Self-standing, metal nanoparticle embedded transperant films from multi-armed cardanol conjugates through *in situ* synthesis

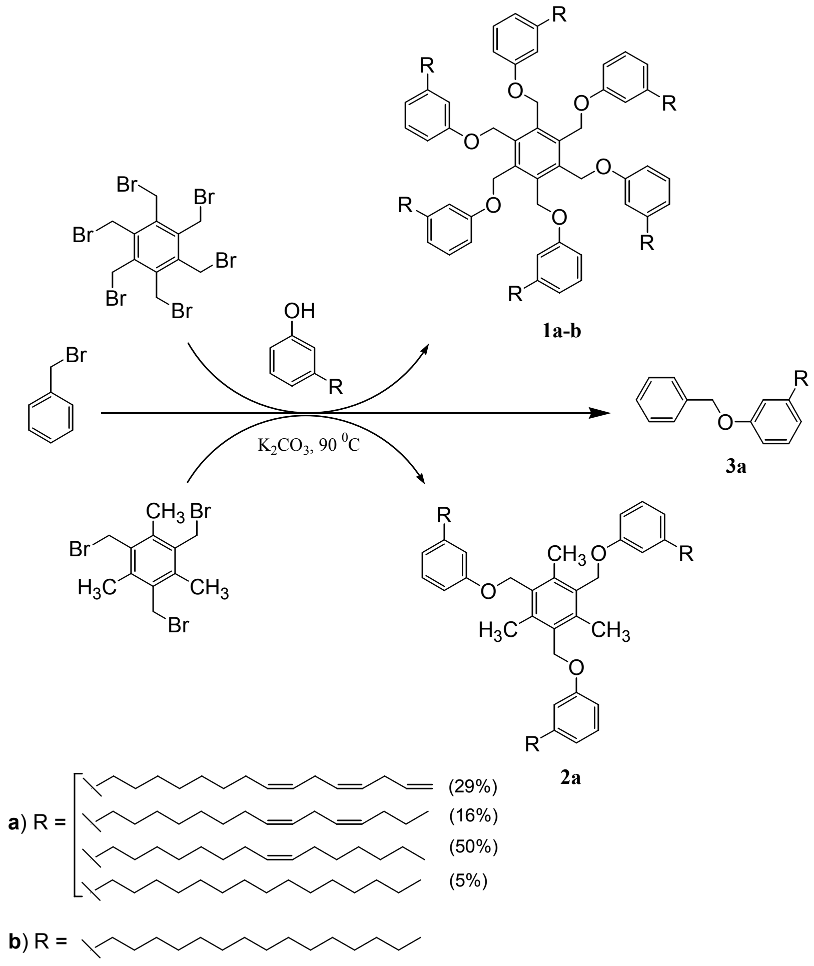
Kuthanapillil Jyothish,[a] Praveen Kumar Vemula,[a] Swapnil R. Jadhav,[a] Lynn C. Franscesconi[b] and George John*[a]

* To whom correspondence should be addressed at:

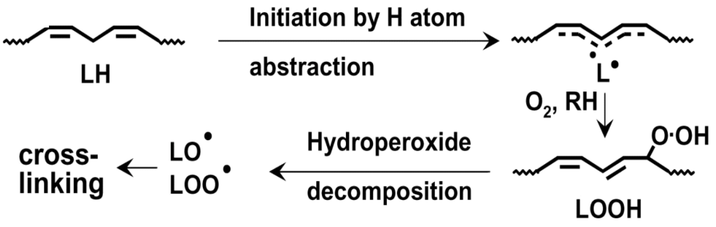
Department of Chemistry
The City College of the City University of New York,
160 Convent Avenue, New York, NY-10031, USA.
Tel: +1 212 650 8353
Fax: +1 212-650-6107
E-mail : john@sci.ccny.cuny.edu

SUPPLEMENTARY SUPPORTING INFORMATION

Synthesis, characterization, preparation and processing of thin films, Schemes S1-S2 showing synthesis route and proposed mechanism of oxidative cross-linking. We also include UV-visible spectra, AFM, SEM and TEM images of MNPs embedded films, DSC curves, Graph showing the size distribution of MNPs, IR spectra before and after cross- linking, and the ^{1}H, ^{13}C NMR and MALDI-TOF spectra of compounds.



Scheme S1. Synthesis of multi-armed cardanol conjugates **1a-b** and **2-3a**.



Scheme S2. Proposed mechanism of cross-linking.

Experimental Section

1. General experimental techniques.

Melting points were determined on a Mel-Temp II melting point apparatus. The IR spectra were recorded on a Nicolete 380 Fourier Transform Infrared Spectrometer. ^{1}H and ^{13}C NMR were recorded on a 300 MHz Varian spectrometer. MALDI-TOF spectra were recorded on an Omniflex Bruker Daltonics spectrometer using α-Cyano-4-hydroxycinnamic acid as the matrix. The electronic absorption spectra were recorded on a CARY100BIO spectrophotometer.

Starting materials. Hexakis(bromomethyl)benzene, 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene, benzylbromide and 3-*n*-Pentadecylphenol were purchased from TCI America and used as such while Cardanol was obtained by double vacuum distillation of cashew-nut shell liquid at 3-4 mm Hg; the fraction distilled at 230-235 ^{O}C was collected.

2. Synthesis of the cardanol conjugates 1a-b and 2-3a

*General Procedure for the Synthesis of **1a-b***: A mixture of cardanol (24 mmol), potassium carbonate (18 mmol) and hexakis(bromomethyl)benzene (1 mmol) in dry DMF (7 mL) were heated at 90 ^{0}C for 12 hours with vigorous stirring (for the synthesis of **1b**, instead of cardanol, 3-n-pentadecylphenol was used). The reaction mixture is cooled to room temperature and filtered to remove unreacted potassium carbonate. The filtrate is poured in to distilled water and is then extracted with ethyl acetate. Removal of the solvent gave a sticky liquid which was then subjected to column chromatography over silica gel. Elution of the column with a mixture of ethyl acetate and hexane (1:19) gave the corresponding cardanol based multi-armed molecules **1a-b** in good yields.

1a: (78 %), IR (KBr) νmax 3009, 2923, 2852, 1583 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.0 (6H, t, J = 7.0 Hz), 6.92-6.82 (9H, m), 5.95-5.82 (0.81H, m), 5.5-5.35 (9H, m), 5.20-5.00 (12 H, m), 2.87 (6H, m), 2.87 (6H, m), 2.68 (6H, t, J = 6.9 Hz), 2.1 (9H, m), 1.7 (6H, m), 1.4 (36H, m), 0.97 (6H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.6, 143.6, 136.9, 129.3, 129.0, 128.87, 128.2, 126.6, 120.4, 114.0, 110.8, 62.6, 35.0, 30.8, 30.5, 30.3, 28.7, 28.4, 28.2, 28.0, 26.2, 24.5, 21.8, 13.1; MALDI-TOF: m/z = 1967.158, 1968.274, 1969.264, 1970.186, 1971.214, 1972.161, 1973.212, 1974.211, 1975.226, 1976.218, 1977.225, 1978.202, 1979.208, 1980.207, 1981.217, 1982.241, (calcd 1975.803 for $C_{138}H_{222}O_6$, the saturated derivative).

1b: (74 %, mp 58 ^{0}C), IR (KBr) νmax 2924, 2848, 1587 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 500 MHz) δ 7.1 (6H, t, J = 7.5 Hz), 6.8-6.7 (18H, m), 5.2 (12H, m), 2.49 (12H, t, J = 7.0 Hz), 1.31-1.25 (156H, m), 0.88 (18H, t, J = 7.0 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 158.8, 145.0, 138.2, 129.5, 121.7, 115.3, 112.1, 64.0, 36.3, 32.2, 31.6, 30.0, 29.8, 29.7, 23.0, 14.4; MALDI-TOF: m/z = 1999.408 (M + Na$^+$), (calcd 1975.803 for $C_{138}H_{222}O_6$).

*Procedure for the Synthesis of **2a***: A mixture of cardanol (7 mmol), potassium carbonate (9 mmol) and 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1 mmol) in dry DMF (7 mL) were heated at 90 ^{0}C for 12 hours with vigorous stirring. The reaction mixture is cooled to room temperature and filtered to remove unreacted potassium carbonate. The filtrate is poured in to distilled water and is then extracted with ethyl acetate. Removal of the solvent gave a sticky liquid which was then subjected to column chromatography over silica gel. Elution of the column with a mixture of ethyl acetate and hexane (1:19) gave **2a** in good yield.

2a: (82 %), IR (KBr) νmax 3013, 2925, 2855, 1583 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.28 (3H, t, J = 8.1 Hz), 6.92-6.82 (9H, m), 5.95-5.82 (0.81H, m), 5.5-5.35 (9H, m), 5.20-5.00 (6H, s), 2.87 (6H, m), 2.87 (6H, m), 2.68 (6H, t, J = 6.9 Hz), 2.51 (9H, s), 2.1 (9H, m), 1.7 (6H, m), 1.4 (36H, m), 0.97 (6H, m); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.6, 145.0, 139.5, 137.1, 132.3, 130.7, 130.2, 129.6, 128.0, 127.2, 121.5, 115.2, 111.9, 65.1, 36.5, 31.9, 31.8, 30.2, 29.8, 29.6, 27.6, 26.0, 23.1, 16.3, 14.6; MALDI-TOF: m/z = 1073.752, 1074.756, 1075.768, 1076.777, 1077.774, 1078.780, 1079.793, 1080.796, 1081.807, 1082.810, 1083.812, 1084.819, 1085.832, 1086.830, 1087.843 (calcd 1068.972 for $C_{75}H_{120}O_3$, the saturated derivative).

*Procedure for the Synthesis of **3a***: A mixture of cardanol (2 mmol), potassium carbonate (5 mmol) and benzyl bromide (1 mmol) were heated at 90 ^{0}C for 12 hours with vigorous stirring. The reaction mixture is cooled to room temperature and filtered to remove unreacted potassium carbonate. The filtrate is poured in to distilled water and is then extracted with ethyl acetate. Removal of the solvent gave a sticky liquid which was then subjected to column chromatography over silica gel. Elution of the column with hexane (1:19) gave **3a** in good yield.

3a: (93 %), IR (KBr) νmax 3013, 2927, 2859, 1585 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.52-7.38 (5H, m), 7.26 (1H, t, J = 7.8 Hz), 5.95-5.82 (0.25H, m), 5.5-5.44 (3H, m), 5.1 (2H, s), 2.87 (2.5H, m), 2.65 (2H, t, J = 7.2 Hz), 2.1 (7.5H, m), 1.68 (2H, m), 1.39 (13H, m), 0.97 (2.5H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.6, 144.9, 137.5, 130.7, 130.4, 130.2, 129.6, 129.5, 128.8, 128.5, 128.2, 127.8, 121.4, 115.4, 112.0, 70.1, 36.3, 32.1, 31.8, 31.7, 30.1, 29.7, 29.6, 29.5, 29.3, 27.5, 26.0, 25.9, 23.1, 23.0, 14.5; HRMS-EI: m/z = 389.363, 391.331, 393.297 (calcd 394.324 for $C_{28}H_{42}O$, the saturated derivative).

3. 1. Preparation of Thin Films on Glass Slides

Thin films were prepared by drop casting a chloroform solution of the desired compound on glass slide and left it room temperature for few minutes. Evaporation of solvent produced sticky thin film on the glass slide for **1a** and **2a**. Such films when exposed to air at ambient conditions for 3 days or upon heating in an air oven at 70 ºC for 7-12 hours caused the oxidative cross-linking (autoxidation) of unsaturated alkyl chains, and produced a transparent, non-sticky and scratch-free film.

3.2. *In situ* Synthesis of Metal Nanoparticles from 1a and 2a

Metal salts (either silver benzoate or chloroauric acid) were dissolved in acetone, and added to the chloroform solution of desired compound at the required concentration. However, since the solubility of silver benzoate is less in acetone, when we needed higher concentration of silver salts, we used silver nitrate in methanol. Thin films were made on glass slides by drop casting a mixture of the desired compound and metal salts solution akin to above-mentioned procedure. The thin films upon exposure to air for 3 days or upon heating at 70 ºC for 7-12 hours produced nanoparticle embedded cross linked films. These films were non-sticky and scratch-free. They also had a pink and yellow color from the AuNPs and AgNPs embedded in the films, respectively.

3.3. UV-vis Spectroscopy

UV-visible spectra of the MNPs embedded cross linked films on the glass slides were directly recorded on CARY100BIO spectrophotometer. Regular uncoated laboratory glass slide was used as reference.

3.4. Transmission Electron Microscopy (TEM)

TEM was recorded by using Zeiss EM 902 transmission electron microscope (80 kV). MNPs embedded thin films were made on laboratory glass slides, and they were microtome to obtain 100 nm thick slices, which were directly placed on Cu-grid and examined under electron microscope.

3.5. Thiobarbituric acid (TBA) test

Five milliliters of both the partially cured solution of **1a** and TBA solution in water (1.0 mM) were mixed in a 10 mL volumetric flask. These solutions were transferred to Pyrex tubes with screw-caps and heated at 80 °C in a water bath for 30 min, then removed and cooled to room temperature and recorded the absorption spectrum.

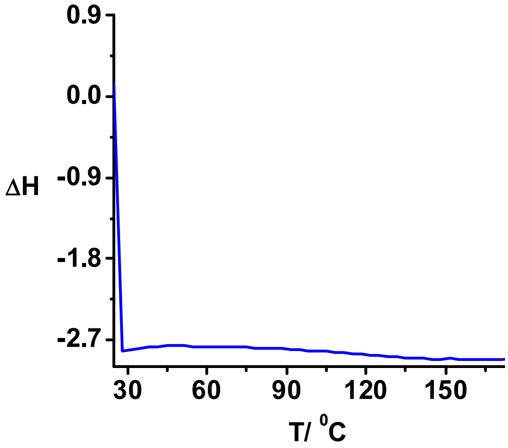


Fig. S1 DSC curve of **1a** obtained at a heating rate of 0.5 °C/min under anaerobic conditions (nitrogen atmosphere).

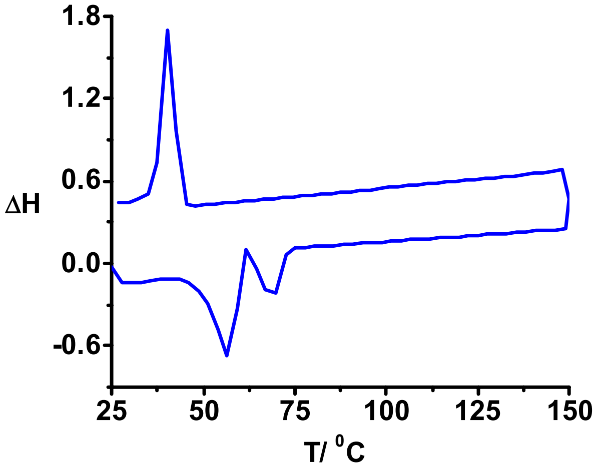


Fig. S2 DSC curve of **1b** obtained at a heating rate of 0.5 °C/min in air (aerobic conditions) (DSC curves obtained in the presence and absence of purged nitrogen for **1b** were the same).

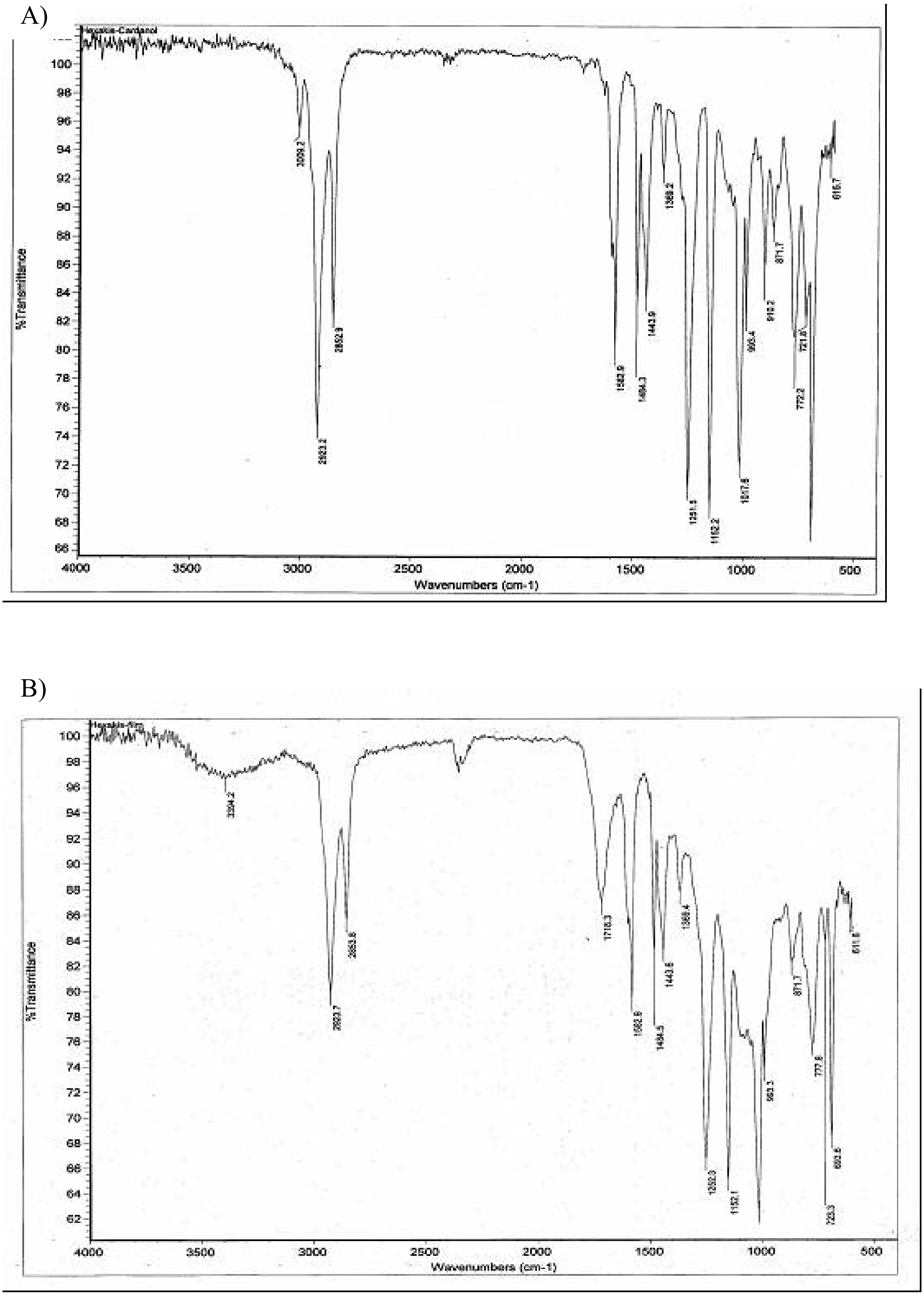


Fig. S3 IR spectrum of A) **1a** before autoxidation B) partially cured thin film of **1a**.

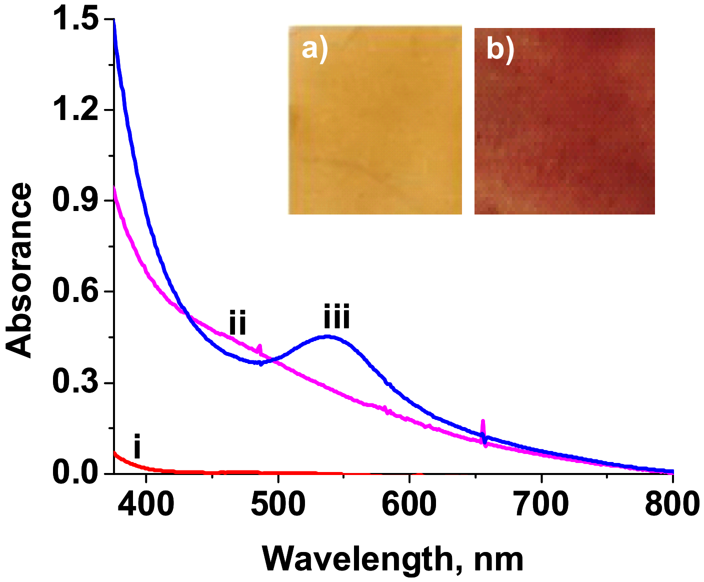


Fig. S4 Absorption spectra of thin films made from **2a**, in the presence of metal salts (i) before and (ii-iii) after the formation of MNPs; ii) AgNPs, iii) AuNPs. Inset shows the photograph of glass slides coated with **2a** containing *in situ* synthesized a) AgNPs, b) AuNPs.

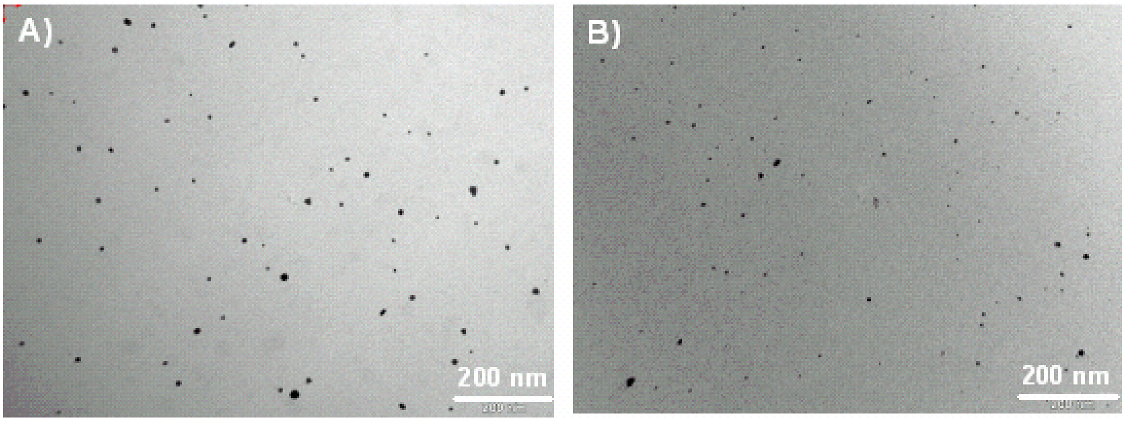


Fig. S5 TEM images of MNPs embedded films obtained from **2a** showing the uniform distribution of MNPs. A) AuNPs; B) AgNPs.

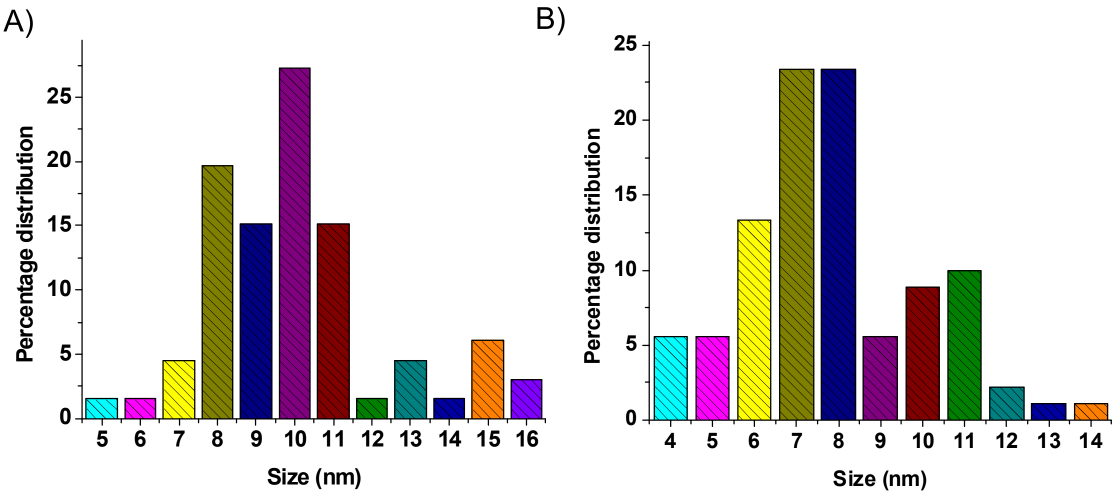


Fig. S6 Size distribution of A) **AuNPs** B) **AgNPs,** *in situ* synthesized from **1a**.

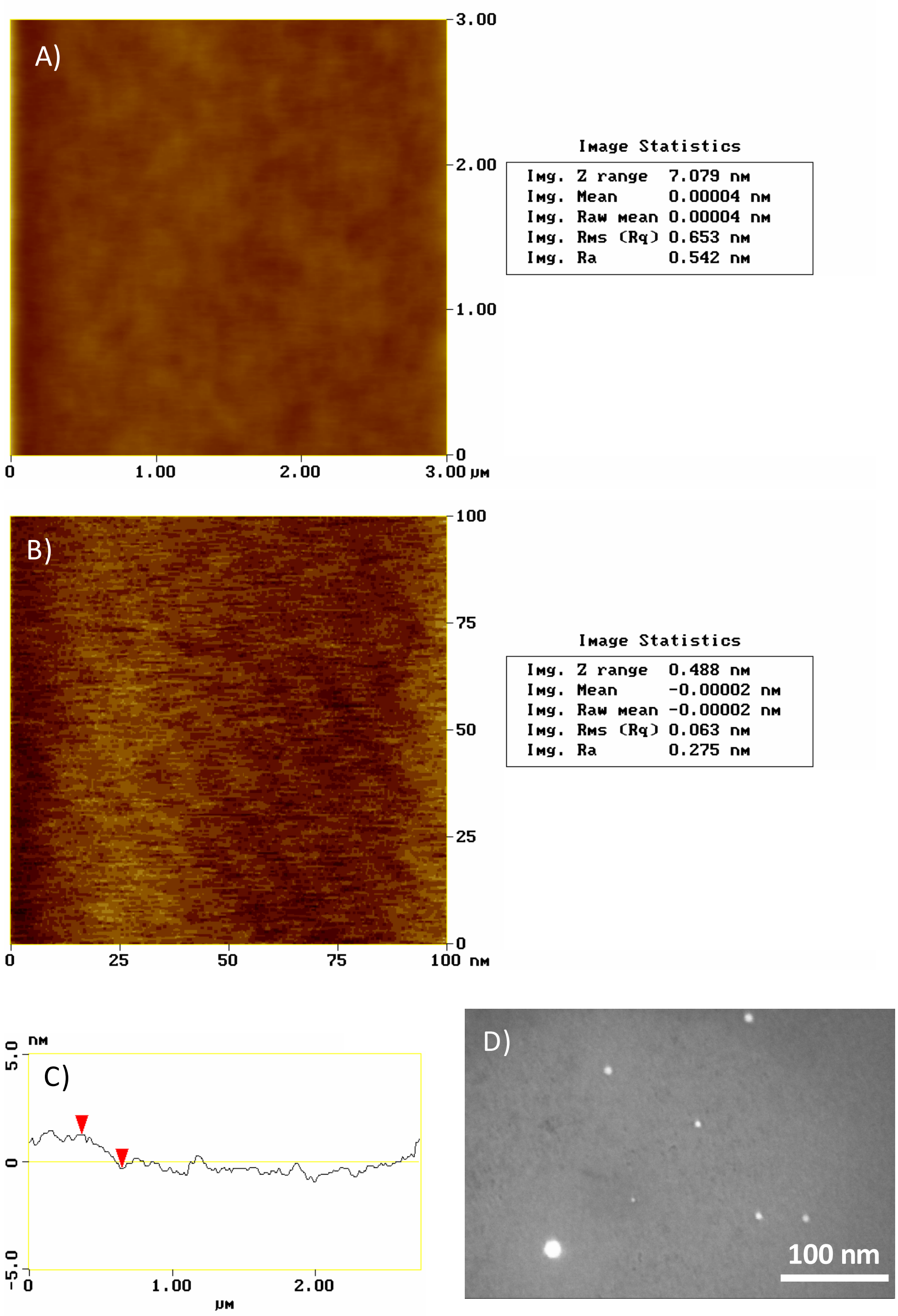


Image Statistics

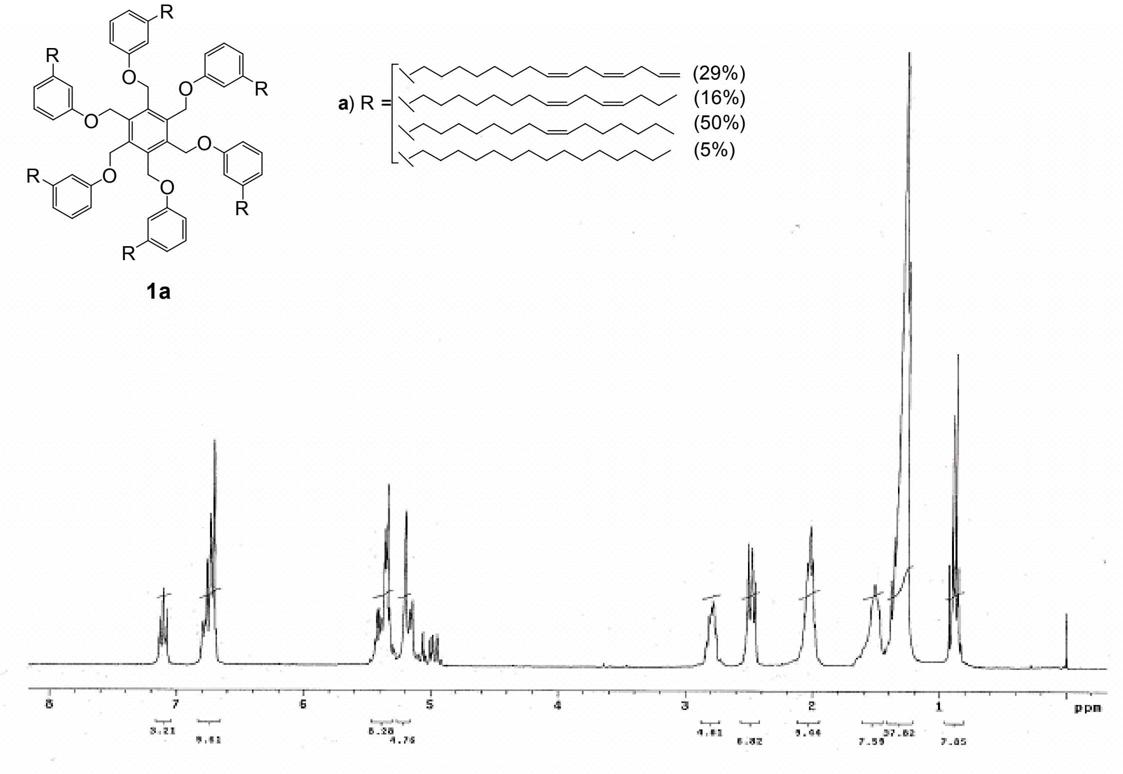
Img. Z range	7.079 nm
Img. Mean	0.00004 nm
Img. Raw mean	0.00004 nm
Img. Rms (Rq)	0.653 nm
Img. Ra	0.542 nm

Image Statistics

Img. Z range	0.488 nm
Img. Mean	-0.00002 nm
Img. Raw mean	-0.00002 nm
Img. Rms (Rq)	0.063 nm
Img. Ra	0.275 nm

Fig. S7 A-B) AFM height images of MNPs embedded films obtained from **1a** with the corresponding roughness analysis; C) Section analysis showing the uniform thickness of the film; D) SEM images of MNPs embedded films obtained from **1a**, white dots in the image are NPs that are on the surface of the film.

A)


R
O
a) R =
(29%)
(16%)
(50%)
(5%)
8
7
6
5
4
3
2
1
ppm
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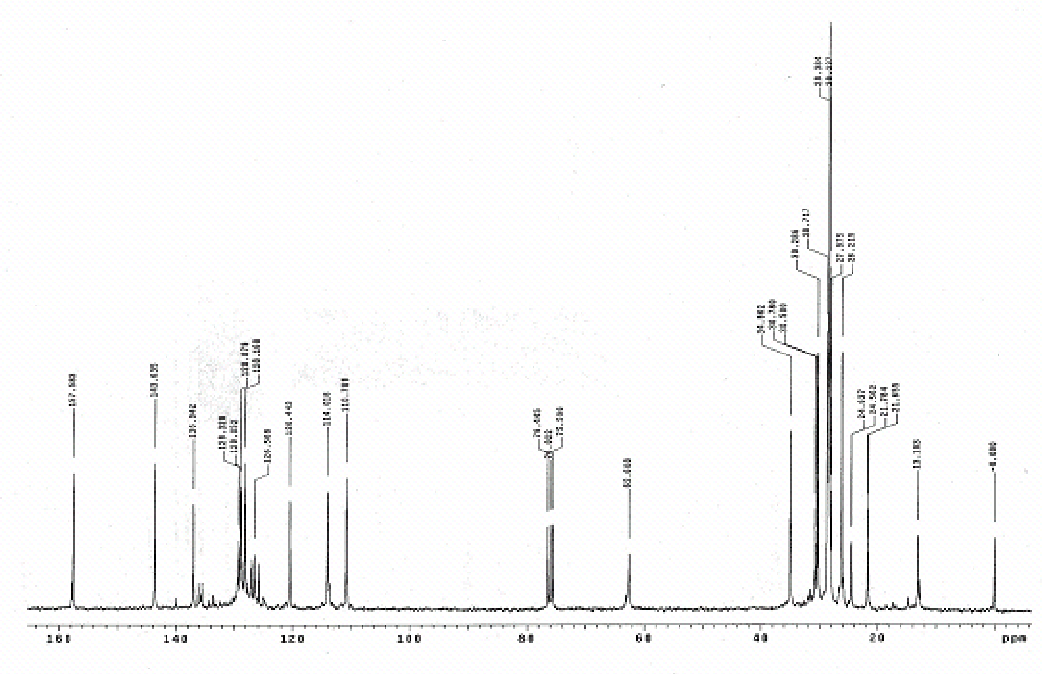
9.81
6.28
4.76
4.01
6.02
9.44
7.59
37.82
7.05

1a

B)


160
140
120
100
80
60
40
20
ppm

C)

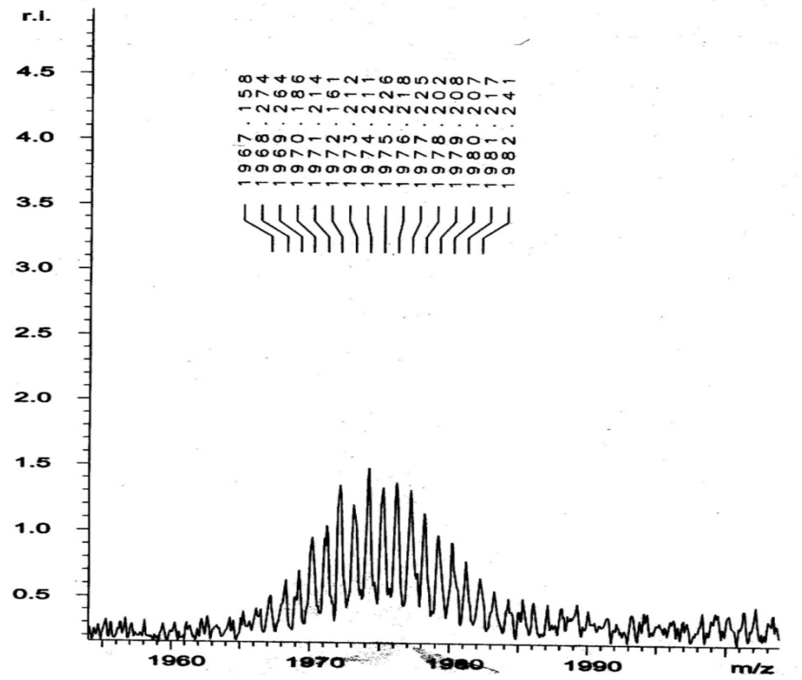


Fig. S8 A-B) ^{1}H (300 MHz), ^{13}C NMR (75 MHz) and MALDI-TOF spectrum, respectively of **1a**.

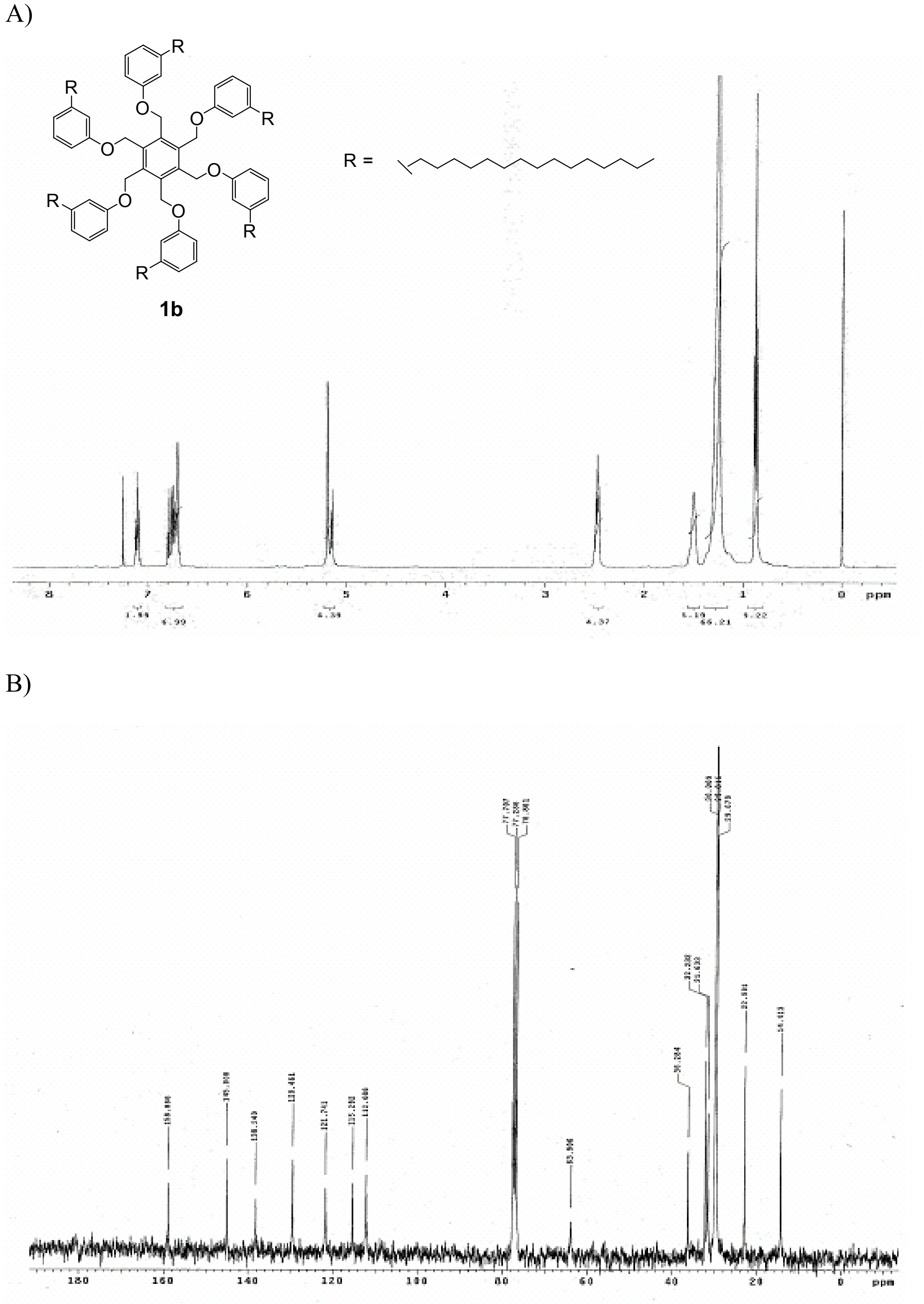
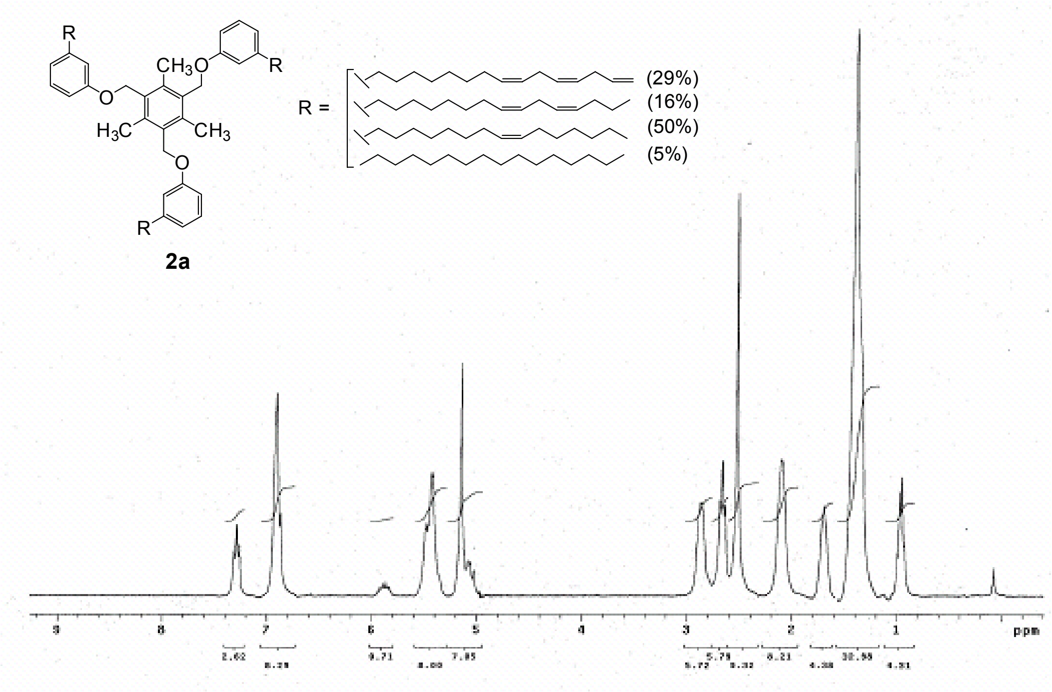
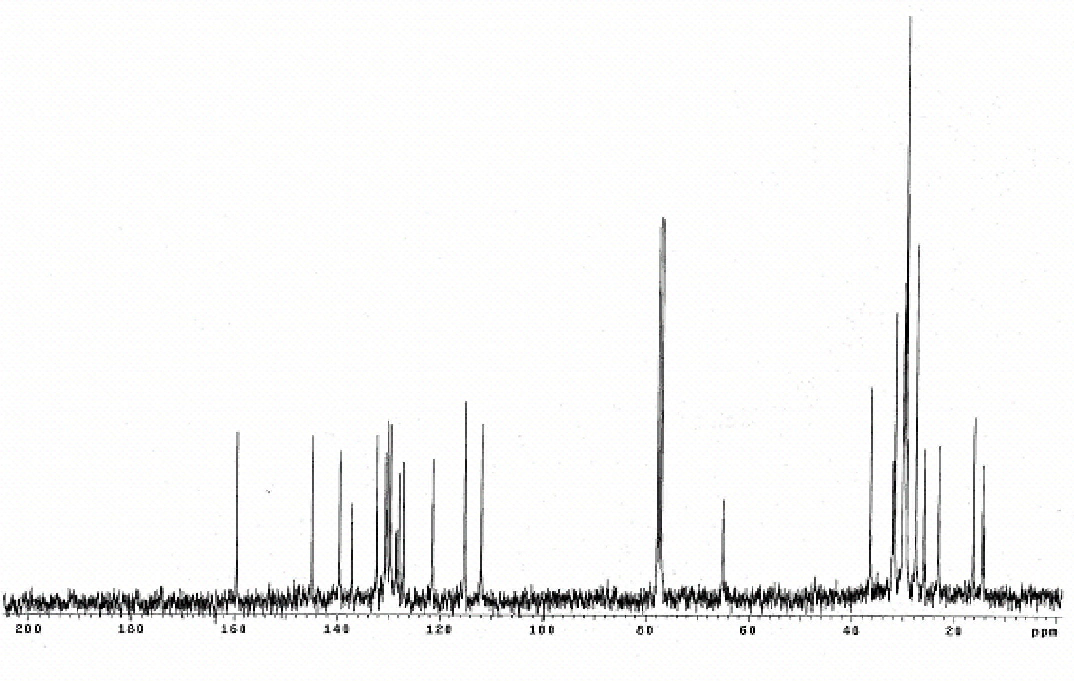


Fig. S9 A-B) ^{1}H (500 MHz) and ^{13}C NMR (75 MHz) spectrum, respectively of **1b** in $CDCl_3$.

A)


R
R
R
O
O
O
CH3
H3C
CH3
R =
(29%)
(16%)
(50%)
(5%)
2a
9
8
7
6
5
4
3
2
1
ppm
2.62
6.28
0.71
6.00
7.85
5.79
5.72
6.32
6.21
4.38
32.55
4.31

B)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100
80
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40
20
ppm

C)

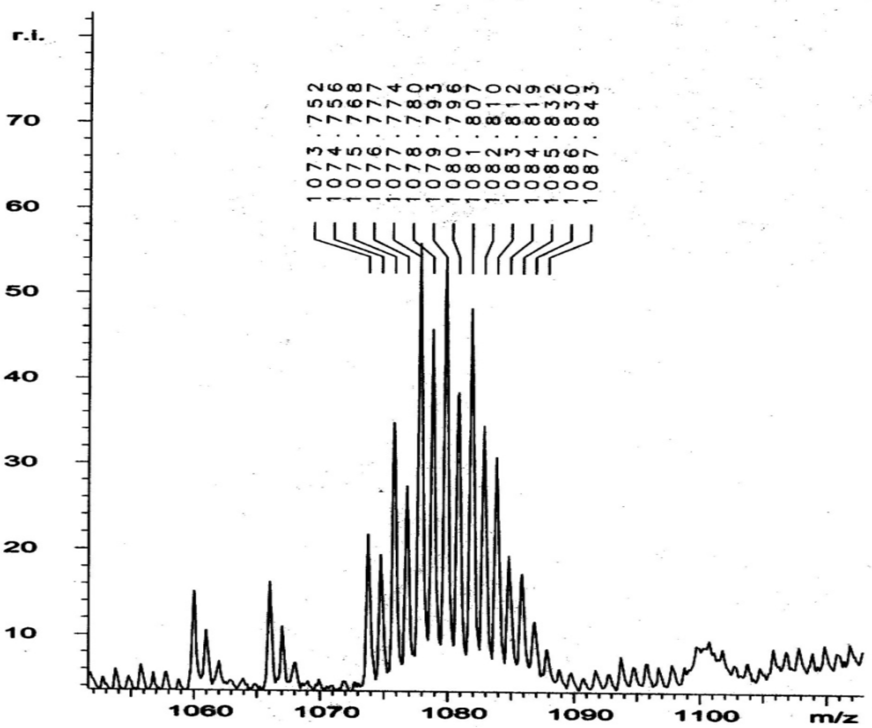

Fig. S10 A-B) ^{1}H (300 MHz) ^{13}C NMR (75 MHz) and MALDI-TOF spectra, respectively of **2a** in CDCl$_3$.

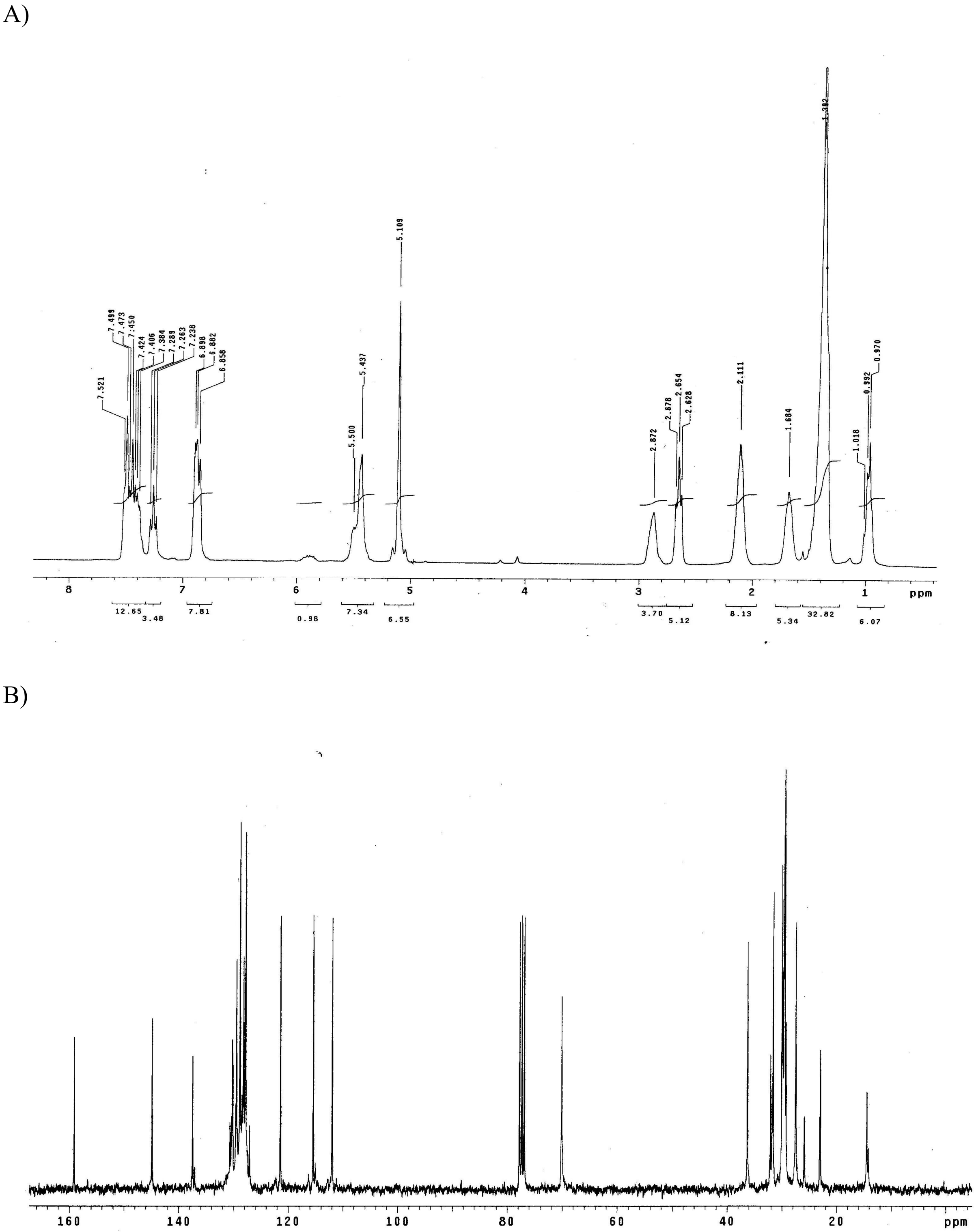

Fig. S11 A-B) ^{1}H (300 MHz) and ^{13}C NMR spectrum (75 MHz), respectively of **3a** in $CDCl_3$.