Supporting Information

Highly Enantioselective Synthesis of Cyclopropylphosphonates Catalysed by Chiral Ruthenium Porphyrins

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General Experiments: All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate drying agent prior to use: benzene from sodium, CH₂Cl₂ from CaH₂ and all other solvents were HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck pre-coated aluminium foil sheets (Silica gel 60 with fluorescent indicator UV₂₅₄). Compounds were visualized with UV light at 254 nm and 365 nm. Column chromatography was carried out using silica gel from Merck (0.063-0.200 mm). ¹H NMR spectra were recorded using Bruker Advance 500dpx at 500 MHz. High-resolution mass spectra were recorded on a ZabSpec TOF Micromass spectrometer in electronic impact mode or ESI positif mode at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest – Rennes FRANCE). Liquid UV-visible spectra were recorded on a UVIKON XL from Biotech. Infra Red spectra were performed in KBr disk on a IFS 28 Bruker. Ethyl diazoacetate was purchased from Aldrich CAS 623-73-4.

5-spirofluorenyldipyrromethane : Pyrrole (22 mL, 316.8 mmol), 9,9'-spirobifluorene-2-carbaldehyde (5 g, 14.5 mmol) and benzene (20 mL) were added to a dry 100-mL round-bottomed distillation flask and degassed with a stream of Ar for 5 minutes. *P*-toluene sulfonic acid (620 mg, 1.63 mmol) was then added and the solution was heated in order to eliminate the water formed during the reaction. After three hours of heating, the reaction was quenched

with triethylamine. Solvents were removed under vacuum to give a black oil which was dissolved in 100 mL of dichloromethane, washed with NaHCO₃, brined, then dried over MgSO₄. The crude product, obtained after concentration, was purified by chromatography on silica with a mixture of ethyl acetate and pentane (8/2). After recrystallization from ethanol, there was obtained 4.1 g of 5-spirobifluorenyldipyrromethane, yield 61 %. ¹H NMR (CDCl₃, ppm) 5.28 (s, 1H); 5.81 (q, 2H); 6.10 (q, 2H); 6.64 (q, 2H); 6.75 (m, 4H); 7.15 (m, 4H); 7.39 (m, 3H); 7.84 (m, 4H); 7.93 (br s, 2H). ¹³C NMR : 66.4; 107.6; 108.7; 117.6; 120.5; 120.7; 124.4; 124.5; 124.8; 128.2; 128.3; 128.4; 132.9; 141.3; 141.8; 142.1; 142.2; 149.1; 149.5; 149.6. Mass (EI) : (m/z): calculated for C₃₄ H₂₄ N₂ [M⁺] : 460.1939; found : 460.1920.

Synthesis of porphyrins:

5,10,15,20-tetrakis-[(1S,4R,5R,8S)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]-porphyrin = **1**

5,10,15-tri-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-20-monospirobifluorenylporphyrin = **2**

5,15-bis-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-10,20-bis-spirobifluorenylporphyrin = **3**

5-mono-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-10,15,20-tri- spirobifluorenylporphyrin = **4**

Method A : 9,9'-spirobifluorenyldipyrromethane (3g, 6.51 mmol) and dimethanoanthracene-9-carbaldehyde (1.55g, 6.51 mmol) were allowed to react at room temperature in dry and degassed dichloromethane (553 mL) , under an argon atmosphere and protected from light, with acid catalysis (BF₃O(Et)₂ :180 µL, 1.23 mmol). Under these conditions, the reaction reached an equilibrium in about 2 hours. A stoichiometric amount of p-chloranil was added to irreversibly oxidize the porphyrinogene. After addition of several drops of triethylamine and the ordinary work-up, concentration, washing, drying, the crude reaction mixture was purified by chromatography on silica gel (CH₂Cl₂). The purple fraction which eluted first was a mixture of six different porphyrins based on the ¹H NMR spectrum (internal NH). After a second chromatography (pentane/CH₂Cl₂: 8/2), the porphyrins were separated on preparative silica plates affording isolation of four different porphyrins which contained 1, 2, 3 or 4 chiral units. R_f (**1**): 0.82; R_f (**2**): 0.56; R_f (**3**): 0.30; R_f (**4**): 0.17. Yield : **1** (3%); **2** (5 %); **3** (7%); **4** (2%).

Method B : 9,9'-spirobifluorene-2-carbaldehyde (0.191g, 0.556 mmol), dimethanoanthracene-9-carbaldehyde (0.4 g, 1.667 mmol) and pyrrole (155 μ L, 2.2 mmol) were allowed to react at room temperature in dry and degassed chloroform (31 mL) under an argon atmosphere and protected from light, with acid catalysis ($\text{BF}_3\text{O}(\text{Et})_2$: 70 μ L, 0.49 mmol). Under these conditions, the reaction reached an equilibrium in about 2 hours. A stoichiometric amount of DDQ was added to irreversibly oxidize the porphyrinogene. After addition of several drops of triethylamine and the ordinary work-up, concentration, washing, drying, the crude reaction mixture was purified by chromatography on basic alumina (CH_2Cl_2 / pentane : 1/1). The purple fraction which eluted first was a mixture of three different porphyrins based on TLC. In fact, there were only porphyrins **1** (10%), **2** (18%) and **3** (8%) which were isolated on silica column (pentane/ CH_2Cl_2 : 8/2). Only traces of **4** were detected.

5,10,15-tri-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-20-monospirobifluorenylporphyrin

2 : NMR ^1H (CDCl_3 , ppm) : -2.60 (s, 2H); 1.02 (m, 6H); 1.41 (m, 18H); 1.79 (m, 6H); 2.06 (m, 6H); 2.84 (m, 6H); 3.62 (s, 6H); 6.92 (d, 2H); 7.18 (td, 2H); 7.27 (m, 2H); 7.33 (t, 1H); 7.39 (t, 1H); 7.43 (m, 3H); 7.54 (t, 1H); 7.83 (m, 3H); 8.13 (d, 1H); 8.19 (dd, 2H); 8.76 (m, 8H). UV-VIS (CH_2Cl_2): $\lambda_{\text{max/nm}}$ (log ϵ) : 224 (4.78); 274 (4.54); 423 (5.38); 517 (4.17); 553 (3.87); 592 (3.79); 647 (3.61); Mass (ESI, CH_2Cl_2 /MeOH 9/1) (m/z): calculated for $\text{C}_{93}\text{H}_{77}\text{N}_4$ $[\text{M} + \text{H}]^+$: 1249.6148; found: 1249.6129.

5,15-bis-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-10,20-bis-spirobifluorenylporphyrin

3 : NMR ^1H (CDCl_3 , ppm) : -2.78 (s, 2H); 1.18 (m, 4H); 1.35 (m, 12H); 1.86 (m, 4H); 2.00 (m, 4H); 2.98-2.42 (m, 4H); 3.57 (s, 4H); 6.89 (t, 2H); 7.06 (m, 5H); 7.26 (m, 5H); 7.38 (m, 5H); 7.52 (t, 2H); 7.69 (d, 1H); 7.78 (m, 5H); 7.98 (d, 1H); 8.09 (m, 3H); 8.16 (m, 3H); 8.66 (m, 8H). UV-VIS (CH_2Cl_2): $\lambda_{\text{max/nm}}$ (log ϵ) 227 (4.83); 270 (4.58); 308 (4.42); 423 (5.41); 517 (4.11); 553 (3.90); 591 (3.65); 647 (3.60). Mass (ESI, CH_2Cl_2 /MeOH 9/1) (m/z): calculated for $\text{C}_{102}\text{H}_{75}\text{N}_4$ $[\text{M} + \text{H}]^+$: 1355.7142 found : 1355.7135.

5-mono-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-10,15,20-tri-spirobifluorenylporphyrin

4 : NMR ^1H (CDCl_3 , ppm) : -2.62 (s, 2H); 1.14 (m, 2H); 1.37 (m, 6H); 1.97 (m, 4H); 3.00-2.46 (m, 2H); 3.60 (m, 2H); 6.64 (m, 2H); 6.92 (m, 2H); 7.13 (m, 7H); 7.47-7.21 (m br, 15H); 7.53 (m, 5H); 7.79 (m, 6H); 7.98 (m, 3H); 8.12 (m, 3H); 8.19 (m, 3H); 9.02-8.58 (m, 8H). UV-VIS (CH_2Cl_2): $\lambda_{\text{max/nm}}$ (log ϵ) : 228 (4.82); 308 (4.60); 426 (5.34); 516 (4.14); 553

(3.85); 590 (3.77); 648 (3.60). Mass (ESI, CH₂Cl₂/MeOH 9/1) (m/z): calculated for C₁₁₁ H₇₃ N₄ [M + H]⁺: 1461.5835 found 1461.5837.

[(1S,4R,5R,8S)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]-porphyrin **1** was previously described (Halterman).

5,10,15-tri-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-20-monospirobifluorenyl

porphyrinatorutheniumcarbonyl 2-Ru(CO) : To a solution of **3** (100 mg, 0.08 mmol) dissolved in commercial degassed o-dichlorobenzene and heated at 180°C was added by portion, Ru₃CO₁₂ (153 mg, 0.24 mmol). The mixture was stirred under an argon atmosphere for 2 hours until the reaction was completed. The solvent was removed under high vacuum and the crude product was purified by chromatography on silica gel using first pentane, then a mixture of pentane/dichloromethane (1/1). The major red-orange band was collected and dried under vacuum to afford a red powder. yield 90 %. NMR ¹H(CDCl₃, ppm) : 1.30 (m, 24 H); 1.87 (m, 6H); 1.99 (m, 6H); 2.71 (m, 6H); 3.58 (s, 6H); 6.87 (t ; 1H); 7.12 (m ; 2H); 7.24 (m, 2H); 7.36 (m, 6H); 7.53 (m, 1H); 7.65 (d, 1H); 7.77 (dd, 2H); 8.20 (m, 3H); 8.54 (m, 8H). UV-VIS (CH₂Cl₂): λ_{max}/nm (log ε): 224 (4.88); 308 (4.47); 413 (5.38); 529 (4.35). Mass (ESI, CH₂Cl₂/MeOH 9/1) (m/z): calculated for C₉₄ H₇₅ N₄ O ¹⁰²Ru [M + H]⁺: 1377.4984 found: 1377.5053; IR (KBr) : ν_{CO} = 1943.9 cm⁻¹

5,15-bis-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-10,20-bis-spirobifluorenyl

porphyrinatorutheniumcarbonyl 3-Ru(CO) : the complex was prepared using the same method as for compound **2-Ru(CO)**. yield 90 %. NMR ¹H (CDCl₃, ppm) : 8.49 (m, 8H); 8.18 (m, 4H); 8.09 (m, 2H); 7.75 (m, 4H); 7.52 (m, 4H); 7.35 (m, 6H); 7.24 (m, 5H); 7.11 (m, 5H); 6.87 (m, 2H); 3.55 (s br, 4H); 2.74-2.52 (m, 4H); 1.91 (m, 8H); 1.34 (m, 12H); 1.11 (m, 4H). UV-VIS (CH₂Cl₂): λ_{max}/nm (log ε) 228 (5.15); 308 (4.81); 415 (5.35); 530 (4.34). Mass (ESI, CH₂Cl₂/MeOH 9/1) (m/z): calculated for C₁₀₃ H₇₂ N₄ O Na ¹⁰²Ru [M + Na]⁺: 1505.4647 found : 1505.4610; IR (KBr) : ν_{CO} = 1943.9 cm⁻¹.

5-mono-[(1S,4R,5R,8S)dimethanoanthracen-9-yl]-10,15,20-tri-spirobifluorenyl

porphyrinatorutheniumcarbonyl 4-Ru(CO) : the complex was prepared using the method used for compound **2-Ru(CO)**. yield 90 % NMR ¹H (CDCl₃, ppm) : 1.14 (m, 2H); 1.35 (m, 6H); 1.90 (m, 4H); 2.88-2.46 (m, 2H); 3.58 (m, 2H); 6.54 (m, 2H); 6.88 (m, 2H); 7.09 (m,

7H); 7.29 (m, 14H); 7.51 (m, 7H); 7.74 (m, 5H); 7.94 (m, 2H); 8.11 (m, 3H); 8.19 (m, 4H); 8.4-8.8 (m, 8H). UV-VIS (CH₂Cl₂): $\lambda_{\text{max/nm}}$ (log ϵ) 228 (5.20); 308 (4.68); 416 (5.34); 530 (4.34). Mass (ESI, CH₂Cl₂/MeOH 9/1) (m/z): calculated for C₁₁₂ H₇₁ N₄ O¹⁰²Ru [M + H]⁺: 1589.4671 found 1589.4714; IR (KBr) : ν_{CO} = 1943.9 cm⁻¹.

Preparation of [Ru(H₄)(CHPO(OiPr)₂)] 5 : to a solution of **1**-Ru(CO) (30 mg, 24 μ mol) in dichloromethane (1 mL) under argon was added a solution of diisopropyldiazomethylphosphonate (6.2 mg, 30 μ mol) in of dichloromethane (0.2 mL) over a period of 30 minutes. The crude product was purified by preparative silica plates (pentane/dichloromethane/ether : 15/10/1) affording the isolation of the pure product (27 mg, 82 %). NMR ¹H (CDCl₃, ppm) : 15.32 (carbene CH, d ²J_{PH} = 46 Hz, 1H); 8.48-8.40 (2d, ³J_{HH} = 5 Hz, 8H); 7.36 (s, 4H); 3.60 (s, 4H); 3.50 (s, 4H); 3.24 (s, 4H); 2.33 (s, 4H); 2.14-1.05 (br m, 50H); 0.31 (dd, J_{HH} = 5.7Hz, 6H); -0.65 (dd, ³J_{HH} = 5.7Hz, 6H). ¹³C NMR (CDCl₃, ppm) : 284.1 (J_{CP} = 180 Hz, carbene C). ³¹P NMR (CDCl₃, ppm) : 16.65. UV-VIS (CH₂Cl₂): $\lambda_{\text{max/nm}}$ (log ϵ) : 408 (5.27); 525 (4.39).

General procedure for cyclopropanation reaction :

The catalyst (0.5%) was placed in an oven-dried hemolysis tube. This tube was evacuated, and backfilled with argon. The solvent (1 mL) was added via syringe, followed by alkene (1 mmol). Then diazo (0.2 mmol) was added slowly to the mixture over a period of 30 minutes. After 2 hours for ethyl diazoacetate and 48 hours for diisopropyl diazomethylphosphonate, the resulting mixture was evaporated and purified by flash silicagel chromatography to give the product. In the case of cyclopropylphosphonate, a second purification by distillation was necessary.

Catalytic reactions were controlled either on a Varian CP-3380 Gas Chromatograph equipped with a CP-Chirasil-Dex Column or on a Merck-Hitachi D-7000 HPLC equipped with both UV Merck-Lachrom L-7400 detector and Jasco OR-1590 polarimeter.

Determination of conversion, diastereoselectivity and enantioselectivity :

Cyclopropanation of styrene with ethyl diazoacetate : GC-column CP-Chirasil-Dex column, injector 200°C (pulsed split mode), detector (FID 220 °C, oven: 120°C; 2.5°C.min⁻¹), pressure = 15 psi. *cis* (1R,2S) τ_r = 13.30 min; *cis* (1S,2R) τ_r = 13.78 min; *trans* (1R,2R) τ_r = 14.21 min; *trans* (1S,2S) τ_r = 14.36 min.

Cyclopropanation of styrene with diisopropyl diazomethylphosphonate :

GC-column CP-Chirasil-Dex column, injector 200°C (pulsed split mode), detector (FID 220 °C, oven: 120°C; 2.5°C.min⁻¹), pressure = 15 psi. τ_r = 35.79 min; τ_r = 35.96 min.

Cyclopropanation of 4-CF₃-styrene with diisopropyl diazomethylphosphonate :

GC-column CP-Chirasil-Dex column, injector 200°C (pulsed split mode), detector (FID 220 °C, oven: 120°C; 2.5°C.min⁻¹), pressure = 15 psi. *trans* τ_r = 35.41 min

Analytical HPLC Chiracel OC column, hexane-isopropanol 98/2 (1 mL.min⁻¹); detection : 254 nm and circular dichroism. τ_r = 10.55 min (-); τ_r = 12.25 min (+).

Cyclopropanation of 4-Cl-styrene with diisopropyl diazomethylphosphonate :

GC-column CP-Chirasil-Dex column, injector 200°C (pulsed split mode), detector (FID 220 °C, oven: 120°C; 2.5°C.min⁻¹), pressure = 15 psi. *trans* τ_r = 34.42 min.

Analytical HPLC Chiracel OC column, hexane-isopropanol 98/2 (1 mL.min⁻¹); detection : 254 nm and circular dichroism. τ_r = 15.23 min (-); τ_r = 16.55 min (+).

Cyclopropanation of 4-Me-styrene with diisopropyl diazomethylphosphonate :

GC-column CP-Chirasil-Dex column, injector 200°C (pulsed split mode), detector (FID 220 °C, oven: 120°C; 2.5°C.min⁻¹), pressure = 15 psi. *trans* τ_r = 30.49 min.

Analytical HPLC Chiracel OC column, hexane-isopropanol 98/2 (1 mL.min⁻¹); detection : 254 nm and circular dichroism. τ_r = 12.84 min (-); τ_r = 15.09 min (+).

Cyclopropanation of 4-OMe-styrene with diisopropyl diazomethylphosphonate :

GC-column CP-Chirasil-Dex column, injector 200°C (pulsed split mode), detector (FID 220 °C, oven: 120°C; 2.5°C.min⁻¹), pressure = 15 psi. *trans* τ_r = 37.47 min

Analytical HPLC Chiracel OJ column, hexane-isopropanol 98.2/1.8 (0.6 mL.min⁻¹); detection : 254 nm and circular dichroism. τ_r = 22.59 min (-); τ_r = 25.08 min (+).