

Supporting Information

Color-tunable fluorescent nanoparticles encapsulating trialkylsilyl-substituted pyrene liquid

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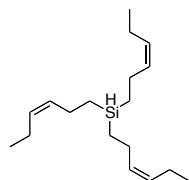
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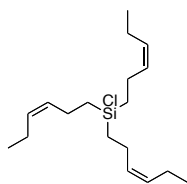
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1. Synthesis of trialkylsilyl-substituted pyrenes

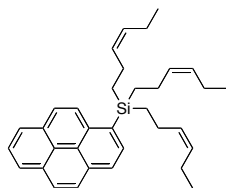
General. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry THF and diethyl ether were purchased from Kanto Chemicals. *t*-BuLi (1.60 M in pentane) was used as received. Reactions were performed under an argon atmosphere. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 100B (Fuji Silysia). Recycling preparative HPLC was performed using LC-918 (Japan Analytical Industry) equipped with silica gel column (Wakosil-II 5-Prep, Wako). Melting points (mp) were measured by SII Exstar 6000 DSC 6200 and determined by the baseline method. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded with a JEOL AL-400 or A-600 spectrometer in CDCl_3 operating at 400 or 600 MHz for ^1H and 100 or 151 MHz for ^{13}C NMR and 79 MHz for ^{29}Si NMR measurements. Chemical shifts are reported in δ ppm using the residual CHCl_3 solvent and CDCl_3 as the internal reference for ^1H ($\delta = 7.26$ ppm) and ^{13}C ($\delta = 77.16$ ppm), respectively, while the external standard of tetramethylsilane was used for ^{29}Si NMR spectra. Mass spectroscopy was measured with a Bruker Daltonics micrOTOF focus using positive mode APCI-TOF method in toluene solutions.



Tri((*Z*)-3-hexen-1-yl)silane. (*Z*)-1-Bromohex-3-ene (48 mL, 357.7 mmol) was slowly added to magnesium turnings (10.7 g, 439.0 mmol) in dry diethyl ether (360 mL) at 0 °C. The resulting mixture was stirred at room temperature for 13 h to prepare a Grignard reagent. The yield determined by Knochel's titration method^[1] was 68% (0.681 M, 245 mmol). Trichlorosilane (8.80 mL, 87.0 mmol) was added into the solution of the Grignard reagent at 0 °C for 15 min, then the solution was warmed up to room temperature and stirred for 3 h. After the solvent was removed under reduced pressure, dry hexane was added and the mixture was filtered and concentrated under reduced pressure. The resulting mixture was distilled under reduced pressure (127–128 °C at 1.5 mmHg) to give 21.0 g (75.2 mmol) of the product in 63% yield as colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 5.40–5.27 (m, 6H), 3.76 (septet, $J_{\text{HH}} = 3.4$ Hz, 1H), 2.13–2.00 (m, 12H), 0.96 (t, $J_{\text{HH}} = 7.6$ Hz, 9H), 0.73–0.68 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.7, 130.7, 22.3, 20.6, 14.5, 11.9; HRMS (APCI): 277.2342 ($[\text{M}-\text{H}]^+$). Calcd for $\text{C}_{18}\text{H}_{33}\text{Si}$: 277.2346.

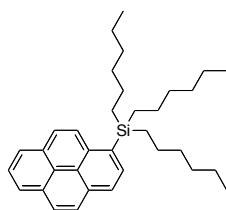


Chlorotri((Z)-3-hexen-1-yl)silane.^[2] To a mixture of CuCl₂ (20.2 g, 151 mmol) and CuI (303 mg, 1.59 mmol) in dry THF (120 mL), tri((Z)-3-hexen-1-yl)silane (20.2 g, 77.3 mmol) was added under an argon atmosphere and the mixture was stirred for 13 h. After the solvent was removed under reduced pressure, dry hexane was added, and the mixture was filtered and concentrated under reduced pressure. The resulting mixture was distilled under reduced pressure (120–121 °C at 1.35 mmHg) to give 8.36 g (26.7 mmol) of the product in 36% yield as colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 5.39–5.30 (m, 6H), 2.19–2.13 (m, 6H), 2.09–2.01 (m, 6H), 0.99–0.95 (t, *J*_{HH} = 7.6 Hz 9H), 0.94–0.89 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 131.3, 130.9, 20.7, 20.6, 16.9, 14.5; HRMS (APCI): 312.2030 (*M*⁺). Calcd for C₁₈H₃₃Cl₁Si₁: 312.2035.

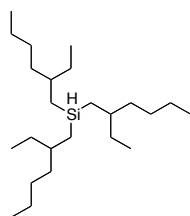


1-[Tri((Z)-3-hexen-1-yl)silyl]pyrene (1). To a solution of 1-bromopyrene (845 mg, 3.02 mmol) in THF (15 mL), *t*-BuLi in pentane (3.90 mL, 1.60 M, 6.00 mmol) was added dropwise at –78 °C. After stirring for 1 h, chlorotri((Z)-3-hexen-1-yl)silane (1.10 mL, 3.30 mmol) was added dropwise at the same temperature, and the mixture was then warmed up to room temperature and stirred for 19 h. After quenching the mixture with an aqueous NH₄Cl solution, the mixture was concentrated under reduced pressure and extracted with hexane. The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography using hexane (*R*_f = 0.33) as an eluent. Further purification by preparative HPLC (hexane) gave 923 mg (1.93 mmol) of the product in 64% yield as pale yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J*_{HH} = 9.3 Hz, 1H), 8.21 (d, *J*_{HH} = 7.8 Hz, 1H), 8.19 (d, *J*_{HH} = 7.1 Hz, 1H), 8.17 (d, *J*_{HH} = 7.1 Hz, 1H), 8.15 (d, *J*_{HH} = 10.0 Hz, 1H), 8.12 (d, *J*_{HH} = 9.3 Hz, 1H), 8.10 (d, *J*_{HH} = 9.8 Hz, 1H), 8.06 (d, *J*_{HH} = 9.0 Hz, 1H), 8.01 (td, *J*_{HH} = 7.6, 0.7 Hz, 1H), 5.42–5.36 (m, 3H), 5.29–5.22 (m, 3H), 2.14–2.08 (m, 6H), 1.95–1.88 (m, 6H), 1.27–1.22 (m, 6H), 0.88 (t, *J*_{HH} = 7.6 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 136.3, 133.2, 132.5, 132.2, 131.9, 131.4, 130.8, 130.6, 128.0,

127.7, 127.5, 127.3, 125.9, 125.3, 125.2, 125.1, 124.8, 124.3; ^{29}Si NMR (79 MHz, CDCl_3) δ -0.090; HRMS (APCI): 478.3054 (M^+). Calcd for $\text{C}_{34}\text{H}_{42}\text{Si}_1$: 478.3050.

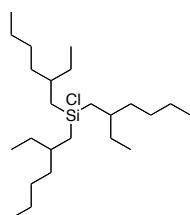


1-(Trihexylsilyl)pyrene (2). To a solution of 1-bromopyrene (5.80 g, 20.6 mmol) in THF (200 mL), *t*-BuLi in pentane (25.8 mL, 1.60 M, 41.2 mmol) was added dropwise at $-78\text{ }^\circ\text{C}$. After stirring for 1 h, chlorotrihexylsilane (7.50 mL, 20.5 mmol) was added dropwise at the same temperature, then the mixture was warmed up to room temperature and stirred for 19 h. After quenching the mixture with an aqueous NH_4Cl solution, the mixture was concentrated under reduced pressure, and extracted with hexane. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography using hexane ($R_f = 0.46$) as an eluent. Further purification by preparative HPLC (hexane) to afford 7.04 g (14.5 mmol) of the product in 71% yield as colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 8.40 (dd, $J_{\text{HH}} = 9.3, 2.4\text{ Hz}$, 1H), 8.23 (d, $J_{\text{HH}} = 7.8\text{ Hz}$, 1H), 8.22 (d, $J_{\text{HH}} = 7.8\text{ Hz}$, 1H), 8.20 (d, $J_{\text{HH}} = 6.3\text{ Hz}$, 1H), 8.18 (d, $J_{\text{HH}} = 7.6\text{ Hz}$, 1H), 8.15 (dd, $J_{\text{HH}} = 9.3, 1.7\text{ Hz}$, 1H), 8.10 (d, $J_{\text{HH}} = 10.0\text{ Hz}$, 1H), 8.07 (d, $J_{\text{HH}} = 10.0\text{ Hz}$, 1H), 8.02 (td, $J_{\text{HH}} = 7.6, 0.7\text{ Hz}$, 1H), 1.40 (m, 12H), 1.30–1.26 (m, 12H), 1.20–1.16 (m, 6H), 0.90–0.86 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.3, 133.9, 133.1, 132.0, 131.5, 130.9, 127.9, 127.8, 127.7, 127.0, 125.8, 125.1, 125.1, 125.1, 124.8, 124.2, 33.6, 31.6, 24.2, 22.8, 14.2, 14.1; ^{29}Si NMR (79 MHz, CDCl_3) δ -0.494; HRMS (APCI): 484.3529 (M^+). Calcd for $\text{C}_{34}\text{H}_{48}\text{Si}_1$: 485.3520.

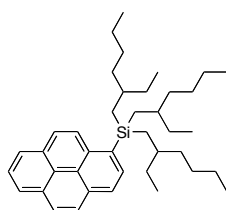


Tris(2-ethylhexyl)silane. 1-Bromo-2-ethylhexane (106 mL, 550 mmol) was added slowly to magnesium turnings (14.7 g, 604 mmol) in dry diethyl ether (550 mL) at $0\text{ }^\circ\text{C}$. The resulting mixture was stirred at room temperature for 14 h to prepare a Grignard reagent. The yield determined by Knochel's titration method was 65% (0.646 M, 358 mmol). Trichlorosilane (10.5 mL, 104 mmol) was added into the solution of the Grignard reagent at $0\text{ }^\circ\text{C}$ for 15 min,

then the mixture was warmed up to room temperature and stirred for 4 h. After the solvent was removed under reduced pressure, dry hexane was added and the mixture was filtered, and concentrated under reduced pressure. The obtained mixture was distilled under reduced pressure (126–127 °C at 0.64 mmHg) to give 28.5 g (77.3 mmol) of the product in 42% yield as colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 3.87 (septet, $J_{\text{HH}} = 3.4$ Hz, 1H), 1.44–1.37 (m, 3H), 1.35–1.19 (m, 24H), 0.91–0.80 (m, 18H), 0.59–0.56 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 36.1, 35.7, 29.1, 28.8, 23.2, 17.7, 14.3, 11.0; HRMS (APCI): 367.3764 ($[\text{M}-\text{H}]^+$). Calcd for $\text{C}_{24}\text{H}_{51}\text{Si}_1$: 367.3755.

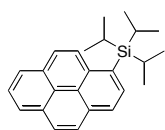


Chlorotris(2-ethylhexyl)silane.^[3] To a solution of tris(2-ethylhexyl)silane (28.5 g, 77.3 mmol) in CCl_4 (23.0 mL, 232 mmol), PdCl_2 (699 mg, 3.94 mmol) was added under an argon atmosphere. Evolution of HCl gas was observed and a little heat was produced. The mixture was warmed up to 90 °C and stirred for 23 h. After the solvent was removed under reduced pressure, the mixture was distilled under reduced pressure (134–135 °C at 0.50 mmHg) to give 29.3 g (72.6 mmol) of the product in 94% yield as colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 1.62–1.54 (m, 3H) 1.39–1.20 (m, 24H), 0.92–0.82 (m, 24H); ^{13}C NMR (100 MHz, CDCl_3) δ 35.6, 35.0, 28.9, 28.7, 23.2, 22.8, 14.3, 10.7; HRMS (APCI): 401.3352 ($[\text{M}-\text{H}]^+$). Calcd for $\text{C}_{24}\text{H}_{50}\text{Cl}_1\text{Si}_1$: 401.3365.



1-[Tris(2-ethylhexyl)silyl]pyrene (3). To a solution of 1-bromopyrene (2.82 g, 10.0 mmol) in THF (120 mL), *t*-BuLi in pentane (12.5 mL, 1.60 M, 20.0 mmol) was added dropwise at –78 °C. After stirring for 1 h, chlorotris(2-ethylhexyl)silane (4.90 mL, 12.0 mmol) was added dropwise at the same temperature, then the mixture was warmed up to room temperature and stirred for 15 h. After quenched with an aqueous NH_4Cl solution, the mixture was extracted with hexane. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography

using hexane ($R_f = 0.49$) as an eluent. Further purification by preparative HPLC (hexane) gave 3.61 g (6.35 mmol) of the product in 64% yield as colorless oil: ^1H NMR (600 MHz, CDCl_3) δ 8.37 (d, $J_{\text{HH}} = 9.2$ Hz, 1H), 8.22 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 8.20 (d, $J_{\text{HH}} = 7.7$ Hz, 1H), 8.17 (d, $J_{\text{HH}} = 7.7$ Hz, 1H), 8.13 (d, $J_{\text{HH}} = 7.7$ Hz, 1H), 8.10 (d, $J_{\text{HH}} = 9.2$ Hz, 1H), 8.07 (d, $J_{\text{HH}} = 8.8$ Hz, 1H), 8.05 (d, $J_{\text{HH}} = 8.8$ Hz, 1H), 8.00 (t, $J_{\text{HH}} = 7.3$ Hz, 1H), 1.51 (m, 3H), 1.26–1.17 (m, 18H), 1.14–1.00 (m, 12H), 0.74–0.69 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.1, 135.6, 132.9, 131.9, 131.5, 130.9, 128.4, 127.8, 127.7, 126.7, 125.7, 125.2, 125.1, 125.0, 124.8, 124.3, 35.6, 35.6, 28.8, 28.8, 23.1, 20.1, 14.2, 10.8; ^{29}Si NMR (79 MHz, CDCl_3) δ -2.214; HRMS (APCI): 568.4461 (M^+). Calcd for $\text{C}_{40}\text{H}_{60}\text{Si}_1$: 568.4459.



1-(Triisopropylsilyl)pyrene (4). To a solution of 1-bromopyrene (8.45 g, 30.1 mmol) in THF (200 mL), $t\text{-BuLi}$ in pentane (37.8 mL, 1.60 M, 60.2 mmol) was added dropwise at -78°C . After stirring for 1 h, chlorotriisopropylsilane (7.10 mL, 33.0 mmol) was added dropwise at the same temperature, then the mixture was warmed up to room temperature and stirred for 14 h. After quenched with an aqueous NH_4Cl solution, the mixture was extracted with hexane. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography using hexane ($R_f = 0.39$) as an eluent. Further purification by recrystallization from a hot hexane solution gave 9.21 g (25.5 mmol) of the product in 85% yield as colorless crystals: mp $99\text{--}100^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J_{\text{HH}} = 9.3$ Hz, 1H), 8.29 (d, $J_{\text{HH}} = 7.8$ Hz, 1H), 8.20–8.16 (m, 3H), 8.10 (d, $J_{\text{HH}} = 9.3$ Hz, 1H), 8.10 (d, $J_{\text{HH}} = 9.0$ Hz, 1H), 8.07 (d, $J_{\text{HH}} = 9.0$ Hz, 1H), 8.00 (t, $J_{\text{HH}} = 7.6$ Hz, 1H), 1.80 (septet, $J_{\text{HH}} = 7.6$ Hz, 3H), 1.22 (d, $J_{\text{HH}} = 7.6$ Hz, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.0, 134.1, 132.4, 131.9, 131.5, 130.8, 129.0, 128.0, 127.6, 126.8, 125.8, 125.1, 125.1, 125.0, 125.0, 124.1, 19.4, 13.3; ^{29}Si NMR (79 MHz, CDCl_3) δ 4.922; HRMS (APCI): 358.2104 (M^+). Calcd for $\text{C}_{25}\text{H}_{30}\text{Si}_1$: 358.2111.

2. Characterization of liquid pyrenes

Photophysical measurements. UV/Vis absorption spectra of neat pyrene **1–4** and their diluted solutions in cyclohexane were measured with a Shimadzu UV-3150 spectrometer. Excitation and emission spectra were measured with Hitachi F-2500 or Hitachi F-4500 spectrometers with a resolution of 1 nm. Absolute fluorescence quantum yields were determined with a Hamamatsu photonics PMA-11 calibrated integrating sphere system. For the emission spectral measurement of neat pyrenes at 77 K, the samples in a 1 cm square quartz cell were cooled by an Oxford Optistat DN cryostat.

Thermal analysis. Differential scanning calorimetry (DSC) was performed using a DSC6200 (SII EXSTAR 6000, Seiko) instrument at a heating rate of 1 °C/min under a nitrogen atmosphere.

Viscosity measurements. Temperature-dependent viscosity measurements were performed with a Haake MARS Thermo Scientific.

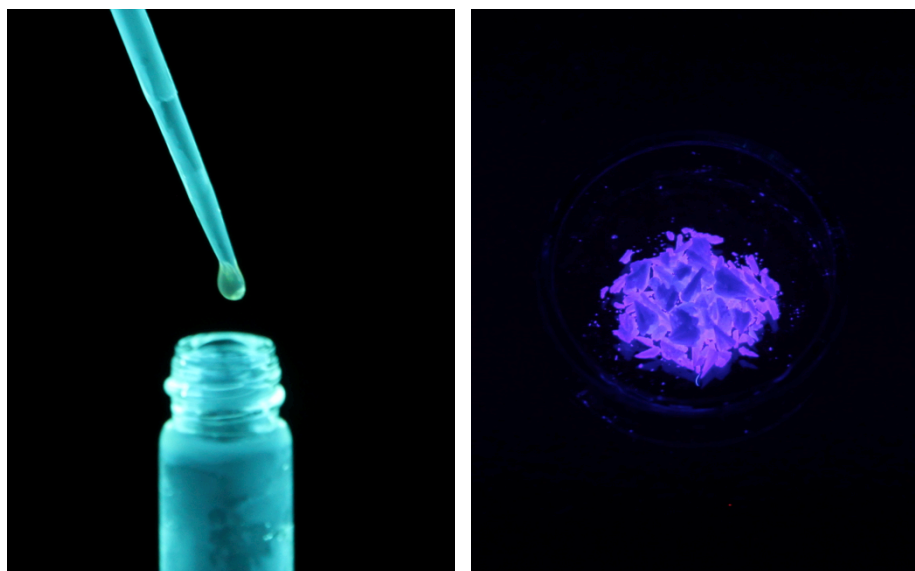


Figure S1. Photographs of trialkylsilyl-substituted liquid pyrene **1** (left) and solid pyrene **4** (right) under irradiation of a light at 365 nm.

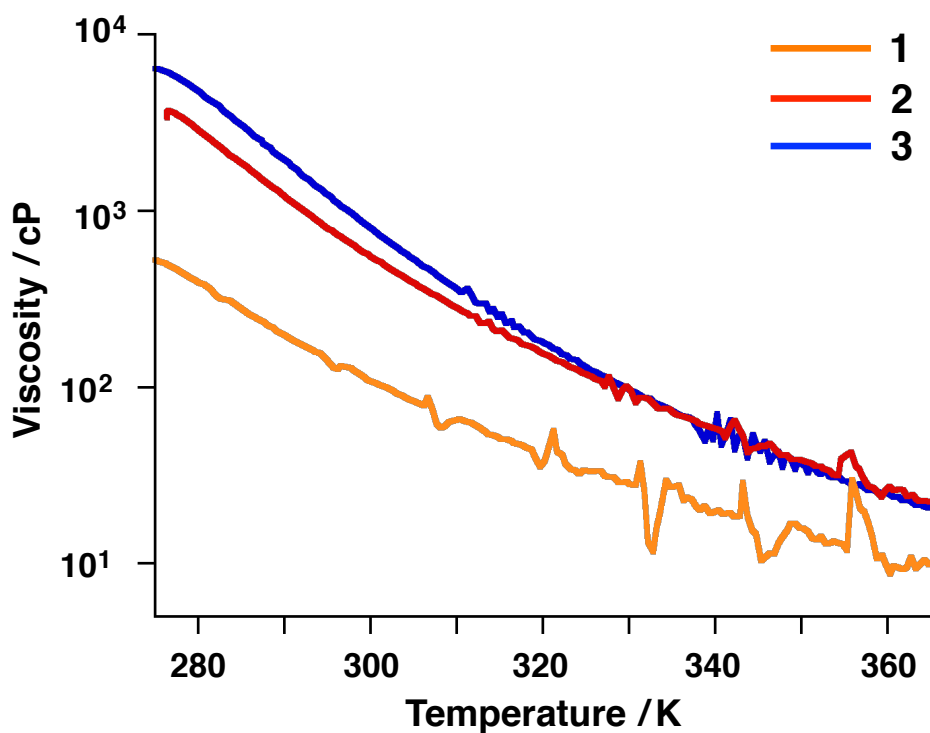


Figure S2. Viscosity of liquid pyrenes 1–3 as a function of temperature.

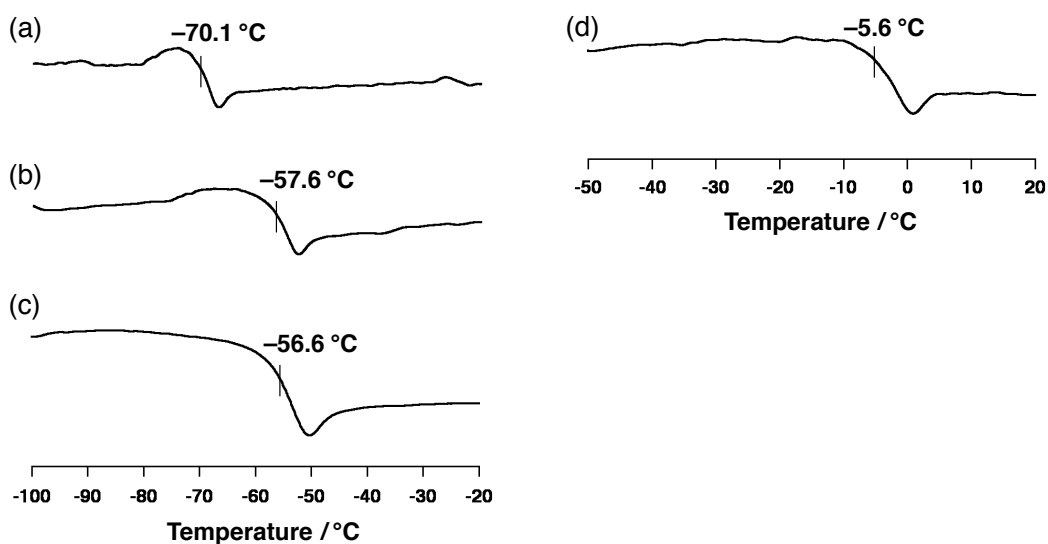


Figure S3. DSC thermograms of (a) 1, (b) 2, (c) 3, and (d) 4 in the heating trace showing the glass transition temperatures (T_g).

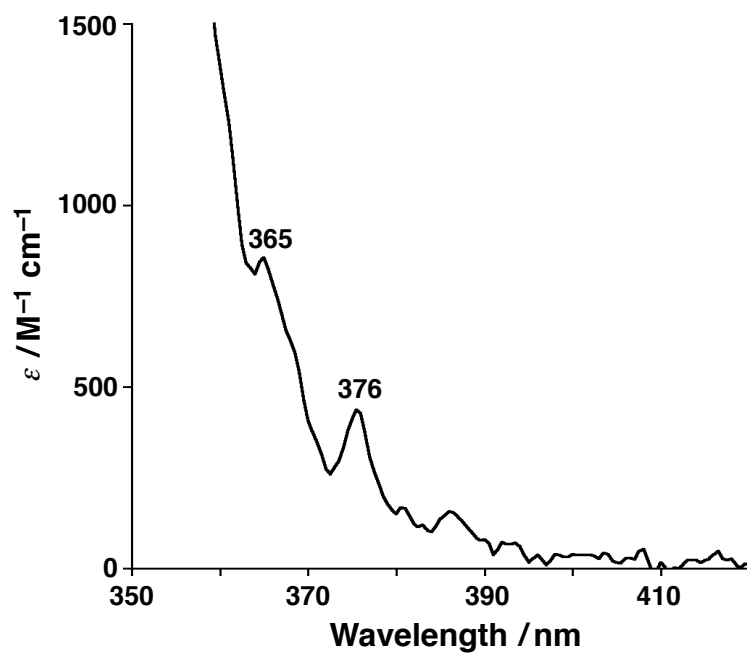


Figure S4. Expanded absorption spectrum of pyrene **1** in the range of 350–410 nm in cyclohexane.

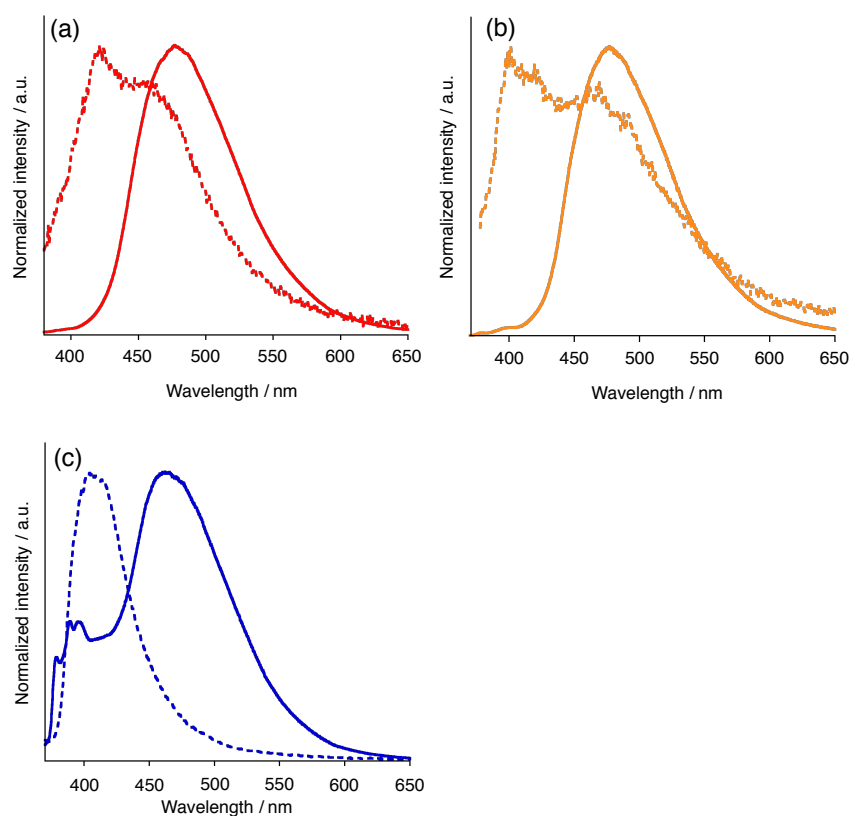


Figure S5. Emission spectra of liquid pyrenes (a) **1**, (b) **2**, and (c) **3** at room temperature (solid line) and at 77 K (dashed line) upon excitation at $\lambda_{\text{ex}} = 350$ nm.

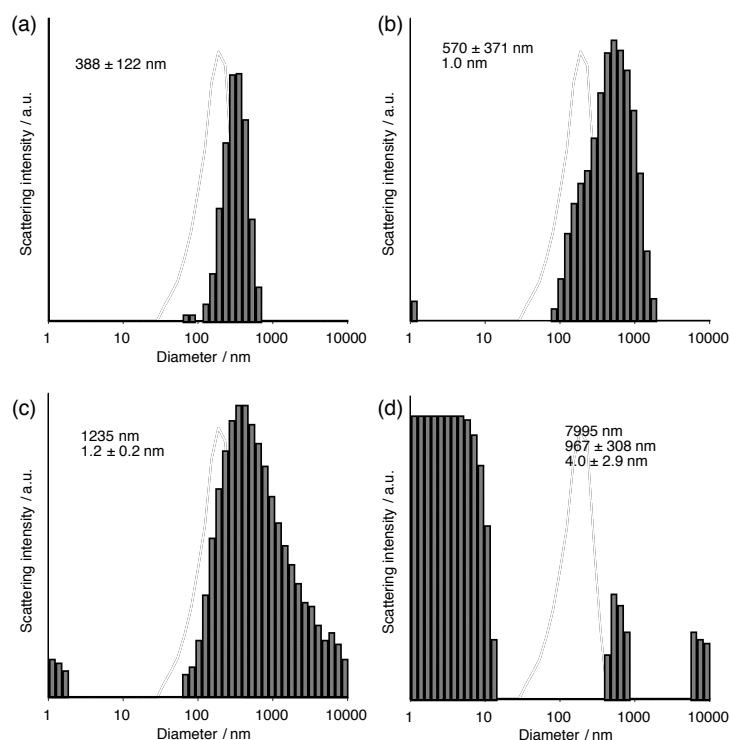


Figure S6. Particle size distributions determined by dynamic light scattering (DLS) of as-prepared (a) NP1, (b) NP2, (c) NP3, and (d) NP4.

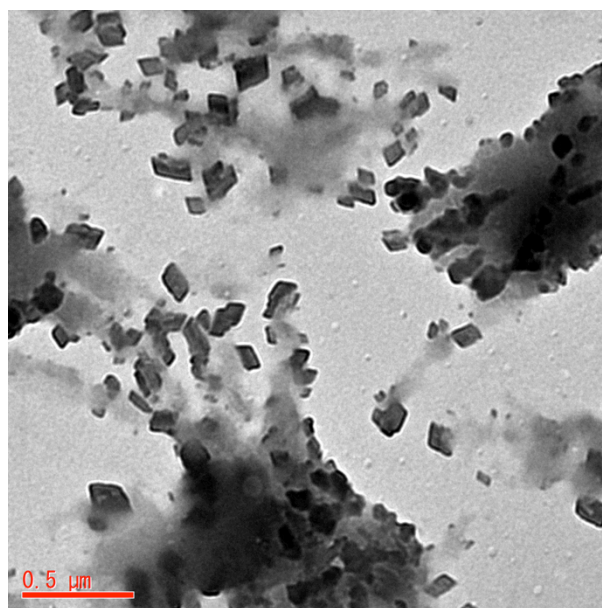


Figure S7. Transmission electron microscope (TEM) image of NP4 after filtration through a 0.2 μm of syringe filter. The filtrate was mounted on a 400 mesh Cu TEM grid and dried. The TEM image showed the formation of aggregated structures with larger sizes than the pore size of the membrane filter and also crystalline-like particles with the size of ~ 100 nm.

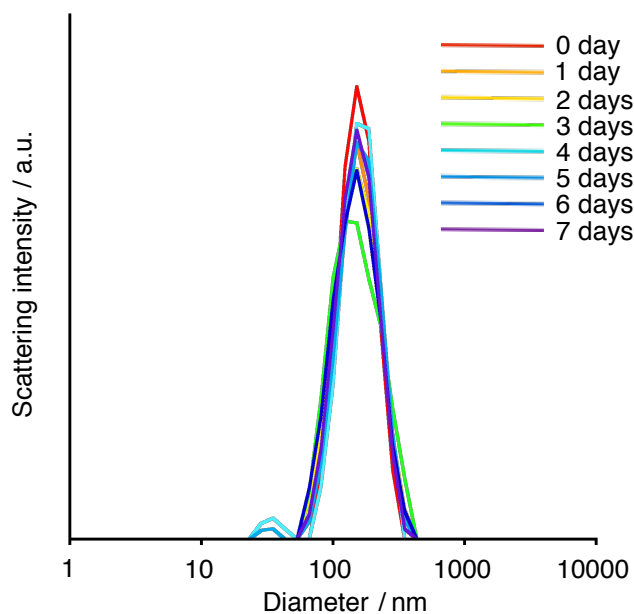


Figure S8. Evaluation of stability of **NP1** in water by monitoring the size distributions with the DLS measurements for 1 week.

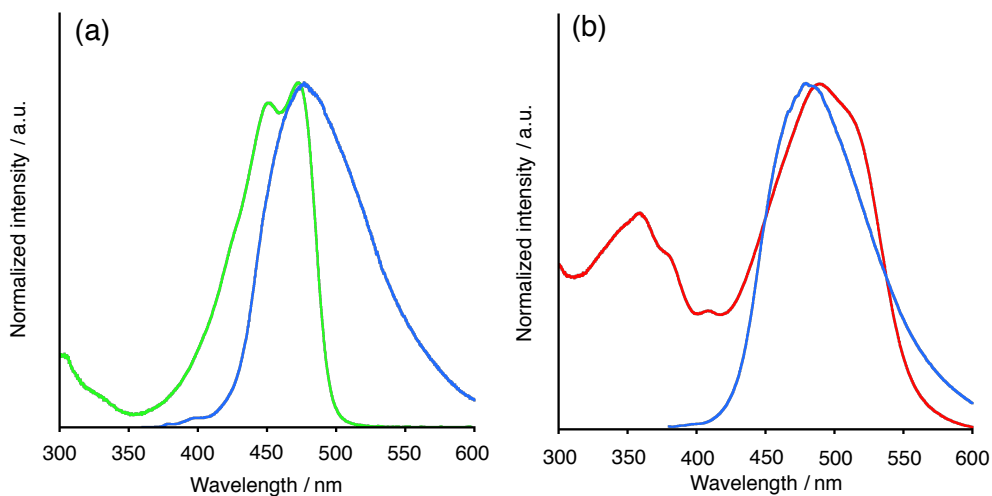


Figure S9. Overlap of the emission spectrum of pyrene excimer of **NP1** (blue line) and the absorption spectrum of (a) C545T (green line) and (b) DCJT B (red line).

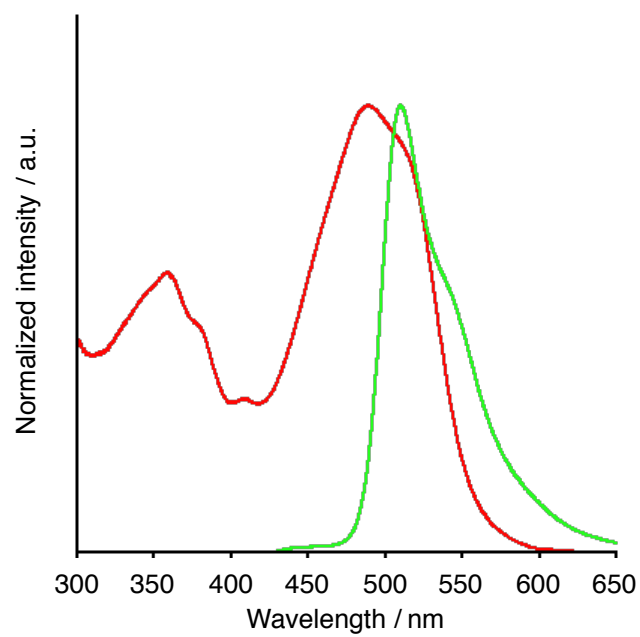


Figure S10. Overlap of the emission spectrum of C545T (green line) and the absorption spectrum of DCJTb (red line).

3. References

- 1 A. Krasovskiy and P. Knochel, *Synlett*, 2006, **5**, 890.
- 2 S. T. Phan, W. Setake and M. Kira, *Chem. Lett.*, 2007, **36**, 1180.
- 3 V. Pongkittiphan, E. A. Theodorakis and W. Chavasiri, *Tetrahedron Lett.*, 2009, **50**, 5080.

4. NMR Spectra

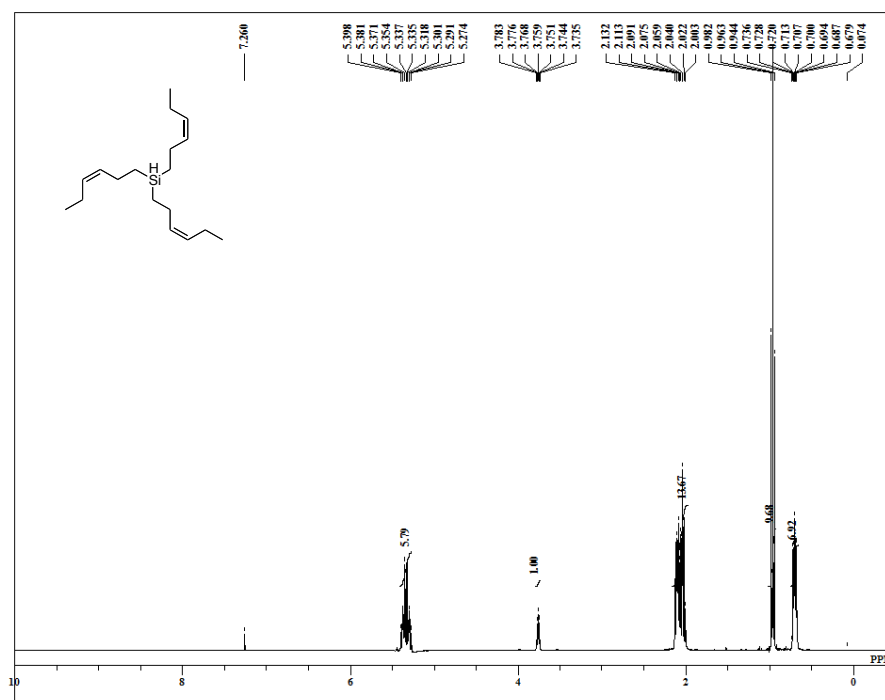


Figure S11. ^1H NMR spectrum (400 MHz) of tri((Z)-3-hexen-1-yl)silane in CDCl_3 .

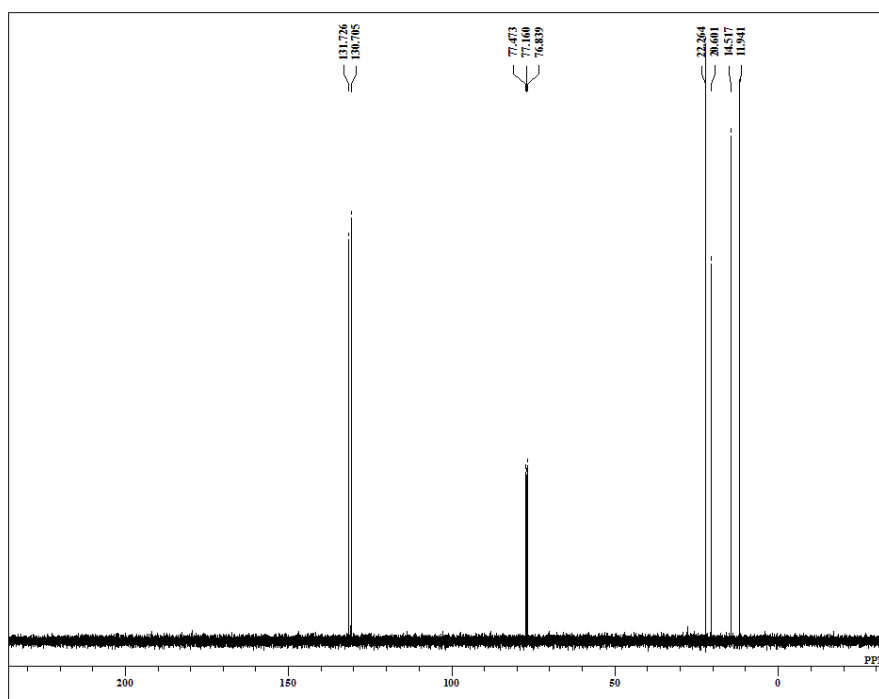


Figure S12. ^{13}C NMR spectrum (100 MHz) of tri((Z)-3-hexen-1-yl)silane in CDCl_3 .

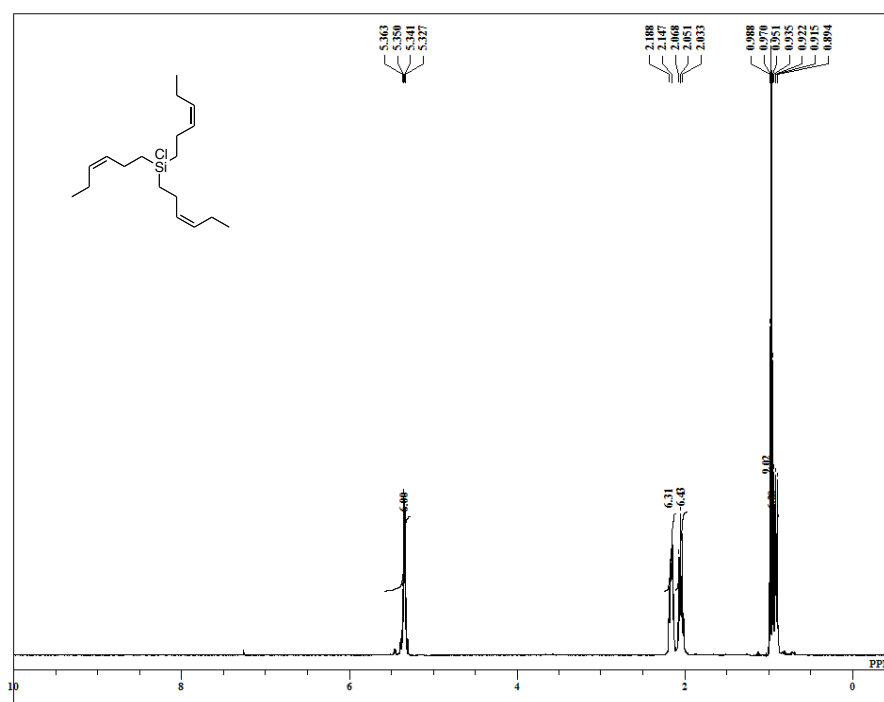


Figure S13. ^1H NMR spectrum (400 MHz) of chlorotri((Z)-3-hexen-1-yl)silane in CDCl_3 .

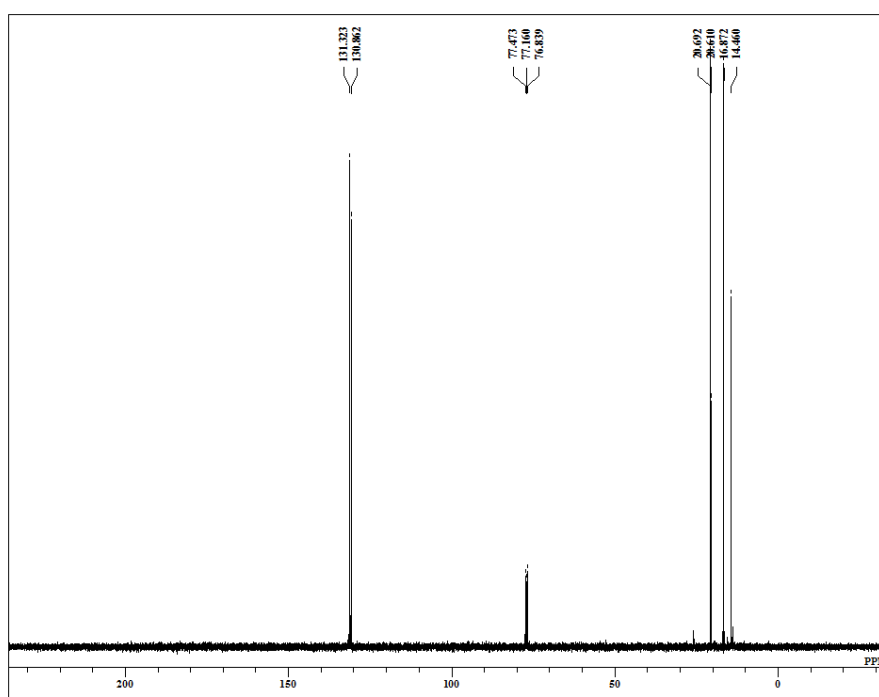


Figure S14. ^{13}C NMR spectrum (100 MHz) of chlorotri((Z)-3-hexen-1-yl)silane in CDCl_3 .

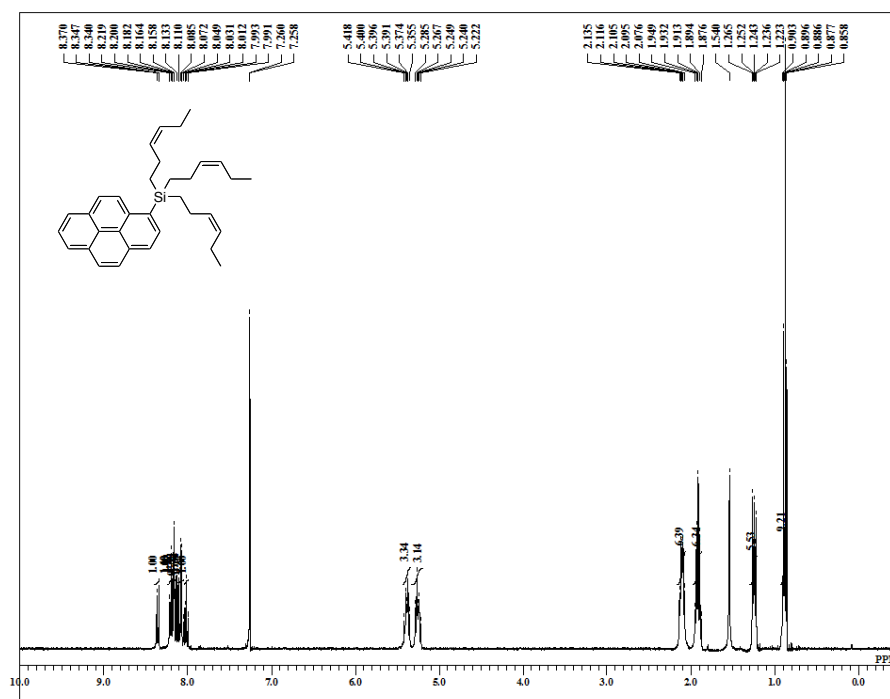


Figure S15. ¹H NMR spectrum (400 MHz) of 1 in CDCl₃.

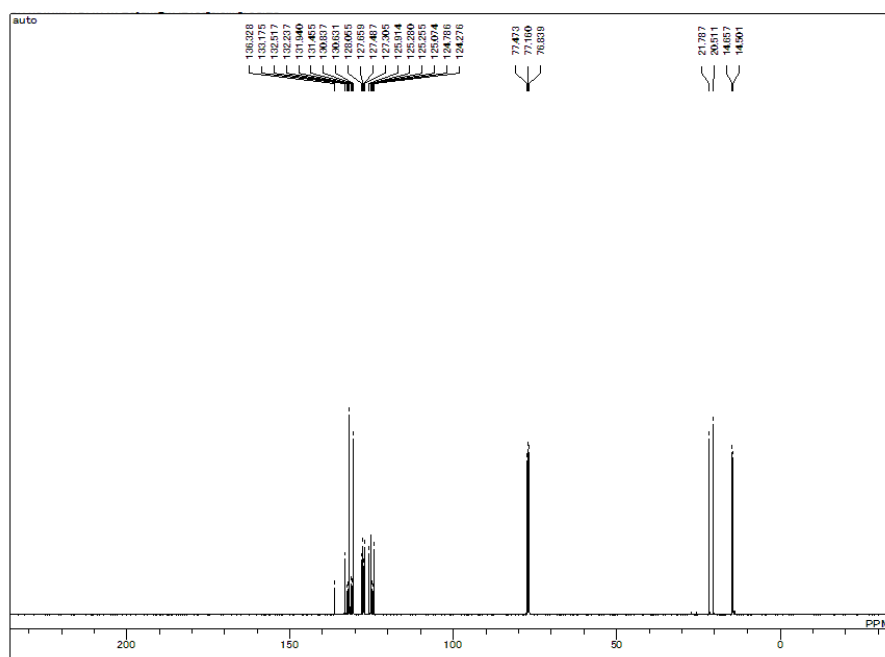


Figure S16. ¹³C NMR spectrum (100 MHz) of 1 in CDCl₃.

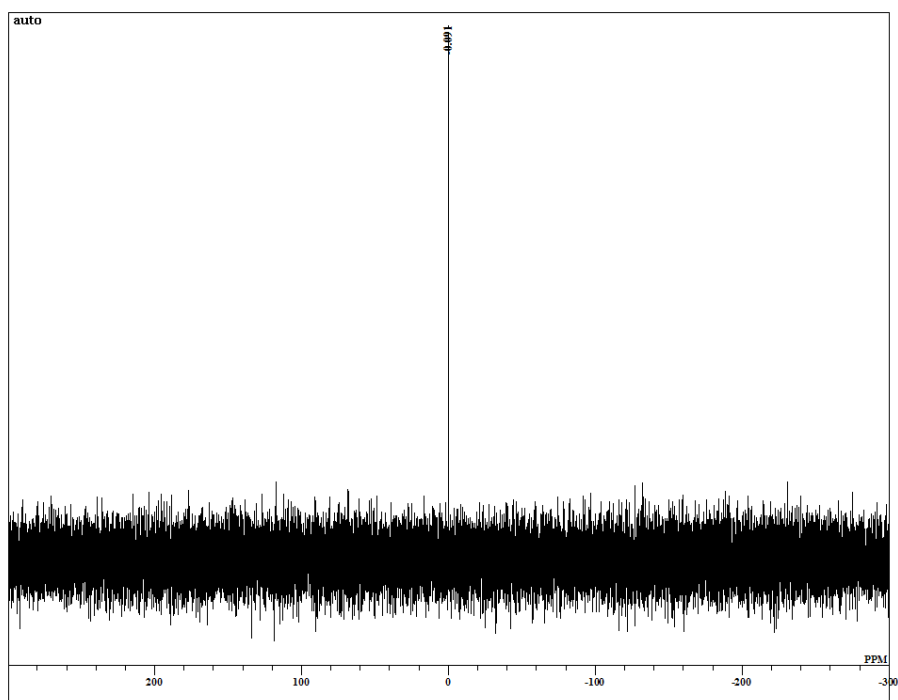


Figure S17. ^{29}Si NMR spectrum (79 MHz) of **1** in CDCl_3 .

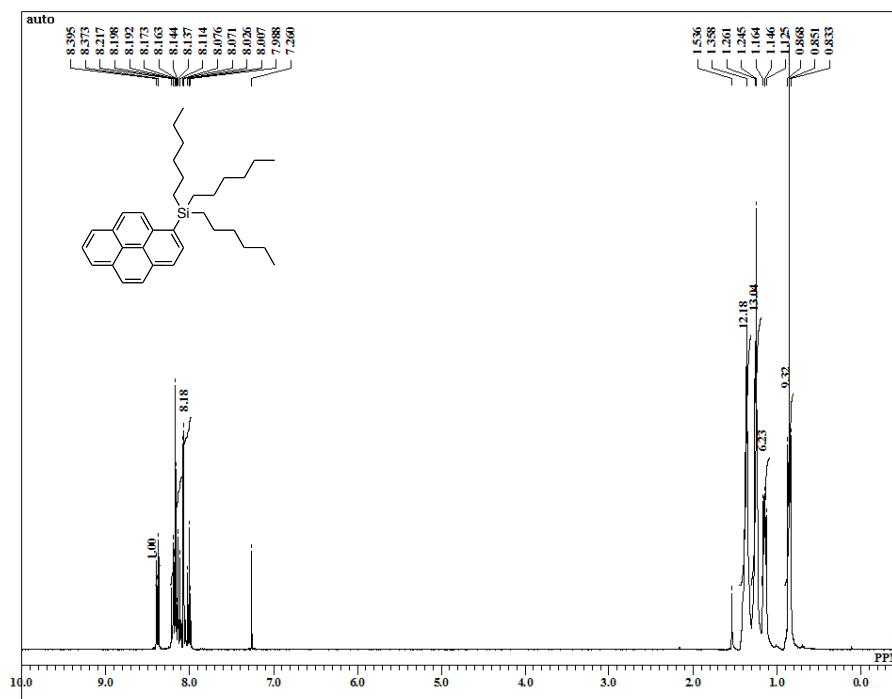


Figure S18. ^1H NMR spectrum (400 MHz) of **2** in CDCl_3 .

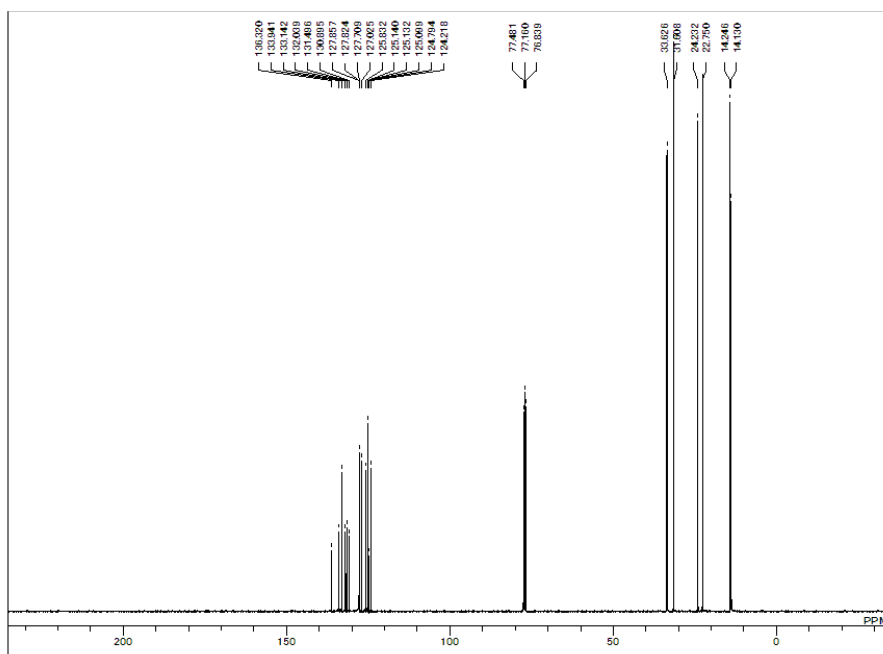


Figure S19. ^{13}C NMR spectrum (100 MHz) of **2** in CDCl_3 .

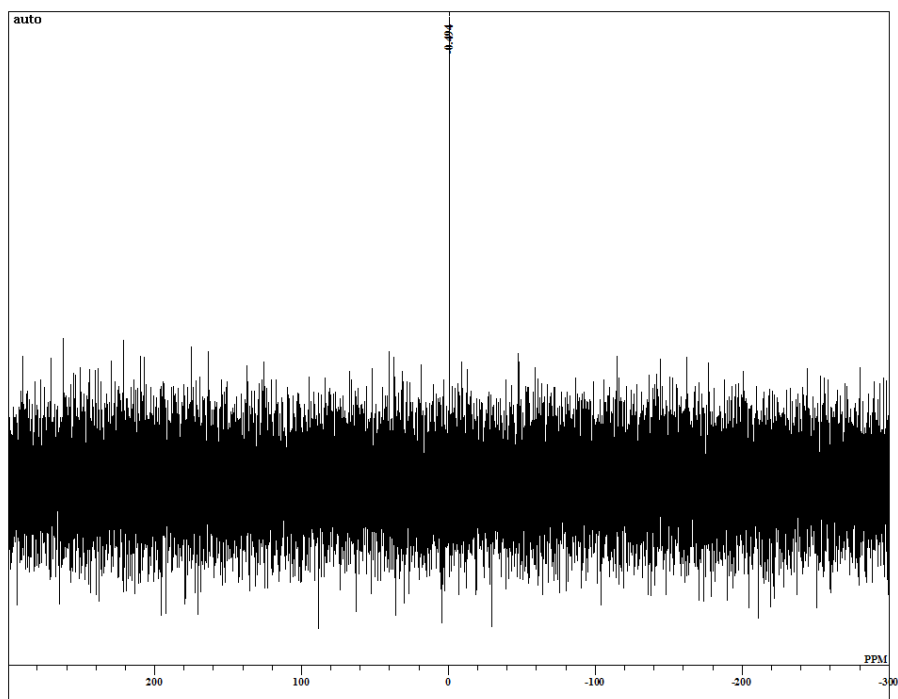


Figure S20. ^{29}Si NMR spectrum (79 MHz) of **2** in CDCl_3 .

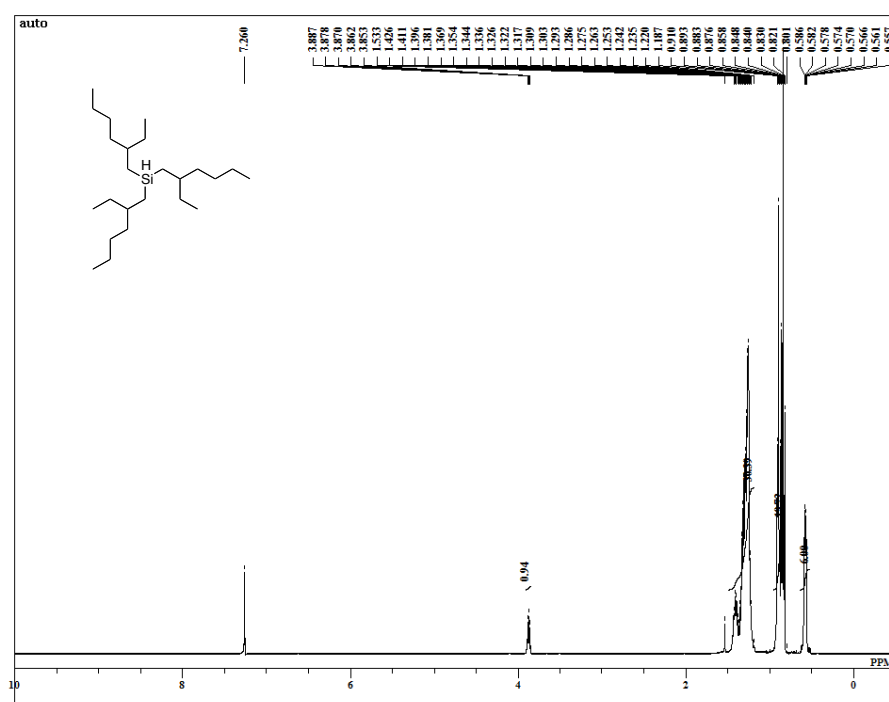


Figure S21. ^1H NMR spectrum (400 MHz) of tris(2-ethylhexyl)silane in CDCl_3 .

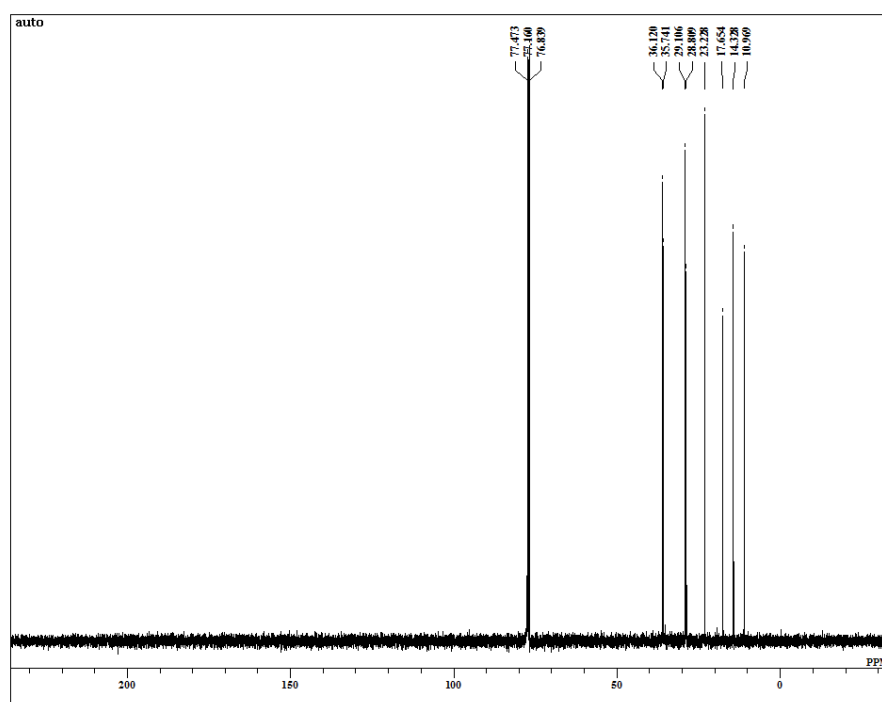


Figure S22. ^{13}C NMR spectrum (100 MHz) of tris(2-ethylhexyl)silane in CDCl_3 .

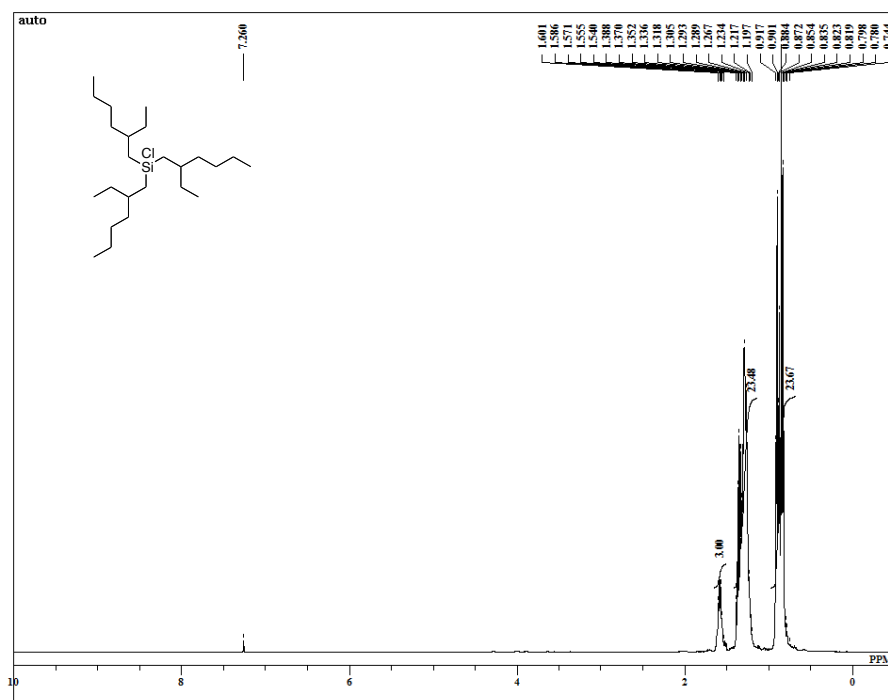


Figure S23. ^1H NMR spectrum (400 MHz) of chlorotris(2-ethylhexyl)silane in CDCl_3 .

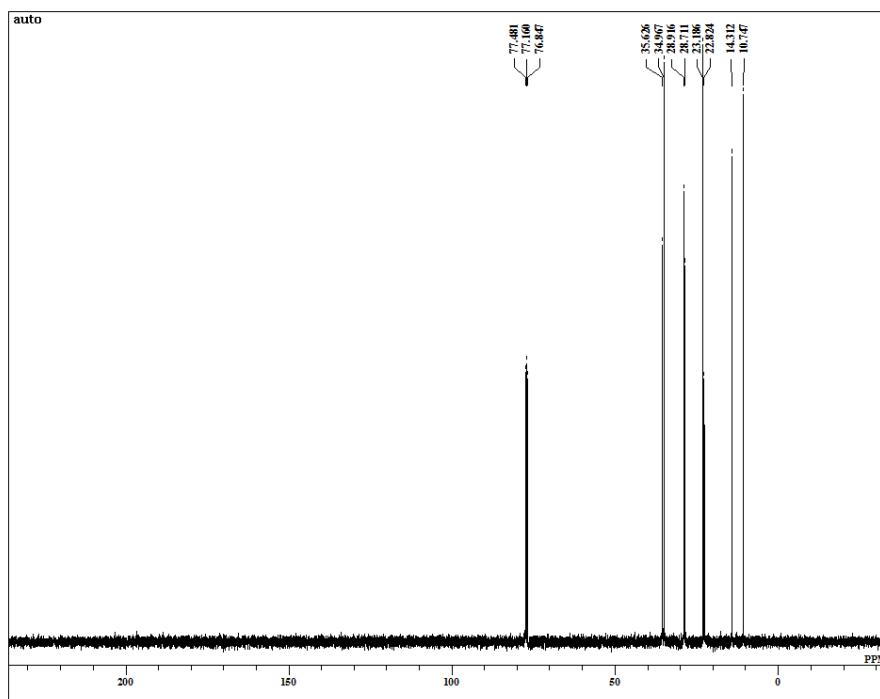


Figure S24. ^{13}C NMR spectrum (100 MHz) of chlorotris(2-ethylhexyl)silane in CDCl_3 .

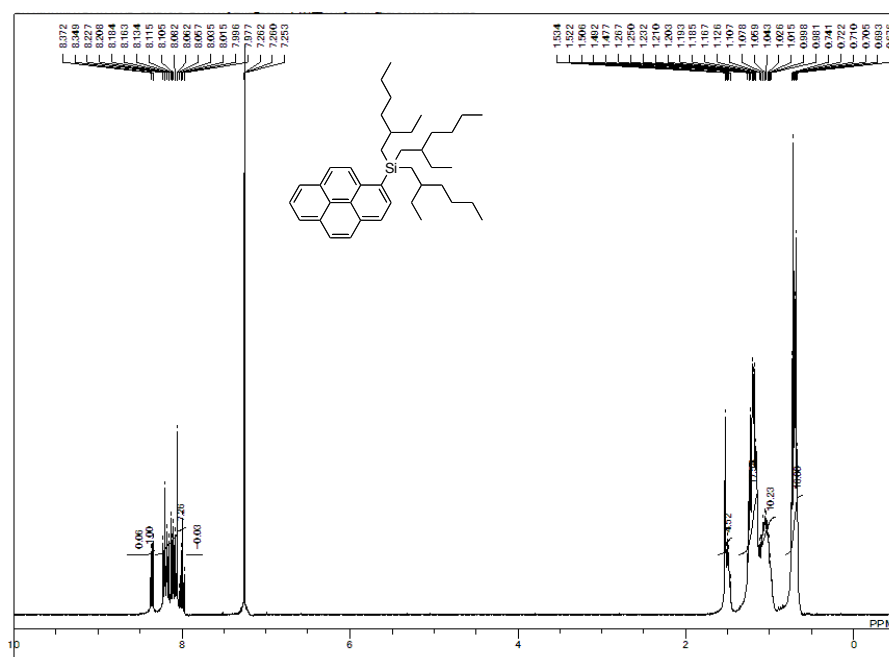


Figure S25. ^1H NMR spectrum (400 MHz) of **3** in CDCl_3 .

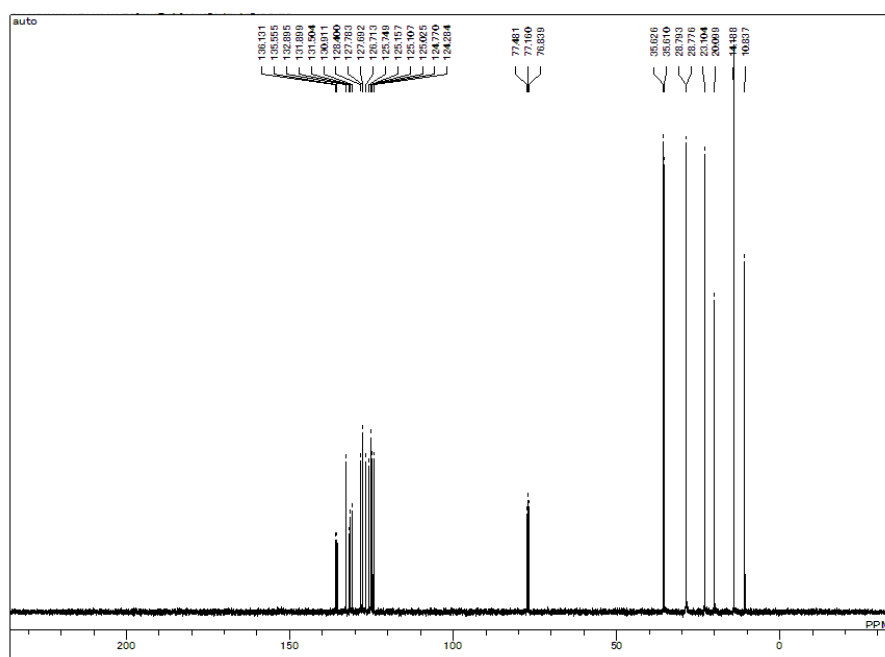


Figure S26. ^{13}C NMR spectrum (100 MHz) of **3** in CDCl_3 .

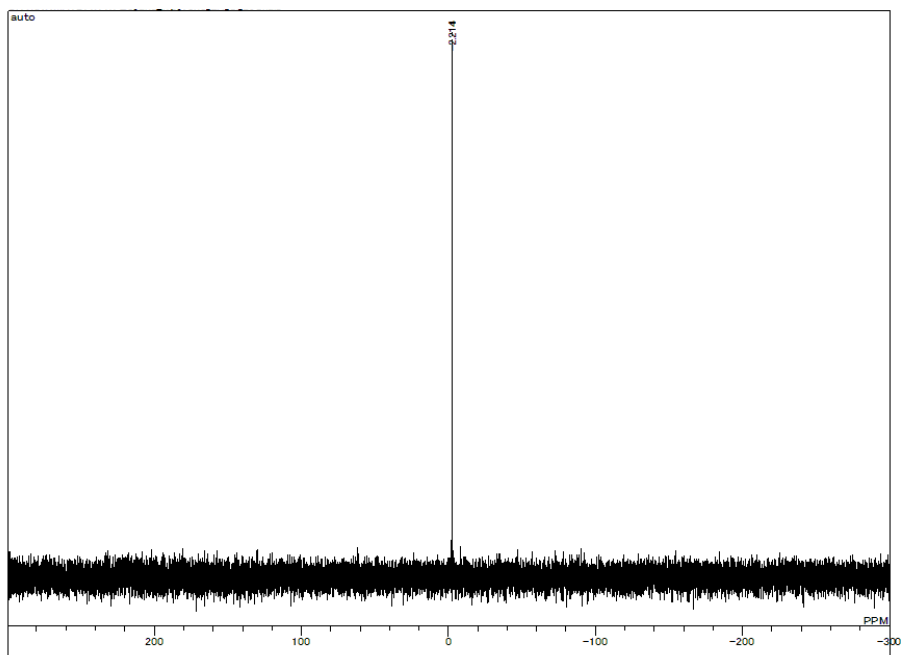


Figure S27. ^{29}Si NMR spectrum (79 MHz) of **3** in CDCl_3 .

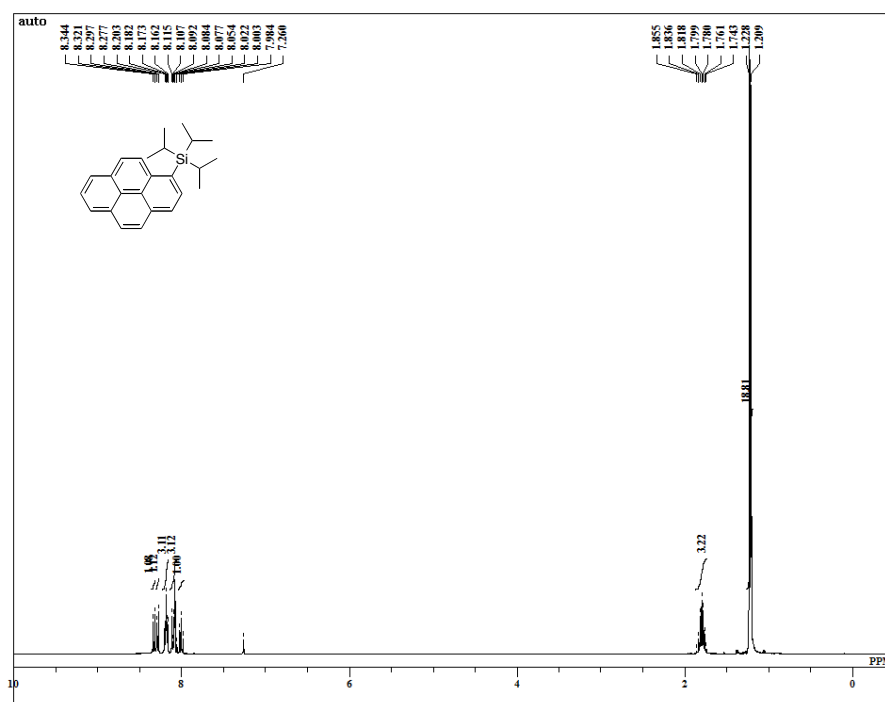


Figure S28. ^1H NMR spectrum (400 MHz) of **4** in CDCl_3 .

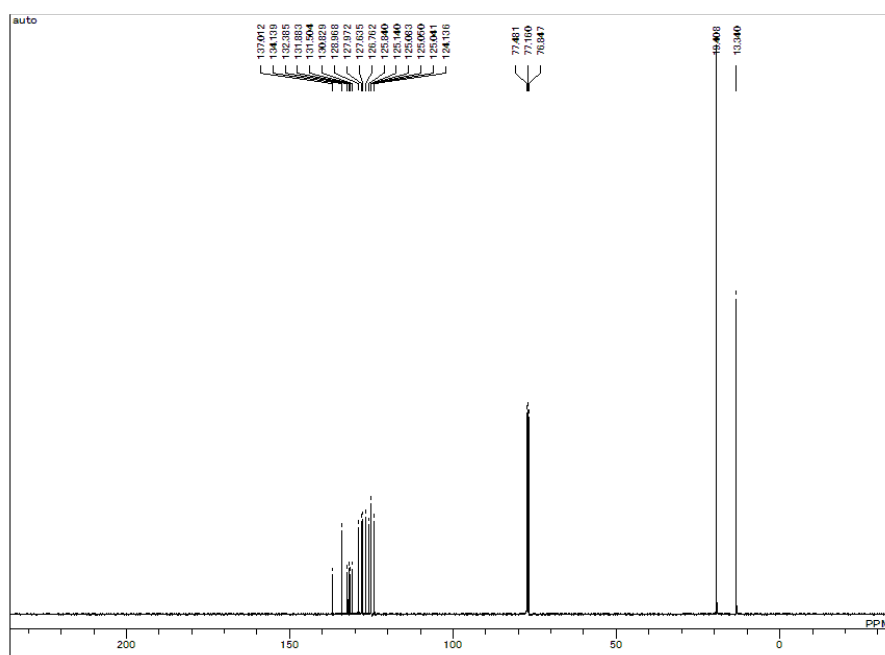


Figure S29. ^{13}C NMR spectrum (100 MHz) of **4** in CDCl_3 .

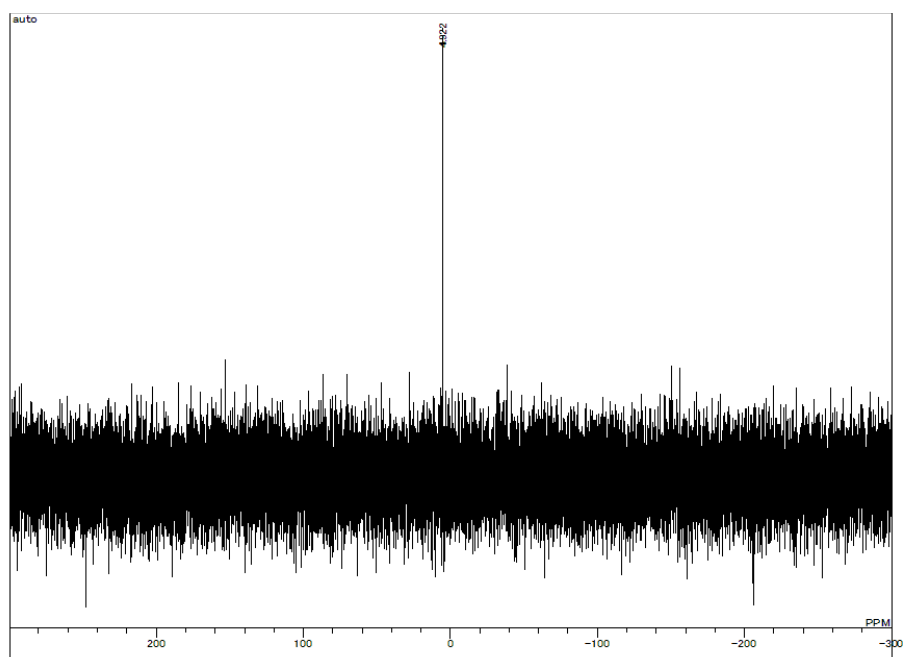


Figure S30. ^{29}Si NMR spectrum (79 MHz) of **4** in CDCl_3 .