Chapter 6

Summary and future scopes of the present work

6.1 Summary of the present work

The major findings of our thesis are highlighted chapter wise below:

Chapter 2

- A new series of ionic liquid 1, 3-disulfonic acid imidazolium carboxylate, [DSIM][CX_3COO] where X= H, Cl and F were prepared from the reaction of 1, 3-disulfonic acid imidazolium chloride [DSIM][Cl] with corresponding acetic acid derivatives at 50 ºC.
- All these ionic liquids were characterized using different spectroscopic tools such as FT-IR, ^{1}HNMR, ^{13}CNMR and elemental analysis. The thermal stability and Brønsted acidity of these IL were determined using thermogravimetric analysis and Hammett functions.
- The catalytic activity of these acidic ILs was examined as homogeneous catalyst for one-pot synthesis of 14-alkyl/aryl-14-*H*-dibenzo[a,j]xanthenes derivatives under solvent free medium and 1,8-dioxodecahydroacridines in solvent-free or aqueous medium in thermal condition.
- The strong acidic ILs [DSIM][CF_3COO] and [DSIM][CCl_3COO] were optimized as best catalysts with good to excellent yields for synthesis of both heterocycles within short time.
- The reusability of the best catalysts were also studied with the model reaction and found to be reusable for three consecutive runs.

Chapter 3

- In the **Chapter 3A,** the three-component preparation of *anti*-2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazine was developed as a single diastereomer from the reaction of 2-naphthol, aryl aldehyde and electron rich primary amines in solution at room temperature or at 100 ºC under solvent free heating in presence of trichloroacetic acid as catalyst.
- The exact orientation of H-2 and H-4 protons of naphthoxazine derivatives was determined as *anti* from the COSY and NOESY interaction of basic oxazine ring of the compound.
- The same synthesis was extended in the **Chapter 3B** with three environmentally benign reusable Brønsted acidic catalysts *viz* sulfamic acid, PTSA and

[DSIM][CF_3COO] IL in aqueous ethanol at room temperature or at 80 ºC in neat condition.

- A new series of triphenylsulfophosphonium chlorometallates were prepared in the **Chapter 3C** from the reaction of triphenylsulfophosphonium chloride ([TPSP][Cl]) with different transition metal halides such as $FeCl_3$, $ZnCl_2$, $MnCl_2$ and $NiCl_2$ in appropriate mole fractions at 80 ºC.
- The synthesized chlorometallates were characterized using different spectroscopic and analytical tool such as FT-IR, NMR, solid-UV, UV-visible, Raman spectroscopy, TGA, SEM-EDX, powder XRD, CHN and ICP elemental analysis etc. The structure of anionic complex were confirmed through solid-UV and Raman spectroscopy and thus the chlorometallates were formulated as [TPSP][$FeCl_4$], $[TPSP]_2[Zn_2Cl_6]$, $[TPSP]_2[MnCl_4]$ and $[TPSP]_2[NiCl_4]$.
- These chlorometallates were investigated as reusable heterogeneous catalysts for the multicomponent synthesis of *anti*-2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazine derivatives. Out of the four, [TPSP][$FeCl_4$] and $[TPSP]_2[Zn_2Cl_6]$ were optimized as most efficient catalysts in aqueous ethanol at room temperature and also under solvent free heating. Furthermore both these catalyst were reused for the eight consecutive cycles with very good reactivity which is again supported by their powder XRD pattern after 8^{th} cycle.
- The fluorescence properties of synthesized 1, 2, 3-trisubstituted naphthoxazines were studied and found to be fluorescence active.

Chapter 4

- We have synthesized three novel Brønsted acidic N, N-disulfotetramethylguanidinium carboxylate ionic liquids [DSTMG][CX_3COO] where X= H, Cl and F, by treating [DSTMG][Cl] with corresponding acetic acid derivatives at 60 ºC. All these ILs were fully characterized via different spectroscopic and analytical tools.
- The catalytic activity of these ILs was investigated as homogeneous catalyst for the multicomponent synthesis of tetrahydrobenzo[a]acridinone and tetrahydrobenzo[a]xanthenone derivatives under solvent free heating at 75-85 ºC. The reusability of ILs was tested and found to be reusable for the six consecutive runs and the FT-IR spectra of reused catalyst also support their reactivity.

- This is the first ever four component and also the IL catalyzed synthesis of tetrahydrobenzo[a]acridinone derivatives.

Chapter 5

- In this chapter a new ionic liquid system diethyl-disulfo-ammonium chlorometallates was introduced by treating the parent diethyl-disulfo-ammonium chloride ([DEDSA][Cl]) with $FeCl_3$ ([DEDSA][$FeCl_4$]) and $ZnCl_2$ ([DEDSA]$_2$[Zn_2Cl_6]) in equimolar ratio at 80 ºC.
- The chlorometallates along with parent IL were characterized using different analytical tool such as FT-IR, solid-UV, UV-visible, Raman spectroscopy, TGA, SEM-EDX, powder XRD, CHN and ICP elemental analysis etc. The structures of their anionic species were fully agreed with the literature data of Raman and solid-UV spectra of such type of anionic speciation.
- Both these chlorometallates IL were utilized as efficient and reusable heterogeneous catalyst for the multicomponent synthesis of 14-aryl-7-(N-phenyl)-14*H*-dibenzo[a.j]acridine derivative under solvent free heating at 100 ºC that gives good yield within reasonable reaction time. Furthermore both the catalysts were reused for the six consecutive cycles and the powder XRD pattern after 6th cycle also support their reactivity.
- The dibenzoacridine derivatives were also tested for fluorescence property and all the molecules were found to exhibit fluorescence.

6.2. Future scopes of the present work

- The preparation of -SO_3H functionalized task-specific imidazolium or ammonium based IL systems will be extendable to various anionic combinations which will generate functionalized ILs bearing simple anions or complex metal anions.
- In future apart from the catalytic uses, these functionalized materials can be applicable as surfactant, ligand in complex synthesis, chromatographic stationary phases, mobile phase additives or electroosmotic flow modifiers in high-performance liquid chromatography and capillary electrophoresis, stabilizer in nano-synthesis. They can also be employed in different industrial processes like membrane separation process, metal ion extraction process, removal of pollutants from refinery feedstocks, desulfurization of fuels, electrodepositions of metal etc.

- ❖ Investigation of biological activities of various substituted 1, 2, 3-trisubstituted naphthoxazine and dibenzoacridine derivatives.
- ❖ Asymmetric synthesis of 1, 2, 3-trisubstituted naphthoxazine derivatives, polyhydrobenzo[a]acridinone and polyhydrobenzo[a]xanthenone.
- ❖ Investigation of fluorescence active derivatives of substituted naphthoxazine and dibenzoacridine for further uses as fluorescent material.

Selected NMR spectra of synthesized heterocycles

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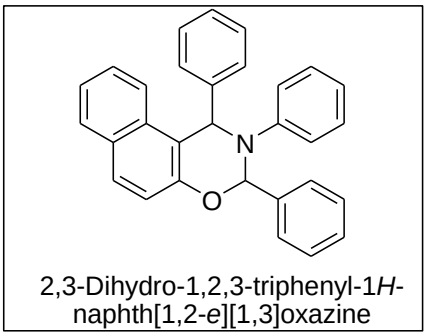
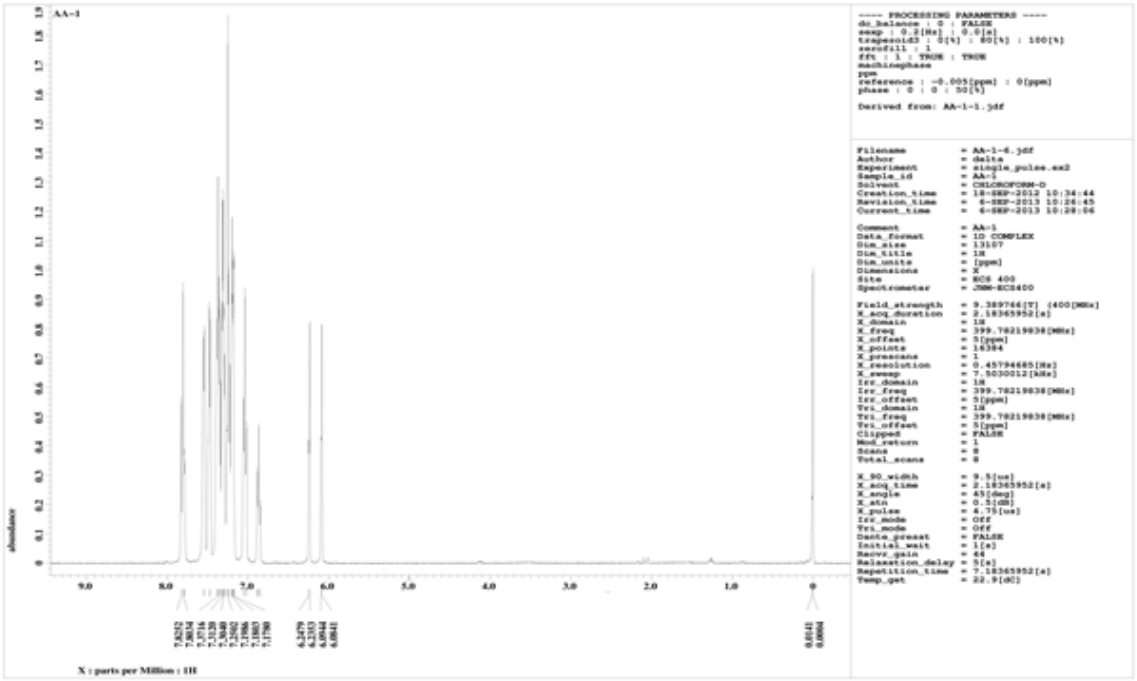
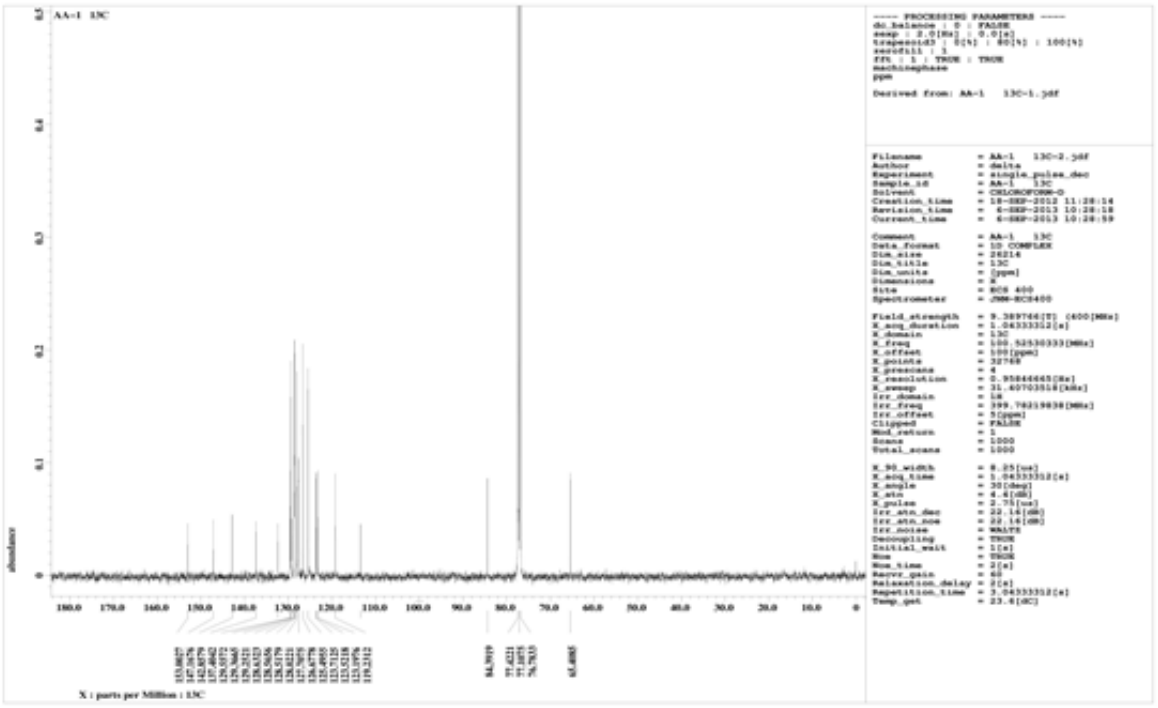


2,3-Dihydro-1,2,3-triphenyl-1*H*-naphth[1,2-*e*][1,3]oxazine

^{1}H-NMR



^{13}C-NMR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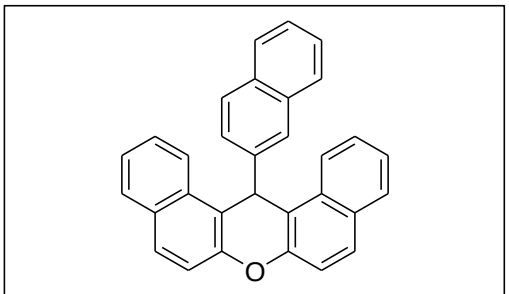
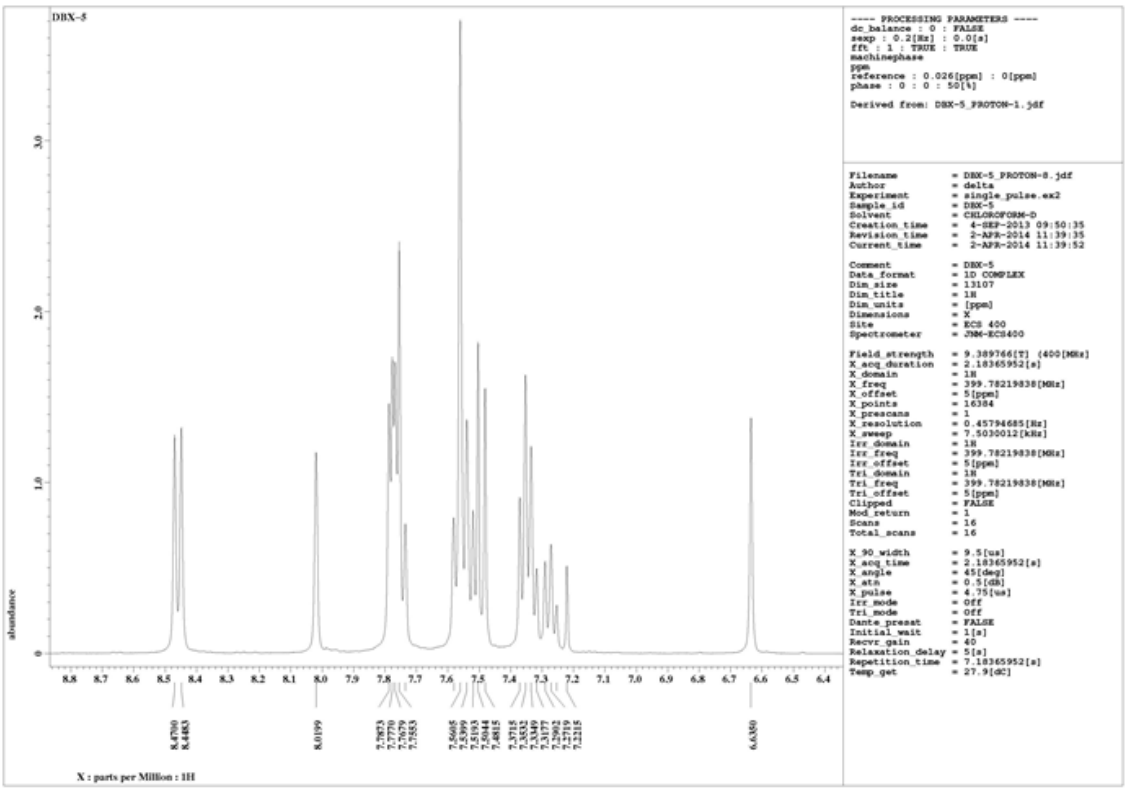
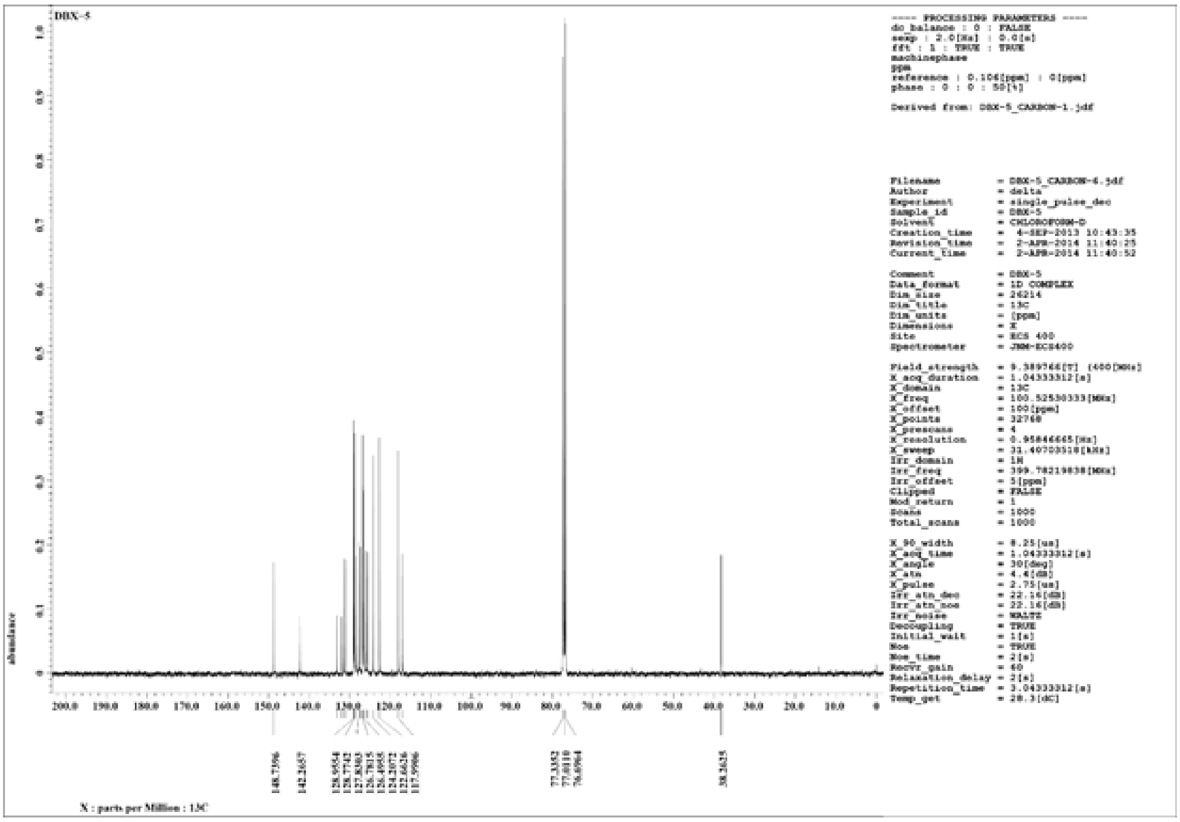


14-Naphthyl-14H-dibenzo [a.j] xanthene

^{1}H-NMR



^{13}C-NMR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77.0110
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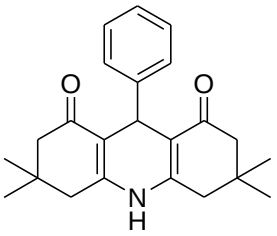
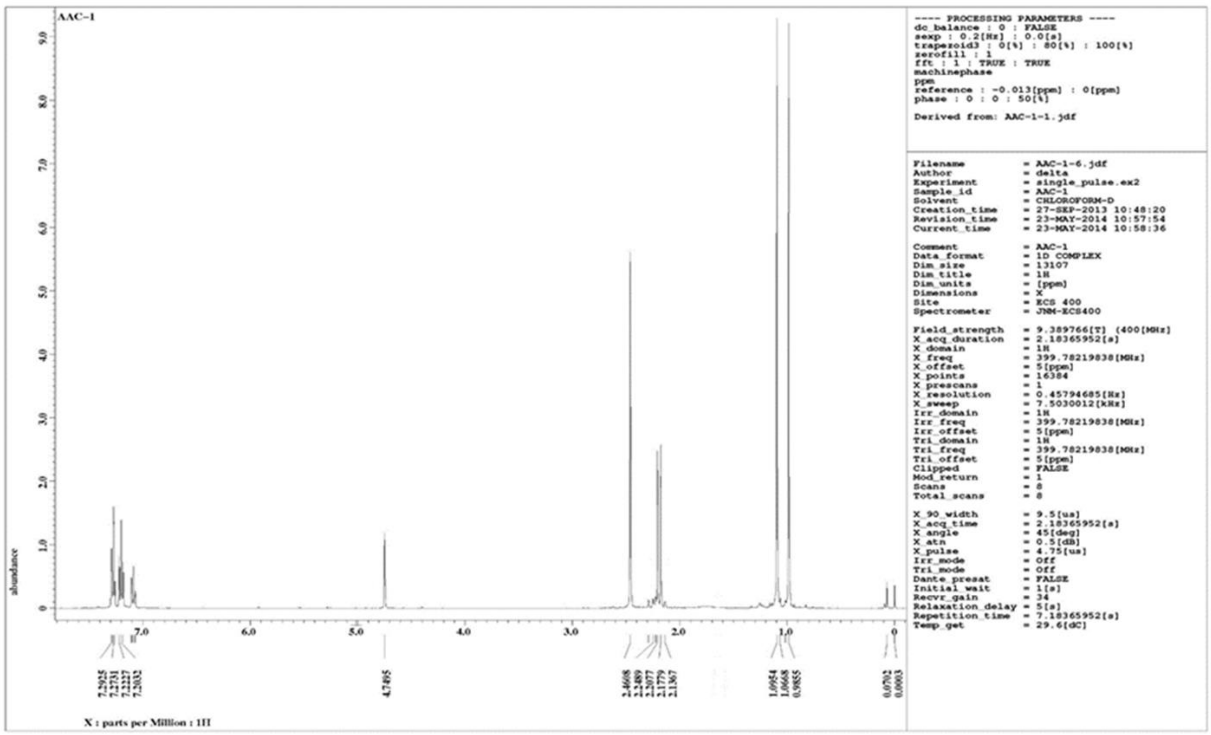
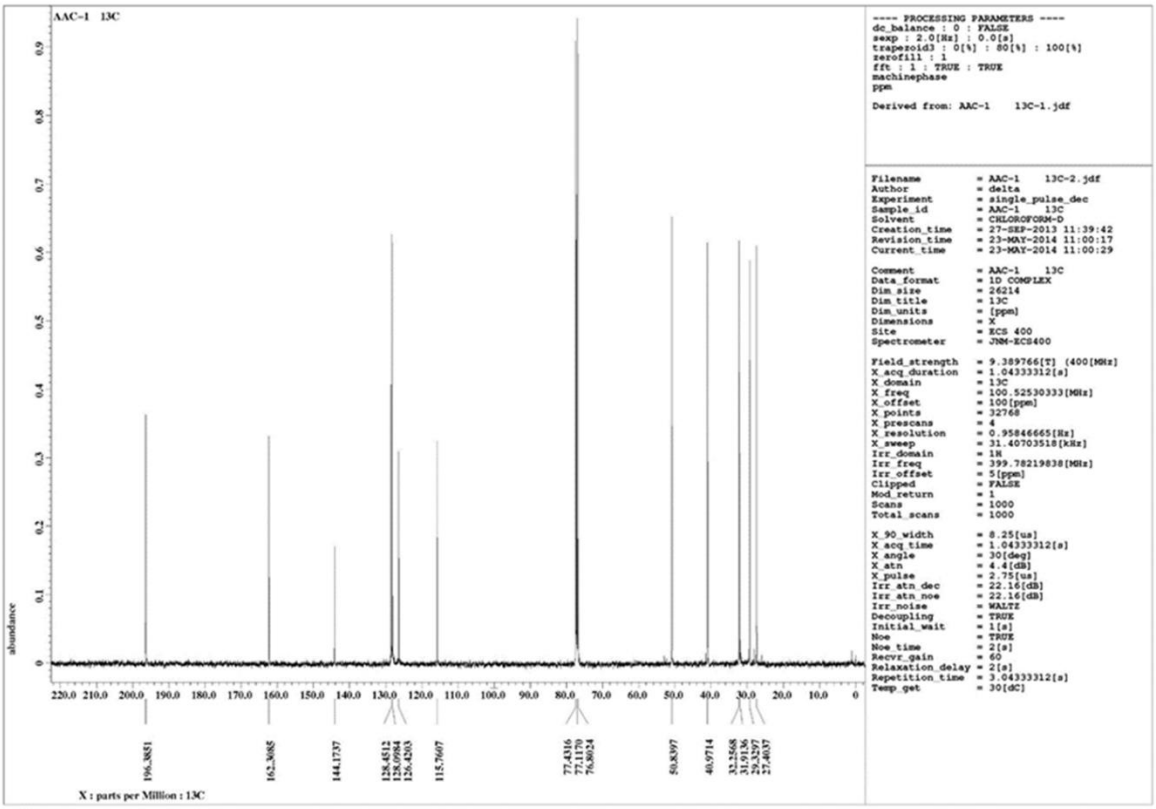


3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-phenylacridine-1,8(2*H*,5*H*,9*H*,10*H*)-dione

^{1}H-NMR



^{13}C-NMR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162.3085
144.1737
128.4512
128.0984
126.4203
115.7607
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29.3297
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ppm
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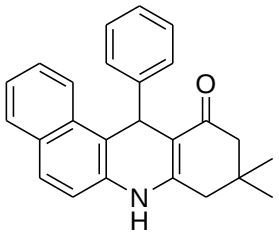
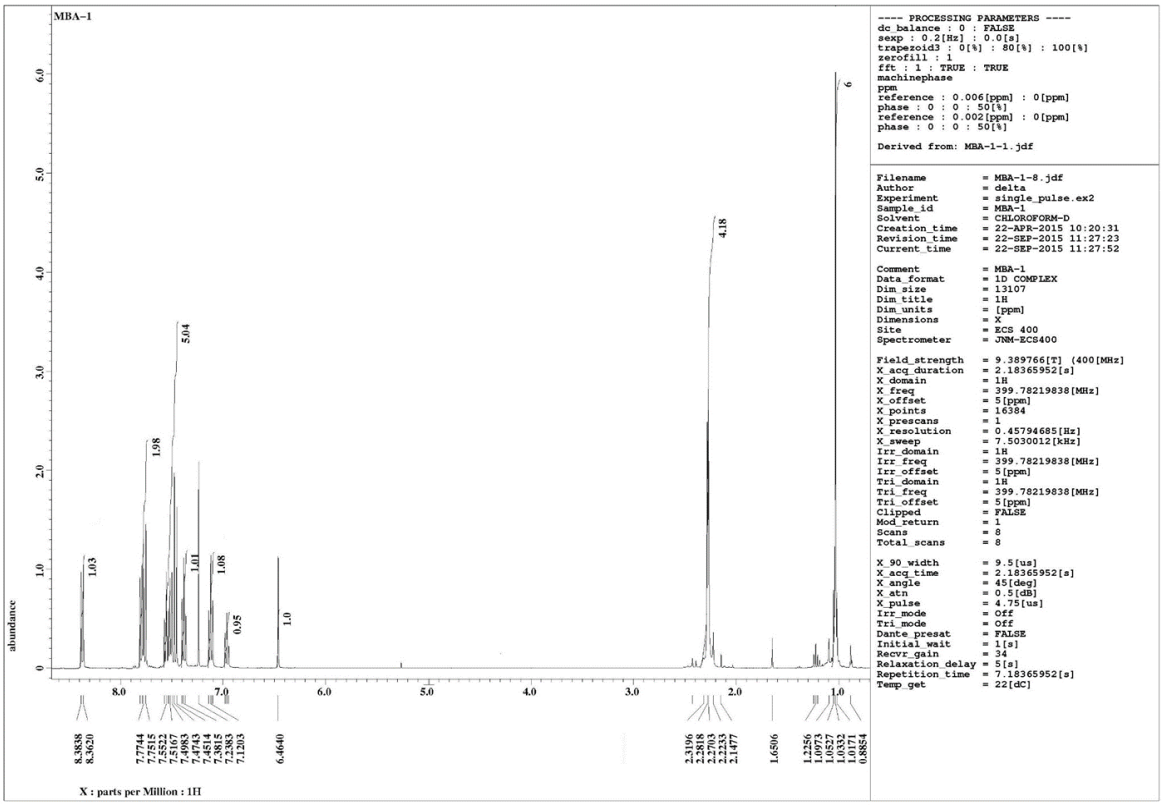
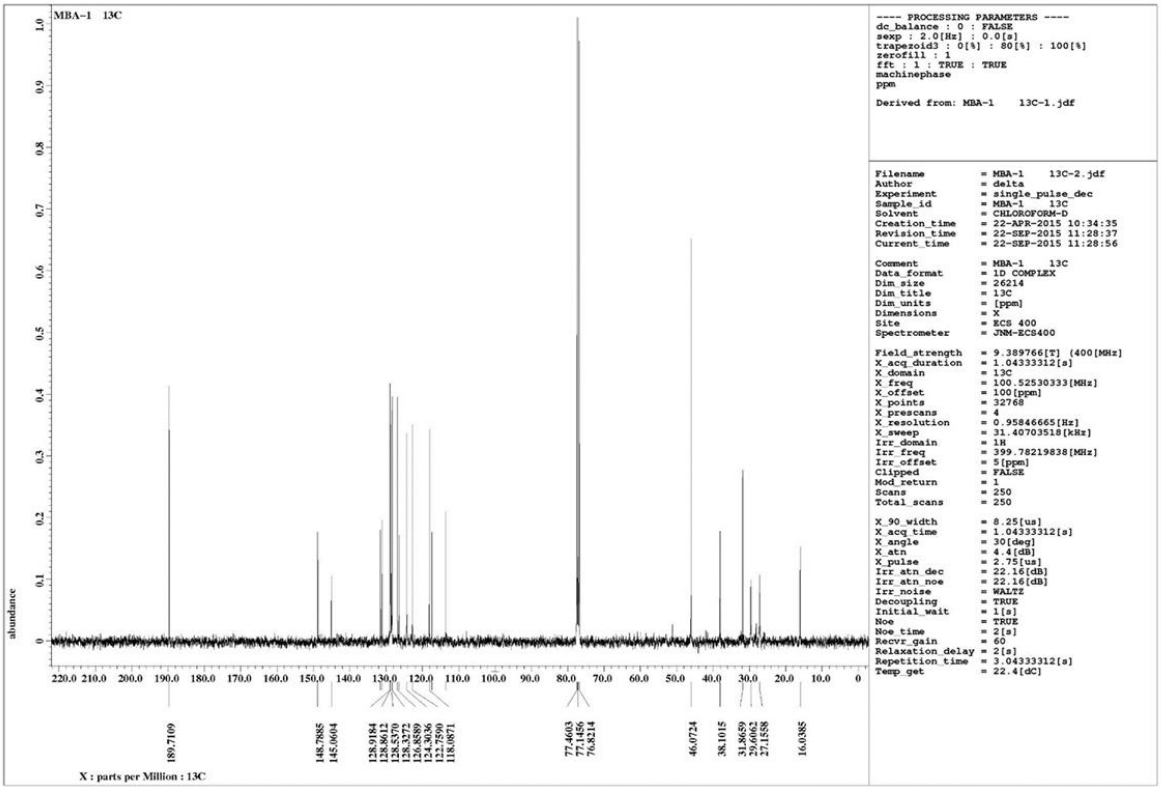


9,10-Dihydro-9,9-dimethyl-12-phenylbenzo[*a*]acridin-11(7*H*,8*H*,12*H*)-one

^{1}H-NMR



^{13}C-NMR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145.0604
128.9184
128.8612
128.5370
128.3372
126.8589
124.3036
122.7590
118.0871
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X : parts per Million : 13C
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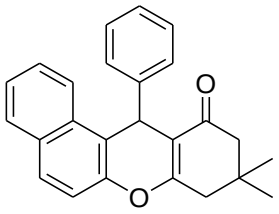
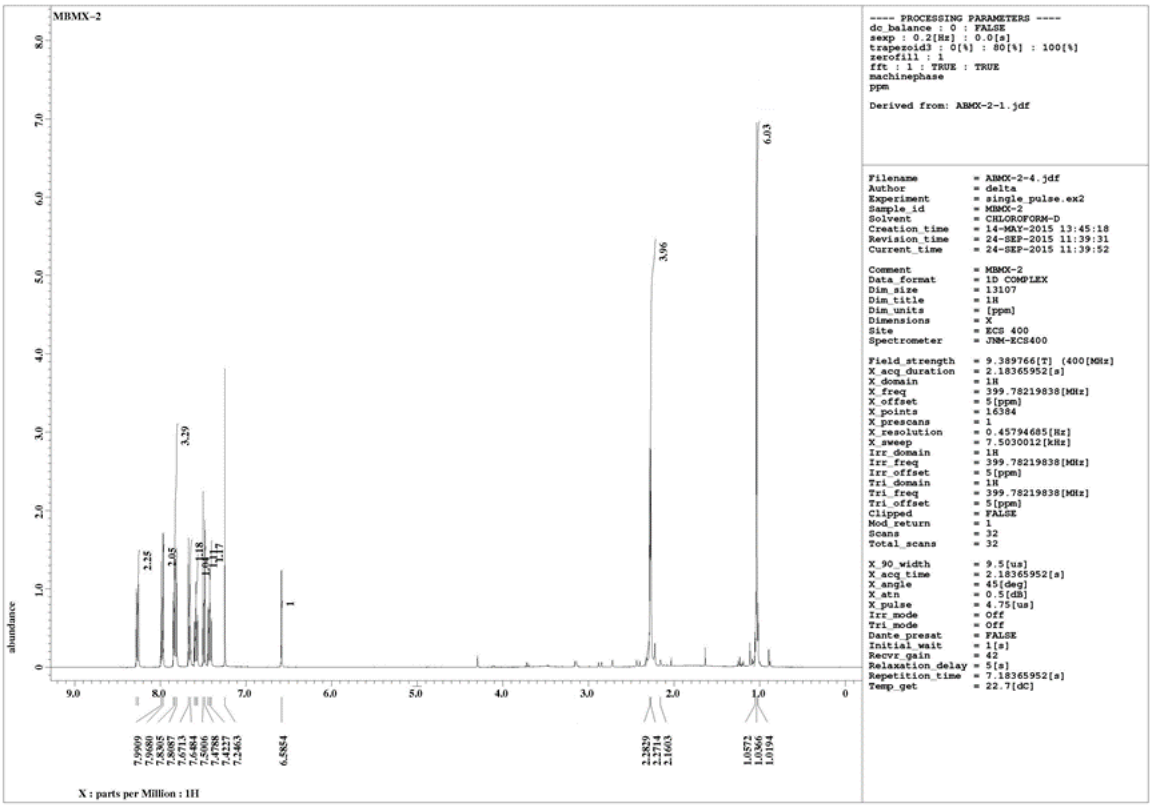
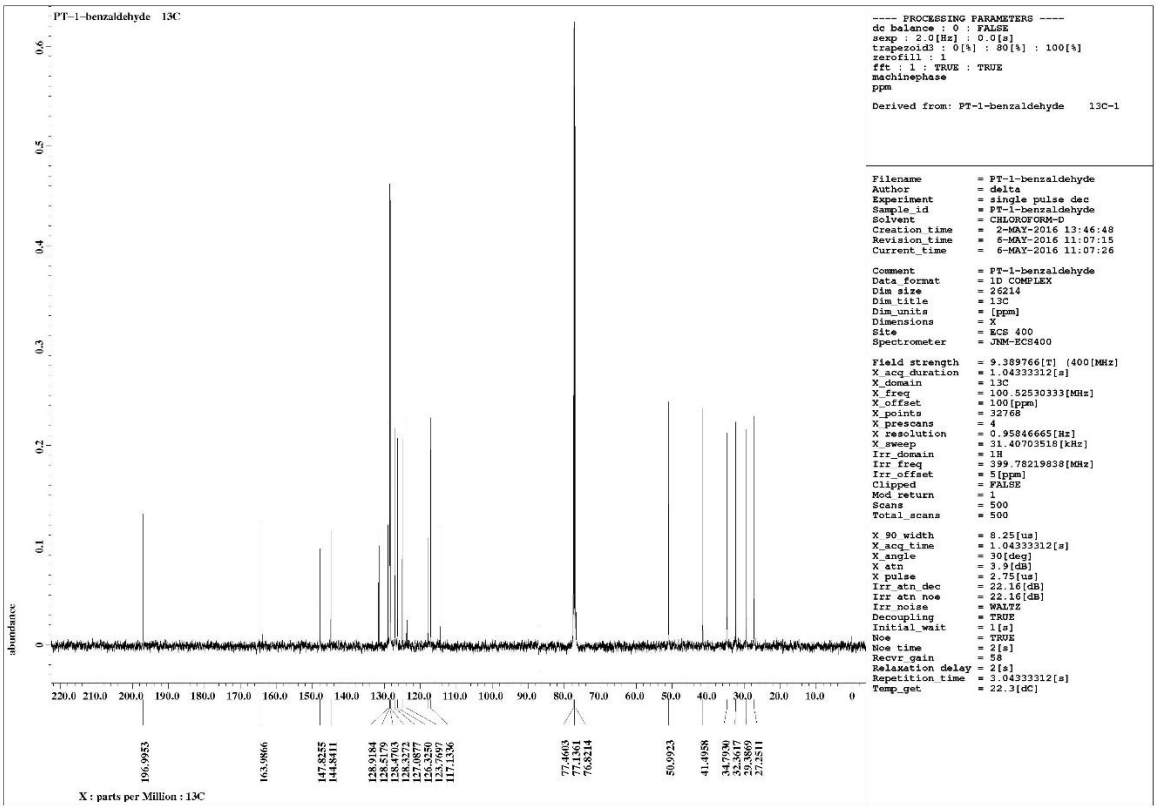


9,10-Dihydro-9,9-dimethyl-12-phenyl-8*H*-benzo[*a*]xanthen-11(12*H*)-one

^{1}H-NMR



^{13}C-NMR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196.9953
163.9866
147.8255
144.8411
128.9184
128.5179
128.4703
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X : parts per Million : 13C
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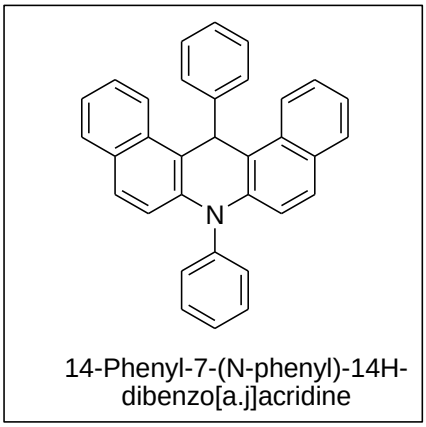
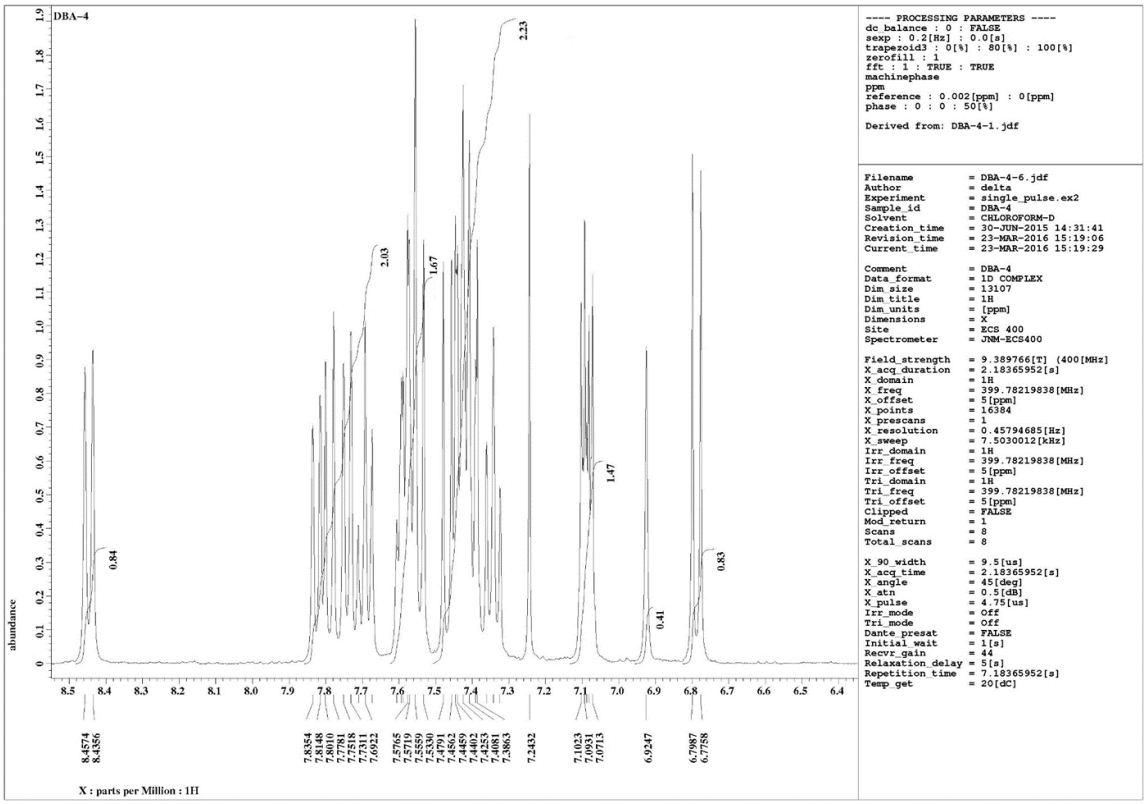
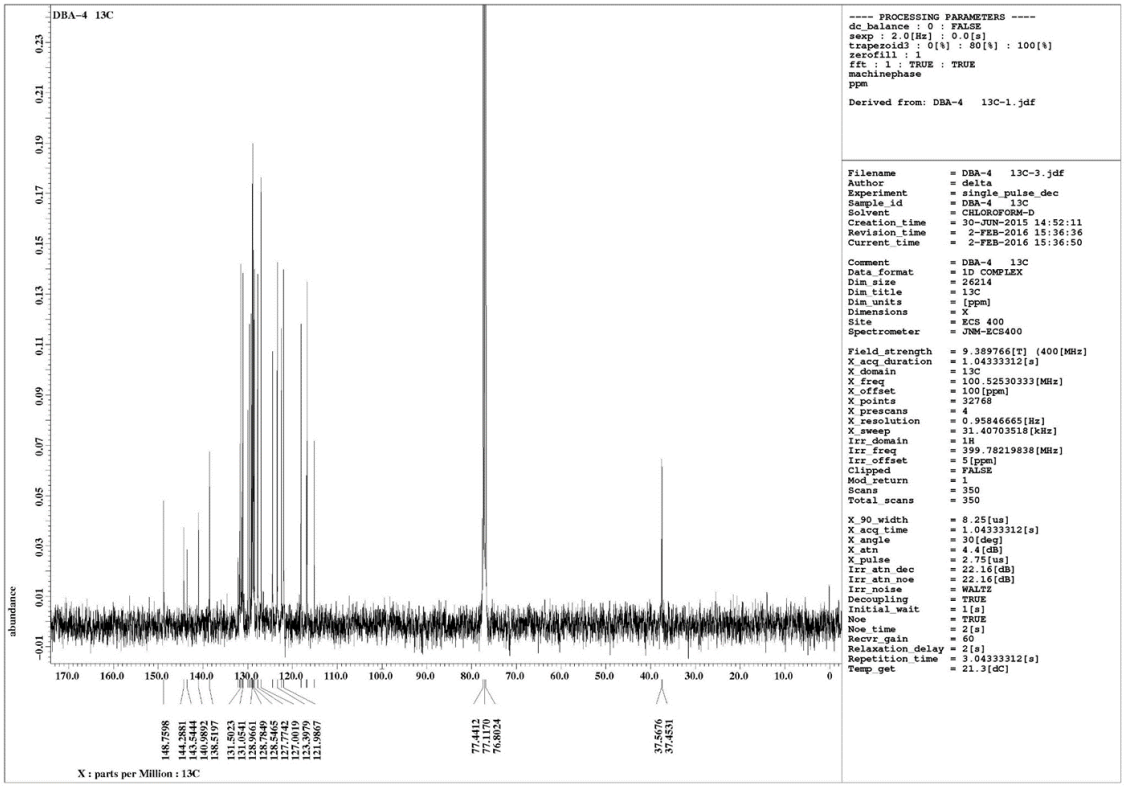


14-Phenyl-7-(N-phenyl)-14H-dibenzo[a.j]acridine

^{1}H-NMR



^{13}C-NMR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X : parts per Million : 13C
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Site = ECS 400
Spectrometer = JNM-ECS400
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 350
Total_scans = 350
X_90_width = 8.25[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.4[dB]
X_pulse = 2.75[us]
Irr_atn_dec = 22.16[dB]
Irr_atn_noe = 22.16[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 21.3[dC]