SUPPORTING INFORMATION

Catalytic, Highly Enantio- and Diastereoselective Pinacol Coupling Reaction with A New Tethered Bis(8-Quinolinolato) (TBOx) Ligand

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Experimental Section.

General Procedures.

All reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin-layer chromatography using Whatman pre-coated silica gel flexible plates (0.25 mm) with F₂₅₄ indicator or Merck pre-coated silica gel plates with F₂₅₄ indicator. Visualization was accomplished by UV light (256 nm), with combination of potassium permanganate and/or phosphomolybdic acid, solution as an indicator. Flash column chromatography was performed according to the method of Still using silica gel 60 (mesh 230-400) supplied by E. Merck. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted.

Commercial grade reagents and solvents were used without further purification except as indicated below. Liquid aldehydes and chlorosilanes were freshly distilled under an atmosphere of dry argon, and solid aldehydes were purified by flash chromatography on silica gel. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl under an atmosphere of dry argon. Dichloromethane (CH₂Cl₂) (anhydrous, 99.9%, 18L in Pure-PacTM) and Acetonitrile (CH₃CN) (anhydrous, 99.8%, 18L in Pure-PacTM) purchased from Aldrich were purified by M. BRAUN solvent purification system (A2 Alumina).

Infrared spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 (400 MHz ¹H, 100 MHz ¹³C), a Bruker Avance 500 (500 MHz ¹H, 125 MHz ¹³C). Chemical shift values (δ) are reported in ppm relative to Me₄Si (δ 0.0 ppm). The proton

spectra are reported as follows δ (multiplicity, coupling constant J , number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (septet), m (multiplet) and br (broad). High-performance liquid chromatography (HPLC) was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter.

7-*tert*-Butyl-8-methoxy-quinoline

To a solution of 7-*tert*-butyl-quinolin-8-ol¹ (17.0 g, 84.5 mmol) in THF (169 mL) was added NaH (60% dispersion in mineral oil, 3.4 g, *ca.* 84.5 mmol) portion-wise at 0 °C. The resulting bright yellow solution was stirred at 0 °C for 30 min. then treated with neat MeI (5.3 mL, 84.5 mmol) and DMF (28 mL). The reaction mixture was allowed to reach room temperature and stirred for 12 h then quenched with saturated NaHCO₃ solution (200 mL) and extracted with diethyl ether (2 x 100 mL). The combined organic layers were washed with saturated NaCl solution (300 mL), dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The resulting crude material was purified by flash chromatography on silica gel (7% EtOAc in hexanes) to afford the title compound as a white solid (16.9 g, 93%). FTIR (CDCl₃) $\nu_{\max}$ 2959, 1505, 1456, 1355, 1129, 991 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.89 (dd, J = 2.0, 4.5 Hz, 1 H), 8.09 (dd, J = 1.5, 8.0 Hz, 1 H), 7.57 (d, J = 8.5 Hz, 1 H), 7.48 (d, J = 8.5 Hz, 1 H), 7.33 (dd, J = 4.0, 8.0 Hz, 1 H), 4.23 (s, 3 H), 1.51 (s, 9 H); ¹³C NMR (125 MHz, CDCl₃) δ 154.8, 148.7, 143.3, 141.5, 135.7, 128.3, 125.9, 121.9, 120.4, 62.5, 35.3, 30.7; MS (CI) Mass Calcd for C₁₄H₁₇NO (M+H)⁺: 216.1. Found: 216.1.

(*R*)-2,2'-Diiodo-1,1'-binaphthyl

The title compound was synthesized according to the literature² as following. (*R*)-2,2'-diamino-1,1'-binaphthyl purchased from Aldrich was converted to the corresponding bis(diazonium zinc iodide), which was washed with commercial reagent-grade anhydrous diethyl ether (used without further purification), affording the title compound in 35–40% yields. Enantiometric excess was determined to be 99% by HPLC with Chiralcel AD-H column with a guard column (AD-H) (99:1 = hexane:2-propanol), 0.5 mL/min.; t_r = 14.6 min.

TBOxMe

To a solution of (*R*)-2,2'-diiodo-1,1'-binaphthyl (1.58 g, 3.12 mmol) in THF (31 mL) was added pentane solution of ^tBuLi (1.7 M, 7.34 mL, 12.48 mmol) drop-wise at $-78\text{ }^{\circ}\text{C}$. The resulting solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h then treated with a solution of 7-*tert*-butyl-8-methoxy-quinoline (2.02 g, 9.36 mmol) in THF (13 mL) drop-wise. The reaction mixture was stirred at $-70\text{ }^{\circ}\text{C}$ for 36 h then quenched with saturated NaHCO_3 solution (50 mL) and extracted with diethyl ether (2 x 50 mL). The combined organic layers were washed with saturated NaCl solution (100 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to afford a crude mixture of the title compound and non-aromatized counterparts. To this was added reagent grade benzene (21 mL) and tetrachloro-1,2-benzoquinone (1.53 g, 6.24 mmol) at room temperature. The resulting mixture was stirred at room temperature for 2 h then quenched with 2N aqueous NaOH solution (20 mL) and extracted with diethyl ether (2 x 20 mL). The combined organic layers were washed with saturated NaCl solution (60 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The resulting crude material was purified by flash chromatography on silica gel (2% EtOAc in hexanes) to afford the title compound as a white solid (1.61 g, 76%). $[\alpha]_D^{26} = +224.4^{\circ}$ ($c = 1.0$, CHCl_3); FTIR (CDCl_3) ν_{max} 3062, 2960, 1540, 1506, 1456, 1362, 1091, 907 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.03 (br s, 4 H), 8.00 (d, $J = 8.0\text{ Hz}$, 2 H), 7.59 (d, $J = 8.5\text{ Hz}$, 2 H), 7.54 (t, $J = 7.0\text{ Hz}$, 2 H), 7.42 (br

d, $J = 8.5$ Hz, 2 H), 7.37 (d, $J = 9.0$ Hz, 2 H), 7.36 (t, $J = 7.5$ Hz, 2 H), 7.17 (d, $J = 8.5$ Hz, 2 H), 6.54 (br d, $J = 8.5$ Hz, 2 H), 3.09 (s, 6 H), 1.37 (s, 18 H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.6, 154.7, 142.5, 140.7, 139.5, 134.5, 134.3, 133.8, 133.3, 129.1, 128.3, 128.2, 127.6, 126.7, 126.3, 126.3, 125.4, 121.3, 121.0, 61.5, 35.1, 30.6; MS (CI) Mass Calcd for $\text{C}_{48}\text{H}_{44}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 681.3. Found: 681.1.

TBOxH

To a solution of TBOxMe (1.61 g, 2.36 mmol) in CH_2Cl_2 (24 mL) was added a CH_2Cl_2 solution of BBr_3 (1.0 M, 9.93 mL, 9.93 mmol) slowly at 0 °C. The resulting bright yellow solution was allowed to reach room temperature and stirred for 3 h. After cooled to 0 °C, the reaction mixture was first quenched with H_2O (4.0 mL) then neutralized with 2N NaOH aqueous solution followed by extraction with CH_2Cl_2 (1 x 20 mL). The combined organic layers were washed with saturated NaCl solution (50 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo* to afford a crude yellow material. To this was added reagent grade toluene (50 mL) and triethanolamine (4.7 mL) then the resulting mixture was refluxed 1 h. After cooled to room temperature, the resulting toluene solution was washed with H_2O (50 mL) then saturated NaCl solution (50 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The resulting crude material was purified by flash chromatography on silica gel (2.5% EtOAc in hexanes) to afford the title compound as a white solid (1.46 g, 95%). $[\alpha]_{\text{D}}^{28} = -93.6^\circ$ ($c = 1.0$, CHCl_3); FTIR (CDCl_3) ν_{max} 3348, 3057, 2958, 2910, 1558, 1472, 1456, 1392, 1133, 908 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, $J = 8.0$ Hz, 2 H), 7.95 (d, $J = 8.5$ Hz, 2 H), 7.68 (br s, 2 H), 7.64 (d, $J = 8.5$ Hz, 2 H), 7.55 – 7.60 (m, 6 H), 7.41 (t, $J = 5.0$ Hz, 2 H), 7.40 (d, $J = 8.5$ Hz, 2 H), 7.07 (d, $J = 8.5$ Hz, 2 H), 6.67 (d, $J = 8.5$ Hz, 2 H), 1.43 (s, 18 H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.2, 150.0, 138.0, 137.3, 135.6, 134.9, 134.1, 133.1, 128.3, 128.3, 127.4, 127.3, 126.9, 126.4, 126.2, 124.5, 121.5, 115.6, 34.6, 29.3; MS (CI) Mass Calcd for $\text{C}_{46}\text{H}_{40}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 653.3. Found: 653.1.

Enantiometric excess was determined to be 99% by HPLC with Chiralcel OD-H column with a guard column (OD-H) (99:1 = hexane:2-propanol), 0.5 mL/min.; t_r = 13.2 min.

TBOxCrCl

An oven-dried round-bottom flask fitted with a reflux condenser was charged with a magnetic stir bar, anhydrous CrCl_2 (63 mg, 0.51 mmol), and TBOxH (300 mg, 0.46 mmol) inside a nitrogen-filled drybox then taken out. To this was added freshly distilled THF (15 mL) and the resulting mixture was refluxed for 24 h under an atmosphere of argon. After cooled to room temperature, the resulting reaction mixture was stirred for 12 h under air, diluted with reagent grade diethyl ether (30 mL), washed with saturated NH_4Cl solution (30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The title compound was obtained as a dark brown solid (340 mg, 99%) and used in the pinacol coupling reaction without any purification.

General Procedure for Pinacol Coupling Reaction of Aromatic Aldehydes

An oven-dried test tube was charged with a magnetic stir bar, TBOxCrCl (12 mg, 0.015 mmol) and Mn powder 50-mesh (83 mg, 1.5 mmol) then flushed thoroughly with argon three times. To this was added anhydrous acetonitrile (2.5 mL) and the resulting yellow-brown mixture was stirred for 10 min. at room temperature. The catalyst solution was treated with neat aldehyde (0.5 mmol) followed by drop-wise addition of neat TESCl (125 μL , 0.75 mmol). The reaction was stirred at room temperature for a specified length of time, at which time it was quenched with saturated NaHCO_3 solution (1 mL) and filtered through a short pad of Celite®. After removal of volatiles *in vacuo*, the residue was taken up into Et_2O (20 mL) then washed with a saturated NaCl solution (20 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The resulting crude silyl ether was treated with aqueous HCl (1M, 2 mL, 2 mmol) in THF (5 mL) at room temperature until it was completely desilylated (by TLC). The reaction mixture was diluted with Et_2O

(20 mL), washed with a saturated NaCl solution (20 mL), and dried over anhydrous Na₂SO₄. The crude product was purified by flash chromatography on silica gel using a specified eluent.

(*R,R*)-(+)-1,2-Diphenyl-ethane-1,2-diol

The reaction was stirred for 10 h. Diastereoselectivity (*dl* : *meso* = 98 : 2) was determined by ¹H NMR analysis of a crude reaction mixture based on the literature.³ Silica gel chromatography (25% EtOAc in hexanes) afforded the title compound as a white solid (51 mg, 94%, 97% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1.0 mL/min.), *t_r*(*S,S*) = 30.2 min., *t_r*(*R,R*) = 33.0 min., *t_r*(*meso*) = 37.2 min. $[\alpha]_D^{28} = +92.7$ (*c* = 1.0, EtOH). The reported value² for *S,S*-enantiomer (100% ee) is $[\alpha]_D = -94.5$ (*c* = 1.0, EtOH).

(*R,R*)-(+)-1,2-Di-*o*-tolyl-ethane-1,2-diol

The reaction was stirred for 18 h. Diastereoselectivity (*dl* : *meso* = 98 : 2) was determined by ¹H NMR analysis of a crude reaction mixture based on the literature.³ Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (56 mg, 93%, 98% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95:5, flow rate = 1.0 mL/min.), *t_r*(*S,S*) = 20.8 min., *t_r*(*R,R*) = 21.9 min., *t_r*(*meso*) = 29.9 min. $[\alpha]_D^{29} = +60.6$ (*c* = 0.83, EtOH). The reported value² for *S,S*-enantiomer (100% ee) is $[\alpha]_D = -64.8$ (*c*=0.83, EtOH).

(*R,R*)-(+)-1,2-Di-*p*-tolyl-ethane-1,2-diol

The reaction was stirred for 12 h. Diastereoselectivity (*dl* : *meso* = 97 : 3) was determined by ^1H NMR analysis of a crude reaction mixture based on the literature.³ Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (56 mg, 93%, 97% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1.0 mL/min.), $t_r(S,S)$ = 29.8 min., $t_r(R,R)$ = 31.4 min., $t_r(\textit{meso})$ = 38.7 min. $[\alpha]_D^{28}$ = +101.0 (c = 1, EtOH). The reported value² for *S,S*-enantiomer (100% ee) is $[\alpha]_D$ = -102.5 (c = 1, EtOH).

(*R,R*)-(+)-1,2-Bis-(3-methoxy-phenyl)-ethane-1,2-diol

The reaction was stirred for 12 h. Diastereoselectivity (*dl* : *meso* = 98 : 2) was determined by ^1H NMR analysis of a crude reaction mixture based on the literature.^{4,5} Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (63 mg, 92%, 97% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1.0 mL/min.), $t_r(S,S)$ = 60.1 min., $t_r(R,R)$ = 63.1 min., $t_r(\textit{meso})$ = 76.1 min. $[\alpha]_D^{29}$ = +94.3 (c = 1.05, CH_2Cl_2). The reported value³ for *R,R*-enantiomer (100% ee) is $[\alpha]_D^{24}$ = +97.9 (c = 1.05, CH_2Cl_2).

(*R,R*)-(+)-1,2-Bis-(4-bromo-phenyl)-ethane-1,2-diol

The reaction was stirred for 10 h. Diastereoselectivity (*dl* : *meso* = 97 : 3) was determined by ^1H NMR analysis of a crude reaction mixture based on the literature.⁶

Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (85 mg, 91%, 98% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1.0 mL/min.), $t_r(R,R)$ = 34.4 min., $t_r(S,S)$ = 37.2 min., $t_r(meso)$ = 44.5 min. $[\alpha]_D^{29}$ = +80.9 (c = 1.0, EtOH). The absolute stereochemistry of the title compound was determined by converting it into 1,2-Diphenyl-ethane-1,2-diol as described below.

A flame-dried round-bottom flask was charged with freshly distilled THF (3 mL) under an argon atmosphere then cooled down to -78 °C. To this was added n BuLi solution in hexanes (1.6M, 200 μ L, 0.32 mmol) followed by a drop-wise addition of 1,2-bis-(4-bromo-phenyl)-ethane-1,2-diol (20 mg, 0.054 mmol) in THF (1 mL). The resulting yellow solution was stirred for 1 h at -78 °C then quenched with a saturated NaHCO_3 solution (1 mL) and extracted with Et_2O (15 mL). The combined organic layers were washed with a saturated NaCl solution (15 mL), dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The purification with preparative TLC (25% EtOAc in hexanes) afforded (*R,R*)-(+)-1,2-diphenyl-ethane-1,2-diol (8 mg, 71%).

(*R,R*)-(+)-1,2-Bis-(4-chloro-phenyl)-ethane-1,2-diol

The reaction was stirred for 9 h. Diastereoselectivity (*dl* : *meso* = 97 : 3) was determined by ^1H NMR analysis of a crude reaction mixture based on the literature.³ Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (67 mg, 94%, 97% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1.0 mL/min.), $t_r(S,S)$ = 30.3 min., $t_r(R,R)$ = 31.6 min., $t_r(meso)$ = 39.3 min. $[\alpha]_D^{29}$ = +90.0 (c = 1, EtOH). The reported value² for *R,R*-enantiomer (100% ee) is $[\alpha]_D$ = +93 (c = 1, EtOH).

(*R,R*)-(+)-1,2-Bis-(4-trifluoromethyl-phenyl)-ethane-1,2-diol

The reaction was stirred for 20 h. Diastereoselectivity (*dl* : *meso* = 97 : 3) was determined by ^1H NMR analysis of a crude reaction mixture based on the literature.⁷ Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (78 mg, 89%, 95% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 95 : 5, flow rate = 1.0 mL/min.), $t_r(S,S)$ = 36.9 min., $t_r(R,R)$ = 42.8 min., $t_r(\textit{meso})$ = 46.9 min. $[\alpha]_D^{29}$ = +67.8 (c = 0.95, CHCl_3). The reported value⁷ for *R,R*-enantiomer (100% ee) is $[\alpha]_D$ = +76.7 (c = 0.95, CHCl_3).

(*R,R*)-(+)-1,2-Di-naphthalen-1-yl-ethane-1,2-diol

The reaction was stirred for 14 h. Diastereoselectivity (*dl* : *meso* = 96 : 4) was determined by ^1H NMR analysis of a crude reaction mixture based on the literature.³ Silica gel chromatography (25% EtOAc in hexanes) afforded the titled compound (72 mg, 92%, 97% ee). $[\alpha]_D^{29}$ = +64.5 (c = 0.86, THF). The reported value² for *R,R*-enantiomer (100% ee) is $[\alpha]_D$ = +68 (c = 0.86, THF). The title compound was mono-benzoylated as described below and its enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1.0 mL/min.), $t_r(S,S)$ = 32.6 min., $t_r(\textit{meso})$ = 35.6 min., $t_r(R,R)$ = 46.1 min.

To a solution of the title compound (20 mg, 0.064 mmol) in pyridine (2 mL) was added 4-DMAP (10 mg, 0.082 mmol) and BzCl (20 μL , 0.17 mmol) at room temperature. The resulting reaction mixture was stirred for 10 h then diluted with Et_2O (20 mL), washed with aqueous HCl (1M, 10 mL) and a saturated NaCl solution, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The purification with preparative TLC (20% EtOAc in hexanes) afforded the corresponding mono-benzoylated product (12 mg, 45%). ^1H NMR (400 MHz, CDCl_3) δ 8.32 (br s, 1H), 8.11 – 7.20 (m, 21H). ^{13}C NMR

(125 MHz, CDCl₃) δ 166.0, 135.2, 133.8, 133.8, 133.4, 131.0, 131.0, 130.2, 130.0, 129.2, 129.2, 128.9, 128.9, 128.6, 128.5, 128.4, 126.4, 126.1, 125.7, 125.7, 125.5, 125.4, 125.1, 123.3, 123.3, 74.0.

(*R,R*)-(+)-1,2-Di-naphthalen-2-yl-ethane-1,2-diol

The reaction was stirred for 14 h. Diastereoselectivity (*dl* : *meso* = 97 : 3) was determined by ¹H NMR analysis of a crude reaction mixture based on the literature.³ Silica gel chromatography (50% EtOAc in hexanes) afforded the titled compound (69 mg, 88%, 95% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column equipped with an OJ-H guard column (hexanes : 2-propanol = 70 : 30, flow rate = 0.9 mL/min.), *t*_r(*R,R*) = 30.3 min., *t*_r(*meso*) = 49.3 min., *t*_r(*R,R*) = 58.3 min. [α]_D²⁹ = +201.4 (*c* = 1.0, THF). The reported value² for *R,R*-enantiomer (100% ee) is [α]_D = +224 (*c* = 1.0, THF).

(*R,R*)-(+)-1,2-Dicyclohexyl-ethane-1,2-diol

An oven-dried test tube was charged with a magnetic stir bar, TBOxCrCl (12 mg, 0.015 mmol) and Mn powder 50-mesh (83 mg, 1.5 mmol) then flushed thoroughly with argon three times. To this was added anhydrous acetonitrile (2.5 mL) and the resulting yellow-brown mixture was stirred for 10 min. at room temperature. The catalyst solution was treated with neat cyclohexanecarboxaldehyde (65 μ L, 0.5 mmol) followed by a drop-wise addition of neat TMSCl (190 μ L, 1.5 mmol). The reaction was stirred at room temperature for a specified length of time, at which time it was quenched with saturated NaHCO₃ solution (1 mL) and filtered through a short pad of Celite®. After removal of volatiles *in vacuo*, the residue was taken up into Et₂O (20 mL) then washed with a saturated NaCl solution (20 mL), dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. To a solution of the resulting material in 1,4-dioxane (6 mL) was added 50%

aqueous H₂SO₄ (0.5 mL), and ethylene glycol at room temperature. The resulting mixture was stirred for 24 h at 90 °C then cooled to room temperature. The reaction mixture was diluted with Et₂O (20 mL), washed with a saturated NaHCO₃ solution (2 x 20 mL) and a saturated NaCl solution (20 mL), dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. Diastereoselectivity (*dl* : *meso* = 93 : 7) was determined by ¹H NMR analysis of a crude reaction mixture based on the literature.⁹ The resulting crude material was purified by flash chromatography on silica gel (25% EtOAc in hexanes) to afford the title compound as a white solid (27 mg, 44%, 84% ee). The title compound was mono-benzoylated as described below and its enantiomeric excess was determined by HPLC with a Chiralcel AD-H column equipped with an AD-H guard column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 1.0 mL/min.), *t*_r(*S,S*) = 17.0 min., *t*_r(*R,R*) = 18.2 min., *t*_r(*meso*-1) = 26.8 min., *t*_r(*meso*-2) = 38.2 min. (The retention time of mono-benzoylated commercially available (*R,R*)-(+)-1,2-dicyclohexyl-ethane-1,2-diol is 18.2 min.)

To a solution of the title compound (20 mg, 0.084 mmol) in pyridine (2 mL) was added 4-DMAP (10 mg, 0.082 mmol) and BzCl (20 µL, 0.17 mmol) at room temperature. The resulting reaction mixture was stirred for 10 h then diluted with Et₂O (20 mL), washed with aqueous HCl (1M, 10 mL) and a saturated NaCl solution, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The purification with preparative TLC (20% EtOAc in hexanes) afforded the corresponding mono-benzoylated product (11 mg, 37%). ¹H NMR (400 MHz, CDCl₃) δ 8.07-7.44 (m, 5H), 5.09 (m, 1H), 3.54 (m, 1H) 1.91-1.05 (m, 22H).

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1,2-Diphenyl-ethane-1,2-diol

2.942

4.750

7.260
7.248
7.241
7.236
7.232
7.225
7.216
7.144
7.134
7.125
7.121
7.116
7.110

ppm

1,2-Di(p-tolyl)ethane-1,2-diol

1,2-Bis-(4-bromo-phenyl)-ethane-1,2-diol

1,2-Bis-(4-trifluoromethyl-phenyl)-ethane-1,2-diol

Crystallographic Experimental Section

[TBO_x(EtOH)₂Cr(III)]Cl

Data Collection

Crystals were obtained by slow diffusion of ethanol into a solution of TBO_xCrCl in bromobenzene. A regular prism (0.30 x 0.30 x 0.20 mm) was selected under a stereomicroscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX CCD diffractometer with nitrogen cooling of the crystal to 100 K. Still images showed diffractions to be sharp although intensity decreased rapidly with 2Θ and were seldom observed beyond 2Θ of ~ 35 degrees. Frames separated in reciprocal space were obtained using SMART¹ software and provided both an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A “full sphere” data set was obtained which samples approximately all of reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω with 10 second integration times for each frame. Data collection was done at 100 K. Integration of intensities, refinement of cell parameters, merging of equivalent diffractions was done using SAINT¹ software. Absorption corrections were applied using SADABS software based on redundant diffractions.

Structure solution and refinement

The space group was determined as P1($\bar{6}$) based of systematic absences and intensity statistics using program XPREP¹. The direct methods routine within program SHELXL-97¹ was used to locate Cr as well as many C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C, N and O atoms. Two large isolated peaks were assigned to Cl ions based on occupancy refinement of almost exactly 1.0 for Cl. One C₆H₅Br molecule was clearly present but disordered where the atoms were out of plane. Other clusters of peaks clearly showed that additional solvent was present and based on inferred shape consisted of C₆H₆ and pentane. Another isolated peak was probably H₂O and yet another disordered solvent molecule appeared to be THF.

Following anisotropic refinement of all non-H atoms of the main molecule and Cl anions, ideal H atom positions were calculated. Following refinement of these two units, the program SQUEEZE² was applied to remove the intensity contributions from the mostly disordered solvent. In total 177 electrons were accounted for in recognized voids. Using the SQUEEZE modified intensities, final refinement of the main molecule and Cl anions was done. Non-H atoms were refined anisotropically while H atoms were refined as isotropic-riding.

Numerous prolate displacement ellipsoids are present some of which probably represent disorder of poorly constrained units; the limited data in 2 Θ probably also contributes to this effect in a general way. All ORTEP¹ diagrams have been drawn with 50% probability ellipsoids.

Equations of interest:

$$R_{\text{int}} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2|$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$$

$$\text{GooF} = S = [\sum [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

$$\text{where: } w = q / \sigma^2 (F_o^2) + (aP)^2 + bP;$$

$$n = \text{number of independent reflections};$$

$$q, a, b, P \text{ as defined in [1]}$$

$$p = \text{number of parameters refined.}$$

References

[1] SMART (v.5.630), SAINTPLUS (v.6.45), SHELXTL(v.6.14), XPREP, SADABS (v.2.03) and ORTEP software are distributed by Bruker AXS, Inc., Madison, WI.

[2] SQUEEZE as implemented in PLATON, A.L. Spek, Multipurpose Crystallographic Tool, J. Appl. Cryst, 2003, 36, 7-13.

Table 1. Crystal and structure refinement for Nori12.

Identification Code	Nori12
Empirical formula	$C_{50}H_{48}CrN_2O_4 + Cl + \text{C}_6\text{H}_5\text{Br} + \text{solvent}$
Formula weight	880.12
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space Group	P1(bar)
Unit cell dimensions	$a = 10.947(3) \text{ Å}$ $\alpha = 105.772(4)^\circ$ $b = 20.288(5) \text{ Å}$ $\beta = 96.529(4)^\circ$ $c = 23.757(6) \text{ Å}$ $\gamma = 90.526(4)^\circ$
Volume	5040(2) Å ³
Z	4
Density (calculated)	1.092 Mg/m ³
Absorption coefficient	0.320 mm ⁻¹
F(000)	1740
Crystal size, color, habit	0.30 x 0.30 x 0.20 mm, pale purple, prism
Theta range for data collection	1.55 – 25.03 °
Index ranges	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -28 ≤ l ≤ 28
Reflections collected	46,976
Independent reflections	17,728 (R _{int} = 0.0720)
Reflections with I > 4σ(F _o)	7,306
Absorption correction	SADABS based on redundant diffractions
Max. and min. transmission	1.0, 0.597
Refinement method	Full-matrix least squares on F ²
Weighting scheme	$w = q [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2F_c^2)/3$, a = 0.1037, b = 0.0, q = 1
Data / restraints / parameters	17728 / 0 / 1061
Goodness-of-fit on F ²	0.931
Final R indices [I > 2 sigma(I)]	R1 = 0.0831, wR2 = 0.2102
R indices (all data)	R1 = 0.1535, wR2 = 0.2314

Largest diff. peak and hole	0.545, -0.408 eÅ ⁻³
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