



**Supporting Information**

**Design and Evaluation of the Thermal Properties of Di-, Tri- and Tetra-Azido-Esters**

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Deepak Kumar, Shaibal Banerjee<sup>\*\*</sup>**

*Organic Synthesis Laboratory, Defence Institute of Advanced Technology,  
(DU), Girinagar, 411025 Pune (Maharashtra), India*

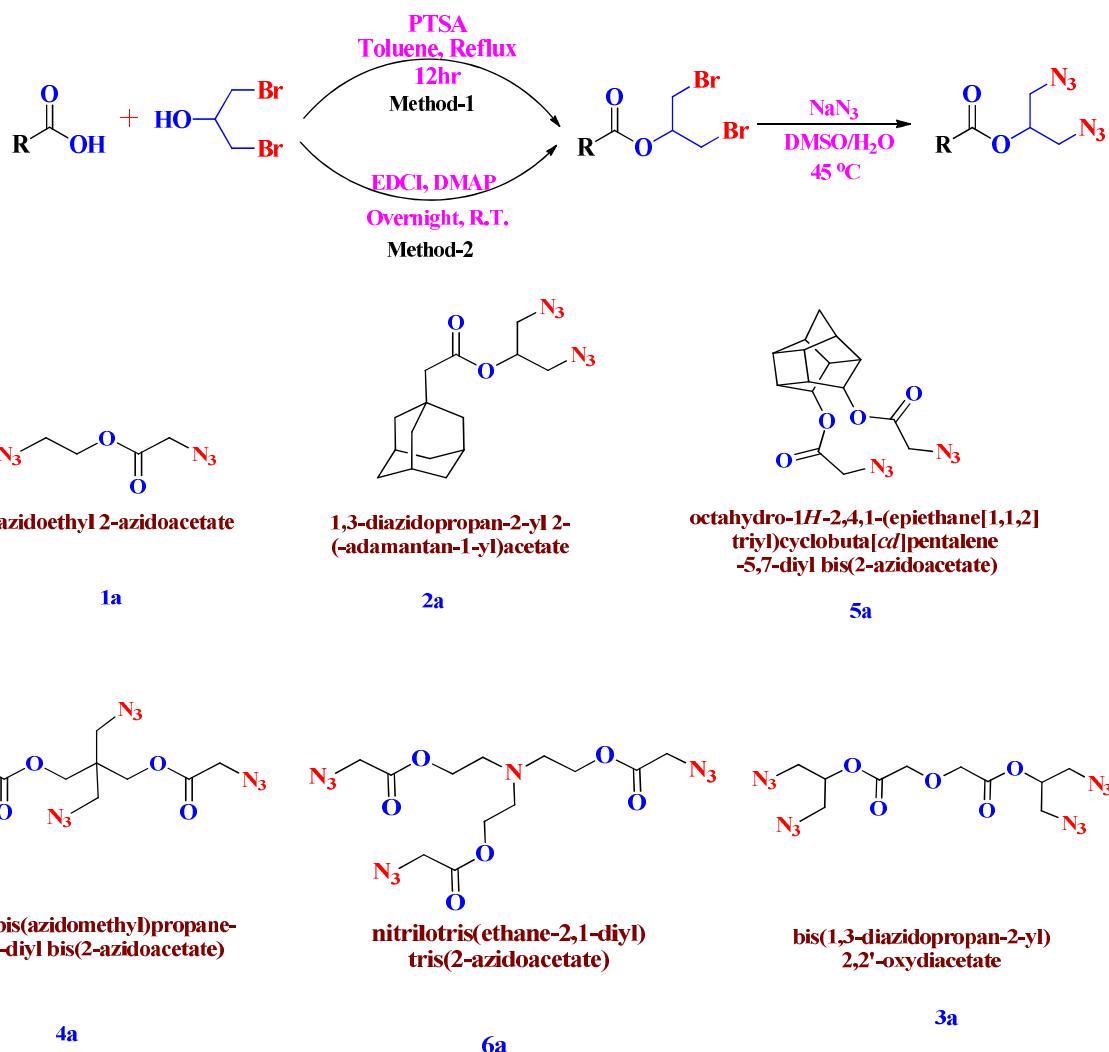
\*E-mail: shaibal.b2001@gmail.com

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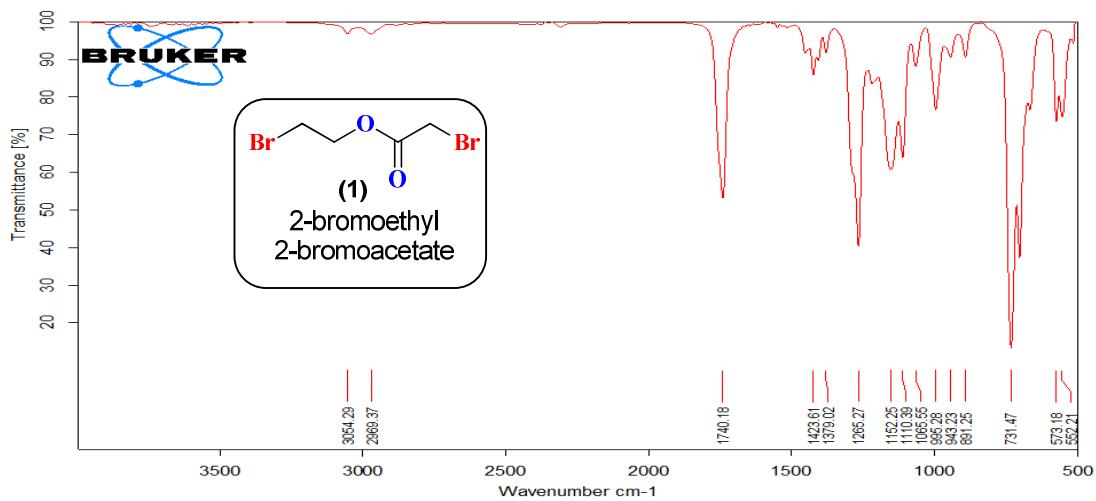
**General Information:**

General Materials: All chemicals and organic solvents were obtained from commercial suppliers and used without further purification. All the reactions were monitored by precoated silica gel 60 F<sub>254</sub> (Merck) TLC plates. Gaussain09 used for computational or DFT calculations.

## Synthetic Scheme and Molecules:

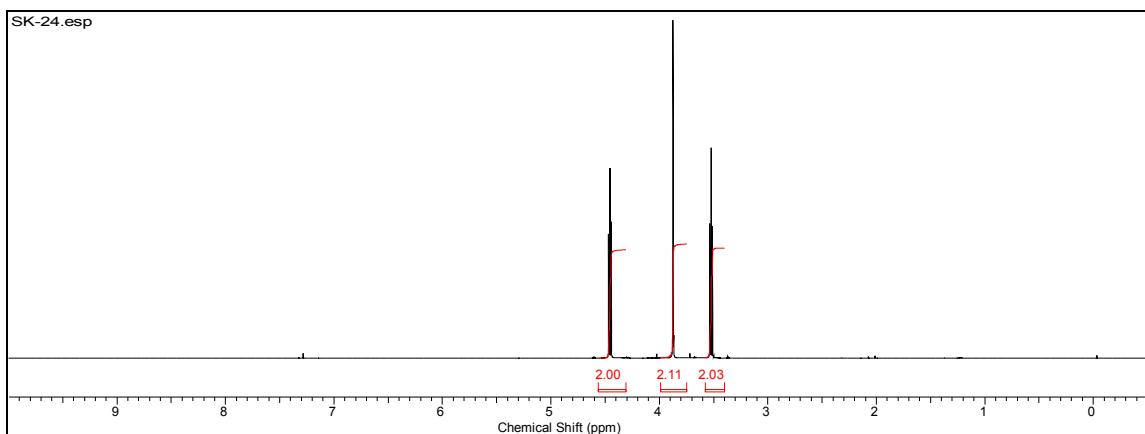


**FT-IR,  $^1\text{H}$  &  $^{13}\text{C}$ -NMRs:**

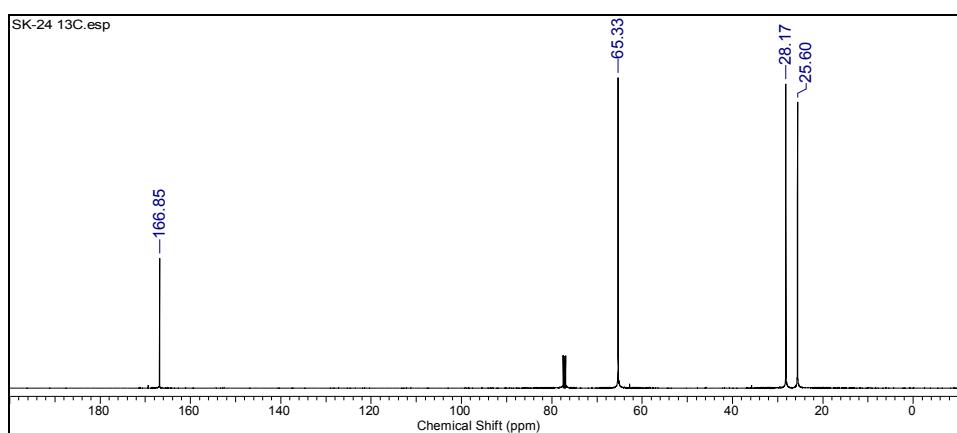


**Fig**

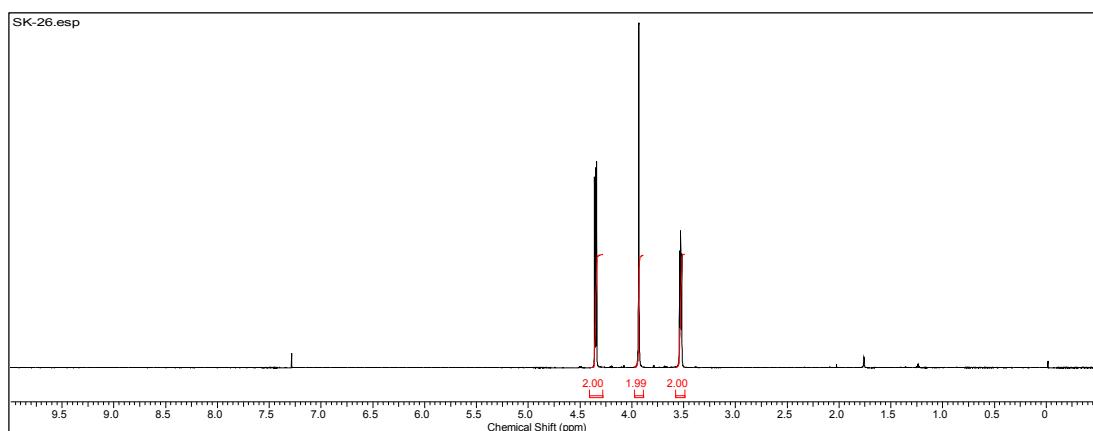
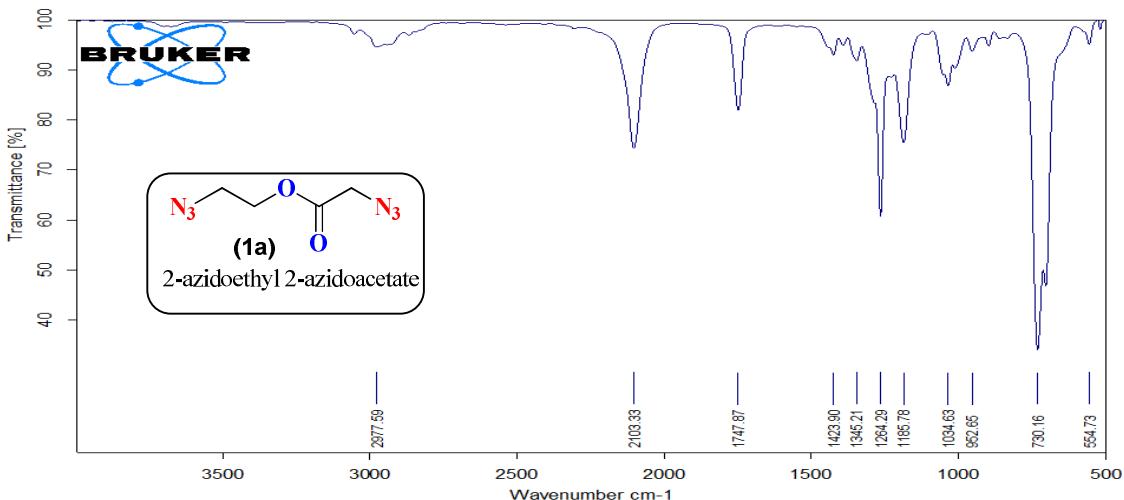
**ure 2.1(a): FT-IR spectrum of 2-bromoethyl 2-bromoacetate (1)**



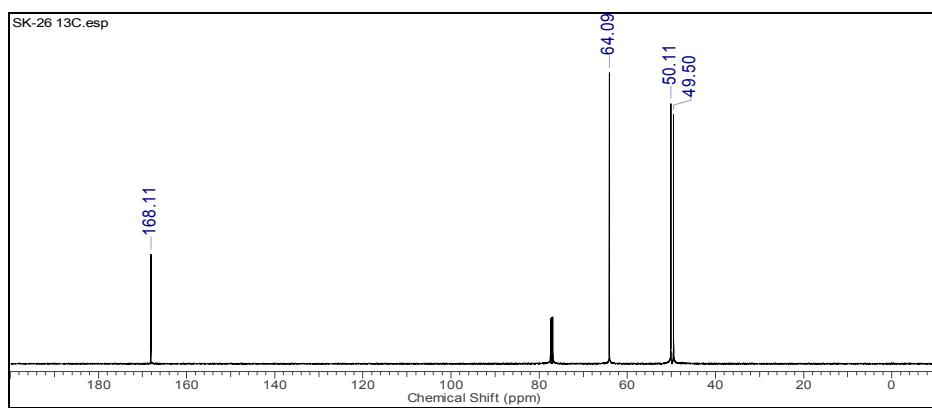
**Figure 2.1(b):  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of 2-bromoethyl 2-bromoacetate (1)**



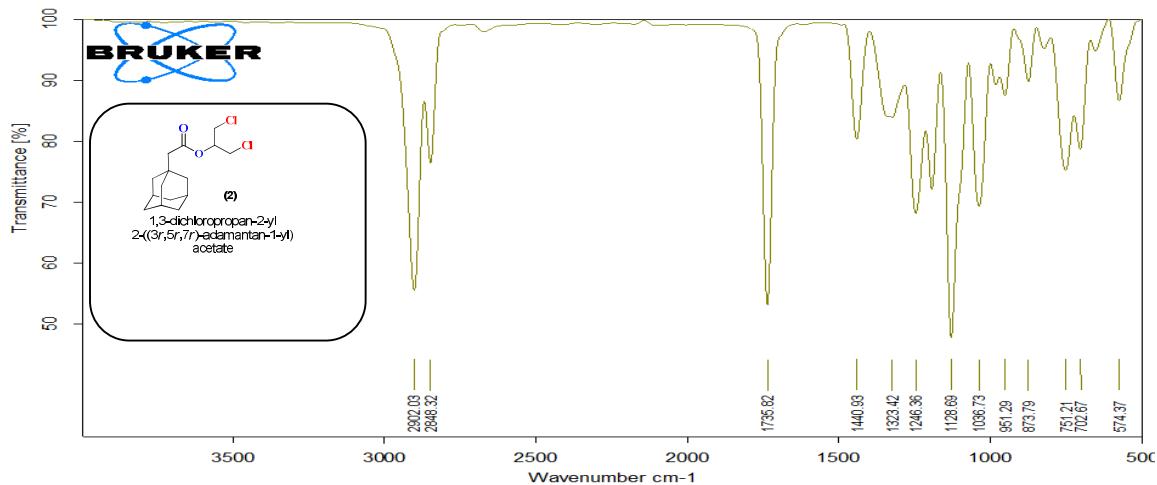
**Figure 2.1(c):  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of 2-bromoethyl 2-bromoacetate (1)**



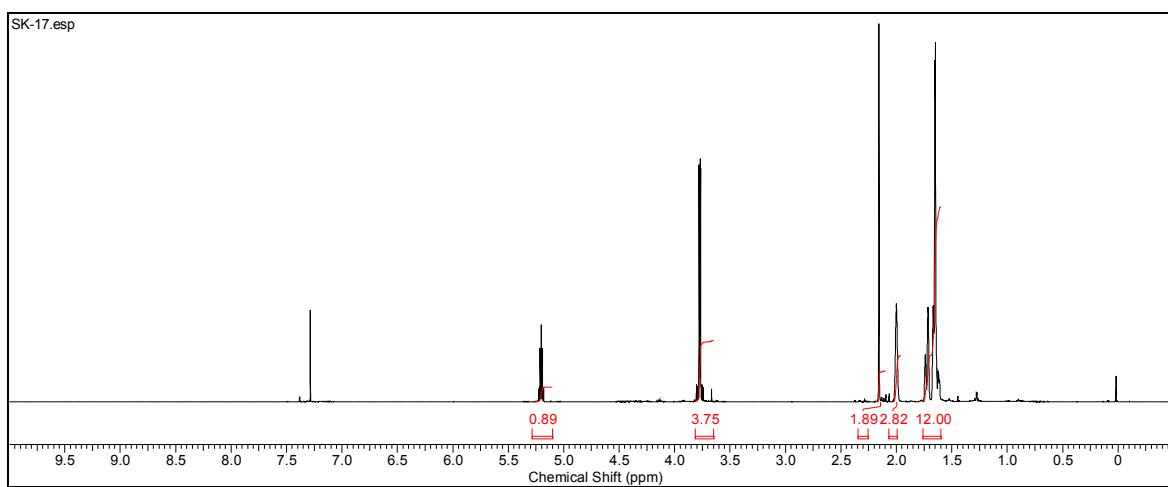
**Figure 2.2(b):**  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of 2-azidoethyl 2-azidoacetate (2a)



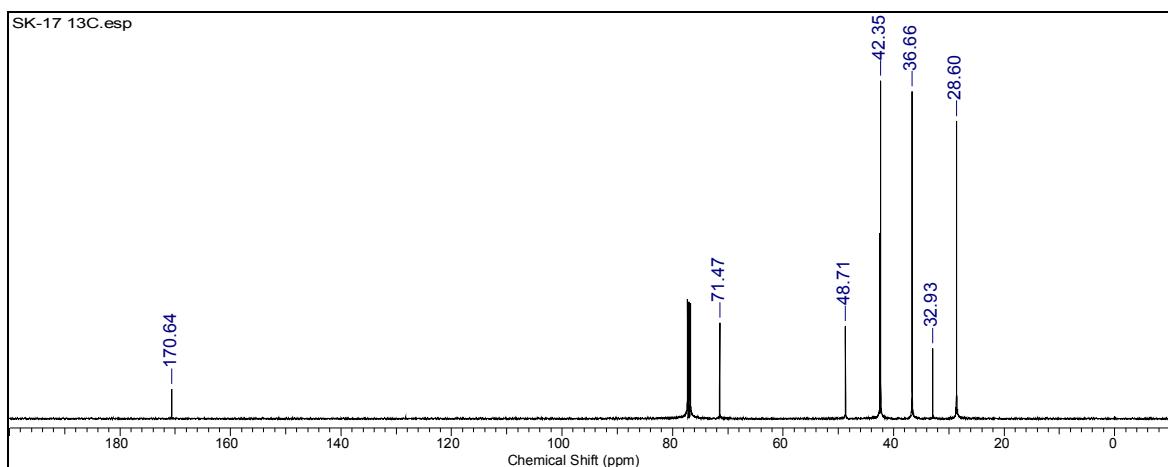
**Figure 2.2(c):**  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of 2-azidoethyl 2-azidoacetate (2a)



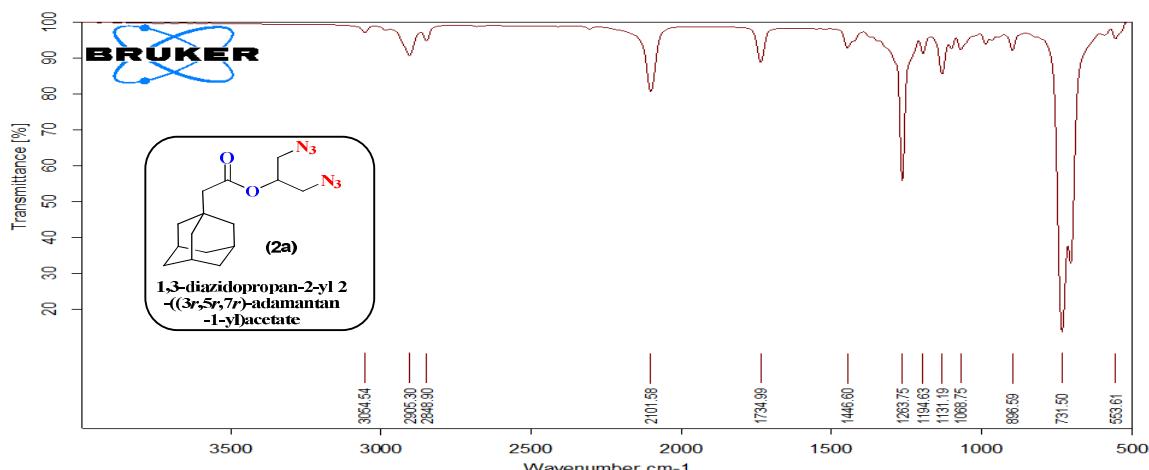
**$^1H$  NMR (500MHz,  $CDCl_3$ )**



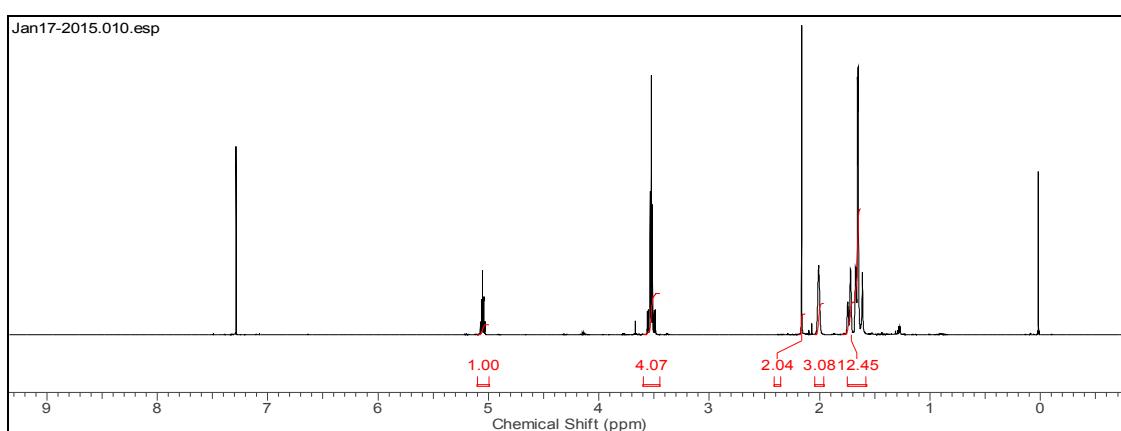
**$^{13}C$  NMR (125MHz,  $CDCl_3$ )**



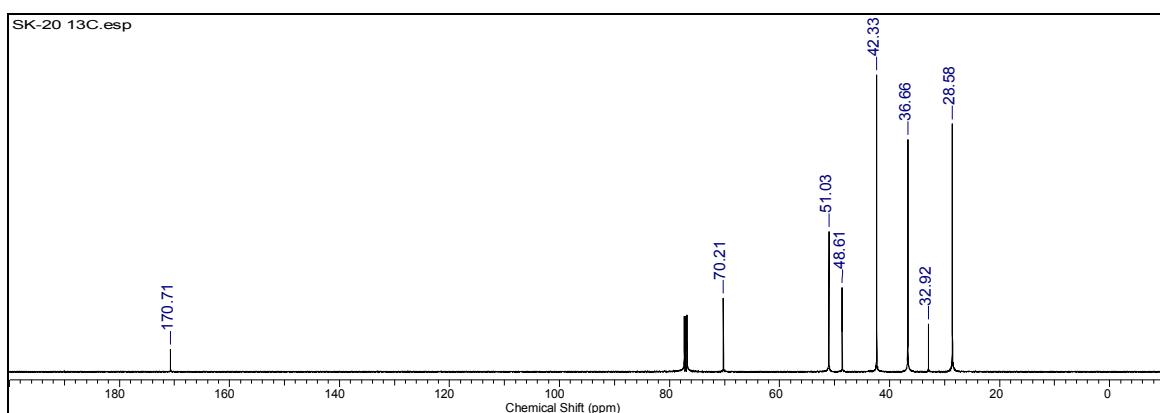
**FT-IR spectrum**



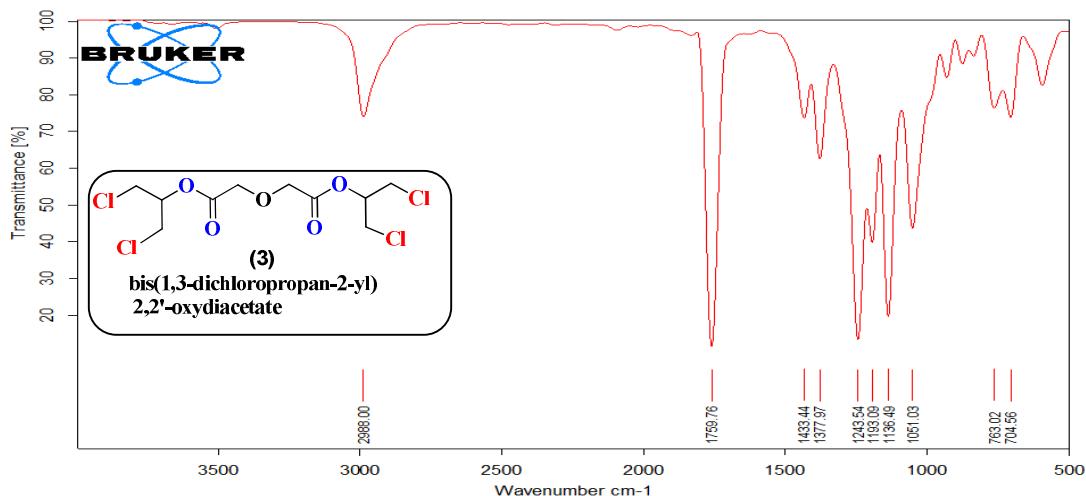
*<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>)*



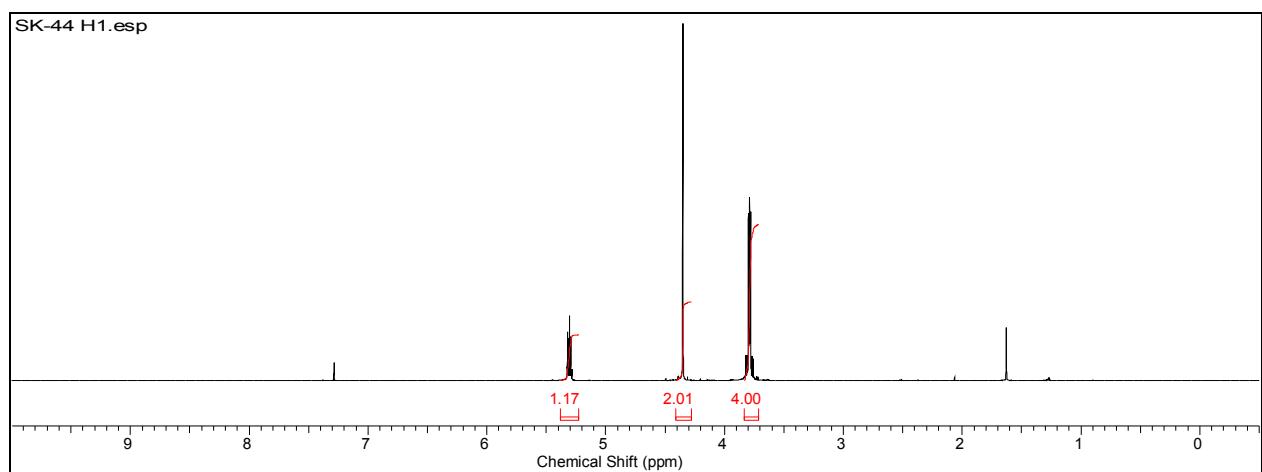
*<sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>)*



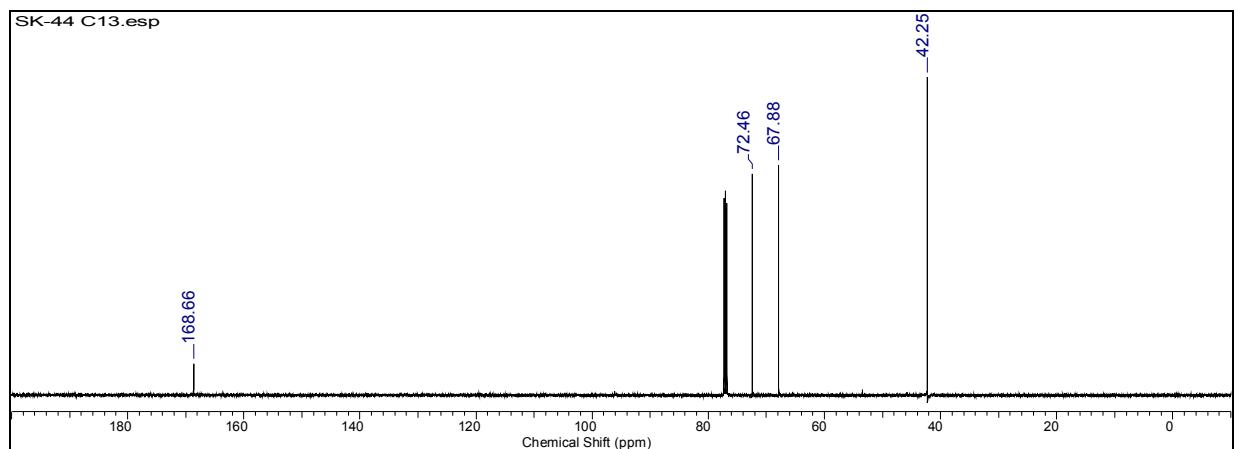
*FT-IR spectrum*



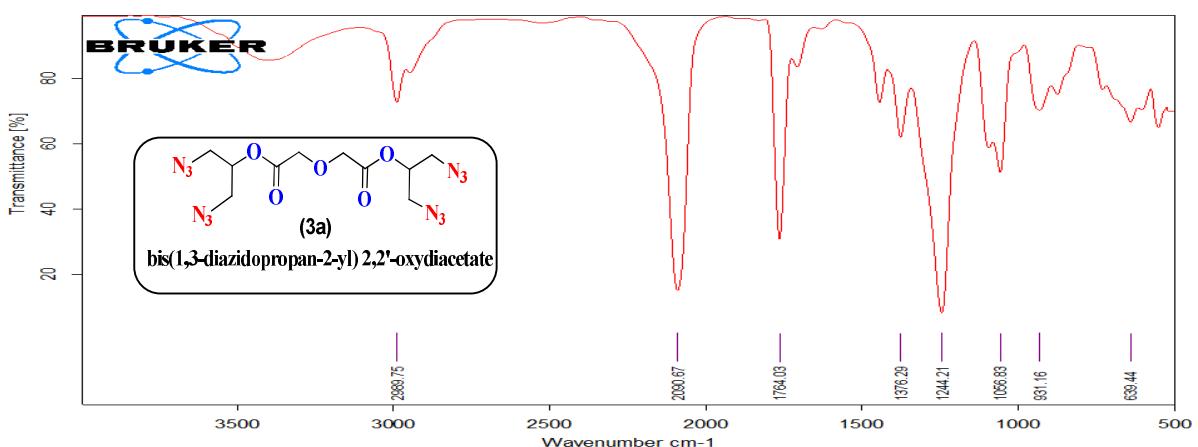
*<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>)*



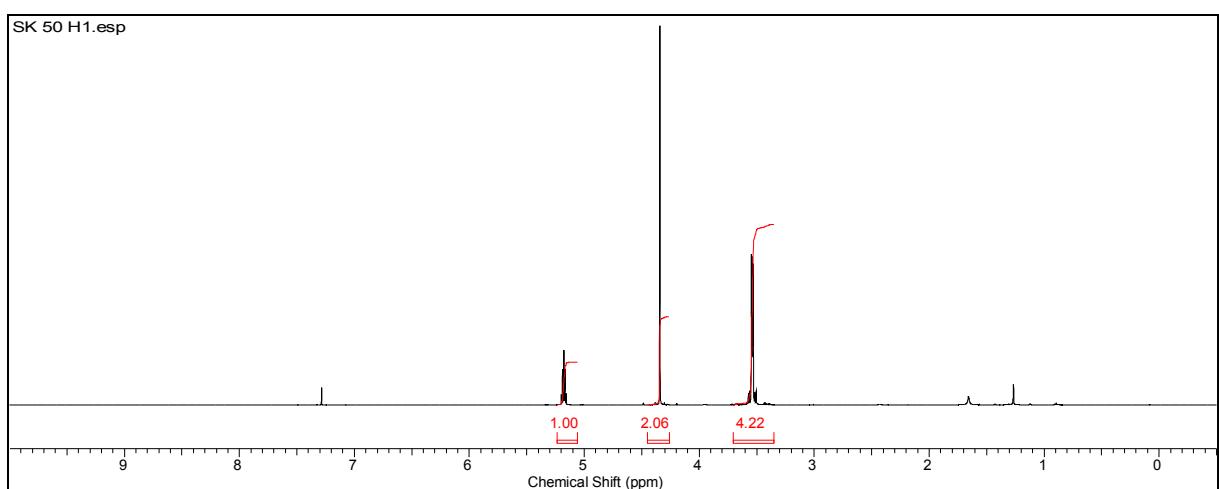
*<sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>)*



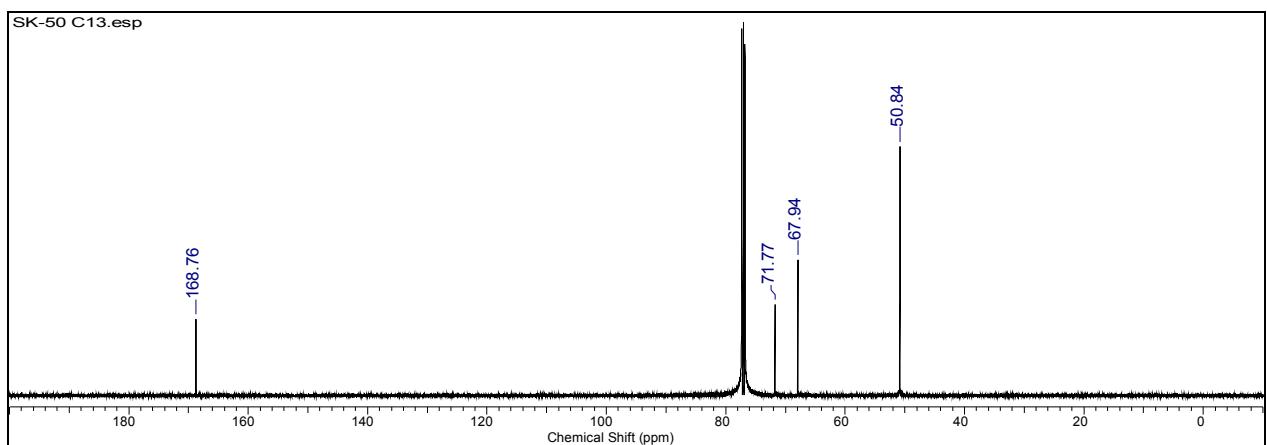
*FT-IR spectrum*

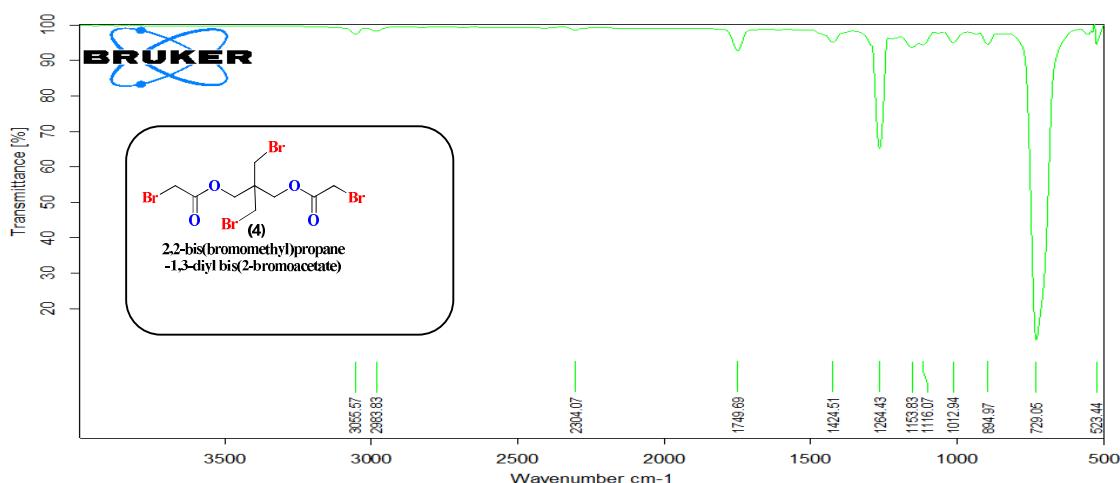


<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>)

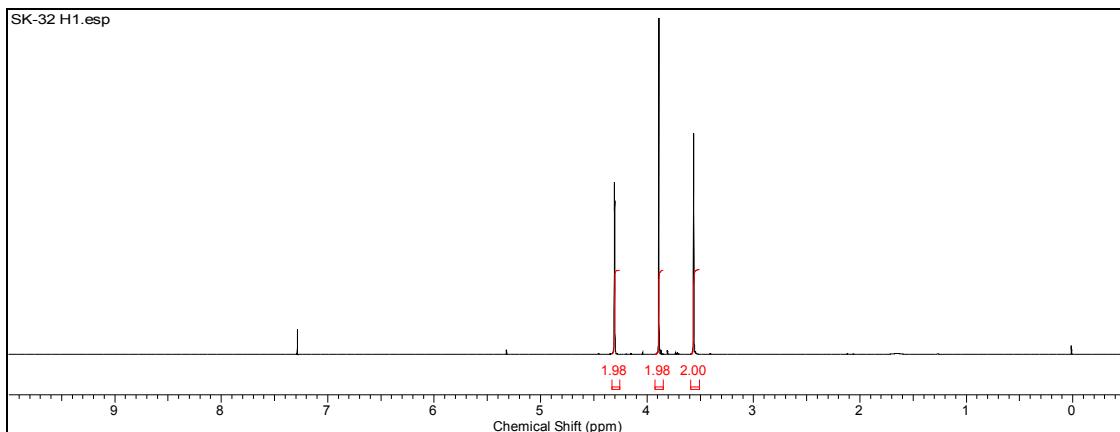


<sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>)

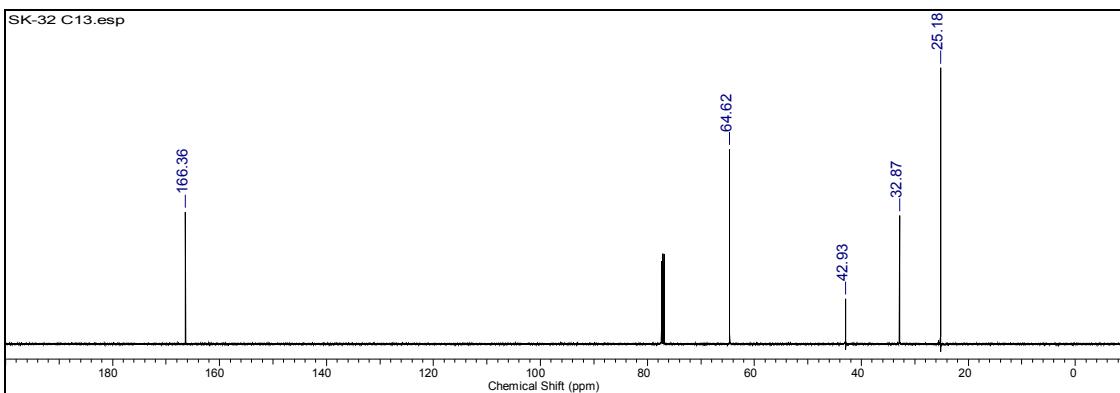




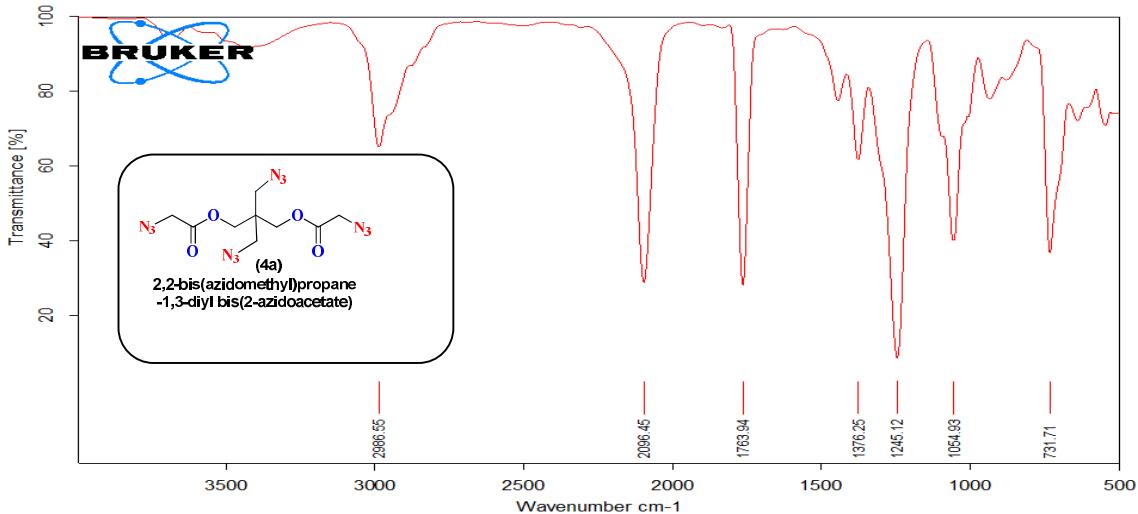
**Figure 2.7(a): FT-IR spectrum of 2,2-bis(bromomethyl)propane -1,3-diyl bis(2-bromoacetate) (7)**



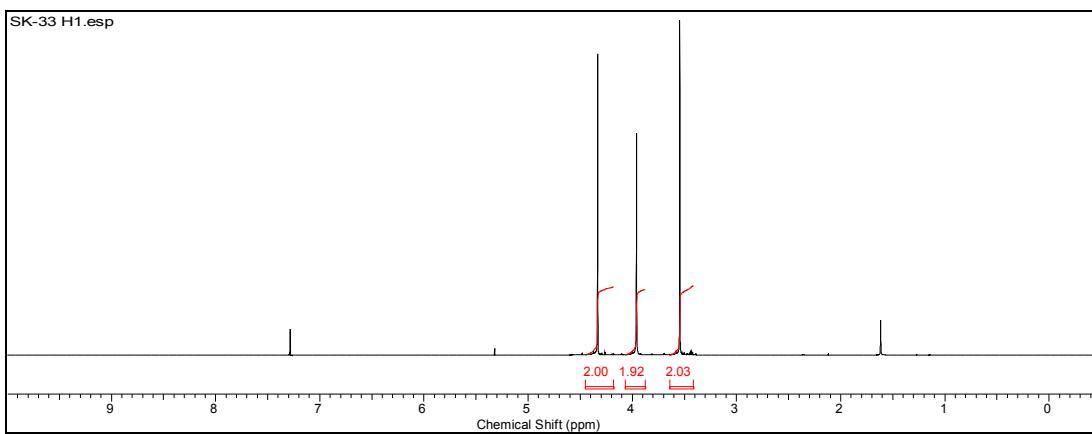
**Figure 2.7(b):  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of 2,2-bis(bromomethyl)propane -1,3-diyl bis(2-bromoacetate) (7)**



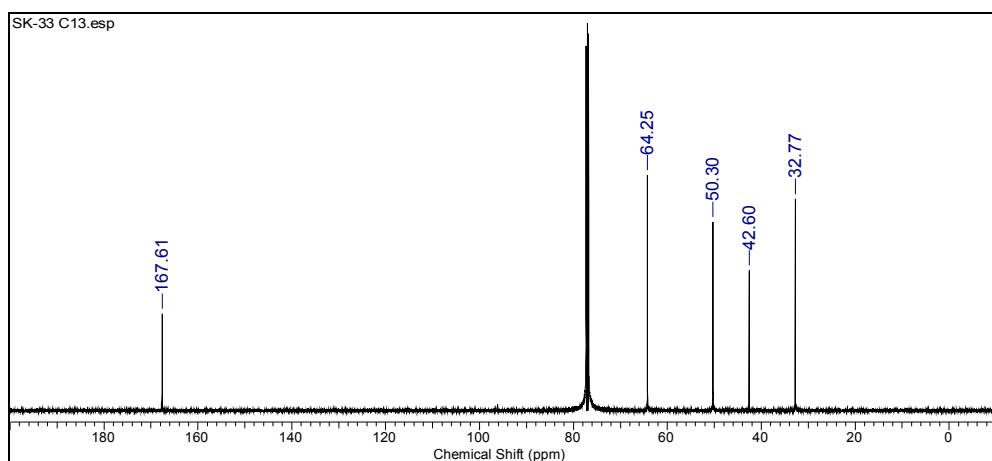
**Figure 2.7(c):  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of 2,2-bis(bromomethyl)propane -1,3-diyl bis(2-bromoacetate) (7)**



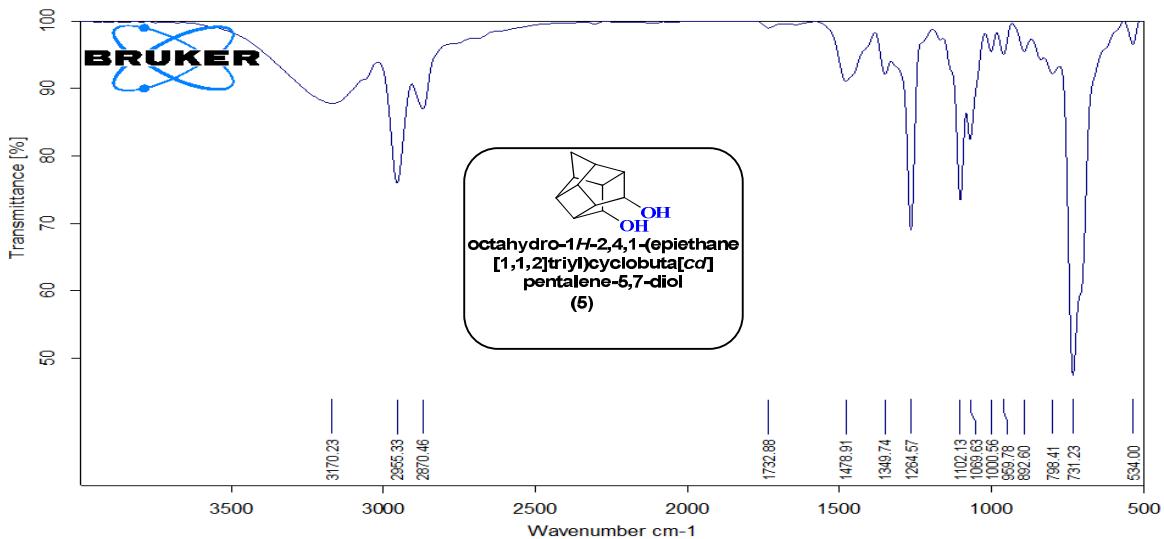
**Figure 2.8(a): FT-IR spectrum of 2,2-bis(azidomethyl)propane -1,3-diyl bis(2-azidoacetate)**



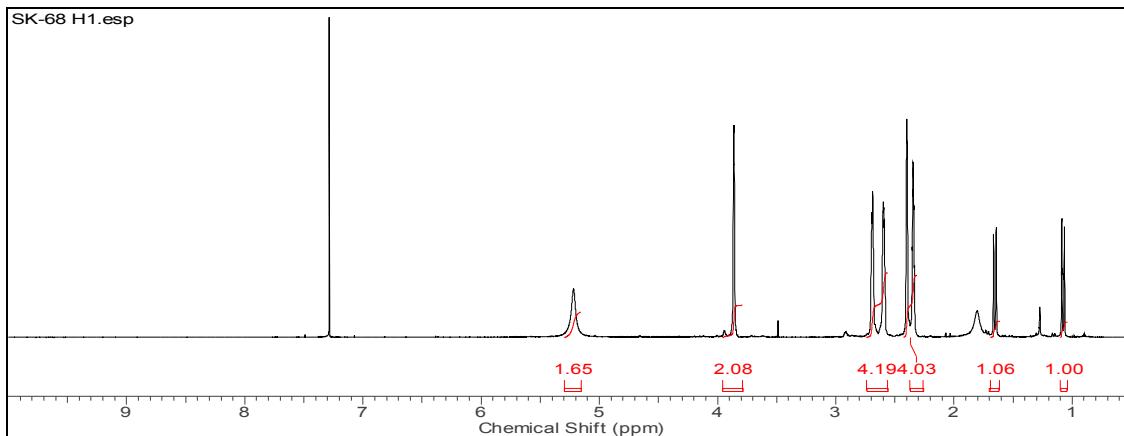
**Figure 2.8(b): <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of 2,2-bis(azidomethyl)propane-1,3-diyl bis(2-azidoacetate)**



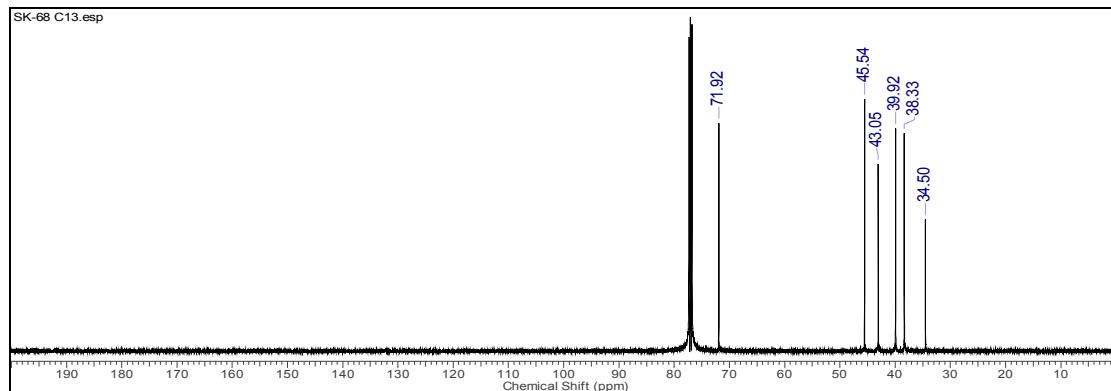
**Figure 2.8(b): <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) of 2,2-bis(azidomethyl)propane-1,3-diyl bis(2-azidoacetate)**



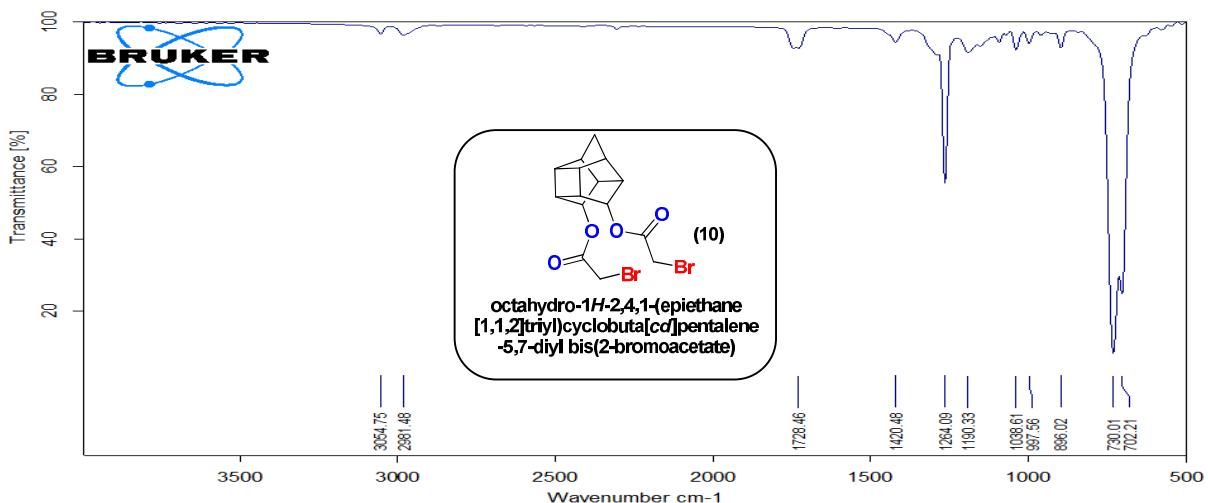
**Figure 2.9(a):** FT-IR spectrum of octahydro-1H-2,4,1(epiethane[1,1,2]triy)cyclobuta[cd]pentalene-5,7-diol (9)



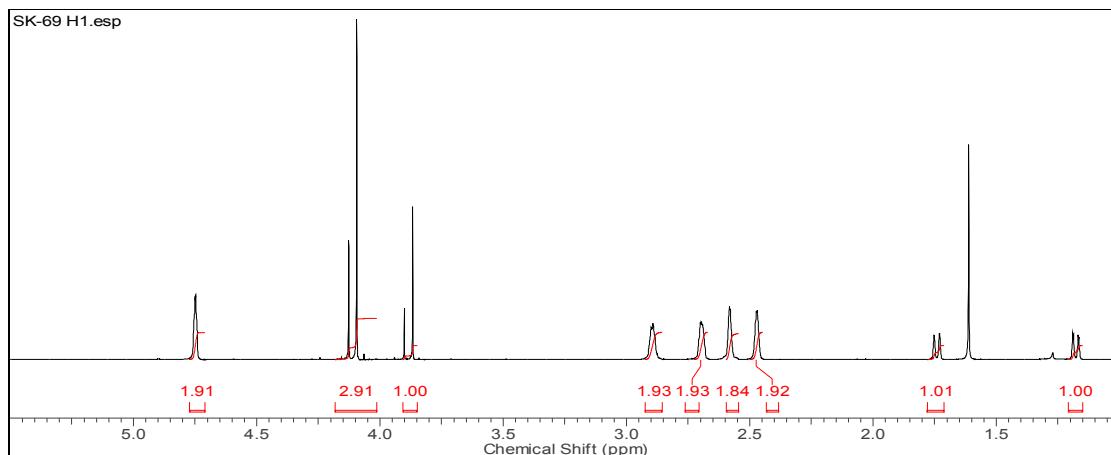
**Figure 2.9(b):**  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of octahydro-1H-2,4,1(epiethane[1,1,2]triy)cyclobuta[cd]pentalene-5,7-diol (9)



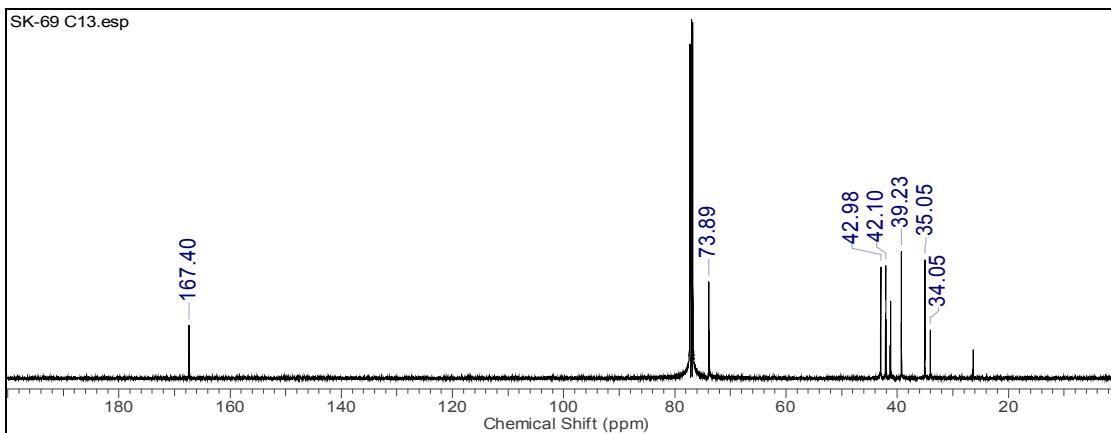
**Figure 2.9(c):**  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of octahydro-1H-2,4,1(epiethane[1,1,2]triy)cyclobuta[cd]pentalene-5,7-diol (9)



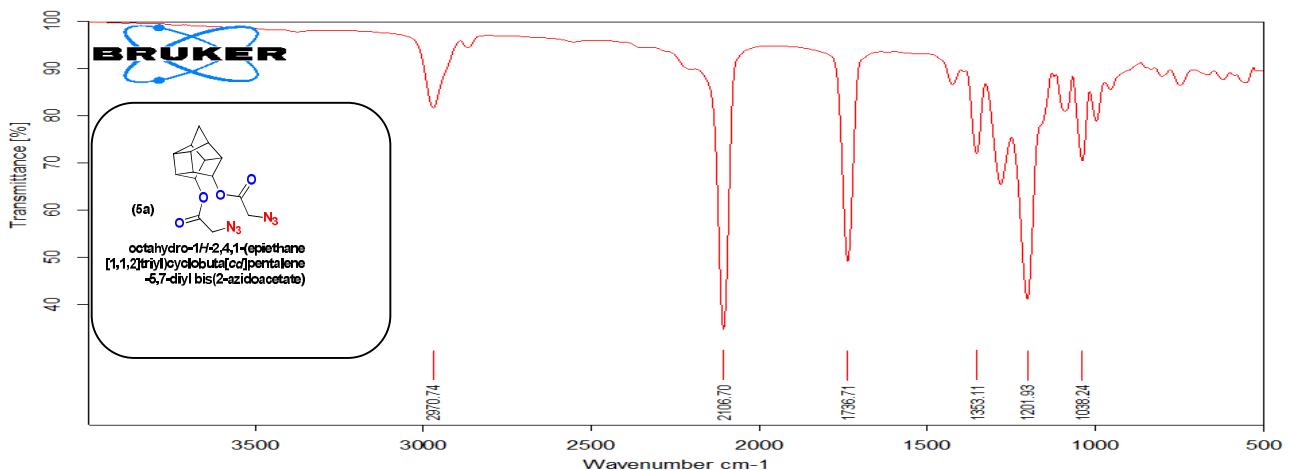
**Figure 2.10(a): FT-IR spectrum of octahydro-1H-2,4,1-(epiethane[1,1,2]triy)cyclobuta[cd]pentalene-5,7-diyl bis(2-bromoacetate) (10)**



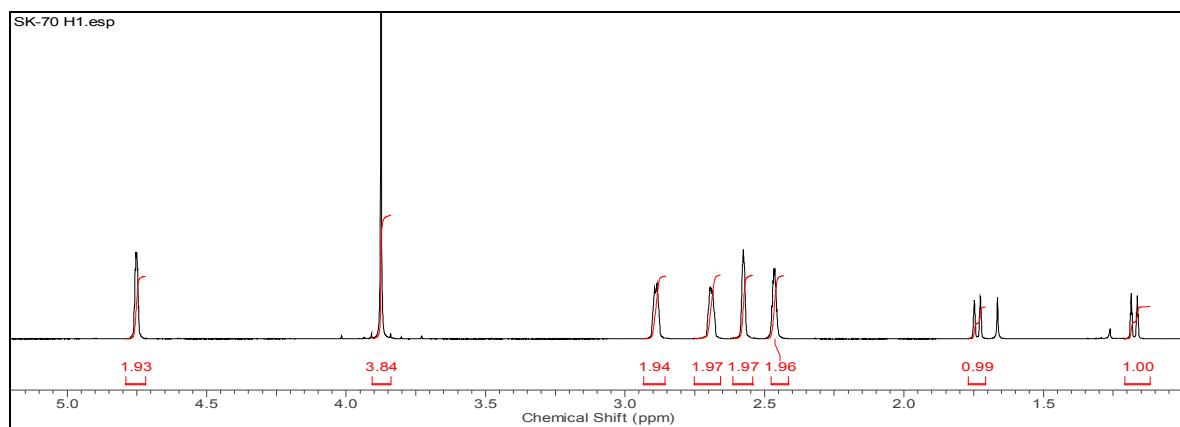
**Figure 2.10(b):  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ ) of octahydro-1H-2,4,1-(epiethane[1,1,2]triy)cyclobuta[cd]pentalene-5,7-diyl bis(2-bromoacetate) (10)**



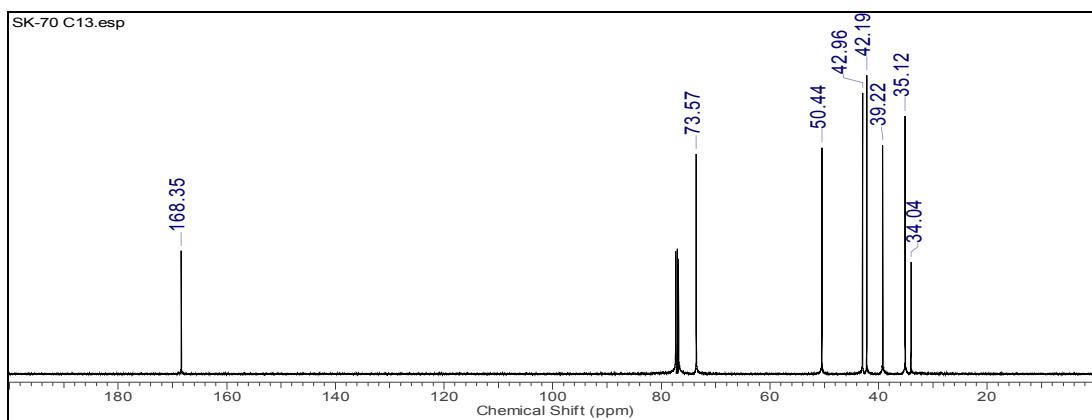
**Figure 2.10(c):  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ ) of octahydro-1H-2,4,1-(epiethane[1,1,2]triy)cyclobuta[cd]pentalene-5,7-diyl bis(2-bromoacetate) (10)**



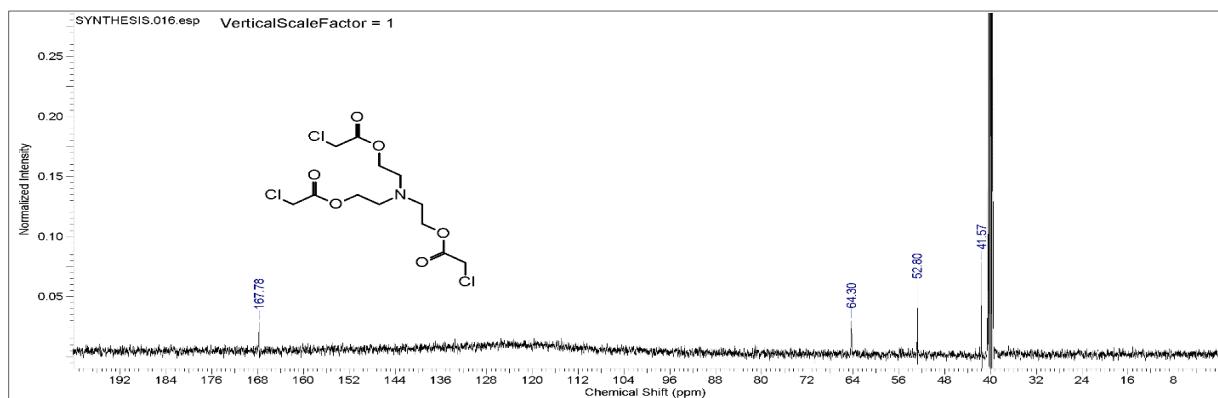
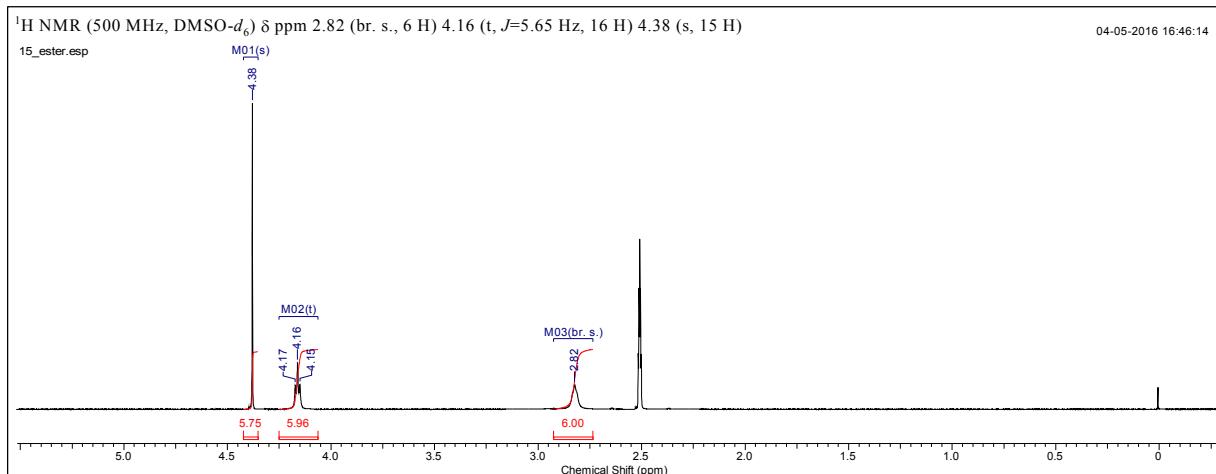
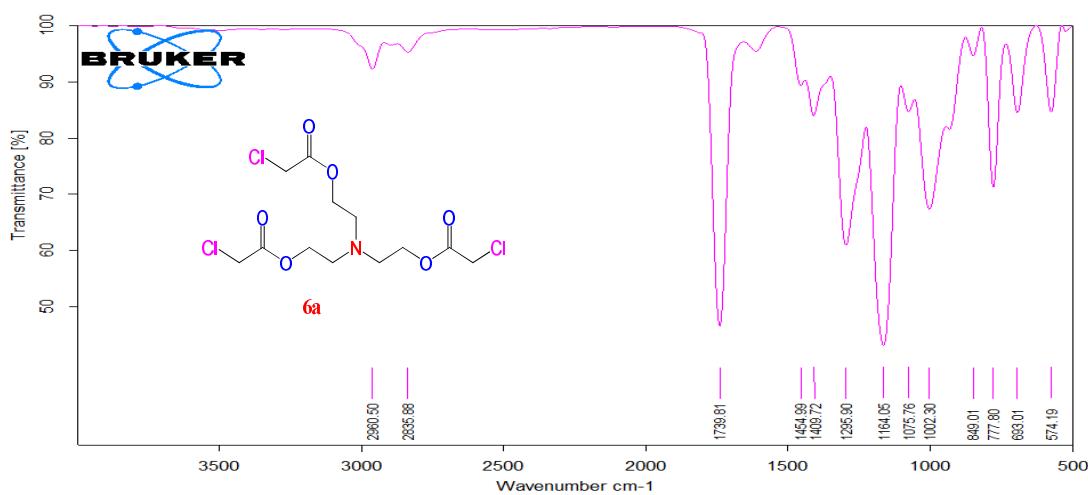
**Figure 2.11(a):** FT-IR spectrum of octahydro-1H-2,4,1-(epiethane[1,1,2]triy) cyclobuta[cd]pentalene-5,7-diyl bis(2-azidoacetate)

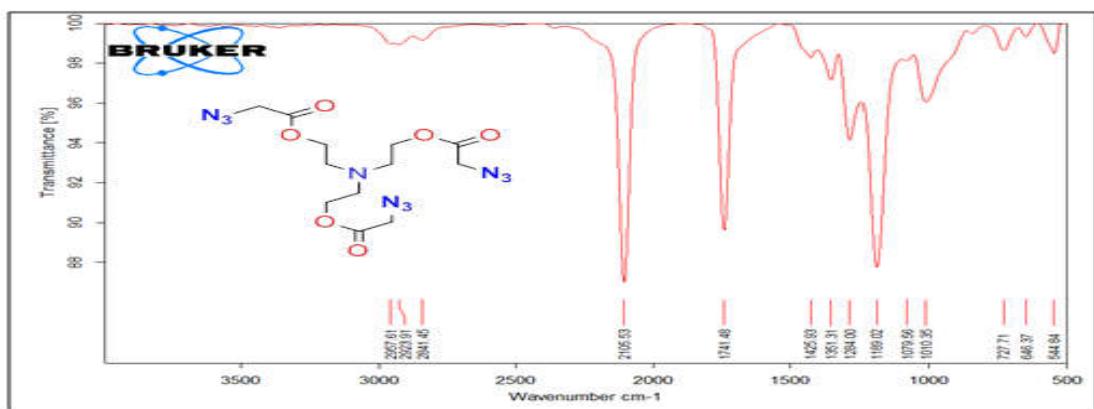


**Figure 2.11(b):** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) of octahydro-1H-2,4,1-(epiethane[1,1,2]triy) cyclobuta[cd]pentalene-5,7-diyl bis(2-azidoacetate) (11e)



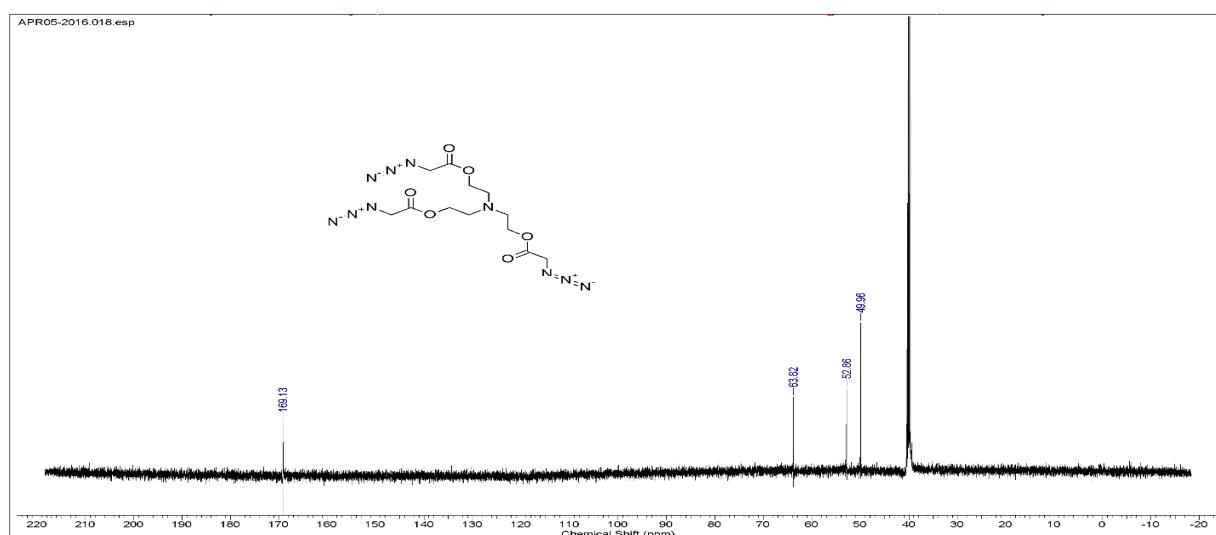
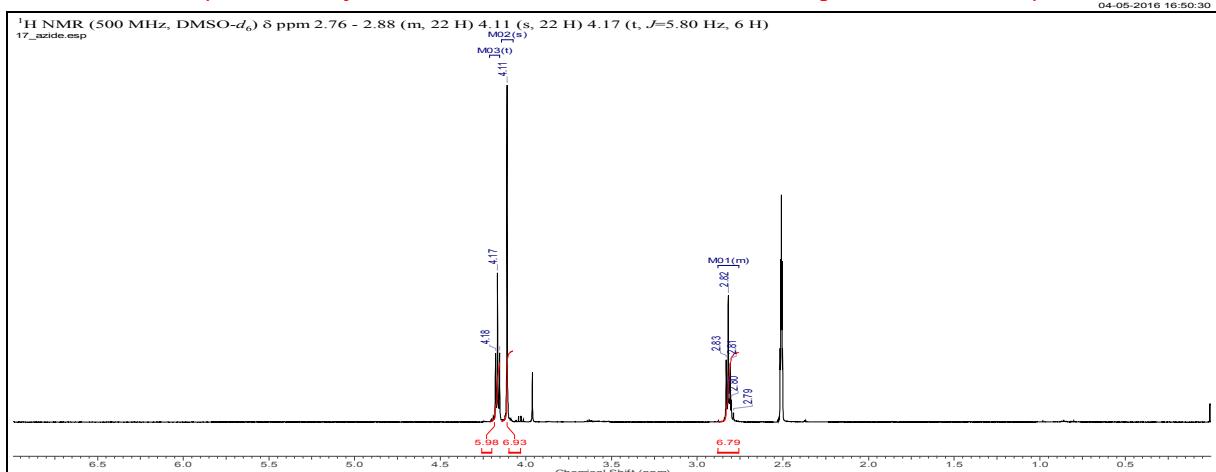
**Figure 2.11(c):** <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) of octahydro-1H-2,4,1-(epiethane[1,1,2]triy) cyclobuta[cd]pentalene-5,7-diyl bis(2-azidoacetate)





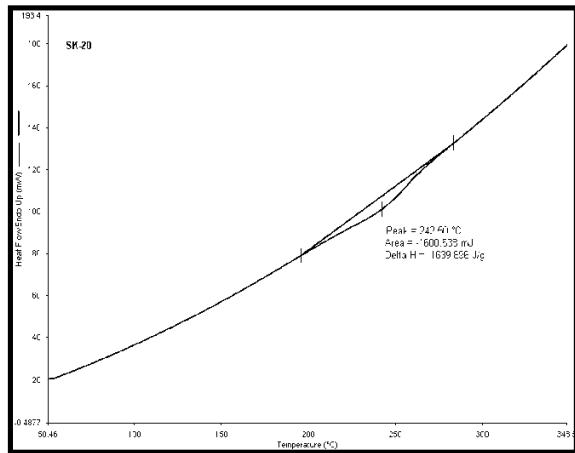
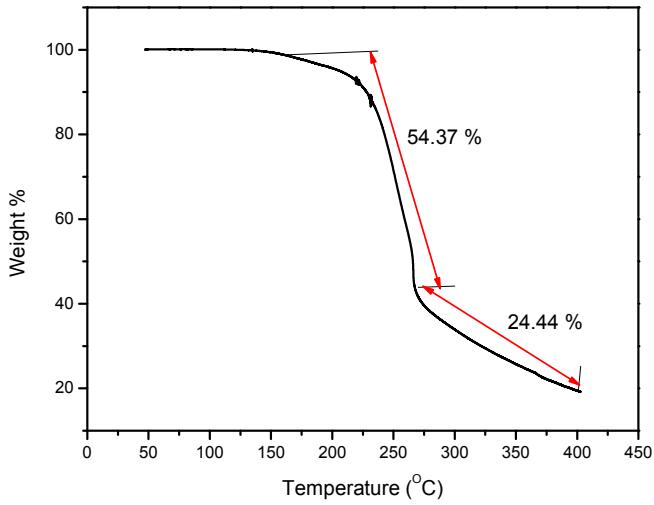
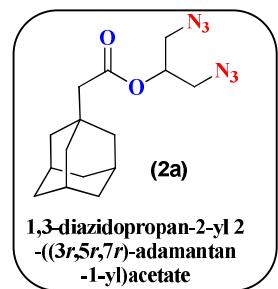
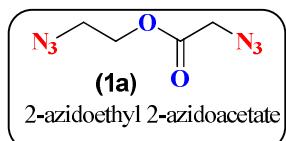
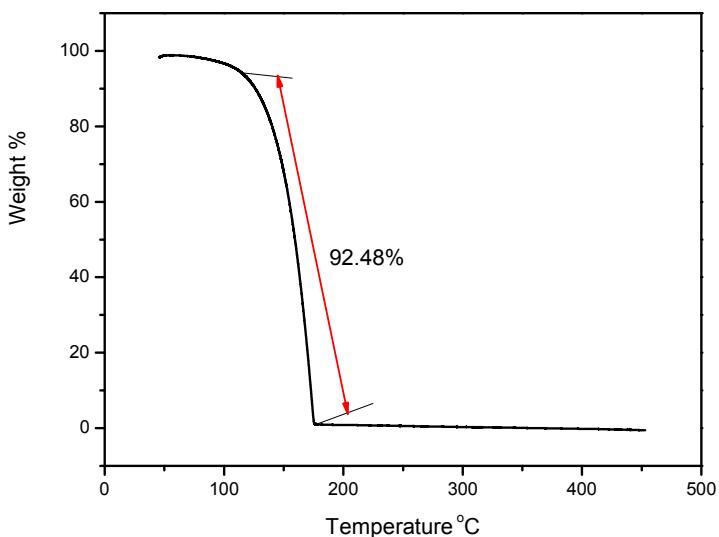
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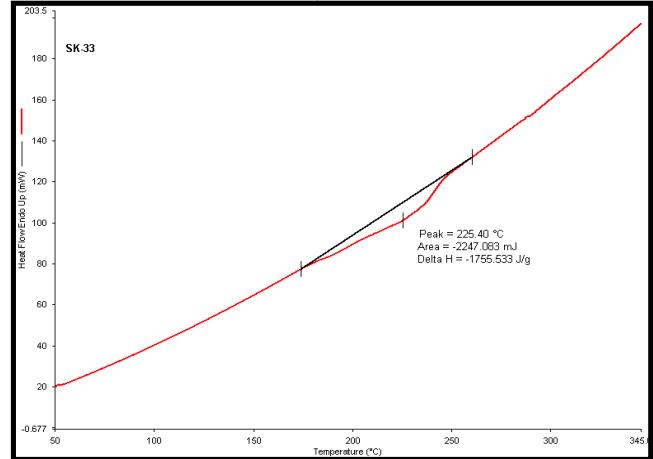
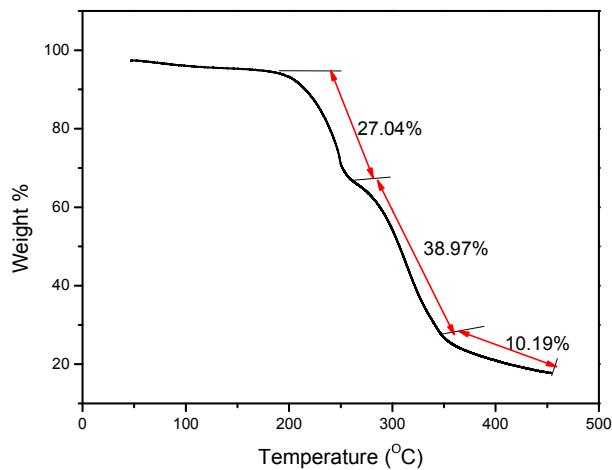
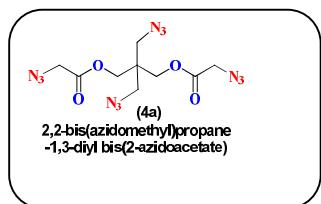
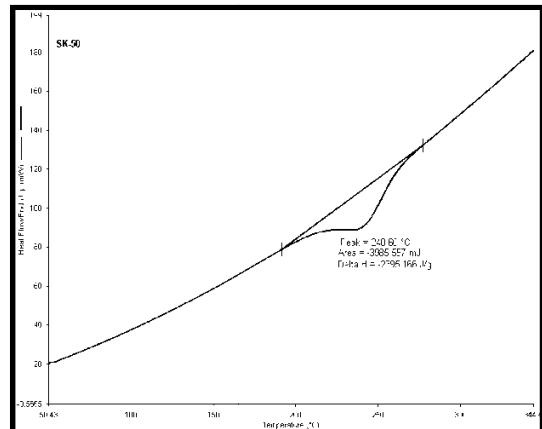
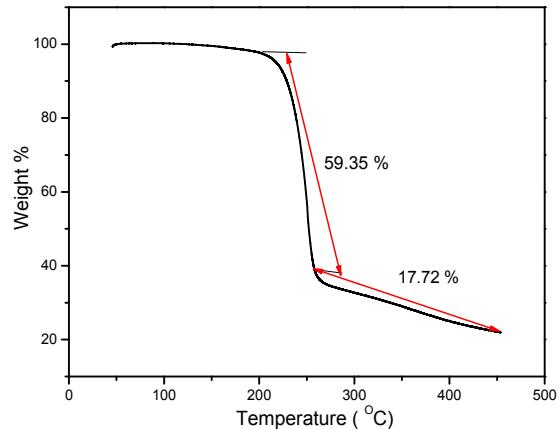
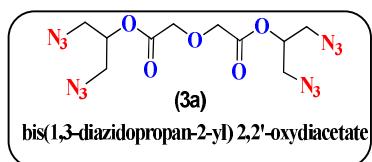
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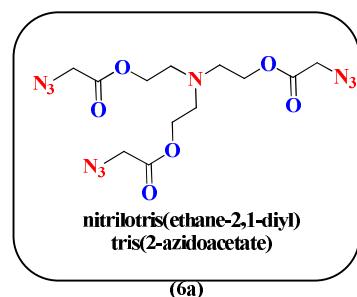
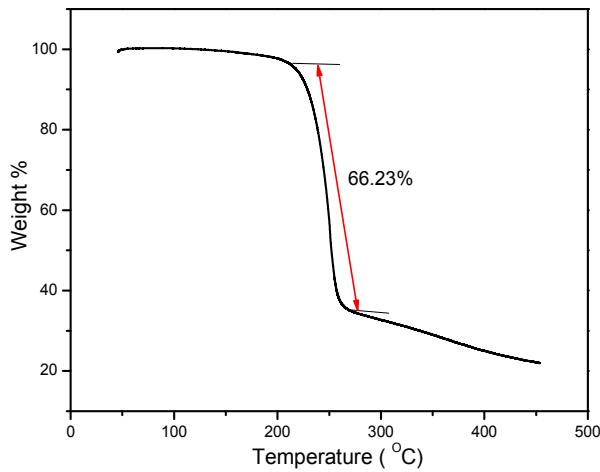
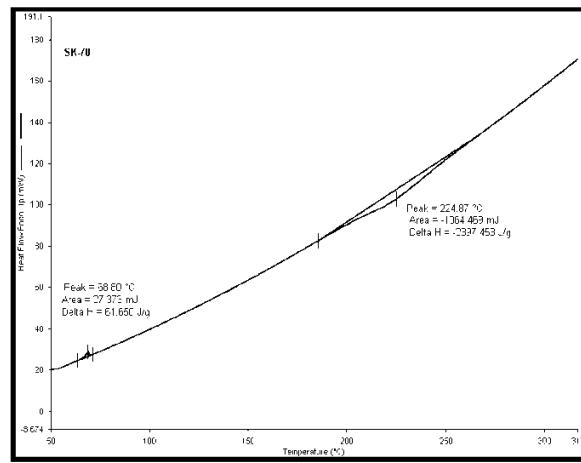
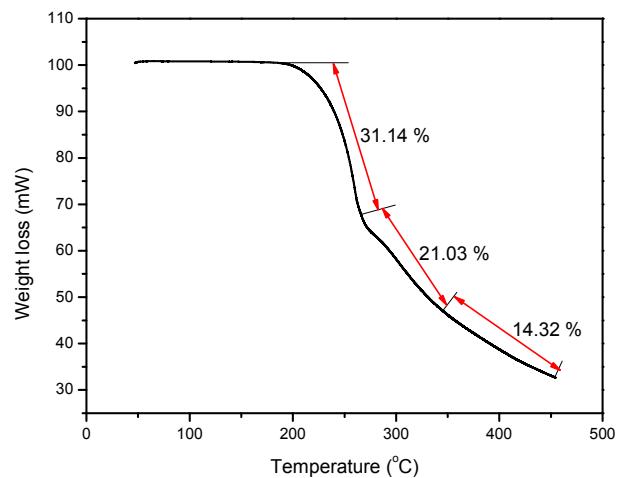
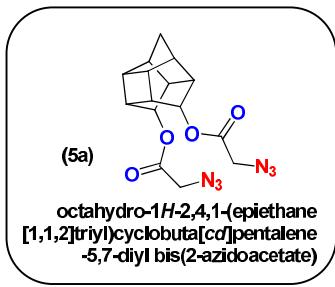


<sup>13</sup>C NMR Spectrum

## DSC and TGA Curves







Electron charge of molecules:

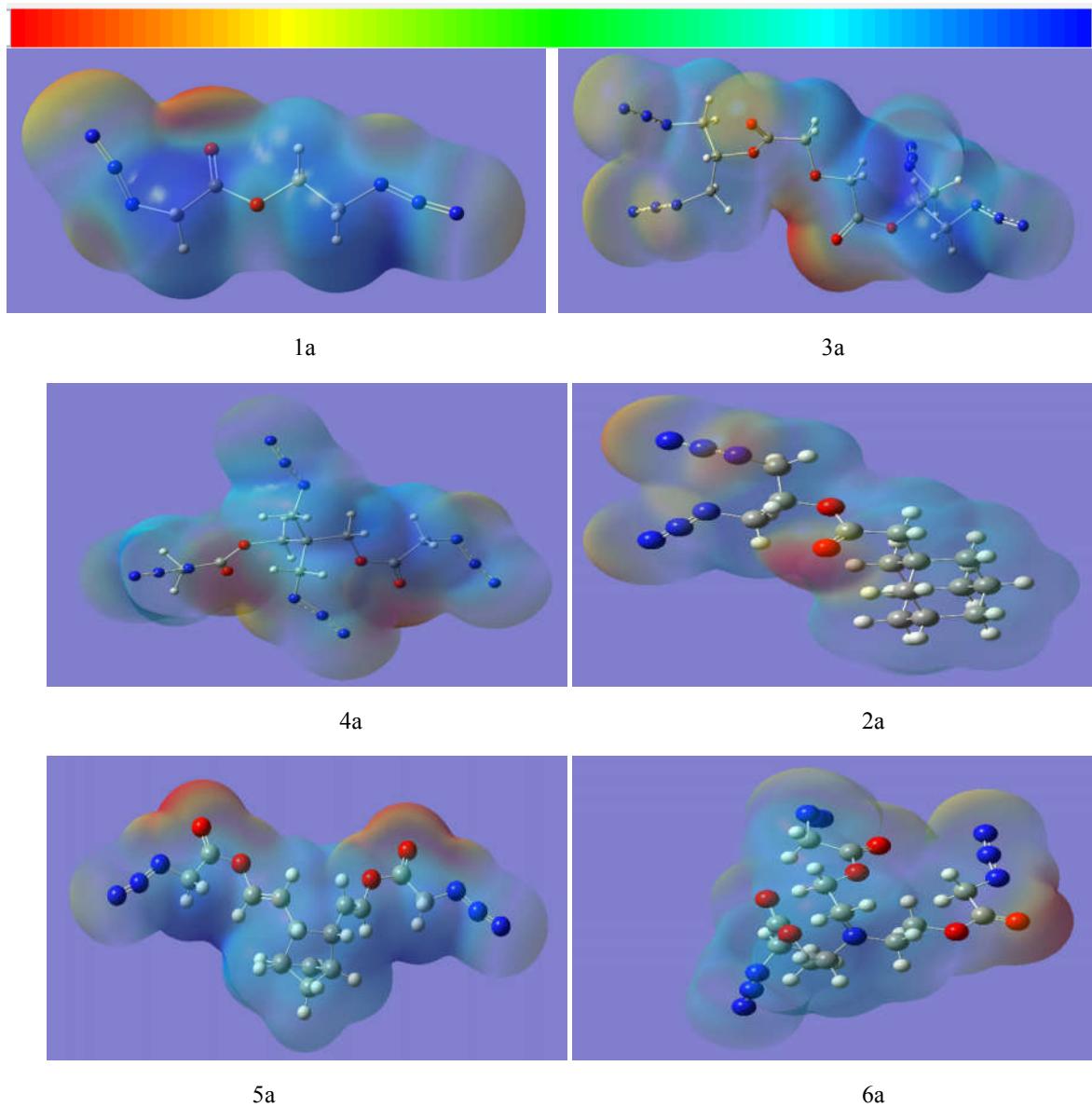


Fig. 6.1: Electron charge density on all the six molecules (M1 – M6)

Table 6.1: Value of electron charge on all three molecules

Molecule	Red color	Blue color
1a	-4.386e-2	4.386e-2
3a	-5.0828e-2	5.0828e-2
4a	-6.708e-2	6.708e-2

2a	-4.029e-2	4.029e-2
5a	-6.156e-2	6.156e-2
6a	-6.834e-2	6.834e-2

Here, we observed that in all molecules electron density is higher on the azido and ester group and lower on carbon atoms. It is due to the strong electron withdrawing effect along with the electronic repulsion within azido group due to several  $\pi$  bonds within a confined location.

### 1.1. IR Spectra

Theoretically determined IR values of M1 molecule are observed at (Neat,  $\text{cm}^{-1}$ ) 3032(C-H str), 2126 ( $\text{N}_3$  str), 1714 (C=O str), 1198 (C-O str) while experimentally reported values are at (Neat,  $\text{cm}^{-1}$ ) 2978 (C-H str) 2103 ( $\text{N}_3$  str) 1748 (C=O str) 1264 (C-O str).

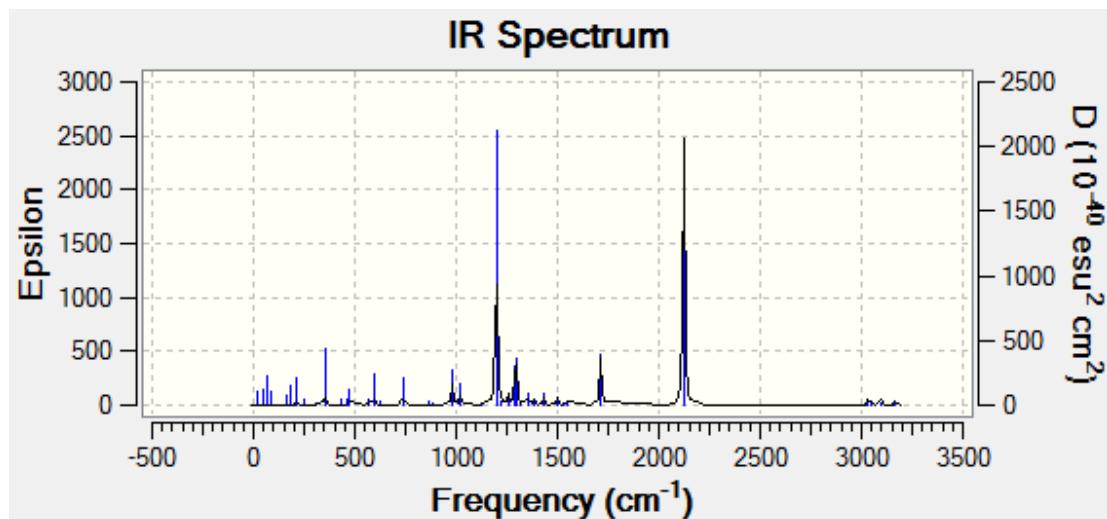


Fig. 6.2: IR-Spectrum of 1a (Theoretical)

In M2, (Neat,  $\text{cm}^{-1}$ ) 2994(C-H str), 2126( $\text{N}_3$  str), 1763(C=O str), 1230(C-C str) and experimental values of M-2 are shown at 2990 (C-H str) 2091 ( $\text{N}_3$  str) 1764 (C=O str) 1244 (C-O str), these values are matching.

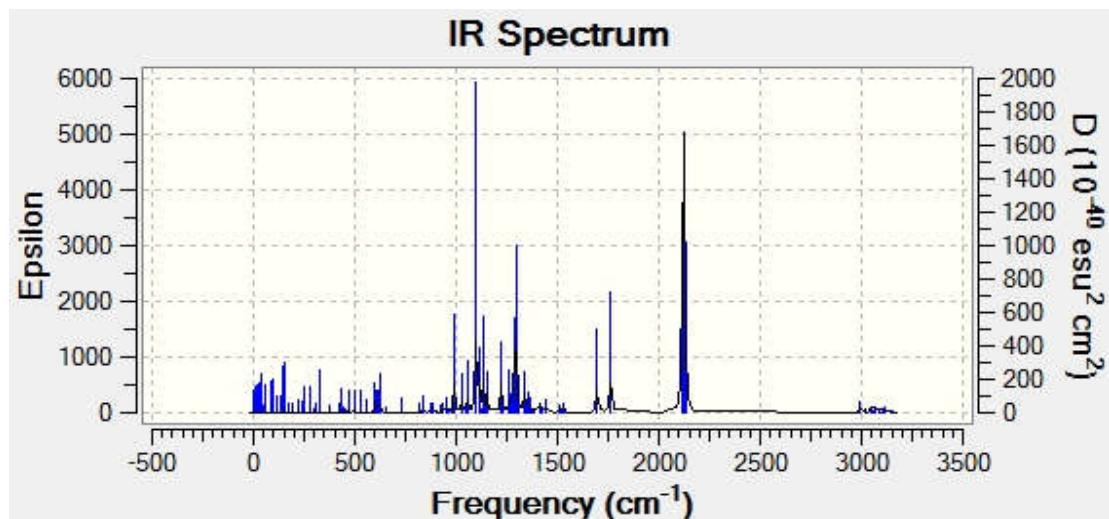


Fig. 6.3: IR-Spectrum of 3a (Theoretical)

In M3, (Neat, cm<sup>-1</sup>) 3037(C-H str), 2124(N<sub>3</sub> str), 1743(C=O str), 1232(C-C str) and experimental value are 2987 (C-H str) 2096 (N<sub>3</sub> str) 1764 (C=O str) 1245 (C-C str).

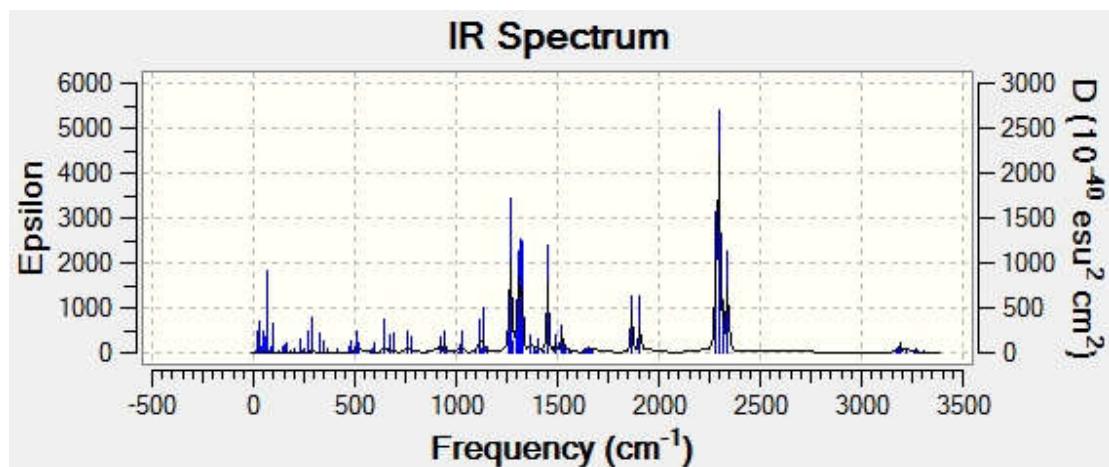


Fig. 6.4: IR-Spectrum of 4a (Theoretical)

In M4, (Neat, cm<sup>-1</sup>) 3037(C-H str), 2160 (N<sub>3</sub> str), 1743(C=O str), 1232(C-C str) and experimental value 2905 (C-H str), 2102 (N<sub>3</sub> str) 1735 (C=O str), 1264 (C-O str).

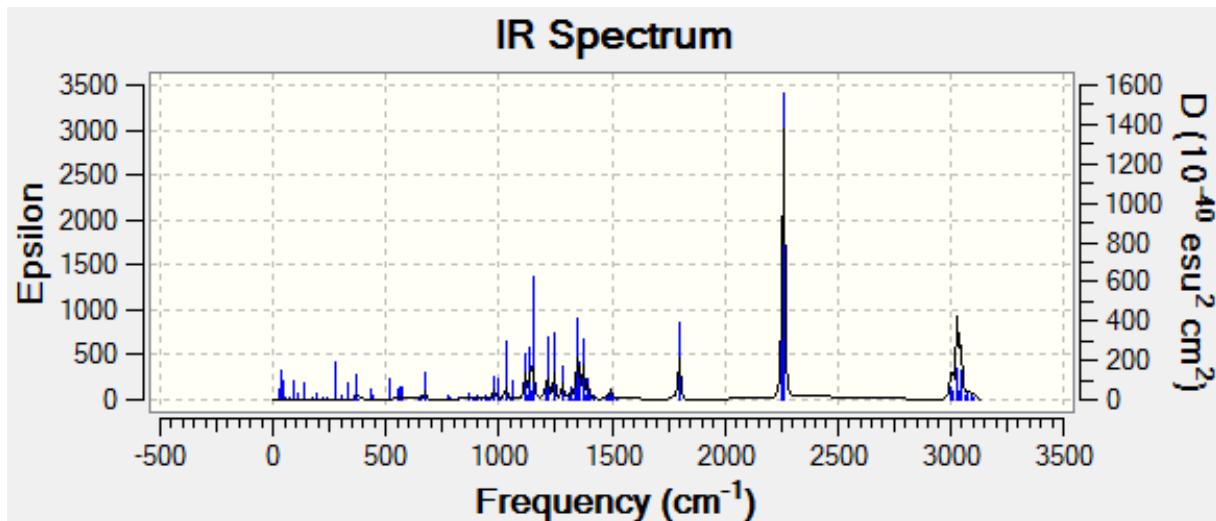


Fig. 6.5: IR-spectra of 2a (Theoretical)

In M5, (Neat,  $\text{cm}^{-1}$ ) 3037(C-H str), 2124( $\text{N}_3$  str), 1743(C=O str), 1232(C-C str) and experimental value 2971 (C-H str) 2107 ( $\text{N}_3$  str) 1737 (C=O str) 1202 (C-O str).

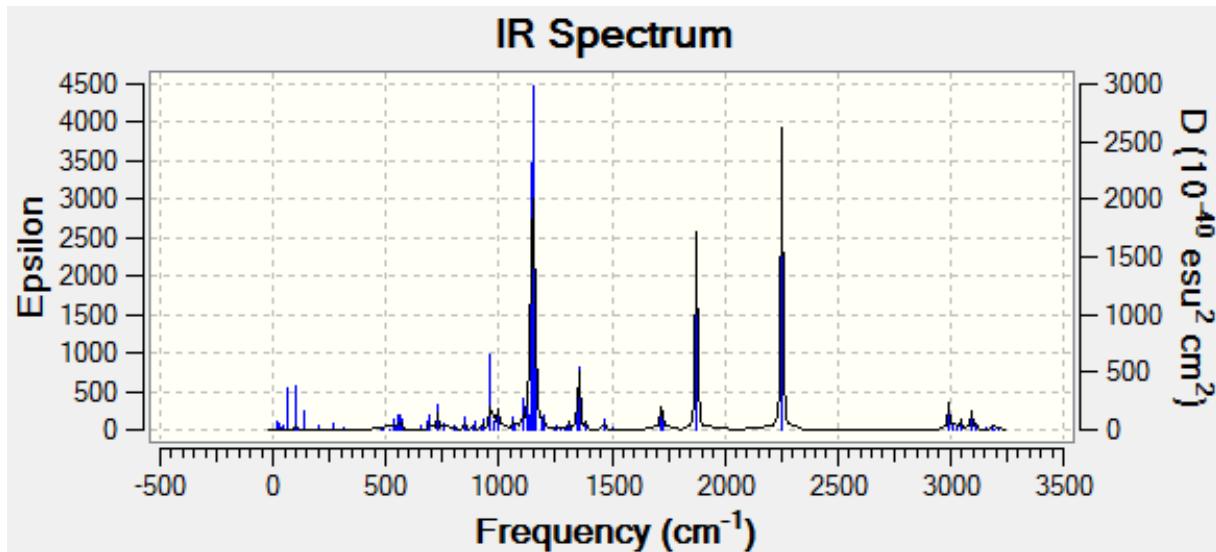


Fig. 6.6: IR-spectra of 5a (Theoretical)

In M6, at (Neat,  $\text{cm}^{-1}$ ) 3037(C-H str), 2124( $\text{N}_3$  str), 1743(C=O str), 1232(C-C str) and experimental value 2975 (C-H str) 2129 ( $\text{N}_3$  str) 1741 (C=O str) 1185 (C-O str).

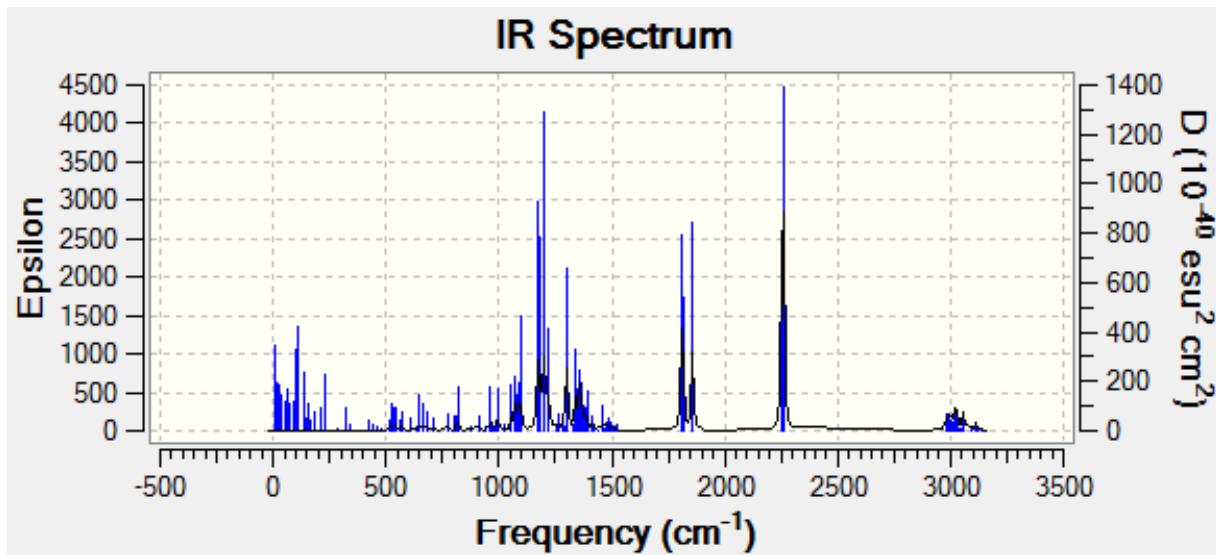


Fig. 6.7: IR-spectra of 6a (Theoretical)

Theoretically predicted IR values were in close agreement with experimental obtained values for the materials M1 to M6. The minor deviation is attributed to the fact that calculations have been done it gas phase whereas neat sample has been used for actual measurement of M1-M6 molecules.

## 1.2. NMR Spectra

The NMR values of M1 to M6 were predicted theoretically by DFT calculations and compared with experimental data. These theoretical values were closing remarkable with experimental values. NMR spectra of six molecules are given below.

Theoretically NMR value of **1a** molecule:

**$^1\text{H NMR}$**  at 5-H( $\delta$  4.5), 6-H( $\delta$  4.3), 12-H( $\delta$  4.3), 2-H( $\delta$  3.8), 3-H( $\delta$  3.8), 11-H( $\delta$  3.5).

**$^{13}\text{C-NMR}$**  at 8-C( $\delta$  181.4), 4-C( $\delta$  73.0), 10-C( $\delta$  58.4), 1-C( $\delta$  56.9).

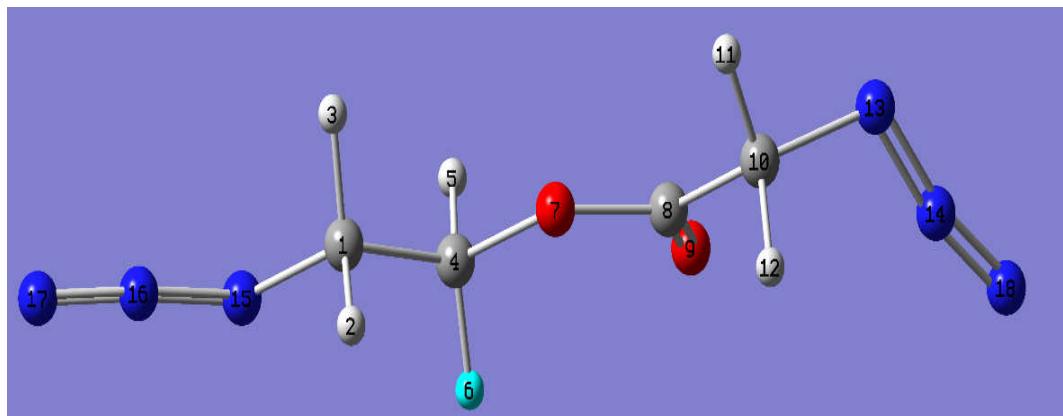


Fig. 6.8: Labelled diagram of M1

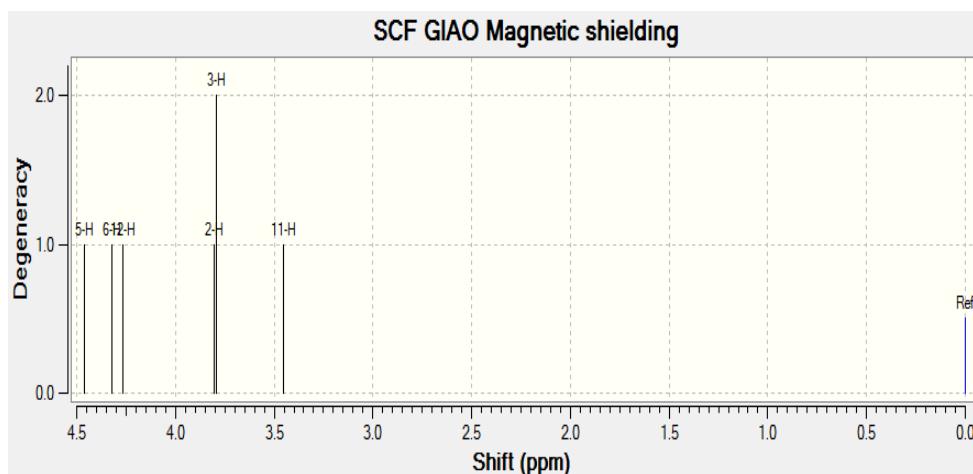


Fig 6.9: NMR spectra of M1 ( $^1\text{H}$ ) (Theoretical)

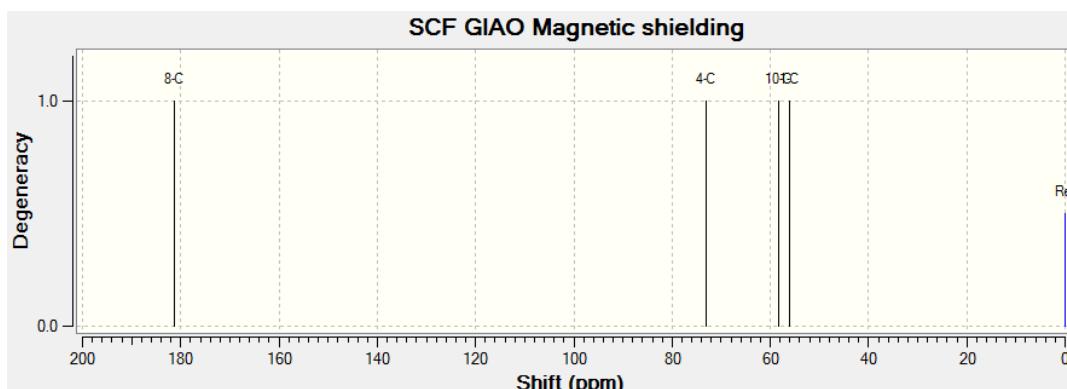


Fig. 6.10: NMR spectra of M1 ( $^{13}\text{C}$ ) (Theoretical)

**$^1\text{H-NMR}$**  It was observed peaks of M-2: 23-H( $\delta$  5.4 ), 14-H( $\delta$  4.9 ), 28-H( $\delta$  4.3 ), 8-H( $\delta$  4.2 ), 18-H( $\delta$  4.1 ), 18,25-H( $\delta$  4.1 ), 2,13-H( $\delta$  4.0), 2,13-H( $\delta$  4.0 ),17-H( $\delta$  4.0 ), 29-H( $\delta$  2.8 ), 7-H( $\delta$  3.4), 26-H( $\delta$  2.8 ).

**$^{13}\text{C-NMR}$**  In M2 9-C( $\delta$  180.0), 10-C( $\delta$  171.8), 1-C( $\delta$  82.3), 22-C( $\delta$  82.3), 16-C( $\delta$  76.6), 12-C( $\delta$  76.7), 27-C( $\delta$  63.2), 6-C( $\delta$  61.8), 24-C( $\delta$  60.9), 3-C( $\delta$  58.6).

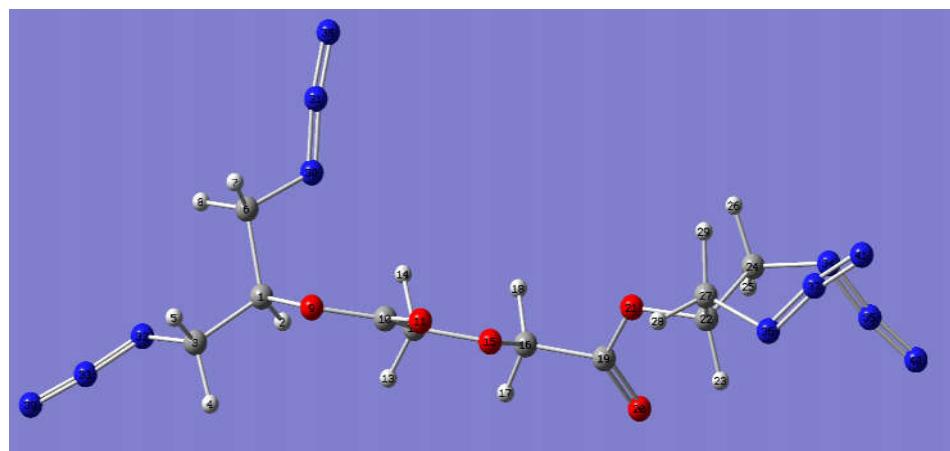


Fig. 6.11: Labelled Diagram of **3a**

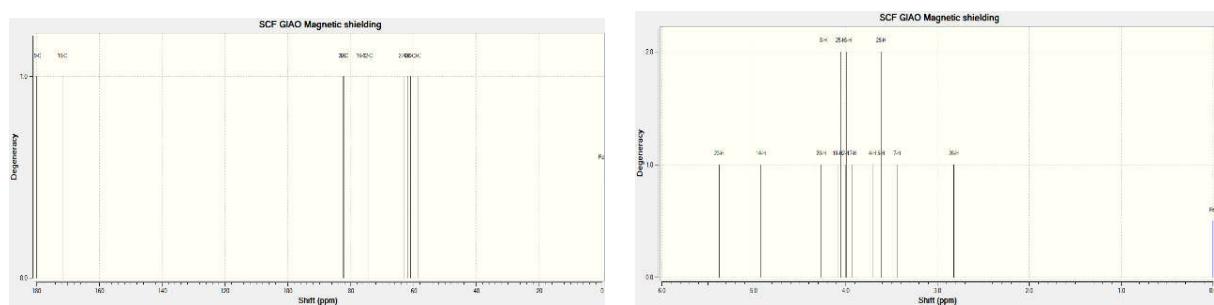


Fig. 6.12: NMR spectra of M2 ( $^{13}\text{C}$ ) (Theoretical)

Fig. 6.13: NMR spectra of M2 ( $^1\text{H}$ ) (Theoretical)

M-3,  **$^1\text{H-NMR}$**  : 11-H ( $\delta$  5.2 ), 12-H ( $\delta$  4.7 ), 16-H( $\delta$  4.6), 2-H( $\delta$  4.5 ), 3-H ( $\delta$  4.4 ), 3,33-H ( $\delta$  4.3 ), 18-H( $\delta$  4.2 ), 15-H( $\delta$  3.9), 21-H ( $\delta$  3.5 ), 34-H ( $\delta$  3.3 ), 19-H( $\delta$  3.2), 22-H ( $\delta$  3.1 ).

**$^{13}\text{C-NMR}$**  7-C ( $\delta$  177.4), 30-C ( $\delta$  176.3), 14-C( $\delta$  82.2), 10-C ( $\delta$  74.0), 20-C( $\delta$  63.9), 1-C( $\delta$  59.9), 17-C ( $\delta$  59.3), 32-C ( $\delta$  56.5), 13-C ( $\delta$  55.4).

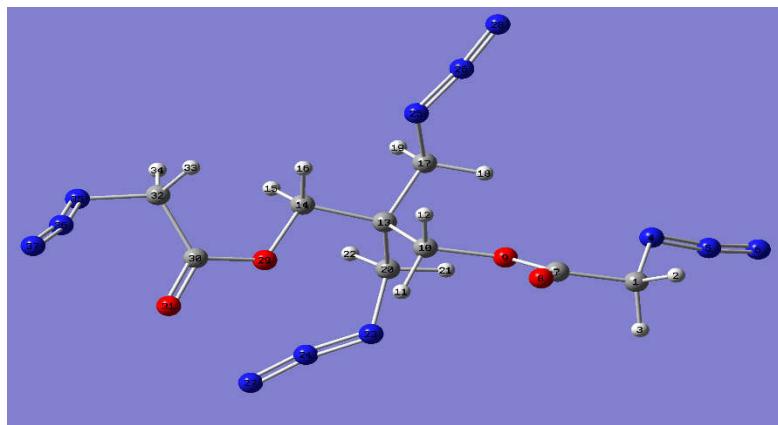


Fig. 6.14: Labelled diagram of **4a**

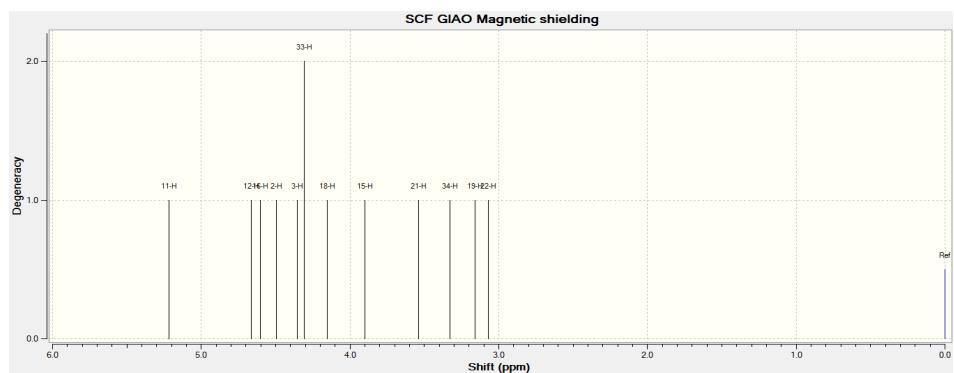


Fig. 6.15: NMR spectra of M3 (<sup>1</sup>H) (Theoretical)

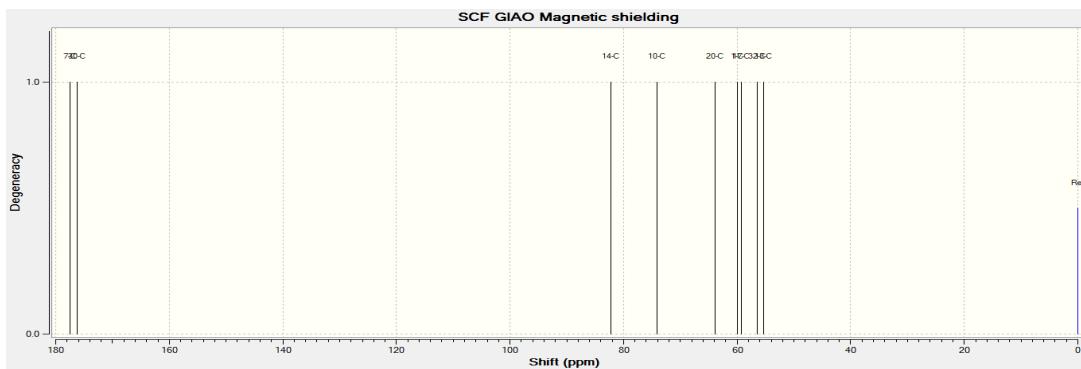


Fig. 6.16: NMR spectra of M3 (<sup>13</sup>C) (Theoretical)

M-4, **<sup>1</sup>H-NMR**: 33-H ( $\delta$  5.1), 38-H ( $\delta$  3.7), 36-H ( $\delta$  3.4), 35-H ( $\delta$  3.3), 39-H ( $\delta$  3.2), 14, 8, 9-H ( $\delta$  1.7), 13, 12, 10, 15, 7, 17-H ( $\delta$  1.6), 18, 20, 24-H ( $\delta$  1.4), 21-H ( $\delta$  1.1).

**<sup>13</sup>C-NMR** of M4: 2-C ( $\delta$  153.7), 4-C ( $\delta$  153.7), 6-C ( $\delta$  153.5), 1-C ( $\delta$  148.5), 5,3-C ( $\delta$  148.4), 25-C ( $\delta$  145.9), 22-C ( $\delta$  144.6), 19-C ( $\delta$  144.4), 16-C ( $\delta$  139.5), 26-C ( $\delta$  136.5), 37-C ( $\delta$  135.0), 34-C ( $\delta$  132.1), 32-C ( $\delta$  109.3).

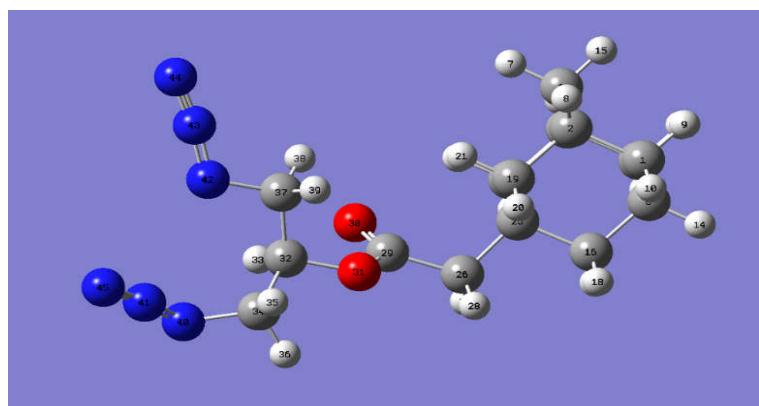


Fig. 6.17: Labelled diagram of **2a**

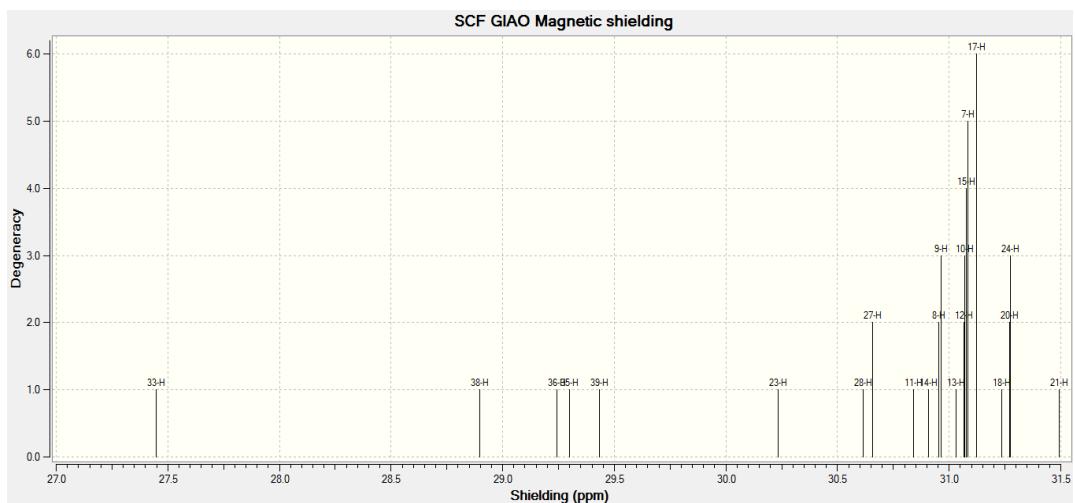


Fig. 6.18: NMR spectra of M4 (<sup>1</sup>H) (Theoretical)

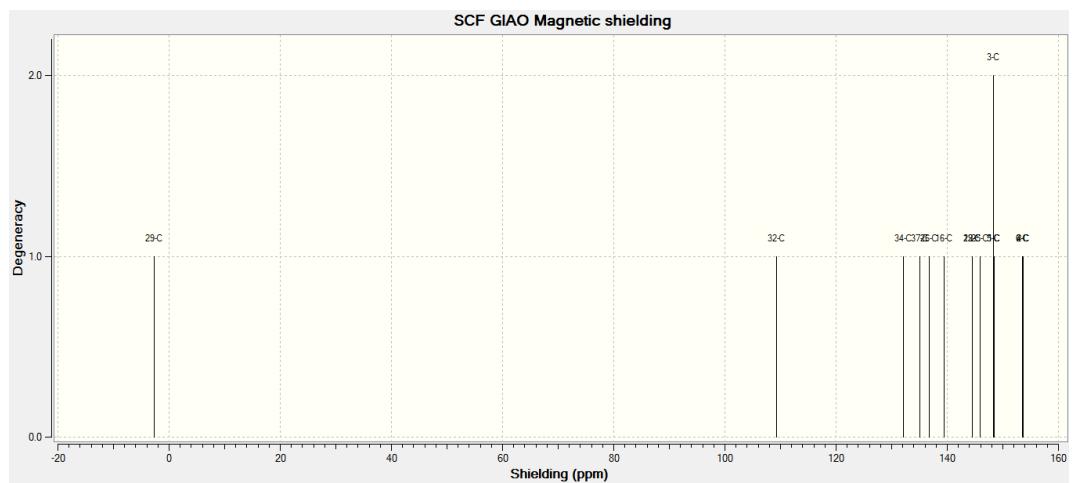


Fig. 6.19: NMR spectra of M4 (<sup>13</sup>C) (Theoretical)

**$^1\text{H-NMR}$**  of M5: 5, 23, 21, 6-H ( $\delta$  4.0), 19, 17-H ( $\delta$  6.1 ), 36, 28-H ( $\delta$  4.4), 37, 27-H ( $\delta$  4.0 ), 11, 13-H ( $\delta$  3.1 ), 14, 15-H ( $\delta$  2.9 ), 9-H ( $\delta$  2.0 ), 8-H( $\delta$  1.7).

**$^{13}\text{C-NMR}$**  of M5: 34-C ( $\delta$  170.0), 25-C ( $\delta$  169.3), 22-C ( $\delta$  142.6), 20-C( $\delta$  142.2), 1-C( $\delta$  140.5), 4-C( $\delta$  140.1), 18-C( $\delta$  128.5), 16-C( $\delta$  127.8), 7-C( $\delta$  59.6), 26-C( $\delta$  58.5), 35-C( $\delta$  58.4), 2,3-C( $\delta$  55.3),12-C( $\delta$  51.6), 10-C( $\delta$  51.1).

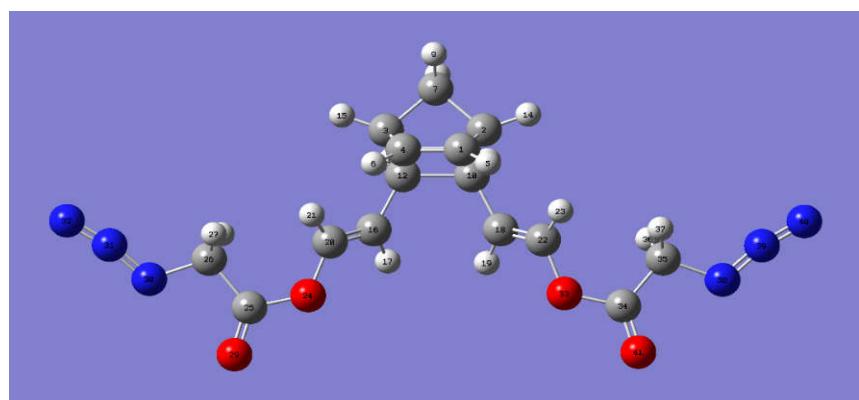


Fig. 6.20: Labelled diagram of **5a**

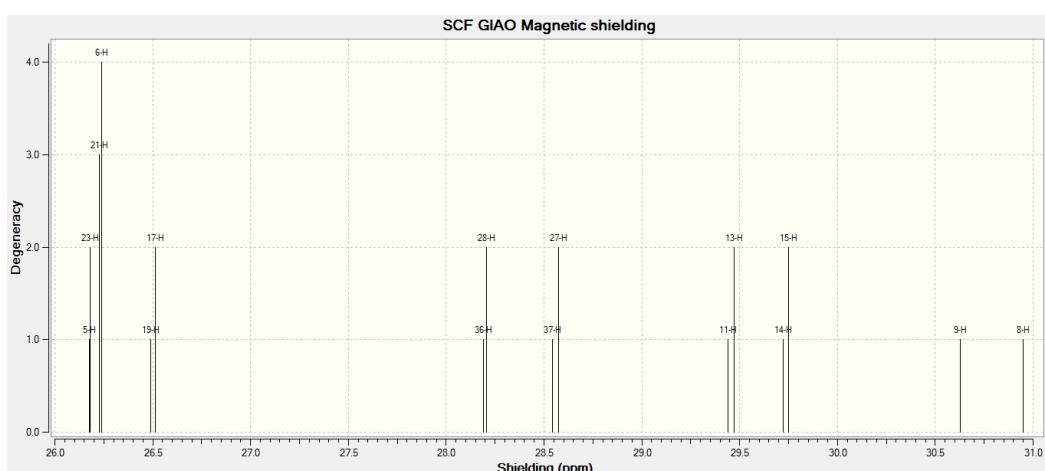


Fig. 6.21: NMR spectra of M5 ( $^1\text{H}$ ) (Theoretical)

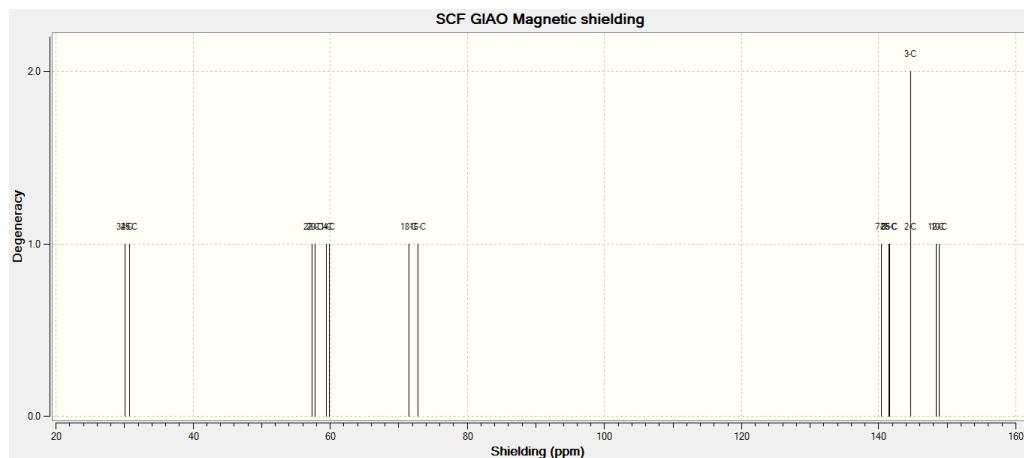


Fig 6.22: NMR spectra of M5 ( $^{13}\text{C}$ ) (Theoretical)

**$^1\text{H-NMR}$  of M6:** 24-H ( $\delta$  5.8), 34, 18-H ( $\delta$  5.5), 16-H( $\delta$  5.3), 12-H ( $\delta$  5.0 ), 43-H ( $\delta$  4.9 ), 42, 33-H( $\delta$  4.7 ), 15,13-H( $\delta$  4.9 ), 19-H( $\delta$  4.0), 10,7,3-H ( $\delta$  3.8), 9,6,4,25-H( $\delta$  3.6).

**$^{13}\text{C}$  NMR of M6:** 21-C( $\delta$  191), 39-C( $\delta$  186.9), 30-C( $\delta$  182.9), 14-C( $\delta$  91.6), 11-C( $\delta$  87.1), 17-C( $\delta$  86.9), 2-C( $\delta$  80.9), 8-C( $\delta$  80.2), 5-C( $\delta$  80.0), 41-C( $\delta$  72.0), 32-C( $\delta$  70.0), 23-C( $\delta$  68.4).

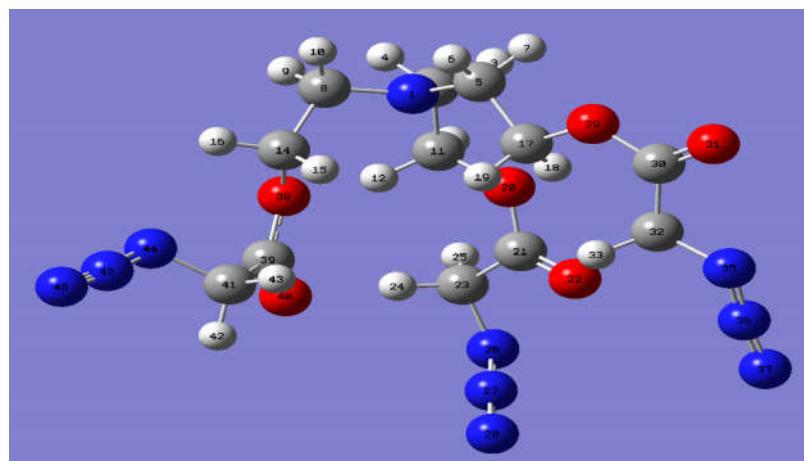


Fig. 6.23: Labelled diagram of **6a**

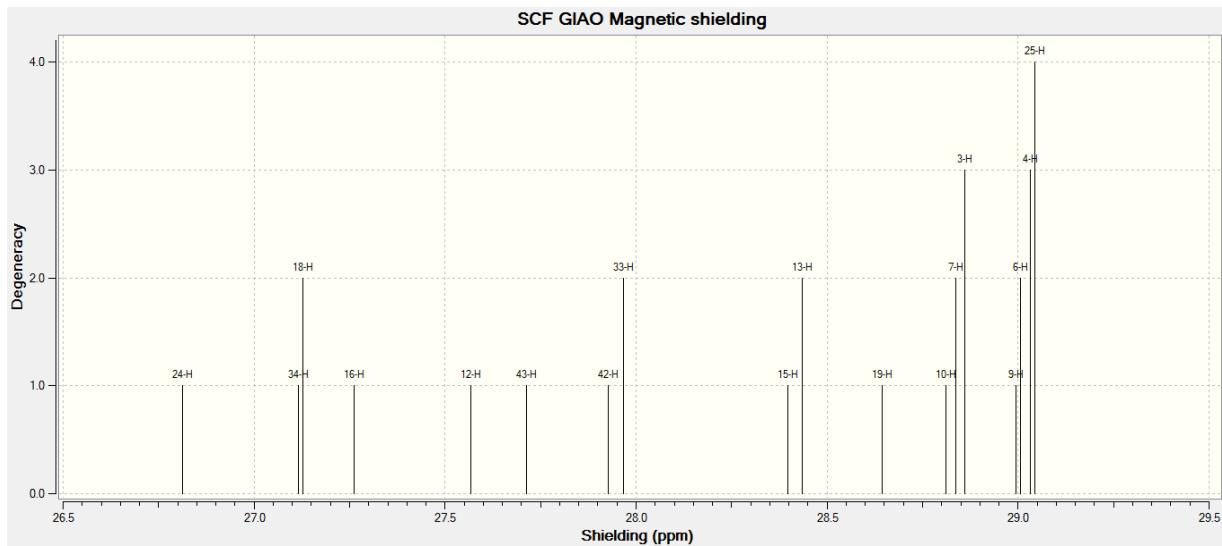


Fig. 6.24: NMR spectra of M6 ( $^{13}\text{C}$ ) (Theoretical)

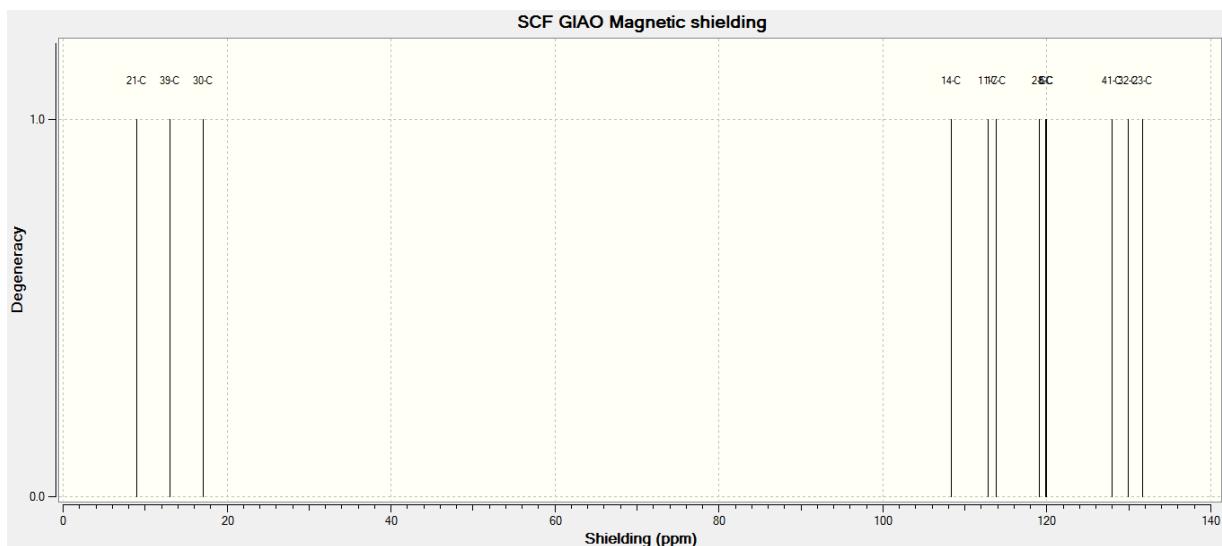


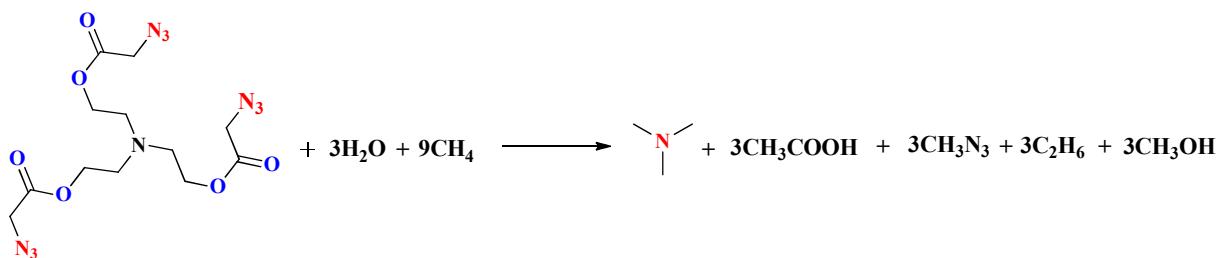
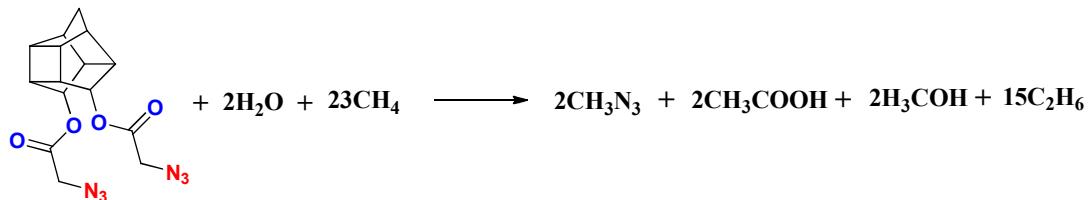
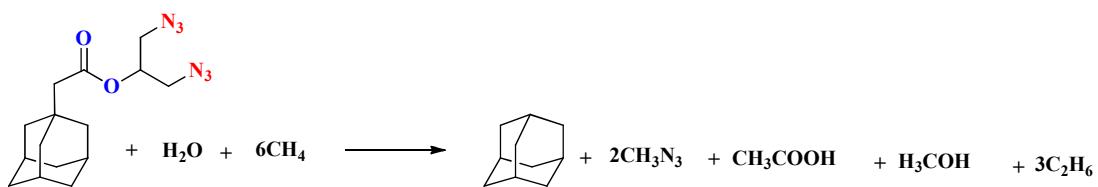
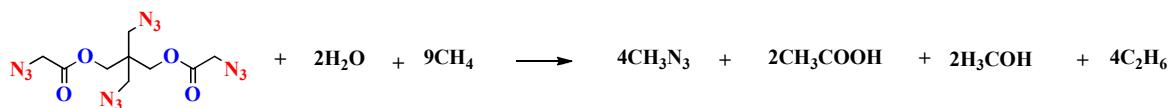
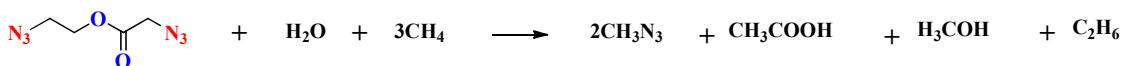
Fig. 6.25: NMR spectra of M6 ( $^{13}\text{C}$ ) (Theoretical)

### Isodesmic Reactions for Heat of formation:



$$\Delta_f H = \Delta_f H(A+B) - \Delta_f H(A-B)$$

$$\Delta_r H = \Delta_f H \text{ products} - \Delta_f H \text{ reactants}$$



Compound	(kcal/mole) (B3LYP/6-31G*)
1a	78.66
3a	144.41
4a	181.33

2a	53.12
5a	131.37
6a	28.43