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Electronic Supplementary Information

2-Mercaptoimidazolium halides: structural diversity, stability and spontaneous racemisation

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1. NMR and IR characterisation of compounds investigated in this study

1.1. Instrumentation

NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer (Billerica, Ma., USA) and analyzed with the MestReNova software (version 9.0.1).[1]

IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument (Billerica, Ma., USA) and analysed with the Bruker Opus software (version 7.2).

1.2. (*RS*)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium bromide (*1*, *RS*-Br)

^{1}H-NMR (300 MHz, [D_6]DMSO): δ = 3.41 (dd, J = 12.7, 5.1 Hz, 1H, S-CH_2), 3.56 (dd, J = 12.6, 2.0 Hz, 1H, S-CH_2), 3.66 (s, 3H, Me), 4.20 (d, J = 3.1 Hz, 2H, N-CH_2), 4.52 – 4.58 (m, 1H, CH), 5.89 (br s, 1H, OH), 7.72 (s, 2H, Im) ppm.

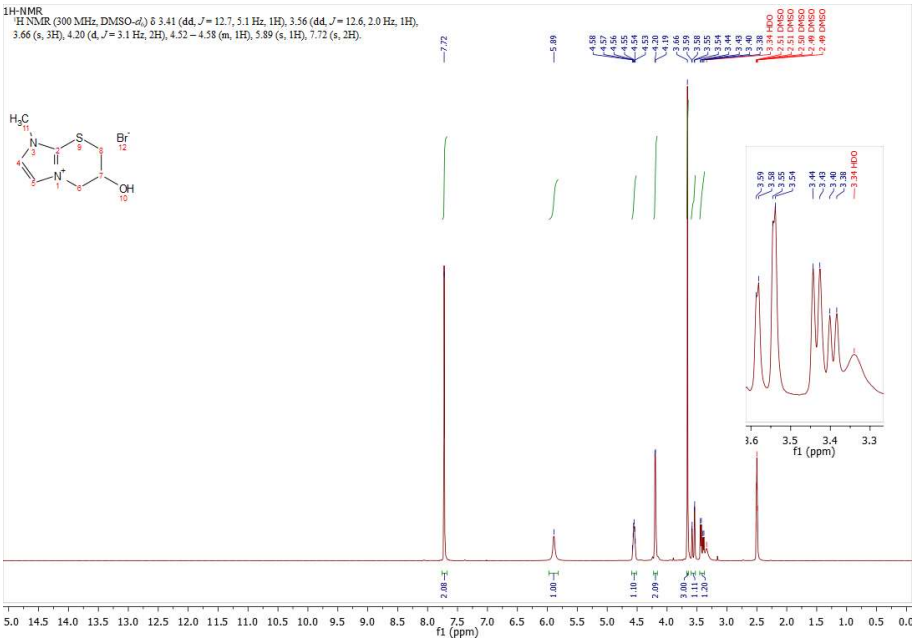


Figure S1. ^{1}H-NMR spectrum of (*RS*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium bromide (***1***, *RS*-**Br**).

^{13}C-NMR (75 MHz, [D_6]DMSO): δ = 31.7 (Me), 34.0 (S-CH_2), 51.5 (N-CH_2), 58.0 (CH), 122.6 (Im), 123.2 (Im), 140.3 (Im) ppm.

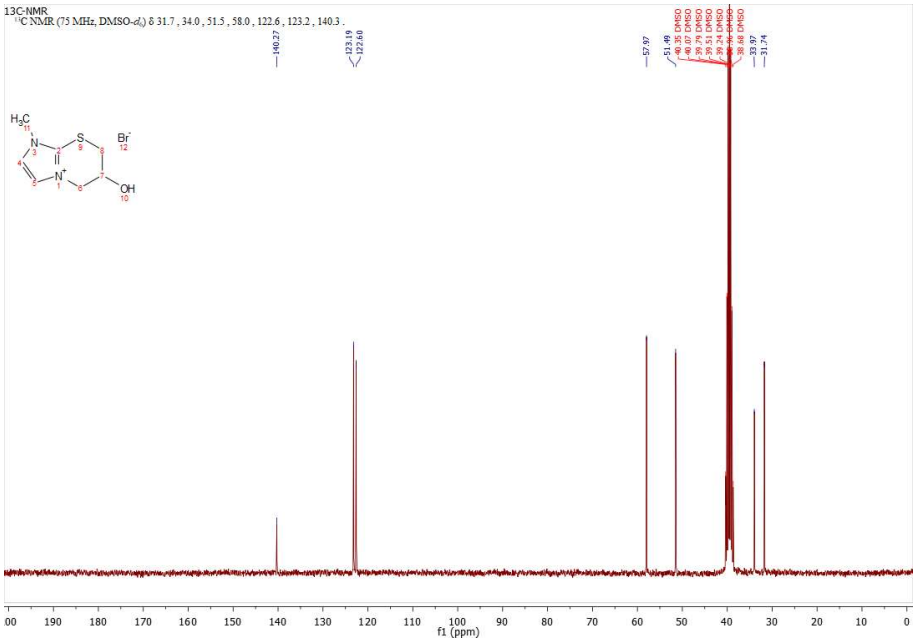


Figure S2. ^{13}C-NMR spectrum of (*RS*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium bromide (***1***, *RS*-**Br**).

FT-IR *(ATR): v* = 3273 (br m) (*v*OH), 3083 (m), 3064 (m), 2996 (w), 2970 (w) (*v*CH, *v*CH_2, *v*CH_3, *v*S-CH_2), 1661 (w), 1570 (m), 1516 (m) (*v*C=N, *v*C=C), 1478 (m), 1449 (m), 1412 (m), 1349 (m), 1311 (m) ($\delta$$CH_2$, $\delta$$CH_3$), 1275 (s), 1219 (s) ($\delta_i$OH), 1187 (m), 1151 (m), 1098 (m) (*v*CC, $\delta_i$$CH_{ar}$), 1078 (s) (*v*CO), 807 (m), 784 (s), 660 (s), 627 (s), 604 (s) (*v*CC, $\delta_o$$CH_{ar}$), 475 (s) cm^{-1}.

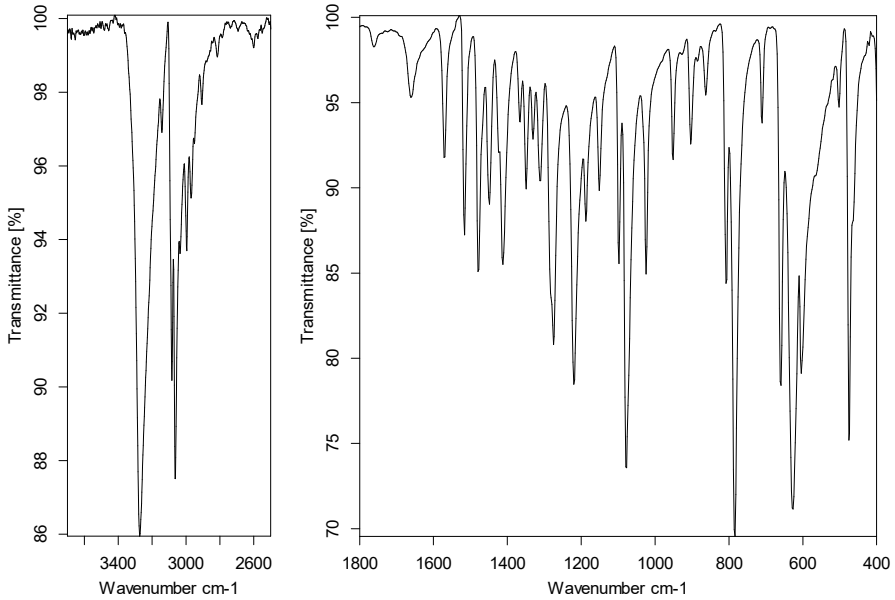


Figure S3. FT-IR spectrum of (*RS*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium bromide (***1***, *RS*-**Br**).

1.3. (RS)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (*2*, *RS*-Cl)

[1]H-NMR (300 MHz, [D_6]DMSO): δ = 3.43 (dd, *J* = 12.8, 5.1 Hz, 1H, S-CH_2), 3.55 (dd, *J* = 12.6, 2.0 Hz, 1H, S-CH_2), 3.66 (s, 3H, Me), 4.20 (d, *J* = 2.6 Hz, 2H, N-CH_2), 4.50 – 4.58 (m, 1H, CH), 6.21 (br s, 1H, OH), 7.73 (s, 2H, Im) ppm.

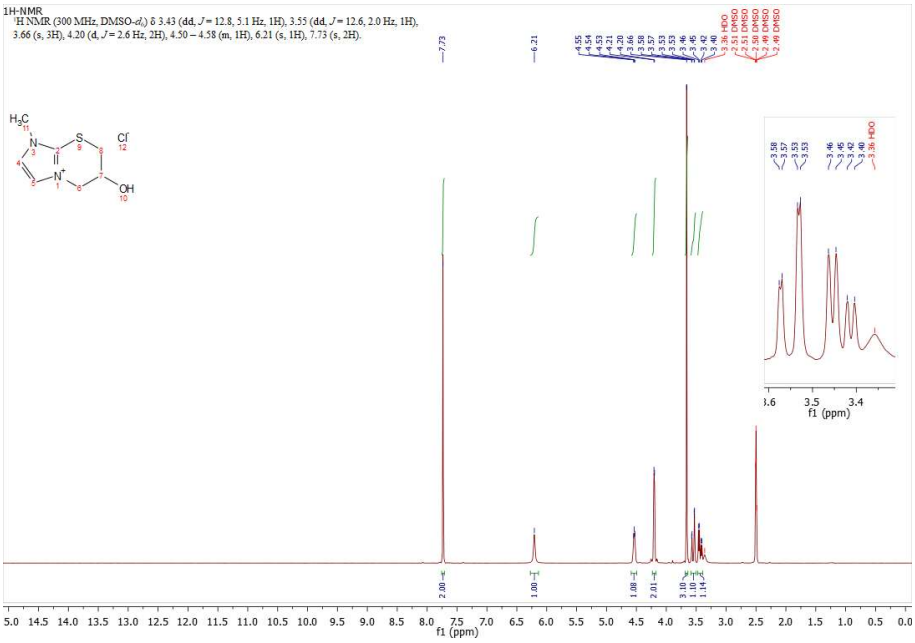


Figure S4. [1]H-NMR spectrum of (*RS*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***2***, *RS*-**Cl**).

[13]C-NMR (75 MHz, [D_6]DMSO): δ = 31.7 (Me), 33.9 (S-CH_2), 51.5 (N-CH_2), 58.0 (CH), 122.6 (Im), 123.2 (Im), 140.3 (Im) ppm.

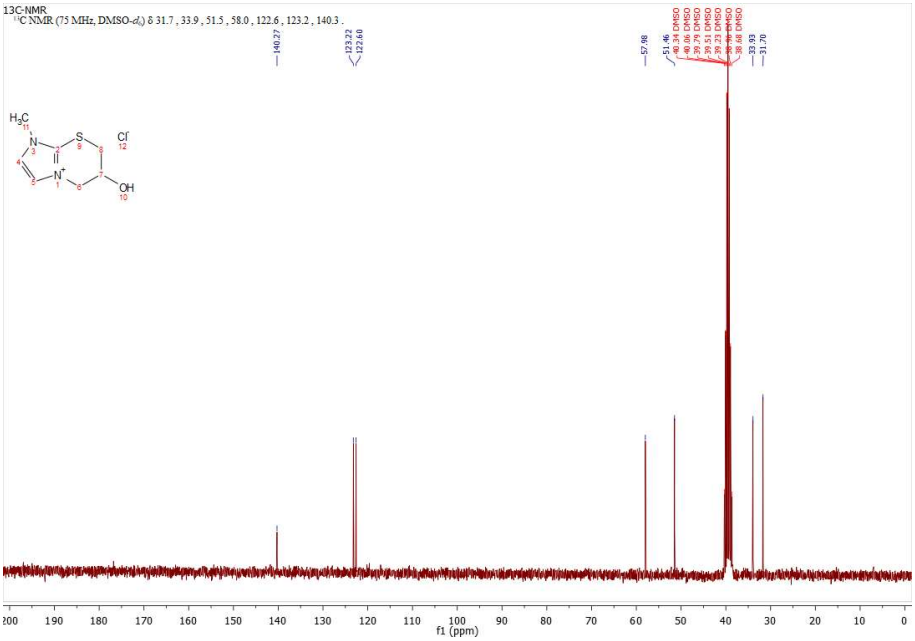


Figure S5. [13]C-NMR spectrum of (*RS*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***2***, *RS*-**Cl**).

FT-IR *(ATR):* ν = 3204 (br m) (νOH), 3084 (m), 3065 (m), 3000 (w), 2971 (w) (νCH, νCH_2, νCH_3, νS-CH_2), 1677 (w), 1569 (m), 1519 (m) (νC=N, νC=C), 1480 (m), 1453 (m), 1413 (m), 1350 (m), 1311 (m) (δCH_2, δCH_3), 1278 (s), 1222 (m) (δ_iOH), 1189 (m), 1153 (m), 1099 (m) (νCC, $\delta_i CH_{ar}$), 1082 (s) (νCO), 808 (m), 795 (s), 686 (s), 659 (s), 600 (m) (νCC, $\delta_o CH_{ar}$), 477 (s) cm^{-1}.

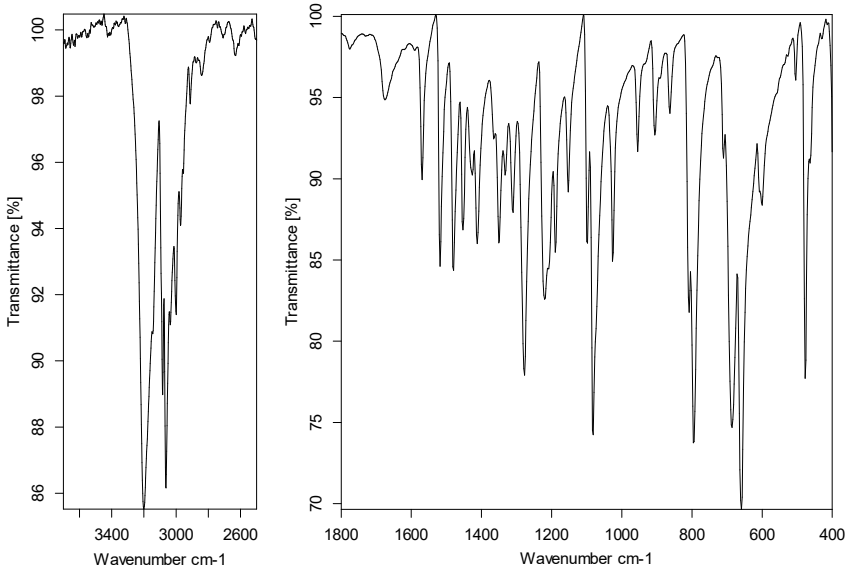


Figure S6. FT-IR spectrum of (*RS*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***2***, *RS*-**Cl**)

1.4. (*R*)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (*3*, *R*-Cl)

^{1}H-NMR (300 MHz, [D_6]DMSO): δ = 3.44 (dd, J = 12.7, 4.9 Hz, 1H, S-CH_2), 3.56 (dd, J = 12.6, 2.1 Hz, 1H, S-CH_2), 3.66 (s, 3H, Me), 4.19 – 4.24 (m, 2H, N-CH_2), 4.48 – 4.59 (m, 1H, CH), 6.26 (br s, 1H, OH), 7.75 (s, 2H, Im) ppm.

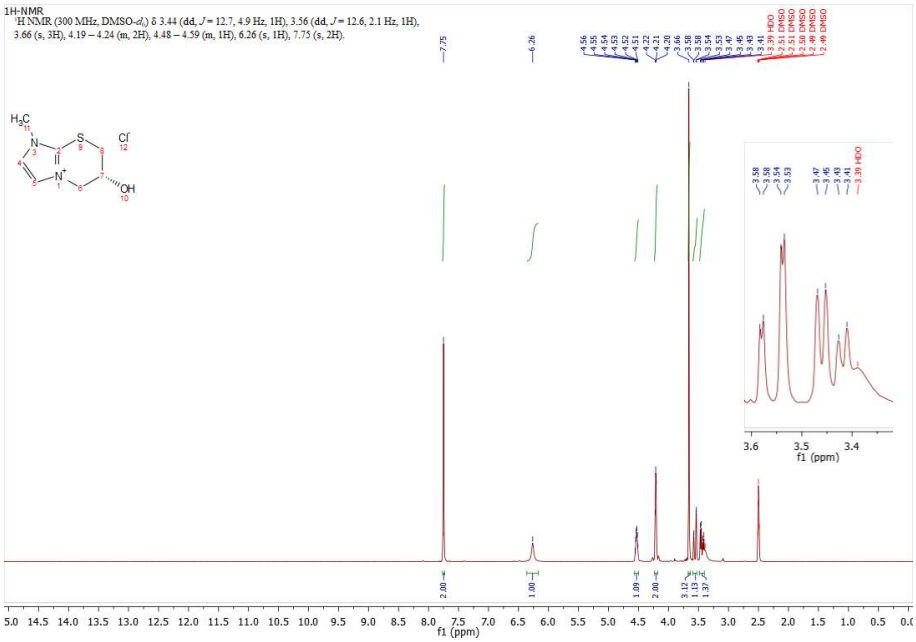


Figure S7. ^{1}H-NMR spectrum of (*R*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***3***, *R*-**Cl**).

[13]C-NMR (75 MHz, [D_6]DMSO): δ = 31.7 (Me), 33.9 (S-CH_2), 51.5 (N-CH_2), 58.0 (CH), 122.6 (Im), 123.2 (Im), 140.3 (Im) ppm.

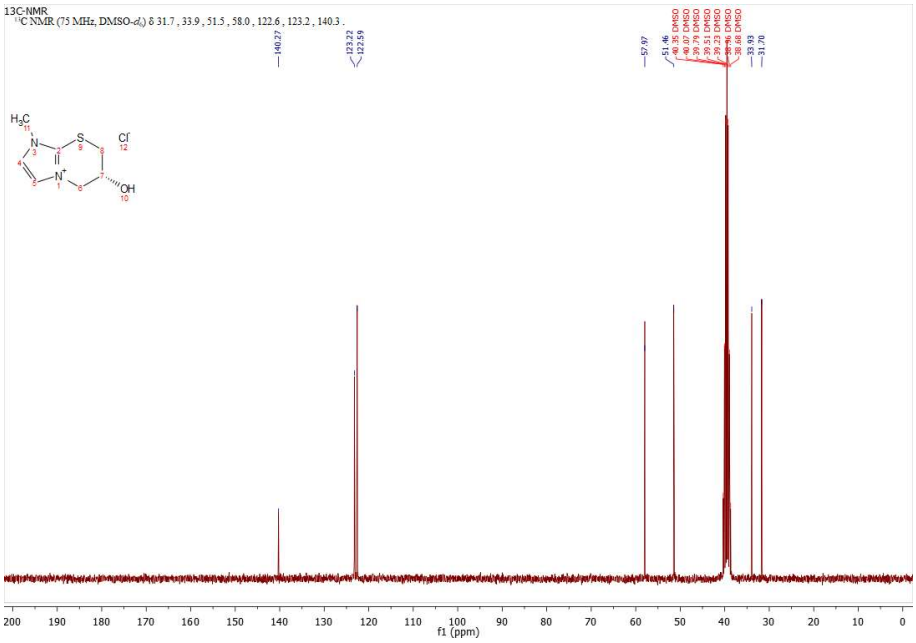


Figure S8. ^{13}C-NMR spectrum of (*R*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***3***, *R*-**Cl**).

FT-IR *(ATR):* ν = 3189, 3148 (br m) (νOH), 3101 (m), 2989 (w), (νCH, νCH_2, νCH_3, νS-CH_2), 1630 (w), 1569 (m), 1515 (m) (νC=N, νC=C), 1480 (m), 1447 (m), 1424 (m), 1343 (m), 1325 (m) (δCH_2, δCH_3), 1290 (m), 1268 (m), 1210 (s) (δ_iOH), 1180 (m), 1149 (w) (νCC, $\delta_i CH_{ar}$), 1086 (s) (νCO), 808 (m), 764 (s), 655 (s), 602 (s) (νCC, $\delta_o CH_{ar}$), 469 (m) cm^{-1}.

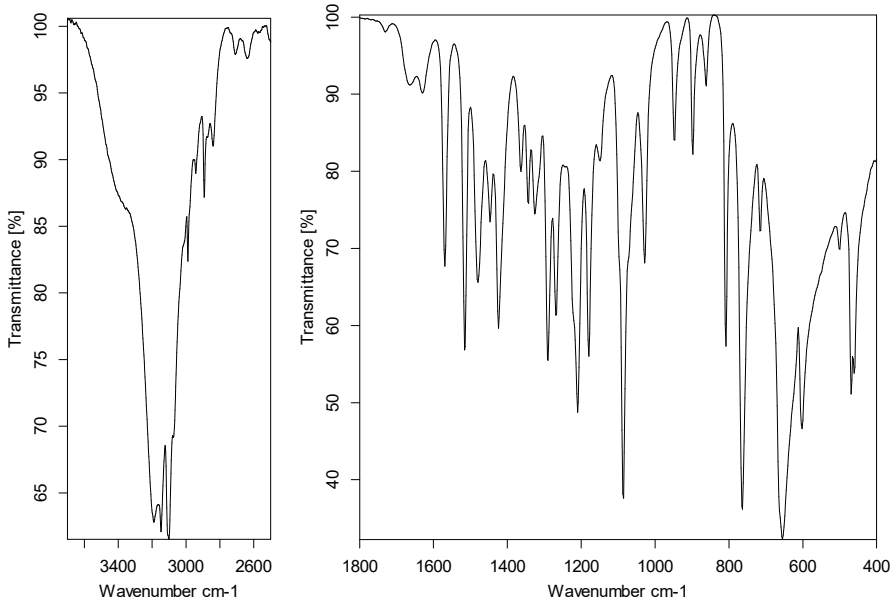


Figure S9. FT-IR spectrum of (*R*)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***3***, *R*-**Cl**).

1.5. (*S*)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***4***, *S*-**Cl**)

[1]H-NMR (300 MHz, [D_6]DMSO): δ = 3.43 (dd, *J* = 12.7, 4.8 Hz, 1H, S-CH_2), 3.55 (dd, *J* = 12.6, 1.9 Hz, 1H, S-CH_2), 3.66 (s, 3H, Me), 4.20 (d, *J* = 2.2 Hz, 2H, N-CH_2), 4.49 – 4.57 (m, 1H, CH), 6.20 (br s, 1H, OH), 7.73 (s, 2H, Im) ppm.

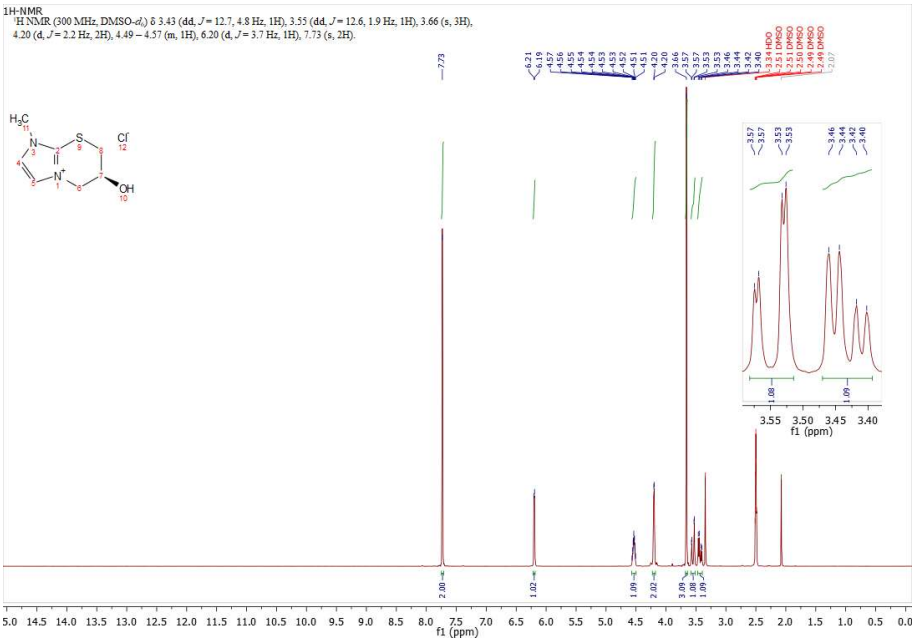


Figure S10. [1]H-NMR spectrum of (S)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***4***, *S*-**Cl**).

[13]C-NMR (75 MHz, [D_6]DMSO): δ = 31.7 (Me), 33.9 (S-CH_2), 51.5 (N-CH_2), 58.0 (CH), 122.6 (Im), 123.2 (Im), 140.3 (Im) ppm.

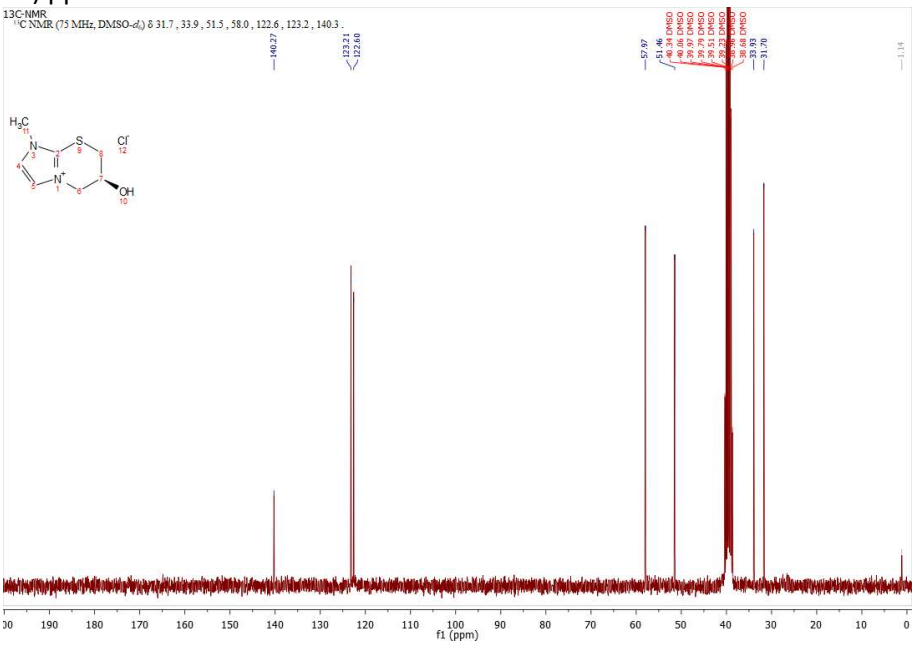


Figure S11. [13]C-NMR spectrum of (S)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***4***, *S*-**Cl**).

FT-IR *(ATR):* ν = 3149 (br m) (νOH), 3068 (m), 3000 (w), 2971 (w) (νCH, νCH_2, νCH_3, νS-CH_2), 1641 (m), 1569 (m), 1520 (m) (νC=N, νC=C), 1481 (m), 1456 (m), 1419 (m), 1347 (m), 1315 (m) (δCH_2, δCH_3), 1248 (s), 1222 (m) (δ_iOH), 1190 (m), 1154 (m) (νCC, $\delta_i CH_{ar}$), 1088 (s) (νCO), 810 (m), 773 (s), 659 (s), 602 (m) (νCC, $\delta_o CH_{ar}$), 475 (m) cm^{-1}.

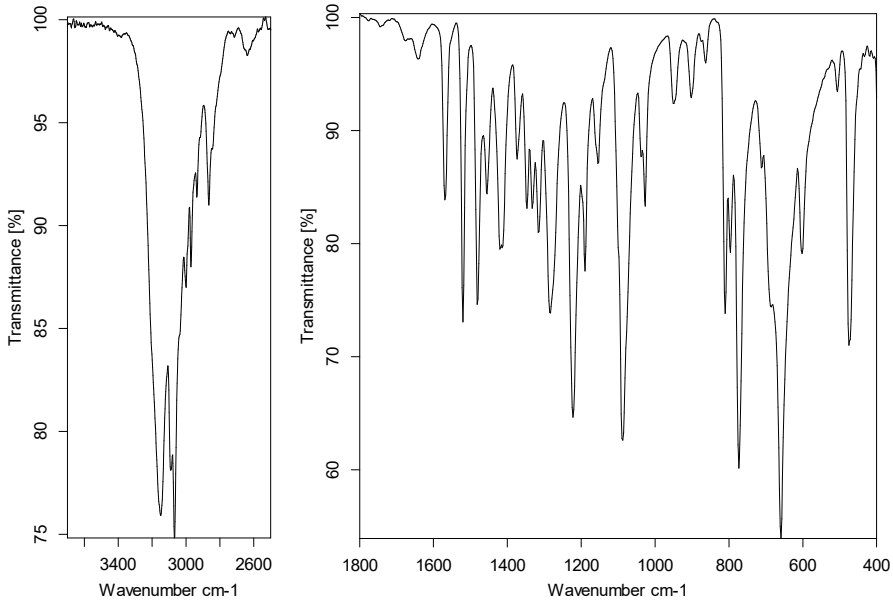


Figure S12. FT-IR spectrum of (S)-6-hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (***4***, *S*-**Cl**).

1.6. (*RS*)-6-Hydroxy-3-methyl-3,5,6,7-tetrahydro-[1,2,4]triazolo[5,1-b][1,3]thiazinium bromide (*5*)

^{1}H-NMR (300 MHz, [D_6]DMSO): δ = 3.49 – 3.65 (m, 2H, S-CH_2), 3.72 (s, 3H, Me), 4.24 – 4.43 (m, 2H, N-CH_2), 4.64 – 4.72 (m, 1H, CH), 6.04 (d, J = 3.9 Hz, 1H, OH), 9.13 (s, 1H, CH_{ar}) ppm.

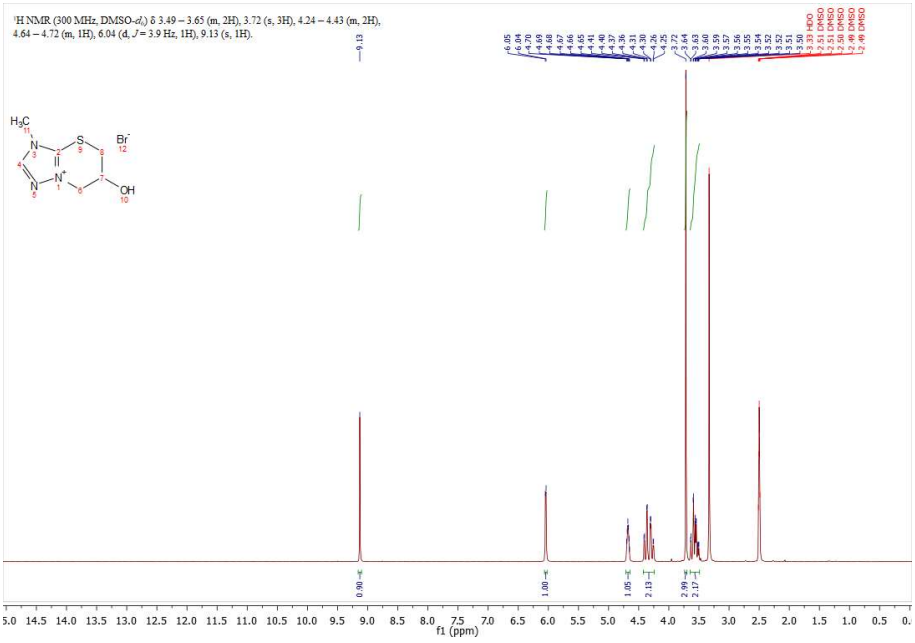


Figure S13. ^{1}H-NMR spectrum of (*RS*)-6-hydroxy-3-methyl-3,5,6,7-tetrahydro-[1,2,4]triazolo[5,1-b][1,3]thiazinium bromide (***5***).

^{13}C-NMR (75 MHz, [D6]DMSO): δ = 32.5 (Me), 32.6 (S-CH2), 54.1 (N-CH2), 58.5 (CH), 144.3 (CH_{ar}), 149.2 (C_{ar}) ppm.

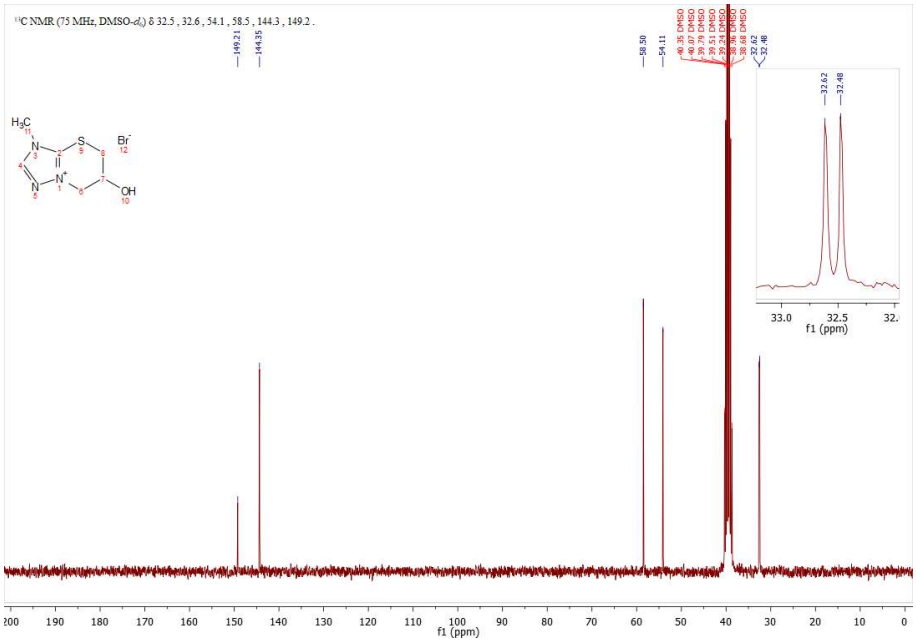


Figure S14. ^{13}C-NMR spectrum of (*RS*)-6-hydroxy-3-methyl-3,5,6,7-tetrahydro-[1,2,4]triazolo[5,1-b][1,3]thiazinium bromide (***5***).

FT-IR *(ATR): ν* = 3272 (br m) (*ν*OH), 3111 (m), 3060 (m), 2971 (m), 2880 (w) (*ν*CH, *ν*CH_2, *ν*CH_3, *ν*S-CH_2), 1550 (m), 1525 (s) (*ν*C=N, *ν*C=C), 1460 (m), 1442 (m), 1400 (m), 1361 (m), 1332 (m) (*δ*CH_2, *δ*CH_3), 1286 (m), 1222 (s) (*δ*$_i$OH), 1173 (m) (*ν*CC), 1090 (s) (*ν*CO), 1039 (s), 943 (m), 889 (m), 867 (s), 805 (s), 722 (m), 661 (m), 633 (s), 611 (s) (*ν*CC) cm^{-1}.

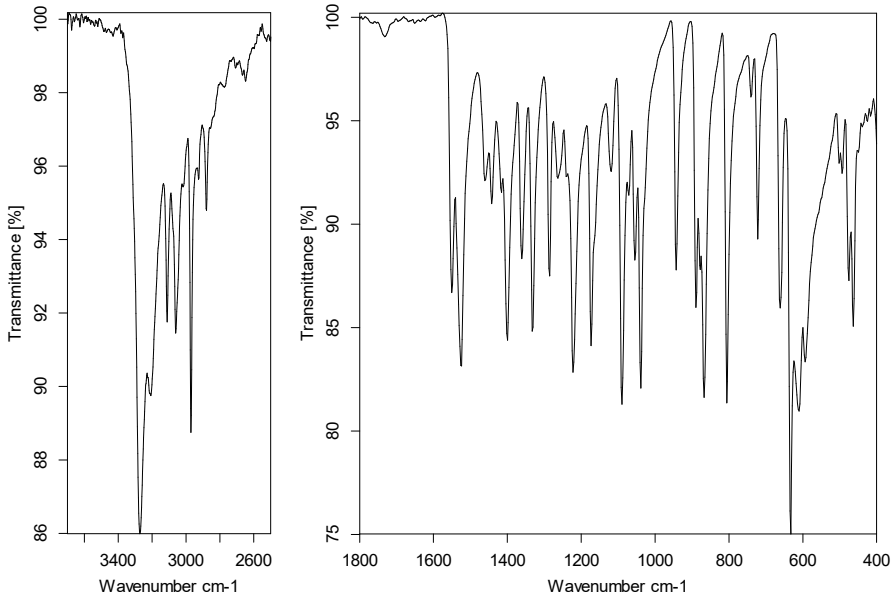


Figure S15. FT-IR spectrum of (*RS*)-6-hydroxy-3-methyl-3,5,6,7-tetrahydro-[1,2,4]triazolo[5,1-b][1,3]thiazinium bromide (***5***).

1.7. (*RS*)-6-Hydroxy-3-methyl-3,5,6,7-tetrahydrotetrazolo[5,1-b][1,3]thiazinium bromide (*6*)

[1]H-NMR (300 MHz, [D_6]DMSO): δ = 3.61 – 3.67 (m, 2H, S-CH_2), 4.15 (s, 3H, Me), 4.55 – 4.63 (m, 1H, CH), 4.70 – 4.84 (m, 2H, N-CH_2), 6.18 (d, *J* = 3.7 Hz, 1H, OH) ppm.

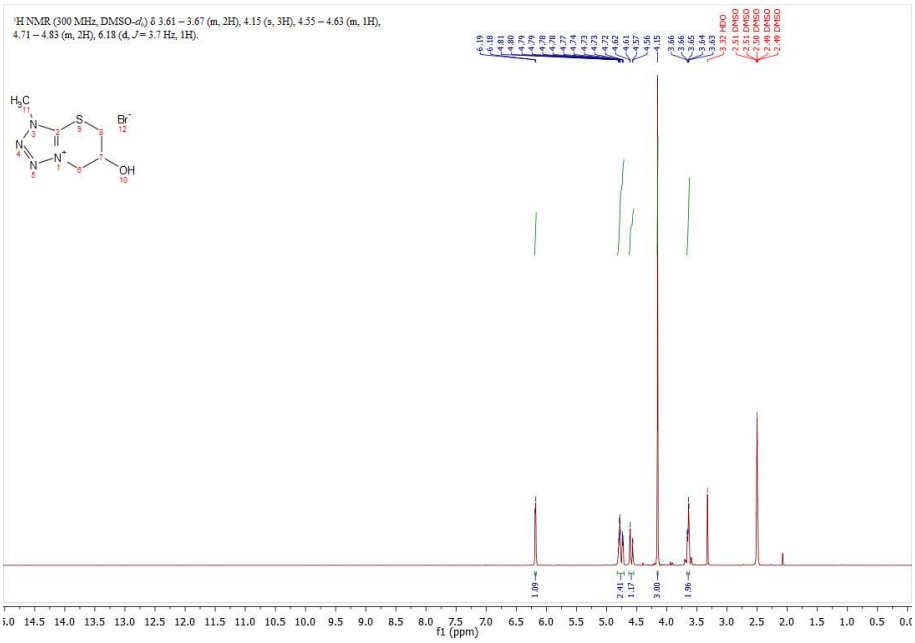


Figure S16. ^{1}H-NMR spectrum of (*RS*)-6-hydroxy-3-methyl-3,5,6,7-tetrahydrotetrazolo[5,1-b][1,3]thiazinium bromide (***6***).

[13]C-NMR (75 MHz, [D_6]DMSO): δ = 33.8 (Me), 35.8 (S-CH_2), 53.4 (N-CH_2), 57.9 (CH), 151.7 (C_{ar}) ppm.

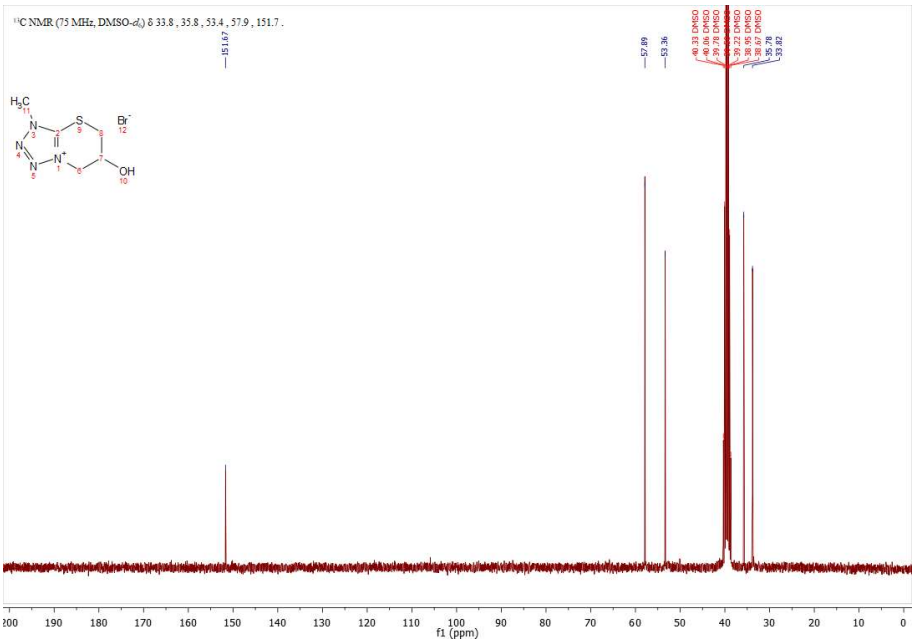


Figure S17. ^{13}C-NMR spectrum of (*RS*)-6-hydroxy-3-methyl-3,5,6,7-tetrahydrotetrazolo[5,1-b][1,3]thiazinium bromide (***6***).

FT-IR *(ATR):* ν = 3216 (br s) (νOH), 3016 (w), 2981 (w), 2949 (w), 2906 (w) (νCH_2, νCH_3, νS-CH_2), 1516 (s), 1489 (m) (νC=N, νC=C), 1420 (m), 1412 (m), 1370 (m), 1336 (m), 1323 (m) (δCH_2, δCH_3), 1299 (m), 1280 (s) (δ_iOH), 1201 (m), 1171 (m), 1099 (m) (νCC), 1077 (s) (νCO), 1036 (m), 1015 (m), 893 (m), 818 (m), 728 (m), 650 (s), 636 (s) (νCC) cm^{-1}.

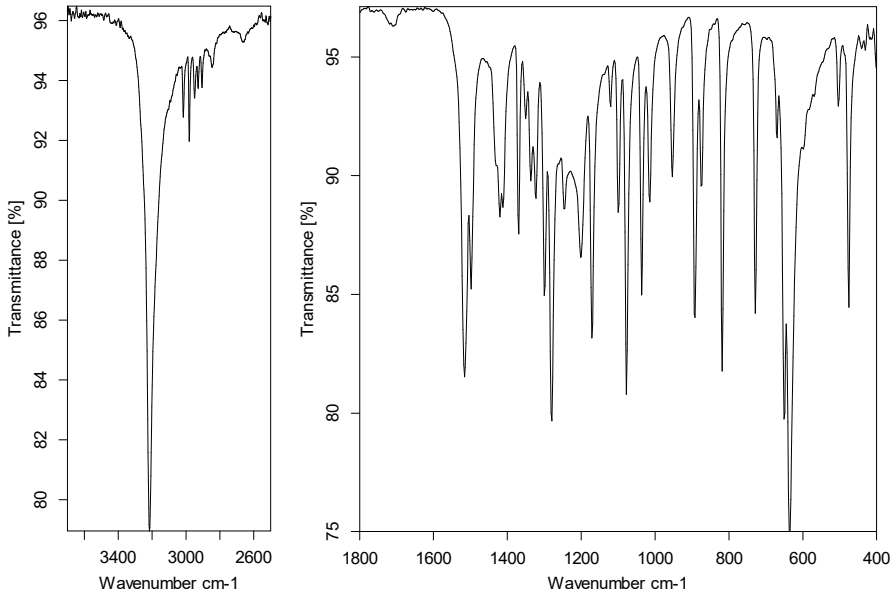


Figure S18. FT-IR spectrum of (*RS*)-6-hydroxy-3-methyl-3,5,6,7-tetrahydrotetrazolo[5,1-b][1,3]thiazinium bromide (***6***).

2. Single crystal X-ray diffraction

Table S1. Crystal data and structure refinement details for compounds ***1***–***3***, ***4*** and ***5***.

Compound	***1*, RS-*Br***	**2, RS-*Cl***	***3*, R-*Cl***	***5***	***6***
Formula	$C_7H_{11}N_2OS{\cdot}Br$	$C_7H_{11}N_2OS{\cdot}Cl$	$C_7H_{11}N_2OS{\cdot}Cl$	$C_6H_{10}N_3OS{\cdot}Br$	$C_5H_9N_4OS{\cdot}Br$
M_r	251.15	206.70	206.70	252.14	253.13
Cryst. size, mm^3	0.40×0.40×0.30	0.40×0.40×0.25	0.30×0.20×0.20	0.12×0.08×0.02	0.36×0.08×0.08
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2	*Pna*2$_1$	*P*2$_1$/*c*
a, Å	11.2359(2)	11.1116(2)	17.1960(8)	15.1584(6)	5.8057(3)
b, Å	14.9020(2)	14.6502(3)	8.4197(5)	6.9422(3)	19.4234(11)
c, Å	12.3361(3)	12.1138(4)	6.6408(3)	8.7807(4)	8.3009(5)
β, °	111.221(2)	111.270(2)	95.281(4)	90	102.153(5)
V, Å^3	1925.46(6)	1837.64(8)	957.41(8)	924.02(7)	915.08(9)
Z/*Z*′	8/1	8/1	4/1	4/1	4/1
D_{calcd}, g cm^{-3}	1.733	1.494	1.434	1.812	1.837
μ, mm^{-1}	4.44	0.60	0.57	4.63	4.68
T, K	233	233	173	203	173
F(000), e	1008	864	432	504	504
	$-14 \le h \le 14$	$-14 \le h \le 14$	$-22 \le h \le 23$	$-18 \le h \le 15$	$-6 \le h \le 5$
hkl range	$-19 \le k \le 19$	$-18 \le k \le 18$	$-11 \le k \le 11$	$-8 \le k \le 6$	$-19 \le k \le 23$
	$-15 \le l \le 13$	$-15 \le l \le 15$	$-8 \le l \le 8$	$-10 \le l \le 10$	$-9 \le l \le 9$
$((\sin\vartheta)/\lambda)_{max}$, Å^{-1}	0.649	0.650	0.676	0.602	0.602
Refl. measured	6560	7134	[a]	5309	5419
Refl. unique / R_{int}	2190 / 0.085	2099 / 0.020	2255 / [a]	1674 / 0.030	1658 / 0.032
Refl. observed	2006	1937	2048	1527	1467
Parameters	115	115	114	116	113
R_1 / wR_2 [$I > 2\,\sigma(I)$]	0.029 / 0.074	0.029 / 0.073	0.029 / 0.076	0.029 / 0.059	0.033 / 0.085
R_1 / wR_2 (all data)	0.032 / 0.076	0.031 / 0.075	0.032 / 0.077	0.034 / 0.061	0.039 / 0.088
Goodness of fit	1.08	1.05	1.02	1.07	1.15
$\Delta\rho_{max\,/\,min}$, e Å^{-3}	0.38 / −0.55	0.25 / −0.25	0.40 / −0.22	0.44 / −0.25	0.85 / −0.36
Flack parameter	–	–	0.34(5)	–	–
CCDC No.	2006014	2006016	2006015	2006017	2006018

[a] Precession-type reconstructions of reciprocal space revealed the presence of non-merohedral twinning for crystals of ***3***. The reciprocal lattices of the two twin domains were related by a rotation of 180° about the crystallographic *c*-axis. The diffraction spots belonging to both domains were indexed in CrysAlisPro and raw data were processed to give an hklf 5 formatted file.

Table S2. Hydrogen bond and short contact parameters (Å, °) of compounds ***1***-***3***, ***5*** and ***6***.

Compound	Interaction	H···A	D···A	D–H···A	Symmetry operation
1	O1–H10···Br1	2.49(2)	3.292(2)	165(2)	*x*, *y*, *z*
	C5–H5B···O1	2.647	3.338(3)	128.7	3/2–*x*, 3/2–*y*, 1–*z*
	C2–H2···Br1	2.836	3.725(2)	158.3	1–*x*, *y*, 3/2–*z*
	C1–H1···Br1	2.860	3.687(2)	147.4	–1/2+*x*, 1/2+*y*, *z*
	C7–H7B···Br1	2.935	3.852(3)	158.0	–1/2+*x*, 1/2+*y*, *z*
	C7–H7C···Br1	2.940	3.894(2)	167.7	–1/2+*x*, 3/2–*y*, –1/2+*z*
	C3–H3B···Br1	2.960	3.761(2)	139.7	*x*, *y*, *z*
	C3–H3A···Br1	2.992	3.918(2)	158.0	1–*x*, 1–*y*, 1–*z*
	C7–H7A···Br1	3.009	3.966(2)	168.9	3/2–*x*, 1/2+*y*, –1/2+*z*
2	O1–H10···Cl1	2.30(2)	3.125(1)	170(2)	*x*, *y*, *z*
	C5–H5B···O1	2.614	3.296(2)	126.8	3/2–*x*, 3/2–*y*, 1–*z*
	C2–H2···Cl1	2.719	3.614(2)	159.4	1–*x*, *y*, 3/2–*z*
	C1–H1···Cl1	2.786	3.592(2)	144.5	–1/2+*x*, 1/2+*y*, *z*
	C7–H7B···Cl1	2.806	3.716(2)	156.7	–1/2+*x*, 1/2+*y*, *z*
	C7–H7C···Cl1	2.855	3.819(1)	173.4	–1/2+*x*, 3/2–*y*, –1/2+*z*
	C3–H3B···Cl1	2.859	3.643(1)	137.5	*x*, *y*, *z*
	C3–H3A···Cl1	2.911	3.843(1)	159.1	1–*x*, 1–*y*, 1–*z*
3	O1–H10···Cl1	2.25(3)	3.050(2)	170(3)	*x*, *y*, –1+*z*
	C2–H2···O1	2.608	3.451(4)	148.0	–*x*, *y*, 2–*z*
	C7–H7B···Cl1	2.713	3.664(3)	163.4	–*x*, 1+*y*, 1–*z*
	C3–H3B···Cl1	2.786	3.709(3)	155.3	*x*, *y*, *z*
	C7–H7A···Cl1	2.802	3.667(4)	147.7	*x*, 1+*y*, *z*
	C5–H5A···Cl1	2.812	3.492(3)	126.4	1/2–*x*, 1/2+*y*, 1–*z*
5	O10–H10···Br	2.34(4)	3.263(4)	165(4)	–x, –y, –1/2+*z*
	C2–H2B···Br	2.811	3.684(5)	148.9	–1/2+x, 1/2–y, z
	C7–H7···Br	2.823	3.570(4)	137.2	–x, 1–y, 1/2+z
	C4–H4A···Br	2.888	3.855(5)	169.6	–x, 1–y, –1/2+z
	C2–H2A···Br	2.975	3.718(5)	133.4	–x, –y, –1/2+z
	C4–H4B···Br	3.005	3.759(5)	134.7	–1/2+x, 1/2–y, z
	C11–H11A···Br	3.041	3.902(6)	148.7	–x, 1–y, 1/2+z
6	O1–H1···Br	2.41(3)	3.228(2)	169(3)	–1+x, y, –1+z
	C5–H5C···O1	2.546	3.428(5)	149.8	2–x, –y, 1–z
	C1–H1A···N2	2.695	3.542(5)	143.8	1–x, –y, 1–z
	C5–H5B···N2	2.702	3.646(5)	161.9	1–x, –y, –z
	C1–H1B···S	2.828	3.496(3)	125.5	–1+x, y, z
	C3–H3B···Br	2.883	3.815(3)	157.2	x, 1/2–y, –1/2+z
	C3–H3A···S	2.924	3.446(4)	113.8	x, 1/2–y, –1/2+z
	C1–H1B···Br	2.927	3.830(4)	152.1	x, 1/2–y, –1/2+z
	C3–H3A···Br	3.038	3.600(4)	117.2	–1+x, 1/2–y, –1/2+z

3. Conformational analysis

3.1. 6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium cation

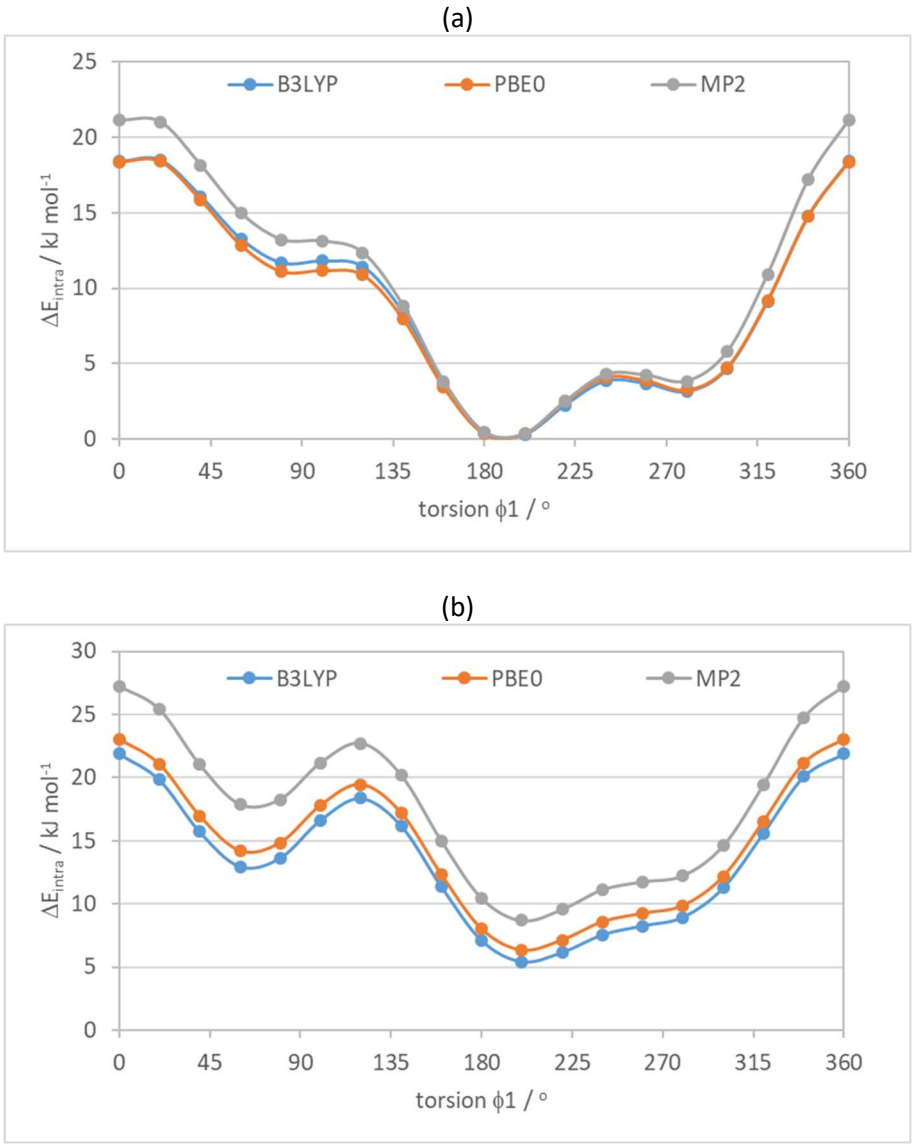
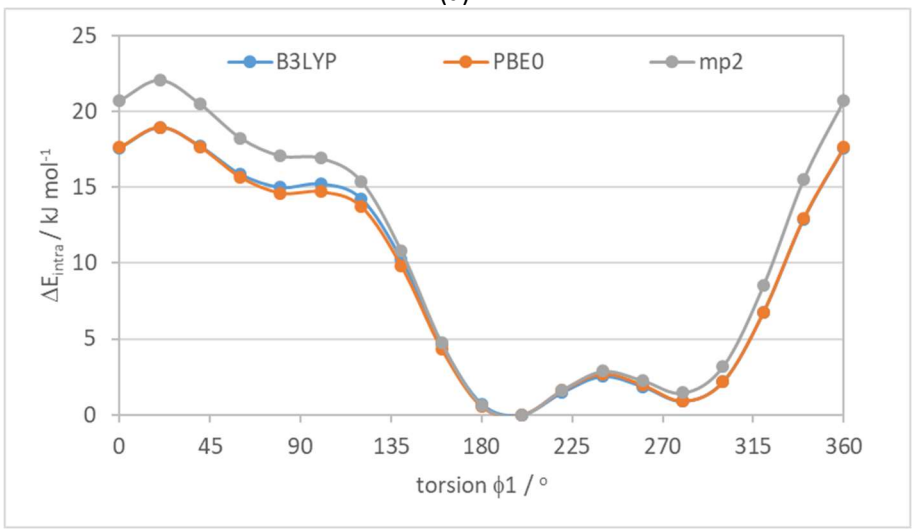


Figure S19. Potential energy scan starting from (a) ring conformation 1 (Fig. 6) and (b) ring conformation 2 and varying the H–O–C3–C4 dihedral. B3LYP/6-31G(d,p), PBE0/6-31G(d,p) and MP2/6-31G(d,p) levels of theory were used.

3.2. 6-Hydroxy-3-methyl-3,5,6,7-tetrahydro-[1,2,4]triazolo[5,1-b][1,3]thiazinium cation

(a)



(b)

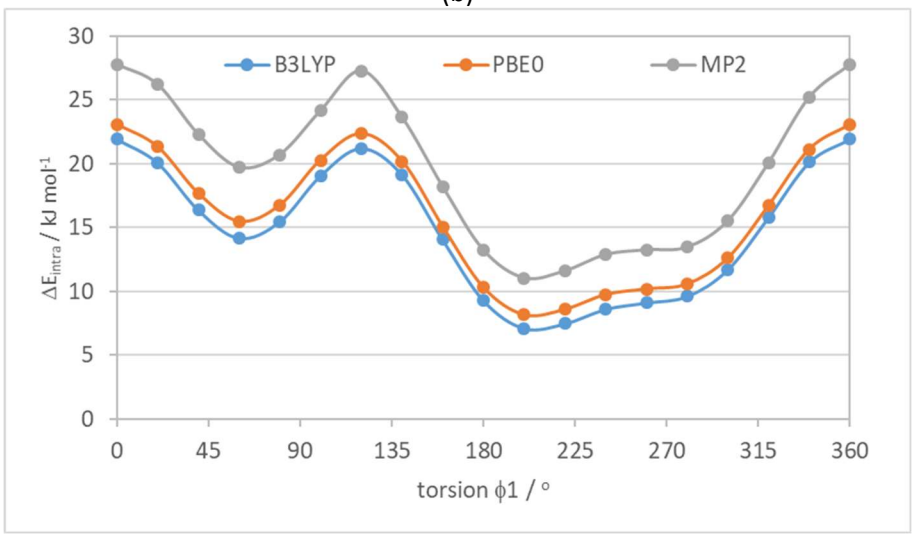


Figure S20. Potential energy scan starting from (a) ring conformation 1 (Fig. 6) and (b) ring conformation 2 and varying the H–O–C3–C4 dihedral. B3LYP/6-31G(d,p), PBE0/6-31G(d,p) and MP2/6-31G(d,p) levels of theory were used.

3.3. 6-Hydroxy-3-methyl-3,5,6,7-tetrahydrotetrazolo[5,1-b][1,3]thiazinium cation

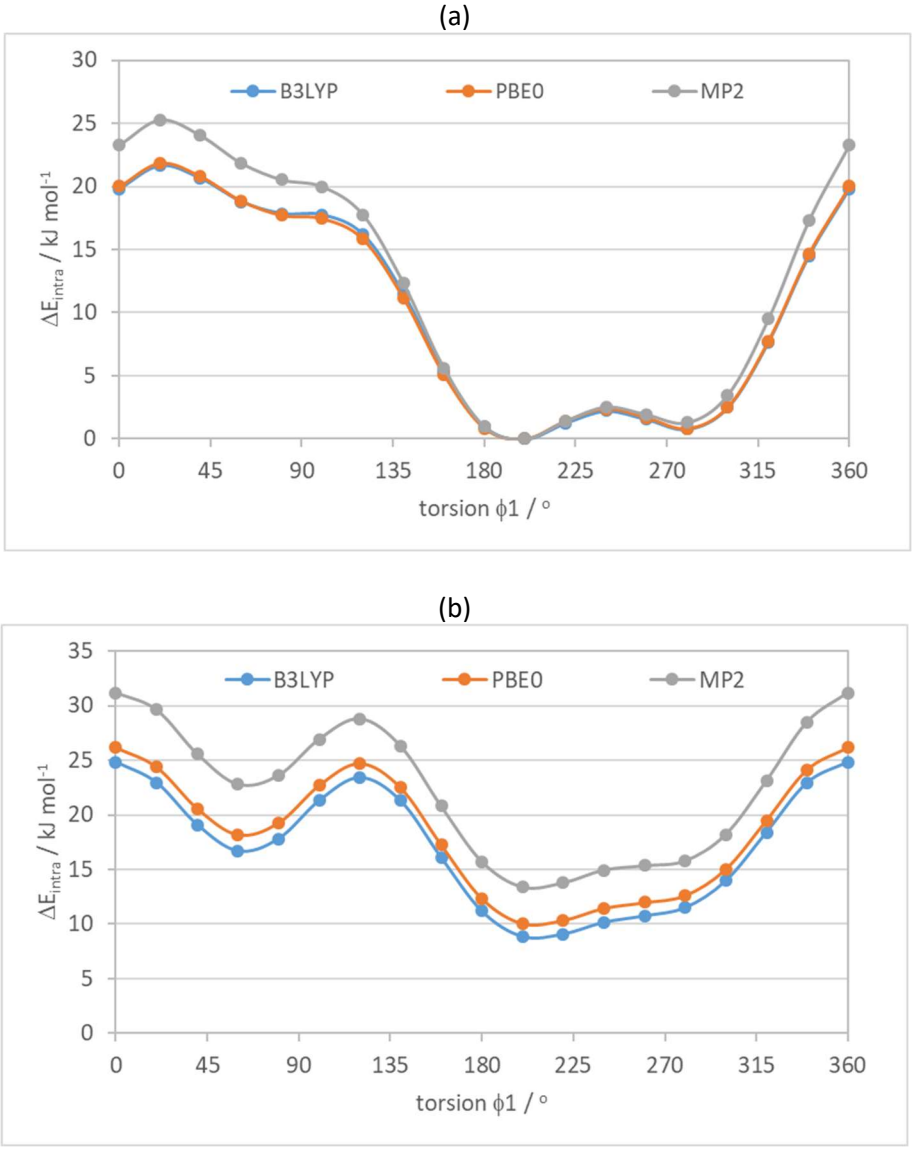


Figure S21. Potential energy scan starting from (a) ring conformation 1 (Fig. 6) and (b) ring conformation 2 and varying the H–O–C3–C4 dihedral. B3LYP/6-31G(d,p), PBE0/6-31G(d,p) and MP2/6-31G(d,p) levels of theory were used.

4. CrystalExplorer pairwise intermolecular energy calculations

Table S3. Overview of stabilising pairwise energetic contributions[a] for compounds **1-3**, **5** and **6**.

Interaction	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
Compound *1*						
O–H···Br$^-$	4.98	-343.7	-65.2	-9.5	54.9	-385.9
C–H···Br$^-$	5.51	-292.8	-40.9	-6.4	18.8	-333.9
C–H···Br$^-$	6.03	-292	-46.3	-8.1	27.8	-332.8
C–H···Br$^-$	5.14	-282.2	-41	-7.4	10.9	-328.4
C–H···Br$^-$	5.95	-250.8	-34.3	-6.6	7.4	-291.7
C–H···Br$^-$	5.42	-253.9	-33.2	-5.5	12.4	-290.2
C–H···Br$^-$	4.67	-248.9	-38.3	-7.1	12.6	-289.9
Compound *2*						
O–H···Cl$^-$	4.85	-361.1	-73.7	-7.2	66.6	-401.5
C–H···Cl$^-$	5.9	-302.4	-51.7	-6.4	30.6	-344.7
C–H···Cl$^-$	5.41	-300	-44.1	-4.8	20	-341.6
C–H···Cl$^-$	5.09	-284.6	-41.5	-5.2	9.4	-330.3
C–H···Cl$^-$	5.28	-259.5	-36	-4.2	12.3	-297.2
C–H···Cl$^-$	4.62	-251.9	-39.9	-5.1	11.3	-293.3
C–H···Cl$^-$	5.94	-250.3	-33.7	-4.3	5.5	-290
Compound *3*						
O–H···Cl$^-$	5.07	-352.5	-67.9	-5.6	72.1	-383.2
C–H···Cl$^-$	5.01	-293	-47.2	-6	14.8	-340.8
C–H···Cl$^-$	5.32	-293.9	-42.8	-5.8	11.5	-340.4
C–H···Cl$^-$	5.99	-292.6	-48.1	-6	26.6	-333.8
C–H···Cl$^-$	4.98	-267.4	-48.6	-6.2	25.1	-308.5
C–H···Cl$^-$	5.72	-254.4	-34.7	-4.1	15.2	-288.9
C–H···Cl$^-$	5.78	-234.5	-25.8	-3	4.2	-267
Compound *5*						
O–H···Br$^-$	3.98	-328.2	-64.9	-13	30.1	-387.7
C–H···Br$^-$	5.37	-341.8	-66.2	-9.9	57.5	-383.5
C–H···Br$^-$	3.64	-289.6	-59.5	-13.9	16.6	-352
C–H···Br$^-$	5.83	-302.5	-46.8	-8.6	27.2	-345.2
C–H···Br$^-$	5.78	-253.7	-28.3	-5	6.5	-289.5
C–H···Br$^-$	5.43	-237	-32.7	-5.7	12.6	-272
Compound *6*						
O–H···Br$^-$	5.32	-353.5	-64.6	-8.9	56.6	-394.3
C–H···Br$^-$	4.65	-323.5	-54	-9.9	24.3	-375.7
C–H···Br$^-$	4.25	-301.8	-49.4	-11.4	12.8	-357.6
C–H···Br$^-$	5.22	-297.7	-43	-8	18.6	-342
C–H···Br$^-$	5.77	-270.1	-35.1	-6.7	7	-313
C–H···Br$^-$	5.85	-252.5	-24.2	-3.9	3.1	-286.3
C–H···Br$^-$	6.72	-196.2	-12.9	-1.7	0.2	-218.4

[a]Electrostatic (E_E), polarisation (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions.
[b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.[2]

5. Crystal16 solubility measurements

5.1. (*RS*)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium bromide (*1*, *RS*-Br)

Table S4. Crystal16 solubility measurements (compound ***1***).

Concentration			Clear point
[g L^{-1}]	[mol L^{-1}]	mole fraction	[°C]
112.37	0.44742	0.03079	20.9
117.48	0.46777	0.03214	22.8
131.05	0.52180	0.03572	27.6
137.02	0.54557	0.03729	30
141.46	0.56325	0.03845	31.4
153.44	0.61095	0.04157	35.5
164.64	0.65554	0.04447	39.5
175.12	0.69727	0.04717	43.3
188.98	0.75246	0.05072	45.9
195.01	0.77647	0.05225	47.7
202.68	0.80701	0.05419	49.9
211.09	0.84051	0.05632	51.7
231.82	0.92303	0.06151	55
244.81	0.97477	0.06473	57.5
259.78	1.03436	0.06842	60
275.59	1.09730	0.07228	62.4

5.2. (*RS*)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (*2*, *RS*-Cl)

Table S5. Crystal16 solubility measurements (compound ***2***).

Concentration			Clear point
[g L^{-1}]	[mol L^{-1}]	mole fraction	[°C]
44.38	0.21471	0.01502	20.6
50.06	0.24219	0.01690	24.3
55.95	0.27068	0.01886	29.5
61.84	0.29918	0.02080	33
64.34	0.31127	0.02162	35.2
69.29	0.33522	0.02325	38.1
76.10	0.36817	0.02547	42.3
78.98	0.38210	0.02641	43.7
84.85	0.41050	0.02832	46.8
88.22	0.42680	0.02941	48.4
95.53	0.46217	0.03177	51.4
99.07	0.47929	0.03291	53.8
107.35	0.51935	0.03556	56.2
120.85	0.58466	0.03986	61.7
139.33	0.67407	0.04567	67.2
163.22	0.78965	0.05309	74.3

5.3. (*R/S*)-6-Hydroxy-1-methyl-1,5,6,7-tetrahydroimidazo[2,1-b][1,3]thiazinium chloride (*3*, *4*)

Table S6. Crystal16 solubility measurements (compound ***3***).

Concentration			Clear point
[g L^{-1}]	[mol L^{-1}]	mole fraction	[°C]
121.40	0.78308	0.05267	22.5
126.63	0.81686	0.05482	25.8
131.53	0.84846	0.05682	28.7
136.33	0.87940	0.05877	32
148.45	0.95757	0.06366	38.3
155.39	1.00235	0.06644	42.8
168.64	1.08785	0.07170	47
178.87	1.15380	0.07572	51.1
189.37	1.22155	0.07981	54.7
199.44	1.28653	0.08370	60.3
211.94	1.36714	0.08848	63.4
222.42	1.43472	0.09245	66.1

Table S7. Crystal16 solubility measurements (compound ***4***).

Concentration			Clear point
[g L^{-1}]	[mol L^{-1}]	mole fraction	[°C]
120.11	0.77477	0.05214	22
126.32	0.81483	0.05469	25.3
130.40	0.84113	0.05636	28.2
138.34	0.89235	0.05958	32.8
149.04	0.96140	0.06390	37.7
161.12	1.03932	0.06872	44.4
167.66	1.08150	0.07131	47.1
173.07	1.11643	0.07345	50
192.35	1.24077	0.08096	55.6
204.32	1.31796	0.08557	59.8
217.56	1.40338	0.09061	63
236.49	1.52551	0.09773	66.6

6. Lattice energy substitution calculations

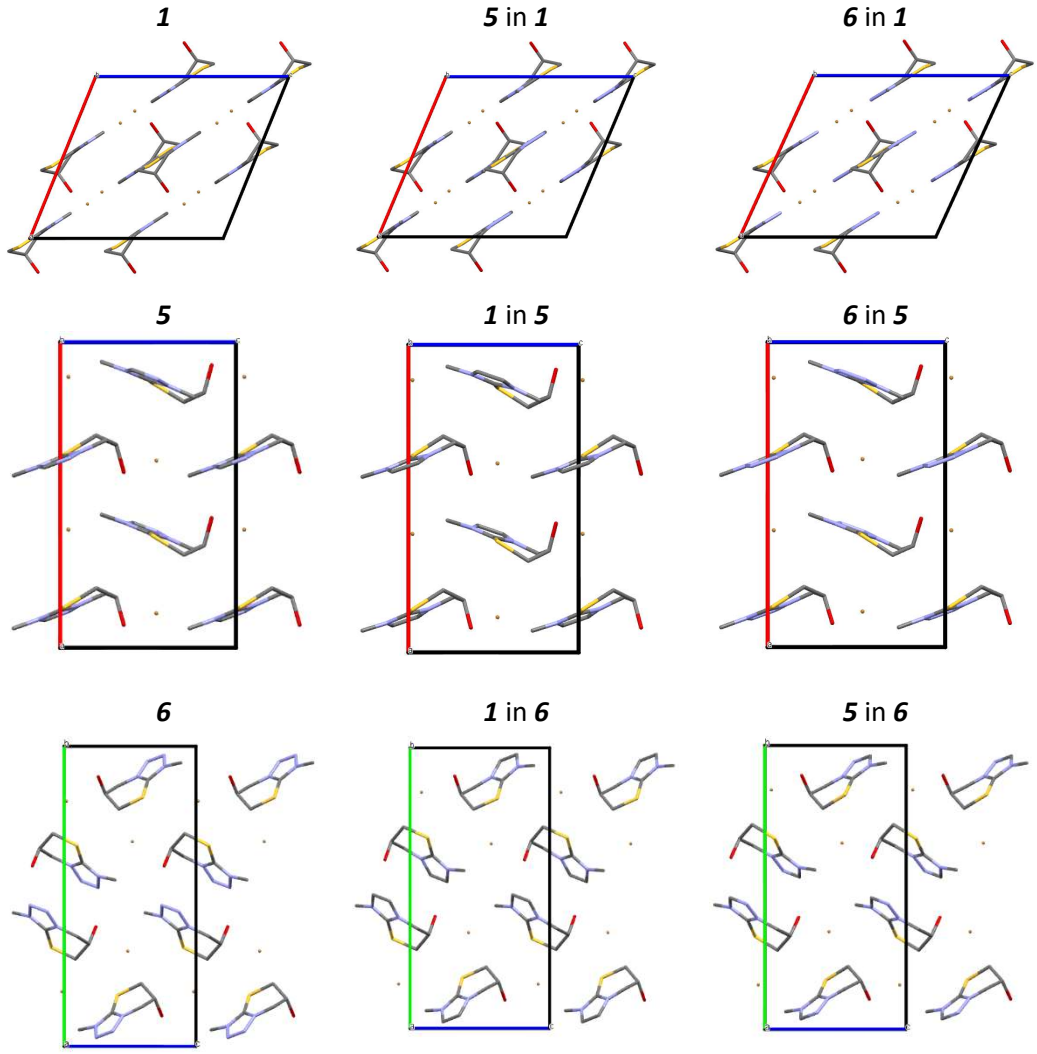


Figure S22. Packing diagrams of experimental and computed structures. The computed structures were obtained by replacing each of the cations of structures ***1***, ***5*** and ***6*** by the other cation in the same structure followed by optimisation (PBE-TS).

References

1. Willcott, M. R., *MestRe Nova*. 2009; Vol. 131, p 13180.
2. Mackenzie, C. F.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A., CrystalExplorer model energies and energy frameworks: extension to metal coordination compounds, organic salts, solvates and open-shell systems. *IUCrJ* **2017,** *4* (5).