Solvent-Dependent Divergent Functions of Sc(OTf)$_3$

in Stereoselective Epoxide-Opening Spiroketalizations

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A. Supplementary Figure S1–S2

Figure S1. Proposed mechanism for formation of benzylidene-dihydrofuranone S3 during the Sc(OTf)3-mediated equilibration reaction in CH2Cl2.

Figure S2. Diversification of 4-bromo-substituted exo-glycal 4h and subsequent TBS deprotection and epoxidation.
**B. COMPLETE DATA ON SPIROCYCLIZATION OF exo-GLYCAL EPOXIDE 6a**

**Table S1. Spirocyclization reactions of exo-glycal epoxide 6a.**

| entry | Table 1 entry | reagent (equiv) | solvent, T (°C) | 7a:8a |
|-------|--------------|----------------|----------------|-------|
| 1     | 1            | MeOH (excess)  | MeOH, rt       | no reaction |
| 2     | 2            | Ti(OiPr)4 (2.0) | CH2Cl2, rt     | no reaction |
| 3     | 3            | –              | toluene, 120   | no reaction |
| 4     |              | Yb(OTf)3 (2.0) | CH2Cl2, –78 → 0 | 60:40 |
| 5     |              | La(OTf)3 (2.0) | CH2Cl2, –78 → 0 | 65:35 |
| 6     |              | In(OTf)3 (2.0) | CH2Cl2, –78 → 0 | 55:45 |
| 7     |              | Zn(OTf)2 (2.0) | CH2Cl2, –78 → 0 | 65:35 |
| 8     |              | AgOTf (2.0)    | CH2Cl2, –78 → 0 | 64:36 |
| 9     |              | Bu3BOTf (2.0)  | CH2Cl2, –78 → 0 | decomposition |
| 10    |              | TMSOTf (2.0)   | CH2Cl2, –78 → 0 | decomposition |
| 11    | 4            | Sc(OTf)3 (2.0) | CH2Cl2, –78 → 0 | 75:25 |
| 12    | 5            | Sc(OTf)3 (2.0) | 1:1 CH2Cl2/THF, –78 → 0 | 95:5 |
| 13    | 6            | Sc(OTf)3 (1.0) | THF, –78 → 0   | 93:7 |
| 14    | 7            | Sc(OTf)3 (0.1) | THF, –78 → 0   | >98:2 |
| 15    | 8            | Sc(OTf)3 (1.0) | THF, –78 → rt  | >98:2 |
| 16    | 9            | Sc(OTf)3 (1.0) | THF, –78 → rt  | >98:2 |
| 17    | 17           | Sc(OTf)3 (1.0) | THF, –20       | >98:2 |
| 18    | 10           | Sc(OTf)3 (1.0) | THF, rt        | 90:10 |
| 19    | 19           | Yb(OTf)3 (2.0) | THF, –78 → rt  | 69:31 |
| 20    | 20           | In(OTf)3 (2.0) | THF, –78 → rt  | 38:62 |
| 21    | 21           | Fe(OTf)3 (2.0) | THF, –78 → rt  | 60:40 |
| 22    | 22           | Ce(OTf)3 (2.0) | THF, –78 → rt  | 33:67 |
| 23    | 23           | Sm(OTf)3 (2.0) | THF, –78 → rt  | 70:30 |
| 24    | 24           | Bi(OTf)3 (2.0) | THF, –78 → rt  | 66:34 |
| 25    | 25           | BF3·OEt 2 (2.0) | THF, –78 → rt | 82:18 |
| 26    | 26           | TiCl4 (2.0)    | THF, –78 → rt  | 92:8 |
| 27    | 27           | Sc(OTf)3 (2.0) | CH2Cl2, 0 → rt | <2:98 |
| 28    | 28           | Sc(OTf)3 (1.0) | CH2Cl2, 0 → rt | <2:98 |
| 29    | 11           | Sc(OTf)3 (0.5) | CH2Cl2, 0 → rt | <2:98 |
| 30    | 12           | Sc(OTf)3 + DTBMP (1.0 + 1.0) | THF, –20 | >98:2 |
| 31    | 13           | ScCl3 (1.0)    | THF, rt        | >98:2 |
| 32    | 14           | TfOH (1.0)     | THF, –20       | 30:70 |
| 33    | 15           | Sc(OTf)3 + DTBMP (0.5 + 0.5) | CH2Cl2, 0 → rt | 75:25 |
| 34    | 16           | TfOH (2.0)     | CH2Cl2, 0 → rt | <2:98 |
| 35    | 17           | TfOH (0.5)     | CH2Cl2, 0 → rt | <2:98 |
| 36    | 18           | TfOH + DTBMP (0.5 + 0.5) | CH2Cl2, 0 → rt | 51:49 |

*Product ratios determined by 1H-NMR analysis of crude reaction products. DTBMP = 2,6-di-tert-butyl-4-methylpyridine.
C. MATERIALS AND METHODS

Reagents were obtained from Aldrich Chemical (www.sigma-aldrich.com), Strem (www.strem.com), or Acros Organics (www.fishersci.com) and used without further purification unless otherwise indicated. Solvents (Optima grade) were obtained from Fisher Scientific (www.fishersci.com), degassed with Ar, and purified on a solvent drying system as described\(^1\) unless otherwise indicated. Dimethyldioxirane (DMDO) was prepared as described\(^2\) and the stock solution in acetone was stored over activated 4 Å molecular sieves at –80 °C.\(^3\) All reactions were performed in flame-dried glassware under positive Ar pressure with magnetic stirring unless otherwise noted. Liquid reagents and solutions were transferred thru rubber septa via syringes flushed with Ar prior to use. Cold baths were generated as follows: 0 °C, wet ice/water; –42 °C, dry ice/acetonitrile; –78 °C, dry ice/acetone.

TLC was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate (KMnO\(_4\)), cerium ammonium molybdenate (CAM). Silica flash chromatography was performed on E. Merck 230–400 mesh silica gel 60. Preparative scale HPLC purification was carried out on a Waters 2545 HPLC with 2996 diode array detector using an Xbridge Prep C18 5 mm column (10 x 150 mm) using a flow rate of 5.0 mL/min and a gradient of 15–40% CH\(_3\)CN in H\(_2\)O over 9 min with UV detection at 254 nm.

Melting point determinations were performed on an Electrothermal 9100 apparatus and are uncorrected (benzoic acid, lit. 121.5 °C, found 122.2–124.8°C). Optical rotations were recorded on a JASCO model P-1020 digital polarimeter with PTC-103T temperature controller. IR spectra were recorded on a Bruker Optics Tensor 27 FTIR spectrometer with peaks reported in cm\(^{-1}\). NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz Avance III NMR or Bruker UltraShield Plus 600 MHz Avance III NMR with DCH CryoProbe at 24 °C in CDCl\(_3\) unless otherwise indicated. Chemical shifts are expressed in ppm relative to TMS (\(^1\)H, 0 ppm) or solvent signals: CDCl\(_3\) (\(^1\)H, 77.0 ppm), CD\(_2\)OD (\(^1\)H, 3.31 ppm; \(^1\)C, 49.048 ppm); coupling constants are expressed in Hz. NMR spectra were processed using Bruker TopSpin or Mnova (www.mestrelab.com/software/mnova-nmr) software. Mass spectra were obtained at the MSKCC Analytical Core Facility on a Waters Acquity SQD LC-MS by electrospray (ESI) ionization or atmospheric pressure chemical ionization (AP-CI). High resolution mass spectra were obtained on a Waters Acquity Premier XE TOF LC-MS by electrospray ionization. X-ray crystallography analysis was carried out at the University of Toledo Instrumentation Center on a Siemens Smart CCD System (http://www.utoledo.edu/nsm/ic/index.html). Crystal structures were visualized using CCDC Mercury software (http://www.ccdc.cam.ac.uk/products/mercury/).

N.B.: Atom numbers used in the text of the article and Supporting Information correspond to the standard carbohydrate numbering system and not to IUPAC nomenclature, which was used solely to name each compound. Compounds not cited in the paper are numbered herein from S1.

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(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518–1520.
(2) Adam, W.; Chan, Y.-Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. J. Org. Chem. 1987, 52, 2800–2803.
(3) Stachel, S. J.; Danishefsky, S. J. Tetrahedron Lett. 2001, 42, 6785–6787.
D. SYNTHESIS OF PROPARGYL ALCOHOLS 2a–h

GENERAL PROCEDURE FOR ALKYNE ADDITION TO SALICYLALDEHYDES

The TBS-protected alkyne (2.5 equiv, commercially available or prepared as previously described) was dissolved in THF (0.2 M) and the solution was cooled to −78 °C. Then, n-BuLi (2.5 equiv, 1.6 M in hexanes) was added dropwise and stirred for 45 min. A precooled (−78 °C) solution of the salicylaldehyde 1 (1.0 equiv) in THF (0.5 M) was added dropwise and stirred for 90 min. The mixture was quenched with satd aq NH₄Cl and the aq layer was separated and extracted with EtOAc. The combined extracts were washed with brine, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography afforded the propargyl alcohols 2a–h.

2-(5-(tert-butyldimethylsilyloxy)-1-hydroxypent-2-ynyl)phenol (2a). Prepared from (but-3-yn-1- yloxy)tert-butyldimethylsilane and salicylaldehyde. Light yellow oil (3.9 g, 77%). TLC: Rᵣ 0.34 (4:1 hexanes/EtOAc). IR (NaCl, film): 3313 (O– H st), 2929, 2856, 1589, 1460, 1254, 1103 (C–O st), 985, 913, 836, 751. ¹H-NMR (600 MHz) δ 7.36 (d, J = 7.8 Hz, 1H), 7.22 (td, J = 7.8, 1.7 Hz, 1H), 6.88 (t, J = 7.7 Hz, 2H), 5.64 (s, 1H), 3.76 (t, J = 6.9 Hz, 2H), 3.02 (s, 1H), 2.51 (td, J = 6.9, 2.0 Hz, 2H), 0.89 (s, 9H), 0.07 (s, 6H). ¹³C-NMR (151 MHz) δ 155.2, 130.0, 128.3, 127.7, 124.8, 120.1, 117.0, 86.3, 79.0, 64.1, 61.6, 25.9, 23.2, 18.3, −5.3. ESI-MS m/z (rel int): (pos) 329.1 ([M+Na]+, 100); (neg) 305.1 ([M–H]−, 100).

2-(6-(tert-butyldimethylsilyloxy)-1-hydroxyhex-2-ynyl)phenol (2b). Prepared from (pent-4-yn-1-yloxy)tert-butyldimethylsilane and salicylaldehyde. Light yellow oil (1.94 g, 75%). TLC: Rᵣ 0.42 (4:1 hexanes/EtOAc). IR (NaCl, film): 3332 (O– H st), 2929, 2856, 1489, 1458, 1361, 1254, 1103 (C–O st), 835, 776, 753. ¹H-NMR (500 MHz) δ 7.45 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 6.92–6.85 (m, 2H), 6.65 (s, 1H), 5.85 (s, 1H), 3.76 (t, J = 6.1 Hz, 2H), 2.45 (td, J = 7.3, 2.2 Hz, 2H), 1.80 (d, J = 6.6 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ¹³C-NMR (126 MHz) δ 155.0, 130.4, 128.6, 123.1, 120.2, 117.0, 91.2, 77.3, 75.1, 68.2, 61.5, 31.5, 25.9, 18.3, 15.4, −5.4. ESI-MS m/z (rel int): (pos) 343.2 ([M+Na]+, 100); (neg) 319.2 ([M–H]−, 100).

2-(6-(tert-butyldimethylsilyloxy)-1-hydroxyhept-2-ynyl)phenol (2c). Prepared from (hex-5-yn-1-yloxy)tert-butyldimethylsilane and salicylaldehyde. Light yellow oil (5.72 g, 78%). TLC:

(4) Cleary, L.; Yoo, H.; Shea, K. J. Org. Lett. 2011, 13, 1781–1783.
Rf 0.45 (4:1 hexanes/EtOAc). IR (NaCl, film): 3332 (O–H st), 1489, 1458, 1361, 1254, 1103 (C–O st), 835, 776, 753. $^1$H-NMR (500 MHz) $\delta$ 7.62–7.58 (m, 1H), 7.34 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.21 (td, $J = 7.8$, 1.8 Hz, 1H), 6.88 (ddd, $J = 7.5$, 3.6, 2.3 Hz, 2H), 5.64 (s, 1H), 3.64 (t, $J = 5.9$ Hz, 2H), 3.41 (s, 1H), 2.31 (td, $J = 6.8$, 2.3 Hz, 2H), 1.62 (tddd, $J = 9.5$, 4.3, 2.6 Hz, 5H), 0.90 (d, $J = 2.6$ Hz, 10H), 0.07 (s, 6H). $^{13}$C-NMR (126 MHz) $\delta$ 155.2, 129.9, 127.7, 125.2, 120.1, 116.9, 89.0, 78.4, 62.8, 31.9, 26.0, 24.9, 18.7, 18.4, –5.24. ESI-MS m/z (rel int): (pos) 357.2 ([M+Na]$^+$, 100); (neg) 333.2 ([M–H]$^-$, 100).

2-(5-(tert-butyldimethylsilyloxy)-1-hydroxypent-2-ynyl)-4-nitrophenol (2d). Prepared from (but-3-yn-1-yl)oxy)tert-butyldimethylsilane and 5-nitrosalicylaldehyde. Yellow oil (955 mg, 91%). TLC: $R_f$ 0.36 (4:1 hexanes/EtOAc). IR (NaCl, film): 3332 (OH st), 1522 (N–O), 1489, 1458, 1361, 1338 (N–O), 1254, 1103 (C–O st), 835, 776, 753. $^1$H-NMR (500 MHz) $\delta$ 8.55 (s, 1H), 8.26 (d, $J = 2.7$ Hz, 1H), 8.12 (dd, $J = 9.0$, 2.8 Hz, 1H), 6.96 (d, $J = 9.0$ Hz, 1H), 5.73 (s, 1H), 3.79 (t, $J = 6.8$ Hz, 2H), 3.49 (d, $J = 4.9$ Hz, 1H), 2.54 (td, $J = 6.8$, 2.0 Hz, 2H), 0.89 (s, 9H), 0.08 (s, 6H). $^{13}$C-NMR (126 MHz) $\delta$ 161.3, 140.8, 126.0, 125.0, 124.1, 117.6, 87.8, 78.0, 63.8, 61.5, 25.9, 23.2, 18.4, –5.30. HRMS m/z calcd for C$_{17}$H$_{24}$NO$_4$Si ([M–H]$^-$) 350.1424; found 350.1429.

2-(5-((tert-butyldimethylsilyl)oxy)-1-hydroxypent-2-yn-1-yl)-4-methoxyphenol (2e). Prepared from (but-3-yn-1-yl)oxy)tert-butyldimethylsilane and 5-methoxysalicylaldehyde. Light yellow oil (890 mg, 81%, >98% purity). TLC: $R_f$ 0.32 (4:1 hexanes/EtOAc). IR (NaCl, film): 3332 (OH st), 1489, 1458, 1361, 1338 (N–O), 1254, 1103 (C–O st), 835, 776, 753. $^1$H-NMR (500 MHz) $\delta$ 6.92 (d, $J = 3.0$ Hz, 1H), 6.86 (s, 1H), 6.82 (d, $J = 8.8$ Hz, 1H), 6.77 (dd, $J = 8.8$, 3.0 Hz, 1H), 5.60 (s, 1H), 3.78–3.72 (m, 5H), 2.95 (s, 1H), 2.51 (td, $J = 6.0$, 2.1 Hz, 2H), 0.89 (s, 9H), 0.07 (s, 6H). $^{13}$C-NMR (126 MHz) $\delta$ 153.1, 148.9, 125.8, 117.8, 114.9, 113.4, 86.3, 79.1, 63.9, 61.7, 55.8, 25.9, 23.2, 18.4, –5.3. HRMS m/z calcd for C$_{18}$H$_{28}$O$_4$SiNa ([M+Na]$^+$) 359.1655; found 359.1671.

2-(5-((tert-butyldimethylsilyl)oxy)-1-hydroxypent-2-yn-1-yl)-4-methylphenol (2f). Prepared from (but-3-yn-1-yl)oxy)tert-butyldimethylsilane and 5-methylsalicylaldehyde. Light Yellow oil (1.45 g, 88%). TLC: $R_f$ 0.34 (4:1 hexanes/EtOAc). IR (NaCl, film): 3332 (OH st), 1489, 1458, 1361, 1254, 1103 (C–O st), 835, 776, 753. $^1$H-NMR (500 MHz) $\delta$ 7.09 (dd, $J = 15.1$, 4.0 Hz, 2H), 7.01 (dt, $J = 8.2$, 2.0 Hz, 1H), 6.78 (dd, $J = 8.1$, 1.8 Hz, 1H), 5.60 (s, 1H), 2.86 (s, 1H), 2.55–2.45 (m, 2H), 2.27 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H). $^{13}$C-NMR
(126 MHz) δ 152.9, 130.4, 130.3, 129.4, 128.1, 124.6, 116.9, 79.3, 64.2, 64.1, 61.7, 25.9, 23.3, 20.5, 18.4, −5.27. **HRMS** m/z calcd for C_{18}H_{28}O_{3}SiNa ([M+Na]^+) 343.1705; found 343.1715.

5-bromo-2-(5-((tert-butyldimethylsilyl)oxy)-1-hydroxypent-2-yn-1-yl)phenol (2g). Prepared from (but-3-yn-1-yloxy)tert-butyldimethylsilane and 4-bromosalicylaldehyde. Yellow oil (920 mg, 96%). **TLC**: R_f 0.36 (4:1 hexanes/EtOAc). The compound was not stable and immediately advanced to the next step for Au(I)-mediated cycloisomerization.

4-bromo-2-(5-((tert-butyldimethylsilyl)oxy)-1-hydroxypent-2-yn-1-yl)phenol (2h). Prepared from (but-3-yn-1-yloxy)tert-butyldimethylsilane and 5-bromosalicylaldehyde. Yellow oil (3.5 g, 91%). **TLC**: R_f 0.36 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3332 (OH st), 1489, 1458, 1361, 1254, 1103 (C–O st), 835, 776, 753. **1H-NMR** (500 MHz) δ 7.47 (s, 1H), 7.44 (dd, J = 2.4, 0.7 Hz, 1H), 7.31 (dd, J = 8.6, 2.5 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 5.60 (s, 1H), 3.77 (t, J = 6.9 Hz, 2H), 3.10 (s, 1H), 2.52 (td, J = 6.8, 2.0 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 6H). **13C-NMR** (126 MHz) δ 154.4, 132.6, 130.3, 126.7, 119.0, 112.0, 87.0, 78.5, 77.3, 63.6, 61.6, 25.9, 25.9, 23.2, 18.4, −5.3. **HRMS** m/z calcd for C_{17}H_{25}O_{3}BrSiNa ([M+Na]^+) 407.0654; found 407.0649.
E. SYNTHESIS OF \textit{exo}-GLYCALs 3a–h

\textbf{GENERAL PROCEDURE FOR AU(I)-MEDIATED CYCLOISOMERIZATION}

The propargyl alcohol 2 (1.0 equiv) was dissolved in acetonitrile (0.05 M). Powdered K$_2$CO$_3$ (1.0 equiv) was added and the solution was stirred for 5 min at rt. AuCl (0.05 equiv) was added and the reaction was stirred for 2–4 h. The solution was filtered through a plug of silica gel with EtOAc and concentrated by rotary evaporation to afford the crude product. Purification by silica gel flash chromatography afforded the \textit{exo}-glycal 3a–h.

\begin{align*}
(Z)-2-(3-(\text{tert}-\text{butyldimethylsilyloxy})\text{propylidene})\text{-2,3-dihydrobenzofuran-3-ol} & (3a). \text{ Prepared from 2a. Yellow oil (810 mg, 63\%). TLC: } R_f 0.46 (4:1 \text{hexanes/EtOAc}). \text{ IR (NaCl, film): 3351 (O–H st), 2928, 2856, 1614, 1600, 1466, 1288, 1254, 1189 1091 (C–O st), 1016, 835, 776, 750. 1H-NMR (600 MHz): } \delta 7.47–7.41 (m, 1H), 7.29 (td, \text{J} = 7.6, 1.4 \text{ Hz}, 1H), 7.02 (td, \text{J} = 7.5, 0.9 \text{ Hz}, 1H), 6.95 (d, \text{J} = 8.1 \text{ Hz}, 1H), 5.59 (s, 1H), 5.15 (td, \text{J} = 7.4, 1.6 \text{ Hz}, 1H), 3.71 (t, \text{J} = 6.8 \text{ Hz}, 2H), 2.63–2.38 (m, 2H), 1.98 (s, 1H), 0.70 (s, 9H), 0.07 (s, 6H). 13C-NMR (151 MHz) \delta 157.8, 157.5, 130.5, 128.3, 127.8, 125.6, 122.2, 110.2, 102.9, 70.9, 62.6, 29.1, 26.0, 18.4, -5.2. \text{ ESI-MS m/z (rel int): (pos) 329.1 ([M+Na]+, 100); (neg) 305.1 ([M–H]–, 100).}

(Z)-2-(4-(\text{tert}-\text{butyldimethylsilyloxy})\text{butylidene})\text{-2,3-dihydrobenzofuran-3-ol} (3b). \text{ Prepared from 2b. Yellow oil (313 mg, 59\%). TLC: } R_f 0.56 (4:1 \text{hexanes/EtOAc}). \text{ IR (NaCl, film): 3367 (O–H st), 2928, 2856, 1614, 1600, 1466, 1287, 1253, 1138 1095 (C–O st), 1017, 902, 835, 775, 750. 1H-NMR (500 MHz): } \delta 7.42 (d, \text{J} = 7.5 \text{ Hz}, 1H), 7.30–7.25 (m, 1H), 7.01 (t, \text{J} = 7.4 \text{ Hz}, 1H), 6.70 (d, \text{J} = 8.1 \text{ Hz}, 1H), 5.56 (d, \text{J} = 9.0 \text{ Hz}, 1H), 5.09 (td, \text{J} = 7.6, 1.6 \text{ Hz}, 1H), 3.67 (t, \text{J} = 6.4 \text{ Hz}, 2H), 2.34 (dp, \text{J} = 17.8, 7.3 \text{ Hz}, 2H), 2.05 (d, \text{J} = 9.0 \text{ Hz}, 1H), 1.66 (dt, \text{J} = 16.5, 8.3 \text{ Hz}, 2H), 0.90 (d, \text{J} = 1.2 \text{ Hz}, 9H), 0.06 (s, 6H). 13C-NMR (126 MHz) \delta 157.6, 156.9, 130.4, 127.7, 125.6, 122.1, 110.3, 106.4, 106.3, 70.9, 70.8, 62.7, 32.6, 26.0, 25.9, 21.7, 18.4, -5.2. \text{ ESI-MS m/z (rel int): (pos) 343.1 ([M+Na]+, 100); (neg) 319.2 ([M–H]–, 100).}
(Z)-2-(6-((tert-butyldimethylsilyl)oxy)hexylidene)-2,3-dihydrobenzofuran-3-ol (3c). Prepared from 2c. Yellow oil (1.0 g, 65%). **TLC:** *R*<sub>t</sub> 0.60 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3367 (O–H st), 2928, 2856, 1614, 1600, 1466, 1287, 1253, 1138 1095 (C–O st), 1017, 902, 835, 775, 750. **<sup>1</sup>H-NMR** (500 MHz): δ 7.42 (d, *J* = 7.4 Hz, 1H), 7.31–7.23 (m, 1H), 7.01 (td, *J* = 7.5, 1.7 Hz, 1H), 5.60–5.50 (m, 1H), 5.07 (td, *J* = 7.5, 1.7 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.39–2.21 (m, 2H), 2.16 (d, *J* = 7.9 Hz, 1H), 1.63–1.55 (m, 2H), 1.54–1.44 (m, 2H), 0.90 (s, 10H), 0.05 (s, 6H). **13C-NMR** (126 MHz) δ 157.6, 156.8, 130.4, 127.8, 125.6, 122.1, 110.2, 106.7, 70.8, 63.0, 32.4, 26.0, 25.7, 25.0, 18.4, –5.24. **ESI-MS** *m/z* (rel int): (pos) 357.2 ([M+Na]<sup>+</sup>, 100); (neg) 333.2 ([M–H]<sup>−</sup>, 100).

(Z)-2-(3-((tert-butyldimethylsilyl)oxy)propylidene)-5-nitro-2,3-dihydrobenzofuran-3-ol (3d). Prepared from 2d. Yellow oil (490 mg, 52%). **TLC:** *R*<sub>t</sub> 0.45 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3367 (O–H st), 2928, 2856, 1614, 1600, 1522 (N–O), 1466, 1324 (N–O), 1287, 1253, 1138 1095 (C–O st), 1017, 902, 835, 775, 750. **<sup>1</sup>H-NMR** (500 MHz): δ 8.35 (s, 1H), 8.26 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 1H), 5.67 (d, *J* = 8.3 Hz, 1H), 5.31 (td, *J* = 7.5, 1.7 Hz, 1H), 3.72 (t, *J* = 6.6 Hz, 2H), 2.59–2.46 (m, 2H), 2.31 (d, *J* = 8.5 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H). **13C-NMR** (126 MHz) δ 162.1, 157.3, 143.2, 129.0, 127.4, 122.3, 110.5, 106.0, 77.2, 69.7, 62.2, 29.1, 25.9, 18.4, –5.2. **HRMS** *m/z* calcd for C<sub>17</sub>H<sub>25</sub>NO<sub>5</sub>SiNa ([M+Na]<sup>+</sup>) 374.1405; found 374.1400.

(Z)-2-(3-((tert-butyldimethylsilyl)oxy)propylidene)-5-methoxy-2,3-dihydrobenzofuran-3-ol (3e). Prepared from 2e. Yellow oil (520 mg, 61%). **TLC:** *R*<sub>t</sub> 0.47 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3351 (O–H st), 2928, 2856, 1614, 1600, 1466, 1288, 1254, 1189 1091 (C–O st), 1016, 835, 776, 750. **<sup>1</sup>H-NMR** (500 MHz) δ 6.96 (dd, *J* = 2.5, 1.1 Hz, 1H), 6.87–6.77 (m, 2H), 5.53 (d, *J* = 8.6 Hz, 1H), 5.08 (tt, *J* = 7.6, 1.4 Hz, 1H), 3.76 (s, 3H), 3.72–3.66 (m, 2H), 2.55–2.39 (m, 2H), 2.35 (dd, *J* = 9.1, 1.5 Hz, 1H), 0.90 (d, *J* = 1.2 Hz, 9H), 0.07 (s, 6H). **13C-NMR** (126 MHz) δ 158.4, 155.2, 151.6, 128.3, 116.5, 110.5, 102.4, 71.3, 62.6, 56.0, 29.1, 26.0, 25.9, 18.4, –5.2. **HRMS** *m/z* calcd for C<sub>18</sub>H<sub>28</sub>O<sub>4</sub>SiNa ([M+Na]<sup>+</sup>) 359.1655; found 359.1658.
(Z)-2-(3-((tert-butyl(dimethyl)silyl)oxy)propylidene)-5-methyl-2,3-dihydrobenzofuran-3-ol (3f). Prepared from 2f. Yellow oil (740 mg, 62%). TLC: R<sub>f</sub> 0.47 (4:1 hexanes/EtOAc). IR (NaCl, film): 3351 (O– H st), 2928, 2856, 1614, 1600, 1466, 1288, 1254, 1189 1091 (C–O st), 1016, 835, 776, 750. <sup>1</sup>H-NMR (500 MHz) δ 7.24–7.18 (m, 1H), 7.07 (dd, J = 8.3, 1.8 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 5.52 (d, J = 4.5 Hz, 1H), 5.10 (td, J = 7.5, 1.6 Hz, 1H), 3.70 (s, 3H), 2.49 (ddt, J = 19.8, 14.2, 7.3, 1.3 Hz, 2H), 2.32 (s, 3H), 2.11 (d, J = 6.6 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H).<sup>13</sup>C-NMR (126 MHz) δ 158.2, 155.6, 131.6, 130.9, 127.6, 126.0, 109.8, 102.5, 77.3, 71.0, 62.6, 29.1, 26.0, 20.9, 18.4, –5.2. HRMS m/z calcd for C<sub>18</sub>H<sub>28</sub>O<sub>3</sub>SiNa ([M+Na]<sup>+</sup>) 343.1705; found 343.1706.

(Z)-6-bromo-2-(3-((tert-butyl(dimethyl)silyl)oxy)propylidene)-2,3-dihydrobenzofuran-3-ol (3g). Prepared from 2g. Yellow oil (610 mg, 68%). TLC: R<sub>f</sub> 0.48 (4:1 hexanes/EtOAc). IR (NaCl, film): 3351 (O– H st), 2928, 2856, 1614, 1600, 1466, 1288, 1254, 1189 1091 (C–O st), 1016, 835, 776, 750. <sup>1</sup>H-NMR (500 MHz) δ 7.29 (d, J = 7.9 Hz, 1H), 7.15 (dd, J = 8.0, 1.6 Hz, 1H), 7.12 (d, J = 1.6 Hz, 1H), 5.53 (d, J = 8.0 Hz, 1H), 5.18 (td, J = 7.4, 1.6 Hz, 1H), 3.70 (t, J = 6.7 Hz, 2H), 2.59–2.38 (m, 2H), 2.02 (d, J = 8.5 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H).<sup>13</sup>C-NMR (126 MHz) δ 158.3, 157.7, 126.9, 126.7, 125.4, 123.7, 113.9, 104.0, 77.3, 70.3, 62.4, 29.1, 26.0, 18.4, –5.23. HRMS m/z calcd for C<sub>17</sub>H<sub>25</sub>O<sub>3</sub>BrSiNa ([M+Na]<sup>+</sup>) 407.0654; found 407.0658.

(Z)-5-bromo-2-(3-((tert-butyl(dimethyl)silyl)oxy)propylidene)-2,3-dihydrobenzofuran-3-ol (3h). Prepared from 2h. Yellow oil (1.8 g, 51%). TLC: R<sub>f</sub> 0.48 (4:1 hexanes/EtOAc). IR (NaCl, film): 3351 (O– H st), 2928, 2856, 1614, 1600, 1466, 1288, 1254, 1189 1091 (C–O st), 1016, 835, 776, 750. <sup>1</sup>H-NMR (500 MHz) δ 7.58–7.51 (m, 1H), 7.39 (dd, J = 8.6, 2.1 Hz, 1H), 6.83 (d, J = 8.6 Hz, 1H), 5.57 (d, J = 8.9 Hz, 1H), 5.16 (td, J = 7.5, 1.6 Hz, 1H), 3.70 (t, J = 6.7 Hz, 2H), 2.58–2.39 (m, 2H), 2.08 (d, J = 9.0 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H).<sup>13</sup>C-NMR (126 MHz) δ 157.5, 156.6, 133.3, 129.9, 129.9, 128.7, 114.2, 111.9, 103.8, 77.3, 70.6, 62.4, 29.1, 26.0, 25.9, 18.4, –5.23. HRMS m/z calcd for C<sub>17</sub>H<sub>25</sub>O<sub>3</sub>BrSiNa ([M+Na]<sup>+</sup>) 407.0654; found 407.0643.
F. SYNTHESIS OF TIPS-PROTECTED exo-GLYCALs 4a–h

GENERAL PROCEDURE FOR TIPS PROTECTION

The exo-glycal 3 (1.0 equiv) was dissolved in CH₂Cl₂ (0.1 M) and cooled down to –78 ºC. 2,6-Lutidine (3.0 equiv) was added to the reaction mixture followed by the addition of triisopropylsilyl triflate (1.5 equiv) and then the reaction was warmed up to –50 ºC over 2 h. The reaction was quenched with a satd aq NaHCO₃ and the aq layer was separated and extracted with CH₂Cl₂. The organic layer was collected, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography afforded the TIPS-protected exo-glycals 4a–h.

(Z)-tert-butyldimethyl(3-(3-(triisopropylsilyloxy)benzofuran-2(3H)-ylidene)propoxy)silane (4a). Prepared from 3a. Yellow oil (630 mg, 83%). TLC: Rₓ 0.40 (9:1 hexanes/EtOAc). IR (NaCl, film): 2947, 2866, 1614, 1600, 1465, 1430, 1386, 1287, 1253, 1191, 1085 (C–O st), 1014, 919, 882, 835, 775, 748. ¹H-NMR (600 MHz): δ 7.36 (s, 1H), 7.24 (dd, J = 7.7, 1.4 Hz, 1H), 6.98 (td, J = 7.5, 1.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.85 (s, 1H), 5.08 (td, J = 7.4, 1.6 Hz, 1H), 3.69 (t, J = 6.8 Hz, 2H), 2.58–2.41 (m, 2H), 1.17 (ddt, J = 13.2, 8.9, 6.0 Hz, 3H), 1.11 (t, J = 6.6 Hz, 18H), 0.90 (s, 9H), 0.07 (s, 6H). ¹³C-NMR (151 MHz): δ 157.5, 157.4, 129.8, 128.3, 128.3, 125.5, 121.7, 110.2, 102.4, 71.4, 62.6, 29.1, 25.9, 18.3, 18.2, 12.9, –5.3. HRMS m/z calcd for C₂₆H₄₆O₃Si₂Na ([M+Na]⁺) 485.2883; found 485.2868.

(Z)-tert-butyldimethyl(4-(3-(triisopropylsilyloxy)benzofuran-2(3H)-ylidene)butoxy)silane (4b). Prepared from 3b. Yellow oil (384 mg, 82%). TLC: Rₓ 0.45 (9:1 hexanes/EtOAc). IR (NaCl, film): 2944, 2864, 1614, 1600, 1465, 1387, 1287, 1252, 1104 (C–O st), 881, 835, 775, 748. ¹H-NMR (500 MHz): δ 7.36 (d, J = 7.4 Hz, 1H), 7.24 (m, 1H), 6.98–6.95 (m, 1H), 6.92 (d, J = 8.1 Hz, 1H), 5.83 (s, 1H), 4.98 (d, J = 1.4 Hz, 1H), 3.66 (t, J = 6.5 Hz, 2H), 2.33 (dt, J = 7.5, 1.3 Hz, 2H), 1.67 (t, J = 6.9 Hz, 2H), 1.18–1.06 (m, 21H), 0.91 (d, J = 0.9 Hz, 9H), 0.05 (d, J = 0.9 Hz, 6H). ¹³C-NMR (151 MHz): δ 157.6, 156.7, 129.8, 128.3, 125.5, 121.7, 110.2, 105.8, 71.4, 62.7, 32.7, 26.0, 21.7, 18.2, 17.7, 13.0, –5.2. ESI-MS m/z (rel int): (pos) 499.4 ([M+Na]⁺, 100).
(Z)-tert-butylidimethyl((6-(3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)hexyl)oxy)silane (4c). Prepared from 3c. Yellow oil (1.07 g, 79%). TLC: Rf 0.50 (9:1 hexanes/EtOAc). IR (NaCl, film): 2944, 2864, 1614, 1600, 1465, 1387, 1287, 1252, 1104 (C–O st), 881, 835, 775, 748. 1H-NMR (500 MHz): δ 7.37 (dt, J = 7.3, 1.1 Hz, 1H), 7.23 (dd, J = 7.8, 1.4 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 5.83 (s, 1H), 4.97 (td, J = 7.5, 1.6 Hz, 1H), 3.64 (t, J = 6.4 Hz, 2H), 2.37–2.22 (m, 2H), 1.63–1.54 (m, 2H), 1.53–1.43 (m, 2H), 1.20–1.08 (m, 21H), 0.90 (s, 9H), 0.05 (s, 6H).

13C-NMR (126 MHz) δ 157.7, 156.6, 129.8, 128.4, 125.5, 121.6, 110.2, 106.2, 71.4, 63.1, 32.4, 26.0, 25.9, 25.1, 18.2, 13.0, –5.3. HRMS m/z calcd for C28H50O3Si2Na ([M+Na]+) 513.3196; found 513.3175.

(Z)-tert-butylidimethyl(3-(5-nitro-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propoxy)silane (4d). Prepared from 3d. Yellow oil (1.06 g, 88%). TLC: Rf 0.42 (9:1 hexanes/EtOAc). IR (NaCl, film): 2944, 2864, 1614, 1600, 1522 (N–O), 1465, 1386, 1324 (N–O), 1287, 1252, 1104 (C–O st), 881, 835, 775, 748. 1H-NMR (600 MHz): δ 8.27 (dd, J = 2.4, 0.9 Hz, 1H), 8.24 (dd, J = 8.9, 2.4 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 5.88 (s, 1H), 5.25 (td, J = 7.4, 1.5 Hz, 1H), 3.70 (t, J = 6.5 Hz, 2H), 2.57–2.45 (m, 2H), 1.23–1.16 (m, 3H), 1.12 (dd, J = 4.8 Hz, 18H), 0.90 (s, 9H), 0.07 (s, 6H). 13C-NMR (151 MHz) δ 157.7, 156.6, 129.8, 128.4, 125.5, 121.6, 110.4, 105.5, 70.3, 62.1, 31.6, 29.1, 25.9, 22.7, 18.3, 18.2, 18.1, 14.1, 12.9, –5.3. HRMS m/z calcd for C26H45NO5Si2Na ([M+Na]+) 530.2734; found 530.2726.

(Z)-tert-butyl(3-(5-methoxy-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propoxymethyl)silane (4e) Prepared from 3e. Yellow oil (620 g, 83%). TLC: Rf 0.41 (9:1 hexanes/EtOAc). IR (NaCl, film): 2944, 2864, 1614, 1600, 1465, 1387, 1287, 1252, 1104 (C–O st), 881, 835, 775, 748. 1H-NMR (500 MHz): δ 6.93 (d, J = 2.6 Hz, 1H), 6.87–6.76 (m, 2H), 5.83 (s, 1H), 5.04 (td, J = 7.4, 1.6 Hz, 1H), 3.77 (s, 3H), 3.68 (t, J = 6.7 Hz, 2H), 2.59–2.39 (m, 2H), 1.19–1.08 (m, 21H), 0.90 (s, 9H), 0.06 (s, 6H). 13C-NMR (126 MHz) δ 157.9, 154.9, 151.7, 129.0, 115.4, 111.0, 110.3, 102.0, 77.3, 71.9, 62.6, 56.0, 29.1, 25.9, 18.2, 13.0, –5.3. HRMS m/z calcd for C27H48O4Si2Na ([M+Na]+) 515.2989; found 515.2969.
**(Z)-**tert-butyl(dimethyl)silyl(3-(5-methyl-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propyoxy)silane (4f). Prepared from 3f. Yellow oil (790 mg, 84%). TLC: Rf 0.42 (9:1 hexanes/EtOAc). IR (NaCl, film): 2947, 2866, 1621, 1600, 1387, 1287, 1251, 1097 (C–O st), 884, 836, 775, 748. $^1$H-NMR (500 MHz): δ 7.15 (m, 1H), 7.03 (dd, J = 8.3, 1.8 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 5.80 (s, 1H), 5.05 (td, J = 7.3, 1.5 Hz, 1H), 3.69 (t, J = 6.8 Hz, 2H), 2.49 (dd, J = 6.9, 1.2 Hz, 2H), 2.31 (s, 3H), 1.19–1.13 (m, 3H), 1.11 (dd, J = 6.8, 4.4 Hz, 18H), 0.90 (s, 9H), 0.07 (s, 6H). $^{13}$C-NMR (126 MHz) δ 157.8, 155.6, 131.0, 130.3, 128.3, 125.9, 109.7, 102.1, 71.6, 62.6, 29.1, 26.0, 21.0, 18.3, 18.2, 13.0, −5.3. HRMS m/z calcd for C$_{27}$H$_{48}$O$_3$Si$_2$Na ([M+Na]$^+$) 499.3040; found 499.3023.

**(Z)-**((6-bromo-2-(3-(tert-butyl(dimethyl)silyl)oxy)propylidene)-2,3-dihydrobenzofuran-3-yl)oxy)triisopropylsilane (4g). Prepared from 3g. Yellow oil (720 mg, 85%). TLC: Rf 0.43 (9:1 hexanes/EtOAc). IR (NaCl, film): 2948, 2866, 1607, 1473, 1387, 1287, 1258, 1097 (C–O st), 881, 835, 776. $^1$H-NMR (500 MHz): δ 7.21 (d, J = 7.8 Hz, 1H), 7.13–7.06 (m, 2H), 5.77 (d, J = 1.7 Hz, 1H), 5.11 (td, J = 7.3, 1.5 Hz, 1H), 3.68 (t, J = 6.7 Hz, 2H), 2.48 (ddt, J = 13.9, 6.9, 1.3 Hz, 2H), 1.18–1.06 (m, 21H), 0.90 (s, 9H), 0.06 (s, 6H). $^{13}$C-NMR (126 MHz) δ 158.3, 157.3, 127.7, 126.5, 124.9, 123.0, 113.9, 103.5, 70.9, 62.4, 29.1, 25.9, 18.3, 18.2, 12.9, −5.28. HRMS m/z calcd for C$_{26}$H$_{45}$O$_3$Si$_2$BrNa ([M+Na]$^+$) 563.1988; found 563.1967.

**(Z)-**((5-bromo-2-(3-(tert-butyl(dimethyl)silyl)oxy)propylidene)-2,3-dihydrobenzofuran-3-yl)oxy)triisopropylsilane (4h). Prepared from 3h. Yellow oil (2.25 g, 94%). TLC: Rf 0.43 (9:1 hexanes/EtOAc). IR (NaCl, film): 2948, 2866, 1611, 1468, 1387, 1287, 1257, 1098 (C–O st), 881, 835, 776. $^1$H-NMR (600 MHz): δ 7.44 (dd, J = 2.1, 0.8 Hz, 1H), 7.35 (dd, J = 8.5, 2.1 Hz, 1H), 6.81 (d, J = 8.5 Hz, 1H), 5.81 (s, 1H), 5.10 (td, J = 7.4, 1.5 Hz, 1H), 3.68 (t, J = 6.7 Hz, 2H), 2.48 (dd, J = 14.1, 11.9, 6.9, 1.3 Hz, 2H), 1.19–1.13 (m, 3H), 1.11 (dd, J = 6.9, 4.0 Hz, 18H), 0.90 (s, 9H), 0.06 (s, 6H). $^{13}$C-NMR (151 MHz) δ 157.1, 156.5, 132.7, 130.6, 128.5, 113.7, 111.8, 103.3, 71.1, 62.4, 29.1, 25.9, 18.3, 18.2, 17.7, 12.9, 12.3, −5.3. HRMS m/z calcd for C$_{26}$H$_{45}$O$_3$Si$_2$BrNa ([M+Na]$^+$) 563.1988; found 563.1979.
G. SYNTHESIS OF 4-SUBSTITUTED exo-GLYCALs (4i–n)

(See Figure S1 for synthetic schemes from 4-bromo substituted exo-glycal 4h.)

(Z)-tert-butyl(dimethyl)[3-(5-phenyl-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propoxy]silane (4i). In a 20 mL vial equipped a magnetic stir bar, aryl bromide 4h (150.0 mg, 0.28 mmol) was dissolved in toluene under an Ar atmosphere. Subsequently, PhB(OH)₂ (68 mg, 0.56 mmol), Cs₂CO₃ (135 mg, 0.42 mmol) and Pd(Ph₃P)₄ (32 mg, 0.028 mmol, 10.0 mol%) were added and the vial was purged with Ar and sealed with a screw cap. The mixture was heated at 105 ºC for 16h. The solution was filtered through a plug of silica gel with EtOAc (100 mL) then washed with water (2x20 mL). The organic layer was collected, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (5–10% EtOAc in hexanes) afforded 4i (70% purity by 1H NMR) as a yellow oil, which was forwarded to the next step without further purification.

(Z)-tert-butyl(3-(5-(3-cyclopentylprop-1-yn-1-yl)-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propoxy)dimethylsilane (4j). In a 20 mL vial equipped a magnetic stir bar, aryl bromide 4h (150.0 mg, 0.28 mmol) was dissolved in DMF under an Ar atmosphere. Subsequently, prop-2-yn-1-ylcyclopentane (109 µL, 0.84 mmol), CuI (21 mg, 0.11 mmol, 40.0 mol%), Et₃N (195 µL, 1.40 mmol) and Pd(Ph₃P)₄ (64 mg, 0.056 mmol, 20.0 mol%) were added and the vial was purged with Ar and sealed with a screw cap. The mixture was heated at 75 ºC for 48h. The solution was filtered through a plug of silica gel with EtOAc (100 mL) then washed with water (2x20 mL). The organic layer was collected, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (5–10% EtOAc in hexanes) afforded 4j (130 mg, 81%) as a yellow oil.

TLC: Rf 0.43 (9:1 hexanes/EtOAc).

IR (NaCl, film): 2948, 2866, 1611, 1468, 1387, 1287, 1257, 1098 (C–O st), 881, 835, 776. ¹H-NMR (600 MHz): δ 7.38 (d, J = 1.7 Hz, 1H), 7.29 (dd, J = 8.3, 1.7 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 5.79 (s, 1H), 5.09 (td, J = 7.4, 1.5 Hz, 1H), 3.68 (t, J = 6.7 Hz, 2H), 2.56–2.44 (m, 2H), 2.40 (d, J = 6.7 Hz, 2H), 2.13 (dt, J = 14.8, 7.4 Hz, 1H), 1.88–1.79 (m, 2H), 1.70–1.62 (m, 2H), 1.61–1.52 (m, 2H), 1.39–1.33 (m, 2H), 1.19–1.14 (m, 3H), 1.11 (dd, J = 7.1, 4.5 Hz, 18H), 0.90 (s, 9H), 0.06 (s, 6H). ¹³C-NMR (151 MHz) δ 157.3, 156.8, 133.5, 128.8, 128.5, 128.5, 117.5, 110.1, 102.9, 88.2, 80.5, 71.1, 62.5, 39.1, 32.0, 29.1, 26.0, 25.9, 25.3, 25.2, 18.3, 18.7, 12.9, –5.3. ESI-MS m/z (rel int): (pos) 591.4 ([M+Na]+, 100).
(Z)-((5-azido-2-(3-((tert-butyldimethylsilyl)oxy)propylidene)-2,3-dihydrobenzofuran-3-yl)oxy)triisopropylsilane (4k). Aryl bromide 4h (160 mg, 0.30 mmol) was dissolved in dry THF (7.0 mL) and the solution was cooled to –78 °C. Then, n-BuLi (351 µL, 1.6 M in hexanes, 0.56 mmol) was added dropwise and warmed to –30 °C over 1.5 h. The reaction was then cooled back to –78 °C and a solution of p-TsN3 (59 mg, 0.30 mmol) in dry THF (3.0 mL) was added. The reaction was warmed to rt over 2h and stirred for 14 h before quenched with a solution of saturated aqueous NH4Cl. The aqueous layer was separated and extracted with ethyl acetate (100 mL). The organic layer was washed with brine, dried over Na2SO4, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (5–10% EtOAc in hexanes) afforded 4k (70% purity by 1H NMR) as a yellow oil, which was forwarded to the next step without further purification.

(Z)-2-(3-((tert-butyldimethylsilyl)oxy)propylidene)-3-(triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-carbaldehyde (4l). Aryl bromide 4h (200 mg, 0.37 mmol) was dissolved in dry THF (8.0 mL) and the solution was cooled to –78 °C. Then, n-BuLi (346 µL, 1.6 M in hexanes, 0.55 mmol) was added dropwise and warmed to –30 °C over 1.5 h. The reaction was then cooled back to –78 °C and dry DMF (571 µL, 7.40 mmol) was added. The reaction was warmed to rt over 2h and quenched with saturated aqueous NH4Cl. The aqueous layer was separated and extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na2SO4, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (5–10% EtOAc in hexanes) afforded 4l (153 mg, 84%) as a yellow oil.

TLC: Rf 0.43 (9:1 hexanes/EtOAc). IR (NaCl, film): 2948, 2866, 1611, 1468, 1387, 1287, 1257, 1098 (C–O st), 881, 835, 776. 1H-NMR (500 MHz) δ 9.90 (s, 1H), 7.94–7.87 (m, 1H), 7.82 (dd, J = 8.4, 1.7 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 5.87 (s, 1H), 5.21 (td, J = 7.4, 1.5 Hz, 1H), 3.70 (t, J = 6.6 Hz, 2H), 2.60–2.42 (m, 2H), 1.25–1.14 (m, 3H), 1.11 (dd, J = 7.0, 5.4 Hz, 18H), 0.90 (s, 9H), 0.07 (s, 6H). 13C-NMR (126 MHz) δ 190.5, 162.4, 157.1, 133.5, 131.5, 129.8, 127.1, 110.7, 104.6, 70.5, 62.3, 29.1, 25.9, 18.3, 18.2, 12.9, –5.30. HRMS m/z calcd for C27H46O4Si2Na ([M+Na]+) 513.2832; found 513.2817.
(Z)-(2-(3-((tert-butyldimethylsilyl)oxy)propyldiene)-3-((triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-yl)methanol (S4). In a 25 mL round bottom flask, aldehyde 4k (400 mg, 0.82 mmol) was dissolved in CH$_2$Cl$_2$/MeOH (2:1, 12 mL) and cooled down to –78 ºC. CeCl$_3$.7H$_2$O (364 mg, 0.98 mmol) was added to the reaction followed by the addition of NaBH$_4$ (31 mg, 0.82 mmol). The reaction was warmed upto 0 ºC over 2 h and quenched with saturated aqueous NH$_4$Cl. The aqueous layer was separated and extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (5–10% EtOAc in hexanes) afforded 4l (354 mg, 86%) as a yellow oil.

TLC: $R_f$ 0.43 (9:1 hexanes/EtOAc).

IR (NaCl, film): 2948, 2866, 1611, 1468, 1387, 1287, 1257, 1098 (C–O st), 881, 835, 776. $^1$H-NMR (500 MHz) $\delta$ 7.38 (d, $J$ = 1.9 Hz, 1H), 7.26– 7.23 (m, 1H), 6.90 (d, $J$ = 8.2 Hz, 1H), 5.84 (s, 1H), 5.09 (td, $J$ = 7.3, 1.6 Hz, 1H), 4.64 (d, $J$ = 5.8 Hz, 2H), 3.69 (t, $J$ = 6.7 Hz, 2H), 2.58–2.41 (m, 2H), 1.53 (t, $J$ = 5.9 Hz, 1H), 1.17 (ddt, $J$ = 12.6, 8.9, 5.8 Hz, 3H), 1.11 (dd, $J$ = 6.9, 4.5 Hz, 18H), 0.90 (s, 9H), 0.07 (s, 6H). $^{13}$C-NMR (126 MHz) $\delta$ 157.6, 157.3, 134.5, 129.2, 128.8, 124.7, 110.1, 102.7, 77.3, 71.3, 65.4, 62.5, 29.1, 25.9, 18.2, 13.0, –5.3. HRMS $m/z$ calcd for C$_{27}$H$_{48}$O$_4$Si$_2$Na ([M+Na]$^+$) 515.2989; found 515.2975.

(Z)-(2-(3-((tert-butyldimethylsilyl)oxy)propyldiene)-3-((triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-yl)methyl acetate (4m). In a 50 mL round bottom flask, the benzyl alcohol S1 (310 mg, 0.63 mmol) was dissolved in CH$_2$Cl$_2$ (12 mL) and cooled down to 0 ºC. Et$_3$N (263 µL, 1.89 mmol) was added to the reaction followed by the addition of AcCl (76 µL, 1.07 mmol). The reaction was warmed upto rt over 30 min and then stirred for 2 h. The solvents were removed by rotary evaporation to afford the crude product. Purification by silica flash chromatography (10% EtOAc in hexanes) afforded 4m (300 mg, 89%) as a yellow oil.

TLC: $R_f$ 0.43 (9:1 hexanes/EtOAc).

IR (NaCl, film): 2948, 2866, 1611, 1468, 1387, 1287, 1257, 1098 (C–O st), 881, 835, 776. $^1$H-NMR (500 MHz) $\delta$ 7.39 ? 7.35 (m, 1H), 7.27–7.22 (m, 1H), 6.90 (d, $J$ = 8.3 Hz, 1H), 5.83 (s, 1H), 5.13 ? 5.06 (m, 2H), 5.02 (d, $J$ = 12.1 Hz, 1H), 3.69 (t, $J$ = 6.7 Hz, 2H), 2.54–2.46 (m, 2H), 2.07 (s, 3H), 1.15 (dd, $J$ = 7.1, 2.9 Hz, 3H), 1.10 (t, $J$ = 6.2 Hz, 18H), 0.90 (d, $J$ = 1.0 Hz, 9H), 0.07 (d, $J$ = 1.0 Hz, 6H). $^{13}$C-NMR (126 MHz) $\delta$ 170.8, 157.6, 157.5, 130.6, 129.5, 128.8, 126.0, 110.1, 102.9, 71.3, 66.2, 62.5, 29.1, 26.0, 25.9, 21.0, 18.3, 18.2, 18.0, 12.9, –5.2. HRMS $m/z$ calcd for C$_{29}$H$_{50}$O$_5$Si$_2$Na ([M+Na]$^+$) 557.3095; found 557.3083.
(Z)-2-((2-(3-((tert-butyldimethylsilyl)oxy)propylidene)-3-((triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-yl)methyl)isoindoline-1,3-dione (4n). In a 10 mL roundbottom flask, the benzyl alcohol S1 (100 mg, 0.20 mmol) was dissolved in THF (2 mL) and cooled down to 0 ºC. Ph₃P (80 mg, 0.30 mmol) and phthalimide (45 mg, 0.30 mmol) were added to the reaction followed by the addition of DEAD (48 µL, 0.30 mmol). The reaction was warmed up to rt over 30 min and then stirred for 12 h. The reaction was diluted with hexanes and purified by silica flash chromatography (10% EtOAc in hexanes) afforded 4n (85 mg, 67%) as a yellow oil.

**TLC:** Rf 0.43 (9:1 hexanes/EtOAc). **IR** (NaCl, film): 2948, 2866, 1611, 1468, 1387, 1287, 1257, 1098 (C–O st), 881, 835, 776. **1H-NMR** (500 MHz) δ 7.83 (dd, J = 5.5, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 7.44 (d, J = 1.8 Hz, 1H), 7.35 (dd, J = 8.3, 1.9 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 5.79 (s, 1H), 5.05 (td, J = 7.4, 1.5 Hz, 1H), 4.87 (d, J = 14.5 Hz, 1H), 4.74 (d, J = 14.5 Hz, 1H), 3.66 (t, J = 6.7 Hz, 2H), 2.53–2.39 (m, 2H), 1.13–1.07 (m, 3H), 1.03 (dd, J = 12.8, 6.9 Hz, 18H), 0.89 (s, 9H), 0.05 (s, 6H). **13C-NMR** (126 MHz) δ 167.9, 157.6, 157.2, 133.9, 132.1, 130.7, 130.1, 130.0, 128.8, 125.9, 123.3, 110.1, 102.6, 71.3, 62.5, 41.2, 29.1, 25.9, 18.2, 18.1, 12.9, −5.29. **HRMS** m/z calcd for C₃₅H₅₁NO₅Si₂Na ([M+Na]+) 644.3204; found 644.3221.
H. SYNTHESIS OF exo-GLYCAL ALCOHOLS 5a–n

GENERAL PROCEDURE FOR TBS DEPROTECTION

In a 50-mL Falcon tube, the TBS-protected exo-glycal 4 (1.0 equiv) was dissolved in THF (0.06 M) and cooled to 0 °C. Pyridine (20.0 equiv, 1.6 mL/mmol) was added followed by dropwise addition of HF-pyridine (70% HF in pyridine, 50 equiv, 1.30 mL/mmol). The reaction was stirred for 2–3 h at 0 °C until completion by TLC analysis. The reaction was quenched slowly using methoxytrimethylsilane (500 equiv) at 0 °C. Following the addition, the reaction was warmed to rt and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography using hexanes/EtOAc/Et3N (79/20/1) as an eluent afforded the free alcohols 5a–n.

(Z)-3-(3-(triisopropylsilyloxy)benzofuran-2(3H)-ylidene)propan-1-ol (5a). Prepared from 4a. Clear oil (171 mg, 65%). TLC: Rf 0.30 (4:1 hexanes/EtOAc). IR (NaCl, film): 3338 (O–H st), 2943, 2866, 1708, 1613, 1599, 1465, 1323, 1287, 1233, 1091, 1059 (C–O st), 881, 749, 721. 1H-NMR (600 MHz): δ 7.40–7.37 (m, 1H), 7.26 (s, 1H), 7.00 (td, J = 7.5, 1.0 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 5.87 (s, 1H), 5.03 (d, J = 1.6 Hz, 1H), 3.80–3.71 (m, 2H), 2.60–2.51 (m, 2H), 1.18 (ddt, J = 13.1, 8.8, 5.9 Hz, 3H), 1.11 (t, J = 7.5 Hz, 1H). 13C-NMR (151 MHz): δ 158.8, 157.4, 130.0, 128.2, 125.5, 121.9, 110.3, 105.1, 71.5, 62.3, 29.1, 18.2, 12.9. HRMS m/z calcd for C20H32O3SiNa ([M+Na]+) 371.2018; found 371.2022.

(Z)-tert-butyldimethyl(4-(3-(triisopropylsilyloxy)benzofuran-2(3H)-ylidene)butoxy)silane (5b). Prepared from 4b. Clear oil (186 mg, 64%). TLC: Rf 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. 1H-NMR (500 MHz): δ 7.39–7.35 (m, 1H), 7.27–7.22 (m, 1H), 7.12 (m, 1H), 6.98 (s, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.85 (s, 1H), 4.99 (td, J = 7.7, 1.6 Hz, 1H), 3.74–3.65 (m, 2H), 2.38 (dp, J = 21.4, 7.2 Hz, 2H), 1.73 (p, J = 6.8 Hz, 2H), 1.51 (d, J = 5.7 Hz, 1H), 1.20–1.14 (m, 3H), 1.11 (t, J = 6.7 Hz, 1H). 13C-NMR (126 MHz): δ 157.4, 157.3, 130.0, 128.2, 125.5, 121.9, 110.2, 105.1, 71.4, 62.2, 32.2, 21.5, 18.2, 17.9, 12.9. HRMS m/z calcd for C21H34O3SiNa ([M+Na]+) 385.2175; found 385.2184.
(Z)-5-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)pentan-1-ol (5c). Prepared from 4c. Clear oil (481 mg, 64%). TLC: R, 0.40 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. 

**1H-NMR** (500 MHz): δ 7.37 (d, J = 7.5 Hz, 1H), 7.25–7.21 (m, 1H), 6.97 (s, 1H), 4.97 (td, J = 7.5, 1.6 Hz, 1H), 3.67 (t, J = 6.5 Hz, 2H), 2.36–2.26 (m, 2H), 1.64 (dq, J = 8.9, 6.6 Hz, 2H), 1.57–1.46 (m, 2H), 1.19–1.14 (m, 3H), 1.11 (t, J = 6.4 Hz, 18H).

**13C-NMR** (126 MHz) δ 157.6, 156.8, 129.9, 128.3, 125.5, 121.7, 110.2, 105.8, 71.4, 62.9, 32.3, 25.7, 25.0, 18.2, 13.0. HRMS m/z: calcd for C_{22}H_{36}O_{3}SiNa ([M+Na]⁺) 399.2331; found 399.2344.

(Z)-3-(5-nitro-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5d). Prepared from 4d. Yellow oil (130 mg, 67%). TLC: R, 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2928, 2856, 1614, 1600, 1522 (N–O), 1466, 1324 (N–O), 1287, 1253, 1138 1095 (C–O st), 1017, 902, 835, 775, 750. 

**1H-NMR** (600 MHz): δ 8.28 (d, J = 2.4 Hz, 1H), 8.25 (dd, J = 8.9, 2.4 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 5.90 (d, J = 1.7 Hz, 1H), 5.19 (td, J = 7.6, 1.5 Hz, 1H), 3.76 (tq, J = 9.3, 4.3 Hz, 2H), 2.62–2.55 (m, 2H), 1.43 (t, J = 5.6 Hz, 1H), 1.19 (ddt, J = 12.8, 8.8, 6.1 Hz, 3H), 1.12 (t, J = 6.9 Hz, 18H).

**13C-NMR** (151 MHz) δ 162.0, 158.1, 143.0, 129.7, 126.9, 121.9, 110.5, 104.7, 70.4, 62.0, 28.9, 18.1, 12.9. HRMS m/z: calcd for C_{20}H_{31}NO_{5}SiNa ([M+Na]⁺) 416.1869; found 416.1876.

(Z)-3-(5-methoxy-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5e). Prepared from 4e. Clear oil (150 mg, 65%). TLC: R, 0.30 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. 

**1H-NMR** (500 MHz): δ 6.94 (d, J = 2.6 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.80 (dd, J = 8.8, 2.6 Hz, 1H), 5.84 (s, 1H), 4.98 (td, J = 7.5, 1.6 Hz, 1H), 3.76 (s, 3H), 3.72 (td, J = 6.6, 2.6 Hz, 2H), 2.54 (q, J = 6.8 Hz, 2H), 1.71 (s, 1H), 1.19–1.13 (m, 3H), 1.11 (dd, J = 6.8, 4.5 Hz, 18H).

**13C-NMR** (126 MHz) δ 159.2, 155.0, 151.5, 128.9, 115.5, 111.1, 110.4, 101.2, 72.0, 62.3, 56.0, 29.0, 18.2, 18.2, 13.0. HRMS m/z: calcd for C_{21}H_{34}O_{3}SiNa ([M+Na]⁺) 401.2124; found 401.2121.
(Z)-3-(5-methyl-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5f). Prepared from 4f. Clear oil (192 mg, 63%). TLC: Rf 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. $^1$H-NMR (600 MHz): δ 7.16 (d, J = 1.8 Hz, 1H), 7.05 (dd, J = 8.2, 1.8 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 5.82 (s, 1H), 4.99 (td, J = 7.5, 1.5 Hz, 1H), 3.82–3.68 (m, 2H), 2.61–2.48 (m, 2H), 2.32 (s, 3H), 1.53 (d, J = 4.1 Hz, 1H), 1.17 (dtt, J = 13.0, 9.0, 5.8 Hz, 3H), 1.11 (t, J = 6.9 Hz, 18H). $^{13}$C-NMR (151 MHz) δ 159.1, 155.3, 131.3, 130.4, 128.0, 125.9, 109.7, 101.2, 71.6, 62.3, 29.0, 21.0, 18.2, 12.9. HRMS m/z calcd for C$_{21}$H$_{34}$O$_3$SiNa ([M+Na]$^+$) 385.2175; found 385.2176.

(Z)-3-(6-bromo-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5g). Prepared from 4g. Yellow oil (225 mg, 71%). TLC: Rf 0.36 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. $^1$H-NMR (500 MHz): δ 7.22 (d, J = 7.9 Hz, 1H), 7.14–7.09 (m, 2H), 5.79 (s, 1H), 5.05 (td, J = 7.5, 1.5 Hz, 1H), 3.73 (td, J = 6.5, 3.0 Hz, 2H), 2.54 (q, J = 6.8, 6.4 Hz, 2H), 1.51 (s, 1H), 1.18–1.12 (m, 3H), 1.10 (t, J = 6.2 Hz, 18H). $^{13}$C-NMR (126 MHz) δ 158.5, 158.2, 127.5, 126.5, 125.1, 123.1, 113.9, 102.6, 70.9, 62.2, 29.0, 18.2, 13.0. HRMS m/z calcd for C$_{20}$H$_{31}$O$_3$BrSiNa ([M+Na]$^+$) 449.1124; found 449.1119.

(Z)-3-(5-bromo-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5h). Prepared from 4h. Yellow oil (103 mg, 65%). TLC: Rf 0.36 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. $^1$H-NMR (500 MHz): δ 7.45 (d, J = 2.0 Hz, 1H), 7.39–7.32 (m, 1H), 6.82 (d, J = 8.5 Hz, 1H), 5.83 (s, 1H), 5.04 (td, J = 7.5, 1.4 Hz, 1H), 3.74 (td, J = 6.5, 3.0 Hz, 2H), 2.55 (dt, J = 7.5, 6.4 Hz, 2H), 1.20–1.08 (m, 21H). $^{13}$C-NMR (126 MHz) δ 158.4, 158.5, 132.8, 130.5, 128.5, 119.1, 111.9, 102.4, 71.2, 62.2, 29.0, 18.2, 12.9. HRMS m/z calcd for C$_{20}$H$_{31}$O$_3$BrSiNa ([M+Na]$^+$) 449.1124; found 449.1133.
(Z)-3-(5-phenyl-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5i). Prepared from 4i. Clear oil (53 mg, 41% over 2 steps). TLC: R$_f$ 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. $^1$H-NMR (500 MHz): δ 7.59 (d, J = 1.9 Hz, 1H), 7.52–7.50 (m, 2H), 7.48 (dd, J = 8.3, 2.0 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.34–7.30 (m, 1H), 7.00 (d, J = 8.3 Hz, 1H), 5.92 (s, 1H), 5.06 (td, J = 7.5, 1.5 Hz, 1H), 3.76 (td, J = 6.5, 2.9 Hz, 2H), 2.58 (q, J = 6.9 Hz, 2H), 1.23–1.17 (m, 3H), 1.13 (dd, J = 7.0, 4.2 Hz, 18H), 0.98 (d, J = 7.1 Hz, 1H). 13C-NMR (126 MHz) δ 159.0, 157.0, 141.1, 129.1, 128.8, 128.8, 126.9, 124.3, 110.4, 101.8, 77.3, 71.6, 62.4, 29.7, 29.1, 18.3, 13.0. HRMS m/z calcd for C$_{26}$H$_{36}$O$_3$SiNa ([M+Na]$^+$) 447.2331; found 447.2328.

(Z)-3-(5-(3-cyclopentylprop-1-yn-1-yl)-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5j). Prepared from 4j. Clear oil (73 mg, 61%). TLC: R$_f$ 0.38 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. $^1$H-NMR (500 MHz): δ 7.38 (d, J = 1.8 Hz, 1H), 7.30 (dd, J = 8.3, 1.8 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.81 (s, 1H), 5.03 (td, J = 7.5, 1.6 Hz, 1H), 3.74 (dq, J = 6.8, 3.6 Hz, 2H), 2.61–2.51 (m, 2H), 2.40 (d, J = 6.7 Hz, 2H), 2.14 (dt, J = 14.7, 7.2 Hz, 1H), 1.87–1.79 (m, 2H), 1.70–1.62 (m, 2H), 1.57 (ddt, J = 11.5, 6.9, 3.6 Hz, 2H), 1.48 (s, 1H), 1.40–1.31 (m, 2H), 1.21–1.13 (m, 3H), 1.11 (t, J = 6.0 Hz, 18H). 13C-NMR (126 MHz) δ 158.7, 156.7, 133.6, 128.8, 128.4, 117.8, 110.2, 102.1, 88.4, 80.4, 77.3, 71.2, 62.3, 39.2, 32.0, 29.1, 25.4, 25.2, 18.2, 13.0. HRMS m/z calcd for C$_{28}$H$_{42}$O$_3$SiNa ([M+Na]$^+$) 477.2801; found 477.2805.

(Z)-3-(5-azido-3-((triisopropylsilyl)oxy)benzofuran-2(3H)-ylidene)propan-1-ol (5k). Prepared from 4k. Clear oil (51 mg, 45% over 2 steps). TLC: R$_f$ 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3583 (O–H st), 2919, 2865, 1717, 1599, 1455, 1286, 1253, 1234, 1170, 1055 (C–O st), 910, 881, 805, 749. $^1$H-NMR (500 MHz): δ 7.03 (d, J = 2.0 Hz, 1H), 6.98–6.88 (m, 2H), 5.84 (s, 1H), 5.04 (td, J = 7.5, 1.5 Hz, 1H), 3.74 (qd, J = 6.1, 2.7 Hz, 2H), 2.55 (q, J = 6.7, 6.0 Hz, 2H), 1.44 (t, J = 5.8 Hz, 1H), 1.21–1.13 (m, 3H), 1.11 (dd, J = 6.7, 4.5 Hz, 18H). 13C-NMR (126 MHz) δ 158.7, 154.8, 133.9, 130.0, 129.9, 120.6, 116.2, 111.3, 102.2, 77.3, 71.4, 62.3, 29.0, 18.2, 12.9. HRMS m/z calcd for C$_{20}$H$_{31}$N$_3$O$_3$SiNa ([M+Na]$^+$) 412.2032; found 412.2039.
(Z)-2-(3-hydroxypropylidene)-3-((triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-carbaldehyde (5l). Prepared from 4l. Clear oil (62 mg, 67%). TLC: Rf 0.36 (4:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1698 (C=C o st), 1613, 1468, 1394, 1287, 1257, 1098 (C=O st), 881, 835, 776. $^1$H-NMR (500 MHz) δ 9.90 (s, 1H), 7.92 (d, $J$ = 1.6 Hz, 1H), 7.83 (dd, $J$ = 8.4, 1.7 Hz, 1H), 7.06 (d, $J$ = 8.3 Hz, 1H), 5.89 (s, 1H), 5.15 (td, $J$ = 7.6, 1.5 Hz, 1H), 3.76 (tt, $J$ = 6.9, 3.3 Hz, 2H), 2.59 (q, $J$ = 6.8 Hz, 2H), 1.26 (s, 1H), 1.19 (ddd, $J$ = 13.8, 6.9, 2.4 Hz, 3H), 1.12 (t, $J$ = 6.9 Hz, 18H). $^{13}$C-NMR (126 MHz) δ 190.5, 162.3, 158.3, 133.6, 131.6, 129.7, 127.0, 110.8, 103.9, 70.5, 62.1, 45.6, 29.7, 29.0, 18.2, 12.9. HRMS m/z calcd for C$_{21}$H$_{32}$O$_4$SiNa ([M+Na]$^+$) 399.1968; found 399.1961.

(Z)-(2-(3-hydroxypropylidene)-3-((triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-yl)-methyl acetate (5m). Prepared from 4m. Clear oil (82 mg, 70%). TLC: Rf 0.38 (4:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1741 (C=O st), 1611, 1468, 1394, 1287, 1257, 1098 (C=O st), 881, 835, 776. $^1$H-NMR (500 MHz) δ 7.38 (d, $J$ = 1.9 Hz, 1H), 7.28–7.22 (m, 1H), 6.91 (d, $J$ = 8.3 Hz, 1H), 5.85 (s, 1H), 5.12–4.99 (m, 3H), 3.74 (td, $J$ = 6.5, 2.6 Hz, 2H), 2.56 (q, $J$ = 6.6 Hz, 2H), 2.07 (s, 3H), 1.26 (s, 1H), 1.16 (ddd, $J$ = 12.2, 9.4, 5.2 Hz, 3H), 1.11 (t, $J$ = 6.9 Hz, 18H). $^{13}$C-NMR (126 MHz) δ 170.9, 158.8, 157.5, 130.7, 129.7, 128.6, 126.0, 110.2, 102.0, 71.3, 66.2, 62.3, 29.7, 29.1, 21.0, 18.2, 12.9. HRMS m/z calcd for C$_{23}$H$_{36}$O$_5$SiNa ([M+Na]$^+$) 443.2230; found 443.2213.

(Z)-2-((2-(3-hydroxypropylidene)-3-((triisopropylsilyl)oxy)-2,3-dihydrobenzofuran-5-yl)-methyl)isoindoline-1,3-dione (5n). Prepared from 4n. Clear oil (36 mg, 55%). TLC: Rf 0.36 (4:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1714 (C=O st), 1611, 1468, 1394, 1287, 1257, 1098 (C=O st), 881, 835, 776. $^1$H-NMR (500 MHz) δ 7.84 (dd, $J$ = 5.5, 3.0 Hz, 2H), 7.70 (dd, $J$ = 5.5, 3.0 Hz, 2H), 7.45 (d, $J$ = 1.8 Hz, 1H), 7.36 (dd, $J$ = 8.2, 1.9 Hz, 1H), 6.87 (d, $J$ = 8.3 Hz, 1H), 5.80 (s, 1H), 5.00 (td, $J$ = 7.5, 1.5 Hz, 1H), 4.87 (d, $J$ = 14.5 Hz, 1H), 4.74 (d, $J$ = 14.5 Hz, 1H), 3.71 (td, $J$ = 6.6, 2.3 Hz, 2H), 2.53 (q, $J$ = 6.8 Hz, 2H), 1.11–1.08 (m, 3H), 1.03 (dd, $J$ = 15.0, 6.9 Hz, 18H), 0.98 (d, $J$ = 6.9 Hz, 1H). $^{13}$C-NMR (126 MHz) δ 167.9, 158.9, 157.1, 134.0, 132.1, 130.8, 130.3, 128.7, 125.9, 123.3, 110.2, 101.8, 77.3, 71.3, 62.3, 41.2, 29.7, 29.0, 18.1, 18.1, 18.0, 17.9, 12.9. HRMS m/z calcd for C$_{29}$H$_{37}$NO$_5$SiNa ([M+Na]$^+$) 530.2339; found 530.2335.
I. SYNTHESIS OF EXO-GLYCAL EPOXIDES 6a–n

GENERAL PROCEDURE FOR DMDO EPOXIDATION

The exo-glycal 5 (1.0 equiv) was dissolved in CH₂Cl₂ (0.02 M) and cooled to −78 °C. Dimethyldioxirane (0.06 M in acetone, 1.5 equiv), stored and maintained in a −80 °C freezer, was added and the reaction stirred for 10 min before warming to rt. The solvents were removed by rotary evaporation to afford the crude epoxides 6a–n that were used immediately without further purification.

2-((2R,3R,3'R)-3-(triisopropylsilyloxy)-3H-spiro[benzofuran-2,2'-oxirane]-3'-yl)ethanol (6a). Prepared from 5a. Clear oil (20 mg, 100%). TLC: Rf 0.20 (4:1 hexanes/EtOAc).

1H-NMR (500 MHz): δ 7.38 (d, J = 7.6 Hz, 1H), 7.28 (dd, J = 7.9, 1.4 Hz, 1H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 5.49 (s, 1H), 3.91 (t, J = 6.1 Hz, 2H), 3.67 (dd, J = 6.7, 5.6 Hz, 1H), 2.13 (p, J = 6.1 Hz, 2H), 1.64 (s, 1H), 1.19–1.12 (m, 3H), 1.09 (dd, J = 16.9, 6.7 Hz, 18H).

3-((2R,3R,3'R)-3-(triisopropylsilyloxy)-3H-spiro[benzofuran-2,2'-oxirane]-3'-yl)propan-1-ol (6b). Prepared from 5b. Clear oil (16 mg, 100%). TLC: Rf 0.25 (4:1 hexanes/EtOAc).

1H-NMR (500 MHz): δ 7.38 (d, J = 7.5 Hz, 1H), 7.29–7.27 (m, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 5.48 (s, 1H), 3.75–3.72 (m, 2H), 3.52 (td, J = 6.3, 1.6 Hz, 1H), 2.05–1.99 (m, 1H), 1.94–1.77 (m, 3H), 1.58 (brs, 1H), 1.16–1.05 (m, 21H).

5-((2R,3R,3'R)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2'-oxiran]-3'-yl)pentan-1-ol (6c). Prepared from 5c. Clear oil (40 mg, 100%). TLC: Rf 0.30 (4:1 hexanes/EtOAc).

1H-NMR (500 MHz): δ 7.38 (d, J = 7.4 Hz, 1H), 7.29–7.25 (m, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 5.48 (s, 1H), 3.73–3.63 (m, 2H), 3.49 (t, J = 6.2 Hz, 1H), 2.01–1.90 (m,
1H), 1.90–1.78 (m, 1H), 1.70–1.59 (m, 4H), 1.42–1.25 (m, 1H), 1.18–1.12 (m, 3H), 1.09 (dd, J = 16.3, 6.6 Hz, 18H).

2-((2R,3R,3′R)-5-nitro-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-3′-yl)-ethanol (6d). exo-Glycal 5d (15 mg, 0.038 mmol) was dissolved in CH₂Cl₂ (2 mL) and cooled to −78 °C. Dimethyldioxirane (1.27 mL, 0.06 M in acetone, 0.076 mmol), stored and maintained in a −80 °C freezer, was added and the reaction stirred for 10 min before it was put inside −20 °C refrigerator for 12 h. The solvents were removed by rotary evaporation to afford the crude epoxide 6d as yellow oil (15.6 mg, 100%) that was used without further purification.

TLC: R$_f$ 0.25 (4:1 hexanes/EtOAc). $^1$H-NMR (500 MHz): δ 8.34–8.21 (m, 2H), 7.01 (d, J = 8.8 Hz, 1H), 5.54 (s, 1H), 3.92 (t, J = 6.1 Hz, 2H), 3.72 (t, J = 6.1 Hz, 1H), 2.13 (q, J = 6.1 Hz, 2H), 1.26 (s, 1H), 1.22–1.14 (m, 3H), 1.11 (dd, J = 13.4, 7.0 Hz, 18H).

2-((2R,3R,3′R)-5-methoxy-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-3′-yl)ethanol (6e). Prepared from 5e. Clear oil (15.6 mg, 100%). TLC: R$_f$ 0.20 (4:1 hexanes/EtOAc). $^1$H-NMR (500 MHz): δ 6.94 (d, J = 1.4 Hz, 1H), 6.83 (d, J = 1.5 Hz, 2H), 5.47 (s, 1H), 3.97–3.84 (m, 2H), 3.78 (s, 3H), 3.65 (dd, J = 6.7, 5.6 Hz, 1H), 2.12 (p, J = 6.1 Hz, 2H), 1.60 (s, 1H), 1.19–1.13 (m, 3H), 1.10 (dd, J = 12.4, 6.6 Hz, 18H).

2-((2R,3R,3′R)-5-methyl-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-3′-yl)ethanol (6f). Prepared from 5f. Clear oil (42 mg, 100%). TLC: R$_f$ 0.25 (4:1 hexanes/EtOAc). $^1$H-NMR (500 MHz): δ 7.16 (d, J = 2.1 Hz, 1H), 7.07 (dd, J = 8.2, 1.9 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 5.45 (s, 1H), 3.90 (t, J = 6.1 Hz, 2H), 3.65 (dd, J = 6.7, 5.5 Hz, 1H), 2.32 (s, 3H), 2.18–2.09 (m, 2H), 1.65 (d, J = 5.0 Hz, 1H), 1.16–1.12 (m, 3H), 1.09 (dd, J = 15.4, 6.7 Hz, 18H).

2-((2R,3R,3′R)-6-bromo-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-3′-yl)ethanol (6g). Prepared from 5g. Clear oil (52 mg, 100%). TLC: R$_f$ 0.25 (4:1 hexanes/EtOAc).
1H-NMR (500 MHz): δ 7.23 (d, J = 8.0 Hz, 1H), 7.15 (dd, J = 8.0, 1.7 Hz, 1H), 7.09 (d, J = 1.7 Hz, 1H), 5.42 (s, 1H), 3.90 (t, J = 6.1 Hz, 2H), 3.66 (t, J = 6.1 Hz, 1H), 2.10 (qd, J = 6.1, 3.2 Hz, 2H), 1.57 (s, 1H), 1.16–1.11 (m, 3H), 1.08 (dd, J = 14.5, 6.5 Hz, 18H).

2-((2R,3R,3'R)-5-bromo-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2'-oxiran]-3'-yl)ethanol (6h). Prepared from 5h. Clear oil (20.8 mg, 100%). 1H-NMR (500 MHz): δ 7.46 (d, J = 2.2 Hz, 1H), 7.38 (dd, J = 8.5, 2.2 Hz, 1H), 6.81 (d, J = 8.5 Hz, 1H), 5.46 (s, 1H), 3.90 (t, J = 6.1 Hz, 2H), 3.66 (t, J = 6.1 Hz, 1H), 2.10 (qd, J = 6.1, 2.7 Hz, 2H), 1.67 (s, 1H), 1.14 (dd, J = 6.8, 2.6 Hz, 3H), 1.09 (dd, J = 12.9, 6.4 Hz, 18H).

2-((2R,3R,3'R)-5-phenyl-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2'-oxiran]-3'-yl)ethanol (6i). Prepared from 5i. Clear oil (10.4 mg, 100%). 1H-NMR (500 MHz): δ 7.59 (d, J = 1.9 Hz, 1H), 7.50 (ddd, J = 7.9, 6.2, 1.8 Hz, 3H), 7.44 (dd, J = 8.5, 6.8 Hz, 2H), 7.35–7.31 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 5.55 (s, 1H), 3.92 (t, J = 6.1 Hz, 2H), 3.70 (dd, J = 6.7, 5.6 Hz, 1H), 2.15 (p, J = 5.9 Hz, 2H), 1.22–1.16 (m, 4H), 1.11 (dd, J = 12.1, 6.9 Hz, 18H).

2-((2R,3R,3'R)-5-(3-cyclopentylprop-1-yn-1-yl)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2'-oxiran]-3'-yl)ethanol (6j).exo-Glycal 5d (12 mg, 0.026 mmol) was dissolved in CH2Cl2 (1.5 mL) and cooled to −78 °C. Dimethyldioxirane (0.77 mL, 0.06 M in acetone, 0.046 mmol), stored and maintained in a −80 °C freezer, was added and the reaction stirred for 10 min before it was put inside −20 °C refrigerator for 12 h. The solvents were removed by rotary evaporation to afford the crude epoxide 6j as clear oil (12.4 mg, 100%) that was used without further purification.

TLC: Rf 0.25 (4:1 hexanes/ EtOAc). 1H-NMR (500 MHz): δ 7.39 (d, J = 1.7 Hz, 1H), 7.32 (dd, J = 8.5, 1.7 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 5.44 (s, 1H), 3.90 (t, J = 6.1 Hz, 2H), 3.66 (t, J = 6.1 Hz, 1H), 2.40 (d, J = 6.7 Hz, 2H), 2.12 (ddd, J = 9.9, 6.1, 3.0 Hz, 3H), 1.86–1.79 (m, 2H), 1.69–1.63 (m, 2H), 1.57 (dt, J = 8.4, 4.0 Hz, 2H), 1.39–1.33 (m, 2H), 1.28 (t, J = 7.2 Hz, 1H), 1.15 (dd, J = 5.8, 3.6 Hz, 3H), 1.10–1.06 (m, 18H).
2-((2R,3R,3′R)-5-azido-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-3′-yl)-ethanol (6k). Prepared from 5k. Clear oil (8.3 mg, 100%). TLC: \( R_f \) 0.25 (4:1 hexanes/EtOAc). \( ^1H-NMR \) (500 MHz): \( \delta \) 7.04 (d, \( J = 2.4 \) Hz, 1H), 6.96 (dd, \( J = 8.7, 2.4 \) Hz, 1H), 6.90 (d, \( J = 8.6 \) Hz, 1H), 5.47 (s, 1H), 3.90 (t, \( J = 6.1 \) Hz, 2H), 3.66 (t, \( J = 6.1 \) Hz, 1H), 2.11 (qd, \( J = 6.1, 3.1 \) Hz, 2H), 1.58 (s, 1H), 1.15 (ddd, \( J = 9.7, 6.2, 4.8 \) Hz, 3H), 1.09 (dd, \( J = 12.0, 6.5 \) Hz, 18H).

(2R,3R,3′R)-3′-(2-hydroxyethyl)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxirane]-5-carbaldehyde (6l). \textit{exo}-Glycal 5i (30 mg, 0.08 mmol) was dissolved in \( \text{CH}_2\text{Cl}_2 \) (4 mL) and cooled to \(-78^\circ\text{C}\). Dimethyldioxirane (2 mL, 0.06 M in acetone, 0.11 mmol), stored and maintained in a \(-80^\circ\text{C}\) freezer, was added and the reaction stirred for 10 min before it was put inside the \(-20^\circ\text{C}\) refrigerator for 12 h. The solvents were removed by rotary evaporation to afford the crude epoxide 6l as clear oil (31.3 mg, 100%) that was used without further purification.

TLC: \( R_f \) 0.25 (4:1 hexanes/EtOAc). \( ^1H-NMR \) (500 MHz): \( \delta \) 9.91 (s, 1H), 7.93 (d, \( J = 1.8 \) Hz, 1H), 7.85 (dd, \( J = 8.4, 1.8 \) Hz, 1H), 7.05 (d, \( J = 8.3 \) Hz, 1H), 5.53 (s, 1H), 3.92 (t, \( J = 6.1 \) Hz, 2H), 3.71 (t, \( J = 6.1 \) Hz, 1H), 2.13 (q, \( J = 6.1 \) Hz, 2H), 1.26 (s, 1H), 1.17 (dt, \( J = 9.5, 6.1 \) Hz, 3H), 1.10 (dd, \( J = 16.6, 7.0 \) Hz, 18H).

((2R,3R,3′R)-3′-(2-hydroxyethyl)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-5-yl)methyl acetate (6m). Prepared from 5m. Clear oil (25.9 mg, 100%). TLC: \( R_f \) 0.25 (4:1 hexanes/EtOAc). \( ^1H-NMR \) (500 MHz): \( \delta \) 7.43 (d, \( J = 2.0 \) Hz, 1H), 7.28–7.25 (m, 1H), 6.80 (dd, \( J = 8.3, 1.6 \) Hz, 1H), 5.48 (s, 1H), 5.13–5.03 (m, 1H), 5.04–5.03 (m, 1H), 4.62 (d, \( J = 4.8 \) Hz, 1H), 4.33 (dt, \( J = 9.0, 7.6 \) Hz, 1H), 4.15 (ddd, \( J = 10.2, 8.1, 2.6 \) Hz, 1H), 3.64–3.54 (m, 1H), 2.47–2.36 (m, 1H), 2.13–2.05 (m, 4H), 1.26 (s, 1H), 1.13–1.05 (m, 12H), 0.95–0.90 (m, 9H).

2-(((2R,3R,3′R)-3′-(2-hydroxyethyl)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2′-oxiran]-5-yl)methyl)isoindoline-1,3-dione (6n). Prepared from 5n. Clear oil (20.6 mg, 100%). TLC: \( R_f \) 0.25 (4:1 hexanes/EtOAc). \( ^1H-NMR \) (500 MHz): \( \delta \) 7.84 (dd, \( J = 5.5, 3.0 \) Hz, 2H), 7.71
(dd, J = 5.4, 3.0 Hz, 2H), 7.46 (d, J = 1.9 Hz, 1H), 7.39 (dd, J = 8.4, 1.9 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 5.42 (s, 1H), 4.88 (d, J = 14.6 Hz, 1H), 4.75 (d, J = 14.5 Hz, 1H), 3.88 (t, J = 6.1 Hz, 2H), 3.63 (dd, J = 6.7, 5.5 Hz, 1H), 2.15–2.03 (m, 2H), 1.10–1.06 (m, 4H), 1.04 (d, J = 6.5 Hz, 9H), 0.98 (d, J = 6.8 Hz, 9H).
J. Sc(OTf)$_3$-mediated Spirocyclization of exo-glycal epoxides 6 in THF with inversion of configuration (7a–n)

The exo-glycal epoxide 6 (1.0 equiv) was dissolved in THF (0.01 M) and cooled to –20 °C. Sc(OTf)$_3$ (1.0 equiv) was added and the reaction was stirred at –20 °C for 2–3 h. The reaction was quenched with satd aq NaHCO$_3$ and the aq layer was separated and extracted with EtOAc. The organic layer was collected, dried over Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography afforded inversion spiroketals 7a–h.

(2S,3R,3'R)-3-(triisopropylsilyloxy)-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan]-3'-ol (7a). Prepared from 6a. Clear oil (15 mg, 96%). TLC: R$_r$ 0.30 (4:1 hexanes/EtOAc). IR (NaCl, film): 3490 (O–H st), 2943, 2866, 1601, 1558, 1463, 1202, 1119, 1067 (C–O st), 1011, 951, 882, 748. $^1$H-NMR (500 MHz): δ 7.33 (d, J = 7.4 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 6.95 (s, 1H), 4.30 (ddd, J = 11.8, 9.7, 7.7 Hz, 1H), 4.22 (td, J = 9.2, 3.1 Hz, 1H), 3.99 (td, J = 9.0, 7.2 Hz, 1H), 2.43 (ddt, J = 12.8, 7.5, 3.1 Hz, 1H), 2.16–2.01 (m, 2H), 1.20 (ddd, J = 13.8, 6.4, 4.3 Hz, 3H), 1.15 (d, J = 5.6 Hz, 18H). $^{13}$C-NMR (126 MHz): δ 156.1, 129.6, 129.0, 124.8, 121.6, 114.0, 110.4, 74.6, 73.2, 65.7, 31.8, 18.1, 18.0, 12.8. HRMS m/z calcd for C$_{20}$H$_{31}$O$_4$Si ([M–H]–) 363.1992; found 363.1989.

(2S,3R,3'R)-3-(((triisopropylsilyl)oxy)-3',4',5',6'-tetrahydro-3H-spiro[benzofuran-2,2'-pyran]-3'-ol (7b). Prepared from 6b. Clear oil (12 mg, 94%). TLC: R$_r$ 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3490 (O–H st), 2943, 2866, 1601, 1558, 1463, 1202, 1119, 1067 (C–O st), 1011, 951, 882, 748, 680. $^1$H-NMR (600 MHz): δ 7.34 (dt, J = 7.5, 1.3 Hz, 1H), 7.21–7.16 (m, 1H), 6.95 (td, J = 7.5, 1.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 5.80 (s, 1H), 3.91 (td, J = 11.6, 2.9 Hz, 1H), 3.82–3.71 (m, 2H), 2.16 (ddt, J = 10.0, 4.8, 1.9 Hz, 1H), 1.89–1.72 (m, 3H), 1.55 (s, 1H), 1.27–1.20 (m, 4H), 1.18 (dd, J = 10.1, 6.5 Hz, 18H). $^{13}$C-NMR (151 MHz): δ 156.7, 129.5, 129.3, 125.1, 121.7, 110.5, 109.1, 77.2, 74.1, 68.6, 61.9, 29.6, 24.8, 18.2, 18.1, 12.9. HRMS m/z calcd for C$_{21}$H$_{34}$O$_4$SiNa ([M+Na]$^+$) 401.2124; found 401.2105.
(2S,3R,3’R)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2’-oxepan]-3’-ol (7c). Prepared from 6c to yield a separable 2:1 mixture of 7c and S2. Clear oil (16 mg, 65%). TLC: Rf 0.40 (4:1 hexanes/EtOAc). IR (NaCl, film): 3490 (O–H st), 2943, 2866, 1601, 1558, 1463, 1202, 1119, 1067 (C–O st), 1011, 951, 882, 748, 680. 1H-NMR (600 MHz) δ 7.34 (dt, J = 7.6, 1.2 Hz, 1H), 7.19 (td, J = 7.8, 1.5 Hz, 1H), 6.95 (td, J = 7.4, 1.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.61 (s, 1H), 4.16 (ddd, J = 12.8, 9.7, 3.1 Hz, 1H), 3.85–3.79 (m, 1H), 3.75 (ddd, J = 12.7, 5.1, 4.1 Hz, 1H), 2.12–2.04 (m, 1H), 2.02 (dd, J = 9.3, 1.4 Hz, 1H), 1.97–1.89 (m, 2H), 1.87–1.80 (m, 1H), 1.74–1.67 (m, 1H), 1.57 (s, 1H), 1.24–1.19 (m, 3H), 1.16 (dd, J = 8.9, 6.7 Hz, 18H). 13C-NMR (151 MHz) δ 156.7, 129.5, 129.4, 125.3, 121.6, 111.1, 110.5, 76.0, 73.8, 63.5, 31.0, 28.7, 21.1, 18.2, 18.1, 13.1. HRMS m/z calcd for C22H36O4SiNa ([M+Na]+) 415.2281; found 415.2276.

(R)-triisopropyl((2-(tetrahydro-2H-pyran-2-yl)benzofuran-3-yl)oxy)silane (S5). Isolated along with 7c as a clear oil (7.5 mg, 30%). TLC: Rf 0.80 (4:1 hexanes/EtOAc). IR (NaCl, film): 2943, 2866, 1601, 1558, 1463, 1202, 1119, 1067 (C–O st), 1011, 951, 882, 748. 1H-NMR (600 MHz) δ 7.54–7.50 (m, 1H), 7.40–7.36 (m, 1H), 7.25–7.22 (m, 1H), 7.17 (td, J = 7.5, 1.0 Hz, 1H), 4.66 (ddd, J = 11.5, 2.2 Hz, 1H), 4.15–4.09 (m, 1H), 3.58 (td, J = 11.8, 2.2 Hz, 1H), 2.15 (tdd, J = 13.0, 11.3, 3.9 Hz, 1H), 2.04–1.98 (m, 1H), 1.81–1.69 (m, 2H), 1.67–1.57 (m, 2H), 1.31 (dq, J = 14.7, 7.4 Hz, 3H), 1.14 (dd, J = 7.5, 2.4 Hz, 18H). 13C-NMR (151 MHz) δ 152.4, 141.8, 135.1, 124.4, 122.0, 118.7, 111.9, 70.5, 69.2, 29.4, 25.7, 23.9, 18.0, 17.9, 13.1. HRMS m/z calcd for C22H35O3Si ([M+Na]+) 375.2355; found 375.2360.

(2S,3R,3’R)-5-nitro-3-((triisopropylsilyl)oxy)-4’,5’-dihydro-3H,3’H-spiro[benzofuran-2,2’-furan]-3’-ol (7d). Prepared from 6d using the general procedure except that the reaction was run at rt for 3 h to afford 7d as a yellow oil (6.3 mg, 90%). TLC: Rf 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2928, 2856, 1614, 1600, 1522 (N–O), 1466, 1324 (N–O), 1287, 1253, 1138 1095 (C–O st), 1017, 902, 835, 775, 750. 1H-NMR (600 MHz) δ 8.22 (dd, J = 2.5, 1.1 Hz, 1H), 8.20 (dd, J = 8.8, 2.5, 0.6 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 5.57 (s, 1H), 4.35 (ddd, J = 9.4, 2.5 Hz, 1H), 4.09–4.02 (m, 1H), 2.00 (dd, J = 9.4, 2.5 Hz, 1H), 1.91 (d, J = 11.6 Hz, 1H), 1.31–1.11 (m, 21H). 13C-NMR (151 MHz) δ 161.4, 142.6, 130.6, 126.8, 121.2, 116.3, 110.6, 74.7, 71.9, 66.5, 31.3, 18.0, 17.9, 12.7. HRMS m/z calcd for C20H30NO6Si ([MH]+) 408.1842; found 408.1836.
(2S,3R,3′R)-5-methoxy-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3H,3′H-spiro[benzofuran-2,2′-furan]-3′-ol (7e). Prepared from 6e. Clear oil (4.5 mg, 89%). \textbf{TLC:} \( R_f \) 0.35 (4:1 hexanes/EtOAc). \textbf{IR} (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. \textbf{^1H-NMR} (600 MHz) \( \delta \) 6.91 (dd, \( J = 2.3, 1.0 \) Hz, 1H), 6.77–6.68 (m, 2H), 5.53 (s, 1H), 4.28 (ddd, \( J = 11.2, 9.7, 7.8 \) Hz, 1H), 3.97 (td, \( J = 9.0, 7.2 \) Hz, 1H), 3.75 (s, 3H), 2.42 (dtd, \( J = 12.3, 7.5, 2.9 \) Hz, 1H), 2.14–2.01 (m, 2H), 1.23–1.10 (m, 21H). \textbf{^13C-NMR} (151 MHz) \( \delta \) 154.8, 150.0, 129.8, 114.7, 114.3, 110.7, 110.6, 74.3, 73.4, 65.9, 56.0, 31.7, 18.1, 18.0, 12.8. \textbf{HRMS} \( m/z \) calcd for C_{21}H_{34}O_{5}SiNa ([M+Na]^+) 417.2073; found 417.2067.

(2S,3R,3′R)-5-methyl-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3H,3′H-spiro[benzofuran-2,2′-furan]-3′-ol (7f). Prepared from 6f. Clear oil (18.4 mg, 92%). \textbf{TLC:} \( R_f \) 0.40 (4:1 hexanes/EtOAc). \textbf{IR} (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. \textbf{^1H-NMR} (600 MHz) \( \delta \) 7.13–7.09 (m, 1H), 6.99 (dd, \( J = 7.9, 1.8 \) Hz, 1H), 6.70 (d, \( J = 8.1 \) Hz, 1H), 5.52 (s, 1H), 4.29 (ddd, \( J = 11.2, 9.7, 7.8 \) Hz, 1H), 4.21 (td, \( J = 9.2, 2.9 \) Hz, 1H), 3.98 (td, \( J = 9.0, 7.2 \) Hz, 1H), 2.42 (dtd, \( J = 12.2, 7.5, 2.9 \) Hz, 1H), 2.30 (s, 3H), 2.14–2.05 (m, 2H), 1.21–1.12 (m, 21H). \textbf{^13C-NMR} (151 MHz) \( \delta \) 153.9, 130.9, 129.9, 128.8, 125.1, 114.0, 109.9, 74.4, 73.1, 65.9, 31.7, 21.1, 18.1, 17.9, 12.8. \textbf{HRMS} \( m/z \) calcd for C_{21}H_{34}O_{5}SiNa ([M+Na]^+) 401.2124; found 401.2108.

(2S,3R,3′R)-6-bromo-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3H,3′H-spiro[benzofuran-2,2′-furan]-3′-ol (7g). Prepared from 6g. Clear oil (17 mg, 85%). \textbf{TLC:} \( R_f \) 0.38 (4:1 hexanes/EtOAc). \textbf{IR} (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. \textbf{^1H-NMR} (600 MHz) \( \delta \) 7.19 (dd, \( J = 7.9, 1.0 \) Hz, 1H), 7.09 (dd, \( J = 7.9, 1.7 \) Hz, 1H), 6.98 (d, \( J = 1.7 \) Hz, 1H), 5.48 (d, \( J = 1.0 \) Hz, 1H), 4.30 (ddd, \( J = 11.6, 10.0, 7.8 \) Hz, 1H), 4.23 (td, \( J = 9.3, 2.7 \) Hz, 1H), 4.00 (td, \( J = 9.1, 7.2 \) Hz, 1H),
2.45 (dt, $J = 12.3, 7.5, 2.7$ Hz, 1H), 2.10 (dq, $J = 12.3, 9.7$ Hz, 1H), 1.97 (d, $J = 11.6$ Hz, 1H), 1.20–1.09 (m, 21H). $^{13}$C-NMR (151 MHz) $\delta$ 156.9, 128.3, 125.8, 124.6, 122.6, 114.7, 114.0, 76.9, 74.6, 72.5, 66.1, 31.5, 18.1, 17.9, 12.7. HRMS m/z calcd for C$_{20}$H$_{31}$O$_4$BrSiNa ([M+Na]$^+$) 465.1073; found 465.1064.

(2$S$,3$R$,3´$R$)-5-bromo-3-((triisopropylsilyl)oxy)-4´,5´-dihydro-3$H$,3´$H$-spiro[benzofuran-2,2´-furan]-3´-ol (7h). Prepared from 6h. Clear oil (9.2 mg, 92%). TLC: $R_f$ 0.38 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. $^{1}$H-NMR (600 MHz) $\delta$ 7.39 (dd, $J = 2.2, 1.0$ Hz, 1H), 7.30 (ddd, $J = 8.5, 2.2, 0.7$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 5.53 (d, $J = 0.9$ Hz, 1H), 4.29 (ddd, $J = 11.6, 10.0, 7.8$ Hz, 1H), 4.22 (td, $J = 9.3, 2.7$ Hz, 1H), 3.99 (td, $J = 9.1, 7.2$ Hz, 1H), 2.44 (ddd, $J = 12.3, 7.5, 2.7$ Hz, 1H), 2.09 (dd, $J = 12.3, 9.8$ Hz, 1H), 1.99 (d, $J = 11.6$ Hz, 1H), 1.21–1.12 (m, 21H). $^{13}$C-NMR (151 MHz) $\delta$ 155.1, 132.4, 131.3, 127.7, 114.6, 113.5, 112.1, 74.3, 72.7, 66.1, 31.5, 18.1, 17.9, 12.7. HRMS m/z calcd for C$_{20}$H$_{31}$O$_4$BrSiNa ([M+Na]$^+$) 465.1073; found 465.1075.

(2$S$,3$R$,3´$R$)-5-phenyl-3-((triisopropylsilyl)oxy)-4´,5´-dihydro-3$H$,3´$H$-spiro[benzofuran-2,2´-furan]-3´-ol (7i). Prepared from 6i. Clear oil (4.3 mg, 87%). TLC: $R_f$ 0.36 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. $^{1}$H-NMR (600 MHz) $\delta$ 7.55–7.54 (m, 1H), 7.50 (ddd, $J = 11.3, 9.7, 7.7$ Hz, 1H), 4.24 (td, $J = 9.2, 2.8$ Hz, 1H), 4.01 (td, $J = 9.0, 7.2$ Hz, 1H), 2.45 (ddd, $J = 12.3, 7.5, 2.8$ Hz, 1H), 2.17–2.04 (m, 2H), 1.25 (d, $J = 3.4$ Hz, 1H), 1.24–1.19 (m, 3H), 1.17 (dd, $J = 6.8, 2.4$ Hz, 18H). $^{13}$C-NMR (151 MHz) $\delta$ 155.7, 141.3, 135.2, 129.6, 128.8, 128.7, 126.8, 126.7, 123.6, 114.5, 110.6, 74.4, 73.1, 66.0, 31.7, 18.1, 18.0, 12.8. HRMS m/z calcd for C$_{26}$H$_{36}$O$_4$SiNa ([M+Na]$^+$) 463.2281; found 463.2282.
(2S,3R,3’R)-5-(3-cyclopentylprop-1-yn-1-yl)-3-((triisopropylsilyl)oxy)-4’,5’-dihydro-3H,3’H-spiro[benzofuran-2,2’-furan]-3’-ol (7j). Prepared from 6j. Clear oil (4.2 mg, 84%). TLC: Rf 0.38 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. 1H-NMR (600 MHz) δ 7.33 (t, J = 1.4 Hz, 1H), 7.25 (dd, J = 8.2, 1.8 Hz, 1H), 6.72 (d, J = 8.3 Hz, 1H), 5.49 (s, 1H), 4.29 (q, J = 9.5 Hz, 1H), 4.21 (td, J = 9.3, 2.9 Hz, 1H), 3.99 (td, J = 9.1, 7.2 Hz, 1H), 2.45–2.41 (m, 1H), 2.39 (d, J = 6.7 Hz, 2H), 2.15–2.06 (m, 2H), 1.99 (d, J = 11.4 Hz, 1H), 1.85–1.79 (m, 2H), 1.68–1.64 (m, 2H), 1.59–1.54 (m, 2H), 1.38–1.32 (m, 2H), 1.18 (d, J = 7.6 Hz, 3H), 1.16–1.13 (m, 18H). 13C-NMR (151 MHz) δ 155.5, 133.3, 129.2, 128.1, 117.4, 114.4, 110.3, 88.0, 80.6, 74.5, 72.8, 66.0, 39.1, 31.9, 31.6, 29.7, 25.4, 25.2, 18.1, 17.9, 12.8. HRMS m/z calcd for C28H42O4SiNa ([M+Na]+) 493.2750; found 493.2739.

(2S,3R,3’R)-5-azido-3-((triisopropylsilyl)oxy)-4’,5’-dihydro-3H,3’H-spiro[benzofuran-2,2’-furan]-3’-ol (7k). Prepared from 6k. Clear oil (3.7 mg, 92%). TLC: Rf 0.40 (4:1 hexanes/EtOAc). IR (NaCl, film): 3583 (O–H st), 2941, 2867, 2114 (N=N=N st), 1482, 1234, 1110 (C–O st), 882, 818. 1H-NMR (600 MHz) δ 6.99 (dd, J = 2.5, 1.1 Hz, 1H), 6.87 (dd, J = 8.5, 2.4 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 5.53 (s, 1H), 4.30 (dd, J = 11.5, 10.0, 7.8 Hz, 1H), 4.22 (td, J = 9.3, 2.7 Hz, 1H), 3.99 (td, J = 9.1, 7.2 Hz, 1H), 2.45 (dt, J = 12.3, 7.5, 2.7 Hz, 1H), 2.10 (dq, J = 12.3, 9.7 Hz, 1H), 2.03 (d, J = 11.6 Hz, 1H), 1.21–1.16 (m, 3H), 1.15 (dd, J = 6.6, 2.1 Hz, 1H). 13C-NMR (151 MHz) δ 153.4, 133.4, 130.8, 120.1, 115.5, 114.4, 110.3, 88.0, 80.6, 74.5, 72.8, 66.1, 31.5, 18.1, 17.9, 12.7. HRMS m/z calcd for C20H31N3O4SiNa ([M+Na]+) 428.1982; found 428.1996.

(2S,3R,3’R)-3’-hydroxy-3-((triisopropylsilyl)oxy)-4’,5’-dihydro-3H,3’H-spiro[benzofuran-2,2’-furan]-5-carbaldehyde (7l). Prepared from 6l. Clear oil (13.7 mg, 86%). TLC: Rf 0.35 (4:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1698 (C=O st), 1613, 1468, 1394, 1287, 1257, 1098 (C–O st), 881, 835, 776. 1H-NMR (600 MHz) δ 9.87 (s, 1H), 7.78 (dd, J = 8.2, 1.8 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 5.57 (s, 1H), 4.35 (q, J =
9.3 Hz, 1H), 4.25 (td, \(J = 9.3, 2.6\) Hz, 1H), 4.03 (td, \(J = 9.2, 7.2\) Hz, 1H), 2.48 (dtd, \(J = 12.3, 7.5, 2.6\) Hz, 1H), 2.13 (dq, \(J = 12.3, 9.8\) Hz, 1H), 1.98 (d, \(J = 11.3\) Hz, 1H), 1.23–1.18 (m, 3H), 1.16 (dd, \(J = 7.0, 1.6\) Hz, 1H). \(^{13}\text{C-NMR}\) (151 MHz) \(\delta 190.5, 161.5, 133.5, 131.2, 130.5, 126.4, 115.5, 110.9, 74.7, 72.1, 66.3, 31.4, 18.1, 17.9, 12.8\). \(\text{HRMS m/z}\) calcd for \(\text{C}_{21}\text{H}_{33}\text{O}_{5}\text{Si} ([\text{M+H}]^+) 393.2097;\) found 393.2083.

\((2S,3R,3'R)-3'\text{-hydroxy-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan]-5-yl}methyl\) acetate (7m). Prepared from 6m. Clear oil (13.7 mg, 91%). \(\text{TLC: } R_r 0.40\) (4:1 hexanes/EtOAc). \(\text{IR (NaCl, film): } 3566\) (O–H st), 2941, 2866, 1741 (C=O st), 1611, 1468, 1394, 1287, 1257, 1098 (C–O st), 881, 835, 776. \(\text{H-NMR (600 MHz): } \delta 7.35–7.31\) (m, 1H), 7.20 (dd, \(J = 8.2, 1.9\) Hz, 1H), 6.79 (d, \(J = 8.2\) Hz, 1H), 5.54 (s, 1H), 5.07 (d, \(J = 12.0\) Hz, 1H), 5.01 (d, \(J = 12.0\) Hz, 1H), 4.30 (ddd, \(J = 11.3, 9.8, 7.7\) Hz, 1H), 4.22 (td, \(J = 9.2, 2.8\) Hz, 1H), 3.99 (td, \(J = 9.0, 7.2\) Hz, 1H), 2.43 (dtd, \(J = 12.3, 7.5, 2.8\) Hz, 1H), 2.14–1.98 (m, 5H), 1.23–1.12 (m, 21H). \(^{13}\text{C-NMR (151 MHz): } \delta 170.9, 156.2, 130.4, 129.5, 129.3, 125.2, 114.5, 110.4, 74.5, 72.9, 66.2, 66.0, 31.7, 21.0, 18.1, 17.9, 12.8\). \(\text{HRMS m/z}\) calcd for \(\text{C}_{23}\text{H}_{36}\text{O}_{6}\text{SiNa} ([\text{M+Na}]^+) 459.2179;\) found 459.2176.

\((2S,3R,3'R)-3'\text{-hydroxy-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan]-5-yl}methyl\) isoindoline-1,3-dione (7n). Prepared from 6n. Clear oil (8.1 mg, 81%, >96% purity). \(\text{TLC: } R_r 0.42\) (9:1 hexanes/EtOAc). \(\text{IR (NaCl, film): } 3566\) (O–H st), 2941, 2866, 1714 (C=O st), 1611, 1468, 1394, 1287, 1257, 1098 (C–O st), 881, 835, 776. \(\text{H-NMR (600 MHz): } \delta 7.82\) (dd, \(J = 5.4, 3.1\) Hz, 2H), 7.69 (dd, \(J = 5.5, 3.0\) Hz, 2H), 7.42–7.37 (m, 1H), 7.31 (dd, \(J = 8.2, 1.9\) Hz, 1H), 6.74 (d, \(J = 8.2\) Hz, 1H), 5.49 (s, 1H), 4.85 (d, \(J = 14.6\) Hz, 1H), 4.73 (d, \(J = 14.5\) Hz, 1H), 4.27 (td, \(J = 10.1, 7.7\) Hz, 1H), 4.18 (td, \(J = 9.3, 2.9\) Hz, 1H), 3.95 (td, \(J = 9.0, 7.2\) Hz, 1H), 2.40 (dtd, \(J = 12.3, 7.5, 2.9\) Hz, 1H), 2.08 (dt, \(J = 12.2, 9.5\) Hz, 1H), 2.00 (d, \(J = 11.3\) Hz, 1H), 1.17–1.12 (m, 3H), 1.10 (d, \(J = 6.5\) Hz, 1H). \(^{13}\text{C-NMR (151 MHz): } \delta 167.9, 155.8, 133.9, 132.2, 130.4, 129.9, 129.5, 125.1, 123.2, 114.4, 110.32, 77.2, 77.0, 76.8, 74.4, 72.9, 65.9, 41.2, 31.7, 18.1, 17.9, 12.7\). \(\text{HRMS m/z}\) calcd for \(\text{C}_{29}\text{H}_{36}\text{O}_{6}\text{SiNa} ([\text{M+Na}]^+) 546.2288;\) found 546.2309.
K. Sc(OTf)₃-MEDIATED SPIROCYCLIZATION OF exo-GLYCAL EPOXIDES 6 IN CH₂Cl₂ WITH RETENTION OF CONFIGURATION (8a–n)

The exo-glycal epoxide 6 (1.0 equiv) was dissolved in CH₂Cl₂ (0.01 M) and cooled down to 0 ºC. Sc(OTf)₃ (0.5 equiv) was added and the reaction was warmed to rt or 60 ºC and stirred for 1–12 h. The reaction was quenched with a satd aq NaHCO₃ and the aq layer was separated and extracted with EtOAc. The organic layer was collected, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography afforded spiroketals 8a–n.

![Diagram of spiroketals 8a–n]

(2R,3R,3’R)-3-(triisopropylsilyloxy)-4’,5’-dihydro-3H,3’H-spiro[benzofuran-2,2’-furan]-3’-ol (8a). Prepared from 6a. Clear oil (22.3 mg, 74%). TLC: Rf 0.60 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. ¹H-NMR (600 MHz): δ 7.43–7.39 (m, 1H), 7.28–7.24 (m, 1H), 6.92 (td, J = 7.5, 1.0 Hz, 1H), 6.83 (dd, J = 8.0, 0.9 Hz, 1H), 6.50 (s, 1H), 4.63 (dt, J = 5.0, 0.8 Hz, 1H), 4.40–4.28 (m, 1H), 4.17 (ddd, J = 9.7, 8.0, 2.7 Hz, 1H), 3.73–3.65 (m, 1H), 2.48–2.36 (m, 1H), 2.10 (ddd, J = 13.4, 7.3, 2.7 Hz, 1H), 1.12–1.06 (m, 12H), 0.96–0.88 (m, 9H). ¹³C-NMR (151 MHz) δ 159.2, 131.0, 125.9, 120.8, 120.3, 111.0, 77.6, 74.6, 68.5, 31.1, 18.1, 17.7, 17.7, 13.3, 12.2. HRMS m/z calcd for C₂₀H₃₁O₄Si ([M–H]–) 363.1992; found 363.1989.

(Z)-2-(2-hydroxybenzylidene)dihydrofuran-3(2H)-one (S3). Byproduct from reaction of 6a. Clear oil (3 mg, 20%). TLC: Rf 0.2 (4:1 hexanes/EtOAc). ¹H-NMR (500 MHz) δ 8.31 (s, 1H), 7.29 (td, J = 7.8, 1.8 Hz, 1H), 7.08 (dd, J = 7.6, 1.7 Hz, 1H), 7.02–6.96 (m, 2H), 6.92 (t, J = 7.4 Hz, 1H), 4.51 (t, J = 6.3 Hz, 2H), 2.67 (td, J = 6.3, 4.5 Hz, 2H). ¹³C-NMR (126 MHz) δ 193.4, 167.4, 154.2, 145.8, 132.8, 130.8, 123.9, 120.8, 118.8, 66.7, 24.9. ESI-MS m/z (rel int): (pos) 213.1 ([M+Na]+, 100).

(2R,3R,3’R)-3-(triisopropylsilyloxy)-4’,5’,6’-tetrahydro-3H-spiro[benzofuran-2,2’-pyran]-3’-ol (8b). Prepared from 6b using the general procedure (60 ºC, 2 h). White solid (16 mg, 62%). Recrystallization from hexanes (slow evaporation method) yielded triclinic clear
crystals for X-ray crystallographic analysis. **TLC**: $R_f$ 0.62 (4:1 hexanes/EtOAc). **$^1$H-NMR** (600 MHz): $\delta$ 7.43 (dd, $J = 7.5$, 1.3 Hz, 1H), 7.30–7.26 (m, 1H), 6.93 (td, $J = 7.4$, 1.0 Hz, 1H), 6.90 (dd, $J = 8.1$, 0.8 Hz, 1H), 5.16 (s, 1H), 4.18 (q, $J = 3.0$ Hz, 1H), 3.99 (ddd, $J = 12.6$, 11.2, 2.7 Hz, 1H), 3.74–3.66 (m, 1H), 3.08 (dd, $J = 3.3$, 1.6 Hz, 1H), 2.22–2.09 (m, 2H), 2.04–1.95 (m, 1H), 1.50–1.41 (m, 1H), 1.10–1.04 (m, 12H), 0.94–0.86 (m, 9H). **$^{13}$C-NMR** (151 MHz): $\delta$ 159.7, 130.8, 126.9, 111.2, 110.9, 78.6, 64.5, 62.6, 25.5, 19.2, 18.2, 17.8, 17.7, 13.4, 12.2. **HRMS** $m/z$ calcd for C$_{21}$H$_{34}$O$_4$SiNa ([M+Na]$^+$) 401.2124; found 401.2123.

**Figure S2.** X-ray crystal structure of spiroketal 8b (0.71 Å resolution).

**(2R,3R,3'R)-3-((triisopropylsilyl)oxy)-3H-spiro[benzofuran-2,2'-oxepan]-3'-ol** (8c). Prepared from 6c. Clear oil (6.2 mg, 55%). **TLC**: $R_f$ 0.68 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. **$^1$H-NMR** (600 MHz) $\delta$ 7.39–7.36 (m, 1H), 7.27–7.24 (m, 1H), 6.92 (td, $J = 7.4$, 1.0 Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 1H), 5.29 (s, 1H), 4.38 (td, $J = 7.4$, 1.8 Hz, 1H), 3.86 (ddd, $J = 12.2$, 8.3, 3.7 Hz, 1H), 3.68 (ddd, $J = 12.5$, 5.8, 4.4 Hz, 1H), 3.57 (d, $J = 7.5$ Hz, 1H), 2.12 (dtd, $J = 14.5$, 7.5, 2.9 Hz, 1H), 2.03–1.96 (m, 1H), 1.92 (ddddd, $J = 14.4$, 12.4, 6.0, 2.5 Hz, 1H), 1.82 (dddd, $J = 20.9$, 9.6, 6.8, 4.3 Hz, 2H), 1.65 (dttdd, $J = 13.4$, 8.1, 5.3, 3.3 Hz, 1H), 1.16–1.13 (m,
3H), 1.12 (d, J = 6.4 Hz, 9H), 0.99 (d, J = 6.9 Hz, 9H). $^{13}$C-NMR (151 MHz) δ 159.1, 130.4, 127.9, 125.9, 120.9, 113.5, 110.9, 80.7, 76.9, 72.4, 64.2, 31.3, 29.6, 21.6, 18.2, 18.0, 17.9, 17.7, 13.3, 12.3. HRMS m/z calcd for C$_{22}$H$_{36}$O$_4$SiNa ([M+Na]$^+$) 415.2281; found 415.2282.

(2R,3R,3'R)-5-nitro-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3H,3'H-spirob[benzofuran-2,2'-furan]-3'-ol (8d). Prepared from 6d. Yellow oil (4.3 mg, 61%). TLC: R$_f$ 0.62 (4:1 hexanes/EtOAc). IR (NaCl, film): 3367 (O–H st), 2928, 2856, 1614, 1600, 1522 (N–O), 1466, 1324 (N–O), 1287, 1253, 1138 1095 (C–O st), 1017, 902, 835, 775, 750. $^1$H-NMR (600 MHz) δ 8.32 (d, J = 2.4 Hz, 1H), 8.26 (dd, J = 8.9, 2.4 Hz, 1H), 6.91 (d, J = 8.9 Hz, 1H), 5.55 (s, 1H), 4.73–4.57 (m, 1H), 4.39 (ddd, J = 9.4, 8.1, 7.2 Hz, 1H), 4.20 (ddd, J = 9.7, 8.1, 2.5 Hz, 1H), 3.46 (t, J = 1.6 Hz, 1H), 2.43 (dddd, J = 16.7, 9.6, 7.0, 4.9, 2.1 Hz, 1H), 2.13 (ddd, J = 13.4, 7.2, 2.5 Hz, 1H), 1.23–1.02 (m, 12H), 1.00–0.90 (m, 9H). $^{13}$C-NMR (151 MHz) δ 164.1, 141.7, 128.6, 127.8, 122.4, 122.3, 111.2, 76.5, 74.5, 69.2, 30.9, 18.1, 17.7, 13.2. HRMS m/z calcd for C$_{20}$H$_{30}$NO$_6$Si ([M–H]$^-$) 408.1842; found 408.1854.

(2R,3R,3'R)-5-methoxy-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3H,3'H-spirob[benzofuran-2,2'-furan]-3'-ol (8e). Prepared from 6e. Clear oil (3.6 mg, 72%). TLC: R$_f$ 0.60 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. $^1$H-NMR (600 MHz) δ 6.98 (d, J = 2.7 Hz, 1H), 6.82 (dd, J = 8.7, 2.7 Hz, 1H), 6.74 (d, J = 8.7 Hz, 1H), 5.48 (s, 1H), 4.61 (d, J = 4.8 Hz, 1H), 4.33 (dt, J = 9.0, 7.5 Hz, 1H), 4.16 (ddd, J = 9.6, 8.0, 2.6 Hz, 1H), 3.77 (s, 3H), 3.69–3.63 (m, 1H), 2.41 (dddt, J = 14.3, 9.4, 4.9, 2.0 Hz, 1H), 2.08 (dddt, J = 13.3, 7.2, 2.6 Hz, 1H), 1.11 (t, J = 1.8 Hz, 12H), 0.96 (dd, J = 4.9, 2.5 Hz, 9H). $^{13}$C-NMR (151 MHz) δ 154.1, 153.2, 127.8, 120.4, 116.2, 112.1, 111.2, 78.1, 74.7, 68.4, 56.2, 31.2, 18.1, 17.8, 13.3. HRMS m/z calcd for C$_{21}$H$_{35}$O$_5$Si ([M–H]$^-$) 393.2097; found 393.2108.

(2R,3R,3'R)-5-methyl-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3H,3'H-spirob[benzofuran-2,2'-furan]-3'-ol (8f). Prepared from 6f. Clear oil (10 mg, 62%). TLC: R$_f$ 0.65 (4:1
hexanes/EtOAc). **IR** (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. **1H-NMR** (600 MHz) δ 7.21–7.15 (m, 1H), 7.06 (dd, $J = 8.2$ Hz, 1H), 5.46 (s, 1H), 4.61 (d, $J = 4.8$ Hz, 1H), 4.33 (dt, $J = 9.1$, 7.6 Hz, 1H), 4.16 (dd, $J = 10.3$, 2.6 Hz, 1H), 3.72–3.67 (m, 1H), 2.30 (s, 3H), 2.11–2.03 (m, 1H), 1.10–1.06 (m, 12H), 0.93 (d, $J = 6.6$ Hz, 9H). **13C-NMR** (151 MHz) δ 157.0, 131.3, 130.1, 126.9, 126.3, 120.3, 110.5, 77.8, 74.6, 68.4, 31.1, 20.9, 18.1, 17.8, 13.3. **HRMS** m/z calcd for C$_{21}$H$_{34}$O$_4$SiNa ([M+Na]$^+$) 401.2124; found 401.2108.

(2R,3R,3'R)-6-bromo-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3'H,3'H-spiro[benzofuran-2,2'-furan]-3'-ol (8g). Prepared from 6a. Clear oil (13 mg, 65%). **TLC:** R$_f$ 0.60 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. **1H-NMR** (600 MHz) δ 7.26 (d, $J = 8.0$ Hz, 1H), 7.06 (dd, $J = 8.0$, 1.7 Hz, 1H), 7.00 (d, $J = 1.6$ Hz, 1H), 5.46 (s, 1H), 4.65–4.57 (m, 1H), 4.34 (dt, $J = 9.2$, 7.6 Hz, 1H), 4.16 (dd, $J = 9.7$, 8.0, 2.6 Hz, 1H), 3.60–3.53 (m, 1H), 2.40 (dtdt, $J = 16.4$, 7.0, 4.9, 2.5 Hz, 1H), 2.09 (dd, $J = 13.4$, 7.2, 2.6 Hz, 1H), 1.13–1.02 (m, 12H), 0.94 (d, $J = 6.7$ Hz, 9H). **13C-NMR** (151 MHz) δ 160.0, 126.9, 126.3, 124.2, 123.9, 121.6, 114.8, 76.9, 74.5, 68.7, 31.0, 18.1, 17.7, 13.3. **HRMS** m/z calcd for C$_{20}$H$_{31}$O$_4$BrSiNa ([M+Na]$^+$) 465.1073; found 465.1064.

(2R,3R,3'R)-5-bromo-3-((triisopropylsilyl)oxy)-4',5'-dihydro-3'H,3'H-spiro[benzofuran-2,2'-furan]-3'-ol (8h). Prepared from 6h. Clear oil (7.6 mg, 76%). **TLC:** R$_f$ 0.60 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. **1H-NMR** (600 MHz) δ 7.48 (d, $J = 2.1$ Hz, 1H), 7.37 (dd, $J = 8.5$, 2.1 Hz, 1H), 6.72 (d, $J = 8.5$ Hz, 1H), 5.46 (s, 1H), 4.63–4.57 (m, 1H), 4.34 (dt, $J = 9.2$, 7.4 Hz, 1H), 4.16 (dd, $J = 9.7$, 8.0, 2.6 Hz, 1H), 3.55 (t, $J = 1.5$ Hz, 1H), 2.40 (dd, $J = 14.3$, 9.5, 4.9, 2.0 Hz, 1H), 2.09 (dd, $J = 13.5$, 7.3, 2.6 Hz, 1H), 1.15–1.03 (m, 12H), 0.98–0.92 (m, 9H). **13C-NMR** (151 MHz) δ 158.1, 133.6, 129.5, 128.8, 120.8, 112.7, 112.6, 74.5, 68.7, 31.1, 18.1, 17.7, 13.3. **HRMS** m/z calcd for C$_{20}$H$_{31}$O$_4$BrSiNa ([M+Na]$^+$) 465.1073; found 465.1080.
(2R,3R,3′R)-5-phenyl-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3H,3′H-spiro[benzofuran-2,2′-furan]-3′-ol (8i). Prepared from 6i. Clear oil (3.6 mg, 72%). TLC: Rf 0.60 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. 1H-NMR (600 MHz) δ 7.60 (d, J = 2.0 Hz, 1H), 7.47 (dd, J = 8.3, 1.7 Hz, 3H), 7.43 (dd, J = 8.6, 6.9 Hz, 2H), 7.36–7.30 (m, 1H), 6.89 (d, J = 8.3 Hz, 1H), 5.56 (s, 1H), 4.66 (d, J = 4.8 Hz, 1H), 4.36 (dt, J = 9.0, 7.5 Hz, 1H), 4.19 (ddd, J = 9.7, 8.0, 2.6 Hz, 1H), 3.70–3.62 (m, 1H), 2.44 (ddtt, J = 16.4, 7.0, 5.0, 2.5 Hz, 1H), 2.11 (ddd, J = 13.4, 7.3, 2.7 Hz, 1H), 1.16–1.11 (m, 12H), 0.95 (dd, J = 5.3, 2.3 Hz, 9H). 13C-NMR (151 MHz) δ 158.8, 141.1, 134.5, 130.2, 128.8, 127.7, 126.8, 124.7, 120.7, 111.2, 77.7, 74.7, 68.6, 31.2, 29.7, 18.2, 17.8, 13.4. HRMS m/z calcd for C26H35O4Si ([M–H]–) 439.2305; found 439.2314.

(2R,3R,3′R)-5-(3-cyclopentylprop-1-yn-1-yl)-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3H,3′H-spiro[benzofuran-2,2′-furan]-3′-ol (8j). Prepared from 6j. Clear oil (3.4 mg, 68%). TLC: Rf 0.65 (4:1 hexanes/EtOAc). IR (NaCl, film): 3547 (O–H st), 2924, 2867, 1723, 1613, 1597, 1465, 1258, 1196, 1084, 1064 (C–O st), 994, 968, 882, 767. 1H-NMR (600 MHz) δ 7.41 (d, J = 1.7 Hz, 1H), 7.30 (dd, J = 8.3, 1.8 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.46 (s, 1H), 4.60 (d, J = 4.8 Hz, 1H), 4.33 (dt, J = 9.1, 7.5 Hz, 1H), 4.15 (ddd, J = 9.7, 8.0, 2.6 Hz, 1H), 3.66–3.54 (m, 1H), 2.40 (d, J = 6.6 Hz, 3H), 2.17–2.11 (m, 1H), 2.10–2.02 (m, 2H), 1.85–1.79 (m, 2H), 1.69–1.64 (m, 3H), 1.35 (ddt, J = 14.4, 8.7, 3.8 Hz, 2H), 1.10 (q, J = 17.1, 1.2 Hz, 12H), 0.95 (dd, J = 5.2, 2.3 Hz, 9H). 13C-NMR (151 MHz) δ 158.5, 134.4, 129.2, 127.3, 120.6, 116.7, 110.9, 88.1, 80.3, 77.4, 76.9, 74.6, 68.6, 39.1, 31.9, 31.1, 29.7, 25.4, 25.2, 18.1, 17.8, 13.3. HRMS m/z calcd for C28H41O4Si ([M–H]–) 469.2774; found 469.2762.

(2R,3R,3′R)-5-azido-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3H,3′H-spiro[benzofuran-2,2′-furan]-3′-ol (8k). Prepared from 6k using general procedure K (60 °C, 12h). Clear oil (2.2 mg, 55%). TLC: Rf 0.62 (4:1 hexanes/EtOAc). IR (NaCl, film): 3583 (O–H st), 2941, 2867, 2114 (N=N=N st), 1482, 1234, 1110 (C–O st), 882, 818. 1H-NMR (600 MHz) δ 7.05 (d, J = 2.4 Hz,
1H), 6.96 (dd, J = 8.5, 2.4 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 5.48 (s, 1H), 4.66–4.56 (m, 1H), 4.34 (dt, J = 9.1, 7.5 Hz, 1H), 4.17 (dd, J = 9.6, 8.1, 2.6 Hz, 1H), 3.62–3.57 (m, 1H), 2.41 (dtdd, J = 16.4, 9.6, 4.9, 2.1 Hz, 1H), 2.09 (dd, J = 13.4, 7.3, 2.6 Hz, 1H), 1.11–1.05 (m, 12H), 0.97–0.94 (m, 9H).  

$^{13}$C-NMR (151 MHz) δ 156.4, 132.6, 128.8, 121.3, 120.8, 116.7, 112.0, 77.5, 74.6, 68.7, 31.1, 29.7, 18.0, 17.7, 13.3. HRMS m/z calcld for C$_{20}$H$_{30}$N$_{3}$O$_{4}$Si ([M–H]$^-$) 404.2006; found 404.2014.

$^{(2R,3R,3'R)}$-3′-hydroxy-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3$H,3'H$-spiro[benzofuran-2,2′-furan]-5-carbaldehyde (8l). Prepared from 6l. Clear oil (5.1 mg, 64%). TLC: R$_{f}$ 0.60 (9:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1698 (C=O st), 1613, 1468, 1394, 1287, 1257, 1098 (C–O st), 881, 835, 776. $^1$H-NMR (600 MHz) δ 9.88 (s, 1H), 7.96 (d, J = 1.7 Hz, 1H), 7.83 (dd, J = 8.3, 1.8 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 5.54 (s, 1H), 4.74–4.57 (m, 1H), 4.43–4.30 (m, 1H), 3.52 (t, J = 1.6 Hz, 1H), 2.43 (dtdd, J = 14.5, 9.6, 4.9, 2.0 Hz, 1H), 2.12 (dd, J = 13.4, 7.2, 2.5 Hz, 1H), 1.13–1.06 (m, 12H), 0.95–0.91 (m, 9H). $^{13}$C-NMR (151 MHz) δ 190.3, 164.3, 134.9, 130.5, 128.7, 127.1, 121.8, 111.5, 76.6, 74.6, 69.0, 31.0, 18.1, 17.7, 13.3. HRMS m/z calcld for C$_{21}$H$_{33}$O$_{5}$Si ([M+H]$^+$) 393.2097; found 393.2086.

$^{(2R,3R,3'R)}$-3′-hydroxy-3-((triisopropylsilyl)oxy)-4′,5′-dihydro-3$H,3'H$-spiro[benzofuran-2,2′-furan]-5-yl)methyl acetate (8m). Prepared from 6m. Clear oil (5.8 mg, 73%). TLC: R$_{f}$ 0.62 (4:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1741 (C=O st), 1611, 1468, 1394, 1287, 1257, 1098 (C–O st), 881, 835, 776. $^1$H-NMR (600 MHz) δ 7.43 (d, J = 1.8 Hz, 1H), 7.31–7.23 (m, 1H), 6.80 (d, J = 8.2 Hz, 1H), 5.48 (s, 1H), 5.08 (d, J = 12.0 Hz, 1H), 5.00 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 4.8 Hz, 1H), 4.34 (dt, J = 9.0, 7.6 Hz, 1H), 4.16 (dd, J = 9.7, 8.0, 2.6 Hz, 1H), 3.63–3.56 (m, 1H), 2.41 (dtdd, J = 14.4, 9.4, 5.0, 2.0 Hz, 1H), 2.06 (s, 4H), 1.11–1.05 (m, 12H), 0.92 (d, J = 6.7 Hz, 9H). $^{13}$C-NMR (151 MHz) δ 170.8, 159.4, 131.9, 128.5, 127.5, 126.8, 120.8, 110.9, 77.4, 74.6, 68.6, 66.2, 31.1, 29.7, 21.0, 18.1, 17.7, 13.3. HRMS m/z calcld for C$_{23}$H$_{36}$O$_{6}$SiNa ([M+Na]$^+$) 459.2179; found 459.2167.
2-(((2R,3R,3’R)-3’-hydroxy-3-((triisopropylsilyl)oxy)-4’,5’-dihydro-3H,3H-spiro[benzofuran-2,2’-furan]-5-yl)methyl)isoindoline-1,3-dione (8n). Prepared from 6n. Clear oil (7.1 mg, 71%). TLC: Rf 0.65 (4:1 hexanes/EtOAc). IR (NaCl, film): 3566 (O–H st), 2941, 2866, 1714 (C=O st), 1611, 1468, 1394, 1287, 1257, 1098 (C–O st), 881, 835, 776. $^1$H-NMR (600 MHz) $\delta$ 7.84 (dd, $J = 5.4$, 3.0 Hz, 2H), 7.71 (dd, $J = 5.5$, 3.0 Hz, 2H), 7.50 (d, $J = 1.9$ Hz, 1H), 7.40 (dd, $J = 8.3$, 1.9 Hz, 1H), 6.77 (d, $J = 8.3$ Hz, 1H), 5.41 (s, 1H), 4.85 (d, $J = 14.5$ Hz, 1H), 4.71 (d, $J = 14.5$ Hz, 1H), 4.59 (d, $J = 4.9$ Hz, 1H), 4.36–4.27 (m, 1H), 4.13 (ddd, $J = 9.8$, 8.1, 2.8 Hz, 1H), 3.55 (t, $J = 1.4$ Hz, 1H), 2.39 (dtdd, $J = 14.5$, 9.5, 5.0, 2.0 Hz, 1H), 2.09–2.05 (m, 1H), 0.99–0.92 (m, 12H), 0.77 (d, $J = 6.9$ Hz, 9H). $^{13}$C-NMR (151 MHz) $\delta$ 167.7, 159.1, 134.0, 132.1, 132.0, 129.2, 127.6, 126.5, 123.3, 120.8, 110.9, 77.4, 74.6, 68.6, 41.1, 31.0, 29.7, 18.0, 17.6, 13.3. HRMS m/z calcd for C$_{29}$H$_{37}$NO$_6$SiNa ([M+Na]$^+$) 546.2288; found 546.2297.
### L. X-RAY DIFFRACTION DATA FOR SPIROKETAL 8b

**Crystal data and structure refinement for 8b**

| Property                                      | Value                  |
|-----------------------------------------------|------------------------|
| Identification code                           | jmw1                   |
| Empirical formula                             | C21 H34 O4 Si          |
| Formula weight                                 | 378.57                 |
| Temperature                                    | 173(2) K               |
| Wavelength                                     | 0.71073 Å              |
| Crystal system                                 | Triclinic              |
| Space group                                    | P-1                    |
| Unit cell dimensions                           | a = 9.0760(7) Å, b = 10.7759(8) Å, c = 11.1491(8) Å |
|                                             | a = 80.423(4)°, b = 84.426(4)°, g = 74.609(4)° |
| Volume                                        | 1035.04(13) Å³         |
| Density (calculated)                          | 1.215 Mg/m³            |
| Absorption coefficient                        | 0.136 mm⁻¹             |
| F(000)                                        | 412                    |
| Crystal size                                   | 0.35 x 0.20 x 0.15 mm³|
| Theta range for data collection                | 1.86 to 26.37°         |
| Index ranges                                   | -11<=h<=11, -13<=k<=13, -13<=l<=13 |
| Reflections collected                          | 13911                  |
| Independent reflections                        | 4222 [R(int) = 0.0386]  |
| Completeness to theta = 26.37°                 | 99.8 %                 |
| Absorption correction                          | Semi-empirical from equivalents |
| Max. and min. transmission                     | 0.9799 and 0.9540       |
| Refinement method                              | Full-matrix least-squares on F² |
| Data / restraints / parameters                 | 4222 / 0 / 327         |
| Goodness-of-fit on F²                          | 1.099                  |
| Final R indices [I>2sigma(I)]                  | R1 = 0.0418, wR2 = 0.0972 |
| R indices (all data)                           | R1 = 0.0595, wR2 = 0.1066 |
| Largest diff. peak and hole                    | 0.249 and -0.240 e.Å⁻³ |
Atomic coordinates \((x10^4)\) and equivalent isotropic displacement parameters \((\text{Å}^2x10^3)\) for 11b. \(U_{eq}\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

|    | x       | y       | z       | \(U_{eq}\) |
|----|---------|---------|---------|------------|
| Si(1) | 2326(1) | 1705(1) | 7472(1) | 27(1)      |
| O(1)  | 1125(1) | 3067(1) | 7803(1) | 26(1)      |
| O(2)  | -178(1) | 5992(1) | 8178(1) | 26(1)      |
| O(3)  | -2123(1)| 5653(1) | 7167(1) | 26(1)      |
| O(4)  | -1892(1)| 3249(1) | 8915(1) | 34(1)      |
| C(1)  | -892(1) | 5027(1) | 7895(1) | 22(1)      |
| C(2)  | 298(2)  | 4203(1) | 7070(1) | 22(1)      |
| C(3)  | 1254(1) | 5130(1) | 6563(1) | 22(1)      |
| C(4)  | 2307(2) | 5157(1) | 5580(1) | 29(1)      |
| C(5)  | 3052(2) | 6141(2) | 5375(1) | 36(1)      |
| C(6)  | 2758(2) | 7076(2) | 6136(1) | 37(1)      |
| C(7)  | 1680(2) | 7084(1) | 7102(1) | 32(1)      |
| C(8)  | 943(2)  | 6107(1) | 7279(1) | 24(1)      |
| C(9)  | -3337(2)| 6538(2) | 7759(1) | 34(1)      |
| C(10) | -3938(2)| 5849(2) | 8918(1) | 34(1)      |
| C(11) | -2639(2)| 5221(1) | 9753(1) | 30(1)      |
| C(12) | -1356(2)| 4320(1) | 9108(1) | 25(1)      |
| C(13) | 2140(3) | 526(2)  | 8888(2) | 29(1)      |
| C(13')| 2731(6) | 697(4)  | 9058(4) | 28(1)      |
| C(14) | 3336(4) | -780(3) | 8915(3) | 37(1)      |
| C(14')| 3002(10)| -767(8) | 8968(6) | 52(2)      |
| C(15) | 2163(4) | 1082(3) | 10072(2)| 49(1)      |
| C(15')| 1523(9) | 1052(7) | 10041(6)| 59(2)      |
| C(16) | 4243(2) | 1995(1) | 6956(1) | 32(1)      |
| C(17) | 5445(2) | 780(2)  | 6650(2) | 51(1)      |
| C(18) | 4846(2) | 2665(2) | 7835(2) | 61(1)      |
| C(19) | 1563(2) | 1059(1) | 6269(1) | 35(1)      |
| C(20) | 1743(2) | 1773(2) | 4980(1) | 38(1)      |
| C(21) | -102(2) | 996(2)  | 6552(2) | 53(1)      |
Bond lengths [Å] and angles [°] for 11b.

| Bond                  | Length  |
|-----------------------|---------|
| Si(1)-O(1)            | 1.6523(9) |
| Si(1)-C(16)           | 1.8680(15) |
| Si(1)-C(19)           | 1.8744(17) |
| Si(1)-C(13)           | 1.879(2) |
| Si(1)-C(13')          | 1.928(4) |
| O(1)-C(2)             | 1.4249(14) |
| O(2)-C(8)             | 1.3725(15) |
| O(2)-C(1)             | 1.4510(16) |
| O(3)-C(1)             | 1.3987(15) |
| O(3)-C(9)             | 1.4383(16) |
| O(4)-C(12)            | 1.4198(17) |
| C(1)-C(12)            | 1.5178(17) |
| C(1)-C(2)             | 1.5400(17) |
| C(2)-C(3)             | 1.4993(18) |
| C(3)-C(8)             | 1.3795(18) |
| C(3)-C(4)             | 1.3848(18) |
| C(4)-C(5)             | 1.379(2) |
| C(5)-C(6)             | 1.380(2) |
| C(6)-C(7)             | 1.382(2) |
| C(7)-C(8)             | 1.368(2) |
| C(9)-C(10)            | 1.509(2) |
| C(10)-C(11)           | 1.515(2) |
| C(11)-C(12)           | 1.5109(18) |
| C(13)-C(14)           | 1.531(4) |
| C(13)-C(15)           | 1.542(4) |
| C(13')-C(15')         | 1.494(8) |
| C(13')-C(14')         | 1.549(9) |
| C(16)-C(18)           | 1.526(2) |
| C(16)-C(17)           | 1.530(2) |
| C(19)-C(20)           | 1.528(2) |
| C(19)-C(21)           | 1.531(2) |
| O(1)-Si(1)-C(16)      | 110.12(6) |
| O(1)-Si(1)-C(19)      | 110.48(6) |
C(16)-Si(1)-C(19) 110.40(7)  
O(1)-Si(1)-C(13) 102.29(8)  
C(16)-Si(1)-C(13) 119.35(9)  
C(19)-Si(1)-C(13) 103.72(10)  
O(1)-Si(1)-C(13') 102.59(14)  
C(16)-Si(1)-C(13') 101.44(16)  
C(19)-Si(1)-C(13') 121.12(16)  
C(13)-Si(1)-C(13') 20.05(15)  
C(2)-O(1)-Si(1) 132.86(8)  
C(8)-O(2)-C(1) 106.81(9)  
C(1)-O(3)-C(9) 113.99(10)  
O(3)-C(1)-O(2) 109.07(10)  
O(3)-C(1)-C(12) 113.58(10)  
O(2)-C(1)-C(12) 106.31(10)  
O(3)-C(1)-C(2) 105.34(10)  
O(2)-C(1)-C(2) 105.57(10)  
C(12)-C(1)-C(2) 116.55(10)  
O(1)-C(2)-C(3) 113.09(11)  
O(1)-C(2)-C(1) 108.68(9)  
C(3)-C(2)-C(1) 101.09(10)  
C(8)-C(3)-C(4) 119.24(13)  
C(8)-C(3)-C(2) 108.07(10)  
C(4)-C(3)-C(2) 132.69(12)  
C(5)-C(4)-C(3) 118.59(13)  
C(4)-C(5)-C(6) 120.72(13)  
C(5)-C(6)-C(7) 121.42(14)  
C(8)-C(7)-C(6) 116.79(14)  
C(7)-C(8)-O(2) 124.06(12)  
C(7)-C(8)-C(3) 123.16(12)  
O(2)-C(8)-C(3) 112.77(11)  
O(3)-C(9)-C(10) 110.94(11)  
C(9)-C(10)-C(11) 109.57(12)  
C(12)-C(11)-C(10) 110.48(11)  
O(4)-C(12)-C(11) 107.89(11)  
O(4)-C(12)-C(1) 109.93(10)  
C(11)-C(12)-C(1) 110.29(11)
Anisotropic displacement parameters (Å² x 10³) for 11b. The anisotropic displacement factor exponent takes the form: \(-2p^2[h^2a^*2U_{11} + ... + 2 h k a^* b^* U_{12}]\)

|        | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|--------|------|------|------|------|------|------|
| Si(1)  | 28(1)| 24(1)| 23(1)| 0(1) | 1(1) | 2(1) |
| O(1)   | 27(1)| 22(1)| 23(1)| 1(1) | 0(1) | 0(1) |
| O(2)   | 28(1)| 26(1)| 24(1)| -9(1)| 3(1) | -8(1)|
| O(3)   | 23(1)| 30(1)| 22(1)| -4(1)| -2(1)| 1(1) |
| O(4)   | 33(1)| 32(1)| 38(1)| -5(1)| 4(1) | -12(1)|
| C(1)   | 21(1)| 24(1)| 20(1)| -4(1)| -2(1)| -4(1)|
| C(2)   | 24(1)| 22(1)| 19(1)| -4(1)| -2(1)| -3(1)|
| C(3)   | 22(1)| 21(1)| 20(1)| -1(1)| -3(1)| -2(1)|
| C(4)   | 29(1)| 27(1)| 23(1)| 0(1) | 1(1) | 0(1) |
| C(5)   | 29(1)| 36(1)| 35(1)| 6(1) | 7(1) | -5(1)|
| C(6)   | 33(1)| 33(1)| 46(1)| 5(1) | -2(1)| -14(1)|
| C(7)   | 34(1)| 29(1)| 36(1)| -6(1)| -3(1)| -11(1)|
| C(8)   | 23(1)| 26(1)| 21(1)| -2(1)| -2(1)| -5(1)|
| C(9)   | 24(1)| 36(1)| 34(1)| -6(1)| 1(1) | 6(1) |
| C(10)  | 23(1)| 40(1)| 35(1)| -8(1)| 5(1) | -1(1)|
| C(11)  | 27(1)| 38(1)| 24(1)| -6(1)| 6(1) | -8(1)|
| C(12)  | 25(1)| 27(1)| 21(1)| -3(1)| 0(1) | -6(1)|
| C(13)  | 30(1) | 30(1) | 28(1) | -1(1) | -5(1) | -7(1) |
|--------|-------|-------|-------|-------|-------|-------|
| C(13')| 32(3) | 22(2) | 27(2) | 4(2)  | -14(2)| -5(2) |
| C(14)  | 44(2) | 14(1) | 44(2) | 9(1)  | -3(1) | -3(1) |
| C(14') | 61(4) | 66(5) | 31(3) | -8(3) | -11(3)| -14(3)|
| C(15)  | 76(2) | 42(2) | 22(1) | 1(1)  | -1(1) | -5(2) |
| C(15') | 82(5) | 66(5) | 31(3) | -8(3) | -11(3)| -14(3)|
| C(16)  | 27(1) | 40(1) | 26(1) | -6(1) | -2(1) | 0(1)  |
| C(17)  | 32(1) | 50(1) | 58(1) | -1(1) | 10(1) | 5(1)  |
| C(18)  | 37(1) | 103(1)| 53(1) | -36(1)| -5(1) | -19(1)|
| C(19)  | 37(1) | 20(1) | 45(1) | -7(1) | 2(1)  | -4(1) |
| C(20)  | 45(1) | 36(1) | 34(1) | -12(1)| -9(1) | -6(1) |
| C(21)  | 46(1) | 44(1) | 76(1) | -17(1)| 3(1)  | -20(1)|

Hydrogen coordinates (x$10^4$) and isotropic displacement parameters (Å$^2x10^3$) for 11b.

|       | x       | y       | z       | U(eq)   |
|-------|---------|---------|---------|---------|
| H(4O) | -1100(20)| 2702(17)| 8620(17)| 66(6)   |
| H(2)  | -233(15)| 3971(12)| 6470(12)| 21(3)   |
| H(4)  | 2488(16)| 4509(13)| 5078(12)| 29(4)   |
| H(5)  | 3782(18)| 6165(14)| 4728(14)| 43(4)   |
| H(6)  | 3277(17)| 7761(14)| 5965(13)| 39(4)   |
| H(7)  | 1426(17)| 7729(14)| 7615(13)| 37(4)   |
| H(9B) | -2907(15)| 7309(13)| 7914(12)| 25(4)   |
| H(9A) | -4133(18)| 6873(14)| 7149(14)| 45(4)   |
| H(10B)| -4785(16)| 6474(14)| 9300(13)| 34(4)   |
| H(10A)| -4384(17)| 5175(14)| 8717(13)| 39(4)   |
| H(11B)| -2996(16)| 4735(13)| 10472(13)| 35(4)  |
| H(11A)| -2218(16)| 5887(14)| 10022(12)| 31(4)  |
| H(12) | -447(15)| 4043(12)| 9577(12)| 24(4)   |
| H(13A)| 1116    | 341     | 8892    | 35      |
| H(13B)| 3703    | 824     | 9310    | 33      |
| H(14A)| 3176    | -1353   | 9669    | 55      |
| H(14B)| 4363    | -638    | 8878    | 55      |
| H(14C) | 3235 | -1187 | 8213 | 55 |
| H(14D) | 3198 | -1279 | 9775 | 78 |
| H(14E) | 3886 | -1034 | 8405 | 78 |
| H(14F) | 2092 | -913  | 8666 | 78 |
| H(15A) | 2054 | 428   | 10776| 74 |
| H(15B) | 1315 | 1861  | 10103| 74 |
| H(15C) | 3135 | 1310  | 10090| 74 |
| H(15D) | 1824 | 483   | 10806| 88 |
| H(15E) | 551 | 947   | 9816 | 88 |
| H(15F) | 1403 | 1959  | 10146| 88 |
| H(16)  | 4077(17)| 2584(14)| 6193(14)| 41(4)|
| H(17A) | 6373 | 1025  | 6283 | 77 |
| H(17B) | 5041 | 376   | 6073 | 77 |
| H(17C) | 5692 | 161   | 7396 | 77 |
| H(18A) | 5013 | 2094  | 8618 | 92 |
| H(18B) | 4097 | 3482  | 7959 | 92 |
| H(18C) | 5815 | 2849  | 7494 | 92 |
| H(19)  | 2167(17) | 169(14) | 6274(13) | 37(4) |
| H(20A) | 1395 | 1338  | 4397 | 57 |
| H(20B) | 2822 | 1763  | 4784 | 57 |
| H(20C) | 1128 | 2675  | 4932 | 57 |
| H(21A) | -763 | 1880  | 6539 | 79 |
| H(21B) | -199 | 494   | 7360 | 79 |
| H(21C) | -410 | 575   | 5938 | 79 |
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2. Synthesis of exo-glycals 3a–h S56
3. Synthesis of TIPS-protected exo-glycals 4a–h S64
4. Synthesis of 4-substituted exo-glycals 4i–n S72
5. Synthesis of exo-glycal alcohols 5a–n S77
6. Synthesis of exo-glycal epoxides 6a–n S91
7. Sc(OTf)\(_3\)-mediated spirocyclization of exo-glycal epoxides 6 in THF with inversion of configuration (7a–n) S105
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