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Synthesis and properties of MQ resins with phenyl groups in monofunctional units

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Materials. TEOS (99.9%, EKOS-1), methyltriethoxysilane (99%, AO Reachem), diethoxydimethylsilane (97%, Sigma-Aldrich), dimethylvinylchlorosilane (97%, Sigma-Aldrich), methyl *tert*-butyl ether (MTBE) (99%, Component-Reaktiv), acetic acid (99.9%, Khimreaktiv), pyridine (99%, Chimmed) were used as received.

Methods. GPC analysis was carried on a chromatographic system consisting of a Staier seriya 2 high-pressure pump (Akvilon, Russia), a Smartline RI 2300 refraction meter detector, and a Jet stream 2 Plus thermostat (Knauer, Germany). The thermostat temperature was 40 °C (±0.1 °C); the eluents were THF or toluene + 2% THF, flow rate 1.0 mL min^{-1}; column 300 x 7.8 mm packed with the sorbent Phenogel (Phenomenex, USA), particle size 5 μm, pore size 10^3 to 10^5 Å. The molecular weight was estimated from the ratio to linear polystyrene standards.

^{1}H NMR spectra were recorded on a Bruker WP250 SY spectrometer, as well as on a BrukerAvance AV300 spectrometer, using tetramethylsilane as internal standard. Spectra were processed using ACDLABS software.

^{29}Si-NMR spectra were recorded on Bruker Avance II 300 (59.6 MHz), with the addition of accelerating the paramagnetic relaxation agent, chromium(III) acetylacetonate. Chemical shifts are reported in ppm and referenced to the internal standard, tetramethylsilane (δ = 0.00 ppm). Spectra were processed using ACDLABS software.

Thermomechanical analysis (TMA) was carried out on UIP-70-M device using the penetration method in the mode of uniaxial constant load (σ =0.2 MPa). Heating of the samples was performed in the temperature range -100 to 350 °C at the rate of 5 °C/min.

Dimethylphenylethoxysilane. A solution of dimethyldiethoxysilane (171 g, 1 mol) and chlorobenzene (56 g, 0.5 mol) was added slowly dropwise to Mg turnings (13.2 g, 0.5 mol) under boiling in argon atmosphere. After the end of the addition, the mixture reacted continually for 5 h under boiling. After completion of the reaction, the mixture was diluted with toluene (200 mL) and filtered on a Schott filter from the precipitate, additionally washing with toluene (3 × 100 ml). The product was isolated as colorless liquid by distillation at atmospheric pressure (BP =196 °C) and a yield 50% (45 g) were obtained. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.39 (s, 6H, $SiCH_3$), 7.39-7.61 (m, 5H, $Si(C_6H_5)$), 3.64-3.73 (m, 2H, $Si(OC\underline{H}_2CH_3)$), 1.20 (t, 3H, $Si(OCH_2C\underline{H}_3)$).

Methyldiphenylethoxysilane. A solution of phenylmagnesium chloride (1 mol) in THF (800 mL) was added slowly dropwise to methyltriethoxysilane (89 g, 0.5 mol) of at room temperature under argon. After the end of the addition, the mixture reacted continually for 10 h under boiling. Then, THF were distilled off, toluene (200 mL) was added, and the mixture was filtered on a Schott filter from the precipitate, additionally washing with toluene (3 × 100 ml). The product was isolated as colorless liquid by distillation under reduced pressure (bp = 117-120

°C / 1 mbar) and a yield 70% (85 g) were obtained. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.65 (s, 3H, $SiCH_3$), 7.35-7.62 (m, 10H, $Si(C_6H_5)$), 3.74-3.82 (m, 2H, $Si(OC\underline{H}_2CH_3)$), 1.23 (t, 3H, $Si(OCH_2C\underline{H}_3)$).

Synthesis of M(Ph)Q resin and M(Ph₂)Q resin. Synthesis of MQ resins with phenyl substituent(s) was carried out by refluxing 30% solution of dimethylphenylethoxysilane (methyldiphenylethoxysilane) and TEOS in glacial acetic acid. The molar ratio of the starting reagents and, correspondingly, M/Q units ratio was varied as follows: 1: 1, 1: 1.5, 1: 2, 1: 3, 1: 4. The reaction product was dissolved in MTBE, washed till neutral pH of the washings and dried over sodium sulfate. After that, the solvent was distilled off on a rotary evaporator and the product was dried in vacuum at 1 Torr.

The analysis of the synthesized products was carried out after they were blocked by dimethylvinylchlorosilane under conditions that did not break the structure, which made it possible to calculate the content of Si-OH groups using the ratio of the proton signals of vinyl and phenyl groups on ^{1}H NMR spectra of the samples. The ratio of M and Q units was determined using ^{29}Si NMR spectroscopy.

^{1}H NMR data (300 MHz, $CDCl_3$; δ, ppm) spectroscopy for dimethylvinylchlorosilane-blocked MQ resins (numbers after MQ correspond to M:Q ratio):

M(Ph)Q 1:1 – -0.37-0.59(20 H Si–CH_3), 6.89-7.69 (11.71 H, Si-C_6H_5), 5.44-6.27 (3 Si–$CH=CH_2$);

M(Ph)Q 1:1.5 – -0.46-0.57(m, 15.8 H, Si–CH_3), 6.86-7.70 (m, 5.43 H, Si-C_6H_5), 5.33-6.25 (m, 3 H, Si–$CH=CH_2$);

M(Ph)Q 1:2 – -0.45-0.69(m, 14.6 H, Si–CH_3), 6.81-7.70 (m, 4.74 H, Si–C_6H_5), 5.26-6.29 (m, 3 H, Si–$CH=CH_2$);

M(Ph)Q 1:3 – -0.79-0.65(m, 10.64 H, Si–CH_3), 6.96-8.05 (m, 3.45 H, Si-C_6H_5), 5.02-6.44 (3 Si–$CH=CH_2$);

M(Ph)Q 1:4 – -0.52-1.06(m, 9.3 H, Si–CH_3), 6.88-7.98 (m, 3.11 H, Si-C_6H_5), 5.24-6.32 (m, 3 H, Si–$CH=CH_2$);

M(Ph₂)Q 1:1 – -0.49-0.84(m, 10.37 H, Si–CH_3), 6.82-7.77 (m, 17.92 H, Si-C_6H_5), 5.27-6.27 (m, 3H, Si–$CH=CH_2$);

M(Ph₂)Q 1:1.5 – -0.46-0.74(m, 8.32 H, Si–CH_3), 6.87-7.74 (m, 9.6 H, Si-C_6H_5), 5.48-6.26 (m, 3H, Si–$CH=CH_2$);

M(Ph₂)Q 1:2 – -0.76-0.79(m, 8.2 H, Si–CH_3), 6.62-7.87 (m, 9.31 H, Si-C_6H_5), 5.12-6.27 (m, 3H, Si–$CH=CH_2$);

M(Ph₂)Q 1:3 – -0.78-0.79(m, 8H, Si–CH_3), 6.97-7.74 (m, 5.77 H, Si-C_6H_5), 5.18-6.31 (m, 3H, Si–$CH=CH_2$);

M(Ph₂)Q 1:4 – -0.58-0.74(m, 7H, Si–CH_3), 6.77-7.99 (m, 6 H, Si-C_6H_5), 5.19-6.36 (m, 3H, Si–$CH=CH_2$).

^{29}Si NMR data (59.6 MHz, toluene; δ, ppm) spectroscopy for dimethylvinylchlorosilane-blocked MQ resins:

M(Ph)Q 1:1 – -71.06 – -133.53 (SiO_2), 9.24 – -3.65 ($C_6H_5(CH_3)_2SiO_{0.5}$);

M(Ph)Q 1:1.5 – -59.01 – -133.11 (SiO_2), 10.61 – -5.16 ($C_6H_5(CH_3)_2SiO_{0.5}$);

M(Ph)Q 1:2 – -86.47 – -129.38 (SiO_2), 7.85 – -4.98 ($C_6H_5(CH_3)_2SiO_{0.5}$);

M(Ph)Q 1:3 – -76.89 – -139.58 (SiO_2), 10.09 – -7.51 ($C_6H_5(CH_3)_2SiO_{0.5}$);

M(Ph)Q 1:4 – -94.01 – -124.29 (SiO_2), 10.52 – -6.25 ($C_6H_5(CH_3)_2SiO_{0.5}$);

M(Ph₂)Q 1:1 – -87.47 – -122.97 (SiO_2), 7.19 – -3.27, -4.32 – -14.50 ($CH_3(C_6H_5)_2SiO_{0.5}$);

M(Ph₂)Q 1:1.5 – -87.89 – -123.46 (SiO_2), 8.04 – -3.12, -4.48 – -14.92 ($CH_3(C_6H_5)_2SiO_{0.5}$);

M(Ph₂)Q 1:2 – -89.29 – -124.01 (SiO_2), 6.92 – -3.17, -4.15 – -12.94 ($CH_3(C_6H_5)_2SiO_{0.5}$);

M(Ph₂)Q 1:3 – - 84.15 – -129.86 (SiO_2), 10.38 – -2.95, -4.31 – -16.46 ($CH_3(C_6H_5)_2SiO_{0.5}$);

M(Ph₂)Q 1:4 – - 92.60 – -128.73 (SiO_2), 8.90 – -3.40, -4.08 – -13.08 ($CH_3(C_6H_5)_2SiO_{0.5}$).

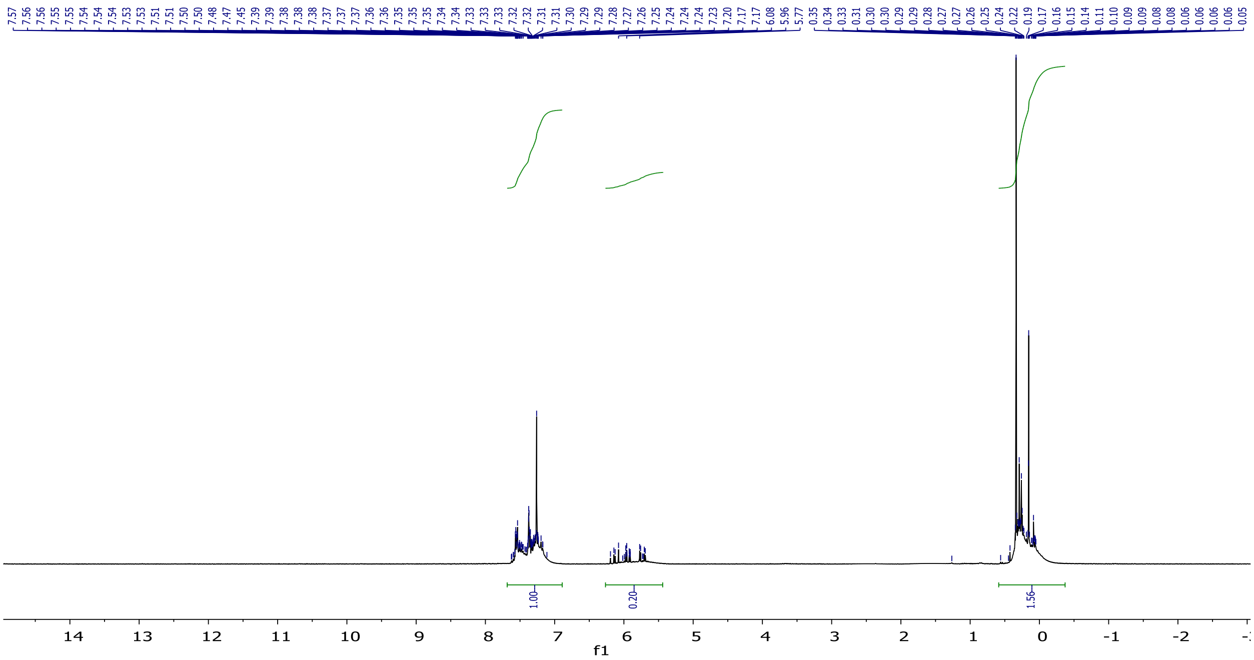

Figure S1 ^{1}H NMR (300 MHz, *CDCl*$_3$) spectrum of resin **1**

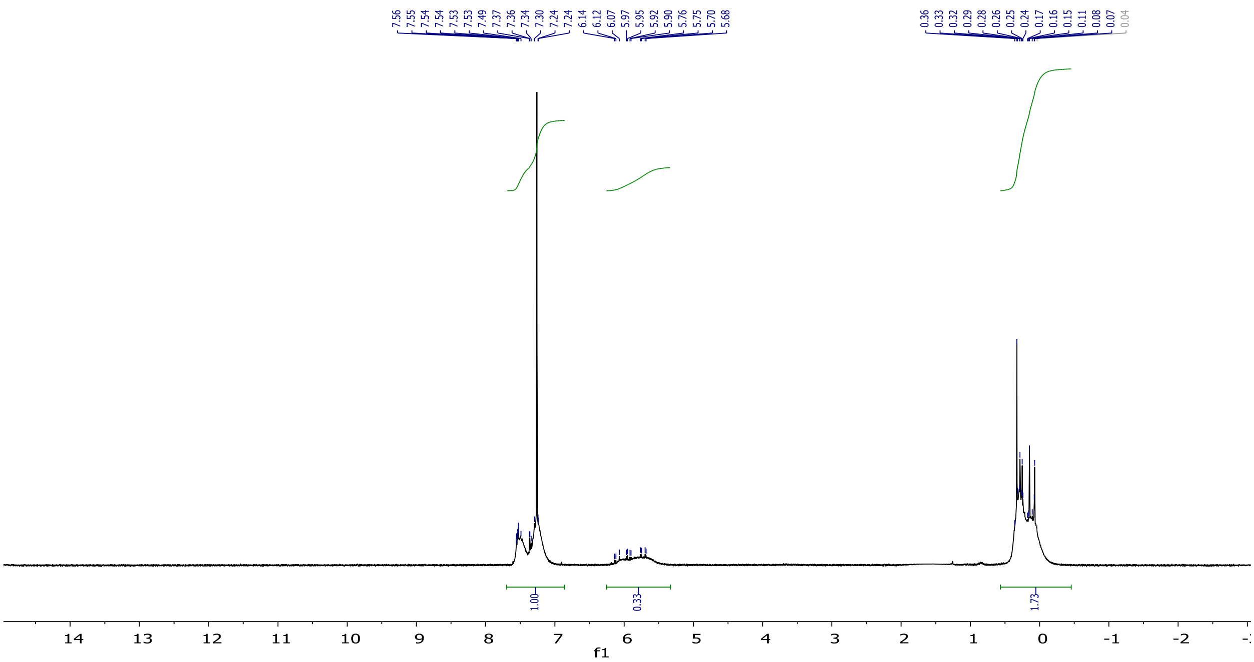

Figure S2 ^{1}H NMR (300 MHz, *CDCl*$_3$) spectrum of resin **2**

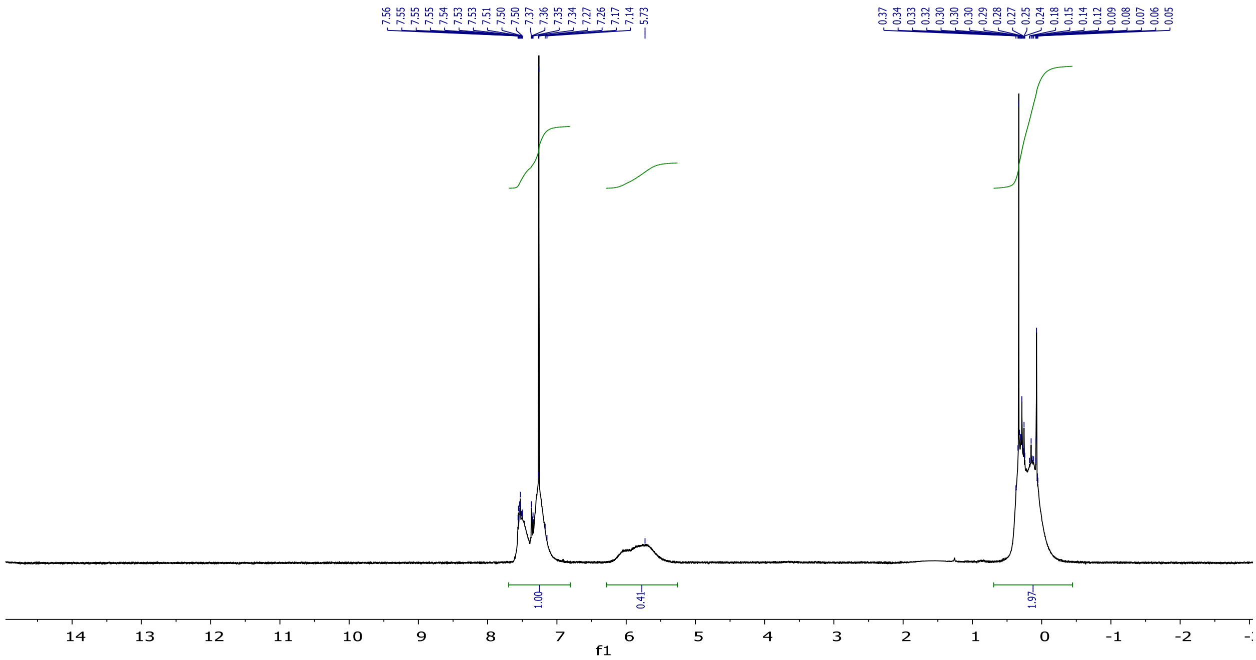

Figure S3 [1]H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **3**

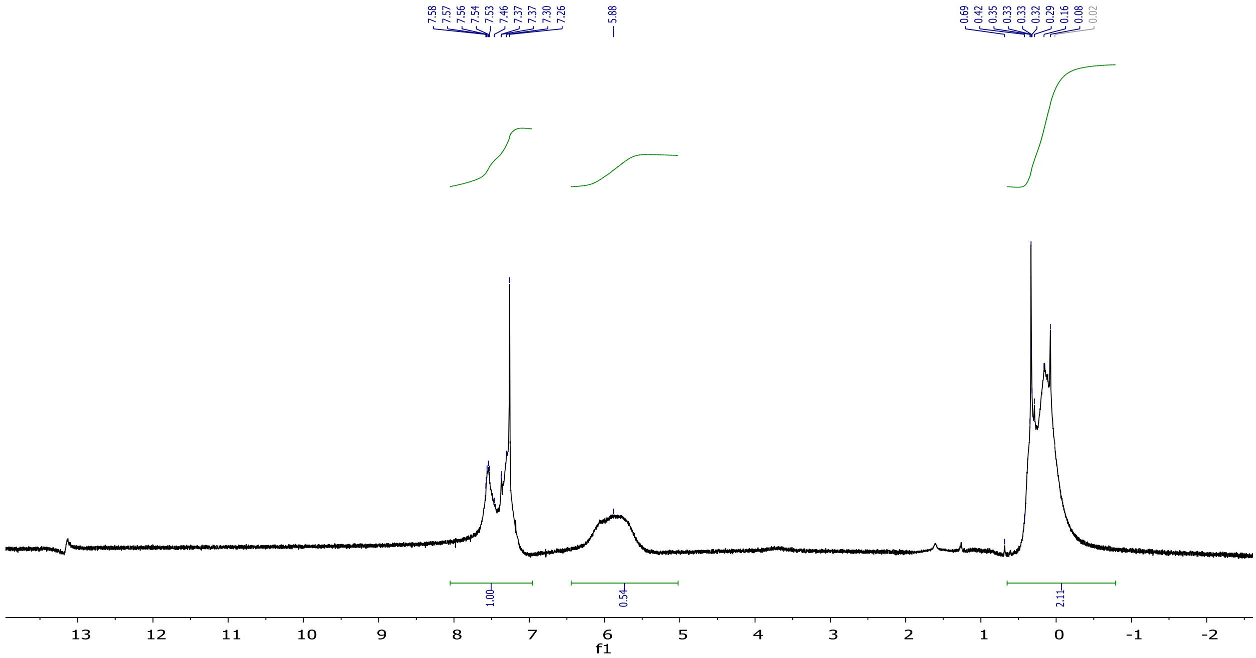

Figure S4 [1]H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **4**

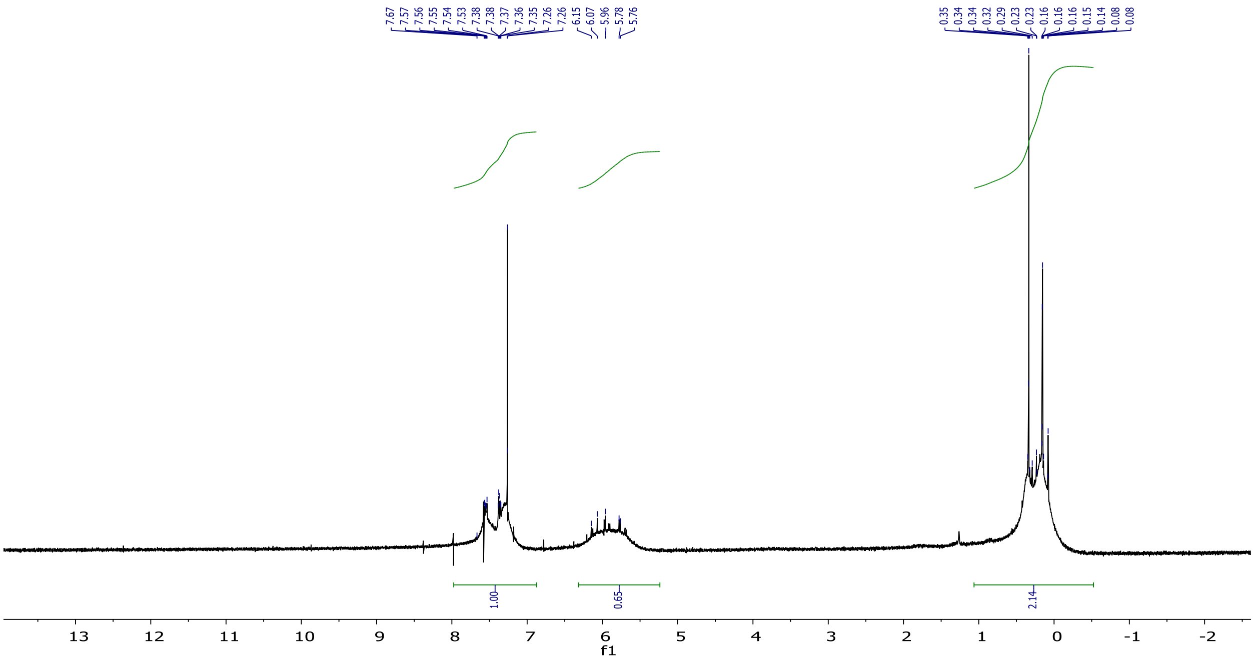

Figure S5 [1]H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **5**

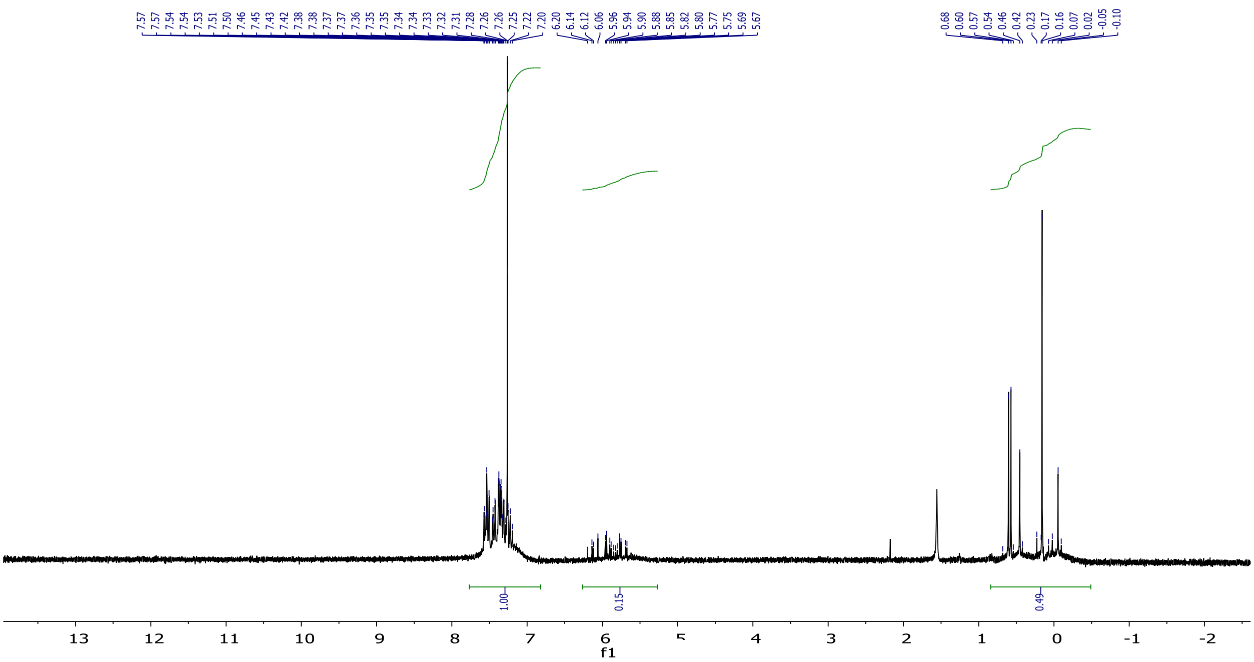

Figure S6 [1]H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **6**

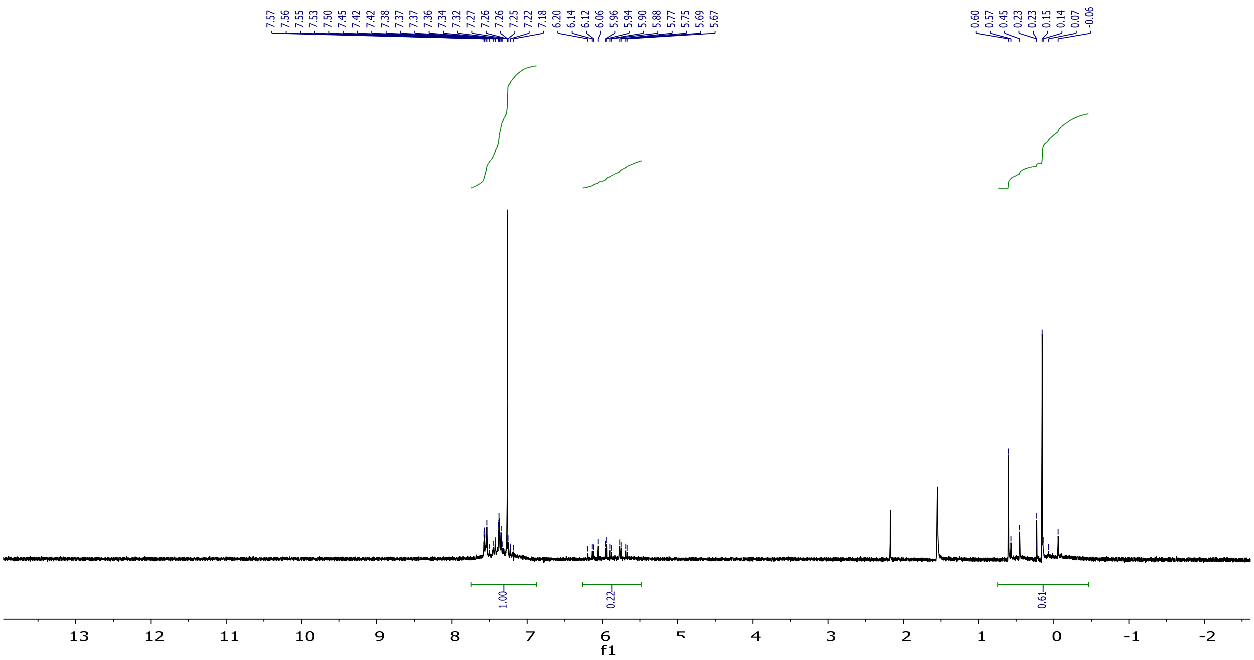

Figure S7 [1]H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **7**

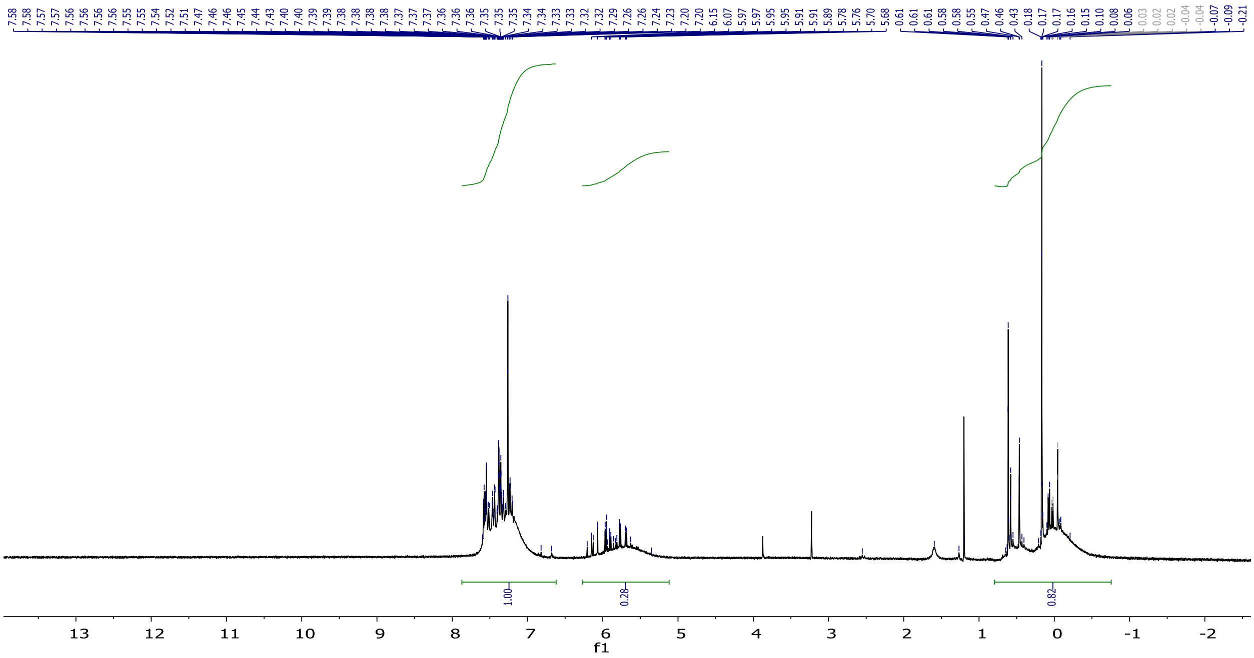

Figure S8 [1]H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **8**

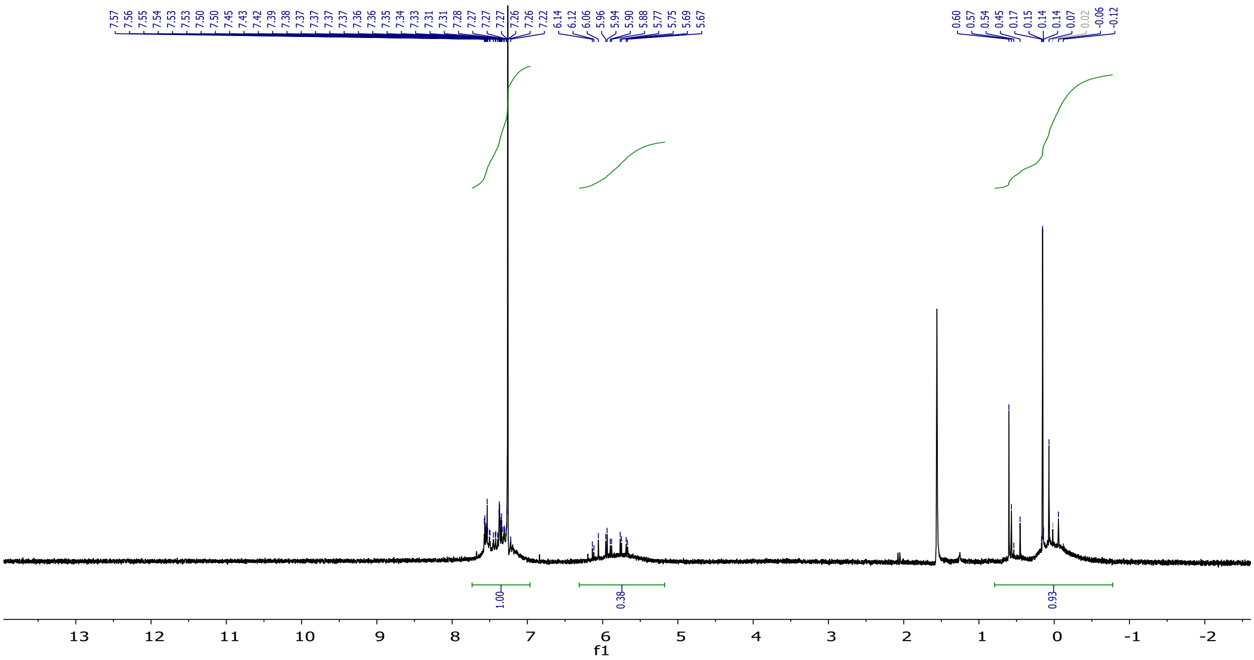

Figure S9 ^{1}H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **9**

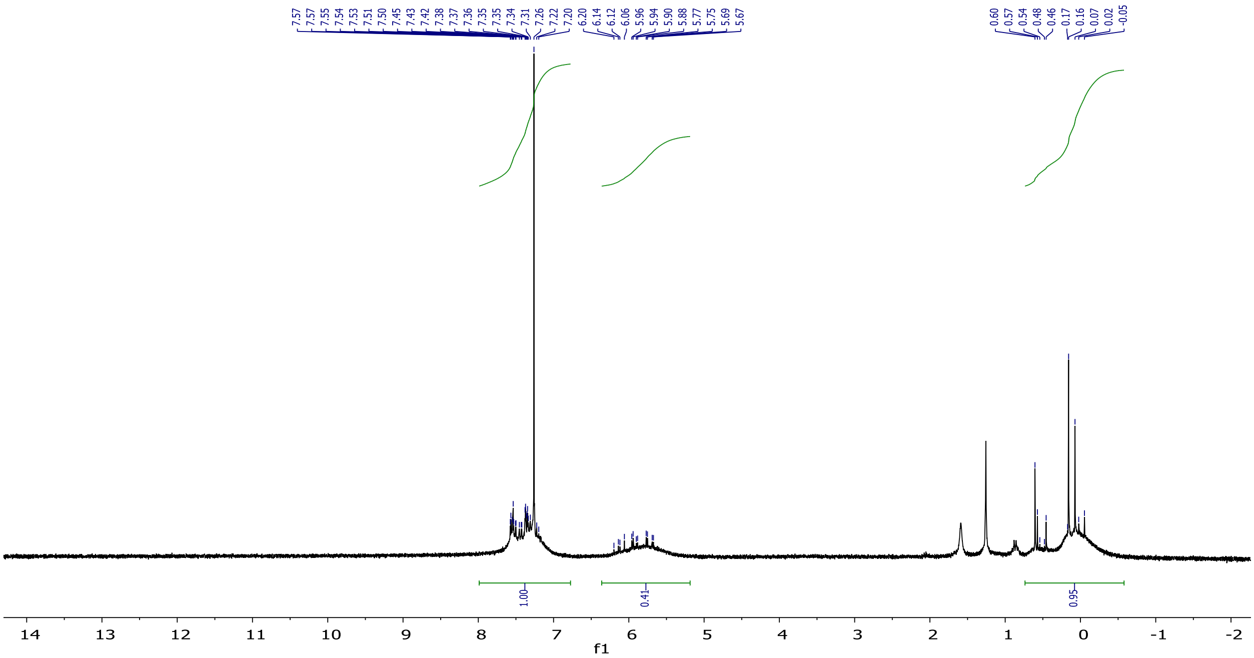

Figure S10 ^{1}H NMR (300 MHz, *$CDCl_3$*) spectrum of resin **10**

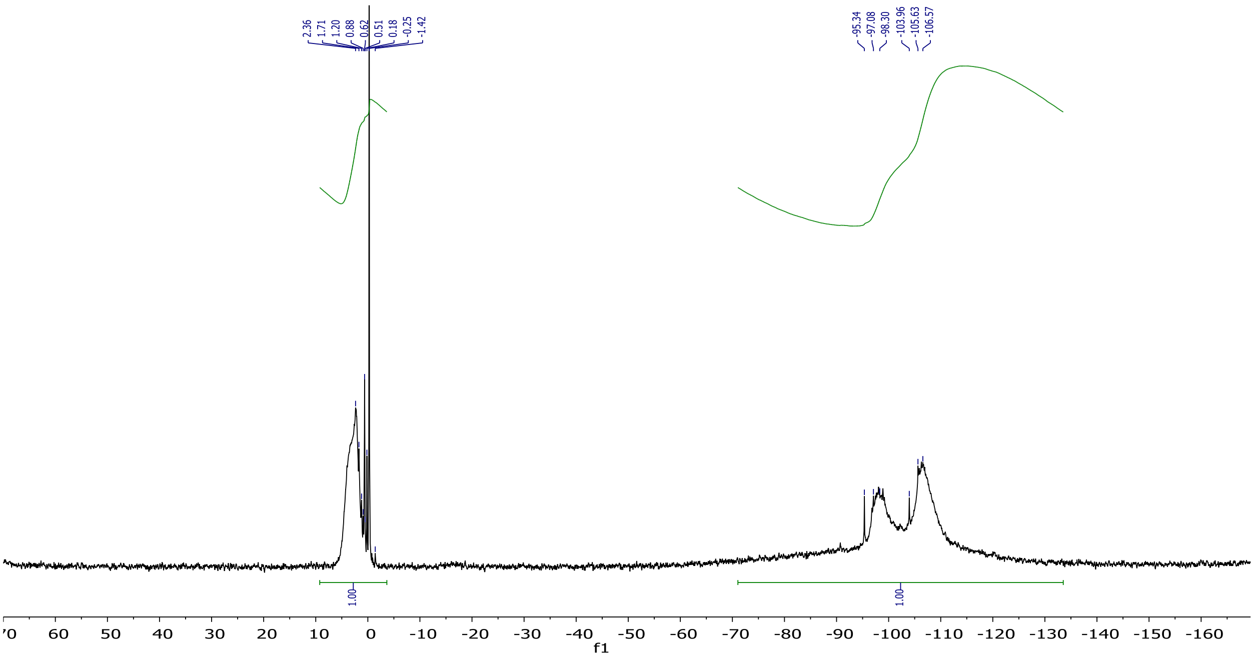

Figure S11 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **1**

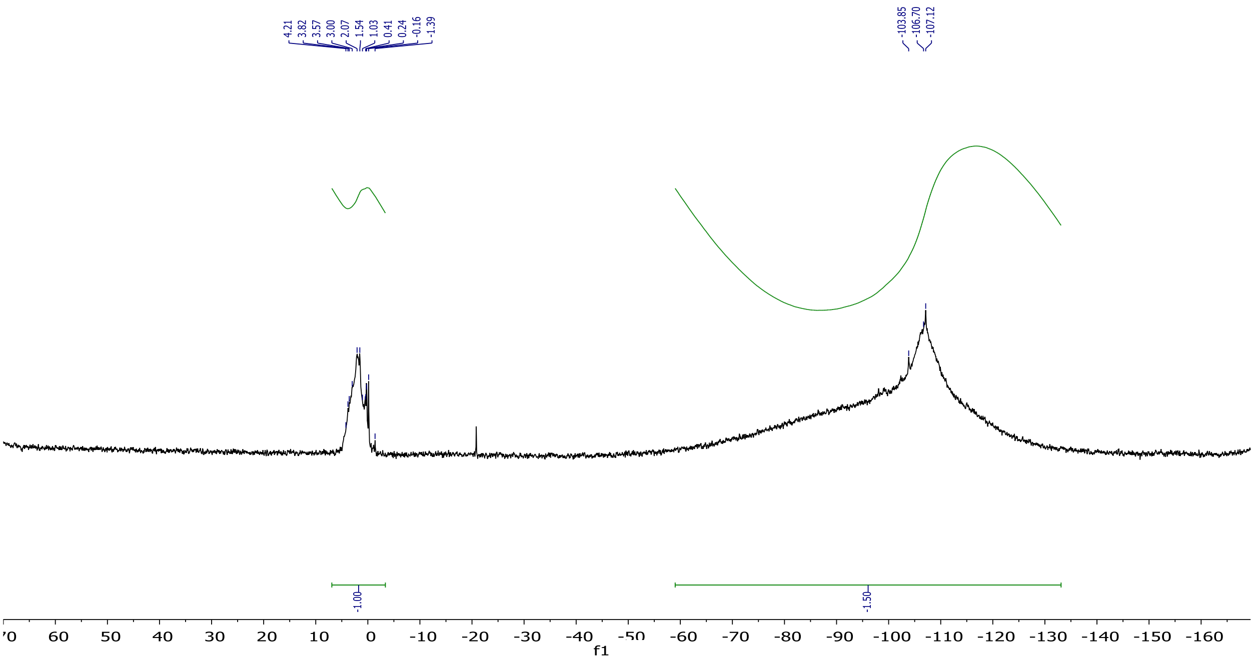

Figure S12 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **2**

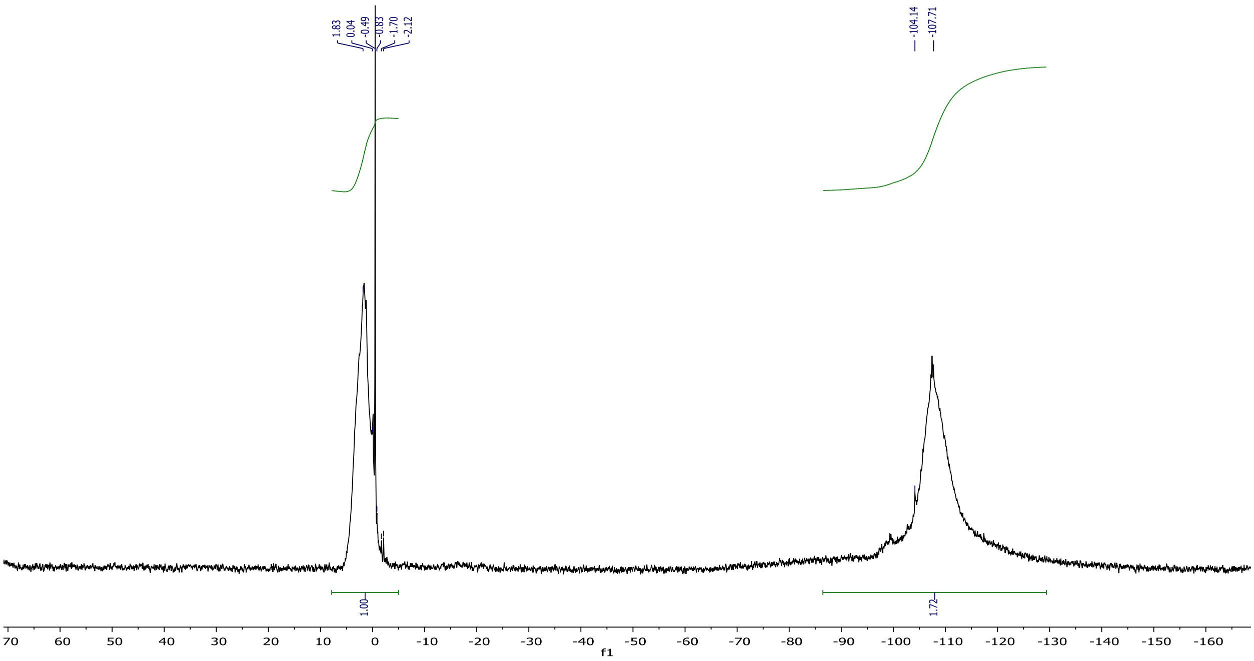

Figure S13 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **3**

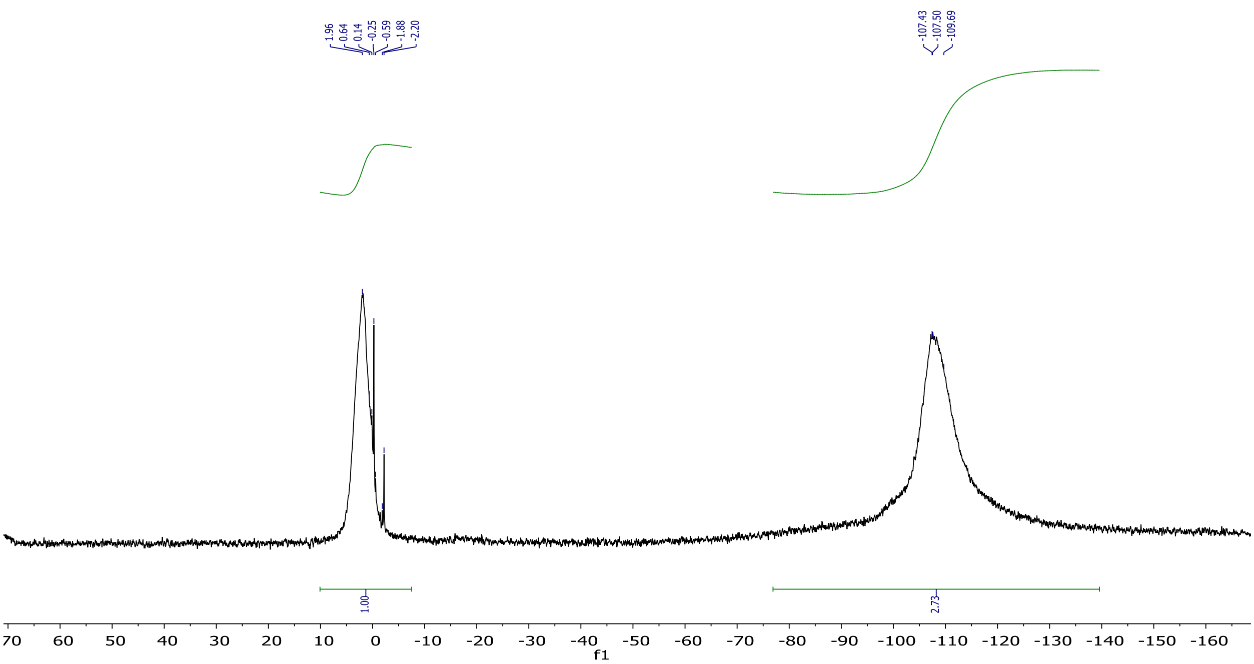

Figure S14 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **4**

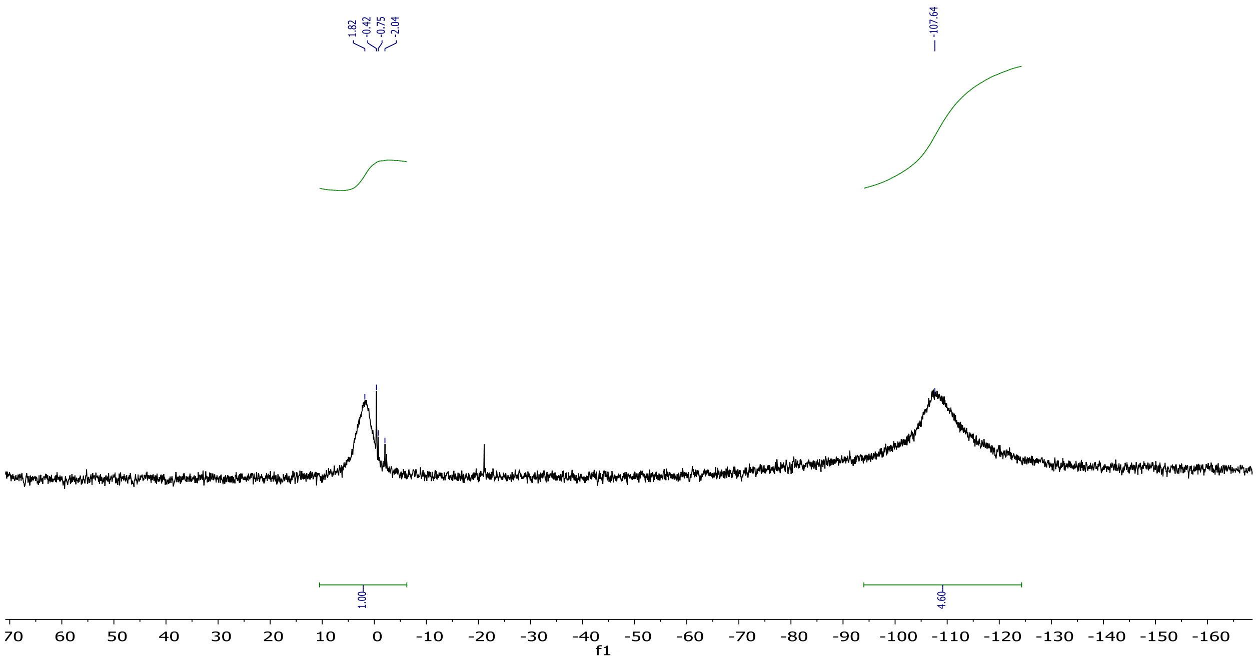

Figure S15 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **5**

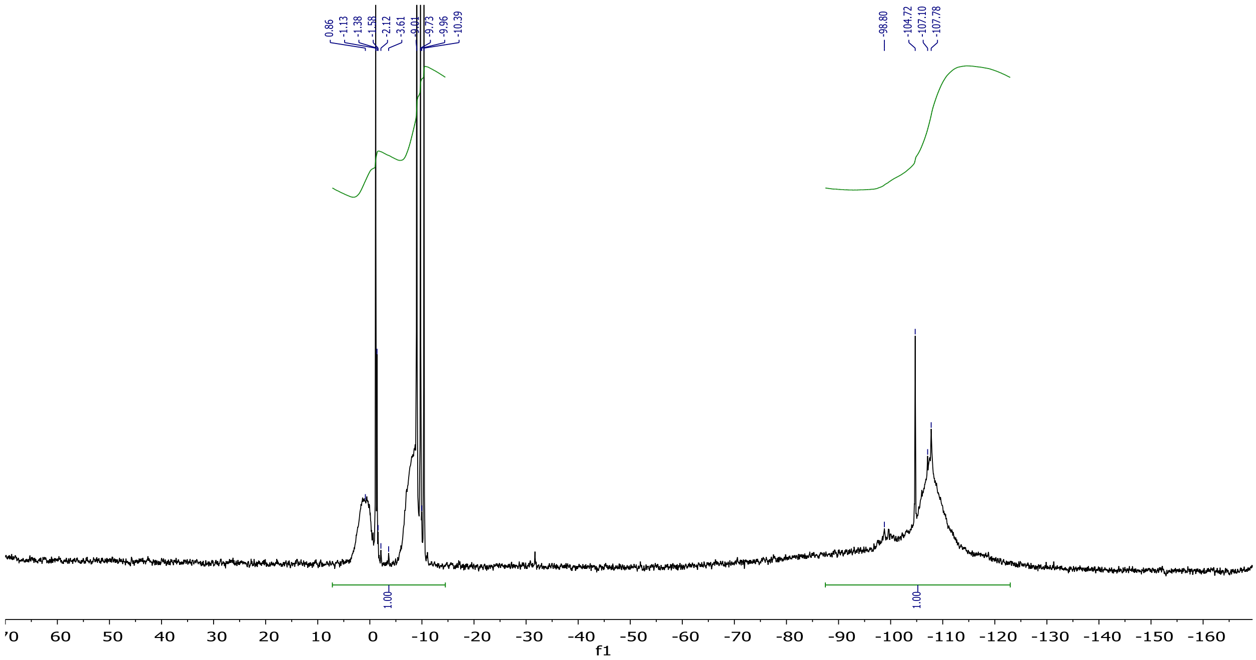

Figure S16 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **6**

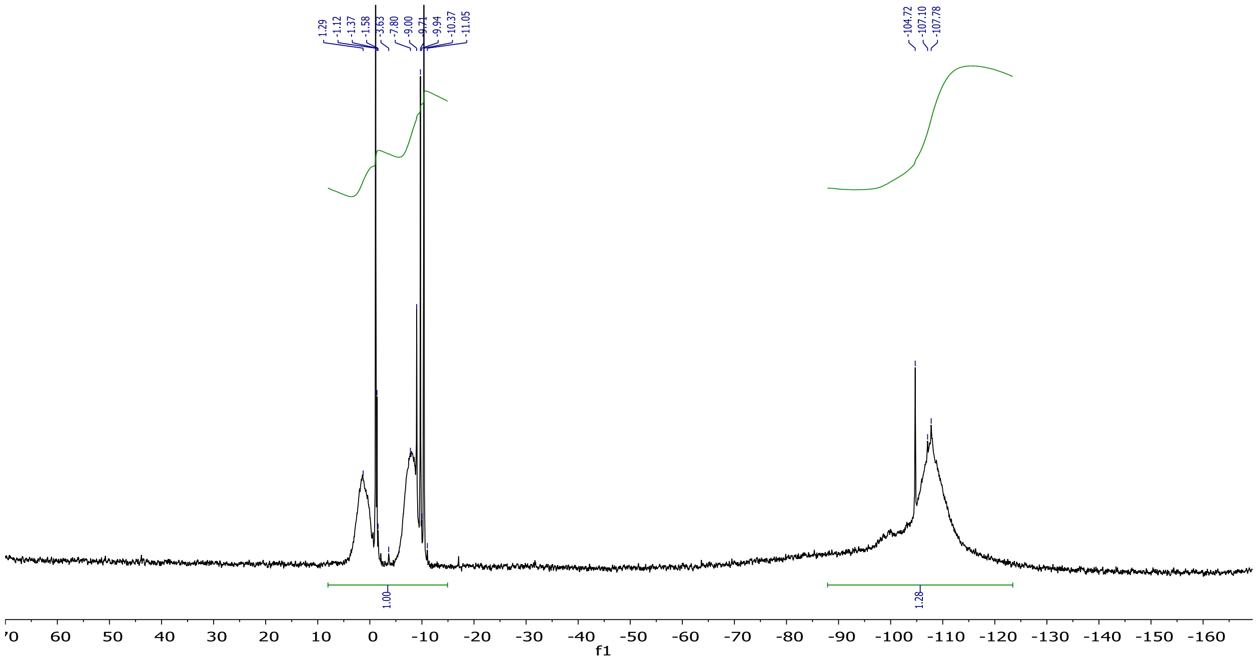

Figure S17 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **7**

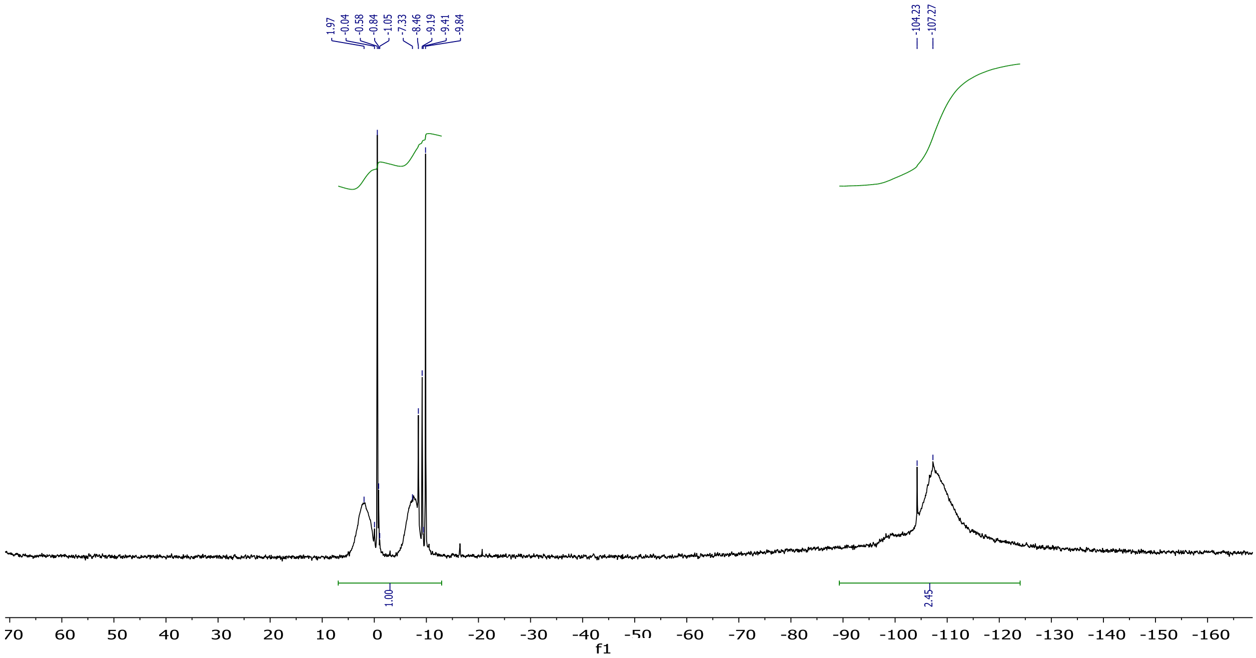

Figure S18 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **8**

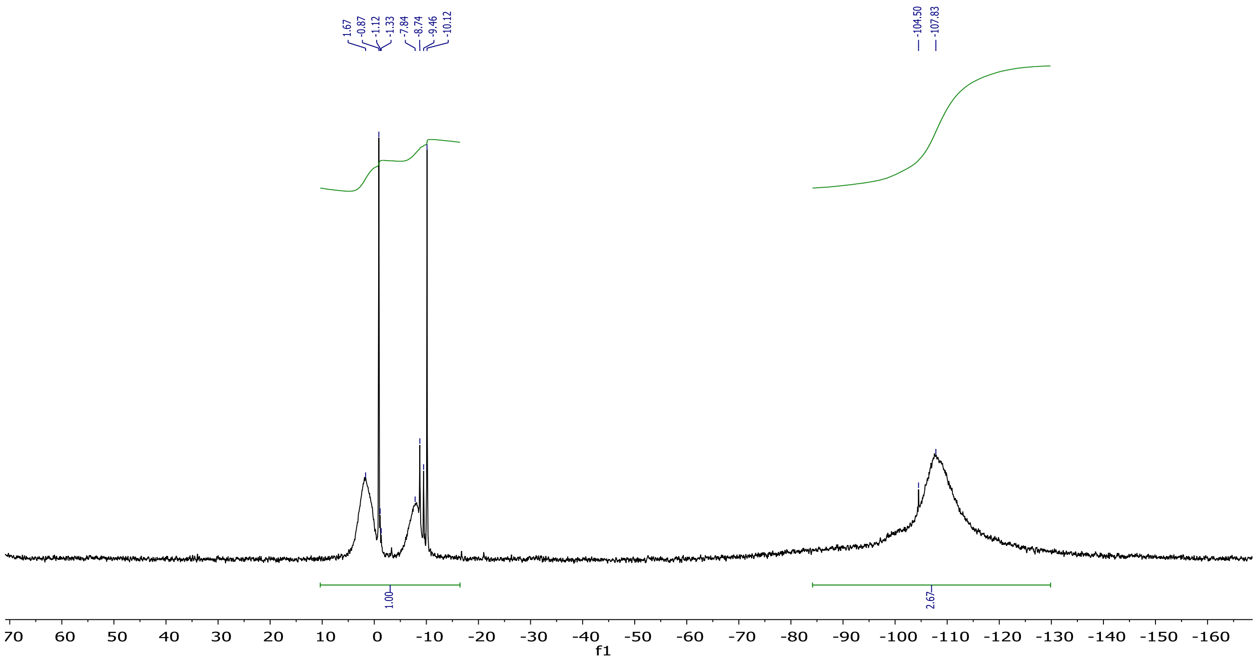

Figure S19 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **9**

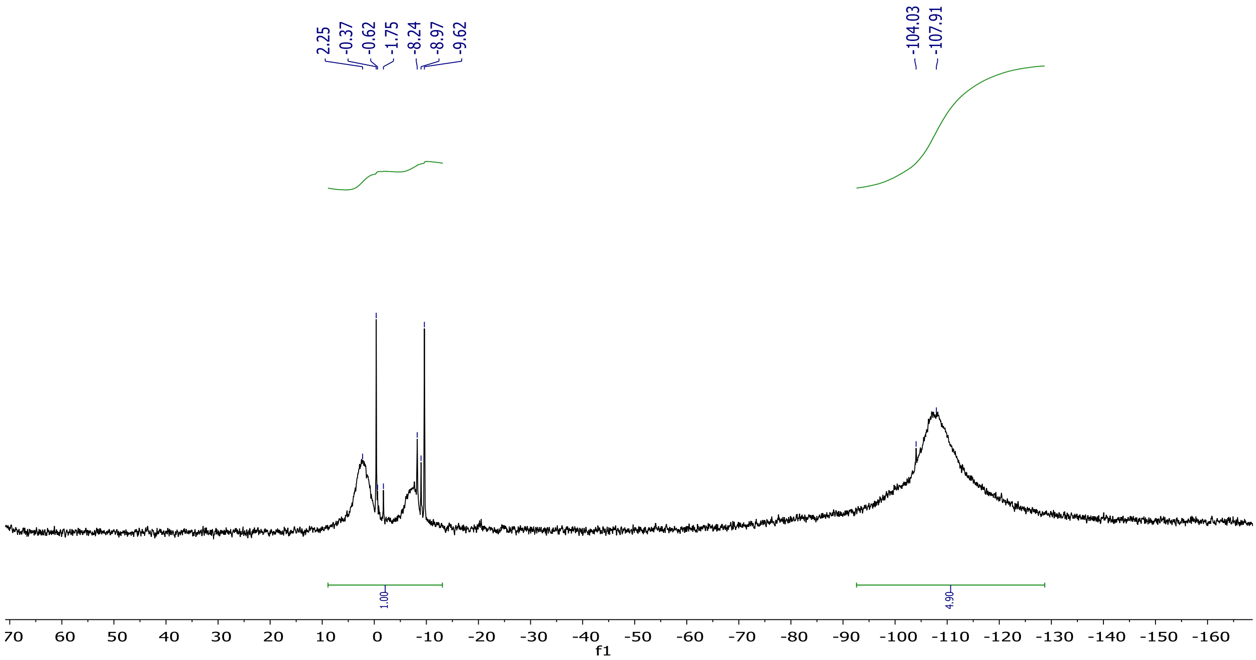

Figure S20 ^{29}Si NMR (59.6 MHz, toluene) spectrum of resin **10**