Protonation and anion-receptor properties of aromatic sulfonylurea derivatives

D. Barišić,[a,b] N. Vidović,[a,c] N. Bregović,[a] N. Cindro,*[a] V. Tomišić[a]

Supplementary Information

Contents

1. NMR spectra of the studied receptors and precursors

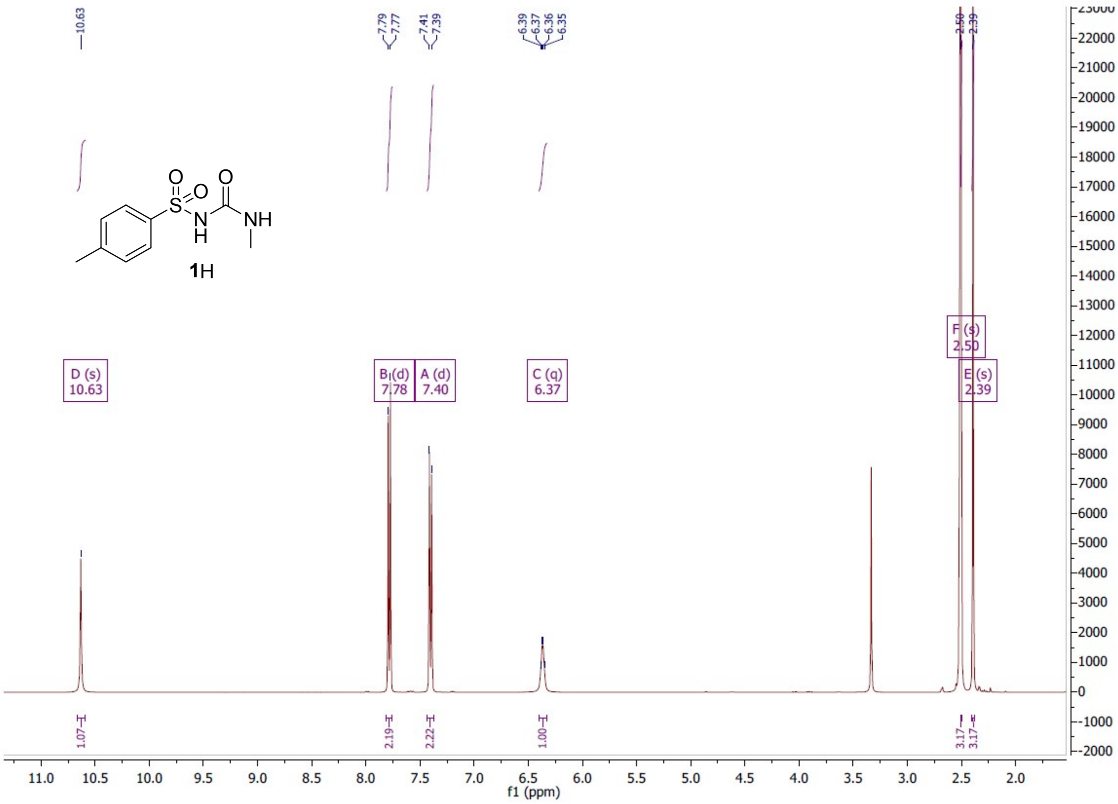


Figure S1. ^{1}H NMR spectrum of **1**H in DMSO-d_6 (400 MHz).

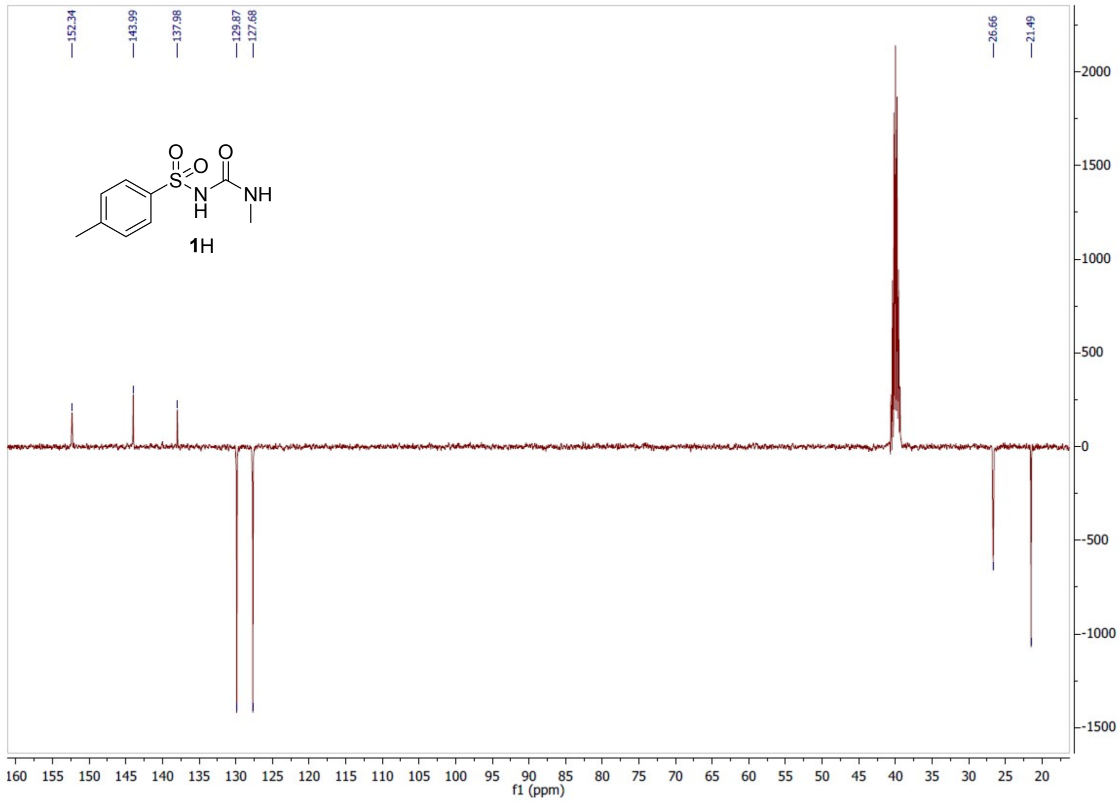


Figure S2. ^{13}C NMR spectrum of **1**H in DMSO-d_6 (101 MHz).

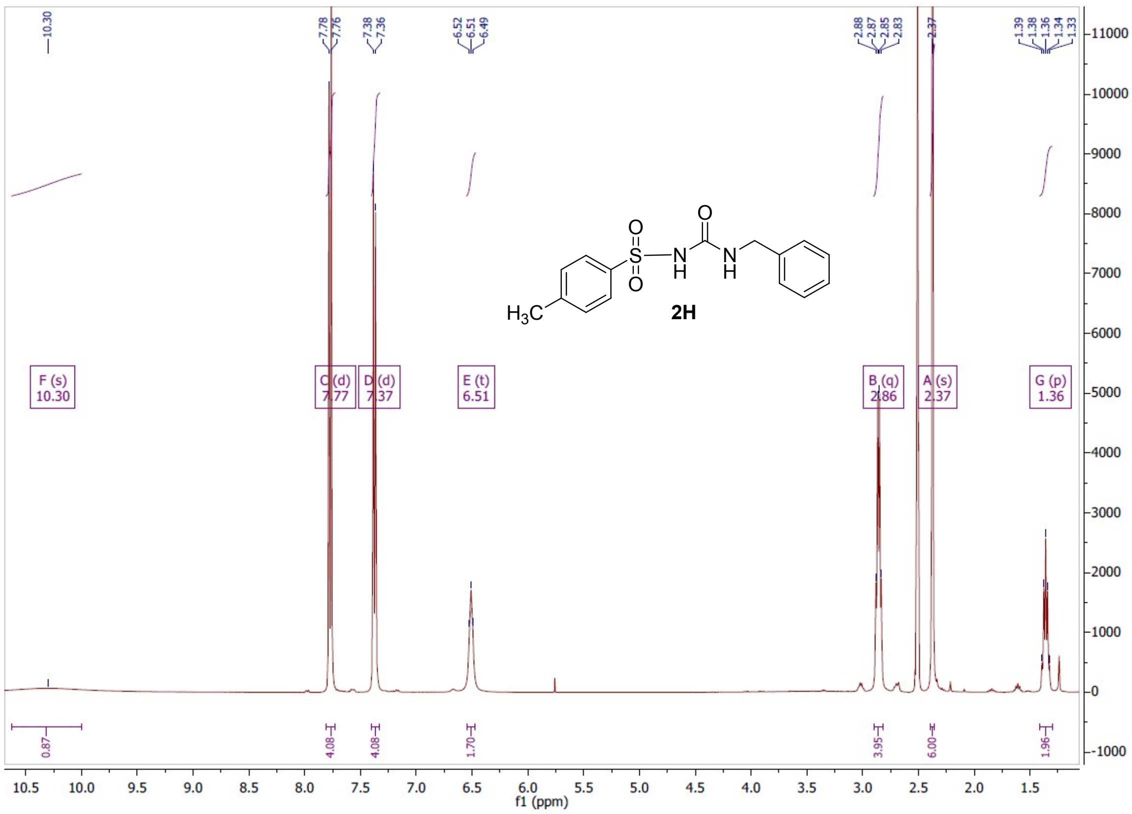


Figure S3. ^{1}H NMR spectrum of **2**H in DMSO-d_6 (400 MHz).

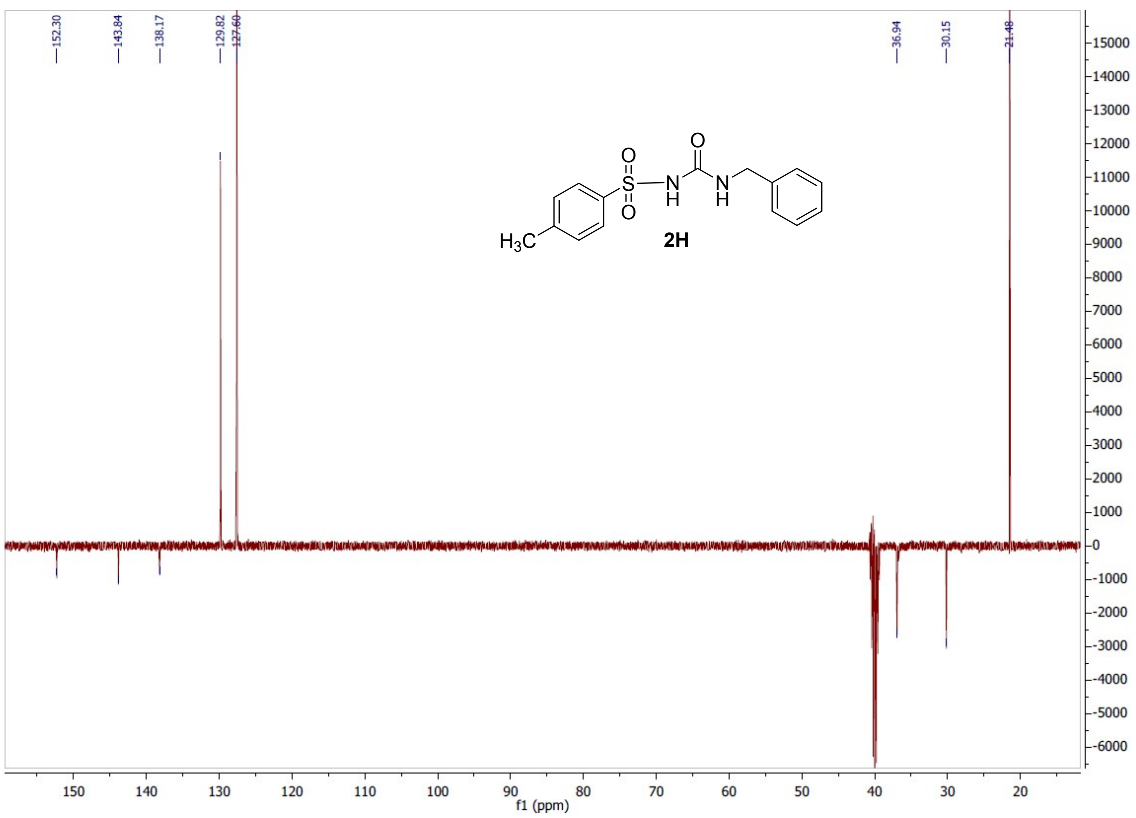


Figure S4 ^{13}C NMR spectrum of **2**H in DMSO-d_6 (101 MHz).

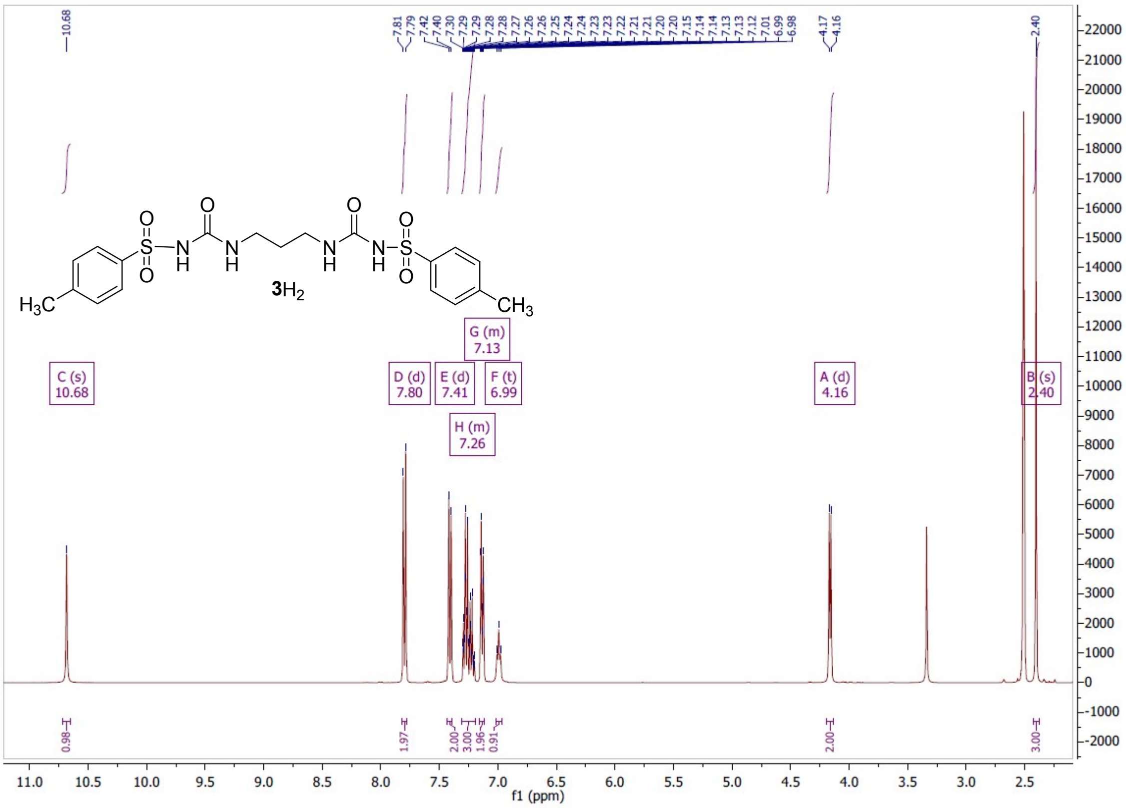


Figure S5. [1]H NMR spectrum of **3**H2 in DMSO-d_6 (400 MHz).

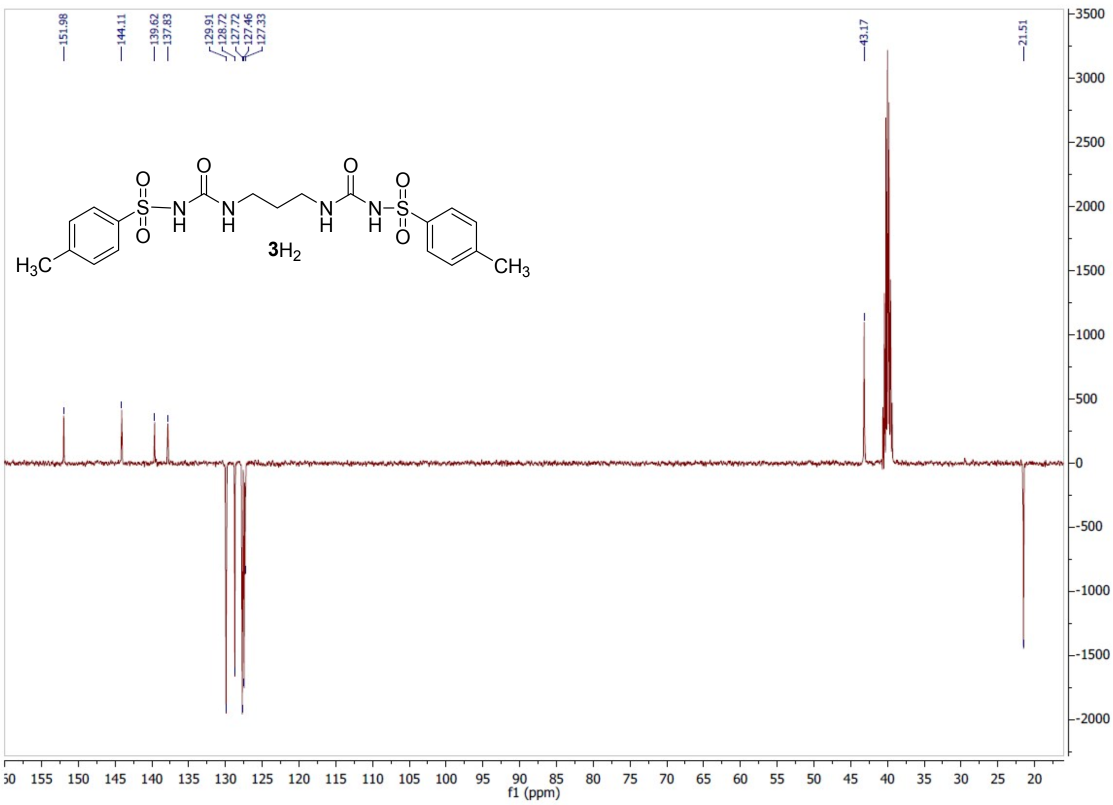


Figure S6 [13]C NMR spectrum of **3**H_2 in DMSO-d_6 (101 MHz).

2. Anion binding - weakly basic anions (Cl^-, Br^-, I^-, NO_3^-, HSO_4^-) in DMSO

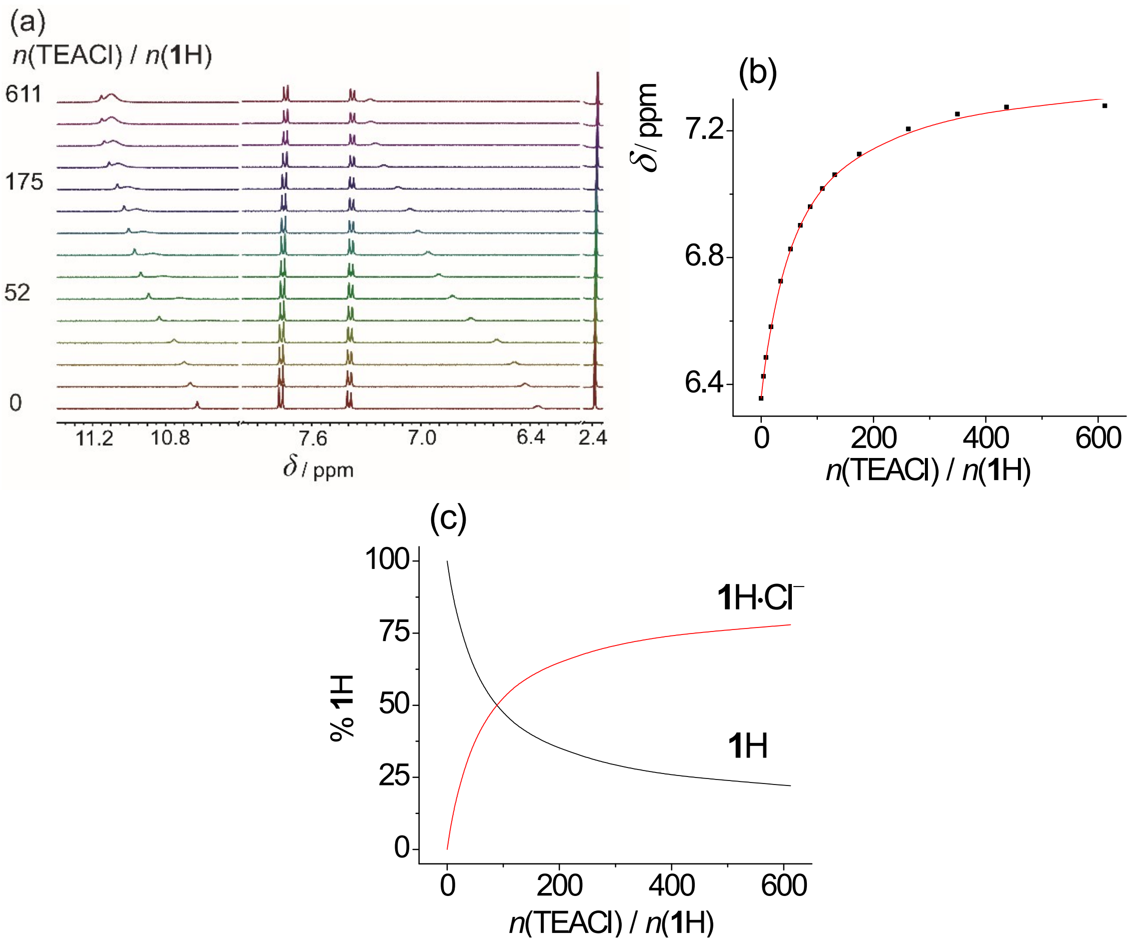


Figure S7. a) ^{1}H NMR titration of **1**H ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) with TEACl ($c = 5.00 \times 10^{-1}$ mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of NH_b proton chemical shift on n(TEACl) / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **1**H with TEACl.

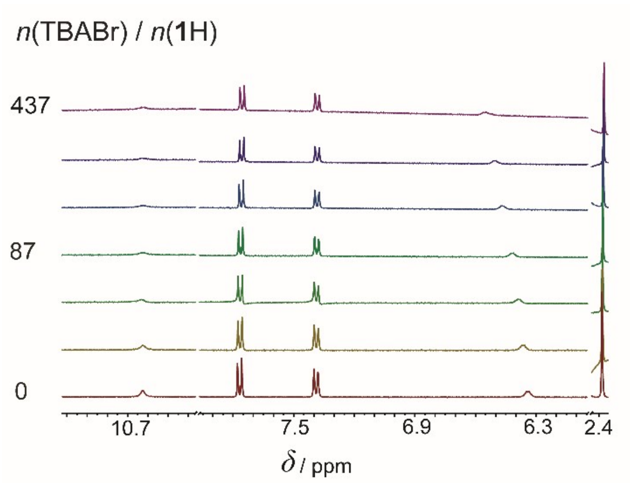


Figure S8. ^{1}H NMR titration of **1**H ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) with TBABr ($c = 5.00 \times 10^{-1}$ mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL.

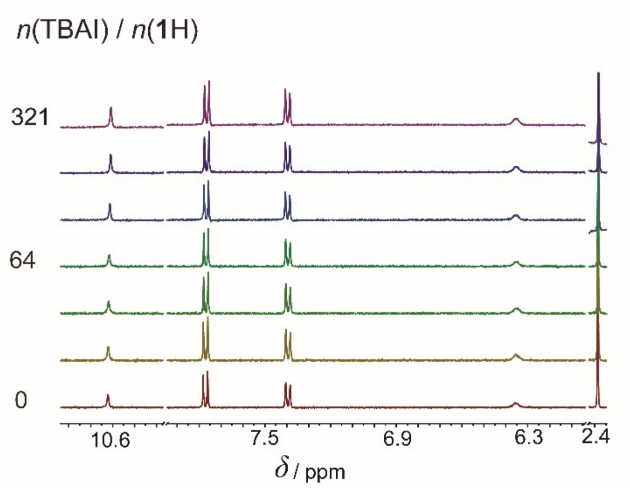
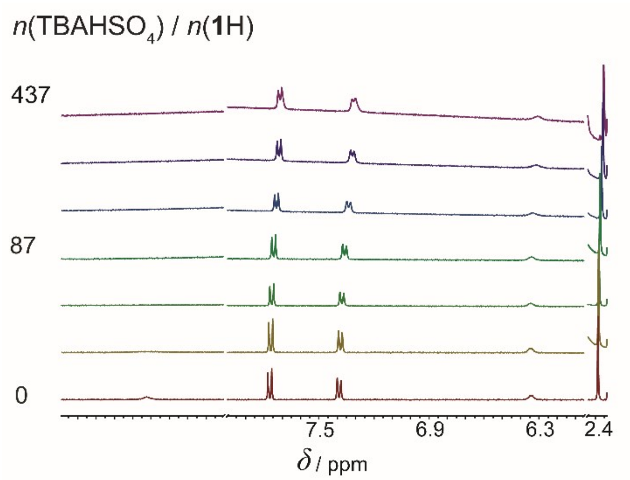


Figure S9. ^{1}H NMR titration of **1**H (c = 1.18 × 10^{-3} mol dm^{-3}) with TBAI (c = 4.03 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.



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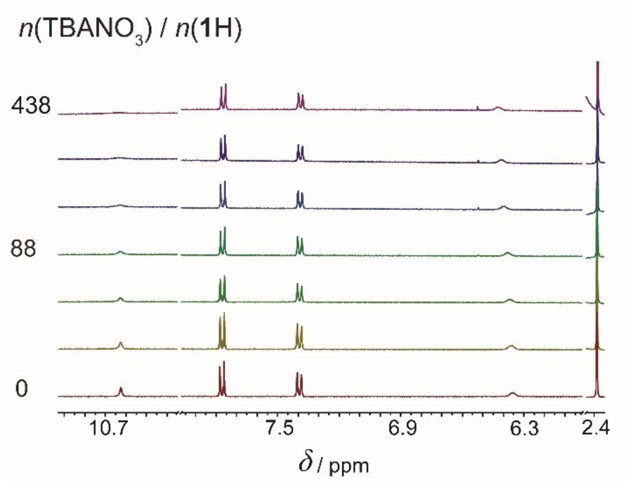

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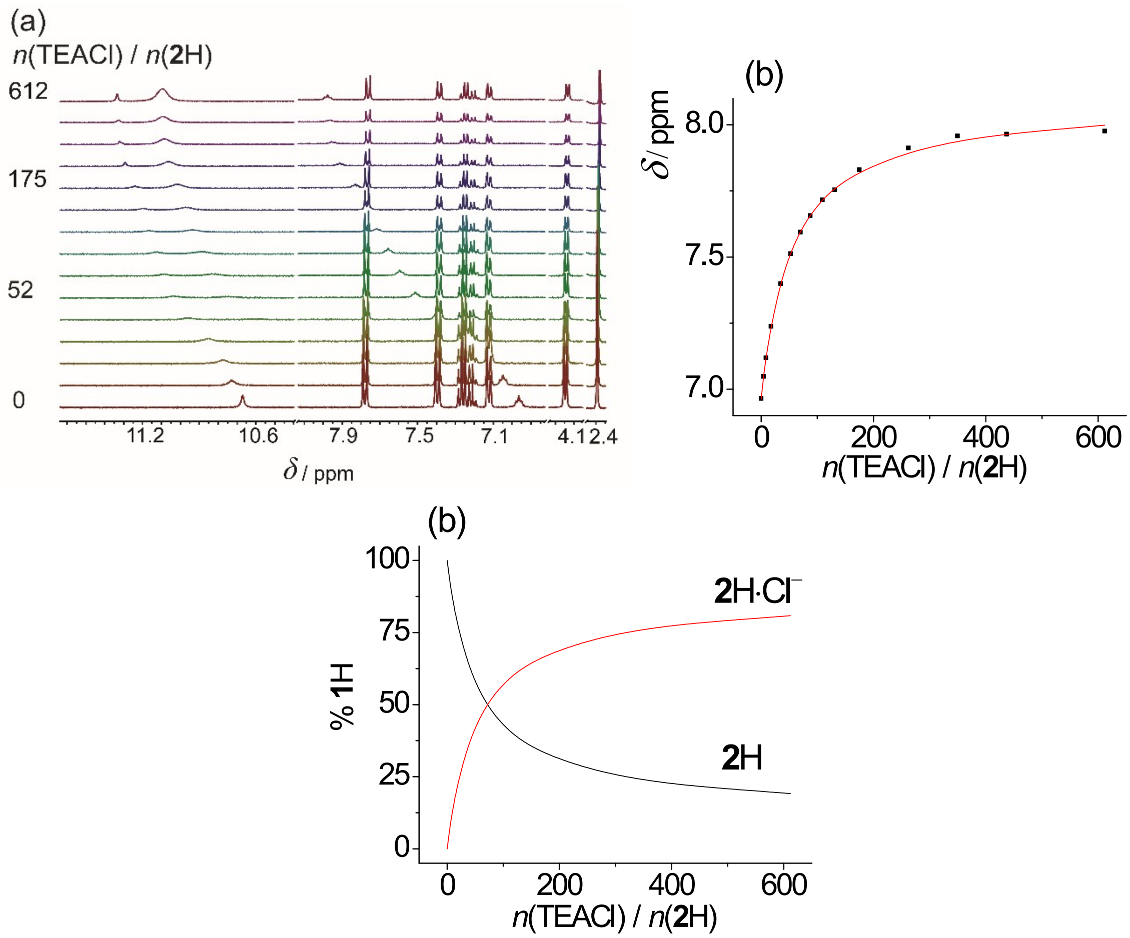


Figure S12. a) ^{1}H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TEACl (c = 5.00 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH$_b$ proton chemical shift on n(TEACl) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **2**H with TEACl.

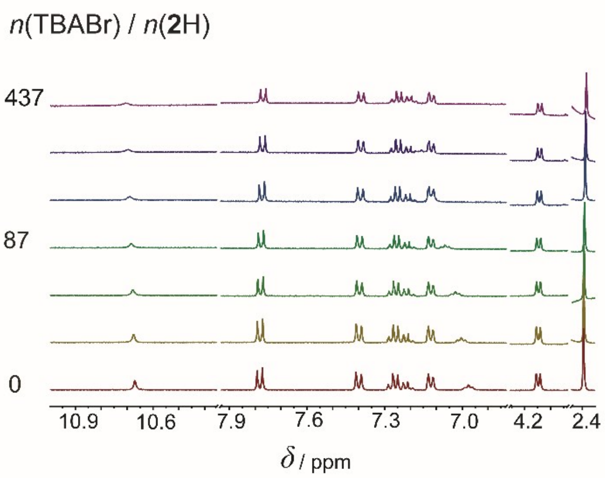


Figure S13. ^{1}H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TBABr (c = 5.00 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

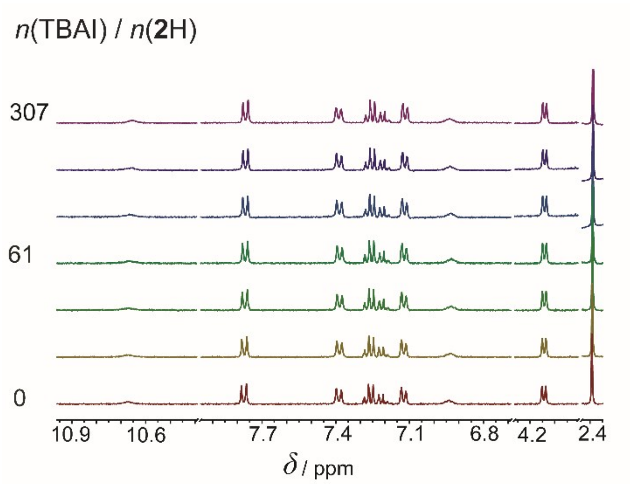


Figure S14. ^{1}H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TBAI (c = 4.03 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

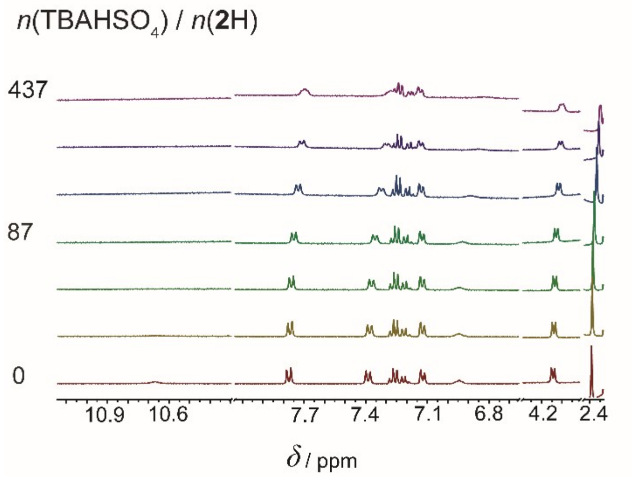


Figure S15. ^{1}H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TBAHSO$_4$ (c = 4.03 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

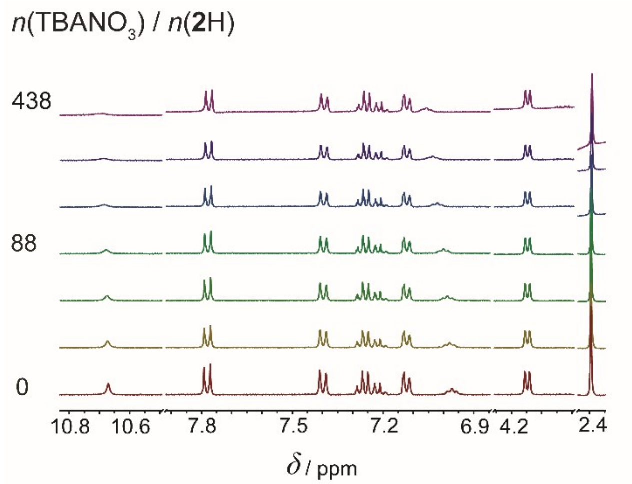


Figure S16. ^{1}H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TBANO$_3$ (c = 5.01 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

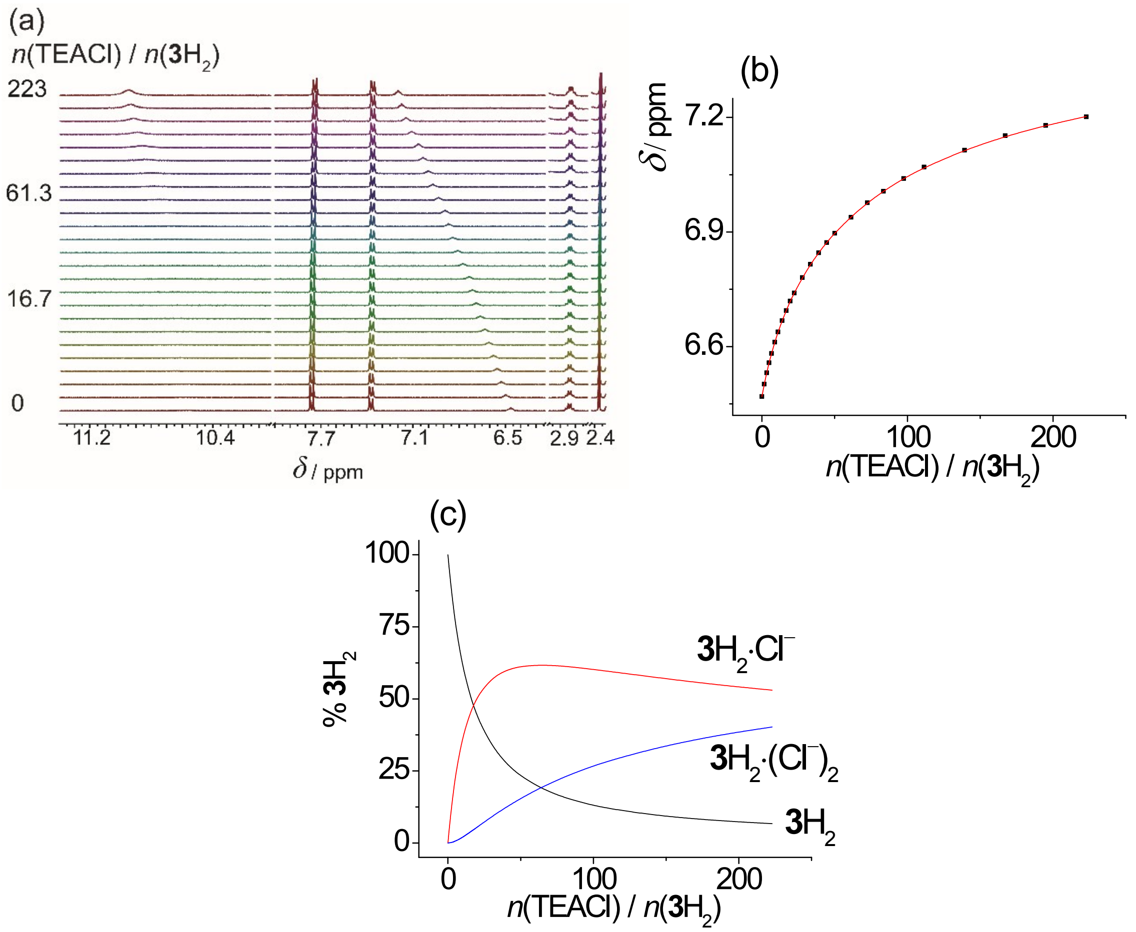


Figure S17. a) ^{1}H NMR titration of **3**H_2 (c = 1.20 × 10^{-3} mol dm^{-3}) with TEACl (c = 3.54 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH_b proton chemical shift on n(TEACl) / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H_2 with TEACl.

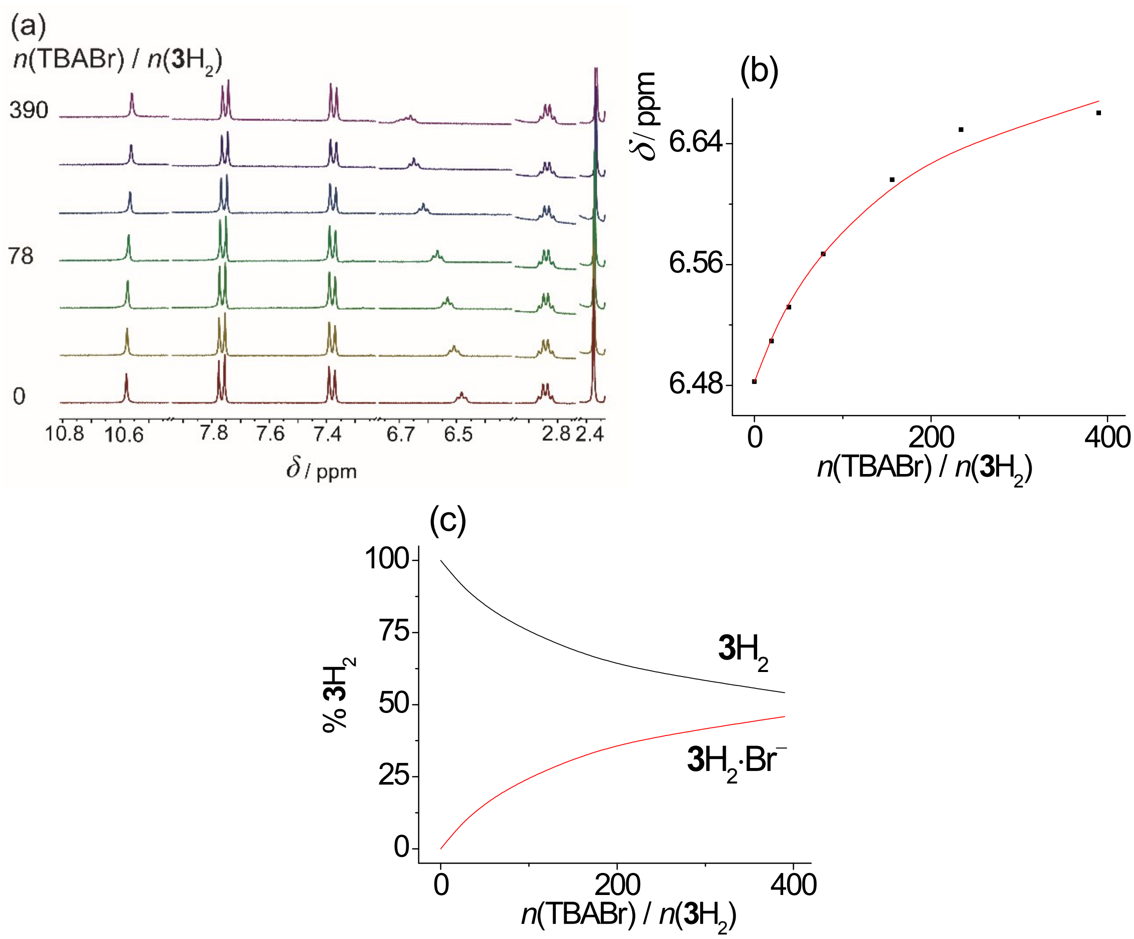


Figure S18. a) [1]H NMR titration of **3**H_2 (c = 1.21 × 10^{-3} mol dm^{-3}) with TBABr (c = 5.00 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH_b proton chemical shift on n(TBABr) / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H_2 with TBABr.

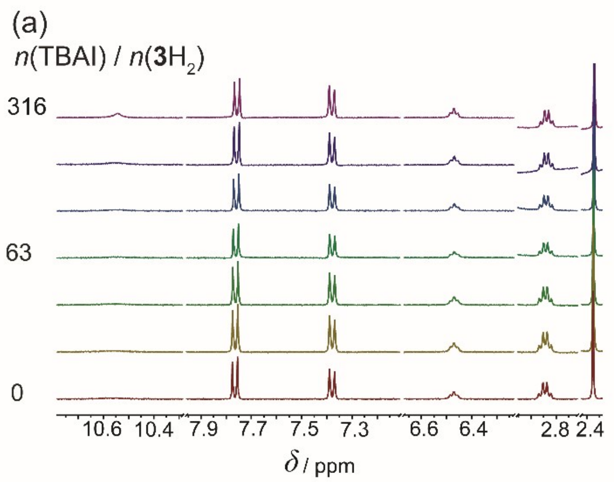


Figure S19. [1]H NMR titration of **3**H_2 (c = 1.20 × 10^{-3} mol dm^{-3}) with TBAI (c = 4.02 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

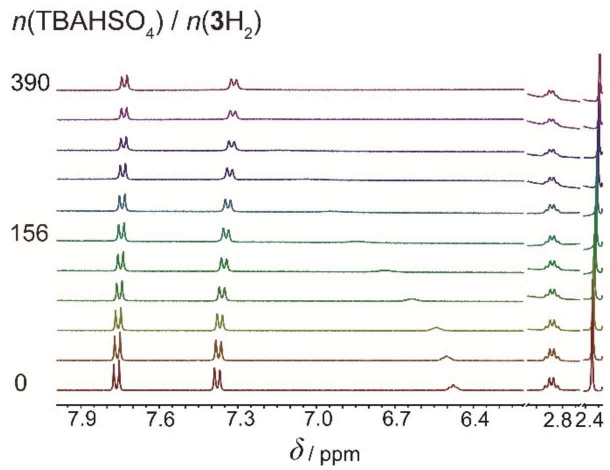


Figure S20. [1]H NMR titration of **3**H_2 (c = 1.21 × 10^{-3} mol dm^{-3}) with $TBAHSO_4$ (c = 5.00 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

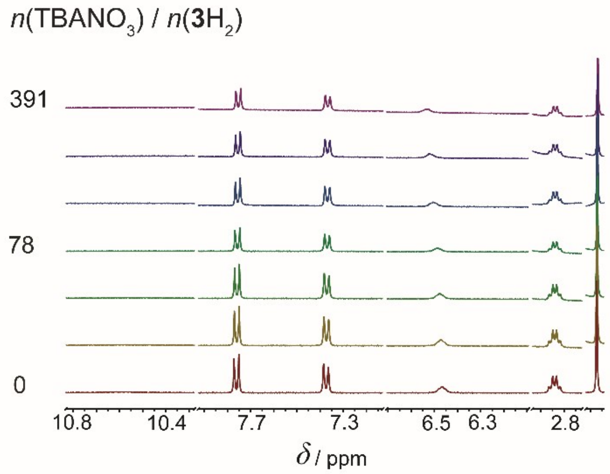


Figure S21. [1]H NMR titration of **3**H_2 (c = 1.21 × 10^{-3} mol dm^{-3}) with $TBANO_3$ (c = 5.01 × 10^{-1} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL.

Table S1. Calculated ^{1}H NMR chemical shifts of **1**H and its chloride complex in DMSO-d_6 at 25 °C.

	NH_a	H_b	H_a	NH_b	H_c
1H	10.325	7.768	7.391	6.356	2.386
1H·Cl^-	11.320	7.738	7.372	7.570	2.367

Table S2. Calculated ^{1}H NMR chemical shifts of **2**H and its chloride complex in DMSO-d_6 at 25 °C.

	NH_a	NH_b
2H	10.671	6.965
2H·Cl^-	11.514	8.245

Table S3. Calculated ^{1}H NMR chemical shifts of **3**H_2 and its chloride and bromide complexes in DMSO-d_6 at 25 °C.

	NH_a	H_b	H_a	NH_b	H_e	H_c
3H_2	10.578	7.764	7.378	6.469	2.842	2.375
3H_2·Cl^-		7.757	7.367	6.826	2.841	2.371
3H_2·$(Cl^-)_2$		7.723	7.363	7.822	2.825	2.354
3H_2·Br^-	10.537	7.738	7.369	6.888	2.827	2.356

3. Anion binding – weakly basic anions (Cl^-, Br^-, I^-, NO_3^-, HSO_4^-) in MeCN

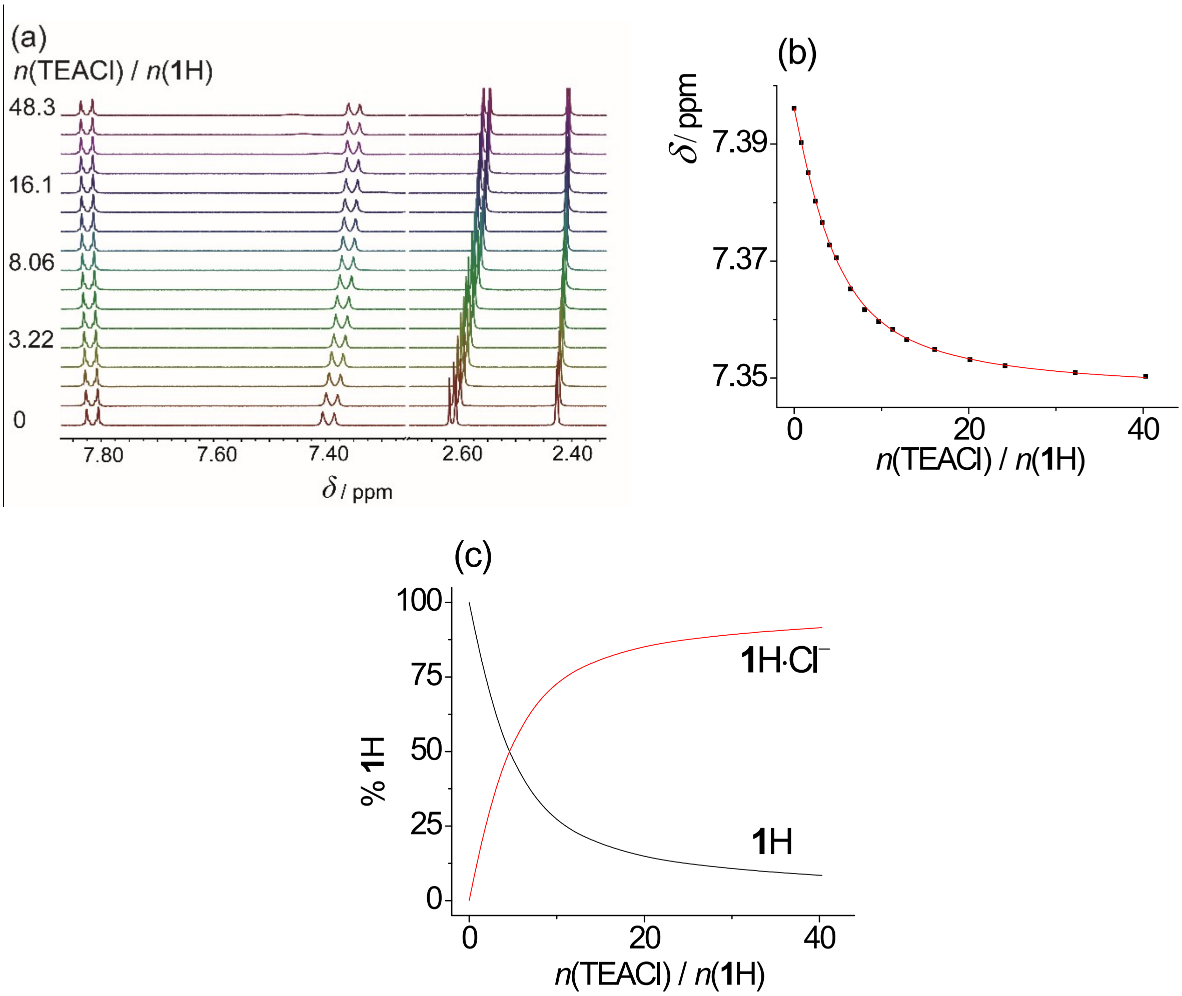


Figure S22. a) ^{1}H NMR titration of **1**H (c = 1.14 × 10^{-3} mol dm^{-3}) with TEACl (c = 2.25 × 10^{-2} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_a proton chemical shift on n(TEACl) / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **1**H with TEACl.

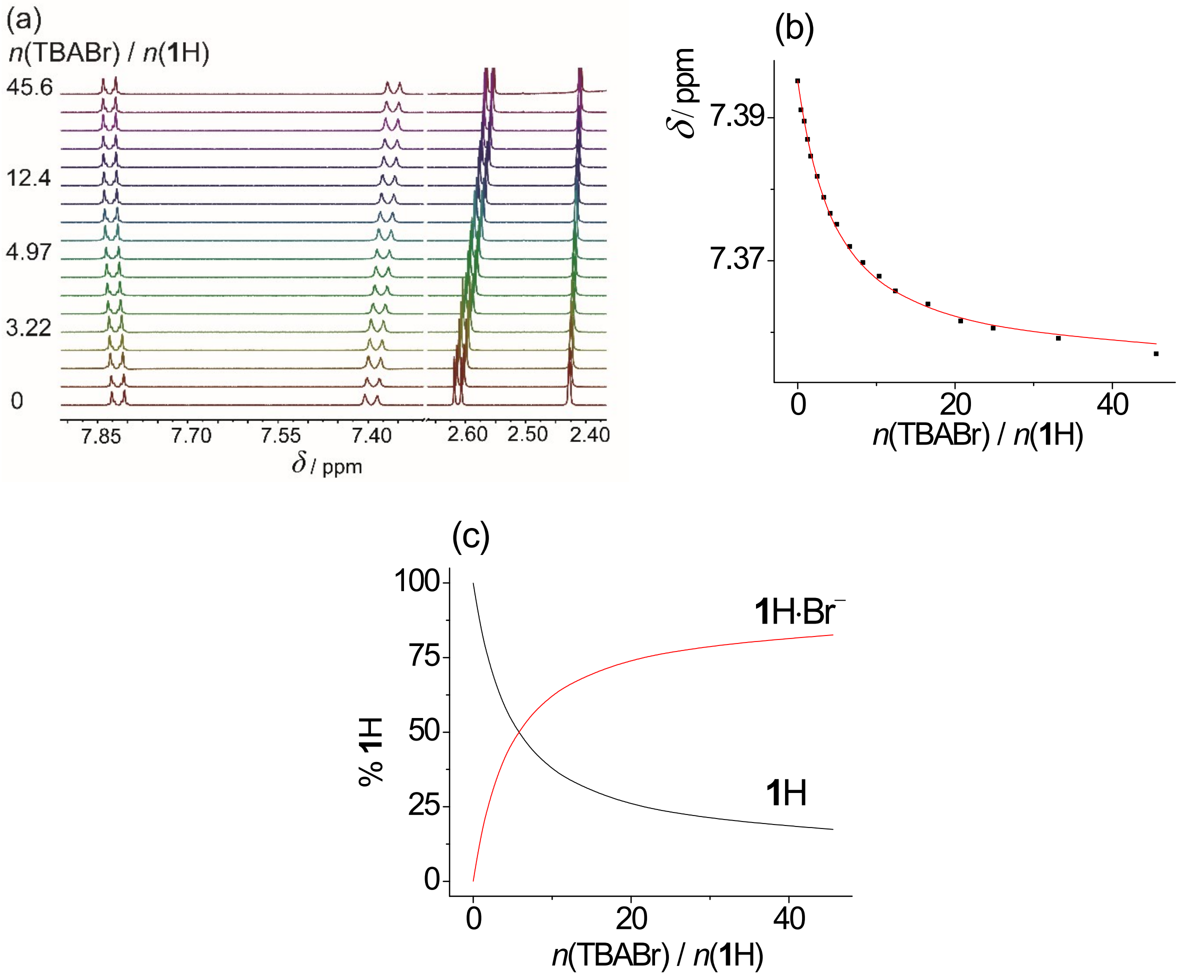


Figure S23. a) ^{1}H NMR titration of **1**H ($c = 1.14 \times 10^{-3}$ mol dm^{-3}) with TBABr ($c = 5.01 \times 10^{-2}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of H_a proton chemical shift on n(TBABr) / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **1**H with TBABr.

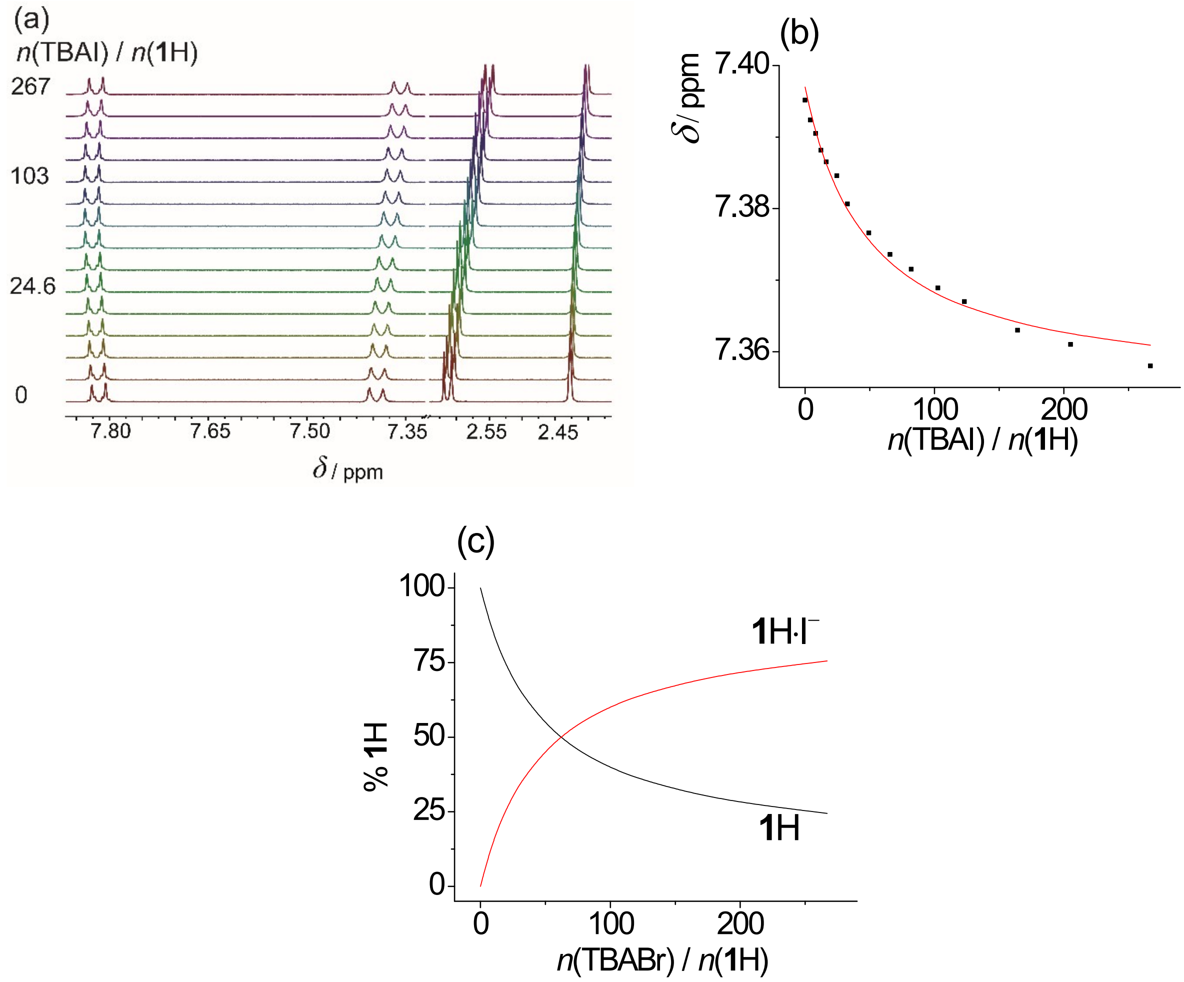


Figure S24. a) ^{1}H NMR titration of **1**H ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with TBAI ($c = 5.01 \times 10^{-1}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of H_a proton chemical shift on n(TBAI) / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **1**H with TBAI.

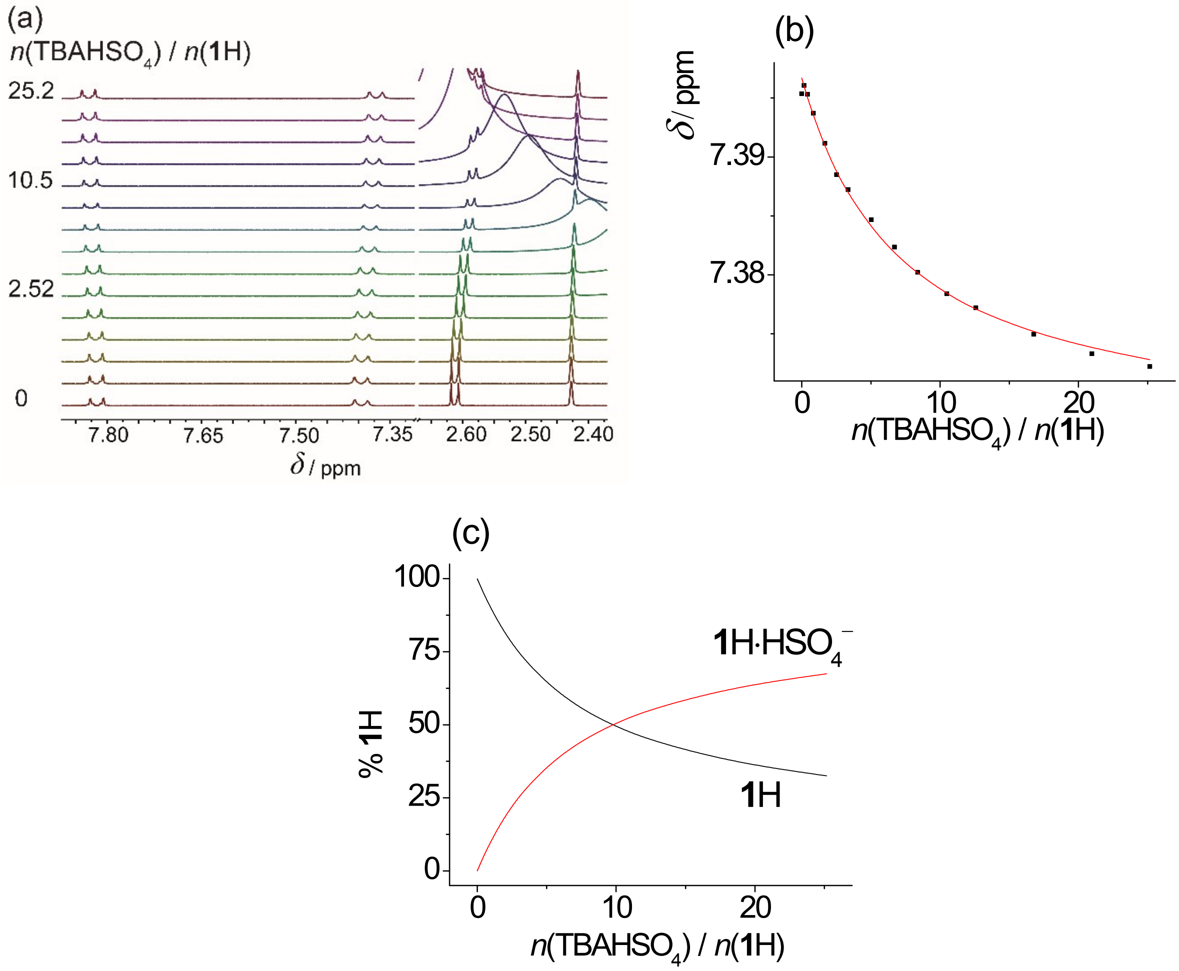
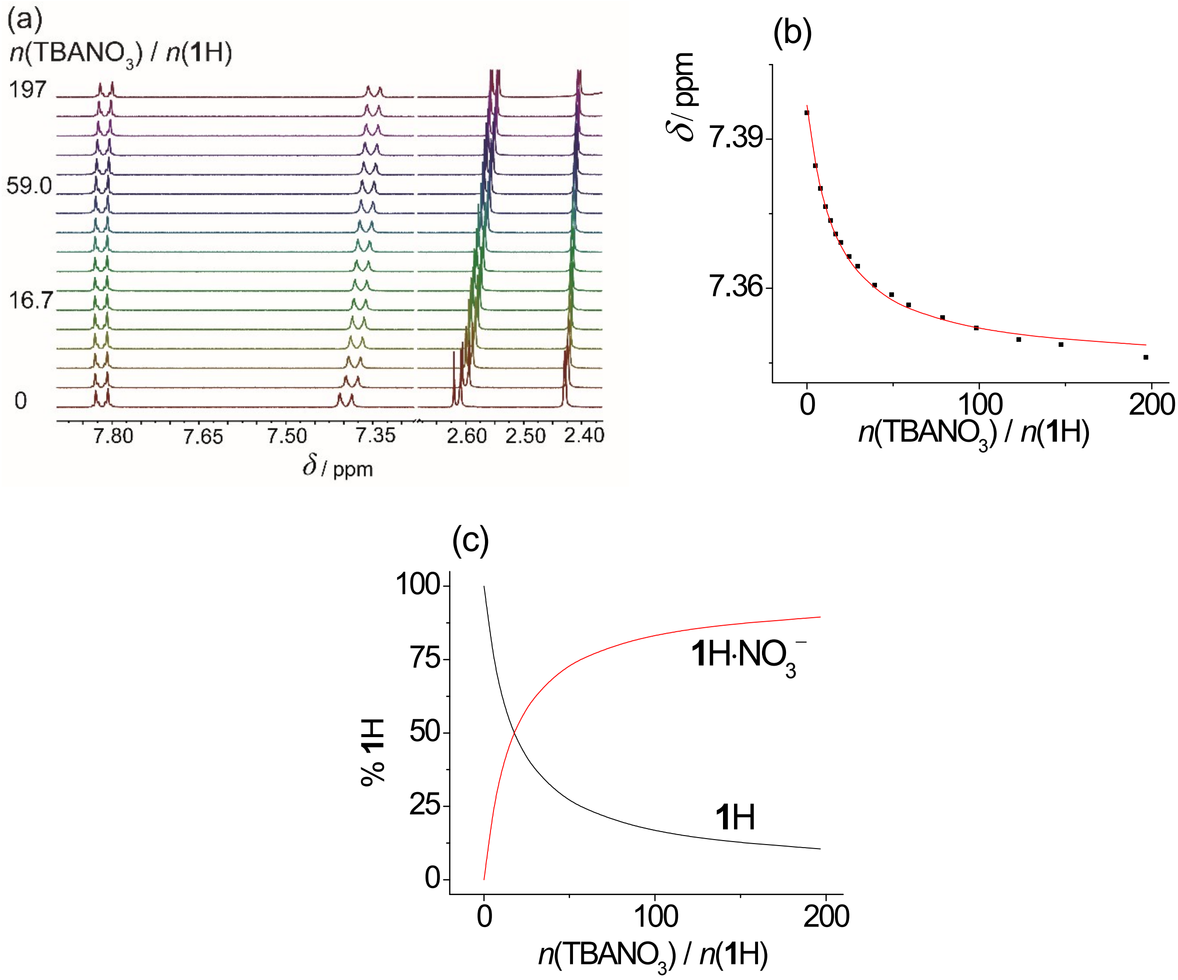


Figure S25. a) ^{1}H NMR titration of **1**H ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with $TBAHSO_4$ ($c = 5.12 \times 10^{-2}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of H_a proton chemical shift on $n(TBAHSO_4)$ / $n(\mathbf{1}H)$ molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **1**H with $TBAHSO_4$.



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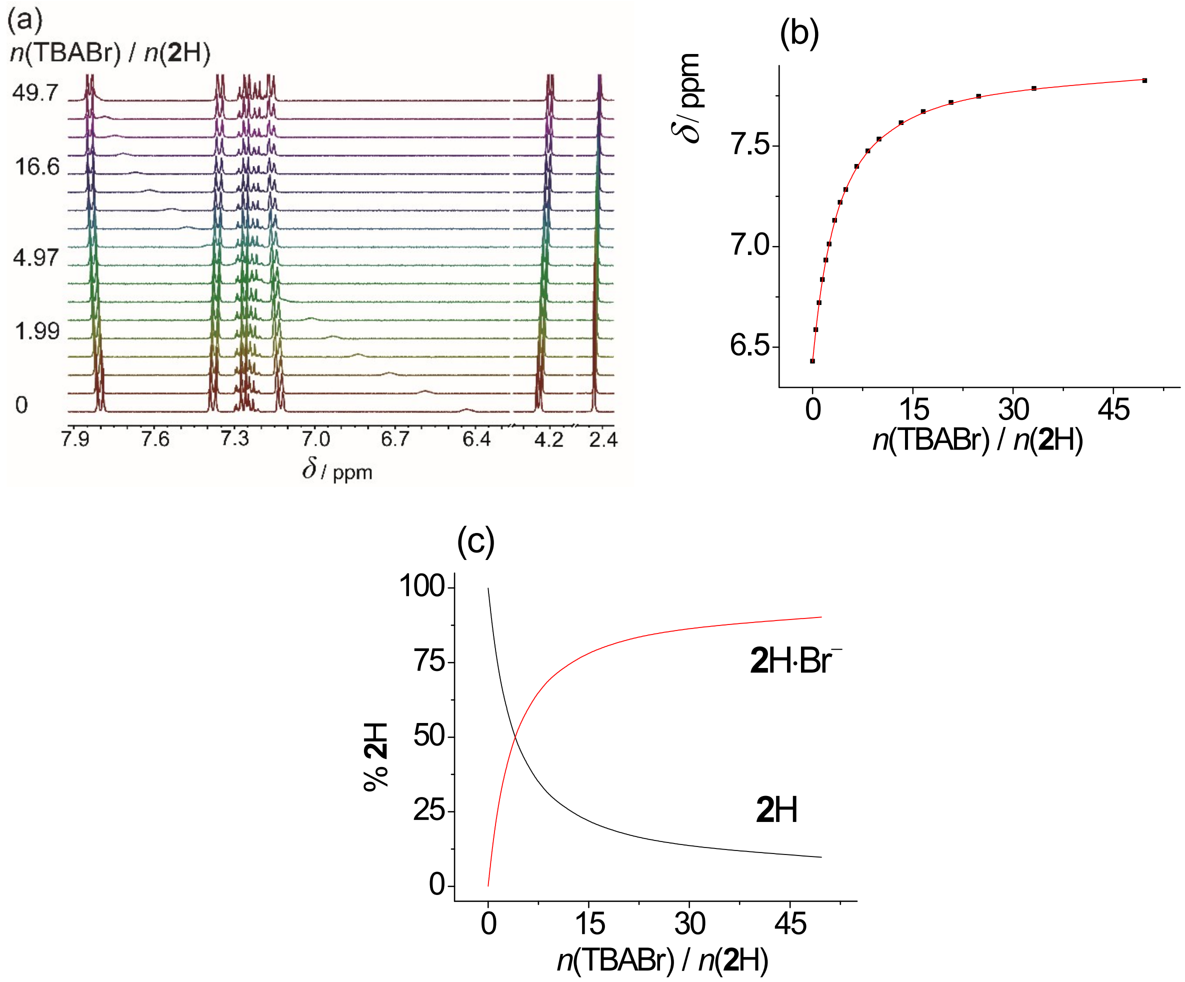

Figure S27. a) ^{1}H NMR titration of **2**H (c = 1.15 × 10^{-3} mol dm^{-3}) with TBABr (c = 1.01 × 10^{-1} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH_b proton chemical shift on n(TBABr) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **2**H with TBABr.

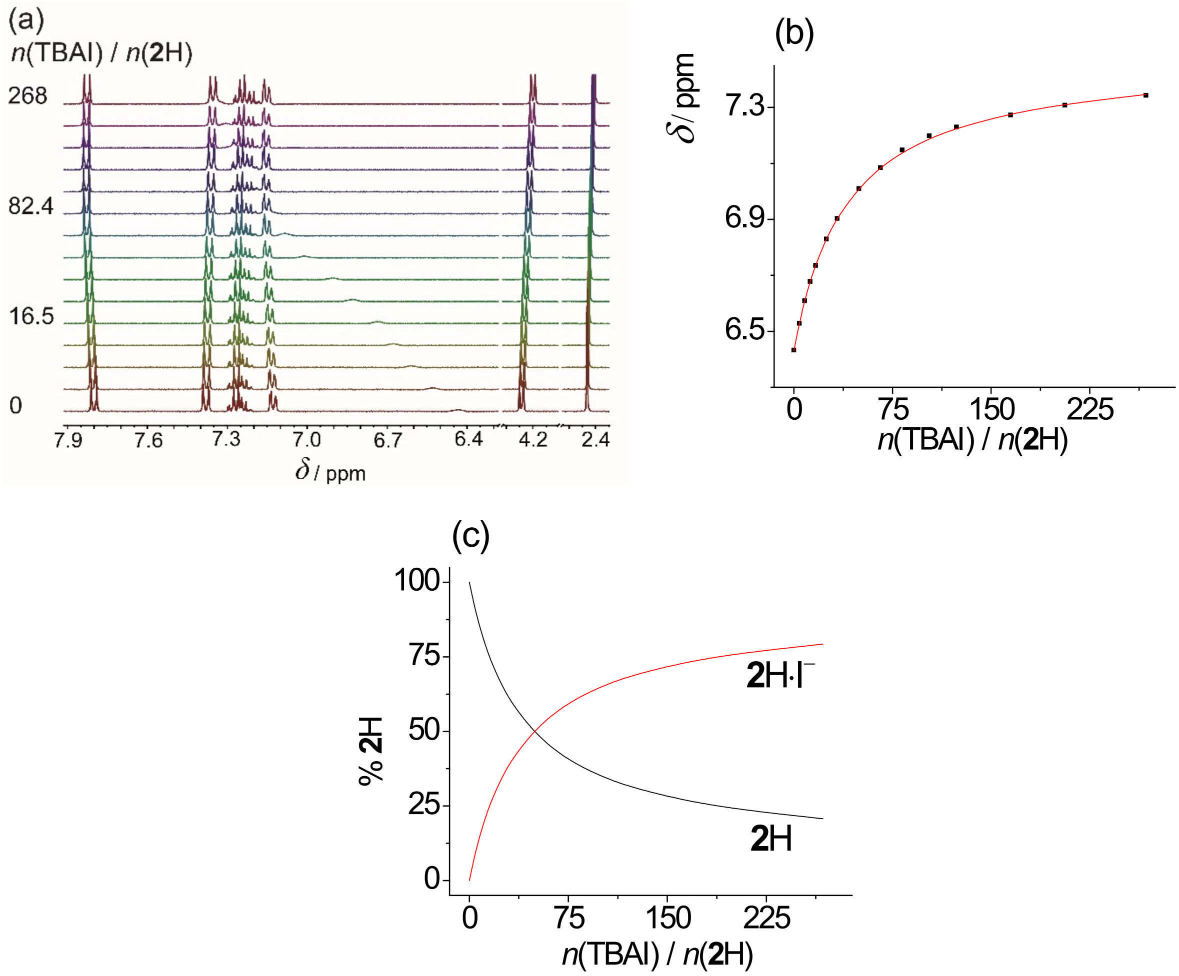

Figure S28. a) ^{1}H NMR titration of **2**H (c = 1.15 × 10^{-3} mol dm^{-3}) with TBAI (c = 5.02 × 10^{-1} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH$_b$ proton chemical shift on n(TBAI) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **2**H with TBAI.

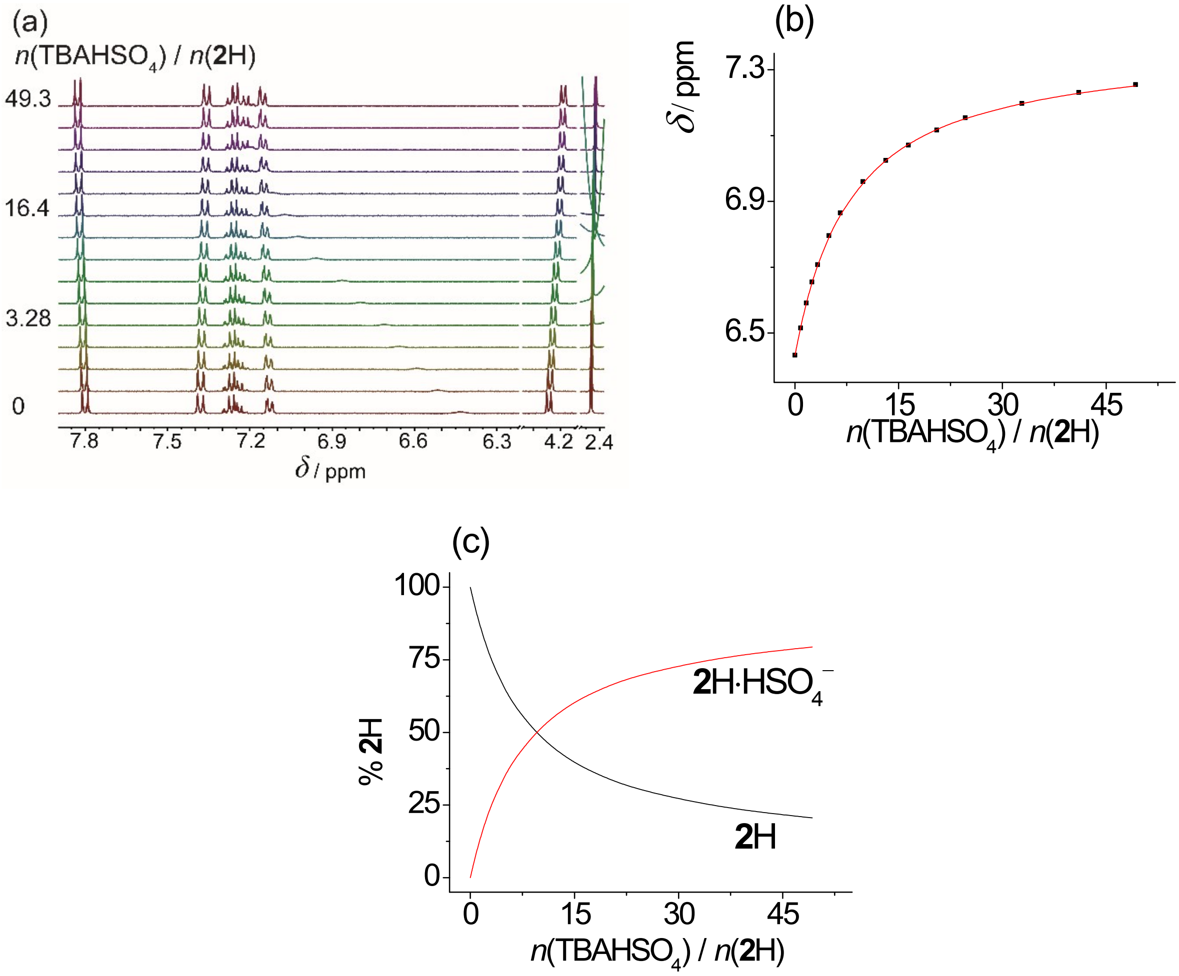

Figure S29. a) ^{1}H NMR titration of **2**H ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with TBAHSO$_4$ ($c = 1.00 \times 10^{-1}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of NH$_b$ proton chemical shift on n(TBAHSO$_4$) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **2**H with TBAHSO$_4$.

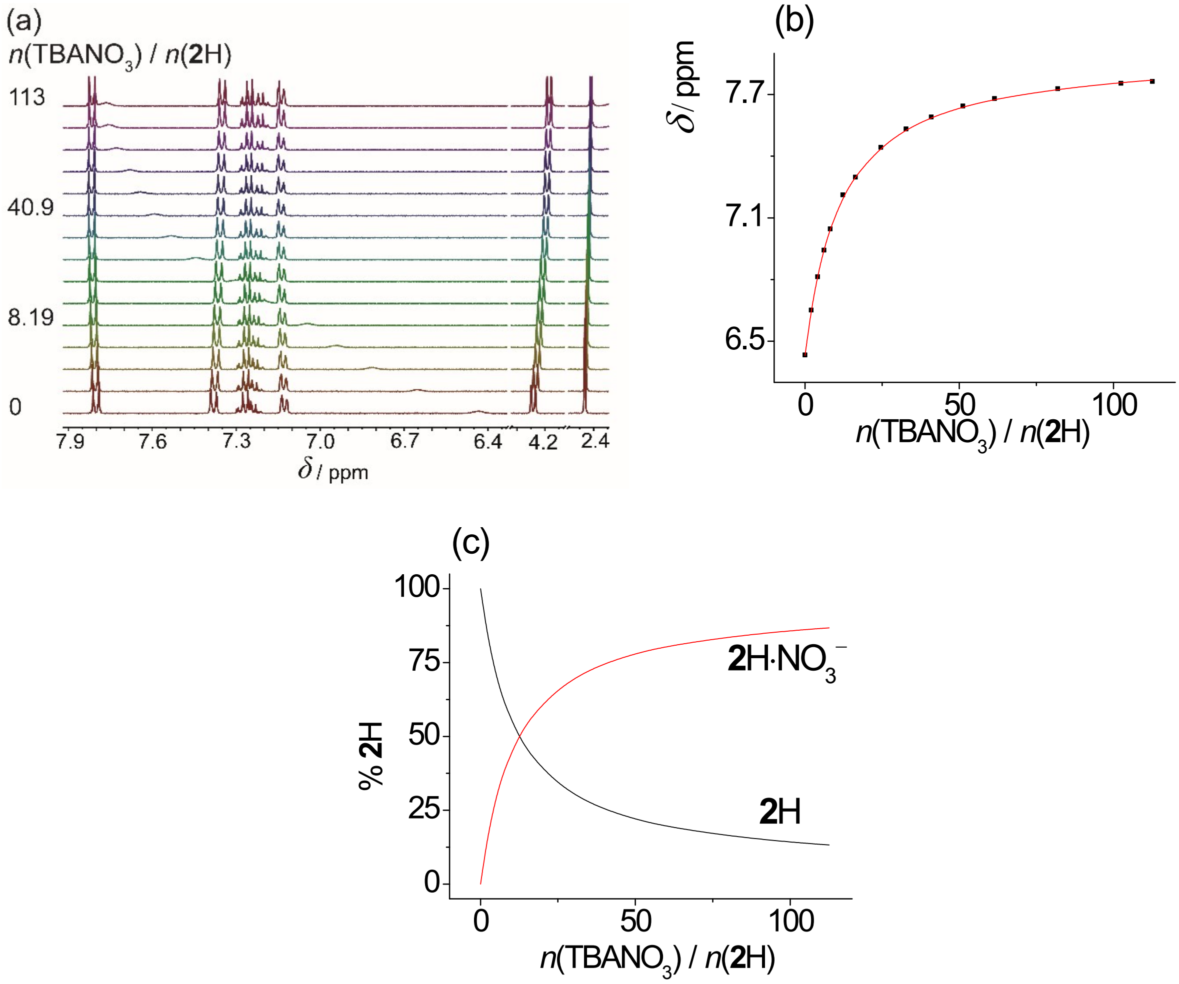

Figure S30. a) [1]H NMR titration of **2**H ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with TBANO$_3$ ($c = 2.50 \times 10^{-1}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of NH$_b$ proton chemical shift on n(TBANO$_3$) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **2**H with TBANO$_3$.

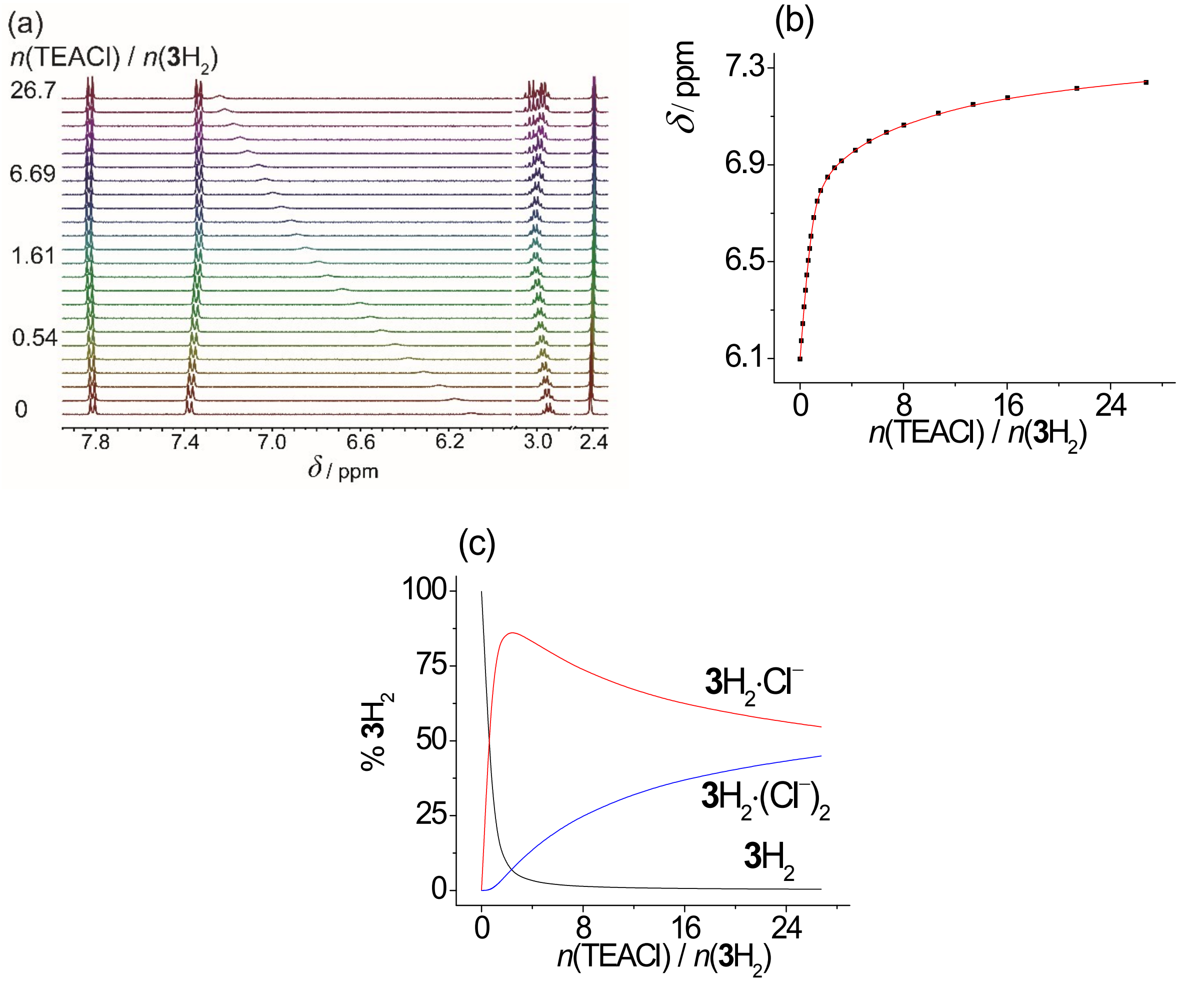

Figure S31. a) ^{1}H NMR titration of **3**H_2 ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) with TEACl ($c = 3.00 \times 10^{-2}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.50$ mL. b) Dependence of NH_b proton chemical shift on n(TEACl) / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H_2 with TEACl.

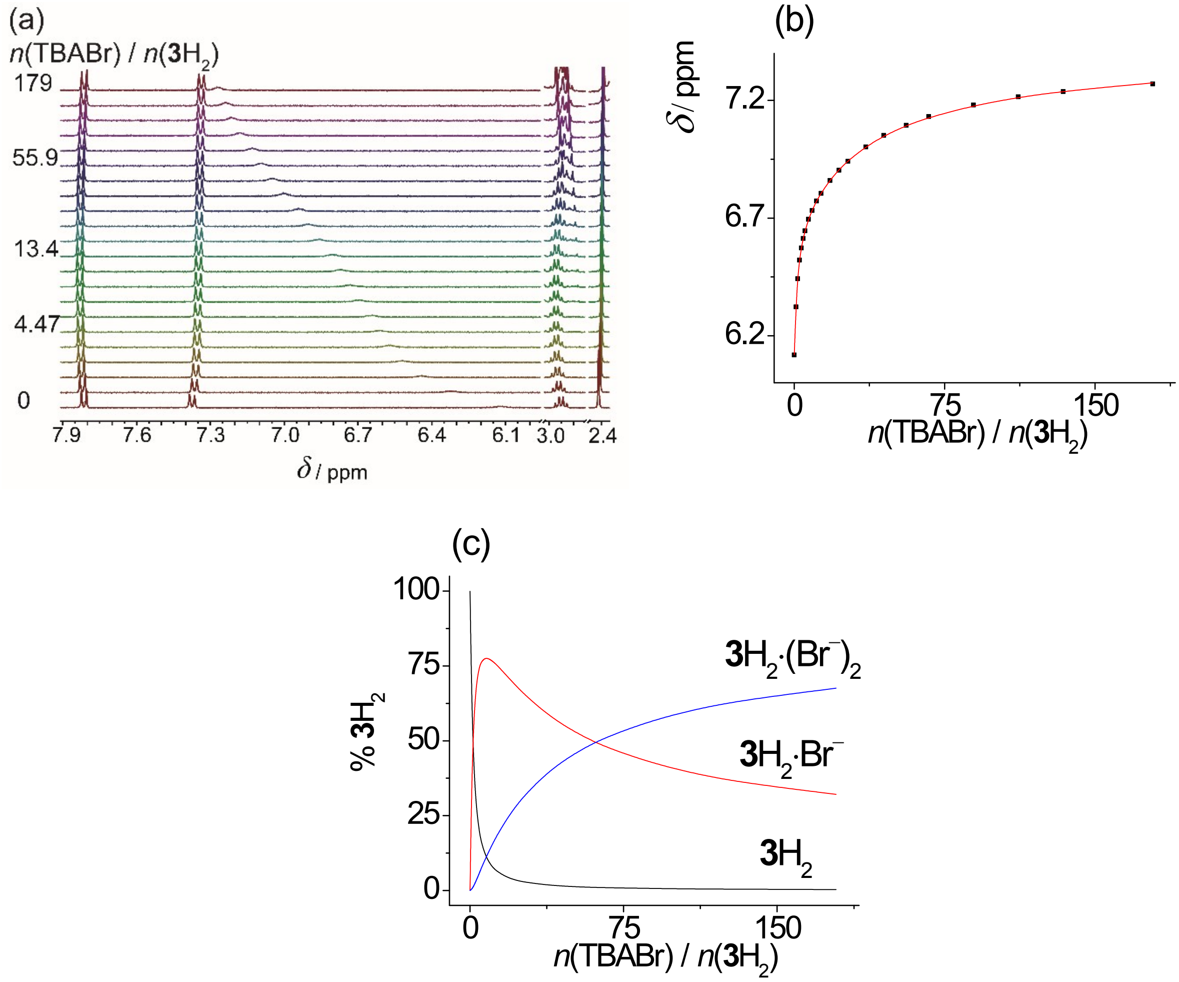

Figure S32. a) ^{1}H NMR titration of **3**H$_2$ ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) with TBABr ($c = 2.50 \times 10^{-1}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.50$ mL. b) Dependence of NH$_b$ proton chemical shift on n(TBABr) / n(**3**H$_2$) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H$_2$ with TBABr.

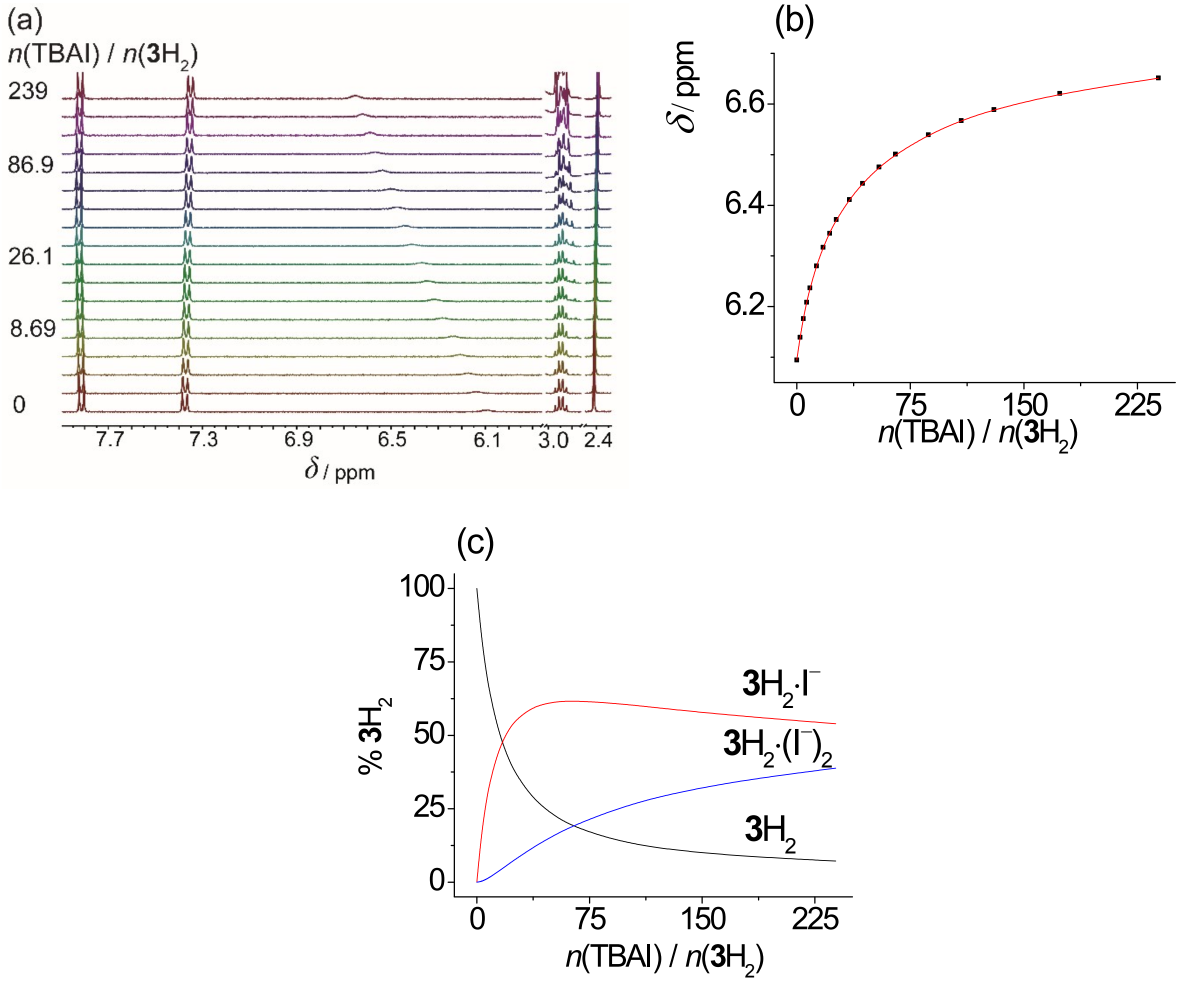

Figure S33. a) ^{1}H NMR titration of **3**H_2 ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with TBAI ($c = 2.50 \times 10^{-1}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.50 mL. b) Dependence of NH_b proton chemical shift on n(TBAI) / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H_2 with TBAI.

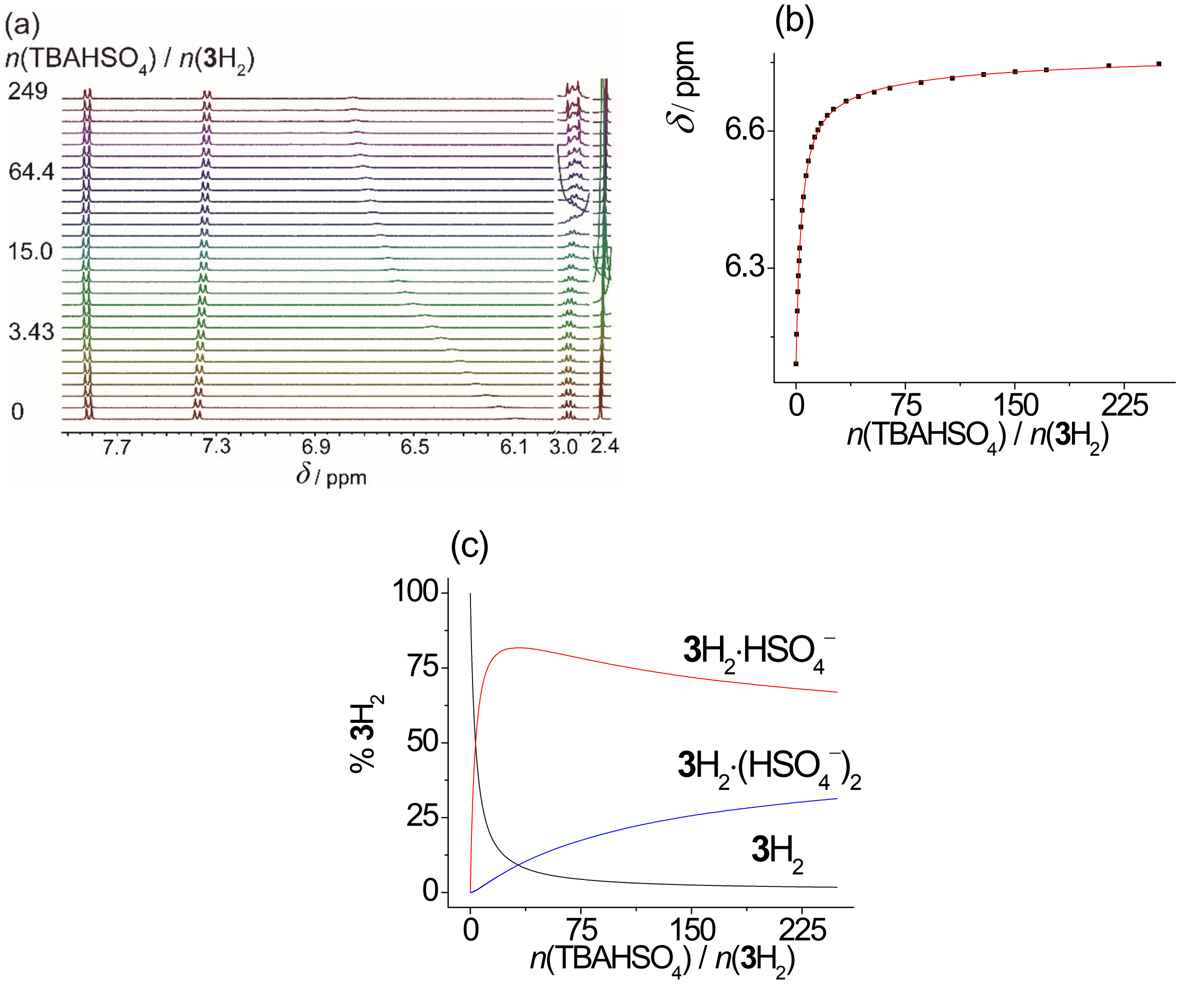

Figure S34. a) ^{1}H NMR titration of **3**H$_2$ ($c = 1.17 \times 10^{-3}$ mol dm^{-3}) with TBAHSO$_4$ ($c = 2.50 \times 10^{-1}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.50$ mL. b) Dependence of NH$_b$ proton chemical shift on n(TBAHSO$_4$) / n(**3**H$_2$) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H$_2$ with TBAHSO$_4$.

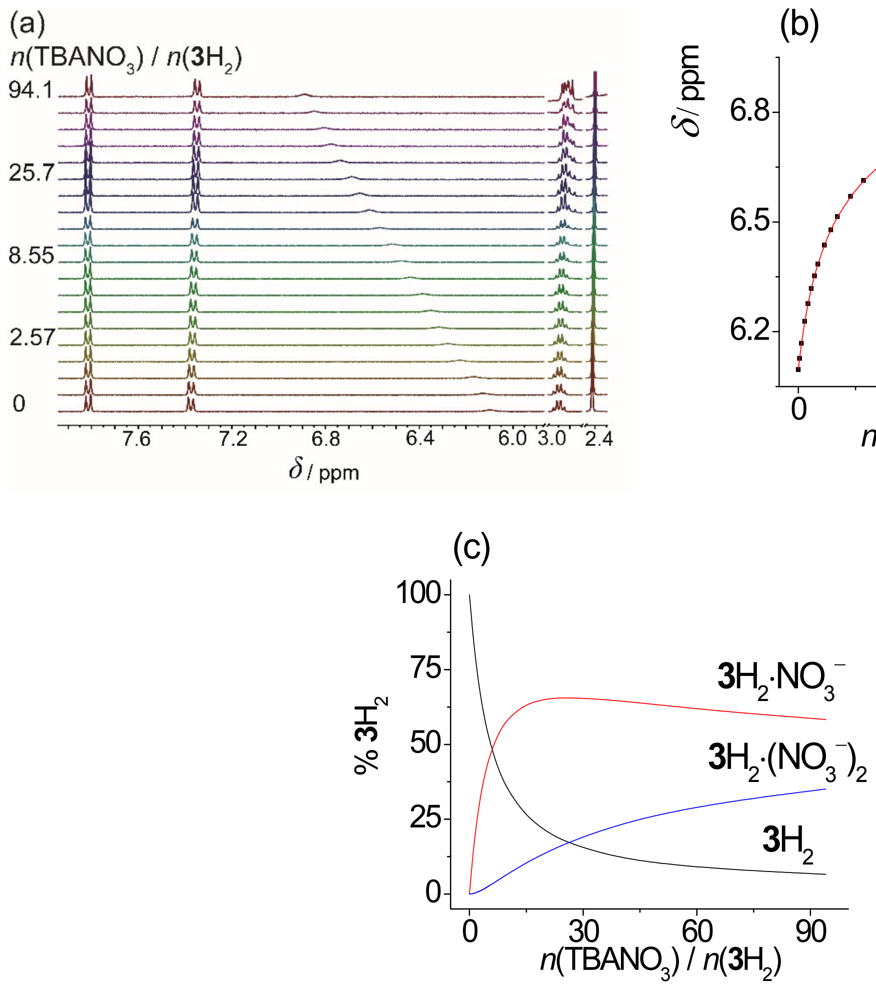

Figure S35. a) ^{1}H NMR titration of **3**H_2 ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with $TBANO_3$ ($c = 9.84 \times 10^{-2}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.50$ mL. b) Dependence of NH_b proton chemical shift on $n(TBANO_3)$ / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of species during the titration of **3**H_2 with $TBANO_3$.

Table S4. Calculated [1]H NMR chemical shifts of **1**H and its chloride, bromide, iodide, hydrogen sulfate and nitrate complexes in MeCN-d_3 at 25 °C.

	H_b	H_a	NH_b	H_d	H_c
1H	7.815	7.389	5.852	2.612	2.426
1H·Cl$^-$	7.828	7.346	7.619	2.547	2.406
1H·Br$^-$	7.835	7.351	7.287	2.549	2.406
1H·I$^-$		7.349	6.903	2.535	2.397
1H·HSO_4^-	8.835	7.361	6.747	2.556	2.412
1H·NO_3^-		7.343	7.334	2.543	2.403

Table S5. Calculated [1]H NMR chemical shifts of **2**H and its chloride, bromide, iodide, hydrogen sulfate and nitrate complexes in MeCN-d_3 at 25 °C.

	H_b	H_a	H_e	H_f	NH_b	H_d	H_c
2H	7.801	7.378	7.266	7.127	6.431	4.245	2.433
2H·Cl$^-$	7.842	7.348	7.258	7.164	8.279	4.192	2.410
2H·Br$^-$	7.847	7.352	7.254	7.168	7.983	4.198	2.410
2H·I$^-$	7.840	7.350	7.242	7.163	7.586	4.194	2.402
2H·HSO_4^-	7.835	7.353	7.251	7.159	7.463	4.178	2.412
2H·NO_3^-		7.346	7.251	7.141	7.974	4.179	2.408

Table S6. Calculated ^{1}H NMR chemical shifts of **3**H_2 and its chloride, bromide, iodide, hydrogen sulfate and nitrate complexes in MeCN-d_3 at 25 °C.

	H_b	H_a	NH_b	H_e	H_c
3H_2	7.815	7.377	5.852	2.949	2.413
3$H_2\cdot Cl^-$	7.835	7.329	6.858	3.019	2.393
3$H_2\cdot(Cl^-)_2$	7.818	7.341	7.724	2.917	2.398
3$H_2\cdot Br^-$	7.836	7.349	6.675	2.983	2.399
3$H_2\cdot(Br^-)_2$	7.808	7.334	7.565	2.909	2.390
3$H_2\cdot I^-$		7.362	6.462		2.403
3$H_2\cdot(I^-)_2$		7.333	7.017		2.378
3$H_2\cdot HSO_4^-$		7.345	6.712		2.395
3$H_2\cdot NO_3^-$		7.354	6.654	2.930	2.401
3$H_2\cdot(NO_3^-)_2$		7.332	7.428	2.885	2.392

4. Protonation properties and interactions with basic anions in DMSO

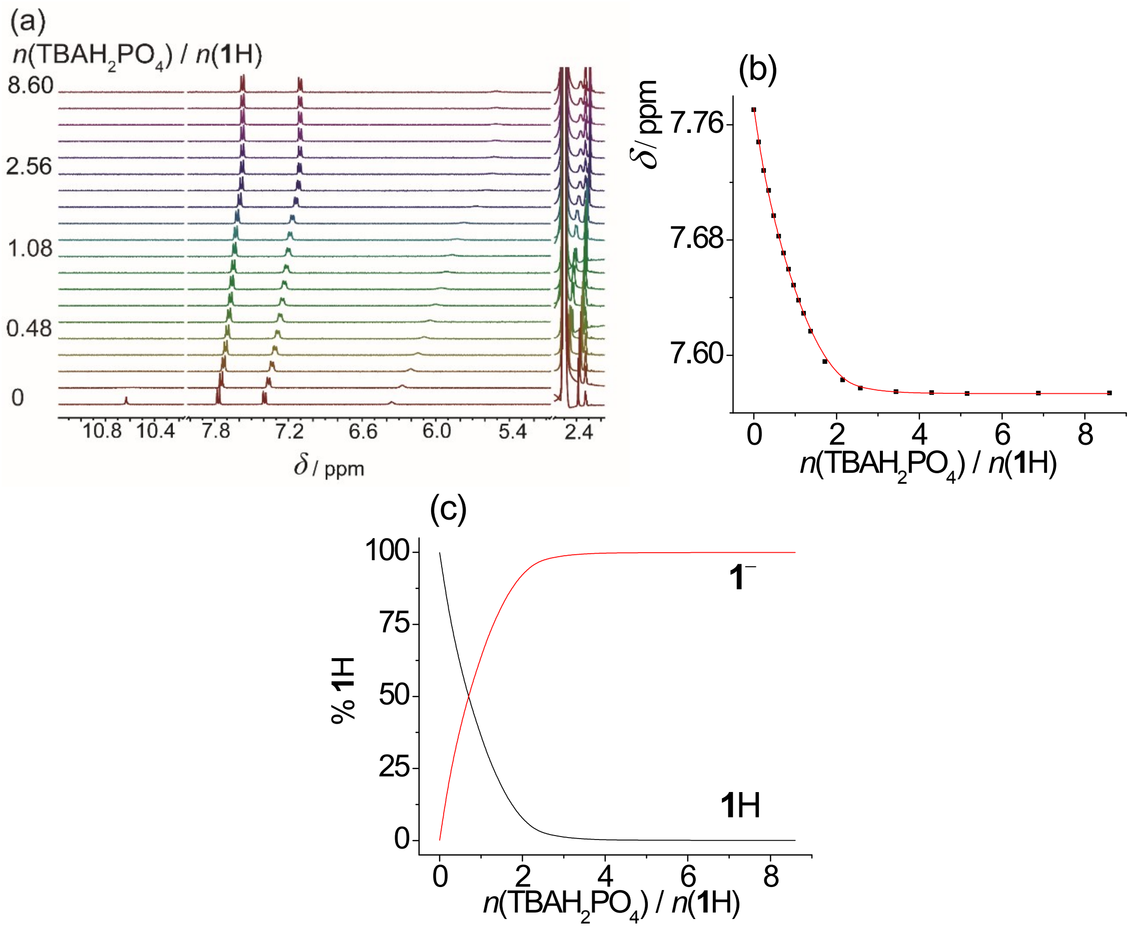

Figure S36. a) ^{1}H NMR titration of **1**H (c = 1.14 × 10^{-3} mol dm^{-3}) with $TBAH_2PO_4$ (c = 1.04 × 10^{-2} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_b proton chemical shift on $n(TBAH_2PO_4)$ / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **1**H during the titration of **1**H solution with $TBAH_2PO_4$.

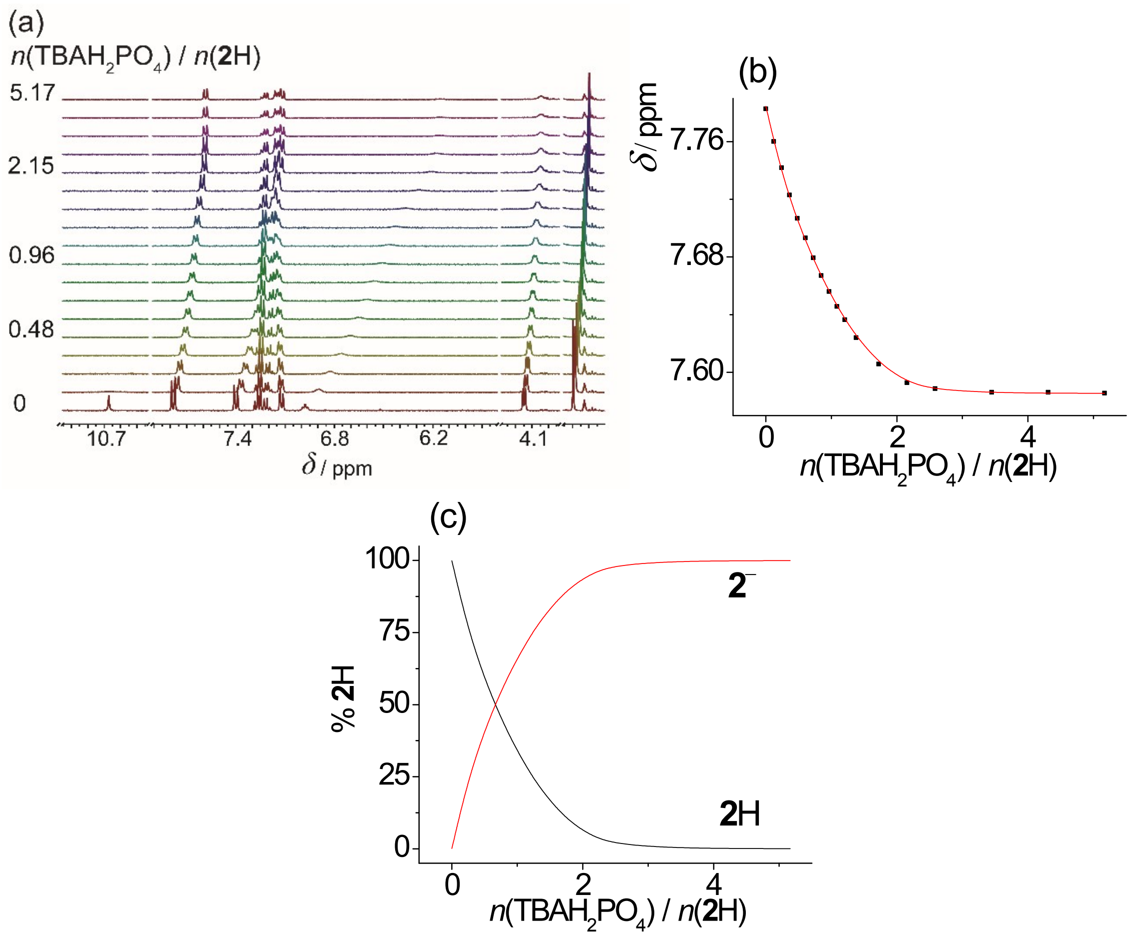

Figure S37. a) ^{1}H NMR titration of **2**H ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) with $TBAH_2PO_4$ ($c = 1.02 \times 10^{-2}$ mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of H_b proton chemical shift on $n(TBAH_2PO_4)$ / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **2**H during the titration of **2**H solution with $TBAH_2PO_4$.

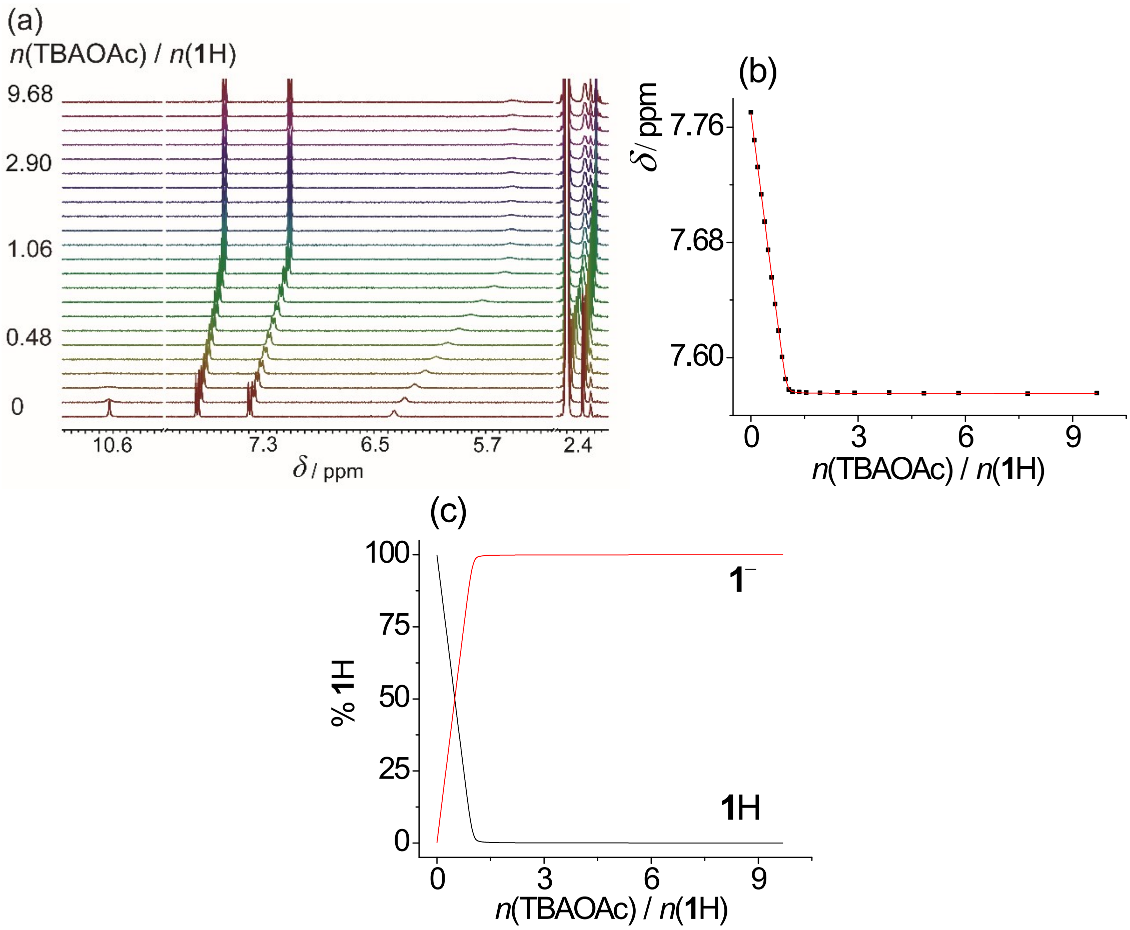

Figure S38. a) ^{1}H NMR titration of **1**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TBAOAc (c = 1.15 × 10^{-2} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_b proton chemical shift on n(TBAOAc) / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **1**H during the titration of **1**H solution with TBAOAc.

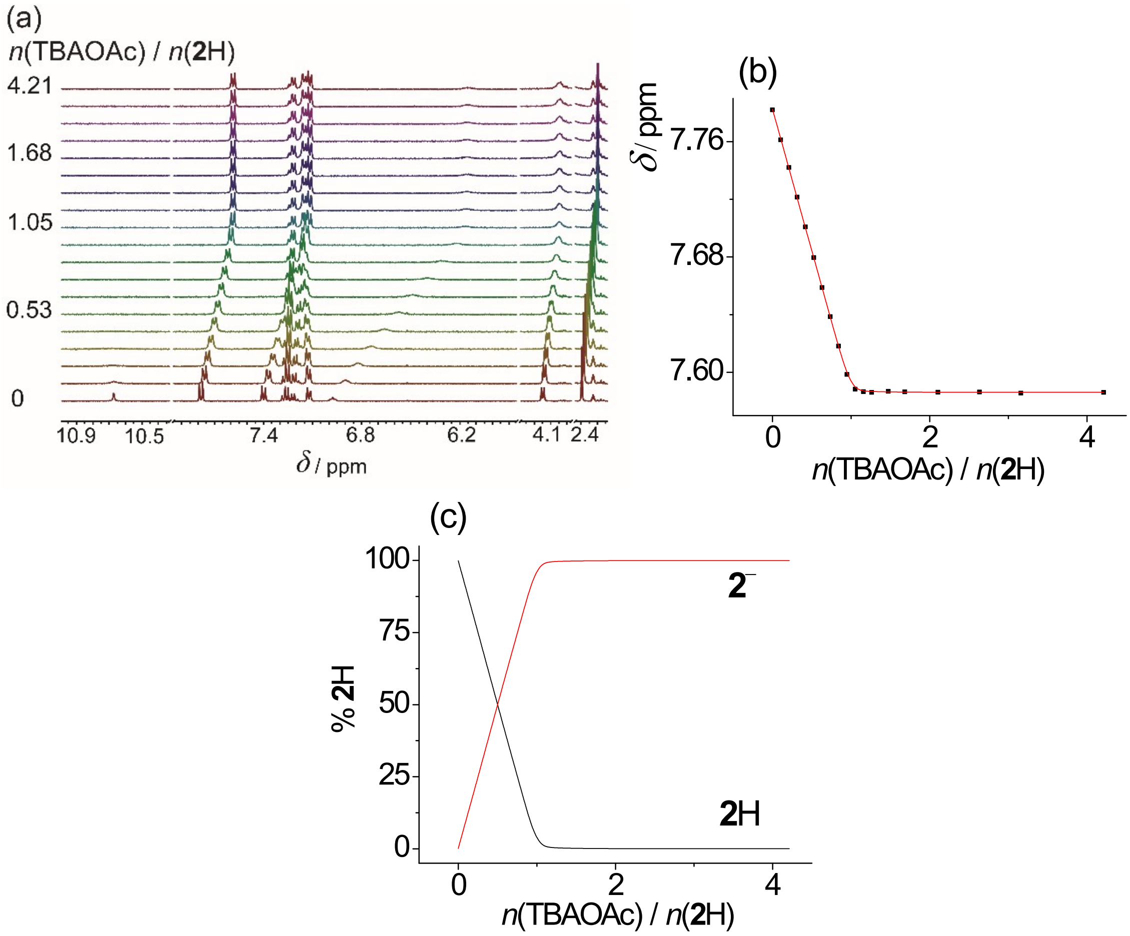

Figure S39. a) [1]H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with TBAOAc (c = 1.25 × 10^{-2} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_b proton chemical shift on n(TBAOAc) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **2**H during the titration of **2**H solution with TBAOAc.

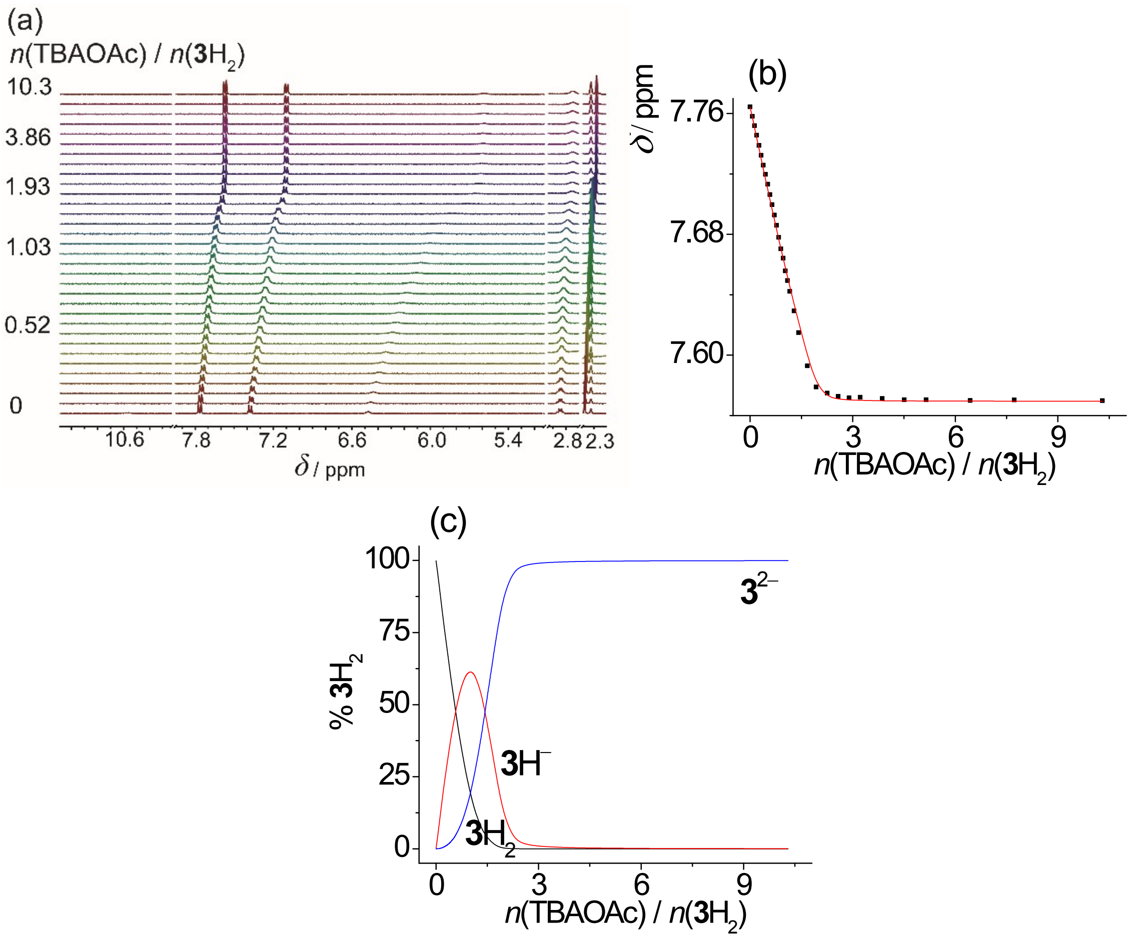

Figure S40. a) ^{1}H NMR titration of **3**H_2 (c = 1.20 × 10^{-3} mol dm^{-3}) with TBAOAc (c = 8.18 × 10^{-3} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_b proton chemical shift on n(TBAOAc) / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **3**H_2 during the titration of **3**H_2 solution with TBAOAc.

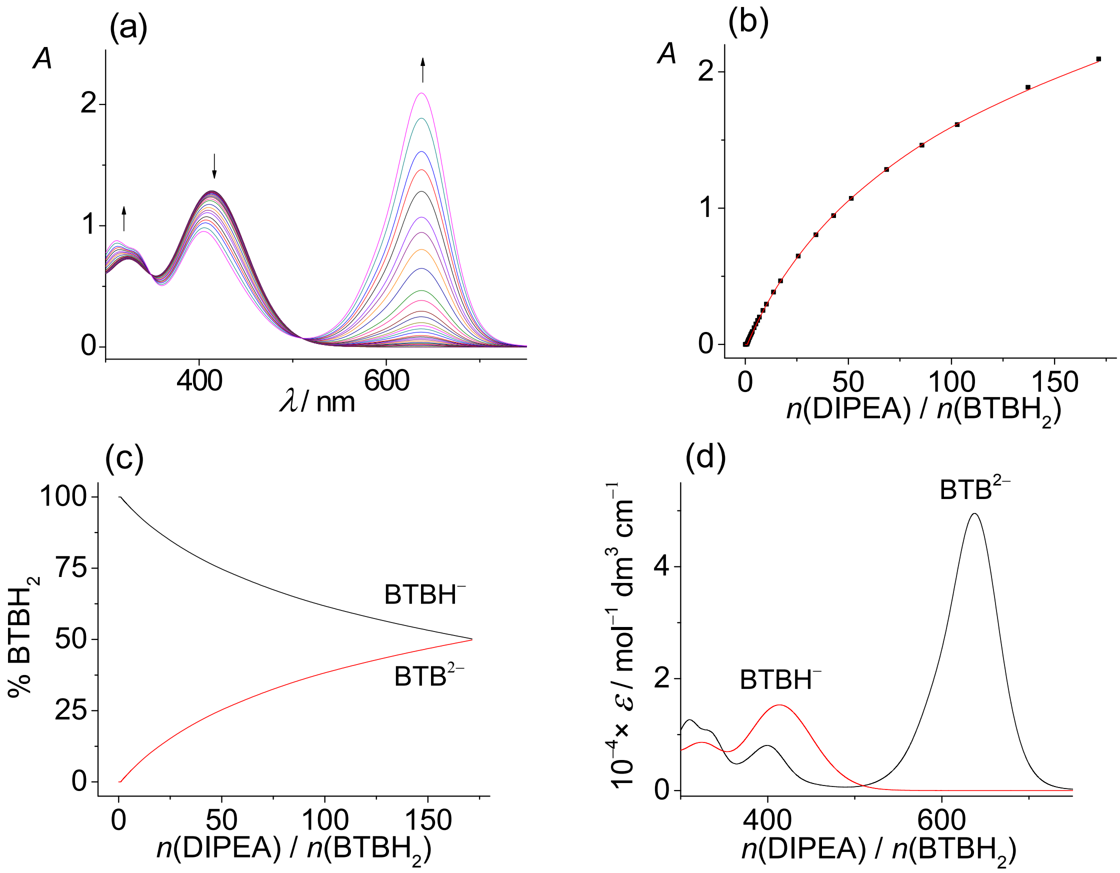

Figure S41. a) Spectrophotometric titration of $BTBH_2$ ($c = 8.41 \times 10^{-5}$ mol dm^{-3}) with DIPEA ($c = 3.40 \times 10^{-2}$ mol dm^{-3}) in DMSO at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.36$ mL. Spectra are corrected for dilution. b) Dependence of absorbance at 638 nm on n(DIPEA) / n($BTBH_2$) molar ratio. ■ experimental, ─ calculated. c) Distribution of protonation species of $BTBH_2$ during the titration of $BTBH_2$ solution with DIPEA. d) Characteristic UV-Vis spectra of bromothymol blue and its deprotonated forms.

$\log K^{H} = 9.23(1)$

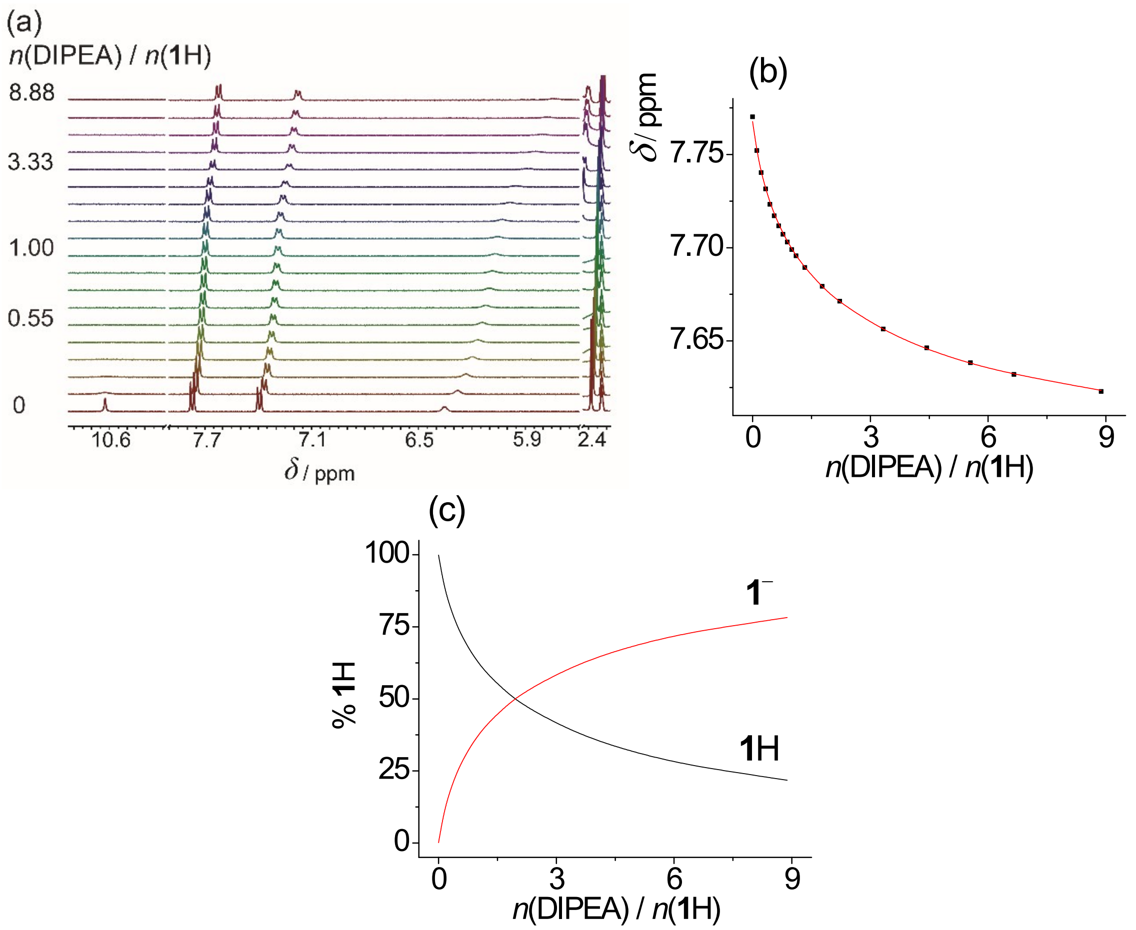

Figure 42. a) ^{1}H NMR titration of **1**H (c = 1.18 × 10^{-3} mol dm^{-3}) with DIPEA (c = 1.39 × 10^{-2} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_b proton chemical shift on n(DIPEA) / n(**1**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **1**H during the titration of **1**H solution with DIPEA.

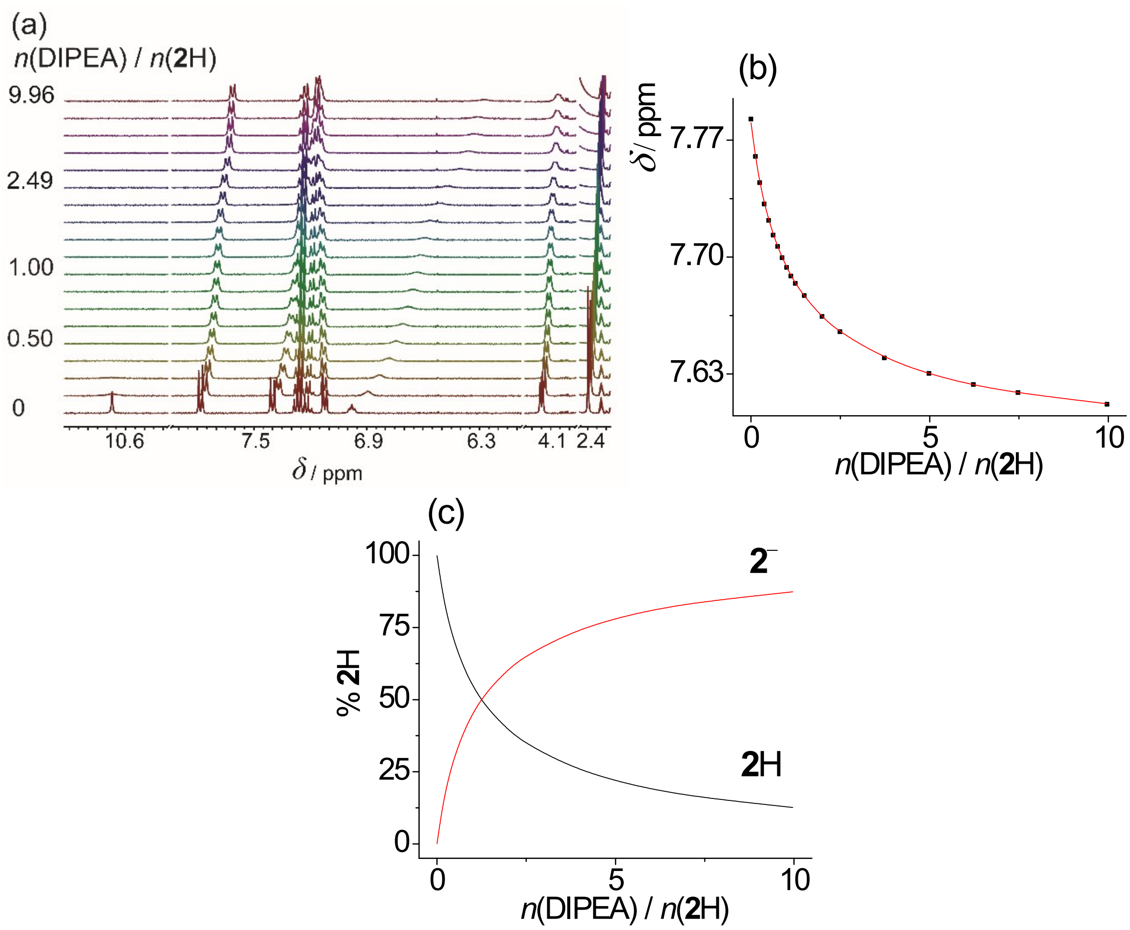

Figure 43. a) ^{1}H NMR titration of **2**H (c = 1.12 × 10^{-3} mol dm^{-3}) with DIPEA (c = 1.48 × 10^{-2} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H$_b$ proton chemical shift on n(DIPEA) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **2**H during the titration of **2**H solution with DIPEA.

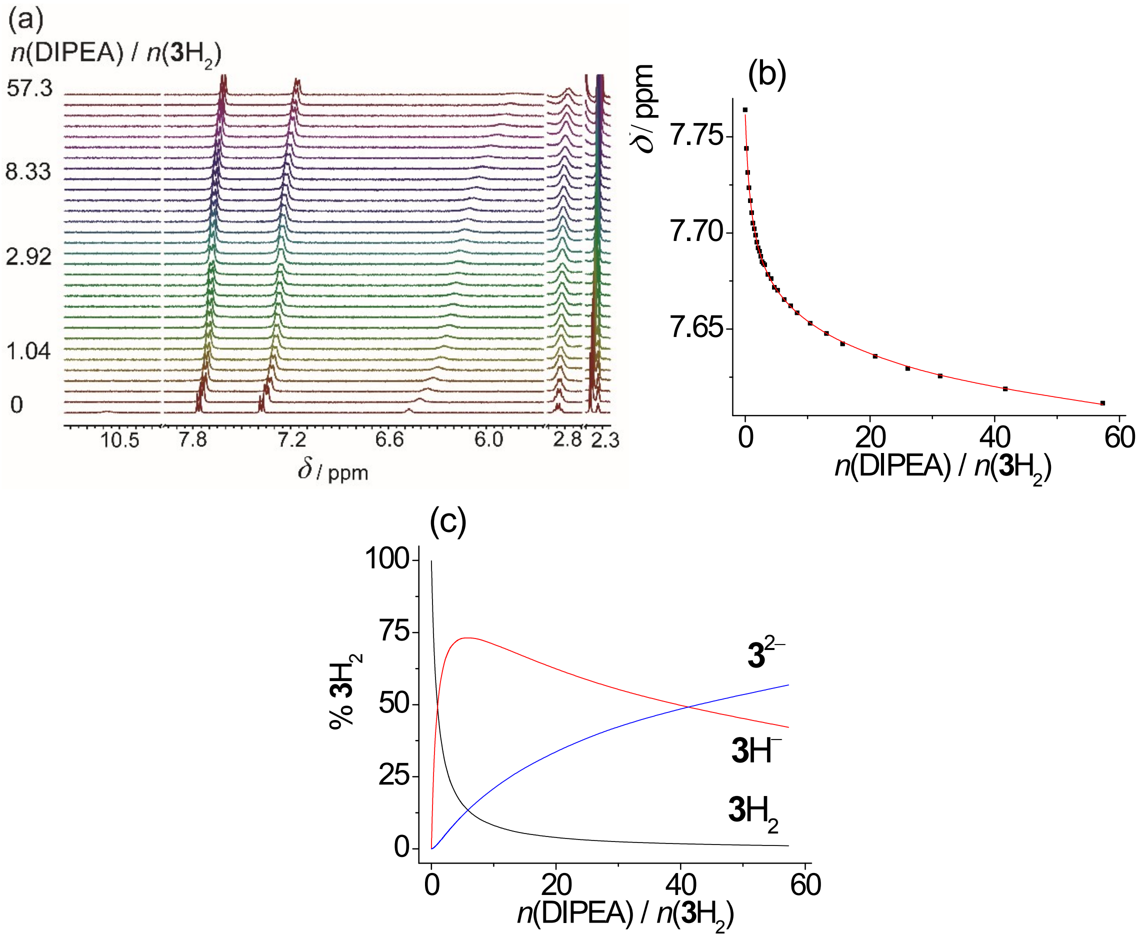

Figure S44. a) ^{1}H NMR titration of **3**H$_2$ (c = 1.20 × 10^{-3} mol dm^{-3}) with DIPEA (c = 6.62 × 10^{-2} mol dm^{-3}) in DMSO-d_6 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H$_b$ proton chemical shift on n(DIPEA) / n(**3**H$_2$) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **3**H$_2$ during the titration of **3**H$_2$ solution with DIPEA.

Table S7. Calculated ^{1}H NMR chemical shifts of **1**H and its deprotonated form in DMSO-d_6 at 25 °C.

	H_b	H_a	H_c
$\mathbf{1}^{-\,a}$	7.583	7.119	2.294
$\mathbf{1}^{-\,b}$	7.575	7.105	2.289
$\mathbf{1}^{-\,c}$	7.573	7.104	2.289
1H	7.768	7.391	2.386

[a] Determined by means of ^{1}H NMR titrations with DIPEA.
[b] Determined by means of ^{1}H NMR titrations with TBAOAc.
[c] Determined by means of ^{1}H NMR titrations with $TBAH_2PO_4$.

Table S8. Calculated ^{1}H NMR chemical shifts of **2**H and its deprotonated form in DMSO-d_6 at 25 °C.

	H_b	H_a	H_f	H_d
$\mathbf{2}^{-\,a}$	7.588	7.123	7.152	4.049
$\mathbf{2}^{-\,b}$	7.586	7.118	7.152	4.046
$\mathbf{2}^{-\,c}$	7.585	7.121	7.153	4.045
2H	7.781	7.398	7.122	4.148

[a] Determined by means of ^{1}H NMR titrations with DIPEA.
[b] Determined by means of ^{1}H NMR titrations with TBAOAc.
[c] Determined by means of ^{1}H NMR titrations with $TBAH_2PO_4$.

Table S9. Calculated ^{1}H NMR chemical shifts of **3**H_2 and its deprotonated forms in DMSO-d_6 at 25 °C.

	H_b	H_a	H_e	H_c
3^{2-} [a]	7.566	7.098	2.753	2.283
3^{2-} [b]	7.570	7.099	2.746	2.284
3^{2-} [c]	7.572	7.103	2.747	2.285
3H^- [a]	7.668	7.233	2.813	2.329
3H^- [b]	7.657	7.216	2.811	2.324
3H^- [c]	7.673	7.237	2.818	2.330
3H_2	7.764	7.378	2.842	2.375

[a] Determined by means of ^{1}H NMR titrations with DIPEA.
[b] Determined by means of ^{1}H NMR titrations with TBAOAc.
[c] Determined by means of ^{1}H NMR titrations with $TBAH_2PO_4$.

5. Protonation properties and interactions with basic anions in MeCN

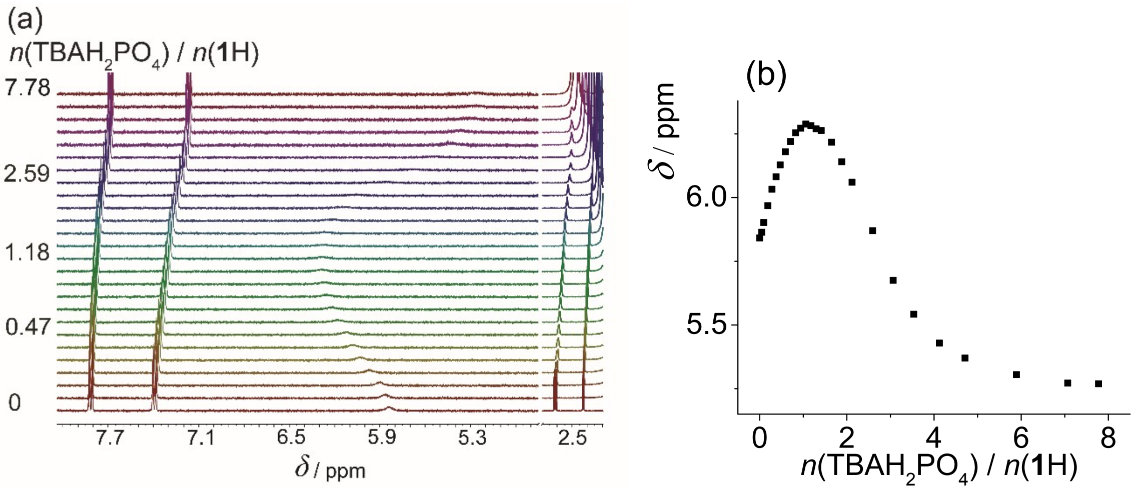

Figure S45. a) ^{1}H NMR titration of **1**H (c = 1.17 × 10^{-3} mol dm^{-3}) with $TBAH_2PO_4$ (c = 1.46 × 10^{-2} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH_b proton chemical shift on $n(TBAH_2PO_4)$ / n(**1**H) molar ratio. ■ experimental

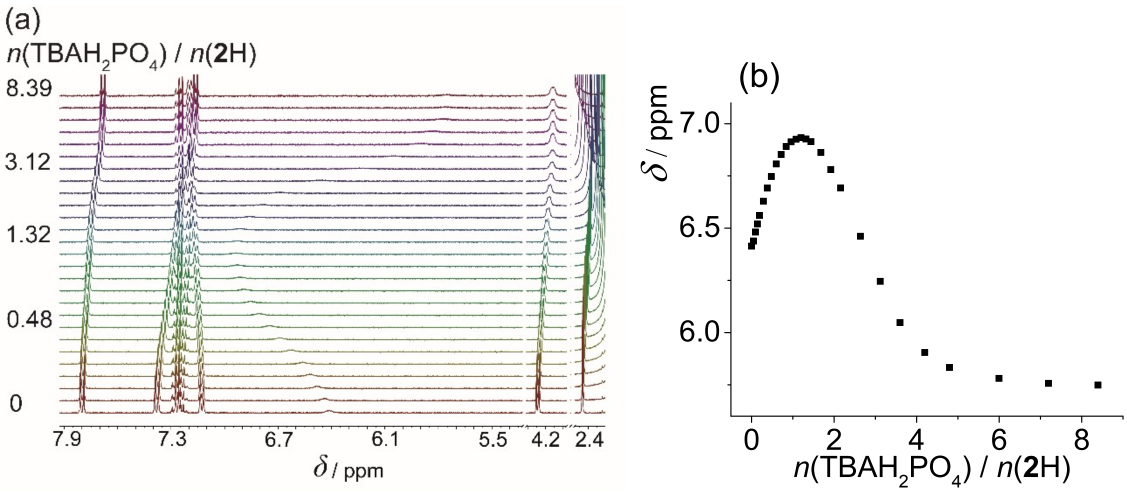

Figure S46. a) ^{1}H NMR titration of **2**H (c = 1.15 × 10^{-3} mol dm^{-3}) with $TBAH_2PO_4$ (c = 1.46 × 10^{-2} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH_b proton chemical shift on $n(TBAH_2PO_4)$ / n(**2**H) molar ratio. ■ experimental

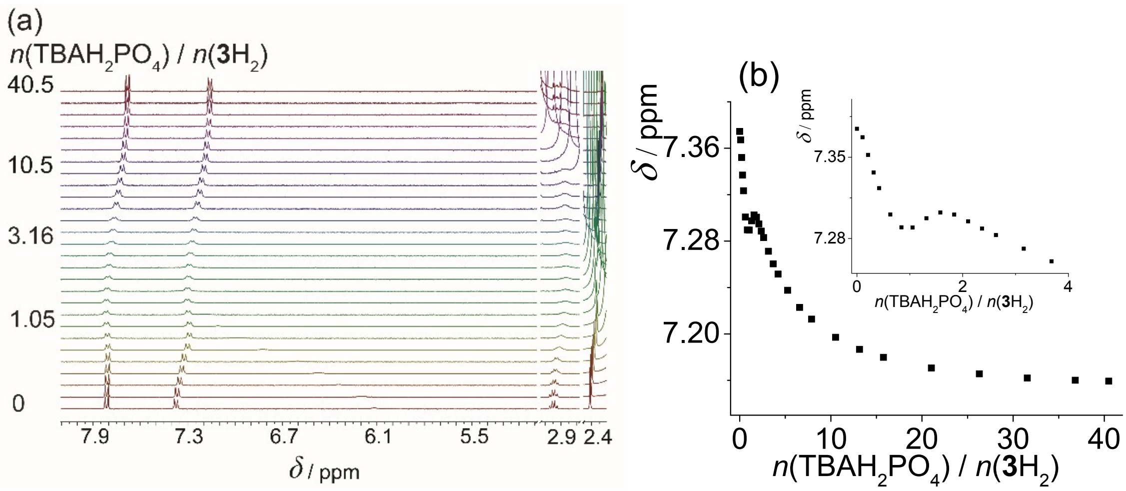

Figure S47. a) ^{1}H NMR titration of **3**H_2 (c = 1.12 × 10^{-3} mol dm^{-3}) with $TBAH_2PO_4$ (c = 2.95 × 10^{-2} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.50 mL. b) Dependence of H_a proton chemical shift on $n(TBAH_2PO_4)$ / n(**3**H_2) molar ratio. Inset: enlarged. ■ experimental

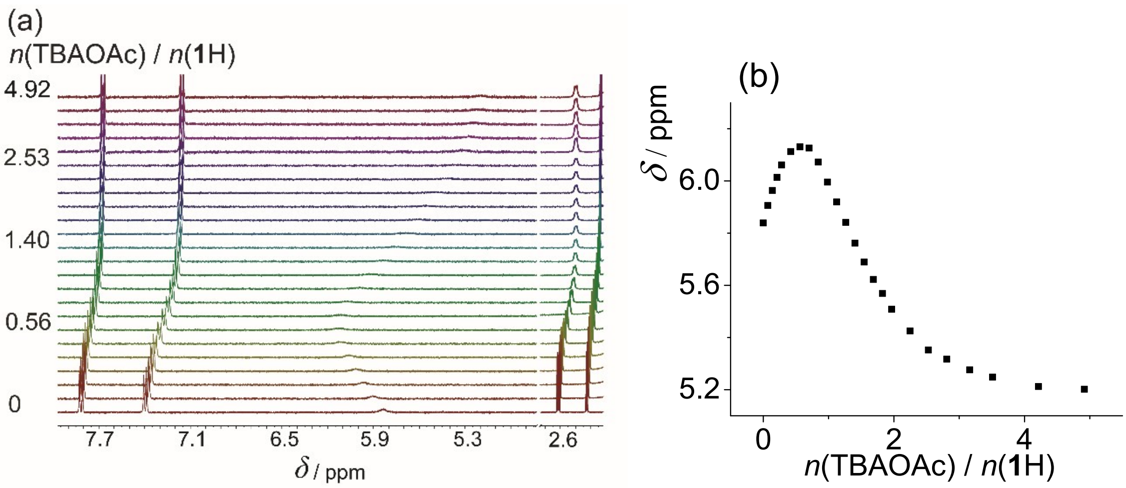

Figure S48. a) ^{1}H NMR titration of **1**H (c = 1.17 × 10^{-3} mol dm^{-3}) with TBAOAc (c = 8.70 × 10^{-3} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of NH_b proton chemical shift on n(TBAOAc) / n(**1**H) molar ratio. ■ experimental

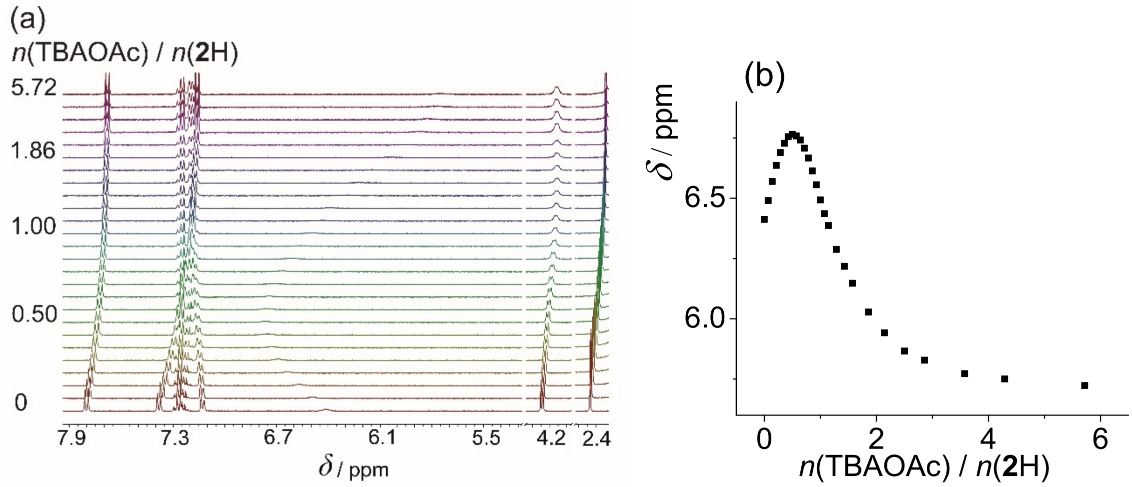

Figure S49. a) ^{1}H NMR titration of **2**H ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with TBAOAc ($c = 8.70 \times 10^{-3}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.53$ mL. b) Dependence of NH_b proton chemical shift on n(TBAOAc) / n(**2**H) molar ratio. ■ experimental

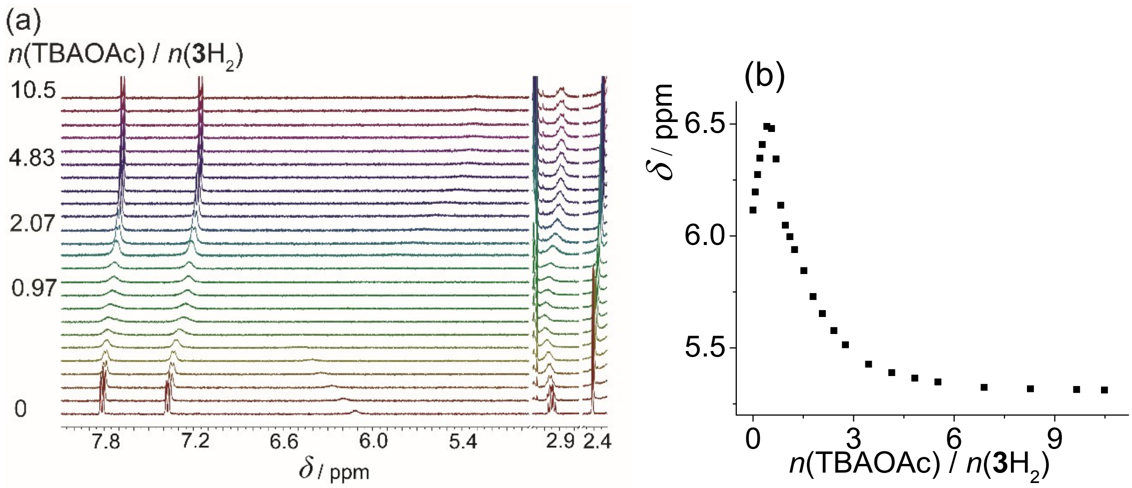

Figure S50. a) ^{1}H NMR titration of **3**H_2 ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) with TBAOAc ($c = 7.73 \times 10^{-3}$ mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, $V_0 = 0.50$ mL. b) Dependence of NH_b proton chemical shift on n(TBAOAc) / n(**3**H_2) molar ratio. ■ experimental

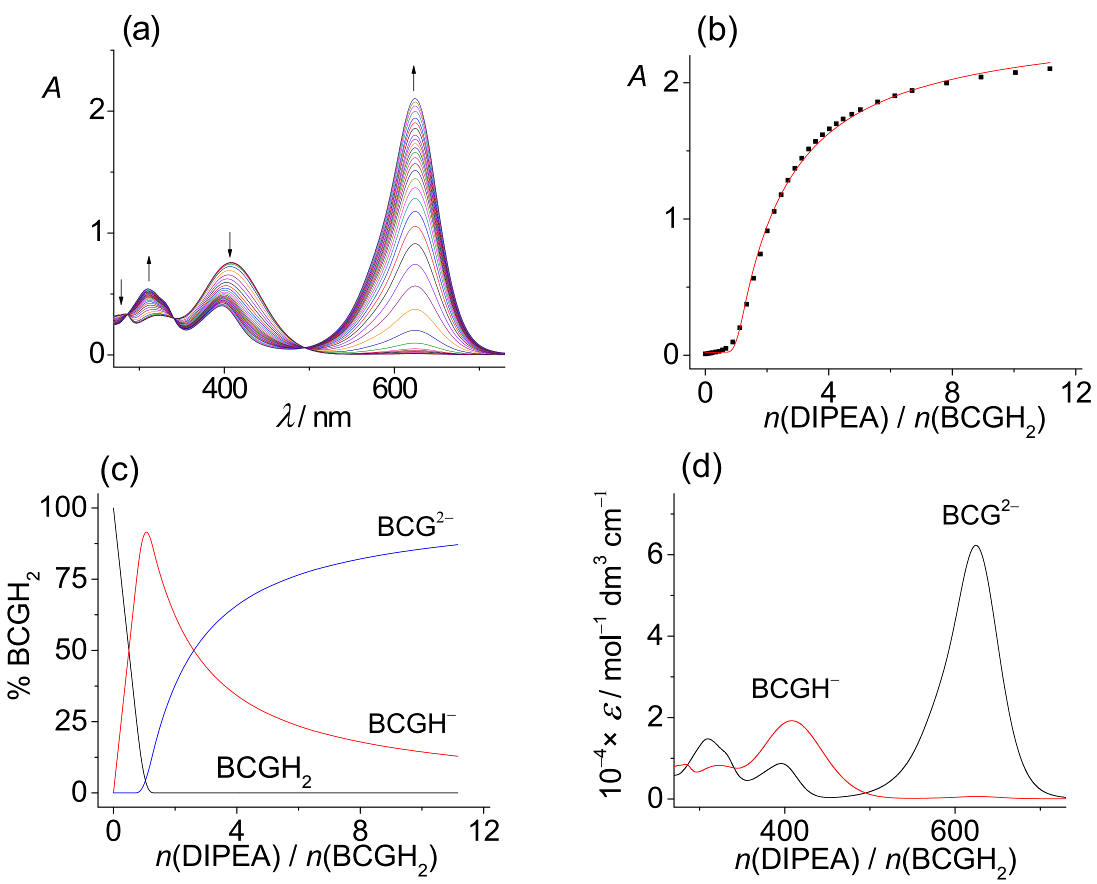

Figure S51. a) Spectrophotometric titration of $BCGH_2$ ($c = 3.95 \times 10^{-5}$ mol dm^{-3}) with DIPEA ($c = 9.17 \times 10^{-4}$ mol dm^{-3}) in MeCN at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.08$ mL. Spectra are corrected for dilution. b) Dependence of absorbance at 638 nm on n(DIPEA) / n($BCGH_2$) molar ratio. ■ experimental, ─ calculated. c) Distribution of protonation species of $BCGH_2$ during the titration of $BCGH_2$ solution with DIPEA. d) Characteristic UV-Vis spectra of $BCGH_2$ deprotonated forms.

$\log K^{H} = 18.64(1)$

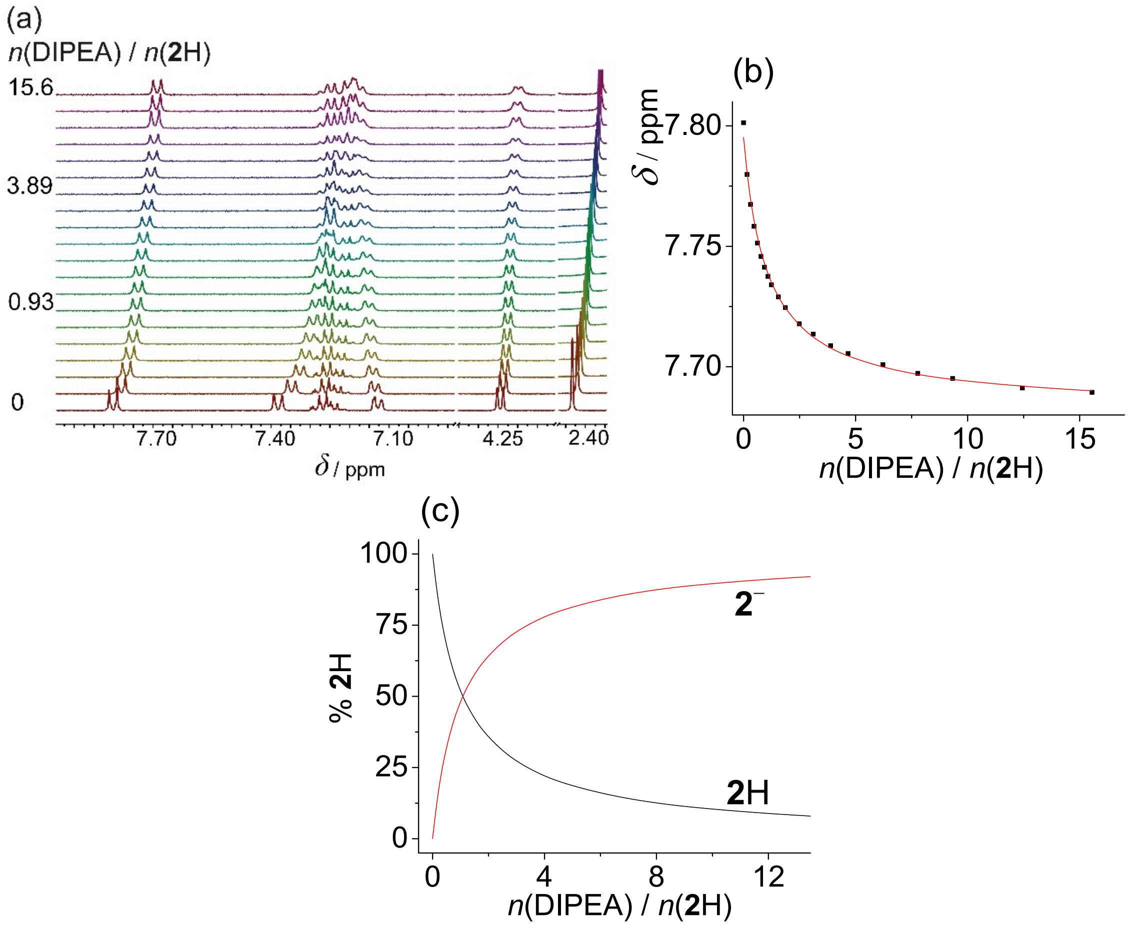

Figure S52. a) ¹H NMR titration of **2**H (c = 1.18 × 10^{-3} mol dm^{-3}) with DIPEA (c = 1.94 × 10^{-2} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.53 mL. b) Dependence of H_b proton chemical shift on n(DIPEA) / n(**2**H) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **2**H during the titration of **2**H solution with DIPEA.

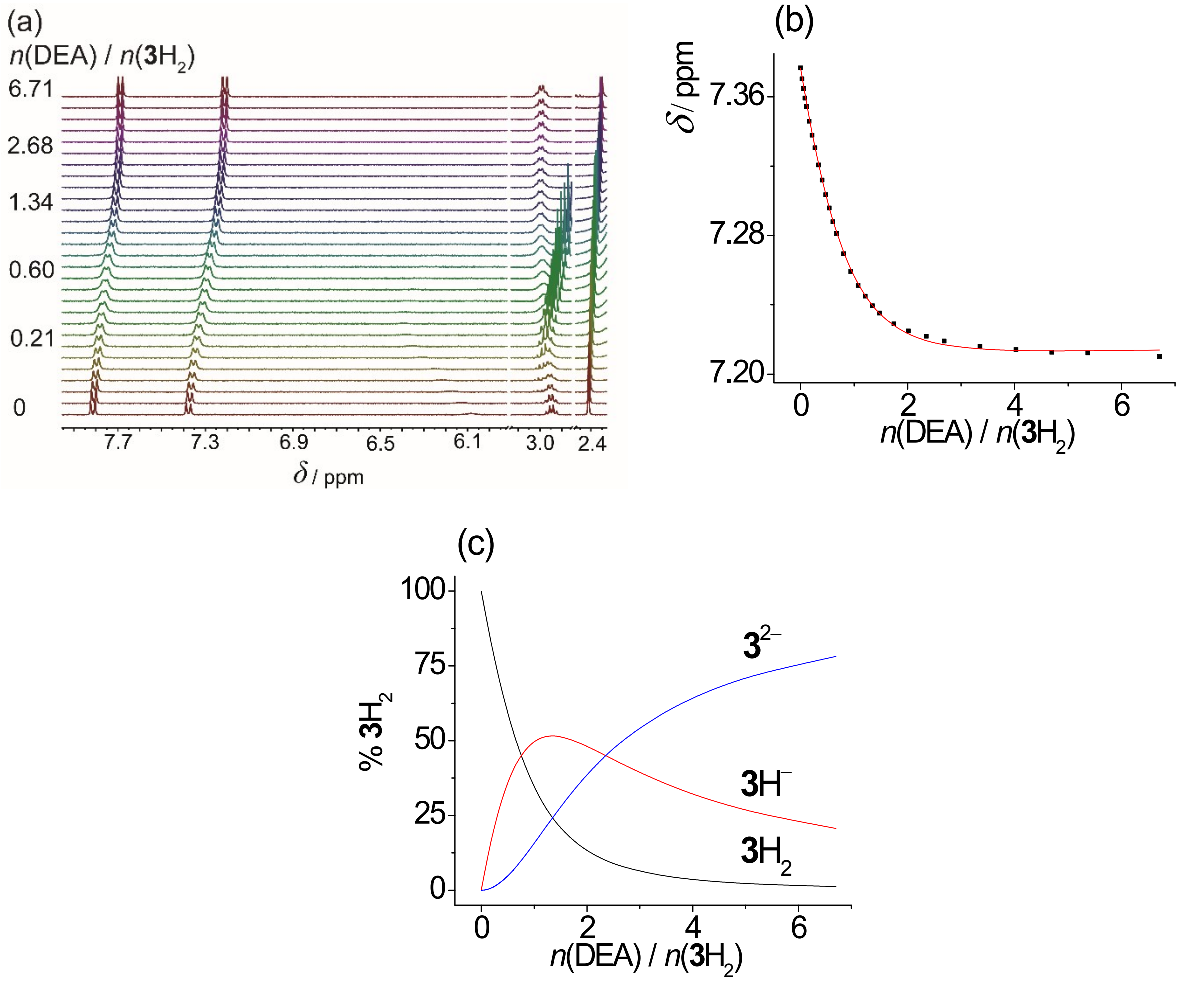

Figure S53. a) ¹H NMR titration of **3**H_2 ($c = 1.15 \times 10^{-3}$ mol dm^{-3}) with DEA (c = 7.72×10^{-3} mol dm^{-3}) in MeCN-d_3 at (25.0 ± 0.1) °C, V_0 = 0.50 mL. b) Dependence of H_a proton chemical shift on n(DEA) / n(**3**H_2) molar ratio. ■ experimental, — calculated. c) Distribution of protonation species of **3**H_2 during the titration of **3**H_2 solution with DEA.

Table S10. Calculated ^{1}H NMR chemical shifts of **1**H and its deprotonated form in MeCN-d_3 at 25 °C.

	H_b	H_a	H_c
1$^-$	7.683	7.191	2.349
1H	7.817	7.396	2.428

Table S11. Calculated ^{1}H NMR chemical shifts of **2**H and its deprotonated form in MeCN-d_3 at 25 °C.

	H_b	H_a	H_d	H_c
2$^-$	7.682	7.194	4.200	2.357
2H	7.801	7.382	4.245	2.434

Table S12. Calculated ^{1}H NMR chemical shifts of **3**H_2 and its deprotonated form in MeCN-d_3 at 25 °C.

	H_a	H_d	H_c
3H^-	7.276	3.003	2.385
3H_2	7.377	2.949	2.413

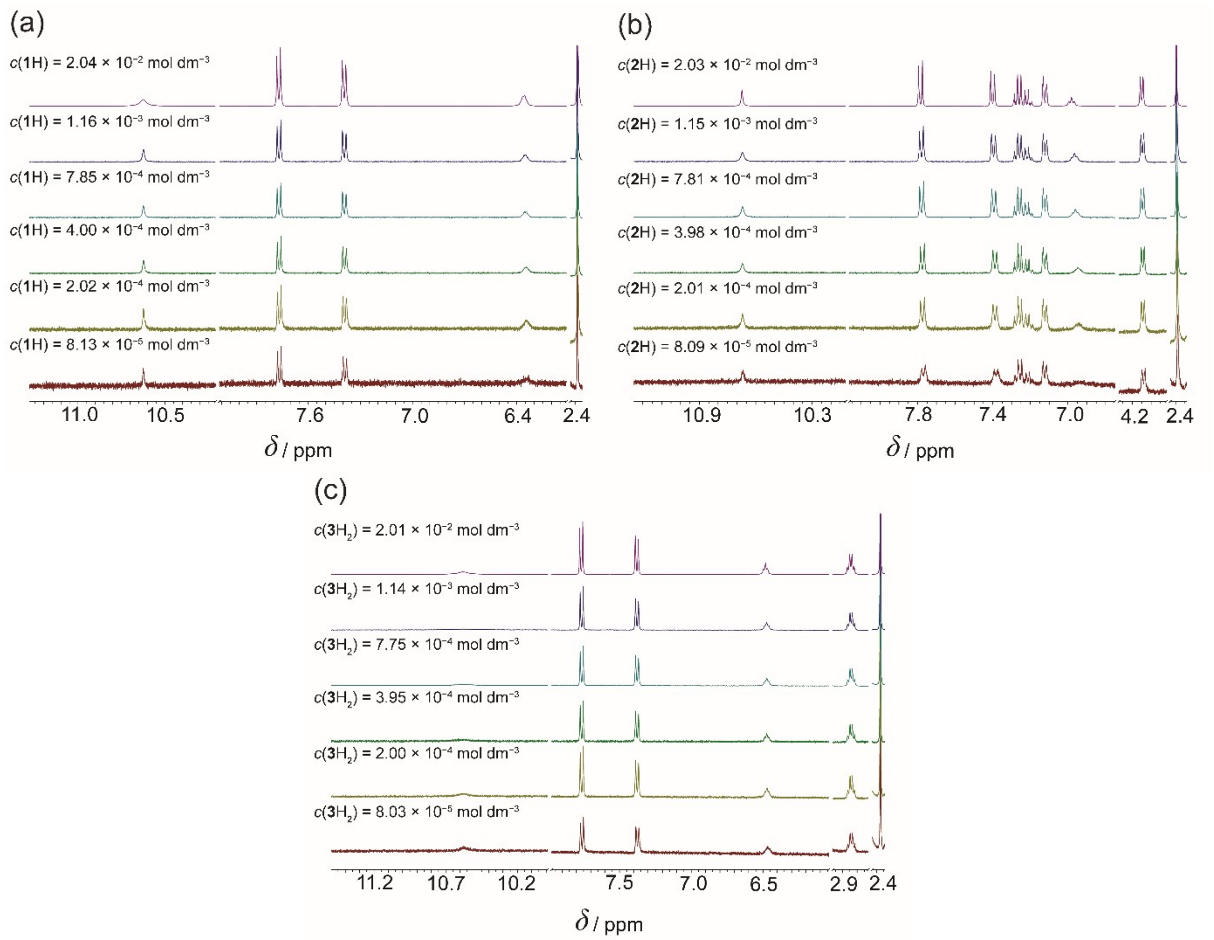

Figure S54. Concentration dependence of ^{1}H NMR spectra of a) **1**H, b) **2**H, and c) **3**H2 in DMSO-d_6 at (25.0 ± 0.1) °C.

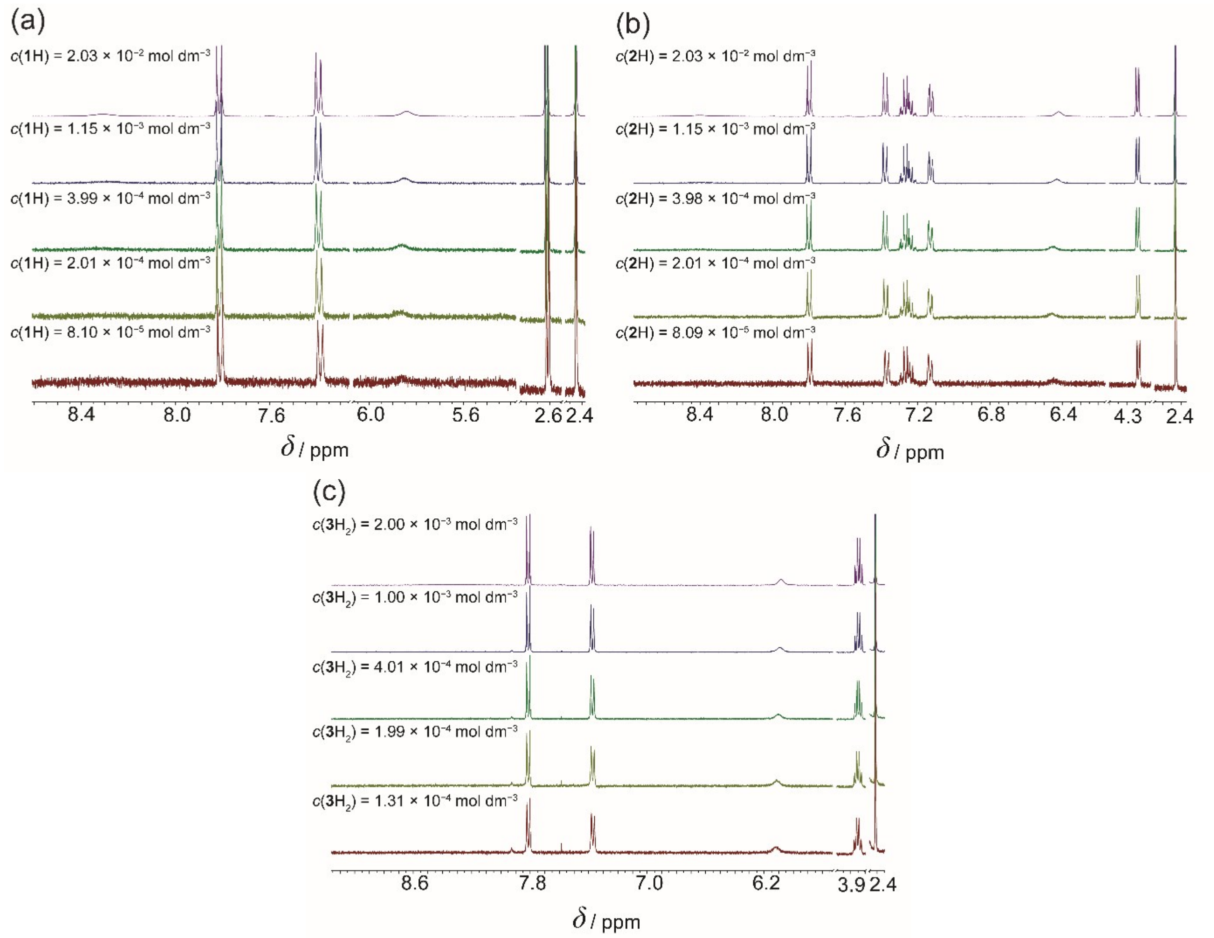

Figure S55. Concentration dependence of ^{1}H NMR spectra of a) **1**H, b) **2**H, and c) **3**H2 in MeCN-d_3 at (25.0 ± 0.1) °C.

6. DOSY NMR experiments

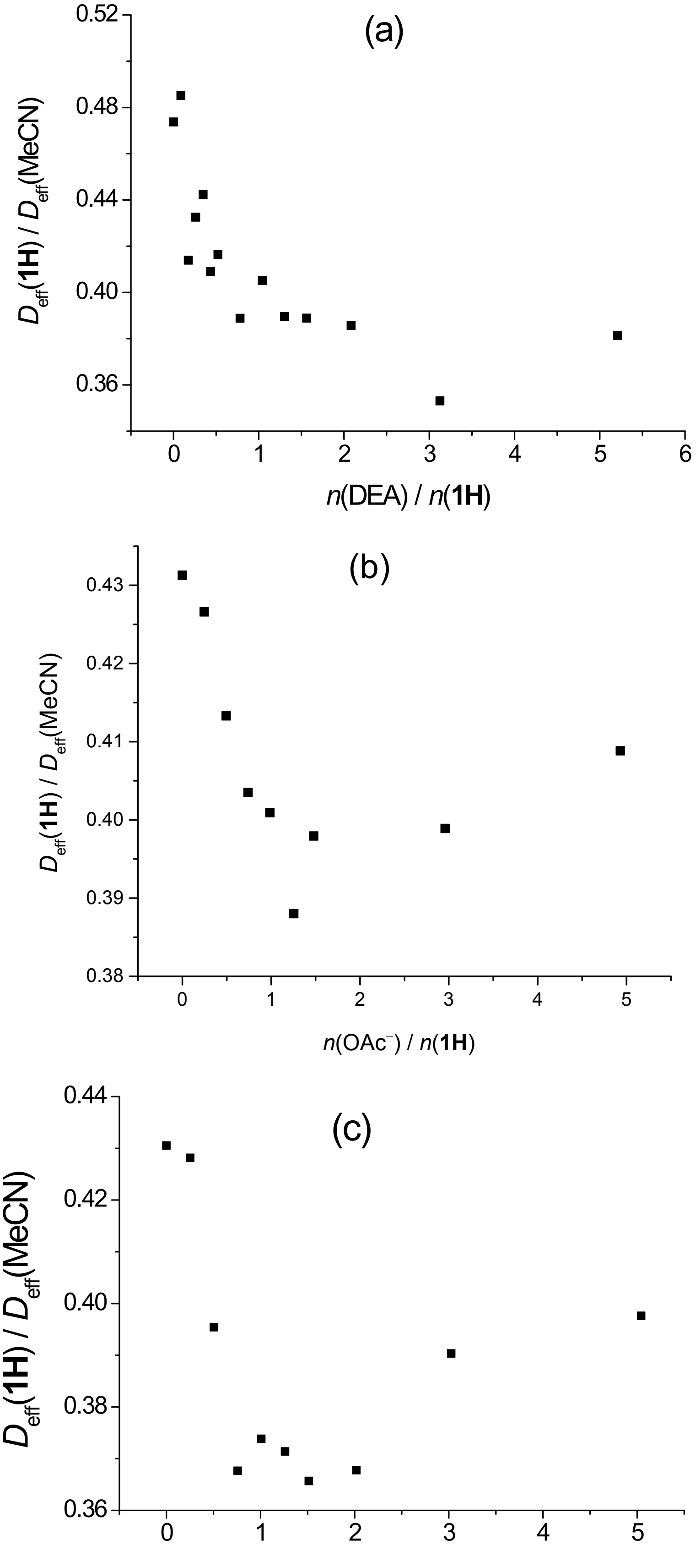

Figure S56. DOSY NMR titration of **1**H with DEA (a), TBAOAc (b), and $TBAH_2PO_4$ (c) in acetonitrile at 25 °C.