Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Janus ring siloxane: a versatile precursor of the extended Janus ring and tricyclic laddersiloxanes

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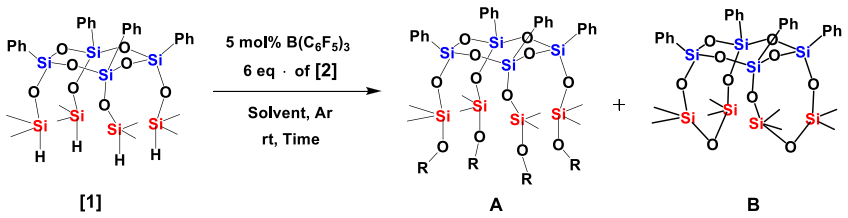
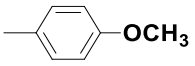
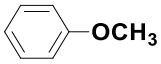
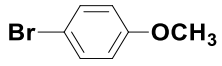
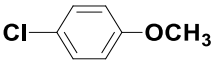
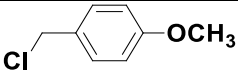
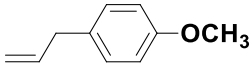
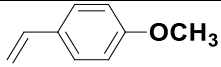
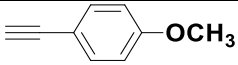
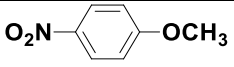
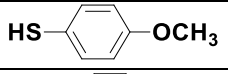
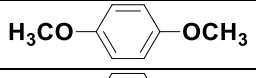
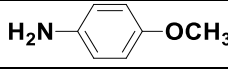
1. Experimental data

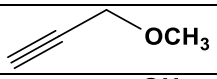
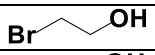
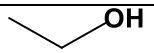
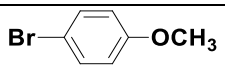
1-1. General

All of reactions were conducted under argon atmosphere. All substrates were purchased from Tokyo Chemical Industry Co. Ltd. and use as receive. The catalyst $B(C_6F_5)_3$ was stored under argon atmosphere. Chromatographic separation of the products were carried out by the Japan Analytical Industry Co. Ltd. LC-5000 recycle-type preparative liquid chromatography using a combination of JAIGEL 1HR+2HR (20 mm × 600 mm) GPC column (eluent: $CHCl_3$). Fourier-transform nuclear magnetic resonance (NMR) spectra were obtained using a JEOL JNM-ECS 300 NMR spectrometer (^1H at 300 MHz, ^{13}C at 75 MHz, ^{29}Si at 59 MHz). Analysis by matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF) was performed on a Shimadzu MALDI-TOF AXIMA®

Table S1: The synthesis and functionalization of the all-cis-cyclotetrasiloxane $[Ph\text{-}Si(O)\text{-}SiMe_2H]_4$ using Pier-Rubinsztajn reaction[a]

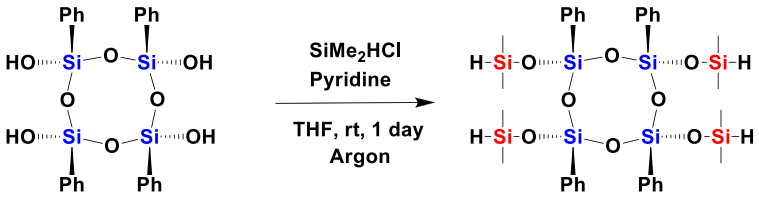


Entry [a]	Compound [2]	Time (h)	Solvent	%Conv.	Isolated Yield	
					A	**B**
1		2	Hexane	100 %	88% **JR-01**	-
2		2	Hexane	100 %	78% **JR-02**	-
3		2	Hexane	100 %	48% **JR-03**	-
4		2	Hexane	100 %	47% **JR-04**	-
5		2	Hexane	100 %	28% **JR-05**	trace
6		2	Hexane	100 %	22% **JR-06**	trace
7		24	Hexane	n.d.		
8		24	Hexane	n.d.		
9		24	$CHCl_3$	n.d.		
10		24	$CHCl_3$	n.d.		
11		24	$CHCl_3$	n.d.		
12		24	$CHCl_3$	no reaction		

13		24	$CHCl_3$	n.d.
14		24	Hexane	n.d.
15		24	Hexane	n.d.
16	 (No catalyst)	24	Hexane	no reaction

[a] Reaction condition: 200 mg of **T_4-SiMe$_2$H** was reacted with 6 eq. of [2]. After aqueous work up, the crude products were purified using 30% EtOAc in hexane and GPC using $CHCl_3$ as an eluents. n.d. = The reactions occur, but there are many of by-products that we cannot isolate. Trace = <5%

1-2. Synthesis of all-*cis*-[PhSi-(O)-OSiMe$_2$H]$_4$ (T_4-O- SiMe$_2$H) using T_4OH



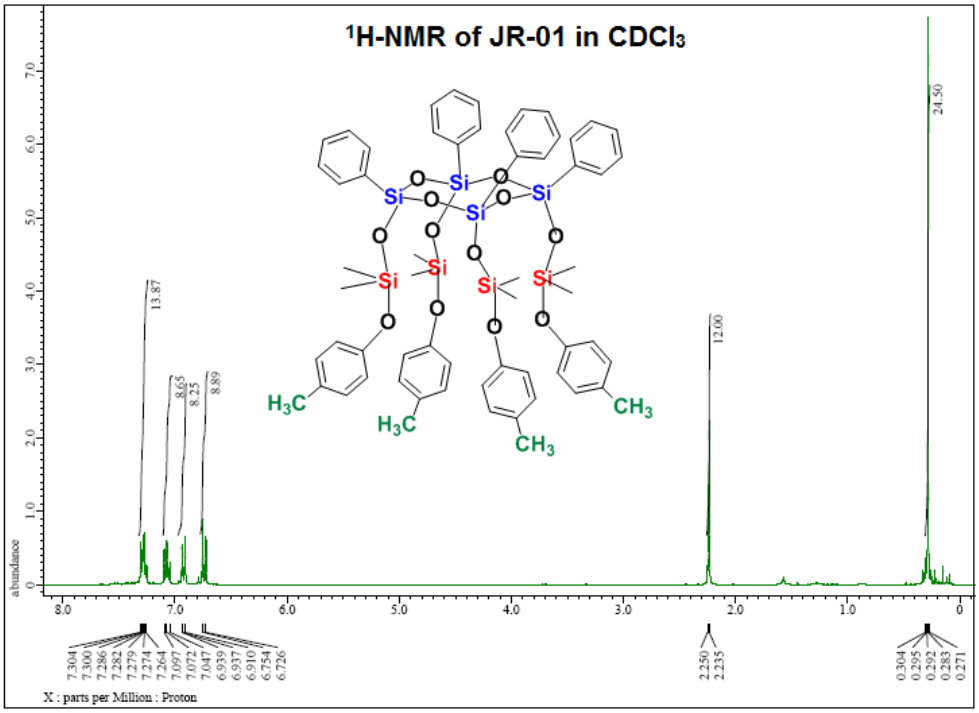
In the 250 mL two-necked round bottom flask equipped with magnetic bar, the white solid of T_4OH (2.0 g, 0.0036 mol) was evacuated and refilled with argon for 3 cycles. Then, 200 mL of anhydrous hexane and 2.79 mL triethylamine (0.0216 mol, 6 equiv.) was added into the reaction flask. After that, the reaction mixture was stirred and cooled to 0 °C for 30 min. Then, 2.39 mL of $SiMe_2HCl$ (0.0216 mol, 6 equiv.) was added dropwise into the reaction flask *via* a glass syringe. After approximately 30 min of dropping time, the reaction mixture was stirred at room temperature for 2 h. For working up, crude product was extracted using 50 mL Hexane and 50 mL of brine for 5 times. Then, the organic layer was washed with saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the product was obtain to yield 2.03 g. (72 %, 0.0026 mol) as a white crystalline and can be used without purification. ^{1}H NMR (300.5 MHz, $CDCl_3$) δ 0.27 (s, 12H, SiMeMe), 0.49 (s, 12H, SiMeMe), 4.87 (sept, 4H, Si-H, J = 3 Hz), 7.10–7.15 (m, 8H, Ar-H), 7.25–7.35 (m, 12H, Ar-H) ppm. ^{13}C NMR (75.57 MHz, $CDCl_3$) δ 0.56 (-Si-CH$_3$), 127.49 (-C=CH), 129.93 ((-C=CH), 132.39 (C), 133.91 ((-C=CH) ppm. ^{29}Si{^{1}H} NMR (59.71 MHz, $CDCl_3$) δ –3.16, –78.08 ppm.

1-3. General procedure for the synthesis of Janus ring JR-01 to JR-06

To the 25 mL two-necked round bottom flask equipped with magnetic bar, **JP-01** (200 mg, 0.254 mmol) was mixed with a solution of 4-arylanisole (1.524 mmol, 6 equiv.) in 4 mL of anhydrous solvent. Then, 5 mol% (6.5 mg.) of $B(C_6F_5)_3$ catalyst was added into the reaction. After the addition of catalyst, we observed that the gas was rapidly forms after the addition of catalyst. The reaction was stirred at room temperature, and quenched with water. Finally, the product was extracted using hexane, brine, and dried over anhydrous Na_2SO_4. After solvent evaporated, the product was purified column chromatography (30% $CHCl_3$/hexane) and GPC ($CHCl_3$).

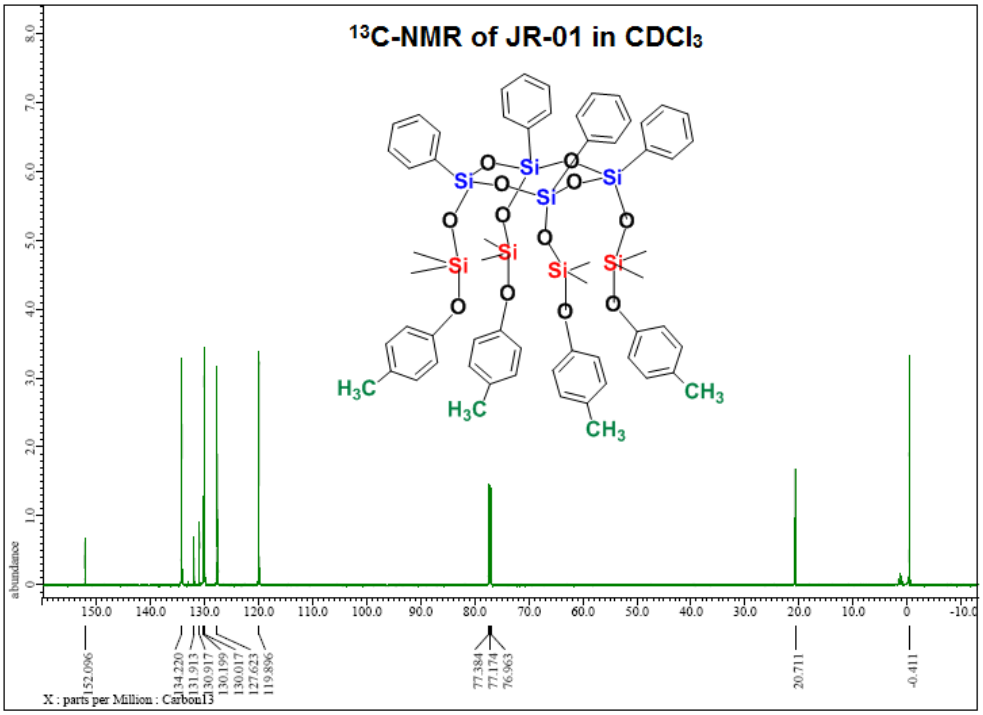
Products	MW	Isolated yield
JR-01 (Colorless oil)	1,209.89	88% (270 mg, 0.22 mol)
JR-02 (Colorless oil)	1,153.78	78% (228 mg, 0.19 mol)
JR-03 (Colorless oil)	1,469.37	48% (179 mg, 0.12 mol)
JR-04 (Colorless oil)	1,290.10	47% (157 mg, 0.11 mol)
JR-05 (Colorless oil)	1,347.67	28% (95 mg, 0.07 mol)
JR-06 (Colorless oil)	1,314.04	22% (73 mg, 0.05 mol)

Figure S1-1: ^{1}H-NMR of **JR-01** in $CDCl_3$



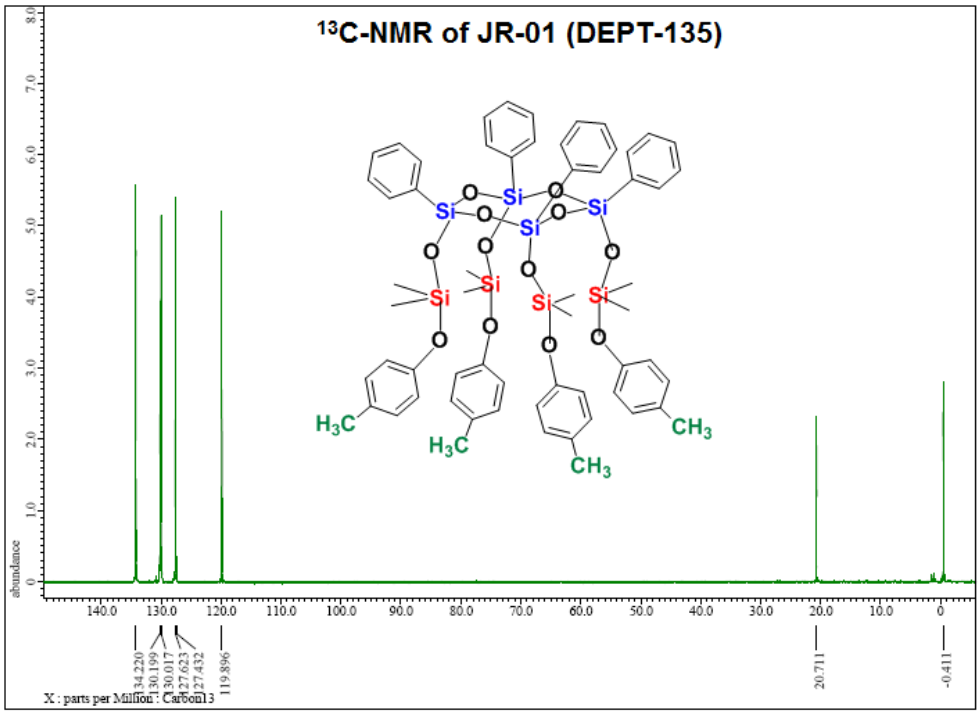
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.29 (s, 24H, $SiMe_2$), 2.25 (s, 12H, CH_3), 6.72-6.75 (m, 8H, C-H at aryl), 6.91-6.93 (m, 8 H, C-H at aryl), 7.04-7.09 (m, 8 H, C-H at aryl), 7.27-7.30 (m, 12 H, C-H at aryl)

Figure S1-2: ^{13}C-NMR of **JR-01** in $CDCl_3$



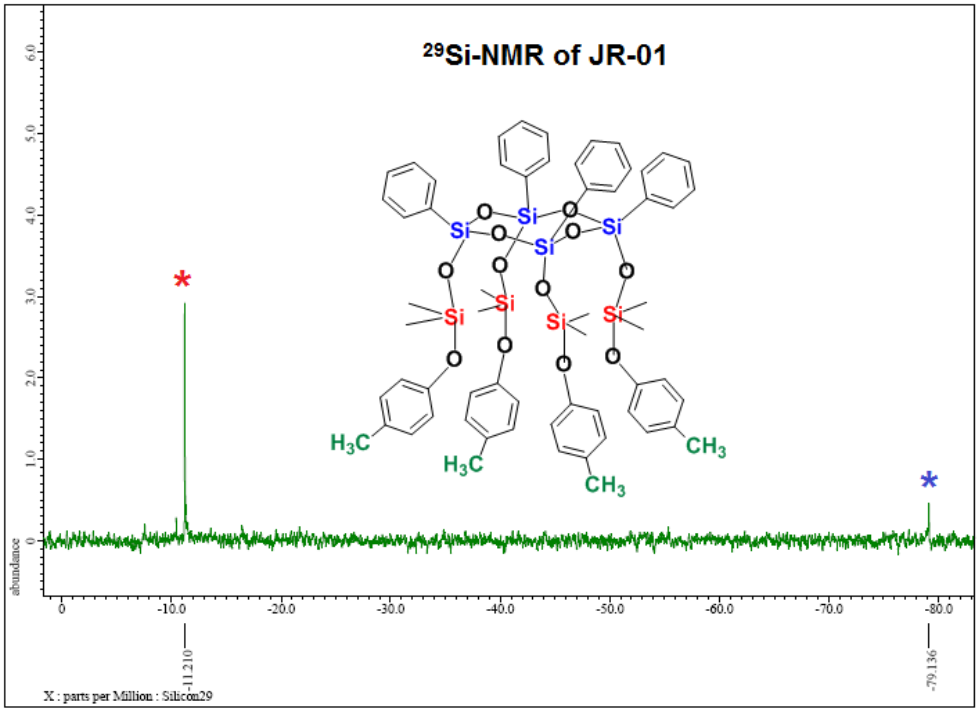
$^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): -0.41, 20.71, 119.89, 127.62, 130.01, 130.19, 130.91, 131.91, 134.22, and 152.09

Figure S1-3: ^{13}C-NMR of **JR-01** in $CDCl_3$ (DEPT-135) Three quaternary carbon atoms



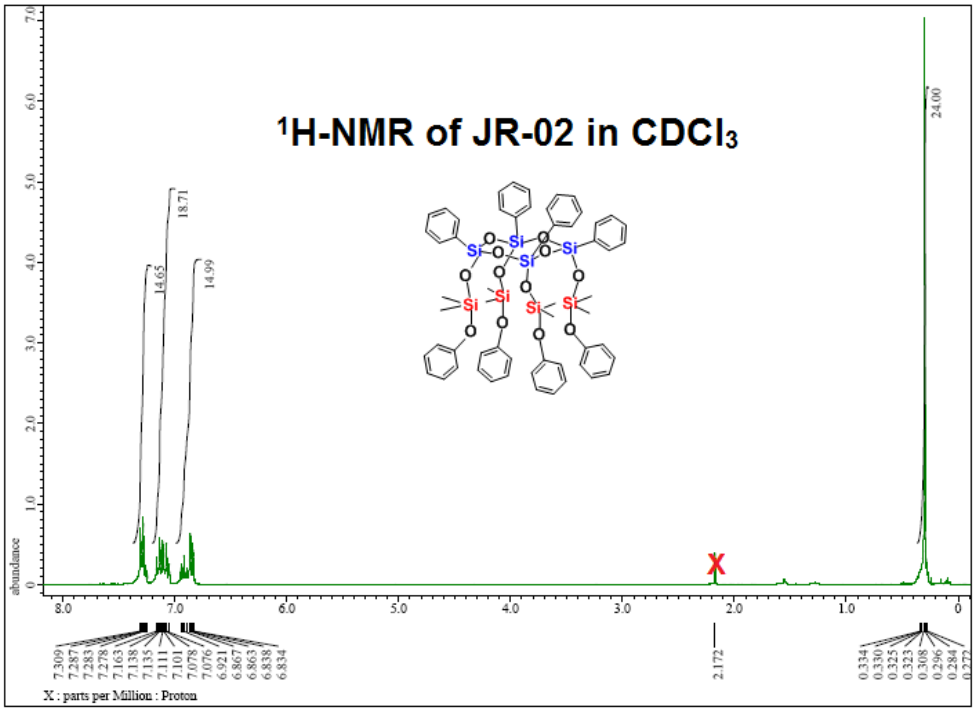
$^{13}C\{^1H\}$ NMR DEPT-135 (75.57 MHz, $CDCl_3$): -0.41, 20.71, 119.89, 127.43, 130.01, 134.22 (The disappearance of quaternary carbon atoms at 130.19, 131.91 and 152.09 were observed.)

Figure S1-4: ^{29}Si-NMR of **JR-01** in $CDCl_3$



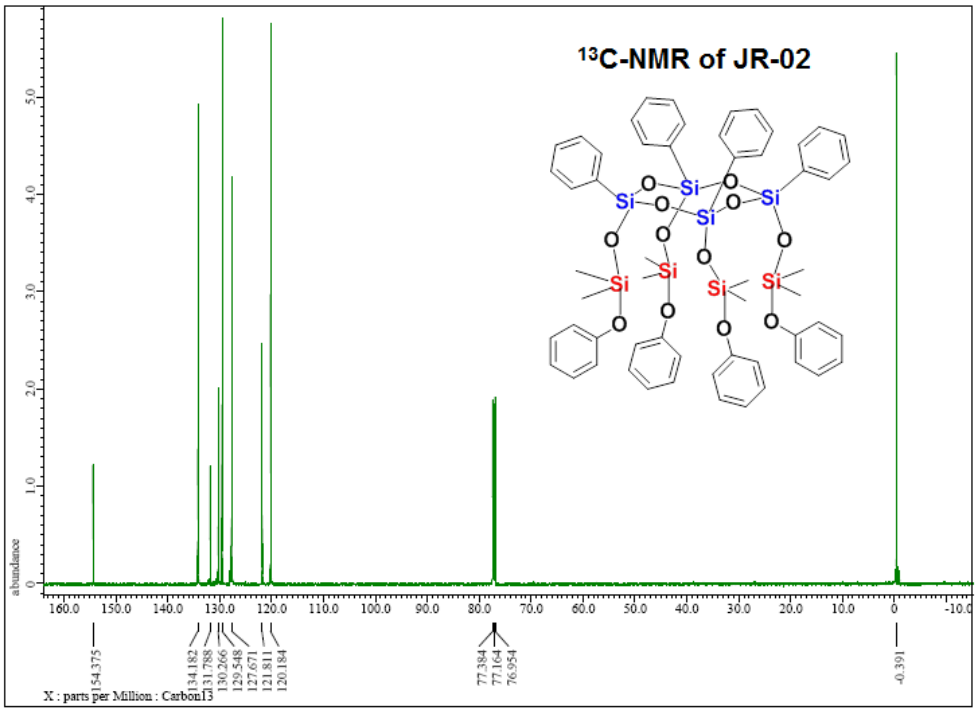
^{29}Si{^{1}H} NMR (59.71 MHz, $CDCl_3$): -11.2 (-O-SiMe_2-O-Ar) and -79.1 (Si-O-Si at T_4 ring).

Figure S2-1: ^{1}H-NMR of **JR-02** in $CDCl_3$



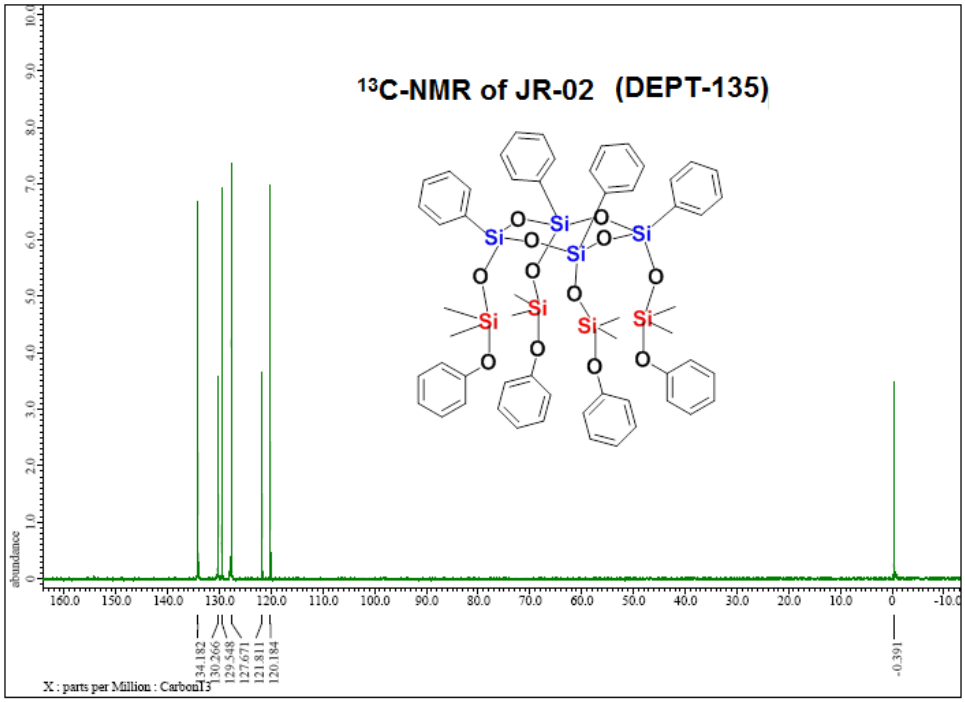
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.29 (s, 24H, SiMe_2), 6.83-6.92 (m, C-H at aryl), 7.07-7.13 (m, C-H at aryl), 7.27-7.30 (m, C-H at aryl), total aryl H = 40H

Figure S2-2: ^{13}C-NMR of **JR-02** in $CDCl_3$



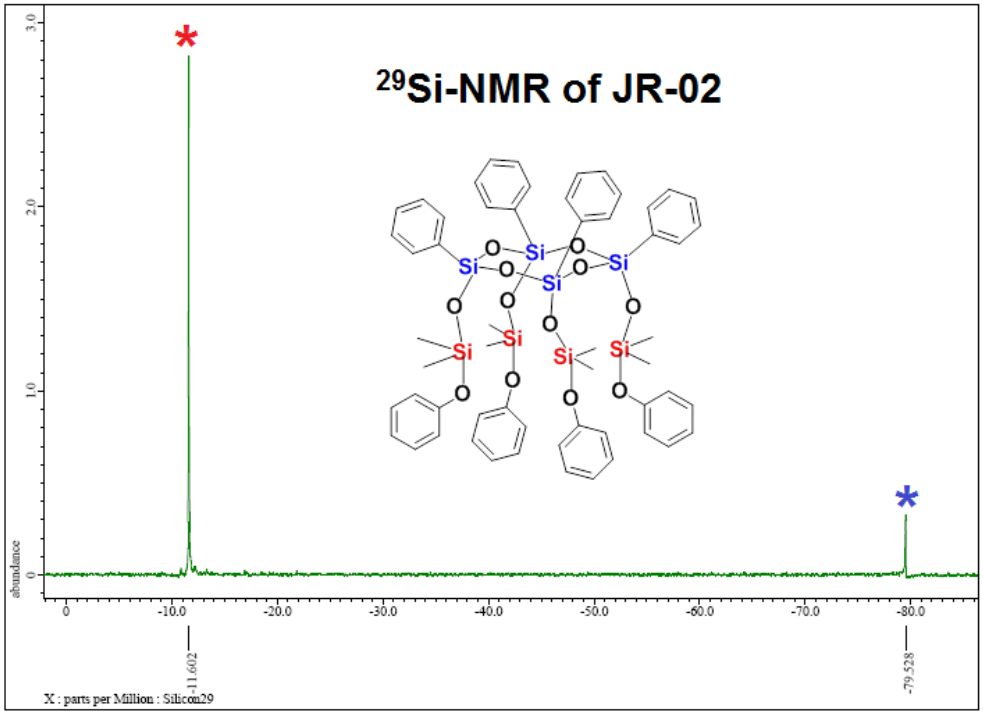
$^{13}C\{^{1}H\}$ NMR (75.57 MHz, $CDCl_3$): -0.39, 120.18, 121.81, 127.67, 129.54, 130.26, 131.78, 134.18, and 154.37

Figure S2-3: ^{13}C-NMR (DEPT-135) of **JR-02** in $CDCl_3$ Two quaternary carbon atoms



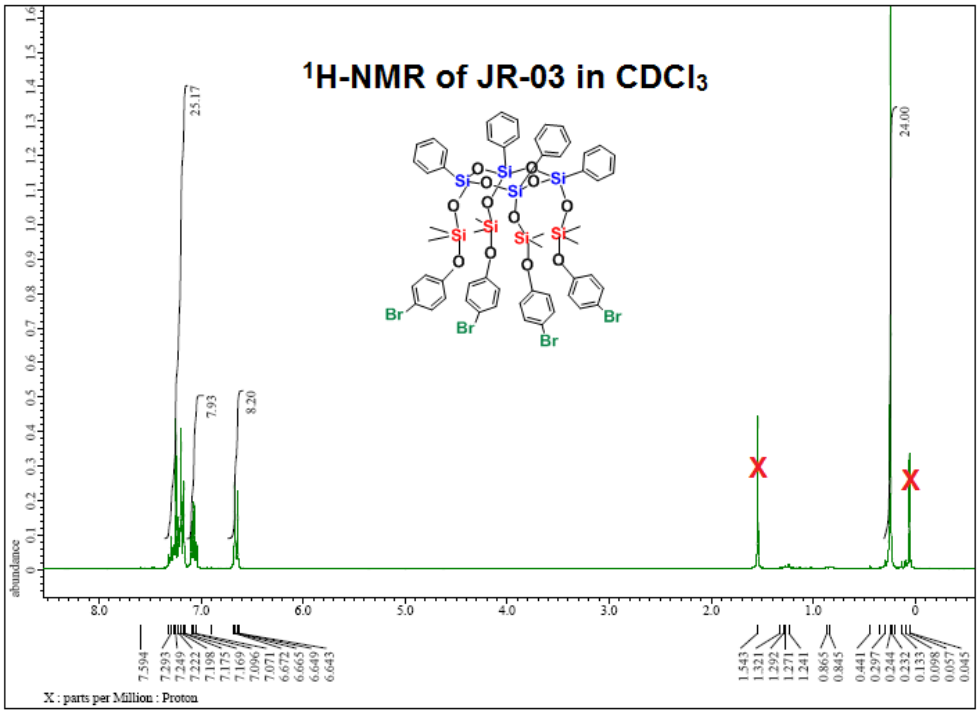
$^{13}C\{^{1}H\}$ NMR (75.57 MHz, CDCl3): -0.39, 120.18, 121.81, 127.67, 129.54, 130.26, and 134.18 (Disappearance of signal at 131.78 and 154.37 ppm refer to quaternary carbon)

Figure S2-4: ^{29}Si-NMR of **JR-02** in $CDCl_3$



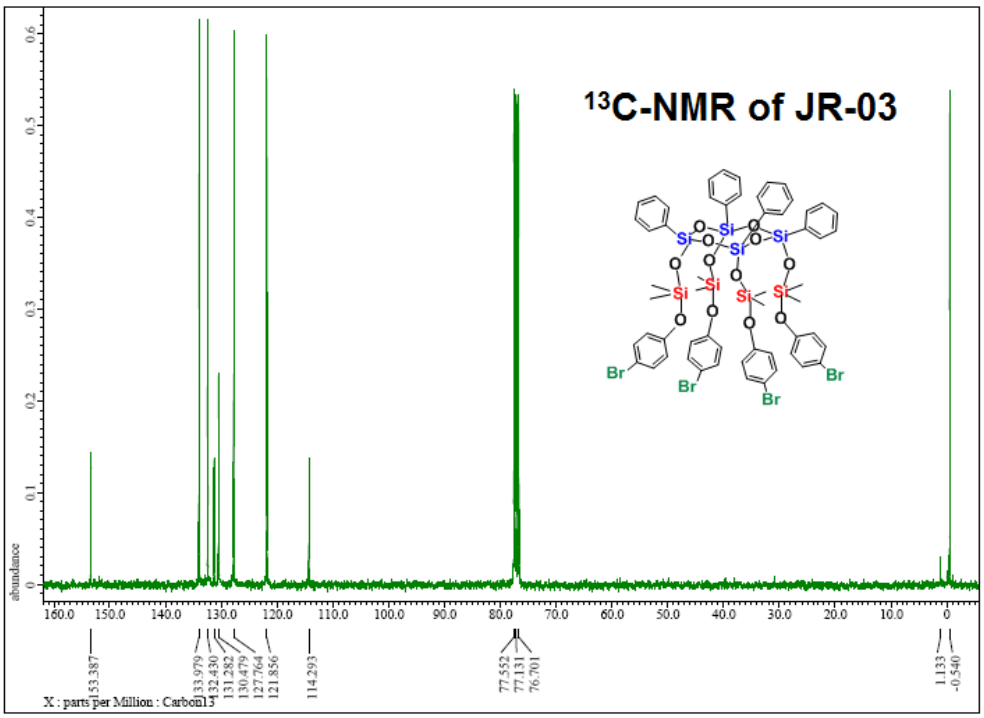
$^{29}Si\{^{1}H\}$ NMR (59.71 MHz, $CDCl_3$): -11.6 (-O-$\underline{Si}Me_2$-O-Ar) and -79.5 (Si-O-Si at T_4 ring).

Figure S3-1: ^{1}H-NMR of **JR-03** in $CDCl_3$ (Note that: This product is an air and moisture sensitive that can be decomposed when exposure to air or water giving unknown pink solid compound.)



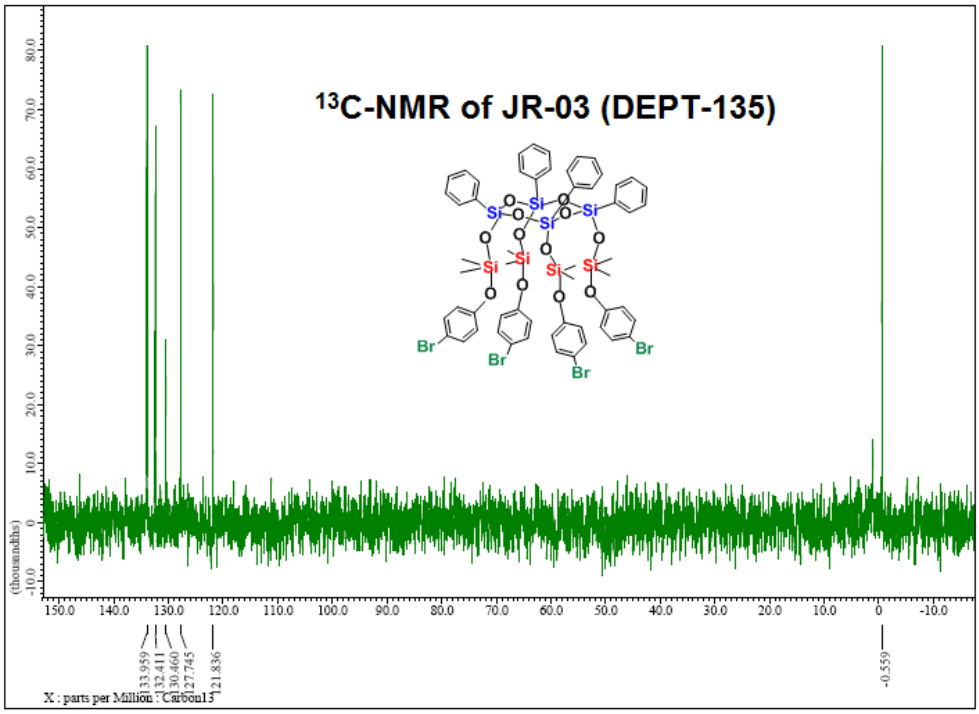
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.24 (s, 24H, $SiMe_2$), 6.65-6.68 (d, 8H, C-H at aryl), 7.10-7.18 (d, 8H, C-H at aryl), 7.23-7.30 (m, 20 H, Ph-H)

Figure S3-2: ^{13}C-NMR of **JR-03** in $CDCl_3$



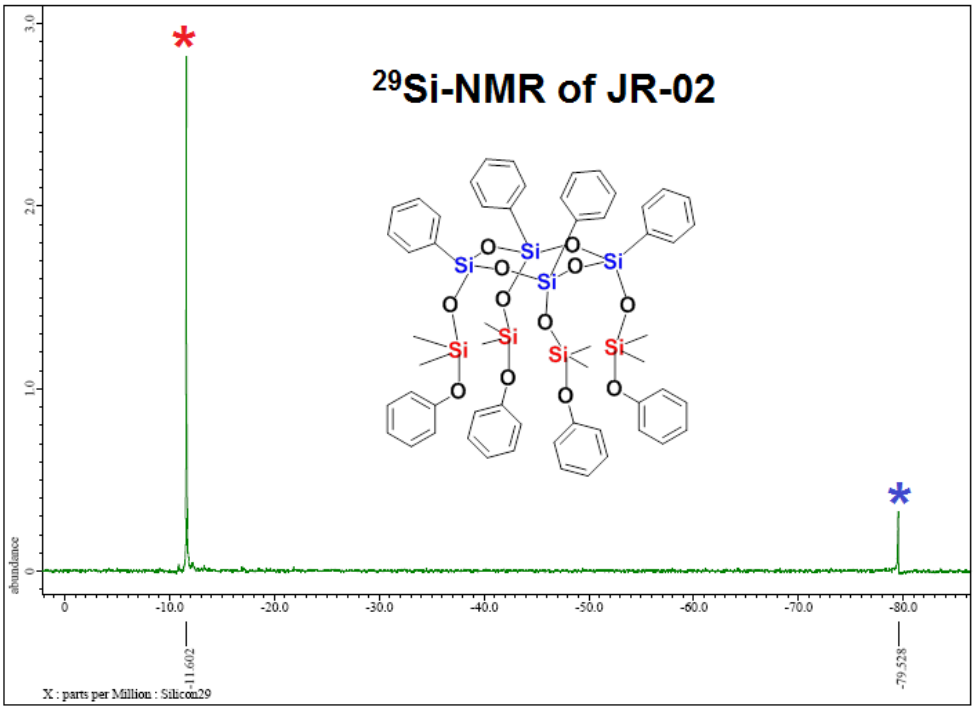
$^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): -0.54 (-Si-$\underline{C}H_3$), 114.29, 121.85, 127,76 130.47, 131.28, 132.43, 133.97, and 153.38

Figure S3-3: ^{13}C-NMR of **JR-03** in $CDCl_3$ (DEPT-135) Three quaternary carbon atoms



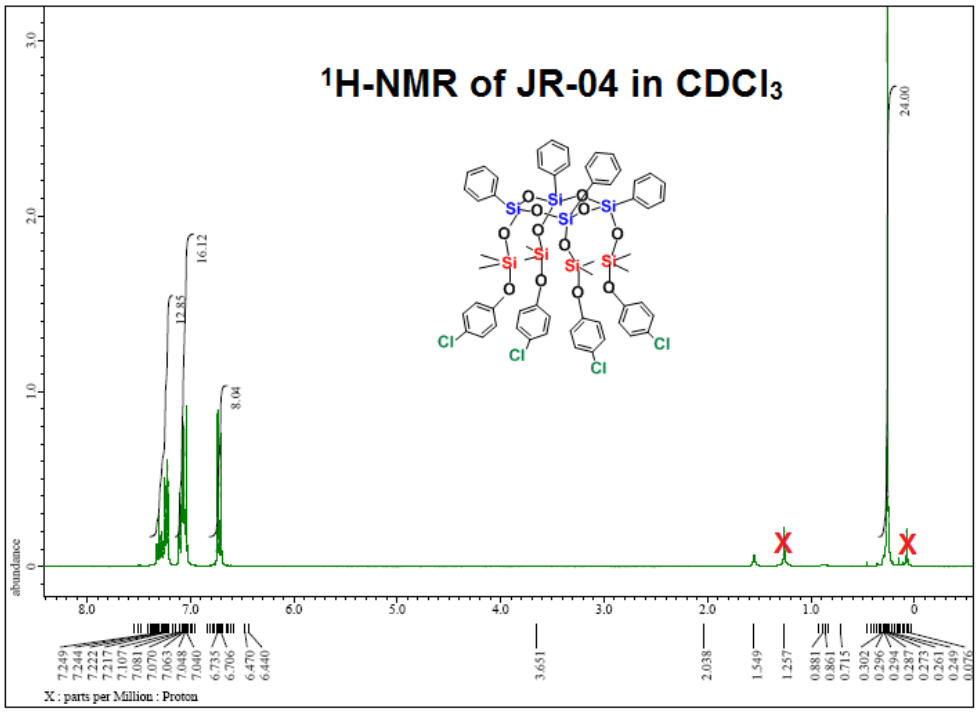
$^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$), (DEPT-135): -0.55 (-Si-$\underline{C}H_3$), 121.83, 127.74, 130.46, 132.41, and 133.95 (The disappearance of quaternary carbon atoms at 114.29, 131.28, and 153.38 were observed.)

Figure S3-4: ^{29}Si-NMR of **JR-03** in $CDCl_3$



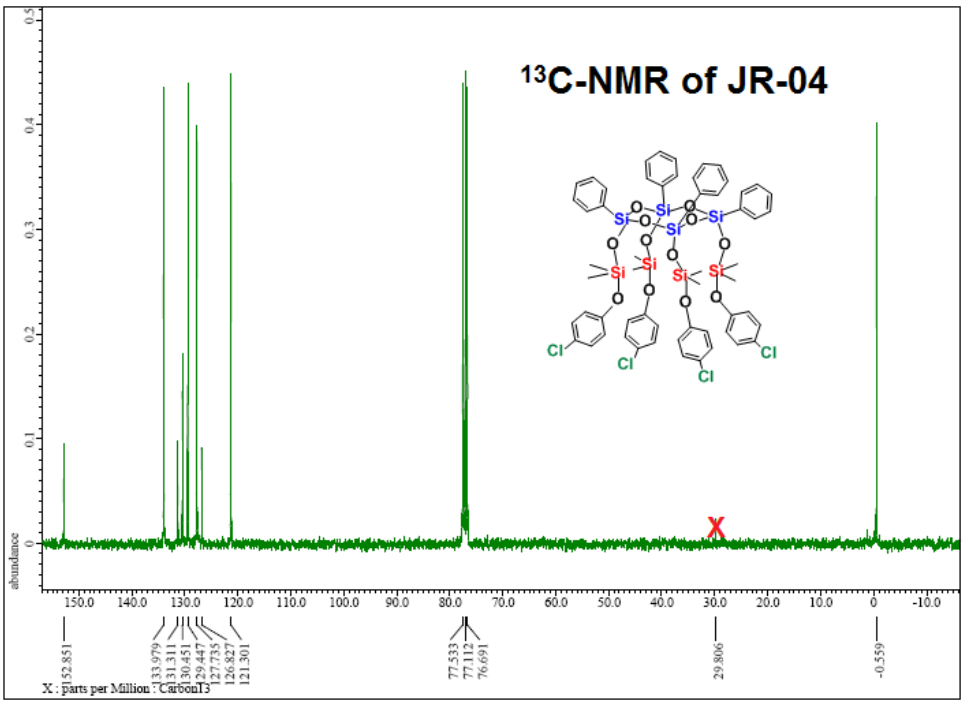
^{29}Si{^{1}H} NMR (59.71 MHz, $CDCl_3$): -11.6 (-O-SiMe_2-O-Ar) and -79.5 (Si-O-Si at T_4 ring).

Figure S4-1: ^{1}H-NMR of **JR-04** in $CDCl_3$



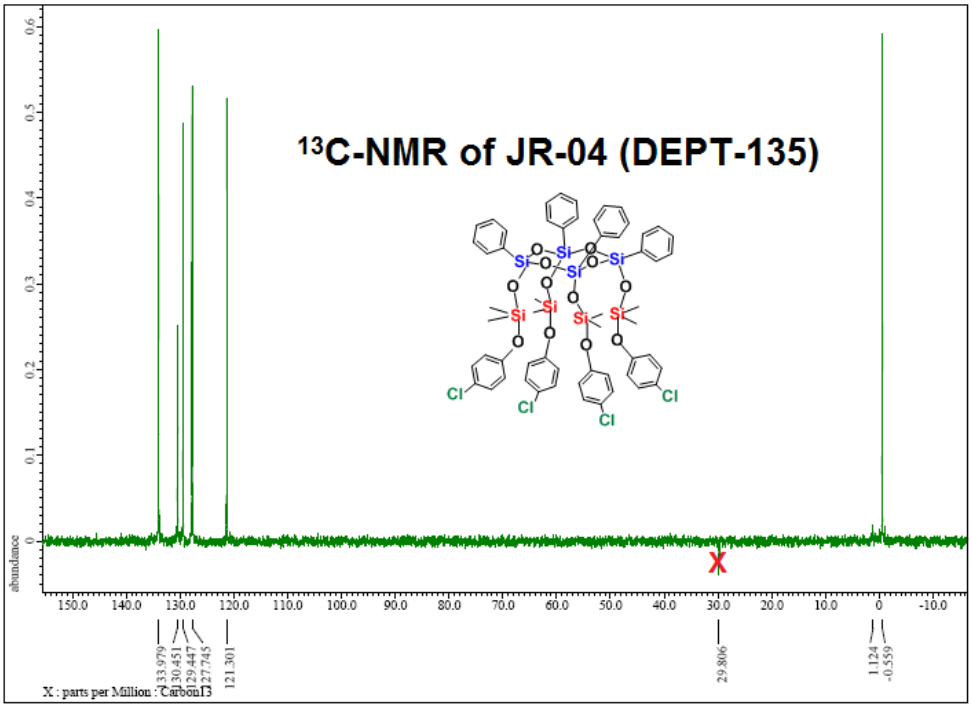
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.25 (s, 24H, $SiMe_2$), 6.70-6.73 (d, 8H, C-H at C-H at aryl), 6.70-6.73 (d, 16H, C-H at aryl), 7.23-7.30 (m, 12 H, C-H at aryl)

Figure S4-2: ^{13}C-NMR of **JR-04** in $CDCl_3$



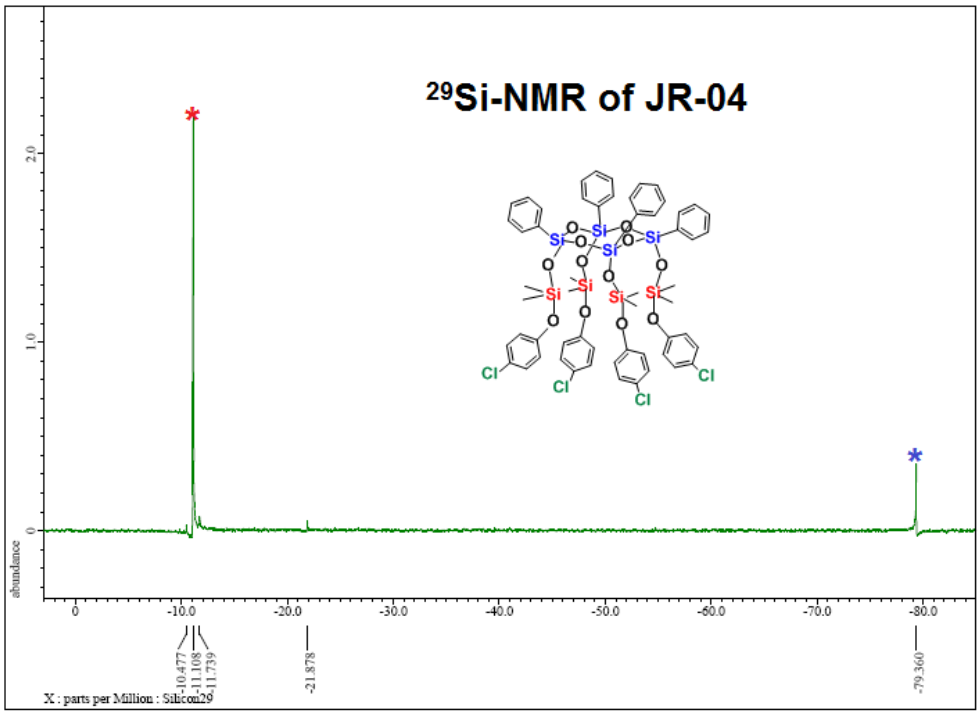
$^{13}C\{^{1}H\}$ NMR (75.57 MHz, $CDCl_3$): -0.55, 121.30, 126.82, 127.73, 129.44, 130.45, 131.31, 133.97, and 152.85

Figure S4-3: ^{13}C-NMR of **JR-04** in $CDCl_3$ (DEPT-135): Three quaternary carbon atoms



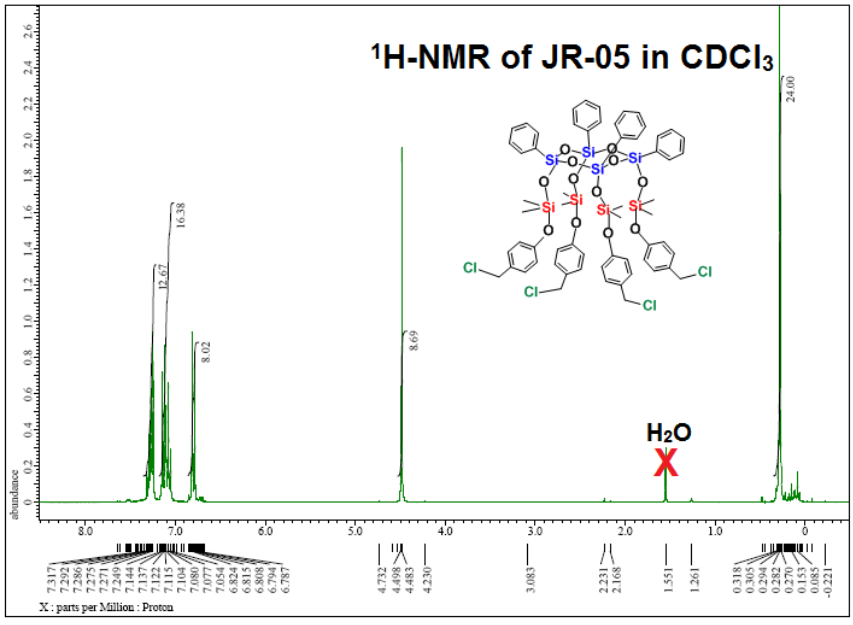
(DEPT-135): -0.56 (-Si-$\underline{C}H_3$), 121.30, 127.74, 129.45, 130.45, and 133.97 (The disappearance of quaternary carbon atoms at 126.82, 131.31 and 152.85 were observed.)

Figure S4-4: ^{29}Si-NMR of **JR-04** in $CDCl_3$



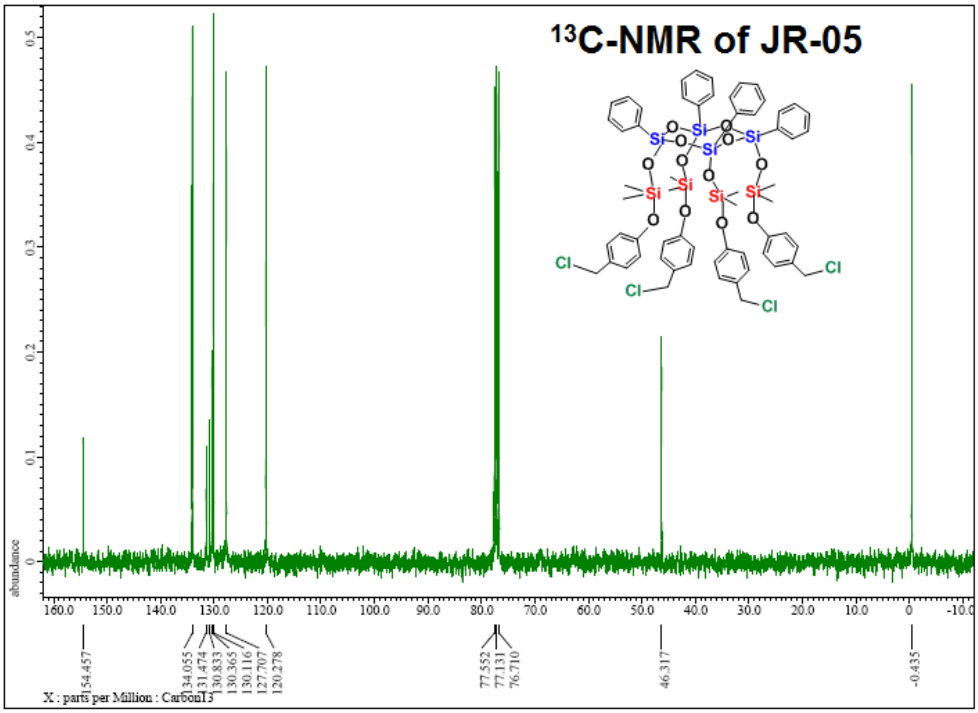
^{29}Si{^{1}H} NMR (59.71 MHz, $CDCl_3$): -11.1 (-O-SiMe_2-O-Ar) and -79.4 (Si-O-Si at T_4 ring).

Figure S5-1: ^{1}H-NMR of **JR-05** in $CDCl_3$



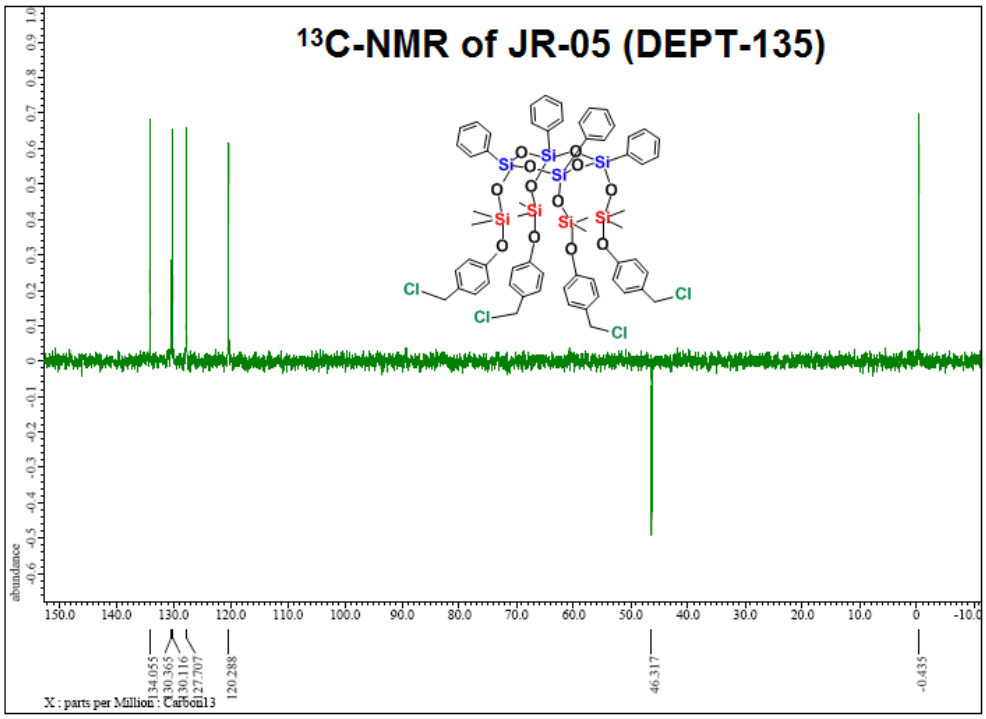
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.27 (s, 24H, SiMe_2), 4.48 (s, 8H, -CH_2), 6.78-6.82 (m, 8H, C-H at aryl), 7.05-7.14 (m, 16 H, C-H at aryl), 7.25-7.32 (m, 12H. C-H at aryl)

Figure S5-2: ^{13}C-NMR of **JR-05** in $CDCl_3$



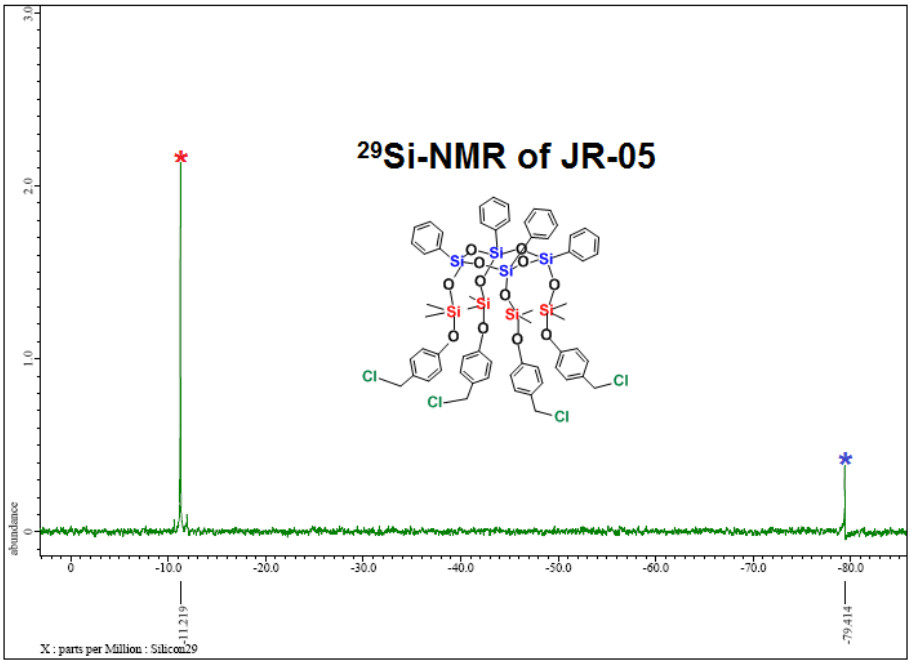
^{13}C{^{1}H} NMR (75.57 MHz, $CDCl_3$): -0.44, 46.32, 120.28, 127.70, 130.11, 130.36, 130.83, 131.47, 134.05, and 154.45.

Figure S5-3: ^{13}C-NMR of **JR-05** in $CDCl_3$ (DEPT-135) Three quaternary carbon atoms



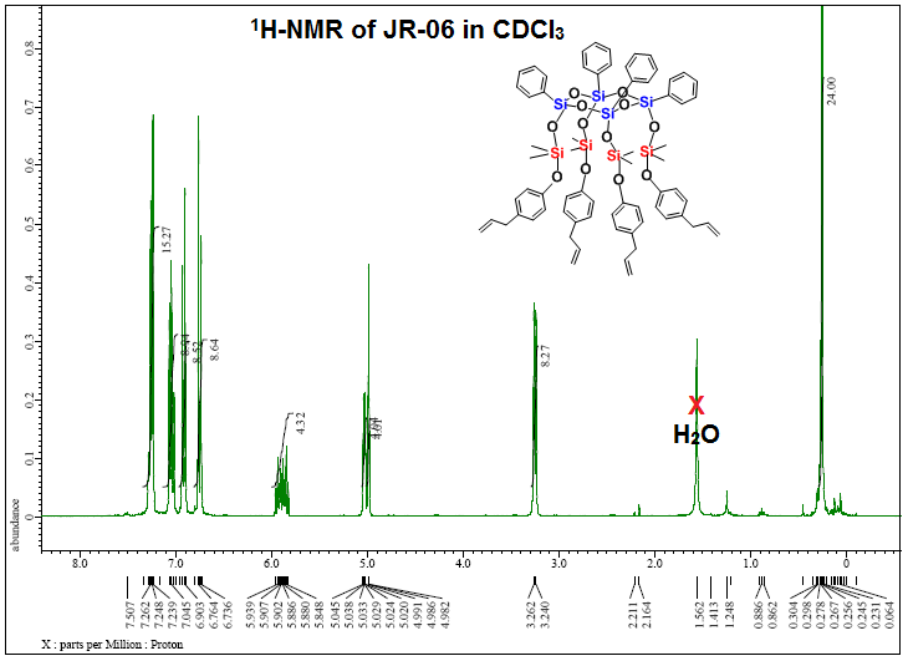
(DEPT-135): -0.44 (-Si-$\underline{C}H_3$), 46.32 (inversion peak of $-CH_2Cl$) 120.28, 127.70, 130.11, 130.36, and 134.05 (C=$\underline{C}$-H). (According to DEPT-135, the disappearance of signals at 130.36, 131.47, and 154.45 ppm refer to quaternary carbon peak)

Figure S5-4: ^{29}Si-NMR of **JR-05** in $CDCl_3$



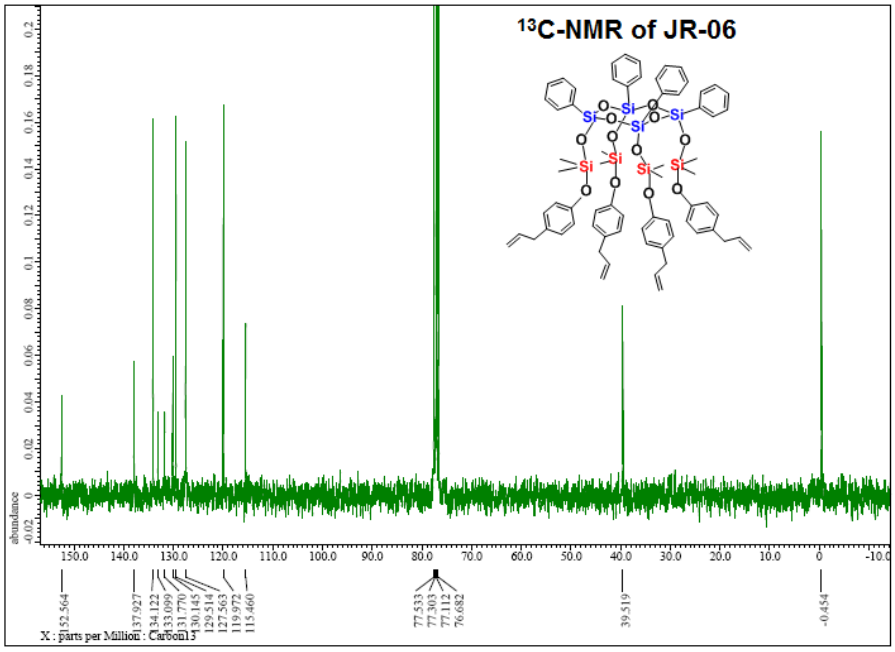
^{29}Si{^{1}H} NMR (59.71 MHz, $CDCl_3$): -11.2 (-O-SiMe_2-O-Ar) and -79.4 (Si-O-Si at T_4 ring).

Figure S6-1: H-NMR of **JR-06** in $CDCl_3$



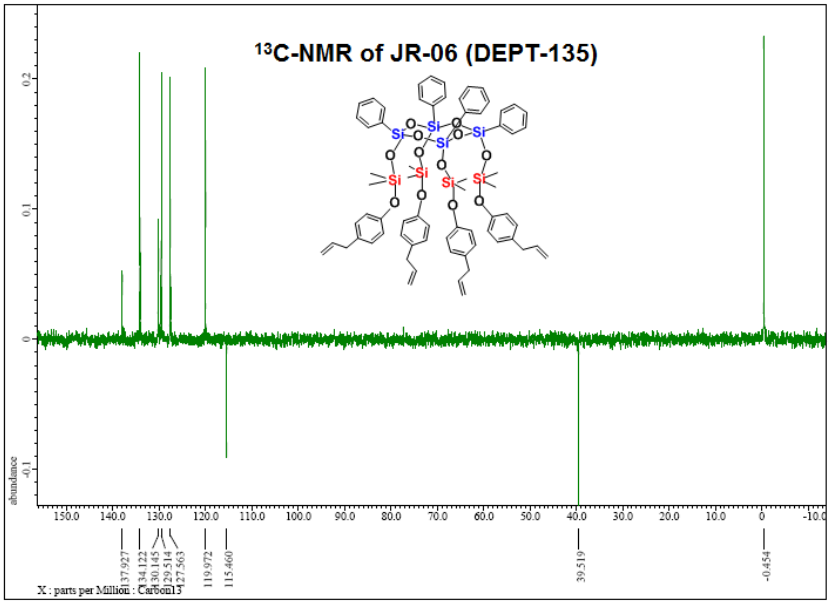
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.26 (s, 24H, SiMe2), 3.26-3.40 (d, 8 H, -CH_2) 4.98-5.04 (dd, 8 H, -C=CH_2), 5.84-5.94 (m, 4H, -CH=CH_2), 6.73-6.76 (m, 8H, C-H at aryl), 6.73-6.76 (m, 8H, C-H at aryl), 6.90-7.05 (m, 8H, C-H at aryl), 7.06-7.10 (d, 8H, C-H at aryl), 7.24-7.26 (m, 8 H, C-H at aryl)

Figure S6-2: ^{13}C-NMR of **JR-06** in $CDCl_3$



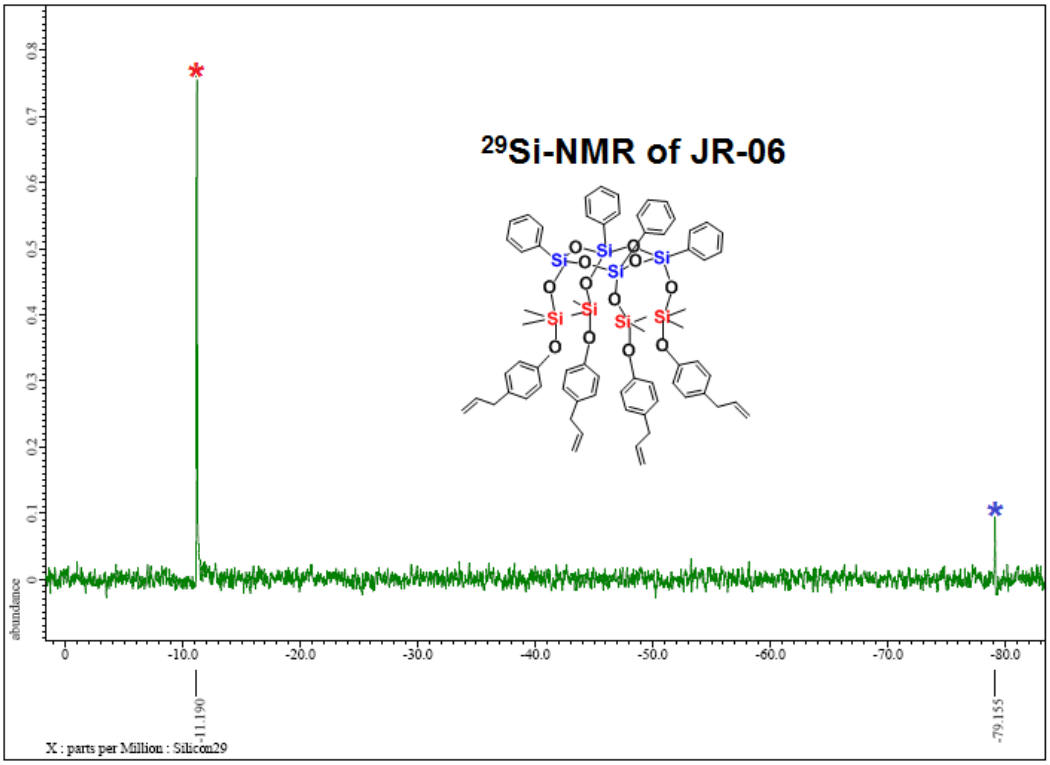
^{13}C{^{1}H} NMR (75.57 MHz, $CDCl_3$): -0.45, 39.51, 115.46, 119.97, 127.56, 129.51, 130.14, 131.77, 133.09, 134.12, 137.92, and 152.56.

Figure S6-3: ^{13}C-NMR of **JR-06** in $CDCl_3$ (DEPT-135) Three quaternary carbon atoms



(DEPT-135):): -0.45 (-Si-$\underline{C}H_3$), 39.52 (inversion peak of -CH_2) , 115.46 (inversion peak of –CH=CH_2), 119.97, 127.56, 129.51, 130.14, 134.12, and 137.92. (According to DEPT-135, the disappearance of signals at 131.77, 133.09, and 152.56. refer to quaternary carbon peak)

Figure S6-4: ^{29}Si-NMR of **JR-06** in $CDCl_3$



^{29}Si{^{1}H} NMR (59.71 MHz, $CDCl_3$): -11.2 (-O-$SiMe_2$-O-Ar) and -79.2 (Si-O-Si at T_4 ring).

Figure S7-1: MALDI-TOF results of **JR-01** (Calculated $[MW+Na]^+$ = 1,232.31, found 1,233.48)

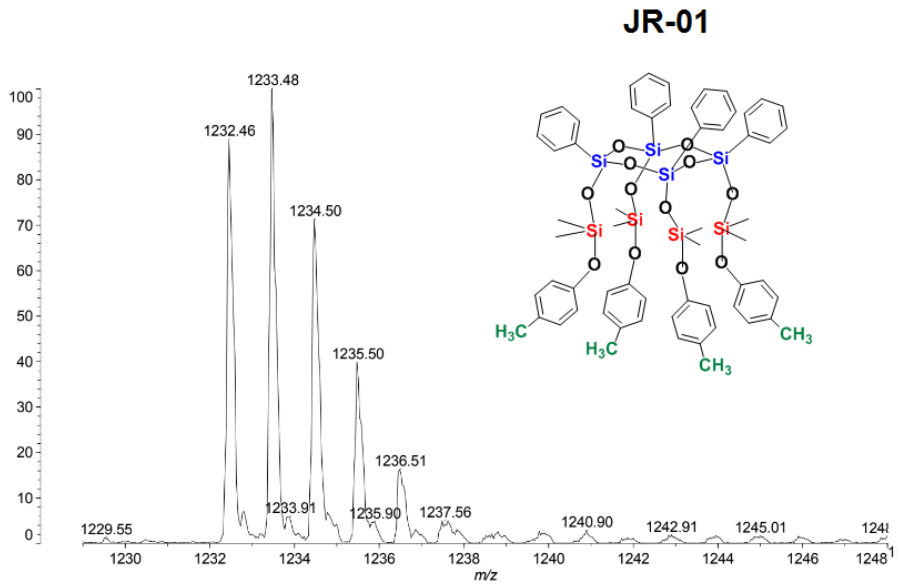


Figure S7-2: MALDI-TOF results of **JR-02** (Calculated $[MW+Na]^+$ = 1,175.24, found 1,175.37)

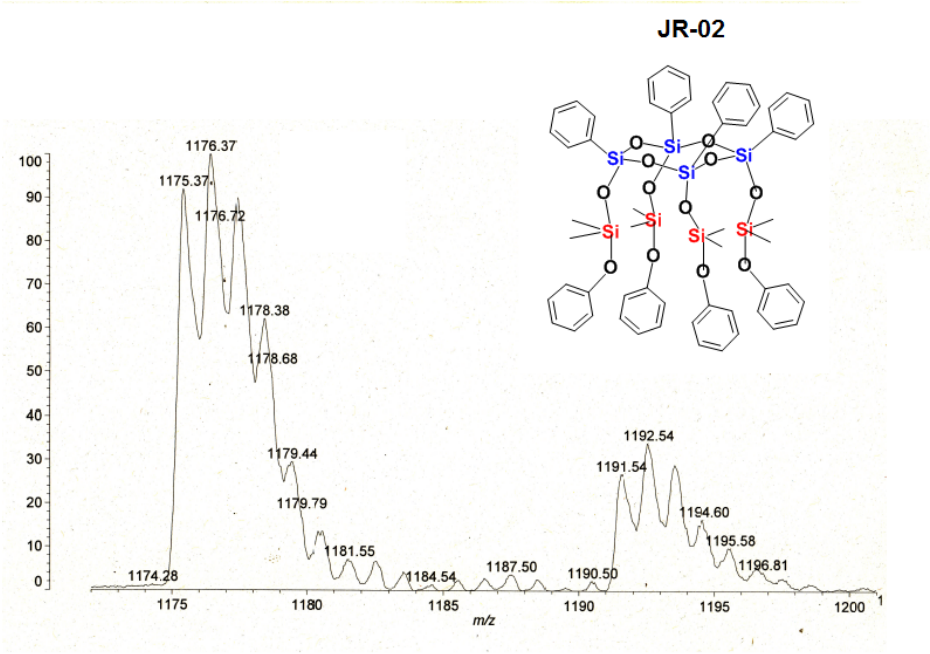


Figure S7-3: MALDI-TOF results of **JR-03** (Calculated $[MW+Na]^+$ = 1,492.88, found 1,492.20)

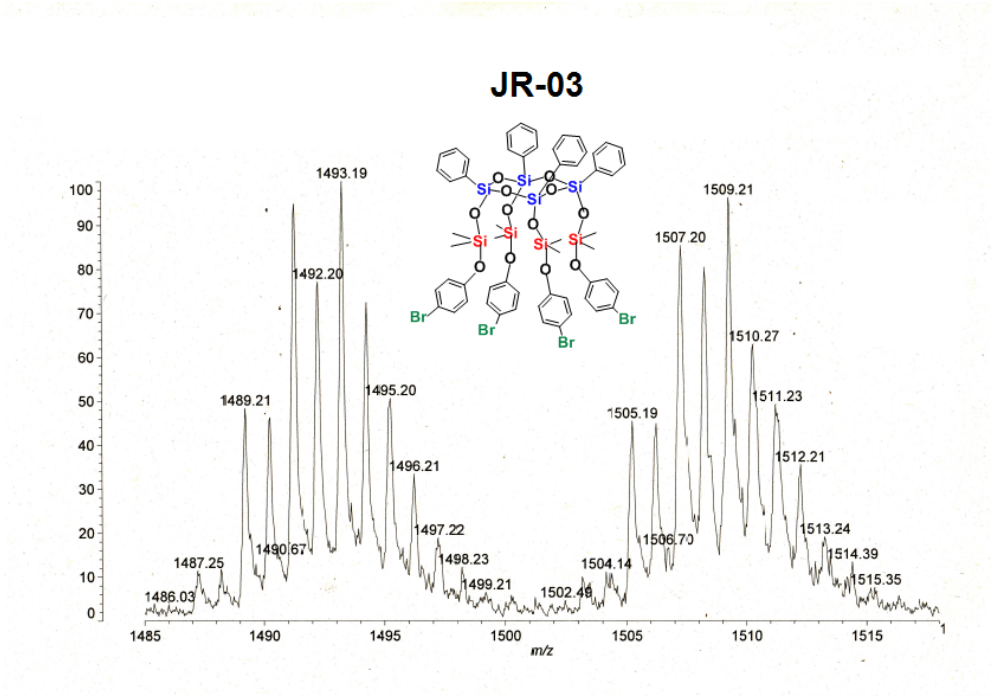


Figure S7-4: MALDI-TOF results of **JR-04** (Calculated $[MW+Na]^+$ = 1,313.09, found 1,313.14)

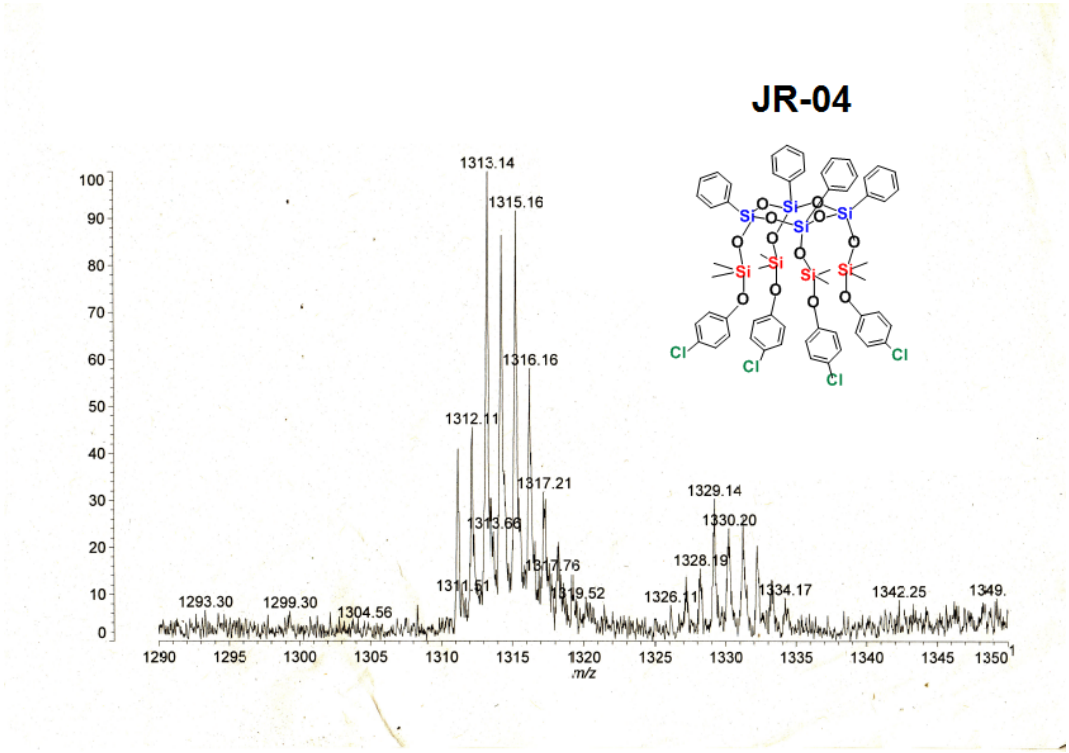


Figure S7-5: MALDI-TOF results of **JR-04** (Calculated $[MW+Na]^+$ = 1,369.15, found 1,369.40)

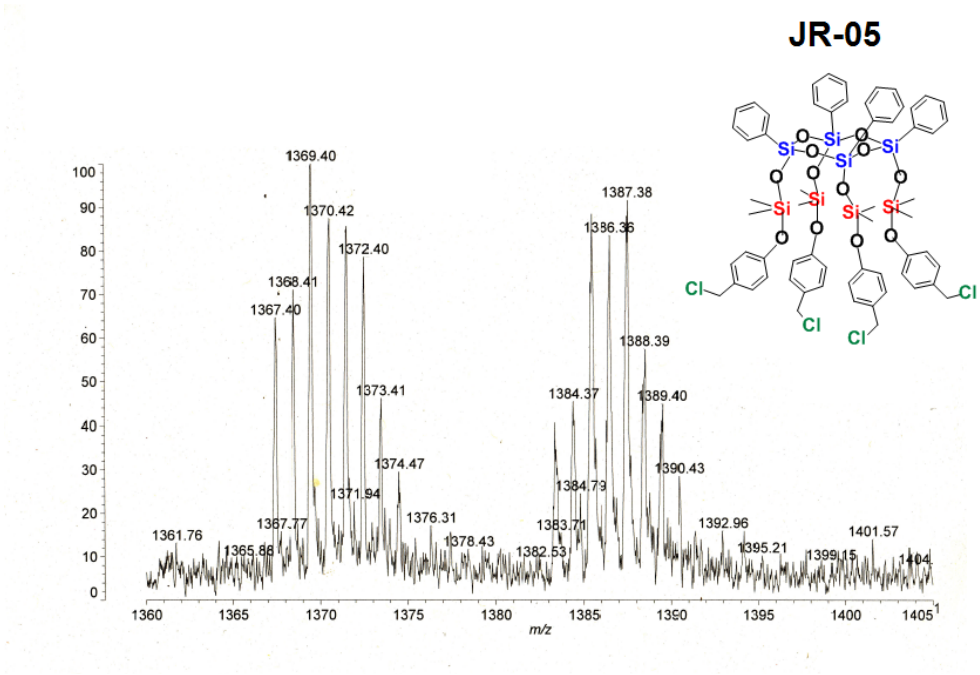
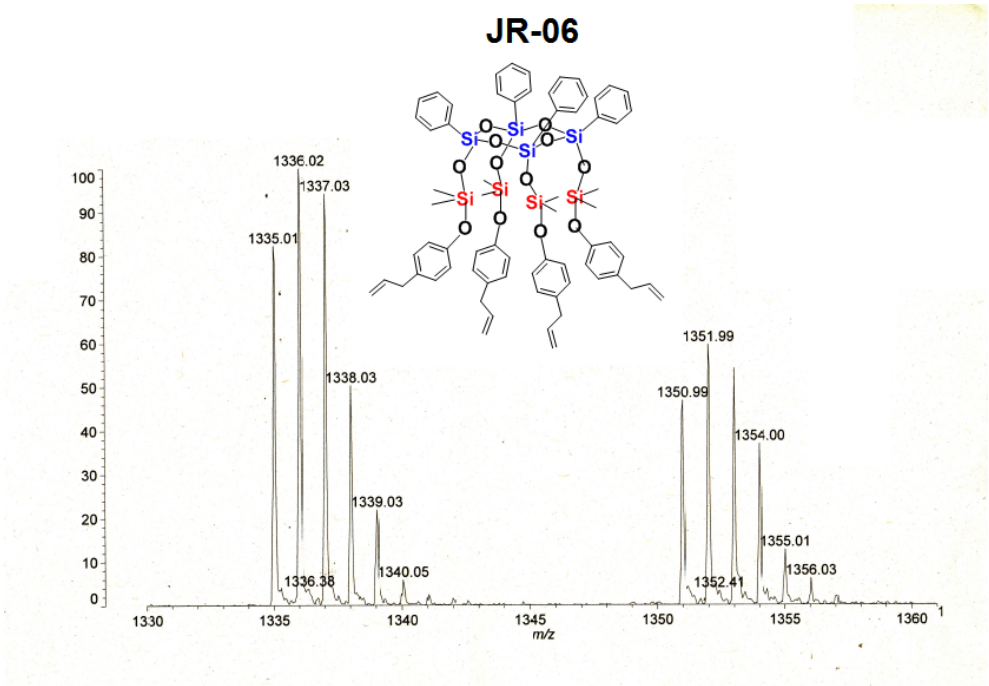


Figure S7-6: MALDI-TOF results of **JR-04** (Calculated $[MW+Na]^+$ = 1,336.37, found 1,336.02)



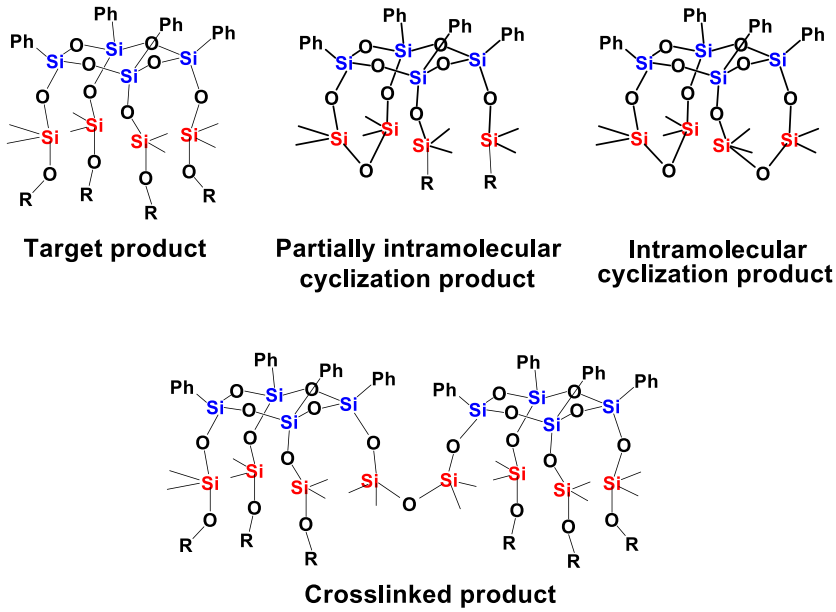
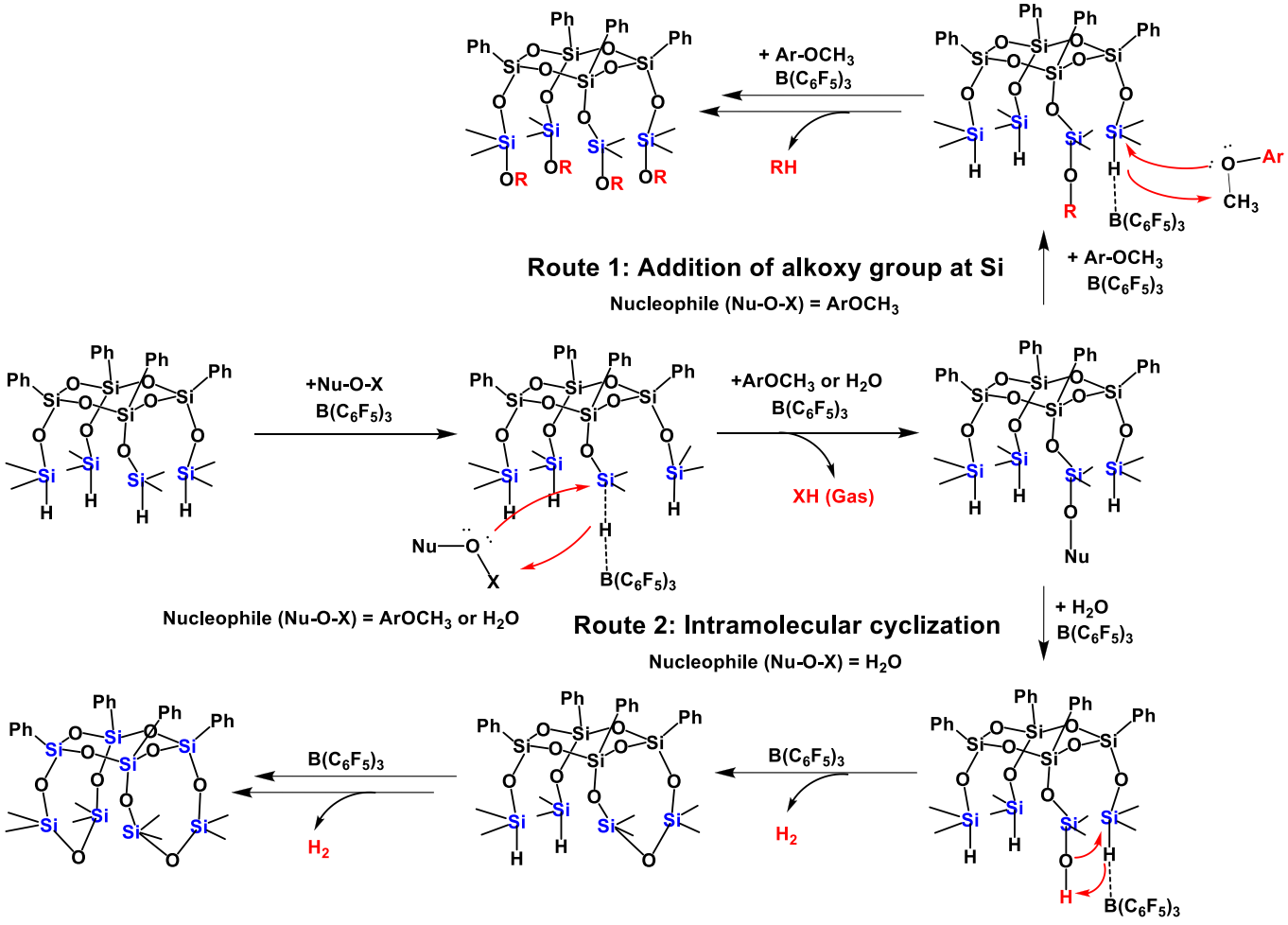
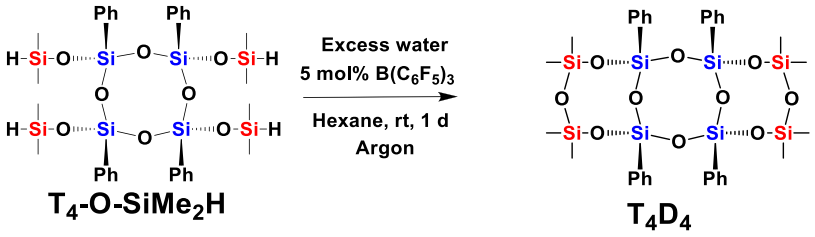


Figure S8: The possible by-products from the functionalization of **T_4-SiMe$_2$H**.



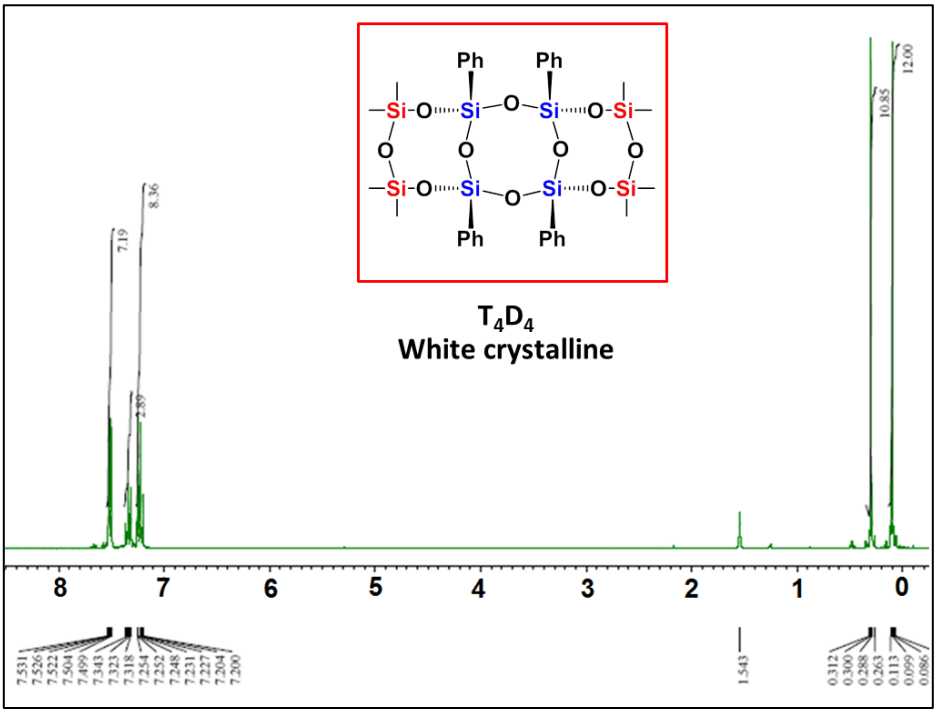
Scheme S9: Possible reaction mechanism

1-4. General procedure for controlled reaction



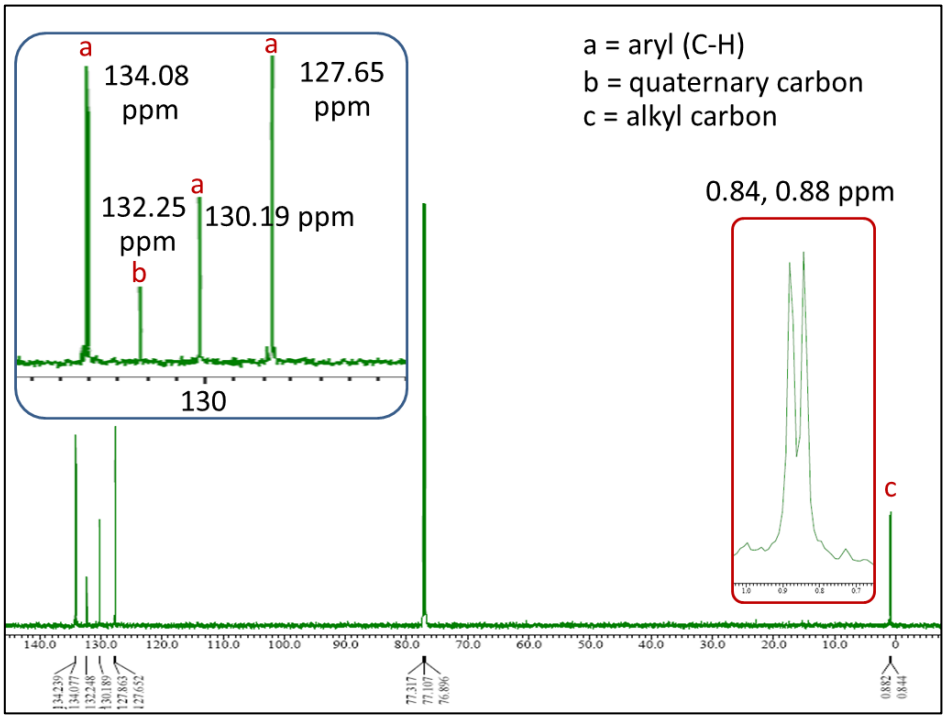
Under anhydrous conditions with argon line, **T_4-O-$SiMe_2H$** (200 mg, 0.255 mmol) with the water were mixed with anhydrous hexane. After stirring for a while, the small amount of $B(C_6F_5)_3$ (7.5 mg, 0.012 mmol) was added into the solution mixture. The reaction was stirred for 24 h at room temperature and quenched with water. The product was extracted using hexane and dried over anhydrous Na_2SO_4. After solvent evaporated, the product was purified using GPC to give the white crystalline of **T_4D_4** as products.

Figure S10-1: ^{1}H -NMR of isolated product **T_4D_4**



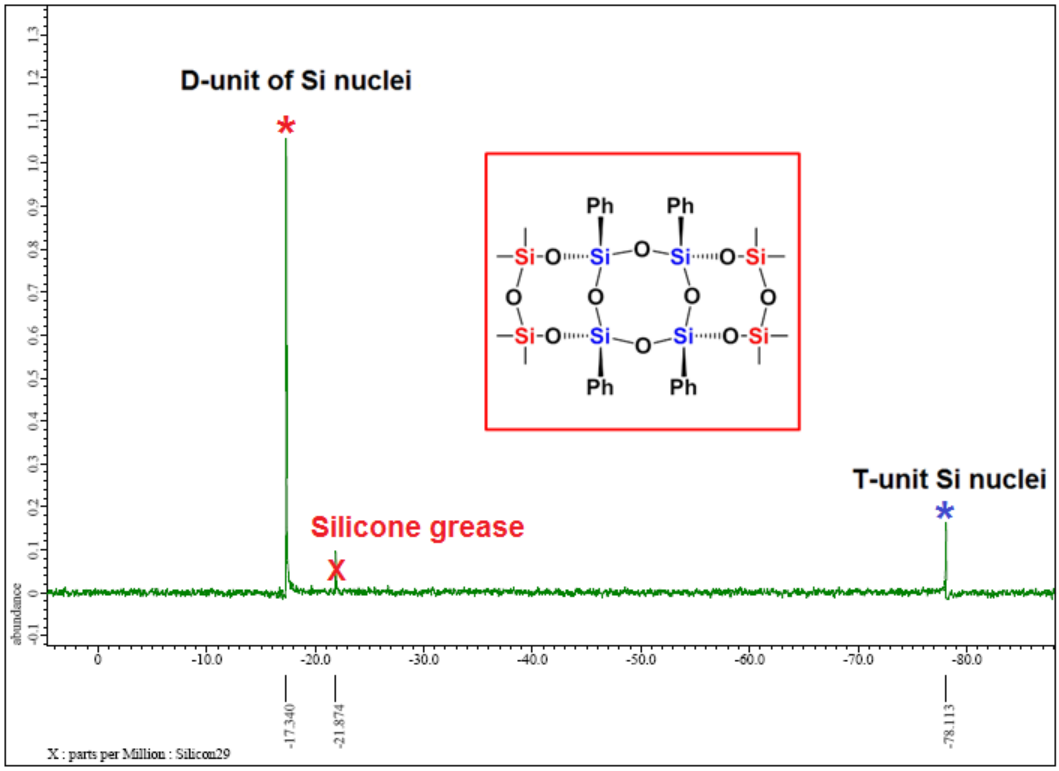
^{1}H NMR (300.5 MHz, $CDCl_3$): δ 0.99 (s, 12H, SiMeMe), 0.300 (s, 12H, SiMeMe), 7.200-7.254 (m, 8H, Ar-H), 7.318-7.343 (m, 4H, Ar-H), 7.499-7.531 (m, 8H, Ar-H)

Figure S10-2: ^{13}C -NMR of isolated product **T_4D_4**



$^{13}C\{^{1}H\}$ NMR (150.91 MHz, $CDCl_3$): δ = 0.84, 0.88 ppm (-$\underline{C}H_3$), 127.65, 130.19, 134.08 ppm (aromatic carbon (-C=$\underline{C}$-H) at phenyl group), and 132.25 ppm (quaternary carbon at phenyl group)

Figure S10-3: ^{29}Si -NMR of isolated product **T_4D_4**



$^{29}Si\{^{1}H\}$ NMR (59.71 MHz, $CDCl_3$): -16.83 (-O-$SiMe_2$-O-Ar) and -77.64 (Si-O-Si at T_4 ring).

Figure S10-4: MALDI-TOF spectra of **T_4D_4**.

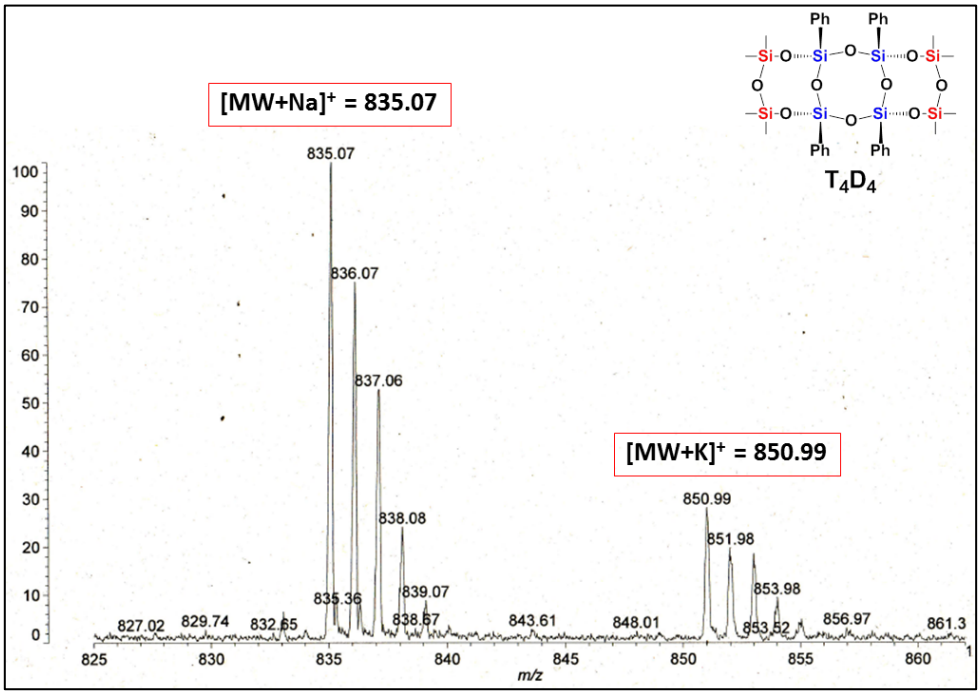


Figure S11: MALDI-TOF spectra of by-products from controlled reaction

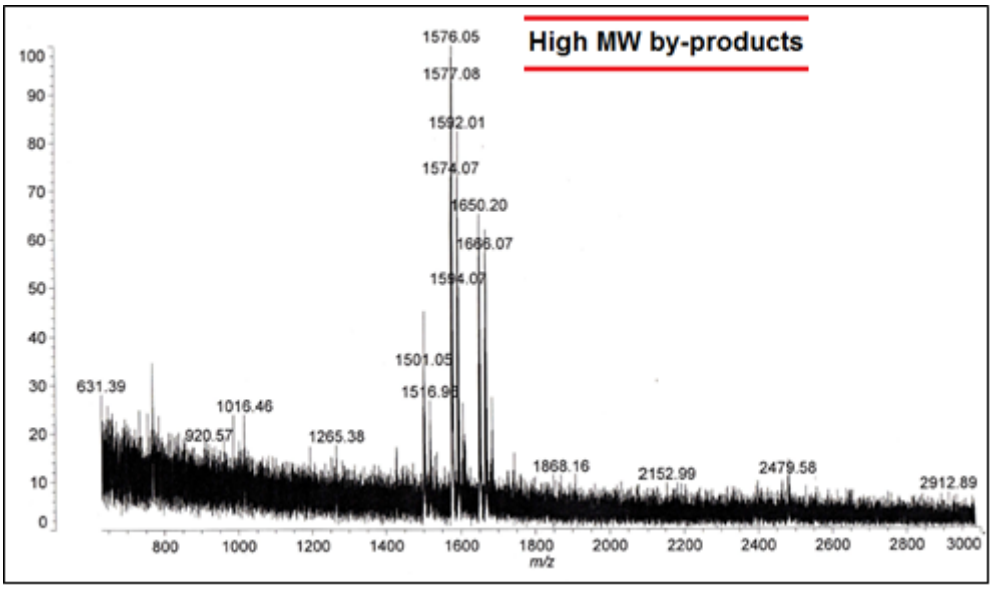


Table S2: Possible by-products from controlled reaction analysed by MALDI-TOF

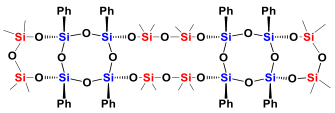
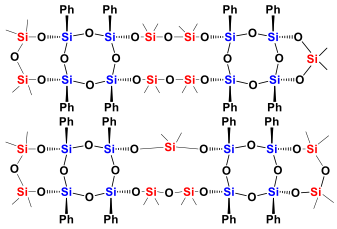
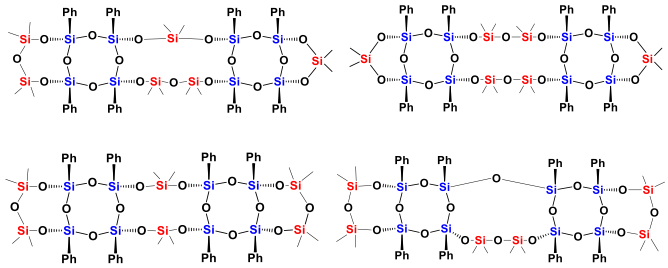
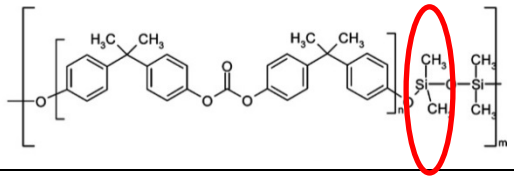
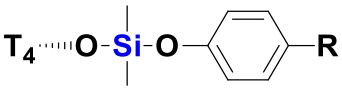
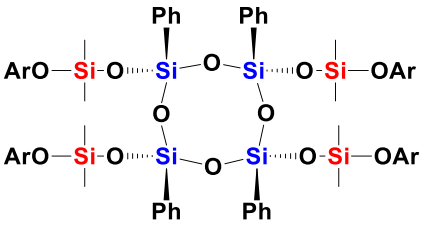
Possible structure of by-products derived from MALDI-TOF results	Calculated $[(M + Na)]^+$	Found
	1648.21	1652.10
		1654.17
		1650.20
	1574.19	1574.02
		1578.05
		1574.07
	1501.02	1501.96
		1501.94
		1501.05

Table S3 The comparison of ^{29}Si-NMR spectra between our results vs the previous studies.

<table>
<tr><td colspan="5">Signal from D-unit silicon atom</td></tr>
<tr><td colspan="2">Structure</td><td>Sample name</td><td>Signals</td><td>References</td></tr>
<tr><td colspan="2">  </td><td>PAS−BPA−PC
Copolymer 8</td><td>-12.3 ppm</td><td>Cella et al.
(Ref. 1)</td></tr>
<tr><td colspan="2">  </td><td>JR-01
JR-02
JR-03
JR-04
JR-05
JR-06</td><td>-11.6 ppm
-11.2 ppm
-11.0 ppm
-11.2 ppm
-11.2 ppm
-11.2 ppm</td><td>This work</td></tr>
<tr><td colspan="5">Signal from all-cis T4
  </td></tr>
<tr><td>R1</td><td>R2</td><td>Sample name</td><td>Signals</td><td></td></tr>
<tr><td>-Ph</td><td>-O-SiMe$_2$-OAr</td><td>JR-01
JR-02
JR-03
JR-04
JR-05
JR-06</td><td>-79.5 ppm
-79.1 ppm
-79.3 ppm
-79.4 ppm
-79.4 ppm
-79.2 ppm</td><td>This work</td></tr>
<tr><td>C$_6$H$_5$</td><td>-O-SiMe$_2$-Vi
-O-SiMe$_2$-Allyl</td><td>CTS-1
CTS-2</td><td>-79.3 ppm
-79.5 ppm</td><td rowspan="3">Panicsh et al.
(Ref. 2)</td></tr>
<tr><td>4-Bromophenyl</td><td>-O-SiMe$_3$</td><td>CTS-6</td><td>-79.9 ppm</td></tr>
<tr><td>4-Chlorophenyl</td><td>-O-SiMe$_3$</td><td>CTS-5</td><td>-79.9 ppm</td></tr>
<tr><td>4-Iodophenyl</td><td>-O-SiMe$_3$
-O-SiMe$_2$-Vi</td><td>CTS-8
CTS-16</td><td>-79.4 ppm
-79.3 ppm</td><td></td></tr>
<tr><td>4-Bromophenyl</td><td>-O-SiMe$_3$</td><td>Compound 5</td><td>-79.9</td><td rowspan="4">Ronchi et al.
(ref. 3)</td></tr>
<tr><td>4-Chlorophenyl</td><td>-O-SiMe$_3$</td><td>Compound 6</td><td>-79.9</td></tr>
<tr><td>4-Styryl</td><td>-O-SiMe$_3$</td><td>Compound 7</td><td>-79.5</td></tr>
<tr><td>4-chlorobenzyl</td><td>-O-SiMe$_3$</td><td>Compound 8</td><td>-79.9</td></tr>
</table>

References

1. R. Panisch, A. R. Bassindale, A. A. Korlyukov, M. B. Pitak, S. J. Coles and P. G. Taylor, *Organometallics*, **2013**, *32*, 1732-1742.

2. M. Ronchi, M. Pizzotti, A. Orbelli Biroli, P. Macchi, E. Lucenti and C. Zucchi, *Journal of Organometallic Chemistry*, **2007**, *692*, 1788-1798.

3. J. Cella, and S. Rubinsztajn, *Macromolecules*, **2008**, *41*, 19, 6965-6971.