Skeletal Diversity *via* Ring Contraction of Glycal-Derived Scaffolds

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Supporting Information

General Information: All reactions were carried out in oven or flame-dried glassware under an atmosphere of argon unless otherwise noted. ^{1}H NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer at ambient temperature and are reported in ppm relative to solvent ($CHCl_3$ at 7.26 ppm). Proton decoupled ^{13}C NMR spectra were recorded at 100.0 MHz at ambient temperature, and are reported in ppm relative to solvent ($CHCl_3$ at 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants (reported in Hz.). High pressure liquid chromatography/mass spectral (LC-MS) analyses were performed using a Micromass 2Q 2000 mass spectrometer in atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) modes. LC separations were performed using a Waters Alliance 2996 module and a Waters Symmetry C8 column (4.6 x 30 mm). ELS detection was performed using a Sedere Sedex 75 ELS detector. Product purities are reported as ELSD area percent. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. Low and high-resolution mass spectra were obtained in the Boston University Mass Spectrometry Laboratory using Finnegan MAT-90 and Waters Q-Tof spectrometers. Microwave mediated reactions were performed using the CEM Discover / Explorer system, equipped with either 10 mL or 80 mL reaction vessels. Chromatography was performed using the ISCO Companion system. Reaction planning and was performed using the Synthematix electronic notebook program (http://www.synthematix.com/). X-ray crystal structures were obtained by Dr. Emil Lobkovsky (Department of Chemistry and Chemical Biology, Cornell University). Analytical thin layer chromatography was performed on 0.25 mm SiO_2 60-F plates. Flash chromatography was performed using 200-400 mesh SiO_2 (Scientific Absorbent Incorporated). Methylene chloride and tetrahydrofuran were purified by passing through two packed columns of neutral alumina (Glass Contour, Irvine, CA). MeOH, dichloroethane, and dimethyformamide were used as supplied from Dri-Solv (EMD) bottles. MP-Carbonate (2.98 mmol/gram) was obtained from Biotage. All other reagents and solvents were used as supplied by Sigma-Aldrich, Fluka, Acros, and Strem Chemicals.

Synthesis of *C*-Glycosides 3c (cf. Scheme 2):

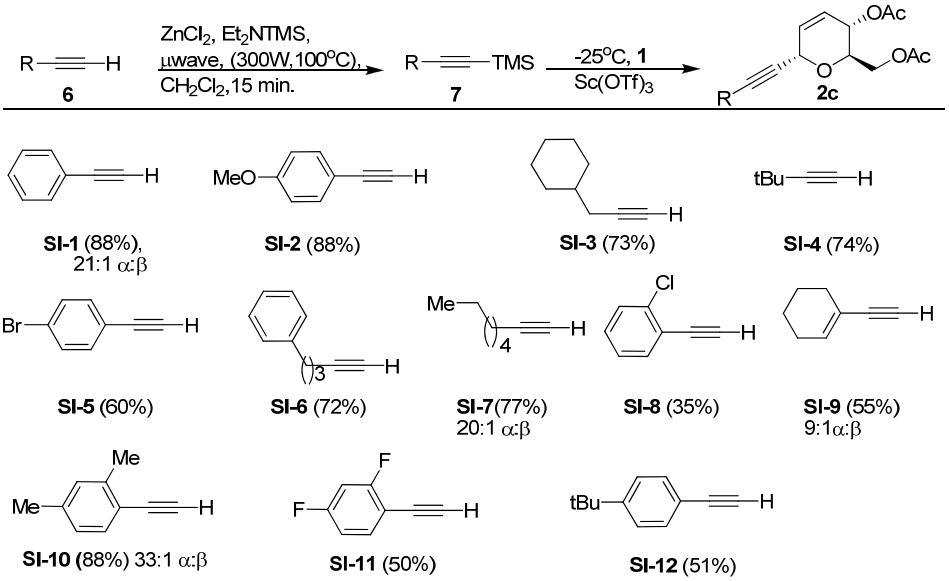
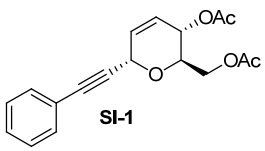
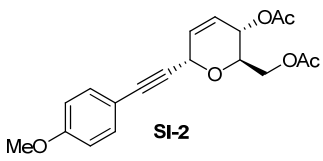


Table SI-1: Alkyne addition to glycals



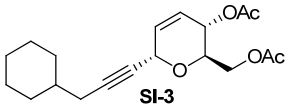
Alkynyl *C*-glycoside SI-1: Zinc chloride (520 mg 3.8 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl- 1,1,1-trimethylsilylamine (0.570 mL, 2.9 mmol) and *p*-methoxyphenylacetylene (0.250 mL, 1.9 mmol). The flask was sealed and heated at 150°C using microwave irradiation (150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (260 mg, 0.96 mmol) and scandium triflate (20 mg, 0.05 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-1** (0.528 g, 88%) as a viscous oil. Spectral data were in agreement with reported literature values.[1]



Alkynyl *C*-glycoside SI-2: Zinc chloride (520 mg 3.8 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (0.570 mL, 2.9 mmol) and *p*-methoxyphenylacetylene (0.250 mL, 1.9 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (260 mg, 0.96 mmol) and scandium triflate

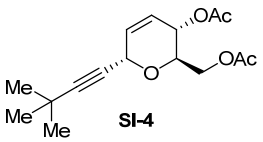
[1] J.S Yaday, B.V.S. Reddy, C.V. Rao, M.S. Reddy, *Synthesis* **2003**, 2, 247-250

(20 mg, 0.05 mmol) were added. After 1.5 h the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-2** (292 mg, 88%) as a viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 2H, *J*=13.2), 6.84 (d, 2H, *J*=11.2), 5.97 (d, 1H, *J*=10.0), 5.97 (d, 1H, *J*= 9.6), 5.34 (d, 1H, *J*=8.8), 5.18 (brs, 1H), 4.26 (d, 2H, *J*=3.2), 4.17 (m, 1H), 3.84 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.3, 159.9, 133.3, 130.2, 129.4, 125.2, 113.9, 86.6, 83.2, 69.8, 64.8, 64.5, 63.0, 55.3, 21.0, 20.8 ppm; IR (neat): 3743, 2955, 2831, 2217, 1740, 1654, 1608, 1507, 1231, 1041 cm^{-1}; $[\alpha]_D^{23}$ = -80° (c = 1.0 $CHCl_3$).



SI-3

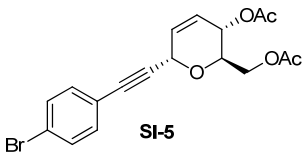
Alkynyl *C*-glycoside SI-3: Zinc chloride (800 mg 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*-diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 3-cyclohexyl-1-propyne (0.530 mL, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.8 mmol) and scandium triflate (20 mg, 0.4 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-3** (451 mg, 73%) as a viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.90 (ddd, 1H, *J*=1.6, 2.8, 10.3), 5.75 (dd, 1H, *J*=2.0, 10.4), 5.28 (dd, 1H, *J*=2.0, 10.0), 4.97 (m, 1H), 4.22 (m, 2H), 4.11 (m, 1H), 2.10 (m 8H), 1.73 (m, 5H), 1.46 (m, 1H), 0.97-1.23 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.2, 129.6, 125.0, 119.8, 88.5, 81.8, 69.7, 64.8, 64.4, 63.0, 28.9, 25.6, 22.1, 21.3, 21.0, 20.8 ppm; IR (neat): 3382, 2939, 2862, 1732, 1650, 1375, 1242 cm^{-1}; $[\alpha]_D^{23}$ = -52° (c = 1.0 CH_2Cl_2).



SI-4

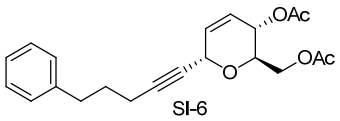
Alkynyl *C*-glycoside SI-4: Zinc chloride (800 mg 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 3,3-dimethyl-1-butyne (300 mg, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.8 mmol) and scandium triflate (140 mg, 0.2 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-4** (0.305 g, 60%) as a viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.84 (ddd, 1H, *J*=1.8, 3.6, 10.2), 5.67 (dt, 1H, *J*=2.0, 10.0), 5.23 (m, 1H), 4.91 (m, 1H) , 4.10 (m, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 1.18 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.2, 130.0, 124.6, 95.6, 74.1, 69.5, 64.9, 64.1, 63.1, 30.7, 20.9, 20.7 ppm; IR (neat): 3436, 2971, 2357, 2225, 1739, 1444, 1375, 1227, 1037 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{22}H_{26}O_5Na$ 393.1678, found 393.1686.

$[\alpha]_D^{23}$ = +2.0° (c = 1.0 CH_2Cl_2).



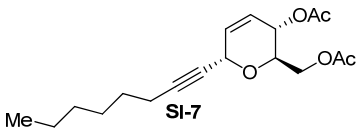
SI-5

Alkynyl *C*-glycoside SI-5: Zinc chloride (800 mg 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 4-bromophenylacetylene (660 mg, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.8 mmol) and scandium triflate (140 mg, 0.2 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-5** (472 mg, 60%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 2H, *J*=8.4), 7.31 (d, 2H, *J*=8.8), 5.96 (ddd, 1H, *J*=1.6, 3.6, 10.0), 5.83 (dt, 1H, *J*= 2.0, 10.0), 5.34 (dq, 1H, *J*=2.0, 8,8), 5.18 (m, 1H), 4.26 (appd, 2H, *J*=4.4), 4.16 (m, 1H), 2.10 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.2, 133.2, 131.6, 128.9, 125.7, 123.1, 121.0, 85.8, 85.5, 70.1, 64.7, 64.3, 62.9, 21.0, 20.8 ppm; IR (neat): 1746, 1487, 1371, 1229, 1044, 825 cm^{-1}; $[\alpha]_D^{23}$ = -111° (c = 1.0 $CHCl_3$).



SI-6

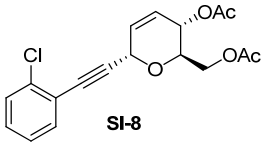
Alkynyl *C*-glycoside SI-6: Zinc chloride (225 mg 1.7 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (0.330 mL, 1.6 mmol) and 5-phenyl-1-propyne (0.220 mL, 1.4 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (250 mg, 0.92 mmol) and scandium triflate (68 mg, 0.14 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-6** (237 mg, 72%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.26 (m, 3H), 5.96 (ddd, 1H, *J*=2.0, 3.2, 10.2), 5.82 (dt, 1H, *J*=1.6, 10.4), 3.56 (dq, 1H, *J*=2.0, 8.8), 5.04 (m, 1H), 4.23 (m, 3H), 2.79 (t, 1H, *J*=6.8), 2.31 (td, 1H, *J*=2.0, 7.2), 2.16(s, 3H), 2.14 (s, 3H), 1.91 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.3, 141.4, 130.0, 128.5, 128.4, 126.0, 124.8, 87.3, 76.4, 69.7, 64.9, 64.2, 63.2, 34.7, 30.0, 21.0, 20.8, 18.2 ppm**;** IR (neat): 3429, 2936, 2236, 1740, 1499, 1363, 1235, 1052 cm^{-1}; $[\alpha]_D^{23}$ = +13° (c = 1.0 $CHCl_3$).



SI-7

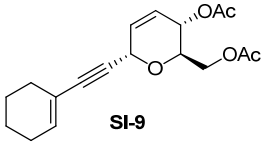
Alkynyl *C*-glycoside SI-7: Zinc chloride (800 mg 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by

N,N-diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 1-octyne (0.540 mL, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.8 mmol) and scandium triflate (90 mg, 0.2 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-7** (458 mg, 77%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (ddd, 1H, *J*=1.4, 3.4, 10.2), 5.75 (appd, 1H, *J*=10.4), 5.29 (dt, 1H, *J*=2.0, 8.8), 4.96 (m, 1H), 4.22 (m, 2H), 4.11 (m, 1H), 2.23 (td, 2H, *J*=2.0, 7.0), 2.10 (s, 3H), 2.09 (s, 3H), 1.51 (m, 2H), 1.24-1.30 (m, 6H), 0.89 (t, 3H, *J*=6.4) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 170.0, 129.9, 124.5, 87.6, 76.7, 75.6, 69.4, 64.7, 64.0, 62.9, 31.1, 28.2, 28.2, 22.3, 20.8, 20.6, 18.5, 13.8 ppm; IR (neat): 2924, 2858, 1744, 1635, 1371, 1235, 1049 cm^{-1}; $[\alpha]_D^{23}$ = +5° (c = 1.0 $CHCl_3$).



SI-8

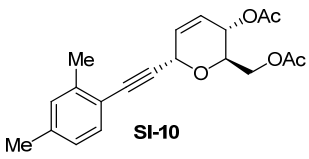
Alkynyl *C*-glycoside SI-8: Zinc chloride (1.05 g 7.7 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (1.20 mL, 6.1 mmol) and 1-chloro-2-ethynyl-benzene (0.490 mL, 4.0 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (550 mg, 2.0 mmol) and scandium triflate (100 mg, 0.2 mmol) were added. After 1.5 h the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-8** (244 mg, 35%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (ddd, 1H, *J*=1.6, 7.2, 26), 7.26 (m, 3H), 6.01 (ddd, 1H, *J*=2.0, 3.6, 10.4), 5.83 (dt, 1H, *J*=2.0, 10.0), 5.34 (d, 1H, *J*=5.2), 5.24 (m, 1H), 4.27 (m, 3H), 2.11 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.2, 136.0, 133.1, 129.6, 129.2, 128.7, 126.3, 125.7, 122.0, 89.9, 83.3, 70.1, 64.6, 64.4, 63.0, 20.9, 20.7 ppm; IR (neat): 2354, 2336, 1743, 1473, 1364, 14229, 1051 cm^{-1}; $[\alpha]_D^{23}$ = -101° (c = 1.0 CH_2Cl_2).



SI-9

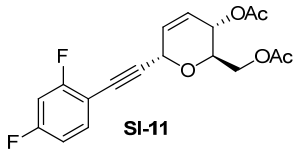
Alkynyl *C*-glycoside SI-9: Zinc chloride (800 mg 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*-diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 1-ethynylcyclohexane (0.430 mL, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.8 mmol) and scandium triflate (100 mg, 0.2 mmol) were added. After 1.5 h, the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40%

EtOAc / pet. ether) provided **SI-9** (372 mg, 60%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.12 (m, 1H), 5.88 (ddd, 1H, *J*=2.0, 3.4, 10.1), 5.74 (dt, 1H, *J*=2.0, 10.0), 5.28 (m, 1H), 5.06 (bs, 1H), 4.21 (m, 2H), 4.09 (m, 1H), 2.06 (s, 3H), 2.05 (m, 10H), 1.61 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.2, 136.0, 130.4, 129.5, 125.0, 119.8, 88.5, 81.8, 74.4, 69.7, 65.7, 64.8, 64.4, 63.4, 63.0, 28.9, 29.8, 25.5, 22.1, 21.3, 21.0, 20.8 ppm; IR (neat): 3449, 2940, 2858, 1744, 1441, 1375, 1231, 1049, 917 cm^{-1}; $[\alpha]_D^{23}$ = -86^o (c = 1.0 $CHCl_3$).



SI-10

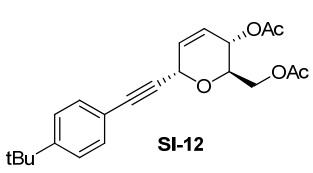
Alkynyl *C*-glycoside SI-10: Zinc chloride (800 mg, 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*-diethyl-1,1,1- trimethylsilylamine (0.520 mL, 4.0 mmol) and 2-ethynyl-1,4-dimethylbenzene (0.520 mL, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150^{o}C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25^{o}C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.80 mmol) and scandium triflate (90 mg, 0.20 mmol) were added. After 5.0 h the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-10** (554 mg, 88%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 1H), 7.05 (m, 2H), 5.99 (dq, 1H, *J*=1.6, 3.6, 10.4), 5.81 (dt, 1H, *J*=2.0, 10.0), 5.33 (dd, 1H, *J*=2.0, 8.8), 5.23 (m, 1H), 4.25 (m, 3H), 2.38 (s, 3H), 2.28 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.3, 137.2, 135.0, 132.4, 129.6, 129.4, 129.3, 125.4, 121.7, 88.1, 85.9, 70.0, 64.9, 64.6, 63.2, 21.0, 20.8, 20.7, 20.1 ppm; IR (neat): 3390, 2916, 1736, 1449, 1375, 1227, 1041 cm^{-1}; $[\alpha]_D^{23}$ = -15^o (c = 1.0 $CHCl_3$).



SI-11

Alkynyl *C*-glycoside SI-11: Zinc chloride (800 mg, 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 1-ethynyl-2,4-difluorobenzene (510 mg, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150^{o}C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25^{o}C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.80 mmol) and scandium triflate (90 mg, 0.20 mmol) were added. After 5.0 h the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-11** (316 mg, 49%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 1H), 6.85 (m, 2H), , 5.97 (dq, 1H, *J*=1.6, 3.6, 10.4), 5.84 (dt, 1H, *J*=2.0, 10.4), 5.34 (dq, 1H, *J*=2.0, 4.0, 8.8), 5.21 (m, 1H), 4.25 (m, 2H), 4.18 (m, 1H), 2.11 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.3, 164.4 (dd, 1C, *J*=46.8, 134.8), 161.9 (dd, 1C, *J*=47.2, 122.8), 134.5 (t, 1C, *J*=12), 128.7, 125.9, 111.6 (dd, 1C, *J*=14.8, 84.8), 107.1 (d, 1C, *J*=46.8), 99.6 (t, 1C, *J*=99.6), 89.7, 79.1, 70.2, 64.7,64.4, 63.0, 21.0, 20.8 ppm; IR (neat): 1743, 1623, 1510, 1425, 1375, 1239, 1052 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for

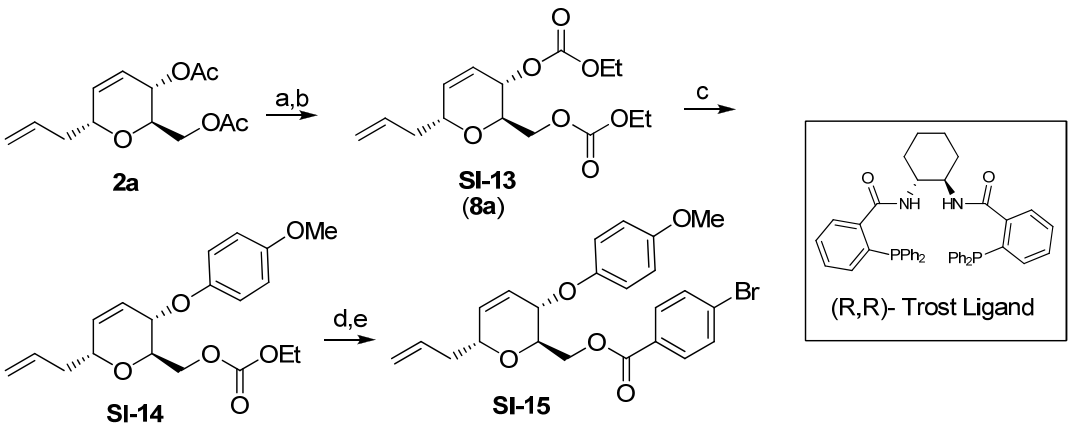
$C_{18}H_{16}O_5NaF_2$ 373.0864, found 373.0799. $[\alpha]_D^{23}$ = -88° (c = 1.0 $CHCl_3$).



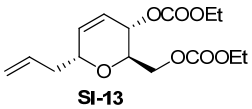
SI-12

Alkynyl *C*-glycoside SI-12: Zinc chloride (800 mg, 5.9 mmol), was added to a flame-dried 80 mL-microwave flask under an inert atmosphere (glove box). The flask was removed from the glove box and placed under argon. Dichloroethane (10 mL) was added, followed by *N,N*- diethyl-1,1,1-trimethylsilylamine (0.800 mL, 4.0 mmol) and 1-*tert*-butyl-4-ethynylbenzene (0.660 mL, 3.7 mmol). The flask was sealed and heated using microwave irradiation (150°C, 150-300 W, Powermax enabled) for 15 min. The reaction was again placed under argon and transferred to a -25°C cold bath. Tri-O-acetyl-D-glucal (500 mg, 1.80 mmol) and scandium triflate (90 mg, 0.20 mmol) were added. After 5.0 h the reaction was diluted with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The organic fraction was washed with sat. brine, dried, and concentrated. Chromatography over SiO_2 (0-40% EtOAc / pet. ether) provided **SI-12** (289 mg, 42%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 2H, *J*=8.4), 7.33 (d, 2H, *J*=9.2), 4.97 (dq, 1H, *J*=2.0, 3.6, 10.0), 5.81 (dt, 1H, *J*= 2.0, 10.0), 5.33 (dq, 1H, *J*=2.0, 4.0, 9.2), 5.18 (m, 1H), 4.26 (d, 2H, *J*=3.6), 4.20 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 1.30 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.3, 152.1, 131.5, 129.3, 125.3, 119.1, 86.8, 84.0, 69.9, 64.8, 64.5, 63.0, 34.8, 31.1, 21.0, 20.8 ppm**;** IR (neat): 2967, 1740, 1375, 1243, 1052, 834 cm^{-1}; $[\alpha]_D^{23}$ = -33° (c = 1.0 $CHCl_3$).

Phenol addition to allyl-C-glycoside 2a



Scheme SI-1. C-glycoside aryl ether formation. a) MP-CO_3, MeOH, (99%); b) ethyl chloroformate, pyridine, DMAP, CH_2Cl_2, (81%); c) $Pd_2(dba)_3$-$CHCl_3$, Trost Ligand, *p*-methoxyphenol, μwave, 100°C (78%); d) MP-CO_3, MeOH (99%), e) *p*-BrBnCl, NEt_3, DMAP, CH_2Cl_2 (X%)

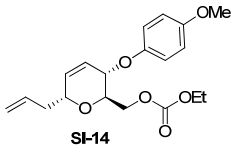


SI-13

Dicarbonate SI-13: Diacetate **2a**[2] (708 mg, 2.8 mmol) was dissolved in MeOH (4.0 mL) and shaken with MP-carbonate resin (230 mg, 0.70 mmol) for 12 h. The reaction was filtered, rinsing with MeOH, then concentrated *in*

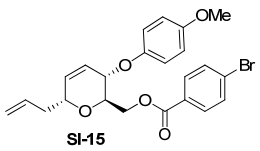
[2] S. Su, D.E. Acquilano, J. Arumugasamy, A.B. Beeler, E.L. Eastwood, J.R. Giguere, P. Lan, X. Lei, G.K. Min, A.R. Yeager, Y. Zhou, J.S. Panek, J.K. Snyder, S.E. Schaus, J.A. Porco Jr., *Org Lett*. **2005**, *7,* 2751-2754.

vacuo. The crude residue was redissolved in methylene chloride (3.0 mL) and pyridine (0.68 mL, 8.5 mmol) was added. The reaction was cooled to 0°C and ethyl chloroformate (0.81 mL, 8.5 mmol) was added. After stirring for 12 h, the reaction was diluted with methylene chloride and washed with sat. aqueous sodium bicarbonate and brine. The organic layer was dried (sodium sulfate), concentrated, and chromatographed over SiO_2 (0-40% ethyl acetate / petroleum ether) to provide **SI-13** (715 mg, 81%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (1H, dt, *J* = 12.0, 2.0), 5.87 (2H, m), 5.14 (1H, appd, *J*=1.6), 5.10 (1H, m), 5.02 (1H, m), 4.23 (7H, m), 4.02 (1H, q, *J*=4.4), 2.45 (1H, m), 2.33 (1H, m), 1.31 (6H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.5, 138.8, 133.2, 126.2, 117.7, 71.5, 69.2, 68.1, 66.0, 61.3, 64.2, 37.7, 14.2, 14.2 ppm; IR (neat): 3740, 3414, 2978, 2912, 1961, 1748, 1375, 1258, 1314 cm^{-1}; $[\alpha]_D^{23}$ = +50° (c = 1.0 CH_2Cl_2).



SI-14

Aryl ether SI-14: Dicarbonate **SI-13** (508 mg, 1.62 mmol), Tris (dibenzylideneacetone) dipalladium (0) chloroform adduct (42 mg, 0.04 mmol), and (1*S*, 2*S*) Trost ligand (56 mg, 0.08 mmol) were added to a flame-dried 10 mL-microwave vessel and were dissolved in degassed dichloromethane (2 mL). After 30 min *p*-methoxyphenol (221 mg, 1.78 mmol) was added and the mixture was heated using microwave irradiation (300W, Powermax enabled) at 100°C for 15 min. The reaction was concentrated and purified over SiO_2 (0-40% ethyl acetate/ petroleum ether) to provide **SI-14** (441 mg, 1.27 mmol, 78%) as a viscous oil. ^{1}H NMR (400MHz; $CDCl_3$): δ 6.85 (4H, m), 5.96 (1H, m), 5.90 (2H, m), 5.13 (2H, m), 4.60 (1H, dd, *J* = 1.6, 8), 4.40 (1H, dd, *J* = 2.8, 11.4), 4.32 (2H, m), 4.17 (2H, q), 4.15 (1H, m), 3.76 (3H, s), 2.52 (1H, m), 2.36 (1H, m), 1.28 (3H, t) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 154.3, 121.0, 134.1, 131.6, 124.6, 117.5, 117.0, 114.7, 72.5, 69.4, 69.4, 66.7, 64.0, 55.7, 37.7, 14.2 ppm.; IR (neat): 2907, 1747, 1506, 1226, 1038, 828 cm^{-1}; $[\alpha]_D^{23}$= +81.9° (c=1.0 CH_2Cl_2).

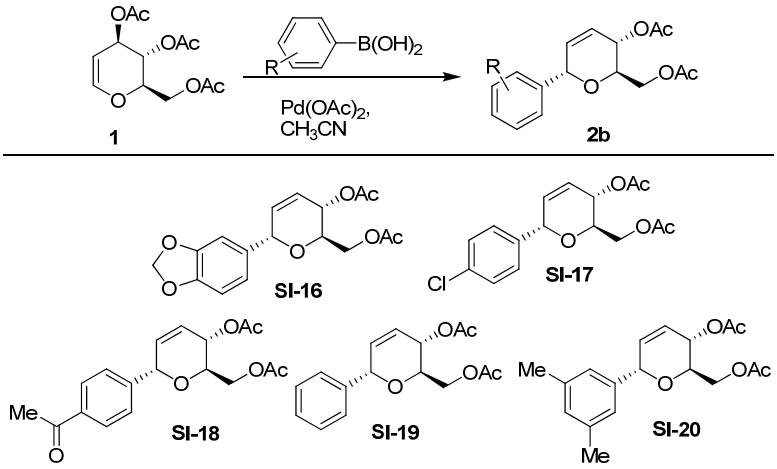


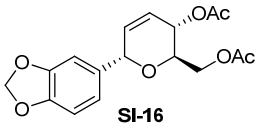
SI-15

***p*-Bromobenzoate ester SI-15**: Ethyl carbonate **SI-14** was dissolved in MeOH and MP-carbonate was added. The reaction was stirred for 5 h and filtered to provide the unprotected alchol as a white solid. ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.85 (4H, m), 6.94 (1H, m), 5.86 (1H, m), 5.18 (1H, q), 5.12 (1H, dd, *J* = 3.2, 9.2), 4.63 (1H, dd, *J* = 1.6, 7.6), 4.31 (1H$^+$, m), 3.86 (1H, dt, *J* = 2.4, 14), 3.76 (2H, m), 3.77 (3H, s) , 2.53 (1H, m), 2.34 (1H, m), 2.10 (1H, bs); ^{13}C NMR (100MHz, $CDCl_3$): δ 154.3, 151.3, 134.4, 131.2, 125.3, 117.5, 117.1, 114.8, 72.6, 71.2, 69.5, 62.4, 55.7, 37.7 ppm; IR (neat): 3459, 2912, 1506, 1225, 1040, 828 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{16}H_{20}O_4Na$ 277.1416, found 277.1417. $[\alpha]_D^{23}$= +113.3° (c=1.0 CH_2Cl_2). The diol (150 mg, 0.54 mmol) was dissolved in dichloromethane. Triethylamine (0.11 mL, 0.81 mmol) and dimethylaminopyridine (7 mg, 0.05 mmol) were added, the reaction was cooled to 0°C and 4-bromo-benzoyl chloride (179 mg, 0.81 mmol) was added. After 10 min the reaction was warmed to room temp and stirred for 4 h. The solution was diluted with dichloromethane, washed with sat. aqueous sodium bicarbonate (1X) and brine (1X), filtered and purified over SiO_2 to yield **SI-15** (172 mg, 0.37 mmol) as a white solid. ^{1}H NMR (400MHz; $CDCl_3$): δ 7.90 (2H, m), 7.57 (2H, m), 6.84 (4H, m), 5.99 (1H, m), 5.89 (2H, m), 4.61 (2H, m), 4.45

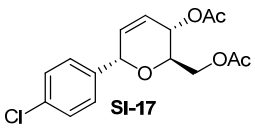
(1H, q), 4.35 (1H$^+$, m), 4.13 (1H, td, *J*= 2.8, 7.2, 14.4), 3.76 (3H, s), 2.54 (1H, m), 2.38 (1H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 165.0, 154.4, 151.1, 134.3, 131.8, 131.2, 128.9, 128.1, 124.7, 117.5, 117.1, 114.8, 72.5, 70.0, 70.0, 64.6, 55.7, 55.7, 37.6 ppm; IR (neat): 2903, 1723, 1505, 1226, 1101, 827, 753 cm^{-1}; $[\alpha]_D^{23}$= 64.8^o (c=1.0 CH_2Cl_2).

General procedure for synthesis of aryl *C*-glycosides 3b (Table S2)



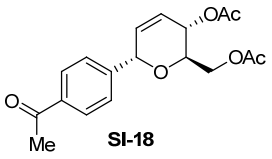


Aryl *C*-Glycoside SI-16: Tri-O-acetyl-D-glucal (0.400g, 1.0 mmol) was dissolved in CH_3CN (8.0 mL). To the reaction was added 3,4-methylenedioxyphenylboronic acid (500 mg, 3.0 mmol) and $Pd(OAc)_2$ (30 mg, 0.1 mmol). After stirring overnight, additional 3,4-methylenedioxyphenylboronic acid (100 mg, 0.6 mmol) and $Pd(OAc)_2$ (20 mg, 0.09 mmol) were added. After 18 h, the reaction was concentrated onto SiO_2 and chromatographed over SiO_2, eluting with 0-60% ethyl acetate / pet. ether to provide **SI-16** (338 mg, 70%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (bs, 1H), 6.86 (d, 1H, *J*=7.6), 6.79 (d, 1H, *J*=8.0), 6.11 (m, 1H), 5.97 (m, 3H), 5.30 (m 1H), 5.22 (m, 1H), 4.26 (dd, 1H, *J*=6.0, 12.0), 4.07 (dd, 1H, *J*=3.2, 12.0), 3.83 (m, 1H), 2.09 (s, 3H), 2.07 (s. 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.5, 147.8, 147.5, 132.6, 131.5, 125.0, 121.7, 108.5, 108.0, 73.5, 69.0, 64.9, 62.8, 21.1, 20.8 ppm; IR (neat): 2889, 1740, 1499, 1491, 1445, 1371, 1231, 1033, 936, 792 cm^{-1}; $[\alpha]_D^{23}$ = +10^o (c = 1.0 CH_2Cl_2).



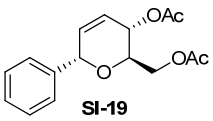
Aryl *C*-Glycoside SI-17: Tri-O-acetyl-D-glucal (400 mg, 1.0 mmol) was dissolved in CH_3CN (8.0 mL). To the reaction was added 4-chlorophenylboronic acid (400 mg, 3.0 mmol) and $Pd(OAc)_2$ (100 mg, 0.4 mmol). After stirring overnight, additional $Pd(OAc)_2$ (50 mg, 0.2 mmol) was added. After 24 h, the reaction was concentrated onto SiO_2 and chromatographed over SiO_2, eluting with 0-50% ethyl acetate / pet. ether to provide **SI-17** (0.241g, 50%) as a viscous oil.[3]

[3] (a) J. Ramnauth, O. Poulin, S. Rakhit, S.P. Maddaford, *Org. Lett*. **2001**, *3*, 2013-2015; (b) N. de la Figuera, P. Forns, J.C. Fernandez, S. Fiol, D.



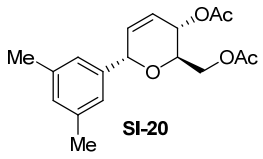
SI-18

Aryl *C*-Glycoside SI-18: Tri-O-acetyl-D-glucal (400 mg, 1.0 mmol) was dissolved in CH_3CN (8.0 mL). To the reaction was added 4-acetylphenylboronic acid (700 mg, 4.0 mmol) and $Pd(OAc)_2$ (100 mg, 0.4 mmol). After stirring overnight, additional 4-acetylphenylboronic acid (200 mg, 1.2 mmol) and $Pd(OAc)_2$ (100 mg, 0.4 mmol) were added. After 24 h, the reaction was concentrated onto SiO_2 and chromatographed (SiO_2), eluting with 0-60% ethyl acetate / pet. ether to provide **SI-18** (363 mg, 70%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=12.4), 7.49 (d, 2H, *J*=8.0), 6.18 (ddd, 1H, *J*=1.6, 2.8, 10.4), 6.01(dt, 1H, *J*=2.4, 5.2), 5.34 (m, 1H), 5.27 (m, 1H), 4.26 (dd, 1H, *J*=6.4, 12), 4.09 (m, 1H), 3.81 (m, 1H)2.59 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 170.7, 170.3, 144.1, 136.7, 130.7, 128.5, 127.7, 125.4, 73.0, 69.7, 64.7, 62.7, 26.6, 20.8 ppm; IR (neat): 2357, 1748, 1682, 1608, 1409, 1367, 1227, 1045 cm^{-1}; $[\alpha]_D^{23} = -7^o$ (c = 1.0 $CHCl_3$).



SI-19

Aryl *C*-Glycoside SI-19: Tri-O-acetyl-D-glucal (2.00 g, 7.3 mmol) was dissolved in CH_3CN (40 mL). Into the reaction was added phenylboronic acid (4.40 g, 36.0 mmol) and $Pd(OAc)_2$ (450 mg, 2.0 mmol). After 24 h, the reaction was concentrated onto SiO_2 and chromatographed over SiO_2, eluting with 0-60% ethyl acetate / pet. ether to provide **SI-16** (1.76 g, 82%) as a viscous oil.[3]



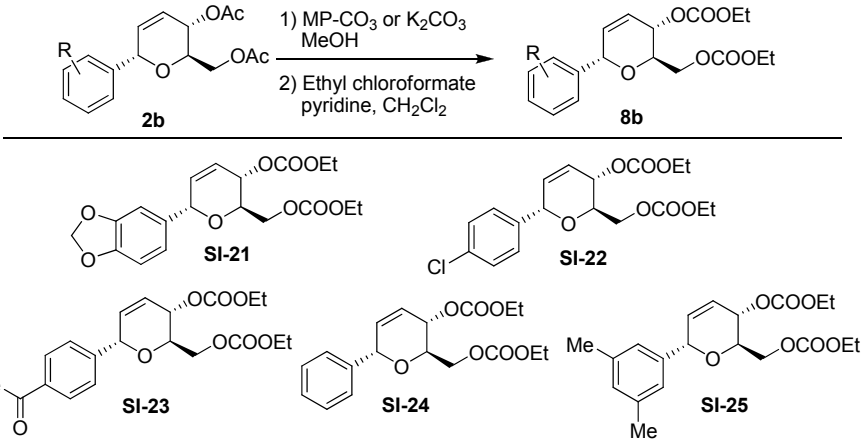
SI-20

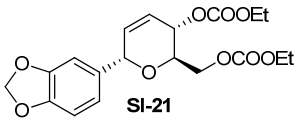
Aryl *C*-Glycoside SI-20: Tri-O-acetyl-D-glucal (750 mg, 2.8 mmol) was dissolved in CH_3CN (30.0 mL). To the reaction was added 3,5-dimethylbenzene boronic acid (1200 mg, 8.3 mmol) and $Pd(OAc)_2$ (200 mg, 0.8 mmol). After 12 h, the reaction was concentrated onto SiO_2 and chromatographed (SiO_2), eluting with 0-60% ethyl acetate / pet. ether to provide **SI-20** (756 mg, 86%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (s, 2H), 6.95 (s, 1H), 6.17 (dq, 1H, *J*=1.6, 3.2, 10.8), 5.96 (dt (1H, *J*=2.0, 10.4), 5.28 (m, 2H), 4.27 (dd, 1H, *J*=6.4, 12.4), 4.10 (dd, 1H, *J*=3.2, 12.0), 3.86 (m, 1H), 2.32 (s, 6H), 2.08 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.3, 138.6, 137.9, 131.7, 129.7, 125.5, 124.6, 73.5, 69.3, 65.0, 62.8, 21.2, 20.9, 20.7 ppm**;** IR (neat): 2913, 1744, 1604, 1441, 1367, 1235, 1045 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{18}H_{22}O_5Na$ 341.1365, found 341.1329. $[\alpha]_D^{23} = 19^o$ (c = 1.0 $CHCl_3$).

Fernandez-Forner, F. Albericia, *Tetrahedron Lett*. **2005**, *46*, 7271-7174.

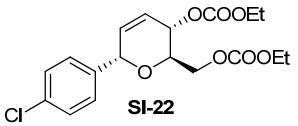
General procedure for conversion of aryl-*C*-glycoside bis-acetates to bis-carbonates 8b

Table SI-3:



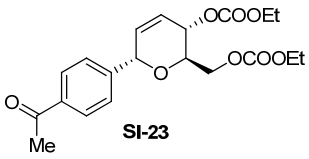


Aryl *C*-Glycoside SI-21: SI-16 (253 mg, 0.76 mmol) was dissolved in anhydrous MeOH (4 mL), and MP-carbonate resin (2.98 mmol/g loading, 63 mg, 0.20 mmol) was added. After orbital shaking for 15 h, the reaction was filtered, rinsed with MeOH, and concentrated *in vacuo* to provide 15 mg of the crude diol, which was dissolved in CH_2Cl_2 (3 mL) and cooled to 0°C. Pyridine (0.13 mL, 1.6 mmol) and ethyl chloroformate (0.15 mL, 1.6 mmol) were added. The reaction was warmed to room temperature, stirred for 12 h, diluted with sat. aqueous sodium bicarbonate and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-21** (14 mg, 68% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, 1H, *J*=1.2), 6.82 (dd, 1H, *J*=2.0, 8.0), 6.76 (d, 1H, *J*=8.0), 6.12 (ddd, 1H, *J*=1.6, 3.2, 10.8), 6.03 (dd, 1H, *J*=2.0, 10.4), 5.95 (m, 2H), 5.22 (m, 1H), 5.17 (m, 1H), 4.29 (dd, 1H, *J*=5.2, 11.6), 4.21 (q, 2H, *J*=7.2), 4.17 (q, 2H, 6.8), 3.86 (m, 1H), 1.31 (t, 3H, *J*=7.6), 1.28 (t, 3H, *J*=6.8) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.5, 147.8, 147.6, 132.1, 131.7, 124.6, 121.8, 108.7, 107.9, 101.1, 73.6, 68.2, 68.2, 66.0, 64.4, 64.1, 14.1 ppm; IR (neat): 2986, 2901, 1740,1487, 1445, 1371, 1262, 1041 cm^{-1}; $[\alpha]_D^{23}$ = -2° (c = 1.0 CH_2Cl_2).



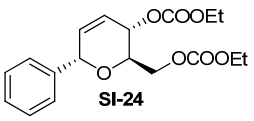
Aryl *C*-Glycoside SI-22: SI-17 (201 mg, 0.62 mmol) was dissolved in anhydrous MeOH (2 mL) and MP-carbonate resin(2.98 mmol/g loading, 100 mg, 0.30 mmol) was added. After orbital shaking for 5 h, the reaction was filtered, rinsed with MeOH, and concentrated *in vacuo* to provide 180 mg of the crude diol, which was dissolved in CH_2Cl_2 (3 mL) and cooled to 0°C. Pyridine (0.16 mL, 2.0 mmol) and ethyl chloroformate (0.19 mL, 2.0 mmol) were added. The reaction was warmed to room temperature, stirred for 12 h, diluted with sat. aqueous sodium bicarbonate and extracted with

CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-22** (108 mg, 42% yield) as viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 4H), 6.16 (ad, 1H, *J*=8.8), 6.07 (d, 1H, *J*=10.4), 5.29 (d, 1H, *J*=2.0), 5.18 (m, 1H), 4.29 (dd, 1H, *J*=5.6, 12.0), 4.22 (m, 5H), 3.86 (m, 1H), 1.31 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.5, 136.9, 134.2, 131.3, 129.4, 128.6, 124.9, 73.0, 68.7, 68.0, 65.9, 64.4, 64.2, 14.2 ppm; IR (neat): 2983, 1748, 1495, 1374, 1262, 1099, 1013, 873 cm^{-1}; $[\alpha]_D^{23}$ = -22° (c = 1.0 $CHCl_3$).



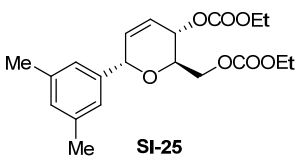
SI-23

Aryl *C*-Glycoside SI-23: SI-18 (108 mg, 0.54 mmol) was dissolved in anhydrous MeOH (3 mL) and MP-carbonate resin(2.98 mmol/g loading, 90 mg, 0.30 mmol) was added. After orbital shaking for 5 h, the reaction was filtered, rinsed with MeOH, and concentrated *in vacuo* to provide 12 mg of the crude diol, which was dissolved in CH_2Cl_2 (2 mL) and cooled to 0°C. Pyridine (0.12 mL, 1.4 mmol) and ethyl chloroformate (0.14 mL, 1.4 mmol) were added. The reaction was warmed to room temperature, stirred for 12 h, diluted with sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-23** (136 mg, 72% yield) as viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 2H, *J*=8.0), 7.50 (d, 2H, *J*=8.8), 6.12 (dt, 1H, *J*=1.6, 10.8), 6.09 (dd, 1H, *J*=1.6, 10.4), 5.34 (m, 1H), 5.19 (appd, 1H, *J*=5.2), 4.33 (dd, 1H, *J*=5.6, 11.6), 4.19 (m, 6H), 3.79 (m, 1H), 2.59 (s, 3H), 2.61 (s, 3H), 1.31 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 155.0, 154.4, 143.7, 136.8, 131.1, 128.6, 127.9, 124.9, 73.1, 69.1, 67.9, 65.9, 64.5, 64.2, 26.7, 14.2, 14.1 ppm; IR (neat): 3440, 2971, 2920, 1732, 1717, 1612, 1390, 1270, 1072 cm^{-1}; $[\alpha]_D^{23}$ = -9° (c = 1.0 CH_2Cl_2).



SI-24

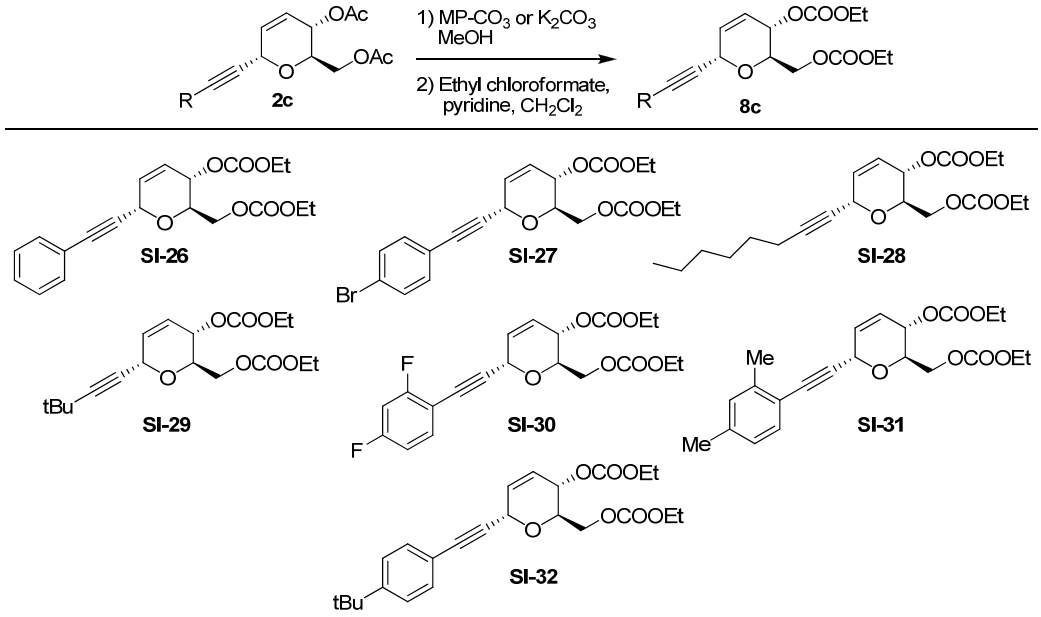
Aryl *C*-Glycoside SI-24: SI-19 (363 mg, 1.1 mmol) was dissolved in anhydrous MeOH (3 mL) and MP-carbonate resin(2.98 mmol/g loading, 200 mg, 0.50 mmol) was added. After orbital shaking for 5 h, the reaction was filtered, rinsed with MeOH and concentrated *in vacuo* to provide 265 mg of the crude diol, which was dissolved in CH_2Cl_2 (4 mL) and cooled to 0°C. Pyridine (0.35 mL, 4.4 mmol) and ethyl chloroformate (0.42 mL, 4.4 mmol) were added. The reaction was warmed to room temperature, stirred for 12 h, diluted with sat. aqueous sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-24** (136 mg, 46% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.31-7.40 (m, 5H), 6.19 (ddd, 1H, *J*=1.6, 3.2, 10.4), 6.06 (dt, 1H, *J*=2.0, 10.0), 5.32 (m, 1H), 5.20 (m, 1H), 5.6 (dd, 1H, *J*=5.6, 11.6), 4.19 (m, 5H), 3.88 (m, 1H), 1.31 (t, 1H, *J*=7.2), 1.28 (s, 1H, *J*=7.2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.5, 138.3, 131.8, 128.4, 128.2, 128.0, 124.4, 73.7, 68.6, 68.2, 66.0, 64.3, 64.1, 14.1 ppm; IR (neat): 2986, 1744, 1456, 1378, 1251, 1107, 1014, 877 cm^{-1}; $[\alpha]_D^{23}$ = -22° (c = 1.0 $CHCl_3$).

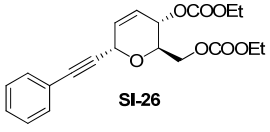


SI-25

Aryl *C*-Glycoside SI-25: **SI-20** (253 mg, 0.8 mmol) was dissolved in anhydrous MeOH (2 mL) and K_2CO_3 (22 mg, 0.16 mmol) was added. After stirring for 2 h, the reaction was filtered, rinsed with MeOH and concentrated *in vacuo* to provide 186 mg of the crude diol, which was dissolved in CH_2Cl_2 (3 mL) and cooled to 0°C. Pyridine (0.26 mL, 3.2 mmol) and ethyl chloroformate (0.30 mL, 3.2 mmol) were added. The reaction was warmed to room temperature, stirred for 2 h, diluted with sat. aqueous sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-25** (218 mg, 73% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.00 (s, 2H), 6.95 (s, 1H), 6.17 (dq, 1H, *J*=1.6, 3.2, 10.8), 5.04 (dt, 1H, *J*=2.4, 10.8), 5.20 (m, 2H), 4.31 (dd, 1H, *J*=5.6, 11.6), 4.22 (m, 5H), 3.90 (m, 1H), 2.31 (s, 6H), 1.31 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.5, 138.1, 137.9, 131.9, 129.8, 125.8, 124.3, 73.8, 68.5, 68.3, 66.0, 64.3, 64.1, 21.2, 14.1 ppm; IR (neat): 2979, 1744, 1612, 1452, 1379, 1270, 1014, 881 cm^{-1}; $[\alpha]_D^{23} = 5^o$ (c = 1.0 $CHCl_3$).

General procedure for conversion of alkynyl-C-glycoside bis-acetates to bis-carbonates, Table SI-4:

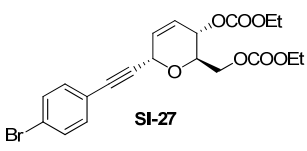




SI-26

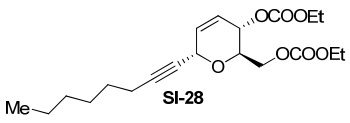
Alkynyl *C*-Glycoside SI-26: **SI-1** (1.60 g, 5.1 mmol) was dissolved in anhydrous MeOH (20 mL) and potassium carbonate (400 mg, 2.0 mmol) was added. After stirring for 2 h, the reaction was concentrated onto SiO_2 and chromatographed (SiO_2) (5-90% ethyl acetate/ hexanes) to provide 1.17 g of the diol, which was dissolved in CH_2Cl_2 (7 mL) and cooled to 0°C. Pyridine (1.50 mL, 19.0 mmol) and ethyl chloroformate (1.40 mL, 15.0 mmol) were added consecutively. The reaction was

warmed to room temperature, stirred for 3 h, diluted ethyl acetate, washed with sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-26** (1.44 g, 99% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.32 (m, 3H), 5.99 (ddd, 1H, *J*=1.6, 3.6, 10.4), 5.89 (dt, 1H, *J*=2.0, 10.0), 5.22 (dq, 1H, *J*=2.0, 8.8), 5.18 (m, 1H), 4.39 (dd, 1H, *J*=2.8, 11.6), 4.34 (dd, 1H, *J*=4.8, 11.6), 4.21 (m, 4H), 1.32 (t, 1H, *J*=7.6), 1.28 (t, 1H, *J*=7.2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.3, 131.8, 129.6, 128.6, 128.2, 124.7, 122.0, 86.7, 84.3, 69.4, 68.0, 66.0, 64.4, 64.3, 64.1, 14.1 ppm; IR (neat): 2967, 1740, 1456, 1371, 1254, 1017 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{20}H_{22}O_7Na$ 397.1263, found 397.1233. $[\alpha]_D^{23}$ = -56° (c = 1.0 $CHCl_3$).



SI-27

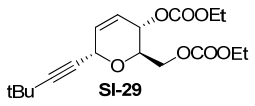
Alkynyl *C*-Glycoside SI-27: Diacetate **SI-5** (38 mg, 0.97 mmol) was dissolved in anhydrous MeOH (3 mL) and MP-carbonate resin (2.98 mmol/g loading, 200 mg, 0.5 mmol) was added. After orbital shaking for 15 h, the reaction was filtered, rinsed with MeOH, and concentrated to provide 304 mg of the diol, which was dissolved in CH_2Cl_2 (4 mL) and cooled to 0°C. Pyridine (0.320 mL, 3.9 mmol) and ethyl chloroformate (0.32 mL, 3.9 mmol) were added. The reaction was warmed to room temperature, stirred for 15 h, diluted methylene chloride, washed with sat. aqeous sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-45% ethyl acetate/pet ether) provided **SI-27** (175 mg, 39% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, 2H, *J*=8.4), 7.29 (d, 2H, *J*=8.8), 5.98 (ddd, 1H, *J*=1.6, 3.2, 10.0), 5.90 (dt, 1H, *J*=2.0, 10.4), 5.21 (dq, 1H, *J*=2.0, 24.4), 5.17 (m, 1H), 4.39 (dd, 1H, *J*=3.2, 12.0), 4.33 (dd, 1H, *J*=4.4, 11.6), 4.21 (q, 2H, *J*=7.2), 4.20 (q, 2H, *J*=7.2), 1.32 (t, 3H, *J*=7.2), 1.29 (t, 3H, *J*=7.6) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.4, 133.3, 131.6, 129.3, 125.0, 123.1, 121.0, 85.7, 85.5, 69.6, 67.9, 66.1, 64.5, 64.3, 64.3, 14.2 ppm**;** IR (neat): 3398, 2974, 1748, 1378, 1247, 1013, 889 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{20}H_{21}O_7NaBr$ 475.0368, found 475.0371. $[\alpha]_D^{23}$ = -75° (c = 1.0 $CHCl_3$).



SI-28

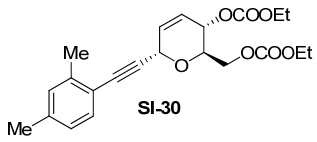
Alkynyl *C*-Glycoside SI-28: Diacetate **SI-7** (357 mg, 1.11 mmol) was dissolved in anhydrous MeOH (5 mL) and MP-carbonate resin(2.98 mmol/g loading, 200 mg, 0.5 mmol) was added. After orbital shaking for 15 h, the reaction filtered, rinsed with MeOH, and concentrated to provide 241 mg diol, which was dissolved in CH_2Cl_2 (3 mL) and cooled to 0°C. Pyridine (0.327 mL, 4.0 mmol) and ethyl chloroformate (0.387 mL, 4.0 mmol) were added. The reaction was warmed to room temperature, stirred for 15 h, diluted with CH_2Cl_2, washed with sat. aqueous sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-28** (324 mg, 39% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, 1H, *J*=2.0, 3.4, 10.3), 5.73 (dt, 1H, *J*=1.6, 10.4), 5.08 (dq, 1H, *J*=2.0, 9.0), 4.86 (m, 1H), 5.08 (m, 1H), 4.85 (m, 1H), 4.17 (m, 7H), 2.12 (td, 2H, *J*=2.0, 7.2), 1.40 (m, 2H), 1.22 (m, 12H), 0.81 (t, 3H, 6*J*=6.8) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 152.2, 130.3, 123.8, 87.8, 75.3, 68.9, 67.9, 66.0, 64.2, 64.0, 63.9, 31.1, 28.2, 28.2, 22.3, 18.5, 14.0, 13.8 ppm; IR (neat): 3452,

2963, 2939, 2854, 2361, 2341, 1740, 1464, 1371, 1266, 1018, 878 cm^{-1}; $[\alpha]_D^{23}$ = -29° (c = 1.0 $CHCl_3$).



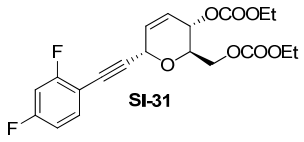
SI-29

Alkynyl *C*-Glycoside SI-29: Diacetate **SI-4** (150 mg, 0.51 mmol) was dissolved in anhydrous MeOH (2 mL) and MP-carbonate resin(2.98 mmol/g loading, 80 mg, 0.2 mmol) was added. After orbital shaking for 15 h, the reaction was filtered, rinsed with MeOH, and concentrated to provide 113 mg of the diol, which was dissolved in CH_2Cl_2 (2 mL) and cooled to 0°C. Pyridine (0.170 mL, 2.1 mmol) and ethyl chloroformate (0.200 mL, 2.1 mmol) were added. The reaction was warmed to room temperature, stirred for 4 h, diluted with CH_2Cl_2, washed with sat. aqeous sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-29** (324 mg, 41% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (m, 1H), 5.80 (m, 1H), 5.15 (m, 1H), 4.93 (m, 1H) , 4.10-4.37 (m, 7H), 1.31 (m, 6H), 1.19 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.4, 130.5, 124.0, 95.9, 73.9, 69.0, 68.2, 66.1, 64.4, 64.2, 64.1, 30.7 27.4, 14.2 ppm; IR (neat): 3425, 2974, 1744, 1378, 1231, 1049 cm^{-1}; $[\alpha]_D^{23}$ = +23.0° (c = 1.0 CH_2Cl_2).



SI-30

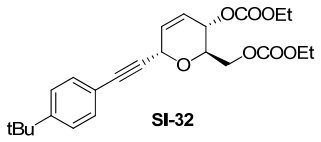
Alkynyl *C*-Glycoside SI-30: Diacetate SI-10 (540 mg, 1.60 mmol) was dissolved in anhydrous MeOH (2 mL) and MP-carbonate resin (2.98 mmol/g loading, 100 mg, 0.32 mmol) was added. After orbital shaking for 2 h, the reaction was filtered, rinsed with MeOH, and concentrated to provide 355 mg of the diol, which was dissolved in CH_2Cl_2 (2 mL) and cooled to 0°C. Pyridine (0.445 mL, 5.5 mmol) and ethyl chloroformate (0.526 mL, 5.5 mmol) were added. The reaction was warmed to room temperature, stirred for 4 h, diluted with CH_2Cl_2, washed with sat. aqeous sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-30** (458 mg, 83% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (s, 1H), 7.03 (m, 2H), 6.00 (dt, 1H, *J*=1.6, 10.0), 5.89 (m, 1H), 5.22, (m, 1H), 4.35 (m, 1H), 4.23 (m, 5H), 2.35 (s, 3H), 2.27 (s, 3H), 1.30 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.4, 137.3, 134.9, 132.5, 129.7, 129.5, 129.2, 124.7, 121.6, 87.8, 86.0, 69.5, 68.1, 66.1, 64.5, 64.4, 64.1, 20.6, 20.0, 14.1 ppm**;** IR (neat): 2994, 1748, 1456, 1371, 1258, 1314 cm^{-1}; $[\alpha]_D^{23}$ = -56° (c = 1.0 CH_2Cl_2).



SI-31

Alkynyl *C*-Glycoside SI-31: Diacetate SI-11 (298 mg, 0.85 mmol) was dissolved in anhydrous MeOH (2 mL) and MP-carbonate resin (2.98 mmol/g loading, 43 mg, 0.13 mmol) was added. After orbital shaking for 3 h, the reaction was filtered, rinsed with MeOH, and concentrated to provide 238 mg of the diol, which was dissolved in CH_2Cl_2 (2 mL) and cooled to 0°C. Pyridine (0.274 mL, 3.4 mmol) and ethyl chloroformate (0.324 mL, 3.4 mmol) were added. The reaction was warmed to room temperature, stirred for 2 h, diluted with CH_2Cl_2, washed with sat. aqeous sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-31** (275 mg, 79% yield) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 1H), 6.83 (m, 2H), 5.99 (dq, 1H, *J*=1.6, 3.2, 10.4), 5.92 (dt, 1H, *J*=1.6, 3.6), 5.21 (m, 2H), 4.39 (dd, 1H,

J=3.2, 12.0), 4.34 (dd, 1H, *J*=4.8, 7.6), 4.22 (m, 5H), 1.30 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3 (dd, 1C, *J*= 46.8, 131.6), 161.8 (dd, 1C, *J*=46.8, 122.8), 155.0, 154.4, 134.4 (dd, 1C, *J*=8.8, 38.4), 129.1, 125.2, 111.5 (dd, 1C, *J*=14.8, 85.2), 104.3 (dd, 1C, *J*=96.8, 102.8), 89.4, 69.6, 67.9, 66.1, 64.5, 64.3, 64.2, 14.2, 14.1 ppm; IR (neat): 2986, 1744, 1619, 1495, 1254, 1153, 1091, 1014 cm^{-1}**;** HRMS (Tof) $[M+Na]^+$: calcd. for $C_{20}H_{20}O_7NaF_2$ 433.1075, found 433.1023. $[\alpha]_D^{23}$ = -67^o (c = 1.0 CH_2Cl_2).

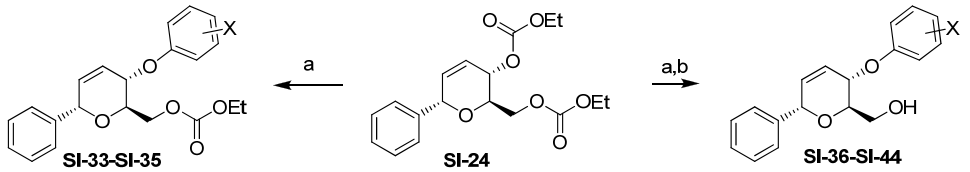


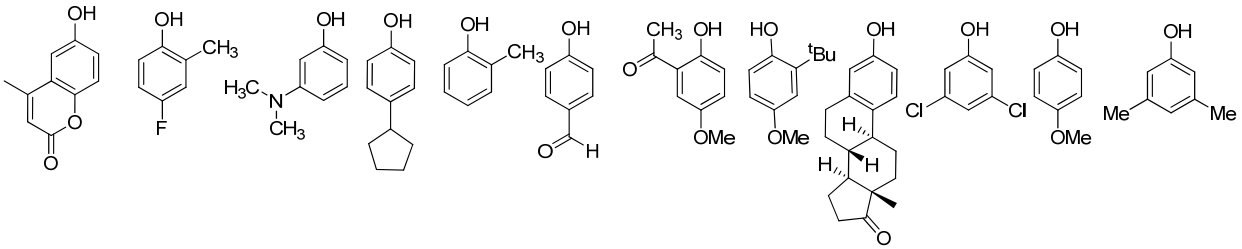
SI-32

Alkynyl *C*-Glycoside SI-32: Diacetate SI-12 (265 mg, 0.71 mmol) was dissolved in anhydrous MeOH (2 mL) and MP-carbonate resin (2.98 mmol/g loading, 36 mg, 0.1 mmol) was added. After orbital shaking for 3 h, the reaction was filtered, rinsed with MeOH, and concentrated to provide 177 mg of the diol, which was dissolved in CH_2Cl_2 (2 mL) and cooled to 0^{o}C. Pyridine (0.188 mL, 2.3 mmol) and ethyl chloroformate (0.222 mL, 2.3mmol) were added. The reaction was warmed to room temperature, stirred for 15 h, diluted with CH_2Cl_2, washed with sat. aqeous sodium bicarbonate and brine, dried, and concentrated. Chromatography over SiO_2 (0-40% ethyl acetate/pet ether) provided **SI-32** (222.4 mg, 89% yield) as a viscous oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 1H, *J*= 8.4), 7.33 (d, 1H, *J*=6.4), 5.99 (dq, 1H, *J*=2.0, 3.6, 10.0), 5.89 (dt, 1H, 2.0, 3.6), 5.23 (dq, 1H, *J*= 2.0, 4.0, 9.2), 5.18 (m, 1H), 4.39 (dd, 1H, *J*=2.8, 12.0), 4.34 (dd, 1H, *J*= 5.2, 12.0), 4.23 (m, 5H), 1.31 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.4, 152.0, 131.6, 129.8, 131.7, 129.8, 125.2, 124.6, 119.0, 86.9, 83.7, 69.4, 68.1, 66.1, 64.5, 64.2, 34.7, 31.1, 14.2 ppm; IR (neat): 2967, 1748, 1371, 1266, 1009, 784 cm^{-1}; $[\alpha]_D^{23}$ = -48^o (c = 1.0 CH_2Cl_2).

Phenol addition to C-glycosides-preliminary rehearsal screen

Table SI- 5: Evaluation of different phenols for allylic addition.

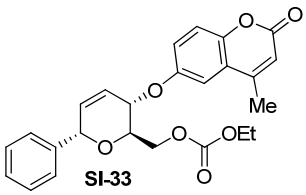




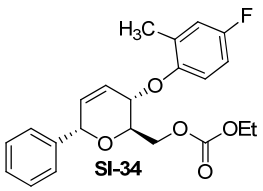
a)$Pd_2(dba)_3$-$CHCl_3$, (S,S)-Trost Ligand, phenol, CH_2Cl_2, μwave (100^{o}C, 300 W), 15 min. b) K_2CO_3, MeOH

General Procedure for phenol addition. (Aryl ethers SI-36-SI-44). Dicarbonate **SI-24** (540 mg, 1.5 mmol), (*1S,2S*)- (-)- 1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl)

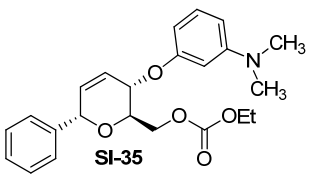
(110 mg, 0.15 mmol), and Tris(dibenzylideneacetone) dipalladium(0)- chloroform adduct (80 mg, 0.08 mmol) were dissolved in degassed CH_2Cl_2 (8.5 mL) and stirred for 15 min. The color of the solution changed from maroon to yellowish-orange. The solution (0.500 mL, 0.09 mmol) was then transferred to separate 10 mL microwave vials containing the appropriate phenol (0.14 mmol). Each reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The solutions were then transferred to 20 mL scintillation vials and concentrated *in vacuo*. Compounds **SI-33-SI-35** were purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide the carbonate- protected aryl ether. For (**SI-36-SI-44**) the crude reaction mixtures were resuspended in MeOH (1.5 mL) and MP-CO_3 or K_2CO_3 (0.25 eq) was added. After shaking for 12 h, the reactions were filtered and concentrated. Purification by SiO_2 chromatography (0-80% ethyl acetate / hexanes) provided the desired aryl ethers **SI-36-SI-44** in the yields described below.



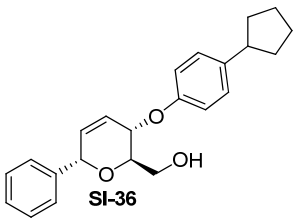
Aryl ether SI-33: Yield: 14.7 (0.04 mmol, 50%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.53 (m, 6H), 6.95 (appd, 1H, *J*=2.4), 6.87 (m, 2H), 6.23 (ddd, 1H, 2.0, 3.2, 10.8), 6.17 (appd, 2H, *J*=4.8), 5.41 (d, 1H, *J*=2.4), 4.98 (dd, 1H, *J*=2.0, 8.0), 4.32 (d, 2H, *J*=4.4), 4.15 (q, 2H, *J*=6.8), 3.95 (m, 1H), 2.41 (s, 3H), 1.27 (t, 1H, *J*=9.6) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.0, 160.1, 155.0, 152.5, 138.5, 131.6, 128.6, 128.3, 127.9, 125.9, 124.3, 114.2, 113.1, 112.3, 103.4, 102.7, 74.3, 68.8, 68.7, 66.2, 64.3, 18.7, 14.2 ppm; IR (neat): 3378, 1957, 1739, 1608, 1440, 1386, 1266, 1141, 1068, 1014 cm^{-1}; $[\alpha]_D^{23}$ = +75° (c = 1.0 CH_2Cl_2).



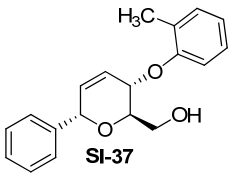
Aryl ether SI-34: Yield: 23 mg (0.07 mmol, 78%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.45 (m, 5H), 6.83 (m, 3H), 6.19 (dd, 1H, *J*=1.2, 2.8), 6.15 (dd, 1H, *J*= 1.6, 3.6), 5.39 (d, 1H, *J*=1.6), 4.81 (dd, 1H, *J*=2.0, 8.8), 4.33 (d, 2H, *J*=3.6), 4.15 (q, 2H, *J*=7.2), 3.94 (m, 1H), 2.17 (s, 3H), 1.27 (t, 3H, *J*=7.2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 155.0, 151.1, 138.9, 130.6, 129.8, 129.7, 128.5, 128.1, 127.8, 117.8, 113.7, 112.6, 74.2, 69.3, 69.1, 66.6, 64.1, 16.5, 14.2 ppm; IR (neat): 3441, 2963, 2920, 1748, 1495, 1456, 1386, 1262, 1204, 1060 cm^{-1}; $[\alpha]_D^{23}$ = +43° (c = 1.0 CH_2Cl_2).



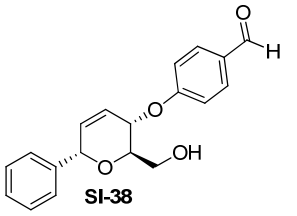
Aryl ether SI-35: Yield: 27 mg (0.12 mmol, 88%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.45 (m, 5H), 7.15 (t, 1H, *J*=8), 6.39 (dd, 1H, *J*=2.0, 8.4), 6.31 (m, 2H), 6.23 (m, 2H), 5.39 (bs, 1H), 4.91 (dd, 1H, *J*=2.0, 8.4), 4.33 (m, 2H), 4.16 (q, 2H, *J*=7.2), 3.92 (m, 1H), 2.94 (s, 6H), 1.28 (t, 3H, *J*=7.2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.0, 158.2, 155.0, 139.0, 130.1, 129.9, 128.5, 128.1, 127.9, 126.1 106.3, 103.0, 100.7, 74.3, 69.1, 68.1, 66.6, 64.0, 40.5, 14.2 ppm; IR (neat): 2912, 1744, 1647, 1612, 1569, 1499, 1449, 1262, 1149 cm^{-1}; $[\alpha]_D^{23}$ = +44° (c = 1.0 CH_2Cl_2).



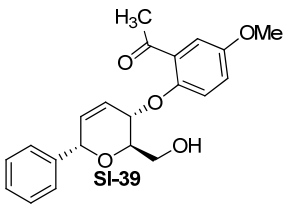
Aryl ether SI-36: Yield: 22 mg (0.12 mmol, 83%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.46 (m, 5H), 7.17 (d, 2H, *J*=8.0), 7.88 (d, 2H, *J*=8.8), 5.37 (m, 1H), 4.88 (m, 1H), 3.74 (m, 3H), 2.92 (m, 1H), 2.03 (m, 2H), 1.67 (m, 7H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 139.4, 139.0, 129.7, 128.5, 128.2, 128.1, 128.0, 126,7, 115.6, 74.4, 70.8, 68.6, 62.3, 45.1, 34.7, 25.4 ppm; IR (neat): 3421, 2951, 2854, 1693, 1511, 1449, 1383, 1223, 1068 cm^{-1}; $[\alpha]_D^{23}$ = +92^{o} (c = 1.0 CH_2Cl_2).



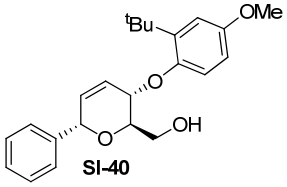
Aryl ether SI-37 Yield: 15 mg (0.10 mmol, 68%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.48 (m, 5H), 7.18 (m, 2H), 6.89 (m, 2H), 6.20 (m, 2H), 5.38 (d, 1H, *J*=2.0), 4.91 (appd, 1H, *J*=6.4), 3.80 (m, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 139.1, 131.1, 129.8, 128.5, 128.2, 128.0, 127.6, 126.8, 126.6, 121.0, 112.5, 74.4, 71.0, 68.5, 62.4, 16.4 ppm; IR (neat): 3433, 2920, 1604, 1491, 1456, 1386, 1235, 1192, 1083 cm^{-1}; $[\alpha]_D^{23}$ = +45^{o} (c = 1.0 CH_2Cl_2).



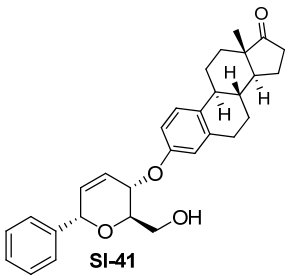
Aryl ether SI-38 Yield: 15 mg (0.10 mmol, 68**%)** as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.85 (d, 2H, *J*=8.4), 7.42 (m, 5H), 7.06 (d, 2H, *J*=8.4), 6.24 (m, 1H), 6.16 (d, 1H, *J*=10.4), 5.39 (d, 1H, *J*=1.6), 5.10 (dd, 1H, *J*=1.2, 7.6), 3.76 (m, 3H), 1.95 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 162.5, 138.6, 132.1, 130.3, 128.6, 128.4, 128.1, 125.4, 115.7, 74.5, 70.4, 68.1, 61.8 ppm; IR (neat): 3421, 2916, 2361, 1957, 1682, 1600, 1510, 1386, 1239, 1165 cm^{-1}; $[\alpha]_D^{23}$ = +98^{o} (c = 1.0 CH_2Cl_2).



Aryl ether SI-39: Yield: 27 mg (0.05 mmol, 38%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 5H), 7.27 (s, 1H), 7.03 (bs, 2H), 6.17 (m, 2H), 5.37 (bs, 1H), 5.02 (d, 1H, *J*=6.8), 3.80 (m, 6H), 2.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 153.9, 150.5, 138.6, 130.7, 129.9, 128.6, 128.4, 128.0, 125.5, 120.4, 115.7, 114.0, 74.4, 70.8, 69.3, 62.1, 55.8, 32.2 ppm; IR (neat): 3421, 2912, 1662, 1491, 1414, 1285, 1219, 1048 cm^{-1}; $[\alpha]_D^{23}$ = +52^{o} (c = 1.0 CH_2Cl_2).

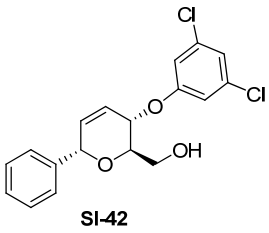


Aryl ether SI-40: Yield: 15 mg (0.07 mmol, 53%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.44 (m, 5H), 6.91 (dd, 2H, *J*=2.8, 12.4), 6.70 (dd, 1H, *J*=2.8, 8.8), 6.14 (m, 2H), 5.27 (bs, 1H), 5.00 (d, *J*=6.4), 3.78 (m, 6H, 1.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 149.1, 140.3, 138.9, 129.8, 128.5, 128.3, 128.1, 126.0, 114.9, 112.9, 109.8, 74.5, 71.0, 67.0, 62.5, 55.6, 34.9, 29.8 ppm; IR (neat): 3425, 2955, 2924, 1957, 1728, 1576, 1484, 1456, 1383, 1266, 1208, 1095, 1052 cm^{-1}; $[\alpha]_D^{23}$ = +77^{o} (c = 1.0 CH_2Cl_2).



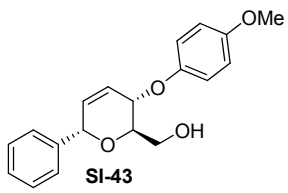
SI-41

Aryl ether SI-41: Yield: 24 mg (0.10 mmol, 68%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 5H), 4.22 (d, 1H, *J*=8.0), 4.77 (dd, 1H, *J*=2.8, 8.4), 6.71 (d, 1H, *J*=2.8), 6.20 (dt, 1H, *J*=2.0, 10.4), 6.14 (dq, 1H, *J*=1.6, 2.8, 10.4), 5.36 (d, 1H, *J*=2.0), 4.88 (dt, 1H, *J*=2.0, 6.4), 3.73 (m, 3H), 2.89 (m, 2H), 2.52 (m, 1H), 2.41 (m, 1H), 2.24 (m, 1H), 2.03 (m, 4H), 1.57 (m, 6H), 0.92 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 138.9, 138.1, 132.8, 129.8, 128.5, 128.2, 128.1, 126.7, 126.6, 115.9, 113.3, 74.5, 70.7, 68.4, 62.3, 50.4, 48.0, 44.0, 38.3, 35.9, 31.6, 29.6, 26.5, 21.6, 13.8 ppm; IR (neat): 3724, 3421, 2916, 1732, 1608, 1495, 1390, 1247, 1068 cm^{-1}; $[\alpha]_D^{23}$ = +150^o (c = 1.0 CH_2Cl_2).



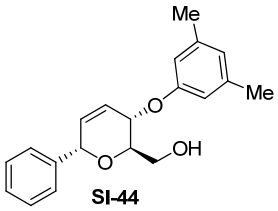
SI-42

Aryl ether SI-42: Yield: 72 mg (0.04 mmol, 30%) as a film.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 5H), 6.99 (1H, t, *J*=1.6), 6.86 (appd, 2H, *J*=1.6), 6.21 (ddd, 1H, *J*=10.4, 2.8, 1.6), 6.13 (dt, 1H, *J*=1.6, 10.4), 5.37 (1H, q, *J*=2.4), 4.93 (m, 1H), 3.70 (m, 3H), 1.92 (t, 1H, *J*=7.2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 138.6, 135.6, 130.9, 128.6, 128.3, 128.1, 125.3, 121.7, 114.7, 74.5, 70.4, 68.7, 61.8 ppm; IR (neat): 3425, 3079, 2951, 2920, 1953, 1584, 1573, 1456, 1386, 1254, 1095 cm^{-1}; $[\alpha]_D^{23}$ = +82^o (c = 1.0 CH_2Cl_2).



SI-43

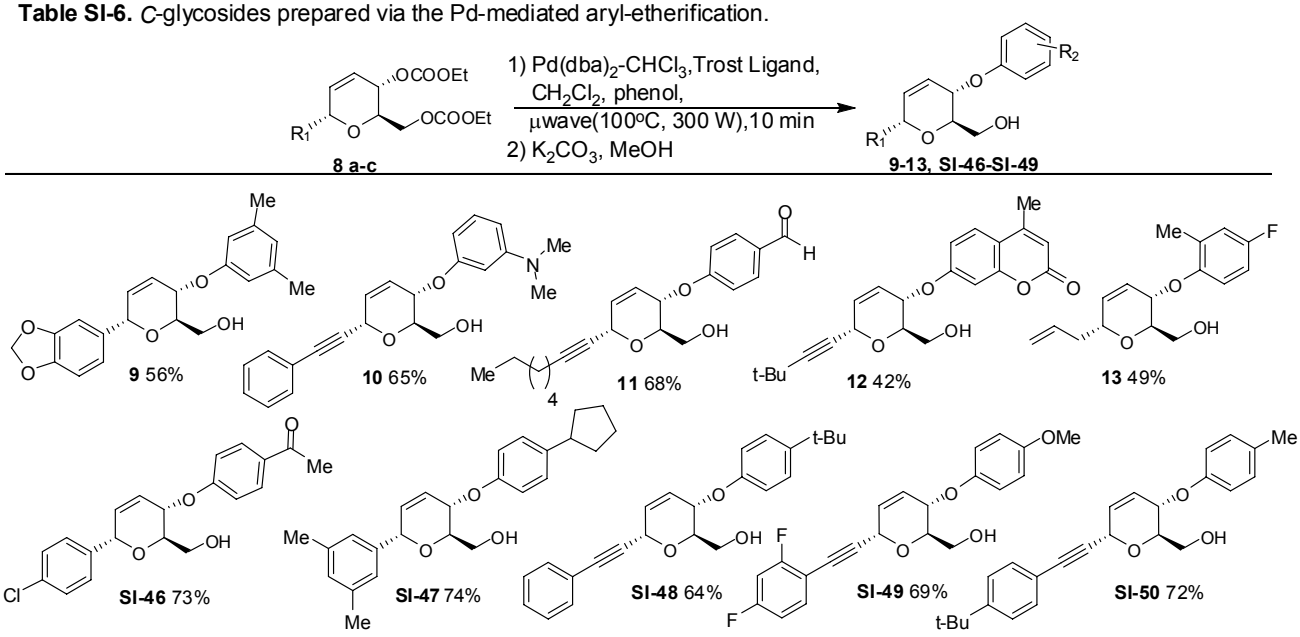
Aryl ether SI-43 (Compound 33): Yield: 34 mg (0.11 mmol, 80%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.46 (m, 5H), 6.91 (d, 1H, *J*=9.2), 6.85 (d, 1H, *J*=9.2), 6.85 (d, 1H, *J*=9.2), 6.20 (dt, 1H, *J*=1.6, 10.4), 6.15 (ddd, 1H, *J*=1.2, 2.8, 10.4), 5.36 (appd, 1H, *J*=2.0), 4.81 (dd, 1H, *J*=1.6, 8.0), 3.75 (m, 6H), 1.86 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 151.4, 138.9, 129.7, 128.5, 128.1, 128.1, 126.6, 117.2, 114.8, 74.4, 70.9, 69.5, 62.2, 55.7 ppm; IR (neat): 4352, 2908, 1511, 1449, 1382, 1223, 1037, 816, 746 cm^{-1}; HRMS (Tof) $[M+H]^+$: calcd. for $C_{19}H_{21}O_4$ 331.1440, found 313.1495. $[\alpha]_D^{23}$ = +95^o (c = 1.0 CH_2Cl_2).

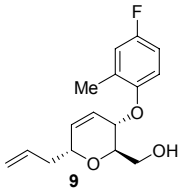


SI-44

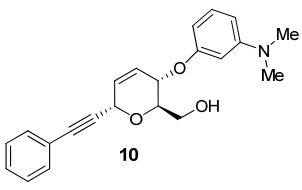
Aryl ether SI-44: Yield: XXmg (0.12 mmol, XX%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.46 (m, 5H), 6.61 (d, 3H, *J*=19.6), 6.21 (ad, 2H, *J*=12.0), 6.15 (as, 2H, *J*=10.4), 5.37, (d, 1H, *J*=2.0), 4.89 (dt, 1H, 1.6, 6.4), 3.73 (m, 3H), 2.29 (bs, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 139.5, 139.0, 129.7, 128.5, 128.2, 128.1, 126.7, 123.1, 113.5, 74.5, 70.8, 68.3, 62.3, 21.4 ppm; IR (neat): 3398, 2920, 2957, 1592, 1460, 1390, 1289, 1157 cm^{-1}; $[\alpha]_D^{23}$ = +101^o (c = 1.0 CH_2Cl_2).

Table SI-6. *C*-glycosides prepared via the Pd-mediated aryl-etherification.



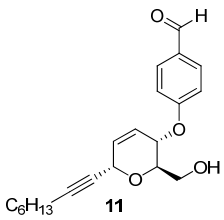


Aryl ether 9: Bis-carbonate **SI-13** (59 mg. 0.19 mmol), (*1S,2S*)-(-)-1,2-Diaminocyclohexane-*N*,*N*'-bis(2'-diphenylphosphinobenzoyl) (13 mg, 0.019 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (10 mg, 0.01 mmol) were dissolved in degassed CH_2Cl_2 (1.0 mL) and stirred for 15 min. The solution changed from maroon to yellowish- orange. 4-Fluoro- 2-methylphenol (26 mg, 0.21 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The crude reaction mixture was transferred to a 20 mL scintillation vial and concentrated *in vacuo*. The reaction was resuspended in MeOH (3.0 mL) and K_2CO_3 (300 mg, 2.0 mmol) was added. After stirring for 5 h, the reaction was concentrated and purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide **13** (26 mg, 49%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (m, 3H), 5.91 (m, 3H), 5.14 (m, 2H), 4.65 (dd, 1H, *J*=1.6, 7.0), 4.33 (m, 1H), 3.84 (m, 2H), 3.72 (m, 1H), 2.53 (m, 1H), 2.35 (m, 1H), 2.19 (s, 3H), 2.07 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 155.9, 151.3, 134.5, 131.4 ,129.5, 125.2, 117.6, 113.5, 112.5, 72.6, 71.2, 69., 62.4, 37.6, 16.5 ppm; IR (neat): 3440, 2917, 1499, 1262, 1204, 1087, 1045, 796 cm^{-1}; $[\alpha]_D^{23}$ = +93° (c = 1.0 CH_2Cl_2).



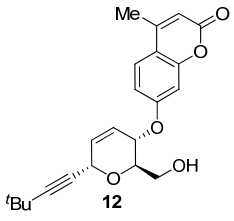
Aryl ether 10: Bis-carbonate **SI-26** (100 mg. 0.27 mmol), (*1S,2S*)- (-)- 1,2-Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (9 mg, 0.01 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (7 mg, 0.01 mmol) were dissolved in degassed CH_2Cl_2 (1.0 mL) and stirred for 15 min. The color of the solution changed from maroon to yellowish-orange. 3-dimethylamino phenol (40 mg, 0.3 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The crude reaction mixture was

transferred to a 20 mL scintillation vial and concentrated *in vacuo*. The reaction was resuspended in MeOH (2.0 mL) and MP-carbonate resin(20 mg, 0.1 mmol) was added. After stirring for 6 h, the reaction was concentrated and purified by SiO_2 chromatography (0-70% ethyl acetate / hexanes) to provide **10** (59 mg, 65%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.33 (m, 3H), 7.15 (t, 1H, *J*=6.8), 6.38 (m, 3H), 6.06 (d, 1H, *J*=2.0, 10.0), 5.95 (ddd, 1H, *J*=1.6, 3.2, 10.4), 5.24 (m, 1H), 4.90 (dd, 1H, *J*=2.0, 8.8), 4.15 (m, 1H), 3.99 (m, 1H, *J*=2.8, 12.0), 3.82 (dd, 1H, *J*=5.2, 12.0), 2.91 (bs, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 152.1, 131.9, 129.9, 128.6, 128.3, 128.2, 126.4, 122.3, 106.3, 103.0, 100.7, 86.4, 85.2, 72.8, 68.0, 64.6, 62.3, 40.5 ppm; IR (neat): 3409, 2924, 2361, 1607, 1581, 1503, 1449, 1390, 1235, 1153, 1079, 757 cm^{-1}; $[\alpha]_D^{23}$ = +12^o (c = 1.0 CH_2Cl_2).



11

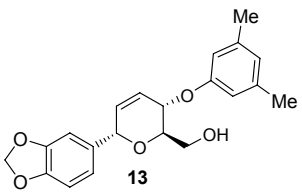
Aryl ether 11: Bis-carbonate **SI-28** (0.081g. 0.21 mmol), (*1S,2S*)- (-)- 1,2-Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (15 mg, 0.021 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (10 mg, 0.01 mmol) were dissolved in degassed CH_2Cl_2 (1.0 mL) and stirred for 15 min. The color of the solution changed from maroon to yellowish-orange. 4-Hydroxybenzaldehyde (28 mg, 0.20 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100^{o}C. The crude reaction mixture was transferred to a 20 mL scintillation vial and concentrated *in vacuo*. The reaction was resuspended in MeOH (3.0 mL) and K_2CO_3 (71 mg (0.21 mmol) was added. After stirring for 15 h, the reaction was concentrated and purified by SiO_2 chromatography (0-70% ethyl acetate / hexanes) to provide **11** (49 mg, 68%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.83 (d, 2H, *J*=9.2), 7.03 (d, 2H, *J*=8.8), 5.91 (m, 2H), 5.02 (m, 2H), 4.08 (m, 1H), 3.93 (dd, 1H, *J*=2.0, 12.0), 3.75 (dd, 1H, *J*=4.4, 12.0), 2.24 (m, 2H), 1.52 (m, 2H), 1.33 (m, 6H), 0.89 (t, 3H, *J*=6.8) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 162.4, 132.1, 130.3, 130.2, 124.1, 115.6, 87.9, 75.8, 71.8, 67.9, 64.4, 61.8, 31.2, 28.5, 28.4, 22.5, 18.7, 14.0 ppm; IR (neat): 3440, 2932, 2858, 1697, 1603, 1577, 1511, 1239, 1161, 1080 cm^{-1}; $[\alpha]_D^{23}$ = +85^o (c = 1.0 CH_2Cl_2).



12

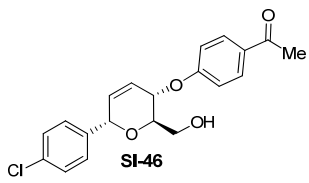
Aryl ether 12: Bis-carbonate **SI-29** (70 mg. 0.20 mmol), (*1S,2S*)- (-)- 1,2-Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (14 mg, 0.021 mmol), and Tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (10 mg, 0.01 mmol) were dissolved in degassed CH_2Cl_2 (1.0 mL) and stirred for 15 min. The solution changed from maroon to yellowish-orange. 7- Hydroxy -4-methylcoumarin (39 mg, 0.22 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100^{o}C. The crude reaction mixture was transferred to a 20 mL scintillation vial and concentrated *in vacuo*. The reaction was resuspended in MeOH (3.0 mL) and K_2CO_3 (370 mg, 2.7 mmol) was added. After stirring for 15 h, the reaction was concentrated and purified by SiO_2 chromatography (0-60% ethyl acetate / hexanes) to provide **12** (31 mg, 42%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 1H, *J*=8.4), 6.88 (m, 2H), 6.15 (bs, 1H), 5.90 (s, 2H), 5.02 (s, 1H), 4.94 (dd, 1H, 1.6, 8.4), 4.05 (m, 1H), 3.94 (m, 1H), 3.76 (m, 1H), 2.39 (s, 3H), 1.23 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 160.3, 155.2, 152.4, 130.4, 125.8, 123.9, 114.1, 112.9, 112.3, 102.8, 95.9, 74.1, 71.7, 68.3, 64.4, 61.9, 30.8, 27.5, 18.7 ppm; IR

(neat): 3441, 2967, 2920, 2233, 1724, 1611, 1386, 1262, 1153, 1072 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{22}H_{24}O_5Na$ 391.1521, found 391.1508. $[\alpha]_D^{23} = +82^o$ (c = 1.0 CH_2Cl_2).



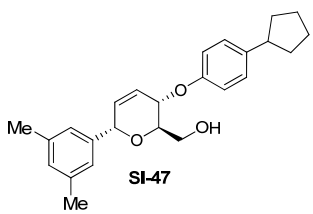
13

Aryl ether 13: Dicarbonate **SI-21** (125 mg 0.32 mmol), (*1S,2S*)- (-)- 1,2-Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (11 mg, 0.02 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (8 mg, 0.02 mmol) were dissolved in degassed CH_2Cl_2 (2.0 mL) and stirred for 15 min. The color of the solution changed from maroon to yellowish-orange. 3,5-Dimethyl phenol (41 mg, 0.3 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The crude reaction mixture was concentrated onto SiO_2 and chromatographed (0-40% ethyl acetate/hexanes) to provide 121 mg of ethyl carbonate-protected **9**. The intermediate was resuspended in MeOH (1.0 mL) and MP-CO_3 (11 mg, 2.98 mmol/g) was added. After stirring for 3 h, the reaction was concentrated and purified by SiO_2 chromatography (0-70% ethyl acetate / hexanes) to provide **9** (33 mg, 56%) as a film. ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (m, 1H), 6.91 (d, 1H, J=7.6), 6.80 (d, 1H, J=8.0), 6.63 (s, 1H), 6.58 (s, 2H), 6.2 (m 1H), 6.09 (m, 1H), 5.98 (s, 2H), 5.25 (m, 1H), 4.86 (dd, 1H, J=1.6, 8.0), 3.71 (m, 3H), 2.29 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 147.8, 147.6, 139.4, 132.8, 129.7, 126.8, 123.1, 121.9, 113.5, 108.9, 108.1, 101.1, 74.2, 70.5, 68.3, 62.3, 21.4 ppm**;** IR (neat): 3433, 2909, 1713, 1596, 1487, 1441, 1285, 1223, 1161, 1072, 928 cm^{-1}; $[\alpha]_D^{23} = +68^o$ (c = 1.0 CH_2Cl_2).



SI-46

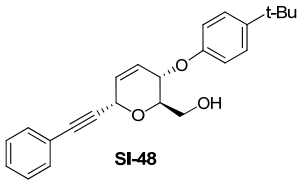
Aryl ether SI-46: Bis-carbonate **SI-22** (111 mg. 0.29 mmol), (*1S,2S*)- (-)- 1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (10 mg, 0.014 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (8 mg, 0.007 mmol) were dissolved in degassed CH_2Cl_2 (1.5 mL) and stirred for 15 min. The solution changed from maroon to yellowish-orange. 4'-hydroxyacetophenone (41 mg, 0.30 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The reaction mixture concentrated onto SiO_2 and chromatographed over SiO_2 (0-50% ethyl acetate / pet. ether) to provide the crude carbonate (104 mg, approx 84%) as a viscous oil. The mixture was resuspended in MeOH (3.0 mL) and K_2CO_3 (8 mg, 0.05 mmol) was added. After stirring for 6 h, the reaction was concentrated and purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide **SI-46** (59 mg, 73%) as a film. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 2H, *J*=8.8), 7.37 (s, 4H), 6.98 (d, 2H, *J*=9.2), 6.17 (2, 2H), 5.34 (m, 1H), 5.05 (dd, 1H, *J*=2.0, 7.6), 3.73 (m, 3H), 2.56 (s, 3H), 1.99 (t, -OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 161.3, 137.2, 134.3, 130.7, 130.2, 129.4, 128.8, 126.0, 115.1, 73.7, 70.6, 68.0, 61.8, 26.3 ppm; IR (neat): 3425, 1674, 1592, 1506, 1250, 1173, 1087 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{20}H_{19}O_4NaCl$ 381.0870, found 381.0887. $[\alpha]_D^{23} = +120^o$ (c = 1.0 CH_2Cl_2).



SI-47

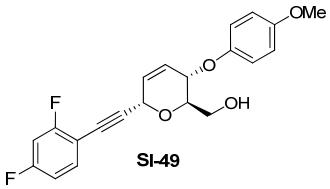
Aryl ether SI-47: Bis-carbonate **SI-25** (108 mg. 0.29 mmol), (*1S,2S*)- (-)- 1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (10 mg, 0.014 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (8 mg, 0.007 mmol) were dissolved in degassed CH_2Cl_2 (1.0 mL)

and stirred for 15 min. The solution changed from maroon to yellowish- orange. 4-cyclopentylphenol (47 mg, 0.29 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The reaction mixture concentrated onto SiO_2 and chromatographed over SiO_2 (0-50% ethyl acetate / pet. ether) to provide the crude carbonate (120 mg, approx 80%) as a viscous oil. The mixture was resuspended in MeOH (2.0 mL) and K_2CO_3 (6.3 mg, 0.05 mmol) was added. After stirring for 5 h, the reaction was concentrated and purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide **SI-47** (64 mg, 74%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, 2H, *J*=2.0), 7.05 (s, 2H), 6.98 (s, 1H), 6.91 (d, 2H, *J*=6.4), 6.19 (dt, 1H, *J*=2.0, 12), 6.11 (dq, 1H, *J*=1.6, 2.8, 10.4), 5.29 (m, 1H), 4.88 (dq, 1H, *J*= 1.6, 3.6, 5.6), 3.77 (m, 3H), 2.95 (m, 1H), 2.35 (m, 2H), 2.04 (m, 2H), 1.78 (m, 2H), 1.69 (m, 2H), 1.58 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 139.4, 138.8, 138.0, 129.9, 129.8, 128.1, 126.4, 126.0, 115.6, 74.6, 70.8, 68.7, 62.2, 45.1, 34.7, 25.4, 21.3 ppm; IR (neat): 3452, 2931, 2874, 1608, 1518, 1239, 1177, 1049, 831 cm^{-1}; $[\alpha]_D^{23}$ = +78° (c = 1.0 CH_2Cl_2).



SI-48

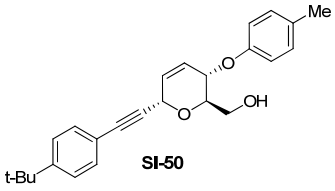
Aryl ether SI-48: Bis-carbonate **SI-26** (200 mg. 0.53 mmol), (*1S,2S*)- (-)- 1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (18 mg, 0.027 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct 14 mg, 0.013 mmol) were dissolved in degassed CH_2Cl_2 (1.0 mL) and stirred for 15 min. The solution changed from maroon to yellowish-orange. *p-tert*-Butyl-phenol (84 mg, 0.56 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The reaction mixture concentrated onto SiO_2 and chromatographed over SiO_2 (0-50% ethyl acetate / pet. ether) to provide the crude carbonate (221 mg, approx 95%) as viscous oil. The mixture was resuspended in MeOH (3.0 mL) and K_2CO_3 (34 mg, 0.1 mmol) was added. After stirring for 15 h, the reaction was concentrated and purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide **SI-48** (117 mg, 64%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 2H), 7.33 (m, 5H), 6.90 (d, 2H, *J*=8.8), 6.04 (d, 1H, *J*=10.4), 5.95 (dq, 1H, *J*=2.0, 3.2, 10.4), 5.24 (m, 1H), 4.89 (dd, 1H, *J*=1.6, 8.8), 4.15 (m, 1H), 3.98 (dd, 1H, *J*=2.8, 9.2), 3.81 (dd, 1H, *J*=4.8, 11.6), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 144.3, 131.9, 128.7, 128.3, 126.5, 126.4, 121.1, 115.2, 86.5, 85.3, 72.7, 68.2, 64.6, 62.3, 34.1, 31.5 ppm; IR (neat): 2955, 1654, 1608, 1507, 1227, 1075 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{24}H_{26}O_3Na$ 385.1780, found 385.1769. $[\alpha]_D^{23}$ = +19° (c = 1.0 CH_2Cl_2).



SI-49

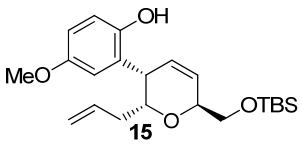
Aryl ether SI-49: Bis-carbonate **SI-13** (138 mg. 0.34 mmol), (*1S,2S*)- (-)- 1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (12 mg, 0.017 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (9 mg, 0.008 mmol) were dissolved in degassed CH_2Cl_2 (1.5 mL) and stirred for 15 min. The solution changed from maroon to yellowish- orange. *p*-Methoxyphenol (44 mg, 0.35 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. The reaction mixture concentrated onto SiO_2 and chromatographed over SiO_2 (0-50% ethyl acetate / pet. ether) to provide the crude carbonate (115 mg, approx 77%) as a viscous oil. The mixture was resuspended in MeOH

(2.0 mL) and K_2CO_3 (7.2 mg, 0.05 mmol) was added. After stirring for 4 h, the reaction was concentrated and purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide **SI-49** (67 mg, 69%) as a film**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 1H), 6.87 (m, 6H), 6.03 (dt, 1H, *J*=1.6, 9.6), 5.94 (dq, 1H, *J*=1.2, 2.8, 10.0), 5.24 (m, 1H), 4.79 (dq, 1H, *J*=2.0, 3.6, 8.8), 4.10 (m, 1H), 3.98 (dd, 1H, *J*=2.4, 12.0), 3.82 (dd, 1H, *J*=4.4, 11.6), 3.77 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4 (dd, 1C, *J*=46.8, 143.6), 161.8 (dd, 1C, *J*=46.8, 134.8), 154.5, 151.2, 134.6 (dd, 1C, 8.8, 38.4), 127.7, 126.5, 117.2, 114.8, 111.5 (dd, 1C, *J*=17.6, 88), 107.1, 104.3 (t, 1C, *J*=96.8), 90.2, 78.9, 72.9, 69.2, 64.5, 62.2, 55.7 ppm; IR (neat): 3465, 2908, 1619, 1499, 1437, 1223, 1145, 1079, 1036, 827 cm^{-1}; HRMS (Tof) $[M+H]^+$: calcd. for $C_{21}H_{18}O_4F$ 373.1251, found 373.1253. $[\alpha]_D^{23}$ = +15^o (c = 1.0 CH_2Cl_2).



SI-50

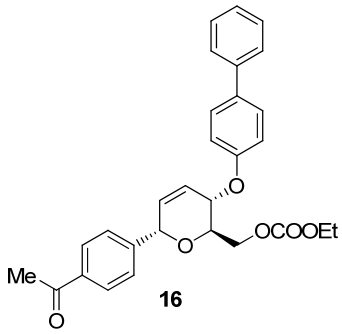
Aryl ether SI-50: Bis-carbonate **SI-32** (148 mg. 0.34 mmol), (*1S,2S*)-(-)- 1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (10 mg, 0.014 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (8 mg, 0.007 mmol) were dissolved in degassed CH_2Cl_2 (1.5 mL) and stirred for 15 min. The solution changed from maroon to yellowish- orange. 4-Methylphenol (38 mg, 0.29 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100^{o}C. The reaction mixture concentrated onto SiO_2 and chromatographed over SiO_2 (0-50% ethyl acetate / pet. ether) to provide the crude carbonate (124 mg, approx 81%) as a viscous oil. The mixture was resuspended in MeOH (2.0 mL) and K_2CO_3 (4 mg, 0.03 mmol) was added. After stirring for 3 h, the reaction was concentrated and purified by SiO_2 chromatography (0-40% ethyl acetate / hexanes) to provide **SI-50** (75 mg, 72%) as a film**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, 2H, *J*=6.8), 7.34 (d, 2H, *J*=8.8), 7.10 (d, 1H, *J*=8.0), 6.86 (m, 2H), 6.02 (dt, 1H, *J*=1.6, 10.4), 5.95 (dq, 1H, *J*=1.6, 3.2, 10), 5.23 (m, 1H), 4.86 (dq, 1H, *J*=1.6, 3.2, 8.8), 4.15 (m, 1H), 3.97 (dd, 1H, *J*=2.8, 11.6), 3.80 (dd, 1H, *J*= 4.8, 12.4), 2.30 (s, 3H), 1.32 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 152.0, 131.6, 130.8, 130.1, 128.4, 126.0, 125.3, 119.2, 115.7, 86.6, 84.4, 72.6, 68.4, 64.7, 62.2, 34.8, 311, 20.5 ppm; IR (neat): 3441, 3037, 2951, 2870, 1708, 1612, 1507, 1386, 1235, 1173, 1084, 1025, 835 cm^{-1}; $[\alpha]_D^{23}$ = +2^o (c = 1.0 CH_2Cl_2).



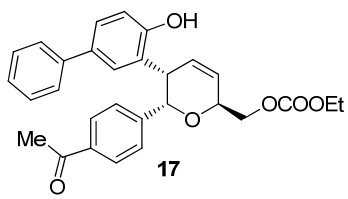
15

Phenol 15: Aryl ether **14**[2] (110 mg, 0.28 mmol) was dissolved in chlorobenzene (0.60 mL) in a 10 mL microwave tube. $Eu(fod)_3$ (30 mg, 0.03 mmol) was added and the reaction was heated with microwave irradiation (300W, 200^{o}C) for 30 min. Concentration *in vacuo*, followed by purification over SiO_2 (0-40 % EtOAc / hexanes) provided **17** (36 mg, 60%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (bs, 1H), 6.82 (d, 1H, *J*=8.8), 6.74 (dd, 1H, *J*=3.2, 8.8), 6.56 (d, 1H, *J*=3.2), 5.92 (ddd, 1H, *J*=2.0, 6.0, 10.8), 5.85 (ddd, 1H, *J*=1.2, 2.8, 10.0), 5.80 (m, 1H), 5.01 (m, 1H), 4.47 (m, 1H), 4.32 (m, 1H), 3.81 (ddd, 2H, *J*=6.0, 11.2, 31.2), 3.72 (t, 1H, *J*=4.4), 2.17 (m, 2H), 0,91

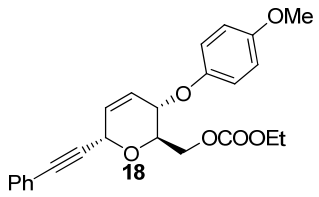
(s, 9H), 0.09 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 149.3, 134.0, 128.1, 125.2, 124.1, 118.0, 117.6, 117.4, 113.6, 75.2, 72.3, 63.8, 55.7, 37.3, 25.8, 18.3, -5.4 ppm**;** IR (neat): 3387, 2920, 1654, 1390, 1083 cm^{-1}; $[\alpha]_D^{23}$ = -210^o (c = 1.0 CH_2Cl_2).



Aryl ether 16: Bis-carbonate SI-23 (200 mg, 0.50 mmol), (*1S,2S*)- (-)-1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (18 mg, 0.013 mmol), and Tris(dibenzylideneacetone) dipalladium(0) chloroform adduct (13 mg, 0.025 mmol) were dissolved in degassed methylene chloride (2.0 mL) and stirred for 15 min. The color of the solution changed from maroon to yellowish-orange. *p*-hydroxybiphenyl (91 mg, 0.54 mmol) was added and the reaction was irradiated in a microwave oven for 15 min (150-300 W, Powermax enabled) at 100^{o}C. The reaction mixture concentrated onto SiO_2 and chromatographed over SiO_2 (0-50% ethyl acetate / pet. ether) to provide **16** (170 mg, 85%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 2H, *J*=8.4), 7.56 (m, 6H), 7.43 (t, 2H, *J*= 7.2), 7.33 (t, 1H, *J*=8.4), 7.00 (d, 2H, *J*=8.4), 6.24 (bs, 2H), 5.43 (bs, 1H), 4.94 (dd, 1H, *J*= 2.0, 8.4), 4.38 (m, 2H), 4.17 (q, 2H, *J*= 7.2, 14.4), 3.93 (m, 1H), 2.62 (s, 3H), 1.29 (t, 3H, *J*=6.8) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 156.4, 155.0, 144.2, 140.5, 136.7, 134.7, 129.9, 128.7, 128.6, 128.4, 127.7, 126.7, 125.9, 115.9, 104.7, 73.6, 69.6, 68.2, 66.4, 64.2, 26.6, 14.2 ppm; IR (neat): 3037, 2982, 2900, 1743, 1677, 1607, 1487, 1258, 1009 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{229}H_{28}O_6Na$ 495.1784, found 495.1798. $[\alpha]_D^{23}$ = +60^o (c = 1.0 CH_2Cl_2).

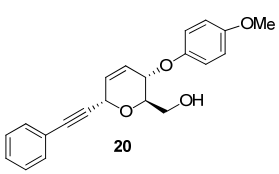


Phenol 17: Aryl ether **16** (20 mg, 0.04 mmol) was dissolved in chlorobenzene (0.50 mL) in a 10 mL microwave tube. $Eu(fod)_3$ (44 mg, 0.04 mmol) was added and the reaction was heated with microwave irradiation (300W, 200^{o}C) for 60 min. Concentration *in vacuo*, followed by purification over SiO_2 (0-80 % EtOAc / hexanes) provided **17** (14 mg, 70%) as a film. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 2H, *J*=7.2), 7.39 (m, 6H), 7.27 (m, 4H), 6.77 (d, 1H, *J*=8.0), 6.20 (m, 1H), 5.97 (dq, 1H, *J*=1.6, 3.2, 10), 5.45 (d, 1H, *J*=3.6), 4.98 (m, 1H), 4.64 (appq, 1H, *J*=8.0, 12.0), 4.22(dd, 1H, *J*=3.6, 12.4), 4.14 (q, 3H, *J*=7.2, 14.4), 3.93 (m, 1H), 2.49 (s, 3H), 1.25 (t, 1H, *J*=7.6) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 155.0, 154.0, 144.0, 140.6 ,135.9, 133.0, 130.4, 130.3, 128.6, 128.0, 127.4, 126.6, 125.7, 123.4, 123.1, 117.2, 73.3, 73.2, 66.0, 64.4, 26.5, 14.1 ppm; IR (neat): 3348, 2920, 1744, 1678, 1604, 1487, 1405, 1277, 1107, 998 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{29}H_{28}O_6Na$ 495.1784, found 495.1787. $[\alpha]_D^{23}$ = -228^o (c = 1.0 CH_2Cl_2).



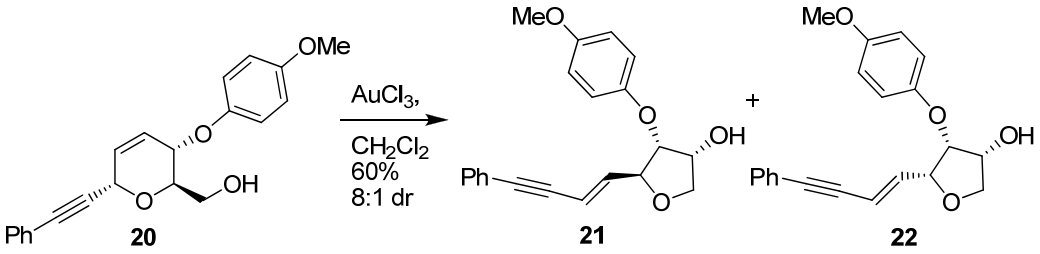
Aryl ether 18: Bis-carbonate **SI-21** (569 mg. 1.52 mmol), (*1S,2S*)- (-)-1,2- Diaminocyclohexane- N,N'-bis(2'-diphenylphosphinobenzoyl) (50 mg, 0.08 mmol), and Tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (39 mg, 0.04 mmol) were dissolved in degassed methylene chloride (4.0 mL) and stirred for 15 min. The color of the solution changed from

maroon to yellowish-orange. *p*-Methoxyphenol (198 mg, 1.60 mmol) was added and the reaction was irradiated for 15 min (150-300 W, Powermax enabled) at 100°C. Purification by SiO_2 chromatography (0-40% ethyl acetate / petroleum ether) provided **18** (583 mg, 94%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 2H), 7.85 (m, 4H), 6.01 (dt, 1H, *J*=1.2, 10.4), 5.95 (ddd, 1H, *J*=1.6, 3.2, 10.4), 5.23 (m, 1H), 4.77 (m, 1H), 4.53 (dd, 1H, *J*=2.4, 11.6), 4.39 (dd, 1H, *J*=4.8, 11.6), 4.29 (m, 1H), 4.17 (q, 2H, *J*=7.2), 3.77 (s, 3H), 1.28 (t, 3H, *J*=7.2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.5, 150.9, 131.8, 128.6, 128.5, 128.3, 125.6, 122.2, 117.1, 114.8, 86.6, 84.9, 70.6, 69.1, 66.5, 64.7, 64.1, 55.7, 14.2 ppm**;** IR (neat): 2959, 1743, 1503, 1444, 1382, 1266, 1227, 1041, 827 cm^{-1}; HRMS (Tof) $[M+H]^+$: calcd. for $C_{224}H_{25}O_6N$ 409.1651, found 409.1654. $[\alpha]_D^{23}$ = -27° (c = 1.0 CH_2Cl_2).

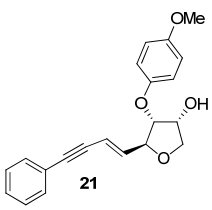


Aryl ether 20: Ethyl ester **18** (337 mg, 0.83 mmol) was dissolved in MeOH (5.0 mL). K_2CO_3 (28 mg, 0.21 mmol) was added and the reaction was stirred for 2 h. Purification over SiO_2 (0-60% ethyl acetate / petroleum ether) provided **20** (278 mg, 100%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.33 (m, 3H), 6.91 (appd, 2H, *J*=9.2), 6.83 (appd, 2H, *J*=9.2), 6.02 (dt, 1H, *J*=1.6, 10.4), 5.95 (ddd, 1H, *J*=2.0, 3.6, 10.0), 5.23 (m, 1H), 4.80 (dq, 1H, *J*=1.6, 8.8), 4.13 (m, 1H), 4.00 (m, 1H), 3.84 (m, 1H), 3.77 (s, 3H), 2.04 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 151.3, 131.9, 128.7, 128.3, 128.2, 126.2, 122.2, 117.2, 114.8, 86.4, 85.1, 72.7, 69.2, 64.6, 62.2, 55.7 ppm; IR (neat): 3464, 2935, 1507, 1219, 1087, 1037, 827, 761, 691 cm^{-1}**;** HRMS (Tof) $[M+H]^+$: calcd. for $C_{21}H_{21}O_4$ 337.1440, found 337.1453. $[\alpha]_D^{23}$ = +6° (c = 1.0 CH_2Cl_2).

Gold(III)- catalyzed ring contraction of *C*-glycosides

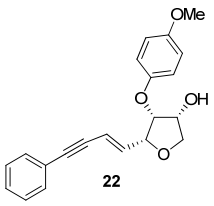


Procedure: **20** (7 mg, 0.02 mmol) was dissolved in CH_2Cl_2 (1.0 mL) under argon. $AuCl_3$ (0.6 mg, 0.002 mmol) was added. After 12 hours the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **21** (major), **22** (minor).

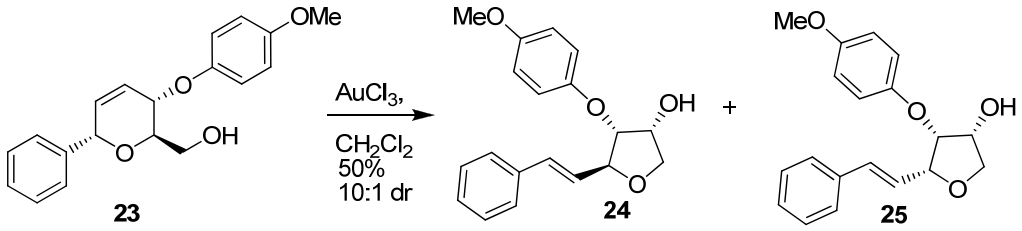


Ene-yne 21: 3.7 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.312 (m, 3H), 6.92 (d, 2H, *J*=8.8), 6.86 (d, 2H), *J*=6.8), 6.23 (dd, 1H, *J*=6.0, 15.6), 6.05 (dd, 1H, *J*=1.6, 15.6), 4.57 (td, 1H, *J*=1.6, 6.0), 4.51 (q, 1H, *J*=5.2), 4.34 (t, 1H, *J*=5.6), 4.23 (dd, 1H, *J*=5.2, 9.6), 3.92 (dd, 1H, *J*=4.4, 9.2), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 151.1, 139.7, 131.5, 128.4, 128.3, 123.0, 117.4, 114.9, 112.1, 90.9, 87.0, 83.0, 80.5, 72.9, 70.2, 55.7 ppm; IR (neat):

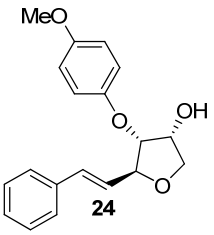
3441, 2948, 1499, 1445, 1227, 1037 cm^{-1}; HRMS (Tof) $[M+H]^+$: calcd. for $C_{21}H_{21}O_4N$ 337.1440, found 337.1410. $[\alpha]_D^{23} = -118^o$ (c = 1.0 CH_2Cl_2).



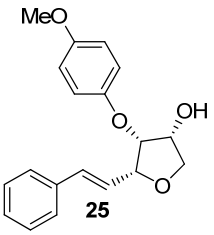
Ene-yne 22: 0.5 mg (7%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.31 (m, 3H), 6.95 (d, 2H, *J*=9.2), 6.84 (d, 2H, *J*=9.2), 6.35 (dd, 1H, *J*=6.4, 16.0), 5.99 (dd, 1H, *J*=1.2, 15.6), 4.67 (m, 2H), 4.54 (m, 1H), 4.06 (dd, 1H, *J*=5.2, 9.2), 3.99 (dd, 1H, *J*=4.4, 10.0), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 152.0, 138.5, 131.5, 128.3, 128.2, 123.2, 117.4, 114.8, 112.7, 90.6, 87.3, 81.0, 79.8, 72.6, 71.7, 55.7 ppm.



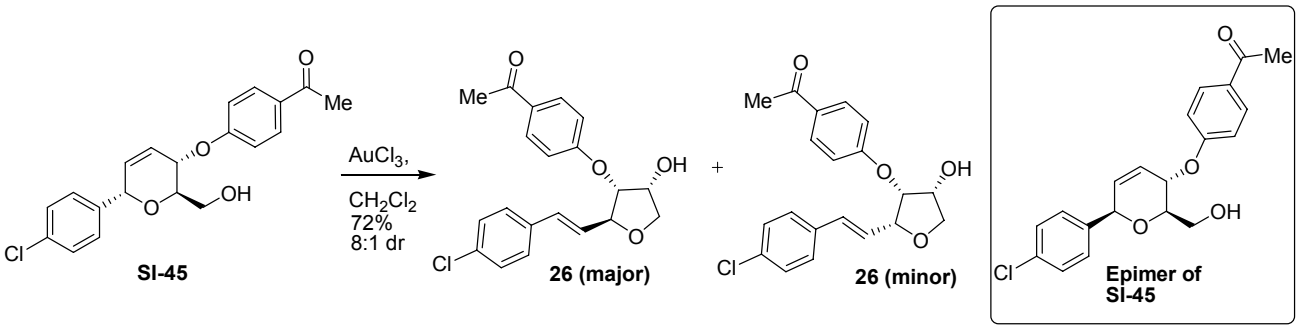
Procedure: **23** (86 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (1.0 mL) under argon. $AuCl_3$ (20 mg, 0.08 mmol) was added. After 8 hours the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **24** (major), **25** (minor).



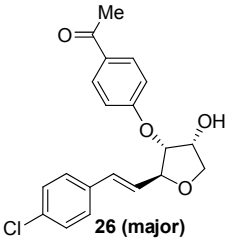
Tetrahydrofuran 24: 39 mg (45%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 5H), 6.93 (d, 2H, *J*=9.6), 6.83 (d, 2H, *J*=9.2), 6.71 (d, 1H, *J*=16.0), 6.21 9dd, 1H, *J*=7.2, 16.0), 4.64 (t, 1H, *J*=6.0), 4.53 (appd, 1H, *J*=4.89), 4.38 (t, 1H, *J*=5.2), 4.27 (dd, 1H, *J*=5.6, 10.0), 3.93 (dd, 1H, *J*=4.4, 9.6), 3.77 (s, 3H), 2.59 (s, -OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 151.3, 132.7, 128.6, 127.9, 126.6, 126.5, 117.4, 114.8, 83.2, 81.2, 72.8, 70.3, 55.7 ppm; IR (neat): 3351, 2959, 1643, 1499, 1262, 1219, 1033 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{19}H_{20}O_4Na$ 335.1259, found 335.1243. $[\alpha]_D^{23} = +60^o$ (c = 1.0 CH_2Cl_2).



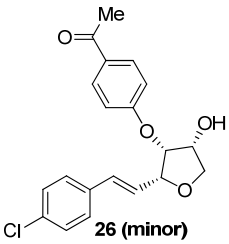
Tetrahydrofuran 25: 4 mg (5%). ^1H NMR (400 MHz, $CDCl_3$): 7.28 (m, 5H), 6.92 (d, 2H, *J*=9.2), 6.79 (d, 2H, *J*=9.2), 6.64 (d, 1H, *J*=15.6), 6.35 (dd, 1H, *J*=7.2, 16.4), 4.69 (m, 1H), 4.59 (m, 1H), 4.03 (dd, 1H, *J*=6.0, 9.2), 3.99 (dd, 1H, *J*=4.8, 9.2), 3.76 (s, 3H), 2.63 (d, 1H, *J*=7.2 (-OH))155.0, 151.3, 136.3, 132.7, 128.6, 127.9, 126.6, 126.5, 117.5, 114.8, 83.2, 81.2, 72.8, 70.3, 55.7 ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 132.7, 126.0, 122.7, 115.9, 93.8, 92.5, 67.0, 66.1, 61.4, 60.9, 54.1, 49.3, 25.7 24.3, 18.0, -4.6, -4.8 ppm; IR (neat): 3436, 1506, 1234, 1041, 753 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{19}H_{20}O_4Na$ 335.1259, found 335.1229. $[\alpha]_D^{23} = -78^o$ (c = 1.0 CH_2Cl_2).



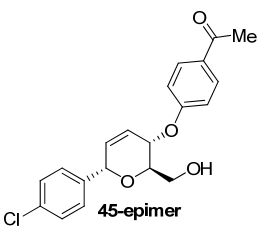
Procedure: **SI-45** (25 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (0.5 mL) under argon. $AuCl_3$ (6 mg, 0.02 mmol) was added. After 6 hours the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **26** (major), **26** (minor) and the epimer of **SI-45**.



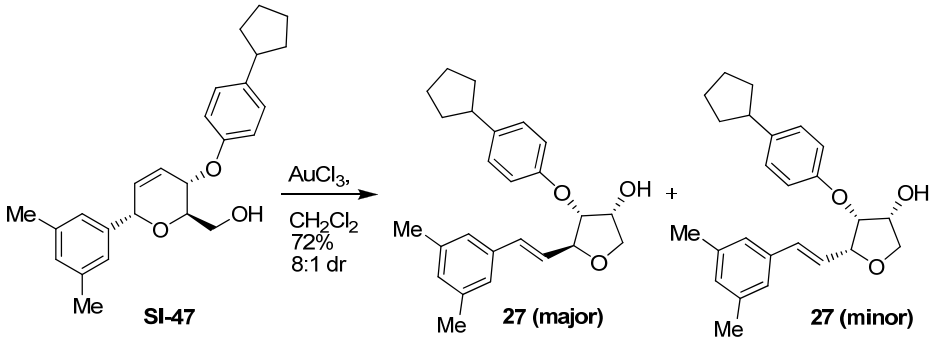
Tetrahydrofuran 26 (major): 15.9 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=9.2), 7.3 (m, 4H), 7.02 (d, 2H, *J*=9.2), 6.68 (d, 1H, *J*=15.6), 6.20 (dd, 1H, *J*=6.8, 16.0), 4.62 (m, 2H), 4.33 (dd, 1H, *J*=5.2, 9.6), 3.93 (dd, 1H, *J*=4.4, 9.2), 2.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 160.9, 134.5, 133.8, 131.9, 131.6, 130.8, 128.8, 127.8, 126.6, 115.4, 81.6, 81.2, 77.9, 72.8, 70.3, 26.4 ppm; IR (neat): 3748, 3580, 2920, 1736, 1647, 1565, 1409 cm^{-1}; HRMS (Tof) $[M+H]^+$: calcd. for $C_{20}H_{20}O_4Cl$ 359.1050, found 359.1052. $[\alpha]_D^{23}$ = +52° (c = 1.0 CH_2Cl_2).



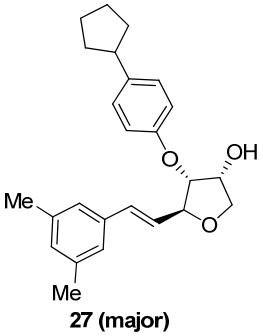
Tetrahydrofuran 26 (minor): 2 mg (8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, 2H, *J*=8.4), 7.3 (m, 4H), 7.01 (d, 2H, *J*=8.0), 6.56 (d, 1H, *J*=16.0), 6.23 (dd, 1H, *J*=7.2, 16.0), 4.92 (t, 1H, *J*=4.8), 4.76 (t, 1H, *J*=7.2), 4.6 (t, 1H, *J*=4.4), 4.12 (dd, 1H, *J*=6.0, 10.0), 4.02 (dd, 1H, *J*=4.8, 10.0), 2.56 (s, 3H), 2.38 (d, 1H, *J*=6.8 (-OH)) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 174.2, 152.7, 151.6, 140.3, 134.9, 132.8, 130.9, 128.9, 128.0, 152.5, 115.7, 104.2, 80.7, 79.5, 77.9, 77.6, 72.3, 72.0, 26.4 ppm; IR (neat): 3401, 2924, 1673, 1603, 1502, 1405, 1254, 1095 cm^{-1}; $[\alpha]_D^{23}$ = +52° (c = 1.0 CH_2Cl_2).



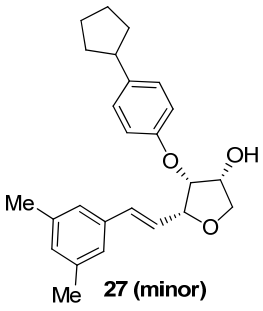
Tetrahydropyran 26 (epimer of 45): 6.5 mg (26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, 2H, *J*= 6.8), 7.31 (m, 4H), 7.01 (d, 2H, *J*=7.2), 6.04 (dt, H, *J*=2.4, 10.0), 5.93 (dt, 1H, *J*=1.6, 10.4), 5.08 (dt, 1H, *J*=1.6, 8.4), 3.93 (m, 2H), 3.79 (m, 1H), 2.57 (s, 3H), 1.99 (s, 1H, -OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 161.2, 138.3, 134.3, 132.3, 130.9, 130.9, 130.8, 128.9, 128.7, 124.9, 115.1, 77.6, 68.1, 62.2, 26.4 ppm; HRMS (Tof) $[M+H]^+$: calcd. for $C_{20}H_{20}O_4Cl$ 359.1050, found 359.1000. IR (neat): 3374, 2916, 1669, 1600, 1499, 1351, 1243, 1165, 1091 cm^{-1}; $[\alpha]_D^{23}$ = +140° (c = 1.0 CH_2Cl_2).



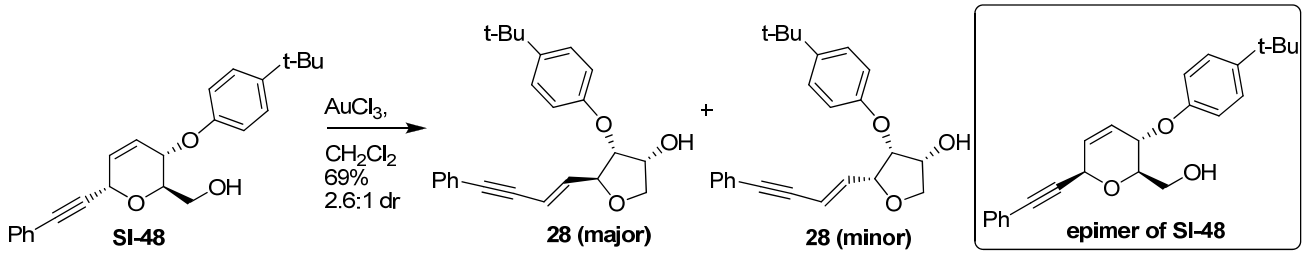
Procedure: **SI-47** (42 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (1.0 mL) under argon. $AuCl_3$ (5 mg, 0.02 mmol) was added. After 2 hours the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **27** (major), **27** (minor).



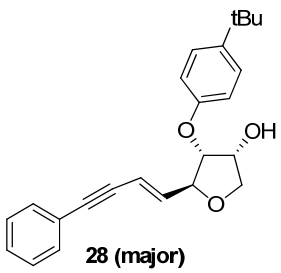
Tetrahydrofuran 27 (major): 14.5 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.17 (d, 2H, *J*=8.0), 7.00 (s, 2H), 6.9 (m, 3H), 6.65 (d, 1H, *J*=15.6), 6.19 (dd, 1H, *J*=6.4, 15.6), 4.64 (t, 1H, *J*=5.6), 4.55 (t, 1H, *J*=4.8), 4.43 (t, 1H, *J*=5.2), 4.28 (dd, 1H, *J*=5.6, 9.6), 3.92 (dd, 1H, *J*=4.8, 9.6)2.94 (m, 1H), 2.30 (s, 6H), 2.05 (m, 2H), 1.81 (m, 2H), 1.68 (m, 2H), 1.54 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 140.4, 138.0, 136.2, 132.9, 129.7, 128.3, 126.0, 124.5, 115.8, 82.2, 81.4, 72.8, 70.3, 45.1, 34.7, 25.4, 21.2 ppm; IR (neat): 3413, 2955, 2850, 1615, 1507, 144, 1238, 1099 cm^{-1}; $[\alpha]_D^{23}$ = -75^o (c = 1.0 CH_2Cl_2).



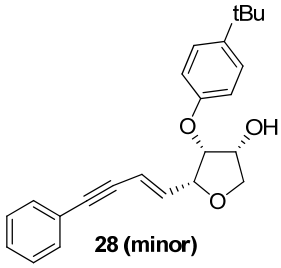
Tetrahydrofuran 27 (minor): 5.6 mg (13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, 2H, *J*=8.0), 6.91 (m, 5H), 6.56 (d, 1H, *J*=15.6), 6.29 (dd, 1H, *J*=7.6, 16.0), 4.76 (t, 1H, *J*=5.2), 4.69 (m, 1H), 4.60 (t, 1H, *J*=4.8), 4.08 (dd, 1H, *J*=6.0, 9.6), 3.99 (dd, 1H, *J*=4.8, 9.2), 2.92 (m, 1H), 2.26 (s, 6H), 2.02 (m, 2H), 1.78 (m, 2H), 1.67 (m, 2H), 1.56 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 137.9, 133.6, 129.5, 128.1, 124.8, 124.6, 116.0, 81.3, 80.3, 77.9, 72.5, 72., 49.3, 45.1, 34.7, 25.4, 21.22 ppm; IR (neat3371, 2959, 2862, 1720, 1603, 1507, 1238, 1102, 1037 cm^{-1}; $[\alpha]_D^{23}$ = +21^o (c = 1.0 CH_2Cl_2).



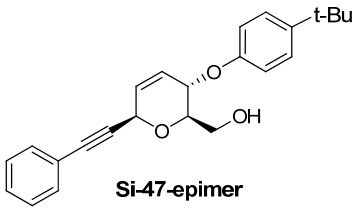
Procedure: **SI-48** (71 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (0.5 mL) under argon. $AuCl_3$ (18 mg, 0.06 mmol) was added. After 5 hours the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **28** (major), **28** (minor) and the epimer of **SI-48**.



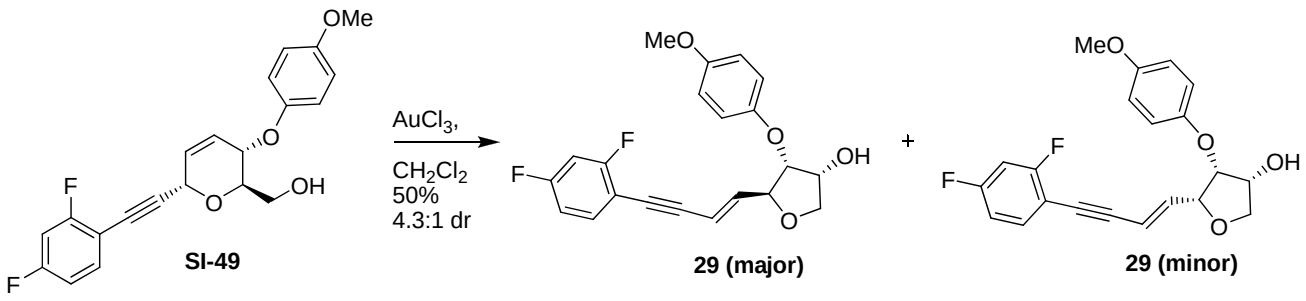
Ene-yne 28 (major): 37 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.33 (m, 5H), 6.91 (dd, 2H, *J*=2.4, 7.2), 6.25 (dd, 1H, *J*=5.6, 15.6), 6.06 (dd, 1H, *J*=1.2, 16.0), 4.58 (dt, 1H, *J*=1.2, 6.0), 4.54 (q, 1H, *J*=4.8), 4.42 (t, 1H, *J*=5.6), 4.25 (dd, 1H, *J*=5.6, 10.0), 3.93 (dd, 1H, *J*=4.8, 9.6) 1.3 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 145.3, 139.6 ,131.5, 128.3, 126.6, 126.4, 123.0, 115.4, 112.2, 90.9, 87.0, 81.9, 80.5, 72.9, 70.2, 34.2, 31.4 ppm; IR (neat): 3440, 3045, 2963, 2866, 1600, 1511, 1363, 1227, 1071 cm^{-1}; $[\alpha]_D^{23}$ = -100^o (c = 1.0 CH_2Cl_2).



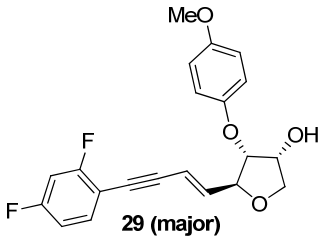
Ene-yne 28 (minor): 14 mg (20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 2H0, 7.31 (m, 5H), 6.94 (d, 2H, *J*=8.4), 6.35 (dd, 1H, *J*=6.8, 16.0), 6.00 (dd, 1H, *J*=1.2, 15.6), 4.77 (t, 1H, *J*=5.2), 4.67 (t, 1H, *J*=6.4), 4.55 (m, 1H), 4.07 (dd, 1H, *J*=5.6, 10.0), 4.00 (dd, 1H, *J*=3.6, 9.6), 2.52 (d, 1H, *J*=6.0 (-OH), 1.30 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 145.2, 138.4, 131.5, 128.7, 128.4, 128.3, 128.2, 126.5, 115.6, 112.7, 90.6, 87.4, 80.1, 79.8, 72.6, 71.7, 34.2, 31.4 ppm; IR (neat): 3440, 2963, 1685, 1600, 1503, 1359, 1255, 1184 cm^{-1}; $[\alpha]_D^{23}$ = +110^o (c = 1.0 CH_2Cl_2).



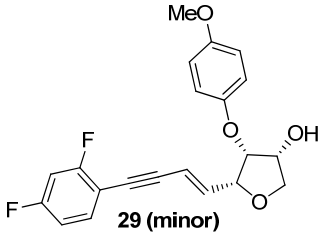
Tetrahydropyran 28 (epimer of SI-47): 9 mg (13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.33 (m, 5H), 6.89 (d, 2H, *J*=8.8), 6.04 (d, 1H, *J*=10.0), 5.95 (dq, 1H, *J*=1.6, 3.2, 10.0), 5.23 (m, 1H), 4.88 (dd, 1H, *J*=2.0, 9.2), 4.15 (m, 1H), 3.9 (m, 1H), 3.82 (m, 1H), 1.30 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 144.2, 131.9, 128.7, 128.3, 128.3, 126.5, 126.2, 122.2, 115.2, 86.4, 85.1, 72.7, 68.2, 64.6, 62.3, 34.1, 61.5 ppm; IR (neat): 3378, 2959, 1705, 1611, 1506, 1371, 1254, 1180, 1067 cm^{-1}; $[\alpha]_D^{23}$ = +19^o (c = 1.0 CH_2Cl_2).



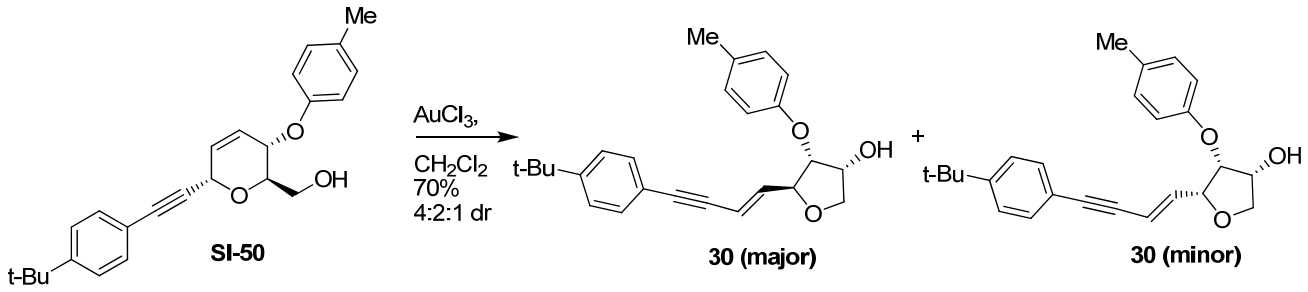
Procedure: **SI-49** (46 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (1.0 mL) under argon. $AuCl_3$ (6 mg, 0.02 mmol) was added. After 2 hours the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **29**(major), **29** (minor).



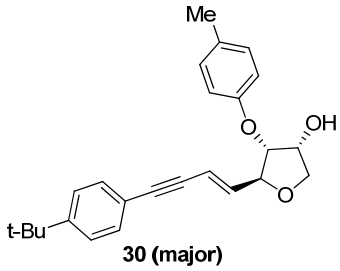
Ene-yne 29 (major): 18.7 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 1H), 6.87 (m, 6H), 6.27 (dd, 1H, *J*=6.0, 15.6), 6.06 (dd, 1H, *J*=1.6, 16.0), 4.58 (t, 1H, *J*=5.2), 4.49 (m, 1H0, 4.33 (t, 1H, *J*=5.2), 4.23 (dd, 1H, *J*=4.8, 9.2), 3.92 (dd, 1H, *J*=4.4, 9.2), 3.78 (s, 3H0, 2.52 (d, 1H, *J*=5.6 (-OH)) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0 (t, 1C, *J*=38.0), 161.6 (t, 1C, *J*=50.0), 155.1, 151.1, 140.6, 134.2 (dd, 1C, *J*=11.6, 49.6), 117.4, 114.9. 111.7 (t, 1C, *J*=14.4), 107.9, 104.3 (t, 1C, *J*=102.8), 91.8, 83.1, 82.9, 80.4, 77.9, 72.9, 70.3, 55.7 ppm; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{21}H_{18}O_4NaF_2$ 395.1071, found 395.1060. IR (neat): 3436, 2932, 1619, 1514, 1464, 1425, 1266, 1227, 1141, 1095, 959 cm^{-1}; $[\alpha]_D^{23}$ = -112° (c = 1.0 CH_2Cl_2).



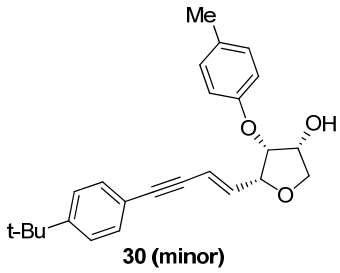
Ene-yne 29 (minor): 4.3 mg (9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 1H), 6.94 (m, 2H), 6.83 (m, 4H), 6.38 (dd, 1H, *J*=6.0, 15.6), 6.00 (dd, 1H, *J*=1.2, 15.6), 4.67 (m, 2H), 4.55 (m, 1H), 4.06 (dd, 1H, *J*=5.2, 10.0), 3.99 (dd, 1H, *J*=4.4, 9.6), 3.77 (s, 3H), 2.53 (d, 1H, *J*=6.0 (-OH)) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 151.9, 139.5, 134.2, 117.4, 114.8, 112.1, 111.6, 111.4, 104.2, 81.0, 79.6, 77.7, 726, 71.6, 55.7 ppm; IR (neat): 3425, 2959, 2920, 1716, 1615, 1506, 1429, 1262, 1223, 1099, 1040 cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{21}H_{18}O_4NaF_2$ 395.1071, found 395.1067. $[\alpha]_D^{23}$ = +121.8° (c = 1.0 CH_2Cl_2).



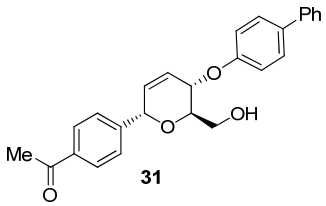
Procedure: **SI-50** (40 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (0.5 mL) under argon. $AuCl_3$ (6 mg, 0.02 mmol) was added. After 15 minutes the reaction was concentrated onto SiO_2 and chromatographed over SiO_2 (0-80% ethyl acetate /pet. ether) to provide diastereomers **30**(major), **30** (minor).



Ene-yne 30 (major): 22 mg (56%). Procedure ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 4H), 7.13 (d, 1H, *J*=9.2), 6.87 (d, 1H, *J*=8.8), 6.22 (dd, 1H, *J*=6.4, 15.6), 6.05 (dd, 1H, *J*=1.6, 15.6), 4.57 (dt, 1H, *J*=1.2, 6.0), 4.51 (m, 1H), 4.4 (t, 1H, *J*=4.8), 4.24 (dd, 1H, *J*=5.6, 10.0), 3.91 (dd, 1H, *J*=4.8, 9.6), 2.31 (s, 3H), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 151.6, 139.1, 1319, 131.3, 130.3, 125.3, 119.9, 115.9, 112.4, 91.1, 86.4, 82.0, 80.6, 72.9, 70.3, 34.8, 31.1, 20.5 ppm; IR (neat): 3347, 2951, 2916, 2854, 1662, 1409, 1266, 1095 cm^{-1}; $[\alpha]_D^{23}$ = -6.0^o (c = 1.0 CH_2Cl_2).

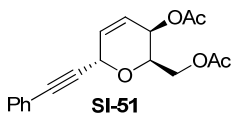


Ene-yne 30 (minor): 6 mg (14%). Procedure ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 4), 7.10(d, 1H, *J*=8.4), 6.89 (d, 1H, *J*=2.4, 6.8), 6.31 (dd, 1H, *J*=6.4, 16.0), 5.98 (dd, 1H, *J*=1.2, 16.0), 4.74 (t, 1H, *J*=5.20, 4.67 (t, 1H, *J*=5.6), 4.55 (m, 1H), 4.06 (dd, 1H, *J*=5.2, 9.6), 3.99 (dd, 1H, *J*=4.4, 9.6), 2.23 (s, 3H), 1.32 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 151.5, 137.9, 131.7, 131.3, 130.2, 125.3, 120.2, 116.0, 112.9, 90.8, 86.7, 80.1, 79.8, 72.5, 71.7, 34.8, 31.1, 20.5 ppm; IR (neat): 3445, 2955, 1616, 1502, 1460, 1359, 1234, 1091, 955 cm^{-1}; $[\alpha]_D^{23}$ = -102^o (c = 1.0 CH_2Cl_2).



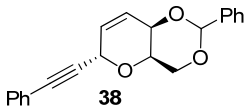
Aryl ether 31: Carbonate **16** was dissolved in MeOH (1.5 mL) and MP-CO_3 (2.98 mmol/g loading, 17 mg, 0.05 mmol) was added. After shaking for 15 h, the reaction was concentrated and purified by SiO_2 chromatography (0-80% ethyl acetate / hexanes) to provide **31** (70 mg, 69%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 2H, *J*=8.4), 7.56 (m, 6H), 7.42 (t, 2H, *J*=7.2), 7.32 (t, 1H, *J*=7.2), 7.03 (d, 2H, *J*=8.8), 6.22 (m, 2H), 5.42 (s, 1H0, 4.99 (d, 1H, *J*=8.4), 3.75 (m, 3H), 2.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 156.8,144.2, 104.6, 136.8, 134.6, 129.3, 128.7, 128.6, 128.4, 127.9, 127.0, 126.8, 126.7, 116.0, 73.8, 71.3, 68.2, 62.1, 26.7 ppm; IR (neat): 3449, 2897, 1678, 1608, 1515, 1487, 1405, 1262, 1087 cm^{-1}; HRMS (Tof) $[M+H]^+$: calcd. for $C_{26}H_{24}O_4$ 401.1753, found 401.1700. $[\alpha]_D^{23}$ = +105^o (c = 1.0 CH_2Cl_2).

Synthesis of Galactal-Derived tetrahydrofurans 40 and 41:



SI-51

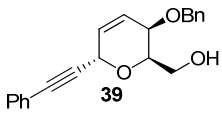
Alkynyl *C*-Galactoside SI-51: Tri-O-Acetyl-D-Galactal (**36**) and 1-phenyl-2-trimethylsilyl- acetylene were dissolved in CH_2Cl_2. The reaction was cooled to -25°C and $Sc(OTf)_3$ was added. After 3.5 h, the reaction was quenched with saturated sodium bicarbonate (at -25°C), diluted with CH_2Cl_2, then washed with sodium bicarbonate (1X) and brine (1X). The organic layer was dried, filtered, concentrated onto silica, and purified over SiO_2 (0-40% ethyl acetate/petroleum ether) yielding **SI-51** as a white solid. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44 (m, 2H), 7.33 (m, 3H), 6.15 (dd, 1H, *J* = 3.6, 10.4), 6.05 (ddd, 1H, *J* = 2.0, 4.8, 6.8), 5.27 (dd, 1H, *J* = 2.0, 4.0), 5.12 (dd, 1H, *J* = 2.4, 5.2), 4.45 (td, 1H, *J* = 2.0, 4.8, 7.2), 4.32 (dd, 1H, *J*= 5.6, 11.6), 4.24 (dd, 1H, *J* = 7.2, 11.2), 2.10 (s, 3H) , 2.10 (s, 3H) ppm ; ^{13}C NMR (100MHz, $CDCl_3$): δ 171.7, 170.4, 132.0, 131.8, 128.8, 128.3, 122.4, 122.1, 86.9, 84.1, 69.7, 64.4, 64.4, 63.3, 62.8, 20.9, 20.8 ppm; IR (neat): 3739, 1744, 1367, 1231, 1076, 1045, 761cm^{-1}; HRMS (Tof) $[M+Na]^+$: calcd. for $C_{18}H_{18}O_5Na$ 337.1052, found 337.0977. $[\alpha]_D^{23}$=-396.9° (c=1.0 CH_2Cl_2).



38

Acetonide 38: Diacetate **SI-51** (600 mg, 1.91 mmol) was dissolved in MeOH (8 mL). K_2CO_3 (132 mg, 9.54 mmol) was added, the reaction was stirred for 40 min at room temperature and was concentrated onto silica and purified over SiO_2 (0-100% ethyl acetate/ petroleum ether) to provide the intermediate diol **37** (409 mg, 1.78 mmol, 93%) as white flakes. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.42 (m, 2H), 7.29 (m, 3H), 6.09 (m, 1H), 6.04 (dd, 1H, *J* = 2.0, 5.6), 5.23 (dd, 1H, *J* = 2.0, 3.6), 4.15 (m 1H), 3.97 (m, 1H), 3.97 (m, 1H), 2.51(bs, 1H), 2.36 (bs, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 131.8, 130.0, 128.7, 128.3, 126.6, 122.1, 86.6, 84.6, 73.4,, 64.5, 62.8 ppm; IR (neat): 3305, 1604, 1317, 1115, 1080, 765 cm^{-1}; $[\alpha]_D^{23}$=-52.6° (c=1.0 CH_2Cl_2).

Diol **37** (100 mg, 0.43 mmol) was dissolved in CH_2Cl_2 (4mL). 10-Camphorsulfonic acid (7 mg, 0.03 mmol) and benzaldehyde dimethyl acetal (0.11 mL, 0.75 mmol) were added, the reaction was stirred for 12 h then diluted with CH_2Cl_2, washed with brine (1X), and back-extracted with CH_2Cl_2. The organic layers were combined, dried, filtered, concentrated onto SiO_2, and purified over SiO_2 (0-40% ethyl acetate/petroleum ether) to provide **38** (68 mg, 0.21 mmol, 49%) as a white solid. ^{1}H NMR (400MHz; $CDCl_3$): δ 7.55 (m, 2H), 7.45 (m,2H), 7.34 (m, 6H), 6.17 (dd, 1H, *J* = 3.6, 10.4), 6.06 (ddd, 1H, *J* = 2.0, 5.6, 10.0), 5.62 (s, 1H), 5.38 (m, 1H), 4.45 (d, 1H, *J* = 12.8), 4.28 (dd, 1H, *J* = 2.8, 17.2), 4.27 (s, 1H), 3.97 (bs, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 137.8, 131.8, 128.8, 128.7, 128.3, 128.1, 126.2, 123.2, 122.2, 100.7, 86.5, 85.1, 71.2, 67.9, 64.6 ppm; IR (neat): 3033, 2909, 1689, 1592, 1328, 750, 694 cm^{-1}; $[\alpha]_D^{23}$= -365.8° (c=1.0 CH_2Cl_2).

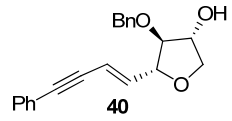


39

Alcohol 39: Acetonide **38** (70 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (2 mL)

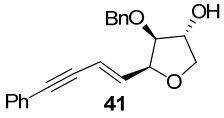
and cooled to 0°C. A 1M solution of Diisobutylaluminum hydride in hexanes (1.76 mL, 1.76 mmol) was added and stirred for 2 hours. The reaction was quenched with saturated ammonium chloride and saturated sodium tartrate, stirred for one hour, then diluted with CH_2Cl_2 and washed with sodium bicarbonate. The organic layer was dried, filtered, concentrated onto silica, and purified over SiO_2 (0-40% ethyl acetate/petroleum ether) to provide **39** (35 mg, 0.11 mmol) as a white solid. ^{1}H NMR (400MHz; $CDCl_3$): δ 7.43 (m, 2H), 7.32 (m, 8H), 6.14 (m, 2H), 5.30 (d, 1H, *J* = 1.2), 4.71 (d, 1H, *J* = 11.6), 4.56 (d, 1H, *J* = 12.0), 4.19 (m, 1H), 4.02 (m, 1H), 3.85 (m, 1H), 2.20 (bs, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 138.0, 131.8, 131.3, 128.6, 128.5, 128.3, 128.0, 127.8, 123.6, 122.2, 86.5, 84.9, 73.5, 70.7, 68.2, 64.4, 62.7 ppm; IR (neat): 3939, 3052, 2916, 1631, 1588, 1324, 1087, 757, 699 cm^{-1}; $[\alpha]_D^{23}$= -265.5° (c=1.0 CH_2Cl_2).

Furan 40,41: Alcohol **39** (72 mg, 0.22mmol) and gold (III) chloride (27 mg, 0.09 mmol) were added to a round bottom flask, and dissolved in CH_2Cl_2 (1mL). After 4 h, the reaction was concentrated onto silica gel and purified over SiO_2 (0-40% ethyl acetate/ petroleum ether) to provide **40** (26.4 mg, 37%) as an oil and **41** (10.6 mg, 15%) as a film.



40

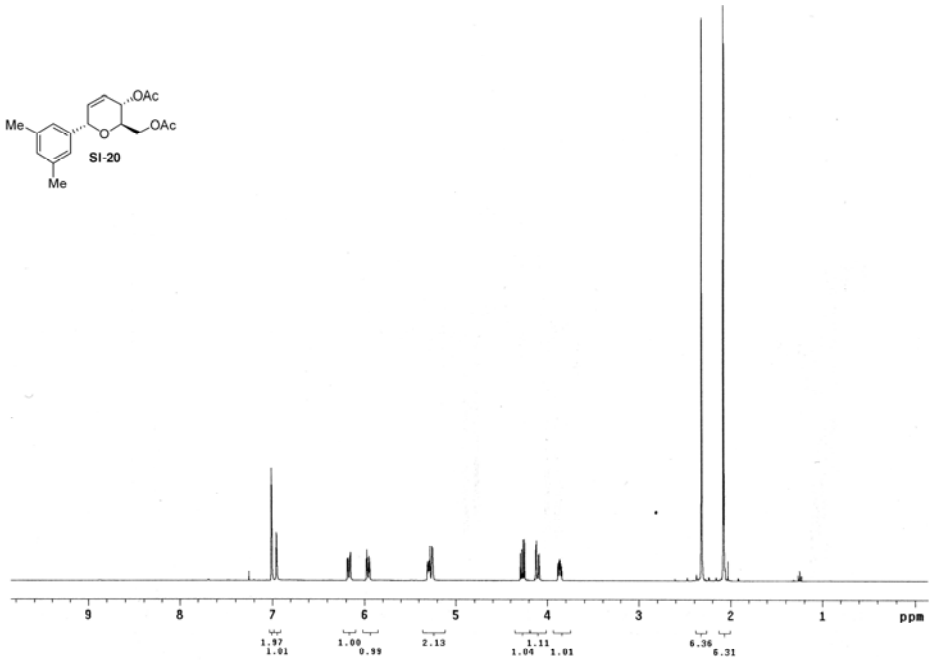
Compound **40**: ^{1}H NMR (400MHz; $CDCl_3$): δ 7.40 (m, 2H), 7.08 (m, 3H), 6.93 (m, 3H), 6.37 (dd, 1H, *J*=6.0, 15.6), 6.08 (dd, 1H, *J*=1.6, 15.6), 4.33 (m, 1H), 4.21 (s, 2H), 3.87 (bs, 1H), 3.75 (dd, 1H, *J*=4.4, 10.0), 3.58 (dd, 1H, *J*=2.0, 10.0), 3.54 (dd, 1H, *J*=1.6, 3.6) ppm; ^{13}C NMR (400M; $CDCl_3$): δ 140.9, 137.5, 131.5, 128.6, 128.3, 128.0, 127.7, 123.1, 111.2, 90.7, 89.6, 87.1, 83.9, 76.4, 74.2, 72.2 ppm; IR (neat): 3424, 3032, 3870, 1094, 959, 753, 694 cm^{-1}; $[\alpha]_D^{23}$= +80.0° (c=13.4 mg/mL)

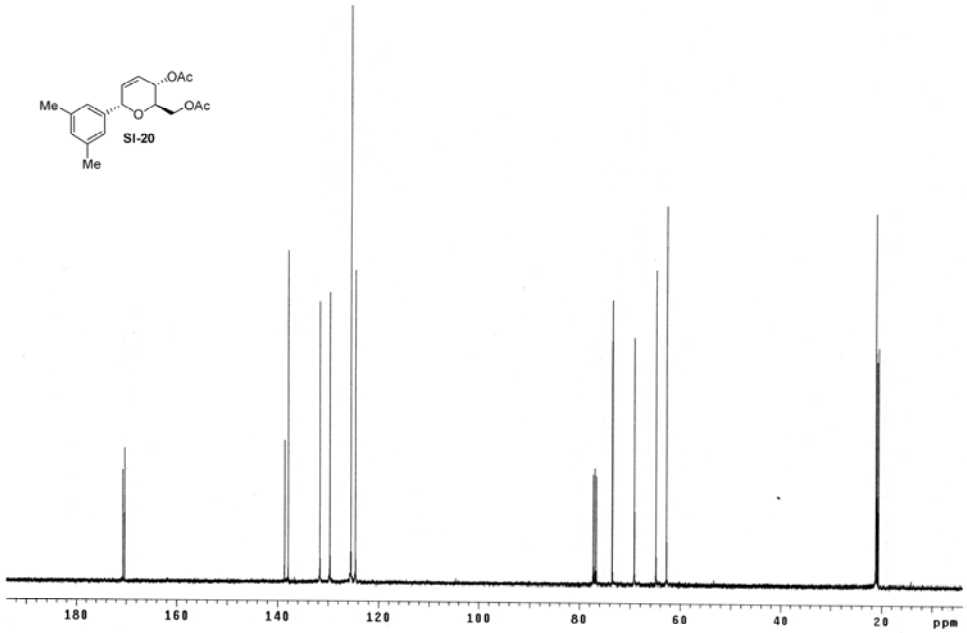


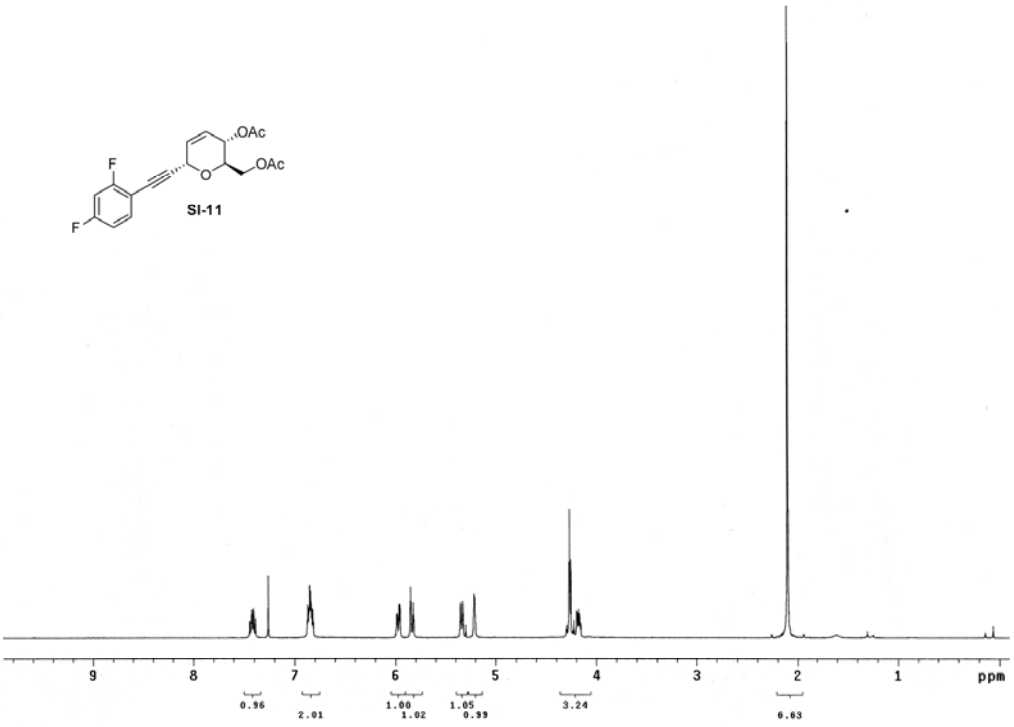
41

Compound **41**: ^{1}H NMR (400MHz; $CDCl_3$): δ 7.37 (m, 2H), 7.19 (m, 2H), 7.09 (m, 2H), 6.90 (m, 3H), 6.56 (dd, 1H, *J*=6.8, 16.0), 6.13 (dd, 1H, *J*=1.6, 13.2), 4.46, (m, 1H), 4.20 (s, 2H), 3.96 (dd, 1H, *J*=4.4, 9.2), 3.84 (m, 1H), 3.46 (dd, 1H, *J*=1.6, 4.0), 3.43 (dd, 1H, *J*=2.0, 9.2) ppm; ^{13}C NMR (400M; $CDCl_3$): δ138.3, 137.7, 131.6, 128.5, 128.3, 128.2, 127.9, 127.7, 123.3, 112.7, 90.3, 87.5, 85.7, 80.7, 75.7, 73.6, 72.5 ppm; IR (neat): 3408, 3032, 2925, 1091, 962, 755, 693cm^{-1};$[\alpha]_D^{23}$= -18.8° (c=1.0 CH_2Cl_2)

Examples of Selected Spectral Data



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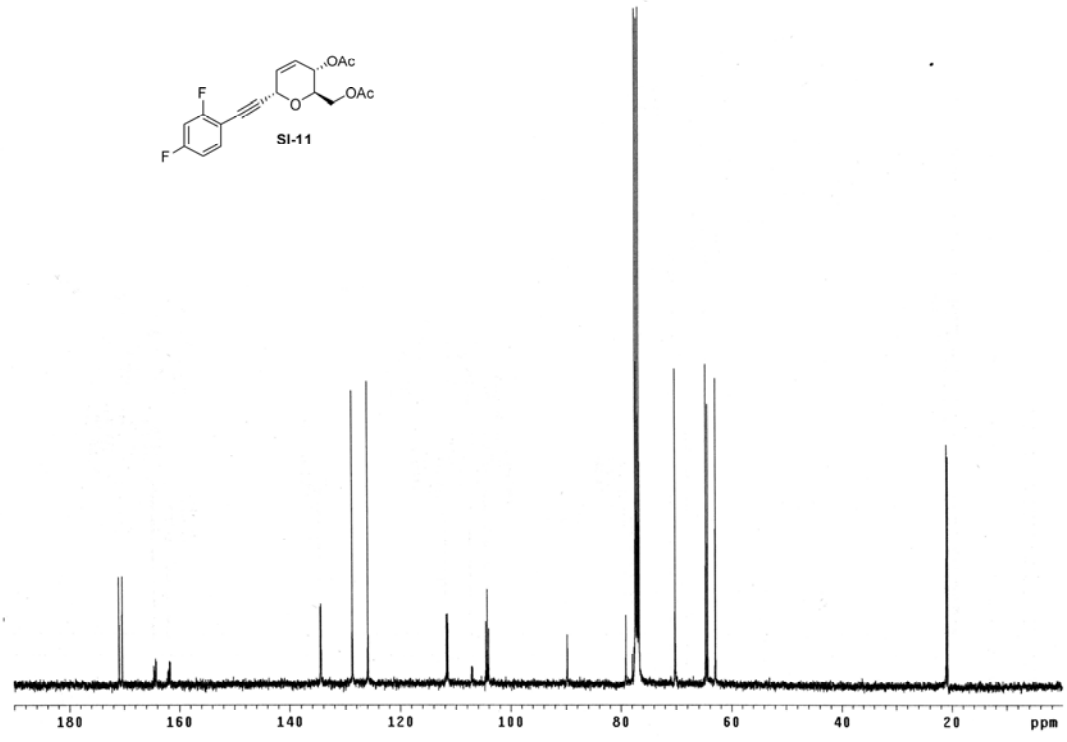
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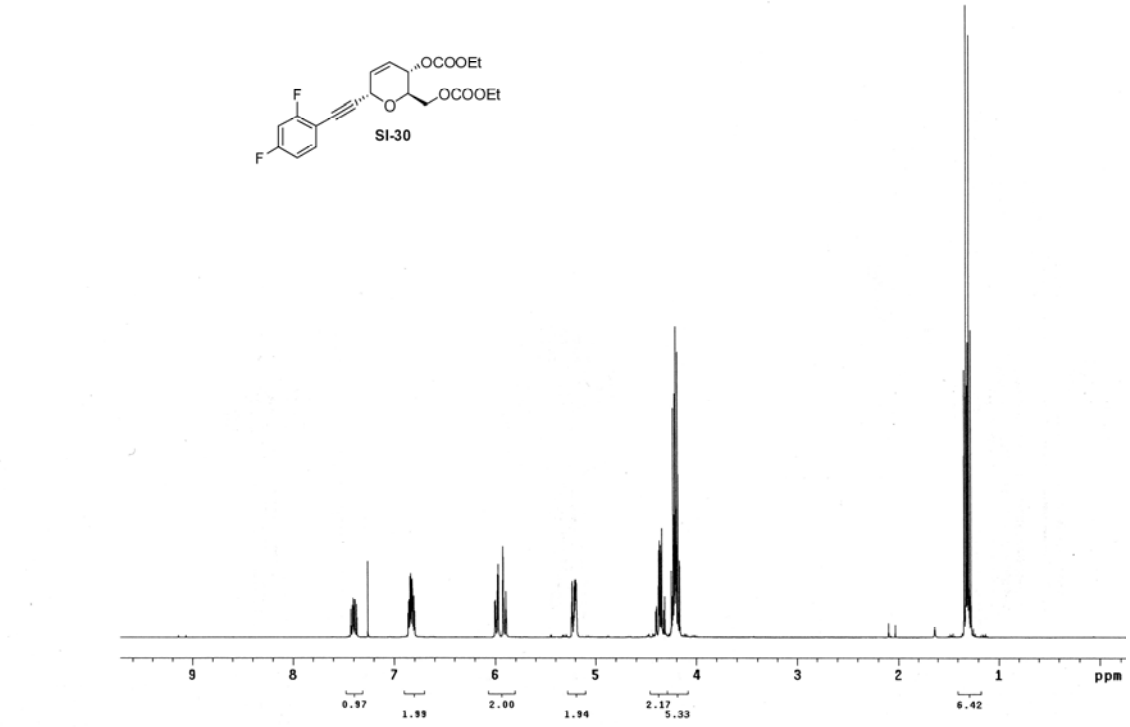
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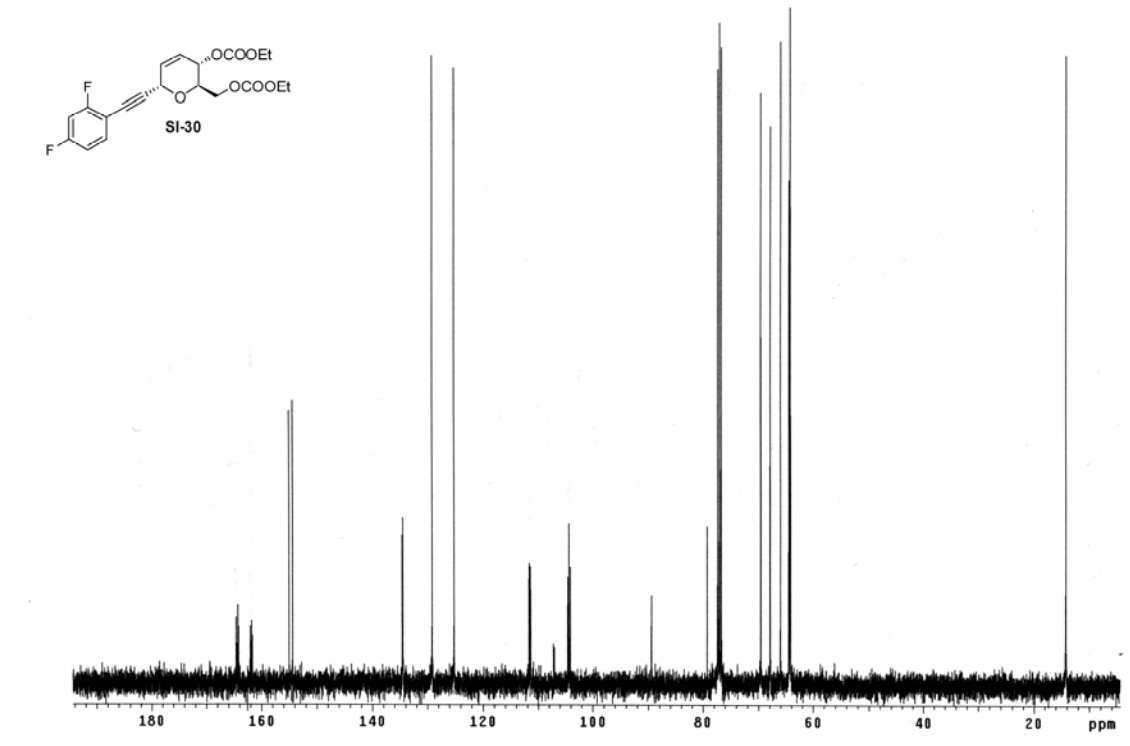
6.42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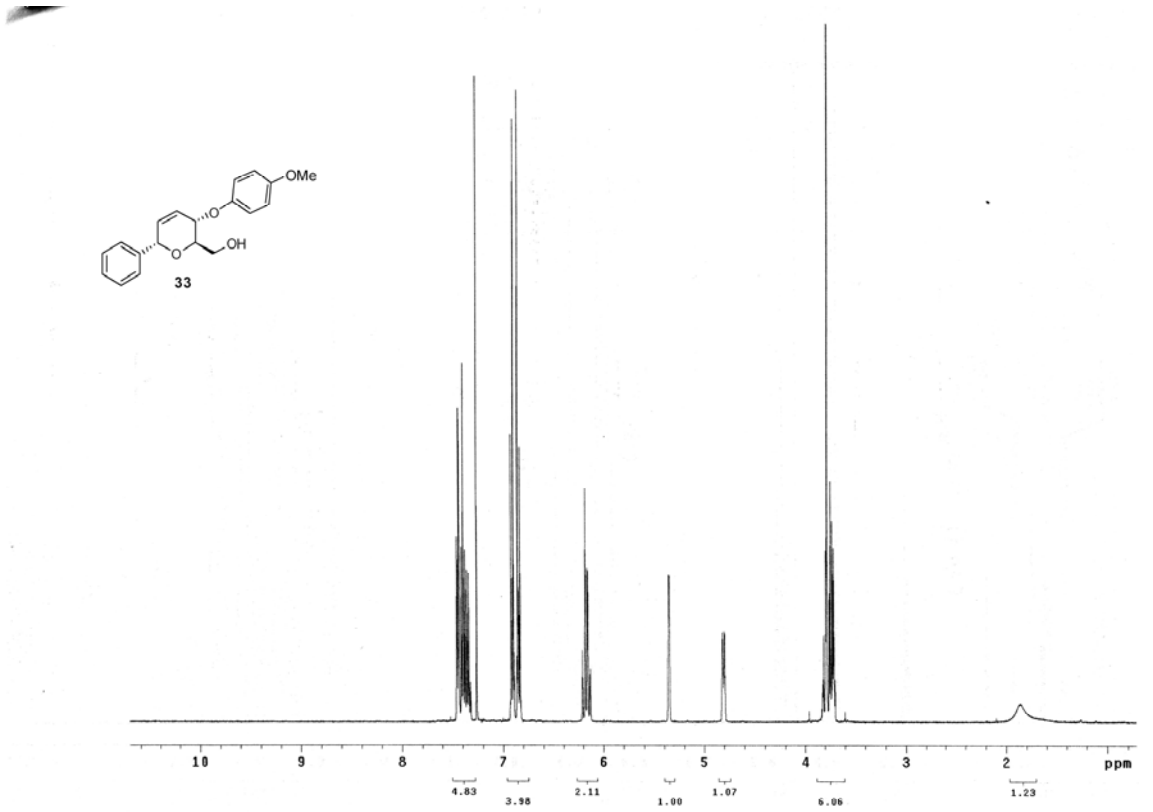
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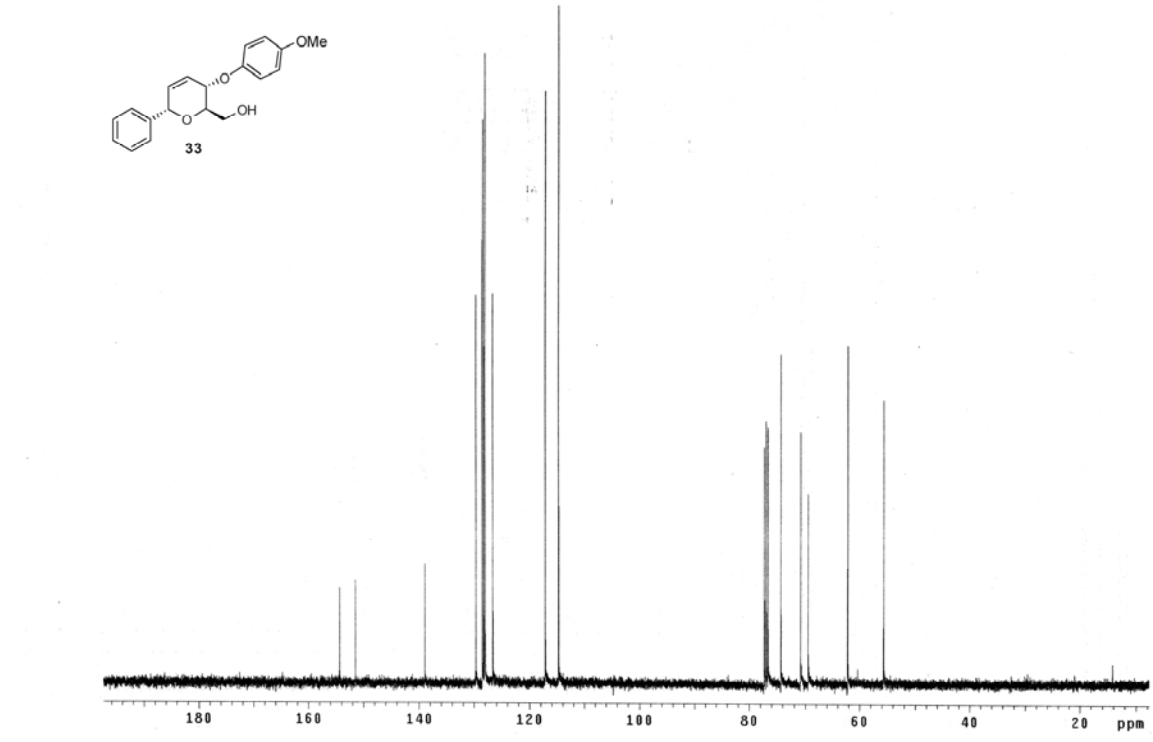
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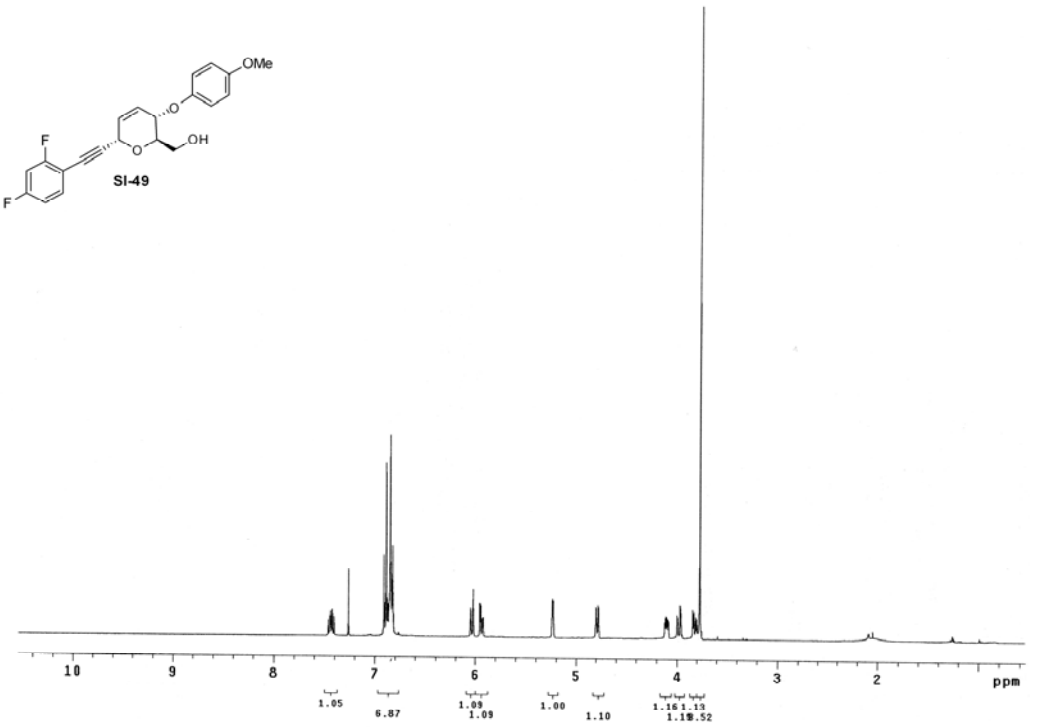
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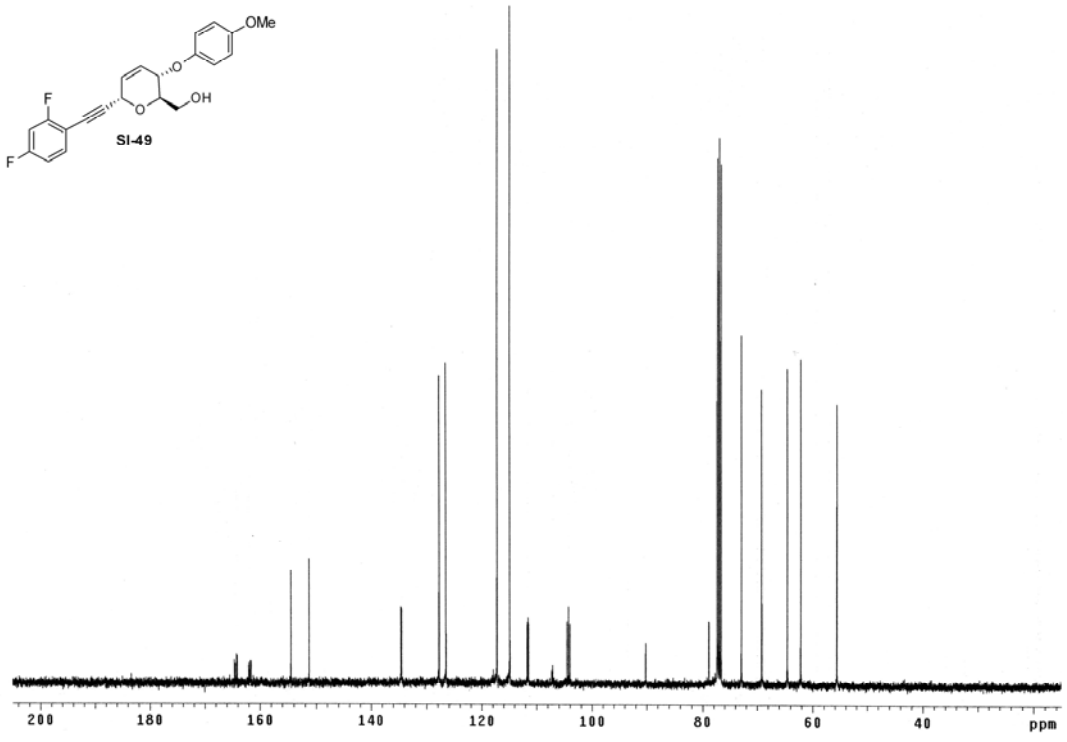
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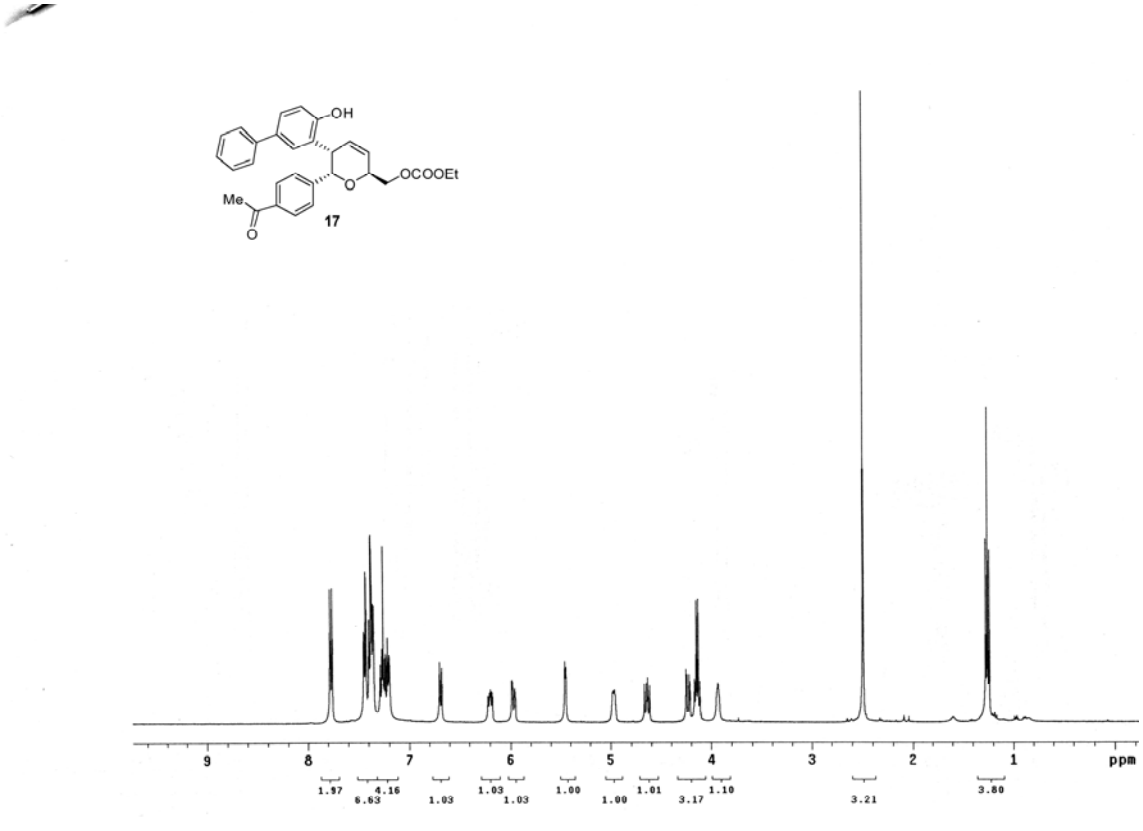
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1.00
1.01
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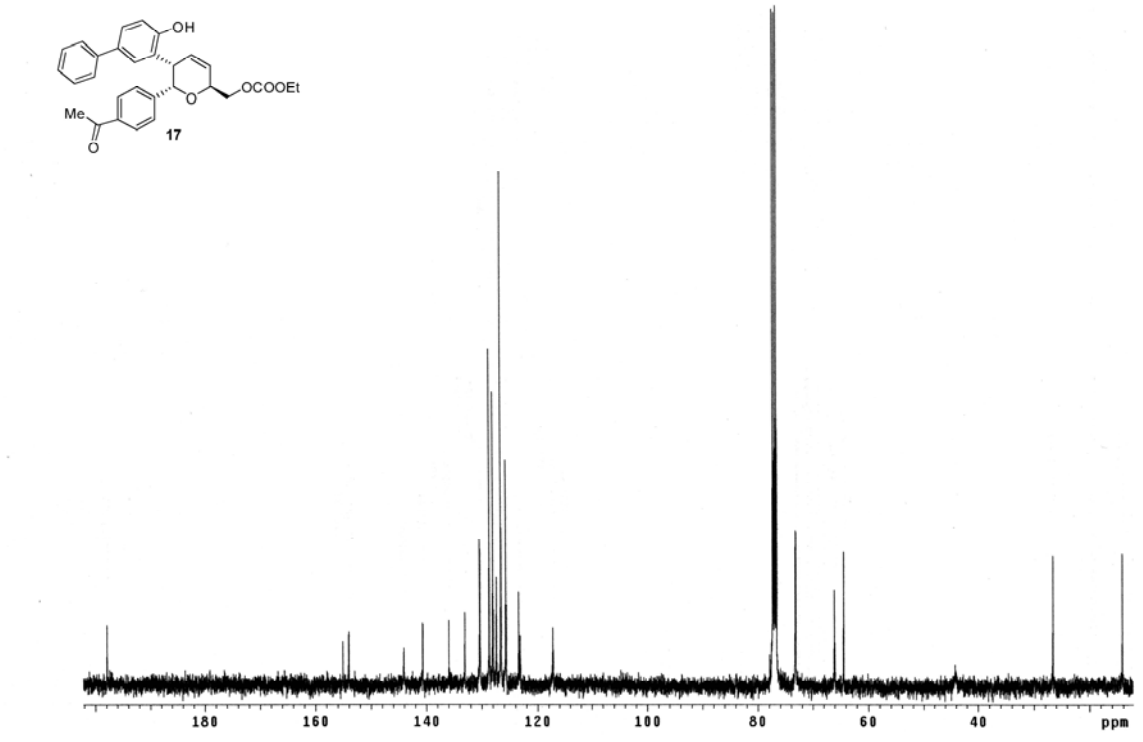
1.10
3.21
3.80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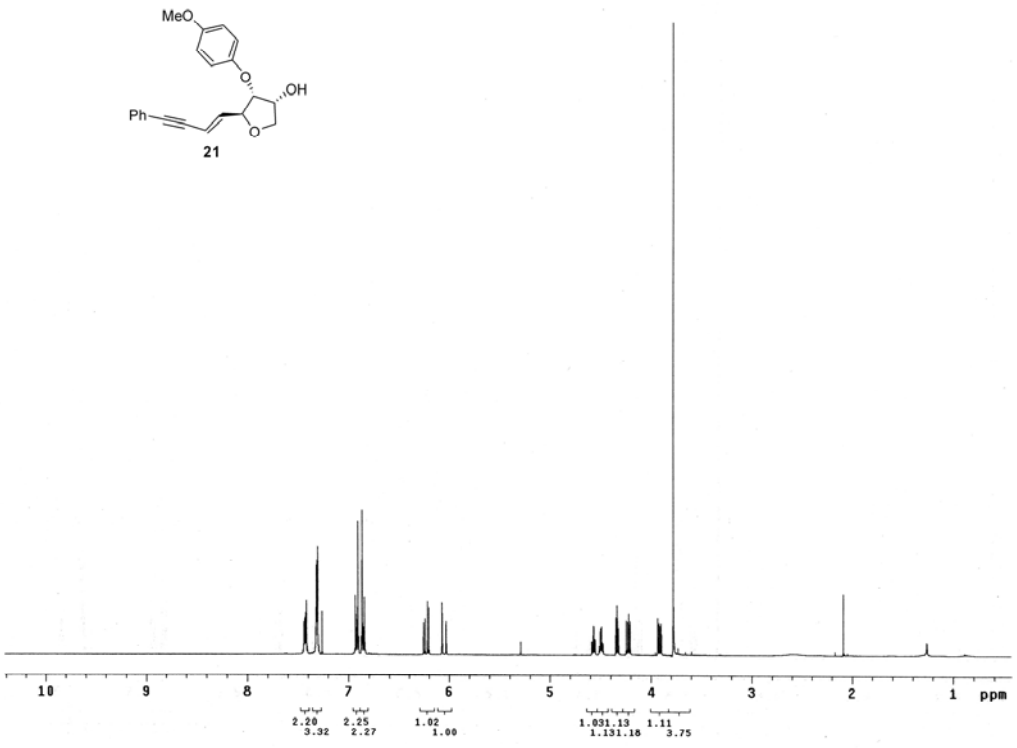
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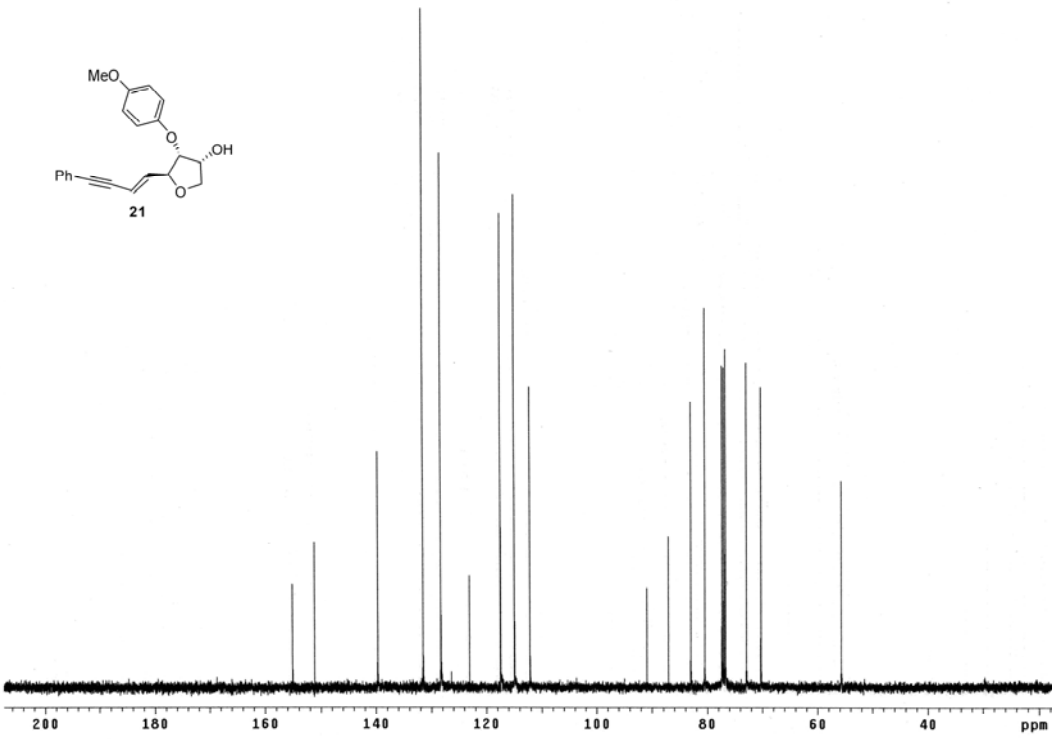
3.75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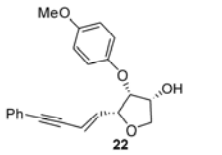
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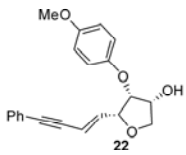
3.85
1.00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O
OH
Ph
O
22

180
160
140
120
100
80
60
40
20
ppm

Figure 1. Time dependent ^{1}H NMR experiments of $AuCl_3$-mediated formation of tetrahydrofurans **24** and **25**. ^{1}H NMR's taken in C_6D_6 of crude SiO_2-filtered reaction mixtures.

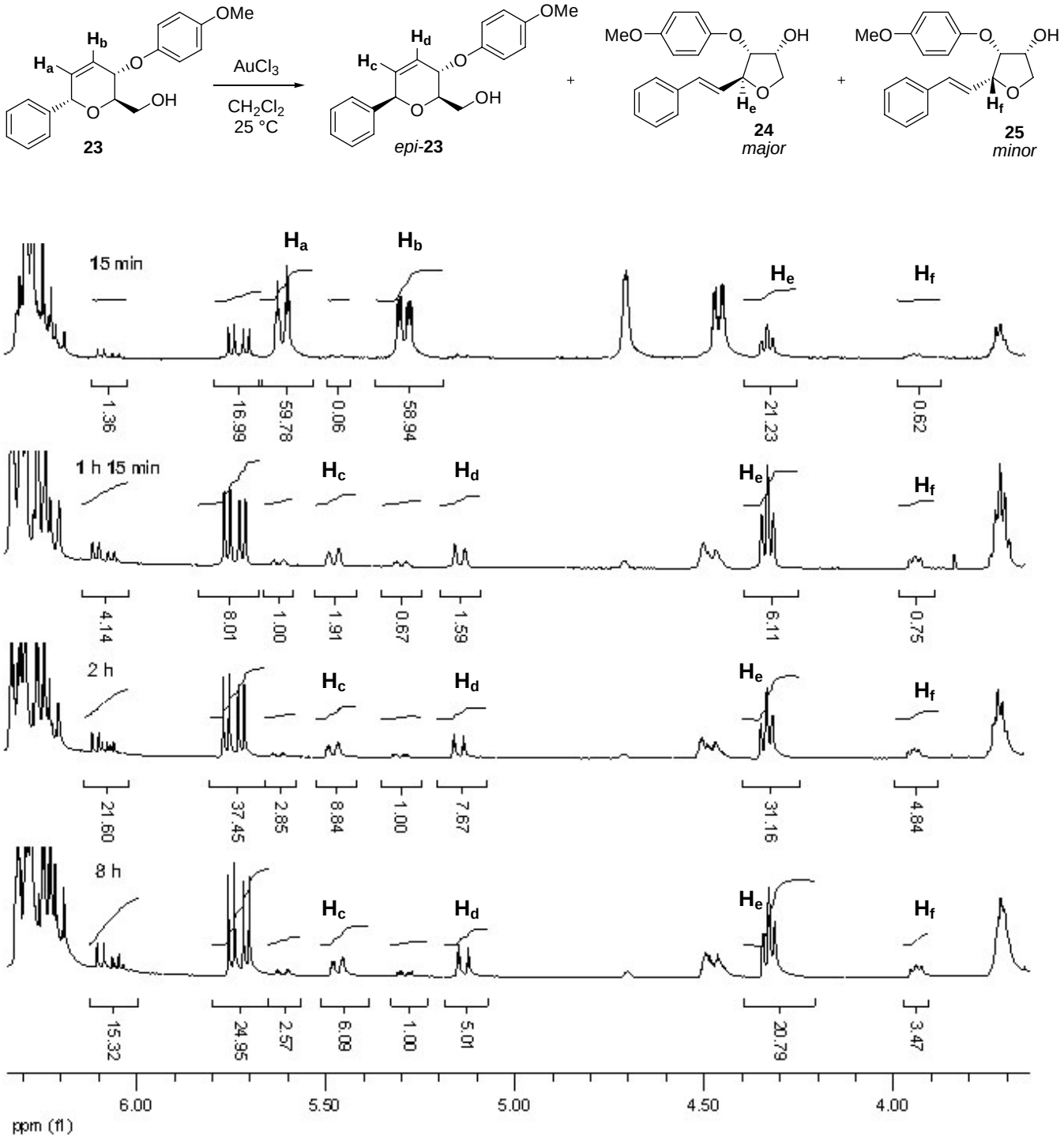
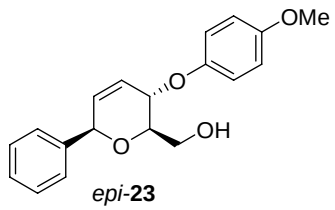
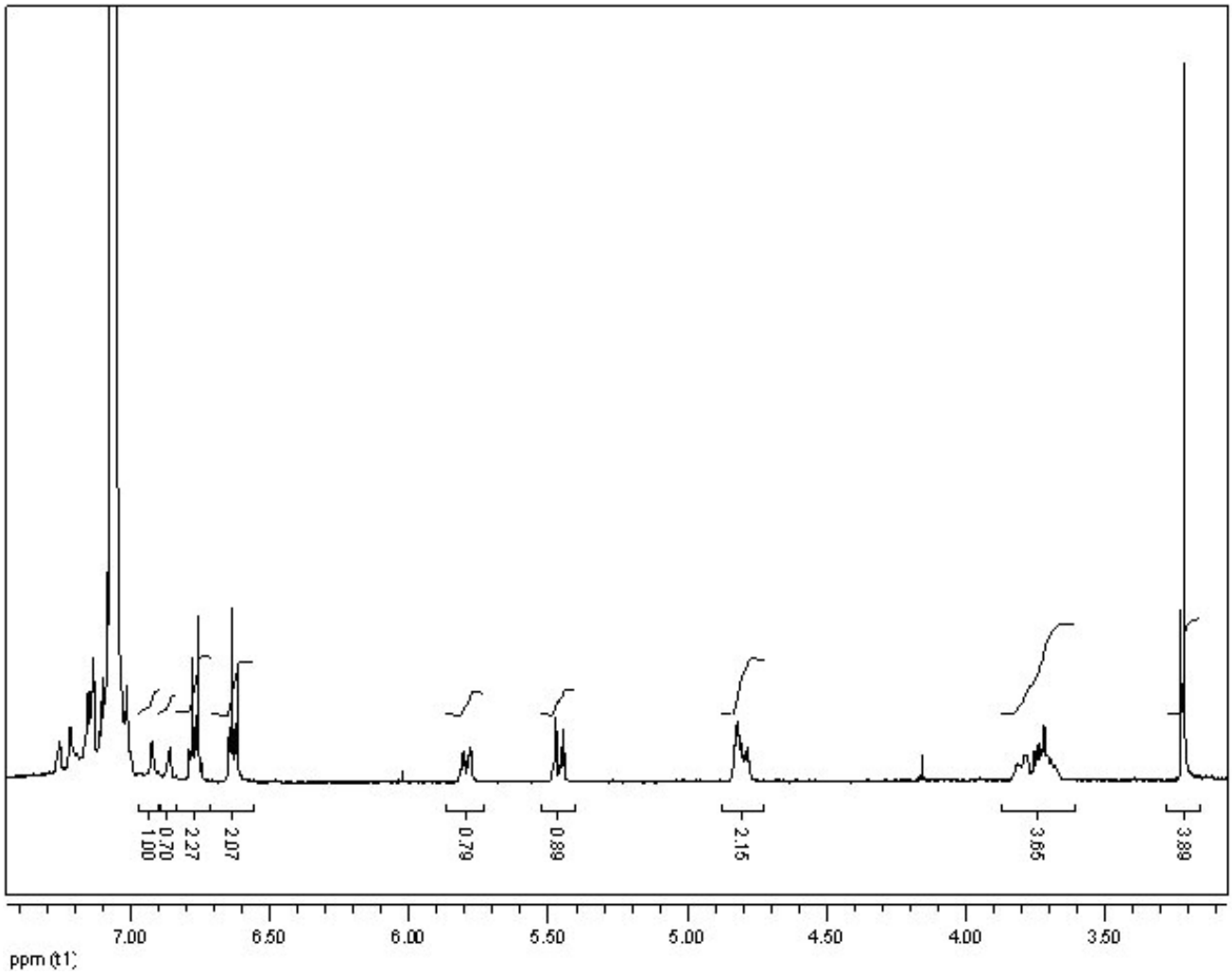


Figure 2. ^{1}H NMR experiments of epimeric **23** produced during the ring contraction reaction. ^{1}H NMR taken in C_6D_6.



epi-**23**



X-ray Crystal Structure of Compound SI-15:

Crystals of compound **SI-15** suitable for x-ray analysis were obtained by slow evaporation from hexanes. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 260139). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

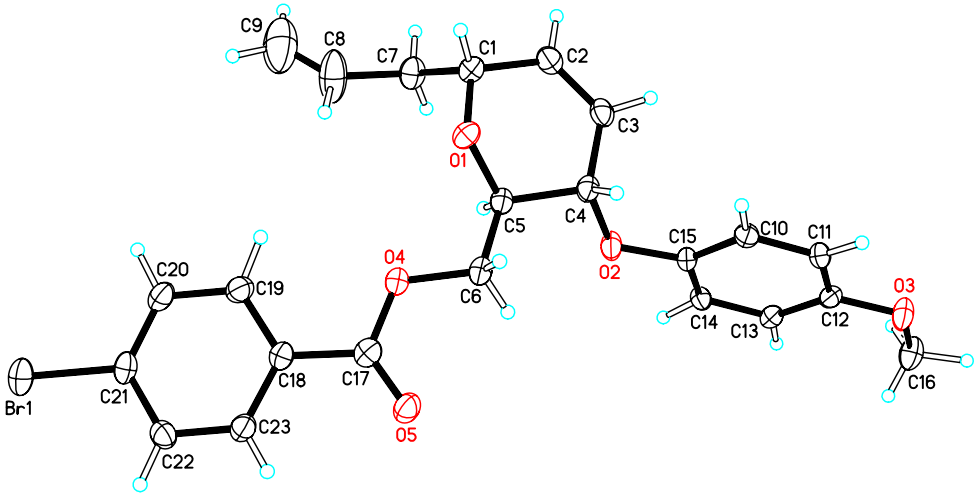


Table 1. Crystal data and structure refinement for porco29.

Identification code	porco29	
Empirical formula	C23 H23 Br O5	
Formula weight	459.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.0462(7) Å	α= 90°.
	b = 5.3870(4) Å	β= 100.504(2)°.
	c = 19.6191(14) Å	γ = 90°.
Volume	1043.97(13) $Å^3$	
Z	2	
Density (calculated)	1.461 Mg/m^3	
Absorption coefficient	2.000 mm^{-1}	
F(000)	472	

Crystal size	1.00 x 0.30 x 0.15 mm^3
Theta range for data collection	2.48 to 30.51°.
Index ranges	-14<=h<=14, -6<=k<=7, -24<=l<=28
Reflections collected	8041
Independent reflections	5322 [R(int) = 0.0252]
Completeness to theta = 30.51°	97.8 %
Absorption correction	SADABS
Max. and min. transmission	0.7535 and 0.2396
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5322 / 1 / 343
Goodness-of-fit on F^2	0.964
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0819
R indices (all data)	R1 = 0.0539, wR2 = 0.0869
Absolute structure parameter	0.055(10)
Largest diff. peak and hole	0.567 and -0.503 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for porco29. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	944(1)	2677(1)	4190(1)	41(1)
O(1)	-5019(2)	14447(4)	2779(1)	27(1)
O(2)	-8105(2)	11847(3)	1833(1)	30(1)
O(3)	-12856(2)	12867(6)	-91(1)	36(1)
O(4)	-4033(2)	9901(4)	2407(1)	30(1)
O(5)	-3783(2)	7402(5)	1524(1)	33(1)
C(1)	-5547(3)	15648(6)	3321(1)	29(1)
C(2)	-6994(3)	16409(6)	3081(2)	31(1)
C(3)	-7704(3)	15654(5)	2481(2)	29(1)
C(4)	-7166(3)	13852(5)	2019(1)	26(1)
C(5)	-5894(2)	12602(7)	2422(1)	25(1)
C(6)	-5117(3)	11212(6)	1960(2)	30(1)
C(7)	-5341(3)	14054(7)	3983(2)	34(1)
C(8)	-3884(3)	13459(10)	4251(2)	64(2)
C(9)	-3230(5)	13519(10)	4787(3)	89(2)

C(10)	-9526(3)	14298(5)	912(1)	26(1)
C(11)	-10738(3)	14430(6)	440(1)	27(1)
C(12)	-11707(2)	12573(8)	407(1)	25(1)
C(13)	-11482(3)	10585(5)	859(1)	25(1)
C(14)	-10262(3)	10435(5)	1333(1)	24(1)
C(15)	-9288(2)	12262(5)	1353(1)	23(1)
C(16)	-13857(3)	10966(8)	-119(2)	41(1)
C(17)	-3451(2)	8036(7)	2117(1)	27(1)
C(18)	-2340(2)	6859(5)	2619(1)	24(1)
C(19)	-1939(2)	7774(9)	3294(1)	31(1)
C(20)	-944(3)	6523(6)	3761(1)	32(1)
C(21)	-371(2)	4424(6)	3545(1)	28(1)
C(22)	-721(3)	3513(6)	2878(2)	31(1)
C(23)	-1715(3)	4776(6)	2413(1)	29(1)

Table 3. Bond lengths [Å] and angles [°] for porco29.

Br(1)-C(21)	1.903(3)
O(1)-C(5)	1.423(4)
O(1)-C(1)	1.427(3)
O(2)-C(15)	1.393(3)
O(2)-C(4)	1.437(3)
O(3)-C(12)	1.379(3)
O(3)-C(16)	1.429(4)
O(4)-C(17)	1.341(4)
O(4)-C(6)	1.451(3)
O(5)-C(17)	1.200(3)
C(1)-C(2)	1.501(4)
C(1)-C(7)	1.540(4)
C(2)-C(3)	1.323(4)
C(3)-C(4)	1.495(4)
C(4)-C(5)	1.531(3)
C(5)-C(6)	1.501(4)
C(7)-C(8)	1.497(4)
C(8)-C(9)	1.134(6)
C(10)-C(15)	1.391(4)
C(10)-C(11)	1.391(3)
C(11)-C(12)	1.389(5)
C(12)-C(13)	1.382(5)
C(13)-C(14)	1.399(3)
C(14)-C(15)	1.383(4)
C(17)-C(18)	1.489(3)
C(18)-C(23)	1.381(4)
C(18)-C(19)	1.402(4)
C(19)-C(20)	1.399(4)
C(20)-C(21)	1.371(4)
C(21)-C(22)	1.382(4)
C(22)-C(23)	1.400(4)
C(5)-O(1)-C(1)	113.72(19)
C(15)-O(2)-C(4)	119.4(2)

C(12)-O(3)-C(16)	116.0(3)
C(17)-O(4)-C(6)	116.4(2)
O(1)-C(1)-C(2)	111.2(2)
O(1)-C(1)-C(7)	111.4(2)
C(2)-C(1)-C(7)	113.0(2)
C(3)-C(2)-C(1)	122.0(3)
C(2)-C(3)-C(4)	122.8(3)
O(2)-C(4)-C(3)	110.4(2)
O(2)-C(4)-C(5)	104.3(2)
C(3)-C(4)-C(5)	109.4(2)
O(1)-C(5)-C(6)	107.6(2)
O(1)-C(5)-C(4)	109.2(3)
C(6)-C(5)-C(4)	112.60(19)
O(4)-C(6)-C(5)	107.0(2)
C(8)-C(7)-C(1)	112.8(3)
C(9)-C(8)-C(7)	133.1(5)
C(15)-C(10)-C(11)	119.0(3)
C(12)-C(11)-C(10)	121.0(3)
O(3)-C(12)-C(13)	124.1(3)
O(3)-C(12)-C(11)	116.0(3)
C(13)-C(12)-C(11)	119.8(2)
C(12)-C(13)-C(14)	119.4(3)
C(15)-C(14)-C(13)	120.5(2)
C(14)-C(15)-C(10)	120.2(2)
C(14)-C(15)-O(2)	114.7(2)
C(10)-C(15)-O(2)	125.1(2)
O(5)-C(17)-O(4)	124.0(3)
O(5)-C(17)-C(18)	124.3(3)
O(4)-C(17)-C(18)	111.7(2)
C(23)-C(18)-C(19)	119.7(3)
C(23)-C(18)-C(17)	118.5(2)
C(19)-C(18)-C(17)	121.8(3)
C(20)-C(19)-C(18)	119.8(3)
C(21)-C(20)-C(19)	119.1(3)
C(20)-C(21)-C(22)	122.5(3)
C(20)-C(21)-Br(1)	118.8(2)

C(22)-C(21)-Br(1)	118.7(2)
C(21)-C(22)-C(23)	118.2(3)
C(18)-C(23)-C(22)	120.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for porco29. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	33(1)	52(1)	36(1)	10(1)	-4(1)	4(1)
O(1)	22(1)	31(1)	27(1)	-1(1)	5(1)	-7(1)
O(2)	26(1)	24(1)	36(1)	7(1)	-7(1)	-2(1)
O(3)	29(1)	42(1)	32(1)	8(1)	-7(1)	0(1)
O(4)	25(1)	33(1)	29(1)	-3(1)	-2(1)	4(1)
O(5)	29(1)	46(1)	23(1)	-3(1)	2(1)	3(1)
C(1)	27(1)	30(2)	28(1)	-2(1)	1(1)	-2(1)
C(2)	32(1)	29(2)	32(1)	3(1)	6(1)	5(1)
C(3)	29(1)	24(1)	33(1)	7(1)	2(1)	2(1)
C(4)	23(1)	25(1)	27(1)	3(1)	-1(1)	-2(1)
C(5)	22(1)	25(1)	25(1)	3(2)	1(1)	-1(1)
C(6)	27(1)	35(2)	26(1)	0(1)	-3(1)	4(1)
C(7)	30(1)	43(2)	29(2)	6(1)	6(1)	0(1)
C(8)	39(2)	109(5)	43(2)	32(2)	7(1)	12(2)
C(9)	51(2)	91(4)	115(4)	38(3)	-13(3)	-15(2)
C(10)	28(1)	21(1)	27(1)	1(1)	2(1)	-2(1)
C(11)	33(1)	24(2)	23(1)	5(1)	0(1)	5(1)
C(12)	25(1)	28(1)	22(1)	-5(2)	1(1)	2(2)
C(13)	24(1)	27(2)	22(1)	-2(1)	3(1)	-2(1)
C(14)	26(1)	22(1)	24(1)	3(1)	3(1)	4(1)
C(15)	22(1)	23(2)	22(1)	1(1)	-1(1)	4(1)
C(16)	30(1)	51(2)	36(2)	4(2)	-5(1)	-2(1)
C(17)	20(1)	34(2)	27(1)	0(1)	9(1)	-6(1)
C(18)	19(1)	29(2)	24(1)	3(1)	5(1)	-4(1)
C(19)	29(1)	35(1)	28(1)	-6(2)	5(1)	-2(2)

C(20)	29(1)	41(2)	23(1)	-3(1)	-1(1)	-3(1)
C(21)	20(1)	38(2)	26(1)	7(1)	2(1)	-2(1)
C(22)	26(1)	33(2)	32(1)	0(1)	6(1)	5(1)
C(23)	24(1)	37(2)	24(1)	-3(1)	3(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for porco29.

	x	y	z	U(eq)
H(1)	-5020(30)	17010(60)	3393(14)	22(7)
H(2)	-7360(20)	17400(70)	3401(12)	15(6)
H(3)	-8530(40)	16480(80)	2332(19)	58(12)
H(4)	-6930(30)	14820(60)	1573(14)	19(7)
H(5)	-6170(30)	11490(60)	2741(15)	24(8)
H(6B)	-4790(30)	12500(90)	1638(15)	35(8)
H(6A)	-5680(30)	10180(60)	1684(14)	19(7)
H(7B)	-5840(40)	12860(110)	3869(18)	50(10)
H(7A)	-5640(30)	14890(70)	4336(16)	33(9)
H(8)	-3410	12923	3900	76
H(9B)	-3610	14031	5174	107
H(9A)	-2304	13056	4849	107
H(10)	-8930(40)	15600(80)	911(17)	46(10)
H(11)	-10890(30)	15700(70)	130(16)	33(9)
H(13)	-12030(30)	9340(60)	829(14)	16(7)
H(14)	-10090(30)	8960(60)	1596(15)	27(8)
H(16C)	-13490(30)	9490(70)	-219(16)	29(8)
H(16B)	-14200(40)	10850(80)	330(20)	57(12)
H(16A)	-14700(40)	11440(80)	-501(19)	60(12)
H(19)	-2220(30)	9390(70)	3442(16)	31(8)
H(20)	-740(30)	7230(80)	4223(15)	44(9)
H(22)	-340(30)	2130(80)	2713(17)	45(11)
H(23)	-1940(40)	4140(90)	2000(20)	63(13)

X-ray Crystal Structure of Compound 22:

Crystals of compound **22** suitable for x-ray analysis were obtained by slow evaporation from methylene chloride. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 287119). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

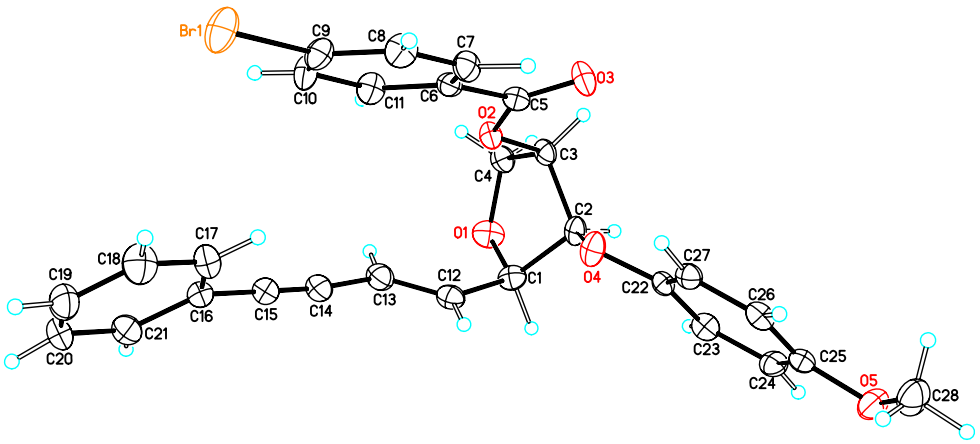


Table 1. Crystal data and structure refinement for porco40.

Identification code	porco40	
Empirical formula	C28 H23 Br O5	
Formula weight	519.37	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.0107(3) Å	α= 90°.
	b = 15.0074(7) Å	β= 90°.
	c = 25.3448(11) Å	γ = 90°.
Volume	2286.23(19) $Å^3$	
Z	4	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	1.837 mm^{-1}	
F(000)	1064	
Crystal size	0.40 x 0.10 x 0.05 mm^3	

Theta range for data collection	1.58 to 28.81°.
Index ranges	-8<=h<=7, -20<=k<=20, -34<=l<=26
Reflections collected	15307
Independent reflections	5894 [R(int) = 0.0265]
Completeness to theta = 28.81°	99.4 %
Absorption correction	Semiempirical by SADABS
Max. and min. transmission	0.9138 and 0.5270
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5894 / 0 / 399
Goodness-of-fit on F^2	0.982
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0685
R indices (all data)	R1 = 0.0456, wR2 = 0.0727
Absolute structure parameter	0.000(6)
Largest diff. peak and hole	0.760 and -0.418 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for porco40. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	5574(1)	5493(1)	1756(1)	44(1)
O(1)	-4883(2)	904(1)	1707(1)	35(1)
O(2)	-2036(2)	2357(1)	1129(1)	24(1)
O(3)	-816(3)	2601(1)	299(1)	34(1)
O(4)	-288(2)	788(1)	809(1)	32(1)
O(5)	3564(3)	-1708(1)	-510(1)	38(1)
C(1)	-2764(4)	548(1)	1578(1)	29(1)
C(2)	-2520(3)	771(1)	983(1)	26(1)
C(3)	-3591(3)	1688(1)	946(1)	25(1)
C(4)	-5412(4)	1629(1)	1354(1)	28(1)
C(5)	-741(4)	2753(1)	765(1)	25(1)
C(6)	774(4)	3412(1)	1017(1)	23(1)
C(7)	2636(4)	3693(1)	741(1)	29(1)
C(8)	4072(4)	4306(1)	960(1)	31(1)
C(9)	3618(4)	4641(1)	1457(1)	30(1)
C(10)	1783(4)	4373(1)	1736(1)	33(1)
C(11)	367(4)	3745(1)	1520(1)	30(1)

C(12)	-912(4)	927(1)	1907(1)	29(1)
C(13)	-1207(4)	1501(2)	2297(1)	32(1)
C(14)	571(5)	1937(1)	2569(1)	34(1)
C(15)	2007(4)	2367(1)	2775(1)	33(1)
C(16)	3762(4)	2882(1)	3005(1)	31(1)
C(17)	5234(4)	3347(2)	2689(1)	37(1)
C(18)	6942(5)	3840(2)	2902(1)	45(1)
C(19)	7215(5)	3871(2)	3440(1)	41(1)
C(20)	5770(5)	3426(2)	3761(1)	40(1)
C(21)	4045(5)	2929(2)	3551(1)	36(1)
C(22)	505(4)	154(1)	461(1)	23(1)
C(23)	-368(4)	-700(1)	403(1)	29(1)
C(24)	694(4)	-1296(1)	66(1)	30(1)
C(25)	2619(4)	-1056(1)	-200(1)	27(1)
C(26)	3461(4)	-208(1)	-143(1)	27(1)
C(27)	2384(3)	395(1)	187(1)	25(1)
C(28)	5415(5)	-1458(2)	-827(1)	43(1)

Table 3. Bond lengths [Å] and angles [°] for porco40.

Br(1)-C(9)	1.895(2)
O(1)-C(1)	1.419(3)
O(1)-C(4)	1.445(3)
O(2)-C(5)	1.346(2)
O(2)-C(3)	1.448(2)
O(3)-C(5)	1.203(2)
O(4)-C(22)	1.381(2)
O(4)-C(2)	1.414(3)
O(5)-C(25)	1.377(2)
O(5)-C(28)	1.422(3)
C(1)-C(12)	1.503(3)
C(1)-C(2)	1.550(3)
C(2)-C(3)	1.523(3)
C(3)-C(4)	1.508(3)
C(5)-C(6)	1.488(3)
C(6)-C(7)	1.386(3)

C(6)-C(11)	1.391(3)
C(7)-C(8)	1.379(3)
C(8)-C(9)	1.383(3)
C(9)-C(10)	1.370(3)
C(10)-C(11)	1.383(3)
C(12)-C(13)	1.321(3)
C(13)-C(14)	1.431(3)
C(14)-C(15)	1.198(3)
C(15)-C(16)	1.431(3)
C(16)-C(17)	1.382(3)
C(16)-C(21)	1.398(3)
C(17)-C(18)	1.377(4)
C(18)-C(19)	1.372(4)
C(19)-C(20)	1.365(4)
C(20)-C(21)	1.384(4)
C(22)-C(27)	1.375(3)
C(22)-C(23)	1.392(3)
C(23)-C(24)	1.391(3)
C(24)-C(25)	1.387(3)
C(25)-C(26)	1.378(3)
C(26)-C(27)	1.391(3)

C(1)-O(1)-C(4)	109.72(16)
C(5)-O(2)-C(3)	117.45(15)
C(22)-O(4)-C(2)	121.00(15)
C(25)-O(5)-C(28)	117.20(18)
O(1)-C(1)-C(12)	113.20(17)
O(1)-C(1)-C(2)	103.23(17)
C(12)-C(1)-C(2)	112.87(17)
O(4)-C(2)-C(3)	111.44(17)
O(4)-C(2)-C(1)	113.48(17)
C(3)-C(2)-C(1)	102.38(17)
O(2)-C(3)-C(4)	106.86(16)
O(2)-C(3)-C(2)	109.54(16)
C(4)-C(3)-C(2)	102.22(17)
O(1)-C(4)-C(3)	107.98(18)

O(3)-C(5)-O(2)	124.55(19)
O(3)-C(5)-C(6)	124.76(19)
O(2)-C(5)-C(6)	110.69(16)
C(7)-C(6)-C(11)	119.75(19)
C(7)-C(6)-C(5)	118.62(18)
C(11)-C(6)-C(5)	121.63(19)
C(8)-C(7)-C(6)	120.28(19)
C(7)-C(8)-C(9)	119.1(2)
C(10)-C(9)-C(8)	121.5(2)
C(10)-C(9)-Br(1)	119.39(16)
C(8)-C(9)-Br(1)	119.09(16)
C(9)-C(10)-C(11)	119.4(2)
C(10)-C(11)-C(6)	120.0(2)
C(13)-C(12)-C(1)	124.2(2)
C(12)-C(13)-C(14)	123.9(2)
C(15)-C(14)-C(13)	174.4(2)
C(14)-C(15)-C(16)	178.0(2)
C(17)-C(16)-C(21)	118.0(2)
C(17)-C(16)-C(15)	120.6(2)
C(21)-C(16)-C(15)	121.3(2)
C(18)-C(17)-C(16)	121.4(2)
C(19)-C(18)-C(17)	119.8(3)
C(20)-C(19)-C(18)	120.0(3)
C(19)-C(20)-C(21)	120.7(2)
C(20)-C(21)-C(16)	120.0(2)
C(27)-C(22)-O(4)	115.14(17)
C(27)-C(22)-C(23)	119.86(18)
O(4)-C(22)-C(23)	124.86(19)
C(24)-C(23)-C(22)	118.9(2)
C(25)-C(24)-C(23)	120.97(19)
O(5)-C(25)-C(26)	124.4(2)
O(5)-C(25)-C(24)	115.93(19)
C(26)-C(25)-C(24)	119.6(2)
C(25)-C(26)-C(27)	119.6(2)
C(22)-C(27)-C(26)	121.00(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for porco40. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	42(1)	39(1)	52(1)	-14(1)	9(1)	-18(1)
O(1)	29(1)	38(1)	40(1)	9(1)	6(1)	-3(1)
O(2)	26(1)	28(1)	20(1)	-1(1)	0(1)	-6(1)
O(3)	39(1)	45(1)	19(1)	-3(1)	-1(1)	-9(1)
O(4)	21(1)	36(1)	37(1)	-14(1)	0(1)	-8(1)
O(5)	41(1)	31(1)	43(1)	-5(1)	2(1)	7(1)
C(1)	26(1)	26(1)	36(1)	2(1)	0(1)	-2(1)
C(2)	20(1)	29(1)	28(1)	-8(1)	-4(1)	-6(1)
C(3)	23(1)	28(1)	24(1)	-2(1)	-7(1)	-6(1)
C(4)	23(1)	33(1)	28(1)	-2(1)	-4(1)	-4(1)
C(5)	24(1)	26(1)	26(1)	3(1)	-2(1)	2(1)
C(6)	24(1)	23(1)	22(1)	2(1)	-2(1)	0(1)
C(7)	30(1)	33(1)	23(1)	-1(1)	6(1)	0(1)
C(8)	28(1)	33(1)	33(1)	1(1)	13(1)	-6(1)
C(9)	31(1)	24(1)	35(1)	-4(1)	2(1)	-5(1)
C(10)	37(1)	33(1)	28(1)	-10(1)	6(1)	-7(1)
C(11)	26(1)	34(1)	29(1)	-1(1)	9(1)	-5(1)
C(12)	28(1)	28(1)	30(1)	6(1)	-2(1)	-2(1)
C(13)	35(1)	33(1)	29(1)	3(1)	-2(1)	-1(1)
C(14)	42(1)	34(1)	26(1)	1(1)	-2(1)	6(1)
C(15)	42(1)	29(1)	29(1)	-1(1)	-6(1)	4(1)
C(16)	38(1)	27(1)	29(1)	-3(1)	-7(1)	7(1)
C(17)	46(2)	39(1)	26(1)	-5(1)	-6(1)	0(1)
C(18)	45(2)	49(1)	40(2)	-3(1)	5(1)	-7(1)
C(19)	40(1)	41(1)	41(1)	-9(1)	-9(1)	-1(1)
C(20)	53(2)	40(1)	28(1)	-5(1)	-15(1)	4(1)
C(21)	44(2)	35(1)	29(1)	3(1)	-1(1)	1(1)
C(22)	23(1)	26(1)	20(1)	-2(1)	-6(1)	1(1)
C(23)	25(1)	32(1)	29(1)	3(1)	-1(1)	-4(1)

C(24)	35(1)	21(1)	33(1)	2(1)	-5(1)	-4(1)
C(25)	27(1)	29(1)	24(1)	1(1)	-8(1)	6(1)
C(26)	24(1)	34(1)	23(1)	4(1)	-2(1)	-2(1)
C(27)	25(1)	24(1)	27(1)	1(1)	-6(1)	-3(1)
C(28)	34(1)	50(1)	46(2)	-10(1)	3(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for porco40.

	x	y	z	U(eq)
H(1)	-2770(50)	-151(18)	1651(10)	50(7)
H(2)	-3310(30)	443(13)	785(7)	13(5)
H(3)	-4030(40)	1839(12)	594(8)	17(5)
H(4B)	-5610(40)	2162(14)	1529(8)	25(5)
H(4A)	-6770(40)	1501(13)	1178(8)	16(5)
H(7)	2970(40)	3428(14)	379(9)	31(6)
H(8)	5280(40)	4471(14)	807(9)	29(6)
H(10)	1520(40)	4611(14)	2058(9)	29(6)
H(11)	-830(40)	3568(13)	1698(8)	20(5)
H(12)	500(40)	749(14)	1822(9)	29(6)
H(13)	-2780(50)	1650(16)	2390(10)	42(7)
H(17)	4990(50)	3307(16)	2336(11)	45(7)
H(18)	7860(60)	4156(19)	2682(12)	63(9)
H(19)	8410(60)	4189(19)	3585(11)	62(9)
H(20)	5890(50)	3405(15)	4138(10)	40(7)
H(21)	3120(50)	2621(16)	3740(10)	42(8)
H(23)	-1730(40)	-831(14)	575(9)	30(6)
H(24)	90(40)	-1864(13)	42(7)	23(5)
H(26)	4720(40)	-65(14)	-314(9)	24(6)
H(27)	2900(40)	964(15)	207(8)	31(6)
H(28C)	5060(50)	-990(19)	-1067(11)	55(8)
H(28B)	6570(50)	-1314(17)	-639(11)	47(8)
H(28A)	5890(70)	-1980(20)	-1033(13)	84(11)

X-ray Crystal Structure of Compound 24:

Crystals of compound **24** suitable for x-ray analysis were obtained by slow evaporation from methylene chloride. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 287120). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

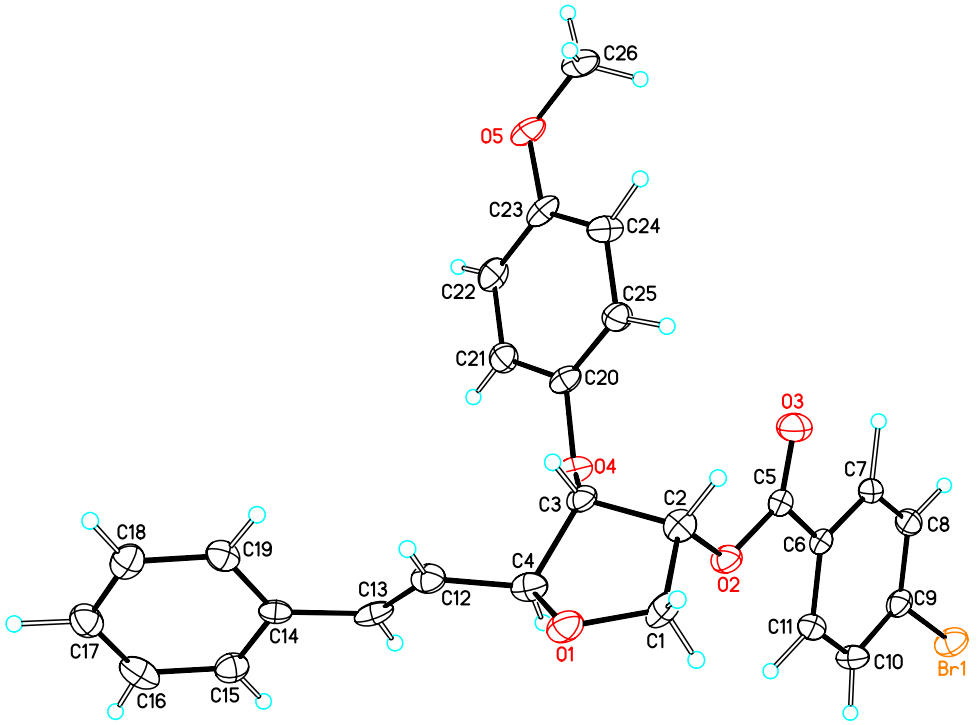


Table 1. Crystal data and structure refinement for porco41.

Identification code	porco41	
Empirical formula	C26 H23 Br O5	
Formula weight	495.35	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 13.1894(18) Å	α= 90°.
	b = 5.1990(10) Å	β= 110.015(7)°.

	c = 17.152(3) Å γ = 90°.
Volume	1105.1(3) $Å^3$
Z	2
Density (calculated)	1.489 Mg/m^3
Absorption coefficient	1.896 mm^{-1}
F(000)	508
Crystal size	1.00 x 0.10 x 0.02 mm^3
Theta range for data collection	2.39 to 23.25°.
Index ranges	-13<=h<=14, -5<=k<=5, -18<=l<=19
Reflections collected	8090
Independent reflections	3034 [R(int) = 0.0515]
Completeness to theta = 23.25°	97.5 %
Absorption correction	Semiempirical by SADABS
Max. and min. transmission	0.9631 and 0.2529
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3034 / 1 / 370
Goodness-of-fit on F^2	0.979
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0816
R indices (all data)	R1 = 0.0514, wR2 = 0.0857
Absolute structure parameter	0.021(11)
Largest diff. peak and hole	0.872 and -0.401 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for porco41. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	1976(1)	625(1)	6242(1)	36(1)
O(1)	-1072(3)	11408(6)	9596(2)	32(1)
O(2)	-656(3)	9035(6)	7929(2)	27(1)
O(3)	-1476(3)	10027(7)	6580(2)	39(1)
O(4)	-2648(3)	7511(6)	7904(2)	29(1)
O(5)	-6583(3)	7718(7)	5321(2)	34(1)
C(1)	-583(4)	12058(12)	9005(4)	34(1)
C(2)	-1274(4)	11035(11)	8161(3)	26(1)
C(3)	-2228(4)	9778(10)	8353(3)	25(1)
C(4)	-1734(4)	9168(11)	9272(4)	29(1)

C(5)	-838(4)	8770(10)	7119(3)	24(1)
C(6)	-166(4)	6698(9)	6940(3)	23(1)
C(7)	-326(4)	6164(10)	6122(3)	24(1)
C(8)	295(4)	4299(11)	5906(4)	30(1)
C(9)	1094(4)	3087(10)	6535(3)	26(1)
C(10)	1287(4)	3566(11)	7363(4)	29(1)
C(11)	641(3)	5411(14)	7567(3)	28(1)
C(12)	-2502(4)	8835(11)	9729(3)	28(1)
C(13)	-2597(4)	6705(12)	10117(3)	30(1)
C(14)	-3300(4)	6256(8)	10610(3)	23(1)
C(15)	-3120(4)	4139(11)	11136(4)	31(1)
C(16)	-3717(5)	3796(13)	11661(4)	38(2)
C(17)	-4507(4)	5549(16)	11653(3)	34(1)
C(18)	-4705(4)	7609(11)	11124(4)	32(1)
C(19)	-4120(4)	7982(11)	10598(3)	28(1)
C(20)	-3636(4)	7744(9)	7239(3)	25(1)
C(21)	-4409(4)	5838(14)	7188(3)	30(1)
C(22)	-5386(4)	5920(14)	6545(3)	31(1)
C(23)	-5591(4)	7839(10)	5947(3)	29(1)
C(24)	-4830(4)	9709(10)	5995(4)	32(2)
C(25)	-3833(4)	9635(10)	6652(3)	30(1)
C(26)	-6799(4)	9614(11)	4689(3)	36(2)

Table 3. Bond lengths [Å] and angles [°] for porco41.

Br(1)-C(9)	1.909(5)
O(1)-C(1)	1.417(7)
O(1)-C(4)	1.448(6)
O(2)-C(5)	1.334(6)
O(2)-C(2)	1.457(6)
O(3)-C(5)	1.208(6)
O(4)-C(20)	1.412(6)
O(4)-C(3)	1.413(6)
O(5)-C(23)	1.381(6)
O(5)-C(26)	1.420(6)
C(1)-C(2)	1.519(7)

C(2)-C(3)	1.551(7)
C(3)-C(4)	1.520(8)
C(4)-C(12)	1.488(7)
C(5)-C(6)	1.492(7)
C(6)-C(7)	1.374(6)
C(6)-C(11)	1.398(7)
C(7)-C(8)	1.398(7)
C(8)-C(9)	1.376(7)
C(9)-C(10)	1.377(7)
C(10)-C(11)	1.404(8)
C(12)-C(13)	1.319(8)
C(13)-C(14)	1.472(7)
C(14)-C(15)	1.392(7)
C(14)-C(19)	1.401(7)
C(15)-C(16)	1.395(8)
C(16)-C(17)	1.381(9)
C(17)-C(18)	1.371(9)
C(18)-C(19)	1.386(7)
C(20)-C(25)	1.367(7)
C(20)-C(21)	1.403(8)
C(21)-C(22)	1.381(7)
C(22)-C(23)	1.390(8)
C(23)-C(24)	1.380(7)
C(24)-C(25)	1.409(8)

C(1)-O(1)-C(4)	106.2(4)
C(5)-O(2)-C(2)	116.1(4)
C(20)-O(4)-C(3)	116.7(4)
C(23)-O(5)-C(26)	116.9(4)
O(1)-C(1)-C(2)	109.1(4)
O(2)-C(2)-C(1)	107.5(4)
O(2)-C(2)-C(3)	109.1(4)
C(1)-C(2)-C(3)	102.2(4)
O(4)-C(3)-C(4)	109.9(4)
O(4)-C(3)-C(2)	115.5(4)
C(4)-C(3)-C(2)	102.6(4)

O(1)-C(4)-C(12)	108.7(4)
O(1)-C(4)-C(3)	102.6(4)
C(12)-C(4)-C(3)	116.3(4)
O(3)-C(5)-O(2)	124.9(5)
O(3)-C(5)-C(6)	122.7(5)
O(2)-C(5)-C(6)	112.4(4)
C(7)-C(6)-C(11)	120.0(5)
C(7)-C(6)-C(5)	117.5(4)
C(11)-C(6)-C(5)	122.4(5)
C(6)-C(7)-C(8)	120.8(5)
C(9)-C(8)-C(7)	118.1(5)
C(8)-C(9)-C(10)	123.2(5)
C(8)-C(9)-Br(1)	118.2(4)
C(10)-C(9)-Br(1)	118.6(4)
C(9)-C(10)-C(11)	117.8(5)
C(6)-C(11)-C(10)	120.1(5)
C(13)-C(12)-C(4)	124.2(5)
C(12)-C(13)-C(14)	127.5(5)
C(15)-C(14)-C(19)	118.4(5)
C(15)-C(14)-C(13)	119.8(5)
C(19)-C(14)-C(13)	121.7(5)
C(14)-C(15)-C(16)	120.8(6)
C(17)-C(16)-C(15)	120.0(6)
C(16)-C(17)-C(18)	119.6(5)
C(17)-C(18)-C(19)	121.2(5)
C(18)-C(19)-C(14)	120.0(5)
C(25)-C(20)-C(21)	120.7(5)
C(25)-C(20)-O(4)	123.2(5)
C(21)-C(20)-O(4)	116.0(5)
C(22)-C(21)-C(20)	119.2(6)
C(21)-C(22)-C(23)	120.3(6)
C(24)-C(23)-O(5)	123.7(5)
C(24)-C(23)-C(22)	120.5(5)
O(5)-C(23)-C(22)	115.8(5)
C(23)-C(24)-C(25)	119.3(5)
C(20)-C(25)-C(24)	120.0(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for porco41. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	28(1)	40(1)	40(1)	-5(1)	10(1)	7(1)
O(1)	24(2)	38(3)	31(2)	-9(2)	5(2)	-2(2)
O(2)	22(2)	33(2)	26(2)	-2(2)	8(2)	6(2)
O(3)	31(2)	52(3)	31(2)	8(2)	9(2)	13(2)
O(4)	23(2)	26(2)	31(2)	-2(2)	2(2)	2(2)
O(5)	15(2)	43(2)	38(2)	-6(2)	1(2)	-4(2)
C(1)	20(3)	43(4)	42(4)	-15(3)	13(3)	-2(3)
C(2)	29(3)	19(4)	32(3)	-3(3)	11(2)	3(3)
C(3)	19(3)	31(3)	25(3)	-2(2)	7(2)	7(2)
C(4)	27(3)	29(3)	27(4)	-6(3)	4(3)	5(3)
C(5)	19(3)	30(3)	23(3)	2(3)	8(3)	-1(2)
C(6)	16(2)	29(3)	24(3)	2(2)	7(2)	-3(2)
C(7)	21(2)	29(4)	22(3)	5(3)	8(2)	3(2)
C(8)	27(3)	43(3)	18(4)	-3(3)	7(3)	-5(3)
C(9)	21(3)	27(3)	33(4)	0(3)	12(3)	3(2)
C(10)	25(3)	32(3)	26(4)	-1(3)	2(3)	6(3)
C(11)	25(2)	37(3)	21(3)	0(4)	6(2)	-1(3)
C(12)	27(3)	28(4)	27(3)	-3(3)	7(3)	8(3)
C(13)	18(3)	27(3)	36(4)	-4(3)	-1(3)	8(3)
C(14)	21(2)	22(4)	18(3)	-5(2)	-2(2)	-4(2)
C(15)	26(3)	29(3)	33(4)	-1(3)	6(3)	-4(3)
C(16)	51(4)	32(4)	25(4)	4(3)	5(3)	-5(3)
C(17)	36(3)	35(3)	30(3)	3(4)	11(2)	-5(4)
C(18)	28(3)	32(3)	35(4)	-10(3)	10(3)	-6(3)
C(19)	32(3)	23(3)	27(3)	3(3)	7(3)	-4(2)
C(20)	19(3)	24(3)	29(3)	-8(3)	6(3)	2(2)
C(21)	30(3)	30(3)	31(3)	2(4)	14(3)	5(3)
C(22)	25(3)	26(4)	42(3)	-4(3)	12(3)	-11(3)
C(23)	16(3)	30(3)	40(4)	-11(3)	8(3)	-2(2)

C(24)	27(3)	30(3)	32(4)	3(3)	1(3)	2(2)
C(25)	23(3)	32(3)	31(3)	5(2)	6(3)	-5(2)
C(26)	25(3)	44(4)	33(4)	-5(3)	0(3)	5(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for porco41.

	x	y	z	U(eq)
H(26A)	-6837	11311	4926	54
H(26B)	-7489	9232	4253	54
H(26C)	-6221	9607	4451	54
H(11)	780(30)	5420(120)	8190(30)	21(11)
H(12)	-2860(40)	10580(150)	9780(30)	43(13)
H(17)	-4950(40)	5520(150)	12060(30)	54(14)
H(24)	-5010(40)	11220(100)	5590(30)	30(15)
H(2)	-1450(30)	12360(90)	7740(30)	11(12)
H(8)	180(30)	4170(80)	5320(30)	17(13)
H(22)	-5810(40)	4690(100)	6530(30)	27(16)
H(21)	-4260(40)	4710(100)	7580(30)	26(16)
H(10)	1860(40)	2870(100)	7780(30)	36(16)
H(15)	-2600(40)	2950(100)	11140(30)	28(15)
H(13)	-2200(30)	5490(100)	10130(20)	1(11)
H(7)	-990(40)	7140(100)	5600(30)	42(15)
H(3)	-2740(40)	10890(120)	8360(30)	27(14)
H(19)	-4230(40)	9330(90)	10210(30)	32(15)
H(4)	-1320(30)	7680(90)	9330(20)	3(11)
H(25)	-3340(40)	10900(130)	6610(30)	35(14)
H(18)	-5250(40)	9010(100)	11110(30)	30(14)
H(1B)	100(40)	11230(90)	9130(30)	24(13)
H(1A)	-570(40)	14020(120)	9070(30)	53(18)
H(16)	-3540(40)	2580(110)	12020(30)	42(18)