Supporting Information

Synthetic Studies on the Kigamicins

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1. General.

Unless otherwise stated, reactions were performed under argon using freshly purified solvents, which were purified using solvent purification columns purchased from Glass Contour, Laguna Beach, CA. All Reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). All work-up and purification procedures were carried out with reagent-grade solvents in air. Flash chromatography was performed with indicated solvents using silica gel (particle size 40-63 μm) purchased from Sorbent Technologies. 1H and 13C NMR spectra were recorded on Varian Inova-400 MHz, 500 MHz, or MR-400 spectrometer. Chemical shift are reported relative to internal chloroform (CDCl3: $^1$H, δ = 7.26 ppm, $^{13}$C, δ = 77.36 ppm). Coupling constants are in Hz and are reported as d (doublet), t (triplet), q (quartet), b (broad peak), and m (multiplet). Mass spectra were acquired on an Agilent Technologies 1200 series LC/MS using indicated ionization methods.

**Materials.** Chemicals were purchased from Aldrich, Fisher or Alfa Aesar, TCI, and Chemical Strem and used without purification.
2. Experimental Procedures and Characterization Data

A mixture of Dudley’s reagent (18.08 g, 2.0 equiv), MgO (2.07 g, 2.0 equiv), and alcohol 11(1) (6.27 g, 25.91 mmol, 1.0 equiv) in DCE (65 mL, 0.4 M) was heated at 80-85 °C for 48 h. The reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The crude was purified by flash chromatography (10:1 to 5:1 Hexane/EtOAc) to yield of compound 13 (7.15 g, 85%) as a pale yellow oil.

1H NMR (400 MHz, CDCl₃) δ 7.39 – 7.28 (m, 5H), 6.80 (dd, J = 10.2, 2.3 Hz, 1H), 5.98 (ddd, J = 10.3, 1.9, 1.0 Hz, 1H), 4.85 – 4.70 (m, 2H), 4.19 – 4.06 (m, 2H), 2.74 (ddd, J = 16.3, 4.3, 1.1 Hz, 1H), 2.46 (dd, J = 16.3, 10.2 Hz, 1H), 0.90 (s, 9H), 0.09 (d, J = 3.0 Hz, 6H).

13C NMR (100 MHz, CDCl₃) δ 197.7, 148.4, 137.8, 129.7, 128.5, 127.9, 127.8, 79.0, 73.3, 72.3, 45.7, 25.7, 18.0, -4.7, -4.8. [α]D²₀ = -95 (c = 1.0, CHCl₃). MS (ESI) calculated for C₁₉H₂₈SiO₃ [M+1]+ 333.2, found 333.2. HRMS calcd for C₁₉H₂₈O₃Si (M+H)+ 333.1881, found 333.1883.

To a stirred solution of enone 13 (9.66 g, 30.02 mmol, 1.0 equiv) in dry CH₂Cl₂ (100 mL, 0.3 M) and pyridine (24.2 mL, 10 equiv) at room temperature was added sequentially DMAP (0.36 g, 0.1 equiv) and I₂ (11.44 g, 1.5 equiv), and the solution was stirred until complete by TLC (~5 h). The reaction was quenched by a 1:1 mixture of saturated NaHCO₃ and saturated Na₂S₂O₃ and allowed to stir for ~10 min. The reaction was then diluted with water and extracted with ethyl acetate (3x). The organic layers were combined and washed with brine and dried over MgSO₄. Evaporation of solvent afforded the crude iodo-enone which was used directly in the next step.

The vinyl iodide was dissolved in MeOH (120 mL, 0.25 M) and cooled to -78 °C under N₂. CeCl₃·7H₂O (22.37 g, 2.0 equiv) was added followed by NaBH₄ (5.7 g, 5.0 equiv) portionwise and stirred for 1.5 h. The reaction was carefully quenched by sequentially adding saturated NH₄Cl solution then a solution of citric acid. After stirring for 0.5 h, the reaction was extracted with ethyl acetate (4x) and the combined organic layers was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure to afford the crude vinyl iodide, which was used directly for the next step.

To a solution of crude vinyl iodide in THF (100 mL, 0.3 M) was added 60% NaH (1.80 g, 1.5 equiv) at 0 °C. After being stirred for 0.5 h at 0 °C, BnBr (5.48 mL, 1.5 equiv) and catalytic TBAI were added to the mixture. The resulting mixture was stirred for 2 h at room temperature. The mixture was diluted with ethyl ether and poured into water, and the aqueous phase was extracted with ether (3x). The combined organic layers was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (15:1 to 10:1 Hexane/EtOAc) provided iodide 14, (10.56 g, 64% yield over 3 steps). 1H NMR (400 MHz, CDCL₃) δ 7.45 (d, J = 7.0 Hz, 2H), 7.41 – 7.27 (m, 8H), 6.42 (t, J = 1.8 Hz, 1H), 4.71 – 4.58 (m, 4H), 4.07 (dt, J = 10.1, 5.4, 2.3 Hz, 1H), 3.88 (dt, J = 7.7, 2.4 Hz, 1H), 3.79 (ddd, J = 11.6, 7.6, 3.6 Hz, 1H), 2.14 (ddd, J = 12.6, 5.8, 3.6 Hz, 1H), 1.83 (td, J = 12.4, 9.8 Hz, 1H), 0.90 (s, 9H), 0.08 (d, J = 2.9 Hz, 6H). 13C NMR (100 MHz, CDCl₃) δ 140.0, 138.0, 137.7, 128.4, 128.4, 128.1, 127.8, 127.8, 127.8, 127.7,
Iodide 14 (4.78 g, 8.69 mmol) was dissolved in THF and toluene (1:5, 43.4 mL, 0.2 M) and cooled to -78 °C. A solution of t-BuLi in hexanes (1.7 M, 10.22 mL, 2.02 equiv) was added dropwise and stirred for 0.5 h. A solution of benzaldehyde 15[26] (3.63 g, 1.1 equiv) in THF (0.5 M) was added dropwise via cannulation. The reaction was allowed to stir for 2 hours at -78 °C and quenched by the addition of a saturated solution of NH₄Cl and diluted with ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the viscous yellow oil by flash chromatography (10:1 Hexane/EtOAc) provided alcohol as a 1:1 mixture of diastereomers.

A solution of above alcohols in DCM (35 mL, 0.2 M) was cooled to 0 °C and Dess-Martin periodinane was added (5.95 g, 2.0 equiv). After 5 minutes the bath was removed and the reaction was stirred at room temperature until complete by TLC (~overnight). Once complete the reaction was cooled to 0 °C and quenched with a 1:1 mixture of saturated NaHCO₃ and saturated Na₂S₂O₃. After stirring for 0.5 h the reaction was diluted with saturated NaHCO₃ and extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (12:1 Hexane/EtOAc) provided compound 16. (4.81 g, 69% yield over 2 steps). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.20 (m, 15H), 6.84 (s, 1H), 6.30 (s, 1H), 5.01 (dd, J = 8.0, 5.6 Hz, 2H), 4.87 (s, 2H), 4.72 (d, J = 12.0 Hz, 1H), 4.64 – 4.58 (m, 1H), 4.58-4.48 (m, 3H), 4.02 (dt, J = 7.6, 2.4 Hz, 1H), 3.77 (s, 3H), 3.67 – 3.58 (m, 1H), 3.35 (s, 3H), 2.28 – 2.20 (m, 1H), 1.72 (dt, J = 12, 8 Hz, 1H), 0.87 (s, 9H), 0.03 (d, J = 5.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 192.6, 152.2, 148.5, 144.7, 142.9, 141.4, 138.6, 135.9, 128.5, 128.1, 128.0, 127.0, 124.5, 118.9, 112.5, 99.5, 80.7, 73.3, 71.8, 71.7, 71.5, 70.8, 60.8, 57.7, 37.5, 25.8, 18.0, -4.6, -4.8. [α]D²⁰ = -37 (c = 1.0, CHCl₃). MS (ESI) calculated for C₄₃H₅₁BrOSi [M+H]+ 803.2, found 803.2. HRMS calcd for C₄₃H₅₁BrOSi (M+H)+ 803.2609, found 803.2435.

A solution of TFA/H₂O 10:1 (60 mL) was added dropwise to a stirred solution of compound 16 (9.40 g, 11.70 mmol) in THF (15 mL) at 0 °C. After 10 min, the reaction mixture was neutralized with 5N NaOH and extracted with EtOAc (3x). The organic layer was washed with saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (4:1 to 1:1 Hexane/EtOAc) provided diol 16'. (7.82 g, 67% yield). ¹H NMR (400 MHz, CDCl₃) δ 10.77 (s, 1H), 7.40 – 7.21 (m, 13H), 7.13 – 7.08 (m, 2H), 6.61 (s, 1H), 6.22 (d, J = 2.8 Hz, 1H), 4.83 (dd, J = 29.0, 11.2 Hz, 2H), 4.55 (t, J = 5.6 Hz, 1H), 4.57 (dd, J = 11.6, 9.2 Hz, 2H), 4.42 (dd, J = 25.6, 11.6 Hz, 2H), 3.88 (s, 3H), 3.87 – 3.83 (m, 1H), 3.50 – 3.42 (m, 1H), 2.83 (d, J = 6.0 Hz, 1H), 2.10 – 20.2 (m, 1H), 1.82 – 1.76 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 155.1, 154.4, 143.2, 140.5, 137.9, 137.5, 135.0, 133.8, 128.7, 128.5, 128.4, 128.3, 127.9, 127.9, 127.9, 127.8, 127.7, 123.3, 112.4, 106.9, 78.4, 71.9, 71.3, 71.1, 70.6, 68.4, 607, 32.2.
$[\alpha]_D^{20} = + 10$ (c = 1.0, CHCl$_3$). MS (ESI) calculated for C$_{35}$H$_{33}$BrO$_7$[M+1$^+$] 645.1, found 645.2. HRMS calced for C$_{35}$H$_{33}$BrO$_7$ (M+H)$^+$ 645.1482, found 645.1479.

To a solution of compound 16' (5.04 g, 7.82 mmol, 1.0 equiv) in t-Butanol (78.2 mL, 0.1 M) was added SeO$_2$ (3.45 g, 4.0 equiv) at room temperature. The resulting mixture was refluxed until completion of the reaction (TLC monitoring, ~4 days). Once complete the reaction was cooled to room temperature and quenched with H$_2$O. The resulting mixture was extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (8:1 Hexane/EtOAc) provided compound 17. (3.97 g, 79%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.6$ Hz, 2H), 7.42 – 7.27 (m, 13H), 6.98 (s, 1H), 5.26 (s, 2H), 5.06 (brs, 1H), 4.88 – 4.83 (m, 4H), 4.36 (s, 1H), 4.32 – 4.30 (m, 1H), 3.86 (s, 3H), 2.39 (d, $J = 14.8$ Hz, 1H), 2.07 (d, $J = 14.8$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.7, 160.2, 154.6, 152.0, 140.6, 138.1, 137.5, 136.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 127.1, 122.7, 120.2, 115.8, 112.7, 76.5, 73.9, 71.7, 69.3, 68.7, 61.7, 28.6.

$[\alpha]_D^{20} = + 42$ (c = 0.2, CHCl$_3$). MS (ESI) calculated for C$_{35}$H$_{31}$BrO$_7$[M+1$^+$] 643.1, found 643.2. HRMS calcd for C$_{35}$H$_{31}$BrO$_7$(M+H)$^+$ 643.1326, found 643.1340.

To a stirred solution of compound 17 (2.02 g, 3.18 mmol, 1.0 equiv) in dry CH$_2$Cl$_2$ (32 mL, 0.1 M) and 2,6-lutidine (1.11 mL, 3.0 equiv) at 0 °C was added TBSOTf (1.46 mL, 2.0 equiv) and the solution was stirred until complete by TLC (~2 h). The reaction was quenched by saturated NaHCO$_3$. Then the mixture was extracted with ethyl acetate (3x). The organic layers were combined and washed with brine and dried over MgSO$_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography (15:1 Hexane/EtOAc) provided compound 18 as a colorless oil. (2.12 g, 89% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 6.9$ Hz, 2H), 7.48 – 7.23 (m, 13H), 6.97 (s, 1H), 5.30 – 5.17 (m, 2H), 5.02 (d, $J = 11.4$ Hz, 1H), 4.91 (d, $J = 10.8$ Hz, 1H), 4.88 (s, 1H), 4.86 (d, $J = 6.0$ Hz, 1H), 4.78 (d, $J = 10.8$ Hz, 1H), 4.29 (d, $J = 5.1$ Hz, 1H), 4.08 (ddd, $J = 7.3$, 5.2, 3.5 Hz, 1H), 3.79 (s, 3H), 2.20 (ddd, $J = 14.2$, 6.0, 3.5 Hz, 1H), 2.03 (ddd, $J = 14.3$, 7.4, 4.9 Hz, 1H), 0.84 (s, 9H), 0.03 (d, $J = 2.9$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.5, 159.7, 154.2, 151.5, 140.1, 139.8, 137.5, 136.2, 128.6, 128.5, 128.5, 128.1, 128.0, 127.8, 127.4, 126.7, 121.8, 120.9, 115.6, 112.1, 77.9, 74.5, 73.5, 71.3, 69.6, 68.8, 61.4, 33.5, 25.8, 18.1, 4.8, 4.8. $[\alpha]_D^{20} = + 8$ (c = 0.5, CHCl$_3$). MS (ESI) calculated for C$_{41}$H$_{45}$SiBrO$_3$ [M+1$^+$] 757.2, found 757.2. HRMS calcd for C$_{41}$H$_{45}$BrO$_7$Si (M+H)$^+$ 757.2191, found 757.2191.
To a solution of isopropenyl acetate (15.12 mL, 6.0 equiv) in toluene (15 mL) was added nBu3SnOMe (27.32 mL, 4.1 equiv) under Ar, and the mixture was heated at 110 °C for 0.5 h. After cooling to room temperature, Pd2(dba)3•CHCl3 (2.40 g, 0.1 equiv), PhDave-Phos (Aldrich) (5.29 g, 0.6 equiv), and LiCl (3.92 g, 4.0 equiv) were added to the reaction mixture. After heating at 110 °C for 10 min, a solution of compound 19 [3] (10 g, 23.15 mmol) in toluene (15 mL) was added. After being stirred for 7~10 min at 110 °C, the reaction mixture was cooled to room temperature and evaporated in vacuo. Purification of the crude by flash chromatography (5:1 to 2:1 Hexane/EtOAc) provided compound 20. (6.30 g, 80% yield). 1H NMR (400 MHz, CDCl3) δ 7.44 – 7.32 (m, 5H), 6.48 (d, J = 2.4 Hz, 1H), 6.45 (d, J = 2.5 Hz, 1H), 5.06 (s, 2H), 4.12 (s, 2H), 2.30 (s, 3H), 1.70 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 205.2, 164.1, 160.8, 159.0, 140.7, 135.6, 128.7, 128.7, 128.4, 127.6, 114.7, 105.5, 101.1, 70.4, 49.3, 30.2, 25.6. MS (ESI) calculated for C20H20O5 [M+H]+ 341.4, found 341.2. HRMS calcld for C20H20O5 (M+H)+ 341.1384, found 341.1399.

To a solution of D-serine (5.0 g, 1.2 equiv) in MeOH (50 mL, 0.8M) was added the 5.4 M solution of MeONa in MeOH (7.4 mL, 1.0 equiv) under Ar, and the mixture was stirred at 0 °C for 15 min. Then compound 20 (13.5 g, 39.7 mmol) in MeOH (30 mL) was added, and the resulting mixture was heated at 60 °C. After being stirred for 48~72 h, the reaction mixture was cooled to room temperature and evaporated in vacuo to give the mixed solid, which was dissolved in H2O and extracted with ethyl acetate (3x). The organic layers were combined and washed with brine, dried over MgSO4, and filtered. The solvent was removed under reduced pressure to afford the crude intermediate, which was used directly for the next step without further purification.

To a solution of crude intermediate in DMF (132 mL, 0.3 M) was added K2CO3 (32.87 g, 6.0 equiv) followed by BuBr (14.14 mL, 3.0 equiv). After being stirred for overnight at 45 °C, the mixture was cooled to room temperature and diluted with water, extracted with ether (3x). The combined organic layers was washed with brine, dried over MgSO4, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (10:1 to 4:1 Hexane/EtOAc) provided compound 21 as a single diastereomer as judged by 1H NMR and LC/MS. (17.4 g, 79% yield over 2 steps). 1H NMR (400 MHz, CDCl3) δ 7.51 (d, J = 6.9 Hz, 2H), 7.41 – 7.27 (m, 13H), 6.50 (d, J = 2.3 Hz, 1H), 6.41 (d, J = 1.2 Hz, 1H), 5.24 (s, 2H), 5.20 (d, J = 3.6 Hz, 2H), 5.05 (dd, J = 7.7, 5.6 Hz, 1H), 5.02 (s, 2H), 4.35 (dd, J = 8.9, 7.7 Hz, 1H), 4.21 (dd, J = 8.9, 5.5 Hz, 1H), 3.11 (d, J = 14.7 Hz, 1H), 2.91 (d, J = 14.7 Hz, 1H), 1.43 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 170.2, 162.2, 160.6, 160.3, 139.3, 136.8, 136.0, 135.4, 128.7, 128.6, 128.5, 128.3, 128.1, 127.6, 126.8, 111.0, 106.8, 100.9, 93.8, 70.8, 70.2, 67.7, 67.3, 57.3, 42.2, 23.2. [α]D[O]20 = -30 (c = 1.0, CHCl3). MS (ESI) calculated for C34H31NO6 [M+1]+ 550.2, found 550.2. HRMS calcld for C34H31NO6 (M+H)+ 550.2224, found 550.2254.
To the solution of compound 21 (9.0 g, 16.39 mmol) in 150 mL THF-H$_2$O (4:1, v:v) was added LiOH•H$_2$O (4.82 g, 7.0 equiv) and the mixture was stirred overnight. The reaction was then quenched by careful addition of aqueous 1 N HCl until the pH of the solution was approximately 6.5. The aqueous solution was saturated with solid NaCl. The two layers were separated and the aqueous phase was extracted with EtOAc (3x). The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, and then concentrated. Purification of the crude by flash chromatography (2:1 to 0:1 Hexane/EtOAc) provided acid 21'. (6.7 g, 89% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, $J = 7.0$ Hz, 2H), 7.42 – 7.35 (m, 7H), 7.32–7.28 (m, 1H), 6.54 (d, $J = 2.0$ Hz, 1H), 6.43 (d, $J = 1.1$ Hz, 1H), 5.17 (dd, $J = 29.6, 12.4$ Hz, 2H), 5.06 (dd, $J = 11.6, 6.4$ Hz, 2H), 4.86 (t, $J = 8$ Hz, 1H), 4.60–4.43 (m, 2H), 4.17 – 4.03 (m, 3H), 3.63 – 3.56 (m, 1H), 3.11 (d, $J = 14.7$ Hz, 1H), 2.94 (d, $J = 14.7$ Hz, 1H), 1.31 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.8, 164.3, 163.5, 161.4, 140.0, 136.2, 135.7, 128.0, 128.6, 128.5, 127.9, 127.6, 126.7, 108.7, 107.1, 100.6, 93.7, 70.8, 70.4, 65.6, 57.7, 42.2, 22.5. $[\alpha]_D^{20} = + 48$ (c = 1.0, CHCl$_3$). MS (ESI) calculated for C$_{27}$H$_{25}$NO$_6$ [M+1'] 460.2, found 460.2. HRMS calcd for C$_{27}$H$_{25}$NO$_6$ (M+H)$^+$ 460.1755, found 460.1777.

To the solution of acid 21' (6.7 g, 14.60 mmol) in THF (73 mL, 0.5 M) were added NMP (3.21 mL, 2.0 equiv) and isobutyl chloroformate (3.8 mL, 2.0 equiv) at -10 °C. The solution was stirred at -10 °C for 20 min and for another 20 min at room temperature. The resulting mixture was again cooled to -10 °C. The solution of sodium phenylselenide in THF, which was prepared by reaction of benzeneselenol (3.1 mL, 2.0 equiv) and 60% NaH (1.29 g, 2.2 equiv) in anhydrous THF (30 mL) at 0 °C, was added through a syringe. The resulting mixture was stirred at -10 °C for 30 min and then for another 3.5 h at room temperature. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography (6:1 to 2:1 Hexane/EtOAc) give the phenylselenyl ether.

To the solution of above phenylselenyl ether and AIBN (1.99 g, 1.0 equiv) in anhydrous benzene (73 mL, 0.5 M) at reflux was added Bu$_3$SnH (10 mL, 3.0 equiv). The mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and the solvent was then removed under reduced pressure. Purification of the crude by flash chromatography (4:1 to 1:1 Hexane/EtOAc) provided compound 22. (3.8 g, 63% yield over 2 steps). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, $J = 7.0$ Hz, 2H), 7.43 – 7.32 (m, 7H), 7.29 (d, $J = 7.4$ Hz, 2H), 6.43 (d, $J = 2.3$ Hz, 1H), 6.43 (d, $J = 1.1$ Hz, 1H), 5.17 (d, $J = 40.0, 12.3$ Hz, 2H), 5.04 (s, 2H), 4.17 – 4.03 (m, 3H), 3.63 – 3.56 (m, 1H), 3.11 (d, $J = 14.7$ Hz, 1H), 2.94 (d, $J = 14.7$ Hz, 1H), 1.31 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.0, 160.4, 139.5, 136.7, 136.1, 128.7, 128.6, 128.5, 127.9, 127.6, 126.7, 126.8, 111.4, 106.6, 100.6, 91.9, 70.7, 70.2, 64.5, 42.9, 42.3, 22.8. $[\alpha]_D^{20} = - 50$ (c = 1.0, CHCl$_3$). MS (ESI) calculated for C$_{26}$H$_{25}$NO$_4$ [M+1'] 416.2, found 416.2. HRMS calcd for C$_{26}$H$_{25}$NO$_4$ (M+H)$^+$ 416.1856, found 416.1877.
30% palladium on carbon (0.97 g, 0.3 equiv) was added to a solution of compound 22 (3.8 g, 9.16 mmol) in ethyl acetate
(48 mL, 0.2 M) under an atmosphere of nitrogen, which was replaced a hydrogen atmosphere using a balloon. The
suspension was then stirred overnight. The resulting solution was filtered through a pad of Celite, which was subsequently
washed with ethyl acetate (3x). The solution concentrated under vacuum. Purification of the crude mixture by flash
chromatography (2:1 to 1:4 Hexane/EtOAc) provided compound 22' (2.0 g, 95% yield).

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\begin{align*}
\text{H NMR (400 MHz, CDCl}_3 & \text{)} \delta 11.99 (s, 1H), 6.29 (s, 1H), 6.22 (s, 1H), 4.20 (t, J = 6.9 Hz, 2H), 3.94 (dt, J = 11.2, 7.2 Hz, 1H), 3.64 (dt, J = 11.2, 6.5 Hz, 1H), 3.11 - 2.93 (m, 2H), 1.35 (s, 3H). \\
\text{C NMR (100 MHz, CDCl}_3 & \text{)} \delta 164.7, 163.0, 161.1, 138.1, 107.5, 104.0, 102.1, 92.5, 64.3, 41.6, 40.6, 22.4. \\
[\alpha]_D^{20} &= \text{ - 56 (c = 1.0, CHCl}_3). \\
\text{MS (ESI) calculated for C}_{12}H_{13}NO_4 \text{[M+1}^+] \text{ 236.2, found 236.2. HRMS calcld for C}_{12}H_{13}NO_4 \text{(M+H)}^+ \text{ 236.0917, found 236.0923.}
\end{align*}
\]

To a solution of compound 22' (2.15 g, 9.16 mmol) and 2,6-lutidine (2.14 mL, 2.0 equiv) was added dropwise Tf₂O (1.43
mL, 1.0 equiv) over 0.5 h. The reaction mixture was stirred at 0 °C for 1 h, then at room temperature for 3 h. The reaction
was washed with water, 1M HCl, sat. NaHCO₃, and brine. It was then dried over MgSO₄ and concentrated under reduced.
The resultant residue was purified by flash chromatography (6:1 to 3:1 Hexane/EtOAc) to give compound 23 (3.19 g, 95%).

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\begin{align*}
\text{H NMR (400 MHz, CDCl}_3 & \text{)} \delta 12.29 (s, 1H), 6.77 (d, J = 2.5 Hz, 1H), 6.64-6.63 (m, 1H), 4.24 (t, J = 6.9 Hz, 2H), 3.98 (dt, J = 11.4, 6.5 Hz, 1H), 3.18 – 3.08 (m, 2H), 1.37 (s, 3H). \\
\text{C NMR (100 MHz, CDCl}_3 & \text{)} \delta 163.4, 162.6, 152.5, 138.4, 120.2, 117.0, 111.7, 110.6, 109.5, 92.3, 64.4, 41.7, 40.5, 22.6. \\
[\alpha]_D^{20} &= \text{ - 112 (c = 0.5, CHCl}_3). \\
\text{MS (ESI) calculated for C}_{13}H_{12}F_3NSO_6 \text{[M+1}^+] \text{ 368.3, found 368.0. HRMS calcld for C}_{13}H_{12}F_3NSO_6 \text{(M+H)}^+ \text{ 368.0410, found 368.0429.}
\end{align*}
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To a solution of compound 23 (3.36 g, 9.16 mmol) in toluene (20 mL, 0.5M) was added i-Pr₂NH (2.6 mL, 2.0 equiv),
Pd(PPh₃)₂Cl₂ (0.646 g, 0.1 equiv), and CuI (0.175 g, 0.1 equiv) under Ar. After being stirred at room temperature for 5 min, trimethylsilylacetylene (2.54 mL, 2.0 equiv) was added. After stirring for overnight, the reaction mixture was evaporated in
vacuo. The crude residue was purified by flash column chromatography (6:1 to 3:1 Hexane/EtOAc) to give the intermediate
silyl alkyne.
To a solution of above intermediate in THF (20 mL, 0.5M) was added 1 N TBAF solution (10 mL, 1.05 equiv) in THF at 0 °C. After stirring for 20 min, the mixture was extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude mixture by flash chromatography (4:1 Hexane/EtOAc) provided alkyne 24. (1.7 g, 77% yield over 2 step.)

1H NMR (400 MHz, CDCl₃) δ 11.91 (s, 1H), 6.97 (s, 1H), 6.81 (s, 1H), 4.22 (t, J = 6.9 Hz, 2H), 4.01 – 3.92 (m, 1H), 3.65 (dt, J = 11.4, 6.5 Hz, 1H), 3.16 (s, 1H), 3.12 – 3.01 (m, 2H), 1.34 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ 164.1, 160.7, 135.9, 127.7, 122.3, 120.0, 110.9, 92.5, 82.5, 79.5, 64.3, 41.7, 40.3, 33.8, 29.7, 25.8, 22.5, 18.1, -4.8, -4.8. [α]D²⁰ = -154 (c = 1.0, CHCl₃). MS (ESI) calculated for C₁₄H₁₃NO₃ [M+1]⁺ 244.3, found 244.2. HRMS calcd for C₁₄H₁₃NO₃ (M+H)⁺ 244.0968, found 244.0989.

A modified procedure reported by Soheili and coworkers was used for the Sonogashira cross-coupling. Accordingly, bromide 18 (1.905 g, 2.519 mmol) was combined with [Pd(allyl)Cl]₂ (92 mg, 0.10 equiv), DABCO (0.622 g, 2.2 equiv), and tBu₃PHBF₄ (0.292 g, 0.40 equiv) in a vial fitted with an efficient stir bar under an atmosphere of Ar. CH₃CN (2.51 mL, 1.0 M) was then added and the solution was sparged for 0.5 h. In a separate vial alkyne 24 (1.224 g, 2.0 equiv) was dissolved in degassed DMF (10.10 mL, 0.5 M) and sparged for 0.5 h before being loaded into a syringe. The solution of alkyne was then added via syringe pump over 7 hours at 45 °C in an aluminum block with vigorous stirring. Once the addition was finished, stirring at this temperature was maintained for an additional 24 h. When complete, the reaction mixture was filtered through a plug of silica gel, washing with DCM. The eluent was then concentrated under reduced pressure and purified by flash chromatography (10:1 to 4:1 Hexane/EtOAc) to give 1.62 g of alkyne 25 (70% yield) as an white foam.

1H NMR (400 MHz, CDCl₃) δ 11.99 (s, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.51 – 7.21 (m, 13H), 7.06 (s, 1H), 6.90 (s, 1H), 6.87 (s, 1H), 5.29 (d, J = 12.6 Hz, 1H), 5.06 (d, J = 11.4 Hz, 1H), 4.94 – 4.85 (m, 3H), 4.79 (d, J = 10.8 Hz, 1H), 4.31 (d, J = 5.3 Hz, 1H), 4.23 (t, J = 6.9 Hz, 2H), 4.07 (ddd, J = 7.7, 5.3, 3.5 Hz, 1H), 4.03 – 3.94 (m, 1H), 3.93 (s, 3H), 3.67 (dt, J = 11.4, 6.5 Hz, 1H), 3.16-3.07 (m, 2H), 2.27–2.15 (m, 1H), 2.09 – 1.98 (m, 1H), 1.37 (s, 3H), 0.85 (s, 9H), 0.04 (d, J = 3.2 Hz, 6H). 13C NMR (100 MHz, CDCl₃) δ 175.6, 164.0, 160.8, 160.1, 151.2, 138.9, 137.6, 136.5, 136.1, 128.6, 128.5, 128.5, 128.1, 128.1, 128.0, 127.9, 127.7, 127.4, 126.7, 121.9, 120.9, 120.7, 119.5, 116.6, 111.1, 111.0, 95.4, 92.5, 86.6, 77.9, 74.6, 73.4, 71.2, 69.7, 68.9, 64.3, 61.9, 41.7, 40.3, 33.8, 29.7, 25.8, 22.5, 18.1, -4.8, -4.8. [α]D²⁰ = +6 (c = 0.1, CHCl₃). HRMS calcd for C₅₅H₅₇NO₁₀Si (M+Na)⁺ 942.3644, found 942.3614.
In a sealed 20 mL reaction vial equipped with a magnetic stirring bar, alkyne 25 (20 mg, 0.02 mmol), [(IPr)AuCl] (5 mol%) and AgSbF₆ (5 mol%) was added to 1,4-dioxane (degassed by bubbling N₂ for 10 minutes) (1.3 mL) and H₂O (degassed by bubbling Ar for 10 minutes) (0.7 mL). The reaction mixture was then heated for 36 h at 82 °C. The reaction was cooled to room temperature and quenched with H₂O. The resulting mixture was extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (6:1 to 3:1 Hexane/EtOAc) provided desired ketone 27 (15.1 mg, 57%, yield) and regio-isomer 26 (3.9 mg, 19% yield). This reaction was frequently carried out in multiple 20 mg aliquots, and the combined crude materials were purified together. The regiochemistry was assigned through the HMBCs of Bn-protected substrate.

**Desired ketone 27:** ¹H NMR (400 MHz, CDCl₃) δ 11.87 (s, 1H), 7.57 (d, J = 7.3 Hz, 2H), 7.46-7.23 (m, 13H), 6.94 (s, 1H), 6.72 (s, 1H), 5.27 (d, J = 12.7 Hz, 1H), 5.22 (d, J = 12.6 Hz, 1H), 4.98 (d, J = 11.5 Hz, 1H), 4.93-4.85 (m, 5H), 4.77 (d, J = 15.0 Hz, 1H), 3.77 (m, 3H), 3.68-3.61 (m, 1H), 3.09 (d, J = 15.0 Hz, 1H), 3.02 (d, J = 15.0 Hz, 1H), 2.04 (m, 1H), 2.00-1.95 (m, 1H), 1.33 (m, 3H), 0.84 (s, 9H), 0.04 (d, J = 4.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 197.9, 175.6, 164.4, 161.1, 153.8, 151.5, 141.5, 140.6, 138.8, 137.5, 136.3, 136.0, 134.9, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.5, 126.8, 121.3, 120.2, 118.4, 117.6, 109.5, 107.0, 92.5, 78.1, 74.5, 73.5, 71.0, 69.5, 68.7, 64.3, 62.7, 49.6, 41.6, 40.4, 33.4, 29.7, 25.8, 22.5, 18.1, -4.7, -4.8. [α]D²⁰ = -11 (c = 0.25, CHCl₃). HRMS calcd for C₅₅H₅₉NO₁₀Si (M+Na)⁺ 960.3750, found 960.3746.

**Regio-isomer 26:** ¹H NMR (400 MHz, CDCl₃) δ 12.00 (s, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.52-7.20 (m, 15H), 6.61 (s, 1H), 5.22 (m, J = 12.8, 9.0 Hz, 1H), 4.92-4.85 (m, 4H), 4.77 (d, J = 10.8 Hz, 1H), 4.33 – 4.19 (m, 5H), 4.11- 4.06 (m, 1H), 4.01-3.95 (m, 1H), 3.71 (s, 3H), 3.69-3.61 (m, 1H), 3.14 (s, 2H), 2.52 – 2.45 (m, 1H), 2.23 – 2.17 (m, 1H), 2.06 – 2.00 (m, 1H), 1.35 (s, 3H), 0.84 (s, 9H), 0.03 (m, J = 2.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 175.8, 163.7, 161.2, 159.4, 153.8, 151.2, 145.5, 140.6, 140.4, 139.1, 137.6, 136.7, 136.5, 132.6, 130.9, 128.5, 128.4, 128.0, 127.9, 127.8, 127.5, 127.3, 126.7, 124.2, 123.4, 120.6, 117.9, 116.8, 115.6, 114.0, 110.1, 92.6, 78.2, 74.5, 73.3, 71.1, 69.6, 68.8, 64.2, 61.5, 41.7, 40.4, 33.6, 38.8, 25.8, 24.6, 22.5, 18.1, -4.7, -4.8. [α]D²⁰ = -24 (c = 1.0, CHCl₃). HRMS calcd for C₅₅H₅₉NO₁₀Si (M-H)⁻ 936.3785, found 936.3789.
To a solution of (R,R)-Ru-catalyst (23.4 mg, 20%) in 2.0 mL CH₂CN (degassed by bubbling N₂ for 10 minutes) was added Et₃N (0.33 mL, 12.0 equiv), followed by formic acid (70 μL, 10.0 equiv) under N₂ at room temperature. The mixture turned into a yellow solution from purple upon the addition of formic acid, and it was stirred for 10 minutes. At the same time, the ketone 27 (0.173 g, 0.18 mmol, 1.0 equiv) was dissolved in degassed CH₂CN (4 mL) and added via cannula, rinsing with additional 1 mL CH₂CN. The reaction was stirred overnight, at which time the reaction was complete by TLC analysis. The reaction was quenched with a saturated solution of NaHCO₃ and extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography (4:1 to 2:1 Hexane/EtOAc) provided alcohol 28 as a single diastereomer as judged by 1H NMR analysis (0.130 g, 75%, yield). ¹H NMR (400 MHz, CDCl₃) δ 11.83 (s, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.47-7.23 (m, 13H), 6.90 (s, 1H), 6.77 (s, 1H), 6.46 (s, 1H), 5.30-5.21 (m, 3H), 5.03 (d, J = 3.2 Hz, 1H), 4.93-4.87 (m, 3H), 4.78 (d, J = 10.8 Hz, 1H), 4.31 (d, J = 5.2 Hz, 2H), 4.20 (t, J = 6.8 Hz, 2H), 4.12-4.04 (m, 1H), 4.00-3.93 (m, 1H), 3.72 (s, 3H), 3.69-3.61 (m, 1H), 3.09-2.94 (m, 3H), 2.77 (dd, J = 8.4, 5.6 Hz, 1H), 2.24-2.16 (m, 1H), 2.08-1.98 (m, 1H), 1.32 (s, 3H), 0.84 (s, 9H), 0.04 (d, J = 4.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ176.9, 164.4, 161.0, 159.4, 154.3, 150.8, 145.1, 141.4, 139.0, 138.5, 137.6, 136.8, 136.0, 128.5, 128.4, 128.0, 127.9, 127.7, 127.5, 127.3, 126.8, 126.0, 120.3, 116.9, 115.2, 109.1, 105.6, 92.5, 78.2, 74.5, 73.4, 70.8, 69.6, 69.4, 68.8, 64.2, 61.7, 44.8, 41.5, 40.4, 33.6, 25.8, 22.4, 18.1, -407, -4.8, [α]D° = -28 (c = 0.1, CHCl₃). HRMS calcd for C₅₅H₄₁NO₇Si (M+Na)⁺ 962.3906, found 962.3919.

To a stirred solution of compound 28 (0.23 g, 0.245 mmol, 1.0 equiv) in dry CH₂Cl₂ (4.9 mL, 0.05 M) and DIPEA (0.256 mL, 6.0 equiv) at 0 °C was added dropwise MOMCl (0.0744 mL, 4.0 equiv) and the solution was stirred at room temperature until complete by TLC (~12 h). The reaction was quenched by saturated NaHCO₃. Then the mixture was extracted with ethyl acetate (3x). The organic layers were combined and washed with brine and dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude by flash chromatography (5:1 to 2:1 Hexane/EtOAc) provided compound 28' as a colorless oil. (0.203 g, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ 11.89 (s, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.47-7.22 (m, 13H), 6.79 (s, 2H), 6.45 (s, 1H), 5.31-5.21 (m, 3H), 5.00 (d, J = 11.6 Hz, 1H), 4.93-4.87 (m, 3H), 4.79 (d, J = 11.2 Hz, 1H), 4.34-4.24 (m, 3H), 4.19 (t, J = 6.8 Hz, 2H), 4.11-4.01 (m, 1H), 3.99-3.92 (m, 1H), 3.69 (s, 3H), 3.66-3.60 (m, 1H), 3.09-2.98 (m, 2H), 2.96 (s, 3H), 2.89-2.77 (m, 2H), 2.21-2.16 (m, 1H), 2.05-1.99 (m, 1H), 1.29 (s, 3H), 0.83 (s, 9H), 0.03 (d, J = 2.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ176.0, 164.5, 160.9, 159.5, 153.9, 151.0,
145.3, 139.4, 139.1, 137.6, 136.8, 135.6, 128.5, 128.5, 128.5, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 126.9, 126.9, 120.7, 120.3, 112.7, 115.6, 108.9, 106.2, 91.2, 92.6, 78.3, 74.6, 73.4, 71.9, 71.0, 70.0, 68.8, 64.3, 61.8, 43.6, 41.6, 40.4, 33.7, 25.8, 22.4, 18.2, -4.7, -4.8. [α]D<br>20 = -18 (c = 0.2, CHCl₃). HRMS calcd for C₅₇H₆₅NO₁₂Si (M+Na)+ 1006.4166, found 1006.4176.

30% palladium on carbon (7 mg, 20%) was added to a solution of compound 28’ (98 mg, 0.10 mmol) in THF (4 mL, 0.025 M) under an atmosphere of argon. The atmosphere was replaced with hydrogen using a balloon. The suspension was then stirred at room temperature until complete by TLC analysis (~2 h). The resulting solution was filtered through a pad of silica gel, which was subsequently washed with ethyl acetate (3x). The solution concentrated under vacuum. Purification of the crude by flash chromatography (6:1 to 3:1 Hexane/EtOAc) provided compound 29 (85 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 12.26 (s, 1H), 11.82 (s, 1H), 7.43-7.27 (m, 10H), 6.87 (s, 1H), 6.82 (s, 1H), 6.60 (s, 1H), 5.28 – 5.24 (m, 1H), 4.96 (d, J = 11.2 Hz, 1H), 4.88 – 4.78 (m, 3H), 4.74 (d, J = 10.8 Hz, 1H), 4.46 – 4.41 (m, 2H), 4.28 (d, J = 4.8 Hz, 1H), 4.21 (t, J = 6.4 Hz, 2H), 4.14 – 4.11 (m, 1H), 4.00 - 3.94 (m, 1H), 3.75 (s, 3H), 3.66-3.60 (m, 1H), 3.11 – 3.02 (m, 2H), 3.02 (s, 3H), 2.94 – 2.88 (m, 2H), 2.21 – 2.15 (m, 1H), 2.12 – 2.06 (m, 1H), 1.32 (s, 3H), 0.81 (s, 9H), 0.01 (d, J = 3.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 182.0, 164.6, 163.0, 160.9, 156.3, 148.8, 145.6, 142.7, 138.5, 137.3, 137.1, 135.6, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 127.8, 127.6, 120.5, 118.5, 117.1, 111.0, 108.9, 108.0, 94.4, 92.6, 77.7, 74.5, 73.2, 72.1, 69.1, 68.1, 64.3, 61.9, 55.4, 43.7, 41.6, 40.5, 32.5, 25.8, 22.4, 18.1, -4.8, -4.9. [α]D<br>20 = -14 (c = 0.1, CHCl₃). HRMS calcd for C₅₀H₅₉NO₁₂Si (M+Na)+ 916.3699, found 916.3642.

To a solution of the compound 29 (16.9 mg, 0.019 mmol) in DMF (1.0 mL, 0.2 M) was added CuCl(OH)(NMI)₂ complex (15.9 mg, 3.0 equiv). The resulting mixture was stirred at 135 °C for 6 min. The reaction was cooled to 0 °C and quenched with saturated KHSO₄. Then the resulting mixture was extracted with ethyl acetate (3x). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the crude mixture by flash chromatography (4:1 to 1:1 Hexane/EtOAc) provided compound 30 (11.5 mg, 69%, yield). ¹H NMR (400 MHz, CDCl₃) δ 13.20 (s, 1H), 12.65 (s, 1H), 7.43-7.20 (m, 10H), 6.70 (s, 1H), 5.24 (t, J = 2.8 Hz, 1H), 4.96 (d, J = 11.2 Hz, 1H), 4.85 – 4.81 (m, 3H), 4.78 – 4.73 (m, 2H), 4.58 (d, J = 6.8 Hz, 1 H), 4.29 (d, J = 4.8 Hz, 1H), 4.23 (t, J = 6.4 Hz, 2H), 4.15 – 4.11 (m, 1H), 4.05 - 3.98 (m, 1H), 3.84 (s, 3H), 3.70-3.64 (m, 1H), 3.23 – 3.18 (m, 1H), 3.21 (s, 3H), 3.10 (dd, J = 16.0, 14.8 Hz, 2H), 2.80 – 2.74 (m, 1H), 2.23 – 2.17 (m, 1H), 2.13 – 2.07 (m, 1H), 1.40 (s, 3H), 0.82 (s, 9H), 0.02 (d, J = 4.4 Hz,
To a solution of the compound 30 (23.0 mg, 0.026 mmol) in CH$_3$CN/H$_2$O (2:1, 2.6 mL) was added PhI(OAc)$_2$ (16.6 mg, 2.0 equiv) at 0 °C. After the reaction was completed by TLC (1.5 h), a solution of Na$_2$S$_2$O$_4$ (0.5 g in 3 mL H$_2$O) was added quickly. The reaction mixture turned from red to bright yellow and was diluted by adding water and extracted with ethyl acetate. The combined organic layers was washed with brine, dried with anhydrous Na$_2$SO$_4$, filtered and concentrated to give triol 31 as orange residue. (20.1 mg, 89% yield). This crude triol residue was dried under vacuum and was sufficiently pure for characterization in crude form. Efforts to purify it further on silica gel led to decomposition. $^1$H NMR (400 MHz, CDCl$_3$) δ 12.93 (s, 1H), 12.73 (brs, 1H), 7.50 (d, J = 6.8 Hz, 2H), 7.42 (d, J = 7.4 Hz, 2H), 7.37 - 7.21 (m, 6H), 6.96 (s, 1H), 6.68 (s, 1H), 5.12 - 5.01 (m, 3H), 4.86 (d, J = 11.8 Hz, 1H), 4.82 - 4.78 (m, 2H), 4.74 (d, J = 10.9 Hz, 2H), 4.64 (brs, 1H), 4.32 (d, J = 5.0 Hz, 1H), 4.23 (t, J = 6.9 Hz, 2H), 4.06 - 3.98 (m, 3H), 3.70 - 3.64 (m, 1H), 3.45 (brs, 3H), 3.11 (q, J = 11 Hz, 2H), 2.96 (brs, 1H), 2.37 - 2.18 (m, 1H), 2.09 - 2.00 (m, 1H), 1.38 (s, 3H), 0.83 (s, 9H), 0.00 (d, J = 4.4 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 182.3, 165.0, 163.3, 141.0, 138.6, 137.6, 137.4, 135.1, 130.2, 128.6, 128.5, 128.0, 127.5, 118.4, 110.0, 94.5, 92.6, 72.9, 74.5, 73.1, 69.4, 68.4, 64.3, 56.0, 41.7, 40.5, 36.6, 31.9, 29.7, 29.4, 28.4, 25.8, 22.7, 18.1, 14.1, -4.8, -4.9. [α]$_{D}^{20}$ = +92 (c = 0.05, CHCl$_3$). HRMS calcd for C$_{49}$H$_{55}$NO$_{12}$Si (M-2)$^+$ 876.3494, found 876.3689. (Hydroquinone was oxidized to quinone under the conditions of LC/MS).

3. References

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4. $^1$H, $^{13}$C NMR and HMBC Spectra of Products
HMBC spectrum of compound A in CDCl₃
HMBC spectrum of compound B in CDCl₃