# Supporting Information

# Synthesis of functionalized disiloxanes with nonconventional fluorescence by oxa-Michael addition reaction

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## Experimental Section

*Materials and Methods*

All materials are used directly without purification unless otherwise specified. 1,3-Bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane was provided by Shandong Dongyue Organosilicon Materials Co, LTD. Acrylonitrile (99%, containing MEHQ), methyl vinylsulfone (96%), phenylvinyl sulfone (99%), ethyl acrylate (99%, containing MEHQ), methyl acrylate (99.0%, containing ≤100 pppm MEHQ), N,N-dimethylpropanamide (≥95.0%), phenyl acrylate (97%), and *t*-Bu$P_2$ (100 μL, 2 M THF solution) were purchased from aladdin Co., LTD, China. Proton nuclear magnetic resonance ($^1$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) and silicon nuclear magnetic resonance ($^{29}$Si NMR) spectra were recorded on a Bruker AVANCE 400 spectrometer at 25 °C using $CDCl_3$ as the solvent and without tetramethylsilane as an interior label. FT-IR were detected at room temperature with Bruker Tensor 27 Fourier Transform Infrared Spectrometer. Ultraviolet absorption (UV) spectra were detected at room temperature by using a Beijing TU-1901 double beam UV-vis

spectrophotometer. The fluorescent spectra of the samples were determined at room temperature with a Hitachi F-7000 fluorescence spectrophotometer using a monochromated Xe lamp as an excitation source.

*Synthesis of 3,3'-((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propane-3,1-diyl))bis(oxy)di propionitrile (FDSi-1).* Under argon atmosphere, 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (BHTDS) (0.25 g, 1 mmol), acrylonitrile (0.106 g, 2 mmol), dichloromethane (5 mL), and *t*-Bu$P_2$ (100 μL, 2 M THF solution) were added in a flask. The mixture was stirred at room temperature for 3 h. Then, acetic acid (2 mmol) was added in the mixture to neutralize the catalyst. The mixture was stood and the organic layer was separated and washed with water. After separating the organic layer, it was dried by anhydrous magnesium sulfate for 2 h. After filtration and removal of the solvent, the crude product was obtained and purified by column chromatography (using dichloromethane and methanol as eluents). The product was afforded as a brown liquid (0.333 g, yield: 93.5%). IR (KBr pellet $cm^{-1}$): 2933, 2874, 2250, 1415, 1368, 1255, 1187, 1116, 1055, 840. $^{1}$H NMR (400 MHz, $CDCl_3$, ppm) δ 3.58 (t, *J* = 6.4 Hz, 4H), 3.38 (t, *J* = 6.9 Hz, 4H), 2.54 (t, *J* = 6.4 Hz, 4H), 1.61–1.48 (m, 4H), 0.52–0.40 (m, 4H), -0.01 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 118.0, 73.59, 64.74, 23.19, 18.85, 14.01, 0.30. $^{29}$Si NMR (75 MHz, $CDCl_3$, ppm) δ 7.73. HR-MS calcd for $C_{16}H_{32}N_2O_3Si_2$ $[M+H]^+$: 357.2024, found 357.2031.

*Synthesis of 1,1,3,3-tetramethyl-1,3-bis(3-(2-(methylsulfonyl)ethoxy)propyl)disiloxane (FDSi-2).* The synthetic procedure and post-treatment of FDSi-2 were similar to those of FDSi-1 except acrylonitrile was replaced by methyl vinylsulfone (0.212 g, 2 mmol). The product was afforded as a yellow liquid (0.405 g, yield: 87.6%). IR (KBr pellet $cm^{-1}$): 2950, 1609, 1479, 1367, 1312, 1254, 1182, 1126, 1060, 782, 689, 487. $^{1}$H NMR (400 MHz, $CDCl_3$, ppm) δ 3.80 (dd, *J* = 5.8, 4.9 Hz, 4H), 3.38 (t, *J* = 6.9 Hz, 4H), 3.20–3.14 (m, 4H), 2.97–2.88 (m, 6H), 1.59–1.46 (m, 4H), 0.49–0.40 (m, 4H), 0.00 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 73.88,

64.08, 55.03, 42.77, 23.01, 14.04, 0.29. $^{29}$Si NMR (75MHz, $CDCl_3$, ppm) δ 7.71. HR-MS calcd for $C_{16}H_{38}O_7S_2Si_2$ $[M+NH_4]^+$: 480.1935, found 480.1926.

*Synthesis of 1,1,3,3-tetramethyl-1,3-bis(3-(2-(phenylsulfonyl)ethoxy)propyl)disiloxane (FDSi-3).* The synthetic procedure and post-treatment of FDSi-3 were similar to those of FDSi-1 except acrylonitrile was replaced by phenylvinyl sulfone (0.336 g, 2 mmol). The product was afforded as a yellow liquid (0.490 g, yield: 83.5%). IR (KBr pellet $cm^{-1}$): 2949, 1951, 1587, 1448, 1366, 1311, 1254, 1145, 1064, 840, 778, 733, 690, 531. $^1$H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94–7.88 (m, 4H), 7.68–7.60 (m, 2H), 7.57–7.52 (m, 4H), 3.77 (td, *J* = 6.3, 2.2 Hz, 4H), 3.40 (td, J = 6.3, 2.1 Hz, 4H), 3.25 (td, *J* = 6.9, 4.3 Hz, 4H), 1.43–1.33 (m, 4H), 0.40–0.30 (m, 4H), 0.01 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 139.72, 133.37, 128.84, 127.82, 73.71, 63.65, 56.04, 22.91, 13.87, 0.04. $^{29}$Si NMR (75 MHz, $CDCl_3$, ppm) δ 7.50. HR-MS calcd for $C_{26}H_{42}O_7S_2Si_2$ $[M+NH_4]^+$: 604.2248, found 604.2235.

*Synthesis of diethyl 3,3'-(((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propane-3,1-diyl)) bis(oxy))dipropionate (FDSi-4).* The synthetic procedure and post-treatment of FDSi-4 were similar to those of FDSi-1 except acrylonitrile was replaced by ethyl acrylate (0.202 g, 2 mmol). The product was afforded as a pale yellow liquid (0.316 g, yield: 70.2%). IR (KBr pellet $cm^{-1}$): 2956, 1739, 1411, 1369, 1255, 1186, 1066, 841, 797. $^1$H NMR (400 MHz, $CDCl_3$, ppm) δ 4.17–4.02 (m, 4H), 3.65 (t, *J* = 6.2, 4.2 Hz, 4H), 3.52–3.28 (m, 4H), 2.59–2.44 (m, 4H), 1.67–1.49 (m, 4H), 1.26–1.14 (m, 6H), 0.52–0.41 (m, 4H), 0.01 (s, 12H). $^{13}$C NMR (101 MHz, $CDCl_3$, ppm) δ 171.46, 73.52, 65.77, 60.23, 34.94, 23.03, 22.32, 13.89, -0.54. $^{29}$Si NMR (75 MHz, $CDCl_3$, ppm) δ 7.72. HR-MS calcd for $C_{18}H_{38}O_7Si_2$ $[M+NH_4]^+$: 468.2807, found 468.2736.

*Synthesis of dimethyl 3,3'-(((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propane-3,1-diyl))bis(oxy))dipropionate (FDSi-5).* The synthetic procedure and post-treatment of FDSi-5 were similar to those of FDSi-1 except acrylonitrile was replaced by methyl acrylate (0.172 g, 2 mmol). The product was afforded as a pale yellow liquid (0.17 g, yield: 40.2%). IR (KBr

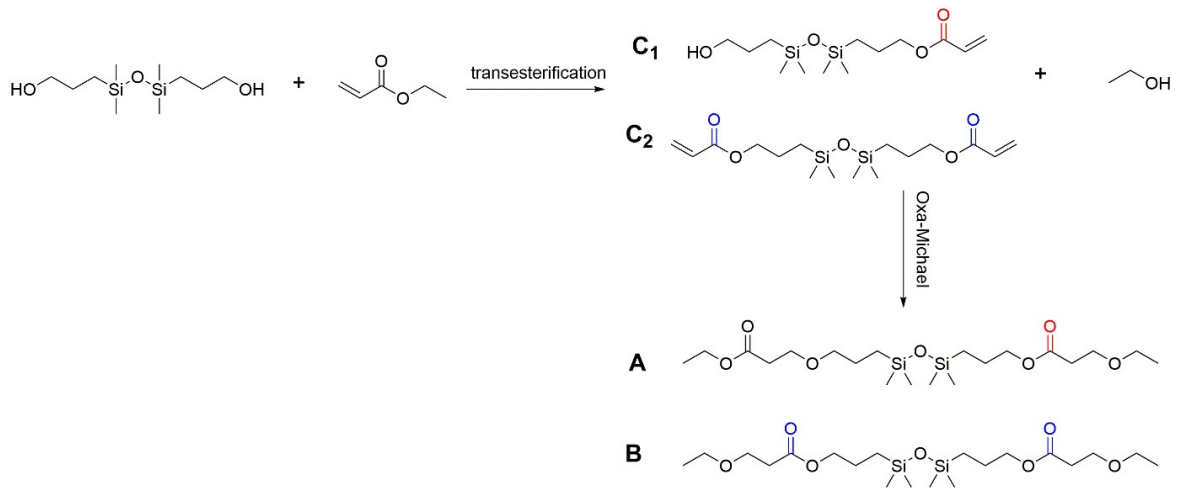
pellet $cm^{-1}$): 2949, 1739, 1411, 1368, 1256, 1184, 1064, 840, 798, 704. $^{1}H$ NMR (400 MHz, $CDCl_3$, ppm) δ 4.12–3.96 (m, 4H), 3.74–3.58 (m, 6H), 3.43–3.26 (m, 4H), 2.54 (td, *J* = 6.4, 1.4 Hz, 4H), 1.69–1.44 (m, 4H), 0.53–0.40 (m, 4H), 0.04– -0.03 (m, 12H).$^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) δ 171.90, 73.61, 66.75, 51.38, 34.70, 23.12, 22.34, 14.16, -0.28. $^{29}Si$ NMR (75 MHz, $CDCl_3$, ppm) δ 8.30. HR-MS calcd for $C_{20}H_{42}O_7Si_2$ $[M+NH_4]^+$: 440.2493, found 440.2407.

*Synthesis of 3,3'-(((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propane-3,1-diyl))bis(oxy)) diphenyldipropionate (FDSi-6).* The synthetic procedure and post-treatment of FDSi-6 were similar to those of FDSi-1 except acrylonitrile was replaced by phenyl acrylate (0.297 g, 2 mmol). The product was afforded as a pale yellow liquid (0.054 g, yield: 10.0%). IR (KBr pellet $cm^{-1}$): 2956, 1732, 1600, 1500, 1401, 1365, 1298, 1254, 1183, 1110, 1068, 988, 840, 797, 485. $^{1}H$ NMR (400 MHz, $CDCl_3$, ppm) δ 7.33–7.31 (m, 4H), 7.28–7.14 (m, 2H), 7.07–7.04 (m, 4H), 4.05 (t, *J* = 6.9 Hz, 2H), 3.51 (t, *J* = 6.9 Hz, 2H), 2.57 (t, *J* = 6.9 Hz, 4H), 1.65–1.48 (m, 4H), 0.50–0.42 (m, 4H), 0.00 (s, 12H). $^{13}C$ NMR (101 MHz, $CDCl_3$, ppm) δ 170.76, 166.26, 130.43, 129.14, 128.32, 121.32, 119.74, 115.12, 73.64, 67.00, 35.09, 26.27, 22.35, 13.80, -0.15. $^{29}Si$ NMR (75 MHz, $CDCl_3$, ppm) δ 7.77. HR-MS calcd for $C_{20}H_{44}N_2O_5Si_2$ $[M+H]^+$: 449.2861, found 449.2865.

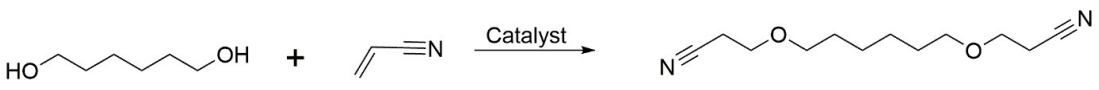
*Synthesis of 3,3'-(((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propane-3,1-diyl))bis(oxy))bis (N,N-dimethylpropanamide) (FDSi-7).* The synthetic procedure and post-treatment of FDSi-7 were similar to those of FDSi-1 except acrylonitrile was replaced by N,N-dimethylpropanamide (0.1983 g, 2 mmol). The product was afforded as a pale yellow liquid (0.0381 g, yield: 8.5%). IR (KBr pellet $cm^{-1}$): 2929, 1648, 1401, 1366, 1298, 1255, 1183, 1110, 1060, 988, 840, 797, 485. $^{1}H$ NMR (400 MHz, $CDCl_3$, ppm) δ 3.69 (t, *J* = 6.9 Hz, 4H), 3.36 (t, *J* = 7.1 Hz, 4H), 2.99 (s, 6H), 2.90 (s, 6H), 2.57 (t, *J* = 6.9 Hz, 4H), 1.55–1.49 (m, 4H), 0.49–0.41 (m, 4H), 0.00 (s, 12H). $^{13}C$ NMR (101 MHz, $CDCl_3$, ppm) δ 170.76, 73.64, 66.63, 36.75,

34.97, 33.47, 23.17, 13.90, 0.14. $^{29}$Si NMR (75 MHz, $CDCl_3$, ppm) δ 8.01. HR-MS calcd for $C_{20}H_{44}N_2O_5Si_2$ $[M+H]^+$: 449.2861, found 449.2865.

*Synthesis of 3,3'-(hexane-1,6-diylbis(oxy))dipropionitrile (FD-J).* The synthetic procedure and post-treatment of FD-J were similar to those of FDSi-1 except BHTDS was replaced by 1,6-hexanediol (0.1181 g, 1 mmol). The product was afforded as a brown liquid (0.222 g, yield: 99.0%). IR (KBr pellet $cm^{-1}$): 2933, 2245, 1461, 1366, 1185, 1114, 1064, 989, 817, 747, 666, 487. $^1$H NMR (400 MHz, $CDCl_3$, ppm) δ 3.65 (t, $J$ = 6.4 Hz, 4H), 3.50 (t, $J$ = 6.5 Hz, 4H), 2.61 (t, $J$ = 6.4 Hz, 4H), 1.64–1.57 (m, 4H), 1.40 (ddd, $J$ = 7.3, 4.5, 3.1 Hz, 4H).




**Scheme S1** The possible mechanism of transesterification reaction of BHTDS and ethyl acrylate during the oxa-Michael addition reaction




**Scheme S2** Synthetic route of FD-J

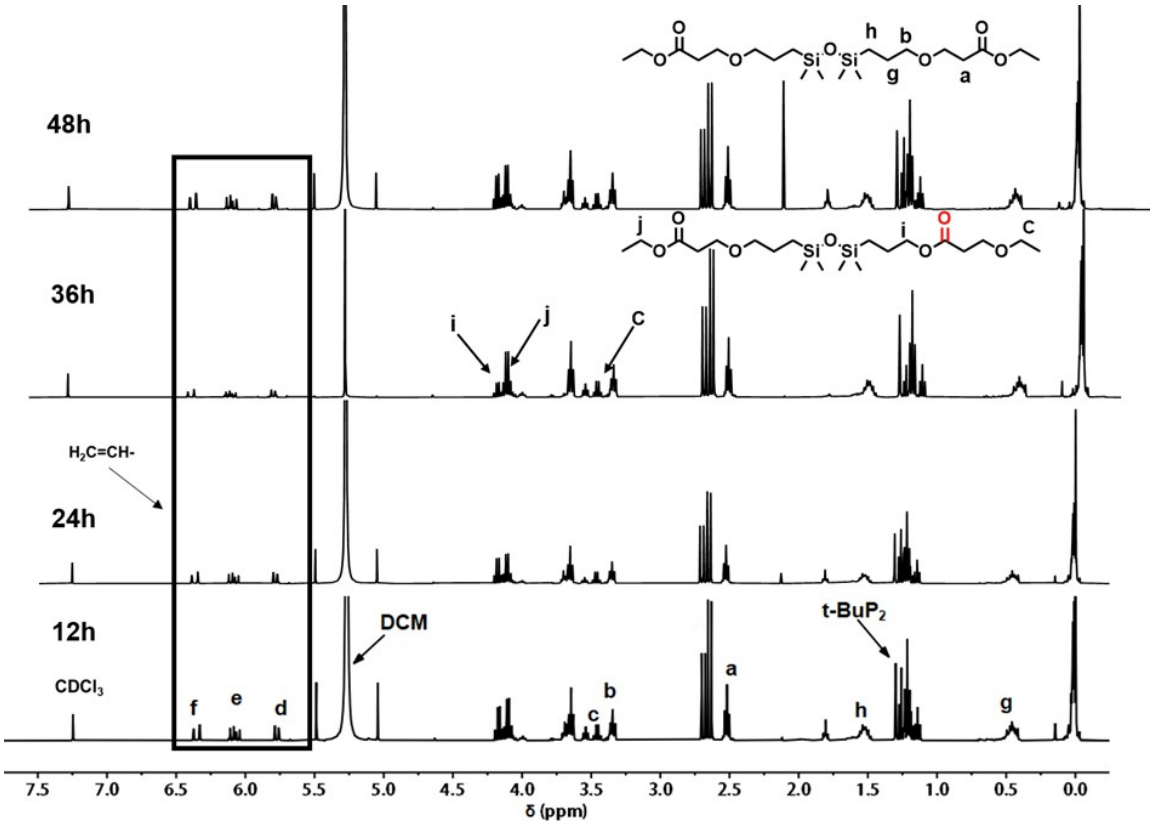



**Fig. S1** [1]H NMR spectra of the mixture of 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane and ethyl acrylate at different reaction times

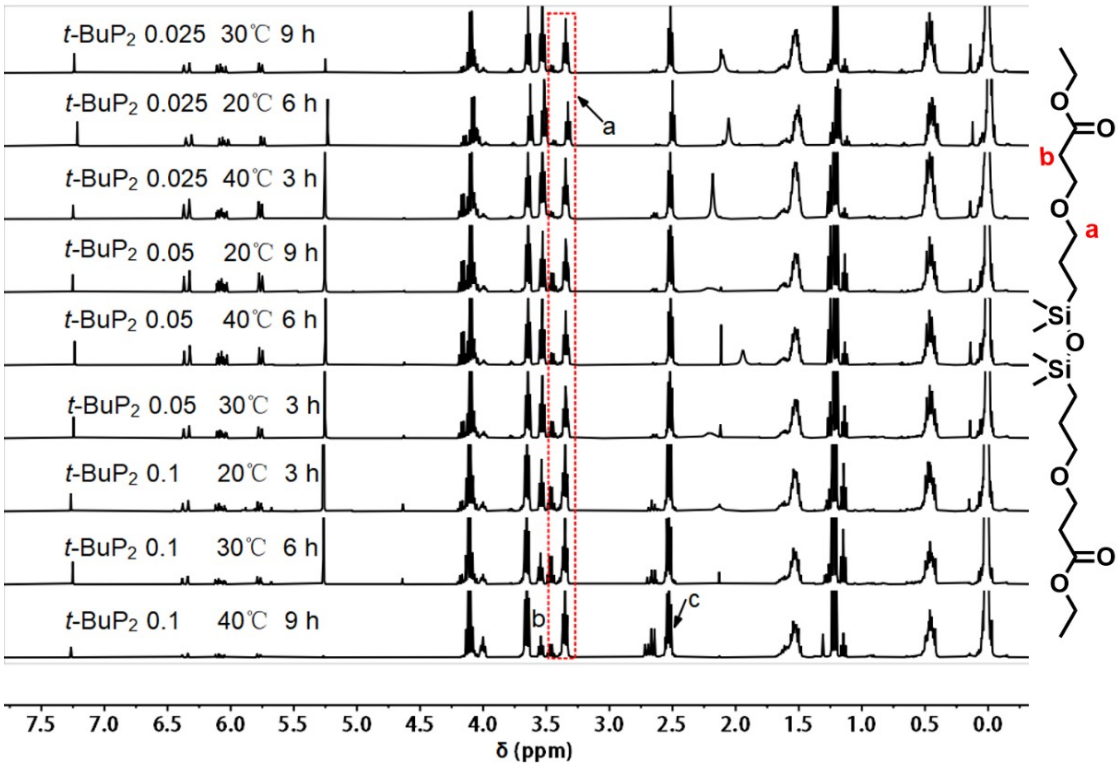



**Fig. S2** [1]H NMR spectra of the products from orthogonal experiments

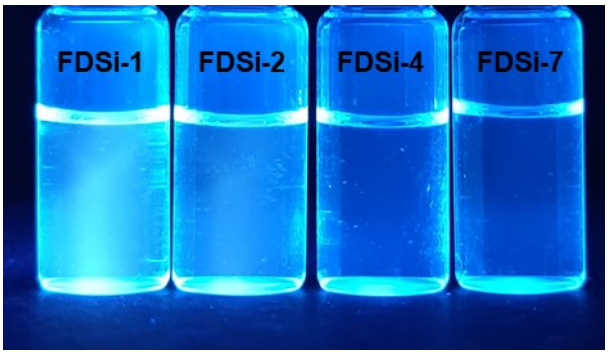



**Fig. S3** The photographs of functionalized disiloxanes (FDSi) in $CH_2Cl_2$ solution (M = $10^{-7}$ mol/L) under 365 nm UV light

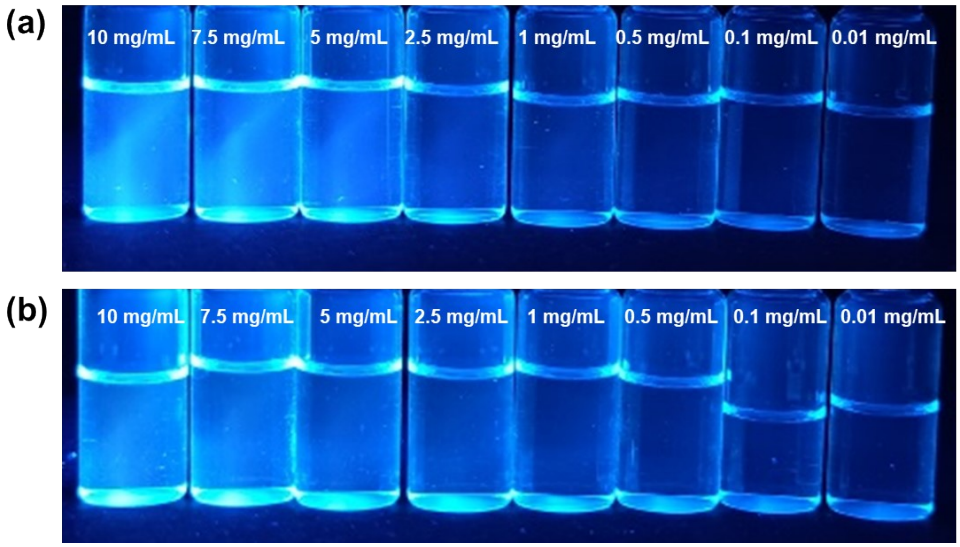



**Fig. S4** The photographs of functionalized disiloxane FDSi-1 (a) and FDSi-2 (b) at different concentrations in $CH_2Cl_2$ solution under 365 nm UV light

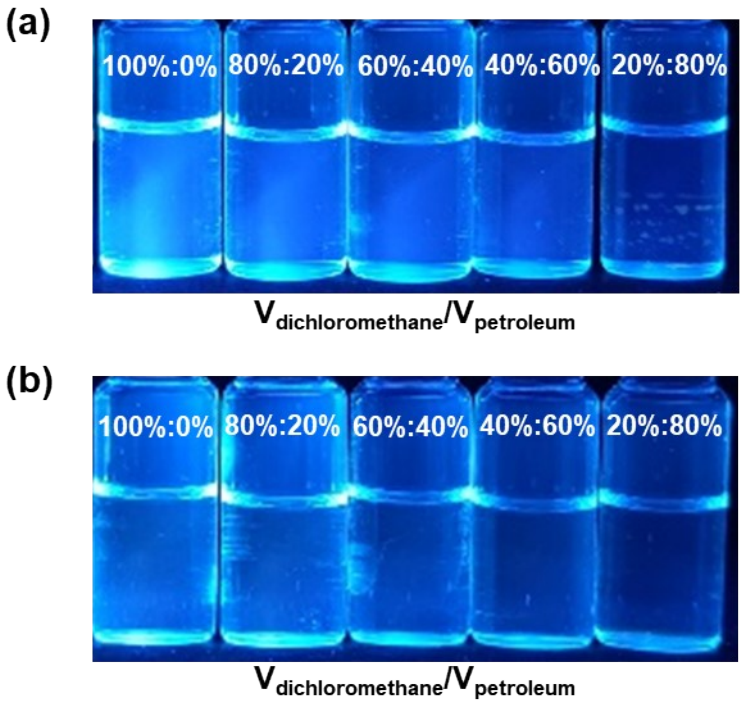



**Fig. S5** The photographs of FDSi-1 (a) and FDSi-2 (b) in dichloromethane-petroleum ether solvent mixture (0.01 mol/L) under 365 nm UV light

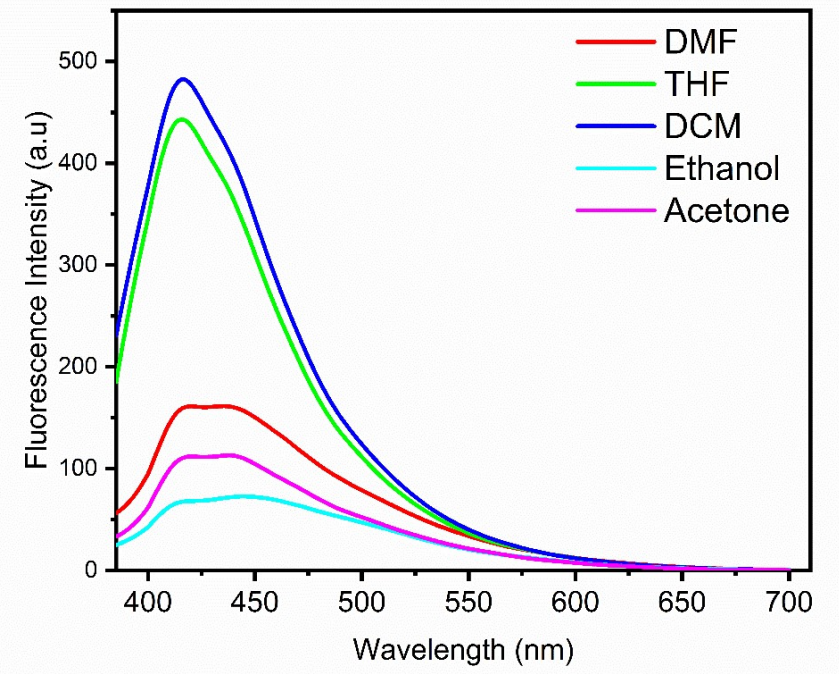



**Fig. S6** Fluorescence spectra of FDSi-2 dissolved in different solvents (0.01 mol/L, $\lambda_{ex}$ =365 nm)

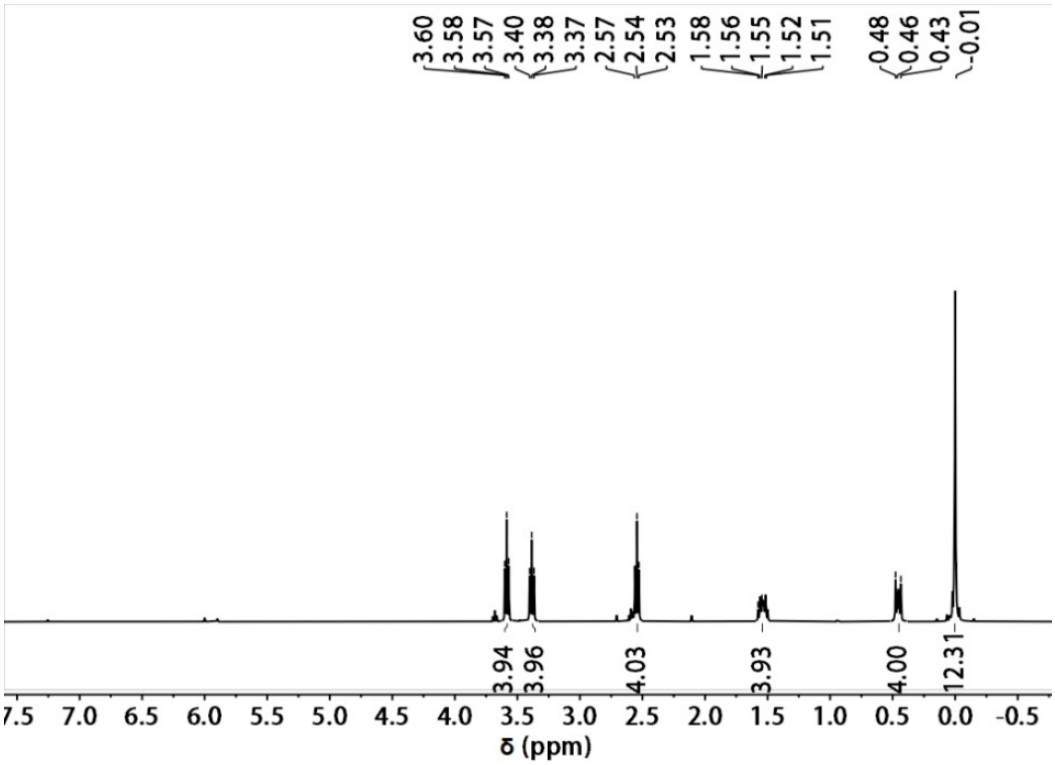



**Fig. S7** $^{1}$H NMR spectra of FDSi-1

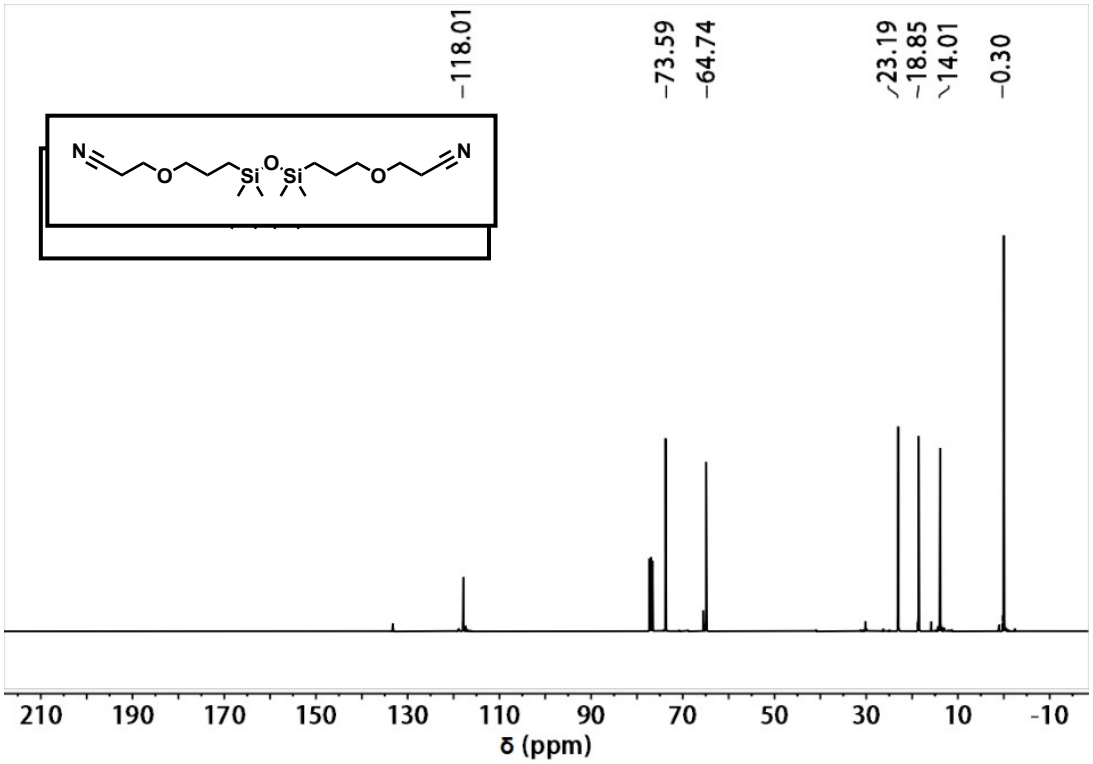



**Fig. S8** $^{13}$C NMR spectra of FDSi-1

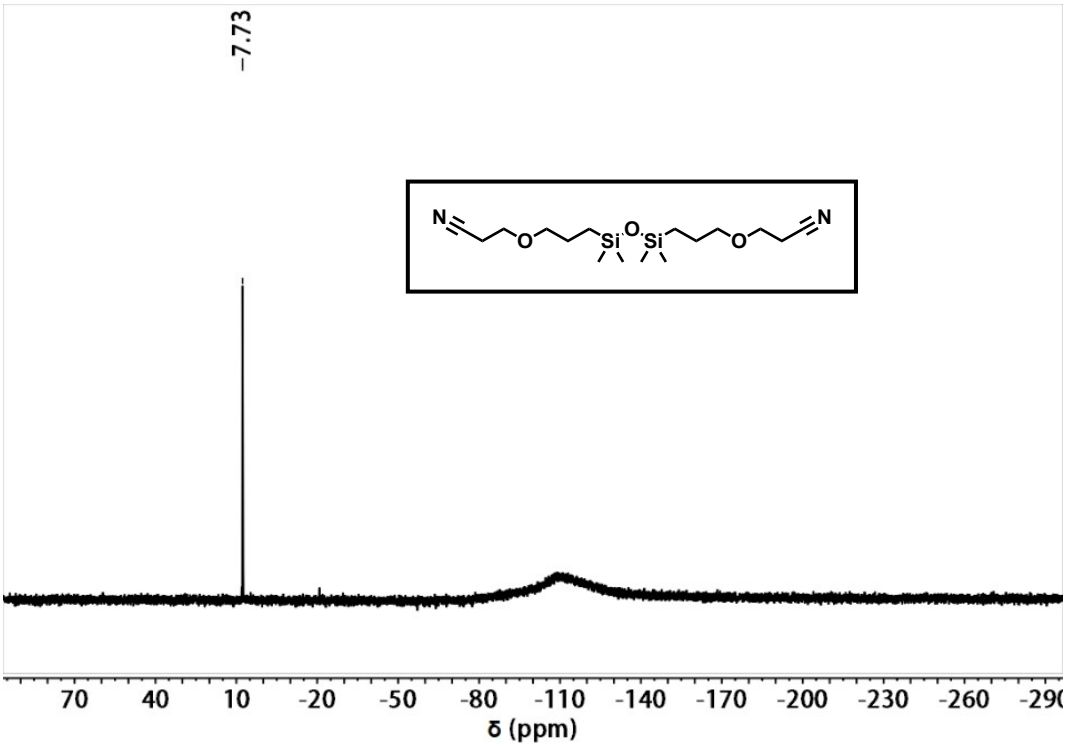



**Fig. S9** $^{29}$Si NMR spectra of FDSi-1

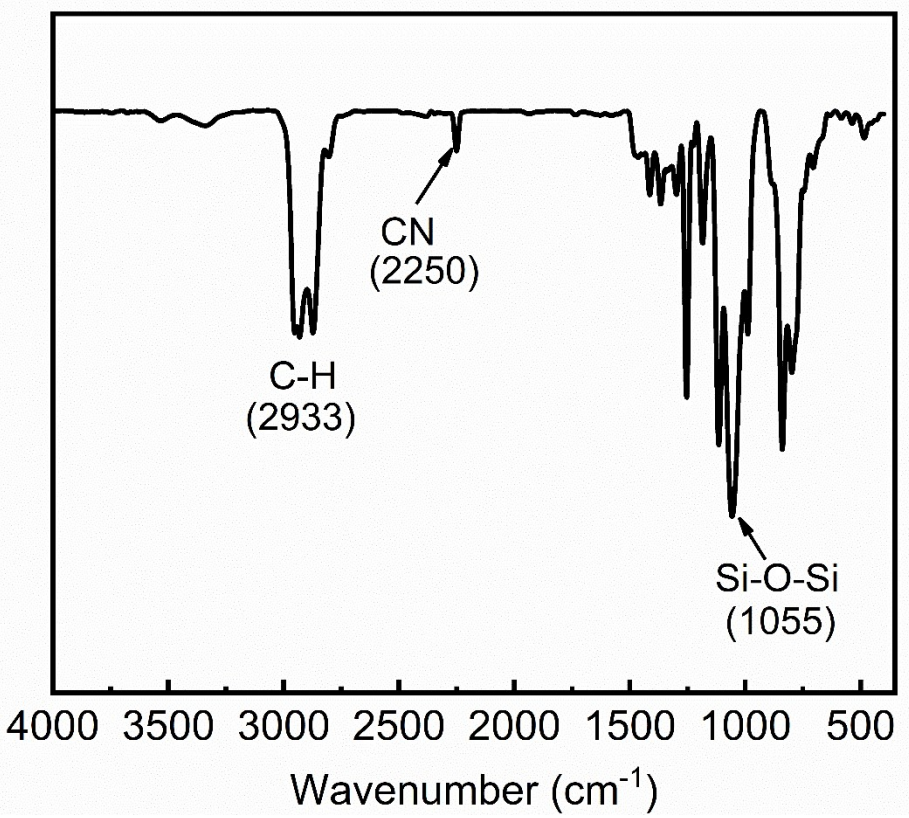



**Fig. S10** FT-IR spectra of FDSi-1

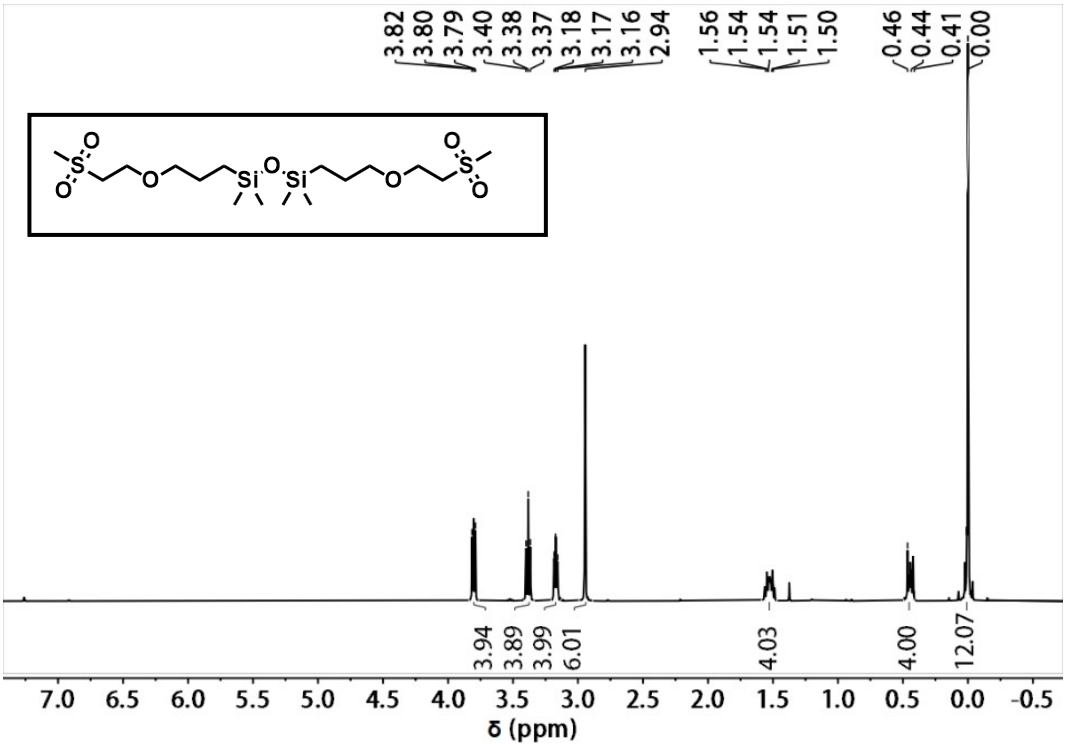



**Fig. S11** $^{1}$H NMR spectra of FDSi-2

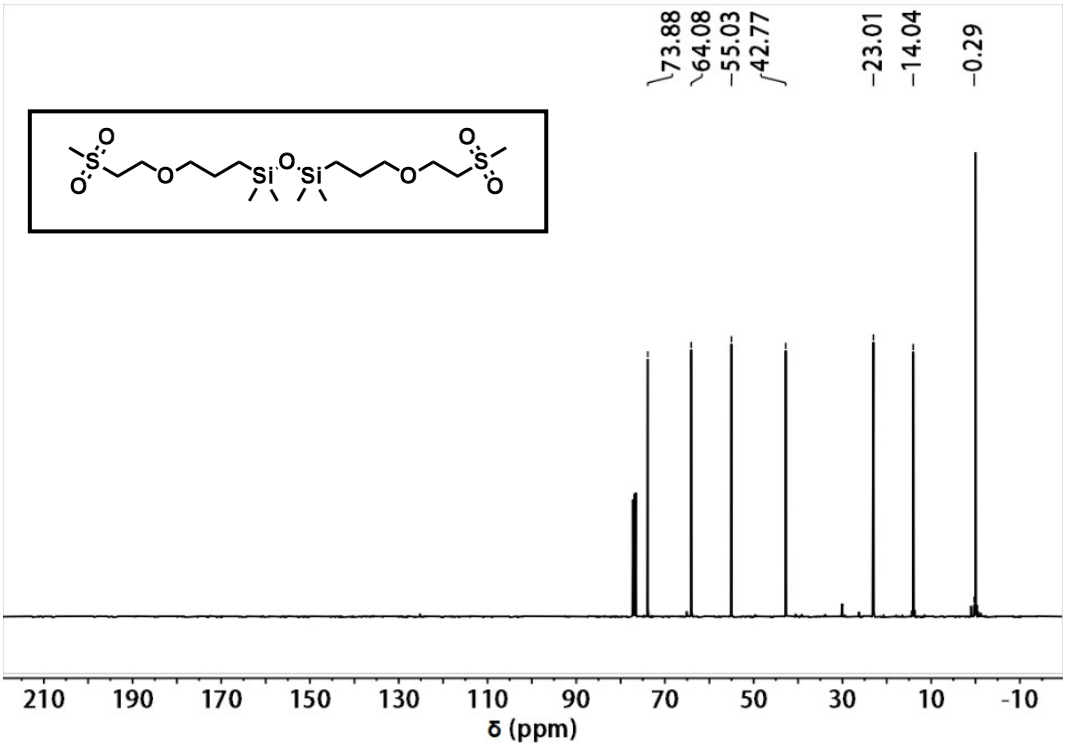



**Fig. S12** $^{13}$C NMR spectra of FDSi-2

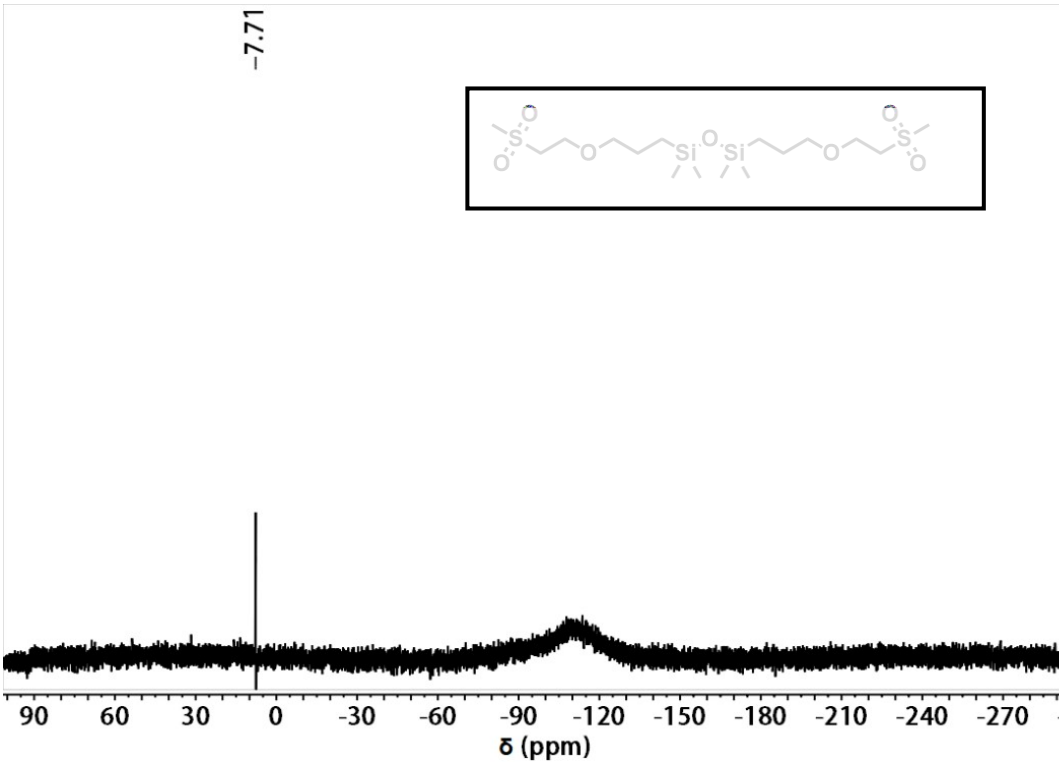



**Fig. S13** $^{29}$Si NMR spectra of FDSi-2

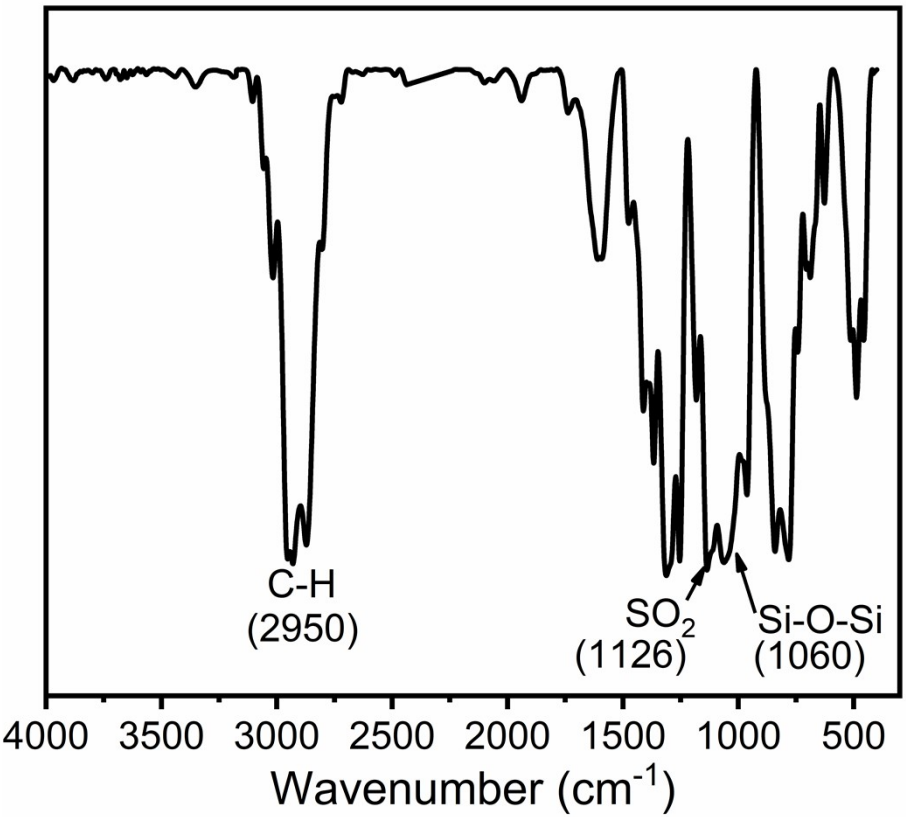



**Fig. S14** FT-IR spectra of FDSi-2

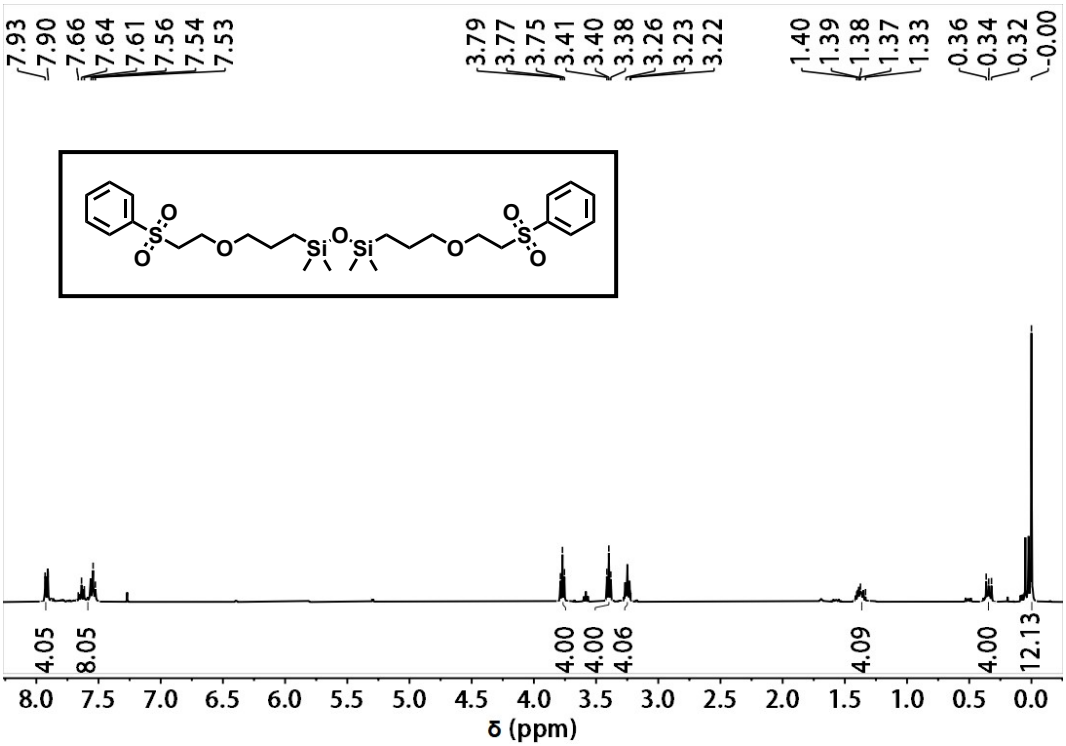



**Fig. S15** $^{1}$H NMR spectra of FDSi-3

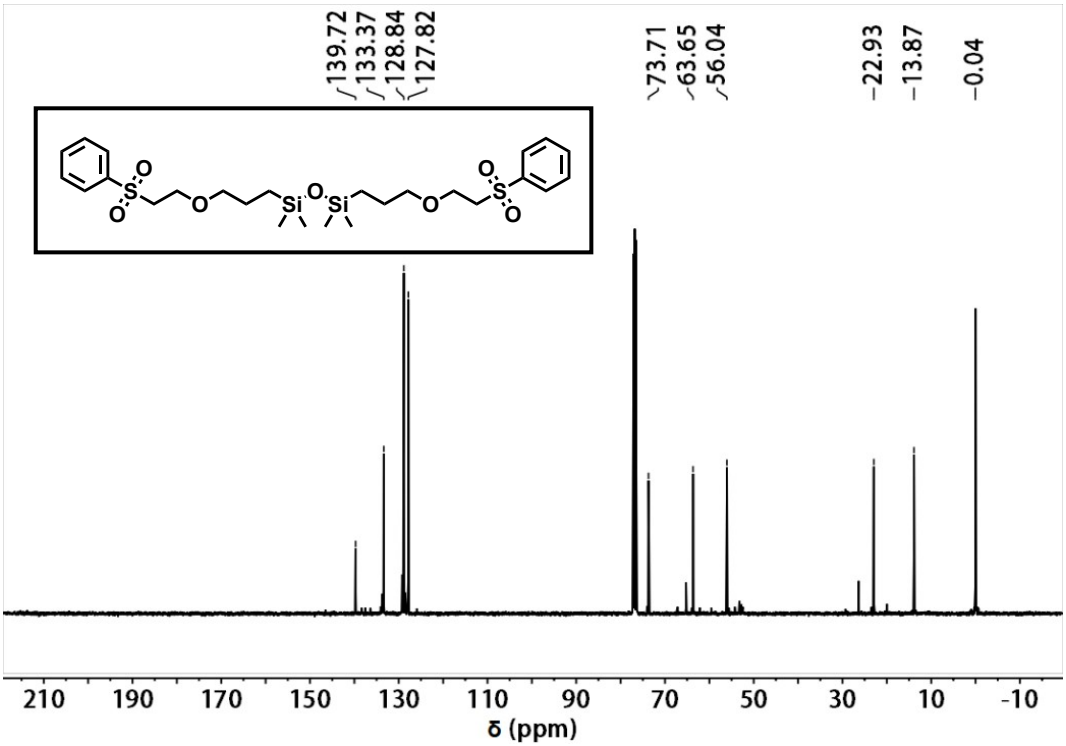



**Fig. S16** $^{13}$C NMR spectra of FDSi-3

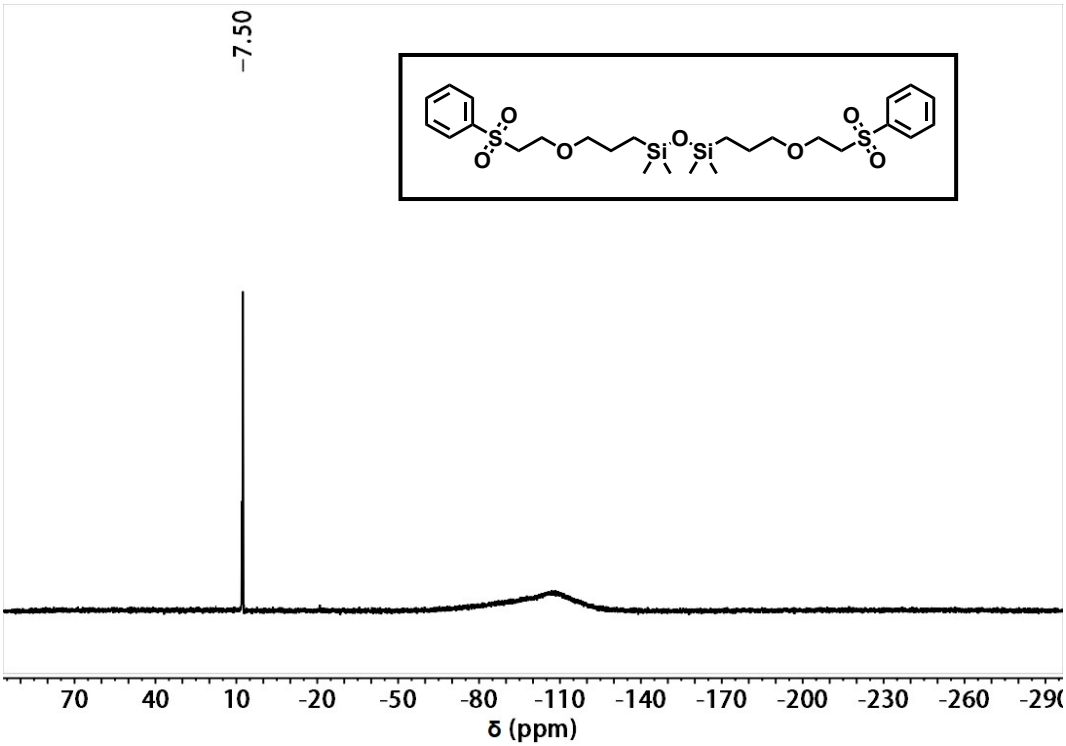



**Fig. S17** $^{29}$Si NMR spectra of FDSi-3

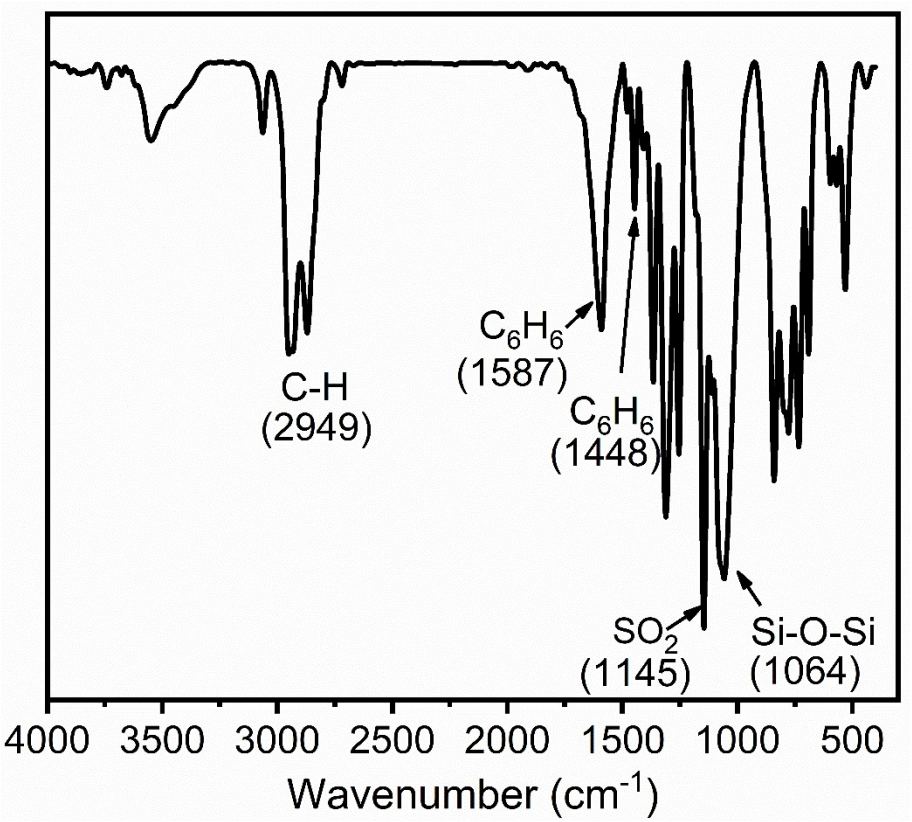



**Fig. S18** FT-IR spectra of FDSi-3

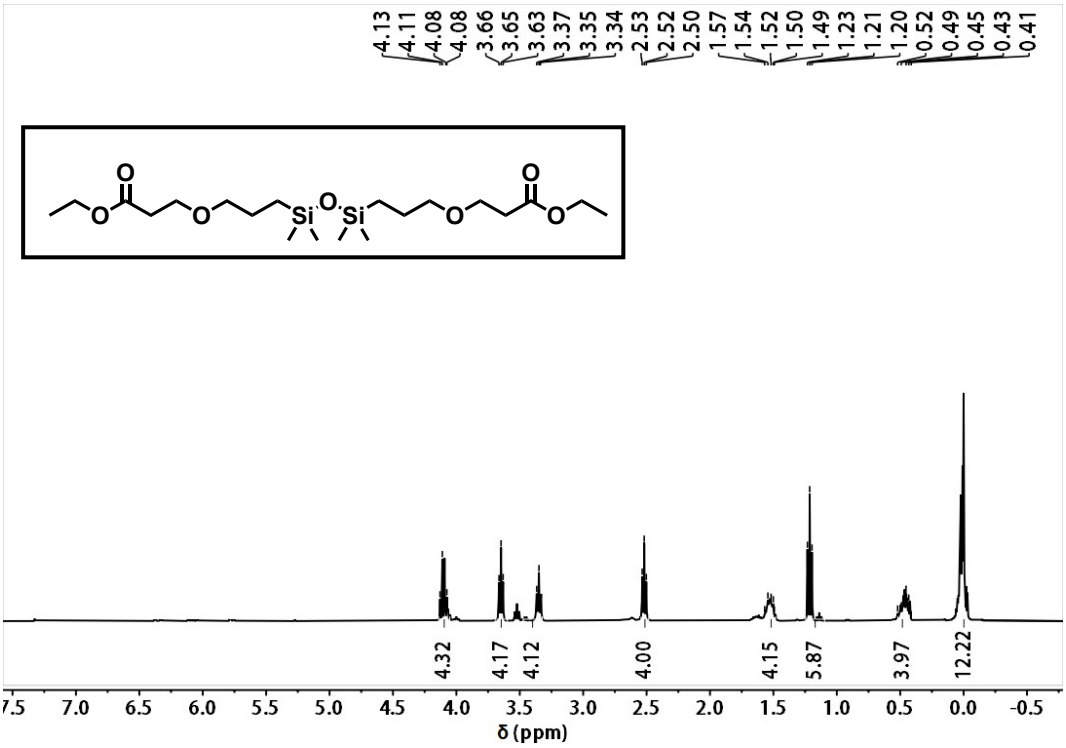



**Fig. S19** $^{1}$H NMR spectra of FDSi-4

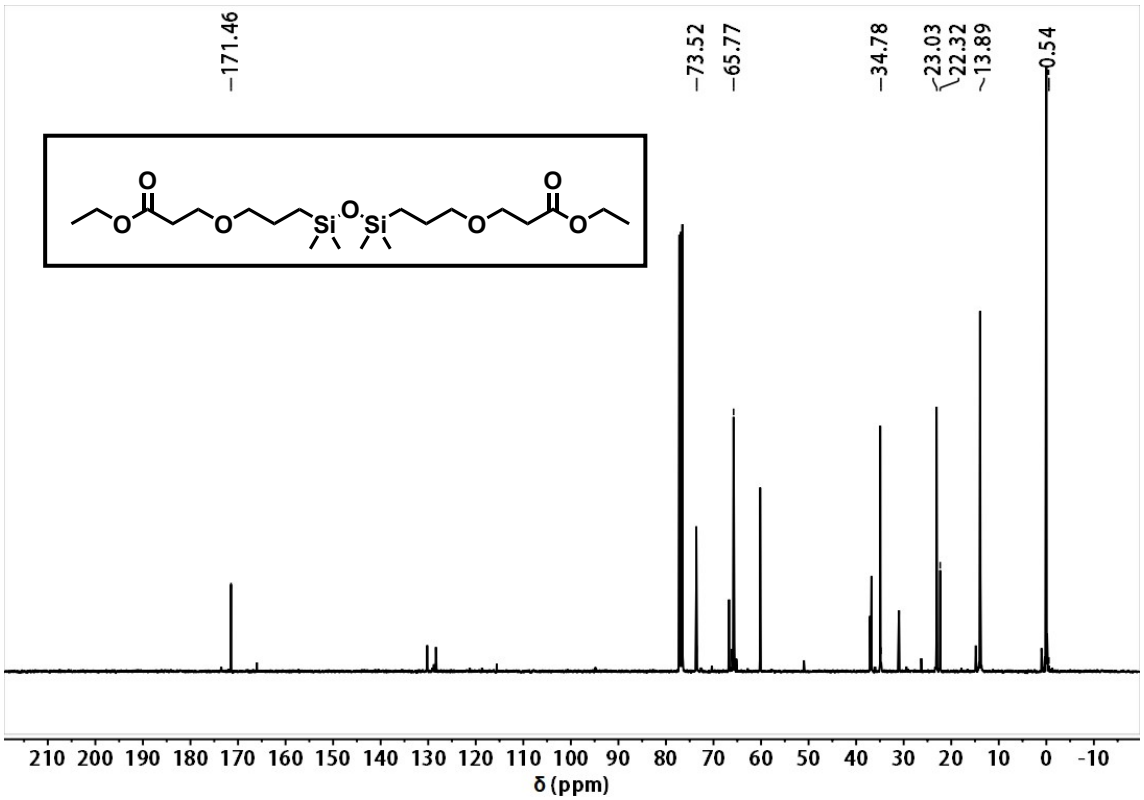



**Fig. S20** $^{13}$C NMR spectra of FDSi-4

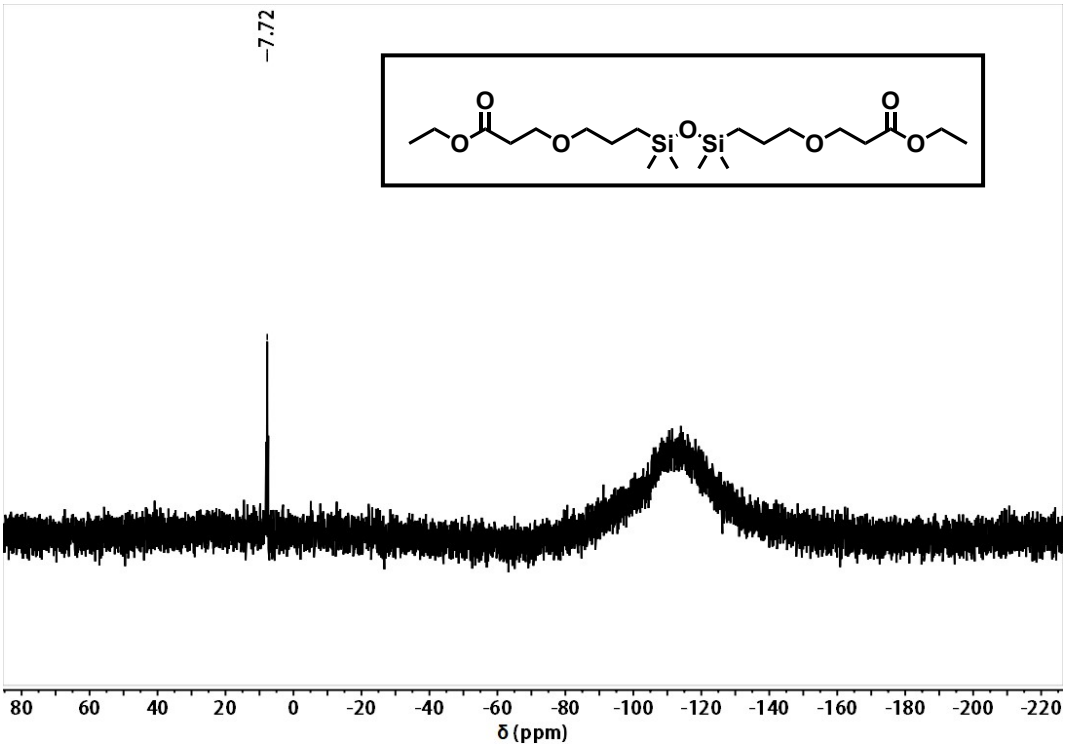



**Fig. S21** $^{29}$Si NMR spectra of FDSi-4

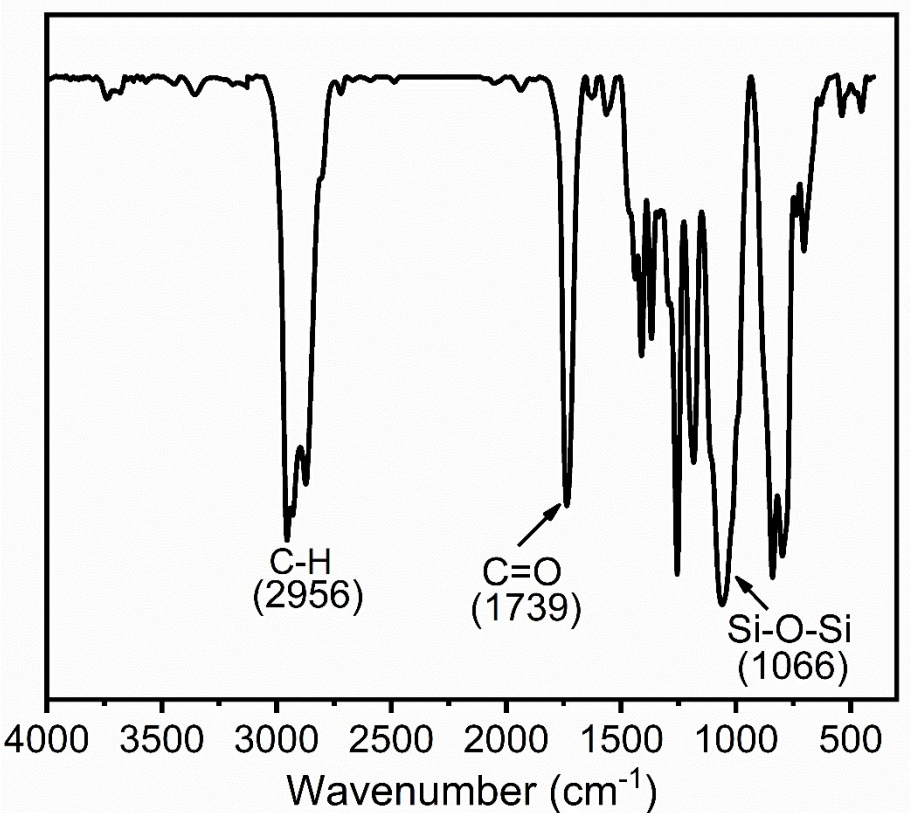



**Fig. S22** FT-IR spectra of FDSi-4

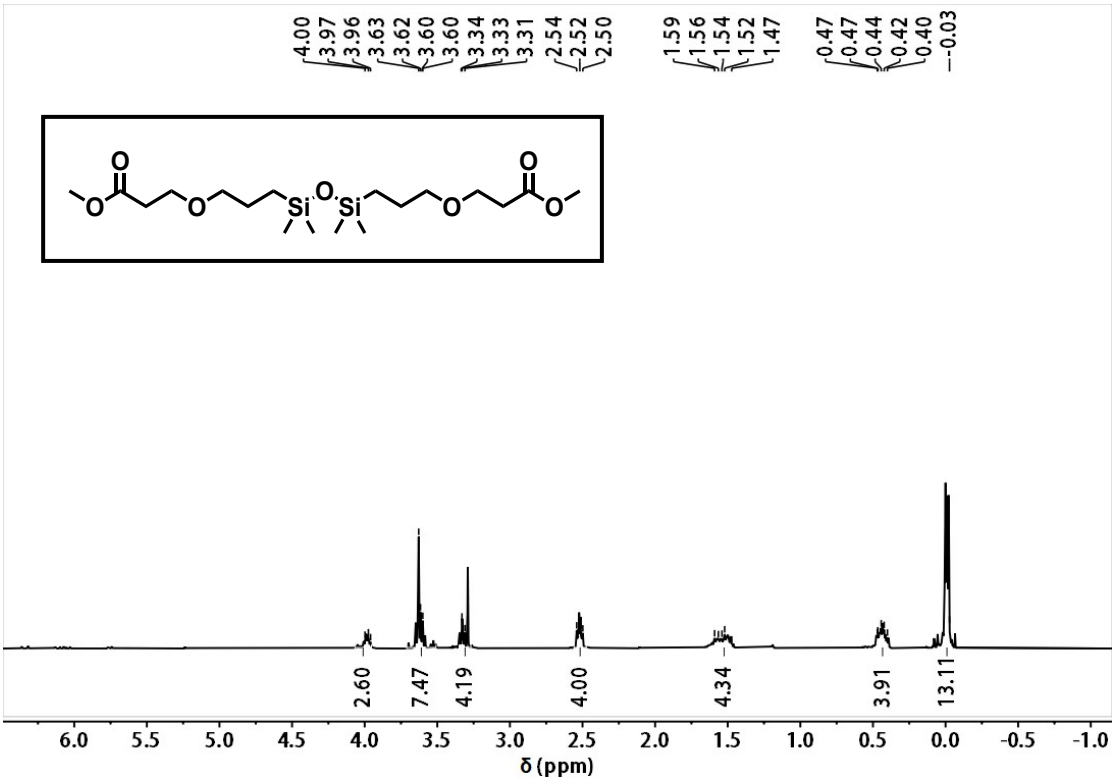



**Fig. S23** $^{1}$H NMR spectra of FDSi-5

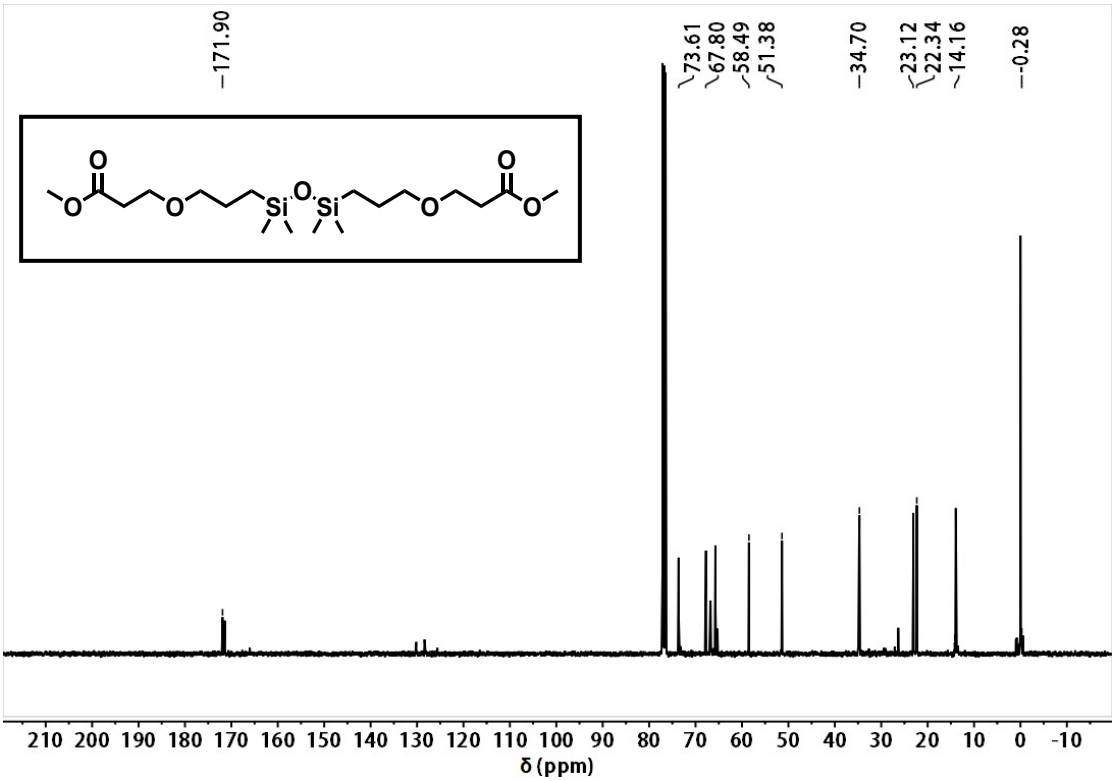



**Fig. S24** $^{13}$C NMR spectra of FDSi-5

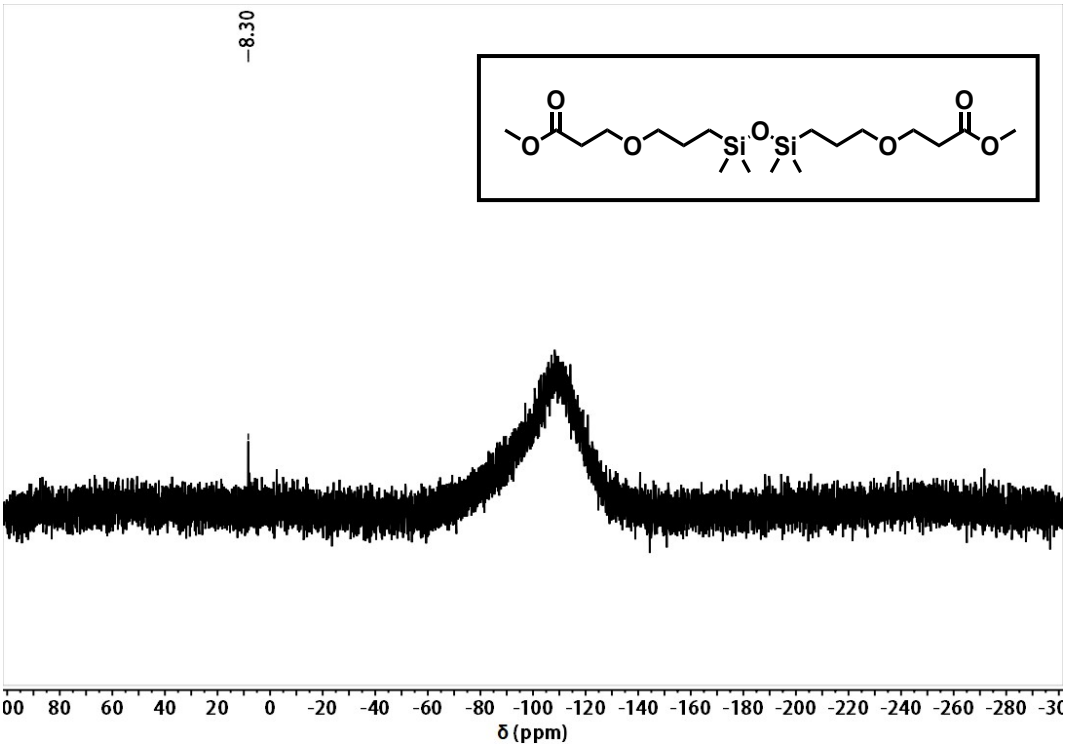



**Fig. S25** $^{29}$Si NMR spectra of FDSi-5

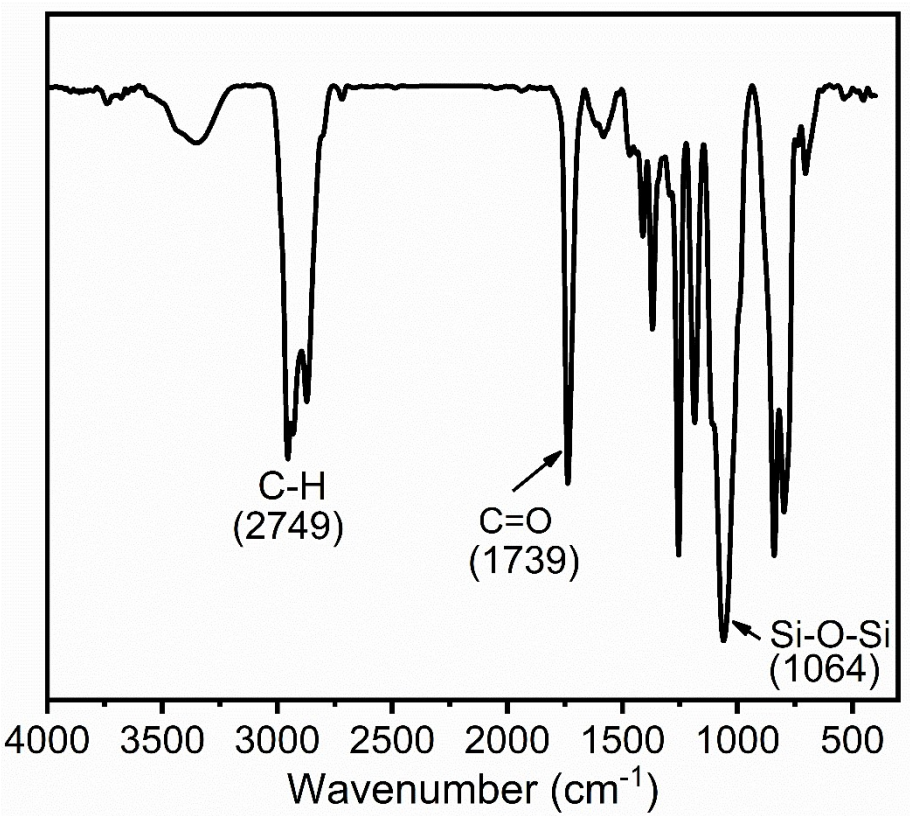



**Fig. S26** FT-IR spectra of FDSi-5

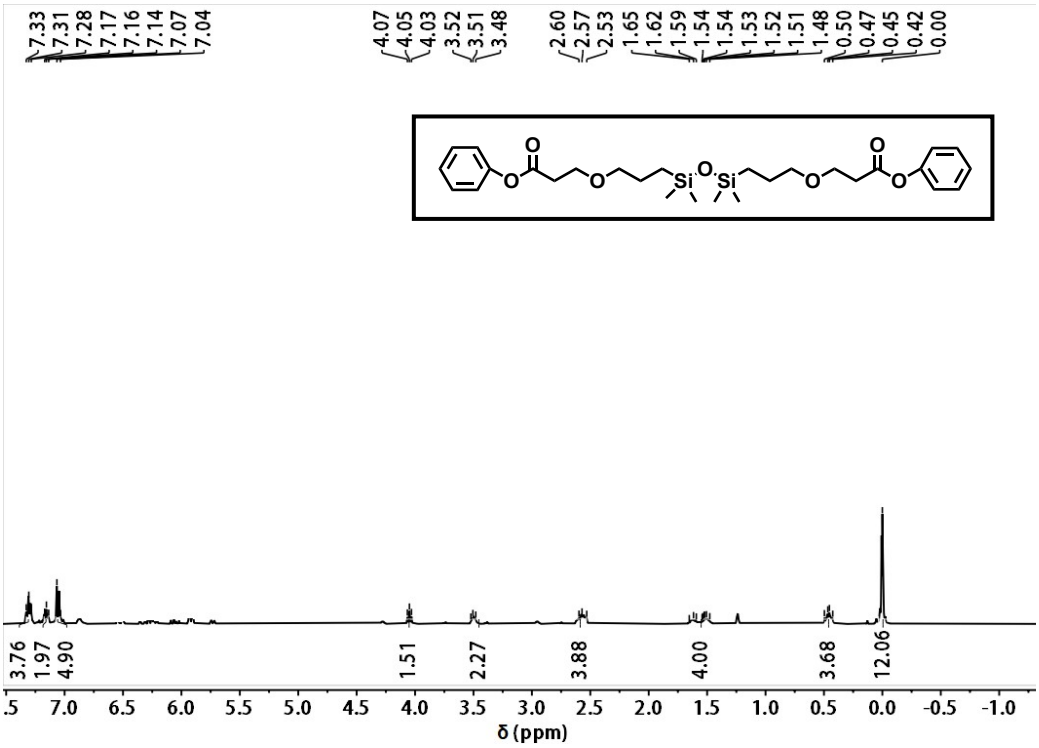



**Fig. S27** $^{1}$H NMR spectra of FDSi-6

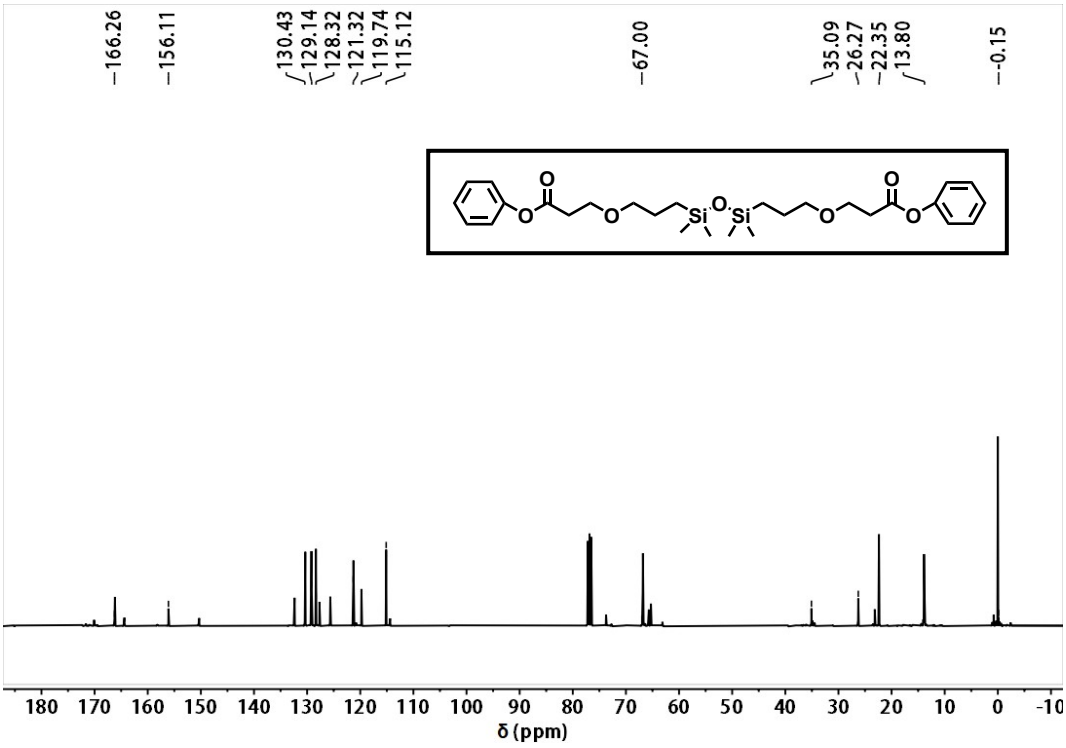



**Fig. S28** $^{13}$C NMR spectra of FDSi-6

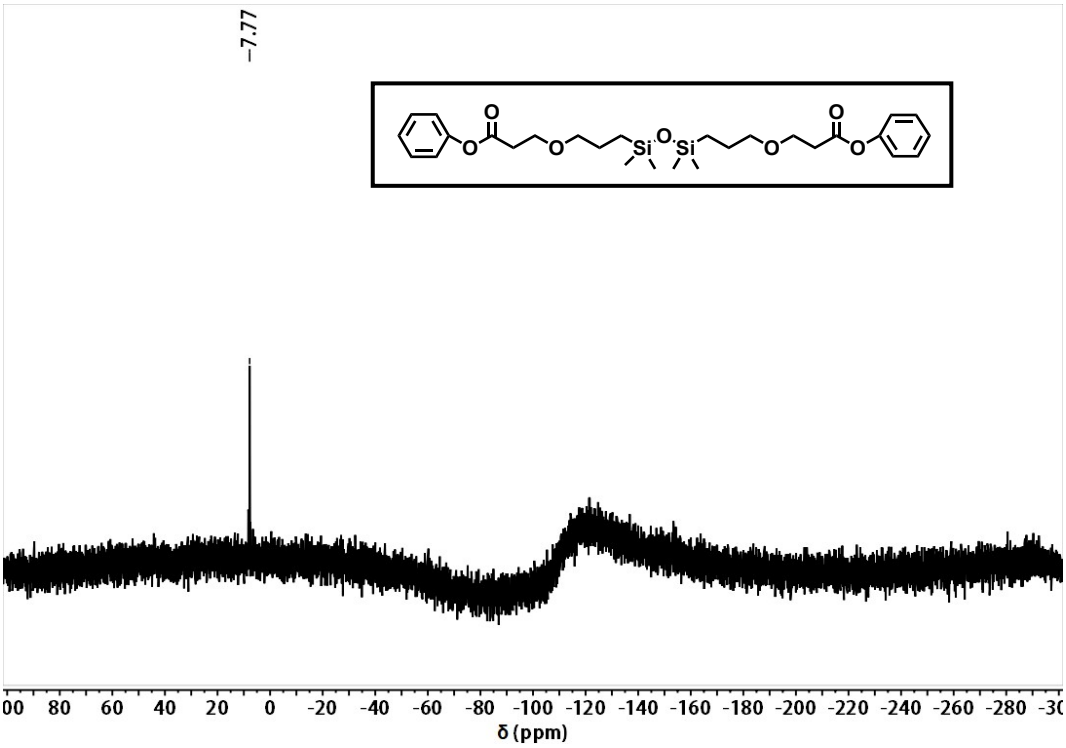



**Fig. S29** $^{29}$Si NMR spectra of FDSi-6

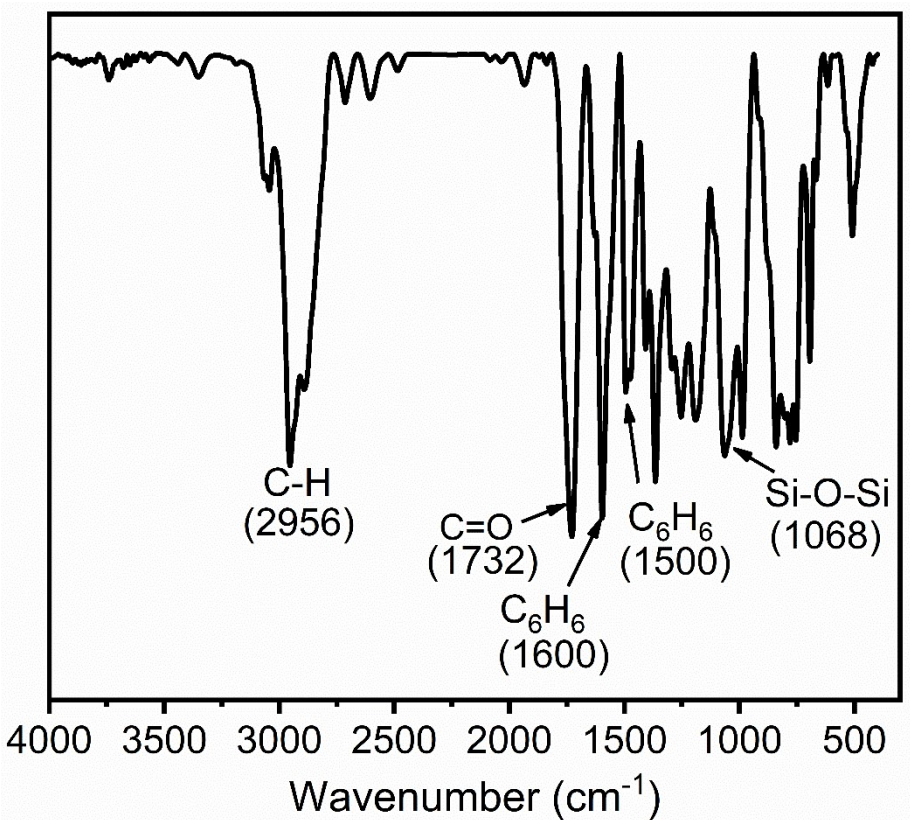



**Fig. S30** FT-IR spectra of FDSi-6

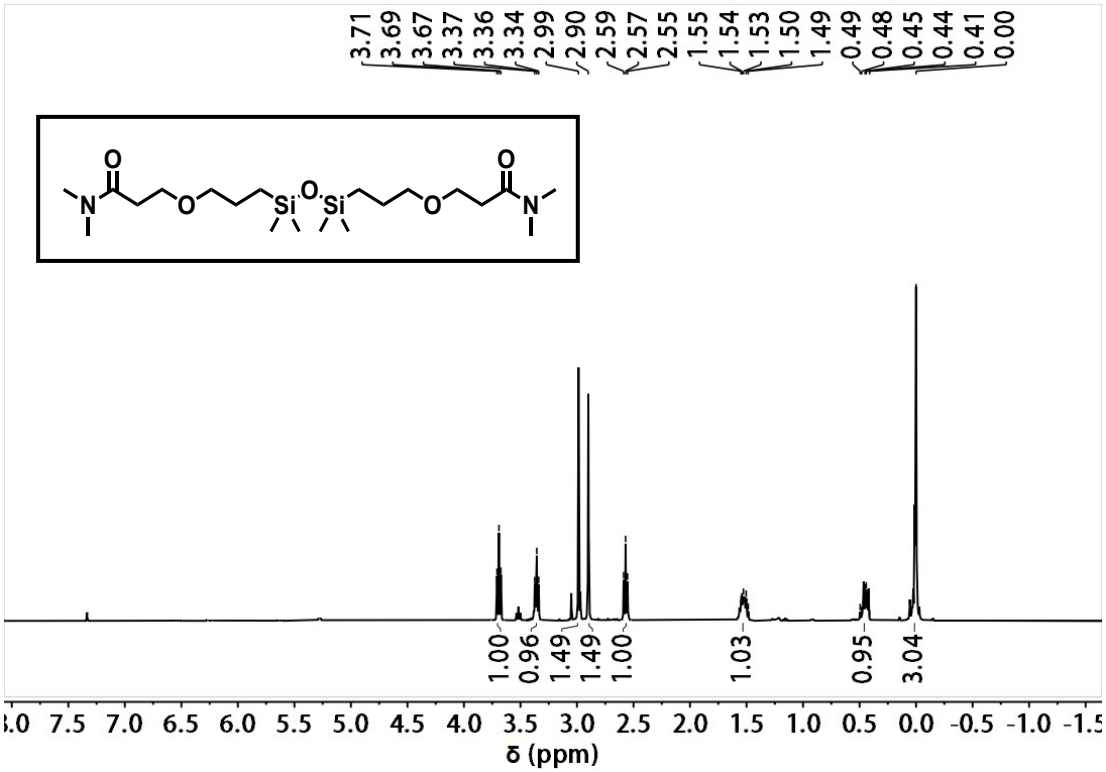



**Fig. S31** $^{1}$H NMR spectra of FDSi-7

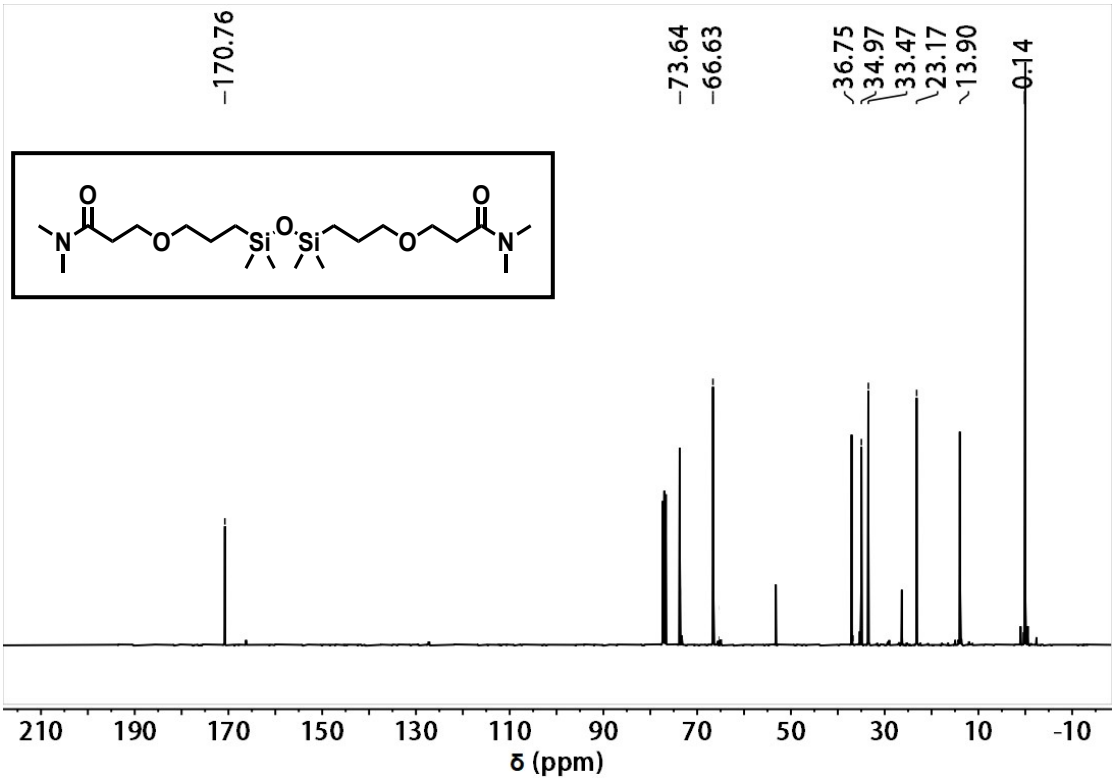



**Fig. S32** $^{13}$C NMR spectra of FDSi-7

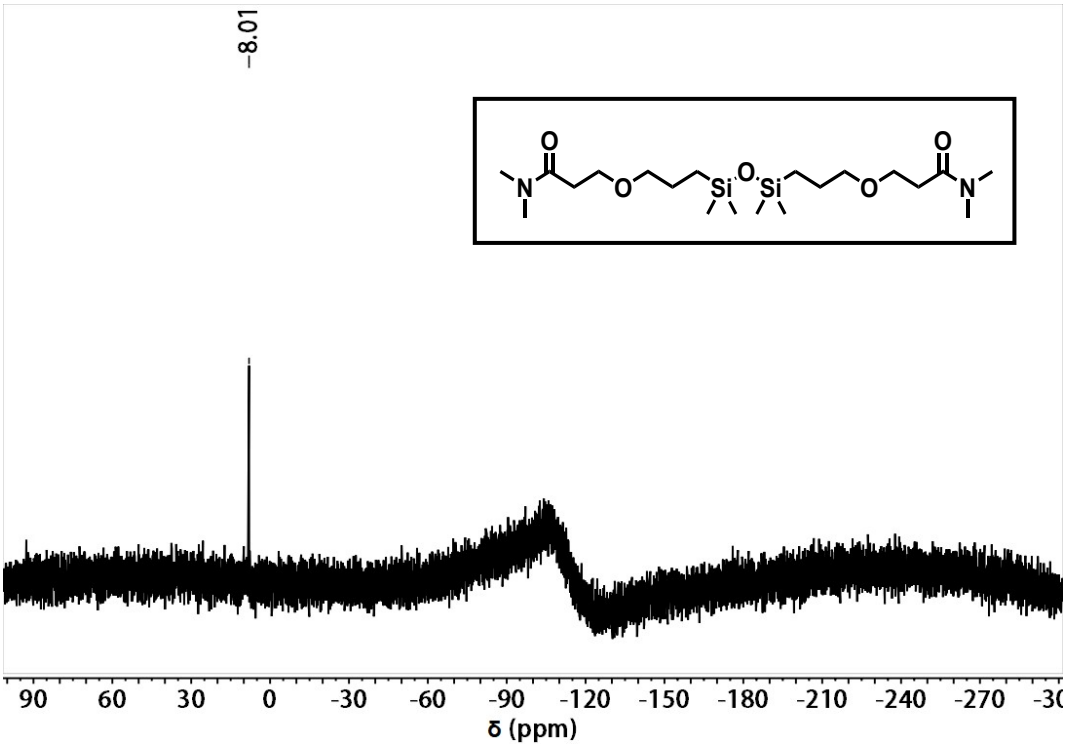



**Fig. S33** $^{29}$Si NMR spectra of FDSi-7

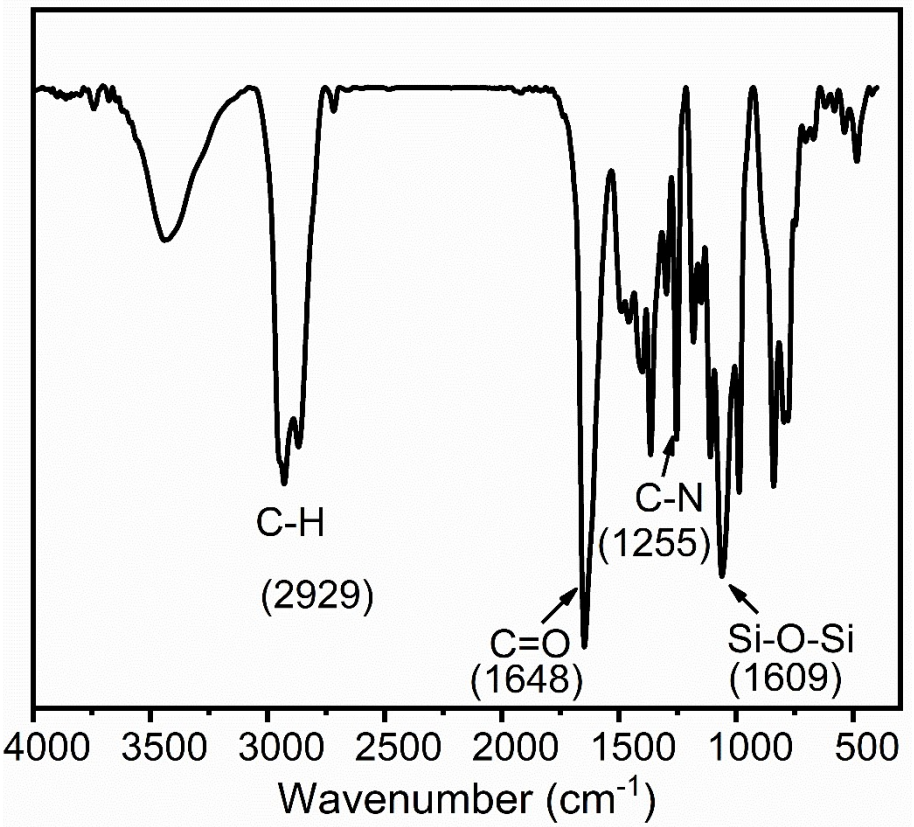



**Fig. S34** FT-IR spectra of FDSi-7

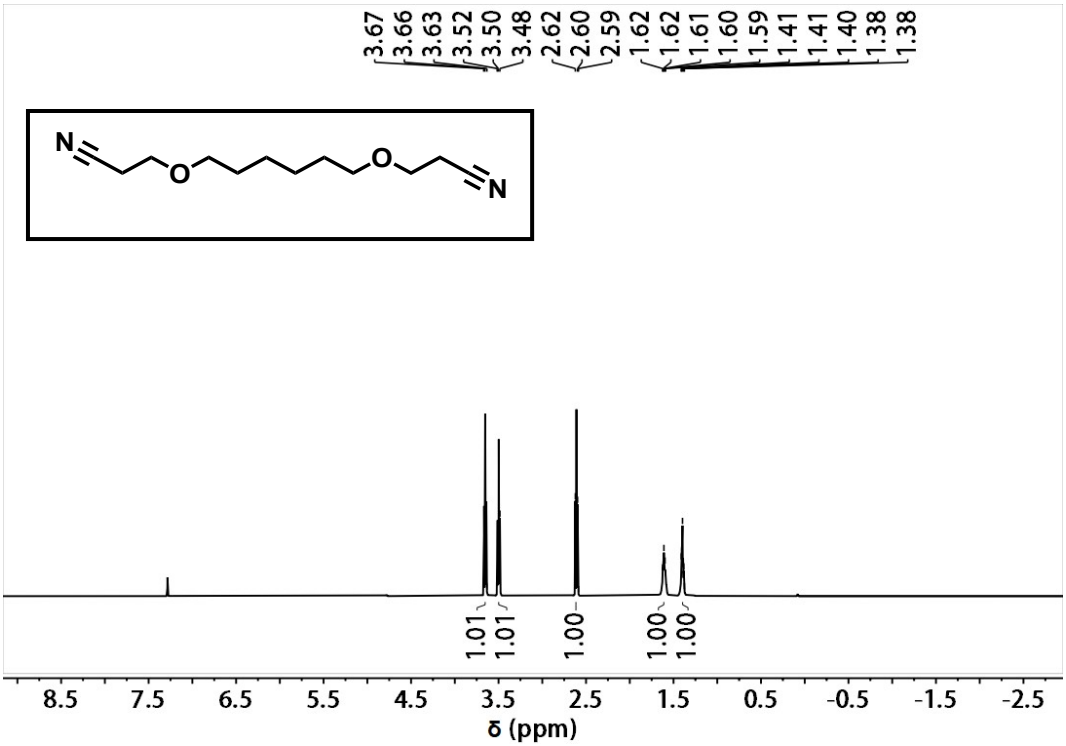



**Fig. S35** $^{1}$H NMR spectra of FD-J

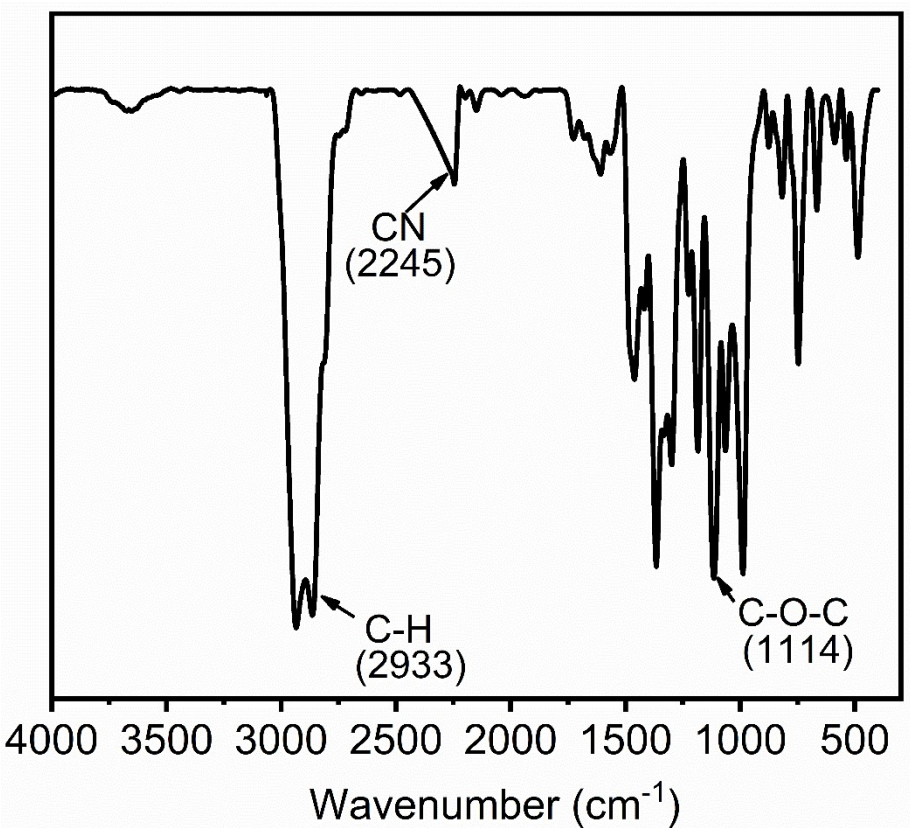



**Fig. S36** FT-IR spectra of FD-J

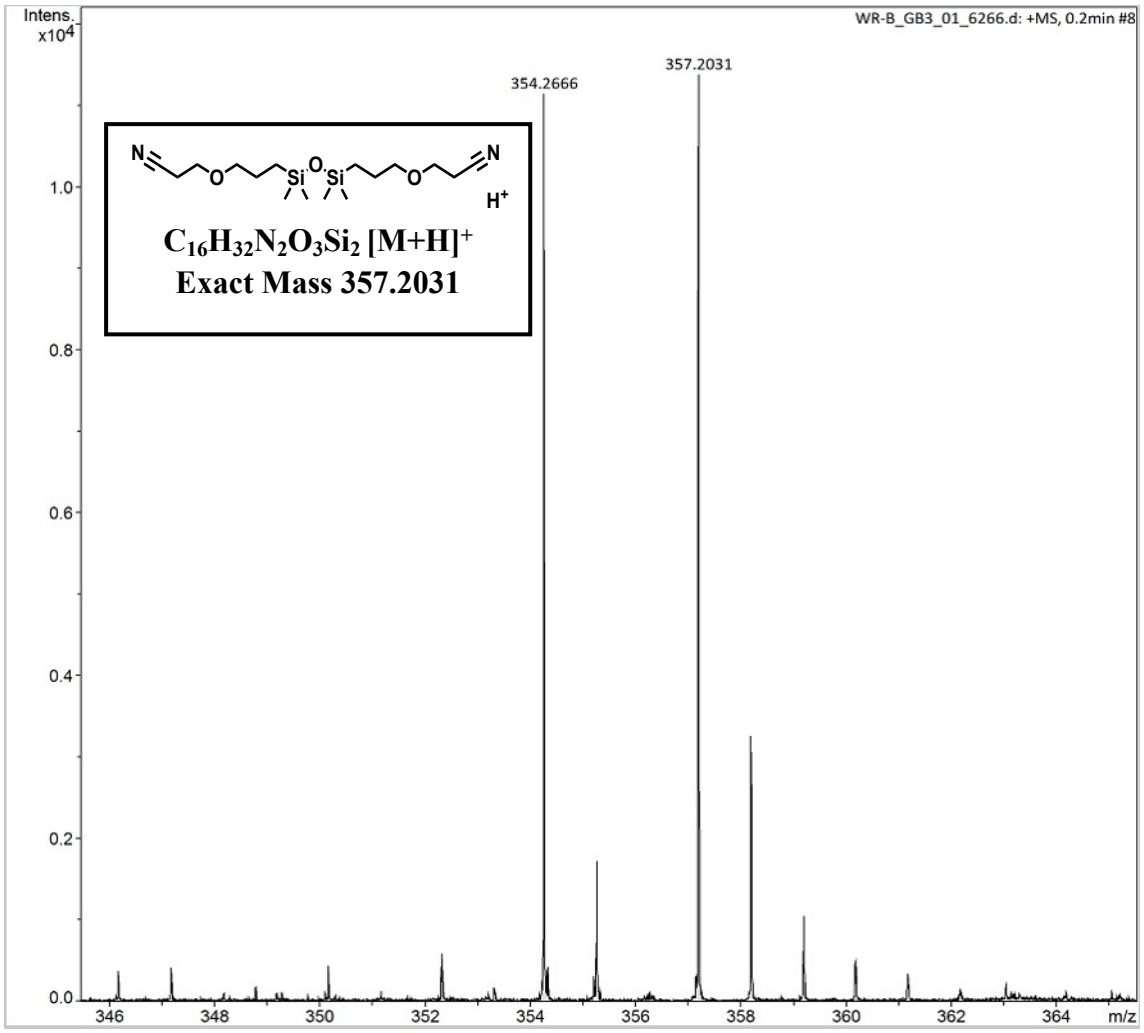



**Fig. S37** HR-MS spectra of FDSi-1

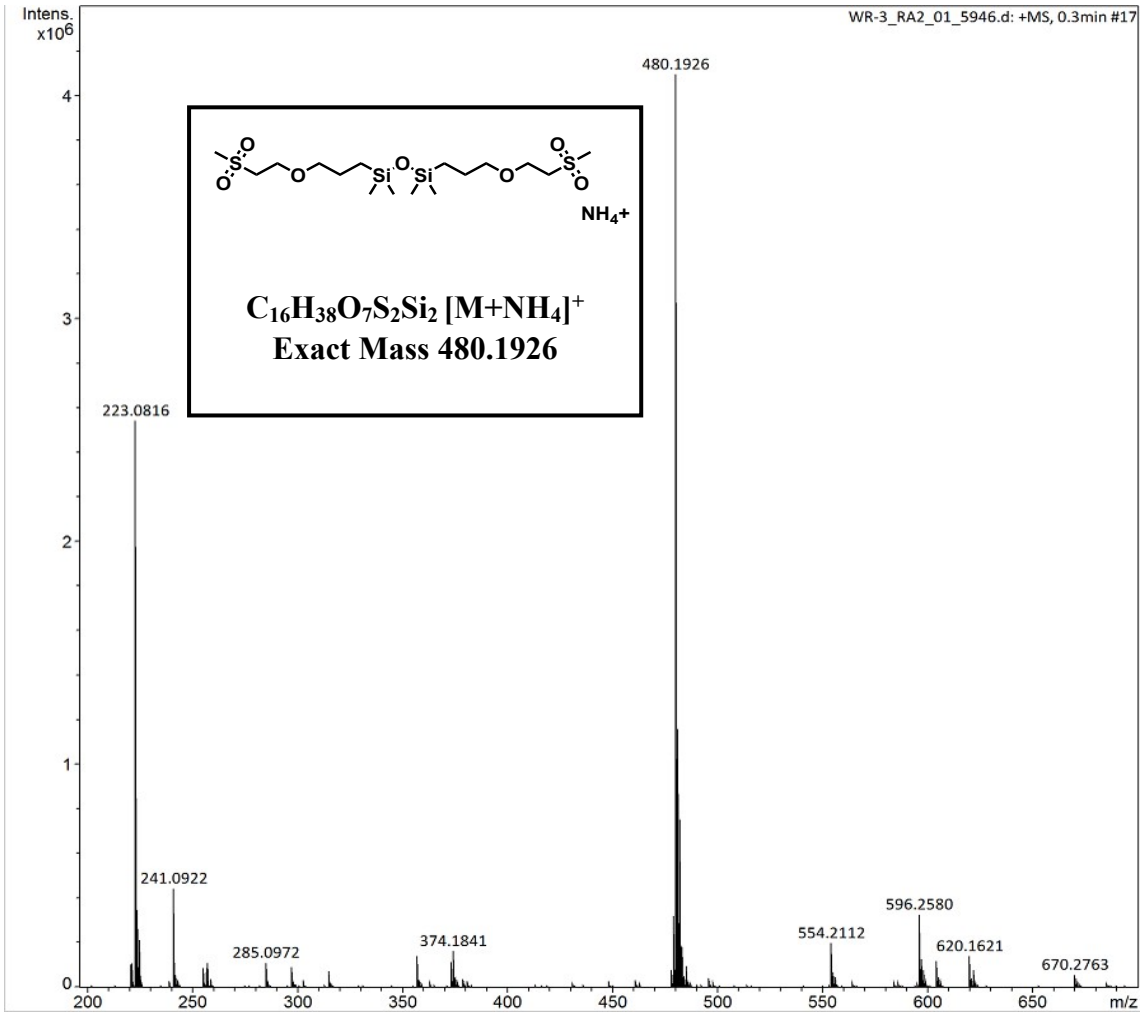



**Fig. S38** HR-MS spectra of FDSi-2

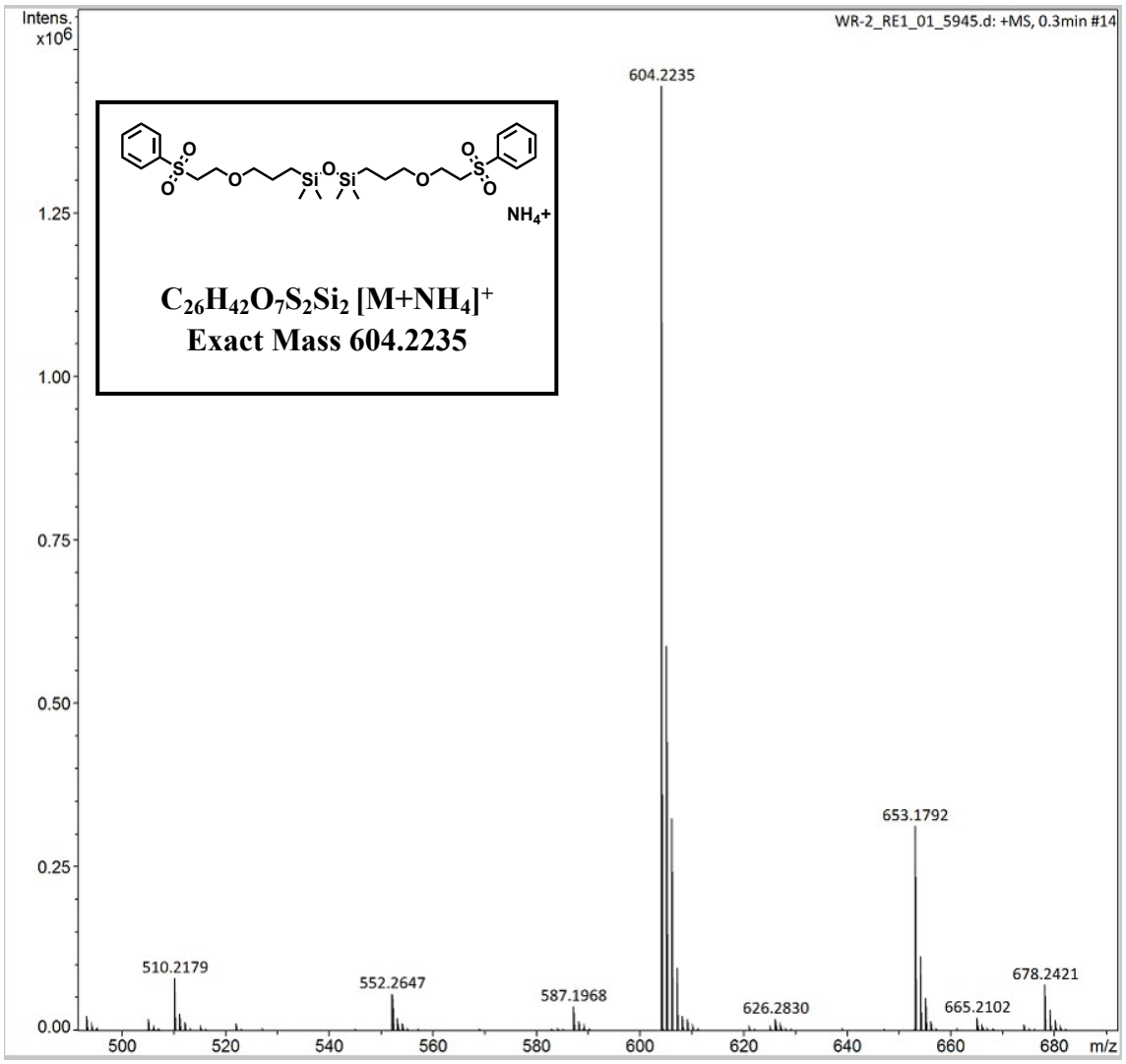



**Fig. S39** HR-MS spectra of FDSi-3

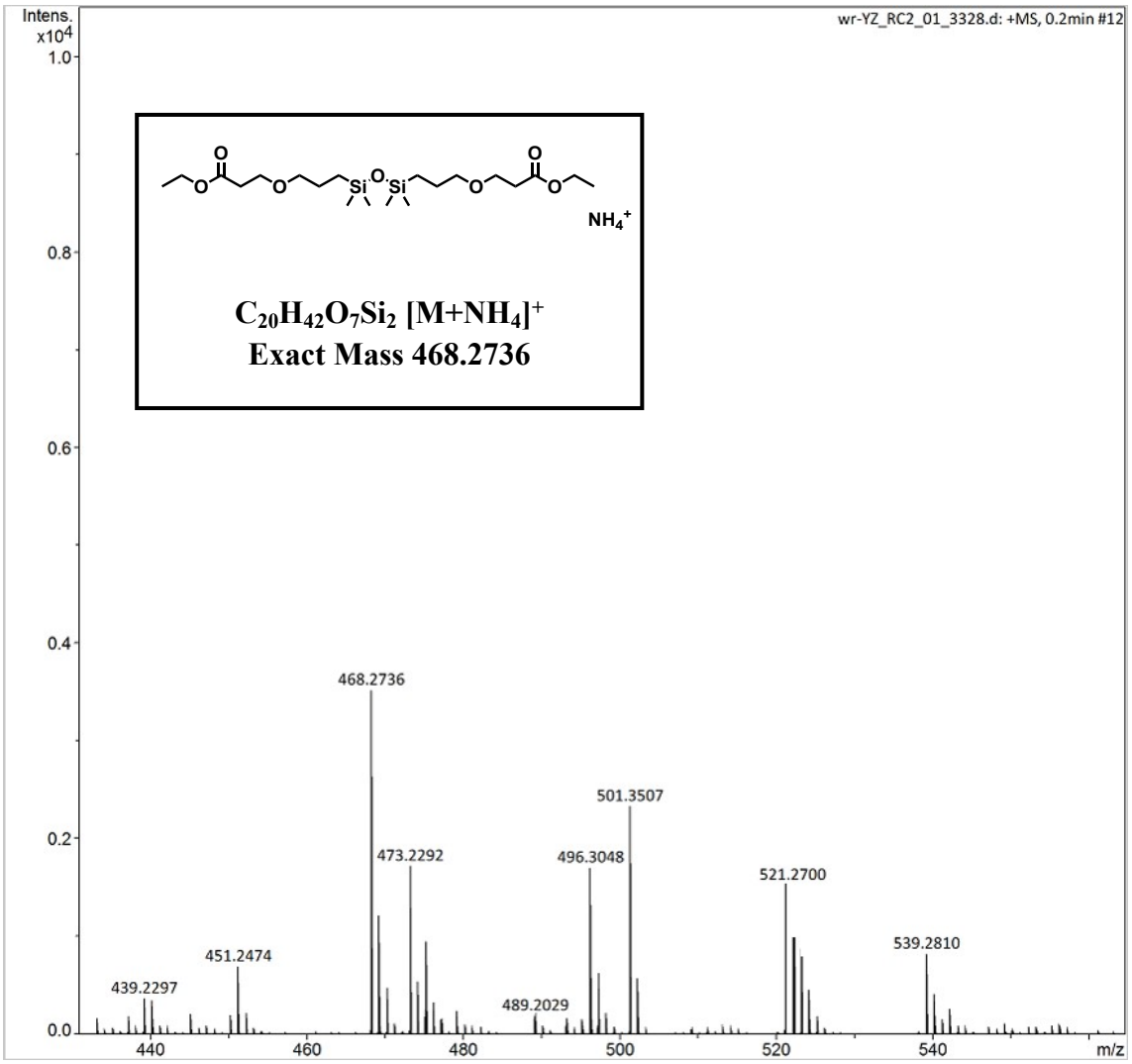



**Fig. S40** HR-MS spectra of FDSi-4

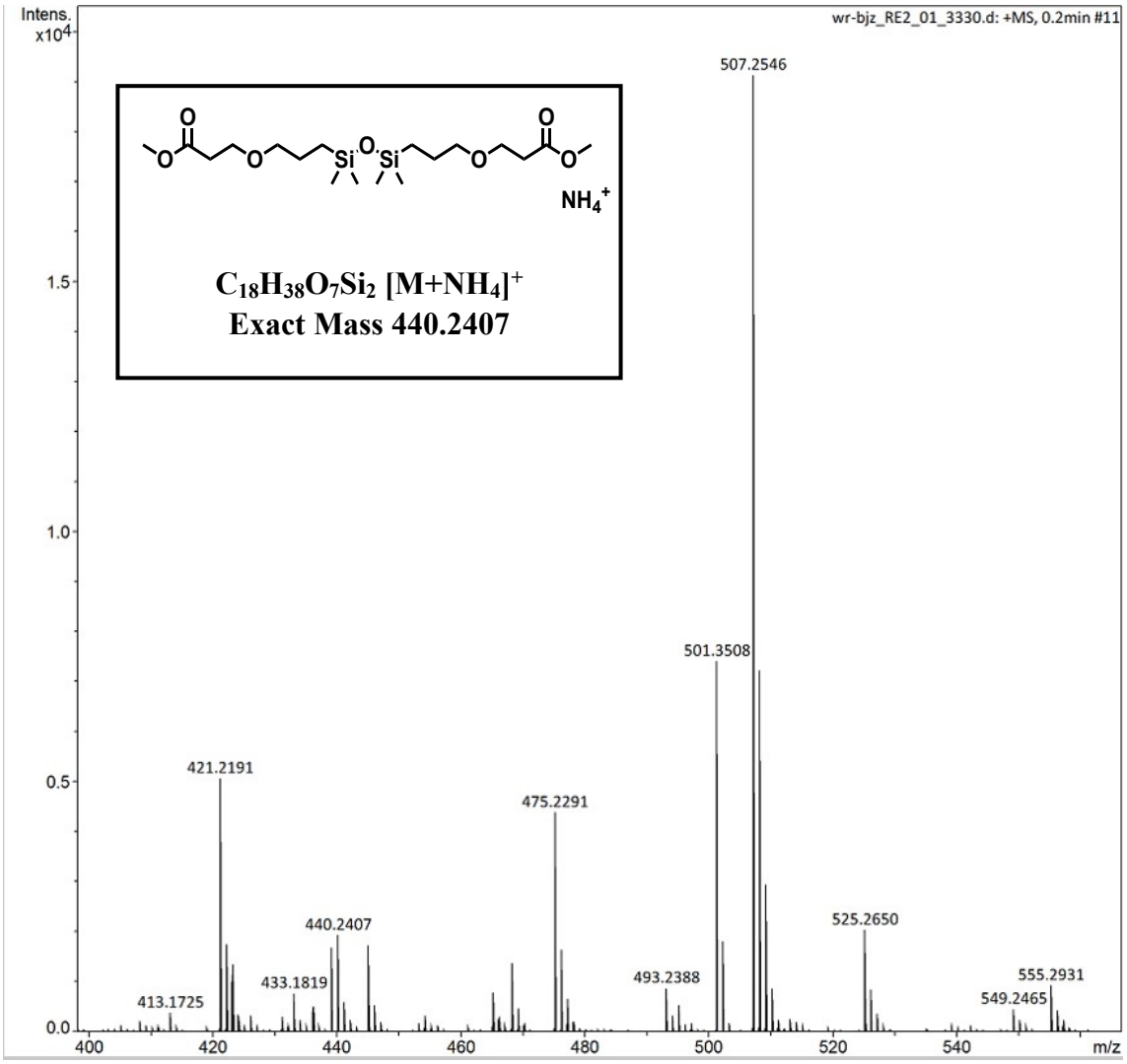



**Fig. S41** HR-MS spectra of FDSi-5

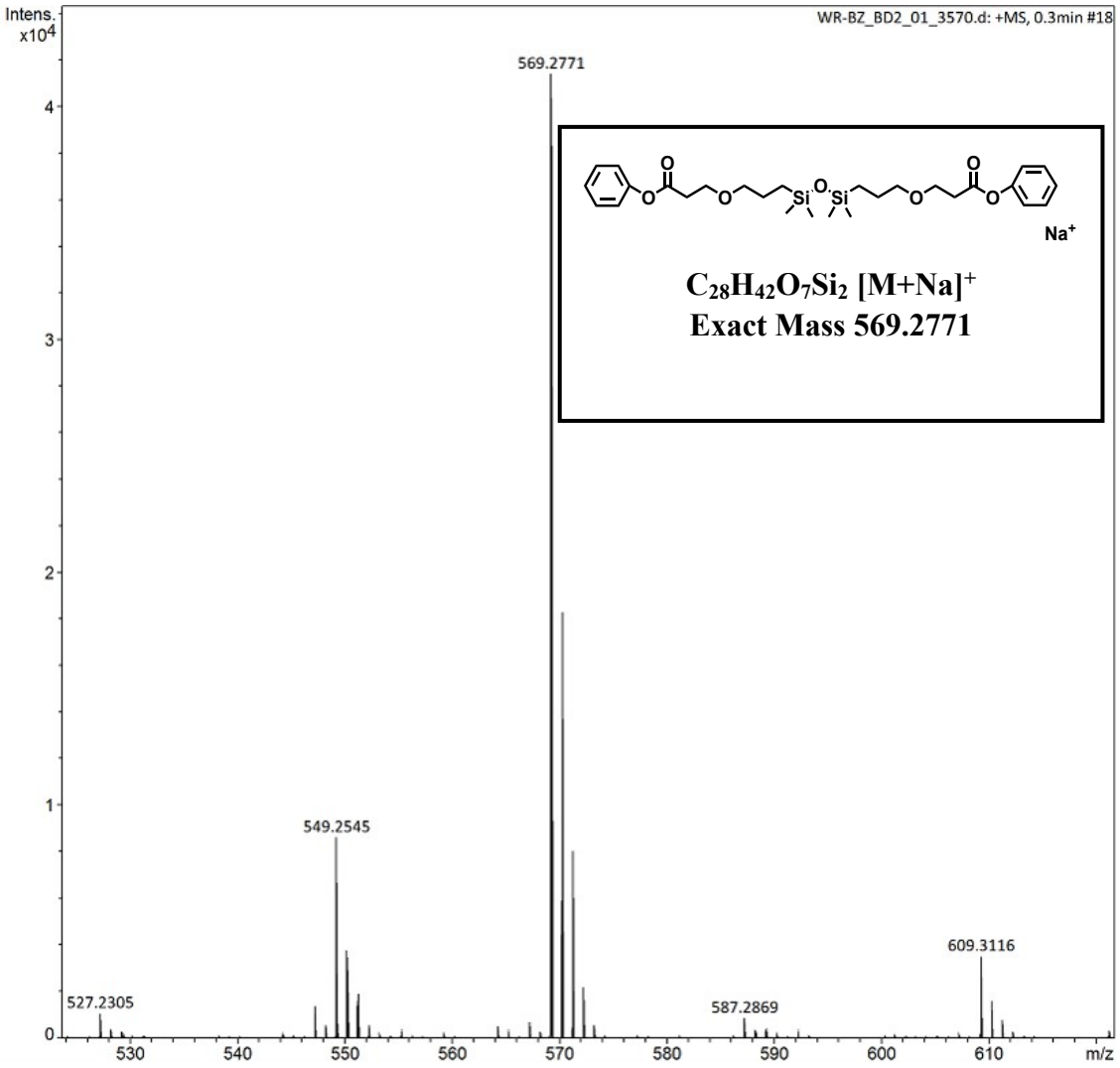



**Fig. S42** HR-MS spectra of FDSi-6

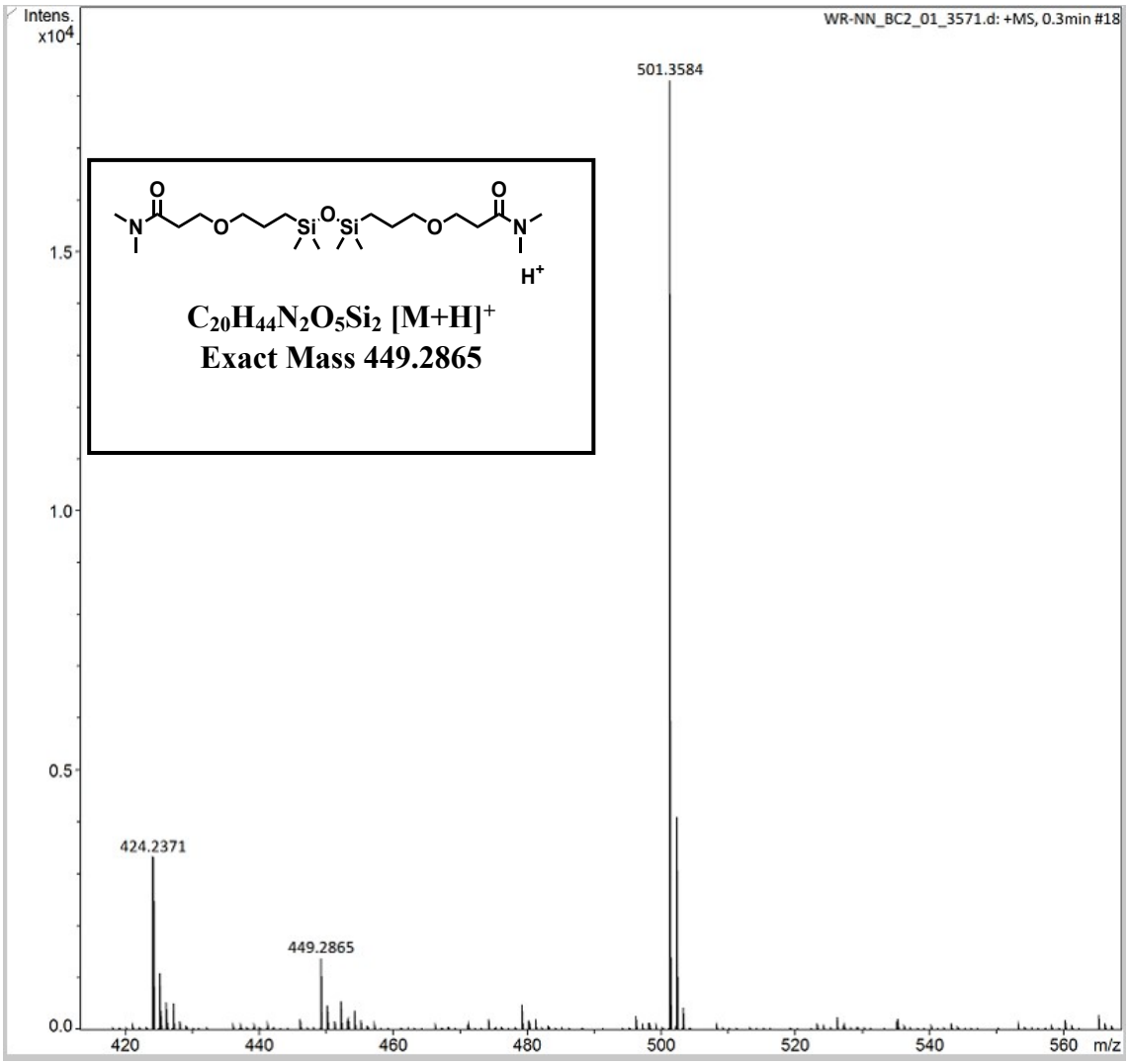



**Fig. S43** HR-MS spectra of FDSi-7