Supporting Information

One-step Synthesis of Triethynylvinylmethanes and Tetraethynylmethanes by GaCl₃-Promoted Diethynylation of 1,4-Enynes and 1,4-Diynes

Ryo Amemiya, Katsunori Suwa, Jyunji Toriyama, Yoshio Nishimura, and Masahiko Yamaguchi^{†*}

*Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences,
Tohoku University, Aoba, Sendai 980-8578, Japan*

[†]Tohoku University 21st Century COE Program CRESCENDO, Sendai, Japan

Melting points were determined with a Yanaco micro melting point apparatus with out correction. ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury NMR (400 MHz) with Me₄Si as an internal standard. ¹³C-NMR spectra taken in CDCl₃ (δ 77.0) was referenced to the residual solvent. IR spectra were measured on a JASCO FT/IR-400. Mass spectra were recorded on a JEOL JMS-DX-303 or a JEOL JMS-AX-500, a JEOL JMS-700.

3,3-Bis(triethylsilylethynyl)-5-triethylsilyl-1-penten-4-yne 4. Under an argon atmosphere, to a mixture of 2,6-di(*t*-butyl)-4-methylpyridine (1 mmol, 205.3 mg) and *t*-butyldiphenylsilanol (0.5 mmol, 128.2 mg) in *o*-dichlorobenzene (0.75 mL) was added a solution of GaCl₃ (1.0 M, 1 mmol) in methylcyclohexane (1 mL) at 0 °C. The mixture was cooled to 0 °C, and a solution of 1-triethylsilyl-4-penten-1-yne **1** (0.5 mmol, 90.1 mg) and chlorotriethylsilylacetylene **2** (2 mmol, 348.0 mg) in *o*-dichlorobenzene (0.75 mL) was added. Then, the mixture was stirred at 130 °C for 12 h, when 2 M HCl was added. The organic materials were extracted with ether. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (hexane) to give **4** (164 mg, 72%). ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (18H, q, *J* = 8.0 Hz), 0.99 (27H, t, *J* = 8.0 Hz), 5.19 (1H, d, *J* = 9.6 Hz), 5.68 (1H, d, *J* = 16.8 Hz) 5.94 (1H, dd, *J* = 9.6 Hz, *J* = 16.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.5, 33.6, 84.2, 102.8, 114.3, 136.2. IR (neat) 2956, 2912, 2876, 2803, 2180, 1458, 1236, 1162, 1101, 1017, 728, 668 cm⁻¹. MS (EI) *m/z* 456 (M⁺,

20%), 399 (M^+ -C₄H₉, 100%). HRMS Calcd for C₂₇H₄₈Si₃: 456.3064. Found: 456.3075.

Reaction of 1 and 2 without silanol and pyridine. Under an argon atmosphere, to a solution of GaCl₃ (1.0 M, 0.1 mmol) in methylcyclohexane (0.1 mL) and *o*-dichlorobenzene (0.75 mL) was added a solution of **1** (0.5 mmol, 90.1 mg) and chlorotriethylsilylacetylene **2** (2 mmol, 348.0 mg) in *o*-dichlorobenzene (0.75 mL) at 0 °C. The mixture was heated at 130 °C for 4 h. The mixture was cooled to 0 °C, and 2 M HCl was added. The organic materials were extracted with ether. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (hexane) to give **4** (9 mg, 4% based on **1**, 20% based on GaCl₃).

1-Triethylsilyl-3,3-bis(tributylsilylethynyl)-4-penten-1-yne 5. ¹H-NMR (400 MHz, CDCl₃) δ 0.50-0.56 (18H, m), 0.82 (18H, t, *J* = 7.2 Hz), 0.93 (9H, t, *J* = 8.0 Hz), 1.21-1.31 (24H, m), 5.11 (1H, d, *J* = 9.6 Hz), 5.59 (1H, d, *J* = 16.4 Hz), 5.85 (1H, dd, *J* = 9.6, 16.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.6, 13.1, 13.9, 26.1, 26.4, 33.5, 84.0, 84.9, 102.3, 102.8, 114.2, 136.3. IR (neat) 2957, 2923, 2873, 2182, 2034, 1634, 1464, 1410, 1377, 1341, 1296, 1261, 1193, 1082, 975, 927, 886, 790, 729 cm⁻¹. MS (EI) *m/z* 624 (M^+ , 7%), 143 (M^+ -C₃₁H₅₃Si₂, 100%). HRMS Calcd for C₃₉H₇₂Si₃: 624.4942. Found: 624.4937.

5-Tributylsilyl-3,3-bis(triethylsilylethynyl)-1-penten-4-yne 8a. ¹H-NMR (400 MHz, CDCl₃) δ 0.57-0.63 (18H, m), 0.88 (9H, t, *J* = 7.2 Hz), 0.99 (18H, t, *J* = 8.0 Hz), 1.33-1.36 (12H, m), 5.19 (1H, d, *J* = 9.6 Hz), 5.67 (1H, d, *J* = 16.4 Hz), 5.93 (1H, dd, *J* = 9.6, 16.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.5, 13.0, 13.9, 26.2, 26.5, 33.6, 84.0, 84.8, 102.3, 102.7, 114.3, 136.2. IR (neat) 2956, 2920, 2875, 2734, 2182, 1635, 1459, 1413, 1377, 1236, 1165, 1102, 1017, 975, 927, 728 cm⁻¹. MS (EI) *m/z* 540 (M^+ , 18%), 143 (M^+ -C₂₅H₄₄Si₂, 100%). HRMS Calcd for C₃₃H₆₀Si₃: 540.4003. Found: 540.4003.

5-(*t*-Butyldimethylsilylethynyl)-3,3-bis(triethylsilyl)-1-penten-4-yne 8b. ¹H-NMR (400 MHz, CDCl₃) δ 0.10 (6H, s), 0.60 (12H, q, *J* = 8.0 Hz), 0.94 (9H, s), 0.99 (18H, t, *J* = 8.0 Hz), 5.19 (1H, d, *J* = 9.6 Hz), 5.67 (1H, d, *J* = 16.8 Hz), 5.93 (1H, dd, *J* = 9.6, 16.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ -4.7, 4.5, 7.5, 17.0, 26.1, 33.5, 84.3, 85.1, 101.9, 102.5, 114.4, 136.1. IR (neat) 2955, 2928, 2876, 2733, 2183, 1641, 1461, 1415, 1250, 1165, 1101, 1016, 975, 928, 830, 797, 777, 729 cm⁻¹. MS (EI) *m/z* 456 (M^+ , 10%), 399 (M^+ -C₄H₉, 49%), 371 (M^+ -C₆H₁₃, 100%). HRMS Calcd for C₂₇H₄₈Si₃: 456.3064. Found: 456.3090.

5-(1-Adamantyl)-3,3-bis(triethylsilylethynyl)-1-penten-4-yne 8c. Under an argon atmosphere, to a mixture of 2,6-di(*t*-butyl)-4-methylpyridine (1 mmol, 205.3 mg) and trihexylsilanol (0.5 mmol, 150.3 mg) in *o*-dichlorobenzene (0.75 mL) were added a solution of GaCl₃ (1.0 M, 1 mmol) in methylcyclohexane (1 mL) at 0 °C. The mixture was cooled to 0 °C, and a solution of 1-(1-adamantyl)-4-penten-1-yne **7c**

(0.5 mmol, 100.2 mg) and **2** (2 mmol, 348.0 mg) in *o*-dichlorobenzene (0.75 mL) was added. Then, the mixture was stirred at 170 °C for 12 h, when 2 M HCl was added. The organic materials were extracted with ether. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (hexane) to give **8c** (116 mg, 49%). ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (12H, q, *J* = 7.6 Hz), 0.99 (18H, t, *J* = 8.0 Hz), 1.67 (6H, s), 1.86 (6H, s), 1.93 (3H, s), 5.15 (1H, d, *J* = 9.6 Hz), 5.64 (1H, d, *J* = 16.4 Hz), 5.92 (1H, dd, *J* = 9.6, 16.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.6, 28.1, 29.6, 32.7, 36.5, 42.5, 75.7, 83.4, 90.5, 103.7, 113.6, 136.9. IR (neat) 2955, 2909, 2875, 2852, 2248, 2180, 1634, 1453, 729 cm⁻¹. MS (EI) *m/z* 476 (M⁺, 37%), 419 (M⁺-C₄H₉, 100%). HRMS Calcd for C₃₁H₄₈Si₂: 476.3295. Found: 476.3299. The same reaction at 130 °C did not give the product, and starting materials were recovered in quantitative yields.

5-Cyclohexyl-3,3-bis(triethylsilylethynyl)-1-penten-4-yne 8d. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (12H, q, *J* = 8.0 Hz), 0.99 (18H, t, *J* = 8.0 Hz), 1.27-1.32 (3H, m), 1.43-1.48 (3H, m), 1.69-1.73 (4H, m), 2.39-2.44 (1H, m), 5.16 (1H, d, *J* = 9.6 Hz), 5.65 (1H, d, *J* = 16.0 Hz), 5.94 (1H, dd, *J* = 9.6, 16.0 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.6, 24.7, 26.0, 29.0, 32.3, 32.7, 76.8, 83.6, 86.7, 103.4, 113.8, 136.8. IR (neat) 2955, 2934, 2875, 2739, 2180, 1457, 729 cm⁻¹. MS (EI) *m/z* 424 (M⁺, 17%), 367 (M⁺-C₄H₉, 86%), 87 (M⁺-C₂₁H₃₉Si₂, 100%). HRMS Calcd for C₂₇H₄₄Si₂: 424.2982. Found: 424.2962.

3,3-Bis(triethylsilylethynyl)-1-nonen-4-yne 8e. ¹H-NMR (400 MHz, CDCl₃) δ 0.62 (12H, q, *J* = 6 Hz), 0.90 (3H, t, *J* = 7.2 Hz), 0.99 (18H, t, *J* = 8.0 Hz), 1.42-1.56 (4H, m), 2.22 (2H, t, *J* = 7.2 Hz), 5.16 (1H, d, *J* = 8.0 Hz), 5.64 (1H, d, *J* = 16.0 Hz), 5.93 (1H, dd, *J* = 8.0, 16.0 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.5, 13.7, 18.6, 22.0, 30.6, 33.0, 76.7, 82.8, 83.7, 103.3, 113.8, 136.8. IR (neat) 2956, 2935, 2912, 2875, 2739, 2181, 1632 cm⁻¹. MS (EI) *m/z* 398 (M⁺, 20%), 341 (M⁺-C₄H₉, 100%). HRMS Calcd for C₂₅H₄₂Si₂: 398.2825. Found: 398.2834.

(*E*)-1-Triethylsilyl-3,3-Bis(triethylsilylethynyl)-4-hexen-1-yne 10a. Under an argon atmosphere, to a mixture of 2,6-di(*t*-butyl)-4-methylpyridine (1 mmol, 205.3 mg) and *t*-butyldiphenylsilanol (0.5 mmol, 128.2 mg) in *o*-dichlorobenzene (0.75 mL) was added a solution of GaCl₃ (1.0 M, 1 mmol) in methylcyclohexane (1 mL) at 0 °C. The mixture was cooled to 0 °C, and a solution of (*E*)-1-triethylsilyl-4-hexen-1-yne **9a** (0.5 mmol, 97.2 mg) and **2** (2 mmol, 348.0 mg) in *o*-dichlorobenzene (0.75 mL) was added. Then, the mixture was stirred at 130 °C for 12 h, when 2 M HCl was added. The organic materials were extracted with ether. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (hexane) to give

10a (190.4 mg, 72%). ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (18H, q *J* = 8.0 Hz), 0.98 (27H, t, *J* = 8.0 Hz), 1.74 (3H, dd, *J* = 2.0 Hz, *J* = 6.4 Hz), 5.55 (1H, dd, *J* = 2.0 Hz, *J* = 14.8 Hz), 6.05-6.10 (1H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.5, 17.3, 32.7, 83.5, 103.5, 125.7, 129.1. IR (neat) 2956, 2913, 2876, 2174, 1458, 1415, 1236, 1150, 1097, 1016, 956, 831, 727 cm⁻¹. MS (EI) *m/z* 470 (M⁺, 43%), 115 (M⁺-C₂₂H₃₅Si₂, 100%). HRMS Calcd for C₂₈H₅₀Si₃: 470.3220. Found: 470.3199.

5-Methyl-1-triethylsilyl-3,3-bis(triethylsilylethynyl)-4-hexen-1-yne 10b. ¹H-NMR (400 MHz, CDCl₃) δ 0.59 (18H, q *J* = 8.0 Hz), 0.98 (27H, t, *J* = 8.0 Hz), 1.73 (3H, d *J* = 1.6 Hz), 1.92 (3H, d *J* = 1.2 Hz), 5.45-5.49 (1H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.5, 19.4, 26.2, 33.6, 81.6, 104.8, 124.6, 138.4. IR (neat) 2955, 2916, 2875, 2733, 2158, 1458, 1419, 1373, 1236, 1217, 1096, 1016, 968, 857, 812, 727 cm⁻¹. MS (EI) *m/z* 484 (M⁺, 40%), 201 (M⁺-C₁₈H₃₅Si₂, 100%). HRMS Calcd for C₂₉H₅₂Si₃: 484.3377. Found: 484.3402.

2-Methyl-5-triethylsilyl-3,3-bis(triethylsilylethynyl)-1-penten-4-yne 10c. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (18H, q *J* = 8.0 Hz), 0.99 (27H, t, *J* = 8.0 Hz), 2.03 (3H, s), 4.96 (1H, s), 5.59 (1H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.5, 18.4, 31.7, 84.0, 103.3, 112.8, 141.6. IR (neat) 2955, 2913, 2875, 2733, 2171, 1652, 1507, 1458, 1415, 1236, 1125, 1097, 1016, 974, 908, 727 cm⁻¹. MS (EI) *m/z* 470 (M⁺, 37%), 115 (M⁺-C₂₂H₃₅Si₂, 100%). HRMS Calcd for C₂₈H₅₀Si₃: 470.3220. Found: 470.3242.

Reaction of Allyltrimethylsilane 11 and 2. Under an argon atmosphere, to a mixture of 2,6-di(*t*-butyl)-4-methylpyridine (1 mmol, 205.3 mg) and *t*-butyldiphenylsilanol (0.5 mmol, 128.2 mg) in *o*-dichlorobenzene (0.75 mL) was added a solution of GaCl₃ (1.0 M, 1 mmol) in methylcyclohexane (1 mL) at 0 °C. The mixture was cooled to 0 °C, and a solution of **11** (0.5 mmol, 57.2 mg) and **2** (1.5 mmol, 261.0 mg) in *o*-dichlorobenzene (0.75 mL) was added. Then, the mixture was stirred at 170 °C for 12 h. 2 M HCl was added, and the organic materials were extracted with ether. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (hexane) to give **4** (126 mg, 55%). The same reaction at 130 °C gave **4** in 31% yield.

3-Methyl-5-triethylsilyl-3-triethylsilylethynyl-1-penten-4-yne 14. ¹H-NMR (400 MHz, CDCl₃) δ 0.59 (12H, q *J* = 8.0 Hz), 0.99 (18H, t, *J* = 8.0 Hz), 1.57 (3H, s), 5.08 (1H, dd, *J* = 1.2 Hz, *J* = 9.6 Hz), 5.53 (1H, dd, *J* = 1.2 Hz, *J* = 16.8 Hz), 5.83 (1H, dd, *J* = 9.6 Hz, *J* = 16.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.5, 31.1, 35.1, 83.4, 107.7, 113.2, 139.9. IR (neat) 2956, 2914, 2733, 2171, 1458, 1415, 1235, 1161, 1016, 976, 925, 789, 726, 537 cm⁻¹. MS (EI) *m/z* 332 (M⁺, 7%), 303 (M⁺-C₂H₅, 100%). HRMS Calcd for C₂₀H₃₆Si₂: 332.2356. Found: 332.2373.

6,6-Dimethyl-1-triethylsilyl-3,3-bis(triethylsilylethynyl)hepta-1,4-diyne 16a. Under an argon atmosphere, to a mixture of 2,6-di(*t*-butyl)-4-methylpyridine (1 mmol, 205.3 mg) and *t*-butyldiphenylsilanol (0.5 mmol, 128.2 mg) in *o*-dichlorobenzene (0.75 mL) was added a solution of GaCl₃ (1.0 M, 1 mmol) in methylcyclohexane (1 mL) at 0 °C. The mixture was cooled to 0 °C, and a solution of 6,6-dimethyl-1-triethylsilylhepta-1,4-diyne (117.2 mg, 0.5 mmol) and **2** (2 mmol, 348.0 mg) in *o*-dichlorobenzene (0.75 mL) was added. Then, the mixture was stirred at 150 °C for 6 h, when 2 M HCl was added. The organic materials were extracted with Et₂O. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography (petroleum ether) to give the title compound (166.1 mg, 65%). ¹H-NMR (400 MHz, CDCl₃) δ 0.61 (18H, q, *J* = 8.0 Hz), 1.00 (27H, t, *J* = 8.0 Hz), 1.21 (9H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 4.4, 7.5, 23.2, 27.4, 30.5, 74.5, 81.9, 88.5, 101.7. IR (neat) 2956, 2873, 2195, 2151, 1459, 1090, 1017, 728 cm⁻¹. MS (EI) *m/z* 366 (M⁺-C₈H₂₀Si, 100%), 454 (M⁺-C₄H₈, 50%), 510 (M⁺, 63%). HRMS Calcd for C₃₁H₅₄Si₃, 510.3533; Found, 510.3526. The same reaction at 130 °C gave the product in 49% yield.

5-(1-Adamantyl)-1-triethylsilyl-3,3-bis(triethylsilylethynyl)penta-1,4-diyne 16b. ¹H-NMR (400 MHz, CDCl₃) δ 0.61 (18H, q, *J* = 8.0 Hz), 1.00 (27H, t, *J* = 8.0 Hz), 1.67 (6H, m), 1.87 (6H, m), 1.94 (3H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 4.4, 7.5, 23.2, 28.0, 29.5, 36.5, 42.2, 74.8, 81.8, 88.1, 101.8. IR (KBr) 2956, 2874, 2195, 2162, 1457, 1093, 1017, 728 cm⁻¹. MS (EI) *m/z* 135 (M⁺-C₂₇H₄₅Si₃, 100%), 444 (M⁺-C₈H₂₀Si, 93%), 532 (M⁺-C₄H₈, 71%), 588 (M⁺, 59%). HRMS Calcd for C₃₅H₆₀Si₃: 588.4003. Found: 588.4005.

5-Cyclohexyl-1-triethylsilyl-3,3-bis(triethylsilylethynyl)penta-1,4-diyne 16c. ¹H-NMR (400 MHz, CDCl₃) δ 0.61 (18H, q, *J* = 8.0 Hz), 0.99 (27H, t, *J* = 8.0 Hz), 1.25-1.38 (3H, m), 1.25-1.50 (3H, m), 1.67-1.75 (3H, m), 2.40-2.44 (1H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.5, 22.3, 24.6, 26.1, 28.9, 32.0, 76.0, 81.9, 84.7, 101.7. IR (KBr) 2955, 2876, 2193, 2157, 1459, 1090, 1016, 728 cm⁻¹. MS (EI) *m/z* 115 (M⁺-C₂₇H₄₁Si₂, 100%), 392 (M⁺-C₈H₂₀Si, 98%), 480 (M⁺-C₄H₈, 43%), 536 (M⁺, 59%). HRMS Calcd for C₃₃H₅₆Si₃: 536.3690. Found: 536.3682.

2,2,8,8-Tetramethyl-5,5-bis(triethylsilylethynyl)nona-3,6-diyne 16d. Mp 62.8-64.0 °C (methanol). ¹H-NMR (400 MHz, CDCl₃) δ 0.61 (12H, q, *J* = 8.0 Hz), 1.00 (18H, t, *J* = 8.0 Hz), 1.21 (18H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 4.4, 7.5, 22.4, 27.4, 30.5, 75.0, 81.3, 88.0, 102.6. IR (KBr) 2958, 2875, 2195, 2155, 1458, 1084, 1016, 728 cm⁻¹. MS (EI) *m/z* 395 (M⁺-C₂H₅, 50%), 452 (M⁺, 13%). HRMS Calcd for C₂₉H₄₈Si₂: 452.3295. Found: 452.3309.

1-(1-Adamantyl)-6,6-Dimethyl-3,3-bis(triethylsilyl)hepta-1,4-diyne 16e. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.61 (12H, q, $J = 8.0$ Hz), 1.00 (18H, t, $J = 8.0$ Hz), 1.21 (9H, s), 1.67 (6H, t, $J = 3.2$ Hz), 1.87 (6H, d, $J = 2.4$ Hz), 1.93 (3H, m). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 4.5, 7.6, 22.5, 27.4, 28.0, 29.5, 30.5, 36.5, 42.2, 75.2, 75.4, 81.2, 87.7, 87.9, 102.7. IR (KBr) 2957, 2909, 2870, 2852, 2190, 2171, 1452, 1265, 1084, 1017, 729 cm^{-1} . MS (EI) m/z 135 ($\text{M}^+ - \text{C}_{25}\text{H}_{39}\text{Si}_2$, 100%), 386 ($\text{M}^+ - \text{C}_8\text{H}_{20}\text{Si}$, 35%), 473 ($\text{M}^+ - \text{C}_4\text{H}_9$, 35%), 474 ($\text{M}^+ - \text{C}_4\text{H}_8$, 41%), 530 (M^+ , 22%). HRMS Calcd for $\text{C}_{35}\text{H}_{54}\text{Si}_2$: 530.3764. Found: 530.3776.

1,5-Bis(triethylsilyl)-3,3-bis(triethylsilyl)hepta-1,4-diyne 16f. Under an argon atmosphere, to a mixture of 2,6-di(*t*-butyl)-4-methylpyridine (1 mmol, 205.3 mg) and *t*-butyldiphenylsilanol (0.05 mmol, 12.8 mg) in *o*-dichlorobenzene (0.75 mL) was added a solution of GaCl_3 (1.0 M, 1 mmol) in methylcyclohexane (1 mL) at 0 $^\circ\text{C}$. The mixture was cooled to 0 $^\circ\text{C}$, and solution of 1,5-bis(triethylsilyl)hepta-1,4-diyne (146.3 mg, 0.5 mmol) and **2** (2 mmol, 348.0 mg) in *o*-dichlorobenzene (0.75 mL) was added. Then, the mixture was warmed to 150 $^\circ\text{C}$ during a period of 15 min, and heated at 150 $^\circ\text{C}$ for 7.5 h. Then 2 M HCl was added, and the organic materials were extracted with Et_2O . The organic layer was washed with brine, dried over MgSO_4 , and concentrated. The residue was purified by flash column chromatography (petroleum ether) to give the title compound (161.2 mg, 56%). Mp 98.0-100.2 $^\circ\text{C}$ (methanol). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.61 (24H, q, $J = 7.6$ Hz), 0.99 (36H, t, $J = 7.6$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 4.4, 7.5, 23.9, 82.5, 100.9. IR (KBr) 2956, 2911, 2875, 2201, 2150, 1458, 1413, 1238, 1090, 1018, 739 cm^{-1} . MS (EI) m/z 424 ($\text{M}^+ - \text{C}_8\text{H}_{20}\text{Si}$, 100%), 455 ($\text{M}^+ - \text{C}_6\text{H}_{13}\text{Si}$, 12%), 484 ($\text{M}^+ - \text{C}_4\text{H}_8\text{Si}$, 17%), 512 ($\text{M}^+ - \text{C}_4\text{H}_8$, 100%), 568 (M^+ , 63%). HRMS Calcd for $\text{C}_{33}\text{H}_{60}\text{Si}_4$: 568.3772. Found: 568.3751.

Figure 3. ¹H-NMR spectra of **5** in CDCl₃.

Figure 4. ¹³C-NMR spectra of **5** in CDCl₃.

Figure 5. ^1H -NMR spectra of **8a** in CDCl₃.

Figure 6. ^{13}C -NMR spectra of **8a** in CDCl₃.

Figure 7. ¹H-NMR spectra of **8b** in CDCl₃.

Figure 8. ¹³C-NMR spectra of **8b** in CDCl₃.

Figure 9. ¹H-NMR spectra of **8c** in CDCl₃.

Figure 10. ¹³C-NMR spectra of **8c** in CDCl₃.

Figure 11. ¹H-NMR spectra of **8d** in CDCl₃.

Figure 12. ¹³C-NMR spectra of **8d** in CDCl₃.

Figure 13. ¹H-NMR spectra of **8e** in CDCl₃.

Figure 14. ¹³C-NMR spectra of **8e** in CDCl₃.

Figure 15. ^1H -NMR spectra of **10a** in CDCl_3 .

Figure 16. ^{13}C -NMR spectra of **10a** in CDCl_3 .

Figure 17. ¹H-NMR spectra of **10b** in CDCl₃.

Figure 18. ¹³C-NMR spectra of **10b** in CDCl₃.

Figure 19. ¹H-NMR spectra of **10c** in CDCl₃.

Figure 20. ¹³C-NMR spectra of **10c** in CDCl₃.

Figure 21. ¹H-NMR spectra of **14** in CDCl₃.

Figure 22. ¹³C-NMR spectra of **14** in CDCl₃.

Figure 23. ¹H-NMR spectra of **16a** in CDCl_3 .

Figure 24. ¹³C-NMR spectra of **16a** in CDCl_3 .

Figure 25. ^1H -NMR spectra of **16b** in CDCl_3 .

Figure 26. ^{13}C -NMR spectra of **16b** in CDCl_3 .

Figure 29. ¹H-NMR spectra of **16d** in CDCl₃.

Figure 30. ¹³C-NMR spectra of **16d** in CDCl₃.

Figure 31. ^1H -NMR spectra of **16e** in CDCl_3 .

Figure 32. ^{13}C -NMR spectra of **16e** in CDCl_3 .

Figure 33. $^1\text{H-NMR}$ spectra of **16f** in CDCl_3 .

Figure 34. $^{13}\text{C-NMR}$ spectra of **16f** in CDCl_3 .