SUPPORTING INFORMATION

Three modes of interactions between anions and phenolic macrocycles: a comparative study

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1. General information

All solvents and chemicals used were purchased from Sigma Aldrich, TCI Europe N.V., Roth and Euriso-top, were of reagent grade and were used without further purification.

^{1}H NMR spectra were recorded at 303 K on Bruker 400 MHz and Varian 600 MHz instruments with residual solvent signal as internal standard.

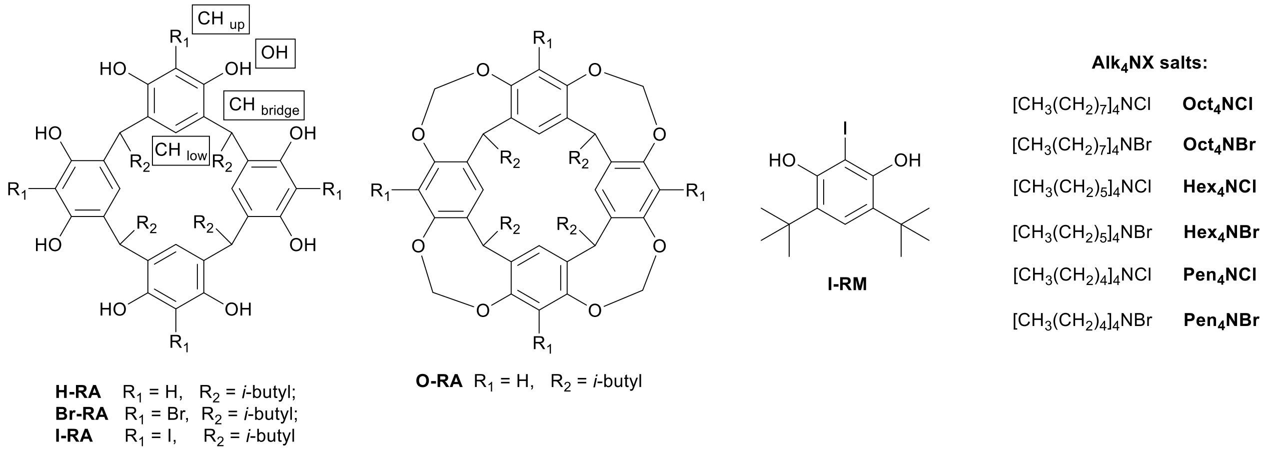
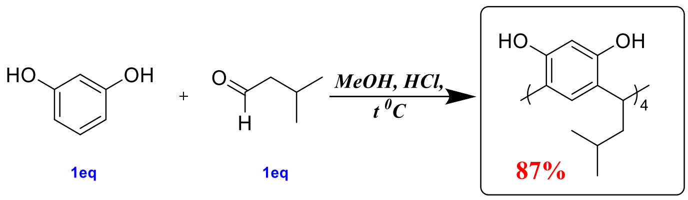


Figure S1. Chemical structures of the macrocycles (**M**), reference compounds, and the salts used in this work and notation of NMR signals.

2. Synthesis of resorcin[4]arenes

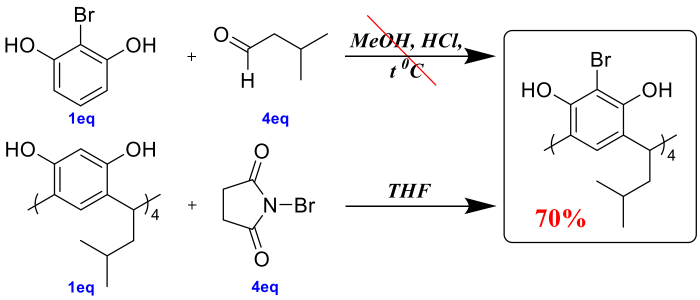
Synthesis of 2,8,14,20–tetraisobutylresorcin[4]arene (H-RA)



Resorcin[4]arene **H-RA** was obtained by acid-catalyzed condensation of resorcinol with isovaleraldehyde in a simple one-pot reaction by the literature procedure.[1]

Analytical data in agreement with literature data.[1]

Synthesis of 1,3,5,7-tetrabromo- 2,8,14,20–tetraisobutylresorcin[4]arene (Br-RA)

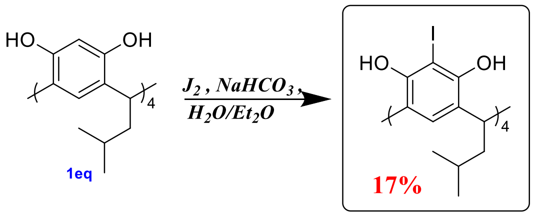


Resorcin[4]arene **Br-RA** was obtained by the slightly modified literature procedure.[2] 2,8,14,20–Tetraisobutylresorcin[4]arene **H-RA** (1.0 g, 1.4 mmol, 1.0 eq.) was dissolved in tetrahydrofuran (20 mL) to give a colorless solution. Subsequently, *N*-bromosuccinimide (1.0 g, 5.6 mmol, 4.0 eq.) was added portion wise over 15 minutes at room temperature. The reaction mixture was stirred under argon atmosphere overnight. Afterwards, the solvent was removed under reduced pressure (40 mbar) at 40 °C to give a light yellow solid. Then methanol (50 mL) was added and the mixture was heated to 85 °C for 40 minutes, followed by hot filtration. The resulting solid was washed with methanol (25 mL) and then dried under vacuum (20 mbar) at 40 °C to give **Br-RA** (1.1 g, 1.0 mmol, 70%) as a colourless powder.

Analytical data in agreement with literature data.[2]

^{1}H-NMR (400 MHz, DMSO-d6, 303 K) δ [ppm] = 9.12 (s, 8H, 4 × OH), 7.34 (s, 4H, 4 × CH_{arom}), 4.48 (t, J = 7.5 Hz, 4H, 4 × CH_{meth}), 2.05 (t, J = 6.7 Hz, 8H, 4 × CH_2), 1.40-1.25 (m, 4H, 4 × CH), 0.90 (s, 12H, 4 × CH_3) 0.89 (s, 12H, 4 × CH_3).

Synthesis of 1,3,5,7-Tetraiodo- 2,8,14,20–tetraisobutylresorcin[4]arene (I-RA)

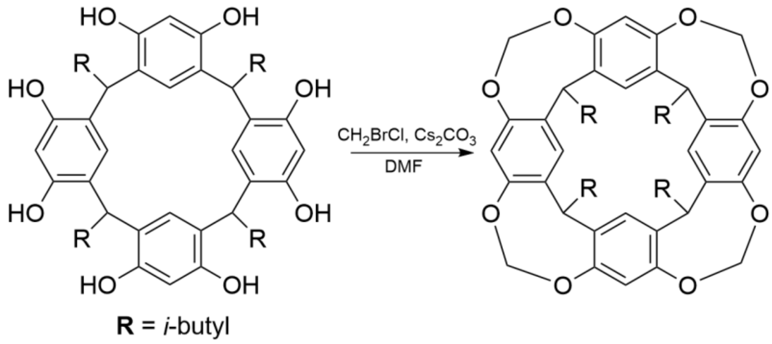


Resorcin[4]arene **Br-RA** was obtained according to the literature procedure.[3] To a solution of 2,8,14,20–tetraisobutylresorcin[4]arene **H-RA** (3.0 g, 4.2 mmol, 1.0 eq.) in water and ether (1 : 1), sodium hydrogen carbonate (1.5 g, 17.7 mmol, 4.0 eq.) and iodine (4.5 g, 17.7 mmol, 4.0 eq.) were added at room temperature under an argon atmosphere. The solution was stirred for 24 h at room temperature. The precipitate was filtered off and the solid residue was washed with cold acetone and dichloromethane several times to afford desired product **I-RA** as a yellow solid (0.9 g, 17%).

Analytical data in agreement with literature data.[3]

^{1}H-NMR (400 MHz, DMSO-d6, 303 K) δ [ppm] = 9.36 (s, 8H, 4 × OH), 7.48 (s, 4H, 4 × CH_{arom}), 4.43 (t, J = 7.5 Hz, 4H, 4 × CH_{meth}), 2.16 (t, J = 6.7 Hz, 8H, 4 × CH_2), 1.37-1.29 (m, 4H, 4 × CH), 0.91 (s, 12H, 4 × CH_3) 0.90 (s, 12H, 4 × CH_3).

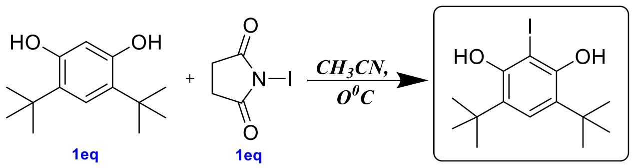
Synthesis of tetraisobutylresorcin[4]arene (O-RA)



Resorcin[4]arene **O-RA** was obtained accordingly literature procedure.[4]

Analytical data in agreement with literature data.[4]

Synthesis of 4,6-di(tert-butyl)-2-iodoresorcinol



2-Iodoresorcinol **I-RM** was obtained according to the literature procedure. [5]

To a mixture of resorcinol (1.0 g, 4.5 mmol, 1.0 eq.) dissolved in MeCN (20mL) was added N-iodosuccinimide (1.03 g, 4.5 mmol, 1.0 eq.) at 0 °C. After stirring for 10 min at the same temperature, to the mixture was added an aqueous saturated solution of sodium thiosulfate (10 mL). The mixture was extracted with EtOAc (10 mL ×3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 30g, n-hexane/EtOAc = 1/1) to give 4,6-di(tert-butyl)-2-iodoresorcinol (1.0 g, 2.8 mmol, 64%) as a colourless solid.

Analytical data in agreement with literature data.[5]

^{1}H-NMR (400 MHz, $CDCl_3$, 303 K) δ [ppm] = 7.18 (s, 1H, aromatic), 5.14 (s, 2H, OH), 1.35 (s, 18H, CH_3×6);**^{13}C NMR** ($CDCl_3$, 126 MHz) δ 29.7 (6C), 35.0 (2C), 85.8 (1C), 125.6 (1C), 127.5 (2C), 150.6 (2C).

Table 1. Solubility of resorcin[4]arenes

N	Solvent	I-RA	Br-RA
1	$CHCl_3$	insoluble	insoluble
2	CH_2Cl_2	insoluble	insoluble
3	Ethyl acetate	insoluble	cloudy solution
4	Benzene	cloudy solution	cloudy solution
5	Acetonitrile	insoluble	insoluble
6	Tetrahydrofuran	**soluble**	**soluble**
7	Methanol	**soluble**	**soluble**
8	Acetone	**soluble**	**soluble**
9	1,4-Dioxane	**soluble**	cloudy solution
10	1-Propanol	-	insoluble
11	Dimethylsulfoxide	**soluble**	**soluble**

3. General procedures for titrations

^{1}H NMR titrations

To the solution of **macrocycle** (C = 0.0067 M, 0.0033 mmol) in THF-d8 (0.5 ml) a solution containing **Alk$_4$NX** (C = 0.1 M, 0.1 mmol) and the **macrocycle** (C = 0.0067 M, 0.0067 mmol) in THF-d8 (1 ml) was added. ^{1}H NMR spectra were recorded at 303 K using Bruker 400 MHz.

^{1}H NMR competitive titrations

To the solution of **Br-RA** (C = 0.0067 M, 0.0033 mmol) and **H-RA** or **O-RA** (C = 0.0067 M, 0.0033 mmol) in THF-d8 (0.5 ml) a solution containing **Alk$_4$NX** (C = 0.1 M, 0.1 mmol) and the **macrocycle** (C = 0.0067 M, 0.0134 mmol) in THF-d8 (1 ml) was added. ^{1}H NMR spectra were recorded at 303 K using Bruker 400 MHz.

DOSY titrations

To the solution of **macrocycle** (C = 0.0025 M, 0.00125 mmol) in THF-d8 (0.5 ml) a solution containing **Alk$_4$NX** (C = 0.0656 M, 0.0656 mmol) and the **macrocycle** (C = 0.0025 M, 0.0025 mmol) in THF-d8 (1 ml) was added. ^{1}H NMR spectra and DOSY measurement were recorded at 303 K using Bruker 600 MHz.

^{1}H DOSY experiments were performed on a Varian VNMRS-600 spectrometer at 298 K equipped with a 5 mm PFG AutoXID (^{1}H/X=^{15}N-^{31}P) probe. DOSY experiments were run with the DPFGDSTE (with convection compensation) pulse sequence for measurements in THF-d8 solutions. The gradient strengths were incremented as a square dependence in the range from 6 to 55 G/cm. 16 transients (with interleave option) were recorded for each increment with 3.2 s acquisition time and 1 s relaxation delay (overall experiment time *ca.* 18 - 20 min). The duration of magnetic field gradients (δ) was 1.5 – 2 ms, whereas a diffusion delay (Δ) was chosen as 50 – 150 ms. Other parameters include the following: a sweep width of 12 000 Hz, 32 K data points. The data were processed using Varian DOSY software. The hydrodynamic diameters d_H ($d_H = 2r_H$) of the species were calculated using the Einstein-Stokes equation from D_{min}

$$\boldsymbol{r_H = \frac{k_b T}{6\pi\eta D}}$$

$\boldsymbol{k_b - Boltzmann\ constant}$

$\boldsymbol{T - temperature}$

$\boldsymbol{\eta - viscosity\ coefficient}$

$\boldsymbol{D - diffusion\ coeffcient}$

4. Titrations of I-RM

4.1. Titration of I-RM with Pen_4NCl in THF

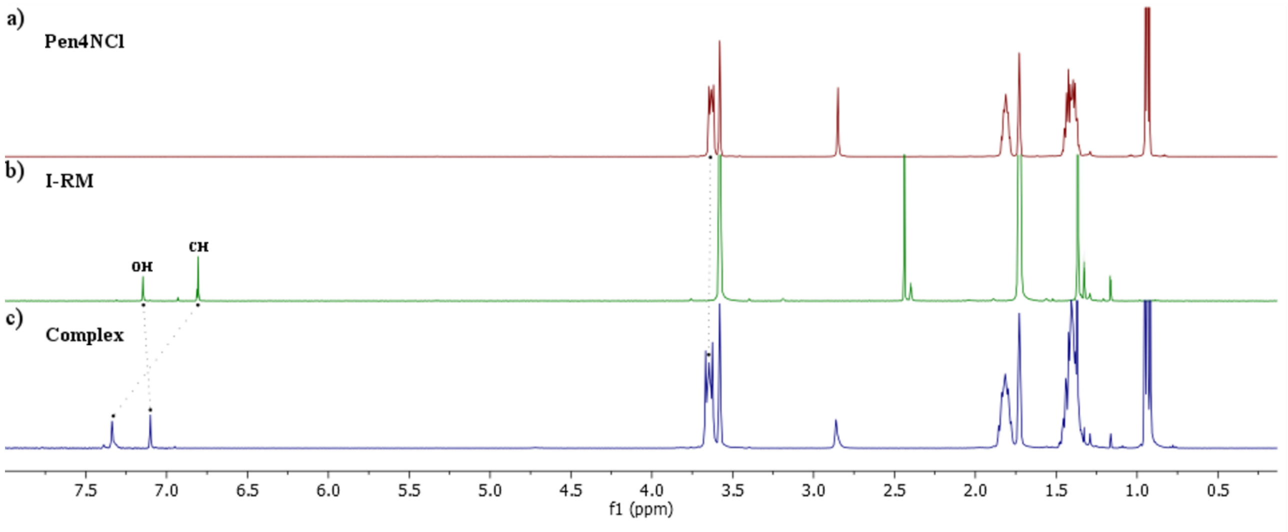


Figure S2. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **I-RM**; (c) complex of **I-RM** and **Pen_4NCl** (400 MHz, 303 K, THF-d8).

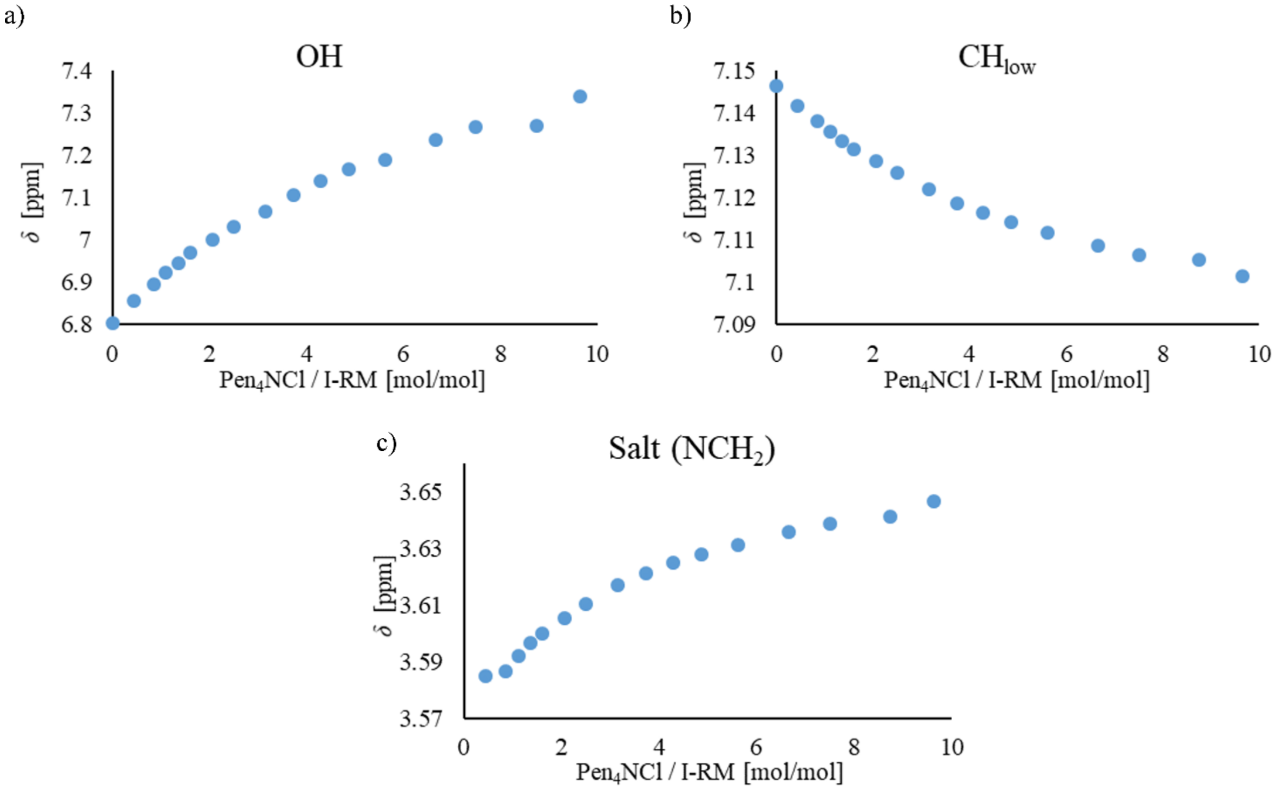


Figure S3. [1]H NMR titration curves for titration of **I-RM** with **Pen_4NCl**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) NCH_2 from salt (400 MHz, 303 K, THF-d8).

5. Titrations of Br-RA

5.1. Titration of Br-RA with Oct_4NCl in THF

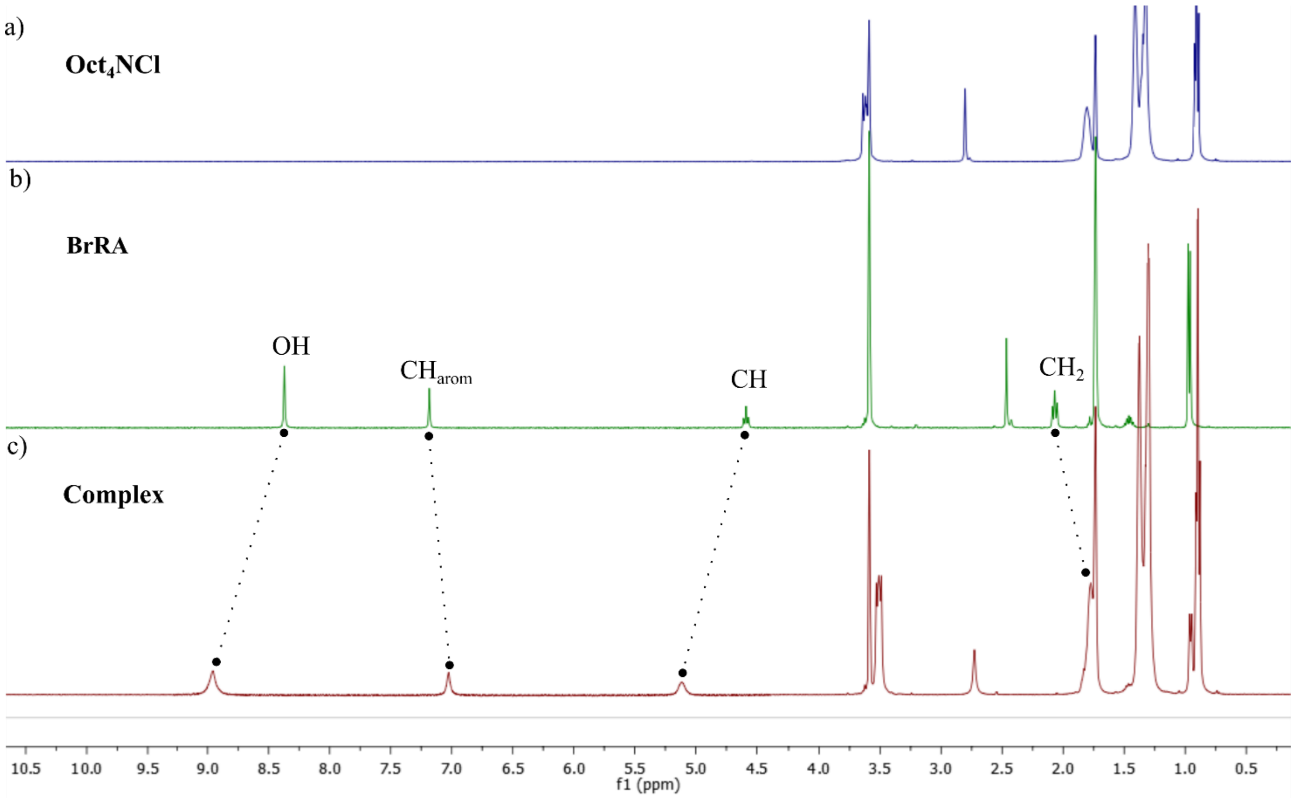
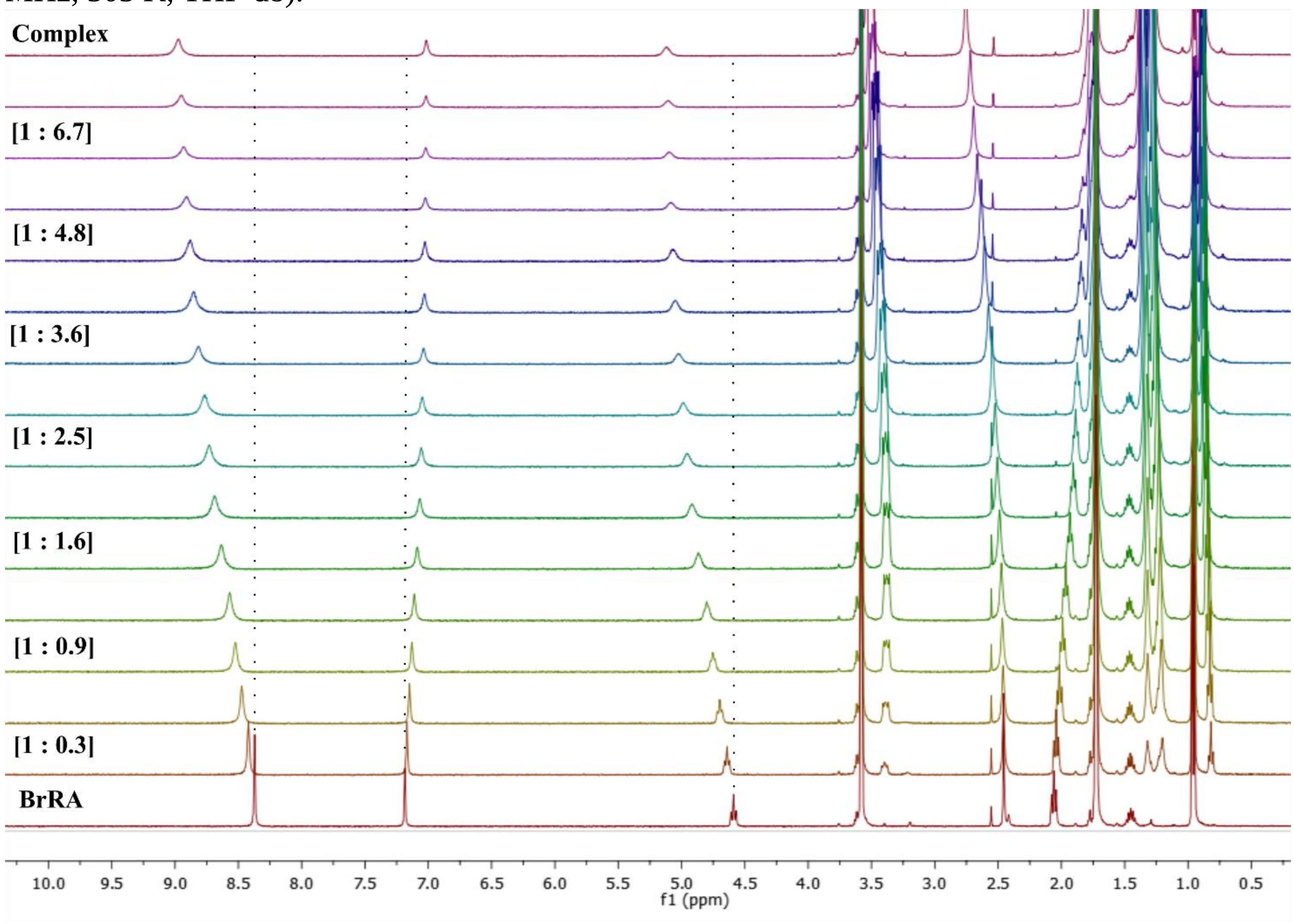


Figure S4. [1]H NMR spectra of (a) **Oct_4NCl**; (b) **Br-RA**; (c) complex of **Br-RA** and **Oct_4NCl** (400 MHz, 303 K, THF-d8).



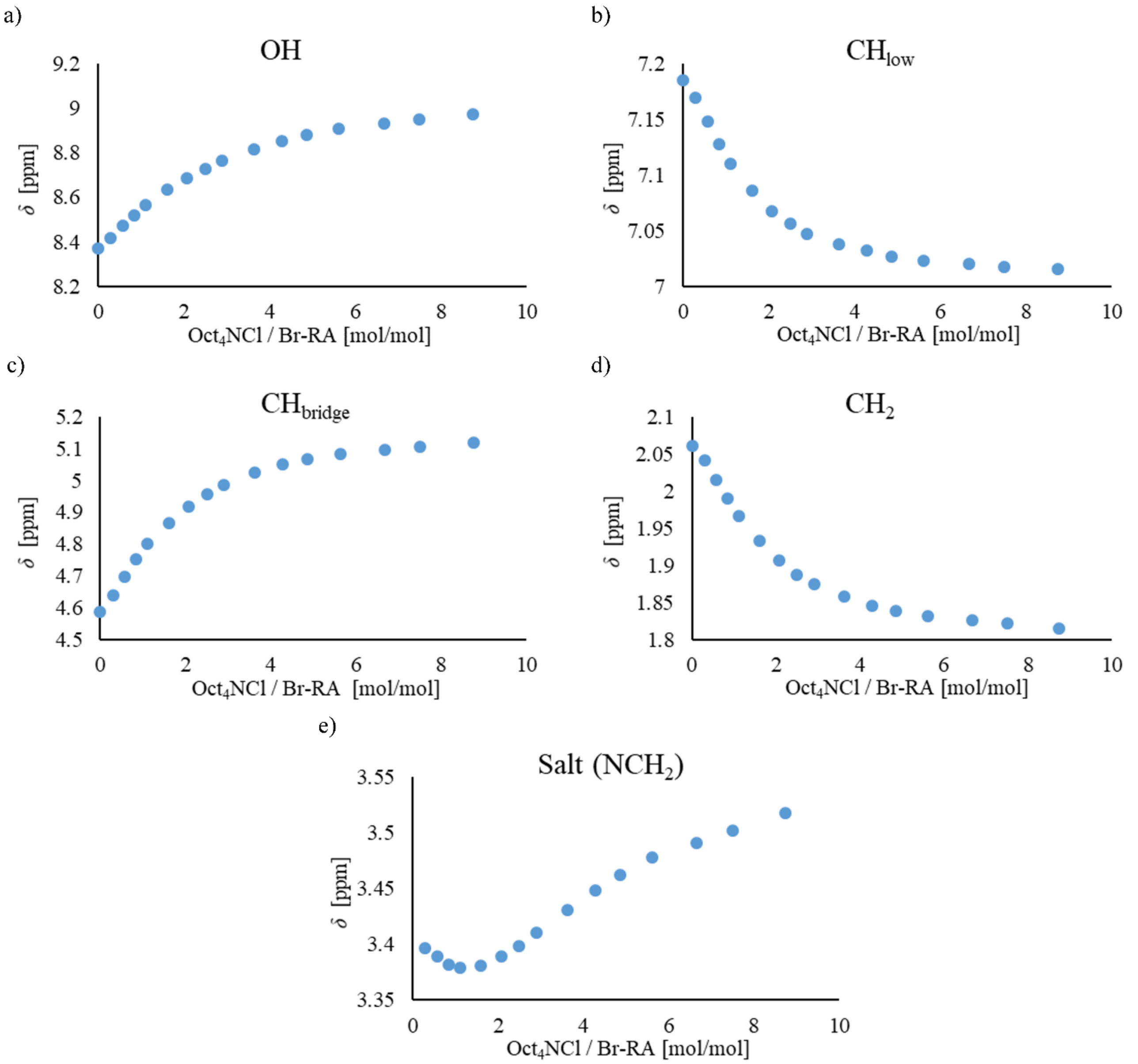


Figure S5. ^{1}H NMR titration curves for titration of **Br-RA** with **Oct4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

5.2. Titration of Br-RA with Oct_4NCl in acetone

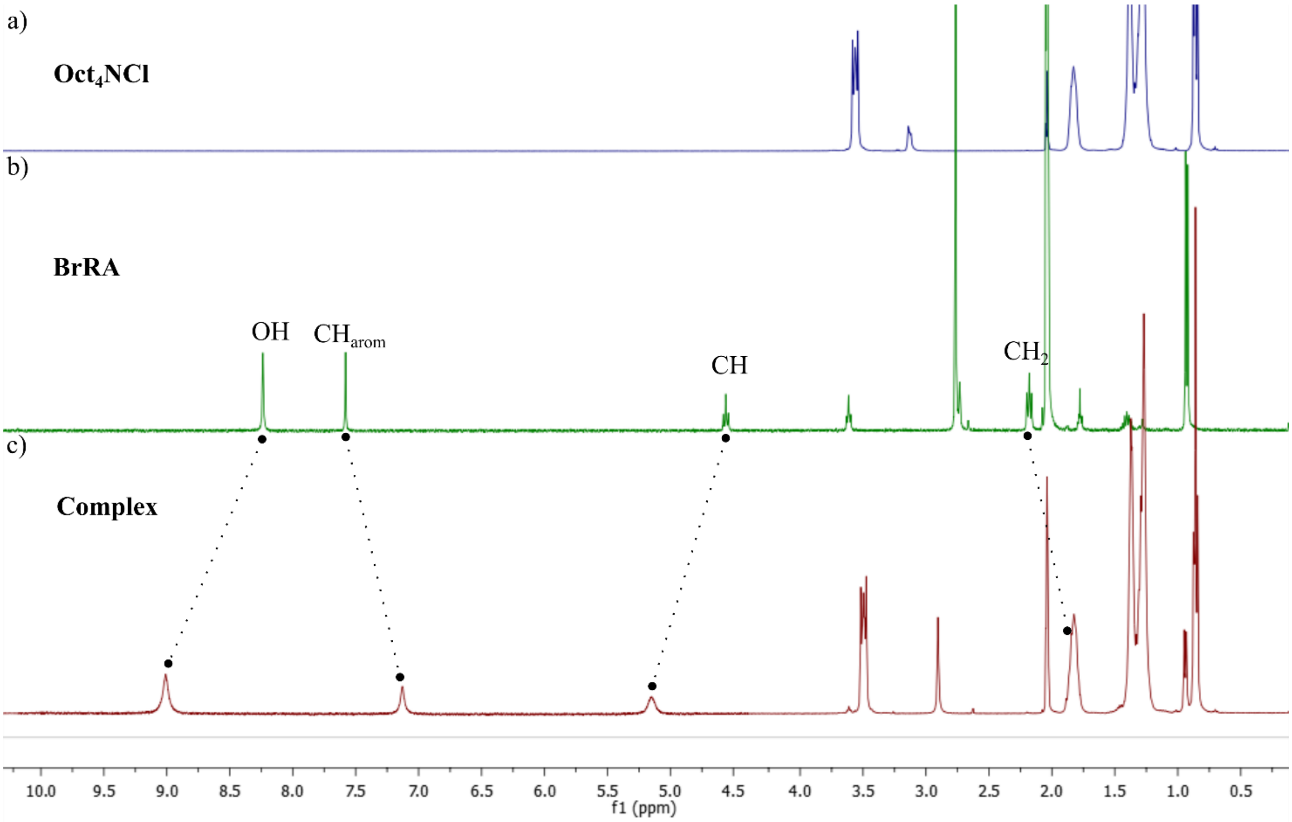
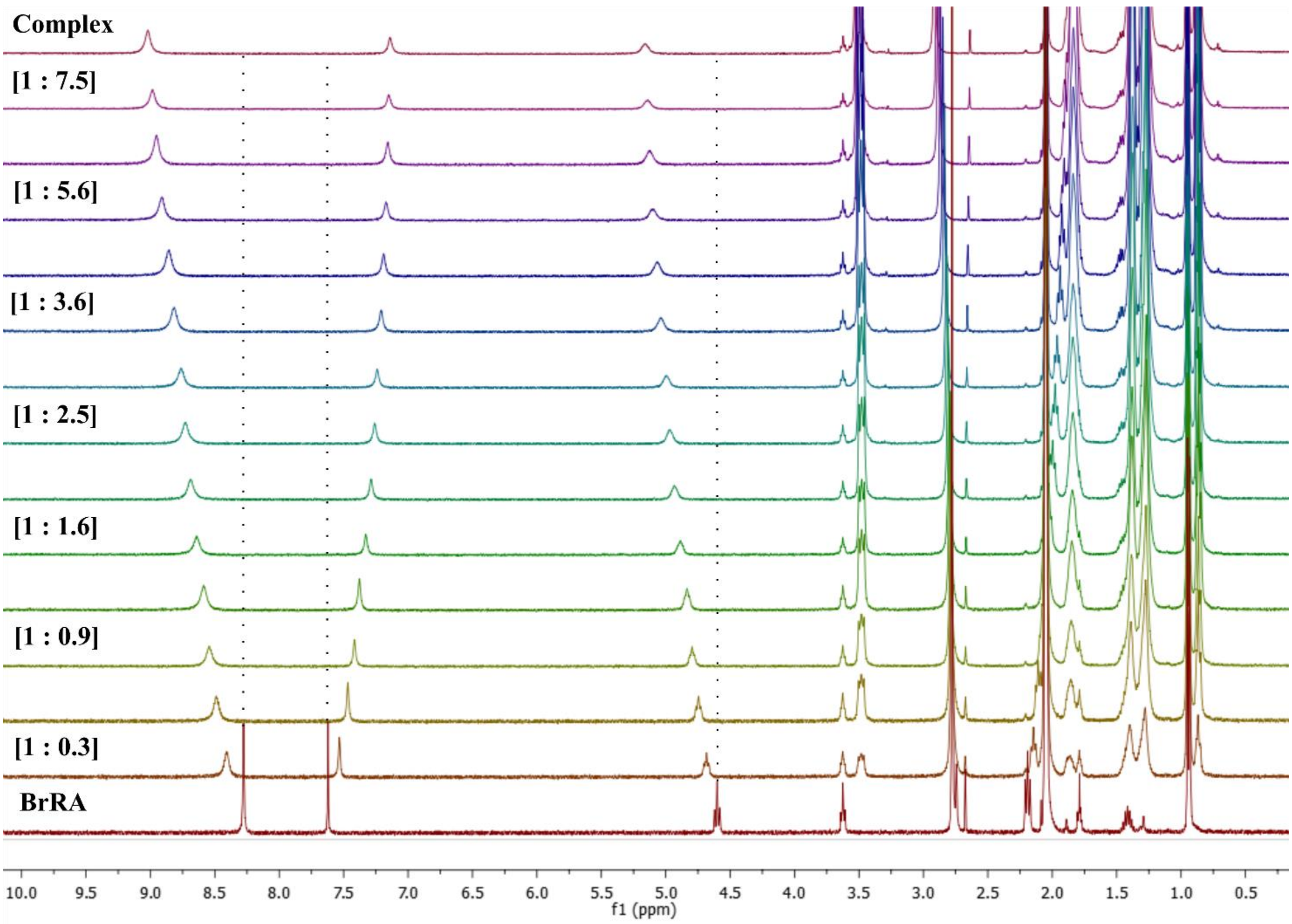


Figure S6. [1]H NMR spectra of (a) **Oct_4NCl**; (b) **Br-RA**;(c) complex of **Br-RA** and **Oct_4NCl** (400 MHz, 303 K, Acetone-d6).



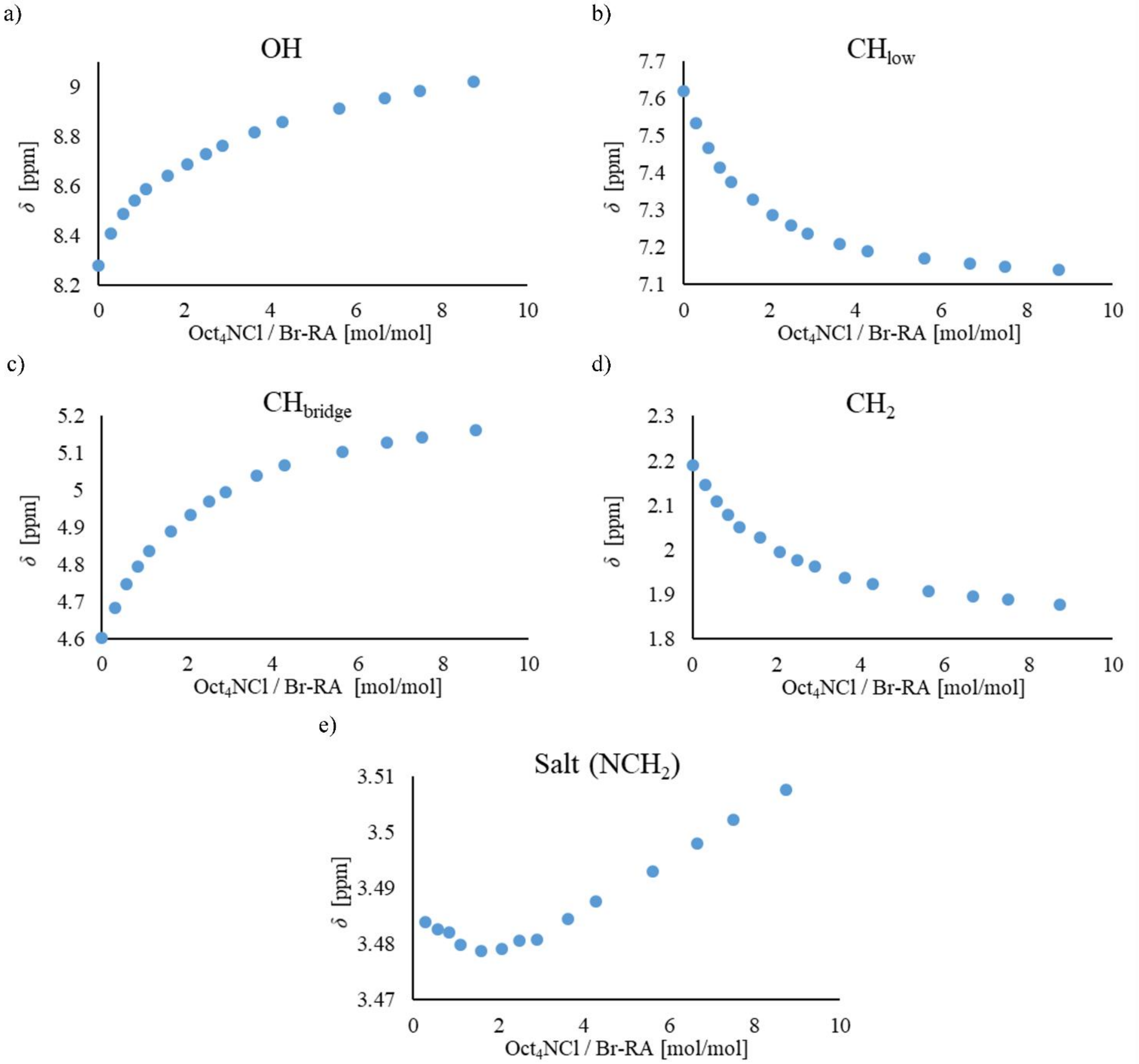


Figure S7. ^{1}H NMR titration curves for titration of **Br-RA** with **Oct_4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

5.3. Titration of Br-RA with Hex_4NCl in THF

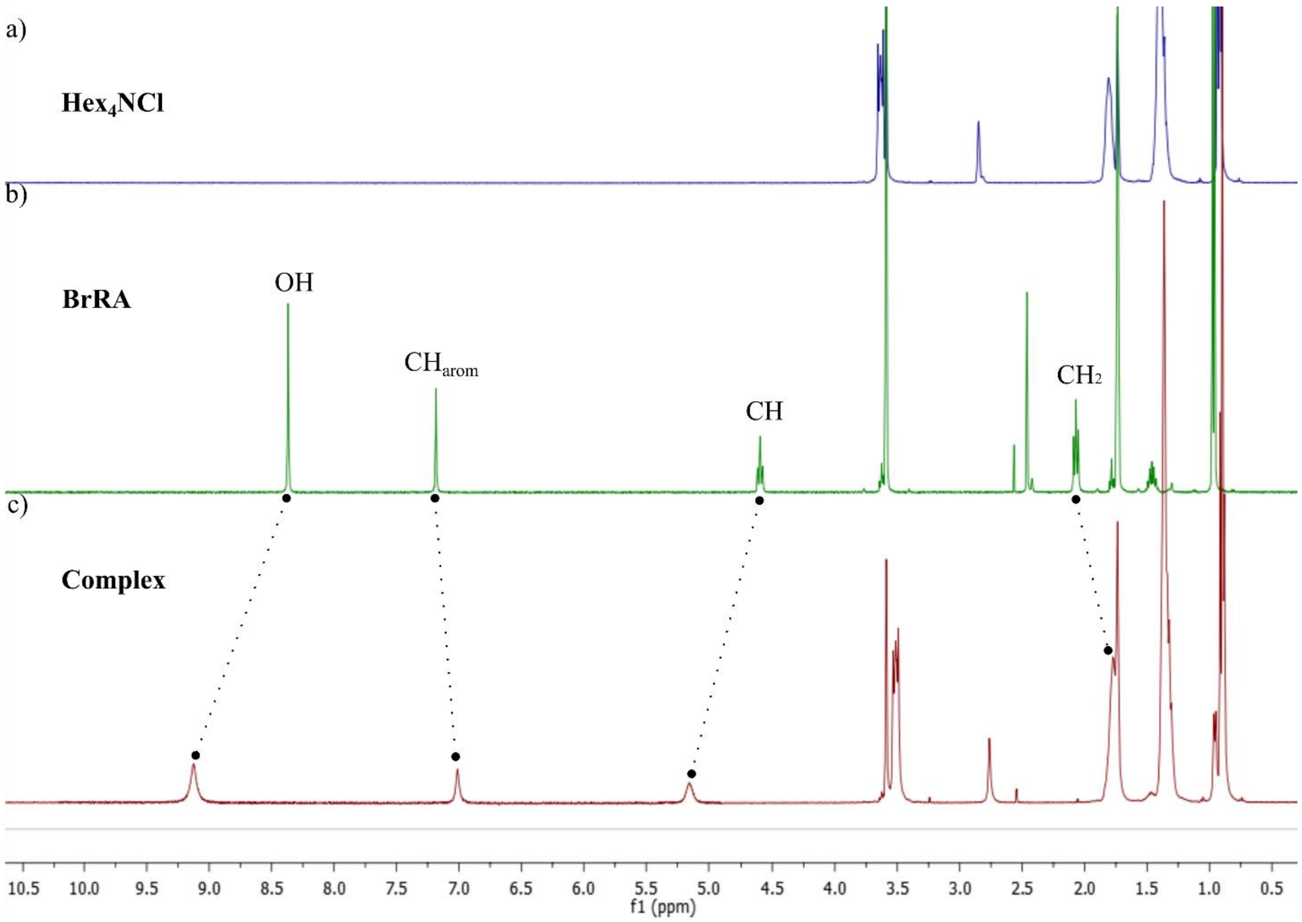
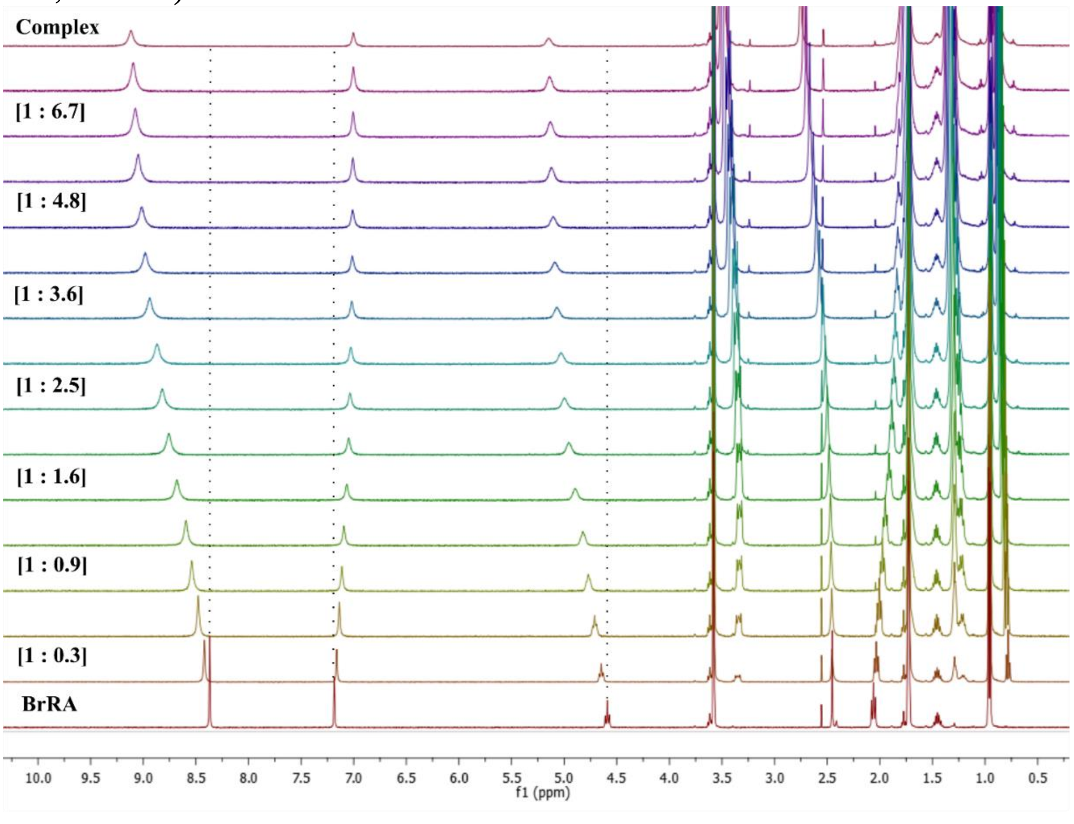


Figure S8. ^{1}H NMR spectra of (a) **Hex_4NCl**; (b) **Br-RA**; (c) complex of **Br-RA** and **Hex_4NCl** (400 MHz, 303 K, THF-d8).



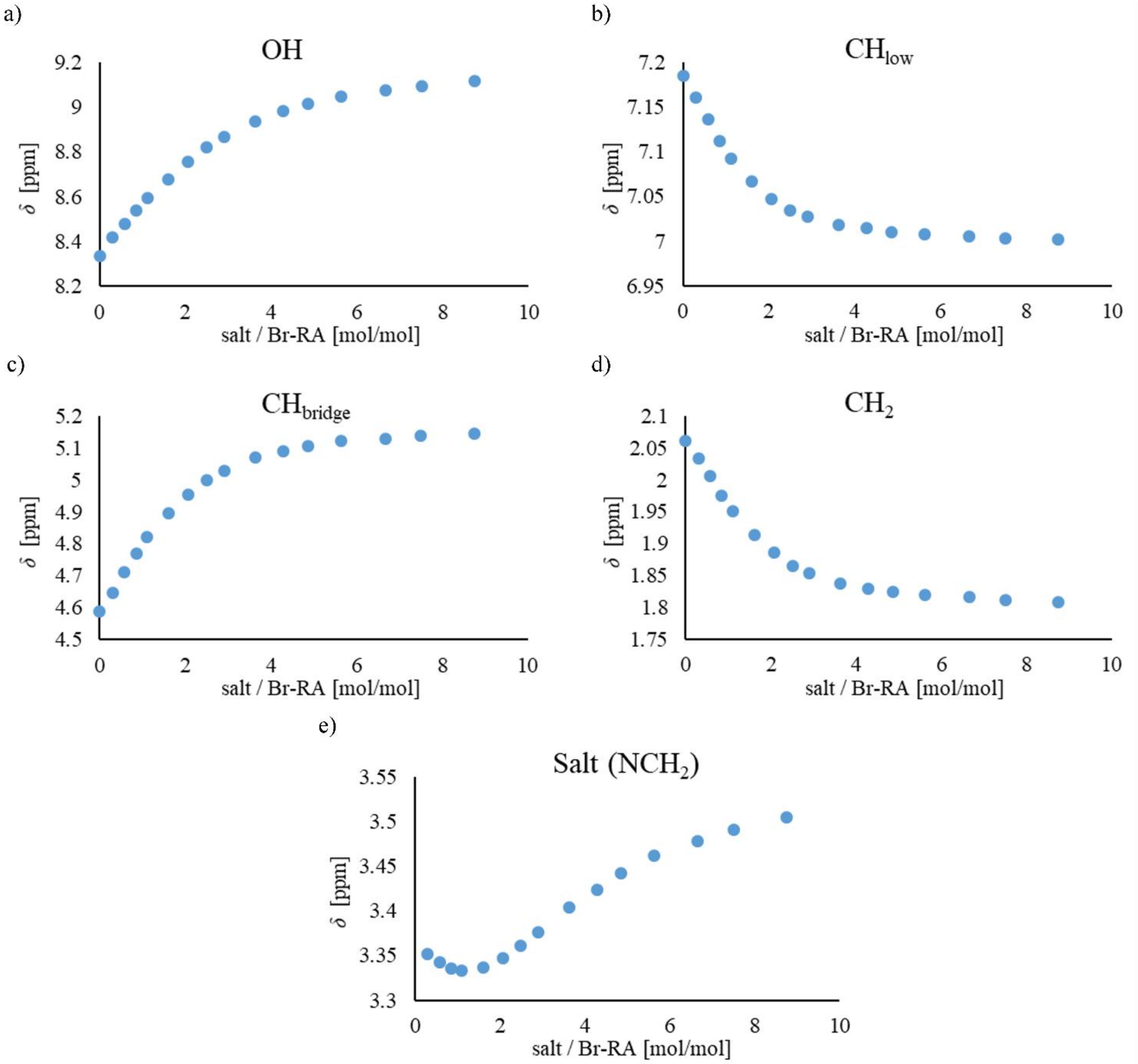


Figure S9. ^{1}H NMR titration curves for titration of **Br-RA** with **Hex_4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

5.4. Titration of Br-RA with Hex_4NCl in acetone

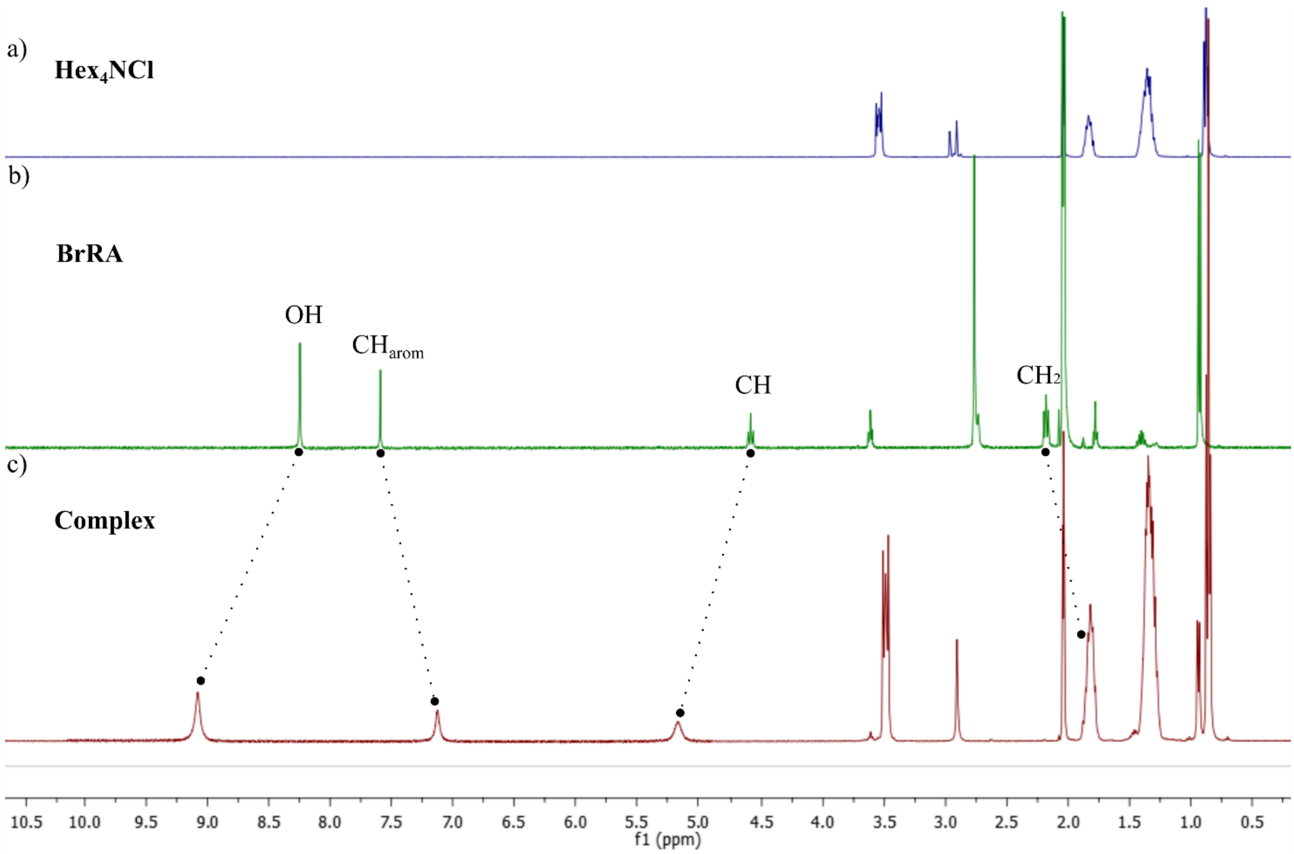
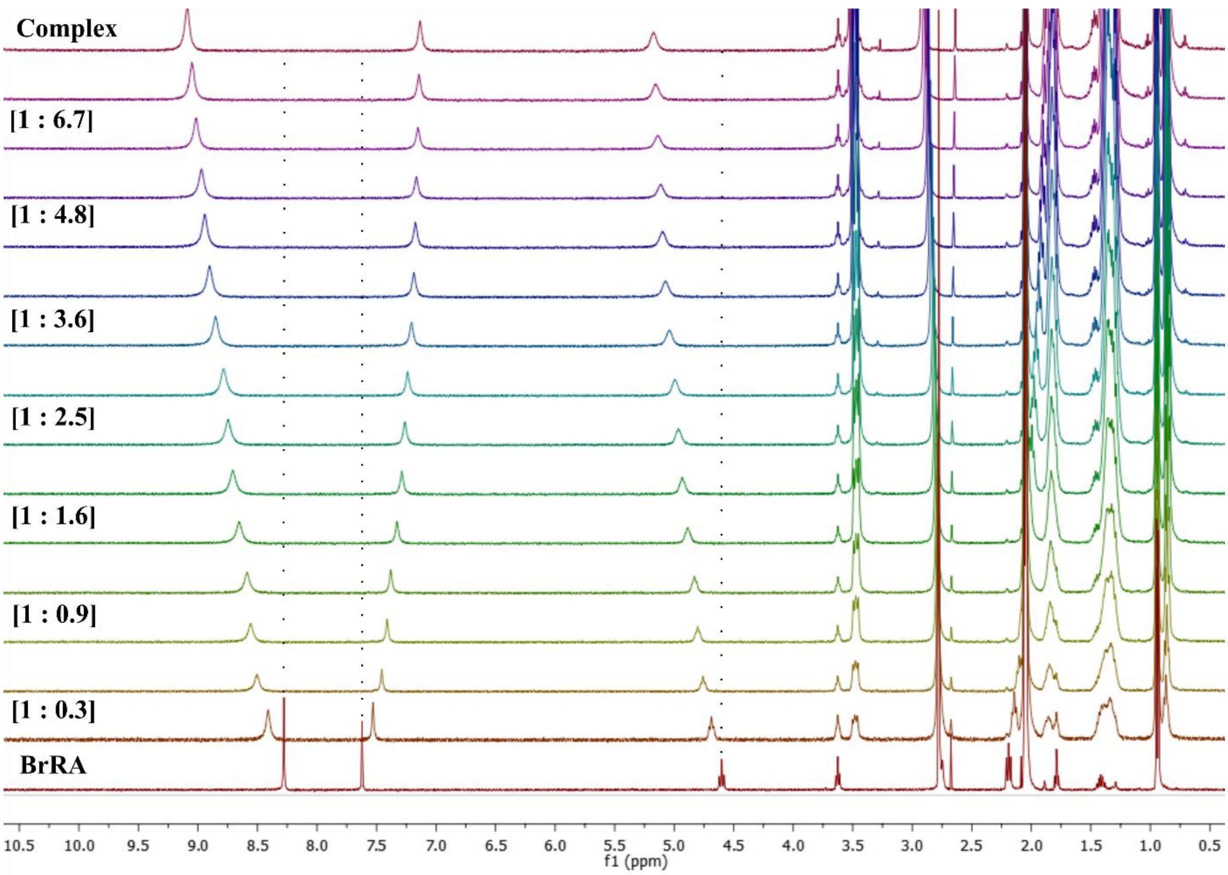


Figure S10. [1]H NMR spectra of (a) **Hex_4NCl**; (b) **Br-RA**; (c) complex of **Br-RA** and **Hex_4NCl** (400 MHz, 303 K, Acetone-d6).



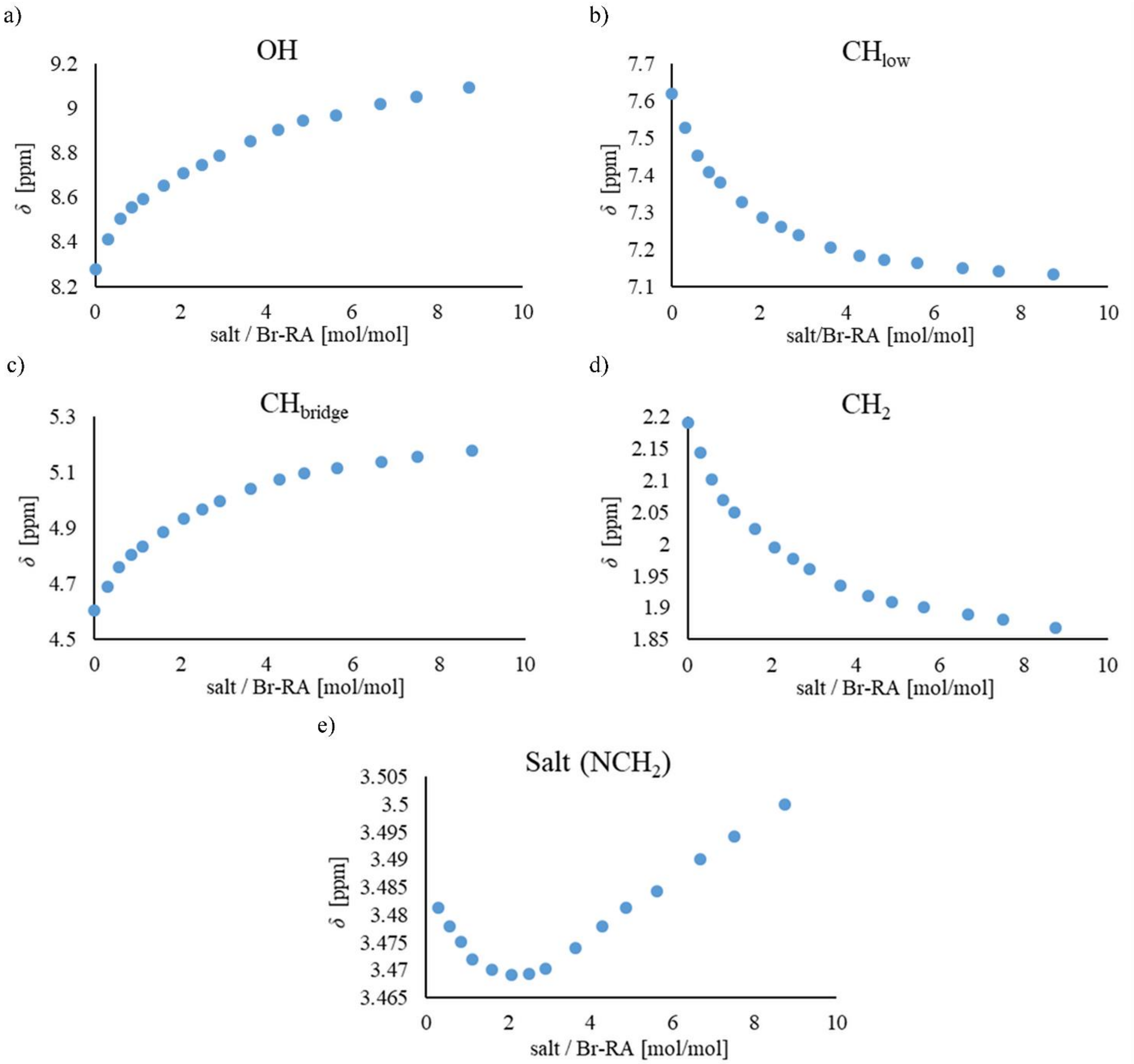


Figure S11. ^{1}H NMR titration curves for titration of **Br-RA** with **Hex$_4$NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

5.5. Titration of Br-RA with Pen_4NCl in THF

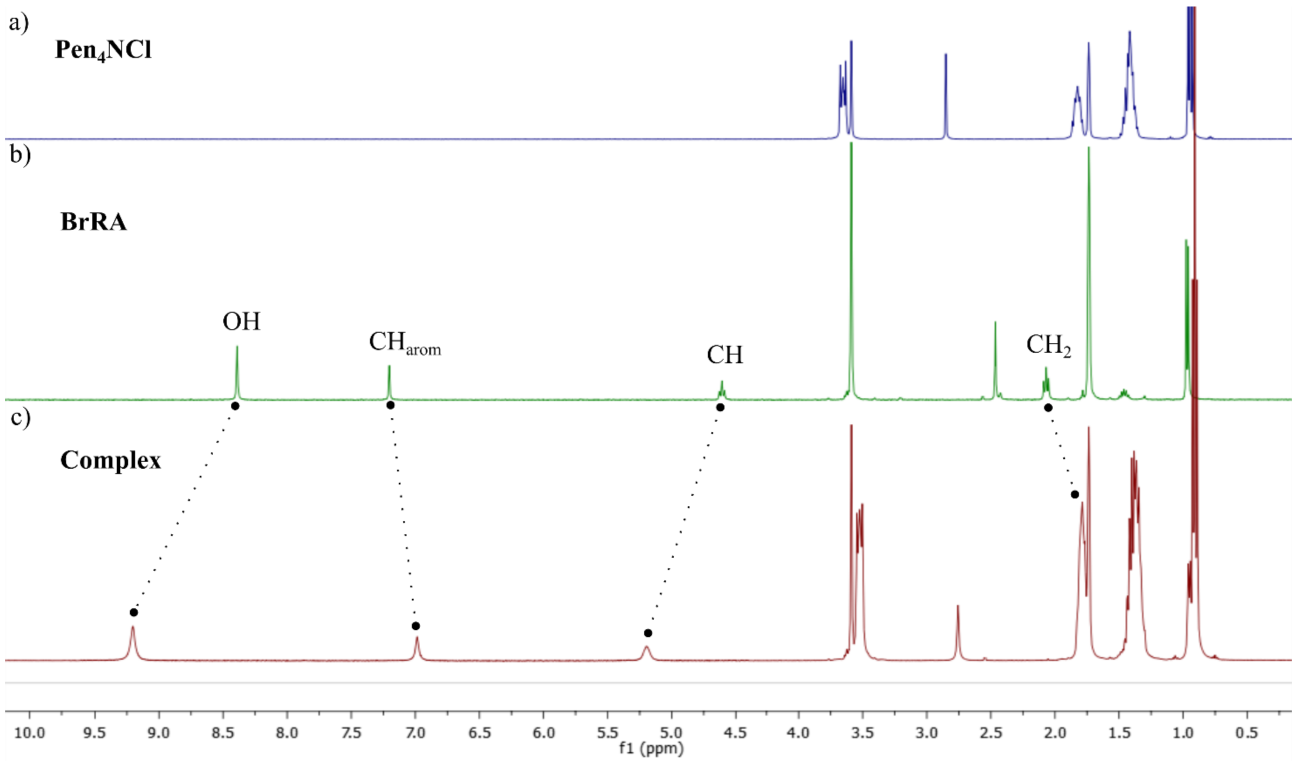
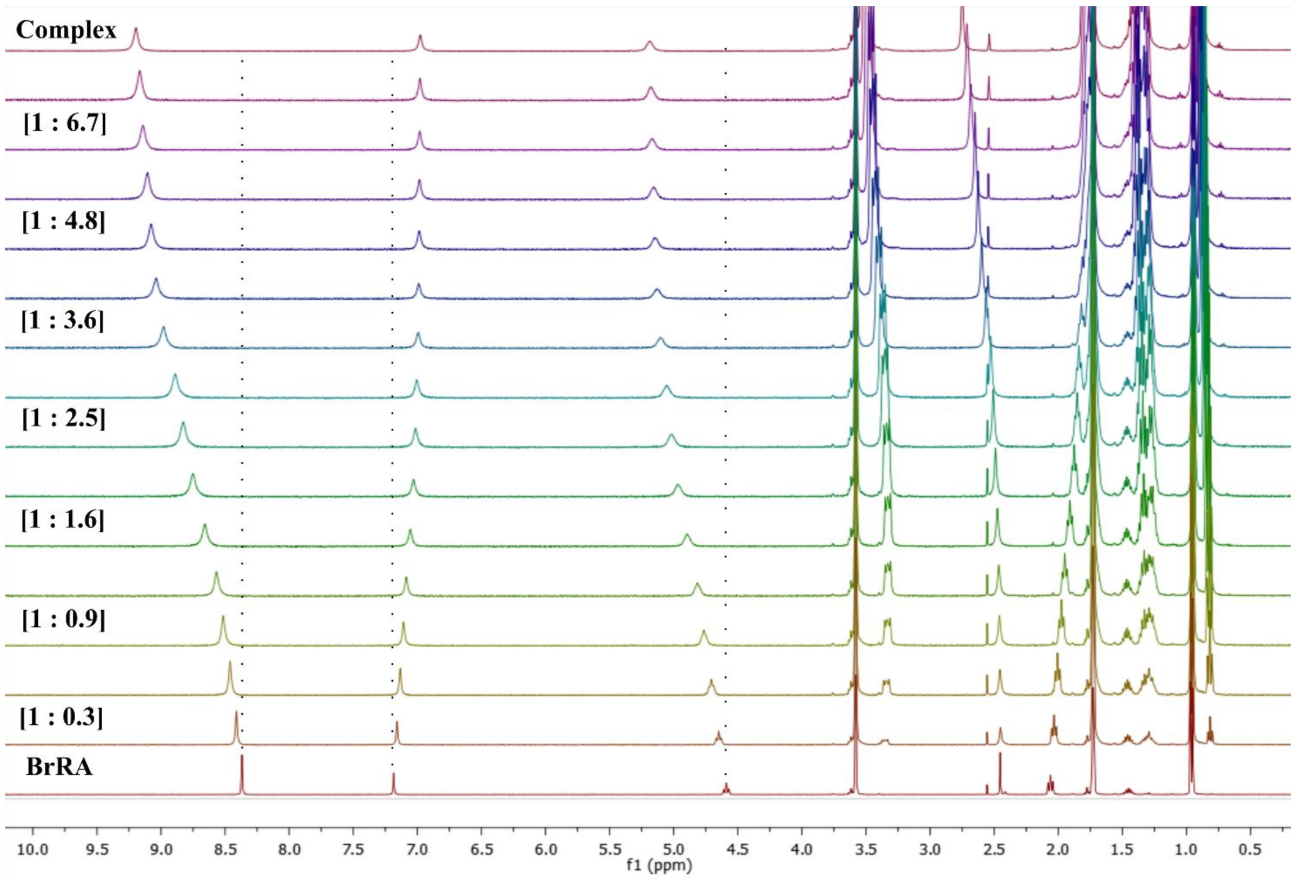


Figure S12. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **Br-RA**; (c) complex of **Br-RA** and **Pen_4NCl** (400 MHz, 303 K, THF-d8).



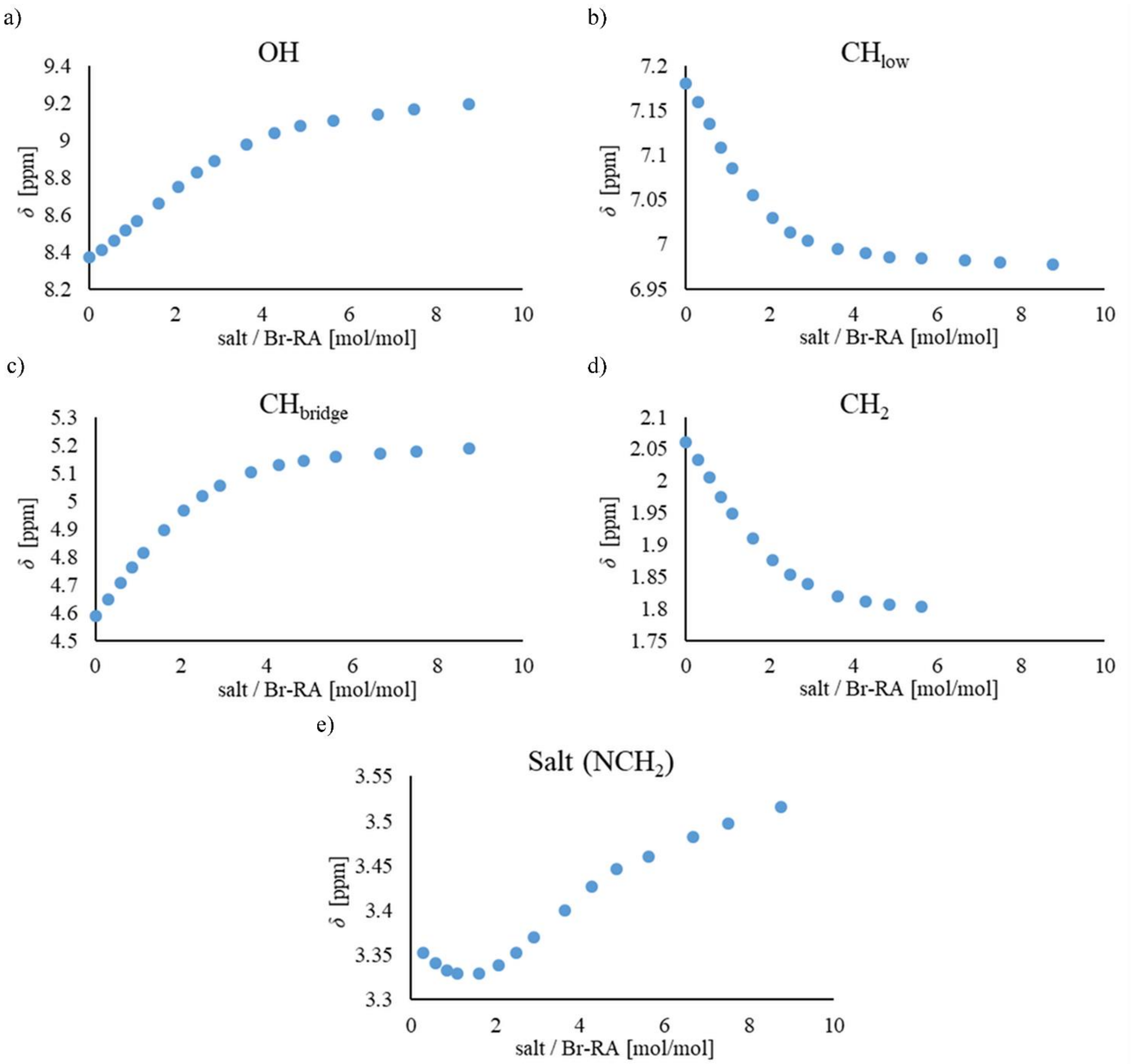
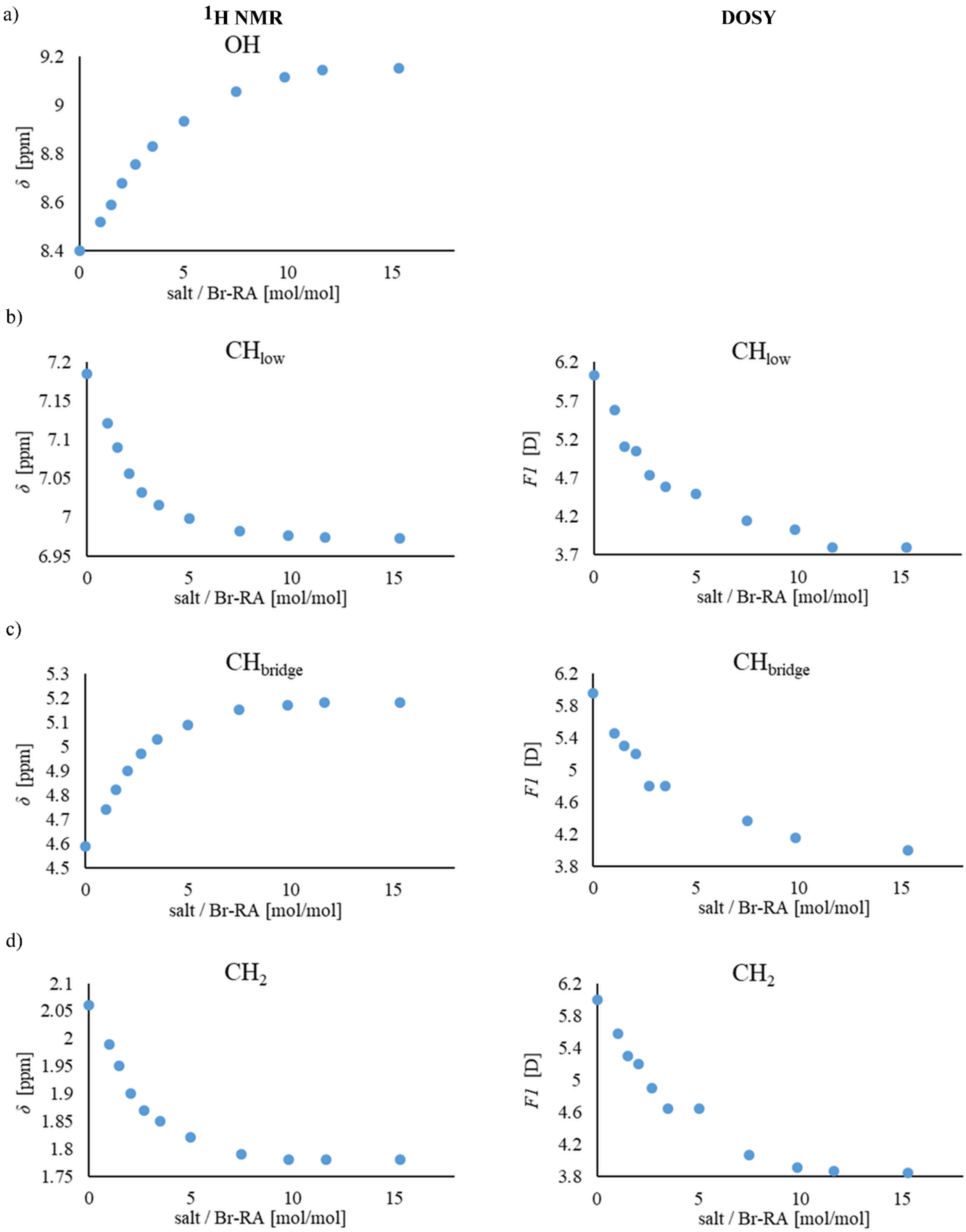


Figure S13. [1]H NMR titration curves for titration of **Br-RA** with **Pen$_4$NCl**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

5.6. DOSY titration curves for titration of Br-RA with Pen_4NCl in THF



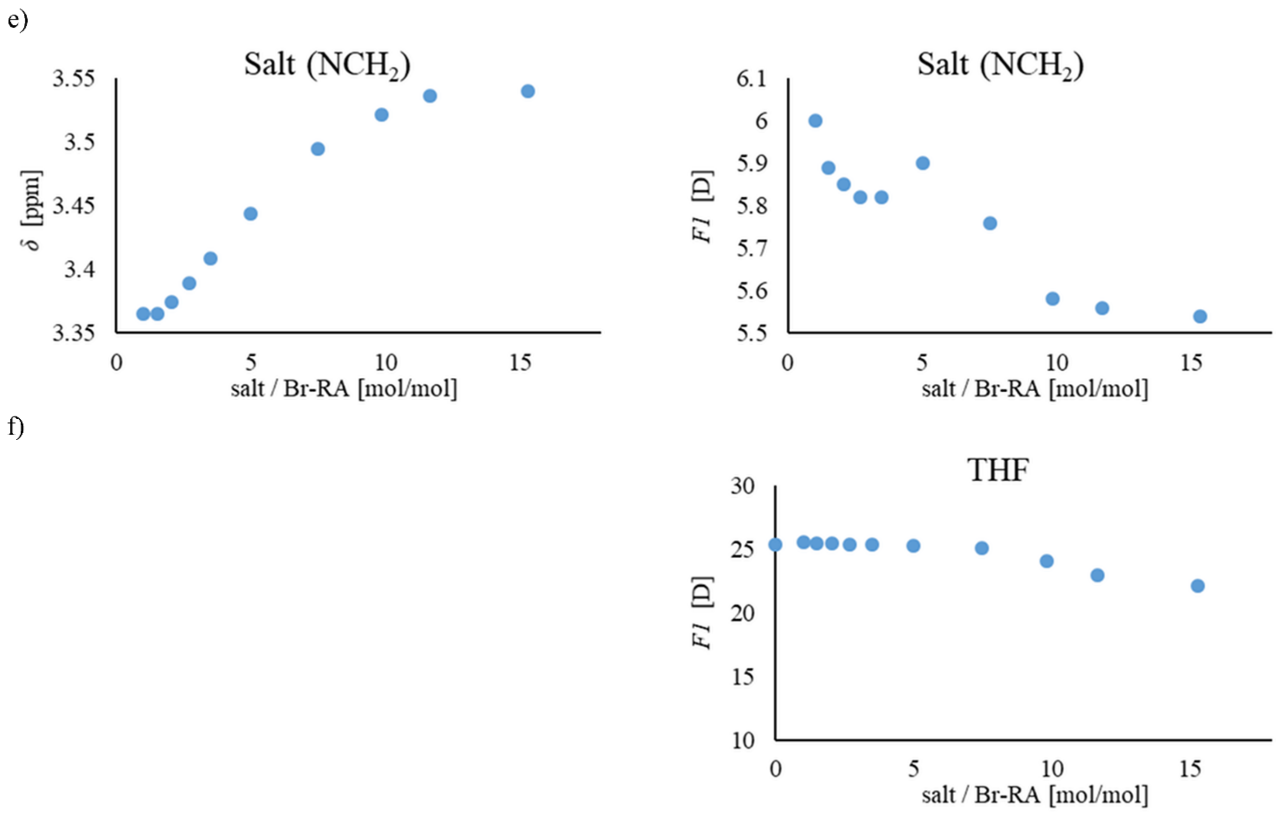
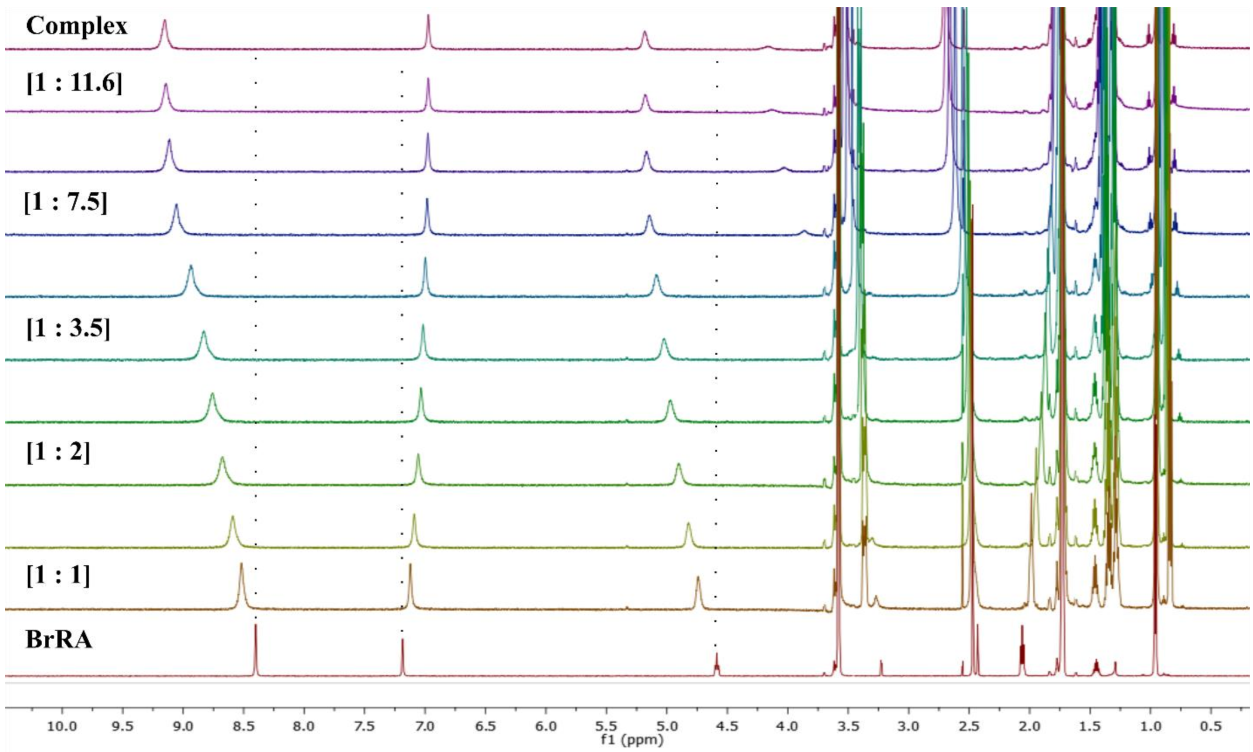


Figure S14. DOSY titration curves for titration of **Br-RA** with **Pen$_4$NCl**. ^{1}H NMR chemical shifts and diffusion coefficient changes for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt; (f) THF signal (600 MHz, 303 K, THF-d8).



5.7. Titration of Br-RA with Pen_4NCl in acetone

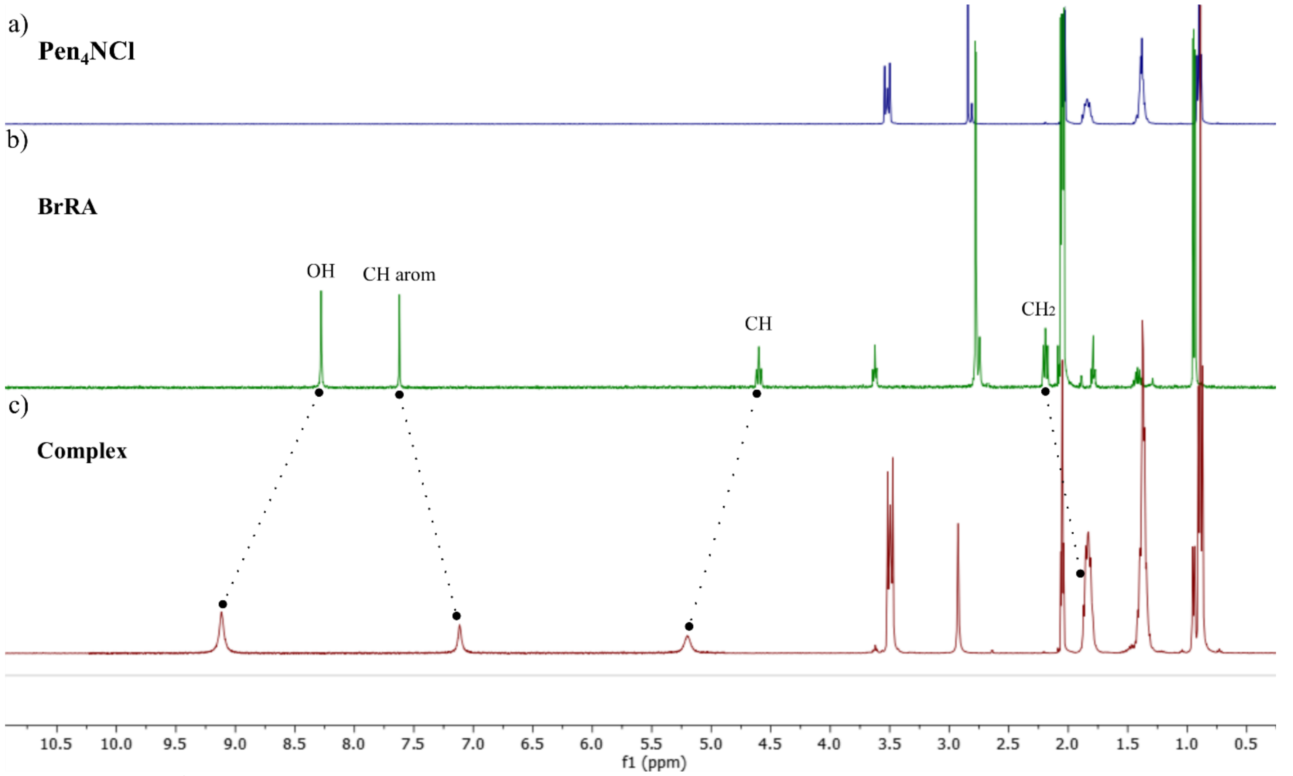
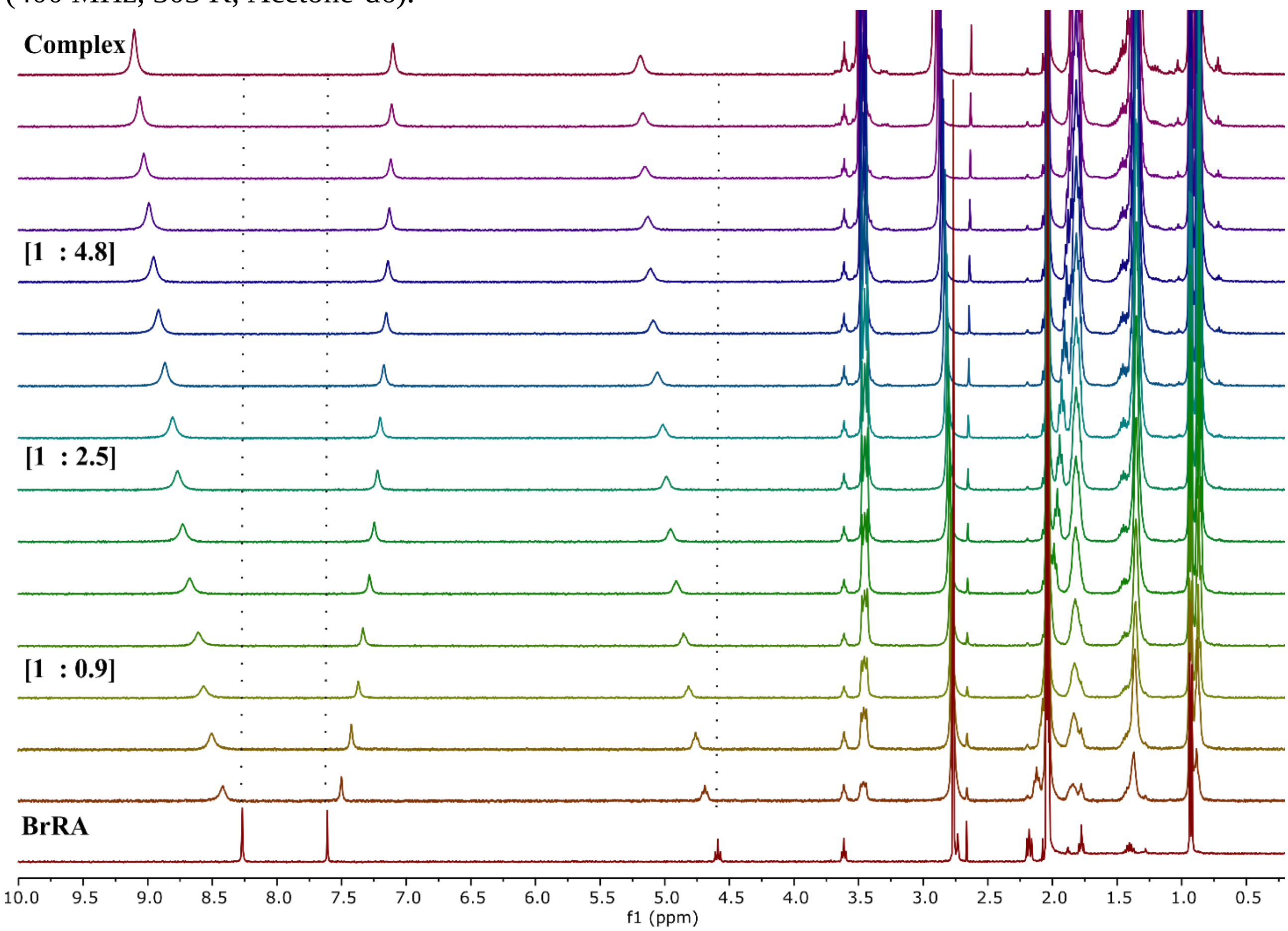


Figure S15. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **Br-RA**; (c) complex of **Br-RA** and **Pen_4NCl** (400 MHz, 303 K, Acetone-d6).



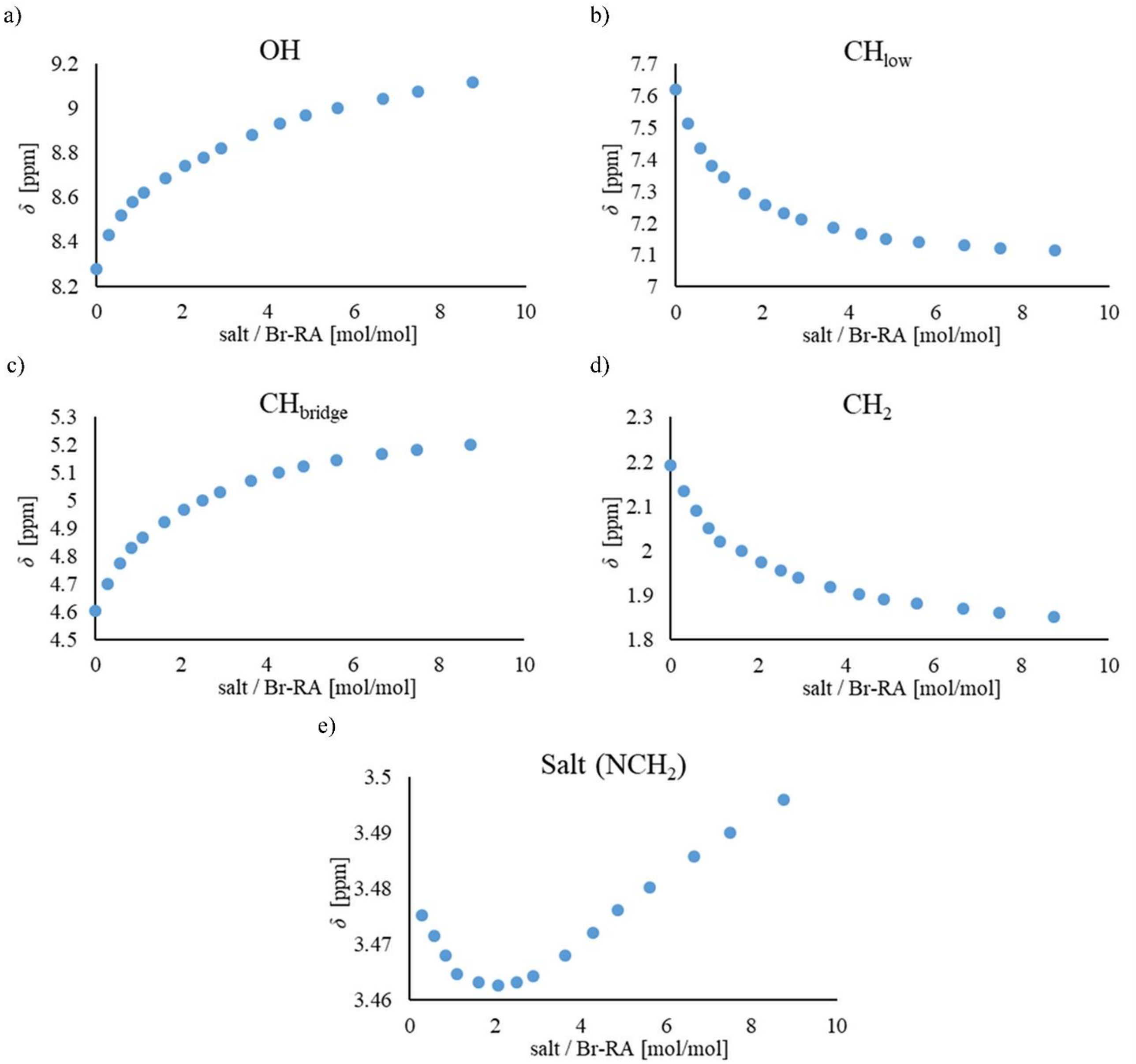


Figure S16. [1]H NMR titration curves for titration of **Br-RA** with **Pen_4NCl**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

5.8. Titration of Br-RA with Pen_4NBr in THF

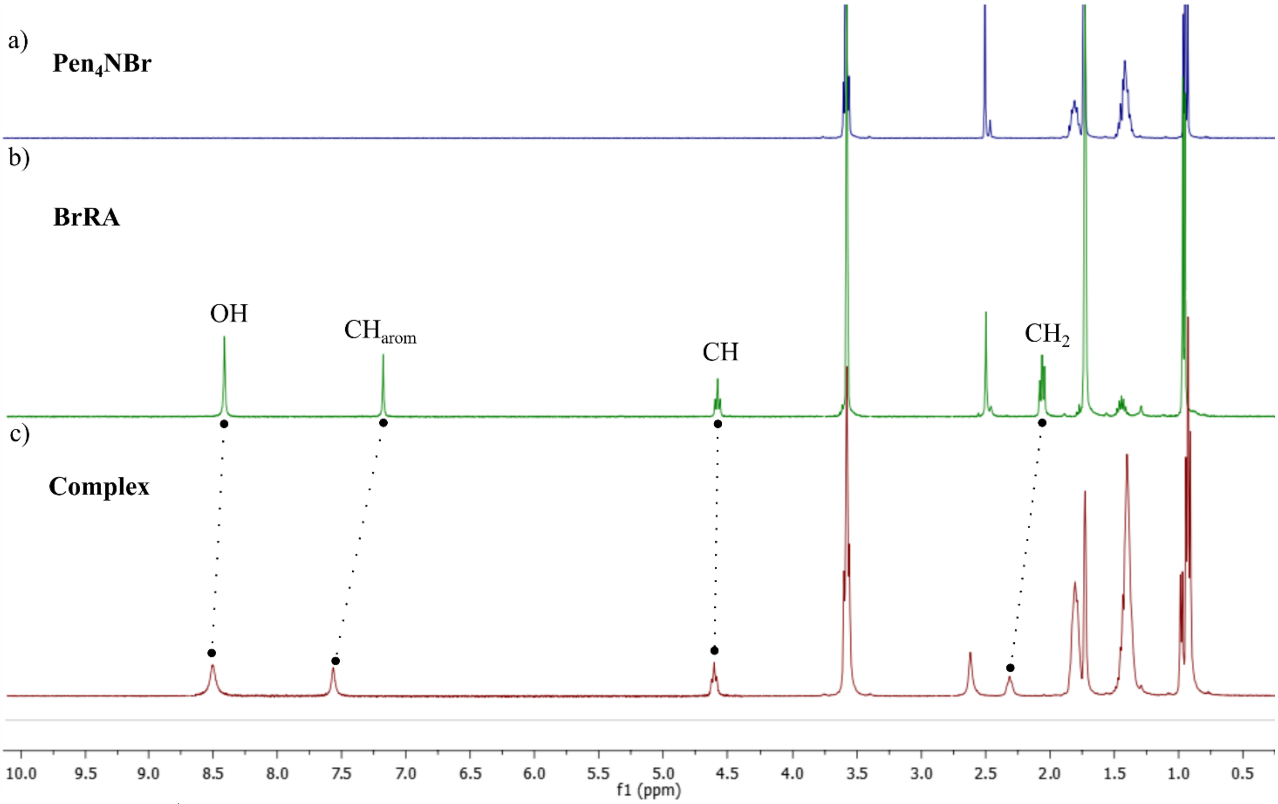
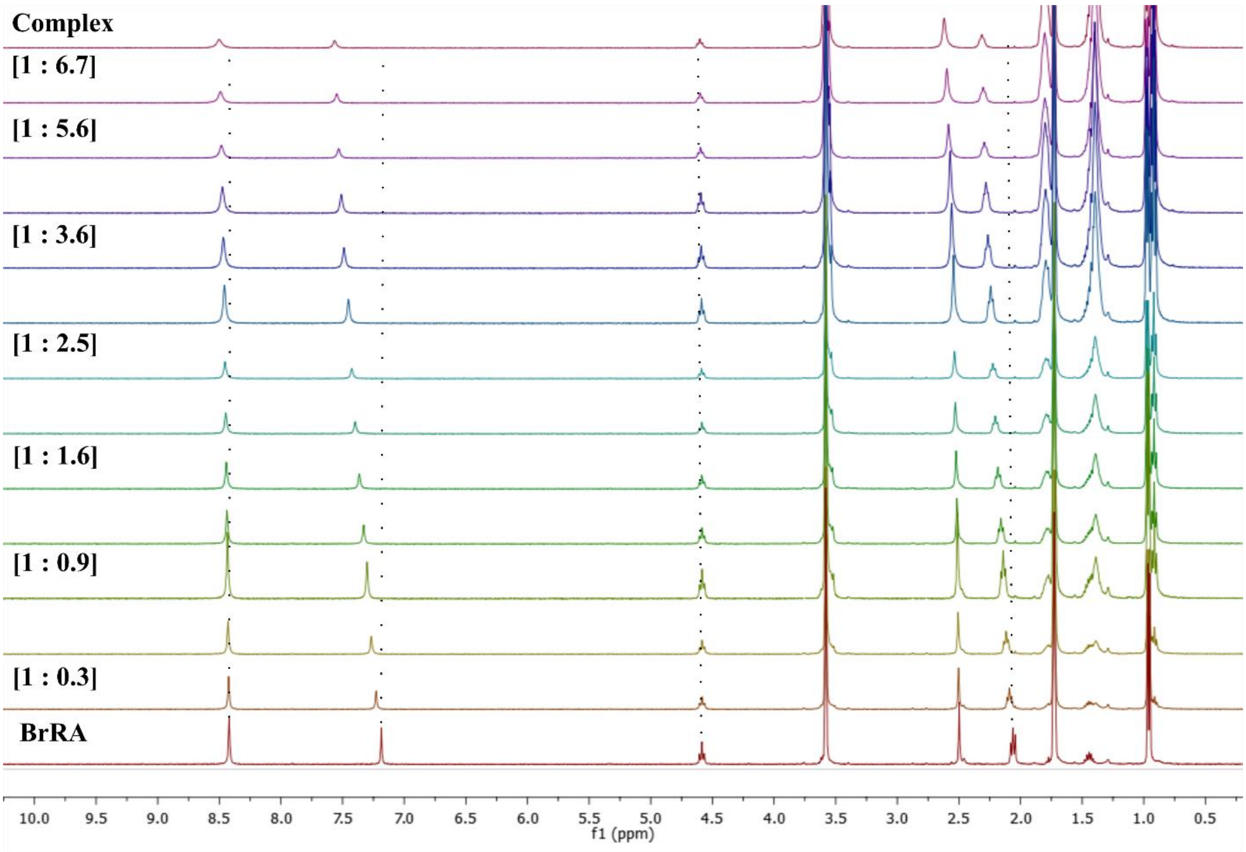


Figure S17. [1]H NMR spectra of (a) **Pen4NBr**; (b) **Br-RA**; (c) complex of **Br-RA** and **Pen4NBr** (400 MHz, 303 K, THF-d8).



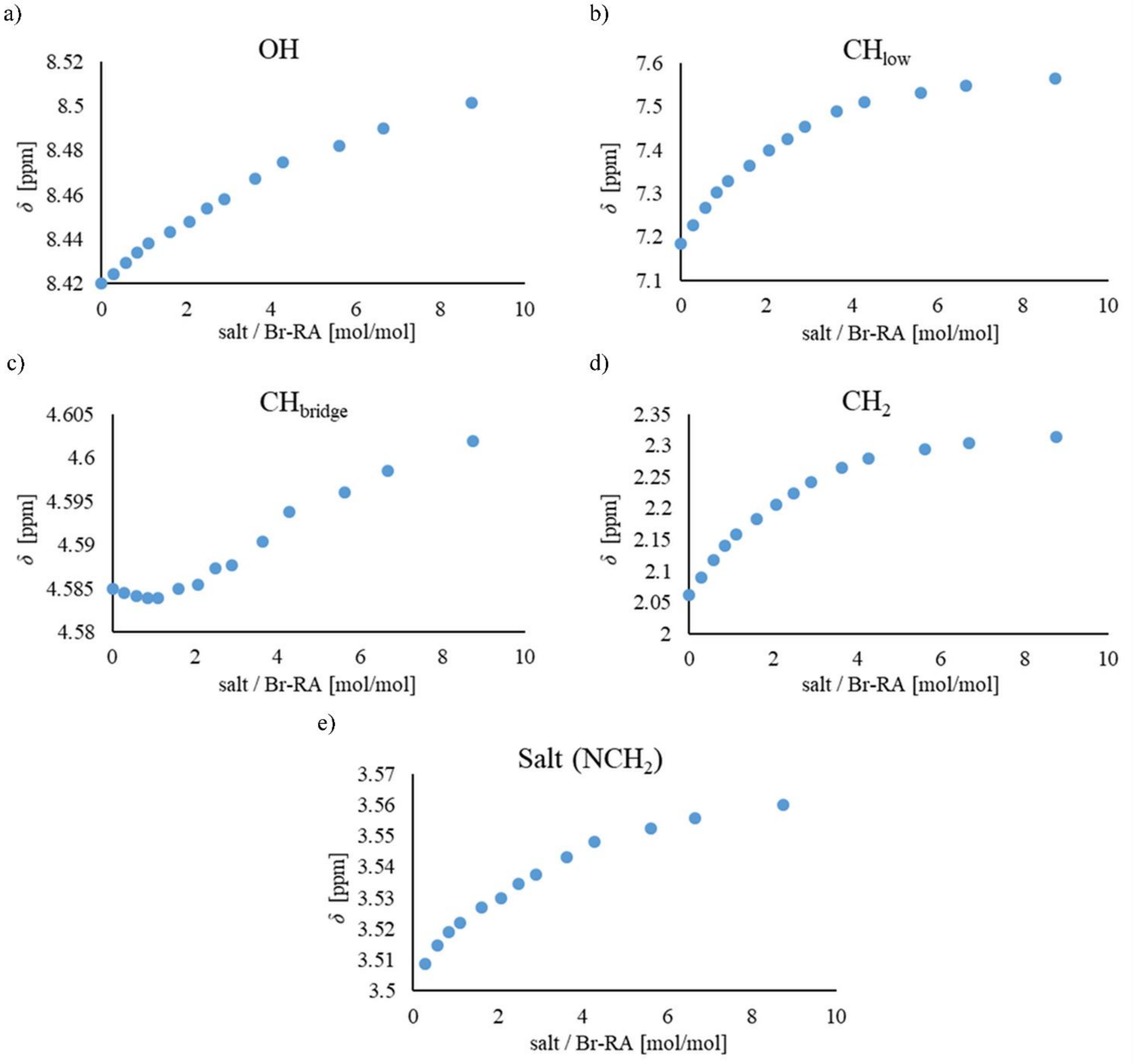
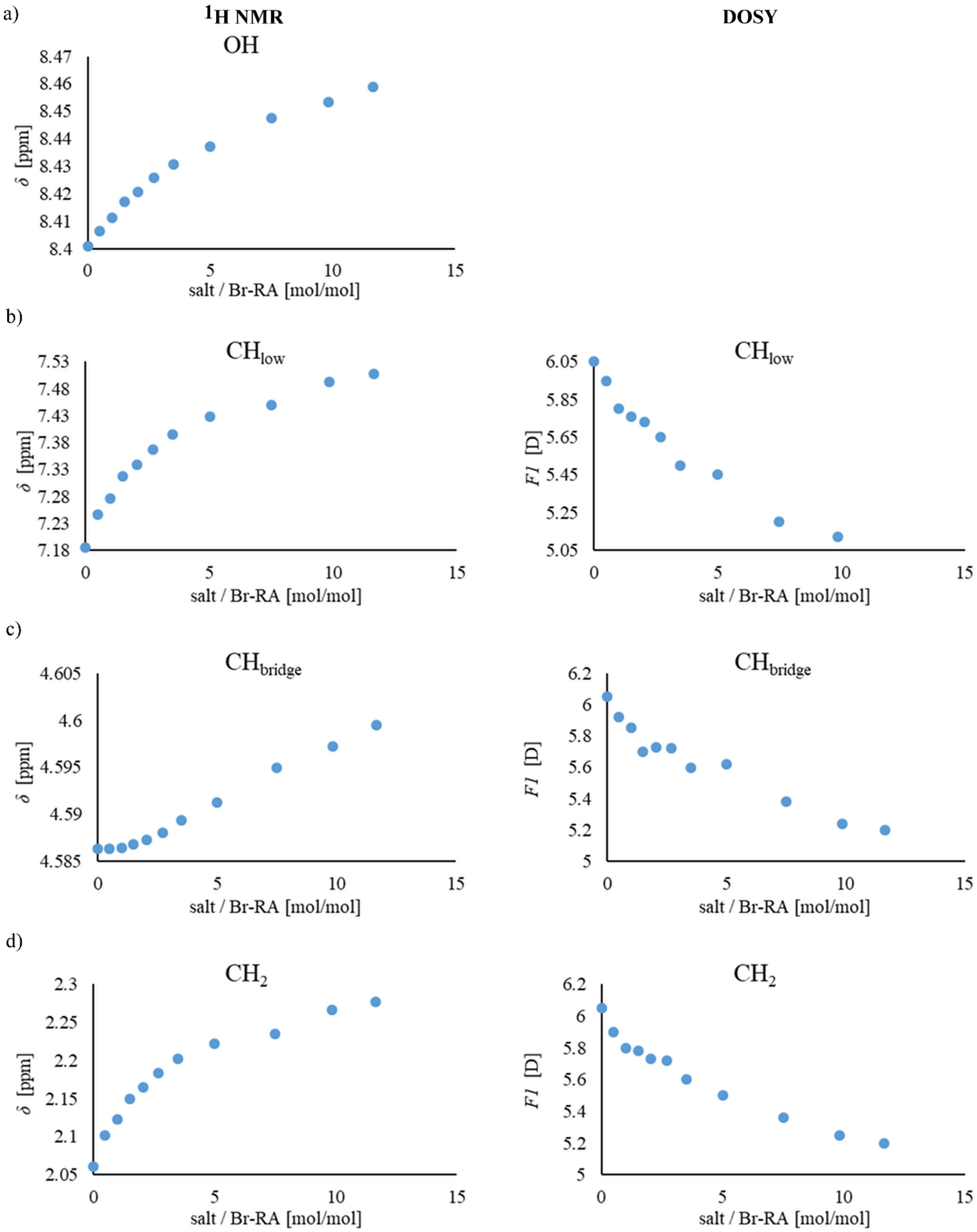
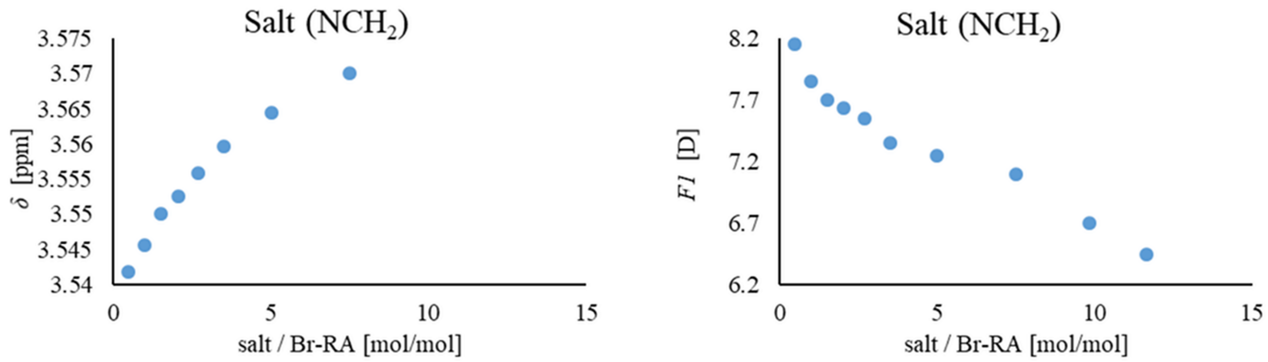


Figure S18. ^{1}H NMR titration curves for titration of **Br-RA** with **Pen$_4$NBr**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

5.9. DOSY titration curves for titration of Br-RA with Pen_4NBr in THF



e)



f)

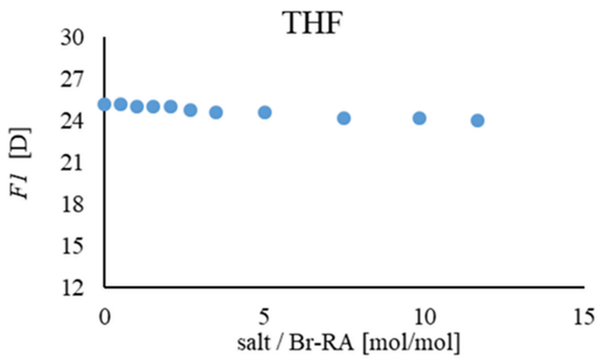
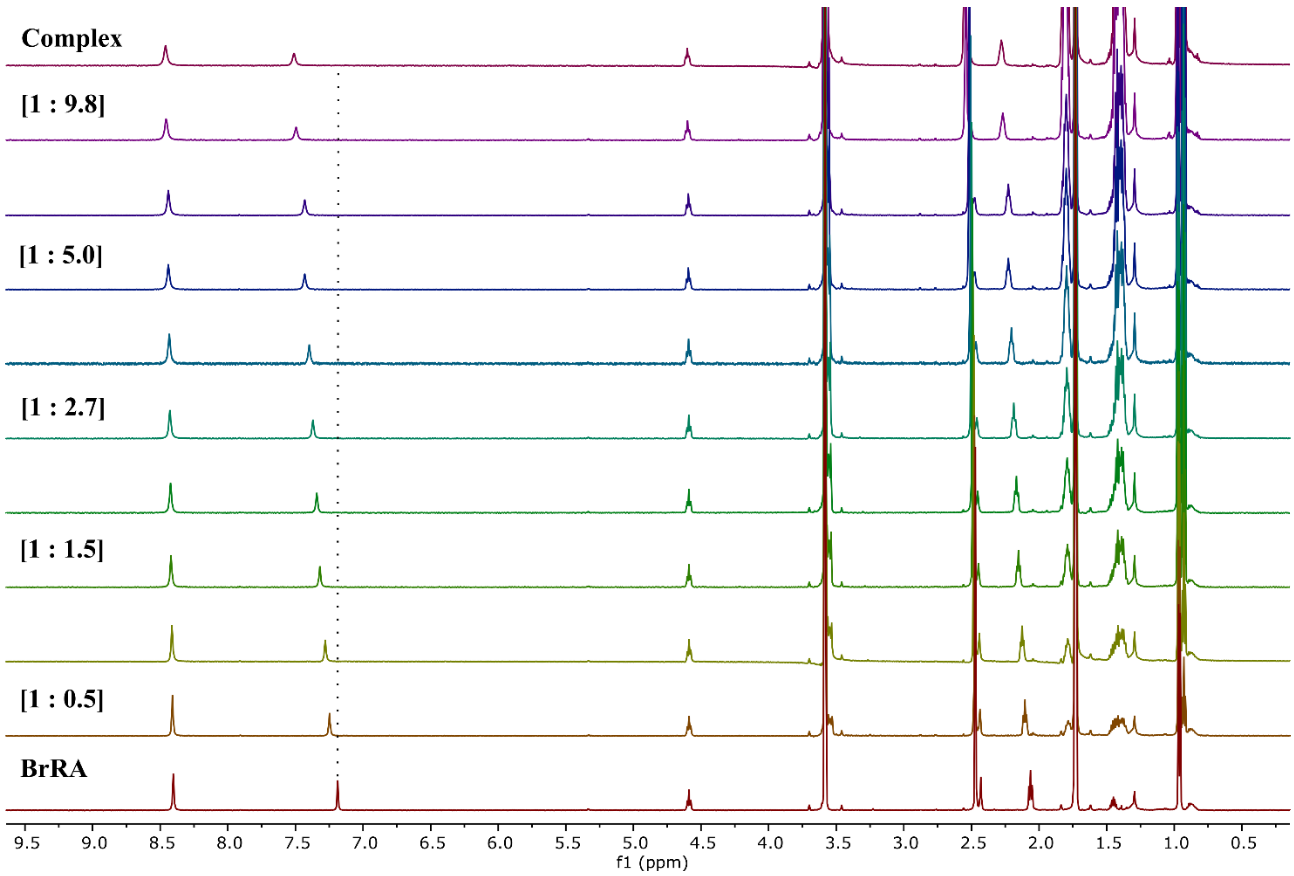


Figure S19. DOSY titration curves for titration of **Br-RA** with **Pen$_4$NBr**. ^{1}H NMR chemical shifts and diffusion coefficient changes for: a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt; (f) THF signal (600 MHz, 303 K, THF-d8).



6. Titrations of I-RA

6.1. Titration of I-RA with Oct_4NCl in THF

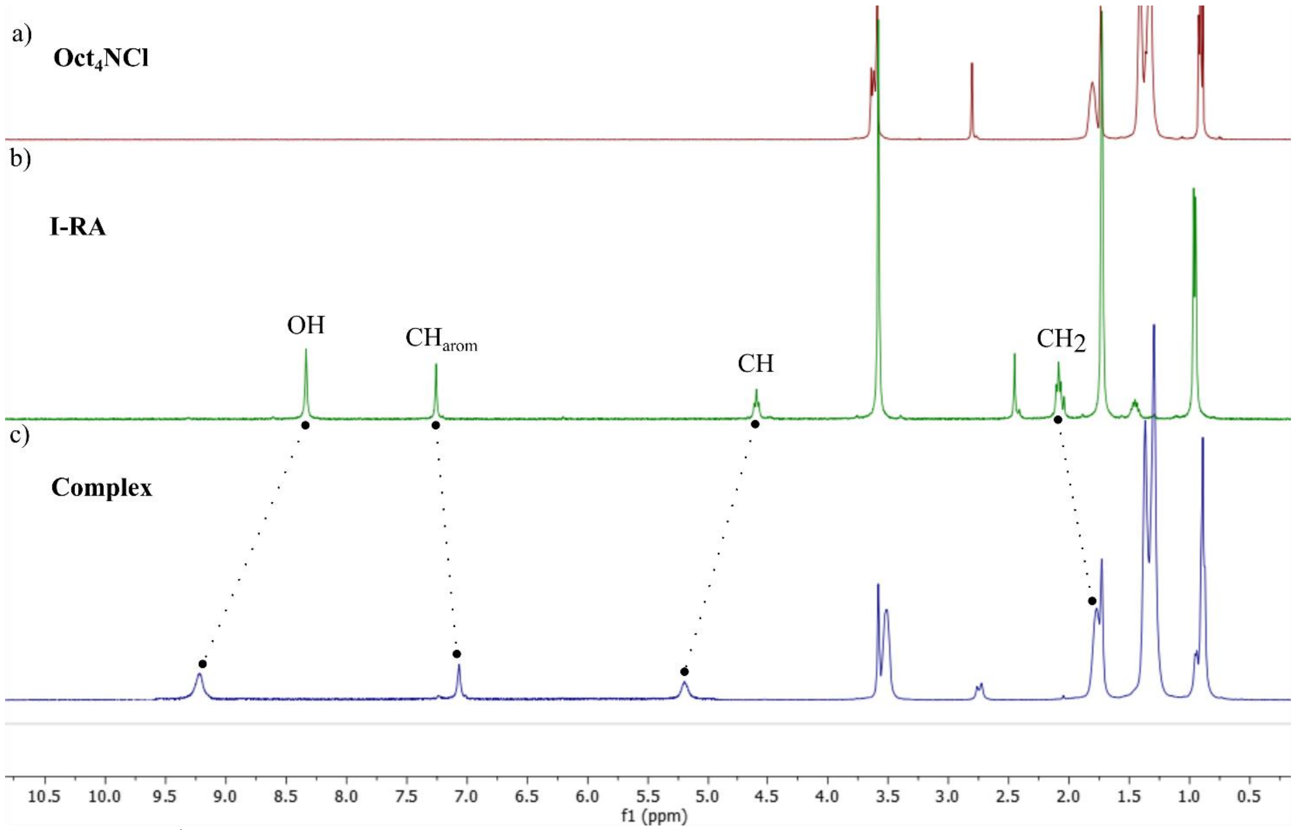
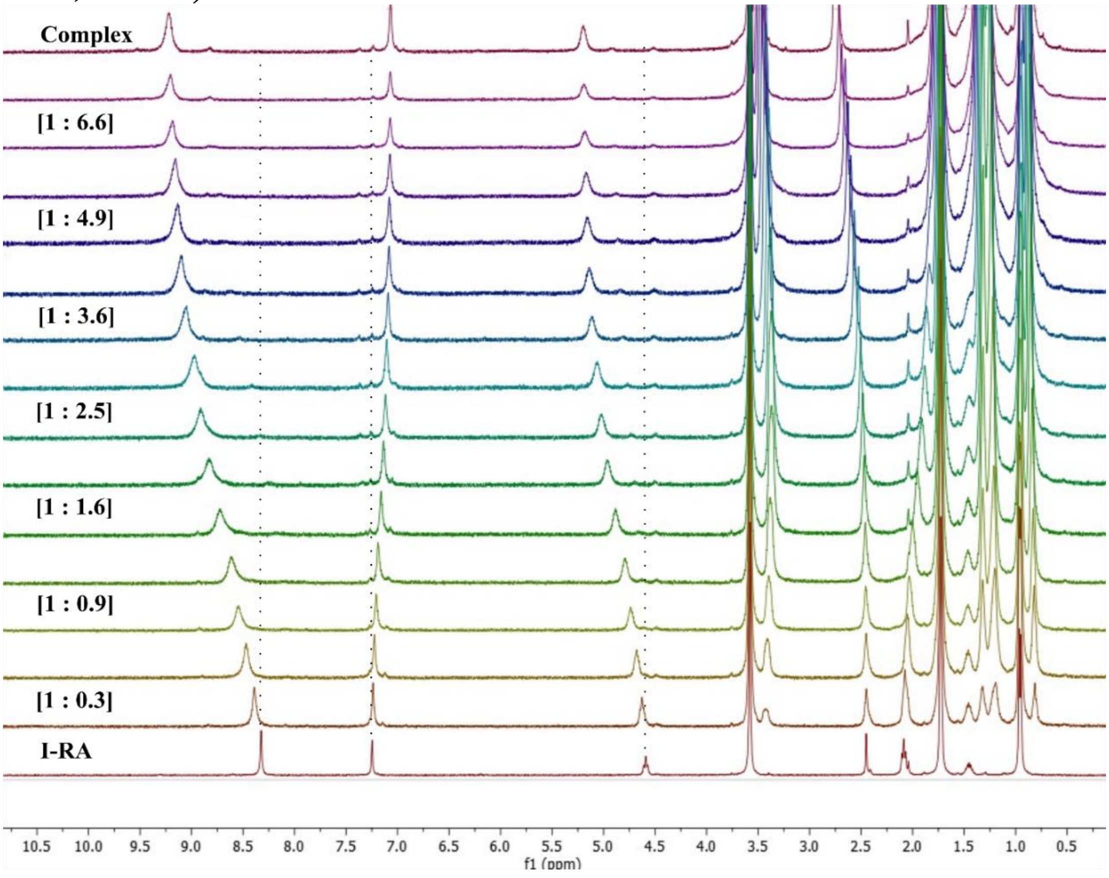


Figure S20. [1]H NMR spectra of (a) **Oct_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Oct_4NCl** (400 MHz, 303 K, THF-d8).



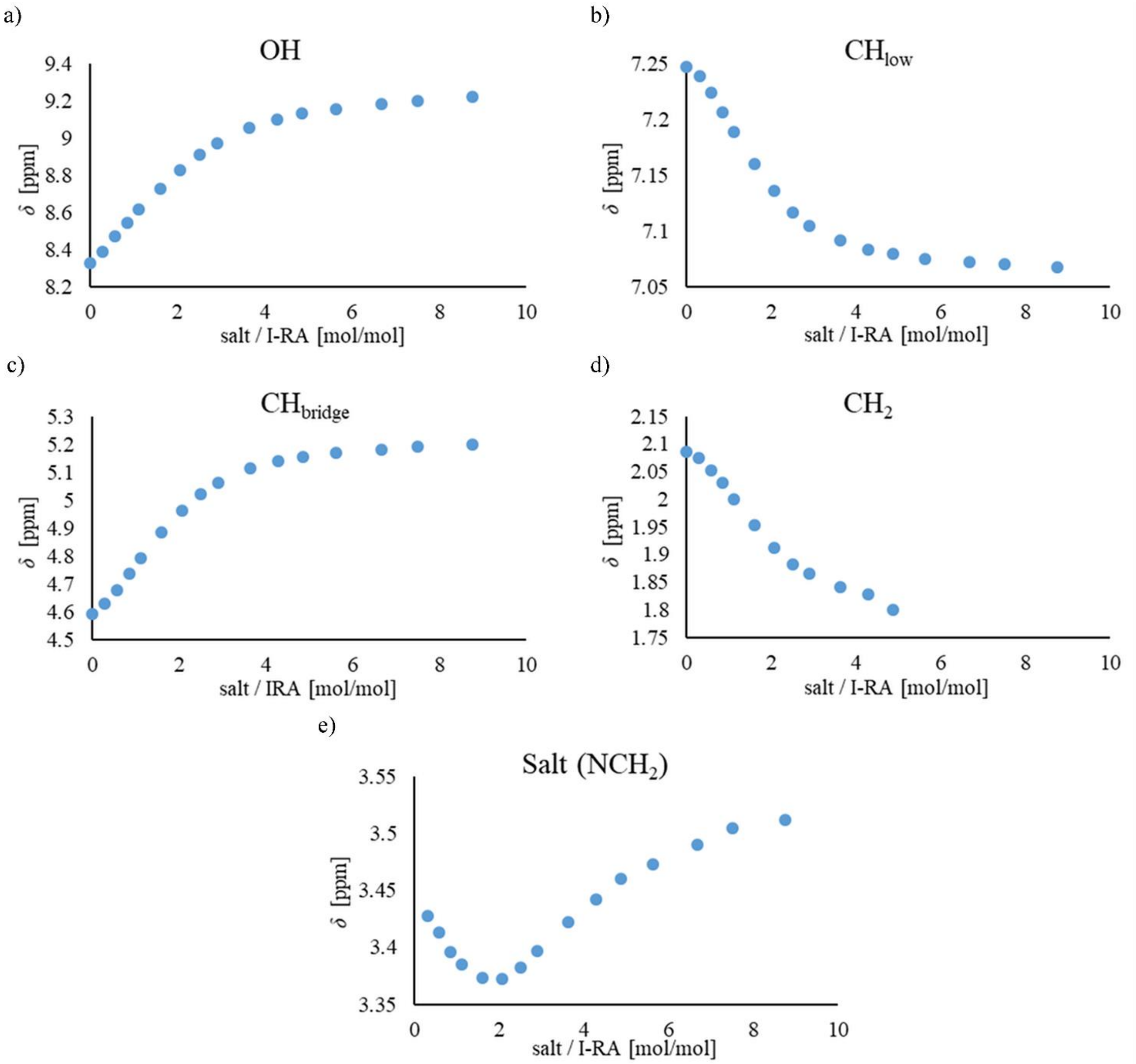


Figure S21. ^{1}H NMR titration curves for titration of **I-RA** with **Oct_4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

6.2. Titration of I-RA with Oct_4NCl in acetone

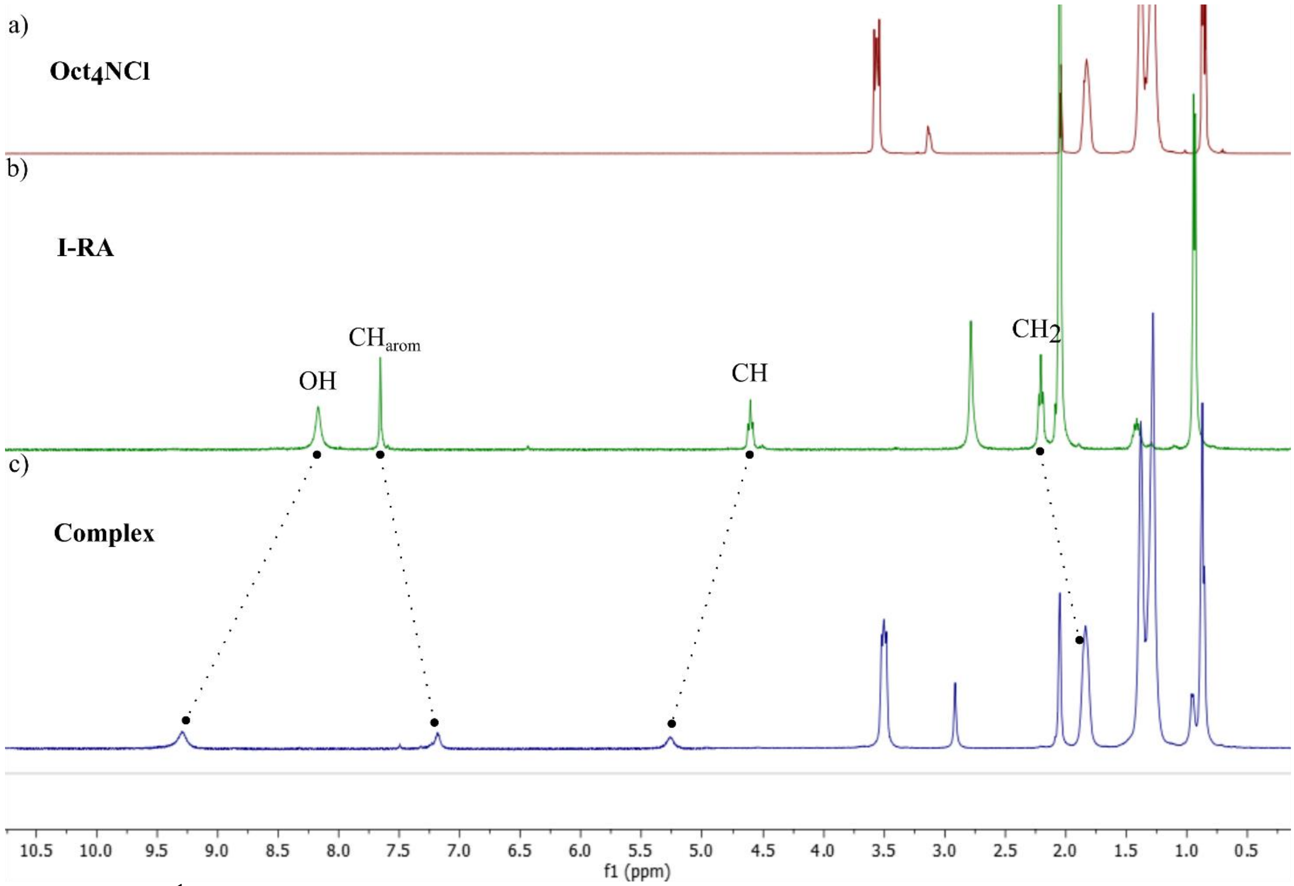
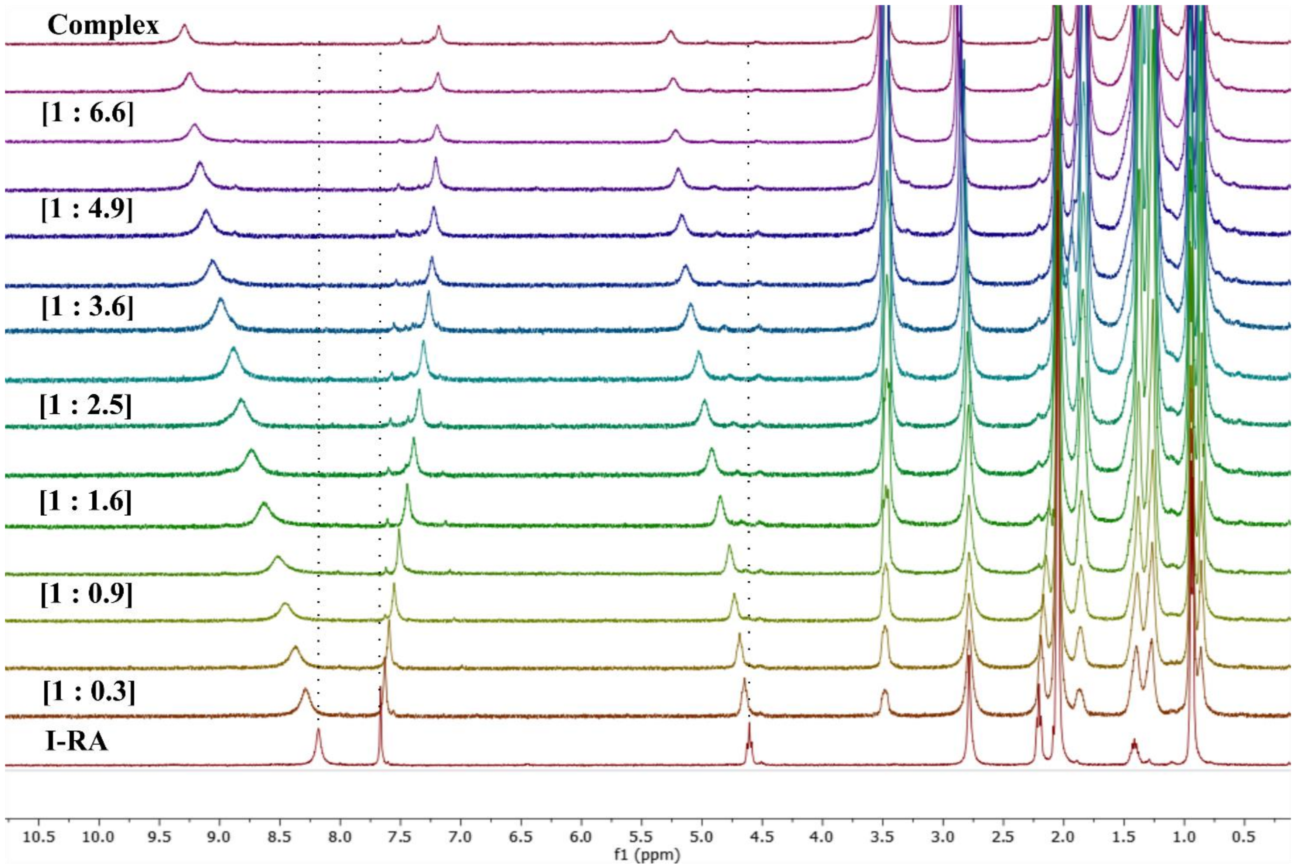


Figure S22. [1]H NMR spectra of (a) **Oct_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Oct_4NCl** (400 MHz, 303 K, Acetone-d6).



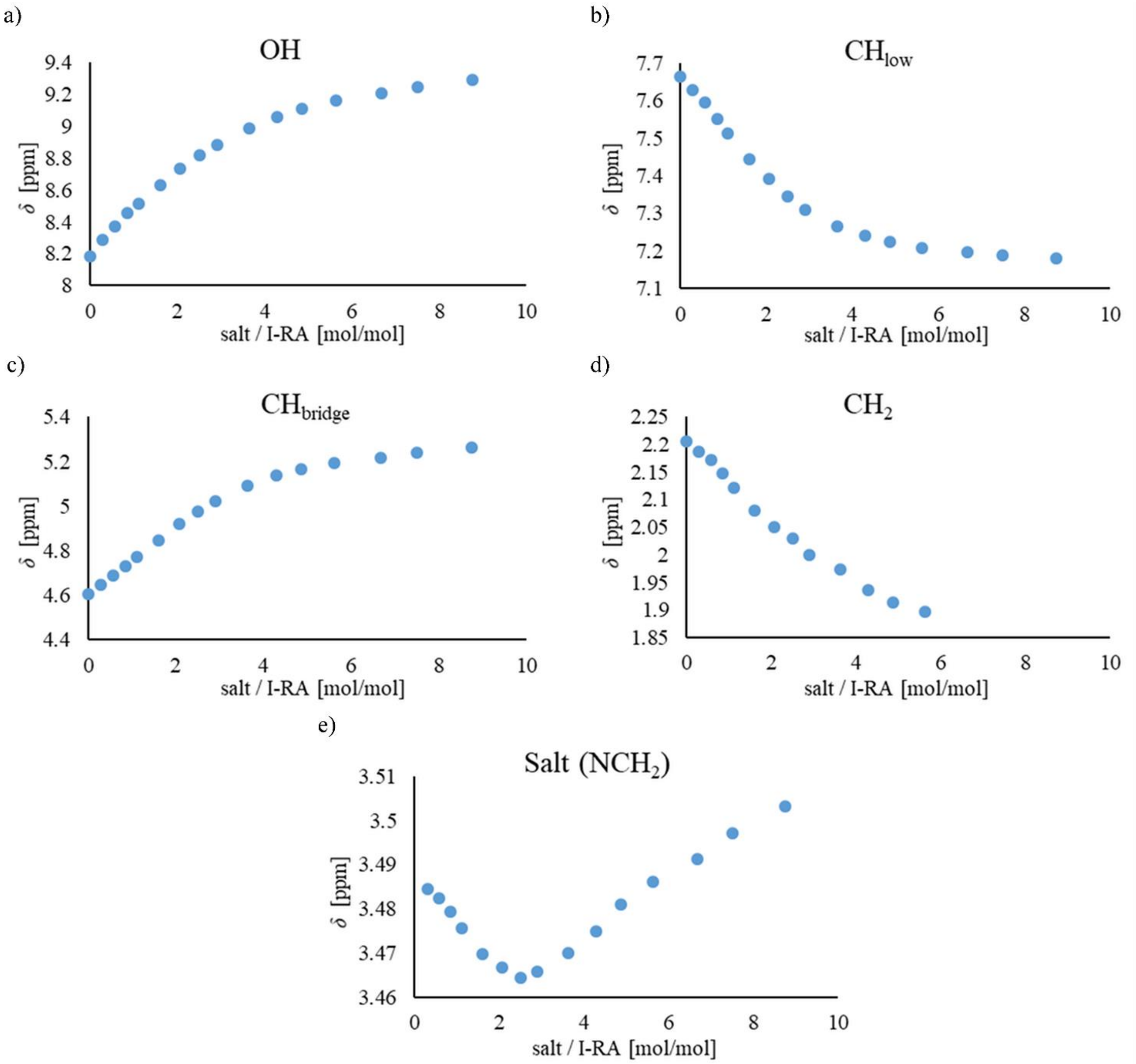


Figure S23. [1]H NMR titration curves for titration of **I-RA** with **Oct_4NCl**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

6.3. Titration of I-RA with Hex_4NCl in THF

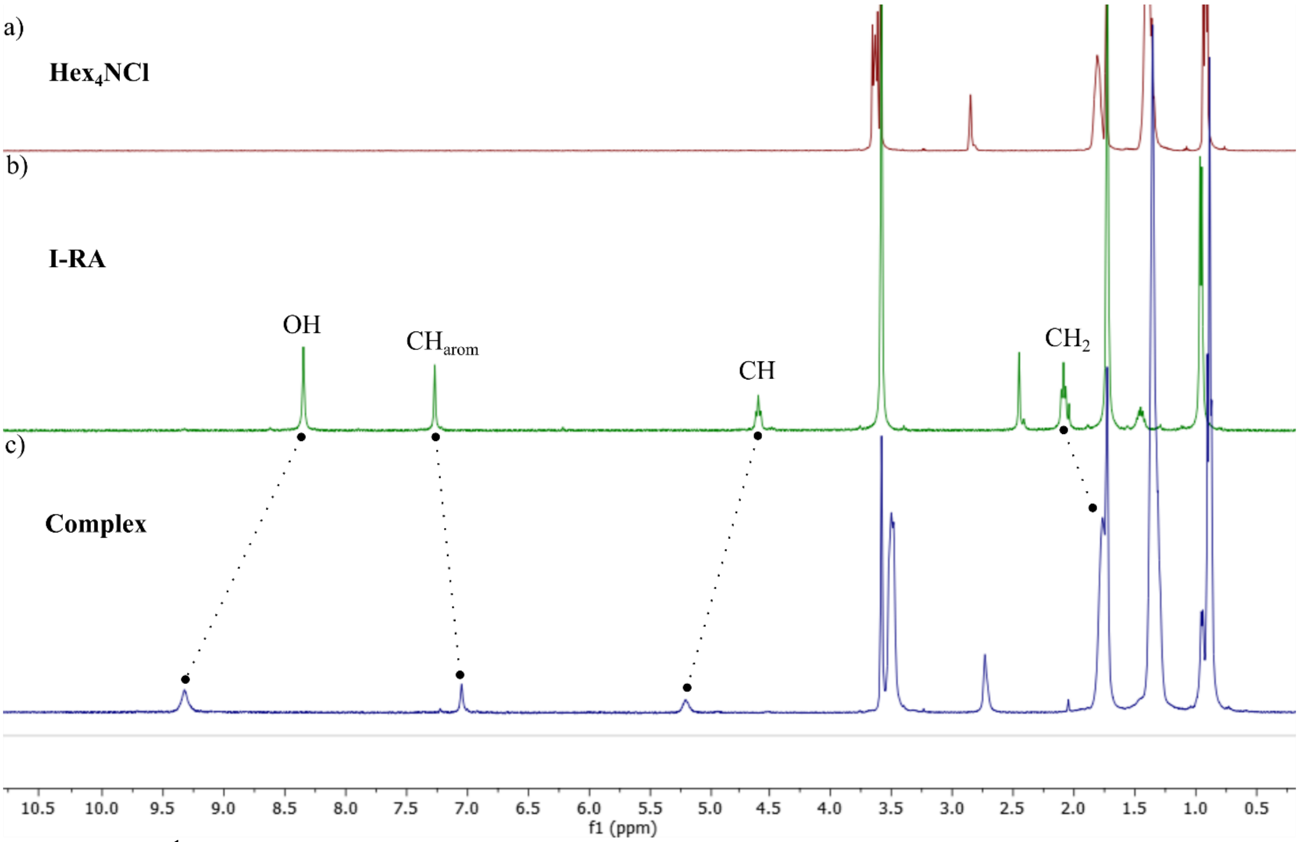
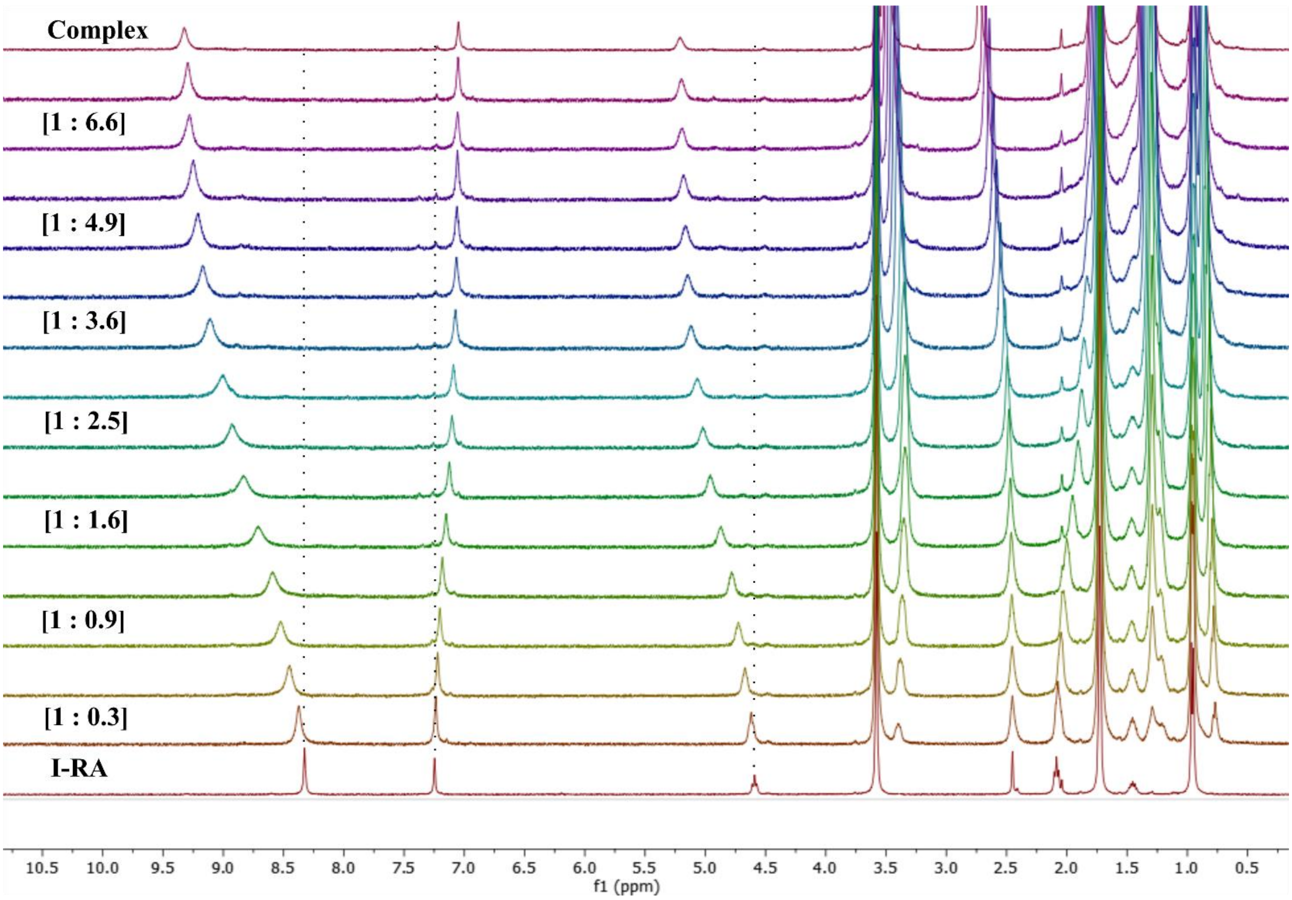


Figure S24. ^{1}H NMR spectra of (a) **Hex_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Hex_4NCl** (400 MHz, 303 K, THF-d8).



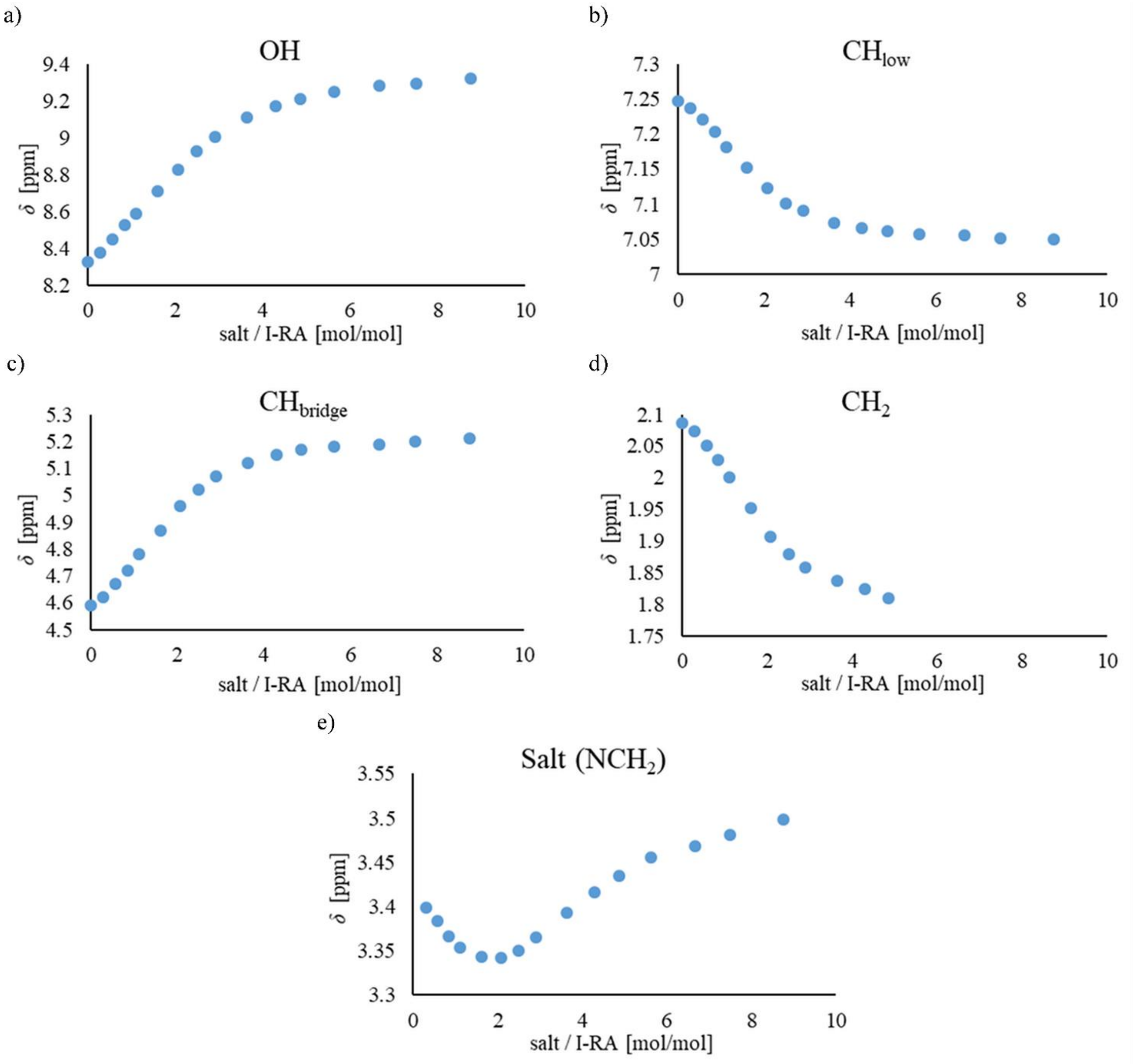


Figure S25. ^{1}H NMR titration curves for titration of **I-RA** with **Hex_4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

6.4. Titration of I-RA with Hex_4NCl in acetone

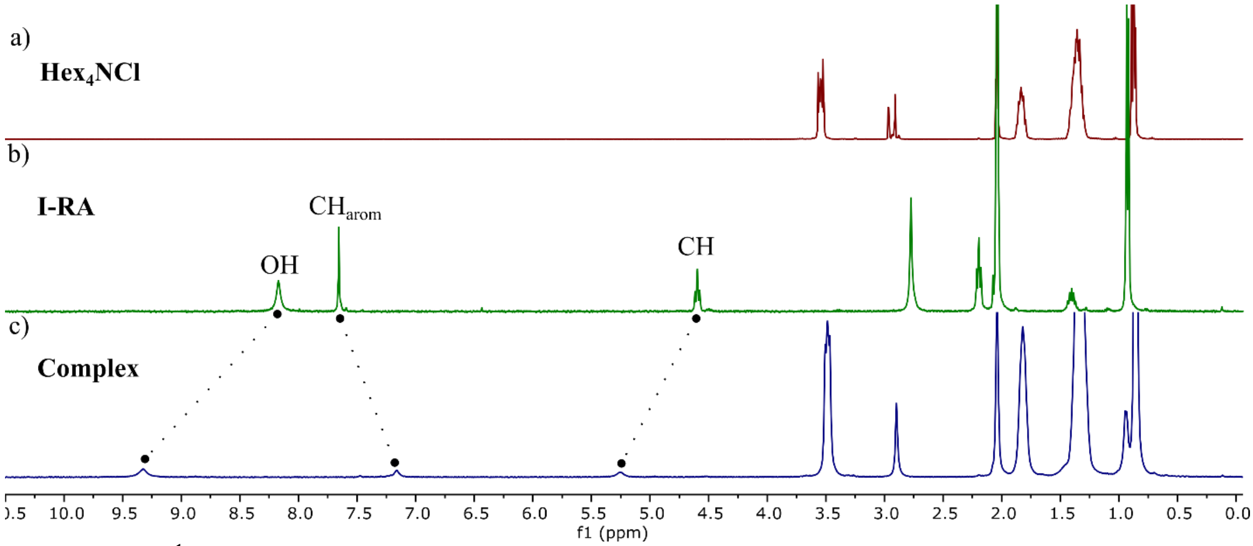
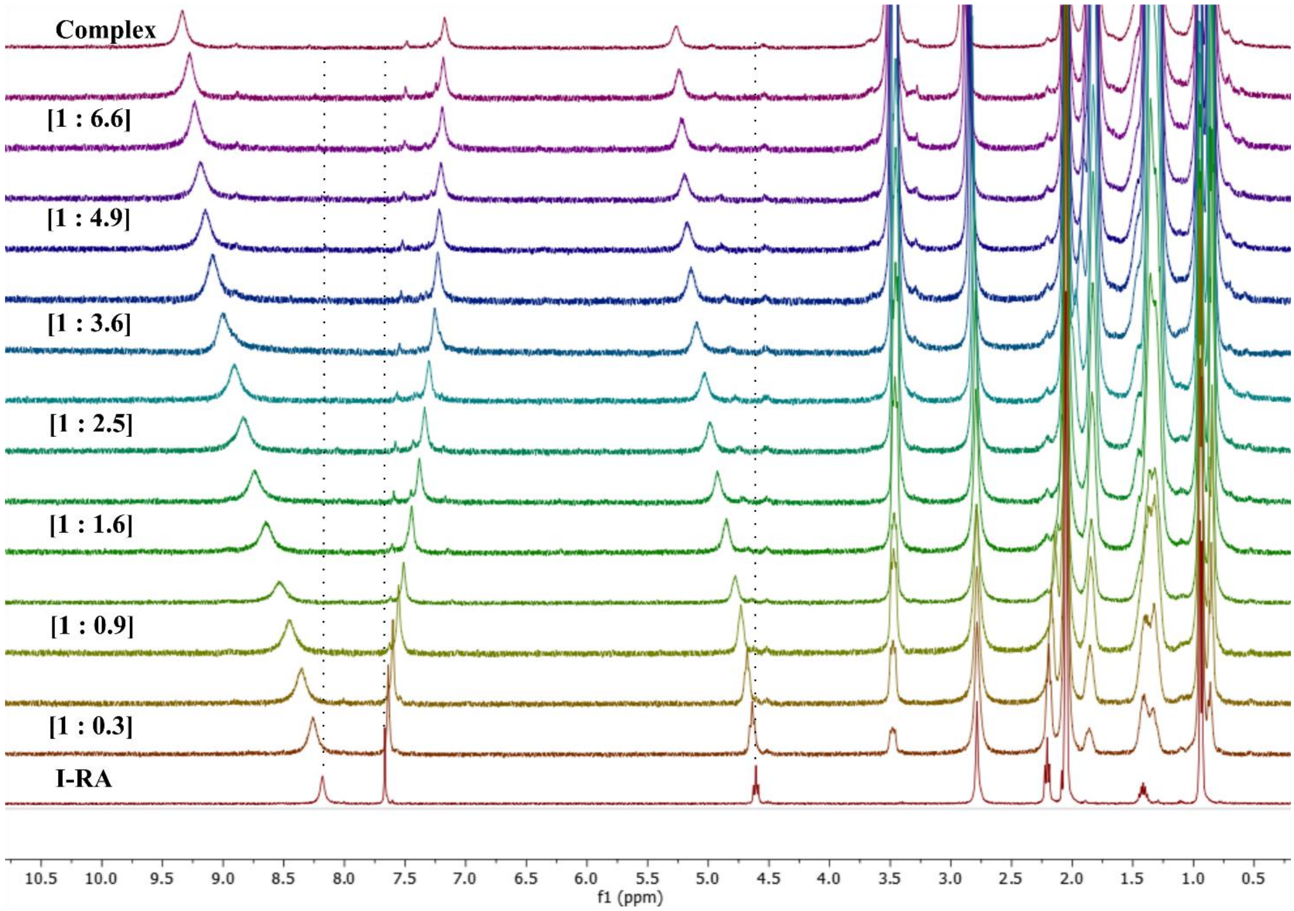


Figure S26. ^{1}H NMR spectra of (a) **Hex_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Hex_4NCl** (400 MHz, 303 K, Acetone-d6).



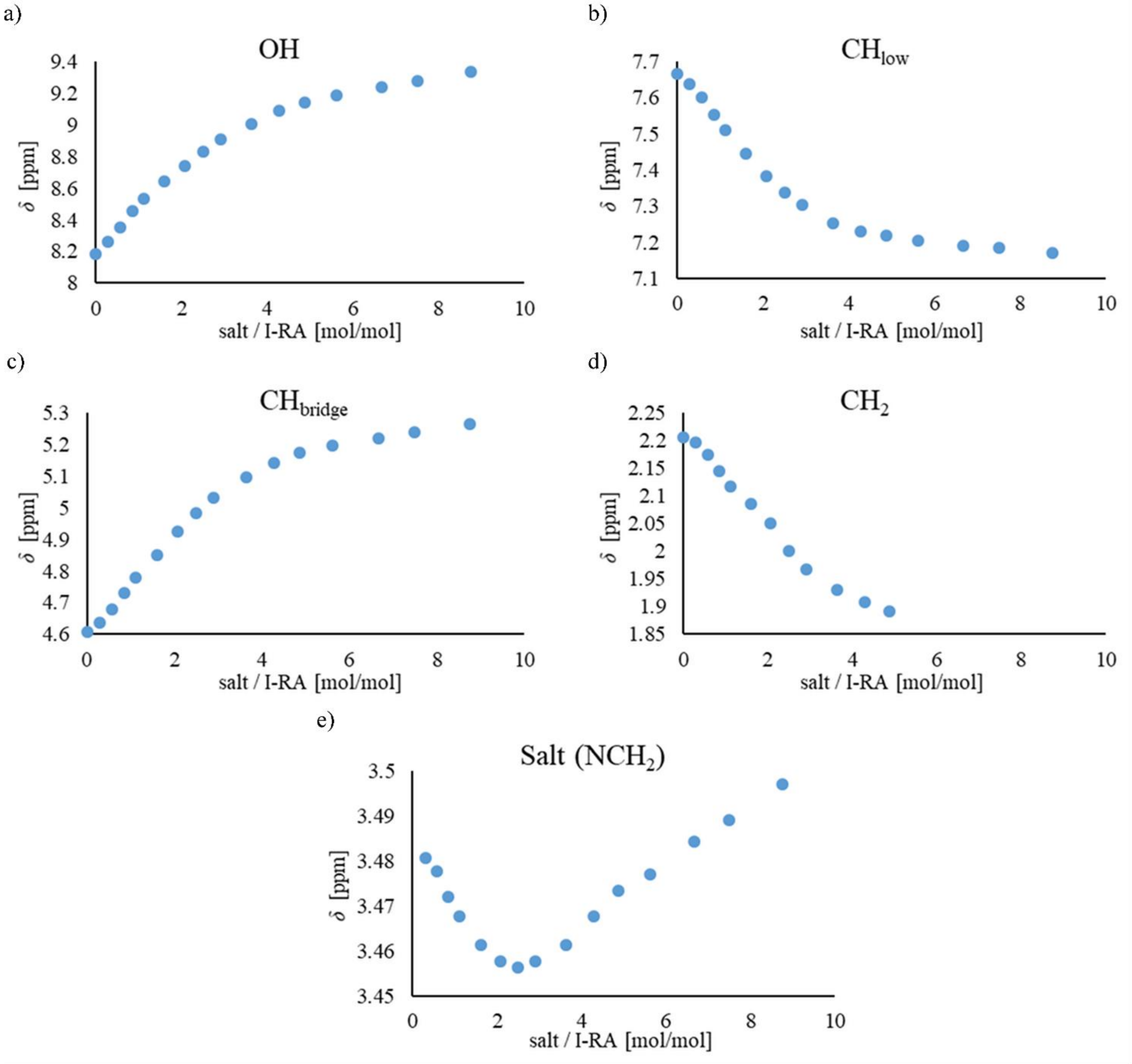


Figure S27. ^{1}H NMR titration curves for titration of **I-RA** with **Hex$_4$NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

6.5. Titration of I-RA with Pen_4NCl in THF

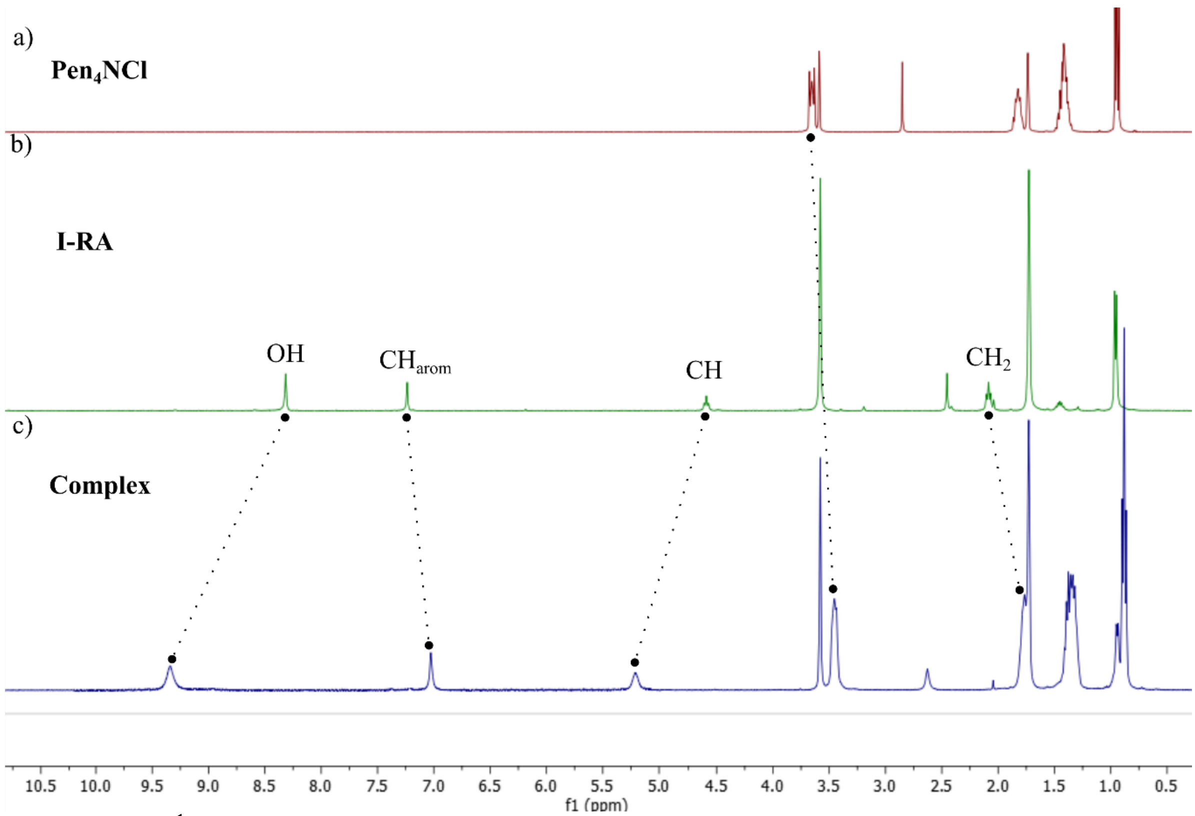
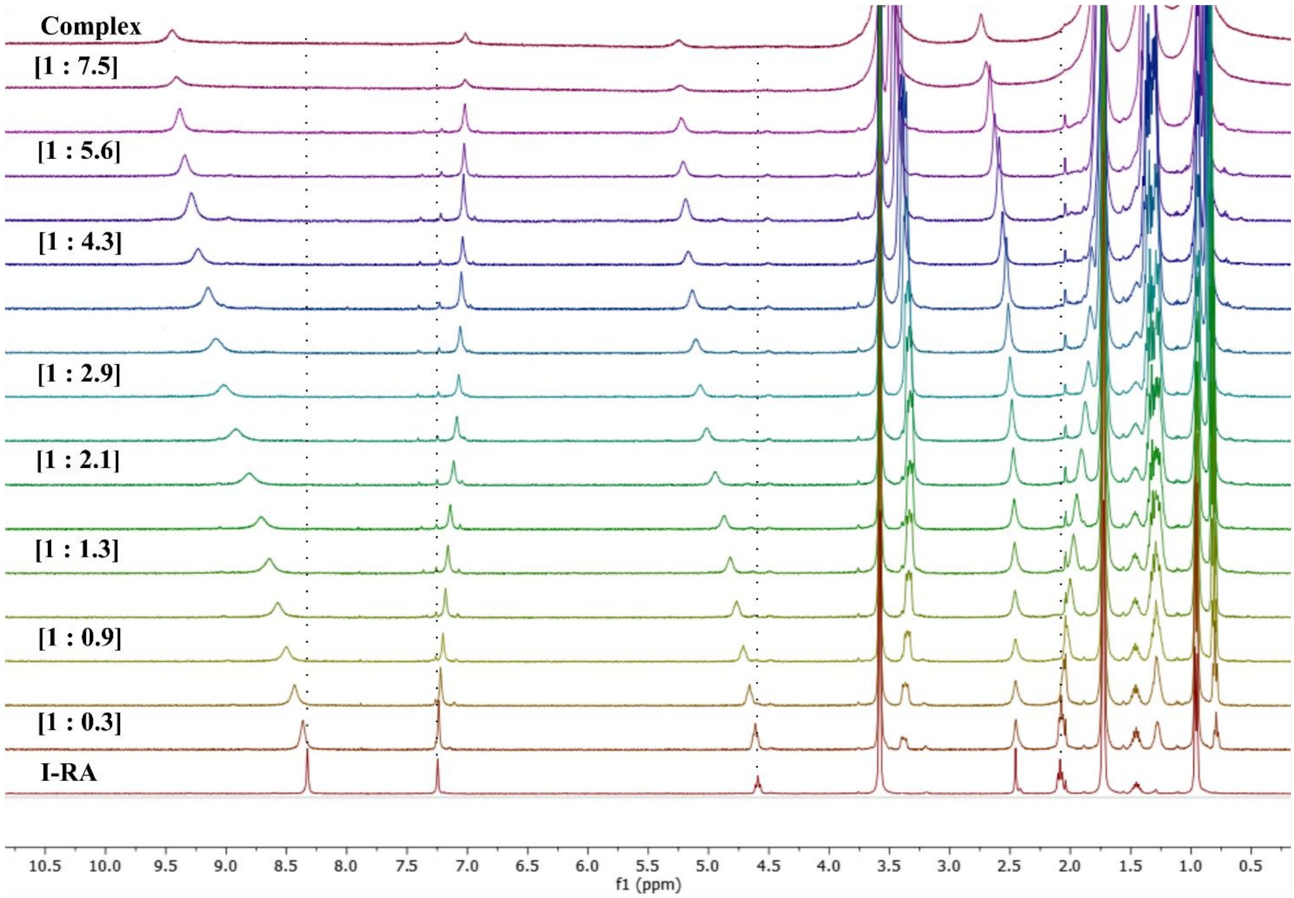


Figure S28. ^{1}H NMR spectra of (a) **Pen_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Pen_4NCl** (400 MHz, 303 K, THF-d8).



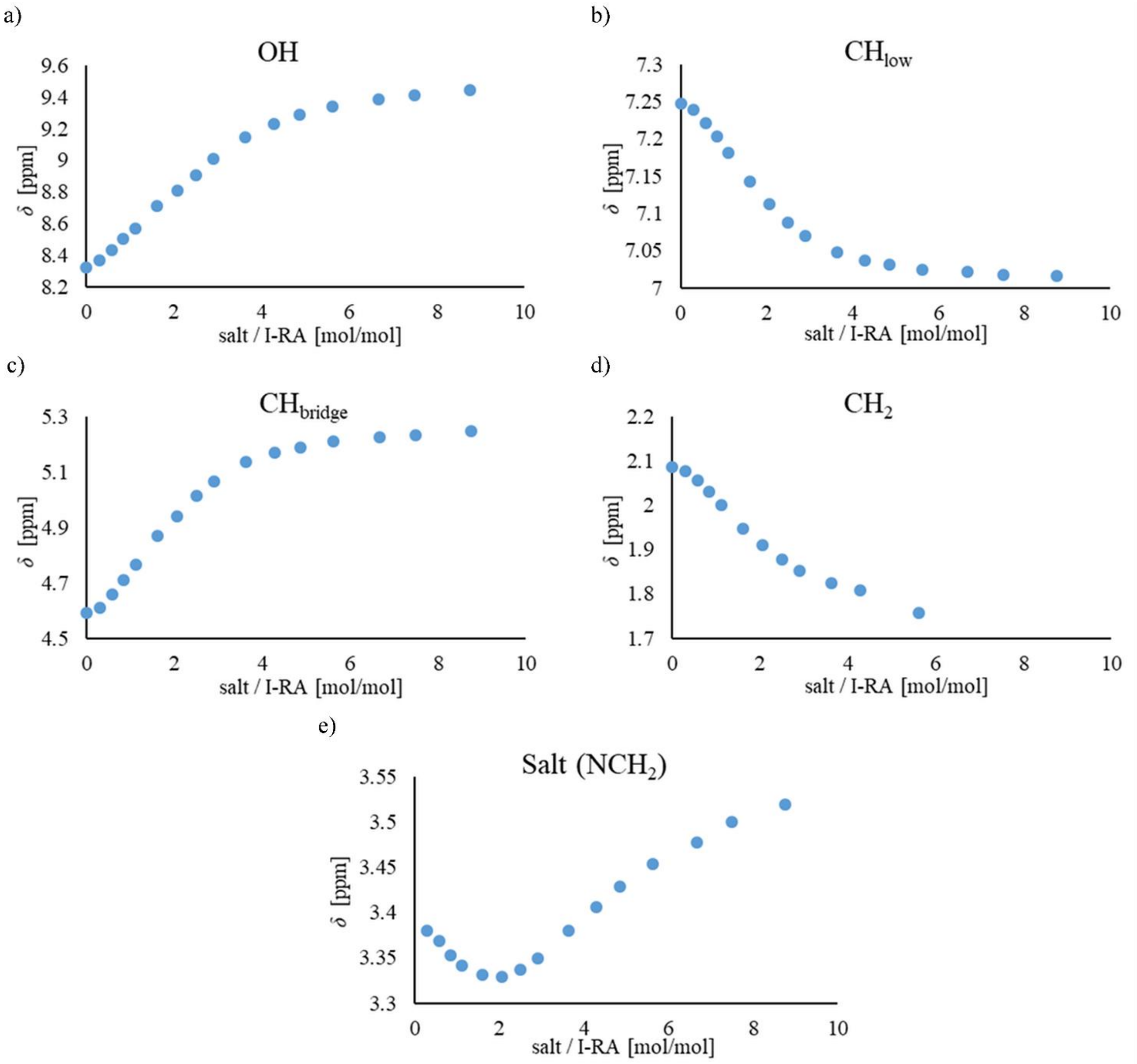
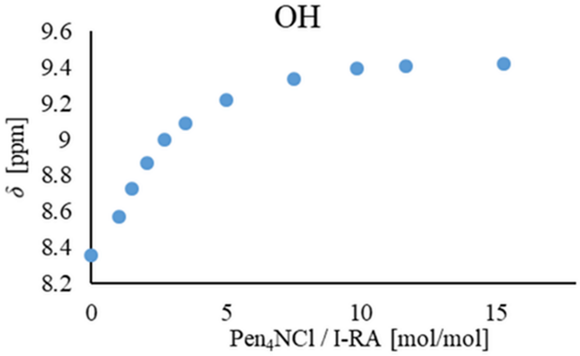


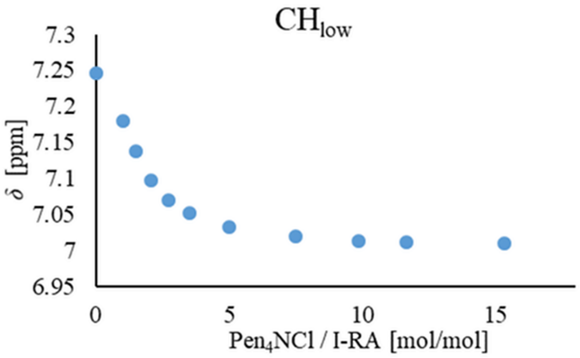
Figure S29. ^{1}H NMR titration curves for titration of **I-RA** with **Pen$_4$NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

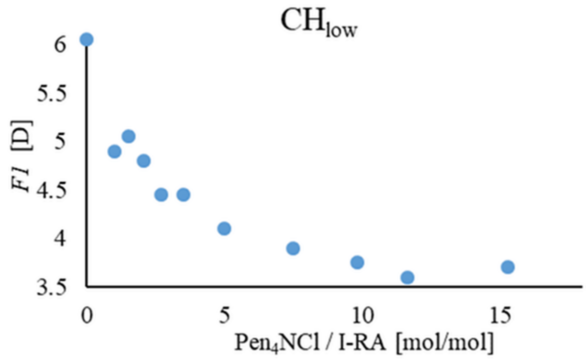
6.6. DOSY titration curves for titration of I-RA with Pen_4NCl in THF

a) ^1H NMR | DOSY

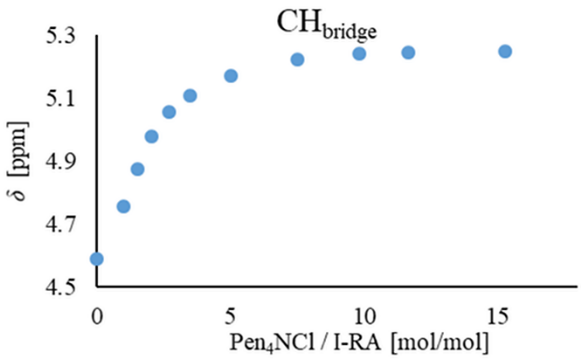


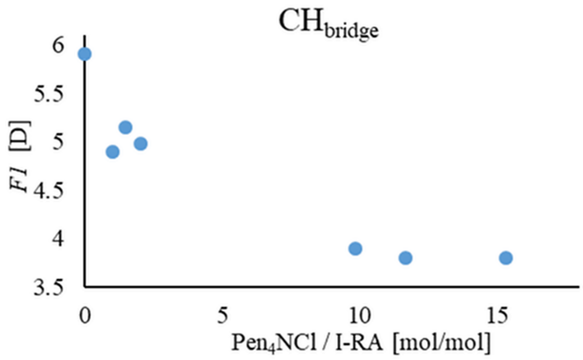
b)



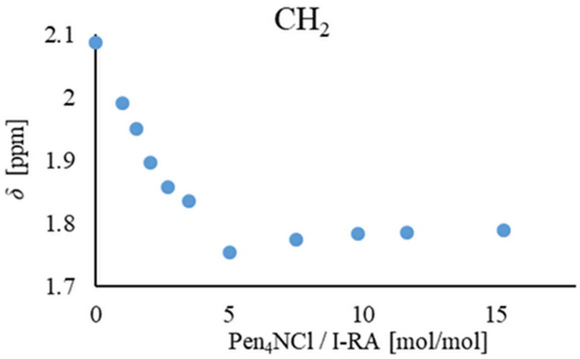


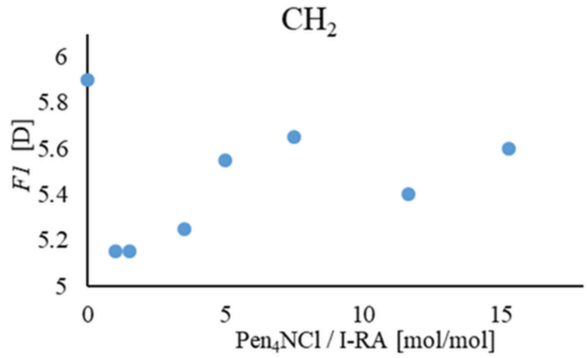
c)





d)





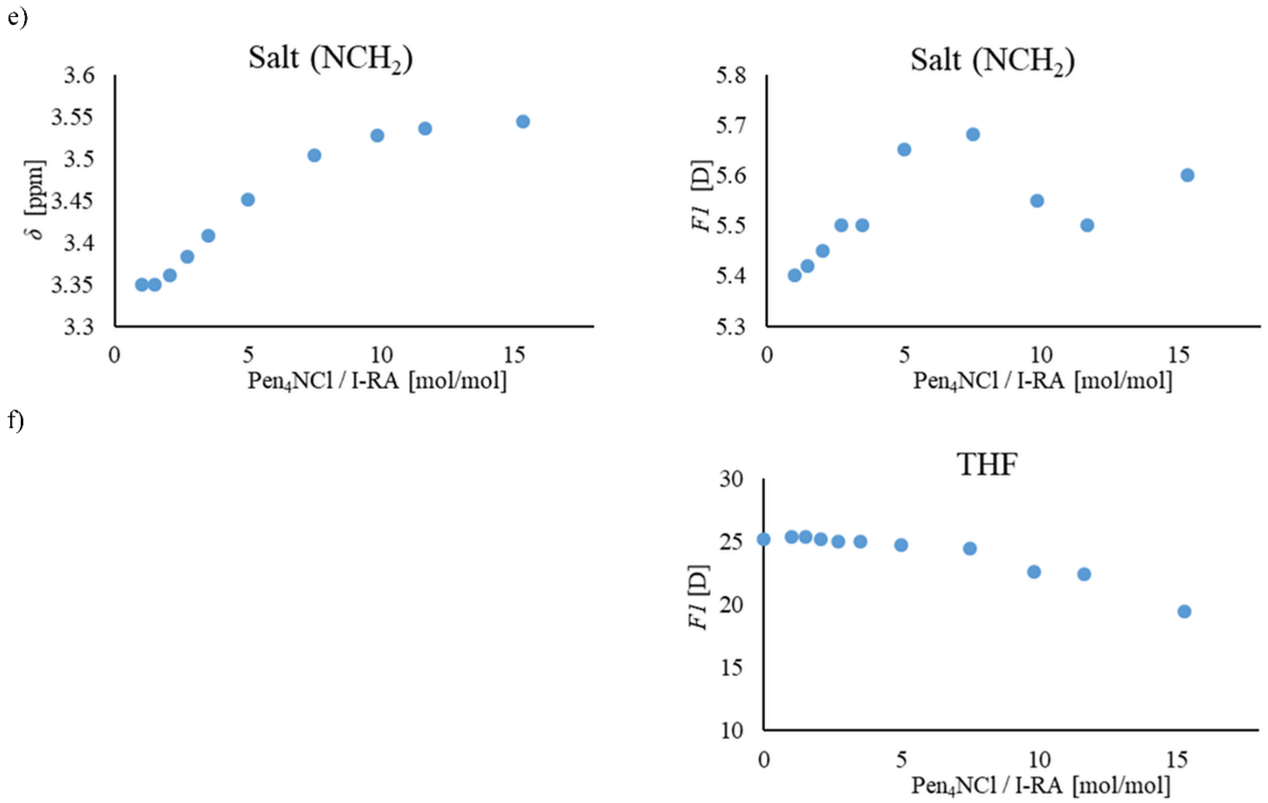
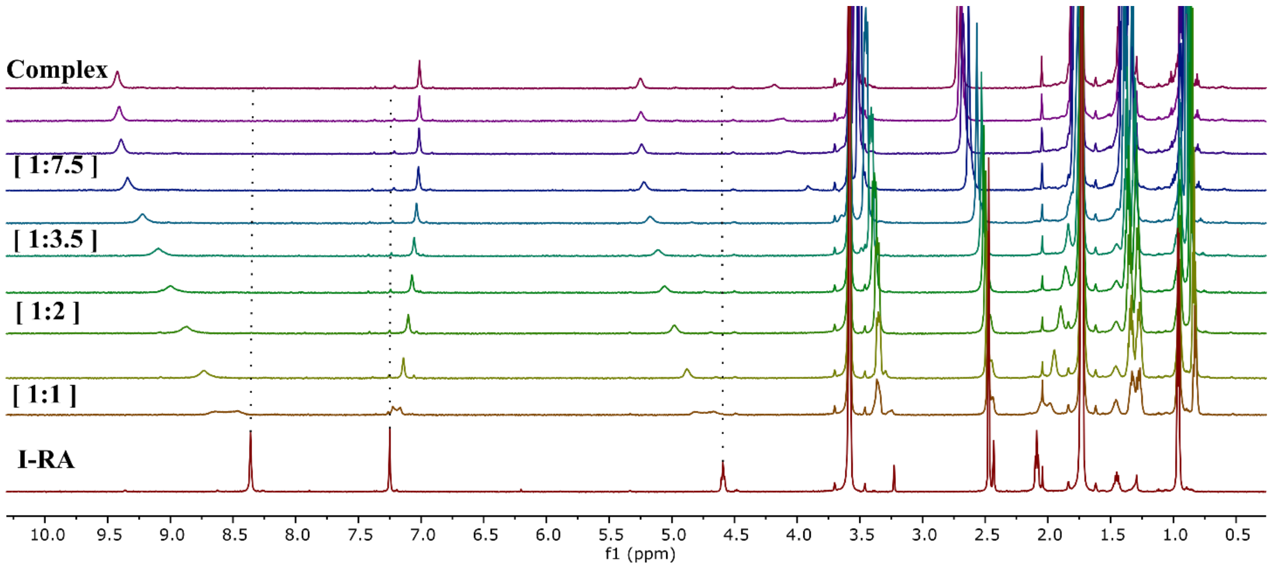


Figure S30. DOSY titration curves for titration of **I-RA** with **Pen_4NCl**. ^{1}H NMR chemical shifts and diffusion coefficient changes for: a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt; (f) THF signal (600 MHz, 303 K, THF-d8).



6.7.Titration of I-RA with Pen_4NCl in acetone

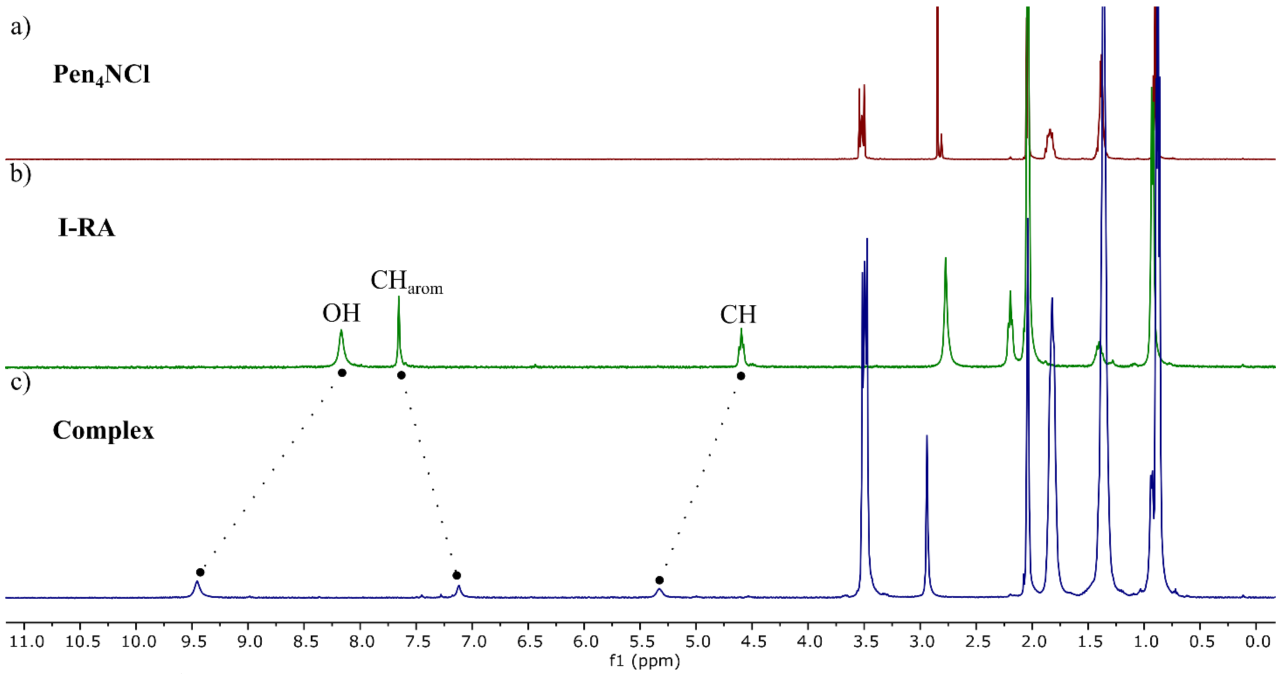
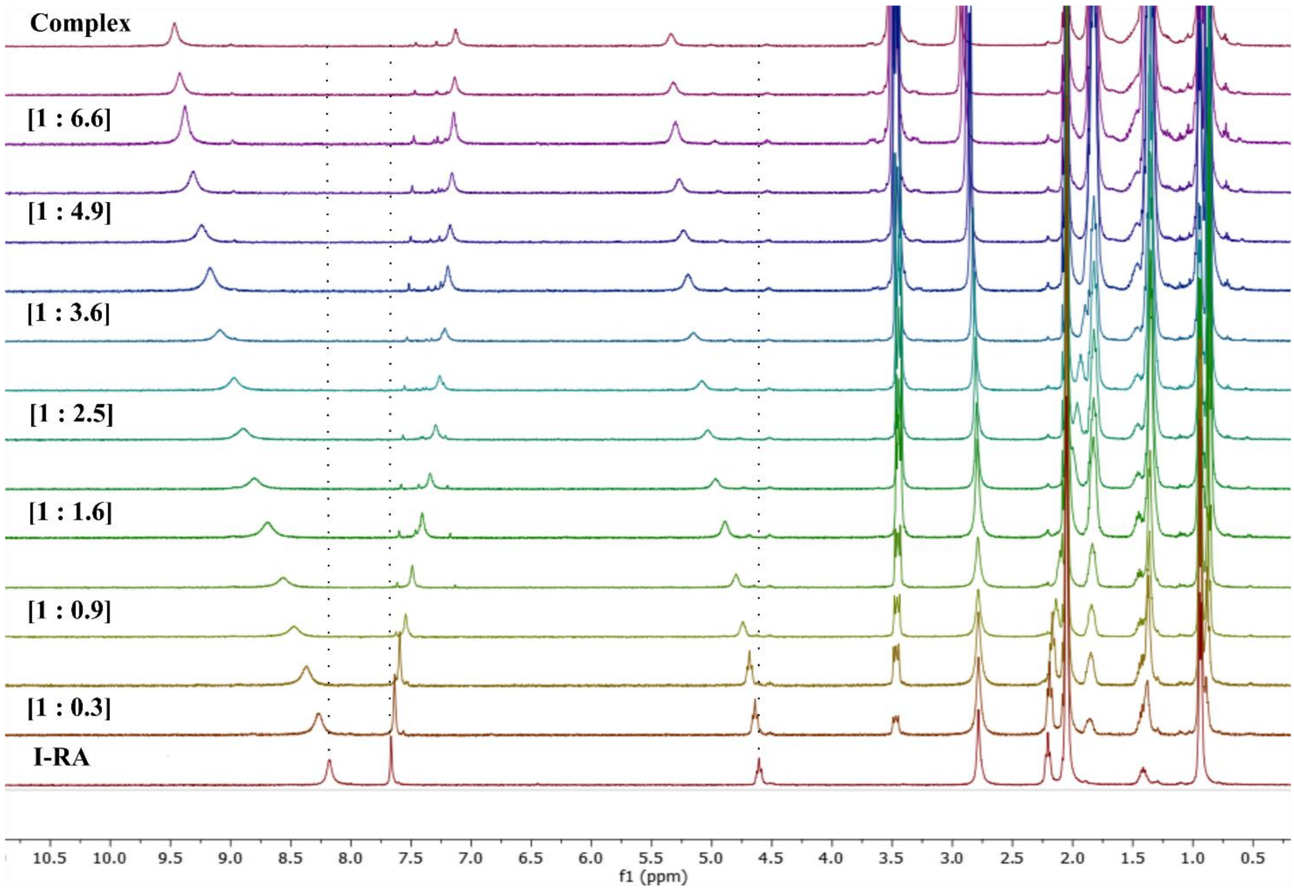


Figure S31. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Pen_4NCl** (400 MHz, 303 K, Acetone-d6).



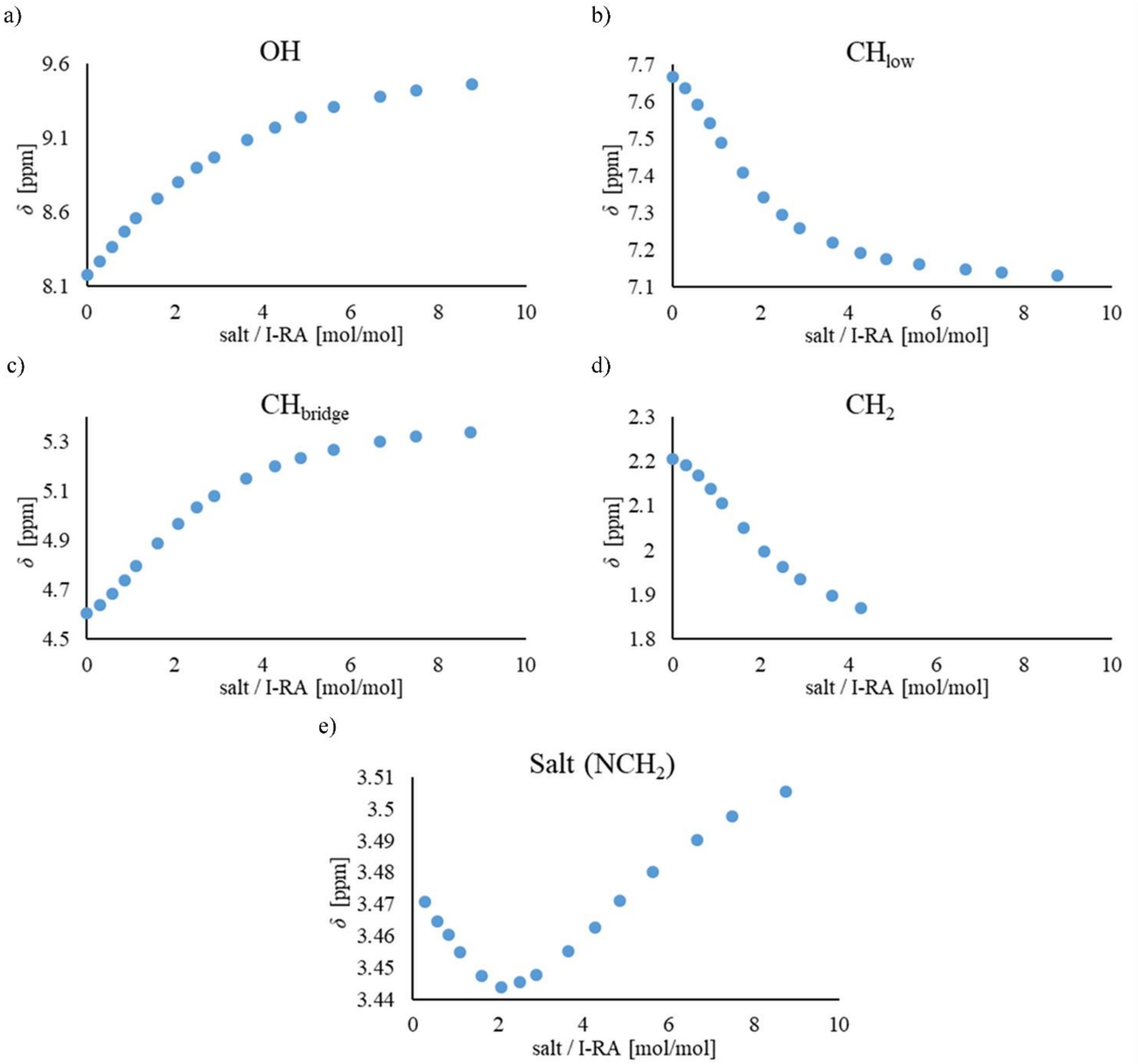


Figure S32. [1]H NMR titration curves for titration of **I-RA** with **Pen$_4$NCl**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

6.8. Titration of I-RA with Pen_4NCl in acetonitrile

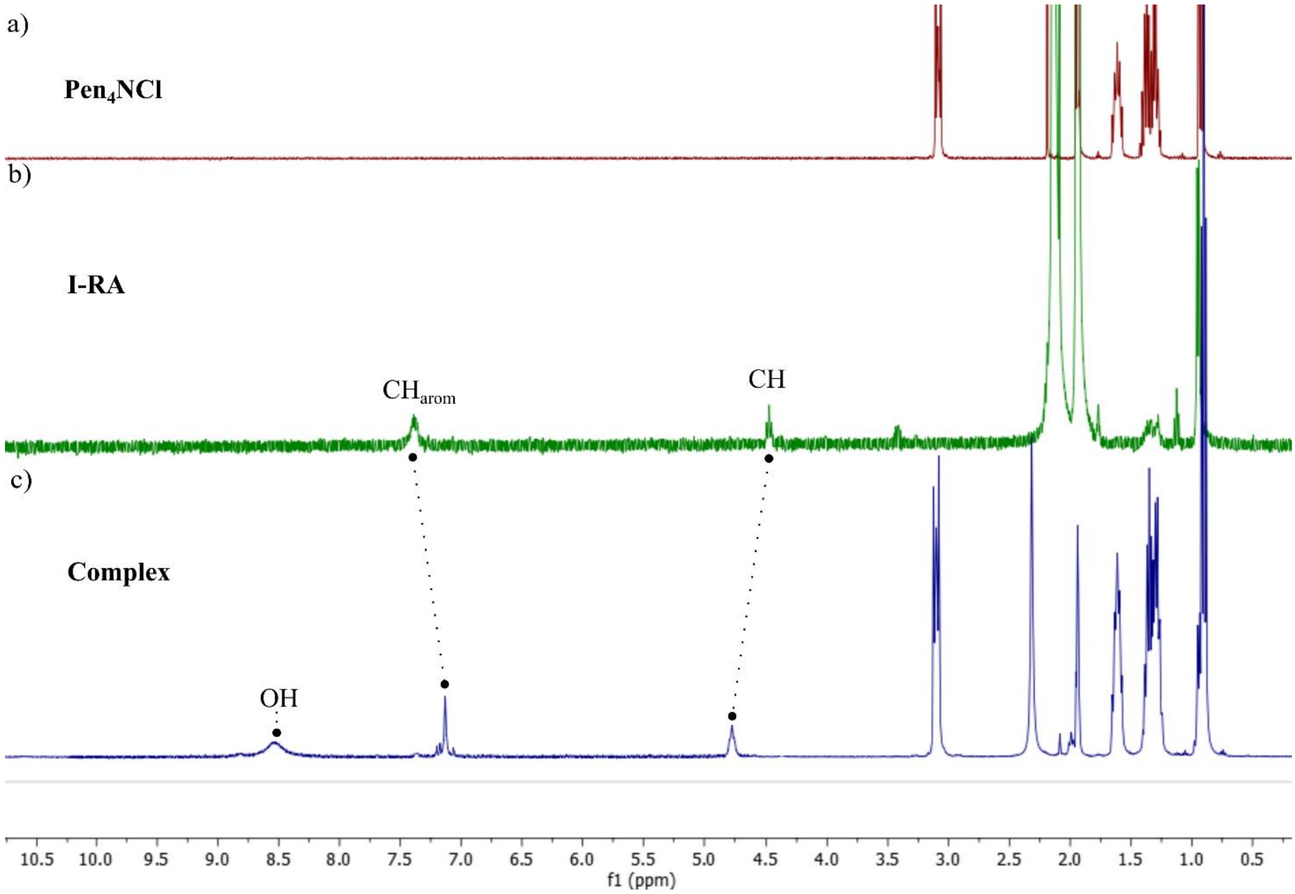
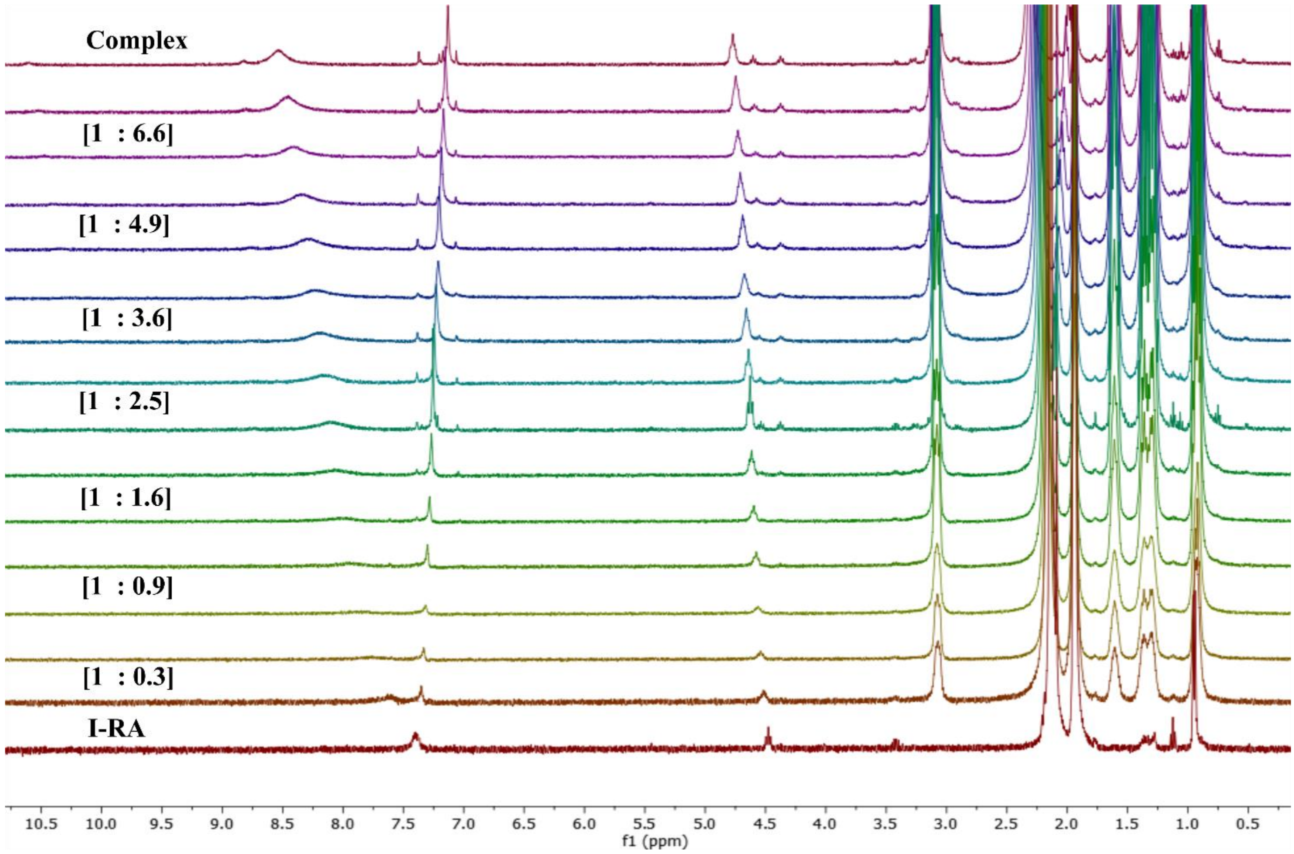


Figure S33. ^{1}H NMR spectra of (a) **Pen_4NCl**; (b) **I-RA**; (c) complex of **I-RA** and **Pen_4NCl** (400 MHz, 303 K, Acetonitrile-d3).


Complex
[1 : 6.6]
[1 : 4.9]
[1 : 3.6]
[1 : 2.5]
[1 : 1.6]
[1 : 0.9]
[1 : 0.3]
I-RA
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

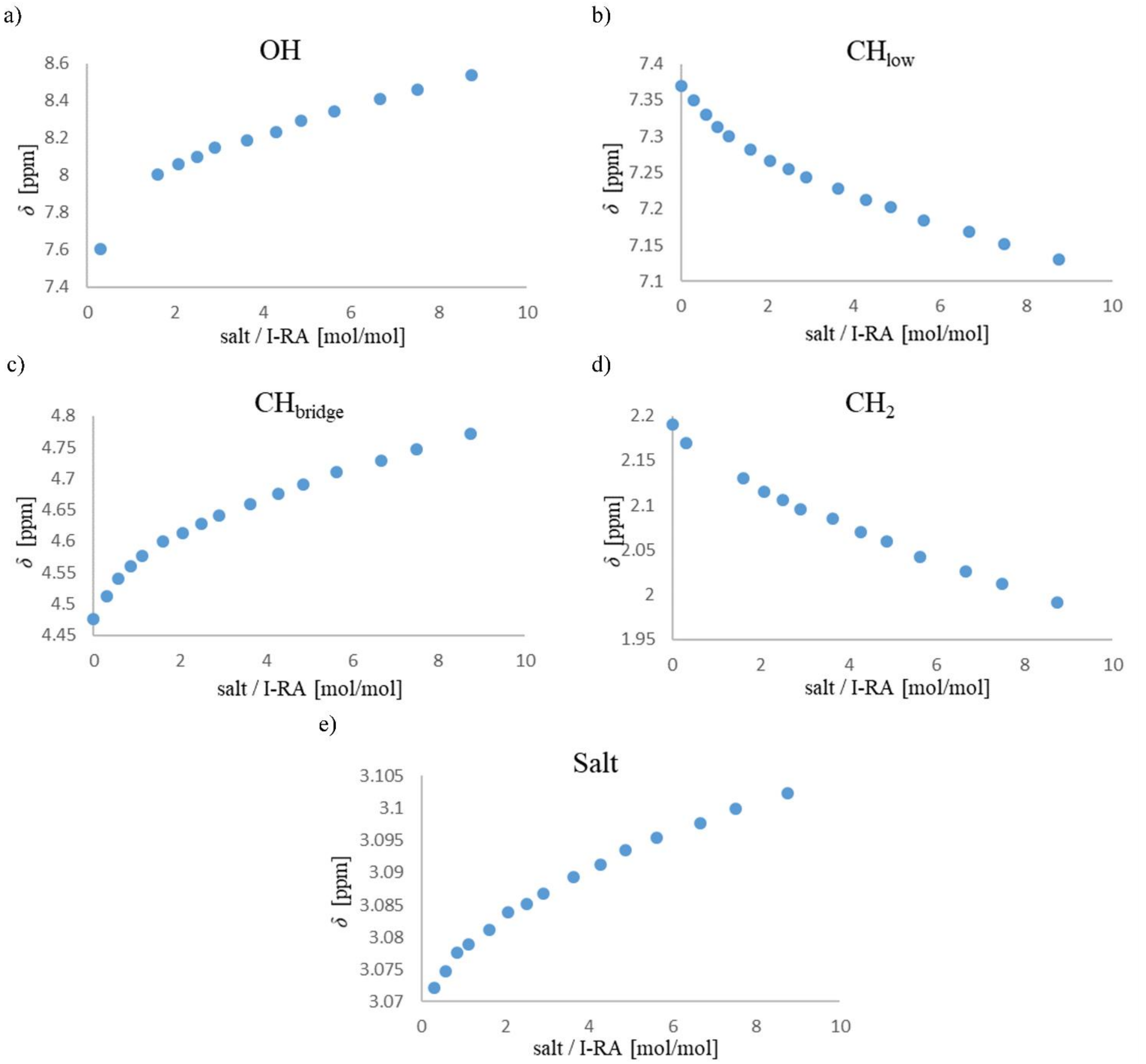


Figure S34. ^{1}H NMR titration curves for titration of **I-RA** with **Pen$_4$NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetonitrile-d3).

6.9. Titration of I-RA with Oct_4NBr in THF

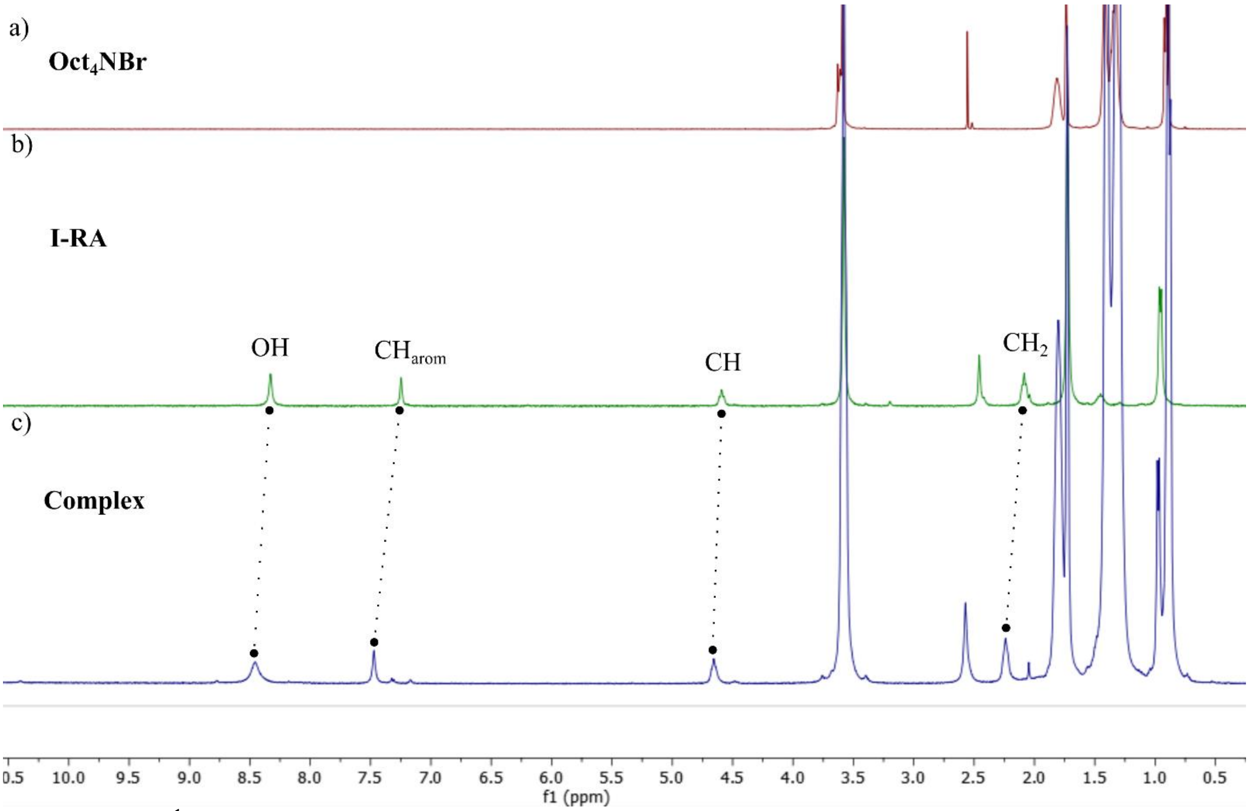
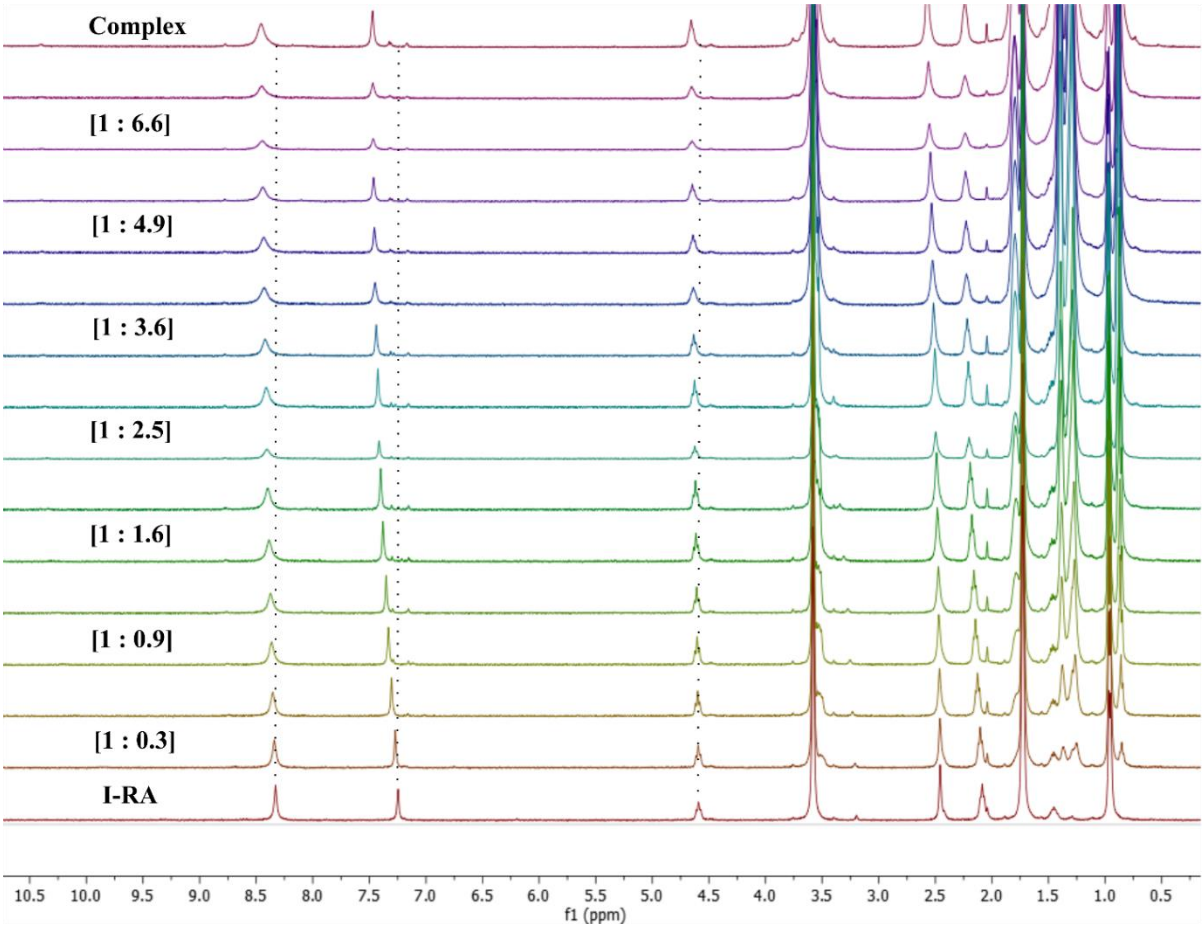


Figure S35. ^{1}H NMR spectra of (a) **Oct_4NBr**; (b) **I-RA**; (c) complex of **I-RA** and **Oct_4NBr** (400 MHz, 303 K, THF-d8).



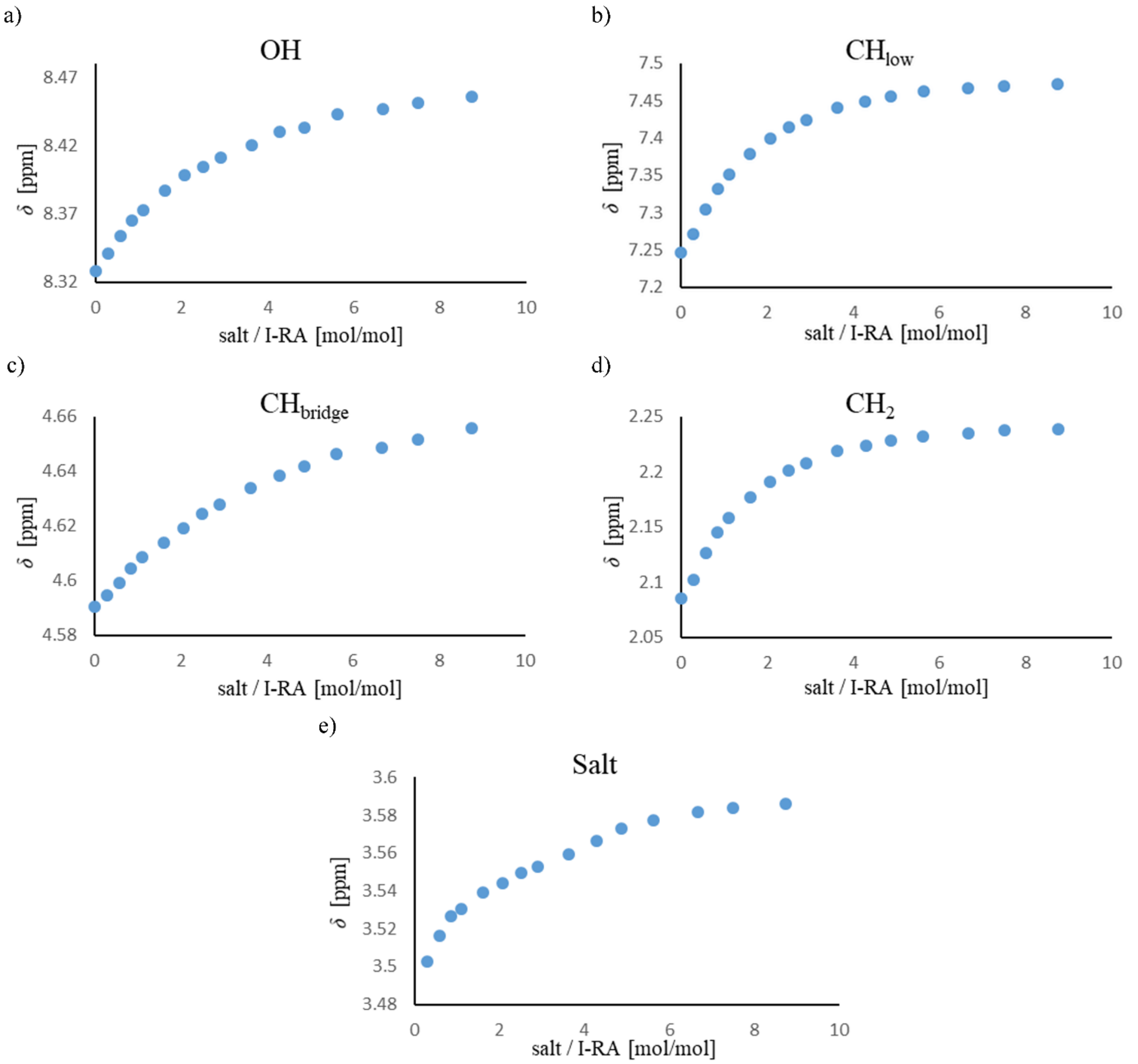


Figure S36. [1]H NMR titration curves for titration of **I-RA** with **Oct₄NBr**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

6.10. Titration of I-RA with Pen_4NBr in THF

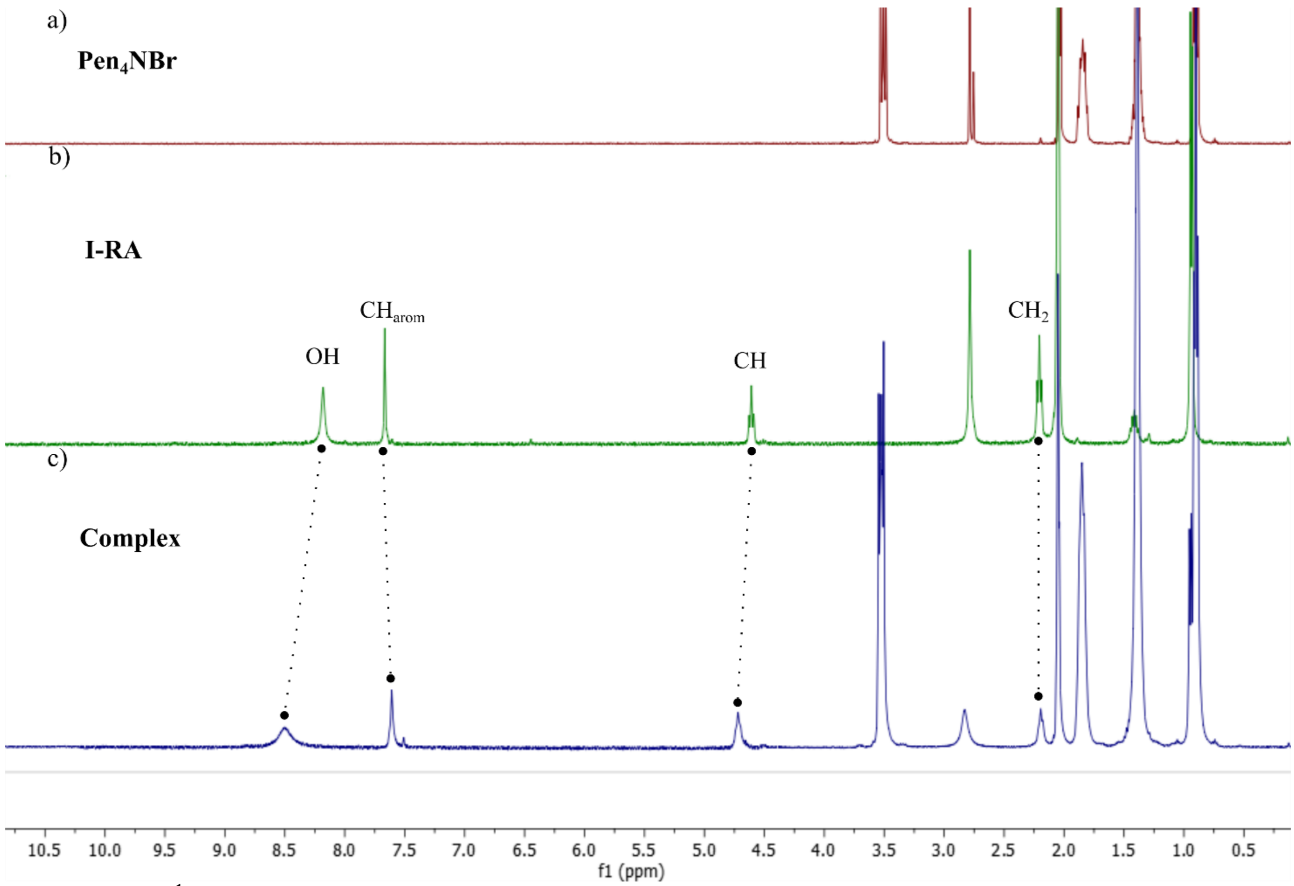
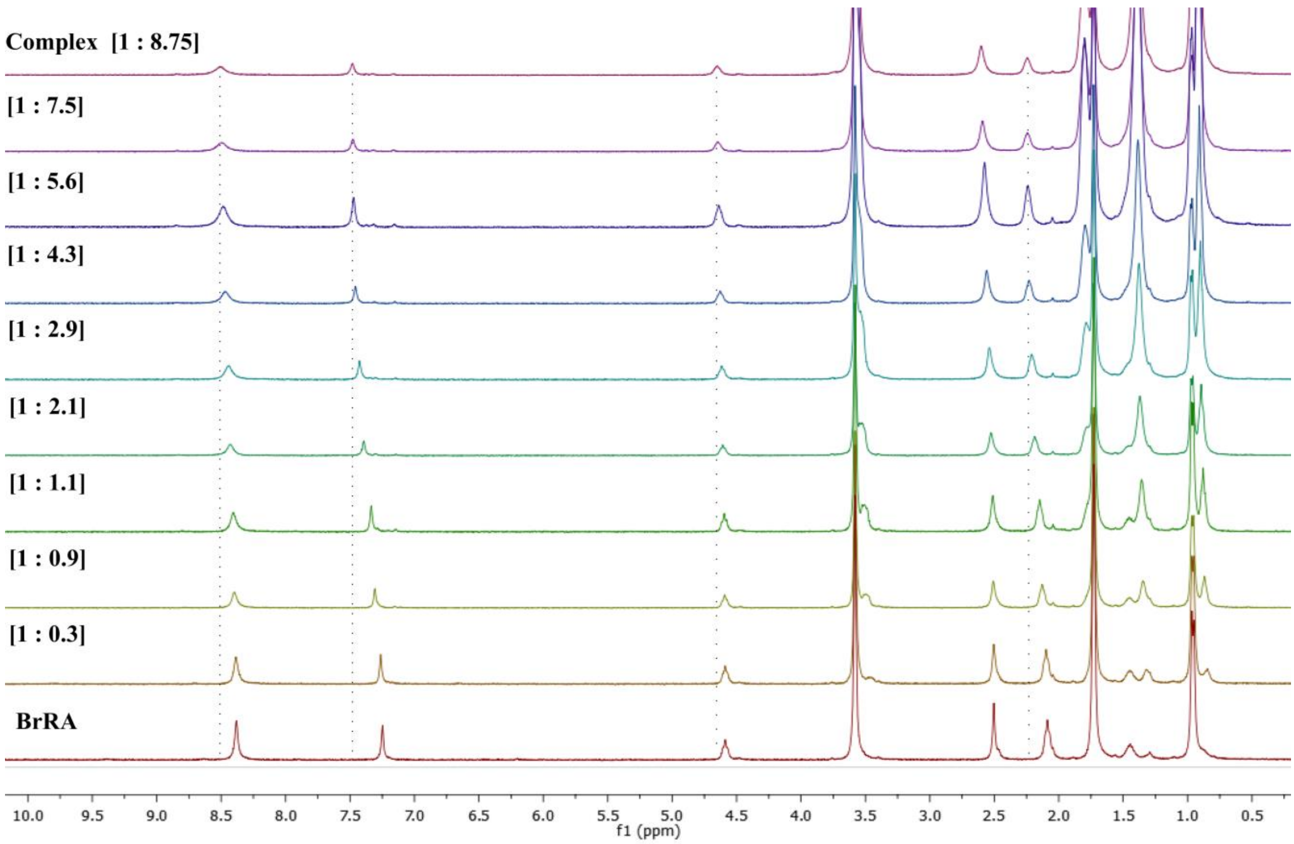


Figure S37. ^{1}H NMR spectra of (a) **Pen_4NBr**; (b) **I-RA**; (c) complex of **I-RA** and **Pen_4NBr** (400 MHz, 303 K, THF-d8).



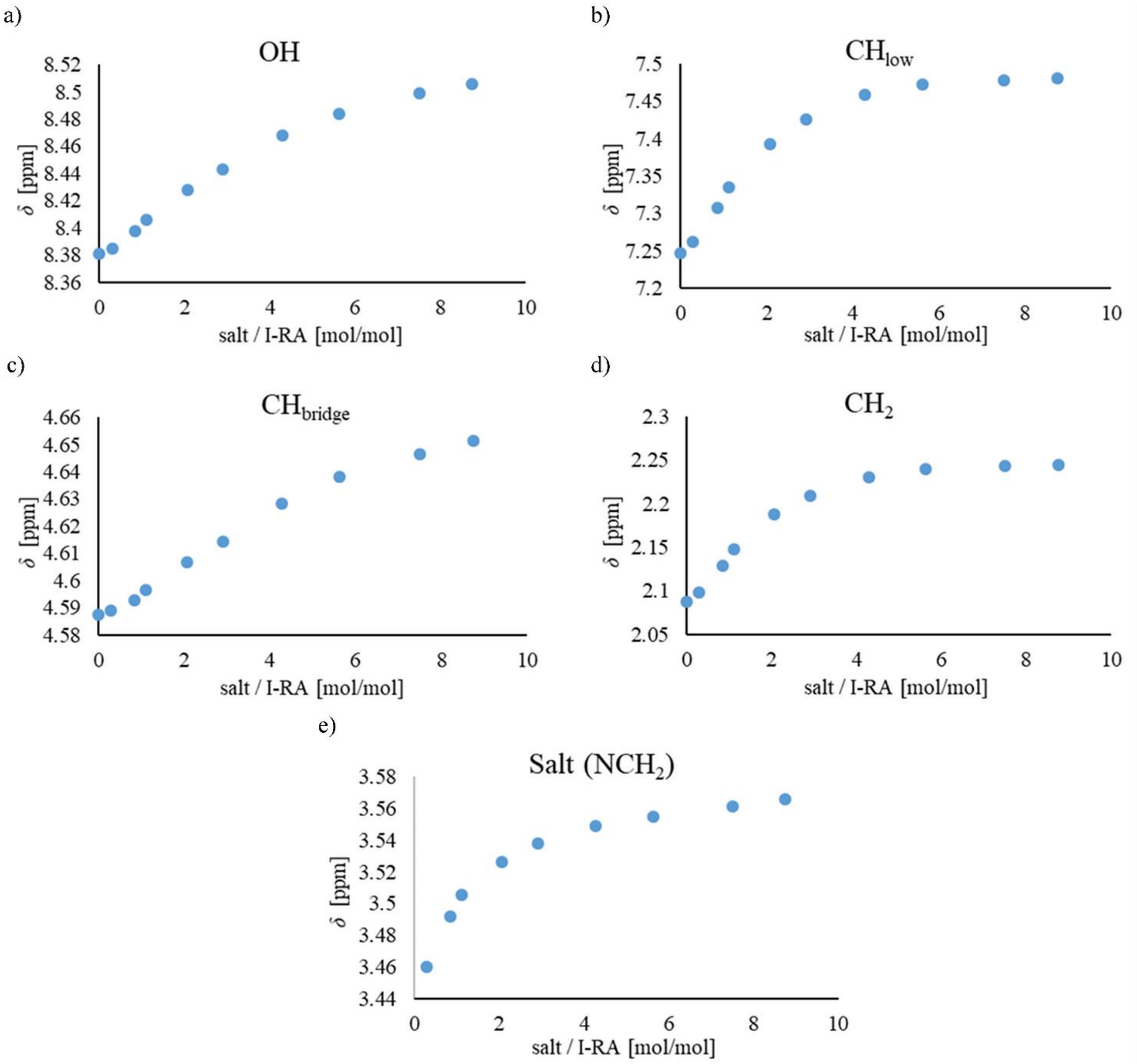
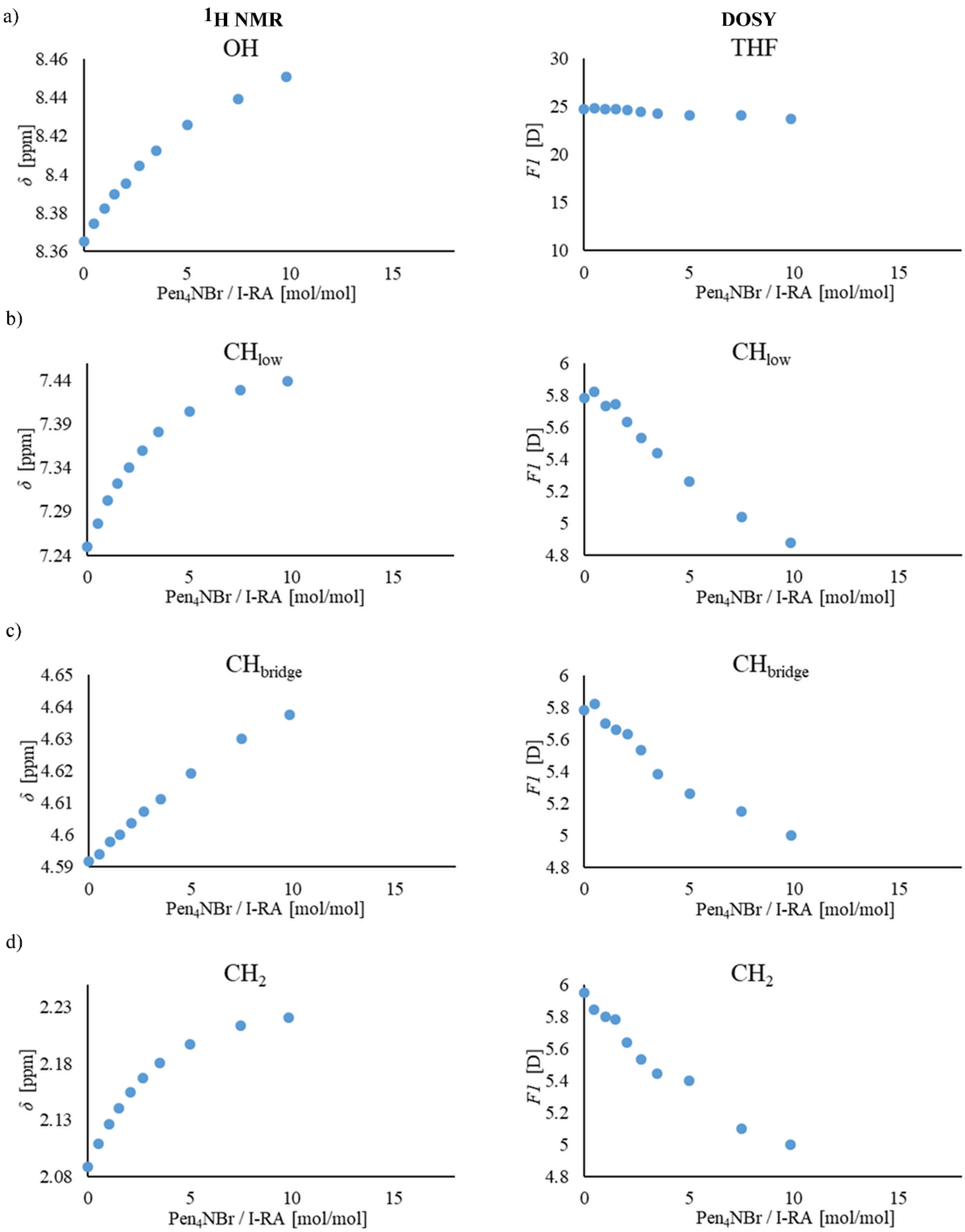


Figure S38. ^{1}H NMR titration curves for titration of **I-RA** with **Pen_4NBr**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

6.11. DOSY titration curves for titration of I-RA with Pen_4NBr in THF



e)

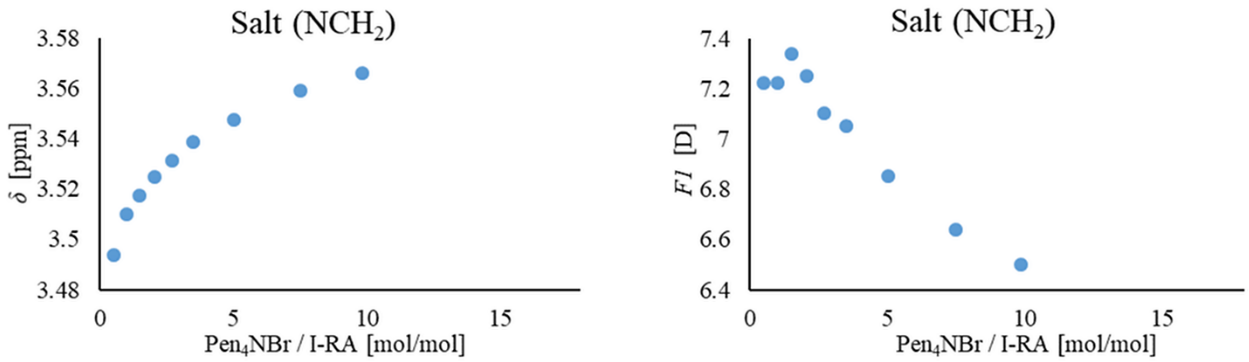
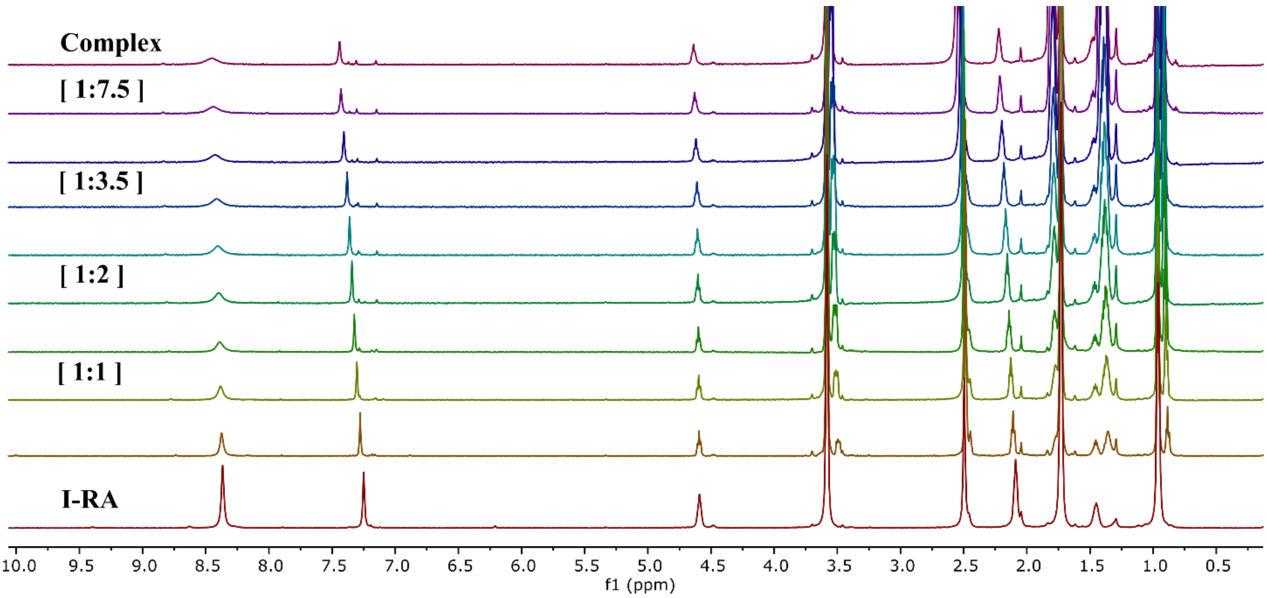


Figure S39. DOSY titration curves for titration of **I-RA** with **Pen4NBr**. [1]H NMR chemical shifts and diffusion coefficient changes for: a) OH and THF signal; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (600 MHz, 303 K, THF-d8).



6.12. Titration of I-RA with Pen_4NBr in acetone

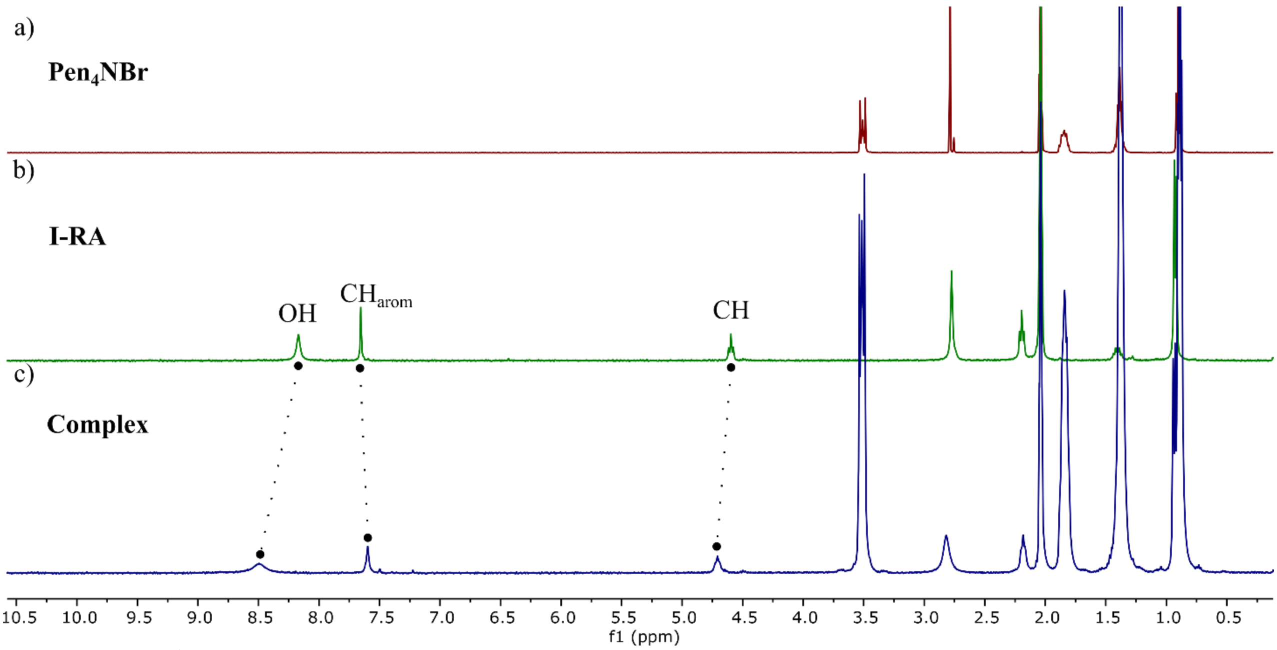
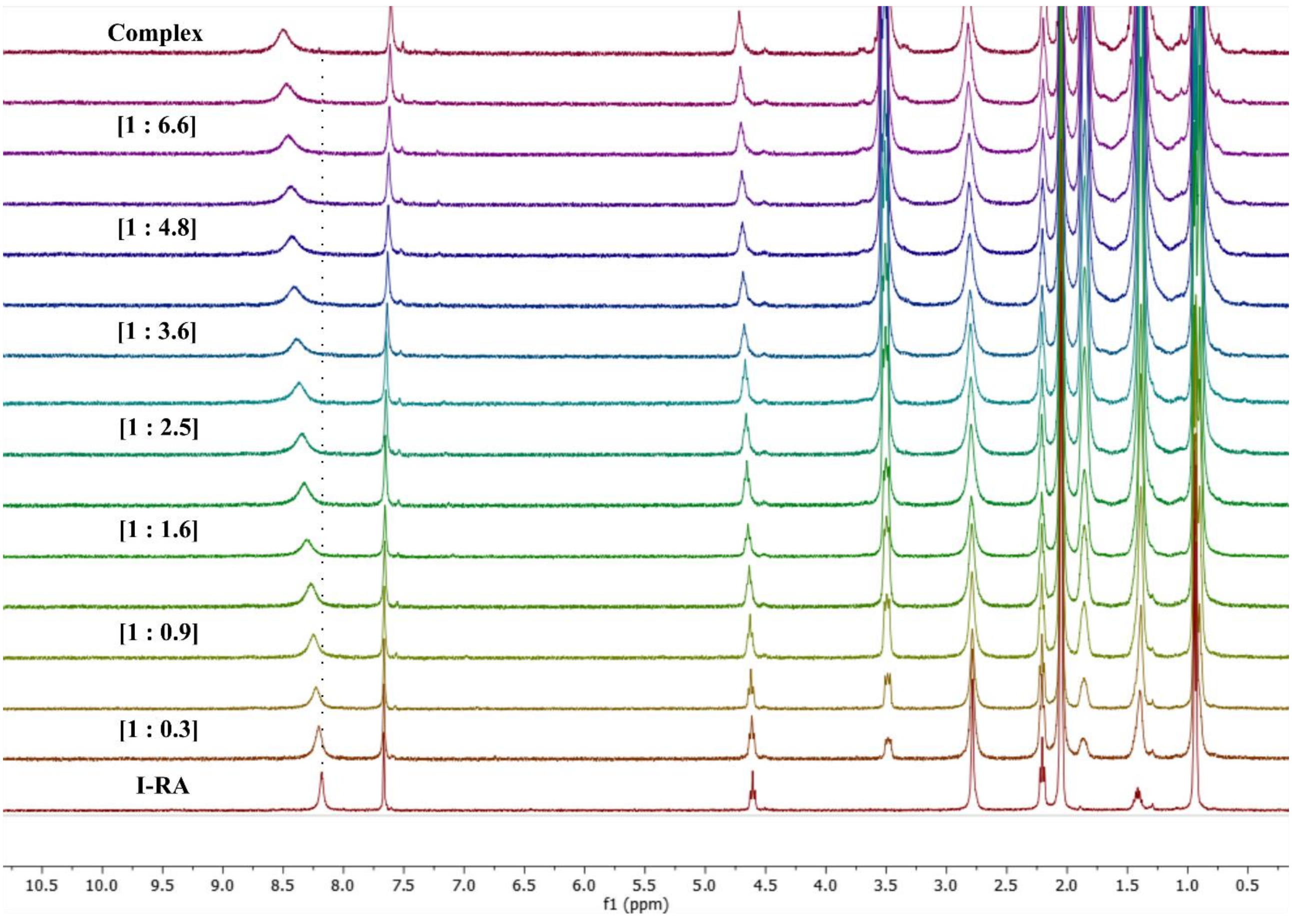


Figure S40. [1]H NMR spectra of (a) **Pen_4NBr**; (b) **I-RA**;(c) complex of **I-RA** and **Pen_4NBr** (400 MHz, 303 K, Acetone-d6).



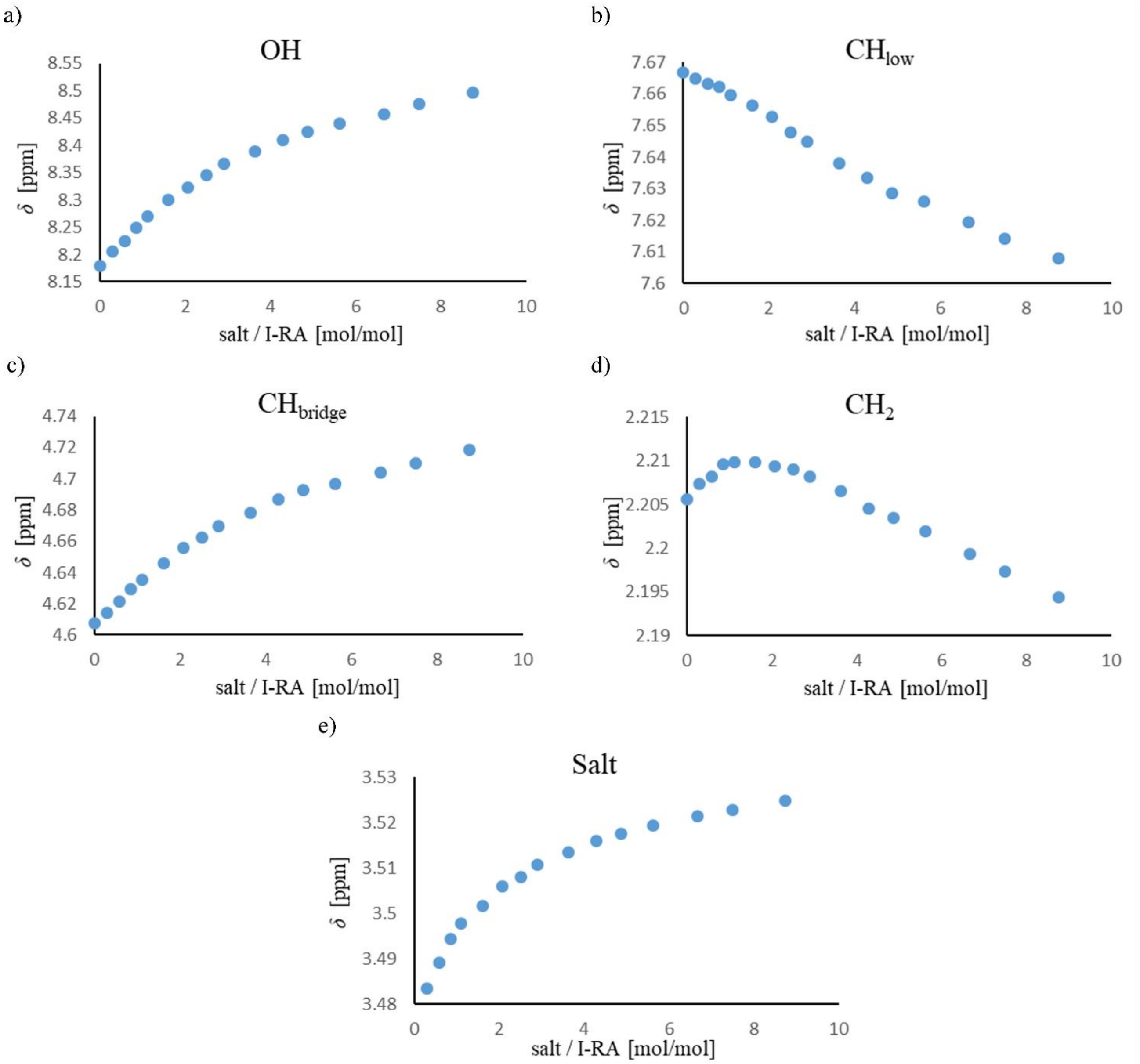


Figure S41. ^{1}H NMR titration curves for titration of **I-RA** with **Pen$_4$NBr**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

7. Titration of H-RA

7.1. Titration of H-RA with Pen_4NCl in THF

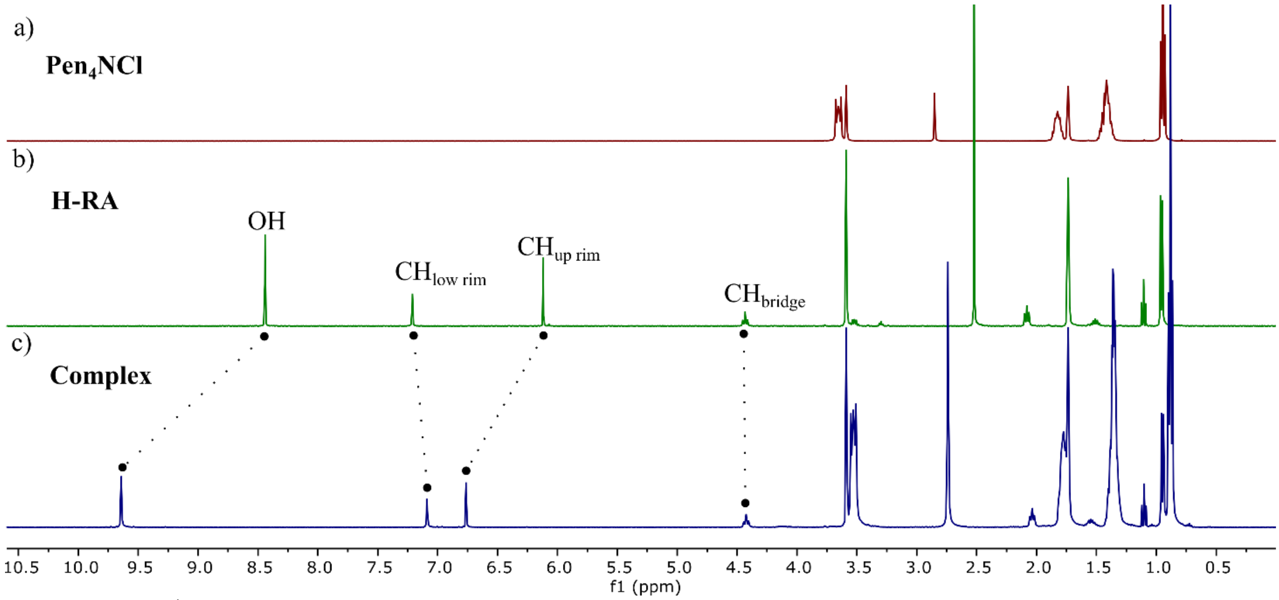
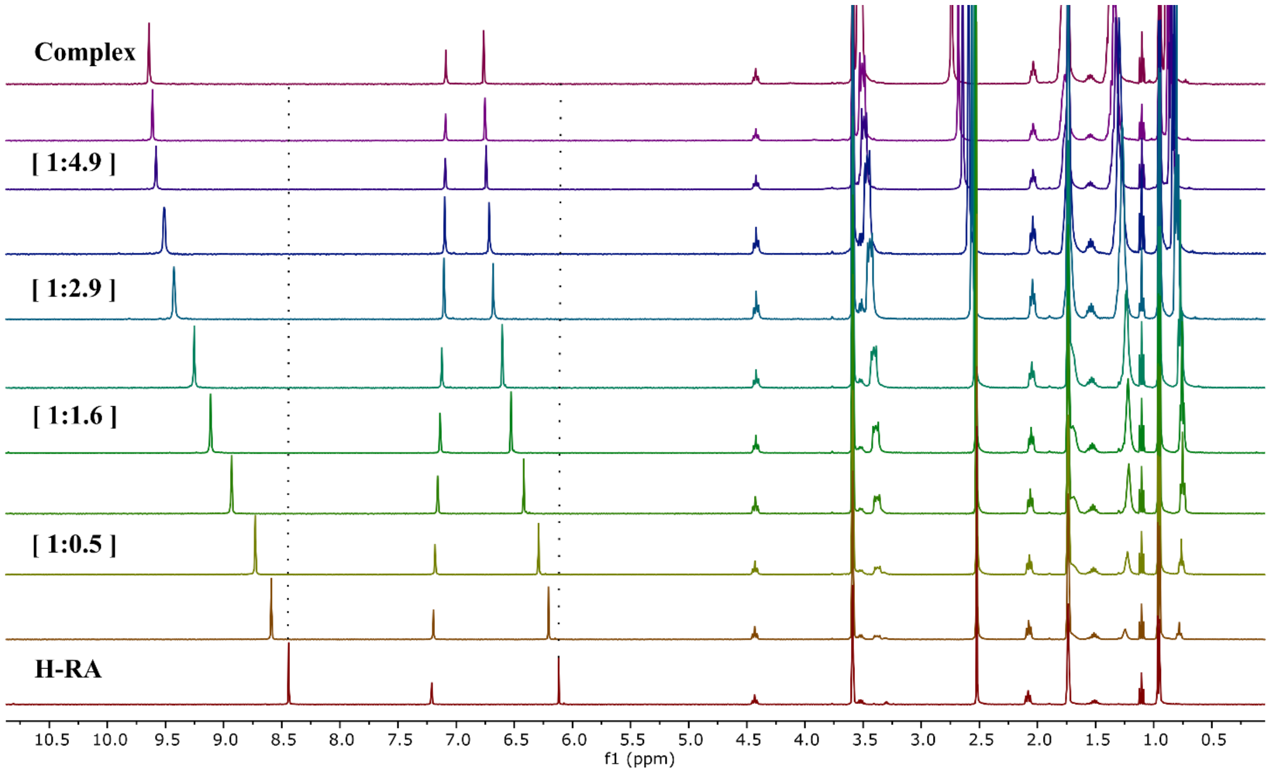


Figure S42. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **H-RA**; (c) complex of **H-RA** and **Pen_4NCl** (400 MHz, 303 K, THF-d8).



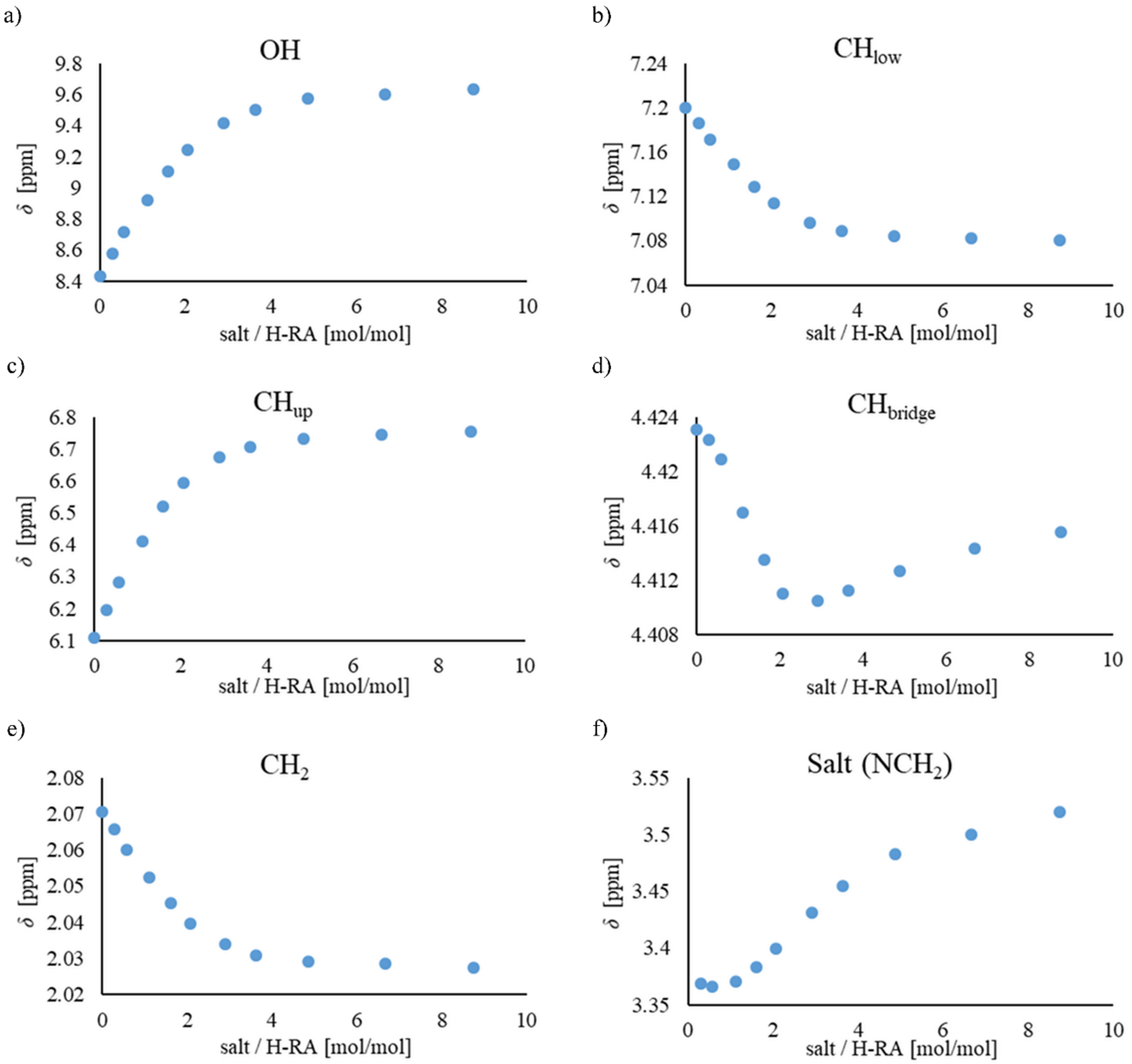


Figure S43. ^{1}H NMR titration curves for titration of **H-RA** with **Pen_4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{up}; (d) CH_{bridge}; (e) CH_2 from lower rim alkyl chain; (f) NCH_2 from salt (400 MHz, 303 K, THF-d8).

7.2. Titration of H-RA with Pen_4NCl in acetone

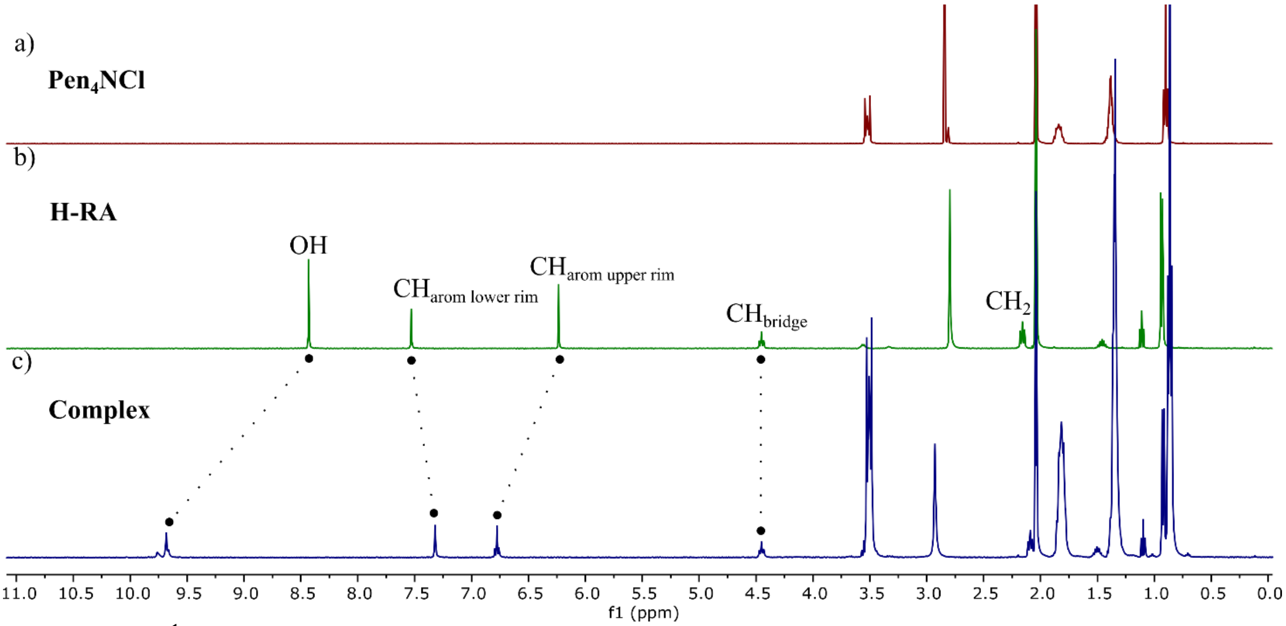
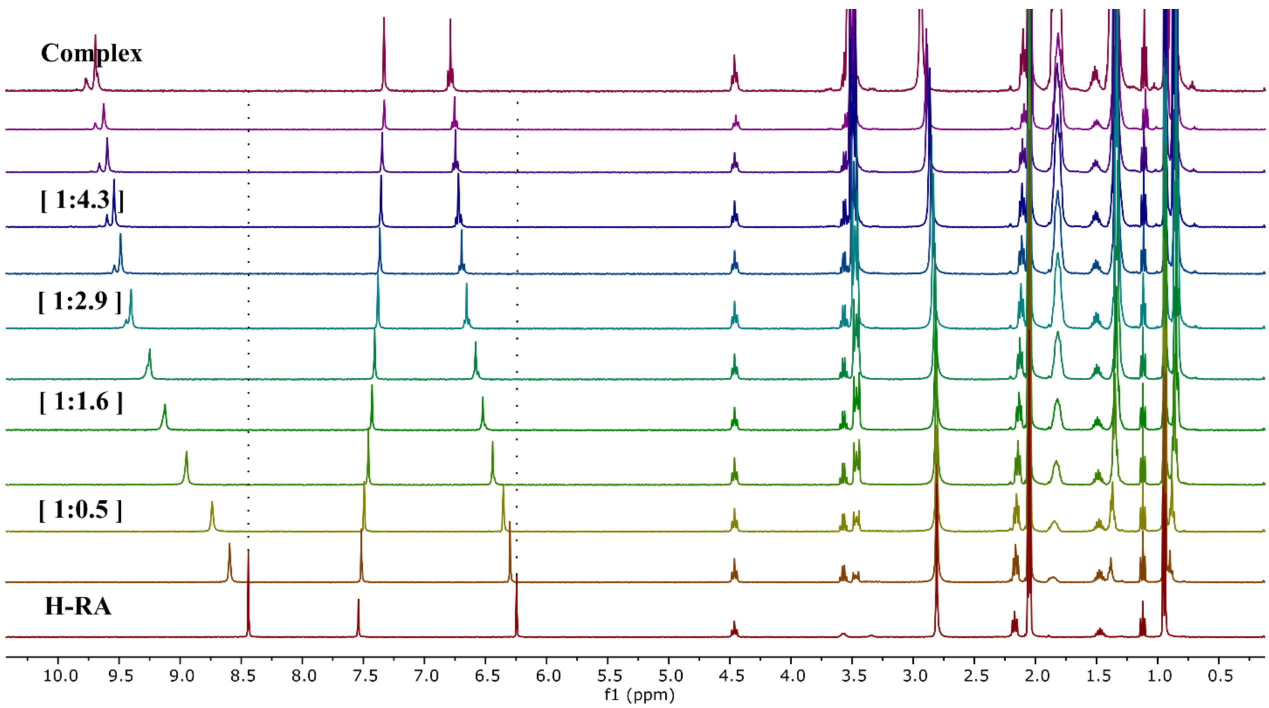


Figure S44. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **H-RA**; (c) complex of **H-RA** and **Pen_4NCl** (400 MHz, 303 K, Acetone-d6).



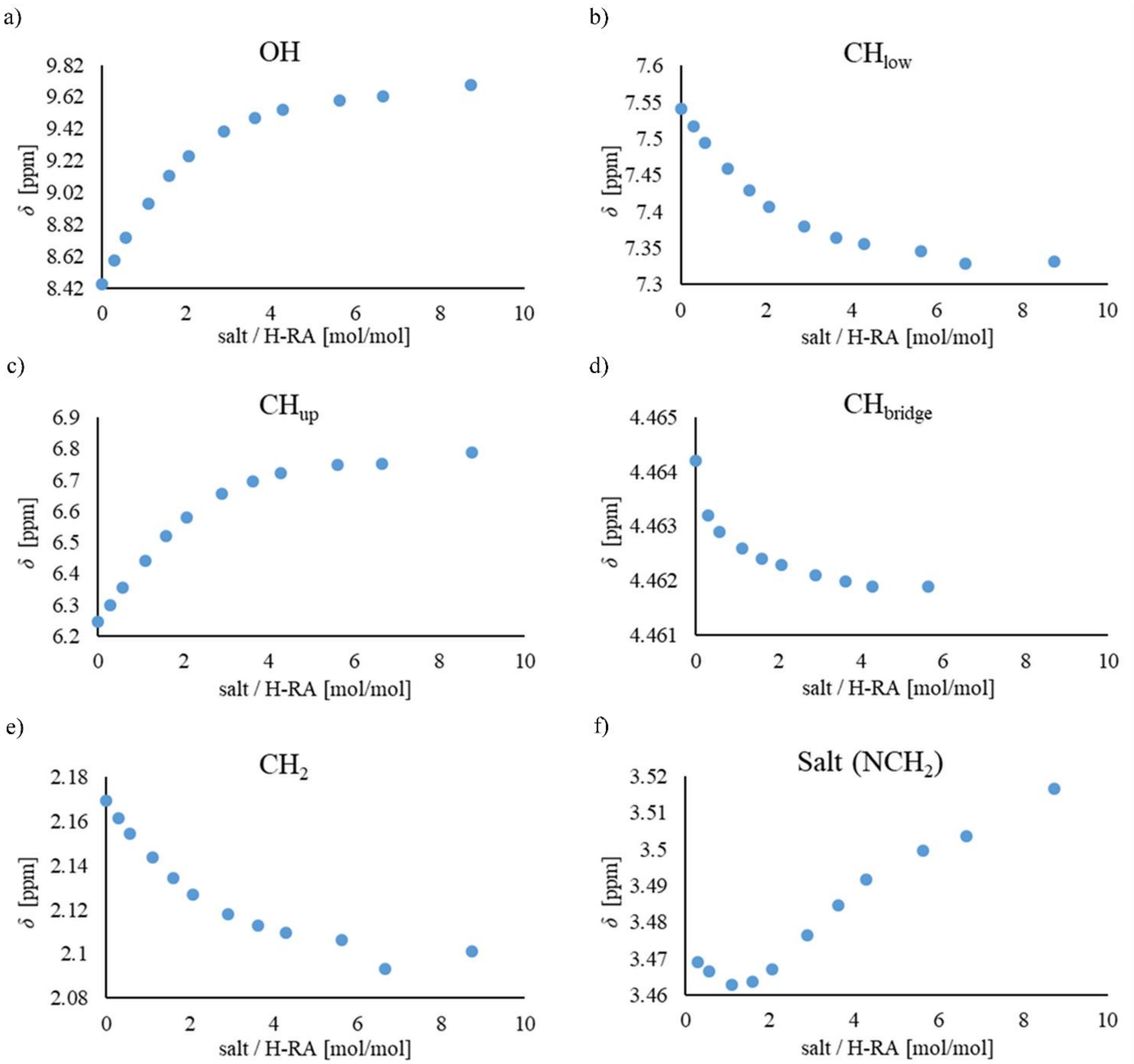


Figure S45. ^{1}H NMR titration curves for titration of **H-RA** with **Pen$_4$NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{up}; (d) CH_{bridge}; (e) CH_2 from lower rim alkyl chain; (f) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

8. Titrations of O-RA

8.1. Titration of O-RA with Pen_4NCl in THF

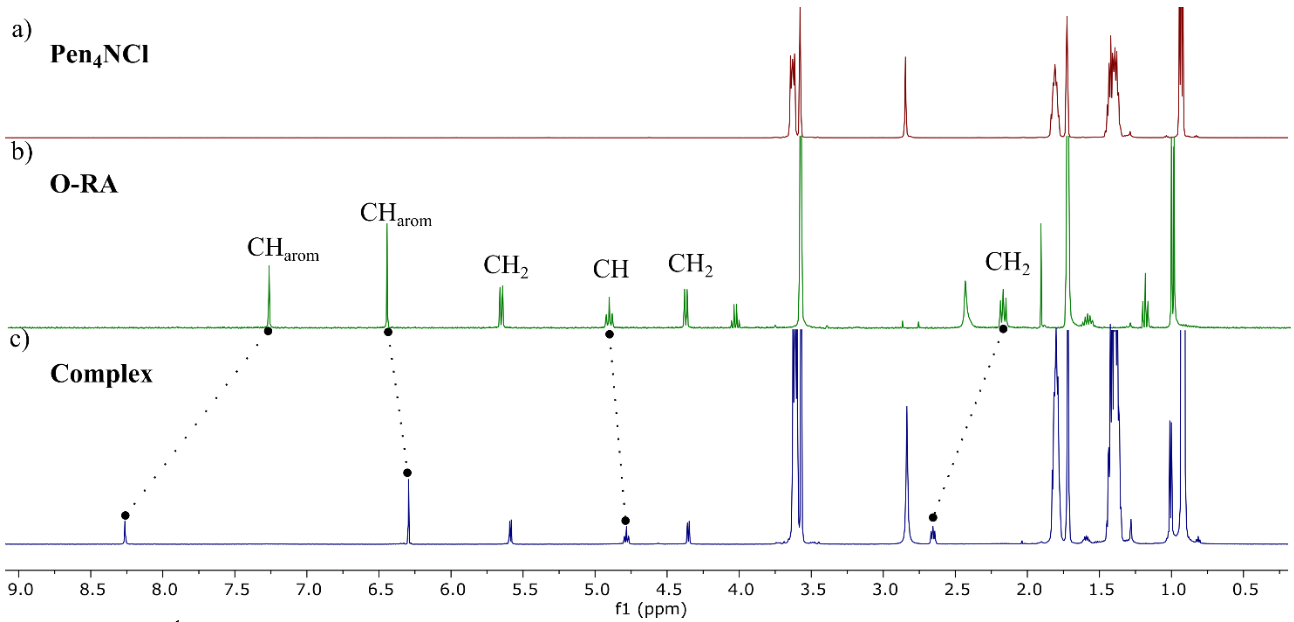
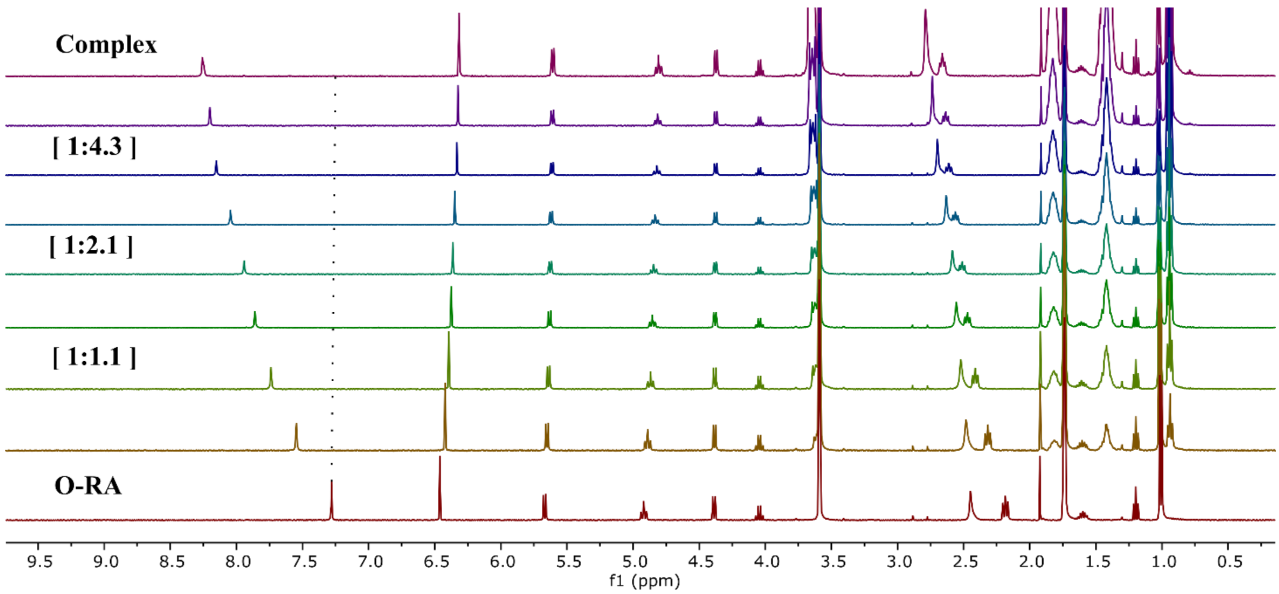


Figure S46. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **O-RA**; (c) complex of **O-RA** and **Pen_4NCl** (400 MHz, 303 K, THF-d8).



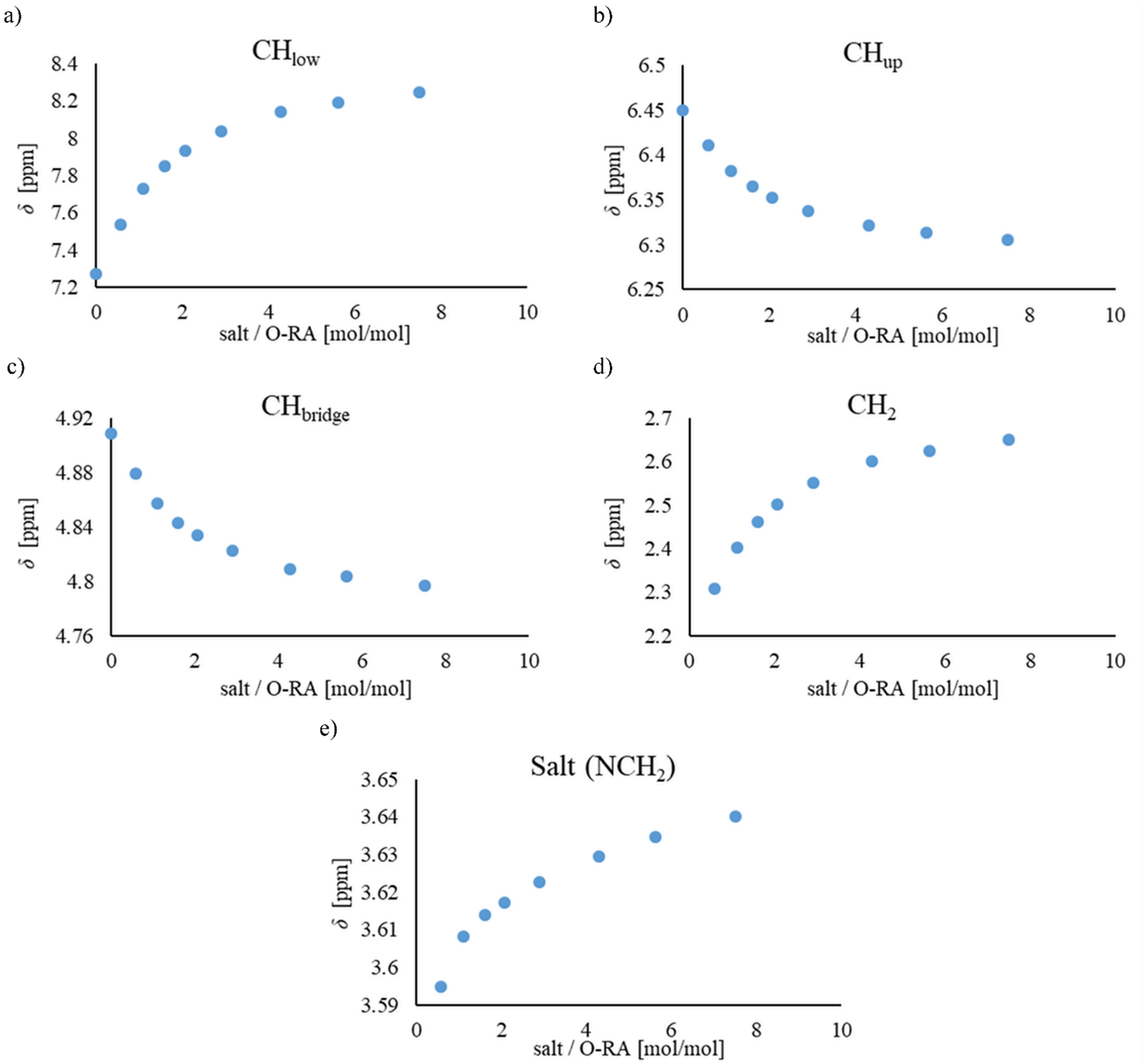
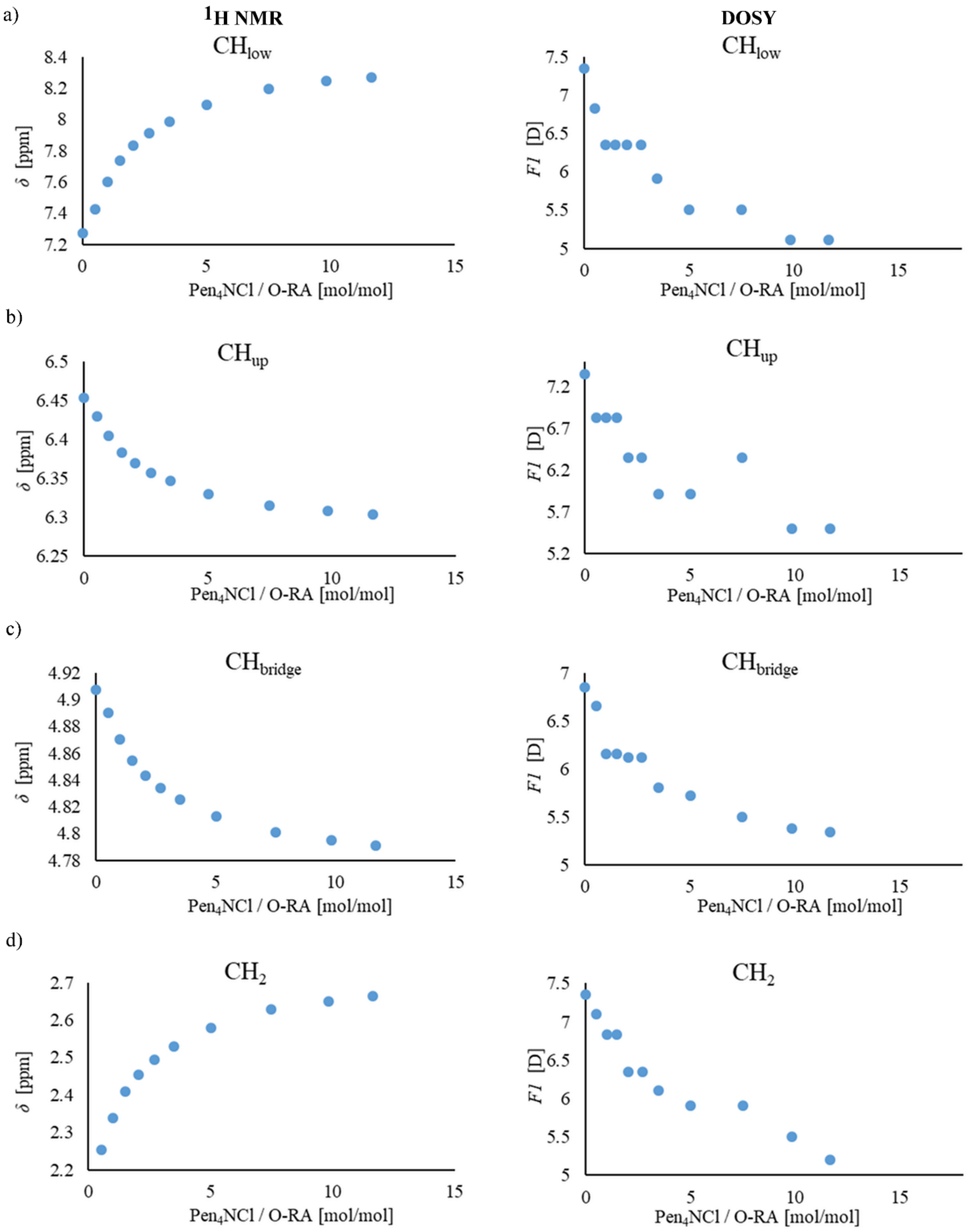


Figure S47. ^{1}H NMR titration curves for titration of **O-RA** with **Pen$_4$NCl**. ^{1}H NMR chemical shifts change for: (a) CH$_{low}$; (b) CH$_{up}$; (c) CH$_{bridge}$; (d) CH$_2$ from lower rim alkyl chain; (e) NCH$_2$ from salt (400 MHz, 303 K, THF-d8).

8.2. DOSY titration curves for titration of O-RA with Pen_4NCl in THF



e)

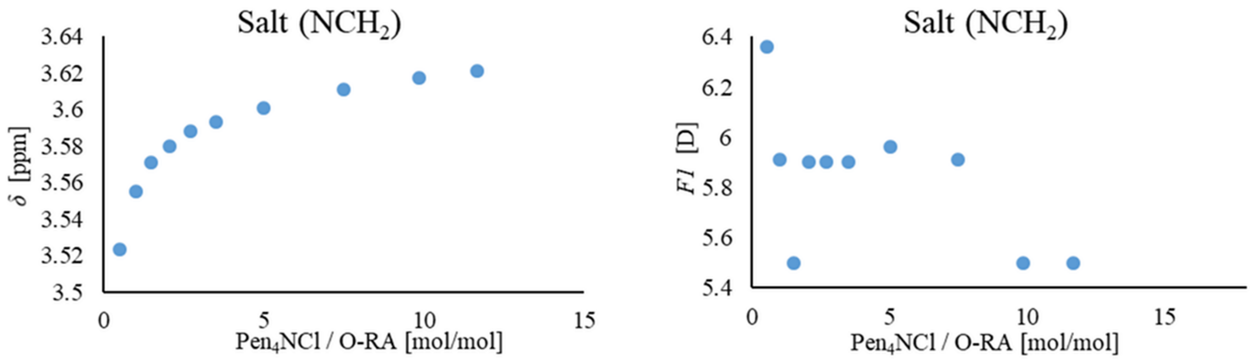
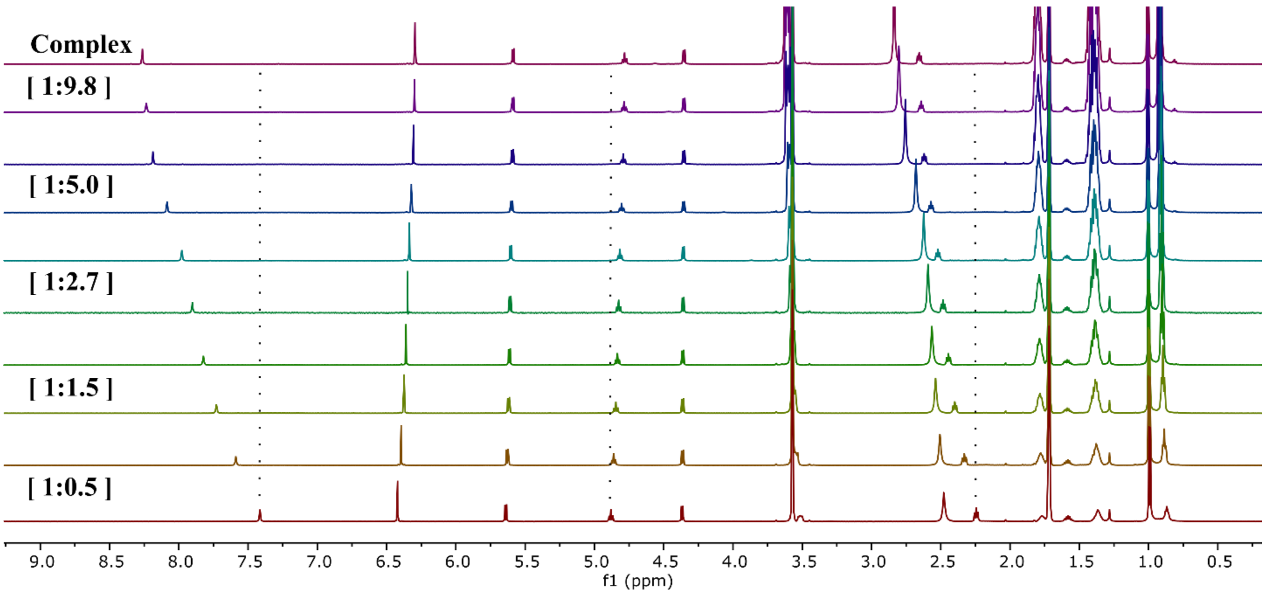


Figure S48. DOSY titration curves for titration of **O-RA** with **Pen4NCl**. [1]H NMR chemical shifts and diffusion coefficient changes for: (a) CH_{low}; (b) CH_{up}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (600 MHz, 303 K, THF-d8).



8.3. Titration of O-RA with Pen_4NBr in THF

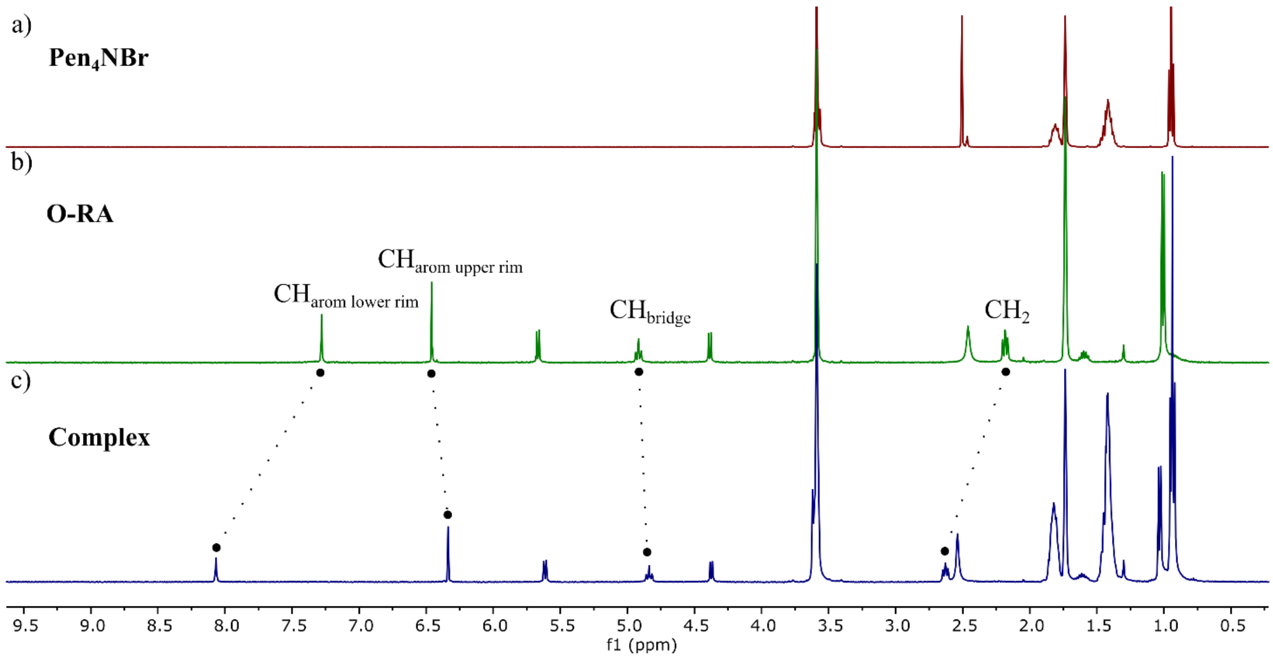
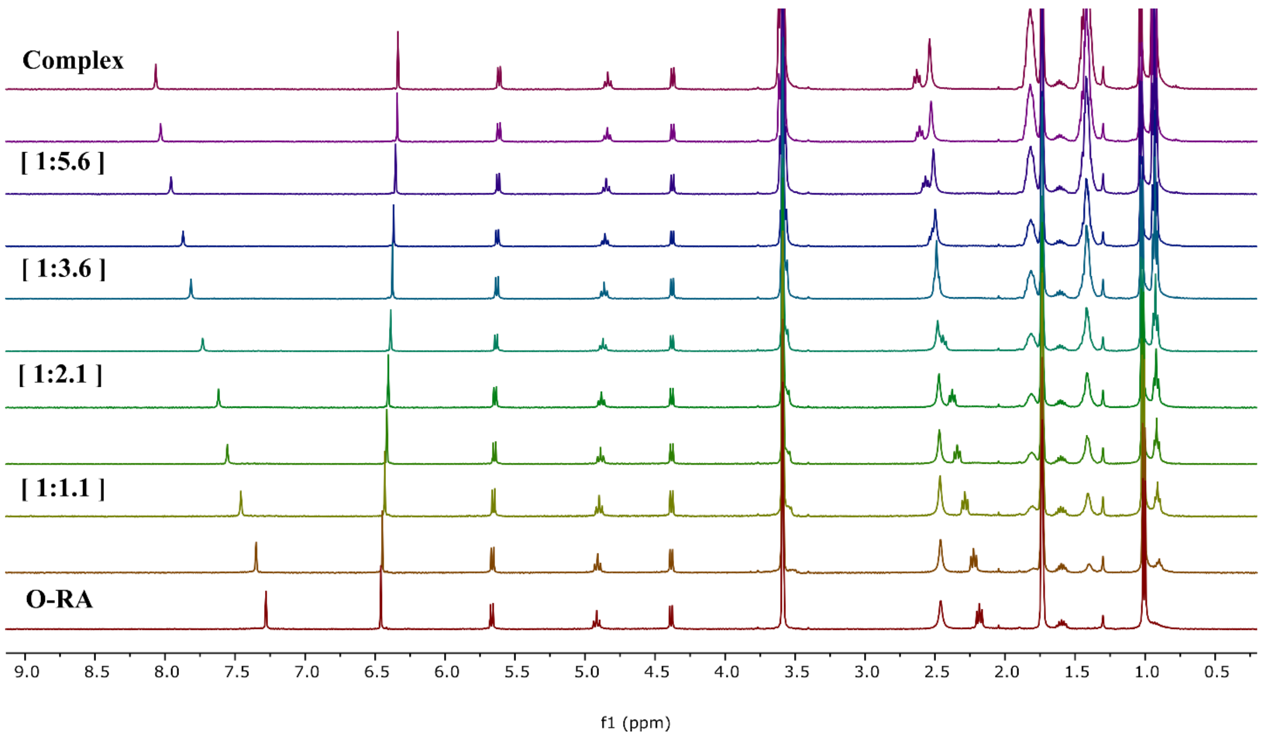


Figure S49. ^{1}H NMR spectra of (a) **Pen_4NBr**; (b) **O-RA**; (c) complex of **O-RA** and **Pen_4NBr** (400 MHz, 303 K, THF-d8).



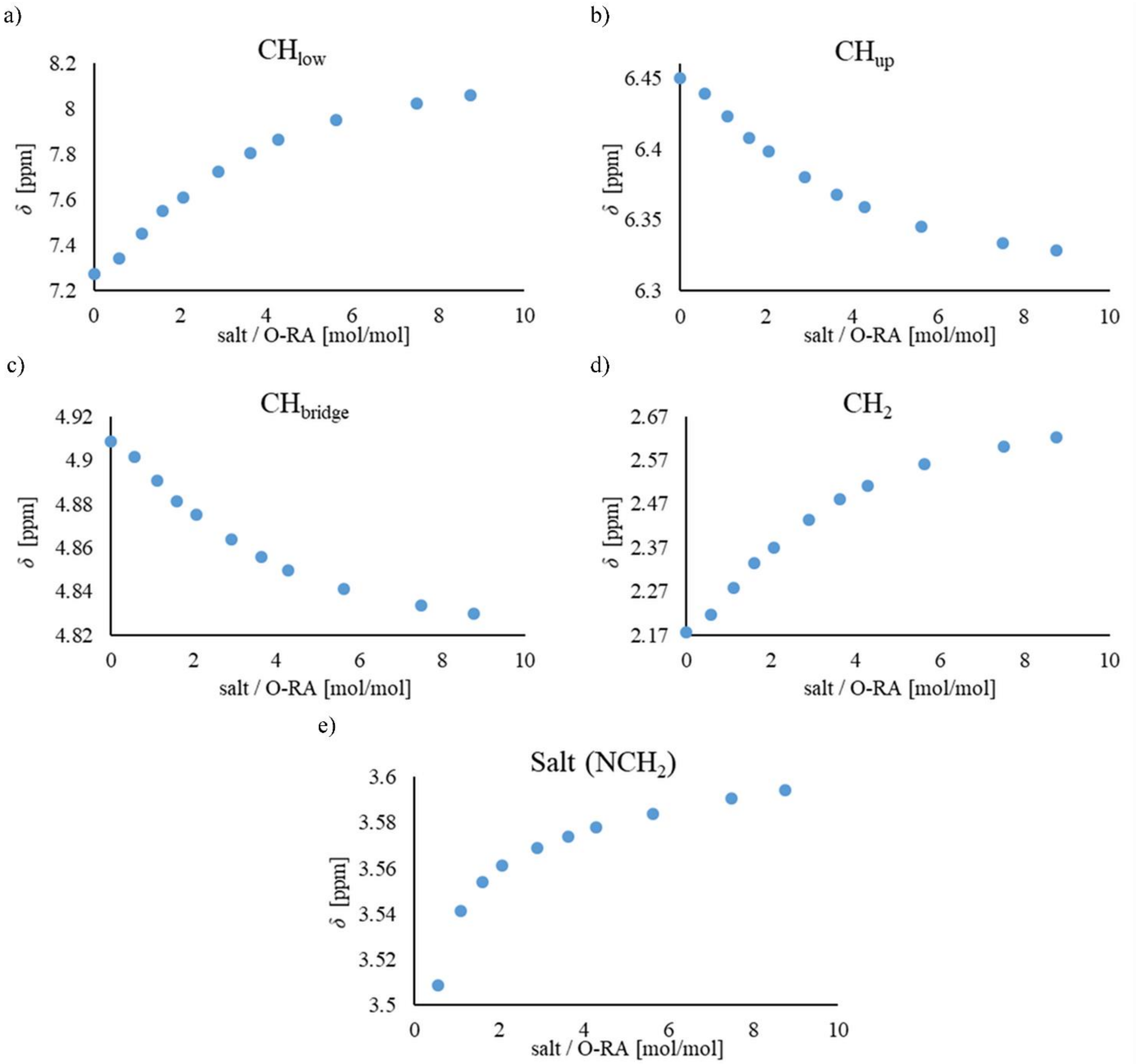


Figure S50. ^{1}H NMR titration curves for titration of **O-RA** with **Pen$_4$NBr**. ^{1}H NMR chemical shifts change for: (a) CH_{low}; (b) CH_{up}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

8.4. Titration of O-RA with Pen_4NCl in acetone

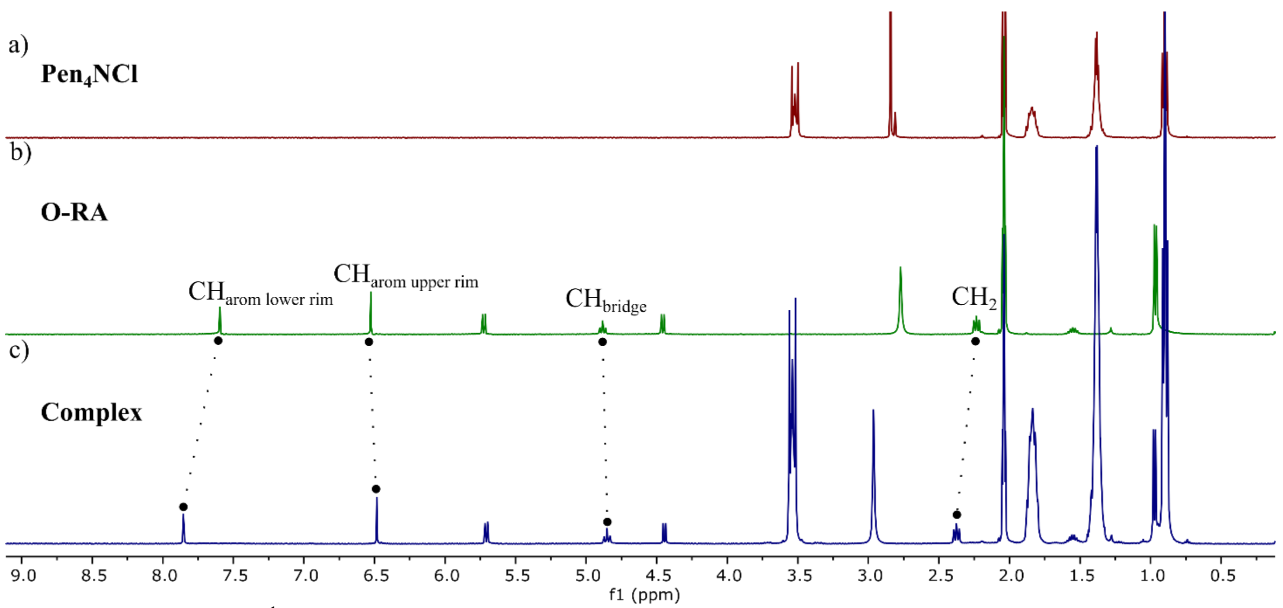
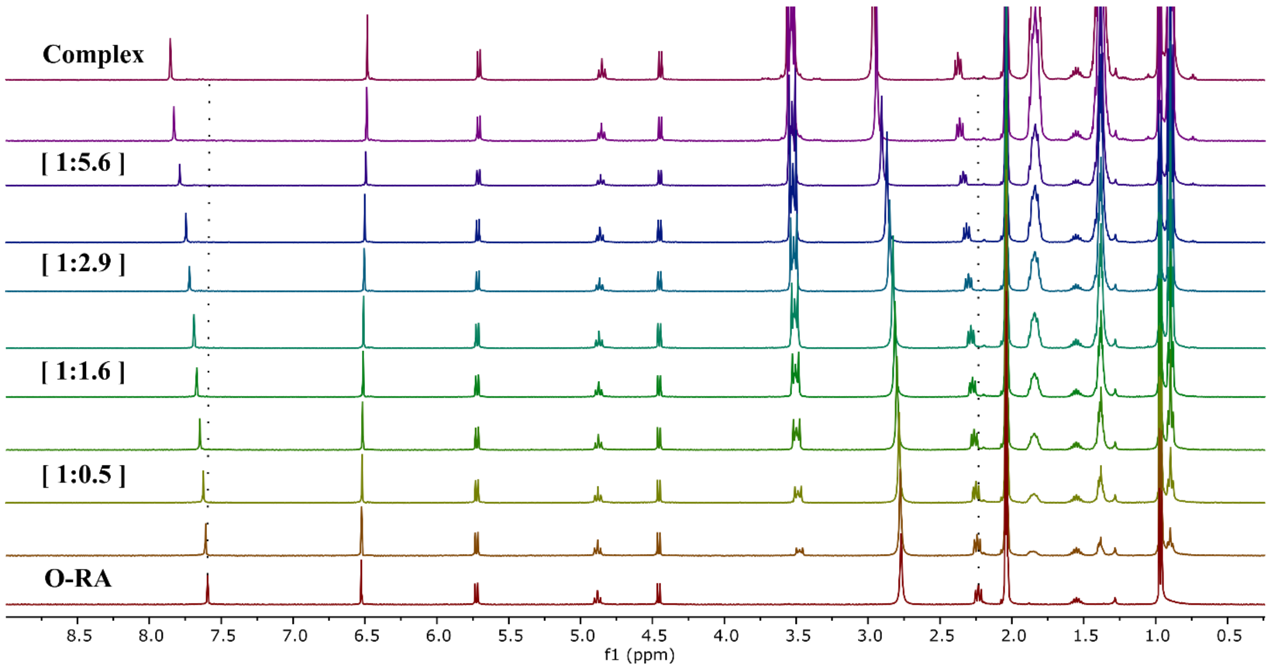


Figure S51. [1]H NMR spectra of (a) **Pen_4NCl**; (b) **O-RA**; (c) complex **O-RA** and **Pen_4NCl** (400 MHz, 303 K, Acetone-d6).



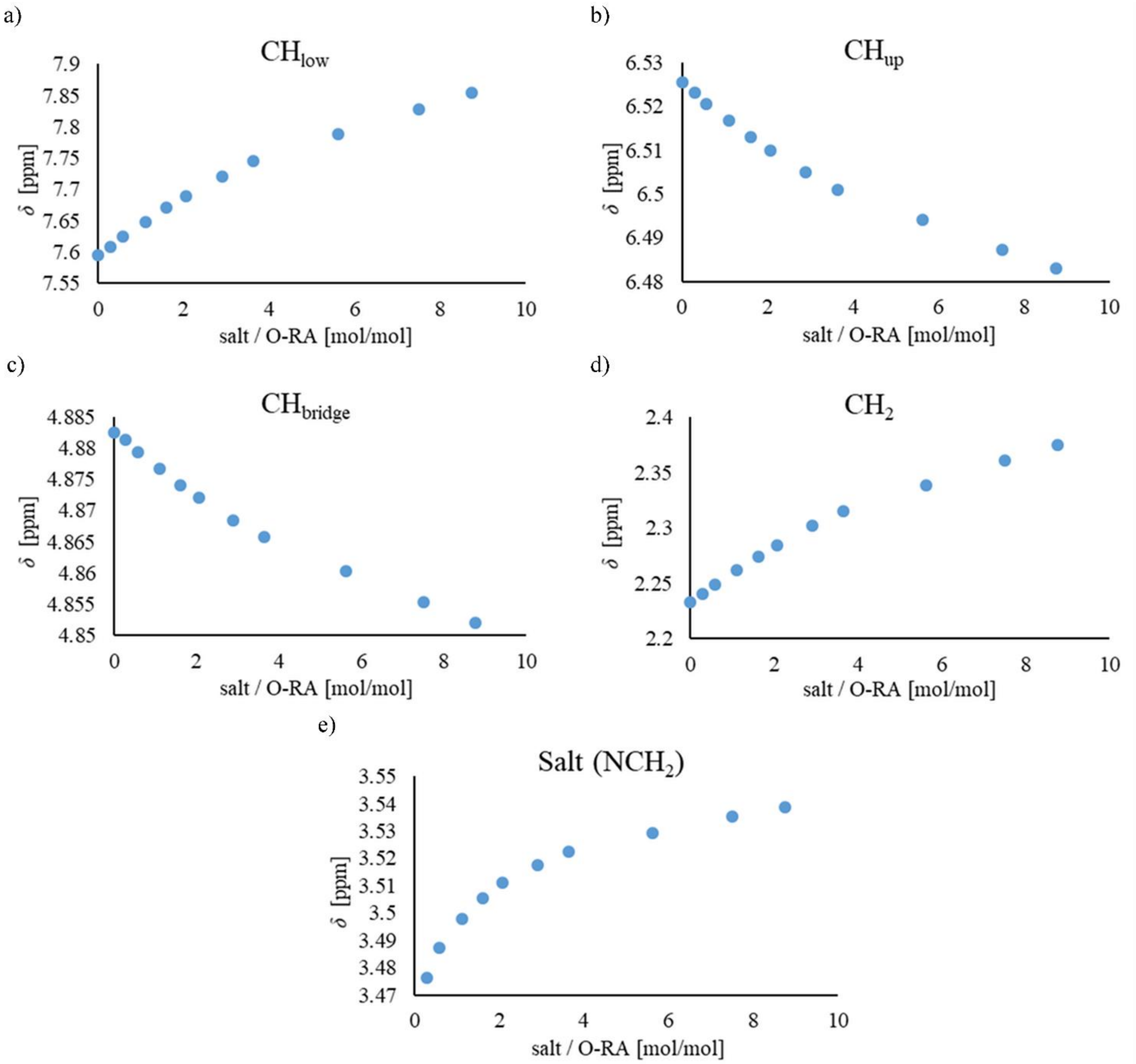


Figure S52. [1]H NMR titration curves for titration of **H-RA** with **Pen_4NCl**. [1]H NMR chemical shifts change for: (a) CH_{low}; (b) CH_{up}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, Acetone-d6).

9. Competitive titrations

9.1. Titration of H-RA+Br-RA with Pen_4NCl in THF

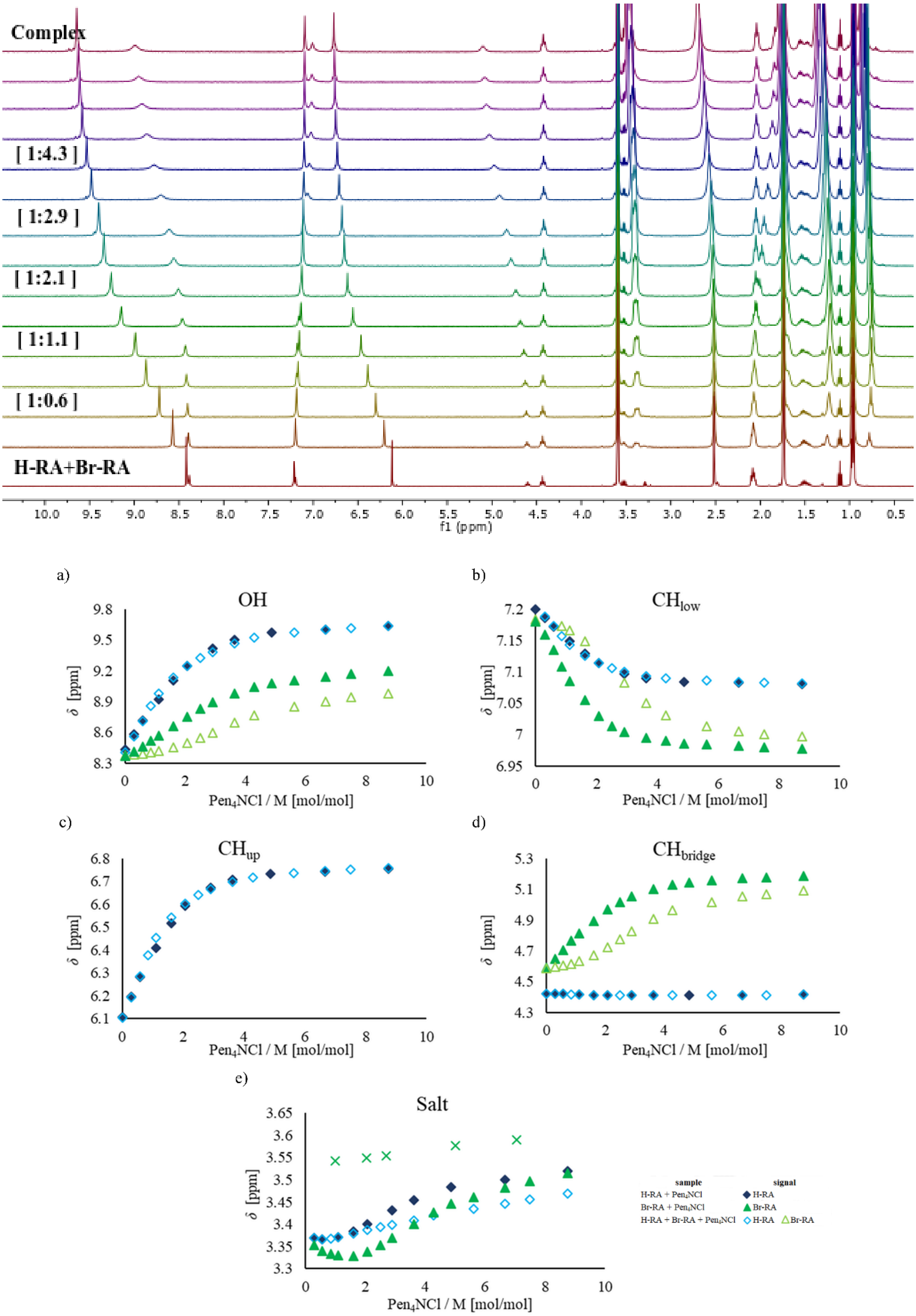


Figure S53. ^{1}H NMR titration curves for titration of **H-RA + Br-RA** with **Pen_4NCl**. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{up}; (d) CH_{bridge}; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

9.2. Titration of O-RA+Br-RA with Pen_4NCl in THF

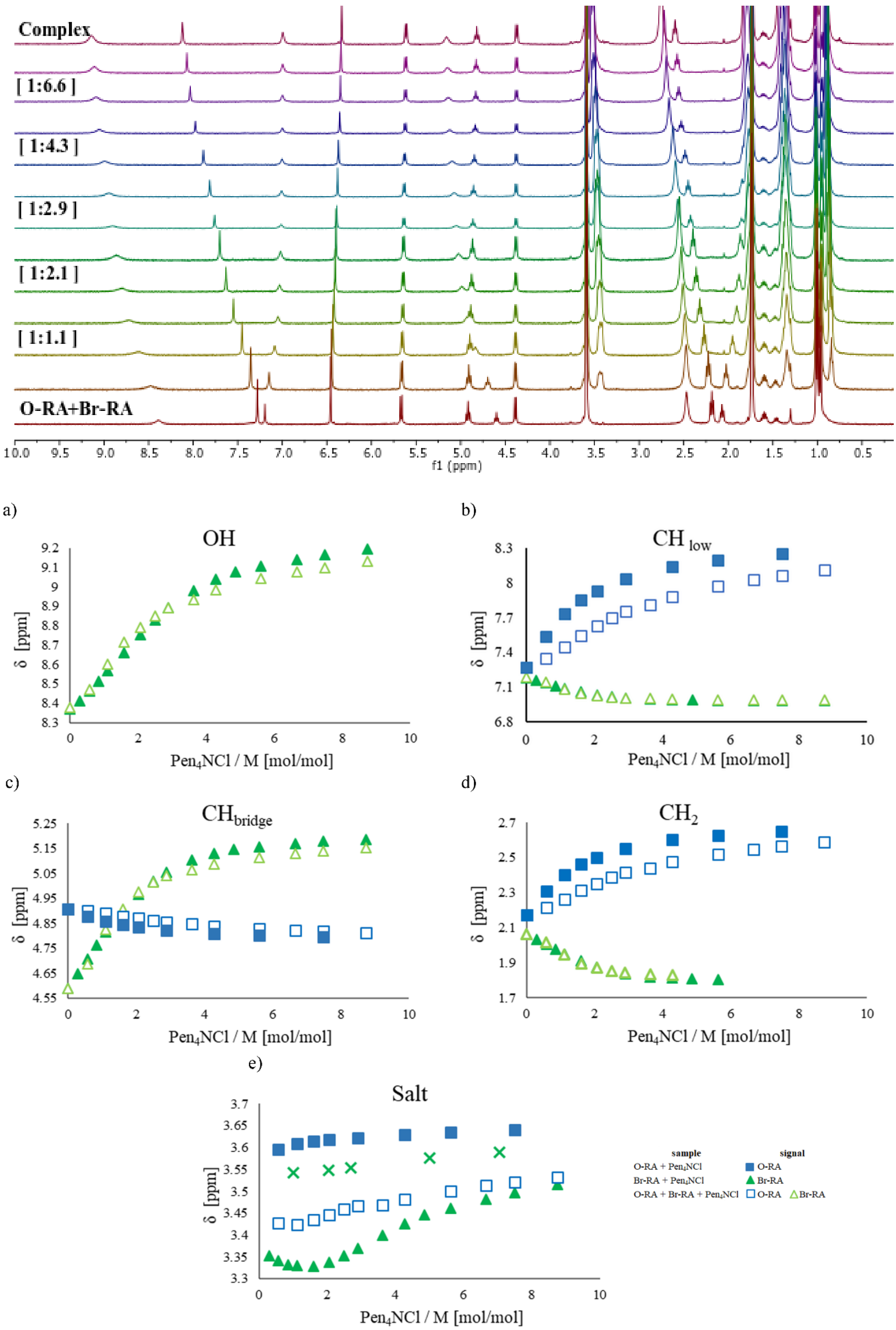


Figure S54. [1]H NMR titration curves for titration of **O-RA + Br-RA** with **Pen_4NCl**. [1]H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

10.Additional comparisons

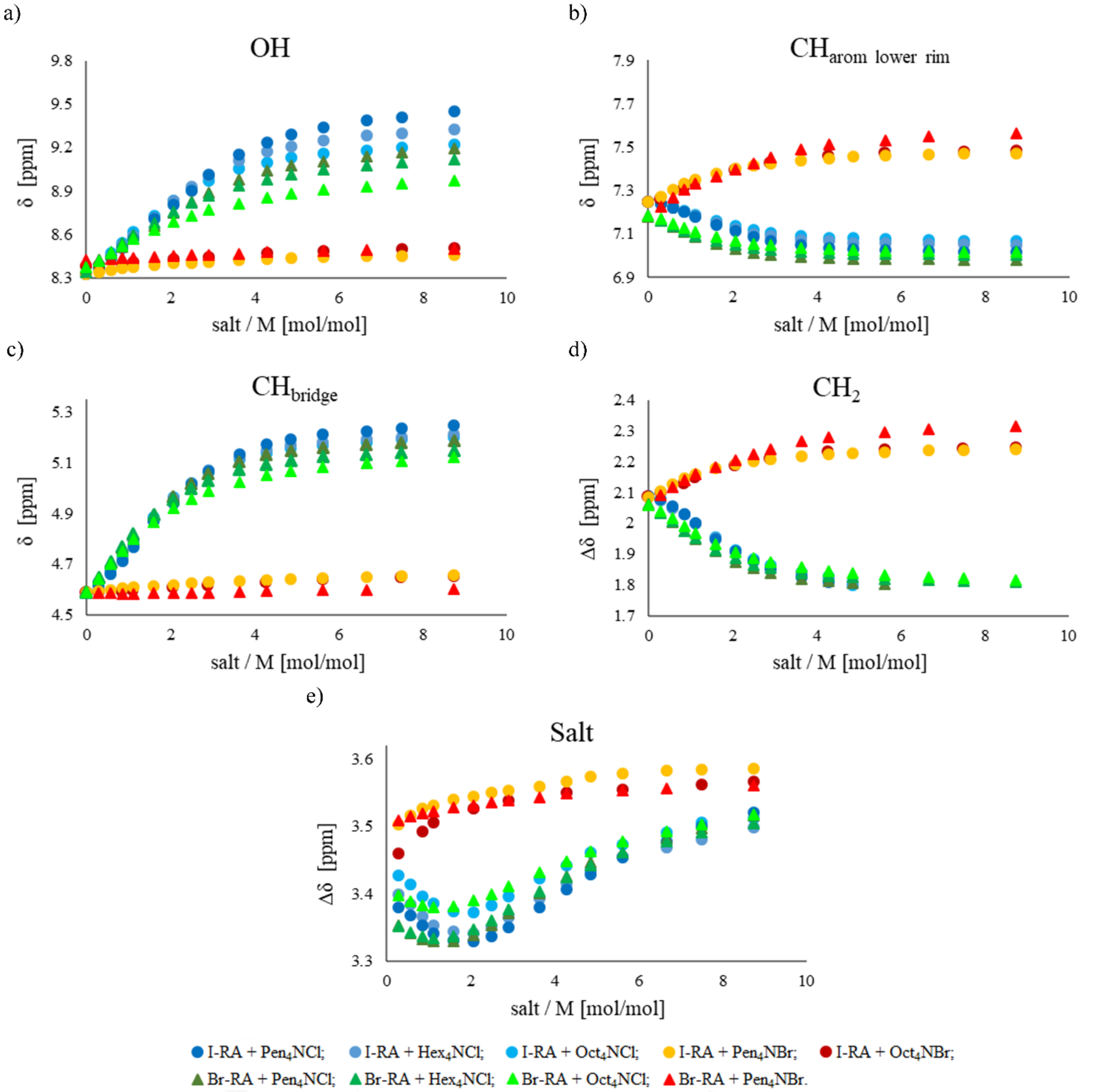


Figure S55. Comparison of interactions **Br-RA** and **I-RA** with **Alk_4NX** salts in THF. ^{1}H NMR chemical shifts change for: (a) OH; (b) CH_{low}; (c) CH_{bridge}; (d) CH_2 from lower rim alkyl chain; (e) NCH_2 from salt (400 MHz, 303 K, THF-d8).

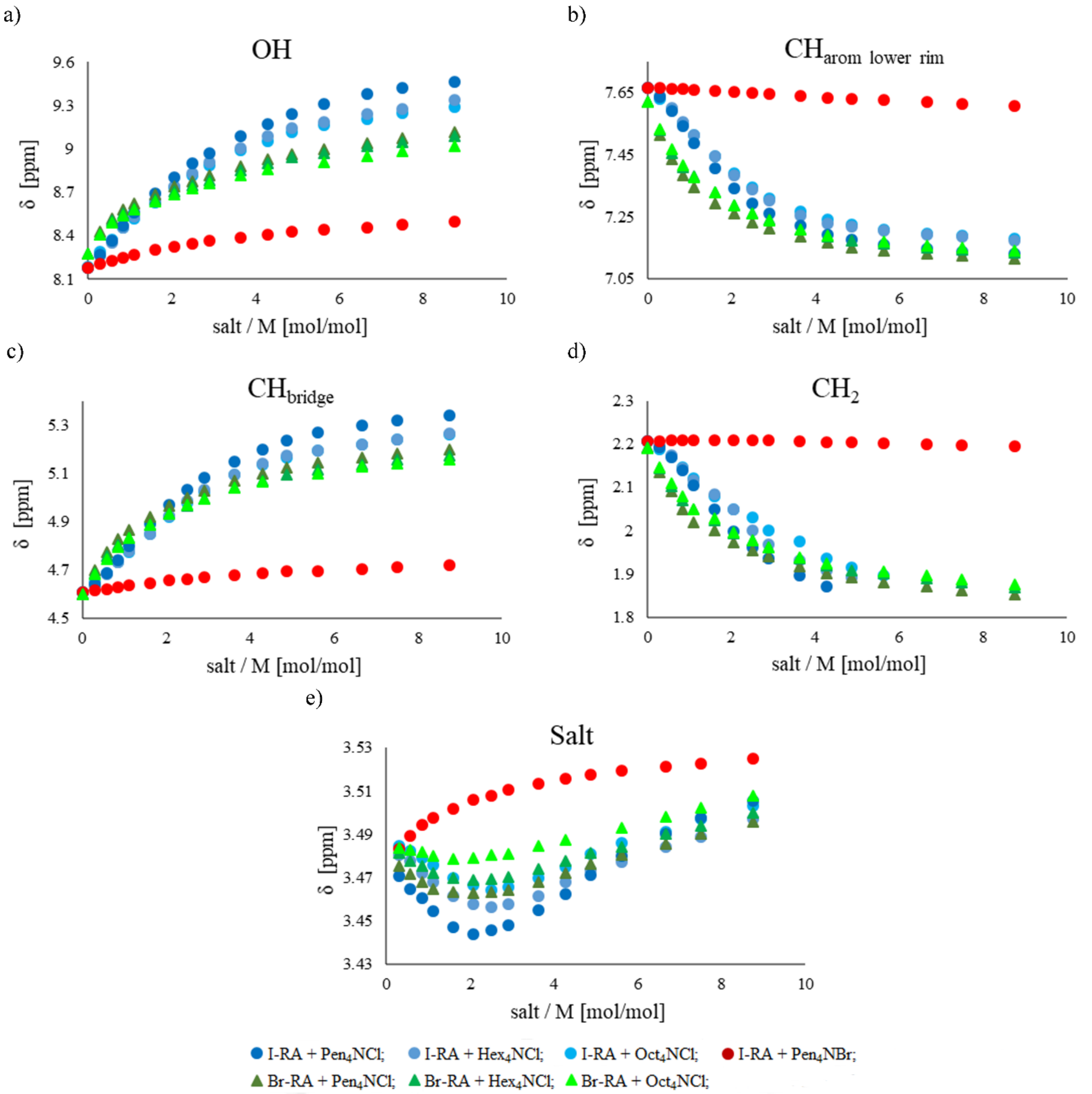


Figure S56. Comparison of interactions **Br-RA** and **I-RA** with **Alk$_4$NX** salts in Acetone. ^{1}H NMR chemical shifts change for: a) OH; (b) CH$_{low}$; (c) CH$_{bridge}$; (d) CH$_2$ from lower rim alkyl chain; (e) NCH$_2$ from salt (400 MHz, 303 K, Acetone-d6).

11.The search of the CCDC database

Search Overview

Search: search22

Date/Time done: Thu Jan 13 15:04:08 2022

Database(s): CSD version 5.41 updates (Mar 2020)
CSD version 5.41 (November 2019)
CSD version 5.41 updates (May 2020)

Restriction Info: No refcode restrictions applied

Filters: None

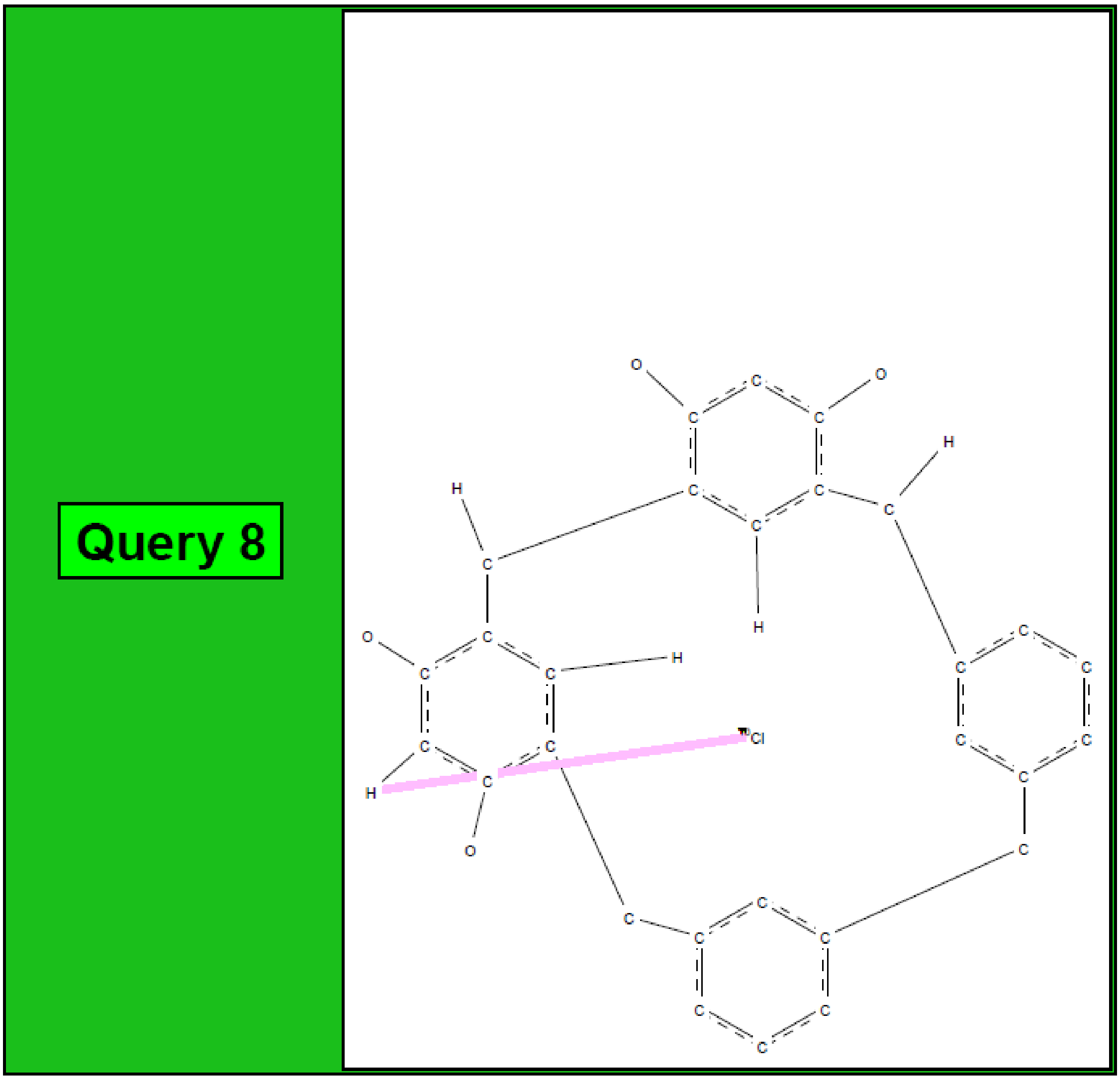
Percentage Completed: 100%

Number of Hits: 13

Single query used. Search found structures that:

match

Query 8



Search: search22 (Thu Jan 13 15:04:08 2022): Hits 1-13

AJUROM

Reference: J.L.Atwood, A.Szumna (2002) *J.Supramol.Chem.* ,**2,**479

AJUSAZ

Reference: J.L.Atwood, A.Szumna (2002) *J.Supramol.Chem.* ,**2,**479

IKASAO

Reference: P.O.Brown, G.D.Enright, J.A.Ripmeester (2002) *J.Supramol.Chem.* ,**2,**497

ITAMIZ

Reference: H.Mansikkamaki, M.Nissinen, K.Rissanen (2004) *Angew.Chem.,Int.Ed.* ,**43,**1243

QOFMIH

Reference: A.Shivanyuk, E.F.Paulus, K.Rissanen, E.Kolehmainen, V.Bohmer (2001) *Chem.-Eur.J.* ,**7,**1944

QOFMON

Reference: A.Shivanyuk, E.F.Paulus, K.Rissanen, E.Kolehmainen, V.Bohmer (2001) *Chem.-Eur.J.* ,**7,**1944

QOFNAA

Reference: A.Shivanyuk, E.F.Paulus, K.Rissanen, E.Kolehmainen, V.Bohmer (2001) *Chem.-Eur.J.* ,**7,**1944

QOFNUU

Reference: A.Shivanyuk, E.F.Paulus, K.Rissanen, E.Kolehmainen, V.Bohmer (2001) *Chem.-Eur.J.* ,**7,**1944

TOJFII

Reference: S.Busi, H.Saxell, R.Frohlich, K.Rissanen (2008) *CrystEngComm* ,**10,**1803

VEKRUA

Reference: S.V.Shishkina, A.Tarnovskiy, V.Rozhkov, O.V.Shishkin, O.Lukin, A.Shivanyuk (2012) *Tetrahedron* ,**68,**9429

VEKSEL

Reference: S.V.Shishkina, A.Tarnovskiy, V.Rozhkov, O.V.Shishkin, O.Lukin, A.Shivanyuk (2012) *Tetrahedron* ,**68,**9429

XUTBET

Reference: H.Mansikkamaki, M.Nissinen, C.A.Schalley, K.Rissanen (2003) *New J.Chem.* ,**27,**88

XUTBIX

Reference: H.Mansikkamaki, M.Nissinen, C.A.Schalley, K.Rissanen (2003) *New J.Chem.* ,**27,**88

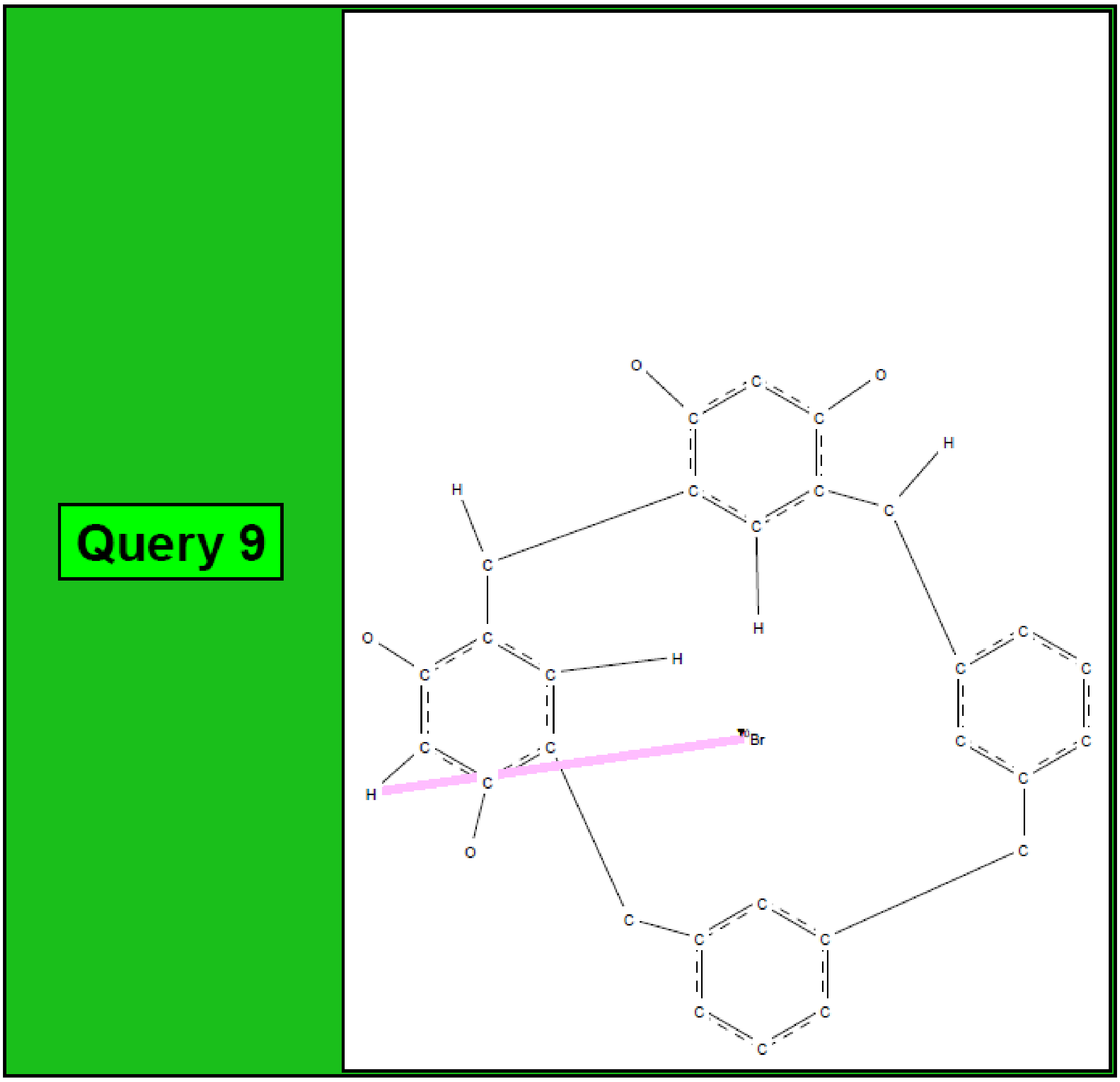
Search Overview

Search:	search23
Date/Time done:	Thu Jan 13 15:27:32 2022
Database(s):	CSD version 5.41 updates (Mar 2020) CSD version 5.41 (November 2019) CSD version 5.41 updates (May 2020)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	11

Single query used. Search found structures that:

match

Query 9



Search: search23 (Thu Jan 13 15:27:32 2022): Hits 1-11

DOXTIU

Reference: N.K.Beyeh, A.Valkonen, K.Rissanen (2009) *Supramol.Chem.* ,**21,**142

FEQQUO

Reference: H.Mansikkamaki, C.A.Schalley, M.Nissinen, K.Rissanen (2005) *New J.Chem.* ,**29,**116

FEQRID

Reference: H.Mansikkamaki, C.A.Schalley, M.Nissinen, K.Rissanen (2005) *New J.Chem.* ,**29,**116

FEQROJ

Reference: H.Mansikkamaki, C.A.Schalley, M.Nissinen, K.Rissanen (2005) *New J.Chem.* ,**29,**116

ITAMOF

Reference: H.Mansikkamaki, M.Nissinen, K.Rissanen (2004) *Angew.Chem.,Int.Ed.* ,**43,**1243

QEHYEI

Reference: H.Mansikkamaki, S.Busi, M.Nissinen, A.Ahman, K.Rissanen (2006) *Chem.-Eur.J.* ,**12,**4289

QEHYIM

Reference: H.Mansikkamaki, S.Busi, M.Nissinen, A.Ahman, K.Rissanen (2006) *Chem.-Eur.J.* ,**12,**4289

QEMLAW

Reference: H.Mansikkamaki, S.Busi, M.Nissinen, A.Ahman, K.Rissanen (2006) *Chem.-Eur.J.* ,**12,**4289

TOJFAA

Reference: S.Busi, H.Saxell, R.Frohlich, K.Rissanen (2008) *CrystEngComm* ,**10,**1803

XUTBOD

Reference: H.Mansikkamaki, M.Nissinen, C.A.Schalley, K.Rissanen (2003) *New J.Chem.* ,**27,**88

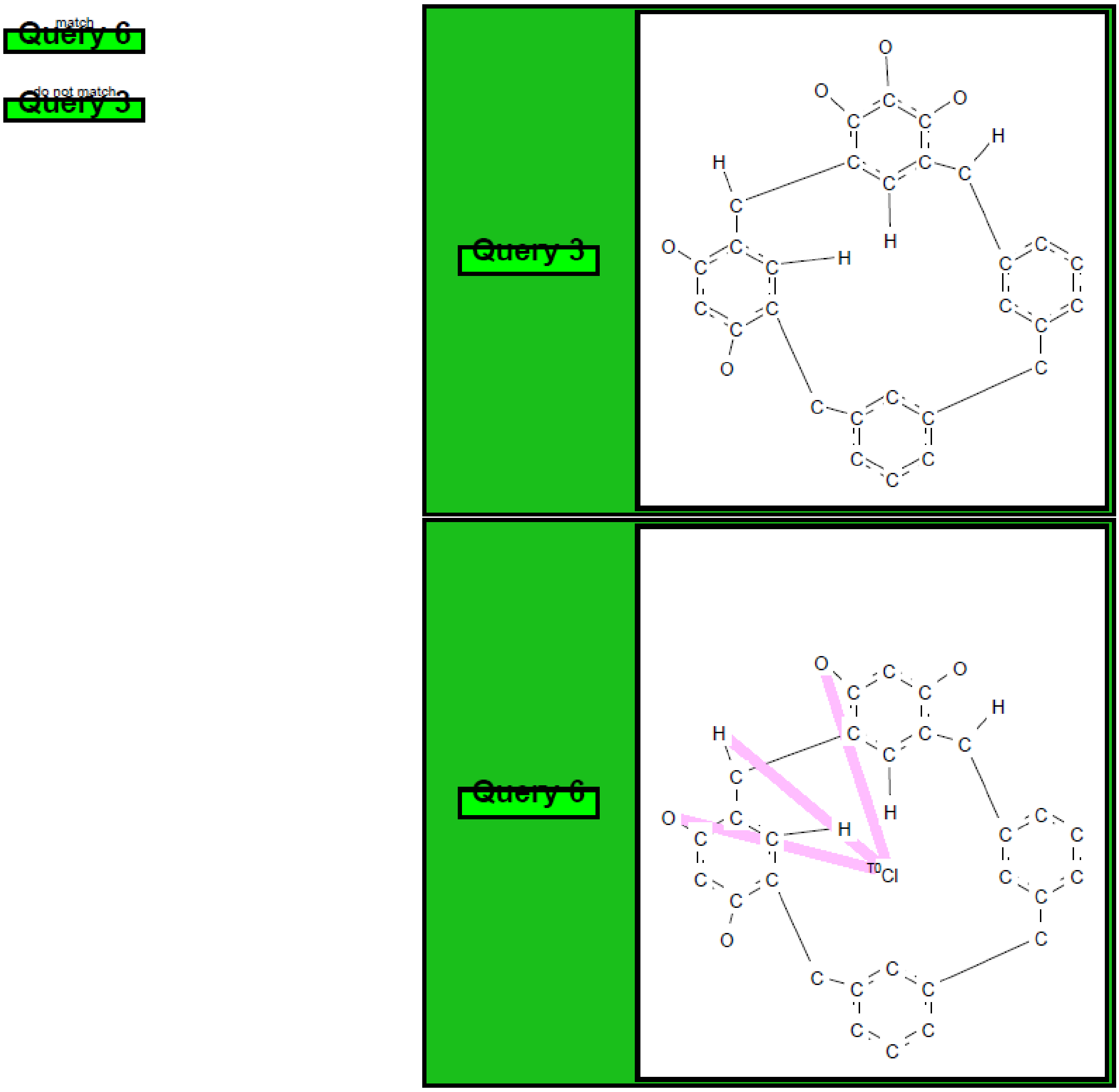
XUTBUJ

Reference: H.Mansikkamaki, M.Nissinen, C.A.Schalley, K.Rissanen (2003) *New J.Chem.* ,**27,**88

Search Overview

Search:	search14
Date/Time done:	Thu Jan 13 14:37:29 2022
Database(s):	CSD version 5.41 updates (Mar 2020) CSD version 5.41 (November 2019) CSD version 5.41 updates (May 2020)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	4

Summary of queries used. Search found structures that:



Search: search14 (Thu Jan 13 14:37:29 2022): Hits: 1-4

IZOLAM

Reference: Fangfang Pan, Ngong Kodiah Beyeh, R.H.A.Ras, K.Rissanen (2016) *Cryst.Growth Des.* ,**16,**6729

KOGQUS

Reference: A.T.Gubaidullin, Y.E.Morozova, A.R.Mustafina, E.Kh.Kazakova, I.A.Litvinov, A.I.Konovalov (1999) *Mendeleev Commun.* ,9

WUNWEJ

Reference: N.Kodiah Beyeh, A.Ala-Korpi, Fangfang Pan, Hyun Hwa Jo, E.V.Anslyn, K.Rissanen (2015) *Chem.-Eur.J.* ,**21,**9556

XAGVAC

Reference: A.Shivanyuk, T.P.Spaniol, K.Rissanen, E.Kolehmainen, V.Bohmer (2000) *Angew.Chem.,Int.Ed.* ,**39,**3497

Search Overview

Search: search20

Date/Time done: Thu Jan 13 14:56:35 2022

Database(s): CSD version 5.41 updates (Mar 2020)
CSD version 5.41 (November 2019)
CSD version 5.41 updates (May 2020)

Restriction Info: No refcode restrictions applied

Filters: None

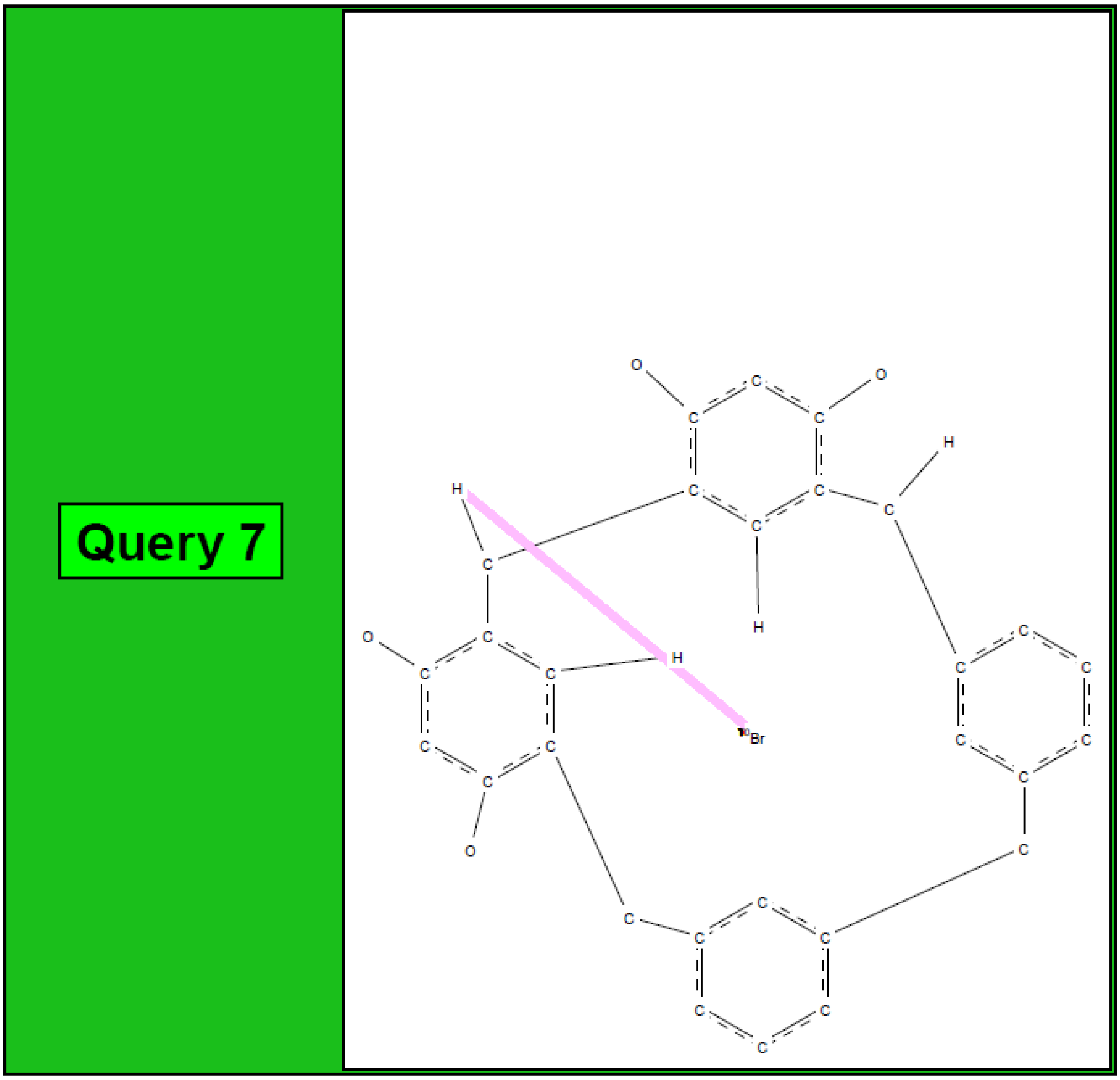
Percentage Completed: 100%

Number of Hits: 7

Single query used. Search found structures that:

match

Query 7



Search: search20 (Thu Jan 13 14:56:35 2022): Hits: 1-7

QACNIT

Reference: N.K.Beyeh, M.Cetina, M.Lofman, M.Luostarinen, A.Shivanyuk, K.Rissanen (2010) *Supramol.Chem.* ,**22,**737

QACNOZ

Reference: N.K.Beyeh, M.Cetina, M.Lofman, M.Luostarinen, A.Shivanyuk, K.Rissanen (2010) *Supramol.Chem.* ,**22,**737

QACPER

Reference: N.K.Beyeh, M.Cetina, M.Lofman, M.Luostarinen, A.Shivanyuk, K.Rissanen (2010) *Supramol.Chem.* ,**22,**737

QEHYEI

Reference: H.Mansikkamaki, S.Busi, M.Nissinen, A.Ahman, K.Rissanen (2006) *Chem.-Eur.J.* ,**12,**4289

SUPTII

Reference: Fangfang Pan, Ngong Kodiah Beyeh, K.Rissanen (2015) *J.Am.Chem.Soc.* ,**137,**10406

UQELEJ

Reference: Fangfang Pan, Ngong Kodiah Beyeh, R.H.A.Ras, K.Rissanen (2016) *CrystEngComm* ,**18,**5724

VUCQER

Reference: N.Kodiah Beyeh, A.Valkonen, S.Bhowmik, Fangfang Pan, K.Rissanen (2015) *Org.Chem.Front.* ,**2,**340

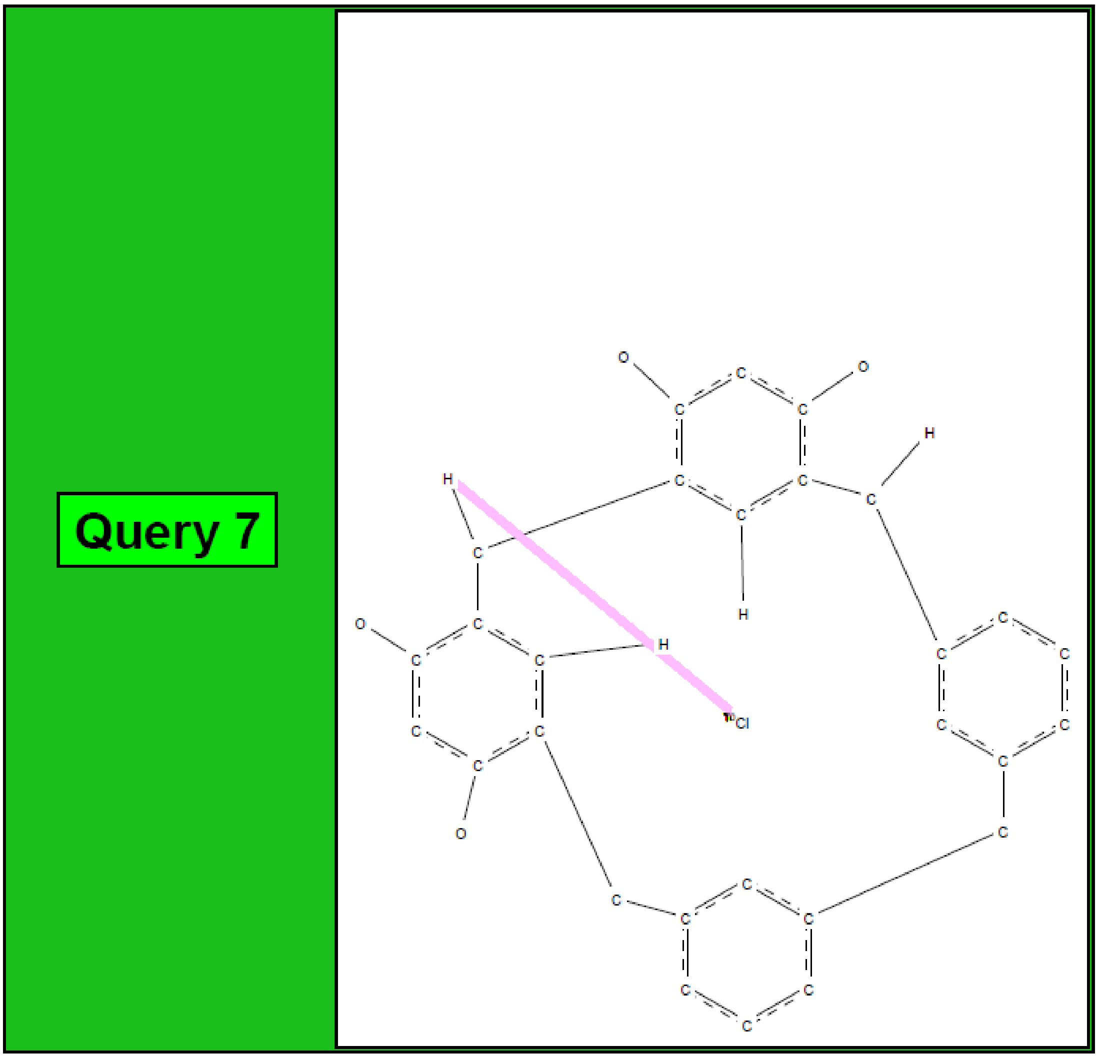
Search Overview

Search:	search21
Date/Time done:	Thu Jan 13 15:02:37 2022
Database(s):	CSD version 5.41 updates (Mar 2020) CSD version 5.41 (November 2019) CSD version 5.41 updates (May 2020)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	13

Single query used. Search found structures that:

match

Query 7



Search: search21 (Thu Jan 13 15:02:37 2022): Hits 1-11

CALJUX

Reference: Ngong Kodiah Beyeh, Fangfang Pan, K.Rissanen (2015) *Angew.Chem.,Int.Ed.* ,**54,**7303

DOQTUA

Reference: N.Kodiah Beyeh, A.Ala-Korpi, M.Cetina, A.Valkonen, K.Rissanen (2014) *Chem.-Eur.J.* ,**20,**15144

DOQVAI

Reference: N.Kodiah Beyeh, A.Ala-Korpi, M.Cetina, A.Valkonen, K.Rissanen (2014) *Chem.-Eur.J.* ,**20,**15144

IZOLAM

Reference: Fangfang Pan, Ngong Kodiah Beyeh, R.H.A.Ras, K.Rissanen (2016) *Cryst.Growth Des.* ,**16,**6729

KATQEC

Reference: H.Mansikkamaki, M.Nissinen, K.Rissanen (2005) *CrystEngComm* ,**7,**519

KOGQUS

Reference: A.T.Gubaidullin, Y.E.Morozova, A.R.Mustafina, E.Kh.Kazakova, I.A.Litvinov, A.I.Konovalov (1999) *Mendeleev Commun.* ,9

LAJXIG

Reference: N.Kodiah Beyeh, Fangfang Pan, S.Bhowmik, T.Makela, R.H.A.Ras, K.Rissanen (2016) *Chem.-Eur.J.* ,**22,**1355

QACNEP

Reference: N.K.Beyeh, M.Cetina, M.Lofman, M.Luostarinen, A.Shivanyuk, K.Rissanen (2010) *Supramol.Chem.* ,**22,**737

QACNUF

Reference: N.K.Beyeh, M.Cetina, M.Lofman, M.Luostarinen, A.Shivanyuk, K.Rissanen (2010) *Supramol.Chem.* ,**22,**737

UREBAW

Reference: Ngong Kodiah Beyeh, Fangfang Pan, R.H.A.Ras (2016) *Asian J.Org.Chem* ,**5,**1027

WUNWEJ

Reference: N.Kodiah Beyeh, A.Ala-Korpi, Fangfang Pan, Hyun Hwa Jo, E.V.Anslyn, K.Rissanen (2015) *Chem.-Eur.J.* ,**21,**9556

Search: search21 (Thu Jan 13 15:02:37 2022): Hits: 12-13

XAGVAC

Reference: A.Shivanyuk, T.P.Spaniol, K.Rissanen, E.Kolehmainen, V.Bohmer (2000) *Angew.Chem.,Int.Ed.* ,**39,**3497

ZISGAL

Reference: N.Kodiah Beyeh, M.Cetina, K.Rissanen (2014) *Chem.Commun.* ,**50,**1959

Search Overview

Search: search5

Date/Time done: Thu Jan 13 13:28:12 2022

Database(s): CSD version 5.41 updates (Mar 2020)
CSD version 5.41 (November 2019)
CSD version 5.41 updates (May 2020)

Restriction Info: No refcode restrictions applied

Filters: None

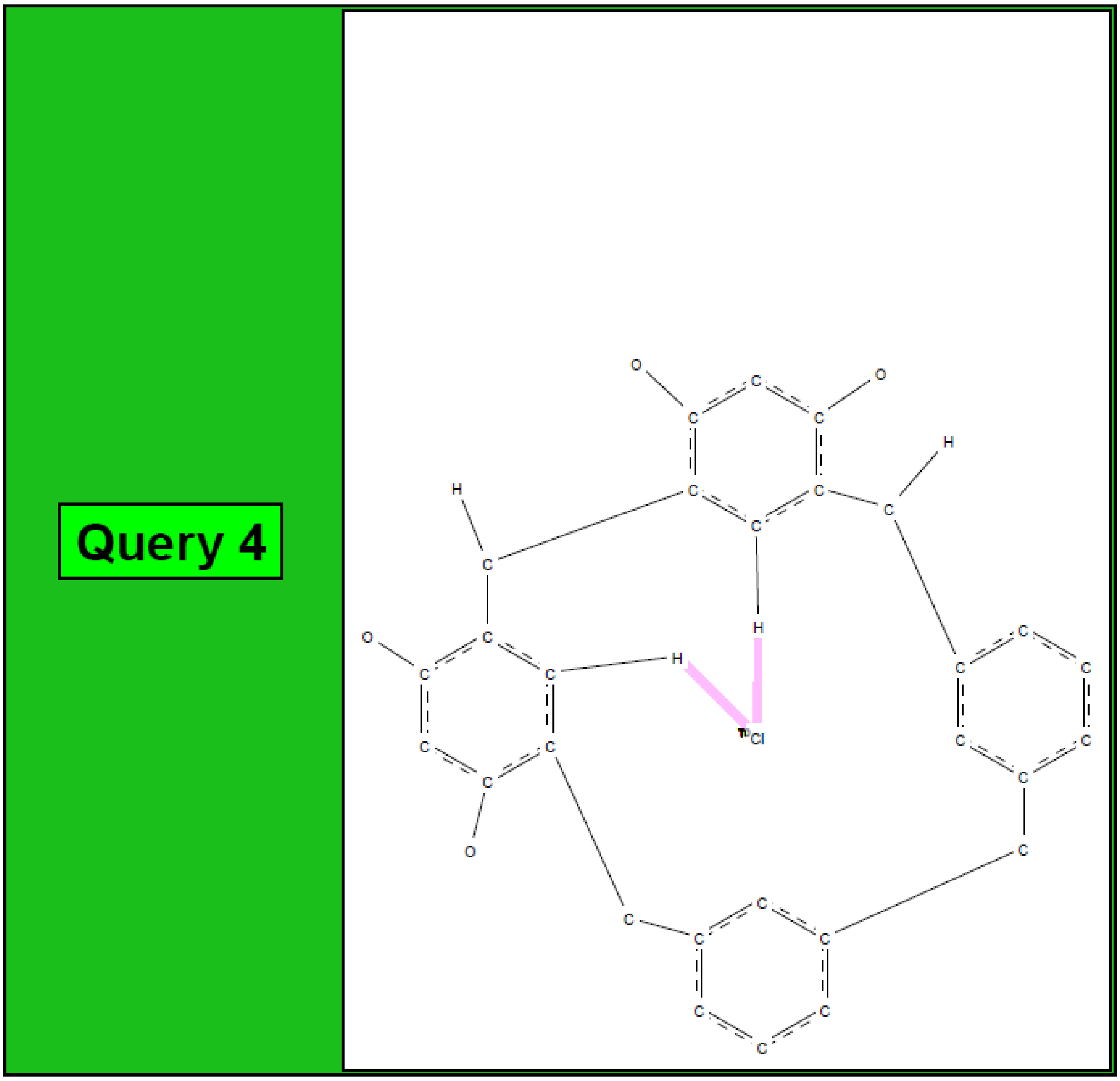
Percentage Completed: 100%

Number of Hits: 17

Single query used. Search found structures that:

match

Query 4



Search: search5 (Thu Jan 13 13:28:12 2022): Hits 1-11

AHOHIQ

Reference: R.Pinalli, G.Brancatelli, A.Pedrini, M.Melegari, S.Geremia, E.Dalcanale (2015) *CSD Communication(Private Communication) ,*

CUYZIG

Reference: M.Melegari, C.Massera, F.Ugozzoli, E.Dalcanale (2010) *CrystEngComm ,***12,**2057

GIPPED

Reference: G.Bracantelli (2018) *CSD Communication(Private Communication) ,*

GIPPIH

Reference: G.Bracantelli (2018) *CSD Communication(Private Communication) ,*

GIYPIQ

Reference: E.Biavardi, C.Massera (2019) *Acta Crystallogr.,Sect.E:Cryst.Commun. ,***75,**277

MIQJEE

Reference: G.Bracantelli (2018) *CSD Communication(Private Communication) ,*

MOXROI

Reference: E.Biavardi, F.Ugozzoli, C.Massera (2015) *Chem.Commun. ,***51,**3426

MOXSAV

Reference: E.Biavardi, F.Ugozzoli, C.Massera (2015) *Chem.Commun. ,***51,**3426

MOXSID

Reference: E.Biavardi, F.Ugozzoli, C.Massera (2015) *Chem.Commun. ,***51,**3426

SORREY

Reference: E.Biavardi, S.Federici, C.Tudisco, D.Menozzi, C.Massera, A.Sottini, G.G.Condorelli, P.Bergese, E.Dalcanale (2014) *Angew.Chem.,Int.Ed. ,***53,**9183

SORROI

Reference: E.Biavardi, S.Federici, C.Tudisco, D.Menozzi, C.Massera, A.Sottini, G.G.Condorelli, P.Bergese, E.Dalcanale (2014) *Angew.Chem.,Int.Ed. ,***53,**9183

Search: search5 (Thu Jan 13 13:28:12 2022): Hits: 12-17

SORRUO

Reference: E.Biavardi, S.Federici, C.Tudisco, D.Menozzi, C.Massera, A.Sottini, G.G.Condorelli, P.Bergese, E.Dalcanale (2014) *Angew.Chem.,Int.Ed.* ,**53,**9183

TUGVAU

Reference: R.Pinalli, G.Brancatelli, A.Pedrini, M.Melegari, S.Geremia, E.Dalcanale (2015) *CSD Communication(Private Communication) ,*

UHEXIQ

Reference: R.Pinalli, G.Brancatelli, A.Pedrini, M.Melegari, S.Geremia, E.Dalcanale (2015) *CSD Communication(Private Communication) ,*

UHEZOY

Reference: R.Pinalli, G.Brancatelli, A.Pedrini, M.Melegari, S.Geremia, E.Dalcanale (2015) *CSD Communication(Private Communication) ,*

XOTKUM

Reference: H.Mansikkamaki, M.Nissinen, K.Rissanen (2002) *Chem.Commun.* ,1902

XUSZOA

Reference: H.Mansikkamaki, M.Nissinen, C.A.Schalley, K.Rissanen (2003) *New J.Chem.* ,**27,**88

Search Overview

Search: search8

Date/Time done: Thu Jan 13 13:50:37 2022

Database(s): CSD version 5.41 updates (Mar 2020)
CSD version 5.41 (November 2019)
CSD version 5.41 updates (May 2020)

Restriction Info: No refcode restrictions applied

Filters: None

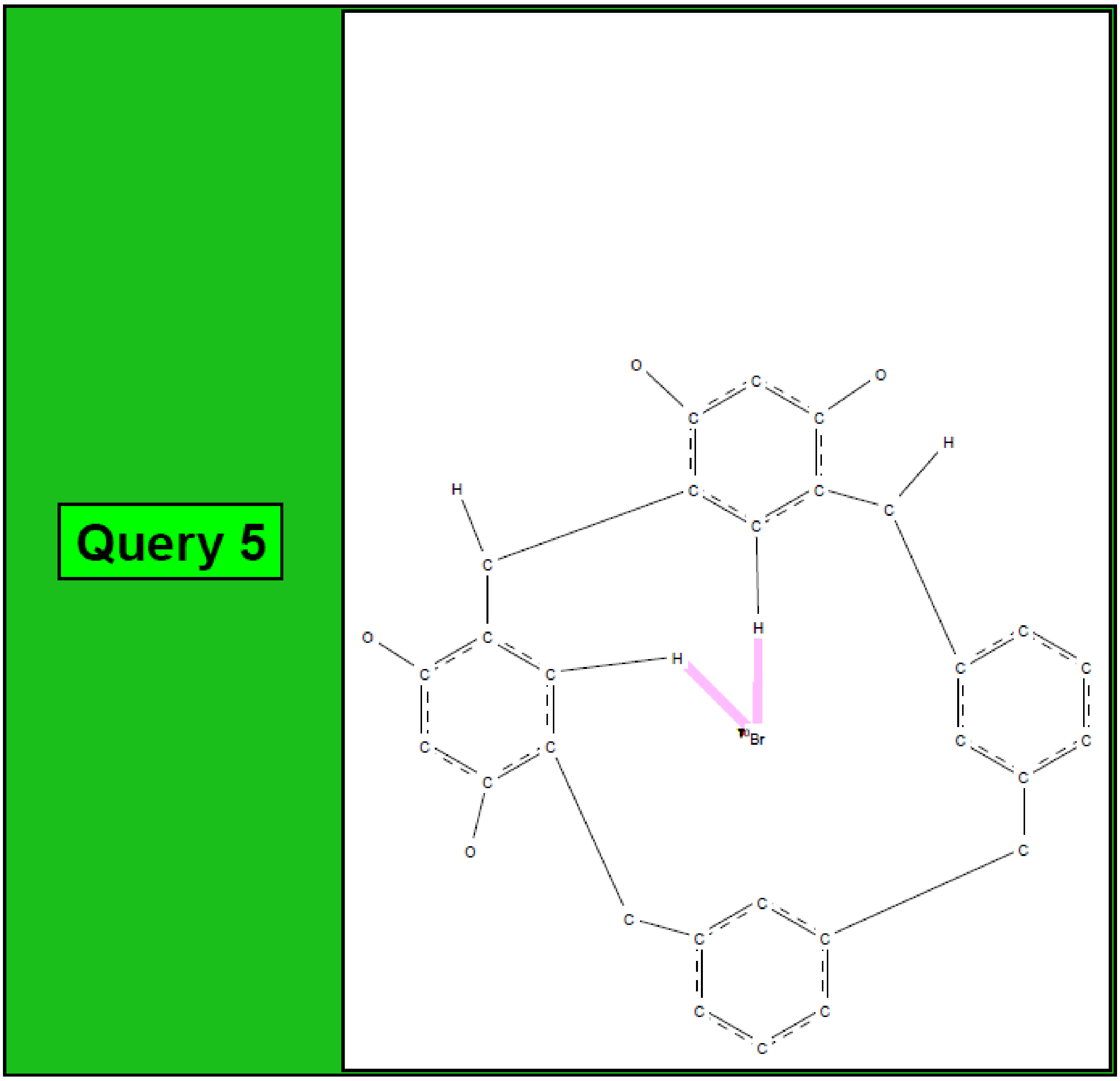
Percentage Completed: 100%

Number of Hits: 5

Single query used. Search found structures that:

match

Query 5



Search: search8 (Thu Jan 13 13:50:37 2022): Hits: 1-5

DIFPEP

Reference: N.Sahin, D.Semeril, E.Brenner, D.Matt, I.Ozdemir, C.Kaya, L.Toupet (2013) *Eur.J.Org.Chem.* ,4443

DOXTEQ

Reference: N.K.Beyeh, A.Valkonen, K.Rissanen (2009) *Supramol.Chem.* ,**21,**142

LICTIC

Reference: N.Sahin, D.Serneril, E.Brenner, D.Matt, I.Ozedmir, C.Kaya, L.Toupet (2013) *ChemCatChem* ,**5,**1116

MUTHOA

Reference: G.BRANCATELLI, T.Barbosa, E.Dalcanale, S.Geremia (2015) *CSD Communication(Private Communication) ,*

VAJXIQ

Reference: N.Sahin, D.Semeril, E.Brenner, D.Matt, C.Kaya, L.Toupet (2015) *Turk.J.Chem.* ,**39,**1171

12.References

[1] P.Timmerman, W. Verboom, D. N. Reinhoudt, *Tetrahedron*, 1996, **52**, 2663.
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