Supplementary data

1. General methods
1H and 13C NMR spectra were recorded at room temperature in CDCl3 with a Bruker ACF300 (300MHz) or AMX500 (500MHz) spectrometer. Chemical shifts (d) are reported in parts per million (ppm). Coupling constants are given as absolute values expressed in Hz. Low resolution mass spectra were obtained on a VG Micromass 7035 spectrometer in EI mode, a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Infrared spectra were recorded on a BIO-RAD FTS 165 FTIR spectrometer. Enantiomeric excesses were determined by chiral HPLC analysis on Jasco HPLC units, including a Jasco DG-980-50 Degasser, a LG-980-02 Ternary Gradient Unit, a PU-980 Intelligent HPLC Pump, UV-975 Intelligent UV/VIS Detectors, and an AS-950 Intelligent Sampler. Optical rotations were recorded on a Jasco DIP-1000 polarimeter. Melting points were determined on a BÜCHI B-540 melting point apparatus. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063mm) mesh silica gel. All distilled solvents were stored under N2. All other reagents and solvents are commercial grade and were used as supplied without further purification, unless otherwise stated.
2. Experimental procedures

General procedures for bicyclic guanidine catalyzed reactions between substituted anthrone and maleimides.

To a 5 ml RBF containing catalyst 1 (5.8 mg, 0.02 mmol, 10 mol %) and a stirring bar, anhydrous CH$_2$Cl$_2$ (1.0 ml), 1, 8-dichloro-9-anthrone 2a (58 mg, 0.22 mmol) and N-acetoxymaleimide 3a (31.0 mg, 0.2 mmol) were added in this sequence. After stirring at -20 °C for 8 hrs, the reaction mixture was loaded onto a short silica gel column, followed by flash chromatography (gradient elution with hexane/EtOAc mixtures; 9/1 to 4/1). Product 4a (72 mg) was obtained as a white solid in 86% yield and 92% ee.

General procedures for the chiral anthrone-derived NHPI analogue mediated oxidations of benzylic compounds and diol.

A solution of substrate 6 (0.2 mmol), catalyst 5 (0.02 mmol), and Co(OAc)$_2$ (0.002 mmol) in anhydrous acetonitrile (1 ml) was placed in a round bottom flask. The flask was equipped with a balloon filled with O$_2$ (1 atm). The mixture was vigorously stirred at 60 °C for 10 h, evaporation of the solvent followed by flash chromatography on silica gel afforded product as a white solid.

General Procedures for the synthesis of β-hydroxy ketal 17.

A solution of substrate 15a (1 mmol), substrate 16a (0.2 mmol), catalyst 14 (0.02 mmol), and Co(OAc)$_2$ (0.002 mmol) was placed in a round bottom flask. The flask was equipped with a balloon filled with O$_2$ (1 atm). The mixture was vigorously stirred at rt for 5 h. The recovery of unreacted 15a under a reduced pressure followed by flash chromatography on silica gel ($n$-hexane–AcOEt = 1:2) afforded product 17a (60% yield) as a colorless liquid.

Procedures for the synthesis of α-hydroxy-γ-lactone 19.

To a solution of alcohol 18 (2 mmol), catalyst 14 (0.02 mmol), Co(OAc)$_2$ (0.002 mmol) in acetonitrile (0.5 ml) placed in a round bottom flask, 16a (0.2 mmol) was was added. The flask was equipped a ballon filled with O$_2$ (1 atm). After the mixture was stirred at rt for 8 h, rotary evaporation of the solvent and unreacted alcohol followed by flash chromatography on silica gel afforded product 19 in 65 % yield.
3. Characterization of the oxidation products

(4a) 2-Acetoxy-5, 13-dichloro-4-hydroxy-3a, 4, 9, 9a-tetrahydro-4, 9-[1’, 2’] benzeno -1H-benz[f]isoindole-1, 3(2H)-dione

White solid. mp 251.9-252.7 °C. 86% yield, 92% ee. \([\alpha]^{25}_D +58 \ (c \ 0.25, \ CHCl_3)\). \(^1\)H NMR (500 MHz, CDCl₃, ppm): \(\delta 2.15 \ (s, 3H), 3.32 \ (dd, 1H, J = 3.1, 8.8Hz), 3.43 \ (d, 1H, J = 9.5Hz), 4.69 \ (d, 1H, J = 3.2Hz), 4.86 \ (s, 1H), 7.12-7.27 \ (m, 6H). \(^13\)C NMR 125 MHz, CDCl₃, ppm): 17.3, 43.0, 44.9, 48.6, 81.3, 122.7, 124.2, 128.5, 129.1, 130.0, 130.1, 131.3, 134.8, 138.7, 141.5, 168.4, 168.6. IR (film): 1215.4, 1637.8, 3019.0 cm⁻¹. LRMS(FAB) m/z 417.8 (M⁺), HRMS(FAB) m/z 418.0249 (M+H⁺), calc. for C₂₀H₁₄Cl₂NO₅ 418.0249.

The ee determined by chiral HPLC; CHIRALCEL AD-H (4.6 mm i.d. x 250 mm); hexane/2-propanol 80/20; flow rate 1.0 ml/min; temp 25 °C; detection UV 230 nm; retention time: 18.1 min and 22.2 min.

(4b) 8, 10-Dichloro-2-acetoxy-4-hydroxy-3a, 4, 9, 9a-tetrahydro-4, 9-[1’, 2’] benzeno-1H-benz[f]isoindole-1, 3(2H)-dione
White solid. mp 244.1-245.0 °C. 85% yield, 12% ee. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 2.16 (s, 3H), 3.20 (d, 1H, \(J = 8.7\)Hz), 3.42 (dd, 1H, \(J = 3.1, 8.4\)Hz), 4.33 (s, 1H), 5.87 (d, 1H, \(J = 3.1\)Hz), 7.20-7.60 (m, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 14.1, 17.3, 36.9, 43.4, 47.1, 119.5, 119.9, 127.7, 128.2, 128.4, 128.6, 130.0, 131.1, 133.3, 142.4, 144.3, 167.7, 169.9. IR (film): 1216.0, 1643.3, 3019.5 cm\(^{-1}\). LRMS(FAB) m/z 418.0 (M\(^+\)), HRMS(FAB) m/z 418.0248 (M+H\(^+\)), calc. for C\(_{20}\)H\(_{14}\)Cl\(_2\)NO\(_5\) 418.0249.

The ee determined by chiral HPLC; CHIRALCEL AD-H (4.6 mm i.d. x 250 mm); hexane/2-propanol 80/20; flow rate 1.0 ml/min; temp 25 °C; detection UV 230 nm; retention time: 27.0 min and 32.1 min.

\((4c)\) 2-benzoyloxy-5, 13-dichloro-4-hydroxy-3a, 4, 9, 9a-tetrahydro-4, 9-[1', 2'] benzeno -1\(H\)-benz[f]isoindole-1, 3(2\(H\))-dione

White solid. mp 176.5 -177.2 °C. 83% yield, 64% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\), ppm): \(\delta\) 3.40 (dd, 1H, \(J = 3.1, 8.8\)Hz), 3.51 (d, 1H, \(J = 8.8\)Hz), 4.74 (d, 1H, \(J = 3.2\)Hz), 4.90 (s, 1H), 7.14-7.97 (m, 11H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), ppm): \(\delta\) 41.8, 43.6, 47.4, 80.0, 121.4, 122.9, 123.4, 127.2, 127.4, 127.8, 128.6, 128.7, 129.2, 129.9,
130.0, 133.5, 137.3, 140.2, 167.2, 167.5. IR (film): 1216.0, 1641.9, 3018.7 cm$^{-1}$.
LRMS(FAB) m/z 479.9 (M$^+$), HRMS(FAB) m/z 480.0400 (M+H$^+$), calc. for C$_{20}$H$_{13}$Cl$_2$NO$_5$ 480.0406.

The ee determined by chiral HPLC; CHIRALCEL AD-H (4.6 mm i.d. x 250 mm); hexane/2-propanol 80/20; flow rate 1.0 ml/min; temp 25 °C; detection UV 230 nm; retention time: 12.3 min and 14.8 min.

(4d) 8, 10-Dichloro-2-benzoyloxy-4-hydroxy-3a, 4, 9, 9a-tetrahydro-4, 9-[1', 2'] benzeno-1H-benz[f]isoindole-1, 3(2H)-dione

White solid. mp 253.3-254.2 °C. 84% yield, 87% ee. $^1$H NMR (500 MHz, CDCl$_3$, ppm): δ 3.26 (d, 1H, $J = 8.8$Hz), 3.49 (dd, 1H, $J = 3.7$, 8.8Hz), 4.35 (s, 1H), 5.92 (d, 1H, $J = 3.2$Hz), 7.22-7.97 (m, 11H). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): δ 37.0, 43.6, 47.2, 77.2, 119.5, 120.0, 124.7, 127.7, 128.3, 128.6 (two peaks), 128.7, 130.1, 130.5, 131.2, 133.4, 134.9, 142.5, 144.5, 167.8, 170.1. IR (film): 1216.0, 1735.4, 3018.2 cm$^{-1}$. LRMS (FAB) 480.0 m/z (M$^+$), HRMS (FAB) m/z 480.0378 (M+H$^+$), calc. for C$_{25}$H$_{16}$Cl$_2$NO$_5$ 480.0406.
The ee determined by chiral HPLC; CHIRALCEL AD-H (4.6 mm i.d. x 250 mm); hexane/2-propanol 80/20; flow rate 1.0 ml/min; temp 25 °C; detection UV 230 nm; retention time: 15.6 min and 19.4 min.

(5) 2-Hydroxy-5, 13-dichloro-4-hydroxy-3a, 4, 9a-tetrahydro-4, 9-[1’, 2’] benzeno -1H-benz[f]isoindole-1, 3(2H)-dione

White solid. mp 191.0 -191.8 °C. 92% yield. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO, ppm): $\delta$ 3.40 (dd, 1H, $J = 3.1, 8.8$Hz), 3.43 (d, 1H, $J = 8.8$Hz), 4.82 (d, 1H, $J = 2.5$Hz), 4.97 (s, 1H), 7.16-7.49 (m, 6H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO, ppm): $\delta$ 42.7, 44.8, 48.3, 81.2, 123.3, 124.2, 128.5, 128.8, 129.3, 129.4, 130.6 (two peaks), 135.9, 137.5, 140.2, 142.7, 170.6, 172.2. IR (film): 1215.9, 1642.0, 3018.2, 3433.0 cm$^{-1}$. LRMS(ESI) m/z 376.3 (M$^+$), HRMS(ESI) m/z 397.9957 (M+Na$^+$), calc. for C$_{18}$H$_{11}$Cl$_2$NO$_4$Na 397.9963.

(7a) 1-Acenaphthenol
Yellow solid. 42% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 3.27 (d, 1H, $J =$ 17.8Hz), 3.82 (dd, 1H, $J =$ 7.4, 17.8Hz), 5.75 (dd, 1H, $J =$ 2.4, 7.3Hz), 7.31-7.78 (m, 6H). LRMS (FAB) m/z 170.1 (M$^+$$)$. 

The ee determined by chiral HPLC; CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol 95/5; flow rate 0.5 ml/min; temp 25 °C; detection UV 230 nm; retention time: 21.8 min and 23.2 min.

(9) 2-Methoxy-2-phenyldindan-1-one

White solid. 55% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 3.34 (s, 3H), 3.59 (s, 2H), 7.29-7.79 (m, 9H). LRMS (FAB) m/z 237.0 (M-H$^+$).

The ee determined by chiral HPLC; CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol 97/3; flow rate 0.3 ml/min; temp 25 °C; detection UV 230 nm; retention time: 27.5 min and 28.9 min.

(11) 1-Phenylethanol

The ee determined by chiral HPLC; CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol 95/5; flow rate 0.5 ml/min; temp 25 °C; detection UV 230 nm; retention time: 11.0 min and 15.1 min.
(13) Benzoin

White solid. 35% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 4.57 (d, 1H, $J = 6.0$Hz), 5.96 (d, 1H, $J = 6.3$Hz), 7.26-7.93 (m, 10H). LRMS (FAB) m/z 213.0 (M+H$^+$).

The ee determined by chiral HPLC; CHIRALPAK IA (4.6 mm i.d. x 250 mm); hexane/2-propanol 95/5; flow rate 1.0 ml/min; temp 25 °C; detection UV 230 nm; retention time: 40.0 min and 46.5 min.

(14) 4-Hydroxy-2-hydroxy -3a, 4, 9, 9a-tetrahydro-4, 9[1', 2']-benzeno-1H-benz[f]isoindole-1, 3(2H)-dione

White solid. mp 225.0-225.9 °C. 92% yield. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO, ppm): $\delta$ 3.14 (d, 1H, $J = 8.8$Hz), 3.34 (dd, 1H, $J = 3.2$, 8.2Hz), 4.76 (d, 1H, $J = 3.2$Hz), 7.13-7.66 (m, 8H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO, ppm): $\delta$ 44.0, 44.7, 47.8, 76.9, 120.5, 121.0, 123.7, 124.5, 126.3, 126.5, 126.6, 126.8, 137.4, 139.9, 141.3, 144.0, 170.9, 171.2. IR (film): 1215.7, 1638.2, 3018.0, 3429.3 cm$^{-1}$. LRMS(ESI) m/z 306.2 (M-H$^+$), HRMS(ESI) m/z 330.0734 (M+Na$^+$), calc. for C$_{18}$H$_{13}$NO$_4$Na 330.0742.

(17a) Methyl 2-hydroxy-3-(2-methyl-1,3-dioxolan-2-yl)propanoate
Colorless liquid. 60% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 1.38 (s, 3H), 2.14 (dd, 1H, $J = 7.6, 14.8$ Hz), 2.27 (dd, 1H, $J = 3.3, 14.8$ Hz), 3.77 (s, 3H), 3.99 (m, 4H), 4.40 (m, 1H). LRMS(ESI) m/z 213.0 (M+Na$^+$)

(17b) Methyl 3-(1,3-dioxolan-2-yl)-2-hydroxypropanoate

Colorless liquid. 56% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 2.85 (dd, 1H, $J = 6.3, 16.4$ Hz), 2.92 (dd, 1H, $J = 4.4, 16.4$ Hz), 3.66 (s, 3H), 3.81 (m, 4H), 4.26 (m, 1H), 4.52 (t, 1H, $J = 5.4$ Hz). LRMS(FAB) m/z 177.0 (M+H$^+$)

(17c) 2-Hydroxy-3-(2-methyl-1,3-dioxolan-2-yl)propanenitrile

Colorless liquid. 58% yield. $^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 1.39 (s, 3H), 2.26 (dd, 1H, $J = 5.7, 15.1$ Hz), 2.44 (dd, 1H, $J = 7.6, 15.1$ Hz), 4.01 (m, 4H), 4.92 (dd, 1H, $J = 5.6, 7.6$ Hz). LRMS(ESI) m/z 176.1 (M+NH$_4^+$)

(17d) 3-(1,3-Dioxolan-2-yl)-2-hydroxypropanenitrile

Colorless liquid. 52% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 2.21 (m, 1H), 2.32 (m, 1H), 3.67 (1H, d, 1H, $J = 6.6$ Hz), 3.92-4.09 (m, 4H), 4.74 (dd, 1H, $J = 3.8, 6.6$ Hz), 5.18 (dd, 1H, $J = 3.5, 5.2$ Hz). LRMS(EI) m/z 142.1 (M-H$^+$)

(19) Dihydro-3-hydroxy-5,5-dimethyl-2(3H)-furanone

Colorless liquid. 65% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 1.39 (s, 3H), 1.50 (s, 3H), 2.04 (dd, 2H, $J = 2.8, 9.1$ Hz), 2.50(dd, 1H, $J = 8.7, 12.9$ Hz), 4.65 (t, 4H, $J = 9.1$). LRMS(FAB) m/z 147.1 (M+NH$_4^+$)
4. Copies of NMR spectrum

(4a)
(4b)
(17b)

(17c)
(17d)

JL3DUL5.1 SHJ217 regroup 15-20 after column 14-16 more scans

(19)

H normal range AC393 se Oul14.1 se(S30) G2-29