ELECTRONIC SUPPLEMENTARY INFORMATION

A model compound for pyridinechalcone-based multistate systems. Ring Opening-Closure as the Slowest Kinetic Step of the Multistate.

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1. Titration of the chalcones in the acidic region in H_2O:MeOH 1:1 (v/v)

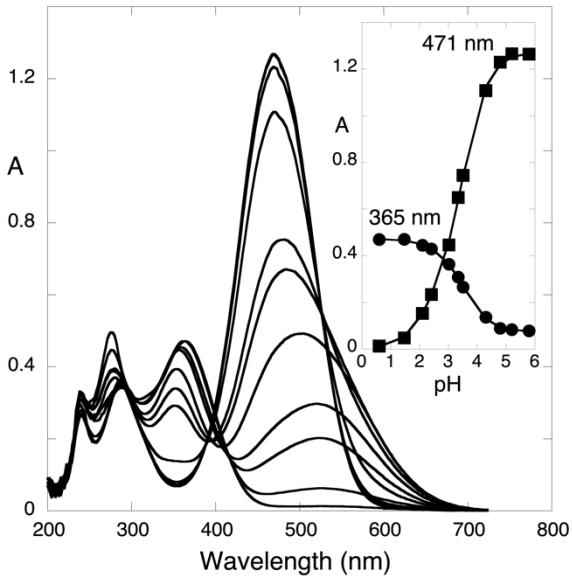


Figure S1. Spectral variations of compound **1** after pH jumps from the neutral *trans*-chalcone at pH=6.4 to the pH range 0.6<pH<5.8; inset: fitting of the absorption data leads to the determination of the acid-base constants for $pK_{Ct^{2+}/Ct^{+}}$=2.2 and $pK_{Ct^{+}/Ct}$=3.5.

2. NMR peak assignment of compound 1 at pD=6.5

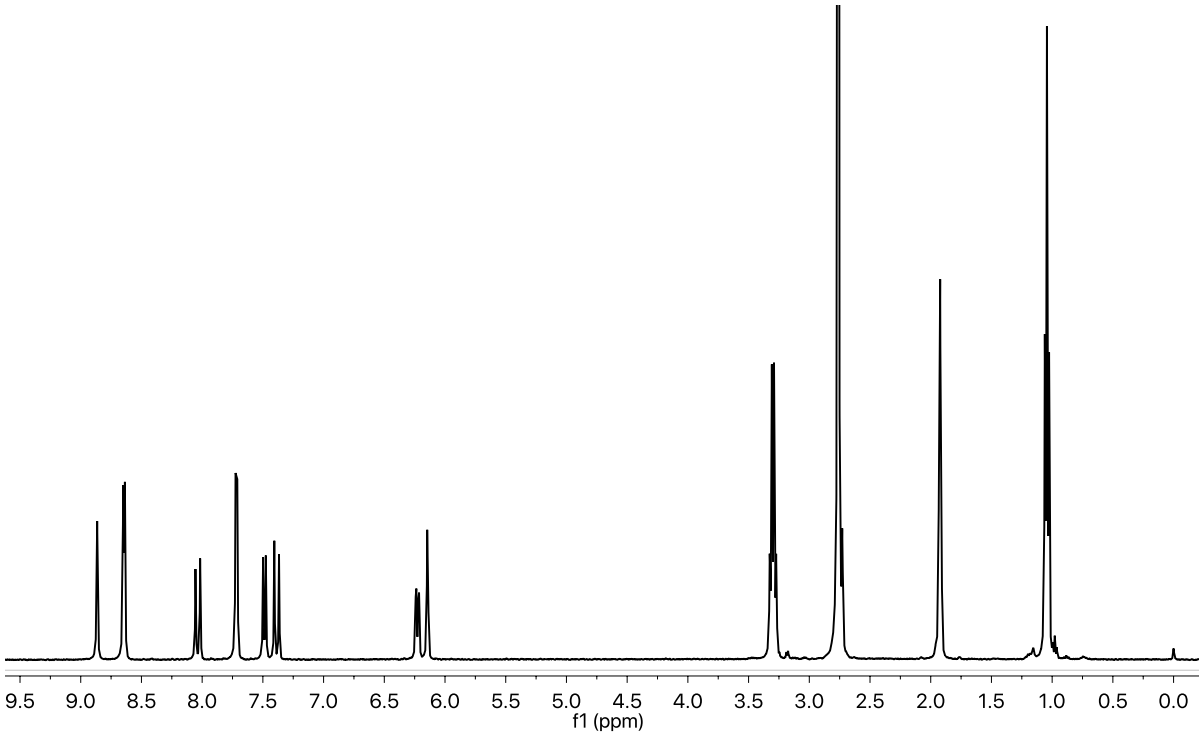


Figure S2. ^{1}H NMR of compound **1** in $(CD_3)_2CO$ at pD=6.5 (**Ct** species).

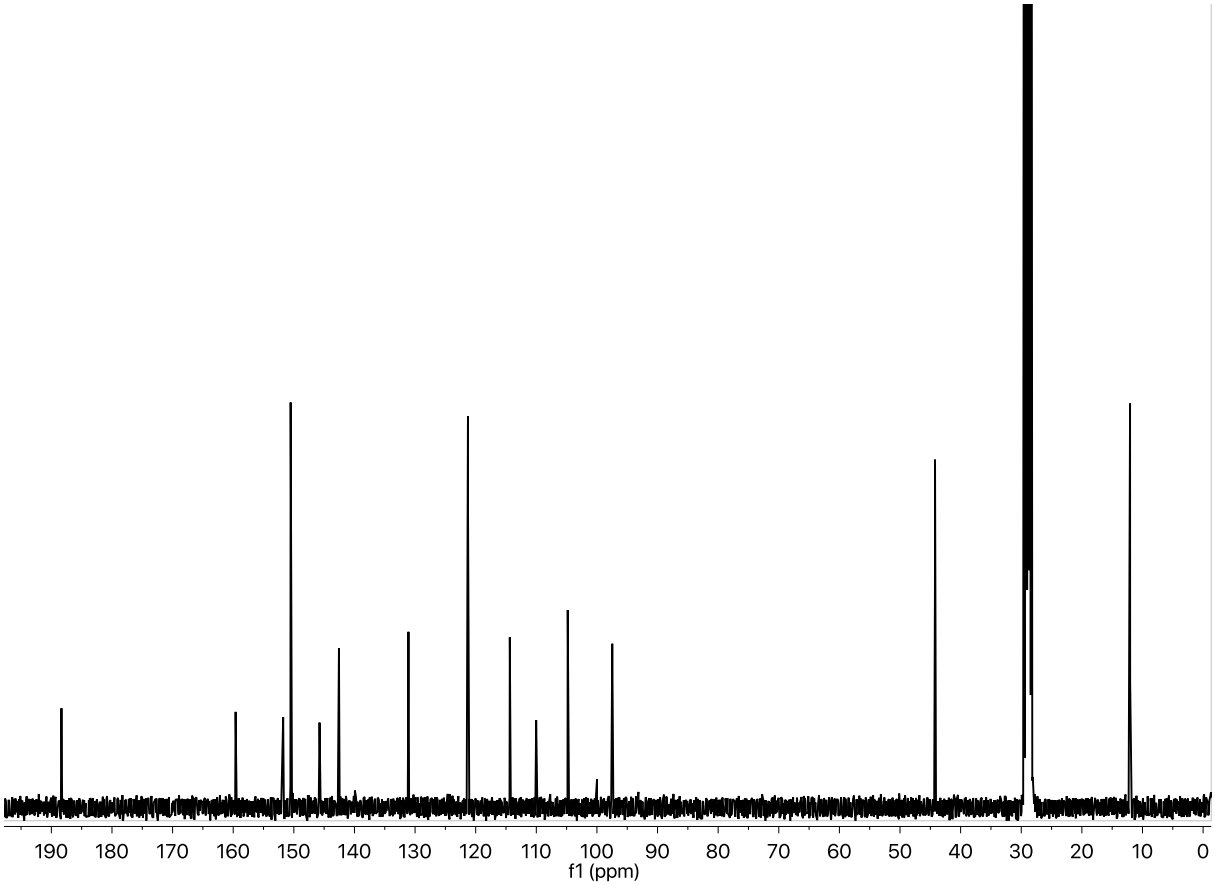


Figure S3. ^{13}C NMR of compound **1** in $(CD_3)_2CO$ at pD=6.5 (**Ct** species).

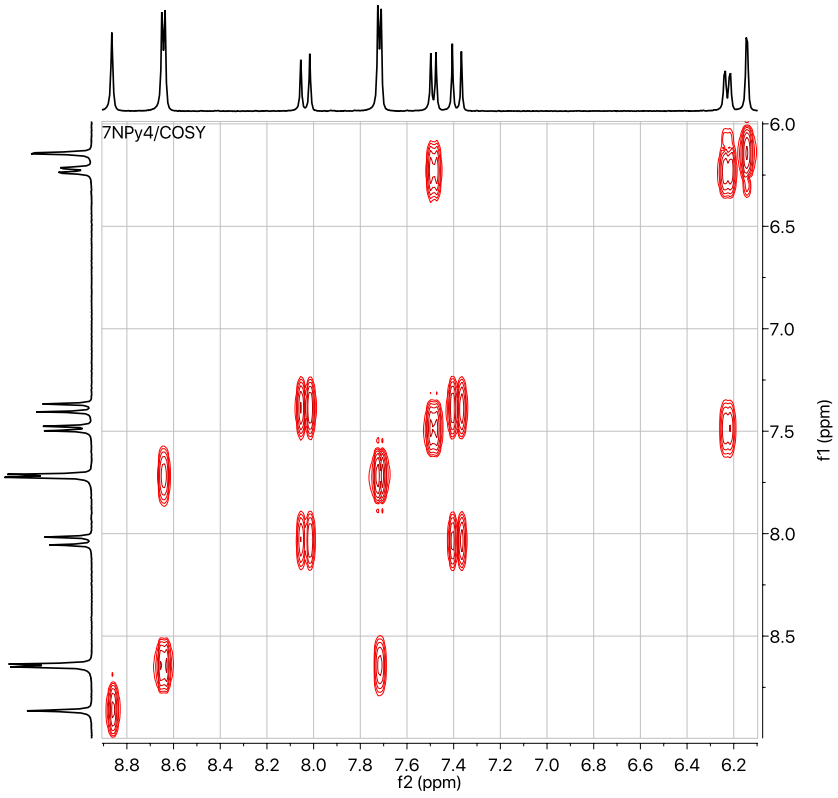


Figure S4. ^{1}H-^{1}H-COSY of compound **1** in $(CD_3)_2CO$ at pD=6.5 (**Ct** species).

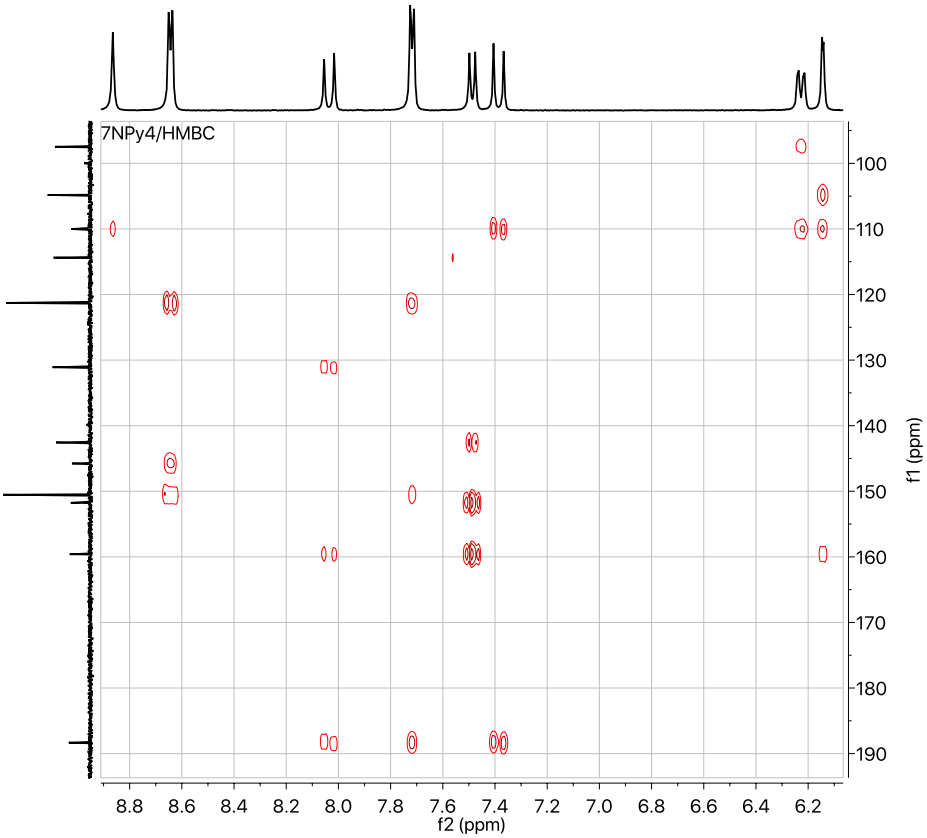
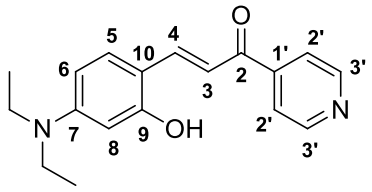


Figure S5. ^{1}H-^{13}C-HMBC of compound **1** in $(CD_3)_2CO$ at pD=6.5 (**Ct** species).

Table S1 – ^{1}H-NMR and ^{13}C-NMR full peak assignment of compound **1** as **Ct** species at pD=6.5 in $(CD_3)_2CO$.

			
Position[a]	**^{1}H δ/ppm (J/Hz)**	**^{13}C δ/ppm**	**HMBC**
OH	8.86 (*s*, 1H)	-	-
2	-	188.3	4, 3, 2’
3	7.39 (*d*, 16.0)	114.4	
4	8.04 (*d*, 16.0)	142.6	5
5	7.49 (*d*, 8.9)	131.1	
6	6.23 (*dd*, 8.9, 2.5)	104.8	8
7	-	151.7	5, CH_2
8	6.14 (*d*, 2.6)	97.5	6
9	-	159.6	4, 5, 6
10	-	110.0	3, 6, 8
1’	-	145.7	3’
2’	7.73 (*d*, 7.0)	121.3	2’, 3’
3’	8.64 (*d*, 7.0)	150.5	3’, 2’
7-N-($\underline{CH_2}$-CH_3)$_2$	3.30 (*q*, 7.0)	44.2	CH_2, CH_3
7-N-(CH_2-$\underline{CH_3}$)$_2$	1.04 (*t*, 7.0)	12.0	CH_2

[a] This numbering was made according to the numbering of the flavylium structure, see Table S2.

3. NMR variations and full peak assignment of the compound 1 after a pD jump from pD=6.5 to pD=3 in $CD_3OD:D_2O$ 1:1 (v/v)

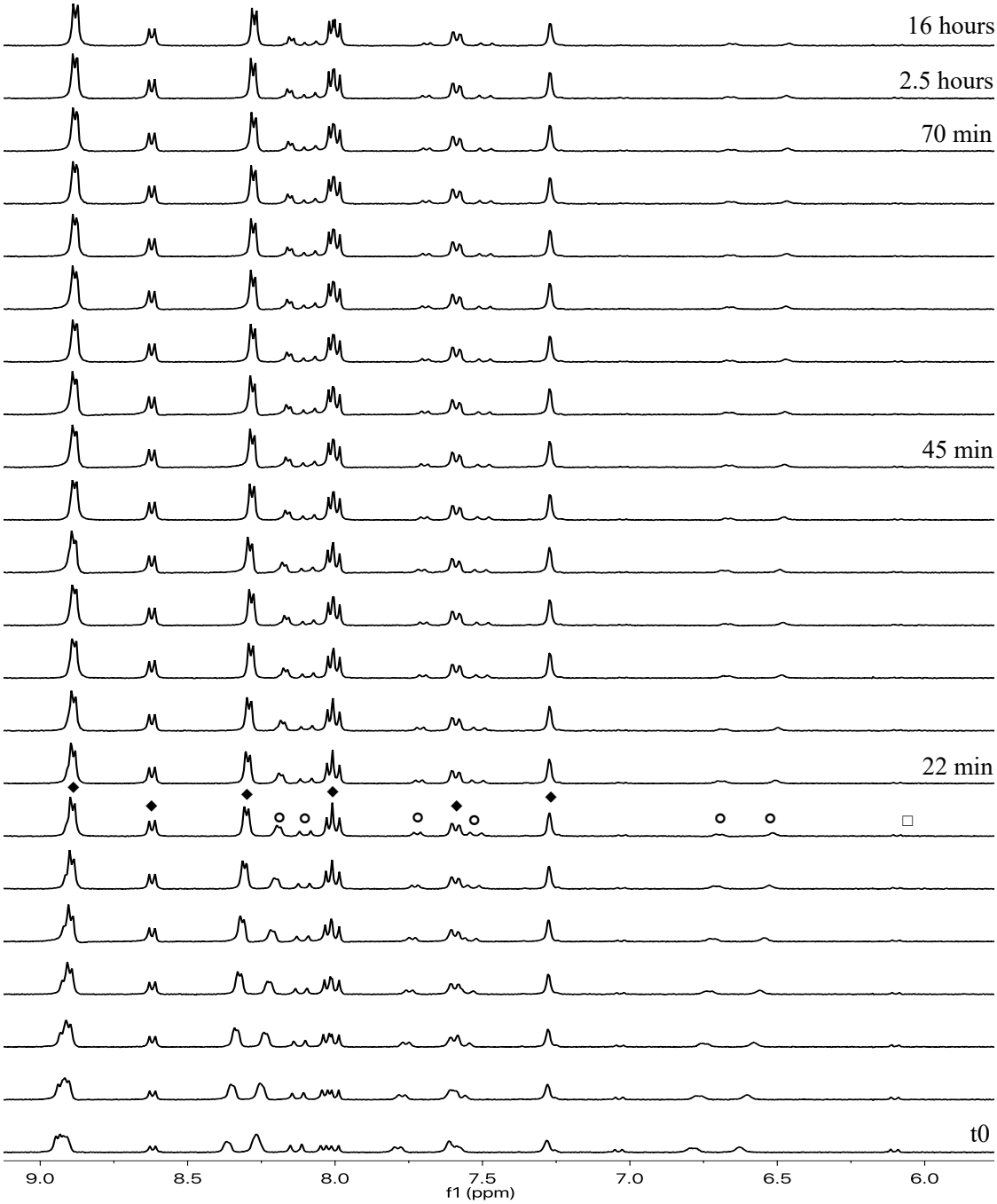


Figure S6 - ^{1}H NMR spectra variations of compound **1** after a pD jump from pD=6.5 to pD=3 in $CD_3OD:D_2O$ 1:1 (v/v); $\mathbf{AH}^+$ (◆), $\mathbf{Ct}^+$ (○), $\mathbf{B}^+$ + $\mathbf{Cc}^+$ (□).

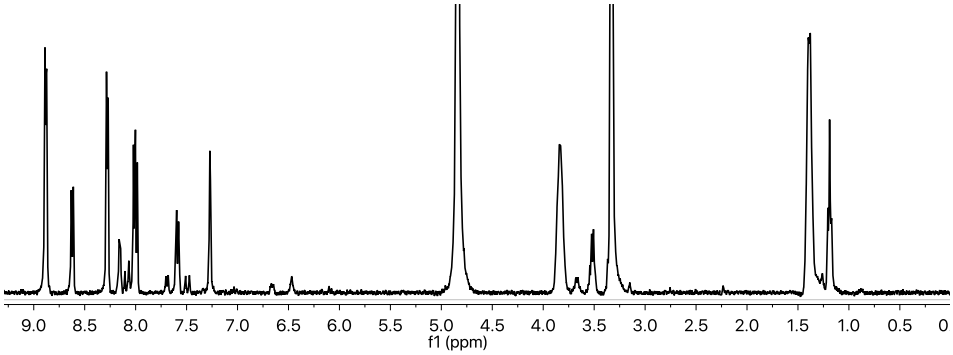


Figure S7. ^{1}H NMR of compound **1** in CD_3OD:D_2O (1:1) at pD=3.0 (**AH**$^{+}$ species is predominant).

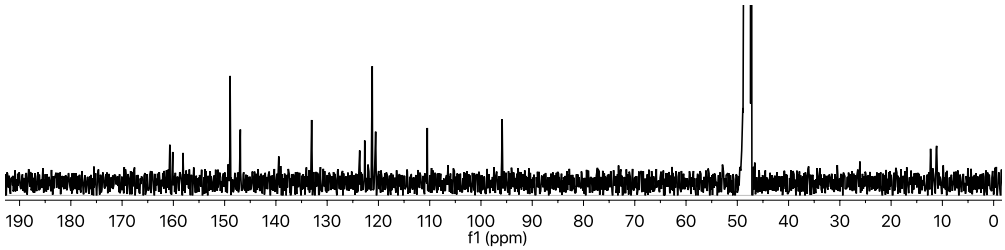


Figure S8. ^{13}C NMR of compound **1** in CD_3OD:D_2O (1:1) at pD=3.0 (**AH**$^{+}$ species is predominant).

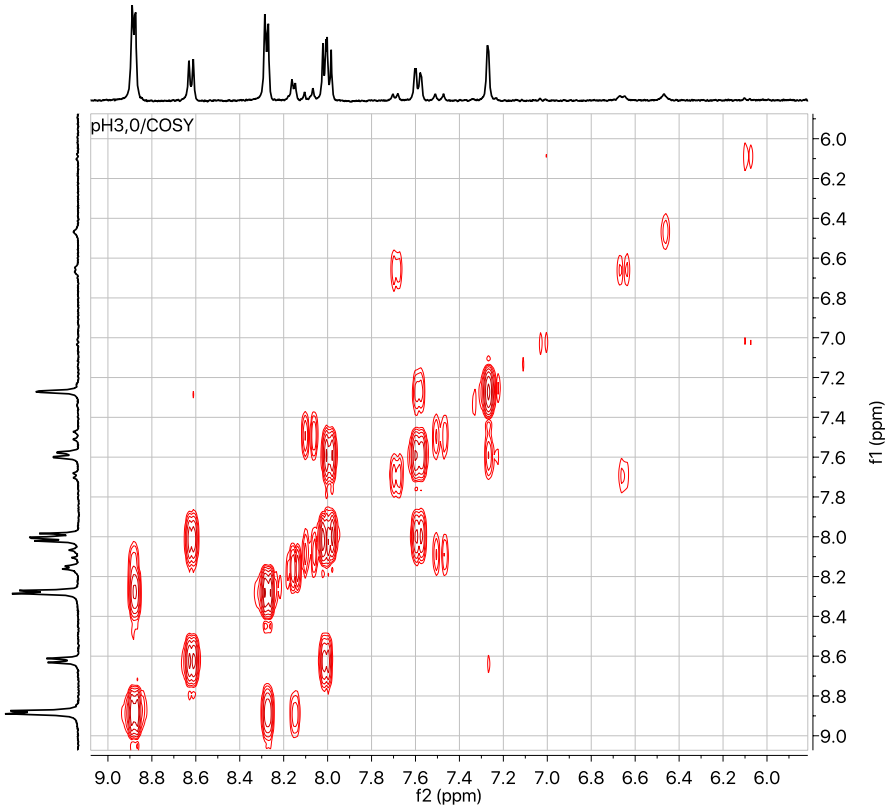


Figure S9. ^{1}H-^{1}H-COSY of compound **1** in CD_3OD:D_2O (1:1) at pD=3.0 (**AH**$^{+}$ species).

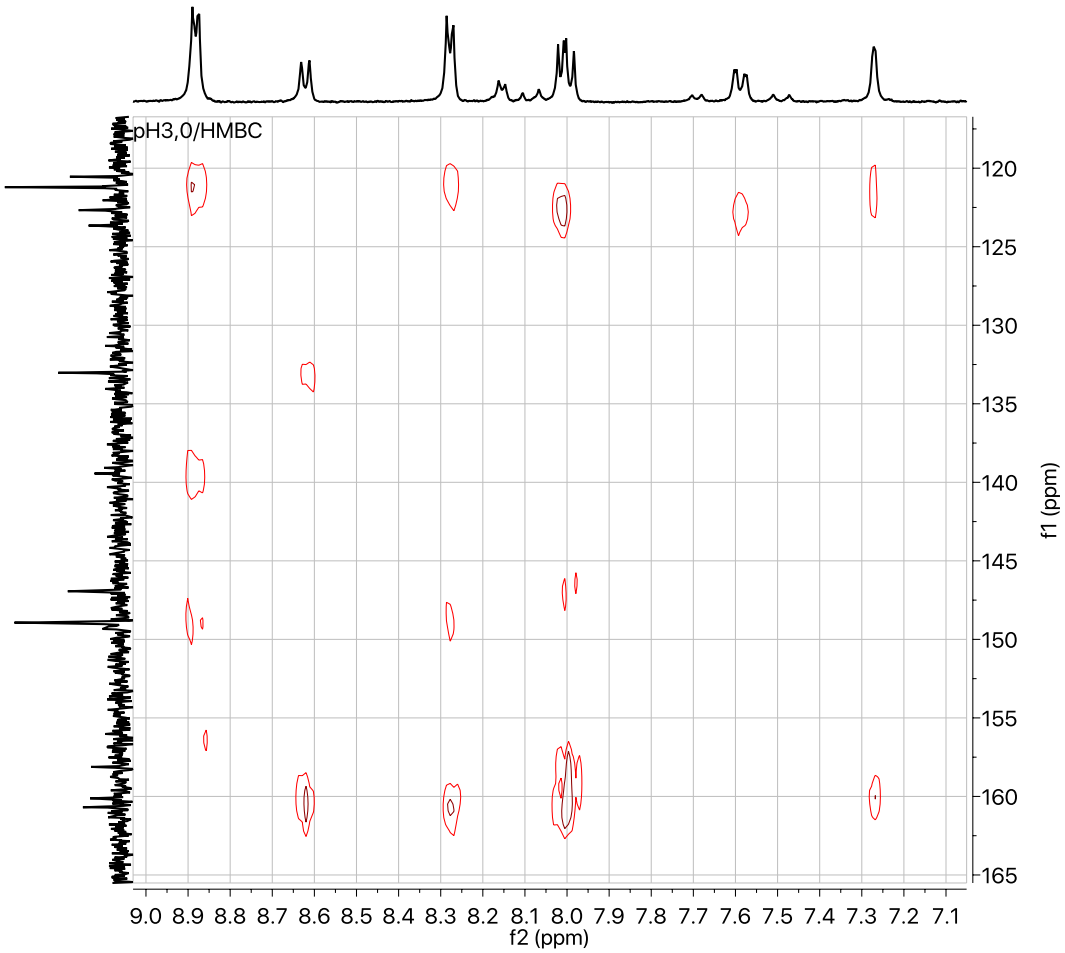
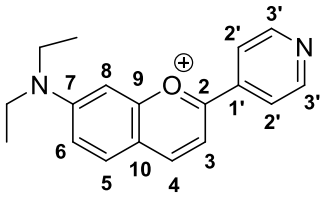


Figure S10. ^{1}H-^{13}C-HMBC of compound **1** in CD_3OD:D_2O (1:1) at pD=3.0 (**AH**$^{+}$ species).

Table S2 – ^{1}H-NMR and ^{13}C-NMR full peak assignment of compound **1** as **AH^{+}** species at pD=3 in CD_3OD:D_2O (1:1).

Major compound (75.8%)

			
Position	**^{1}H δ/ppm (J/Hz)** MeOD:D_2O (1:1)	**^{13}C δ/ppm** MeOD:D_2O (1:1)	**HMBC** MeOD:D_2O (1:1)
1	-	-	-
2	-	160.7	4, 2’
3	8.00 (*d*, ov, 7.5)	132.9	4
4	8.62 (*d*, 8.9)	146.9	5
5	8.00 (*d*, ov, 7.5)	110.5	
6	7.59 (*dd*, 8.9, 2.3)	120.6	8
7	-	160.1	5, 8, CH2
8	7.27 (*d*, 2.3)	95.9	6
9	-	158.14	5
10	-	122.7	3, 6
1’	-	139.4	3’, 3
2’	8.28 (*m*)	121.2	3’, 2’
3’	8.84 (*m*)	149.0	2’, 3’
7-N-($\underline{CH_2}$-CH_3)$_2$	3.84 (*m*)	46.9	-
7-N-(CH_2-$\underline{CH_3}$)$_2$	1.39 (*m*)	11.8	-

4. NMR variations and full peak assignment of the compound 1 after a pD jump from pD=6.5 to pD=0.5 in $CD_3OD:D_2O$ 1:1 (v/v)

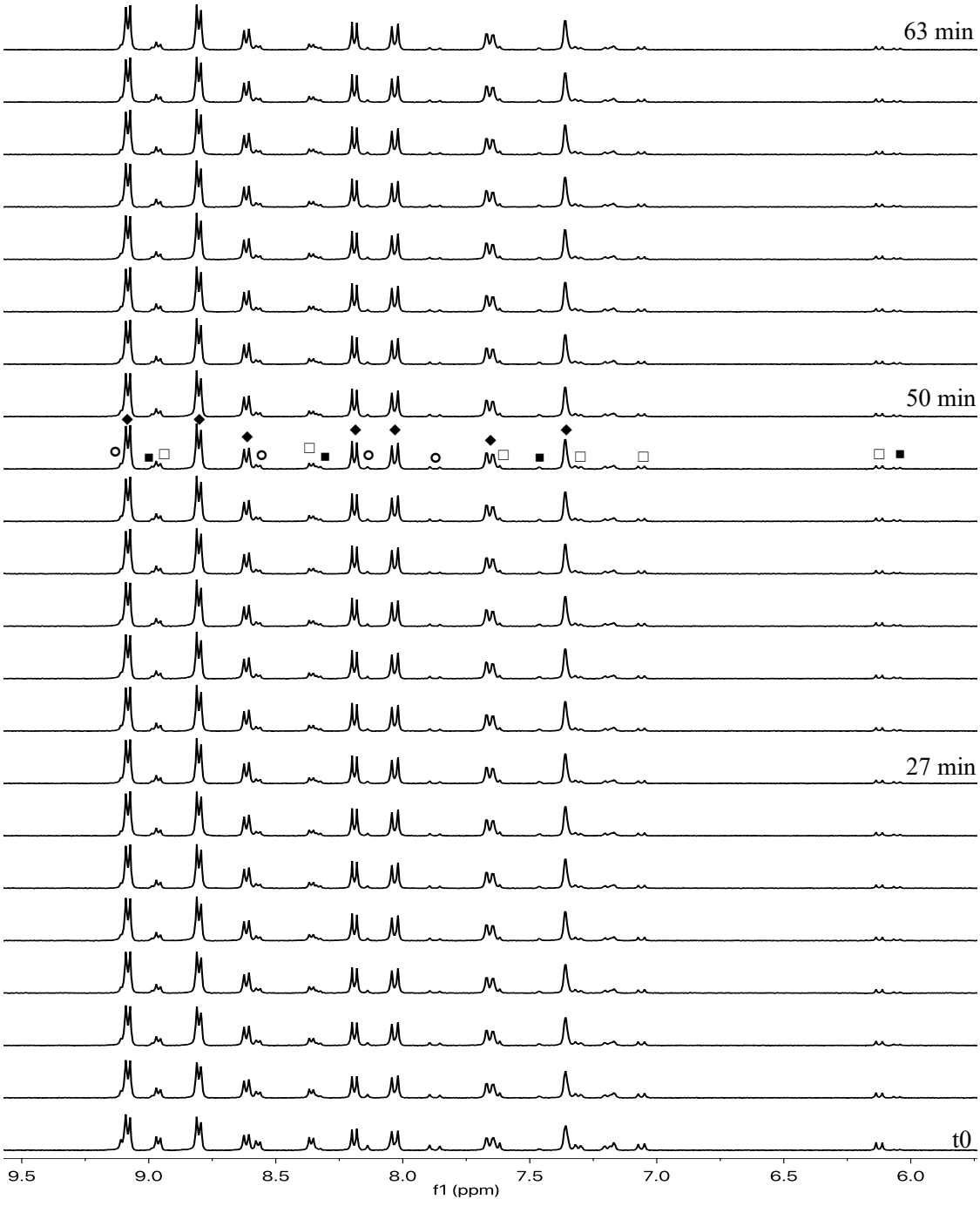


Figure S11 - ^{1}H NMR spectral variations of compound **1** after a pD jump from pD=6.5 to pD=0.5 in $CD_3OD:D_2O$ 1:1 (v/v); $\mathbf{AH^{2+}}$ (◆), $\mathbf{Ct^{2+}}$ (⊙), $\mathbf{Cc^{2+}}$ (□), $\mathbf{B^{2+}}$ (■).

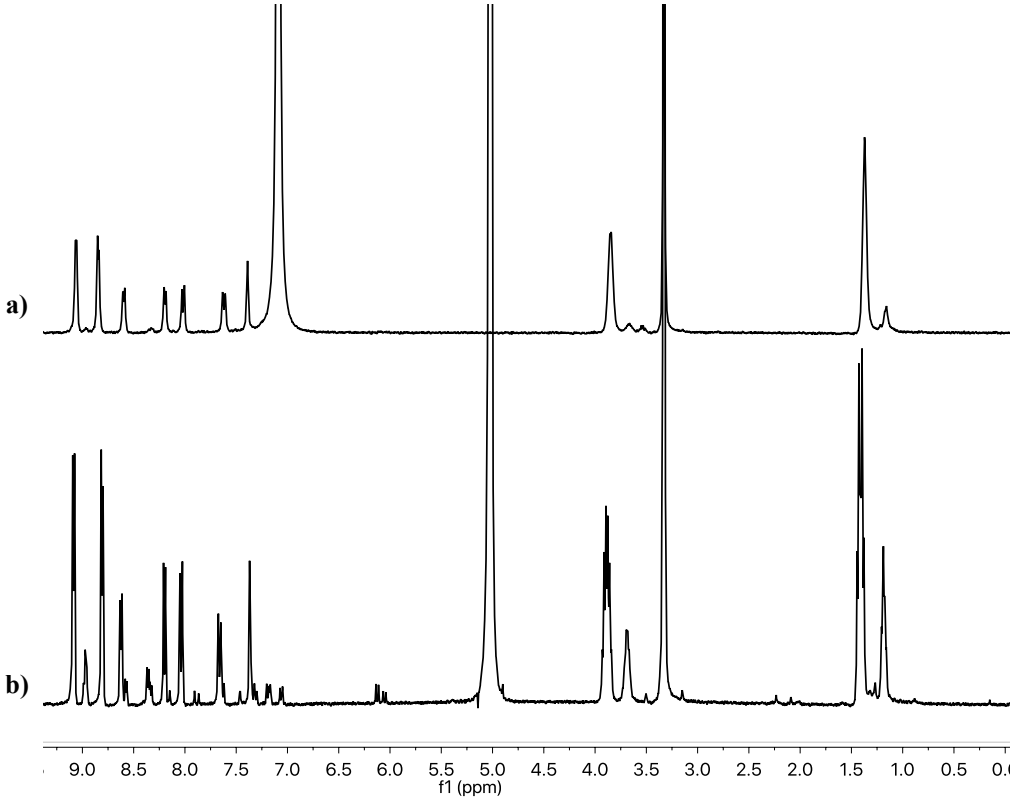


Figure S12. a) ^{1}H NMR of compound **1** in DCl at pD = –1 (**AH^{2+}**); **b)** ^{1}H NMR of compound **1** in CD_3OD:D_2O (1:1) at pD=0.5 (**AH^{2+}** Major species 78.1%).

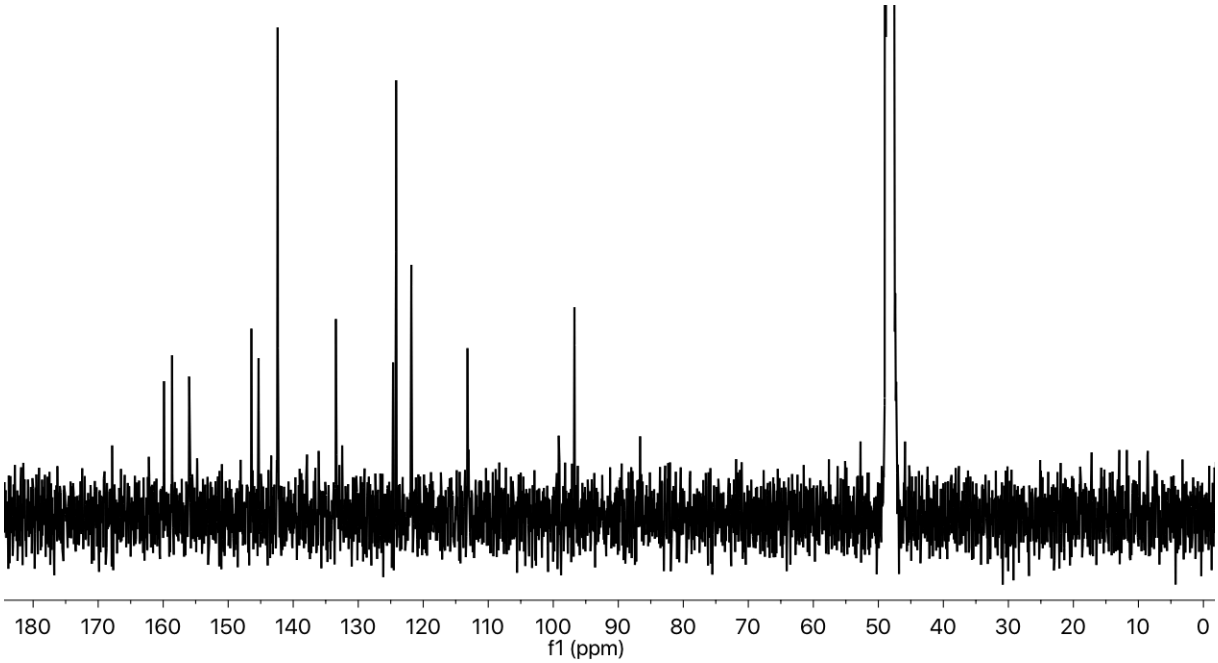


Figure S13. ^{13}C NMR of compound **1** in CD_3OD:D_2O (1:1) at pD = –1 (**AH^{2+}** species).

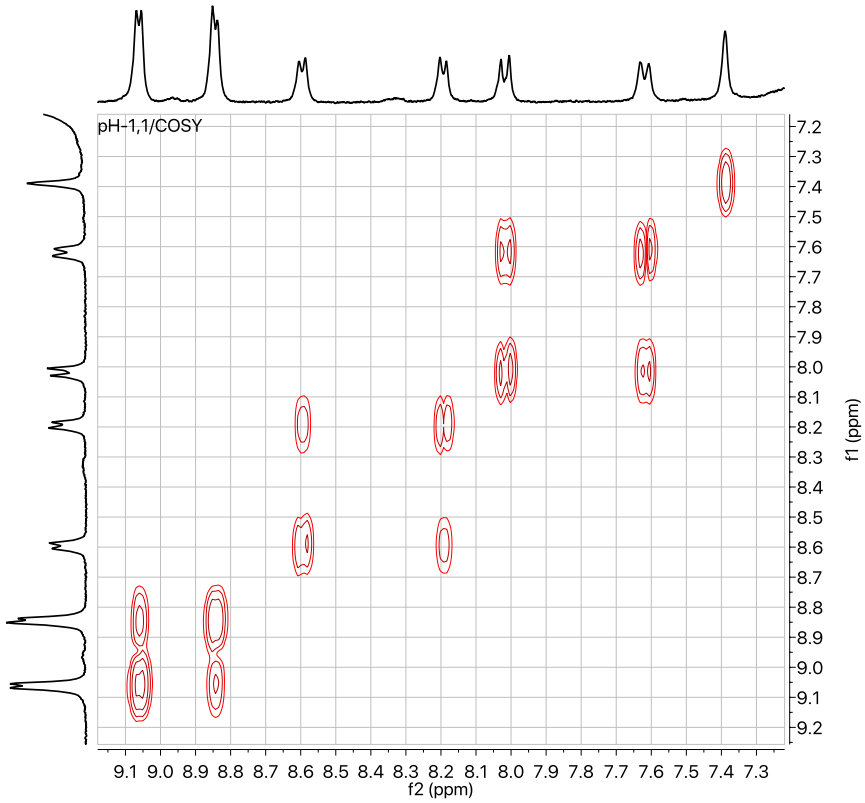
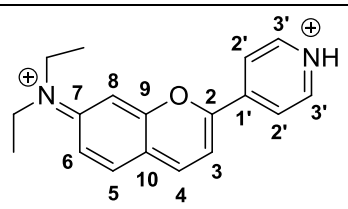


Figure S14. ^{1}H-^{1}H-COSY of compound **1** in DCl at pD = –1 (**AH**$^{2+}$).

Table S3 – ^{1}H-NMR of compound **1** in DCl at pD = –1 (**AH^{2+}**).

		
Position	**^{1}H δ/ppm (J/Hz)**	**^{13}C δ/ppm**
1	-	
2	-	159.8*
3	8.02 (dd, 9.5, 4.2)	133.3$^{\#}$
4	8.60 (d, 7.5)	145.4
5	8.19 (d, 7.5)	113.2$^{\#}$
6	7.62 (d, 9.6)	121.8$^{\#}$
7	-	158.5*
8	7.39 (s,)	96.8
9	-	155.8*
10	-	124.6$^{\$}$
1’	-	146.4$^{\$}$
2’	8.84 (d, 6.1)	
3’	9.06 (d, 5.9)	142.5
7-N-($\underline{CH_2}$-CH_3)$_2$	3.85 ((*br* m)	48.0
7-N-(CH_2-$\underline{CH_3}$)$_2$	1.38 ((*br* m)	12.0

$^{\$, *, \#}$ These signals may be interchangeable.