Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

The *Syn* and *Anti* isomers of the Porphyrinogen-like Precursor of Calix[4]phyrin: Isolation, X-ray Structure, Anion Binding and Fluoride-ion-Mediated Proton-Deuterium Exchange Studies

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Contents

1. Experimental section

General

Solvents were purchased from commercial sources and distilled before use by following standard procedures.

2. NMR and IR spectra

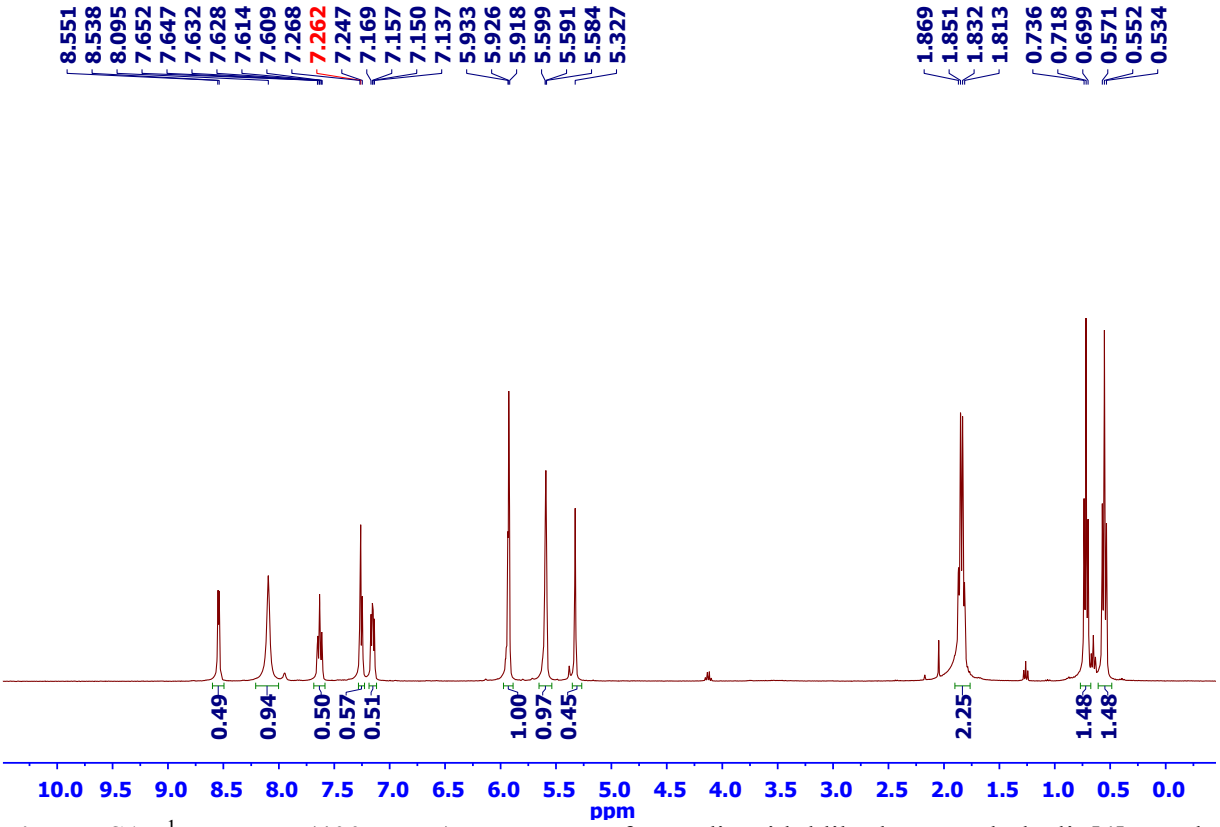


Figure S1. ^{1}H NMR (400 MHz) spectrum of *syn*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2a** in $CDCl_3$.

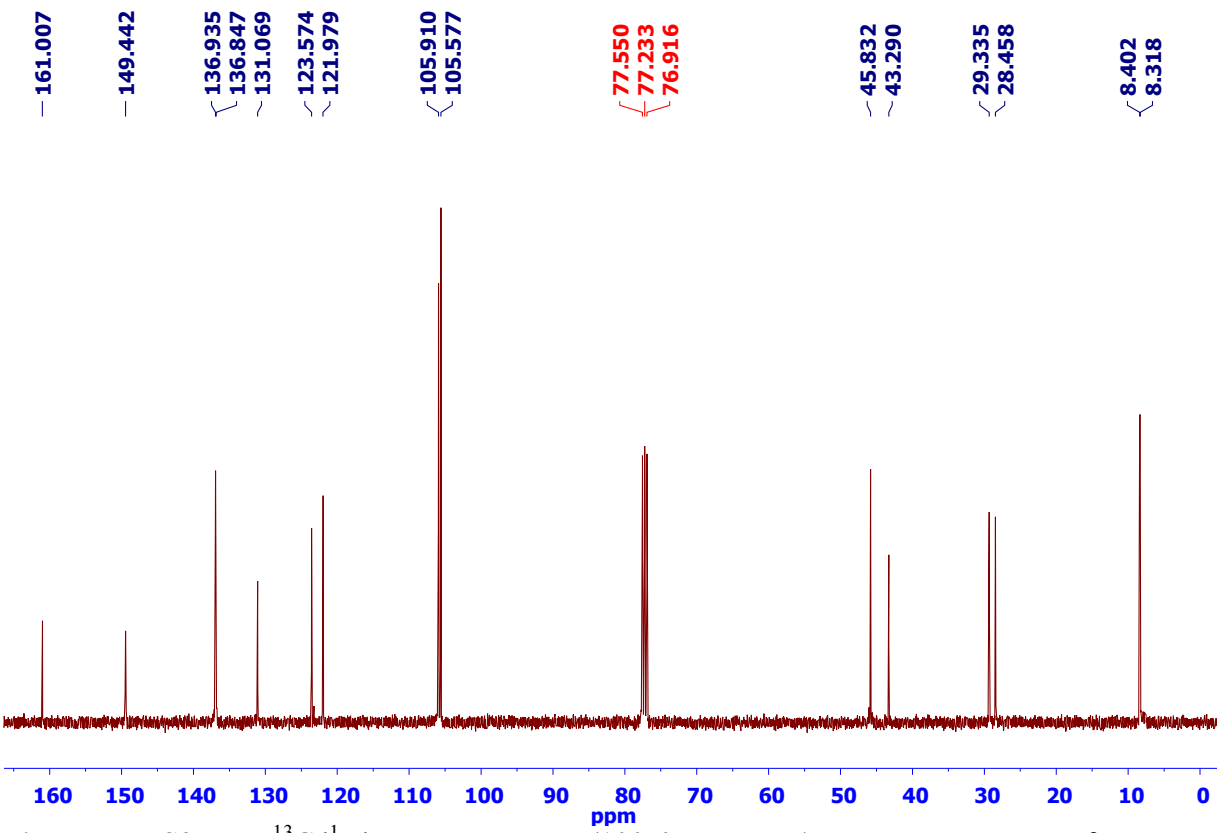


Figure S2. $^{13}C\{^{1}H\}$ NMR (100.6 MHz) spectrum of *syn*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2a** in $CDCl_3$.

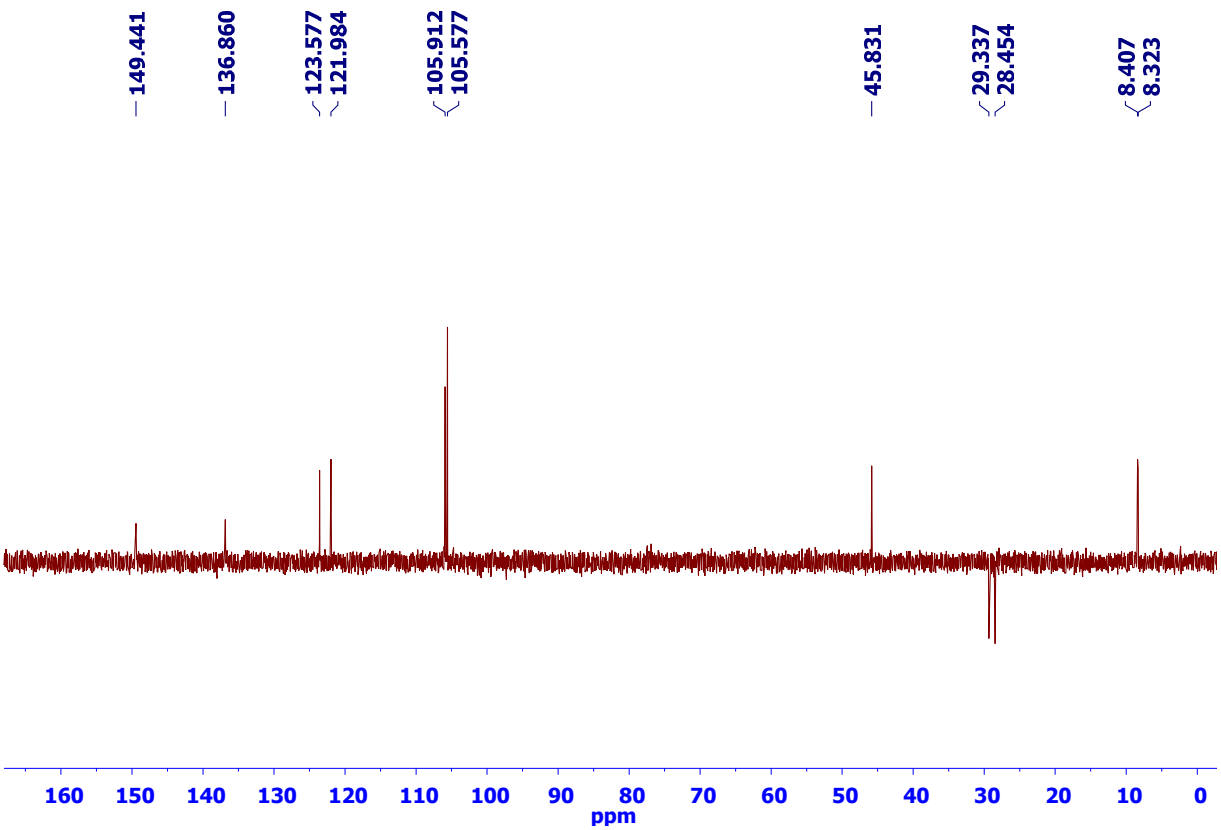


Figure S3. DEPT-135{^{1}H} (100.6 MHz) NMR spectrum of *syn*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2a** in $CDCl_3$.

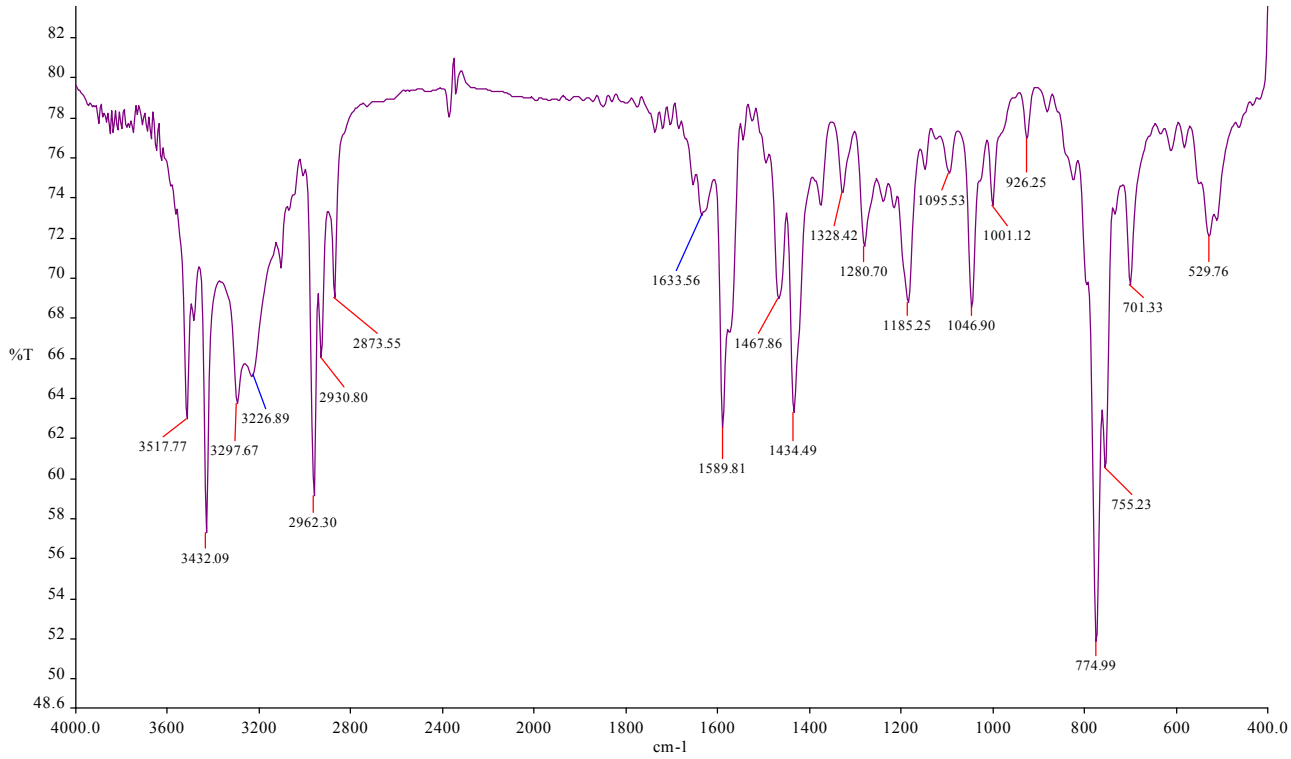


Figure S4. IR spectrum of *syn*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2a** recorded as a KBr disc.

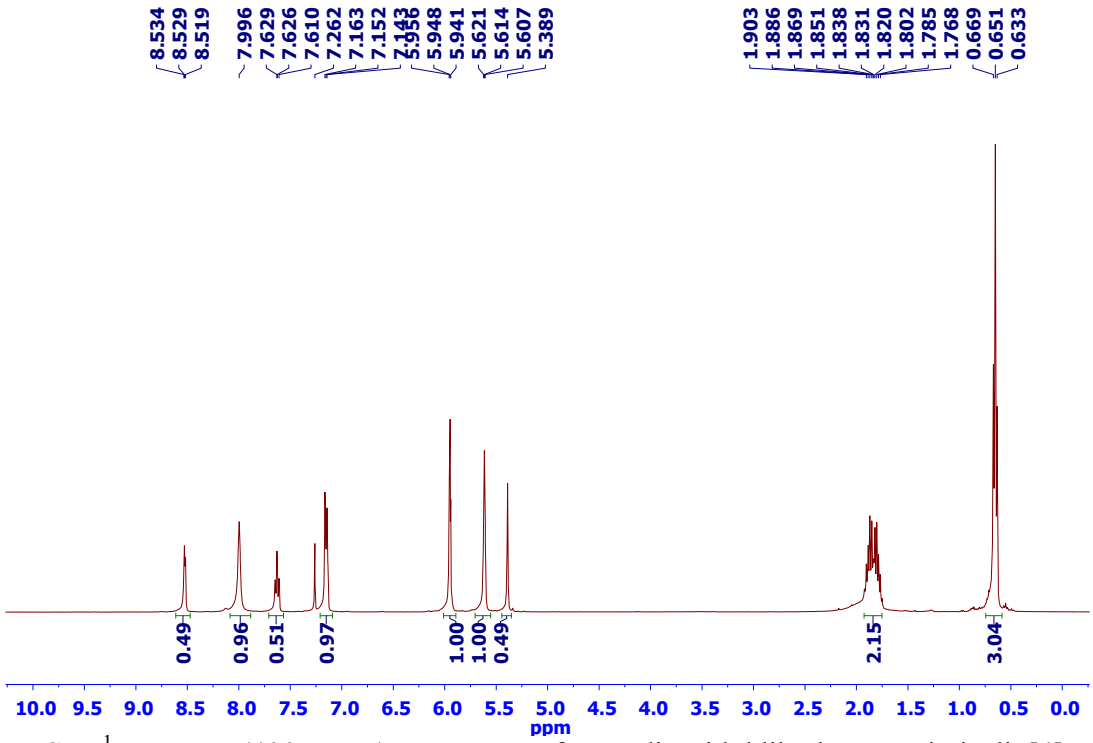


Figure S5. ^{1}H NMR (400 MHz) spectrum of *anti*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2b** in $CDCl_3$.

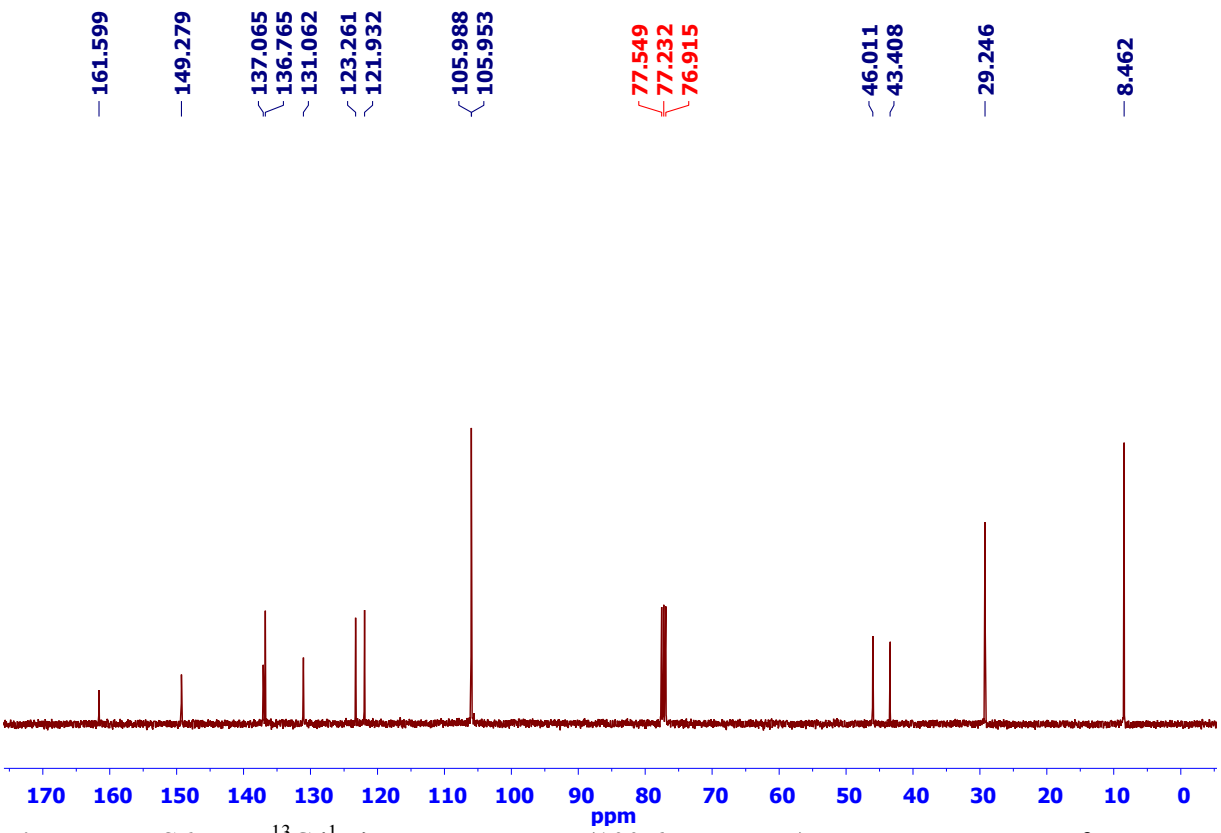


Figure S6. $^{13}C\{^{1}H\}$ NMR (100.6 MHz) spectrum of *anti*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2b** in $CDCl_3$.

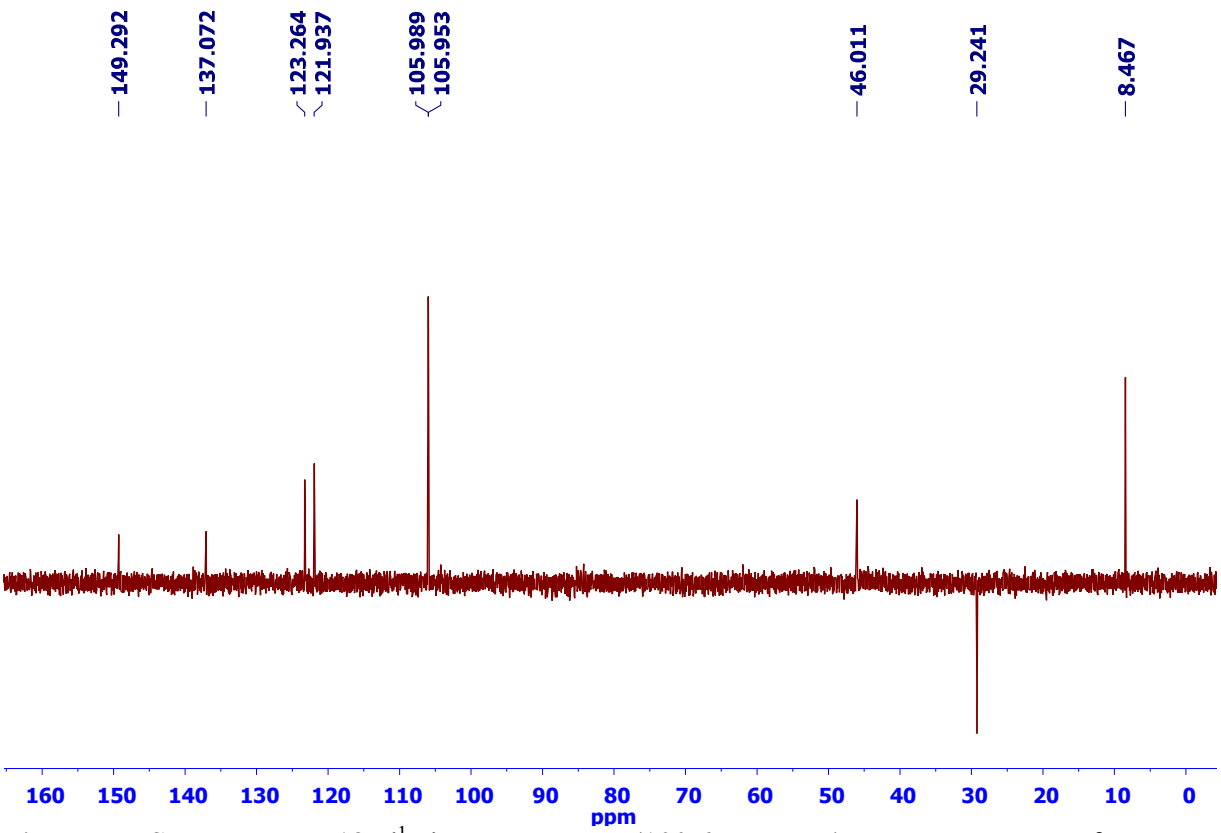


Figure S7. DEPT-135{^{1}H} NMR (100.6 MHz) spectrum of *anti*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2b** in $CDCl_3$.

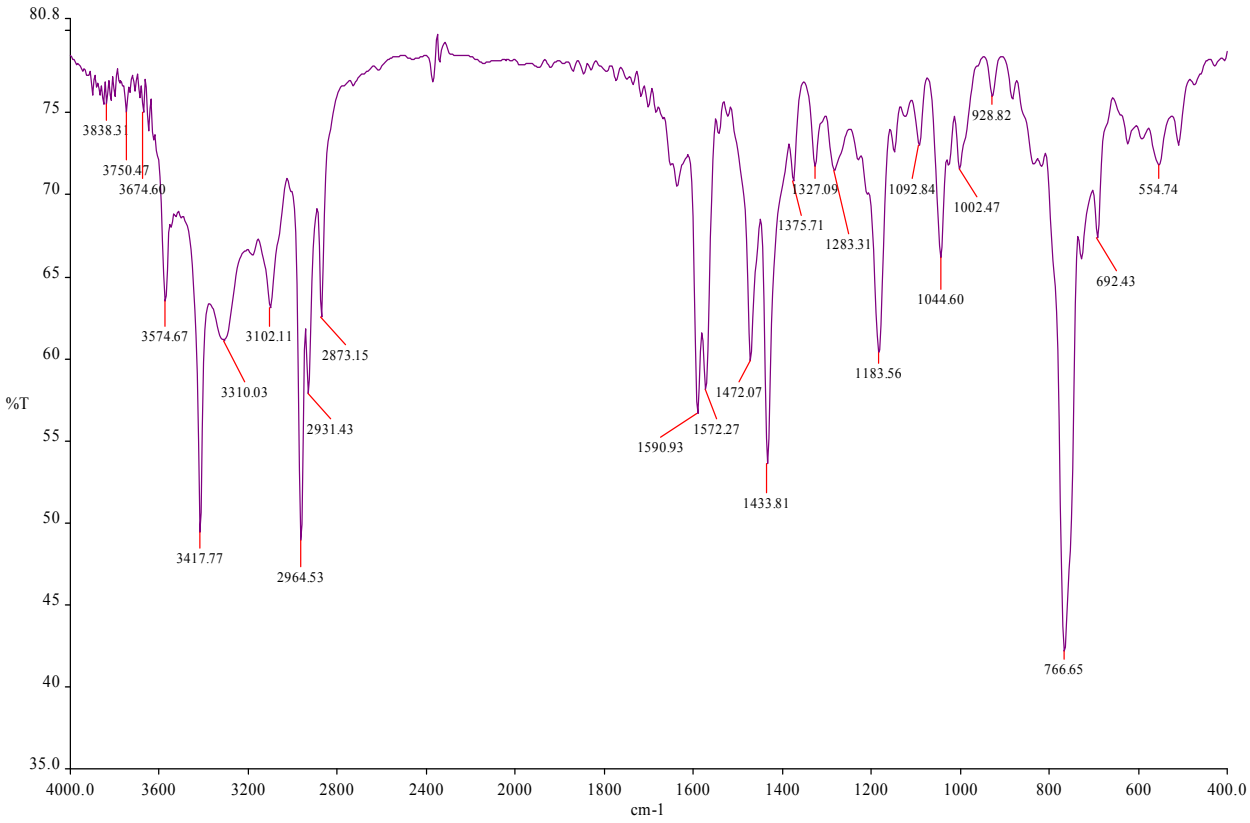


Figure S8. IR spectrum of *anti*-dipyridyldihydrotetraethylcalix[4]pyrrole isomer **2b** recorded as a KBr disc.

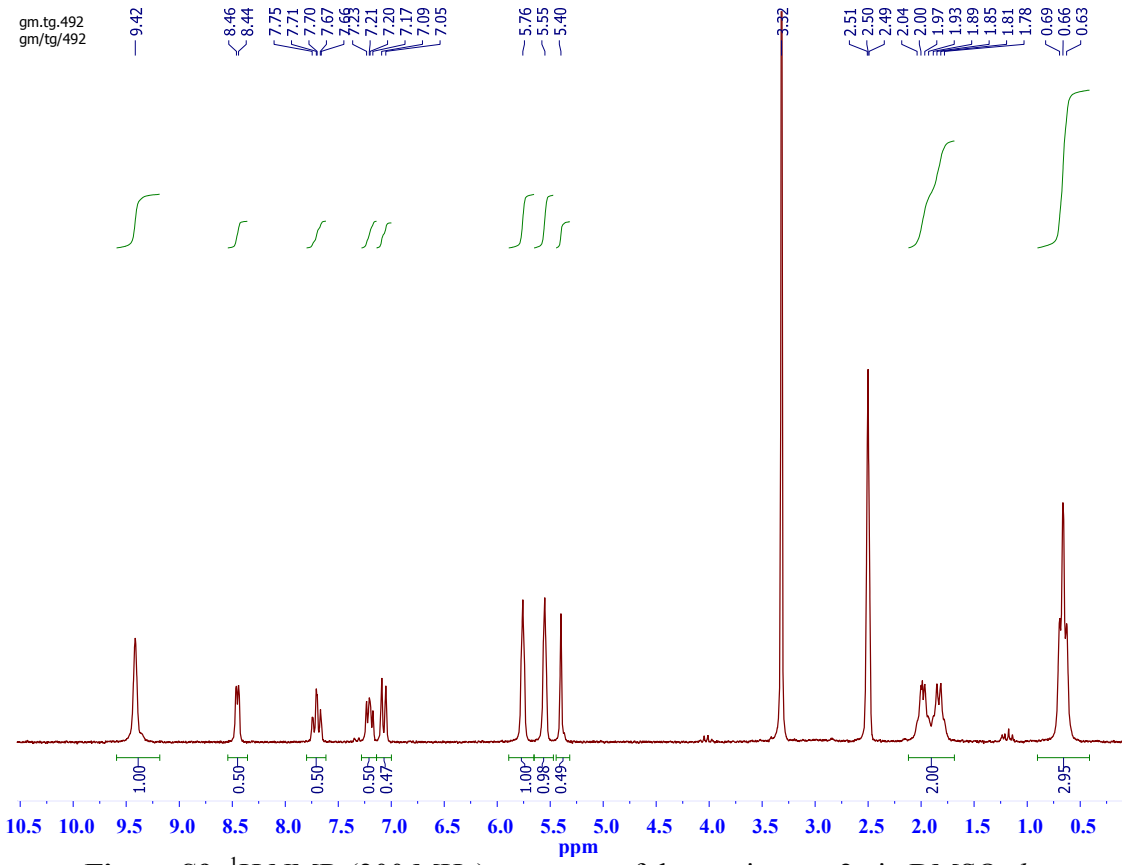


Figure S9. ^{1}H NMR (200 MHz) spectrum of the *syn* isomer **2a** in DMSO-d_6.

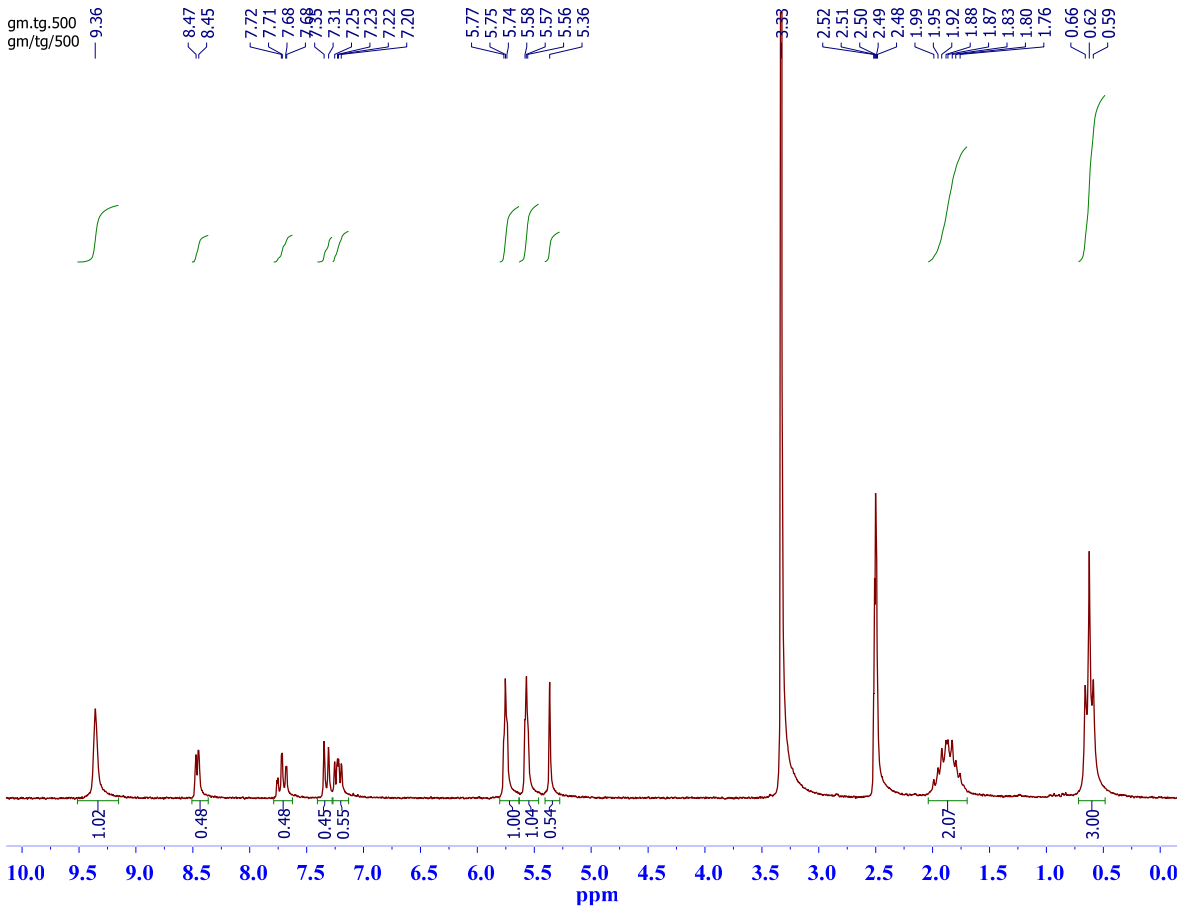


Figure S10. ^{1}H NMR (200 MHz) spectrum of the *anti* isomer **2b** in DMSO-d_6.

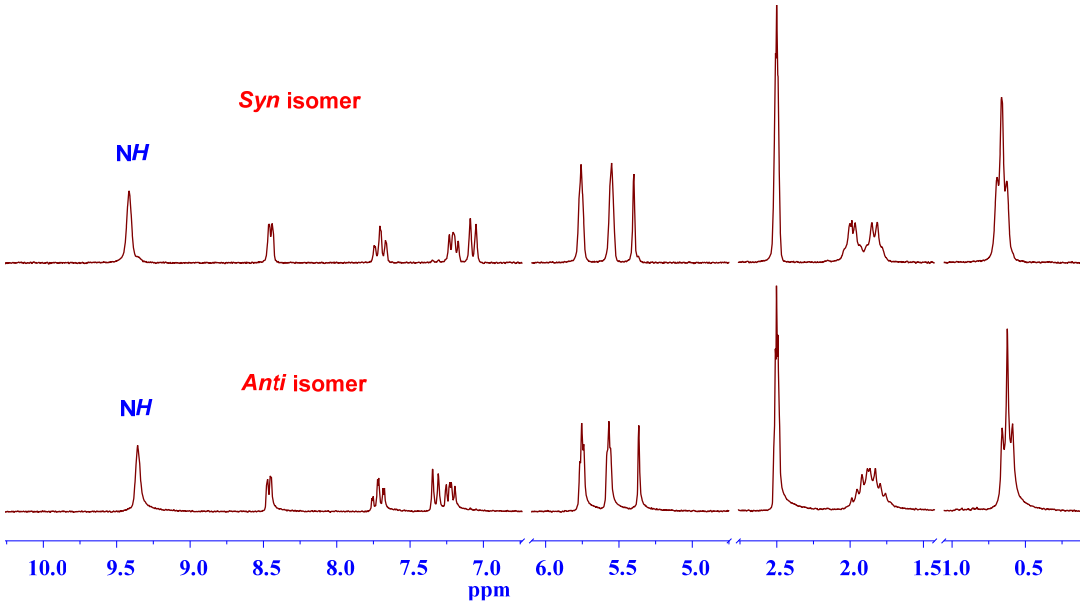


Figure S11. Comparison of the ^{1}H NMR (200 MHz) spectrum of the *syn* **2a** isomer with that of the *anti* **2b** isomer in DMSO-d_6.

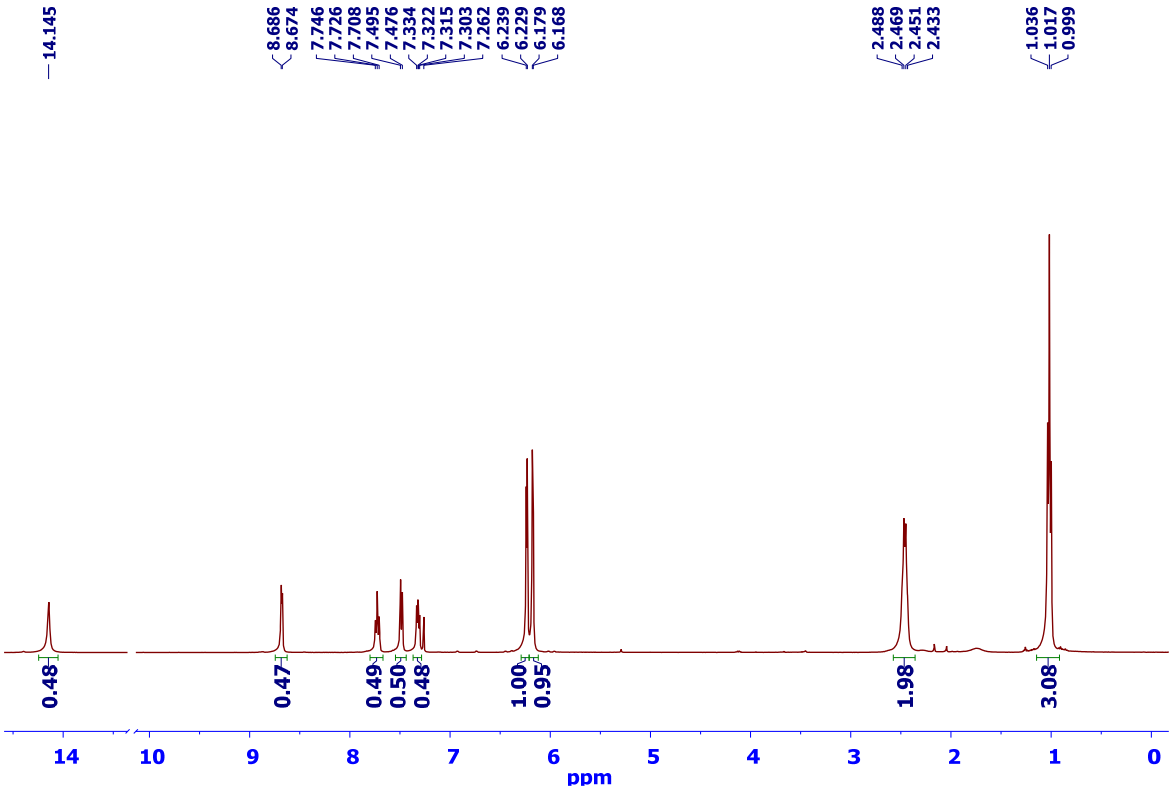


Figure S12. ^{1}H NMR (400 MHz) spectrum of calix[4]phyrin **3** in $CDCl_3$.

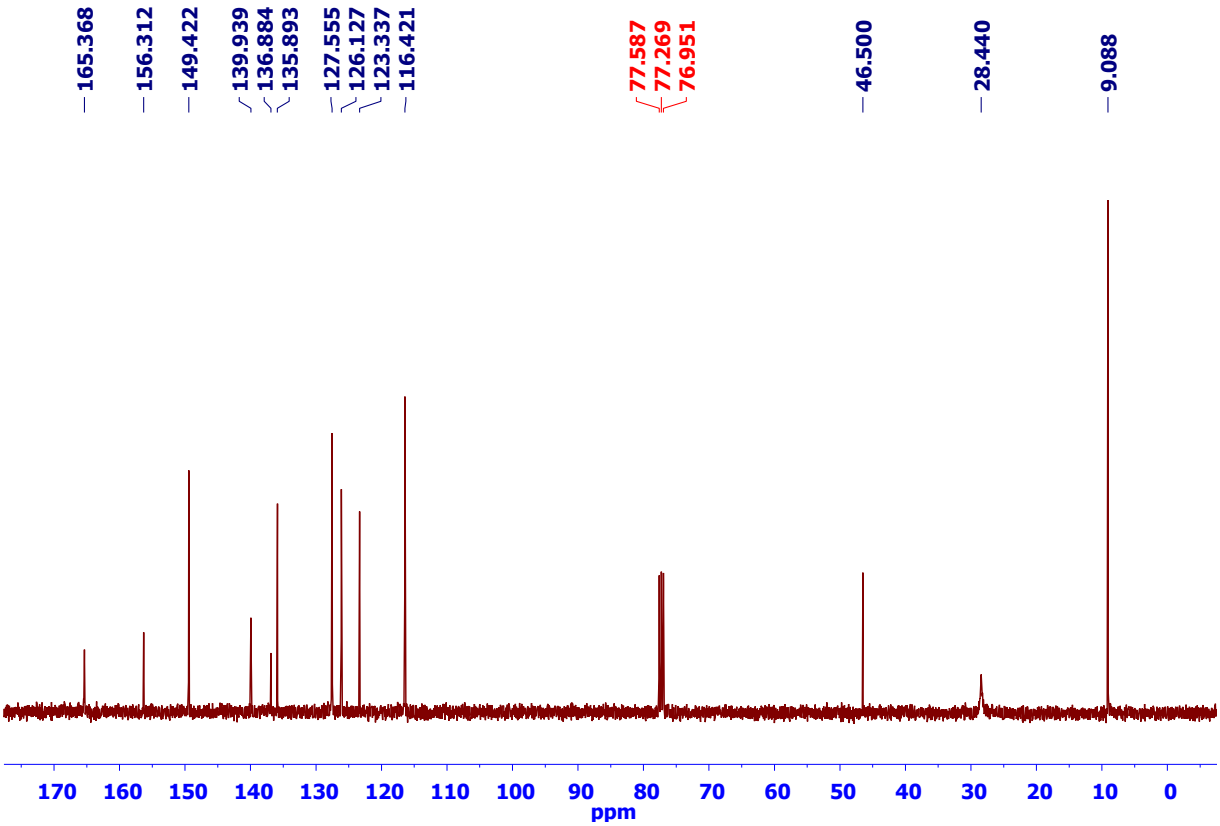


Figure S13. $^{13}C\{^{1}H\}$ NMR (100.6 MHz) spectrum of calix[4]phyrin **3** in $CDCl_3$.

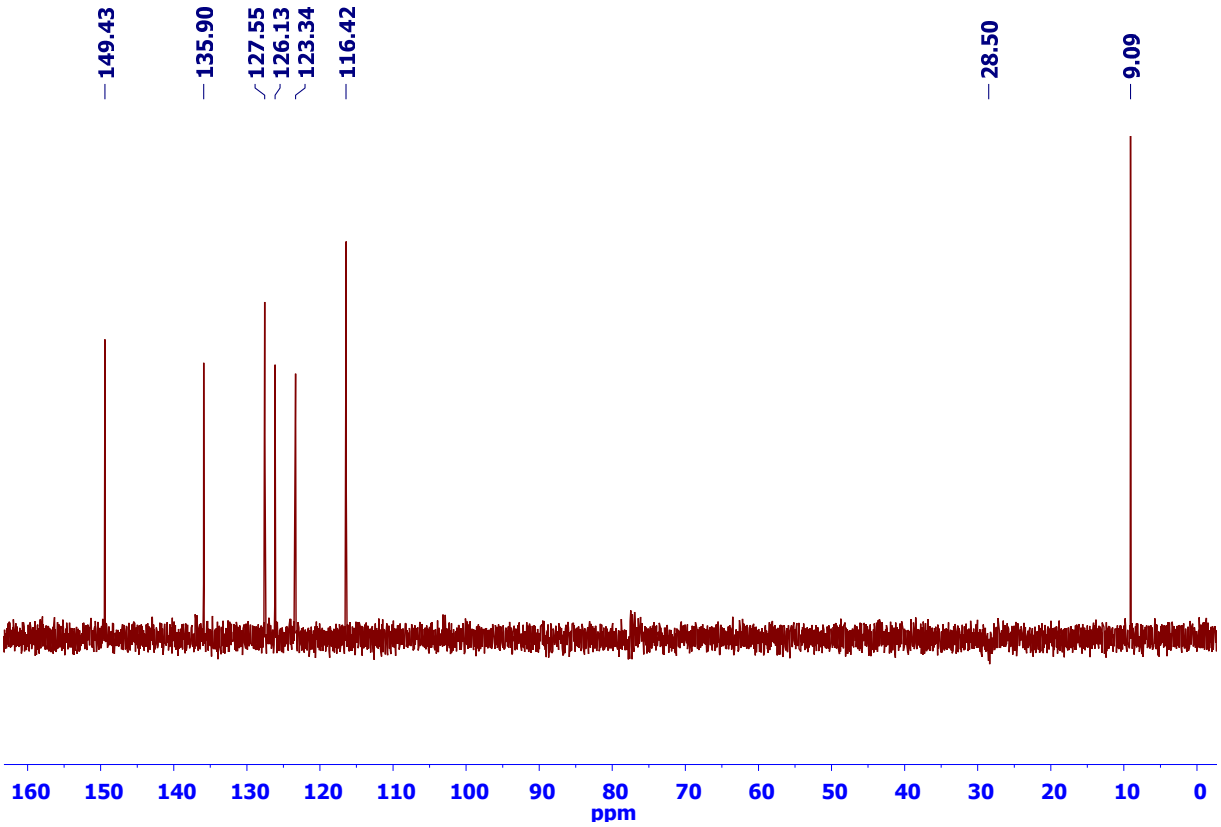


Figure S14. DEPT-135{^{1}H} NMR (100.6 MHz) spectrum of calix[4]phyrin **3** in $CDCl_3$.

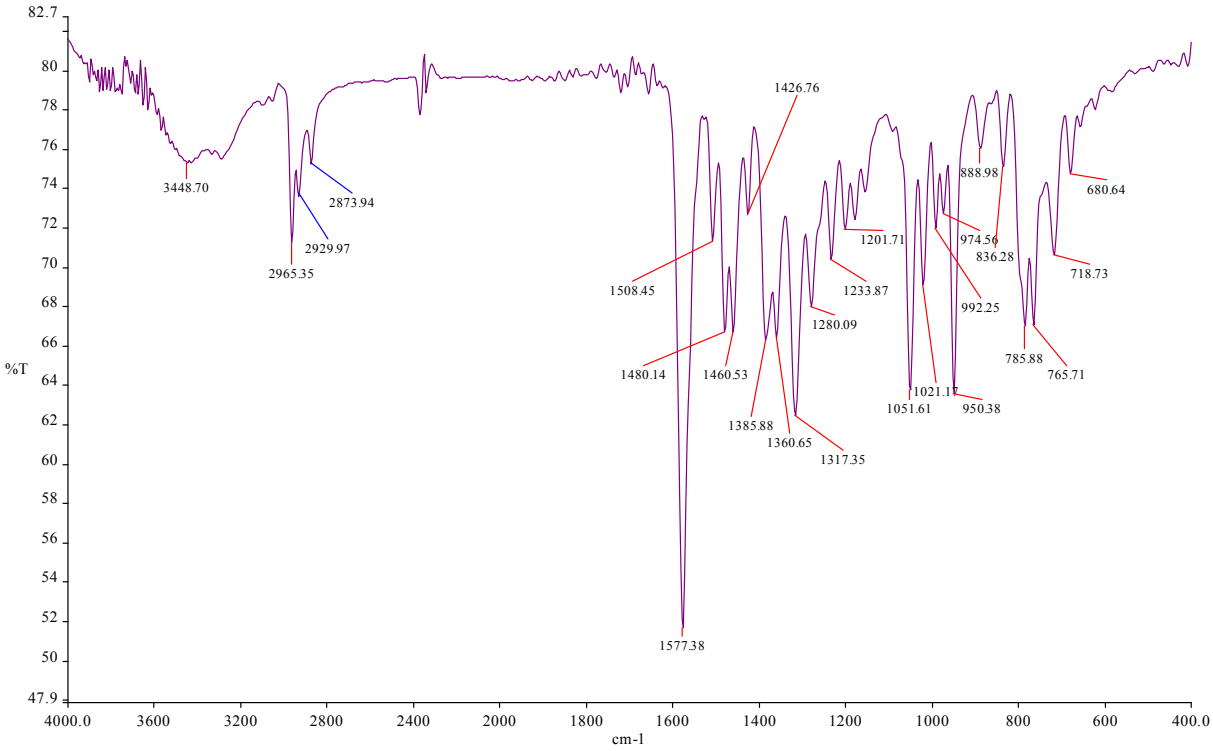


Figure S15. IR spectrum of calix[4]phyrin **3** recorded as a KBr disc.

3. X-ray crystallography

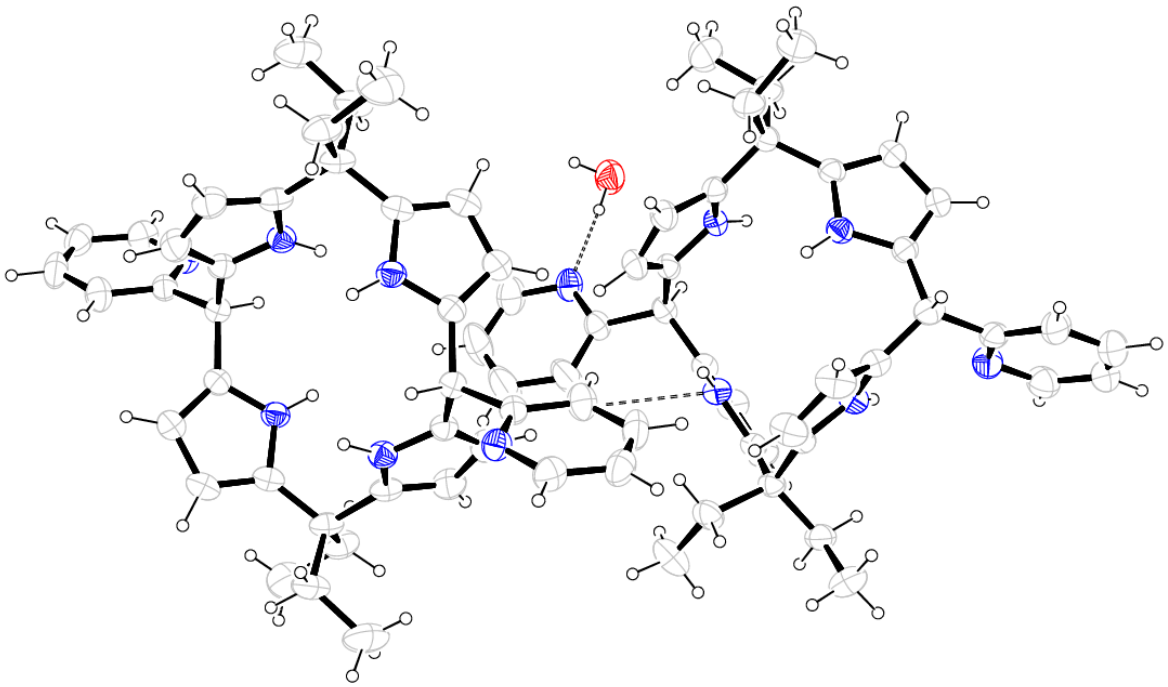


Figure S16. ORTEP diagram of the *anti* isomers **2b** and **2b'** generated by the inversion center with 30% probability ellipsoids.

4. UV-vis spectrum of calix[4]phyrin

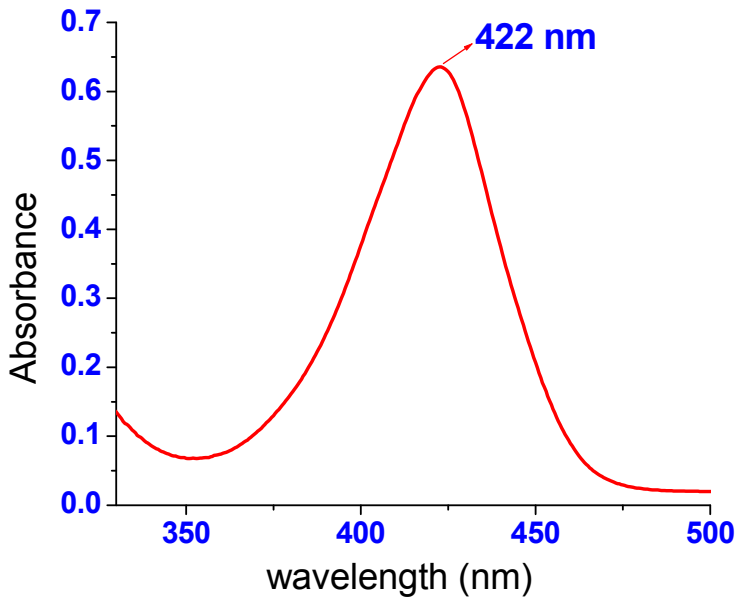


Figure S17. UV-vis spectrum of calix[4]phyrin **3** in acetone (ε = 62300 $M^{-1}cm^{-1}$).

5. NMR titrations and determination of binding constants

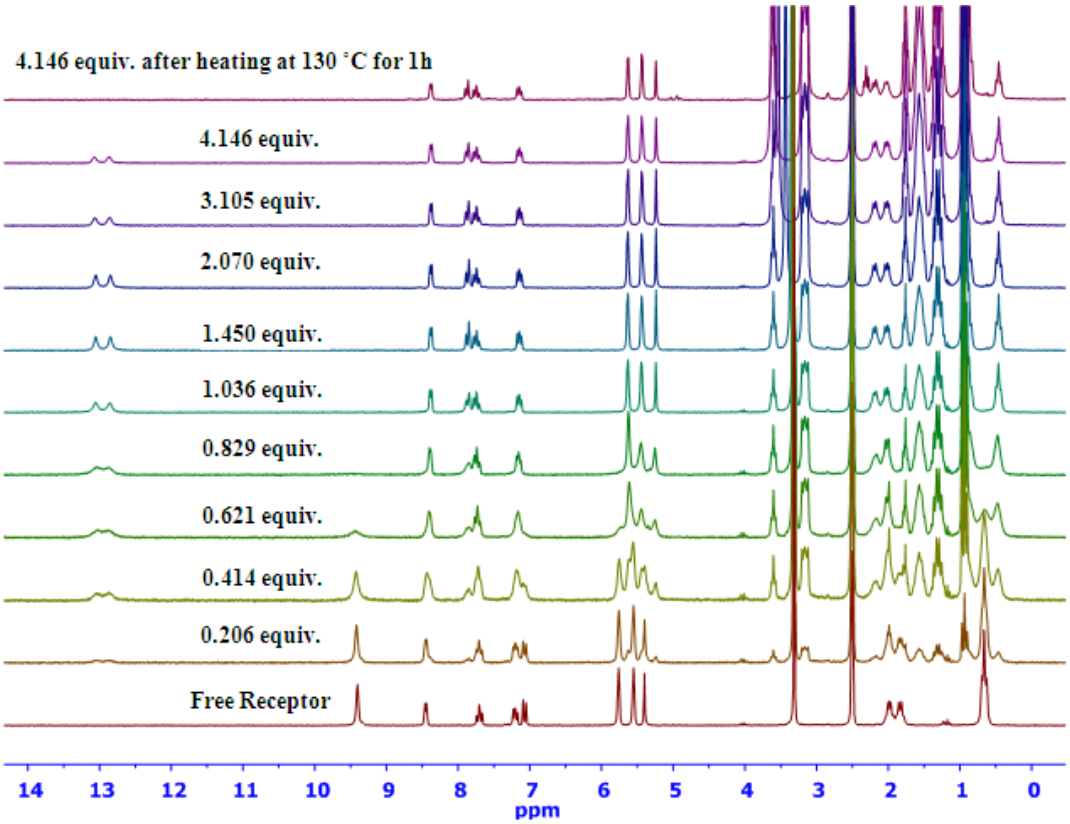


Figure S18. ^{1}H NMR (200 MHz) titration spectra of **2a**·H_2O with the fluoride anion in DMSO-d_6 at room temperature.

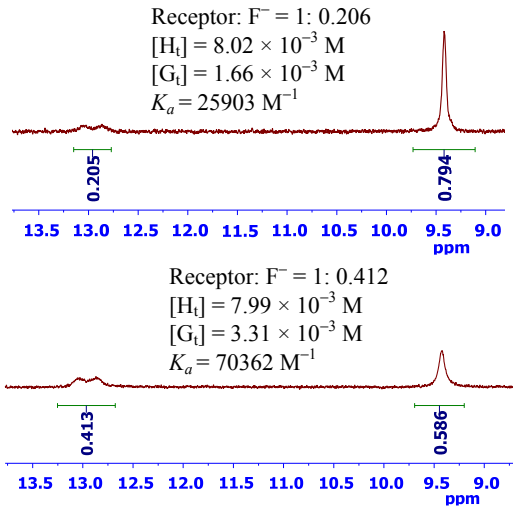


Figure S19. Binding constants K_a determination from the slow exchange process observed during the titration of **2a**·H_2O with F^- as its *n*-Bu_4N^+ salt in DMSO-d_6 at 298 K.

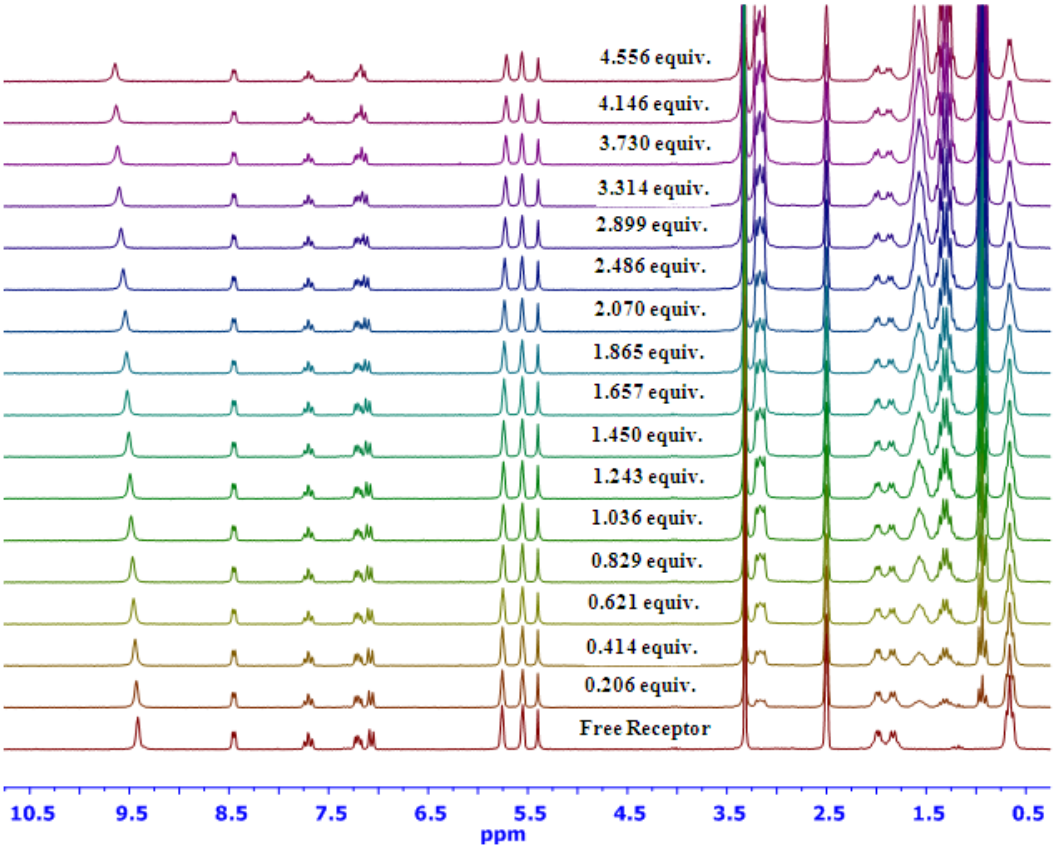


Figure S20. ^{1}H NMR (200 MHz) titration spectra of **2a**·H_2O with the chloride anion in DMSO-d_6 at room temperature.

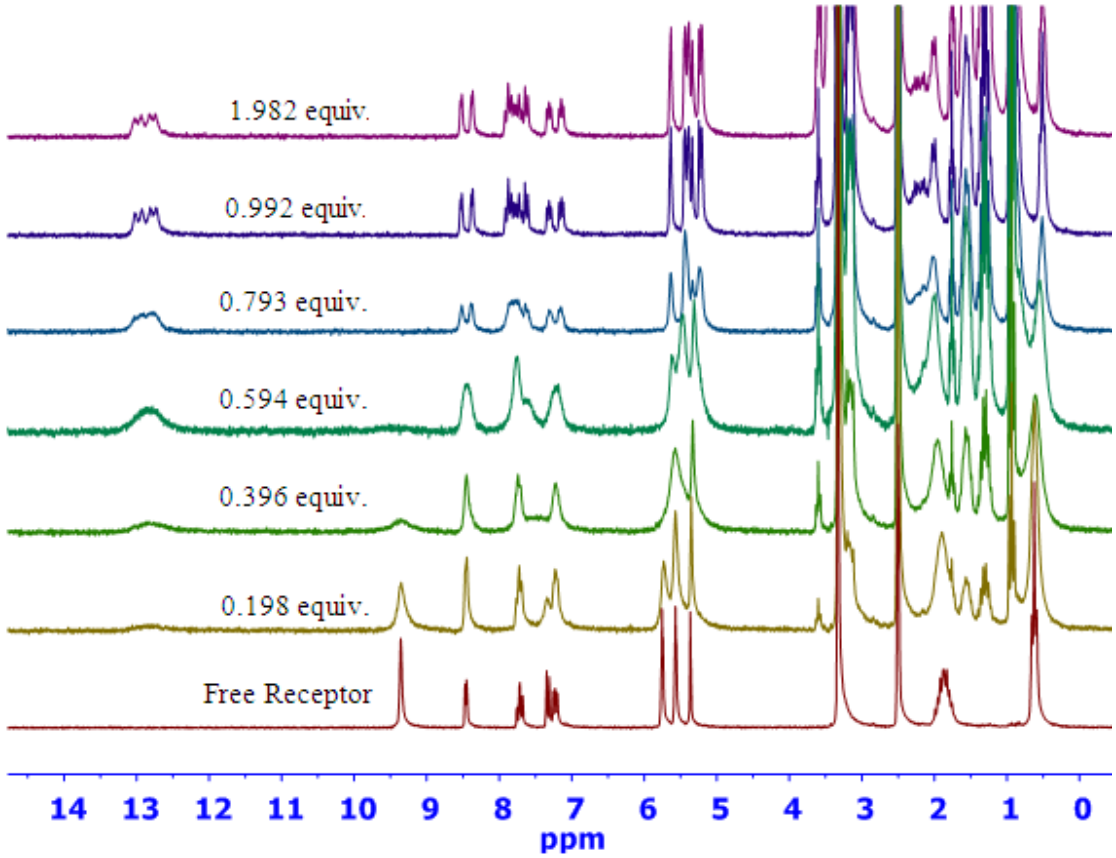


Figure S21. ^{1}H NMR (200 MHz) titration spectra of **2b**·(0.66)H_2O with the fluoride anion in DMSO-d_6 at room temperature.

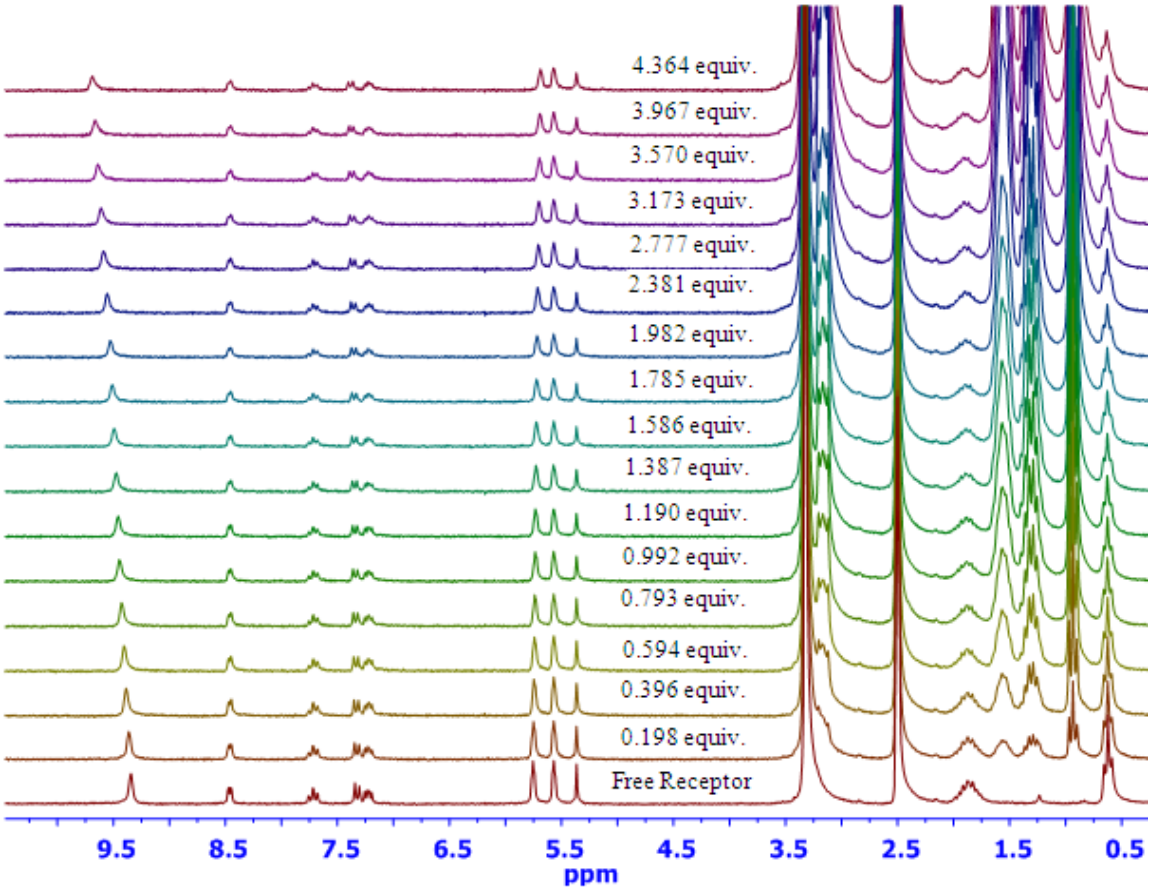


Figure S22. ^{1}H NMR (200 MHz) titration spectra of **2b**·(0.66)H_2O with the chloride anion in DMSO-d_6 at room temperature.

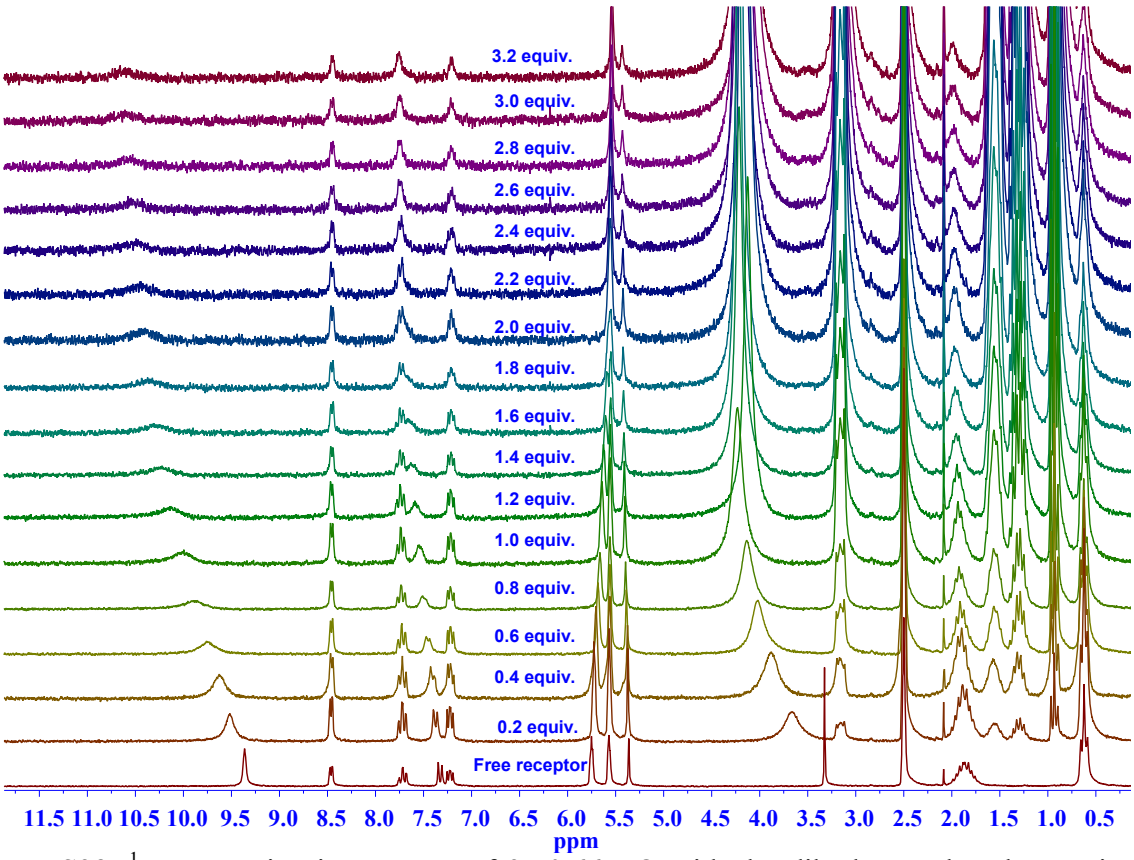
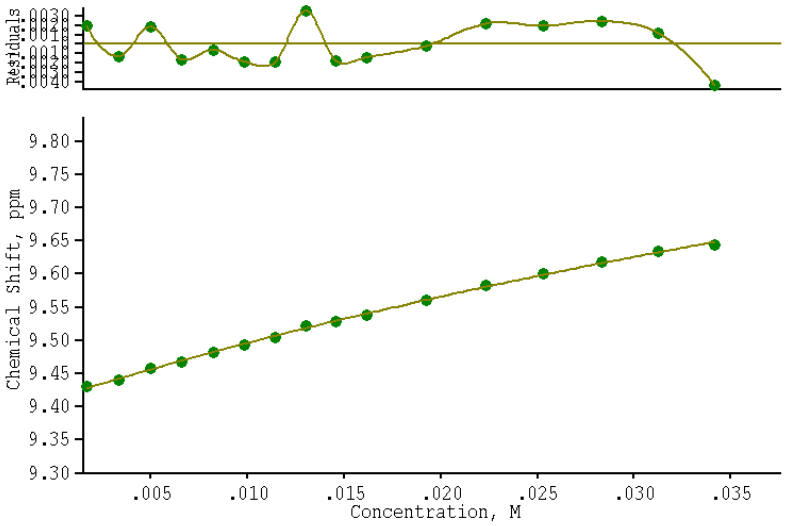


Figure S23. ^{1}H NMR titration spectra of **2b**·0.66H_2O with the dihydrogenphosphate anion in DMSO-d_6 at room temperature.

Figure S24. Determination of K_a using NH resonances by the EQNMR program for the titration of **2a**·H_2O with Cl^- ion in DMSO-d_6 at room temperature.

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Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 12:11:43   on 10/03/2012
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Using NH proton

Equilibrium constants are floating point numbers

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2	1	9.41327E+00	9.410E-02	1.831E-03	7.345E+00	free ligand
3	1	1.03400E+01	1.038E-01	9.766E-02	5.603E+02	complex

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1	1	9.4300E+00	9.4280E+00	1.9732E-03	2.0924E-02	1.0000E+00	1.6600E-03	8.0200E-03	0.0000E+00
2	1	9.4410E+00	9.4423E+00	-1.2922E-03	-1.3687E-02	1.0000E+00	3.3100E-03	7.9900E-03	0.0000E+00
3	1	9.4580E+00	9.4561E+00	1.9121E-03	2.0217E-02	1.0000E+00	4.9500E-03	7.9700E-03	0.0000E+00
4	1	9.4680E+00	9.4696E+00	-1.6136E-03	-1.7043E-02	1.0000E+00	6.5800E-03	7.9400E-03	0.0000E+00
5	1	9.4820E+00	9.4826E+00	-5.8651E-04	-6.1855E-03	1.0000E+00	8.2000E-03	7.9100E-03	0.0000E+00
6	1	9.4930E+00	9.4949E+00	-1.8778E-03	-1.9781E-02	1.0000E+00	9.8100E-03	7.8900E-03	0.0000E+00
7	1	9.5050E+00	9.5069E+00	-1.9293E-03	-2.0298E-02	1.0000E+00	1.1400E-02	7.8600E-03	0.0000E+00
8	1	9.5220E+00	9.5184E+00	3.6011E-03	3.7818E-02	1.0000E+00	1.2990E-02	7.8400E-03	0.0000E+00
9	1	9.5280E+00	9.5298E+00	-1.7538E-03	-1.8407E-02	1.0000E+00	1.4570E-02	7.8100E-03	0.0000E+00
10	1	9.5390E+00	9.5404E+00	-1.4210E-03	-1.4896E-02	1.0000E+00	1.6130E-02	7.7900E-03	0.0000E+00
11	1	9.5610E+00	9.5611E+00	-1.4591E-04	-1.5261E-03	1.0000E+00	1.9240E-02	7.7400E-03	0.0000E+00
12	1	9.5830E+00	9.5808E+00	2.2192E-03	2.3158E-02	1.0000E+00	2.2300E-02	7.6900E-03	0.0000E+00
13	1	9.6010E+00	9.5990E+00	1.9646E-03	2.0462E-02	1.0000E+00	2.5320E-02	7.6400E-03	0.0000E+00
14	1	9.6190E+00	9.6165E+00	2.4700E-03	2.5679E-02	1.0000E+00	2.8310E-02	7.5900E-03	0.0000E+00
15	1	9.6340E+00	9.6328E+00	1.1930E-03	1.2384E-02	1.0000E+00	3.1260E-02	7.5400E-03	0.0000E+00
16	1	9.6440E+00	9.6484E+00	-4.4003E-03	-4.5627E-02	1.0000E+00	3.4170E-02	7.5000E-03	0.0000E+00

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TOLERANCE ON SUM OF SQUARES     0.0100
TOLERANCE ON EIGEN VALUES     0.0001
CONVERGANCE AFTER     2   ITERATIONS
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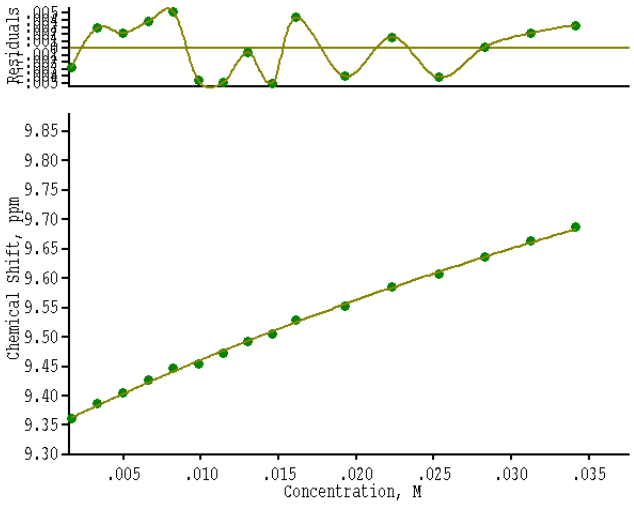
Figure S25. Determination of K_a using NH resonances by the EQNMR program for the titration of **2b**·(0.66)H_2O with Cl^- ion in DMSO-d_6 at room temperature.

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Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 16:43:16   on 10/04/2012

Using NH proton

Equilibrium constants are floating point numbers
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1 1 9.75334E+00 9.900E-02 1.744E+00 7.591E+02 K1
2 1 9.34261E+00 9.340E-02 2.933E-03 6.851E+00 free ligand
3 1 1.07634E+01 1.075E-01 1.863E-01 6.753E+02 complex

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2	1	9.3870E+00	9.3841E+00	2.9192E-03	3.1098E-02	1.0000E+00	3.3100E-03	8.3500E-03	0.0000E+00
3	1	9.4060E+00	9.4038E+00	2.1572E-03	2.2934E-02	1.0000E+00	4.9500E-03	8.3200E-03	0.0000E+00
4	1	9.4270E+00	9.4232E+00	3.8500E-03	4.0840E-02	1.0000E+00	6.5800E-03	8.3000E-03	0.0000E+00
5	1	9.4470E+00	9.4418E+00	5.2433E-03	5.5502E-02	1.0000E+00	8.2000E-03	8.2700E-03	0.0000E+00
6	1	9.4550E+00	9.4595E+00	-4.5490E-03	-4.8112E-02	1.0000E+00	9.8100E-03	8.2400E-03	0.0000E+00
7	1	9.4720E+00	9.4769E+00	-4.8895E-03	-5.1620E-02	1.0000E+00	1.1400E-02	8.2200E-03	0.0000E+00
8	1	9.4930E+00	9.4936E+00	-5.7697E-04	-6.0779E-03	1.0000E+00	1.2990E-02	8.1900E-03	0.0000E+00
9	1	9.5050E+00	9.5100E+00	-4.9868E-03	-5.2465E-02	1.0000E+00	1.4570E-02	8.1600E-03	0.0000E+00
10	1	9.5300E+00	9.5256E+00	4.4413E-03	4.6603E-02	1.0000E+00	1.6130E-02	8.1400E-03	0.0000E+00
11	1	9.5520E+00	9.5560E+00	-4.0035E-03	-4.1913E-02	1.0000E+00	1.9240E-02	8.0800E-03	0.0000E+00
12	1	9.5860E+00	9.5844E+00	1.6298E-03	1.7002E-02	1.0000E+00	2.2300E-02	8.0300E-03	0.0000E+00
13	1	9.6070E+00	9.6112E+00	-4.1542E-03	-4.3241E-02	1.0000E+00	2.5320E-02	7.9800E-03	0.0000E+00
14	1	9.6370E+00	9.6368E+00	2.2984E-04	2.3849E-03	1.0000E+00	2.8310E-02	7.9300E-03	0.0000E+00
15	1	9.6630E+00	9.6608E+00	2.2068E-03	2.2838E-02	1.0000E+00	3.1260E-02	7.8800E-03	0.0000E+00
16	1	9.6870E+00	9.6838E+00	3.2387E-03	3.3433E-02	1.0000E+00	3.4170E-02	7.8300E-03	0.0000E+00

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TOLERANCE ON SUM OF SQUARES     0.0100
TOLERANCE ON EIGEN VALUES     0.0001
CONVERGANCE AFTER     2   ITERATIONS
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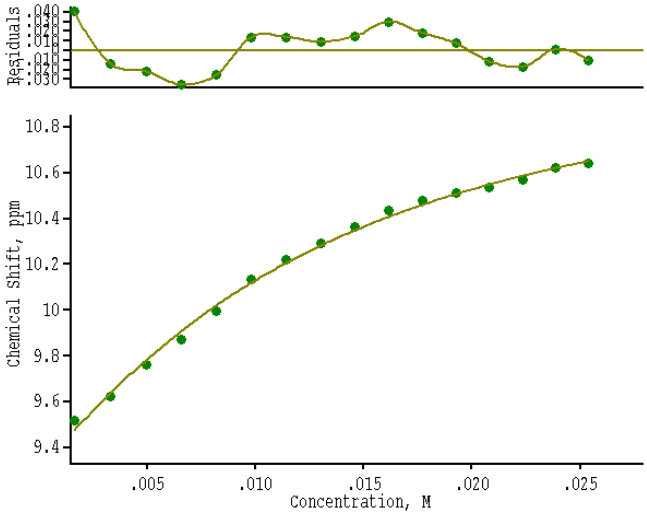
Figure S26. Determination of K_a using NH resonance by EQNMR for the **2b**·0.66H_2O and $H_2PO_4^-$ ion in DMSO-d_6 at room temperature.



Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 18:04:09 on 01/15/2013

Using NH proton

Equilibrium constants are floating point numbers

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2	1	9.29606E+00	9.360E-02	2.368E-02	5.492E+00	free ligand
3	1	1.12411E+01	1.120E-01	9.364E-02	6.764E+01	complex

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RFACTOR = 0.2006 PERCENT

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2	1	9.6250E+00	9.6384E+00	-1.3435E-02	-1.3959E-01	1.0000E+00	3.3200E-03	8.3500E-03	0.0000E+00
3	1	9.7600E+00	9.7819E+00	-2.1862E-02	-2.2400E-01	1.0000E+00	4.9600E-03	8.3200E-03	0.0000E+00
4	1	9.8730E+00	9.9084E+00	-3.5351E-02	-3.5806E-01	1.0000E+00	6.5900E-03	8.3000E-03	0.0000E+00
5	1	9.9960E+00	1.0021E+01	-2.5184E-02	-2.5194E-01	1.0000E+00	8.2100E-03	8.2700E-03	0.0000E+00
6	1	1.0134E+01	1.0120E+01	1.4124E-02	1.3937E-01	1.0000E+00	9.8200E-03	8.2400E-03	0.0000E+00
7	1	1.0220E+01	1.0206E+01	1.4003E-02	1.3701E-01	1.0000E+00	1.1420E-02	8.2200E-03	0.0000E+00
8	1	1.0291E+01	1.0282E+01	8.9827E-03	8.7287E-02	1.0000E+00	1.3010E-02	8.1900E-03	0.0000E+00
9	1	1.0364E+01	1.0349E+01	1.4919E-02	1.4395E-01	1.0000E+00	1.4590E-02	8.1600E-03	0.0000E+00
10	1	1.0438E+01	1.0408E+01	3.0091E-02	2.8829E-01	1.0000E+00	1.6150E-02	8.1400E-03	0.0000E+00
11	1	1.0479E+01	1.0461E+01	1.8385E-02	1.7545E-01	1.0000E+00	1.7710E-02	8.1100E-03	0.0000E+00
12	1	1.0515E+01	1.0508E+01	7.4806E-03	7.1142E-02	1.0000E+00	1.9260E-02	8.0800E-03	0.0000E+00
13	1	1.0538E+01	1.0549E+01	-1.1258E-02	-1.0683E-01	1.0000E+00	2.0800E-02	8.0600E-03	0.0000E+00
14	1	1.0570E+01	1.0587E+01	-1.6994E-02	-1.6078E-01	1.0000E+00	2.2330E-02	8.0300E-03	0.0000E+00
15	1	1.0622E+01	1.0621E+01	1.3132E-03	1.2363E-02	1.0000E+00	2.3850E-02	8.0100E-03	0.0000E+00
16	1	1.0641E+01	1.0651E+01	-1.0413E-02	-9.7859E-02	1.0000E+00	2.5360E-02	7.9800E-03	0.0000E+00

TOLERANCE ON SUM OF SQUARES 0.0100
TOLERANCE ON EIGEN VALUES 0.0001
CONVERGANCE AFTER 5 ITERATIONS

6. H/D Exchange

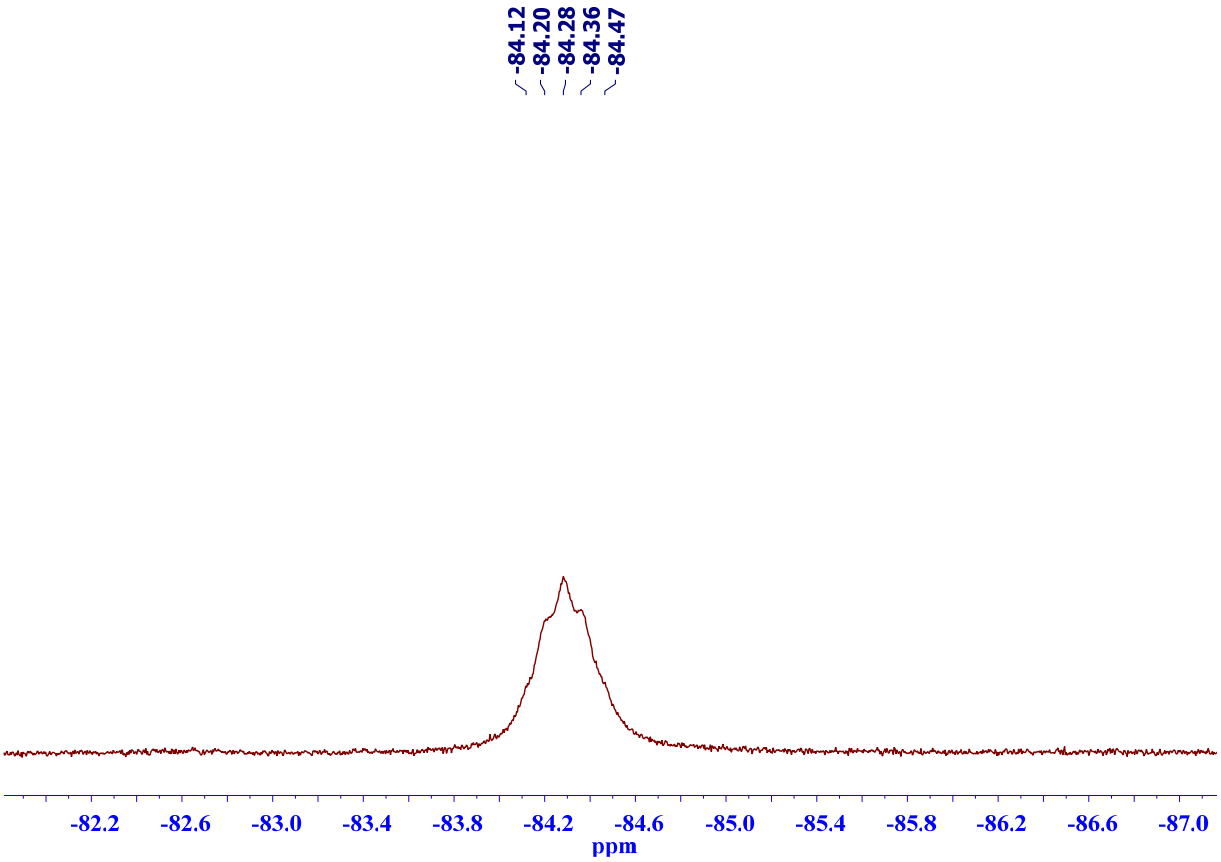

Figure S27. Partial proton coupled ^{19}F NMR spectrum of the *syn* isomer with one equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing a broad multiplet for the formation of 1:1 F^- ion complex containing no deuterium atom.

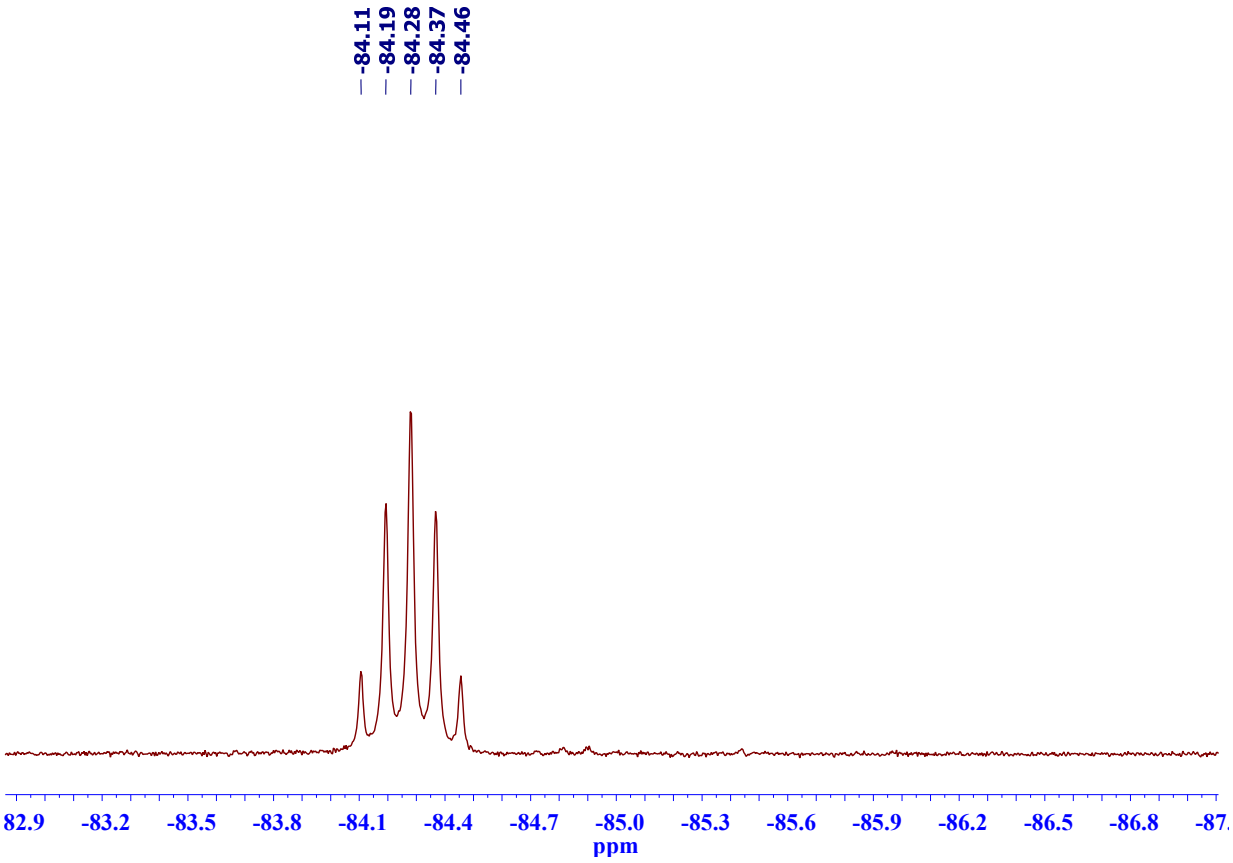

Figure S28. Partial proton coupled ^{19}F NMR spectrum of the *syn* isomer with two equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing a quintet for the formation of 1:1 F^- ion complex containing no deuterium atom.

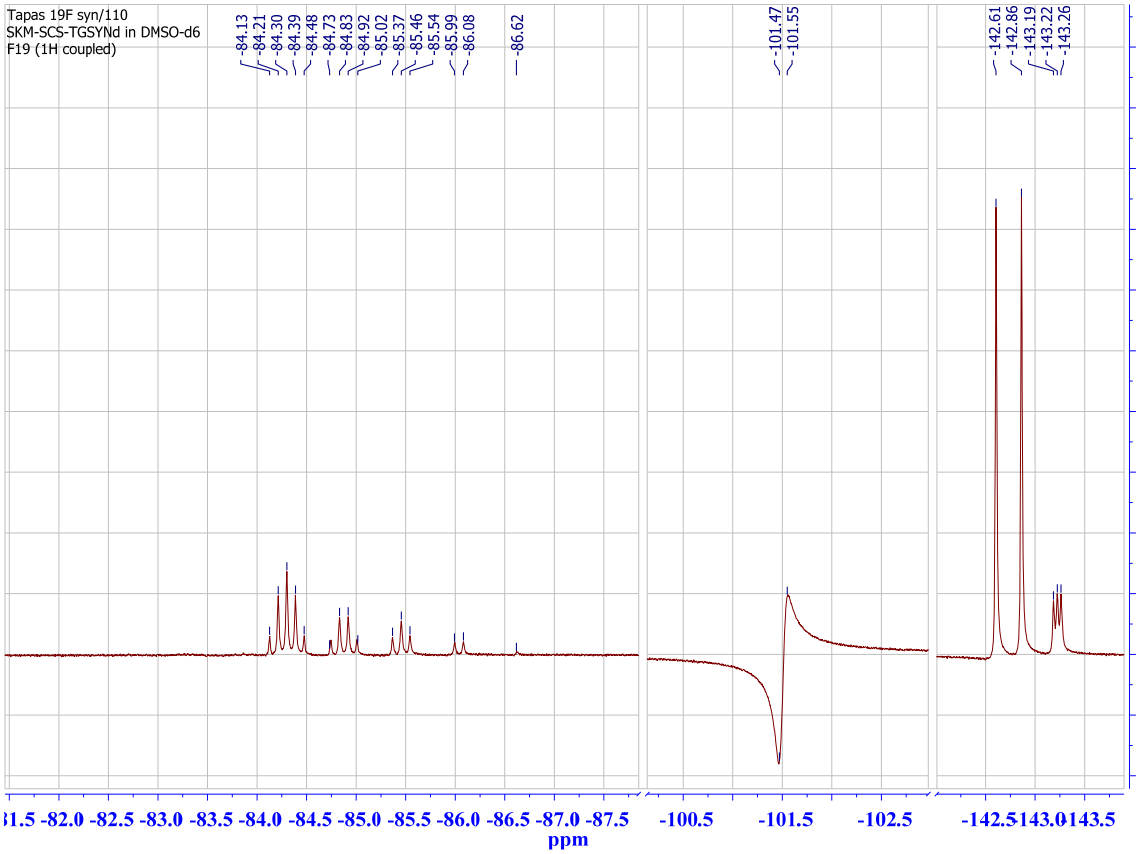

Figure S29. The proton coupled ^{19}F NMR spectrum of the *syn* isomer after the addition of four equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing multiplets for the formation of different 1:1 F^- ion complexes containing deuterium atom. The resonances corresponding to the formation of HF_2^- (δ = –142.7(d), *J*(HF) = 117.6 Hz) and DF_2^- (δ = –143.2(t), *J*(DF) = 16.5 Hz) in the solution are also appeared.

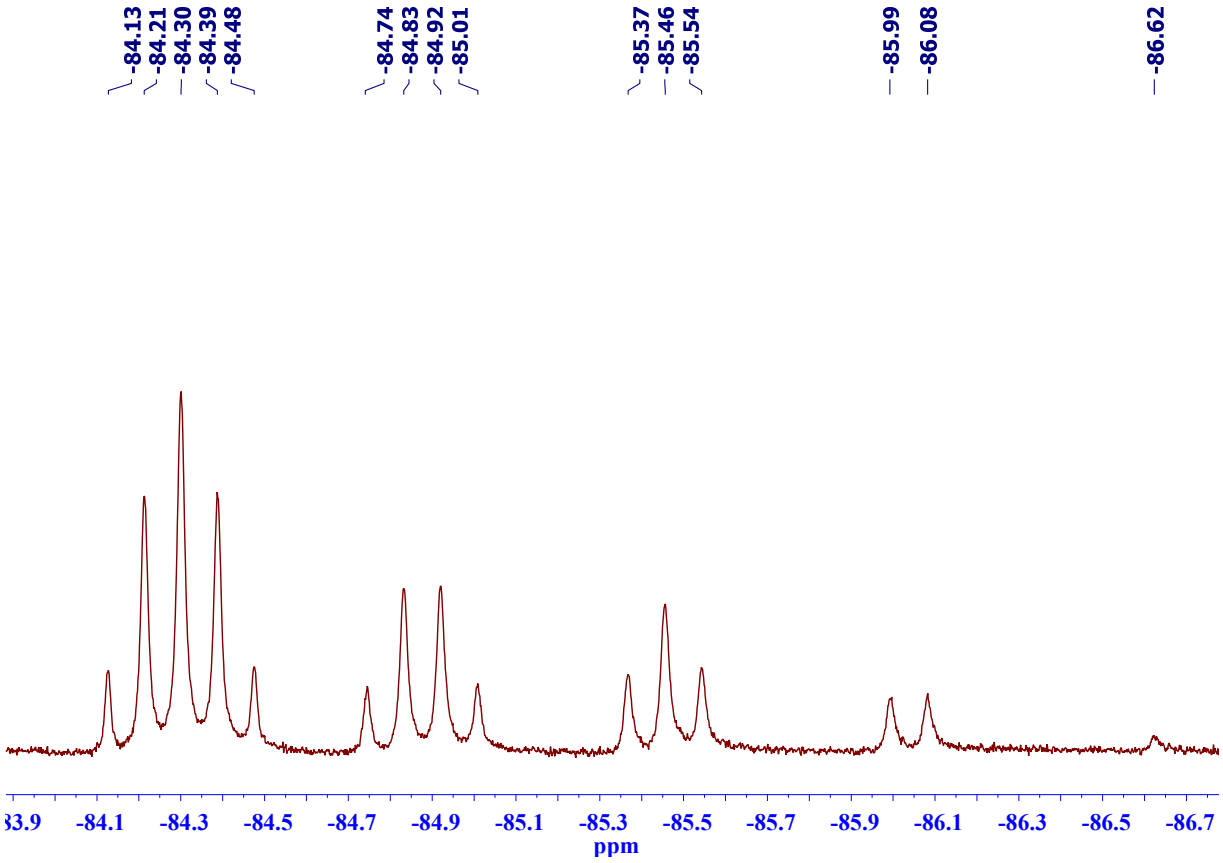

Figure S30. Partial proton coupled ^{19}F NMR spectrum of the *syn* isomer after the addition of four equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing multiplets for the formation of different 1:1 F^- ion complexes containing deuterium atom.

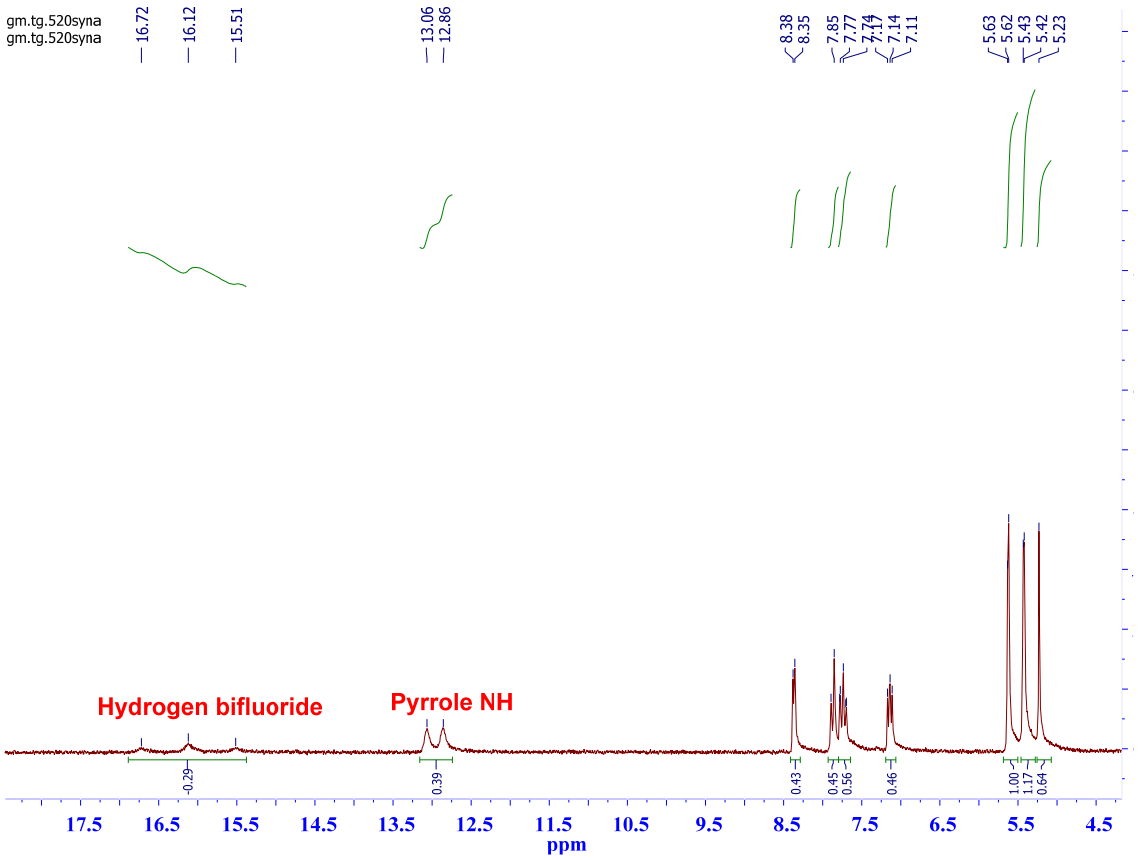

Figure S31. Partial ^{1}H NMR spectrum recorded after one day for the *syn* isomer with four equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing appearance of HF_2^- with J(HF) = 121 Hz and the pyrrolic NH resonance split into a doublet. The appearance of the NH resonance even after the addition of four equiv of F^- and 24 h indicates that H/D exchange process can be slow.

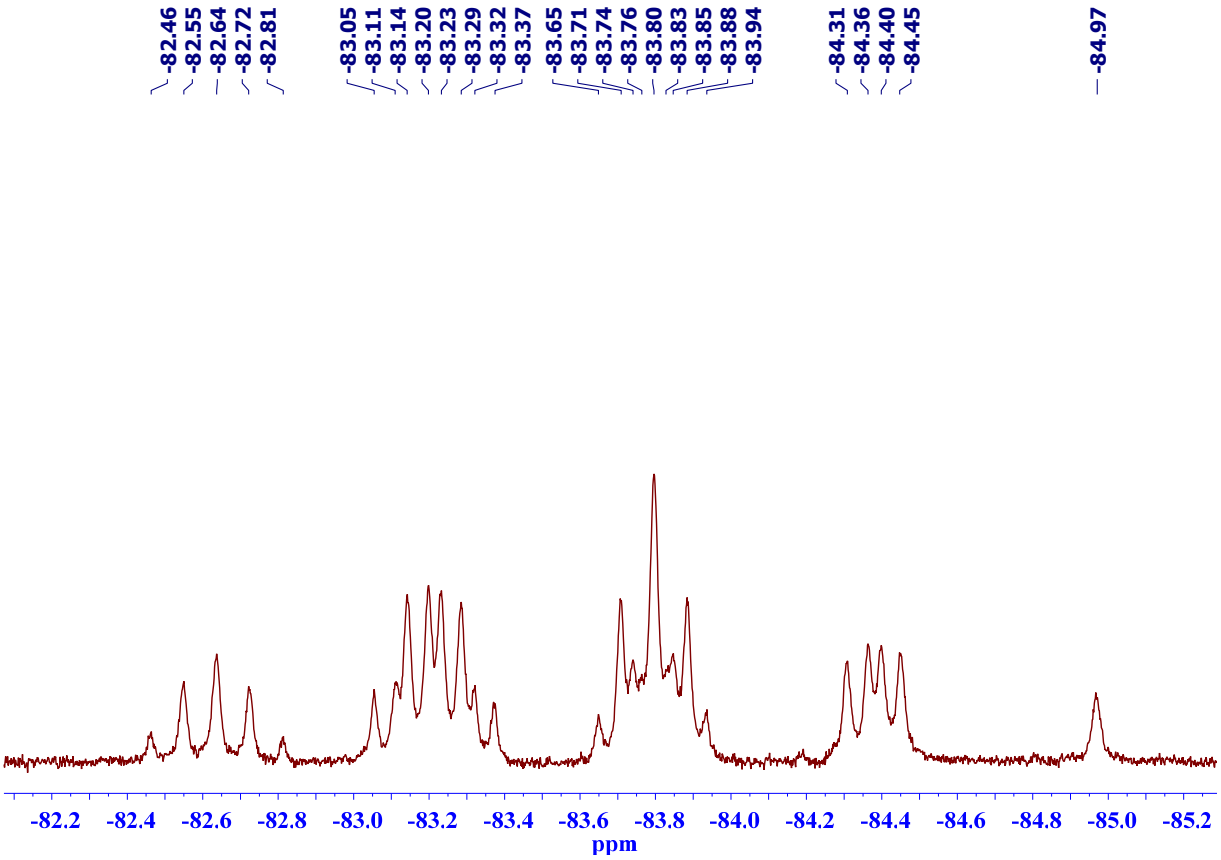

Figure S32. Partial proton coupled ^{19}F NMR spectrum of the *anti* isomer after the addition of two equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing multiplets for the formation of different 1:1 F^- ion complexes containing deuterium atom.

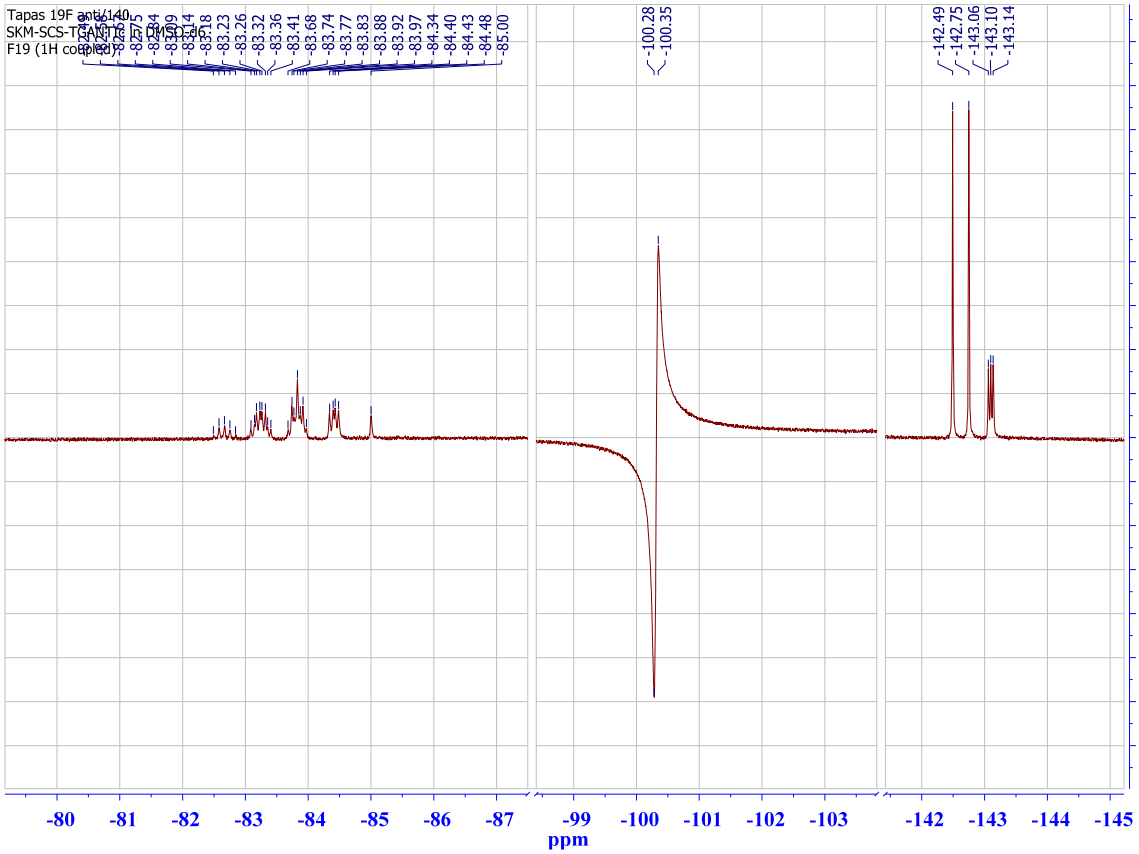

Figure S33. The proton coupled ^{19}F NMR spectrum of the *anti* isomer after the addition of three equiv of F^- ion as its *n*-Bu_4N^+ salt in DMSO-d_6, showing multiplets for the formation of different 1:1 F^- ion complexes containing deuterium atom. The resonances corresponding to the formation of HF_2^- (δ = –142.6(d), *J*(HF) = 122.4 Hz) and DF_2^- (δ = –143.1(t), *J*(DF) = 18.8 Hz) in the solution are also appeared.

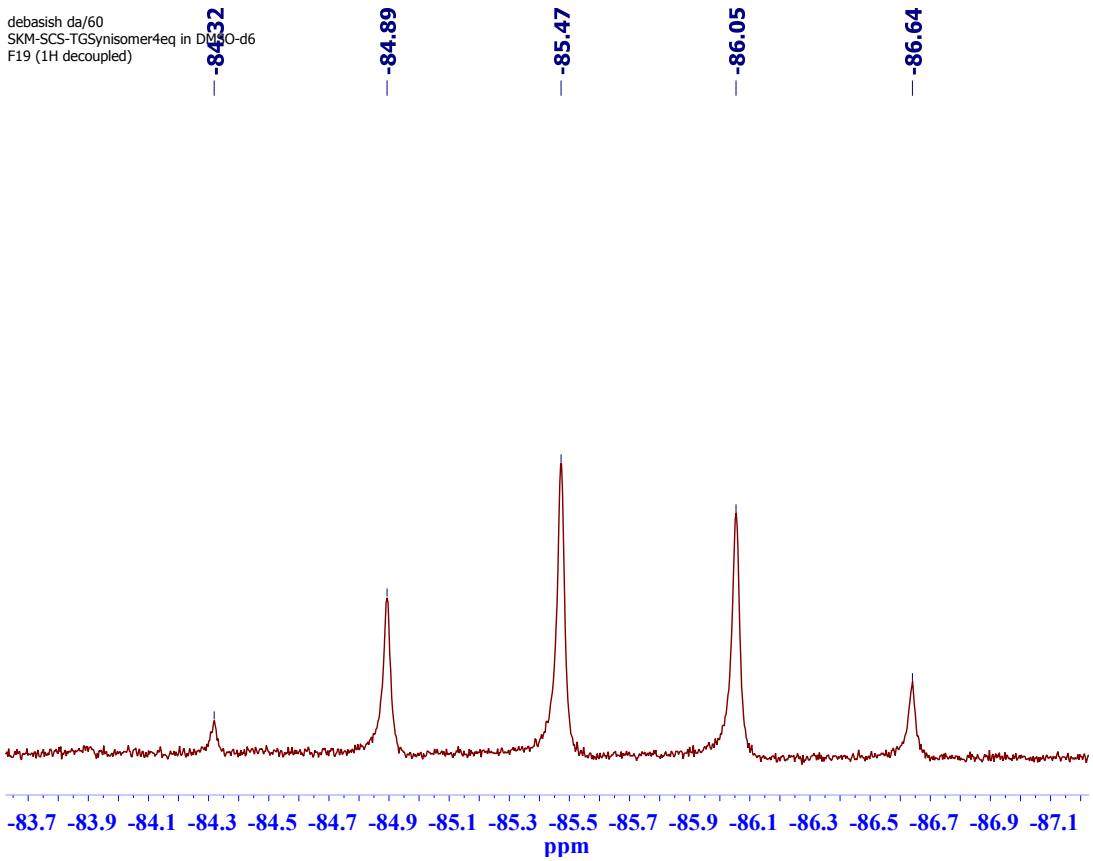

Figure S34. The proton decoupled ^{19}F NMR spectrum of the *syn* isomer with five equiv of the F^- ion in DMSO-d_6, showing one singlet for each type of F^- ion complex formed in solution.

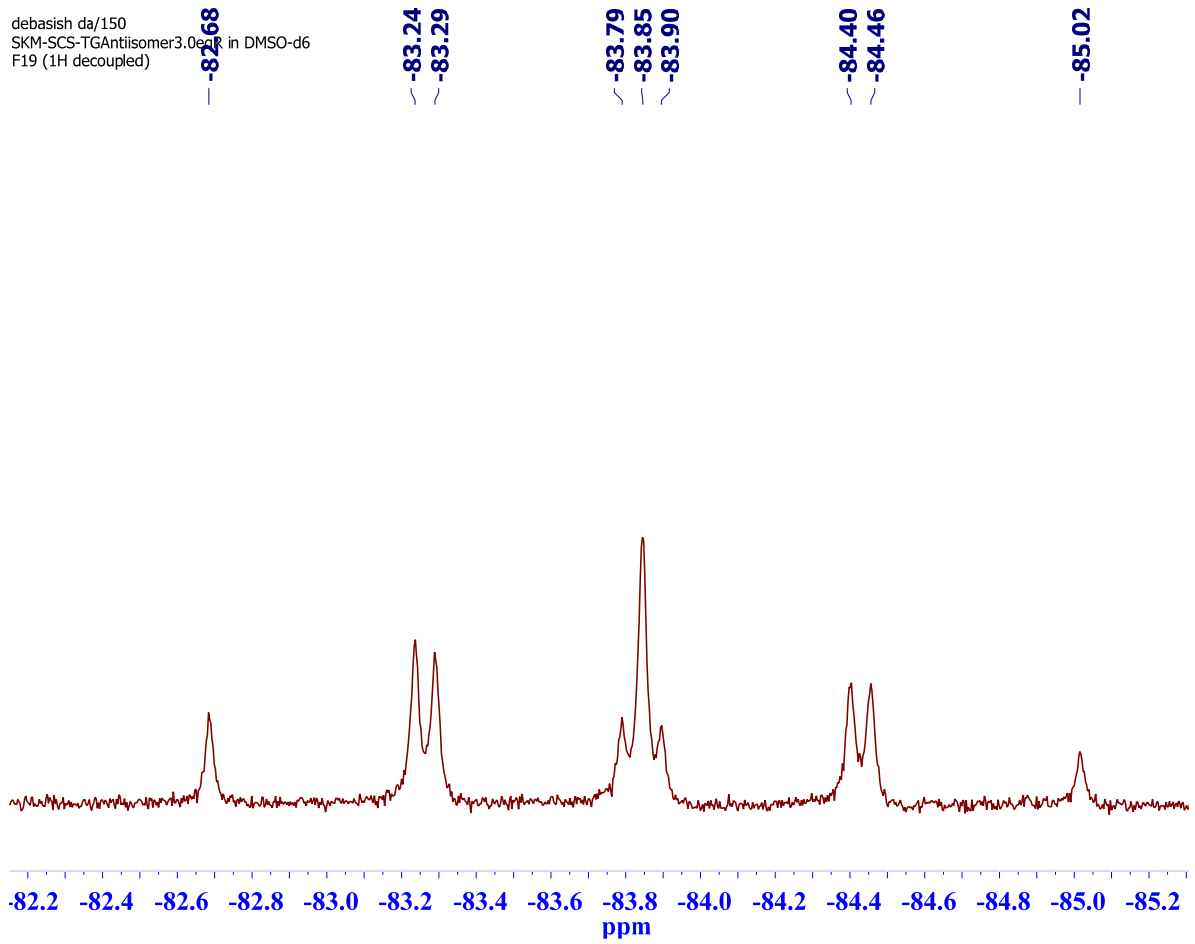

Figure S35. The proton decoupled ^{19}F NMR spectrum of the *anti* isomer with three equiv of the F^- ion in DMSO-d_6, showing one singlet for each type of F^- ion complex formed in solution as explained in Fig. 8 of the paper.

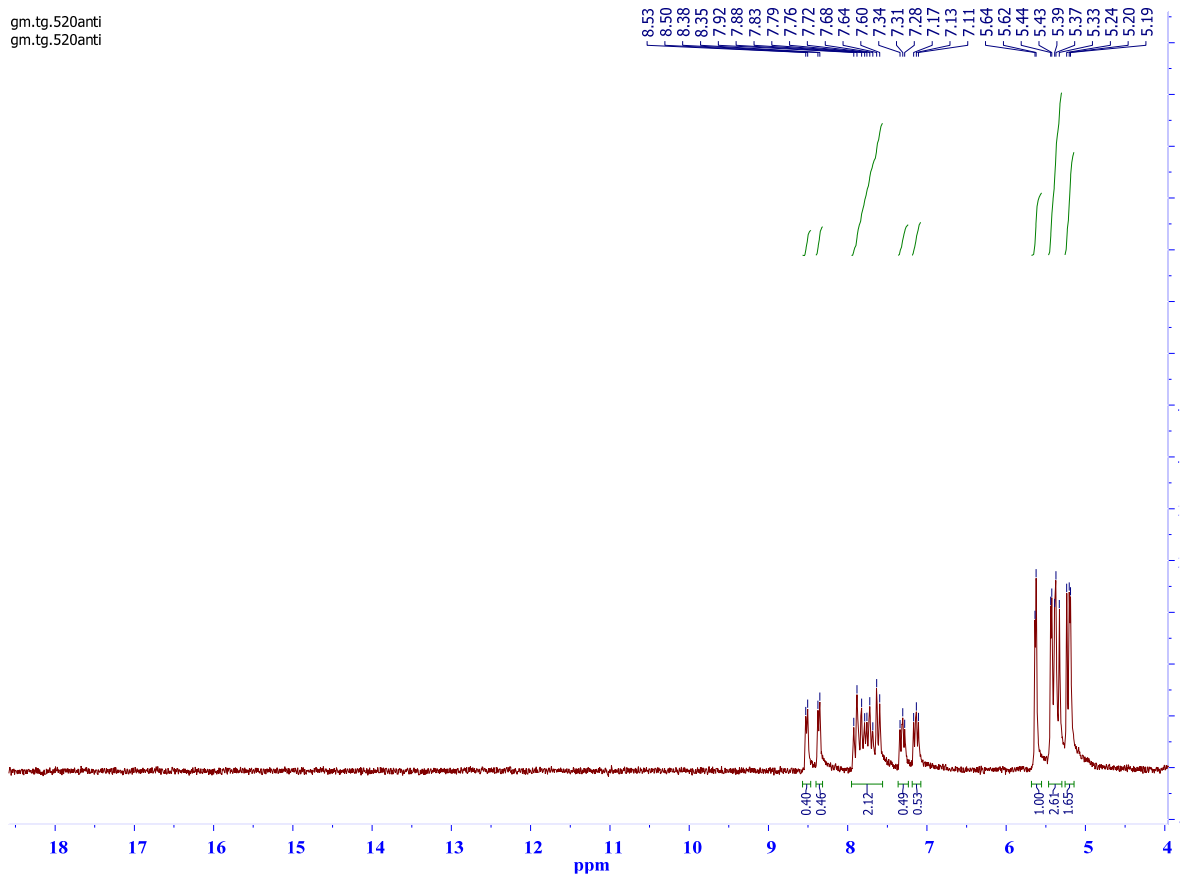

Figure S36. Partial ^{1}H NMR spectrum recorded after one day for the *anti* isomer with three equiv of F^{-} ion as its *n*-Bu_4N^{+} salt in DMSO-d_6. The NH resonance is completely disappeared owing to H/D exchange.