

**Rosin-based dielectric polymer with intrinsic low dielectric constant
and comprehensively excellent properties**

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This electronic supplementary information is composed of the total of 14 pages, including 22 figures.

Synthesis of Compound 1

Dehydroabiatic acid (0.017 mol, 5.00 g) was dissolved in anhydrous acetonitrile (337 mL), and NBS (0.031 mol, 5.54 g) was added. The mixture was allowed to react in darkness at room temperature for 24 h. The mixture was suction filtered, yielding a white solid that was dissolved in ethyl acetate (50 mL). The solution was subsequently washed with water (50 mL, 3 times) and dried over anhydrous Na₂SO₄. After filtration and concentration, Compound 1 was purified using column chromatography with a mixture of petroleum ether and ethyl acetate as the eluent (5:1, v/v). Yield: 53%. ¹H NMR (400 MHz, DMSO) δ 12.20 (s, 1H), 7.36 (s, 1H), 7.00 (s, 1H). ¹³C NMR (101 MHz, DMSO) δ 179.2 (m), 149.2 (s), 143.2 (s), 134.5 (s), 128.0 (s), 127.2 (s), 120.8 (m), 46.2 (s), 44.2 (s), 37.5 (s), 36.5 (s), 36.1 (s), 31.9 (s), 28.9 (s), 24.6 (s), 22.7 (s), 22.6 (s), 20.8 (m), 18.0 (s), 16.3 (s); MS (ESI) m/z 377 [M-H]⁻.

Synthesis of Compound 2

Compound 1 (1.00 mmol, 0.379 g), tripotassium phosphate (2.00 mmol, 0.425 g) and benzocyclobutene-4-boronic acid (1.25 mmol, 0.185 g) were dissolved in a water/ethanol mixture (6 mL, 1:1, v/v) in a N₂ atmosphere. Tetrakis(triphenylphosphine)palladium (0) (0.01 mmol, 0.0116 g) was added, and the mixture was subsequently heated at 60 °C for 10 h. The mixture was allowed to cool to room temperature and suction filtered with diatomite. The organic phases washed with water (50 mL, 3 times), dried over anhydrous Na₂SO₄, filtered and concentrated to yield the crude product. Compound 2 was purified using column chromatography with a mixture of petroleum ether and ethyl acetate as the eluent (5:1, v/v). Yield: 85%. ¹H

NMR (400 MHz, DMSO) δ 12.16 (s, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.02 (dd, $J = 7.5$, 0.9 Hz, 1H), 7.00 (s, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 3.18 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 179.4 (s), 146.27 (s), 144.9 (s), 143.4 (s), 142.5 (s), 140.6 (s), 138.9 (s), 133.5 (s), 127.7 (s), 125.4 (s), 125.3 (s), 123.2 (s), 122.0 (s), 46.3 (s), 44.6 (s), 37.7 (s), 36.3 (s), 36.2 (s), 29.2 (s), 29.0 (s), 28.9 (s), 28.3 (s), 24.8 (s), 24.2 (s), 24.0 (s), 21.1 (s), 18.1 (s), 16.3 (s); MS (ESI) m/z 401 [M-H] $^-$.

Synthesis of Compound 3

Lithium aluminum hydride (68.4 mmol, 2.60 g) and tetrahydrofuran (40 mL) were added to a round bottom flask containing magnetons. A solution of compound **2** (12.4 mmol, 5.00 g) dissolved in tetrahydrofuran (40 mL) was added dropwise at 0 °C. After dripping, stir for 0.5 h, then stir at room temperature for 2 h. At the end of the reaction, deionized water and 10% HCl were added at 0 °C successively to annihilate. The organic phases were washed with water (50 mL, 3 times), dried over anhydrous Na_2SO_4 , filtered and concentrated to yield the crude product. Compound **3** was purified using column chromatography with a mixture of petroleum ether and ethyl acetate as the eluent (5:1, v/v). Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 7.09 (dd, $J = 7.5$, 1.1 Hz, 1H), 7.06 (d, $J = 7.4$ Hz, 1H), 7.02 (s, 1H), 7.00 (s, 1H), 6.96 (s, 1H), 3.48 (dd, $J = 10.9$, 5.0 Hz, 1H), 3.23 (d, $J = 11.5$ Hz, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.88 (s), 145.31 (s), 143.94 (s), 143.09 (s), 141.38 (s), 139.53 (s), 134.08 (s), 128.17 (s), 126.24 (s), 125.69 (s), 123.75 (s), 121.98 (s), 72.28 (s), 43.97 (s), 38.48 (s), 37.92 (s), 37.41 (s), 35.15 (s), 29.96 (s), 29.64 (s), 29.48 (s), 28.94 (s), 25.38 (s), 24.59 (s), 24.36 (s), 18.97 (s), 18.67 (s), 17.46 (s). MS (EI) m/z 388.

Preparation of BCB films for the measurement of the surface roughness

A solution of BCB-DA-Si dissolved in xylene (35 mg/mL) was spin-coated on a monocrystalline silicon wafer to form a smooth film which was dried for 24 h at room temperature. The silicon wafer was heated stepwise at 130 °C for 0.5 h, 180 °C for 1.0 h, 210 °C for 1.0 h, 230 °C for 1.5 h and 250°C for 1.5 h in an argon atmosphere.

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Measurement of crosslinking density of BCB polymers

The cross-linking density (ρ) of a thermoset polymer may be estimated from its elastic modulus in the rubbery region by using the following eq (1):¹

$$\rho = \frac{E'}{3\Phi RT} \quad (1)$$

where ρ is the number of moles of network chains per unit volume of the cured polymer, Φ is the front factor and equals to 1, E' is the storage modulus of the polymer at the $T_g + 40$ °C, and R and T are the gas constant and the absolute temperature, respectively. The cross-linking density of P-BCB-DA-Si and P-BCB-Si are 629.65 mol/m³ and 1480.89 mol/m³, respectively. The crosslinking density of P-BCB-DA-Si is smaller than that of P-BCB-Si, because the huge hydrogenated phenanthrene ring hinders the crosslinking of the polymer.

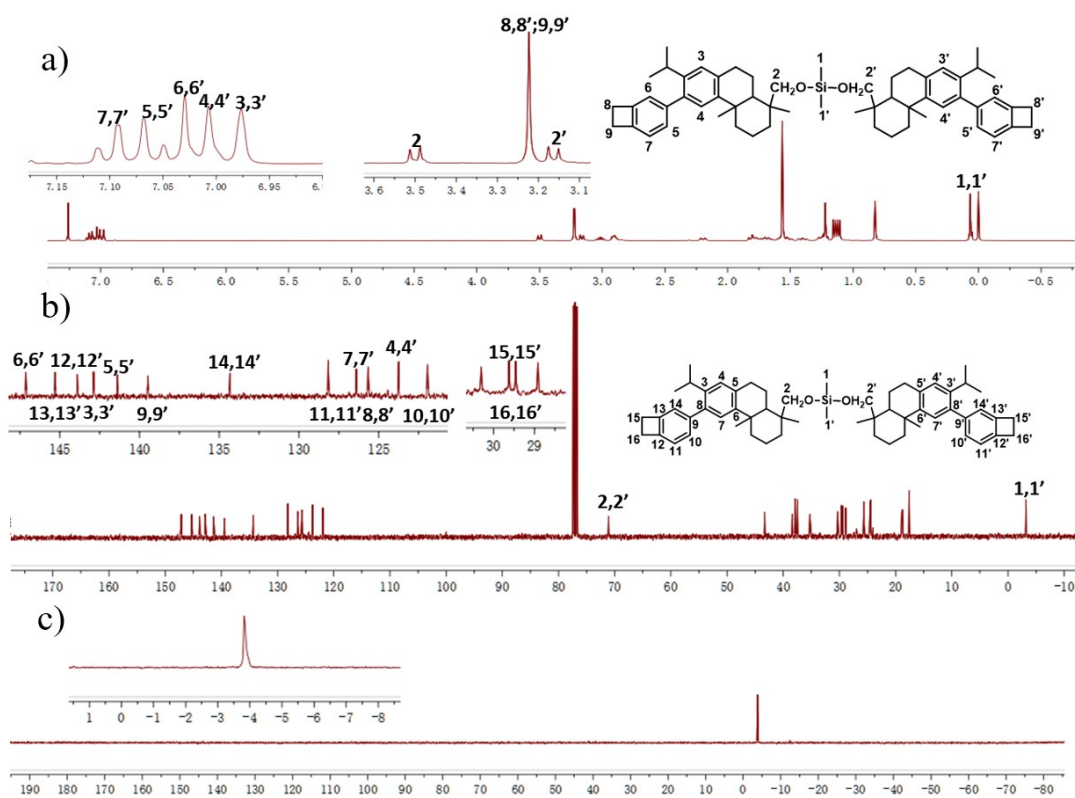


Fig. S1 a) ^1H , b) ^{13}C , and c) ^{29}Si NMR spectra of BCB-DA-Si.

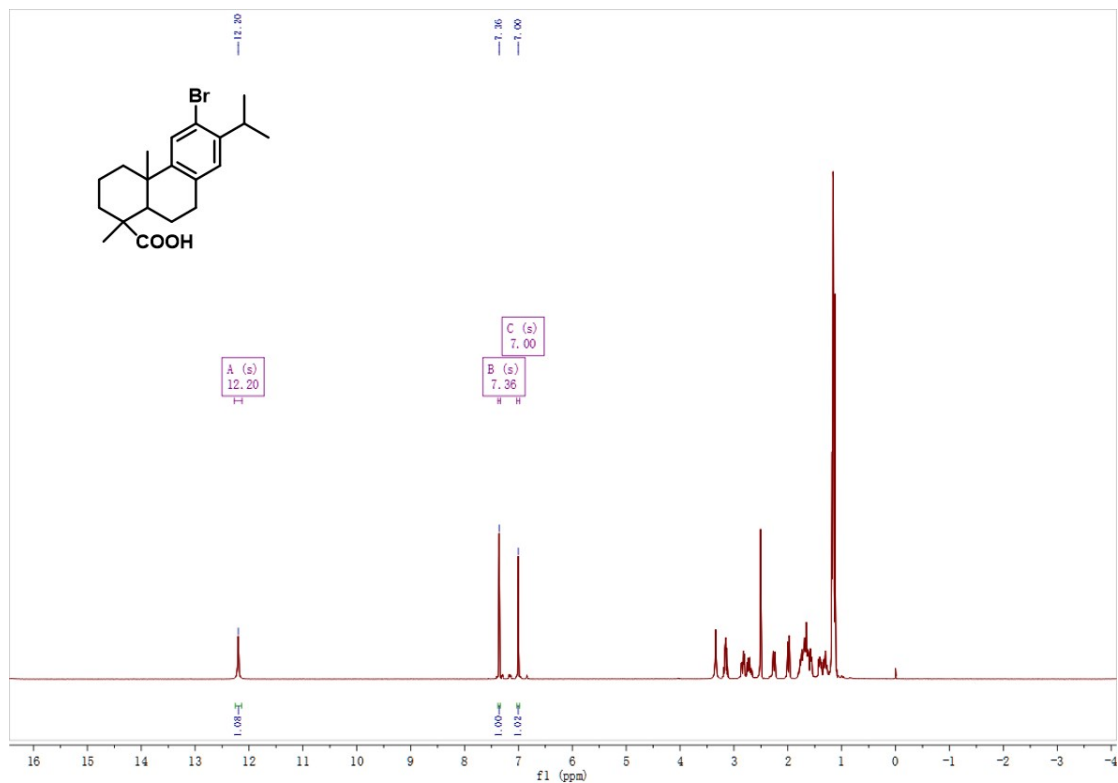


Fig. S2 ^1H NMR spectrum of Compound 1.

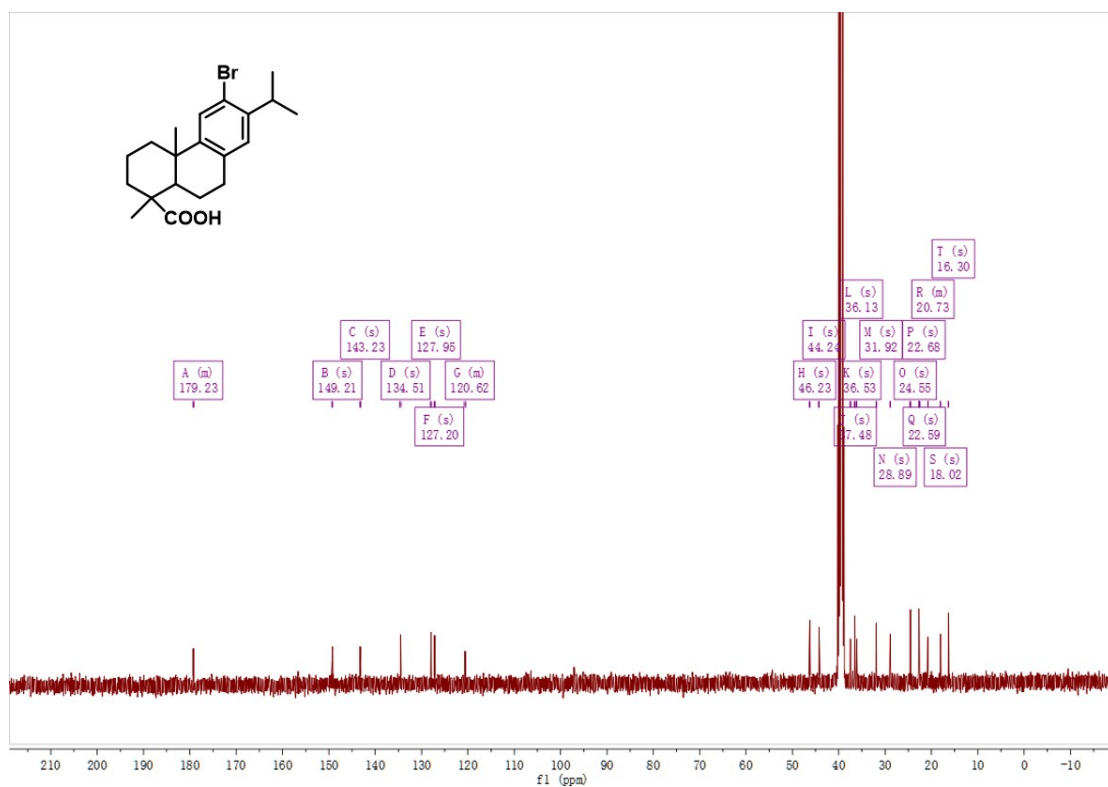


Fig. S3 ^{13}C NMR spectrum of Compound 1.

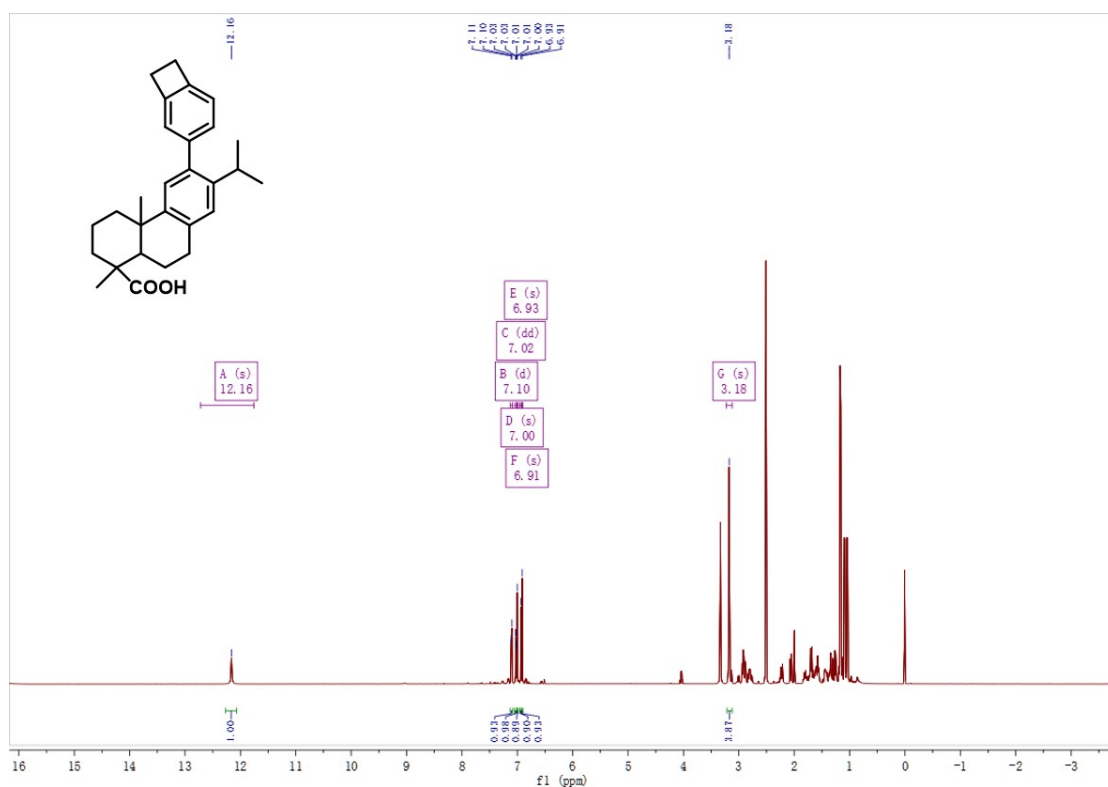


Fig. S4 ^1H NMR spectrum of Compound 2.

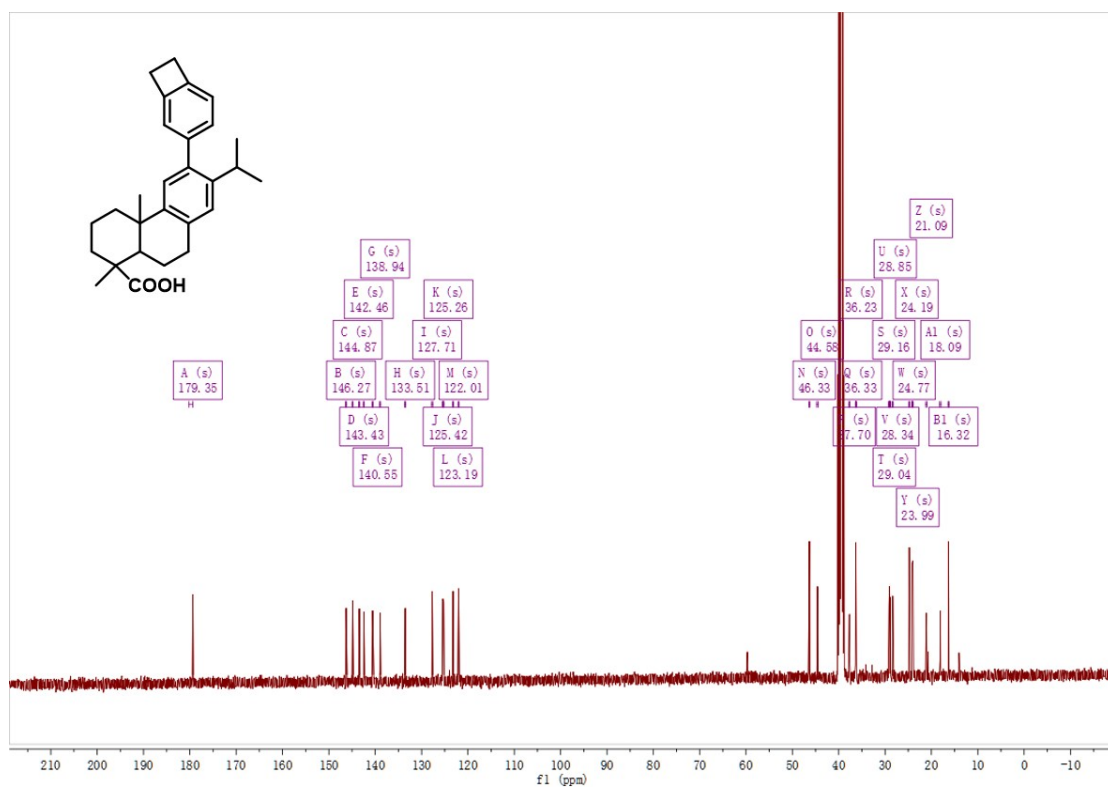


Fig. S5 ^{13}C NMR spectrum of Compound 2.

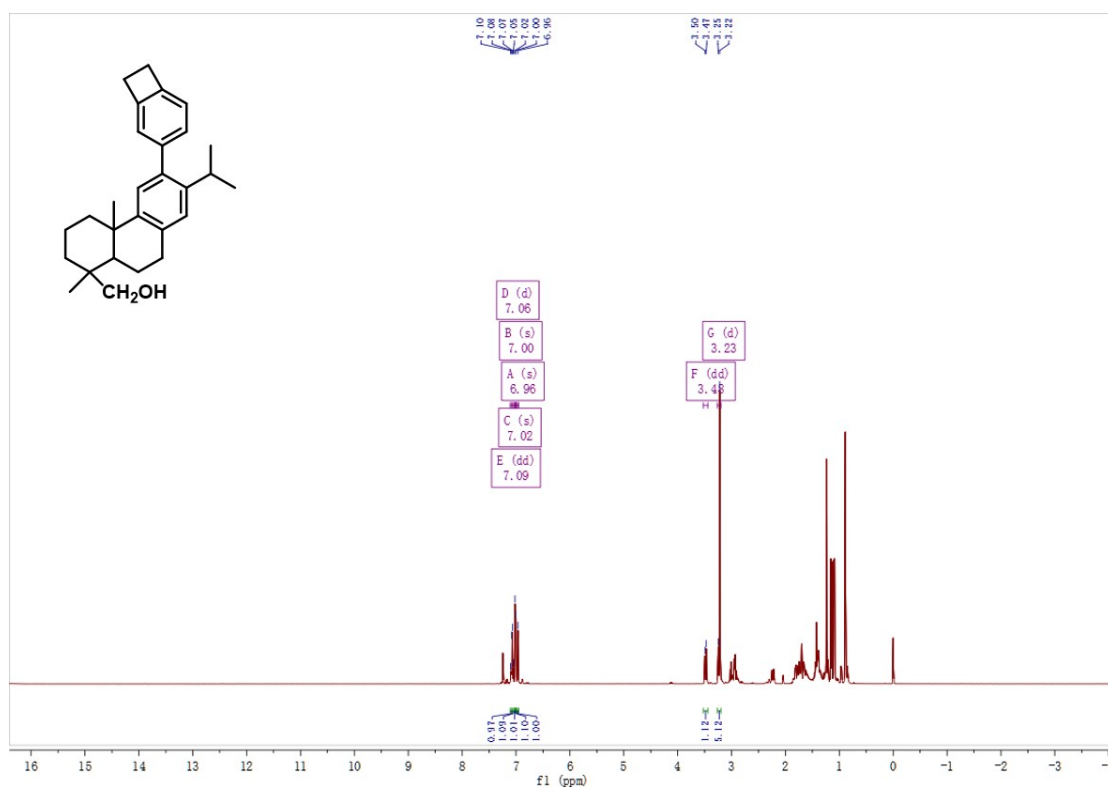


Fig. S6 ^1H NMR spectrum of Compound 3.

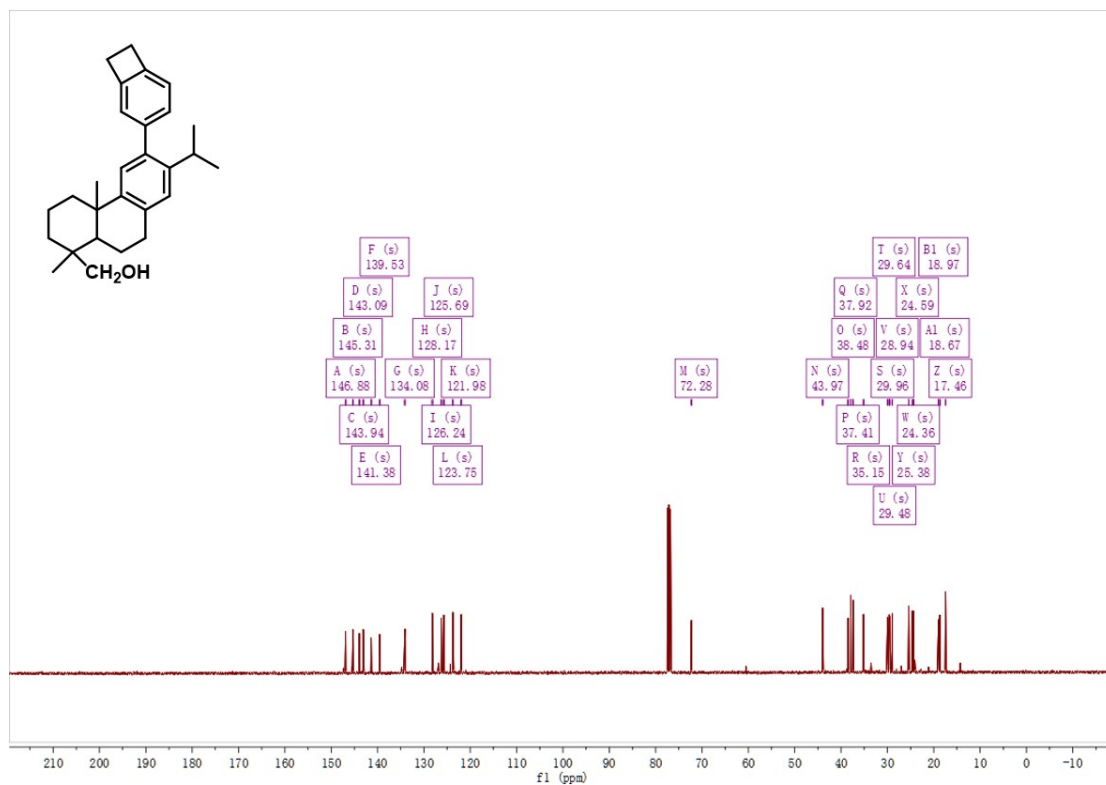


Fig. S7 ^{13}C NMR spectrum of Compound 3.

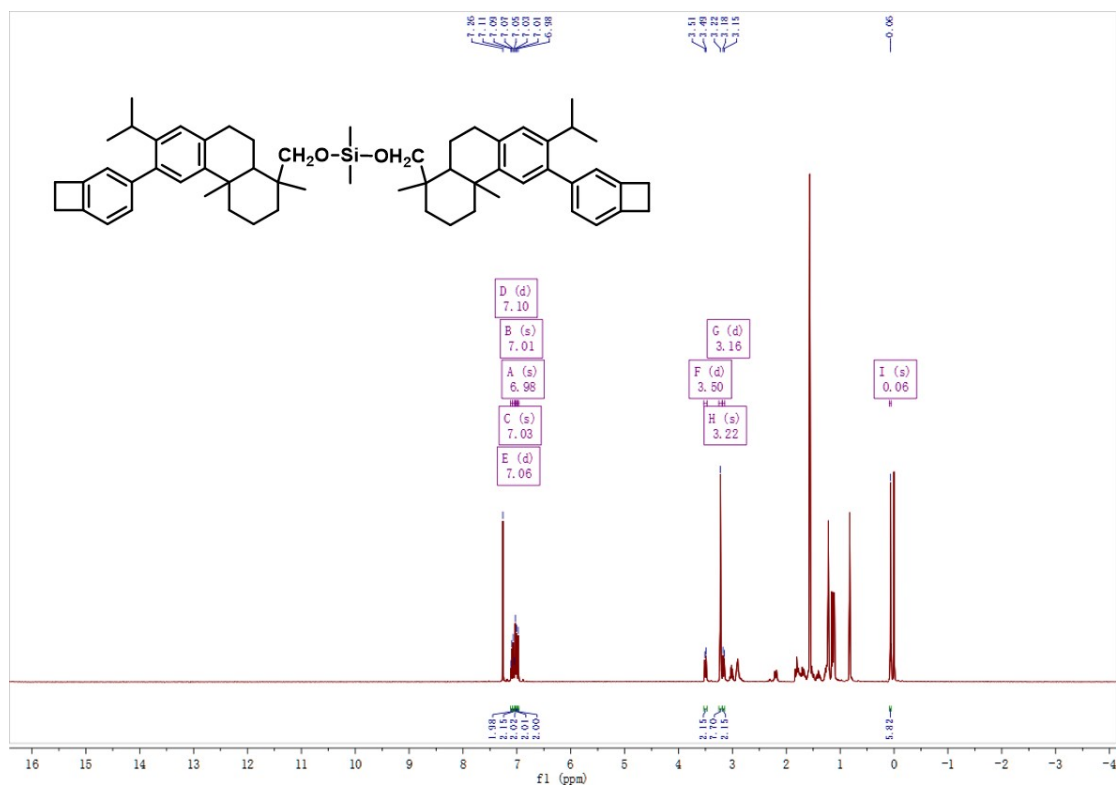


Fig. S8 ^1H NMR spectrum of BCB-DA-Si.

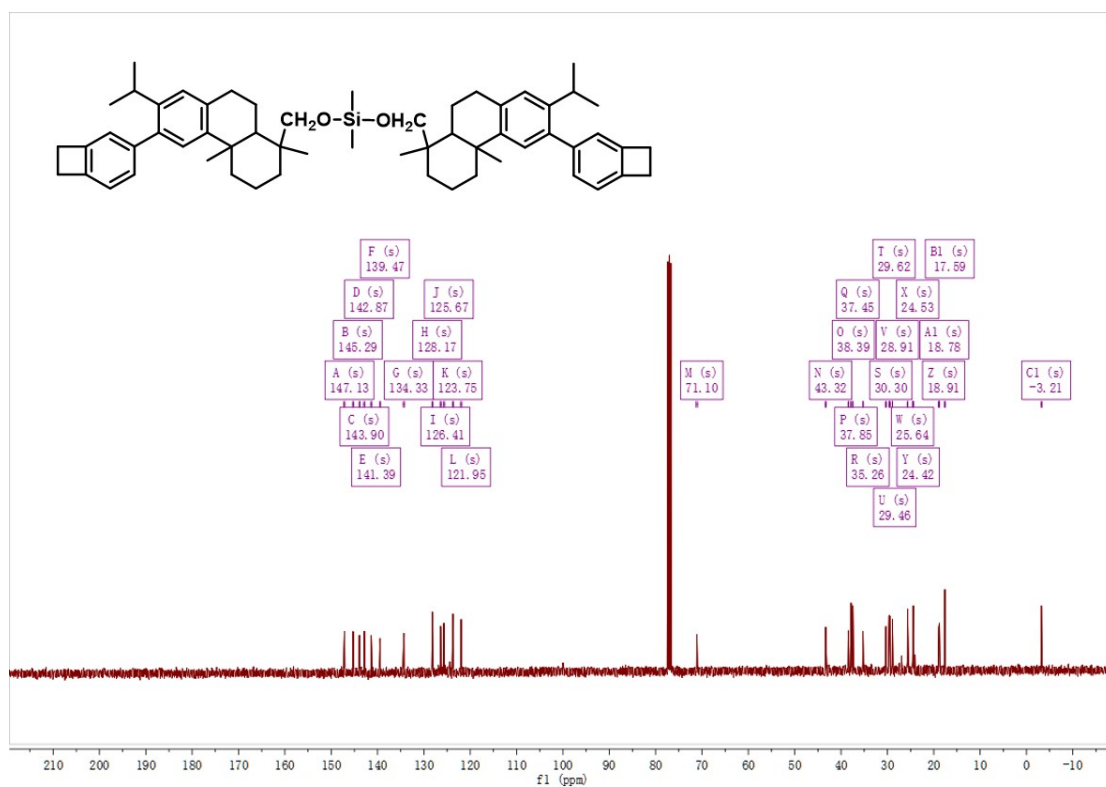


Fig. S9 ^{13}C NMR spectrum of BCB-DA-Si.

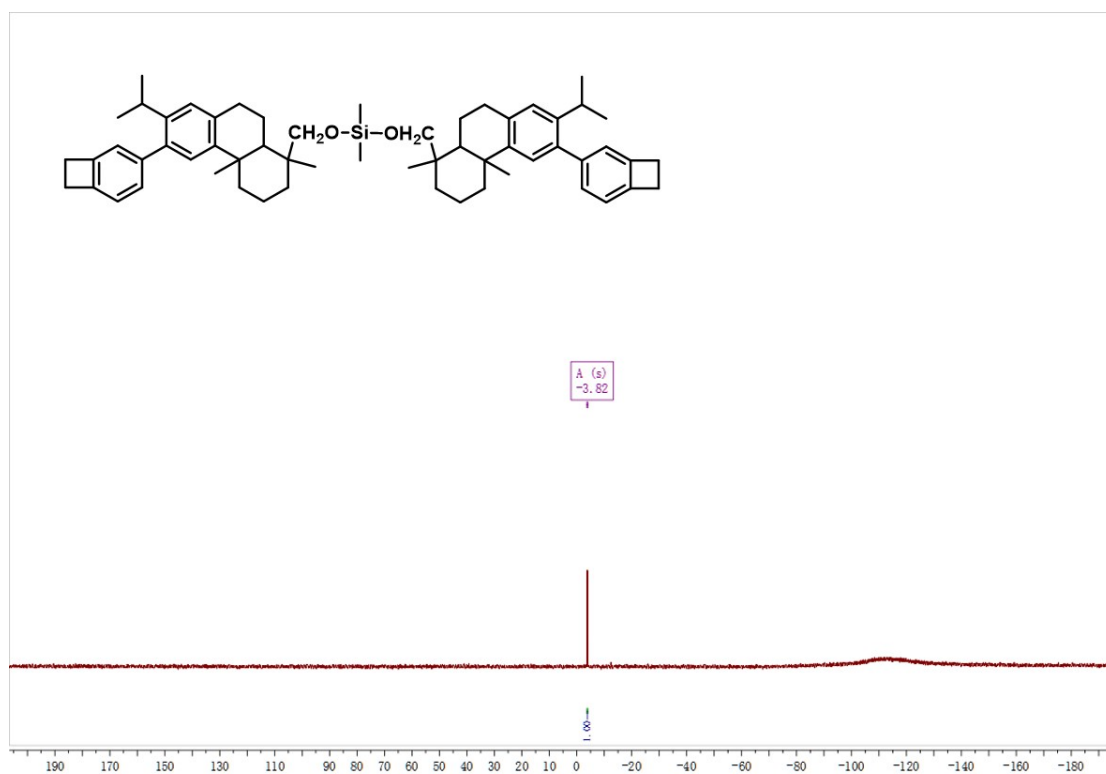


Fig. S10 ^{29}Si NMR spectrum of BCB-DA-Si.

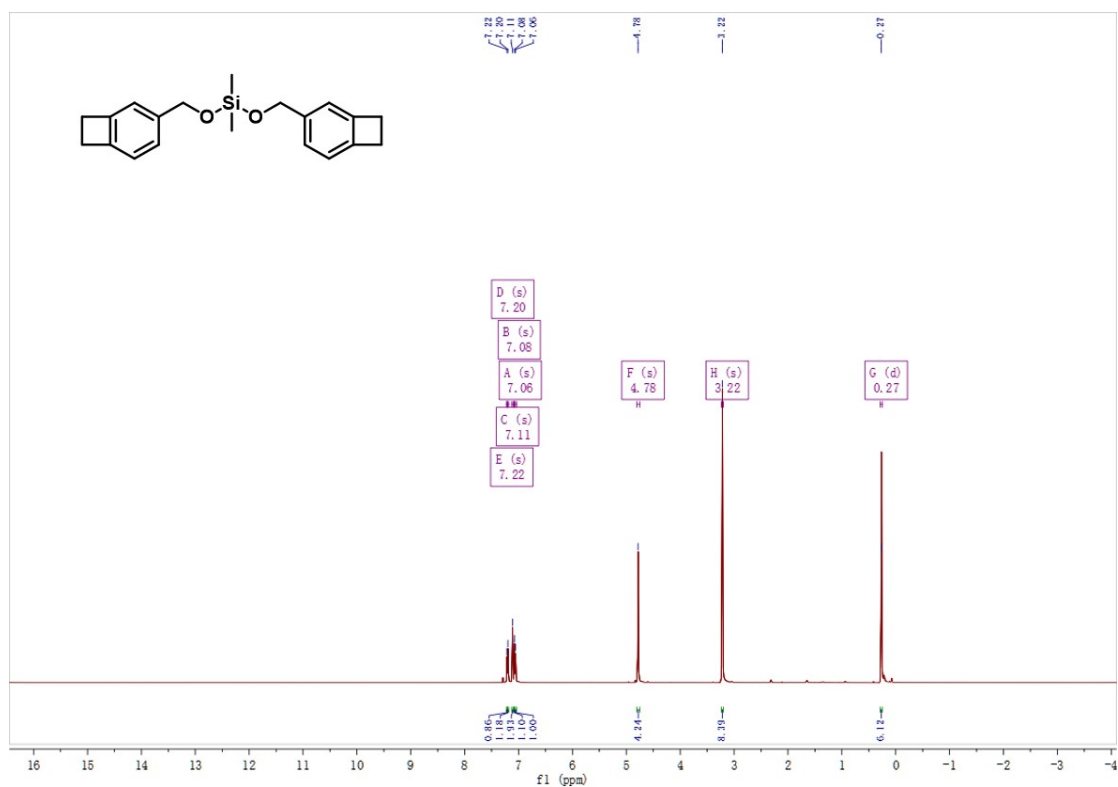


Fig. S11 ^1H NMR spectrum of BCB-Si.

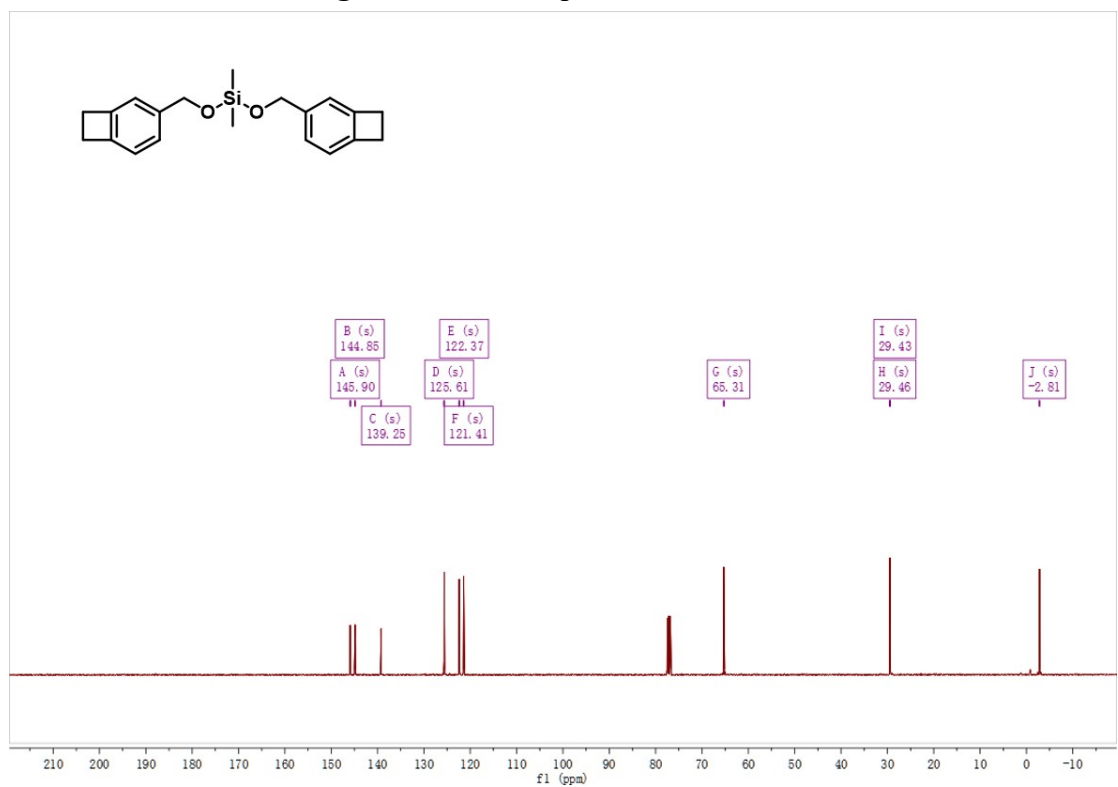


Fig. S12 ^{13}C NMR spectrum of BCB-Si.

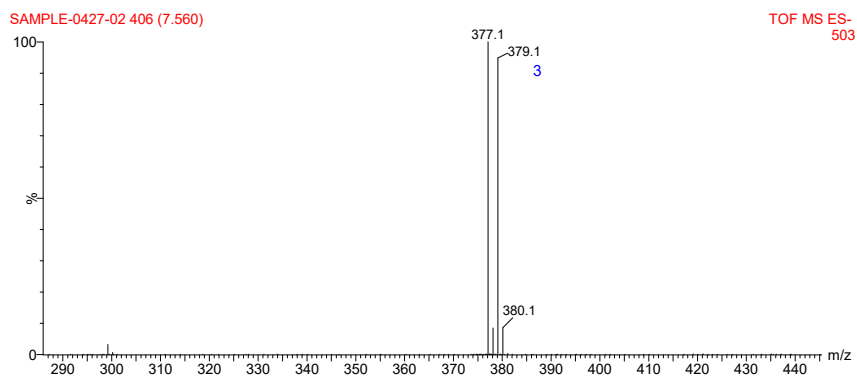


Fig. S13 MS spectrum of Compound 1.

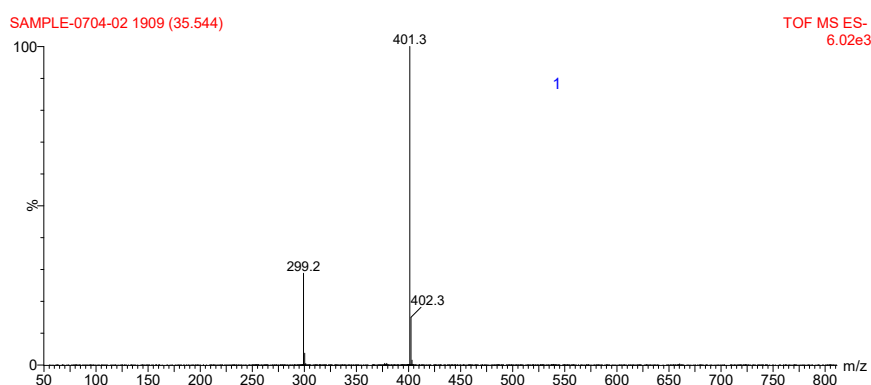


Fig. S14 MS spectrum of Compound 2.

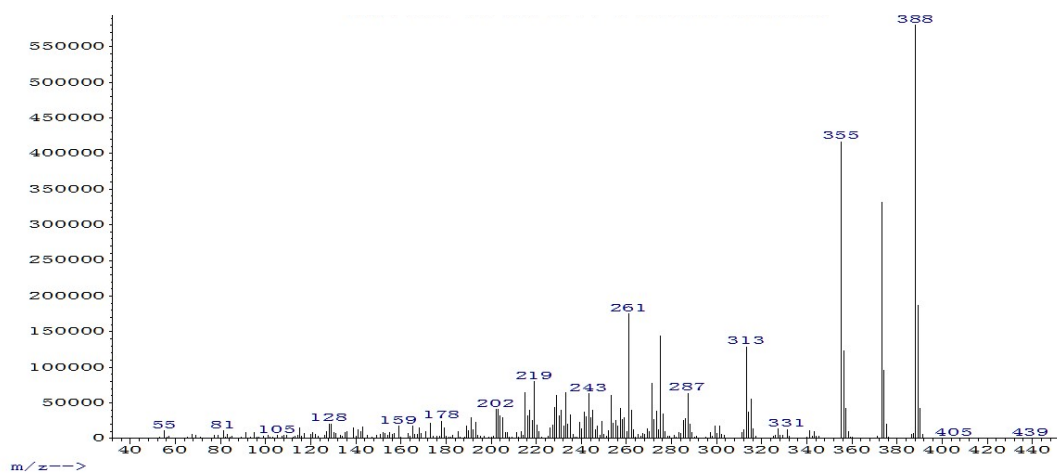


Fig. S15 MS spectrum of Compound 3.

FF4 #38 RT: 0.20 AV: 1 NL: 1.14E5
T: FTMS + p NSI Full ms [500.0000-2000.0000]

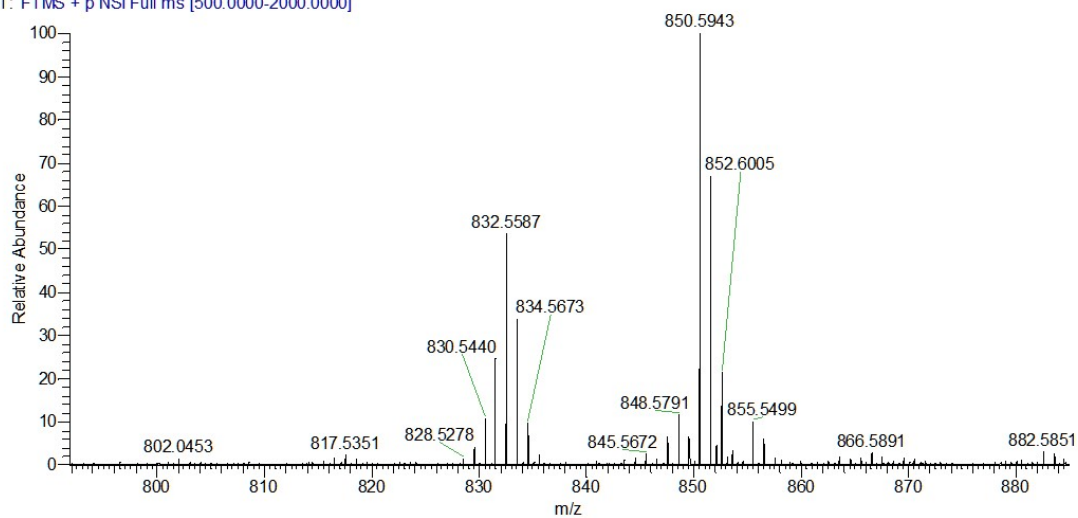


Fig. S16 MS spectrum of BCB-DA-Si.

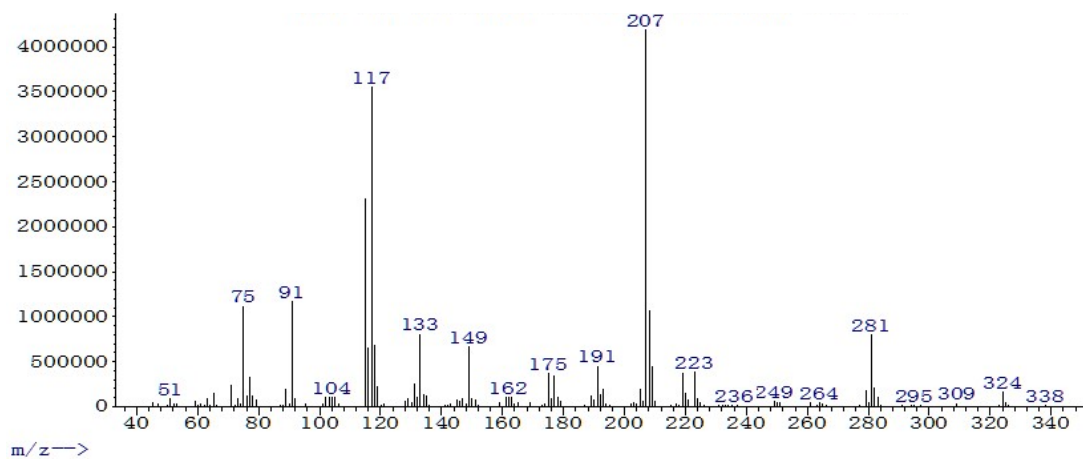


Fig. S17 MS spectrum of BCB-Si.

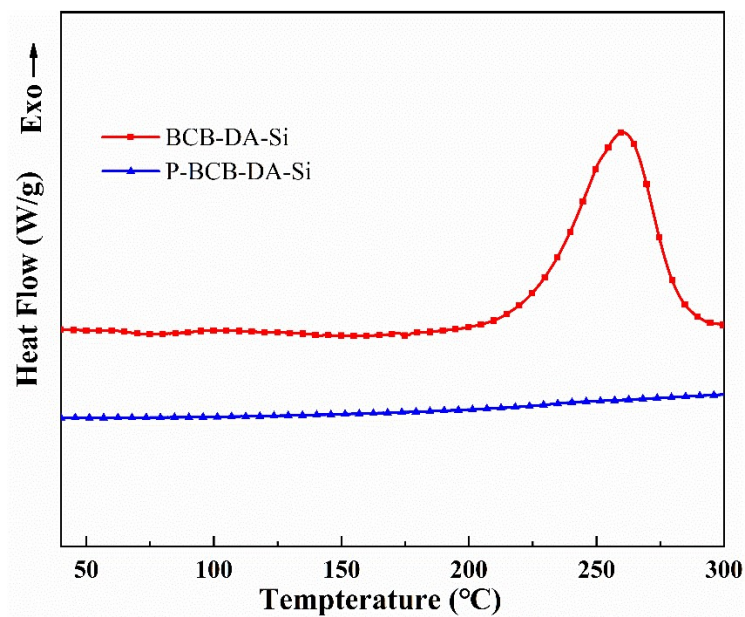


Fig. S18 DSC curves of BCB-DA-Si and P-BCB-DA-Si.



Fig. S19 Solvent resistance of P-BCB-DA-Si.

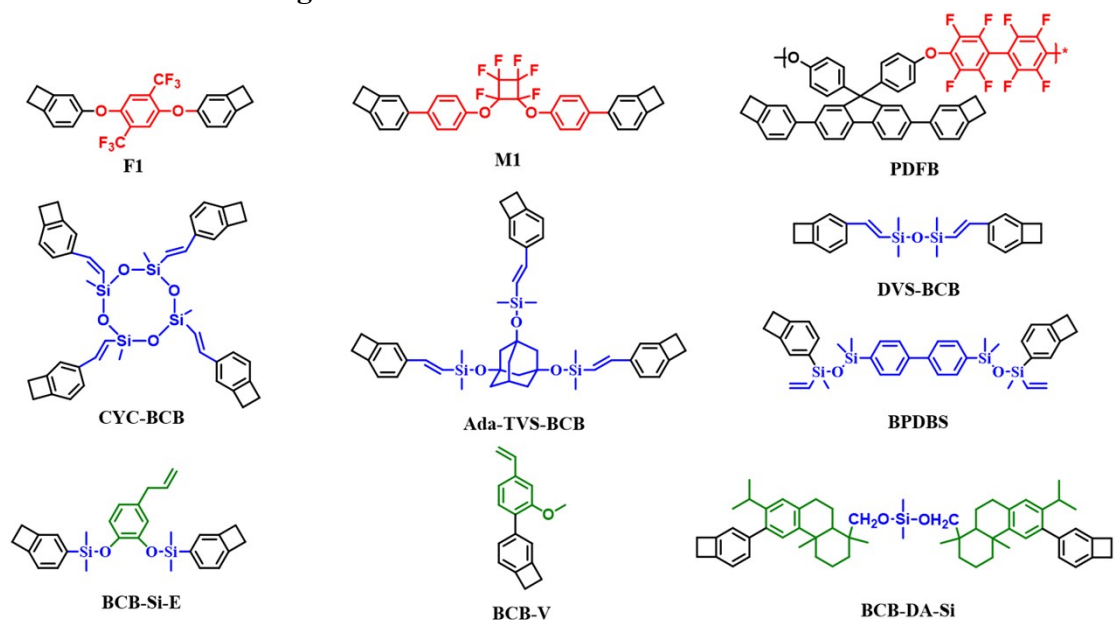


Fig. S20 The structures of reported BCB monomers.

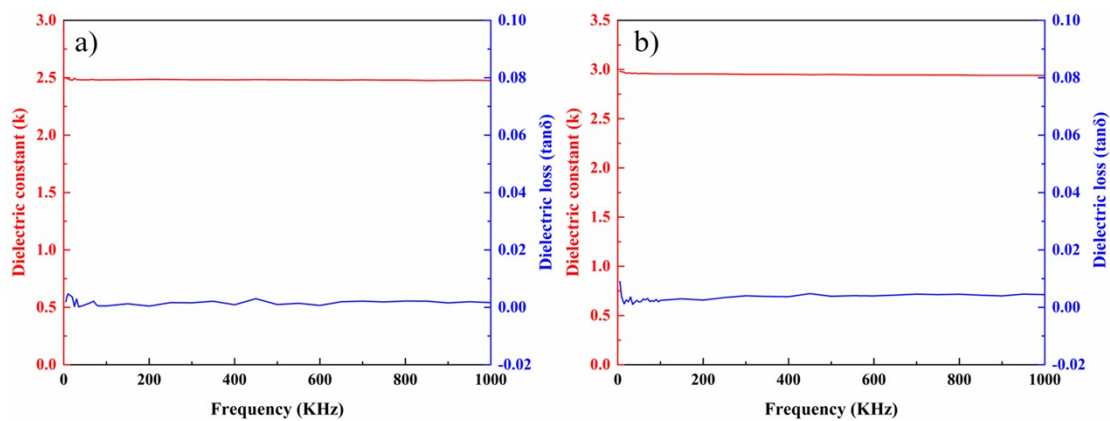


Fig. S21 Dielectric properties of BCB resins at frequencies ranging from 5 to 1000 KHz. a) P-BCB-DA-Si; b) P-BCB-Si.

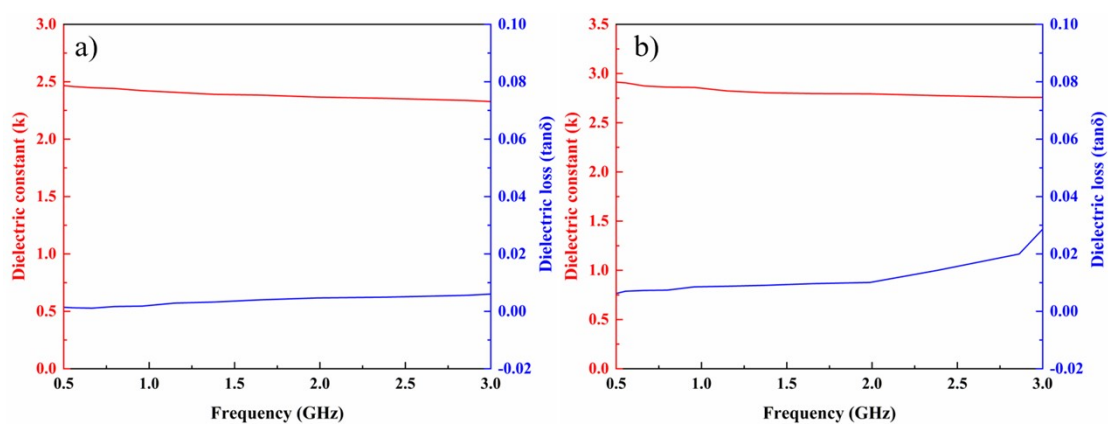


Fig. S22 Dielectric properties of BCB resins at frequencies ranging from 0.5 to 3.0 GHz. a) P-BCB-DA-Si; b) P-BCB-Si.

Notes and references

1. J. Chen, M. Zeng, Z. Feng, T. Pang, Y. Huang and Q. Xu, *ACS Appl. Polym. Mater.*, 2019, **1**, 625-630.