Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Biasing hydrogen bond donating host systems towards chemical warfare agent recognition

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Experimental

General Experimental Methods All reactions were performed under slight positive pressure of nitrogen using oven dried glassware. NMR spectra were determined on a Bruker AVII 400 and a Bruker AVII 500 spectrometer with the chemical shifts reported in parts per million (ppm), calibrated to the centre of the solvent peak set (s = singlet, d = doublet, t = triplet, q = quartet, br = broad) for 1H and 13C spectra. Chemicals shifts (δ) are reported in ppm relative to TMS for ^{1}H or ^{13}C NMR spectra and to $CFCl_3$ for ^{19}F NMR spectra. All solvents and starting materials were purchased from chemical stores where available. Low resolution mass spectra were recorded on a Waters Acquity UHPLC-MS system. High resolution mass spectra were recorded on a Bruker Maxis ESI-TOF system by the mass spectrometry service at the University of Southampton. Melting points were recorded in open capillaries on a Gallenkamp melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR), and reported in wavenumbers (cm^{-1}).

*Compound **1*** 1-Isocyanato-4-(trifluoromethyl)benzene (0.43 mL, 3.00 mM) was added to a stirring solution of **(**3-aminophenyl)boronic acid (0.41 g, 3.00 mM) in anhydrous dimethylformamide (5 mL) under an inert atmosphere. The mixture was allowed to stir overnight and then added to water (100 mL) and sonicated for 15 mins. The crude product was then isolated as a cream solid, dissolved in ethyl acetate (15 mL) and hexane added until a white precipitate has formed, which was removed by filtration and washed with a 1:1 hexane:ethyl acetate mixture (10 mL). Yield: 36 % (0.35 g, 1.06 mM); Decomposition Point: 249 ºC; IR (film): ν = broad 3330, 3300 (urea NH stretch), 1640 (CO stretch), 1320 (BO stretch); HRMS (ESI^-): m/z: act: 323.0829 $[M-H]^-$ cal: 323.0823 $[M-H]^-$; ^{1}H NMR (500 MHz, MeCN-d_3): δ: 6.00 (s, 2H, OH), 7.33 (t, J = 7.73 Hz, 1H), 7.38 (br s, 1H, NH), 7.45 (dt, J_1 = 0.80 Hz, J_2 = 7.12 Hz, 1H),

7.66-7.59 (m, 6H), 7.76 (d, J = 1.25 Hz, 1H); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.26 (s, 3F); ^{13}C NMR (100 MHz, MeCN-d_3): δ: 118.9 (CH), 121.9 (CH), 123.6 (C), 124.4 (C, q, J = 32.0 Hz), 125.5 (CH), 127.0 (CH, q, J = 5.0 Hz), 129.1 (CH), 129.4 (CH), 129.8 (C), 139.8 (C), 144.8 (C), 153.8 (CO) (a drop of DMSO was added to aid the solubility of the sample).

*Compound **2*** 1-Isocyanato-4-(trifluoromethyl)benzene (0.26 mL, 1.82 mM) was added to a stirring solution of **(**2-aminophenyl)boronic acid (0.25 g, 1.82 mM) in anhydrous dimethylformamide (5 mL) under an inert atmosphere. The mixture was allowed to stir overnight and then added to water (100 mL) and sonicated for 15 mins. The crude product was then isolated as a cream solid, and heated at 70 ºC in ethyl acetate (15 mL) for 2 hrs. The white solid was then removed and washed with ethyl acetate (5 mL). Yield: 55 % (0.31 g, 1.00 mM); Melting Point: > 250 ºC; IR (film): ν = 3370 (NH stretch), 1660 (CO stretch), 1320 (BO stretch); HRMS (ESI$^-$): m/z: act: 307.0857 [M-H]$^-$ cal: 307.0863 [M-H]$^-$; ^{1}H NMR (500 MHz, MeCN-d_3): δ: 6.64 (br s, 1H, OH), 7.07 (d, J = 8.13 Hz, 1H), 7.13 (td, J_1 = 0.86 Hz, J_2 = 7.42 Hz, 1H), 7.42 (d, J = 8.13 Hz, 2H), 7.53 (ddd, J_1 = 1.49 Hz, J_2 = 7.19 Hz, J_3 = 8.28 Hz, 1H), 7.76 (d, J = 8.25 Hz, 2H), 7.83 (d, J = 6.87 Hz, 1H), 8.50 (br s, 1H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.80 (s, 3F); ^{13}C NMR (125 MHz, MeCN-d_3): δ: 115.22 (CH), 122.6 (CH), 124.4 (C), 126.6 (C), 126.9 (CH, q, J = 3.0 Hz), 129.5 (C, d, J = 10 Hz), 130.9 (CH), 133.3 (CH), 134.2 (CH), 144.0 (C), 146.6 (C), 155.0 (CO).

*Compound **3*** A 50 % solution of TBA HF_2 in acetonitrile (1.64 mL, 2.54 mM) was added to a stirring solution of compound **1** (0.25 g, 0.77 mM) in methanol (4 mL). The mixture was allowed to stir overnight and then taken to dryness giving a clear oil which was dissolved in methanol (1 mL) and added to water (20 mL) this gave the crude product which was isolated as a white solid. The pure product was recrystallized from ethyl acetate (9 mL) giving a white solid. Yield: 68 %

(0.31 g, 0.53 mM); Melting Point: 134 ºC; IR (film): ν = 3370 (NH stretch), 1660 (CO stretch); HRMS (ESI^-): m/z: act: 347.0799 $[M]^-$ cal: 347.0798 $[M]^-$; ^1H NMR (500 MHz, MeCN-d_3): δ: 0.93 (t, J = 7.39 Hz, 12H, CH_3), 1.27-1.35 (m, 8H, CH_2), 1.51-1.57 (m, 8H, CH_2), 3.00-3.03 (m, 8H, CH_2), 7.12-7.18 (m, 2H), 7.32 (d, J_1 = 1.60 Hz, 1H), 7.55-7.58 (m, 3H), 7.65 (br s, 1H, NH), 7.70 (d, J_1 = 8.48 Hz, 2H), 8.06 (br s, 1H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.10 (s, 3F), -139.68 (s, 3F); ^{13}C NMR (100 MHz, MeCN-d_3): δ: 13.9 (CH_3), 20.4 (CH_2), 24.3 (CH_2), 59.3 (CH_2), 117.7 (CH), 119.0 (CH), 123.5 (CH), 123.7 (C), 124.5 (C), 127.0 (CH, q, J = 4.0 Hz), 127.2 (CH), 127.4 (C), 128.2 (CH), 138.7 (C), 145.0 (C), 153.6 (CO).

*Compound **4*** A 50 % solution of TBA HF_2 in acetonitrile (1.64 mL, 2.54 mM) was added to a stirring solution of compound **2** (0.25 g, 0.82 mM) in methanol (4 mL). The mixture was allowed to stir overnight and then added to water (100 mL) this gave the crude product which was isolated as a white solid. The pure product was recrystallized from ethyl acetate (14 mL) giving a white solid. Yield: 65 % (0.32 g, 0.53 mM); Melting Point: 169 ºC; IR (film): ν = 3370 (NH stretch), 1680 (CO stretch); HRMS (ESI^-): m/z: act: 347.0800 $[M]^-$ cal: 347.0798 $[M]^-$; ^1H NMR (500 MHz, MeCN-d_3): δ: 0.97 (t, J = 7.39 Hz, 12H, CH_3), 1.31-1.38 (m, 8H, CH_2), 1.54-1.61 (m, 8H, CH_2), 3.03-3.06 (m, 8H, CH_2), 6.91 (t, J = 7.23 Hz, 1H), 7.31 (t, J = 7.68 Hz, 1H), 7.45 (dd, J_1 = 1.40 Hz, J_2 = 7.20 Hz, 1H), 7.59 (d, J = 8.54 Hz, 2H), 7.71 (d, J = 8.48 Hz, 2H), 7.95 (d, J – 8.12 Hz, 1H), 8.15 (br s, 1H, NH), 8.17 (br s, 1H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.33 (s, 3F), -138.86 (s, 3F); ^{13}C NMR (100 MHz, MeCN-d_3): δ: 13.9 (CH_3), 20.4 (CH_2), 24.4 (CH_2), 59.4 (CH_2), 119.1 (CH), 119.8 (CH), 122.6 (CH), 123.5 (C, d, J = 30 Hz), 124.6 (C), 126.9 (CH, q, J = 5.0 Hz), 127.1 (CH), 127.3 (C), 133.4 (CH, q, J = 3.0 Hz), 142.8 (C), 145.3 (C), 153.8 (CO).

*Compound **5*** 1-Isothiocyanato-4-(trifluoromethyl)benzene (0.37 g, 1.82 mM) was added to a stirring solution of **(**3-aminophenyl)boronic acid (0.25 g, 1.82 mM) in anhydrous dimethylformamide (3 mL) under an inert atmosphere. The mixture was allowed to stir overnight and then added to water (100 mL) and sonicated for 15 mins. The crude product was then isolated as a cream solid, dissolved in an ethyl acetate (2 mL)/methanol (0.2 mL) mixture and precipitated out with the addition of hexane as a cream solid. The white solid was then removed and washed with hexane (5 mL). Yield: 74 % (0.59 g, 1.35 mM); Melting Point: 163 ºC; IR (film): ν = broad 3330, 3210 (urea NH stretch), 1530 (CS stretch), 1320 (BO stretch); HRMS (ESI⁻): m/z: act: 339.0598 $[M-H]^-$ cal: 339.0594 $[M-H]^-$; ^{1}H NMR (500 MHz, MeCN-d_3): δ: 6.14 (s, 2H, OH), 7.41 (t, J = 7.50 Hz, 1H), 7.49 (d, J = 7.91 Hz, 1H), 7.63-7.67 (m, 5H), 7.72 (s, 1H), 8.46 (br s, 1H, NH), 8.53 (br s, 1H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.64 (s, 3F); ^{13}C NMR (100 MHz, MeCN-d_3): δ: 124.2 (C), 124.5 (CH), 126.2 (C, d, J = 30 Hz), 126.5 (CH, q, J = 4 Hz), 126.9 (C), 127.9 (CH), 128.9 (CH), 131.4 (CH), 132.4 (CH), 139.3 (C), 144.4 (C), 181.5 (CS) (a drop of DMSO was added to aid the solubility of the sample).

*Compound **6*** 1-Isothiocyanato-4-(trifluoromethyl)benzene (0.37 g, 1.82 mM) was added to a stirring solution of **(**2-aminophenyl)boronic acid (0.25 g, 1.82 mM) in anhydrous dimethylformamide (3 mL) under an inert atmosphere. The mixture was allowed to stir overnight and then added to water (100 mL) and sonicated for 15 mins. The crude product was then isolated as a cream solid, dissolved in ethyl acetate (2 mL) and precipitated out with the addition of hexane as a cream solid. The white solid was then removed and washed with hexane (5 mL). Yield: 95 % (0.44 g, 1.73 mM); Melting Point: > 250 ºC; IR (film): ν = broad 3190 (urea NH stretch), 1640 (CS stretch), 1320 (BO stretch); HRMS (ESI⁻): m/z: act: 321.0490 $[M-H]^-$ cal: 321.0489 $[M-H]^-$; ^{1}H NMR (500 MHz, MeCN-d_3): δ: 7.01 (s, 1H, OH), 7.23-7.27 (m, 2H), 7.39

(d, J = 7.80 Hz, 2H), 7.61 (t, J = 8.40 Hz, 1H), 7.77 (d, J = 8.18 Hz, 2H), 7.89 (d, J = 7.54 Hz, 1H), 10.23 (br s, 1H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -60.61 (s, 3F); ^{13}C NMR (125 MHz, DMSO-d_6): δ: 115.8 (CH), 116.5 (C), 123.2 (CH), 123.8 (C), 126.0 (CH), 127.6 (C, q, J = 33 Hz), 130.5 (CH), 133.1 (CH), 133.6 (CH), 146.3 (C), 146.8 (C), 180.0 (CS).

*Compound **7*** A 50 % solution of TBA HF_2 in acetonitrile (1.64 mL, 2.54 mM) was added to a stirring solution of compound **5** (0.25 g, 0.74 mM) in methanol (10 mL). The mixture was allowed to stir for three days and then added to water (100 mL) this gave the crude product which was isolated cream semi-solid, which was dissolved in methanol (10 mL) and taken to dryness to give a cream solid. Yield: 81 % (0.37 g, 0.60 mM); Melting Point: 161 ºC; IR (film): ν = 3330 (NH stretch), 1540 (CS stretch); HRMS (ESI$^-$): m/z: act: 363.0572 [M]$^-$ cal: 363.0570 [M]$^-$; ^{1}H NMR (500 MHz, MeCN-d_3): δ: 0.95 (t, J = 7.33 Hz, 12H, CH_3), 1.30-1.37 (m, 8H, CH_2), 1.54-1.61 (m, 8H, CH_2), 3.04-3.07 (m, 8H, CH_2), 7.18-7.24 (m, 2H), 7.35-7.38 (m, 2H), 7.61 (d, J = 8.48 Hz, 2H), 7.73 (d, J = 8.48 Hz, 2H), 8.58 (br s, 2H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.52 (s, 3F), -141.65 (s, 3F); ^{13}C NMR (125 MHz, MeCN-d_3): δ: 13.9 (CH_3), 20.4 (CH_2), 24.4 (CH_2), 59.4 (CH_2), 122.04 (C), 123.5 (CH), 124.5 (C), 125.3 (CH), 126.4 (CH, q, J = 4.0 Hz), 126.7 (C, q, J = 20 Hz), 128.6 (CH), 129.2 (CH), 131.1 (CH), 137.1 (C), 144.3 (C), 181.2 (CS).

*Compound **8*** A 50 % solution of TBA HF_2 in acetonitrile (1.64 mL, 2.54 mM) was added to a stirring solution of compound **6** (0.25 g, 0.78 mM) in methanol (10 mL). The mixture was allowed to stir overnight and then added to water (100 mL) this gave the crude product which was isolated as a white solid. The pure product was recrystallized from ethyl acetate giving a white solid. Yield: 77 % (0.35 g, 0.60 mM); Melting Point: 175 ºC; IR (film): ν = 3230 (NH stretch), 1520 (CS stretch); HRMS (ESI$^-$): m/z: act: 343.0513 [M]$^-$ cal: 343.0508 [M]$^-$; ^{1}H NMR

(500 MHz, MeCN-d_3): δ: 0.95 (t, J = 7.33 Hz, 12H, CH_3), 1.30-1.37 (m, 8H, CH_2), 1.54-1.61 (m, 8H, CH_2), 3.04-3.07 (m, 8H, CH_2), 7.18-7.24 (m, 2H), 7.35-7.38 (m, 2H), 7.61 (d, J = 8.48 Hz, 2H), 7.73 (d, J = 8.48 Hz, 2H), 8.58 (br s, 2H, NH); ^{19}F NMR (500 MHz, MeCN-d_3): δ: -62.34 (s, 3F), -135.95 (s, 3F); ^{13}C NMR (125 MHz, DMSO-d_6): δ: 14.0 (CH_3), 20.2 (CH_2), 23.5 (CH_2), 58.0 (CH_2), 113.7 (CH), 121.4 (CH), 124.2 (C), 124.6 (CH), 125.7 (C, q, J = 31.25 Hz), 126.3 (C), 127.2 (CH), 130.6 (CH), 131.0 (CH), 141.5 (C), 150.2 (C), 177.0 (CS).

Characterization NMR

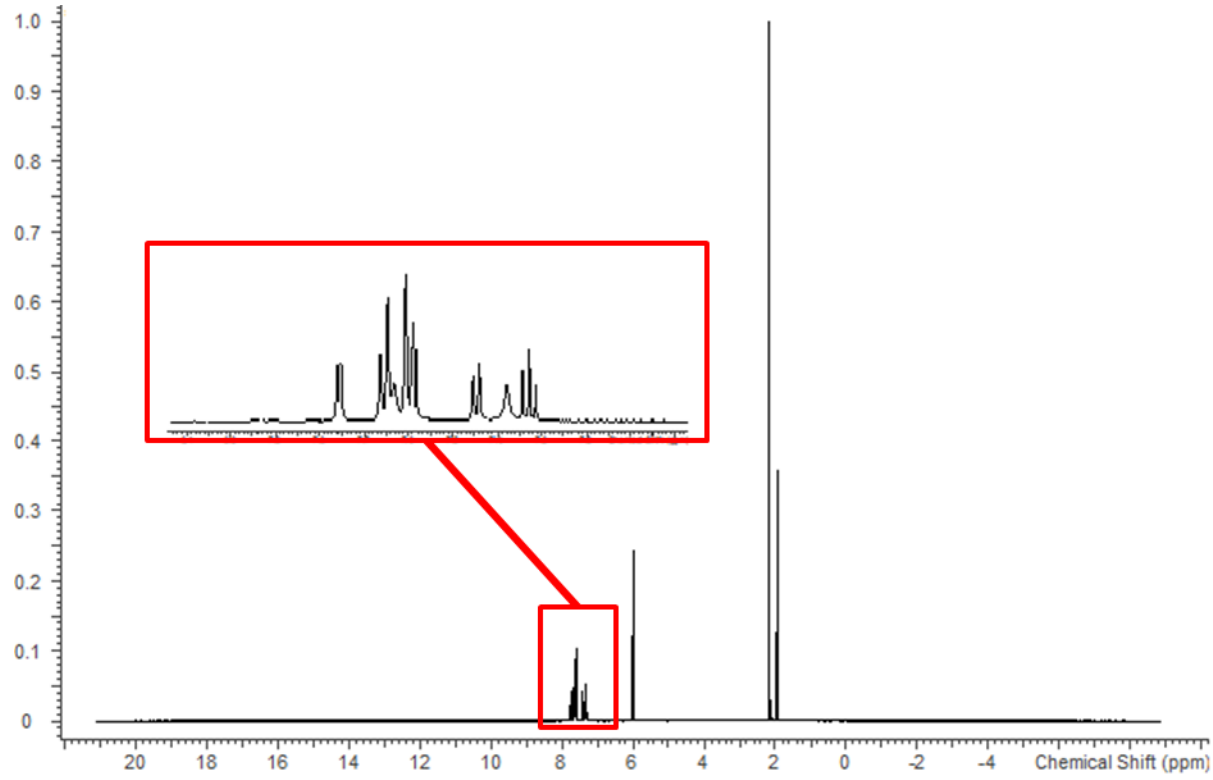

Figure S1. ^{1}H NMR of compound **1** in CD_3CN.

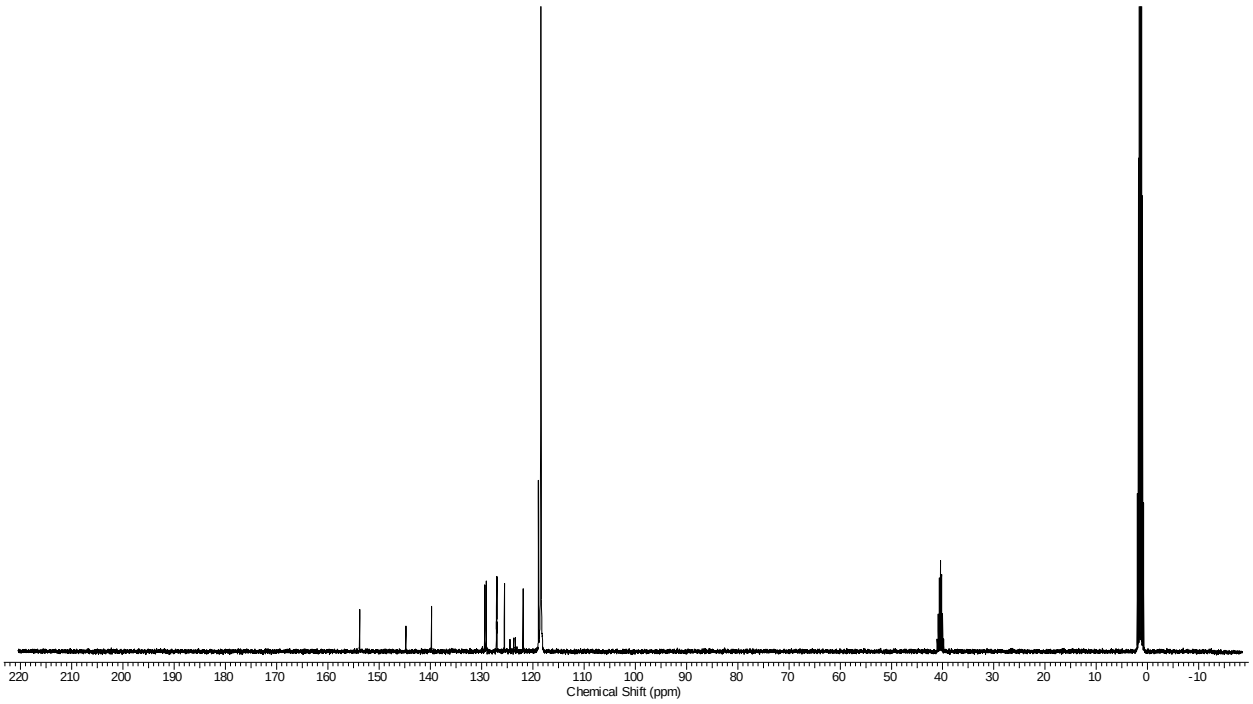

Figure S2. ^{13}C NMR of compound **1** in CD_3CN/DMSO-d_6.

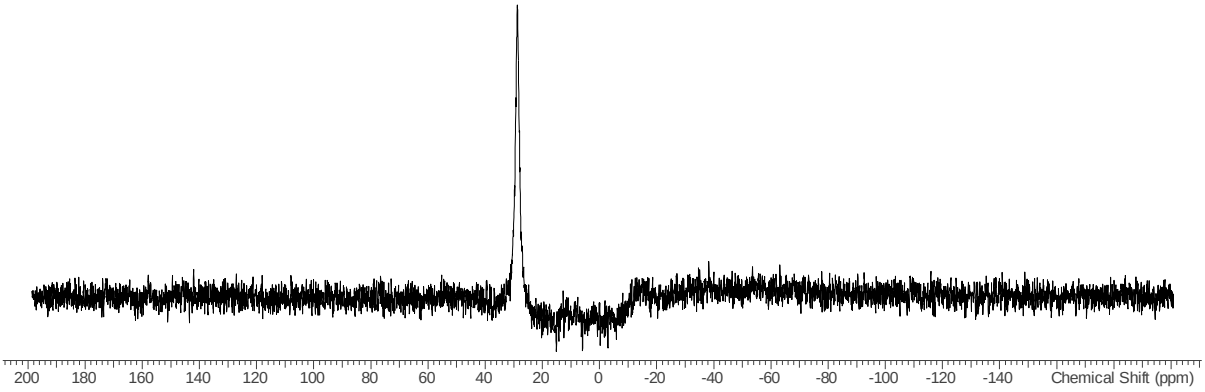

Figure S3. ^{11}B NMR of compound **1** in CD_3CN– the resonance corresponding to the boron silicate glass has been subtracted.

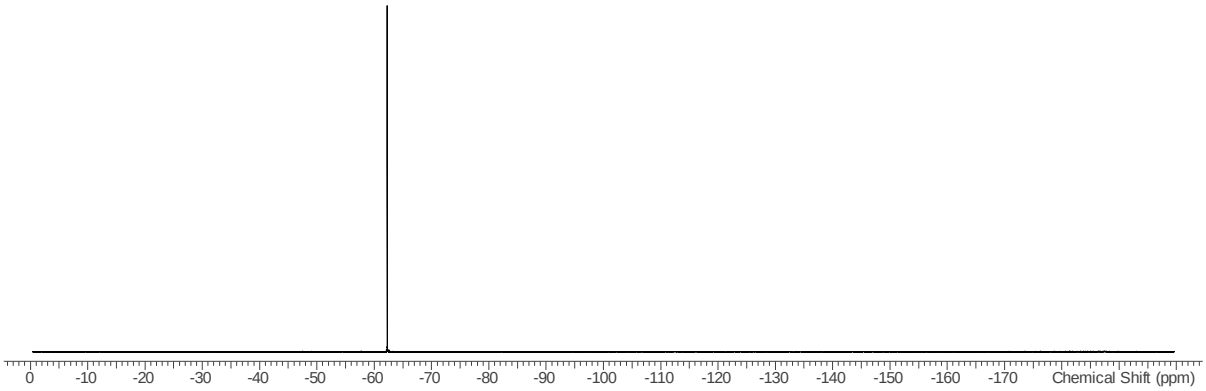

Figure S4. ^{19}F NMR of compound **1** in CD_3CN.

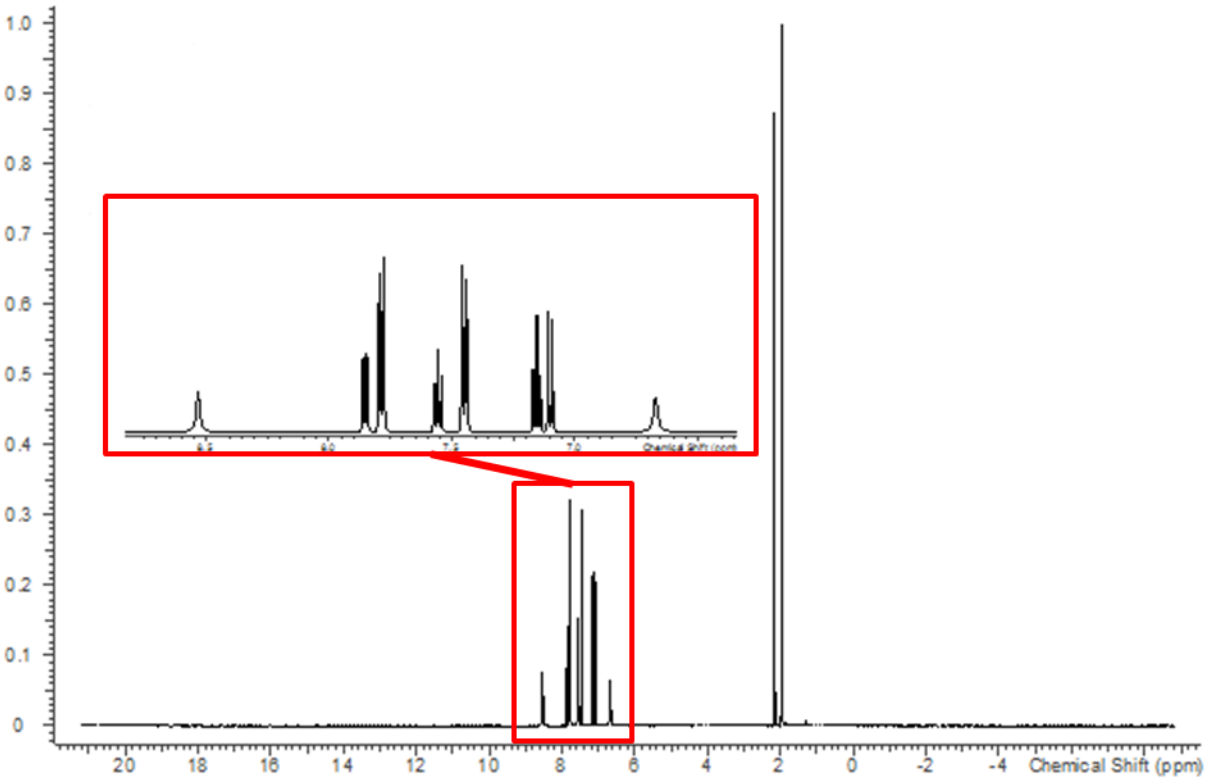

Figure S5. ^{1}H NMR of compound **2** in CD_3CN.

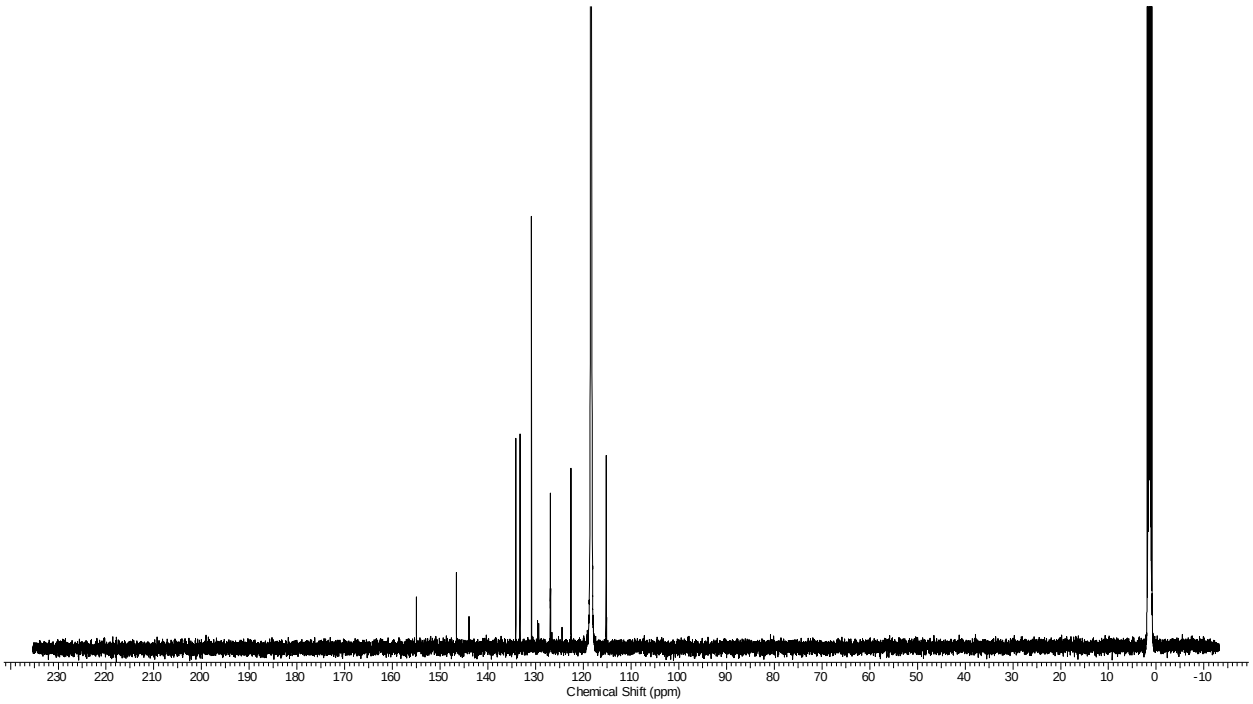

Figure S6. ^{13}C NMR of compound **2** in CD_3CN.

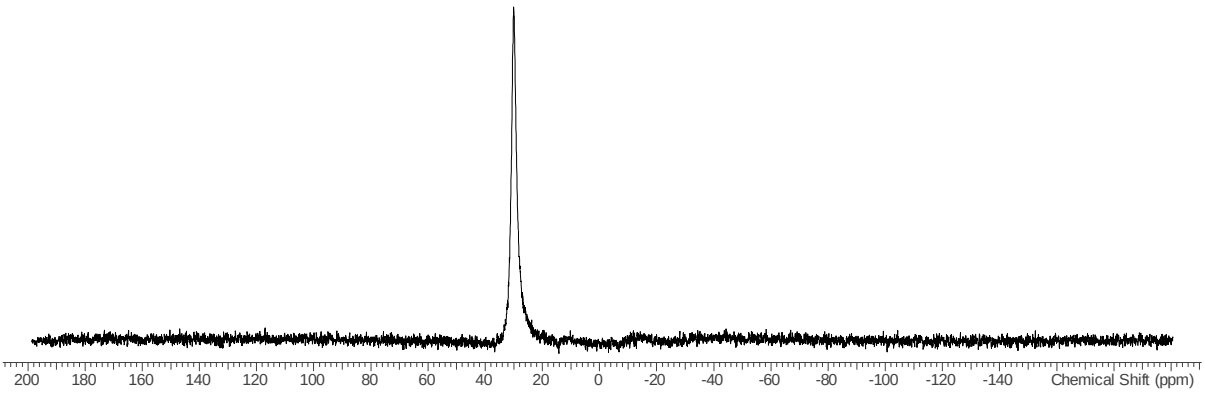

Figure S7. ^{11}B NMR of compound **2** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

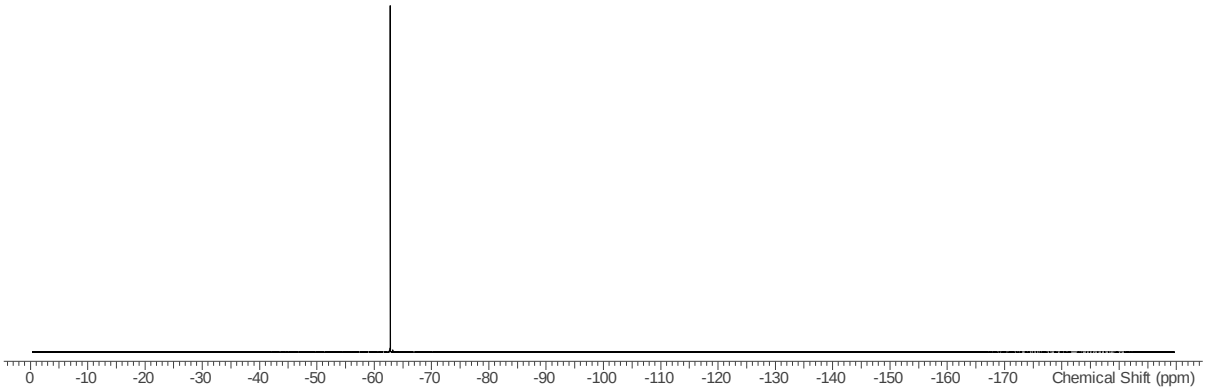

Figure S8. ^{19}F NMR of compound **2** in CD_3CN.

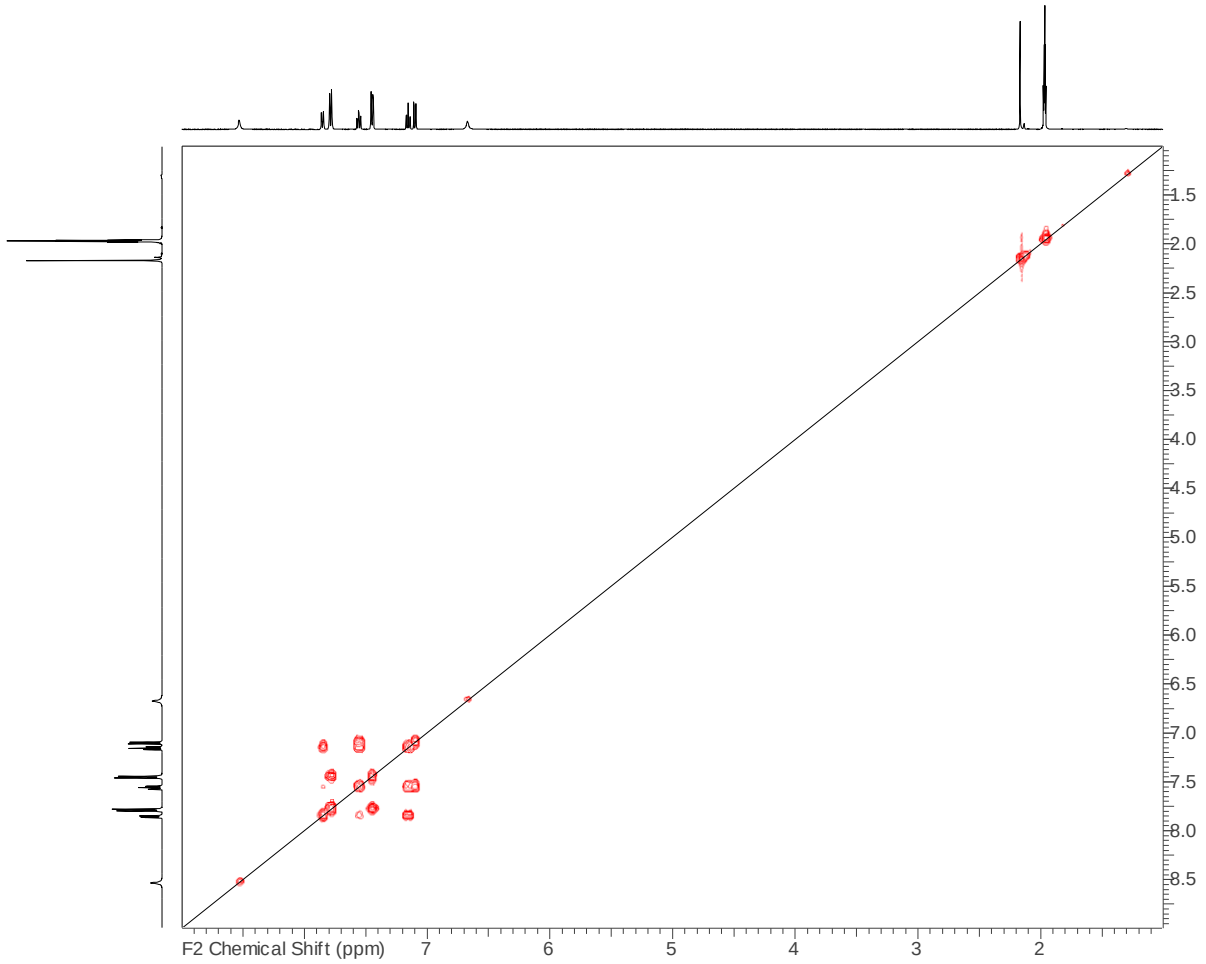

Figure S9.COSY NMR of compound **2** in CD_3CN.

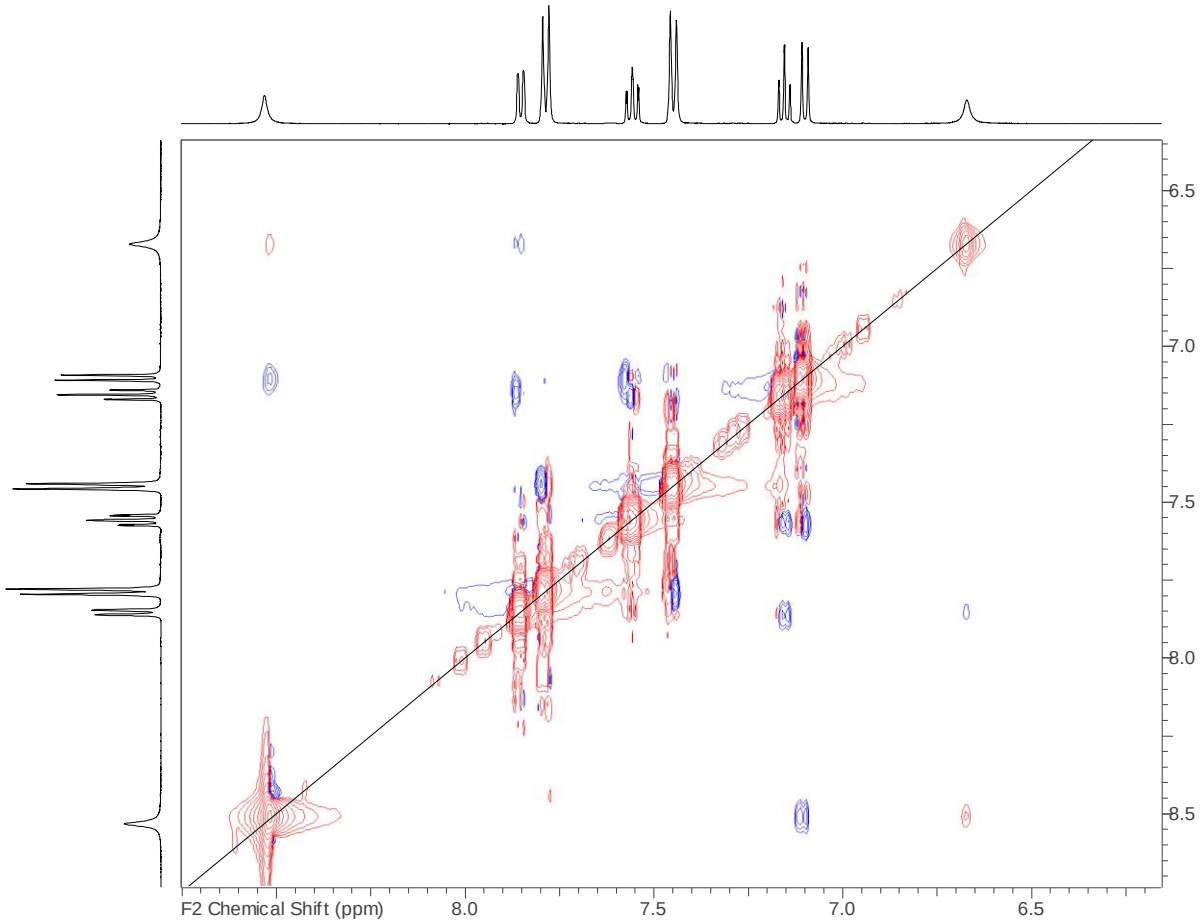

Figure S10. ROESY NMR of compound **2** in CD_3CN.

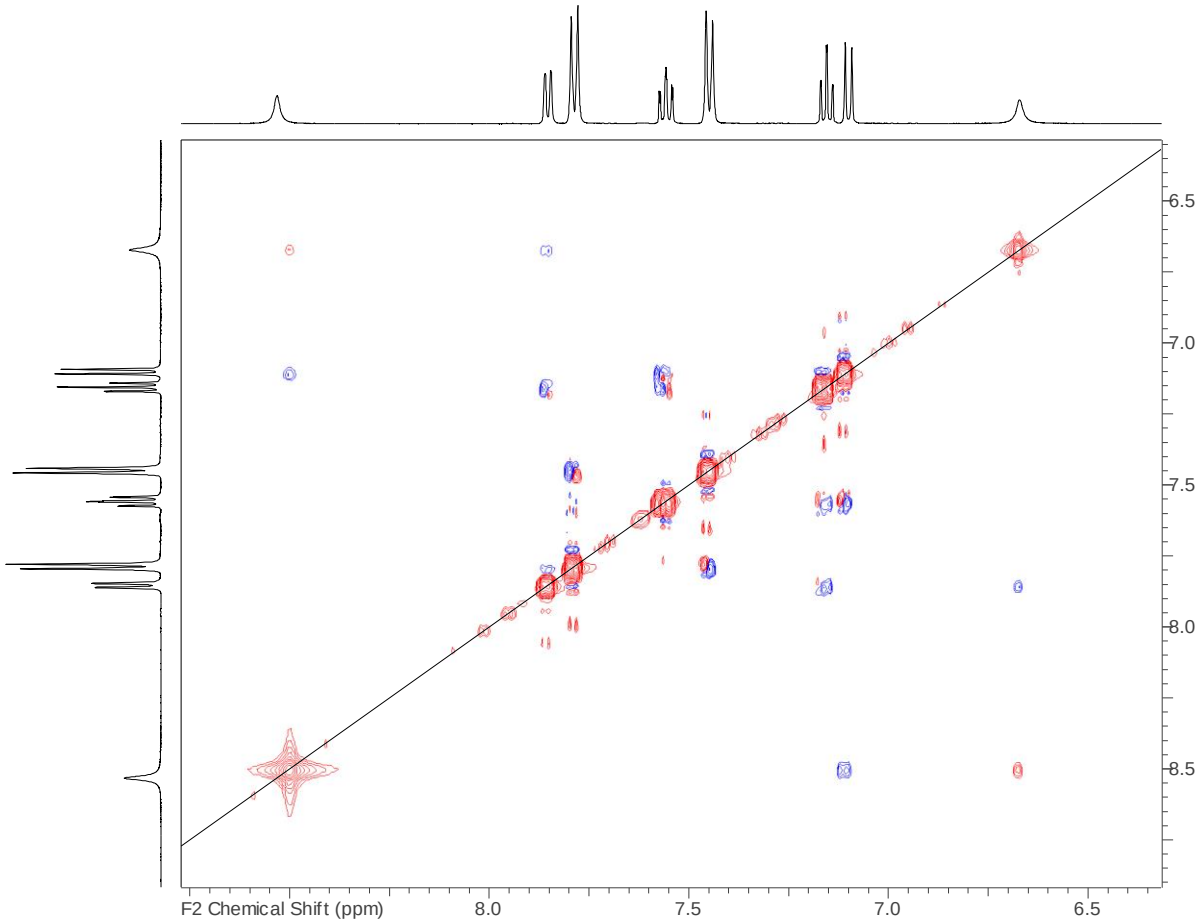

Figure S11. NOESY NMR of compound **2** in CD_3CN.

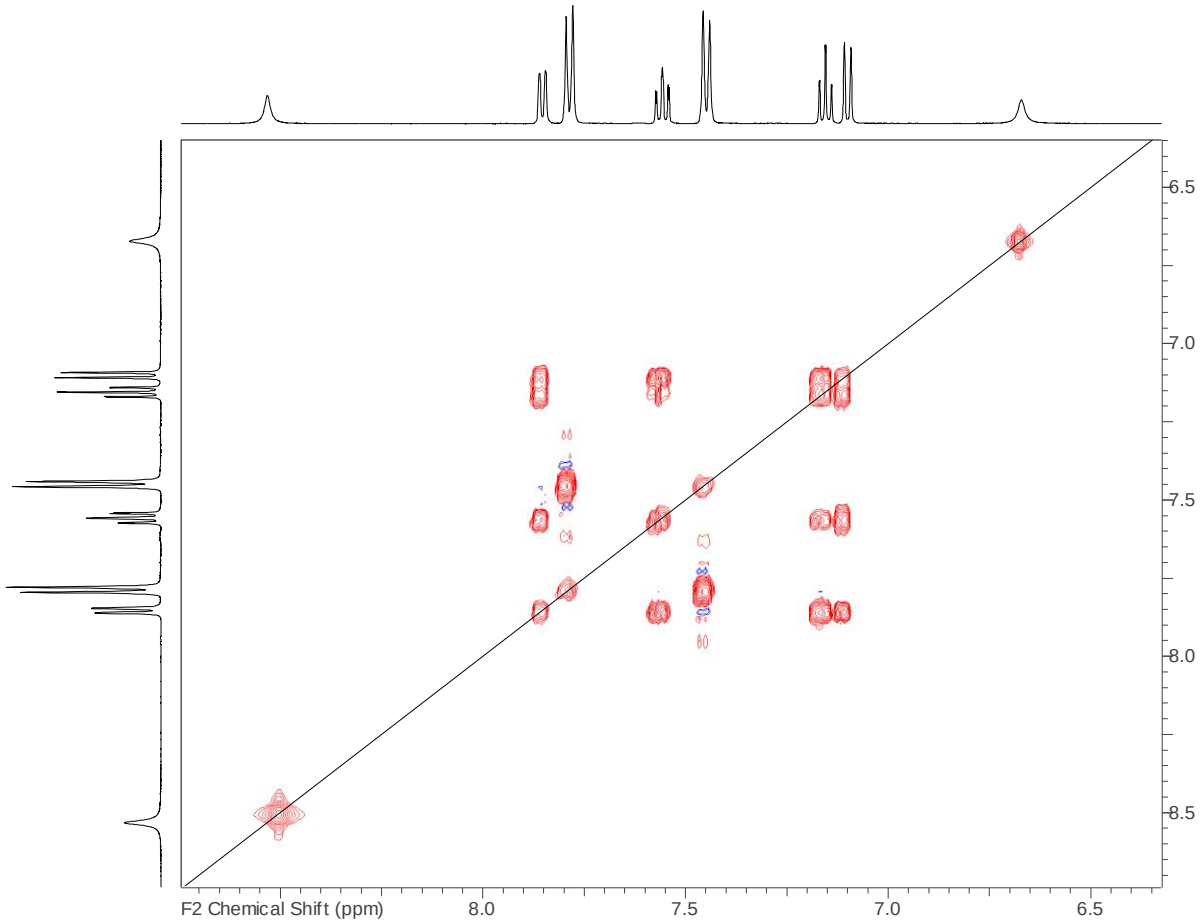

Figure S12. TOCSY NMR of compound **2** in CD_3CN.

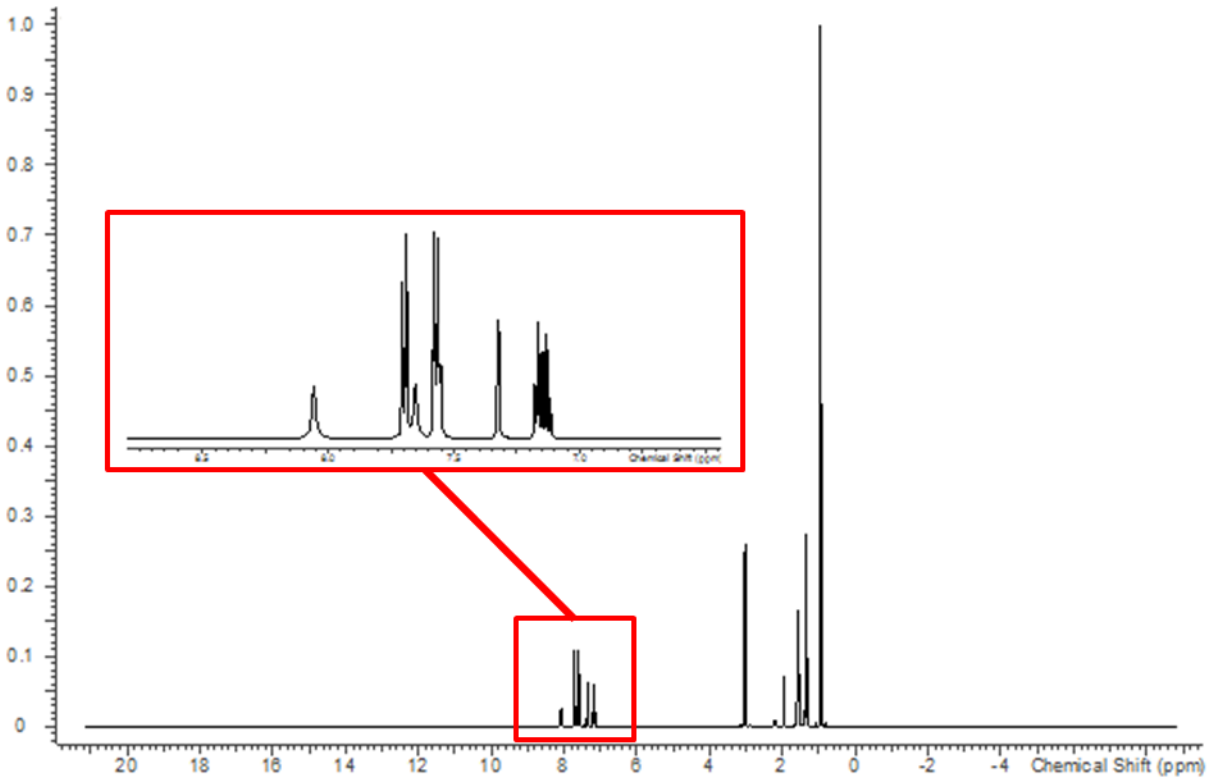

Figure S13. ^{1}H NMR of compound **3** in CD_3CN.

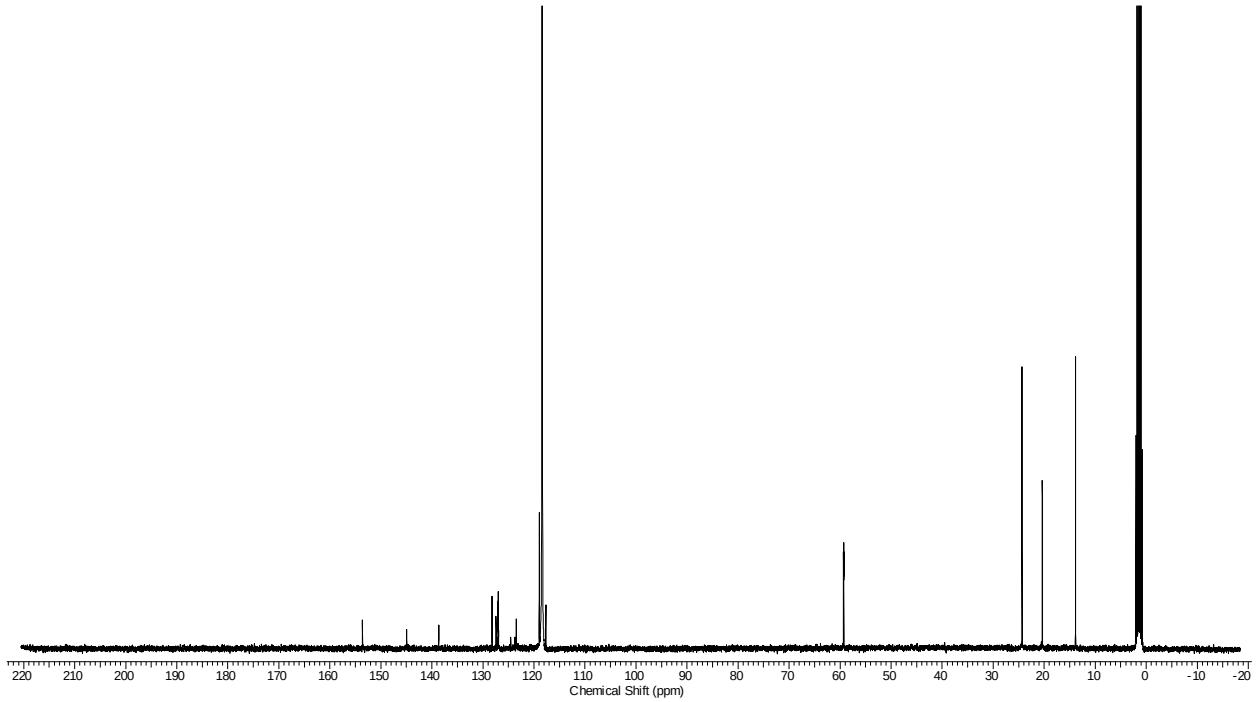

Figure S14. ^{13}C NMR of compound **3** in CD_3CN.

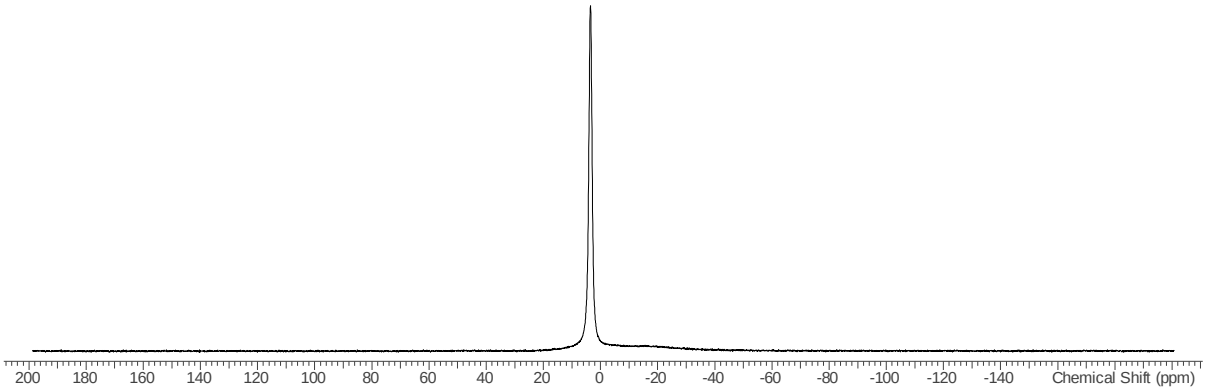

Figure S15. ^{11}B NMR of compound **3** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

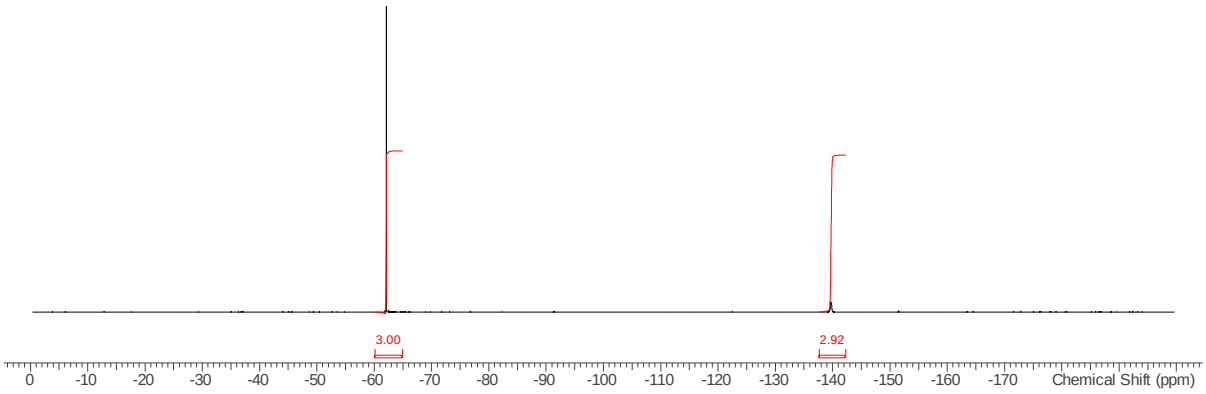

Figure S16. ^{19}F NMR of compound **3** in CD_3CN.

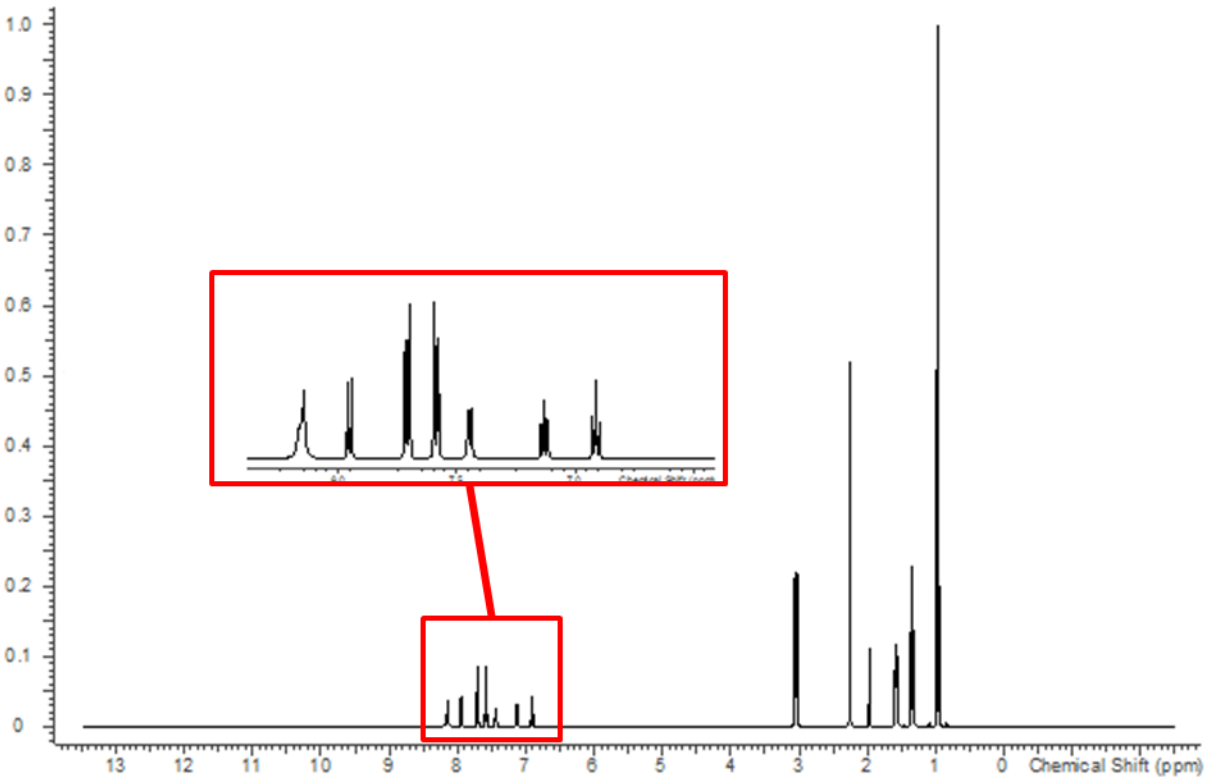

Figure S17. ^{1}H NMR of compound **4** in CD_3CN.

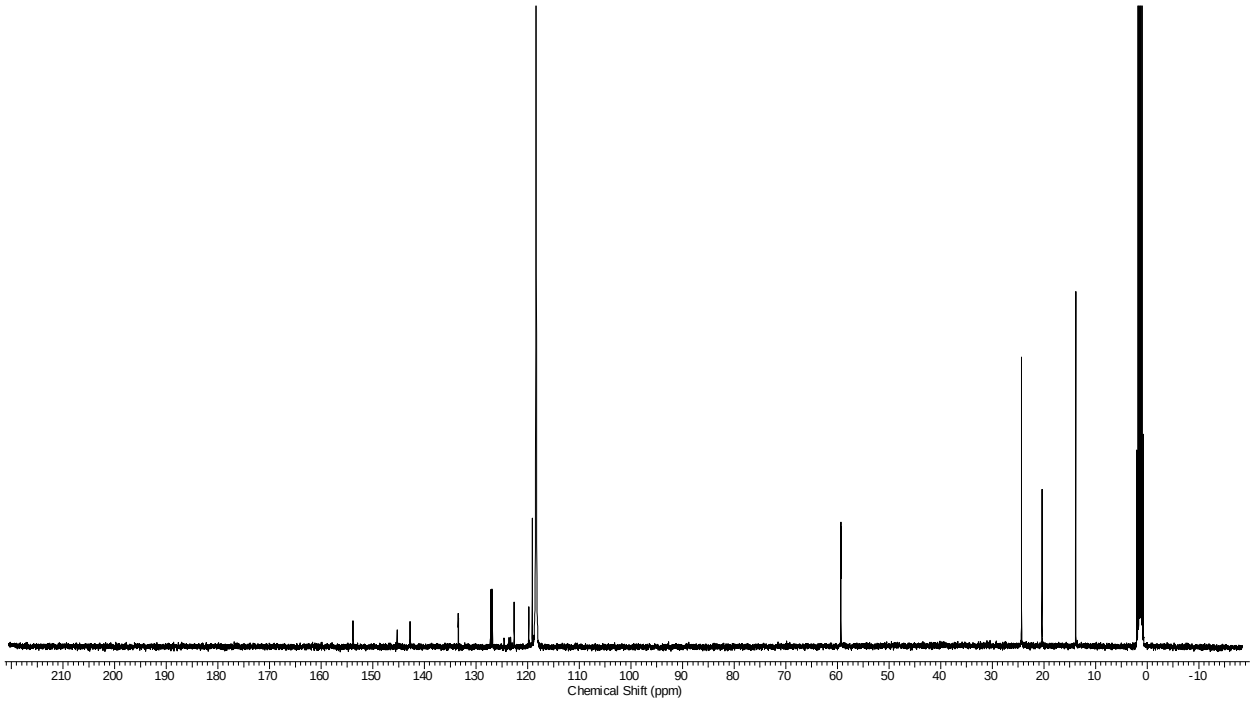

Figure S18. ^{13}C NMR of compound **4** in CD_3CN.

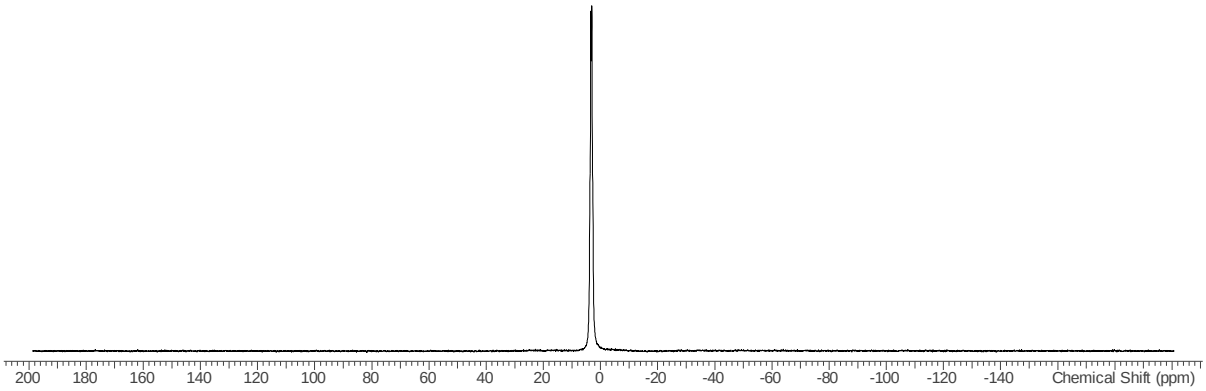

Figure S19. ^{11}B NMR of compound **4** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

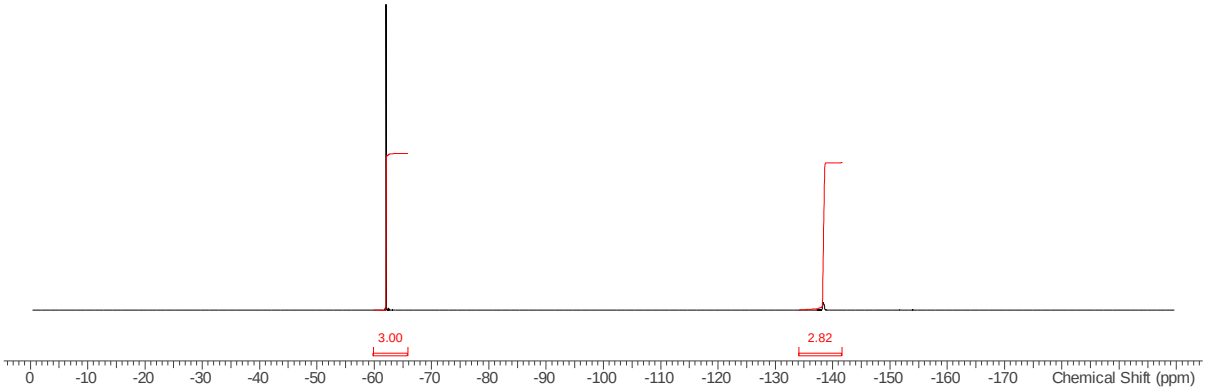

Figure S20. ^{19}F NMR of compound **4** in CD_3CN.

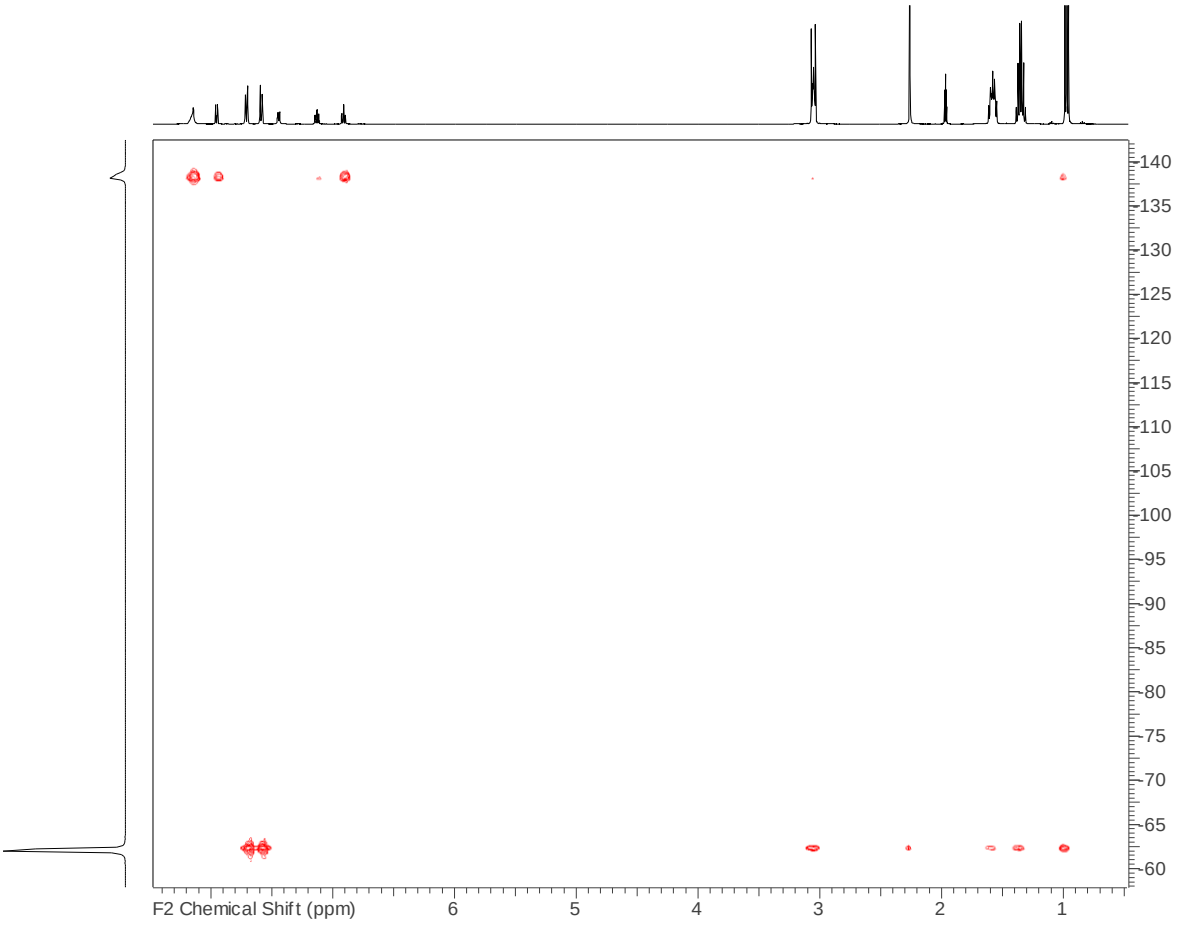

Figure S21. $^{1}H/^{19}F$ HMBC NMR of compound **4** in CD_3CN.

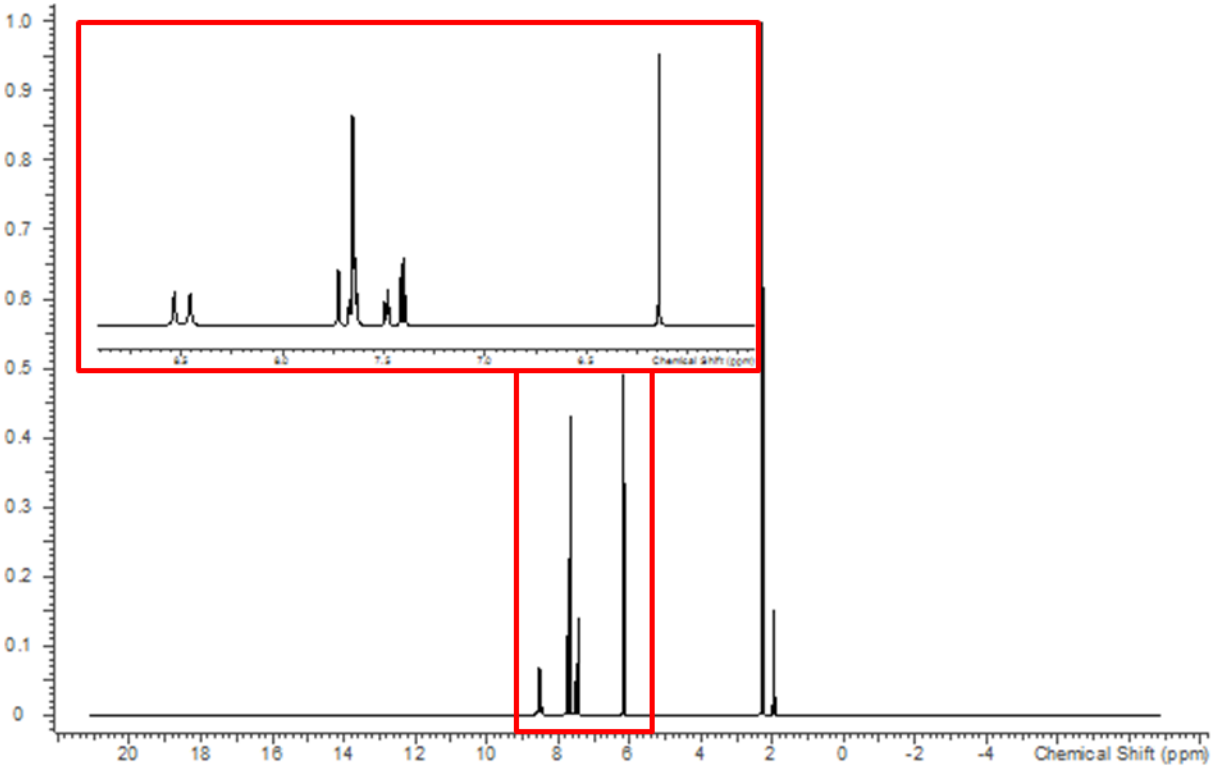

Figure S22. ^{1}H NMR of compound **5** in CD_3CN.

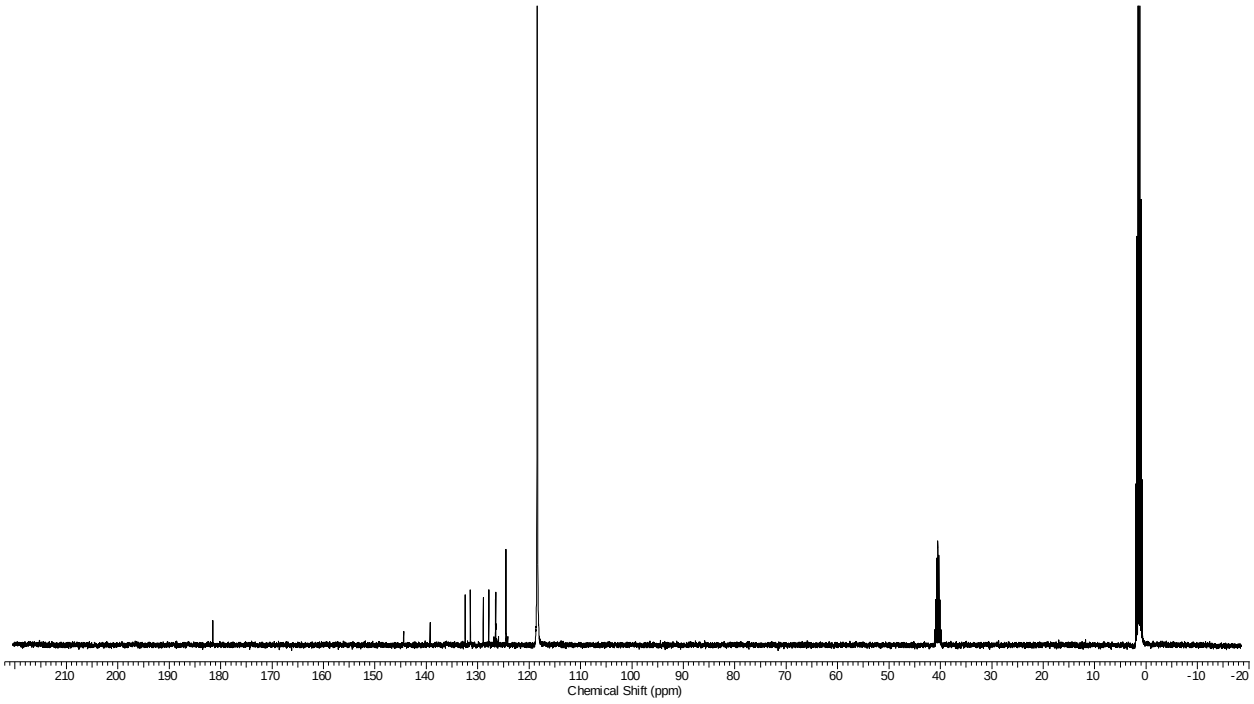

Figure S23. ^{13}C NMR of compound **5** in CD_3CN/DMSO-d_6.

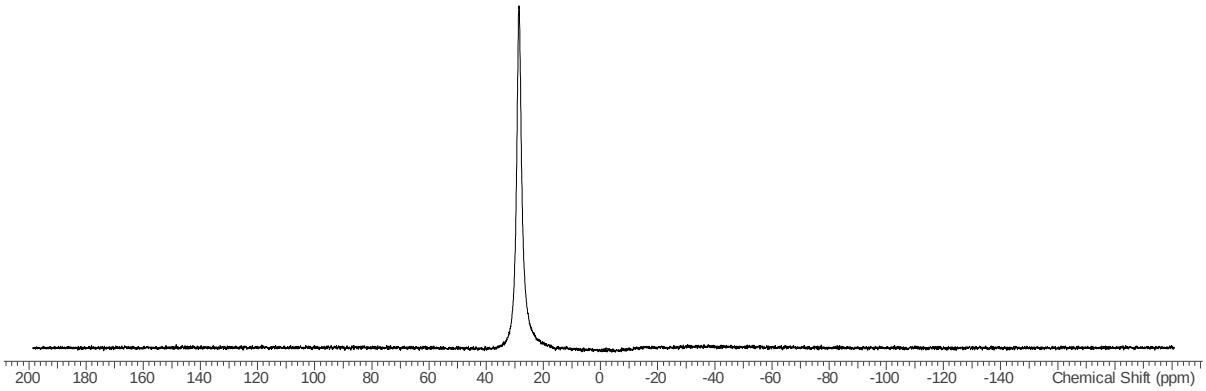

Figure S24. ^{11}B NMR of compound **5** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

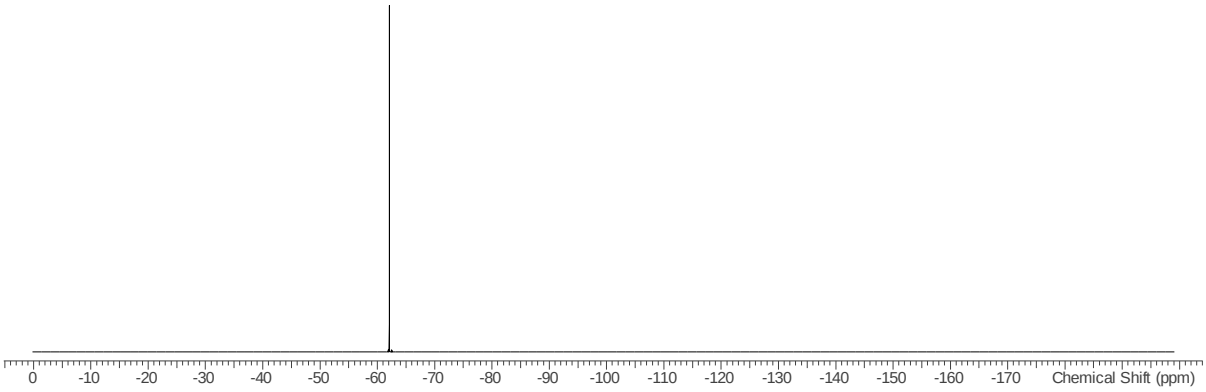

Figure S25. ^{19}F NMR of compound **5** in CD_3CN.

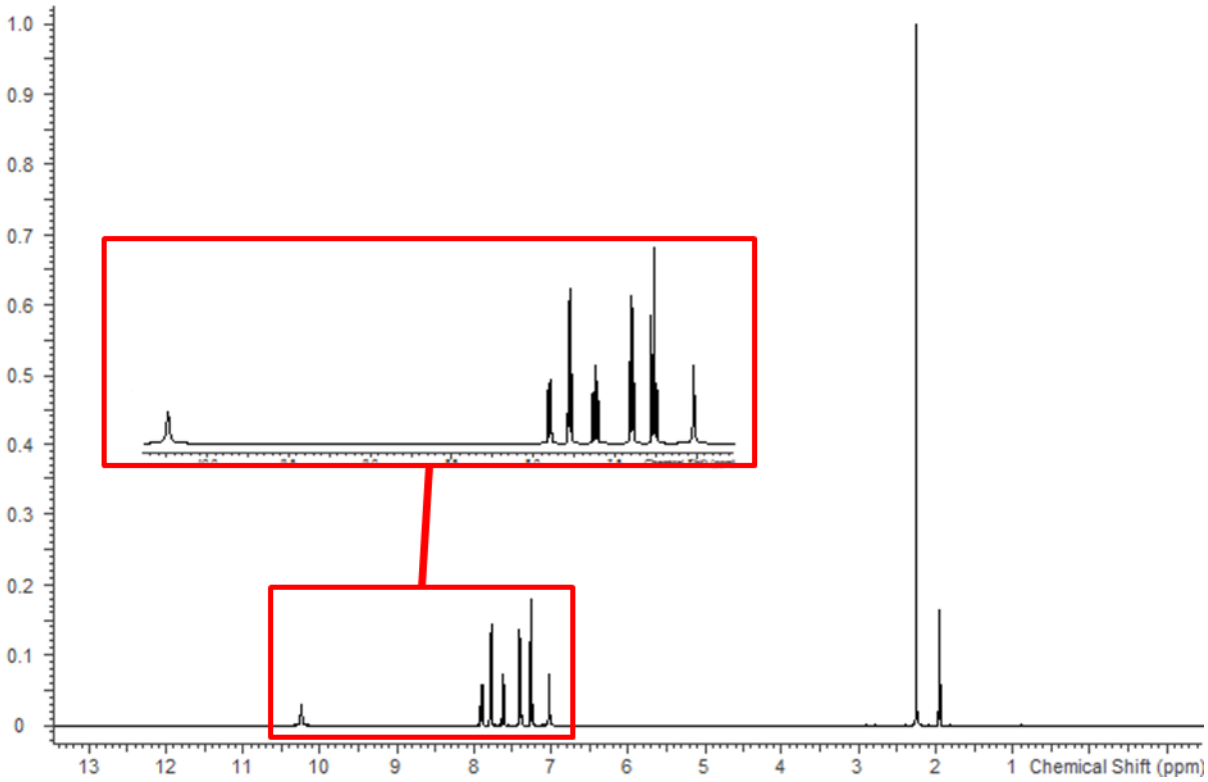

Figure S26. ^{1}H NMR of compound **6** in CD_3CN.

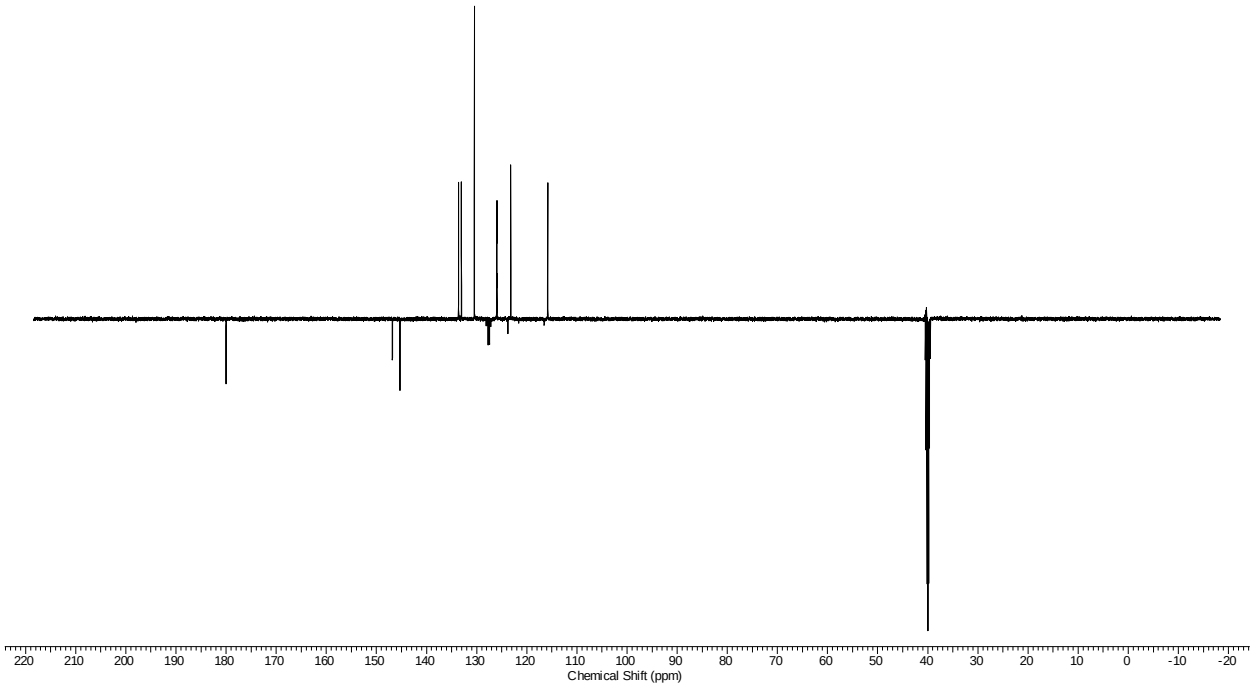

Figure S27. ^{13}C DEPTQ NMR of compound **6** in DMSO-d_6.

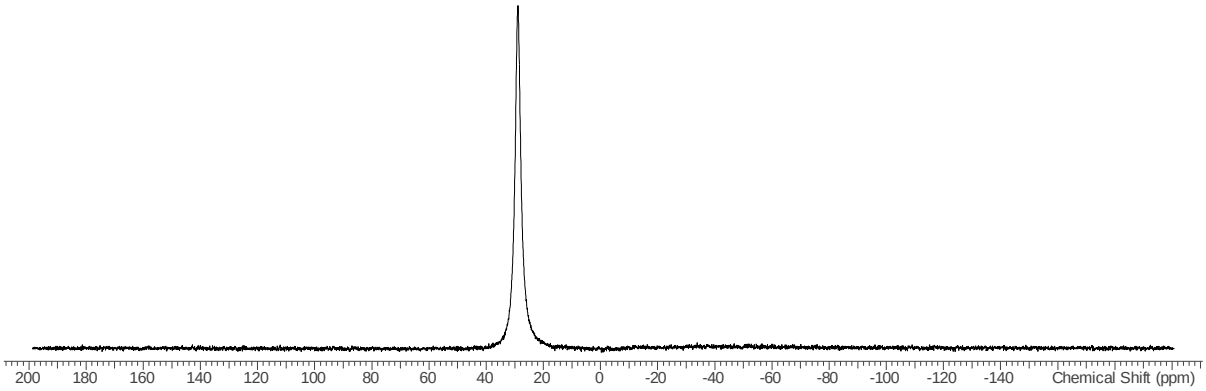

Figure S28. ^{11}B NMR of compound **6** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

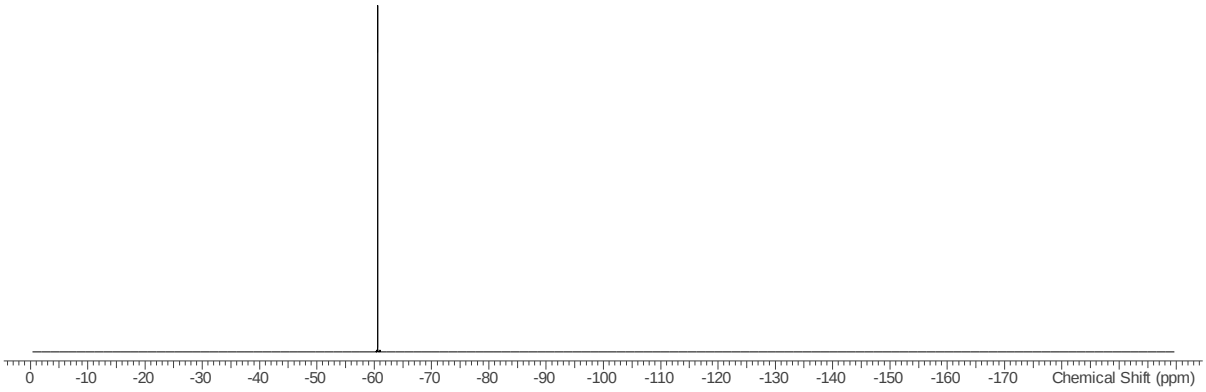

Figure S29. ^{19}F NMR of compound **6** in CD_3CN.

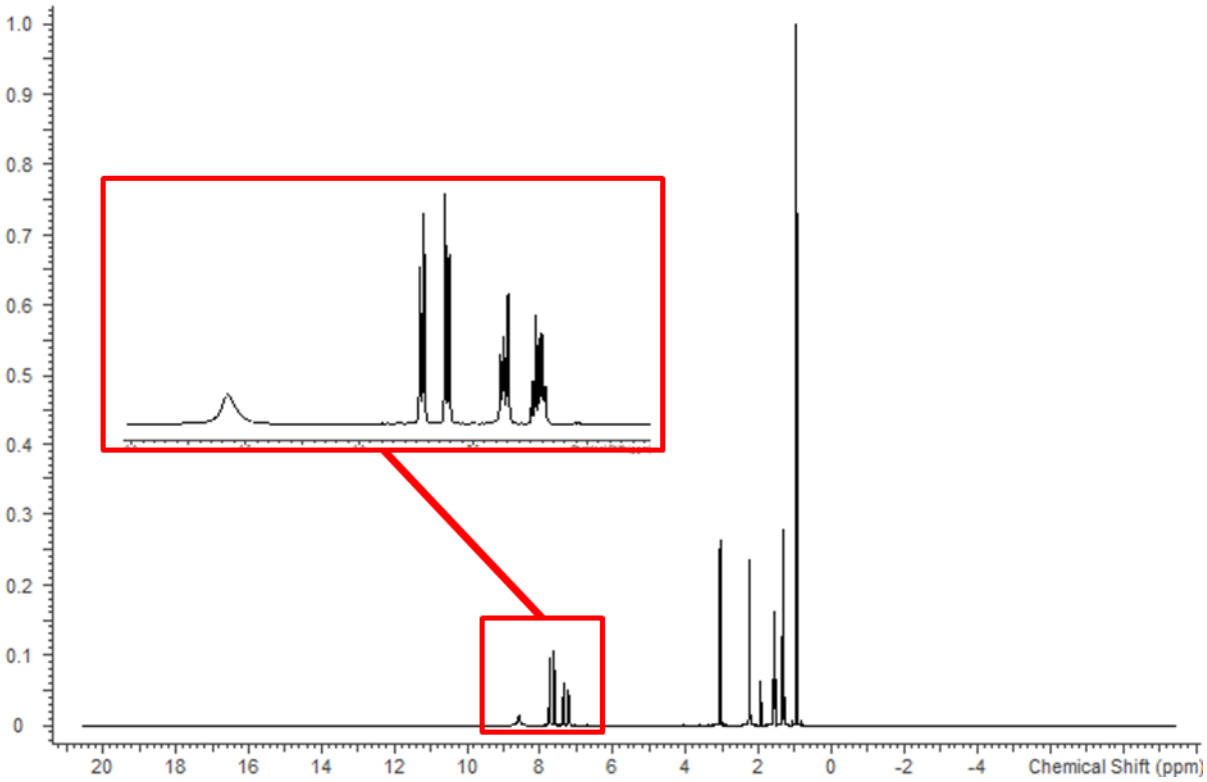

Figure S30. ^{1}H NMR of compound **7** in CD_3CN.

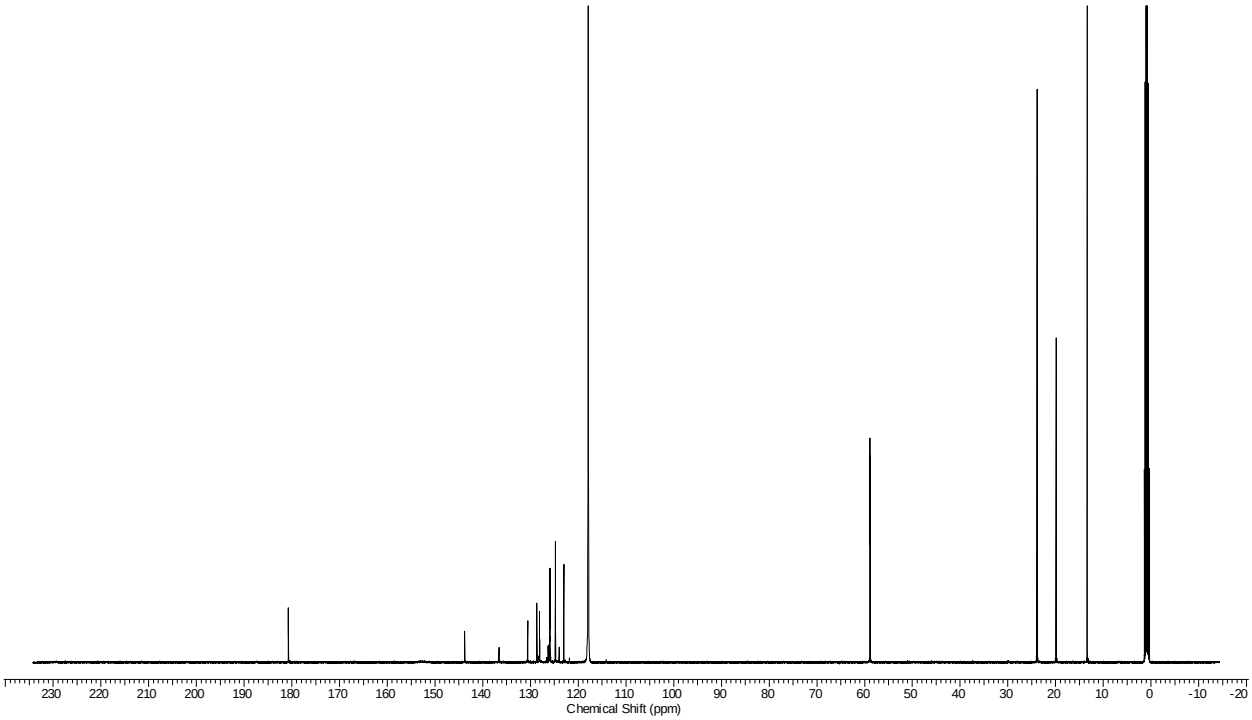

Figure S31. ^{13}C NMR of compound **7** in CD_3CN.

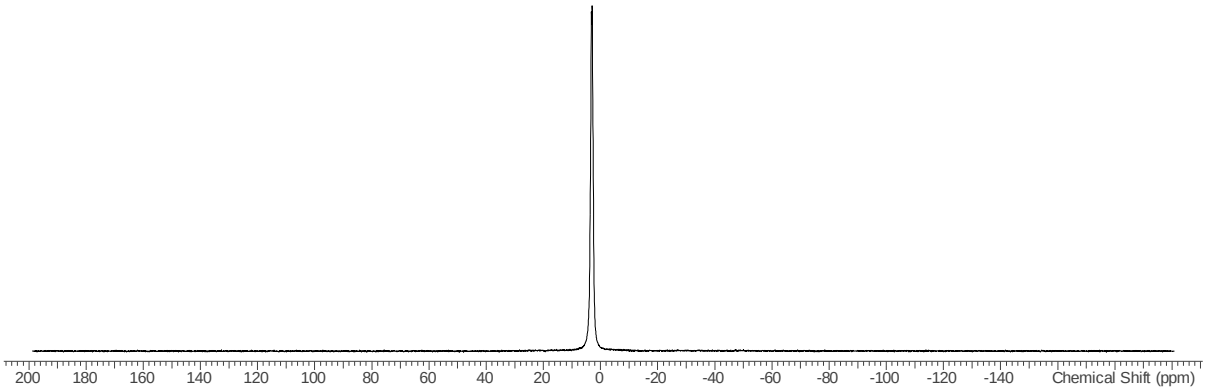

Figure S32. ^{11}B NMR of compound **7** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

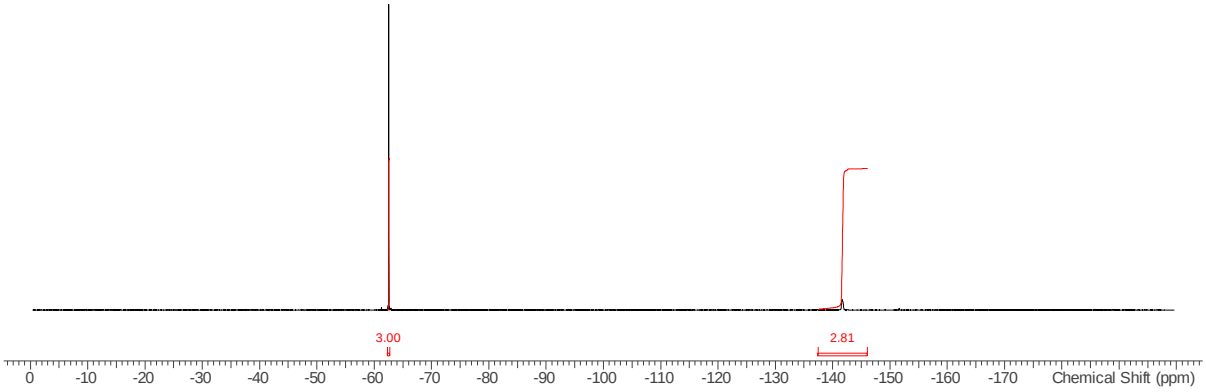

Figure S33. ^{19}F NMR of compound **7** in CD_3CN.

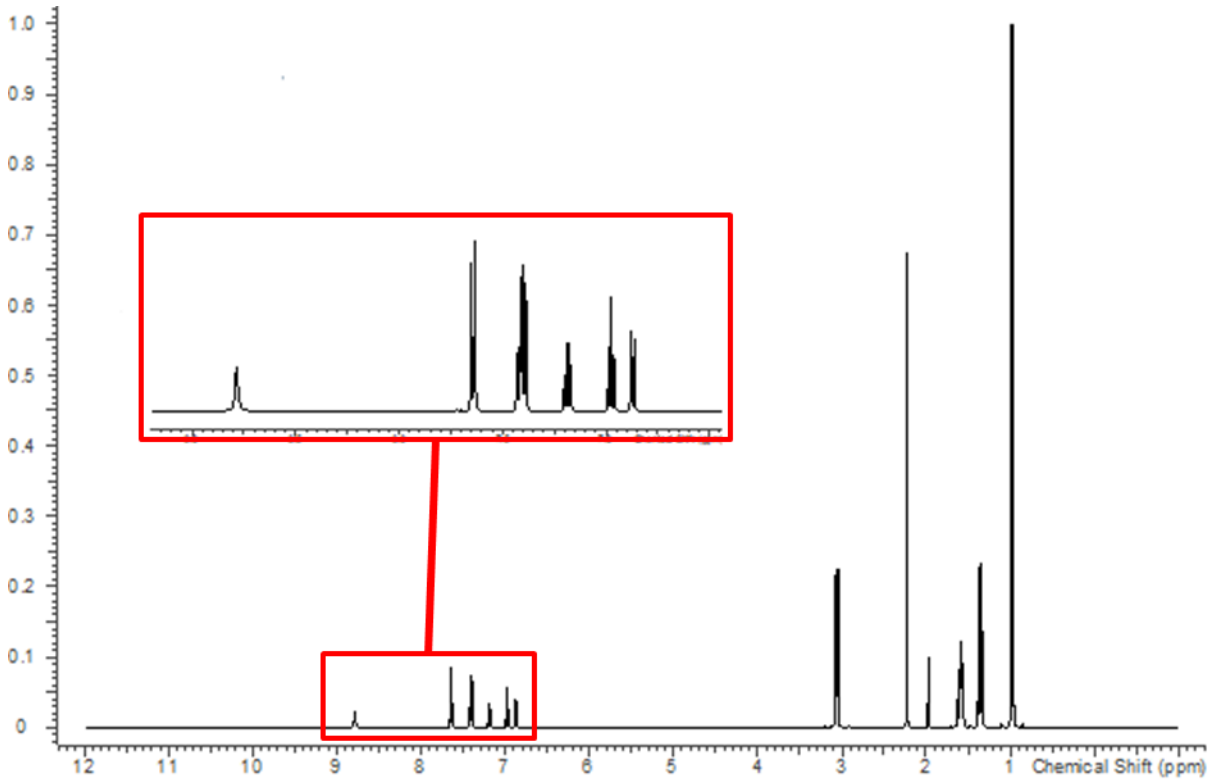

Figure S34. ^{1}H NMR of compound **8** in CD_3CN.

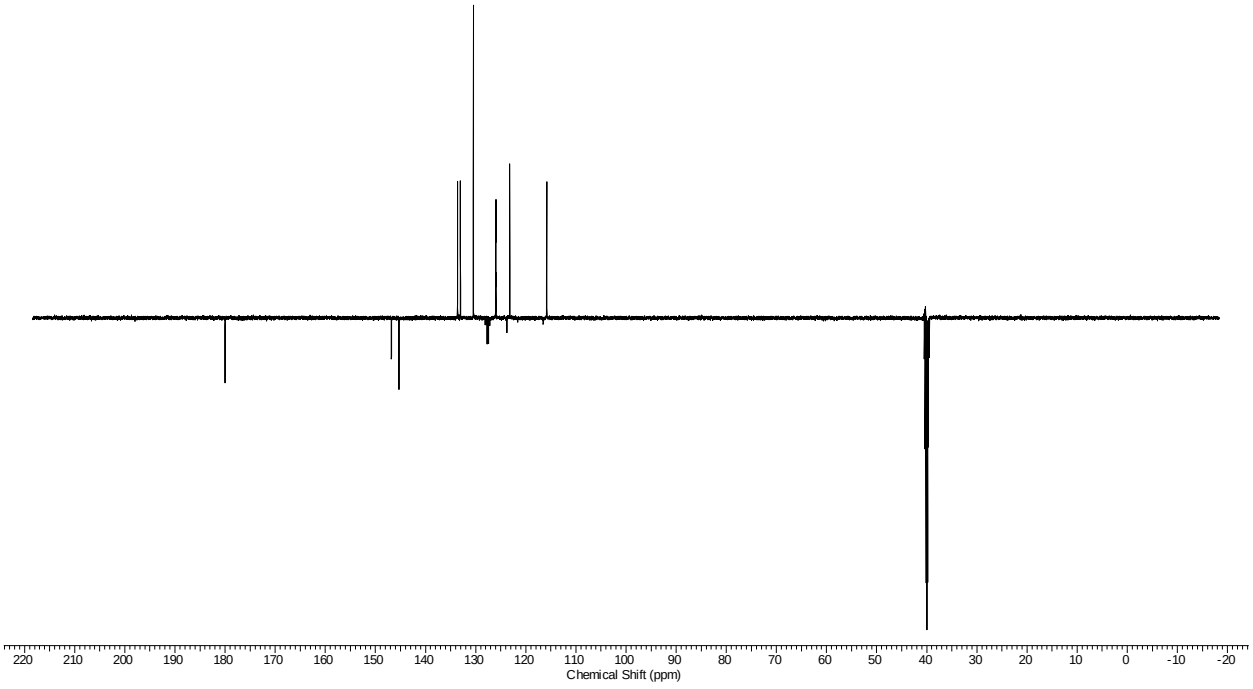

Figure S35. ^{13}C DEPTQ NMR of compound **8** in DMSO-d_6.

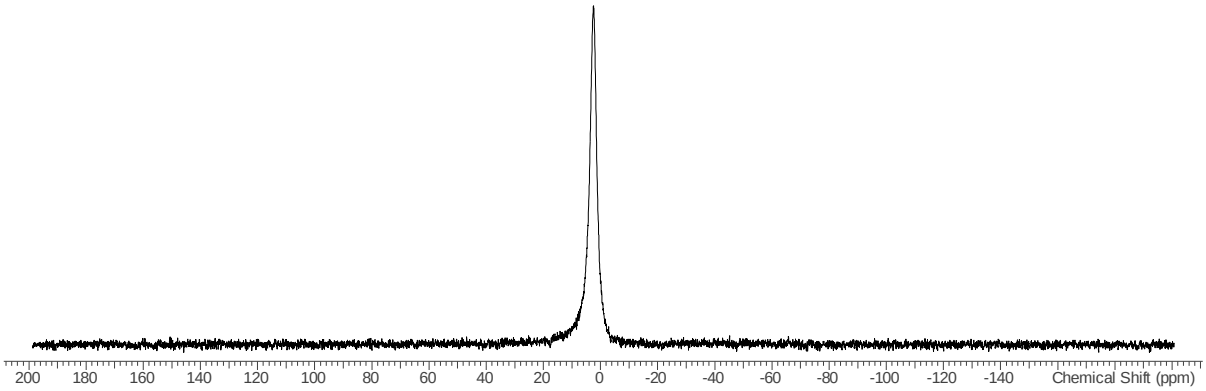

Figure S36. ^{11}B NMR of compound **8** in CD_3CN – the resonance corresponding to the boron silicate glass has been subtracted.

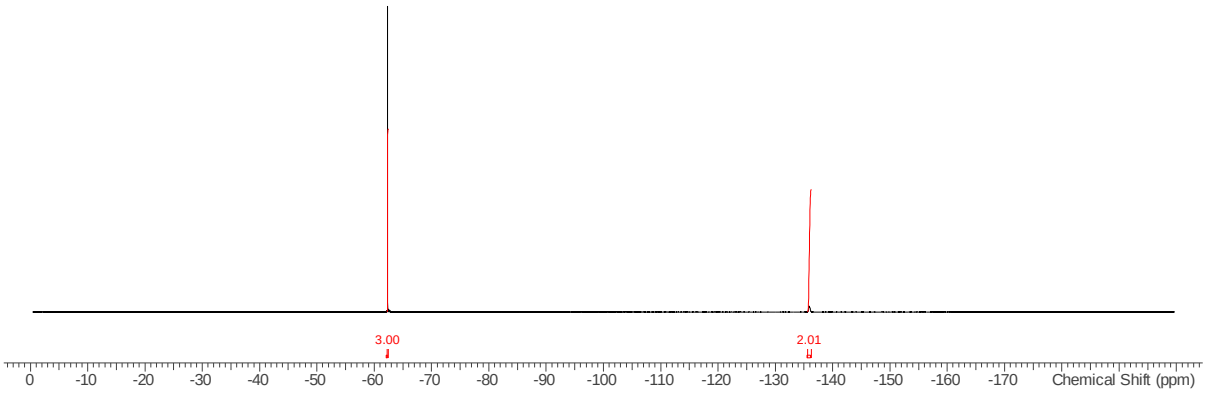

Figure S37. ^{19}F NMR of compound **8** in CD_3CN.

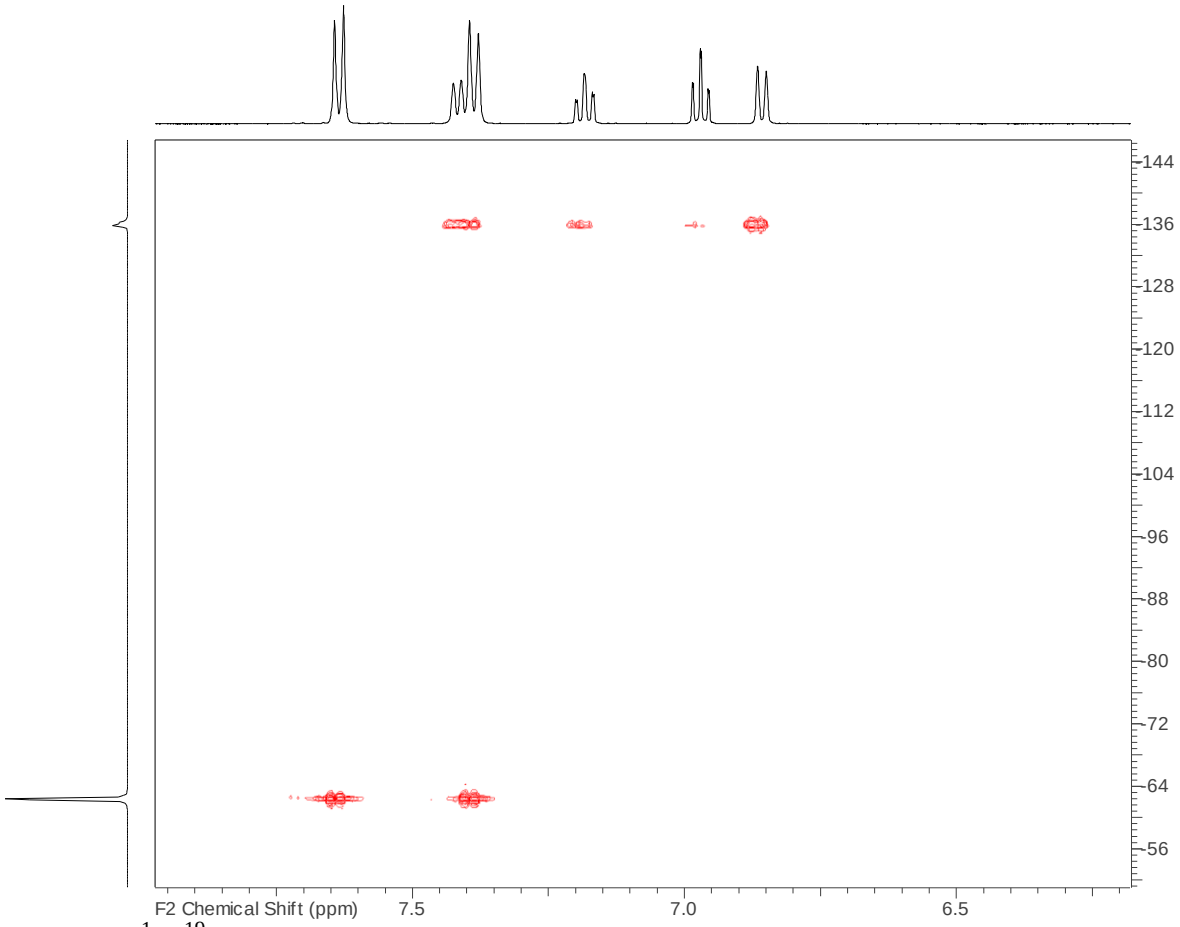

Figure S38. $^{1}H/^{19}F$ HMBC NMR of compound **8** in CD_3CN. Correlations between the BF_2^- functionality and CH groups of both aromatic rings proves that this compound adopts a similar conformation to compound **6**.

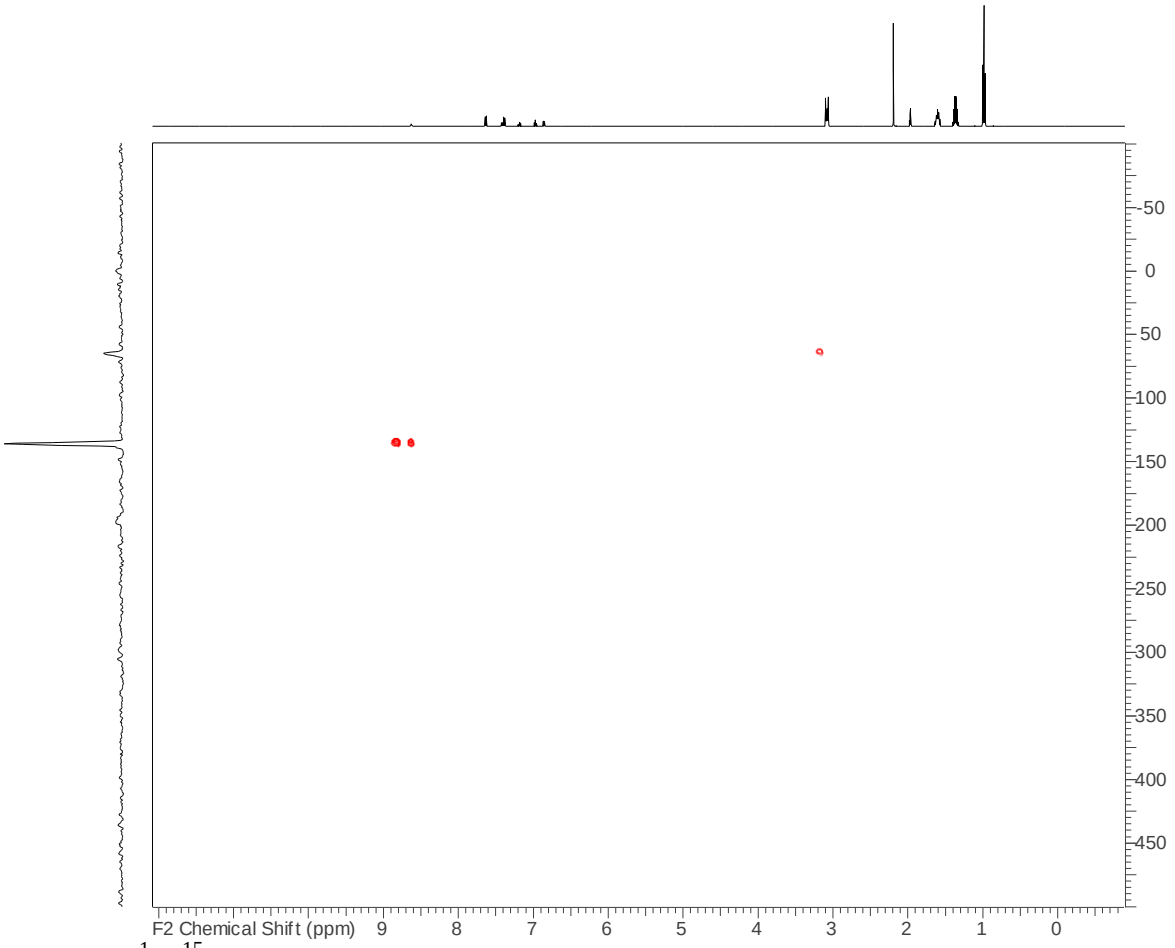

Figure S39. $^{1}H/^{15}N$ HMBC NMR of compound **8** in CD_3CN. Correlations confirm the presence of NH functionality at 8.46 ppm.

Reactions of receptors 1-8

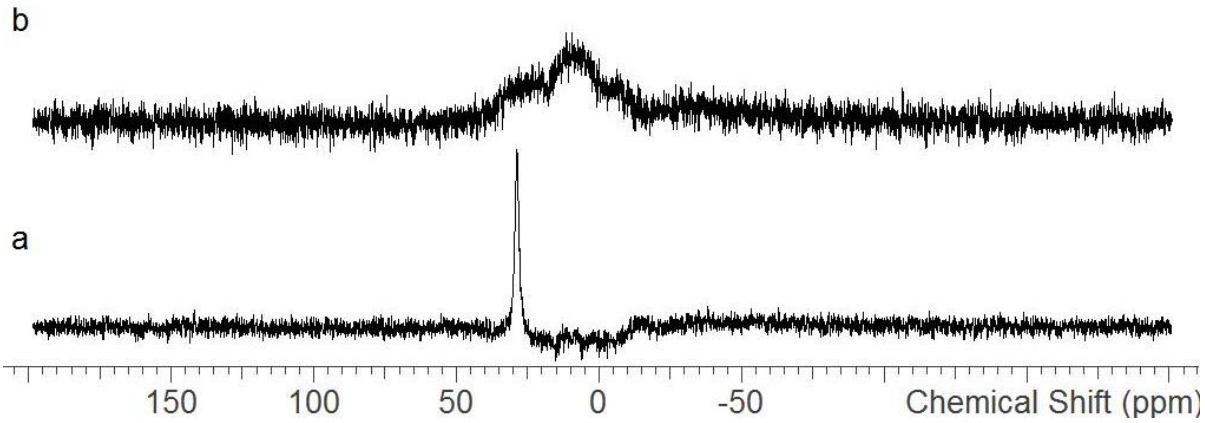

Figure S40. ^{11}B NMR spectrum of a) receptor **1** in CD_3CN, b) with 1 equiv. TBA H_2PO_4 – the resonance corresponding to the boron silicate glass has been subtracted.

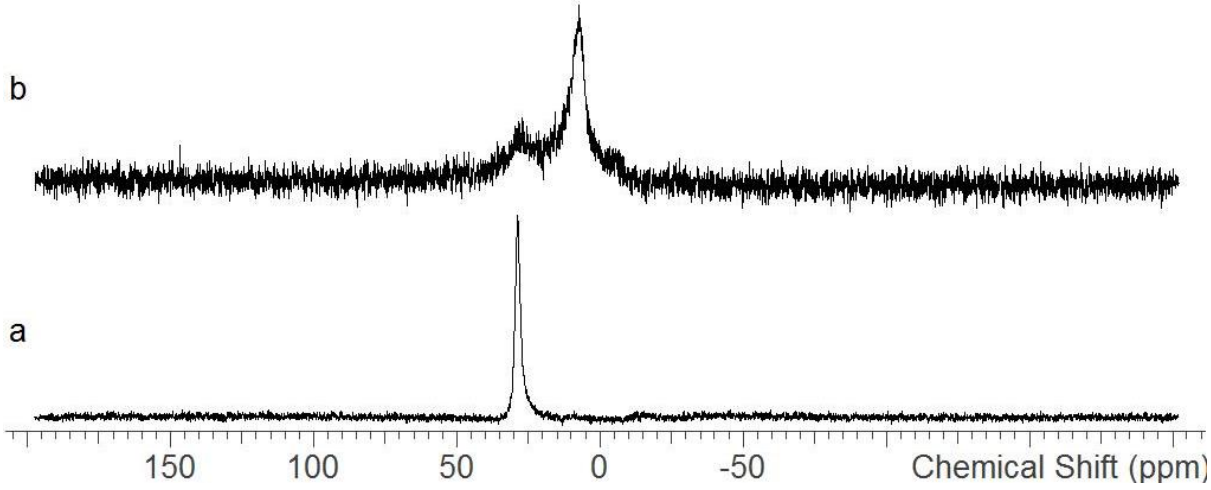

Figure S41. ^{11}B NMR spectrum of a) receptor **2** in CD_3CN, b) with 1 equiv. TBA H_2PO_4– the resonance corresponding to the boron silicate glass has been subtracted.

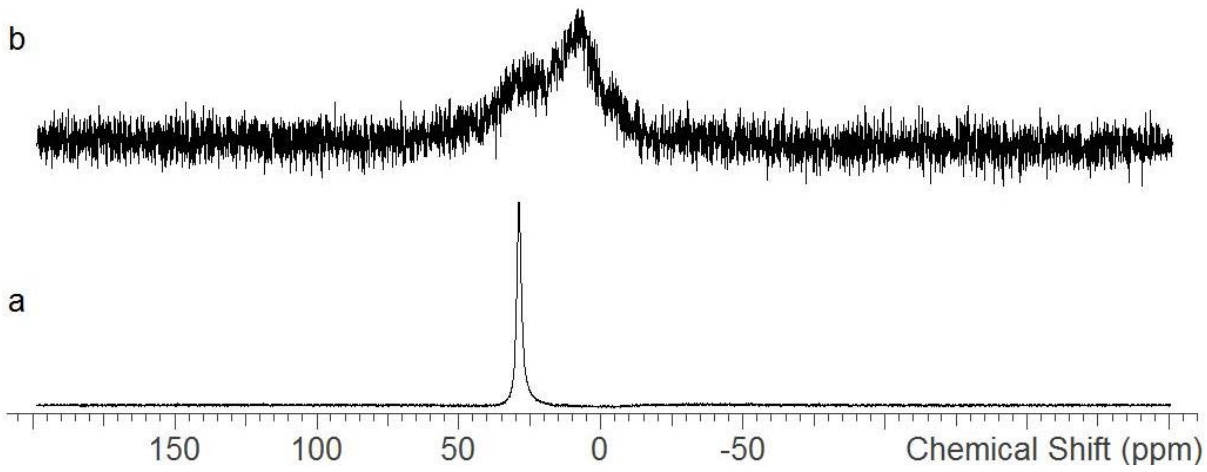

Figure S42. ^{11}B NMR spectrum of a) receptor **5** in CD_3CN, b) with 1 equiv. TBA H_2PO_4 – the resonance corresponding to the boron silicate glass has been subtracted.

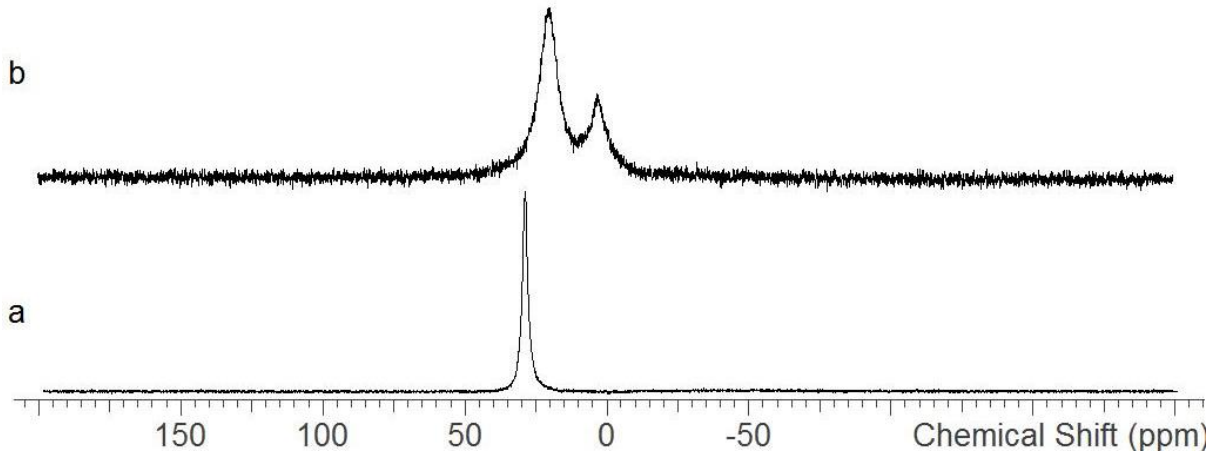

Figure S43. ^{11}B NMR spectrum of a) receptor **6** in CD_3CN, b) with 1 equiv. TBA H_2PO_4– the resonance corresponding to the boron silicate glass has been subtracted.

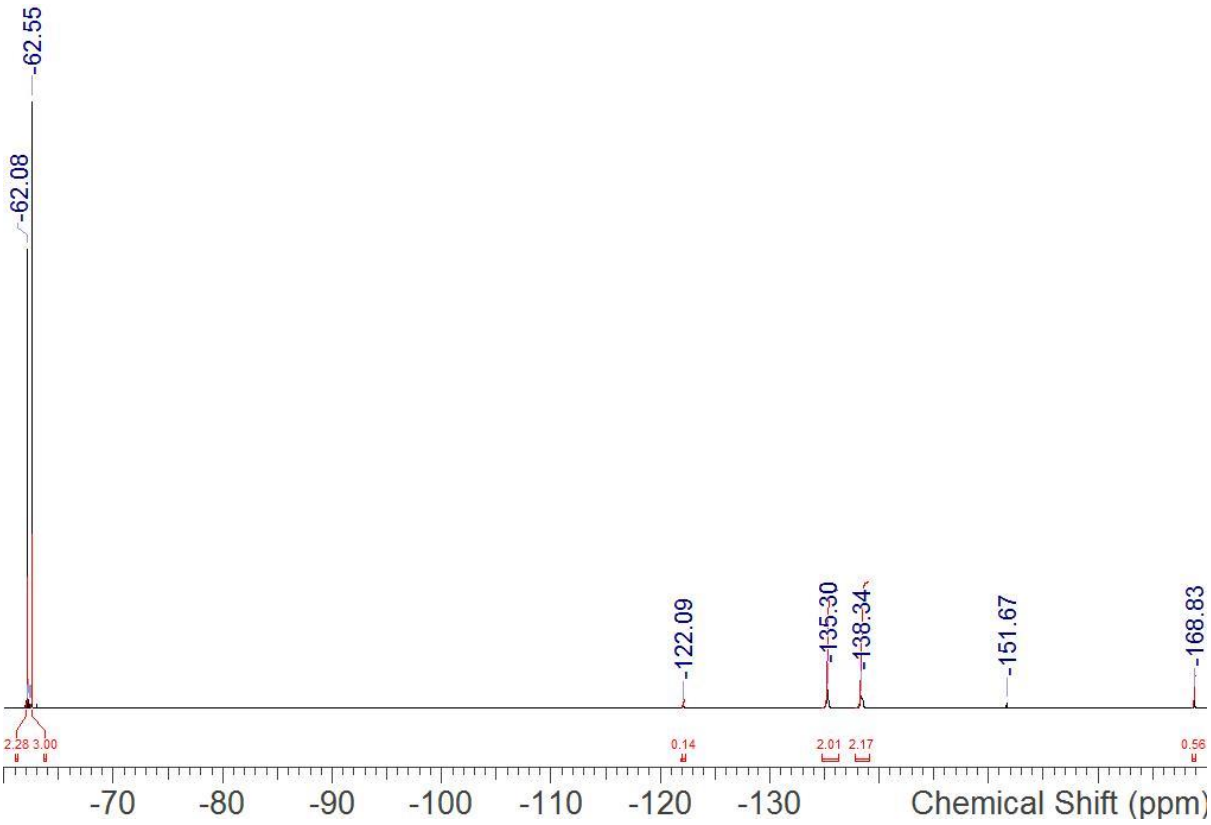

Figure S44. ^{19}F NMR spectrum in CD_3CN of receptor **4** with 1 equiv. PMP.

General binding constant calculation information

Table S1. Chemical shift (ppm) of the NH resonance of the free host used to calculate binding constants through titration experiments.

Compound	Cl^-	$H_2PO_4^-$	PMP	DMMP	GD
1	7.37	N/A	N/A	7.68	7.40
2	8.51	N/A	8.51	8.51	n/a
3	7.29	7.84	N/A	7.85	7.20
4	8.09	8.06	N/A	8.07	8.00
5	8.40	N/A	8.50	8.50	8.42
6	10.12	N/A	10.26	10.12	n/a
7	8.34	8.45	N/A	8.45	8.42
8	8.57	8.49	8.49	8.49	8.5

Calculation of binding constants with chloride

All ^1H NMR titration data was fit using EQNMR.

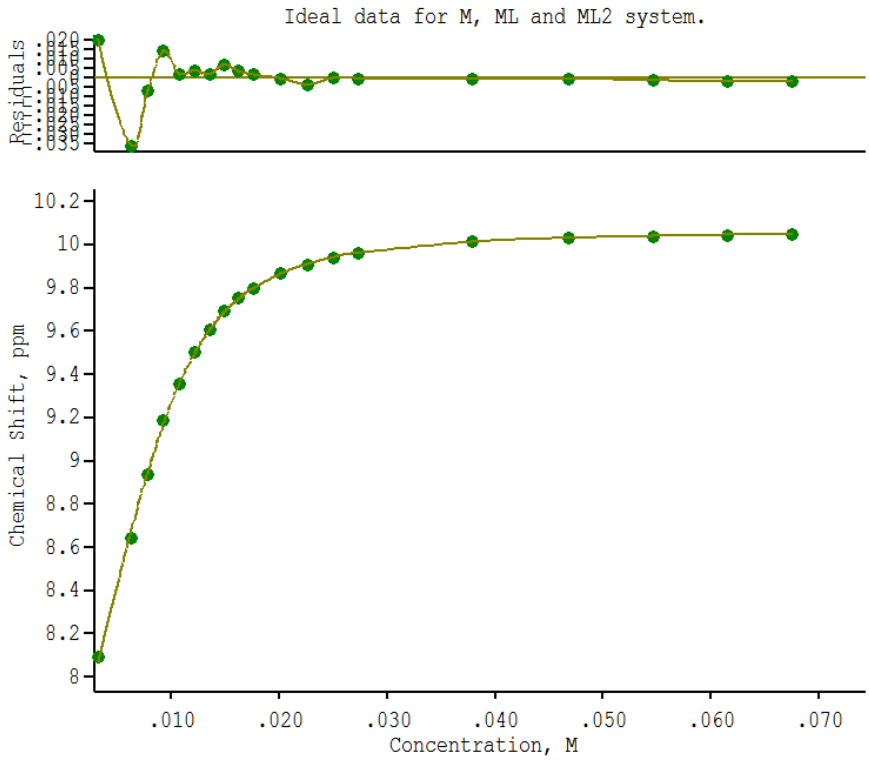

Figure S45. ^{1}H NMR titration in CD_3CN with receptor **1** vs chloride following the NH.

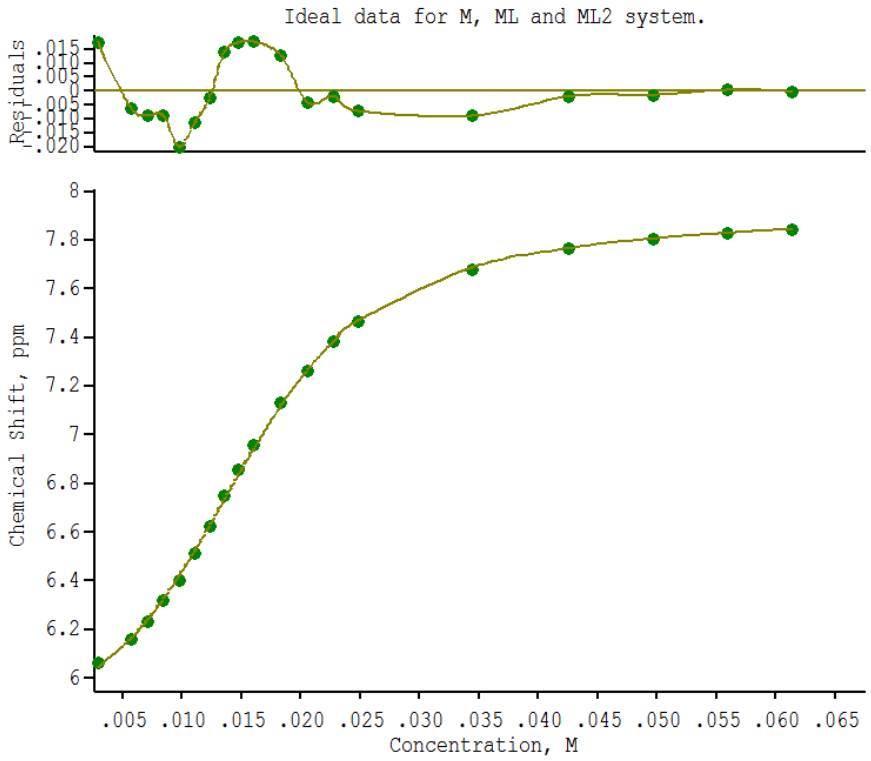

Figure S46. ^{1}H NMR titration in CD_3CN with receptor **1** vs chloride following the OH.

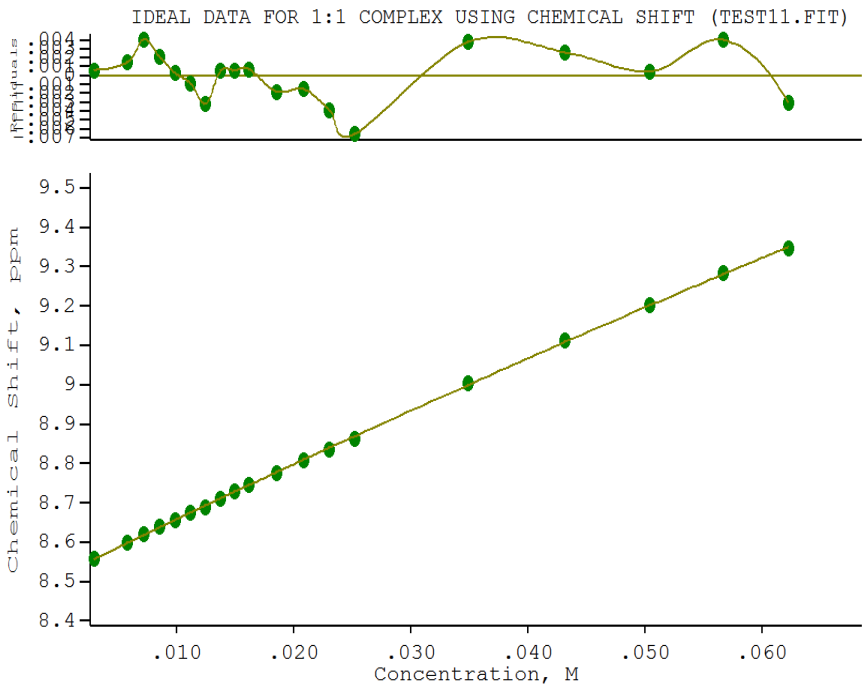

Figure S47. ^{1}H NMR titration in CD_3CN with receptor **2** vs following the NH.

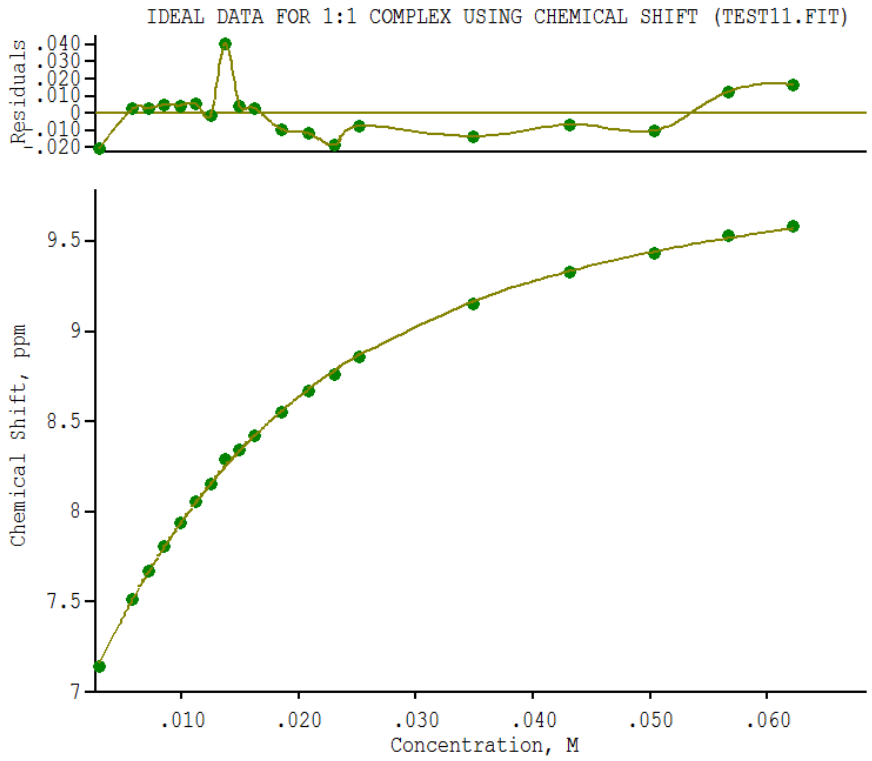

Figure S48. ^{1}H NMR titration in CD_3CN with receptor **2** vs chloride following the OH.

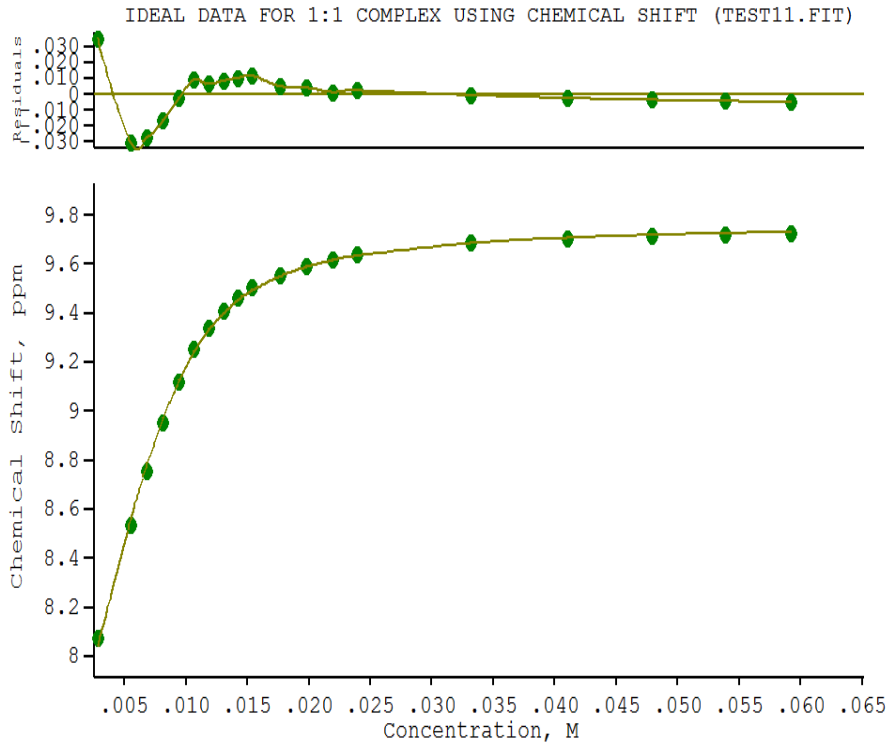

Figure S49. ^{1}H NMR titration in CD_3CN with receptor **3** vs chloride following the NH.

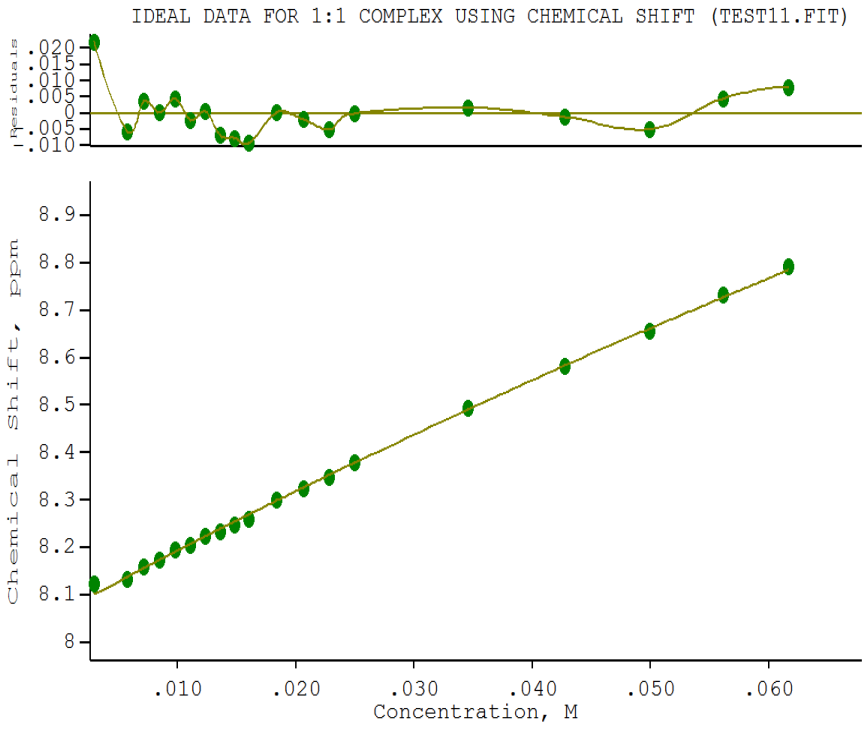

Figure S50. ^{1}H NMR titration in CD_3CN with receptor **4** vs chloride following the NH.

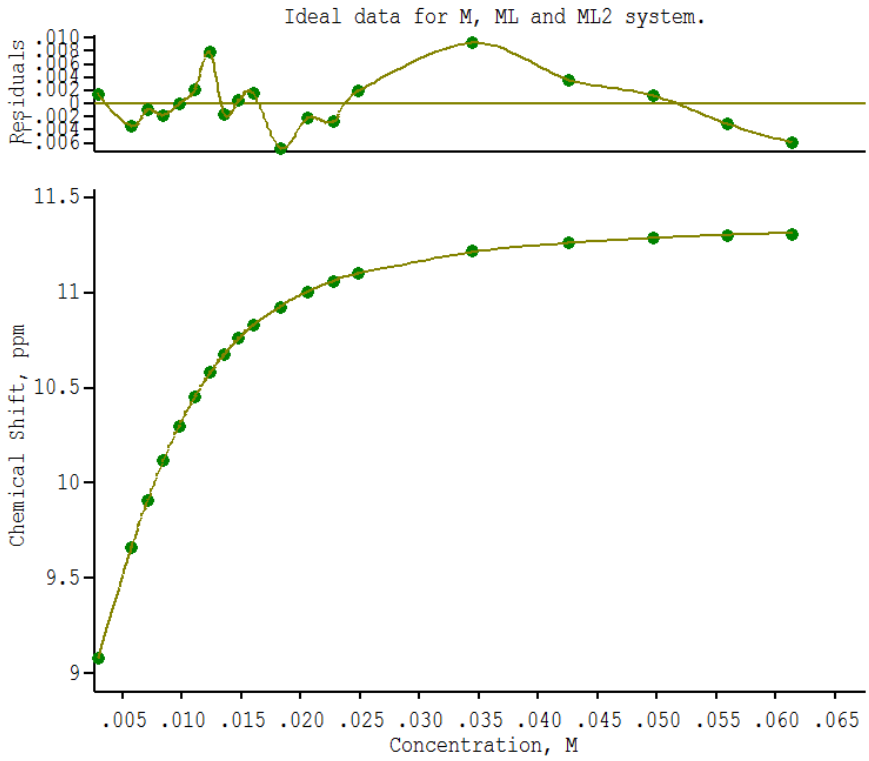

Figure S51. ^{1}H NMR titration in CD_3CN with receptor **5** vs chloride following the NH.

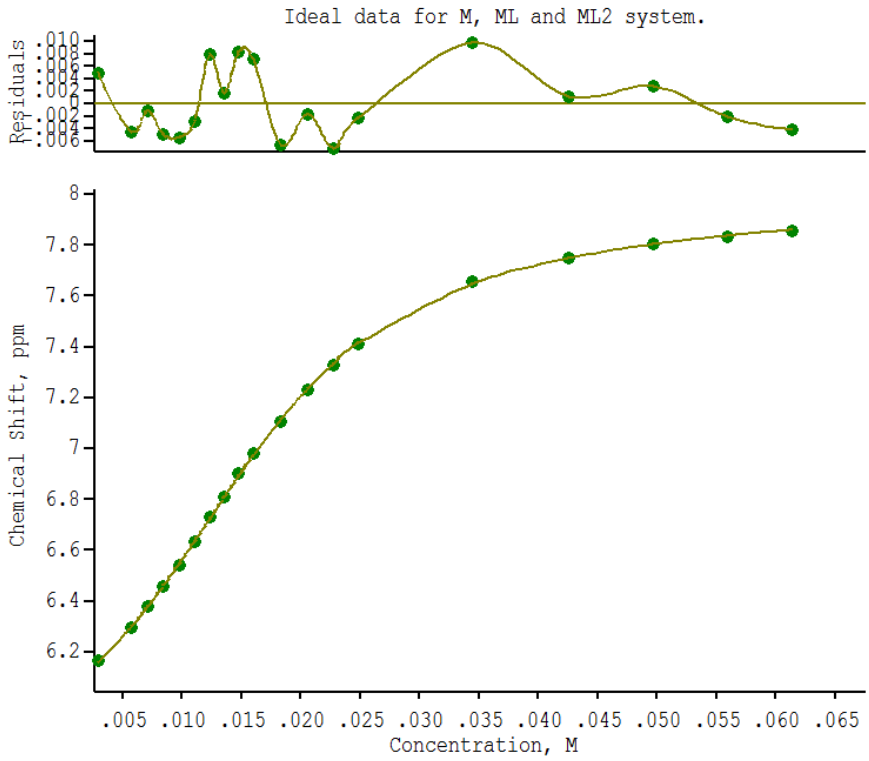

Figure S52. ^{1}H NMR titration in CD_3CN with receptor **5** vs chloride following the OH.

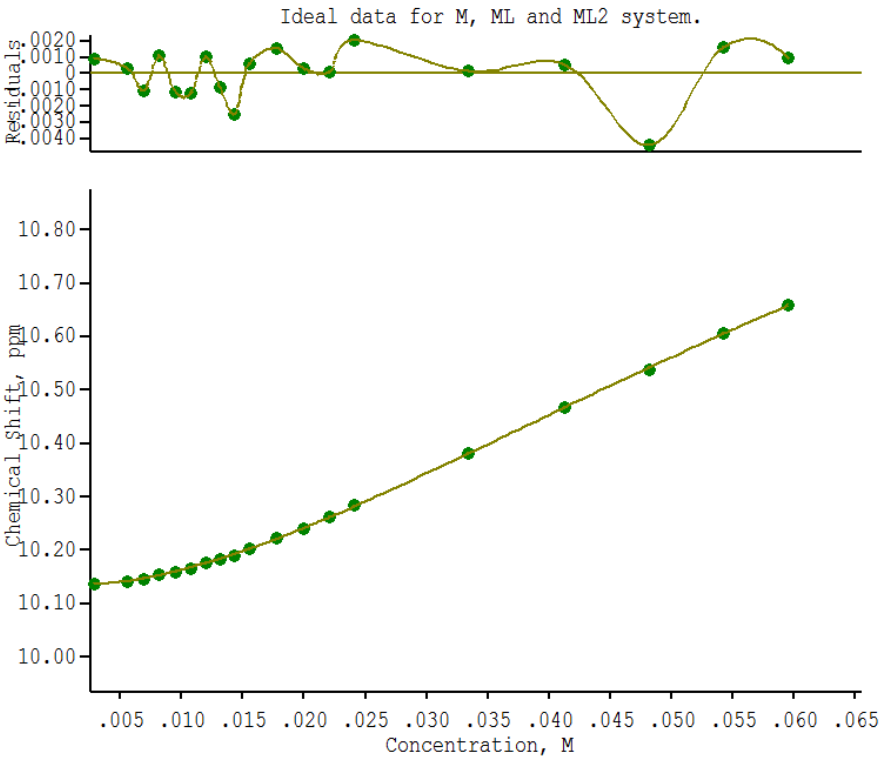

Figure S53. ^{1}H NMR titration in CD_3CN with receptor **6** vs chloride following the NH.

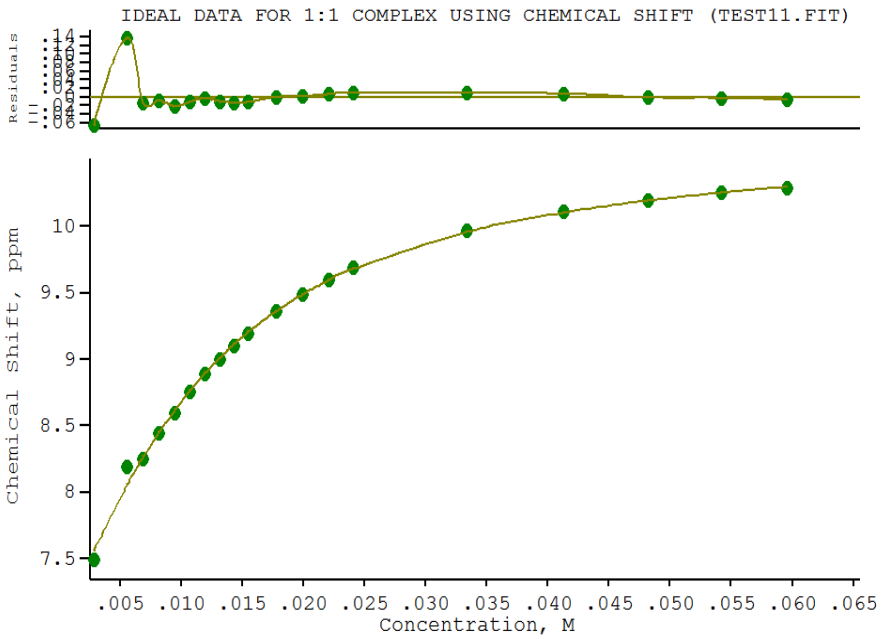

Figure S54. ^{1}H NMR titration in CD_3CN with receptor **6** vs chloride following the OH.

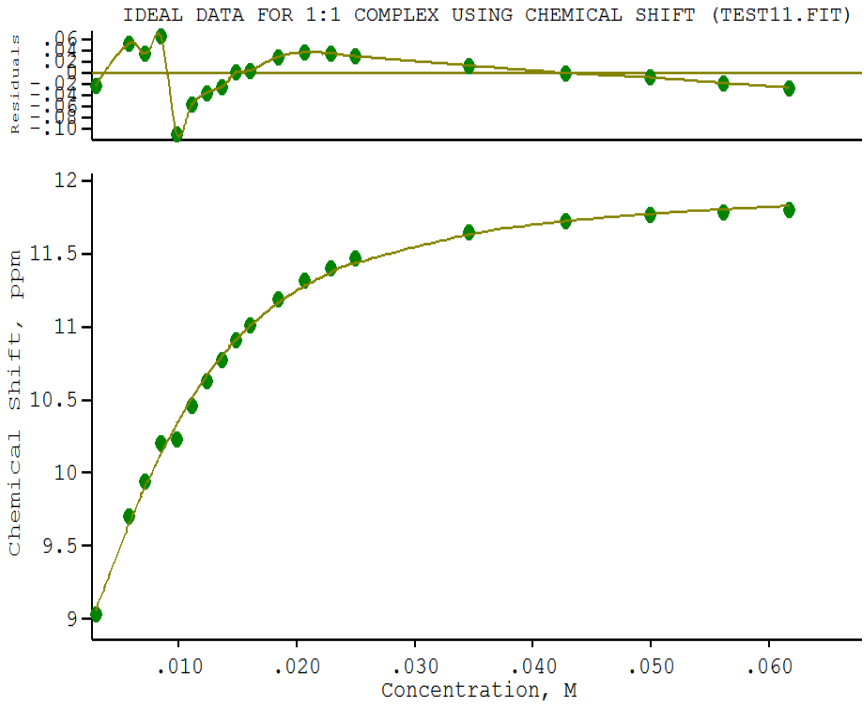

Figure S55. ^{1}H NMR titration in CD_3CN with receptor **7** vs chloride following the NH.

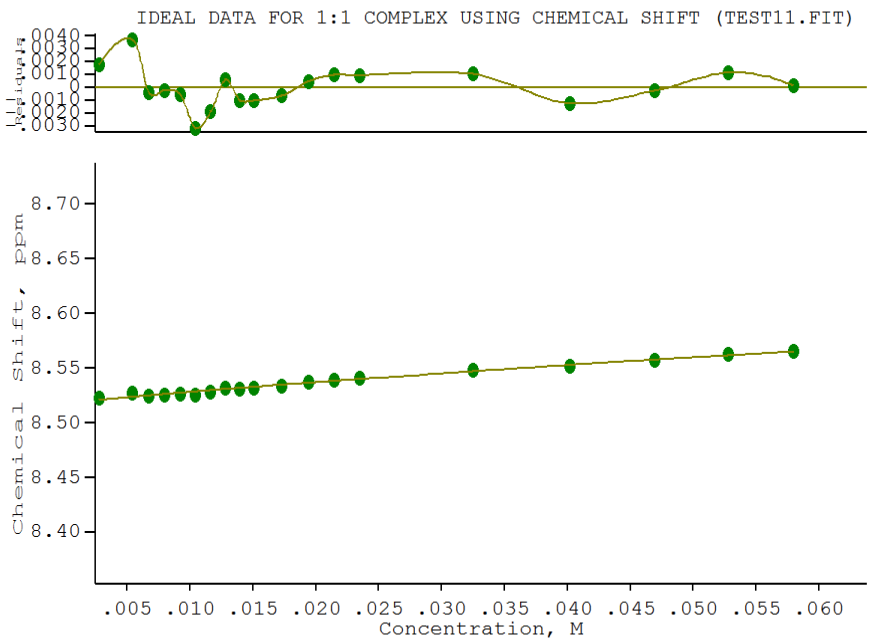

Figure S56. ^{1}H NMR titration in CD_3CN with receptor **8** vs chloride following the NH.

Calculation of binding constants with dihydrogen phosphate

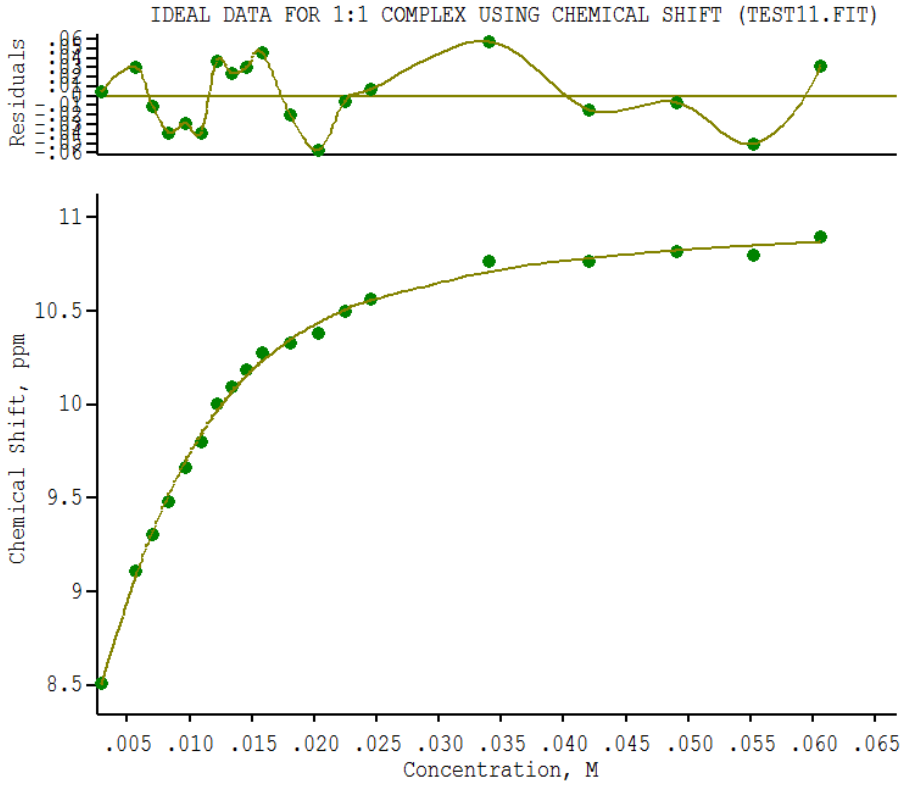

Figure S57. ^{1}H NMR titration in CD_3CN with receptor **3** vs dihydrogen phosphate following the NH.

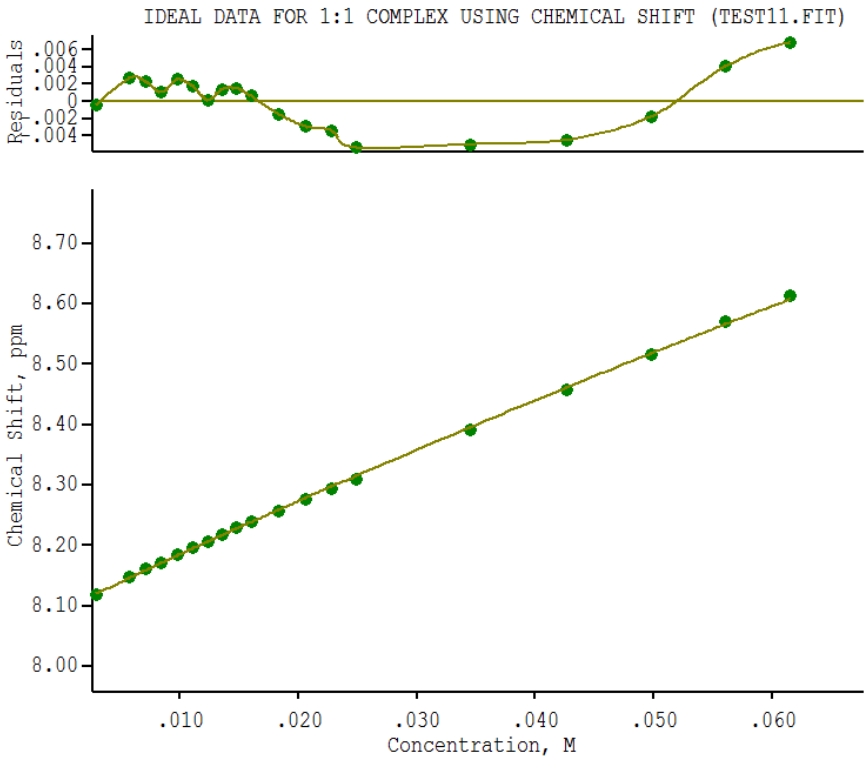

Figure S58. ^{1}H NMR titration in CD_3CN with receptor **4** vs dihydrogen phosphate following the NH.

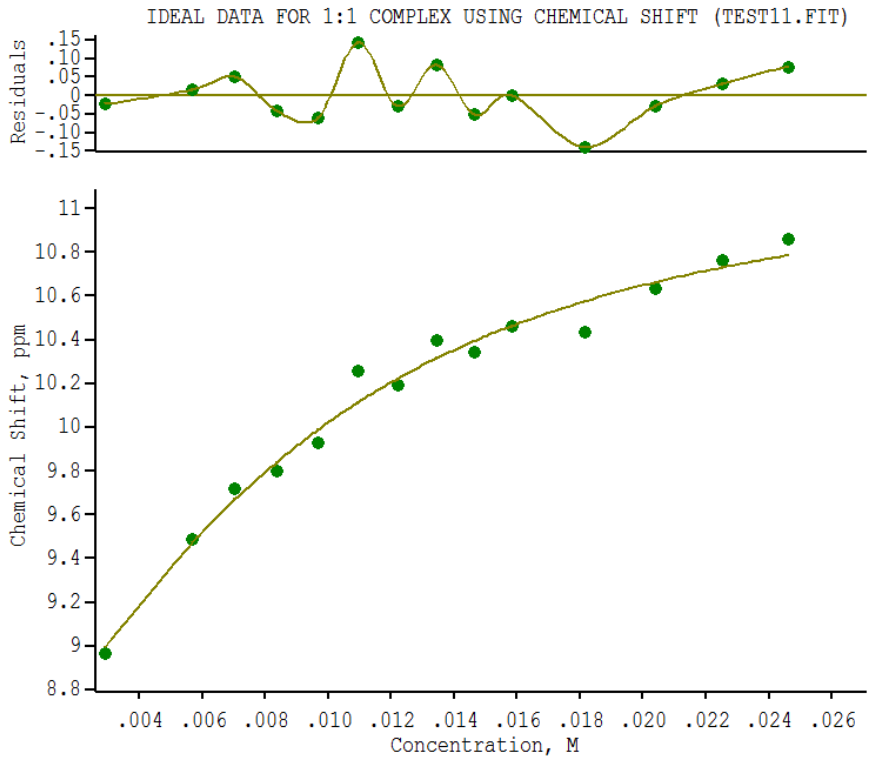

Figure S59. ^{1}H NMR titration in CD_3CN with receptor **7** vs dihydrogen phosphate following the NH.

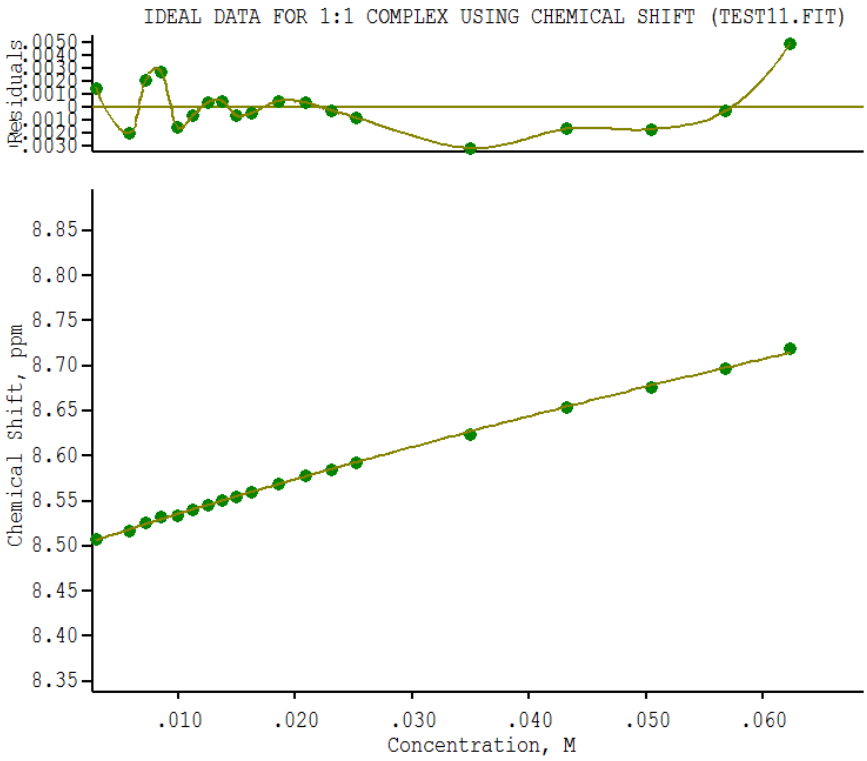

Figure S60. ^{1}H NMR titration in CD_3CN with receptor **8** vs dihydrogen phosphate following the NH.

Calculation of binding constants with PMP

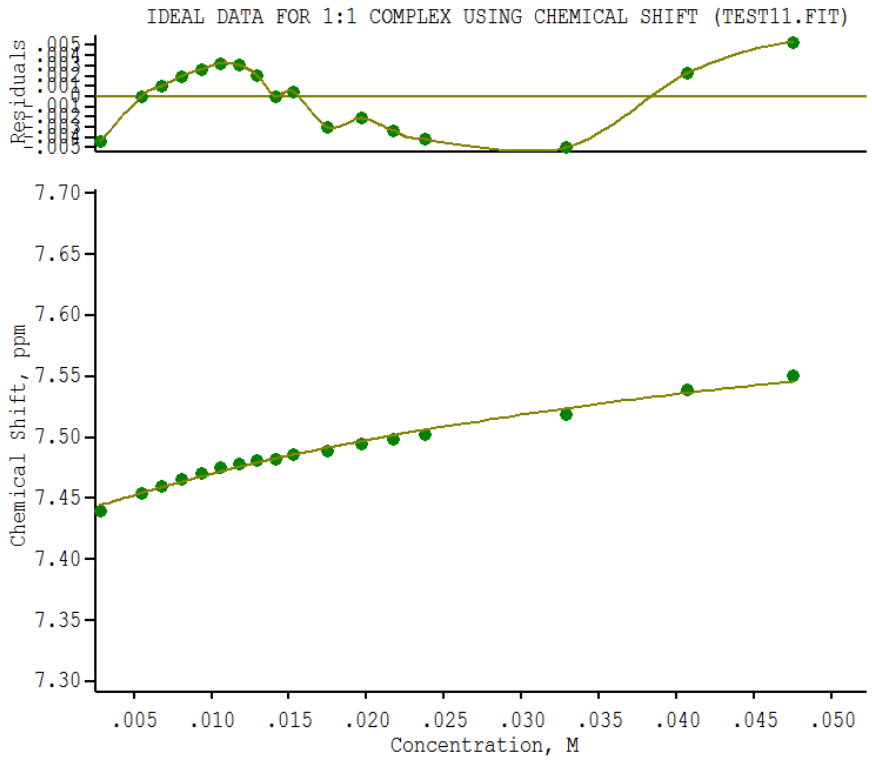

Figure S61. ^{1}H NMR titration in CD_3CN with receptor **1** vs PMP following the NH.

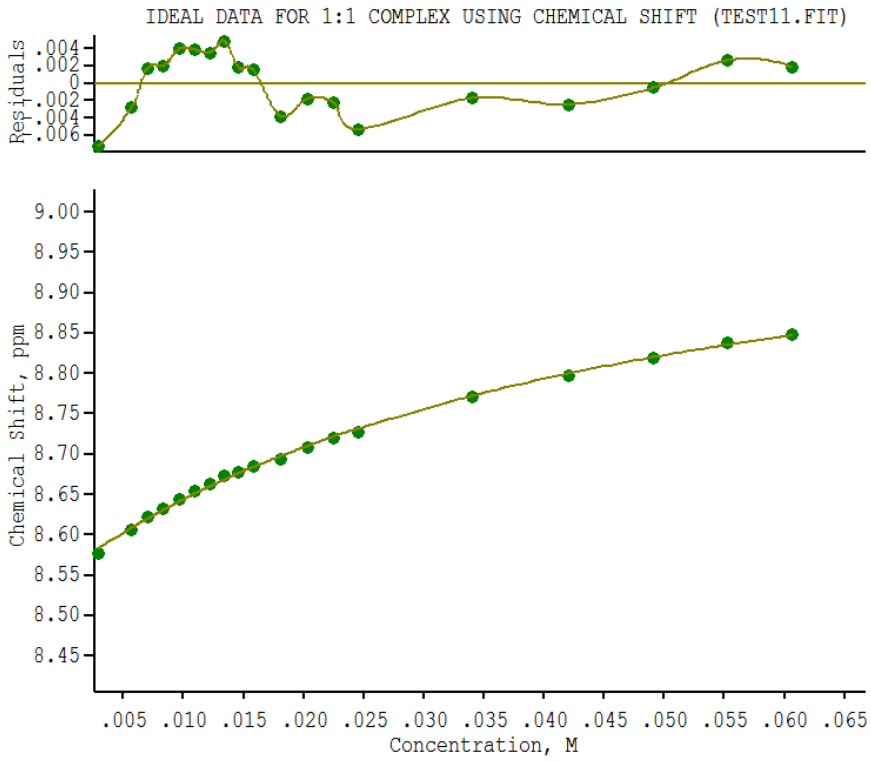

Figure S62. ^{1}H NMR titration in CD_3CN with receptor **2** vs PMP following the NH.

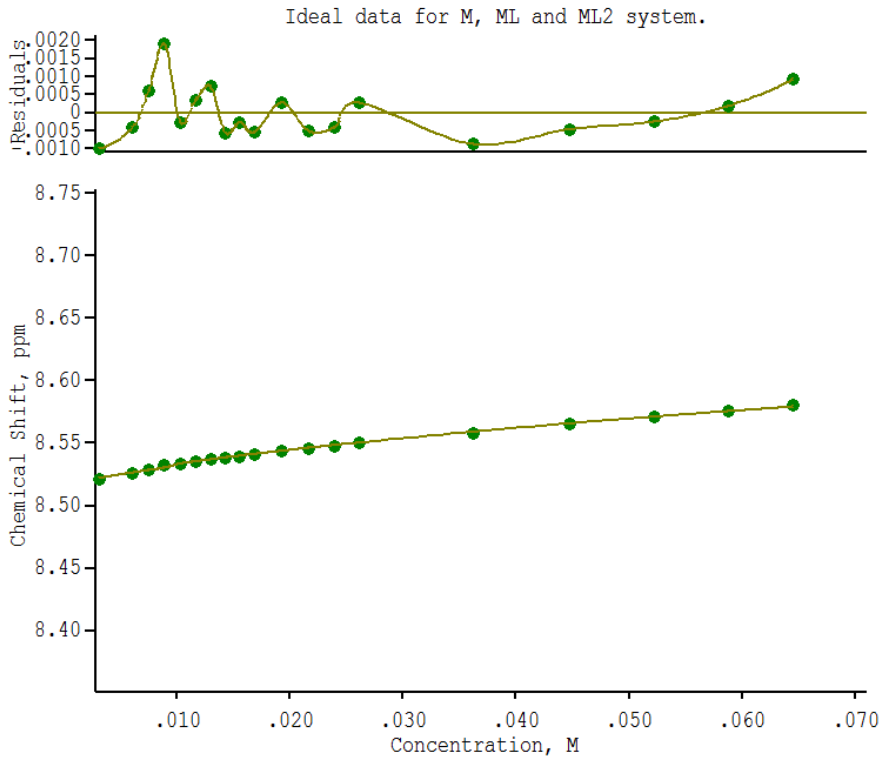

Figure S63. ^{1}H NMR titration in CD_3CN with receptor **5** vs PMP following the NH.

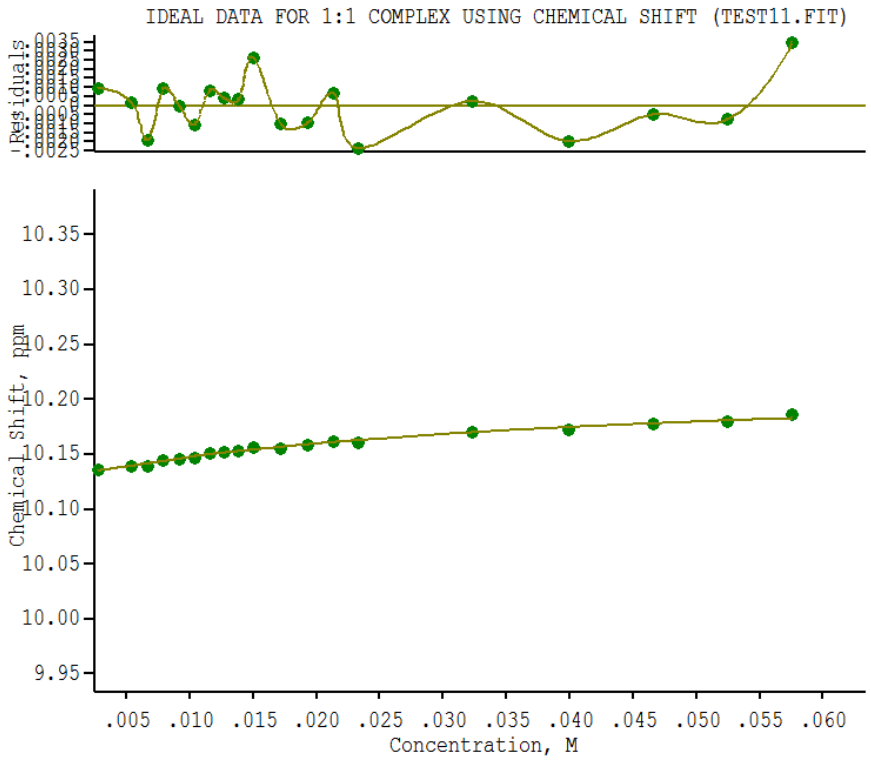

Figure S64. ^{1}H NMR titration in CD_3CN with receptor **6** vs PMP following the NH.

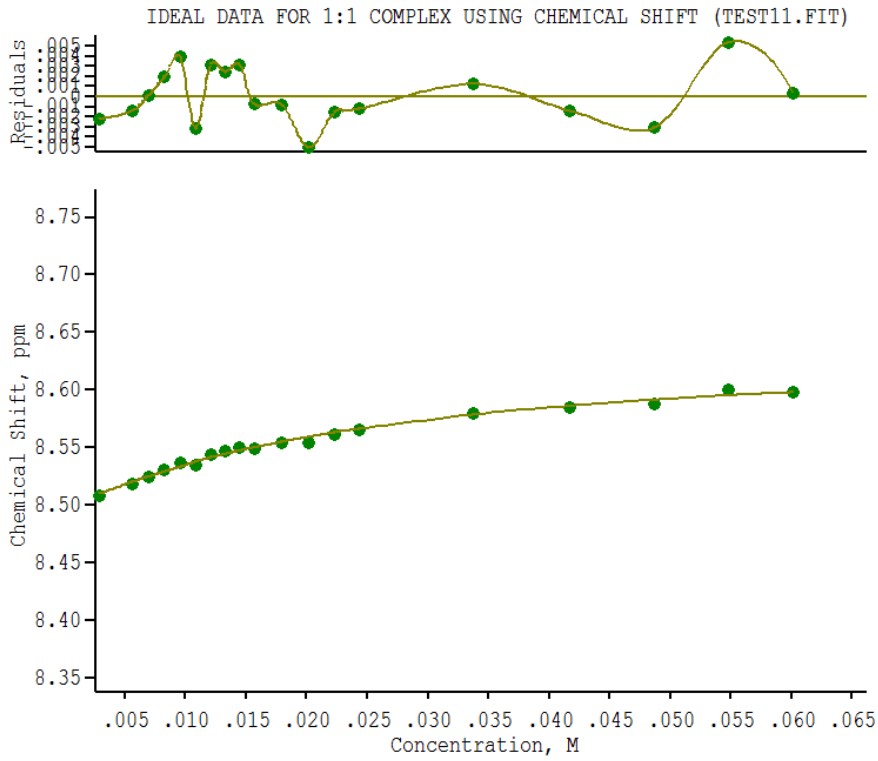

Figure S65. ^{1}H NMR titration in CD_3CN with receptor **8** vs PMP following the NH.

Calculation of binding constants with DMMP

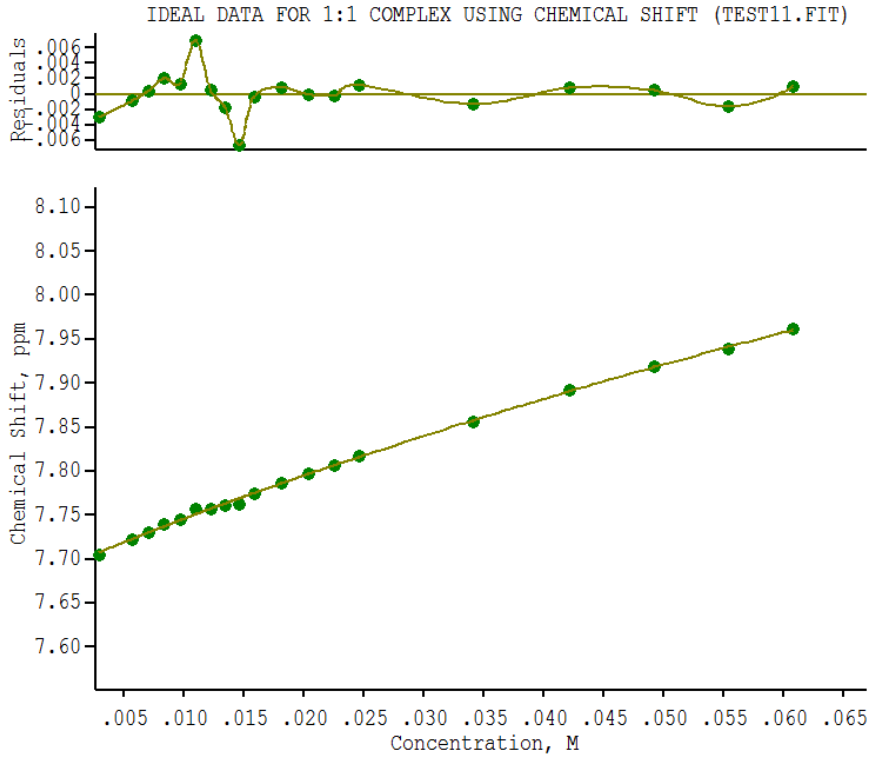

Figure S66. ^{1}H NMR titration in CD_3CN with receptor **1** vs DMMP following the NH.

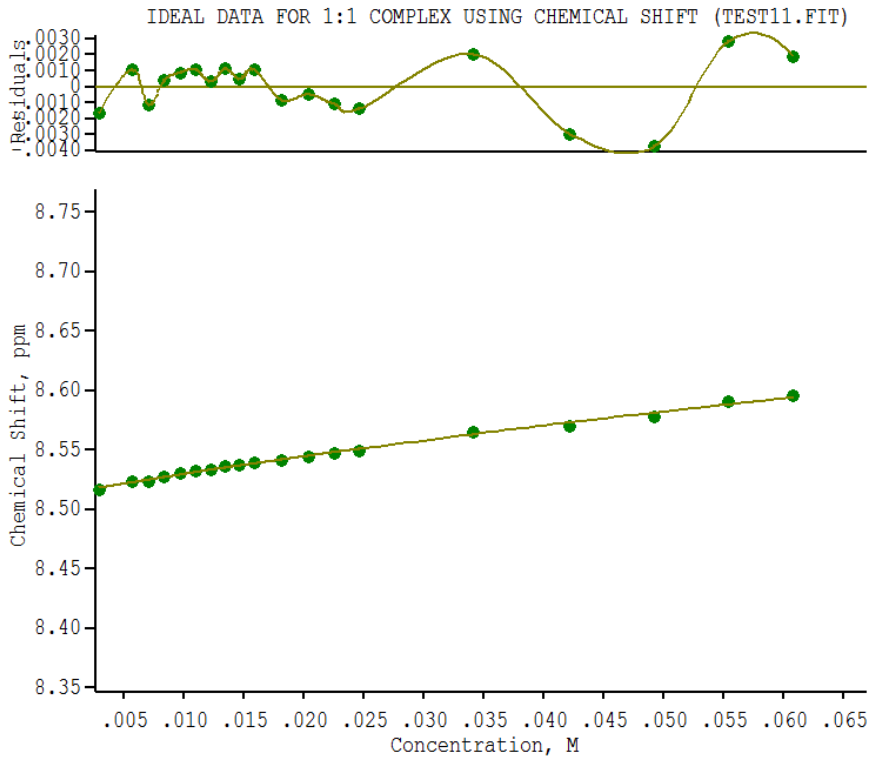

Figure S67. ^{1}H NMR titration in CD_3CN with receptor **1** vs DMMP following the NH.

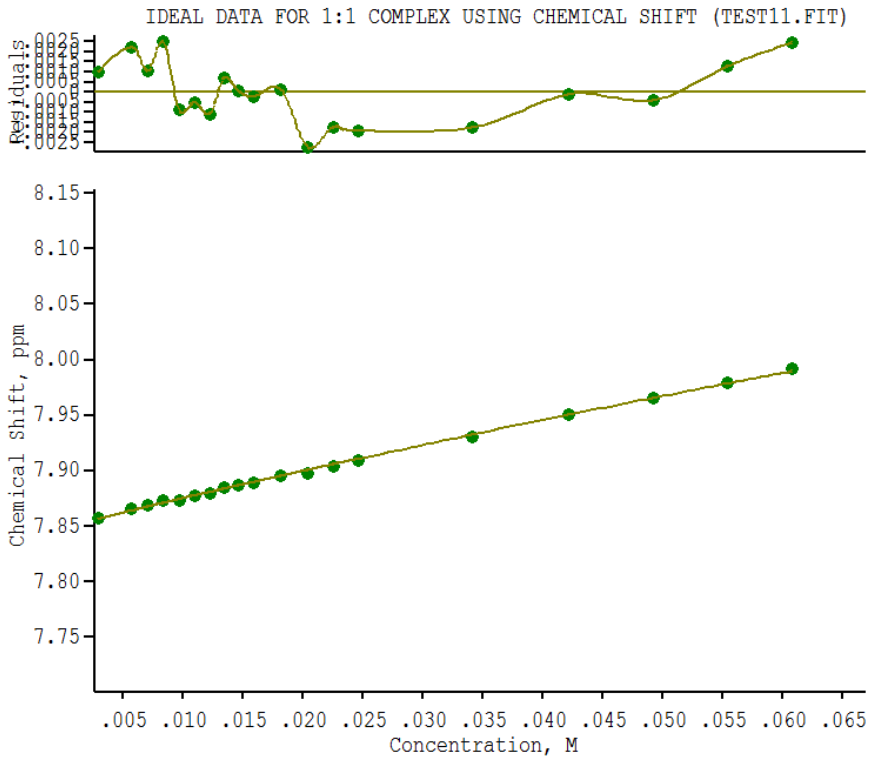

Figure S68. ^{1}H NMR titration in CD_3CN with receptor **3** vs DMMP following the NH.

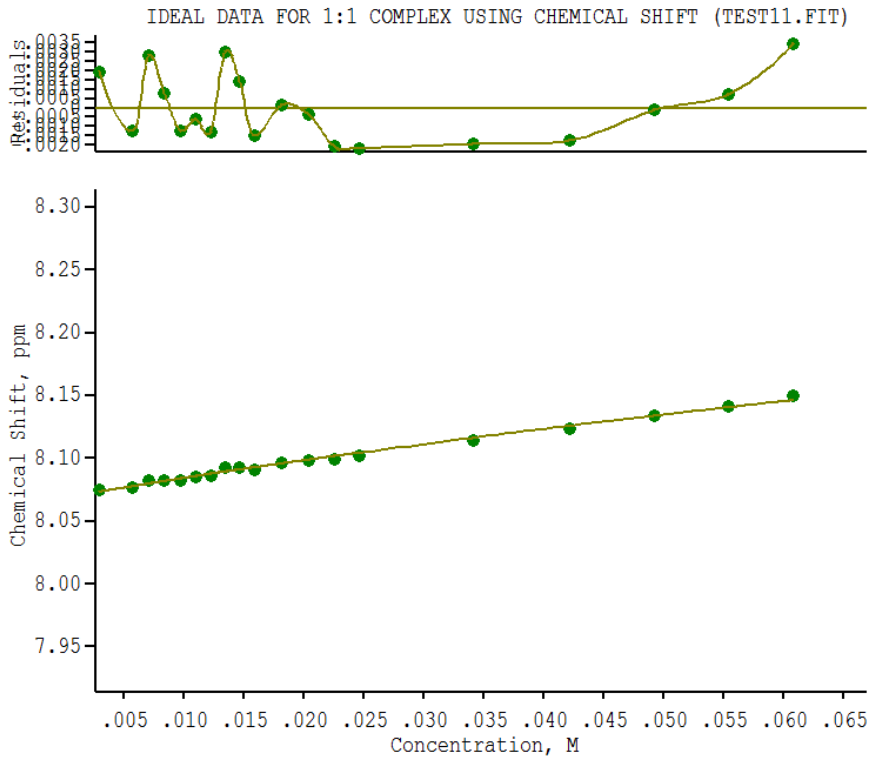

Figure S69. ^{1}H NMR titration in CD_3CN with receptor **5** vs DMMP following the NH.

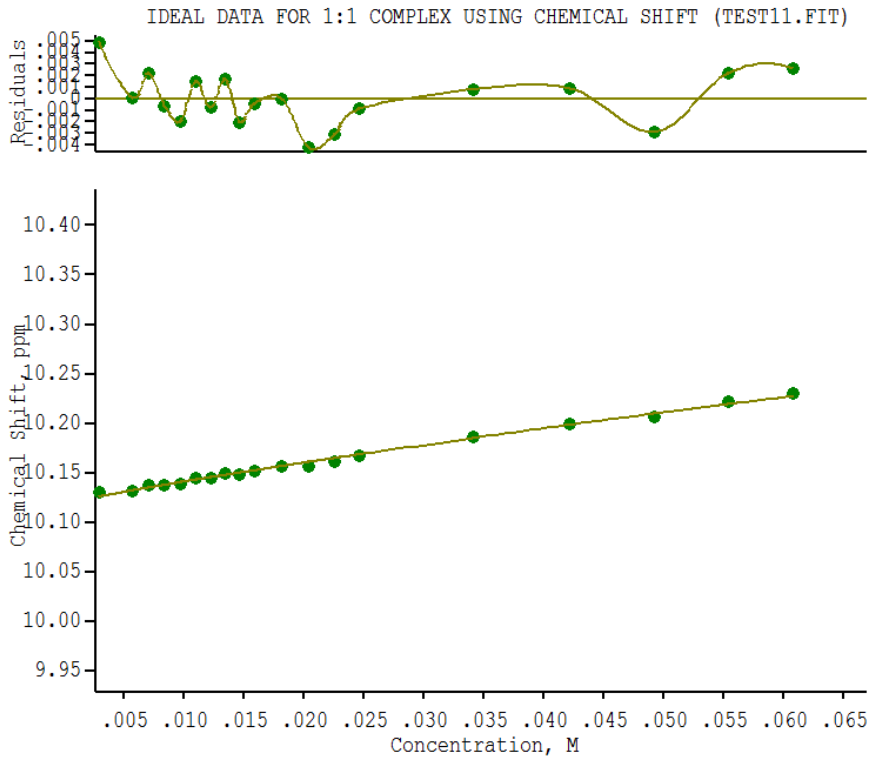

Figure S70. ^{1}H NMR titration in CD_3CN with receptor **6** vs DMMP following the NH.

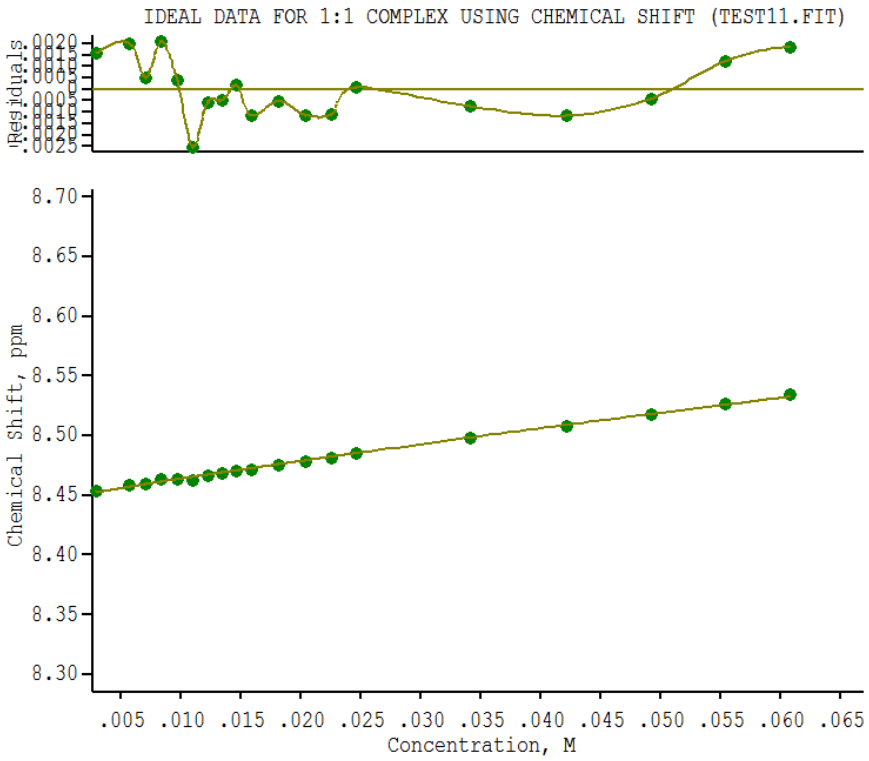

Figure S71. ^{1}H NMR titration in CD_3CN with receptor **7** vs DMMP following the NH.

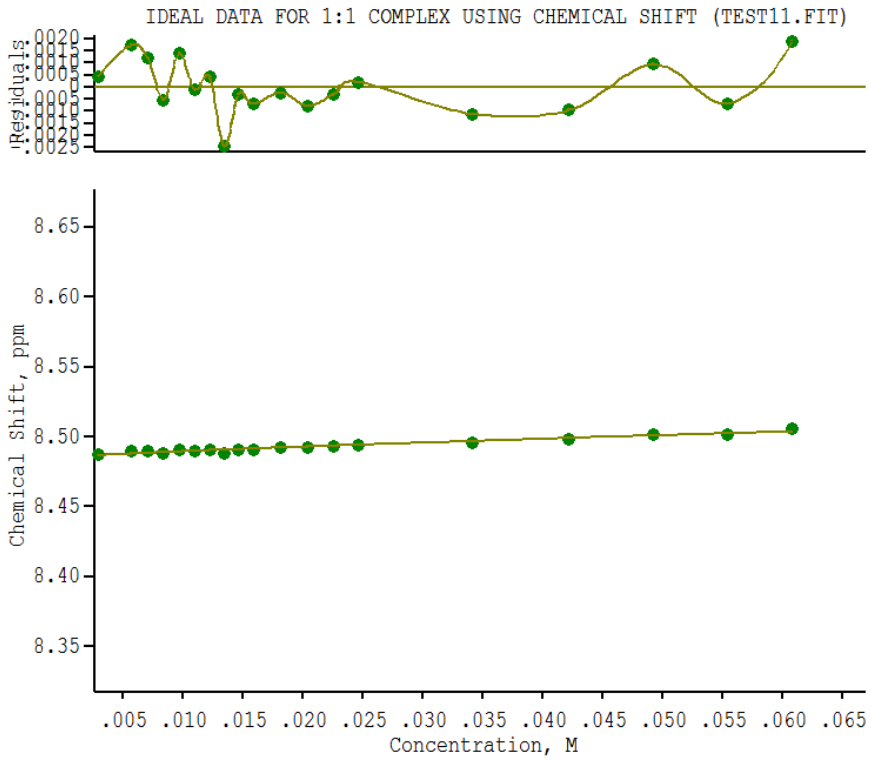

Figure S72. ^{1}H NMR titration in CD_3CN with receptor **8** vs DMMP following the NH.

Titration data and calculation of binding constants with GD

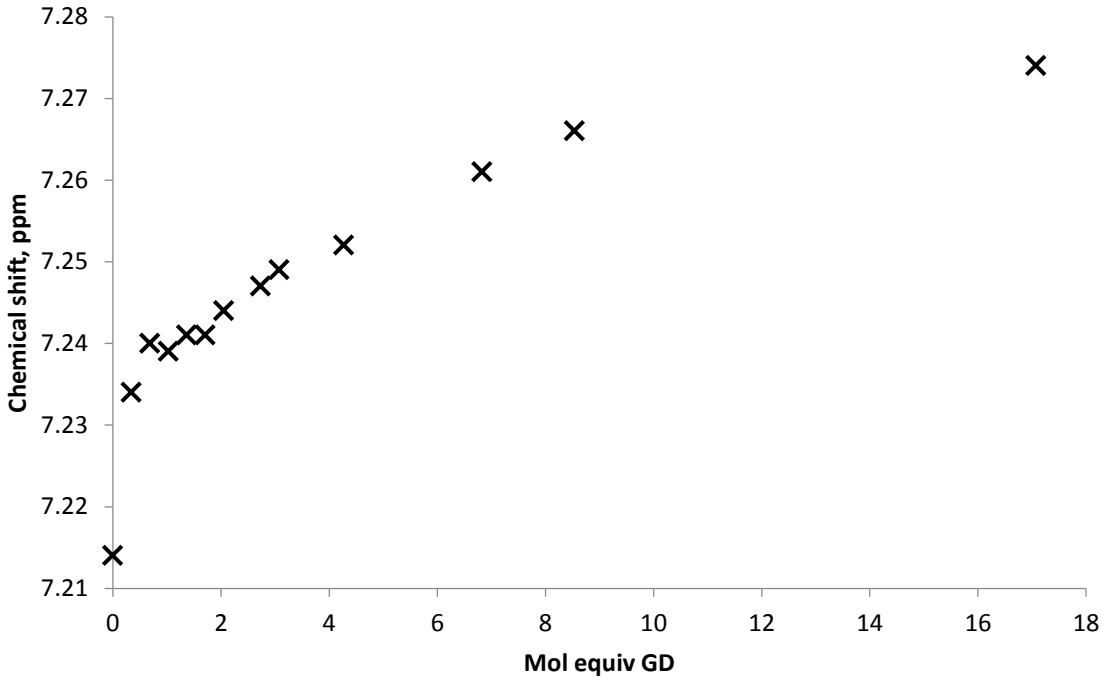

Figure S73. Binding curve generated by the titration of receptor **3** with GD in CD_3CN.

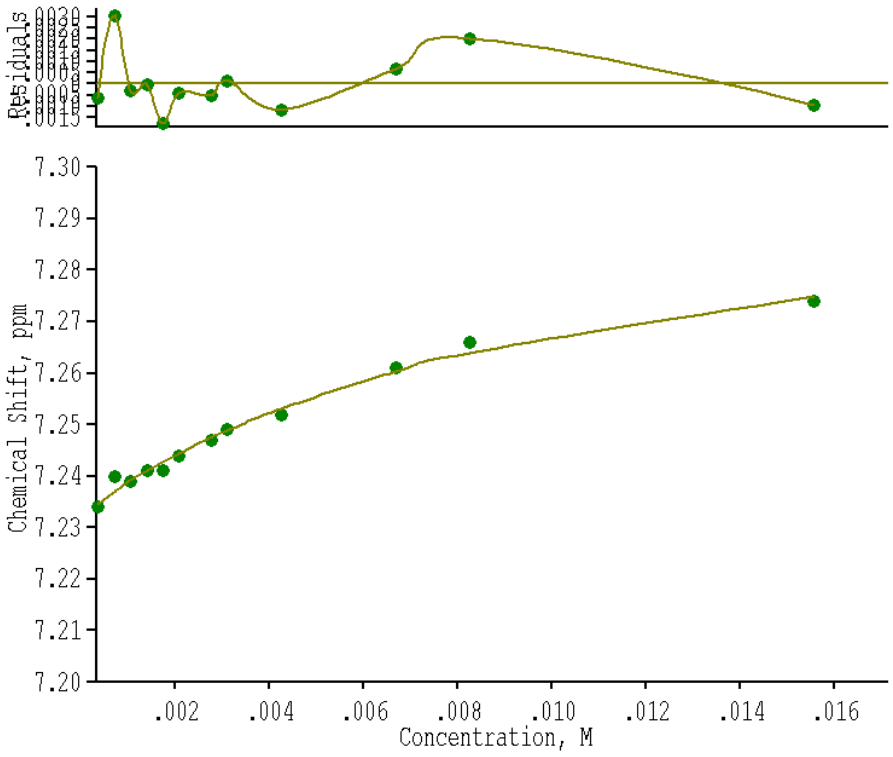

Figure S74. ^{1}H NMR titration in CD_3CN with receptor **3** vs GD following the NH.

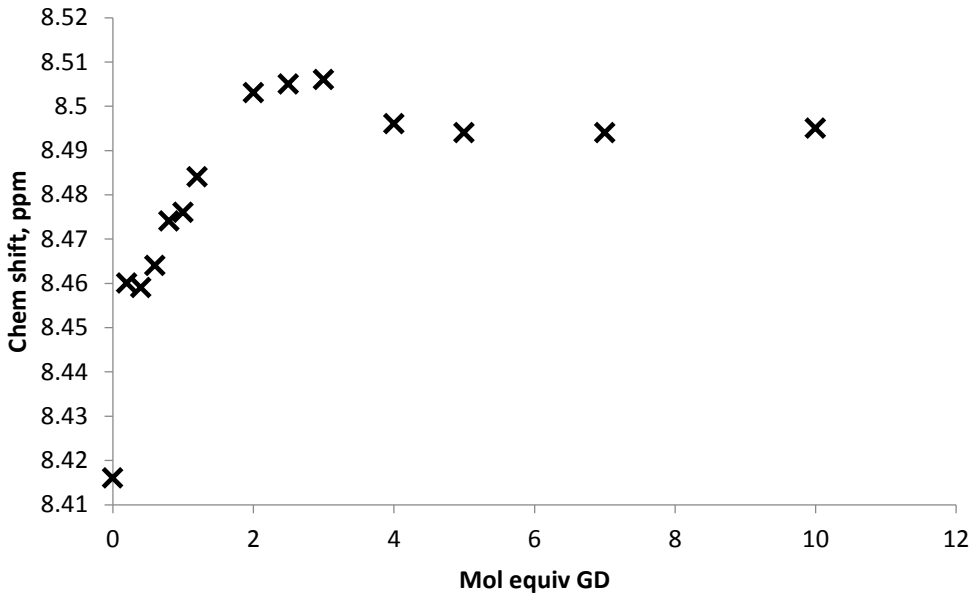

Figure S75. Binding curve generated by the titration of receptor **5** with GD in CD_3CN.

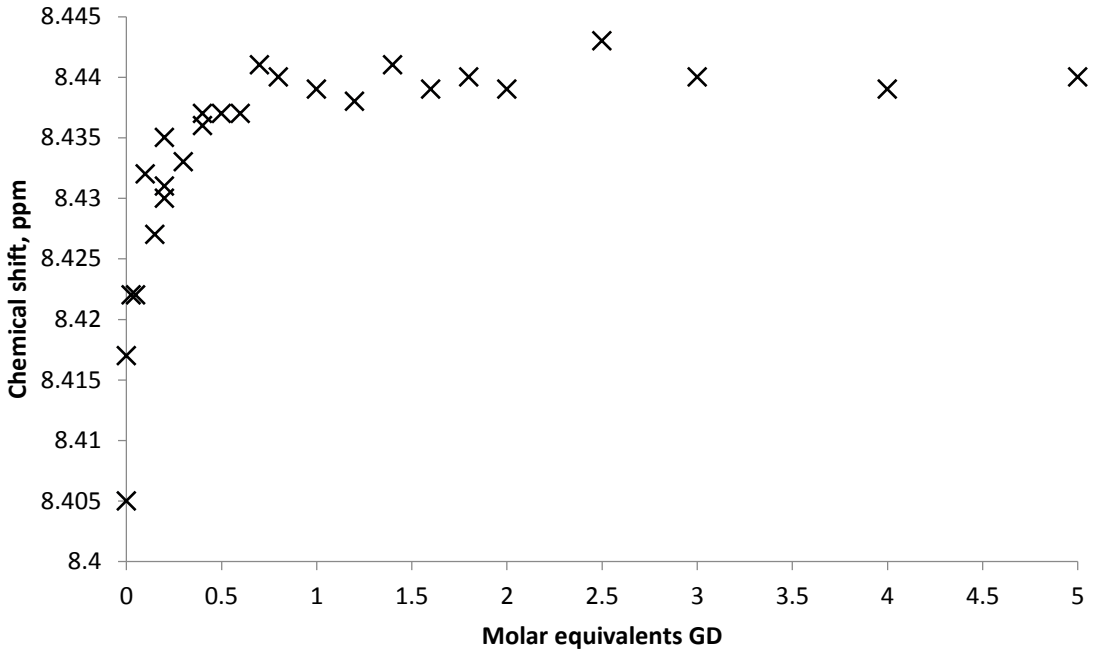

Figure S76. Binding curve generated by the titration of receptor **7** with GD in CD_3CN.

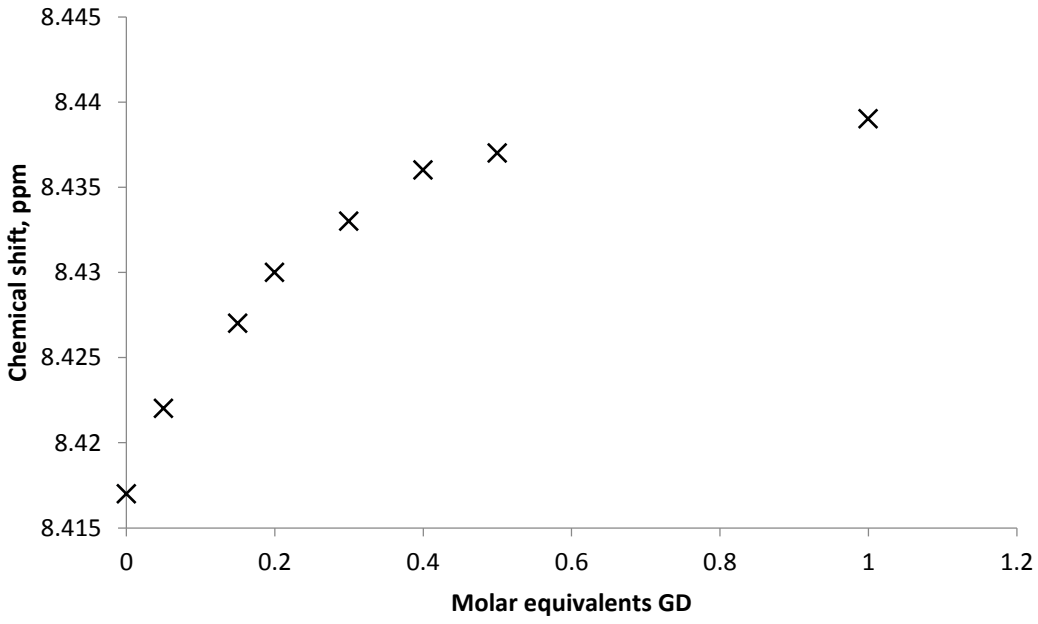

Figure S77. Selected region (approx. 10-90 % complex formation) of the binding curve generated by the titration of receptor **7** with GD in CD_3CN.

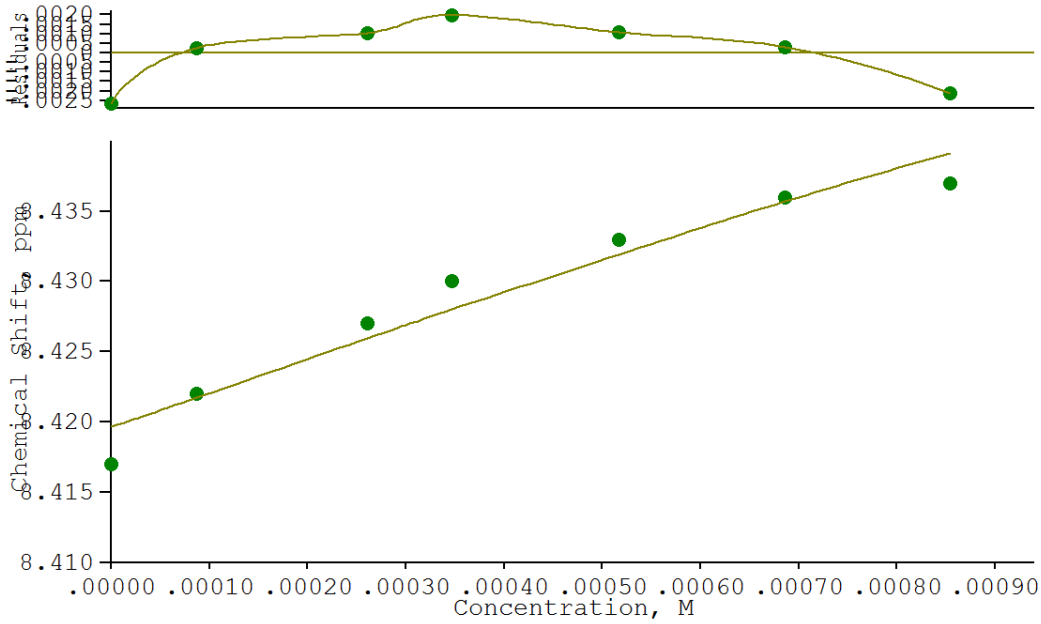

Figure S78. ^{1}H NMR titration in CD_3CN with receptor **3** vs GD following the NH; K_{assoc} = 1500 M^{-1}

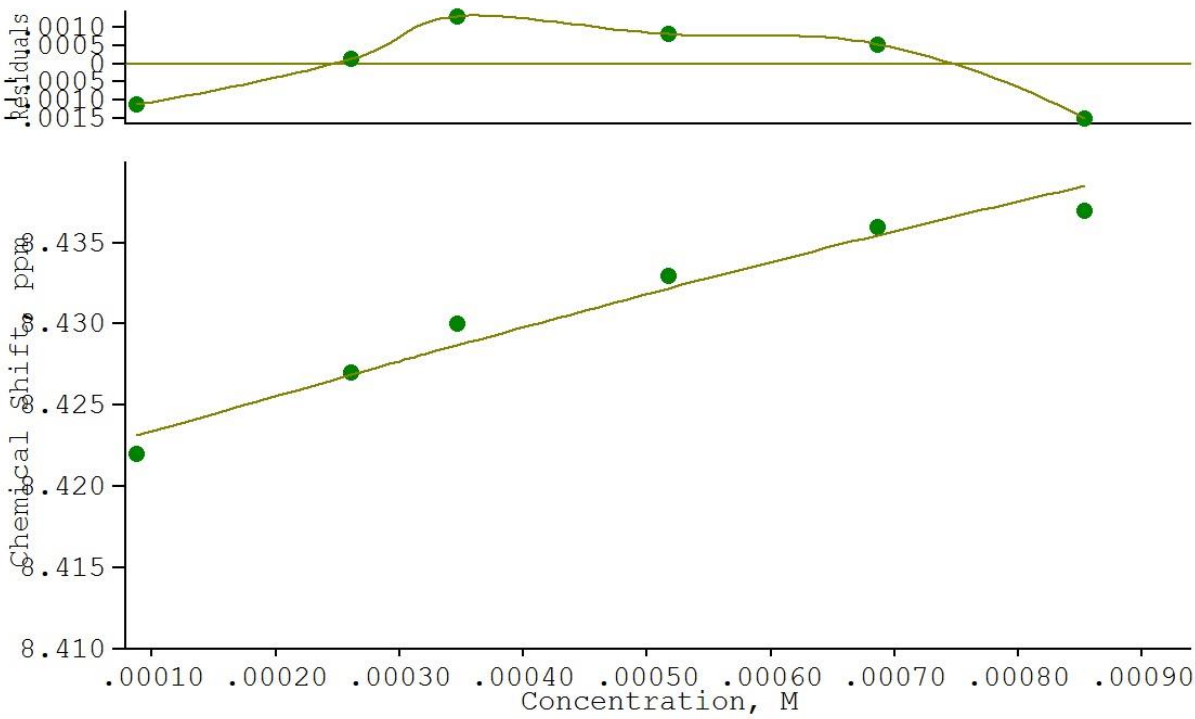

Figure S79. Additional data fitting of the ^{1}H NMR titration in CD_3CN with receptor **3** vs GD following the NH; K_{assoc} = 1500 M^{-1}

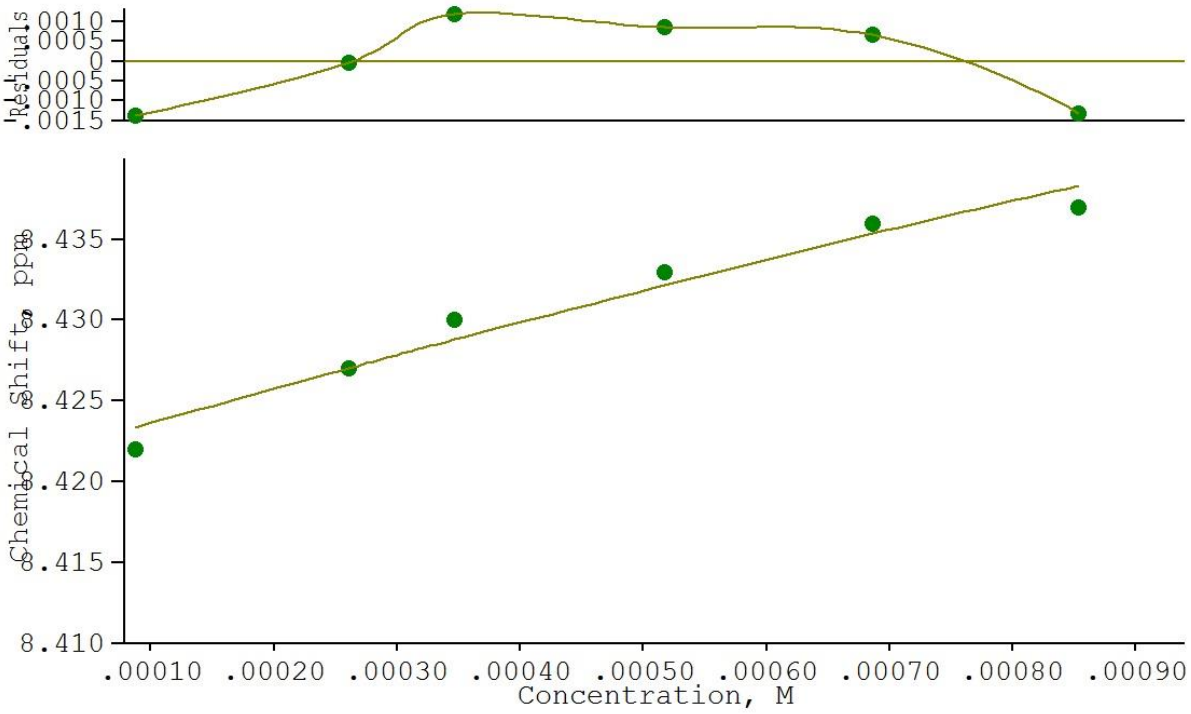

Figure S80. Additional data fitting of the ^{1}H NMR titration in CD_3CN with receptor **3** vs GD following the NH; K_{assoc} = 1350 M^{-1}

Crystallographic data

X-ray data were collected on a Rigaku AFC 12 diffractometer mounted on Rigaku FR-E+ Super Bright Ultra High Flux rotating anode CCD diffractometer equipped with VariMax very high flux (VHF) optics and Saturn 724+ CCD detector.

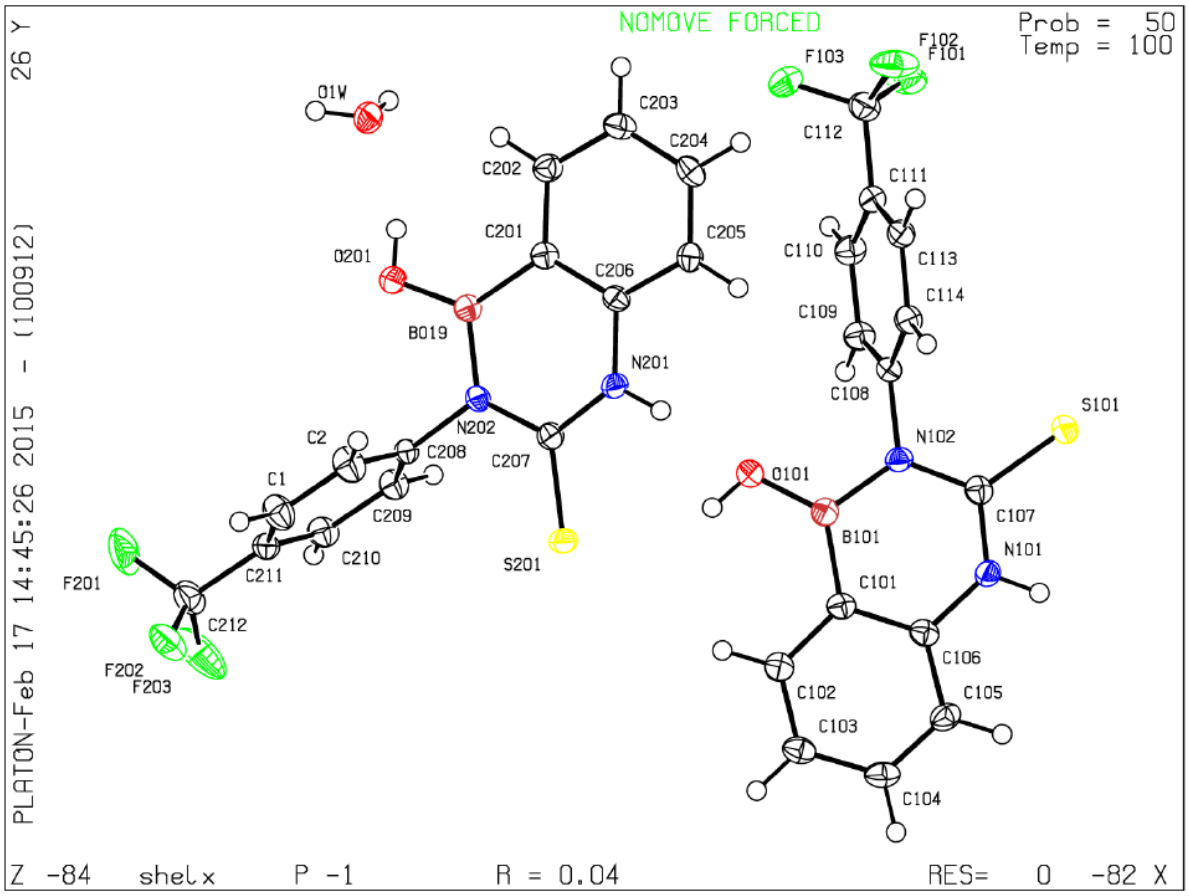

Figure S81. Crystal data for receptor **6**. CCDC 1430064, $C_{28}H_{22}B_2F_6N_4O_3S_2$ (M =662.23): triclinic, space group P-1 (no. 2), a = 9.018(2) Å, b = 12.159(3) Å, c = 14.878(4) Å, α = 107.953(2)°, β = 95.582(2)°, γ = 107.978(3)°, V = 1442.5(6) Å^3, Z = 2, T = 100(2) K, μ(MoKα) = 0.263 mm^{-1}, *Dcalc* = 1.525 g/mm^3, 31777 reflections measured (5.554 ≤ 2Θ ≤ 55.078), 6635 unique (R_{int} = 0.0859, R_{sigma} = 0.0629) which were used in all calculations. The final R_1 was 0.0430 (I > 2σ(I)) and wR_2 was 0.1199 (all data).

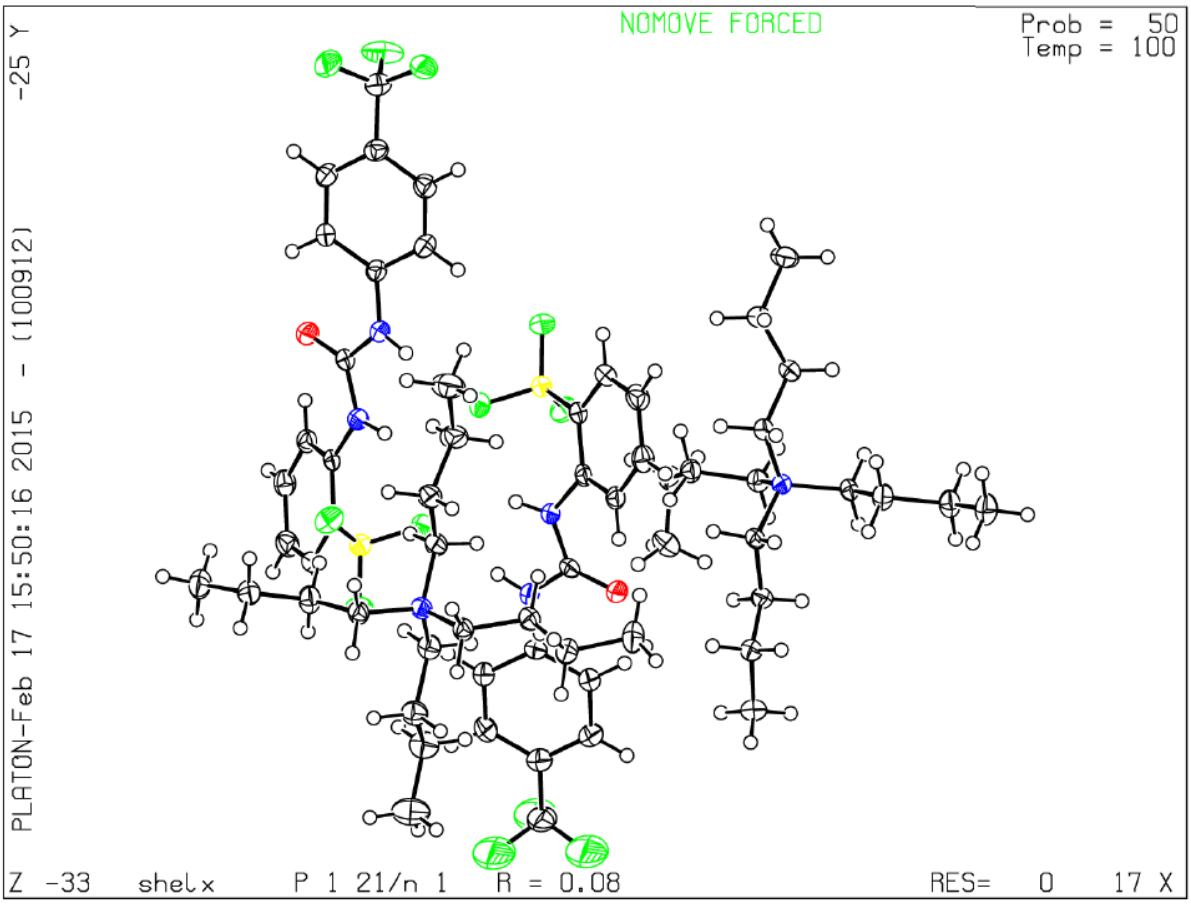

Figure S82. Crystal data for receptor **4**. CCDC 1430065, $C_{30}H_{46}BF_6N_3O$ (M =589.51): monoclinic, space group $P2_1/n$ (no. 14), a = 17.561(6) Å, b = 16.385(5) Å, c = 23.157(8) Å, β = 103.246(5)°, V = 6486(4) Å^3, Z = 8, T = 100(2) K, μ(MoKα) = 0.096 mm^{-1}, *Dcalc* = 1.207 g/mm^3, 63627 reflections measured ($4.972 \leq 2\Theta \leq 54.98$), 14809 unique ($R_{int}$ = 0.0855, R_{sigma} = 0.0660) which were used in all calculations. The final R_1 was 0.0763 ($I > 2\sigma(I)$) and wR_2 was 0.2461 (all data).