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## General Methods.

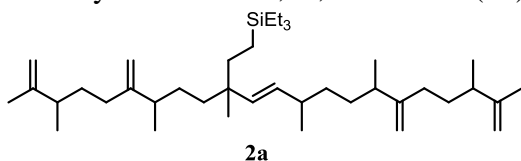
The  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectroscopic data in  $\text{CDCl}_3$  were recorded on a Bruker AV400 spectrometer using  $\text{Me}_4\text{Si}$  ( $\delta = 0$  ppm) and  $\text{CDCl}_3$  (centerline of the triplet,  $\delta = 77.1$  ppm), respectively, as internal standards. Signal patterns are indicated as br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants ( $J$ ) are given in hertz (Hz). DEPT-90 and DEPT-135 were used to identify primary, secondary, tertiary and quaternary carbons. The solvents that were distilled prior to use are 2-propanol (from Mg), toluene (from  $\text{CaH}_2$ ), THF (from Na/benzophenone), and 1,2-dichloroethane (from  $\text{CaH}_2$ ). After the reactions were completed, the organic extracts were concentrated by using an evaporator, and then the residues were purified by chromatography on silica gel (Kanto, spherical silica gel 60N). Botryococcene **1** was provided by the Algae Biomass and Energy System R&D Center, University of Tsukuba.

### General Procedure for Hydrosilylation of Botryococcene (1).

To a mixture of botryococcene **1** (1 equiv) and an organosilane (2 equiv) in a solvent ( $0.2 \text{ mol dm}^{-3}$ ) was added a Pt catalyst ( $\sim 1 \text{ mol}\%$ ) under an Ar atmosphere. The mixture was stirred at  $80^\circ\text{C}$  and concentrated under reduced pressure. The crude oily product was purified by column chromatography on silica gel to give a hydrosilylated botryococcene (**2**).

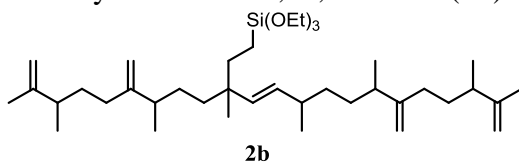
### Hydrosilylated Botryococenes (2).

Synthesis of (*E*)-10-[2-(triethylsilyl)ethyl]-2,3,7,10,13,16,20,21-octamethyl-6,17-dimethylenedocosa-1,11,21-triene (**2a**):



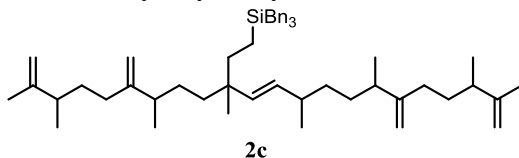
According to the general procedure for the hydrosilylation a mixture of **1** (100 mg, 0.21 mmol), triethylsilane (68  $\mu\text{L}$ , 0.43 mmol) and Karstedt's catalyst in xylene (Pt  $\sim 2\%$ , 10  $\mu\text{L}$ , 1.0  $\mu\text{mol}$ ) was stirred at  $80^\circ\text{C}$  for 24 h to afford the silane **2a** (108 mg, 86% isolated yield):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.31–0.39 (m, 2 H), 0.48 (q,  $J = 7.8$  Hz, 6 H), 0.84–1.04 (m, 27 H), 1.13–1.59 (m, 14 H), 1.66 (s, 6 H), 1.84–2.21 (m, 9 H), 4.69 (br s, 8 H), 5.03 (dd,  $J = 15.7, 7.3$  Hz, 1 H), 5.11 (d,  $J = 15.7$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  3.3 ( $\text{CH}_2 \times 3$ ), 4.6 ( $\text{CH}_2$ ), 7.6 ( $\text{CH}_3 \times 3$ ), 19.0 ( $\text{CH}_3 \times 2$ ), 19.9 ( $\text{CH}_3 \times 2$ ), 20.4 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_3$ ), 30.2 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 31.8 ( $\text{CH}_2$ ), 33.48 ( $\text{CH}_2$ ), 33.51 ( $\text{CH}_2$ ), 33.6 ( $\text{CH}_2$ ), 35.29 ( $\text{CH}_2$ ), 35.32 ( $\text{CH}_2$ ), 37.6 (CH), 38.7 ( $\text{CH}_2$ ), 39.3 (C), 40.3 (CH), 40.8 (CH), 41.1 (CH  $\times 2$ ), 107.3 ( $\text{CH}_2 \times 2$ ), 109.6 ( $\text{CH}_2 \times 2$ ), 133.8 (CH), 137.2 (CH), 150.1 (C  $\times 2$ ), 155.0 (C  $\times 2$ ) ppm; GC-MS (EI,  $m/z$ ) 583 ( $\text{M}^+$ ), 554, 513, 439; IR (neat) 2956, 2874, 1456, 887, 729  $\text{cm}^{-1}$ .

Synthesis of (*E*)-10-[2-(triethoxysilyl)ethyl]-2,3,7,10,13,16,20,21-octamethyl-6,17-dimethylenedocosa-1,11,21-triene (**2b**):



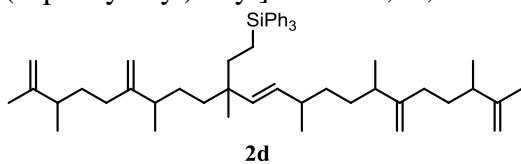
According to the general procedure for the hydrosilylation a mixture of **1** (100 mg, 0.21 mmol), triethoxysilane (78  $\mu$ L, 0.43 mmol) and Karstedt's catalyst in xylene (Pt ~2%, 10  $\mu$ L, 1.0  $\mu$ mol) was stirred at 80  $^{\circ}$ C for 24 h to afford the silane **2b** (106 mg, 78% isolated yield):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.46–0.55 (m, 2 H), 0.79–1.05 (m, 18 H), 1.10–1.61 (m, 14 H), 1.22 (t,  $J = 7.0$  Hz, 9 H), 1.66 (s, 6 H), 1.82–2.20 (m, 9 H), 3.80 (q,  $J = 7.0$  Hz, 6 H), 4.64–4.72 (m, 8 H), 5.07 (dd,  $J = 15.7, 7.1$  Hz, 1 H), 5.11 (d,  $J = 15.7$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  4.2 ( $\text{CH}_2$ ), 18.4 ( $\text{CH}_3 \times 3$ ), 18.97 ( $\text{CH}_3$ ), 18.98 ( $\text{CH}_3$ ), 19.8 ( $\text{CH}_3$ ), 19.9 ( $\text{CH}_3$ ), 20.4 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 22.3 ( $\text{CH}_3$ ), 30.1 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 33.39 ( $\text{CH}_2$ ), 33.43 ( $\text{CH}_2$ ), 33.5 ( $\text{CH}_2$ ), 33.6 ( $\text{CH}_2$ ), 34.1 ( $\text{CH}_2$ ), 35.3 ( $\text{CH}_2$ ), 37.7 ( $\text{CH}$ ), 38.9 ( $\text{CH}_2$ ), 39.2 (C), 40.3 ( $\text{CH}$ ), 40.7 ( $\text{CH}$ ), 41.1 ( $\text{CH} \times 2$ ), 58.4 ( $\text{CH}_2 \times 3$ ), 107.3 ( $\text{CH}_2 \times 2$ ), 109.58 ( $\text{CH}_2$ ), 109.60 ( $\text{CH}_2$ ), 134.2 ( $\text{CH}$ ), 136.7 ( $\text{CH}$ ), 150.07 (C), 150.08 (C), 154.97 (C), 155.02 (C) ppm; GC-MS (EI,  $m/z$ ) 631 ( $\text{M}^+$ ), 561, 451, 439; IR (neat) 2964, 2927, 1455, 1081, 786  $\text{cm}^{-1}$ .

Synthesis of (*E*)-2,3,7,10,13,16,20,21-octamethyl-6,17-dimethylene-10-[2-(tribenzylsilyl)ethyl]docosa-1,11,21-triene (**2c**):

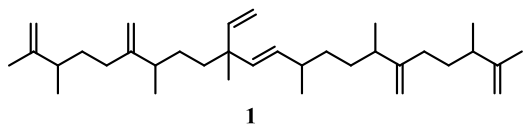


According to the general procedure for the hydrosilylation a mixture of **1** (103 mg, 0.22 mmol), tribenzylsilane (134 mg, 0.44 mmol) and Karstedt's catalyst in xylene (Pt ~2%, 10  $\mu$ L, 1.0  $\mu$ mol) was stirred at 80  $^{\circ}$ C for 24 h to afford the silane **2c** (142 mg, 84% isolated yield):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.29–0.41 (m, 2 H), 0.68–1.61 (m, 32 H), 1.62–1.70 (m, 6 H), 1.82–2.21 (m, 9 H), 2.08 (s, 6 H), 4.63–4.73 (m, 6 H), 4.90–5.14 (m, 4 H), 6.93 (d,  $J = 6.1$  Hz, 6 H), 7.07 (t,  $J = 5.9$  Hz, 3 H), 7.18 (dd,  $J = 6.1, 5.9$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  5.5 ( $\text{CH}_2$ ), 12.4 ( $\text{CH}_3$ ), 19.0 ( $\text{CH}_3$ ), 19.2 ( $\text{CH}_3$ ), 19.9 ( $\text{CH}_3 \times 2$ ), 20.2 ( $\text{CH}_3$ ), 20.5 ( $\text{CH}_3$ ), 21.7 ( $\text{CH}_3$ ), 21.9 ( $\text{CH}_2 \times 3$ ), 30.1 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2 \times 2$ ), 33.5 ( $\text{CH}_2 \times 2$ ), 33.7 ( $\text{CH}_2$ ), 34.8 ( $\text{CH}_2$ ), 35.3 ( $\text{CH}_2$ ), 37.8 ( $\text{CH}$ ), 39.2 ( $\text{CH}_2$ ), 39.3 (C), 40.3 ( $\text{CH}$ ), 40.7 ( $\text{CH}$ ), 41.1 ( $\text{CH}$ ), 41.5 ( $\text{CH}$ ), 107.3 ( $\text{CH}_2 \times 2$ ), 109.6 ( $\text{CH}_2 \times 2$ ), 124.3 ( $\text{CH} \times 3$ ), 128.4 ( $\text{CH} \times 6$ ), 128.6 ( $\text{CH} \times 6$ ), 134.2 ( $\text{CH}$ ), 136.6 ( $\text{CH}$ ), 139.5 (C  $\times 3$ ), 150.1 (C), 150.3 (C), 154.9 (C), 155.0 (C) ppm.

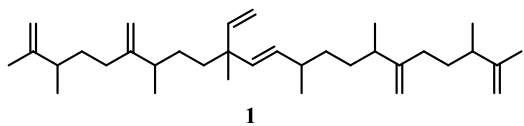
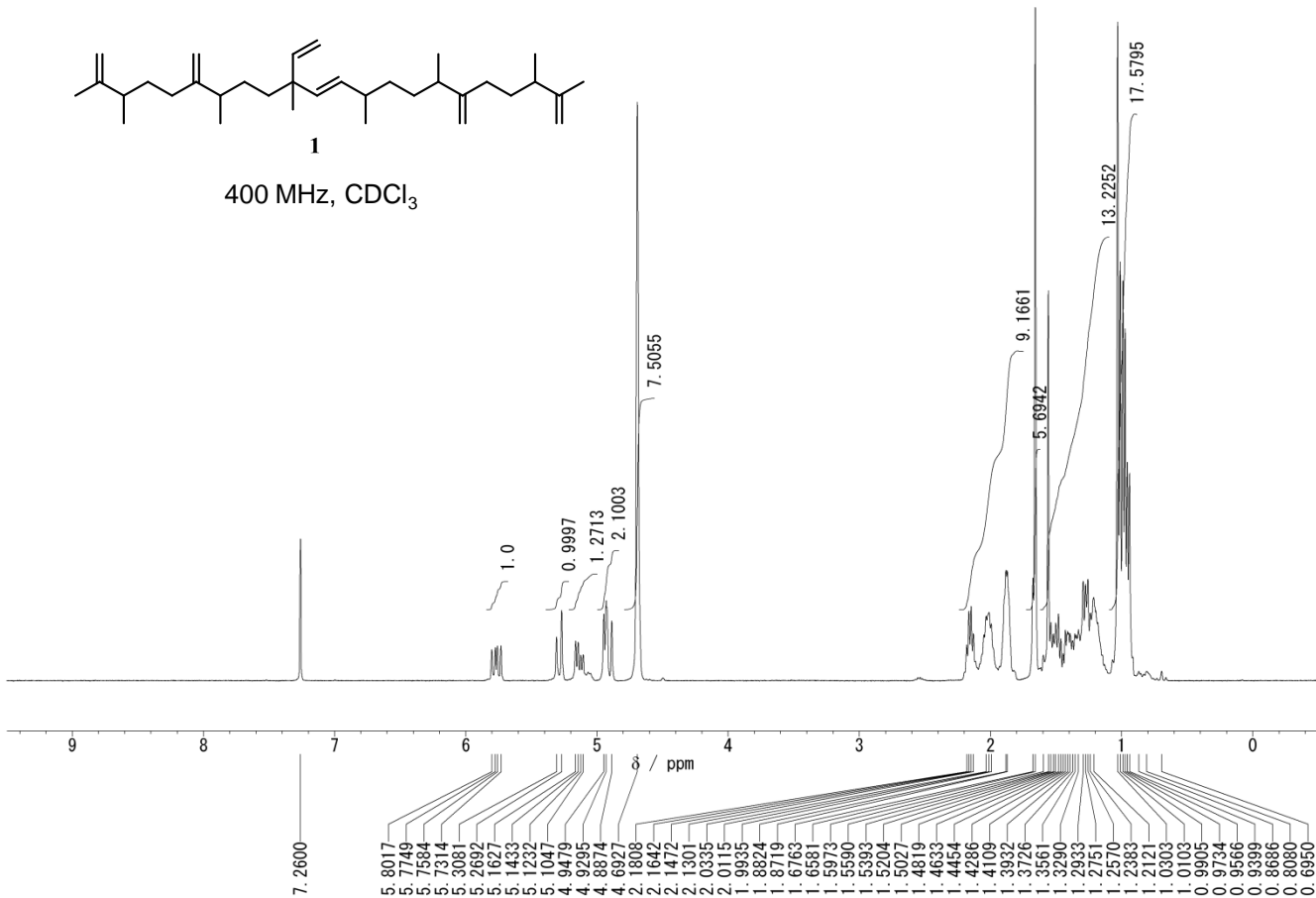
Synthesis of (*E*)-2,3,7,10,13,16,20,21-octamethyl-6,17-dimethylene-10-[2-(triphenylsilyl)ethyl]docosa-1,11,21-triene (**2d**):



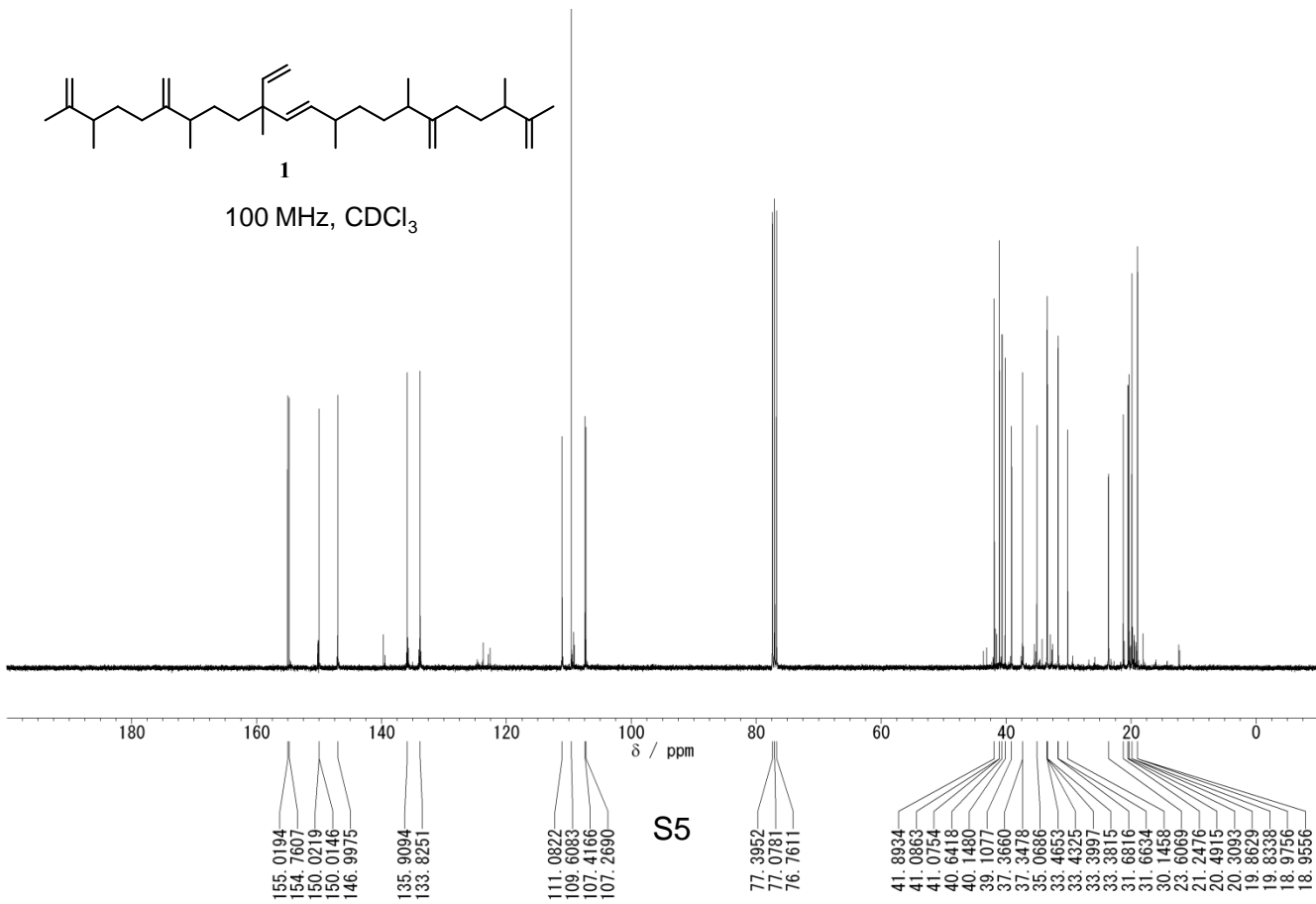
According to the general procedure for the hydrosilylation a mixture of **1** (102 mg, 0.22 mmol), triphenylsilane (114 mg, 0.44 mmol) and Karstedt's catalyst in xylene (Pt ~2%, 10  $\mu$ L, 1.0  $\mu$ mol) was stirred at 80 °C for 24 h to afford the silane **2d** (123 mg, 77% isolated yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.86–1.03 (m, 18 H), 1.08–1.56 (m, 16 H), 1.61–1.68 (m, 6 H), 1.77–2.20 (m, 9 H), 4.60–4.74 (m, 8 H), 5.04 (dd,  $J$  = 15.8, 6.8 Hz, 1 H), 5.10 (d,  $J$  = 15.8 Hz, 1 H), 7.31–7.42 (m, 9 H), 7.47–7.52 (m, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  6.9 (CH<sub>2</sub>), 19.0 (CH<sub>3</sub> x 2), 19.86 (CH<sub>3</sub>), 19.87 (CH<sub>3</sub>), 20.4 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 22.3 (CH<sub>3</sub>), 30.1 (CH<sub>2</sub>), 31.69 (CH<sub>2</sub>), 31.70 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 33.5 (CH<sub>2</sub>), 33.7 (CH<sub>2</sub>), 35.3 (CH<sub>2</sub>), 35.5 (CH<sub>2</sub>), 37.6 (CH), 38.9 (CH<sub>2</sub>), 39.6 (C), 40.3 (CH), 40.7 (CH), 41.06 (CH), 41.08 (CH), 107.31 (CH<sub>2</sub>), 107.32 (CH<sub>2</sub>), 109.60 (CH<sub>2</sub>), 109.61 (CH<sub>2</sub>), 127.9 (CH x 5), 128.0 (CH), 129.4 (CH x 3), 134.3 (CH), 135.5 (C x 3), 135.7 (CH x 5), 136.5 (CH), 136.7 (CH), 150.06 (C), 150.08 (C), 154.9 (C), 155.0 (C) ppm; GC-MS (EI,  $m/z$ ) 727 ( $M^+$ ), 575, 547, 439; IR (neat) 2960, 2926, 1428, 1110, 888, 700  $\text{cm}^{-1}$ .



400 MHz, CDCl<sub>3</sub>

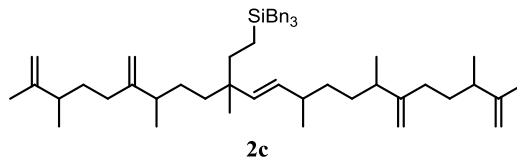


100 MHz, CDCl<sub>3</sub>

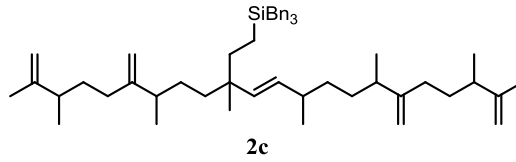
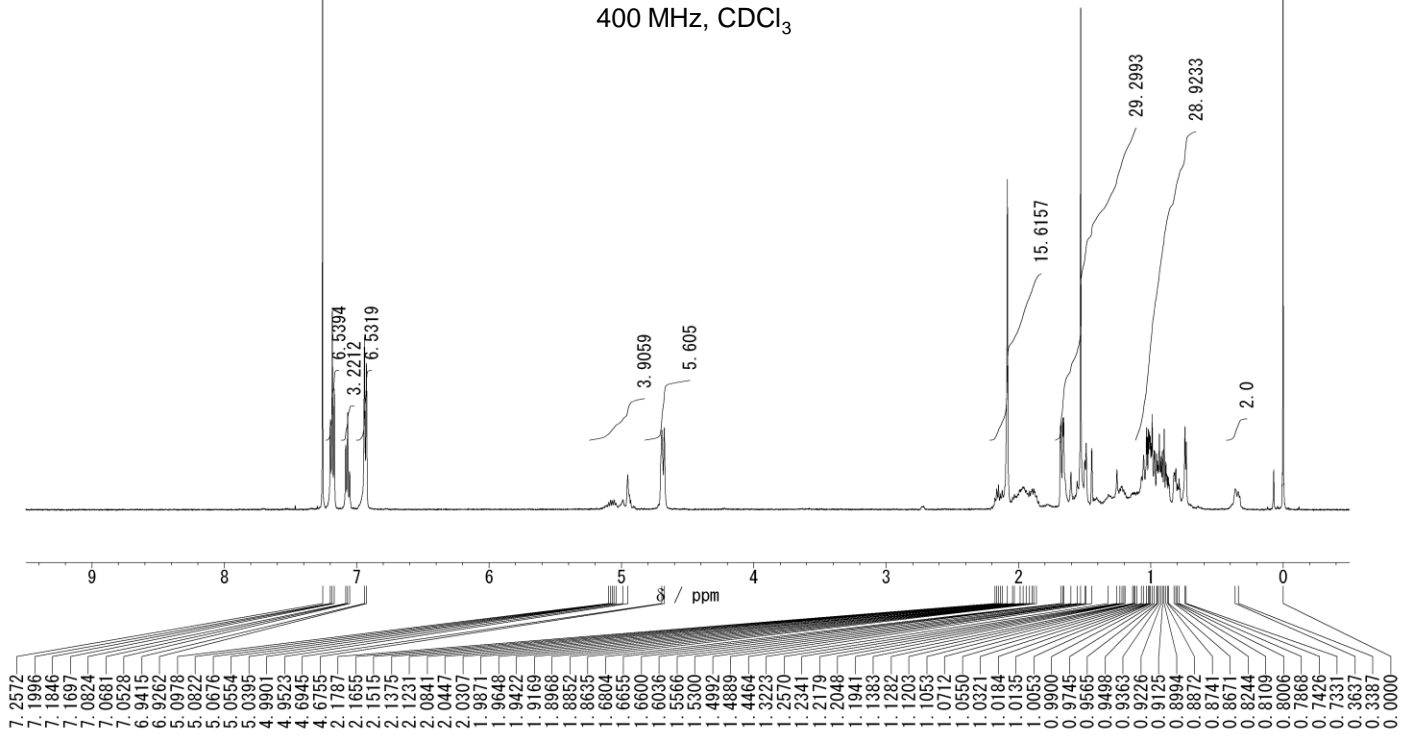




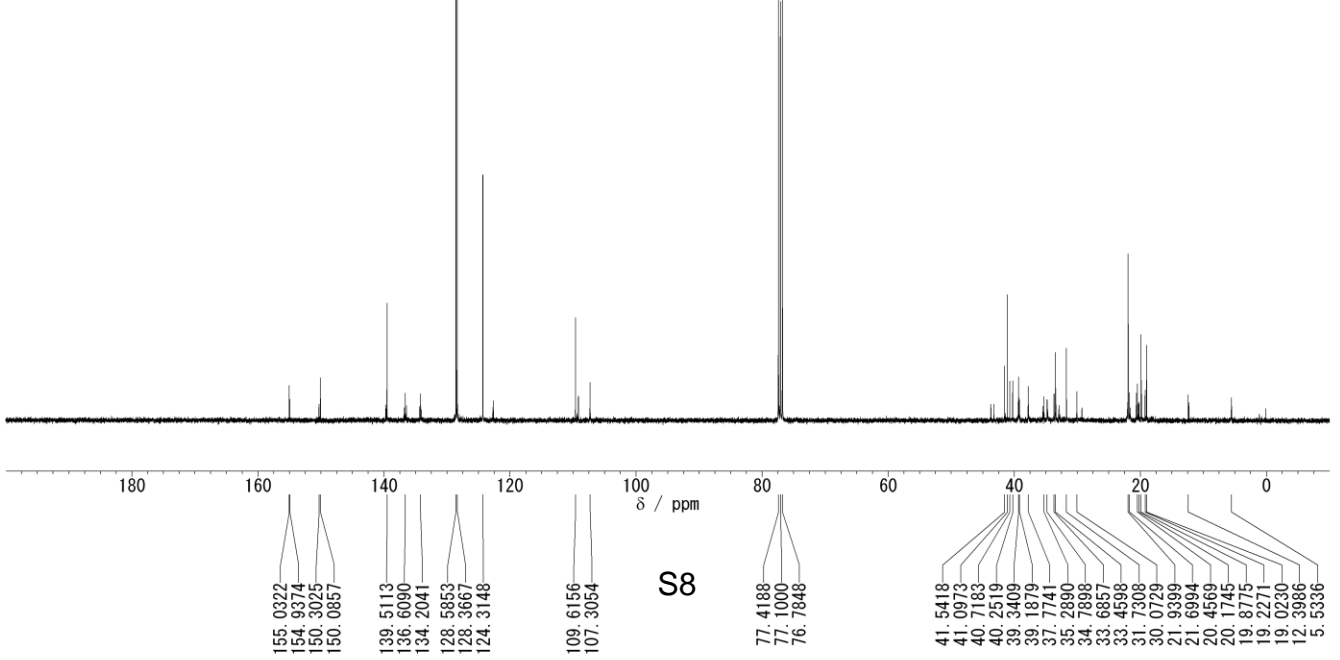




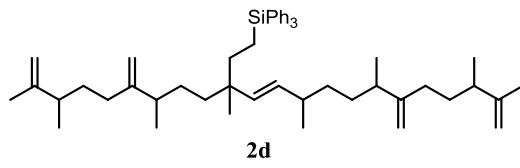
400 MHz, CDCl<sub>3</sub>



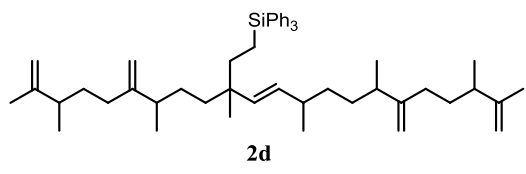
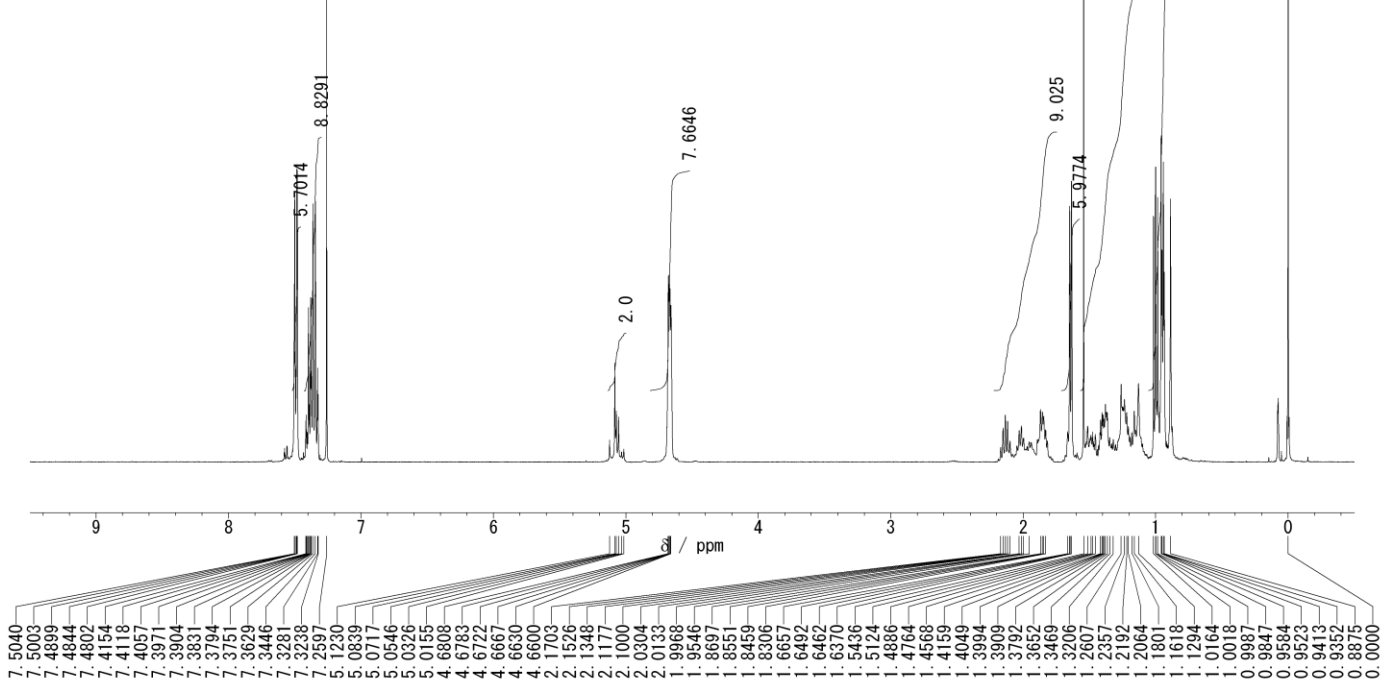
100 MHz, CDCl<sub>3</sub>







400 MHz, CDCl<sub>3</sub>



100 MHz, CDCl<sub>3</sub>

