Supporting Materials

Regioselectivity Control in a Ruthenium-catalyzed Cycloisomerization of Diyne-ols.

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General experimental: All reactions were performed under an argon atmosphere unless otherwise noted. Dry acetone was distilled over drierite. Dry tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl or purified on an alumina column purification system. All other solvents were purified on an alumina column purification system. Catalysts 3.1 was prepared according to literature. Flash chromatography was performed with EM Science silica gel. Proton and broad band decoupled $^{13}$C nuclear magnetic resonance data were acquired on Varian GEM300, Inova Unity 400, or Inova Unity 500 spectrometer as indicated. Chemical shifts are reported in ppm relative to TMS, CDCl$_3$, or C$_6$D$_6$. Infrared (IR) data were recorded on sodium chloride plates on a Perkin Elmer Paragon 500 FT-IR spectrometer. The water used in all reactions was deionized water. All other chemicals were obtained from Aldrich, Acros, or GFS Chemical Companies and distilled prior to use.

Cyclization Procedure A:
To a solution of diyne-ol (0.2 mmol) in distilled acetone (2 mL) was added water (1.5 mmol, 27 µL) and [CpRu(CH$_3$CN)$_3$]PF$_6$ (I) (0.02 mmol, 8.5 mg). The yellow/orange solution was then sealed and heated in a 60 °C oil bath until consumption of starting material was complete as judged by TLC (generally 1-8 hr). The crude reaction mixture was then cooled to room temperature, diluted with petroleum ether (10 mL) and filtered through a plug of celite using ether as the eluent to remove most of the ruthenium components. The solvent was removed in vacuo to yield the crude product, which was purified using silica gel chromatography.

Cyclization Procedure A':
To a solution of diyne-ol (0.2 mmol) in distilled acetone (2 mL) was added water (1.5 mmol, 27 µL) and [CpRu(CH$_3$CN)$_3$]PF$_6$ (I) (0.02 mmol, 8.5 mg). The yellow/orange solution was then sealed and heated in a 50 °C oil bath until consumption of starting material was complete as judged by TLC (2hr). The crude reaction mixture was then cooled to room temperature, diluted with petroleum ether (10 mL) and filtered through a plug of celite using ether as the eluent to remove most of the ruthenium components. The solvent was removed in vacuo to yield the crude product, which was purified using silica gel chromatography.

Cyclization Procedure B:
To a solution of diyne-ol (0.2 mmol) in distilled acetone (1.2 mL) was added water (0.8 mL) and [CpRu(CH$_3$CN)$_3$]PF$_6$ (I) (0.02 mmol, 8.5 mg). The yellow/orange solution was then sealed and heated in a 60 °C oil bath until consumption of starting material was complete as judged by TLC (generally 1-8 hr). The crude reaction mixture was then cooled to room temperature, diluted with petroleum ether (10 mL) and filtered through a plug of celite using ether as the eluent to remove most of the ruthenium components. The solvent was removed in vacuo to yield the crude product, which was purified using silica gel chromatography.

Cyclization Procedure B':

To a solution of diyne-ol (0.2 mmol) in distilled acetone (1.2 mL) was added water (0.8 mL) and [CpRu(CH$_3$CN)$_3$]PF$_6$ (1) (0.03 mmol, 13 mg). The yellow/orange solution was then sealed and heated in a 60 °C oil bath until consumption of starting material was complete as judged by TLC (generally 1-8 hr). The crude reaction mixture was then cooled to room temperature, diluted with petroleum ether (10 mL) and filtered through a plug of celite using ether as the eluent to remove most of the ruthenium components. The solvent was removed in vacuo to yield the crude product, which was purified using silica gel chromatography.

Cyclization Procedure B'':
To a solution of diyne-ol (0.2 mmol) in distilled acetone (2 mL) was added Water (1.5 mmol, 27 µL) and [CpRu(CH$_3$CN)$_3$]PF$_6$ (1) (0.02 mmol, 8.5 mg). The yellow/orange solution was then stirred at room temperature until consumption of starting material was complete as judged by TLC (15 min). The crude reaction mixture was diluted with petroleum ether (10 mL) and filtered through a plug of celite using ether as the eluent to remove most of the ruthenium components. The solvent was removed in vacuo to yield the crude product, which was purified using silica gel chromatography.

To a solution of dimethyl(bis)propargyl malonate (0.5 g, 2.4 mmol) in THF (20 mL) cooled to -78 °C was added n-BuLi (1.5 mL of 1.6 M solution in hexanes, 2.4 mmol). After stirring for 1 hr, TMS-Cl (0.31 mL, 2.4 mmol) was added and stirred for 2 hr. A second aliquot of n-BuLi (1.5 mL of 1.6 M solution in hexanes, 2.4 mmol) was added and stirred 1 hr. Freshly distilled acetone (0.36 mL, 4.8 mmol) was then added and the reaction was stirred 2 hr more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO$_4$, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 275 mg of 2 (34%).

Rf (40% Et$_2$O/PE): 0.3. IR (neat): 3495, 2980, 2957, 2931, 2361, 1745, 1437, 1364, 1324, 1294, 1251, 1211, 1029, 957, 846, 761, 699 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$): 3.72 (s, 6H), 2.92 (s, 2H), 2.91 (s, 2H), 2.27 (bs, 1H), 1.43 (s, 6H), 0.1 (s,9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 169.3, 100.8, 88.6, 88.5, 76.5, 65.0, 57.2, 53.0, 31.5, 24.1, 22.9, -0.04. Anal Cal’d for C$_{17}$H$_{26}$O$_5$Si: C, 60.32; H, 7.74. Found: C, 60.50; H, 7.90.

Procedure: B with 5% 1 for 20 hr.

Rf (50% Et$_2$O/PE): 0.5. IR (neat): 2956, 1739, 1434, 1378, 1355, 1249, 1021, 1161, 1076, 901, 840, 754, 696 cm$^{-1}$. $^1$H NMR (400 MHz, C$_6$D$_6$): 4.81 (m, 1H), 3.28 (s, 6H),
Supporting Materials

3.27 (s, 2H), 3.10, (d, J = 2 Hz, 2H), 1.27 (s, 6H), 0.22 (s, 9H). $^{13}$C NMR (100 MHz, C$_6$D$_6$): 171.5, 151.8, 133.9, 123.5, 116.7, 73.9, 60.3, 52.3, 37.9, 36.6, 27.5, -1.8. Anal Cal'c for C$_{17}$H$_{26}$O$_5$Si: C, 60.32; H, 7.74. Found: C, 60.32; H, 7.87.

**Procedure:** A for 2hr.

Rf (50% Et$_2$O/PE): 0.5. IR (neat): 2955, 2895, 2840, 1737, 1608, 1434, 1382, 1367, 1321, 1249, 1195, 1171, 1074, 931, 867, 840, 754 cm$^{-1}$. $^1$H NMR (300 MHz, C$_6$D$_6$): 171.6, 150.9, 140.5, 127.7, 120.6, 72.9, 65.1, 52.7, 36.5, 34.4, 26.4, -2.0. HRMS (EI, [M]$^+$) Cal’c for C$_{17}$H$_{26}$O$_5$Si: 338.1550. Found: 338.1547 (17.4), 279.1402 (92.1), 175.07 (22.1).

To a solution of dimethyl(bis)propargyl malonate (0.5 g, 2.4 mmol) in THF (20 mL) cooled to -78 °C was added LHMDS (2.4 mL of 1.0 M solution in THF, 2.4 mmol). After stirring for 30 minutes, Me$_2$Si(OiPr)Cl (0.33 g, 2.4 mmol) was added and stirred for 1 hr. A second aliquot of LHMDS (2.8 mL of 1.0 M solution in THF, 2.8 mmol) was added and stirred 15 minutes. Freshly distilled acetone (0.36 mL, 4.8 mmol) was then added and the reaction was stirred 1 hr more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO$_4$, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 490 mg of 6 (56%).

Rf (40% Et$_2$O/PE): 0.35. IR (neat): 3490, 2971, 2930, 2179, 1745, 1437, 1368, 1324, 1293, 1257, 1211, 1122, 1081, 1029, 952, 885, 832, 793, 667 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): 4.15 (sep, J = 6 Hz, 1H), 3.37 (s, 6H), 3.30 (s, 2H), 3.28 (s, 2H), 2.57 (bs, 1H), 1.39 (s, 6H), 1.19 (d, J = 6 Hz, 6H), 0.23 (s, 6H). $^{13}$C NMR (100 MHz, C$_6$D$_6$): 169.3, 101.2, 89.9, 87.6, 76.1, 66.2, 64.7, 57.4, 52.7, 31.6, 25.7, 24.5, 23.4, 0.9. HRMS (EI, [M-OH]$^+$) Cal’c for C$_{19}$H$_{29}$O$_5$Si: 365.1784. Found: 365.1799 (0.6), 339.1254 (35.1), 307.0992 (49.1).

Procedure: A' for 2hr (some amount of dimer also formed).

Rf (20% Et$_2$O/PE): 0.40. IR (neat): 3530, 2956, 2853, 1736, 1611, 1435, 1382, 1367, 1321, 1252, 1196, 1171, 1148, 1079, 932, 865, 823, 781 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$): 5.52 (bs, 1H), 3.74 (s, 6H), 3.21 (s, 1H), 2.39 (s, 2H), 1.90 (bs, 1H), 1.18 (s, 6H), 1.09 (s, 9H).
To a solution of dimethyl(bis)propargyl malonate (1.0 g, 4.8 mmol) in THF (35 mL) cooled to -78 °C was added LHMDS (4.8 mL of 1.0 M solution in THF, 4.8 mmol). After stirring for 30 minutes, BnMe₂SiCl (0.87 mL, 4.8 mmol) was added and stirred for 1 hr. A second aliquot of LHMDS (6.2 mL of 1.0 M solution in THF, 6.2 mmol) was added and stirred 30 minutes. Freshly distilled acetone (0.36 mL, 4.8 mmol) was then added and the reaction was stirred 1 hr more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 1.41 g of 8 (71%).

Rf (40% Et₂O/PE): 0.2. IR (neat): 3495, 3025, 2958, 2898, 2180, 1744, 1600, 1494, 1452, 1436, 1364, 1324, 1294, 1249, 1209, 1028, 839, 764, 700 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): 7.20 (m, 2H), 7.05 (m, 3H), 3.71 (s, 6H), 2.97 (s, 2H), 2.92 (s, 2H), 2.37 (s, 1H), 2.15 (s, 2H), 1.46 (s, 6H). ¹³C NMR (75MHz, CDCl₃): 169.2, 138.8, 128.3, 128.2, 124.3, 102.1, 88.7, 86.9, 76.4, 64.9, 57.0, 52.9, 31.5, 26.1, 24.1, 22.8, -2.1. HRMS (EI, [M]+) Cal’c for C₂₂H₂₅O₅Si: 399.1628. Found: 399.1635 (1.7), 323.1300 (12.3), 263.1099 (90.7). LRMS (Cl, [M + H]+) Cal’c for C₂₃H₃₁O₅Si: 415.2, Found: 415.3, 432.3 [M + NH₃]+.

Procedure: A for 2 hr.

Rf (40% Et₂O/PE): 0.4. mp = 59-61 °C. IR (neat): 3067, 3021, 2954, 2899, 1737, 1600, 1494, 1434, 1367, 1321, 1250, 1148, 1075, 823, 649 cm⁻¹. ¹H NMR (300 MHz, C₆D₆): 7.13 (m, 3H), 7.01 (m, 2H), 5.74 (s, 1H), 3.71 (s, 6H), 3.40 (s, 2H), 3.33 (s, 6H), 2.22 (s, 2H), 2.13 (s, 2H), 1.08 (s, 6H). ¹³C NMR (75MHz, C₆D₆): 171.0, 149.4, 140.0, 139.4, 128.9, 128.4, 128.2, 124.1, 121.8, 72.8, 65.3, 52.0, 36.3, 34.7, 26.2, 24.3, -4.2. HRMS (EI, [M]+) Cal’c for C₂₃H₃₀O₅Si: 414.1863. Found: 414.1863 (33.3), 355.1717 (100).
the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (50% ether/pet. ether) to yield 650 mg of 10 (67%).

Rf (30% Et₂O/PE): 0.15. IR (neat): 3500, 3070, 2958, 2844, 2246, 2180, 1731, 1435, 1265, 1324, 1294, 1208, 1116, 1026, 952, 818, 782, 733, 703, 665 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.57 (m, 2H), 7.36 (m, 3H), 3.72 (s, 6H), 3.02 (s, 2H), 2.98 (s, 2H), 2.40 (bs 1H), 1.46 (s, 6H), 0.37 (s, 6H). ¹³C NMR (100MHz, CDCl₃): 169.4, 137.1, 133.8, 129.6, 128.1, 102.9, 88.9, 86.7, 76.6, 65.2, 57.3, 31.7, 24.4, 23.2, -0.6. HRMS (EI, [M]+) Cal’c for C₂₂H₂₈O₅Si: 400.1706. Found: 400.1709 (0.1), 285.1478 (3.4), 135.0672 (100).

Procedure: A for 2.5 hr

Rf (30% Et₂O/PE): 0.4. IR (neat): 3070, 2973, 2954, 2901, 1737, 1607, 1430, 1382, 1367, 1321, 1250, 1195, 1171, 1148, 1111, 1076, 865, 812, 780, 701 cm⁻¹. ¹H NMR (400 MHz, C₆D₆): 7.58 (m, 2H), 7.15 (m, 3H), 5.70 (bs, 1H), 3.34 (s, 2H), 3.26 (s, 6H), 2.05 (d, J = 1.2 Hz, 2H), 1.02 (s, 6H), 0.39 (s, 6H). ¹³C NMR (100 MHz, C₆D₆): 171.2, 149.4, 140.4, 137.3, 134.3, 129.7, 129.4, 128.0, 122.3, 73.2, 65.5, 52.2, 36.5, 35.1, 26.4, -3.2. HRMS (EI, [M]+) Cal’c for C₂₂H₂₈O₃Si: 400.1706. Found: 400.1713 (29.7), 342.1613 (23.1), 341.1568 (85.7), 135.0637 (100).

To a solution of dimethyl(bis)propargyl malonate (0.5 g, 2.4 mmol) in THF (20 mL) cooled to -78 °C was added LHMDS (2.4 mL of 1.0 M solution in THF, 2.4 mmol). After stirring for 30 minutes, TES-Cl (0.36 g, 2.4 mmol) was added and stirred for 1 hr. A second aliquot of LHMDS (2.8 mL of 1.0 M solution in THF, 2.8 mmol) was added and stirred 15 minutes. Freshly distilled acetone (0.36 mL, 4.8 mmol) was then added and the reaction was stirred 1 hr more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 627 mg of 12 (66%).

Rf (40% Et₂O/PE): 0.4. IR (neat): 3494, 2956, 2178, 1745, 1437, 1324, 1294, 1211, 1028, 952, 850, 727 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 3.72 (s, 6H), 2.96 (s, 2H), 2.94 (s, 2H), 1.44 (s, 6H), 0.94 (t, J = 8 Hz, 9H), 0.55 (q, J = 8 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): 169.3, 101.8, 88.6, 85.7, 76.7, 65.1, 57.1, 53.0, 31.6, 24.2, 22.9, 7.5, 4.4. Anal Cal’c for C₂₂H₃₀O₃Si: C, 64.70; H, 8.88. Found: C, 63.93; H, 8.31.
Supporting Materials

Procedure: A for 2 hr.

Rf (40% Et₂O/PE): 0.55. IR (neat): 2954, 2875, 1738, 1434, 1366, 1251, 1073, 1004, 721 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 5.42 (s, 1H), 3.71 (s, 6H), 3.12 (s, 2H), 2.34 (s, 2H), 1.14 (s, 6H), 0.93 (t, J = 8Hz, 9H), 0.66 (q, J = 8Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): 171.9, 150.1, 140.9, 128.6, 73.2, 65.2, 53.0, 36.8, 34.9, 26.8, 7.6, 2.9. HRMS Cal’c for C₂₀H₃₂O₅Si: 380.2019. Found: 380.2017 (72.9), 321.0914 (97.1), 87.0631 (100).

To a solution of 7 or 9 (0.15 mmol) in THF (1.6 mL) cooled to 0 °C was added TBAF (0.3 mL of a 1M solution in THF, 0.3 mmol). The solution was then warmed to room temperature, and stirred until starting material was consumed (30 minutes). The crude reaction was filtered through a plug of silica with ether, and the solvent was removed in vacuo. The crude product was then purified on silica (30% ether/pet. ether) to yield 14 (39 mg, 99%).

Rf (20% Et₂O/PE): IR (neat): 3072, 2968, 2845, 1732, 1658, 1620, 1434, 1369, 1332, 1248, 1168, 1124, 1091, 1057, 965, 811, 702 cm⁻¹. ¹H NMR (500 MHz, C₆D₆): 6.06 (bs, 1H), 5.65 (bs, 1H), 3.29 (s, 3H), 3.28 (s, 3H), 3.25 (d, J = 2 Hz, 2H), 2.02 (s, 2H), 1.02 (s, 6H). ¹³C NMR (100 MHz, C₆D₆): 171.2, 140.2, 135.9, 121.2, 118.7, 74.4, 65.7, 52.2, 36.3, 33.2, 26.2. Compound 14 is highly unstable, and satisfactory elemental analysis or HRMS with EI ionization were unable to be obtained. Additional characterization was obtained upon conversion to the known compound 3-formyl-4-(2-methyl-propenyl)-cyclopent-3-ene-1,1-dicarboxylic acid dimethyl ester (40).²

To a solution of 7 (20 mg, 0.058 mmol) in 50/50 THF/MeOH (1 mL total) was added KHCO₃ (12 mg, 0.117 mmol) and H₂O₂ (20 µL of a 30% solution in water, 0.176 mmol). The reaction was then heated to 65 °C for 1 hr, cooled to room temperature, extracted with ether, dried over MgSO₄, and the solvent was removed in vacuo. The crude product was purified on silica (80% ether/pet. ether) to yield 15 (16 mg, 98%).

Rf (80% Et₂O/PE): 0.2. IR (neat): 2976, 2932, 2849, 1732, 1709, 1433, 1386, 1255, 1193, 1152, 1112, 1070, 1021 cm⁻¹. ¹H NMR (400 MHz, C₆D₆): 3.50 (app. p, J = 2Hz, 2H), 3.22 (s, 6H), 2.93 (app. t, J = 1.6 Hz, 2H), 1.44 (s, 2H), 0.96 (s, 6H). ¹³C NMR (100 MHz, C₆D₆): 171.5, 161.6, 152.4, 126.1, 79.8, 57.7, 52.4, 43.9, 38.9, 35.9, 27.6. HRMS (EI, [M⁺]) Cal’c for C₁₄H₁₈O₅: 282.1103. Found: 282.1105 (11.9), 223.0944 (61.0), 205.0872 (76.0), 164.0485 (100).
To a solution of bispropargyltosylamine (0.505 g, 2.04 mmol) in THF (8 mL) cooled to -78 °C was added LHMDS (2.9 mL of 0.7 M solution in THF, 2.04 mmol). After stirring for 20 minutes, TMS-Cl (0.26 mL, 2.04 mmol) was added and stirred for 15 minutes. A second aliquot of LHMDS (4.37 mL of 0.7 M solution in THF, 3.06 mmol) was added and stirred 15 minutes. Freshly distilled acetone (0.3 mL, 4.08 mmol) was then added and the reaction was stirred 15 minutes more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 560 mg of 16 (73%).

Rf (50% Et₂O/PE): 0.35. mp = 78-80 °C. IR (neat): 3524, 2980, 2179, 1654, 1598, 1495, 1437, 1401, 1352, 1250, 1163, 1095, 1002, 952, 903, 843, 756, 665 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.70 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 4.14 (s, 2H), 4.13 (s, 2H), 2.40 (s, 3H), 1.52 (bs, 1H), 1.35 (s, 6H), 0.04 (s, 9H).

To a solution of 1,6-heptadiyne (0.530 g, 5.75 mmol) in THF (40 mL) cooled to -78 °C was added LHMDS (11.5 mL of 0.5 M solution in THF, 5.75 mmol). After stirring for 30 minutes, TMS-Cl (0.73 mL, 5.75 mmol) was added and stirred for 30 minutes. A second aliquot of LHMDS (13.8 mL of 0.5 M solution in THF, 6.90 mmol) was added and stirred 30 minutes. Freshly distilled acetone (0.63 mL, 8.63 mmol) was then added and the reaction was stirred 30 minutes more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 60 mg of 17 (95%).
720 mg of 16 (60%). The product still contained some minor impurities which could not be totally eliminated upon distillation, and was used as is after distillation.

Rf (25% Et2O/PE): 0.3. IR (neat): 3374, 2958, 2237, 2175, 1454, 1362, 1249, 1165, 1044, 949, 843, 760, 698, 638 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): 2.27 (q, J = 7.8 Hz, 4H), 2.1 (bs, 1H), 1.66 (m, 2H), 1.45 (s, 6H), 0.11 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 106.4, 85.8, 85.1, 81.5, 65.3, 31.8, 28.8, 19.1, 17.8, 0.2.

Anal Cal’d for C₁₄H₂₂O₃Si: C, 70.21; H, 9.97. Found: C, 70.15; H, 10.13.

Procedure: A for 15 hr.

Rf (20% Et₂O/PE): 0.9. IR (neat): 2926, 2852, 1656, 1446, 1366, 1246, 1066, 836, cm⁻¹. ¹H NMR (400 MHz, C₆D₆): 5.33 (bs, 1H), 2.52 (m, 2H), 2.38 (m, 2H), 2.20 (q, J = 1.6 Hz, 2H), 1.17 (s, 6H), 0.26 (s, 9H). ¹³C NMR (100 MHz, C₆D₆): 147.2, 137.1, 132.9, 125.4, 72.2, 37.3, 31.7, 26.7, 25.9, -1.5. HRMS (EI, [M-H]+) Cal’d for C₁₃H₂₂O₃Si: 222.1440. Found: 222.1433 (50.3), 207.1194 (43.0), 73.0474 (100).

To a solution of bispropargylether (0.258 g, 2.72 mmol) in THF (8 mL) cooled to -78 °C was added LHMDS (3.9 mL of 0.7 M solution in THF, 2.72 mmol). After stirring for 20 minutes, TMS-Cl (0.35 mL, 2.72 mmol) was added and stirred for 15 minutes. A second aliquot of LHMDS (5.8 mL of 0.7 M solution in THF, 4.08 mmol) was added and stirred 15 minutes. Freshly distilled acetone (0.40 mL, 5.4 mmol) was then added and the reaction was stirred 30 minutes more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (30% ether/pet. ether) to yield 475 mg of 20 (78%).

Rf (30% Et₂O/PE): 0.4. IR (neat): 3418, 2961, 2855, 2174, 1443, 1363, 1251, 1168, 1088, 1001, 950, 845, 761 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 4.22 (s, 2H), 4.19 (s, 2H), 2.1 (bs, 1H), 1.49 (s, 6H), 0.15 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): 100.6, 92.1, 91.6, 77.2, 65.2, 57.4, 56.9, 31.4, -0.1. HRMS (EI, [M-H]+) Cal’d for C₁₂H₁₉O₂Si: 223.1154. Found: 223.1158 (12.0), 209.0996 (33.0), 179.0890 (85.0).

Procedure: A for 2hr.

Rf (30% Et₂O/PE): 0.6. IR (neat): 2962, 2851, 1460, 1358, 1248, 1164, 1084, 1047, 905, 840, cm⁻¹. ¹H NMR (400 MHz, C₆D₆): 4.62 (bs, 1H), 4.56 (s, 2H), 4.29 (d, J = 2Hz,
To a solution of 4-pentyn-1-ol (2 mL, 21.4 mmol) in THF (125 mL) cooled to -78 °C was added EtMgBr (42.8 mL of a 1 M solution in THF, 42.8 mmol). The mixture was allowed to warm to room temperature and stir for 3 hours. After cooling back to -78 °C, freshly distilled acetone (4.72 mL, 64.2 mmol) was added slowly. The reaction was warmed to room temperature and stirred an additional 2.5 hr, quenched with saturated ammonium chloride, extracted with ether, dried over MgSO₄, and the solvent was removed in vacuo. The crude product was purified on silica (90% ether/pet. ether) to yield 1.63 g (54%) of the expected tertiary propargyl alcohol.

To a solution of DMSO (1.48 mL, 20 mmol) in DCM (66 mmol) at -78 °C was added oxaly chloride (0.9 mL, 10 mmol) dropwise and stirred15 minutes. The tertiary propargyl alcohol product of the first reaction (0.99 g, 6.96 mmol) was then in DCM (15 mL) to the activated DMSO slowly. This solution was then stirred 15 minutes, Et₃N (4.9 mL, 35 mmol) was added, and stirred a further 30 min. The reaction was quenched with water, extracted with ether, dried over MgSO₄, and the solvent was removed in vacuo to yield crude aldehyde (830 mg, 85%) which was used for the following reaction.

To a solution of TMS-acetylene (4 mL, 28 mmol) in THF (50 mL) cooled to -78 °C was added n-BuLi (11 mL of a 2.5 M solution in hexanes, 27.5 mmol), and the mixture was stirred for 1 hr. The aldehyde product from the previous reaction was then added in THF (12 mL), warmed to room temperature and stirred an additional 30 minutes, quenched with saturated ammonium chloride, extracted with ether, dried over MgSO₄, and the solvent was removed in vacuo. The crude product was purified on silica (50% ether/pet. ether) to yield 641 mg (50%) of 22red.

Rf (100% Et₂O): 0.85. IR (neat): 3555, 2960, 2934, 2238, 2173, 1423, 1408, 1363, 1333, 1250, 1164, 1069, 1006, 945, 904, 843, 760, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 4.46 (m, 1H), 2.42-2.24 (m, 2H), 2.20 (bs, 1H), 1.86 (q, J = 7.2 Hz, 2H), 1.46 (s, 6H), 0.14 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): 105.9, 89.9, 85.9, 81.3, 65.4, 61.7, 36.4, 31.7, 14.7, -0.08. Anal Cal’d for C₁₃H₂₂O₂Si: C, 65.50; H, 9.30. Found: C, 65.52; H, 9.50.

To a solution of 22red (99 mg, 0.415 mmol) in DCM (2 mL) at 0 °C was added NaHCO₃ (1.0 mL of 5wt% in water), TEMPO (0.65 mg, 0.00415 mmol), KBr (5 mg, 0.04 mmol), and NaOCl (10% in water, 0.62 mmol). The mixture was stirred for 1 hr, extracted with DCM, dried over MgSO₄, and the solvent was removed in vacuo. The crude product was purified on silica (50% ether/pet. ether) to yield 67 mg (67%) of 22.
Rf (50% Et₂O/PE): 0.35. **IR** (neat): 3416, 2980, 2933, 2151, 1679, 1363, 1253, 1166, 1114, 847, 762 cm⁻¹. **¹H NMR** (400 MHz, C₆D₆): 2.40 (m, 2H), 2.29 (m, 2H), 1.74 (bs, 1H), 1.39 (s, 6H), 0.03 (s, 9H). **¹³C NMR** (100 MHz, C₆D₆): 184.3, 102.5, 97.1, 86.8, 79.9, 64.8, 44.3, 31.7, 13.5, -1.0. **Anal Cal’c** for C₁₃H₂₀O₂Si: C, 66.05; H, 8.53. Found: C, 65.88; H, 8.42.

Procedure: B” for 15 minutes.

Rf (50% Et₂O/PE): 0.6. **IR** (neat): 2972, 2926, 1702, 1654, 1553, 1460, 1412, 1380, 1361, 1287, 1267, 1246, 1175, 1092, 1019, 891, 843, 762, 701 cm⁻¹. **¹H NMR** (400 MHz, C₆D₆): 4.57 (bs, 1H), 2.075 (s, 2H), 2.073 (s, 2H), 1.21 (s, 6H), 0.44 (s, 9H). **¹³C NMR** (100 MHz, C₆D₆): 203.0, 173.5, 135.3, 124.1, 113.6, 78.6, 37.2, 28.4, 23.6, -2.6. **HRMS** (EI, [M]+) Cal’c for C₁₃H₂₀O₂Si: 236.1233. Found: 236.1226 (52.3), 221.0998 (70.8), 208.1278 (61.5), 73.0484 (100).

Procedure: A for 18 hr.

Rf (50% Et₂O/PE): 0.61. **IR** (neat): 2975, 2933, 2888, 1705, 1568, 1369, 1347, 1246, 1215, 1162, 1128, 1094, 1006, 978, 918, 842, 760, 717. **¹H NMR** (400 MHz, C₆D₆): 5.15 (p, J = 2 Hz, 1H), 2.69 (q, J = 2.4 Hz, 2H), 2.04 (q, J = 1.6 Hz, 2H), 1.01 (s, 6H), 0.47 (s, 9H). **¹³C NMR** (100 MHz, C₆D₆): 202.4, 169.0, 136.6, 127.9, 116.9, 76.2, 43.1, 36.9, 26.5, -2.6. **HRMS** (EI, [M]+) Cal’c for C₁₃H₂₀O₂Si: 236.1233. Found: 236.1226 (52.3), 221.0998 (70.8), 208.1278 (61.5), 73.0484 (100).

To a solution of tosyl-protected propargyl amine (2 g, 9.56 mmol), 4-trimethylsilanylbut-3-yn-1-ol (1.28 g, 8.93 mmol), and triphenylphosphine (2.46 g, 9.38 mmol) in THF (70 mL) cooled to 0 °C was added DIAD (1.83 mL, 9.29 mmol) dropwise. The mixture was warmed slowly to room temperature and stirred an additional 8 hr. Silica gel was then added to crude reaction mixture, and filtered through silica gel with ether as the eluent. The solvent was removed in vacuo, and the crude product was purified on silica (20% ether/pet. ether) to yield 4-methyl-N-prop-2-ynyl-N-(4-trimethylsilanyl-but-3-ynyl)-benzenesulfonamide (1.5 g, 50%) as a white solid (mp = 89-92 °C).

To a solution of the product of the previous reaction (390 mg, 0.89 mmol) in THF (10 mL) at -78 °C was added n-BuLi (0.74 mL of a 1.56 M solution in hexanes, 1.157 mmol). Following 30 minutes stirring, freshly distilled acetone (0.098 mL, 1.34 mmol) was added dropwise, and stirring was continued for 30 minutes more. Saturated ammonium chloride was added, the reaction mixture was warmed to room temperature,
extracted with ether, and the solvent was removed in vacuo to yield the crude product which was purified on silica (50% ether/pet. ether) to give pure 25 (249 mg, 71%).

Rf (50% Et2O/PE): 0.35. IR (neat): 3512, 2980, 2177, 1598, 1493, 1451, 1348, 1250, 1161, 1097, 843 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 7.75 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 4.2 (s, 2H), 3.36 (t, J = 7 Hz, 2H), 2.56 (t, J = 7 Hz, 2H), 2.43 (s, 3H), 1.30 (s, 6H), 0.16 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): 143.6, 136.3, 129.6, 127.7, 103.3, 90.3, 86.9, 74.9, 64.8, 45.5, 37.6, 31.0, 21.5, 20.6, 0.01.

Anal Cal’c for C₂₀H₂₉NO₃SSi: C, 61.34; H, 7.46; N, 3.58. Found: C, 61.18; H, 7.47; N, 3.68.

Procedure: B’ for 8 hr (a small amount of a less polar compound, presumably the isomerized compound is formed upon extended heating, but can be easily separated by silica gel chromatography).

Rf (20% Et₂O/PE): IR (neat): 2971, 2926, 2945, 1598, 1461, 1348, 1248, 1165, 1091, 1019, 952, 929, 900, 840, 747, 711, 660. ¹H NMR (400 MHz, C₆D₆): 7.68 (d, J = 8 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 4.56 (t, J = 1.6 Hz, 1H), 3.62 (d, J = 1.6 Hz, 2H), 2.94 (t, J = 6 Hz, 2H), 2.16 (t, J = 6 Hz, 2H), 1.93 (s, 3H), 1.15 (s, 6H), 0.12 (s, 9H). ¹³C NMR (100 MHz, C₆D₆): 153.6, 142.9, 134.6, 129.5, 128.3, 126.1, 121.3, 118.5, 73.3, 48.4, 45.7, 26.6, 25.1, 21.1, -1.3. HRMS (EI, [M]+) Cal’c for C₂₀H₂₉NO₃SSi: 391.1637. Found: 391.1625 (0.9), 376.1405 (8.2), 308.1136 (7.7), 280.0997 (89.8).


To a solution of triethyl sodiomethanecarboxylate (4.0 g, 15.7 mmol) in toluene:DMF (1:1, 50 mL) was added 3-trimethylsilylpropargyl bromide (3.0 g, 15.7 mmol), and the mixture was stirred and heated at 80 °C overnight. The resulting yellow suspension was cooled to room temperature, diluted with toluene (100 mL), washed with water, saturated Na₂CO₃, and brine. The combined aqueous layers were extracted with toluene and the combined organic layers were dried (MgSO₄), and the solvent was removed in vacuo to afford 2-ethoxycarbonyl-2-(3-trimethylsilanyl-2-propynyl)malonic acid diethyl ester as a yellow oil (5.53 g, 99 %).

A solution of this product in THF (20 mL) was added dropwise to a suspension of sodium ethoxide (1.30 g, 1.91 mmol) in THF (30 mL). After stirring at room temperature for 2 h, 1N HCl was added until the solution was acidic. The reaction mixture was then diluted with ether (150 mL), washed with water (30 mL), saturated NaHCO₃ solution, brine, dried (MgSO₄), concentrated in vacuo, and purified on silica (25% ether/pet. ether) to afford 2-(3-trimethylsilanyl-2-propynyl)malonic acid diethyl ester (4.15 g, 100 %).
Following stirring for 30 minutes, propargyl bromide (1.67 mL of an 80% solution in toluene, 15 mmol) was added, and the reaction was stirred an additional 3 hours. Water was then added, and extracted with ether, and dried over Na$_2$SO$_4$. The solvent removed in vacuo and the crude product was purified on silica (10% ether/pet. ether) to yield 2-prop-2-ynyl-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid diethyl ester (4.34 g, 94%).

Rf (40% Et$_2$O/PE): 0.80. IR (neat): 3286, 2962, 2180, 1740, 1427, 1367, 1288, 1207, 1031, 845, 761, 643 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): 4.19 (m, 4H), 2.96 (s, 2H), 2.93 (d, J = 3 Hz, 2H), 1.99 (t, J = 3 Hz, 1H), 1.23 (t, J = 7.2 Hz, 6H), 0.09 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): 168.8, 101.0, 88.5, 78.9, 71.7, 62.2, 56.8, 24.1, 22.7, 14.2, 0.1. Anal Cal’c for C$_{16}$H$_{24}$O$_4$Si: C, 62.30; H, 7.84. Found: C, 62.48; H, 8.01.

To a solution of 2-prop-2-ynyl-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid diethyl ester (308 mg, 1 mmol) in THF (10 mmol) at -78 °C was added n-BuLi (0.4 mL of a 2.5 M solution in hexanes, 1 mmol), and after stirring for 30 minutes, 2-pentanone (103 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred 30 minutes, quenched with saturated ammonium chloride, extracted with ether, dried over Na$_2$SO$_4$, and the solvent was removed in vacuo. The resulting crude product was then purified on silica (20% ether/pet. ether) to yield 29 (193 mg, 49%).

Rf (40% Et$_2$O/PE): 0.45. IR (neat): 3498, 2960, 1736, 1447, 1366, 1247, 1186, 1155, 1070, 840. $^1$H NMR (500 MHz, CDCl$_3$): 4.17 (m, 4H), 2.93 (s, 2H), 2.92 (s, 2H), 1.90 (bs, 1H), 1.65-1.40 (m, 4H), 1.39 (s, 3H), 1.22 (t, J = 7 Hz, 6H), 0.91 (t, J = 7 Hz, 3H), 0.10 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): 168.9, 101.1, 88.4, 87.6, 78.1, 68.4, 62.1, 57.0, 46.2, 30.1, 24.1, 22.9, 18.2, 14.4, 14.3, 0.1. Anal Cal’c for C$_{21}$H$_{34}$O$_5$Si: C, 63.92; H, 8.69. Found: C, 64.12; H, 8.74.

Procedure: B for 1.5 hr.

Rf (20% Et$_2$O/PE): IR (neat): 3498, 2960, 2180, 1741, 1466, 1367, 1289, 1251, 1192, 1031, 845, 761 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): 4.82 (t, J = 2 Hz, 1H), 3.95 (q, J = 7.2 Hz, 4H), 3.31 (d, J = 2 Hz, 2H), 3.15 (t, J = 2.5 Hz, 2H), 1.6-1.3 (m, 4H), 1.26 (s, 3H), 0.90 (t, J = 7 Hz, 6H), 0.89 (m, 3H), 0.23 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): 171.0, 151.5, 134.1, 123.0, 115.8, 76.3, 61.3, 60.0, 43.7, 38.1, 36.5, 25.8, 17.6, 14.7, 13.9, -1.9. HRMS (EI, [M]$^+$) Cal’c for C$_{21}$H$_{34}$O$_5$Si: 394.2176. Found: 394.2173 (52.1), 379.1931 (57.9), 351.1602 (100).
Procedure: A for 2 hr (product still contains a small amount of 30).

Rf (20% Et$_2$O/PE): IR (neat): 2959, 1735, 1467, 1446, 1366, 1247, 1186, 1154, 1070, 839. $^1$H NMR (400 MHz, C$_6$D$_6$): 5.84 (t, J = 1.6 Hz, 1H), 3.98 (m, 4H), 3.63 (d, J = 16 Hz, 1H), 3.58 (d, J = 16 Hz, 1H), 2.25 (dd, J1 = 15.6 Hz, J2 = 1.6 Hz, 2H), 1.30 (m, 4H), 1.06 (s, 3H), 0.93 (t, J = 7 Hz, 6H), 0.82 (t, J = 7 Hz, 3H), 0.20 (s, 9H.

$^{13}$C NMR (100 MHz, C$_6$D$_6$): 170.9, 150.6, 140.3, 128.5, 122.1, 75.0, 65.8, 42.2, 35.3, 35.0, 29.9, 23.2, 17.0, 14.7, 13.9, -1.9. HRMS (EI, [M]$^+$) Cal’c for C$_{21}$H$_{34}$O$_5$Si: 394.2176. Found: 394.2173 (42.4), 351.1606 (82.6), 73.0474 (100).

To a solution of bispropargyltosylamine (0.505 g, 2.04 mmol) in THF (8 mL) cooled to -78 °C was added LHMDS (4.08 mL of 0.5 M solution in THF, 2.04 mmol). After stirring for 45 minutes, TMS-Cl (0.26 mL, 2.04 mmol) was added and stirred for 30 minutes. A second aliquot of LHMDS (4.9 mL of 0.5 M solution in THF, 2.45 mmol) was added and stirred 30 minutes. Freshly distilled cyclohexanone (0.317 mL, 3.06 mmol) was then added and the reaction was stirred 1 hour more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO$_4$, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (35% ether/pet. ether) to yield 340 mg of 32 (40%).

Rf (40% Et$_2$O/PE): 0.3. mp = 85-87 °C. IR (neat): 3520, 2934, 2858, 2179, 1597, 1494, 1446, 1353, 1250, 1164, 1094, 1002, 965, 846, 846, 759, 667 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): 7.69 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.17 (s, 2H), 4.13 (s, 2H), 2.40 (s, 3H), 1.77 (bs, 1H), 1.69-1.56 (m, 5H), 1.45-1.31 (m, 5H), 0.03 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): 143.9, 135.4, 129.7, 128.1, 97.5, 91.3, 89.5, 76.6, 68.6, 39.7, 37.3, 36.5, 25.1, 23.3, 21.6, -0.3. Anal Cal’c for C$_{22}$H$_{31}$NO$_3$Si: C, 63.27; H, 7.48. Found: C, 63.24; H, 7.46.

Procedure: A for 1 hr.

Rf (25% Et$_2$O/PE): 0.45. IR (neat): 2932, 2857, 1597, 1448, 1349, 1248, 1164, 1091, 840, 666. $^1$H NMR (400 MHz, C$_6$D$_6$): 7.75 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 4.56 (bs, 1H), 4.18 (s, 2H), 3.87 (d, J = 2 Hz, 2H), 1.88 (s, 3H), 1.76 (m, 2H), 1.58 (m, 2H), 1.44 (m, 2H), 1.30 (m, 2H), 1.15 (m, 2H), 0.05 (s, 9H). $^{13}$C NMR (100 MHz, C$_6$D$_6$):
To a solution of dimethyl(bis)propargyl malonate (0.3 g, 1.44 mmol) in THF (10 mL) cooled to -78 °C was added LHMDS (1.6 mL of 0.9 M solution in THF, 1.44 mmol). After stirring for 30 minutes, TMS-Cl (0.18 mL, 1.44 mmol) was added and stirred for 1.5 hours. A second aliquot of LHMDS (1.9 mL of 0.9 M solution in THF, 1.73 mmol) was added and stirred 30 minutes. Freshly distilled i-butyraldehyde (0.2 mL, 2.16 mmol) was then added and the reaction was stirred 1 hour more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 310 mg of 34 (62%).

Rf (40% Et₂O/PE): 0.35. IR (neat): 3501, 2958, 2987, 2180, 1744, 1436, 1324, 1293, 1251, 1211, 1029, 844, 761, 644 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 4.11 (dt, J₁ = 5.6 Hz, J₂ = 2 Hz, 1H), 3.72 (s, 6H), 2.98 (d, J = 2 Hz, 2H), 2.95 (s, 2H), 1.80 (m, 1H), 1.68 (bs, 1H), 0.93 (t, J = 6.8 Hz, 6H), 0.10 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 169.2, 100.6, 88.5, 83.3, 79.8, 67.7, 56.9, 52.9, 34.4, 24.1, 22.9, 18.0, 17.1, -0.1. HRMS (EI, [M-CH₃]⁺) Cal’d for C₁₇H₂₅O₅Si: 337.1471. Found: 337.1467 (5.1), 309.1163 (12.5), 277.1225 (13.7), 249.0934 (32.7), 73.0496 (100).
stirring for 30 minutes, TMS-Cl (0.31 mL, 2.4 mmol) was added and stirred for 1.5 hours. A second aliquot of LHMDS (3.6 mL of 1 M solution in THF, 3.6 mmol) was added and stirred 30 minutes. Freshly distilled benzaldehyde (0.37 mL, 3.6 mmol) was then added and the reaction was stirred 1 hour more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 560 mg of 34 (60%).

Rf (50% Et₂O/PE): 0.25. IR (neat): 3486, 3021, 2957, 2900, 2180, 1732, 1603, 1494, 1436, 1352, 1294, 1250, 1211, 1139, 1028, 844, 761, 731, 699, 637 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): 7.5 (m, 2H), 7.3 (m, 3H), 5.41 (bs, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.06 (d, J = 2 Hz, 2H), 2.99 (s, 2H), 0.13 (s, 9H).

13C NMR (125 MHz, CDCl₃): 169.4, 140.9, 128.8, 128.6, 126.9, 100.9, 88.9, 83.6, 81.7, 64.9, 57.2, 53.3, 24.5, 23.4, 0.2.


To a solution of bispropargyltosylamine (0.514 g, 2.08 mmol) in THF (25 mL) cooled to -78 °C was added LHMDS (4.16 mL of 0.5 M solution in THF, 2.08 mmol). After stirring for 30 minutes, TMS-Cl (0.26 mL, 2.08 mmol) was added and stirred for 30 minutes. A second aliquot of LHMD (4.99 mL of 0.5 M solution in THF, 2.49 mmol) was added and stirred 30 minutes. Freshly distilled benzaldehyde (0.317 mL, 3.12 mmol) was then added and the reaction was stirred 1 hour more. Saturated ammonium chloride was then added to the reaction at -78 °C and the mixture was warmed to room temperature, extracted with ether, dried over MgSO₄, and the solvent removed in vacuo. The crude product was then purified using silica gel chromatography (40% ether/pet. ether) to yield 530 mg of 38 (60%).

Rf (20% Et₂O/PE): IR (neat): 2954, 2842, 1737, 1613, 1576, 1535, 1493, 1434, 1252, 1199, 1170, 1075, 969, 843, 823, 752, 692. ¹H NMR (400 MHz, C₆D₆): 8.15 (d, J = 16.4 Hz, 1H), 7.32 (m, 2H), 7.02 (m, 3H), 6.68 (d, J = 16.4 Hz, 1H), 3.75 (s, 2H), 3.55 (s, 2H), 3.12 (s, 6H), 0.19 (s, 9H). ¹³C NMR (100 MHz, C₆D₆): 235.3, 171.6, 141.9, 138.8, 136.9, 128.8, 128.6, 128.4, 127.4, 123.8, 58.0, 52.5, 42.1, 41.1, -2.6. Anal Cal’c for C₂₁H₂₆O₅Si: C, 65.26; H, 6.78. Found: C, 65.14; H, 6.81.

**Procedure:** A for 2 hr (product contains a trace amount of impurity (possibly [6H]-pyran).
Supporting Materials

3H), -0.005 (s, 9H). $^{13}$C NMR (100 MHz, C$_6$D$_6$): 143.4, 141.0, 136.2, 129.6, 128.6, 126.8, 98.6, 90.9, 86.3, 79.2, 64.3, 37.6, 36.9, 21.1. Anal Cal’d for C$_{23}$H$_{27}$NO$_3$Si: C, 64.90; H, 6.39; N, 3.29. Found: C, 64.92; H, 6.46; N, 3.17.

$$\begin{align*}
\text{TsN} & \quad \text{Ph} \quad \text{OH} \\
\xrightarrow{A \ 87\%} & \quad \text{TsN} \quad \text{Ph} \quad \text{TMS} \\
38 & \quad 39
\end{align*}$$

Procedure: A for 1hr.

Rf (20% Et$_2$O/PE): reddish crystals mp = 120-122 IR (neat): 2923, 2853, 1618, 1597, 1546, 1493, 1448, 1347, 1250, 1165, 1098, 843, 816, 752, 667. $^1$H NMR (400 MHz, C$_6$D$_6$): 7.82 (d, J = 8 Hz, 2H), 7.80 (d, J = 16 Hz, 1H), 7.25 (m, 2H), 7.02 (m, 3H), 6.78 (d, J = 8 Hz, 2H), 6.37 (d, J = 16 Hz, 1H), 4.67 (t, J = 3.6 Hz, 2H), 4.48 (dd, J1 = 4 Hz, J2 = 3.2 Hz, 2H), 1.85 (s, 3H), 0.04 (s, 9H). $^{13}$C NMR (100 MHz, C$_6$D$_6$): 233.1, 143.4, 139.5, 137.8, 136.4, 135.4, 134.9, 129.9, 129.2, 129.0, 127.8, 12.5, 121.2, 56.0, 55.2, 21.0, -2.7. HRMS (EI, [M$^+$]) Cal’d for C$_{23}$H$_{27}$NO$_3$Si: 425.1481. Found: 425.1488(37.6), 242.1264 (78.5).
Supporting Materials
### Supporting Materials

**S21**

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<tr>
<td>Flg</td>
<td>6.000</td>
<td>ppm</td>
</tr>
</tbody>
</table>

![NMR Spectrogram](image)

**NMR Spectrogram:**
- Peaks at 6.00, 2.35, 2.14, 6.34, and 6.47 ppm.
- Assignments for peaks visible.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Jan 14 2003</td>
</tr>
<tr>
<td>Solvent</td>
<td>CDCl3</td>
</tr>
<tr>
<td>File</td>
<td>nmr</td>
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<tr>
<td>NMR</td>
<td>600.23 G</td>
</tr>
<tr>
<td>Ratio</td>
<td>2:1</td>
</tr>
<tr>
<td>Processing</td>
<td>4000.0 Hz</td>
</tr>
<tr>
<td>Temp</td>
<td>293 K</td>
</tr>
<tr>
<td>NMR</td>
<td>390.20 Hz</td>
</tr>
<tr>
<td>Peak Width</td>
<td>1.20</td>
</tr>
</tbody>
</table>

**Diagram**

- Chart showing NMR spectrum with peaks at various ppm values.
- Chemical structures are shown with annotations:
  - E = 4-Me - 13
  - OH
  - SiMe2Bn

**Note:** The image contains textual data related to NMR spectroscopy settings and parameters, along with a diagram of the spectrum and chemical structures.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
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<tr>
<td>Sample</td>
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<tr>
<td>Solvent</td>
<td>Benzene</td>
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<td>NMR</td>
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<td>Acquisition</td>
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<td>PPG</td>
<td>90/90</td>
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<tr>
<td>TMS</td>
<td>0.00 ppm</td>
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<tr>
<td>ppm</td>
<td>0.00 ppm</td>
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<tr>
<td>TOF</td>
<td>0.00 sec</td>
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<tr>
<td>Footnote</td>
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<tr>
<td>Lock</td>
<td>not used</td>
</tr>
<tr>
<td>Gain</td>
<td>0.00 mT/m</td>
</tr>
</tbody>
</table>

**Notes:**
- DISPLAY: 462.3
- WET: 16.7
- SG: 1.39
- pH: 9.0
- Rf: 0.33
- TH: 20
- Membrane: 6.886

**Graph:**
- X-axis: ppm
- Y-axis: Signal intensity
- Peaks at 3.02 ppm, 7.08 ppm, and 1.00 ppm
Supporting Materials