Supplementary Material (ESI) for Chemical Communications

Reversible self-assembly of dendrimer based on polyhedral oligomeric silsesquioxane (POSS)

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Supplementary Information

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Experimental Materials

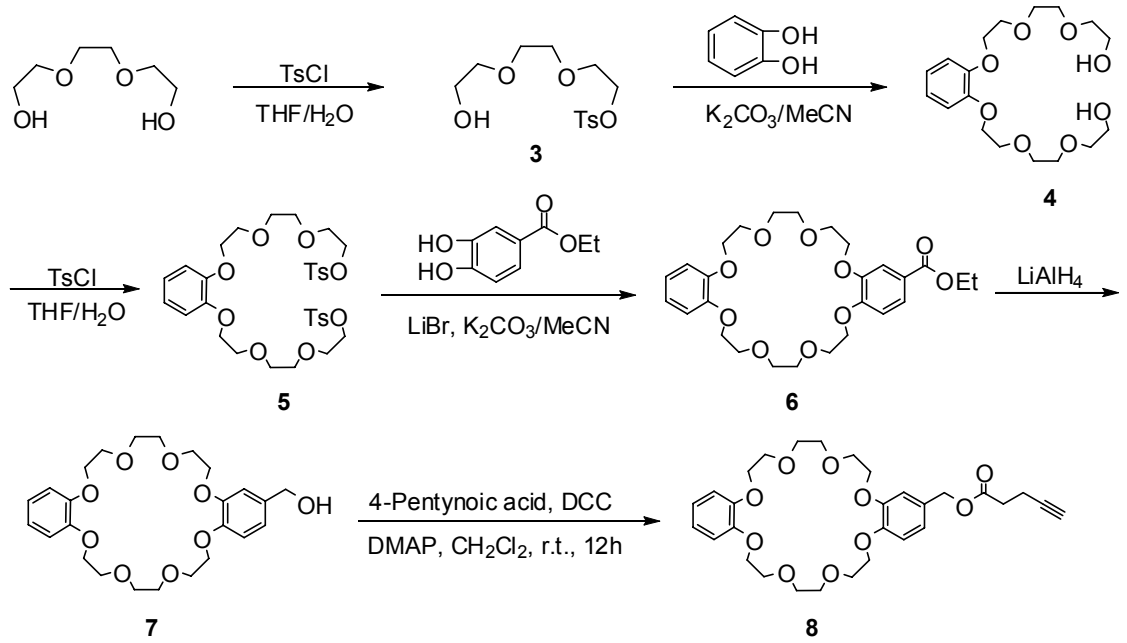
Triethylene glycol (99%), *p*-toluenesulfonyl chloride, pyrocatechol (99%), ethyl 3, 4-dihydroxybenzoate (97%), 4-pentynoic acid (95%), N,N′-dicyclohexylcarbodiimide (99%), 4-di(methylamino)pyridine (99%), 4-bromobenzaldehyde (99%), lithium bromide (99%), ethynyltrimethylsiane, bis(triphenylphosphine)palladium(Ⅱ) dichloride (99.99%), benzylamine (99%), triethylamine (99.5%), copper(Ⅰ) iodide (98%), copper (Ⅱ) sulfate pentahydrate (99.99%), (+)-sodium L-ascorbate (98%), ammonium hexafluorophosphate, anhydrous methanol, anhydrous dichloromethane and anhydrous acetonitrile were purchased from Sigma Aldrich Co. and used without further purification. Lithium aluminium hybride (92.0%) was purchased from Kanto Chemical CO., INC. 1-Ethynylpyrene (96%) was purchased from Alfa Aesar. Reagents and solvents were used without further purification, except for tetrahydrofuran (THF) and toluene, which were distilled in the presence of calcium hydride.

Characterization

^{1}H (500 MHz), ^{13}C (125 MHz), and ^{29}Si (99 MHz) NMR spectra were obtained in $CDCl_3$ on a Varian 500 MHz spectrometer model Unity INOVA. Chemical shifts were reported in ppm relative to $CHCl_3$ (δ 7.26, ^{1}H), $CDCl_3$ (δ 77.0, ^{13}C), acetone (δ 2.05, ^{1}H), acetone (δ 29.84, 206.15, ^{13}C) and tetramethylsilane (δ 0.00, ^{29}Si). ^{1}H NMR of complex at different ratio was obtained on a Bruker 400 MHz spectrometer. Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS) was taken on a Shimadzu Kratos Kompact MALDI III. The matrix 2,5-dihydroxybenzoic acid (DHBA) was dissolved in CH_2Cl_2 (10 mg/ml), and mixed with the sample solution (0.5-1 mg/ml in CH_2Cl_2) in 1 : 1 v/v ratio. Elemental analysis (EA) was performed on a

Vario EL III elemental analyzer. Gas chromatography-mass spectroscopic (GC-MS) analysis was carried out on a Shimadzu QP-5000 mass spectrometer. Gel permeation chromatography (GPC) analysis was performed on a JASCO HPLC Gulliver 900 with a combination of KF-803L (30 cm, exclusion limit: 7.0×10^4, polystyrene) and KF-804 (30 cm, exclusion limit: 4.0×10^5, polystyrene) columns (linear calibration down to M_n = 100) with THF as an eluent. Thin-layer chromatography (TLC) was performed on silica gel sheet coated with silica gel 60 F_{254} from E. Merck, visualized by UV light. Column chromatography was performed on silica gel 60 N (Kanto Chemical CO., INC, Cat. No. 37563-79, 40-50 μm). Air and moisture sensitive manipulations were performed under nitrogen using standard Schlenk techniques.

General procedures for dibenzo-24-crown-8



Preparation of 8-tosyloxy-3,6-dioxaoctanol (3): To a mixture of triethylene glycol (35 ml, 0.26 mol) and sodium hydroxide (8 g, 0.2 mol) in THF (40 ml)/H_2O (40 ml) in an ice bath was added dropwise tosyl chloride (24 g, 0.13 mmol) in THF (80 ml) for 3 h. The reaction mixture was stirred overnight; THF was then evaporated under reduced

pressure. The residue was extracted with ethyl acetate and dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the crude product was purified by column chromatography over silica gel (eluent: ethyl acetate) to afford product (18.2 g, 46%). δ_H(500 MHz; $CDCl_3$; 298 K) 2.36 (3 H, s, C*H*$_3$), 2.79 (1 H, br, s, O*H*), 3.51 (6 H, m, 3 × OC*H*$_2$), 3.61 (4 H, m, 2 × OC*H*$_2$), 4.02 (2 H, m, OC*H*$_2$), 7.26 (2 H, d, Ar*H*), 7.72 (2 H, d, Ar*H*); δ_C(125 MHz; $CDCl_3$; 298 K) 21.79 (*C*H$_3$), 61.78, 68.81, 69.45, 70.04, 70.84, 72.70 (O*C*H$_2$), 128.11, 130.06, 133.06, 145.10(Ar*C*).

Preparation of 1,2-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzene (4): Mixture of catechol (2.83 g, 0.026 mol), compound **3** (16.0 g, 0.052 mol) and K_2CO_3 (16 g, 0.12 mol) in dry acetonitrile (200 ml) was refluxed for 60 h. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: ethyl acetate/methanol = 4 : 1) to afford the desired product (7.59 g, 78 %). δ_H(500 MHz; $CDCl_3$; 298 K) 3.16 (2 H, s, br, OH), 3.59-3.60 (4 H, m), 3.67-3.75 (4 H, m,), 3.87-3.89 (4 H, m), 4.16-4.18 (8 H, m), 6.90 (4 H, s); δ_C(125 MHz; $CDCl_3$; 298 K) 61.94, 68.83, 69.97, 70.58, 71.07, 72.97, 114.56, 121.86, 148.95.

Preparation of 1,2-Bis[2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy]benzene (5): To a mixture of compound **4** (7.32 g, 19.6 mmol) and sodium hydroxide (3 g, 75 mmol) in THF/H_2O (20 ml/20 ml) in an ice bath was added dropwise tosyl chloride (7.5 g, 39.5 mmol) in THF (60 ml) for 3 h. The mixture solution was continued to stir overnight, then THF was evaporated under reduced pressure. The residue was extracted with ethyl acetate and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the crude product was purified by column chromatography (eluent: ethyl acetate/hexane = 4 : 1) to afford the desired product (11.5 g, 86%). δ_H(500 MHz; $CDCl_3$; 298 K) 2.42 (6 H, s),

3.58-3.60 (4 H, m), 3.65-3.69 (4 H, m), 3.80-3.82 (4 H, m), 4.12-4.15 (8 H, m), 6.90 (4 H, s), 7.32 (4 H, dd), 7.78 (4 H, dd); δ_C(125 MHz; $CDCl_3$; 298 K) 21.66, 68.72, 68.85, 69.33, 69.85, 70.78, 70.83, 114.90, 121.69, 127.99, 129.87, 132.99, 144.85, 148.98.

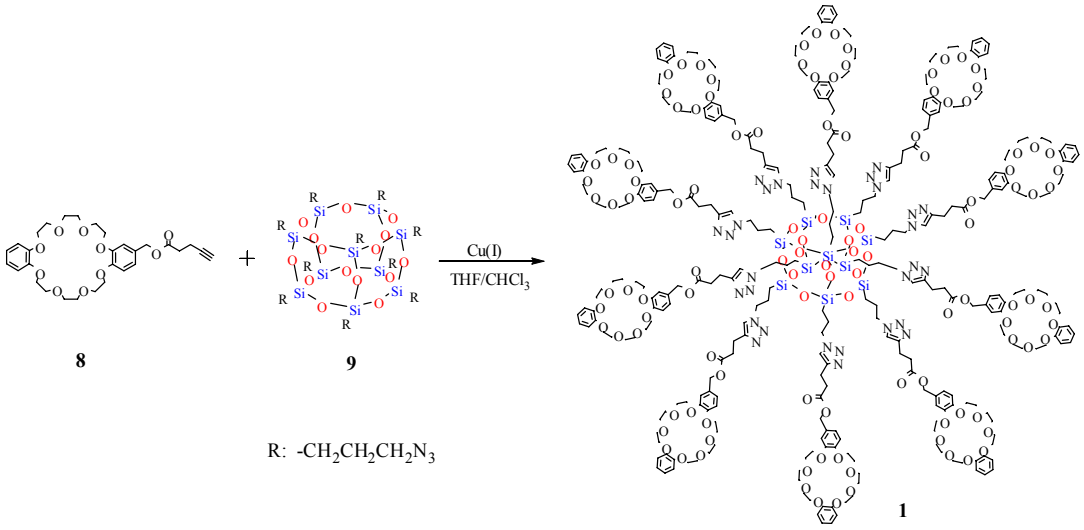
Preparation of ethyl 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo [b, n] [1,4,7,10,13,16,19,22] octaoxacyclotetracosine-2-carboxylate (6)[1]: A solution of ethyl 3,4-dihydroxybenzoate (0.81 g, 4.5 mmol), K_2CO_3 (3.0 g, 18 mmol) and a catalytic amount of LiBr in MeCN (500 ml) was heated to reflux under N_2 for 1 h. A solution of compound **5** (3.07 g, 4.5 mmol) in MeCN (250 ml) was added dropwise over 12 h and the mixture was heated to reflux for 48 h. Filtration and concentration of the filtrate *in vacuo* left an oil which was taken up in CH_2Cl_2 (150 ml) and washed with 0.1 M aq. HCl (2 × 100 ml) and sat. aq. NaCl solution (100 ml). Drying ($MgSO_4$) and evaporation *in vacuo* followed by column chromatography (eluent: ethyl acetate/methanol = 10 : 1) afforded product (1.75 g, 74.7%). δ_H(500 MHz; $CDCl_3$; 298 K) 1.37 (3 H, t), 3.83 (8 H, m), 3.90- 3.94 (8 H, m), 4.13-4.19 (8 H, m), 4.33 (2 H, q), 6.83 (1 H, d), 6.85-6.90 (4 H, m), 7.51 (1 H, d), 7.63-7.65 (1 H, dd); δ_C(125 MHz; $CDCl_3$; 298 K) 14.50, 60.90, 69.38, 69.44, 69.50, 69.60, 69.74, 69.89, 70.05, 71.39, 71.47, 71.56, 112.06, 114.10, 114.40, 121.52, 123.31, 123.93, 128.08, 129.94, 148.30, 148.99, 152.88, 166.47.

Preparation of 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b, n]-[1,4,7,10, 13,16,19,22]octaoxacyclotetracosin-2-ylmethanol (7): A solution of compound **6** (1.4 g, 2.68 mmol) in THF (50 ml) was added dropwise to a suspension of $LiAlH_4$ (0.51 g, 13.4 mmol) in THF (150 ml) during 1 hour under ice bath. The mixture was stirred for 1 h at room temperature, and then heated to reflux for 2 h. The solution was filtered on Celite, then evaporation, 150 ml CH_2Cl_2 was added, 0.1 M HCl (100 ml for two times) was added to the mixture, then separate to get organic layer. The organic layer was

washed with brine (2 × 40 ml), dried over $MgSO_4$ and evaporation *in vacuo* yielded product (1.2 g, 93.6%) as a white powder. δ_H(500 MHz; $CDCl_3$; 298 K) 3.82 (8 H, s), 3.89-3.91 (8 H, m), 4.13-4.15 (8 H, m), 4.57 (2 H, s), 6.81-6.90 (7 H, m); δ_C(125 MHz; $CDCl_3$; 298 K) 65.24, 69.45, 69.64, 69.99, 71.37, 113.04, 113.94, 114.13, 120.00, 121.52, 134.37, 148.46, 149.00, 149.09.

Preparation of (6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n] [1,4,7,10, 13,16,19,22] octaoxacyclotetracosin-2-yl)methyl pent-4-ynoate (8)[2]: A mixture of compound **7** (1.0 g, 2.1 mmol), 4-pentynoic acid (0.24 g, 2.31 mmol), DCC (4.1 ml, 4.1 mmol), and DMAP (53.0 mg) in CH_2Cl_2 (20 ml) was stirred at room temperature for 12 h. The solution was then filtered through a short pad of Celite, and the filtrate obtained was evaporated under reduced pressure. The residue was purified by column chromatography (eluent: $CHCl_3/CH_3OH$ = 5 : 1, and then $CHCl_3/CH_3OH$ = 15 : 1) to afford the monomer product (1.02 g, 87%) as a white solid. δ_H (500 MHz; $CDCl_3$; 298 K) 1.97 (1 H, s), 2.51 (2 H, m), 2.56 (2 H, m), 3.83 (8 H, s), 3.91 (8 H), 4.14 (8 H, quin), 5.04 (2 H, s), 6.81-6.90 (7 H, m); δ_C(125 MHz; $CDCl_3$; 298 K) 14.32, 33.34, 66.49, 69.05, 69.36, 69.44, 69.47, 69.81, 69.82, 69.90, 71.27, 71.30, 82.43, 113.48, 113.96, 114.30, 121.37, 121.74, 128.69, 148.81, 148.87, 148.99, 171.61.

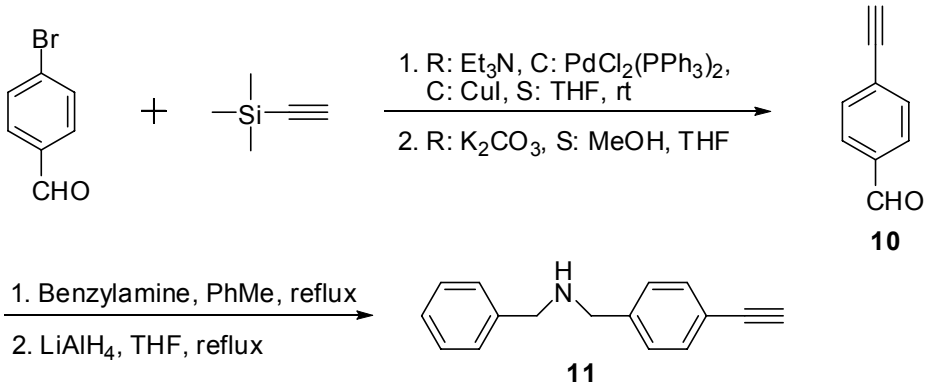
General procedures for dibenzo-24-crown-8 terminated POSS-core dendrimer (1)



A solution of compound **9**[3] (0.05 g, 0.0367 mmol) and **8** (0.215 g, 0.385 mmol) in $THF/CHCl_3$ (12 ml/3 ml) was placed in a 30 ml round-bottom flask sealed with a rubber septum and degassed by nitrogen bubbling during 15 min. Then, a freshly prepared aqueous solution of $CuSO_4 \cdot 5H_2O$ (5 mol%, 4.82 mg, 0.0193 mmol) in 0.3 ml of water was added to the mixture, followed by addition of a solution of sodium ascorbate (10 mol%, 7.63 mg, 0.0385 mmol) in 0.3 ml of water. Nitrogen bubbling was continued for further 3 min. Upon the addition of copper, the reaction mixture turned brown for a few seconds and then changed to a yellow-orange color, which persisted for several hours at 40 °C under nitrogen atmosphere. Reactions that had reached completion, usually 48 h, had become yellow-green. The solution was then filtered through a short pad of Celite, and the filtrate obtained was evaporated under reduced pressure. The residue was purified by column chromatography (eluent: $CHCl_3/CH_3OH$ = 40 : 1, and then $CHCl_3/CH_3OH$ = 10 : 1) to afford the desired product (0.23 g, 89.0%) as a gelatinous solid. δ_H(500 MHz; $CDCl_3$; 298 K) 0.54 ($SiCH_2CH_2CH_2$), 1.92 ($SiCH_2CH_2$ CH_2), 2.73-2.76 (CH_2CH_2CO), 3.0-3.03 (CH_2CH_2CO), 3.81 (8 H, s), 3.89 (8 H, m), 4.11 -4.13 (8 H, m), 4.25 (2 H, m, $SiCH_2CH_2CH_2$), 4.99 ($-OCH_2$), 6.79-6.89 (7 H, m), 7.51

(C*H*=C); δ_C(125 MHz; $CDCl_3$; 298 K) 9.22, 20.87, 24.0, 33.57, 52.16, 66.27, 69.33, 69.41, 69.45, 69.78, 69.87, 71.21, 113.55, 113.99, 114.30, 121.36, 121.64, 122.03, 128.78, 145.99, 148.78, 148.86, 148.93, 172.50; δ_{Si}(99 MHz; $CDCl_3$; 298 K) -69.24 (Si-O-Si). MALDI-TOF MS $[C_{330}H_{440}N_{30}O_{115}Si_{10}+Na]^+$: Calcd. 6965.71, found 6964.61.

General procedures for N-benzyl-1-(4-ethynylphenyl) methanamine

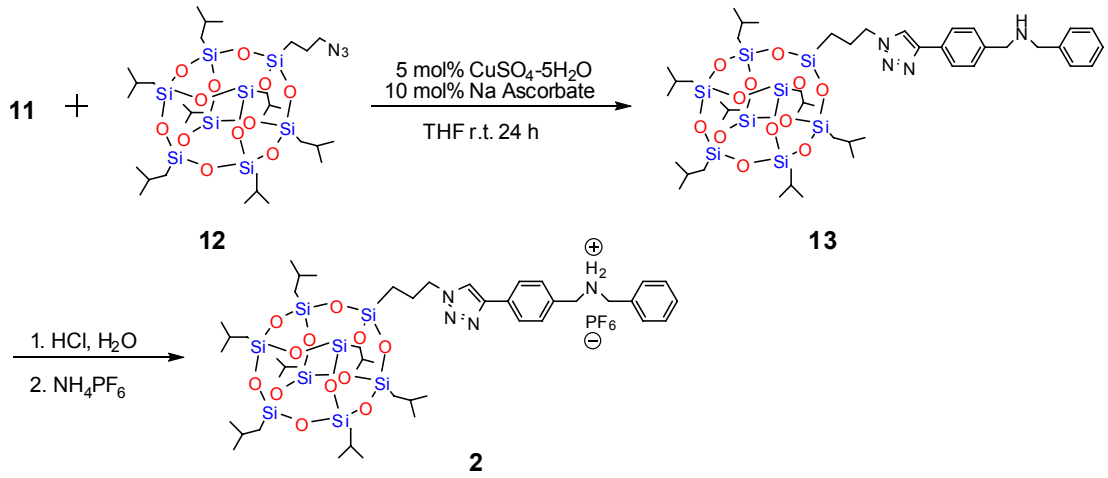


Synthesis of 4-ethynylbenzaldehyde(10)[4]: To a stirred mixture of 4.63 g (25.0 mmol) of 4-bromobenzaldehyde, 190 mg (1.0 mmol) of CuI, and 350 mg (0.50 mmol) of $Pd(PPh_3)_2Cl_2$ in 35 ml of THF was added 5.1 g (36.42 mmol) of triethylamine. A solution of trimethylsilylacetylene (3.7 ml, 26.3 mmol) in 9 ml of THF was then added over 1 h. The solvent was evaporated, and the residue was treated by pentane. Filtration through Celite and evaporation of the solvent under vacuum to give a thick oil, which was purified by column chromatography (eluent: CH_2Cl_2/hexane = 1 : 1) afforded 4-(tri methylsilylethinyl)benzaldehyde **(**5.0 g, 99%). 4-(Trimethylsilylethinyl)benzaldehyde (3.4 g, 16.8 mmol) and K_2CO_3 (0.23 g, 1.68 mmol) were dissolved in 60 ml of MeOH. The reaction was stirred at room temperature for 3 h, and the solvent was removed under vacuum. The solid was redissolved in CH_2Cl_2 and was washed with aqueous $NaHCO_3$ three times. The organic layer was dried over Na_2SO_4 and evaporated under

vacuum. The yellow residue was purified by column chromatography (eluent: CH_2Cl_2/ hexane = 3 : 1) afforded product (2.14 g, 98%). δ_H(500 MHz; acetone-d_6; 298 K) 3.98 (1 H, s, ethynyl H), 7.71 (2 H, d, ArH), 7.94 (2 H, d, ArH), 10.07 (1 H, s, CHO); δ_C(125 MHz; acetone-d_6; 298 K) 82.98, 83.39, 128.99, 130.37, 133.51, 137.38, 192.39.

Synthesis of N-benzyl-1-(4-ethynylphenyl)methanamine (11): A solution of benzyl amine (1.10 ml, 10 mmol) and 4-ethynylbenzaldehyde (1.30 g, 10 mmol) in toluene (70 ml) was stirred under reflux in a Dean-Stark apparatus for 18 h. After the reaction mixture was cooled down to room temperature, the solvent was evaporated under vacuum to give a yellow solid, which was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1: 1) afforded the imine product (2.10 g, 95%). δ_H(500 MHz; $CDCl_3$; 298 K) 3.18(1 H, ethynyl H), 4.84(2 H, -C*H*$_2$), 7.34-7.76(5 H, Ar*H*), 8.38(1 H, -C*H*-N). A solution of imine (0.50 g, 2.28 mmol) in THF (30 ml) was added dropwise to a suspension of $LiAlH_4$ (0.47 g, 11.39 mmol) in THF (80 ml) during 1 h under ice bath. The mixture was stirred for 1 h at room temperature, and then heated to reflux for 8 h. The reaction progress was monitored by GC-MS until total disappearance of the starting materials. The solution was filtered on Celite, then evaporation, the residue was purified by column chromatography (eluent: ethyl acetate/$CHCl_3$ = 1 : 2) afforded product (0.41 g, 81%). δ_H(500 MHz; acetone-d_6; 298 K) 3.61(1 H, ethynyl H), 3.76(2 H, -C*H*$_2$), 3.78(2 H, -C*H*$_2$), 7.23-7.46(5 H, Ar*H*); δ_C(125 MHz; acetone-d_6; 298 K) 53.16, 53.55, 78.66, 84.32, 121.34, 127.45, 128.86, 128.97, 132.58, 141.75, 143.08.

General procedures for dibenzylammonium hexafluorophosphate salt based on POSS (2)



A solution of compound **11** (0.25 g, 1.11 mmol) and **12**[3] (1.0 g, 1.11 mmol) in 30 ml THF was placed in a 50 ml round-bottom flask sealed with a rubber septum and degassed by nitrogen bubbling during 15 min. Then, a solution of $CuSO_4 \cdot 5H_2O$ (5 mol%, 0.014 g, 0.056 mmol) in 0.5 ml of water was added to the mixture, followed by addition of a solution of sodium ascorbate (10 mol%, 0.022 g, 0.11 mmol) in 0.5 ml of water. Upon the addition of copper, the reaction mixture turned brown for a few seconds and then changed to a yellow-orange color, which persisted for several hours at room temperature under nitrogen atmosphere. Reactions that had reached completion, usually 24 h, had become yellow-green. The solution was then filtered through a short pad of Celite, and the filtrate obtained was evaporated under reduced pressure. The residue was purified by column chromatography (eluent: ethyl acetate/hexane = 1 : 1) to afford the desired product (1.15 g, 92%) as a white solid. δ_H(500 MHz; $CDCl_3$; 298 K) 0.59-0.62 (-Si-C*H*$_2$-CH(CH_3)), 0.94-0.96(-Si-CH_2-CH(C*H*$_3$)), 1.81-1.88(-Si-CH_2-C*H*(CH_3)), 2.05 (Si-CH_2C*H*$_2$$CH_2$-N), 3.83-3.85(-C*H*$_2$-NH-C*H*$_2$), 4.39 (Si-$CH_2$$CH_2$C*H*$_2$-N), 7.34-7.42 (7 H, Ar*H*), 7.71 (1 H, -C*H*=C), 7.79-7.81(2 H, Ar*H*); δ_C(125 MHz; $CDCl_3$; 298 K) 9.20, 22.40, 22.43, 23.81, 23.87, 24.20, 25.66, 52.49, 52.72, 52.98, 119.14, 125.72, 127.04, 128.23, 128.43, 128.68, 129.50, 139.96, 147.59; δ_{Si}(99 MHz; $CDCl_3$; 298 K) -67.52,

-67.83, -68.50. MALDI-TOF MS [$C_{47}H_{84}N_4O_{12}Si_8$]: Calcd. 1120.42, found 1120.09.

Compound **13** (0.1 g, 0.089 mmol) was dissolved THF (5 ml), 3 ml of 5 N aq. HCl was added (pH<2) and the reaction mixture was stirred for 30 min. Evaporation of the solvent afforded a yellow solid, which was dissolved again in THF (5 ml). A solution of NH_4PF_6 (0.15 g, 0.92 mmol) in 0.2 ml of water was added to the solution and stirred for 5 min. Evaporation of solvent afforded pale solid **2**, which were isolated, washed with H_2O, and dried in vacuum to afford product (0.11 g, 95%). ^{1}H NMR (500 MHz; $CDCl_3$; 298 K) 0.59-0.67 (-Si-C*H*$_2$-CH(CH_3)), 0.92-0.96 (-Si-CH_2-CH (C*H*$_3$)), 1.80-1.87 (-Si-CH_2-C*H*(CH_3)), 2.08 (Si-CH_2C*H*$_2$$CH_2$-N), 4.01 (-C*H*$_2$-$NH_2^+$-), 4.42 (-C*H*$_2$-$NH_2^+$-), 4.50 (Si-$CH_2CH_2$C*H*$_2$-N), 7.1-7.2 (4 H, Ar*H*), 7.44-7.63 (5 H, Ar*H*), 7.93 (1 H, -C*H*=C). MALDI-TOF MS [$C_{47}H_{84}N_4O_{12}Si_8$ –PF_6]$^+$: Calcd. 1121.43, found 1121.06.

Copies of NMR and MALDI-TOF-MS data of compounds

The ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR and MALDI-TOF MS of dibenzo-24-crown-8 terminated POSS-core dendrimer (**1**) were shown in **Figure 1-4**.

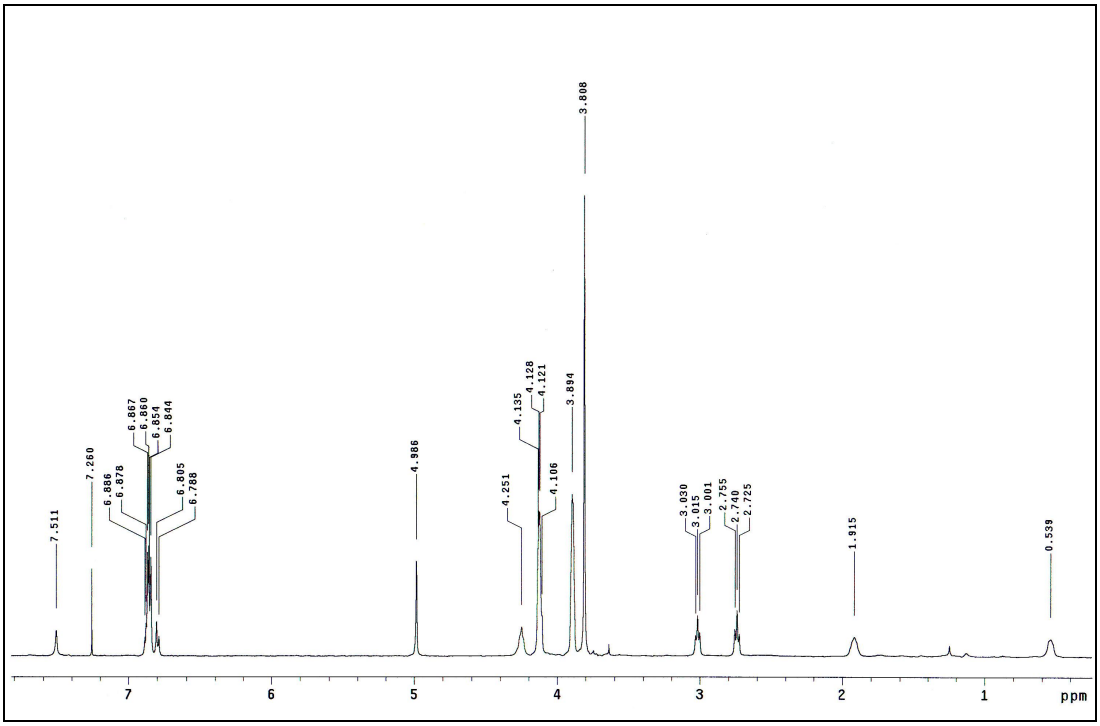


Fig. 1 ^{1}H NMR (500 MHz; $CDCl_3$; 298K) of **1**

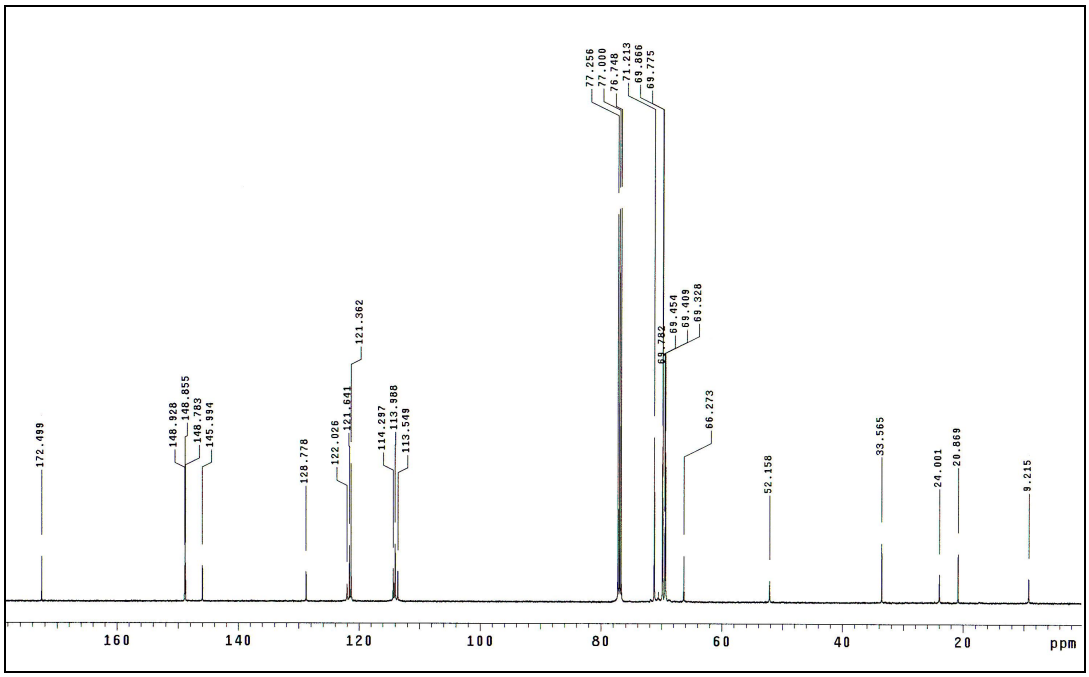


Fig. 2 ^{13}C NMR (125 MHz; $CDCl_3$; 298K) of **1**

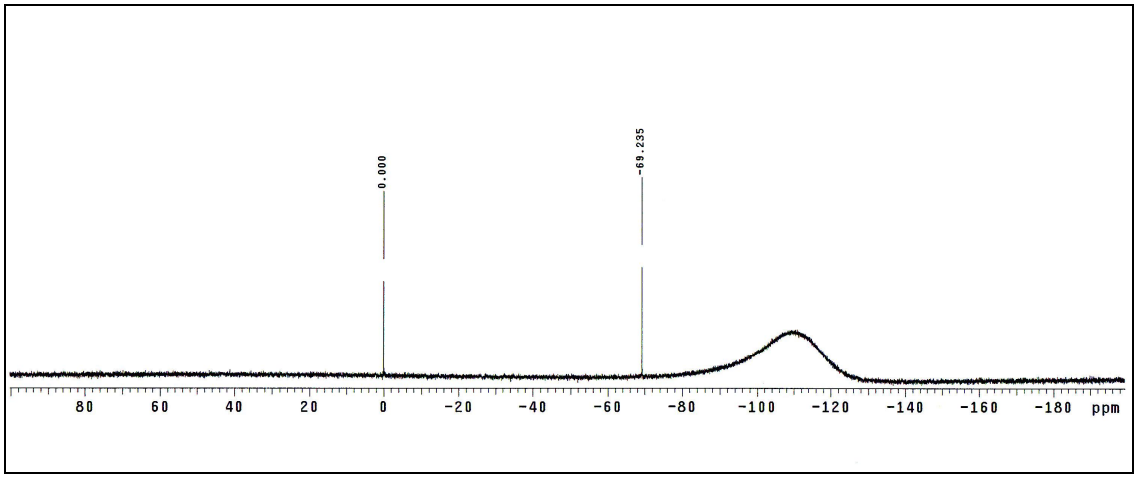


Fig. 3 ^{29}Si NMR (99 MHz; $CDCl_3$; 298K) of **1**

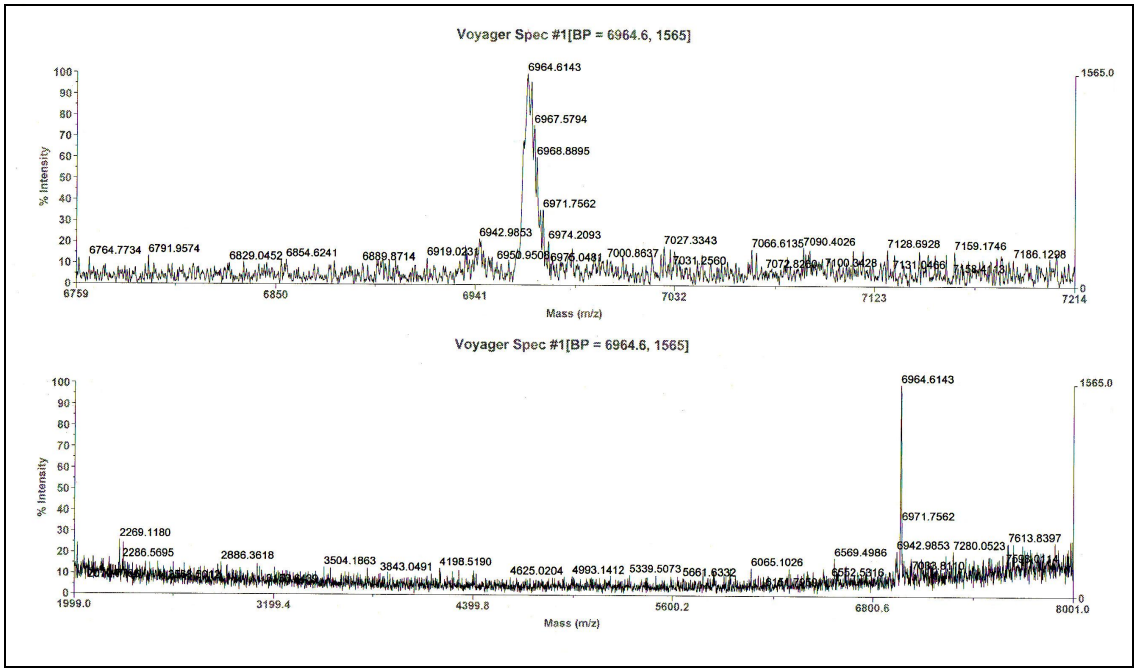


Fig. 4 MALDI-TOF MS of **1**

The ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR and MALDI-TOF MS of dibenzylammonium based on POSS (**13**) and its dibenzylammonium hexafluorophosphate salt based on POSS (**2**) were shown in **Figure 5-10**.

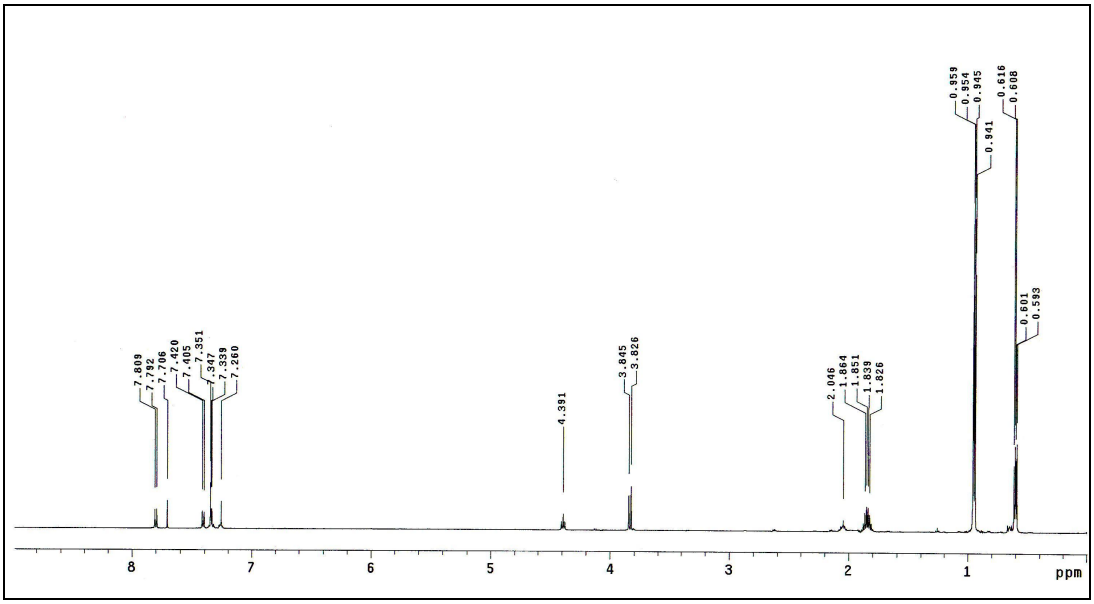


Fig. 5 ^{1}H NMR (500 MHz; $CDCl_3$; 298K) of **13**

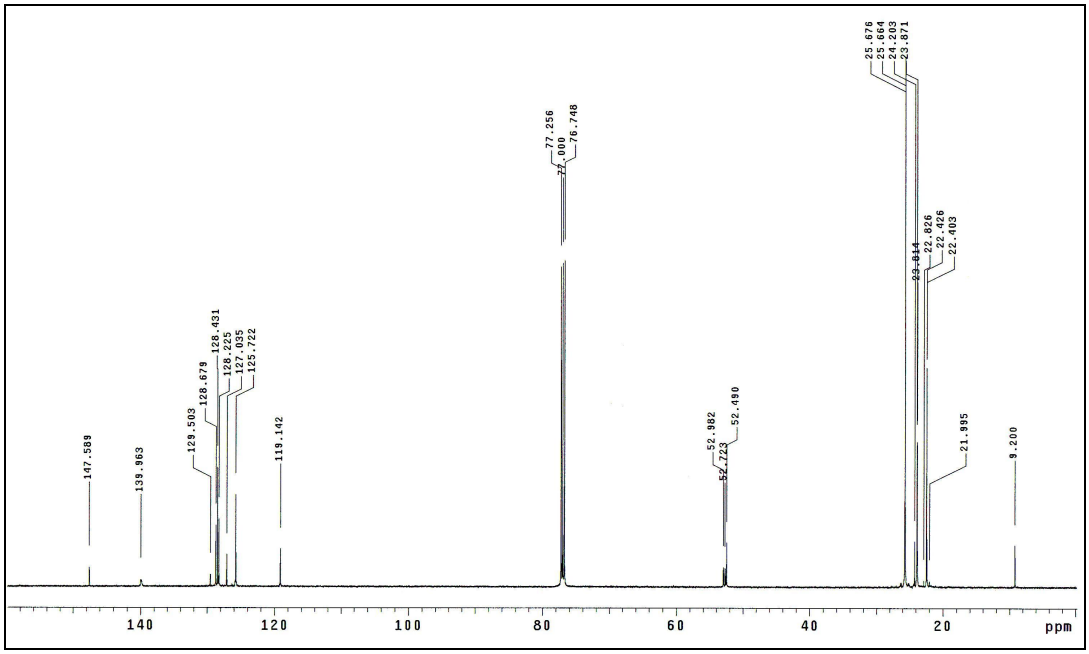


Fig. 6 ^{13}C NMR (125 MHz; $CDCl_3$; 298K) of **13**

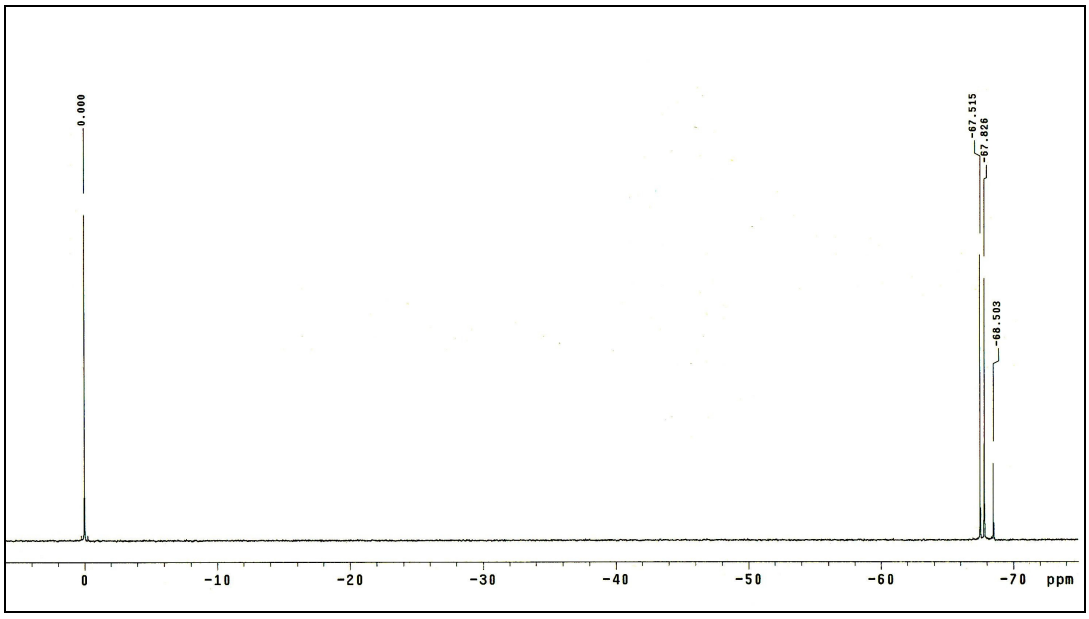


Fig. 7 ^{29}Si NMR (99 MHz; $CDCl_3$; 298K) of **13**

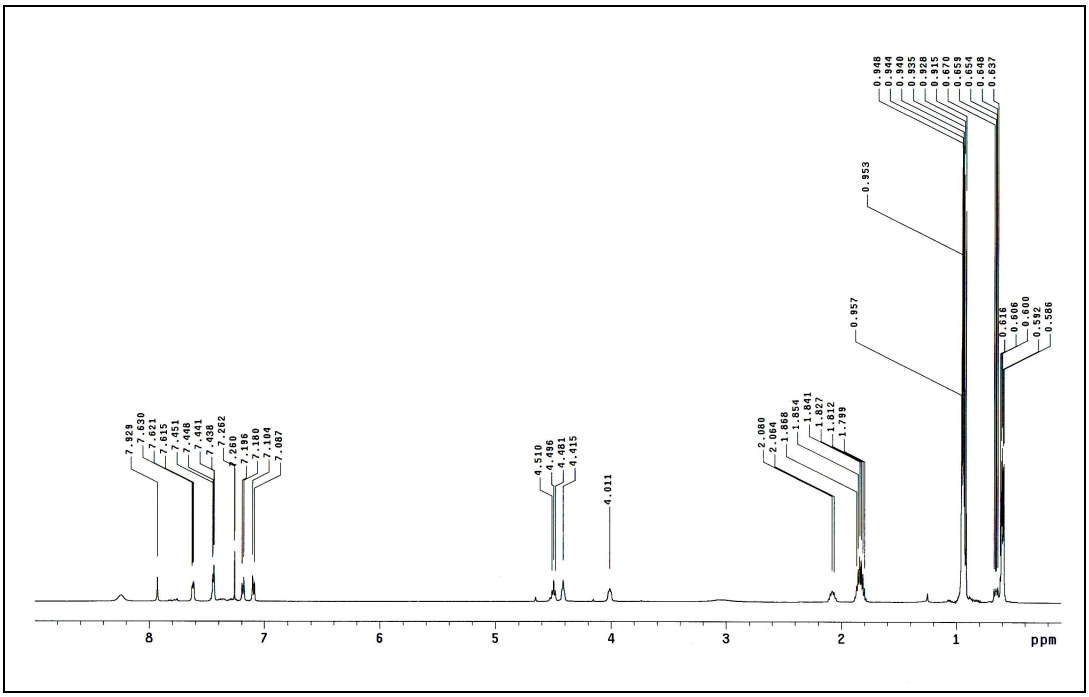


Fig. 8 ^{1}H NMR (500 MHz; $CDCl_3$; 298K) of **2**

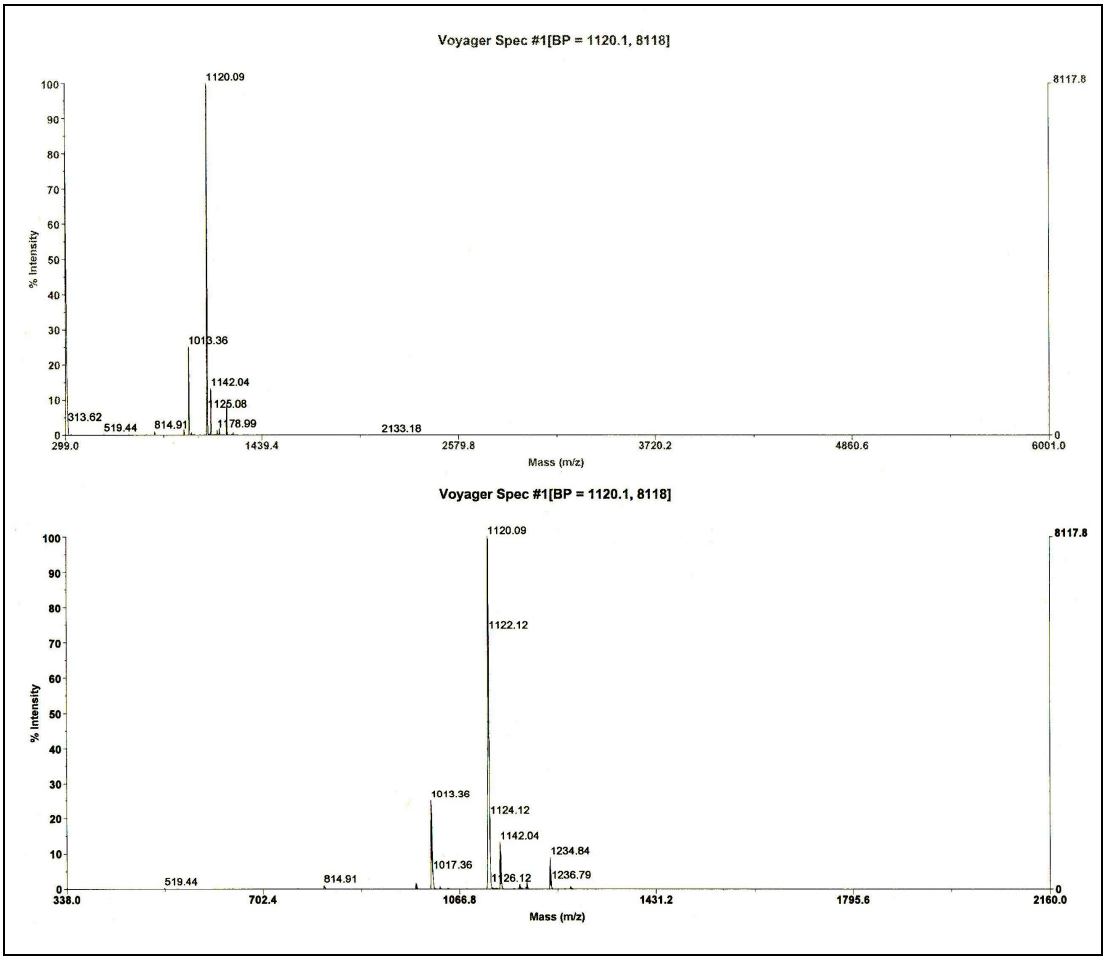


Fig. 9 MALDI-TOF MS of **13**

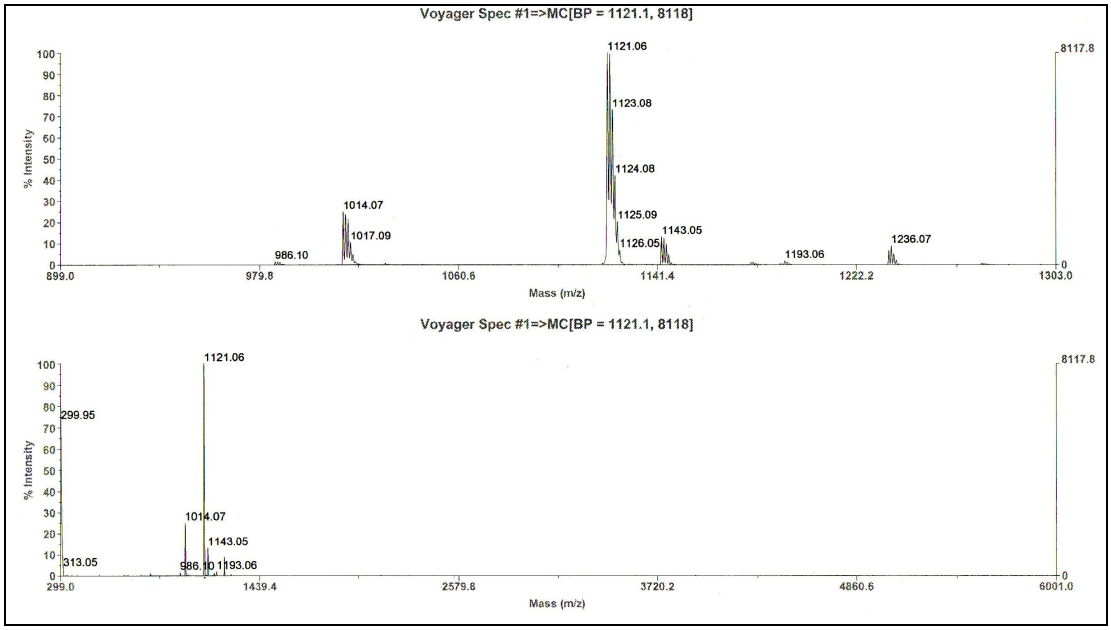


Fig. 10 MALDI-TOF MS of **2**

The ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR of dendritic complex constructed by **1** and 10 equiv of **2** was shown in **Figure 11-13**.

Conditions for preparing dendritic complex:

- **1**: 0.016g, 2.36×10^{-3} mmol
- **2**: 0.03g, 2.36×10^{-2} mmol
- n_1: n_2 = 1 : 10
- Solvent ($CDCl_3$): 0.6 ml; C_1 = 3.93 mM, C_2 = 39.3 mM
- The ^{1}H NMR spectra were obtained after 15 min of mixing.

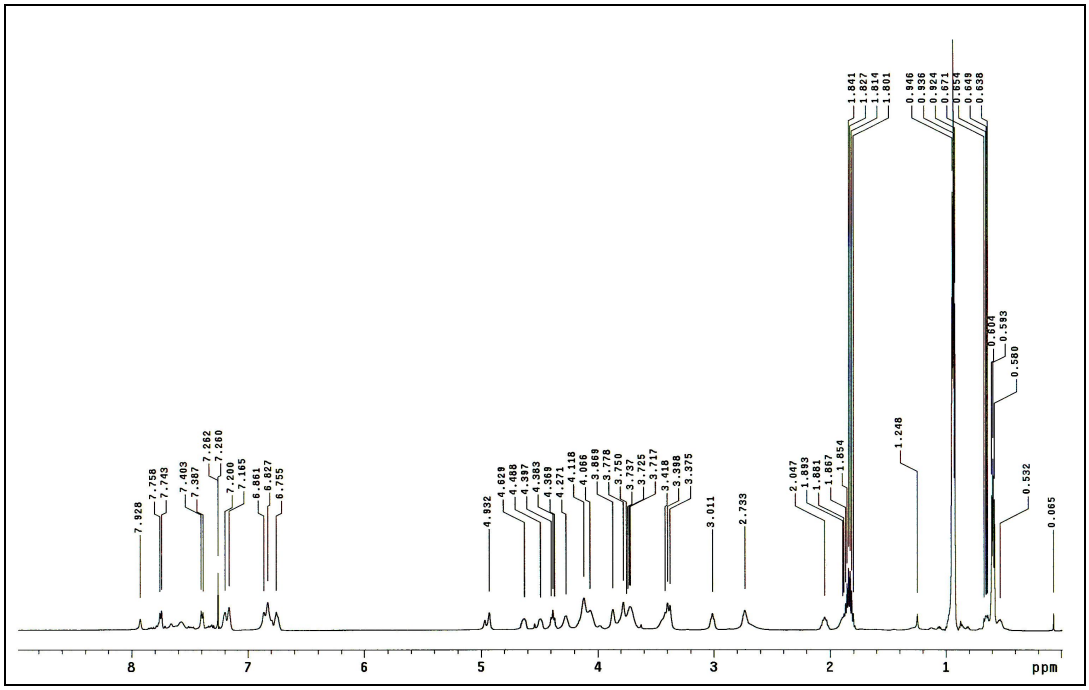


Fig. 11 ^{1}H NMR (500 MHz; $CDCl_3$; 298K) of complex constructed by **1** and 10 equiv of **2**

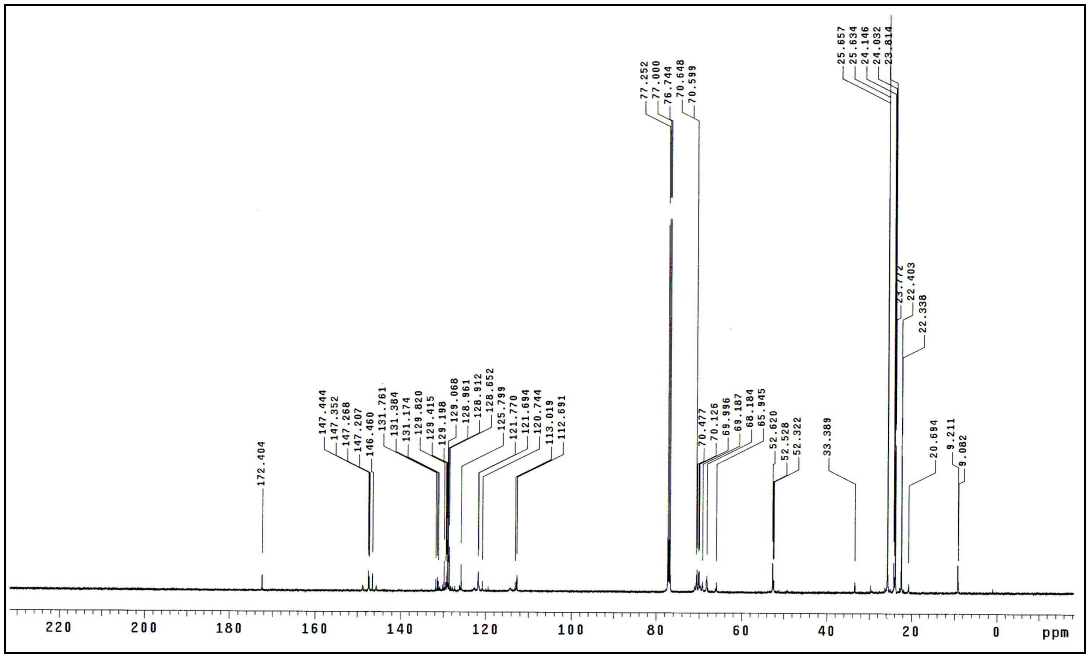


Fig. 12 ^{13}C NMR (125 MHz; $CDCl_3$; 298K) of complex constructed by **1** and 10 equiv of **2**

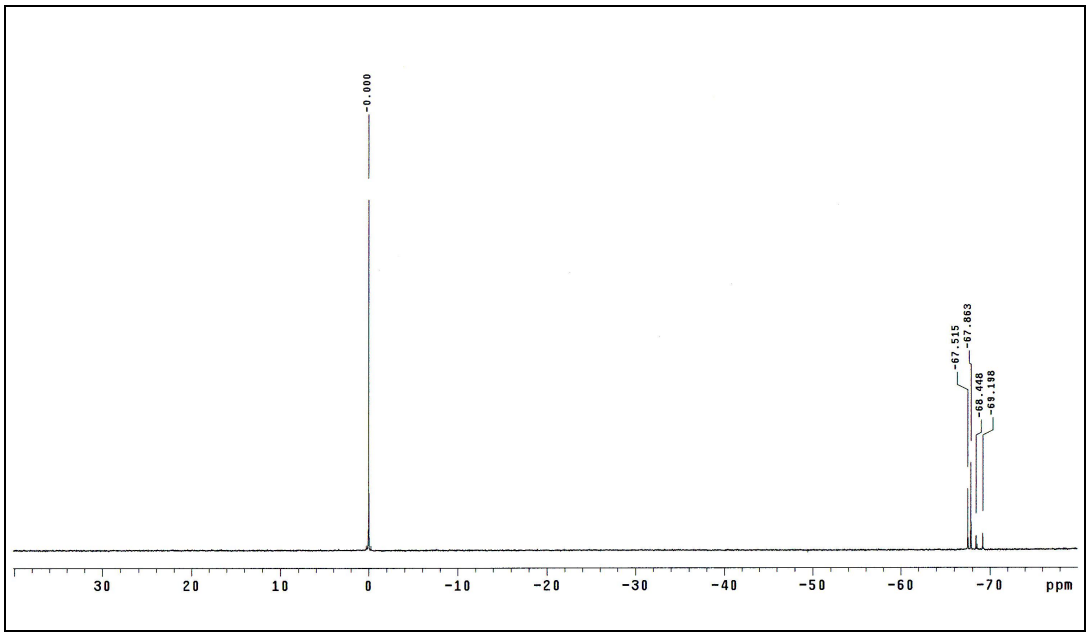


Fig. 13 ^{29}Si NMR (99 MHz; $CDCl_3$; 298K) of complex constructed by **1** and 10 equiv of **2**

The ^{1}H NMR of complex at different ratio of **1** and **2** was shown in **Figure 14-18**.

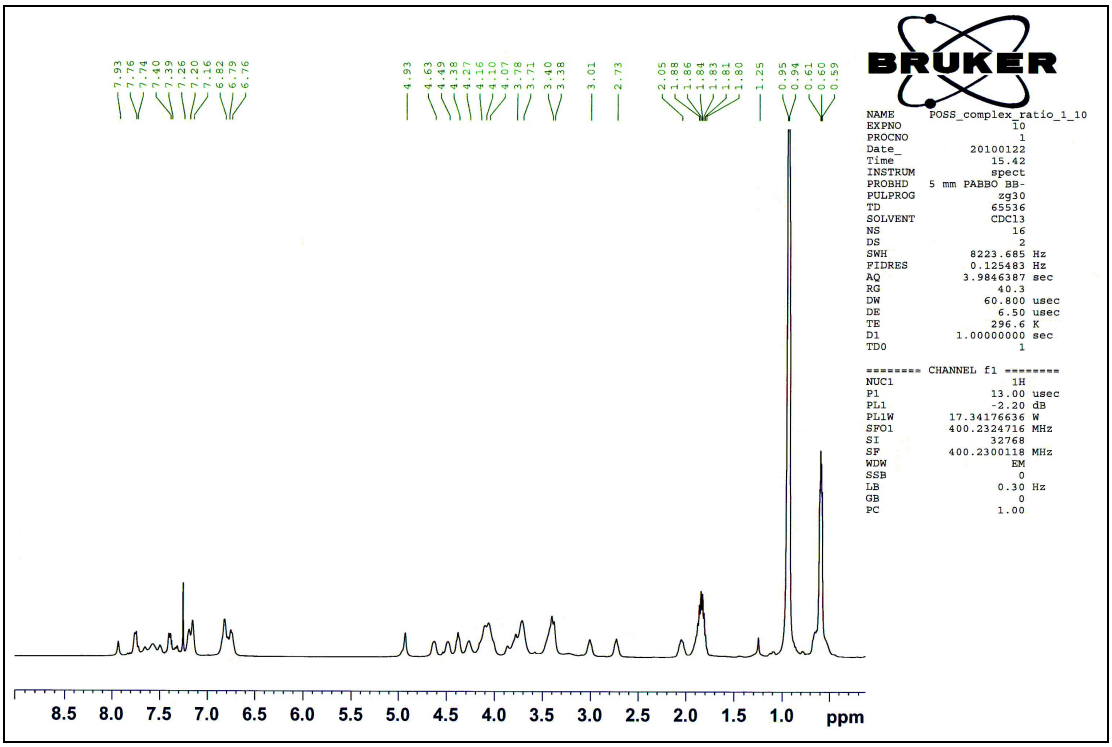


Fig. 14 ^{1}H NMR (400 MHz; $CDCl_3$; 298K) of complex at the ratio of 1 : 10 of **1** and **2**

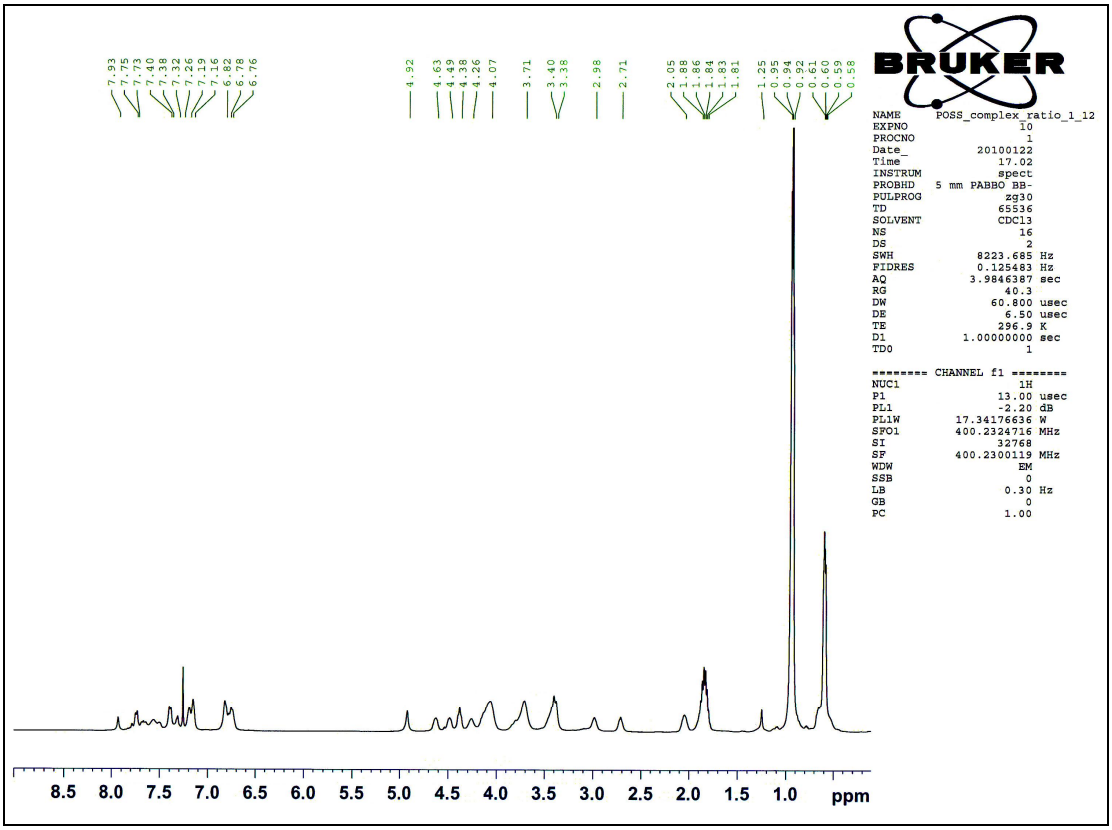


Fig. 15 ^{1}H NMR (400 MHz; $CDCl_3$; 298K) of complex at the ratio of 1 : 12 of **1** and **2**

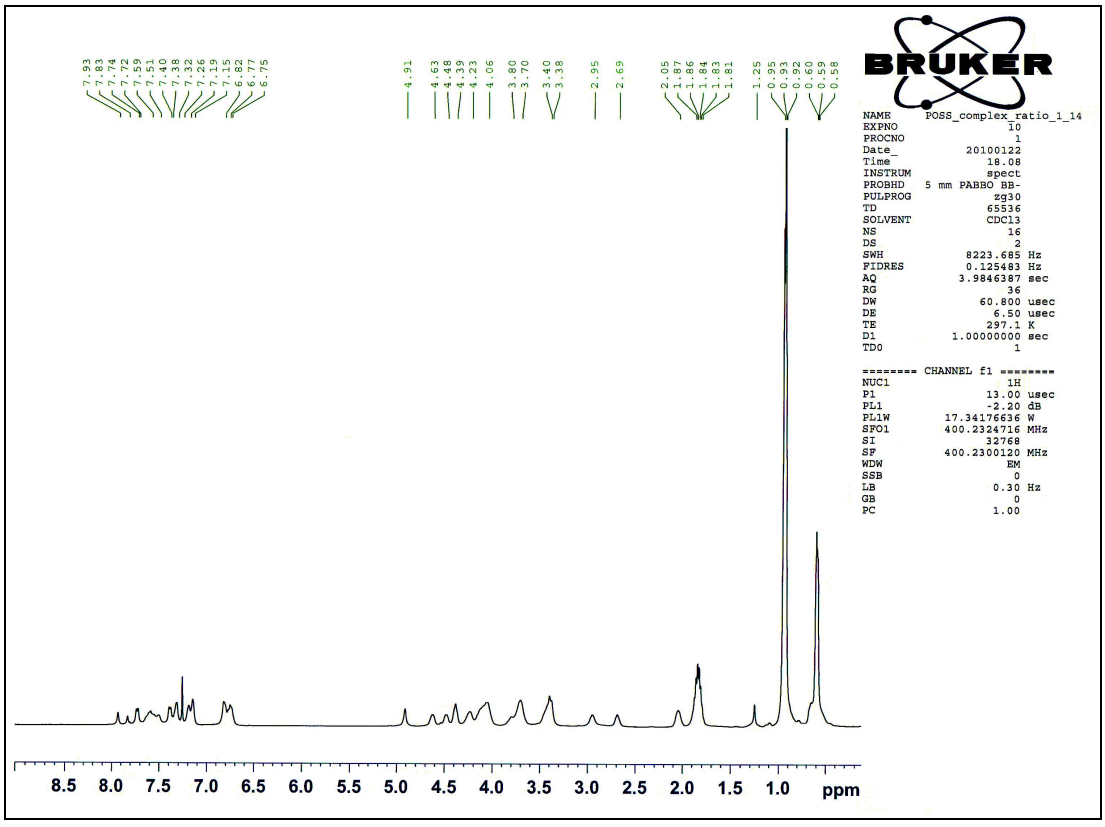


Fig. 16 ^{1}H NMR (400 MHz; $CDCl_3$; 298K) of complex at the ratio of 1 : 14 of **1** and **2**

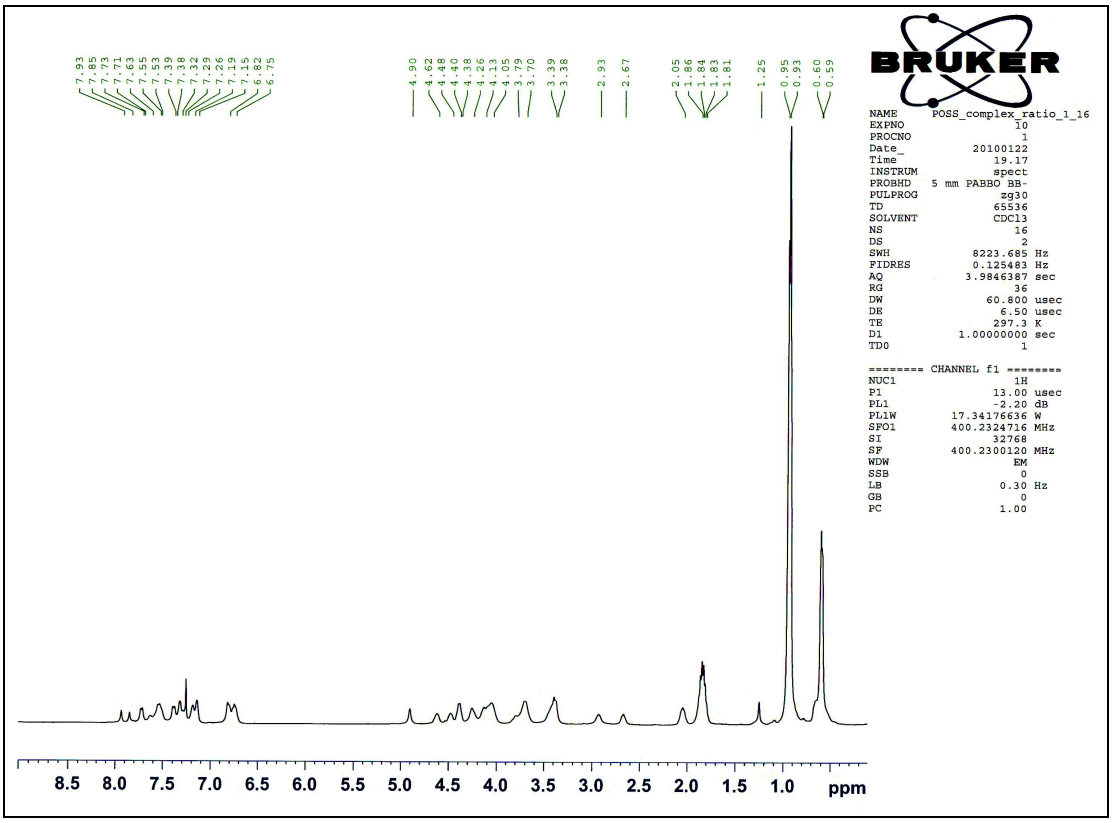


Fig. 17 ^{1}H NMR (400 MHz; $CDCl_3$; 298K) of complex at the ratio of 1 : 16 of **1** and **2**

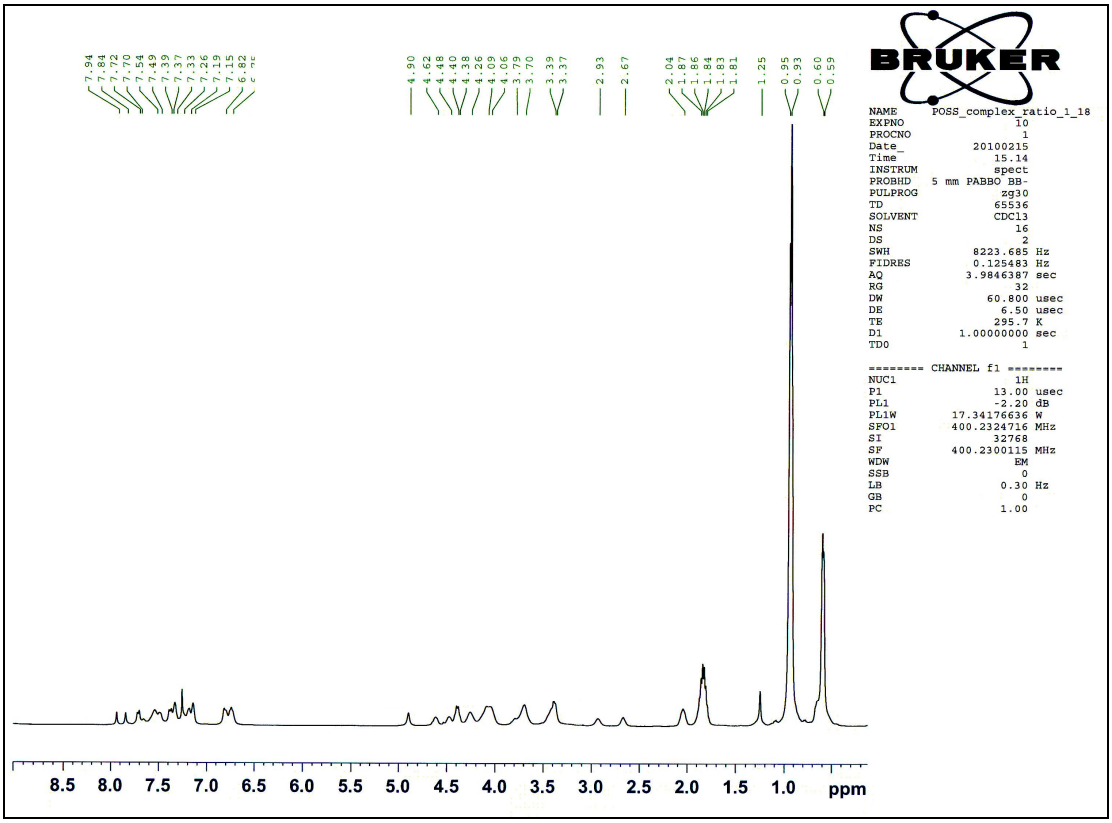


Fig. 18 ^{1}H NMR (400 MHz; $CDCl_3$; 298K) of complex at the ratio of 1 : 18 of **1** and **2**

The ^{1}H NMR of complex treated with base and acid was shown in **Figure 19-20**.

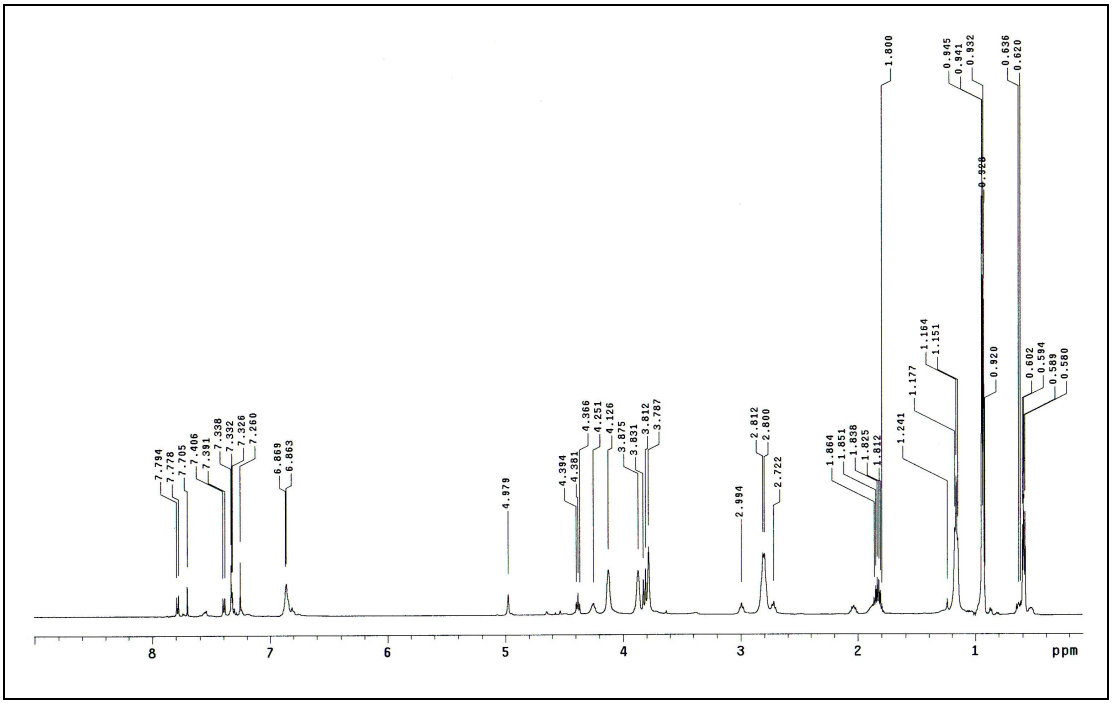


Fig. 19 ^{1}H NMR (500 MHz; $CDCl_3$; 298K) of complex after TEA base-treated

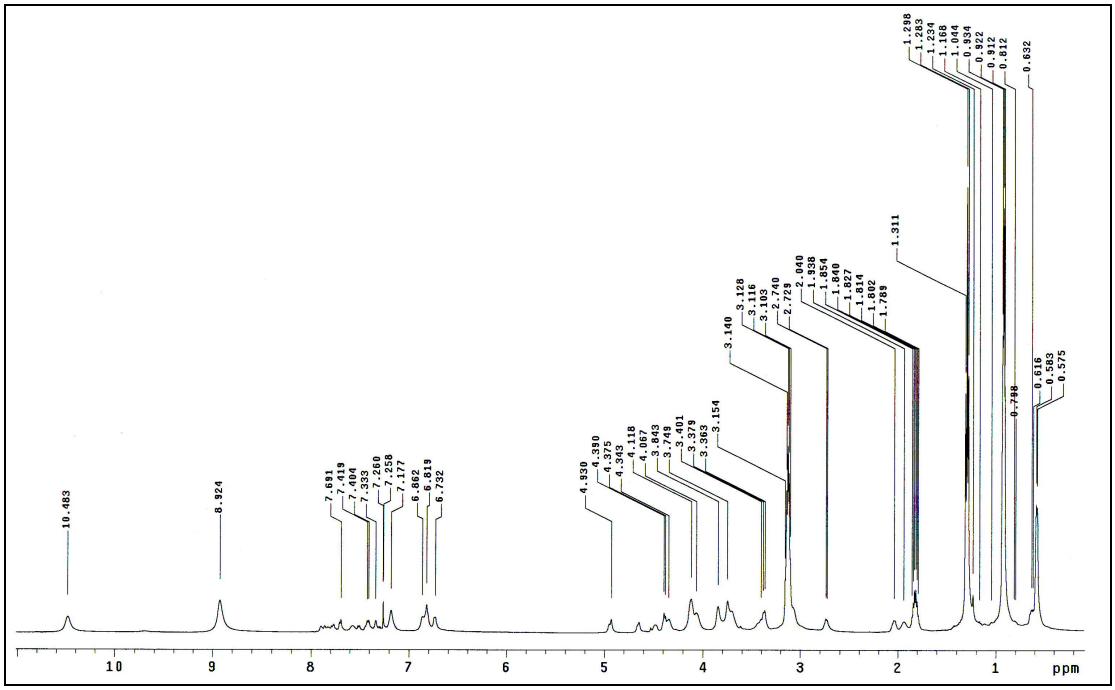


Fig. 20 ^{1}H NMR (500 MHz; $CDCl_3$; 298K) of complex after TFA acid-treated

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