

**Enantio- and Structure-Selective Diels-Alder Reactions of Unsymmetrical Quinones
Catalyzed by a Chiral Oxazaborolidinium Cation. Predictive Selection Rules.**

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Supplementary Material

Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm). Flash chromatography was performed using Baker silica gel (40 µm particle size). NMR spectra were recorded on Varian Innova-500, or Mercury-400 instruments and calibrated using residual undeuterated solvent as an internal reference. IR spectra were recorded on Avatar 360 FT-IR spectrometer. Low-resolution mass (CI) spectra were obtained by using a Platform II mass spectrometer. High-resolution mass spectral analyses were performed at the Harvard University Mass Spectrometry Center. Analytical high performance liquid chromatography (HPLC) was performed on Isco 2350 Series or Waters 626 HPLC using the indicated chiral column. Gas chromatography (GC) analyses were performed on Hewlett-Packard 6850 Series GC System equipped with flame ionization detector using a J & W Scientific Cyclosil-B column (30 m x 0.25 mm). Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from calcium hydride. Toluene was distilled from sodium. 2-Methylnaphthalene-1, 4-dione (Aldrich), naphthalene-1, 4-dione (Aldrich), 2-bromo-6-methyl-1,4-benzoquinone (Sigma-Aldrich), 1,4-benzoquinone (Aldrich) and 2-*t*-butyl-1,4-benzoquinone were used after recrystallization with a mixture of ethyl acetate and hexanes. 2-Triisopropylsilyloxy-1,3-butadiene,¹ 2, 3, 5-trimethyl-1,4-benzoquinone,² 1-bromo-2, 4-

¹ Corey, E. J.; Guzman-Perez, A.; Loh, T.-P. *J. Am. Chem. Soc.* **1994**, *116*, 3611.

² Ito, S.; Aihara, K.; Matsumoto, M. *Tetrahedron Lett.* **1983**, *24*, 5249.

dimethyl-1, 4-benzoquinone,³ 1-methoxy-2-methyl-1, 4-benzoquinone,⁴ 2, 3-dimethyl-1, 4-benzoquinone,⁵ 2-methoxy-6-methyl-1, 4-benzoquinone⁶ and 3-iodo-2, 5-dimethyl-1, 4-benzoquinone⁷ were prepared according to literature procedures.

General Procedure for the Preparation and Use of Chiral Diels-Alder Catalysts. A 100-mL, two-necked, round-bottomed flask equipped with a stir bar, a glass stopper and a 50-mL pressure-equalizing addition funnel (containing a cotton plug and ca. 10 g of 4 molecular sieves,⁸ and functioning as a Soxhlet extractor) fitted on top with a reflux condenser and a nitrogen inlet adaptor was charged with (*S*)-(-)- α,α -diphenyl-2-pyrrolidinemethanol (82.0 mg, 0.324 mmol, from Lancaster), tri-*o*-tolylboroxine⁹ (38.0 mg, 0.107 mmol) and 25 mL of toluene. The resulting solution was heated to reflux (bath temperature ~ 145 °C). After 3 h, the reaction mixture was cooled to ca. 60 °C and the addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume of ca. 5 mL. This distillation protocol was repeated three times by re-charging with 3 x 5 mL of toluene. The solution was then allowed to cool to room temperature and the distillation head was quickly replaced with a vacuum adaptor. Concentration *in vacuo* (ca. 0.1 mmHg, 1 h) afforded the corresponding oxazaborolidine as clear oil, which can then be dissolved in CH₂Cl₂ and used in two Diels-Alder experiments.

To an aliquot of the oxazaborolidine precursor (0.160 mmol, theoretical) in 1.0mL of CH₂Cl₂ at -25 °C was added trifluoromethanesulfonimide (0.20 M solution in CH₂Cl₂, freshly prepared, 667 μ L, 0.133 mmol) dropwise. After 10 min at -25 °C, a colorless homogeneous catalyst solution was ready for use in the Diels-Alder reactions.

³ a) Smith, L. I.; Wiley, P.F. *J. Am. Chem. Soc.* **1946**, 68, 887. b) Smith, L. I.; Wiley, P.F. *J. Am. Chem. Soc.* **1946**, 68, 894.

⁴ Knolker, H.-J.; Frohner, W.; Reddy, K. R. *Synthesis* **2002**, 4, 557.

⁵ Fischl, S.; Mulbaier, M.; Giannis, A. *Tetrahedron* **2001**, 57, 4863.

⁶ Stevens, R. V.; Angle, S. R.; Kloc, K.; Mak, K. F.; Trueblood, K. L.; Liu, Y.-X. *J. Org. Chem.* **1986**, 51, 4347.

⁷ Cressman, H. W. J.; Thirtle, J. R. *J. Org. Chem.* **1966**, 31, 1279.

⁸ Molecular sieves (pellets) were dried *in vacuo* at ca. 200 °C with a gas burner for 10 min prior to use.

⁹ Corey, E. J.; Shibata, T.; Lee, T. W. *J. Am. Chem. Soc.* **2002**, 124, 3803.

To a catalyst solution in CH_2Cl_2 (1.0 mL) were successively added a solution of 1, 4-benzoquinone (0.665 mmol) in CH_2Cl_2 (0.7~1.0 mL) and 2-triisopropylsilyloxy-1,3-butadiene (194 μL , 166 mg, 0.732 mmol) at -78°C . The reaction mixture was stirred at the temperature indicated in Table 1-3 and monitored by ^1H NMR or TLC. When it was judged to be complete, dichloromethane was removed by rotary evaporation and water (5mL) and hexanes (3mL) were added. The aqueous layer was extracted with hexanes (4 x 5mL).¹⁰ The combined extract was dried over anhydrous Na_2SO_4 and concentrated to afford the corresponding adduct which was pure enough for the most purposes. Further purification was performed by silica gel chromatography (Table 1), low temperature (-78°C) silica gel chromatography or recrystallization (Table 2, 3).¹¹

The corresponding racemic products for the determination of enantioselectivity were prepared by using ethylaluminum dichloride (20 mol %) or anhydrous LiClO_4 ¹² as a Lewis acid catalyst or thermal reaction.

Determination of Regioselectivity, Enantioselectivity and Absolute Configuration of the Diels-Alder Adducts Reported in Tables 1-3.

Table 1, entry 1: Regioselectivity and enantioselectivity were determined by HPLC analysis using a Regis (*S, S*)-Whelk-O1 column (0.2% *i*-PrOH in hexanes for elution; 1mL/min; λ 254 nm); retention times: 13.1 min (major), 15.5 min (minor), 18.6 min (regioisomer). The absolute configuration was determined by comparison with an authentic sample prepared from (-)-(4*aR*, 8*aS*)-3-iodo -2, 4*a* -dimethyl-6 -(triisopropylsilyl)oxy - 4*a*, 5, 8, 8*a* - tetrahydro -1, 4-naphthoquinone (substitution of iodine with methyl group¹³) and HPLC analysis.

¹⁰ After hexanes extraction, the aqueous solution was treated with aqueous 2N NaOH solution and extracted with dichloromethane. The combined extract was dried over Na_2SO_4 , concentrated and purified by column chromatography (elution with EtOAc) to afford pure ligand (95-99% recovery).

¹¹ Quinone adducts in Table 2 and 3 are unstable under silica gel chromatography at ambient temperature.

¹² Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595.

¹³ The solution of iodoquinone adduct (Table 1, entry 3) in THF was treated with dimethylzinc (2.0 eq.) in the presence of catalytic amount of dichlorobis(triphenylphosphine)palladium for 3 h at 20°C to provide the corresponding methyl quinone adduct (Table 1, entry 1, 56% yield).

Table 1, entry 2: Regioselectivity and enantioselectivity were determined by HPLC analysis using a Daicel Chiralcel OD-H column (0.2% *i*-PrOH in hexanes for elution; 1 mL/min; λ 254 nm); retention times: 12.2 min (major), 14.6 min (regioisomer), 15.6 min (regioisomer), 16.3 min (minor). The absolute configuration was determined by X-ray crystallographic analysis.

Table 1, entry 3: Enantioselectivity was determined by subsequent desilylation with 10% HF, reduction with *n*Bu₃SnH to the ketone compound and GC analysis (120 °C, 25 psi); retention times: 169.4 (major), 172.5 min (minor). The absolute configuration was assigned by X-ray crystallographic analysis of (*4aR*, *8aS*)-3-iodo-2,4a-dimethyl-4a,7,8,8a-tetrahydro-5H-naphthalene-1,4,6-trione; Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388.

Table 1, entry 4: Regioselectivity and enantioselectivity were determined by HPLC analysis using a Daicel Chiralcel OD-H column (0.1% *i*-PrOH in hexanes for elution; 1 mL/min; λ 254 nm); retention times: 34.5 min (major), 42.6 min (minor), 38.7 min (regioisomer), 40.1 min (regioisomer). The absolute configuration was determined by analogy with (-)-(*4aR*, *8aS*)-2-bromo-4a,5,8,8a-tetrahydro-6-(triisopropylsilyl)oxy-3,4a-dimethyl-naphthalene-1,4-dione.

Table 1, entry 5: Enantioselectivity was determined by HPLC analysis using a Daicel Chiralcel OD-H column (0.4% *i*-PrOH in hexanes for elution; 1 mL/min; λ 254 nm); retention times: 9.7 min (major), 11.8 min (minor). The absolute configuration was determined by selective reduction with NaBH₄, *p*-bromobenzoylation, desilylation and X-ray crystallographic analysis of (*4aS*, *9R*, *9aR*)-1,2,3,4,4a,9,9a,10-octahydro-9a-methyl-2,10-dioxoanthracen-9-yl-4-bromobenzoate (*vide infra*).

Table 2, entry 1: Enantioselectivity was determined by reduction with NaBH₄ to the corresponding diol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 6.64 (dd, 1H, *J* = 5.0 Hz, major), 6.51 (d, 1H, *J* = 4.5 Hz, minor). The absolute configuration was determined by analogy with (+)-(*4aR*, *8aS*)-4a,5,8,8a-tetrahydro-6-(triisopropylsilyl)oxynaphthalene-1,4-dione and (+)-(*4aS*, *9aR*)-1,4,4a,9a-tetrahydro-2-(triisopropylsilyl)oxy-9a-methylanthracene-9,10-dione.

Table 2, entry 2: Enantioselectivity was determined by desilylation with 10% HF to the corresponding ketone and GC analysis (155 °C, 25 psi); retention times: 58.4 (major), 59.7 min (minor). The absolute configuration was determined by analogy with (+)-(4*aR*, 8*aS*)-2, 3, 6-trimethyl-4*a*, 5, 8, 8*a*-tetrahydro-1, 4-naphthoquinone; Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388.

Table 2, entry 3: Regioselectivity was determined by ¹H NMR analysis of the crude mixture: δ 3.25 (dd, 1H, *J* = 15.0, 8.0 Hz, major), 3.20 (dd, 1H, *J* = 15.0, 8.0 Hz, minor). Enantioselectivity was determined by selective Luche reduction with NaBH₄ to the corresponding alcohol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 6.26 (dd, 1H, *J* = 5.5, 3.2 Hz, major), 6.13 (d, 1H, *J* = 4.0 Hz, minor). The absolute configuration was determined by analogy with (+)-(4*aR*, 8*aS*)-2, 3-Dimethyl-6-(triisopropylsilyl)oxy - 4*a*, 5, 8, 8*a* -tetrahydro -1, 4-naphthoquinone; Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388.

Table 2, entry 4: Enantioselectivity was determined by desilylation to the corresponding ketone and HPLC analysis using a Daicel Chiralcel OJ column (50% *i*-PrOH in hexanes for elution; 0.5 mL/min; λ 254 nm); retention times: 39.7 min (minor), 44.1 min (major). The absolute configuration was assigned by comparison with an authentic sample prepared from (-)-(4*aS*, 8*aR*)-4*a*, 5, 8, 8*a*-tetrahydro-2-bromo-7-(triisopropylsilyl)oxy-8*a*-methylnaphthalene-1, 4-dione (substitution of bromine with methoxy group,¹⁴ desilylation) and HPLC analysis.

Table 2, entry 5: Enantioselectivity was determined by substitution of bromine with methoxy group, desilylation and HPLC analysis using a Daicel Chiralcel OJ column (50% *i*-PrOH in hexanes for elution; 0.5 mL/min; λ 254 nm); retention times: 39.7 min (minor), 44.1 min (major). The absolute configuration was determined by desilylation and X-ray crystallographic

¹⁴ The bromoquinone adduct (Table 2, entry 5) was stirred for 24hr at 20 °C under basic methanol solution (1N NaOH:MeOH=1:50) to give the corresponding methoxy quinone adduct (Table 2, entry 4) and its trans isomer (= 1:1, 85% yield).

analysis of (*4aR,8aS*)-3-bromo-4a, 5, 8, 8a-tetrahydro-4a-methylnaphthalene-1, 4, 6(*7H*)-trione (*vide infra*).

Table 3, entry 1: Enantioselectivity was determined by reduction with NaBH₄ to the corresponding diol, then acid-catalyzed cyclization to cyclic ketal monoalcohol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 6.03 (dd, 0.5H, *J* = 2.0 Hz, minor), 5.97 (dd, 0.5H, *J* = 2.0 Hz, major); ¹⁹F NMR integration (376.2 MHz, CDCl₃): δ -71.79 (s, CF₃, major), -71.89 (s, CF₃, minor). The absolute configuration was assigned by selective Luche reduction, acid-catalyzed ketal formation, *p*-bromobenzoylation, desilylation with 10%HF (in CH₃CN) and X-ray crystallographic analysis of (*1R,4S,4aR,8aS*)-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1-hydroxy-6-oxonaphthalen-4-yl-4-bromobenzoate (*vide infra*).

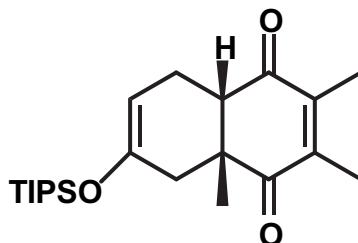
Table 3, entry 2: Regioselectivity and enantioselectivity were determined by reduction with NaBH₄ to the corresponding alcohol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 6.65 (t, 1H, *J* = 2.0 Hz, minor), 6.63 (t, 1H, *J* = 2.0 Hz, regioisomer), 6.58 (t, 1H, *J* = 2.0 Hz, regioisomer), 6.55 (t, 1H, *J* = 2.0 Hz, major). The absolute configuration was determined by analogy with (+)-(4*aS*, 8*aR*)-4a, 5, 8, 8a-tetrahydro-2-methoxy-7-(triisopropylsilyl)oxy-naphthalene-1,4-dione.

Table 3, entry 3: Regioselectivity was determined by ¹H NMR analysis of the crude mixture: δ 3.04 (dd, 1H, *J* = 12.4, 6.4 Hz, major), 3.08 (dd, 1H, *J* = 11.6, 5.6 Hz, minor). Enantioselectivity was determined by reduction with NaBH₄ to the corresponding alcohol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 4.71 (d, 1H, *J* = 5.2 Hz, major), 4.63 (m, 1H, minor). The absolute configuration was determined by analogy with (+)-(4*aS*, 8*aR*)-4a, 5, 8, 8a-tetrahydro-2-methoxy-7-(triisopropylsilyl)oxy-naphthalene-1,4-dione.

Table 3, entry 4: Enantioselectivity was determined by HPLC analysis using a Daicel Chiralcel OD-H column (0.4% *i*-PrOH in hexanes for elution; 1 mL/min; λ 254 nm); retention times: 9.7 min (major), 11.8 min (minor). The absolute configuration was determined by selective reduction with NaBH₄, *p*-bromobenzoylation, desilylation and X-ray crystallographic analysis of

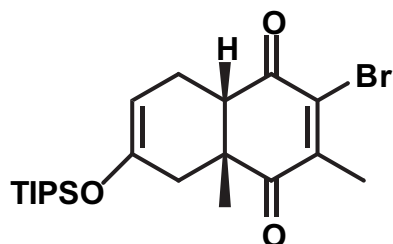
(4*aS*, 9*R*, 9*aR*)-1, 2, 3, 4, 4*a*, 9, 9*a*, 10- octahydro- 9*a*- methyl- 2, 10- dioxoanthracen-9-yl 4-bromobenzoate (*vide infra*).

Experimental Procedure and Physical Data of the Diels-Alder Products:¹⁵

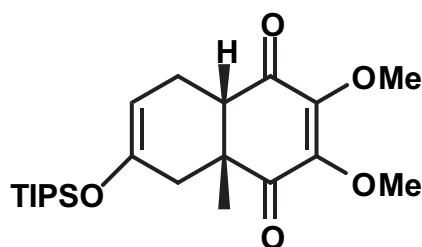


(4*aR*, 8*aS*)-4*a*, 5, 8, 8*a*-Tetrahydro-6-(triisopropylsilyl)oxy-2, 3, 4*a*-trimethylnaphthalene-1, 4-dione (Table 1, entry 1). Purification by column chromatography (elution with pentane) afforded 246 mg (98%) of product as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 4.80 (t, 1H, *J* = 3.6 Hz), 2.74 (dd, 1H, *J* = 6.0, 5.2Hz), 2.56-2.68 (m, 1H), 2.52(dd, 1H, *J* = 17.2, 1.6Hz), 2.12-2.22 (m, 1H), 1.99 (s, 3H), 1.96 (s, 3H), 1.79 (d, 1H, *J* = 17.2 Hz), 1.32 (s, 3H), 1.01-1.12 (m, 3H), 1.03 (d, 18H, *J* = 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.9, 199.6, 147.8, 143.6, 142.6, 99.9, 51.8, 48.8, 37.1, 23.6, 23.1, 18.2 (x6), 13.4, 13.1, 12.8 (x3); FTIR (neat) 2924, 1674, 1489, 1204; LRMS (CI) calcd for [C₂₂H₃₇O₃Si] ([MH]⁺): 377; found 377; [α]_D²³ -33.8 (*c* 1.1, CHCl₃, 99% ee).

¹⁵ The physical and spectral data of two Diels-Alder adducts are known. For (4*aR*, 8*aS*)- 3 -iodo -2,4*a* -dimethyl -6 -(triisopropyl silyl)oxy - 4*a*, 5, 8, 8*a* - tetrahydro -1,4- naphthoquinone and (4*aR*, 8*aS*)- 2, 3 - dimethyl - 6 - (triisopropyl silyl)oxy - 4*a*, 5, 8, 8*a* - tetrahydro -1,4 naphthoquinone, see Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, 125, 6388.

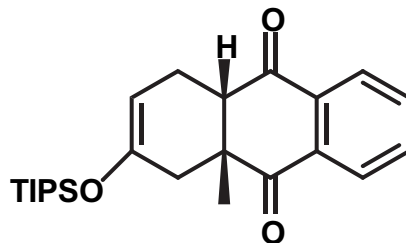


(4aR, 8aS)-2-Bromo-4a, 5, 8, 8a-tetrahydro-6-(triisopropylsilyl)oxy-3, 4a-dimethylnaphthalene-1, 4-dione (Table 1, entry 2). Purification by column chromatography (gradient elution with 1% Et₂O-pentane) afforded 282 mg (96%) of product as a pale yellow solid: mp 68.0-70.0 °C: ¹H NMR (500 MHz, CDCl₃) δ 4.80 (t, 1H, *J* = 4.0 Hz), 2.87 (dd, 1H, *J* = 6.0, 6.0 Hz), 2.60-2.64 (m, 1H), 2.54-2.58 (dd, 1H, *J* = 17.5, 1.5 Hz), 2.23-2.67 (m, 1H), 2.22 (s, 3H), 1.85 (d, 1H, *J* = 17.5 Hz), 1.36 (s, 3H), 1.01-1.15 (m, 3H), 1.04 (d, 18H, *J* = 6.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 197.9, 191.7, 147.9, 147.7, 138.7, 99.4, 51.4, 49.0, 36.7, 23.6, 23.57, 18.4, 18.2 (x6), 12.8 (x3); FTIR (neat) 2941, 2864, 1688, 1462, 1202; LRMS (CI) calcd for [C₂₁H₃₃BrO₃Si] ([M]⁺): 440, 442; found 440, 442; [α]_D²³ -2.0 (*c* 0.8, CHCl₃, 97 % ee).



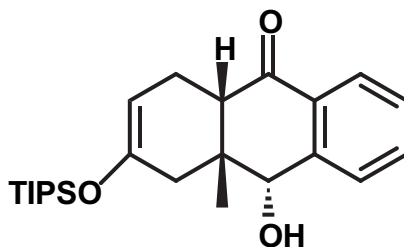
(4aR, 8aS)-4a, 5, 8, 8a-Tetrahydro-2, 3-dimethoxy-6-(triisopropylsilyl)oxy-4a-methylnaphthalene-1, 4-dione (Table 1, entry 4). Purification by column chromatography (gradient elution with hexanes and 5% Et₂O-pentane) afforded 230 mg (85%) of product as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 4.79 (m, 1H), 3.96 (s, 6H), 2.68 (m, 1H), 2.63-2.69 (m, 1H), 2.53-2.58 (dd, 1H, *J* = 17.2, 1.5 Hz), 2.19-2.23 (m, 1H), 1.85 (d, 1H, *J* = 17.2 Hz), 1.35 (s, 3H), 1.01-1.24 (m, 3H), 1.04 (d, 18H, *J* = 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 195.4, 147.8, 147.6, 147.0, 99.4, 60.84, 60.78, 50.9, 48.0, 37.0, 23.6, 22.9, 18.2 (x6), 12.8 (x3); FTIR (neat)

2942, 2865, 1677, 1599, 1281, 1208; HRMS (CI) calcd for $[C_{22}H_{37}O_5Si]$ ($[MH]^+$): 409.2410; found 409.2420; $[\alpha]_D^{23}$ -6.6 (c 1.5, $CHCl_3$, 95 % ee).



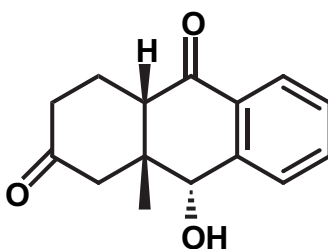
(4aS,9aR)-1,4,4a,9a-Tetrahydro-2-(triisopropylsilyl)oxy-9a-methylanthracene-9,10-dione

(Table 1, entry 5). Purification by column chromatography (5% EtOAc-hexanes) afforded 255 mg (96%) of product as a white solid: mp 45.0-46.0 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.05-8.06 (m, 1H), 8.00-8.02 (m, 1H), 7.69-7.74 (m, 2H), 4.81-4.83 (m, 1H), 2.94 (dd, 1H, J = 7.0, 5.5 Hz), 2.72 (dd, 1H, J = 17.0, 1.5 Hz), 2.50-2.56 (m, 1H), 2.24-2.30 (m, 1H), 1.90 (dd, 1H, J = 17.0, 1.5 Hz), 1.38 (s, 3H), 1.07-1.16 (m, 3H), 1.04 (d, 18H, J = 6.5Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 198.0, 147.9, 134.2, 134.0, 133.3, 132.8, 127.2, 126.4, 99.3, 52.6, 48.8, 36.4, 23.8 (x2), 17.8 (x6), 12.4 (x3); FTIR (neat) 2941, 2864, 1693, 1674, 1202; LRMS (CI) calcd for $[C_{24}H_{34}O_3Si]$ ($[M]^-$): 398; found 398; $[\alpha]_D^{23}$ +23.6 (c 1.0, $CHCl_3$, 91% ee).



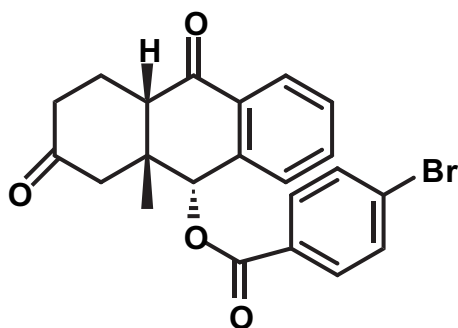
(4aS, 9R, 9aR)-1, 4, 4a, 9a-Tetrahydro-9-hydroxy-2-(triisopropylsilyl)oxy-9a-methylanthracen-10 (9H)-one. To a stirred solution of the (triisopropylsilyl)oxy quinone adduct (99.6 mg, 0.25 mmol) in MeOH (3.5 mL) was added sodium borohydride (11.3 mg, 0.29 mmol) at 0 °C and the reaction mixture was stirred for 30 min at 0 °C. Water (4 mL) and EtOAc (4 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (4 mLx3). The combined extract was dried over sodium sulfate and concentrated *in vacuo* to give a

white solid product (99.1mg, 99%): mp 108.0-109.0 °C (EtOAc-hexanes): ^1H NMR (500 MHz, CDCl_3) δ 7.98 (dd, 1H, $J = 7.5, 1.0$ Hz), 7.76 (d, 1H, $J = 8.5$ Hz), 7.58 (ddd, 1H, $J = 7.5, 7.5, 1.0$ Hz), 7.35 (dd, 1H, $J = 7.5, 7.5$ Hz), 4.84 (s, 1H), 4.81-4.82 (m, 1H), 3.02 (dd, 1H, $J = 17.0, 5.5$ Hz), 2.92 (brs, 1H), 2.34 (d, 1H, $J = 5.5$ Hz), 2.21-2.27 (m, 1H), 1.95 (d, 1H, $J = 17.5$ Hz), 1.76 (d, 1H, $J = 17.5$ Hz), 1.38 (s, 3H), 0.99-1.08 (m, 3H), 0.95 (d, 9H, $J = 7.0$ Hz), 0.94 (d, 9H, $J = 6.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 196.9, 148.2, 143.8, 134.0, 130.3, 127.6, 126.8, 126.4, 100.7, 75.6, 50.0, 41.8, 32.0, 23.7, 20.2, 17.8 (x6), 12.4 (x3); FTIR (neat) 2940, 2864, 1665, 1206; LRMS (CI) calcd for $[\text{C}_{24}\text{H}_{33}\text{O}_3\text{Si}]$ ($[\text{M}-\text{H}]^-$): 399; found 399; $[\alpha]_{\text{D}}^{23}$ -67.5 (c 1.0, CHCl_3 , 91% ee).

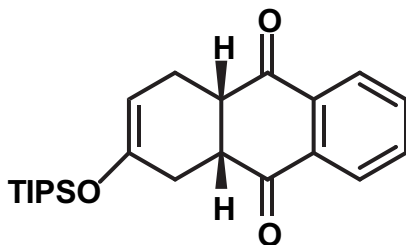


(4aS, 9R, 9aR)-1, 4, 4a, 9a-Tetrahydro-9-hydroxy-9a-methylanthracene-2, 10(3H, 9H)-dione. Deprotection of TIPS group¹⁶ afforded 35 mg (95%) of ketone product as a colorless oil: ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, 1H, $J = 7.5$ Hz), 7.62-7.69 (m, 2H), 7.45-7.49 (m, 1H), 4.82 (d, 1H, $J = 4.5$ Hz), 2.77-2.83 (m, 1H), 2.65 (t, 1H, $J = 5.0$ Hz), 2.32-2.42 (m, 2H), 2.30 (d, 1H, $J = 15.0$ Hz), 2.24 (d, 1H, $J = 15.0$ Hz), 2.04-2.12 (m, 1H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.1, 197.8, 142.7, 134.7, 129.4, 128.4, 127.8, 127.1, 74.8, 51.7, 46.1, 45.0, 38.5, 25.1, 23.9; FTIR (neat) 2952, 1684, 1676, 1286; LRMS (CI) calcd for $[\text{C}_{15}\text{H}_{16}\text{O}_3]$ ($[\text{M}]^+$): 244; found 244.

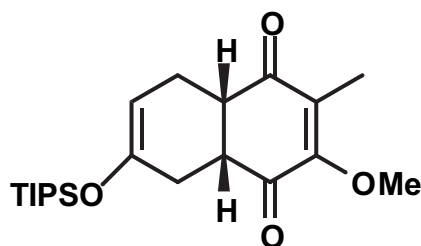
¹⁶ Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, 125, 6388.



(4aS, 9R, 9aR)-1, 2, 3, 4, 4a, 9, 9a, 10-Octahydro-9a-methyl-2, 10-dioxoanthracen-9-yl 4-bromobenzoate. To a stirred solution of the alcohol (30 mg, 0.12 mmol) in pyridine (0.5 mL) were added *p*-bromobenzoyl chloride (11.3 mg, 0.29 mmol) and a catalytic amount of 4-(dimethylamino) pyridine at 20 °C and the reaction mixture was stirred for 10 hrs at 65 °C. Pyridine was evaporated *in vacuo* and water (4 mL) and dichloromethane (4 mL) were added. The aqueous layer was extracted with dichloromethane (4 mLx3). The combined extract was dried over sodium sulfate and concentrated *in vacuo* to give pale yellow oily residue. The residue was purified by column chromatography (gradient elution with 10-20% EtOAc-hexanes) to afford 10 mg (20%) of *trans* product and 31mg (59%) of *cis* product as a white solid. Recrystallization of *cis* product from benzene provided colorless crystals suitable for X-ray structure determination: mp 149.0-150.0 °C: ¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.91 (d, 2H, *J* = 8.4 Hz), 7.58-7.65 (m, 1H), 7.63 (d, 2H, *J* = 8.4 Hz), 7.49 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.29 (d, 1H, *J* = 8.0 Hz), 6.49 (s, 1H), 2.83-2.89 (m, 1H), 2.80 (t, 1H, *J* = 4.8 Hz), 2.46 (d, 1H, *J* = 14.8 Hz), 2.34-2.46 (m, 2H), 2.34 (d, 1H, *J* = 14.8 Hz), 2.12-2.20 (m, 1H), 1.24 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 208.8, 196.4, 165.5, 138.7, 134.8, 132.1 (x2), 131.4 (x2), 129.9, 129.1, 129.0, 127.8, 127.6, 127.3, 75.5, 51.5, 46.1, 44.4, 38.3, 25.0, 23.2 ; FTIR (neat) 1711, 1721, 1680, 1258, 1097; LRMS (CI) calcd for [C₂₂H₁₉BrO₄] ([M]⁺): 426, 428; found 426, 428.

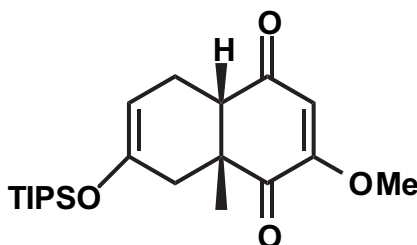


(4a*S*, 9a*R*)-1, 4, 4a, 9a-Tetrahydro-2-(triisopropylsilyl)oxy-anthracene-9, 10-dione (Table 2, entry 1). After quenched with MeOH-H₂O at -78°C and warmed up to room temperature, the reaction mixture was extracted with hexanes and the combined organic phase was washed with water and brine. After dried over Na₂SO₄, the solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography at -78°C to afford 250 mg (98%) of the Diels-Alder adduct as colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.05 (m, 2H), 7.73-7.76 (m, 2H), 4.87 (m, 1H), 3.47 (dd, 1H, $J = 11.0, 5.5$ Hz), 3.29-3.31 (m, 1H), 2.63-2.68 (m, 1H), 2.47-2.53 (m, 1H), 2.25-2.31 (m, 2H), 1.08-1.27(m, 3H), 1.07 (d, 18H, $J = 7.2$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 198.5, 197.6, 148.5, 134.6, 134.5, 134.3, 134.1, 127.12, 127.13, 100.5, 47.6, 46.8, 28.7, 24.4, 18.2(x6), 13.0(x3); FTIR (neat) 2941, 2864, 1694, 1187, 881; LRMS (CI) calcd for [C₂₃H₃₃O₃Si] ([MH]⁺): 385; found 385; [α]_D²³ +9.2 (c 1.7, CHCl₃, 97 % ee).

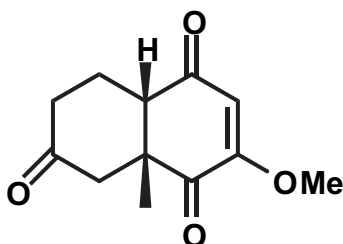


(4a*R*,8a*S*)-4a,5,8,8a-Tetrahydro-3-dimethoxy-6-(triisopropylsilyl)oxy-2-methylnaphthalene-1, 4-dione (Table 2, entry 3). After quenched with MeOH-H₂O at -78°C and warmed up to room temperature, the reaction mixture was extracted with hexanes and the combined organic phase was washed with water and brine. After dried over Na₂SO₄, the solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography at -78°C to afford 242 mg (96%) of an inseparable mixture of Diels-Alder adduct as yellow oil. After reduction with NaBH₄ to the corresponding alcohols, the minor diastereomer could be

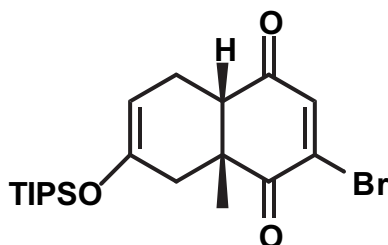
separated by silica gel chromatography to afford pure major diastereomer, which was reoxidized by Dess-Martin periodinane to give pure (4*aR*, 8*aS*)-4a, 5, 8, 8a-tetrahydro-3-dimethoxy-6-(triisopropylsilyl)oxy-2-methylnaphthalene-1,4-dione as colorless oil: ^1H NMR (500 MHz, CDCl_3) δ 4.79 (m, 1H), 3.94 (s, 3H), 3.25 (dd, 1H, $J = 14.0, 7.0$ Hz), 3.02 (m, 1H), 2.55-2.59 (m, 1H), 2.22-2.31 (m, 1H), 2.13-2.20 (m, 2H), 1.86 (s, 3H), 1.02-1.16 (m, 3H), 1.02 (d, 18H, $J = 7.2$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 200.1, 195.2, 159.1, 148.2, 130.8, 100.3, 60.1, 47.1, 46.6, 27.9, 24.9, 18.2(x6), 12.8(x3), 9.5; FTIR (neat) 2942, 2864, 1673, 1601, 1195, 1126; HRMS (CI) calcd for $[\text{C}_{21}\text{H}_{35}\text{O}_4\text{Si}]$ ($[\text{MH}]^+$): 379.2304; found 379.2299; $[\alpha]_{\text{D}}^{23} +36.8$ (c 2.4, CHCl_3 , 90 % ee).



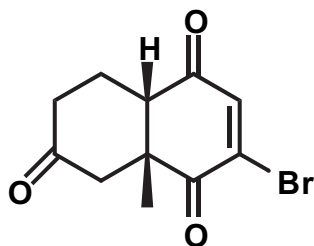
(4*aS*, 8*aR*)-4a, 5, 8, 8a-Tetrahydro-2-methoxy-7-(triisopropylsilyl)oxy -8a-methylnaphthalene-1, 4-dione (Table 2, entry 4). Aqueous work-up and treatment with pentane afforded 247 mg (98%) of product as white solid: mp 76.0-77.0 °C (pentane): ^1H NMR (400 MHz, CDCl_3) δ 5.86 (s, 1H), 4.80-4.82 (m, 1H), 3.78 (s, 3H), 2.71 (dd, 1H, $J = 5.6, 5.6$ Hz), 2.61-2.69 (m, 1H), 2.61 (dd, 1H, $J = 16.8, 1.6$ Hz), 2.18-2.25 (m, 1H), 1.83 (d, 1H, $J = 16.8\text{Hz}$), 1.39 (s, 3H), 1.06-1.16 (m, 3H), 1.04 (d, 18H, $J = 6.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 196.3, 160.0, 147.2, 109.8, 99.5, 56.3, 51.3, 48.4, 36.3, 22.8, 22.9, 17.9 (x6), 12.5 (x3); FTIR (neat) 2944, 2862, 1704, 1672, 1604, 1188; LRMS (CI) calcd for $[\text{C}_{21}\text{H}_{34}\text{O}_4\text{Si}]$ ($[\text{M}]^+$): 378; found 378; $[\alpha]_{\text{D}}^{23} -2.4$ (c 1.0, CHCl_3 , 92% ee).



(4aR, 8aS)-4a, 5, 8, 8a-Tetrahydro-3-methoxy-4a-methylnaphthalene-1,4,6(7H)-trione. Deprotection of TIPS group afforded 10 mg (89%) of ketone product as a white solid: ^1H NMR (500 MHz, CDCl_3) δ 5.99 (s, 1H), 3.82 (s, 3H), 2.91 (dd, 1H, $J = 5.0, 5.0$ Hz), 2.84 (d, 1H, $J = 15.0$ Hz), 2.32-2.46 (m, 3H), 2.13 (d, 1H, $J = 15.0$ Hz), 2.06-2.13 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.1, 197.2, 194.4, 160.1, 110.4, 56.5, 53.2, 51.9, 47.7, 38.3, 25.1, 23.6; FTIR (neat) 1709, 1665, 1604, 1228, 1067; LRMS (CI) calcd for $[\text{C}_{12}\text{H}_{14}\text{O}_4]$ ($[\text{M}]^+$): 222; found 222.

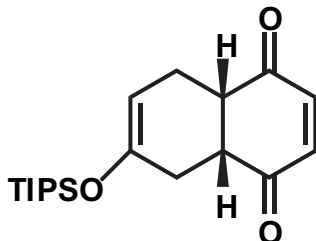


(4aS, 8aR)-4a, 5, 8, 8a-Tetrahydro-2-bromo-7-(triisopropylsilyl)oxy-8a-methylnaphthalene-1,4-dione (Table 2, entry 5). Aqueous work-up afforded 270 mg (95%) of product as a pale yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 7.18 (s, 1H), 4.77-4.79 (m, 1H), 2.78 (dd, 1H, $J = 5.4, 5.4$ Hz), 2.59-2.67 (m, 1H), 2.52 (dd, 1H, $J = 17.2, 2.0$ Hz), 2.16-2.23 (m, 1H), 1.84 (d, 1H, $J = 17.6$ Hz), 1.40 (s, 3H), 1.04-1.13 (m, 3H), 1.04 (d, 18H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 193.7, 147.1, 140.5, 139.8, 99.0, 51.7, 48.4, 36.7, 22.9, 22.1, 17.8 (x6), 12.4 (x3); FTIR (neat) 2942, 2865, 1690, 1208; LRMS (CI) calcd for $[\text{C}_{20}\text{H}_{32}\text{BrO}_3\text{Si}]$ ($[\text{MH}]^+$): 427, 429; found 427, 429; $[\alpha]_{\text{D}}^{23} -14.3$ (c 1.0, CHCl_3 , 91% ee).



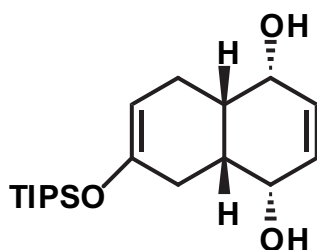
(4aR, 8aS)-3-Bromo-4a, 5, 8, 8a-tetrahydro-4a-methylnaphthalene-1, 4, 6(7H)-trione.

Deprotection of TIPS group and recrystallization from a mixture solvent (EtOAc: Hexanes=1:7) afforded 56 mg (65%) of ketone product as golden crystals suitable for X-ray structure determination: mp 113-114 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (s, 1H), 3.00 (dd, 1H, J = 5.6, 5.6 Hz), 2.80 (d, 1H, J = 14.8 Hz), 2.29-2.48 (m, 3H), 2.16 (d, 1H, J = 14.8 Hz), 2.04-2.14 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.2, 195.3, 192.1, 140.8, 140.1, 53.7, 51.9, 48.0, 38.0, 24.6, 24.0; FTIR (neat) 2932, 1683, 1588, 1181; LRMS (CI) calcd for $[\text{C}_{11}\text{H}_{11}\text{BrO}_3]$ ($[\text{M}]^-$): 270, 272; found 270, 272; $[\alpha]_{\text{D}}^{23}$ -12.8 (c 1.0, CHCl_3 , >91% ee).

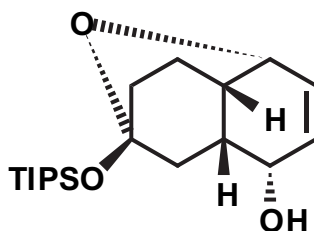


(4aR, 8aS)-4a, 5, 8, 8a-Tetrahydro-6-(triisopropylsilyl)oxy-naphthalene-1, 4-dione (Table 3, entry 1). After quenched with $\text{MeOH-H}_2\text{O}$ at -78°C and warmed up to room temperature, the reaction mixture was extracted with hexanes and the combined organic phase was washed with water and brine. After dried over Na_2SO_4 , the solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography at -78°C to afford 190 mg (85%) of the Diels-Alder adduct as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 6.69 (d, 1H, J = 10.4Hz), 6.64 (d, 1H, J =10.4Hz), 4.83 (m, 1H), 3.30 (dd, 1H, J =12.0, 6.0Hz), 3.12 (dd, 1H, J = 12.0, 6.0 Hz), 2.53-2.60 (m, 1H), 2.43-2.49 (m, 1H), 2.18-2.24 (m, 2H), 0.88-1.25 (m, 3H), 1.05 (d, 18H, J = 6.6 Hz); ^{13}C NMR (100MHz, CDCl_3) δ 200.3, 199.2, 148.3, 139.6, 139.4, 100.3, 47.4, 46.5, 28.4,

24.2, 18.1(x6), 12.8 (x3); FTIR (neat) 2864, 1684, 1653, 1194, 881; $[\alpha]_D^{23} +18.0$ (*c* 1.8, CHCl_3 , 88 % ee).



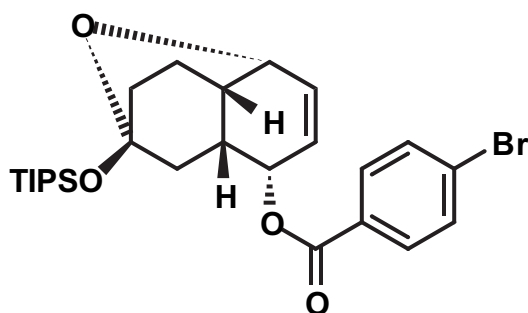
(1R, 4S, 4aR, 8aS)-1, 4, 4a, 5, 8, 8a-hexahydro-6-(triisopropylsilyl)oxy-naphthalene-1, 4-diol. To a stirred solution of the (triisopropylsilyl)oxy quinone adduct (66.8 mg, 0.20 mmol) in MeOH (5 mL) was added a $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (59.2 mg, 0.24 mmol) and sodium borohydride (9.1 mg, 0.24 mmol) at 0 °C and the reaction mixture was stirred for 10 min at 0 °C. Water (4 mL) and hexanes (4 mL) were added and the organic layers were separated. The aqueous layer was extracted with hexanes and ether (10 ml x 3). The combined extract was dried over sodium sulfate and concentrated *in vacuo* to give pale yellow oil, which was purified by silica gel chromatography to afford diol as a colorless oil (45.4 mg, 68%): ^1H NMR (400 MHz, CDCl_3) δ 5.74 (s, 2H), 4.94 (m, 1H), 4.24 (m, 2H), 2.09-2.31 (m, 6H), 1.01-1.24 (m, 3H), 1.04 (d, 18H, *J* = 6.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 152.0, 129.9, 129.8, 101.9, 68.7, 68.4, 35.4, 34.2, 29.9, 23.6, 18.2 (x6), 12.9 (x3); FTIR (neat) 2863, 1662, 1193, 677; LRMS (CI) calcd for $[\text{C}_{19}\text{H}_{34}\text{O}_3\text{Si}]$ ($[\text{M}-\text{H}]^-$): 337; found 337; $[\alpha]_D^{23} -15.0$ (*c* 0.8, CHCl_3).



TIPS cyclic ketal.

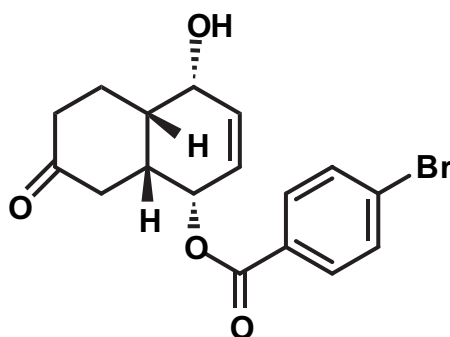
To a stirred solution of diol obtained previously (33.8 mg, 0.10 mmol) in 5 mL of THF, $\text{BF}_3 \cdot \text{OEt}_2$ (2.8mg, 0.02 mmol) was added by syringe at -78 °C. The mixture was stirred at -78 °C

for 2 h and then diluted with 10 mL of diethyl ether and 5mL of saturated aqueous NaHCO_3 . The mixture was warmed up to room temperature and the two phases were separated. The aqueous phase was extracted with diethyl ether (2 x 10 mL) and the combined organic phase was washed with saturated aqueous NaCl , dried over Na_2CO_3 . The solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography to afford 28.7 mg (85%) of ketal as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 6.00 (ddd, 1H, $J = 9.6, 5.2, 2.0\text{Hz}$), 5.65 (dt, 1H, $J = 9.6, 1.6\text{Hz}$), 4.34 (m, 1H), 4.10 (m, 1H), 2.40 (m, 1H), 1.52-1.96 (m, 7H), 1.01-1.08 (m, 3H), 1.03 (d, 18H, $J = 6.6\text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3) δ 131.5, 131.2, 96.6, 70.9, 70.3, 37.1, 35.1, 33.2, 29.9, 25.4, 18.4 (x6), 13.3 (x3); FTIR (neat) 2940, 2863, 1339, 1180, 994; LRMS (CI) calcd for $[\text{C}_{19}\text{H}_{35}\text{O}_3\text{Si}]$ ($[\text{MH}]^+$): 339; found 339; $[\alpha]_D^{23}$ -108 (c 1.9, CHCl_3).



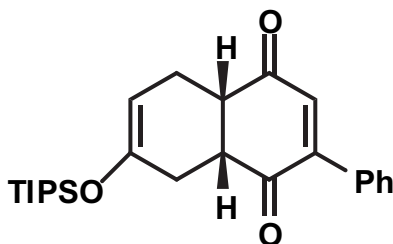
***p*-Bromobenzoate.**

Protection of monoalcohol obtained previously with *p*-bromobenzoyl chloride afforded bromobenzoate (87%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 7.87(d, 2H, $J = 6.4\text{Hz}$), 7.58 (d, 2H, $J = 6.4\text{Hz}$), 6.13 (ddd, 1H, $J = 9.6, 4.8, 2.4\text{Hz}$), 5.73 (dt, 1H, $J = 9.6, 1.2\text{Hz}$), 5.63 (m, 1H), 4.19 (m, 1H), 2.65 (m, 1H), 2.15 (m, 1H), 1.59-1.99 (m, 6H), 1.01-1.10 (m, 3H), 1.04 (d, 18H, $J = 6.6\text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 133.2, 132.0(x2), 131.4(x2), 129.4, 128.4, 127.3, 96.3, 74.1, 70.1, 35.6, 34.3, 33.0, 29.7, 25.3, 18.5 (x6), 13.3 (x3); FTIR (neat) 2922, 2862, 1719, 1265, 995; LRMS (CI) calcd for $[\text{C}_{26}\text{H}_{37}\text{BrO}_4\text{Si}]$ ($[\text{M}]^+$): 520, 522; found 520, 522; $[\alpha]_D^{23}$ -43.8 (c 2.6, CHCl_3).



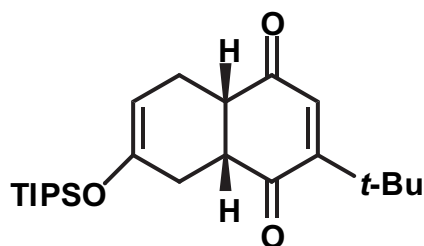
(1R, 4S, 4aR, 8aS)-1, 4, 4a, 5, 6, 7, 8, 8a-Octahydro-1-hydroxy-6-oxonaphthalen-4-yl-4-bromobenzoate. After desilylation with 10% HF(CH₃CN), residue was purified by silica gel chromatography to afford the hydroxyketone as a white solid. Recrystallization from a mixture solvent (diethyl ether-hexanes 2 : 1) at 0 °C for 2 days provided the colorless crystal suitable for the X-ray structure determination: mp 138 – 139 °C: ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, 2H, *J*=6.8 Hz), 7.54 (d, 2H, *J*=6.8 Hz), 5.82-5.86 (m, 2H), 5.62 (m, 1H), 4.56 (dd, 1H, *J*=6.4, 1.2 Hz), 2.07-2.65 (m, 8H); ¹³C NMR (100MHz, CDCl₃) δ 209.8, 171.4, 165.5, 134.4, 131.9, 131.4, 128.7, 128.6, 124.5, 69.1, 68.9, 42.9, 40.3, 37.7, 37.2, 21.0; FTIR (neat) 1722, 1182, 1025, 909, 730; LRMS (CI) calcd for [C₁₇H₁₇BrO₄] ([M]⁺): 364, 366; found 364, 366.

(4aS, 8aR)-4a, 5, 8, 8a-Tetrahydro-7-(triisopropylsilyloxy)-2-phenylnaphthalene-1, 4-dione

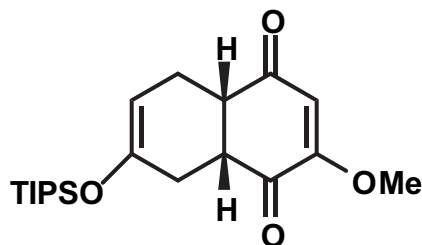


(Table 3, entry 2). After quenched with MeOH-H₂O at -78 °C and warmed up to room temperature, the reaction mixture was extracted with hexanes and the combined organic phase was washed with water and brine. After dried over Na₂SO₄, the solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography at -78 °C to afford 246 mg

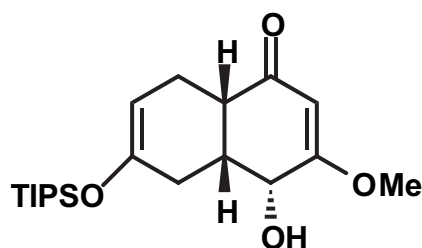
(90%) of the Diels-Alder adduct as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.48 (m, 5H), 6.77 (s, 1H), 4.86 (m, 1H), 3.52 (dd, 1H, $J = 9.6, 4.4$ Hz), 3.18 (dd, 1H, $J = 10.0, 4.4$ Hz), 2.66-2.71 (m, 1H), 2.47-2.53 (m, 1H), 2.52-2.30 (m, 2H), 1.12-1.31 (m, 3H), 1.08 (d, 18H, $J = 6.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 200.2, 199.0, 149.53, 148.4, 134.8, 133.3, 130.6, 129.5, 129.3, 128.8(x2), 100.3, 48.8, 46.7, 28.4, 24.5, 18.2(x6), 12.8(x3); FTIR (neat) 2941, 2863, 1673, 1189, 881; HRMS (CI) calcd for $[\text{C}_{25}\text{H}_{35}\text{O}_3\text{Si}]$ ($[\text{MH}]^+$): 411.2355; found 411.2352; $[\alpha]_{\text{D}}^{23} +47.8$ (c 2.9, CHCl_3 , 94% ee).



(4a*S*, 8a*R*)-2-*tert*-Butyl-4a, 5, 8, 8a-tetrahydro-7-(triisopropylsilyloxy)-naphthalene-1, 4-dione (Table 3, entry 3). After quenched with $\text{MeOH-H}_2\text{O}$ at -78°C and warmed up to room temperature, the reaction mixture was extracted with hexanes and the combined organic phase was washed with water and brine. After dried over Na_2SO_4 , the solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography at -78°C to afford 238 mg (92%) of the Diels-Alder adduct as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 6.46 (s, 1H), 4.82 (m, 1H), 3.25 (dd, 1H, $J = 11.2, 5.6$ Hz), 3.03 (dd, 1H, $J = 12.4, 6.0$ Hz), 2.47-2.53 (m, 1H), 2.36-2.42 (m, 1H), 2.12-2.21 (m, 2H), 1.24 (s, 9H), 1.12-1.32 (m, 3H), 1.09 (d, 18H, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0, 199.9, 160.6, 148.4, 133.6, 100.4, 49.3, 46.4, 30.1, 29.0(x3), 28.4, 24.2, 18.2(x6), 12.8(x3); FTIR (neat) 2942, 2865, 1675, 1212, 753; HRMS (CI) calcd for $[\text{C}_{23}\text{H}_{39}\text{O}_3\text{Si}]$ ($[\text{MH}]^+$): 391.2668; found 391.2670; $[\alpha]_{\text{D}}^{23} +23.9$ (c 2.2, CHCl_3 , 91% ee).

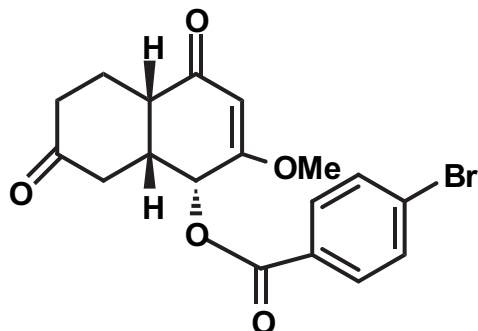


(4aS, 8aR)-4a, 5, 8, 8a-Tetrahydro-2-methoxy-7-(triisopropylsilyloxy)-naphthalene-1, 4-dione (Table 3, entry 4). Aqueous work-up and treatment with pentane afforded 230 mg (95%) of product as a white solid: mp 79.0-80.0 °C (pentane): ^1H NMR (400 MHz, CDCl_3) δ 5.87 (s, 1H), 4.81-4.83 (m, 1H), 3.78 (s, 3H), 3.32 (dd, 1H, $J = 12.0, 5.2$ Hz), 3.04 (dd, 1H, $J = 13.2, 6.0$ Hz), 2.60-2.66 (m, 1H), 2.38-2.46 (m, 1H), 2.18-2.29 (m, 2H), 1.10-1.18 (m, 3H), 1.05 (d, 18H, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 193.7, 161.3, 147.9, 110.2, 100.1, 56.3, 46.6, 45.8, 27.9, 24.6, 17.9 (x6), 12.5 (x3); FTIR (neat) 2941, 2865, 1701, 1672, 1598, 1184; LRMS (CI) calcd for $[\text{C}_{20}\text{H}_{32}\text{O}_4\text{Si}]$ ($[\text{M}]^+$): 364; found 364; $[\alpha]_{\text{D}}^{23} +83.6$ (c 1.0, CHCl_3 , 91% ee).

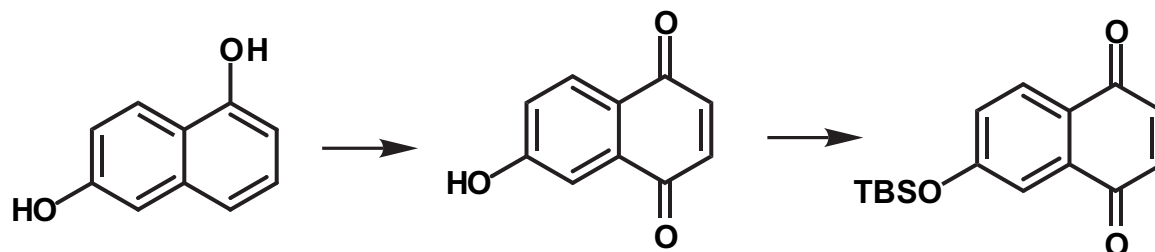


(4R,4aR,8aS)-4a,5,8,8a-Tetrahydro-4-hydroxy-3-methoxynaphthalene-1,6(4H,7H)-dione.

Selective reduction of quinone with sodium borohydride afforded crude mono alcohol product as a pale yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 5.36 (s, 1H), 4.84-4.85 (m, 1H), 4.81 (d, 1H, $J = 5.0$ Hz), 3.77 (s, 3H), 2.81-2.88 (m, 2H), 2.51-2.53 (m, 1H), 2.19 (dd, 1H, $J = 18.0, 5.0$ Hz), 2.03-2.14 (m, 1H), 1.06-1.15 (m, 3H), 1.04 (d, 9H, $J = 7.0$ Hz), 1.03 (d, 9H, $J = 7.0$ Hz).



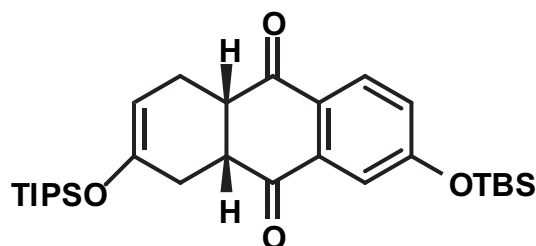
(4*R*, 4*aR*, 8*aS*)-1, 4, 4*a*, 5, 6, 7, 8, 8*a*-Octahydro-3-methoxy-1, 6-dioxonaphthalen-4-yl 4-bromobenzoate. *p*-Bromobenzoylation of the alcohol at 20 °C and deprotection of TIPS group provided crude ketone product. The crude product was purified by column chromatography (gradient elution with 30-60% EtOAc-hexanes) to afford 30 mg (48% for two steps) of product as a white solid. Recrystallization from a mixture solvent (dichloromethane: hexanes=1:5) provided colorless crystals suitable for X-ray structure determination: mp 191-192 °C: ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, 2H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), 6.26 (d, 1H, *J* = 4.8 Hz), 5.55 (s, 1H), 3.73 (s, 3H), 3.03 (dt, 1H, *J* = 15.2, 5.2 Hz), 2.85 (dd, 1H, *J* = 9.6, 4.8 Hz), 2.74 (ddd, 1H, *J* = 13.6, 10.8, 5.2 Hz), 2.57 (dd, 1H, *J* = 14.8, 5.2 Hz), 2.39-2.52 (m, 2H), 2.34 (dt, 1H, *J* = 14.8, 5.2 Hz), 1.80-1.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 208.7, 196.7, 170.6, 164.8, 131.9 (x2), 131.3 (x2), 128.9, 127.8, 102.6, 69.3, 56.6, 44.1, 40.3, 39.2, 38.4, 25.4 ; FTIR (neat) 2944, 1719, 1654, 1607, 1584, 1199, 1007; LRMS (CI) calcd for [C₁₈H₁₇BrO₅] ([M]⁺): 392, 394; found 392, 394.



6-Hydroxynaphthalene-1, 4-dione : Oxygen was bubbled rapidly into a stirring solution of naphthalene-1,6-diol (3 g, 18.7 mol) and bis(salicylidene)ethylenediaminocobalt (II) hydrate (salcomine, 0.3 g) in anhydrous DMF (20ml) for 10 h. The reaction mixture was passed through a Celite pad and the filtrate was concentrated *in vacuo* to give gummy residue. Water (100mL) and EtOAc (20mL) were added and the aqueous layer was extracted with EtOAc (4x 20mL). The combined extract was dried over anhydrous Na_2SO_4 and concentrated to afford black red solid residue. The crude product was purified by column chromatography (gradient elution with 30-60% EtOAc-hexanes) to afford 2.3 g (67% yield) of product as orange solid: ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, 1H, $J = 8.5$ Hz), 7.47 (d, 1H, $J = 2.5$ Hz), 7.18 (dd, 1H, $J = 8.5, 2.5$ Hz), 6.94 (s, 2H), 5.51 (s, 1H); LRMS (CI) calcd for $[\text{C}_{10}\text{H}_6\text{O}_3]$ ($[\text{M}-\text{H}]^-$): 173; found 173.

6- *t*-Butyldimethyl silyloxy naphthalene-1, 4-dione : To a stirred solution of the phenol (530 mg, 3.0 mmol) in anhydrous DMF (6 mL) were added imidazole (576 mg, 9.13 mmol) and *t*-butyldimethylsilyl chloride (688 mg, 4.56 mmol) at 20 °C and the reaction mixture was stirred for 20 min at 20 °C. Water (60 mL) and diethyl ether (10 mL) were added. The aqueous layer was extracted with diethyl ether (10 mLx3). The combined extract was dried over sodium sulfate and concentrated *in vacuo* to give brown oily residue. The residue was purified by column chromatography (gradient elution with 1-3% EtOAc-hexanes) to afford 319 mg (36%) of TBS ether product as green oil: ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, 1H, $J = 8.4$ Hz), 7.45 (d, 1H, $J = 2.4$ Hz), 7.15 (dd, 1H, $J = 8.4, 2.4$ Hz), 6.92 (d, 2H, $J = 0.8$ Hz), 1.00 (s, 9H), 0.27 (s, 6H); ^{13}C

NMR (125 MHz, CDCl_3) δ 185.1, 184.1, 161.1, 138.9, 138.3, 133.9, 129.0, 125.9, 125.4, 116.9, 25.5 (x3), 18.2, -4.4 (x2) ; FTIR (neat) 2857, 1664, 1589, 1305, 1239; LRMS (CI) calcd for $[\text{C}_{16}\text{H}_{21}\text{O}_3\text{Si}]$ ($[\text{MH}]^+$): 289; found 289.



(4aR, 9aS)-2-(Triisopropylsilyl)oxy-1, 4, 4a, 9a-tetrahydro-7-t-butylidimethylsilyloxyanthracene-9, 10-dione. Aqueous work-up and silica gel filtration afforded 342 mg (95%) of product as pale orange oil: ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, 1H, J = 8.0 Hz), 7.38 (d, 1H, J = 2.5 Hz), 7.12 (dd, 1H, J = 8.0, 2.5 Hz), 4.84-4.85 (m, 1H), 3.43 (dd, 1H, J = 12.0, 5.5 Hz), 3.04 (dt, 1H, J = 7.5, 5.5 Hz), 2.64-2.70 (m, 1H), 2.42-2.47 (m, 1H), 2.23-2.27 (m, 2H), 1.08-1.17 (m, 3H), 1.05 (d, 18H, J = 7.0 Hz), 0.98 (s, 9H), 0.25 (s, 6H) ; ^{13}C NMR (125 MHz, CDCl_3) δ 197.2 (x2), 161.2, 148.2, 136.2, 129.4, 127.5, 125.9, 116.6, 100.3, 47.4, 46.3, 28.3, 25.4 (x3), 24.4, 17.9 (x6), 18.1, 12.5 (x3), -4.5, -4.4; FTIR (neat) 2964, 1690, 1591, 1288; LRMS (CI) calcd for $[\text{C}_{29}\text{H}_{46}\text{O}_4\text{Si}_2]$ ($[\text{M}]^-$): 514; found 514; $[\alpha]_{\text{D}}^{23}$ +15.4 (c 1.0, CHCl_3 , >99% ee). Regioselectivity was determined by ^1H NMR analysis of the crude mixture: δ 3.43 (dd, 1H, J = 12.0, 5.5 Hz, major), 3.38 (dd, 1H, J = 11.5, 6.0 Hz, minor), 3.25 (dd, 1H, J = 12.0, 6.0 Hz, minor), 3.04 (dt, 1H, J = 7.5, 5.5 Hz, major). Enantioselectivity was determined by HPLC analysis using a Daicel Chiralcel OD-H column (0.2% *i*-PrOH in hexanes for elution; 1 mL/min; λ 254 nm); retention times: 9.43 min (regioisomer), 10.19 min (major), 12.30 min (minor). The absolute configuration was determined by analogy with (+)-(4a*S*, 9a*R*)-1, 4, 4a, 9a-tetrahydro-2-(triisopropylsilyl)oxy-anthracene-9, 10-dione.