Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supplementary Information (ESI)

Controllable preparation of nanocomposites through convenient structural modification of cobalt contained organometallic precursors: nanotubes and nanospheres with high selectivity, and their magnetic properties

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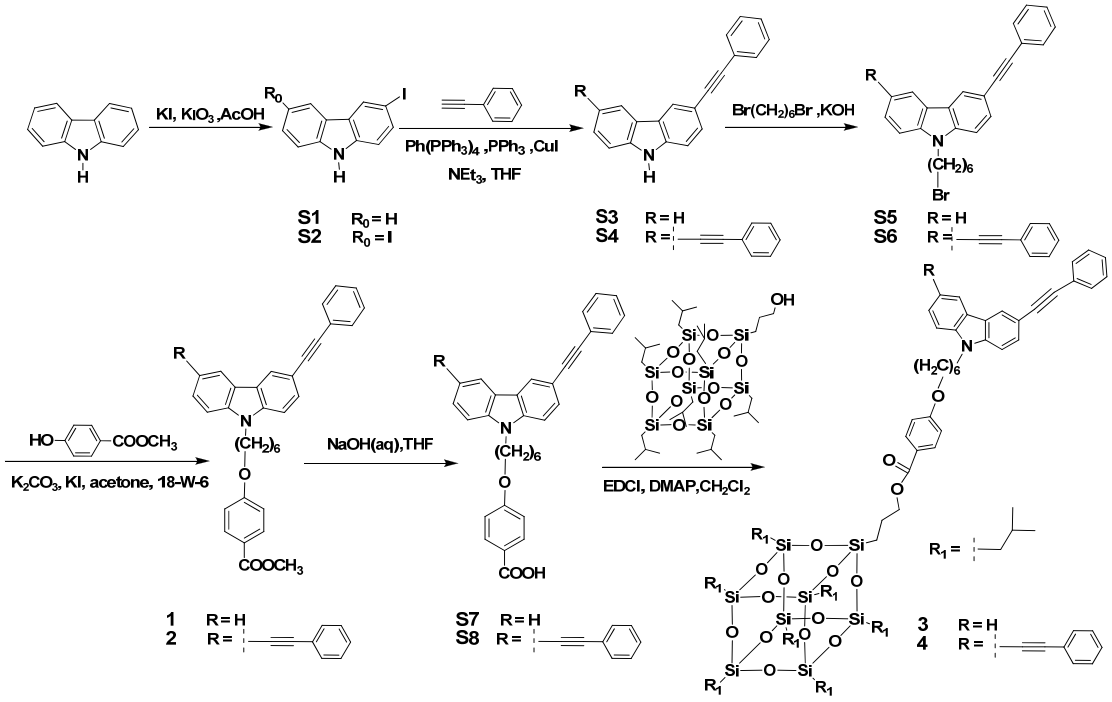

Scheme S1 Synthetic pathway of the compounds **1**, **2**, **3** and **4**.

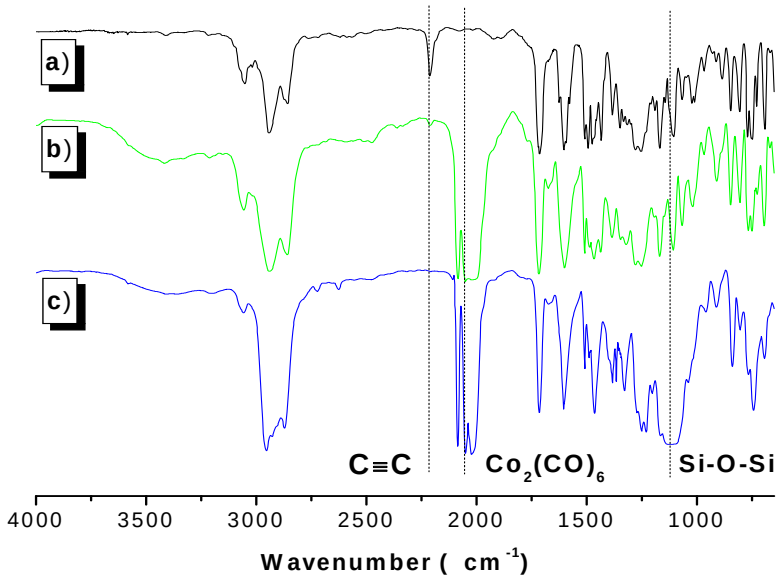

Figure S1 IR spectra of a) **1**, b) **M1**, and c) **PM1**.

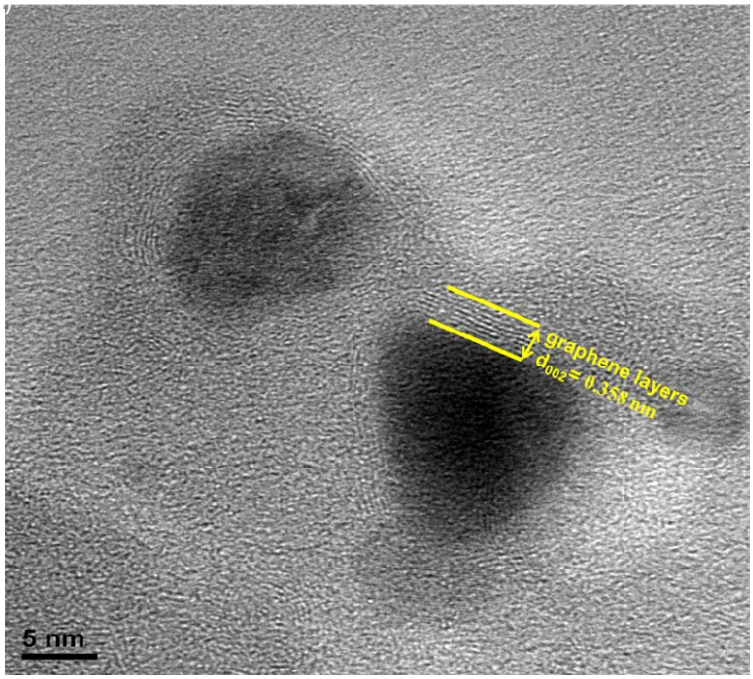

Figure S2 HRTEM image of the materials obtained through thermolysis of compound **M1** as the same as figure 3h in a large size.

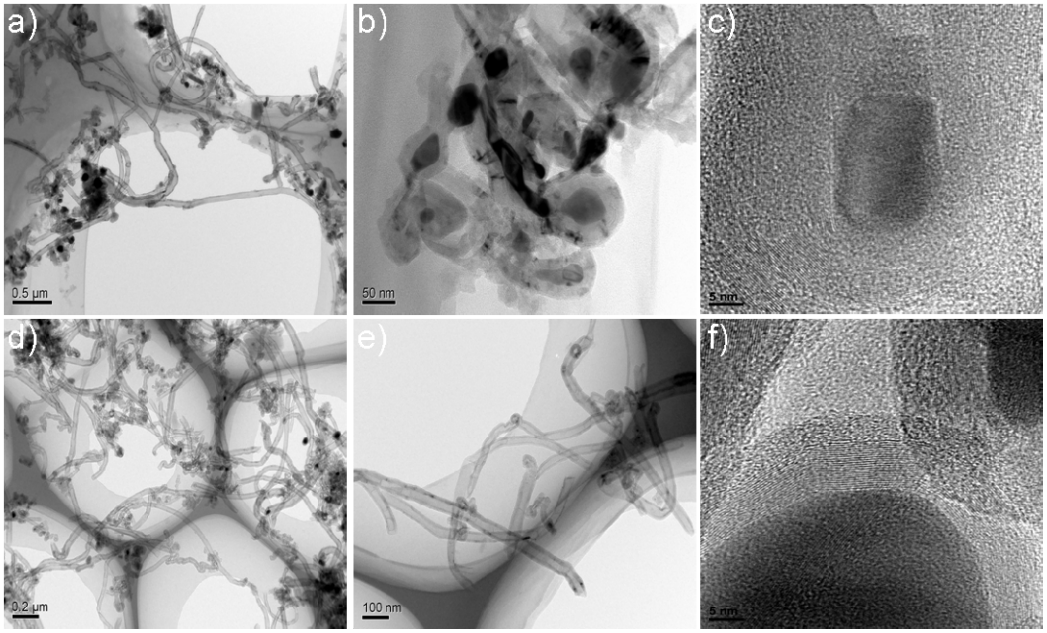

Figure S3 TEM images of the materials obtained through thermolysis of compounds **M2** and **PM2**. (a, b, c) for precursor **M2**, (e, f, g) for precursor **PM2**.

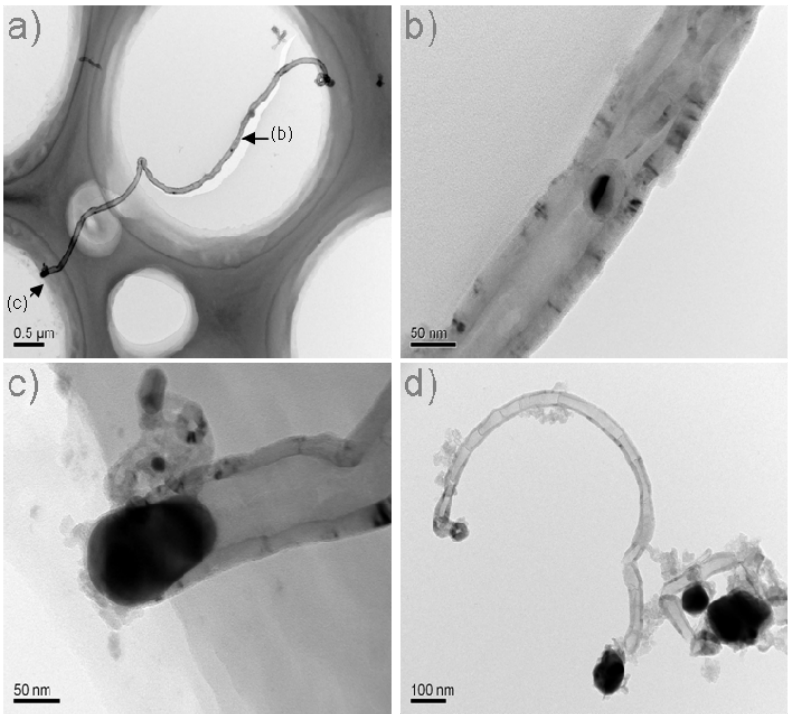

Figure S4 TEM images of the materials obtained through thermolysis of compound **M2**.

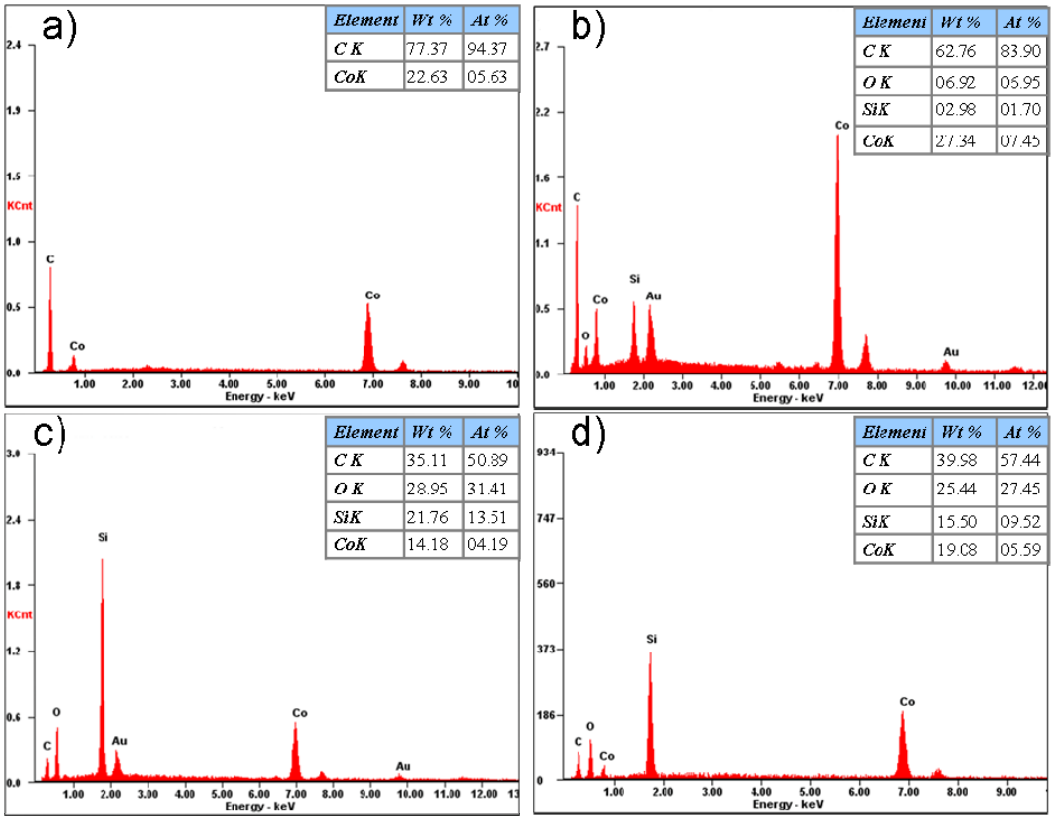

Figure S5 SEM-EDX spectra of the materials obtained through thermolysis of compounds: a) **M1-S**, b) **M2-S**, c) **PM1-S** and d) **PM2-S**.

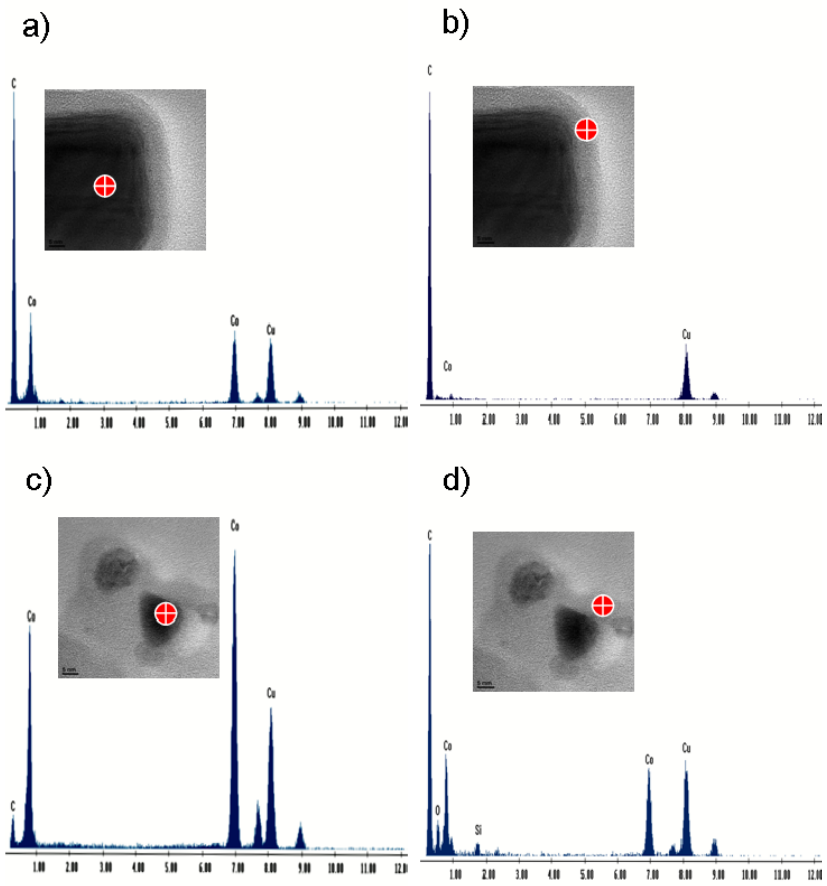

Figure S6 TEM-EDX spectra of **M1-S** (a, b) and **PM1-S** (c, d) core-shell nanospheres.

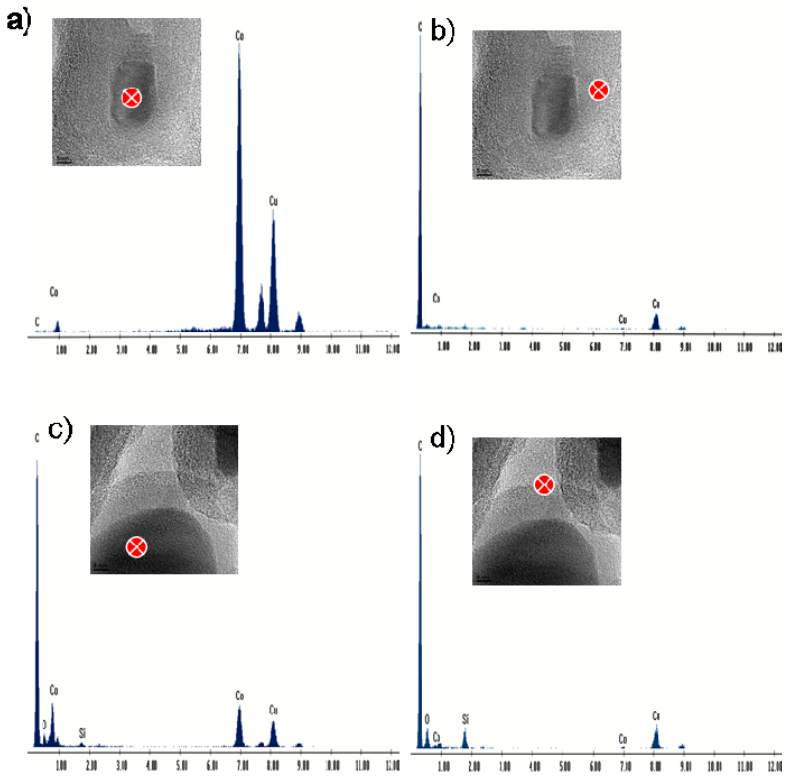

Figure S7 TEM-EDX spectra of **M2-S** (a, b) and **PM2-S** (c, d) nanotubes.

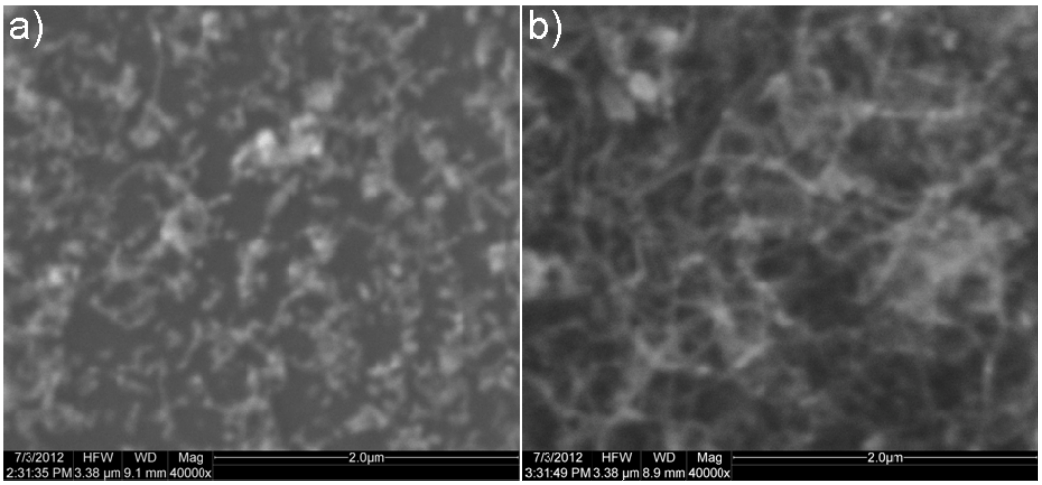

Figure S8 SEM images of the materials obtained through thermolysis of compounds **M2** and **PM2**, carried out without coating with gold metal.

Table S1 Compositions of **M1**, **PM1**, **M2**, and **PM2**.

sample	C (%)	Co(%)	Si(%)	O(%)	H(%)	N(%)
M1	61.00	14.97	0.00	18.28	3.97	1.78
PM1	51.55	7.23	13.78	20.60	5.99	0.86
M2	55.26	20.09	0.00	20.45	3.01	1.19
PM2	50.02	11.69	11.14	21.42	5.05	0.69

Experimental Section

3-iodo-9H-carbazole (**S1**) and 3,6-diiodo-9H-carbazole (**S2**) were prepared according to the literatures.[1]

General procedure for the synthesis of compounds S3 and S4: A mixture of compound **S1** or **S2** (1.00 equiv), CuI (20% equiv), triphenylphosphine (PPh_3) (10% equiv), tetrakis (triphenylphosphine) palladium ($Pd(PPh_3)_4$) (5 mol%) and THF/triethylamine (2:1 in volume), was charged with argon, and then phenylacetylene (1.50 equiv in case of compound **S3**, 3.00 equiv in case of compound **S4**) was added dropwise by syringe. The reaction was stirred at 50 ^oC for 12 h. After cooled to room temperature, the mixture was filtered. The filtrate was evaporated to remove the solvent. The crude product was purified by column chromatography.

Compound **S3**: Compound **S1** (2.35 g, 8 mmol), phenylacetylene (1.22 g, 12 mmol). Purified by column chromatography on silica gel using THF/PE (1/4) as eluent to afford white powder (1.62 g, 76%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 1H, ArH), 8.17 (s, 1H, N-H), 8.08 (d, J = 7.5 Hz, 1H, ArH), 7.61 (d, J = 6.9 Hz, 1H, ArH), 7.58 (d, J = 7.5 Hz, 2H, ArH), 7.42 (m, 6H, ArH), 7.32 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 131.8, 129.8, 128.6, 128.1, 126.7, 124.3, 124.2, 120.8, 120.3, 111.1, 110.9, 87.9. MS (EI), *m/z* [M^+]: 267.2, calcd: 267.1. Anal. calcd for $C_{20}H_{13}N$: C 89.86, H 4.90, N 5.24; found: C 89.70, H 5.11, N 5.40.

Compound **S4**: Compound **S2** (2.10 g, 5 mmol), phenylacetylene (1.53 g, 15 mmol). Purified by column chromatography on silica gel using THF/PE (1/4) as eluent to afford white

powder (1.43 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.27 (s, 2H, ArH), 8.24 (s, 1H, N-H), 7.64 (s, 2H, ArH), 7.59 (d, J = 9 Hz, 4H, ArH), 7.40 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 139.7, 131.8, 130.3, 128.7, 128.2, 124.5, 123.3, 115.0, 111.1, 104.2, 90.7, 88.2. MS (EI), *m*/*z* [M^+]: 367.1, calcd: 367.1. Anal. calcd for $C_{28}H_{17}N$: C 91.52, H 4.66, N 3.81; found: C 91.35, H 4.82, N 3.69.

General procedure for the synthesis of compounds S5 and S6: A mixture of compound **S3** or **S4** (1.00 equiv), KOH (3.00 equiv) and 1,6-dibromohexane (5.00 equiv) in DMF (20 mL). Stirred at room temperature overnight. Then, the reaction mixture was poured into saturated NaCl aqueous solution and extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the resulting crude product was purified by column chromatography.

Compound **S5**: Compound **S3** (2.67 g, 10 mmol). Purified by column chromatography on silica gel using $CHCl_2$/PE (1/4) as eluent to afford white-off powder (2.78 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 1H, ArH), 8.10 (d, J = 7.8 Hz, 1H, ArH), 7.64 (d, J = 9.0 Hz, 1H, ArH), 7.58 (d, J = 6.0 Hz, 2H, ArH), 7.48 (d, J = 7.2 Hz, 1H, ArH) 7.38 (m, 6H, ArH), 4.32 (t, J = 6.4 Hz, 2H, -N-CH_2-), 3.37 (t, J = 6.3 Hz, 2H, -CH_2Br), 1.91 (t, J = 6.9 Hz, 2H, -CH_2CH_2Br), 1.82 (t, J = 6.9 Hz, 2H, -N-CH_2CH_2-), 1.42 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 141.0, 140.3, 131.7, 129.5, 128.6, 128.0, 126.4, 124.3, 123.2, 122.7, 120.8, 119.7, 113.6, 109.1, 108.9, 87.8, 43.2, 33.9, 32.8, 29.0, 28.1, 26.7. MS (EI), *m*/*z* [M^+]: 429.1, calcd: 429.1. Anal. calcd for $C_{26}H_{24}BrN$: C 72.56, H 5.62, N 3.25; found: C 72.42, H 5.91, N 3.28.

Compound **S6**: Compound **S4** (1.29 g, 3.5 mmol). Purified by column chromatography on silica gel using $CHCl_2$/PE (1/2) as eluent to afford white-off powder (1.45 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 7.66 (d, J = 8.4 Hz, 2H, ArH), 7.59 (d, J = 7.8 Hz, 4H, ArH), 7.36 (m, 8H, ArH), 4.32 (t, J = 6.9 Hz, 2H, -N-CH_2-), 3.38 (t, J = 6.6 Hz, 2H, -CH_2Br), 1.91 (t, J = 7.0 Hz, 2H, -CH_2CH_2Br), 1.82 (t, J = 6.8 Hz, 2H, -N-CH_2CH_2-), 1.41 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 140.6, 131.7, 130.3, 128.6, 128.1, 124.4, 124.0, 122.8, 114.3, 109.2, 90.7, 88.1, 43.4, 33.8, 32.7, 29.0, 28.1, 26.6. MS (EI), *m*/*z* [M^+]: 529.0, calcd: 529.1. Anal. calcd for $C_{34}H_{28}BrN$: C 76.98, H 5.32, N 2.64; found: C 76.84, H 5.56, N 2.80.

General procedure for the synthesis of compound 1 and 2: A mixture of compound **S5** or **S6** (1.00 equiv), K_2CO_3 (7.50 equiv), KI (1.00 equiv), methyl 4-hydroxybenzoate (1.50 equiv) and a bit of 18-crown-6, was charged with argon. And then anhydrous acetone (20 mL) was added by syringe. The reaction was stirred under reflux overnight. After cooled to room temperature, the mixture was filtered, the filtrate was evaporated to remove the solvent. The crude product was purified by column chromatography.

Compound **1**: Compound **S5** (2.58 g, 6 mmol). Purified by column chromatography on silica gel using $CHCl_2$/petroleum ether (1/2) as eluent to afford grey solid (2.46 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 1H, ArH), 8.10 (d, J = 7.5 Hz, 1H, ArH), 7.96 (d, J = 9.0 Hz, 2H, ArH), 7.63 (d, J = 8.7 Hz, 1H, ArH), 7.58 (d, J = 7.5 Hz, 2H, ArH), 7.47 (d, J = 6.9 Hz, 1H, ArH), 7.36 (m, 6H, ArH), 6.85 (d, J = 9.0 Hz, 2H, ArH), 4.33 (t, J = 7.1 Hz, 2H, -O-CH_2-), 3.95 (t, J = 6.3 Hz, 2H, -N-CH_2-), 3.87 (s, 3H, -O-CH_3), 1.93 (t, J = 7.1 Hz, 2H, -N-CH_2CH_2-), 1.76 (t, J = 6.6 Hz, 2H, -O-CH_2CH_2-), 1.48 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 167.3, 163.2, 141.2, 140.5, 131.9, 129.7, 128.7, 126.5, 124.5, 124.4, 123.3, 122.9, 120.9, 119.9, 114.6, 114.2, 113.7, 109.2, 91.2, 88.0, 68.2, 43.4, 29.3, 27.4, 26.2. MS (EI), *m/z* [M^+]: 501.4, calcd: 501.2. Anal. calcd for $C_{34}H_{31}NO_3$: C 81.41, H 6.23, N 2.79; found: C 81.31, H 6.36, N 2.74.

Compound **2**: Compound **S6** (2.12 g, 4 mmol). Purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether (1/2) as eluent to afford grey solid (2.00 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 7.98 (d, J = 9.0 Hz, 2H, ArH), 7.66 (d, J = 8.1 Hz, 2H, ArH), 7.59 (d, J = 7.2 Hz, 4H, ArH), 7.36 (m, 8H, ArH), 6.86 (d, J = 8.7 Hz, 2H, ArH), 4.33 (t, J = 6.9 Hz, 2H, -O-CH_2-), 3.95 (t, J = 6.4 Hz, 2H, -N-CH_2-), 3.87 (s, 3H, -O-CH_3), 1.94 (t, J = 6.8 Hz, 2H, -N-CH_2CH_2-), 1.76 (t, J = 6.9 Hz, 2H, -O-CH_2CH_2-), 1.48 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 167.2, 163.0, 140.7, 131.8, 130.0, 128.6, 128.2, 124.5, 124.1, 122.8, 114.3, 109.2, 90.8, 88.2, 66.1, 52.1, 43.4, 29.2, 27.2, 26.1. MS (EI), *m/z* [M^+]: 601.1, calcd: 601.3. Anal. calcd for $C_{42}H_{35}NO_3$: C 83.83, H 5.86, N 2.33; found: C 84.02, H 6.16, N 2.32.

General procedure for the synthesis of compound S7 and S8: Compound **1** or **2** (1.00 equiv) was dissolved in methanol (30 mL). Then, a solution of NaOH (30 equiv) in H_2O (15 mL) was added dropwise by syringe. The reaction was stirred under reflux overnight. The reaction

mixture was evaporated under vacuum, after evaporation of the THF solvent, HCl (2 M) was added dropwise to adjust the pH value to 1, then the mixture was filtered.

Compound **S7**: Compound **1** (1.50 g, 3 mmol). Filtration to afford **S7** as white solid (1.17 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 1H, ArH), 8.11 (d, J = 8.1 Hz, 1H, ArH), 8.03 (d, J = 8.1 Hz, 2H, ArH), 7.64 (d, J = 8.7 Hz, 1H, ArH), 7.58 (d, J = 6.6 Hz, 2H, ArH), 7.48 (d, J = 7.5 Hz, 1H, ArH), 7.36 (m, 6H, ArH), 6.88 (d, J = 8.7 Hz, 2H, ArH), 4.34 (t, J = 7.0 Hz, 2H, -O-CH_2-), 3.97 (t, J = 6.2 Hz, 2H, -N-CH_2-), 1.94 (t, J = 6.6 Hz, 2H, -N-CH_2CH_2-), 1.77 (t, J = 7.2 Hz, 2H, -O-CH_2CH_2-), 1.48 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 167.5, 162.7, 141.0, 140.3, 131.8, 131.6, 129.5, 129.3, 128.7, 126.8, 124.3, 123.5, 122.8, 122.2, 121.2, 119.8, 114.7, 112.6, 110.3, 91.5, 87.9, 68.1, 42.8, 28.9, 26.6, 25.7. MS (EI), *m/z* [M^+]: 487.1, calcd: 487.2. Anal. calcd for $C_{33}H_{29}NO_3$: C 81.29, H 5.99, N 2.87; found: C 81.37, H 6.19, N 2.76.

Compound **S8**: Compound **2** (1.81 g, 3 mmol). Filtration to afford **S8** as white solid (1.67 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 8.03 (d, J = 8.4 Hz, 2H, ArH), 7.65 (d, J = 8.7 Hz, 2H, ArH), 7.59 (d, J = 6.6 Hz, 4H, ArH), 7.37 (m, 8H, ArH), 6.87 (d, J = 8.4 Hz, 2H, ArH), 4.33 (br, 2H, -O-CH_2-), 3.96 (br, 2H, -N-CH_2-), 1.93 (br, 2H, -N-CH_2CH_2-), 1.77 (br, 2H, -O-CH_2CH_2-), 1.47 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 167.9, 162.7, 140.9, 132.0, 131.9, 130.3, 129.5, 129.0, 125.0, 123.6, 122.5, 114.7, 113.5, 110.9, 91.5, 88.4, 68.3, 43.2, 29.1, 26.8, 26.0. MS (EI), *m/z* [M^+]: 587.5, calcd: 587.2. Anal. calcd for $C_{41}H_{33}NO_3$: C 83.79, H 5.66, N 2.38; found: C 83.76, H 5.86, N 2.51.

General procedure for the synthesis of compounds 3 and 4: PSS-(3-Hydroxypropyl)-heptaisobutyl substituted (POSS) (1.00 equiv) and compound **S7** or **S8** (1.50 equiv) were dissolved in anhydrous CH_2Cl_2 under argon atmosphere. DMAP (5 mol%) and EDCI (3.00 equiv) were added, and the mixture was stirred at room temperature overnight. Then, the reaction mixture was poured into saturated citric acid aqueous solution and extracted with dichloromethane. The organic layer was combined, washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the raw product was purified by column chromatography.

Compound **3**: Compound **S7** (0.15 g, 0.3 mmol). Purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether (1/2) as eluent to afford white powder (0.22 g, 80%). ^{1}H

NMR (300 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 1H, ArH), 8.10 (d, J = 8.1 Hz, 1H, ArH), 7.97 (d, J = 8.1 Hz, 2H, ArH), 7.64 (d, J = 7.8 Hz, 1H, ArH), 7.58 (d, J = 7.2 Hz, 2H, ArH), 7.47 (d, J = 7.2 Hz, 1H, ArH), 7.39 (m, 6H, ArH), 6.86 (d, J = 8.1 Hz, 2H, ArH), 4.33 (br, 2H, -O-CH_2-), 4.24 (br, 2H, $Si(CH_2)_2CH_2O$-), 3.96 (br, 2H, -N-CH_2-), 1.85 (m, 13H), 1.49 (br, 4H), 0.95 (d, J=6.0, 42H,-CH_3), 0.72 (br, 2H, Si-$CH_2(CH_2)_2$-), 0.60 (d, J=6.3, 14H, Si-$CH_2CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm): 166.6, 163.0, 141.0, 140.3, 131.8, 131.7, 129.6, 128.6, 128.0, 126.4, 124.3, 123.1, 120.8, 119.7, 114.2, 113.5, 109.1, 108.9, 91.1, 87.9, 68.1, 66.8, 43.3, 29.2, 27.3, 26.0, 24.1, 22.8, 8.8. MS (MALDI-TOF), *m/z* $[M+H]^+$: 1344.6, calcd: 1344.5. Anal. calcd for $C_{64}H_{97}NO_{15}Si_8$: C 57.15, H 7.27, N 1.04; found: C 57.23, H 7.44, N 0.98.

Compound **4**: Compound **S8** (0.18 g, 0.3 mmol). Purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether (1/2) as eluent to afford white powder (0.27 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 2H, ArH), 7.98 (d, J = 9.3 Hz, 2H, ArH), 7.66 (d, J = 8.4 Hz, 2H, ArH), 7.59 (d, J = 6.9 Hz, 4H, ArH), 7.37 (m, 8H, ArH), 6.87 (d, J = 8.4 Hz, 2H, ArH), 4.33 (br, 2H, -O-CH_2-), 4.24 (br, 2H, $Si(CH_2)_2CH_2O$-), 3.97 (br, 2H, -N-CH_2-), 1.86 (m, 13H), 1.49 (br, 4H), 0.95 (d, J=6.3, 42H, -CH_3), 0.72 (br, 2H, Si-$CH_2(CH_2)_2$-), 0.60 (d, J=6.6, 14H, Si-$CH_2CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm): 167.0, 163.3, 141.0, 132.1, 130.4, 129.0, 128.5, 124.8, 124.4, 123.4, 123.1, 114.6, 109.6, 91.1, 88.5, 68.4, 67.2, 43.8, 29.6, 29.5, 27.6, 26.5, 26.3, 24.5, 23.1, 9.1. MS (MALDI-TOF), *m/z* $[M-2H]^+$: 1441.2, calcd: 1441.5. Anal. calcd for $C_{72}H_{101}NO_{15}Si_8$: C 59.84, H 7.04, N 0.97; found: C 59.90, H 7.22, N 0.98.

Reference:

(1) Wu, Y.; Guo, H.; James, T. D.; Zhao, J. *J. Org. Chem.*, 2011, **76**, 5685.

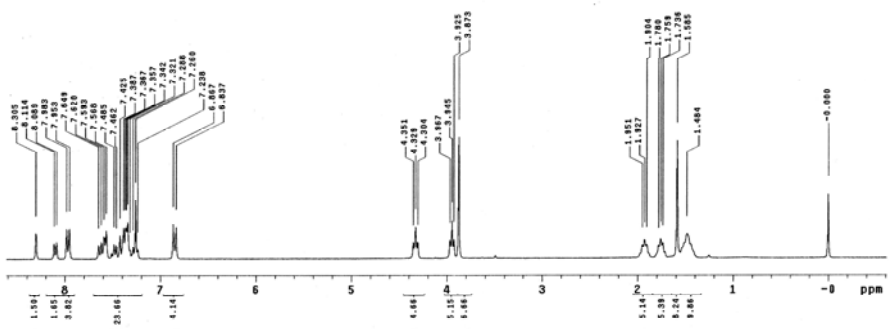

Figure S9. ^{1}H NMR spectra of **1** in $CDCl_3$.

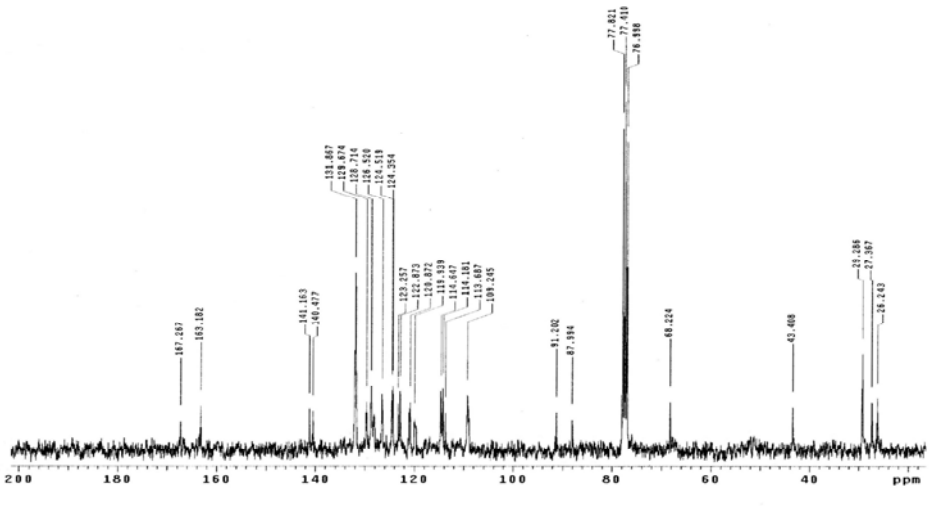

Figure S10. ^{13}C NMR spectra of **1** in $CDCl_3$.

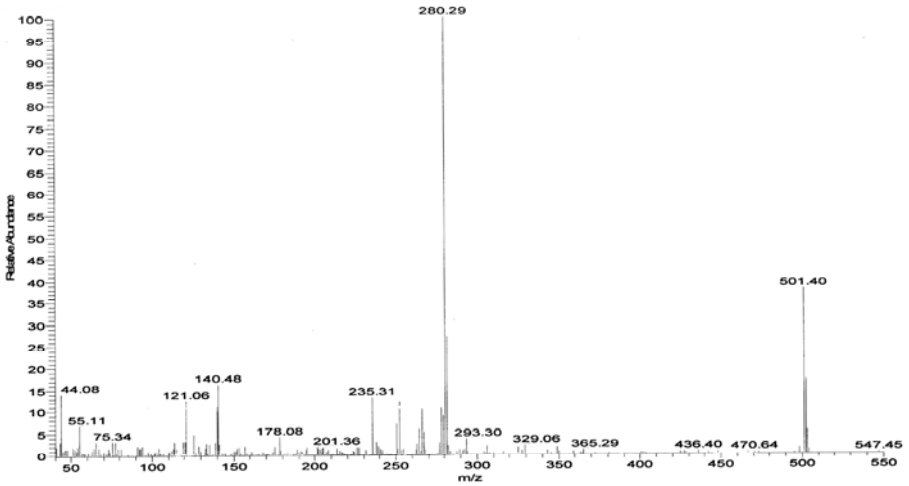

Figure S11. MS (EI) spectrum of **1**.

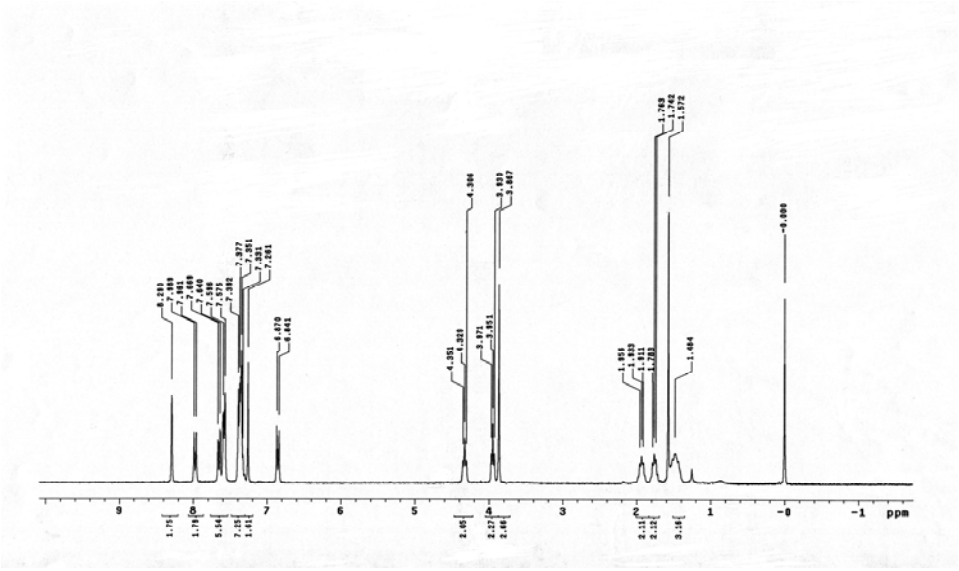

Figure S12. ^{1}H NMR spectra of **2** in $CDCl_3$.

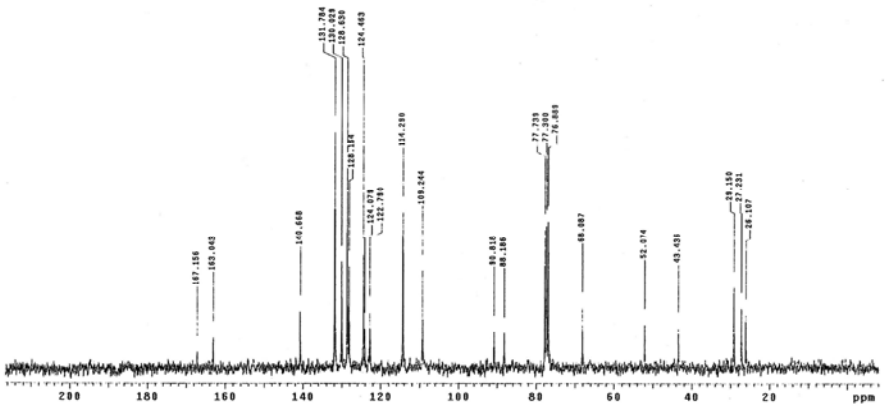

Figure S13. ^{13}C NMR spectra of **2** in $CDCl_3$.

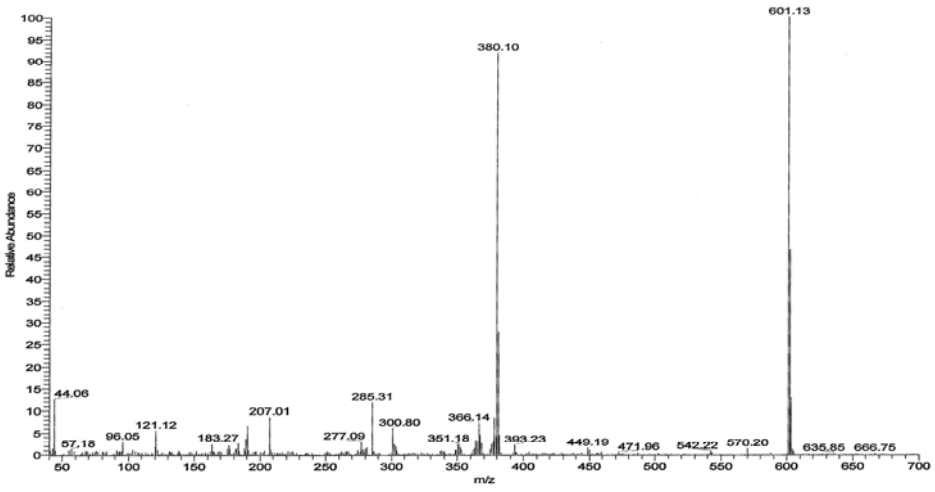

Figure S14. MS (EI) spectrum of **2**.

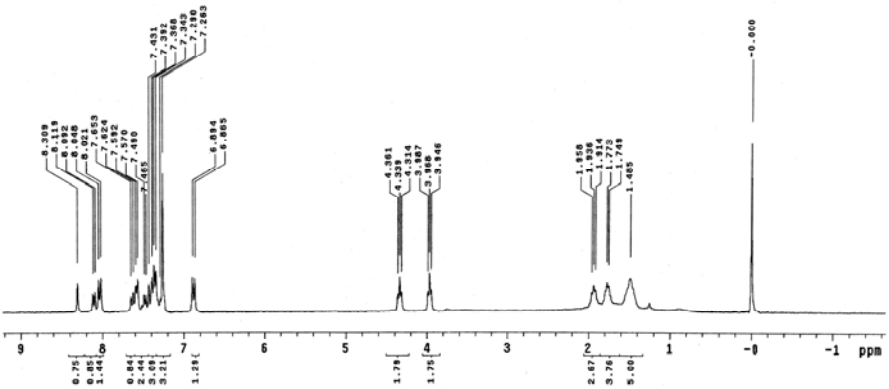

Figure S15. ^{1}H NMR spectra of **S7** in $CDCl_3$.

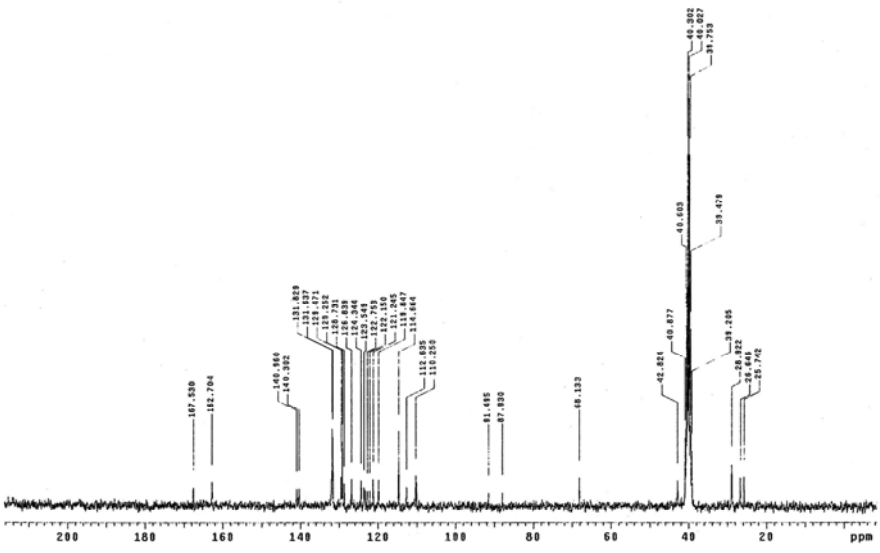

Figure S16. ^{13}C NMR spectra of **S7** in DMSO-d_6.

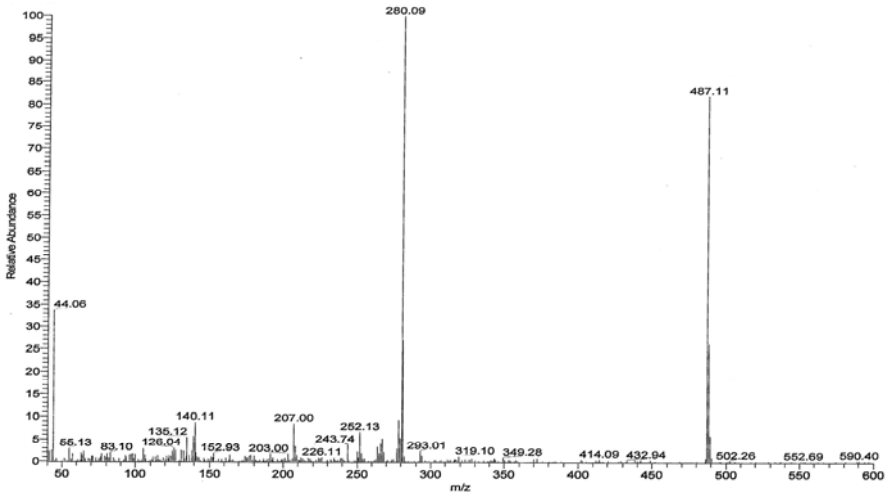

Figure S17. MS (EI) spectrum of **S7**.

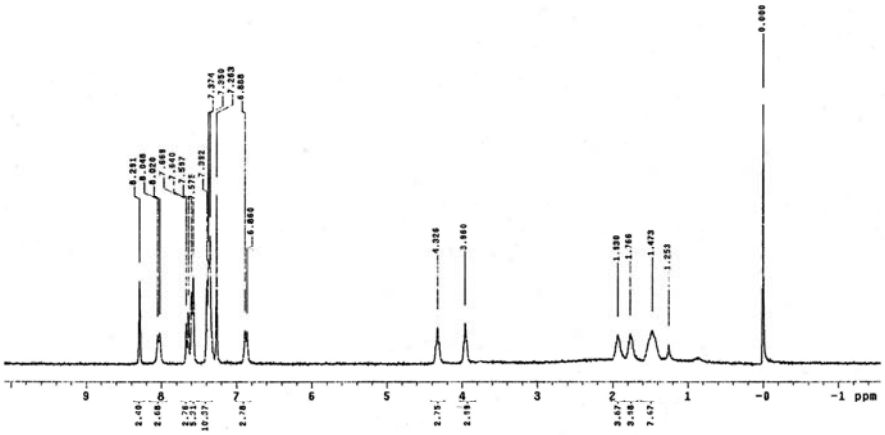

Figure S18. ^{1}H NMR spectra of **S8** in $CDCl_3$.

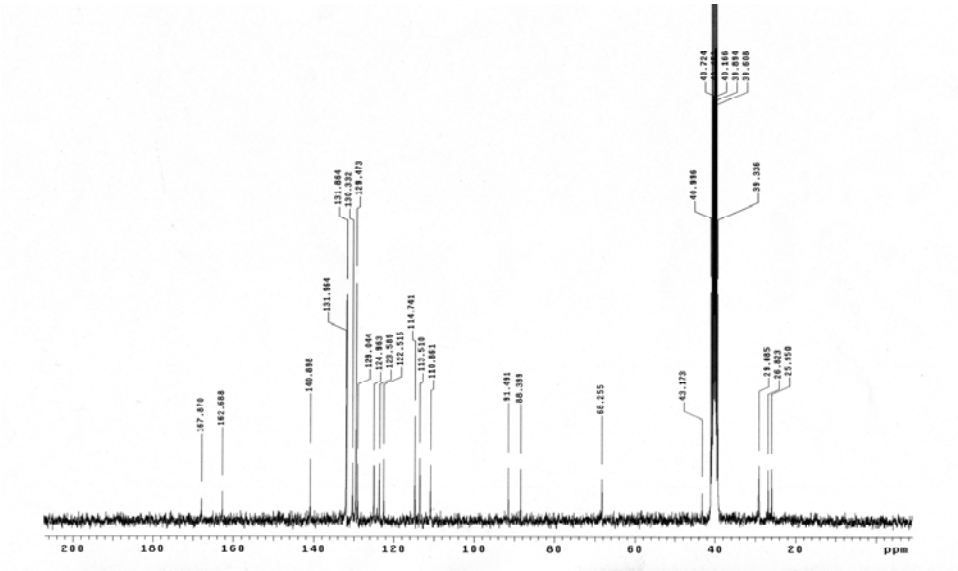

Figure S19. ^{13}C NMR spectra of **S8** in DMSO-d_6.

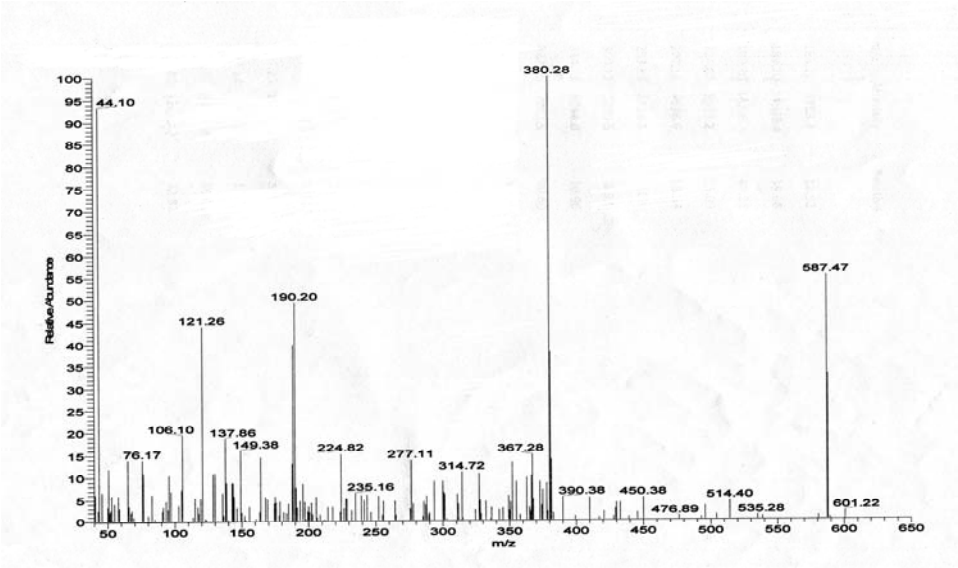

Figure S20. MS (EI) spectrum of **S8**.

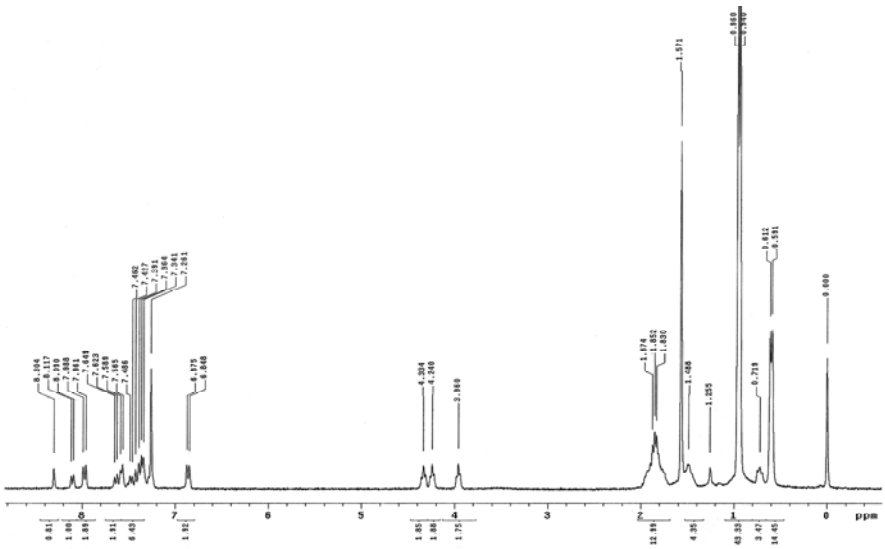

Figure S21. ^{1}H NMR spectra of **3** in $CDCl_3$.

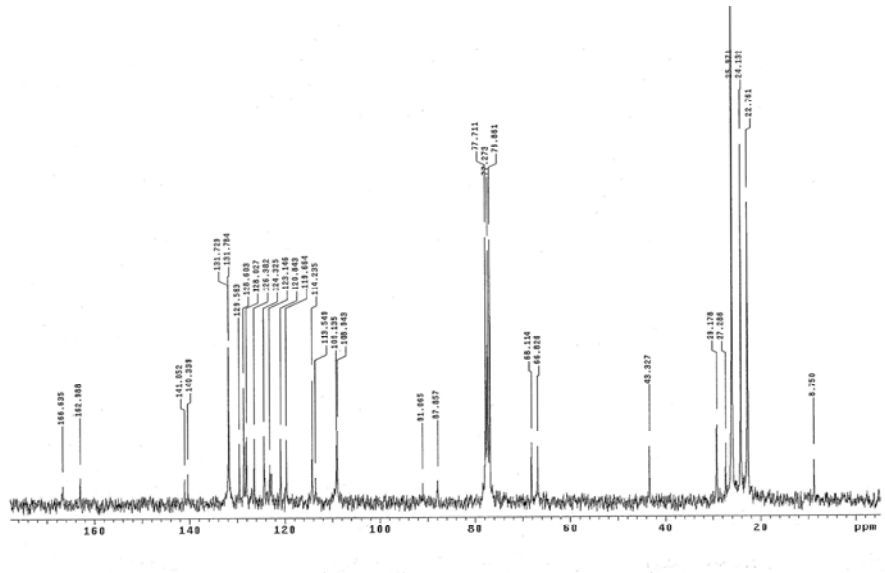

Figure S22. ^{13}C NMR spectra of **3** in $CDCl_3$.

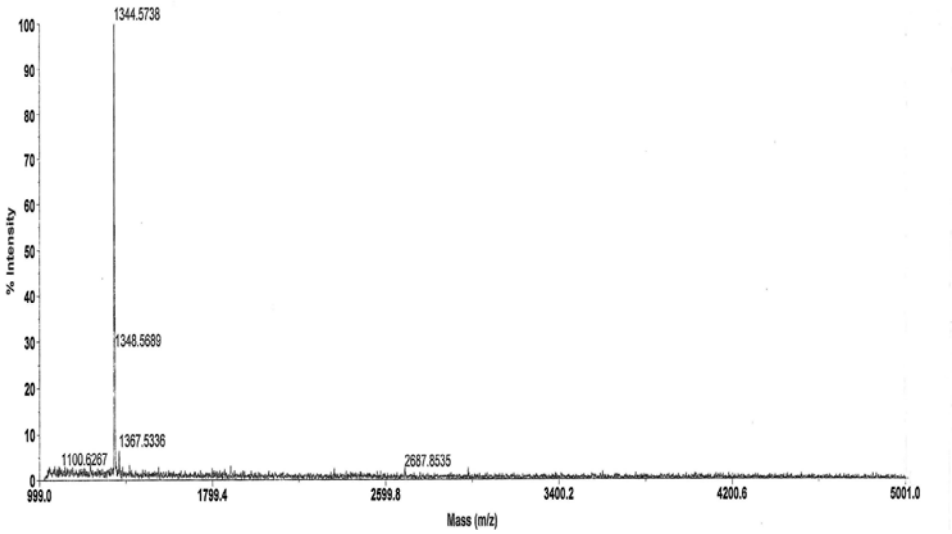

Figure S23. MALDI-TOF spectrum of **3**.

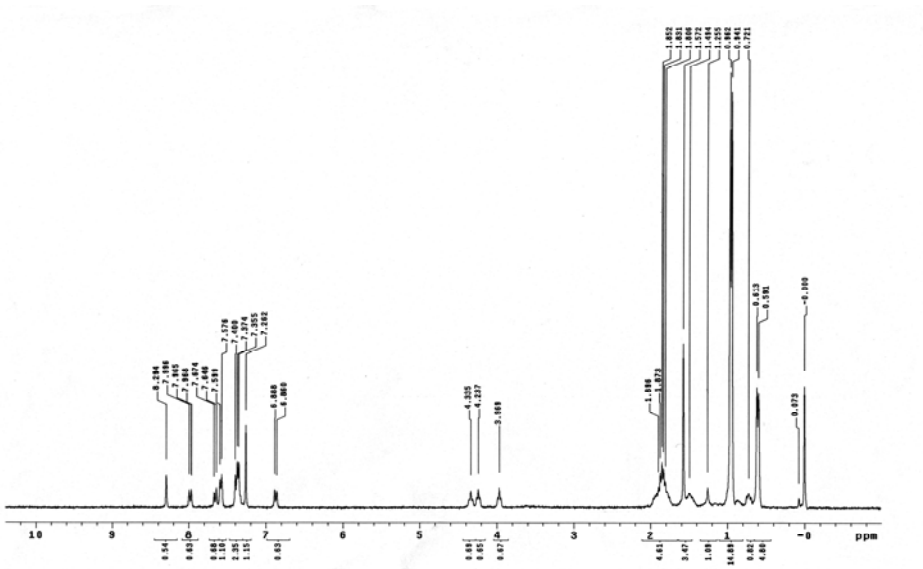

Figure S24. ^{1}H NMR spectra of **4** in $CDCl_3$.

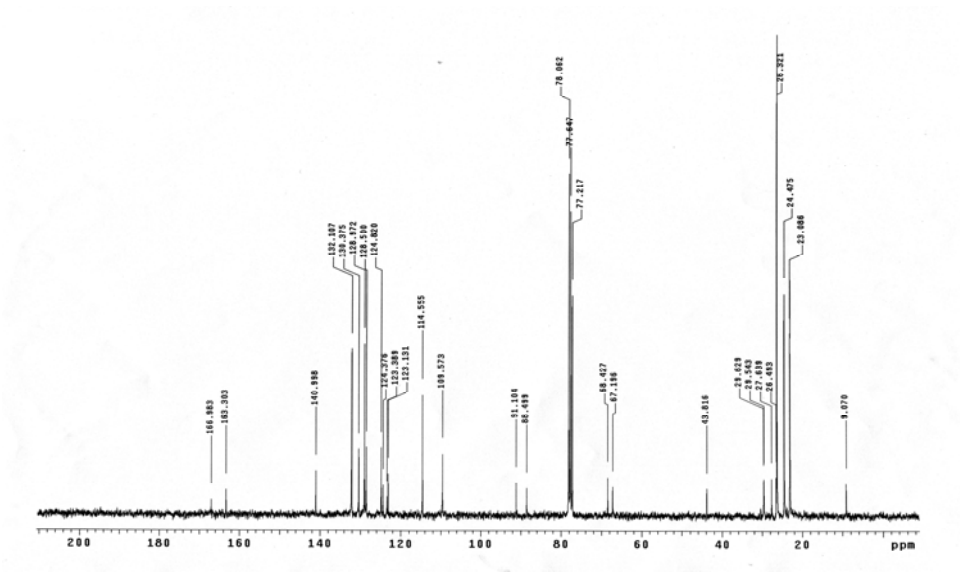

Figure S25. ^{13}C NMR spectra of **4** in $CDCl_3$.

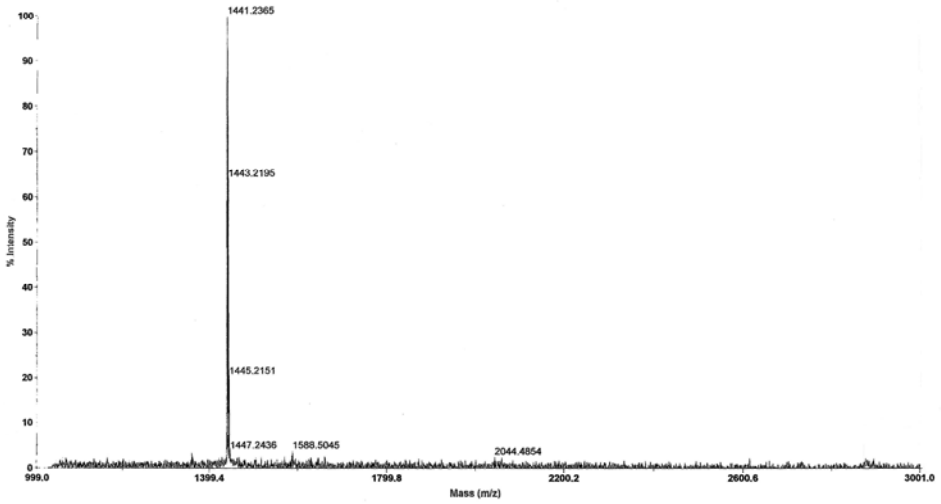

Figure S26. MALDI-TOF spectrum of **4**.

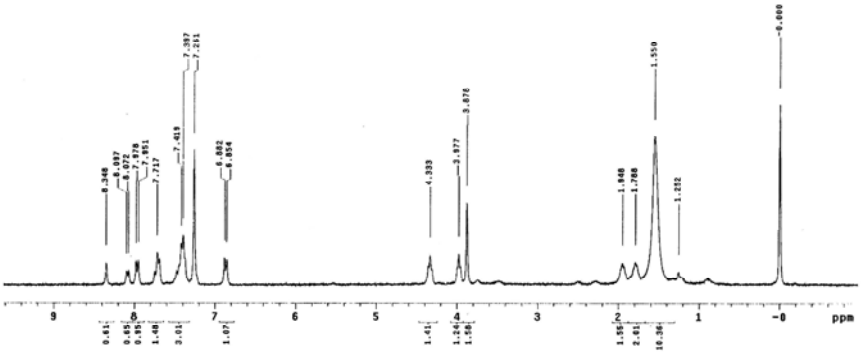

Figure S27. ^{1}H NMR spectra of **M1** in $CDCl_3$.

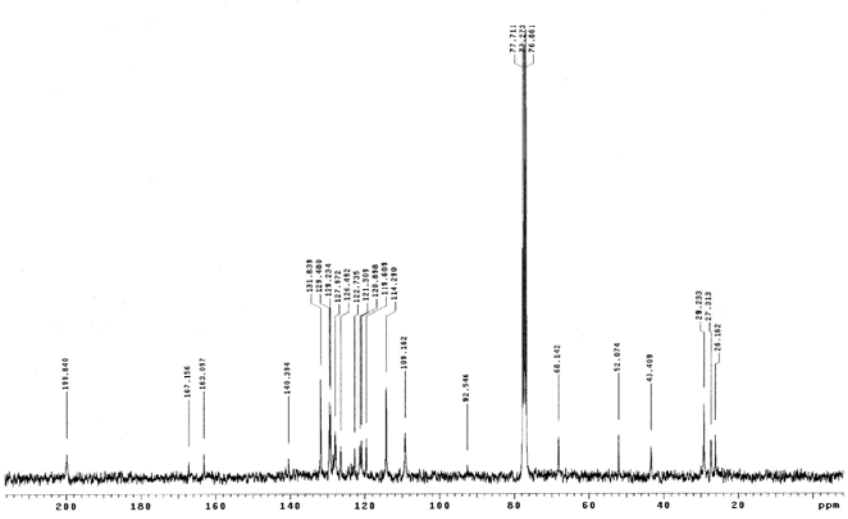

Figure S28. ^{13}C NMR spectra of **M1** in $CDCl_3$.

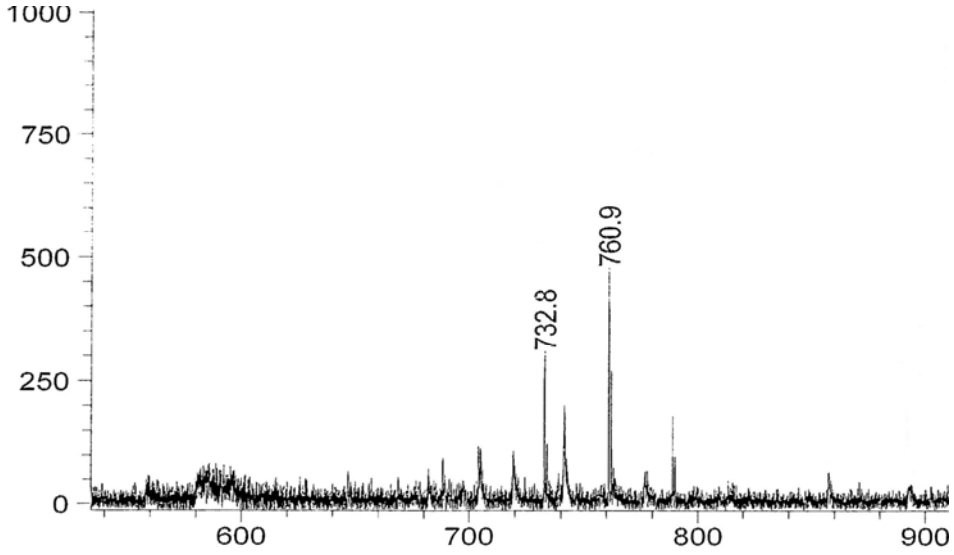

Figure S29. MALDI-TOF spectrum of **M1**.

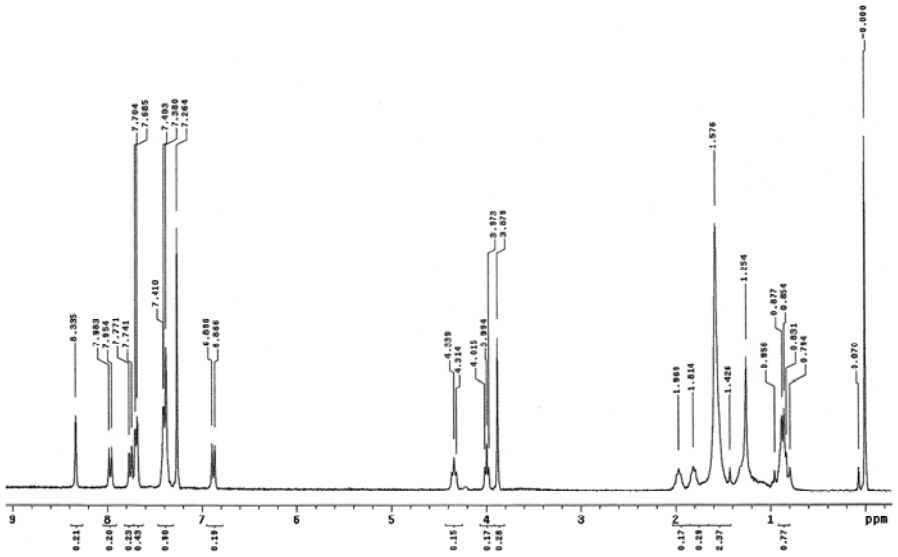

Figure S30. ^{1}H NMR spectra of **M2** in $CDCl_3$.

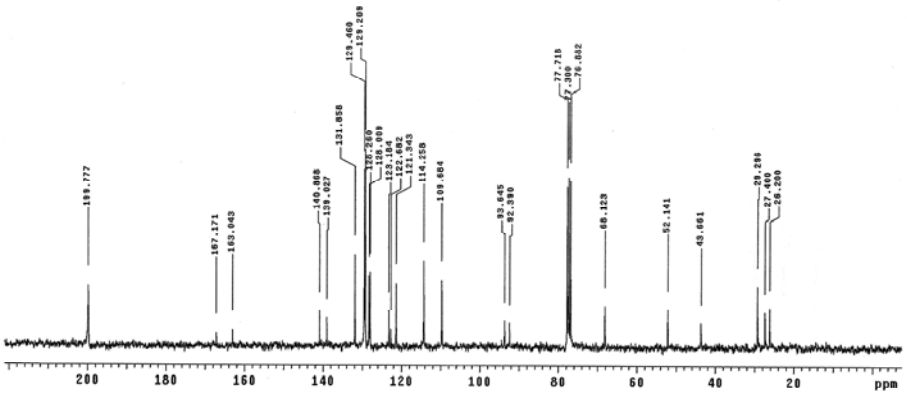

Figure S31. ^{13}C NMR spectra of **M2** in $CDCl_3$.

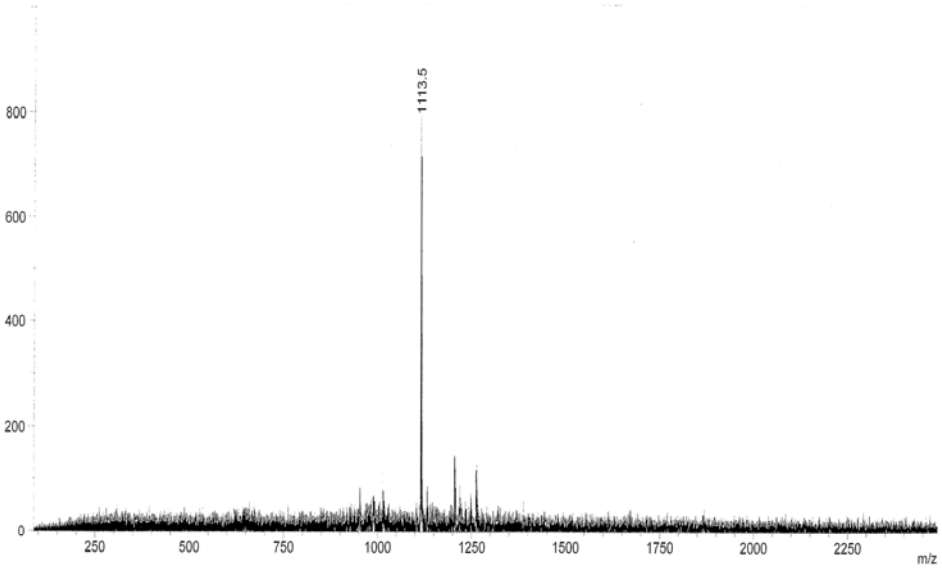

Figure S32. MALDI-TOF spectrum of **M2**.

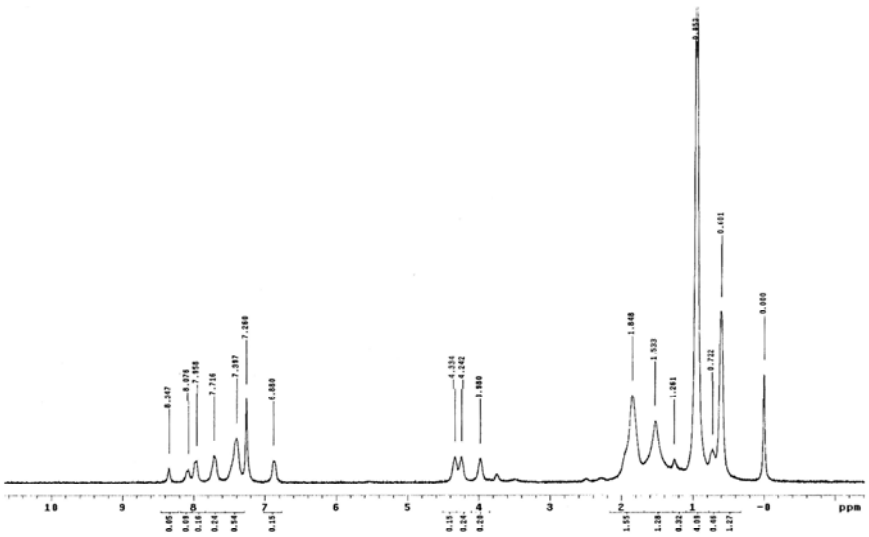

Figure S33. ^{1}H NMR spectra of P**M1** in $CDCl_3$.

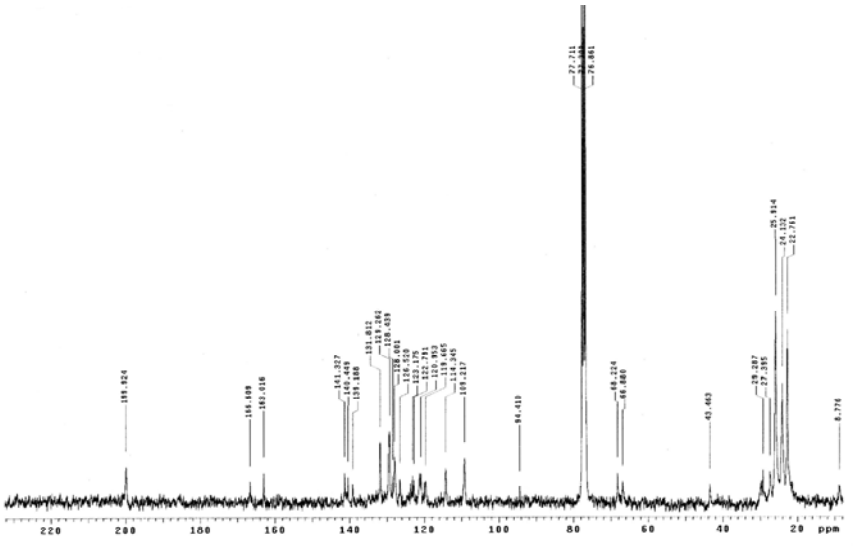

Figure S34. ^{13}C NMR spectra of P**M1** in $CDCl_3$.

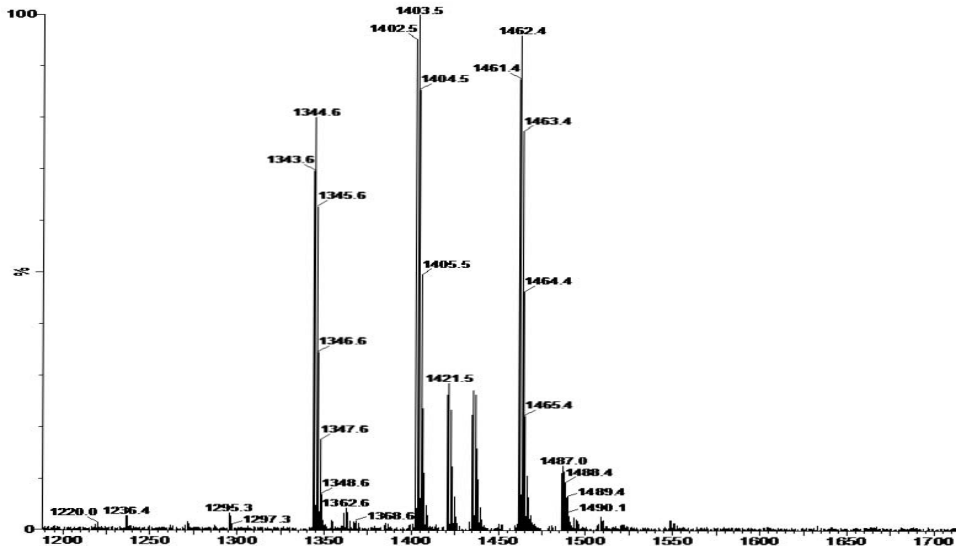

Figure S35. MALDI-TOF spectrum of **PM1**.

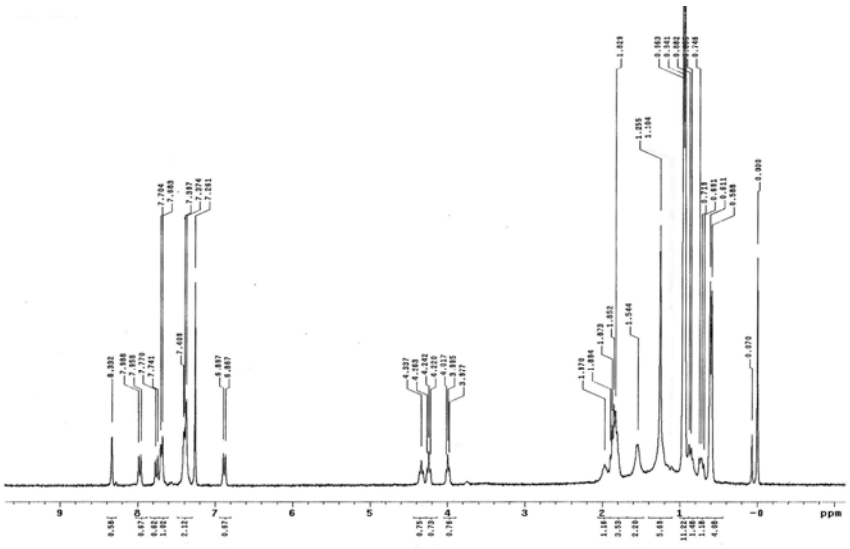

Figure S36. ^{1}H NMR spectra of P**M2** in $CDCl_3$.

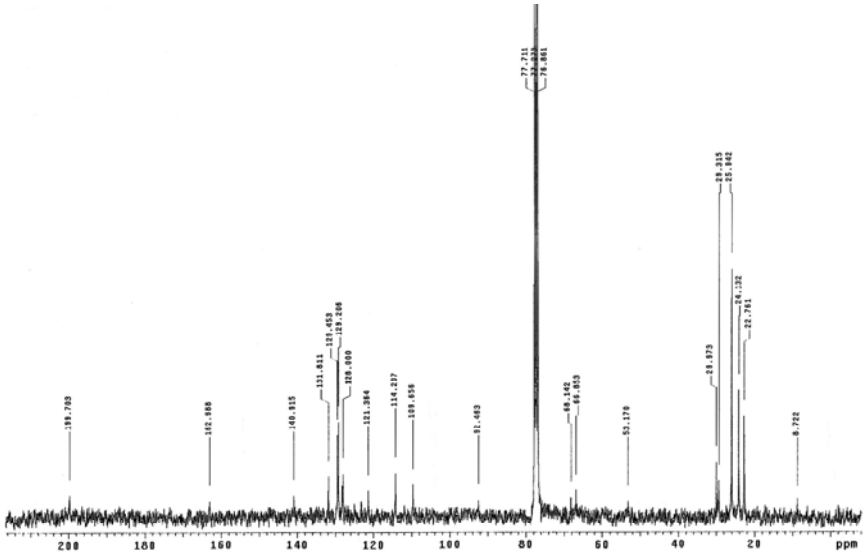

Figure S37. ^{13}C NMR spectra of P**M2** in $CDCl_3$.

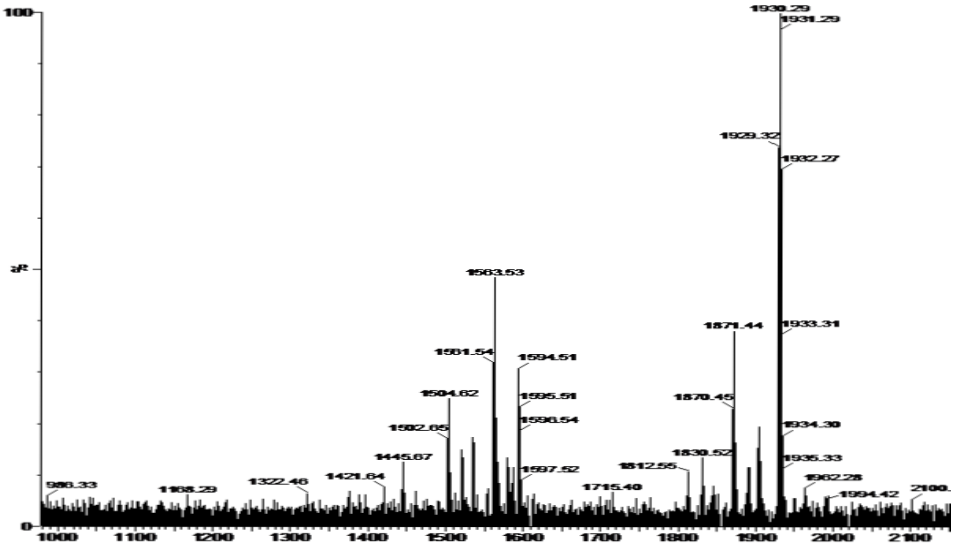

Figure S38. MALDI-TOF spectrum of **PM2**.