Supporting Information

Synthetic Study on Carthamin. 2. Stereoselective Approach to C-Glycosyl Quinochalcone via Desymmetrization

Taiki Hayashi, Ken Ohmori, Keisuke Suzuki*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

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**General Experimental Procedure**

All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry argon. Ethereal solvents, CH$_2$Cl$_2$ and toluene (anhydrous; Kanto Chemical Co., Inc.) were used as received. BF$_3$·OEt$_2$, i-Pr$_2$NH and MeCN were distilled prior to use according to the standard protocols. ASCA-2 catalyst was purchased from N.E.CHEMCAT Co. Other reagents were used without further purification as received from commercial. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (TLC silica gel 60 F$_{254}$, Art 5715, 0.25 mm) were used. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck silica gel 60 PF$_{254}$ (Art 7747). For flash column chromatography, silica gel 60N (spherical, neutral, 63–210 µm) from Kanto Chemical was used. Higher-accuracy purifications were performed by a Yamazen Smart Flash EPCLC W-Prep 2XY system. Melting point (mp) determinations were performed by using a METTLER TOLEDO MP70 melting point system, and is uncorrected. $^1$H- and $^{13}$C-NMR were measured on a Bruker Avance-III (600 MHz) or a JEOL ECS-400 (400 MHz) spectrometer in the solvent indicated; Chemical shifts (δ) are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane 0.00 ppm or 2.09 ppm for toluene-d$_8$), and coupling constants (J) are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer or a Thermo SCIENTIFIC NICOLET iS5 FTIR spectrometer. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded by using a Perkin-Elmer Spectrum 100 FTIR spectrometer equipped with a universal ATR sampling accessory or a Thermo SCIENTIFIC NICOLET iS5 FTIR spectrometer equipped with a iD5 ATR accessory. Ultraviolet-Visible (UV-Vis) spectra were recorded on a Jasco V-670 spectrophotometer. Elemental analyses were recorded on an Elementar vario MICRO cube analyzer. Optical rotation ([α]$_D$) were measured on a Jasco P-2300 polarimeter. High-resolution mass spectra (HRMS) were obtained with a Bruker Daltonics micrOTOF-QII. Recycling preparative gel permeation chromatography (GPC) was performed using a Japan Analytical Industry LC-918 equipped with SHIMAMURA YRU-880 midget UV/RI detector (EtOAc) or a Japan Analytical Industry LC-9201 equipped with UV-254 UV detector and RI-50s RI detector (CHCl$_3$). X-ray crystallographic data were recorded with a Rigaku R-AXIS RAPID diffractometer.
Molecular sieves 4A (92 g) was placed in a 1 L three-necked round-bottom flask, and dried by heating with a heat gun under vacuum. After cooling to room temperature, the flask was purged with argon and charged with d-glucosyl fluoride 2 (36.7 g, 67.6 mmol, α/β = 15/85), silyl ether 3 (29.2 g, 74.4 mmol) and CH₂Cl₂ (230 mL). To the mixture was added BF₃·OEt₂ (9.20 mL, 74.5 mmol) at −78 °C, and the mixture was allowed to warm to 0 °C over 1.5 h, and stirred for 0.5 h. The reaction was quenched by adding saturated aqueous NaHCO₃. After filtration through a Celite® pad (washed with EtOAc), the mixture was extracted with EtOAc (∗3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 95/5→1/1) to afford crude product. A flask, thoroughly purged with argon, was charged with ASCA2® (16.9 g), to which was added a solution of this crude material in THF/MeOH (1/1, 700 mL). The atmosphere was changed from argon to H₂ (1 atm), and the mixture was stirred for 1 d at room temperature. After changing the atmosphere from H₂ to argon, the mixture was filtered through a Celite® pad (washed with MeOH) and was concentrated in vacuo. To a solution of this crude material in CH₂Cl₂ (490 mL) was added Boc₂O (148 g, 678 mmol) and DMAP (826 mg, 6.76 mmol) at 0 °C. After stirring overnight, the reaction was quenched by adding saturated aqueous NaHCO₃. The mixture was extracted with CH₂Cl₂ (∗3). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 9/1→1/1) to afford crude product. To a solution of this crude material in THF (340 mL) was added AcOH (7.75 mL, 135 mmol) and n-Bu₄NF (1.0 M in THF, 101 mL, 101 mmol) at 0 °C. After stirring for 15 min, the reaction was diluted with water and was extracted with EtOAc (∗3). The combined organic extracts were washed with saturated aqueous NaHCO₃ and brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 75/25→65/35) to afford para-glycoside 4 (22.5 g, 46%) as a white solid and ortho-glycoside 5 (17.7 g, 37%) as a white solid.

4: mp 139–142 °C (acetone/hexane, partially decomposed); [α]D20 +2.2 (c 1.21, CHCl₃); Rf 0.33 (hexane/EtOAc = 6/4); ¹H NMR (600 MHz, CDCl₃) δ 1.24 (s, 9H), 1.43 (s, 9H), 1.44 (s, 9H), 1.48 (s, 9H), 3.72 (s, 3H), 3.75 (s, 3H), 3.80 (m, 1H), 4.15 (dd, 1H, J = 11.8, 2.5 Hz), 4.22 (dd, 1H, J = 11.8, 5.9 Hz), 4.91 (dd, 1H, J = 9.8, 9.5 Hz), 4.99 (d, 1H, J = 10.0 Hz), 5.08 (dd, 1H, J = 9.7, 9.5 Hz), 5.22 (s, 1H), 5.69 (dd, 1H, J = 10.0, 9.7 Hz), 5.96 (s, 1H), 5.965 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 27.4, 27.67, 27.70, 27.73, 55.9, 56.0, 65.7, 71.7, 72.1, 72.3, 75.8, 77.6, 81.8, 82.2, 82.3, 82.9, 91.7, 93.1, 103.9, 151.9, 152.3, 152.6, 153.2, 158.0, 160.0, 161.5; IR (ATR) 3446, 2981, 2940, 1748, 1601, 1504, 1477, 1457, 1433, 1396, 1370, 1272,

5: mp 137–139 °C (Et₂O/hexane, partially decomposed); [α]D²⁰ +7.7 (c 1.02, CHCl₃); Rf 0.60 (hexane/EtOAc = 6/4); ¹H NMR (600 MHz, CDCl₃) δ 1.24 (s, 9H), 1.44 (s, 9H), 1.46 (s, 9H), 1.48 (s, 9H), 3.73 (s, 3H), 3.74 (s, 3H), 3.87 (ddd, 1H, J = 9.7, 4.9, 2.3 Hz), 4.16 (dd, 1H, J = 12.3, 2.3 Hz), 4.35 (dd, 1H, J = 12.3, 4.9 Hz), 5.01 (dd, 1H, J = 9.7, 9.4 Hz), 5.09 (d, 1H, J = 9.5 Hz), 5.12 (dd, 1H, J = 9.5, 8.9 Hz), 5.16 (dd, 1H, J = 9.4, 8.9 Hz), 5.98 (d, 1H, J = 2.2 Hz), 6.11 (d, 1H, J = 2.2 Hz), 7.23 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 27.4, 27.6, 27.65, 27.67, 55.3, 55.8, 64.1, 71.2, 73.0, 74.0, 76.2, 76.5, 82.2, 82.57, 82.60, 83.3, 91.3, 94.8, 101.7, 151.4, 152.0, 152.4, 153.1, 158.2, 158.3, 161.9; IR (ATR) 3432, 2981, 2939, 1747, 1626, 1593, 1506, 1457, 1396, 1370, 1346, 1271, 1249, 1209, 1148, 1098, 1039, 988, 964, 923, 854, 786 cm⁻¹; Anal. Calcd for C₃₄H₅₂O₁₆: C, 56.97; H, 7.31. Found: C, 56.73; H, 7.32; HRMS (ESI-TOF) m/z Calcd for C₃₄H₅₂NaO₁₆ [M+Na]⁺: 739.3148; Found: 739.3138.

Diagnostic HMBC correlations for compound 5

**Synthesis of cyclic carbonate 6 and iodobenzene S1**

To a mixture of PhI(OCOCF₃)₂ (99.0 mg, 0.230 mmol) and NaHCO₃ (44.9 mg, 0.534 mmol) in MeCN (2 mL) was added a solution of phenol 4 (127 mg, 0.177 mmol) in MeCN (3 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃ and 10% aqueous Na₂S₂O₃. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 65/35→44/56) to afford a mixture of 6 and S1 with some impurities, which was further purified by gel permeation chromatography [JAIGEL-2H® (2.0 cm φ×60 cm)+JAIGEL-1H® (2.0 cm φ×60 cm), CHCl₃, flow rate 3.5 mL/min] to afford cyclic carbonate 6 (76.3 mg, 66%) as a white amorphous and iodobenzene S1 (6.8 mg, ca.4%, contaminated with small amount of impurities) as a white amorphous.
$\alpha$D 20 –3.5 (c 1.16, CHCl₃); $R_f$ 0.27 (hexane/EtOAc = 6/4); $^1$H NMR (600 MHz, CDCl₃) $\delta$ 1.45 (s, 9H), 1.47 (s, 9H), 1.50 (s, 9H), 3.78–3.84 (1H, overlapped), 3.79 (s, 3H), 3.82 (s, 3H), 3.97 (dd, 1H, $J = 12.3, 2.5$ Hz), 4.09 (d, 1H, $J = 10.3$ Hz), 4.25 (dd, 1H, $J = 12.3, 4.9$ Hz), 4.77 (dd, 1H, $J = 9.7, 9.5$ Hz), 4.86 (dd, 1H, $J = 10.3, 9.9$ Hz), 5.12 (dd, 1H, $J = 9.9, 9.5$ Hz), 5.52 (s, 1H), 5.53 (s, 1H); $^{13}$C NMR (150 MHz, CDCl₃) $\delta$ 27.58, 27.64, 27.7, 56.6, 56.9, 63.9, 70.7, 71.8, 73.1, 74.6, 76.4, 82.7, 83.6, 83.8, 102.7, 104.0, 146.5, 151.9, 152.0, 152.8, 163.8, 164.4, 185.4; IR (ATR) 2982, 2944, 1786, 1747, 1669, 1640, 1614, 1458, 1396, 1370, 1340, 1275, 1245, 1210, 1152, 1095, 1007, 979, 922, 854, 786 cm⁻¹; HRMS (ESI-TOF) $m/z$ Calcd for C₃₀H₄₂NaO₁₆ [M+Na]$^+$: 681.2365; Found: 681.2346.

$S1$: $R_f$ 0.45 (hexane/THF = 6/4); $^1$H NMR (400 MHz, toluene-d₈, 333 K, contaminated with small amount of impurities) $\delta$ 1.33 (s, 9H), 1.34 (s, 9H), 1.36 (s, 9H), 1.38 (s, 9H), 3.13 (s, 3H), 3.15 (s, 3H), 3.26 (m, 1H), 4.03 (dd, 1H, $J = 11.6, 2.4$ Hz), 4.11 (dd, 1H, $J = 11.6, 7.2$ Hz), 4.53 (d, 1H, $J = 10.0$ Hz), 4.92 (dd, 1H, $J = 9.7, 8.6$ Hz), 5.20 (dd, 1H, $J = 10.0, 8.6$ Hz), 5.40 (s, 1H), 5.60 (s, 1H), 6.92 (d, 2H, $J = 8.8$ Hz), 7.49 (d, 2H, $J = 8.8$ Hz); $^{13}$C NMR (100 MHz, toluene-d₈, 333 K, contaminated with small amount of impurities) $\delta$ 27.7, 27.87 (2C), 27.92, 55.3, 55.4, 56.7, 65.6, 72.5, 73.2, 77.2, 78.5, 79.3, 81.6, 81.7, 82.2, 82.4, 93.1, 102.6, 104.9, 130.8, 137.4, 138.4, 152.0, 153.0, 153.2, 153.6, 170.0, 170.4, 185.5; IR (ATR) 2981, 2939, 1747, 1654, 1627, 1593, 1487, 1457, 1396, 1368, 1209, 1152, 1096, 1038, 982, 964, 917, 852, 813, 784, 723, 710 cm⁻¹; HRMS (ESI-TOF) $m/z$ Calcd for C₄₀H₅₅INaO₁₆ [M+Na]$^+$: 941.2427; Found: 941.2425.

**Diagnostic HMBC correlations for compound S1**

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**Synthesis of cyclic carbonate 6**

To a mixture of C₆F₅I(OCOCF₃)₂ (120 mg, 0.231 mmol) and NaHCO₃ (44.5 mg, 0.530 mmol) in MeCN (2 mL) was added a solution of phenol 4 (127 mg, 0.177 mmol) in MeCN (3 mL) at 0 °C. After stirring for 45 min, the reaction was quenched by adding saturated aqueous NaHCO₃ and 10% aqueous Na₂S₂O₃. The mixture was extracted with EtOAc ($\times$3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel,
hexane/EtOAc = 65/35→44/56) and gel permeation chromatography [JAIGEL-2H® (2.0 cm φ×60 cm)+JAIGEL-1H® (2.0 cm φ×60 cm), CHCl₃, flow rate 3.5 mL/min] to afford cyclic carbonate 6 (88.6 mg, 76%) as a white amorphous.

**Synthesis of bromoquinol 8, 10 and S2**

To a solution of cyclic carbonate 6 (262 mg, 0.398 mmol) in AcOH (4 mL) was added N-bromosaccharin (136 mg, 0.519 mmol) at room temperature. After stirring for 15 min at room temperature, the reaction mixture was diluted with CH₂Cl₂ and water and was extracted with CH₂Cl₂ (∼3). The combined organic extracts were washed with a mixture of saturated aqueous NaHCO₃ and 10% aqueous Na₂S₂O₃. A white precipitate was formed. After filtration through a Celite® pad (washed with CH₂Cl₂), the filtrate was re-extracted with CH₂Cl₂ (∼3). The combined organic extracts were dried (Na₂SO₄), and concentrated in vacuo. To a solution of this crude material in CH₂Cl₂ (2 mL) was added NEt₃ (110 µL, 0.794 mmol) at 0 °C. After stirring for 20 min, the reaction was quenched by adding saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (∼3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 77/23→4/6) to afford bromoquinol 8 (256 mg, 87%) as a white solid, bromoquinol 10 and dibromide S2. Both 10 and S2 contained small amount of impurities. Further purification by PTLC (hexane/Et₂O = 2/8) and by PTLC (CHCl₃/EtOAc = 95/5) gave bromoquinol 10 (1.1 mg, trace) as a colorless oil and dibromide S2 (12.4 mg, 4%) as a white amorphous, respectively.

**8:** mp 165–166 °C (Et₂O/hexane, partially decomposed); [α]D²⁰ −65.7 (c 1.06, CHCl₃); Rf 0.31 (hexane/EtOAc = 7/3); ¹H NMR (600 MHz, CDCl₃) δ 1.44 (s, 9H), 1.46 (s, 9H), 1.50 (s, 9H), 3.80 (dd, 1H, J = 9.8, 4.5, 2.5 Hz), 3.82 (s, 3H), 3.95 (dd, 1H, J = 12.3, 2.5 Hz), 4.09 (d, 1H, J = 10.3 Hz), 4.15 (s, 3H), 4.27 (dd, 1H, J = 12.3, 4.5 Hz), 4.78 (dd, 1H, J = 9.8, 9.5 Hz), 4.84 (dd, 1H, J = 10.3, 9.9 Hz), 5.12 (dd, 1H, J = 9.9, 9.5 Hz), 5.72 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 27.58, 27.64, 27.67, 56.9, 62.7, 63.6, 70.5, 71.2, 73.1, 74.5, 76.4, 81.6, 82.6, 83.7, 83.8, 103.2, 110.8, 146.3, 151.9, 152.0, 152.8, 161.5, 164.5, 178.9; IR (ATR) 2981, 2942, 1790, 1747, 1659, 1610, 1458, 1396, 1371, 1275, 1248, 1237, 1207, 1151, 1096, 1040, 973, 913, 886, 854, 785, 746, 728, 718 cm⁻¹; Anal. Caled for C₃₀H₄₁BrO₁₆·C, 48.86; H, 5.60. Found: C, 48.67; H, 5.50; HRMS (ESI-TOF) m/z Caled for C₃₀H₄₁BrNaO₁₆ [M+Na]⁺: 759.1470; Found: 759.1455.
Diagnostic ROESY correlations for compound 8

10: \([\alpha]_D^{20} +9.5 \text{ (c 0.73, CHCl}_3\); \(R\) \(t\) 0.38 (hexane/EtOAc = 6/4); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 1.44 (s, 9H), 1.47 (s, 9H), 1.51 (s, 9H), 3.83 (ddd, 1H, \(J = 9.8, 5.2, 2.5\) Hz), 3.85 (s, 3H), 4.00 (dd, 1H, \(J = 12.3, 2.5\) Hz), 4.07 (d, 1H, \(J = 10.3\) Hz), 4.17 (s, 3H), 4.27 (dd, 1H, \(J = 12.3, 5.2\) Hz), 4.77 (dd, 1H, \(J = 9.8, 9.5\) Hz), 4.86 (dd, 1H, \(J = 10.3, 9.9\) Hz), 5.12 (dd, 1H, \(J = 9.9, 9.5\) Hz), 5.71 (s, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 27.58, 27.64, 27.7, 57.3, 62.6, 64.0, 70.8, 72.2, 73.3, 74.5, 76.8 (overlapped by a signal of CDCl\(_3\)), 81.2, 82.8, 83.8, 83.9, 101.7, 110.9, 146.2, 151.9, 152.0, 152.7, 161.2, 165.1, 179.0; IR (ATR) 2983, 2947, 1790, 1747, 1659, 1608, 1458, 1396, 1370, 1354, 1274, 1250, 1237, 1206, 1150, 1094, 1058, 1029, 984, 968, 901, 855, 786, 749, 730, 705 \(\text{cm}^{-1}\); HRMS (ESI-TOF) \(m/z\) Calcd for C\(_{30}\)H\(_{41}\)BrNaO\(_{16}\)[M+Na\(^+\): 759.1470; Found: 759.1452.

Bromoquinol 10 was also obtained by other method (see below).
Na$_2$S$_2$O$_3$, dried (Na$_2$SO$_4$), and concentrated in vacuo. Recrystallization of the residue (vapor diffusion, Et$_2$O/pentane) gave single crystal (colorless needles, 2:1 co-crystal of 7 and pentane) of 7 for X-ray diffraction analysis.

**7: ($\alpha$)$_{D}^{20}$= −12.6 (c 0.113, CHCl$_3$); $R_{f}$ 0.41 (hexane/ EtOAc = 6/4); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.44 (s, 9H), 1.46 (s, 9H), 1.49 (s, 9H), 2.08 (s, 3H), 3.69 (s, 3H), 3.78 (ddd, 1H, $J = 9.6, 4.7, 2.5$ Hz), 3.82 (s, 3H), 3.95 (dd, 1H, $J = 12.2, 2.5$ Hz), 4.32 (dd, 1H, $J = 12.2, 4.7$ Hz), 4.40 (d, 1H, $J = 10.3$ Hz), 4.47 (dd, 1H, $J = 10.3, 9.7$ Hz), 4.77 (dd, 1H, $J = 9.6, 9.3$ Hz), 5.17 (dd, 1H, $J = 9.7, 9.3$ Hz), 5.29 (s, 1H), 5.56 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 22.3, 27.6, 27.6, 27.6, 43.7, 54.3, 57.2, 63.7, 69.9, 71.1, 73.5, 74.4, 75.9, 82.4, 83.6 (2C), 85.2, 103.4, 104.6, 146.4, 152.01, 152.03, 152.9, 166.8, 168.0, 187.0; IR (ATR) 2981, 2946, 1791, 1748, 1675, 1623, 1458, 1396, 1370, 1348, 1288, 1275, 1251, 1222, 1206, 1153, 1114, 1096, 1038, 1013, 978, 924, 899, 855, 786, 762, 739, 726, 713 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ Calcd for C$_{32}$H$_{45}$BrNaO$_{18}$ [M+Na$^+$]: 819.1682; Found: 819.1654.

**Synthesis of bromide 9**

To a solution of phenol 4 (36.7 mg, 0.0512 mmol) in CH$_2$Cl$_2$ (2 mL) was added N-bromosuccinimide (9.1 mg, 0.051 mmol) at 0 °C. After stirring for 15 min, the reaction mixture was quenched by adding saturated aqueous NaHCO$_3$ and 10% aqueous Na$_2$S$_2$O$_3$. The mixture was extracted with EtOAc ($\times$3). The combined organic extracts were washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by PTLC (CHCl$_3$/EtOAc = 9/1) to afford bromophenol 9 (34.9 mg, 86%) as a white amorphous.

**9: ($\alpha$)$_{D}^{20}$= +4.63 (c 1.05, CHCl$_3$); $R_{f}$ 0.50 (hexane/EtOAc = 6/4); $^1$H NMR (600 MHz, CDCl$_3$, ratio of rotamers = 55/45, signals for the minor rotamer are marked with an asterisk) $\delta$ 1.22 (s, 9H+9H*), 1.40–1.47 (18H+18H*, overlapped), 1.48 (s, 9H+9H*), 3.76* (s, 3H), 3.79–3.84 (1H+1H*, overlapped), 4.28* (dd, 1H, $J = 11.5, 4.6$ Hz), 4.78 (d, 1H, $J = 10.0$ Hz), 4.89–4.96 (1H+1H*, overlapped), 5.00* (d, 1H, $J = 9.8$ Hz), 5.08 (dd, 1H, $J = 9.7, 9.5$ Hz), 5.10* (dd, 1H, $J = 9.7, 9.6$ Hz), 5.56* (dd, 1H, $J = 9.8, 9.6$ Hz), 5.66 (s, 1H), 5.68* (s, 1H), 5.73 (dd, 1H, $J = 10.0, 9.7$ Hz), 6.36* (s, 1H), 6.41 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$, ratio of rotamers = 55/45, discernible signals for the minor rotamer are marked with an asterisk, several signals are missing, possibly due to overlapping) $\delta$ 27.3, 27.6, 27.7, 56.2*, 56.3, 62.3, 62.6*, 65.1*, 65.4, 71.5*, 71.7, 72.0, 73.3*, 73.5, 75.8*, 76.0, 77.4, 81.9, 82.1, 82.2, 82.3*, 82.4, 83.0, 94.8*, 96.3, 96.6, 98.0*, 111.0, 111.9*, 151.4*, 151.8, 152.2*, 152.3, 152.6 (C+C*), 153.1, 153.2*, 154.4*, 154.5, 157.3, 158.7* (2C*), 160.6; IR (ATR) 3451, 2982, 2941, 1747, 1601, 1583, 1458, 1420, 1396, 1369, 1272, 1249, 1153, 1099, 1039, 990,
963, 932, 919, 853, 787, 767, 732 cm⁻¹; HRMS (ESI-TOF) m/z Calcd for C₃₄H₅₁BrNaO₁₆ [M+Na]⁺: 817.2253; Found: 817.2234.

**Synthesis of bromoquinol 8 and 10**

To a mixture of bromophenol 9 (66.1 mg, 0.0831 mmol) and NaHCO₃ (41.9 mg, 0.499 mmol) in MeCN (3 mL) was added PhI(OOCOCF₃)₂ (89.4 mg, 0.208 mmol) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was quenched by adding saturated aqueous NaHCO₃ and 10% aqueous Na₂S₂O₃. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 6/4) to afford bromoquinol 10 (17.4 mg, 28%) as a white amorphous, along with some mixed fractions including bromoquinol 8. Further purification by PTLC (CHCl₃/EtOAc = 95/5) gave bromoquinol 8 (21.4 mg, 35%) as a white solid.

**Synthesis of ether 12**

To a suspension of bromoquinol 8 (2.65 g, 3.59 mmol) in MeOH (90 mL) was added K₂CO₃ (1.49 g, 10.8 mmol) at 0 °C. After stirring for 45 min, the reaction was quenched by adding saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. This crude material, including diol 11 and ether 12 (the ratio was 28/72, which was analyzed by ¹H NMR), was azeotropically dried with toluene (×2). To a mixture of the crude material and dried Molecular sieves 4Å (3.4 g) in CH₂Cl₂ (18 mL) was added DBU (804 µL, 5.39 mmol) at 0 °C. After stirring for 20 min at room temperature, the mixture was diluted with EtOAc. After filtration through a Celite® pad (washed with EtOAc), saturated aqueous NH₄Cl was added to the filtrate and the mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, toluene/acetone = 85/15) to afford ether 12 (2.33 g, 96%) as a white amorphous.
12: [α]D^20 +58.1 (c 1.03, CHCl₃); Rf 0.55 (CH₂Cl₂/Et₂O = 8/2); ^1H NMR (600 MHz, CDCl₃) δ 1.48 (s, 9H), 1.49 (s, 9H), 1.51 (s, 9H), 1.77 (d, 1H, J = 9.2 Hz), 3.78 (s, 3H), 3.99 (ddd, 1H, J = 9.7, 4.5, 2.5 Hz), 4.17 (dd, 1H, J = 12.4, 2.5 Hz), 4.37 (dd, 1H, J = 12.4, 4.5 Hz), 4.76 (dd, 1H, J = 10.4, 9.2 Hz), 4.90 (dd, 1H, J = 9.7, 8.7 Hz), 5.24 (dd, 1H, J = 10.4, 8.7 Hz), 5.51 (s, 1H); ^13C NMR (150 MHz, CDCl₃) δ 27.6, 27.66, 27.73, 56.8, 64.2, 71.7, 72.7, 75.7, 78.4, 80.2, 80.4, 82.7, 83.5, 83.8, 86.4, 98.2, 101.0, 151.9, 152.1, 153.0, 167.3, 168.0, 180.9; IR (ATR) 3184, 2982, 2941, 1748, 1676, 1603, 1459, 1396, 1370, 1356, 1292, 1275, 1241, 1230, 1158, 1131, 1111, 1096, 1074, 1053, 1002, 976, 954, 942, 918, 906, 849, 786, 779, 747, 720 cm⁻¹; Anal. Calcd for C₂₈H₃₉BrO₁₄: C, 49.49; H, 5.79. Found: C, 49.30; H, 5.75; HRMS (ESI-TOF) m/z Calcd for C₂₈H₃₉BrNaO₁₄ [M+Na]^+: 701.1415; Found: 701.1408.

Diagnostic NOESY correlations for compound 12

Analytical sample of 11 was obtained by the following procedure.

To a suspension of bromoquinol 8 (7.1 mg, 9.6 µmol) in MeOH (1 mL) was added K₂CO₃ (4.5 mg, 33 µmol) at 0 °C. After stirring for 2 h, the reaction was quenched by adding saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (silica gel, CH₂Cl₂/Et₂O = 8/2) to afford diol 11 (2.3 mg, 34%) as a colorless oil and ether 12 (4.2 mg, 64%) as a white amorphous.

11: [α]D^20 +36 (c 0.30, CHCl₃); Rf 0.45 (CH₂Cl₂/Et₂O = 8/2); ^1H NMR (600 MHz, CDCl₃) δ 1.45 (s, 9H), 1.46 (s, 9H), 1.48 (s, 9H), 3.65 (ddd, 1H, J = 9.7, 6.1, 2.4 Hz), 3.70 (d, 1H, J = 3.8 Hz), 3.81 (s, 3H), 3.84 (d, 1H, J = 9.8 Hz), 3.97 (dd, 1H, J = 12.0, 2.4 Hz), 4.10 (ddd, 1H, J = 9.8, 9.4, 3.8 Hz), 4.13 (s, 3H), 4.14 (dd, 1H, J = 12.0, 6.1 Hz), 4.67 (dd, 1H, J = 9.7, 9.2 Hz), 4.78 (dd, 1H, J = 9.4, 9.2 Hz), 4.80 (s, 1H), 5.65 (s, 1H); ^13C NMR (150 MHz, CDCl₃) δ 27.60, 27.63, 27.7, 56.8, 64.2, 70.6, 71.2, 75.9, 77.5, 78.1, 79.9, 82.4, 83.4, 83.9, 101.8, 110.8, 152.0, 153.0, 154.2, 165.7, 169.7, 180.5; IR (neat) 3383, 2982, 2941, 1748, 1676, 1603, 1459, 1370, 1356, 1292, 1275, 1241, 1230, 1158, 1131, 1111, 1096, 1074, 1053, 1002, 976, 954, 942, 918, 906, 849, 786, 779, 747, 720 cm⁻¹; HRMS (ESI-TOF) m/z Calcd for C₂₉H₄₃BrNaO₁₅ [M+Na]^+: 733.1678; Found: 733.1658.
A mixture of ether 12 (1.46 g, 2.15 mmol), Pd(PhCN)₂Cl₂ (82.5 mg, 0.215 mmol), t-Bu₃PH·BF₄ (143 mg, 0.493 mmol) and Cul (61.4 mg, 0.322 mmol) was dissolved in MeCN/i-Pr₂NH (19/1, 20 mL, degassed by purging with argon under sonication). Trimethylsilylacetylene (0.75 mL, 5.4 mmol) was added to the mixture at room temperature. After stirring for 1 d, Florisil (3.1 g) was added to the mixture and the reaction mixture was stirring for 2 h under air. After filtration through a Celite ™ pad (washed with EtOAc), the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 53/47 → 32/68) to afford crude product including silane S₃. To a solution of this crude material in THF (14 mL) was added AcOH (246 µL, 4.30 mmol) and n-Bu₄NF (1.0 M in THF, 3.2 mL, 3.2 mmol) at room temperature. After stirring for 30 min, the reaction mixture was diluted with water at 0 °C and was extracted with EtOAc (×3). The combined organic extracts were washed with saturated aqueous NaHCO₃ and brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 53/47 → 32/68) and PTLC (hexane/acetone = 6/4) to afford alkyne 13 (1.17 g, 87%) as a white amorphous.

13: [α]D₂₀ +36.7 (c 1.06, CHCl₃); Rₚ 0.39 (hexane/EtOAc = 4/6); ¹H NMR (600 MHz, CDCl₃) δ 1.48 (s, 9H), 1.49 (s, 9H), 1.50 (s, 9H), 3.36 (s, 1H), 3.73 (brs, 1H), 3.75 (d, 1H, J = 9.2 Hz), 3.77 (s, 3H), 3.99 (ddd, 1H, J = 9.7, 4.4, 2.5 Hz), 4.17 (dd, 1H, J = 12.4, 2.5 Hz), 4.37 (dd, 1H, J = 12.4, 4.4 Hz), 4.78 (dd, 1H, J = 10.5, 9.2 Hz), 4.90 (dd, 1H, J = 9.7, 8.7 Hz), 5.25 (dd, 1H, J = 10.5, 8.7 Hz), 5.44 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 27.60, 27.64, 27.7, 56.7, 64.2, 71.2, 71.9, 72.5, 75.6, 78.3, 80.1, 80.4, 82.7, 83.4, 83.8, 86.5, 99.2, 101.3, 151.9, 152.1, 153.0, 167.9, 173.9, 184.6; IR (ATR) 3284, 2982, 2941, 1747, 1667, 1634, 1612, 1457, 1396, 1370, 1277, 1250, 1238, 1153, 1099, 1050, 1009, 974, 947, 922, 851, 786, 770, 749, 729, 712 cm⁻¹; HRMS (ESI-TOF) m/z Calcd for C₃₀H₄₁O₁₄ [M+H⁺]: 625.2491; Found: 625.2471.

**Synthesis of nitrone 14**

A solution of aldehyde S₄ (4.48 g, 20.2 mmol) in EtOH/H₂O (1/1, 90 mL) was added NaOAc (2.49 g, 30.4 mmol) and CH₃NH₂·HCl (2.19 g, 26.2 mmol) at room temperature. After stirring for 75 min, the mixture was concentrated in vacuo. The residue was dissolved in CH₂Cl₂ and water. The mixture was extracted with
CH₂Cl₂ (×3), dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/acetone = 1/1→4/6) to afford nitron 14 (4.71 g, 93%) as a white solid. 14: mp 101–102 °C; Rf 0.30 (hexane/acetone = 1/1); ¹H NMR (600 MHz, CDCl₃) δ 1.56 (s, 9H), 3.89 (s, 3H), 7.24 (d, 2H, J = 8.8 Hz), 7.37 (s, 1H), 8.26 (d, 2H, J = 8.8 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 27.7, 54.3, 83.9, 121.2, 128.0, 129.7, 134.2, 151.3, 152.0; IR (ATR) 3098, 3043, 3007, 2979, 2936, 1758, 1716, 1602, 1576, 1500, 1479, 1454, 1431, 1407, 1395, 1370, 1311, 1253, 1225, 1211, 1175, 1137, 1045, 1012, 966, 947, 896, 871, 855, 812, 778, 747, 703 cm⁻¹; Anal. Calcd for C₁₃H₁₈N₂O₄: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.03; H, 6.62; N, 5.73; HRMS (ESI-TOF) m/z Calcd for C₁₃H₁₈N₂O₄ [M+H]+: 252.1230; Found: 252.1228.

Diagnostic NOE correlations for compound 14

**Synthesis of hydroxyamine 15**

To a solution of alkyne 13 (2.11 g, 3.38 mmol) and nitron 14 (1.10 g, 4.38 mmol) in toluene (28 mL) was added ZnEt₂ (0.86 M in hexane, 9.8 mL, 8.43 mmol) at room temperature. After stirring for 4 h, the reaction was quenched by adding saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 4/6→1/9) to afford hydroxyamine 15 (2.26 g, 76%, diastereomixture) as a white amorphous.

15: Rf 0.30 (hexane/EtOAc = 3/7); ¹H NMR (600 MHz, CDCl₃, diastereomixture, signals for the minor diastereomer are marked with an asterisk) δ 1.44 (s, 9H+9H*), 1.48 (s, 9H+9H*), 1.49 (s, 9H+9H*), 1.55 (s, 9H+9H*), 1.56 (s, 9H+9H*), 1.86 (s, 3H+3H*), 3.58–4.08 (br, 1H+1H*), 3.75–3.80 (1H+1H*, overlapped), 3.77 (s, 3H+3H*), 3.99 (m, 1H+1H*), 4.17 (dd, 1H+1H*, J = 12.3, 2.0 Hz), 4.38 (dd, 1H+1H*, J = 12.3, 4.4 Hz), 4.67–5.28 (br, 2H+2H*), 4.78 (dd, 1H+1H*, J = 10.1, 9.5 Hz), 4.90 (dd, 1H+1H*, J = 9.4, 9.2 Hz), 5.21–5.27 (1H+1H*, overlapped), 5.429 (s, 1H), 5.433* (s, 1H), 7.14* (d, 2H, J = 8.5 Hz), 7.15 (d, 2H, J = 8.4 Hz), 7.60* (d, 2H, J = 8.5 Hz), 7.61 (d, 2H, J = 8.4 Hz); ¹³C NMR (150 MHz, CDCl₃, diastereomixture, discernible signals for the minor diastereomer are marked with an asterisk, several signals are missing, 252.1228.
possibly due to overlapping) δ 27.6, 27.68, 27.72, 45 (very broad), 56.7, 64.29*, 64.32, 65.6*, 65.7, 71.2, 71.8, 75.7, 78.0 (br), 78.3, 80.2, 80.36*, 80.38, 82.7, 83.2, 83.3*, 83.4, 83.72, 83.74*, 93.5, 93.6*, 99.79, 99.81*, 101.4, 121.09*, 121.11, 129.9*, 130.0, 134.3 (br), 150.78*, 150.80, 151.71, 151.72, 151.9, 152.1, 153.0, 167.9*, 168.0, 172.7*, 172.8, 184.5*, 184.6; IR (ATR) 3308, 2982, 2939, 1748, 1668, 1613, 1508, 1476, 1457, 1396, 1370, 1275, 1251, 1144, 1098, 1076, 1052, 1017, 974, 949, 918, 896, 850, 784, 739 cm⁻¹; HRMS (ESI-TOF) m/z Calcd for C₄₃H₅₈N₈O₁₈ [M+H]⁺: 876.3648; Found: 876.3623.

**Synthesis of triketone 18**

Molecular sieves 4A (4.25 g) was placed in a 300 mL three-necked round-bottom flask, and dried by heating with a heat gun under vacuum. After cooling to room temperature, the flask was purged with argon and charged with hydroxyamine 15 (2.25 g, 2.57 mmol, diastereomixture), NEt₃ (1.07 mL, 7.72 mmol) and CH₂Cl₂ (85 mL). To the mixture was added AgOTf (132 mg, 0.514 mmol) at room temperature, and the mixture was stirred for 1 h. The reaction was quenched by adding saturated aqueous NaHCO₃. After filtration through a Celite® pad (washed with EtOAc), the filtrate was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 49/51→28/72) to afford crude material of isoaxazoline 16 (1.89 g). Diastereomer ratio of 16 was analyzed by ¹H NMR (more polar/less polar = 65/35). To a mixture of this crude material and cyclohexene (219 µL, 2.16 mmol) in CH₂Cl₂ (85 mL) at 0 °C was added dimethyldioxirane (0.074 M in acetone, 32 mL, 2.4 mmol) dropwise over 20 min. After further stirring for 10 min, the mixture was concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 36/64→15/85) to afford crude material of quinohalcone 17 (1.16 g). E/Z ratio of 17 was analyzed by ¹H NMR (E/Z = 96/4). To a solution of this crude material in CH₂Cl₂ (46 mL) was added TsOH·H₂O (391 mg, 2.06 mmol) at 0 °C. After stirring for 15 min, the reaction was quenched by adding saturated aqueous NH₄Cl. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/acetone = 7/3) and Smart Flash EPCLC
W-Prep 2XY system (ULTRA PACK, DIOL-40B, hexane/EtOAc = 6/4) to afford triketone 18 (891 mg, 40%) as a yellow solid.

18: mp 164–165 °C (hexane/acetone, partially decomposed); [α]_D^{20} –238 (c 1.01, CHCl₃); Rₐ 0.47 (hexane/acetone = 6/4); ¹H NMR (600 MHz, CDCl₃) δ 1.41 (s, 9H), 1.44 (s, 9H), 1.47 (s, 9H), 1.57 (s, 9H), 3.44 (d, 1H, J = 9.5 Hz), 3.59 (d, 1H, J = 2.0 Hz), 3.62 (dd, 1H, J = 9.9, 6.6 Hz), 3.90 (s, 3H), 3.92 (dd, 1H, J = 9.5, 2.0 Hz), 3.98 (dd, 1H, J = 11.8, 6.6 Hz), 4.00 (dd, 1H, J = 9.9, 3.2 Hz), 4.03 (s, 1H), 4.53 (s, 1H), 4.59 (dd, 1H, J = 9.9, 9.8 Hz), 4.84 (dd, 1H, J = 9.8, 9.4 Hz), 5.55 (s, 1H), 7.23 (d, 2H, J = 8.6 Hz), 7.65 (d, 2H, J = 8.6 Hz), 7.91 (d, 1H, J = 15.8 Hz), 7.97 (d, 1H, J = 15.8 Hz), 18.20 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 27.6, 27.7 (3C), 57.0, 65.4, 70.1, 71.1, 75.5, 78.75, 78.78, 82.2, 82.97, 82.98, 83.2, 84.0, 100.5, 106.2, 121.3, 121.8, 130.1, 132.4, 144.3, 151.2, 152.2, 153.0, 153.1, 153.2, 170.4, 183.5, 192.1, 193.9; IR (ATR) 3462, 2982, 2939, 1748, 1662, 1625, 1601, 1585, 1525, 1507, 1456, 1428, 1396, 1369, 1348, 1274, 1252, 1227, 1141, 1005, 1039, 1016, 974, 920, 894, 856, 839, 784, 751, 739 cm⁻¹; Anal. Calcd for C₄₂H₅₆O₁₉: C, 58.33; H, 6.53. Found: C, 58.11; H, 6.51; HRMS (ESI-TOF) m/z Calcd for C₄₂H₅₆NaO₁₉ [M+Na⁺]: 887.3308; Found: 887.3284; UV-Vis (MeCN) 236, 377 nm.

Analytical sample of 16 (less polar and more polar) was obtained by following procedure.

Molecular sieves 4A (125 mg) was placed in a 30 mL two-necked round-bottom flask, and dried by heating with a heat gun under vacuum. After cooling to room temperature, the flask was purged with argon and charged with hydroxyamine 15 (66.5 mg, 0.0759 mmol, diastereomixture), NEt₃ (31.6 µL, 0.228 mmol) and CH₂Cl₂ (2.5 mL). To the mixture was added AgOTf (3.9 mg, 0.015 mmol) at room temperature, and the mixture was stirred for 1 h. The reaction was quenched by adding saturated aqueous NaHCO₃. After filtration through a Celite® pad (washed with EtOAc), the filtrate was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (CHCl₃/acetone = 8/2) to afford isoxazoline 16 (15.9 mg, 24%, less polar) as a yellow solid and isoxazoline 16 (20.7 mg, 31%, more polar) as a yellow solid.

16 (less polar): mp 118–126 °C (partially decomposed); [α]_D^{20} –90.1 (c 0.520, acetone); Rₐ 0.48 (CHCl₃/acetone = 8/2); ¹H NMR (600 MHz, acetone-d₆) δ 1.48 (s, 27H), 1.52 (s, 9H), 2.81 (s, 3H), 3.79 (s, 3H), 4.10 (m, 1H), 4.14 (dd, 1H, J = 12.3, 2.6 Hz), 4.17 (d, 1H, J = 9.2 Hz), 4.33 (dd, 1H, J = 12.3, 4.0 Hz), 4.74 (dd, 1H, J = 10.3, 9.2 Hz), 4.80 (d, 1H, J = 2.8 Hz), 4.93 (dd, 1H, J = 9.7, 9.1 Hz), 5.36 (dd, 1H, J = 10.3, 9.1 Hz), 5.40 (s, 1H), 5.52 (d, 1H, J = 2.8 Hz), 6.12 (s, 1H), 7.12 (d, 2H, J = 8.6 Hz), 7.41 (d, 2H, J =...
Analytical sample of 17 was obtained by following procedure.

To a solution of isoxazoline 16 [15.1 mg, 0.0172 mmol, diasteremoer ratio (more palar/less polar) = 6/4] in CH₂Cl₂ (1 mL) at 0 °C was added dimethyldioxirane (0.075 M in acetone, 0.34 mL, 0.026 mmol) dropwise over 20 min. After further stirring for 10 min, the reaction mixture was quenched by adding saturated aqueous NaHCO₃ and 10% aqueous Na₂S₂O₃. The mixture was extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 6/4→4/6) and Smart Flash EPCLC W-Prep 2XY system (ULTRA PACK, DIOL-40A, hexane/EtOAc = 4/6) to afford quinochalcone 17 (4.9 mg, 34%, E/Z = 95/5) as a white amorphous.
1275, 1252, 1227, 1140, 1074, 1051, 1017, 975, 964, 948, 922, 893, 851, 784, 749 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ Calcd for C$_{42}$H$_{55}$O$_{18}$ [M+H]$^+$: 847.3383; Found: 847.3361; UV-Vis (MeCN) 232, 246, 304 nm.
References


 Compound 4 (\(^1\)H NMR, 600 MHz, CDCl\(_3\))

Current Data Parameters
NAME    DH1-1922-pr4-recry
EXPNO    10
PROCNO  1

F2 - Acquisition Parameters
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PULPROG zg30
TD       65536
SOLVENT CDCl3
MS       16
DS       2
SNR     12019.230 Hz
FIDRES  0.183399 Hz
AQ       2.7262976 sec
RG       31.94
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TE       10.00 usec
D1         298.0 K
D1   1.00000000 sec
TDD      1

======== CHANNEL f1 ========
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D1                1.00000000 sec
TE                298.0 K
DE                10.00 usec
AQ       2.7262976 sec
FIDRES  0.183399 Hz
AQ       2.7262976 sec
FIDRES  0.183399 Hz

F2 - Processing parameters
SI       65536
SF      600.1337060 MHz
WON     EM
LSB      0
LB       0.30 Hz
CB      0
PC       1.00
Compound 4 (\(^{13}\)C NMR, 150 MHz, CDCl\(_3\))
Compound 5 (\(^1\)H NMR, 600 MHz, CDCl\(_3\)
Compound 5 ($^{13}$C NMR, 150 MHz, CDCl$_3$)
Compound 6 (\(^1\)H NMR, 600 MHz, CDCl\(_3\))

Current Data Parameters
NAME  DH1-2036-pr3-non
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
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PRGBHD  5 mm CPMG BBO B4
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MS  16
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SNR  12019.230 Hz
FIDRES  0.183399 Hz
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RG  31.94
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TE  10.00 usec
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D1  1.0000000 sec
TDO  1

======== CHANNEL f1 ========
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FIDRES  0.183399 Hz
SWH  12019.230 Hz
DS  2
NS  16
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PULPROG  zg30
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INSTRUM  spect
Time  14:41
Date_  20150609

F2 - Processing parameters
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WDW  EM
LSB  0
GB  0
PC  1.00

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O
BocO
OBoc
BocO
OMe

O
MeO
Compound 6 ($^{13}$C NMR, 150 MHz, CDCl$_3$)
Compound S1 (\textsuperscript{1}H NMR, 400 MHz, toluene-\textit{d}_8, 333 K, contaminated with small amount of impurities)
Compound S1 (\(^{13}\)C NMR, 100 MHz, toluene-\(\text{d}_8\), 333 K, contaminated with small amount of impurities)
Compound 7 (\(^1\)H NMR, 600 MHz, CDCl\(_3\))
Compound 8 (1H NMR, 600 MHz, CDCl₃)

Current Data Parameters
NAME   DH1-1944-pr3-recry
EXPNO  10
PROCNO 1

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BG    31.94
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DE    10.00 use
TE   298.0 K
D1   1.000000 sec
TDS   1

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PLW1  23.00000000 W

F2 - Processing parameters
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SF   600.1300151 MHz
WDW   EM
ESR   0
LB     0.30 Hz
GB   0
PC    1.00

8

O
BocO
BocO
BocO
OMe
OMe
MeO
O
Br
Compound 8 ($^{13}$C NMR, 150 MHz, CDCl$_3$)

Current Data Parameters
NAME  DH1-1944-pr3-recry
EXPNO  11
PROCNO 1

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PULPROG  zgpg30
TD  35536
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DS  4
DM  36057.69 Hz
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RG  175.56
DM  13.867 usec
SE  18.00 usec
TE  298.0 K
D1  2.00000000 sec
DII  0.03000000 sec
TDII  1

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NUC1  1H
P1  10.00 usec
PLW1  70.00000000 W

----------- CHANNEL f2 -----------
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NUC2  13C
CPDPRG2  waltz16
PCPD2  70.00 usec
PLW2  26.00000000 W
PLW12  0.76407999 W
PLW13  0.37439999 W

F2 - Processing parameters
SL  1
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NOW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
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Compound 10 ($^1$H NMR, 600 MHz, CDCl$_3$)
Compound 10 ($^{13}$C NMR, 150 MHz, CDCl$_3$)

Current Data Parameters
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EXPNO    30
PROCNO   1

F2 - Acquisition Parameters
Data_    20160916
Time     5.13
INSTRUM  spect
PROBHD   5 mm CPPBBO BB
PULPROG  zgpg30
TD       5536
SOLVENT  CDCl$_3$
NS       2560
DS       4

--- CHANNEL f2 ---
SF01     150.9178981 MHz
NUC1     1H
P1       10.00 usec
PLW1     70.00000000 W

 --- CHANNEL f2 ---
SF02     600.1324005 MHz
NUC2     13C
CPDPRG2  waltz16
PCPD2    70.00 usec
PLW2     26.00000000 W
PLW12    0.76407999 W
PLW13    0.37439999 W

F2 - Processing parameters
SI       12768
SF       150.9028129 MHz
NOW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40

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Compound 10 (NOE, 600 MHz, CDCl₃)
Compound S2 (¹H NMR, 600 MHz, CDCl₃)
Compound S2 ($^{13}$C NMR, 150 MHz, CDCl$_3$)
Compound 9 (¹H NMR, 600 MHz, CDCl₃, ratio of rotamers = 55/45)
Compound 9 (\(^{13}\)C NMR, 150 MHz, CDCl\(_3\), ratio of rotamers = 55/45)
Compound 11 (1H NMR, 600 MHz, CDCl₃)
Compound 11 (\textsuperscript{13}C NMR, 150 MHz, CDCl\textsubscript{3})
Compound 12 (\(^1\)H NMR, 600 MHz, CDCl\(_3\))

Current Data Parameters
NAME  DH1-1984-pr2-non
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
Data_  20150501
Time  18.18
INSTRUM  spect
PROBHD  5 mm CPPro B8
PULPROG  zg30
TD  65536
SOLVENT  CDCl3
NS  16
DS  2
DM  12019.230 Hz
FIDRES  0.183399 Hz
AQ  2.7262976 sec
BG  31.94
SN  41.800 use
SE  10.00 use
TE  300.0 K
D1  1.0000000 sec
TDS  1

****** CHANNEL f1 ******
SP01  600.133760 MHz
NUC1  1H
P1  12.00 use
PLW1  23.00000000 W

F2 - Processing parameters
ST  65536
SF  600.1300162 MHz
WOW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Compound 12 (\(^{13}\)C NMR, 150 MHz, CDCl\(_3\))
Compound 13 ($^1$H NMR, 600 MHz, CDCl$_3$)
Compound 13 ($^{13}$C NMR, 150 MHz, CDCl$_3$)
Compound 14 (\(^1\)H NMR, 600 MHz, CDCl\(_3\))

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Current Data Parameters
- **NAME**: DHI-2020-pr1-non
- **EXPNO**: 10
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Data**: 20150528
- **Time**: 2.27
- **INSTRUM**: spect
- **PROBH**: 5 mm CPPBBO BB
- **PULPROG**: zg30
- **TD**: 85536
- **SOLVENT**: CDCl\(_3\)
- **NS**: 16
- **DS**: 2
- **BW**: 12019.230 Hz
- **FIDRES**: 0.183399 Hz
- **AQ**: 2.7262976 sec
- **RG**: 31.94
- **DM**: 41.800 use
- **DE**: 10.00 use
- **TE**: 291.5 K
- **D1**: 1.0000000 sec
- **TDS**: 1

**F2 - Processing Parameters**
- **SI**: 65536
- **SF**: 600.133706 MHz
- **WDF**: EM
- **ESB**: 0
- **LB**: 0.30 Hz
- **GB**: 0
- **PC**: 1.00

---

Me

N

\(\text{OBoc}^{+}\)

14
Compound 14 (\textsuperscript{13}C NMR, 150 MHz, CDCl\textsubscript{3})
Compound 15 (\(^1\)H NMR, 600 MHz, CDCl\(_3\), diastereomixture)
Compound 15 ($^{13}$C NMR, 150 MHz, CDCl$_3$, diastereomixture)

Current Data Parameters
NAME DH1-2310-re2-13c
EXPN0 20
PROCNO 1

F2 - Acquisition Parameters
Data_ 2016092
Time 8.09
INSTRUM spect
PRBBD 5 mm CPPBBO BR
PULPAC zgpg30
TD 65536
SOLVENT CDCl$_3$
NS 6144
DS 4
ANW 36057.69 Hz
FIDRES 0.550197 Hz
AQ 0.9087659 sec
BG 175.56
Sm 13.867 use
SE 18.00 use
TE 298.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

F1 - Acquisition Parameters
SFO1 150.917898 MHz
NUC1 1H
F1 100.00 use
PLW1 70.0000000 W

F1 - Processing parameters
SI 12746
SF 150.9028118 MHz
WDM EM
SSB 0
LD 1.00 Hz
GB 0
PC 1.40

(diastereomixture)
Compound 16 (¹H NMR, 600 MHz, acetone-<i>d</i><sub>6</sub>, less polar)

<table>
<thead>
<tr>
<th>Compound</th>
<th>16</th>
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</thead>
<tbody>
<tr>
<td>Description</td>
<td>1H NMR, 600 MHz, acetone-&lt;i&gt;d&lt;/i&gt;&lt;sub&gt;6&lt;/sub&gt;, less polar</td>
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Current Data Parameters
- NAME: DH1-2569-prl-non
- EXPNO: 10
- PROCNO: 1
- F2 - Acquisition Parameters
  - Data_020160903
  - Time: 16.07
  - INSTRUM: spect
  - PROBHD: 5 mm CPPBB8 BB
  - PULPROG: zg30
  - TD: 65536
  - SOLVENT: Acetone
- NS: 16
- DS: 2
- DM: 12019.2 Hz
- FIDRES: 0.183399 Hz
- AQ: 2.7262976 sec
- RG: 17.5
- DM: 41.800 usec
- DE: 10.000 usec
- TE: 298.0 K
- D1: 1.000000000 sec
- TDS: 1

F2 - Processing Parameters
- SI: 65536
- SF: 600.1330128 MHz
- WDM: EM
- ESB: 0
- LB: 0.30 Hz
- GB: 0
- PC: 1.00
Compound 16 (\(^1^3\)C NMR, 150 MHz, acetone-\(d_6\), less polar)

![NMR spectrum of compound 16](image)
Compound 16 (\(^1\)H NMR, 600 MHz, acetone-\(d_6\), more polar)
Compound 16 ($^{13}$C NMR, 150 MHz, acetone-$d_6$, more polar)
Compound 17 (\(^1\)H NMR, 600 MHz, CDCl\(_3\), ratio of E/Z isomers = 95/5)
Compound 17 ($^{13}$C NMR, 150 MHz, CDCl$_3$, ratio of E/Z isomers = 95/5)
Compound 18 (\(^1\)H NMR, 600 MHz, CDCl\(_3\))
Compound 18 ($^{13}$C NMR, 150 MHz, CDCl$_3$)
Compound 18 (HMBC, CDCl₃)