3)-phenylpyrazole-d_4 in CD_3OD.

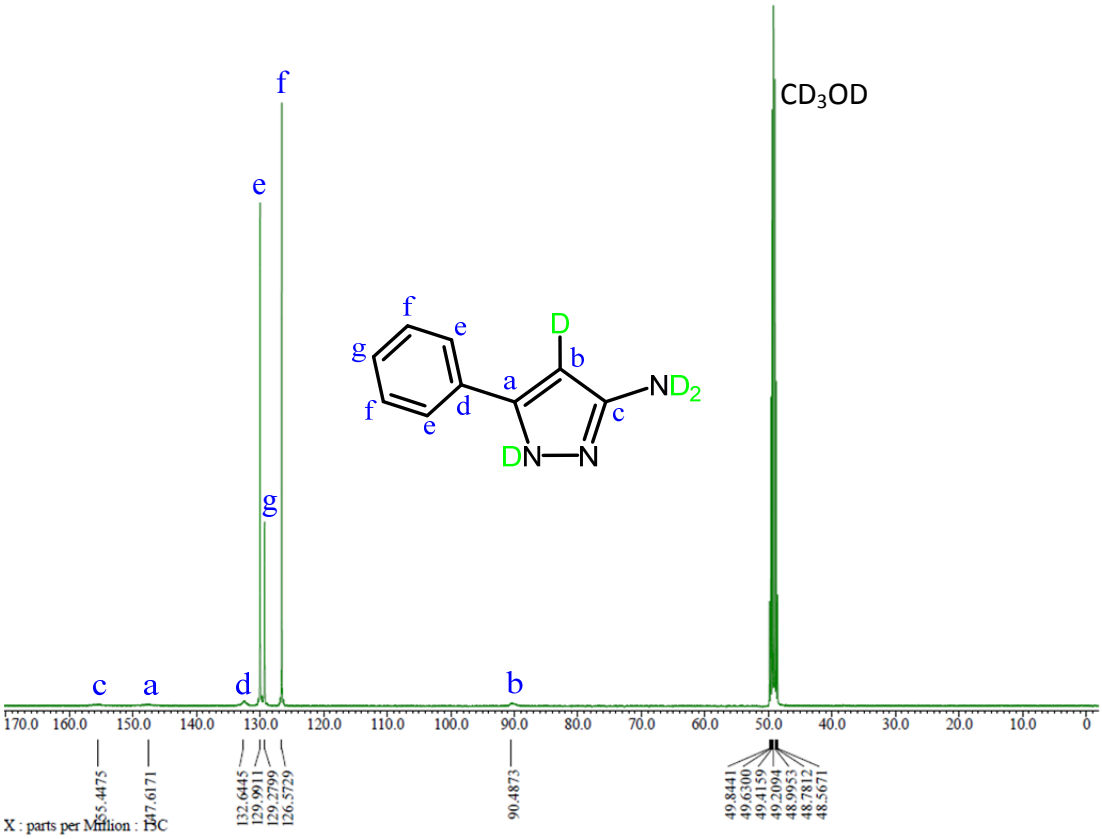

Figure S44. ^{13}C NMR spectrum of 3(5)-amino-5(3)-phenylpyrazole-d_4 in CD_3OD.