Supporting information

The Synthesis of Highly Functionalized 2-Pyranone from Silyl Ketene

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General Considerations. All operations were conducted under an inert atmosphere. All $^1$H, $^{13}$C, $^{29}$Si, HSQC, HMBC and NOESY NMR were collected on Bruker Ascend III HD 500MHz NMR instrument equipped with prodigy probe and shifts are reported relative to residual solvent peak, as noted. All NMR spectra were collected using CDCl$_3$ as the solvent unless otherwise noted. FTIR spectra were acquired using an Aglient Cary 630 FT-IR in ATR mode. Melting points were determined using. Melt-TEMP 50/60 cycle apparatus. ESI spectra were obtained on THERMO Finniagn LCQ DECA ion trap mass spectrometer equipped with an external AP ESI ion source.

Materials. All purchased chemicals were used directly as received, unless otherwise stated. LDA solution, tert-butyldiphenylsilylchloride, $^{1}$BuOLi solution and acetic acid was purchased from sigma aldrich. Dioxane was purchased from fishier and dried over CaH$_2$ under reflux for 8 hours and used immediately or stored in the schlenk flask.

Other Systems Explored. The transformation reported herein (silyl ketene to 2-pyranone) was attempted with many other silyl groups, solvents, and catalysts; the formation of 2 in high yield was only realized with the system reported herein, with all other conditions leading to a complex mixture of products, as determined by TLC and $^1$H NMR. Similar reactions were explored with trimethylsilyl (TMS) ketene, triethylsilylketene (TES), tert-butylmethyldimethylsilyl ketene (TBDMS), triisopropylsilyl (TIPS) ketene, methyldiphenylsilyl (MDPS) ketene, phenyldimethyldimethylsilyl (PDMS) ketene, and triphenylsilyl (TPhS) ketene in dry hexane, cyclohexane, toluene, THF and 1,4-dioxane, with the counterion of Li$^+$, Na$^+$, K$^+$ and NH$_4^+$ and anion of MeO$^-$, $^{1}$BuO$^-$ and LDA.

Materials Preparation
Preparation of Triisopropylsilylketene (TBDPS ketene, 1): (Z)-1-bromo-2-tert-butoxylethene (S1) was prepared using the previously established protocol. [1] An LDA (2mol/L in THF-ethylbenzene-hexane) in THF (48 mL, 0.096 mol LDA) was added to dry THF (48 mL) in an oven-dried round bottom flask placed under N₂, cooled to -78 °C in a dry ice-acetone bath. A mixture S1 (7.08 g, 0.04 mol) and dry THF (16 mL) was prepared in an addition funnel and added dropwise to LDA solution. After complete addition, the reaction was warmed to room temperature naturally and stirred for 3 hours. The vessel was then cooled to -20 °C using a salt water ice bath and tert-butyldiphenylsilyl chloride (12.1 mL, 0.048 mol) was then added and the resulting solution again warmed to room temperature and stirred for 4 hours. The mixture was then transferred to a separation funnel containing an aqueous solution of saturated NaHCO₃ (80 mL). The organic layer was isolated and the aqueous layer washed with hexane (2 x 20 mL). The combined organic layers were washed with 0.5 N HCl (2 x 80 mL), water (120 mL), and an aqueous solution of saturated NaCl (120 mL); the organic phase was dried over Na₂SO₄, then filtered and solvent removed under reduced pressure. The isolated crude product was run through a plug column of silica gel, with eluent of 2.5 vol% NEt₃ in hexanes. A pale, yellow oil was obtained, placed under an inert environment (N₂) and then heated to 85 °C for 2 hours (or until disappearance of the alkyne stretching frequency in the FTIR spectrum). Compound 1 was isolated by vacuum distillation (41%, 4.2 g, 0.016 mol) as a transparent oil. ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 6.5 Hz, 4H), 7.46 (dq, J = 14.0, 7.0 Hz, 6H), 2.30 (s, 1H), 1.14 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 178.96, 135.99, 134.15, 129.99, 128.14, 27.49, 19.45, -3.23. ²⁹Si NMR (99 MHz, CDCl₃) δ -3.59.
Preparation of (Z)-4,6-bis( tert-butyldiphenylsilyl)-3-((tert-butyldiphenylsilyl)oxy)-hex-2-en-5-ynoic acid (2): To a round bottom flask, a THF solution of tBuOLi (1 M, 0.33 mmol) was diluted with dry dioxane (2 mL) at 25°C. Then TBDPS-ketene (1mmol, 0.28g) was added dropwise. After the addition, the mixture was stirred at 25°C for ~30 s. Then neat acetic acid (0.02 g, 0.33mmol) was add. Then the whole mixture was loaded on the column and the final product was obtained by eluting with Hexane : Et₂O = 2 :1 and was pure enough for the next step reaction with the yield of 50%. The spectrum pure title product was obtained after recrystallization from diethyl ether as a white solid (mp = 166 °C). 

\[ ^1H \text{NMR (500 MHz, CDCl}_3\text{)} \delta 8.08 \text{ (d, J = 7.0 Hz, 2H), 7.70 (dd, J = 15.0, 6.8 Hz, 5H), 7.59 (d, J = 7.0 Hz, 2H), 7.54 (d, J = 7.0 Hz, 2H), 7.40 – 7.24 (m, 15H), 7.18 – 7.06 (m, 7H), 6.03 (s, 1H), 4.43 (s, 1H), 1.16 (s, 9H), 1.03 (s, 9H), 0.73 (s, 9H).} \]

\[ ^{13}C \text{NMR (126 MHz, CDCl}_3\text{)} \delta 170.98, 170.52, 137.22, 136.96, 135.96, 135.94, 135.42, 135.24, 133.72, 132.48, 132.01, 131.33, 130.10, 129.96, 129.88, 129.56, 129.43, 129.20, 129.17, 127.79, 127.73, 127.56, 127.52, 127.43, 127.27, 108.25, 99.49, 82.87, 28.73, 27.35, 26.41, 25.27, 19.63, 19.25, 18.70. \]

\[ ^{29}Si \text{NMR (99 MHz, CDCl}_3\text{)} \delta -2.13, -2.74, -18.31. \]

Preparation of 5-(tert-butyldiphenylsilyl)-6-((tert-butyldiphenylsilyl)methyl)-4-((tert-butyldiphenylsilyl)oxy)-2H-pyran-2-one (3): Compound 2 (0.3g,0.36mmol) was dissloved in dry dioxane (2 mL) under N₂ and stirred at 70°C. After complete consumption of 2, the solvent was removed under reduced pressure, and the viscous residue was subjected to column chromatography (elutent of hexanes:ethyl acetate, 10:1, v:v). Byproduct 10 and the compound 3 were isolated (R_f values of 0.8 and 0.5, respectively).
**Compound 3** (75%, 0.23g, 0.27mmol, white solid, mp = 160 °C): $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 – 7.25 (m, 25H), 7.17 (t, J = 7.5 Hz, 4H), 7.02 (d, J = 7.0 Hz, 4H), 5.16 (s, 1H), 2.43 (s, 2H), 0.96 (s, 9H), 0.86 (s, 9H), 0.74 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.21, 172.87, 163.43, 136.80, 136.49, 136.30, 135.43, 133.95, 131.75, 130.34, 129.67, 129.63, 128.34, 128.09, 127.78, 104.50, 97.14, 30.85, 28.77, 28.16, 24.82, 20.22, 20.14, 18.84. $^{29}$Si NMR (99 MHz, CDCl$_3$) δ 1.09, -2.24, -6.13.

**Compound 10** (15%, 0.045g, 0.054mmol, light yellow oil): $^1$H NMR (500 MHz, CDCl$_3$) δ 7.75 – 7.70 (m, 4H), 7.64 (d, J = 7.0 Hz, 4H), 7.57 – 7.53 (m, 4H), 7.38 – 7.13 (m, 26H), 5.00 (s, 1H), 2.87 (s, 2H), 1.01 (s, 18H), 0.94 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.99, 157.32, 136.13, 136.04, 135.92, 135.87, 135.78, 135.73, 135.48, 134.16, 133.03, 131.75, 130.47, 130.45, 129.56, 128.35, 128.17, 128.03, 127.88, 105.35, 93.68, 93.14, 43.86, 27.57, 27.18, 26.96, 19.91, 19.58, 19.00. $^{29}$Si NMR (99 MHz, CDCl$_3$) δ -0.58, -4.98, -17.47.

**Preparation of 5-(tert-butyldiphenylsilyl)-6-((tert-butyldiphenylsilyl)methyl)-4-hydroxy-2H-pyran-2-one (11):** First, 0.23g (0.27 mmol) 3 was dissloved with MeCN/H$_2$O (10 : 1) at room temperature. Then 0.03ml DB ws added and the mixture was stirred at room temperature for 30mins. Then the mixture was washed with 10ml sat. NH$_4$Cl solution. The aqueous phase was washed with DCM. Then the organic phase was combined and dried under Na$_2$SO$_4$ for 30min. Then the solvent was evaporated and the residue was laded on the column and eluted with Hex : EA = 5 : 1 first to get rid of the tert-butyldiphenylsilyl alcohol and then Hex : EtOH = 10 : 1 to get the titled compound as a white solid (0.1g, 0.16mmol, 61%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 (d, J = 7.0 Hz, 4H), 7.32 (t, J = 7.0 Hz, 3H), 7.26 (t, J = 7.0 Hz, 5H), 7.18 – 7.10 (m, 7H), 7.04 (t, J = 7.5 Hz, 4H), 5.44 (s, 1H), 2.03 (s, 2H), 1.00 (s, 10H), 0.63 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 176.87, 174.81, 166.53, 105.13, 89.13, 30.21, 27.90, 23.35, 20.08, 18.51. $^{29}$Si NMR (99 MHz, CDCl$_3$) δ -2.90, -6.29.
Preparation of 5-(tert-butyldiphenylsilyl)-6-((tert-butyldiphenylsilyl)methyl)-4-((tert-butyldiphenylsilyl)oxy)-2-bromo-pyran-2-one (12): First, 0.5g 3 was diluted with 3ml dry DCM and stirred at room temperature. Then 0.4ml Br$_2$/DCM solution (1.66M) was added dropwisely. After the addition, the mixture was kept stirred in the dark for 3hrs. Then the mixture was loaded on the column and eluted with Hex:EA = 5 : 1 to get the titled compound as a white solid with the yield of 30% (0.12g). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 (d, J = 6.5 Hz, 3H), 7.43 (d, J = 7.0 Hz, 3H), 7.34 – 7.31 (m, 5H), 7.26 (t, J = 7.0 Hz, 7H), 7.20 (d, J = 7.0 Hz, 4H), 6.42 (s, 1H), 2.08 (s, 2H), 1.00 (s, 9H), 0.68 (s, 10H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.73, 167.82, 158.96, 102.00, 87.84, 30.05, 27.90, 23.15, 20.05, 18.62. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ 2.33, -1.27.
Figure S1: Characterization of 1: A) $^1$H NMR; B) $^{13}$C NMR; C) $^{29}$Si NMR; D) FTIR; E) Gas chromatogram; F) Mass spectrum from GC-MS.

A) 

B)
Figure S2: Characterization of 2: A) $^1$H NMR; B) $^{13}$C NMR; C) $^{29}$Si NMR; D) HSQC NMR; E) HMBC NMR; F) NOESY NMR; G) FTIR; H) Electrospray ionization mass spectrum.

A) 

B)
G)

H)
Figure S3: Characterization of 3: A) $^1$H NMR; B) $^{13}$C NMR; C) $^{29}$Si NMR; D) HSQC NMR; E) HMBC NMR; F) NOESY NMR; G) FTIR; H) Electrospray ionization mass spectrum.

A)

B)
Figure S4: Full $^1$H NMR spectra before and after 13 and 78 hours of heating 2 in dioxane with the chemical shifts of starting material 2, product 3, intermediate 6, and byproduct 10 identified by boxes of the relevant colors.
Figure S5. Characterization of 10: A) $^1$H NMR; B) $^{13}$C NMR; C) $^{29}$Si NMR; D) HSQC NMR; E) HMBC NMR; F) NOESY NMR; G) FTIR; H) Electrospray ionization mass spectrum.

A)

B)
**Figure S6.** Proposed structure of compound 6 based on NMR spectrum of the reaction mixture at 13 hours: A) $^1$H NMR; B) $^{13}$C NMR; C) HSQC NMR; D) HMBC NMR. (Peaks labeled as 2, 10, 3 stand for compound 2, compound 10 and compound 3, respectively.)
Figure S7. Characterization data for compound 11: A) $^1$H NMR; B) $^{13}$C NMR; C) $^{29}$Si NMR; D) FTIR; E) Electronspray ionization mass spectrum.

A)
Figure S8. Characterization data for compound 12: A) $^1$H NMR; B) $^{13}$C NMR; C) $^{29}$Si NMR; D) FTIR; E) Electronspray ionization mass spectrum.

A)

B)
Appendix 1. XRD characterization data. The thermal ellipsoid probability of the X-ray structures is 50%.

Table S1. Crystal data and structure refinement for Compound 2.

| Identification code | Compound 2 |
|---------------------|------------|
| Empirical formula   | C54 H60 O3 Si3 |
| Formula weight      | 841.29 |
| Temperature         | 100.0 K |
| Wavelength          | 1.54178 Å |
| Crystal system      | Triclinic |
| Space group         | P-1 |
| Unit cell dimensions| \(a = 13.7333(5) \text{ Å}\) \(\beta = 90.326(2)^\circ\) |
|                     | \(b = 14.5236(5) \text{ Å}\) \(\beta = 109.495(2)^\circ\) |
|                     | \(c = 15.4513(5) \text{ Å}\) \(\beta = 93.507(2)^\circ\) |
| Volume              | 2898.63(18) Å³ |
| \(Z\)               | 2 |
| Density (calculated) | 0.964 Mg/m³ |
| Absorption coefficient | 1.015 mm⁻¹ |
| \(F(000)\)          | 900 |
| Crystal size        | 0.3 x 0.27 x 0.24 mm³ |
| Theta range for data collection | 3.035 to 68.326°. |
| Index ranges        | -14<=h<=16, -17<=k<=17, -18<=l<=18 |
| Reflections collected | 36276 |
| Independent reflections | 10419 \([R(int) = 0.0523]\) |
| Completeness to theta | 67.679° | 97.90% |
| Description                                           | Value                                           |
|-------------------------------------------------------|-------------------------------------------------|
| Absorption correction                                 | Semi-empirical from equivalents                 |
| Max. and min. transmission                            | 0.7531 and 0.6285                                |
| Refinement method                                     | Full-matrix least-squares on F$_2$              |
| Data / restraints / parameters                         | 10419 / 0 / 551                                  |
| Goodness-of-fit on F$_2$                              | 1.068                                           |
| Final R indices [I>2sigma(I)]                         | R$_1$ = 0.0516, wR$_2$ = 0.1340                  |
| R indices (all data)                                  | R$_1$ = 0.0646, wR$_2$ = 0.1417                  |
| Extinction coefficient                                | n/a                                             |
| Largest diff. peak and hole                           | 1.129 and -0.387 eÅ$^3$                         |
| SQUEEZE                                               | 155e/uc (4 DCM = 168e/uc)                       |
Table S2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound 2. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | x      | y      | z      | $U(\text{eq})$ |
|-------|--------|--------|--------|----------------|
| Si(1) | 7230(1)| 7633(1)| 5169(1)| 22(1)         |
| Si(2) | 5712(1)| 8485(1)| 1845(1)| 26(1)         |
| Si(3) | 7346(1)| 4711(1)| 2772(1)| 23(1)         |
| O(3)  | 6377(1)| 8002(1)| 2837(1)| 24(1)         |
| O(1)  | 9021(1)| 10313(1)| 3954(1)| 32(1)        |
| O(2)  | 9359(1)| 8997(1)| 4713(1)| 30(1)         |
| C(6)  | 8783(2)| 9443(1)| 4091(1)| 23(1)         |
| C(28) | 7734(2)| 2961(1)| 3605(2)| 31(1)         |
| C(3)  | 7732(2)| 7528(1)| 4135(1)| 21(1)         |
| C(45) | 6551(2)| 8532(1)| 1112(2)| 30(1)         |
| C(29) | 5932(2)| 4325(1)| 2269(2)| 24(1)         |
| C(12) | 6443(2)| 9417(2)| 4974(2)| 31(1)         |
| C(1)  | 7462(2)| 5867(1)| 3314(2)| 25(1)         |
| C(35) | 8050(2)| 4766(2)| 1902(2)| 29(1)         |
| C(24) | 8723(2)| 4231(2)| 4547(2)| 29(1)         |
| C(5)  | 7792(2)| 9098(1)| 3440(1)| 23(1)         |
| C(2)  | 7572(2)| 6611(1)| 3690(1)| 22(1)         |
| C(17) | 5843(2)| 7171(1)| 4872(2)| 29(1)         |
| C(7)  | 7280(2)| 8904(1)| 5450(2)| 25(1)         |
| C(25) | 9183(2)| 3625(2)| 5231(2)| 37(1)         |
| C(23) | 7988(2)| 3914(1)| 3719(2)| 24(1)         |
| C(39) | 5364(2)| 9665(2)| 2094(2)| 30(1)         |
| C(27) | 8200(2)| 2354(2)| 4287(2)| 35(1)         |
| C(44) | 5778(2)| 10472(2)| 1819(2)| 35(1)        |
| C(40) | 4695(2)| 9772(2)| 2599(2)| 37(1)         |
| C(51) | 4560(2)| 7637(2)| 1324(2)| 37(1)         |
| C(46) | 7402(2)| 7981(2)| 1299(2)| 33(1)         |
| C(36) | 8160(2)| 3792(2)| 1568(2)| 36(1)         |
| C(4)  | 7318(2)| 8261(1)| 3450(1)| 21(1)         |
| C(33) | 4400(2)| 3635(2)| 1091(2)| 36(1)         |
| C(32) | 3814(2)| 3749(2)| 1642(2)| 41(1)         |
| C     | 5527(2) | 11337(2) | 2027(2) | 41(1) |
|-------|---------|----------|---------|-------|
| C(10) | 7281(2) | 10806(2) | 5815(2) | 48(1) |
| C(8)  | 8120(2) | 9381(2)  | 6104(2) | 39(1) |
| C(11) | 6444(2) | 10357(2) | 5153(2) | 43(1) |
| C(50) | 6326(2) | 9050(2)  | 308(2)  | 38(1) |
| C(34) | 5442(2) | 3923(2)  | 1398(2) | 34(1) |
| C(16) | 7748(3) | 5913(2)  | 5961(2) | 48(1) |
| C(13) | 8087(2) | 6952(2)  | 6153(2) | 33(1) |
| C(18) | 5255(2) | 7483(2)  | 5373(2) | 38(1) |
| C(37) | 7488(2) | 5347(2)  | 1078(2) | 39(1) |
| C(38) | 9141(2) | 5219(2)  | 2385(2) | 40(1) |
| C(9)  | 8121(2) | 10317(2) | 6285(2) | 49(1) |
| C(15) | 7936(2) | 7242(2)  | 7058(2) | 38(1) |
| C(30) | 5331(2) | 4412(2)  | 2824(2) | 46(1) |
| C(26) | 8920(2) | 2687(2)  | 5101(2) | 37(1) |
| C(53) | 4956(2) | 6688(2)  | 1242(2) | 36(1) |
| C(19) | 4252(2) | 7127(2)  | 5236(2) | 42(1) |
| C(41) | 4443(2) | 10637(2) | 2804(2) | 47(1) |
| C(49) | 6910(2) | 9032(2)  | -263(2) | 46(1) |
| C(47) | 7984(2) | 7952(2)  | 724(2)  | 43(1) |
| C(48) | 7740(2) | 8483(2)  | -61(2)  | 48(1) |
| C(31) | 4286(2) | 4129(2)  | 2523(2) | 58(1) |
| C(20) | 3798(2) | 6464(2)  | 4589(2) | 51(1) |
| C(42) | 4856(2) | 11422(2) | 2513(2) | 49(1) |
| C(14) | 9232(2) | 7085(2)  | 6250(2) | 52(1) |
| C(52) | 3836(2) | 7576(2)  | 1882(3) | 66(1) |
| C(22) | 5322(2) | 6550(2)  | 4142(2) | 52(1) |
| C(54) | 3957(2) | 7960(2)  | 350(2)  | 61(1) |
| C(21) | 4310(2) | 6209(2)  | 3999(3) | 61(1) |
Table S3. Bond lengths [Å] and angles [°] for compound 2.

| Bond                  | Length [Å]  |
|-----------------------|-------------|
| Si(1)-C(3)            | 1.947(2)    |
| Si(1)-C(17)           | 1.883(2)    |
| Si(1)-C(7)            | 1.887(2)    |
| Si(1)-C(13)           | 1.908(2)    |
| Si(2)-O(3)            | 1.6828(15)  |
| Si(2)-C(45)           | 1.865(3)    |
| Si(2)-C(39)           | 1.878(2)    |
| Si(2)-C(51)           | 1.889(2)    |
| Si(3)-C(29)           | 1.883(2)    |
| Si(3)-C(1)            | 1.846(2)    |
| Si(3)-C(35)           | 1.900(2)    |
| Si(3)-C(23)           | 1.881(2)    |
| O(3)-C(4)             | 1.352(2)    |
| O(1)-H(1)             | 0.8400      |
| O(1)-C(6)             | 1.321(2)    |
| O(2)-C(6)             | 1.237(2)    |
| C(6)-C(5)             | 1.454(3)    |
| C(28)-H(28)           | 0.9500      |
| C(28)-C(23)           | 1.402(3)    |
| C(28)-C(27)           | 1.388(3)    |
| C(3)-H(3)             | 1.0000      |
| C(3)-C(2)             | 1.466(3)    |
| C(3)-C(4)             | 1.504(3)    |
| C(45)-C(46)           | 1.408(3)    |
| C(45)-C(50)           | 1.410(3)    |
| C(29)-C(34)           | 1.394(3)    |
| C(29)-C(30)           | 1.384(3)    |
| C(12)-H(12)           | 0.9500      |
| C(12)-C(7)            | 1.401(3)    |
| C(12)-C(11)           | 1.392(3)    |
| C(1)-C(2)             | 1.201(3)    |
| C(35)-C(36)           | 1.534(3)    |
| C(35)-C(37)           | 1.537(3)    |
| C(35)-C(38)           | 1.537(3)    |
C(24)-H(24)  0.9500
C(24)-C(25)  1.387(3)
C(24)-C(23)  1.393(3)
C(5)-H(5)  0.9500
C(5)-C(4)  1.346(3)
C(17)-C(18)  1.384(3)
C(17)-C(22)  1.404(4)
C(7)-C(8)  1.396(3)
C(25)-H(25)  0.9500
C(25)-C(26)  1.384(4)
C(39)-C(44)  1.403(3)
C(39)-C(40)  1.404(4)
C(27)-H(27)  0.9500
C(27)-C(26)  1.378(4)
C(44)-H(44)  0.9500
C(44)-C(43)  1.387(3)
C(40)-H(40)  0.9500
C(40)-C(41)  1.385(3)
C(51)-C(53)  1.532(3)
C(51)-C(52)  1.517(4)
C(51)-C(54)  1.547(4)
C(46)-H(46)  0.9500
C(46)-C(47)  1.380(4)
C(36)-H(36A)  0.9800
C(36)-H(36B)  0.9800
C(36)-H(36C)  0.9800
C(33)-H(33)  0.9500
C(33)-C(32)  1.369(4)
C(33)-C(34)  1.386(3)
C(32)-H(32)  0.9500
C(32)-C(31)  1.390(4)
C(43)-H(43)  0.9500
C(43)-C(42)  1.378(4)
C(10)-H(10)  0.9500
C(10)-C(11)  1.382(4)
C(10)-C(9)  1.382(4)
C(8)-H(8)  0.9500
C(8)-C(9)  1.385(4)
C(11)-H(11)  0.9500
C(50)-H(50)  0.9500
C(50)-C(49)  1.377(4)
C(34)-H(34)  0.9500
C(16)-H(16A)  0.9800
C(16)-H(16B)  0.9800
C(16)-H(16C)  0.9800
C(16)-C(13)  1.548(4)
C(13)-C(15)  1.541(3)
C(13)-C(14)  1.530(4)
C(18)-H(18)  0.9500
C(18)-C(19)  1.388(4)
C(37)-H(37A)  0.9800
C(37)-H(37B)  0.9800
C(37)-H(37C)  0.9800
C(38)-H(38A)  0.9800
C(38)-H(38B)  0.9800
C(38)-H(38C)  0.9800
C(9)-H(9)  0.9500
C(15)-H(15A)  0.9800
C(15)-H(15B)  0.9800
C(15)-H(15C)  0.9800
C(30)-H(30)  0.9500
C(30)-C(31)  1.387(4)
C(26)-H(26)  0.9500
C(53)-H(53A)  0.9800
C(53)-H(53B)  0.9800
C(53)-H(53C)  0.9800
C(19)-H(19)  0.9500
C(19)-C(20)  1.347(4)
C(41)-H(41)  0.9500
C(41)-C(42)  1.386(4)
C(49)-H(49)  0.9500
C(49)-C(48)  1.381(4)
| Bond                  | Length   |
|----------------------|----------|
| C(47)-H(47)          | 0.9500   |
| C(47)-C(48)          | 1.397(4) |
| C(48)-H(48)          | 0.9500   |
| C(31)-H(31)          | 0.9500   |
| C(20)-H(20)          | 0.9500   |
| C(20)-C(21)          | 1.385(4) |
| C(42)-H(42)          | 0.9500   |
| C(14)-H(14A)         | 0.9800   |
| C(14)-H(14B)         | 0.9800   |
| C(14)-H(14C)         | 0.9800   |
| C(52)-H(52A)         | 0.9800   |
| C(52)-H(52B)         | 0.9800   |
| C(52)-H(52C)         | 0.9800   |
| C(22)-H(22)          | 0.9500   |
| C(22)-C(21)          | 1.391(4) |
| C(54)-H(54A)         | 0.9800   |
| C(54)-H(54B)         | 0.9800   |
| C(54)-H(54C)         | 0.9800   |
| C(21)-H(21)          | 0.9500   |
| C(17)-Si(1)-C(3)     | 112.20(10)|
| C(17)-Si(1)-C(7)     | 107.32(10)|
| C(17)-Si(1)-C(13)    | 109.37(11)|
| C(7)-Si(1)-C(3)      | 106.60(9) |
| C(7)-Si(1)-C(13)     | 113.44(10)|
| C(13)-Si(1)-C(3)     | 107.95(9) |
| O(3)-Si(2)-C(45)     | 107.38(9) |
| O(3)-Si(2)-C(39)     | 109.40(9) |
| O(3)-Si(2)-C(51)     | 103.69(10)|
| C(45)-Si(2)-C(39)    | 111.89(11)|
| C(45)-Si(2)-C(51)    | 109.85(11)|
| C(39)-Si(2)-C(51)    | 114.11(11)|
| C(29)-Si(3)-C(35)    | 114.06(10)|
| C(1)-Si(3)-C(29)     | 108.46(9) |
| C(1)-Si(3)-C(35)     | 108.74(10)|
| C(1)-Si(3)-C(23)     | 106.57(9) |
C(23)-Si(3)-C(29)  108.63(9)
C(23)-Si(3)-C(35)  110.11(10)
C(4)-O(3)-Si(2)  129.69(13)
C(6)-O(1)-H(1)  109.5
O(1)-C(6)-C(5)  112.31(17)
O(2)-C(6)-O(1)  122.07(19)
O(2)-C(6)-C(5)  125.61(18)
C(23)-C(28)-H(28)  119.3
C(27)-C(28)-H(28)  119.3
C(27)-C(28)-C(23)  121.4(2)
Si(1)-C(3)-H(3)  106.1
C(2)-C(3)-Si(1)  115.56(14)
C(2)-C(3)-H(3)  106.1
C(2)-C(3)-C(4)  111.54(17)
C(4)-C(3)-Si(1)  110.75(13)
C(4)-C(3)-H(3)  106.1
C(46)-C(45)-Si(2)  120.69(18)
C(46)-C(45)-C(50)  116.5(2)
C(50)-C(45)-Si(2)  122.61(18)
C(34)-C(29)-Si(3)  125.72(17)
C(30)-C(29)-Si(3)  117.35(17)
C(30)-C(29)-C(34)  116.9(2)
C(7)-C(12)-H(12)  119.3
C(11)-C(12)-H(12)  119.3
C(11)-C(12)-C(7)  121.5(2)
C(2)-C(1)-Si(3)  177.5(2)
C(36)-C(35)-Si(3)  110.72(16)
C(36)-C(35)-C(37)  109.98(19)
C(36)-C(35)-C(38)  108.24(19)
C(37)-C(35)-Si(3)  111.16(16)
C(38)-C(35)-Si(3)  107.63(16)
C(38)-C(35)-C(37)  109.0(2)
C(25)-C(24)-H(24)  119.4
C(25)-C(24)-C(23)  121.2(2)
C(23)-C(24)-H(24)  119.4
C(6)-C(5)-H(5)  117.2
C(4)-C(5)-C(6) 125.62(19)
C(4)-C(5)-H(5) 117.2
C(1)-C(2)-C(3) 178.1(2)
C(18)-C(17)-Si(1) 119.26(17)
C(18)-C(17)-C(22) 115.7(2)
C(22)-C(17)-Si(1) 125.03(18)
C(12)-C(7)-Si(1) 119.26(16)
C(8)-C(7)-Si(1) 123.72(17)
C(8)-C(7)-C(12) 117.0(2)
C(24)-C(25)-H(25) 119.9
C(26)-C(25)-C(24) 120.2(2)
C(26)-C(25)-H(25) 119.9
C(28)-C(23)-Si(3) 120.01(17)
C(24)-C(23)-Si(3) 122.57(16)
C(24)-C(23)-C(28) 117.4(2)
C(44)-C(39)-Si(2) 122.35(19)
C(44)-C(39)-C(40) 117.0(2)
C(40)-C(39)-Si(2) 120.58(18)
C(28)-C(27)-H(27) 120.0
C(26)-C(27)-C(28) 119.9(2)
C(26)-C(27)-H(27) 120.0
C(39)-C(44)-H(44) 119.3
C(43)-C(44)-C(39) 121.3(3)
C(43)-C(44)-H(44) 119.3
C(39)-C(40)-H(40) 119.3
C(41)-C(40)-C(39) 121.5(2)
C(41)-C(40)-H(40) 119.3
C(53)-C(51)-Si(2) 108.50(16)
C(53)-C(51)-C(54) 108.8(2)
C(52)-C(51)-Si(2) 112.51(18)
C(52)-C(51)-C(53) 110.1(2)
C(52)-C(51)-C(54) 108.8(3)
C(54)-C(51)-Si(2) 108.00(19)
C(45)-C(46)-H(46) 119.2
C(47)-C(46)-C(45) 121.6(2)
C(47)-C(46)-H(46) 119.2
C(35)-C(36)-H(36A) 109.5
C(35)-C(36)-H(36B) 109.5
C(35)-C(36)-H(36C) 109.5
H(36A)-C(36)-H(36B) 109.5
H(36A)-C(36)-H(36C) 109.5
H(36B)-C(36)-H(36C) 109.5
O(3)-C(4)-C(3) 112.41(16)
C(5)-C(4)-O(3) 122.07(18)
C(5)-C(4)-C(3) 125.49(18)
C(32)-C(33)-H(33) 119.9
C(32)-C(33)-C(34) 120.2(2)
C(34)-C(33)-H(33) 119.9
C(33)-C(32)-H(32) 120.4
C(33)-C(32)-C(31) 119.1(2)
C(31)-C(32)-H(32) 120.4
C(44)-C(43)-H(43) 119.8
C(42)-C(43)-C(44) 120.4(3)
C(42)-C(43)-H(43) 119.8
C(11)-C(10)-H(10) 120.3
C(11)-C(10)-C(9) 119.4(2)
C(9)-C(10)-H(10) 120.3
C(7)-C(8)-H(8) 119.2
C(9)-C(8)-C(7) 121.6(2)
C(9)-C(8)-H(8) 119.2
C(12)-C(11)-H(11) 120.0
C(10)-C(11)-C(12) 120.1(2)
C(10)-C(11)-H(11) 120.0
C(45)-C(50)-H(50) 118.9
C(49)-C(50)-C(45) 122.2(2)
C(49)-C(50)-H(50) 118.9
C(29)-C(34)-H(34) 119.0
C(33)-C(34)-C(29) 121.9(2)
C(33)-C(34)-H(34) 119.0
H(16A)-C(16)-H(16B) 109.5
H(16A)-C(16)-H(16C) 109.5
H(16B)-C(16)-H(16C) 109.5
| Bond                        | Angle  |
|-----------------------------|--------|
| C(13)-C(16)-H(16A)         | 109.5  |
| C(13)-C(16)-H(16B)         | 109.5  |
| C(13)-C(16)-H(16C)         | 109.5  |
| C(16)-C(13)-Si(1)          | 108.52(18) |
| C(15)-C(13)-Si(1)          | 109.53(16) |
| C(15)-C(13)-C(16)          | 108.4(2) |
| C(14)-C(13)-Si(1)          | 112.36(16) |
| C(14)-C(13)-C(16)          | 108.1(2) |
| C(14)-C(13)-C(15)          | 109.8(2) |
| C(17)-C(18)-H(18)          | 118.8   |
| C(17)-C(18)-C(19)          | 122.4(2) |
| C(19)-C(18)-H(18)          | 118.8   |
| C(35)-C(37)-H(37A)         | 109.5   |
| C(35)-C(37)-H(37B)         | 109.5   |
| C(35)-C(37)-H(37C)         | 109.5   |
| H(37A)-C(37)-H(37B)        | 109.5   |
| H(37A)-C(37)-H(37C)        | 109.5   |
| H(37B)-C(37)-H(37C)        | 109.5   |
| C(35)-C(38)-H(38A)         | 109.5   |
| C(35)-C(38)-H(38B)         | 109.5   |
| C(35)-C(38)-H(38C)         | 109.5   |
| H(38A)-C(38)-H(38B)        | 109.5   |
| H(38A)-C(38)-H(38C)        | 109.5   |
| H(38B)-C(38)-H(38C)        | 109.5   |
| C(10)-C(9)-C(8)            | 120.4(2)|
| C(10)-C(9)-H(9)            | 119.8   |
| C(8)-C(9)-H(9)             | 119.8   |
| C(13)-C(15)-H(15A)         | 109.5   |
| C(13)-C(15)-H(15B)         | 109.5   |
| C(13)-C(15)-H(15C)         | 109.5   |
| H(15A)-C(15)-H(15B)        | 109.5   |
| H(15A)-C(15)-H(15C)        | 109.5   |
| H(15B)-C(15)-H(15C)        | 109.5   |
| C(29)-C(30)-H(30)          | 119.2   |
| C(29)-C(30)-C(31)          | 121.7(2)|
| C(31)-C(30)-H(30)          | 119.2   |
C(25)-C(26)-H(26) 120.1
C(27)-C(26)-C(25) 119.8(2)
C(27)-C(26)-H(26) 120.1
C(51)-C(53)-H(53A) 109.5
C(51)-C(53)-H(53B) 109.5
C(51)-C(53)-H(53C) 109.5
H(53A)-C(53)-H(53B) 109.5
H(53A)-C(53)-H(53C) 109.5
H(53B)-C(53)-H(53C) 109.5
C(18)-C(19)-H(19) 119.6
C(20)-C(19)-C(18) 120.8(2)
C(20)-C(19)-H(19) 119.6
C(40)-C(41)-H(41) 119.9
C(40)-C(41)-C(42) 120.1(3)
C(42)-C(41)-H(41) 119.9
C(50)-C(49)-H(49) 120.0
C(50)-C(49)-C(48) 119.9(3)
C(48)-C(49)-H(49) 120.0
C(46)-C(47)-H(47) 119.9
C(46)-C(47)-C(48) 120.1(3)
C(48)-C(47)-H(47) 119.9
C(49)-C(48)-C(47) 119.7(3)
C(49)-C(48)-H(48) 120.2
C(47)-C(48)-H(48) 120.2
C(32)-C(31)-H(31) 119.9
C(30)-C(31)-C(32) 120.2(3)
C(30)-C(31)-H(31) 119.9
C(19)-C(20)-H(20) 120.6
C(19)-C(20)-C(21) 118.7(3)
C(21)-C(20)-H(20) 120.6
C(43)-C(42)-H(41) 119.6(2)
C(43)-C(42)-H(42) 120.2
C(41)-C(42)-H(42) 120.2
C(13)-C(14)-H(14A) 109.5
C(13)-C(14)-H(14B) 109.5
C(13)-C(14)-H(14C) 109.5
| Bond                  | Angle  |
|----------------------|--------|
| H(14A)-C(14)-H(14B) | 109.5  |
| H(14A)-C(14)-H(14C) | 109.5  |
| H(14B)-C(14)-H(14C) | 109.5  |
| C(51)-C(52)-H(52A)  | 109.5  |
| C(51)-C(52)-H(52B)  | 109.5  |
| C(51)-C(52)-H(52C)  | 109.5  |
| H(52A)-C(52)-H(52B) | 109.5  |
| H(52A)-C(52)-H(52C) | 109.5  |
| H(52B)-C(52)-H(52C) | 109.5  |
| C(17)-C(22)-H(22)   | 119.4  |
| C(21)-C(22)-C(17)   | 121.2(3) |
| C(21)-C(22)-H(22)   | 119.4  |
| C(51)-C(54)-H(54A)  | 109.5  |
| C(51)-C(54)-H(54B)  | 109.5  |
| C(51)-C(54)-H(54C)  | 109.5  |
| H(54A)-C(54)-H(54B) | 109.5  |
| H(54A)-C(54)-H(54C) | 109.5  |
| H(54B)-C(54)-H(54C) | 109.5  |
| C(20)-C(21)-C(22)   | 120.5(3) |
| C(20)-C(21)-H(21)   | 119.8  |
| C(22)-C(21)-H(21)   | 119.8  |

Symmetry transformations used to generate equivalent atoms:
Table S4. Anisotropic displacement parameters (Å²x 10³) for compound 2. The anisotropic displacement factor exponent takes the form:

\[-2\pi^2 \left[ h^2 a^* U_{11} + \ldots + 2hk a^* b^* U_{12} \right] \]

|     | U₁₁  | U₂₂  | U₃₃  | U₁₂ | U₁₃  | U₂₃  |
|-----|------|------|------|-----|------|------|
| Si(1) | 23(1) | 17(1) | 28(1) | -2(1) | 10(1) | 1(1) |
| Si(2) | 24(1) | 22(1) | 26(1) | -6(1) | 1(1)  | 2(1) |
| Si(3) | 27(1) | 16(1) | 23(1) | -4(1) | 6(1)  | 1(1) |
| O(3)  | 22(1) | 20(1) | 27(1) | -3(1) | 3(1)  | -2(1)|
| O(1)  | 30(1) | 19(1) | 34(1) | 2(1)  | -2(1) | -7(1)|
| O(2)  | 24(1) | 18(1) | 37(1) | 2(1)  | -2(1) | -2(1)|
| C(6)  | 25(1) | 17(1) | 26(1) | -1(1) | 6(1)  | -1(1)|
| C(28) | 32(1) | 19(1) | 40(1) | -3(1) | 12(1) | 2(1) |
| C(3)  | 20(1) | 17(1) | 25(1) | -3(1) | 6(1)  | -1(1)|
| C(45) | 31(1) | 23(1) | 29(1) | -7(1) | 3(1)  | 0(1) |
| C(29) | 31(1) | 16(1) | 26(1) | 0(1)  | 9(1)  | 0(1) |
| C(12) | 34(1) | 22(1) | 36(1) | -4(1) | 9(1)  | 2(1) |
| C(1)  | 26(1) | 20(1) | 28(1) | 0(1)  | 7(1)  | 1(1) |
| C(35) | 33(1) | 25(1) | 30(1) | -4(1) | 12(1) | 1(1) |
| C(24) | 31(1) | 26(1) | 30(1) | -2(1) | 9(1)  | 3(1) |
| C(5)  | 23(1) | 19(1) | 24(1) | -2(1) | 2(1)  | -2(1)|
| C(2)  | 20(1) | 21(1) | 24(1) | -1(1) | 6(1)  | 1(1) |
| C(17) | 28(1) | 21(1) | 40(1) | -6(1) | 17(1) | -1(1)|
| C(7)  | 29(1) | 23(1) | 25(1) | -4(1) | 11(1) | 0(1) |
| C(25) | 38(1) | 40(1) | 30(1) | 3(1)  | 7(1)  | 7(1) |
| C(23) | 25(1) | 22(1) | 28(1) | -2(1) | 11(1) | 3(1) |
| C(39) | 32(1) | 26(1) | 22(1) | -4(1) | -3(1) | 6(1) |
| C(27) | 38(1) | 21(1) | 53(2) | 7(1)  | 23(1) | 7(1) |
| C(44) | 34(1) | 28(1) | 32(1) | -7(1) | -2(1) | 2(1) |
| C(40) | 52(2) | 33(1) | 26(1) | 0(1)  | 10(1) | 10(1)|
| C(51) | 28(1) | 34(1) | 42(1) | -15(1)| 2(1)  | 0(1) |
| C(46) | 37(1) | 27(1) | 34(1) | -1(1) | 11(1) | 2(1) |
| C(36) | 38(1) | 34(1) | 38(1) | -7(1) | 18(1) | 5(1) |
| C(4)  | 21(1) | 20(1) | 22(1) | -6(1) | 6(1)  | 1(1) |
| C(33) | 32(1) | 45(1) | 28(1) | -5(1) | 5(1)  | -2(1)|
| C(32) | 34(1) | 40(1) | 50(2) | -9(1) | 15(1) | -9(1)|
|   | 53(2) | 24(1) | 34(1) | -2(1) | -3(1) | 4(1) |
|---|-------|-------|-------|-------|-------|-----|
| C(10)| 53(2) | 24(1) | 34(1) | -2(1) | -3(1) | 4(1) |
| C(8)| 42(1) | 30(1) | 38(1) | -5(1) | 4(1)  | -6(1) |
| C(11)| 46(2) | 24(1) | 62(2) | -1(1) | 23(1) | 7(1) |
| C(50)| 41(1) | 35(1) | 29(1) | 0(1)  | 2(1)  | 2(1) |
| C(34)| 31(1) | 42(1) | 29(1) | -8(1) | 8(1)  | 2(1) |
| C(16)| 75(2) | 31(1) | 50(2) | 11(1) | 36(2) | 16(1) |
| C(13)| 35(1) | 34(1) | 36(1) | 10(1) | 20(1) | 9(1) |
| C(18)| 34(1) | 36(1) | 46(2) | -15(1)| 20(1) | -3(1) |
| C(37)| 53(2) | 34(1) | 32(1) | 2(1)  | 18(1) | 4(1) |
| C(38)| 40(1) | 43(1) | 41(1) | -11(1)| 19(1) | -11(1)|
| C(9)| 63(2) | 32(1) | 43(2) | -12(1)| 9(1)  | -15(1)|
| C(15)| 43(2) | 38(1) | 33(1) | 5(1)  | 13(1) | 1(1) |
| C(30)| 52(2) | 47(2) | 40(2) | -21(1)| 25(1) | -22(1)|
| C(26)| 36(1) | 38(1) | 40(1) | 15(1) | 16(1) | 15(1)|
| C(53)| 37(1) | 28(1) | 40(1) | -11(1)| 9(1)  | -5(1)|
| C(19)| 33(1) | 41(1) | 63(2) | -4(1) | 30(1) | 4(1)|
| C(41)| 69(2) | 41(2) | 37(1) | -4(1) | 22(1) | 17(1)|
| C(49)| 58(2) | 45(2) | 30(1) | 0(1)  | 10(1) | -3(1)|
| C(47)| 42(2) | 39(1) | 51(2) | -3(1) | 20(1) | 3(1)|
| C(48)| 57(2) | 51(2) | 42(2) | -6(1) | 26(1) | -10(1)|
| C(31)| 54(2) | 65(2) | 65(2) | -34(2)| 39(2) | -29(2)|
| C(20)| 34(2) | 48(2) | 78(2) | -14(2)| 30(1) | -13(1)|
| C(42)| 75(2) | 31(1) | 34(1) | -7(1) | 8(1)  | 19(1)|
| C(14)| 38(2) | 73(2) | 52(2) | 31(2) | 19(1) | 24(1)|
| C(52)| 42(2) | 71(2) | 90(3) | -41(2)| 32(2) | -22(2)|
| C(22)| 43(2) | 49(2) | 69(2) | -23(1)| 29(2) | -10(1)|
| C(54)| 48(2) | 45(2) | 60(2) | -16(1)| -23(2)| 5(1)|
| C(21)| 47(2) | 58(2) | 77(2) | -26(2)| 25(2) | -18(1)|
Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^-3) for compound 2.

|      | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H(1) | 9569  | 10501 | 4371  | 47    |
| H(28)| 7232  | 2726  | 3049  | 37    |
| H(3) | 8498  | 7666  | 4390  | 25    |
| H(12)| 5861  | 9116  | 4519  | 37    |
| H(24)| 8912  | 4873  | 4644  | 35    |
| H(5) | 7449  | 9497  | 2966  | 28    |
| H(25)| 9681  | 3855  | 5792  | 44    |
| H(27)| 8022  | 1710  | 4193  | 42    |
| H(44)| 6241  | 10426 | 1483  | 42    |
| H(40)| 4408  | 9239  | 2804  | 45    |
| H(46)| 7580  | 7620  | 1834  | 39    |
| H(36A)| 8538| 3433  | 2095  | 53    |
| H(36B)| 8540| 3835  | 1133  | 53    |
| H(36C)| 7471| 3489  | 1265  | 53    |
| H(33)| 4091  | 3357  | 496   | 44    |
| H(32)| 3094  | 3572  | 1426  | 50    |
| H(43)| 5818  | 11875 | 1834  | 50    |
| H(10)| 7280  | 11446 | 5946  | 57    |
| H(8) | 8705  | 9056  | 6434  | 47    |
| H(11)| 5869  | 10691 | 4819  | 51    |
| H(50)| 5752  | 9425  | 154   | 45    |
| H(34)| 5835  | 3845  | 1003  | 41    |
| H(16A)| 7032| 5804  | 5949  | 72    |
| H(16B)| 8203| 5552  | 6447  | 72    |
| H(16C)| 7795| 5726  | 5367  | 72    |
| H(18)| 5548  | 7958  | 5828  | 45    |
| H(37A)| 6812| 5037  | 738   | 59    |
| H(37B)| 7903| 5418  | 673   | 59    |
| H(37C)| 7389| 5956  | 1299  | 59    |
| H(38A)| 9090| 5862  | 2549  | 61    |
| H   | 1st Value | 2nd Value | 3rd Value | 4th Value |
|-----|-----------|-----------|-----------|-----------|
| H(38B) | 9548      | 5197      | 1972      | 61        |
| H(38C) | 9481      | 4884      | 2943      | 61        |
| H(9)   | 8703      | 10624     | 6734      | 59        |
| H(15A) | 8205      | 7884      | 7219      | 57        |
| H(15B) | 8309      | 6841      | 7549      | 57        |
| H(15C) | 7197      | 7188      | 6981      | 57        |
| H(30)  | 5642      | 4672      | 3426      | 55        |
| H(26)  | 9235      | 2274      | 5571      | 44        |
| H(53A) | 5418      | 6734      | 876       | 55        |
| H(53B) | 4368      | 6247      | 942       | 55        |
| H(53C) | 5337      | 6475      | 1856      | 55        |
| H(19)  | 3880      | 7354      | 5604      | 51        |
| H(41)  | 3986      | 10692     | 3144      | 57        |
| H(49)  | 6742      | 9396      | -795      | 55        |
| H(47)  | 8551      | 7571      | 863       | 52        |
| H(48)  | 8143      | 8467      | -455      | 58        |
| H(31)  | 3892      | 4194      | 2919      | 70        |
| H(20)  | 3140      | 6178      | 4538      | 61        |
| H(42)  | 4679      | 12015     | 2648      | 58        |
| H(14A) | 9333      | 6849      | 5692      | 79        |
| H(14B) | 9645      | 6749      | 6780      | 79        |
| H(14C) | 9453      | 7744      | 6338      | 79        |
| H(52A) | 4220      | 7406      | 2511      | 99        |
| H(52B) | 3272      | 7107      | 1602      | 99        |
| H(52C) | 3549      | 8175      | 1894      | 99        |
| H(22)  | 5666      | 6360      | 3737      | 62        |
| H(54A) | 3744      | 8586      | 391       | 92        |
| H(54B) | 3342      | 7540      | 73        | 92        |
| H(54C) | 4402      | 7958      | -31       | 92        |
| H(21)  | 3967      | 5799      | 3493      | 73        |
Table S6. Crystal data and structure refinement for compound 3.

| Identification code | Compound 3 |
|---------------------|------------|
| Empirical formula   | C54 H60 O3 Si3 |
| Formula weight      | 841.29 |
| Temperature         | 100.0 K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Triclinic |
| Space group         | P-1 |
| Unit cell dimensions| \(a = 12.5118(9) \text{ Å}\), \(\alpha = 68.488(2)^\circ\). |
|                     | \(b = 12.5949(11) \text{ Å}\), \(\beta = 89.117(2)^\circ\). |
|                     | \(c = 16.5326(15) \text{ Å}\), \(\gamma = 75.576(2)^\circ\). |
| Volume              | 2339.1(3) Å³ |
| Z                   | 2 |
| Density (calculated)| 1.194 Mg/m³ |
| Absorption coefficient | 0.144 mm⁻¹ |
| F(000)              | 900 |
| Crystal size        | 0.32 x 0.3 x 0.28 mm³ |
| Theta range for data collection | 1.687 to 26.395° |
| Index ranges        | \(-15 < h < 12, -15 < k < 15, -20 < l < 20\) |
| Reflections collected | 33116 |
| Independent reflections | 9529 [R(int) = 0.0718] |
| Completeness to theta | 25.242° |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.4874 and 0.4488 |
| Refinement method   | Full-matrix least-squares on \(F^2\) |
| Data / restraints / parameters | 9529 / 0 / 550 |
|-------------------------------|----------------|
| Goodness-of-fit on F²         | 1.027          |
| Final R indices [I>2sigma(I)] | R₁ = 0.0483, wR₂ = 0.1132 |
| R indices (all data)          | R₁ = 0.0674, wR₂ = 0.1267 |
| Extinction coefficient        | n/a            |
| Largest diff. peak and hole   | 0.366 and -0.376 eÅ⁻³ |
Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for compound 3. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^0$ tensor.

|      | x     | y     | z     | $U_{eq}$ |
|------|-------|-------|-------|---------|
| Si(2) | 4165(1) | 4270(1) | 3246(1) | 13(1)   |
| Si(3) | 1477(1) | 2226(1) | 3443(1) | 14(1)   |
| Si(1) | 2794(1) | 7449(1) | 408(1)  | 16(1)   |
| O(1)  | 3259(1) | 4726(1) | 687(1)  | 17(1)   |
| O(3)  | 2489(1) | 2931(1) | 3116(1) | 15(1)   |
| O(2)  | 2631(1) | 3653(1) | 101(1)  | 26(1)   |
| C(22) | 3062(2) | 4968(2) | 3812(1) | 14(1)   |
| C(3)  | 2822(2) | 3425(2) | 2310(1) | 14(1)   |
| C(38) | 1569(2) | 1891(2) | 4644(1) | 14(1)   |
| C(39) | 1613(2) | 2745(2) | 4984(1) | 16(1)   |
| C(6)  | 3098(2) | 8666(2) | 688(1)  | 20(1)   |
| C(23) | 3213(2) | 4877(2) | 4674(1) | 18(1)   |
| C(4)  | 2549(2) | 3163(2) | 1627(1) | 16(1)   |
| C(1)  | 3574(2) | 4949(2) | 1389(1) | 14(1)   |
| C(27) | 2035(2) | 5646(2) | 3354(1) | 16(1)   |
| C(33) | 6034(2) | 5042(2) | 2400(1) | 18(1)   |
| C(44) | 1867(2) | 817(2)  | 3248(1) | 17(1)   |
| C(2)  | 3471(2) | 4266(2) | 2227(1) | 14(1)   |
| C(5)  | 2804(2) | 3793(2) | 771(1)  | 17(1)   |
| C(31) | 6705(2) | 6615(2) | 2502(1) | 21(1)   |
| C(54) | 3928(2) | 6064(2) | 1051(1) | 17(1)   |
| C(34) | 5033(2) | 2706(2) | 3966(1) | 17(1)   |
| C(29) | 5131(2) | 6118(2) | 3252(1) | 16(1)   |
| C(32) | 6775(2) | 5732(2) | 2170(1) | 20(1)   |
| C(25) | 1359(2) | 6056(2) | 4604(1) | 21(1)   |
| C(40) | 1701(2) | 2480(2) | 5874(1) | 20(1)   |
| C(43) | 1616(2) | 745(2)  | 5242(1) | 21(1)   |
| C(26) | 1191(2) | 6177(2) | 3748(1) | 19(1)   |
| C(11) | 2313(2) | 9748(2) | 532(1)  | 25(1)   |
| C(41) | 1754(2) | 1340(2) | 6451(1) | 24(1)   |
| C(12) | 1383(2) | 7257(2) | 722(1) | 20(1) |
|-------|---------|---------|--------|-------|
| C(7)  | 4176(2) | 8563(2) | 988(1) | 23(1) |
| C(37) | 5481(2) | 2001(2) | 3392(2) | 25(1) |
| C(28) | 5179(2) | 5219(2) | 2939(1) | 15(1) |
| C(42) | 1713(2) | 477(2)  | 6131(2) | 26(1) |
| C(30) | 5892(2) | 6799(2) | 3045(1) | 19(1) |
| C(45) | 2978(2) | 247(2)  | 3269(2) | 24(1) |
| C(50) | 56(2)   | 3216(2) | 2926(1) | 18(1) |
| C(24) | 2374(2) | 5410(2) | 5070(1) | 20(1) |
| C(35) | 4397(2) | 1988(2) | 4671(1) | 21(1) |
| C(17) | 842(2)  | 6638(2) | 384(1)  | 24(1) |
| C(18) | 2876(2) | 7877(2) | -817(1) | 28(1) |
| C(53) | -834(2) | 2686(2) | 3472(2) | 24(1) |
| C(16) | -236(2) | 6581(2) | 550(2)  | 31(1) |
| C(36) | 6031(2) | 2811(2) | 4442(2) | 25(1) |
| C(10) | 2594(2) | 10670(2)| 667(2)  | 31(1) |
| C(47) | 2520(2) | -1365(2)| 3038(2) | 29(1) |
| C(13) | 792(2)  | 7786(2) | 1262(1) | 27(1) |
| C(51) | -62(2)  | 4442(2) | 2962(2) | 23(1) |
| C(52) | -178(2) | 3382(2) | 1972(2) | 28(1) |
| C(14) | -290(2) | 7726(2) | 1434(2) | 34(1) |
| C(19) | 2984(2) | 6859(2) | -1129(2)| 32(1) |
| C(46) | 3299(2) | -824(2) | 3164(2) | 31(1) |
| C(8)  | 4453(2) | 9494(2) | 1115(2) | 29(1) |
| C(9)  | 3661(2) | 10544(2)| 957(2)  | 31(1) |
| C(49) | 1096(2) | 256(2)  | 3111(2) | 35(1) |
| C(15) | -805(2) | 7137(2) | 1064(2) | 34(1) |
| C(48) | 1425(2) | -820(2) | 3012(2) | 41(1) |
| C(20) | 1807(3) | 8838(2) | -1281(2)| 49(1) |
| C(21) | 3883(3) | 8375(3) | -1079(2)| 56(1) |
Table S8. Bond lengths [Å] and angles [°] for compound 3.

| Bond                  | Length [Å] |
|-----------------------|------------|
| Si(2)-C(22)           | 1.875(2)   |
| Si(2)-C(2)            | 1.909(2)   |
| Si(2)-C(34)           | 1.932(2)   |
| Si(2)-C(28)           | 1.8941(19) |
| Si(3)-O(3)            | 1.6951(13) |
| Si(3)-C(38)           | 1.871(2)   |
| Si(3)-C(44)           | 1.864(2)   |
| Si(3)-C(50)           | 1.900(2)   |
| Si(1)-C(6)            | 1.877(2)   |
| Si(1)-C(54)           | 1.907(2)   |
| Si(1)-C(12)           | 1.880(2)   |
| Si(1)-C(18)           | 1.903(2)   |
| O(1)-C(1)             | 1.375(2)   |
| O(1)-C(5)             | 1.392(2)   |
| O(3)-C(3)             | 1.357(2)   |
| O(2)-C(5)             | 1.214(2)   |
| C(22)-C(23)           | 1.400(3)   |
| C(22)-C(27)           | 1.401(3)   |
| C(3)-C(4)             | 1.357(3)   |
| C(3)-C(2)             | 1.456(3)   |
| C(38)-C(39)           | 1.396(3)   |
| C(38)-C(43)           | 1.406(3)   |
| C(39)-H(39)           | 0.9500     |
| C(39)-C(40)           | 1.385(3)   |
| C(6)-C(11)            | 1.404(3)   |
| C(6)-C(7)             | 1.403(3)   |
| C(23)-H(23)           | 0.9500     |
| C(23)-C(24)           | 1.389(3)   |
| C(4)-H(4)             | 0.9500     |
| C(4)-C(5)             | 1.422(3)   |
| C(1)-C(2)             | 1.361(3)   |
| C(1)-C(54)            | 1.485(3)   |
| C(27)-H(27)           | 0.9500     |
| C(27)-C(26)           | 1.390(3)   |
C(33)-H(33)   0.9500  
C(33)-C(32)   1.382(3) 
C(33)-C(28)   1.409(3) 
C(44)-C(45)   1.391(3) 
C(44)-C(49)   1.394(3) 
C(31)-H(31)   0.9500  
C(31)-C(32)   1.392(3) 
C(31)-C(30)   1.379(3) 
C(54)-H(54A)  0.9900  
C(54)-H(54B)  0.9900  
C(34)-C(37)   1.535(3) 
C(34)-C(35)   1.538(3) 
C(34)-C(36)   1.543(3) 
C(29)-H(29)   0.9500  
C(29)-C(28)   1.396(3) 
C(29)-C(30)   1.393(3) 
C(32)-H(32)   0.9500  
C(25)-H(25)   0.9500  
C(25)-C(26)   1.380(3) 
C(40)-H(40)   0.9500  
C(40)-C(41)   1.387(3) 
C(43)-H(43)   0.9500  
C(43)-C(42)   1.383(3) 
C(26)-H(26)   0.9500  
C(11)-H(11)   0.9500  
C(11)-C(10)   1.384(3) 
C(41)-H(41)   0.9500  
C(41)-C(42)   1.384(3) 
C(12)-C(17)   1.404(3) 
C(12)-C(13)   1.399(3) 
C(7)-H(7)     0.9500  
C(7)-C(8)     1.388(3) 
C(37)-H(37A)  0.9800  
C(37)-H(37B)  0.9800  
C(37)-H(37C)  0.9800
C(42)-H(42)  0.9500
C(30)-H(30)  0.9500
C(45)-H(45)  0.9500
C(45)-C(46)  1.382(3)
C(50)-C(53)  1.548(3)
C(50)-C(51)  1.536(3)
C(50)-C(52)  1.535(3)
C(24)-H(24)  0.9500
C(35)-H(35A)  0.9800
C(35)-H(35B)  0.9800
C(35)-H(35C)  0.9800
C(17)-H(17)  0.9500
C(17)-C(16)  1.386(3)
C(18)-C(19)  1.525(3)
C(18)-C(20)  1.545(4)
C(18)-C(21)  1.532(3)
C(53)-H(53A)  0.9800
C(53)-H(53B)  0.9800
C(53)-H(53C)  0.9800
C(16)-H(16)  0.9500
C(16)-C(15)  1.374(4)
C(36)-H(36A)  0.9800
C(36)-H(36B)  0.9800
C(36)-H(36C)  0.9800
C(10)-H(10)  0.9500
C(10)-C(9)  1.378(3)
C(47)-H(47)  0.9500
C(47)-C(46)  1.378(3)
C(47)-C(48)  1.365(3)
C(13)-H(13)  0.9500
C(13)-C(14)  1.394(3)
C(51)-H(51A)  0.9800
C(51)-H(51B)  0.9800
C(51)-H(51C)  0.9800
C(52)-H(52A)  0.9800
C(52)-H(52B)  0.9800
C(52)-H(52C)  0.9800
C(14)-H(14)  0.9500
C(14)-C(15)  1.387(4)
C(19)-H(19A)  0.9800
C(19)-H(19B)  0.9800
C(19)-H(19C)  0.9800
C(46)-H(46)  0.9500
C(8)-H(8)  0.9500
C(8)-C(9)  1.378(3)
C(9)-H(9)  0.9500
C(49)-H(49)  0.9500
C(49)-C(48)  1.385(3)
C(15)-H(15)  0.9500
C(48)-H(48)  0.9500
C(20)-H(20A)  0.9800
C(20)-H(20B)  0.9800
C(20)-H(20C)  0.9800
C(21)-H(21A)  0.9800
C(21)-H(21B)  0.9800
C(21)-H(21C)  0.9800
C(22)-Si(2)-C(2)  107.77(9)
C(22)-Si(2)-C(34)  114.51(9)
C(22)-Si(2)-C(28)  106.87(9)
C(2)-Si(2)-C(34)  111.42(9)
C(28)-Si(2)-C(2)  110.68(9)
C(28)-Si(2)-C(34)  105.50(8)
O(3)-Si(3)-C(38)  101.68(8)
O(3)-Si(3)-C(44)  108.41(8)
O(3)-Si(3)-C(50)  112.08(8)
C(38)-Si(3)-C(50)  110.11(9)
C(44)-Si(3)-C(38)  109.51(9)
C(44)-Si(3)-C(50)  114.28(9)
C(6)-Si(1)-C(54)  105.35(9)
C(6)-Si(1)-C(12)  110.85(10)
C(6)-Si(1)-C(18)  106.93(9)
| Bond                  | Angle (°)  |
|----------------------|------------|
| C(12)-Si(1)-C(54)    | 111.13(9)  |
| C(12)-Si(1)-C(18)    | 110.73(10) |
| C(18)-Si(1)-C(54)    | 111.66(10) |
| C(1)-O(1)-C(5)       | 123.13(15) |
| C(3)-O(3)-Si(3)      | 130.74(12) |
| C(23)-C(22)-Si(2)    | 123.44(15) |
| C(23)-C(22)-C(27)    | 117.16(18) |
| C(27)-C(22)-Si(2)    | 119.38(15) |
| O(3)-C(3)-C(4)       | 121.99(17) |
| O(3)-C(3)-C(2)       | 115.46(17) |
| C(4)-C(3)-C(2)       | 122.55(18) |
| C(39)-C(38)-Si(3)    | 122.16(15) |
| C(39)-C(38)-C(43)    | 117.45(19) |
| C(43)-C(38)-Si(3)    | 120.38(15) |
| C(38)-C(39)-H(39)    | 119.2      |
| C(40)-C(39)-C(38)    | 121.59(18) |
| C(40)-C(39)-H(39)    | 119.2      |
| C(11)-C(6)-Si(1)     | 122.82(16) |
| C(7)-C(6)-Si(1)      | 119.96(16) |
| C(7)-C(6)-C(11)      | 116.93(19) |
| C(22)-C(23)-H(23)    | 119.2      |
| C(24)-C(23)-C(22)    | 121.65(19) |
| C(24)-C(23)-H(23)    | 119.2      |
| C(3)-C(4)-H(4)       | 119.8      |
| C(3)-C(4)-C(5)       | 120.48(18) |
| C(5)-C(4)-H(4)       | 119.8      |
| O(1)-C(1)-C(54)      | 108.14(16) |
| C(2)-C(1)-O(1)       | 122.44(17) |
| C(2)-C(1)-C(54)      | 129.24(18) |
| C(22)-C(27)-H(27)    | 119.3      |
| C(26)-C(27)-C(22)    | 121.42(19) |
| C(26)-C(27)-H(27)    | 119.3      |
| C(32)-C(33)-H(33)    | 118.8      |
| C(32)-C(33)-C(28)    | 122.42(19) |
| C(28)-C(33)-H(33)    | 118.8      |
| C(45)-C(44)-Si(3)    | 119.97(15) |
C(45)-C(44)-C(49) 116.6(2)
C(49)-C(44)-Si(3) 123.38(17)
C(3)-C(2)-Si(2) 119.80(14)
C(1)-C(2)-Si(2) 125.76(14)
C(1)-C(2)-C(3) 114.32(17)
O(1)-C(5)-C(4) 115.51(17)
O(2)-C(5)-O(1) 116.07(18)
O(2)-C(5)-C(4) 128.34(18)
C(32)-C(31)-H(31) 120.1
C(30)-C(31)-H(31) 120.1
C(30)-C(31)-C(32) 119.84(18)
Si(1)-C(54)-H(54A) 108.4
Si(1)-C(54)-H(54B) 108.4
C(1)-C(54)-Si(1) 115.32(14)
C(1)-C(54)-H(54A) 108.4
C(1)-C(54)-H(54B) 108.4
H(54A)-C(54)-H(54B) 107.5
C(37)-C(34)-Si(2) 109.74(14)
C(37)-C(34)-C(35) 108.40(17)
C(37)-C(34)-C(36) 108.06(17)
C(35)-C(34)-Si(2) 114.21(13)
C(35)-C(34)-C(36) 107.03(17)
C(36)-C(34)-Si(2) 109.21(14)
C(28)-C(29)-H(29) 119.2
C(30)-C(29)-H(29) 119.2
C(30)-C(29)-C(28) 121.64(19)
C(33)-C(32)-C(31) 119.36(19)
C(33)-C(32)-H(32) 120.3
C(31)-C(32)-H(32) 120.3
C(26)-C(25)-H(25) 120.1
C(26)-C(25)-C(24) 119.89(19)
C(24)-C(25)-H(25) 120.1
C(39)-C(40)-H(40) 120.1
C(39)-C(40)-C(41) 119.9(2)
C(41)-C(40)-H(40) 120.1
C(38)-C(43)-H(43) 119.5
C(42)-C(43)-C(38) 121.0(2)
C(42)-C(43)-H(43) 119.5
C(27)-C(26)-H(26) 120.0
C(25)-C(26)-C(27) 120.09(19)
C(25)-C(26)-H(26) 120.0
C(6)-C(11)-H(11) 119.3
C(10)-C(11)-C(6) 121.4(2)
C(10)-C(11)-H(11) 119.3
C(40)-C(41)-H(41) 120.2
C(42)-C(41)-C(40) 119.6(2)
C(42)-C(41)-H(41) 120.2
C(17)-C(12)-Si(1) 121.70(17)
C(13)-C(12)-Si(1) 121.55(16)
C(13)-C(12)-C(17) 116.6(2)
C(6)-C(7)-H(7) 119.3
C(8)-C(7)-C(6) 121.4(2)
C(8)-C(7)-H(7) 119.3
C(34)-C(37)-H(37A) 109.5
C(34)-C(37)-H(37B) 109.5
C(34)-C(37)-H(37C) 109.5
H(37A)-C(37)-H(37B) 109.5
H(37A)-C(37)-H(37C) 109.5
H(37B)-C(37)-H(37C) 109.5
C(33)-C(28)-Si(2) 121.99(15)
C(29)-C(28)-Si(2) 121.53(15)
C(29)-C(28)-C(33) 116.47(17)
C(43)-C(42)-C(41) 120.4(2)
C(43)-C(42)-H(42) 119.8
C(41)-C(42)-H(42) 119.8
C(31)-C(30)-C(29) 120.24(19)
C(31)-C(30)-H(30) 119.9
C(29)-C(30)-H(30) 119.9
C(44)-C(45)-H(45) 119.2
C(46)-C(45)-C(44) 121.6(2)
C(46)-C(45)-H(45) 119.2
C(53)-C(50)-Si(3) 108.59(14)
| Bond | Angle |
|------|-------|
| C(51)-C(50)-Si(3) | 109.02(13) |
| C(51)-C(50)-C(53) | 107.74(17) |
| C(52)-C(50)-Si(3) | 114.43(15) |
| C(52)-C(50)-C(53) | 108.81(17) |
| C(52)-C(50)-C(51) | 108.05(17) |
| C(23)-C(24)-H(24) | 120.1 |
| C(25)-C(24)-C(23) | 119.76(19) |
| C(25)-C(24)-H(24) | 120.1 |
| C(34)-C(35)-H(35A) | 109.5 |
| C(34)-C(35)-H(35B) | 109.5 |
| C(34)-C(35)-H(35C) | 109.5 |
| H(35A)-C(35)-H(35B) | 109.5 |
| H(35A)-C(35)-H(35C) | 109.5 |
| H(35B)-C(35)-H(35C) | 109.5 |
| C(12)-C(17)-H(17) | 118.9 |
| C(16)-C(17)-C(12) | 122.1(2) |
| C(16)-C(17)-H(17) | 118.9 |
| C(19)-C(18)-Si(1) | 114.41(15) |
| C(19)-C(18)-C(20) | 108.0(2) |
| C(19)-C(18)-C(21) | 107.9(2) |
| C(20)-C(18)-Si(1) | 108.01(17) |
| C(21)-C(18)-Si(1) | 108.76(16) |
| C(21)-C(18)-C(20) | 109.7(2) |
| C(50)-C(53)-H(53A) | 109.5 |
| C(50)-C(53)-H(53B) | 109.5 |
| C(50)-C(53)-H(53C) | 109.5 |
| H(53A)-C(53)-H(53B) | 109.5 |
| H(53A)-C(53)-H(53C) | 109.5 |
| H(53B)-C(53)-H(53C) | 109.5 |
| C(17)-C(16)-H(16) | 120.1 |
| C(15)-C(16)-C(17) | 119.8(2) |
| C(15)-C(16)-H(16) | 120.1 |
| C(34)-C(36)-H(36A) | 109.5 |
| C(34)-C(36)-H(36B) | 109.5 |
| C(34)-C(36)-H(36C) | 109.5 |
| H(36A)-C(36)-H(36B) | 109.5 |
H(36A)-C(36)-H(36C) 109.5
C(11)-C(10)-H(10) 119.8
C(9)-C(10)-C(11) 120.3(2)
C(9)-C(10)-H(10) 119.8
C(46)-C(47)-H(47) 120.6
C(48)-C(47)-H(47) 120.6
C(48)-C(47)-C(46) 118.9(2)
C(12)-C(13)-H(13) 119.3
C(14)-C(13)-C(12) 121.4(2)
C(14)-C(13)-H(13) 119.3
C(50)-C(51)-H(51A) 109.5
C(50)-C(51)-H(51B) 109.5
C(50)-C(51)-H(51C) 109.5
H(51A)-C(51)-H(51B) 109.5
H(51A)-C(51)-H(51C) 109.5
H(51B)-C(51)-H(51C) 109.5
C(50)-C(52)-H(52A) 109.5
C(50)-C(52)-H(52B) 109.5
C(50)-C(52)-H(52C) 109.5
H(52A)-C(52)-H(52B) 109.5
H(52A)-C(52)-H(52C) 109.5
H(52B)-C(52)-H(52C) 109.5
C(13)-C(14)-H(14) 120.0
C(15)-C(14)-C(13) 120.0(2)
C(15)-C(14)-H(14) 120.0
C(18)-C(19)-H(19A) 109.5
C(18)-C(19)-H(19B) 109.5
C(18)-C(19)-H(19C) 109.5
H(19A)-C(19)-H(19B) 109.5
H(19A)-C(19)-H(19C) 109.5
H(19B)-C(19)-H(19C) 109.5
C(45)-C(46)-H(46) 119.7
C(47)-C(46)-C(45) 120.6(2)
C(47)-C(46)-H(46) 119.7
C(7)-C(8)-H(8) 119.9
| Bond                  | Angle (°) |
|----------------------|-----------|
| C(9)-C(8)-C(7)       | 120.2(2)  |
| C(9)-C(8)-H(8)       | 119.9     |
| C(10)-C(9)-C(8)      | 119.8(2)  |
| C(10)-C(9)-H(9)      | 120.1     |
| C(8)-C(9)-H(9)       | 120.1     |
| C(44)-C(49)-H(49)    | 119.3     |
| C(48)-C(49)-C(44)    | 121.5(2)  |
| C(48)-C(49)-H(49)    | 119.3     |
| C(16)-C(15)-C(14)    | 119.9(2)  |
| C(16)-C(15)-H(15)    | 120.0     |
| C(14)-C(15)-H(15)    | 120.0     |
| C(47)-C(48)-C(49)    | 120.9(2)  |
| C(47)-C(48)-H(48)    | 119.6     |
| C(49)-C(48)-H(48)    | 119.6     |
| C(18)-C(20)-H(20A)   | 109.5     |
| C(18)-C(20)-H(20B)   | 109.5     |
| C(18)-C(20)-H(20C)   | 109.5     |
| H(20A)-C(20)-H(20B)  | 109.5     |
| H(20A)-C(20)-H(20C)  | 109.5     |
| H(20B)-C(20)-H(20C)  | 109.5     |
| C(18)-C(21)-H(21A)   | 109.5     |
| C(18)-C(21)-H(21B)   | 109.5     |
| C(18)-C(21)-H(21C)   | 109.5     |
| H(21A)-C(21)-H(21B)  | 109.5     |
| H(21A)-C(21)-H(21C)  | 109.5     |
| H(21B)-C(21)-H(21C)  | 109.5     |

Symmetry transformations used to generate equivalent atoms:
Table S9. Anisotropic displacement parameters (Å$^2 \times 10^3$) for compound 3. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [ h^2 a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} ]$

|     | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-----|----------|----------|----------|----------|----------|----------|
| Si(2)| 11(1)    | 14(1)    | 15(1)    | -7(1)    | 2(1)     | -4(1)    |
| Si(3)| 14(1)    | 14(1)    | 15(1)    | -6(1)    | 3(1)     | -7(1)    |
| Si(1)| 24(1)    | 14(1)    | 12(1)    | -5(1)    | 1(1)     | -7(1)    |
| O(1) | 24(1)    | 14(1)    | 14(1)    | -5(1)    | 2(1)     | -8(1)    |
| O(3) | 16(1)    | 18(1)    | 13(1)    | -6(1)    | 4(1)     | -8(1)    |
| O(2) | 40(1)    | 27(1)    | 17(1)    | -11(1)   | 3(1)     | -16(1)   |
| C(22)| 15(1)    | 14(1)    | 17(1)    | -7(1)    | 3(1)     | -7(1)    |
| C(3) | 12(1)    | 11(1)    | 16(1)    | -3(1)    | 2(1)     | -1(1)    |
| C(38)| 10(1)    | 17(1)    | 17(1)    | -6(1)    | 4(1)     | -4(1)    |
| C(39)| 14(1)    | 16(1)    | 18(1)    | -5(1)    | 3(1)     | -4(1)    |
| C(6) | 32(1)    | 15(1)    | 14(1)    | -5(1)    | -1(1)    | -7(1)    |
| C(23)| 16(1)    | 19(1)    | 19(1)    | -8(1)    | 0(1)     | -5(1)    |
| C(4) | 18(1)    | 13(1)    | 19(1)    | -7(1)    | 2(1)     | -7(1)    |
| C(1) | 13(1)    | 13(1)    | 18(1)    | -8(1)    | 2(1)     | -2(1)    |
| C(27)| 18(1)    | 16(1)    | 17(1)    | -7(1)    | 3(1)     | -7(1)    |
| C(33)| 16(1)    | 17(1)    | 24(1)    | -12(1)   | 2(1)     | -3(1)    |
| C(44)| 23(1)    | 16(1)    | 15(1)    | -6(1)    | 4(1)     | -7(1)    |
| C(2) | 12(1)    | 12(1)    | 18(1)    | -8(1)    | 2(1)     | -2(1)    |
| C(5) | 19(1)    | 15(1)    | 19(1)    | -8(1)    | 2(1)     | -6(1)    |
| C(31)| 18(1)    | 21(1)    | 26(1)    | -5(1)    | 1(1)     | -10(1)   |
| C(54)| 20(1)    | 15(1)    | 19(1)    | -6(1)    | 5(1)     | -8(1)    |
| C(34)| 14(1)    | 17(1)    | 19(1)    | -6(1)    | 2(1)     | -5(1)    |
| C(29)| 13(1)    | 19(1)    | 16(1)    | -7(1)    | 0(1)     | -3(1)    |
| C(32)| 15(1)    | 24(1)    | 22(1)    | -8(1)    | 4(1)     | -5(1)    |
| C(25)| 18(1)    | 23(1)    | 27(1)    | -16(1)   | 9(1)     | -5(1)    |
| C(40)| 18(1)    | 24(1)    | 20(1)    | -12(1)   | 3(1)     | -6(1)    |
| C(43)| 25(1)    | 19(1)    | 20(1)    | -7(1)    | 6(1)     | -10(1)   |
| C(26)| 15(1)    | 19(1)    | 24(1)    | -10(1)   | 1(1)     | -2(1)    |
| C(11)| 32(1)    | 18(1)    | 22(1)    | -7(1)    | -7(1)    | -4(1)    |
| C(41)| 28(1)    | 29(1)    | 16(1)    | -6(1)    | 5(1)     | -10(1)   |
| C(12)| 23(1)    | 17(1)    | 15(1)    | -2(1)    | -3(1)    | -2(1)    |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C(7) | 29(1) | 17(1) | 22(1) | -7(1) | 1(1) | -7(1) |
| C(37) | 23(1) | 19(1) | 28(1) | -8(1) | 5(1) | 0(1) |
| C(24) | 25(1) | 24(1) | 18(1) | -12(1) | 5(1) | -11(1) |
| C(35) | 19(1) | 18(1) | 20(1) | -3(1) | 0(1) | -4(1) |
| C(45) | 22(1) | 18(1) | 32(1) | -8(1) | 2(1) | -6(1) |
| C(50) | 16(1) | 20(1) | 20(1) | -10(1) | 1(1) | -7(1) |
| C(24) | 25(1) | 24(1) | 18(1) | -12(1) | 5(1) | -11(1) |
| C(35) | 19(1) | 18(1) | 20(1) | -3(1) | 0(1) | -4(1) |
| C(17) | 25(1) | 22(1) | 22(1) | -4(1) | -2(1) | -5(1) |
| C(18) | 51(2) | 22(1) | 16(1) | -7(1) | 7(1) | -19(1) |
| C(53) | 18(1) | 25(1) | 35(1) | -16(1) | 5(1) | -8(1) |
| C(16) | 25(1) | 30(1) | 28(1) | 1(1) | -5(1) | -9(1) |
| C(36) | 18(1) | 26(1) | 27(1) | -5(1) | -4(1) | -5(1) |
| C(10) | 45(2) | 14(1) | 28(1) | -7(1) | -8(1) | 0(1) |
| C(47) | 39(1) | 18(1) | 32(1) | -14(1) | 1(1) | -2(1) |
| C(13) | 32(1) | 24(1) | 19(1) | -5(1) | 1(1) | -3(1) |
| C(51) | 19(1) | 19(1) | 29(1) | -7(1) | -5(1) | -4(1) |
| C(52) | 22(1) | 37(1) | 26(1) | -15(1) | -4(1) | -5(1) |
| C(14) | 32(1) | 30(1) | 22(1) | -1(1) | 9(1) | 5(1) |
| C(19) | 55(2) | 32(1) | 17(1) | -12(1) | 11(1) | -23(1) |
| C(46) | 28(1) | 22(1) | 39(2) | -11(1) | 6(1) | 0(1) |
| C(8) | 32(1) | 23(1) | 34(1) | -10(1) | -2(1) | -10(1) |
| C(9) | 48(2) | 18(1) | 33(1) | -11(1) | -4(1) | -13(1) |
| C(49) | 22(1) | 32(1) | 65(2) | -33(1) | 6(1) | -9(1) |
| C(15) | 23(1) | 32(1) | 29(1) | 6(1) | 1(1) | -4(1) |
| C(19) | 55(2) | 26(1) | 17(1) | -3(1) | -11(1) | -6(2) |
| C(20) | 101(3) | 67(2) | 31(2) | -26(2) | 36(2) | -67(2) |
Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^-3) for compound 3.

|       | x      | y      | z      | U(eq) |
|-------|--------|--------|--------|-------|
| H(39) | 1582   | 3527   | 4594   | 19    |
| H(23) | 3907   | 4441   | 4997   | 21    |
| H(4)  | 2184   | 2555   | 1721   | 20    |
| H(27) | 1913   | 5745   | 2762   | 19    |
| H(33) | 6103   | 4425   | 2187   | 22    |
| H(31) | 7216   | 7088   | 2354   | 26    |
| H(54A)| 4535   | 5972   | 671    | 21    |
| H(54B)| 4231   | 6184   | 1551   | 21    |
| H(29) | 4565   | 6270   | 3616   | 20    |
| H(32) | 7327   | 5607   | 1790   | 24    |
| H(25) | 780    | 6416   | 4873   | 25    |
| H(40) | 1724   | 3077   | 6090   | 23    |
| H(43) | 1582   | 145    | 5031   | 25    |
| H(26) | 497    | 6624   | 3427   | 23    |
| H(11) | 1574   | 9850   | 330    | 30    |
| H(41) | 1820   | 1153   | 7063   | 29    |
| H(7)  | 4728   | 7841   | 1107   | 27    |
| H(37A)| 4861   | 1907   | 3094   | 37    |
| H(37B)| 5947   | 1221   | 3757   | 37    |
| H(37C)| 5923   | 2427   | 2958   | 37    |
| H(42) | 1751   | -305   | 6525   | 32    |
| H(30) | 5851   | 7392   | 3279   | 22    |
| H(45) | 3530   | 602    | 3358   | 29    |
| H(24) | 2495   | 5331   | 5657   | 24    |
| H(35A)| 4103   | 2427   | 5044   | 31    |
| H(35B)| 4899   | 1225   | 5028   | 31    |
| H(35C)| 3784   | 1856   | 4392   | 31    |
| H(17) | 1228   | 6246   | 31     | 29    |
| H(53A)| -817   | 1930   | 3423   | 36    |
| H(53B)| -1567  | 3234   | 3253   | 36    |
| Symbol | Value1 | Value2 | Value3 | Value4 |
|--------|--------|--------|--------|--------|
| H(53C) | -682   | 2558   | 4085   | 36     |
| H(16)  | -580   | 6159   | 309    | 37     |
| H(36A) | 6504   | 3186   | 4011   | 38     |
| H(36B) | 6458   | 2021   | 4825   | 38     |
| H(36C) | 5765   | 3292   | 4791   | 38     |
| H(10)  | 2048   | 11393  | 559    | 37     |
| H(47)  | 2742   | -2104  | 2971   | 35     |
| H(13)  | 1136   | 8194   | 1517   | 32     |
| H(51A) | 96     | 4356   | 3564   | 35     |
| H(51B) | -820   | 4932   | 2752   | 35     |
| H(51C) | 461    | 4820   | 2591   | 35     |
| H(52A) | 321    | 3809   | 1609   | 42     |
| H(52B) | -948   | 3837   | 1772   | 42     |
| H(52C) | -58    | 2607   | 1928   | 42     |
| H(14)  | -674   | 8089   | 1804   | 40     |
| H(19A) | 3699   | 6280   | -896   | 47     |
| H(19B) | 2939   | 7164   | -1768  | 47     |
| H(19C) | 2384   | 6479   | -924   | 47     |
| H(46)  | 4065   | -1190  | 3178   | 37     |
| H(8)   | 5191   | 9408   | 1311   | 35     |
| H(9)   | 3851   | 11179  | 1049   | 38     |
| H(49)  | 329    | 621    | 3085   | 42     |
| H(15)  | -1550  | 7118   | 1166   | 41     |
| H(48)  | 880    | -1185  | 2926   | 49     |
| H(20A) | 1164   | 8517   | -1112  | 74     |
| H(20B) | 1840   | 9090   | -1914  | 74     |
| H(20C) | 1738   | 9519   | -1110  | 74     |
| H(21A) | 3805   | 9069   | -924   | 84     |
| H(21B) | 3930   | 8604   | -1710  | 84     |
| H(21C) | 4557   | 7770   | -771   | 84     |
Appendix 2.

Calculation of the compounds’ concentration at different time points:

Concentration of compound 2 at 0 hour is 0.17M.

Integral of 2 (Proton attached to sp2 hybridized carbon) at 0 hour is 15.89 compared to the internal standard Et₂O.

Integral of 2 (Proton attached to sp2 hybridized carbon) at X hour is $I_2$ compared to Et₂O.

Then the concentration of 2 at X hour is

$$C_2 = \frac{I_2}{15.89} \times 0.17$$

Integral of 3 (Proton attached to sp2 hybridized carbon) at X hour is $I_3$ compared to Et₂O.

Then the concentration of 3 at X hour is

$$C_3 = \frac{I_3}{15.89} \times 0.17$$

Integral of 6 (Proton attached to sp2 hybridized carbon) at X hour is $I_6$ compared to Et₂O.

Then the concentration of 6 at X hour is

$$C_6 = \frac{I_6}{15.89} \times 0.17$$

Integral of 10 (Proton attached to sp2 hybridized carbon) at X hour is $I_{10}$ compared to Et₂O.

Then the concentration of 10 at X hour is

$$C_{10} = \frac{I_{10}}{15.89} \times 0.17$$
Table S11. Concentration of compound 2, 3, 10 and total concentration of 3&6 at different time points

| Time (h) | Concentration of compound 2 integral (M) | Concentration of compound 3 integral (M) | Concentration of compound 6 integral (M) | Concentration of compound 10 integral (M) | Total concentration of 3 and 6 (M) |
|----------|--------------------------------------|---------------------------------------|---------------------------------------|-----------------------------------------|----------------------------------|
| 0        | 15.89                                | 0                                     | 0                                     | 0                                        | 0.01925739                      |
| 1        | 15.11                                | 0.17                                  | 0.18                                  | 0.001925739                              | 0.00908175                      |
| 2        | 14.39                                | 0.153952171                          | 0.55                                  | 0.005684204                              | 0.000213971                      |
| 3        | 13.88                                | 0.148495909                          | 0.87                                  | 0.009307741                              | 0.000855884                      |
| 4        | 13.46                                | 0.144002517                          | 1.16                                  | 0.012410321                              | 0.001604783                      |
| 5        | 12.97                                | 0.138760227                          | 1.54                                  | 0.016475771                              | 0.002674683                      |
| 6        | 12.37                                | 0.132341095                          | 1.8                                   | 0.01925739                               | 0.003637508                      |
| 7        | 12.01                                | 0.128489616                          | 2.16                                  | 0.023108874                              | 0.004921334                      |
| 8        | 11.5                                 | 0.123033354                          | 2.39                                  | 0.025569541                              | 0.005991189                      |
| 9        | 11.06                                | 0.118325991                          | 2.67                                  | 0.028565153                              | 0.007595972                      |
| 10       | 10.49                                | 0.112227816                          | 2.88                                  | 0.030811831                              | 0.008665828                      |
| 11       | 10.26                                | 0.10976149                           | 3.18                                  | 0.034021397                              | 0.010056639                      |
| 12       | 9.89                                 | 0.105806885                          | 3.4                                   | 0.036375079                              | 0.011447451                      |
| 13       | 9.46                                 | 0.101208307                          | 3.6                                   | 0.038514789                              | 0.012731278                      |
| 19       | 6.39                                 | 0.068363751                          | 4.74                                  | 0.050711139                              | 0.021825047                      |
| 26       | 4.11                                 | 0.043971051                          | 5.43                                  | 0.05809314                               | 0.033700441                      |
| 32       | 2.71                                 | 0.028993077                          | 5.44                                  | 0.058200126                              | 0.046752675                      |
| 37       | 1.88                                 | 0.020113279                          | 5.04                                  | 0.053920705                              | 0.057665198                      |
| 42       | 1.38                                 | 0.014764003                          | 4.46                                  | 0.047715544                              | 0.067721838                      |
| 48       | 0.87                                 | 0.009407741                          | 3.65                                  | 0.039049717                              | 0.081095078                      |
| 54       | 0.54                                 | 0.005777218                          | 2.74                                  | 0.029314034                              | 0.093505349                      |
| 60       | 0.29                                 | 0.00310258                          | 1.82                                  | 0.019471366                              | 0.108269352                      |
| 66       | 0.12                                 | 0.001283826                          | 0.99                                  | 0.010501567                              | 0.118539062                      |
| 72       | 0.06                                 | 0.000641913                          | 0.4                                   | 0.004279421                              | 0.12410321                      |
| 78       | 0                                   | 0                                     | 0                                     | 0                                        | 0.130094399                      |
Appendix 3.

Rate law derivation.

Consumption rate of $2 = -(k_1+k_5)[2]$

The rate law of compound $2$ can be described as:

$$\frac{d[2]}{dt} = -(k_1+k_5)[2] \quad (\text{Eq. 1})$$

Based on (Eq 1)

$$[2] = 0.17*e^{-(k_1+k_5)t}. \quad (\text{Eq. 2})$$

To obtain the rate law of $6+3$:

Production rate of $4 = k_1[2]$

Consumption rate of $4 = k_2[4]$

Production rate of $5 = k_2[4]$

Consumption rate of $5 = k_3[5]$

With stead-state approximation:

$$k_1[2] = k_2[4] = k_3[5] \quad (\text{Eq. 3})$$

Since compound $6$ can be observed, the rate of its generation and consumption cannot be treated as equal based SSA. Thus the rate law of compound $6$ can be expressed as:

$$\frac{d[6]}{dt} = k_3[5] - k_4[6]^\alpha \quad (\text{Eq. 4})$$

The rate law of compound $3$ can be expressed as:

$$\frac{d[3]}{dt} = k_4[6]^\alpha \quad (\text{Eq. 5})$$

Combination of (Eq. 3), (Eq. 4) and (Eq. 5)

$$[3]+[6] = -\frac{0.17k_1}{k_1+k_5} e^{-(k_1+k_5)t} + \frac{0.17k_1}{k_1+k_5} \quad (\text{Eq. 6})$$

To obtain the rate law of compound $10$:

Production rate of $7 = k_5[2]$

Consumption rate of $7 = k_6[7]$

Production rate of $8 = k_6[7]$

Consumption rate of $8 = k_7[8]$
Production rate of $9 = k_7[8]$
Consumption rate of $9 = k_8[9]$

With stead-state approximation:

$$k_5[2] = k_6[7] = k_7[8] = k_8[9]$$  \hspace{1cm} (Eq. 7)

The rate law of compound 10 can be described as:

$$\frac{d[10]}{dt} = k_8[9]$$ \hspace{1cm} (Eq. 8)

Combine (Eq 7) and (Eq 8)

$$[10] = -\frac{0.17k_5}{k_1+k_5} e^{-(k_1+k_5)t} + \frac{0.17k_5}{k_1+k_5}$$  \hspace{1cm} (Eq. 9)
Figure S7. Fitting result of the kinetic data with the derived rate law.
Reference:

1 Y. Xiang, D. J. Burrill, K. K. Bullard, B. J. Albrecht, L. E. Tragesser, J. McCaffrey, D. S. Lambrecht and E. Pentzer, *Polym. Chem.*, 2017, 8, 5381–5387.