

Supporting Information

BINOL and triazole-containing Janus ring and 29-8-29-membered tricyclic ladder-type hybridized siloxane: Application for the fluorescence sensing of anions

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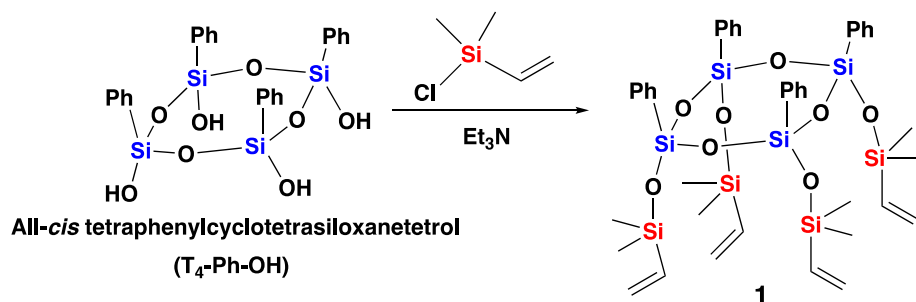
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1. General information

THF, DMF and toluene were dried using mBRAUN purification system. Triethylamine was distilled from potassium hydroxide, stored on potassium hydroxide under an argon atmosphere. Karstedt's catalyst (in xylene, 2% Pt) and (chloromethyl)dimethylsilane were purchased from Sigma-Aldrich, sodium azide was purchased from TCI, sodium iodide and copper (I) iodide were purchased from FUJIFILM Wako Pure Chemical Co., all reagents were used as received. Flash column chromatography was performed over silica gel (63-210 μm). The Fourier transformation nuclear magnetic resonance (NMR) spectra were acquired using a JEOL JNM-ECA 400 (^1H at 399.78 MHz) and JEOL JNM-ECA 600 instrument (^1H at 600.17 MHz, ^{13}C at 150.91 MHz, ^{29}Si at 119.24 MHz). For ^1H NMR, chemical shifts were reported as δ units (ppm) relative to SiMe_4 (TMS), with the residual solvents peaks used as standards. For ^{13}C NMR and ^{29}Si NMR, chemical shifts were reported as δ units (ppm) relative to SiMe_4 (TMS), the residual solvents peaks were used as standards and spectra were obtained with complete proton decoupling. UV/Vis spectra were recorded on a Hitachi U-3000 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer with a xenon arc lamp as light source. MALDI-TOF mass analysis was conducted using a Shimadzu AXIMA Performance instrument with 2,5-dihydroxybenzoic acid (dithranol) as the matrix. Thin layer chromatography was performed using Silica gel 60 F₂₅₄.

2. Experimental procedures and characterization data for synthetic compounds 1, 2, 3, 5, 7.

2.1 Preparation of tetravinyl-substituted all-*cis*-T₄ [Ph-Si-(O)-OSiMe₂Vin]₄ (**1**)



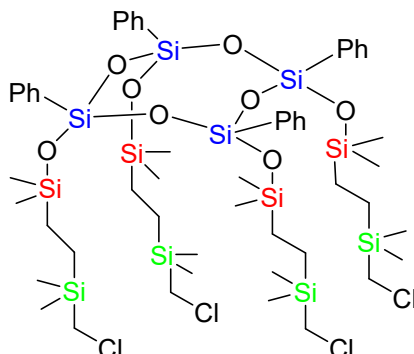
An argon-purged three-necked round bottom flask equipped with a stir bar was charged with **T₄-Ph-OH**¹ (1.0 g, 1.8 mmol), dry THF (100 mL) and distilled triethylamine (1.5 mL, 10.8 mmol). The mixture was cooled down to 0 °C. Chlorodimethylvinylsilane (1.5 mL, 10.8 mmol) was added dropwise via a microsyringe into the reaction mixture at 0 °C. After addition, the reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 23 h. After the reaction, water (~100 mL) was added into the reaction medium which was extracted 3 times with hexane. The gathered organic layer was washed 3 times with brine, dried over anhydrous Na₂SO₄, evaporated on the rotavapor and then dried under vacuum at room temperature for 1 day to afford the pure product **1** (1.537 g, 96%). The physical data were identical in all respects to those previously reported.²

¹ R. Ito, Y. Kakihana, Y. Kawakami, *Chem. Lett.* **2009**, *38*, 364-365.

² (a) O. I. Shchegolikhina, Y. A. Pozdnyakova, Y. A. Molodtsova, S. D. Korin, S. S. Bukalov, L. A. Leites, K. A. Lyssenko, A. S. Peregudov, N. Auner, D. E. Katsoulis, *Inorg. Chem.*, **2002**, *41*, 6892-6904; (b) A. A. Anisimov, Y. N. Kononevich, M. I. Buzin, A. S. Peregudov, O. I. Shchegolikhina, A. M. Muzafarov, *Macroheterocycles*, **2016**, *9*, 442-452.

2.2 Tetrachloro-substituted all-*cis*-T₄ [Ph-Si(O)-OSiMe₂(CH₂CH₂)SiMe₂CH₂Cl]₄

(2)



An argon-purged 100 mL Schlenk flask was charged with pre-synthesized **1** (1.94 g, 2.18 mmol), (chloromethyl)dimethylsilane (1.6 mL, 13.1 mmol) and dry toluene (14 mL). Karstedt's catalyst (2.18 μ mol of [Pt], 25 μ L of a commercial bottle with 2% Pt in xylene) was then added at room temperature. After addition, the mixture was heated to 40 °C and stirred at 40 °C for 18 h. Then, the reaction mixture was cooled down to room temperature and passed through a silica plug which was washed twice with dichloromethane. The gathered eluate was concentrated under reduced pressure and dried under vacuum to give the pure product **2** as a slightly yellowish liquid (2.88 g, 99%) without any further purification.

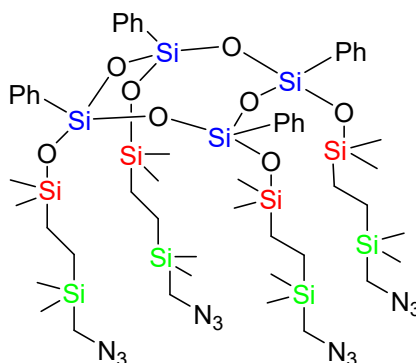
¹H-NMR (600 MHz, CDCl₃): δ 7.28-7.25 (m, 12H), 7.06-7.08 (m, 8H), 2.70 (s, 8H), 0.49-0.42 (m, 16H), 0.19 (s, 24H), 0.02 (s, 24H) ppm.

¹³C NMR (150.91 MHz, CDCl₃): δ 134.03, 133.06, 129.86, 127.49, 30.02, 9.74, 5.08, -0.33, -5.11 ppm.

²⁹Si NMR (119.24 MHz, CDCl₃): δ 11.78, 5.78, -78.96 ppm.

MALDI-TOF MS (m/z): 1347.14 ([M+Na]⁺, calcd 1347.11); 1363.11 ([M+K]⁺, calcd 1363.22).

2.3 Tetraazido-substituted all-*cis*-T₄ [Ph-Si(O)-OSiMe₂(CH₂CH₂)SiMe₂CH₂N₃]₄ (3)



An argon-purged 100 mL Schlenk flask was charged with **2** (0.75 g, 0.57 mmol), NaN₃ (0.45 g, 6.84 mmol), NaI (0.043 g, 0.28 mmol), dry DMF (41 mL) and dry THF (16 mL). The reaction mixture was heated to 60 °C and stirred for 24h at 60 °C. Then, The reaction mixture was cooled down to room temperature, CH₂Cl₂ (80 mL) was slowly added (stirred for about 10 minutes), followed by the addition of water (100 mL). The organic phase was washed 5 times with water to remove DMF, then dried over anhydrous Na₂SO₄ and concentrated on the rotavapor (with dichloromethane several times to remove traces of DMF) to give the target compound **3** as a yellow liquid (0.734 g, 96%), without any further purification.

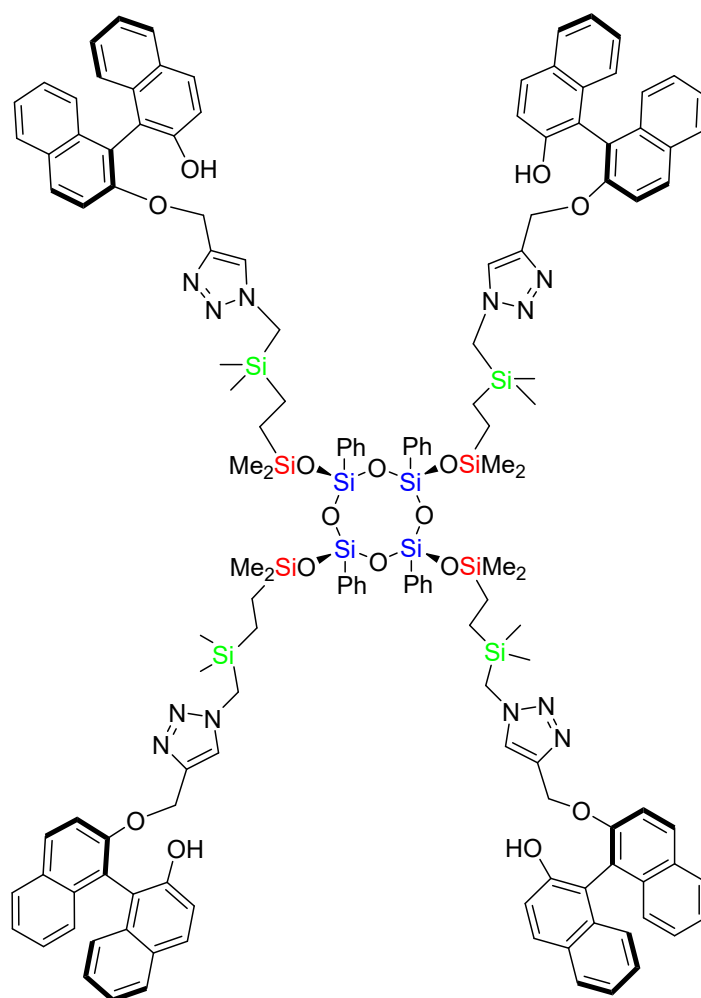
¹H-NMR (600 MHz, CDCl₃): δ 7.26-7.27 (m, 12H), 7.06-7.09 (m, 8H), 2.68 (s, 8H), 0.43 (s, 16H), 0.20 (s, 24H), 0.004 (s, 24H) ppm.

¹³C NMR (150.91 MHz, CDCl₃): δ 134.02, 133.02, 129.91, 127.51, 40.64, 9.75, 5.49, -0.33, -4.73 ppm.

²⁹Si NMR (119.24 MHz, CDCl₃): δ 11.76, 5.59, -78.92 ppm.

Elemental analysis: Calcd for C₅₂H₉₂N₁₂O₈Si₁₂: C, 46.25; H, 6.87; N, 12.45; Found: C, 46.54; H, 6.52; N, 11.41.

2.4 BINOL and triazole containing all-*cis*-T₄ (5)



To a 100 mL flask was added **3** (0.20 g, 0.15 mmol), pre-prepared monopropargyl BINOL **4** (0.21 g, 0.65 mmol), NEt₃ (20 μ L, 0.15 mmol), CuI (14 mg, 74 μ mol) and THF (12 mL). The mixture was stirred at room temperature for 20 h, then another portion of CuI (14 mg, 74 μ mol) was added into the reaction mixture which was allowed to stir for an additional 20 h at room temperature. The resulting mixture was quenched by sat. NH₄Cl aq. and extracted with EtOAc. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated in vacuo to afford the crude product. The crude product was purified by column chromatograph on silica gel (hexane/EtOAc = 1:1) to give a white powder (0.26 g, 66%).

¹H-NMR (600 MHz, acetone-*d*₆): δ 8.05 (s, 4H), 7.95 (d, *J* = 8.9 Hz, 4H), 7.88-7.82 (m, 12H), 7.61 (d, *J* = 9.3 Hz, 4H), 7.36-7.20 (m, 30H), 7.14-7.09 (m, 20H), 6.94 (d, *J*

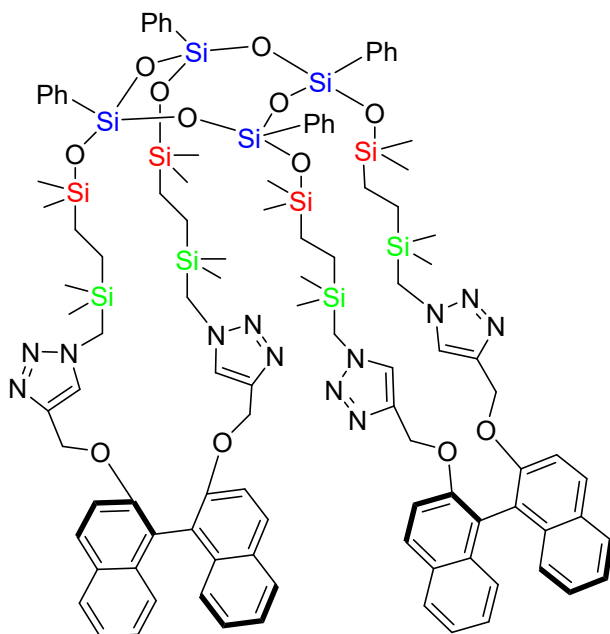
= 8.2 Hz, 4H), 5.19-5.11 (ABq, $J = 13.2$ Hz, 8H), 3.74 (s, 8H), 0.50 (s, 16H), 0.21 (s, 24H), -0.09 (s, 24H) ppm.

$^{13}\text{C-NMR}$ (150.91 MHz, acetone- d_6): δ 155.64, 153.69, 144.56, 135.25, 135.08, 134.72, 133.75, 130.95, 130.64, 130.53, 130.06, 129.71, 128.87, 128.82, 128.42, 127.16, 126.82, 125.91, 125.53, 124.60, 124.50, 123.53, 120.14, 119.57, 117.24, 116.58, 64.15, 40.40, 10.24, 6.07, 0.04, -4.49 ppm.

$^{29}\text{Si NMR}$ (119.24 MHz, acetone- d_6): δ 12.08, 4.86, -78.79 ppm.

MALDI-TOF MS (m/z): 2667.54 ($[\text{M}+\text{Na}]^+$, calcd 2667.88).

2.5 BINOL and triazole containing 29-8-29 membered-ring ladder-type siloxane (7)



To a 100 mL flask was added **3** (0.33 g, 0.24 mmol), dipropargyl BINOL **6** (0.18 g, 0.49 mmol), NEt_3 (27 μL , 0.23 mmol), CuI (36 mg, 0.19 mmol) and THF (20 mL). The mixture was stirred at room temperature for 20 h, then another portion of CuI (36 mg, 0.19 mmol) was added into the reaction mixture which was allowed to stir for an additional 20 h at room temperature. The resulting mixture was quenched by sat. NH_4Cl aq. and extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford the crude product. The crude product was purified by column chromatograph on silica gel (hexane/EtOAc = 2:1) to

give a white powder (0.065 g, 13%).

¹H-NMR (400 MHz, acetone-*d*₆): δ 7.98-7.88 (m, 8H), 7.62-7.59 (m, 4H), 7.41-7.28 (m, 20H), 7.20 (t, *J* = 7.2 Hz, 4H), 7.12 (t, *J* = 7.6 Hz, 8H), 7.02 (d, *J* = 8.5 Hz, 4H), 5.23-5.03 (ABq, *J* = 12.4 Hz, 8H), 3.88-3.79 (ABq, *J* = 16.8 Hz, 4H), 0.56-0.53 (m, 16H), 0.26-0.12 (m, 24H), -0.03 (s, 6H), -0.06 (s, 6H), -0.08 (s, 6H), -0.11 (s, 6H) ppm.

¹³C-NMR (151.91 MHz, acetone-*d*₆): δ 154.08, 143.58, 134.19, 133.95, 130.14, 129.61, 129.29, 128.07, 127.62, 126.25, 125.12, 124.22, 123.67, 120.25, 115.92, 63.18, 39.55, 13.52, 9.49, 5.32, -0.56, -0.62, -0.93, -5.15, -5.22, -5.28 ppm.

²⁹Si NMR (119.24 MHz, acetone-*d*₆): δ 12.05, 4.95, -78.84 ppm.

MALDI-TOF MS (m/z): 2096.85 ([M+Na]⁺, calcd 2096.69).

3. Fluorescence spectra of compound **5** in THF in the presence of various anions

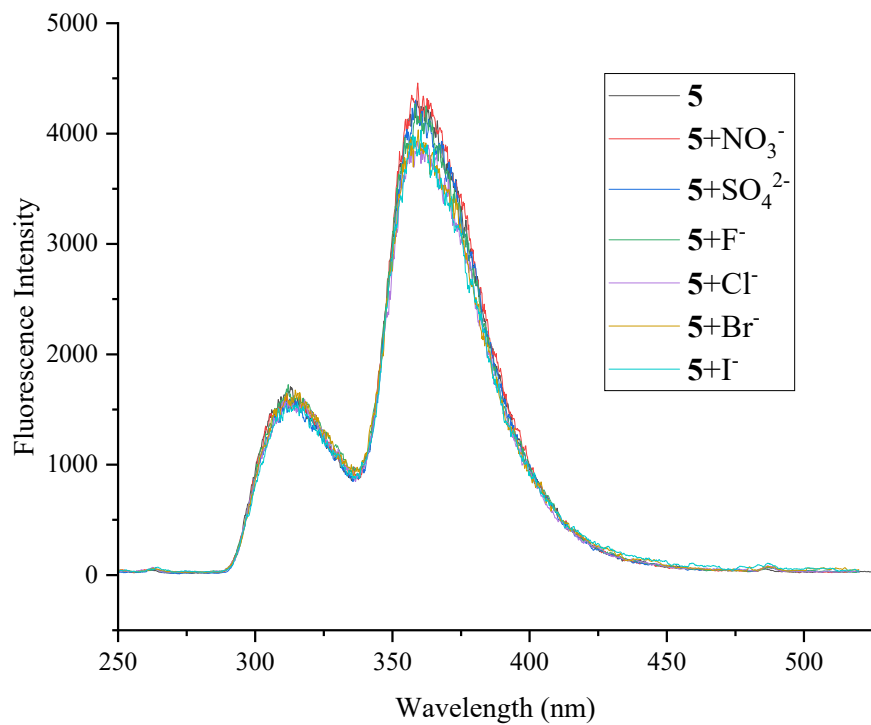


Figure S1 Fluorescence emission spectra of compound **5** in THF (1 μ M) in the presence of various anions (20 equiv.)

4. The Stern–Volmer plot of compound 7 at lower concentration of I⁻

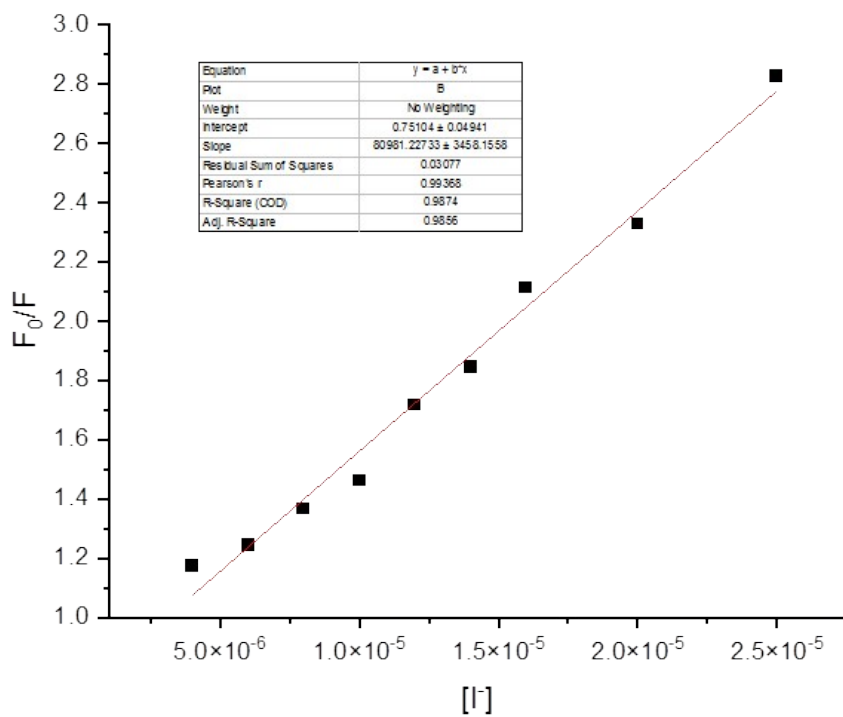


Figure S2 The Stern–Volmer plot of compound 7 at low concentration of I⁻.

5. UV-Vis titration spectra of compound 7 in THF with increasing concentration of I⁻.

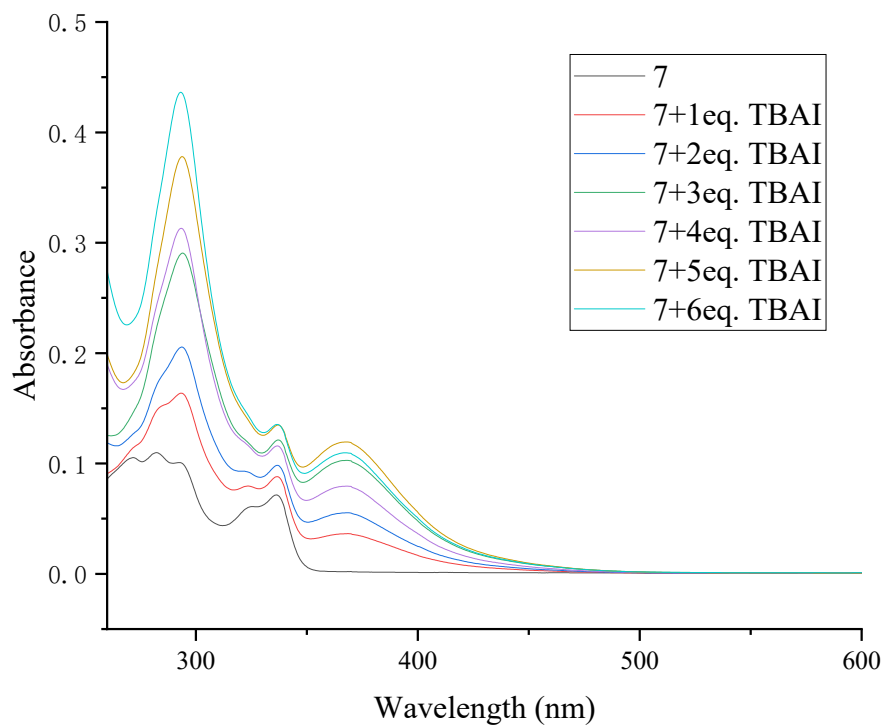


Figure S3 UV-Vis titration spectra of compound 7 in THF (5.0 μM) with increasing concentration of I⁻ (0-6 equiv.)

6. NMR spectra for compounds 2, 3, 5 and 7

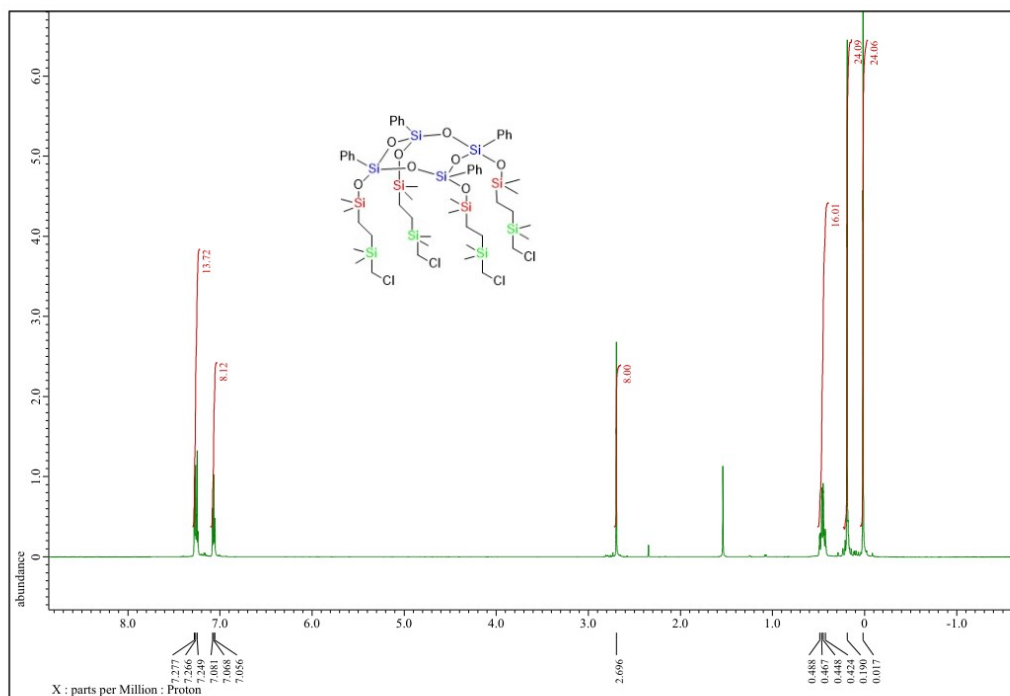


Figure S4: ¹H NMR spectrum of compound 2

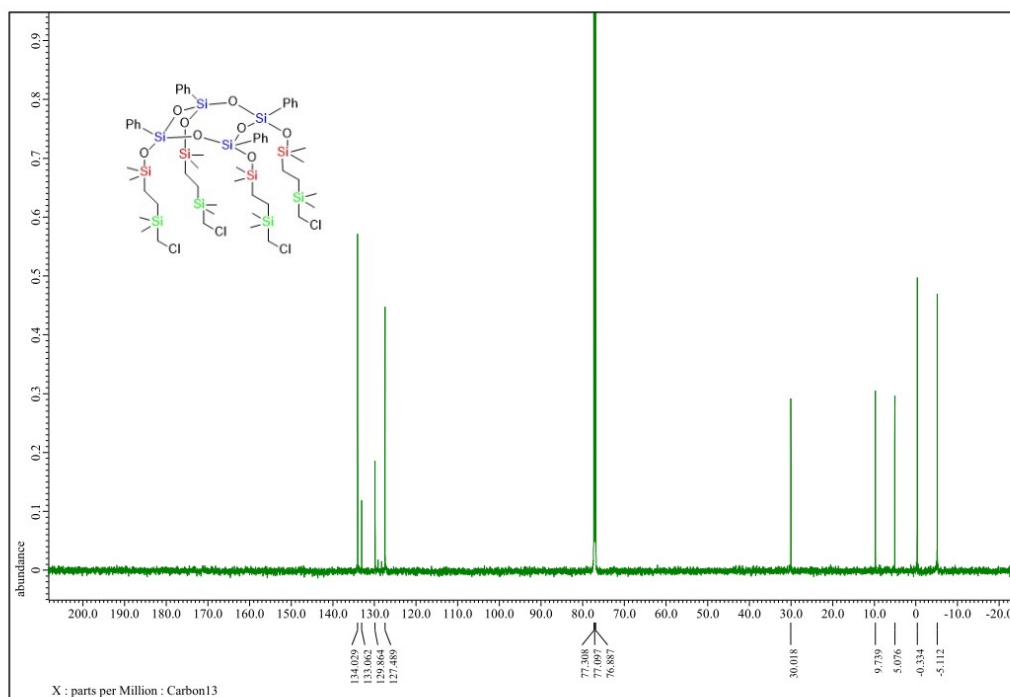


Figure S5: ¹³C NMR spectrum of compound 2

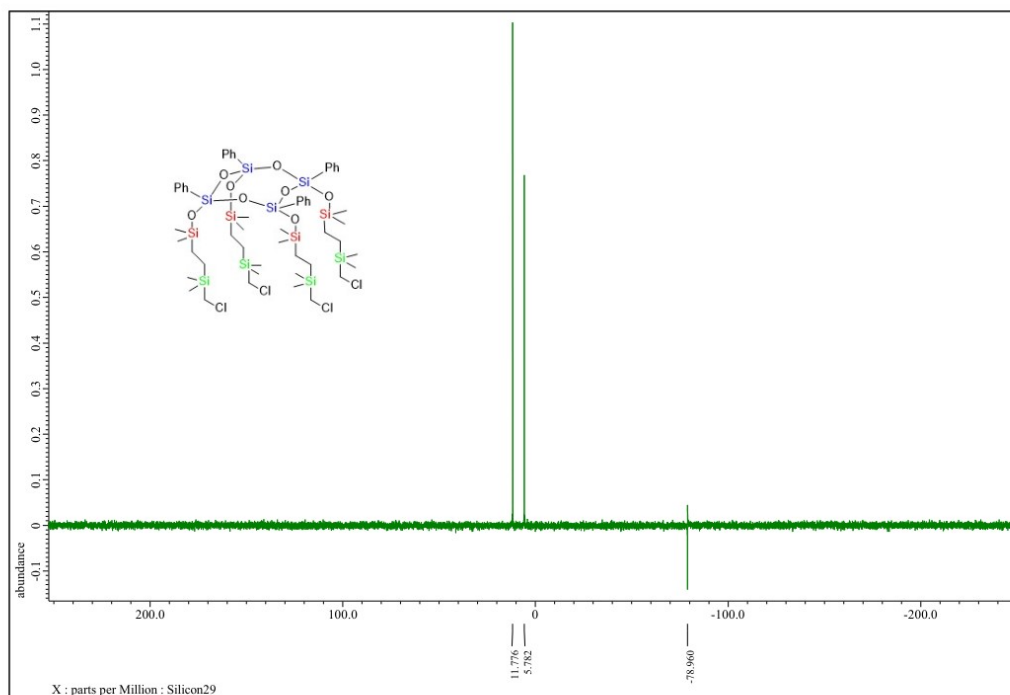


Figure S6: ^{29}Si NMR spectrum of compound 2

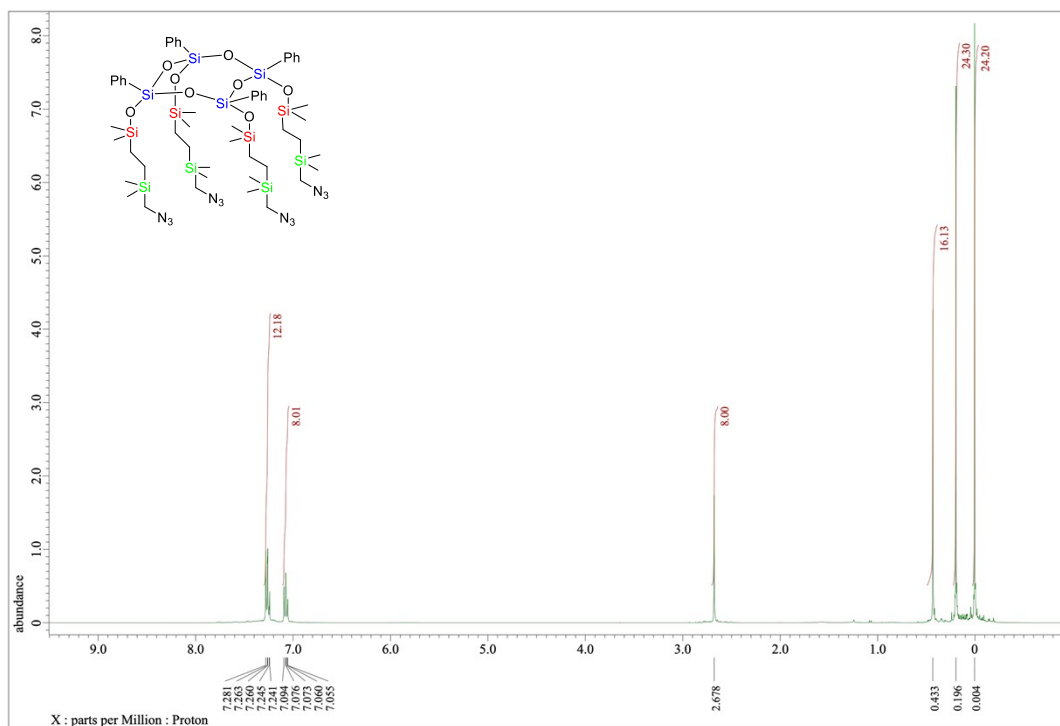


Figure S7: ^1H NMR spectrum of compound **3**

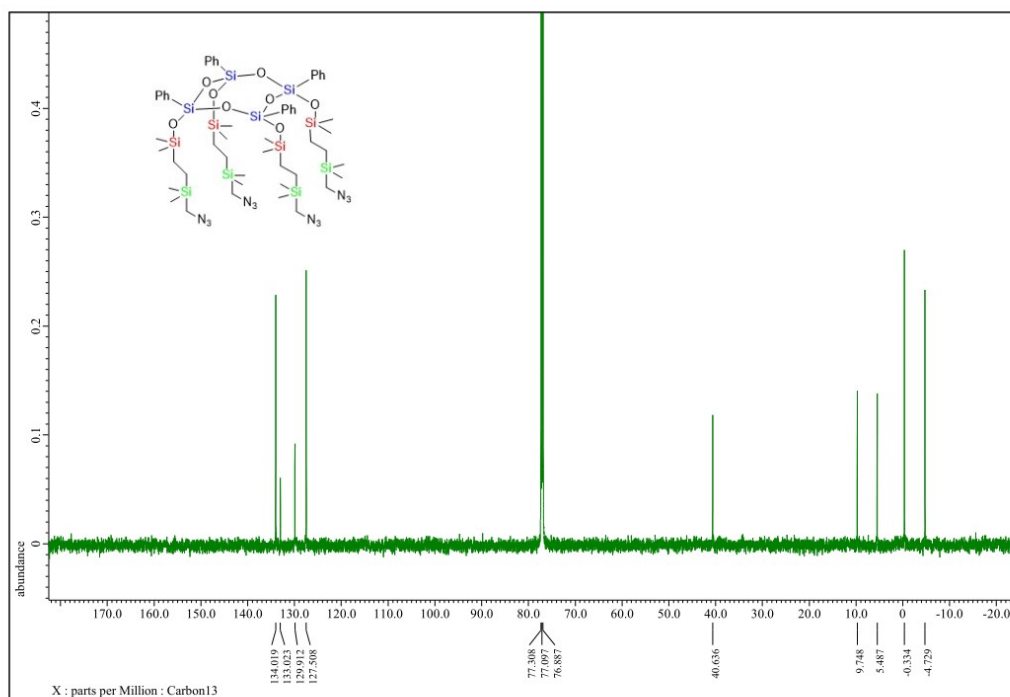


Figure S8: ^{13}C NMR spectrum of compound **3**

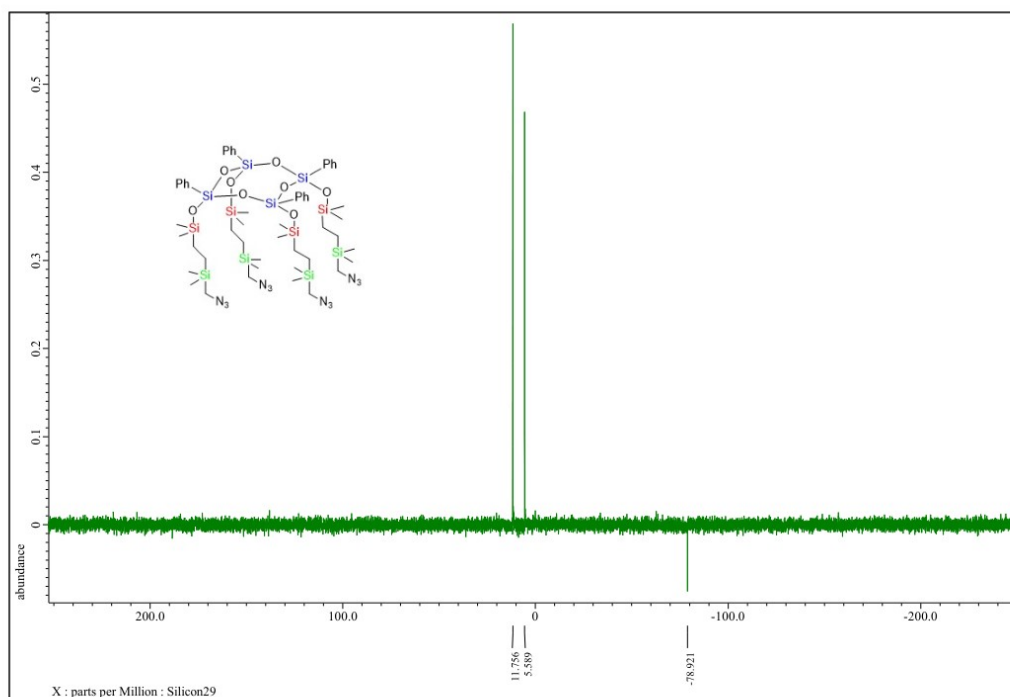


Figure S9: ^{29}Si NMR spectrum of compound **3**

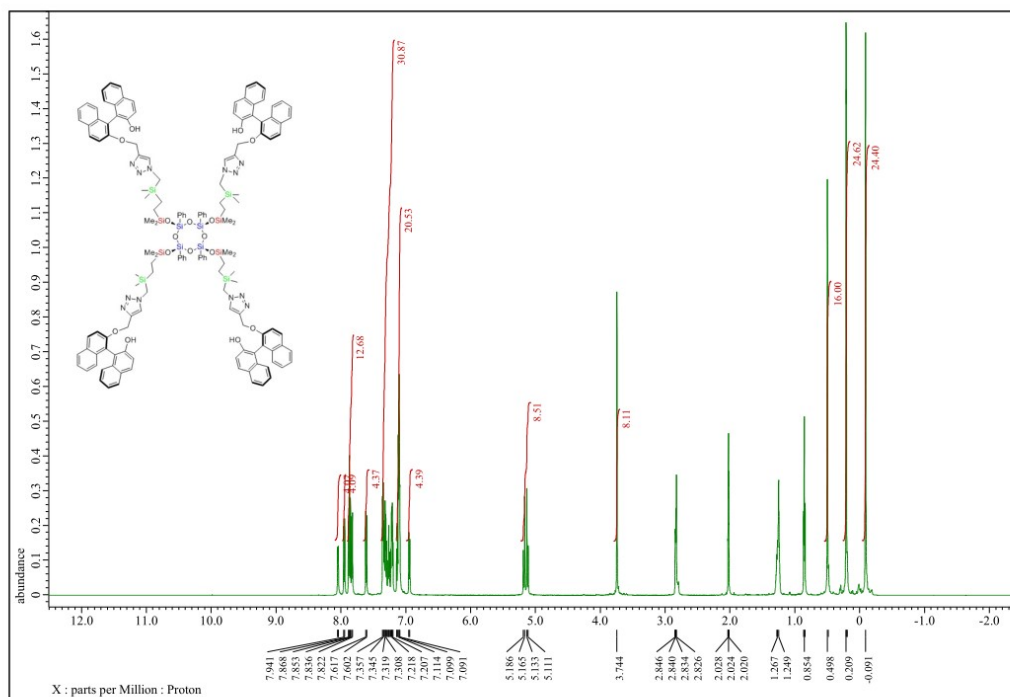


Figure S10: ^1H NMR spectrum of compound **5**

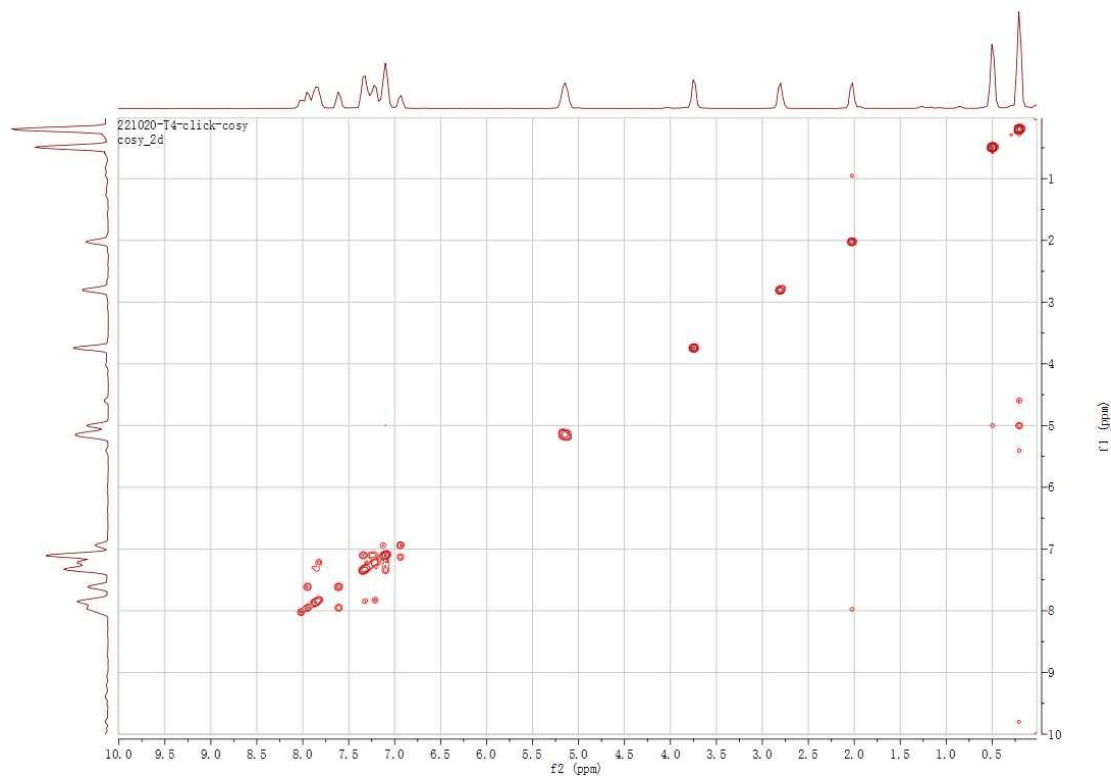


Figure S11: COSY-2D NMR spectrum of compound **5**

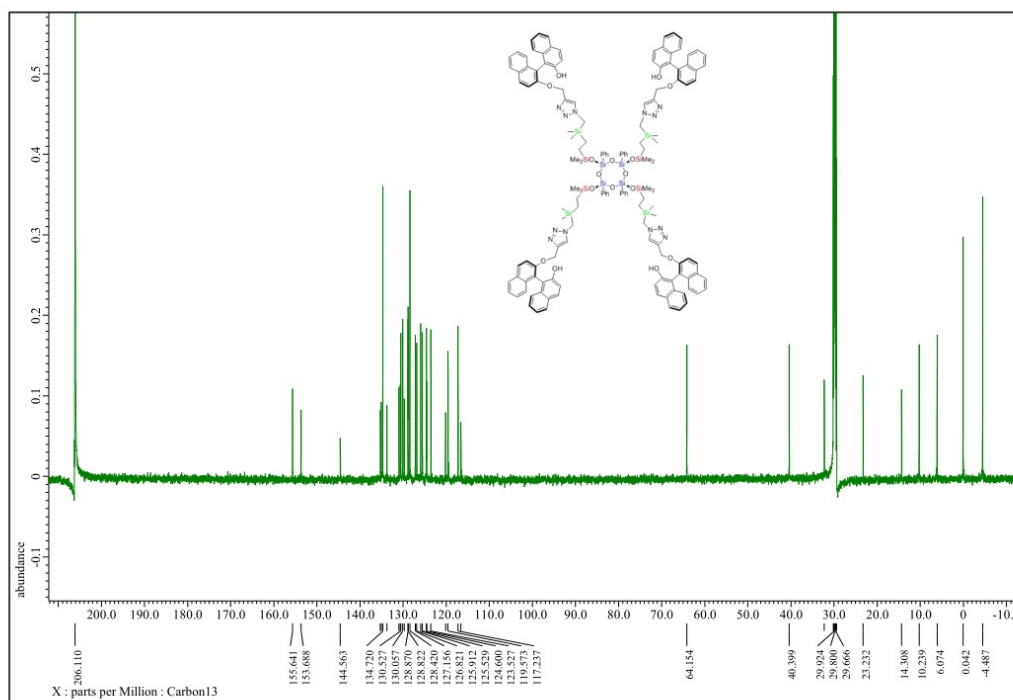


Figure S12: ^{13}C NMR spectrum of compound 5

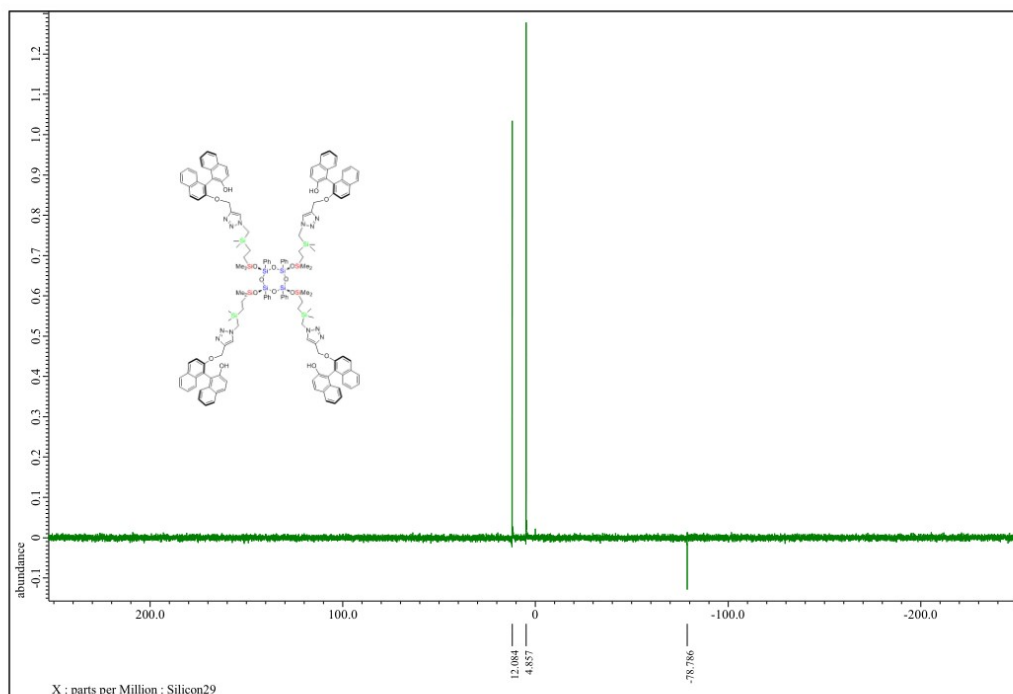


Figure S13: ^{29}Si NMR spectrum of compound 5

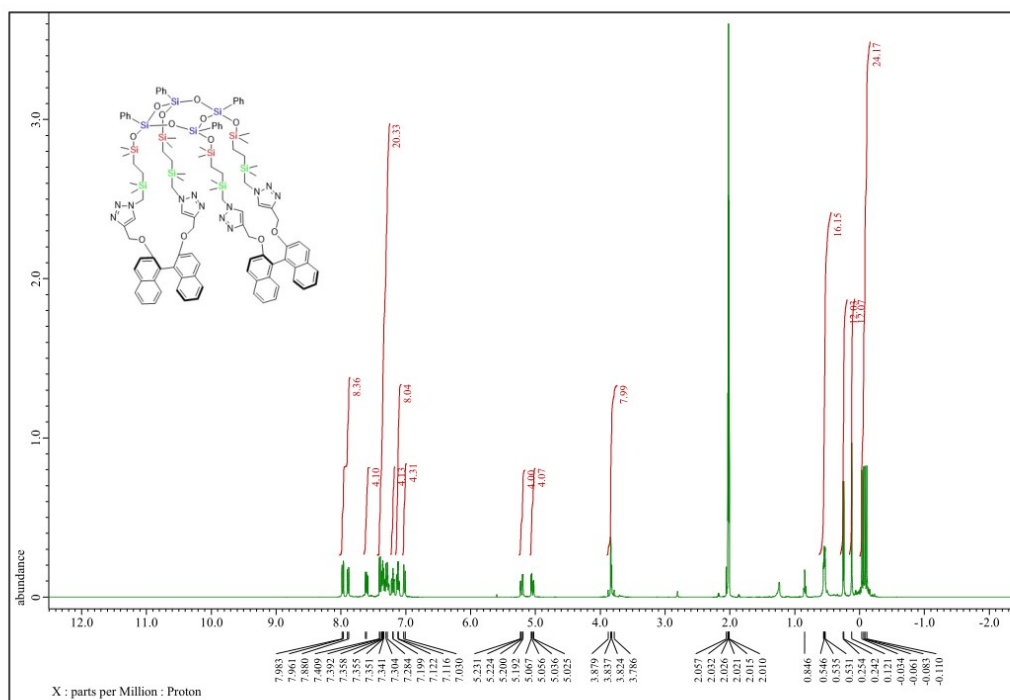


Figure S14: ^1H NMR spectrum of compound 7

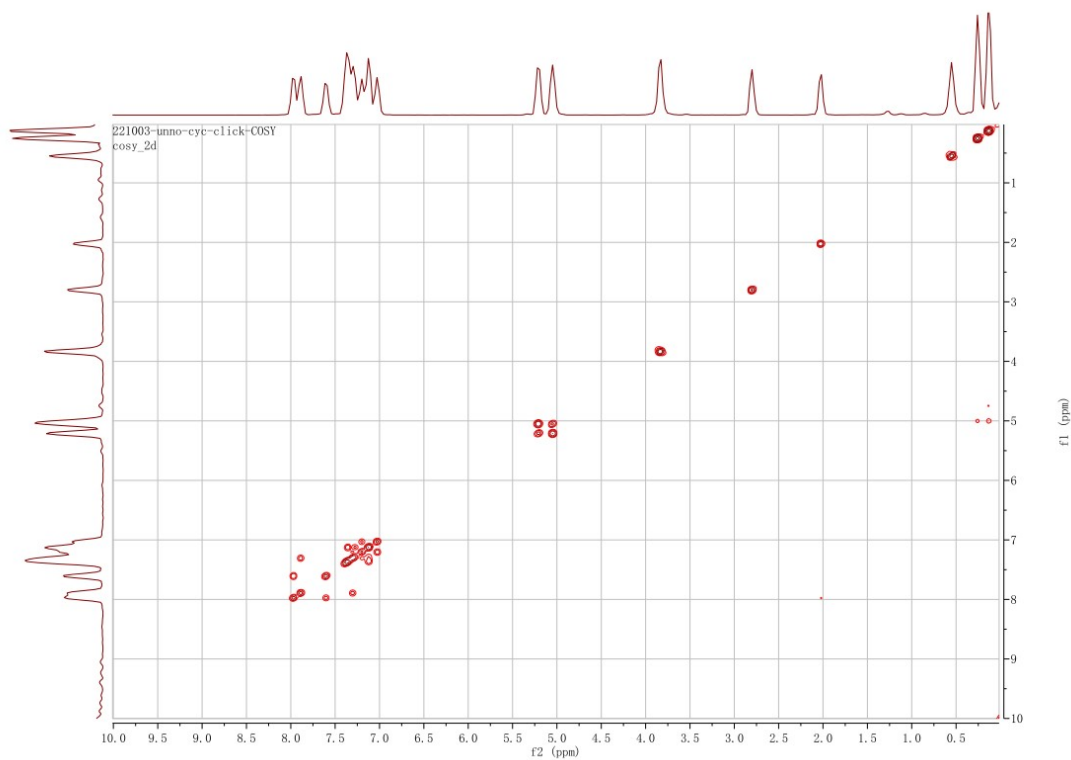


Figure S15: COSY-2D NMR spectrum of compound 7

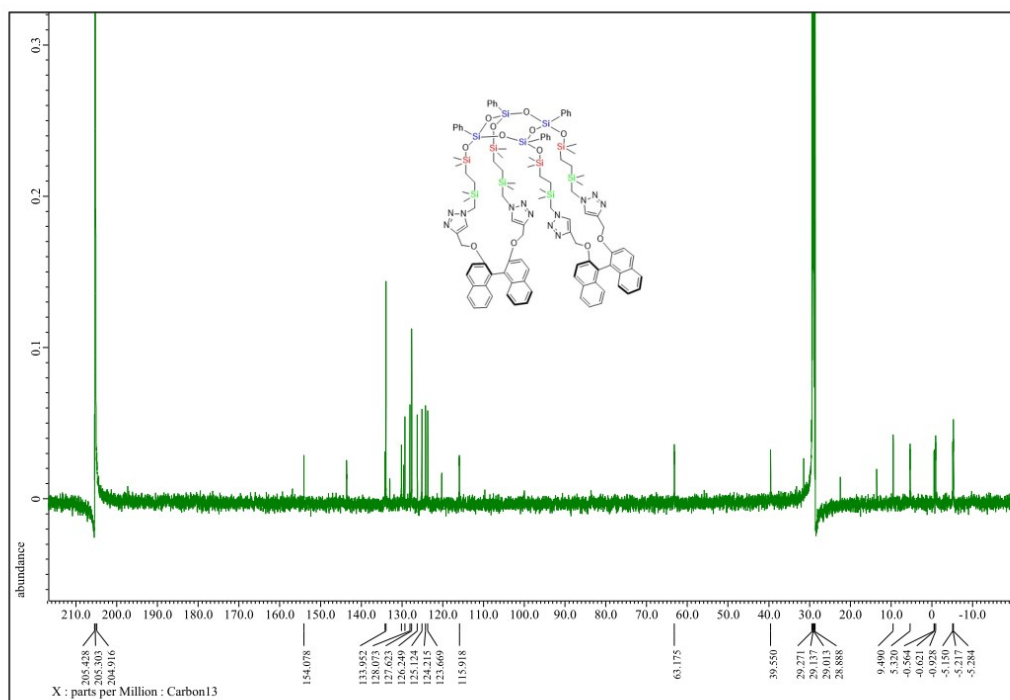


Figure S16: ^{13}C NMR spectrum of compound 7

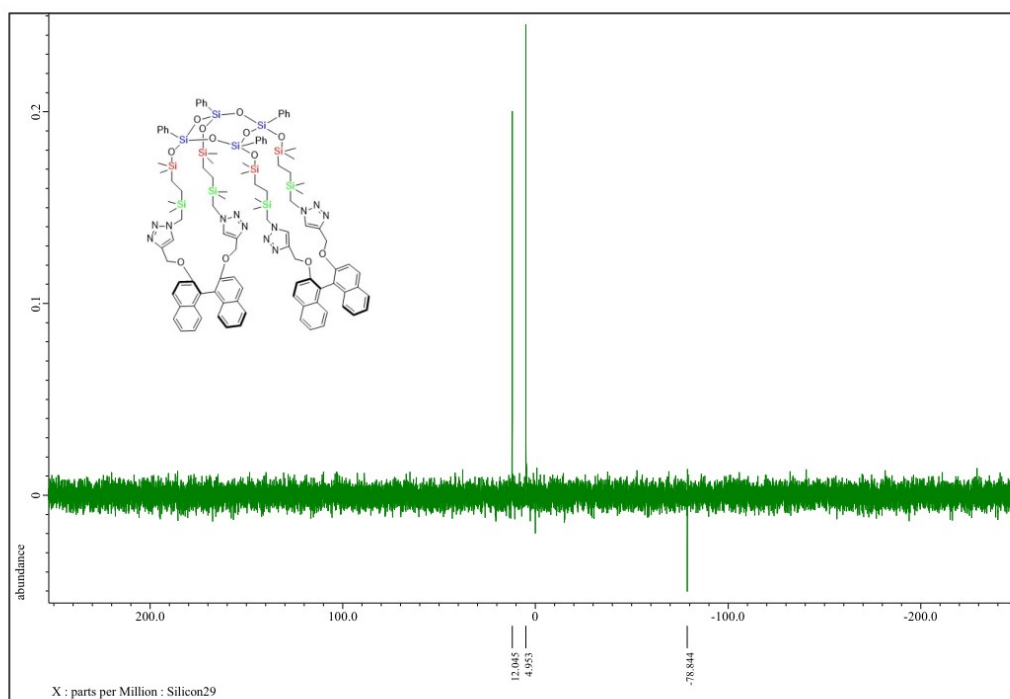


Figure S17: ^{29}Si NMR spectrum of compound 7

7. MALDI-TOF spectra for compounds 2, 5 and 7.

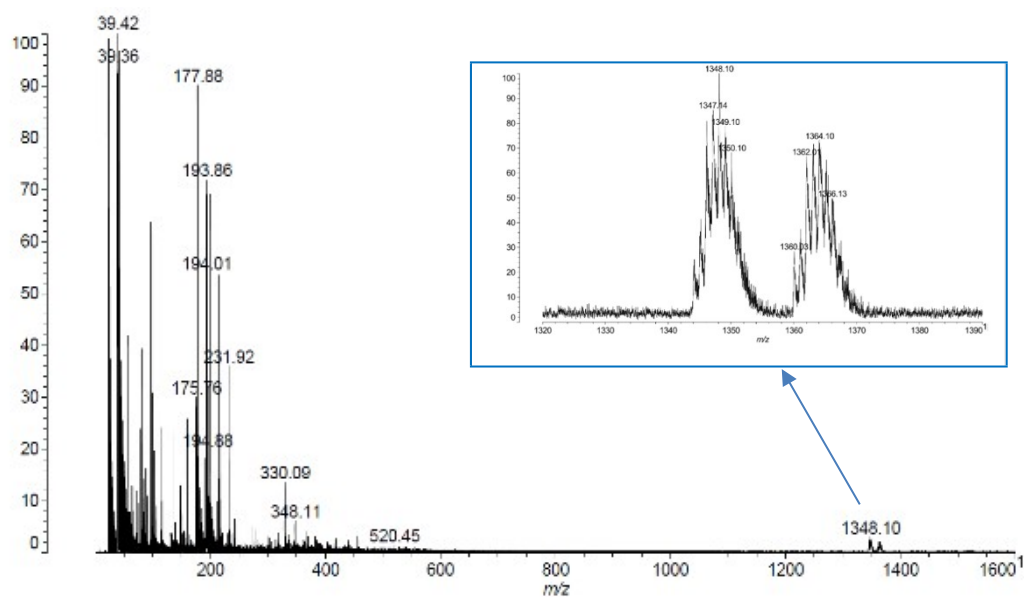


Figure S18 MALDI-TOF spectrum of compound 2

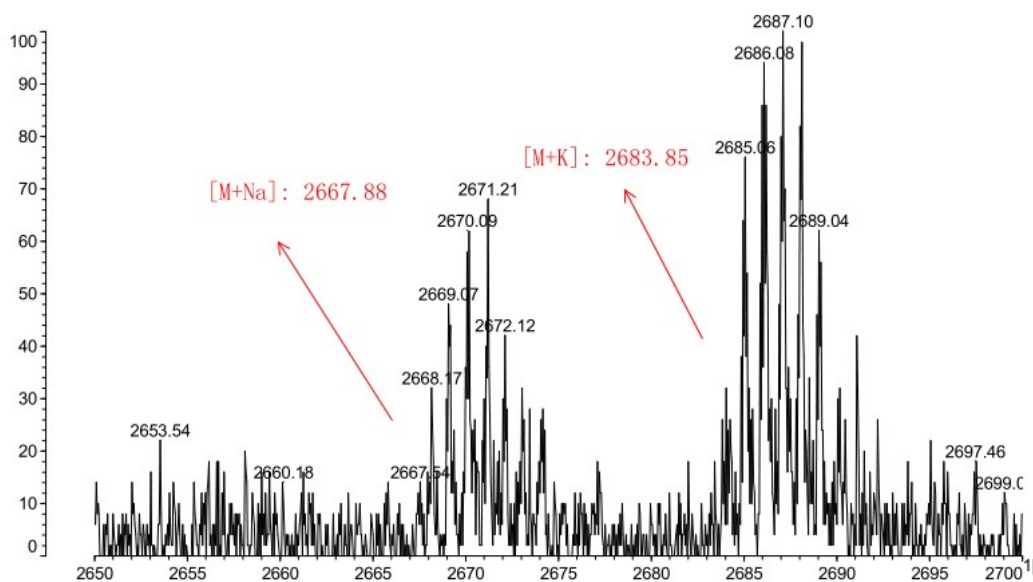


Figure S19 MALDI-TOF spectrum of compound 5

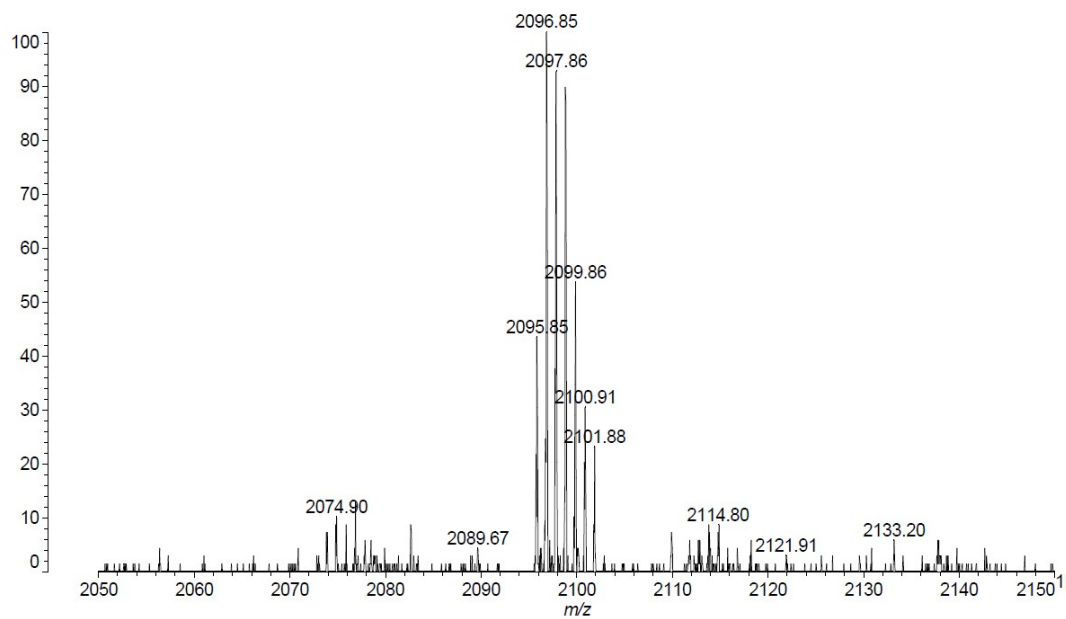


Figure S20 MALDI-TOF spectrum of compound 7

8. Molecular model of the 7/iodide anion complex by Gaussian 09 suites of programs.

Calculations were performed with the Gaussian09 suites of programs. Geometries were fully optimized without symmetry constraints in gas phase by using the B3LYP functional in conjunction with the standard 6-31G(d,p) basis was employed for the C, H, O, N and Si atoms, whereas the Lanl2DZ valence basis set in combination with the corresponding effective core potential were used for the I atom.

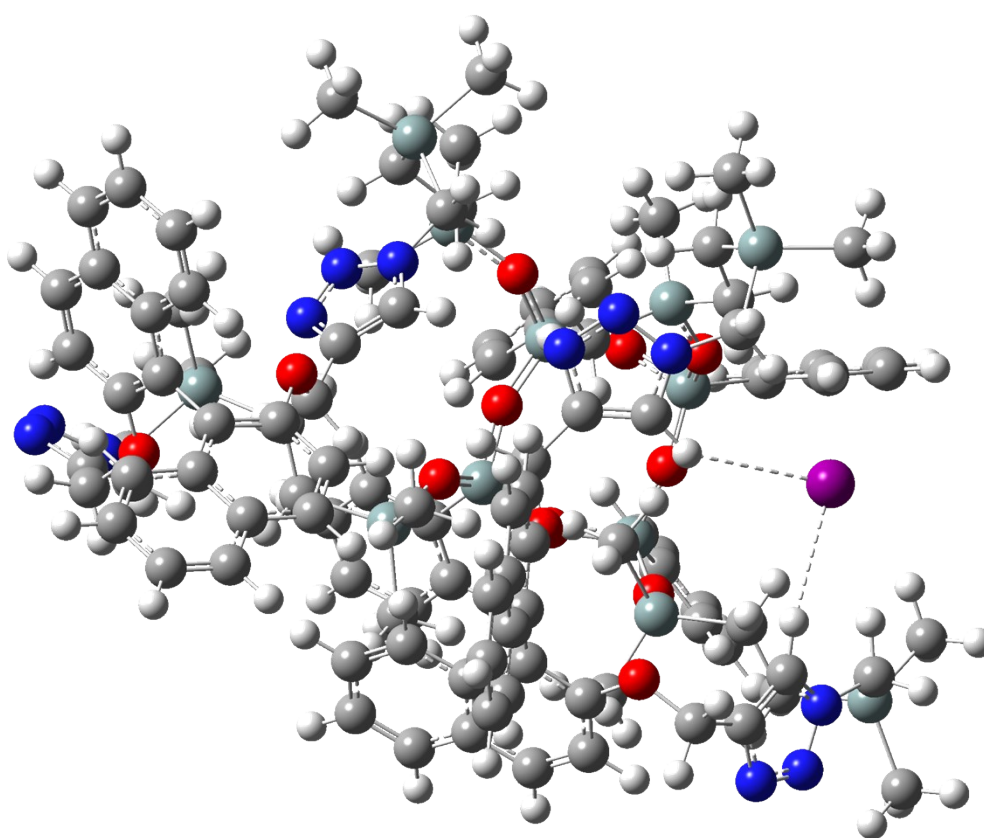


Figure S21 Molecular model of the 7/iodide anion complex by Gaussian 09 suites of programs. Carbons are gray, hydrogens are white, oxygens are red, silicons are blue grey, nitrogens are blue, and iodide anion is purple. ($I \dots H_1 = 3.060 \text{ \AA}$, $I \dots H_2 = 3.128 \text{ \AA}$)