Revisiting the Salicylidene-based Anion Receptors

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(1) Materials and experimental methods

All chemicals and solvents used in the synthesis of Schiff bases were purchased from commercial sources and used without further purification. Tris(2-aminoethyl)amine, 4-nitrobenzoyl chloride, 2-hydroxybenzaldehyde, 4-aminobenzonitrile, *ortho*-phenylene diamine, 5-nitro-2-hydroxybenzaldehyde and dimethylsulfoxide-d_6 (99.9 atom % D) were purchased from Sigma-Aldrich (Germany/China). Pd (10%) on carbon, hydrazine monohydrate and tetrabutylammonium salts were purchased from TCI (Japan).

NMR experiments were carried out on a Bruker Advance FT-400 MHz instrument using DMSO-d_6 and chemical shifts were recorded in parts per million (ppm) on the scale using residual solvent peak (2.50 ppm) as a reference. In a typical ^{1}H-NMR experiment to demonstrate the hydrolysis of imine bond in the presence of a tetrabutylammonium salt, 15 mg of a salicylidene Schiff base compound was dissolved in 0.5 ml of DMSO-d_6 (Molar strength: 3.7 x10^{-2} mol/L for **SL**, 1.3 x10^{-1} mol/L for **CL1**, 1.0 x10^{-1} mol/L for **CL2**) and an excess of a tetrabutylammonium salt (10 equiv. in the case of **SL** and 5 equiv. in the cases of **CL1**, **CL2** and **NCL2**) was added into the DMSO-d_6 solution. ^{1}H-NMR of the solution mixture was recorded on the same day in an hour, and the sealed NMR tubes were kept at room temperature under ambient condition. The NMR solution mixtures were recorded on subsequent days to monitor the progress of imine bond hydrolysis.

In a typical ^{1}H-NMR control experiment to demonstrate the hydrolysis of imine bond in the presence of water, 15 mg of a salicylidene Schiff base compound was dissolved in 0.5 ml of DMSO-d_6 (Molar strength: 3.7 x10^{-2} mol/L for **SL**, 1.3 x10^{-1} mol/L for **CL1**, 1.0 x10^{-1} mol/L for **CL2**) and an excess of deionized water (30 equiv. in the case of **SL** and 15 equiv. in the cases of **CL1** and **CL2**) was added into the solution. ^{1}H-NMR of the solution mixture was recorded on the same day. The sealed NMR tubes were kept at room temperature under ambient condition and the NMR solution mixtures were recorded on subsequent days to monitor the progress of imine bond hydrolysis. Similarly, ^{1}H-NMR control experiments of salicylidene compounds (**SL**, **CL1** and **CL2**) in the presence of water and one equiv. of (n-Bu_4N^+)Cl^- were prformed to demonstrate the role of anion in the hydrolysis of imine bonds in the presence of moisture.

Variable temperature ^{1}H-NMR spectra of **CL2** in the presence of tetrabutylammonium dihydrogenphosphate was recorded in $CDCl_3$ (Sigma-Aldrich) at room temperature, 0 ^{o}C and at −20 ^{o}C on a Bruker Advance FT-400 MHz instrument.

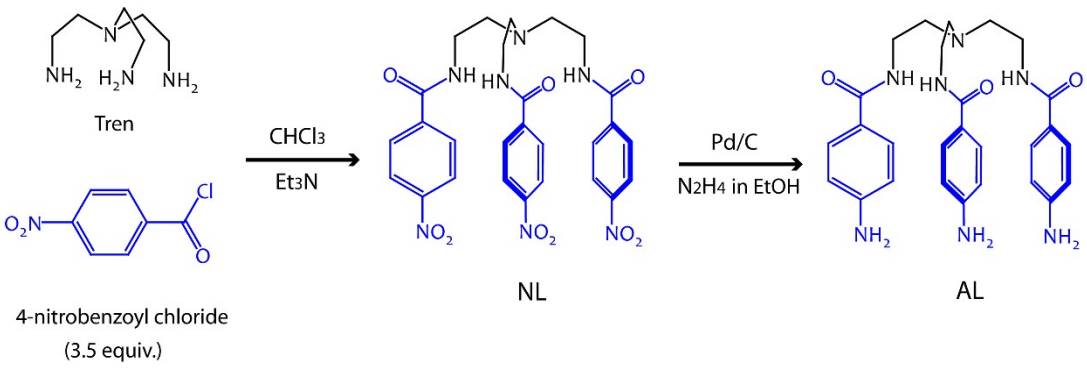
(2) Synthesis and Characterization of Salicylidene Schiff Base Compounds

(A) Synthesis of tris(4-amino-N-ethylbenzamide)amine (AL): Tris(4-amino-N-ethylbenzamide)amine (**AL**) was synthesized by reduction of its nitro analogue (Tris(4-nitro-N-ethylbenzamide)amine**, NL**) which was synthesized by modification of a reported literature procedure (Scheme S1). **NL** was synthesized by the reaction of tris(2-aminoethyl)amine, (Tren) with 4-nitrobenzoyl chloride in 1 : 3.5 molar ratio at room temperature in dry chloroform. In a 100 mL flat bottom flask, 0.73 mL (5 mmol) of tris(2-aminoethyl)amine was dissolved in 25 mL of chloroform and 3.2 g of 4-nitrobenzoyl chloride (17.5 mmol) was added in portions into the above solution with constant stirring at room temperature. The reaction mixture was allowed to stir overnight at room temperature followed by the addition of 3 ml (excess) triethylamine and stirred for another 1 hour. Reaction of Tren with 4-nitrobenzoyl chloride generates HCl in the reaction medium, which eventually protonate the tertiary nitrogen of the formed **NL**. Triethylamine was added to basify the reaction mixture so that **NL** can be obtained in its neutral form. The precipitate obtained was then filtered, collected in a 250 ml flat bottom flask and washed with 50 ml of methanol in the presence of 1 ml of triethylamine under stirring. The compound was finally filtered again and washed with another 50 ml of methanol over the filter paper to ensure its purity for subsequent reduction reaction.

In a 250 ml flat bottom flask, 1 g of **NL** (1.6 mmol) as dispersed in 100 ml of ethanol and 100 mg of Pd/C and 1 ml of hydrazine hydrate was added in to the flask. The reaction mixture was then refluxed overnight at about 70 °C and filtered to remove the heterogeneous Pd/C catalyst. The filtrate was then allowed to evaporate in a beaker at room temperature when colorless crystals of **AL** were obtained in quantitative yield within a day or two. The crystals were collected by decantation/filtration and washed with 10 ml of ethanol to ensure its purity for spectroscopy analysis. The compound was characterized by NMR spectroscopy.

Isolated yield of **AL**: 590 mg (percentage yield 70%). The compound is highly soluble in dimethylformamide, and dimethyl sulfoxide, soluble in methanol/ethanol on heating, and insoluble in tetrahydrofuran, chloroform and acetonitrile.

Characterization of **AL**: ^{1}H-NMR (400 MHz, DMSO-d_6) chemical shift in δ ppm: 2.50 (DMSO-CH_3), 2.64 (t, 6x$N\mathbf{CH_2}$), 3.30 (t, 6x$NCH_2\mathbf{CH_2}$), 3.37 (HOD/H_2O), 5.56 (s, 3x$\mathbf{NH_2}$), 6.50 (d, 6xCH), 7.55 (d, 6xCH), 7.94 (t, 3x**NH**).



Scheme S1. Synthesis of **AL** from tris(2-aminoethylamine) and 4-nitrobenzoyl chloride.

(B) Synthesis of tris-4-(2-hydroxybenzylideneamino)-N-(2-aminoethyl)benzamide (SL): Salicylidene based tripodal amide receptor **SL** was synthesized by Schiff base condensation reaction of **AL** with salicylaldehyde in methanol under reflux (Scheme 1, main manuscript). In a 250 ml flat bottom flask, 500 mg of **AL** (1.0 mmol) and 420 mg (0.360 mL) of 2-hydroxybenzaldehyde (3.5 mmol) were mixed in 100 ml of methanol. After overnight refluxing of the reaction mixture at 60 °C, the yellow precipitate formed was filtered and washed with 40 ml of

methanol (2 x 20 ml) to ensure its purity for spectroscopy analysis. The compound was characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy (Figure S2 and S3).

Isolated yield of **SL**: 550 mg (percentage yield 67%). The compound is highly soluble in dimethylformamide, and dimethyl sulfoxide, soluble in methanol/ethanol on heating, and insoluble in tetrahydrofuran, chloroform and acetonitrile.

Characterization of **SL**: **^{1}H-NMR** (400 MHz, DMSO-d_6) chemical shift in δ ppm: 2.75 (3xN**CH_2**), 3.42 (3xNCH$_2$**CH_2**), 6.95 (6xCH), 7.42 (9xCH), 7.57 (3xCH), 7.88 (6xCH), 8.40 (3xNH), 8.94 (3x**CH**=N), 12.84 (3x**OH**). **^{13}C-NMR** (100 MHz, DMSO-d_6) chemical shift in δ ppm: 31.16 (3xCH_3OH), 38.10 (3x-NCH_2), 53.63 (3x-NCH$_2$$CH_2$), 117.07 (3x-CH), 119.63 (3x-CH), 119.68 (3x-CH), 121.60 (3x-CH), 128.94 (3x-CH), 132.98 (3x-CH), 133.06 (3x-CH), 134.05 (3x-CH), 150.81 (3x-CH), 160.75 (3x-CH), 164.67 (3xC=N), 166.16 (3xC=O).

(C) Synthesis of 4-(2-hydroxybenzylideneamino)benzonitrile (CL1): 500 mg of 4-aminobenzonitrile (4.2 mmol) was dissolved in 20 ml of methanol in a flat bottomed flask and 0.53 ml (620 mg) of 2-hydroxybenzaldehyde (5.0 mmol) was added into the above solution. The solution mixture was then stirred at room temperature (c.a. 30^{o} C) for about 12 hrs. and the yellow precipitate formed was then filtered and washed with 15 ml (3 x 5 ml) of methanol to obtain **CL1**. The compound was then air dried at room temperature and characterized by ^{1}H-NMR and ^{13}C NMR spectroscopy (Figure S4 and S5).

Isolated yield of **CL1**: 790 mg (percentage yield 83%). The compound is soluble in dimethylformamide, dimethyl sulfoxide, chloroform and tetrahydrofuran soluble in methanol/ethanol on heating.

^{1}H-NMR (400 MHz, DMSO-d_6) chemical shift in δ ppm: 2.50 (DMSO-CH_3), 3.35 (HOD/H_2O), 7.00 (m, 2xCH), 7.46 (t, 1xCH), 7.54 (d, 2xCH), 7.70 (d, 1xCH), 7.91 (d, 2xN=CH), 12.43 (s, 1xOH). **^{13}C-NMR** (100 MHz, DMSO-d_6) δ ppm: 108.83, 116.72, 118.79, 119.30, 119.35, 122.46, 132.54, 133.64, 134.09, 152.57, 160.24, 165.39.

(D) Synthesis of 1,2-(2-hydroxybenzylideneamino)benzene (CL2): 500 mg of 1,2-phenylenediamine (4.6 mmol) was dissolved in 20 ml of methanol in a flat bottomed flask and 1.24 g (1.0 ml) of 2-hydroxybenzaldehyde (10.1 mmol) was added into the solution. The solution mixture was then stirred at room temperature (30^{o} C) for about 12 hours and the yellow precipitate formed was then filtered and washed with 20 ml (2 x 10 ml) of methanol to obtain **CL2**. The compound was then air dried at room temperature and characterized by ^{1}H-NMR and ^{13}C NMR spectroscopy (Figure S6 and S7).

Isolated yield of **CL2**: 1.2 g (percentage yield 82%). The compound is soluble in dimethylformamide, dimethyl sulfoxide, chloroform and tetrahydrofuran.

^{1}H-NMR (400 MHz, DMSO-d_6) chemical shift in δ ppm: 2.51 (DMSO-CH_3), 3.35 (HOD/H_2O), 6.98 (m, 4xCH), 7.42 (m, 6xCH), 7.68 (d, 2xCH), 8.94 (s, 2xN=CH), 12.95 (s, 2xOH). **^{13}C-NMR** (100 MHz, DMSO-d_6) δ ppm: 116.65, 119.05, 119.47, 119.72, 127.78, 132.44, 133.41, 142.24, 160.37, 164.01.

(E) Synthesis of 4-(5-nitro-2-hydroxybenzylideneamino)benzonitrile (NCL1): 500 mg of 4-aminobenzonitrile (4.2 mmol) was dissolved in 15 ml of methanol in a flat bottomed flask. 780 mg of 5-nitro-2-hydroxybenzaldehyde (4.6 mmol) dissolved in 15 ml of methanol was added into the above solution. The solution mixture was then stirred at room temperature (30^{o} C) for about 12 hours. and the yellow precipitate formed was then filtered and washed with 15 ml (3 x 5 ml) of methanol to obtain **NCL1**. The compound was then air dried at room temperature. Isolated yield of **NCL1**: 850 mg (percentage yield 75%). The compound is not stable in the solution-state and thus could not be characterized by NMR spectroscopy. Unlike **CL1** and **CL2**, it was observed to undergo hydrolysis of -N=CH- bond in neat DMSO-d_6 (Figure S9).

(F) Synthesis of 1,2-(5-nitro-2-hydroxybenzylideneamino)benzene (NCL2): 108 mg of 1,2-phenylenediamine (1.0 mmol) was dissolved in 10 ml of methanol in a flat bottomed flask. 355 mg of 5-nitro-2-hydroxybenzaldehyde (2.1 mmol) dissolved in 15 ml of methanol was added into the above solution. The solution mixture was then stirred at room temperature (30^{o} C) for about 12 hours and the yellow precipitate formed was then filtered and washed with 20 ml (2 x 10 ml) of methanol to obtain **NCL2**. The compound was then air dried at room temperature. Isolated yield of **NCL2**: 310 mg (percentage yield 78%). The isolated compound is barely soluble in any solvents such as dimethyl sulfoxide, chloroform, acetonitrile and methanol and thus could not be characterized by NMR spectroscopy in deuterated solvents (DMSO-d_6 or $CDCl_3$). **NCL2** was characterized in the presence of (n-Bu_4N^+)$H_2PO_4^-$ where no immediate hydrolysis of -N=CH- bond was observed, and six peaks for six different sets of -CH protons in the aromatic region of the spectrum confirmed the purity of the compound (Figure S8). The -OH peak of **NCL2** was not observed due to proton-exhange processes in solution.

^{1}H-NMR (400 MHz, DMSO-d_6) chemical shift in δ ppm: 8.60 (s, 2x-CH), 8.51 (d, 2x-N=CH), 7.76 (q, 2x-CH), 7.12 (q, 2x-CH), 6.88 (q, 2x-CH), 6.10 (q, 2x-CH), 3.15 (m, N^+-CH_2 of n-Bu_4N^+), 3.60 (s, HOD/H_2O), 2.50 (s, DMSO-CH_3), 1.55 (m, -CH_2 of n-Bu_4N^+), 1.32 (m, -CH_2 of n-Bu_4N^+), 0.90 (m, -CH_3 of n-Bu_4N^+).

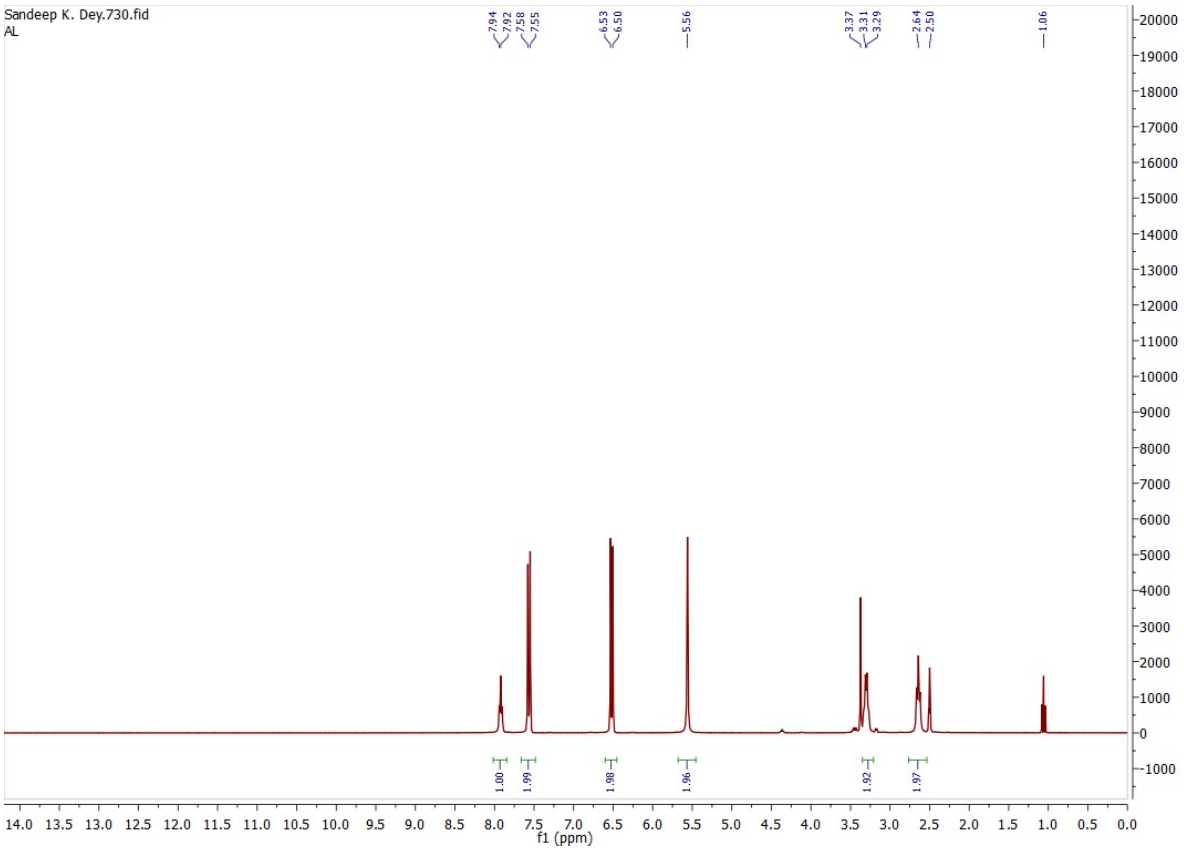


Fig. S1. ^{1}H-NMR spectrum of **AL** in DMSO-d_6.

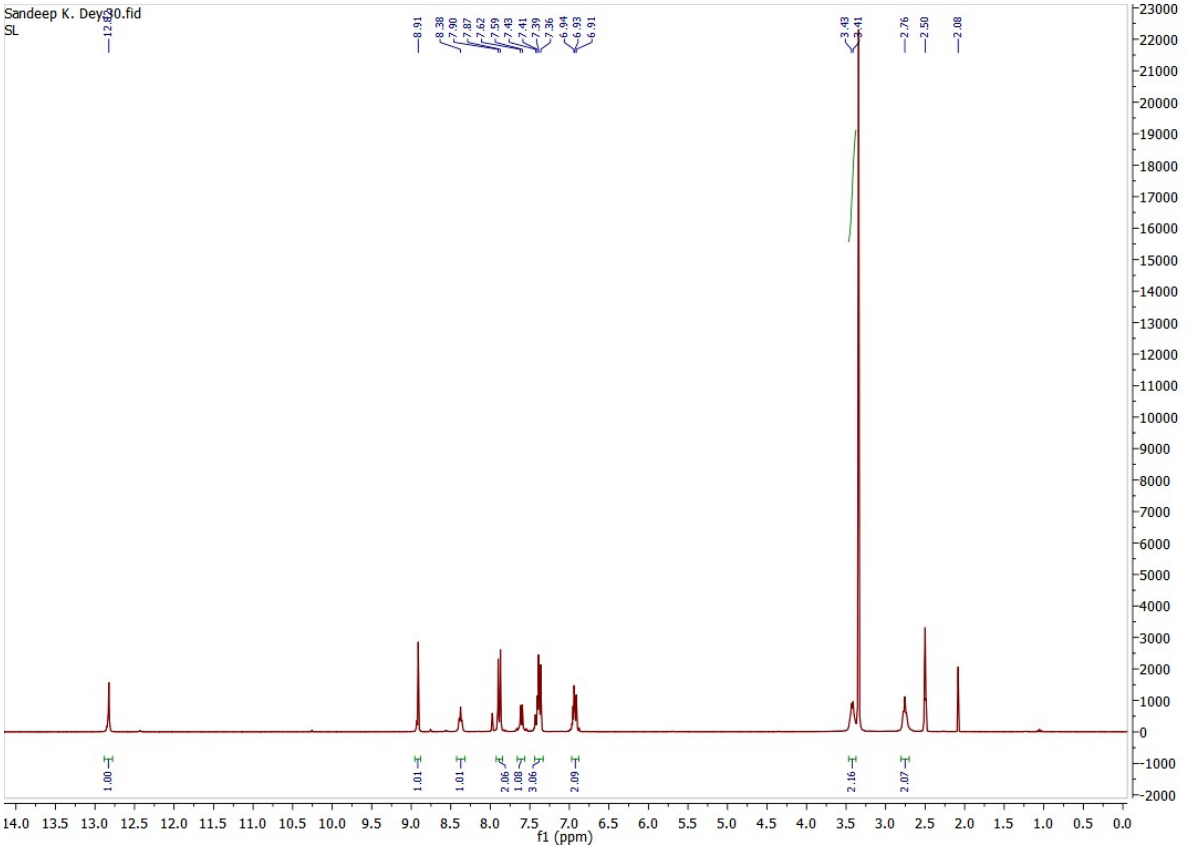


Fig. S2. ^{1}H-NMR spectrum of **SL** in DMSO-d_6.

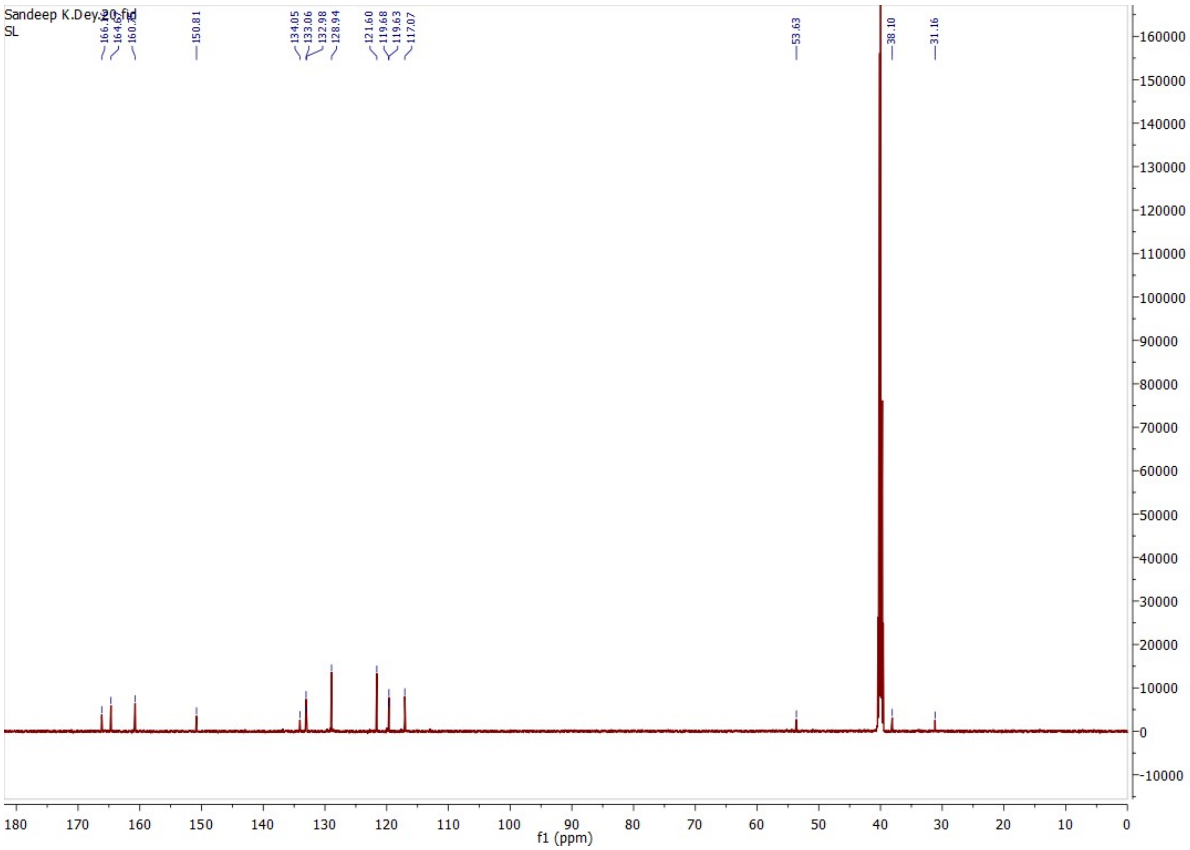


Fig. S3. ^{13}C-NMR spectrum of **SL** in DMSO-d_6.

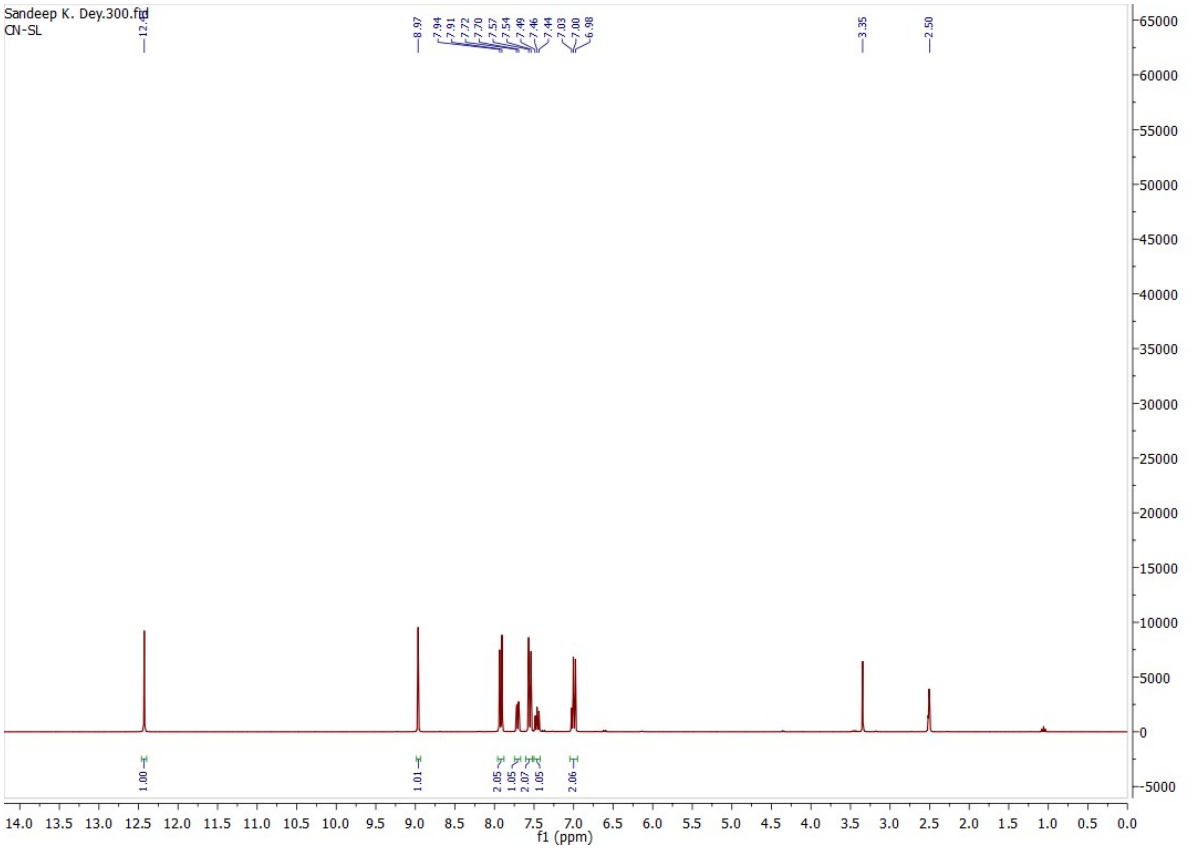


Fig. S4. ^{1}H-NMR spectrum of **CL1** in DMSO-d_6.

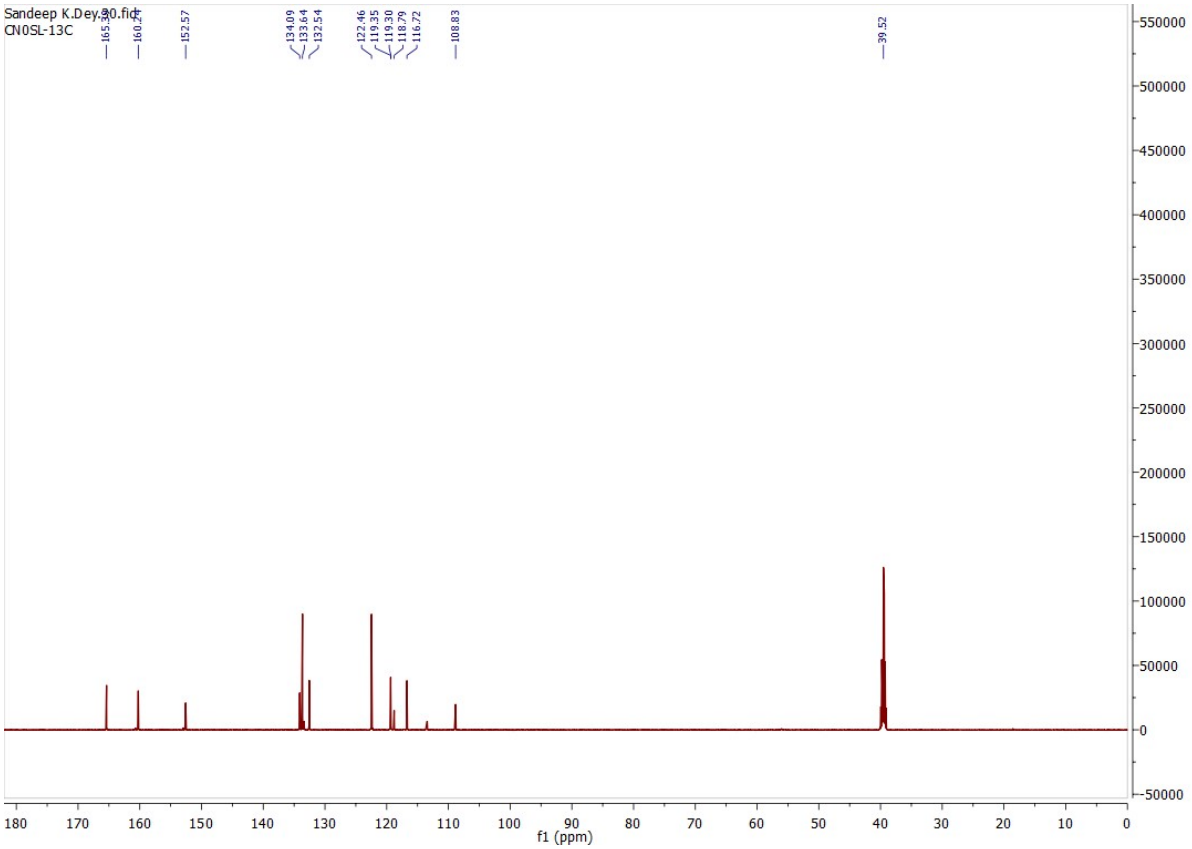


Fig. S5. ^{13}C-NMR spectrum of **CL1** in DMSO-d_6.

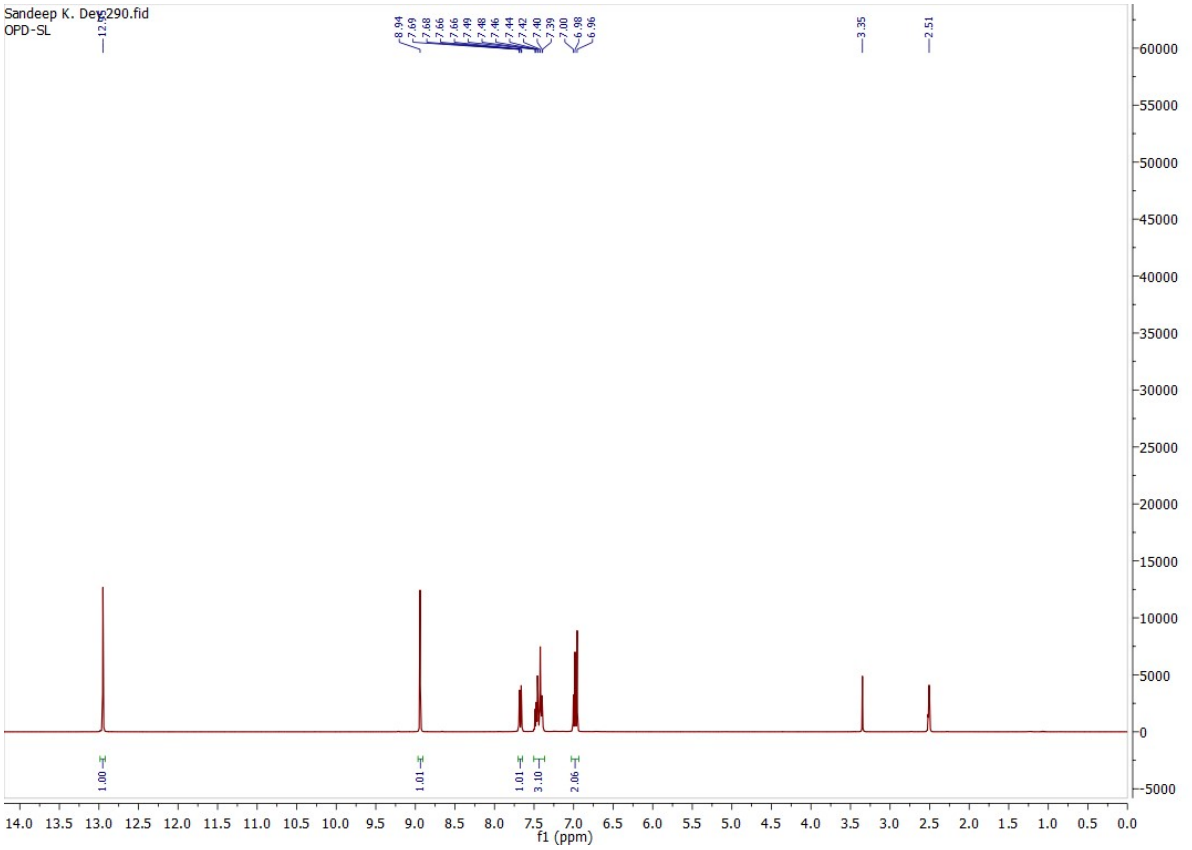


Fig. S6. ^{1}H-NMR spectrum of **CL2** in DMSO-d_6.

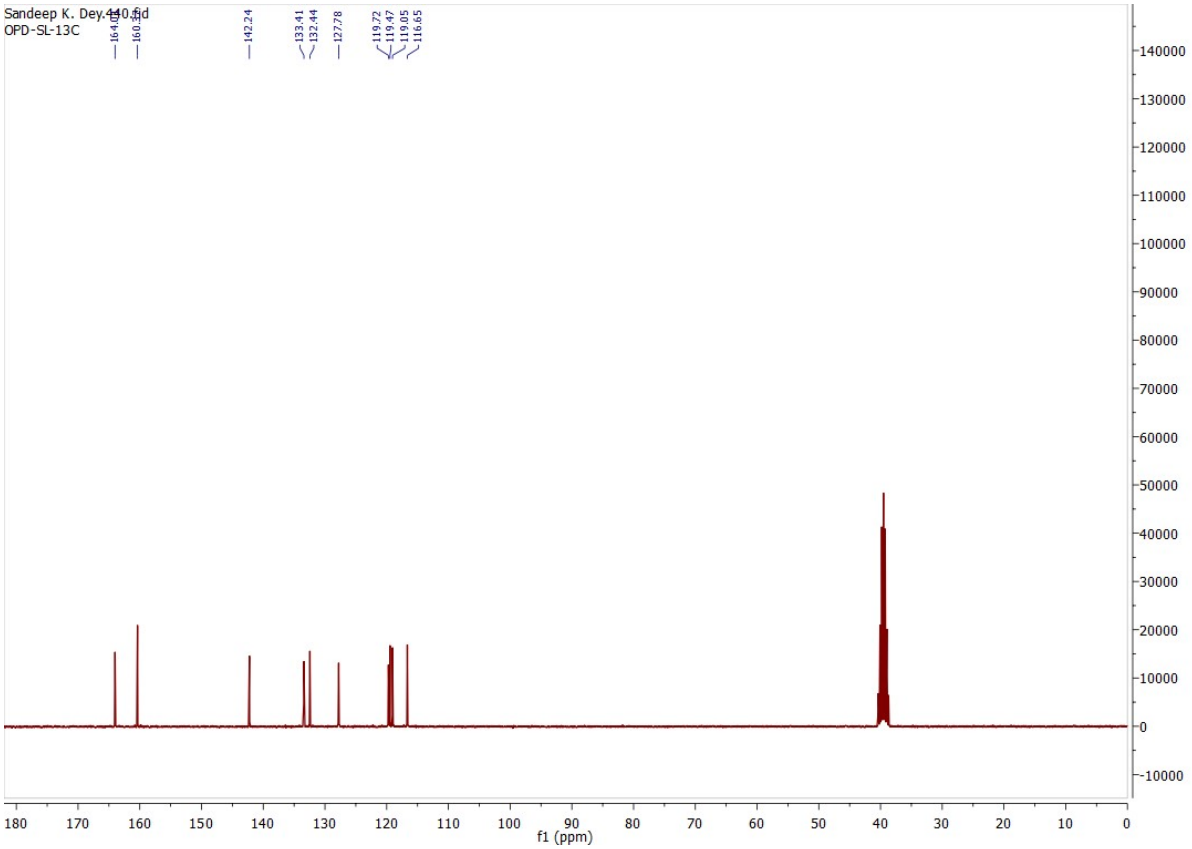


Fig. S7. ^{13}C-NMR spectrum of **CL2** in DMSO-d_6.

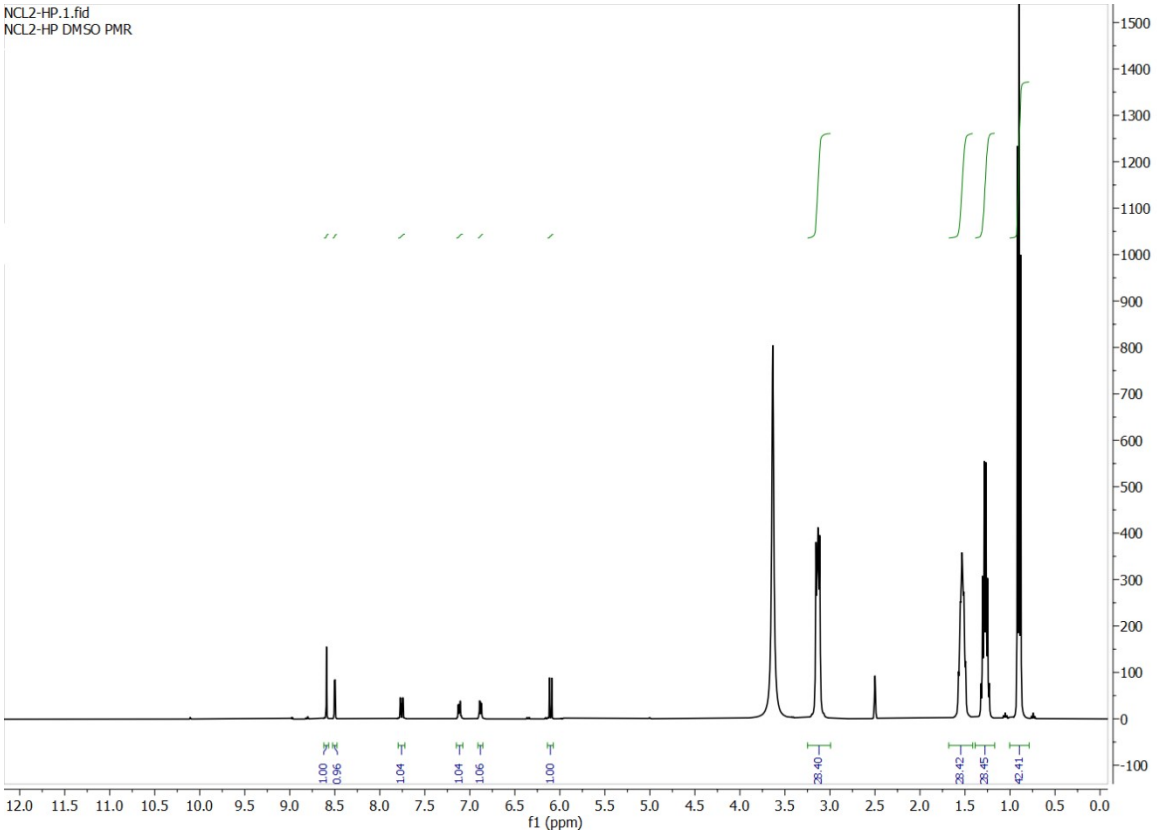


Fig. S8. ^{1}H-NMR spectrum of **NCL2** in DMSO-d_6 in the presence of (n-Bu_4N^+)$H_2PO_4^-$ to solubilize the compound.

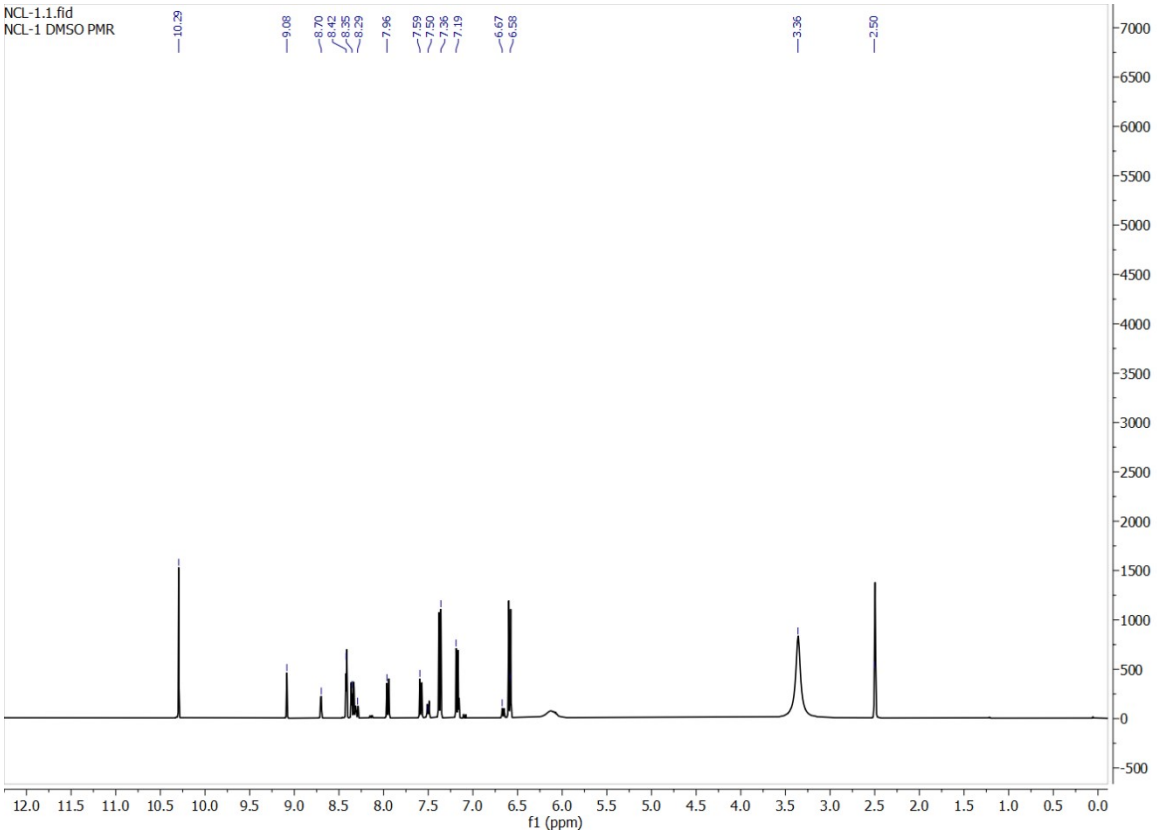


Fig. S9. ^{1}H-NMR spectrum of **NCL1** showing hydrolysis of -N=CH- bond in DMSO-d_6. 70% hydrolysis was observed after 15 min. of sample preparation suggesting instability of compound in solution.

(3) ^{1}H-NMR experiments of SL in the presence of tetrabutylammonium salts in DMSO-d_6.

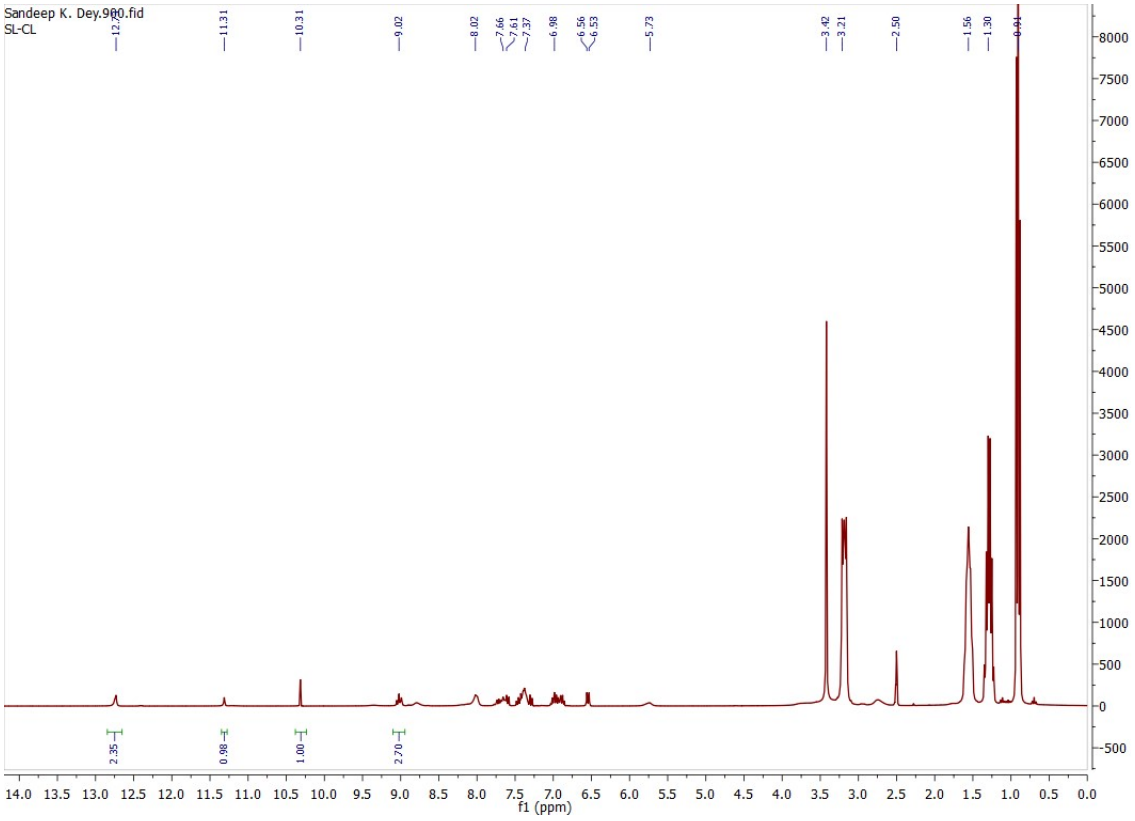


Fig. S10. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equiv. (n-Bu_4N^+)Cl^-, recorded after 24 h.

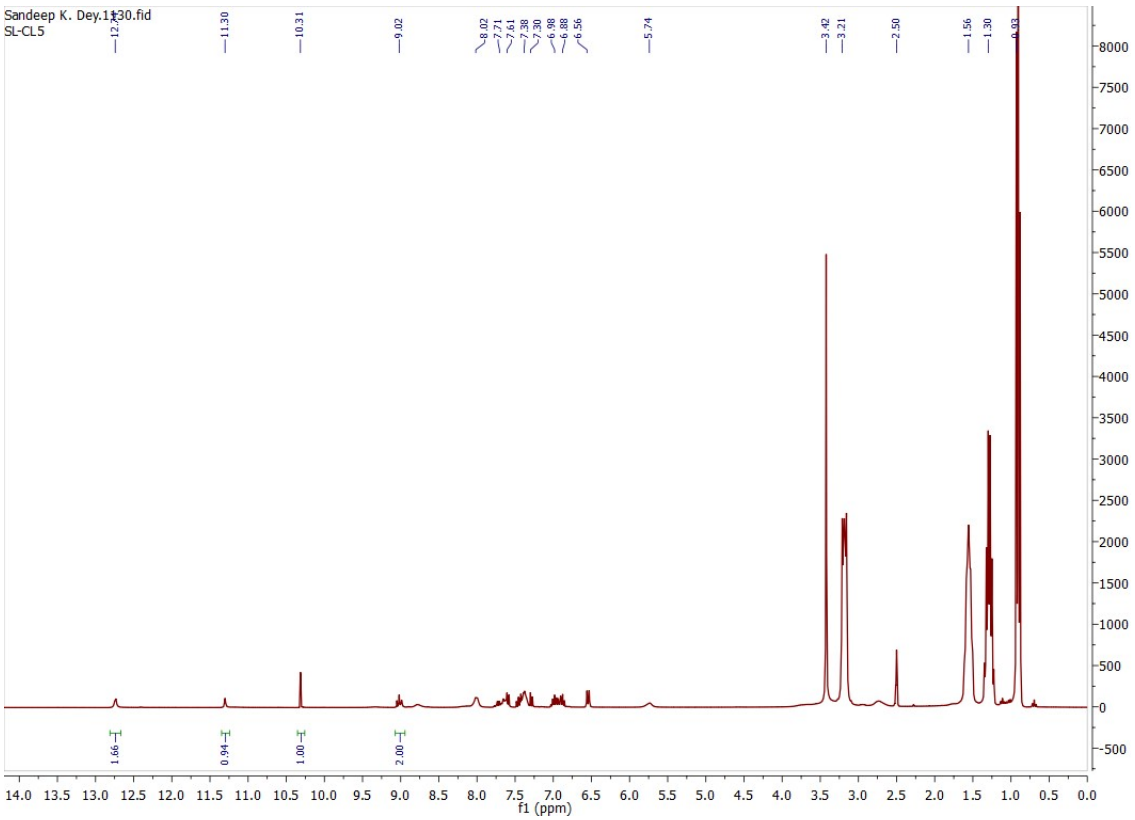


Fig. S11. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equiv. (n-Bu_4N^+)Cl^-, recorded after 72 h.

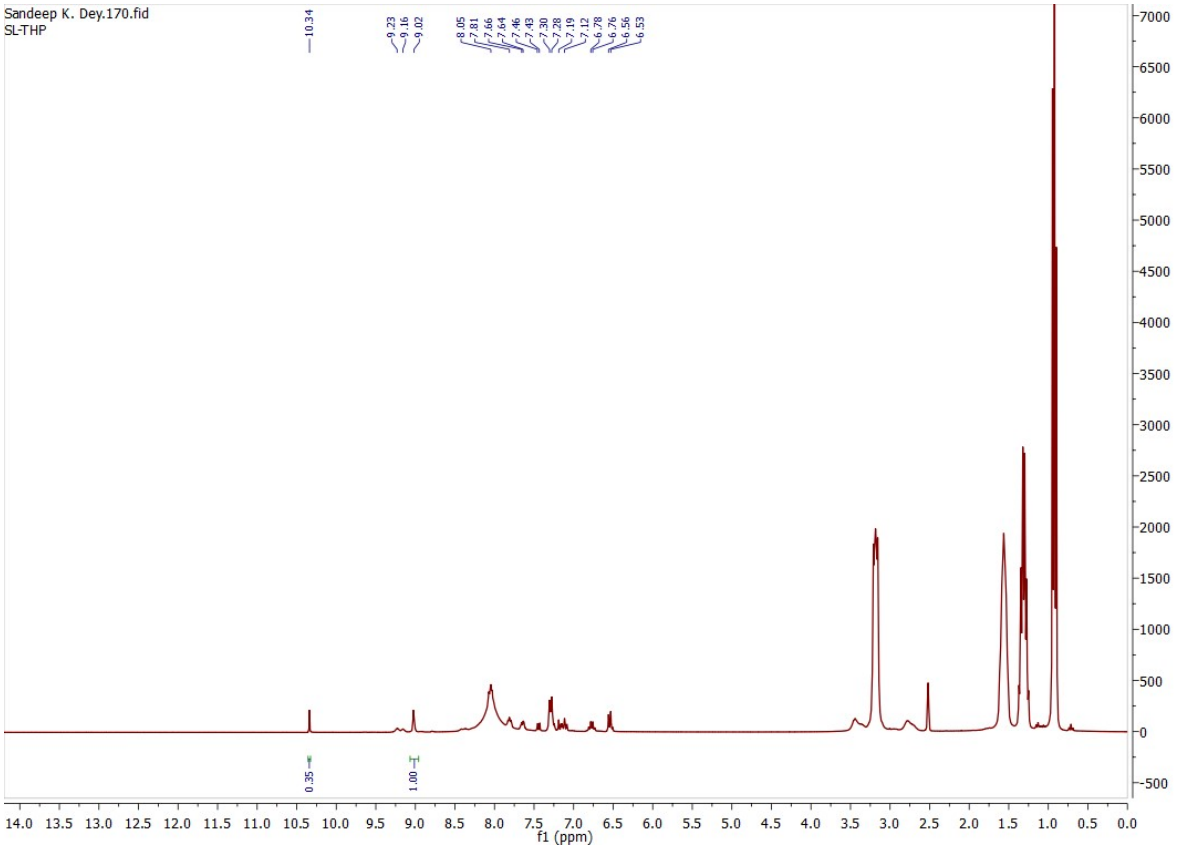


Fig. S12. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equiv. (n-Bu_4N^+)$H_2PO_4^-$, recorded after 1 h.

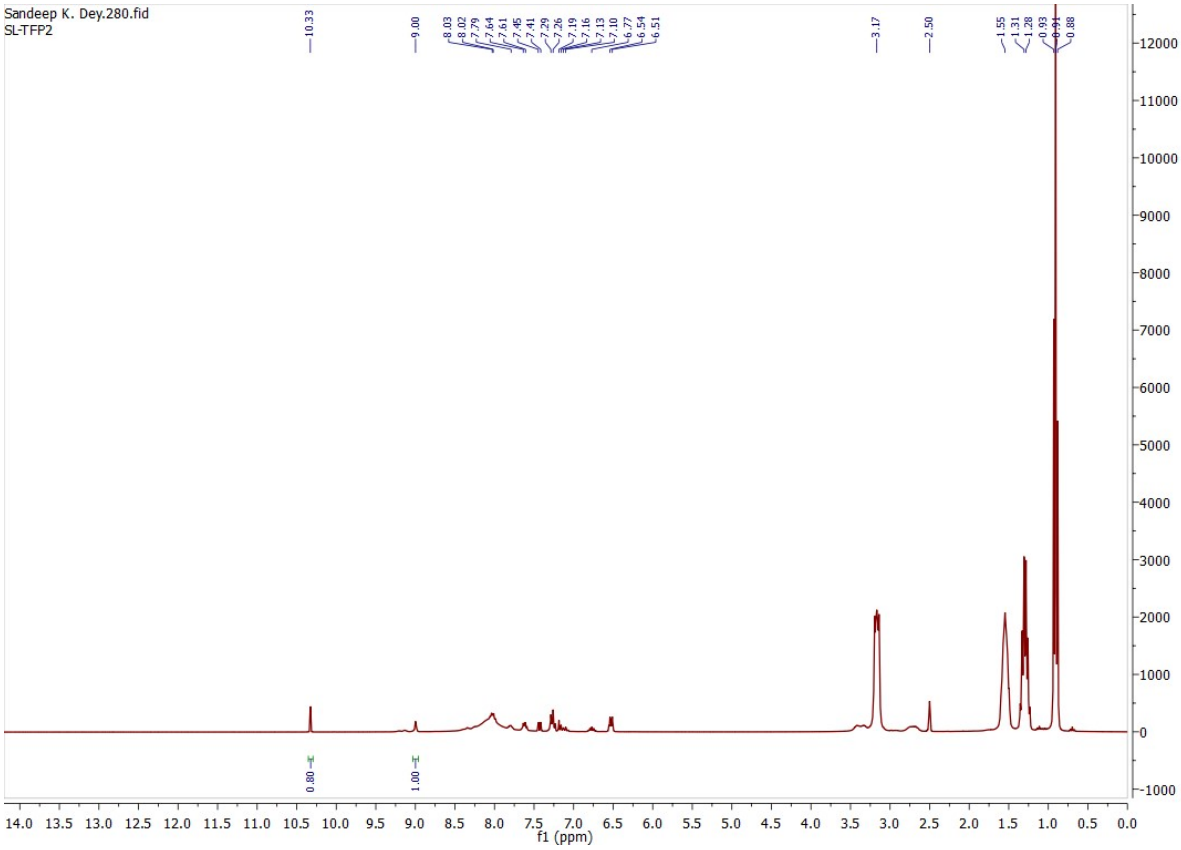


Fig. S13. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equiv. (n-Bu_4N^+)$H_2PO_4^-$, after 24 h.

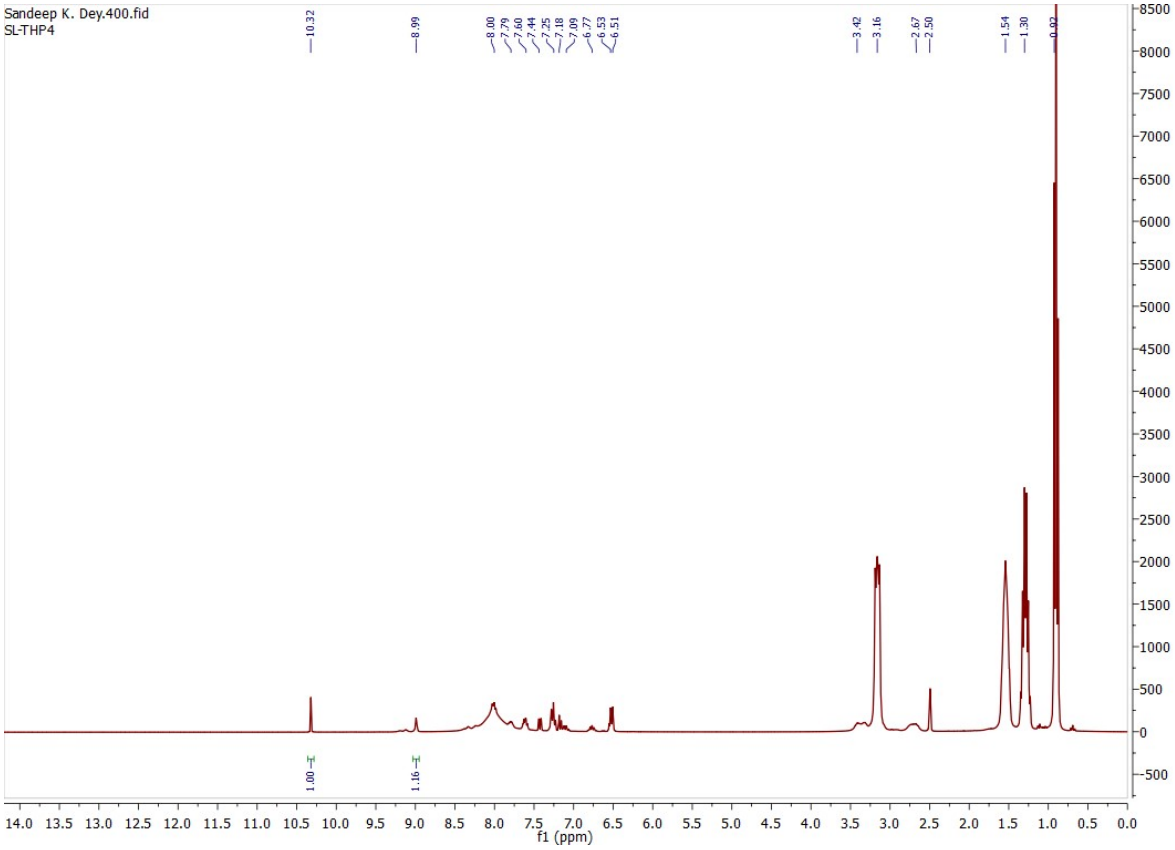


Fig. S14. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equiv. (n-Bu_4N^+)$H_2PO_4^-$, after 72 h.

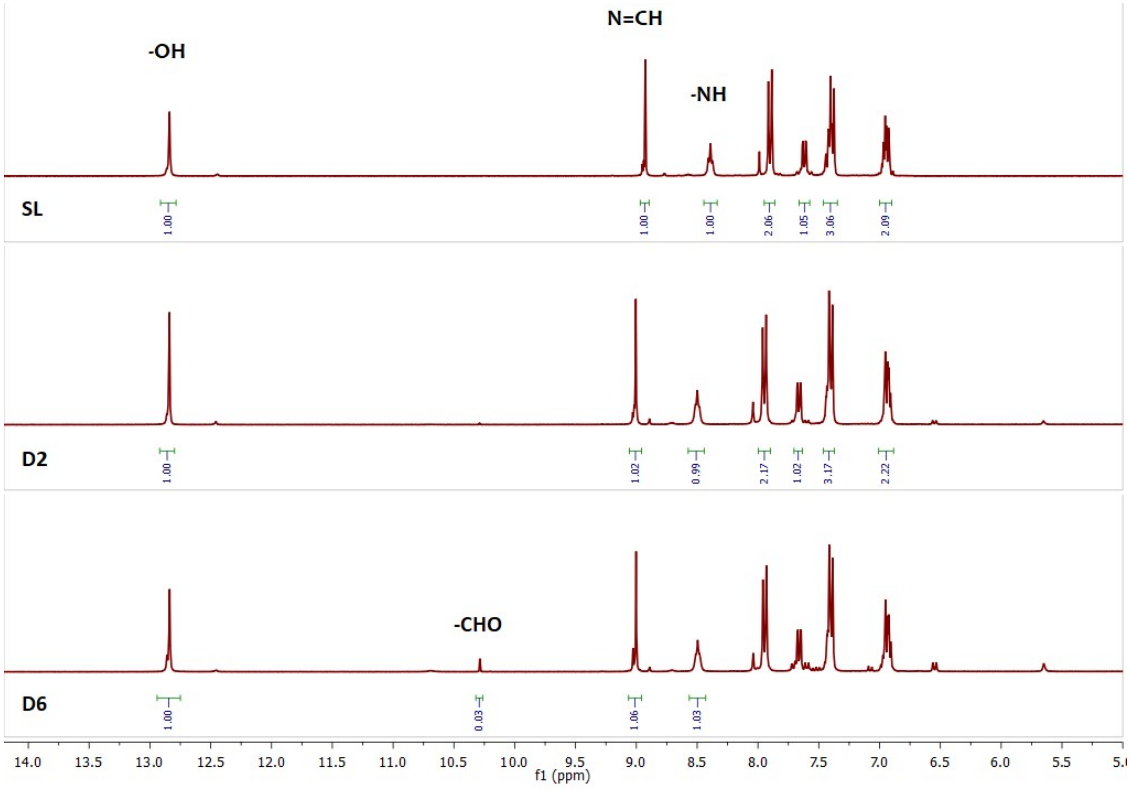


Fig. S15. Aromatic region of ^{1}H-NMR (DMSO-d_6) spectra of **SL** in the presence of 10 equivalents (n-Bu_4N^+)Br^-, recorded after 24 h. (D2), and after 120 h. (D6).

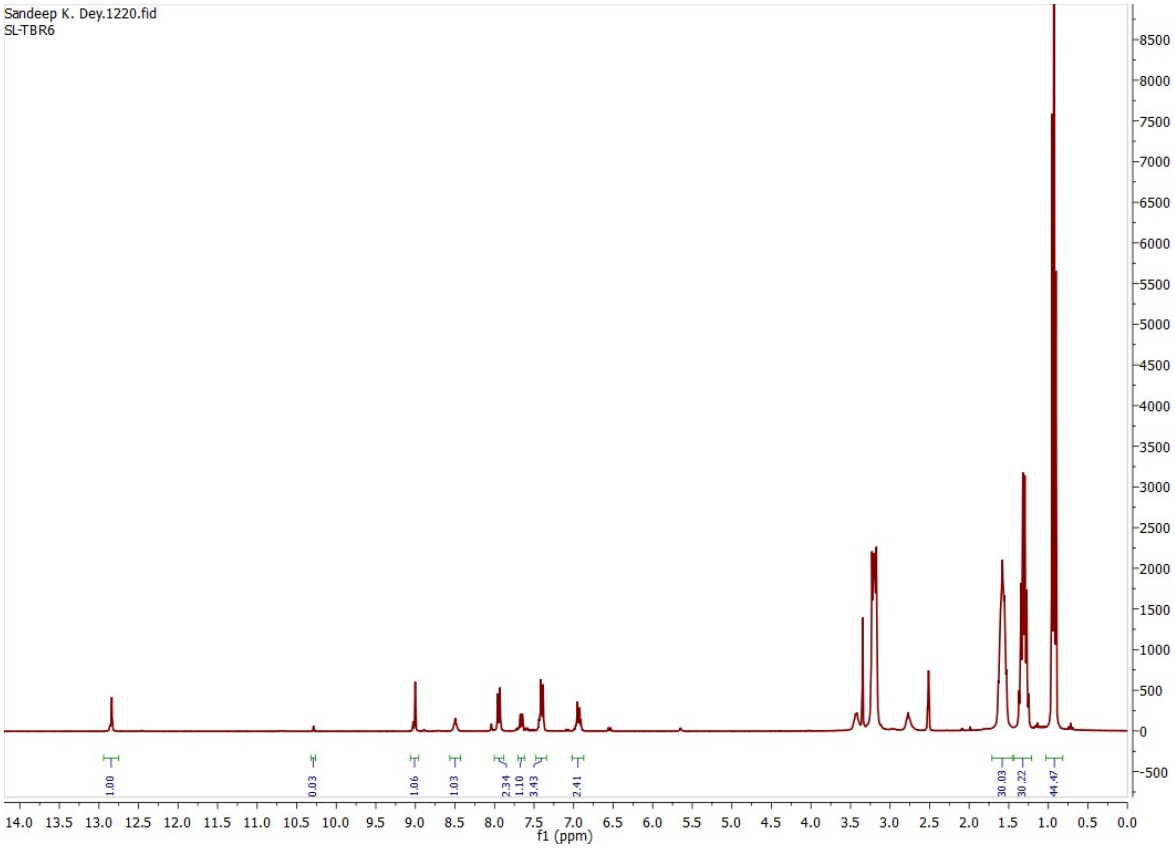


Fig. S16. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equivalents (n-Bu_4N^+)Br^-, after 120 h.

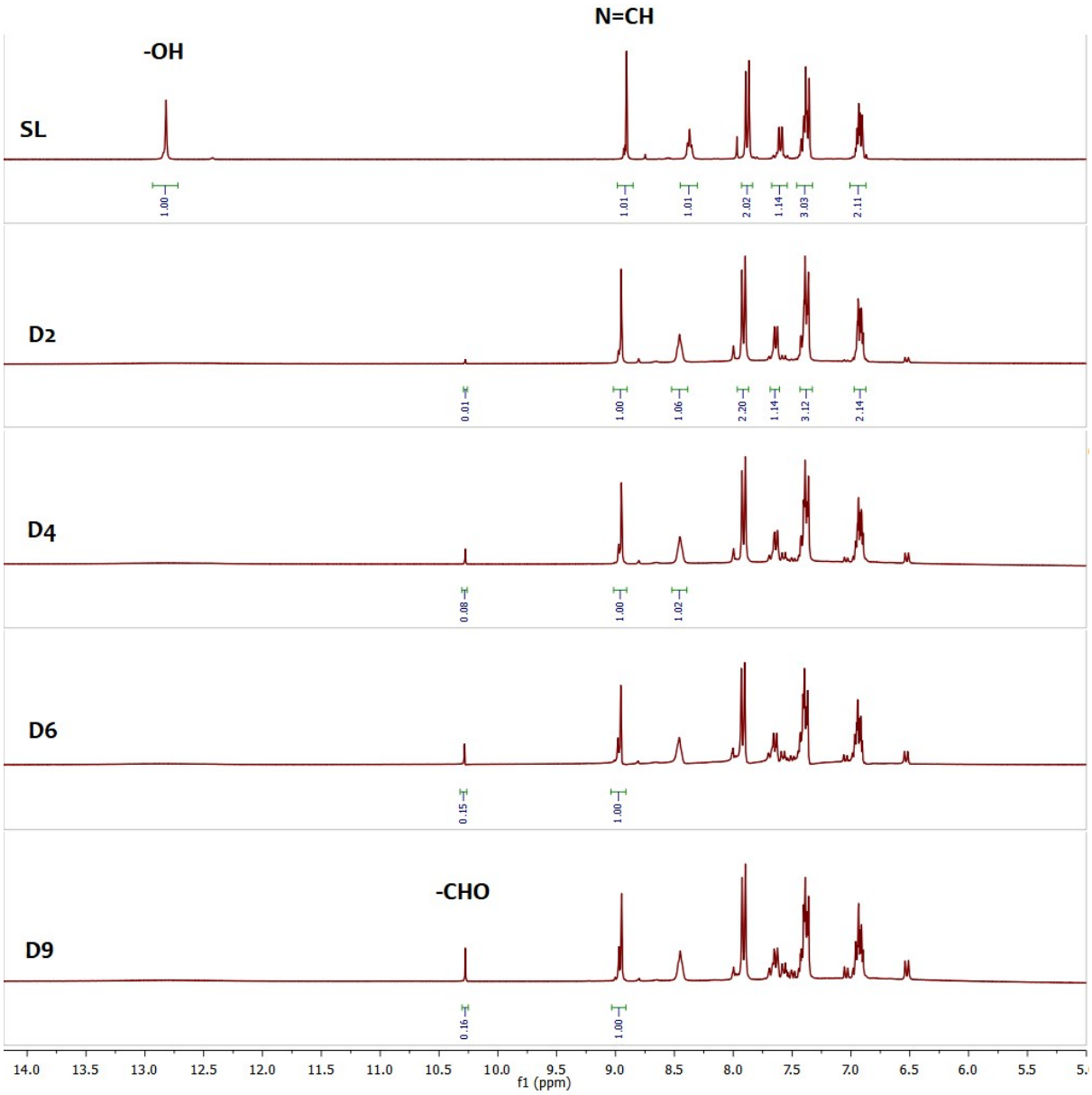


Fig. S17. Aromatic region of ^{1}H-NMR (DMSO-d_6) spectra of **SL** in the presence of 10 equivalents (n-Bu_4N^+)HSO_4^-, recorded after 24 h. (D2), 72 h. (D4), and after 120 h. (D6).

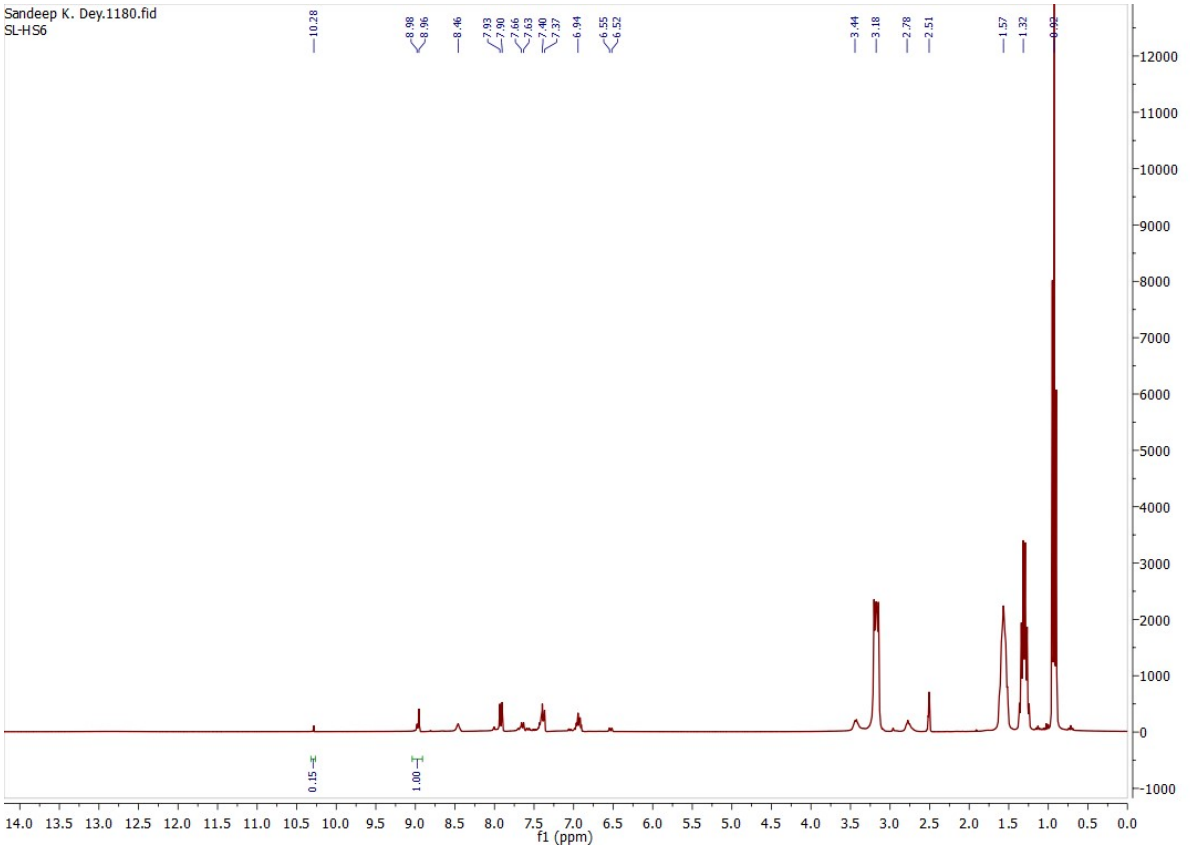


Fig. S18. ^{1}H-NMR spectrum of **SL** (DMSO-d_6) in the presence of 10 equiv. (n-Bu_4N^+)HSO_4^-, after 120 h.

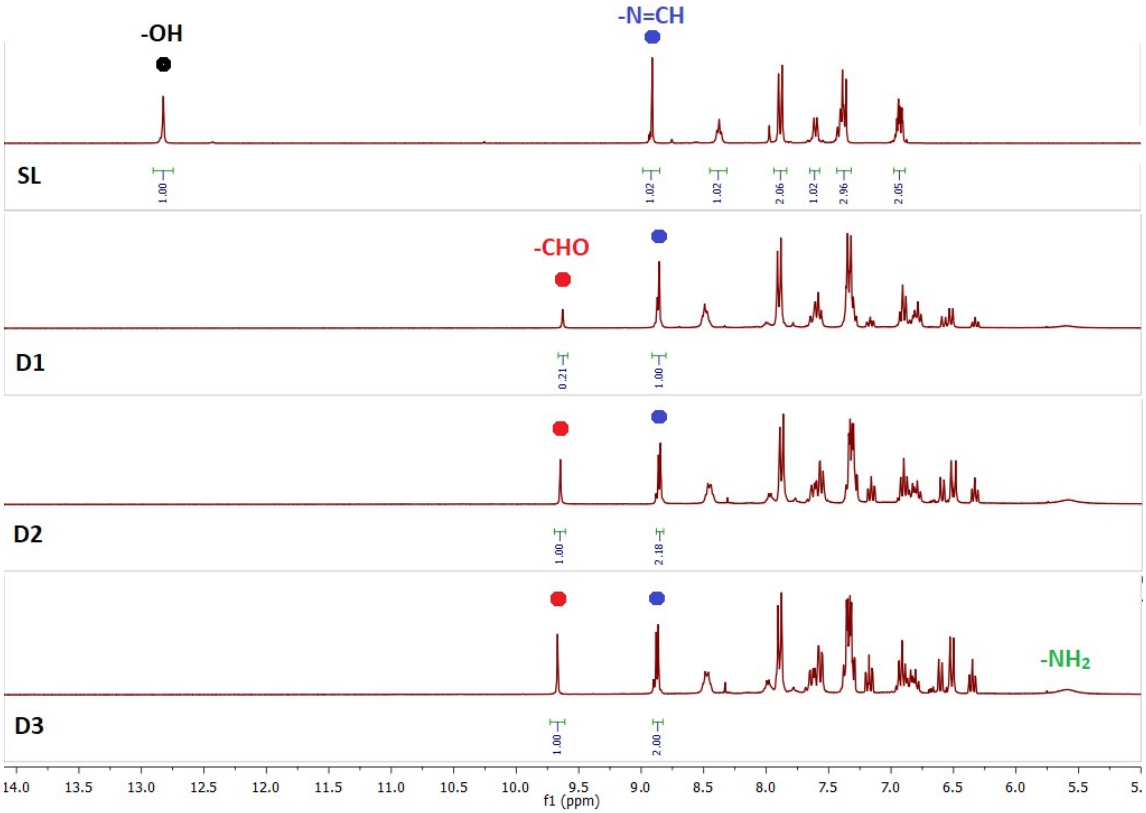


Fig. S19. Aromatic region of ^{1}H-NMR (DMSO-d_6) spectra of **SL** in the presence of 10 equivalents (n-Bu_4N^+)CH_3COO^-, recorded after 1 h. (D1), after 24 h. (D2) and after 48 h. (D3).

(4) ^{1}H-NMR experiments of CL1 in the presence of tetrabutylammonium salts in DMSO-d_6.

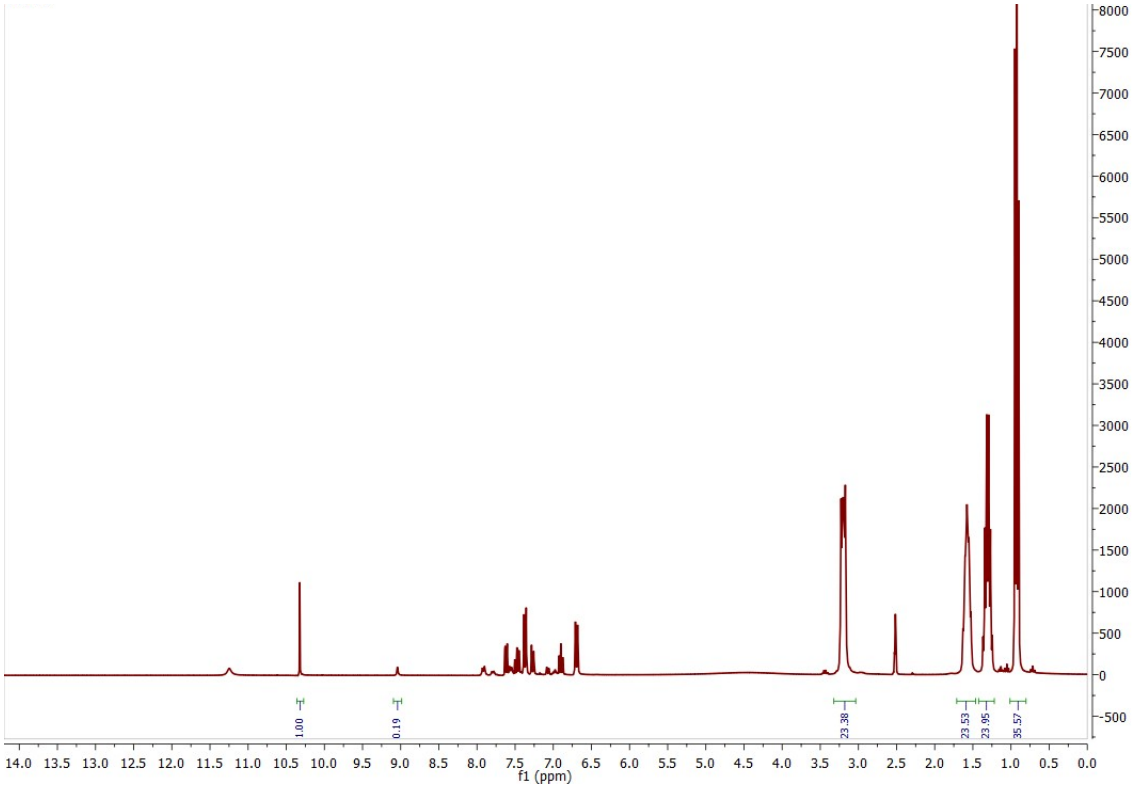


Fig. S20. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)Cl^-, after 24 h.

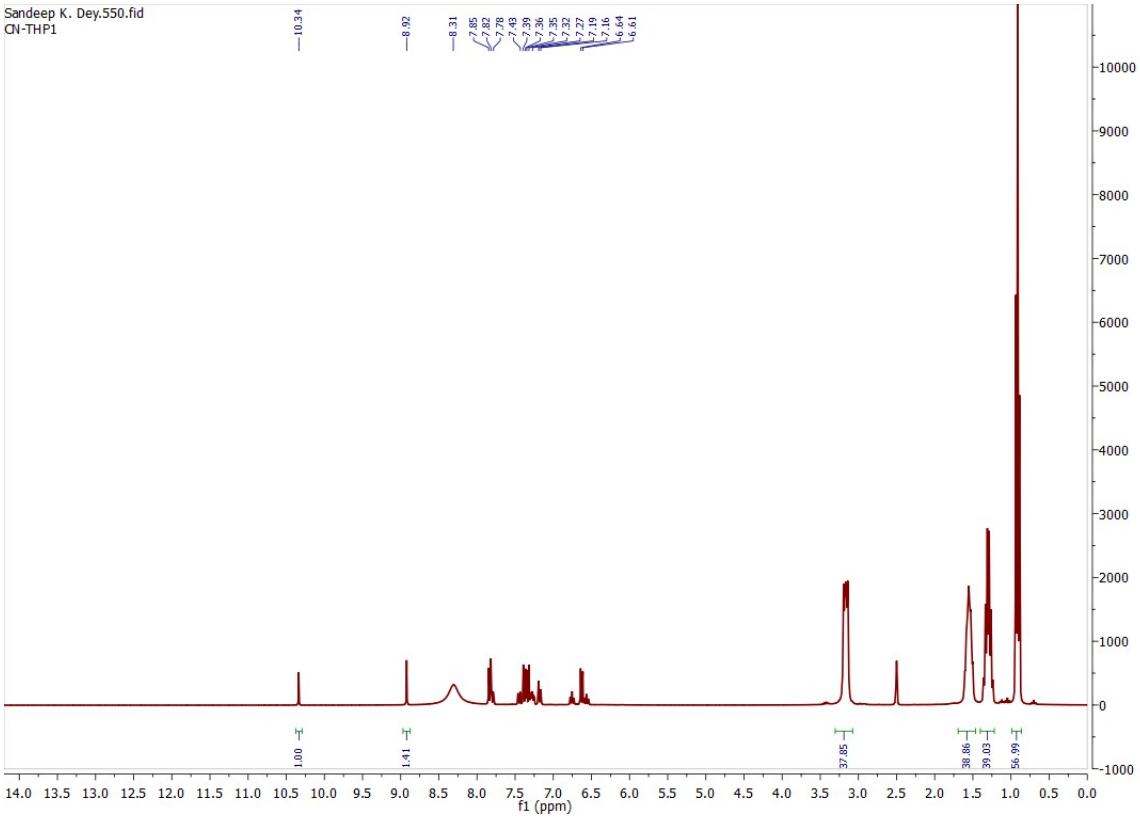


Fig. S21. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)$H_2PO_4^-$, after 1 h.

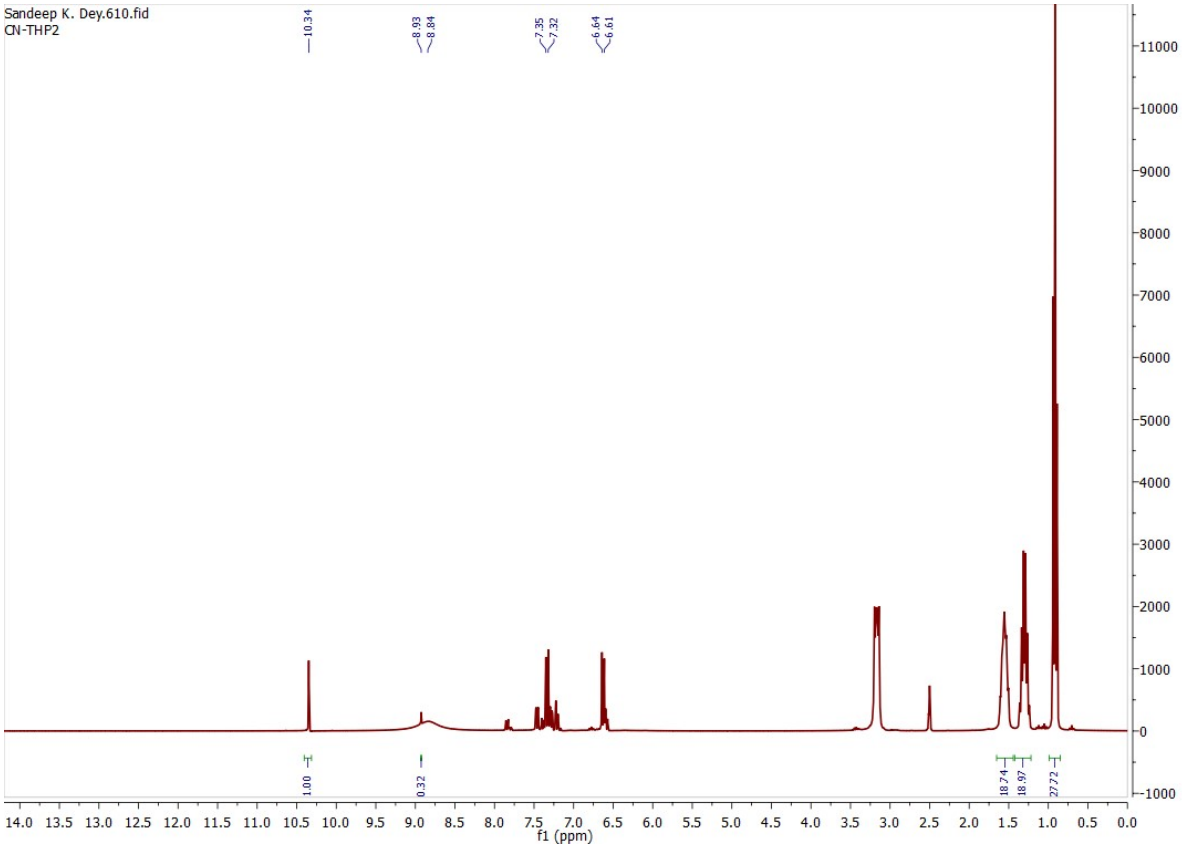


Fig. S22. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)$H_2PO_4^-$, after 24 h.

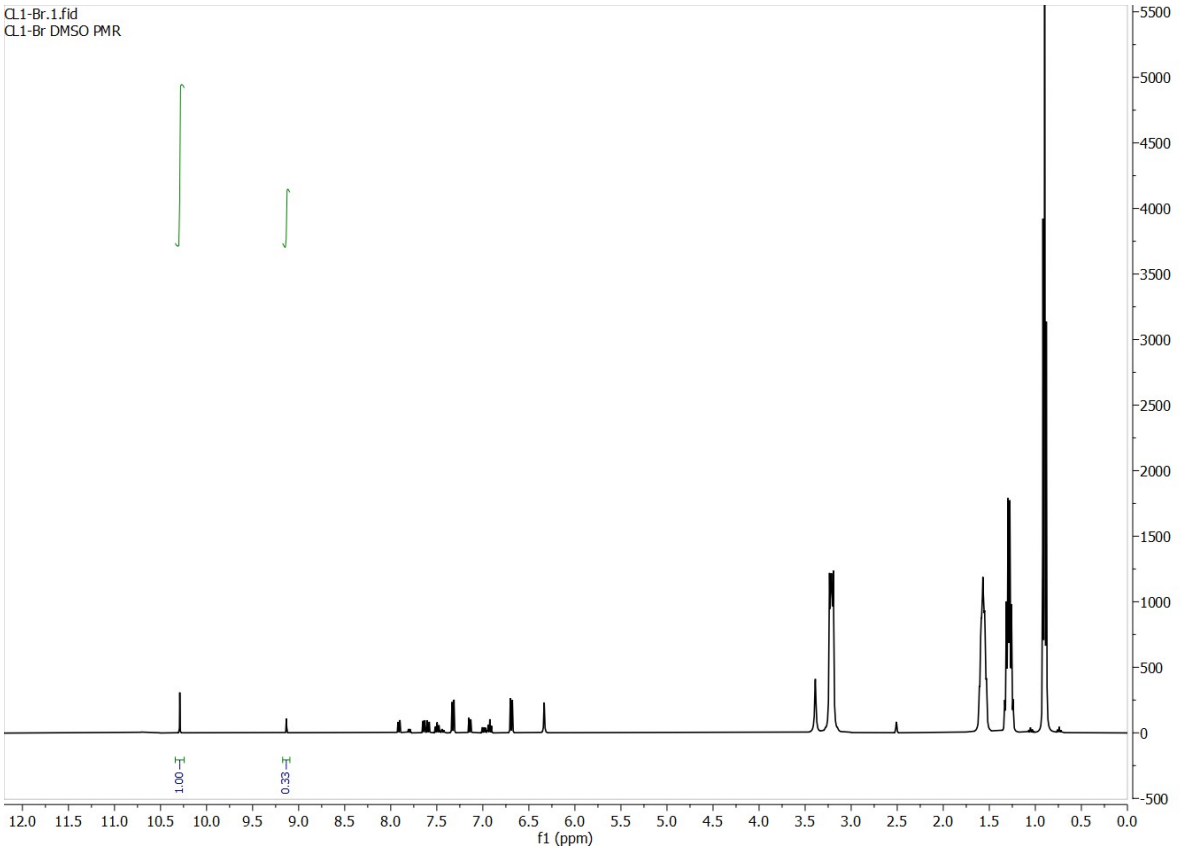


Fig. S23. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)Br^-, after 120 h.

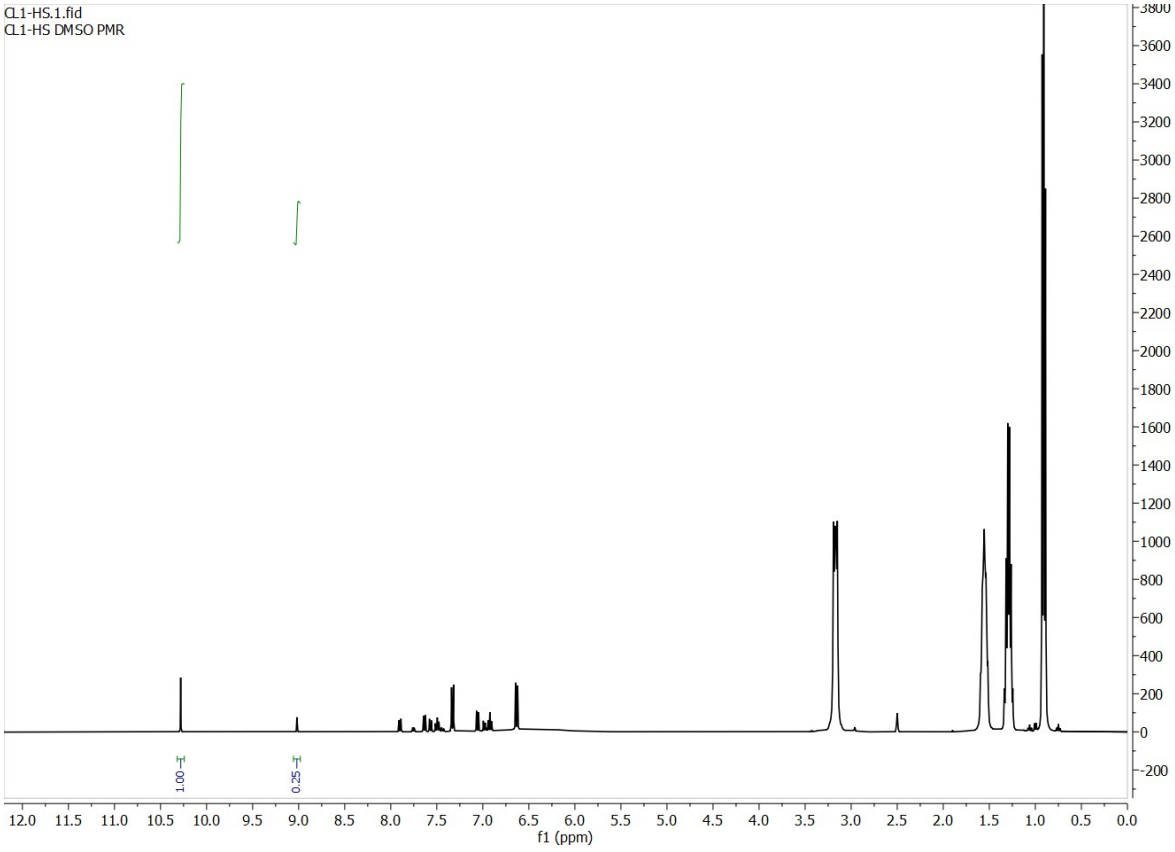


Fig. S24. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equiv. (n-Bu_4N^+)HSO_4^-, after 120 h.

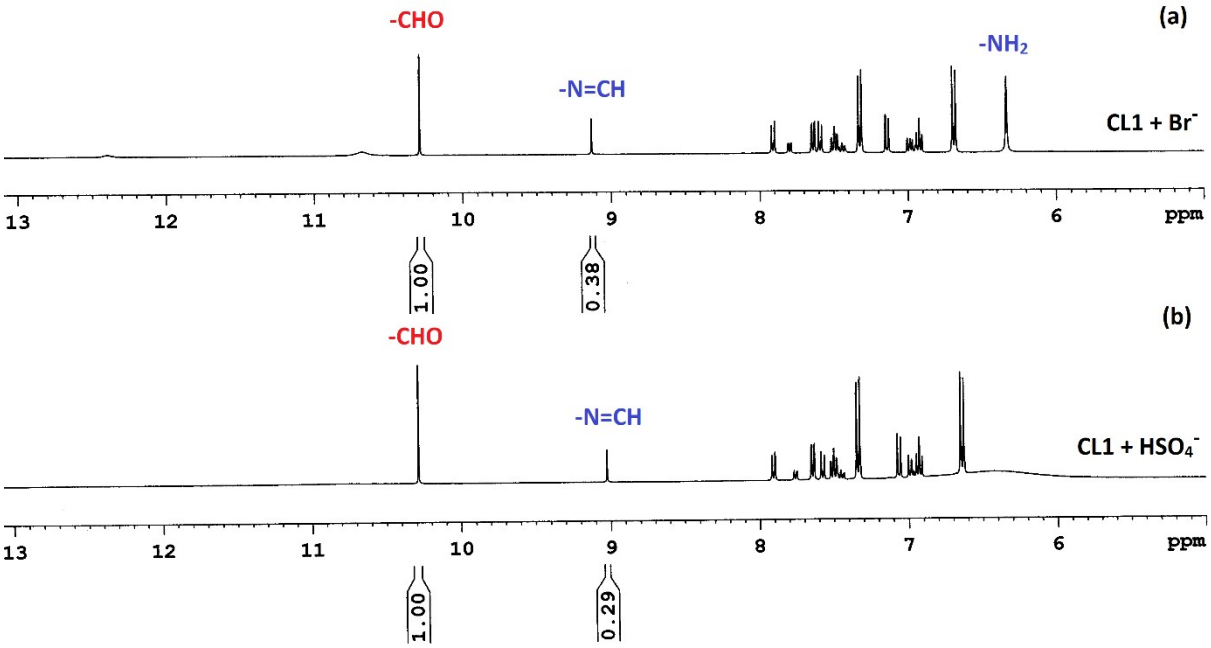


Fig. S25. Comparison of ^{1}H-NMR spectra of **CL1** (DMSO-d_6) in the presence of 5 equiv. (n-Bu_4N^+)Br^- and (n-Bu_4N^+)HSO_4^- after 120 h. (5 days).

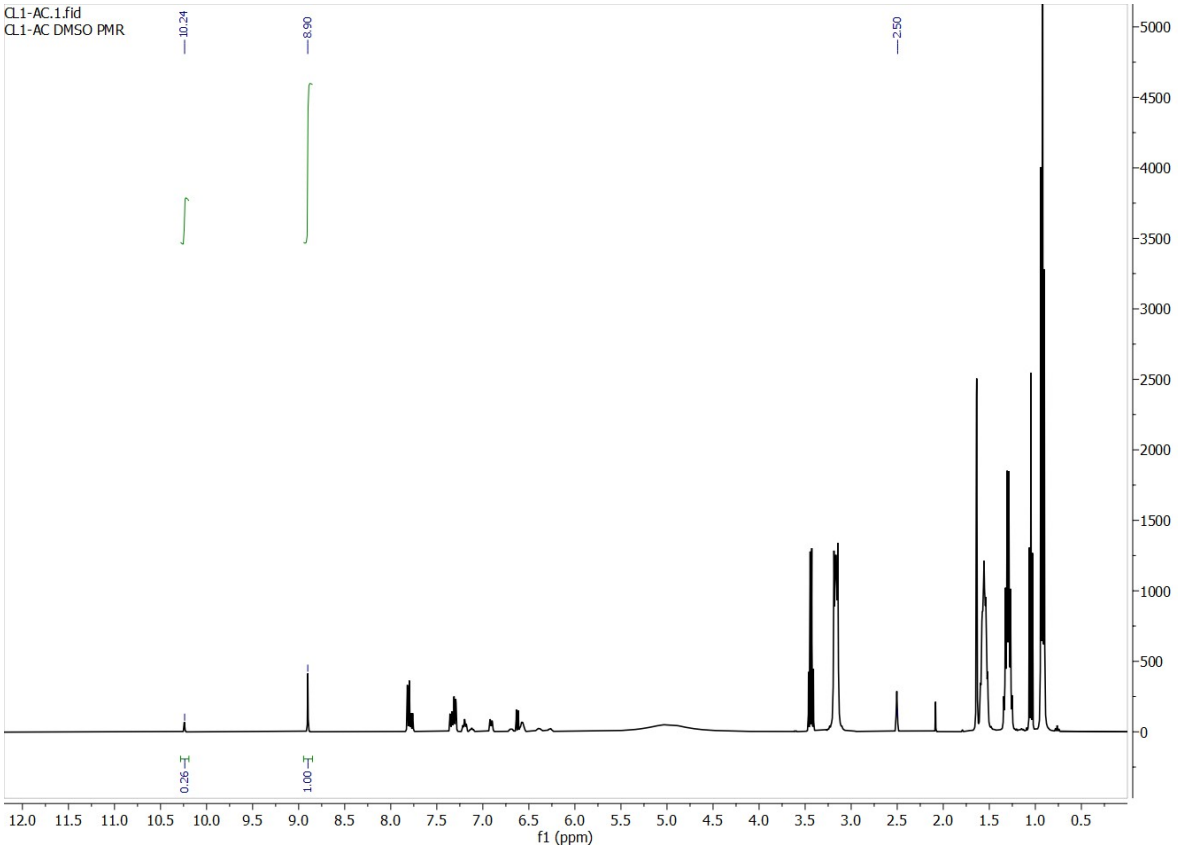


Fig. S26. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equiv. (n-Bu_4N^+)CH_3COO^-, after 1 h.

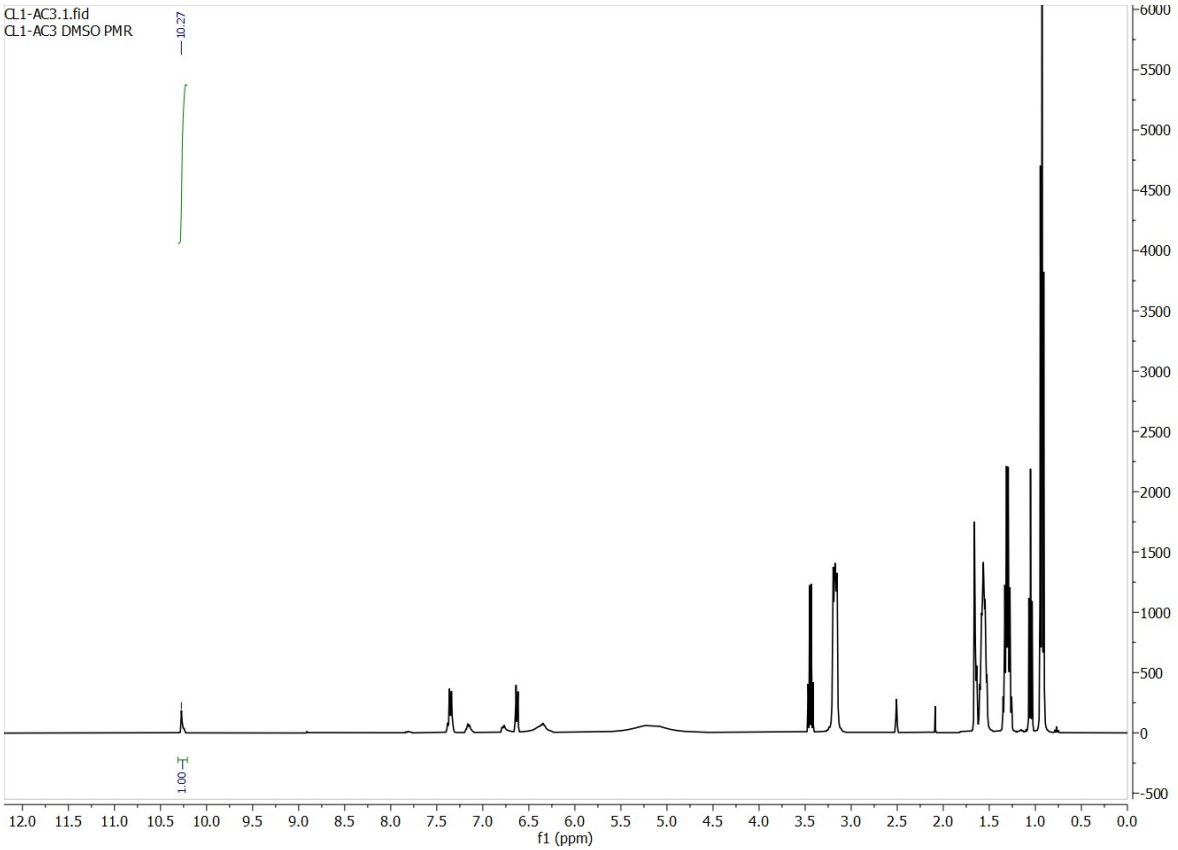


Fig. S27. ^{1}H-NMR spectrum of **CL1** (DMSO-d_6) in the presence of 5 equiv. (n-Bu_4N^+)CH_3COO^-, after 48 h.

(5) ^{1}H-NMR experiments of CL2 in the presence of tetrabutylammonium salts in DMSO-d_6.

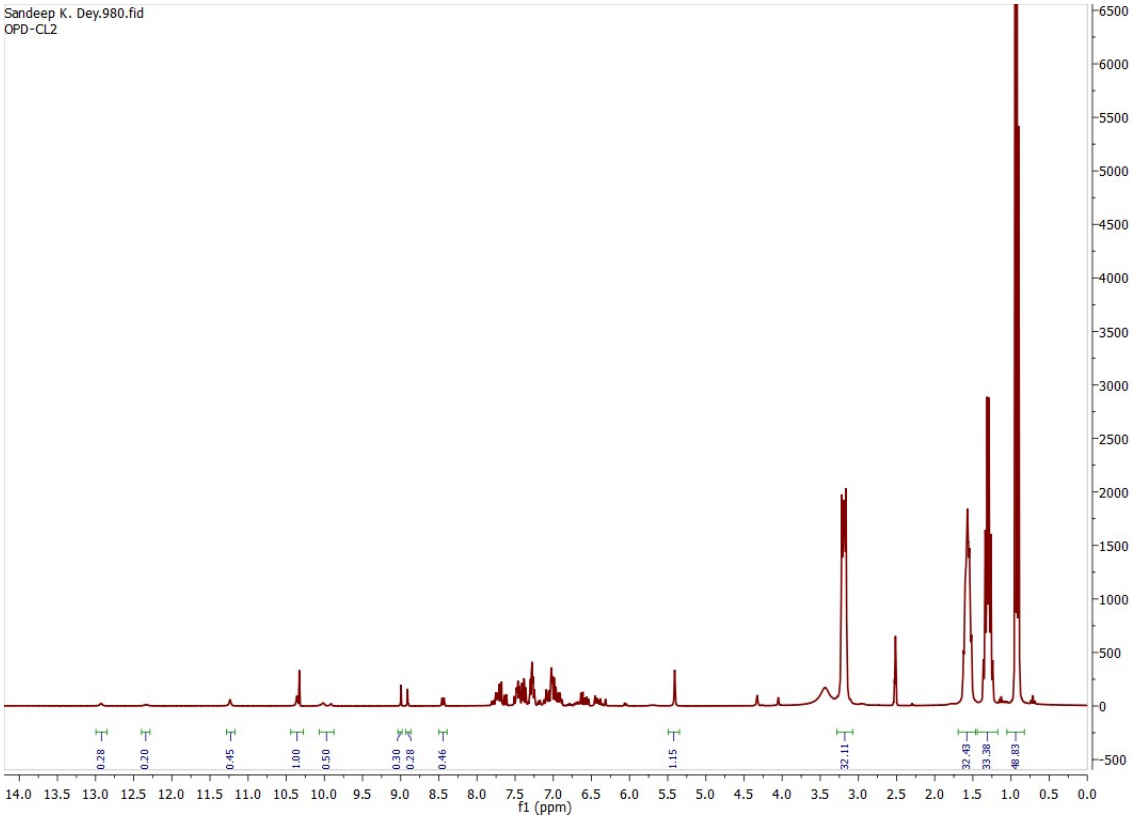


Fig. S28. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)Cl^-, after 24 h.

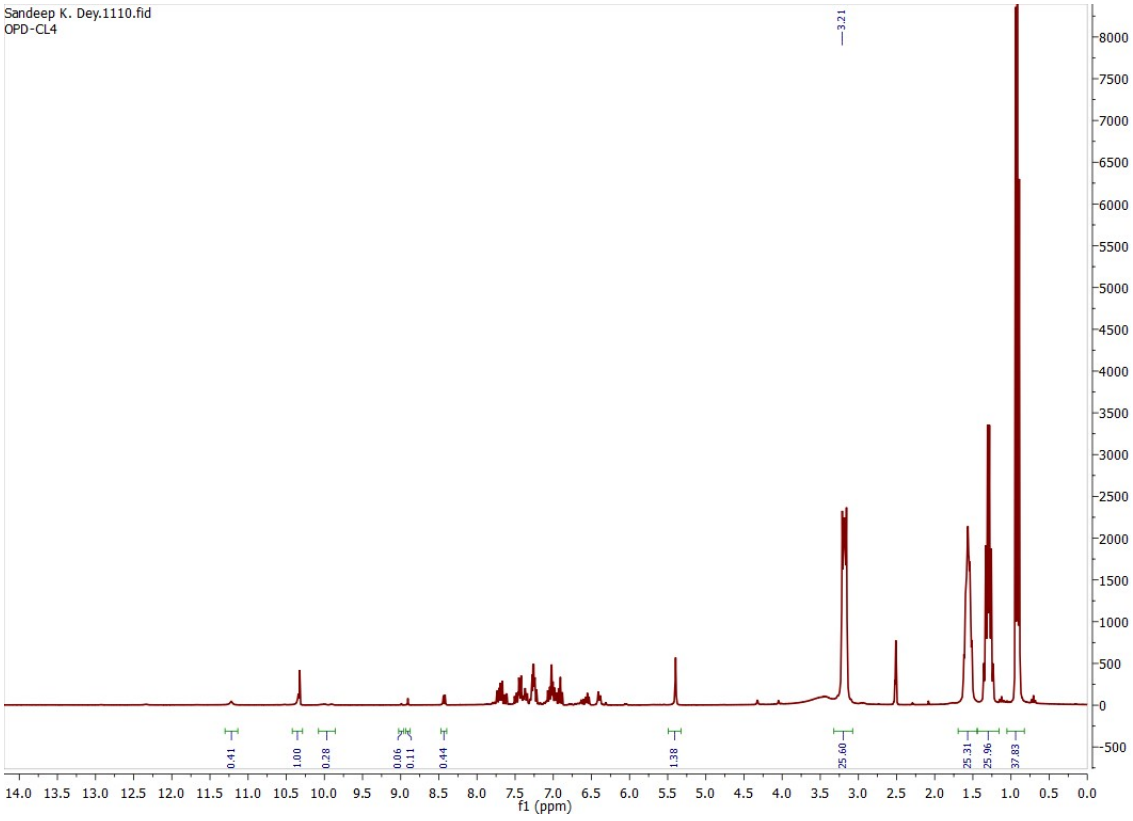


Fig. S29. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)Cl^-, after 72 h.

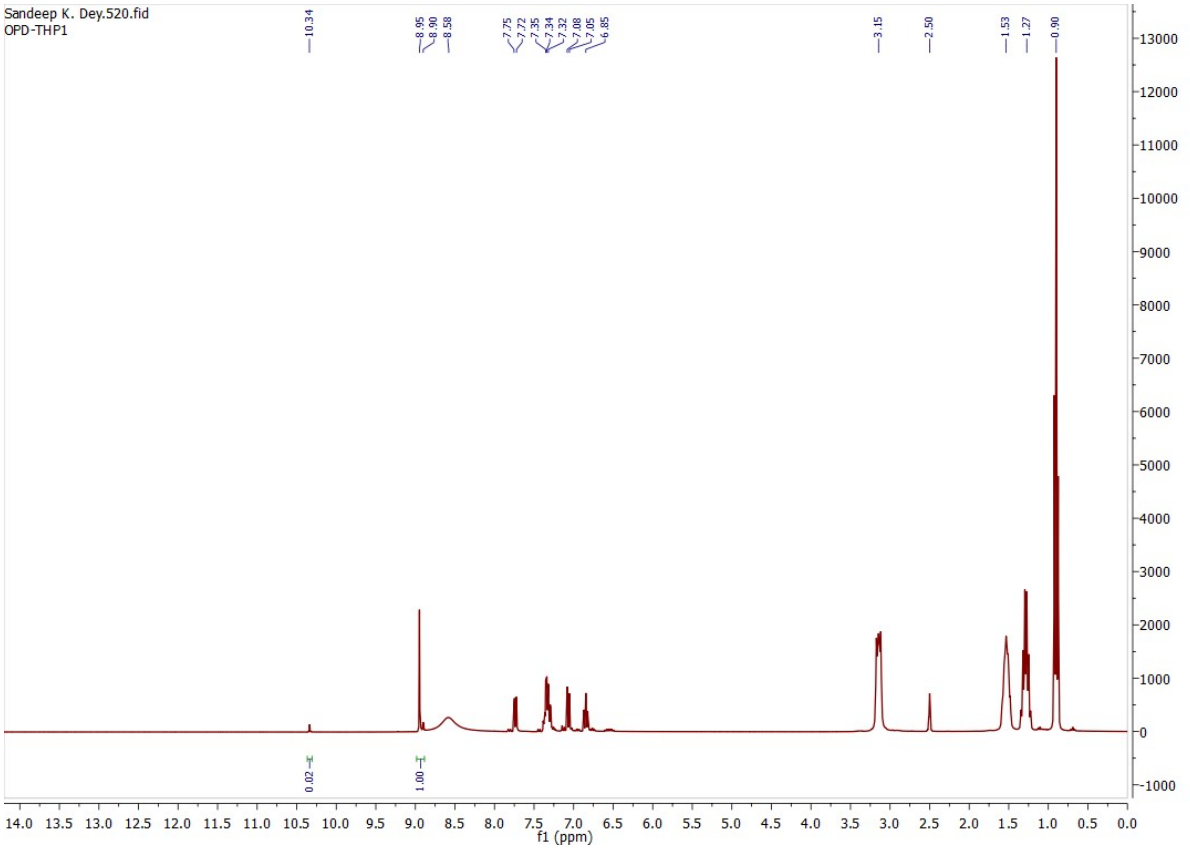


Fig. S30. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)$H_2PO_4^-$, after 1 h.

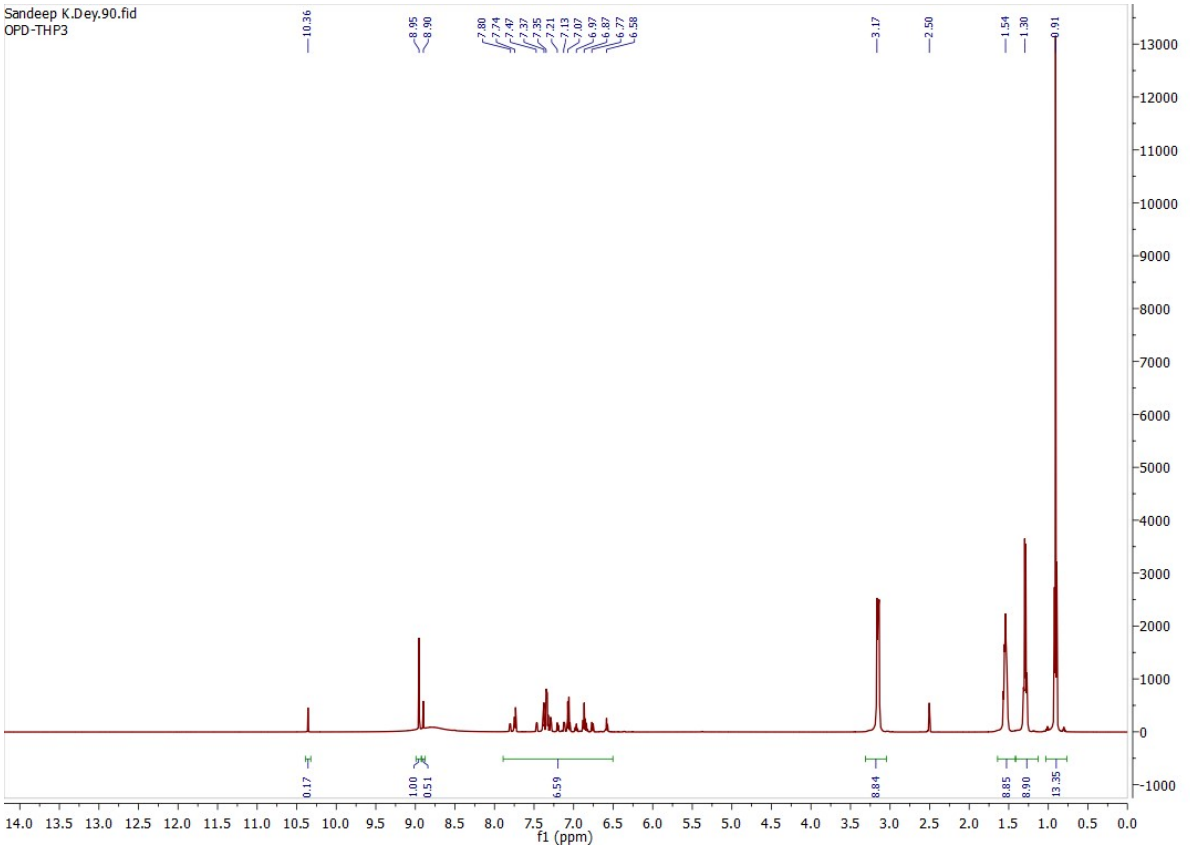


Fig. S31. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)$H_2PO_4^-$, after 24 h.

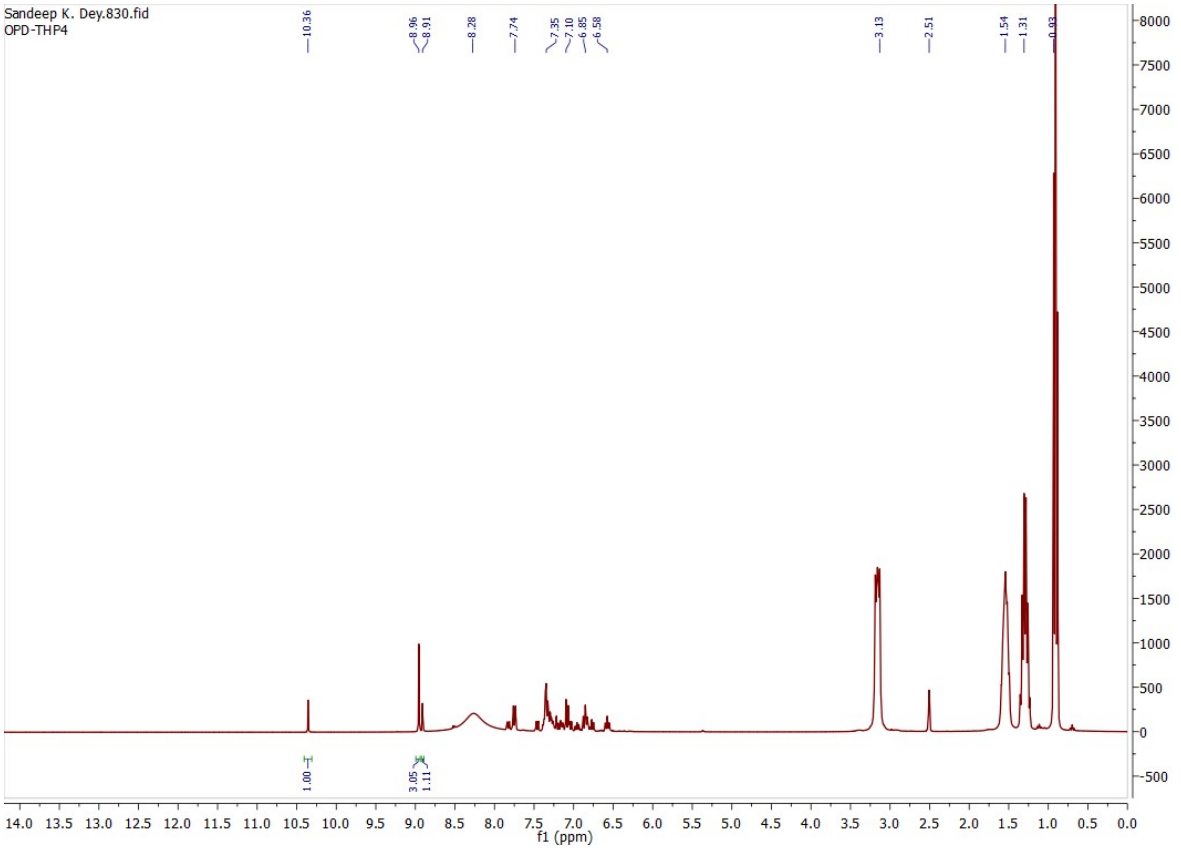


Fig. S32. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)$H_2PO_4^-$, after 48 h.

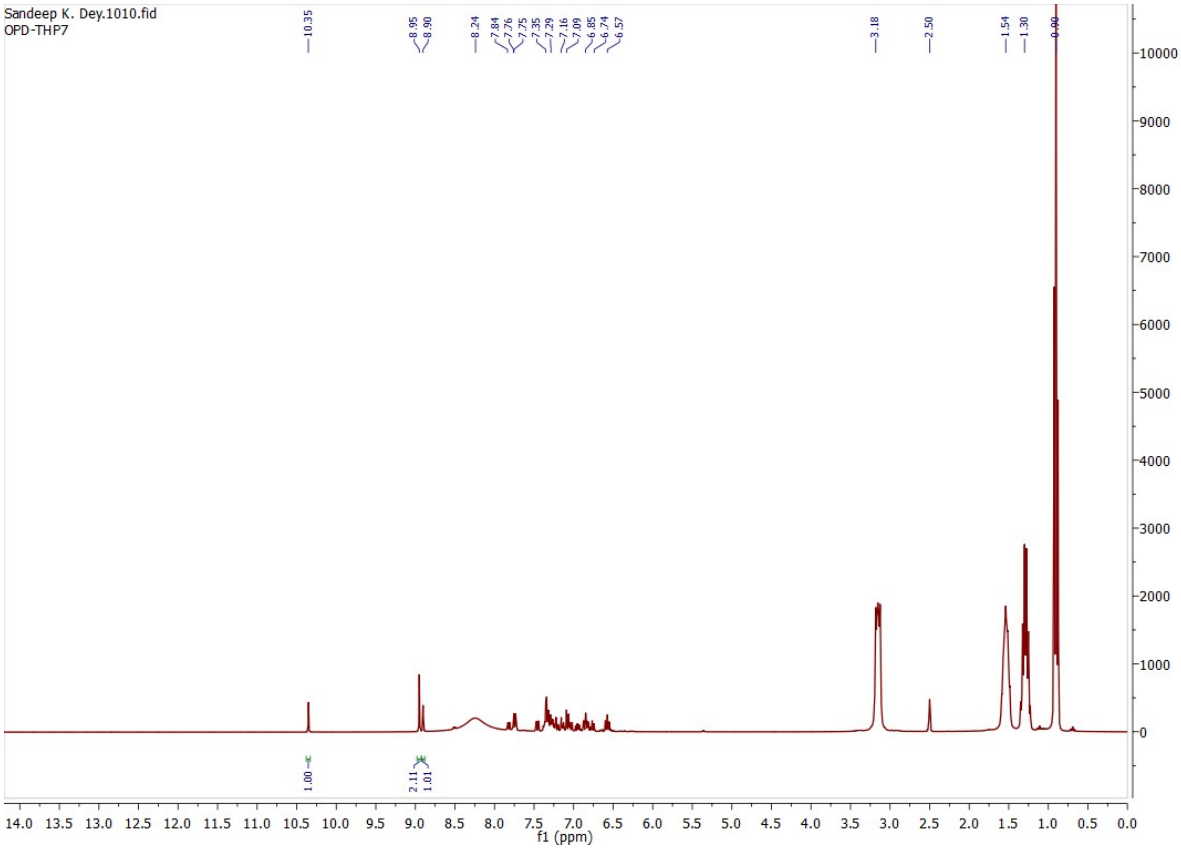


Fig. S33. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)$H_2PO_4^-$, after 72 h.

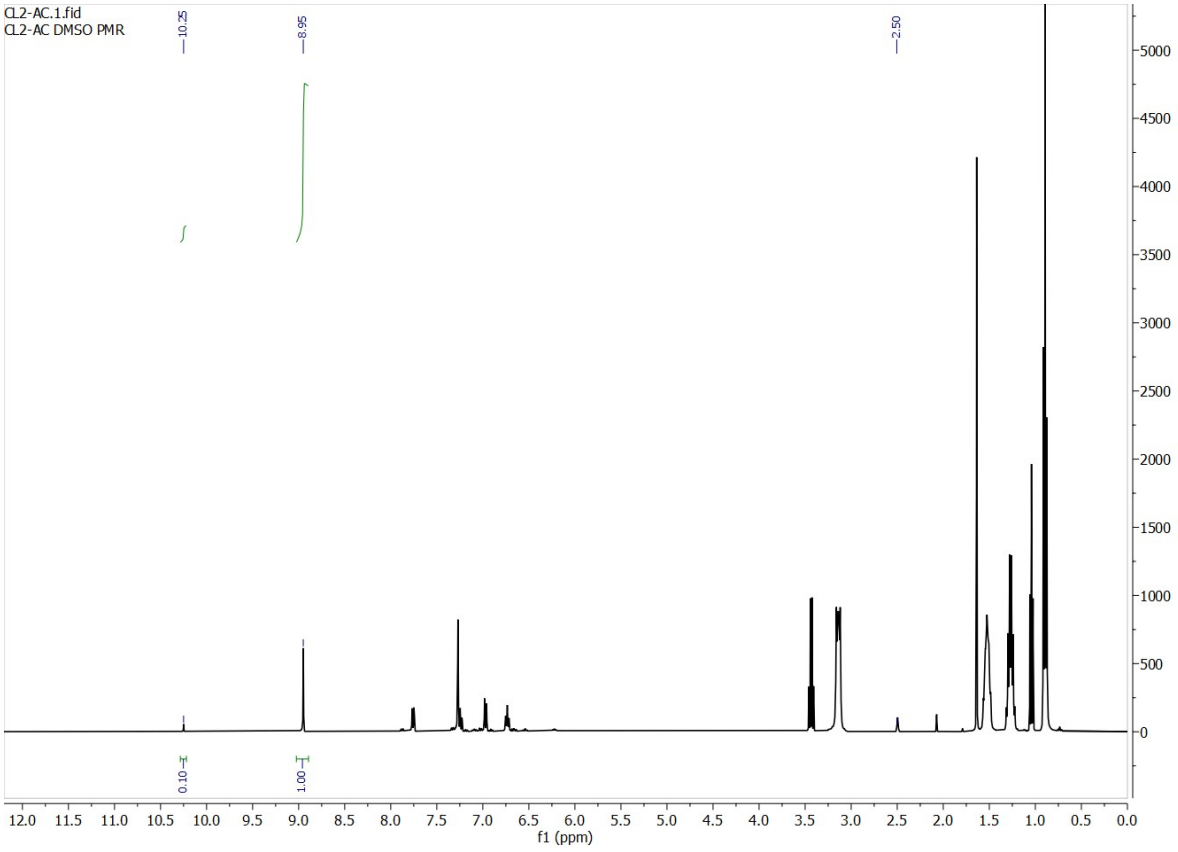


Fig. S34. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)CH_3COO^-, after 1 h.

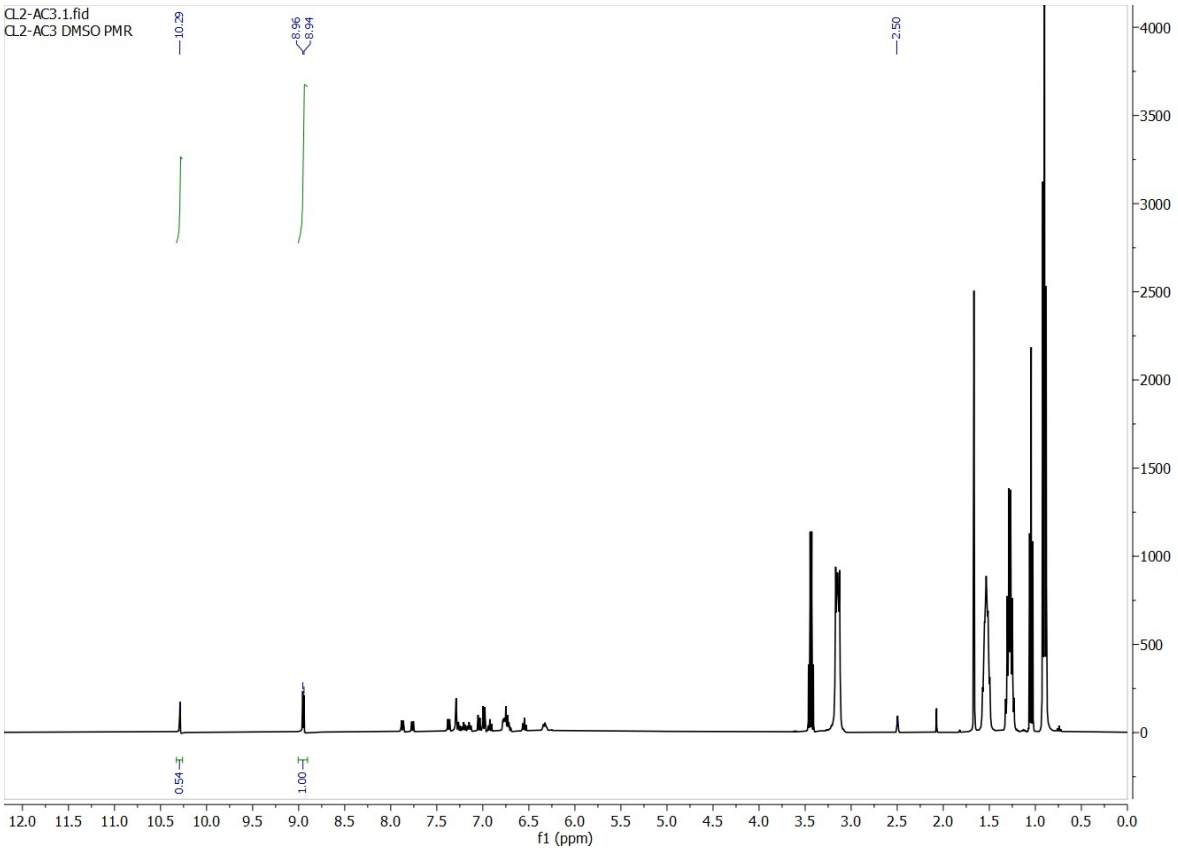


Fig. S35. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)CH_3COO^-, after 48 h.

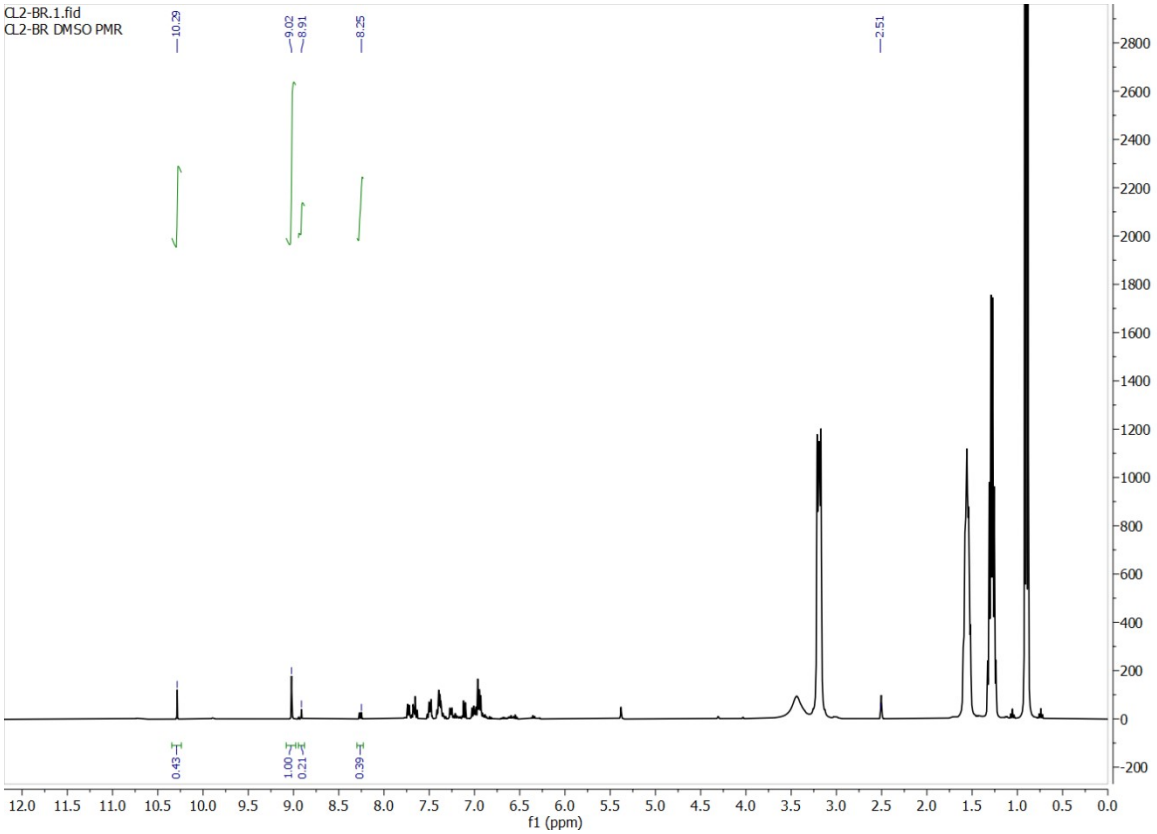


Fig. S36. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)Br^-, after 120 h.

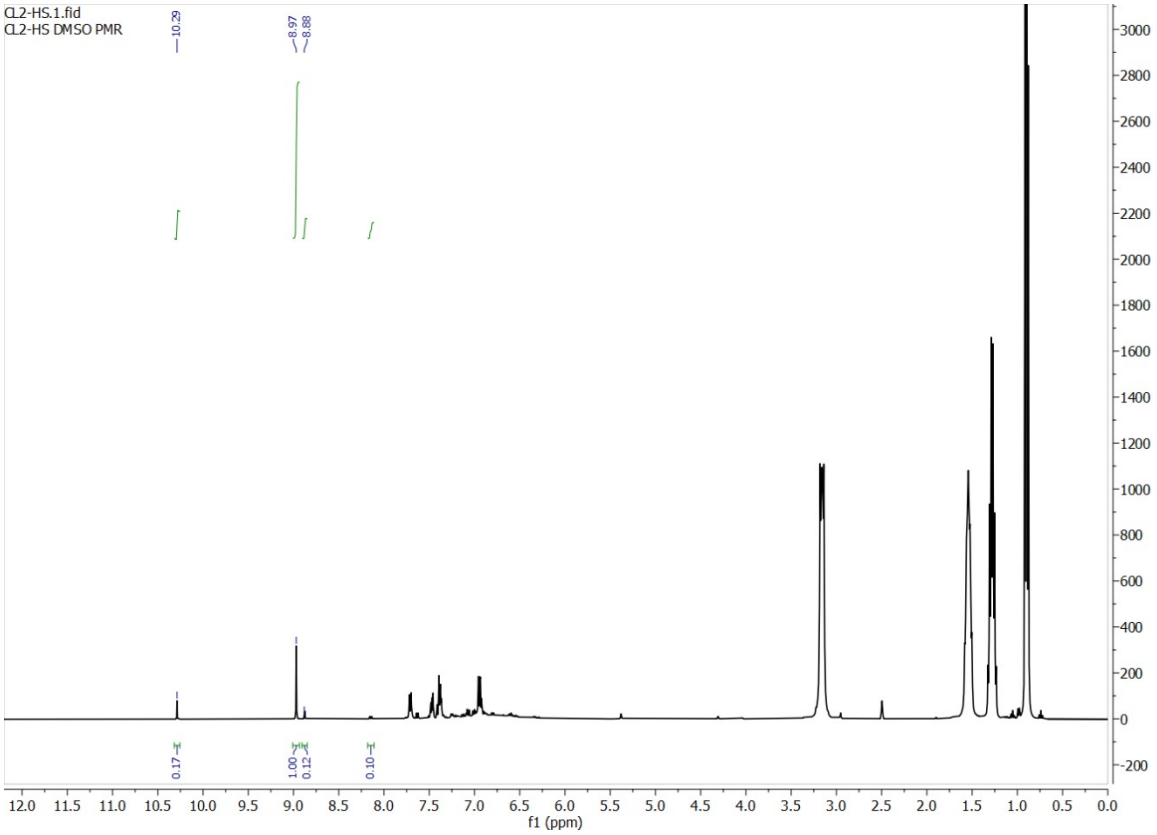


Fig. S37. ^{1}H-NMR spectrum of **CL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)HSO_4^-, after 120 h.

(6) ^{1}H-NMR experiments of NCL2 in the presence of tetrabutylammonium salts in DMSO-d_6.

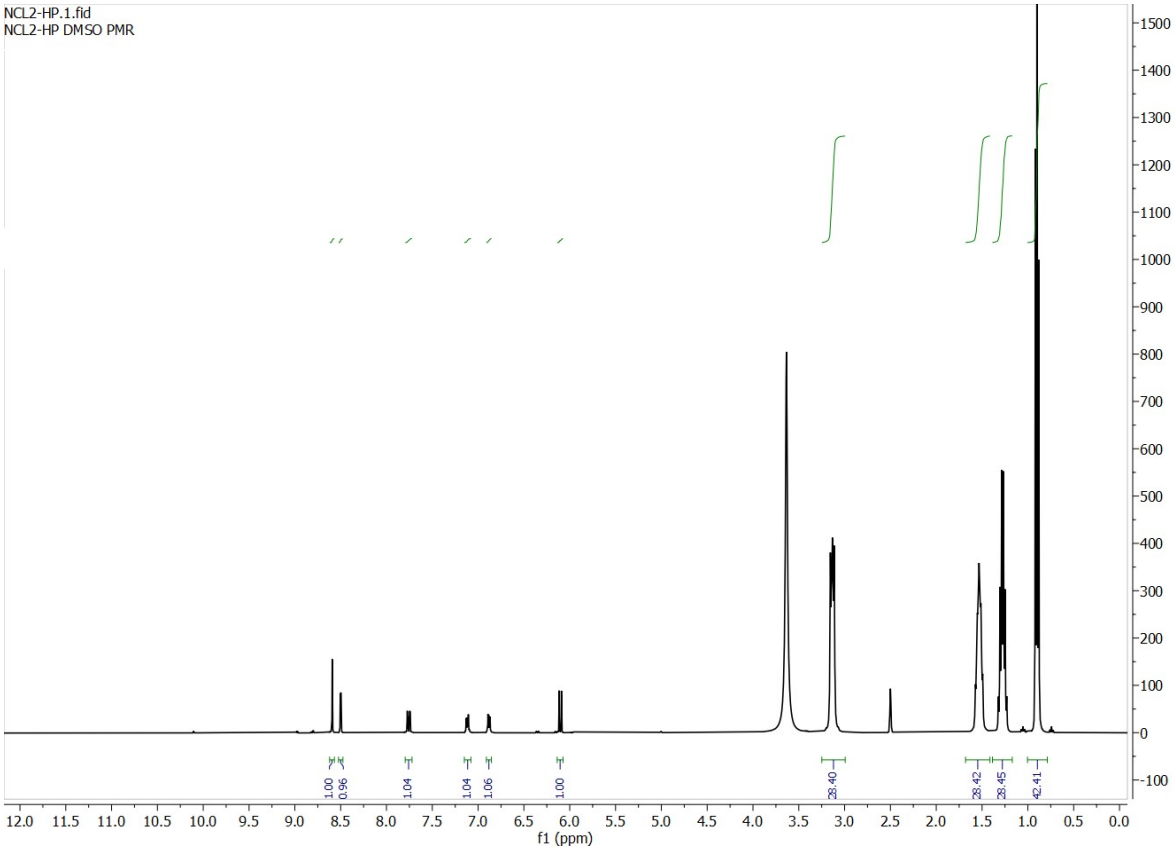


Fig. S38. ^{1}H-NMR spectrum of **NCL2** (DMSO-d_6) in the presence of 5 equiv. (n-Bu_4N^+)$H_2PO_4^-$, after 15 min. of sample preparation. No immediate hydrolysis was observed to take place in the sample except disappearance of -OH due to proton excange processes with $H_2PO_4^-$ ions. This confirms the purity of synthesized **NCL2** as number of -CH peaks and their integral values in the aromatic region matches perfectly expected for **NCL2**.

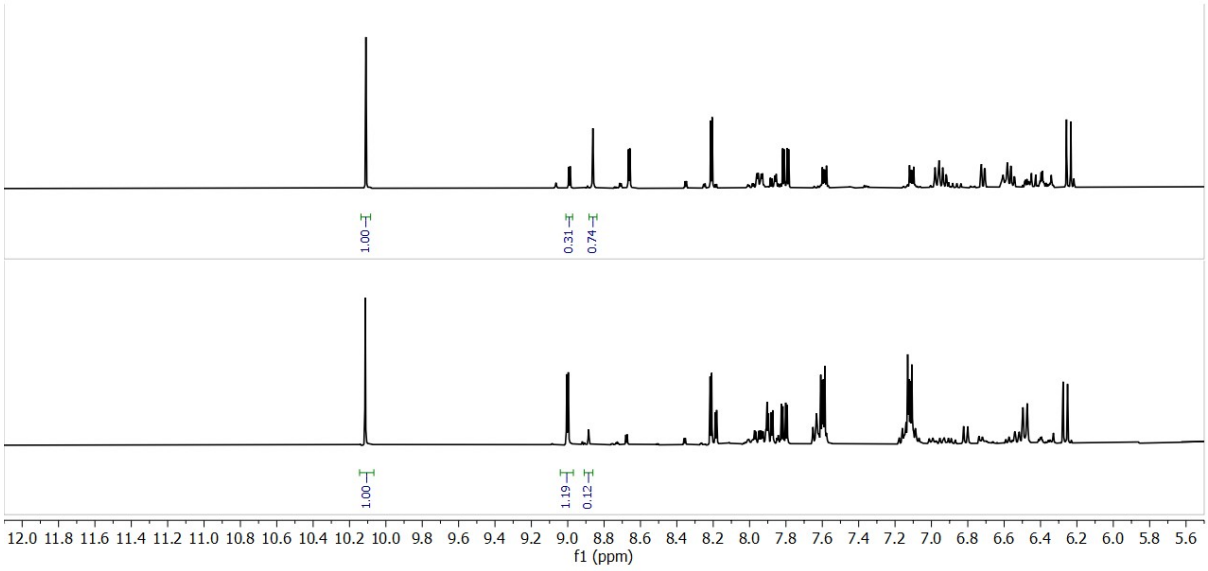


Fig. S39. ^{1}H-NMR spectrum of **NCL2** (DMSO-d_6) in the presence of 5 equivalents (n-Bu_4N^+)F^-, after 1 h. (bottom) and after 24 h. (top).

(7) Control H-NMR experiments

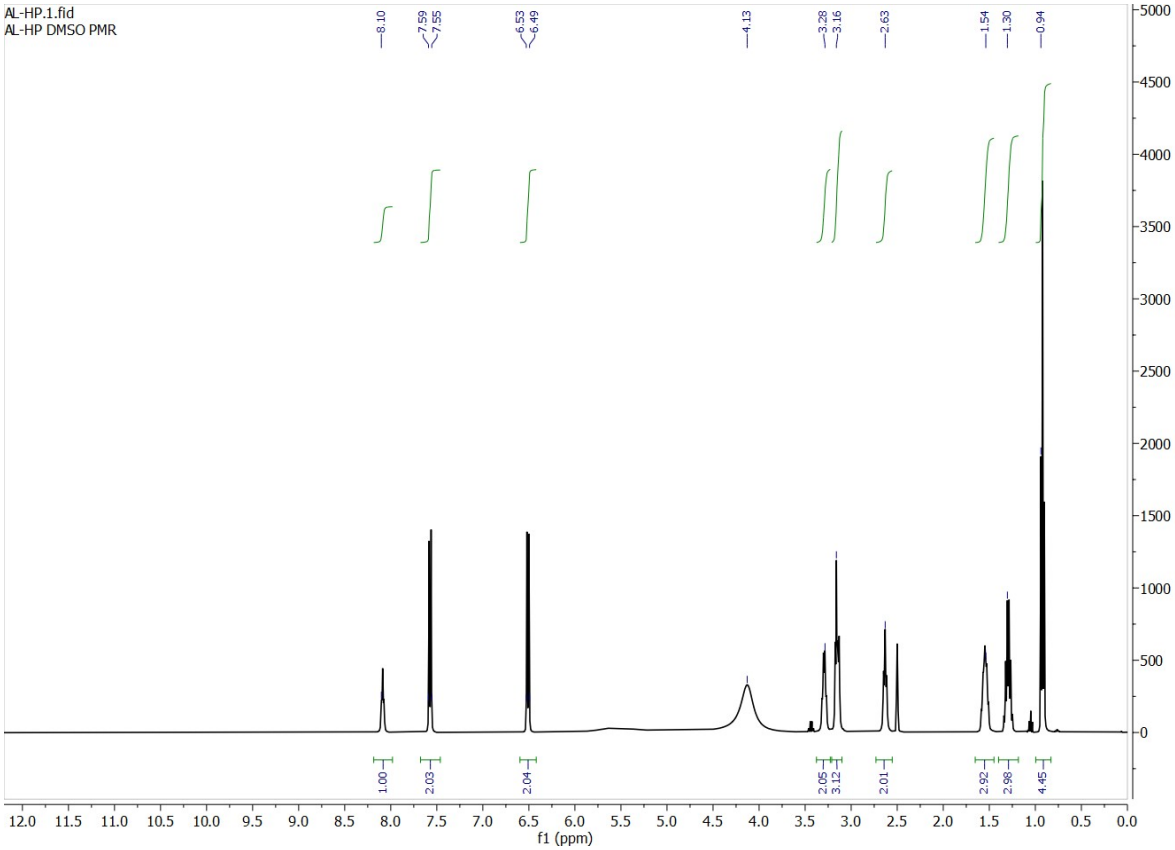


Fig. S40. ^{1}H-NMR spectrum of **AL** (DMSO-d_6) in the presence of one equivalent of (n-Bu_4N^+)$H_2PO_4^-$.

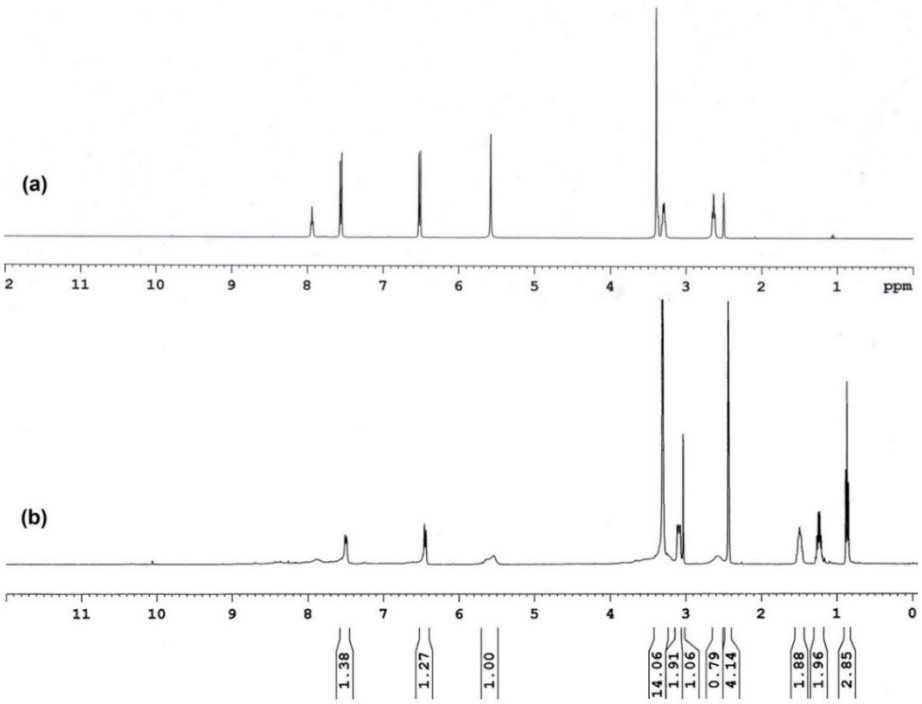


Fig. S41. (a) ^{1}H-NMR spectrum of **AL** in DMSO-d_6 and, (b) ^{1}H-NMR spectrum of **AL** in the presence of one equivalent of (n-Bu_4N^+)Cl^- showing broadening of amide –NH signal (at 7.9 ppm) and amine –NH_2 signals (at 5.6 ppm).

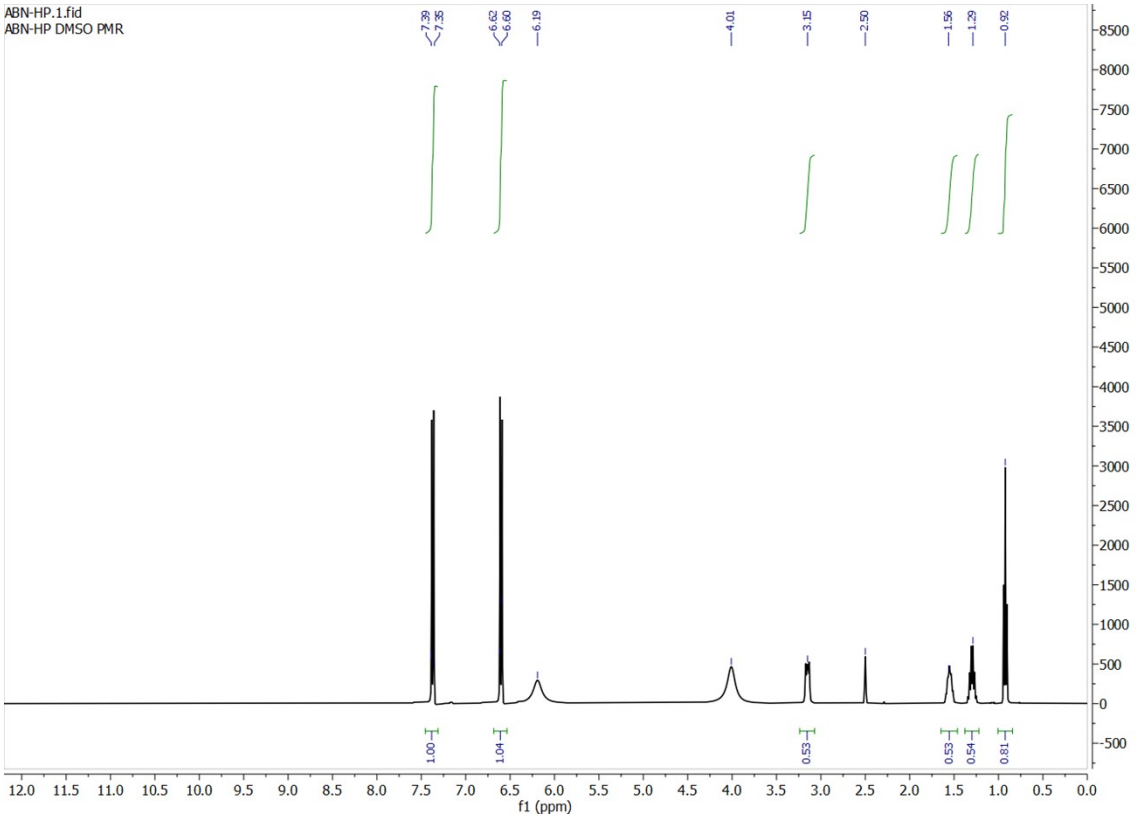


Fig. S42. ^{1}H-NMR spectrum of **4-aminobenzonitrile** (DMSO-d_6) in the presence of (n-Bu_4N^+)$H_2PO_4^-$.

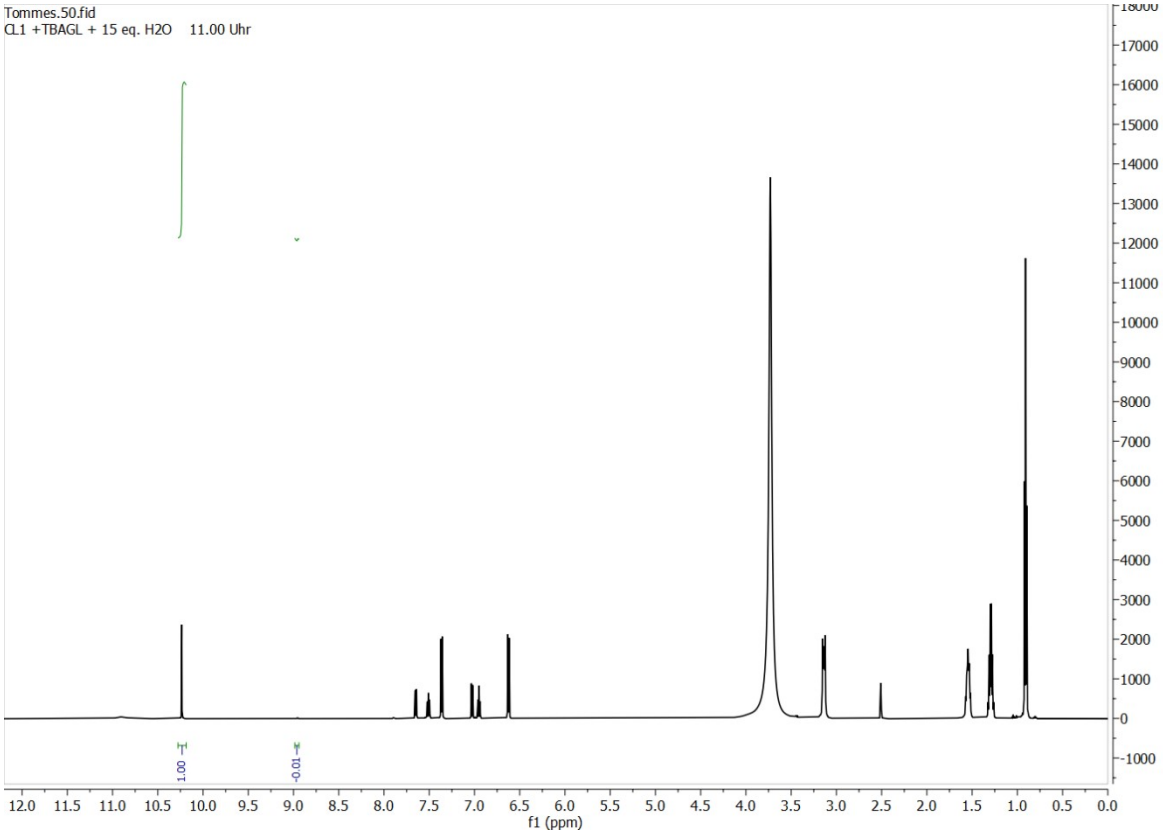


Fig. S43. Aromatic region of ^{1}H-NMR spectrum (DMSO-d_6) of **CL1** in the presence of 15 equivalents of H_2O and 1 equivalent of (n-Bu4N^+)Cl^-, recorded after 1 hour showing complete hydrolysis.

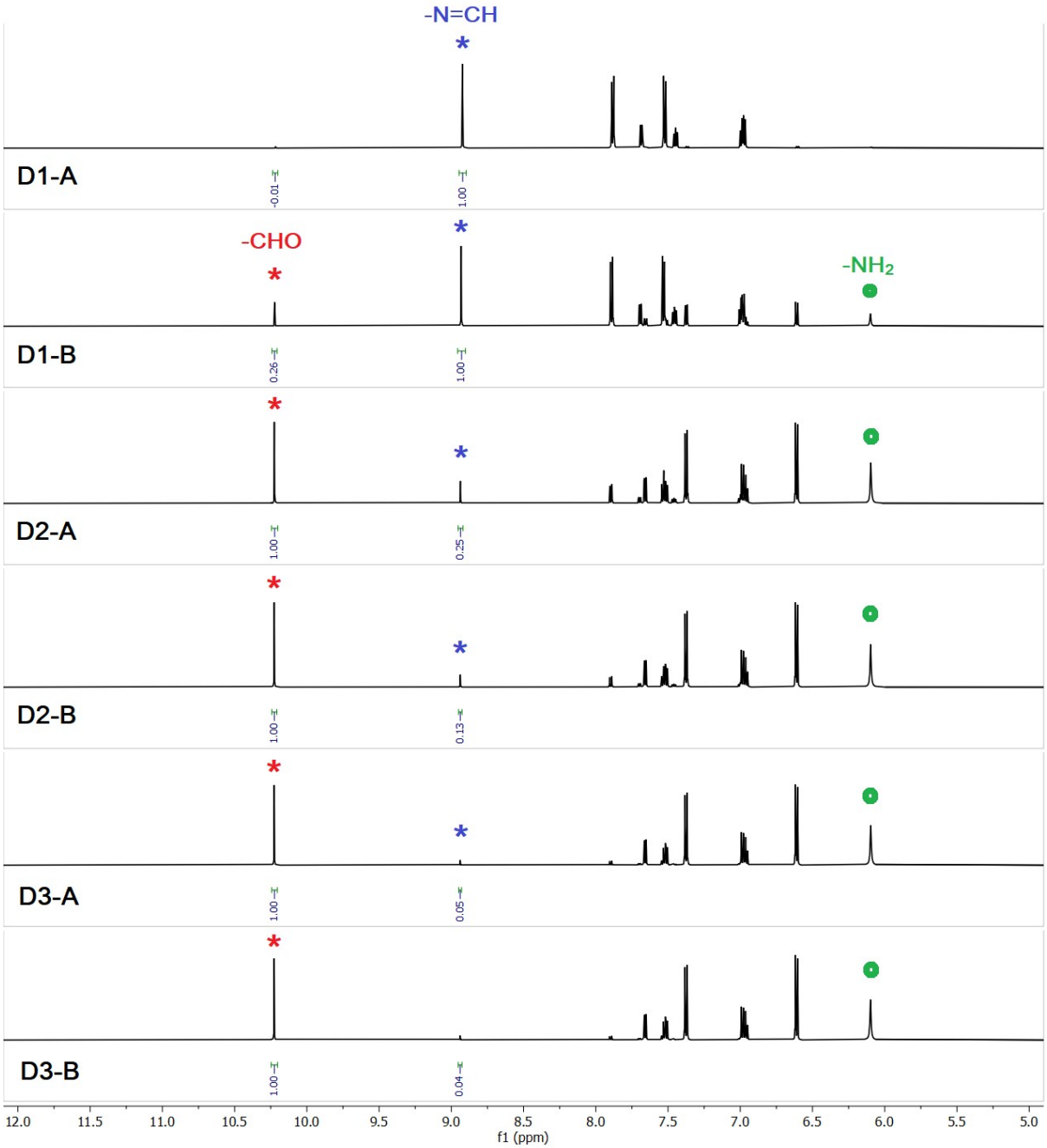


Fig. S44. Aromatic region of ^{1}H-NMR spectra (DMSO-d_6) of **CL1** in the presence of 15 equivalents of H_2O, recorded after 1 hour (D1-A), 6 hours (D1-B), 24 hours (D2-A), 30 hours (D2-B), 48 hours (D3-A) and after 54 hours (D3-B). Signals labelled with red and blue asterisk indicate -CHO and -N=CH- peaks of salicylaldehyde (red) and **CL1** (blue) respectively. Signals labelled with green dots represent -NH_2 peaks of 4-aminobenzonitrile (hydrolysis product).

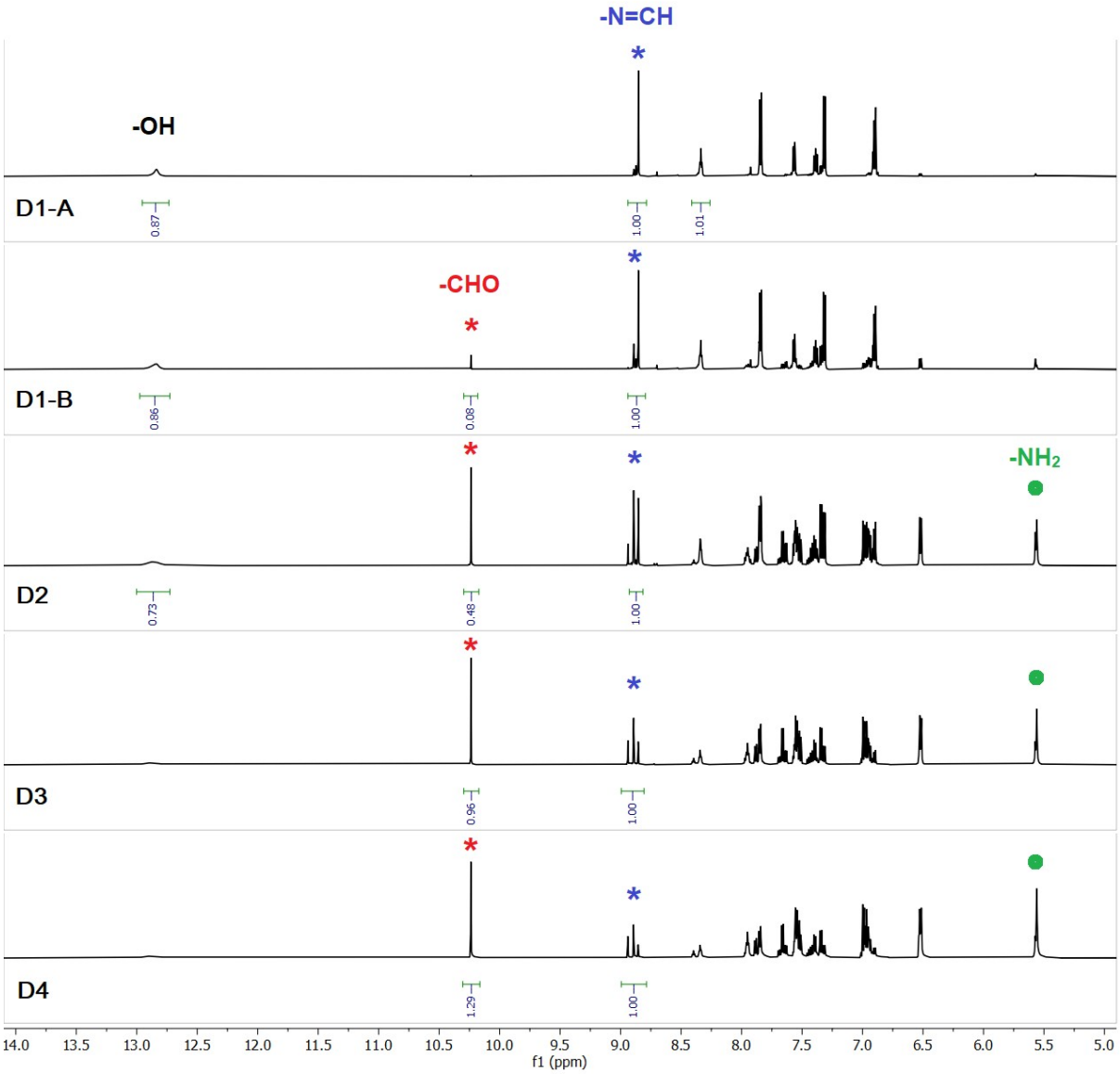


Fig. S45. Aromatic region of ^{1}H-NMR spectra (DMSO-d_6) of **SL** in the presence of 30 equivalents of H_2O, recorded after 1 hour (D1-A), 6 hours (D1-B), 30 hours (D2), 54 hours (D3) and after 72 hours (D4). Signals labelled with red and blue asterisk indicate -CHO and -N=CH- peaks of salicylaldehyde (red) and **SL** (blue) respectively. Signals labelled with green dots represent -NH_2 peaks of **AL** (hydrolysis product).

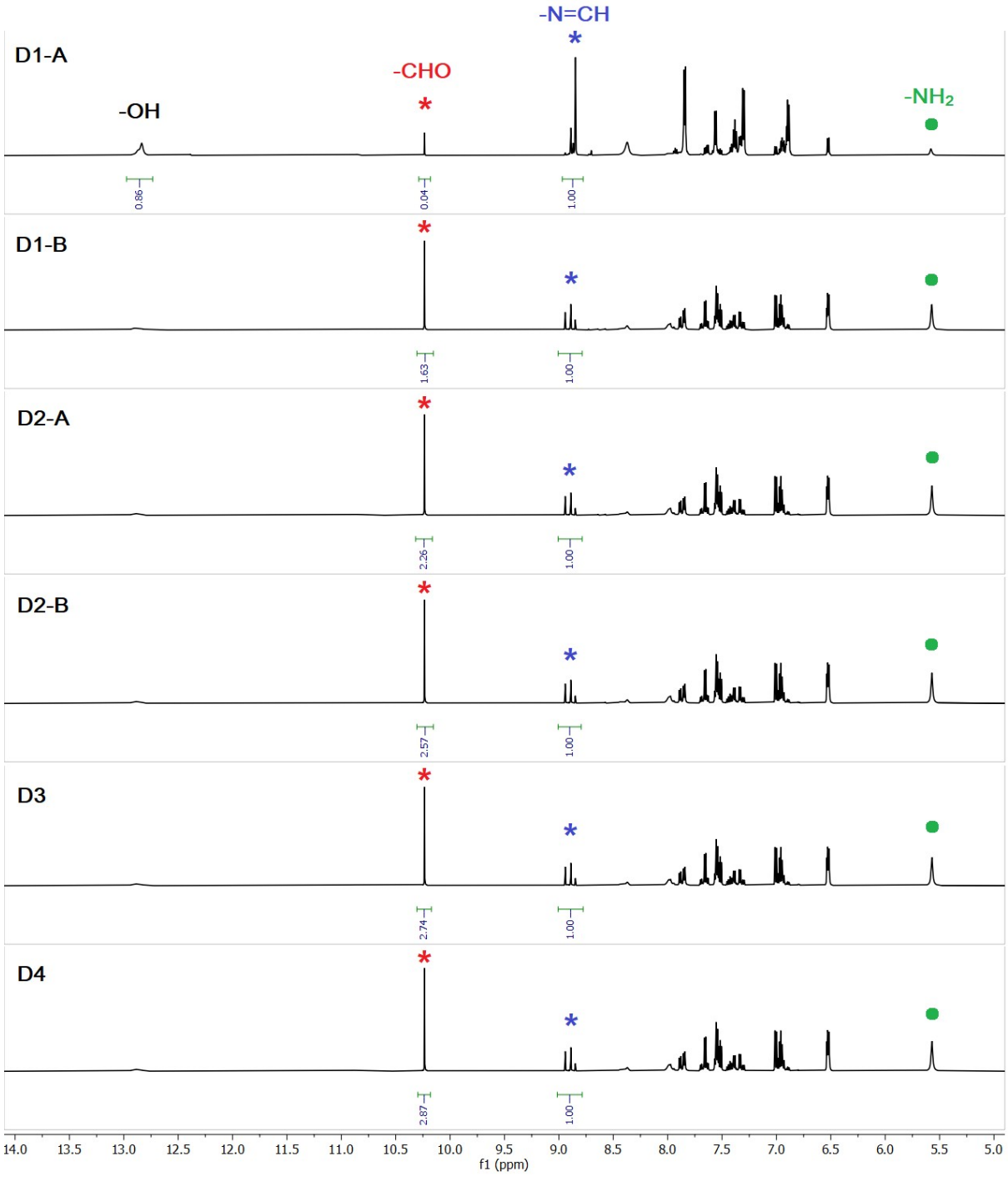


Fig. S46. Aromatic region of ^{1}H-NMR spectra (DMSO-d_6) of **SL** in the presence of 30 equivalents of H_2O and 1 equivalent of (n-Bu4N^{+})Cl^{-}, recorded after 1 hour (D1-A), 6 hours (D1-B), 24 hours (D2-A), 30 hours (D2-B), 48 hours (D3) and after 72 hours (D4). Signals labelled with red and blue asterisk indicate -CHO and -N=CH- peaks of salicylaldehyde (red) and **SL** (blue) respectively. Signals labelled with green dots represent -NH_2 peaks of **AL** (hydrolysis product).

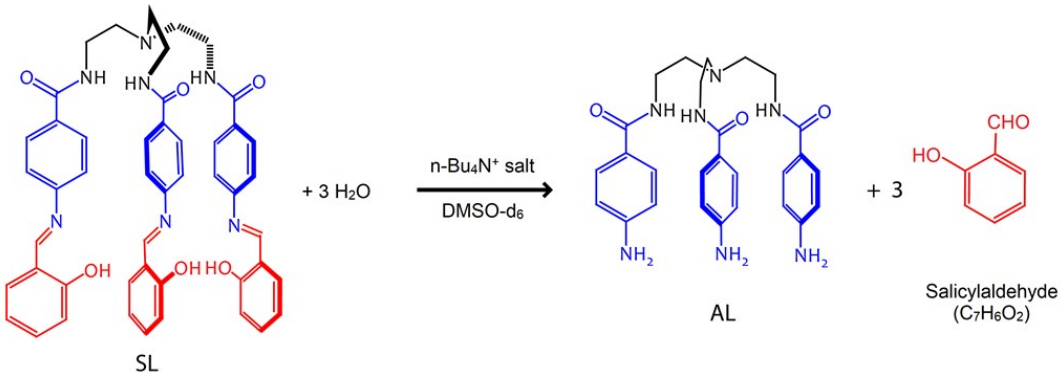
Table S1. Percentage of hydrolysis of Schiff bases **SL**, **CL1** and **CL2** in the presence of $(n\text{-}Bu_4N)^+Cl^-$, $(n\text{-}Bu_4N)^+H_2PO_4^-$ and $(n\text{-}Bu_4N)^+CH_3COO^-$ obtained from ^{1}H-NMR experiments in DMSO-D_6.

NMR Soln. Mix.	After 1 h.	After 24 h.	After 48 h.	After 72 h.
SL + $(n\text{-}Bu_4N)^+Cl^-$ (10 equiv.)	0%	27%	30%	33%
SL + $(n\text{-}Bu_4N)^+H_2PO_4^-$ (10 equiv.)	24%	44%	46%	47%
SL + $(n\text{-}Bu_4N)^+CH_3COO^-$ (10 equiv.)	17%	31%	33%	35%
CL1 + $(n\text{-}Bu_4N)^+Cl^-$ (5 equiv.)	–	84%	–	–
CL1 + $(n\text{-}Bu_4N)^+H_2PO_4^-$ (5 equiv.)	40%	75%	–	–
CL1 + $(n\text{-}Bu_4N)^+CH_3COO^-$ (5 equiv.)	30%	–	99%	–
CL2 + $(n\text{-}Bu_4N)^+Cl^-$ (5 equiv.)	Cannot be determined due to presence of multiple species			
CL2 + $(n\text{-}Bu_4N)^+H_2PO_4^-$ (5 equiv.)	–	15%	22%	25%
CL2 + $(n\text{-}Bu_4N)^+CH_3COO^-$ (5 equiv.)	10%	–	35%	–

Table S2. Percentage of hydrolysis of Schiff bases **SL**, **CL1** and **CL2** in the presence of water and separately in the presence of water and $(n\text{-}Bu_4N)^+Cl^-$ obtained from ^{1}H-NMR experiments in DMSO-d_6 (**Control experiments**).

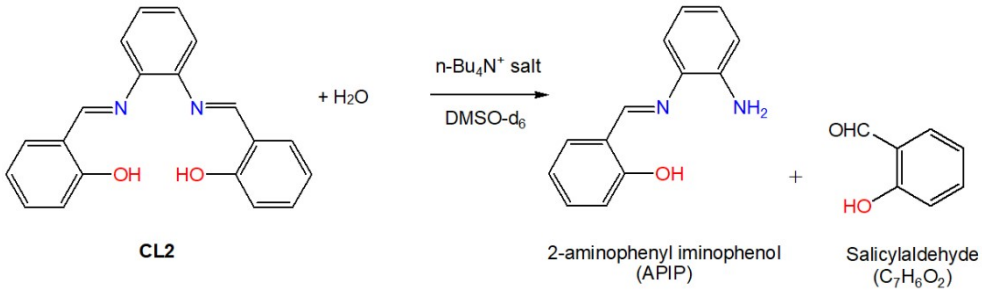
NMR soln. mix.	$(n\text{-}Bu_4N)^+Cl^-$	1 h.	6 h.	24 h.	30 h.	48 h.	54 h.	72 h.
CL1+15 equiv. H_2O	0 equiv.	1%	20%	80%	88%	95%	96%	–
CL1+15 equiv. H_2O	1 equiv.	99%	–	–	–	–	–	–
CL2+15 equiv. H_2O	0 equiv.	0%	2%	18%	18%	21%	21%	26%
CL2+15 equiv. H_2O	1 equiv.	20%	30%	45%	46%	57%	63%	71%
SL + 30 equiv. H_2O	0 equiv.	0%	7%	27%	32%	46%	49%	55%
SL + 30 equiv. H_2O	1 equiv.	4%	62%	69%	72%	73%	73%	73%

Table S3. Calculation of equilibrium constant (**K**) for the hydrolysis of **SL** in DMSO-d_6 in the presence of tetrabutylammonium salts and control experiments in the presence of water (Table S1 and S2 are referred for equilibrium concentration calculations).



SL + 3 H_2O $\xrightarrow{X}$ AL + 3 $C_7H_6O_2$	[**SL**] (mol/L)	[AL] (mol/L)	[$C_7H_6O_2$] (mol/L)	**K** [H_2O]^3 = [AL]x[$C_7H_6O_2$]^3/[SL] (mol^3 L^{-3})
X = 10 equiv. Cl^-	2.48 x 10^{-2}	1.22 x 10^{-2}	3.66 x 10^{-2}	**2.411 x 10^{-5}**
X = 10 equiv. $H_2PO_4^-$	1.96 x 10^{-2}	1.74 x 10^{-2}	5.22 x 10^{-2}	**1.262 x 10^{-4}**
X = 10 equiv. CH_3COO^-	2.40 x 10^{-2}	1.29 x 10^{-2}	3.87 x 10^{-2}	**3.115 x 10^{-5}**
X = 30 equiv. H_2O	1.66 x 10^{-2}	2.03 x 10^{-2}	6.10 x 10^{-2}	**2.780 x 10^{-4}**
X = 30 equiv. H_2O + 1 equiv. Cl^-	1.00 x 10^{-2}	2.70 x 10^{-2}	8.10 x 10^{-2}	**1.434 x 10^{-3}**

Table S4. Calculation of equilibrium constant (**K**) for the hydrolysis of **CL2** in DMSO-d_6 in the presence of tetrabutylammonium salts and control experiments in the presence of water (Table S1 and S2 are referred for equilibrium concentration calculations).



CL2 + H_2O $\xrightarrow{X}$ APIP + $C_7H_6O_2$	[**CL2**] (mol/L)	[APIP] (mol/L)	[$C_7H_6O_2$] (mol/L)	**K** [H_2O] = [APIP]x[$C_7H_6O_2$]/[**CL2**] (mol L^{-1})
X = 5 equiv. (n-Bu_4N)$^+H_2PO_4^-$	7.50 x10^{-2}	2.50 x10^{-2}	2.50 x10^{-2}	**8.333 x10^{-3}**
X = 5 equiv. (n-Bu_4N)$^+CH_3COO^-$	6.50 x10^{-2}	3.50 x10^{-2}	3.50 x10^{-2}	**1.884 x10^{-2}**
X = 15 equiv. H_2O	7.40 x10^{-2}	2.60 x10^{-2}	2.60 x10^{-2}	**9.135 x10^{-3}**
X = 15 equiv. H_2O + 1 equiv. (n-Bu_4N)$^+Cl^-$	2.90 x10^{-2}	7.10 x10^{-2}	7.10 x10^{-2}	**1.738 x10^{-1}**

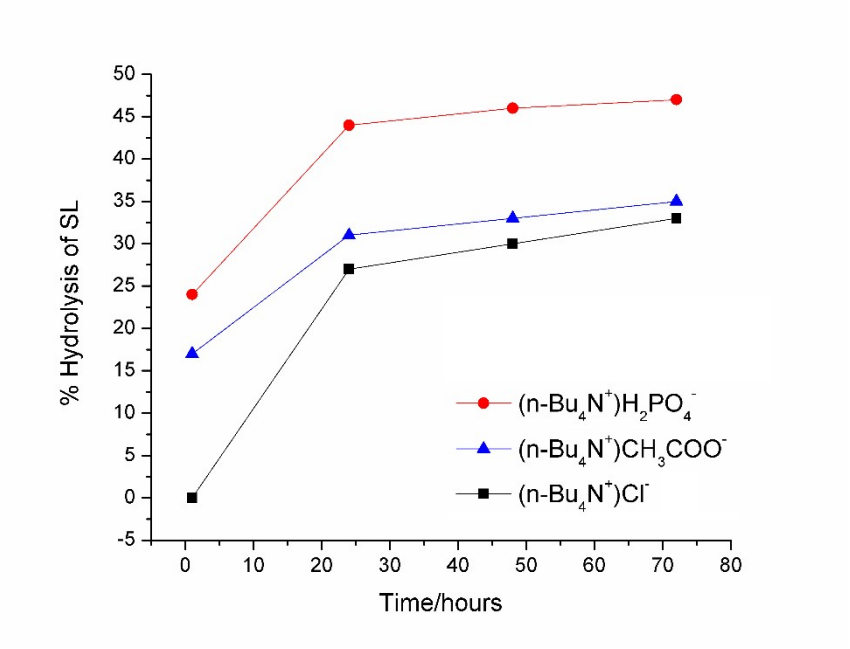


Fig. S47. Plot of hydrolysis percentage of Schiff base **SL** vs. time (hours) in the presence of $(n\text{-}Bu_4N)^+Cl^-$, $(n\text{-}Bu_4N)^+H_2PO_4^-$ and $(n\text{-}Bu_4N)^+CH_3COO^-$ obtained from ^{1}H-NMR experiments in DMSO-D_6 (Refer Table S1).

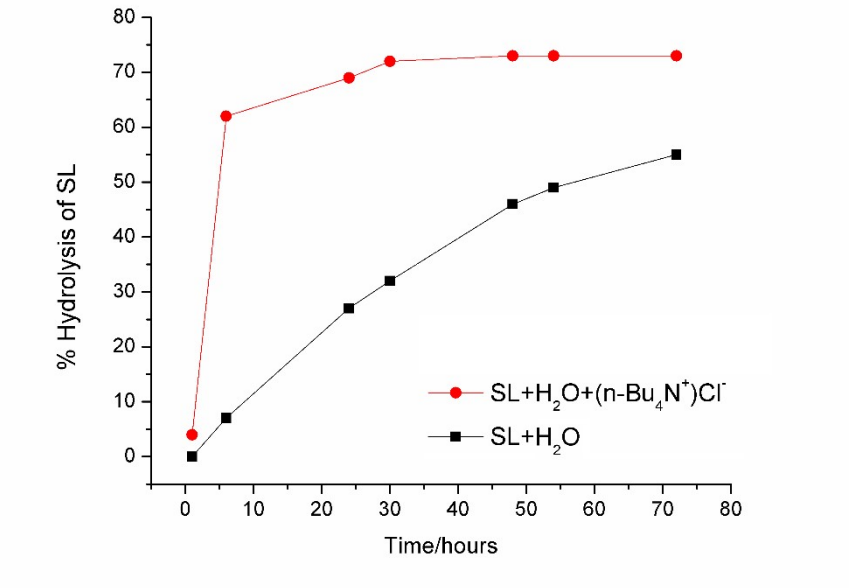


Fig. S48. Plot of hydrolysis percentage of Schiff base **SL** vs. time (hours) in the presence of 30 equiv. water and separately in the presence of water (30 equiv.) and $(n\text{-}Bu_4N)^+Cl^-$ (1 equiv.) obtained from ^{1}H-NMR experiments in DMSO-D_6 (Refer Table S2).

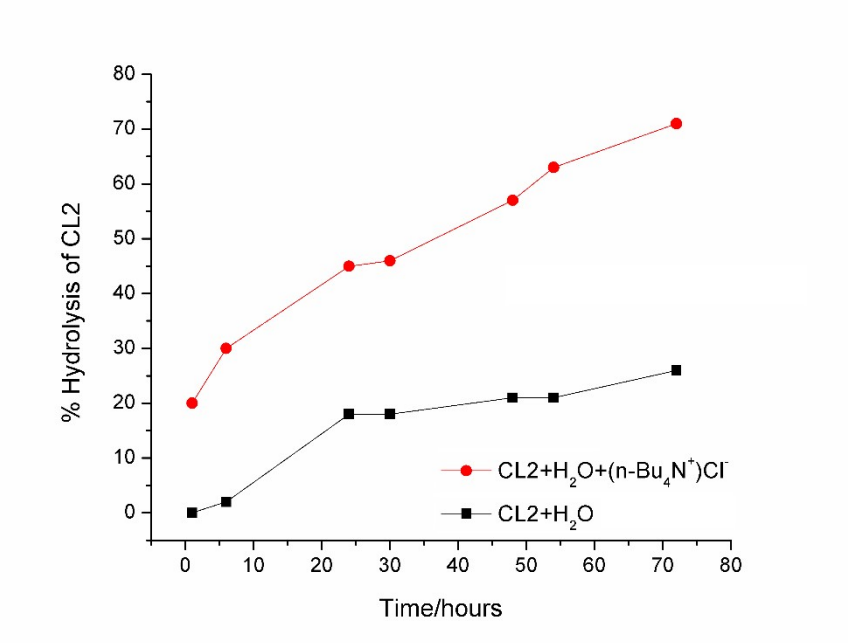


Fig. S49. Plot of hydrolysis percentage of Schiff base **CL2** vs. time (hours) in the presence of 15 equiv. water and separately in the presence of water (15 equiv.) and $(n\text{-}Bu_4N)^+Cl^-$ (1 equiv.) obtained from ^{1}H-NMR experiments in DMSO-D_6 (Refer Table S2).

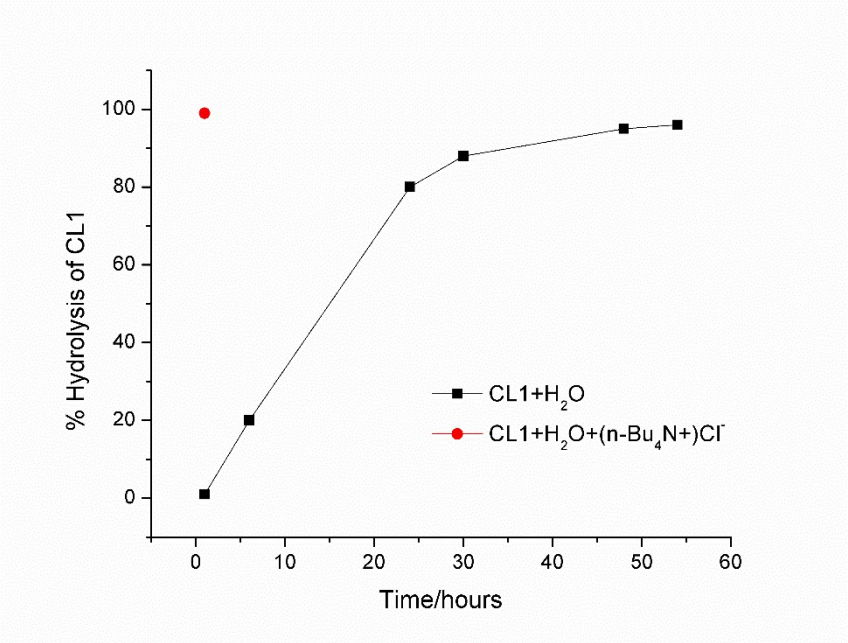


Fig. S50. Plot of hydrolysis percentage of Schiff base **CL1** vs. time (hours) in the presence of 15 equiv. water and separately in the presence of water (15 equiv.) and $(n\text{-}Bu_4N)^+Cl^-$ (1 equiv.) obtained from ^{1}H-NMR experiments in DMSO-D_6 (Refer Table S2).

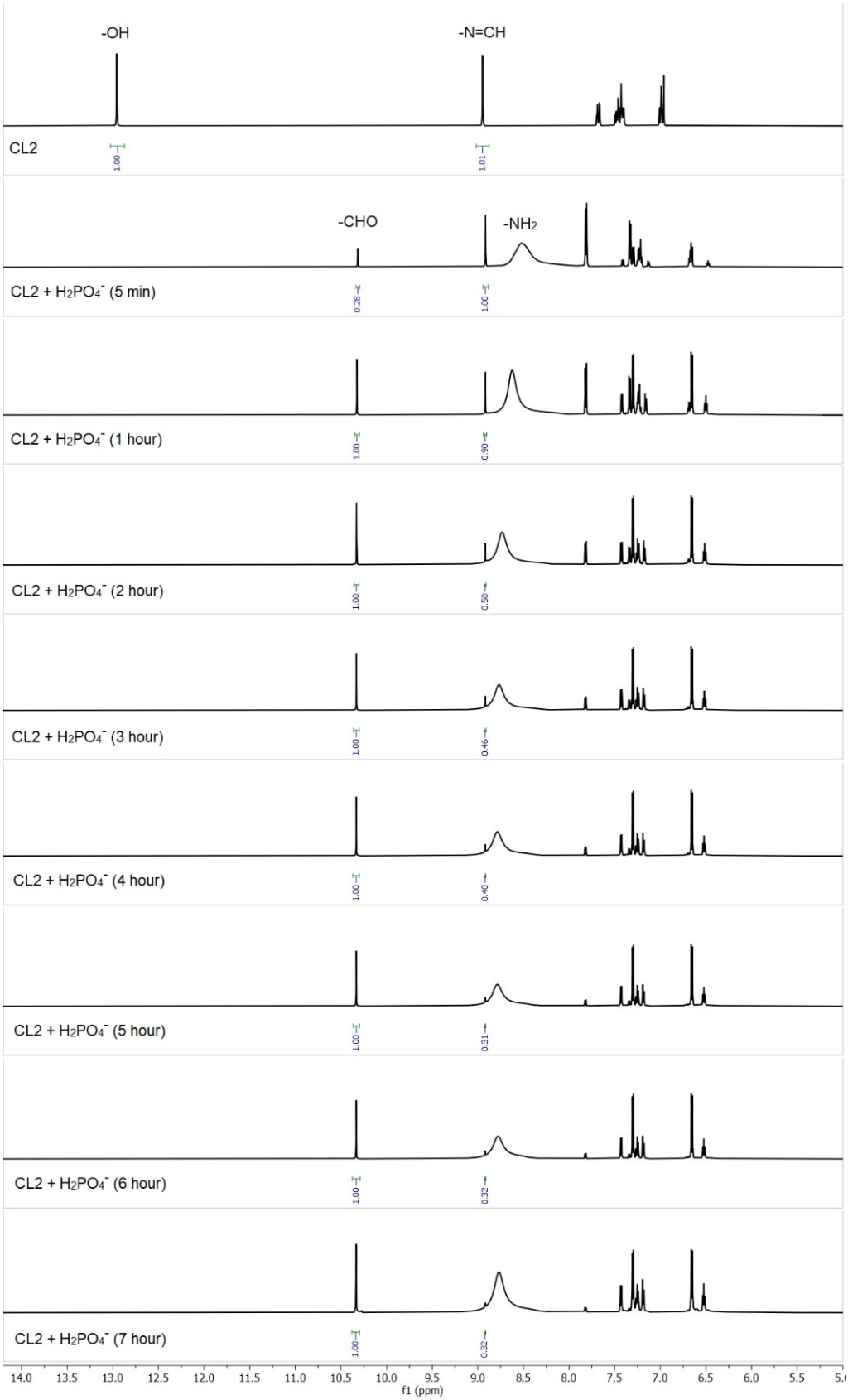


Fig. S51 Aromatic region of ^{1}H-NMR (DMSO-d_6) spectra of **CL1** in the presence of 5 equivalents of (n-Bu_4N^+)$H_2PO_4^-$ recorded after every one hour.

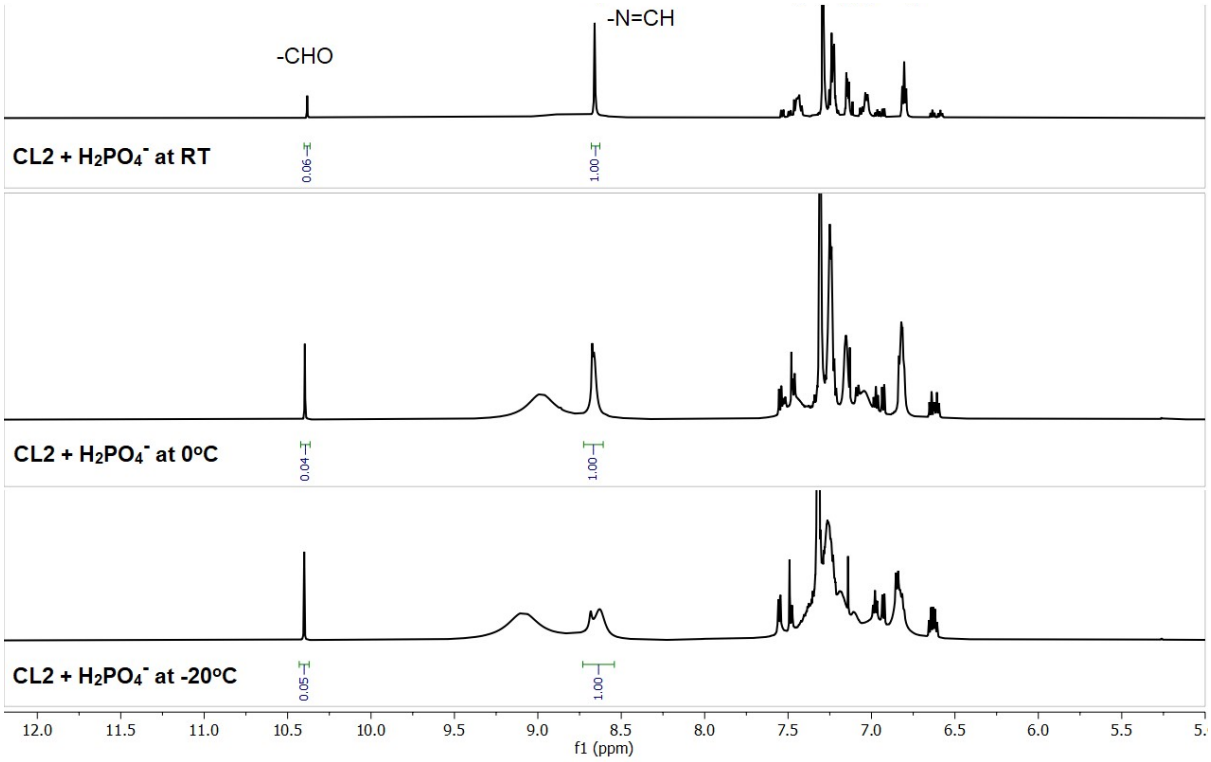


Fig. S52 Aromatic region of ^{1}H-NMR ($CDCl_3$) spectra of **CL2** in the presence of 5 equivalents of (n-Bu_4N^+)$H_2PO_4^-$ recorded at room temperature (RT), 0 ^{o}C and −20 ^{o}C **after one hour** of sample preparation.

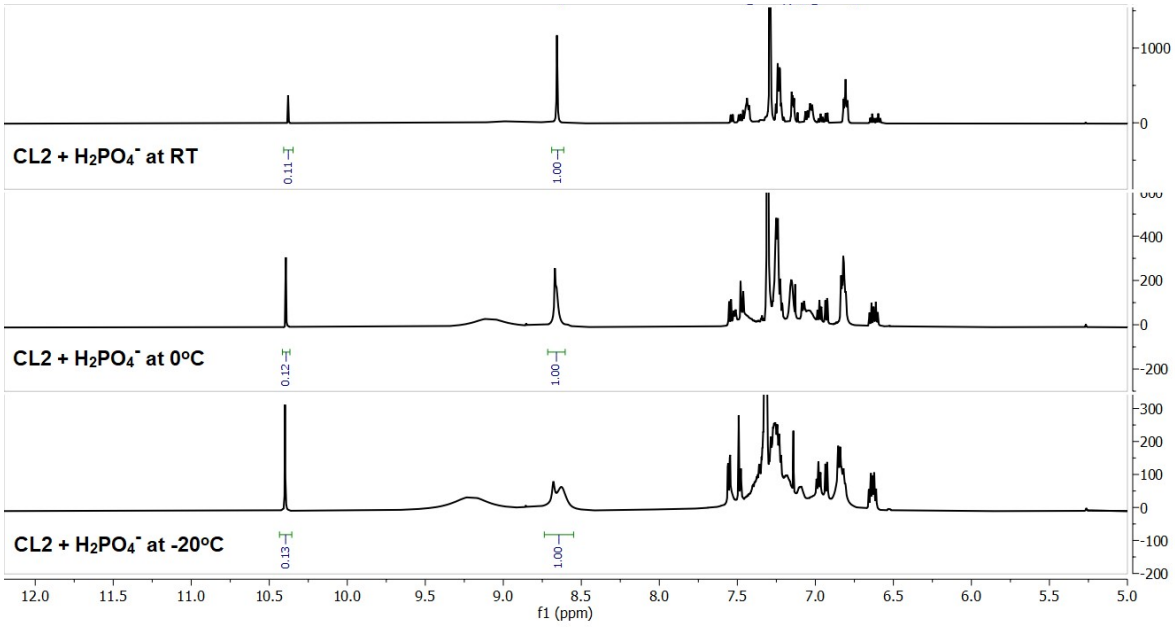


Fig. S53 Aromatic region of ^{1}H-NMR ($CDCl_3$) spectra of **CL2** in the presence of 5 equivalents of (n-Bu_4N^+)$H_2PO_4^-$ recorded at room temperature (RT), 0 ^{o}C and −20 ^{o}C **after six hours** of sample preparation.