**B-Alkyl Suzuki couplings for the stereoselective synthesis of substituted pyrans**

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**General**: All reactions were carried out under Ar in flame-dried glassware. IR: Nicolet FT-7199 spectrometer, wavenumbers (ν) in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). The solvents used were purified by distillation over the drying agents indicated and were transferred under Argon: THF, Et₂O (Mg-anthracene), CH₂Cl₂, MeCN, Et₃N (CaH₂), DMF (Desmodur®, dibutyltin dilaurate), MeOH (Mg), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. The solvent signals were used as references (CD₂Cl₂: δC ≡ 54.0 ppm; residual CH₂Cl₂ in CD₂Cl₂: δH ≡ 5.32 ppm; C₆D₆: δC ≡ 128.0 ppm; residual C₆H₆ in C₆D₆: δH ≡ 7.15 ppm; CDCl₃: δC ≡ 77.0 ppm; residual CHCl₃ in CDCl₃: δH ≡ 7.26 ppm). Where indicated, the signal assignments are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (cosygs and cosydqtp); HSQC (invietgssi) optimized for ¹J(C,H) = 145 Hz; HMBC (inv4gsplrnd) for correlations via ³J(C,H); HSQC-TOCSY (invietgsm) using an MLEV17 mixing time of 120 ms.

**Pyran 7**

To a solution of 9-BBN dimer (274 mg, 1.123 mmol, 2.0 eq) in THF (2.8 ml) at room temperature was added alcohol 6 (175 mg, 0.562 mmol, 1.0 eq) and the resulting solution was stirred for 6 h (no starting material by TLC). To the borane thus obtained was added a degassed solution of NaOH (1.0 M, 1.68 ml, 3.0 eq) and the
mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 5 (218 mg, 1.120 mmol, 2.0 eq), PdCl$_2$(dppf) (41 mg, 0.056 mmol, 0.1 eq), and AsPh$_3$ (17 mg, 0.056 mmol, 0.1 eq) in degassed THF (2.8 ml) and the mixture was stirred at ambient temperature overnight. The reaction was quenched with aq. NH$_4$Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were stirred with HCl (1.0 M, 30 ml) for 50 min, the layers were separated, and the organic phase dried over MgSO$_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (10:1 to 4:1, hexanes:EtOAc) afforded pyran 7 as a mixture of diastereomers$^1$ (148 mg, 62%, d.r > 10:1).

$\left[\alpha\right]_D^{20} = +10.0$ (c 2.0, CH$_2$Cl$_2$). IR (ATR) 2921, 2858, 1697, 1468, 1450, 1410, 1387, 1365, 1326, 1298, 1251, 1167, 1107, 1083, 1006, 977 701, 673 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 – 7.62 (m, 4H), 7.45 – 7.34 (m, 6H), 3.81 – 3.67 (m, 3H), 3.52 (m, 1H), 2.60 (dd, $J = 15.1$, 7.5 Hz, 1H), 2.39 (dd, $J = 15.1$, 5.2 Hz, 1H), 2.11 (s, 3H), 1.80 (m, 1H), 1.74 – 1.50 (m, 5H), 1.23 – 1.11 (m, 2H), 1.05 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.8, 135.5, 134.0, 129.5, 127.6, 74.7, 74.3, 60.4, 50.5, 39.3, 31.5, 31.4, 30.9, 26.9, 23.5, 19.2. HRMS (ESI+): calcd. for C$_{26}$H$_{36}$O$_3$NaSi (M + Na)$^+$: 447.2323; found 447.2326.

**Pyran 9**

To a solution of 9-BBN dimer (92 mg, 0.377 mmol, 2.1 eq) in THF (0.9 ml) at room temperature was added alcohol 8 (15 mg, 0.180 mmol, 1.0 eq) and the resulting solution was stirred for 4 h. To the borane thus obtained was added a degassed solution of NaOH (1.0 M, 0.54 ml, 3.0 eq) and the mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 5 (53 mg, 0.270 mmol, 1.5 eq), PdCl$_2$(dppf) (13 mg, 0.018 mmol, 0.1 eq), and AsPh$_3$ (6 mg, 0.018 mmol, 0.1 eq) in degassed THF (0.9 ml) and the mixture was stirred at ambient temperature overnight. The reaction was quenched with aq. NH$_4$Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were stirred with HCl (1.0 M, 30 ml) for 50 min

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$^1$ Diastereomeric ratios determined by NMR analysis.
and the layers were separated. The organic phase was stirred with a pH = 7 buffer solution (15 ml) and 30% H₂O₂ (5 ml) for 30 min. The layers were separated and the organic phase dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (4:1, hexanes:EtOAc) afforded pyran 9 (20 mg, 73%, d.r > 10:1) as an oil.

\[ \alpha_D^{10} = -31.8 \left( \text{c 0.5, CH}_2\text{Cl}_2 \right). \text{IR (ATR) 1699, 1466, 1371, 1244, 1204, 1091, 1073, 973, 929 cm}^{-1}. {^1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 3.77 (\text{m, 1H}), 3.45 (\text{ddd, } J = 12.5, 8.0, 6.3 \text{ Hz, 1H}), 2.68 (\text{dd, } J = 15.5, 7.6 \text{ Hz, 1H}), 2.42 (\text{dd, } J = 15.5, 5.2 \text{ Hz, 1H}), 2.18 (\text{s, 3H}), 1.84 – 1.76 (\text{m, 1H}), 1.63 – 1.47 (\text{m, 3H}), 1.21 – 1.10 (\text{m, 2H}), 1.13 (\text{d, } J = 6.2 \text{ Hz, 3H}). {^{13}}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 207.7, 74.1, 74.0, 50.4, 33.0, 31.2, 31.0, 23.5, 22.1. \text{HRMS (ESI+): calcd. for C}_9\text{H}_{16}\text{O}_2\text{H}^+ (\text{M + H})^+: 157.1226; \text{found 157.1228.}

\[(+)-(S,S)-(\text{cis-6-methyltetrahydropyran-2-yl})\text{acetic acid (10)}\]

To a solution of pyran 9 (46 mg, 0.293 mmol) in dioxane (2.3 ml) at room temperature was added a sodium hypobromite solution (4.6 ml) (freshly prepared from bromine (1.1 ml), aqueous sodium hydroxide (10%, 28.3 ml) and dioxane (6.67 ml)) and the mixture was stirred vigorously for 3 h. The reaction was quenched with aqueous sodium sulfite (10%, 2.0 ml) and acidified to pH = 1 with HCl (3 M). The mixture was extracted with methyl tert-butyl ether (2 x 15 ml) and the combined organic extracts were dried over MgSO₄, filtered, and concentrated in vacuo. Purification of the residue by flash chromatography (4:1 to 2:1 to 1:1, hexanes:EtOAc) afforded 10 (30 mg, 65%) as an oil.

\[ \alpha_D^{10} = +19.1 \left( \text{c 1.0, CHCl}_3 \right) [\text{lit.},^2 \alpha_D^{10} + 18.6 \left( \text{c 2.77, CHCl}_3 \right)]. \text{IR (ATR) 2930, 1714, 1440, 1079, 1040 cm}^{-1}. {^1}\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 3.82 – 3.72 (\text{m, 1H}), 3.64 – 3.52 (\text{m, 1H}), 2.56 (\text{m, 1H}), 2.54 (\text{m, 1H}), 1.89 – 1.81 (\text{m, 1H}), 1.68 – 1.47 (\text{m, 3H}), 1.32 – 1.18 (\text{m, 2H}), 1.22 (\text{d, } J = 6.19 \text{ Hz, 3H}). {^{13}}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 172.8, 74.8, 73.9, 40.9, 32.7, 30.7, 23.0, 22.0. \text{HRMS (ESI+): calcd. for C}_8\text{H}_{14}\text{O}_3\text{Na} (\text{M + Na})^+: 158.0943; \text{found 158.0942.}

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Pyran 12

To a solution of 9-BBN dimer (289 mg, 1.184 mmol, 2.1 eq) in THF (2.8 ml) at room temperature was added allylcyclohexanol (11) (79 mg, 0.564 mmol, 1.0 eq) and the resulting solution was stirred overnight. To the borane thus obtained was added a degassed solution of NaOH (1.0 M, 1.41 ml, 2.5 eq) and the mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 5 (110 mg, 0.564 mmol, 1.0 eq), PdCl$_2$(dppf) (41 mg, 0.056 mmol, 0.1 eq), and AsPh$_3$ (17 mg, 0.056 mmol, 0.1 eq) in degassed THF (2.8 ml) and the mixture was stirred at ambient temperature overnight. The reaction was quenched with aq. NH$_4$Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were stirred with HCl (1.0 M, 30 ml) for 50 min, the layers were separated, and the organic phase dried over MgSO$_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (4:1 to 2:1, hexanes:EtOAc) afforded pyran 12 (83 mg, 70%) as an oil.

IR (ATR) 1713, 1443, 1359, 1184, 1101, 1070, 1004, 908, 882, 823, 741, 702 cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.95 (m, 1H), 2.63 (dd, $J$ = 14.5, 8.3 Hz, 1H), 2.34 (dd, $J$ = 14.5, 4.3 Hz, 1H), 2.20 (s, 3H), 2.09 (m, 1H), 1.87 (m, 1H), 1.72 – 1.42 (m, 6H), 1.42 – 1.28 (m, 4H), 1.28 – 1.08 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.5, 72.5, 66.7, 50.7, 40.4, 35.4, 31.9, 29.6, 27.2, 26.2, 21.7, 21.2, 19.1. HRMS (ESI+): calcd. for C$_{13}$H$_{22}$O$_2$Na (M + Na)$^+$: 233.1511; found 233.1512.

Pyran 14

To a solution of 9-BBN dimer (272 mg, 1.115 mmol, 2.1 eq) in THF (2.7 ml) at room temperature was added alcohol 13 (130 mg, 0.531 mmol, 1.0 eq) and the resulting solution was stirred overnight. To the borane thus obtained was added a degassed solution of NaOH (1.0 M, 1.59 ml, 3.0 eq) and the mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 5 (155 mg, 1.673 mmol, 1.5 eq), PdCl$_2$(dppf) (39 mg, 0.053 mmol, 0.1 eq), and AsPh$_3$ (16 mg, 0.053 mmol, 0.1 eq) in degassed THF (2.7
ml) and the mixture was stirred at ambient temperature overnight. The reaction was quenched with aq. NH₄Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were stirred with HCl (1.0 M, 30 ml) for 50 min, the layers were separated, and the organic phase dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (10:1 to 4:1, hexanes:EtOAc) afforded pyran 14 (107 mg, 64%, d.r > 10:1) as an oil.

\[ \alpha = +33.8 \ (c \ 1.0, \ CH₂Cl₂). \] IR (ATR) 1716, 1462, 1358, 1253, 1086, 1006, 949, 833, 774 cm⁻¹. ¹H NMR (400 MHz, C₆D₆) δ 3.83 (ddd, J = 9.6, 8.4, 6.2 Hz, 1H, H(10a)), 3.78 (ddd, J = 10.0, 7.4, 4.6 Hz, 1H, H(10b)), 3.59 (dddd, J = 11.0, 7.8, 5.0, 2.2 Hz, 1H, H(4)), 2.99 (dt, J = 9.6, 2.2 Hz, 1H, H(8)), 2.39 (dd, J = 15.2, 7.9 Hz, 1H, H(3a)), 2.02 (dd, J = 15.2, 4.8 Hz, 1H, H(3b)), 1.91 (dddd, J = 13.8, 8.0, 7.4, 2.3 Hz, 1H, H(9a)), 1.82 (s, 3H, H(1)), 1.54 (dddd, J = 13.8, 9.6, 6.2, 4.4 Hz, 1H, H(9b)), 1.48 (ddt, J = 13.4, 3.8, 3.0 Hz, 1H, H(6eq.)), 1.34 (ddt, J = 13.0, 3.8, 2.5 Hz, 1H, H(5eq.)), 1.16 (tdq, J = 10.4, 6.7, 4.0 Hz, 1H, H(7)), 1.08 (ddt, J = 13.0, 10.8, 4.0 Hz, 1H, H(5ax.)), 1.00 (s, 9H), 0.94 (ddt, J = 13.2, 11.6, 4.0 Hz, 1H, H(6ax.)), 0.65 (d, J = 6.7 Hz, 3H, Me(7)), 0.11 (s, 3H), 0.09 (s, 3H). ¹³C NMR (100 MHz, C₆D₆) δ 204.9 (C₂), 80.3 (C₈), 74.2 (C₄), 59.9 (C₁₀), 50.1 (C₃), 37.0 (C₉), 35.2 (C₇), 33.0 (C₆), 32.3 (C₅), 30.4 (C₁), 26.2 (Me7), 18.5, 17.7, -5.13, -5.19.

HRMS (ESI+): calcd. for C₁₇H₃₄O₃SiH⁺ (M + H)⁺: 315.2355; found 315.2355.

**rac-tetrahydrofuran 16**

To a solution of 9-BBN dimer (192 mg, 0.787 mmol, 2.1 eq) in THF (1.9 ml) at room temperature was added alcohol 15 (77 mg, 0.375 mmol, 1.0 eq) and the resulting solution was stirred 4 h (no starting material by TLC). To the borane thus obtained was added a
degassed solution of NaOH (1.0 M, 1.12 ml, 3.0 eq) and the mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 5 (109 mg, 0.563 mmol, 1.5 eq), PdCl₂(dpdpf) (27 mg, 0.038 mmol, 0.1 eq), and AsPh₃ (11 mg, 0.038 mmol, 0.1 eq) in degassed THF (1.9 ml) and the mixture was stirred at ambient temperature overnight. The reaction was quenched with aq. NH₄Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were stirred with HCl (1.0 M, 30 ml) for 50 min, the layers were separated, and the organic phase dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (4:1 to 2:1 to 1:1, hexanes:EtOAc) afforded tetrahydrofuran 16 (63 mg, 61%, d.r = 1.7:1) as an oil.

IR (ATR) 1714, 1456, 1358, 1255, 1168, 1086, 973, 834, 776, 736, 697 cm⁻¹. Characteristic data for the major isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.28 (m, 2H), 7.21 (m, 2H), 7.15 (m, 1H), 5.09 (m, 2H), 4.40 (m, 1H), 4.27 (m, 1H), 2.56 (dd, J = 15.1, 7.3 Hz, 1H), 2.43 (dd, J = 15.6, 6.9 Hz, 1H), 2.27 (dd, J = 15.2, 6.1 Hz, 1H), 2.08 (dd, J = 15.7, 6.0 Hz, 1H), 1.81 (s, 3H), 1.86 – 1.65 (m, 2H), 1.45 – 1.15 (m, 2H). ¹³C NMR (100 MHz, C₆D₆) δ 207.2, 171.0, 135.9, 128.5, 128.2, 128.1, 74.8, 74.9, 66.3, 49.6, 40.8, 32.0, 31.7, 30.7. HRMS (ESI+): calcd. for C₁₆H₂₀O₄H⁺ (M + H)⁺: 277.1437; found 277.1440.

Pyrrolidine 17

To a solution of 9-BBN dimer (112 mg, 0.459 mmol, 2.1 eq) in THF (1.1 ml) at room temperature was added N-allylcarbamate (34 mg, 0.219 mmol, 1.0 eq) and the resulting solution was stirred for 6 h. To the borane thus obtained was added a degassed solution of NaOH (1.0 M, 0.66 ml, 3.0 eq) and the mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 5 (64 mg, 0.328 mmol, 1.5 eq), PdCl₂(dpdpf) (16 mg, 0.022 mmol, 0.1 eq), and AsPh₃ (7 mg, 0.022 mmol, 0.1 eq) in degassed THF (1.1 ml) and the mixture was stirred at ambient temperature overnight. The reaction was quenched with aq. NH₄Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were dried over MgSO₄ and
concentrated *in vacuo*. Purification of the residue by flash chromatography (2:1 to 1:1, hexanes:EtOAc) afforded pyrrolidine 17 (27 mg, 55%) as an oil.

IR (ATR) 1714, 1692, 1455, 1394, 1366, 1255, 1167, 1098, 835, 775, 735, 698 cm\(^{-1}\). 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.14 (br, 1H), 3.32 (br, 2H), 2.45 – 2.30 (m, 1H), 2.15 (s, 3H), 2.12 – 2.02 (m, 1H), 1.81 (m, 2H), 1.67 – 1.52 (m, 2H), 1.46 (s, 9H). HRMS (ESI\(^+\)): calcd. for C\(_{12}\)H\(_{21}\)NO\(_3\)H\(^+\) (M + H\(^+\)): 228.1599; found 228.1600.

**Alkynone 19**

![Alkynone 19](attachment:alkynone_19.png)

To a solution of amide 18 (1.08 g, 2.80 mmol, 1.0 eq) in THF (5.6 ml) at 0 °C was added a solution of ethynyl magnesium bromide (0.5 M, 6.72 ml, 3.36 mmol, 1.2 eq) and the mixture was stirred for 2 h. The reaction was quenched with aq. NH\(_4\)Cl (25 ml) and extracted with methyl tert-butyl ether (2 x 20 ml). The combined organic extracts were dried over MgSO\(_4\), filtered, and concentrated *in vacuo*. Purification of the residue by flash chromatography (10:1, hexanes:EtOAc) afforded alkynone 19 (0.86 g, 88%) as an oil.

\([\alpha]_D^{20}\) = +13.2 (c 1.0, CH\(_2\)Cl\(_2\)). IR (ATR) 1684, 1566, 1462, 1427, 1030, 948, 822, 738, 700 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.66 (m, 4H), 7.46 – 7.35 (m, 6H), 3.92 (dd, \(J = 10.2, 6.5\) Hz, 1H), 3.88 (dd, \(J = 10.2, 5.3\) Hz, 1H), 3.17 (s, 1H), 2.83 (m, 1H), 1.18 (d, \(J = 7.0\) Hz, 3H), 1.04 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 189.5, 135.6, 133.3, 129.7, 127.7, 80.7, 79.1, 65.1, 51.0, 26.7, 19.3, 12.3. HRMS (ESI\(^+\)): calcd. for C\(_{22}\)H\(_{26}\)O\(_2\)NaSi (M + Na\(^+\)): 373.1593; found 373.1594.

**Vinyl iodide 20**

![Vinyl iodide 20](attachment:vinyl_20.png)

To a solution of alkynone 19 (149 mg, 0.425 mmol, 1.0 eq) in CH\(_2\)Cl\(_2\) (4.2 ml) at –78 °C was added TMSI (153 mg, 0.765 mmol, 1.8 eq) and the mixture was stirred for 10 min. The reaction was quenched by the addition of an Et\(_2\)O:H\(_2\)O solution (1:1, 0.75 ml) and allowed to warm to 5 °C. The mixture was diluted with CH\(_2\)Cl\(_2\) (15 ml) and washed
successively with aq. satd. NaHCO₃ (10 ml) and aq. satd. Na₂S₂O₃ (10 ml). The organic phase was dried over MgSO₄ and filtered before i-Pr₂NEt (0.75 ml) was added slowly to the filtrate. The resulting mixture was stirred for 2 h and then washed with HCl (1.0 N, 10 ml) and aq. satd. NaHCO₃ (10 ml). The organic phase was dried over MgSO₄ and concentrated in vacuo. Rapid purification of the residue by flash chromatography (10:1, hexanes:EtOAc) yielded the sensitive iodide 20 (195 mg, 96%) that was used immediately.

\[ [\alpha]_D^{20} = +17.8 \text{ (c 1.0, CH₂Cl₂).} \]

IR (ATR) 1693, 1564, 1471, 1427, 1388, 1361, 1105, 1029, 947, 822, 799, 700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 14.8 Hz, 1H), 7.65 – 7.60 (m, 4H), 7.48 – 7.37 (m, 6H), 7.27 (d, J = 14.8 Hz, 1H), 3.80 (dd, J = 10.1, 7.4 Hz, 1H), 3.70 (dd, J = 10.0, 5.5 Hz, 1H), 2.97 (m, 1H), 1.05 (d, J = 6.9 Hz, 3H), 1.02 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 145.8, 137.2, 134.9, 134.8, 131.3, 129.3, 100.3, 67.6, 48.0, 28.1, 20.6, 14.2. HRMS (ESI+): calcd. for C₂₂H₂₇O₂NaSiI (M + Na)⁺: 501.0714; found 501.0717.

Pyran 21

To a solution of 9-BBN dimer (147 mg, 0.602 mmol, 2.1 eq) in THF (1.4 ml) at room temperature was added alcohol 8 (25 mg, 0.287 mmol, 1.0 eq) and the resulting solution was stirred overnight. To the borane thus obtained was added a degassed solution of NaOH (1.0 M, 0.86 ml, 3.0 eq) and the mixture was stirred for 10 min. The resulting boronate solution was transferred via syringe to a Schlenk tube containing iodide 20 (137 mg, 0.287 mmol, 1.5 eq), PdCl₂(dppf) (21 mg, 0.029 mmol, 0.1 eq), and AsPh₃ (9 mg, 0.029 mmol, 0.1 eq) in degassed THF (1.4 ml) and the mixture was stirred at 65 °C for 8 h. The reaction was cooled to room temperature, quenched with aq. NH₄Cl (15 ml) and extracted with EtOAc (2 x 15 ml). The combined organic extracts were stirred with HCl (1.0 M, 30 ml) for 50 min, the layers were separated, and the organic phase dried over MgSO₄ and concentrated in vacuo. Purification of the residue by flash chromatography (10:1 to 4:1, hexanes:EtOAc) afforded pyran 21 (68 mg, 54%) along with the minor diastereomer 22 (11 mg, 9%) as an oil.
$[\alpha]_D^{19} = -28.6 \ (c \ 1.0, \ CH_2Cl_2)$. IR (ATR) 1712, 1567, 1471, 1388, 1370, 1110, 1074, 1019, 998, 823, 739, 700 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 – 7.62 (m, 4H), 7.45 – 7.35 (m, 6H), 3.81 (dd, $J$ = 9.9, 7.4 Hz, 1H), 3.80 (m, 1H), 3.65 (dd, $J$ = 9.9, 5.5 Hz, 1H), 3.43 (m, 1H), 2.85 (m, 1H), 2.81 (dd, $J$ = 16.1, 6.8 Hz, 1H), 2.51 (dd, $J$ = 16.1, 5.9 Hz, 1H), 1.78 (m, 1H), 1.70 – 1.40 (m, 3H), 1.20 – 1.09 (m, 2H), 1.11 (d, $J$ = 6.2 Hz, 3H), 1.03 (s, 9H), 1.01 (d, $J$ = 2.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 211.8, 135.6, 133.5, 133.4, 129.7, 127.7, 74.1, 73.9, 66.1, 49.5, 49.3, 33.1, 31.4, 26.8, 23.5, 22.1, 19.2, 12.7. HRMS (ESI+): calcd. for C$_{27}$H$_{38}$O$_3$NaSi (M + Na)$^+$: 461.2486; found 461.2482.

Pyran 22

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 – 7.62 (m, 4H), 7.45 – 7.35 (m, 6H), 4.31 (m, 1H), 3.87 (m, 1H), 3.81 (dd, $J$ = 10.0, 7.7 Hz, 1H), 3.63 (dd, $J$ = 10.0, 4.4 Hz, 1H), 2.88 (m, 1H), 2.84 (dd, $J$ = 15.7, 7.1 Hz, 1H), 2.62 (dd, $J$ = 15.7, 9.1 Hz, 1H), 1.75 – 1.57 (m, 4H), 1.36 – 1.24 (m, 2H), 1.15 (d, $J$ = 6.5 Hz, 3H), 1.03 (s, 9H), 1.02 (d, $J$ = 5.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 211.7, 135.6, 134.8, 129.7, 127.7, 67.4, 67.2, 66.1, 48.4, 46.7, 31.3, 29.8, 26.8, 19.5, 19.2, 18.2, 12.9.