Diastereoselective Intramolecular Temporary Silicon-Tethered Rhodium-Catalyzed [4+2+2] Cycloisomerization Reactions: Regiospecific Incorporation of Substituted 1,3-Butadienes

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Representative Experimental Procedures and Supplemental Data

N-((2Z)-4-{{tert-Butyl(dimethyl)silyl}oxy}but-2-en-1-yl)-4-methyl-N-prop-2-yn-1-ylbenzenesulfonamide 6.

A 100 mL, three-necked round-bottom flask equipped with a magnetic stir bar, thermometer, subaseal and glass stopper was charged with triphenylphosphine (2.076 g, 7.9 mmol), (2Z)-4-{{tert-butyl(dimethyl)silyl}oxy}but-2-en-1-ol **5** (1.750 g, 8.7 mmol), 4-methyl-N-prop-2-yn-1-ylbenzenesulfonamide **4** (1.478 g, 7.1 mmol) and tetrahydrofuran (70 mL). The resulting clear, colorless solution was cooled with stirring to *ca.* -5 °C under an atmosphere of nitrogen, and diisopropylazodicarboxylate (DIAD) (1.6 mL, 8.1 mmol) added dropwise over 5 minutes *via* syringe, keeping the temperature below 0 °C. The resultant reaction mixture was stirred for 6 hours, slowly warming to room temperature (t.l.c. control; 20% ethyl acetate/hexanes). The reaction mixture was concentrated *in vacuo* onto silica gel. Purification *via* FCC on silica gel (eluting with 10-20% ethyl acetate/hexane gradient) provided **6** (2.612 g, 94%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.72 (dtt, *J* = 11.0, 4.6, 1.4 Hz, 1H), 5.34 (dtt, *J* = 11.0, 5.5, 1.7 Hz, 1H), 4.20 (dd, *J* = 6.1, 1.5 Hz, 2H), 4.04 (d, *J* = 2.4 Hz, 2H), 3.84 (d, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 1.97 (t, *J* = 2.4 Hz, 1H), 0.83 (s, 9H), 0.00 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 143.64 (e), 136.00 (e), 135.51 (o), 129.56 (o), 127.82 (o), 123.94 (o), 76.79 (e), 73.76 (e), 59.11 (e), 43.32 (e), 35.87 (e), 25.94 (o), 21.59 (o), 18.31 (e), -5.17 (o).

IR (Neat): 3274 (m), 2930 (s), 2857 (s), 2119 (w), 1655 (w), 1599 (m), 1350 (vs), 1256 (s), 1163 (vs), 1092 (s), 838 (s), 778 (s), 661 (s) cm^{-1} .

HRMS (CI, $\text{M}+\text{H}^+$): calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{NSSi}$ 394.1872, found 394.1869.

***N*-[*(2Z)*-4-Hydroxybut-2-en-1-yl]-4-methyl-*N*-prop-2-yn-1-ylbenzene sulfonamide.** A 100 mL one-necked round-bottom flask equipped with a magnetic stir bar and a subaseal was charged with **6** (1.970 g, 5.0 mmol) and THF (50 mL), then cooled with stirring using an external ice bath.

Tetrabutylammonium fluoride (TBAF) (7.0 mL, 7.0 mmol, 1.0M solution in THF) was added dropwise *via* syringe, and the resultant solution stirred overnight at room temperature (t.l.c. control; 50% diethyl ether/hexane). The reaction was quenched by the addition of H_2O (20 mL) and stirred at ambient temperature for *ca.* 10 minutes. The solution was extracted diethyl ether, washed with brine, dried (MgSO_4), filtered and concentrated *in vacuo* to afford a crude oil. Purification *via* FCC on silica gel (30% ethyl acetate/hexane) provided the desired alcohol (1.382 g, 99%) as a white crystalline solid.

^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 5.80 (dt, J = 11.0, 6.7 Hz, 1H), 5.42 (dt, J = 11.0, 7.3 Hz, 1H), 4.15 (d, J = 6.4 Hz, 2H), 4.03 (d, J = 2.4 Hz, 2H), 3.83 (d, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.17 (bs, 1H), 2.01 (t, J = 2.4 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.84 (e), 135.61 (e), 134.46 (o), 129.62 (o), 127.74 (o), 125.27 (o), 76.62 (e), 74.06 (e), 57.95 (e), 43.02 (e), 36.03 (e), 21.58 (o).

IR (Neat): 3526 (m), 3399 (bm), 3290 (s), 3028 (m), 2925 (m), 2873 (m), 2119 (w), 1654 (w), 1598 (m), 1345 (vs), 1161 (vs), 1091 (vs), 895 (s), 768 (m) cm^{-1} .

HRMS (ESI, $\text{M}+\text{Na}^+$): calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{NNaS}$ 302.0827, found 302.0827.

Representative Procedure for the Preparation of the Silicon-Tethered 1,6-Enynes:¹ A 25 mL one-necked round-bottom flask equipped with a magnetic stir bar and a subaseal was charged with (*1E*)-buta-1,3-dien-1-yl(diisopropyl)silane² (4.0 mmol) and dichloromethane (10 mL). *N*-bromosuccinimide (NBS) (3.6 mmol) was then added to the solution in portions (*ca.* 5-10 min.) under a stream of nitrogen, and stirred for a further 10 minutes at room temperature. Silyl bromide **7** was then added to a 50 mL one-necked

round-bottom flask containing the requisite allylic alcohol (2 mmol), (4-*N,N*-dimethylamino)pyridine (DMAP) (0.003 mmol), Et₃N (6 mmol) and dichloromethane (10 mL) *via* teflon® cannula. The resultant solution was stirred overnight at room temperature (t.l.c. control; 30% ethyl acetate/hexane). The reaction mixture was concentrated *in vacuo* onto silica gel. Purification *via* FCC on silica gel (2.5-10% Et₂O/Pentane gradient) provided **1**.

***N*-((*2E*)-4-{[(*1E*)-Buta-1,3-dien-1-yl(diisopropyl)silyl]oxy}but-2-en-1-yl)-4-methyl-*N*-prop-2-yn-1-ylbenzenesulfon-amide.**

¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.63 (dd, *J* = 18.6, 9.8 Hz, 1H), 6.34 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.79 (ddt, *J* = 15.3, 4.5, 0.8 Hz, 1H), 5.70 (d, *J* = 18.6 Hz, 1H), 5.61 (dt, *J* = 15.3, 6.7 Hz, 1H), 5.25 (dd, *J* = 16.8, 0.6 Hz, 1H), 5.16 (d, *J* = 10.1, 0.6 Hz, 1H), 4.19 (dd, *J* = 2.6, 1.1 Hz, 2H), 4.06 (d, *J* = 2.4 Hz, 2H), 3.82 (d, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 1.97 (t, *J* = 2.4 Hz, 1H), 1.01-0.97 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 148.09 (o), 143.61 (e), 139.80 (o), 136.18 (e), 135.37 (o), 129.59 (o), 127.88 (o), 126.95 (o), 123.11 (o), 118.82 (e), 76.67 (e), 73.80 (e), 63.20 (e), 47.98 (e), 35.77 (e), 21.66 (o), 17.52 (o), 17.47 (o), 12.51 (o).

IR (Neat): 3306 (m), 3086 (w), 2944 (s), 2893 (s), 2120 (vw), 1624 (w), 1598 (m), 1575 (m), 1463 (m), 1351 (vs), 1163 (vs), 1127 (s), 1094 (s), 883 (m), 660 (s) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₄H₃₅O₃NSSi 445.2107, found 445.2101.

Representative Procedure for the Intramolecular Temporary Silicon-Tethered Rhodium-Catalyzed [4+2+2] Cycloisomerization: A 10 mL sealed tube was charged with (*E*)- or (*Z*)-**1** (0.25 mmol), Rh(COD)(C₁₀H₈)SbF₆ (0.05 mmol) and acetonitrile (3.0 mL) under a stream of nitrogen *via* syringe. The sealed tube was then heated in a 110 °C oil bath *ca.* 16 hours. Concentration *in vacuo* and subsequent purification by FCC on silica gel (eluting with 5-20% Et₂O/Pentane gradient) provided **2a** and **3a** respectively.

**(4Z,7E)-3,3-Diisopropyl-9-[(4-methylphenyl)sulfonyl]-
3,3a,6,8,9,10,10a,10b-octahydro-1H-[1,2]oxasilolo[3',4':7,8]
cycloocta[1,2-c]pyrrole.**

¹H NMR (400 MHz, C₆D₆): δ 7.70 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 2H), 5.66 (ddd, *J* = 11.0, 7.9, 4.0 Hz, 1H), 5.51 (dt, *J* = 10.6, 2.7 Hz, 1H), 4.95 (t, *J* = 1.5 Hz, 1H), 3.90 (dd, *J* = 8.9, 6.4 Hz, 1H), 3.78 (d, A of AB, *J*_{AB} = 12.8 Hz, 1H), 3.51 (dd, B of ABX, *J*_{AB} = 13.0 Hz, *J*_{BX} = 2.0 Hz, 1H), 3.19 (dd, *J* = 11.5, 9.4 Hz, 1H), 3.10 (dd, A of ABX, *J*_{AB} = 9.8 Hz, *J*_{AX} = 3.1 Hz, 1H), 2.93 (dd, B of ABX, *J*_{AB} = 9.8 Hz, *J*_{BX} = 7.0 Hz, 1H), 2.87-2.84 (m, 1H), 2.78-2.71 (m, 1H), 2.37-2.29 (m, 1H), 2.24 (dd, *J* = 11.0, 6.7 Hz, 1H), 2.10 (tt, *J* = 11.2, 6.4 Hz, 1H), 1.93 (s, 3H), 1.29-1.02 (m, 7H), 0.94 (2t, *J* = 7.2 Hz, 6H), 0.89-0.78 (m, 1H).

¹³C NMR (100 MHz, C₆D₆): δ 143.23 (e), 137.86 (e), 133.22 (e), 129.78 (o), 129.61 (o), 128.56 (o), 121.08 (o), 69.22 (e), 54.30 (e), 52.46 (e), 47.85 (o), 39.52 (o), 28.76 (e), 25.06 (o), 21.18 (o), 18.07 (o), 17.77 (o), 17.61 (o), 12.98 (o), 12.76 (o).

IR (Neat): 3019 (m), 2943 (s), 2865 (s), 1638 (w), 1598 (m), 1463 (s), 1349 (vs), 1167 (vs), 1032 (s), 883 (m), 783 (s), 665 (s), 551 (s) cm⁻¹.

HRMS (ESI, M+Na⁺): calcd for C₂₄H₃₅O₃NNaSSi 468.2005, found 468.2017.

***N*-[(2E)-4-({Diisopropyl[(1E)-3-methylbuta-1,3-dien-1-yl]
silyl}oxy)but-2-en-1-yl]-4-methyl-*N*-prop-2-yn-1-
ylbenzene sulfonamide.**

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 19.2 Hz, 1H), 5.79 (dt, *J* = 15.3, 4.5 Hz, 1H), 5.64 (d, *J* = 19.5 Hz, 1H), 5.66-5.57 (m, 1H), 5.09 (s, 1H), 5.02 (s, 1H), 4.19 (dd, *J* = 4.3, 1.5 Hz, 2H), 4.06 (d, *J* = 2.1 Hz, 2H), 3.82 (d, *J* = 6.7 Hz, 2H), 2.39 (s, 3H), 1.97 (t, *J* = 2.4 Hz, 1H), 1.83 (s, 3H), 1.57-0.87 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 150.01 (o), 143.61 (e), 143.41 (e), 136.21 (e), 135.44 (o), 129.59 (o), 127.90 (o), 123.12 (o), 121.48 (o), 118.30 (e), 76.68 (e), 73.80 (e), 63.20 (e), 47.99 (e), 35.77 (e), 21.66 (o), 17.93 (o), 17.59 (o), 17.54 (o), 12.57 (o).

IR (Neat): 3295 (m), 3080 (w), 2943 (s), 2892 (s), 2120 (w), 1619 (w), 1598 (m), 1575 (m), 1463 (m), 1351 (vs), 1163 (vs), 894 (s), 660 (s) cm⁻¹.

HRMS (EI, M-C₃H₇⁺): calcd for C₂₂H₃₀O₃NSSi 416.1716, found 416.1719.

(4Z,7E)-3,3-Diisopropyl-5-methyl-9-[(4-methylphenyl)sulfonyl]-3a,6,8,9,10,10a,10b-octahydro-1H-[1,2]oxasilolo[3',4':7,8]cycloocta[1,2-c]pyrrole.

¹H NMR (400 MHz, C₆D₆): δ 7.69 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 2H), 5.33 (d, *J* = 11.0 Hz, 1H), 4.99 (t, *J* = 2.1 Hz, 1H), 3.87 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.73 (dd, A of ABX, *J*_{AB} = 12.8 Hz, *J*_{AX} = 1.2 Hz, 1H), 3.58 (d, B of AB, *J*_{AB} = 13.1 Hz, 1H), 3.21 (dd, *J* = 11.2, 9.4 Hz, 1H), 3.01 (d, *J* = 5.5 Hz, 2H), 2.94 (dd, *J* = 19.1, 2.0 Hz, 1H), 2.79 (bs, 1H), 2.20-2.05 (m, 3H), 1.93 (s, 3H), 1.66 (s, 3H), 1.15-1.04 (m, 7H), 0.95 (2t, *J* = 6.7 Hz, 6H), 0.89-0.80 (m, 1H).

¹³C NMR (100 MHz, C₆D₆): δ 143.33 (e), 138.18 (e), 135.24 (e), 133.06 (e), 129.67 (o), 128.58 (o), 123.02 (o), 120.34 (o), 69.33 (e), 54.72 (e), 52.76 (e), 49.49 (o), 39.44 (o), 34.13 (e), 25.76 (o), 25.61 (o), 21.21 (o), 18.09 (o), 17.81 (o), 17.67 (o), 12.97 (o), 12.79 (o).

IR (Neat): 3025 (m), 2943 (s), 2891 (s), 1656 (w), 1598 (m), 1463 (m), 1349 (vs), 1168 (vs), 1036 (s), 883 (m), 780 (s), 666 (s), 550 (s) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₃₇O₃NSSi 459.2263, found 459.2266.

N-((2Z)-4-[(1E)-Buta-1,3-dien-1-yl(diisopropyl)silyl]oxy}but-2-en-1-yl)-4-methyl-N-prop-2-yn-1-ylbenzenesulfonamide.

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.63 (dd, *J* = 18.5, 10.2 Hz, 1H), 6.33 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.78 (dt, *J* = 11.5, 5.8 Hz, 1H), 5.70 (d, *J* = 18.6 Hz, 1H), 5.40-5.34 (m, 1H), 5.23 (d, *J* = 17.1 Hz, 1H), 5.15 (d, *J* = 9.8 Hz, 1H), 4.28 (d, *J* = 6.1 Hz, 2H), 4.05 (d, *J* = 2.1 Hz, 2H), 3.85 (d, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.96 (t, *J* = 2.3 Hz, 1H), 1.02-0.96 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 148.13 (o), 143.67 (e), 139.83 (o), 136.08 (o), 135.55 (o), 129.60 (o), 127.91 (o), 127.03 (o), 124.02 (o), 118.80 (e), 73.80 (e), 59.53 (e), 43.44 (e), 35.94 (e), 21.68 (o), 17.50 (o), 17.46 (o), 12.43 (o).

IR (Neat): 3307 (m), 3029 (w), 2944 (s), 2866 (s), 2119 (vw), 1624 (vw), 1598 (m), 1575 (m), 1350 (vs), 1163 (vs), 1092 (s), 896 (m), 814 (m), 661 (s) cm^{-1} .

HRMS (ESI, $\text{M}+\text{Na}^+$): calcd for $\text{C}_{24}\text{H}_{35}\text{O}_3\text{NNaSSi}$ 468.2005, found 468.2019.

(4Z,7E)-3,3-Diisopropyl-9-[(4-methylphenyl)sulfonyl]-3,3a,6,8,9,10,10a,10b-octahydro-1H-[1,2]oxasilolo[3',4':7,8]cycloocta[1,2-c]pyrrole.

^1H NMR (400 MHz, C_6D_6): δ 7.71 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 7.9 Hz, 2H), 5.52-5.41 (m, 2H), 5.04-5.03 (m, 1H), 4.19 (dd, J = 9.3, 5.7 Hz, 1H), 3.77 (dd, A of ABX, J_{AB} = 13.3 Hz, J_{AX} = 1.6 Hz, 1H), 3.48 (dd, B of ABX, J_{AB} = 13.3 Hz, J_{BX} = 2.0 Hz, 1H), 3.41 (dd, J = 10.7, 9.4 Hz, 1H), 3.17 (dd, A of ABX, J_{AB} = 9.3 Hz, J_{AX} = 3.0 Hz, 1H), 2.98 (bs, 1H), 2.89 (dd, B of ABX, J_{AB} = 9.2 Hz, J_{BX} = 7.6 Hz, 1H), 2.59-2.46 (m, 2H), 2.21 (dd, J = 13.1, 8.4 Hz, 1H), 2.17-2.09 (m, 1H), 1.87 (s, 3H), 1.10-0.97 (m, 14H).

^{13}C NMR (100 MHz, C_6D_6): δ 143.19 (e), 134.34 (e), 133.64 (e), 130.27 (o), 129.61 (o), 128.44 (o), 128.36 (o), 127.13 (o), 122.92 (o), 69.31 (e), 53.87 (e), 51.58 (e), 44.67 (o), 39.60 (o), 29.11 (e), 28.86 (o), 21.13 (o), 17.74 (o), 17.63 (o), 17.61 (o), 17.56 (o), 13.10 (o), 12.66 (o).

IR (Neat): 3007 (m), 2936 (s), 2858 (s), 1638 (w), 1596 (m), 1461 (m), 1344 (vs), 1163 (vs), 1014 (s), 663 (s), 550 (s) cm^{-1} .

HRMS (ESI, $\text{M}+\text{Na}^+$): calcd for $\text{C}_{24}\text{H}_{35}\text{O}_3\text{NNaSSi}$ 468.2005, found 468.2005.

N-[(2Z)-4-({Diisopropyl[(1E)-3-methylbuta-1,3-dien-1-yl]silyl}oxy)but-2-en-1-yl]-4-methyl-N-prop-2-yn-1-ylbenzenesulfonamide.

^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 19.2 Hz, 1H), 5.79 (dt, J = 11.0, 6.0 Hz, 1H), 5.63 (d, J = 19.2 Hz, 1H), 5.39-5.33 (m, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 4.28 (d, J = 5.2 Hz, 2H), 4.05 (d, J = 2.1 Hz, 2H), 3.84 (d, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.95 (t, J = 2.3 Hz, 1H), 1.81 (s, 3H), 1.03-0.96 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 150.03 (o), 143.66 (e), 143.41 (e), 136.05 (e), 135.64 (o), 129.59 (o), 127.90 (o), 123.95 (o), 121.54 (o), 118.29 (e), 76.84 (e), 73.75 (e), 59.50 (e), 43.40 (e), 35.91 (e), 21.68 (o), 17.92 (o), 17.55 (o), 17.50 (o), 12.46 (o).

IR (Neat): 3308 (m), 3080 (w), 3029 (w), 2943 (s), 2892 (m), 2119 (w), 1619 (w), 1598 (m), 1576 (m), 1463 (m), 1351 (vs), 1163 (vs), 1092 (s), 895 (s), 661 (s) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₃₇O₃NSSi 459.2263, found 459.2267.

(4Z,7E)-3,3-Diisopropyl-5-methyl-9-[(4-methylphenyl)sulfonyl]-3,3a,6,8,9,10,10a,10b-octahydro-1H-[1,2]oxasilolo[3',4':7,8]cycloocta[1,2-c]pyrrole.

¹H NMR (400 MHz, C₆D₆): δ 7.71 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 5.24 (d, *J* = 9.7 Hz, 1H), 5.03 (dt, *J* = 6.9, 2.3 Hz, 1H), 4.22 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.48-3.40 (m, 2H), 3.21 (dd, A of ABX, *J*_{AB} = 9.3 Hz, *J*_{AX} = 2.5 Hz, 1H), 2.98 (bs, 1H), 2.87 (dd, B of ABX, *J*_{AB} = 9.3 Hz, *J*_{BX} = 7.6 Hz, 1H), 2.73 (d, A of AB, *J*_{AB} = 20.7 Hz, 1H), 2.31 (dd, B of ABX, *J*_{AB} = 20.0 Hz, *J*_{BX} = 2.6 Hz, 1H), 2.19 (dd, *J* = 13.1, 9.7 Hz, 1H), 2.14-2.03 (m, 1H), 1.88 (s, 3H), 1.60 (s, 3H), 1.13-0.98 (m, 14H).

¹³C NMR (100 MHz, C₆D₆): δ 143.26 (e), 134.91 (e), 134.14 (e), 133.51 (e), 129.63 (o), 128.47 (o), 123.62 (o), 122.26 (o), 68.95 (e), 54.01 (e), 51.81 (e), 45.83 (o), 39.31 (o), 35.11 (e), 29.04 (o), 26.30 (o), 21.16 (o), 17.82 (o), 17.75 (o), 17.65 (o), 13.21 (o), 12.64 (o).

IR (Neat): 3027 (w), 2942 (s), 2864 (s), 1656 (vw), 1598 (m), 1463 (m), 1349 (vs), 1163 (vs), 1003 (s), 788 (s), 668 (s), 580 (s) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₃₇O₃NSSi 459.2263, found 459.2256.

(1E)-Buta-1,3-dien-1-yl(diisopropyl){[(2E)-4-(prop-2-yn-1-yl)oxy]but-2-en-1-yl}oxy)silane.

¹H NMR (400 MHz, CDCl₃): δ 6.65 (dd, *J* = 18.7, 10.1 Hz, 1H), 6.34 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.87-5.76 (m, 2H), 5.72 (d, *J* = 18.7 Hz, 1H), 5.24 (dd, *J* = 17.1, 0.7 Hz, 1H), 5.15 (dd, *J* = 10.0, 0.6 Hz, 1H), 4.22 (d, *J* = 3.1 Hz, 2H), 4.12 (d, *J* = 2.3 Hz, 2H), 4.06 (d, *J* = 4.3 Hz, 2H), 2.40 (t, *J* = 2.4 Hz, 1H), 1.07-0.82 (m, 14H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.05 (o), 139.85 (o), 133.53 (o), 127.07 (o), 125.36 (o), 118.67 (e), 79.86 (e), 74.44 (e), 69.80 (e), 63.40 (e), 57.03 (e), 17.54 (o), 17.49 (o), 12.54 (o).

IR (Neat): 3309 (m), 3086 (w), 3043 (w), 2944 (s), 2866 (s), 2117 (w), 1624 (w), 1575 (m), 1464 (m), 1105 (s), 995 (s), 882 (s), 667 (s) cm^{-1} .

HRMS (ESI, $\text{M}+\text{Na}^+$): calcd for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{NaSi}$ 315.1756, found 315.1760.

(4Z,7E)-3,3-Diisopropyl-1,3,3a,6,8,10,10a,10b-octahydrofuro[3',4':3,4]cycloocta[1,2-c][1,2]oxasilole.

^1H NMR (400 MHz, C_6D_6): δ 5.81-5.75 (m, 1H), 5.66 (dt, J = 10.6, 2.3 Hz, 1H), 5.07 (t, J = 2.0 Hz, 1H), 4.21 (dd, A of ABX, J_{AB} = 12.0 Hz, J_{AX} = 1.3 Hz, 1H), 4.05 (dd, B of ABX, J_{AB} = 12.0 Hz, J_{BX} = 2.0 Hz, 1H), 3.87 (dd, J = 9.2, 6.4 Hz, 1H), 3.57-3.54 (m, 2H), 3.26 (dd, A of ABX, J_{AB} = 11.4 Hz, J_{AX} = 9.2 Hz, 1H), 2.93-2.87 (m, 2H), 2.49-2.44 (m, 1H), 2.40 (dd, B of ABX, J_{AB} = 10.9 Hz, J_{BX} = 6.8 Hz, 1H), 2.30 (tt, J = 11.1, 6.6 Hz, 1H), 1.18-0.89 (m, 14H).

^{13}C NMR (100 MHz, C_6D_6): δ 141.91 (e), 130.27 (o), 127.87 (o), 117.71 (o), 73.48 (e), 72.95 (e), 69.49 (e), 48.94 (o), 40.59 (o), 28.75 (e), 25.25 (o), 18.16 (o), 17.87 (o), 17.62 (o), 12.94 (o), 12.83 (o).

IR (Neat): 3017 (m), 2942 (s), 2865 (s), 1639 (w), 1464 (m), 1028 (s), 882 (s), 784 (s), 681 (m) cm^{-1} .

HRMS (EI, M^+): calcd for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{Si}$ 292.1859, found 292.1857.

Diisopropyl[(1E)-3-methylbuta-1,3-dien-1-yl][(2E)-4-(prop-2-yn-1-yloxy)but-2-en-1-yl]oxy silane.

^1H NMR (400 MHz, CDCl_3): δ 6.75 (d, J = 19.2 Hz, 1H), 5.88-5.76 (m, 2H), 5.66 (d, J = 19.3 Hz, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.23 (d, J = 3.2 Hz, 2H), 4.12 (d, J = 2.1 Hz, 2H), 4.07 (d, J = 4.2 Hz, 2H), 2.40 (t, J = 2.1 Hz, 1H), 1.83 (s, 3H), 1.07-1.00 (m, 14H).

^{13}C NMR (100 MHz, CDCl_3): δ 149.91 (o), 143.46 (e), 133.62 (o), 125.39 (o), 121.63 (o), 118.18 (e), 79.89 (e), 74.44 (e), 69.83 (e), 63.42 (e), 57.05 (e), 17.95 (o), 17.61 (o), 12.61 (o).

IR (Neat): 3309 (m), 3081(w), 2944 (s), 2865 (s), 2117 (w), 1620 (w), 1575 (m), 1464 (s), 1105 (s), 992 (s), 883 (s), 665 (s) cm^{-1} .

HRMS (CI, $\text{M}-\text{C}_3\text{H}_7^+$): calcd for $\text{C}_{15}\text{H}_{23}\text{O}_2\text{Si}$ 263.1467, found 263.1469.

(4Z,7E)-3,3-Diisopropyl-5-methyl-1,3,3a,6,8,10,10a,10b-octahydrofuro[3',4':3,4]cycloocta[1,2-c][1,2]oxasilole.

^1H NMR (400 MHz, C_6D_6): δ 5.46 (d, $J = 10.7$ Hz, 1H), 5.10 (dt, $J = 8.2, 2.4$ Hz, 1H), 4.19 (dq, A of ABX, $J_{AB} = 11.9$ Hz, $J_{AX} = 1.7$ Hz, 1H), 4.07 (dd, B of ABX, $J_{AB} = 11.9$ Hz, $J_{BX} = 2.1$ Hz, 1H), 3.85 (dd, $J = 8.9, 6.1$ Hz, 1H), 3.61 (dd, A of ABX, $J_{AB} = 8.9$ Hz, $J_{AX} = 6.7$ Hz, 1H), 3.52 (dd, B of ABX, $J_{AB} = 9.1$ Hz, $J_{BX} = 4.5$ Hz, 1H), 3.28 (dd, $J = 10.9, 9.4$ Hz, 1H), 3.10 (dd, $J = 18.6, 2.7$ Hz, 1H), 2.86 (bs, 1H), 2.35-2.21 (m, 3H), 1.74 (d, $J = 0.9$ Hz, 3H), 1.22-1.17 (m, 4H), 1.15-1.02 (m, 9H), 0.99-0.90 (m, 1H).

^{13}C NMR (100 MHz, C_6D_6): δ 142.33 (e), 135.32 (e), 123.41 (o), 116.88 (o), 73.71 (e), 73.16 (e), 69.60 (e), 50.20 (o), 40.56 (o), 34.19 (e), 25.86 (o), 25.81 (o), 18.19 (o), 17.93 (o), 17.71 (o), 12.95 (o), 12.89 (o).

IR (Neat): 2942 (s), 2865 (s), 1680 (vw), 1657 (vw), 1463 (m), 1027 (s), 883 (s), 782 (s), 678 (m) cm^{-1} .

HRMS (EI, M^+): calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ 306.2015, found 306.2019.

(1E)-Buta-1,3-dien-1-yl(diisopropyl){[(2Z)-4-(prop-2-yn-1-yloxy)but-2-en-1-yl]oxy}silane.

^1H NMR (400 MHz, CDCl_3): δ 6.66 (dd, $J = 18.6, 10.1$ Hz, 1H), 6.35 (dt, $J = 16.8, 10.1$ Hz, 1H), 5.77-5.56 (m, 2H), 5.55-5.52 (m, 1H), 5.25 (d, $J = 17.1$ Hz, 1H), 5.15 (dd, $J = 10.3, 0.6$ Hz, 1H), 4.30 (dd, $J = 6.1, 0.6$ Hz, 2H), 4.11-4.10 (m, 4H), 2.39 (t, $J = 2.3$ Hz, 1H), 1.02-0.99 (m, 14 H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.14 (o), 139.86 (o), 133.76 (o), 127.06 (o), 125.96 (o), 118.74 (e), 79.77 (e), 74.55 (e), 65.38 (e), 59.95 (e), 57.21 (e), 17.51 (o), 17.47 (o), 12.47 (o).

IR (Neat): 3308(m), 3086 (w), 3027 (w), 2944 (s), 2893 (s), 2117 (w), 1624 (w), 1575 (m), 1464 (m), 1087 (vs), 882 (s), 668 (s) cm^{-1} .

HRMS (CI, $M+H^+$): calcd for $C_{17}H_{29}O_2Si$ 293.1937, found 293.1945.

(4Z,7E)-3,3-Diisopropyl-1,3,3a,6,8,10,10a,10b-octahydrofuro

[3',4':3,4]cycloocta[1,2-c][1,2]oxasilole.

1H NMR (400 MHz, C_6D_6): δ 5.63 (ddd, $J = 10.3, 6.4, 3.6$ Hz, 1H), 5.57 (dt, $J = 9.7, 2.1$ Hz, 1H), 5.17 (dt, $J = 6.9, 2.5$ Hz, 1H), 4.23 (dd, $J = 9.4, 6.0$ Hz, 1H), 4.12 (dt, A of ABX, $J_{AB} = 12.5$ Hz, $J_{AX} = 1.8$ Hz, 1H), 4.02 (dd, B of ABX, $J_{AB} = 12.5$ Hz, $J_{BX} = 2.1$ Hz, 1H), 3.66 (dd, A of ABX, $J_{AB} = 9.1$ Hz, $J_{AX} = 2.6$ Hz, 1H), 3.56 (dd, B of ABX, $J_{AB} = 8.9$ Hz, $J_{BX} = 6.4$ Hz, 1H), 3.46 (dd, $J = 11.2, 9.4$ Hz, 1H), 3.16 (bs, 1H), 2.78-2.62 (m, 2H), 2.38 (dd, $J = 13.1, 9.2$ Hz, 1H), 2.20 (dq, $J = 17.3, 6.2$ Hz, 1H), 1.14-1.00 (m, 14H).

^{13}C NMR (100 MHz, C_6D_6): δ 138.44 (e), 130.54 (o), 127.53 (o), 119.52 (o), 72.87 (e), 72.16 (e), 69.56 (e), 44.70 (o), 40.67 (o), 29.62 (e), 29.11 (o), 17.73 (o), 13.19 (o), 12.70 (o).

IR (Neat): 3012 (m), 2941 (s), 2890 (s), 1638 (w), 1463 (m), 1011 (s), 881 (s), 787 (s), 684 (m) cm^{-1} .

HRMS (CI, $M+H^+$): calcd for $C_{17}H_{29}O_2Si$ 293.1937, found 293.1934.

Diisopropyl[(1E)-3-methylbuta-1,3-dien-1-yl]{[(2Z)-4-(prop-2-yn-1-yloxy)but-2-en-1-yl]oxy}silane.

1H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, $J = 19.2$ Hz, 1H), 5.75 (dt, $J = 11.3, 5.8, 1.4$ Hz, 1H), 5.66 (d, $J = 19.2$ Hz, 1H), 5.55 (dt, $J = 11.3, 6.6, 1.7$ Hz, 1H), 5.09 (s, 1H), 5.03 (s, 1H), 4.30 (dd, $J = 6.0, 0.8$ Hz, 2H), 4.11 (d, $J = 0.6$ Hz, 2H), 4.10 (d, $J = 2.4$ Hz, 2H), 2.38 (t, $J = 2.3$ Hz, 1H), 1.83 (s, 3H), 1.06-0.98 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.04 (o), 143.45 (e), 133.83 (o), 133.83 (o), 125.94 (o), 121.62 (o), 118.22 (e), 79.79 (e), 74.52 (e), 65.41 (e), 59.95 (e), 57.21 (e), 17.93 (o), 17.58 (o), 17.54 (o), 12.54 (o).

IR (Neat): 3309 (m), 3081 (w), 3027 (w), 2944 (s), 2892 (s), 2117 (w), 1619 (w), 1575 (m), 1464 (m), 1087 (vs), 883 (s), 666 (s) cm^{-1} .

HRMS (CI, $M+H^+$): calcd for $C_{18}H_{31}O_2Si$ 307.2093, found 307.2097.

(4Z,7E)-3,3-Diisopropyl-5-methyl-1,3,3a,6,8,10,10a,10b-octahydrofuro[3',4':3,4]cycloocta[1,2-c][1,2]oxasilole.

¹H NMR (400 MHz, C₆D₆): δ 5.38 (dq, *J* = 9.5, 1.4 Hz, 1H), 5.15 (dt, *J* = 6.7, 2.3 Hz, 1H), 4.25 (dd, *J* = 9.4, 6.0 Hz, 1H), 4.13 (dt, A of ABX, *J*_{AB} = 12.5 Hz, *J*_{AX} = 2.0 Hz, 1H), 4.00 (dd, B of ABX, *J*_{AB} = 12.5 Hz, *J*_{BX} = 2.4 Hz, 1H), 3.68 (dd, A of ABX, *J*_{AB} = 8.9 Hz, *J*_{AX} = 2.1 Hz, 1H), 3.55 (dd, B of ABX, *J*_{AB} = 8.9 Hz, *J*_{BX} = 6.4 Hz, 1H), 3.49 (dd, *J* = 11.2, 9.4 Hz, 1H), 3.12 (bs, 1H), 2.91 (d, A of AB, *J*_{AB} = 19.5 Hz, 1H), 2.46 (dd, B of ABX, *J*_{AB} = 19.8 Hz, *J*_{BX} = 2.7 Hz, 1H), 2.34 (dd, *J* = 13.1, 10.1 Hz, 1H), 2.19 (dq, *J* = 17.3, 6.4 Hz, 1H), 1.69 (s, 3H), 1.17-1.03 (m, 14H).
¹³C NMR (100 MHz, C₆D₆): δ 138.38 (e), 135.14 (e), 123.92 (o), 118.79 (o), 72.99 (e), 72.36 (e), 69.25 (e), 45.81 (o), 40.43 (o), 35.54 (e), 29.30 (o), 26.36 (o), 17.91 (o), 13.28 (o), 12.66 (o).

IR (Neat): 2941 (s), 2865 (s), 1657 (w), 1463 (m), 1011 (s), 918 (m), 881 (s), 791 (s), 668 (s) cm⁻¹.

HRMS (CI, M⁺): calcd for C₁₈H₃₀O₂Si 306.2015, found 306.2013.

Diethyl ((2E)-4-(((1E)-buta-1,3-dien-1-yl(diisopropyl)silyl)oxy}but-2-en-1-yl)(prop-2-yn-1-yl)malonate.

¹H NMR (400 MHz, CDCl₃): δ 6.63 (dd, *J* = 18.6, 10.1 Hz, 1H), 6.34 (dt, *J* = 17.1, 10.1 Hz, 1H), 5.70 (d, *J* = 18.6 Hz, 2H), 5.47 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.26 (dd, *J* = 17.1, 0.6 Hz, 1H), 5.17 (dd, *J* = 10.0, 0.7 Hz, 1H), 4.17 (2q, *J* = 7.2 Hz, 4H), 4.16-4.14 (m, 2H), 2.78 (d, *J* = 7.6 Hz, 2H), 2.75 (d, *J* = 2.7 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.22 (2t, *J* = 7.2 Hz, 6H), 1.02-0.97 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 169.82 (e), 148.03 (o), 139.89 (o), 134.64 (o), 127.09 (o), 123.26 (o), 118.65 (e), 79.07 (e), 71.46 (e), 63.72 (e), 61.73 (e), 56.83 (e), 34.83 (e), 22.61 (e), 17.51 (o), 17.45 (o), 14.19 (o), 12.53 (o).

IR (Neat): 3312 (m), 2943 (s), 2894 (s), 2124 (vw), 1738 (vs), 1624 (vw), 1575 (m), 1464 (m), 1204 (s), 1097 (s), 882 (m), 667 (m) cm⁻¹.

HRMS (ESI, M+Na⁺): calcd for C₂₄H₃₈O₅NaSi 457.2386, found 457.2380.

Diethyl (4Z,7Z)-3,3-diisopropyl-1,3,3a,6,8,10,10a,10b-octahydro-9H-cyclopenta[3,4]cycloocta[1,2-c][1,2]oxasilole-9,9-dicarboxylate.

¹H NMR (400 MHz, C₆D₆): δ 5.74 (ddd, *J* = 12.5, 9.9, 4.7 Hz, 1H), 5.61 (dt, *J* = 10.8, 2.1 Hz, 1H), 5.27 (d, *J* = 2.4 Hz, 1H), 4.03-3.87 (m, 5H), 3.32 (dd, A of ABX, *J*_{AB} = 11.5 Hz, *J*_{AX} = 9.4 Hz, 1H), 3.31-3.26 (m, 2H), 2.95-2.91 (m, 2H), 2.67 (ddd, A of ABMX, *J*_{AB} = 12.9 Hz, *J*_{AM} = 8.3 Hz, *J*_{AX} = 1.4 Hz, 1H), 2.45 (dd, B of ABX, *J*_{AB} = 10.8 Hz, *J*_{BX} = 7.1 Hz, 1H), 2.47-2.39 (m, 1H), 2.16 (tt, *J* = 11.3, 6.6 Hz, 1H), 1.93 (dd, B of ABX, *J*_{AB} = 13.0 Hz, *J*_{BX} = 7.5 Hz, 1H), 1.14-0.96 (m, 14H), 0.92 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, C₆D₆): δ 171.48 (e), 171.21 (e), 141.89 (e), 130.51 (o), 127.77 (o), 120.89 (o), 69.41 (e), 61.32 (e), 61.24 (e), 59.52 (e), 52.16 (o), 44.80 (e), 39.40 (e), 38.62 (o), 28.89 (e), 25.63 (o), 18.21 (o), 17.91 (o), 17.63 (o), 14.06 (o), 12.98 (o), 12.83 (o).

IR (Neat): 2942 (s), 2866 (s), 1733 (vs), 1639 (w), 1464 (m), 1191 (s), 1031 (s), 883 (m), 785 (s), 681 (m) cm⁻¹.

HRMS (ESI, M+Na⁺): calcd for C₂₄H₃₈O₅NaSi 457.2386, found 457.2382.

Diethyl [(2E)-4-({diisopropyl[(1E)-3-methylbuta-1,3-dien-1-yl]silyl}oxy)but-2-en-1-yl](prop-2-yn-1-yl)malonate.

¹H NMR (400 MHz, CDCl₃): δ 6.73 (d, *J* = 19.2 Hz, 1H), 5.71 (dt, *J* = 15.2, 4.8 Hz, 1H), 5.63 (d, *J* = 19.3 Hz, 1H), 5.48 (dt, *J* = 15.2, 7.6, 1.6 Hz, 1H), 5.08 (s, 1H), 5.04 (s, 1H), 4.17 (2q, *J* = 7.1 Hz, 4H), 4.16-4.14 (m, 2H), 2.78 (dd, *J* = 7.5, 0.8 Hz, 2H), 2.75 (d, *J* = 2.7 Hz, 2H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.83 (s, 3H), 1.22 (2t, *J* = 7.1 Hz, 6H), 1.08-0.97 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 169.82 (e), 149.91 (o), 143.46 (e), 134.69 (o), 123.29 (o), 121.62 (o), 118.12 (e), 79.09 (e), 71.44 (e), 63.73 (e), 61.71 (e), 56.85 (e), 34.85 (e), 22.63 (e), 17.91 (o), 17.56 (o), 17.49 (o), 14.18 (o), 12.58 (o).

IR (Neat): 3312 (m), 2943 (s), 2893 (m), 2124 (vw), 1738 (vs), 1620 (w), 1575 (m), 1464 (m), 1204 (s), 1097 (s), 882 (m), 666 (m) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₄₀O₅Si 448.2645, found 448.2637.

Diethyl (4Z,7Z)-3,3-diisopropyl-5-methyl-1,3,3a,6,8,10,10a,10b-octahydro-9H-cyclopenta[3,4]cycloocta[1,2-c][1,2]oxasilole-9,9-dicarboxylate.

¹H NMR (400 MHz, C₆D₆): δ 5.44 (d, *J* = 11.0 Hz, 1H), 5.29 (d, *J* = 2.8 Hz, 1H), 4.03-3.86 (m, 5H), 2.64 (ddd, *J* = 12.9, 8.2, 1.6 Hz, 1H), 3.36 (dd, A of ABX, *J*_{AB} = 11.4 Hz, *J*_{AX} = 9.4 Hz, 1H), 3.29 (dq, A of ABX, *J*_{AB} = 15.2 Hz, *J*_{AX} = 2.2 Hz, 1H), 3.19-3.11 (m, 2H), 2.94 (d, B of AB, *J*_{AB} = 15.2 Hz, 1H), 2.39 (dd, B of ABX, *J*_{AB} = 11.0 Hz, *J*_{BX} = 7.1 Hz, 1H), 2.25-2.14 (m, 2H), 1.94 (dd, *J* = 12.9, 7.5 Hz, 1H), 1.73 (s, 3H), 1.17-0.96 (m, 14H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, C₆D₆): δ 171.46 (e), 171.23 (e), 142.27 (e), 135.23 (e), 123.34 (o), 119.99 (o), 69.59 (e), 61.31 (e), 61.19 (e), 59.48 (e), 53.04 (o), 44.89 (e), 39.50 (e), 38.68 (o), 34.42 (e), 26.22 (o), 25.62 (o), 18.25 (o), 17.96 (o), 17.71 (o), 14.08 (o), 12.97 (o), 12.88 (o).

IR (Neat): 2941 (s), 2866 (s), 1733 (vs), 1464 (m), 1245 (s), 1032 (s), 883 (m), 784 (m), 678 (m) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₄₀O₅Si 448.2645, found 448.2637.

Diethyl ((2Z)-4-{[(1E)-buta-1,3-dien-1-yl(diisopropyl)silyl]oxy}but-2-en-1-yl)(prop-2-yn-1-yl)malonate.

¹H NMR (400 MHz, CDCl₃): δ 6.65 (dd, *J* = 18.9, 10.1 Hz, 1H), 6.34 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.74-5.68 (m, 2H), 5.24 (dd, *J* = 16.8, 0.6 Hz, 1H), 5.21-5.17 (m, 1H), 5.14 (dd, *J* = 10.1, 0.6 Hz, 1H), 4.31 (dd, *J* = 6.1, 1.5 Hz, 2H), 4.29-4.11 (m, 4H), 2.77 (d, *J* = 7.9 Hz, 2H), 2.74 (d, *J* = 2.7 Hz, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.22 (2t, *J* = 7.2 Hz, 6H), 1.01-0.98 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 169.79 (e), 148.06 (o), 139.91 (o), 134.99 (o), 127.20 (o), 122.82 (o), 118.62 (e), 79.11 (e), 71.52 (e), 61.84 (e), 59.87 (e), 56.72 (e), 30.31 (e), 22.59 (e), 17.51 (o), 17.47 (o), 14.15 (o), 12.47 (o).

IR (Neat): 3311(m), 3086 (w), 2943 (s), 2866 (s), 2124 (vw), 1738 (vs), 1624 (vw), 1575 (m), 1464 (m), 1207 (s), 1095 (s), 882 (m), 674(m) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₄H₃₈O₅Si 434.2489, found 434.2496.

Diethyl (4Z,7Z)-3,3-diisopropyl-1,3,3a,6,8,10,10a,10b-octahydro-9H-cyclopenta[3,4]cycloocta[1,2-c][1,2] oxasilole-9,9-dicarboxylate.

¹H NMR (400 MHz, C₆D₆): δ 5.59-5.44 (m, 3H), 4.08 (dd, *J* = 9.1, 6.6 Hz, 1H), 4.03-3.86 (m, 4H), 3.50 (dd, *J* = 11.0, 9.2 Hz, 1H), 3.34-3.29 (m, 1H), 3.14 (d, A of AB, *J*_{AB} = 15.6 Hz, 1H), 3.04 (dt, B of ABX, *J*_{AB} = 15.5 Hz, *J*_{BX} = 2.0 Hz, 1H), 2.94 (dt, *J* = 17.4, 6.1 Hz, 1H), 2.78 (tt, *J* = 11.8, 5.9 Hz, 1H), 2.67 (dd, A of ABX, *J*_{AB} = 12.7 Hz, *J*_{AX} = 8.7 Hz, 1H), 2.47-2.37 (m, 2H), 2.19 (dd, B of ABX, *J*_{AB} = 13.0 Hz, *J*_{BX} = 10.5 Hz, 1H), 1.10 (2t, *J* = 6.9 Hz, 6H), 1.06-0.97 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, C₆D₆): δ 171.68 (e), 171.53 (e), 139.37 (e), 130.58 (o), 126.16 (o), 122.71 (o), 70.63 (e), 61.34 (e), 58.40 (e), 44.34 (o), 44.16 (e), 40.85 (o), 36.26 (e), 29.49 (o), 27.57 (e), 17.60 (o), 17.48 (o), 17.45 (o), 14.06 (o), 13.05 (o), 12.84 (o).

IR (Neat): 2942 (s), 2892 (s), 1733 (vs), 1640 (w), 1464 (s), 1245 (s), 1039 (s), 881 (m), 784 (m), 670 (m) cm⁻¹.

HRMS (ESI, M+Na⁺): calcd for C₂₄H₃₈O₅NaSi 457.2386, found 457.2386.

Diethyl [(2Z)-4-({diisopropyl[(1E)-3-methylbuta-1,3-dien-1-yl]silyl}oxy)but-2-en-1-yl](prop-2-yn-1-yl) malonate.

¹H NMR (400 MHz, CDCl₃): δ 6.74 (d, *J* = 19.2 Hz, 1H), 5.72 (dt, *J* = 11.1, 5.8 Hz, 1H), 5.65 (d, *J* = 19.3 Hz, 1H), 5.22-5.15 (m, 1H), 5.07 (s, 1H), 5.02 (s, 1H), 4.31 (dd, *J* = 6.0, 1.2 Hz, 2H), 4.23-4.10 (m, 4H), 2.77 (d, *J* = 7.8 Hz, 2H), 2.73 (d, *J* = 2.7 Hz, 2H), 1.95 (t, *J* = 2.7 Hz, 1H), 1.83 (s, 3H), 1.21 (2t, *J* = 7.1 Hz, 6H), 1.08-0.97 (m, 14H).

¹³C NMR (100 MHz, CDCl₃): δ 169.78 (e), 149.95 (o), 143.47 (e), 135.05 (o), 122.78 (o), 121.72 (o), 118.11 (e), 79.11 (e), 71.49 (e), 61.83 (e), 59.83 (e), 56.72 (e), 30.31 (e), 22.59 (e), 17.91 (o), 17.56 (o), 14.13 (o), 12.52 (o).

IR (Neat): 3312 (m), 2943 (s), 2894 (s), 2124 (vw), 1755 (vs), 1738 (vs), 1620 (w), 1575 (m), 1464 (s), 1187 (s), 1095 (s), 883 (s), 667 (s) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₄₀O₅Si 448.2645, found 448.2640.

Diethyl (4Z,7Z)-3,3-diisopropyl-5-methyl-1,3,3a,6,8,10,10a,10b-octahydro-9H-cyclopenta[3,4]cycloocta[1,2-c][1,2]oxasilole-9,9-dicarboxylate.

¹H NMR (400 MHz, C₆D₆): δ 5.44 (bs, 1H), 5.31 (d, *J* = 8.2 Hz, 1H), 4.12 (dd, *J* = 8.7, 6.3 Hz, 1H), 4.04-3.85 (m, 4H), 3.50 (dd, *J* = 11.0, 8.9 Hz, 1H), 3.40-3.39 (m, 1H), 3.10 (d, A of AB, *J*_{AB} = 15.9 Hz, 1H), 3.06 (d, A of AB, *J*_{AB} = 17.4 Hz, 1H), 2.79 (dd, A of ABX, *J*_{AB} = 18.3 Hz, *J*_{AX} = 6.7 Hz, 1H), 2.73 (dd, A of ABX, *J*_{AB} = 13.3 Hz, *J*_{AX} = 9.1 Hz, 1H), 2.62 (ddd, *J* = 18.0, 12.4, 6.0 Hz, 2H), 2.37 (dd, B of ABX, *J*_{AB} = 12.8 Hz, *J*_{BX} = 8.2 Hz, 1H), 2.12 (dd, B of ABX, *J*_{AB} = 13.1 Hz, *J*_{BX} = 10.1 Hz, 1H), 1.65 (s, 3H), 1.13-0.99 (m, 14H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, C₆D₆): δ 171.40 (e), 171.30 (e), 139.11 (e), 133.88 (e), 123.47 (o), 121.73 (o), 69.98 (e), 61.14 (e), 61.11 (e), 58.74 (e), 44.95 (o), 44.67 (e), 39.92 (o), 36.28 (e), 33.78 (e), 29.46 (o), 26.45 (o), 17.55 (o), 17.48 (o), 17.43 (o), 13.88 (o), 13.86 (o), 13.03 (o), 12.62 (o).

IR (Neat): 2941 (s), 2865 (s), 1733 (vs), 1464 (m), 1244 (s), 1069 (m), 881 (m), 782 (m), 666 (w) cm⁻¹.

HRMS (EI, M⁺): calcd for C₂₅H₄₀O₅Si 448.2645, found 448.2641.

References:

- (1) Modification of procedure reported by Petit, M.; Chouraqui, G.; Aubert, C.; Malacria, M. *Org. Lett.* **2003**, 5, 2037.
- (2) Denmark, S. E.; Cottell, J. J. *J. Org. Chem.* **2001**, 66, 4276.

Indiana University Molecular Structure Center

Report 04055: C₂₅H₃₇NO₃SSi 2a

John C. Huffman

March 7, 2004

Empirical Formula: C₂₅H₃₇NO₃SSi
Color of Crystal: colorless
Crystal System: Triclinic
Space Group: P-1
Cell Dimensions (at 112(2) K; 929 data)
a = 8.5445(8)
b = 22.090(2)
c = 26.409(3)
alpha = 85.199(3)
beta = 84.017(3)
gamma = 89.845(3)

Z (Molecules/cell): 8
Volume: 4940.1(8)
Calculated Density: 1.236
Molecular Weight: 459.71
Linear Absorption Coefficient: 0.206
Final residuals are:
R(F) (observed data) = 0.0511
Rw(F2) (refinement data) = 0.1074

The sample was submitted by Erich W. Baum from the research group of Prof. Andrew Evans, Department of Chemistry, Indiana University. The crystals occur as transparent colorless rectangular plates that tend to grow in clumps or affixed to the wall of the sample vial. A fragment of one of the plates of approximate dimensions 0.30 × 0.25 × 0.20 mm onto the tip of a 0.1 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 112(2) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 30 frames. The data collection was carried out using graphite monochromated Mo K α radiation with a frame time of 15 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Two sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at -43° in 2 θ . Final cell constants were calculated from the xyz centroids of 929 strong reflections from the actual data collection after integration (SAINT).

Complete data are available at

<http://bl-chem-iumsc110.chem.indiana.edu/recipnet/showsample.jsp?sampleId=59057753&sampleHistoryId=-1>

Indiana University Molecular Structure Center

Report 04052: $\text{C}_{25}\text{H}_{37}\text{NO}_3\text{SSi}$ 2c

John C. Huffman

February 26, 2004

Empirical Formula: $\text{C}_{25}\text{H}_{37}\text{NO}_3\text{SSi}$
Color of Crystal: colorless
Crystal System: Monoclinic
Space Group: $P2(1)/c$
Cell Dimensions (at 115(2) K; 999 data)
a = 19.1175(17)
b = 8.4638(7)
c = 17.2327(15)
alpha = 90
beta = 116.296(2)
gamma = 90

Z (Molecules/cell): 4
Volume: 2499.8(4)
Calculated Density: 1.221
Molecular Weight: 459.71
Linear Absorption Coefficient: 0.203
Final residuals are:
R(F) (observed data) = 0.0425
Rw(F2) (refinement data) = 0.0860

The sample was submitted by Erich W. Baum from the research group of Prof. Andrew Evans, Department of Chemistry, Indiana University. The crystals occur as transparent colorless rectangular plates that tend to grow in clumps or affixed to the wall of the sample vial. A fragment of one of the plates of approximate dimensions $0.30 \times 0.20 \times 0.09$ mm onto the tip of a 0.1 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 115(2) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20 frames. The data collection was carried out using graphite monochromated Mo $K\alpha$ radiation with a frame time of 3 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Two sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at -43° in 2θ . Final cell constants were calculated from the xyz centroids of 999 strong reflections from the actual data collection after integration (SAINT).

Complete data are available at

<http://bl-chem-iumsc110.chem.indiana.edu/recipnet/jamm.jsp?sampleId=59057535&sampleHistoryId=-1>