SUPPORTING INFORMATION

FOR

Regioselective Synthesis of Unsymmetrical C-Aryl Glycosides Using Silicon Tethers as Disposable Linkers

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TD 16384
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S2

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S5

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S16

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28

hrp3-188

exp1 s2pul

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S20

Bromomethyl-[5-(4(*R*),5(*S*)-dimethoxy-6(*R*)-methoxymethyltetrahydropyran-2-(*R*)-yl)furan-2-yl]dimethylsilane (8). A solution of lithium diisopropylamide (LDA) in THF/hexanes (0.51 M, 2.51 mL, 1.28 mmol) was added to a solution of **7** (218 mg, 0.85 mmol) in THF (4 mL) at -78 °C. After 3.5 h at -78 °C, (bromomethyl)chlorodimethylsilane (freshly distilled from CaH₂, 128 μ L, 0.94 mmol) was added, and the reaction was warmed to rt. After 12 h at rt, saturated aqueous NaHCO₃ (40 mL) was added, and the aqueous mixture was extracted with CH₂Cl₂ (3 x 30 mL). The combined organic layers were washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 20% EtOAc/hexanes to give 254 mg (73%) of **8** as an oil: ¹H NMR (250 MHz) δ 6.62 (d, *J* = 3.2 Hz, 1 H), 6.28 (d, *J* = 3.2 Hz, 1 H), 4.44 (dd, *J* = 11.9, 1.9 Hz, 1 H), 3.68-3.60 (comp, 2 H), 3.54 (s, 3 H), 3.45 (s, 3 H), 3.43-3.35 (comp 2 H), 3.37 (s, 3 H), 3.15 (app t, *J* = 5.3 Hz, 1 H), 2.58 (s, 2 H), 2.34 (ddd, *J* = 12.9, 5.0, 2.0 Hz, 1 H), 1.78 (app dt, *J* = 12.9, 11.6 Hz, 1 H), 0.36 (s, 6 H); ¹³C NMR (65 MHz) δ 158.3, 156.0, 122.0, 107.3, 82.4, 79.8, 79.2, 71.7, 71.1, 60.6, 59.3, 57.1, 34.4, 15.9, -4.4; IR (neat) 2930, 2894, 2830, 1253, 1188, 1111, 1083 cm⁻¹; HRMS (CI) *m/z* 406.0817 [C₂₇H₂₇O₅SiBr (M + H) requires 406.0811].

(2,6-Dichloro-4-methoxyphenoxyethyl)-[5-(4(*R*),5(*S*)-dimethoxy-6(*R*)-methoxymethyltetrahydropyran-2-(*R*)-yl)furan-2-yl]dimethylsilane (10). A mixture of tetrabutylammonium iodide (65 mg, 0.18 mmol), K₂CO₃ (100 mg, 0.80 mmol), **8** (65 mg, 0.16 mmol), and 2,6-dichloro-4-methoxyphenol (**9**) (36 mg, 0.17 mmol) in acetone (1.7 mL) was stirred for 48 h at rt. H₂O (5 mL) was added, and the aqueous mixture was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed with brine (9 mL), dried (MgSO₄), and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 20% EtOAc/hexanes to give 75 mg (83%) of **10** as a colorless oil: ¹H NMR (250 MHz, acetone-d₆) δ 6.96 (s, 2 H), 6.84 (d, *J* = 3.2 Hz, 1 H), 6.36 (dd, *J* = 3.2, 0.5 Hz, 1 H), 4.50 (br dd, *J* = 11.9, 2.0 Hz, 1 H), 3.90 (s, 2 H), 3.80 (s, 3 H), 3.54-3.53 (comp, 2 H), 3.49 (s, 3 H), 3.45-3.34 (comp, 2 H), 3.41 (s, 3 H), 3.29 (s, 3 H), 3.04 (app t, *J* = 9.4 Hz, 1 H), 2.36 (ddd, *J* = 12.8, 5.0, 1.9 Hz, 1 H), 1.67 (ddd, *J* = 12.8, 11.8, 11.5 Hz, 1 H), 0.44 (s, 3 H), 0.44 (s, 3 H); ¹³C NMR (65 MHz) δ 160.1, 156.8, 156.5, 148.4, 129.8, 123.1, 115.4, 107.7, 83.2, 80.6, 80.0, 72.7, 71.5, 67.0, 60.5, 59.1, 56.9, 56.4, 35.4, -4.7; IR (neat) 2930, 2833, 1560, 1474, 1437, 1221, 1112, 1076, 1043 cm⁻¹; HRMS (CI) *m/z* 518.1291 [C₂₃H₃₂O₇SiCl₂ (M) requires 518.1294].

Cycloadduct (11). A solution of *s*-butyllithium in cyclohexane (1.30 M, 49 μ L, 0.06 mmol) was added to a solution of **10** (30 mg, 0.06 mmol) in THF (0.8 mL) at -95 °C. The solution was stirred for 10 min at -95 °C, and then warmed to -5 °C over 40 min. Saturated aqueous NH₄Cl (2 mL) and H₂O (1 mL) were added, and the aqueous mixture was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (6 mL), dried (MgSO₄), and concentrated under reduced pressure. The residue was purified by column chromatography eluting with 40% EtOAc/hexanes to give 19 mg (68%) of **11** as an oil: ¹H NMR (250 MHz) δ 7.08 (d, *J* = 5.3 Hz, 0.5 H), 7.00 (d, *J* = 0.5 H), 6.97 (d, *J* = 5.3 Hz, 0.5 H), 6.95 (d, *J* = 5.3 Hz, 0.5 H), 6.59 (s, 0.5 H), 6.58 (s, 0.5 H), 4.65 (br d, *J* = 11.5 Hz, 0.5 H), 4.24 (br d, *J* = 10.0 Hz, 0.5 H), 4.17 (d, *J* = 15.2 Hz, 0.5 H), 4.16 (d, *J* = 15.0 Hz, 0.5 H), 3.75 (s, 1.5 H), 3.74 (s, 1.5 H), 3.71-3.38 (comp, 5 H), 3.57 (s, 1.5 H), 3.55 (s, 1.5 H), 3.44 (s, 1.5 H), 3.42 (s, 1.5 H), 3.41 (s, 1.5 H), 3.35 (s, 1.5 H), 3.18 (app t, *J* = 9.1 Hz, 0.5 H), 3.00 (app t, *J* = 9.1 Hz, 0.5 H), 2.27-2.15 (comp, 1 H), 1.79-1.53 (comp, 1 H), 0.36 (s, 1.5 H), 0.35 (s, 1.5 H), 0.34 (s, 1.5 H), 0.32 (s, 1.5 H); HRMS (CI) *m/z* 483.1597 [C₂₃H₃₂O₇SiCl (M + H) requires 483.1606].

5-Chloro-1-(4(*R*),5(*S*)-dimethoxy-6(*R*)-methoxymethyltetrahydropyran-2(*R*)-yl)-3,6-dimethoxy-11-oxatricyclo[6.2.1.0^{0,0}]undeca-2(7),3,5,9-tetraene (12). A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M, 62 μ L, 0.06 mmol) was added to a solution of **11** (10 mg, 0.02 mmol) in DMF (0.5 mL) at rt, and the reaction was stirred for 15 min. Saturated aqueous NaHCO₃ (2 mL) and H₂O (0.5 mL) were added. The aqueous mixture was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (6 mL), dried (MgSO₄), and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 50% EtOAc/hexanes to give 7 mg (79%) of **12** as a colorless oil: ¹H NMR (250 MHz) δ 7.07 (d, *J* = 5.5 Hz, 0.5 H), 7.04 (dd, *J* = 5.5, 1.8 Hz, 0.5 H), 6.99 (dd, *J* = 5.5, 1.8 Hz, 0.5 H), 6.84 (d, *J* = 5.5 Hz, 0.5 H), 6.63 (s, 0.5 H), 6.62 (s, 0.5 H), 5.95-5.93 (comp, 1 H), 4.61 (dd, *J* = 11.5, 1.5 Hz, 0.5 H), 4.42 (dd, *J* = 12.0, 1.8 Hz, 0.5 H), 3.85 (s, 1.5 H), 3.84 (s, 1.5 H), 3.77 (s, 1.5 H), 3.75 (s, 1.5 H), 3.73-3.41 (comp, 4 H), 3.55 (s, 1.5 H), 3.55 (s, 1.5 H), 3.45 (s, 1.5 H), 3.40 (s, 1.5 H), 3.39 (s, 1.5 H), 3.28 (s, 1.5 H), 3.04 (app t, *J* = 9.0 Hz, 0.5 H), 2.99 (app t, *J* = 9.0 Hz, 0.5 H), 2.24-2.17 (comp, 1 H), 1.78-1.54 (comp, 1 H); HRMS (CI) *m/z* 427.1524 [C₂₁H₂₈O₇Cl (M + H) requires 427.1524].

7-Chloro-4-(4(*R*),5(*S*)-dimethoxy-6(*R*)-methoxymethyltetrahydropyran-2(*R*)-yl)-5,8-dimethoxynaphthalen-1-ol (13). A solution containing trifluoroacetic acid (TFA) (3 drops) and **12** (7 mg, 0.02 mmol) in CH₂Cl₂ (0.5 mL) was stirred for 5 h at rt in a reaction vessel that was sealed with a glass stopper. The reaction mixture was diluted with CH₂Cl₂ (2 mL), and the solution was washed with saturated aqueous NaHCO₃ (2 mL) and brine (2 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure to give 7 mg (quant.) of **13** as a colorless oil: ¹H NMR (500 MHz) δ 9.72 (s, 1 H), 7.74 (br d, *J* = 8.1 Hz, 1 H), 6.94 (d, *J* = 8.1 Hz, 1 H), 6.72 (s, 1 H), 5.49 (br d, *J* = 10.2 Hz, 1 H), 3.96 (s, 3 H), 3.90 (s, 3 H), 3.68 (app d, *J* = 3.4 Hz, 2 H), 3.58 (s, 3 H), 3.51-3.46 (comp, 2 H), 3.43 (s, 3 H), 3.42 (s, 3 H), 3.18 (dd, *J* = 9.6, 8.6 Hz, 1 H), 2.51 (ddd, *J* = 12.7, 4.8, 1.4 Hz, 1 H), 1.34 (app dt, *J* = 12.7, 11.2 Hz, 1 H); ¹³C NMR (125 MHz) δ 154.0, 152.6, 145.4, 129.9, 125.9, 124.0, 121.0, 118.9, 112.5, 107.2, 83.5, 80.1, 79.4, 75.6, 72.4, 62.5, 60.6, 59.5, 56.5, 55.8, 39.4; IR (CDCl₃) 3346, 2938, 2841, 1599, 1516, 1467, 1385, 1351, 1111 cm⁻¹; HRMS (CI) *m/z* 426.1438 [C₂₁H₂₇O₇Cl (M) requires 426.1445].

[5-(4,5-Dimethoxy-6-methoxymethyltetrahydropyran-2-yl)]dimethylvinylsilane (16). *n*-BuLi (0.44 mL of a 2.3 M solution in THF, 1.01 mmol) was added dropwise to a solution of furan **7** (0.20 g, 0.78 mmol) in THF (3.9 mL) at -78 °C. The reaction was stirred for 3.5 h and freshly distilled chlorodimethylvinylsilane (0.13 g, 1.09 mmol) was added in one portion. The reaction was stirred for 45 min and quenched by addition of saturated NaHCO₃ (3 mL). The organic layer was separated and washed with brine (3 mL), dried (MgSO₄), and concentrated. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc (4:1) to furnish 0.22 g (88%) of vinyl silane **16** as a pale yellow oil. ¹H NMR (500 MHz) δ 6.53 (d, *J* = 3.0 Hz, 1 H), 6.26 (d, *J* = 3.0 Hz, 1 H), 6.19 (dd, *J* = 20.2, 14.7 Hz, 1 H), 6.00 (dd, *J* = 14.7, 3.6 Hz, 1 H), 5.74 (dd, *J* = 20.2, 3.6 Hz, 1 H), 4.44 (dd, *J* = 11.8, 1.8 Hz, 1 H), 3.65 (dd, *J* = 10.8, 2.0 Hz, 1 H), 3.59 (dd, *J* = 10.6, 4.6 Hz, 1 H), 3.54 (s, 3 H), 3.45 (s, 3 H), 3.41-3.35 (m, 2 H), 3.37 (s, 3 H), 3.15 (dd, *J* = 9.5, 8.5 Hz, 1 H), 2.34 (ddd, *J* = 13.0, 5.5, 2.0 Hz, 1 H), 1.78 (app q, *J* = 11.5 Hz, 1 H), 0.29 (s, 6 H); ¹³C NMR (125 MHz) δ 158.0, 157.9, 136.6, 133.2, 121.2, 107.1, 82.5, 79.8, 79.3, 71.8, 71.3, 60.6, 59.3, 57.1, 34.5, -3.3; IR (NaCl film) 3050, 2929, 2831, 1593, 1112 cm⁻¹; MS (CI) *m/z* 340, 309 (base), 235; HRMS (CI) *m/z* 340.1716 [C₁₇H₂₈O₅Si (M) requires 340.1706].

2-([5-(4,5-Dimethoxy-6-methoxymethyltetrahydropyran-2-yl)]dimethylsilanyl)ethanol (17). 9-BBN (10.2 mL of a 0.5 M solution in THF, 5.11 mmol) was added to a solution of vinyl silane **16**

(1.16 g, 3.41 mmol) dissolved in THF (5 mL) at ambient temperature. The solution was stirred for 12 h and then 6 mL of 3 N NaOH was added dropwise followed by 2 mL of 30% H₂O₂. The mixture was stirred for 45 min and the aqueous layer was separated, the organic layer was washed with brine (10 mL), dried (MgSO₄), and concentrated. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc (2:3) to afford 1.08 g (88%) of alcohol **17** as a colorless oil. ¹H NMR (250 MHz) δ 6.54 (d, *J* = 3.2 Hz, 1 H), 6.27 (d, *J* = 3.2 Hz, 1 H), 4.45 (dd, *J* = 11.9, 1.8 Hz, 1 H), 3.78-3.72 (m, 2 H), 3.67 (dd, *J* = 10.6, 2.1 Hz, 1 H), 3.60 (dd, *J* = 10.6, 4.4 Hz, 1 H), 3.55 (s, 3 H), 3.46 (s, 3 H), 3.45-3.34 (m, 2 H), 3.38 (s, 3 H), 3.16 (dd, *J* = 9.4, 8.9 Hz, 1 H), 2.35 (ddd, *J* = 12.9, 4.9, 1.9 Hz, 1 H), 1.79 (dt, *J* = 12.8, 11.7 Hz, 1 H), 1.19-1.11 (m, 2 H), 0.25 (s, 6 H); ¹³C NMR (62.5 MHz) δ 158.2, 157.9, 121.0, 107.1, 82.4, 79.9, 79.2, 71.7, 71.2, 60.5, 59.6, 59.3, 57.1, 34.4, 20.6, -3.0; IR (NaCl film) 3443, 2926, 1112 cm⁻¹; MS (CI) *m/z* 358, 327, 313 (base); HRMS (CI) *m/z* 358.1795 [C₁₇H₃₀O₆Si (M) requires 358.1811].

[2-(2,6-Dichloro-4-methoxyphenoxy)ethyl]-[5-(4,5-dimethoxy-6-methoxymethyltetrahydropyran-2-yl)furan-2-yl]dimethylsilane (18). Alcohol **17** (0.35 g, 0.97 mmol), 2,6-dichloro-4-methoxyphenol (**9**) (0.37 g, 1.95 mmol) and PPh₃ (0.33 g, 1.27 mmol) were dissolved in THF (3.3 mL) and DIAD (0.25 g, 1.27 mmol) was added dropwise. The solution was heated to reflux for 1 h and then cooled and concentrated. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc (4:1) to afford 0.39 g (75%) of aryl ether **18** as a pale orange oil. ¹H NMR (250 MHz) δ 6.82 (s, 2 H), 6.56 (d, *J* = 3.2 Hz, 1 H), 6.28 (d, *J* = 3.2 Hz, 1 H), 4.45 (dd, *J* = 12.0, 1.8 Hz, 1 H), 4.10-4.02 (m, 2 H), 3.75 (s, 3 H), 3.68 (dd, *J* = 10.6, 2.1 Hz, 1 H), 3.62 (dd, *J* = 10.6, 4.4 Hz, 1 H), 3.56 (s, 3 H), 3.51-3.36 (m, 2 H), 3.47 (s, 3 H), 3.39 (s, 3 H), 3.17 (app t, *J* = 9.2 Hz, 1 H), 2.36 (ddd, *J* = 12.8, 4.7, 2.1 Hz, 1 H), 1.79 (dt, *J* = 12.7, 11.5 Hz, 1 H), 1.50-1.41 (m, 2 H), 0.30 (s, 6 H); ¹³C NMR (62.5 MHz) δ 158.0, 157.9, 155.5, 145.3, 129.7, 121.1, 114.4, 107.1, 82.5, 79.8, 79.2, 71.7, 71.2, 71.1, 60.6, 59.3, 57.0, 55.9, 34.5, 17.4, -3.0; IR (NaCl film) 2930, 1557, 1110, 1043 cm⁻¹; MS (CI) *m/z* 531, 501, 281 (base); HRMS (CI) *m/z* 531.1358 [C₂₄H₃₃O₇SiCl₂ (M-H) requires 531.1372].

Cycloadduct (19). Furan **18** (34 mg, 65 μ mol) was dissolved in Et₂O (1.0 mL) and the solution was cooled to -95 °C with an Et₂O/Liquid N₂ bath. *t*-BuLi (63 μ L of a 1.56 M solution in pentane, 97 μ mol) was added dropwise and the bath temperature was maintained below -90 °C for 15 min and then allowed to slowly warm to -10 °C. The reaction was quenched by addition of saturated aqueous NaHCO₃.

(2 mL) and the mixture was extracted with EtOAc (2 x 3 mL). The combined extracts were dried (MgSO₄) and concentrated. The residue was purified by flash chromatography on silica gel eluting with hexanes/EtOAc (65:35) to afford 26 mg (81%) of cycloadduct **19** as a colorless oil. ¹H NMR (250 MHz) δ 7.05 (d, *J* = 5.2 Hz, 1 H), 6.98 (d, *J* = 5.4 Hz, 1 H), 6.93 (d, *J* = 5.3 Hz, 1 H), 6.98 (d, *J* = 5.4 Hz, 1 H), 6.58 (s, 2 H), 4.64-4.50 (m, 3 H), 4.26 (d, *J* = 11.8 Hz, 1 H), 3.99-3.80 (m, 2 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.70-3.60 (m, 4 H) 3.57 (s, 3 H), 3.56 (s, 3 H), 3.48-3.35 (m, 4 H), 3.45 (s, 3 H), 3.42 (s, 3 H), 3.41 (s, 3 H), 3.34 (s, 3 H), 3.17 (t, *J* = 9.0 Hz, 1 H), 3.10 (t, *J* = 9.0 Hz, 1 H), 2.37-2.15 (m, 2 H), 1.73 (app q, *J* = 12.2 Hz, 1 H), 1.66-1.42 (m, 3 H), 1.15-1.00 (m, 2 H), 0.36 (s, 6 H), 0.23 (s, 3 H), 0.21 (s, 3 H); MS (CI) *m/z* 496 (base), 465, 437; HRMS (CI) *m/z* 496.1694 [C₂₄H₃₃O₇SiCl (M) requires 496.1684].

7-Chloro-4-(4(*R*),5(*S*)-dimethoxy-6(*R*)-methoxymethyltetrahydropyran-2(*R*)-yl)-5,8-dimethoxynaphthalen-1-ol (14). A solution of TBAF (0.16 mL of a 1.0 M solution in THF, 0.16 mmol) was added to a solution of cycloadduct **19** (26 mg, 52 μ mol) in DMF (1.0 mL) and heated to 70 °C for 30 min. The solution was then cooled, brine (3 mL) and EtOAc (3 mL) were added, and the solution was vigorously stirred. The organic layer was separated, dried (MgSO₄), and concentrated. The residue was purified by flash chromatography on silica gel eluting with hexanes/EtOAc (1:4) to provide 17 mg (80%) of phenol **14** as a colorless oil. ¹H NMR (250 MHz) δ 7.08-6.98 (m, 3 H), 6.83 (d, *J* = 5.5 Hz, 1 H), 6.59 (s, 1 H), 6.57 (s, 1 H), 5.91 (d, *J* = 1.7 Hz, 2 H), 5.24 (br s, 2 H), 4.61 (d, *J* = 11.3 Hz, 1 H), 4.41 (d, *J* = 11.9 Hz, 1 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.69-3.39 (m, 8 H), 3.55 (s, 3 H), 3.54 (s, 3 H), 3.44 (s, 3 H), 3.40 (s, 3 H), 3.39 (s, 3 H), 3.28 (s, 3 H), 3.05 (app t, *J* = 9.1 Hz, 1 H), 2.99 (app t, *J* = 9.1 Hz, 1 H), 2.26-2.21 (m, 1 H), 2.21-2.15 (m, 1 H), 1.78-1.55 (m, 2 H); MS (CI) *m/z* 413, 412 (base); HRMS (CI) *m/z* 413.1375 [C₂₀H₂₆ClO₇ (MH) requires 413.1367].