

# DABCO Catalyzed One-Pot Synthesis of Ester Derivatives of Tris (2-Aminoethyl)amine

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## Abstract



Here, 2, 7R = CH<sub>3</sub>; 3, 8R = C<sub>2</sub>H<sub>5</sub>; 4, 9R = C<sub>4</sub>H<sub>9</sub>; 5, 10R = C<sub>3</sub>H<sub>6</sub>SiO<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>; 6, 11 R = C<sub>2</sub>H<sub>4</sub>OH

Tris (2-aminoethyl) amine (Tren) is a commercially available tripodal amine. Tren has been widely used as a ligand in the preparation of metal complexes. Tris (2-aminoethyl) amine (Tren)-based esters have been synthesized in a single-pot-reaction of tren with six equivalent each of alkyl acrylates, 3-trimethoxysilyl propyl methacrylate and 2-hydroxyethylmethacrylate in presence of 10 mol% DABCO in mild conditions. The higher yield of the product was obtained in case of alkyl acrylates. The reaction was accomplished at room temperature and in a short reaction time. All synthesized compounds were characterized by IR, UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR, GC-mass and elemental analysis.

**Keywords** Tris (2-aminoethyl) amine, Alkylacrylates, 1, 4-Diaza bicyclo [2. 2. 2] octane (DABCO), Ester

## 1. Introduction

Tris (2-aminoethyl) amine (Tren) [*N,N*-Bis (2-aminoethyl)-1, 2-ethane diamine] is a commercially available tripodal amine. Tren has been widely used as a ligand in the preparation of metal complexes [1-3]. Sterically hindered triamidoamine ligands with a C<sub>3</sub> symmetrical tren-based backbone Tren have been found to coordinate to a variety of transition metals stabilizing unusual complexes thereby allowing exceptional reactivities [4,5]. Ligands of the type [(RNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N<sup>3+</sup> (R=H [6], methyl [7], benzyl [8]) have been shown to form complexes with transition metals or main group elements [9,10].

Over the past several years triamidoamine ligands based on tris (2-aminoethyl) amine (Tren) have been explored extensively to coordinate a variety of transition metals forming important complexes which showed versatile activities [11-15]. Greco and Schrock reported the synthesis

of triamidoamine ligands of the type (ArylNHCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N and Molybdenum and Tungsten complexes that contain an [(ArylNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sup>3+</sup> ligand [16]. The copper (II) complexes [Cu(Bz<sub>3</sub>tren)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub> and [Cu(Bz<sub>3</sub>tren)Cl]Cl were synthesized and structurally characterized [17] by M. Schatz *et al.* Mösch-Zanetti *et al.* reported the synthesis of a C<sub>6</sub>F<sub>5</sub> substituted unsymmetrical triamidoamine ligand along with the preparation of two rhenium (V) oxo compounds [18]. Recently, Guillaume Barre *et al.* have prepared the hexa substituted tetramine ligand [19] by refluxing tris (2-aminoethyl) amine, 1-iodooctadecane and potassium carbonate in acetonitrile for 2 days and they have reported its catalytic effects for living radical polymerization of methylmethacrylate. It has been reported that tris (2-aminoethyl) amine based tetradentate chelating ligand forms stable complexes with transition metals which is used as a carbon dioxide absorbent [20]. The synthesis of cationic lipids, tris (2-aminoethyl) amine-based  $\alpha$ -branched fatty acid amides has been reported resulting a series of lipids with specific variations in the lipophilic as well as the hydrophilic part of the lipids [21]. Tripodal ligand based on tris (2-aminoethyl) amine was prepared that served as potential Fe (III) binding chelator and to detect Fe for further

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modification to develop a better potent fluorescence sensor [22]. In this paper, a novel approach to synthesize ester derivatives of tris (2-aminoethyl) amine is described.

## 2. Experimental

### 2.1. General Remarks

Melting points were determined in open capillary tube on Gallenkamp (England) melting point apparatus and uncorrected. IR spectra were recorded on a Shimadzu FTIR spectrophotometer and UV spectra were recorded in dry MeOH with Shimadzu visible spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400 spectrophotometer (400 MHz) using tetramethylsilane as internal reference and solvent  $\text{CDCl}_3$ . Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 240 C Analyser. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60F-254 (E. Merck), and the spots were visualized with UV light. Column chromatography was performed on silica gel (60-120 mesh). DABCO (1, 4-diazabicyclo [2. 2. 2] octane), tris (2-aminoethyl) amine, acrylates, 3-(trimethoxysilyl) propylmethacrylate, 2-hydroxyethyl methacrylate and other reagents were purchased from E. Merck (Germany) and Fluka (Switzerland).

### 2.2. General Procedure for the Synthesis of Compound (7-11)

Compounds **7-11** were prepared from the reaction of tris (2-aminoethyl) amine with different acrylates in presence of DABCO at room temperature. To a stirred solution of tris (2-aminoethyl) amine (0.5 g, 0.0034 mol) and DABCO (0.038 g, 10 mol %) in methanol (5 mL) at r. t. and methyl acrylate (1.90 g, 0.02 mol) was added. Then the mixture was stirred for 3-4 hours. The progress of the reaction was monitored by TLC. Then the solvent of the reaction mixture was removed by distillation and extracted by  $\text{CHCl}_3$  solution (3 x 50 ML), the organic layer was washed by distilled water (3 x 50 ML) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product obtained after evaporation of the solvent was purified by chromatography on a column of silica gel (60-120 mesh) with ethyl acetate in n-hexane to yield yellowish liquid pure compound **7**.

**Compound 7:** Yellowish liquid, Yield: 92%, IR (KBr):  $\nu_{\text{max}}$  = 3448.84 (N-H), 2845.10-2956.01 (C-H), 1736.96 (C=O), 1438.94 ( $\text{CH}_2$ ), 1330.93-1364.68 (C-N), 1202.66 (-O-), 700-1000  $\text{cm}^{-1}$ . UV (MeOH):  $\lambda_{\text{max}}$  = 335.20, 280.80, 231.80 nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 3.68 (s, 3H,  $\text{CH}_3$ ), 2.55 (s, 1H, NH), 2.80 (t, 2H,  $J$  = 6.8 Hz, CON- $\text{CH}_2$ ), 2.48 (t, 2H,  $J$  = 6.8, 7.2 Hz,  $\text{NCH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.87, 51.57, 49.65, 32.44. HRMS (CI) Calcd for  $\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_6$   $[\text{M}+\text{H}]^+$  320.34, found  $[\text{M}+\text{H}]^+$  320.49. Anal. Calcd. (%) for  $\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_6$ : C 44.99, H 7.55, N 17.49; Found (%) C 45.12, H 7.38, N 17.68.

**Compound 8:** The product was obtained from tris (2-aminoethyl) amine (0.5 g, 0.0034 mol), ethyl acrylate (2.21 g, 0.02 mol) and DABCO (0.038 g, 10 mol %). Yellowish liquid, Yield: 90%, IR (KBr) 34.50 (N-H), 2826.77-2890.05 (C-H), 1740 (C=O), 1469.81 ( $\text{CH}_2$ ), 1372.40 (C-N), 1190.30 (-O-)  $\text{cm}^{-1}$ ; UV 340.30, 282.20, 232.00, 230.80 nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 4.11 (q, 2H,  $J$  = 7.2, 6.8 Hz,  $\text{OCH}_2$ ), 2.78 (t, 2H,  $J$  = 7.2 Hz, CON- $\text{CH}_2$ ), 2.44 (t, 2H,  $J$  = 7.2 Hz,  $\text{NCH}_2$ ), 2.55 (s, 1H, NH), 1.25 (t, 3H,  $J$  = 7.2 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.49, 60.44, 49.72, 32.71, 14.22. HRMS (CI) calcd for  $\text{C}_{15}\text{H}_{30}\text{N}_4\text{O}_6$   $[\text{M}+\text{H}]^+$  362.42, found  $[\text{M}+\text{H}]^+$  362.29. Anal. Calcd. (%) for  $\text{C}_{15}\text{H}_{30}\text{N}_4\text{O}_6$ : C 49.71, H 8.34, N 15.46; Found (%) C 49.74, H 8.43, N, 15.62.

**Compound 9:** The product was obtained from tris (2-aminoethyl) amine (0.5 g, 0.0034 mol), butyl acrylate (2.82 g, 0.02 mol) and DABCO (0.038 g, 10 mol %). Yellowish liquid, Yield: 80%, IR 34.88.13 (N-H), 2840.10-2880.83 (C-H), 1736.00 (CO), 1462.09 ( $\text{CH}_2$ ), 1280-1320 (C-N), 1180 (-O-)  $\text{cm}^{-1}$ ; UV (MeOH):  $\lambda_{\text{max}}$  = 279.60, 231.60 nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 4.04 (t, 2H,  $J$  = 6.8 Hz,  $\text{OCH}_2$ ), 2.76 (t, 2H,  $J$  = 6.8 Hz, CON- $\text{CH}_2$ ), 2.52 (s, 1H, NH), 2.42 (t, 2H,  $J$  = 7.2, 6.8 Hz,  $\text{NCH}_2$ ), 1.60 (quint, 2H,  $J$  = 6.8 Hz, aliphatic H-3), 1.36 (quint, 2H,  $J$  = 7.2, 7.6 Hz, aliphatic H-2), 0.930 (t, 3H,  $J$  = 7.2, 7.6 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.54, 64.25, 49.72, 32.67, 30.67, 19.12, 13.68. HRMS (CI) calcd for  $\text{C}_{21}\text{H}_{42}\text{N}_4\text{O}_6$   $[\text{M}+\text{H}]^+$  446.58, found  $[\text{M}+\text{H}]^+$  446.51. Anal. Calcd. (%) for  $\text{C}_{21}\text{H}_{42}\text{N}_4\text{O}_6$ : C 56.48, H 9.48, N 12.55; Found (%) C 56.65, H 9.30, N 12.72.

Compound **10-11** were also prepared through the above reaction procedure. After usual workup the solid compounds were obtained without any separation technique. It is mentioned here that the compound **10-11** were not soluble in any organic solvent.

**Compound 10:** The product was obtained from tris (2-aminoethyl) amine (0.5 g, 0.0034 mol), 3-(trimethoxysilyl) propyl methacrylate (5.47 g, 0.02 mol) and DABCO (0.038 g, 10 mol %). Yield: 89%, Colourless solid, mp 187-188 °C: IR 3467.16 (N-H), 2933.83 (C-H), 1726.35 (CO), 1460.16 ( $\text{CH}_2$ ), 1280.05 (-O-), 940.33 (Si-O)  $\text{cm}^{-1}$ . The SEM and EDX of this compound were carried out.

**Compound 11:** The product was obtained from tris (2-aminoethyl) amine (0.5 g, 0.0034 mol), 2-hydroxyethyl methacrylate (2.87 g, 0.02 mol) and DABCO (0.038 g, 10 mol %). Yellowish solid, Yield: 85%, mp 145-146 °C: IR 3537.57 (N-H), 3417.01 (OH), 2853.78-2954.22 (C-H), 1725.38 (CO), 1462.09 ( $\text{CH}_2$ ), 1274.03 (C-N), 1151.54 (-O-)  $\text{cm}^{-1}$ . The SEM and EDX of this compound were taken.

## 3. Results and Discussion

It is reported here that the coupling between tris (2-aminoethyl) amine with acrylates were accomplished in presence of DABCO in good yield% (Scheme 1, Table 1). A

divergent synthesis of the polyamidoamine type compound by using two monomers is developed. A straightforward methodology to highly substituted alkyltren ester compounds is demonstrated. A single pot base catalyzed synthetic protocol has been employed to assemble alkylacrylates, 3-(trimethoxysilyl) propyl methacrylate, 2-hydroxy-ethylmethacrylate, with Tren base ester macro molecules. The reaction of a central Tren unit bearing three primary amine moieties with six equiv. each of alkyl acrylates provides access to a series of functionalized tripodal esters (**Scheme 1**). Tris (2-aminoethyl) amine is taken as the core molecule and alkyl acrylate is considered as coupling monomer. The additions of three alkylacrylate molecules to tris (2-aminoethyl) amine in solvent MeOH was occurred rapidly in presence of DABCO. The nucleophilic addition involves by the electron pair on the nitrogen to the electropositive carbonyl carbon with release of alkene group.

It was observed that the reaction of Tris (2-aminoethyl) amine **1** and methyl, ethyl, n-butyl acrylate **2, 3, 4** afforded dendrimer type compounds **7, 8, 9** in good yields (table-1, entry 1-3). Then the reaction between Tris (2-aminoethyl) amine **1** and 3-(trimethoxysilyl) propyl methacrylate **5**, 2-hydroxyethyl methacrylate **6** afforded dendrimeric compounds **10, 11** in good yields (table-1, entry 4, 5). The results are demonstrated in Table-1. The synthesized

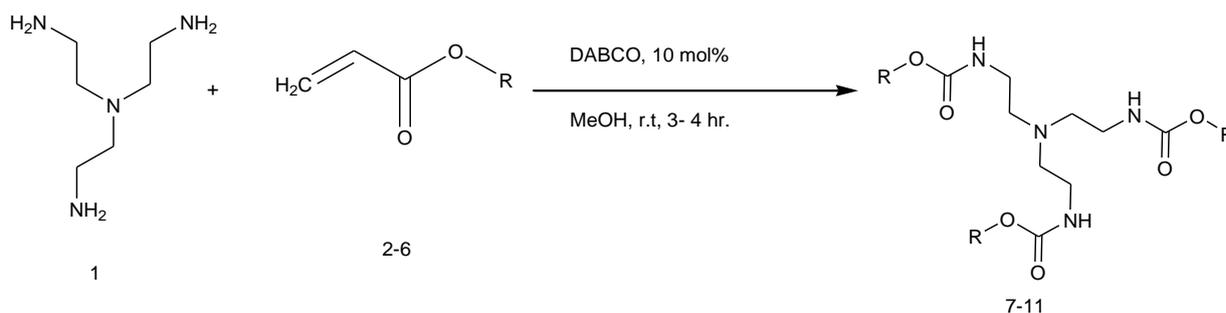
compounds **7-9** were characterized by IR, UV,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR, GC-mass and elemental analysis and the compounds **10-11** were characterized by their satisfactory spectroscopic (IR, SEM, EDX) data analyses.

The SEM and EDX of compound **10** are shown in fig. 1, 2. The SEM images are represented as the agglomerate globular size of surface morphology of the ligands. The morphology is clean and compact with even surface and less voids. From EDX analysis, the presence of silicon is well observed and it is 5.45% of mass weight and 2.65% of atomic wt. of the compound. From EDX analysis carbon, nitrogen, oxygen was found to be 56.77%, 5.51%, 32.27% of mass weight and 64.47%, 5.37%, 27.51% of atomic wt. of the compound.

**Table 1.** DABCO Catalyzed carbon-nitrogen bond formation reaction between Tris (2-aminoethyl) amine with different acrylates

Entry	Tren	Acrylates	Products	<sup>a</sup> Yield%
1	1	2	7	92
2		3	8	90
3		4	9	80
4		5	10	89
5		6	11	85

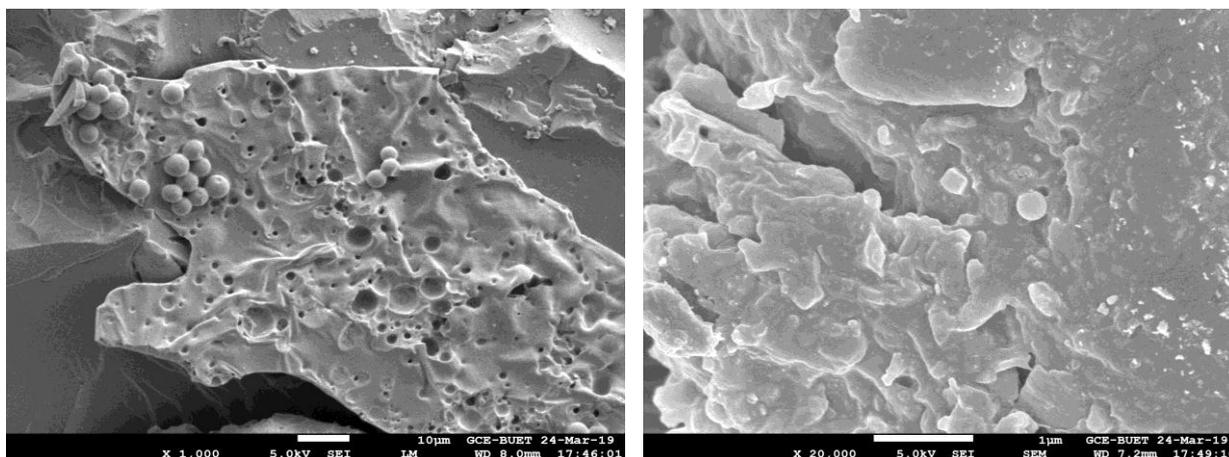
<sup>a</sup>Yield% is based on Tris (2-aminoethyl) amine



Here, **2**, **7R** = CH<sub>3</sub>; **3**, **8R** = C<sub>2</sub>H<sub>5</sub>; **4**, **9R** = C<sub>4</sub>H<sub>9</sub>; **5**, **10R** = C<sub>3</sub>H<sub>6</sub>SiO<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>; **6**, **11 R** = C<sub>2</sub>H<sub>4</sub>OH

**Scheme 1**

SEM images of compound **10**



**Figure 1.** SEM for the compound **10** by applying from 5.0 kv 7.2 mm x 50 (SEM) to 5.0 kv 7.2mm x 20,000 (SEM)

EDX spectrum of compound 10

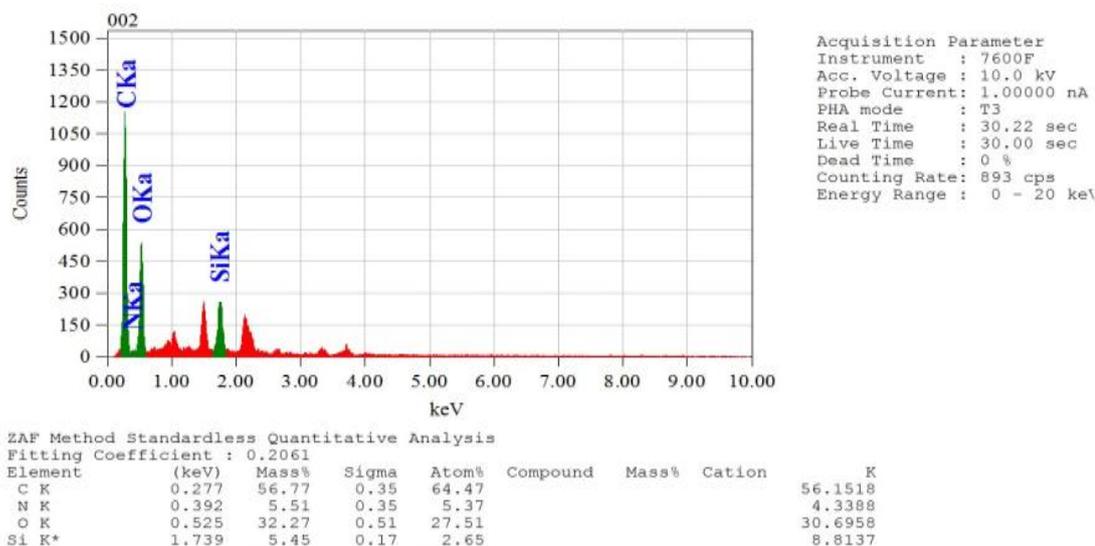


Figure 2. EDX spectra of the compound 10

SEM images of compound 11

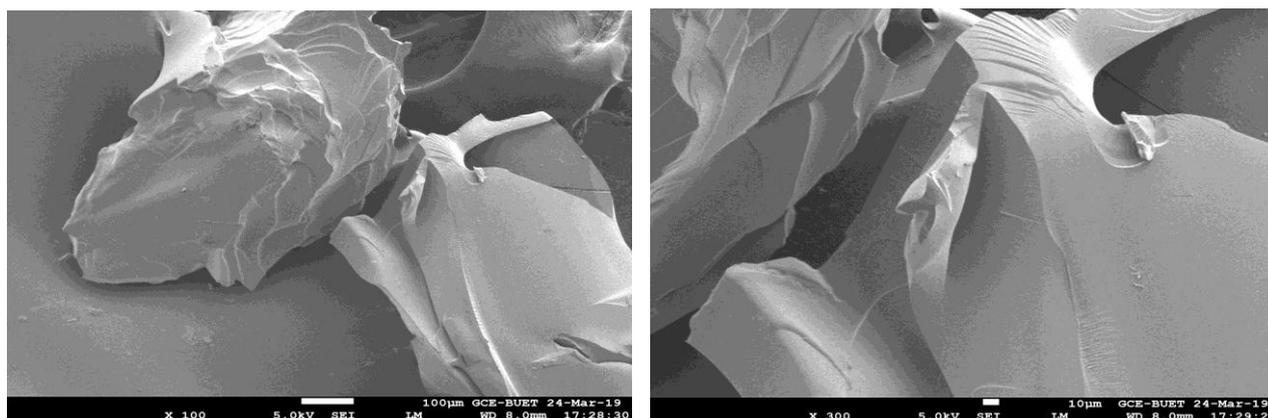


Figure 3. SEM for the compound 11 by applying from 5.0 kv 8 mm x 100 (SEM) to 5.0 kv 8 mm x 1,000 (SEM)

EDX spectrum of compound 11

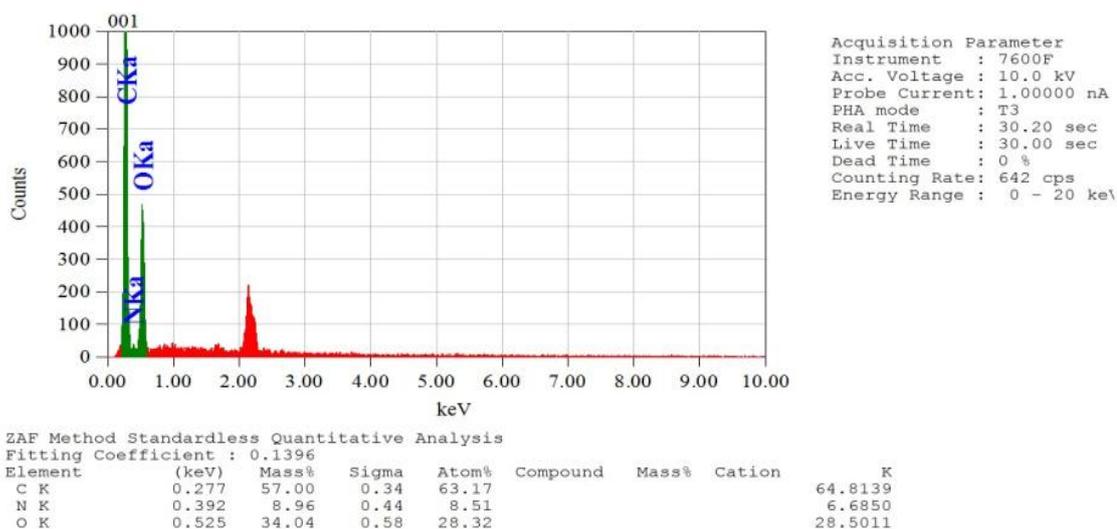
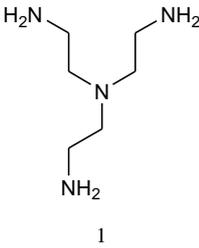
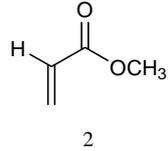
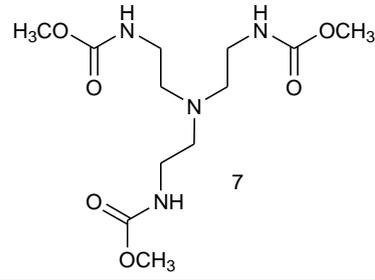
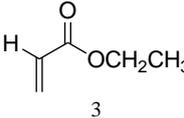
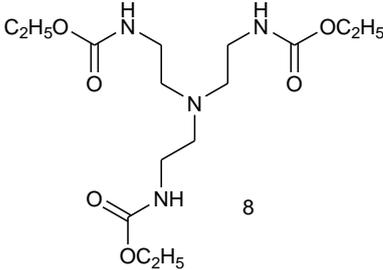
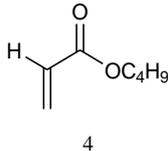
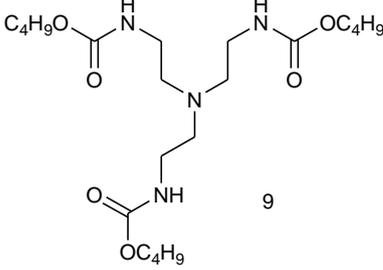
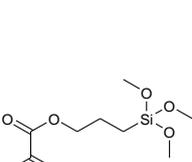
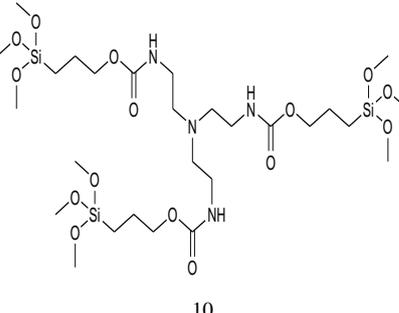
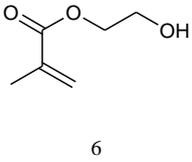
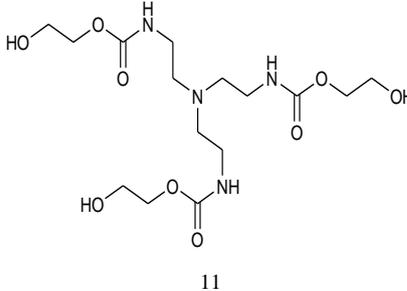


Figure 4. EDX spectra of the compound 11

**Table 2.** DABCO Catalyzed carbon-nitrogen bond formation reaction between Tris (2-aminoethyl) amine with different acrylates

Entry	Tren	Acrylates	Product	<sup>a</sup> Yield%
1.	 1	 2	 7	92
2.		 3	 8	90
3.		 4	 9	80
4.		 5	 10	89
5.		 6	 11	85

<sup>a</sup>Yield % is based on Tren

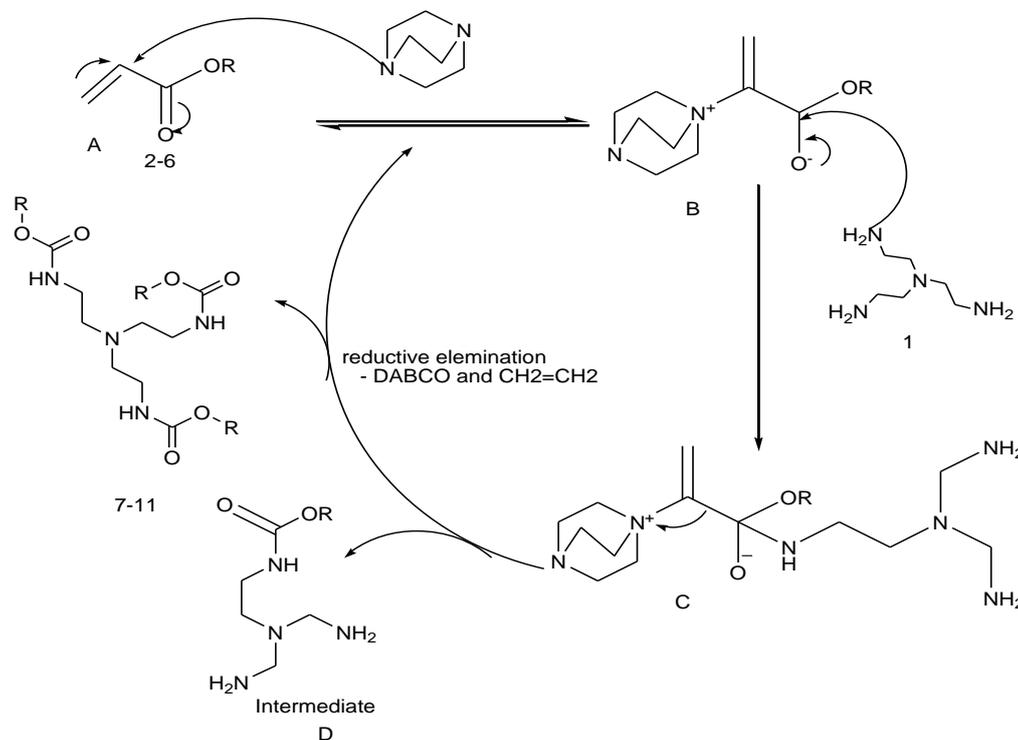
The SEM and EDX of compound **11** are shown in fig. 3, 4. The images are represented as “irregular-rough surface” structure. From EDX analysis carbon, nitrogen, oxygen was

found to be 57.00%, 8.96%, 34.04% of mass weight and 63.17%, 8.51%, 28.32% of atomic wt. of the compound.

## 4. Mechanism

It can be perceived that the reactions proceed according to **Scheme-2** although the detailed mechanism of the reaction is yet to be clarified. It was observed that the presence of DABCO was very essential for the success of this C-N bond forming reactions. Tris (2-aminoethyl) amine is taken as the

core molecule and alkyl acrylate is considered as coupling monomer. The additions of three alkylacrylate molecules to Tris (2-aminoethyl) amine in solvent MeOH was occurred rapidly in presence of DABCO. The nucleophilic addition involves by the electron pair on the nitrogen to the electropositive carbonyl carbon with release of alkene group.



Scheme 2

The key steps of the possible mechanism were based on the following observations. The mechanism is proposed to be consisting of 3 Steps: a) Elimination of the catalyst and proton transfer. b) Michael addition of the nucleophilic trigger catalyst to the activated alkene. c) Quenching the Zwitterionic adduct with an electrophile.

Invariably, it has been concluded by all the studies that the reaction is the outcome of an addition elimination sequence involving activated alkene, electrophile and tertiary amine.

In the first step of the nucleophilic addition of DABCO with electrophile carbon of  $\alpha$ ,  $\beta$ -unsaturated ester to produce BH adducts **B**. In the next step, this adducts react with nucleophile nitrogen of Tris (2-aminoethyl) amine to produce complex compound **C**. Then reductive elimination of DABCO to give compound **D**. Finally compounds **7-11** were obtained in good yield. The regenerated DABCO usually participate in the reaction as a base catalyst.

## 5. Conclusions

A convenient method for the synthesis of macro molecule of ester derivatives from the reaction of Tris (2-aminoethyl) amine with acrylates using 10 mol% 1, 4-Diaza bicyclo [2. 2. 2] octane (DABCO) in MeOH has been developed under

mild conditions at room temperature. The synthesized compounds would be important ligands and potent intermediate for the synthesis of medicinal compounds. The most important features of these methods were that, the readily available inexpensive materials were used under relatively mild conditions and got relatively higher yield. No toxic and hazardous compounds were produced by this procedure. Therefore, this methodology could be utilized to synthesize the biologically important dendrimer type compounds in mild conditions.

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