Ratiometric fluorescent Zn^{2+} and In^{3+} receptor of fused pyrazine with an aminopropanol chain in acetonitrile
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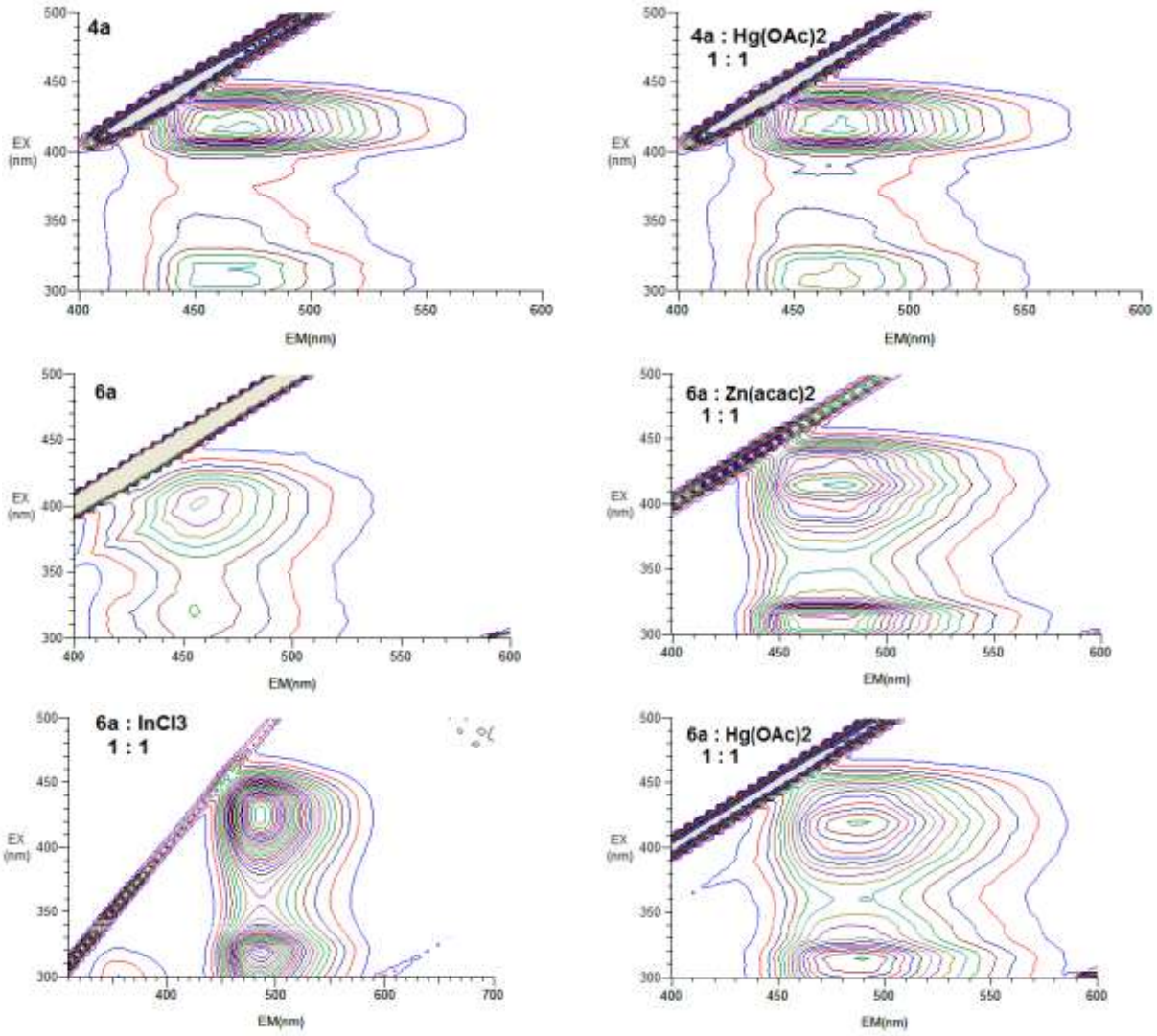
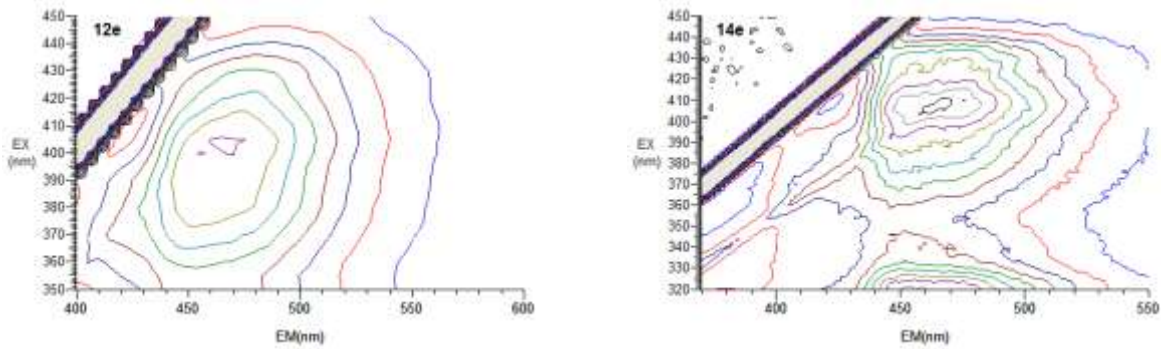
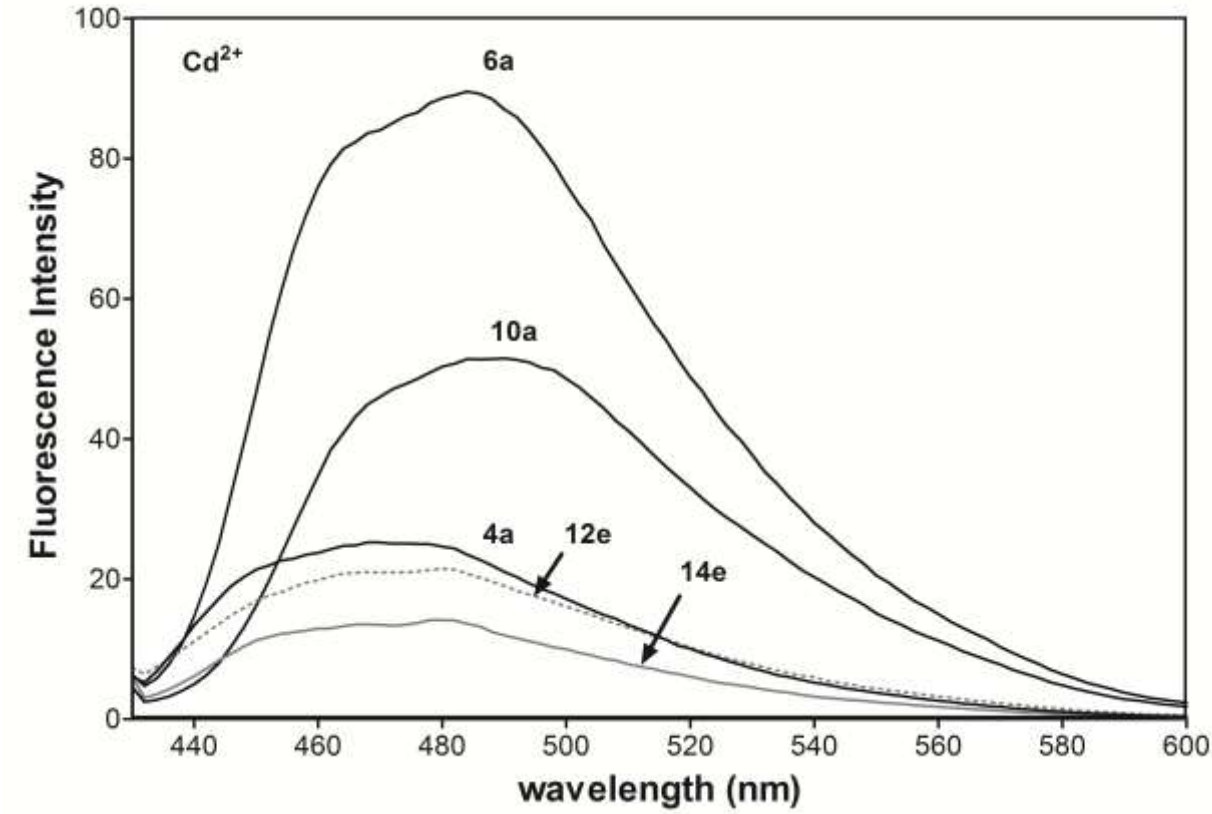
Supplementary Information
2D fluorescence spectra:

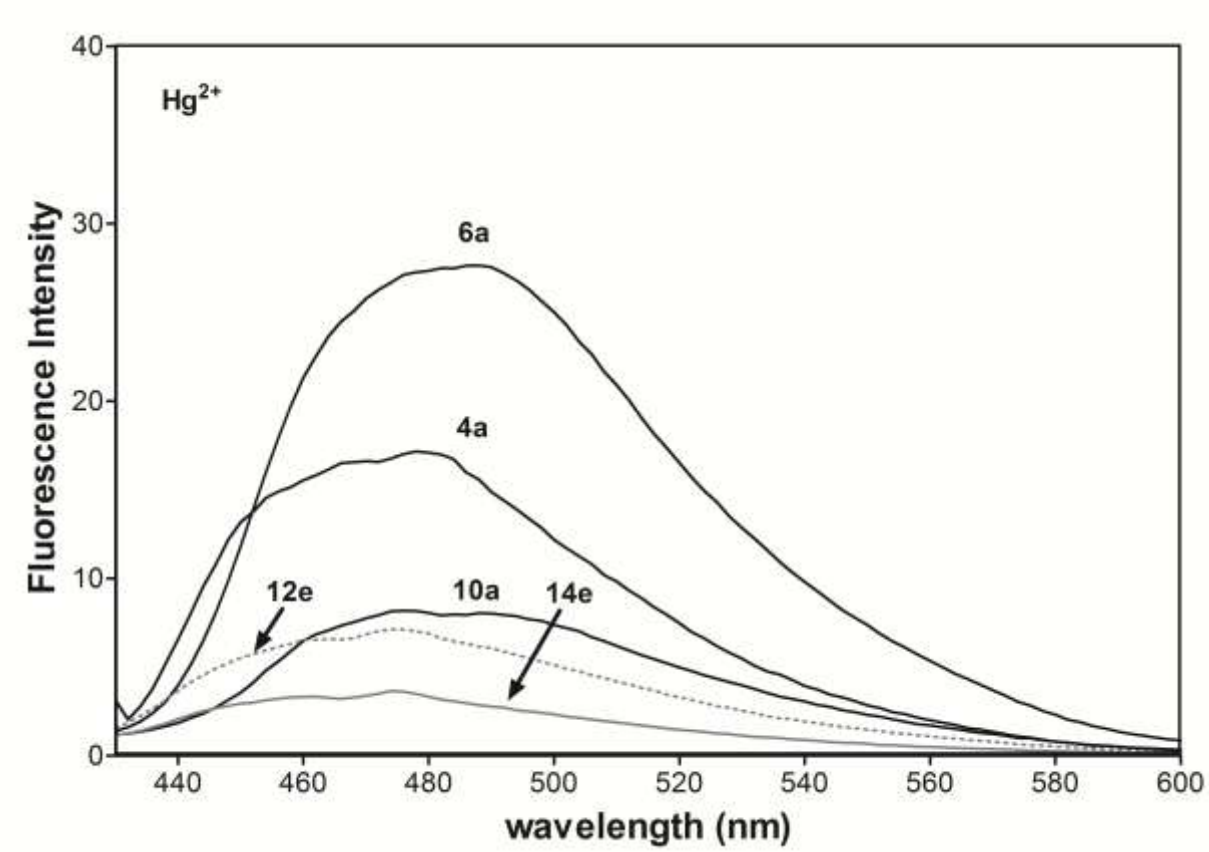




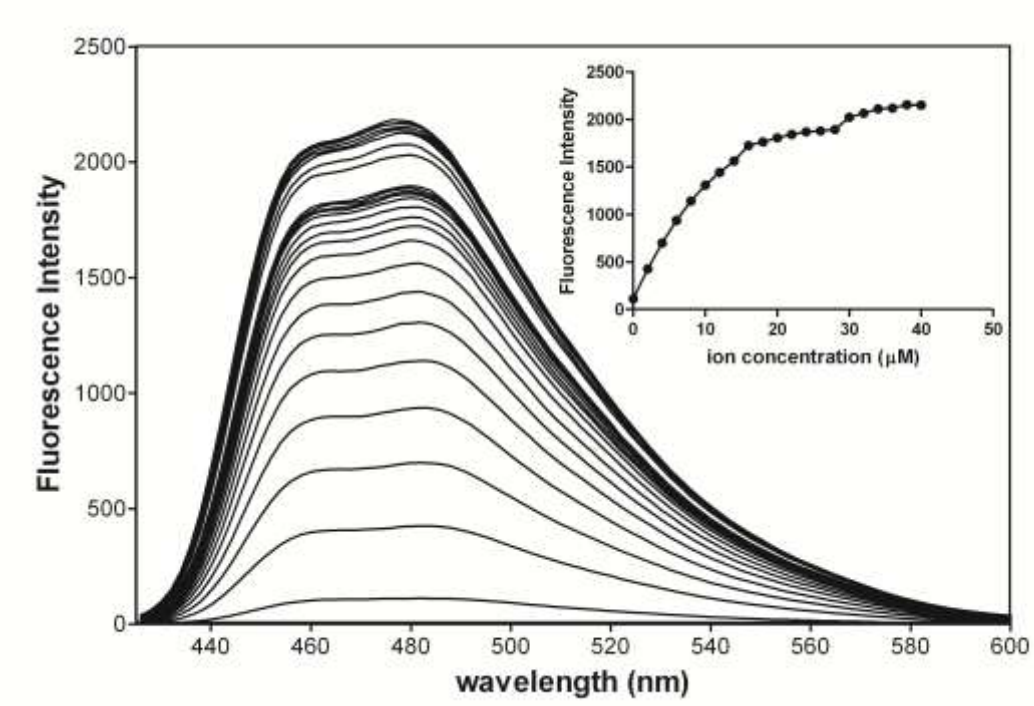
luorescence spectra of **4a**, **6a**, **10a**, **12e**, and **14e** (10 μM) in CH_3CN with 1 equiv. of Cd^{2+} (λ_{ex} = 420 nm, voltage 450 V).



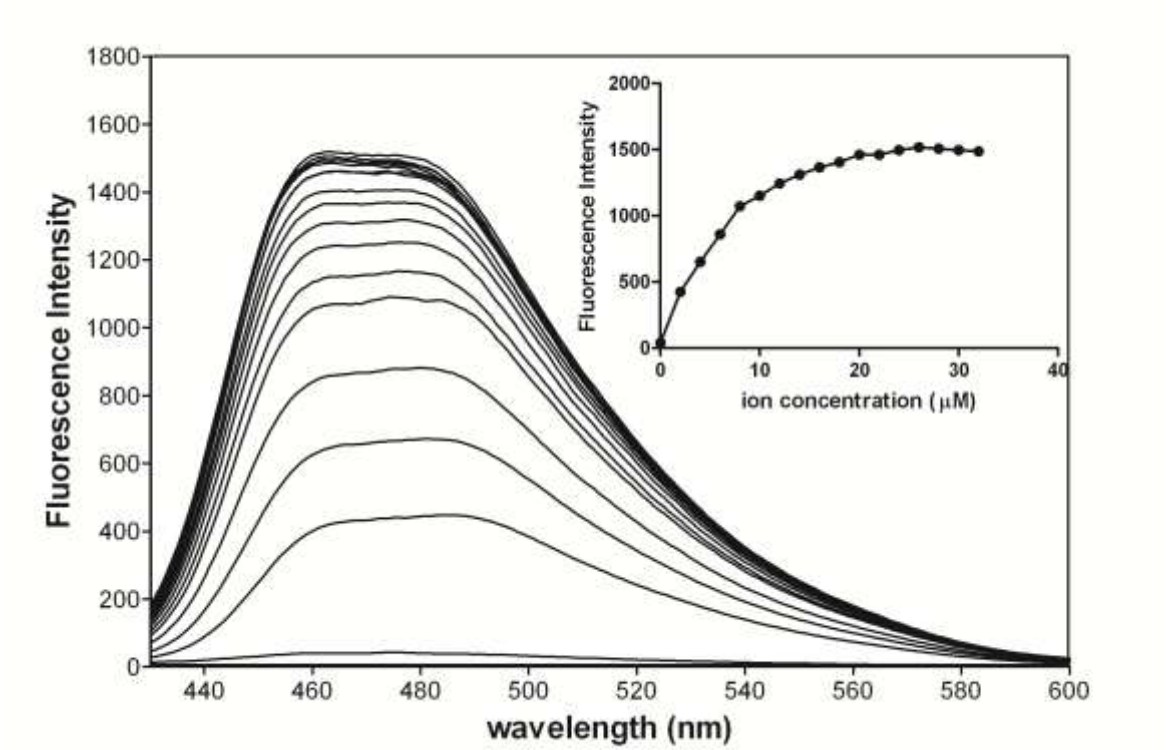
Fluorescence spectra of **4a**, **6a**, **10a**, **12e**, and **14e** (10 μM) in CH_3CN with 1 equiv. of Hg^{2+} (λ_{ex} = 415 nm, voltage 400 V).



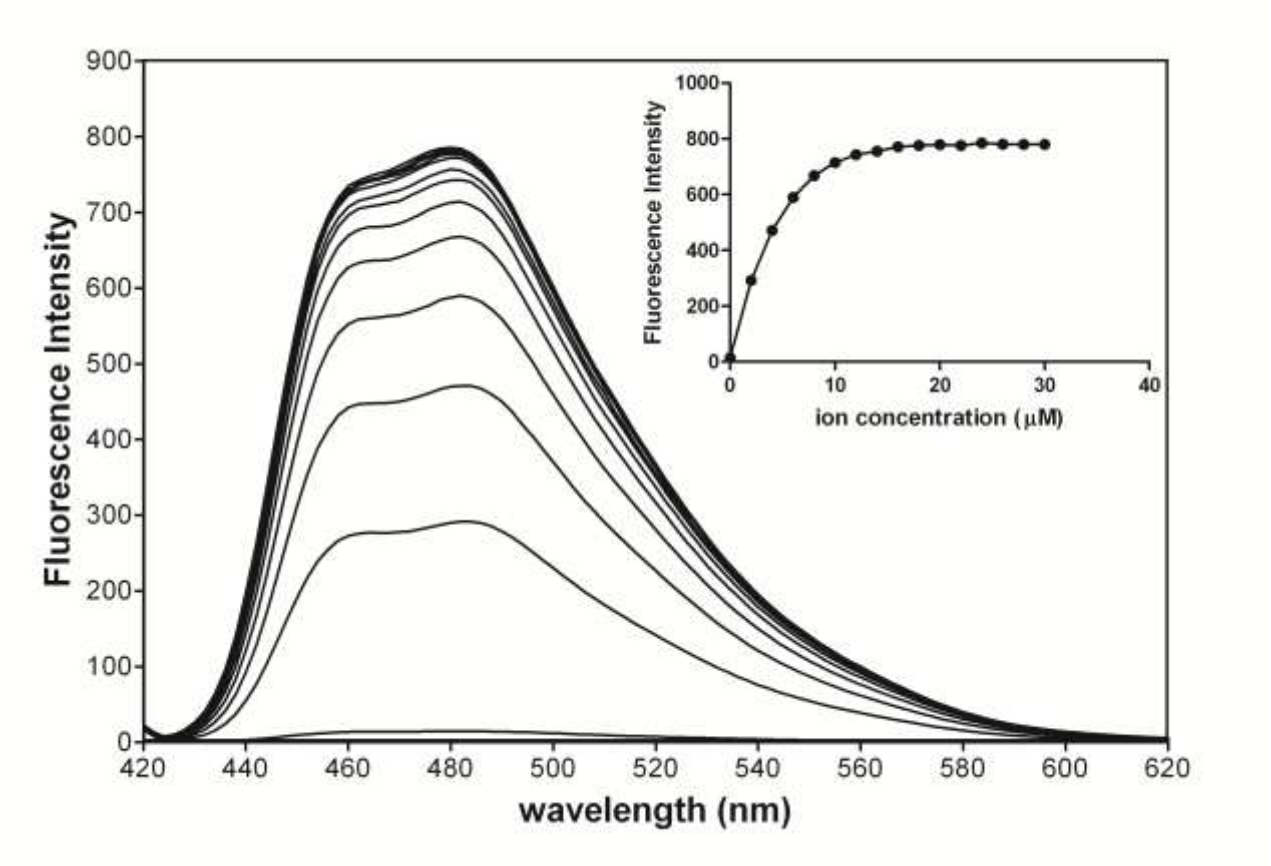
luorescence titration (λ_{ex} = 415 nm, 450 V) of **6a** (10 μM) in CH_3CN with $Zn(OAc)_2$. The concentration of Zn^{2+} was increased from 0 to 40 μM. Inset: increase in fluorescenct intensity at λ_{em} = 482 nm as the function of Zn^{2+} concentration. concentration.



Fluorescence titration (λ_{ex} = 415 nm, 550 V) of **6a** (10 μM) in CH_3CN with $ZnCl_2$. The concentration of Zn^{2+} was increased from 0 to 30 μM. Inset: increase in fluorescenct intensity at λ_{em} = 464 nm as the function of Zn^{2+} concentration.

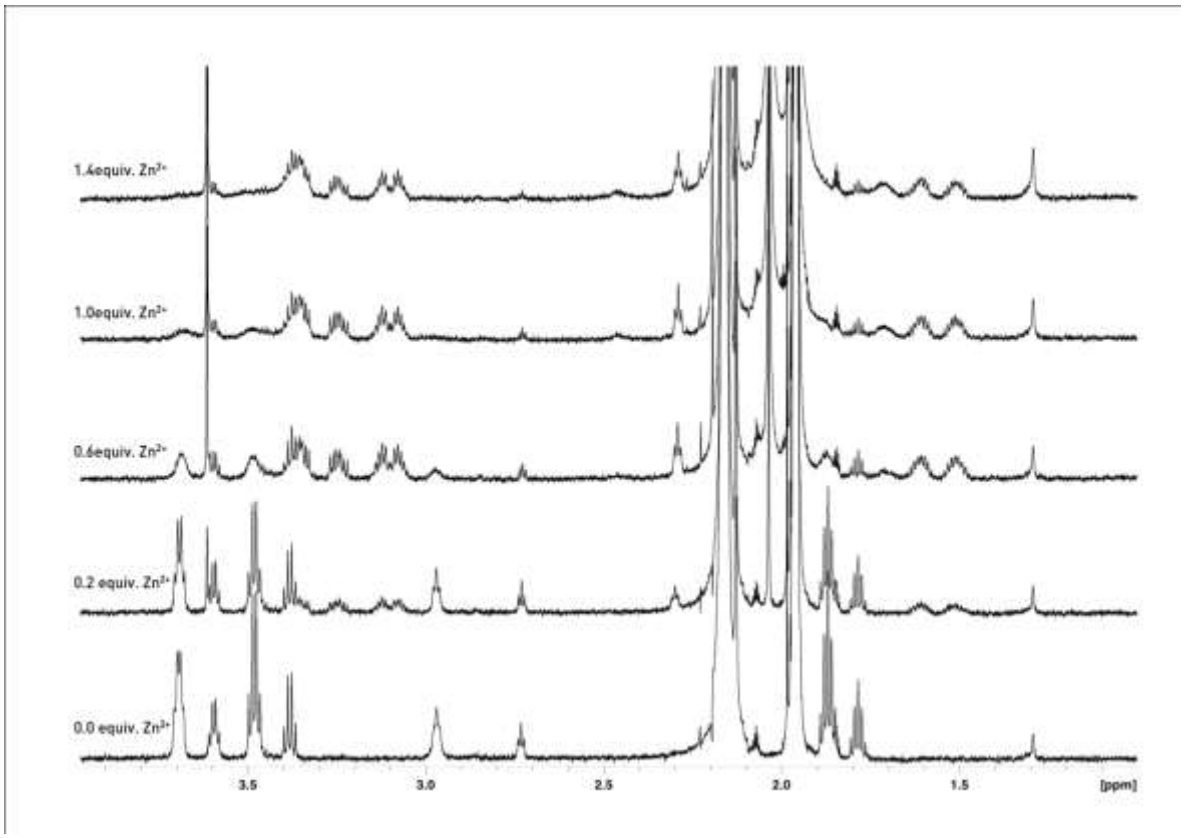


Fluorescence titration (λ_{ex} = 415 nm, 400 V) of **6a** (10 μM) in CH_3CN with $Zn(acac)_2$. The concentration of Zn^{2+} was increased from 0 to 30 μM. Inset: increase in fluorescenct intensity at λ_{em} = 482 nm as the function of Zn^{2+} concentration.

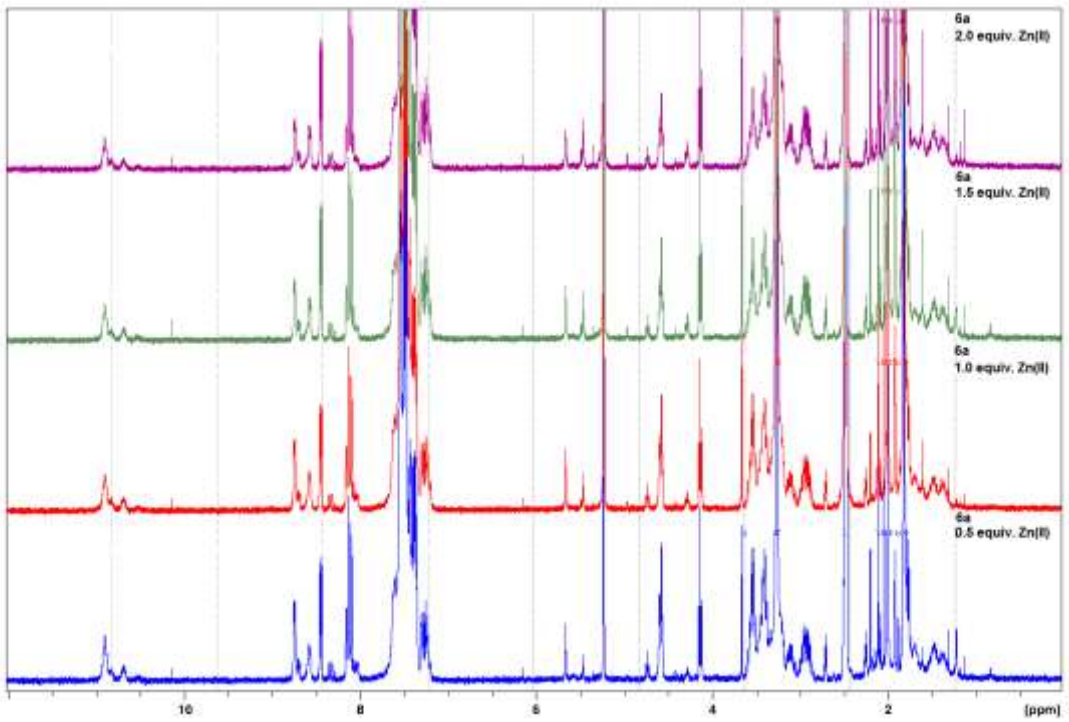


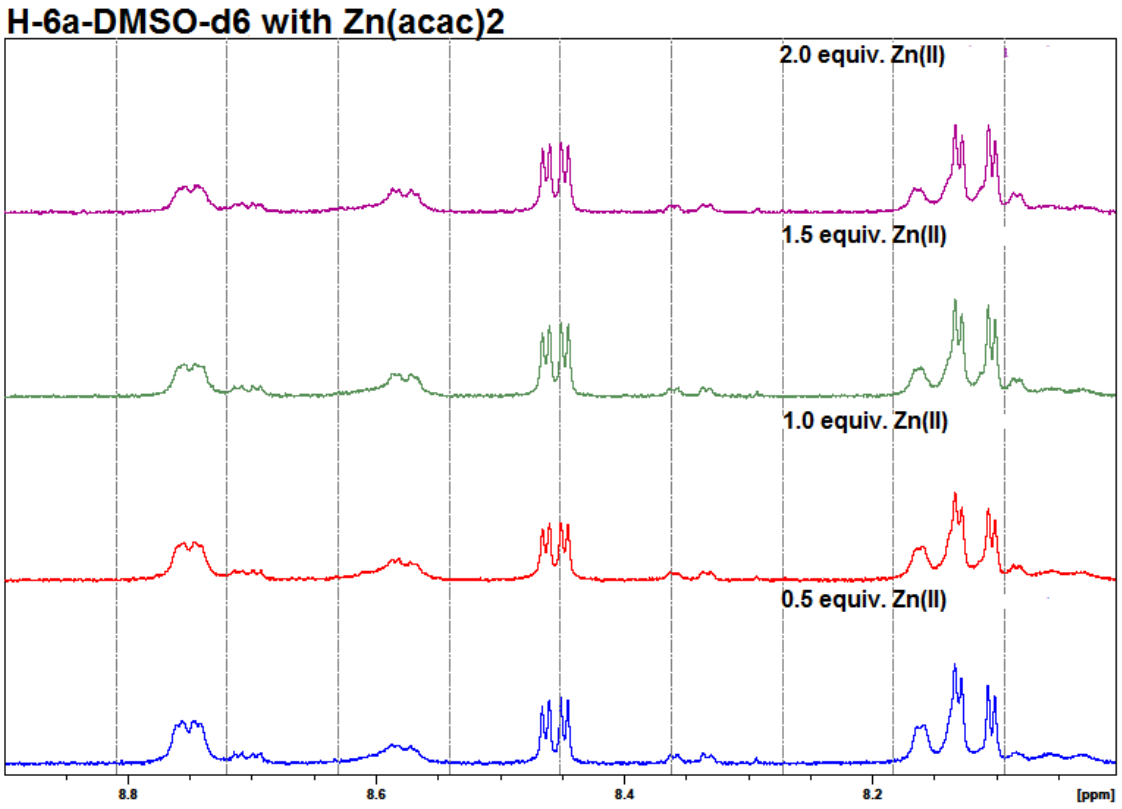
MR spectra

Partial H NMR spectra **6a (**600.206 MHz, CD_3CN) with 0.0 equiv. $Zn(acac)_2$; 0.2 equiv. $Zn(acac)_2$; 0.6 equiv $Zn(acac)_2$; 1.0 equiv. $Zn(acac)_2$; 1.4 equiv. $Zn(acac)_2$

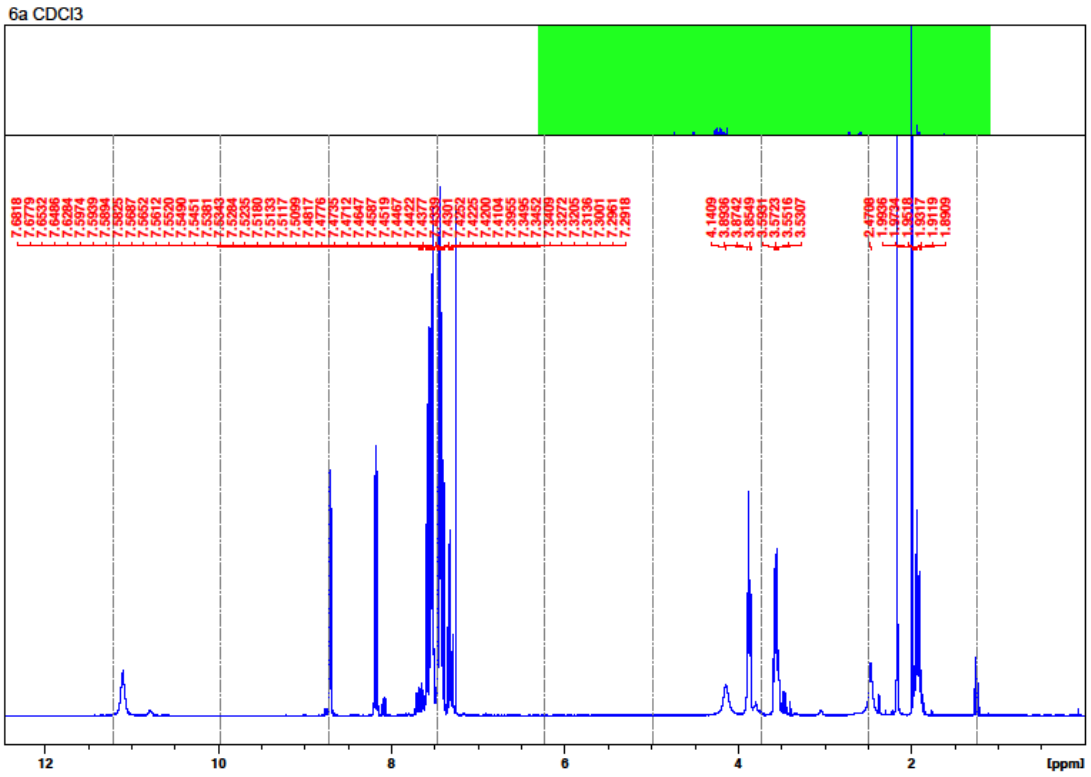


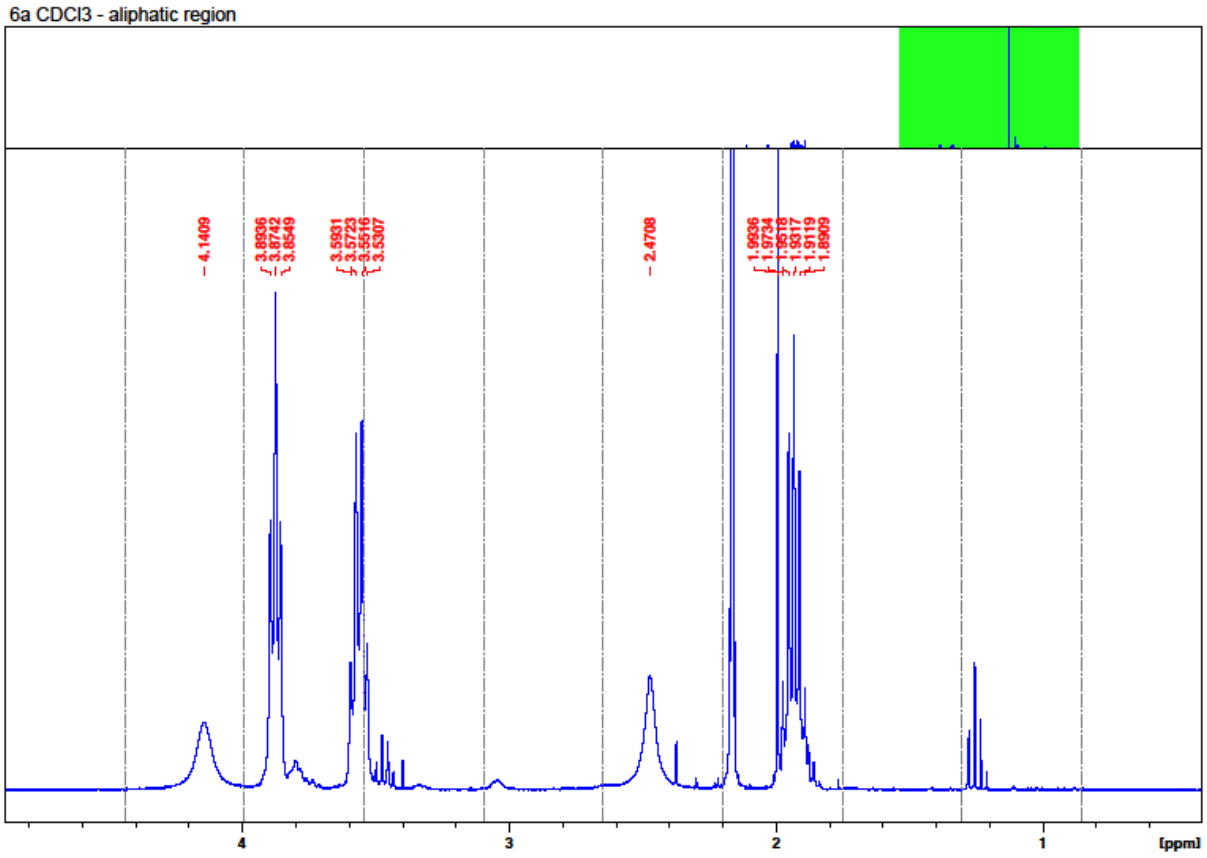
6a (300.13 MHz, DMSO-d_6): 0.5 equiv. Zn(acac)2; 1.0 equiv. Zn(acac)2; 1.5 equiv. Zn(acac)2; 2.0 equiv. Zn(acac)2

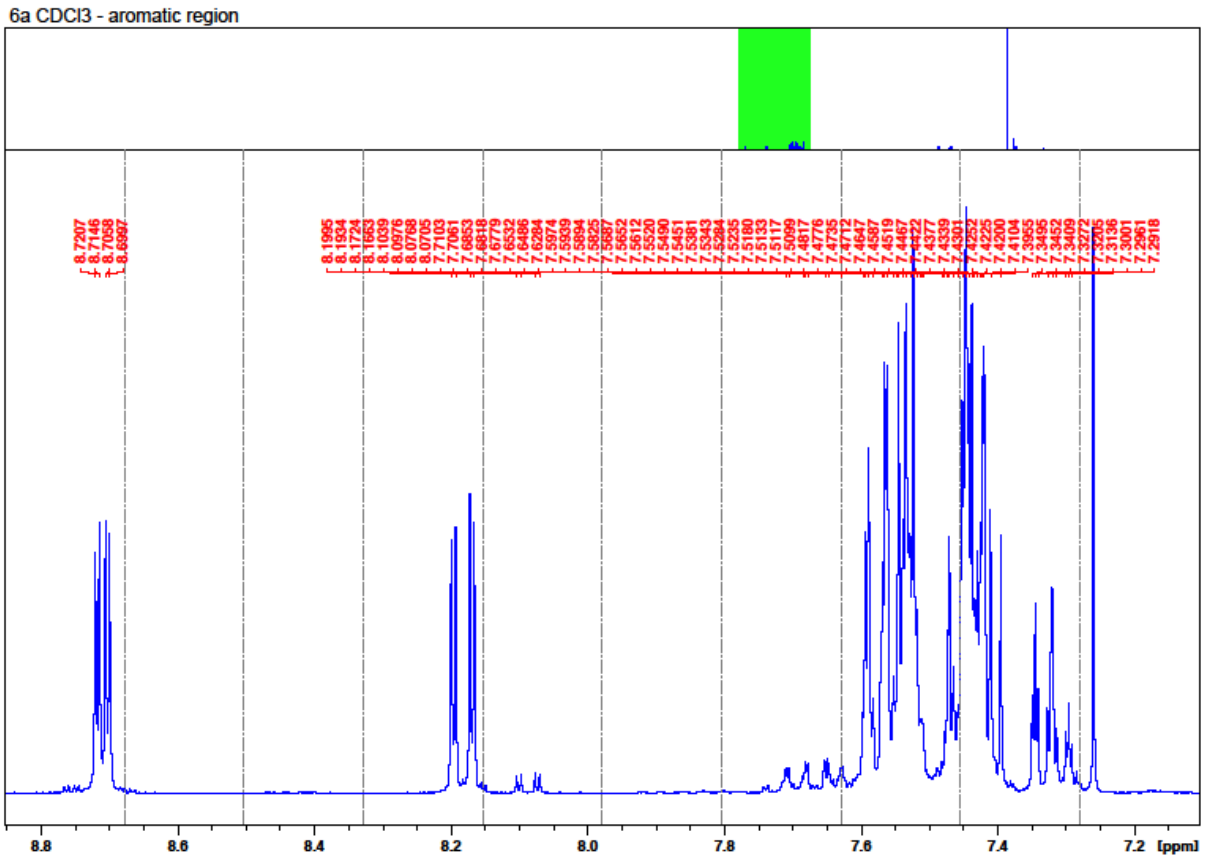




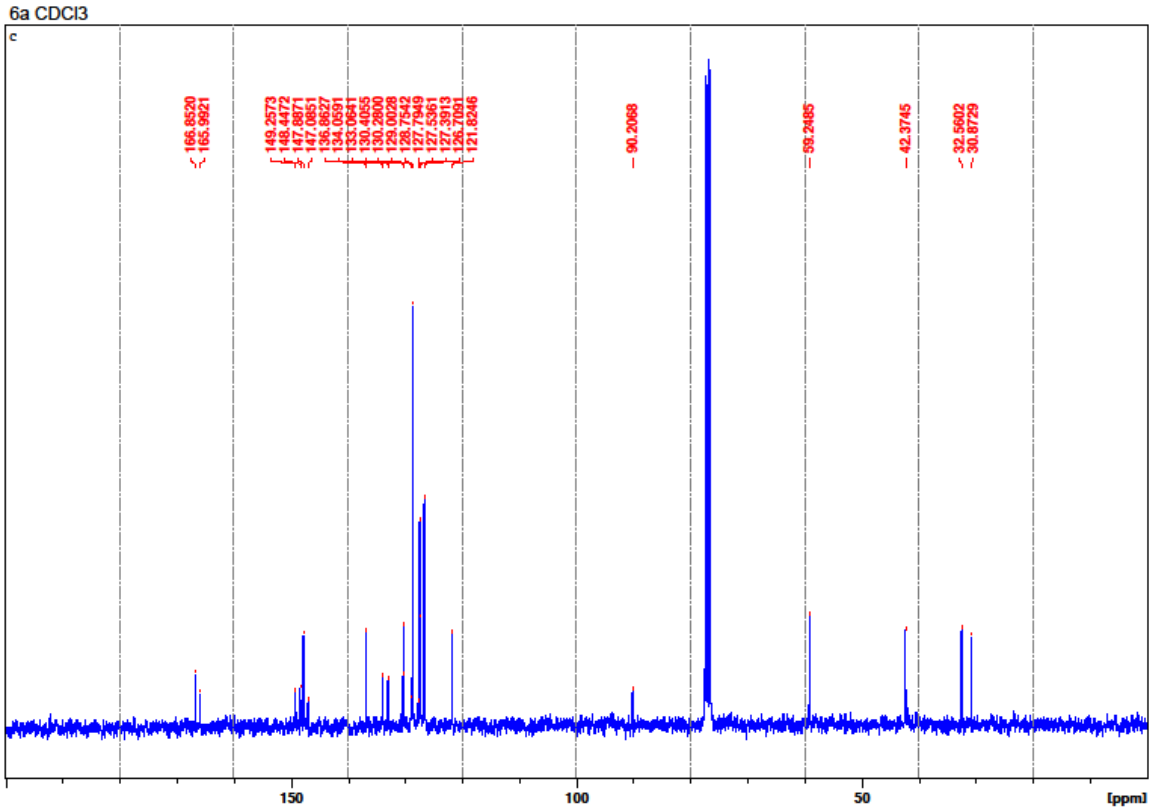
6a (300.13 MHz, $CDCl_3$)



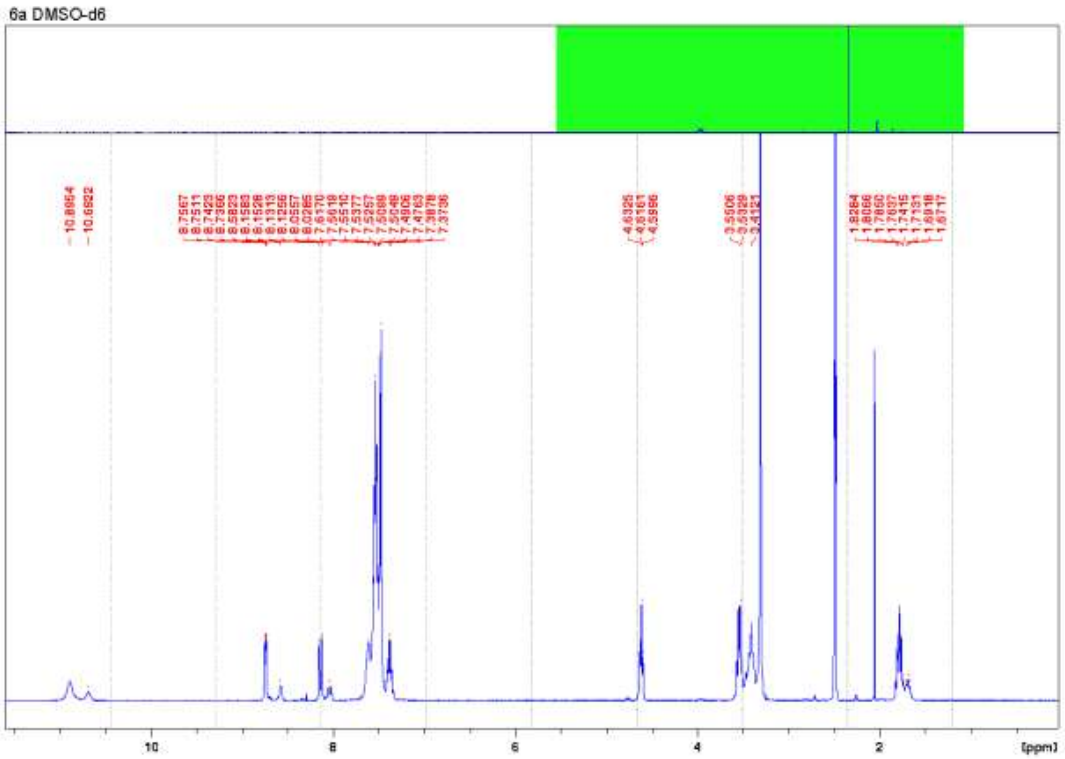




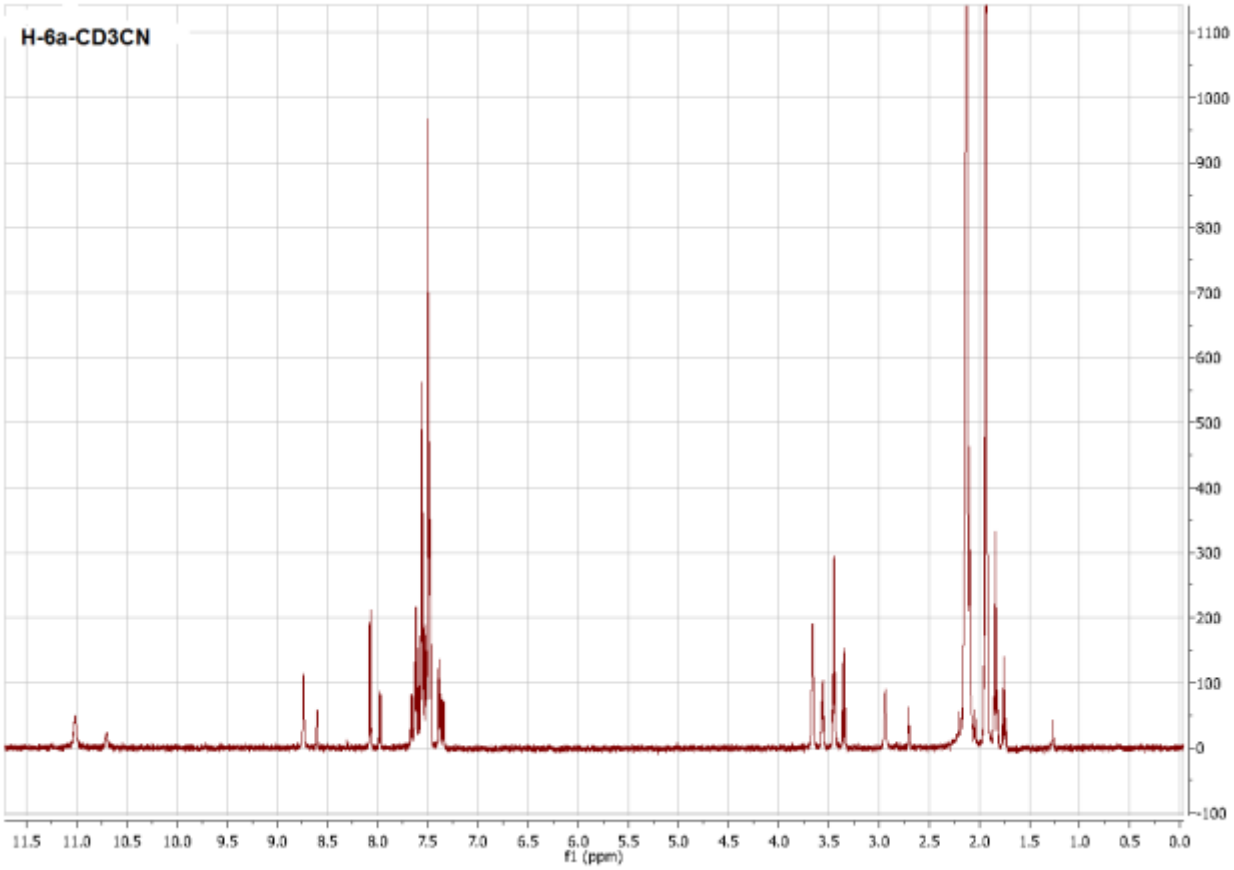
6a (75.47 MHz, CDCl3)



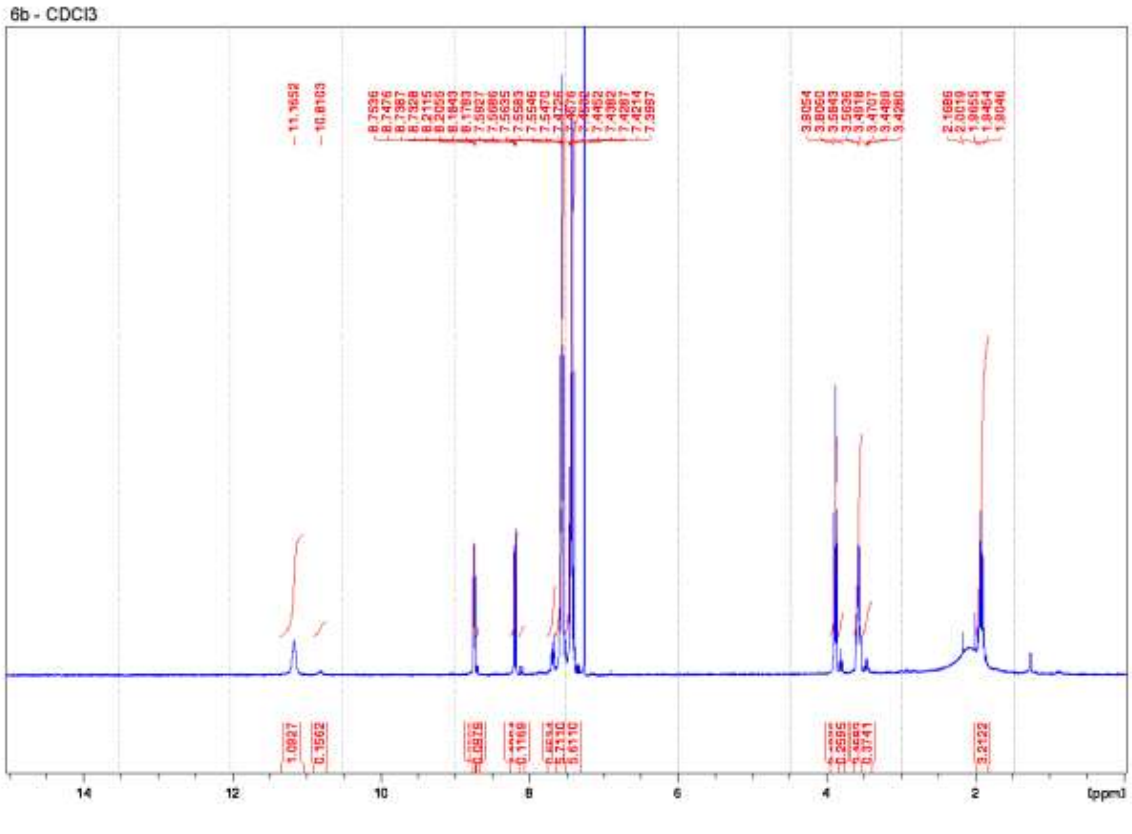
6a (300.13 MHz,)

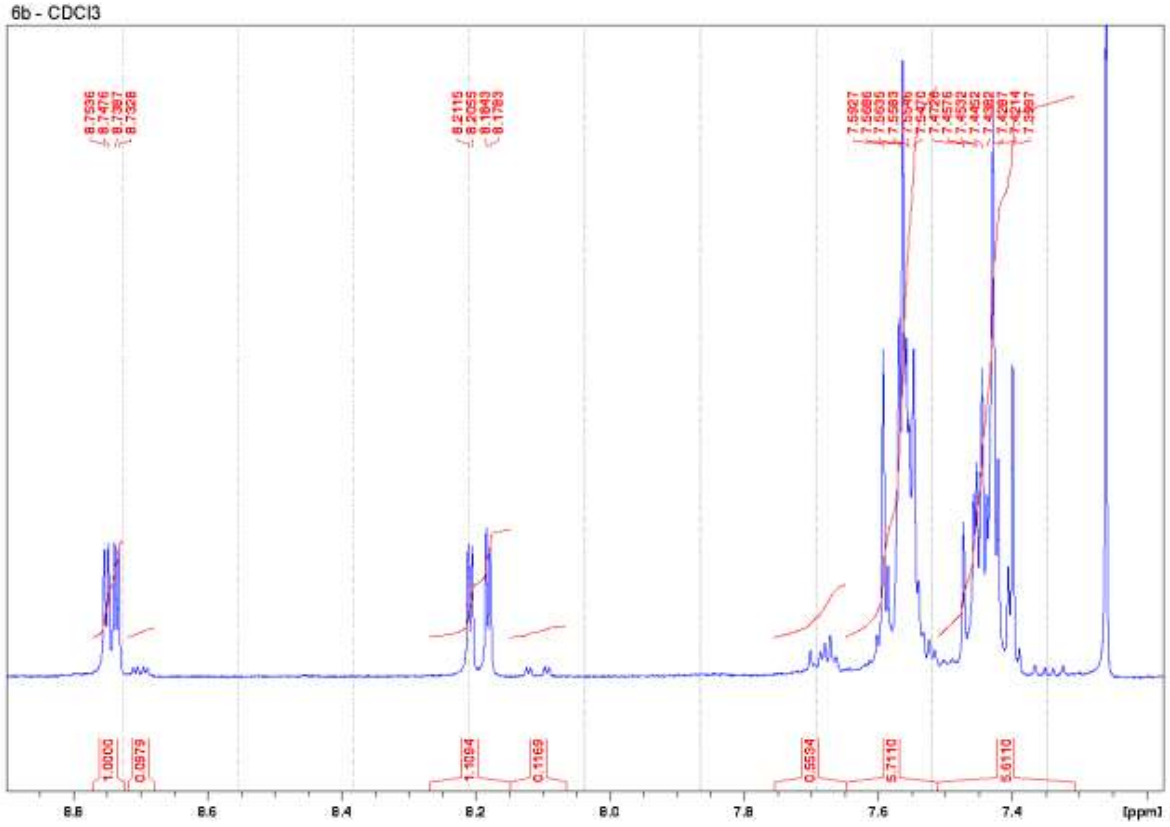


6a (600.206 MHz, CD_3CN)



6b (300.13 MHz, CDCl3)





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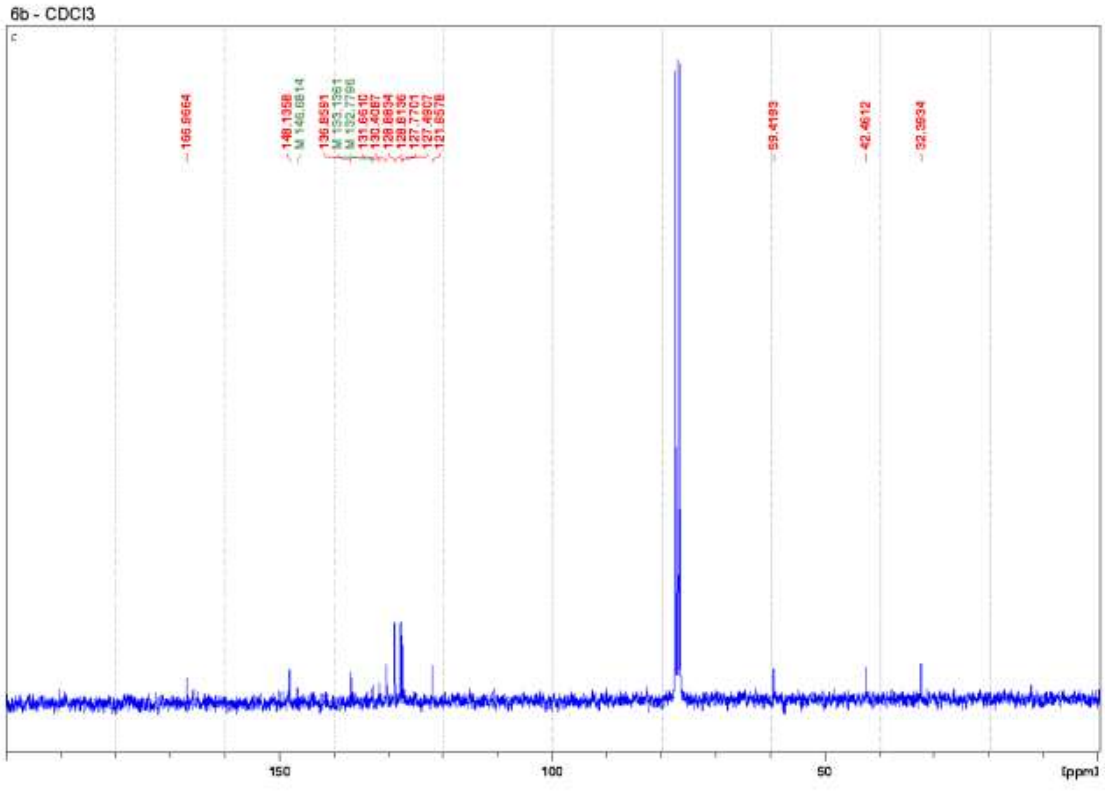
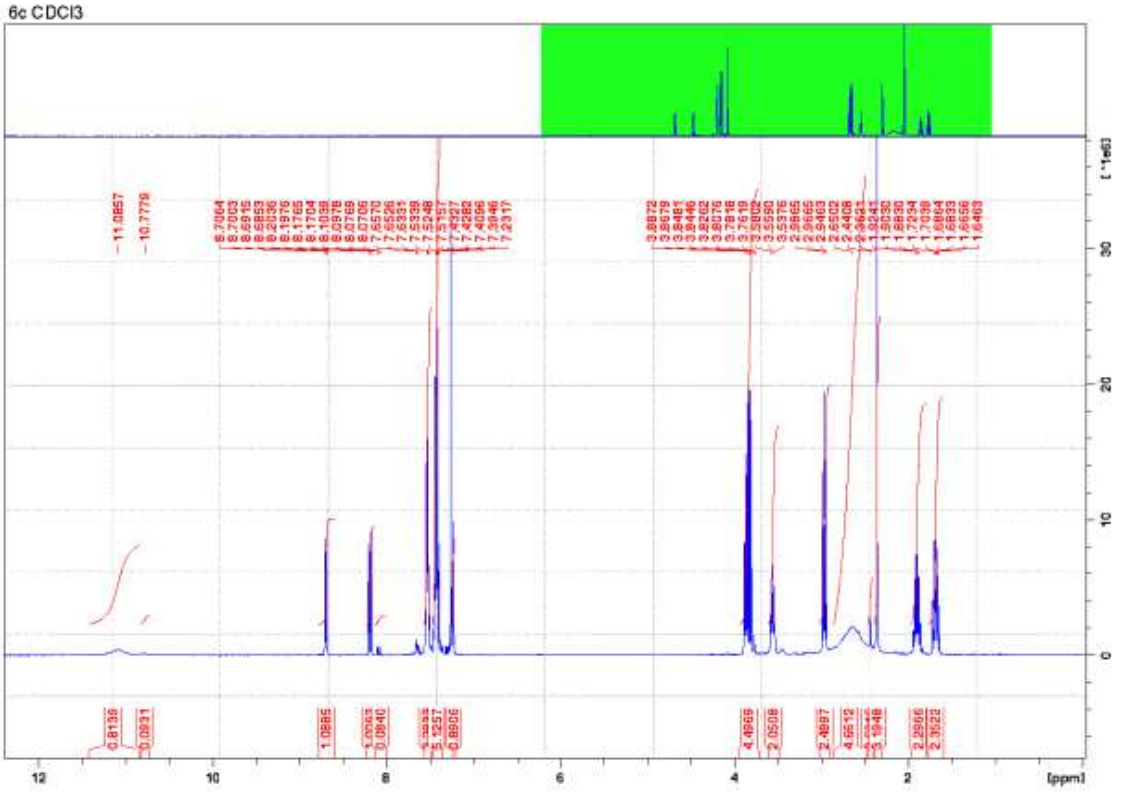


6c (300.13 MHz, CDCl3)



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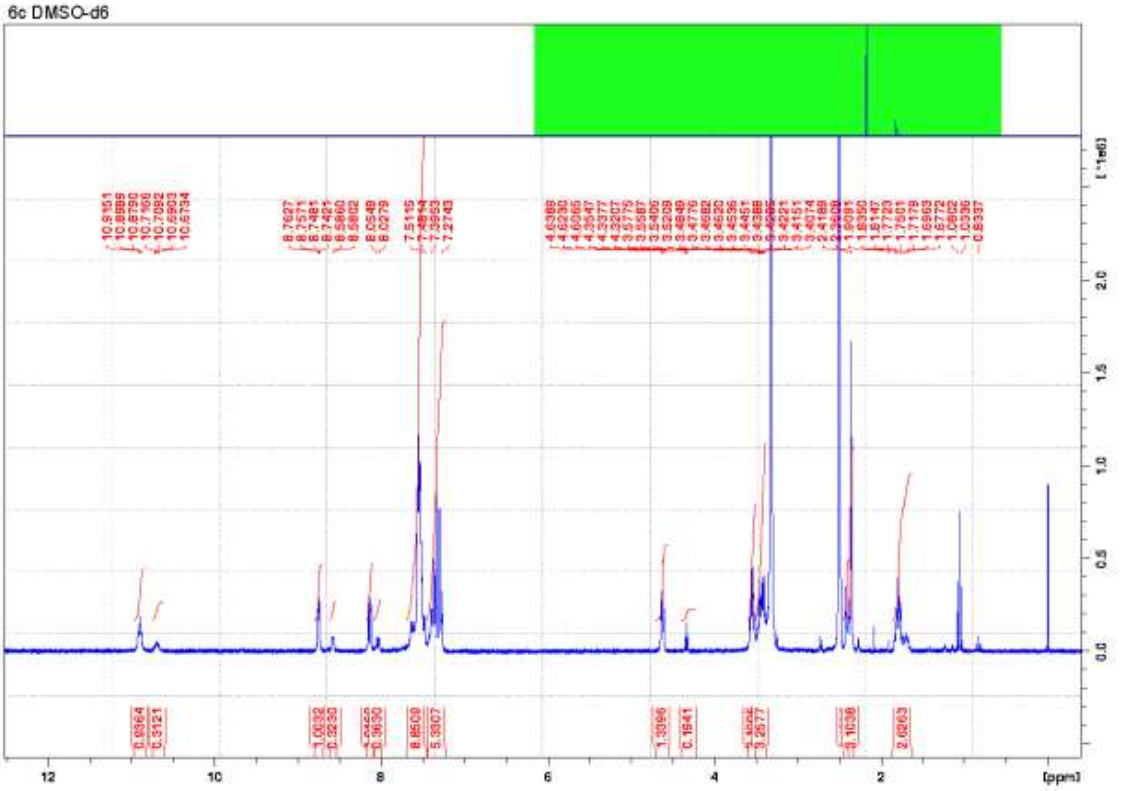

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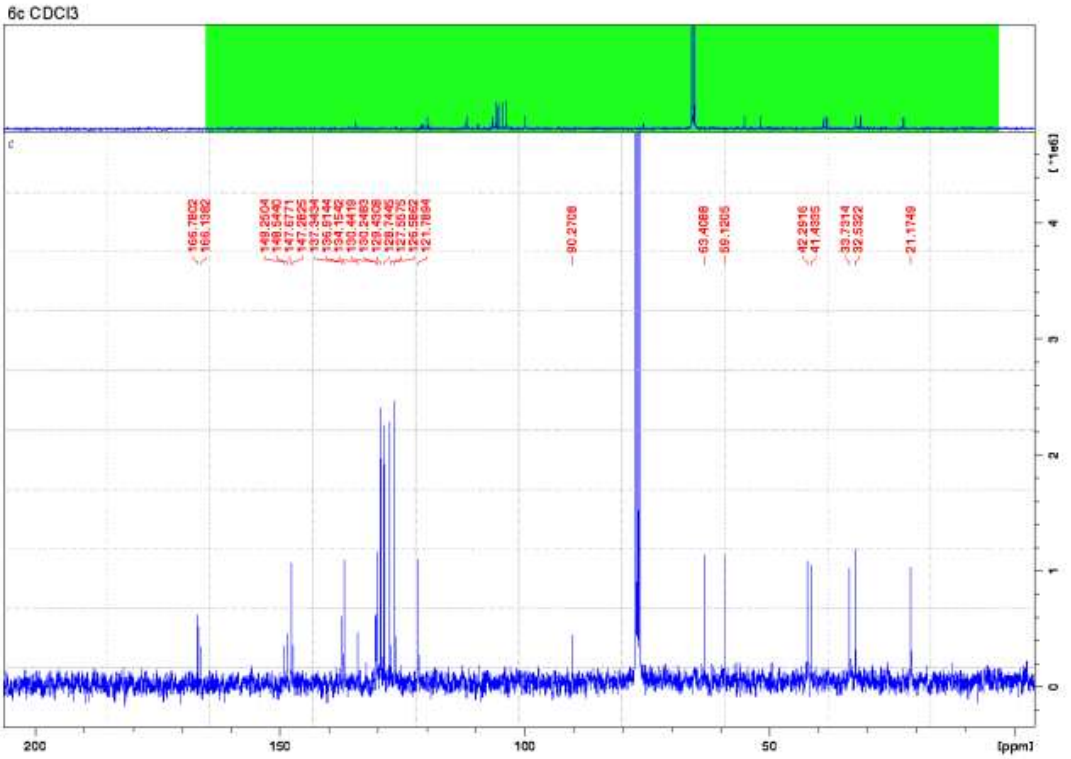
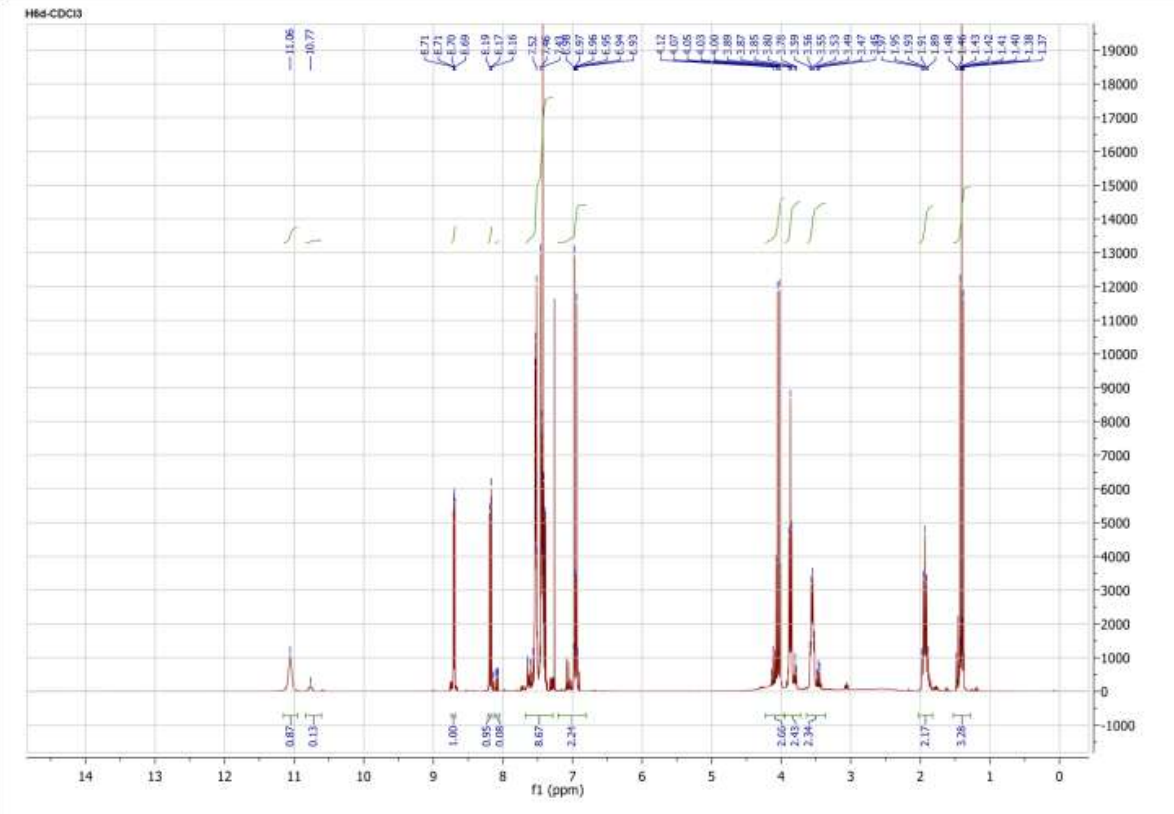
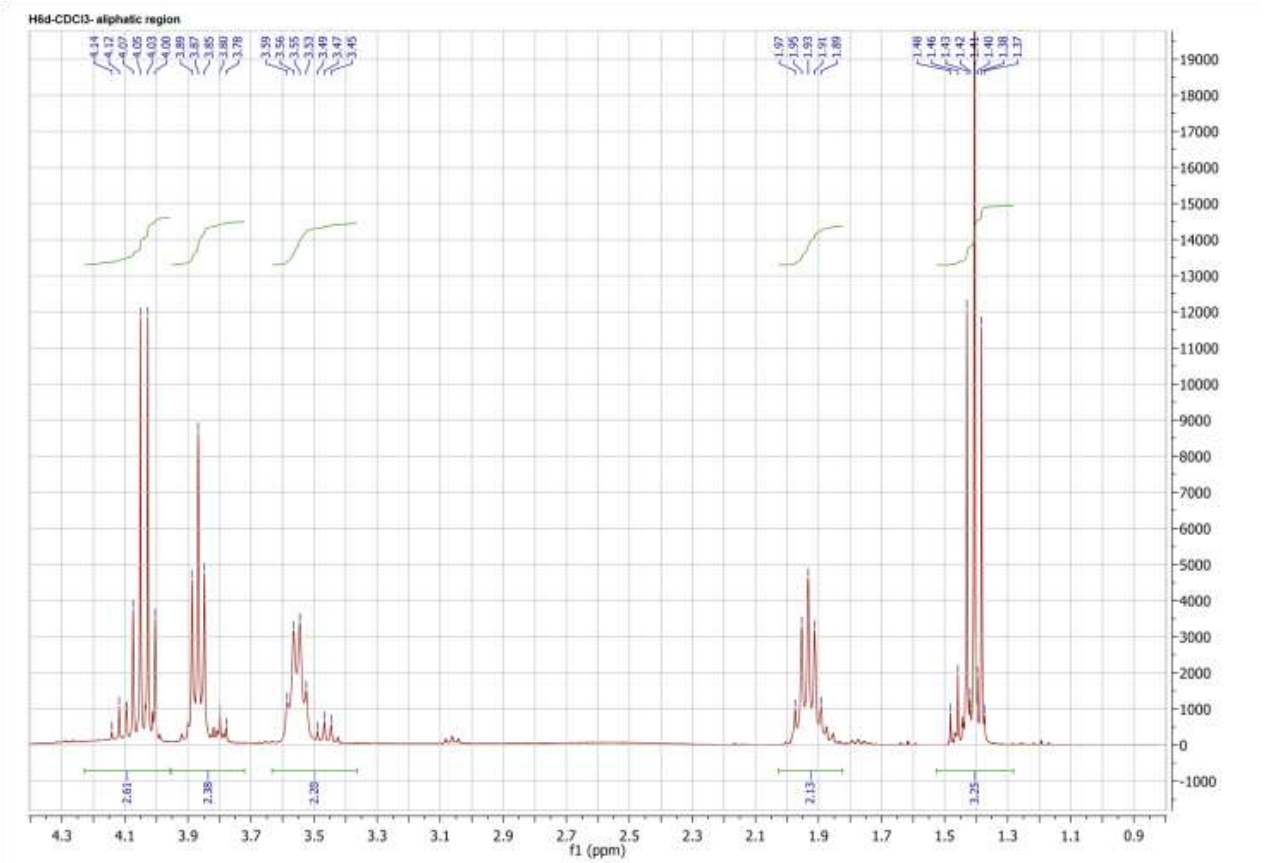
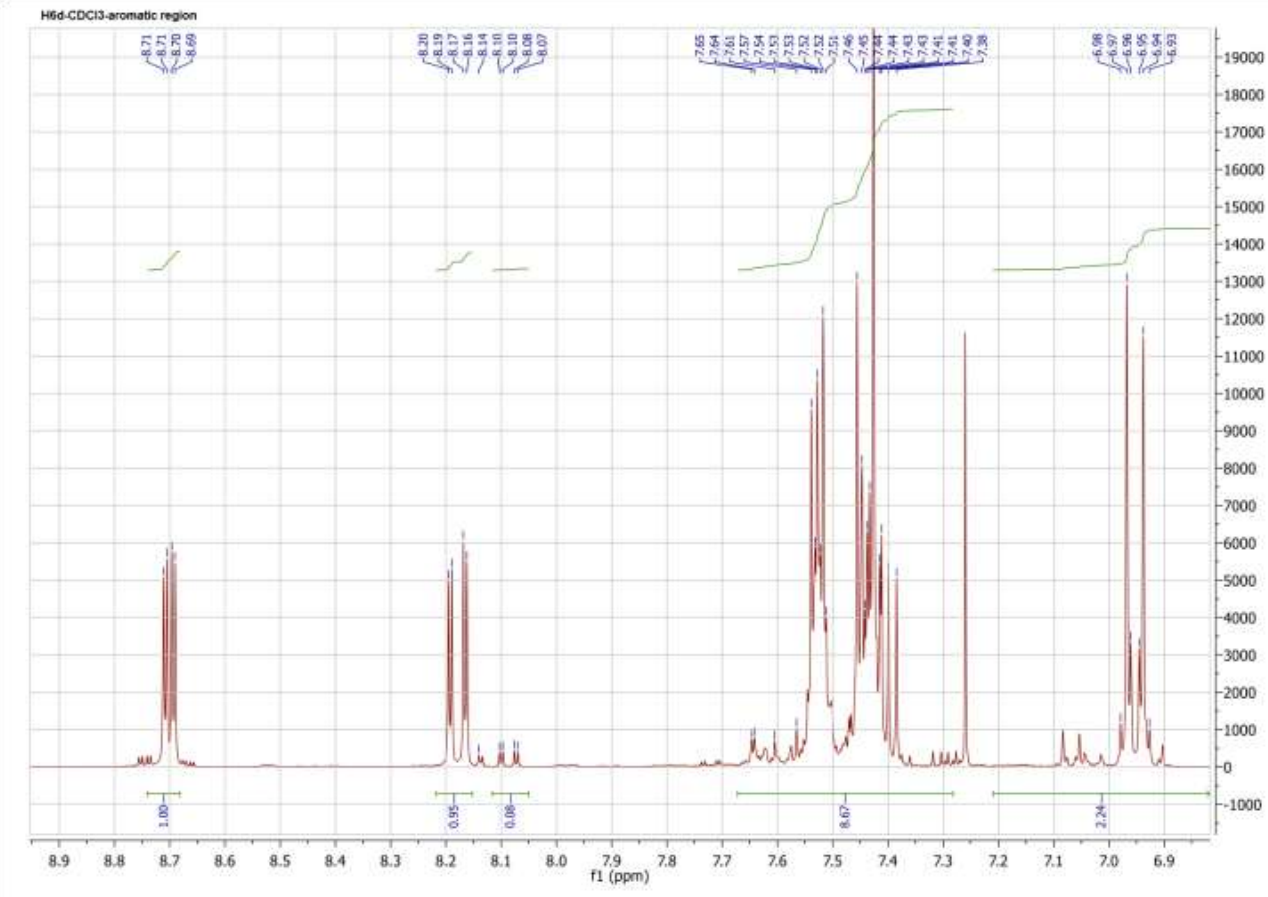


6d (300.13 MHz, CDCl3)







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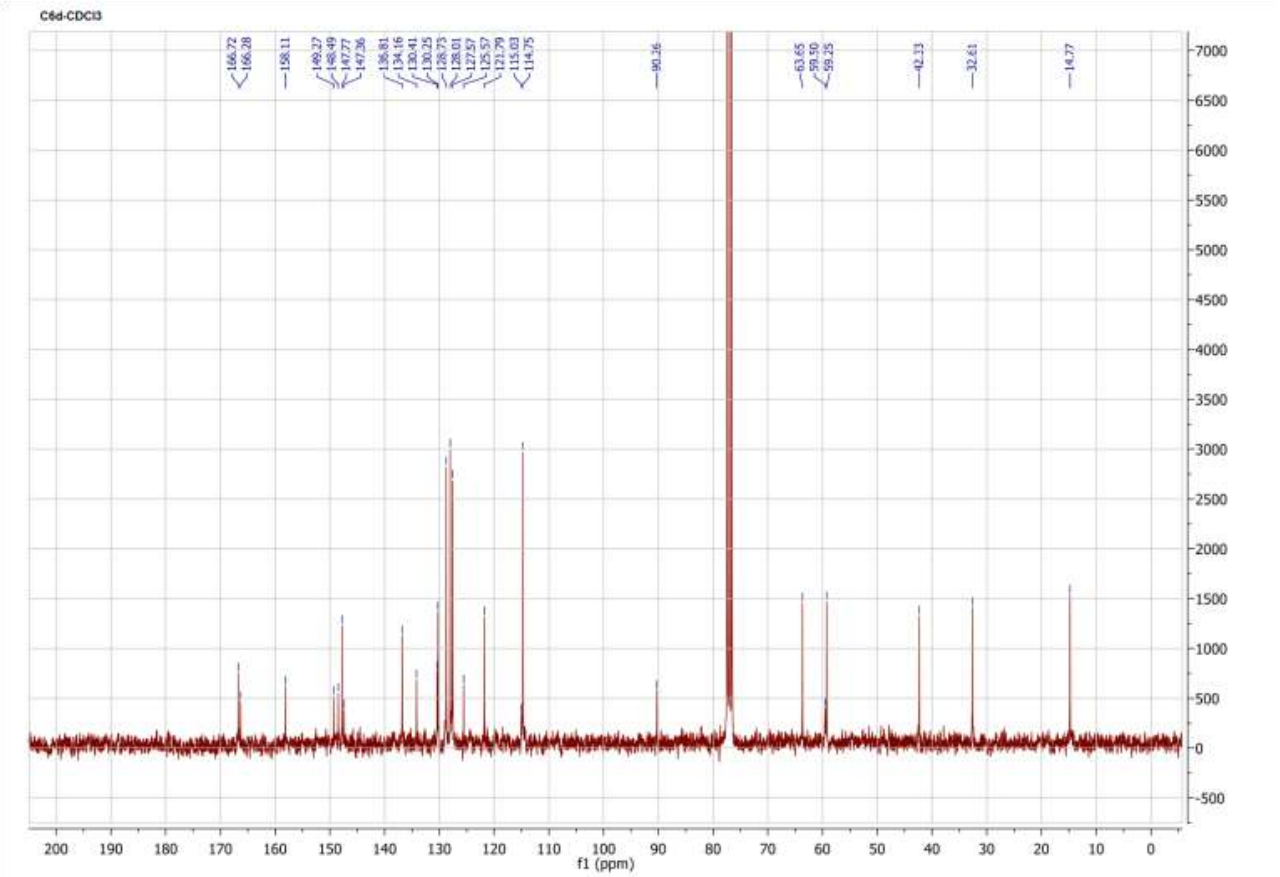
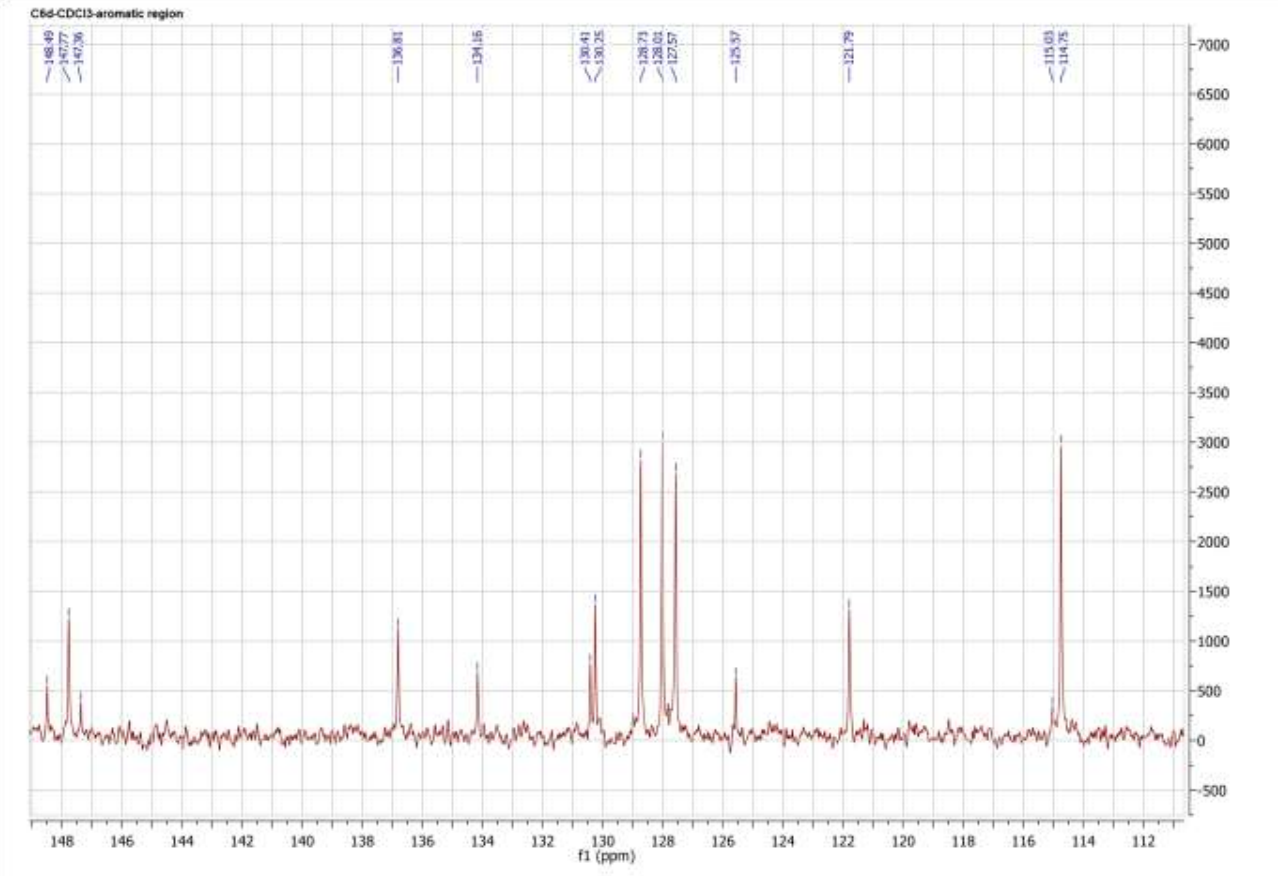
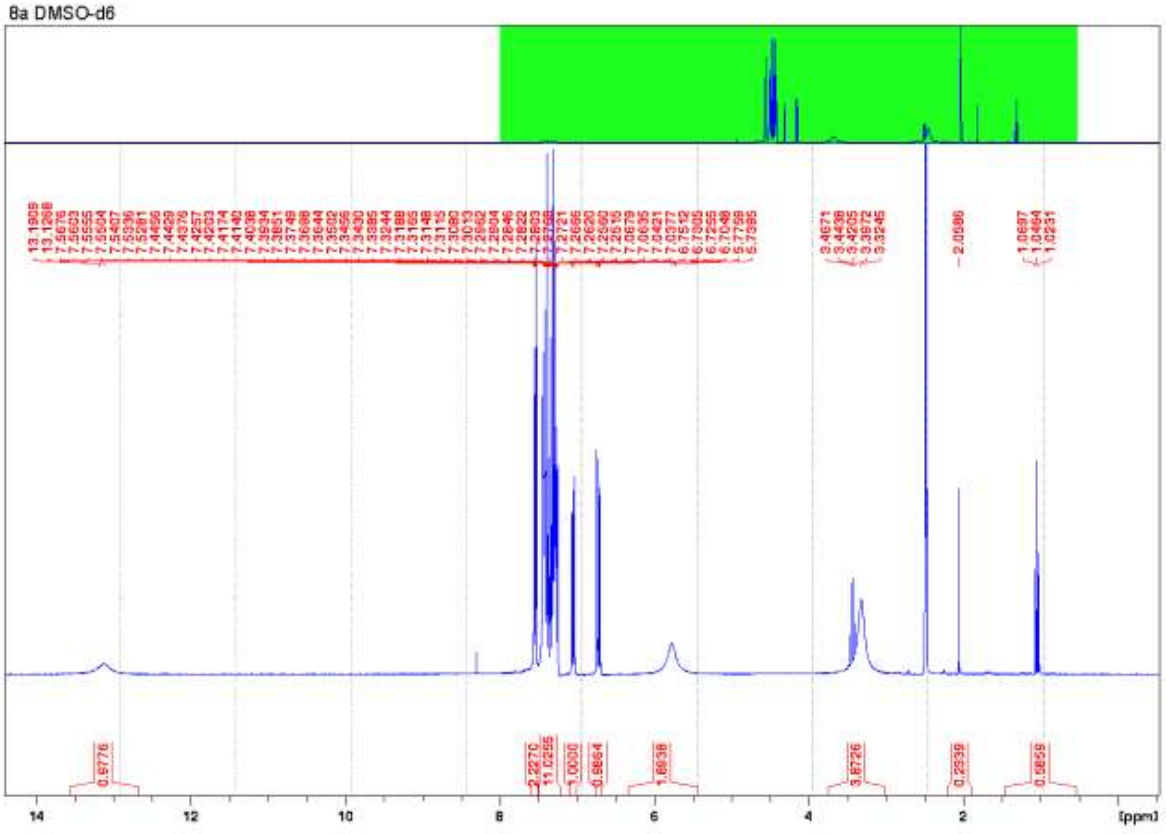
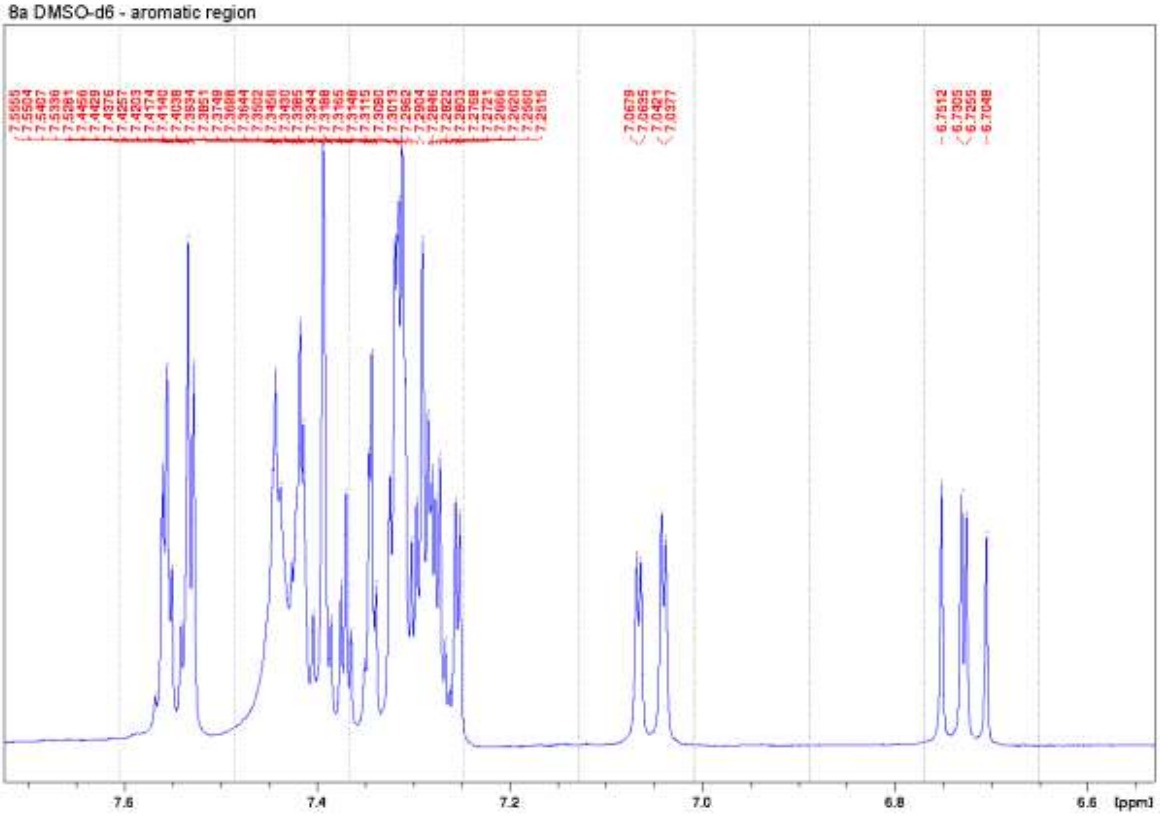


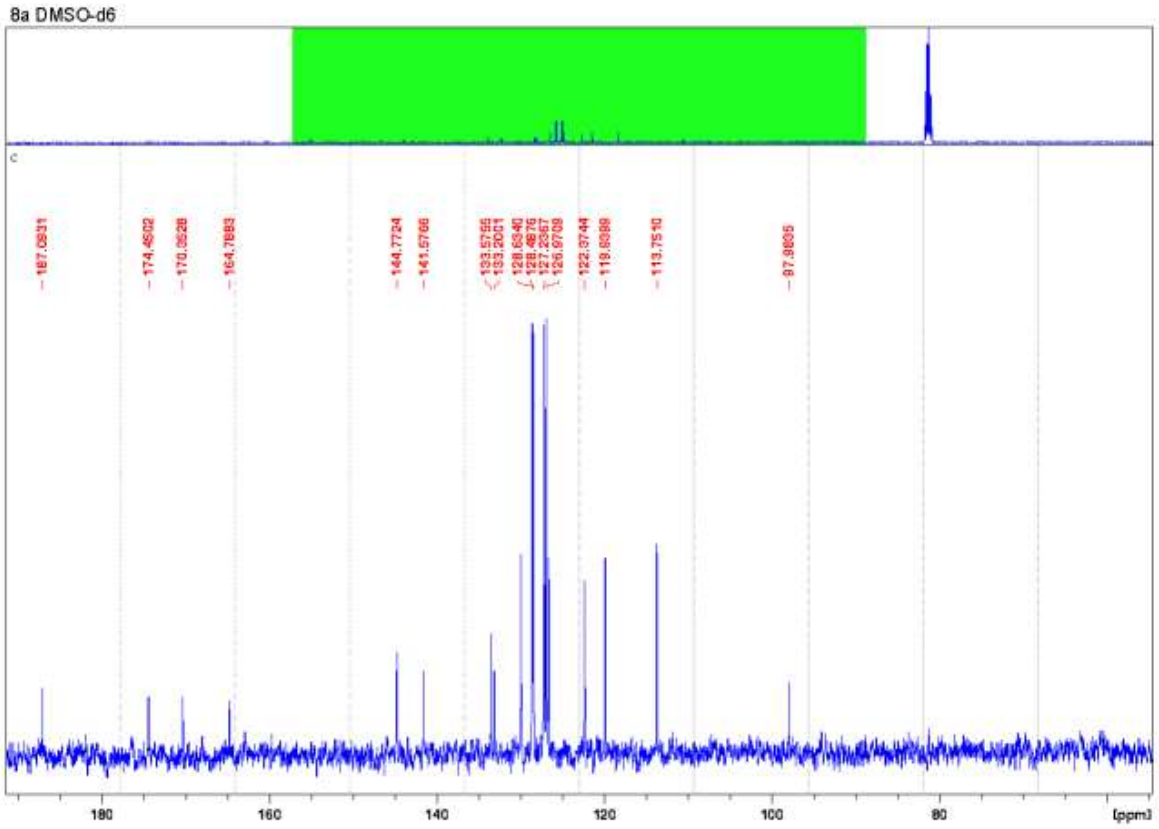


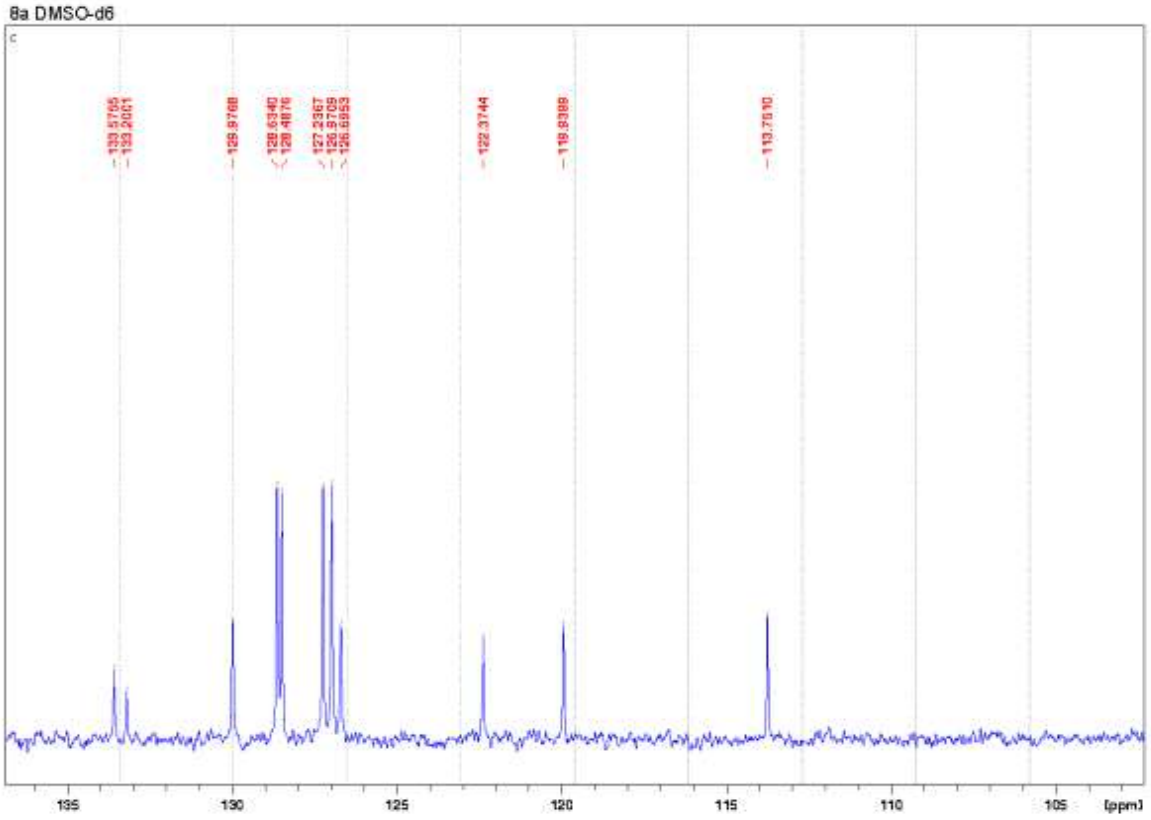
8a (300.13 MHz,)





8a (75.47 MHz,)





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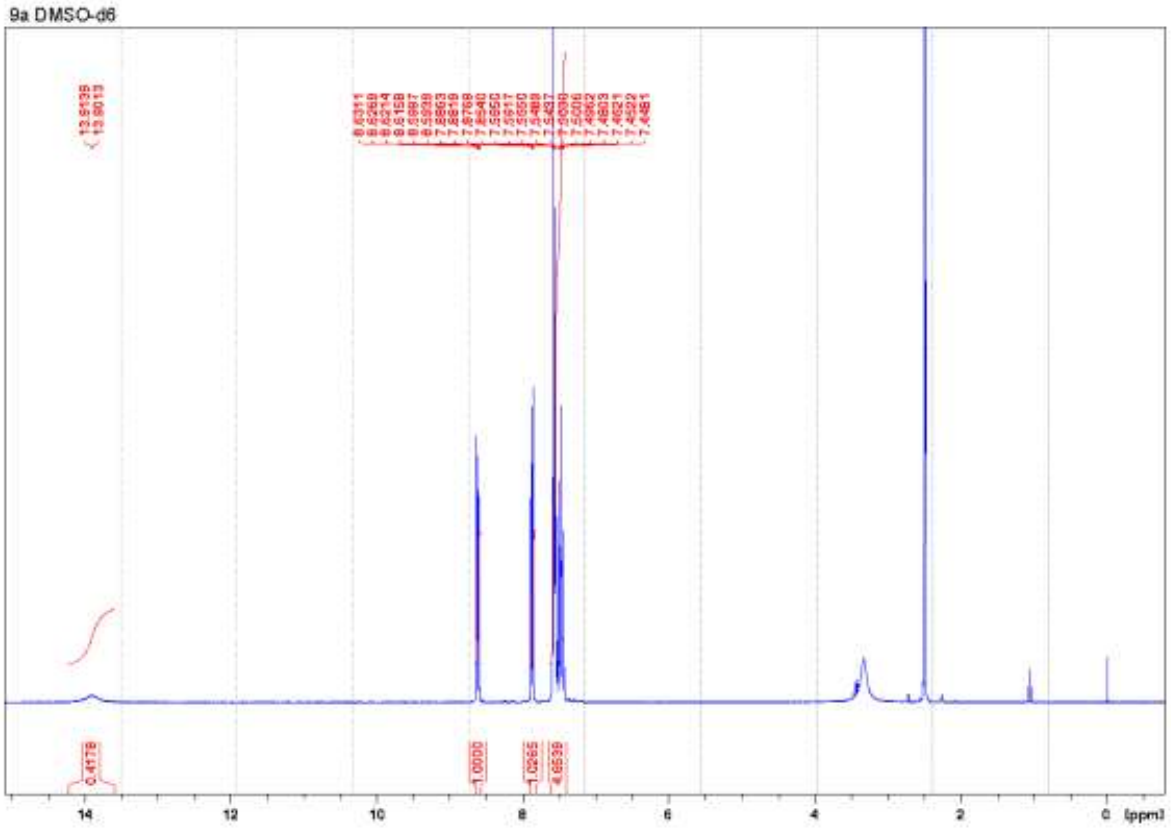
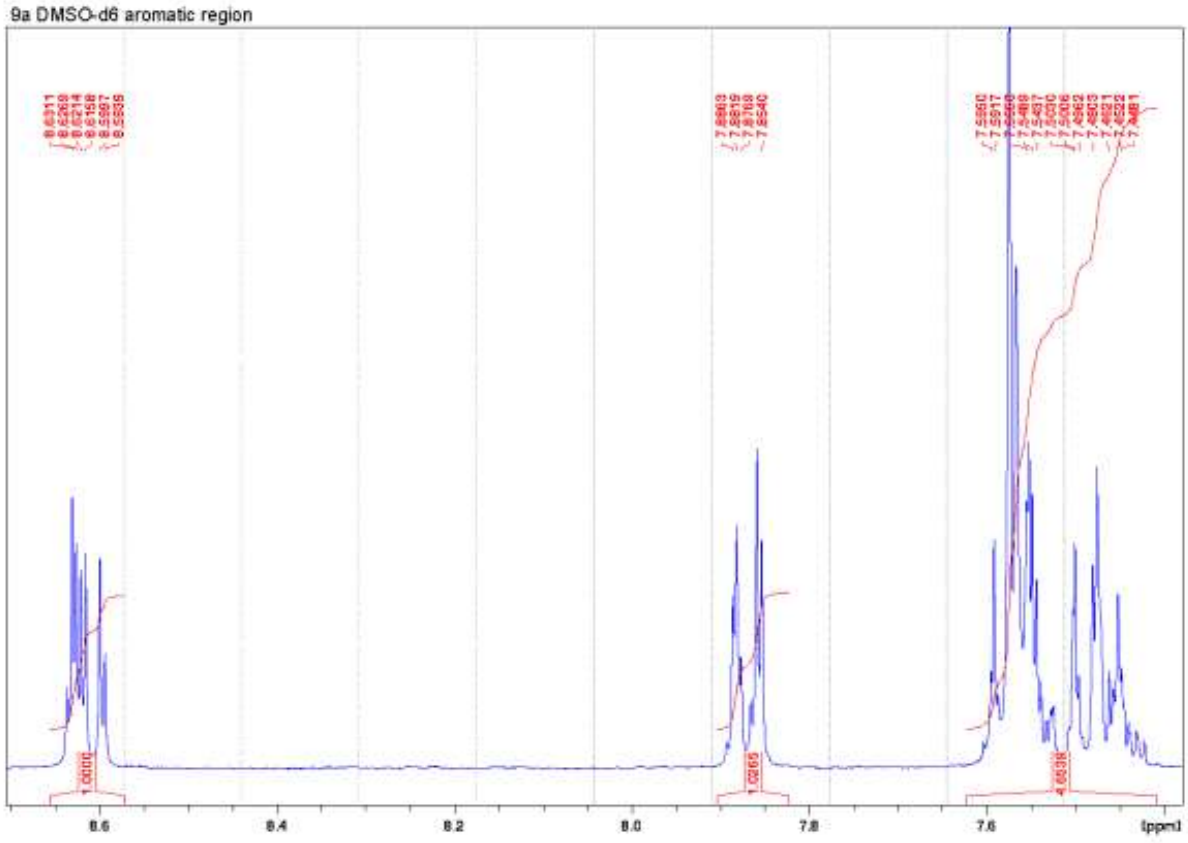
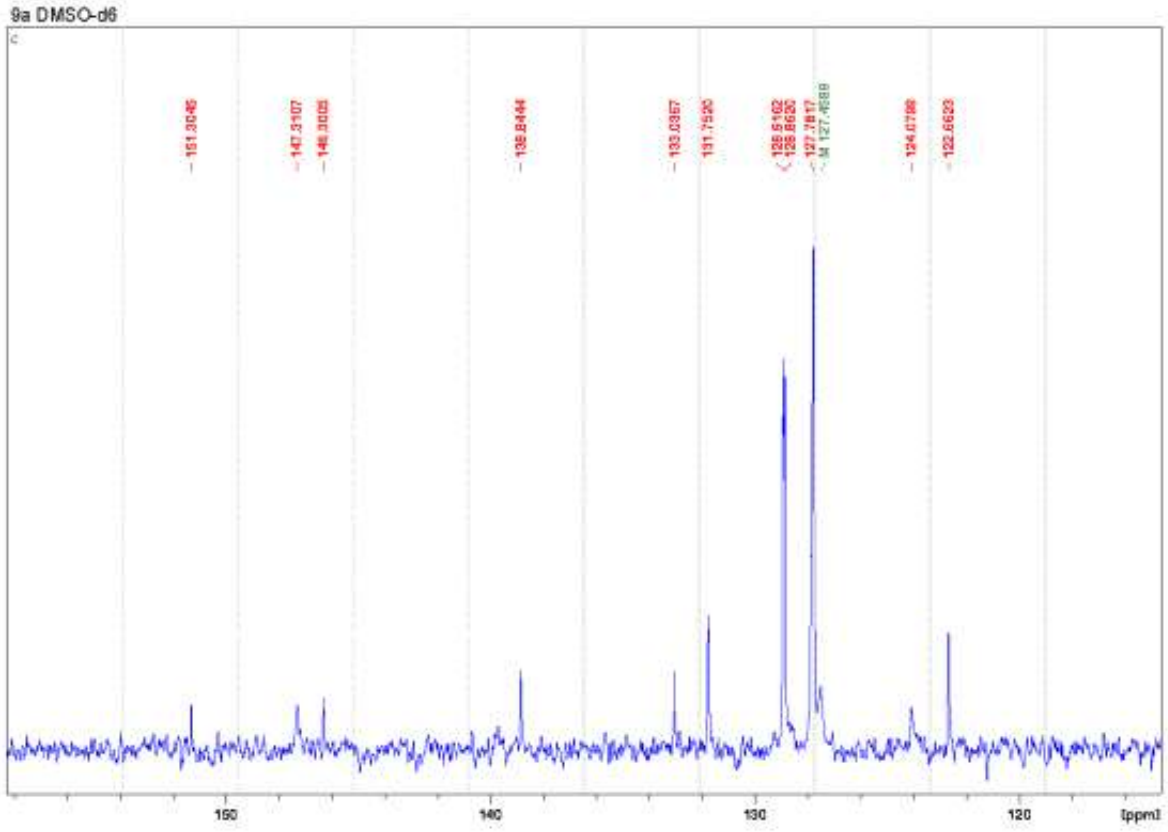
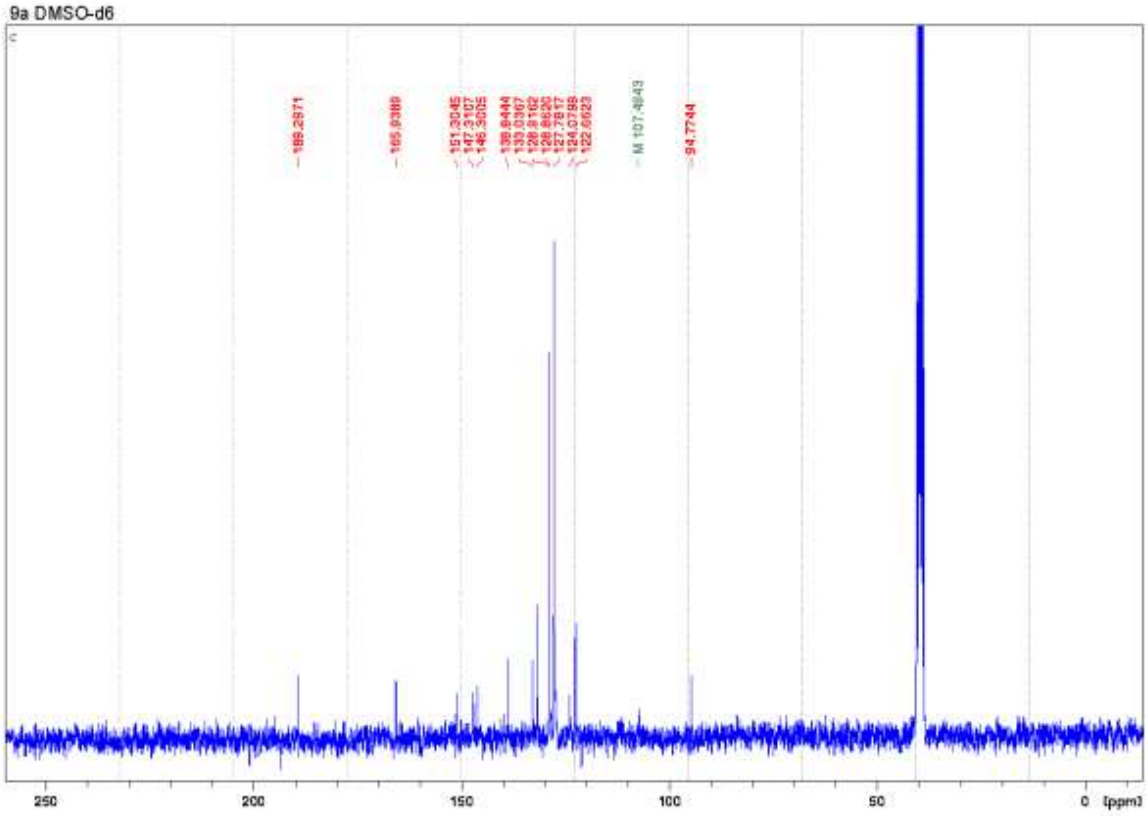


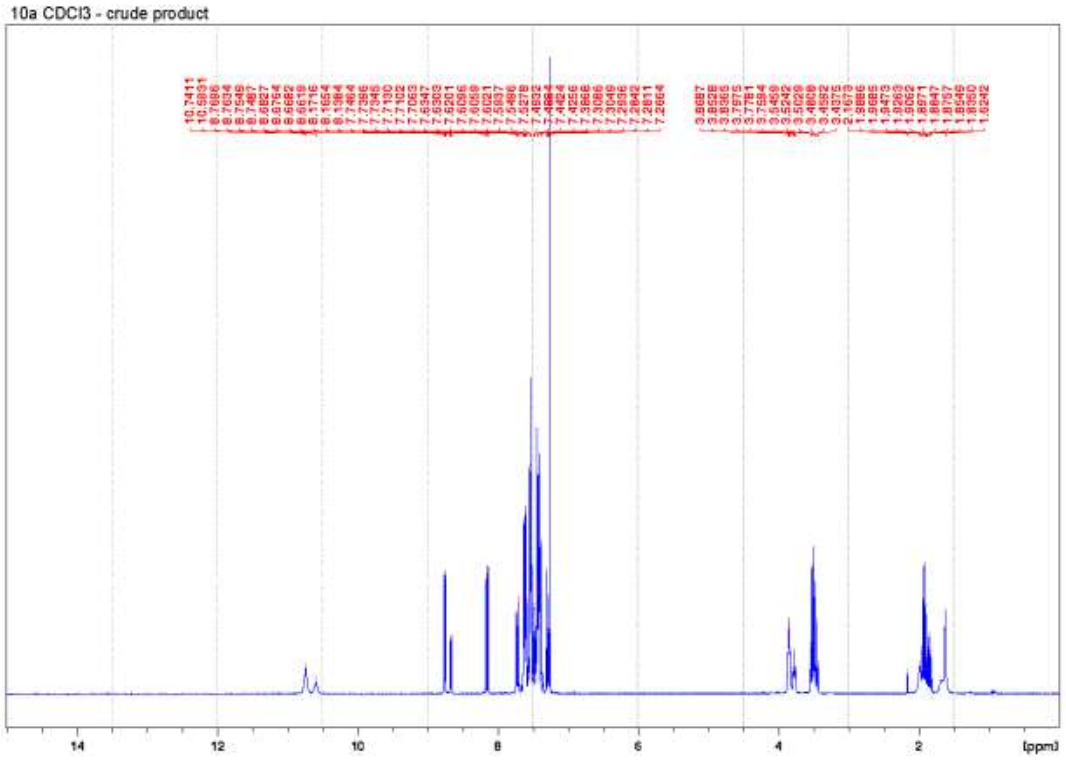


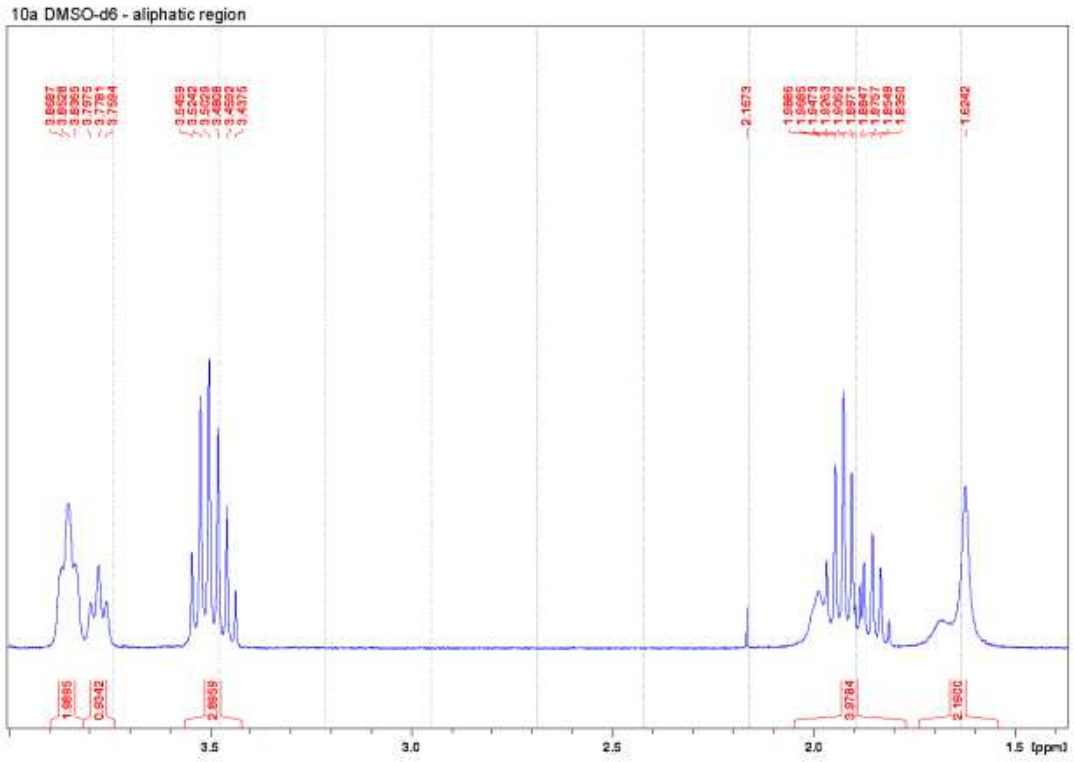
9a (75.47 MHz,)

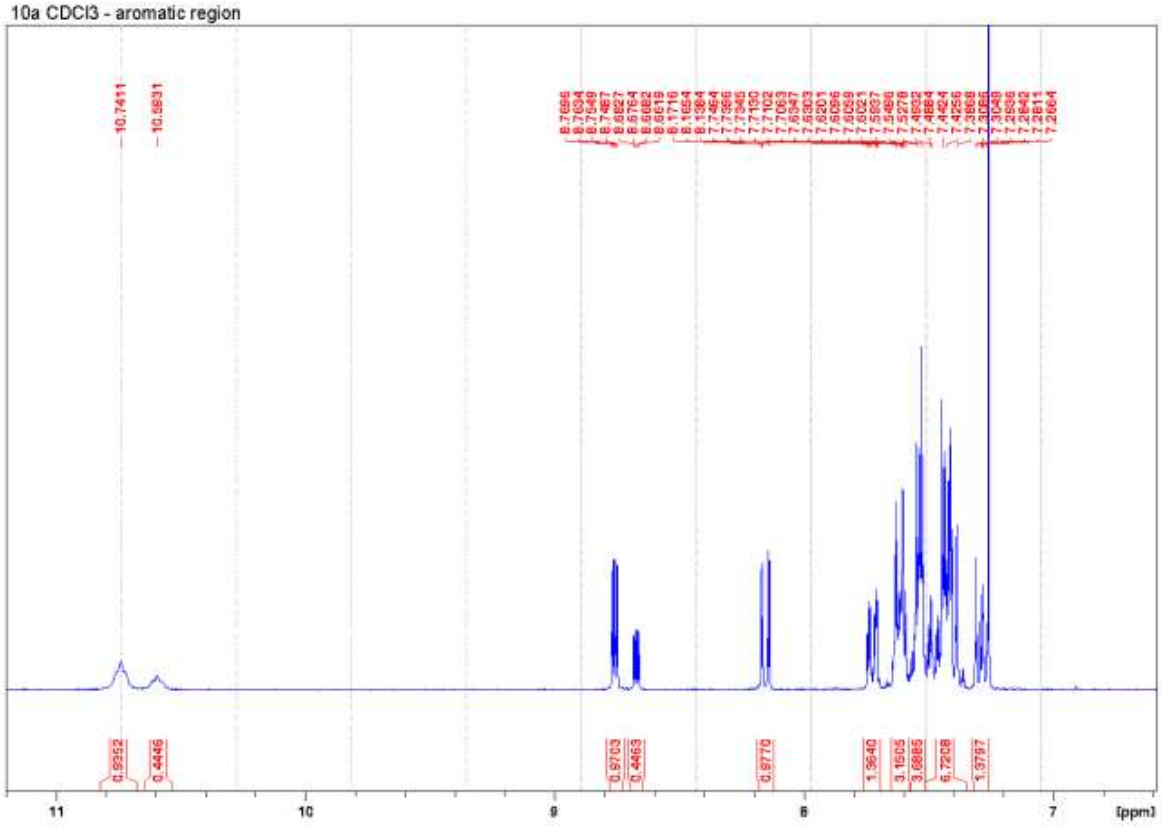




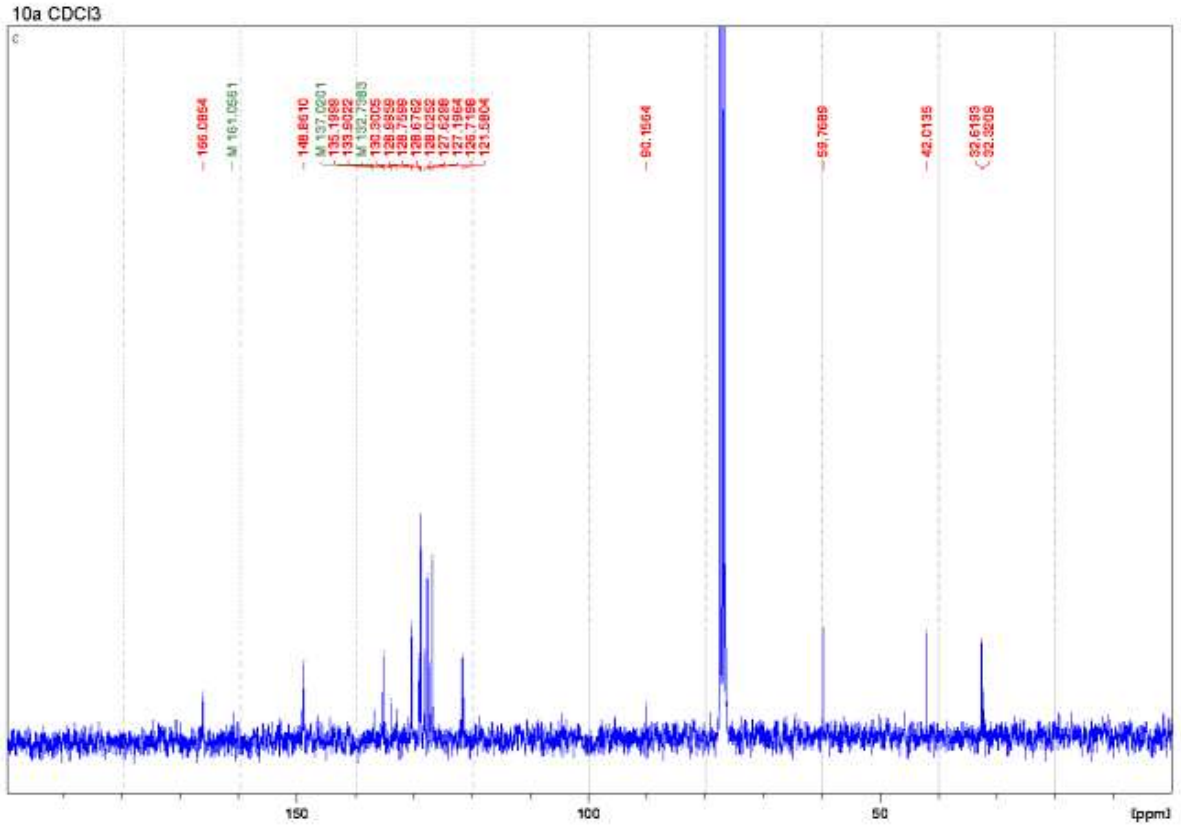
10a (300.13 MHz, CDCl3)



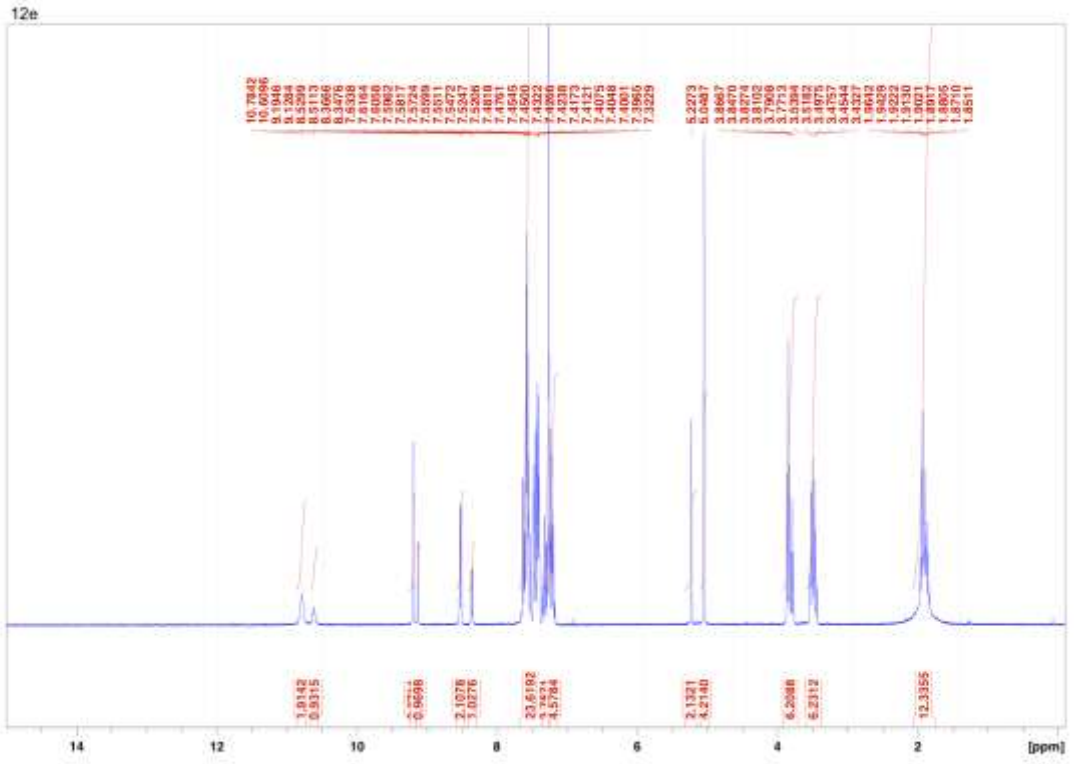


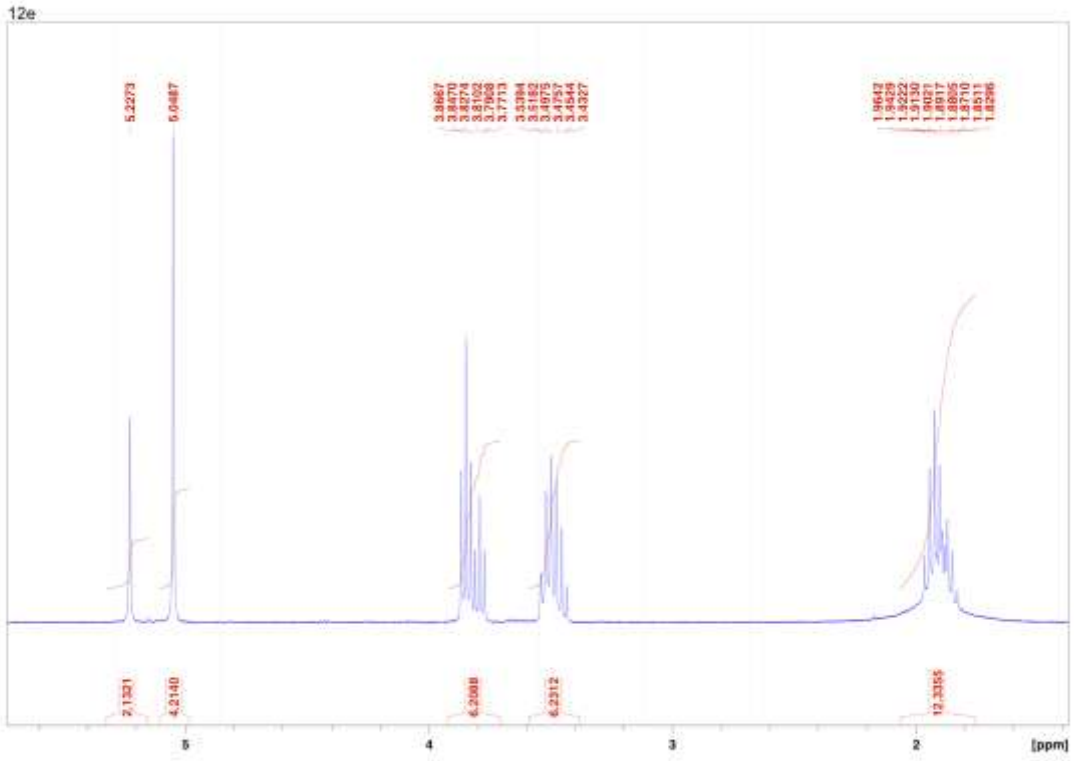


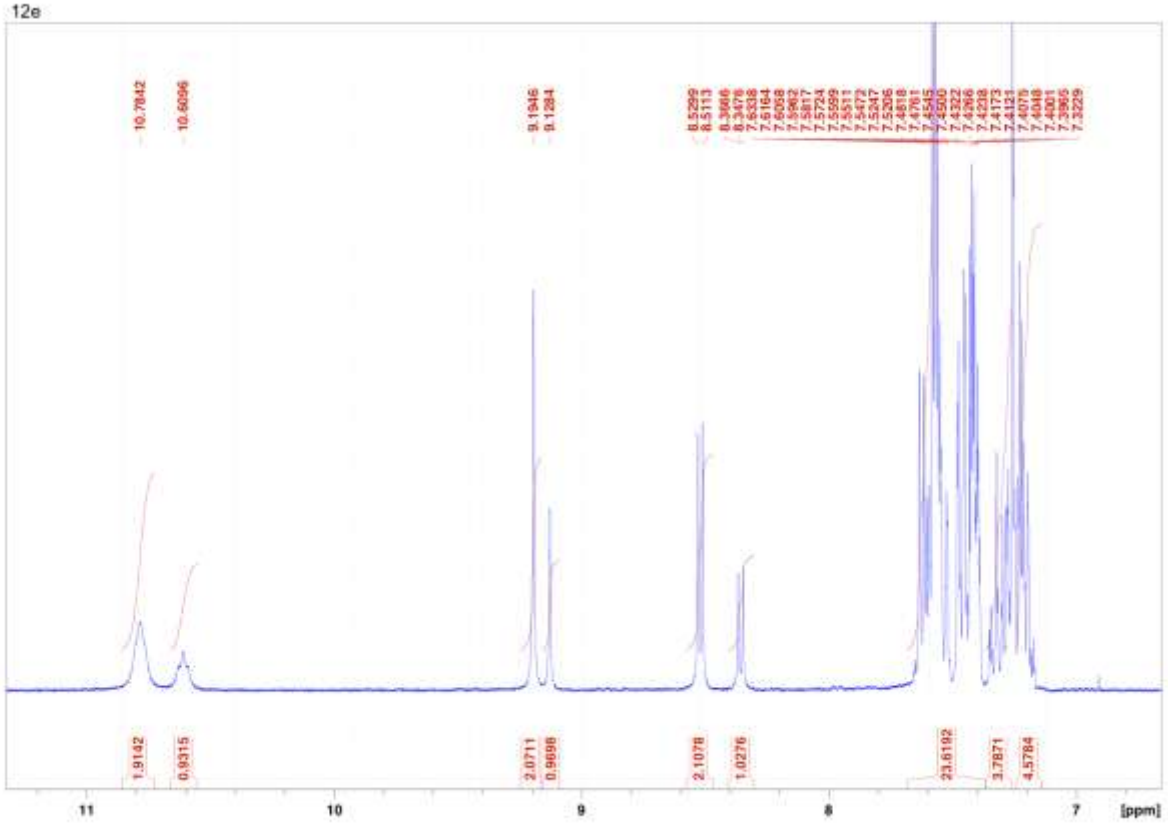
10a (75.47 MHz, CDCl3)



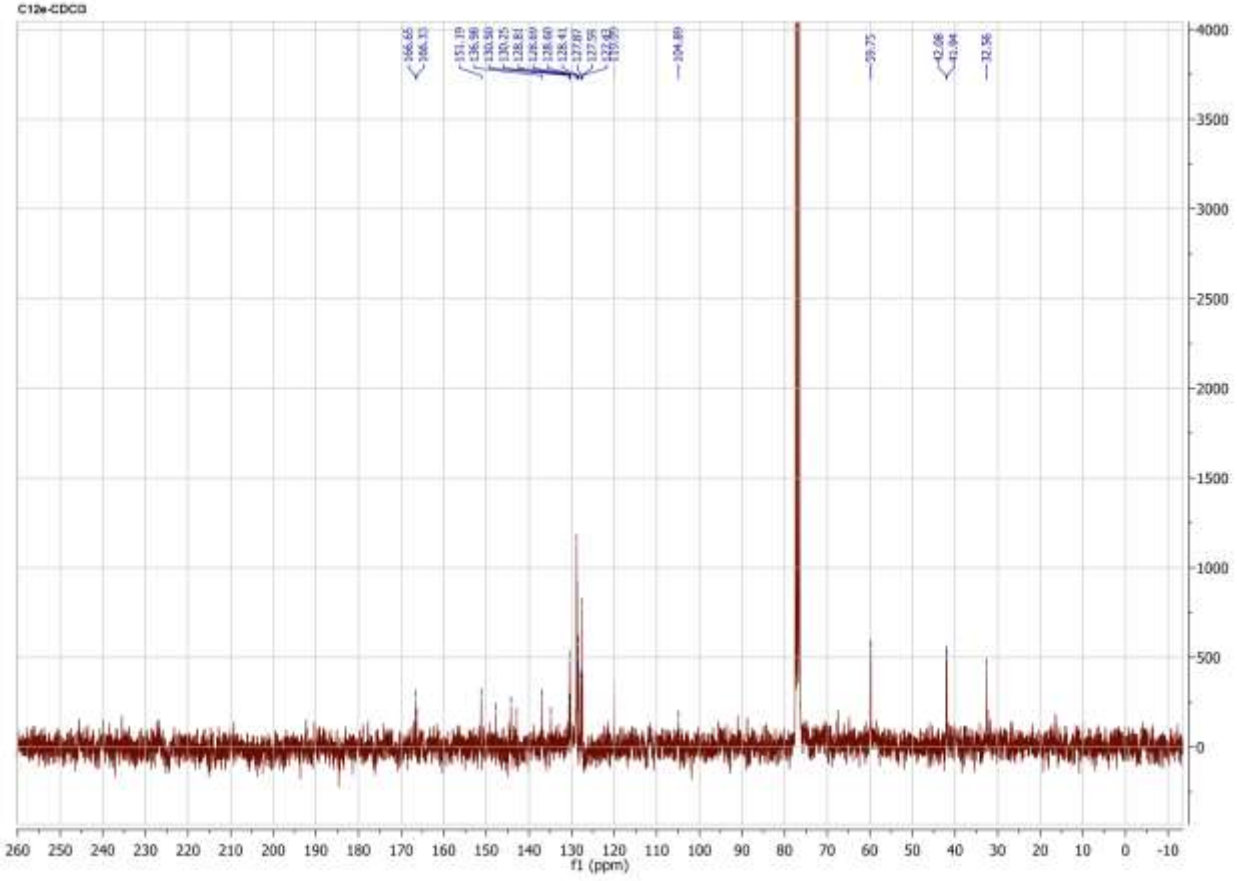
12e (300.13 MHz, CDCl3)



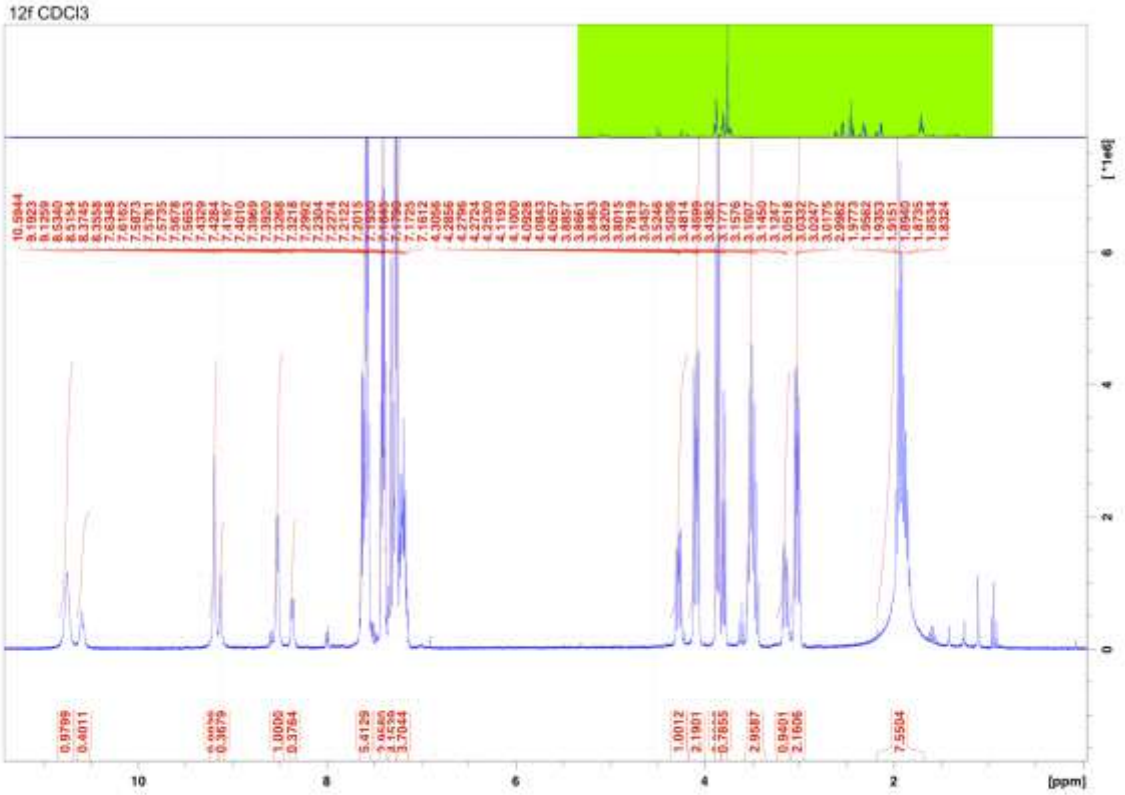




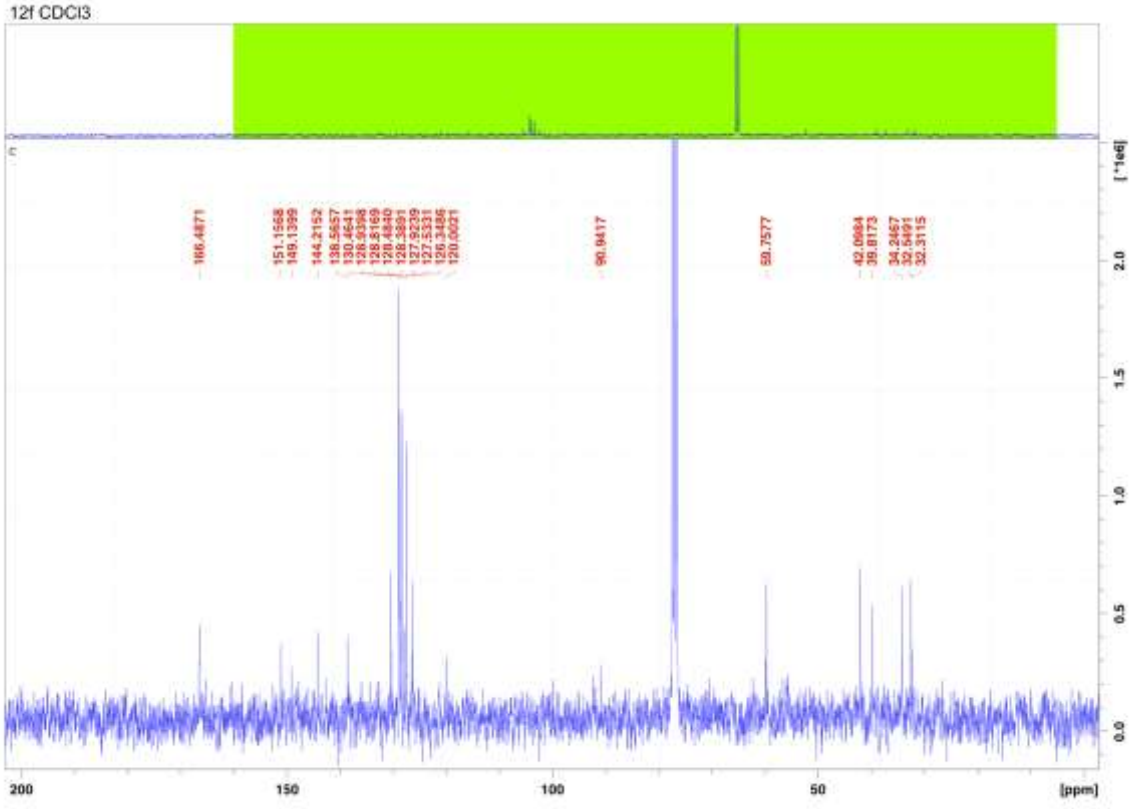
12e (75.47 MHz, CDCl3)



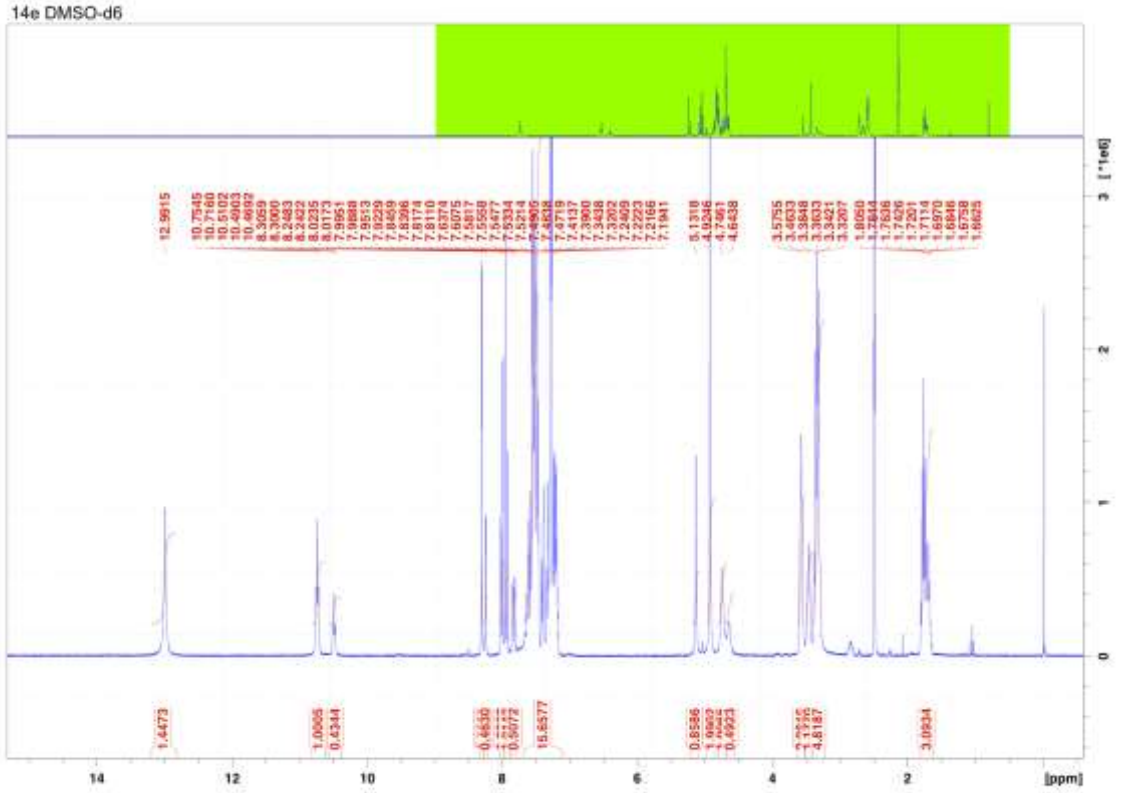
12f (300.13 MHz, CDCl3)



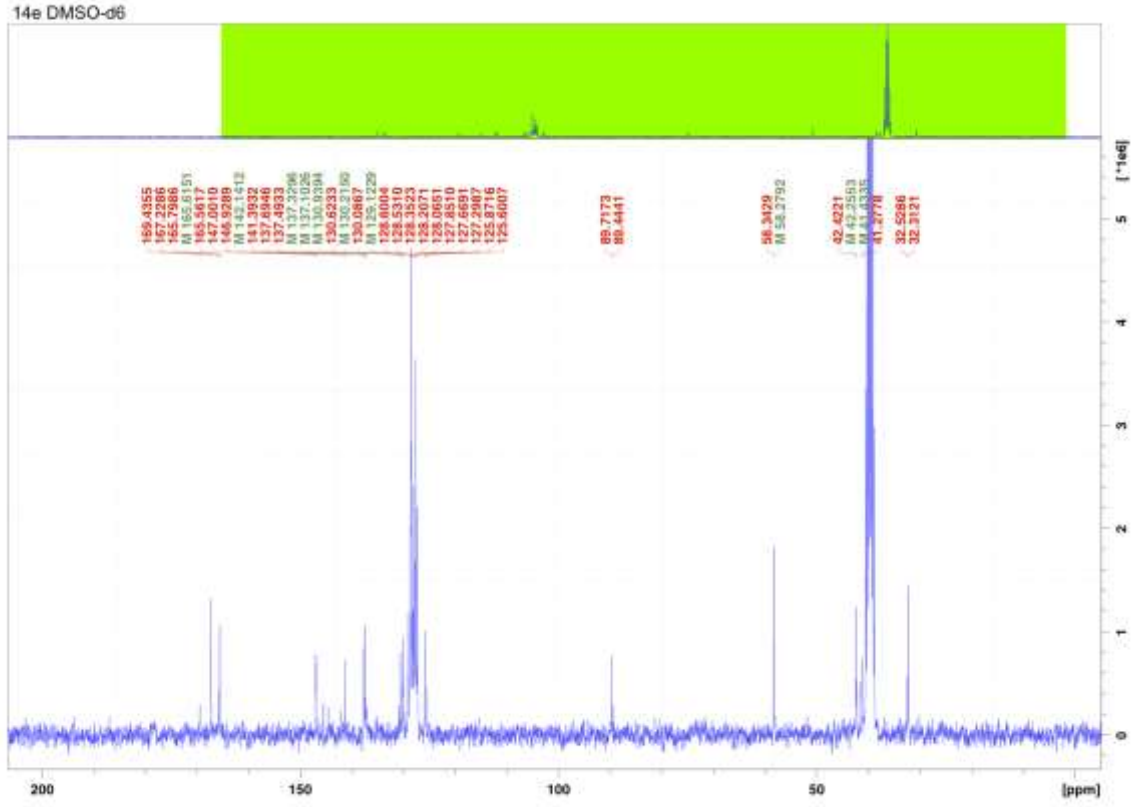
12f (75.47 MHz, CDCl3)



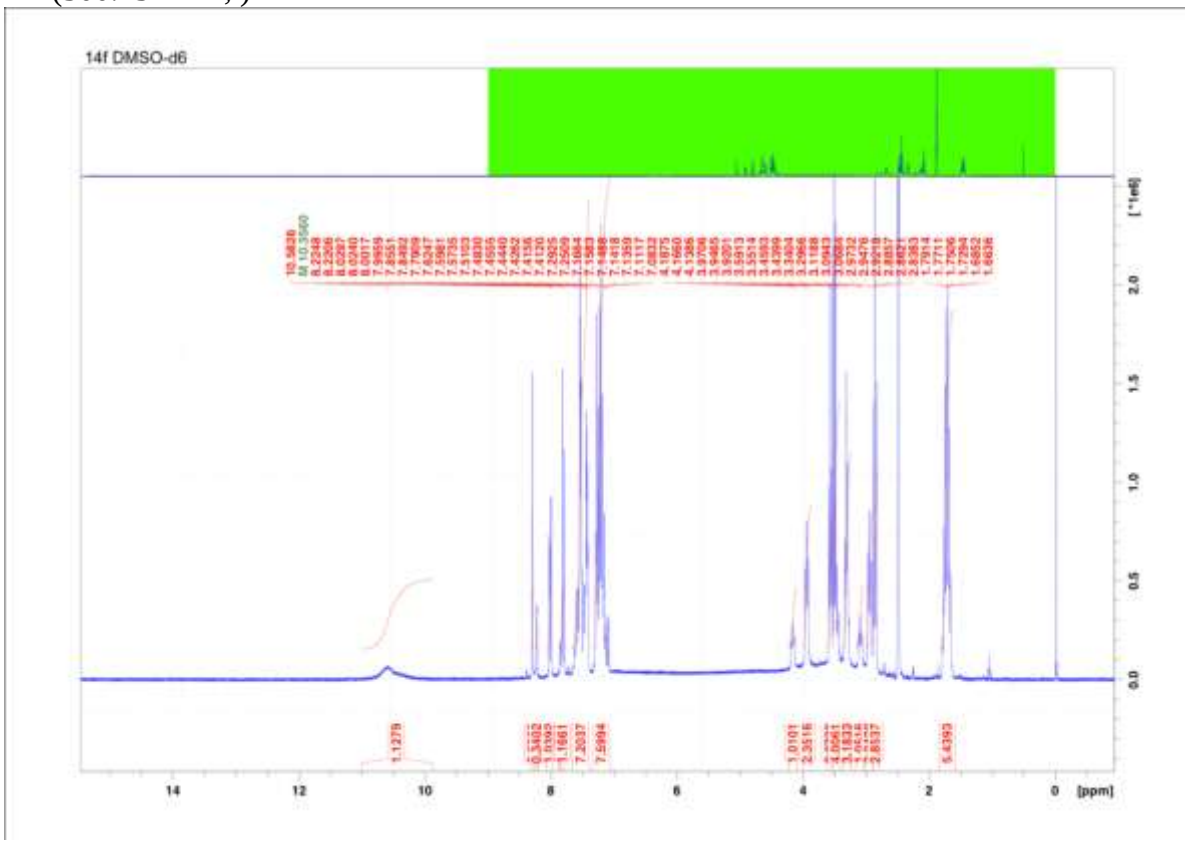
14e (300.13 MHz,)



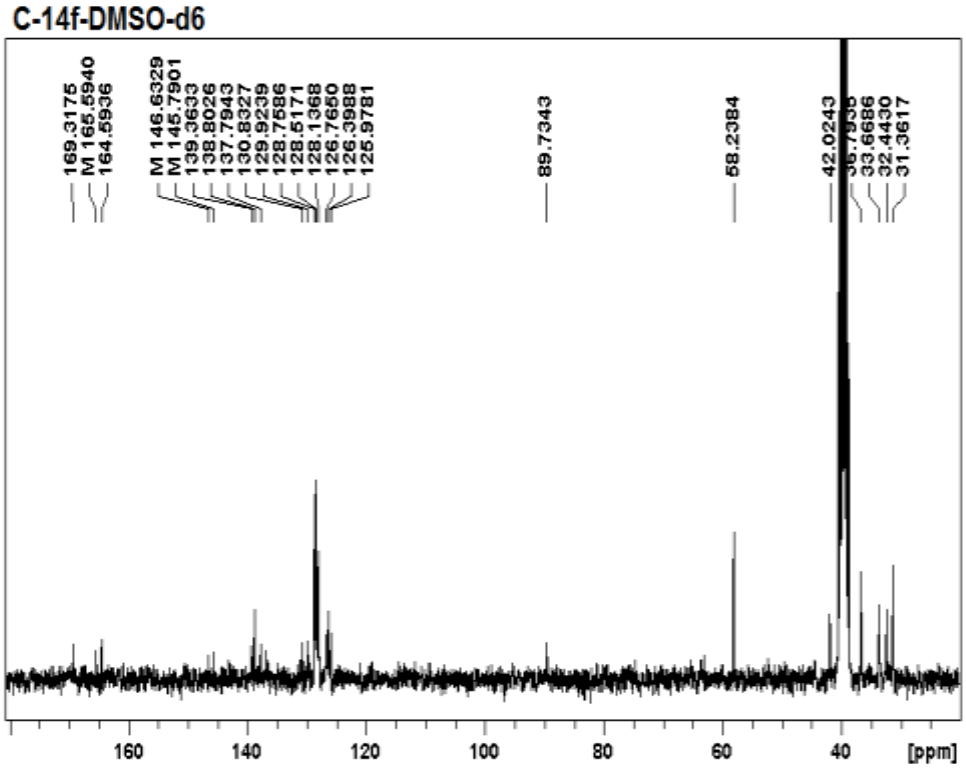
14e (75.47 MHz,)



14f (300.13 MHz,)



14f (75.47 MHz,)



Conformational and intermolecular interaction analysis for crystal structure of 6a and 12e

Compound **6a** crystallises in monohydrate form. In the structure of **12e**, disorder was observed for the hydroxyethyl group, with a site occupancy of 88.4% for the major component. However, the position of the hydroxyl group is defined without disorder due to its stabilisation by the strong intermolecular hydrogen bond O39-H39...N7 with its donor on the molecule related via the c-glide plane: x, -y+1.5, z-0.5 (H39...N7 = 1.962(18) Å, O39...N7 = 2.852(1) Å and O39-H39...N7 = 174.7(15)º). A similar intermolecular hydrogen bond is also observed for 6a with its acceptor on atom N5 of the molecule related via screw axis 21: -x+2, y-0.5, -z+0.5 (H39...N5 = 1.87(2) Å, O39...N5 = 2.745(3) Å and O39-H39...N5 = 173 (5)º).

The three aromatic systems in molecules of both compounds are in different mutual orientations, which influence the π-π interactions observed in the three-dimensional crystal structure. The angle between phenylmetilidene aromatic fragment and the main three-membered heteroatomic ring system is 114.62(7)° and 99.66(3)° for **6a** and **12e**, respectively. Both molecules differ in the substituent attached to N1 atom. The phenyl substituent in case of compound **6a** forms angel 130.92(6)° with the main heteroatomic ring system, whereas in the structure **12e** the mutual orientation of the benzyl substituent to the main ring system is 102.99(3)°. Additional difference in position of nitrogen atom N5 or N7 of the main ring system for **6a** and **12e**, respectively, implicates various π electron properties, resulting in different way of interaction. Stacking is observed between the main ring system for crystal structure of **6a**. This π-π interaction propagates parallel to [031] direction. The overlapping parts are the five-membered ring and six-membered ring of the molecule translated in [010] direction, which are arranged in the step-like construction. The distance between centroids (C_t...C_t) of the overlapping rings is 3.558(3) Å, with shortest interatomic distance C3-C6_2 3.440(2) Å (where _2 is symmetry operator: x, y+1, z). Due to symmetry observed in the crystal structure, molecules involved in stacking propagating parallel to [031] and [03-1] are arranged in a "herring-bone" fashion. Another π-π interaction in the crystal structure of **6a** is observed between phenyl groups of two molecules related *via* inversion centre. The C_t...C_t distance of interacting rings is 3.770(3) Å and the shortest interatomic distance C13...C15_3 is 3.368(2) Å (where _3 is symmetry operator: -x+2, -y+1, -z+1). In structure **12e** a dimer is formed by π-π interaction of the main heteroatomic ring systems of molecules related by inversion centre. The overlapping of rings is however stronger, mainly observed between six-membered rings of the system with shortest C_t...C_t distance 3.542(2) Å. Both other aromatic rings in the molecule of **12e** do not form π-π interactions.