Supporting Information

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(A) General Information

$^1$H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. $^{13}$C NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. The enantiomeric excesses were determined by HPLC analysis on chiral DAICEL CHIRALPAK IA, IE, ADH or IC column at 254 nm. Optical rotations were measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^T$ (c = g/100 mL, CH$_2$Cl$_2$). HRMS was recorded on a commercial apparatus (ESI source). Solvents were dried according to standard procedures. Racemic samples were prepared according to the methods reported in the literature.$^{[1]}$

All reactions were performed in sealed oven-dried glass tubes under an atmosphere of nitrogen unless otherwise noted. The diastereoisomers of the catalytic products have different Rf values and they could be isolated by flash chromatography on silica gel. Malonate 2 and Enynes were prepared according to the literature.$^{[2,3]}$ The N,N’-dioxdes were prepared according to the methods reported in the literature.$^{[4]}$

(B) General experimental procedure for the preparation of polyquinanes

In a test tube, a mixture of L-PiMe$_3$ (5.6 mg, 10 mol%) and Y(OTf)$_3$ (5.4 mg, 10 mol%) in CH$_2$Cl$_2$ (1.0 mL) was stirred at 30 °C for 0.5 hour under N$_2$ atmosphere. After the solvent had been removed under vacuum, enynes (1) (0.1 mmol), malonate (2) (0.1 mmol) and CH$_2$Cl$_2$ (0.5 mL) were added. After being stirred at 30 °C for 10 min, iPr$_2$EtN (8.4 μL, 50 mol%) was added and the mixture was stirred at the same temperature for 48 h. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1/6-1/2) to afford the desired products.

(C) Transformations of 3a and 3o

a): Synthesis of compound 4a from 3a
To a solution of phenylhydrazine (0.24 mmol, 25.9 mg) in toluene (2.0 mL) was added 3a (0.2 mmol, 82.4 mg, 97% ee), and the resulting mixture was stirred for 10 min at room temperature. TSOH (0.24 mmol, 45.6 mg) was then added and the mixture was stirred at 80 °C for another 48 h. The solution was then cooled to room temperature, diluted with water and extracted with dichloromethane. The organic layer was then washed with water, NH₄Cl (0.1 M), and saturated NaHCO₃. The collected organic layer was dried over anhydrous Na₂SO₄, concentrated and purified by silica gel column chromatography (ethyl acetate/petroleum ether 1/6 – 1/3) to give compound 4a as a white solid in 89% (86.1 mg) yield with 97% ee.

b): synthesis of compound 4b from 3a

To a dry Schlenk tube was added 3a (0.2 mmol, 82.4 mg, 97% ee), LiCl (2 mmol, 84 mg), H₂O (2 mmol, 36 mg) and DMF (2.5 mL). The reaction was stirred at 145 °C for 1 hour. The solution was then cooled to room temperature, diluted with water and extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na₂SO₄, concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1 - 3/1) to yield 4b as a colourless oil in 51% yield (36.1 mg) with 97%/97% ee, 76/24 d.r.

c): Synthesis of compound 4c from 3a

To a stirred suspension of LiAlH₄ (3.6 mmol, 136.8 mg) in 15 mL of THF under N₂ atmosphere, was added 3a (0.3 mmol, 123.6 mg, 97% ee ) in 7.5 mL of THF via syringe at room temperature.
After 0.5 h, the reaction was quenched with H₂O, followed by aq. 10% NaOH solution, and then extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na₂SO₄, concentrated and purified by silica gel column chromatography (MeOH/ethyl acetate = 0/1 - 1/10) to afford the product 4c as a colourless oil in 71% yield (70.5 mg) with 97% ee.

d): Synthesis of compound 4d from 3a

To a stirred suspension of 3a (0.2 mmol, 82.4 mg, 97% ee) in 3.5 mL of MeOH/CH₂Cl₂ (6/1), was added NaBH₄ (0.6 mmol, 22.7 mg) at 0 °C. Then the mixture was stirred at room temperature for another 3.5 h. After that, the reaction was quenched with H₂O and extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na₂SO₄, concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1 - 3/1) to afford the product 4d as a colourless oil in 81% yield (67.5 mg) with 97% ee.

e): Synthesis of compound 4e from 3o

To a stirred suspension of 3o (0.28 mmol, 115.1 mg, 91% ee) in 2.5 mL of MeOH, was added K₂CO₃ (0.56 mmol, 77.8 mg) at room temperature. Then the mixture was stirred at the same temperature for another 1.5 h. After that, the reaction was filtered and concentrated under reduced pressure. The crude mixture was directly subjected to the next reaction without further purification. Then, N-hydroxy-4-methoxybenzimidoyl chloride (0.56 mmol, 110.6 mg), Et₃N (0.56 mmol, 56.6 mg) and CH₂Cl₂ (3 mL) was added to the mixture at room temperature. After 21 h, the reaction was concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1 - 2/1) to afford the product 4e as a colourless oil in 72% (98.2 mg) yield with 92% ee.
(D) The X-ray structure for 3h (CCDC 1519972)

The compound 3h was recrystallized from CH$_2$Cl$_2$ and petroleum ether.
CCDC 1519972 contains the supplementary crystallographic data of the adduct 3h for this paper.
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(E) The analytical and spectral characterization data for the compounds

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(phenylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3a)

Colourless oil, 30.1 mg, 73% yield. 97% ee determined by HPLC (chiral ADH column), $n$-hexane/$i$-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 17.0 min, 19.4 min. $\left[\alpha\right]_D^{20}$ = -52.31 ($c = 0.43$ in CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.47 – 7.37 (m, 2H), 7.35 – 7.24 (m, 3H), 3.93 – 3.87 (m, 1H), 3.85 – 3.62 (m, 9H), 3.01 (dd, $J$=14.0, 7.2, 1H), 2.87 – 2.71 (m, 2H), 2.62 – 2.43 (m, 3H), 2.26 – 2.11 (m, 2H), 1.78 – 1.72 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 211.5, 172.5, 171.3, 170.3, 131.9, 128.5, 128.3, 122.7, 87.4, 85.0, 62.8, 58.6, 55.0, 53.2, 52.9, 51.9, 40.8, 39.8, 37.4, 35.7, 22.7.

HRMS (ESI-TOF): calcd for C$_{23}$H$_{24}$NaO$_7^+$ ([M + Na]$^+$) 435.1420, found 435.1416.

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Dimethyl 3a-((4-fluorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3b)

Colourless oil, 28.1 mg, 65% yield. 95% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.0 min, 19.7 min. [α]D20 = -42.97 (c = 0.38 in CH2Cl2).

$^1$H NMR (400 MHz, CDCl3) δ = 7.40 (dd, J=8.0, 5.6, 2H), 6.99 (t, J=8.4, 2H), 3.91 – 3.86 (m, 1H), 3.79 – 3.61 (m, 9H), 3.02 (dd, J=14.0, 7.2, 1H), 2.86 – 2.72 (m, 2H), 2.58 – 2.45 (m, 3H), 2.23 – 2.10 (m, 2H), 1.72 – 1.68 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl3) δ = 211.5, 172.4, 171.3, 170.3, 162.7 (d, J=250), 133.9 (d, J=10), 118.8 (d, J=10), 115.6(d, J=20), 86.4, 84.7, 62.7, 58.7, 55.0, 53.2, 52.9, 51.9, 40.9, 39.8, 37.5, 35.7, 22.7.

Dimethyl 3a-((4-chlorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3c)

Colourless oil, 31.8 mg, 71% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, \( \lambda = 254 \) nm, retention time: 21.1 min, 24.4 min. \([\alpha]_{D}^{20} = -49.02\) (c = 0.51 in CH\(_2\)Cl\(_2\)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.30\) (dd, \( J=30.8, 8.0, 4H\)), 3.91 – 3.86 (m, 1H), 3.85 – 3.63 (m, 9H), 3.02 (dd, \( J=14.0, 7.2, 1H\)), 2.86 – 2.71 (m, 2H), 2.62 – 2.43 (m, 3H), 2.25 – 2.09 (m, 2H), 1.74 – 1.70 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 211.3, 172.3, 171.3, 170.2, 134.6, 133.2, 128.7, 121.1, 86.3, 86.1, 62.7, 58.7, 55.0, 53.2, 52.9, 51.9, 40.9, 39.8, 37.4, 35.7, 22.7.

HRMS (ESI-TOF): calcd for C\(_{23}\)H\(_{23}\)ClNaO\(_7\) (\([M + Na]^+\)) 469.1030, found 469.1028; calcd for C\(_{23}\)H\(_{23}\)ClNaO\(_7\) (\([M + Na]^+\)) 471.1001, found 471.1003.
1,1(2H)-dicarboxylate (3d)

Colourless oil, 29.3 mg, 60% yield. 96% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.7 min, 25.3 min. \([\alpha]_D^{20} = -44.88 \ (c = 0.51 \text{ in CH}_2\text{Cl}_2)\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.42 \ (d, \ J=8.4, 2H), 7.33 – 7.22 \ (m, 2H), 3.97 – 3.81 \ (m, 1H), 3.79 – 3.66 \ (m, 9H), 3.02 \ (dd, \ J=13.6, 7.2, 1H), 2.88 – 2.57 \ (m, 2H), 2.57 – 2.27 \ (m, 3H), 2.27 – 2.03 \ (m, 2H), 1.71 – 1.68 \ (m, 1H)\).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 211.3, 172.3, 171.3, 170.2, 133.4, 131.6, 122.8, 121.6, 86.4, 86.3, 62.7, 58.7, 55.0, 53.2, 52.9, 51.9, 40.9, 39.8, 37.5, 35.7, 22.7\).

HRMS (ESI-TOF): calcd for C\(_{23}\)H\(_{23}\)BrNaO\(_7^+\) ([M + Na]\(^+\) ) 513.0525, found 513.0525; calcd for C\(_{23}\)H\(_{23}\)BrNaO\(_7^+\) ([M + Na]\(^+\) ) 515.0504, found 515.0504.

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Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(p-tolylethynyl)hexahydronapthalene-1,1(2H)-dicarboxylate (3e)

Colourless oil, 30.3 mg, 71% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 20.5 min, 24.0 min. \([\alpha]_D^{20} = -48.52 \ (c = 0.47 \text{ in CH}_2\text{Cl}_2)\).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.30$ (d, $J=8.0$, 2H), 7.09 (d, $J=8.0$, 2H), 3.92 – 3.63 (m, 10H), 3.00 (dd, $J=13.2$, 7.2, 1H), 2.88 – 2.71 (m, 2H), 2.61 – 2.45 (m, 3H), 2.33 (s, 3H), 2.25 – 2.11 (m, 2H), 1.75 – 1.70 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 211.7$, 172.5, 171.3, 170.4, 138.6, 131.8, 129.1, 119.6, 87.6, 84.2, 62.8, 58.6, 55.1, 53.2, 52.9, 51.9, 40.8, 39.8, 37.4, 35.7, 22.6, 21.6.

HRMS (ESI-TOF): calcd for C$_{24}$H$_{26}$NaO$_7$$^+$ ([M + Na]$^+$) 449.1576, found 449.1572.

**Dimethyl 3-(2-methoxy-2-oxoethyl)-3a-((4-methoxyphenyl)ethynyl)-4-oxohexahydropentane-1,1(2H)-dicarboxylate (3f)**

Colourless oil, 30.6 mg, 70% yield. 95% ee determined by HPLC (chiral ADH column), $n$-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 28.5 min, 35.1 min. $[\alpha]_D^{20} = -61.6$ (c = 0.61 in CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.41 – 7.31$ (m, 2H), 6.90 – 6.76 (m, 2H), 3.90 – 3.63 (m, 13H), 2.99 (dd, $J = 13.6$, 7.2 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.62 – 2.43 (m, 3H), 2.24 – 2.11 (m, 2H), 1.74 – 1.70 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 211.8$, 172.5, 171.4, 170.4, 159.8, 133.4, 114.8, 113.9, 87.3, 83.5, 62.8, 58.7, 55.4, 55.1, 53.2, 52.9, 51.9, 40.8, 39.8, 37.4, 35.8, 22.6.

HRMS (ESI-TOF): calcd for C$_{24}$H$_{26}$NaO$_7$$^+$ ([M + Na]$^+$) 465.1525, found 465.1523.
Dimethyl 3a-((4-acetylphenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3g)

Colourless oil, 28.4 mg, 63% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 24.6 min, 26.7 min. $[\alpha]_D^{20} = -48.28$ (c = 0.52 in CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.01 – 7.79$ (m, 2H), 7.64 – 7.40 (m, 2H), 3.91 (dd, $J=9.6$, 8.4, 1H), 3.81 – 3.65 (m, 9H), 3.04 (dd, $J=14.0$, 7.2, 1H), 2.89 – 2.74 (m, 2H), 2.69 – 2.44 (m, 6H), 2.27 – 2.09 (m, 2H), 1.76 – 1.70 (m, 1H).

$^1$C NMR (101 MHz, CDCl$_3$) $\delta = 211.1$, 197.4, 172.3, 171.3, 170.2, 136.5, 132.1, 128.3, 127.5, 88.5, 86.6, 62.7, 58.8, 54.9, 53.2, 52.9, 52.0, 40.9, 39.8, 37.5, 35.6, 26.8, 22.7.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{20}$NaO$_8$ ($[M + Na]^+$) 477.1525, found 477.1525.
Dimethyl 3a-((2-chlorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3h)

Colourless oil, 30.1 mg, 67% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.4 min, 19.9 min. [α]$_{D}^{20}$ = -32.27 (c = 0.50 in CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.41 (m, 1H), 7.37 (d, $J$ = 8.0 Hz, 1H), 7.28 – 7.17 (m, 2H), 3.94 (t, $J$ = 8.0 Hz, 1H), 3.88 – 3.57 (m, 9H), 3.04 (dd, $J$ = 14.0, 7.2 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.67 – 2.45 (m, 3H), 2.28 – 2.14 (m, 2H), 1.74 – 1.71 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 211.2, 172.5, 171.2, 170.4, 136.2, 133.6, 129.5, 129.3, 126.5, 122.6, 90.5, 84.2, 62.7, 58.8, 54.8, 53.2, 52.9, 51.9, 41.1, 40.0, 37.6, 35.5, 22.7.

HRMS (ESI-TOF): calcd for C$_{23}$H$_{23}$ClNaO$_7$ ([M + Na]$^+$) 469.1030, found 469.1031; calcd for C$_{23}$H$_{23}$ClNaO$_7$ ([M + Na]$^+$) 471.1001, found 471.1024.
Dimethyl 3a-((3-chlorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3i)

Colourless oil, 28.1 mg, 63% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.6 min, 24.3 min. \([\alpha]_D^{20} = -49.40\) (c = 0.50 in CHCl₃).

\(^1\)H NMR (400 MHz, CDCl₃) δ = 7.40 (s, 1H), 7.31 – 7.20 (m, 3H), 3.91 – 3.86 (m, 1H), 3.84 – 3.62 (m, 9H), 3.03 (dd, \(J = 14.0, 7.2, 1H\)), 2.85 – 2.72 (m, 2H), 2.61 – 2.44 (m, 3H), 2.24 – 2.09 (m, 2H), 1.71 – 1.68 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl₃) δ = 211.2, 172.3, 171.3, 170.2, 134.2, 131.8, 130.1, 129.6, 128.9, 124.3, 86.4, 86.0, 62.7, 58.7, 54.9, 53.3, 52.9, 51.9, 40.9, 39.8, 37.5, 35.6, 22.7.

HRMS (ESI-TOF): calcd for C₃₂H₃₄ClNaO₇\(^{+}\) ([M + Na]\(^{+}\)) 469.1030, found 469.1029; calcd for C₃₃H₃₆ClNaO₇\(^{+}\) ([M + Na]\(^{+}\)) 471.1001, found 471.1028.

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Dimethyl 3a-((3-fluorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3j)

Colourless oil, 27.0 mg, 63% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm,
Retention time: 24.5 min, 27.2 min. \([\alpha]_{D}^{20} = -52.37\) (c = 0.51 in CH₂Cl₂).

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 7.28 – 7.18\) (m, 2H), 7.17 – 7.07 (m, 1H), 7.07 – 6.93 (m, 1H), 3.89 (dd, \(J=9.6, 8.4, 1H\)), 3.83 – 3.64 (m, 9H), 3.03 (dd, \(J=14.0, 7.2, 1H\)), 2.86 – 2.71 (m, 2H), 2.61 – 2.43 (m, 3H), 2.24 – 2.09 (m, 2H), 1.74 – 1.69 (m, 1H).

\(^13\)C NMR (101 MHz, CDCl₃) \(\delta = 211.2, 172.3, 171.3, 170.2, 162.4\) (d, \(J=250\)), 123.0 (d, \(J=10\)), 127.8 (d, \(J=3\)), 124.5 (d, \(J=10\)), 118.7 (d, \(J=20\)), 115.9 (d, \(J=20\)), 86.2, 86.1, 62.7, 58.6, 54.9, 53.2, 52.9, 51.9, 40.9, 39.8, 37.5, 35.6, 22.7.

HRMS (ESI-TOF): calcd for C\(_{23}\)H\(_{23}\)FNaO\(_7\)\(^+\) ([M + Na]\(^+\)) 453.1326, found 453.1327.

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(m-tolylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3k)

Colourless oil, 30.7 mg, 72% yield. 95% ee determined by HPLC (chiral ADH column), \(n\)-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, \(\lambda = 254\) nm, retention time: 8.6 min, 9.6 min. \([\alpha]_{D}^{20} = -50.98\) (c = 0.51 in CH₂Cl₂).

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 7.27 – 7.06\) (m, 4H), 3.91 – 3.85 (m, 1H), 3.83 – 3.59 (m, 9H), 3.01 (dd, \(J=14.0, 7.2, 1H\)), 2.87 – 2.71 (m, 2H), 2.60 – 2.46 (m, 3H), 2.31 (s, 3H), 2.24 – 2.11 (m, 2H), 1.74 – 1.68 (m, 1H).
$^1$C NMR (101 MHz, CDCl$_3$) $\delta = 211.6, 172.5, 171.3, 170.4, 138.0, 132.5, 129.4, 129.0, 128.2, 122.4, 87.6, 84.6, 62.7, 58.6, 55.0, 53.2, 52.9, 51.9, 40.8, 39.8, 37.5, 35.7, 22.7, 21.3.

HRMS (ESI-TOF): calcd for C$_{24}$H$_{26}$NaO$_7$ ([M + Na$^+$]) 449.1576, found 449.1577.

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$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.23$ (dd, $J=5.2, 1.2, 1H$), 7.18 (dd, $J=3.6, 1.2, 1H$), 6.95 (dd, $J=5.2, 4.0, 1H$), 3.88 (dd, $J=9.2, 8.8, 1H$), 3.75 (s, 6H), 3.68 (s, 3H), 3.04 – 2.96 (m, 1H), 2.84 – 2.73 (m, 2H), 2.56 – 2.43 (m, 3H), 2.24 – 2.11 (m, 2H), 1.79 – 1.69 (m, 1H).

$^1$C NMR (101 MHz, CDCl$_3$) $\delta = 211.3, 172.4, 171.3, 170.3, 132.5, 127.3, 127.0, 122.5, 88.9, 80.6, 62.8, 58.9, 55.0, 53.3, 52.9, 51.9, 40.9, 39.8, 37.4, 35.7, 22.7.

HRMS (ESI-TOF): calcd for C$_{21}$H$_{22}$NaO$_7$S$^+$ ([M + Na$^+$]) 441.0984, found 441.0983.

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(thiophen-2-ylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3l)

Colourless oil, 22.4 mg, 54% yield. 98% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 11.6 min, 13.1 min, $[\alpha]_{D}^{20} = -47.04$ (c = 0.37 in CH$_2$Cl$_2$).
Dimethyl 3-(2-methoxy-2-oxoethyl)-3a-(naphthalen-2-ylethynyl)-4-oxohexahydrpentalen-1,1(2H)-dicarboxylate (3m)

Colourless oil, 32.8 mg, 71% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \), retention time: 14.5 min, 15.8 min. [\( \alpha \)]\text{D}^{20} = -52.18 (c = 0.55 in CH\text{Cl}_2).

\(^1\text{H} \text{ NMR} \) (400 MHz, CDCl\text{3}) \( \delta = 7.94 \) (s, 1H), 7.85 – 7.68 (m, 3H), 7.57 – 7.36 (m, 3H), 3.97 – 3.90 (m, 1H), 3.86 – 3.51 (m, 9H), 3.04 (dd, \( J = 14.0, 7.6, 1 \text{H} \)), 2.92 – 2.75 (m, 2H), 2.67 – 2.45 (m, 3H), 2.30 – 2.15 (m, 2H), 1.80 – 1.69 (m, 1H).

\(^1\text{C} \text{ NMR} \) (101 MHz, CDCl\text{3}) \( \delta = 211.6, 172.5, 171.4, 170.3, 132.9, 131.8, 128.6, 128.0, 127.8, 126.8, 126.7, 119.9, 87.8, 85.3, 62.8, 58.8, 55.1, 53.3, 52.9, 51.9, 40.9, 39.8, 37.5, 35.8, 22.70.

HRMS (ESI-TOF) calculated for C\text{27}H\text{30}NaO\text{7}+ ([M + Na]\text{+}) 485.1576, found 485.1573.
((3-(2-Methoxy-2-oxoethyl)-1,1-bis(methoxycarbonyl)-4-oxohexahydropentalen-3a(1H)-yl)ethyl)ferrocene (3n)

Colourless oil, 18.3 mg, 35% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 35.0 min, 38.2 min. [α]D20 = -25.80 (c = 0.31 in CH2Cl2).

1H NMR (400 MHz, CDCl3) δ = 4.45 – 4.35 (m, 2H), 4.21 (s, 4H), 4.16 (d, J=2.0, 2H), 3.94 – 3.64 (m, 10H), 3.00 (dd, J=13.6, 6.8, 1H), 2.83 (dd, J=16.0, 4.4, 1H), 2.76 – 2.66 (m, 1H), 2.62 – 2.41 (m, 3H), 2.22 – 2.09 (m, 2H), 1.74 – 1.66 (m, 1H).

13C NMR (101 MHz, CDCl3) δ = 211.9, 172.6, 171.3, 170.4, 86.1, 81.1, 71.7, 70.0, 68.7, 64.7, 62.6, 58.8, 54.9, 53.2, 52.9, 51.9, 40.6, 39.9, 37.5, 35.7, 22.6.


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Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-((trimethylsilyl)ethynyl)hexahydrapentalene-1,1(2H)-dicarboxylate (3o)

Colourless oil, 25.5 mg, 62% yield. 91% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, \( \lambda = 210 \text{ nm} \), retention time: 5.7 min, 6.2 min. \([\alpha]_D^{20} = -42.97 \) (c = 0.38 in CH\(_2\)Cl\(_2\)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 3.66 – 3.57 (m, 7H), 3.53 (s, 3H), 2.80 (dd, \( J = 14.0, 7.2 \text{ Hz} \), 1H), 2.60 (dd, \( J = 16.0, 4.0 \text{ Hz} \), 1H), 2.55 – 2.47 (m, 1H), 2.36 – 2.19 (m, 3H), 2.04 – 1.88 (m, 2H), 1.55 – 1.46 (m, 1H), 0.00 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 211.4, 172.5, 171.1, 170.4, 101.2, 92.5, 62.6, 58.9, 55.0, 53.1, 52.9, 51.9, 40.5, 39.8, 37.4, 35.6, 22.5, 0.0.

HRMS (ESI-TOF): calcd for C\(_{20}\)H\(_{28}\)NaO\(_7\)Si\(^+\) ([M + Na]\(^+\)) 431.1502, found 431.1500.

Dimethyl 3-(2-methoxy-2-oxoethyl)-3a-(phenylethynyl)-2,3,3a,4,9,9a-hexahydro-1H-pentaleno[1,2-b]indole-1,1-dicarboxylate (4a)

White solid, 86.1 mg, 89% yield. 97% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \), retention time: 11.0 min, 32.3 min. \([\alpha]_D^{20} = -46.69 \) (c = 1.72 in CH\(_2\)Cl\(_2\)).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.92\) (s, 1H), 7.35 – 7.16 (m, 7H), 7.07 – 6.92 (m, 2H), 4.14 (d, \(J=6.8\), 1H), 3.66 (d, \(J=17.6\), 6H), 3.37 – 3.20 (m, 4H), 3.14 (dd, \(J=15.2\), 7.6, 1H), 3.00 (d, \(J=15.2\), 1H), 2.87 (dd, \(J=17.2\), 11.6, 1H), 2.69 – 2.50 (m, 2H), 1.86 (t, \(J=12.4\), 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 174.5, 171.7, 170.2, 145.2, 140.9, 131.6, 128.3, 128.1, 124.3, 123.2, 121.3, 119.5, 118.9, 116.3, 112.3, 88.6, 86.2, 66.2, 62.3, 53.0, 52.4, 52.0, 51.3, 42.0, 41.6, 37.6, 26.1.

HRMS (ESI-TOF): calcld for C\(_{29}\)H\(_{27}\)NNaO\(_6^+\) ([M + Na\(^+\)]\(^+\)) 508.1736, found 508.1737.

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Methyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(phenylethynyl)octahydropentalene-1-carboxylate (4b)

Colourless oil, 36.1 mg, 51% yield. 76/24 d.r. determined by \(^1\)H NMR. 97%/97% ee determined by HPLC (chiral IE column), \(n\)-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, \(\lambda = 254\) nm, retention time: 12.3 min, 14.3 min, 15.8 min, 19.5 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.47 – 7.37\) (m, 2H), 7.33 – 7.26 (m, 3H), 3.77 – 3.63 (m, 6H), 3.50 – 3.41 (m, 0.28H), 3.30 – 3.19 (m, 1H), 2.95 – 2.30 (m, 7.86H), 2.11 – 1.84 (m, 2H).
1H NMR (400 MHz, CDCl₃) δ = 7.28 – 7.13 (m, 5H), 5.09 (s, 1H), 4.65 (d, J=32.4, 2H), 4.13 – 3.99 (m, 2H), 3.74 – 3.36 (m, 7H), 2.48 (t, J=8.8, 2H), 2.00 (d, J=7.6, 1H), 1.83 – 1.41 (m, 6H).

13C NMR (101 MHz, CDCl₃) δ = 131.5, 128.3, 127.8, 123.8, 94.6, 84.6, 78.9, 71.6, 64.9, 61.2, 61.1, 58.0, 47.1, 41.3, 37.3, 35.0, 34.5, 23.7, 14.3.

(4-Hydroxy-3-(2-hydroxyethyl)-3a-(phenylethynyl)octahydropentalene-1,1-diyl)dimethanol (4c)

Colourless oil, 70.5 mg, 71% yield. 97% ee determined by HPLC (chiral IC column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 6.9 min, 8.5 min. [α]D²⁰ = -33.51 (c = 1.14 in CH₂Cl₂).
HRMS (ESI-TOF): calcd for C_{20}H_{26}NaO_4^+ ([M + Na]^+) 353.1729, found 353.1730.

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Dimethyl 4-hydroxy-3-(2-methoxy-2-oxoethyl)-3a-(phenylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (4d)

Colourless oil, 67.5 mg, 81% yield. 97% ee determined by HPLC (chiral IE column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \) nm, retention time: 11.0 min, 12.8 min. \([\alpha]_{D}^{20} = -103.07 \) (c = 1.20 in CH_2Cl_2).

\(^1\)H NMR (400 MHz, CDCl_3) \( \delta = 7.41 – 7.34 \) (m, 2H), 7.32 – 7.25 (m, 3H), 4.15 (dd, \( J = 5.6, 3.2, 1H \)), 4.09 – 3.98 (m, 1H), 3.77 – 3.63 (m, 1H), 3.29 – 3.11 (m, 1H), 2.86 (dd, \( J = 17.6, 10.4, 1H \)), 2.69 (dd, \( J = 12.8, 6.0, 1H \)), 2.58 (dd, \( J = 17.6, 4.4, 1H \)), 2.11 – 2.06 (m, 1H), 1.99 – 1.86 (m, 2H), 1.63 – 1.47 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl_3) \( \delta = 175.0, 172.1, 171.1, 131.6, 128.3, 128.0, 123.4, 92.4, 85.9, 78.7, 61.4, 59.8, 58.0, 52.9, 52.4, 52.1, 43.5, 36.4, 36.3, 36.2, 27.2.

HRMS (ESI-TOF): calcd for C_{23}H_{26}NaO_5^+ ([M + Na]^+) 437.1576, found 437.1570.
Dimethyl 3a-(3-(4-methoxyphenyl)isoxazol-5-yl)-3-(2-(methylperoxy)-2(2-ethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (4e)

Colourless oil, 98.2 mg, 72% yield. 92% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.9 min, 23.2 min. [α]$_{20}$ = - 188.55 (c = 1.75 in CH$_2$Cl$_2$, λ = 365 nm).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.77 – 7.67 (m, 2H), 6.99 – 6.92 (m, 2H), 6.51 (s, 1H), 4.13 – 4.10 (m, 1H), 3.86 – 3.75 (m, 9H), 3.63 (s, 3H), 3.08 – 2.95 (m, 2H), 2.64 – 2.44 (m, 3H), 2.30 – 2.19 (m, 2H), 2.03 – 1.97 (m, 1H), 1.90 – 1.81 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 213.4, 171.9, 171.1, 170.7, 168.54, 161.9, 161.1, 128.2, 121.1, 114.3, 101.3, 63.1, 62.0, 60.4, 55.4, 55.3, 53.2, 53.2, 52.9, 52.9, 52.2, 51.8, 41.9, 40.6, 38.0, 34.9, 22.7, 21.1, 14.2.

HRMS (ESI-TOF): calcld for C$_{25}$H$_{27}$NNaO$_9$ $^+$ ([M + Na]$^+$) 508.1584, found 508.1584.
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(F) Reference


(G) Copies of the NMR spectra

3a
3f
3g
3h
3j
4a
4d
(H) Copies of the CD spectra