Supporting Information

Asymmetric total synthesis of (+)-xestoquinone and (+)-adociaquinones A and B

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General experimental procedures

All reactions were carried out under an inert nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise noted. Anhydrous dichloromethane, tetrahydrofuran and toluene were purified by the PS-MD-5 (Innovative Technology) solvent purification system. Dimethyl sulfoxide used for IBX oxidation was purchased from commercially available anhydrous solvent. Anhydrous diethyl ether was distilled from sodium. The solvents used for condition screening of desymmetric intramolecular Michael addition are all commercially available analytical-grade solvents. TLC analyses were performed on EMD 250 µm Silica Gel HSGF$_{254}$ plates and visualized by quenching of UV fluorescence ($\lambda_{\text{max}}$ = 254 nm), or by staining phosphomolybdic acid, or potassium permanganate. Flash column chromatography was performed as described by Still$^{[1]}$, employing SiliCycle UltraPure Silica Gels: SilicaFlash$^{[0]}$ P60 40 – 63 µm (230 – 400 mesh). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker-500, 400 spectrometers. Chemical shifts for $^1$H and $^{13}$C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent (CDCl$_3$: δ 7.26, 77.0 ppm; DMSO: δ 2.50, 40.4 ppm) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were acquired on Waters Micromass GCT Premier or Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS. Mass spectra were acquired on Agilent 5975C. Infrared (IR) spectra was obtained using a Shimatzu IRTracer-100 fourier transform infrared spectroscopy (FTIR). The $[\alpha]_D^{20}$ was recorded at 365 nm using Anton Paar MCP 5500.

General experimental procedure A for desymmetric intramolecular Michael addition without AcOH

A solution of 13, catalyst in analytical-grade solvent was stirred at room temperature for indicated time without inert nitrogen atmosphere. Then the solution was evacuated and purified by flash chromatography or preparation lamella chromatography (20% ethyl acetate – petroleum ether).

General experimental procedure B for desymmetric intramolecular Michael addition with AcOH

A solution of 13, catalyst and additive AcOH in analytical-grade solvent was stirred at room temperature for indicated time without inert nitrogen atmosphere. Then the solution was quenched with saturated NaHCO$_3$ and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated and purified by silica gel flash chromatography or preparation lamella chromatography (20% ethyl acetate – petroleum ether).
Detail of the screening conditions of desymmetric intramolecular Michael addition

Table S1. Screening conditions of desymmetric intramolecular Michael addition to obtain 14′ using S-catalysts.

| entry | cat. (equiv.) | solvent | time | yield/d.r. at C2 | e.e. |
|-------|--------------|---------|------|------------------|------|
| 1     | Et$_3$NH (10.0) | MeOH/H$_2$O (20:1) | 6.0 h | 64% | rac. |
| 2     | (S)-cat.I (0.5) | MeOH/H$_2$O (20:1) | 10.5 h | 48% / 3.0:1 | 14a′: -87%; 14b′: -31% |
| 3     | (S)-cat.II (0.5) | MeOH/H$_2$O (20:1) | 10.5 h | 56% / 2.8:1 | 14a′: -85%; 14b′: -5% |
| 4     | (S)-cat.III (0.5) | MeOH/H$_2$O (20:1) | 48.0 h | trace | 14a′: -80%; 14b′: -15% |
| 5     | (S)-cat.IV (0.5) | MeOH/H$_2$O (20:1) | 48.0 h | trace | 14a′: -84%; 14b′: -6% |
| 6     | (S)-cat.I (0.5) | MeOH | 2.0 h | 63% / 5.0:1 | 14a′: -85%; 14b′: -37% |
| 7     | (S)-cat.I (0.5) | DCM | 24.0 h | 51% / 1.1:1 | 14a′: -93%; 14b′: -86% |
| 8     | (S)-cat.I (0.5) | Et$_2$O | 24.0 h | 50% / 2.8:1 | 14a′: -96%; 14b′: -93% |
| 9     | (S)-cat.I (0.5) | MeCN | 24.0 h | 47% / 1.0:1 | 14a′: -93%; 14b′: -88% |
| 10    | (S)-cat.I (0.5) | toluene | 5.5 h | 42% / 22.0:1 | 14a′: -97%; 14b′: -89% |
| 11    | (S)-cat.I (0.5) | toluene | 11.0 h | 52% / 4.5:1 | 14a′: -97%; 14b′: -89% |
| 12    | (S)-cat.I (0.3) | toluene | 16.0 h | 73% / 1.7:1 | 14a′: -97%; 14b′: -94% |
| 13    | (S)-cat.I (0.2) | toluene | 16.0 h | 86% / 2.0:1 | 14a′: -96%; 14b′: -89% |
| 14    | (S)-cat.I (0.4) | toluene | 12.0 h | 62% / 14.0:1 | 14a′: -96%; 14b′: -89% |

All reactions were performed using 13 (0.8 mg, 0.03 mmol, 1.0 equiv., 0.05 M) and catalyst at room temperature in analytical-grade solvents, unless otherwise noted.

The yields and diastereomeric ratios (d.r.) were determined from the crude $^1$H NMR spectrum of 14′ using [H$_2$Br$_2$] as an internal standard, unless otherwise noted.

The enantiomeric excess (e.e.) values were determined by chiral high-performance liquid chromatography (Chiralpak IG-H). Compound 13: 9.6 mg, 0.05 mmol, 0.1 M. Isolated yield of 14a′+14b′. The d.r. values were determined from the $^1$H NMR spectrum of purified 14′ after purification by silica gel column chromatography. Compound 13: 1.0 g, 5.2 mmol, 0.1 M. Compound 13: 288 mg, 1.5 mmol, 0.1 M. Isolated yield of 12a′+12b′. The d.r. values were determined from the crude $^1$H NMR spectrum of 12′ obtained from the one-pot process.

Table S2. Supplementary experiments as reviewer’s suggestions.

| entry | condition | result |
|-------|-----------|--------|
|       | without 13 |        |
| 1     | (R)-cat.I (0.05 mmol, 16.3 mg, 1.0 equiv.) | (R)-cat.I : stable |
|       | AcOH (0.25 mmol, 15.0 mg, 5.0 equiv.) | TMS group: not deprotected |
|       | toluene (0.5 mL), RT, 9.0 h | |
| 2     | (R)-cat.II (0.05 mmol, 16.3 mg, 1.0 equiv.) | N.R. |
|       | toluene (0.5 mL), RT, 9.0 h | |
| 3     | (R)-cat.II (0.05 mmol, 16.3 mg, 1.0 equiv.) | N.R. |
|       | AcOH (0.25 mmol, 15.0 mg, 5.0 equiv.) | |
|       | toluene (0.5 mL), RT, 9.0 h | |

The entry 1 in Table S2 indicate that the Hayashi–Jørgensen catalyst (R)-cat.I was stable under the stirred solution of 0.5 N AcOH/toluene for more than 9 hours. Besides, we conclude that (R)-cat.I was the effective catalyst in this desymmetrization reaction based on entries 2, 3 in Table S2.
Experimental procedures and spectroscopic data

To a stirred solution of 4-methoxybenzyl alcohol (55.26 g, 49.6 mL, 0.40 mol, 1.0 equiv.) and 1,5-pentanediol (62.5 g, 62.9 mL, 0.60 mol, 1.5 equiv.) in anhydrous DCM (500 mL) at room temperature was added Amberlyst-15 resin (8.29 g, 15% w/w). The mixture was refluxed at 50 °C for 24 hours then filtered through silica gel and washed with DCM (6×50 mL). The filtrate was concentrated and the obtained crude compound S1 was dissolved in anhydrous THF (800 mL). Then imidazole (81.7 g, 1.20 mol, 3.0 equiv.), PPh3 (157.37 g, 0.60 mol, 1.5 equiv.), I2 (152.29 g, 0.6 mol, 1.5 equiv.) was successively added to the solution at 0 °C. After stirred at 0 °C for 1 hour, the solution was quenched with saturated Na2S2O3 (100 mL) then THF was evacuated. The mixture was extracted with ethyl acetate (3×200 mL). The combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate, concentrated, and added 200 mL Et2O. Then the undissolved triphenylphosphine oxide was filtered and washed with Et2O (3×50 mL). The filtrate was concentrated and purified by silica gel flash chromatography (5% to 10% ethyl acetate – petroleum ether) to obtain S2 as a light yellow viscous oil (98.87 g, 74% over two steps). Rf = 0.42 (10% ethyl acetate – petroleum ether). The NMR spectra of S2 were consistent with the previous report [2].

To a stirred solution of diisopropylamine (28 mL, 200 mmol, 2.0 equiv.) in anhydrous THF (300 mL) at 0 °C under nitrogen atmosphere was slowly added n-BuLi (80 mL, 200 mmol, 2.0 equiv., 2.5 M in hexane). After stirring at 0 °C for 30 minutes, the compound S3 (15.4 g, 100 mmol, 1.0 equiv.) in anhydrous THF (50 mL) was slowly added at -78 °C. Then the mixture was stirred for 30 minutes at -78 °C and stirred for 30 minutes at room temperature. After that, compound S2 (66.8 g, 200 mmol, 2.0
equiv.) in anhydrous THF (50 mL) was slowly added to the mixture at -78 °C and slowly warmed to room temperature. After stirring at room temperature overnight, the mixture was quenched with water (100 mL) and extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% to 20% ethyl acetate – petroleum ether) to obtain S4 as a light yellow viscous oil (27.35 g, 79%) and 2.46 g recycling starting material S3. Rf = 0.24 (10% ethyl acetate – petroleum ether); Light yellow viscous oil; 1H NMR (400 MHz, Chloroform-d) δ 7.24 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.22 (s, 1H), 4.41 (s, 2H), 3.87 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 3.41 (t, J = 6.6 Hz, 2H), 2.48 – 2.31 (m, 2H), 1.94 – 1.82 (m, 1H), 1.70 (ddd, J = 13.4, 7.5, 5.7 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.54 – 1.46 (m, 1H), 1.46 – 1.36 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.32 – 1.27 (m, 2H), 1.27 – 1.17 (m, 2H), 1.05 (s, 3H) ppm; 13C NMR (100 MHz, Chloroform-d) δ 204.2, 175.6, 159.1, 130.8, 129.2 (2C), 113.7 (2C), 101.3, 72.5, 70.1, 64.1, 55.2, 43.2, 36.9, 32.2, 29.7, 26.9, 26.1, 23.8, 22.3, 14.2 ppm; IR νmax 2935, 2858, 1653, 1608, 1512, 1458, 1375, 1359, 1246, 1190, 1099, 1035, 896, 846, 821 cm⁻¹; HRMS–EI (m/z): [M]+ calculated for C22H32O4, 360.2301, found, .360.2299.

To a stirred mixture of LiAlH₄ (5.73 g, 151.2 mmol, 1.2 equiv.) in anhydrous Et₂O (400 mL) at 0 °C under nitrogen atmosphere was slowly added compound S4 (43.62 g, 126 mmol, 1.0 equiv.) in anhydrous Et₂O (100 mL). After stirred at 0 °C for 30 minutes, 300 mL saturated NH₄Cl was slowly added to the mixture and then added 300 mL 3 N HCl at 0 °C. The mixture was slowly warmed to room temperature and stirred for another 1 hour. Separated the Et₂O layer and washed with water, saturated NaHCO₃, brine. Then the separated total aqueous layer was extracted with ethyl acetate (3×100 mL) and the separated ethyl acetate layer was washed with water, saturated NaHCO₃, brine. The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% to 20% ethyl acetate – petroleum ether) to obtain S5 as a light yellow viscous oil (26.0 g, 65%). Rf = 0.30 (10% ethyl acetate – petroleum ether); Light yellow viscous oil; 1H NMR (400 MHz, Chloroform-d) δ 7.25 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 10.2 Hz, 1H), 5.86 (d, J = 10.2 Hz, 1H), 4.43 (s, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.5 Hz, 2H), 2.47 – 2.38 (m, 2H), 1.94 (ddd, J = 14.5, 8.9, 5.9 Hz, 1H), 1.74 (dt, J = 12.8, 6.0 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.50 – 1.22 (m, 6H), 1.11 (s, 3H) ppm; 13C NMR (100 MHz, Chloroform-d) δ 199.7, 159.4, 159.1, 130.7, 129.2 (2C), 127.3, 113.8 (2C), 72.6, 69.9, 55.3, 41.0, 35.6, 34.2, 33.5, 29.7, 26.9, 24.9, 24.0 ppm; IR νmax 2933, 2859, 1682, 1612, 1512, 1463, 1301, 1265, 1246, 1097, 1035, 804 cm⁻¹; HRMS–EI
To a stirred solution of S5 (13.0 g, 41.08 mmol, 1.0 equiv.) in anhydrous THF (400 mL) at room temperature was successively added DDQ (28.0 g, 123.24 mmol, 3.0 equiv.), TBSCI (6.81 g, 45.19 mmol, 1.1 equiv.) portion-wisely. After stirring at room temperature for 5 hours, the brown mixture was stirred at 50 °C for further 16 hours. The mixture was concentrated and diluted with ethyl acetate (150 mL) then quenched with saturated Na2S2O3/NaHCO3 (150 mL, v/v = 1:1). Separated the ethyl acetate layer and washed with water, brine. Then the separated total aqueous layer was extracted with ethyl acetate (3×100 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (30% to 60% ethyl acetate – petroleum ether) to obtain S6 as a brown viscous oil (3.43 g, 43%). Rf = 0.20 (30% ethyl acetate – petroleum ether); Brown viscous oil; 1H NMR (500 MHz, Chloroform-d) δ 6.76 (d, J = 10.1 Hz, 2H), 6.26 (d, J = 10.1 Hz, 2H), 3.60 (t, J = 6.5 Hz, 2H), 1.66–1.59 (m, 2H), 1.55–1.47 (m, 2H), 1.47 (br s, 1H), 1.36–1.26 (m, 2H), 1.24 (s, 3H), 1.19–1.09 (m, 2H) ppm; 13C NMR (125 MHz, Chloroform-d) δ 186.4, 155.9 (2C), 128.8 (2C), 62.7, 42.0, 40.5, 32.4, 26.1, 26.0, 24.8 ppm; IR νmax 3051, 2937, 2862, 1718, 1664, 1624, 1458, 1267, 1246, 1037, 862, 704 cm−1; HRMS–EI (m/z): [M]+ calculated for C12H18O2, 194.1307, found, 194.1305.

To a stirred solution of S6 (3.30 g, 17.00 mmol, 1.0 equiv.) in anhydrous DMSO (50 mL) at room temperature was added IBX (9.52 g, 34.00 mmol, 2.0 equiv.) portion-wisely. After stirring at room temperature for 2 hours, the mixture was quenched with saturated Na2S2O3/NaHCO3 (50 mL, v/v = 1:1) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (30% to 40% ethyl acetate – petroleum ether) to obtain 13 as a light brown oil (1.96 g, 60%). Rf = 0.20 (20% ethyl acetate – petroleum ether); Light brown oil; 1H NMR (500 MHz, Chloroform-d) δ 9.69 (s, 1H), 6.72 (d, J = 10.0 Hz, 2H), 6.22 (d, J = 10.0 Hz, 2H), 2.36 (td, J = 7.3, 1.5 Hz, 2H), 1.63–1.57 (m, 2H), 1.57–1.49 (m, 2H), 1.21 (s, 3H), 1.16–1.06 (m, 2H) ppm; 13C NMR (125 MHz, Chloroform-d) δ 202.0, 186.1, 155.5 (2C), 128.8 (2C), 43.5, 41.8, 40.2, 26.0, 24.5, 22.0 ppm; IR νmax 3053, 2937, 2862, 1718, 1664, 1624, 1458,
A solution of 13 (1.54 g, 8.00 mmol, 1.0 equiv.), (R)-cat.I (520 mg, 1.60 mmol, 0.2 equiv.) and AcOH (96 mg, 1.60 mmol, 0.2 equiv.) in analytical-grade toluene (80 mL) was stirred at room temperature for 9.5 hours with inert nitrogen atmosphere. Then 1,3-propanediol (2.44 g, 2.31 mL, 32.00 mol, 4.0 equiv.), 46.5% BF₃·Et₂O (1.14 g, 0.99 mL, 8.0 mmol, 1.0 equiv.) was added to the solution at 0 °C and stirred at room temperature for further 2 hours. The solution was quenched with saturated NaHCO₃ (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (20% ethyl acetate – petroleum ether) to obtain pure 12a (0.95 g), pure 12b (0.15 g) and the mixture of 12a+12b (0.40 g) all as light yellow viscous oil (total 1.6 g, total 80% for one pot synthesis, d.r. = 5.5:1).

R_f = 0.30 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; [α]_D° = -10.5 (c = 1.00 in DCM); ¹H NMR (500 MHz, Chloroform-d) δ 6.62 (d, J = 10.1 Hz, 1H), 5.84 (d, J = 10.1 Hz, 1H), 4.24 (d, J = 7.4 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.76 – 3.63 (m, 2H), 2.46 – 2.35 (m, 1H), 2.30 – 2.20 (m, 2H), 2.10 – 2.02 (m, 1H), 2.01 – 1.94 (m, 1H), 1.81 – 1.69 (m, 1H), 1.67 – 1.60 (m, 1H), 1.54 – 1.44 (m, 3H), 1.33 (d, J = 13.5 Hz, 1H), 1.16 (s, 3H), 1.14 – 1.10 (m, 1H) ppm; ¹³C NMR (125 MHz, Chloroform-d) δ 200.6, 161.5, 126.0, 103.1, 67.00, 66.97, 40.1, 38.3, 36.1, 34.7, 31.3, 25.9, 24.3, 21.3, 20.3 ppm; IR cm⁻¹: νmax 2937, 2860, 1676, 1614, 1375, 1267, 1240, 1143, 1114, 1086, 1014, 935, 852 cm⁻¹; HRMS–EI (m/z): [M⁺] calculated for C₁₃H₂₂O₃, 250.1569, found, 250.1571.

R_f = 0.34 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; [α]_D° = -64.9 (c = 0.60 in DCM); ¹H NMR (500 MHz, Chloroform-d) δ 6.53 (dd, J = 10.1, 2.1 Hz, 1H), 5.88 (d, J = 10.1 Hz, 1H), 4.57 (d, J = 2.4 Hz, 1H), 4.09 – 4.01 (m, 2H), 3.77 – 3.62 (m, 2H), 2.77 – 2.60 (m, 2H), 2.06 – 1.92 (m, 2H), 1.89 – 1.79 (m, 1H), 1.69 – 1.58 (m, 3H), 1.35 – 1.25 (m, 2H), 1.22 (s, 3H), 1.21 – 1.11 (m, 2H) ppm; ¹³C NMR (125 MHz, Chloroform-d) δ 199.4, 159.1, 128.3, 102.2, 67.1, 67.0, 42.0, 40.9, 40.2, 37.53, 37.52, 27.8, 25.8, 25.3, 22.6 ppm; IR cm⁻¹: νmax 2936, 2858, 1676, 1610, 1377, 1238, 1151, 1122, 1016, 997, 941, 893 cm⁻¹; HRMS–EI (m/z): [M⁺] calculated for C₁₃H₂₂O₃, 250.1569, found, 250.1567.
A solution of 13 (288 mg, 1.50 mmol, 1.0 equiv.), (S)-cat.I (195 mg, 0.60 mmol, 0.4 equiv.) in analytical-grade toluene (15 mL) was stirred at room temperature for 12 hours with inert nitrogen atmosphere. Then 1,3-propanediol (457 mg, 0.43 mL, 6.00 mol, 4.0 equiv.), 46.5% BF$_3$-Et$_2$O (213 mg, 0.185 mL, 1.5 mmol, 1.0 equiv.) was added to the solution at 0°C and stirred at room temperature for further 2 hours. The solution was quenched with saturated NaHCO$_3$ (10 mL), and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (20% ethyl acetate – petroleum ether) to obtain pure 12a as a light yellow viscous oil (233 mg, 62% for one pot synthesis, d.r. = 14.0:1).

R$_f$ = 0.30 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; $[\alpha]_{D}^{20}$ = +9.4 (c = 0.60 in DCM); $^1$H NMR: the same to compound 12a; $^{13}$C NMR: the same to compound 12a; IR $\nu_{\text{max}}$ 2928, 2863, 1684, 1676, 1376, 1275, 1240, 1145, 1116, 1015, 934, 852, 764 cm$^{-1}$; HRMS–EI (m/z): [M]$^+$ calculated for C$_{15}$H$_{22}$O$_3$, 250.1569, found, 250.1571.

To a solution of dienophile 12a (2.00 g, 8.00 mmol, 1.0 equiv.), aromatic aldehyde 11 (2.16 g, 12.0 mmol, 1.5 equiv.) in anhydrous and degassed toluene (400 mL) (concentration for dienophile 12a is 0.02 M) was added titanium(IV) isopropoxide (6.82 g, 7.10 mL, 24.0 mmol, 3.0 equiv.) under N$_2$. After homogeneous mixing, the solution was divided into 10 parallel reactions in 10 quartz tubes (10×40 mL). 5 parallel reactions were conducted with 5 quartz tubes once. The solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at $\lambda_{\text{max}} = 366$ nm for 1.5 hours (Note: the atmosphere temperature among quartz tubes was 35 to 40 °C). After the above 5 parallel reactions were over, the reaction mixture was quenched with
saturated NaHCO₃ (50 mL). Then another 5 parallel reactions were conducted for another 1.5 hours, the reaction mixture was also quenched with saturated NaHCO₃ (50 mL). The total mixture was filtered through silica gel and washed with ethyl acetate (6×50 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (10% to 30% ethyl acetate – petroleum ether) to obtain 1.80 g 16a (contain ~ 9% S7) as a yellow viscous oil.

To a solution of above obtained 1.80 g 16a (contain ~ 9% S7) in anhydrous toluene (40 mL) was added DDQ (1.97 g, 8.69 mmol, 2.0 equiv.) at room temperature. After stirred at 80 °C for 3 hours, the mixture was quenched with saturated Na₂S₂O₃/NaHCO₃ (40 mL, v/v = 1:1) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% ethyl acetate – petroleum ether) to obtain pure 10a as a yellow foam solid (1.38 g, 42% over two steps).

![16a](image1)

Rᶠ = 0.36 (30% ethyl acetate – petroleum ether); Yellow viscous oil; [α]²⁰ = +179.0 (c = 1.10 in DCM); ¹H NMR (400 MHz, Chloroform-d) δ 7.81 (d, J = 2.4 Hz, 1H), 6.79 (d, J = 8.9 Hz, 1H), 6.65 (d, J = 8.9 Hz, 1H), 4.41 (d, J = 7.6 Hz, 1H), 4.02 (dd, J = 11.4, 5.0 Hz, 1H), 3.92 (dd, J = 11.5, 5.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.64 (td, J = 12.3, 2.6 Hz, 1H), 3.41 (td, J = 12.0, 2.6 Hz, 1H), 2.99 (dd, J = 15.7, 6.9 Hz, 1H), 2.72 (dd, J = 11.5, 6.9, 2.5 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.57 (d, J = 7.1 Hz, 1H), 2.49 (dd, J = 17.6, 5.7 Hz, 1H), 2.04 – 1.88 (m, 3H), 1.76 (dd, J = 13.8, 7.0, 3.0 Hz, 1H), 1.57 – 1.50 (m, 3H), 1.47 – 1.35 (m, 2H), 1.28 – 1.21 (m, 1H), 0.96 (s, 3H) ppm; ¹³C NMR (100 MHz, Chloroform-d) δ 200.5, 151.7, 150.0, 134.5, 127.0, 126.4, 122.4, 112.5, 108.6, 103.6, 66.9, 66.0, 55.93, 55.91, 41.7, 40.6, 39.1, 38.1, 35.8, 35.5, 25.6, 24.8, 24.0, 21.8, 19.4 ppm; IR νmax 2957, 2925, 2863, 1675, 1599, 1576, 1484, 1465, 1275, 1267, 1110, 1098, 1003, 763, 759 cm⁻¹; HRMS –EI (m/z): [M]+ calculated for C₂₅H₂₅O₅, 412.2250, found, 412.2255.

![10a](image2)

Rᶠ = 0.42 (30% ethyl acetate – petroleum ether); Yellow foam solid, m.p. 110-112 °C; Compound 10a was recrystallized from dichloromethane at room temperature to obtain yellow crystals, CCDC 2050868; [α]²⁰ = +1.5 (c = 1.00 in DCM); ¹H NMR (400 MHz, Chloroform-d) δ 8.93 (s, 1H), 8.23 (s, 1H), 6.69 (d, J = 8.3 Hz, 1H), 6.57 (d, J = 8.3 Hz, 1H), 4.30 (d, J = 7.3 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.912 (s, 3H), 3.908 (s, 3H), 3.77 – 3.64 (m, 2H), 2.78 (dd, J = 16.6, 13.9 Hz, 1H), 2.62 (dd, J = 16.7, 4.2 Hz, 1H), 2.49 (dt, J = 13.9, 4.2 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.11 – 1.98 (m, 1H), 1.80 – 1.69 (m, 2H), 1.69 – 1.61 (m, 3H), 1.60 (s, 3H), 1.36 – 1.20 (m, 2H) ppm; ¹³C NMR (100 MHz, Chloroform-d) δ 198.9, 150.8, 148.9, 148.6, 129.1, 128.6, 124.2, 122.5, 119.4, 105.6, 103.4, 102.7, 66.93, 66.91, 55.6, 55.5, 40.0, 38.2, 37.7, 35.9, 35.8, 25.9, 25.2, 21.4, 21.2 ppm; IR νmax 3055, 2937, 2862, 2837,
To a solution of dienophile 12a' (200 mg, 0.80 mmol, 1.0 equiv.), aromatic aldehyde 11 (216 mg, 1.20 mmol, 1.5 equiv.) in anhydrous and degassed toluene (40 mL) (concentration for dienophile 12a' is 0.02 M) was added titanium(IV) isopropoxide (682 mg, 0.71 mL, 2.40 mmol, 3.0 equiv.) under N₂. After homogeneous mixing, the solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at λ_max = 366 nm for 1.5 hours (Note: the atmosphere temperature among quartz tubes was 35 to 40 °C). After that, the mixture was quenched with saturated NaHCO₃ (10 mL) and filtered through silica gel and washed with ethyl acetate (6×10 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (10% to 30% ethyl acetate – petroleum ether) to obtain 190 mg 16a' as a yellow viscous oil.

To a solution of above obtained 16a' (190 mg, 0.46 mmol, 1.0 equiv.) in anhydrous toluene (10 mL) was added DDQ (218 mg, 0.96 mmol, 2.0 equiv.) at room temperature. After stirred at 80 °C for 3 hours, the mixture was quenched with saturated Na₂S₂O₃/NaHCO₃ (10 mL, v/v = 1:1) and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% ethyl acetate – petroleum ether) to obtain 10a' as a yellow foam solid (161 mg, 49 % over two steps).

To a solution of dienophile 12a' (200 mg, 0.80 mmol, 1.0 equiv.), aromatic aldehyde 11 (216 mg, 1.20 mmol, 1.5 equiv.) in anhydrous and degassed toluene (40 mL) (concentration for dienophile 12a' is 0.02 M) was added titanium(IV) isopropoxide (682 mg, 0.71 mL, 2.40 mmol, 3.0 equiv.) under N₂. After homogeneous mixing, the solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at λ_max = 366 nm for 1.5 hours (Note: the atmosphere temperature among quartz tubes was 35 to 40 °C). After that, the mixture was quenched with saturated NaHCO₃ (10 mL) and filtered through silica gel and washed with ethyl acetate (6×10 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (10% to 30% ethyl acetate – petroleum ether) to obtain 190 mg 16a' as a yellow viscous oil.

To a solution of above obtained 16a' (190 mg, 0.46 mmol, 1.0 equiv.) in anhydrous toluene (10 mL) was added DDQ (218 mg, 0.96 mmol, 2.0 equiv.) at room temperature. After stirred at 80 °C for 3 hours, the mixture was quenched with saturated Na₂S₂O₃/NaHCO₃ (10 mL, v/v = 1:1) and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% ethyl acetate – petroleum ether) to obtain 10a' as a yellow foam solid (161 mg, 49 % over two steps).

R_f = 0.36 (30% ethyl acetate – petroleum ether); Yellow viscous oil; [α]D²⁰ = -144.9 (c = 0.40 in DCM); ¹H NMR: the same to 16a; ¹³C NMR: the same to 16a; IR ν_max 2960, 2925, 2857, 1691, 1675, 1598, 1570, 1483, 1464, 1275, 1260, 1144, 1096, 1016, 802, 799 cm⁻¹; HRMS–EI (m/z): [M]+ calculated for C₂₅H₃₂O₅, 412.2250, found, 412.2248.

R_f = 0.42 (30% ethyl acetate – petroleum ether); Yellow foam solid, m.p. 57-59 °C; [α]D²⁰ = -4.4 (c = 0.60 in DCM); ¹H NMR: the same to 10a; ¹³C NMR: the same to 10a; IR ν_max 2954, 2930, 2927, 2857, 1683, 1627, 1590, 1458, 1435, 1343, 1333, 1268, 1239, 1142, 1119, 1104, 1092, 1009, 934 cm⁻¹; HRMS–EI (m/z): [M]+ calculated for C₂₅H₃₀O₅, 410.2093, found, 410.2097.
To a solution of 10a (1.31 g, 3.2 mmol, 1.0 equiv.) in analytical-grade t-BuOH (60 mL) was added t-BuOK (3.60 g, 32.0 mmol, 10.0 equiv.). Then the mixture was stirred with bubbling O₂ into the mixture at 40 °C for 3 hours. After that, t-BuOH was evacuated and the mixture was diluted with ethyl acetate (50 mL) and water (30 mL). Separated the organic layer and the aqueous layer was washed with ethyl acetate (3×50 mL). The combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate, then concentrated to obtain 1.12 g crude 17a as a yellow foam solid for the next step without further purification.

To a solution of above obtained crude 17a in analytical-grade MeCN (60 mL) was added 2 N HCl (10 mL) at room temperature. Then the solution was stirred at 80 °C for 5 hours and quenched with saturated NaHCO₃ (50 mL). The mixture was extracted with DCM (3×60 mL) and washed with brine. The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain 18 as a yellow solid (668 mg, 60% over two steps). Note: The xestoquinol dimethyl ether 18 was easier to dissolve in DCM than ethyl acetate.  

Rᵣ = 0.38 (30% ethyl acetate – petroleum ether); Yellow solid, m.p. 243-245 °C; Compound 18 was recrystallized from THF/hexane (v/v = 1/2) at room temperature to obtain yellow crystals, CCDC 2050867; [α]ᵣ = +99.6 (c = 1.00 in DCM); ¹H NMR (400 MHz, Chloroform-d) δ 9.23 (s, 1H), 8.23 (s, 1H), 7.42 (t, J = 1.4 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.81 (ddt, J = 16.9, 7.8, 1.7 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.29 – 2.14 (m, 1H), 2.13 – 2.02 (m, 1H), 1.76 (td, J = 13.2, 4.3 Hz, 1H), 1.49 (s, 3H) ppm; ¹³C NMR (100 MHz, Chloroform-d) δ 172.7, 150.6, 148.6, 146.7, 146.6, 144.6, 143.6, 131.2, 127.2, 124.5, 123.9, 121.2, 117.4, 105.9, 103.2, 55.6, 55.5, 36.2, 33.6, 31.9, 18.6, 17.1 ppm; IR νₑₓₘₐₓ 2938, 2835, 1670, 1614, 1541, 1471, 1465, 1423, 1356, 1267, 1244, 1192, 1144, 1091, 1043, 904, 862, 806 cm⁻¹; HRMS–EI (m/z): [M]⁺ calculated for C₂₂H₂₀O₄, 348.1362, found, 348.1360.
The enantiomer compound 18' (136 mg, 65% over two steps) was synthesized according to the above similar procedures using 10a' (246 mg, 0.60 mmol, 1.0 equiv.) as starting material. **Note:** The xestoquinol dimethyl ether 18' was easier to dissolve in DCM than ethyl acetate.

\[
R_f = 0.38 \text{ (30\% ethyl acetate – petroleum ether);} \\
\text{Yellow solid, m.p. 248-250 °C;} \\
\text{Compound 18' was recrystallized from THF/hexane (v/v = 1/2)} \\
\text{at room temperature to obtain yellow crystals, CCDC 2050869;} \\
[\alpha]_{D}^{20} = -95.4 \; (c = 1.00 \text{ in DCM}); \\
\text{H NMR: the same to 18;} \\
\text{C NMR: the same to 18;} \\
\text{IR} \nu_{\text{max}} \; 3102, 2944, 2836, 1666, 1628, 1613, 1533, 1464, 1423, 1357, 1267, 1245, 1190, 1145, 1089, 1044, 905, 865, 802 \text{ cm}^{-1}; \\
\text{HRMS – EI (m/z): [M]^{+} calculated for C}_{22}H_{20}O_{4}, 348.1362, \text{ found, 348.1360.}
\]

To stirred solution of 18 (208 mg, 0.6 mmol, 1.0 equiv.) in MeCN/H2O (50 mL, v/v = 4:1) was added CAN (987 mg, 1.8 mmol, 3.0 equiv.) at 0 °C. Then the solution was stirred at room temperature for 1 hours. After that, the mixture was extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (30% ethyl acetate – petroleum ether) to obtain (+)-xestoquinone (2) as a yellow-brown solid (156 mg, 82%).
R_f = 0.26 (30% ethyl acetate – petroleum ether); Yellow-brown solid, m.p. 213-216 °C; [α]_D\textsuperscript{20} = +11.2 (c = 1.00 in DCM); \textsuperscript{1}H NMR (500 MHz, Chloroform-d) δ 8.98 (s, 1H), 8.22 (s, 1H), 7.54 (br t, J = 1.5 Hz, 1H), 7.05 (d, J = 10.0 Hz, 1H), 7.02 (d, J = 10.0 Hz, 1H), 2.89 (ddt, J = 17.1, 8.0, 1.8 Hz, 1H), 2.66 (dddd, J = 17.0, 10.0, 8.5, 1.5 Hz, 1H), 2.58 (dt, J = 12.9, 3.6 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.23 – 2.15 (m, 1H), 1.76 (td, J = 13.1, 4.4 Hz, 1H), 1.53 (s, 3H) ppm; \textsuperscript{13}C NMR (125 MHz, Chloroform-d) δ 184.6, 183.8, 170.1, 156.2, 147.3, 145.0, 144.0, 139.3, 138.7, 137.9, 133.2, 130.3, 126.9, 123.2, 121.6, 37.4, 32.6, 31.2, 18.4, 16.9 ppm; IR ν_max 3105, 2862, 1670, 1614, 1539, 1444, 1430, 1318, 1274, 1236, 1134, 1092, 986, 845, 764 cm\textsuperscript{-1}; HRMS–EI (m/z): [M]+ calculated for C\textsubscript{20}H\textsubscript{14}O\textsubscript{4}, 318.0892, found, 318.0889.

The (-)-xestoquinone (2') (40 mg, 84%) was synthesized according to the above similar procedures using 18' (52 mg, 0.15 mmol, 1.0 equiv.) as starting material.

R_f = 0.26 (30% ethyl acetate – petroleum ether); Yellow-brown solid, m.p. 96 - 98 °C; [α]_D\textsuperscript{20} = -8.2 (c = 1.00 in DCM); \textsuperscript{1}H NMR: the same to 2; \textsuperscript{13}C NMR: the same to 2; IR ν_max 2953, 2926, 2856, 1669, 1602, 1539, 1444, 1430, 1318, 1274, 1236, 1134, 1092, 1058, 986, 845, 764 cm\textsuperscript{-1}; HRMS–EI (m/z): [M]+ calculated for C\textsubscript{20}H\textsubscript{14}O\textsubscript{4}, 318.0892, found, 318.0894.

Table S3. Screening conditions of the late-stage cyclization.

| entry | additive | temperature/time | ratio of 3:4 | combined yield |
|-------|----------|-----------------|-------------|---------------|
| 1     | –        | -20 °C / 6 h    | 1:2.5       | 28%           |
| 2     | –        | 0 °C / 3 h      | 1:2.2       | 28%           |
| 3     | –        | 20 °C / 1 h     | 1:2.3       | 33%           |
| 4\textsuperscript{a} | – | 50 °C / 3 h | 1:3.0 | 84%\textsuperscript{a} |
| 5     | CeCl\textsubscript{2}+7H\textsubscript{2}O | 50 °C / 1 h | 1:2.2 | 52% |
| 6     | TFA      | 50 °C / 1 h     | 1:1.1       | 13%           |
| 7     | Cs\textsubscript{2}CO\textsubscript{3} | 50 °C / 1 h | – | messy, N.D. |
| 8     | NEt\textsubscript{3} | 50 °C / 1 h | 1:2.5 | 18% |

All reactions were performed using (-)-xestoquinone (2) (3.2 mg, 0.01 mmol, 1.0 equiv.) and hypotaurine 9 (1.7 mg, 0.015 mmol 1.5 equiv.) as starting materials in EtOH/MeCN/H\textsubscript{2}O (0.5 mL, v/v/v = 2:2:1), unless otherwise noted. \textsuperscript{a}The ratios of 3:4 and combined yields were determined from crude \textsuperscript{1}H NMR spectrum of 3+4 using CH\textsubscript{2}Br\textsubscript{2} as an internal standard. \textsuperscript{b}(-)-xestoquinone (2) (32 mg, 0.1 mmol, 1.0 equiv.) and hypotaurine 9 (17 mg, 0.15 mmol, 1.5 equiv) in EtOH/MeCN/H\textsubscript{2}O (5 mL, v/v/v = 2:2:1); \textsuperscript{c}isolated combined yield of 3+4.
To a stirred solution of (+)-xestoquinone (2) (32 mg, 0.1 mmol, 1.0 equiv.) in EtOH/MeCN/H2O (5 mL, v/v/v = 2:2:1) was added hypotaurine 9 (17 mg, 0.15 mmol, 1.5 equiv.) at room temperature. Then the solution was stirred at 50 °C for 3 hours. TLC analysis showed all (+)-xestoquinone (2) was consumed. The solvent was evacuated under vacuum, and the residue was purified by preparation lamella chromatography (7% MeOH-DCM, washed with 10% MeOH-DCM) directly to afford yellow solid (+)-adiciaquinone A (3) (9.0 mg, 21%), (+)-adiciaquinone B (4) (27.0 mg, 63%).

\[ \text{Rf} = 0.52 \text{ (10\% methanol-dichloromethane); Yellow solid, m.p. >320 °C (decomposed); } [\alpha]_{20}^{20} = +65.2 \text{ (c = 0.1 in chloroform-methanol (v/v = 2:1)); } \]

\[ ^1\text{H NMR (500 MHz, DMSO-d}_6\text{)} \delta 9.35 \text{ (br s, 1H, NH), 8.68 (s, 1H), 8.26 (s, 1H), 8.00 (s, 1H), 3.88 (t, } J = 6.0 \text{ Hz, 2H), 3.40 (t, } J = 6.0 \text{ Hz, 2H), 2.84 (dd, } J = 17.0, 8.0 \text{ Hz, 1H), 2.64 – 2.60 (m, 1H), 2.60 – 2.57 (m, 1H), 2.30 – 2.16 (m, 1H), 2.13 – 2.03 (m, 1H), 1.65 (td, } J = 13.0, 4.4 \text{ Hz, 1H), 1.50 (s, 3H ppm); } ^{13}\text{C NMR (125 MHz, DMSO-d}_6\text{)} \delta 177.9, 173.8, 169.4, 157.4, 147.8, 147.2, 146.2, 143.0, 136.0, 134.4, 128.6, 125.4, 123.0, 121.7, 111.7, 48.2, 39.4 (C21, buried in the peak of DMSO-d}_6\text{), 37.2, 31.8, 30.3, 17.9, 16.3 ppm; IR } \nu_{\text{max}} \text{ 3270, 2928, 2858, 1668, 1655, 1589, 1508, 1458, 1344, 1282, 1238, 1116, 1028, 864 cm}^{-1}; \text{ HRMS–ESI (m/z): [M+Na]}^+ \text{ calculated for C}_{22}\text{H}_{17}\text{NO}_6\text{SNa}, 446.0669, \text{ found, 446.0663.} \]
R_f = 0.48 (10% methanol-dichloromethane); Yellow solid, m.p. >320 °C (decomposed); [α]_D^20 = +100.4 (c = 0.05 in chloroform-methanol (v/v = 2:1)); ¹H NMR (500 MHz, DMSO-d_6) δ 9.24 (br s, 1H, NH), 8.72 (s, 1H), 8.28 (s, 1H), 8.00 (s, 1H), 3.88 (t, J = 5.9 Hz, 2H), 3.40 (t, J = 5.9 Hz, 2H), 2.84 (dd, J = 17.1, 7.9 Hz, 1H), 2.65 (dd, J = 13.2, 4.1 Hz, 1H), 2.59 (dd, J = 17.4, 8.9 Hz, 1H), 2.28 – 2.15 (m, 1H), 2.12 – 2.01 (m, 1H), 1.63 (td, J = 12.9, 4.3 Hz, 1H), 1.50 (s, 3H) ppm; ¹³C NMR (125 MHz, DMSO-d_6) δ 178.3, 173.7, 169.4, 154.6, 147.9, 147.1, 146.2, 143.0, 137.9, 131.8, 130.8, 124.7, 123.4, 121.6, 111.3, 48.2, 39.3 (C22, buried in the peak of DMSO-d_6), 36.8, 31.6, 30.3, 17.8, 16.2 ppm; IR ν_max 3274, 2935, 2862, 1716, 1664, 1616, 1541, 1508, 1458, 1267, 1240, 1143, 935, 864, 806 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calculated for C_{22}H_{17}NO_{6}SNa⁺, 446.0669, found, 446.0662.

Note: The (+)-adociaquinones A (3) and B (4) were uneasy to dissolve in organic solution, especially for the major product (+)-adociaquinone B (4), which was uneasy to dissolve in DMSO-d_6.
Comparison of NMR spectroscopic data of natural and synthetic (+)-xestoquinone (2), (+)-adociaquinones A (3) and B (4)

Natural product (+)-xestoquinone: $[\alpha]_D^{25} = +17.2$ (c = 1.16 in DCM)\textsuperscript{[3]}

Our Synthetic (+)-xestoquinone: $[\alpha]_D^{20} = +11.2$ (c = 1.00 in DCM)

**Table S4.** Comparison of $^1$H NMR spectroscopic data of natural\textsuperscript{[4]} and synthetic\textsuperscript{[5]} (+)-xestoquinone with this synthetic work.

| position | natural (a) (Laurent’s work) $\delta^1$H [ppm; mult; J (Hz)], 300 MHz, Chloroform-$d$ | synthetic (b) (Harada’s work) $\delta^1$H [ppm; mult; J (Hz)], 400 MHz, Chloroform-$d$ | synthetic (c) (this work) $\delta^1$H [ppm; mult; J (Hz)], 500 MHz, Chloroform-$d$ | deviation (a-c; b-c) $\Delta\delta$ (ppm) |
|----------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-----------------------------------------|
| 1        | 7.54; t; 1.5                                    | 7.54; br t; 1.5                                  | 7.54; br t; 1.5                                  | 0.00; 0.00                              |
| 3a       | 2.64; dddd; 17.1, 9.8, 8.4, 1.5                  | 2.64; dddd; 17.0, 9.9, 8.4, 1.5                  | 2.66; dddd; 17.0, 10.0, 8.5, 1.5                 | -0.02; -0.02                           |
| 3b       | 2.88; dddd; 17.1, 8.0, 2.5, 1.5                  | 2.88; dddd; 17.0, 8.0, 2.2, 1.5                  | 2.89; ddt; 17.1, 8.0, 1.8                        | -0.01; -0.01                           |
| 4        | 2.22; m, 2H                                      | 2.28; m, 1H                                      | 2.29; m, 1H                                      | -0.07, 0.03; -0.01, 0.00               |
| 5a       | 1.75; ddd; 13.0, 13.0, 4.7                       | 1.76; ddd; 13.0, 13.0, 4.5                       | 1.76; td; 13.1, 4.4                              | -0.01; 0.00                            |
| 5b       | 2.57; ddd; 12.8, 3.6, 3.6                        | 2.58; ddd; 13.0, 4.1, 3.0                        | 2.58; dt; 12.9, 3.6                              | -0.01; 0.00                            |
| 11       | 9.03; s                                          | 9.05; s                                          | 8.98; s                                          | 0.05; 0.07                             |
| 14       | 7.02; s, 2H                                      | 7.06; d; 10.4                                    | 7.05; d; 10.0                                    | -0.03, 0.00; -0.01, 0.01              |
| 15       | 7.03; d; 10.4                                    | 7.02; d; 10.0                                    | 7.02; d; 10.0                                    | 0.01, 0.01                             |
| 18       | 8.23; s                                          | 8.25; s                                          | 8.22; s                                          | 0.01; 0.03                             |
| 20       | 1.53; s                                          | 1.54; s                                          | 1.53; s                                          | 0.00; 0.01                             |
Table S5. Comparison of $^{13}$C NMR spectroscopic data of natural [4] (+)-xestoquinone with this synthetic work.

| position | natural (a) (Laurent’s work) $\delta$ $^{13}$C [ppm], 75 MHz, Chloroform-$d$ | synthetic (b) (this work) $\delta$ $^{13}$C [ppm], 125 MHz, Chloroform-$d$ | deviation (a-b) $\Delta\delta$ (ppm) |
|----------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|---------------------------------|
| 1        | 145.0                                                                              | 145.0                                                                              | 0.0                             |
| 2        | 121.5                                                                              | 121.6                                                                              | -0.1                            |
| 3        | 16.9                                                                               | 16.9                                                                               | 0.0                             |
| 4        | 18.4                                                                               | 18.4                                                                               | 0.0                             |
| 5        | 31.2                                                                               | 31.2                                                                               | 0.0                             |
| 6        | 37.4                                                                               | 37.4                                                                               | 0.0                             |
| 7        | 147.3                                                                              | 147.3                                                                              | 0.0                             |
| 8        | 144.0                                                                              | 144.0                                                                              | 0.0                             |
| 9        | 170.3                                                                              | 170.1                                                                              | 0.2                             |
| 10       | 137.9                                                                              | 137.9                                                                              | 0.0                             |
| 11       | 127.0                                                                              | 126.9                                                                              | 0.1                             |
| 12       | 130.3                                                                              | 130.3                                                                              | 0.0                             |
| 13       | 183.9                                                                              | 183.8                                                                              | 0.1                             |
| 14       | 139.4                                                                              | 139.3                                                                              | 0.1                             |
| 15       | 138.7                                                                              | 138.7                                                                              | 0.0                             |
| 16       | 184.7                                                                              | 184.6                                                                              | 0.1                             |
| 17       | 133.2                                                                              | 133.2                                                                              | 0.0                             |
| 18       | 123.2                                                                              | 123.2                                                                              | 0.0                             |
| 19       | 156.2                                                                              | 156.2                                                                              | 0.0                             |
| 20       | 32.6                                                                               | 32.6                                                                               | 0.0                             |
Natural product (+)-adociaquinone A: $[\alpha]_D = +31.7$ (c = 4.66 in MeCN) $^6$

Harada’s Synthetic (+)-adociaquinone A: $[\alpha]_D^{29} = +70$ (c = 0.107 in chloroform -methanol (v/v = 2:1)) $^7$

Our Synthetic (+)-adociaquinone A: $[\alpha]_D^{29} = +65.2$ (c = 0.1 in chloroform -methanol (v/v = 2:1))

Table S6. Comparison of $^1$H NMR spectroscopic data of natural $^6$ and synthetic $^7$ (+)-adociaquinone A with this synthetic work.

| position | natural (a) (Ireland’s work) | synthetic (b) (Harada’s work) | synthetic (c) (this work) | deviation (a-c; b-c) | Δδ (ppm) |
|----------|-------------------------------|-------------------------------|--------------------------|---------------------|----------|
| 1        | 7.97; s                       | 8.00; s                       | 8.00; s                  | -0.03; 0.00        |
| 3a       | 2.56; dd; 17.0, 9.0           | 2.60; m                       | 2.59; m                  | -0.03; 0.01        |
| 3b       | 2.82; dd; 17.0, 8.5           | 2.84; dd; 17.4, 8.2,         | 2.84; dd; 17.0, 8.0      | -0.02; 0.00        |
| 4a       | 2.06; m                       | 2.08; m                       | 2.08; m                  | -0.02; 0.00        |
| 4b       | 2.21; m                       | 2.23; m                       | 2.22; m                  | -0.01; 0.01        |
| 5a       | 1.63; dt; 13.0, 4.5           | 1.66; ddd; 12.9, 12.9, 4.2   | 1.65; td; 13.0, 4.4      | -0.02; 0.01        |
| 5b       | 2.60; m                       | 2.60; m                       | 2.61; m                  | -0.01; -0.01       |
| 11       | 8.65; s                       | 8.69; s                       | 8.68; s                  | -0.03; 0.01        |
| 18       | 8.24; s                       | 8.26; s                       | 8.26; s                  | -0.02; 0.00        |
| 20       | 1.48; s                       | 1.50; s                       | 1.50; s                  | -0.02; 0.00        |
| 21       | 3.87; m                       | 3.88; br s                    | 3.88; t; 6.0             | -0.01; 0.00        |
| 22       | 3.39; t; 6.0                  | 3.40; t; 6.0                  | 3.40; t; 6.0             | -0.01; 0.00        |
| NH       | 9.33; br s                    | 9.34; br s                    | 9.35; br s               | -0.02; -0.01       |
Table S7. Comparison of $^{13}$C NMR spectroscopic data of natural [6] and synthetic [7] (+)-adiciaquinone A with this synthetic work.

| position | natural (a) (Ireland’s work) $\delta^{13}$C [ppm], 125 MHz, DMSO-$d_6$ | synthetic (b) (Harada’s work) $\delta^{13}$C [ppm], 125 MHz, DMSO-$d_6$ | synthetic (c) (this work) $\delta^{13}$C [ppm], 125 MHz, DMSO-$d_6$ | deviation (a-c) $\Delta\delta$ (ppm) |
|----------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|----------------------------------|
| 1        | 146.2                                                                                           | --                                                                                               | 146.2                                                                                           | 0.0                              |
| 2        | 121.6                                                                                           | --                                                                                               | 121.7                                                                                           | -0.1                             |
| 3        | 16.3                                                                                           | --                                                                                               | 16.3                                                                                           | 0.0                              |
| 4        | 17.8                                                                                           | --                                                                                               | 17.9                                                                                           | -0.1                             |
| 5        | 30.3                                                                                           | --                                                                                               | 30.3                                                                                           | 0.0                              |
| 6        | 37.2                                                                                           | --                                                                                               | 37.2                                                                                           | 0.0                              |
| 7        | 147.7                                                                                           | --                                                                                               | 147.8                                                                                           | -0.1                             |
| 8        | 143.0                                                                                           | --                                                                                               | 143.0                                                                                           | 0.0                              |
| 9        | 169.3                                                                                           | --                                                                                               | 169.4                                                                                           | -0.1                             |
| 10       | 135.9                                                                                           | --                                                                                               | 136.0                                                                                           | -0.1                             |
| 11       | 125.4                                                                                           | --                                                                                               | 125.4                                                                                           | 0.0                              |
| 12       | 128.6                                                                                           | --                                                                                               | 128.6                                                                                           | 0.0                              |
| 13       | 173.7                                                                                           | --                                                                                               | 173.8                                                                                           | -0.1                             |
| 14       | 111.7                                                                                           | --                                                                                               | 111.7                                                                                           | 0.0                              |
| 15       | 147.2                                                                                           | --                                                                                               | 147.2                                                                                           | 0.0                              |
| 16       | 177.9                                                                                           | --                                                                                               | 177.9                                                                                           | 0.0                              |
| 17       | 134.4                                                                                           | --                                                                                               | 134.4                                                                                           | 0.0                              |
| 18       | 122.9                                                                                           | --                                                                                               | 123.0                                                                                           | -0.1                             |
| 19       | 157.3                                                                                           | --                                                                                               | 157.4                                                                                           | -0.1                             |
| 20       | 31.8                                                                                           | --                                                                                               | 31.8                                                                                           | 0.0                              |
| 21       | 39.4                                                                                           | --                                                                                               | 39.4, buried in the peak of DMSO-$d_6$                                                         | 0.0                              |
| 22       | 48.2                                                                                           | --                                                                                               | 48.2                                                                                           | 0.0                              |
Natural product (+)-adociaquinone B: $[\alpha]_D = +21.5$ (c = 1.86 in MeCN) \[6\]
Harada’s Synthetic (+)-adociaquinone B: $[\alpha]_{D}^{20} = +74$ (c = 0.0668 in chloroform -methanol (v/v = 2:1)) \[7\]
Our Synthetic (+)-adociaquinone B: $[\alpha]_{D}^{20} = +100.4$ (c = 0.05 in chloroform -methanol (v/v = 2:1))

Table S8. Comparison of $^1$H NMR spectroscopic data of natural \[6\] and synthetic \[7\] (+)-adociaquinone B with this synthetic work.

| position | natural (a) (Ireland’s work) | synthetic (b) (Harada’s work) | synthetic (c) (this work) | deviation (a-c; b-c) Δδ (ppm) |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
|          | $\delta$ $^1$H [ppm; mult; J (Hz)], 500 MHz, DMSO-$d_6$ | $\delta$ $^1$H [ppm; mult; J (Hz)], 500 MHz, DMSO-$d_6$ | $\delta$ $^1$H [ppm; mult; J (Hz)], 500 MHz, DMSO-$d_6$ |                               |
| 1        | 7.99; s                        | 8.00; s                        | 8.00; s                        | -0.01; 0.00                   |
| 3a       | 2.58; dd; 16.5, 8.5             | 2.59; dd; 16.9, 9.0            | 2.59; dd; 17.4, 8.9            | -0.01; 0.00                   |
| 3b       | 2.83; dd; 16.5, 7.5             | 2.84; dd; 16.9, 7.7            | 2.84; dd; 17.1, 7.9            | -0.01; 0.00                   |
| 4a       | 2.05; m                        | 2.07; m                        | 2.07; m                        | -0.02; 0.00                   |
| 4b       | 2.20; m                        | 2.21; m                        | 2.21; m                        | -0.01; 0.00                   |
| 5a       | 1.62; dt; 13.0, 4.0             | 1.63; ddd; 12.8, 12.8, 4.2     | 1.63; td; 12.9, 4.3            | -0.01; 0.00                   |
| 5b       | 2.64; m                        | 2.65; ddd; 12.8, 3.0, 3.0      | 2.65; dd; 13.2, 4.1            | -0.01; 0.00                   |
| 11       | 8.70; s                        | 8.72; s                        | 8.72; s                        | -0.02; 0.00                   |
| 18       | 8.26; s                        | 8.28; s                        | 8.28; s                        | -0.02; 0.00                   |
| 20       | 1.49; s                        | 1.50; s                        | 1.50; s                        | -0.01; 0.00                   |
| 21       | 3.38; t; 6.0                   | 3.40; buried in the peak of water | 3.40; t; 5.9                  | -0.02; 0.00                   |
| 22       | 3.86; m                        | 3.88; t; 5.9                   | 3.88; t; 5.9                   | -0.02; 0.00                   |
| NH       | 9.23; br s                     | 8.90; br s                     | 9.24; br s                     | -0.01; -0.34                  |
Table S9. Comparison of $^{13}$C NMR spectroscopic data of natural $^6$ and synthetic $^7$ (+)-adociaquinone B with this synthetic work.

| position | natural (a) (Ireland’s work) $\delta^{13}$C [ppm], 125 MHz, DMSO-$d_6$ | synthetic (b) (Harada’s work) $\delta^{13}$C [ppm], 125 MHz, DMSO-$d_6$ | synthetic (c) (this work) $\delta^{13}$C [ppm], 125 MHz, DMSO-$d_6$ | deviation (a-c; b-c) $\Delta\delta$ (ppm) |
|----------|------------------------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|----------------------------------|
| 1        | 146.2                                                            | 146.1                                                            | 146.2                                                            | 0.0; -0.1                        |
| 2        | 121.6                                                            | 121.6                                                            | 121.6                                                            | 0.0; 0.0                         |
| 3        | 16.2                                                             | 16.2                                                             | 16.2                                                             | 0.0; 0.0                         |
| 4        | 17.8                                                             | 17.8                                                             | 17.8                                                             | 0.0; 0.0                         |
| 5        | 30.3                                                             | 30.3                                                             | 30.3                                                             | 0.0; 0.0                         |
| 6        | 36.8                                                             | 36.8                                                             | 36.8                                                             | 0.0; 0.0                         |
| 7        | 147.9                                                            | 147.9                                                            | 147.9                                                            | 0.0; 0.0                         |
| 8        | 143.1                                                            | 143.1                                                            | 143.0                                                            | 0.1; 0.1                         |
| 9        | 169.4                                                            | 169.4                                                            | 169.4                                                            | 0.0; 0.0                         |
| 10       | 137.9                                                            | 137.9                                                            | 137.9                                                            | 0.0; 0.0                         |
| 11       | 124.7                                                            | 124.8                                                            | 124.7                                                            | 0.0; 0.1                         |
| 12       | 130.9                                                            | 130.9                                                            | 130.8                                                            | 0.1; 0.1                         |
| 13       | 173.7                                                            | 173.7                                                            | 173.7                                                            | 0.0; 0.0                         |
| 14       | 147.1                                                            | 147.1                                                            | 147.1                                                            | 0.0; 0.0                         |
| 15       | 111.3                                                            | 111.4                                                            | 111.3                                                            | 0.0; 0.1                         |
| 16       | 178.3                                                            | 178.3                                                            | 178.3                                                            | 0.0; 0.0                         |
| 17       | 131.8                                                            | 131.8                                                            | 131.8                                                            | 0.0; 0.0                         |
| 18       | 123.4                                                            | 123.4                                                            | 123.4                                                            | 0.0; 0.0                         |
| 19       | 154.6                                                            | 154.6                                                            | 154.6                                                            | 0.0; 0.0                         |
| 20       | 31.6                                                             | 31.6                                                             | 31.6                                                             | 0.0; 0.0                         |
| 21       | 48.2                                                             | 48.3                                                             | 48.2                                                             | 0.0; 0.1                         |
| 22       | 39.3                                                             | around 40, buried in the peak of DMSO-$d_6$                     | 39.3, buried in the peak of DMSO-$d_6$                            | 0.0; 0.7                         |
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$^1$H and $^{13}$C NMR, HPLC spectra of the synthetic intermediates and products

Chemical Formula: C$_2$H$_3$O$_4$
400 MHz, CDCl$_3$

Chemical Formula: C$_2$H$_3$O$_4$
100 MHz, CDCl$_3$
Chemical Formula: C_{10}H_{16}O_3
400 MHz, CDCl_3

Chemical Formula: C_{10}H_{16}O_3
100 MHz, CDCl_3
Chemical Formula: $C_{12}H_{14}O_2$
500 MHz, CDCl$_3$
Chemical Formula: \( \text{C}_{12}\text{H}_{14}\text{O}_2 \)
500 MHz, CDCl\(_3\)

Chemical Formula: \( \text{C}_{12}\text{H}_{14}\text{O}_2 \)
125 MHz, CDCl\(_3\)
12a (major)
Chemical Formula: C₁₅H₂₂O₃
500 MHz, CDCl₃

12a (major)
Chemical Formula: C₁₅H₂₂O₃
125 MHz, CDCl₃
**12b (minor)**

Chemical Formula: $\text{C}_{13}\text{H}_{23}\text{O}_3$

500 MHz, CDCl$_3$

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**12b (minor)**

Chemical Formula: $\text{C}_{13}\text{H}_{23}\text{O}_3$

125 MHz, CDCl$_3$
Chemical Formula: $C_{20}H_{30}O_5$

400 MHz, CDCl$_3$

Chemical Formula: $C_{20}H_{30}O_5$

100 MHz, CDCl$_3$
Chemical Formula: C_{26}H_{32}O_{6}
NOESY, CDCl₃

Chemical Formula: C_{22}H_{20}O_{4}
400 MHz, CDCl₃
(+)-xestoquinone (2)
Chemical Formula: C_{20}H_{14}O_{4}
125 MHz, CDCl₃

(+)-adociaquinone A (3)
Chemical Formula: C_{32}H_{27}NO_{5}S
500 MHz, DMSO-d₆
(+)-adoclauquinone A (3)
Chemical Formula: C_32H_27N_0_6S
125 MHz, DMSO-d_6

signal of C21 buried in the peak of DMSO-d_6 δ 39.4 ppm

(+)-adoclauquinone A (3)
Chemical Formula: C_32H_27N_0_6S
DEPT135, DMSO-d_6

C (21) δ 39.4 ppm
(+)-adodiaquinone B (4)
Chemical Formula: C_{22}H_{17}NO_3S
500 MHz, DMSO-d_6

signal of C22
buried in the peak
of DMSO-d_6
δ 39.3 ppm
HPLC spectra of product 14.

1. **Table S1**, entry 1, racemate of product 14a/14a*: HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; $t_1 = 23.774$ min, $t_2 = 27.376$ min.
2. **Table S1,** entry 1, racemate of product **14a/14a'**: HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; $t_{r1} = 30.408$ min, $t_{r2} = 35.231$ min.

![HPLC analysis of 14a/14a'](image1)

| Peak | RetTime Type | Width [min] | Area [mAU] | Height [mAU] | % |
|------|--------------|-------------|------------|--------------|---|
| 1    | 30.408 BB    | 0.5634      | 3081.65405 | 84.29497     | 49.7363 |
| 2    | 35.231 BB    | 0.6613      | 3114.33130 | 72.29312     | 50.2637 |

Totals: 6195.98535 156.58809

3. **Table S1,** entry 1, racemate of product **14b/14b'**: HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; $t_{r1} = 21.321$ min, $t_{r2} = 25.338$ min.

![HPLC analysis of 14b/14b'](image2)

| Peak | RetTime Type | Width [min] | Area [mAU] | Height [mAU] | % |
|------|--------------|-------------|------------|--------------|---|
| 1    | 21.321 BB    | 0.4199      | 782.72742  | 28.85401     | 50.1745 |
| 2    | 25.338 BB    | 0.4885      | 777.28302  | 24.57059     | 49.8255 |

Totals: 1560.01044 55.42460

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4. **Table S1**, entry 1, racemate of product 14b/14b': HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; $t_{r1} = 26.635$ min, $t_{r2} = 32.160$ min.

![HPLC analysis of product 14b/14b'](image)

| Peak RetTime Type Width Area Height Area % |
|---|---|---|---|---|---|
| 1 26.635 BB 0.4890 1877.38310 58.63712 49.6089 |
| 2 32.160 VB 0.5913 1909.01538 49.80637 50.3911 |

Totals: 3708.39656 108.44349

5. **Table 1**, entry 12, 1.31g scale, 97% e.e. for product 14a: HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; $t_{r1}$ (minor) = 30.103 min, $t_{r2}$ (major) = 34.725 min.

![HPLC analysis of product 14a](image)

| Peak RetTime Type Width Area Height Area % |
|---|---|---|---|---|---|
| 1 30.103 BB 0.4274 83.47428 2.36739 1.4422 |
| 2 34.725 BB 0.6506 5704.58008 132.56462 98.5578 |

Totals: 5788.05436 134.93202
6. **Table 1**, entry 12, 1.31g scale, 91% e.e. for product 14b: HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; t\(_r\)\(_1\) (minor) = 26.406 min, t\(_r\)\(_2\) (major) = 31.770 min.

7. **Table S1**, entry 11, -97% e.e. for product 14a': HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; t\(_r\)\(_1\) (major) = 24.030 min, t\(_r\)\(_2\) (minor) = 27.856 min.
8. **Table S1**, entry 11, -89% e.e. for product 14b: HPLC analysis, Chiralpak IG-H, i-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; $t_{r1}$ (major) = 21.637 min, $t_{r2}$ (minor) = 25.830 min.

![HPLC chromatogram](image)

**Signal 1: VWD A, Wavelength=234 nm**

| Peak | RetTime | Type | Width | Area | Height | Area |
|------|---------|------|-------|------|--------|------|
| 1    | 21.637  | VB   | 0.4433| 7187.9414| 248.97035| 94.4512 |
| 2    | 25.830  | MK   | 0.5234| 422.27490| 13.44546 | 5.5488 |

**Totals**: 7610.21631 262.41581