Comparison of binding affinities of water-soluble calixarenes with the organophosphorus nerve agent Soman (GD) and commonly-used nerve agent simulants

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pH measurements

All pH measurements were made using a Metler Toledo SevenCompact ph/ion InLab® Pro ISM probe and data is presented in Table S1.

	pH Measurement of simulant in D2O		
Mol eq calix	PMP	DEMP	DIMP
0	2.86	7.52	7.14
0.2	2.83	3.63	3.27
0.4	2.63	2.84	2.85
0.6	2.37	2.6	2.74
0.8	2.34	2.58	2.57
1	2.34	2.49	2.44
1.2	2.24	2.44	2.38
1.4	2.15	2.26	2.31
1.6	2.14	2.21	2.17
1.8	2.13	2.11	2.08
2	2.08	2.06	2.06
2.5	2	2.01	1.94
3	1.97	1.91	1.84
4	1.82	1.7	1.78
5	1.69	1.67	1.64
7	1.58	1.56	1.56
10	missed	1.5	1.44

Table S1. pH measurements of solutions of PMP, DEMP and DIMP (initial concentration = 0.01 M) in non-buffered D_2O upon addition of SCX4.

NMR Job Plot and Titration Data – *p*-sulfonatocalix[4]arene (SCX4)

Data fit plots obtained using WinEQNMR.[1]

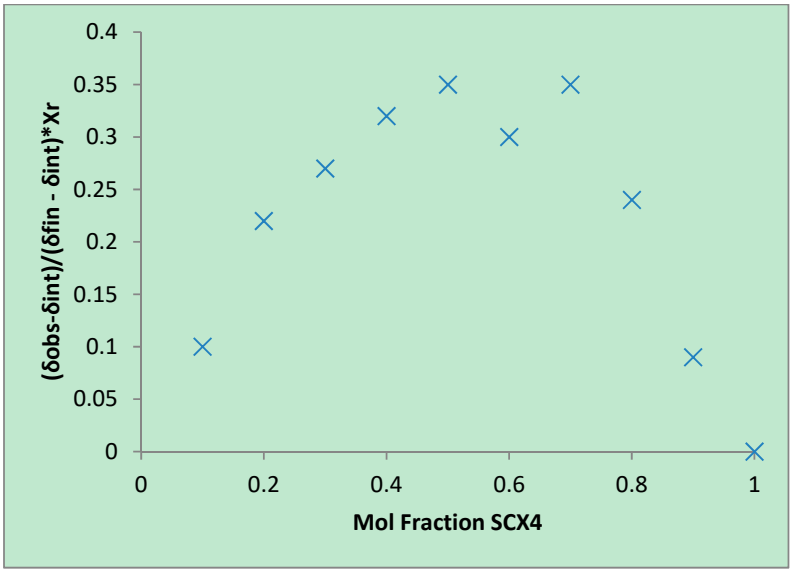

Figure S1. Job plot analysis of SCX4 and DEMP, following SCX4 CH_2 environment (D_2O, 293 K). Total concentration 0.01M.

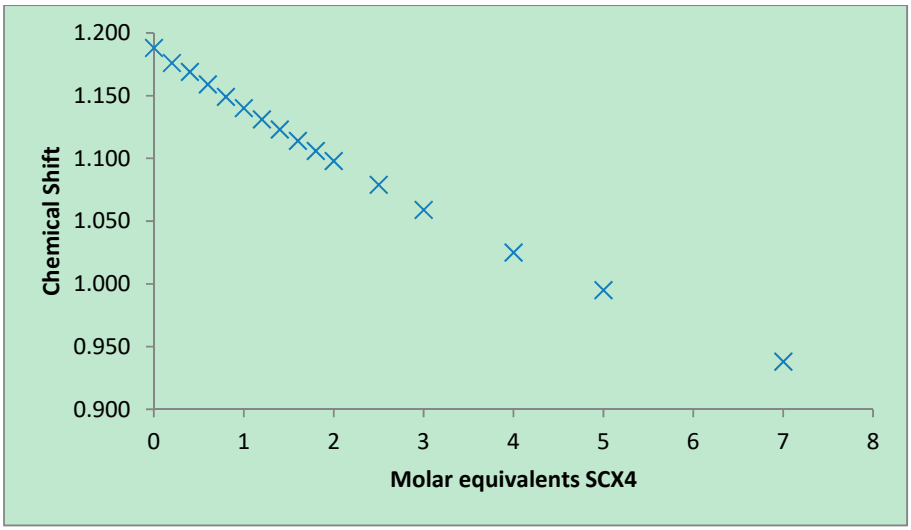

Figure S2. Titration plot of DEMP with SCX4 (D_2O, 293K). Following DEMP ethyl-CH_3 proton environment. Initial concentration of DEMP 0.01M.

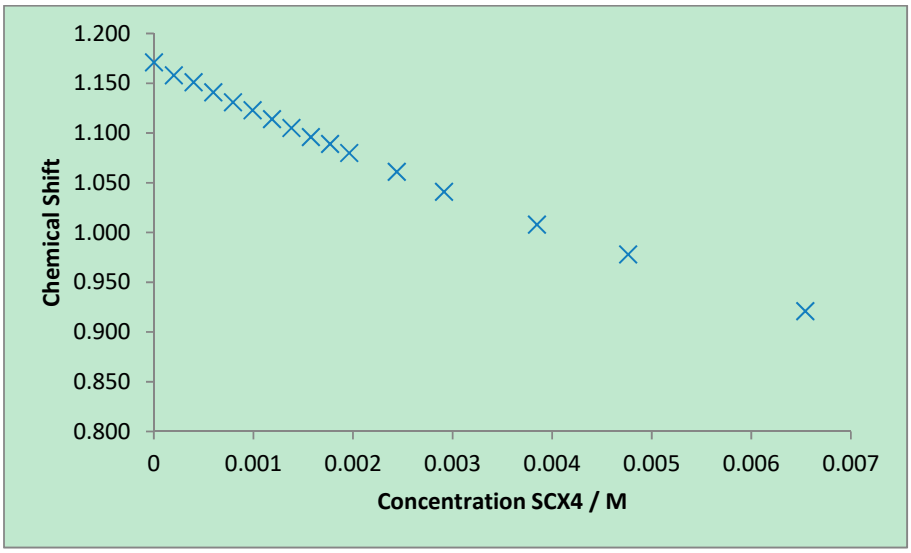

Figure S3. Titration plot of DEMP with SCX4 (0.25 M phosphate buffered D_2O, 293K). Following DEMP ethyl-CH_3 proton environment. Initial concentration of DEMP 0.01M.

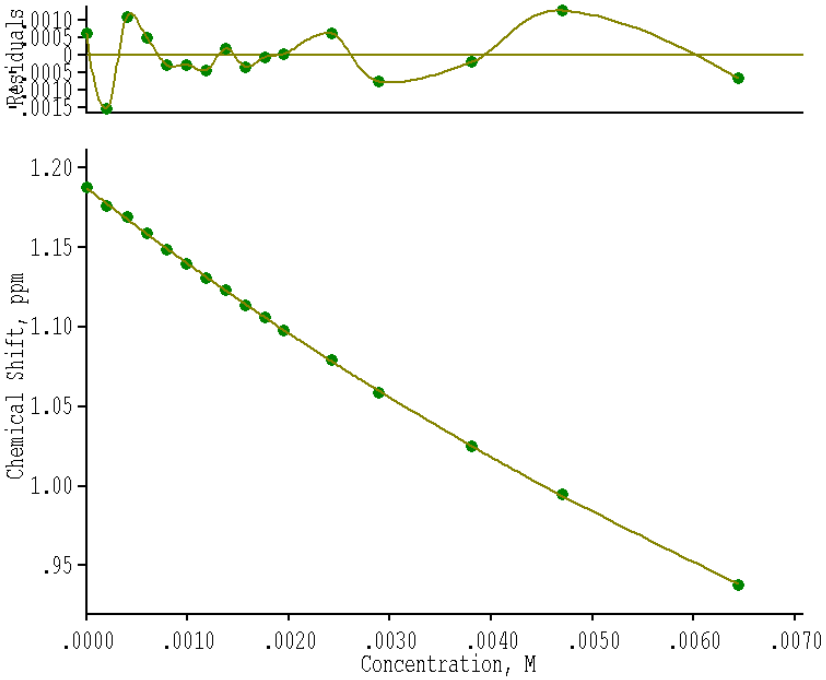

Figure S4. Data fitting of the titration of DEMP with SCX4 in D_2O (293 K). Following DEMP ethyl-CH_3 proton environment.

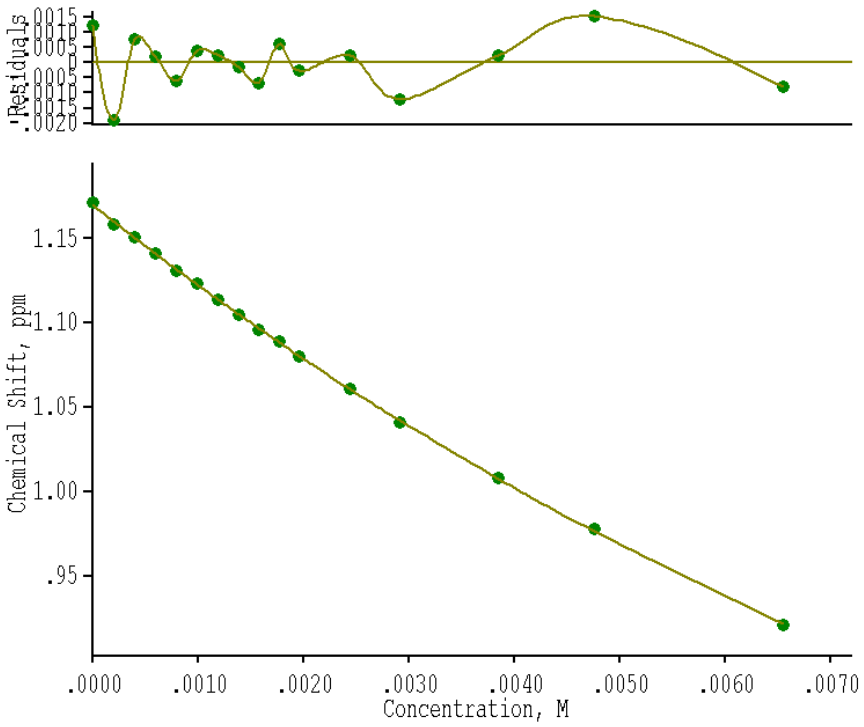

Figure S5. Data fitting of the titration of DEMP with SCX4 in 0.25 M phosphate buffered D_2O (293 K). Following DEMP ethyl-CH_3 proton environment.

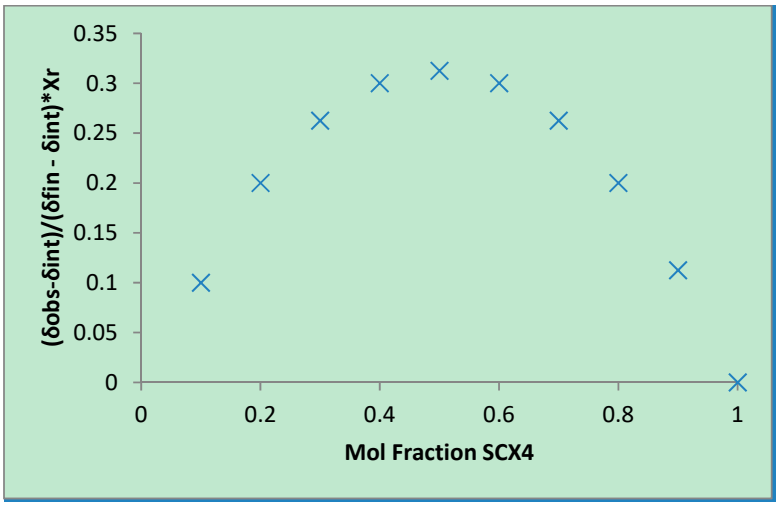

Figure S6. Job plot analysis of SCX4 and DIMP, following SCX4 CH_2 environment (D_2O, 293 K). Total concentration 0.01M.

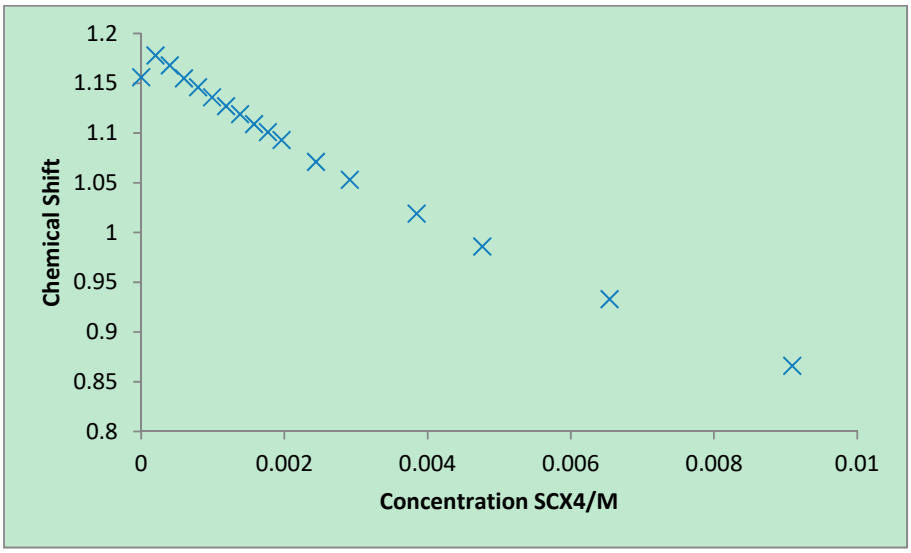

Figure S7. Titration plot of DIMP with SCX4 (D_2O, 293K). Following DIMP alkyl-CH_3 proton environment. Initial concentration of DIMP 0.01M.

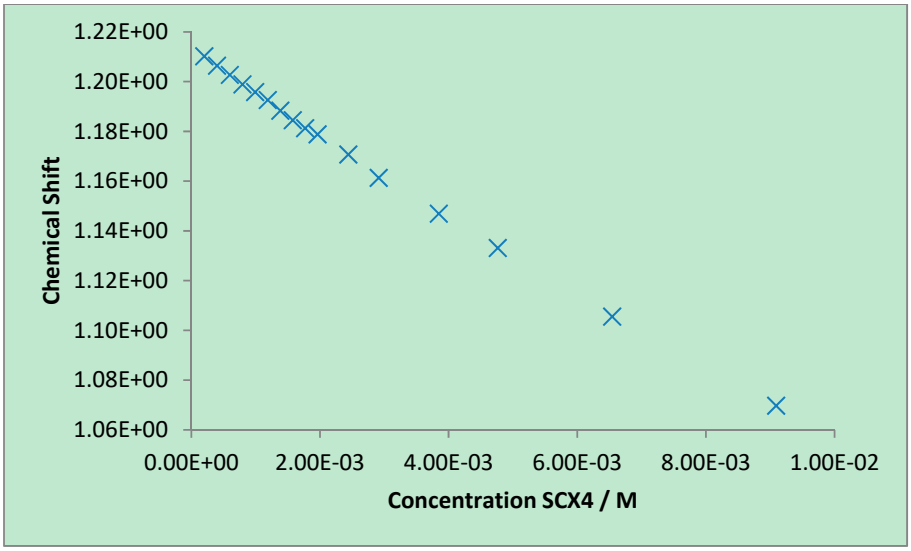

Figure S8. Titration plot of DIMP with SCX4 (0.25 M phosphate buffered D_2O, 293K). Following DIMP alkyl-CH_3 proton environment. Initial concentration of DIMP 0.01M

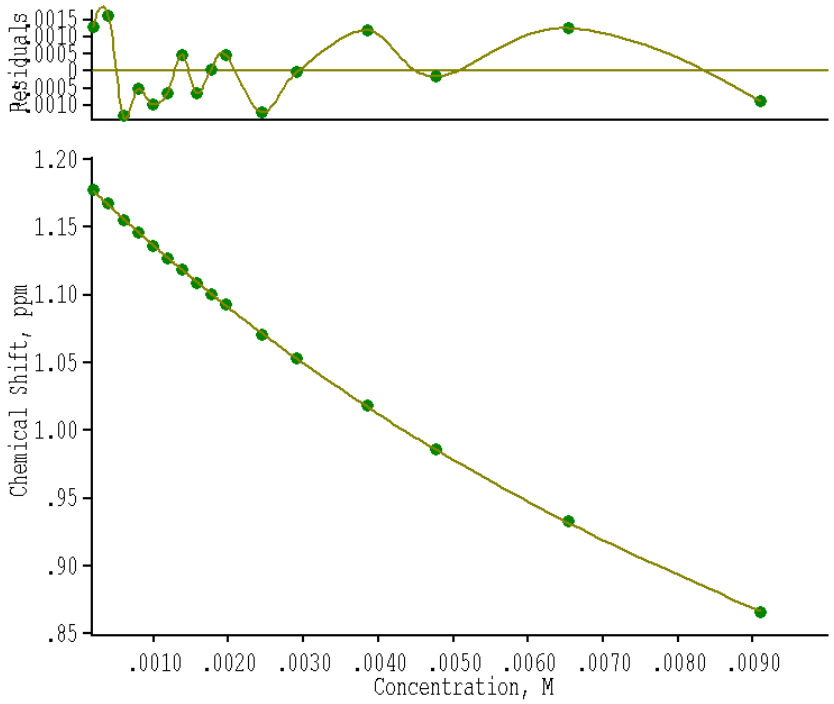

Figure S9. Data fitting of the titration of DIMP with SCX4 in D_2O (293 K). Following DIMP alkyl-CH_3 proton environment.

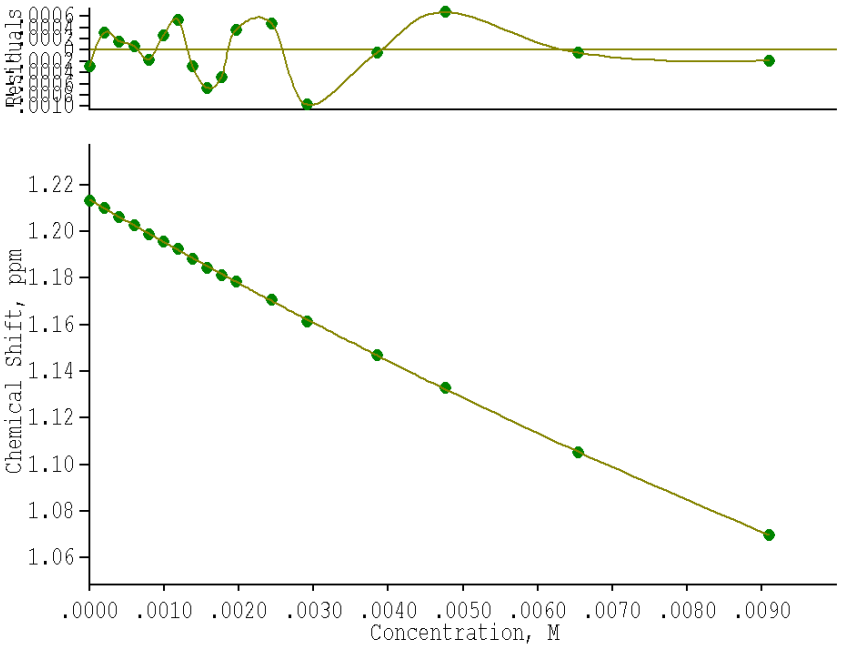

Figure S10. Data fitting of the titration of DIMP with SCX4 in 0.25 M phosphate buffered D_2O (293 K). Following DIMP alkyl-CH_3 proton environment.

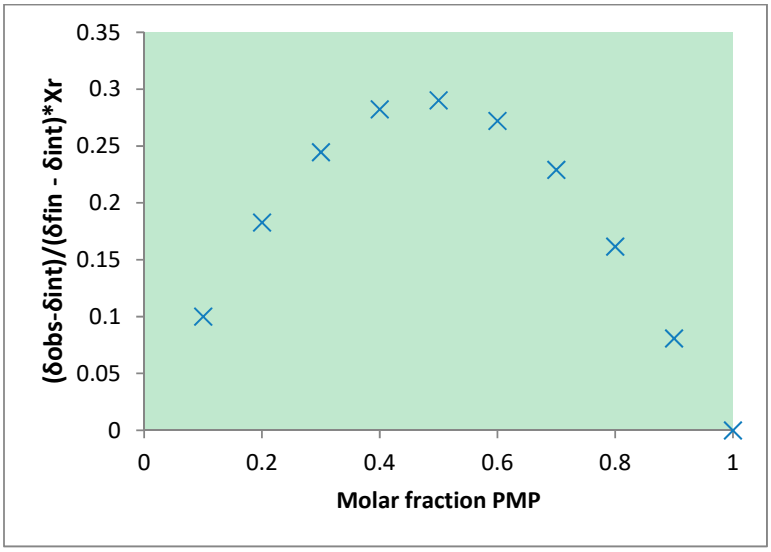

Figure S11. Job plot analysis of SCX4 and PMP, following PMP ^{t}Bu proton environment (D_2O, 293K). Total concentration 0.01M.

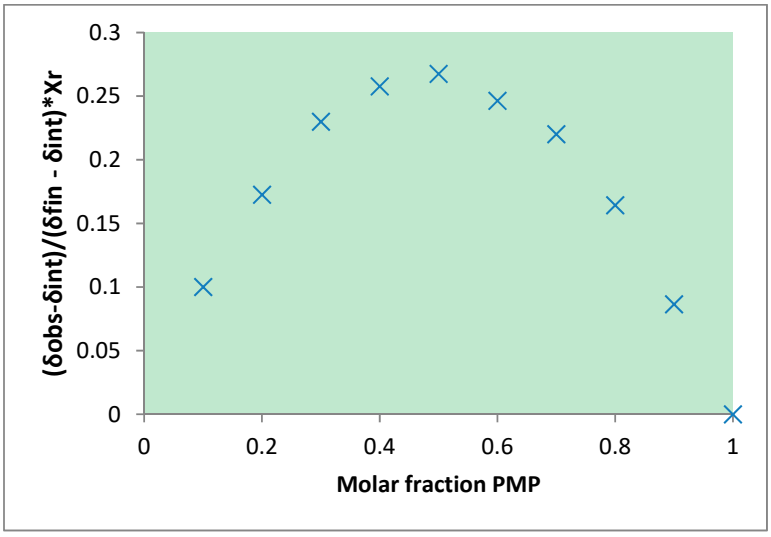

Figure S12. Job plot analysis of SCX4 and PMP, following PMP ^{t}Bu proton environment. (0.25 M phosphate buffered D_2O, 293 K). Total concentration 0.01M.

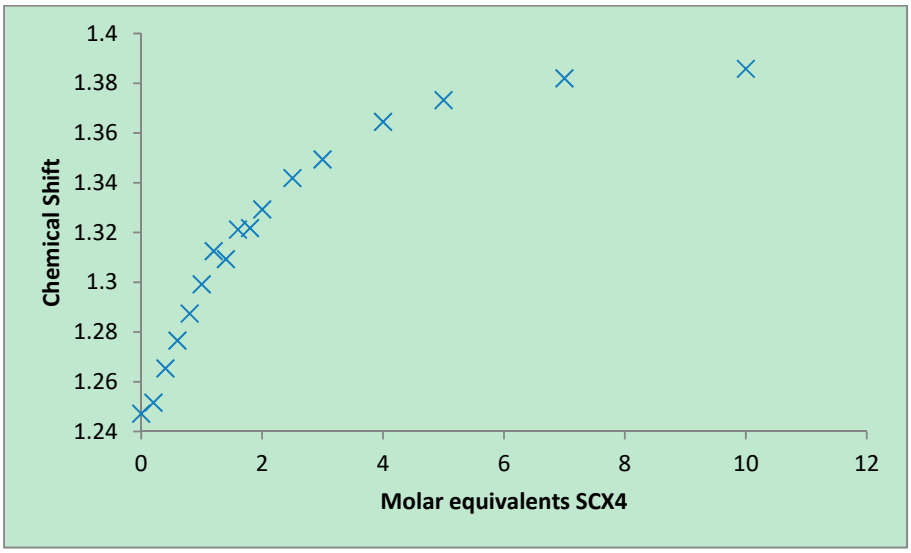

Figure S13. Titration plot of PMP with SCX4 (D_2O, 293K). Following PMP P-Me proton environment. Initial concentration of PMP 0.01M.

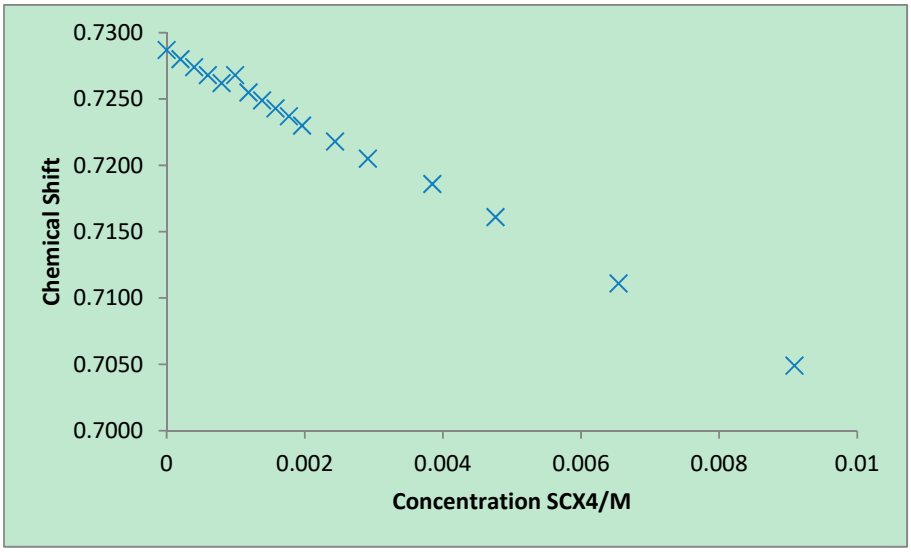

Figure S14. Titration plot of PMP with SCX4 (0.25 M phosphate buffered D_2O, 293K). Following PMP ^{t}Bu proton environment. Initial concentration of PMP 0.01M.

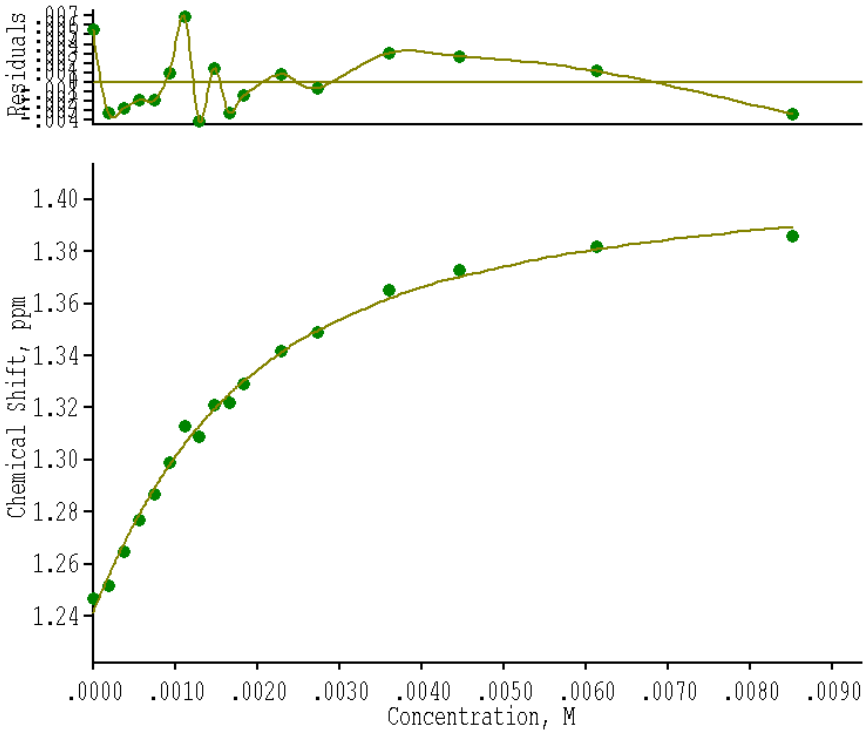

Figure S15. Data fitting of the titration of PMP with SCX4 in D_2O (293 K). Following PMP P-Me proton environment.

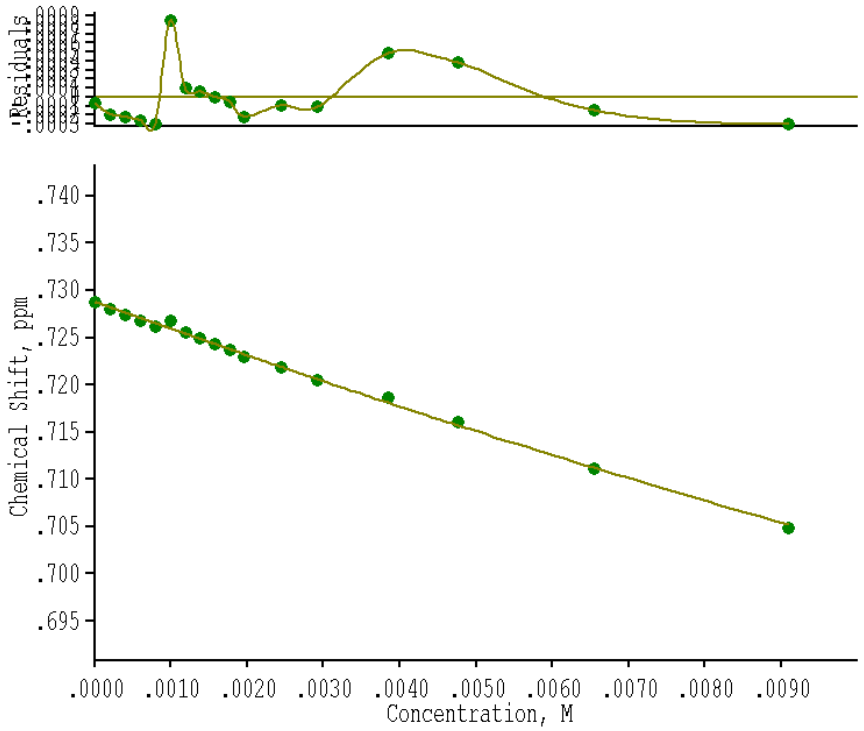

Figure S16. Data fitting of the titration of PMP with SCX4 in 0.25 M phosphate buffered D_2O (293 K). Following PMP ^{t}Bu proton environment.

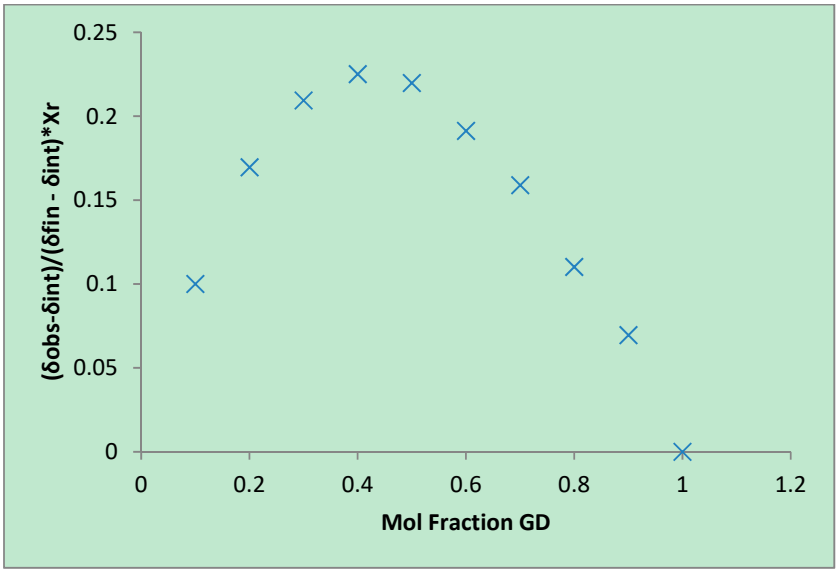

Figure S17. Job plot analysis of SCX4 and GD, following GD ^{t}Bu environment (D_2O, 293 K). Total concentration 0.01M.

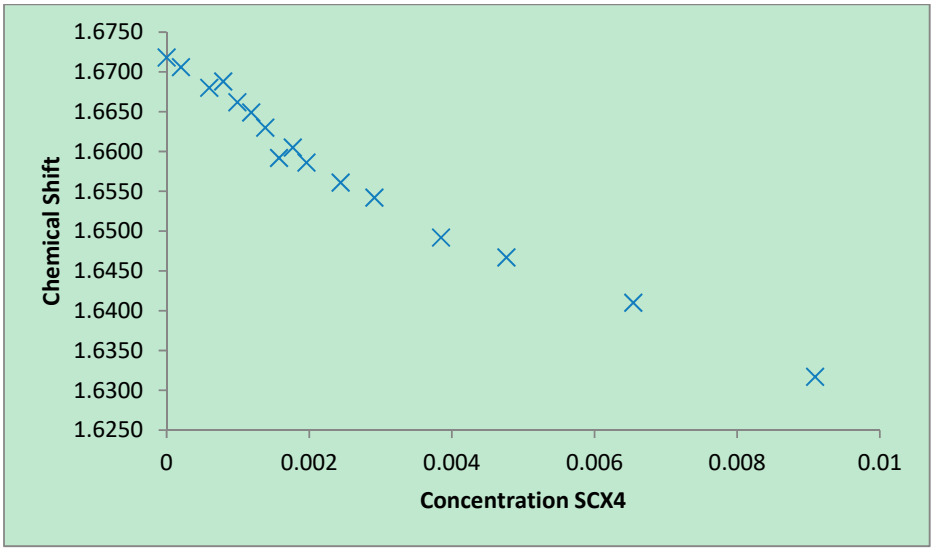

Figure S18. Titration plot of GD with SCX4 (0.25 M phosphate buffered D_2O, 293K). Following GD P-Me proton environment. Initial concentration of DEMP 0.01M.

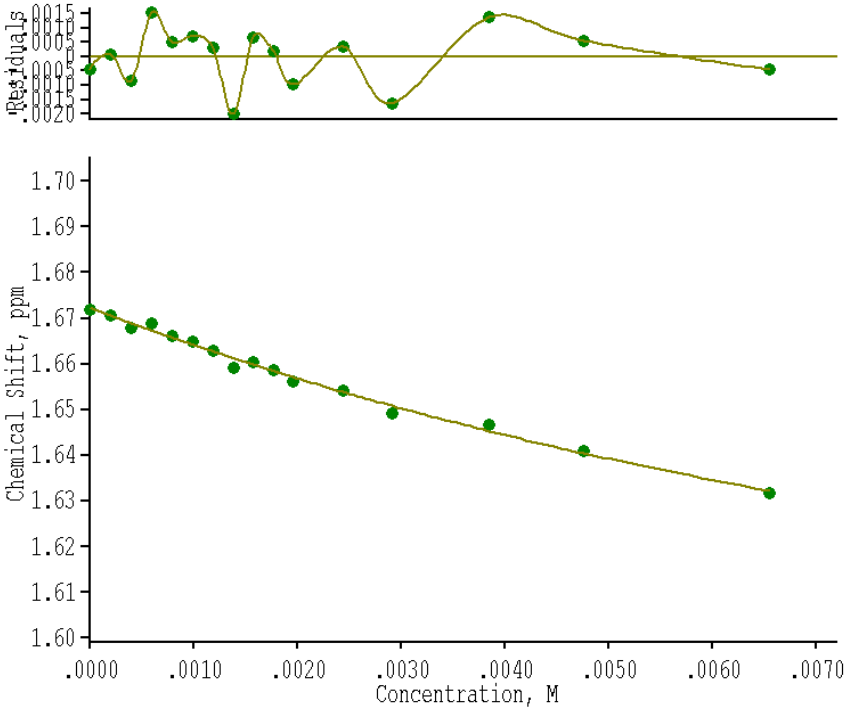

Figure S19. Data fitting of the titration of GD with SCX4 in 0.25 M phosphate buffered D_2O (293 K). Following GD P-Me proton environment.

NMR Job Plot and Titration Data – *p*-sulfonatocalix[6]arene (SCX6)

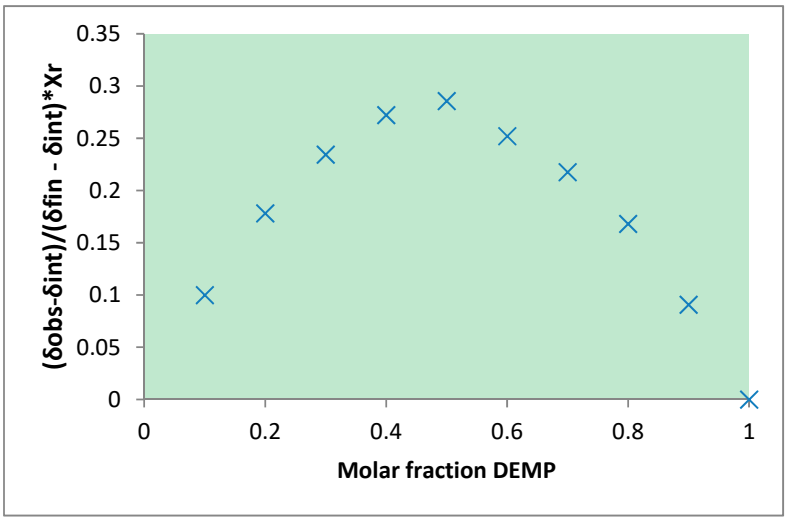

Figure S20. Job plot analysis of SCX6 and DEMP, following DEMP P-Me environment (D_2O, 293 K). Total concentration 0.01M.

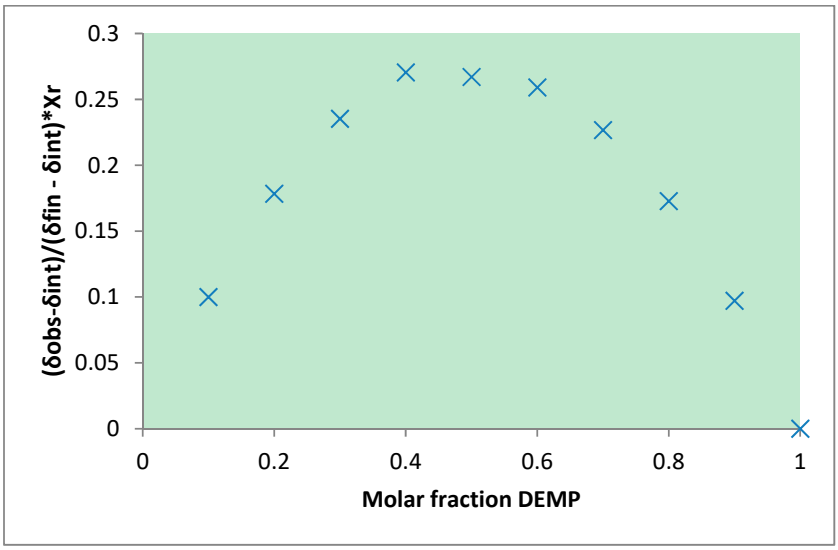

Figure S21. Job plot analysis of SCX6 and DEMP, following DEMP P-Me environment (0.25 M phosphate buffered D_2O, 293 K). Total concentration 0.01M.

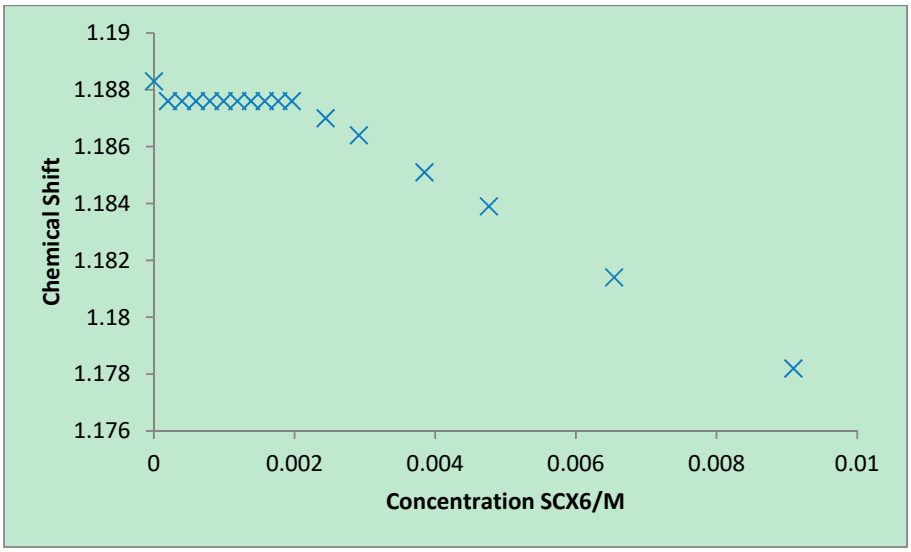

Figure S22. Titration plot of DEMP with SCX6 (D_2O, 293K). Following DEMP ethyl-CH_3 proton environment. Initial concentration of DEMP 0.01M.

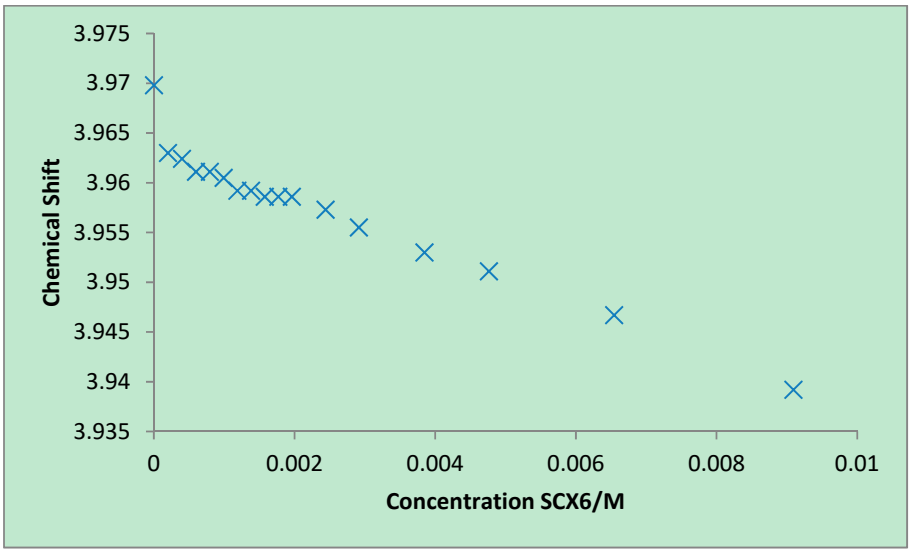

Figure S23. Titration plot of DEMP with SCX6 (0.25 M phosphate buffered D_2O, 293K). Following DEMP ethyl-CH_3 proton environment. Initial concentration of DEMP 0.01M.

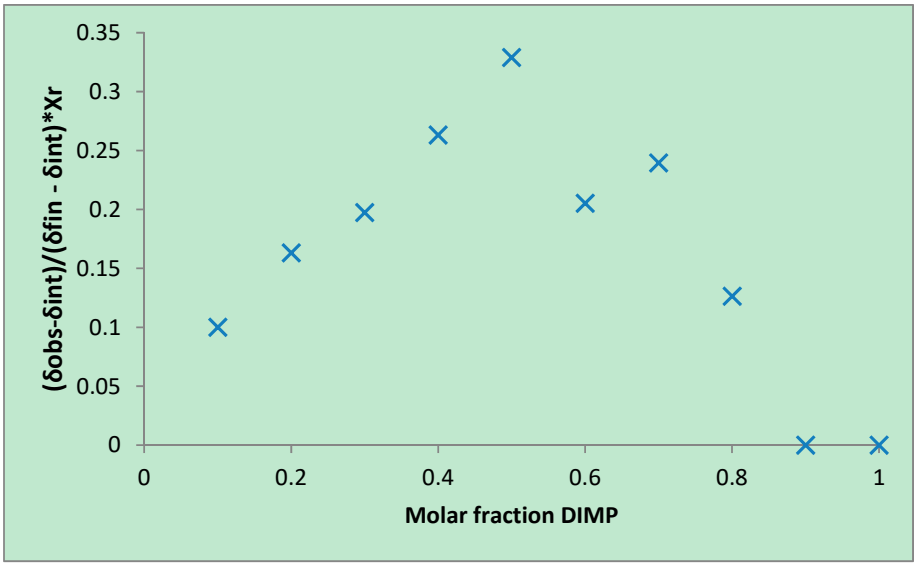

Figure S24. Job plot analysis of SCX6 and DIMP, following DIMP alkyl-CH_3 environment (D_2O, 293 K). Total concentration 0.01M.

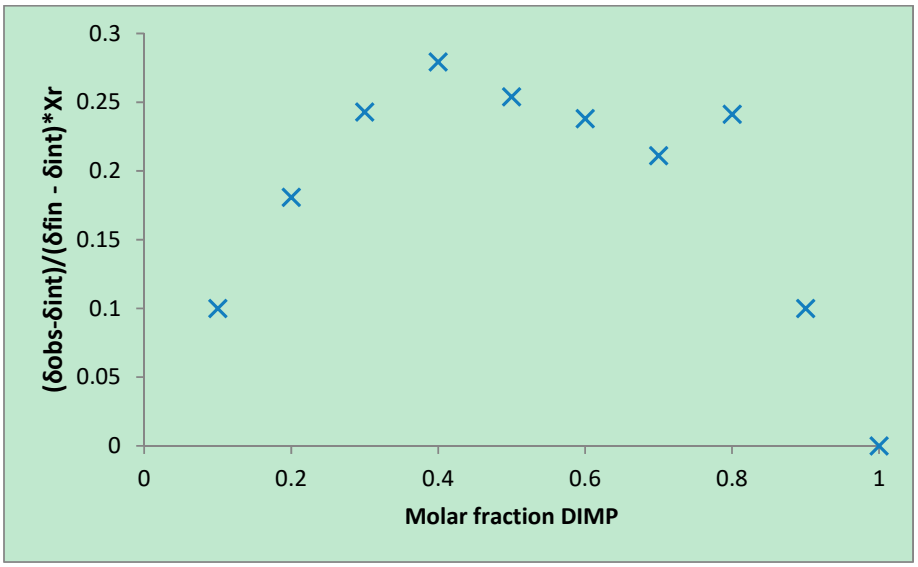

Figure S25. Job plot analysis of SCX6 and DIMP, following DIMP alkyl-CH_3 environment (0.25 M phosphate buffered D_2O, 293 K). Total concentration 0.01M.

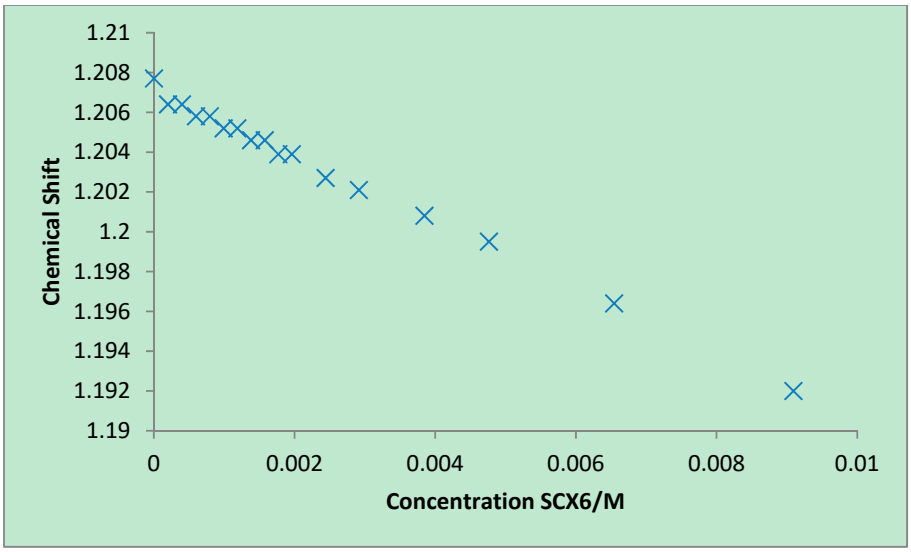

Figure S26. Titration plot of DIMP with SCX6 (D_2O, 293K). Following DIMP alkyl-CH_3 proton environment. Initial concentration of DIMP 0.01M.

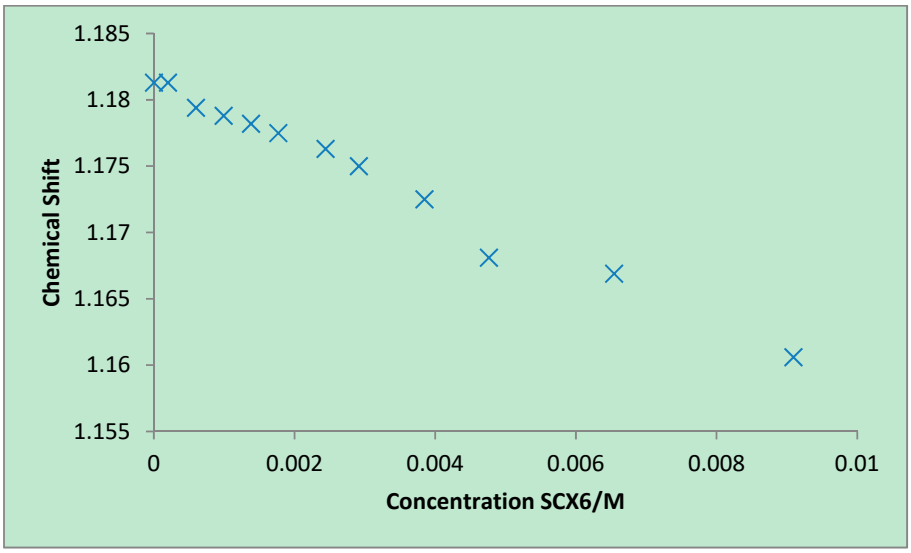

Figure S27. Titration plot of DIMP with SCX6 (0.25 M phosphate buffered D_2O, 293K). Following DIMP alkyl-CH_3 proton environment. Initial concentration of DIMP 0.01M.

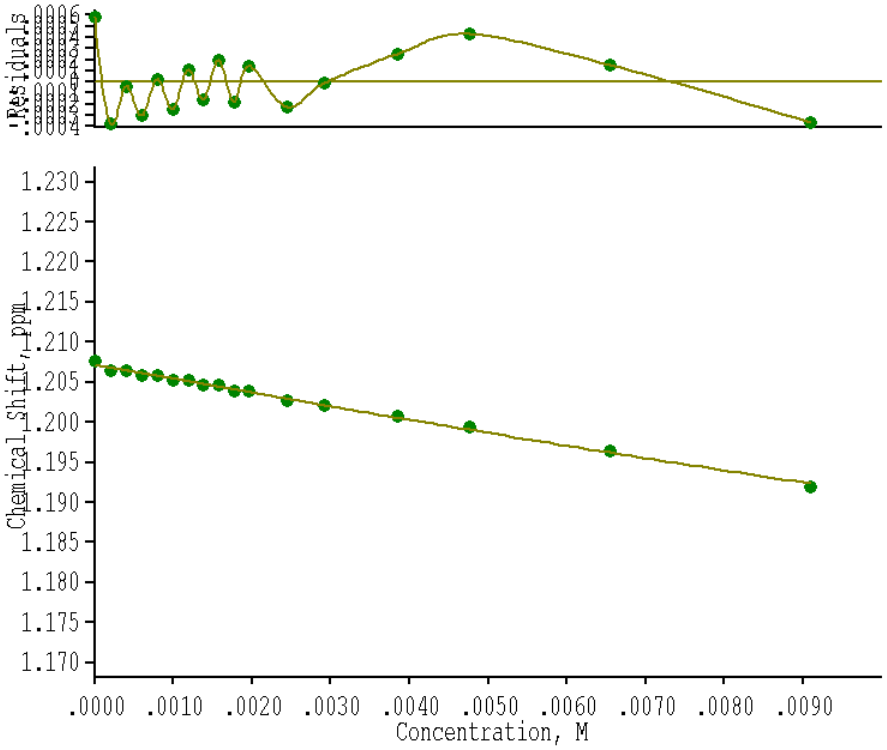

Figure S28. Data fitting of the titration of DIMP with SCX6 in D_2O (293 K). Following DIMP alkyl-CH_3 proton environment.

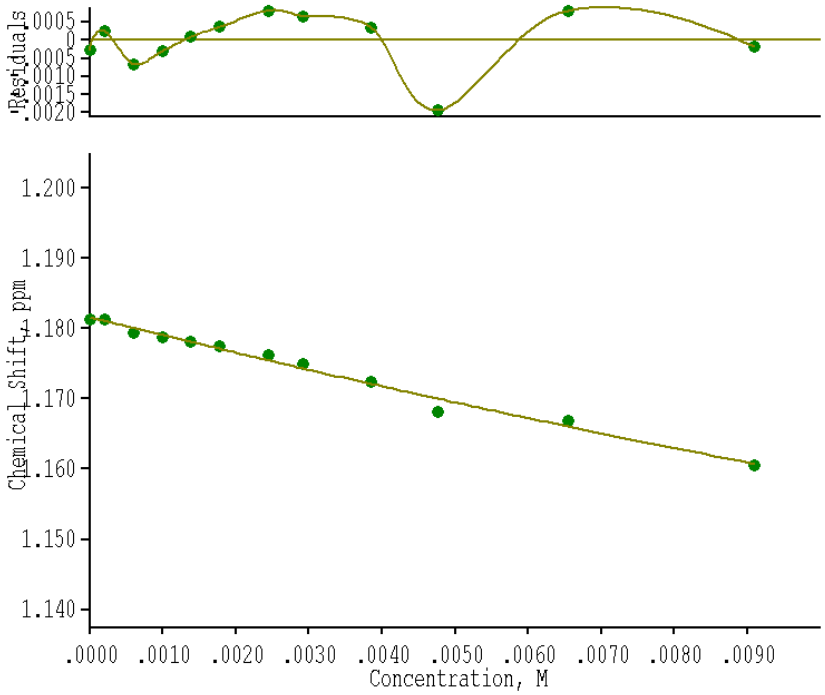

Figure S29. Data fitting of the titration of DIMP with SCX6 in 0.25 M phosphate buffered D_2O (293 K). Following DIMP alkyl-CH_3 proton environment.

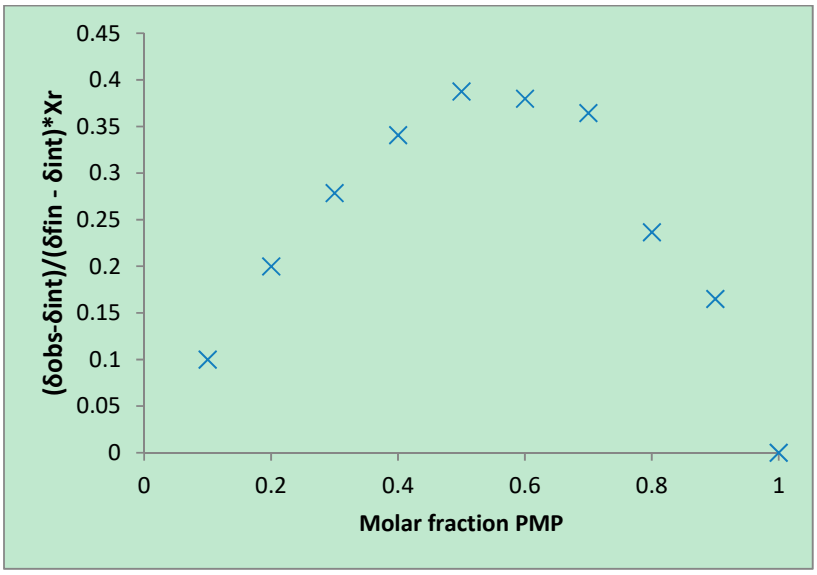

Figure S30. Job plot analysis of SCX6 and PMP, following PMP ^{t}Bu environment (D_2O, 293 K). Total concentration 0.01M

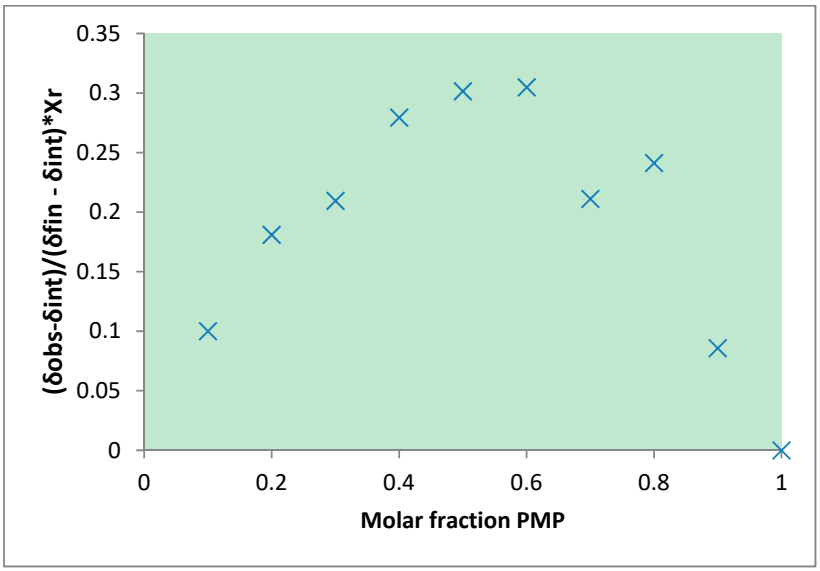

Figure S31. Job plot analysis of SCX6 and PMP, following PMP ^{t}Bu environment (0.25 M phosphate buffered D_2O, 293 K). Total concentration 0.01M.

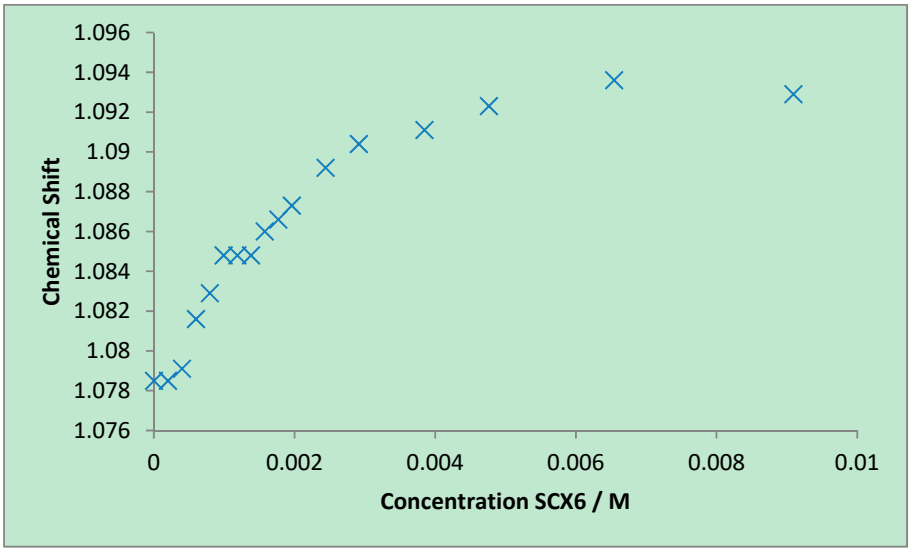

Figure S32. Titration plot of PMP with SCX6 (D_2O, 293K). Following PMP P-Me proton environment. Initial concentration of PMP 0.01M.

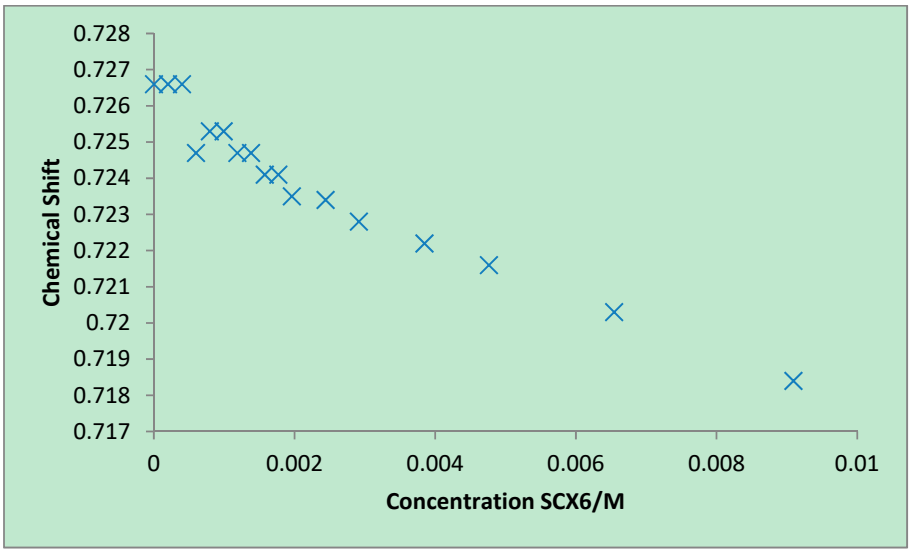

Figure S33. Titration plot of PMP with SCX6 (0.25 M phosphate buffered D_2O, 293K). Following PMP ^{t}Bu proton environment. Initial concentration of PMP 0.01M.

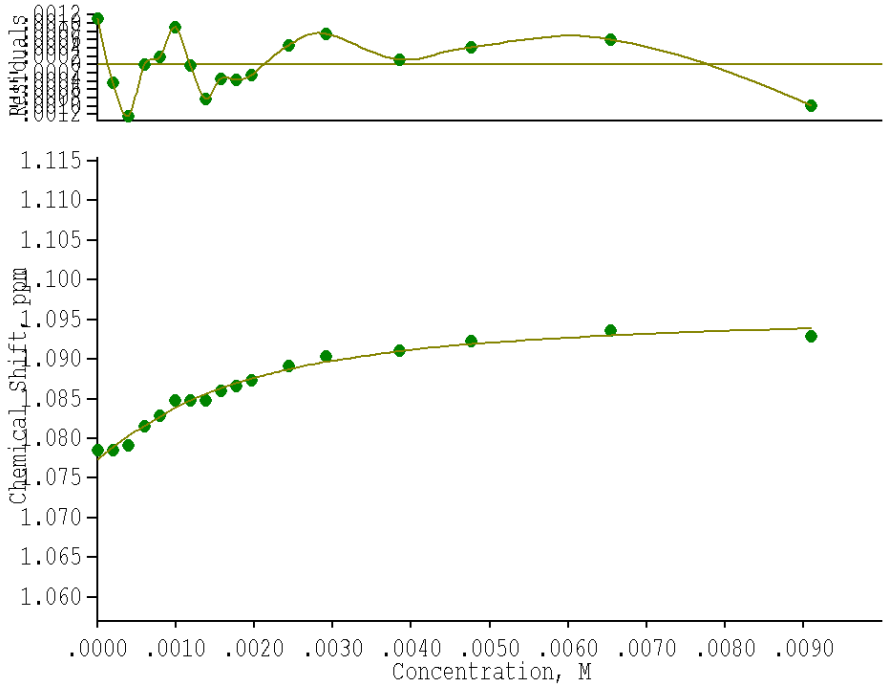

Figure S34. Data fitting of the titration of PMP with SCX6 in D_2O (293 K). Following PMP P-Me proton environment.

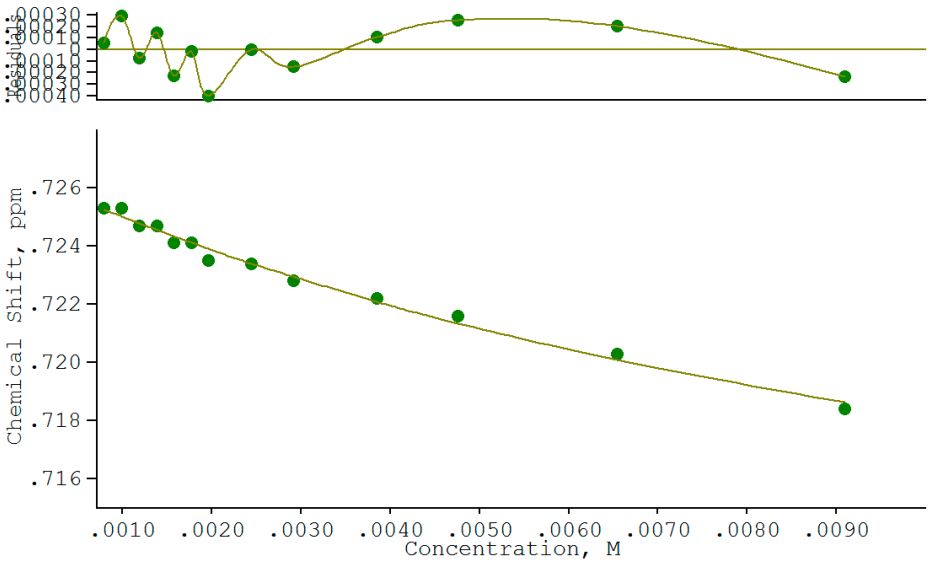

Figure S35. Data fitting of the titration of PMP with SCX6 in 0.25 M phosphate buffered D_2O (293 K). Following PMP ^{t}Bu proton environment.

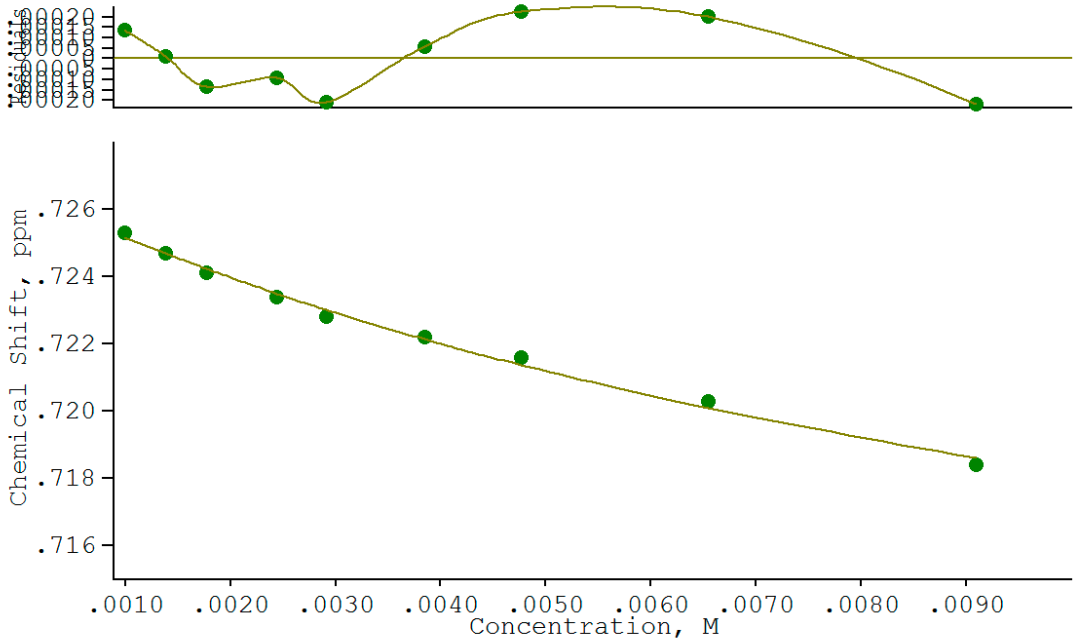

Figure S36. Data fitting of the titration of PMP, using selected data, with SCX6 in 0.25 M phosphate buffered D_2O (293 K). Following PMP ^{t}Bu proton environment.

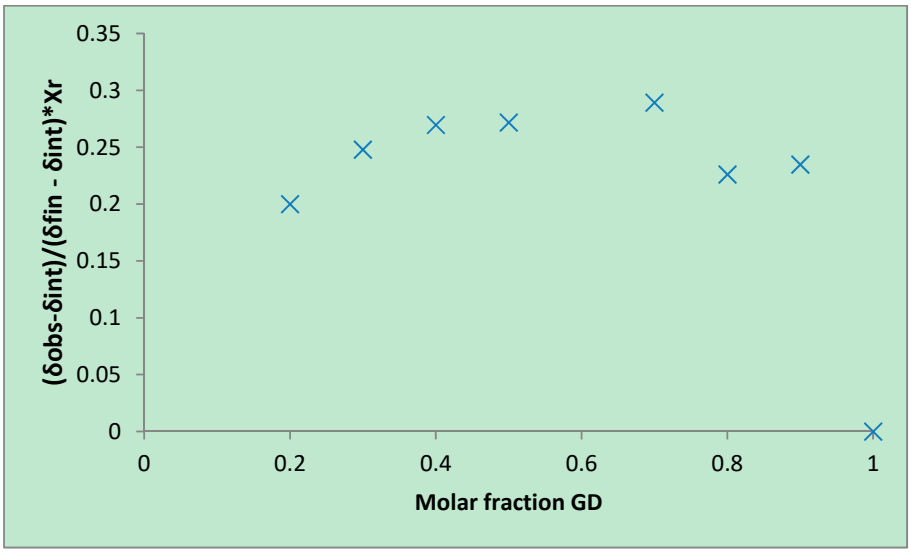

Figure S37. Job plot analysis of SCX6 and GD, following GD ^{t}Bu environment (0.25 M phosphate buffered D_2O, 293 K). Total concentration 0.01M.

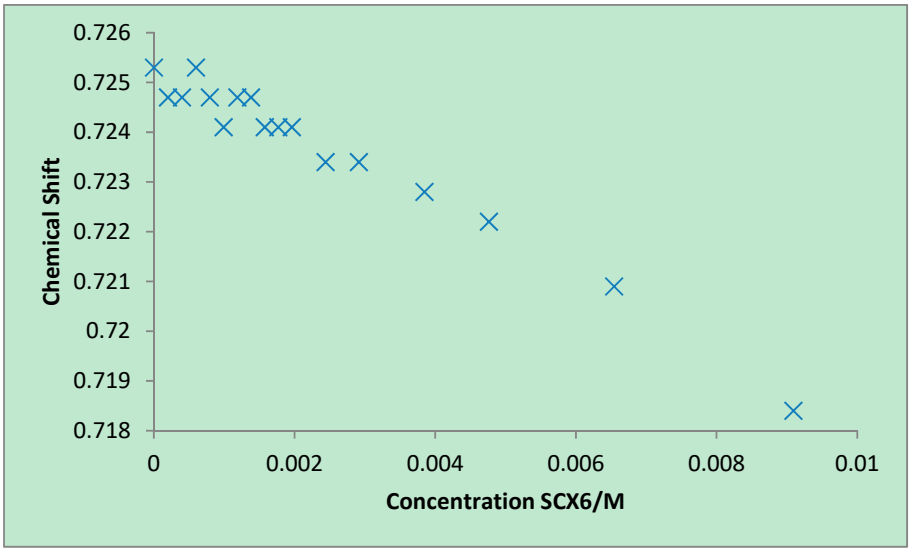

Figure S38. Job plot analysis of SCX6 and GD, following GD ^{t}Bu environment (0.25 M phosphate buffered D_2O, 293 K). Total concentration 0.01M.

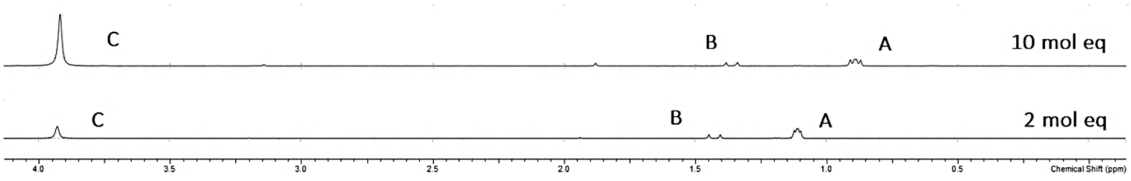

Figure S39. ^{1}H NMR spectra of DIMP in the presence of (bottom) 2 molar equivalents of SCX4 and (top) 10 molar equivalents of SCX4. Proton environment A is observed to shift upfield from 1.1398 ppm to 0.8714 ppm ($\Delta\delta$ = -0.2684 ppm)

References

1. Hynes, M.J., EQNMR: a computer program for the calculation of stability constants from nuclear magnetic resonance chemical shift data, **1993**, 311.