Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Heteroditopic receptor flexibility – an important design principle for effective ion pair extractants based on carboxylates studies

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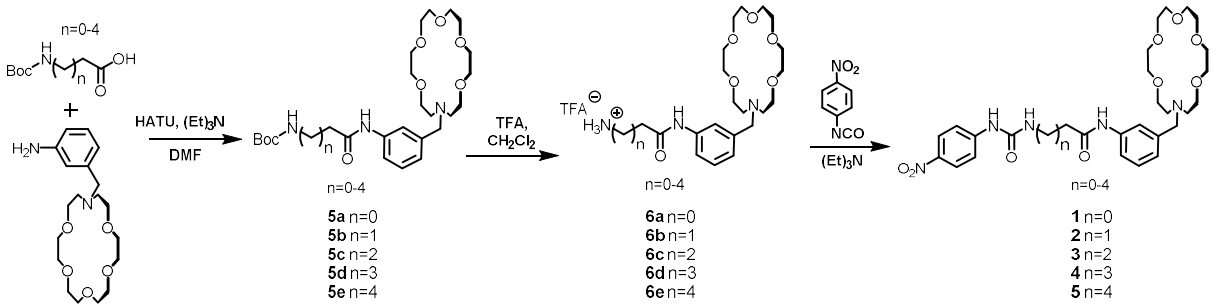
General Information

All solvents and starting materials were purchased from Merc or Fluorochem. All commercial-grade chemicals were used without further purification. The TBAOAc salt and cation ClO_4^- or PF_6^- salts were dried under high vacuum at 30–45 °C before using. ^{1}H and ^{13}C NMR spectra as well as titration experiments were performed on a 300 MHz Bruker Avance spectrometer. ^{1}H NMR chemical shifts δ are reported in ppm with reference to the tetramethylsilane or protonated residual solvent signal ($CDCl_3$/CD_3CN). N-(3-Nitrobenzyl)-aza-18-crown-6 was prepared according to our literature report [1].

1. Synthetic route to the receptors 1-5 with general experimental procedures and NMR spectra



General procedure for compounds 5(a-e)

The solution of 1.65 mmol (1.1 eq) N-Boc-amino acid, 1.65 mmol (1.1 eq) HATU and 0.73 g (1.0 mL, 7.2 mmol) triethylamine, dissolved in 17 mL of dry DMF, was stirred under argon atmosphere at room temperature for 1 h. Then 1.5 mmol of N-(3-nitrobenzyl)-aza-18-crown-6 was added. The reaction mixture was then stirred at room temperature overnight. Then the solvent was evaporated. The oily residue was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The oil was purified by column chromatography on silica gel with chloroform then with 4% methanol/chloroform as eluents to give desired product.

(3-aminobenzyl)-aza-18-crown-6 amide of (tert-butyloxycarbonyl)glycine (5a): 0.66 g (1.26 mmol) of an amorphous solid, 84% of yield; R_f (10%MeOH/DCM) = 0.63; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.64 (s, 1H), 7.74 (s, 1H), 7.62 (m, 1H), 7.40 (m, 1H), 7.20 (d, 1H, J=6 Hz), 5.74 (s, 1H), 4.27 (s, 2H), 3.81 (d, 1H, J=6 Hz), 3.76 (t, 4H, J=6 Hz), 3.60 (m, 18H), 3.22 (bs, 4H),1.43 (s, 9H); ^{13}C NMR (75 MHz, CD_3CN): δ 169.70, 157.20, 140.04, 130.64, 127.53, 123.07, 121.64, 80.17, 70.91, 70.74, 70.60, 65.09, 57.18, 54.26, 45.23, 28.58, 28.04

(3-aminobenzyl)-aza-18-crown-6 amide of 2-(tert-butyloxycarbonyl)amino)propanoic acid (5b): 0.41 g (0.78 mmol) of an amorphous solid, 52% of yield; R_f (10% MeOH/DCM) = 0.5; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.61 (s, 1H), 7.73 (s, 1H), 7.62 (bs, 1H), 7.39 (m, 1H), 7.17 (d, 1 H, J=9 Hz), 5.50 (bs, 1H), 4.25 (bs, 2H), 3.75 (t, 4H, J=6 Hz), 3.59 (m, 16H), 3.35 (dd, 2H, J_1=6 Hz, J_2=12 Hz), 3.21 (m, 4H), 2.51 (t, 2H, J=6 Hz), 1.39 (s, 9H); ^{13}C NMR (75 MHz, CD_3CN): δ 171.24, 156.87, 140.43, 130.55, 127.29, 122.85, 121.40, 79.42, 79.16, 70.87, 70.66, 70.58, 70.53, 65.19, 57.22, 54.50, 37.87, 37.43, 28.62.

(3-aminobenzyl)-aza-18-crown-6 amide of 3-(tert-butyloxycarbonyl)amino)butanoic acid (5c): 0.74 g (1.37 mmol) of an amorphous solid, 92% of yield; R_f (10% MeOH/DCM) = 0.6; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.65 (s, 1H), 7.73 (s, 1H), 7.61 (bs, 1H), 7.39 (m, 1H), 7.17 (d, 1H, J=9 Hz), 5.41 (bs, 1H), 4.30 (bs, 2H), 3.61 (m, 18H), 3.25 (m, 4h), 3.9 (dd, 2H, J_1=6 Hz, J_2=12 Hz), 2.34 (t, 2H, J=6 Hz), 1.78 (q, 2H, J=6 Hz), 1.40 (s, 9H); ^{13}C NMR (75 MHz, CD_3CN): δ 171.52, 156.24, 139.66, 129.56, 126.43, 122.12, 78.18, 70.04, 69.64, 63.78, 55.67, 53.66, 39.52, 33.89, 27.67, 25.70

(3-aminobenzyl)-aza-18-crown-6 amide of 4-(tert-butyloxycarbonyl)amino)pentanoic acid (5d): 0.74 g (1.37 mmol) of an amorphous solid, 69% of yield; R_f (10% MeOH/DCM) = 0.52; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.53 (s, 1H), 7.72 (s, 1H), 7.63 (d, 1H, J=9 Hz), 7.38 (m, 1H), 7.17 (d, 1H, J=6 Hz), 5.35 (bs, 1H), 4.27 (bs, 2H), 3.76 (m, 4H), 3.61 (m, 16H), 3.23 (m, 4H), 3.04 (m, 2H) , 2.34 (m, 2H), 1.64 (m 2H), 1.48 (m 2H), 1.39 (s, 9H);^{13}C NMR (75 MHz, CD_3CN): 172.64, 156.87, 140.55, 130.45, 127.05, 122.69, 121.36, 79.05, 78.92, 70.80, 70.59, 70.47, 64.87, 57.10, 54.24, 40.60, 37.08, 30.22, 28.58, 23.20

(3-aminobenzyl)-aza-18-crown-6 amide of 5-(tert-butyloxycarbonyl)amino)hexanoic acid(5e): 0.4 g (0.7 mmol) of an amorphous solid, 63% of yield; R_f (10% MeOH/DCM) = 0.55; ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 8.27 (bs, 1H), 7.97 (bs, 1H), 7.50 (bs, 2H), 7.06 (m, 2H) , 4.70 (bs, 1H), 4.22 (bs, 1H), 3.60 (m, 18H), 3.52 (m, 2H), 3.05 (m, 2H), 2.36 (bs, 2H), 2.33 (m, 2H), 1.67 (m, 2H), 1.44 (m, 2H), 1.38 (bs, 9H); ^{13}C NMR (75 MHz, CD_3CN): 172.75, 156.98, 140.66, 130.56, 127.16, 122.80, 121.47, 79.16, 79.02, 70.90, 70.69, 70.58, 64.97, 57.21, 54.35, 40.71, 37.19, 30.33, 28.68, 23.31.

General procedure for compounds 6(a-e)

The solution of (3-aminobenzyl)-aza-18-crown-6 amide of N-Boc-aminoacides (1.62 mmol) in 4 mL of DCM was cooled to 0 °C using dry ice/water bath. To this solution 3.0 mL of trifluoroacetic acid was added. Then cooling bath was removed and the reaction mixture was stirred at room temperature for 1 h. The full conversion of the substrate was confirmed by TLC analysis in 10% MeOH/DCM. Then the volatiles were evaporated and the residue was dried

under high vacuum to give desired compound in form of TFA salts. These compounds were used in the next step without further purification.

General procedure for Receptors 1-5:

In round bottom flask the 1.26 mmol of trifluoroacetic acid salt of (3-aminobenzyl)-aza-18-crown-6 amide of amino acids (6a-e) and 2.0 mL (1.45 g, 1.4 mmol, 2 eq.) of triethylamine were dissolved in 5 mL of dry THF. To the resulting mixture 4-nitrophenyl isothiocyanate (1.39 mmol, 1.1 eq.) was added, under argon atmosphere. The reaction mixture was stirred overnight at room temperature. Then the solvent was evaporated and the resulting oil was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. Receptor was absorbed on silica gel and filtered using ethyl acetate to remove isocyanate impurities, and then 20% MeOH/DCM. Then after evaporation the receptor was dissolved in chloroform and some portion of solid $MgSO_4$ was added and left overnight. After filtration and solvent evaporation the receptor●salt complex was purified by column chromatography on silica gel with 10% MeOH/DCM as eluents to give an amorphous solid. For decomplexation of receptor●salt complex, the complexes of receptors **1-5** were dissolved in chloroform and washed 3 times with distilled water. Then solvents were evaporated (without drying) to give "free" desired receptor.

Receptor 1: 0.33 g (0.57 mmol) of an amorphous yellow solid, 45% of yield; R_f (10% MeOH/DCM) = 0.22; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.71 (s, 1H), 8.35 (s, 1H), 8.07 (d, 2H, J=9 Hz), 7.57 (m, 4H), 7.23 (t, 1H, J=9 Hz), 7.02 (d, 1H, J=6 Hz), 6.13 (m, 1H), 3.93 (d, 2H, J=6 Hz), 3.58 (m, 22H), 2.67 (m, 4H); ^{13}C NMR (75 MHz, CD_3CN): 169.43, 155.73, 147.42, 142.59, 139.29, 129.44, 125.83, 125.18, 121.06, 118.18, 71.34, 71.11, 70.87, 70.41, 60.01, 55.18, 44.67; HR-MS (ESI): m/z = 612.2620 $[M+Na]^+$ (calc. for $C_{28}H_{39}N_5O_9Na$: 612.2643)

Receptor 2: 0.28 g (0.46 mmol) of an amorphous light-yellow solid, 60% of yield; R_f (10% MeOH/DCM) = 0.3; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.70 (s, 1H), 8.23 (s, 1H), 8.03 (d, 2H, J=9 Hz), 7.54 (m, 4H), 7.19 (t, 1H, J=6 Hz), 6.97 (d, 1H, J=9 Hz), 6.11 (t, 1H, J= 6Hz), 3.51 (m, 26H), 2.63 (t, 4H, J=6Hz), 2.57 (t, 2H, J=6Hz); ^{13}C NMR (75 MHz, CD_3CN): 171.43, 155.61, 147.64, 142.21, 141.60, 139.52, 129.33, 125.78, 125.05, 120.98, 119.13, 118.26, 118.03, 71.24, 71.03, 70.80, 70.23, 60.03, 54.96, 37.72, 36.84, 2.09, 1.82, 1.54, 1.26, 0.99, 0.71, 0.44; HR-MS (ESI): m/z = 626.2819 $[M+Na]^+$ (calc. for $C_{29}H_{41}N_5O_9Na$: 626.2802)

Receptor 3: 0.45 g (0.74 mmol) of an amorphous yellow solid, 55% of yield; R_f (10% MeOH/DCM) = 0.28; ^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 9.51 (s, 1H), 9.24 (s, 1H), 8.04 (d, 2H, J=9 Hz), 7.71 (s, 1H), 7.63 (m, 3H), 7.30 (m, 1H), 7.10 (m, 2H), 4.11 (bs, 2H), 3.69 (t, 4h, J=6 Hz), 3.55 (m, 15H), 3.25 (m, 2H), 3.09 (m, 4H), 2.39 (m, 2H), 1.85 (m, 2H); ^{13}C NMR (75 MHz, CD_3CN): 172.58, 162.32, 161.88, 156.27, 148.51, 141.88, 140.57, 130.12, 126.34, 125.83, 122.27, 120.84, 120.12,117.82, 116.21, 79.12, 71.00, 70.90, 70.80, 66.42, 58.19, 54.15, 39.47, 34.89, 26.94; HR-MS (ESI): m/z = 640.2950 $[M+Na]^+$ (calc. for $C_{30}H_{43}N_5O_9Na$: 640.2958)

Receptor 4: 0.48 g (0.76 mmol) of an amorphous dark-yellow solid, 58% of yield; R_f (10% MeOH/DCM) = 0.42;^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 9.10 (s, 1H), 8.79 (s, 1H), 8.03 (d, 2H, J=9 Hz), 7.58 (m, 4H), 7.25 (m, 1H), 7.05 (d, 1H, J=9 Hz), 6.63 (m, 1H), 3.88 (bs, 2H), 3.54 (m, 21H), 3.18 (dd, 2H, J_1=6 Hz, J_2=12 Hz), 2.89 (m, 4H), 2.33 (m, 2H), 1.67 (m, 2H), 1.51 (m, 2H); ^{13}C NMR (75 MHz, CD_3CN): 172.72, 156.01, 148.34, 141.95, 140.24, 129.81, 125.84, 121.89, 120.15, 117.86, 71.07, 70.88, 70.75, 67.87, 58.54, 54.72, 39.97, 37.25, 30.21, 23.55; HR-MS (ESI): m/z = 654.3091 $[M+Na]^+$ (calc. for $C_{31}H_{45}N_5O_9Na$: 654.3115)

Receptor 5: 0.28 g (0.43 mmol) of an amorphous orange solid, 63% of yield; R_f (10% MeOH/DCM) = 0.43;^{1}H NMR (300 MHz, CD_3CN, δ_{ppm}): 8.45 (s, 1H), 8.19 (d, 2H, J=9 Hz), 8.01 (s, 1H), 7.58 (m, 4H), 7.22 (m, 1H), 7.00 (d, 1H, J=9 Hz), 5.69 (s, 1H), 3.66 (s, 2H), 3.58 (m, 20H), 3.19 (m, 2H), 2.71 (m, 4H), 2.31 (m, 2H), 1.68 (m, 2H), 1.53 (m, 2H), 1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 172.77, 155.82, 147.46, 140.86, 138.99, 128.85, 124.96, 124.22, 120.97,

117.09, 69.25, 68.13, 53.87, 39.40, 37.19, 29.27, 26.38, 25.27; HR-MS (ESI): m/z = 668.3264 $[M+Na]^+$ (calc. for $C_{32}H_{47}N_5O_9Na$: 668.3271)

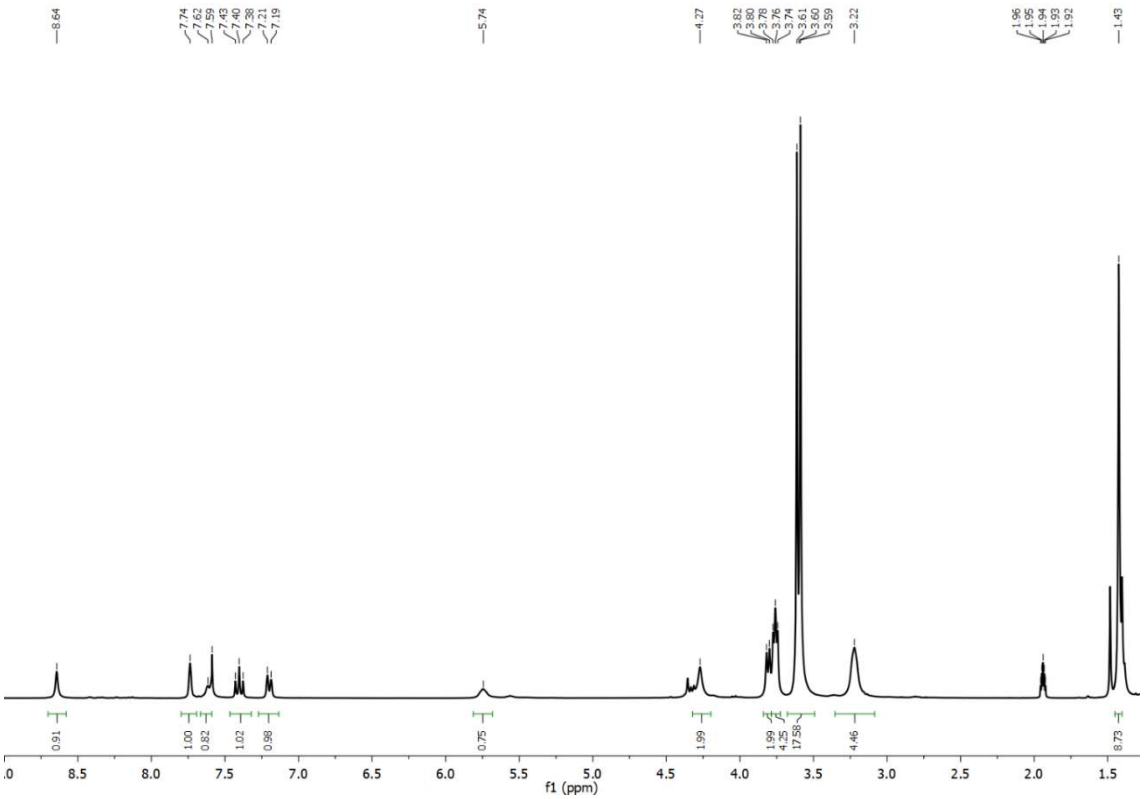


Figure S1. ^{1}H NMR spectrum of **5a**

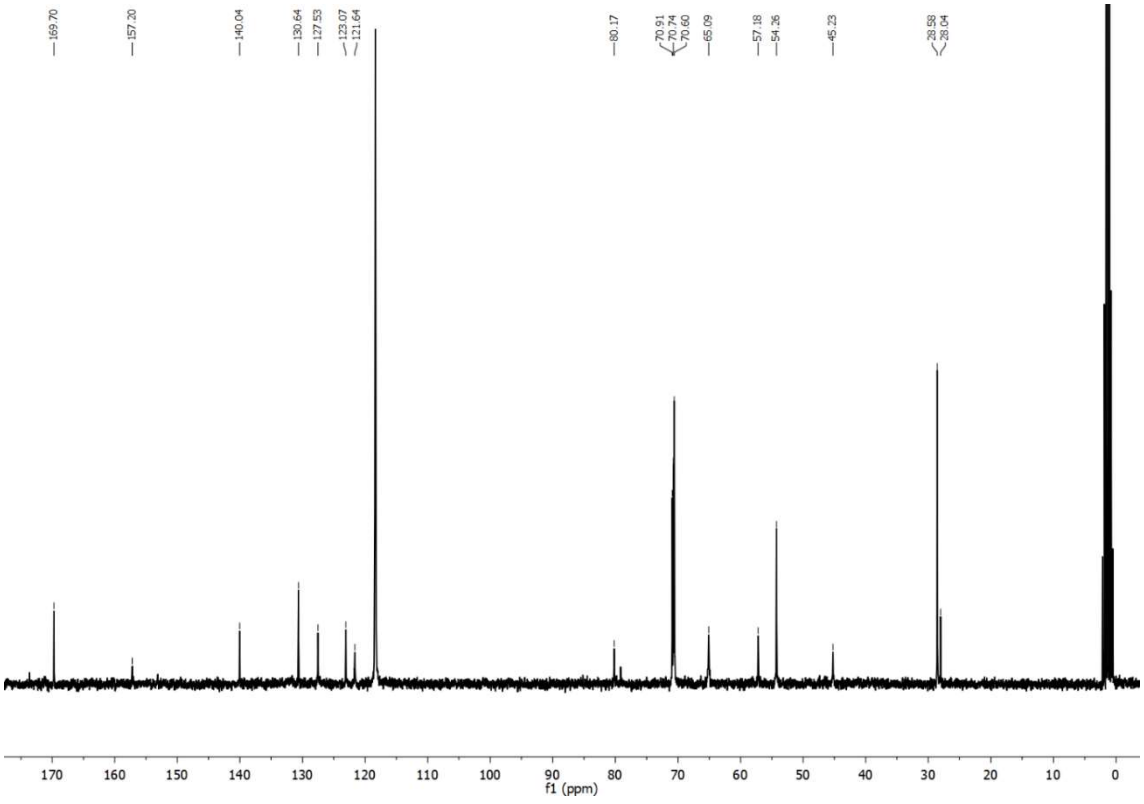


Figure S2. ^{13}C NMR spectrum of **5a**

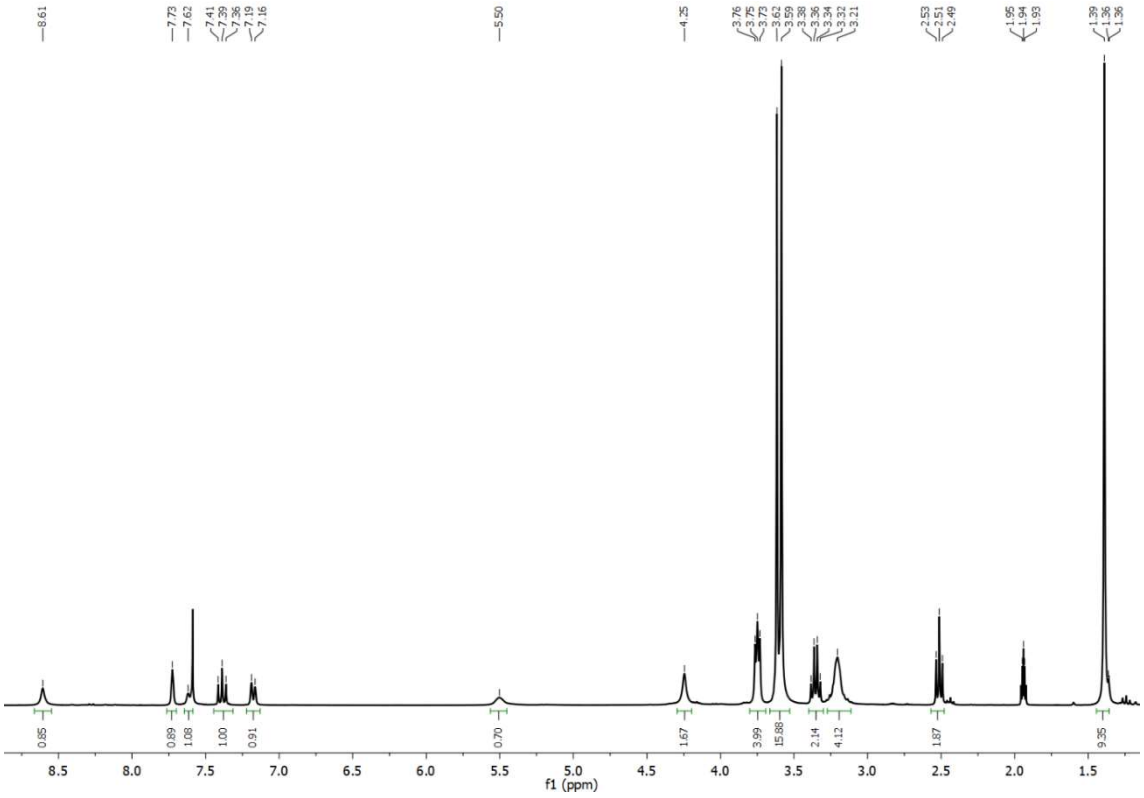


Figure S3. ^{1}H NMR spectrum of **5b**

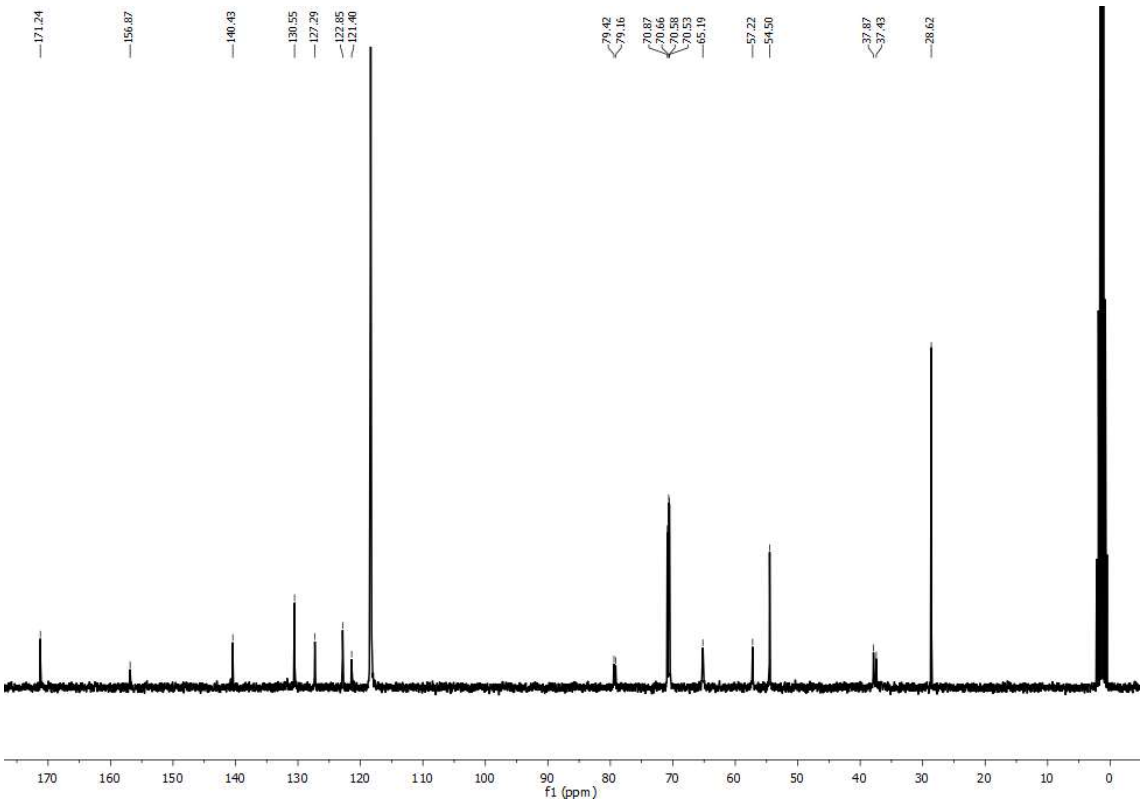


Figure S4. ^{13}C NMR spectrum of **5b**

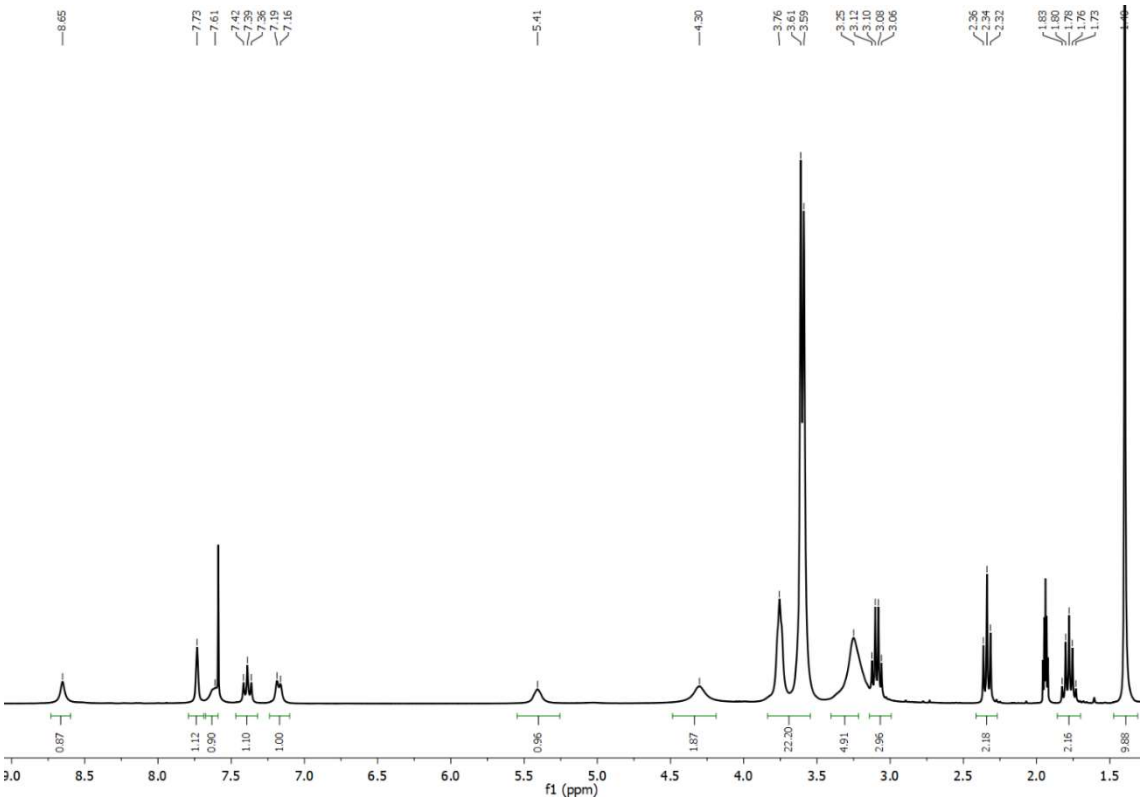


Figure S5. ^{1}H NMR spectrum of **5c**

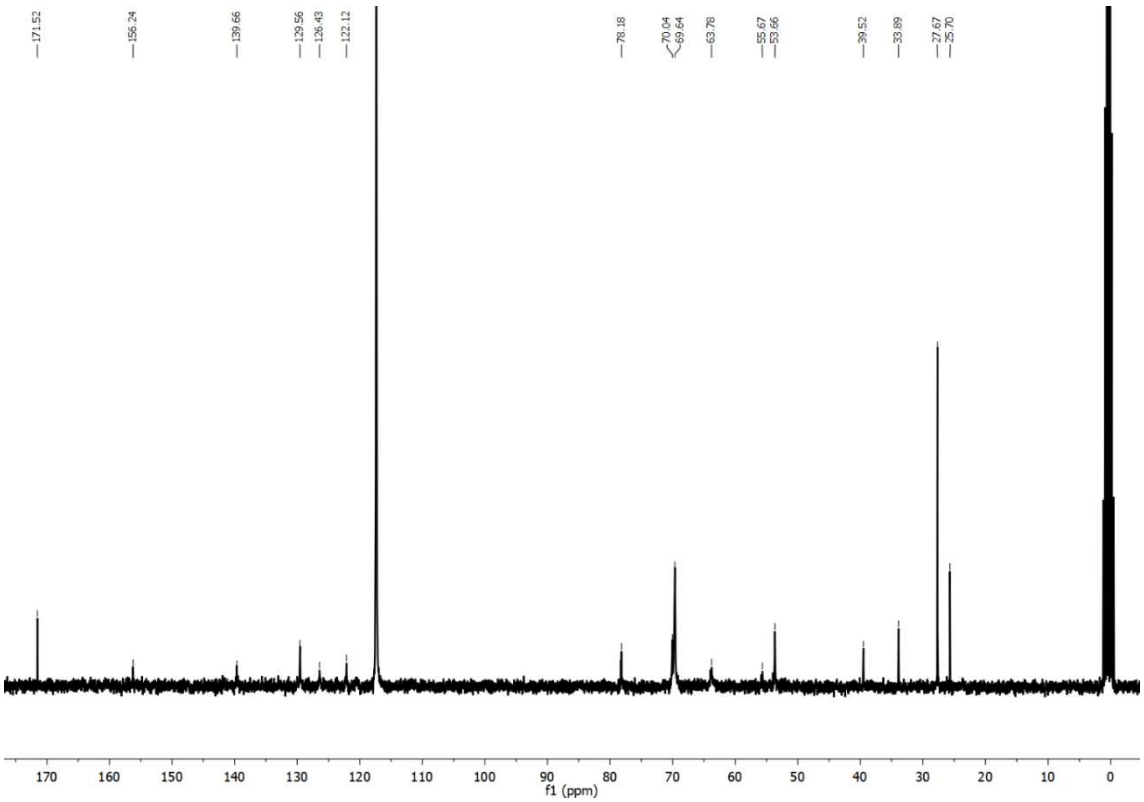


Figure S6. ^{13}C NMR spectrum of **5c**

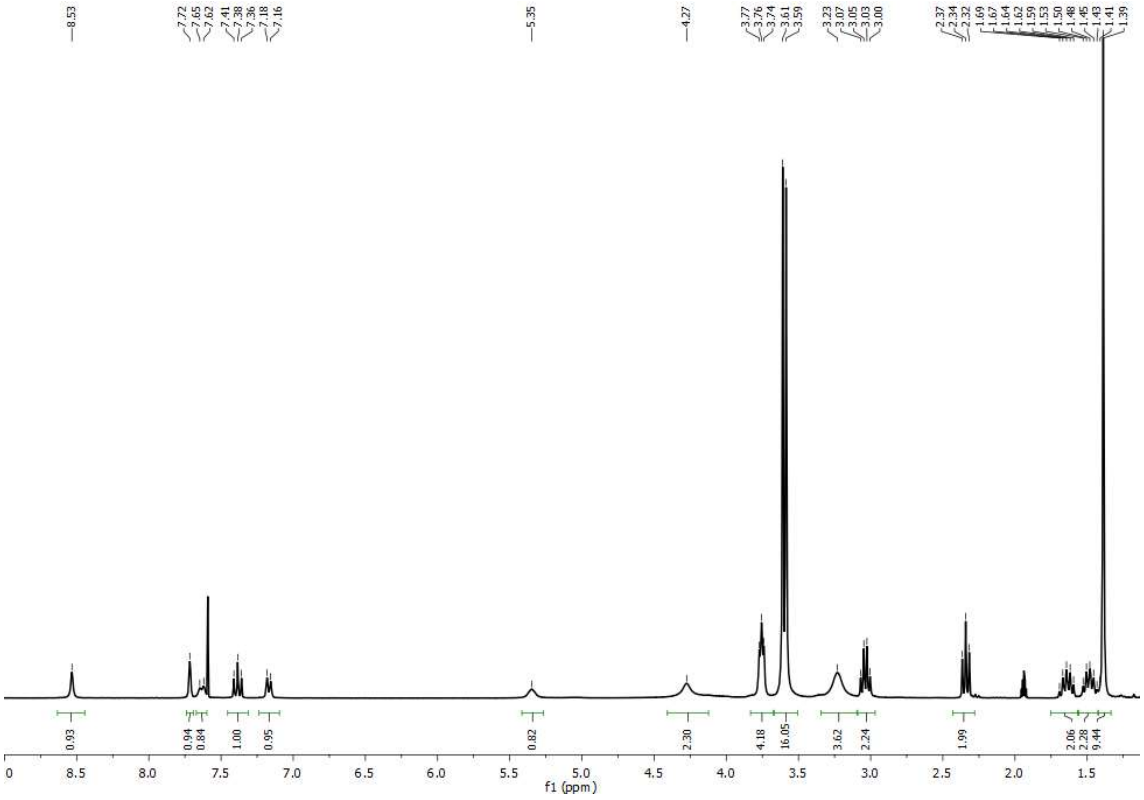


Figure S7. ^{1}H NMR spectrum of **5d**

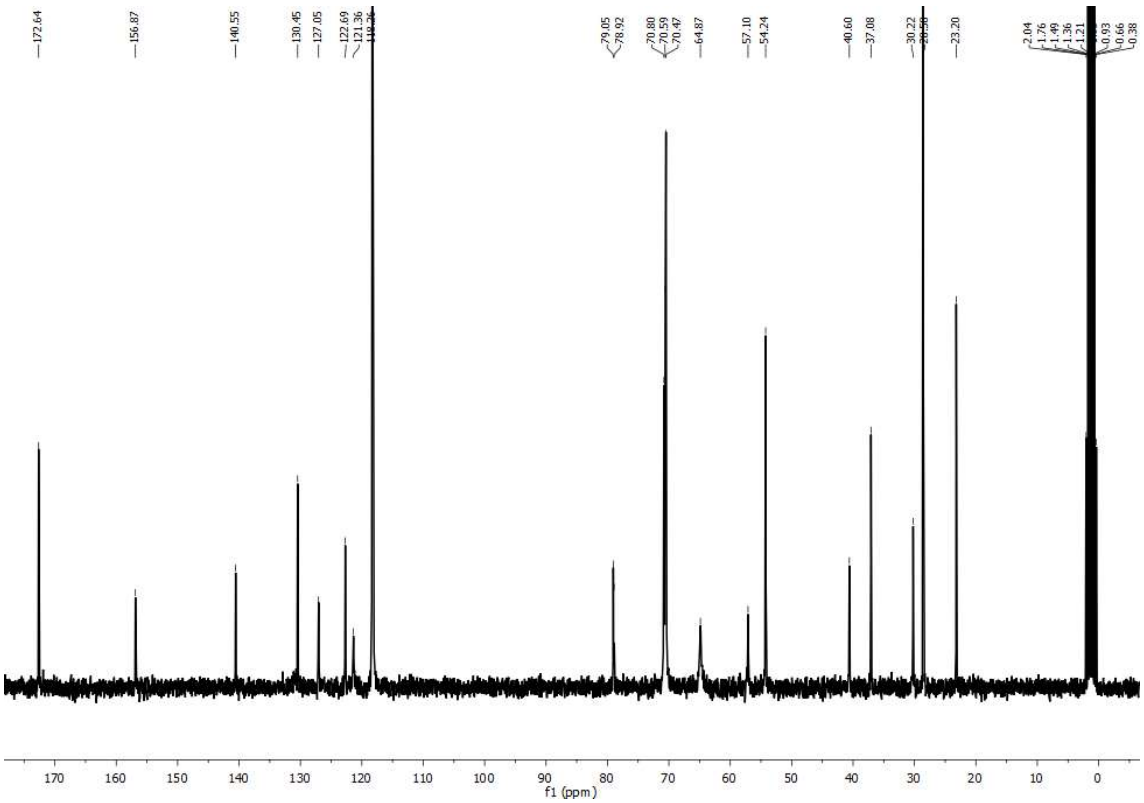


Figure S8. ^{13}C NMR spectrum of **5d**

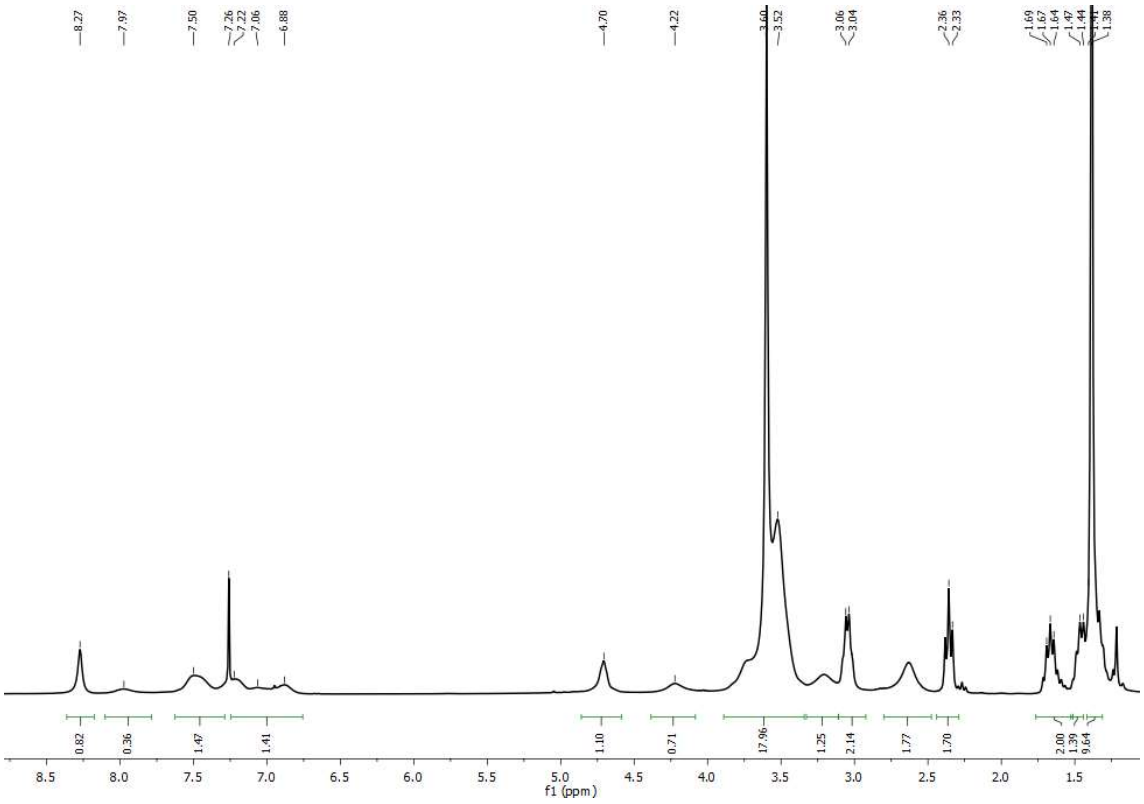


Figure S9. ^{1}H NMR spectrum of **5e**

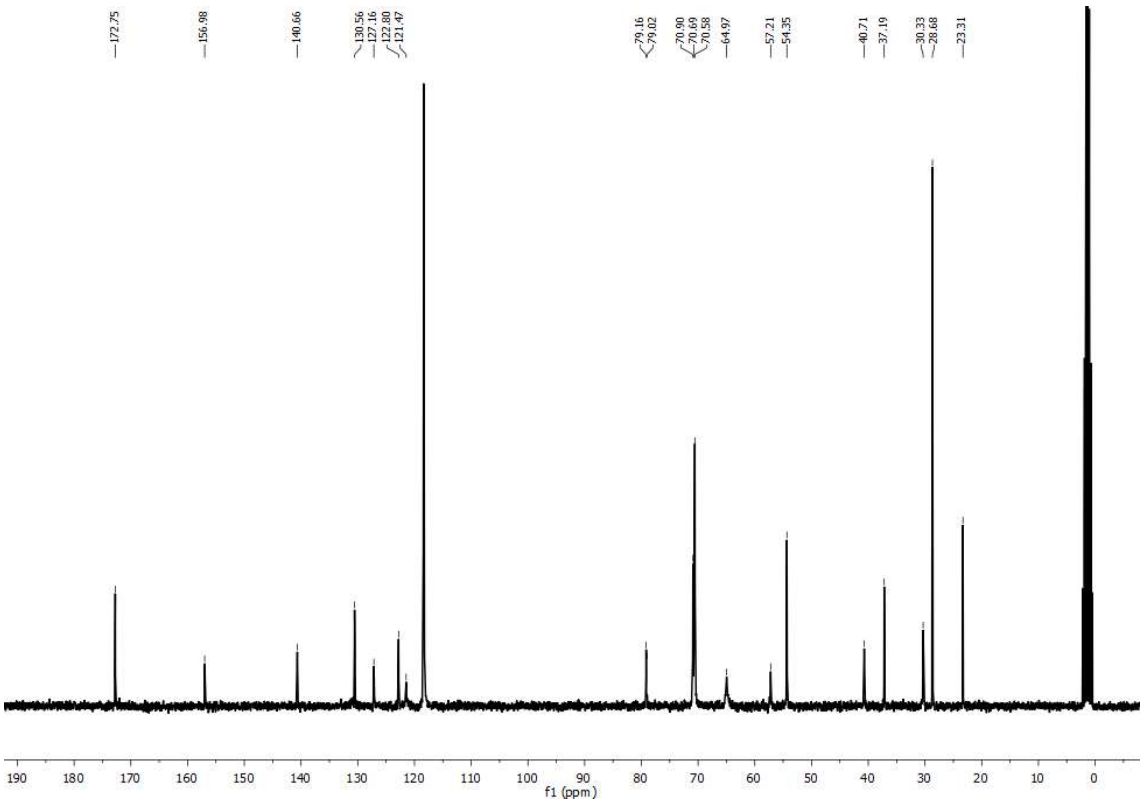


Figure S10. ^{13}C NMR spectrum of **5e**

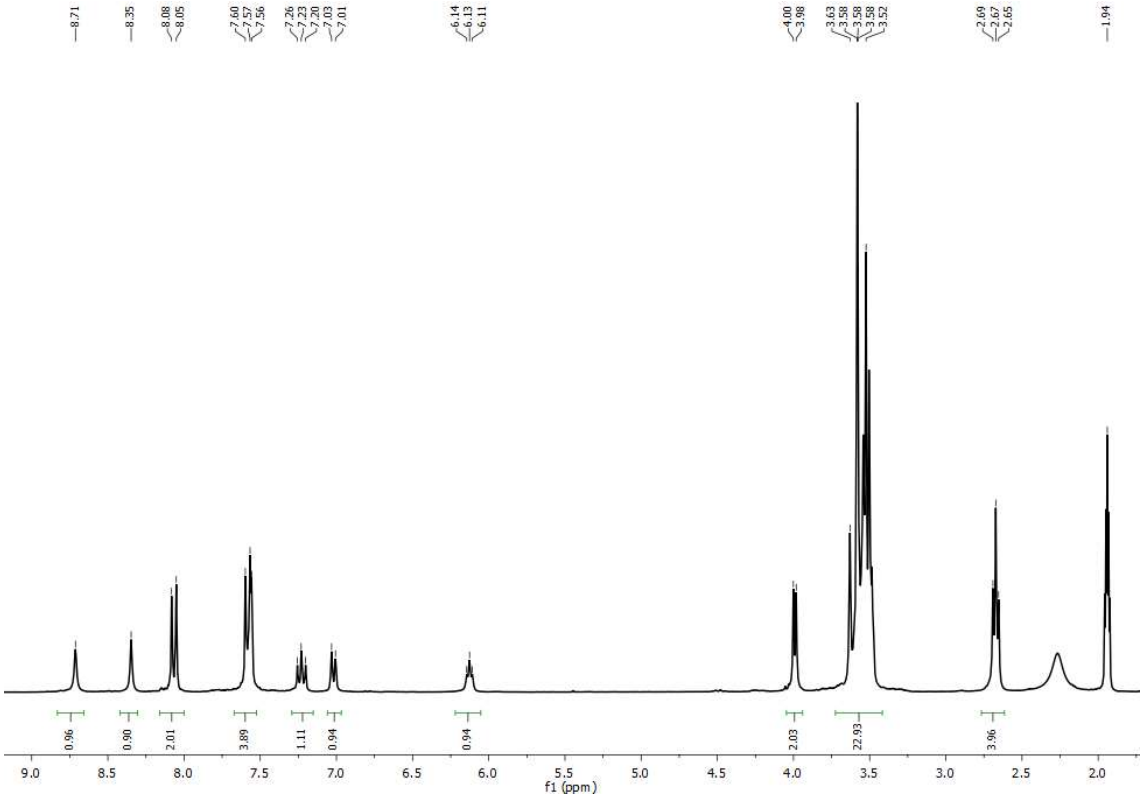


Figure S11. ^{1}H NMR spectrum of the receptor **1**

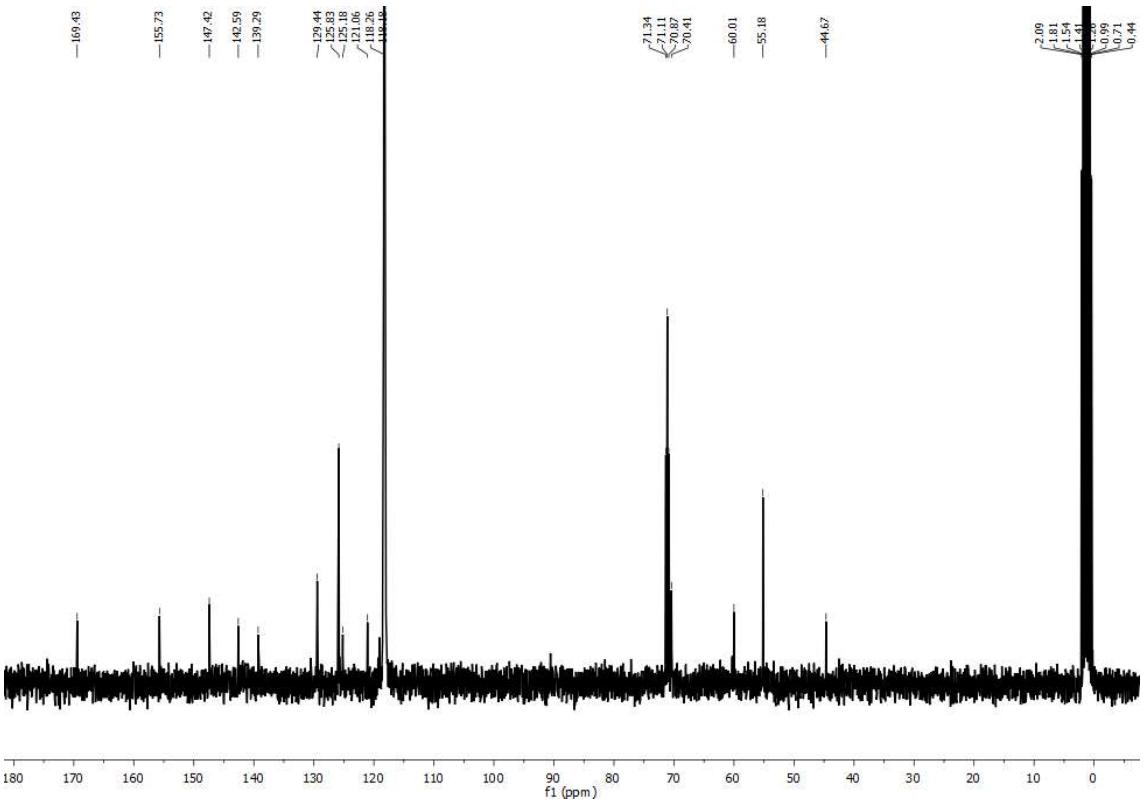


Figure S12. ^{13}C NMR spectrum of the receptor **1**

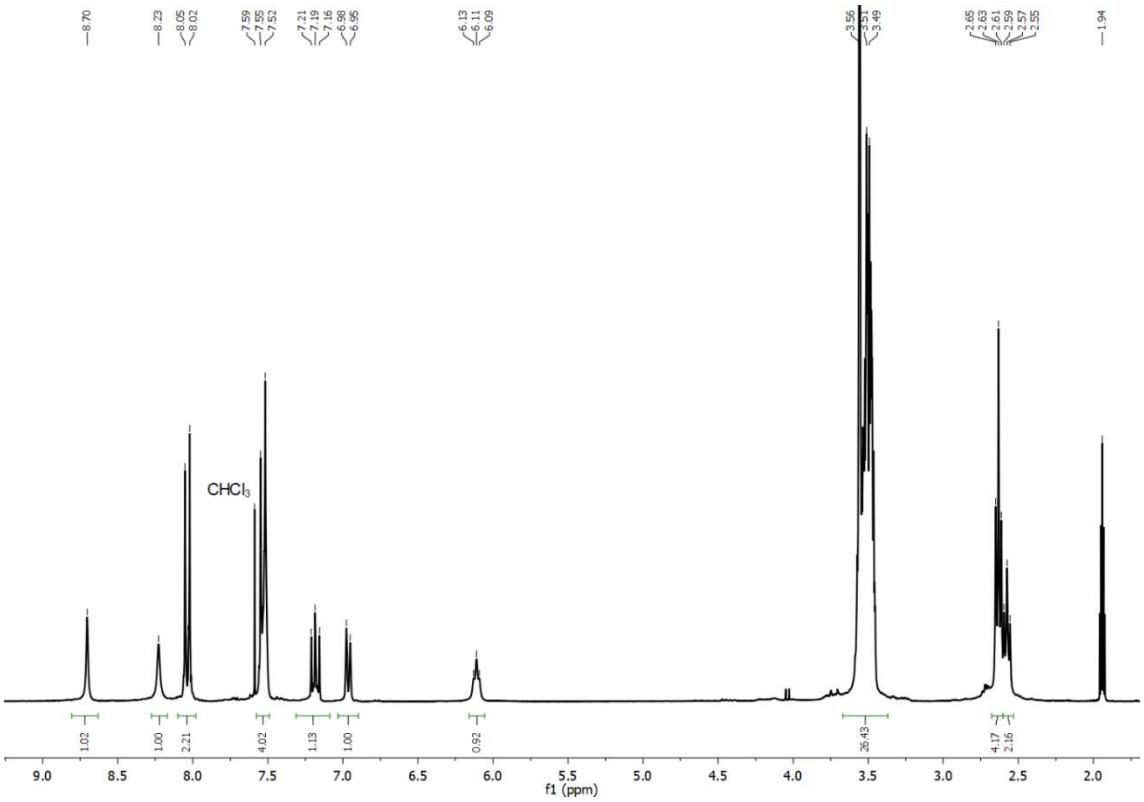


Figure S13. ^{1}H NMR spectrum of the receptor **2**

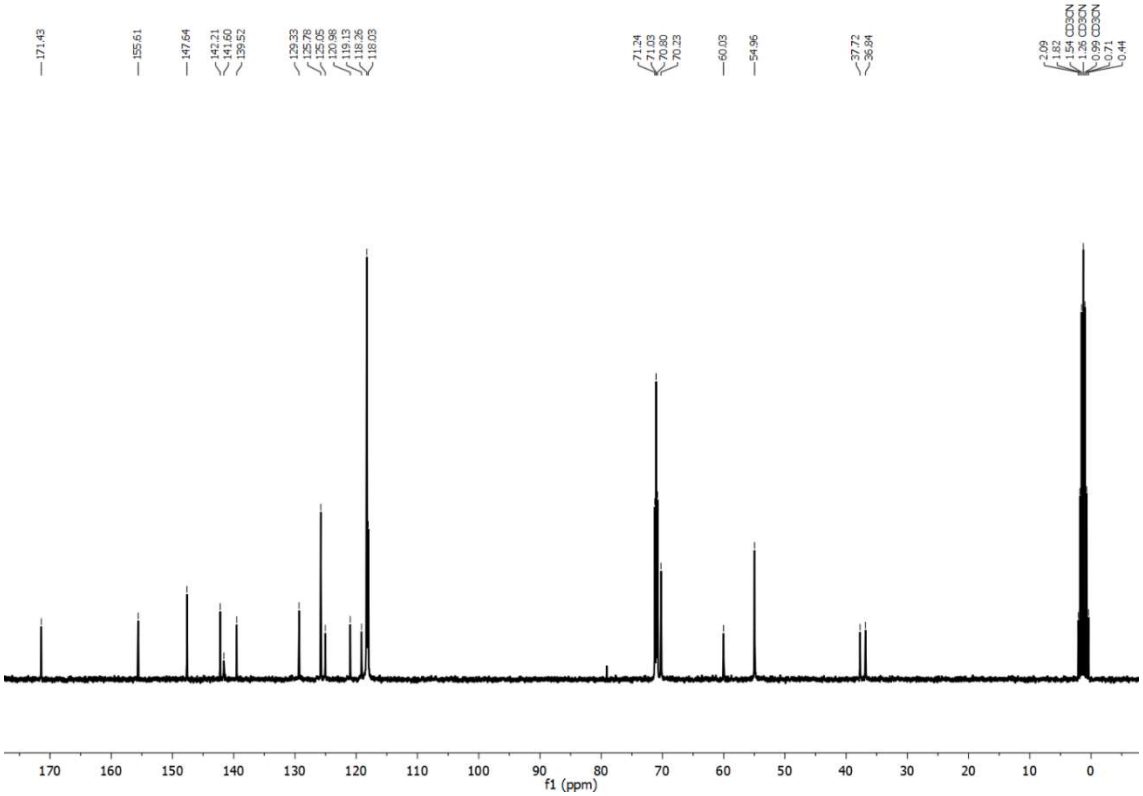


Figure S14. ^{13}C NMR spectrum of the receptor **2**

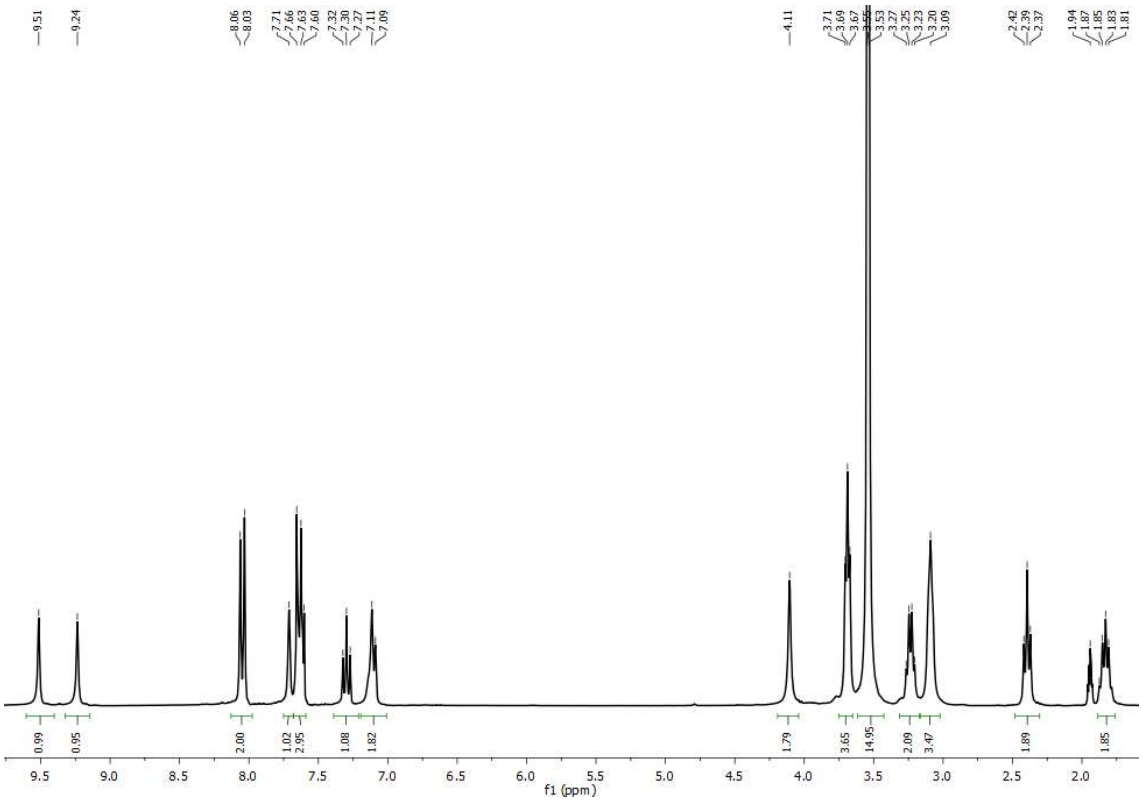


Figure S15. ^{1}H NMR spectrum of the receptor **3**

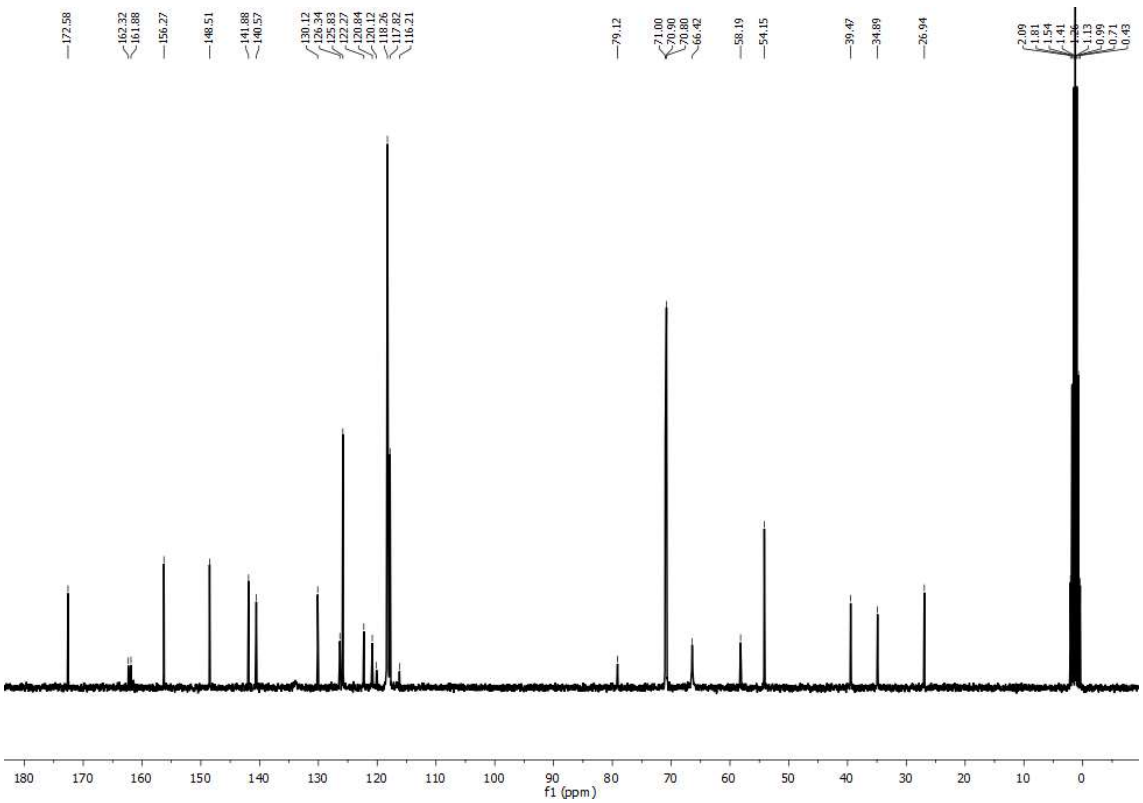


Figure S16. ^{13}C NMR spectrum of the receptor **3**

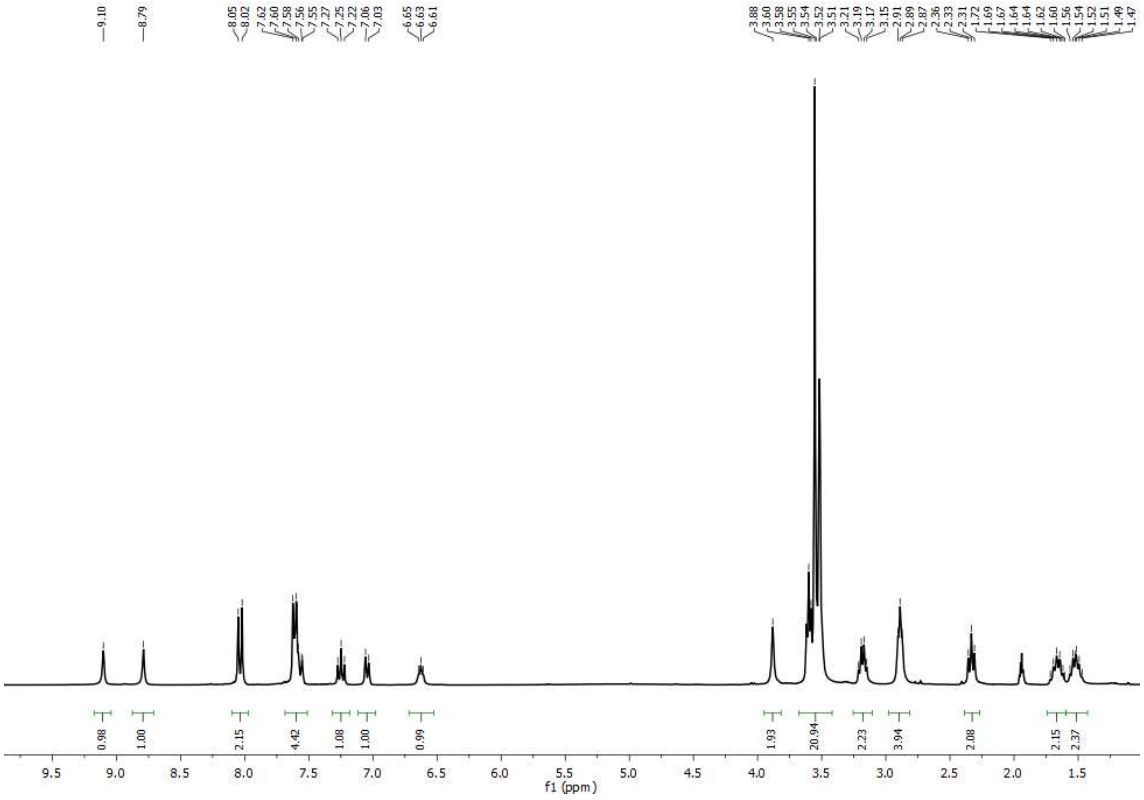


Figure S17. ^{1}H NMR spectrum of the receptor **4**

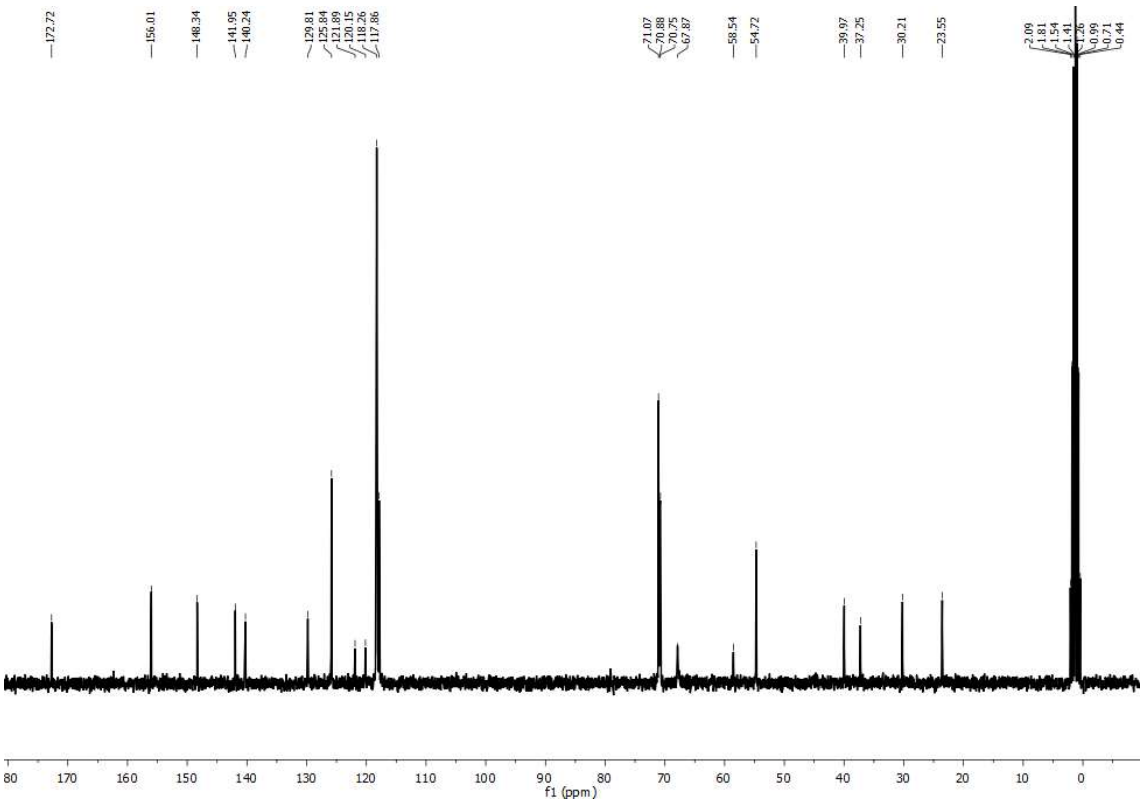


Figure S18. ^{13}C NMR spectrum of the receptor **4**

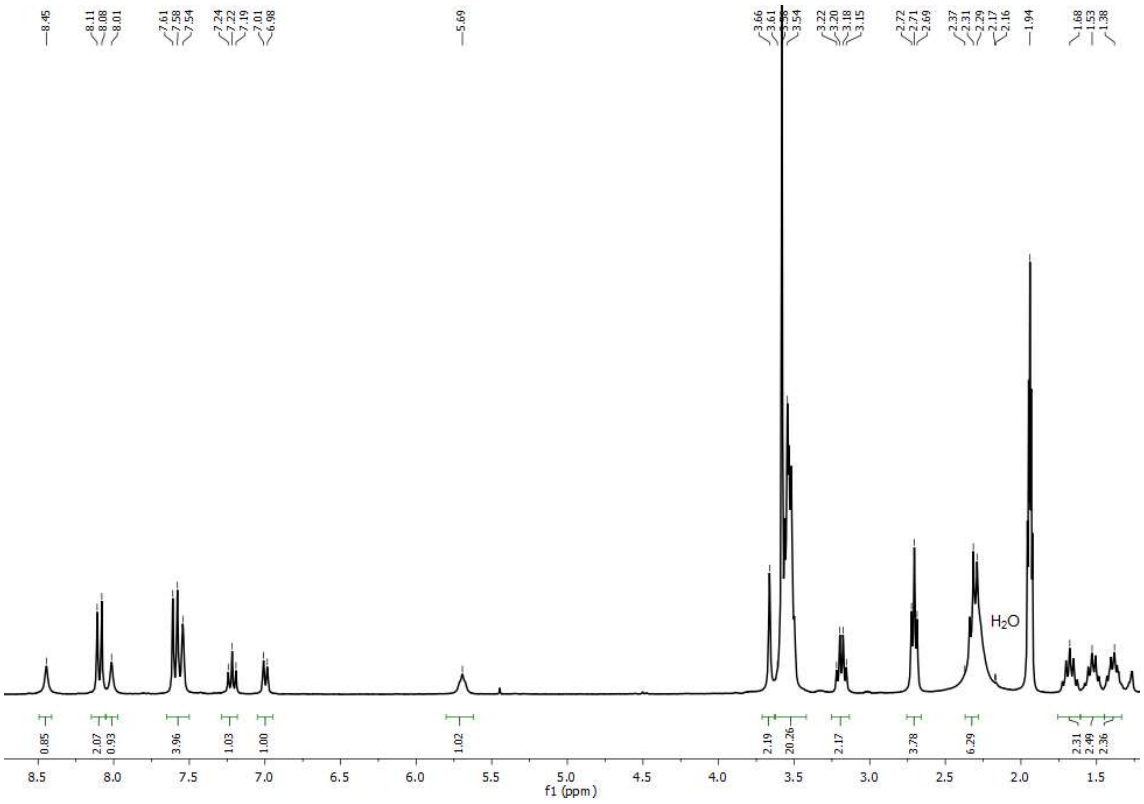


Figure S19. ^{1}H NMR spectrum of the receptor **5**

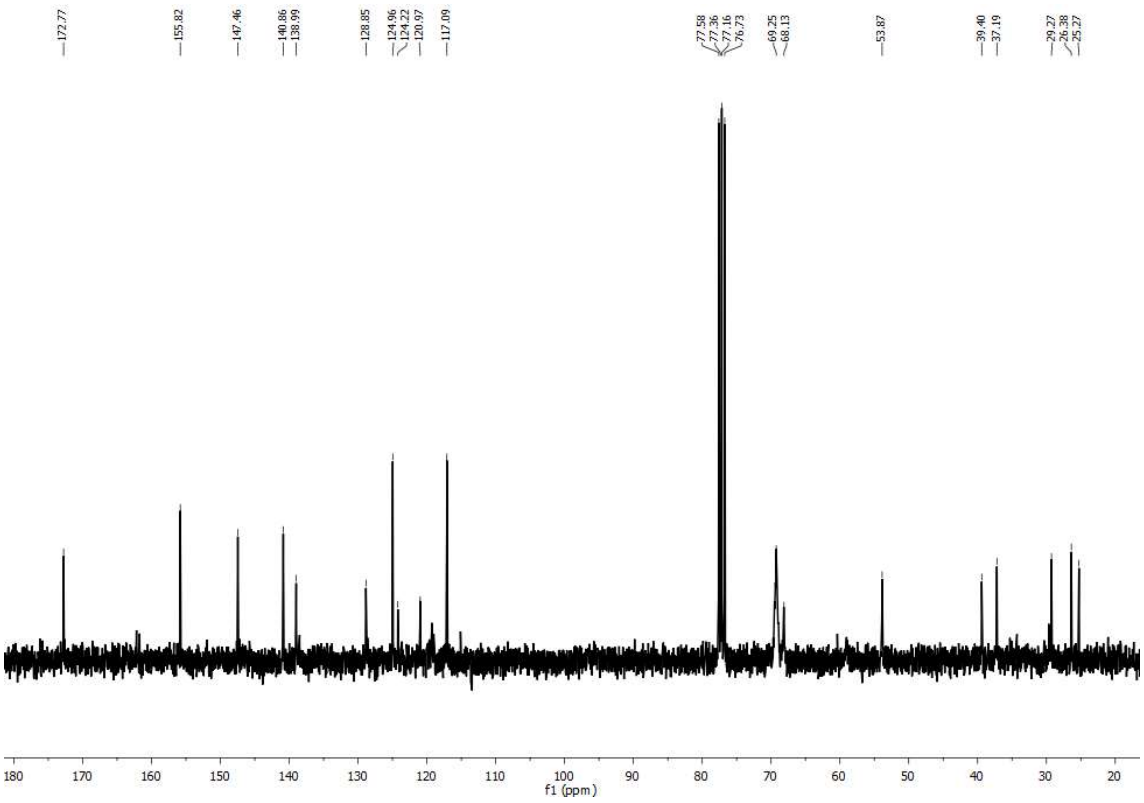


Figure S20. ^{13}C NMR spectrum of the receptor **5**

2. The ^{1}H NMR titration experiments

^{1}H NMR titration experiments were performed on a 300 MHz Bruker Avance spectrometer, at 298 K, in 3% H_2O/CD_3CN solution. In each case 0.5 mL of 4.0 x 10^{-3} M solution of the receptor **1-5** was added to 5 mm NMR tube. The receptor solution contains or not 1 mol eq. of potassium cation. Then to the receptor solution the titrant solution of tetrabutylammonium acetate or chloride in the receptor solution (2.1 x10^{-1} M) was added. After each addition of the titrant, a spectrum was registered. The resulting titration data were analyzed by Bindfit.[2]

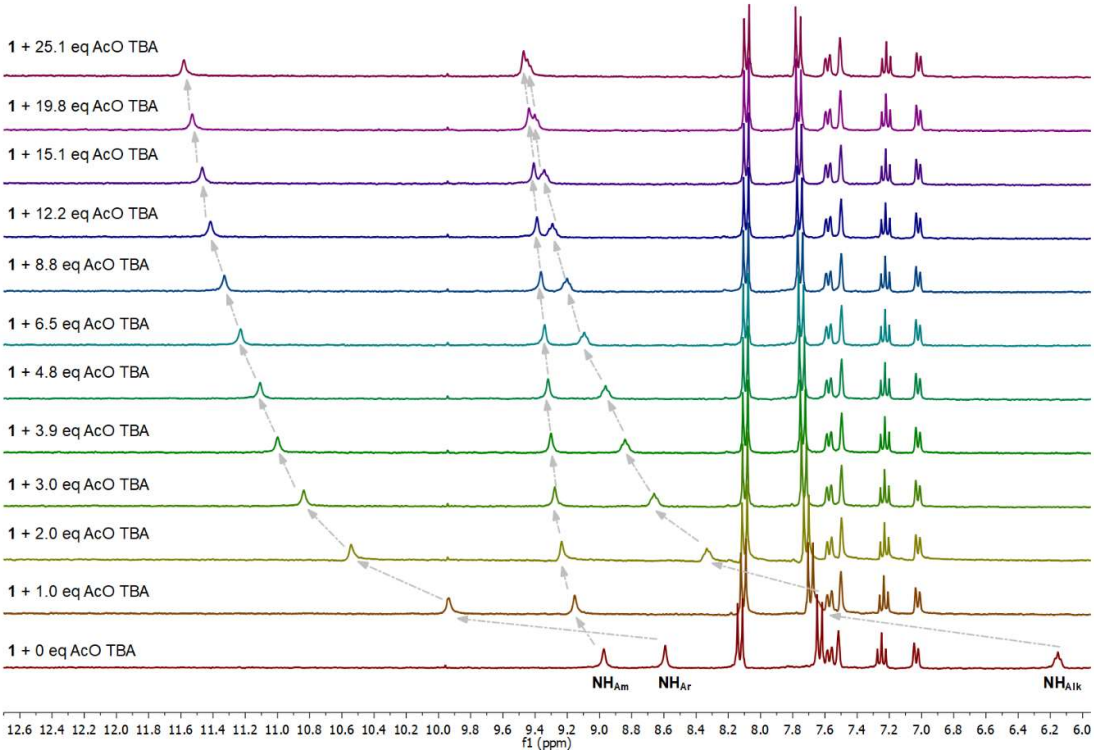


Figure S21. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBAOAc) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

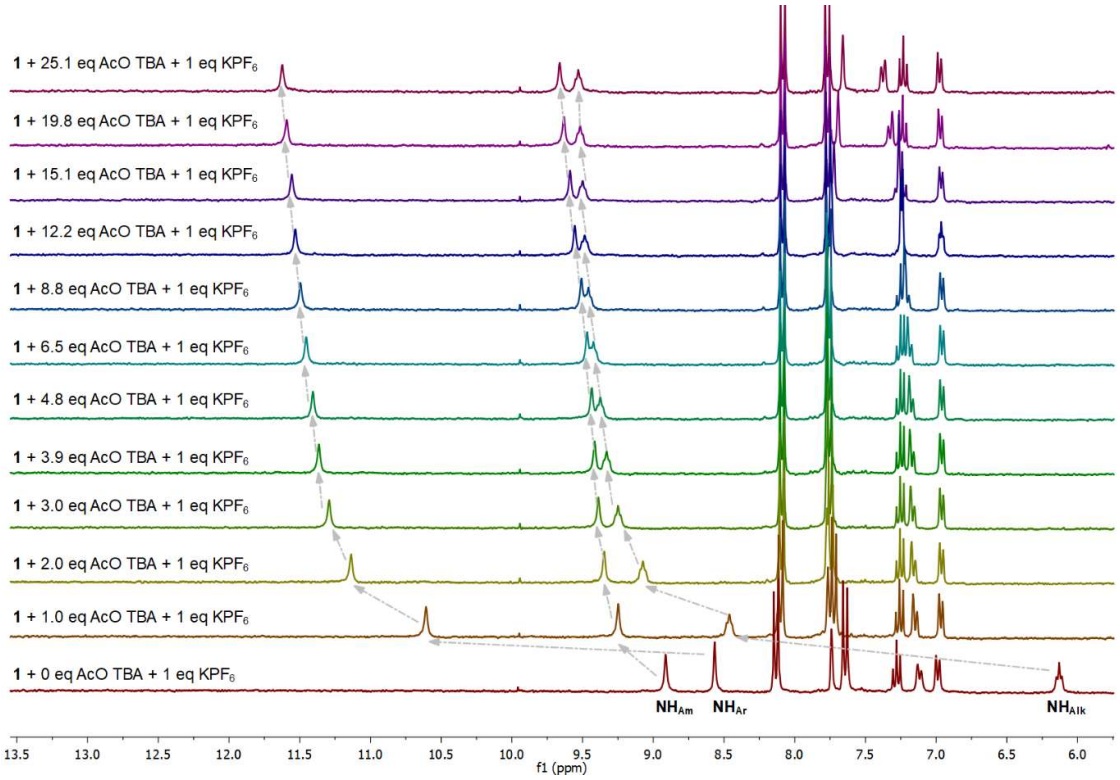


Figure S22. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBAOAc) addition in presence of 1eq. KPF_6,(293 K, 3% H_2O/CD_3CN solution, $C_{titrant}=2.1 \times 10^{-1}$ M, $C_{receptor}=4.0 \times 10^{-3}$ M)

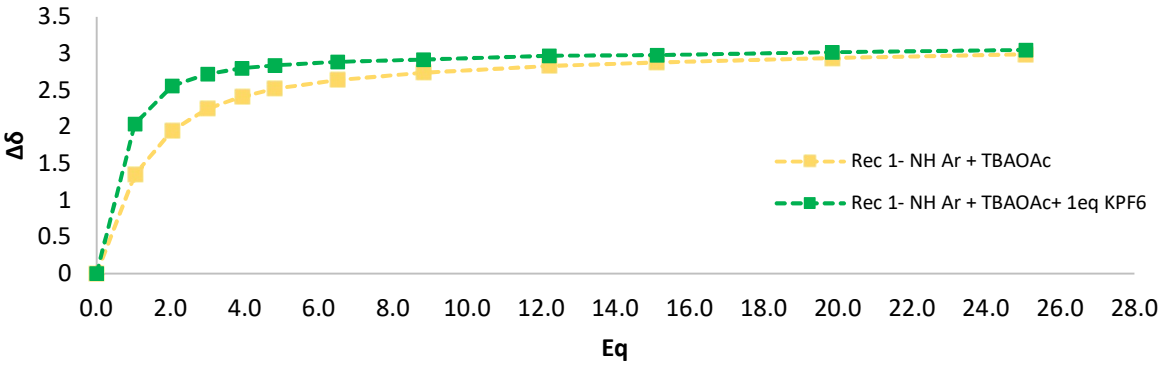


Figure S23. ^{1}H NMR titration binding isotherm of **1** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

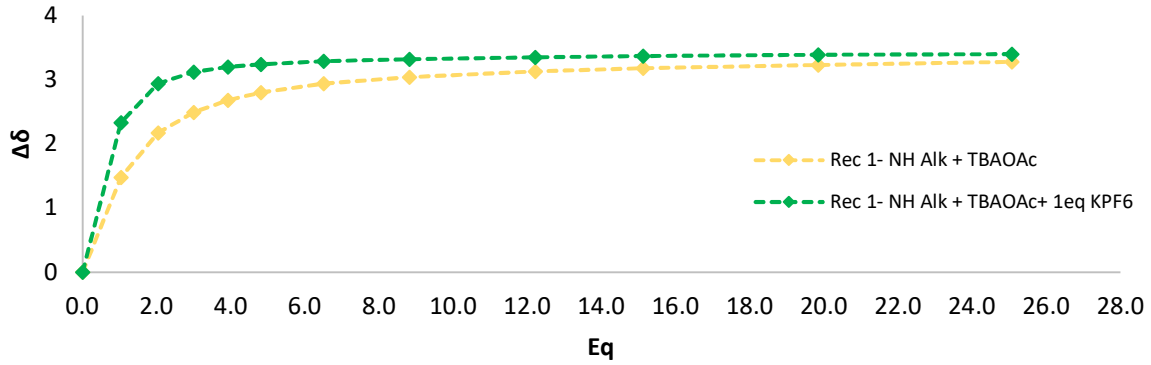


Figure S24. ^{1}H NMR titration binding isotherm of **1** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

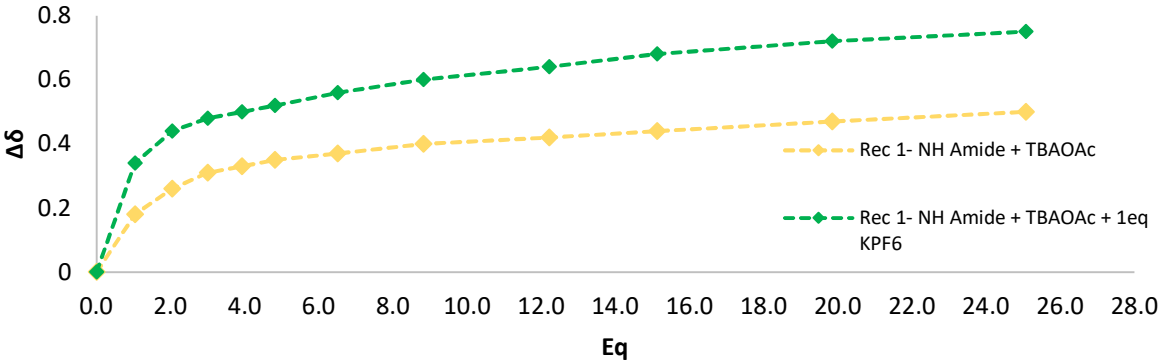


Figure S25. ^{1}H NMR titration binding isotherm of **1** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

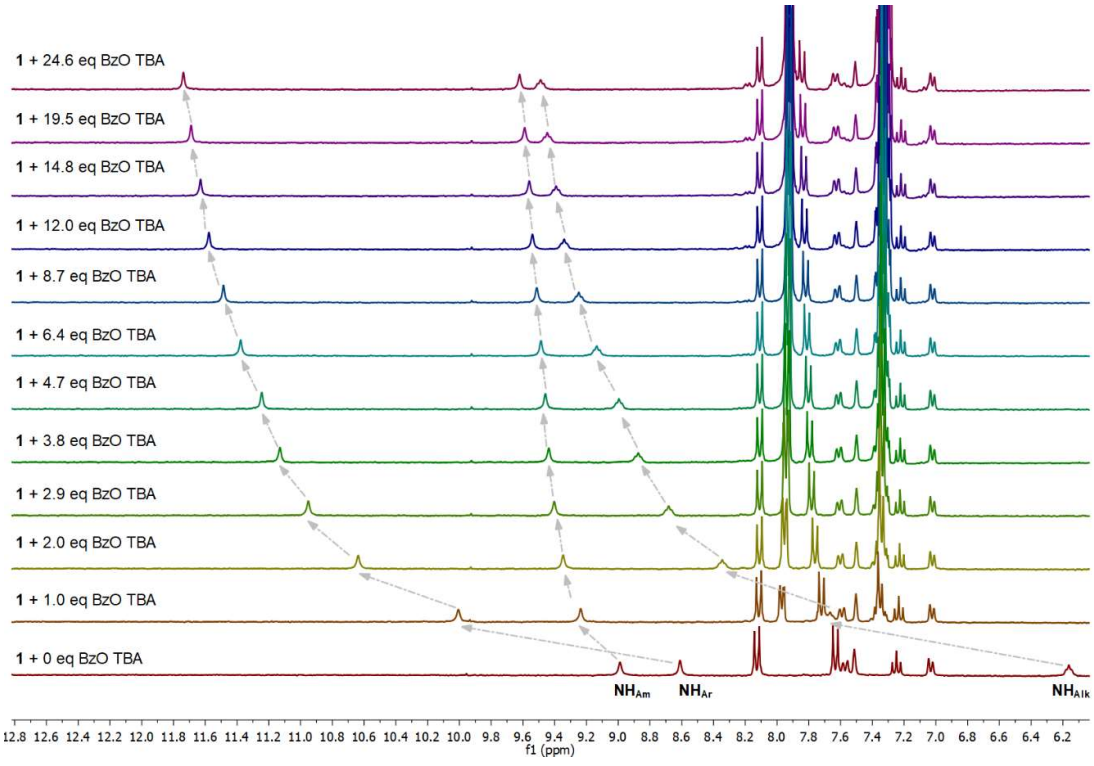


Figure S26. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBAOBz) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

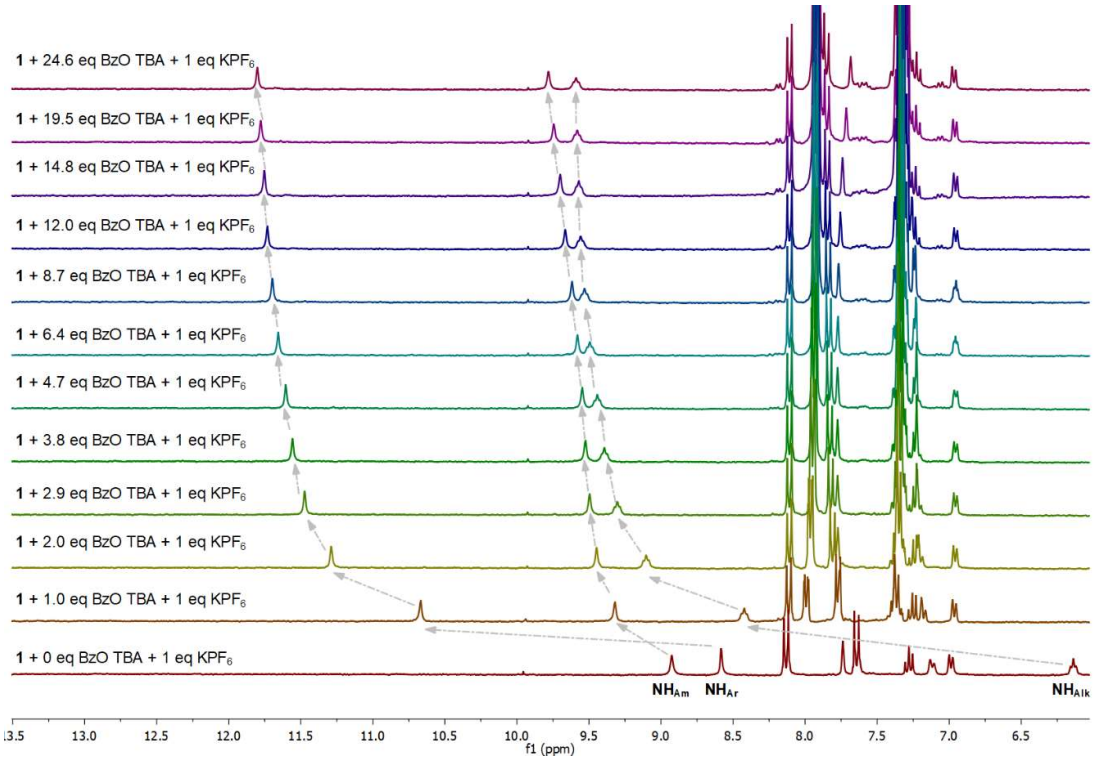


Figure S27. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBAOBz) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

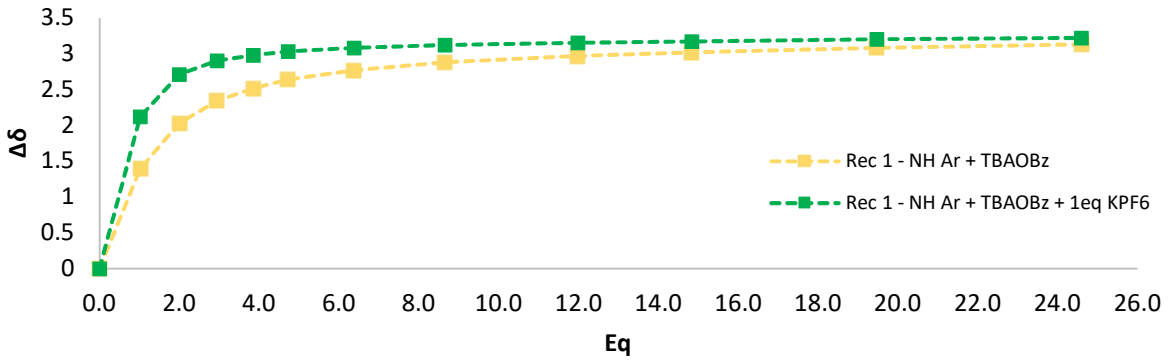


Figure S28. ^{1}H NMR titration binding isotherm of **1** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

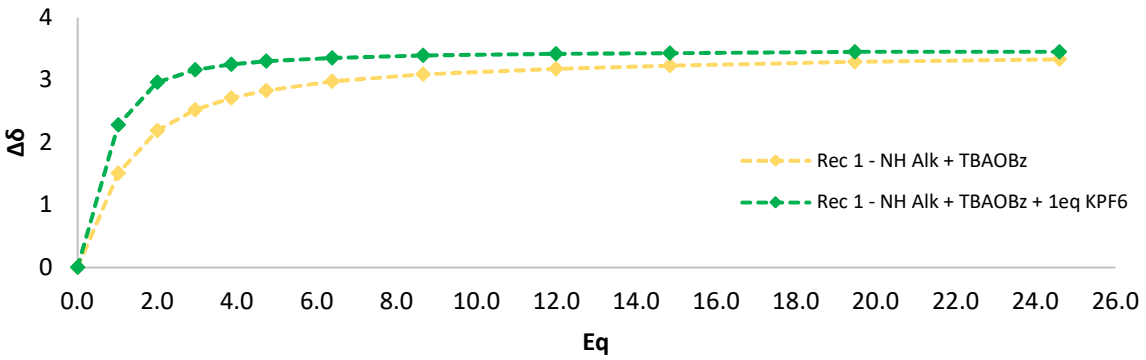


Figure S29. ^{1}H NMR titration binding isotherm of **1** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

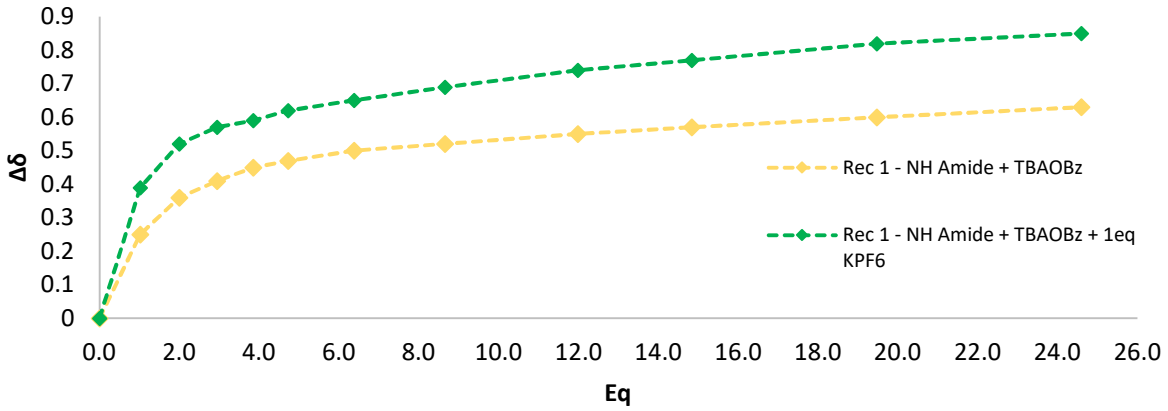


Figure S30. ^{1}H NMR titration binding isotherm of **1** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

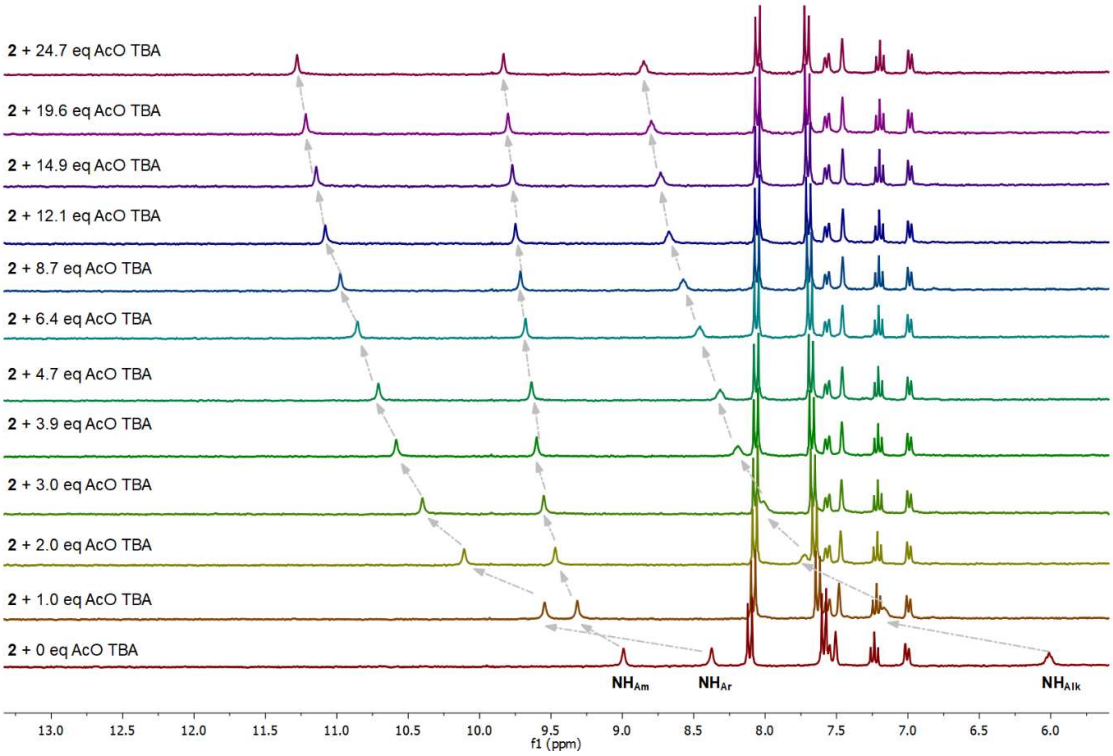


Figure S31. Partial ^{1}H NMR titration experiment of **2** upon titrant (TBAOAc) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

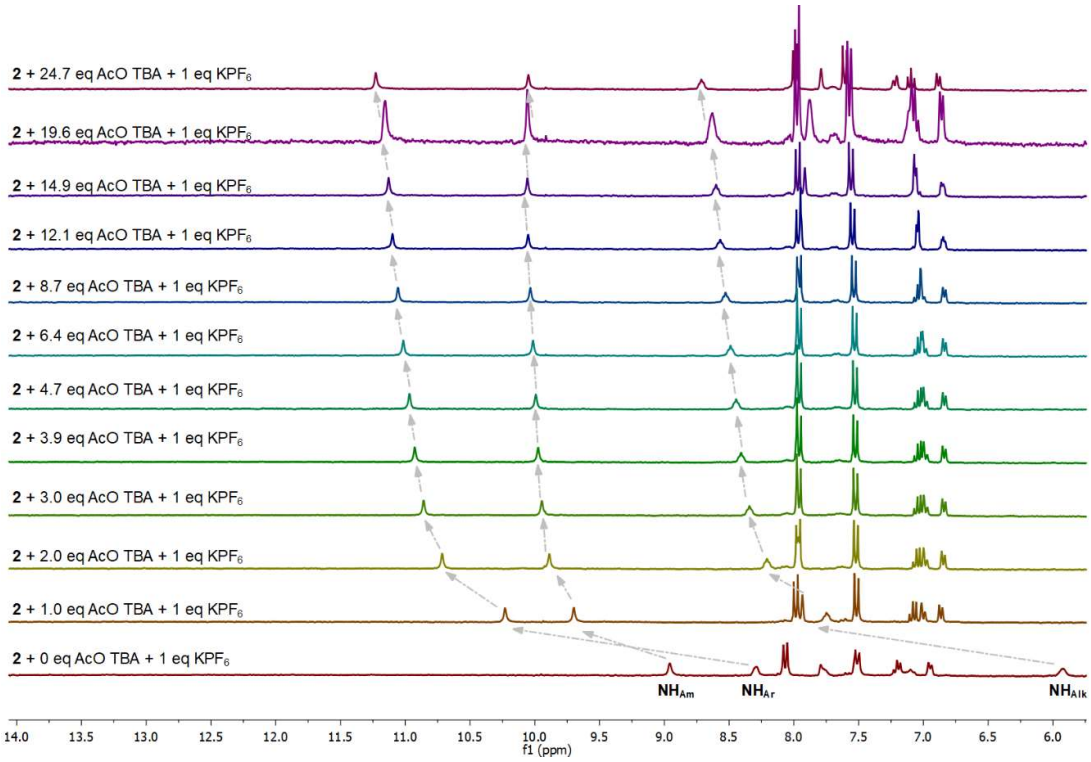


Figure S32. Partial ^{1}H NMR titration experiment of **2** upon titrant (TBAOAc) addition in presence of 1 eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}=2.1 \times 10^{-1}$ M, $C_{receptor}=4.0 \times 10^{-3}$ M)

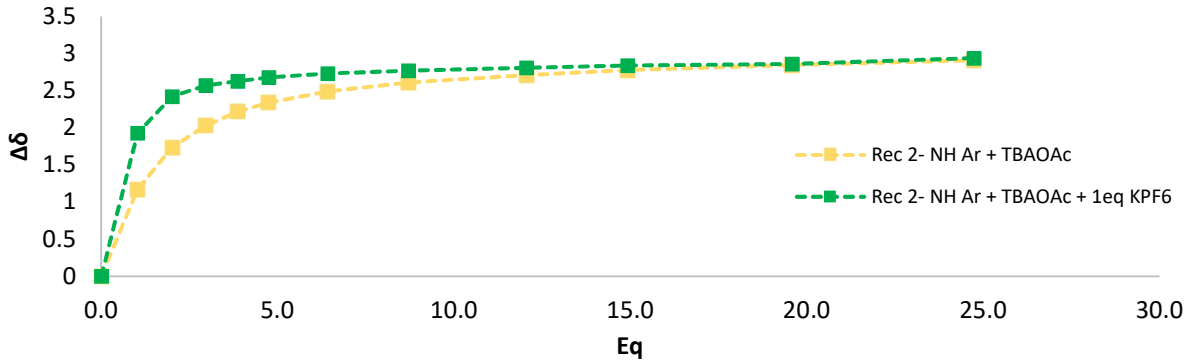


Figure S33. ^{1}H NMR titration binding isotherm of **2** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

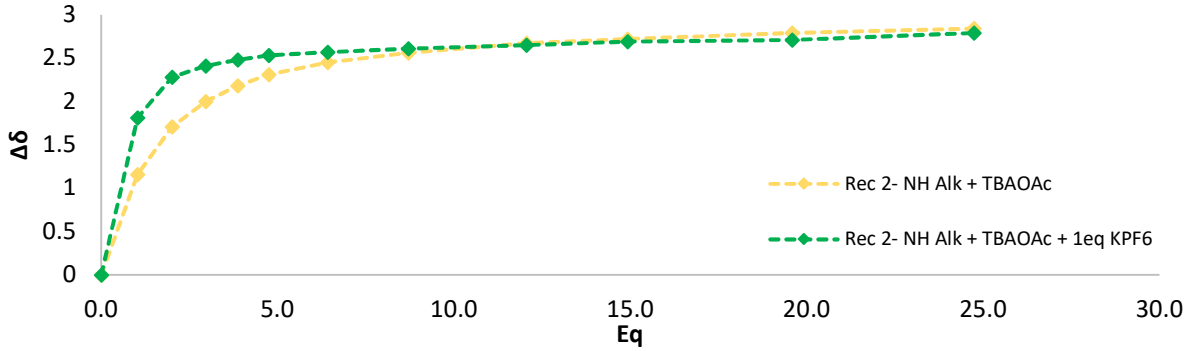


Figure S34. ^{1}H NMR titration binding isotherm of **2** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

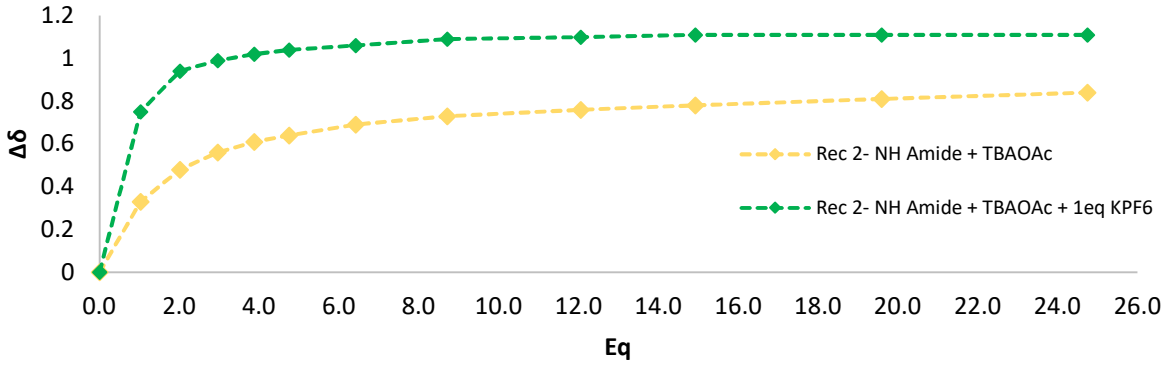


Figure S35. ^{1}H NMR titration binding isotherm of **2** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

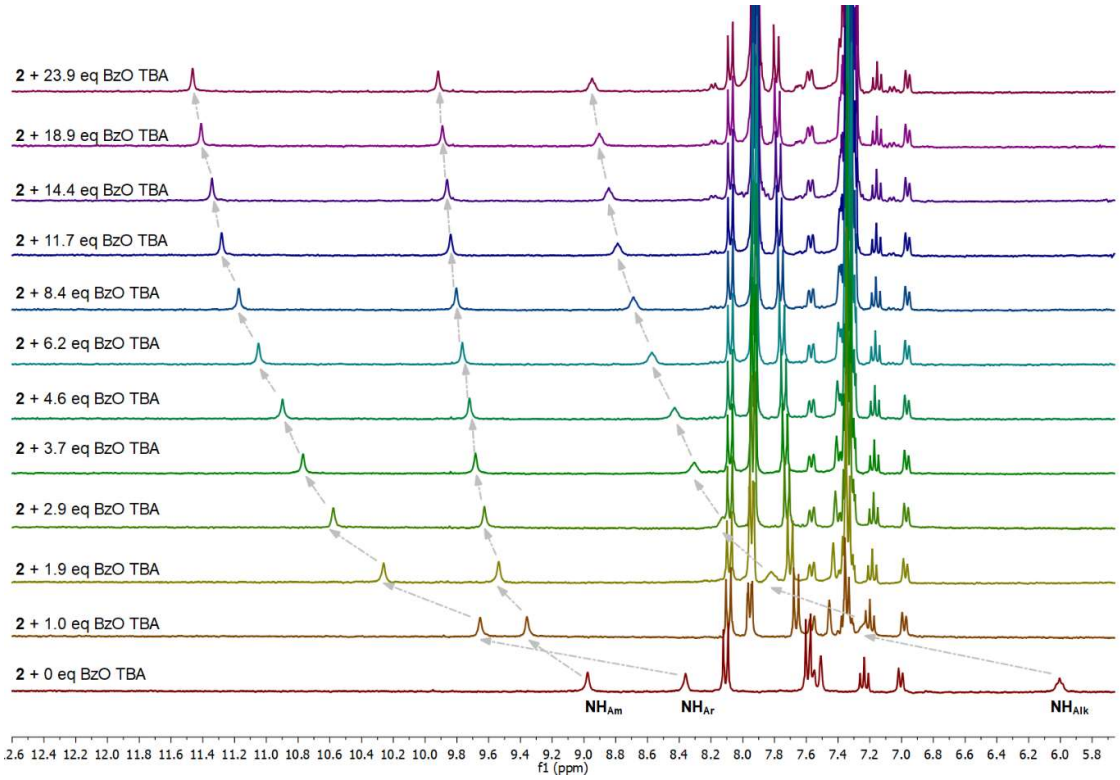


Figure S36. Partial ^{1}H NMR titration experiment of **2** upon titrant (TBAOBz) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.05 x10^{-1} M, $C_{receptor}$=4.1 x10^{-3} M)

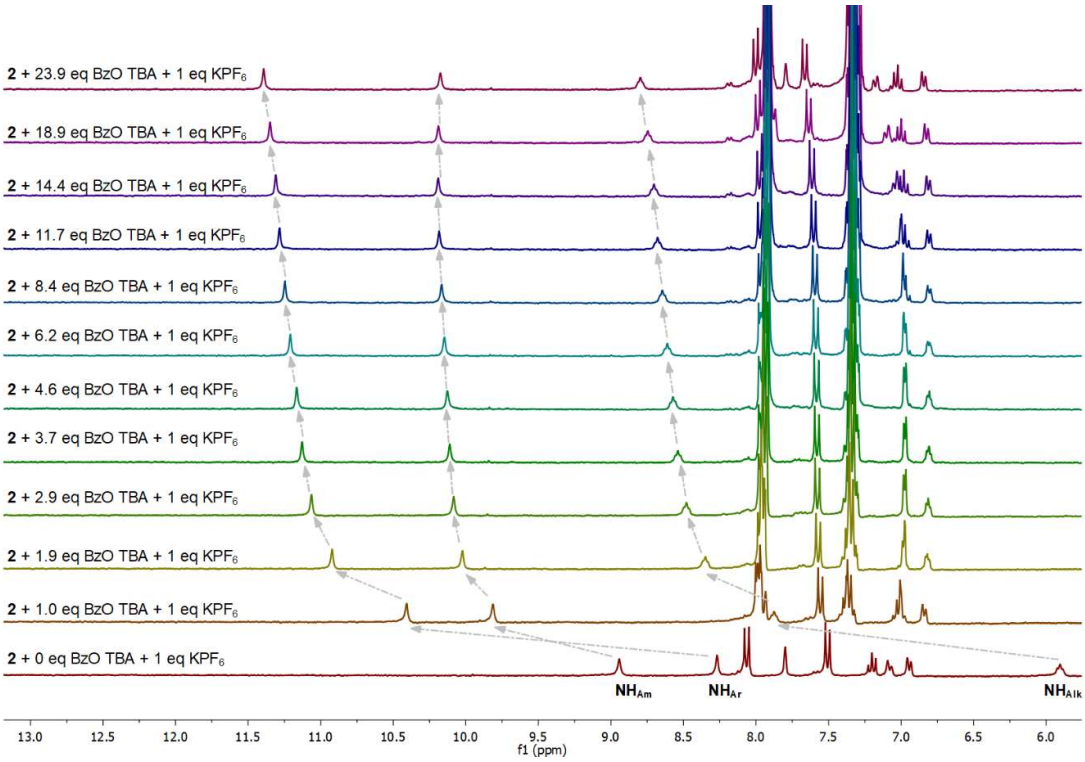


Figure S37. Partial ^{1}H NMR titration experiment of **2** upon titrant (TBAOBz) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.05 x10^{-1} M, $C_{receptor}$=4.1 x10^{-3} M)

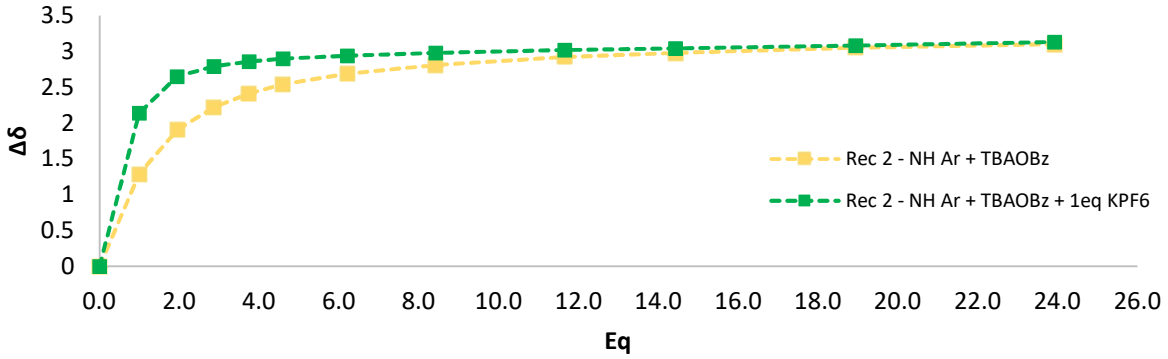


Figure S38. ^{1}H NMR titration binding isotherm of **2** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

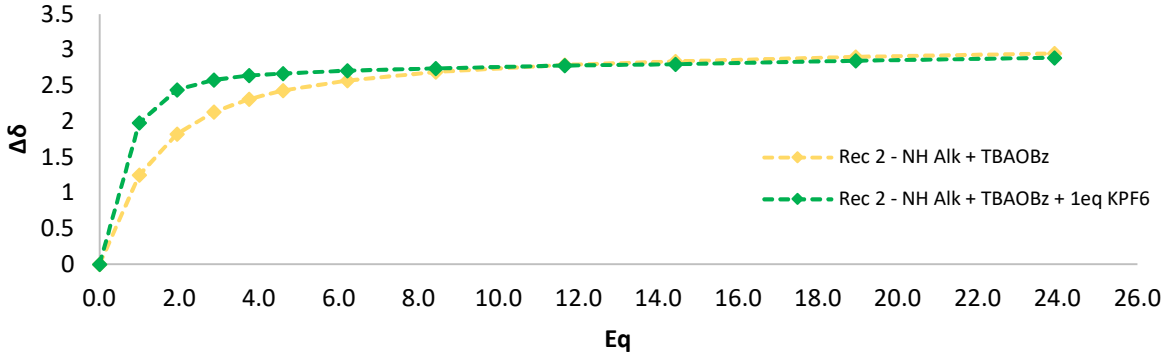


Figure S39. ^{1}H NMR titration binding isotherm of **2** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

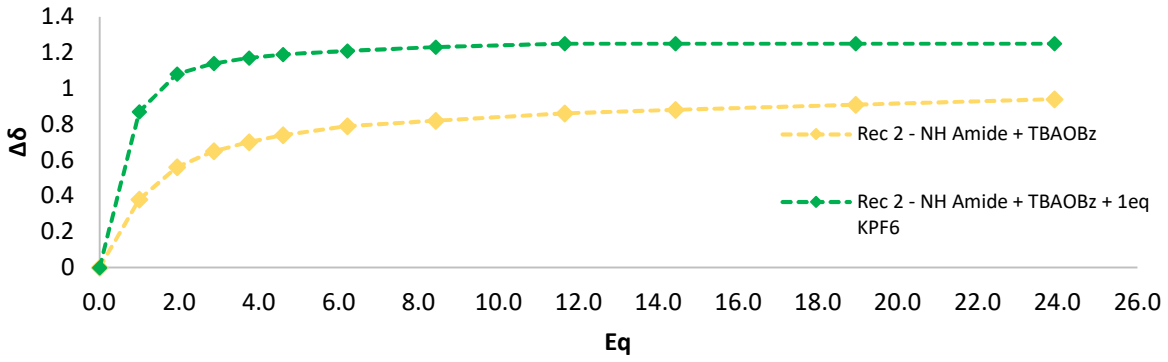


Figure S40. ^{1}H NMR titration binding isotherm of **2** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

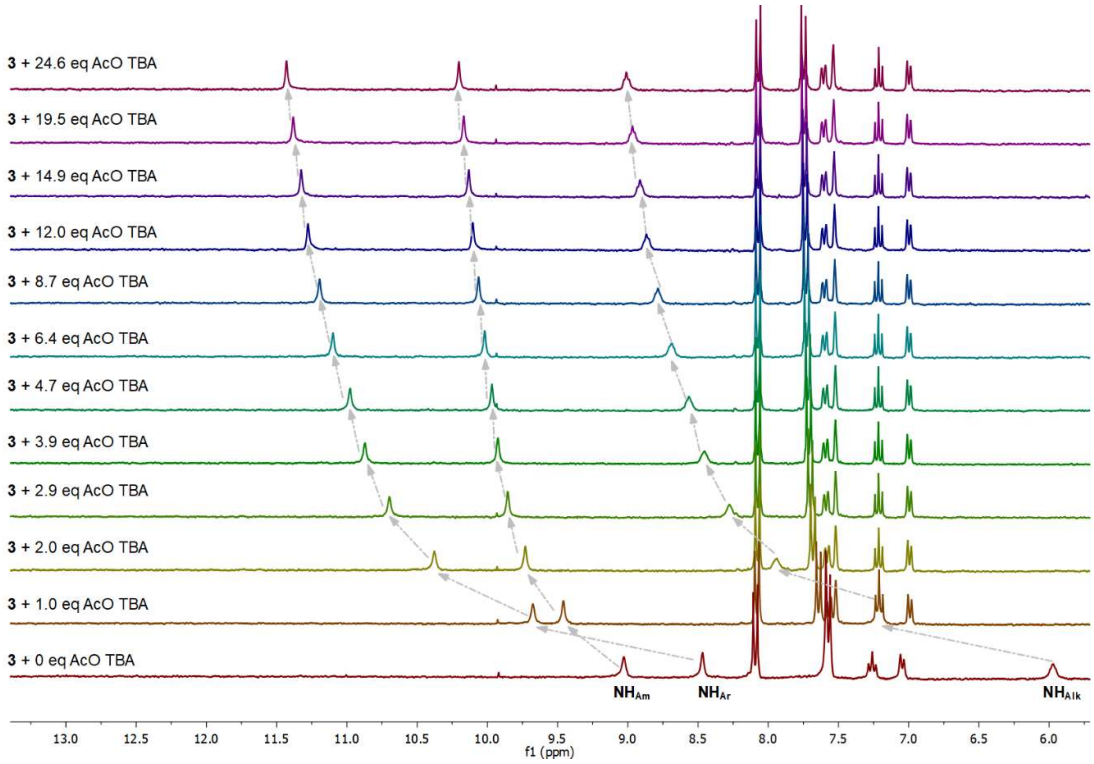


Figure S41. Partial ^{1}H NMR titration experiment of **3** upon titrant (TBAOAc) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

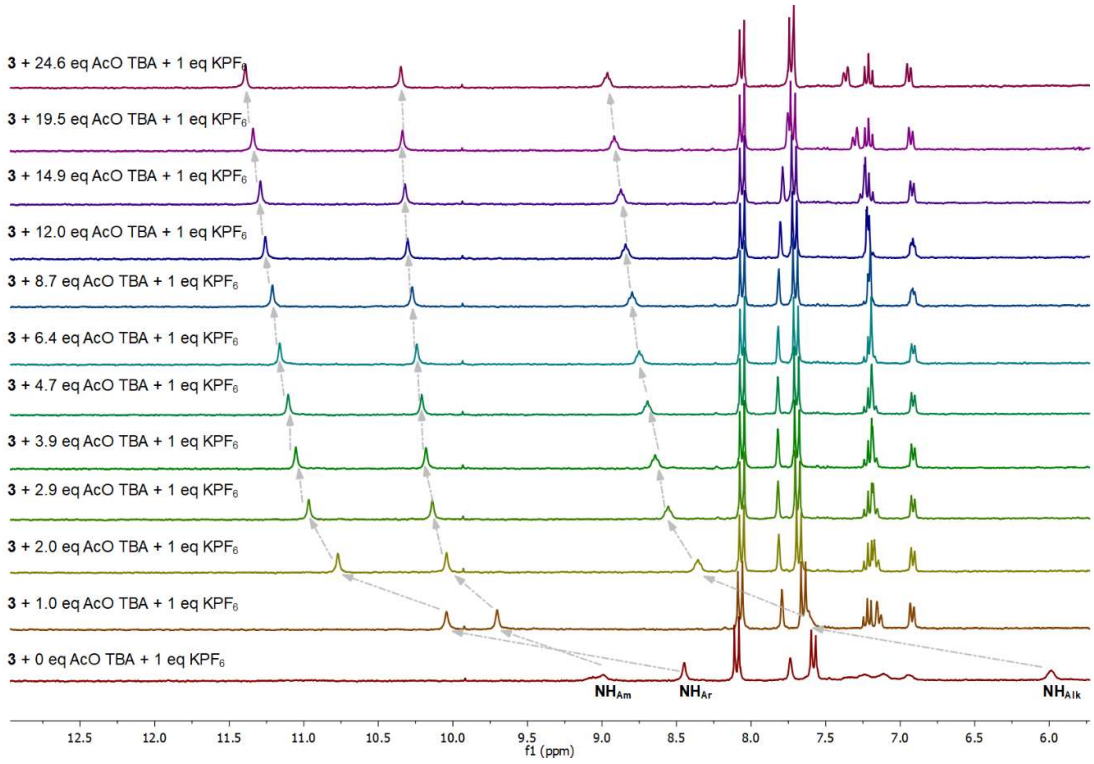


Figure S42. Partial ^{1}H NMR titration experiment of **3** upon titrant (TBAOAc) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

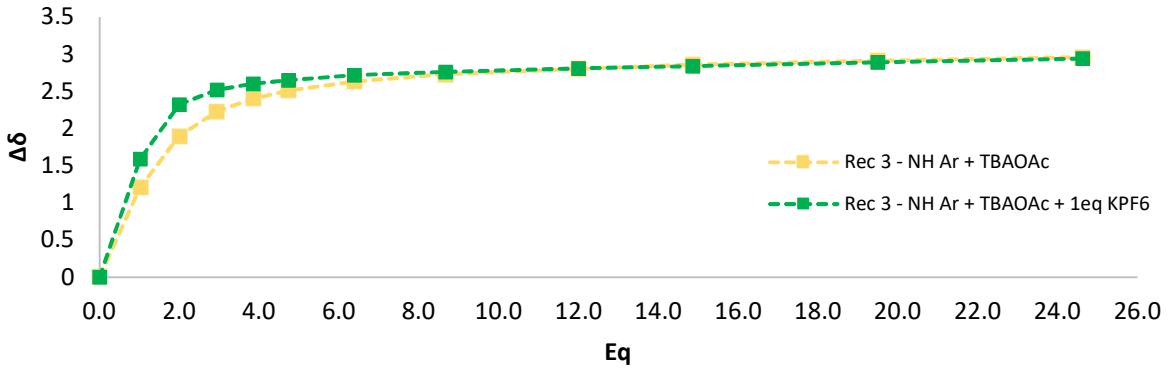


Figure S43. ^{1}H NMR titration binding isotherm of **3** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

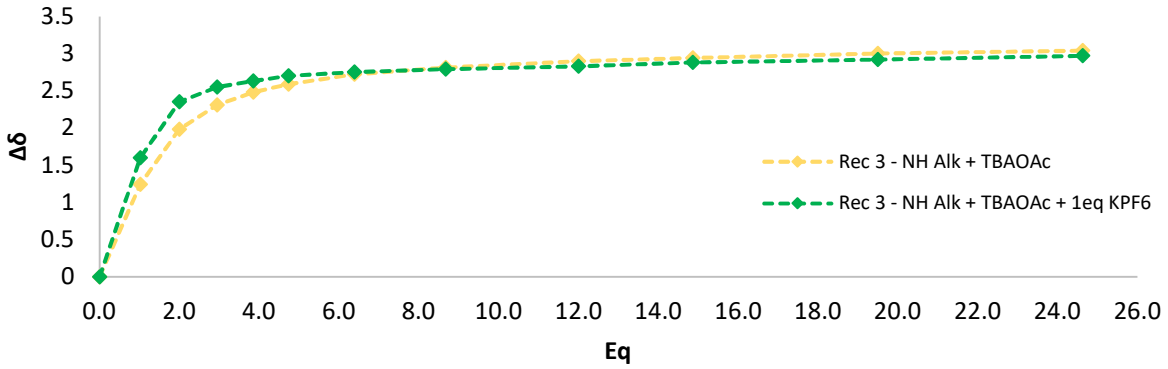


Figure S44. ^{1}H NMR titration binding isotherm of **3** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

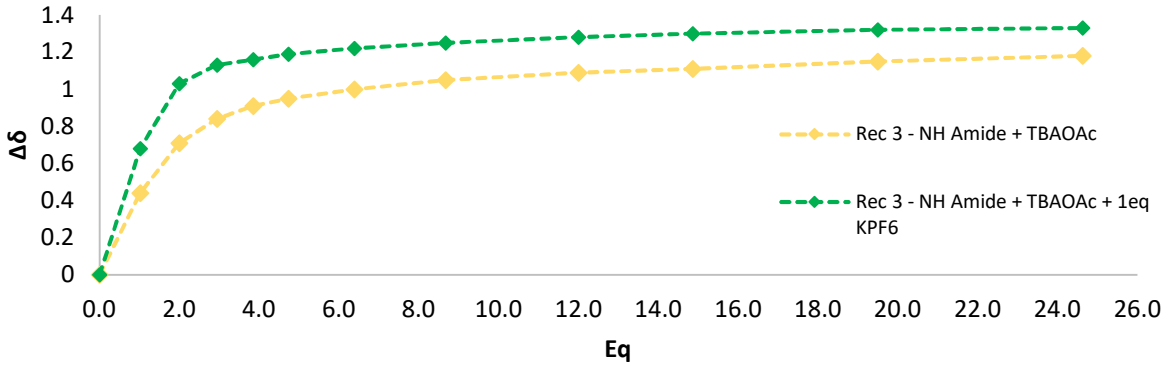


Figure S45. ^{1}H NMR titration binding isotherm of **3** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

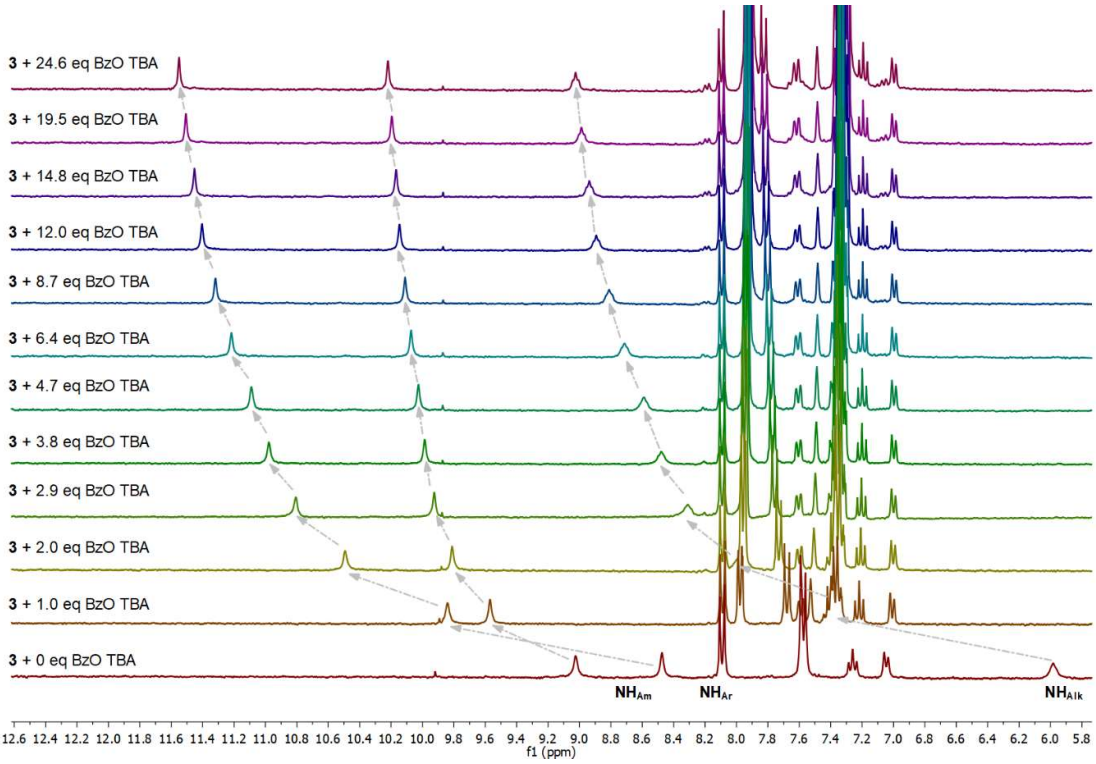


Figure S46. Partial ^{1}H NMR titration experiment of **3** upon titrant (TBAOBz) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

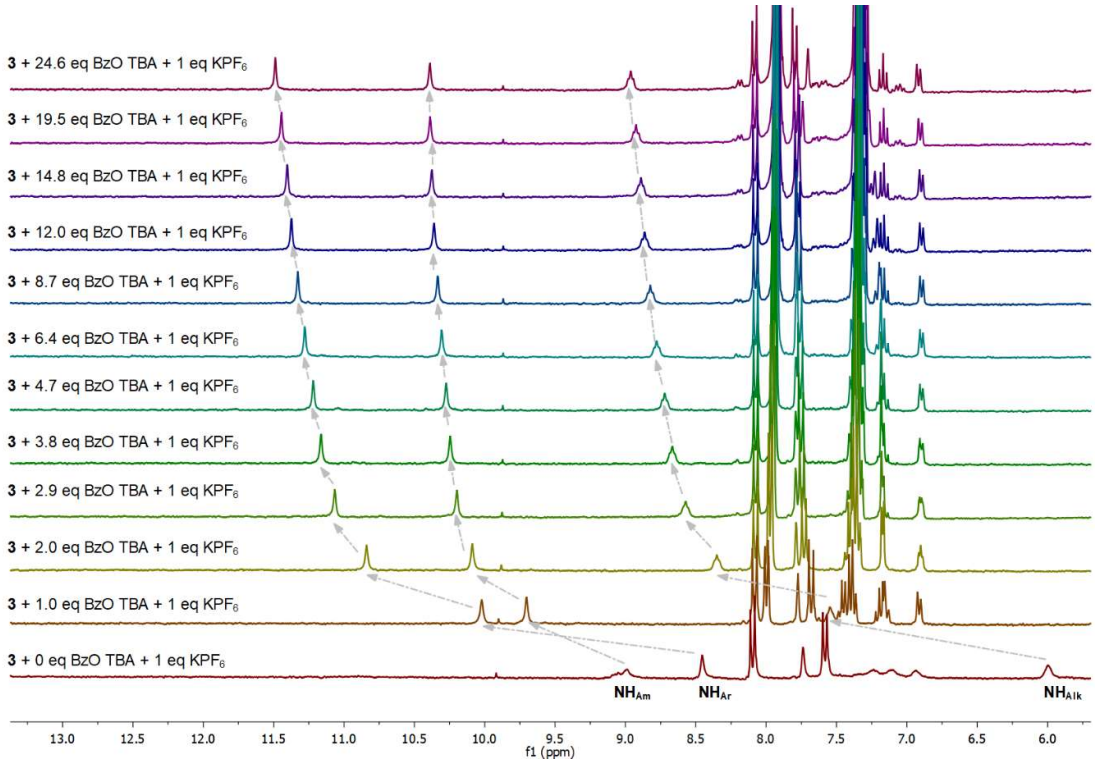


Figure S47. Partial ^{1}H NMR titration experiment of **3** upon titrant (TBAOBz) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

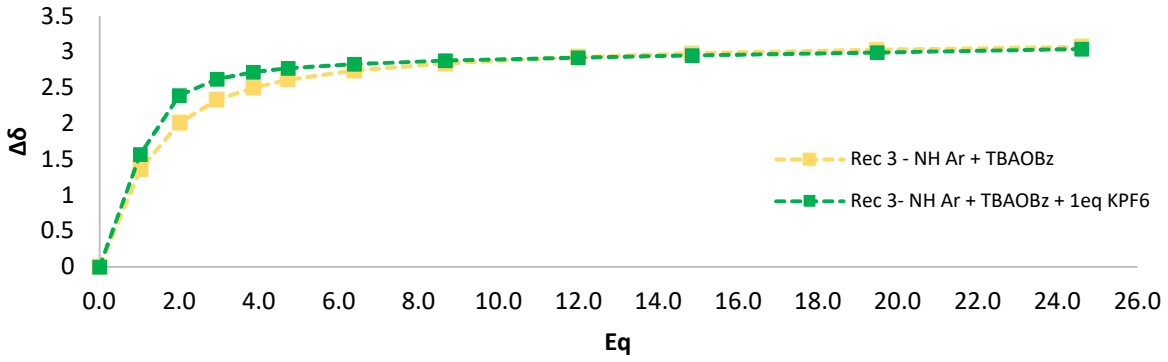


Figure S48. ^{1}H NMR titration binding isotherm of **3** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

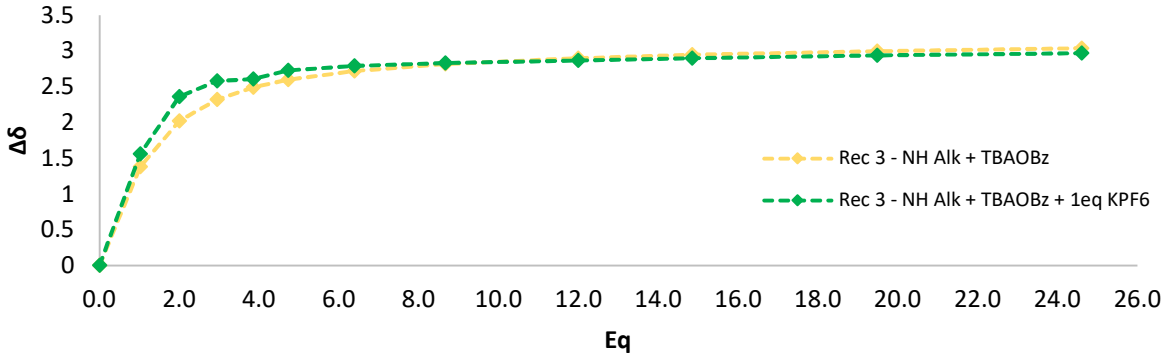


Figure S49. ^{1}H NMR titration binding isotherm of **3** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

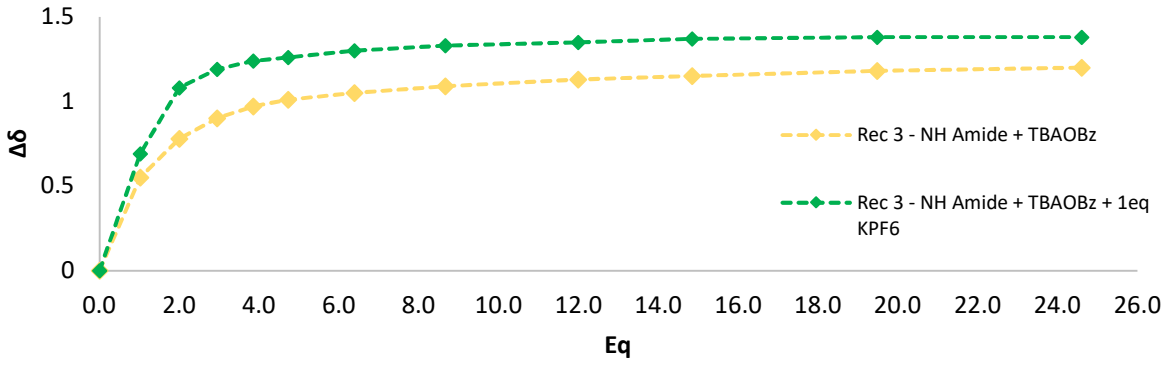


Figure S50. ^{1}H NMR titration binding isotherm of **3** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

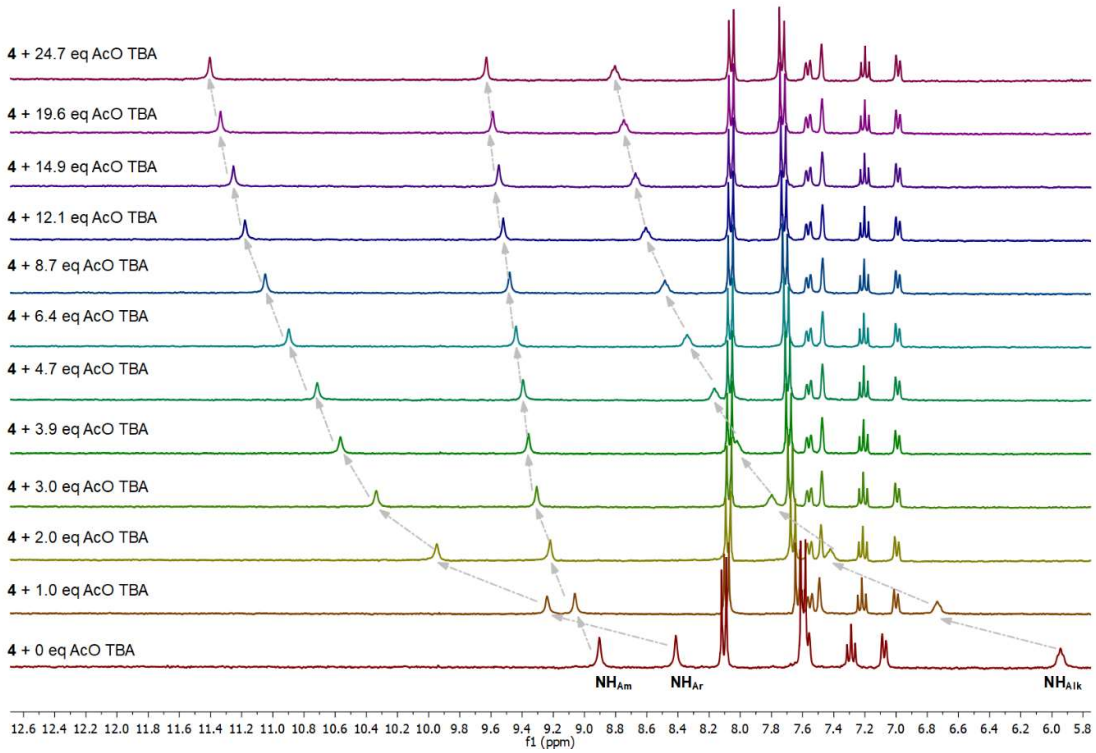


Figure S51. Partial ^{1}H NMR titration experiment of **4** upon titrant (TBAOAc) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

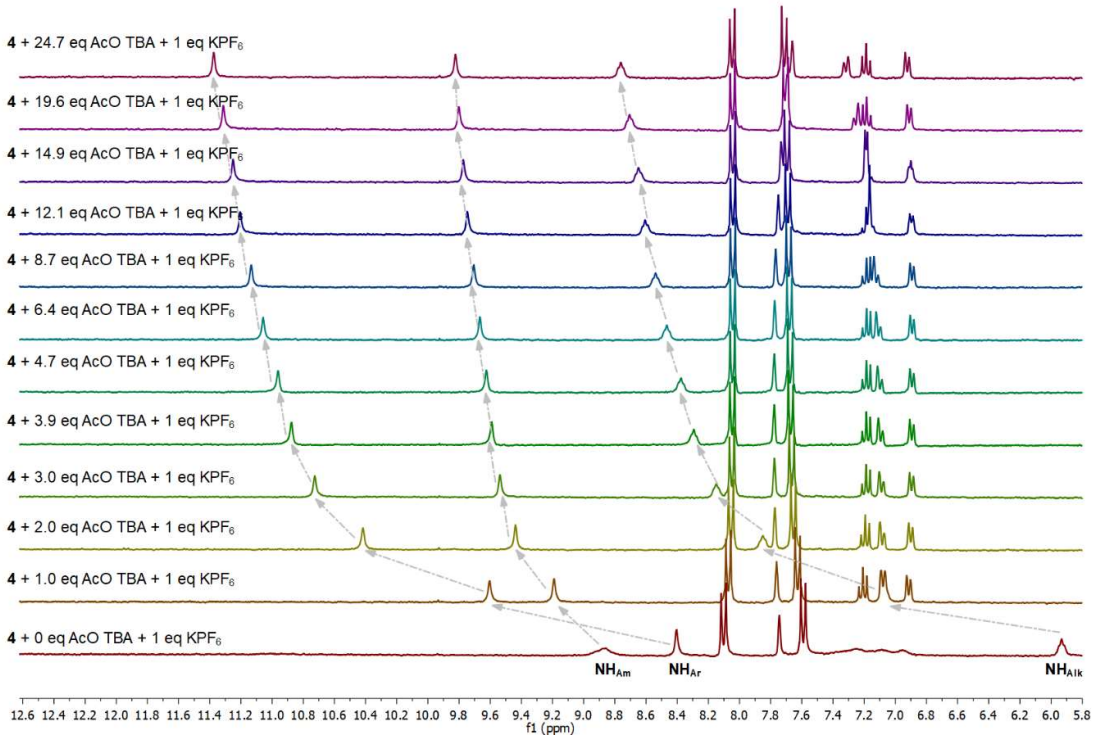


Figure S52. Partial ^{1}H NMR titration experiment of **4** upon titrant (TBAOAc) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

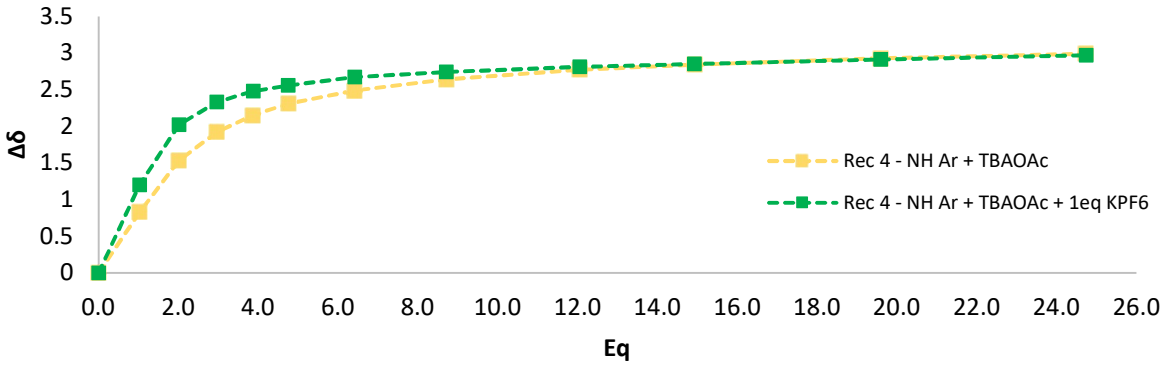


Figure S53. ^{1}H NMR titration binding isotherm of **4** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

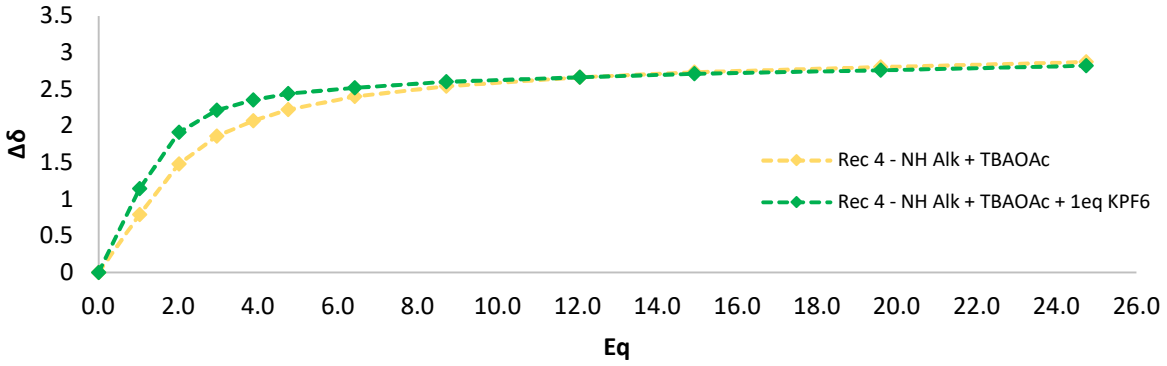


Figure S54. ^{1}H NMR titration binding isotherm of **4** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

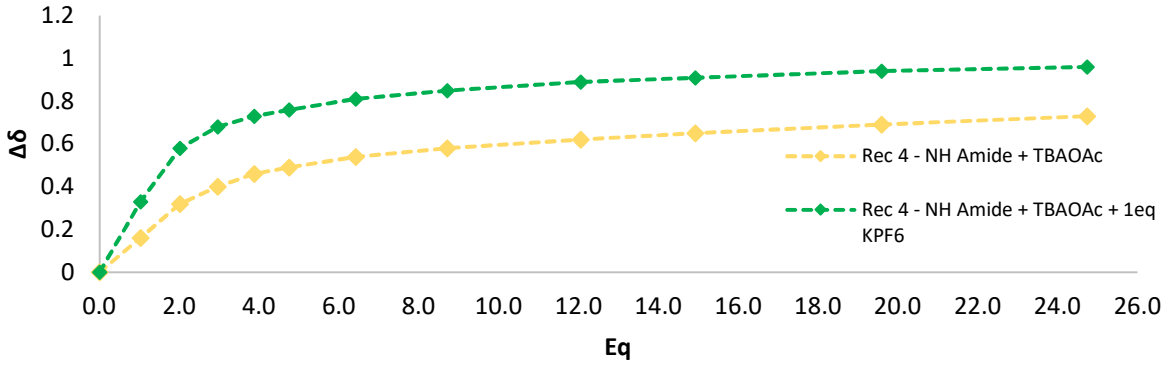


Figure S55. ^{1}H NMR titration binding isotherm of **4** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

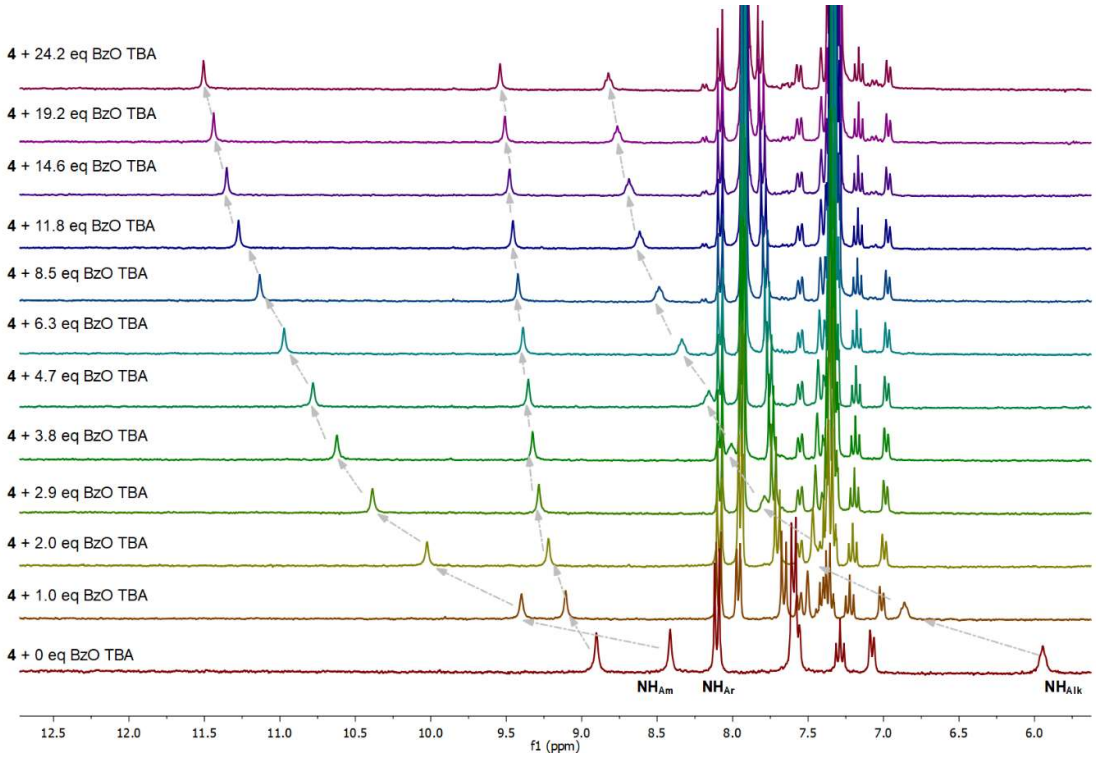


Figure S56. Partial ^{1}H NMR titration experiment of **4** upon titrant (TBAOBz) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

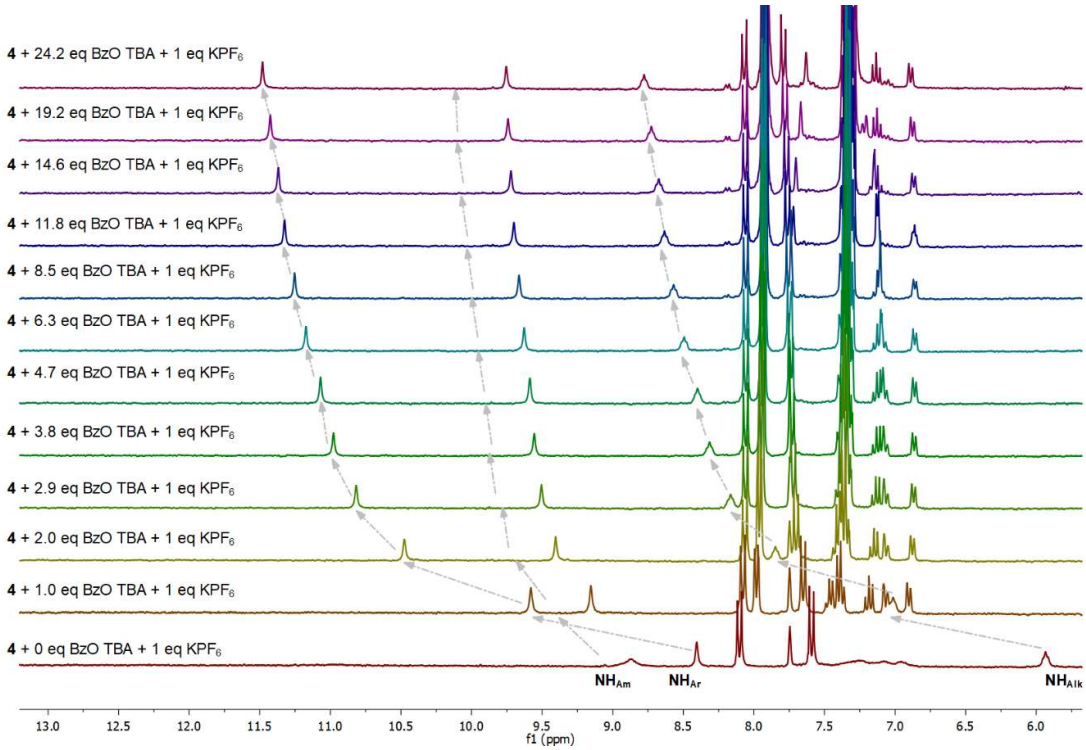


Figure S57. Partial ^{1}H NMR titration experiment of **4** upon titrant (TBAOBz) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

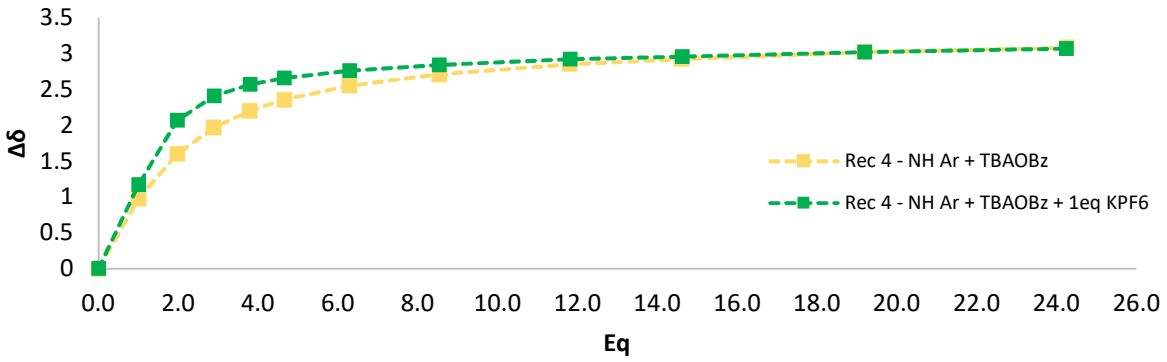


Figure S58. ^{1}H NMR titration binding isotherm of **4** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

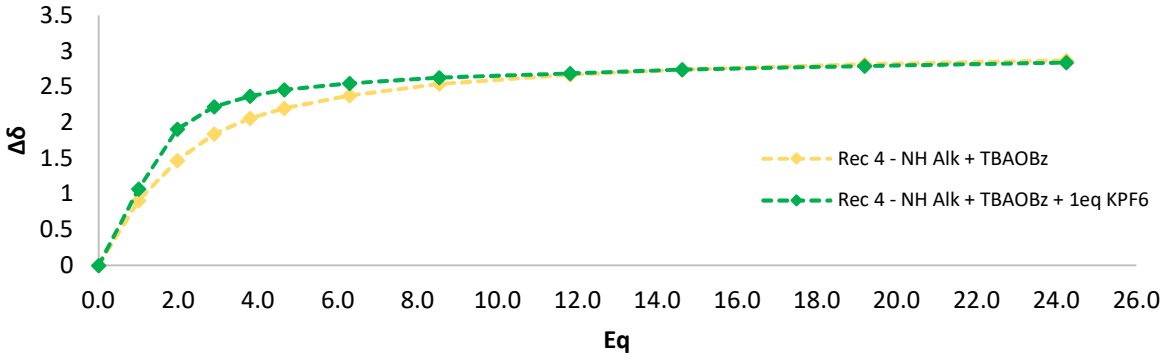


Figure S59. ^{1}H NMR titration binding isotherm of **4** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

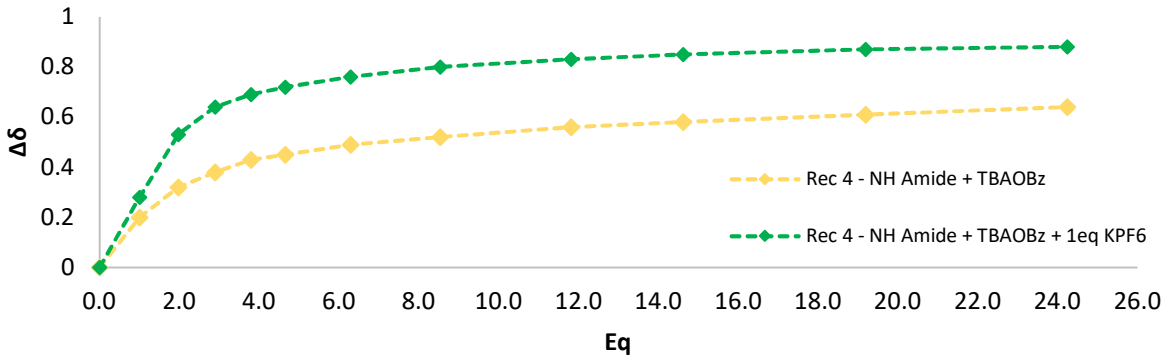


Figure S60. ^{1}H NMR titration binding isotherm of **4** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

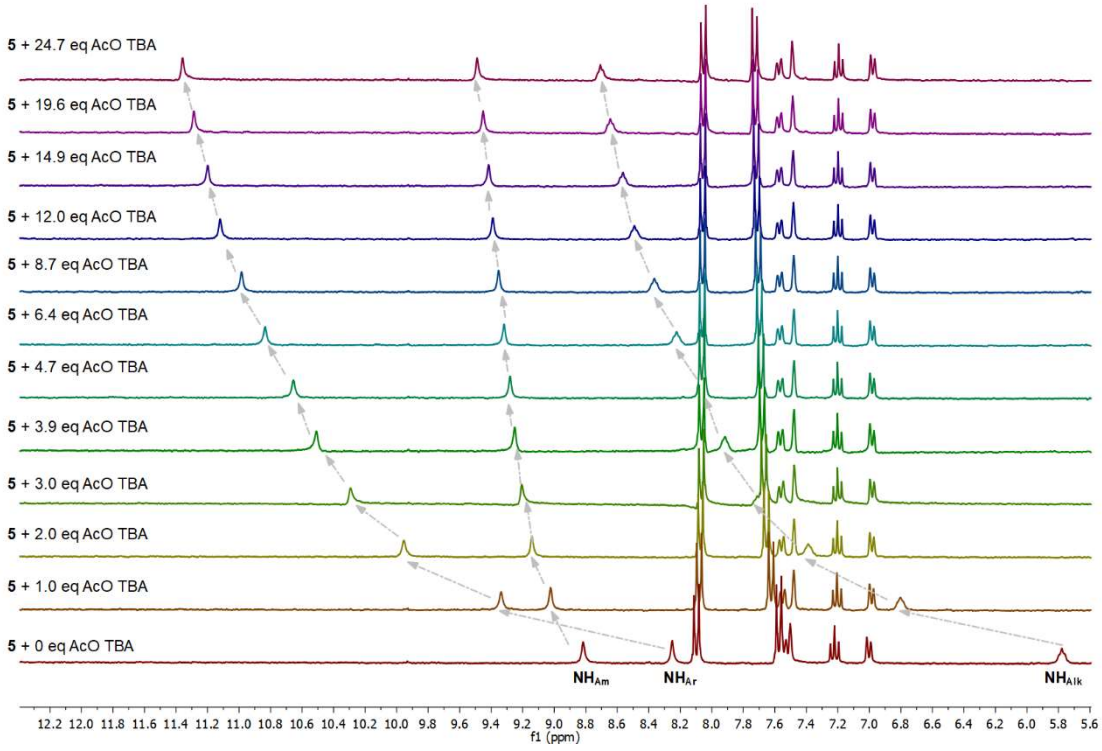


Figure S61. Partial ^{1}H NMR titration experiment of **5** upon titrant (TBAOAc) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.0 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

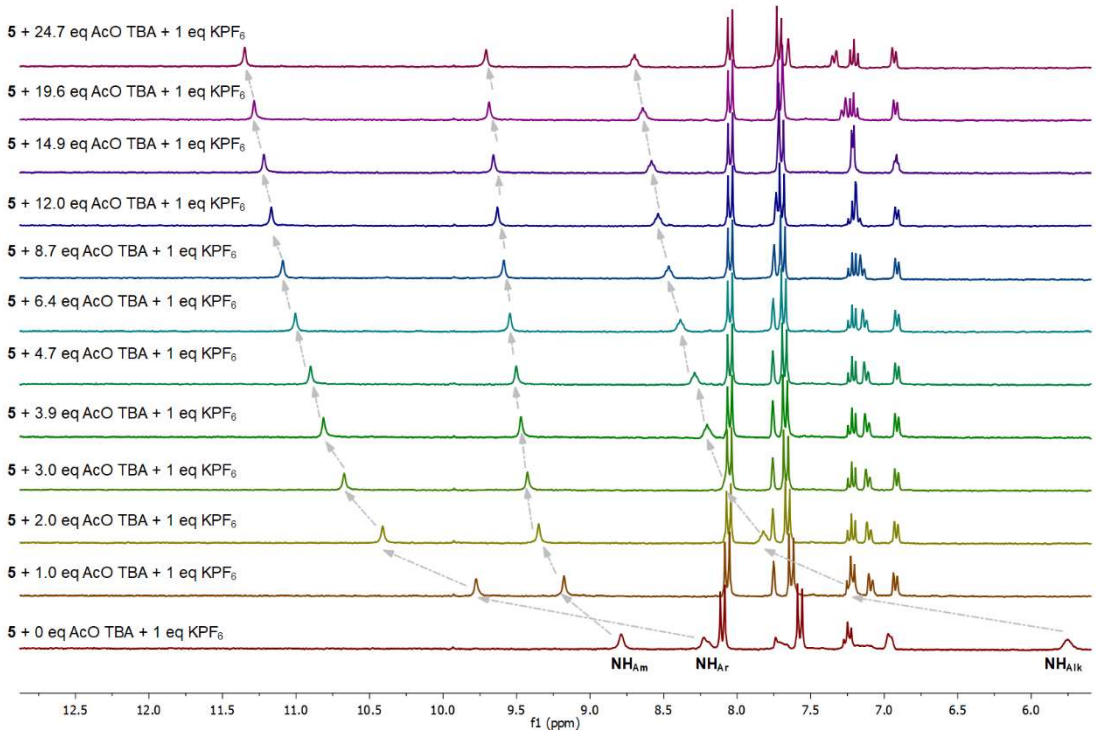


Figure S62. Partial ^{1}H NMR titration experiment of **5** upon titrant (TBAOAc) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.0 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

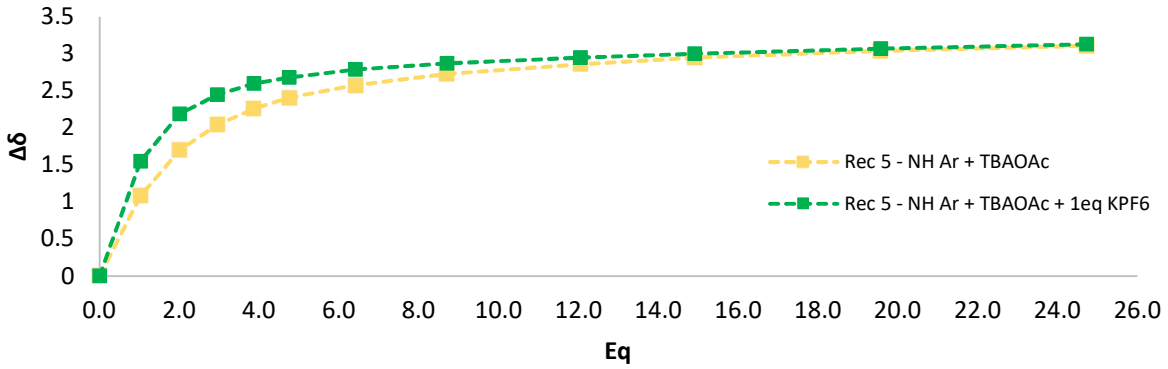


Figure S63. ^{1}H NMR titration binding isotherm of **5** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

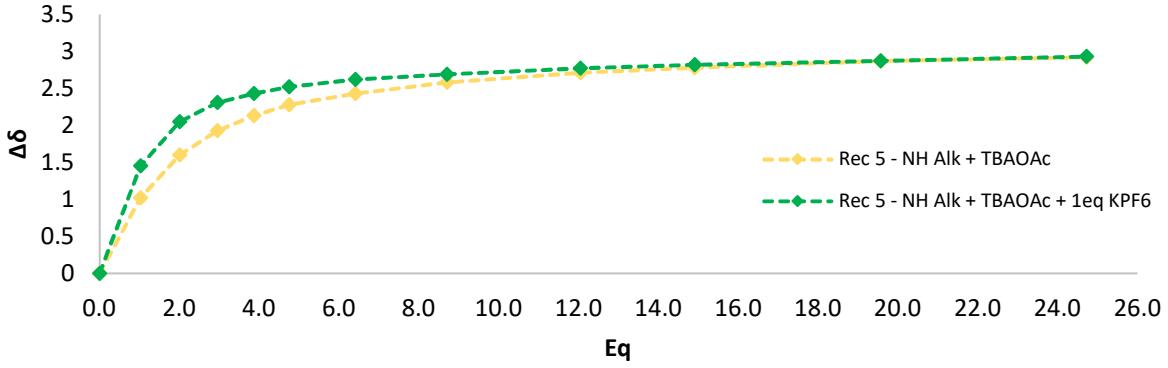


Figure S64. ^{1}H NMR titration binding isotherm of **5** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

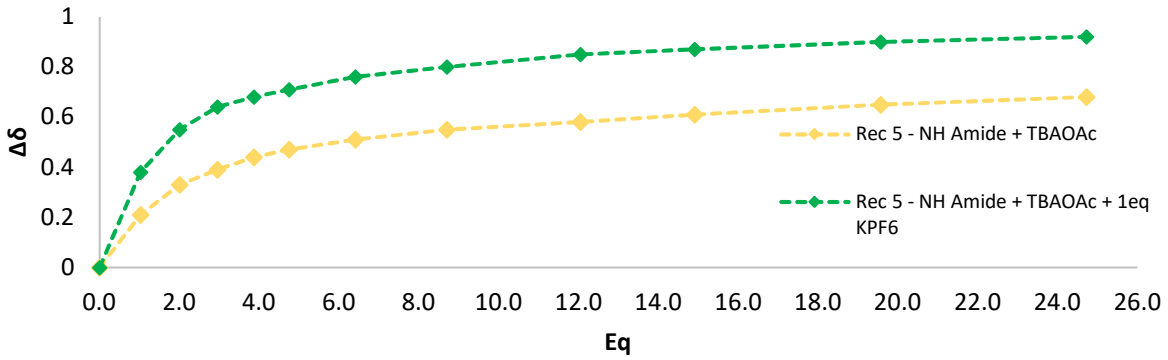


Figure S65. ^{1}H NMR titration binding isotherm of **5** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

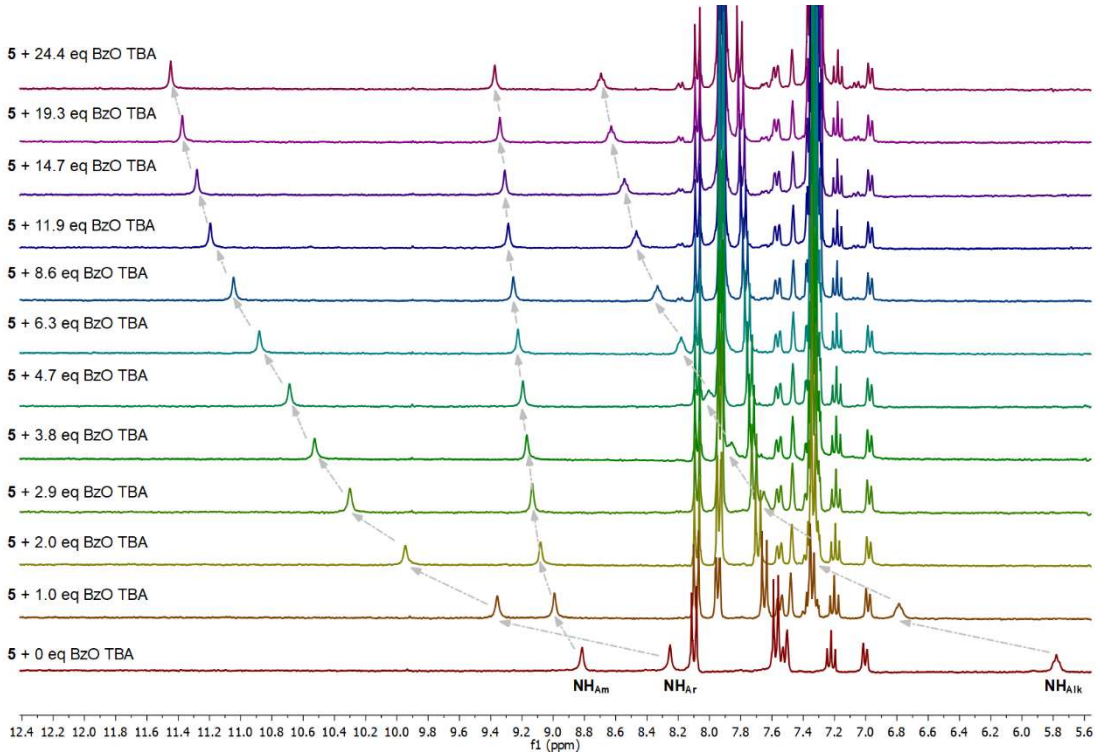


Figure S66. Partial ^{1}H NMR titration experiment of **5** upon titrant (TBAOBz) addition, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

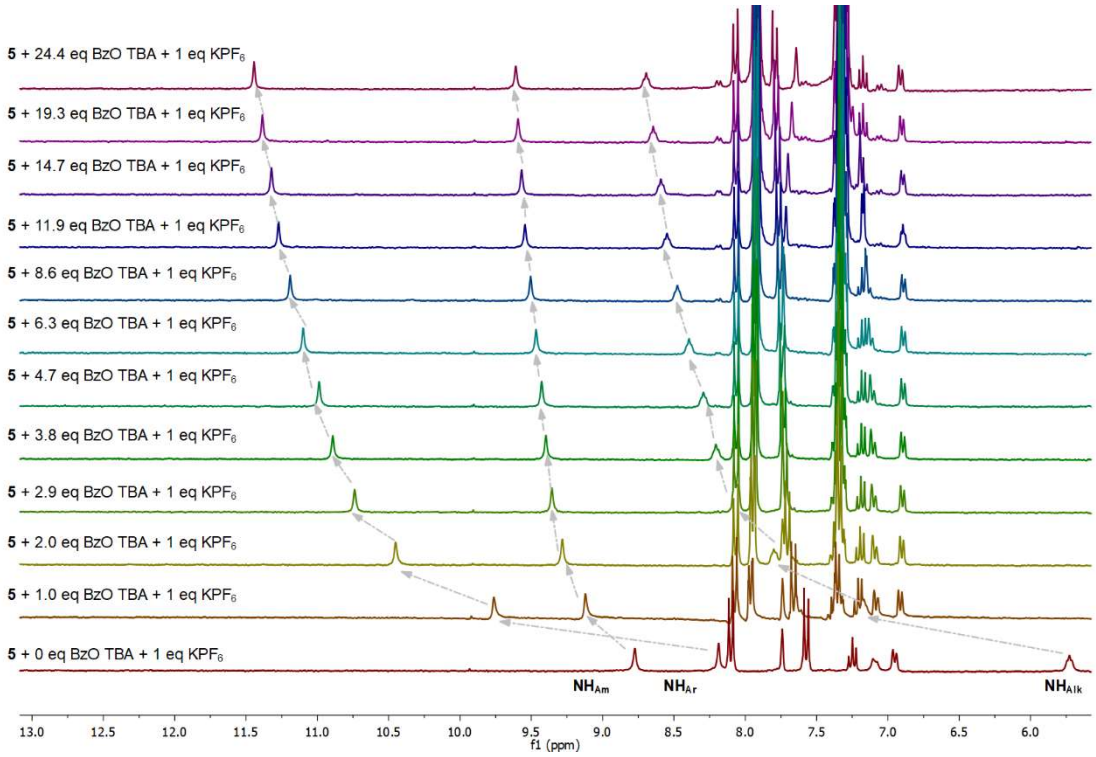


Figure S67. Partial ^{1}H NMR titration experiment of **5** upon titrant (TBAOBz) addition in presence of 1eq. KPF_6, (293 K, 3% H_2O/CD_3CN solution, $C_{titrant}$=2.1 x10^{-1} M, $C_{receptor}$=4.0 x10^{-3} M)

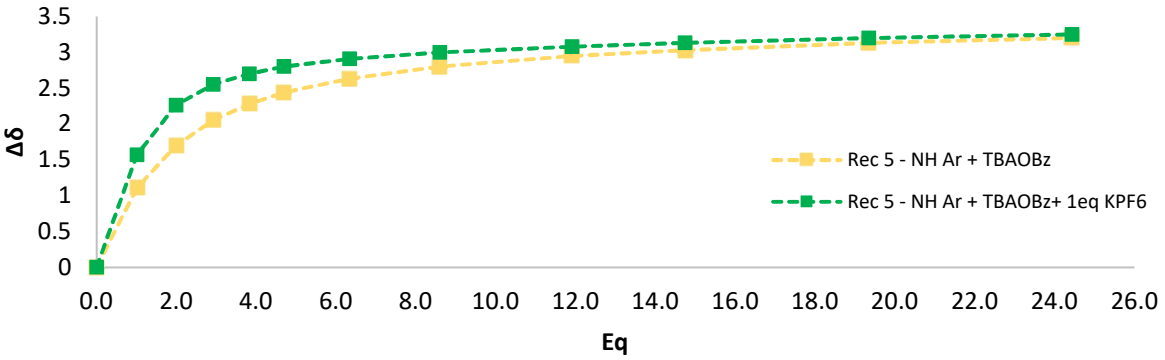


Figure S68. ^{1}H NMR titration binding isotherm of **5** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

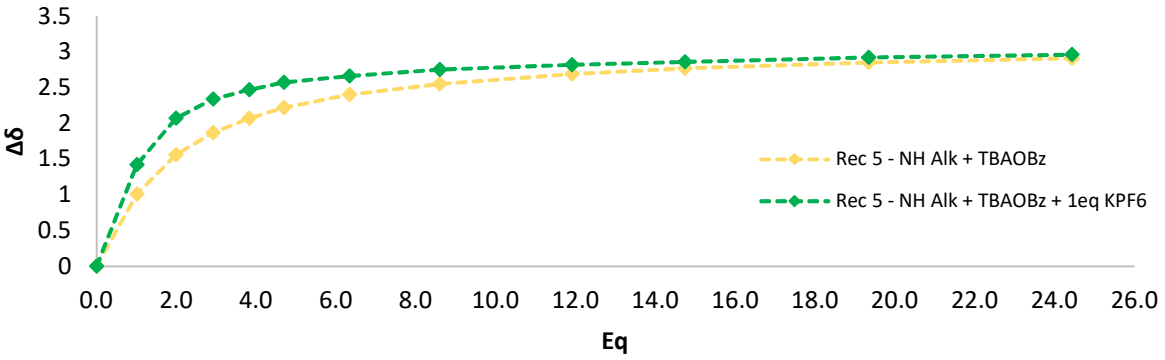


Figure S69. ^{1}H NMR titration binding isotherm of **5** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

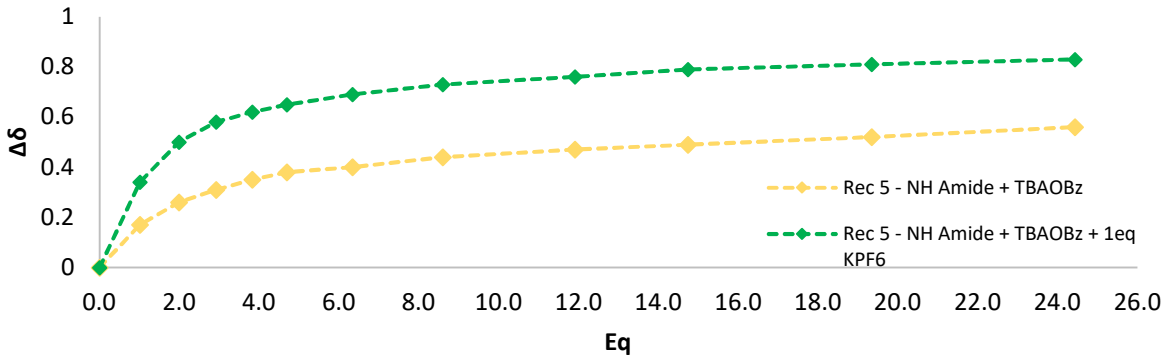


Figure S70. ^{1}H NMR titration binding isotherm of **5** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

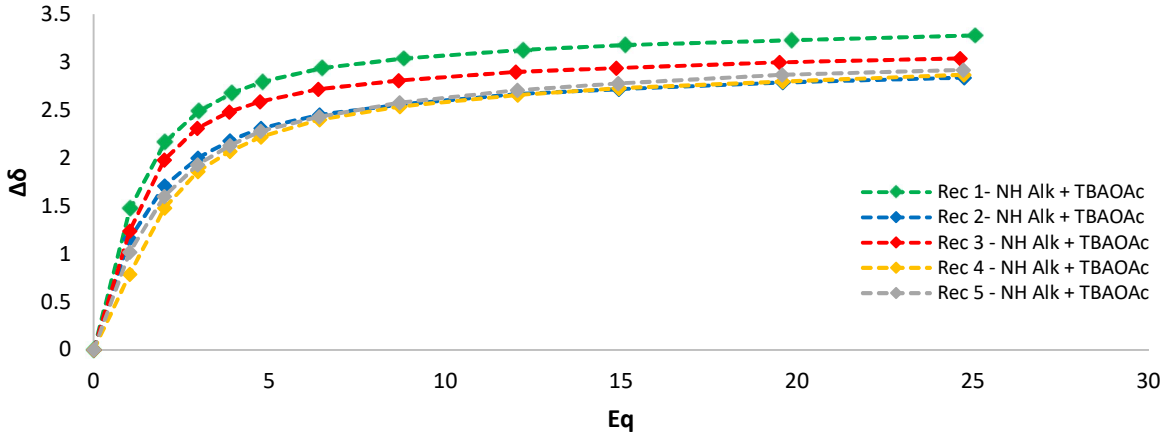


Figure S71. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOAc, 3% H_2O/CD_3CN solution

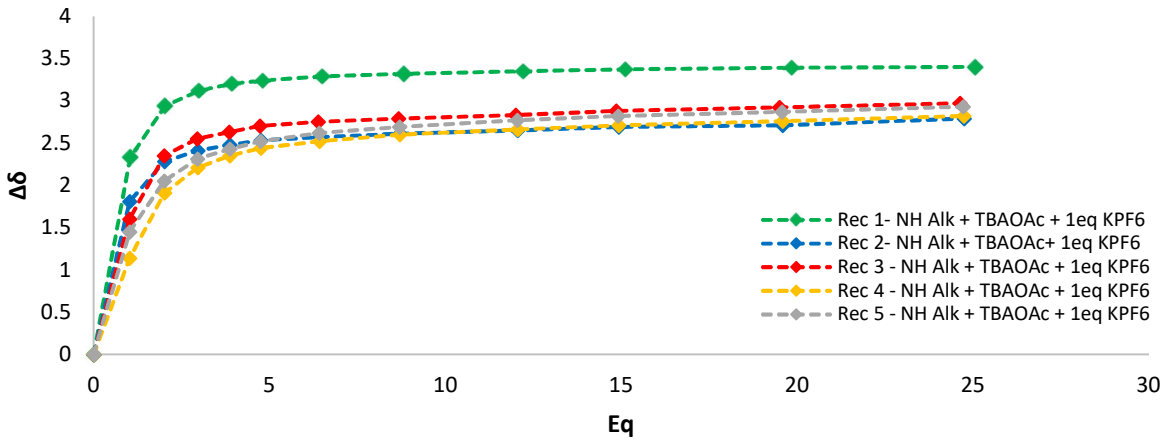


Figure S72. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

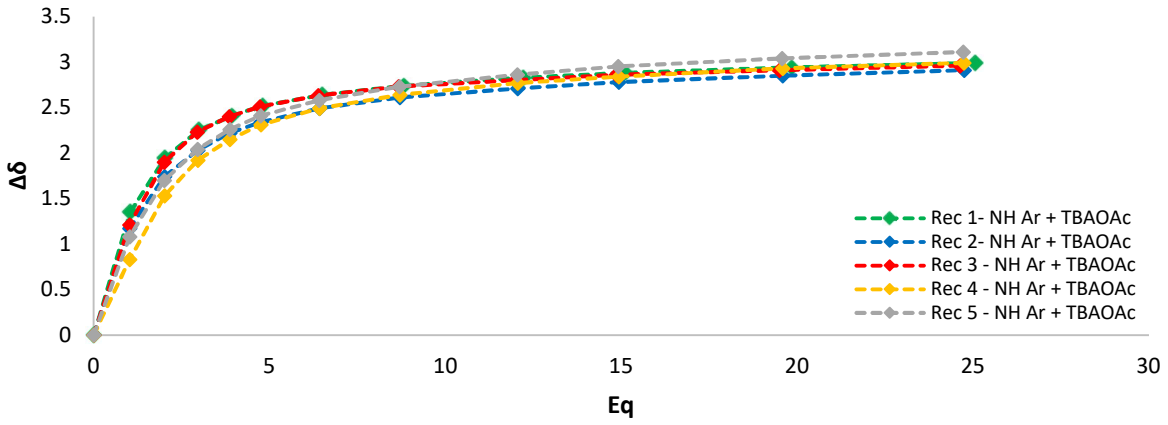


Figure S73. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOAc, 3% H_2O/CD_3CN solution

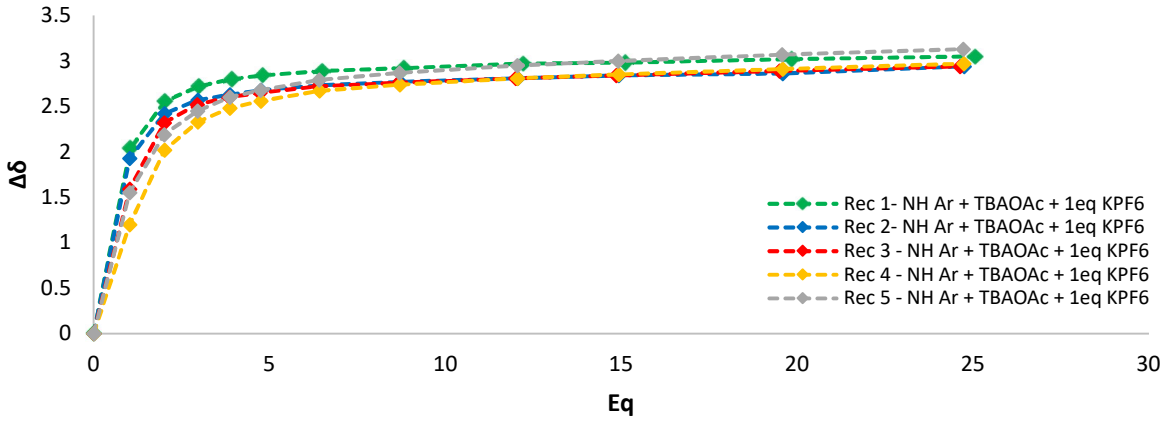


Figure S74. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution.

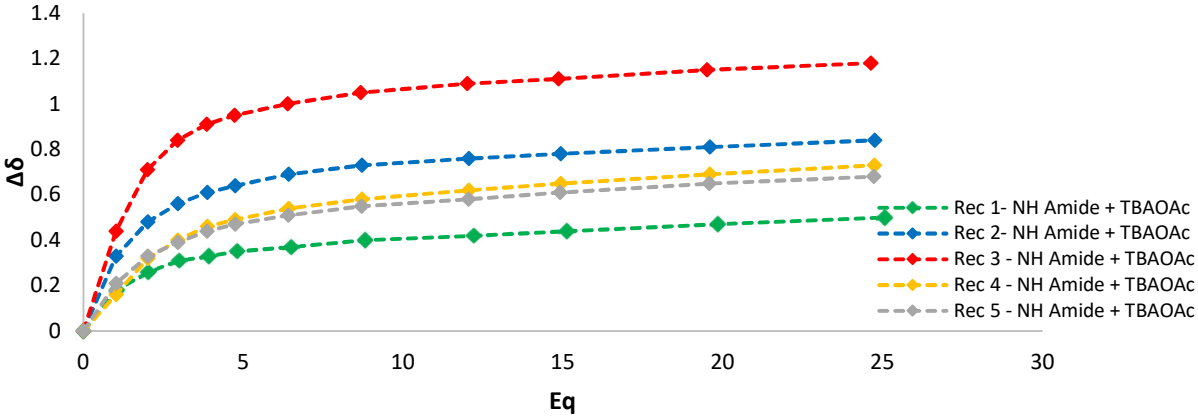


Figure S75. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOAc, 3% H_2O/CD_3CN solution

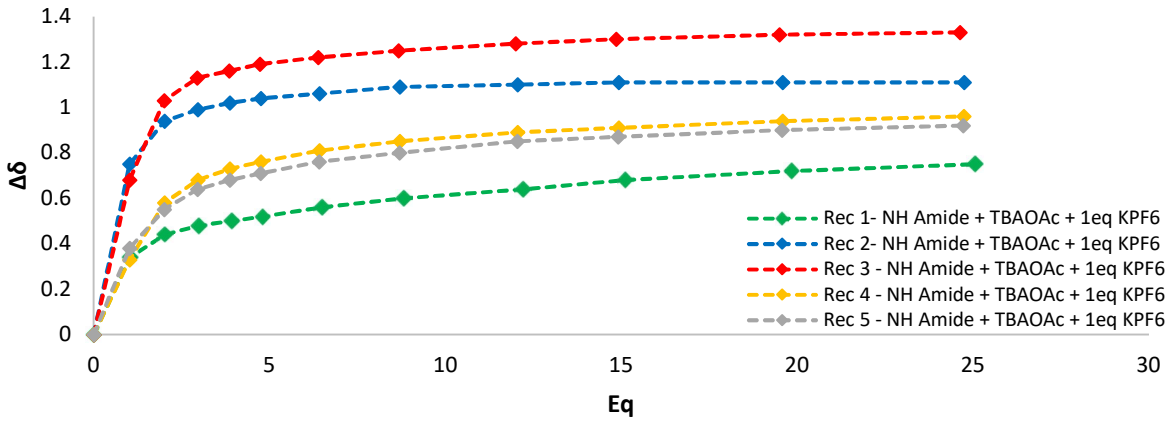


Figure S76. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOAc in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

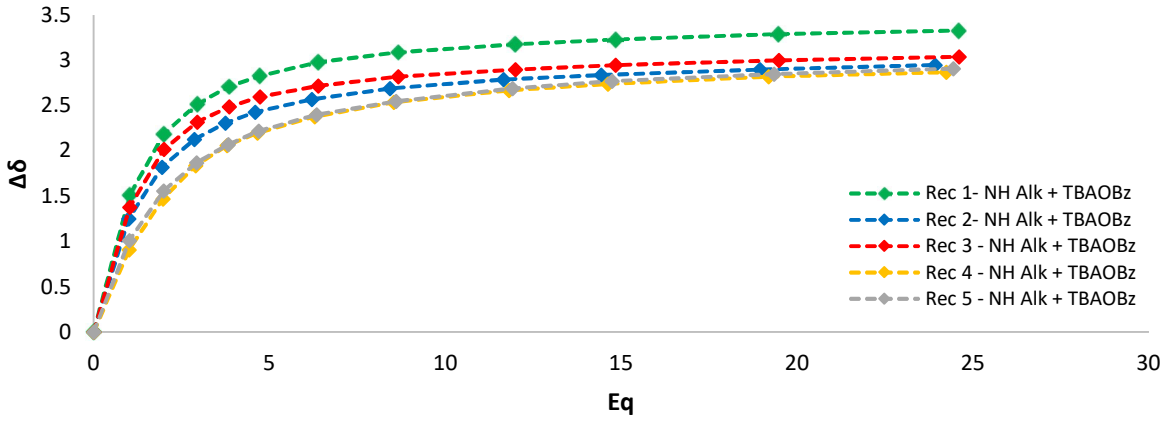


Figure S77. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOBz, 3% H_2O/CD_3CN solution

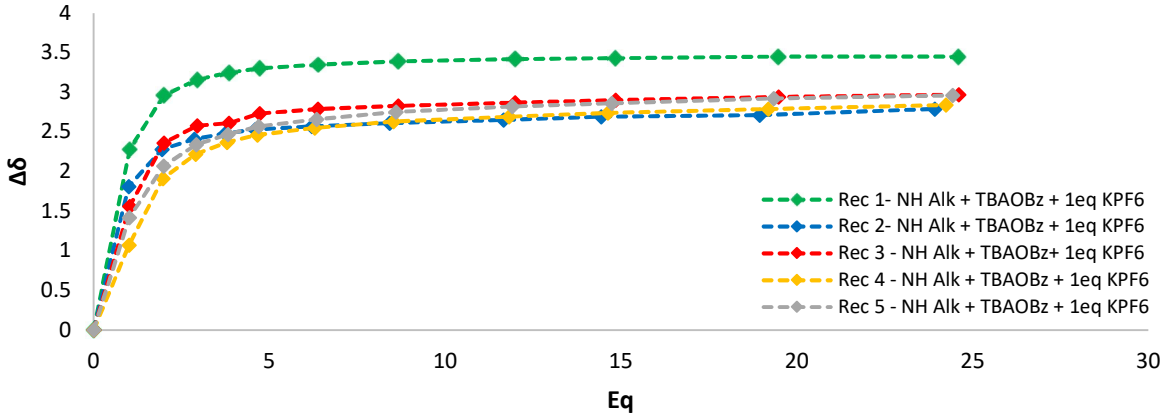


Figure S78. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

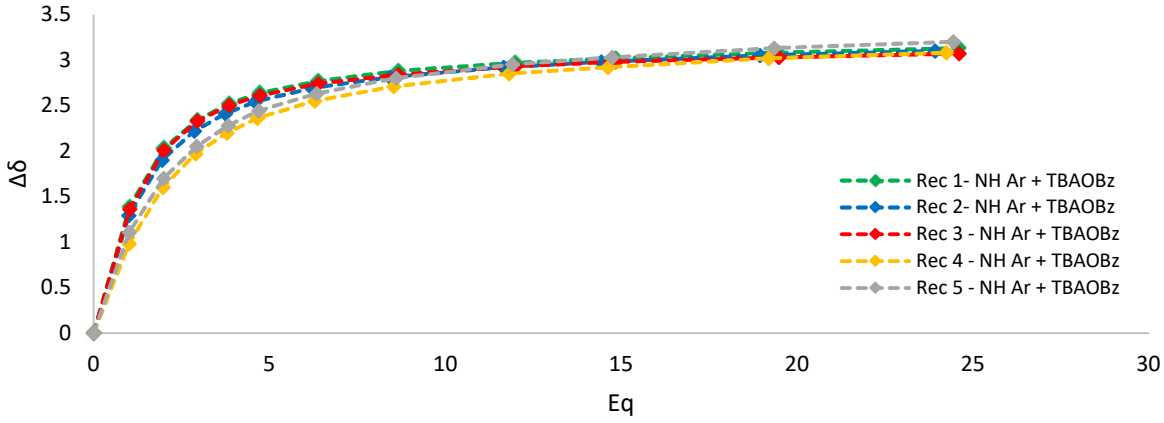


Figure S79. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOBz, 3% H_2O/CD_3CN solution

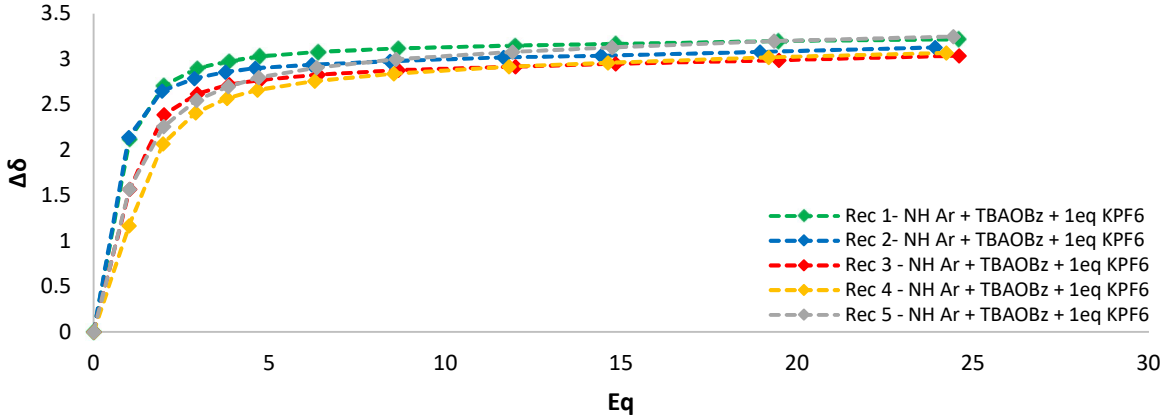


Figure S80. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

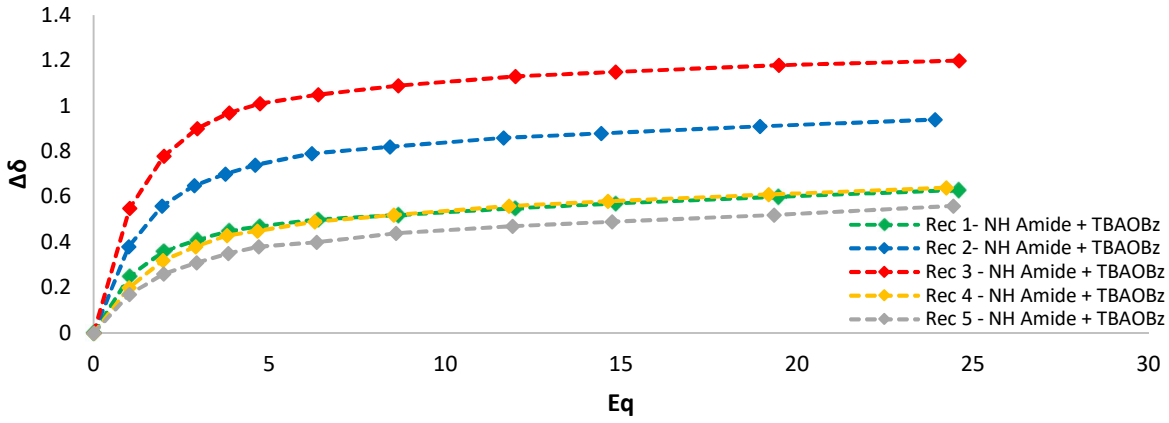


Figure S81. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOBz, 3% H_2O/CD_3CN solution

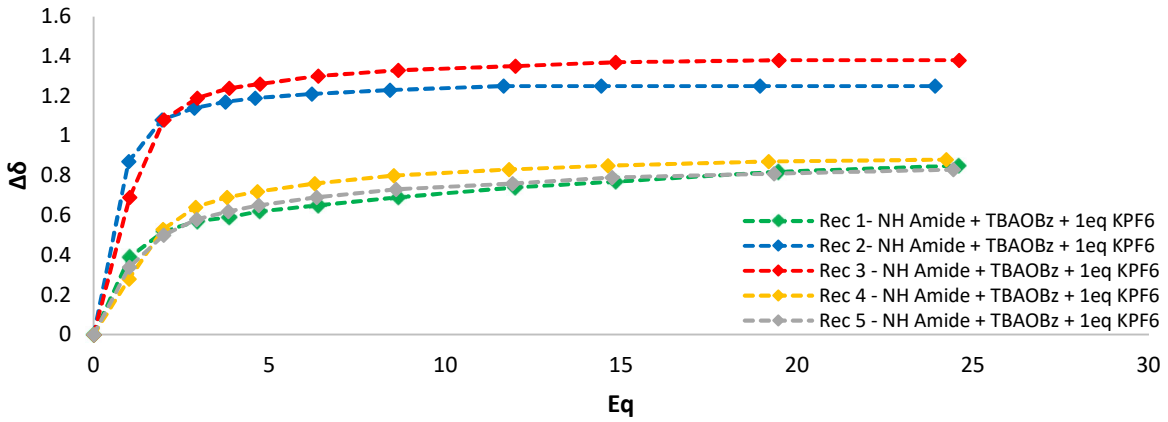


Figure S82. ^{1}H NMR titration binding isotherm of receptors **1-5** with TBAOBz in the presence or absence of 1 eq. of cations, 3% H_2O/CD_3CN solution

Receptor	TBAOAc	KOAc	K_K/K_{TBA}	TBAOBz	KOBz	K_K/K_{TBA}
1	320 (±2.6%)	1330 (±11.2%)	4.15	320 (±2.3%)	1200 (±11.0%)	3.8
2	240 (±2.3%)	1200 (±9.1%)	5.0	270 (±2.2%)	1600 (±9.8%)	5.9
3	290 (±2.7%)	680 (±5.2%)	2.3	330 (±1.6%)	630 (±5.7%)	1.9
4	150 (±3.8%)	330 (±5.6%)	2.2	160 (±1.3%)	320 (±6.7%)	2
5	180 (±1.9%)	420 (±4.9%)	2.3	160 (±1.8%)	400 (±3.7%)	2.5

Figure S83. ^{1}H NMR spectroscopy K_{obs} values (298 K; 3% H_2O/CD_3CN solution) for interactions of the receptors **1-5** with anions in the presence or absence of potassium cation and errors values in parentheses

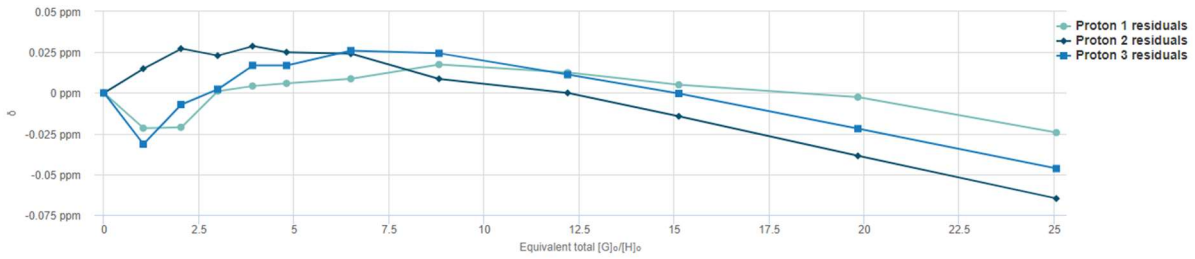


Figure S84. Residual plot for ^{1}H NMR titration experiment for receptor **1** with TBAOAc, 3% H_2O/CD_3CN solution

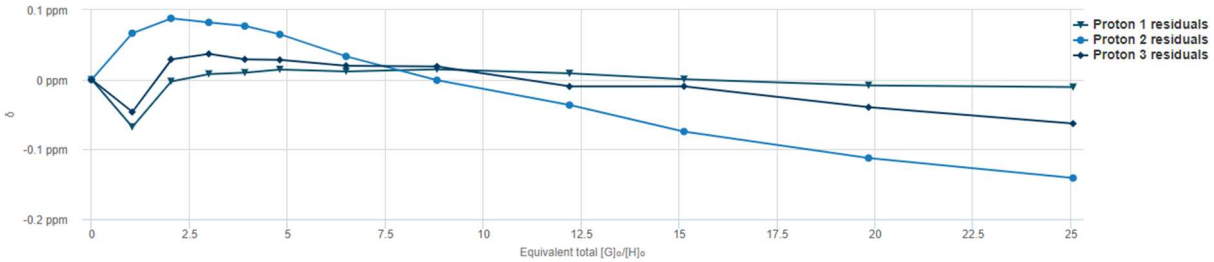


Figure S85. Residual plot for ^{1}H NMR titration experiment for receptor **1** with TBAOAc in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

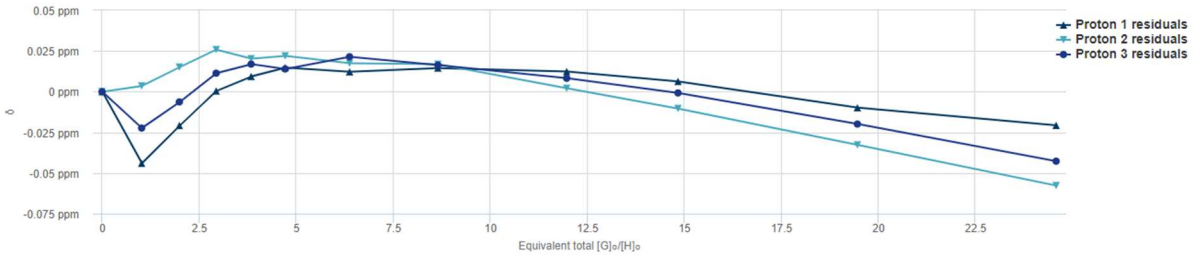


Figure S86. Residual plot for ^{1}H NMR titration experiment for receptor **1** with TBAOBz, 3% H_2O/CD_3CN solution

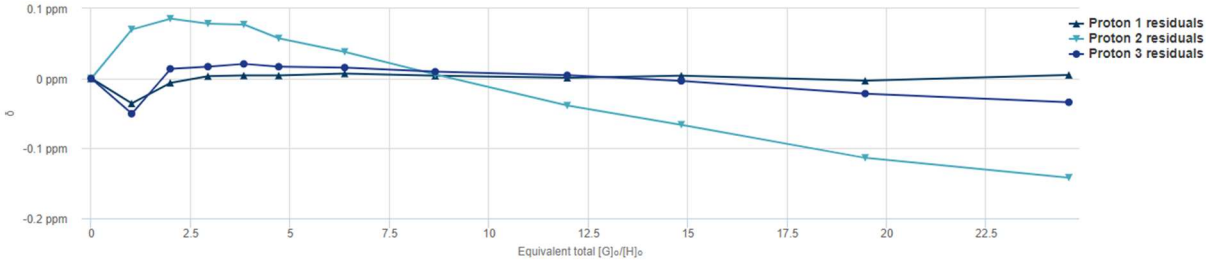


Figure S87. Residual plot for ^{1}H NMR titration experiment for receptor **1** with TBAOBz in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

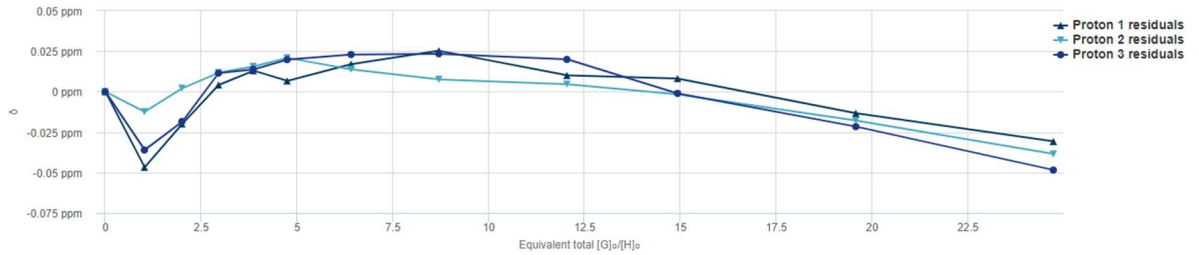


Figure S88. Residual plot for ^{1}H NMR titration experiment for receptor **2** with TBAOAc, 3% H_2O/CD_3CN solution

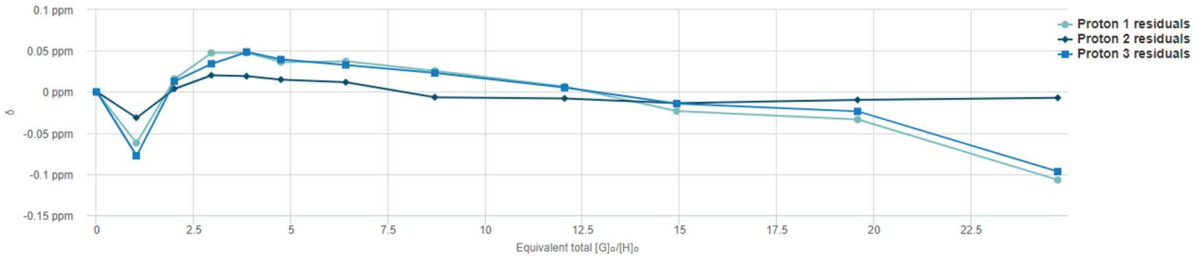


Figure S89. Residual plot for ^{1}H NMR titration experiment for receptor **2** with TBAOAc in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

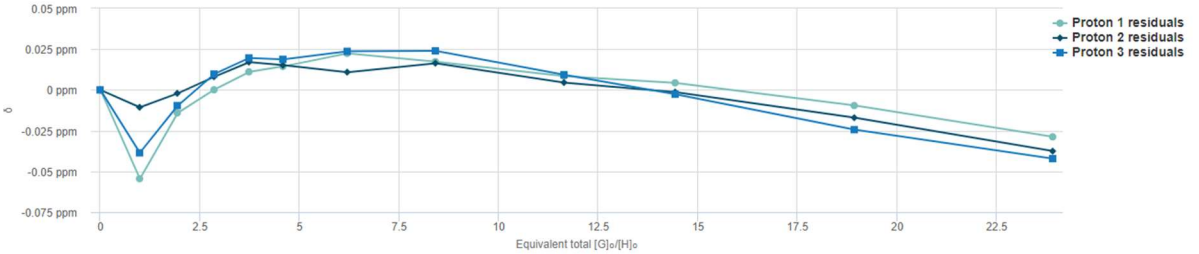


Figure S90. Residual plot for ^{1}H NMR titration experiment for receptor **2** with TBAOBz, 3% H_2O/CD_3CN solution

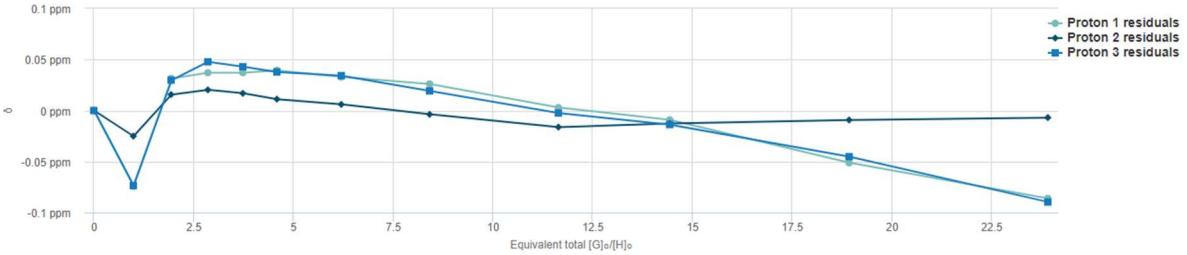


Figure S91. Residual plot for ^{1}H NMR titration experiment for receptor **2** with TBAOBz in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

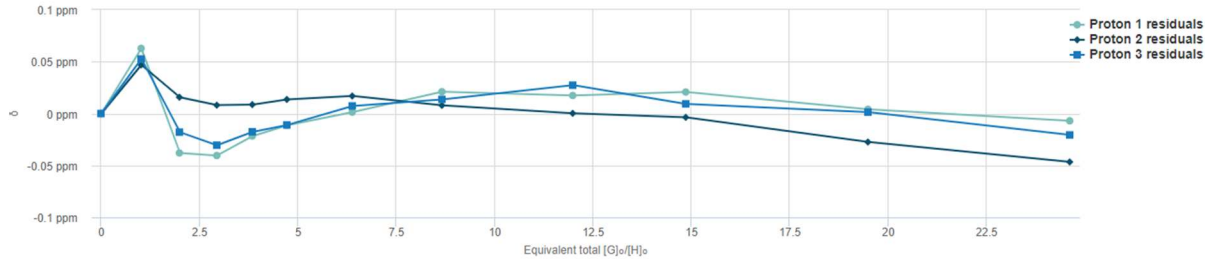


Figure S92. Residual plot for ^{1}H NMR titration experiment for receptor **3** with TBAOAc, 3% H_2O/CD_3CN solution

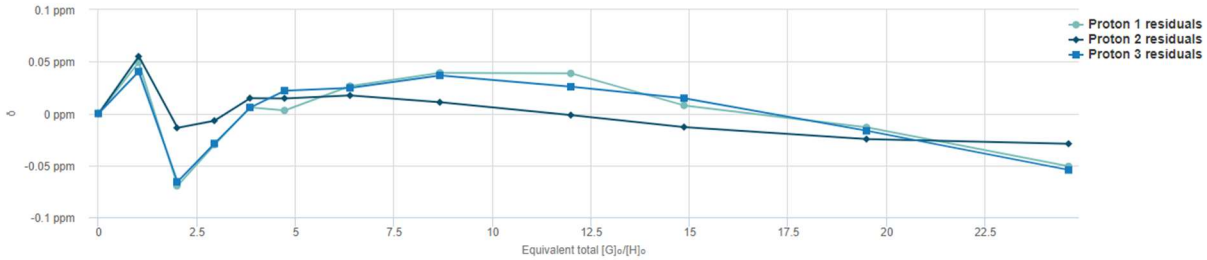


Figure S93. Residual plot for ^{1}H NMR titration experiment for receptor **3** with TBAOAc in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

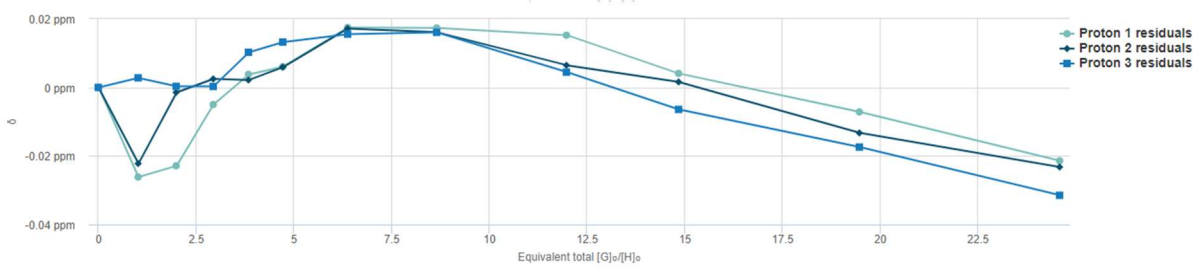


Figure S94. Residual plot for ^{1}H NMR titration experiment for receptor **3** with TBAOBz, 3% H_2O/CD_3CN solution

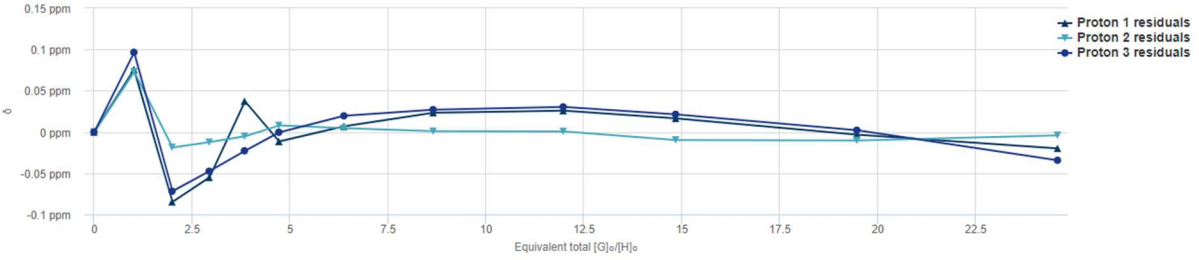


Figure S95. Residual plot for ^{1}H NMR titration experiment for receptor **3** with TBAOBz in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

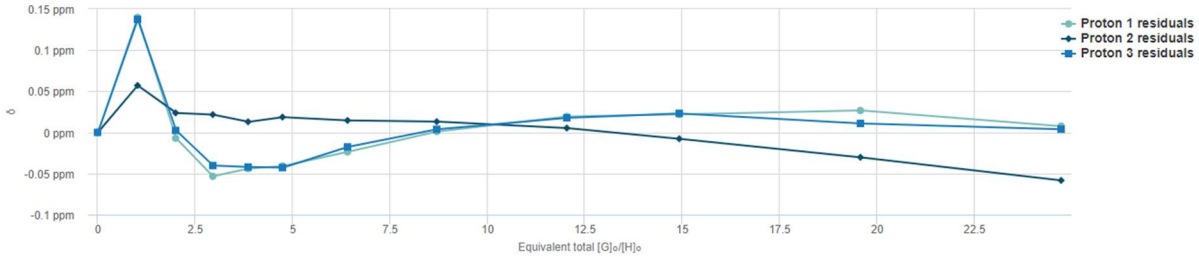


Figure S96. Residual plot for ^{1}H NMR titration experiment for receptor **4** with TBAOAc, 3% H_2O/CD_3CN solution

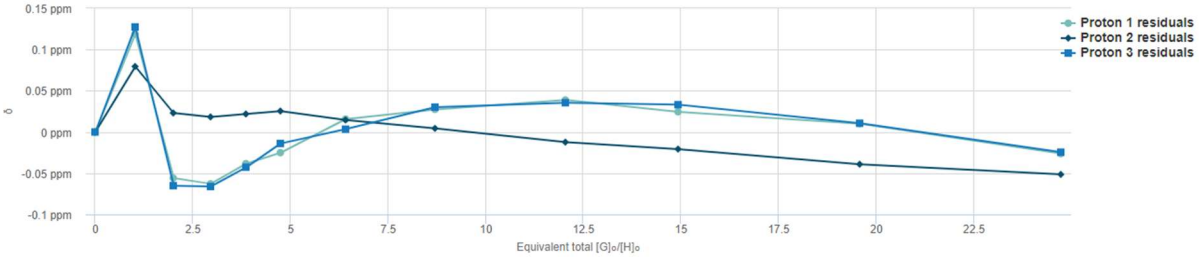


Figure S97. Residual plot for ^{1}H NMR titration experiment for receptor **4** with TBAOAc in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

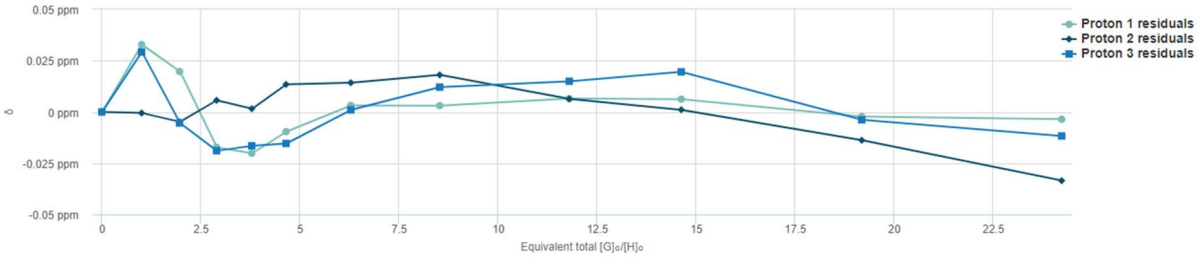


Figure S98. Residual plot for ^{1}H NMR titration experiment for receptor **4** with TBAOBz, 3% H_2O/CD_3CN solution

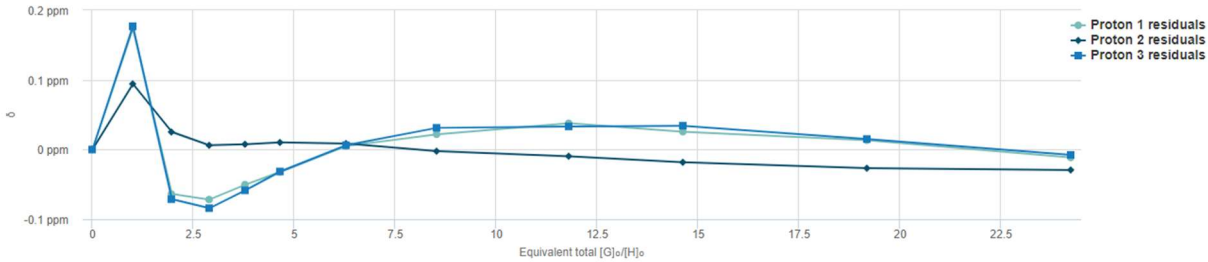


Figure S99. Residual plot for ^{1}H NMR titration experiment for receptor **4** with TBAOBz in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

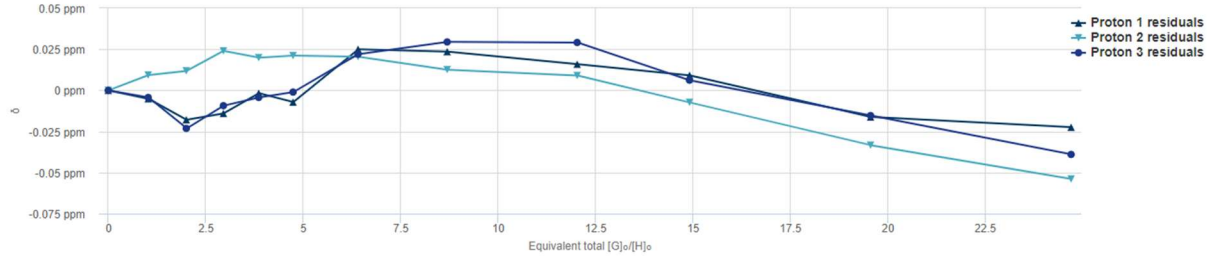


Figure S100. Residual plot for ^{1}H NMR titration experiment for receptor **5** with TBAOAc, 3% H_2O/CD_3CN solution

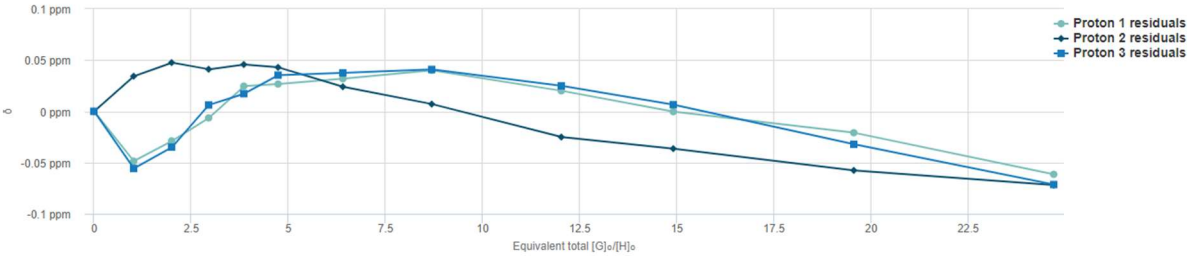


Figure S101. Residual plot for ^{1}H NMR titration experiment for receptor **5** with TBAOAc in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

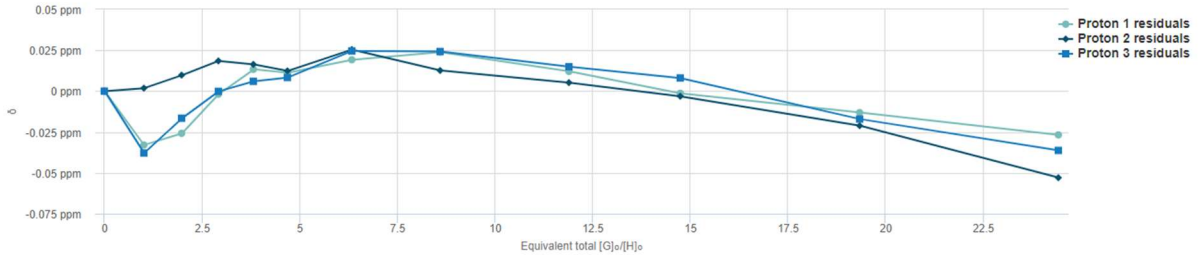


Figure S102. Residual plot for ^{1}H NMR titration experiment for receptor **5** with TBAOBz, 3% H_2O/CD_3CN solution

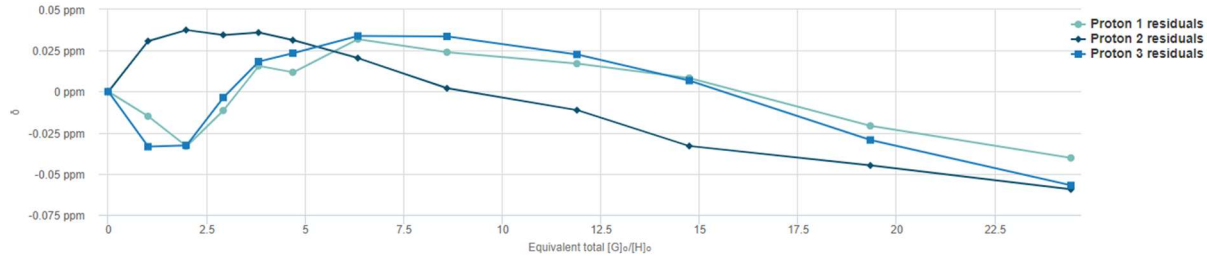


Figure S103. Residual plot for ^{1}H NMR titration experiment for receptor **5** with TBAOBz in the presence of 1 eq. of potassium cations, 3% H_2O/CD_3CN solution

3. The ^{1}H NMR extraction experiments

The^{1}H NMR extraction experiments were performed on a 300 MHz Bruker Avance spectrometer, at 298 K, in $CDCl_3$ solution. In each case 0.5 mL of 1.25-2.5 x 10^{-2} M solution of the receptor **1-5** was washed with water, then after phase separation, the receptor solution was extracted with aqueous solution of salts for 1 minute. The equivalent of salt in water solution was calculated based on molarity of the receptor in chloroform phase. *For example: 0.5 ml of chloroform solution of the receptor **1** (2.5x10^{-2} M) was extracted with 0.5 ml of KOAc water solution (1.25 M) which corresponded to 50 eq.* Then chloroform phase containing receptor-salt complex was washed with water ('back' extraction), to prove the reversibility of extraction process. After each step of the experiment ^{1}H NMR spectrum was registered. The efficiency of the extraction process was calculated on the basis of the carboxylate alkyl signals integration values, assuming the receptor as an internal standard. The 100% efficiency corresponds to fully salt loaded receptor.

- Control experiment checking salt affinity to aqueous phase. Conformation that KOAc in LLE experiment condition was not extracted with chloroform.

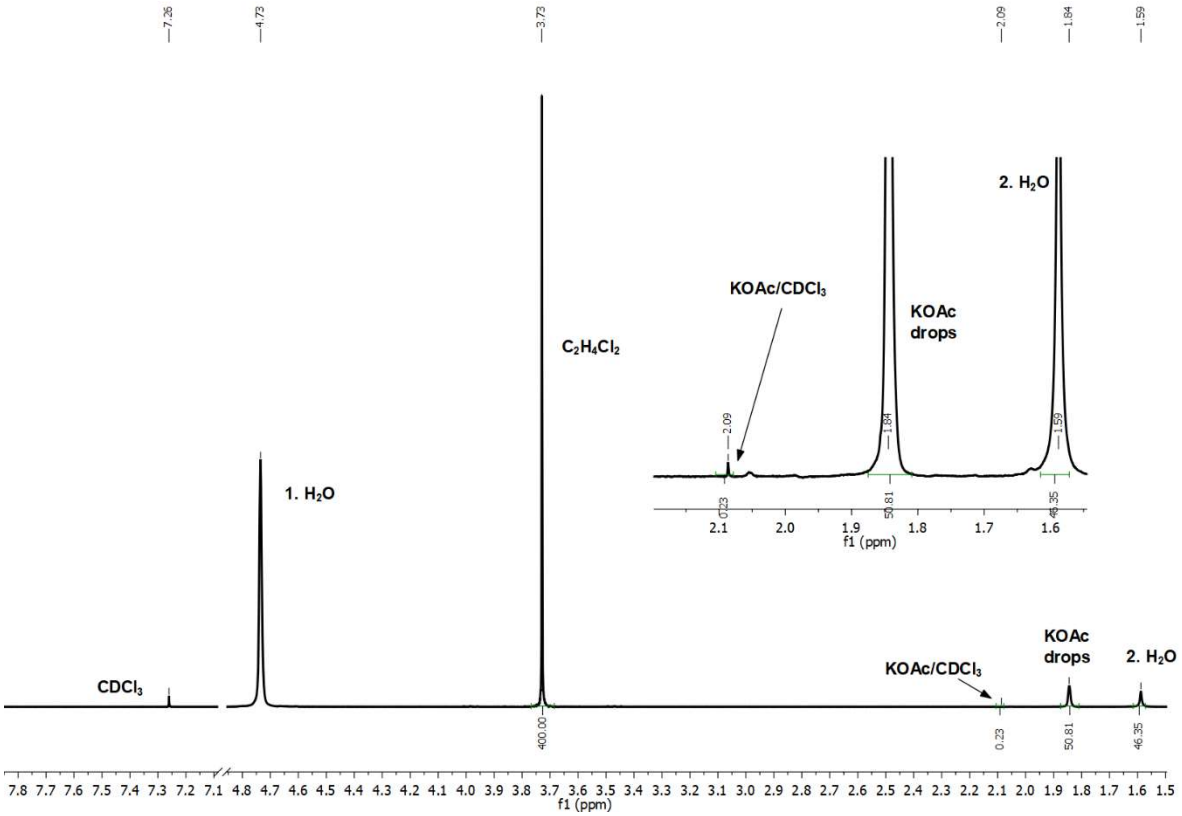


Figure S104. Liquid-Liquid extraction of KOAc aqua solution C=3.2 M which corresponds to 130 eq. when the receptor solution is present with $CDCl_3$. 1 H_2O is peak corresponding to water in drops on the NMR tubes walls. 2 H_2O is water in $CDCl_3$. Potasium acetate concentration was measured based on addition of 10 µL of 1,2-dichloroethane as internal standard and it was 1.93x 10^{-7}. The efficiency of this proces was 6x10^{-6}% based on internal standard.

- On the spectrum above and spectras under the peak 1.84-1.88 can be observed. This peak corresponds to the potassium acetate in water droplets remaining on the walls of NMR tube. The intensity of this signal depended on the concentration of the potassium acetate in water and the quality of phase separation. Nevertheless, the presence of this signal does not affect extraction experiment efficiency and quality, because the peak of potassium acetate in $CDCl_3$ has diferent chemical shift 2.09-2.13 ppm. Moreover, we tried to simulate the most realistic conditions of the extraction proces therefore we did not perform any additional treatments of the NMR sample.

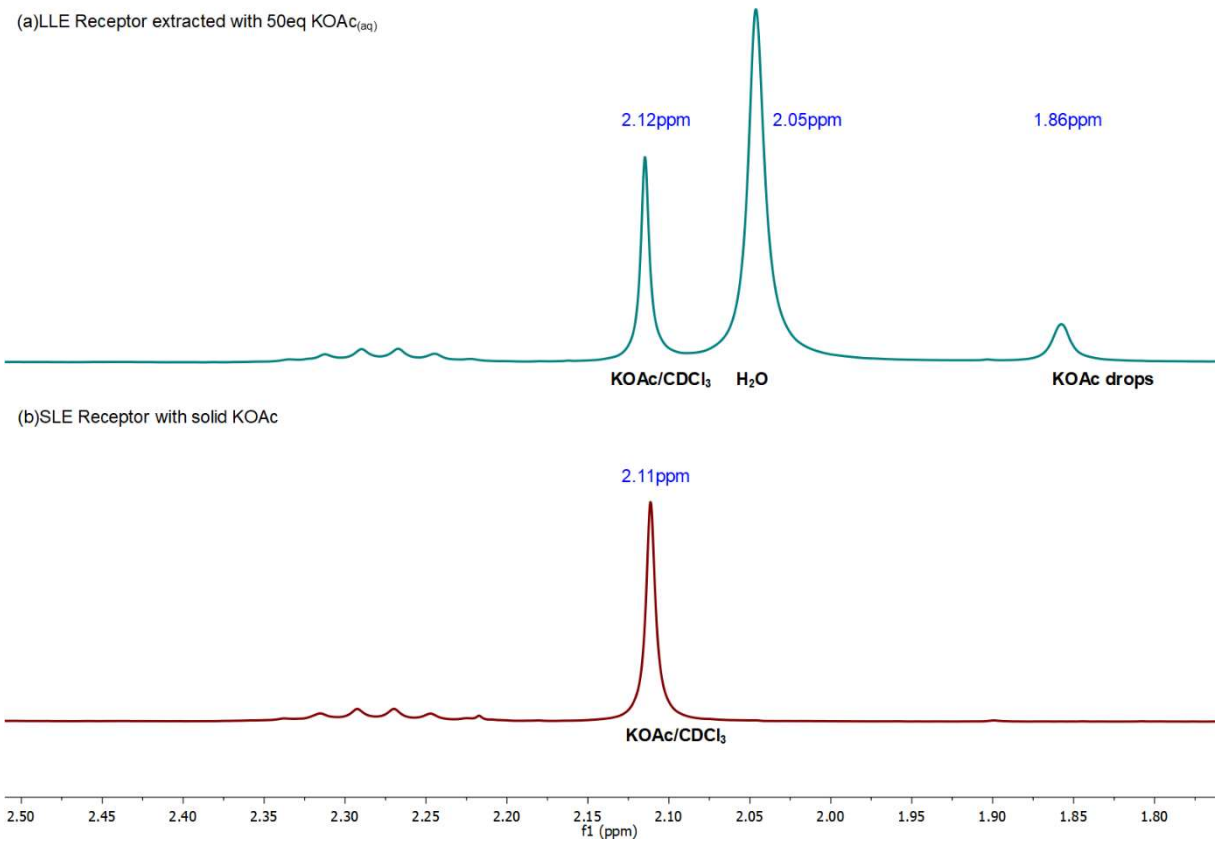


Figure S105. Partial ^{1}H NMR spectrum of the receptor **1** (a) LLE extraction $C_{receptor}$=2.5x10^{-2} M, C_{KOAc}=1.25 M (b) SLE extraction $C_{receptor}$=2.5x10^{-2} M, solid KOAc was added.

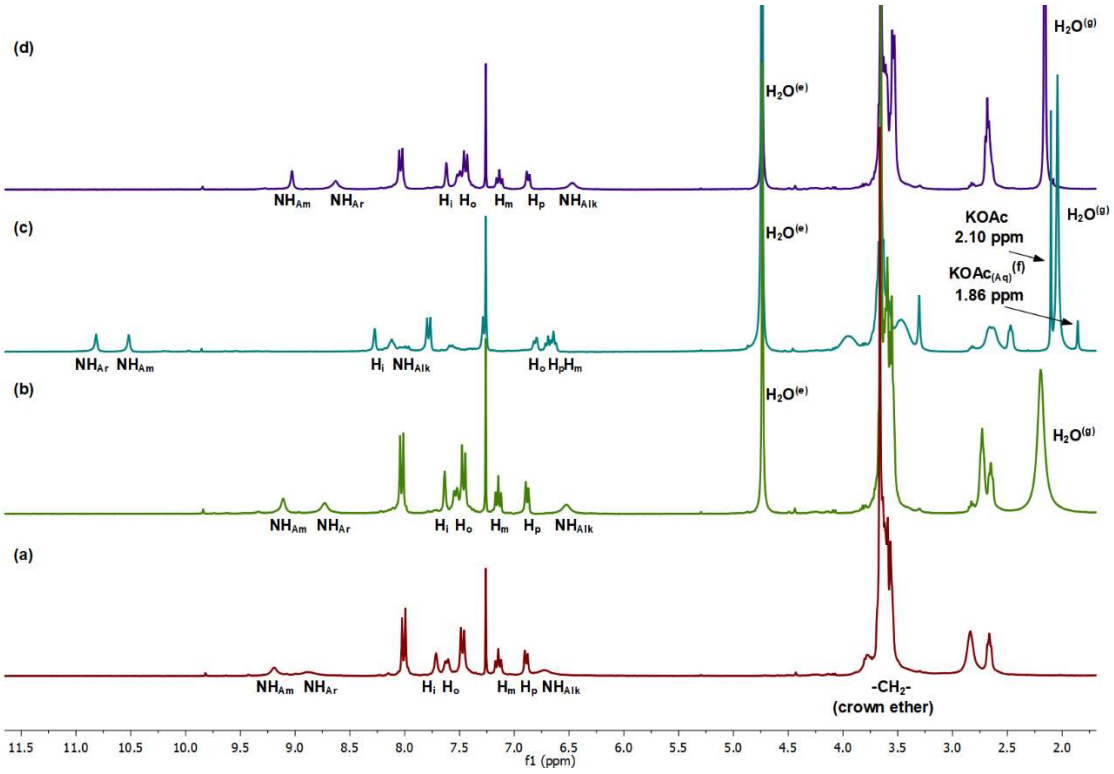


Figure S106. ^{1}H NMR spectra stack of extraction experiments: (a) receptor **2** dissolved in 'dry' CDCl3 ($C_{receptor}$=2.5x10^{-2} M); (b) receptor **2** solution after being washed with deionized water; (c) receptor **2** solution after extraction with 50 eq. KOAc aqueous solution (1.25 M); (d) receptor **2** solution after back-extraction to deionized water; $H_2O^{(e)}$- water signal from droplets on NMR tubes walls; $H_2O^{(g)}$-water signal in $CDCl_3$; $KOAc_{(aq)}{}^{(f)}$ salt present in droplets of water on the NMR tubes walls

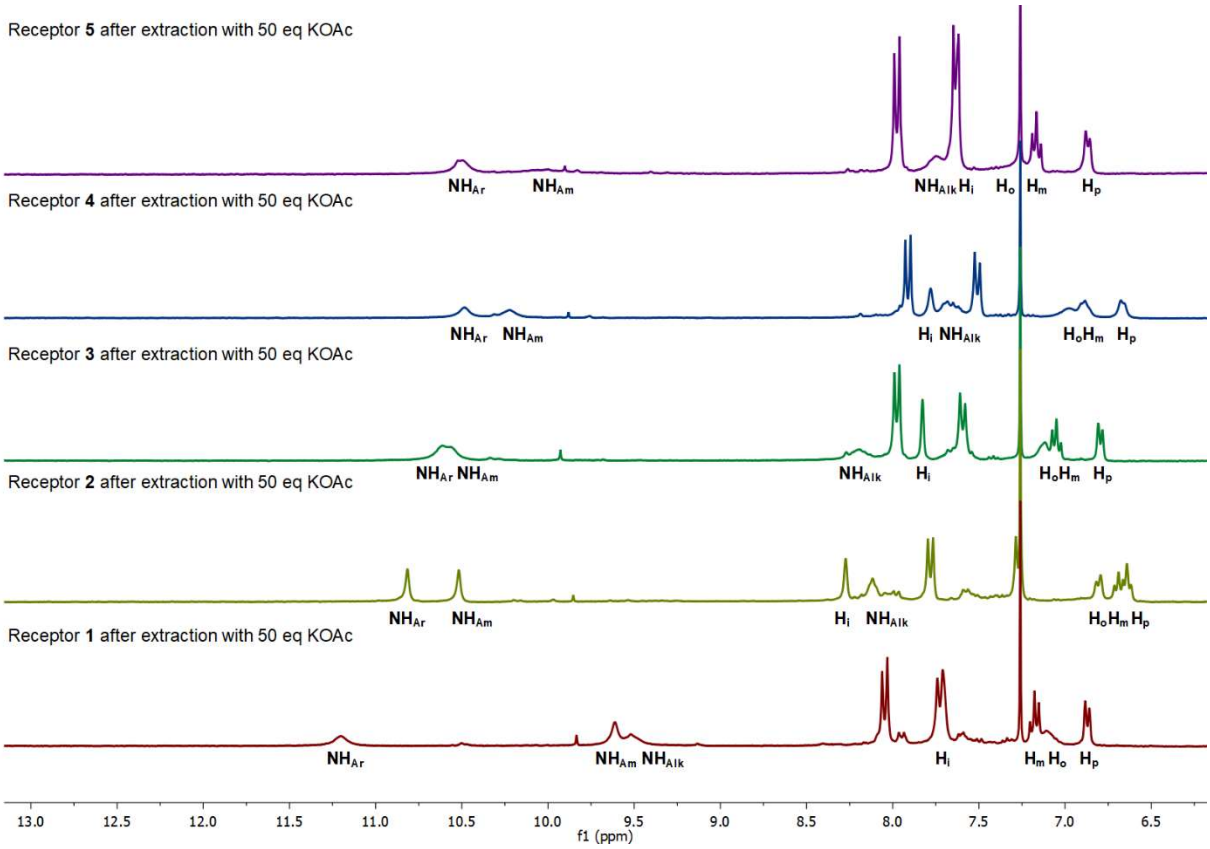


Figure S107. Partial ^{1}H NMR extraction experiment of receptors **1**-**5** after 1 minute extraction with 50 eq. aqueous solution of potassium acetate (293 K, $CDCl_3$, C_{KOAc}=1.25 M, $C_{receptor}$=2.5x10^{-2} M)

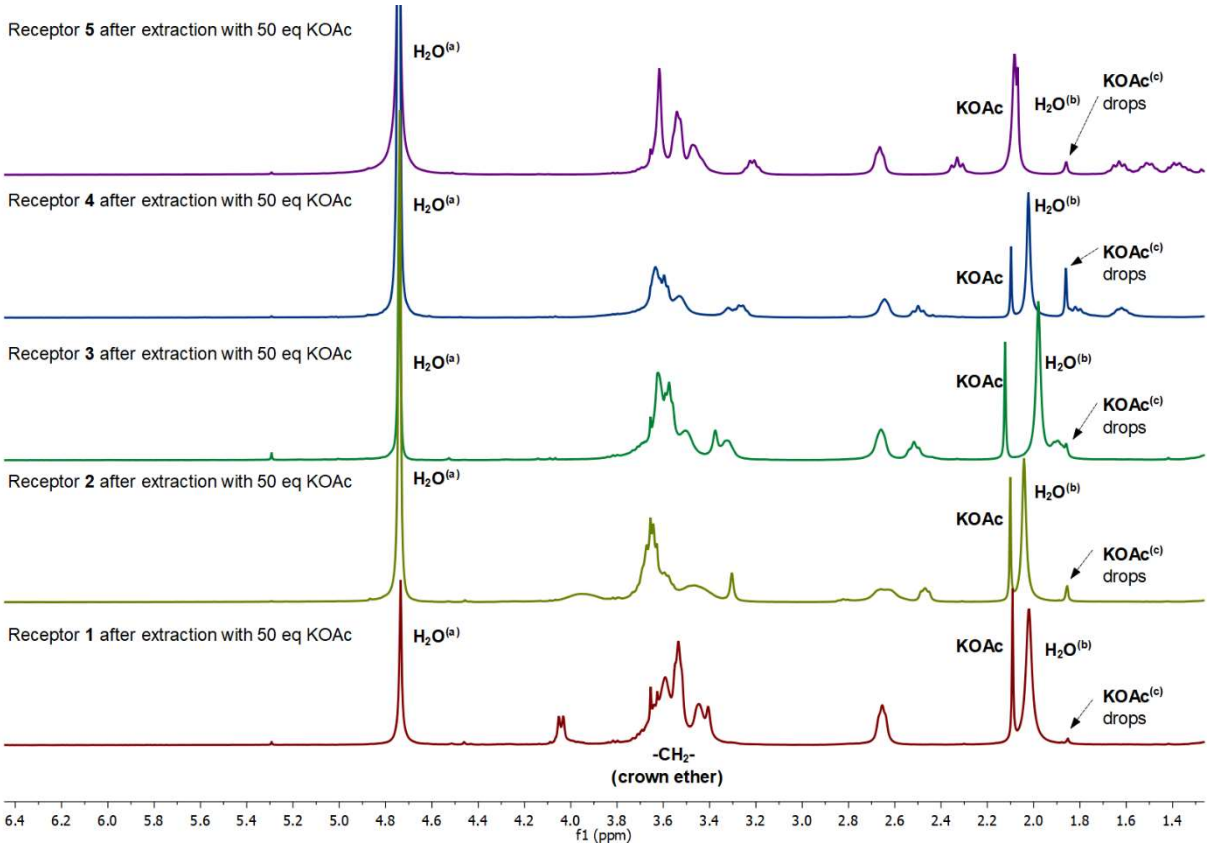


Figure S108. Partial ^{1}H NMR extraction experiment of receptors **1**-**5** after 1 minute extraction with 50 eq. aqueous solution of potassium acetate (293 K, $CDCl_3$, C_{KOAc}=1.25 M, $C_{receptor}$=2.5x10^{-2} M); $H_2O^{(a)}$ - water signal from droplets on NMR tubes walls; $H_2O^{(b)}$-water signal in $CDCl_3$; $KOAc_{(aq)}{}^{(c)}$ salt present in droplets of water on the NMR tubes walls

Receptor	Extraction efficiency for 50 Eq. KOAc [(a)]	Extraction efficiency for 25 Eq. KOAc [(a)]
1	76%	58%
2	85%	73%
3	71%	63%
4	67%	34%
5	33%	27%

Figure S109. Efficiency of extraction process in function of salt concentration. Based on ^{1}H NMR extraction experiments. (293 K, $CDCl_3$; $C_{receptor}$= 2.5 x10^{-2} M; C_{KOAc} =1.25 M (50eq.) or C_{KOAc} =0.625 M (25eq.)); [(a)]units of moles of salt vs. units of moles of the receptor in 0.5 ml of solutions; Extraction efficiency calculated from the integral value of acetate methyl group. Assuming that 100% efficiency is the value of the integral 3.

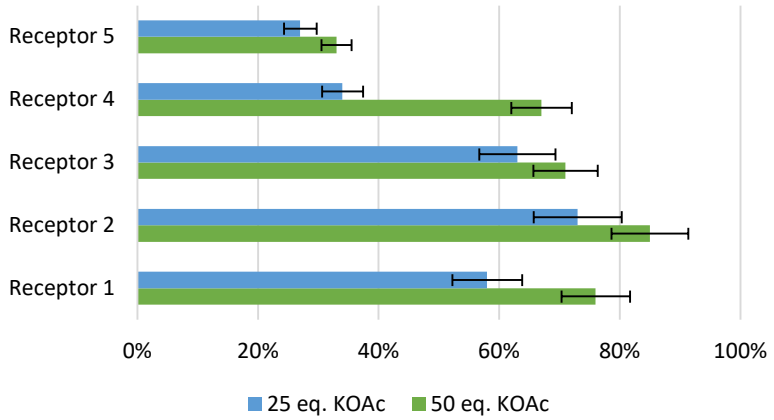


Figure S110. Efficiency of extraction process in function of salt concentration with errors. Based on ^{1}H NMR extraction experiments (293 K, $CDCl_3$; $C_{receptor}$= 2.5 x10^{-2} M; C_{KOAc} =1.25 M (50eq.) or C_{KOAc} =0.625 M (25eq.))

4. The 2D NMR ROESY experiment

2D NMR ROESY experiment was performed on 500 MHz Avance spectrometer, at 298 K in $CDCl_3$ solution. The receptor **2** or **4** solution $C_{receptor}$=3.2x10^{-2} M in chloroform was extracted with KOAc aqueous solution C_{KOAc}=3 M (complex spectres) or with deionized water (ligand spectres). Then after phase separation organic phase was retracted through hydrophobic filter and placed in NMR tube. Filtration was performed to dispose water drops on the NMR tube's walls.

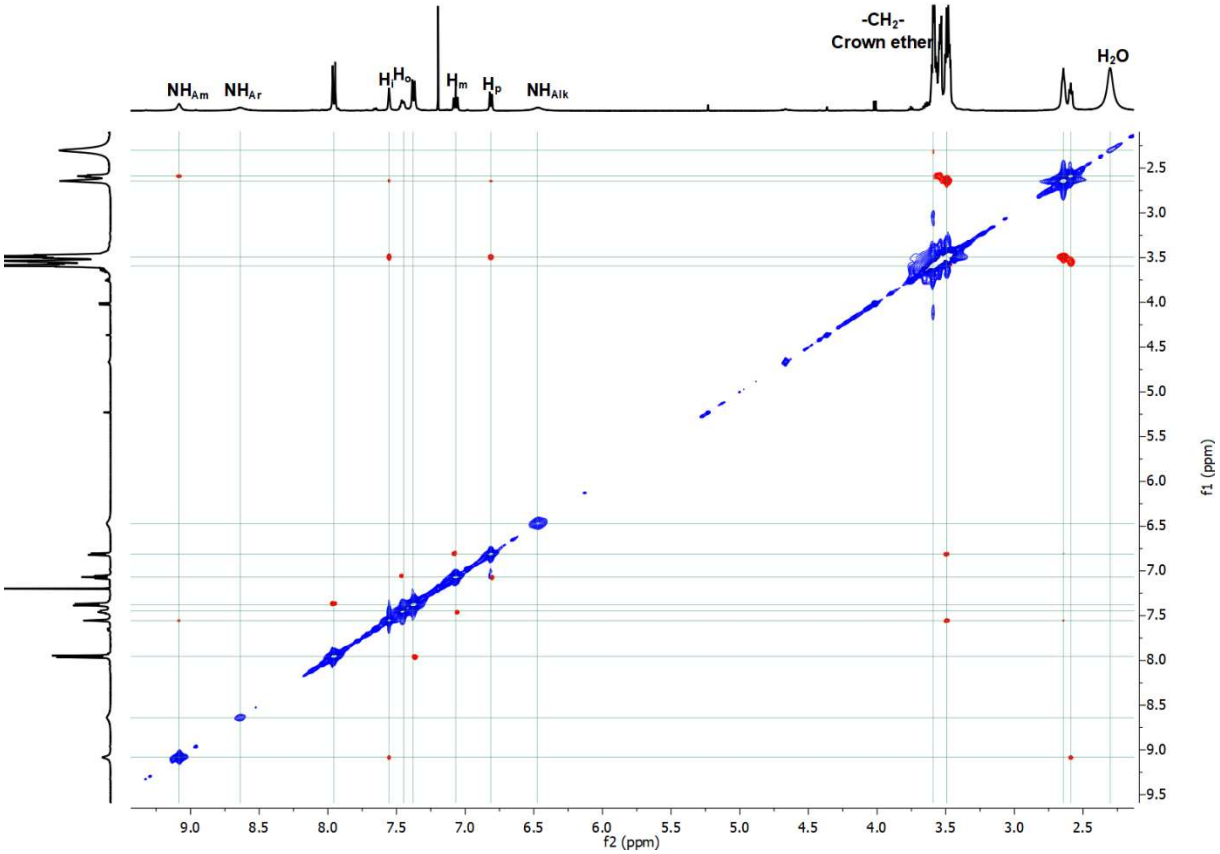


Figure S111. 2D ROESY spectrum of receptor **2** 'free' ligand $CDCl_3$ after extraction with deionized water (500 MHz; $CDCl_3$; 293 K)

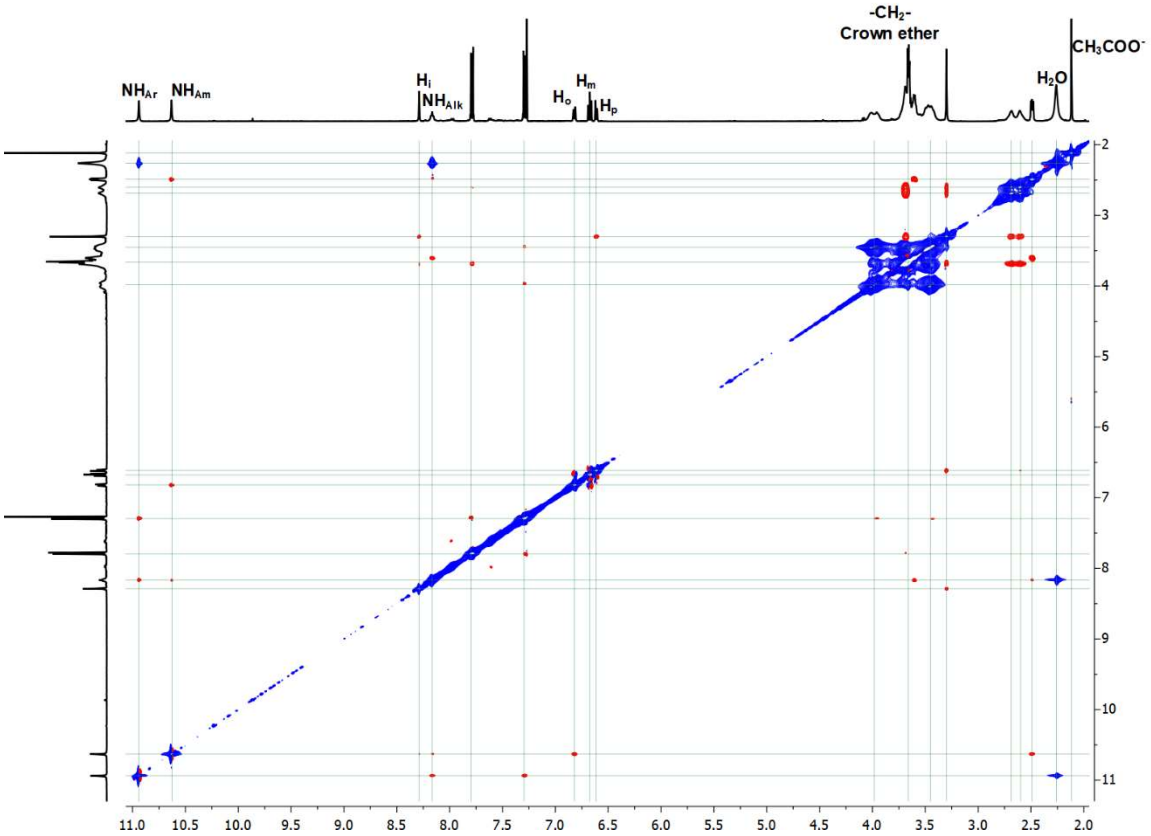


Figure S112. 2D ROESY spectrum of receptor **2**●KOAc complex (500 MHz; $CDCl_3$; 293 K)

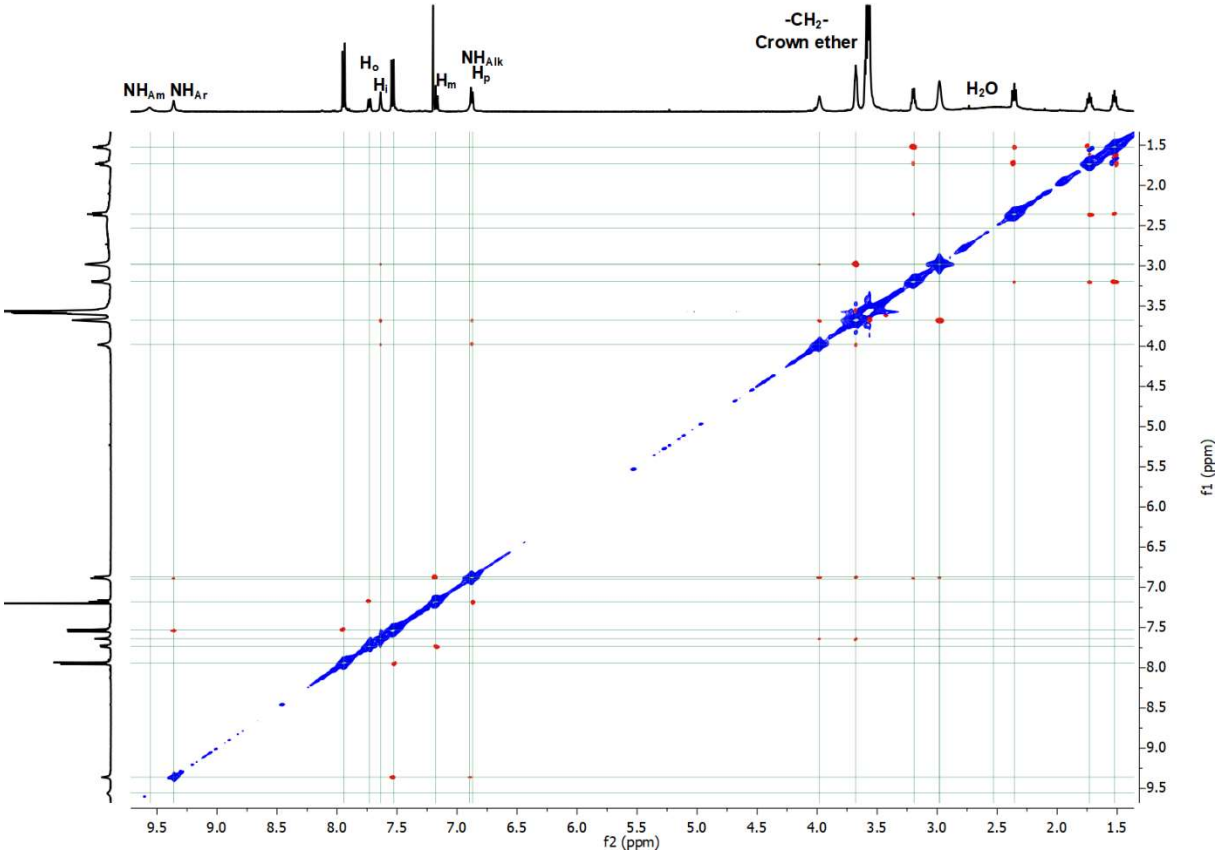


Figure S113. 2D ROESY spectrum of receptor **4** 'free' ligand $CDCl_3$ after extraction with deionized water (500 MHz; $CDCl_3$; 293 K)

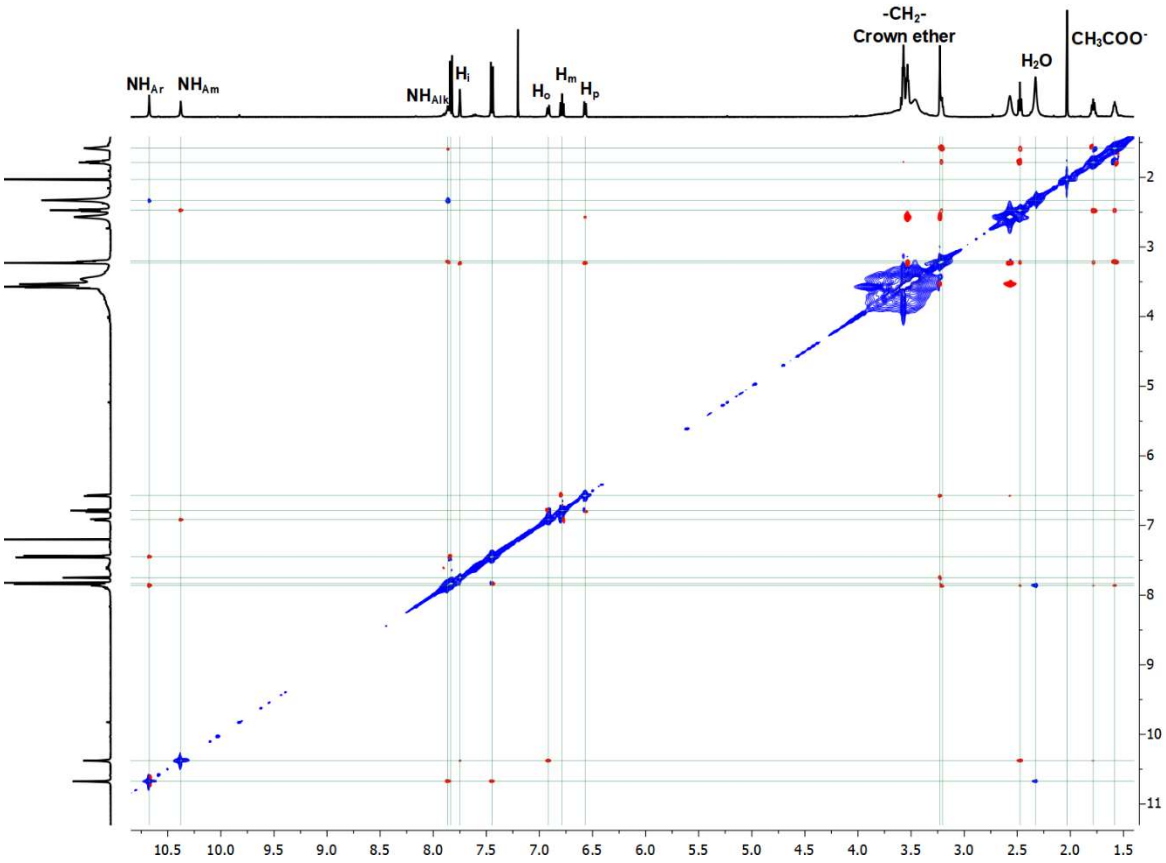


Figure S114. 2D ROESY spectrum of receptor **4**●KOAc complex, (500 MHz; $CDCl_3$; 293 K)

5. DFT cacluation

Theoretical calculations for **2**●KOAc and **4**●KOAc were performed with ORCA Version 4.2.1[3] The initial (starting point) geometry has been established based on 2D ROESY NMR results and was obtained by preoptimization of complexes with universal force field and steepest descent algorithm implemented in Avogadro 1.2.[4] Geometry optimization were done with aim of the B3LYP and dev2-SVP basis set.[5,6] Evaluated energies for obtained final geometries were -8230663.3521759 kJ x mol^{-1} for **2**●KOAc complex and -8436798.23543657 kJ x mol^{-1} for **4**●KOAc.

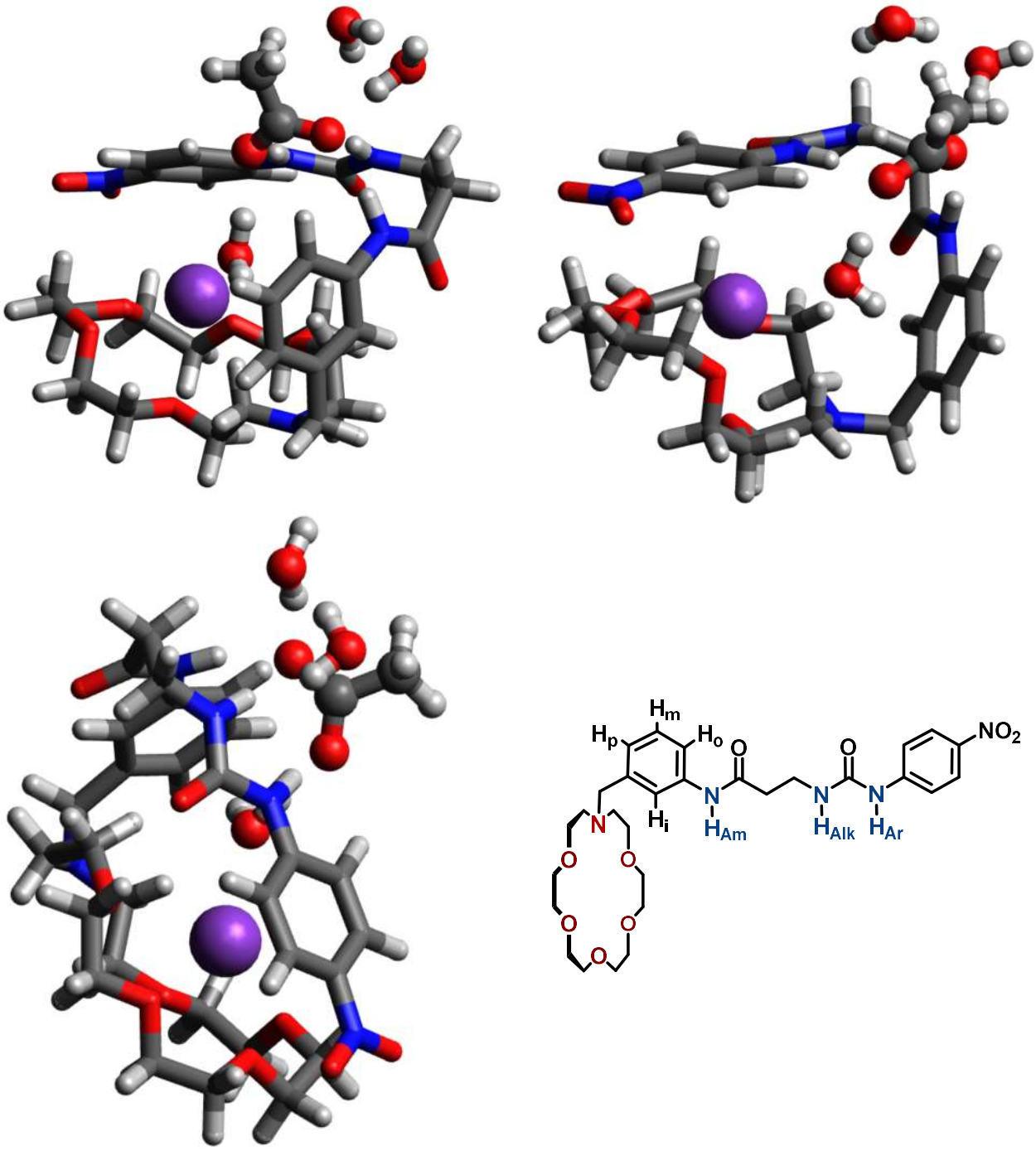


Figure S115. The structures of receptor **2** in complex with KOAc.

Atoms	Distance [Å]
$O(CH_3COO^-)$Y-shape---N(NH_{Alk})	3.097; $\sphericalangle_{NHO}$ 168°
$O(CH_3COO^-)$Y-shape---N(NH_{Alk})	3.582; $\sphericalangle_{NHO}$ 132°
$O(CH_3COO^-)$Y-shape---N(NH_{Ar})	2.806; $\sphericalangle_{NHO}$ 171°
$O(CH_3COO^-)$Y-shape---N(NH_{Ar})	3.829; $\sphericalangle_{NHO}$ 140°
$O(CH_3COO^-)$Y-shape---N(NH_{Am})	2.873; $\sphericalangle_{NHO}$ 164°
$O(CH_3COO^-)$Y-shape---N(NH_{Am})	4.059; $\sphericalangle_{NHO}$ 126°
$O(CH_3COO^-)$Y-shape---H(Bridging H_2O)	1.784; $\sphericalangle_{AcO\text{-}H\text{-}O}$ 173°
$O(CH_3COO^-)$Y-shape---H(Bridging H_2O)	4.252; $\sphericalangle_{AcO\text{-}H\text{-}O}$ 80°
K^+--- O(Bridging H_2O)	2.731
$O(CH_3COO^-)$Y-shape---K^+	4.894

$O(CH_3COO^-)$Y-shape---K^+	6.561
Crow ether-Ar_{ring} π—K^+	5.584
NO_2-Ar_{ring} π—K^+	3.521
H_o---$H(CH_3COO^-)$	4.029
H_o---$H(CH_3COO^-)$	4.590
H_o---$H(CH_3COO^-)$	5.004
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	2.801
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	2.841
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	2.891
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	3.120

Figure S116. Distances between atoms for **2**●KOAc complex

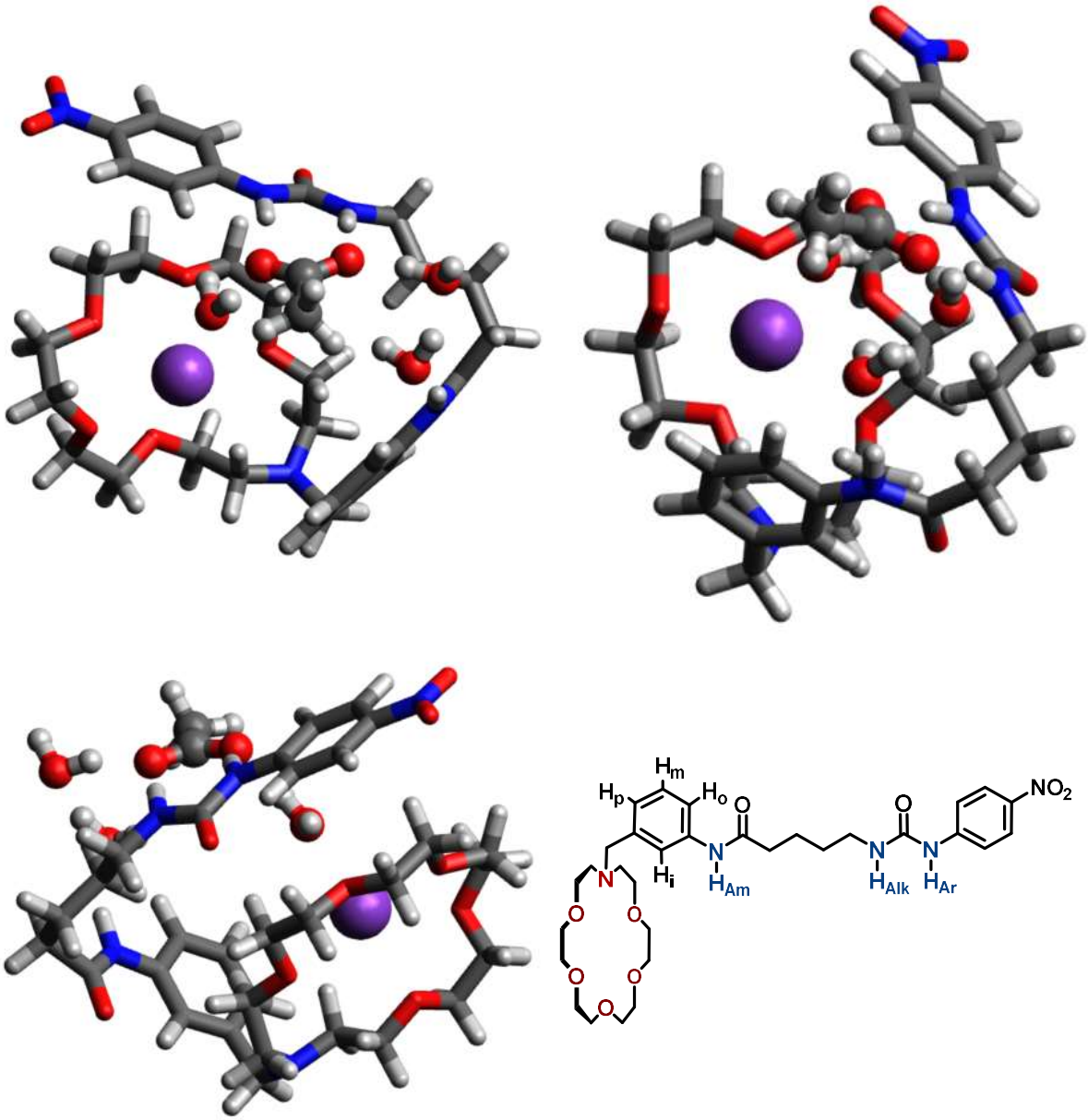


Figure S117. The structures of receptor **4** in complex with KOAc.

Atoms	Distance [Å]
$O(CH_3COO^-)$Y-shape---$N(NH_{Alk})$	2.882; $\sphericalangle_{NHO}$ 168°
$O(CH_3COO^-)$Y-shape---$N(NH_{Alk})$	3.572; $\sphericalangle_{NHO}$ 128°
$O(CH_3COO^-)$Y-shape---$N(NH_{Ar})$	2.825; $\sphericalangle_{NHO}$ 167°
$O(CH_3COO^-)$Y-shape---$N(NH_{Ar})$	3.629; $\sphericalangle_{NHO}$ 137°
$O(CH_3COO^-)$Y-shape---$N(NH_{Am})$	5.332; $\sphericalangle_{NHO}$ 127°
$O(CH_3COO^-)$Y-shape---$N(NH_{Am})$	6.425; $\sphericalangle_{NHO}$ 114°
$O(CH_3COO^-)$Y-shape---H(Bridging H_2O)	1.745; $\sphericalangle_{AcO\text{-}H\text{-}O}$ 166°
$O(CH_3COO^-)$Y-shape---H(Bridging H_2O)	3.546; $\sphericalangle_{AcO\text{-}H\text{-}O}$ 145°
K^+--- O(Bridging H_2O)	2.590
$O(CH_3COO^-)$Y-shape---K^+	5.263
$O(CH_3COO^-)$Y-shape---K^+	6.649
Crow ether-Ar_{ring} π—K^+	5.324
NO_2-Ar_{ring} π—K^+	5.584
H_o---$H(CH_3COO^-)$	3.961
H_o---$H(CH_3COO^-)$	5.154
H_o---$H(CH_3COO^-)$	5.731
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	3.296
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	3.368
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	4.407
Crown ether -CH_2- --- $H(NO_2Ar_{ring})$	4.837

Figure S118. Distances between atoms for **4**●KOAc complex

6. References

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