Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for:

Controlling ring-chain tautomerism through steric hindrance

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Table S1. Diffraction data for *E*-$H_2L^1_{SB}$ and *rac*-$H_2L^2_{TQ}$ and *rac*-$H_2L^2_{TQ}$·$HCCl_3$

	E-$H_2L^1_{SB}$	*rac*-$H_2L^2_{TQ}$	*rac*-$H_2L^2_{TQ}$·$HCCl_3$
Formula	$C_{21}H_{20}N_2O_4S$	$C_{25}H_{28}N_4O_3S$	$C_{25}H_{28}N_4O_3S$·$CHCl_3$
Molecular weight	396.45	464.57	583.94
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a (Å)	8.979 (4)	8.7401 (12)	10.0744 (8)
b (Å)	10.358 (5)	10.3466 (13)	11.5179 (8)
c (Å)	12.109 (6)	12.7780 (18)	13.2903 (9)
α (º)	68.918 (5)	91.204 (6)	64.902 (4)
β (º)	67.153 (4)	91.180 (6)	84.007 (5)
γ (º)	88.425 (6)	91.168 (5)	87.326 (5)
Z	2	2	2
Volume (Å^3)	960.1 (8)	1154.8 (3)	1388.91(18)
Temperature	293(1)	100(2)	100(2)
Density (calculated, Mg/m^3)	1.371	1.336	1.396
Radiation type, wavelength	Cu *K*α, λ = 1.54184 Å	Mo *K*α, λ = 0.71073 Å	Mo *K*α, λ = 0.71073 Å
Absorption coefficient (mm^{-1})	1.76	0.962	1.051
F(000)	416	492	608
Habit, colour	Prism, orange	Plate, colourless	Prism, colourless
Crystal size (mm^3)	0.39 × 0.28 × 0.11	0.28 × 0.25 × 0.08	0.33 × 0.28 × 0.11
θ range for data collection	4.3 to 74.1	1.6 to 23.35°	1.7 to 26.0
Index ranges	$0 \le h \le 11$ $-12 \le k \le 12$ $-13 \le l \le 15$	$-10 \le h \le 10$ $-12 \le k \le 12$ $0 \le l \le 16$	$-12 \le h \le 12$ $-12 \le k \le 12$ $0 \le l \le 16$
Reflections collected	4133	16285	29871
Independent reflections	3877 (R_{int} = 0.017)	4138 (R_{int} = 0.090)	5483(R_{int} = 0.043)
Data / restraints / parameters	3877 / 0 / 272	4138 / 0 / 310	5483 / 0 / 543
Goodness-of-fit on F^2	1.068	1.047	1.058
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0459, wR_2 = 0.0594	R_1 = 0.0692, wR_2 = 0.1155	R_1 = 0.0451, wR_2 = 0.0694
R indices (all data)	R_1 = 0.1280, wR_2 = 0.1375	R_1 = 0.1565, wR_2 = 0.1831	R_1 = 0.1058, wR_2 = 0.1197
Largest diff. peak and hole (e.Å^{-3})	0.400 and -0.296	0.389 and -0.527	0.568 and -0.501

Table S2. Selected bond lengths and angles for $H_2L^1_{SB}$

Atoms	Distances	Atoms	Angles
C1-S1	1.761(2)	N1-S1-C1	106.65(8)
S1-O2	1.4278(15)	C7-N1-S1	117.00(13)
S1-O1	1.4355(14)	N1-C7-C8	114.60(14)
S1-N1	1.6177(19)	C12-C13-N2	122.05(16)
N1-C7	1.474(2)	C8-C13-N2	117.61(14)
C13-N2	1.420(2)	N2-C14-C15	121.38(14)
C14-N2	1.284(2)	O3-C20-C15	122.23(15)
C20-O3	1.3312(19)	O4-C19-C18	119.64(16)6
C19-O4	1.353(2)		

H bond scheme

D-H···*A*	*D*—H	H···*A*	*D*···*A*
N1-H1A···O1[i]	0.84 (3)	2.28 (3)	3.107 (2)
O4-H4P···O3[ii]	0.85 (4)	1.98 (4)	2.747 (2)
O3-H3P···N2	0.92 (7)	1.68(7)	2.561(2)
N2-H3P'···O3	0.76 (6)	1.93(7)	2.561(2)
C14-H14···O2[iii]	0.93	2.59	3.492 (2)
C18-H18···O1[iv]	0.93	2.61	3.464 (3)

(i) -*x*+2, -*y*-1, -*z*+1; (ii) -*x*+2, -*y*, - (iii) -*x*+1, -*y*, -*z*+1; (iv)

Table S3. Selected bond lengths and angles for *rac*-$H_2L^2_{TQ}$ and *rac*-$H_2L^2_{TQ}$·$HCCl_3$

Atoms	Distance[a] $H_2L^2_{TQ}$	Distance[a] $H_2L^2_{TQ}$·$HCCl_3$	Atoms	Angle[b] $H_2L^2_{TQ}$	Angle[b] $H_2L^2_{TQ}$·$HCCl_3$
S1-O1	1.430 (3)	1.4340 (18)	O1-S1-O2	120.12 (15)	119.76 (11)
S1-O2	1.435 (3)	1.4330 (17)	N1-S1-C1	107.08 (16)	108.33 (10)
S1-N1	1.666 (3)	1.669 (2)	C7-N1-S1	115.4 (2)	116.24 (15)
N1-C7	1.491 (4)	1.486 (3)	C7-N1-C14	111.3 (3)	110.91 (18)
N1-C14	1.479 (5)	1.492 (3)	C14-N1-S1	117.5 (2)	115.49 (15)
C13-N2	1.392 (5)	1.391 (3)	C13-N2-C14	118.1 (3)	118.33 (19)
N2-C14	1.447 (4)	1.432 (3)	N2-C14-N1	110.2 (3)	109.22 (18)
C18-N3	1.347 (4)	1.339 (3)	C18-N3-C19	117.4 (3)	117.6 (2)
N3-C19	1.320 (5)	1.335 (3)	N3-C19-N4	116.2 (3)	116.9 (2)
C19-N4	1.427 (4)	1.404 (3)	C19-N4-C20	126.0 (3)	127.0 (2)
N4-C20	1.367 (5)	1.366 (3)	N4-C20-O3	122.8 (3)	122.1 (2)
C20-O3	1.224 (4)	1.228 (3)			
Hydrogen bond scheme for $H_2L^2_{TQ}$					
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*	
N2—H2*A*···O3^{iii}	0.92 (4)	2.02 (4)	2.887 (4)	155 (3)	
N4—H4*A*···N1	0.88 (4)	2.26 (4)	2.892 (4)	128 (3)	
C7—H7*A*···O2^{i}	0.99	2.47	3.282 (4)	139	
C18—H18···O3^{ii}	0.95	2.57	3.461 (4)	156	
C18—H18···N3^{ii}	0.95	2.70	3.393 (5)	130	
Hydrogen bond scheme for $H_2L^2_{TQ}$·$HCCl_3$					
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*	
N2—H2*A*···O3^{iv}	0.80 (3)	2.12 (3)	2.904 (3)	167 (3)	
C2—H2···O2^{v}	0.95	2.46	3.406 (3)	179	
C7—H7*A*···Cl2	0.99	2.99	3.965 (2)	170	
C1*S*—H1*S*···O3^{vi}	1.00	2.20	3.092 (3)	147	

[a] in Å. [b] in º. (i) -*x*, -*y*, -*z*+1; (ii) -*x*-1, -*y*, -*z*+2; (iii) -*x*, -*y*, -*z*+2. (iv) -*x*+1, -*y*, -*z*+2; (v) -*x*+1, -*y*+1, -*z*+1; (vi) -*x*+1, -*y*+1, -*z*+2

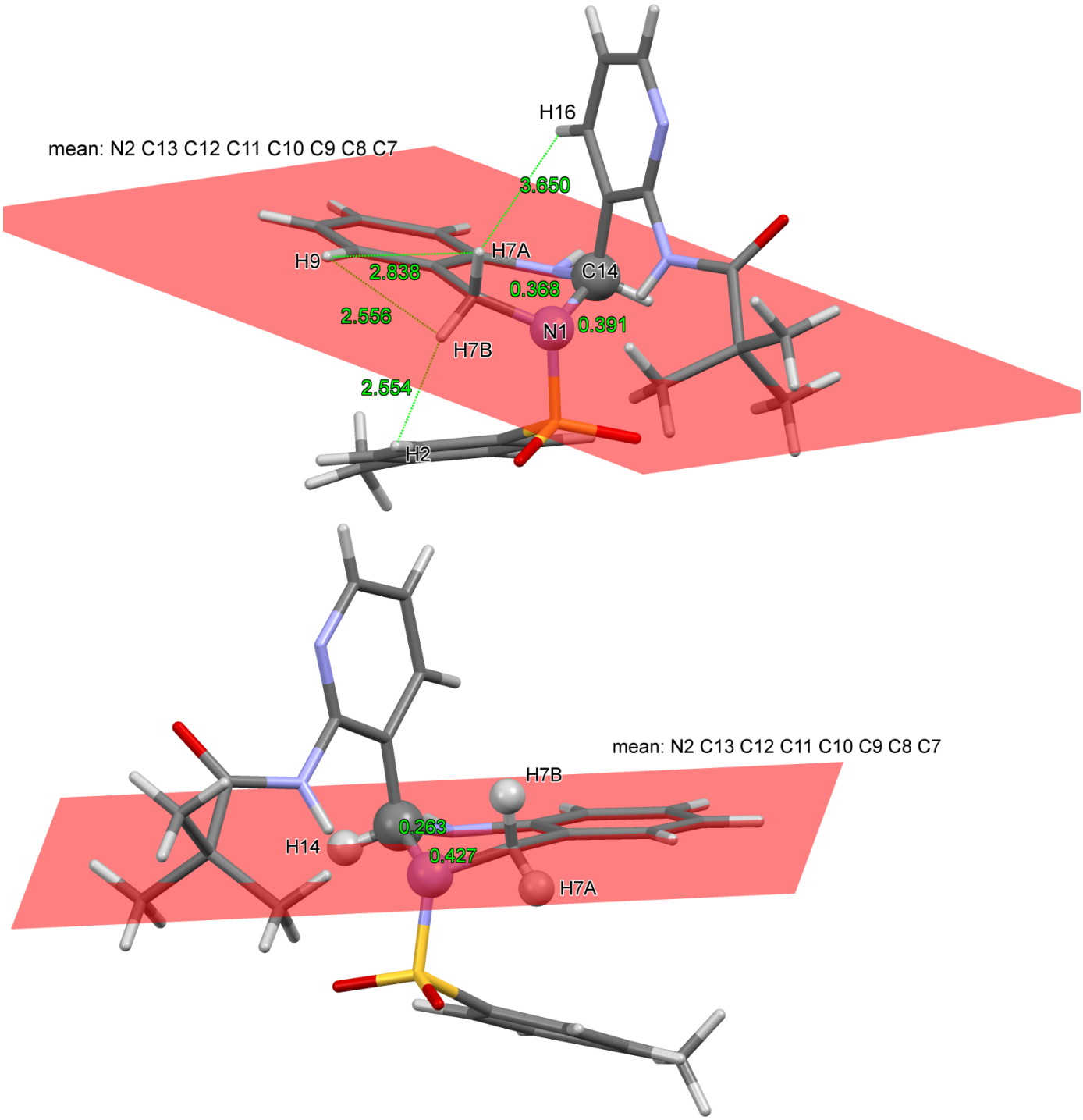

Fig. S1. Balls and sticks diagrams for *C(R),N(R)*-$H_2L^2{}_{TQ}$·$HCCl_3$ (top) and *C(S),N(S)*-$H_2L^2{}_{TQ}$ (bottom). The semi-chair conformation of the tetrahydroquinazoline rings with the corresponding distances between calculated planes and aliphatic atoms is shown. Some distances related to H···H couplings for NMR discussion are also indicated in the top figure.

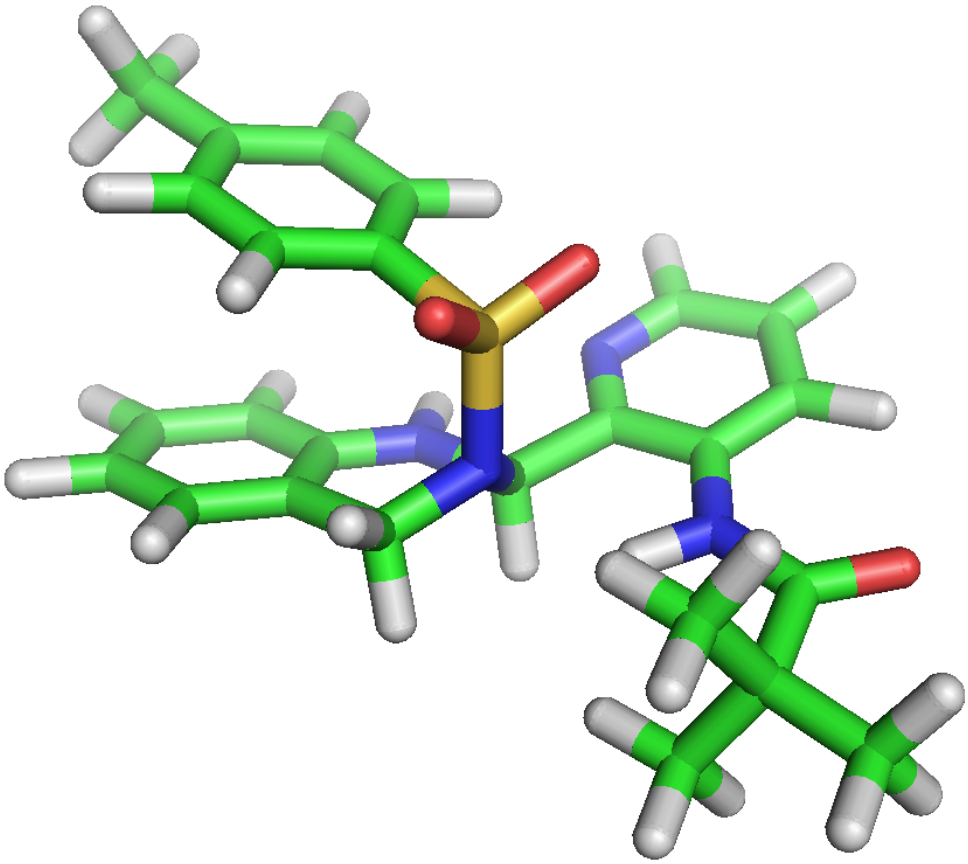

Fig. S2. Lowest energy conformation obtained using molecular mechanics modelling for C(*R*),N(*S*)-$H_2L^2{}_{TQ}$.

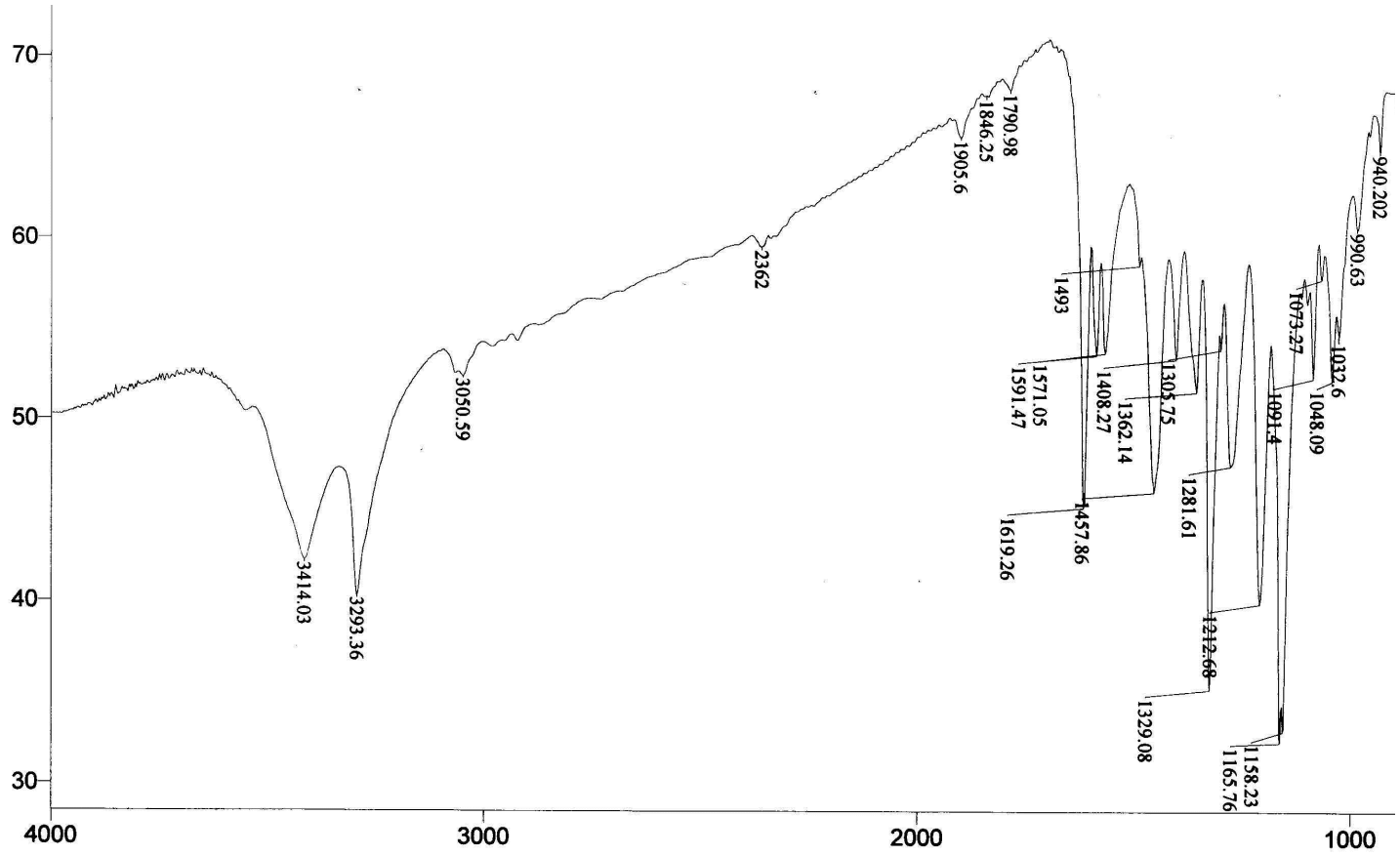

Fig. S3. Partial view of the IR spectrum $H_2L^1{}_{SB}$

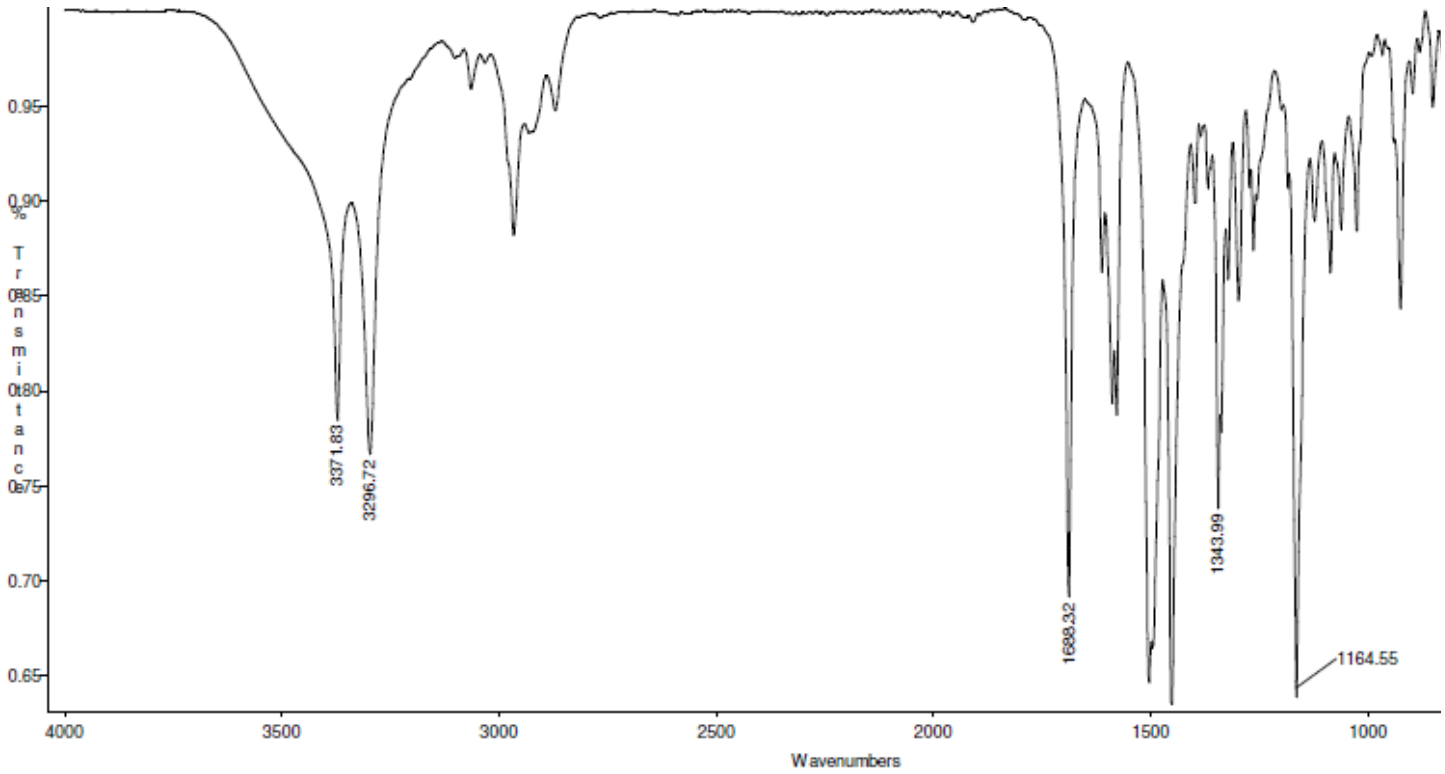

Fig. S4. Partial view of the IR spectrum of $H_2L^2{}_{TQ}$

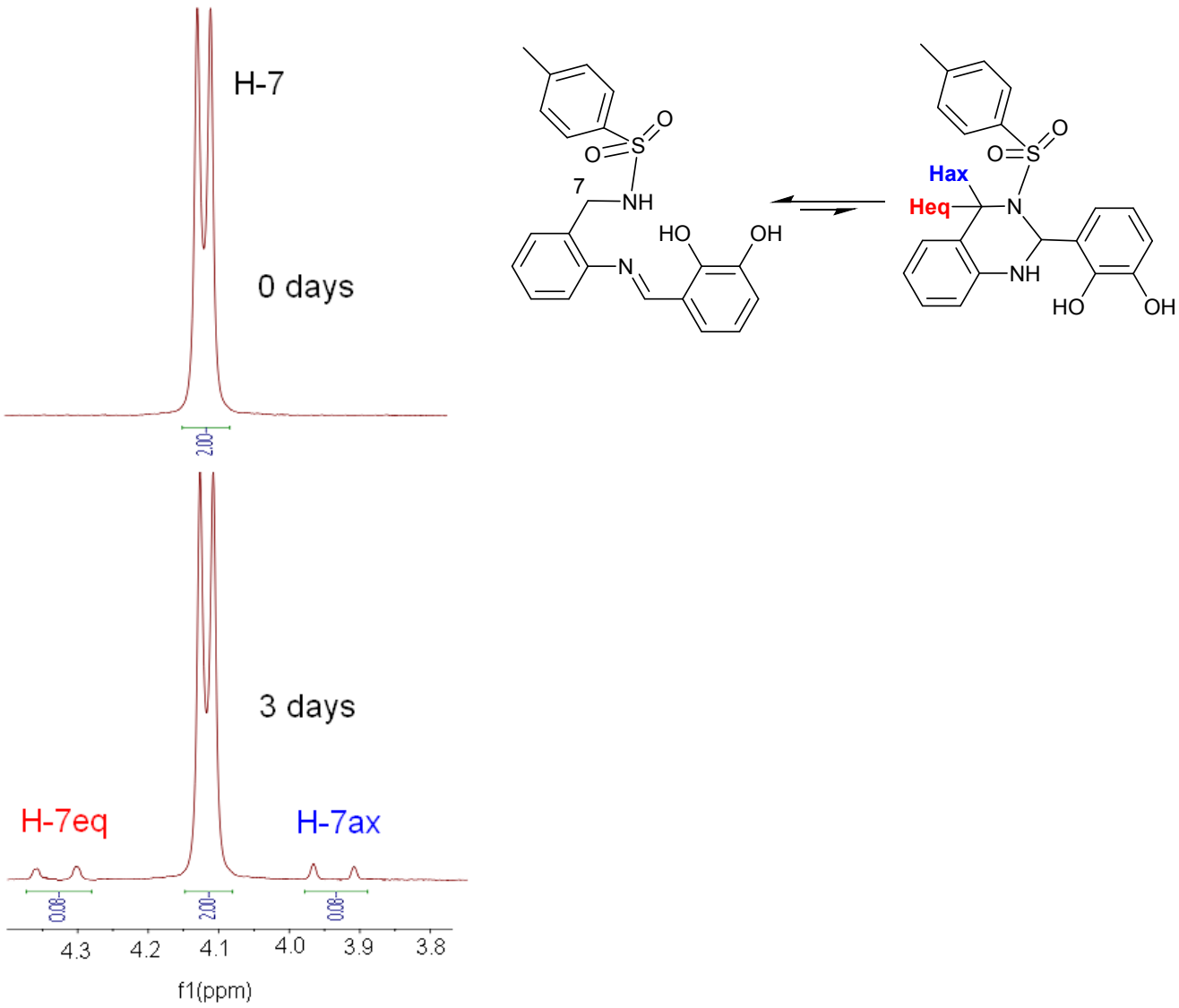

Fig S5. Initial and final spectra of the ^{1}H NMR monitoring of $H_2L^1_{SB}$ based on the changes with time observed in methylene signals. The central doublet corresponds to H-7 of $H_2L^1_{SB}$, while both H-7eq and H-7ax correspond to $H_2L^1_{TQ}$. Integration values are written above each peak.

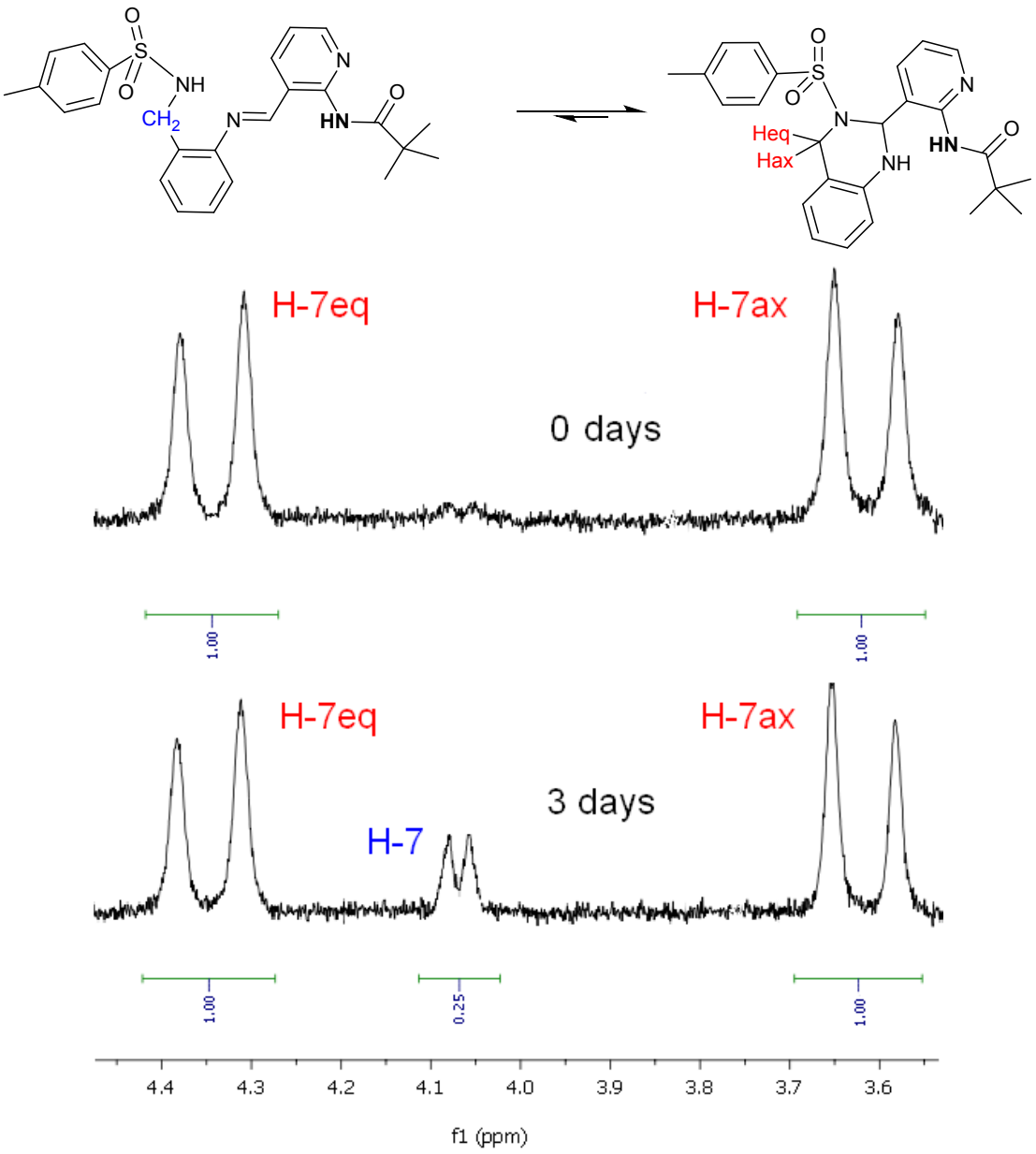

Fig S6. Initial and final spectra of the ^{1}H NMR monitoring of $H_2L^2_{TQ}$ based on the changes with time observed in methylene signals. The central doublet corresponds to H-7 of $H_2L^2_{SB}$, while H-7eq (left) and H-7ax (right) correspond to $H_2L^2_{TQ}$. Integration values are written above each peak.