

CHEMISTRY 
A EUROPEAN JOURNAL

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Enantioselective Synthesis of [7]Helicene: Dramatic Effects of Olefin Additives and Aromatic Solvents in Asymmetric Olefin Metathesis.

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Enantioselective Synthesis of [7]Helicene: Dramatic Effects of Olefin Additives and Aromatic Solvents in Asymmetric Olefin Metathesis.

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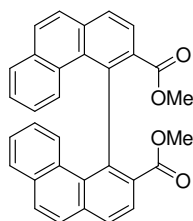
SUPPORTING INFORMATION

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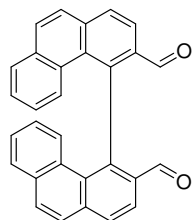
All reactions that were carried out under anhydrous conditions were performed under an inert argon or nitrogen atmosphere in glassware that had previously been dried overnight at 120 °C or had been flame dried and cooled under a stream of argon or nitrogen.^[1] All chemical products were obtained from Sigma-Aldrich Chemical Company or Strem Chemicals and were reagent quality. These products were used without further purification. The preparation of racemic [7]helicene has been described.^[2] The synthesis of catalysts **3**,^[3] **4a** and **4b** were prepared as previously reported.^[4] Olefin additive **15**^[5] and 1,2-divinylbenzene^[6] were prepared as previously reported. All other olefin additives are commercially available. Technical solvents were obtained from VWR International Co. Anhydrous solvents (CH₂Cl₂, Et₂O, THF, Toluene, DMF and n-hexane) were dried and deoxygenated using a GlassContour system (Irvine, CA). Isolated yields reflect the mass obtained following flash column silica gel chromatography. Organic compounds were purified using the method reported by W. C. Still^[7] and using silica gel obtained from Silicycle Chemical division (40-63 nm; 230-240 mesh). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed silica gel 60 coated with a fluorescence indicator (Silicycle Chemical division, 0.25 mm, F₂₅₄). Visualization of TLC plate was performed by UV (254 nm), ninhydrin or KMnO₄ stains. All mixed solvent eluents are reported as v/v solutions. Concentration refers to removal of volatiles at low pressure on a rotary evaporator. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD) and were compared to racemic samples. All reported compounds were homogeneous by thin layer chromatography (TLC) and by ¹H NMR. NMR spectra were taken in deuterated CDCl₃ using Bruker AV-300, AMX 300 and AMX 400 instruments unless otherwise noted. Signals due to the solvent served as the internal standard. The acquisition parameters are shown on all spectra. The ¹H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q

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- [1] D. F. Shriver, M. A. Drezdon in *The Manipulation of Air-Sensitive Compounds*; Wiley-VCH: New York, 1986.
- [2] S. K. Collins, A. Grandbois, M. P. Vachon, J. Côté, *Angew. Chem.* **2006**, *118*, 2989-2992.; *Angew. Chem., Int. Ed.* **2006**, *45*, 2923-2926.
- [3] P.-A. Fournier, S. K. Collins, *Organometallics* **2007**, *26*, 2945-2949
- [4] P.-A. Fournier, J. Savoie, M. Bédard, B. Stenne, A. Grandbois, S. K. Collins, *Chem. Eur. J. Submitted for publication*
- [5] L. Boisvert, F. Beaumier, C. Spino, *Can. J. Chem.* **2006**, *84*, 1290
- [6] R. H. Mitchell, B.N. Ghose, M.E. Williams, *Can. J. Chem.*, **1977**, *55*, 210
- [7] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

(quartet), m (multiplet), br (broad); the list of couplings constants (J) corresponds to the order of the multiplicity assignment. The ^1H NMR assignments were made based on chemical shift and multiplicity and were confirmed, where necessary, by homonuclear decoupling, 2D COSY experiments. The ^{13}C NMR assignments were made on the basis of chemical shift and multiplicity and were confirmed, where necessary, by two dimensional correlation experiments (HSQC). High resolution mass spectroscopy (HRMS) was done by the Centre régional de spectrométrie de masse at the Département de Chimie, Université de Montréal from an Agilent LC-MSD TOF system using ESI mode of ionization.

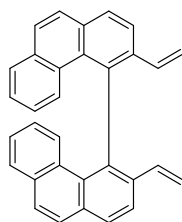


3,3'-dimethyl-4,4'-biphenanthryl-3,3'-dicarboxylate (S1) : In a flame dried 250 mL round bottom flask is added anhydrous dimethylsulfoxide (24.5 mL), methanol (9.1 mL) and freshly distilled *N*-ethyl- *N*-diisopropylamine (3.5 mL). The solvent mixture is degassed by 3 freeze thaw cycles. In a high pressure reaction vessel is added 3,3'-bistrifluoromethanesulfonate-4,4'-biphenanthryl⁸ (3.00 g, 1.0 eq, 4.61 mmol), palladium acetate (207 mg, 0.2 eq, 0.92 mmol), 1,3-bis(diphenylphosphino)propane and the previously degassed solvent mixture. The reaction vessel is sealed and purged three times with carbon monoxide. The reaction vessel is then pressurized with carbon monoxide (130 psi) and heated in an oil bath at 120°C for 72h. The reaction vessel is then cooled to rt and water (75 mL) is added to the reaction mixture. The reaction mixture is then extracted 3 times with ether (75 mL). The organic phases are then combined, dried over sodium sulphate and concentrated under vacuum. Ether (75 mL) is then added to the resulting yellow solid and heated to reflux for 2h. The suspension is then cooled to rt, filtered and the filter cake is washed with cold ether. The resulting solid is pure enough to proceed to the next step. For an analytical sample for characterisation, the product can be purified by silica gel column chromatography (Hexanes: Ethyl Acetate 3:1) to afford pure 3,3'-dimethyl-4,4'-biphenanthryl-3,3'-dicarboxylate (1,5 g, 70%) as an off-white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.2$ Hz, 2H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.86 (d, $J = 8.8$ Hz, 2H), 7.82 (d, $J = 8.8$ Hz, 2H), 7.78 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.33 (ddd, $J = 7.8, 7.0, 1.0$ Hz, 2H), 6.87 (ddd, $J = 8.6, 7.0, 1.5$ Hz, 2H), 3.17 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 139.7, 134.7, 132.9, 130.2 (2c's), 129.3, 129.1, 128.4, 128.1, 126.7, 126.5, 126.2, 125.8, 125.6, 52.2; HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{22}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$, 493.14103, found 493.14230.

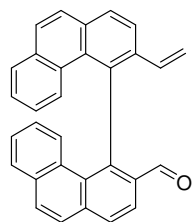


[8] T.H. Hayashi, I.Y. Uozumi, Y. Matsumoto, F. Ozawa, *Synthesis* **1994**, 526.

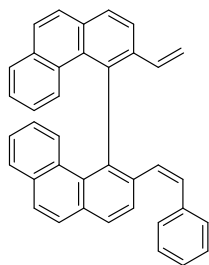
3,3'-dicarboxaldehyde-4,4'-biphenanthryl (S2): In a flame dried 100mL round bottom flask is added 3,3'-dimethyl-4,4'-biphenanthryl-3,3'-dicarboxylate (**XX**) (600 mg, 1.0 eq, 1.28 mmol). Anhydrous tetrahydrofuran (20 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled to 0°C. Lithium aluminium hydride (125 mg, 2.5 eq, 3.19 mmol) is added to the diester solution in small portions. The grey suspension is warmed at rt and stirred overnight. 1N HCl (50 mL) is slowly added and the reaction mixture is stirred until total dissolution of the aluminium salts. Dichloromethane (50 mL) is added to the yellow suspension. The phases are separated and the aqueous phase is extracted two times with dichloromethane. The organic phases are combined, dried over sodium sulphate and concentrated under vacuum. Pyridinium chlorochromate (PCC) (700 mg, 2.5 eq, 3.2 mmol) and anhydrous dichloromethane (12 mL) are added to the resulting solid. The solution is stirred at rt for 3h. The solution is then filtered through celite and washed with dichloromethane. The filtrate is then concentrated under vacuum and the resulting solid is purified by silica gel column chromatography (3:1 Hexanes:Ethyl Acetate) to obtain pure 3,3'-dicarboxaldehyde-4,4'-biphenanthryl as a light yellow solid (500 mg, 95%) ¹H NMR (400 MHz, CDCl₃) δ 9.21 (d, *J* = 0.8 Hz, 2H), 8.33 (d, *J* = 7.9 Hz, 2H), 8.23 (dd, *J* = 8.3, 0.7 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.89 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.77 (dd, *J* = 8.7, 0.4 Hz, 2H), 7.41 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 2H), 6.98 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 191.1, 141.9, 137.2, 134.3, 133.3, 132.1, 130.7, 130.5, 130.4, 129.7, 127.5, 127.3, 127.2, 126.9, 125.2; HRMS (ESI) *m/z* calculated for C₃₀H₁₈O₂Ag [M+Ag]⁺, 517, 03522, found 517.03520.



3,3'-Divinyl-4,4'-biphenanthryl (5): A flame dried round bottom flask is charged with 3,3'-dicarboxaldehyde-4,4'-biphenanthryl **S2** (200 mg, 0.49 mmol, 1.0 eq.). Anhydrous tetrahydrofuran (20 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to -78 °C. A second flame dried round bottom flask is charged methyltriphenylphosphonium bromide (700 mg, 1.96 mmol, 4.0 eq.). Anhydrous tetrahydrofuran (20 mL) is added and the suspension is cooled down to -78 °C. *n*-Butyllithium (3.8 eq, 1.86 mmol, 0.75 mL of a 2.5M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt for 10 min. and then cooled back to -78 °C. The orange solution of phosphorus ylide is slowly transferred via canula to the solution of **S2**. The reaction mixture is warmed to rt and stirred for 1 hour. Silica gel is directly added to the reaction mixture and the solvent is evaporated under vacuum. The product is dry packed and purified by silica gel column chromatography (15:1 Hexanes: Ethyl Acetate) to afford pure 3,3'-divinyl-4,4'-biphenanthryl (190 mg, 94 %) as an off-white solid; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 9.4 Hz, 2H), 7.75 (app d, *J* = 8.1 Hz, 4H), 7.65 (d, *J* = 9.4 Hz, 2H), 7.28 (m, 2H), 6.82 (ddd, *J* = 9.4, 7.4, 1.5 Hz, 2H), 5.99 (dd, *J* = 18.0, 9.0 Hz, 2H), 5.48 (d, *J* = 18.0 Hz, 2H), 4.76 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 137.9, 135.7, 135.0, 133.5, 133.4, 131.0, 129.5, 129.2, 128.5, 128.0, 127.4, 126.2, 125.9, 125.8, 124.7, 115.4; HRMS (ESI⁺) *m/z* calculated for C₃₂H₂₂Ag [M+Ag]⁺, 513.0773, found 513.07669.

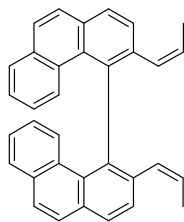


3-Carboxaldehyde-3'-vinyl-4,4'-biphenanthryl (S2): To a flame dried round bottom flask was added 3,3'-dicarboxaldehyde-4,4'-biphenanthryl **S2** (120 mg, 1.0 eq, 0.29 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the mixture is stirred until dissolution of the substrate and the solution is cooled down to -78 °C. To a second flame dried round bottom flask was added methyltriphenylphosphonium bromide (0.22 mmol, 0.75 eq, 79 mg). Anhydrous tetrahydrofuran (5 mL) was added and the suspension was cooled down to -78 °C. *n*-Butyllithium (0.21 mmol, 0.7 eq, 0.1 mL of a 2.5M solution in hexanes) was added to the suspension of the phosphonium salt. The orange solution was warmed to rt for 10 min. and then cooled back to -78 °C. The orange solution of phosphorus ylide was slowly transferred via canula to the solution of 3,3'-dicarboxaldehyde-4,4'-biphenanthryl. The reaction mixture was warmed to rt and stirred for 1 hour. Silica gel is directly added to the reaction mixture and the solvent is evaporated under vacuum. The product is dry packed and purified by silica gel column chromatography (4:1 Hexanes:Ethyl Acetate) to afford pure 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl (40 mg, 34 %) as an off-white solid; ¹H NMR (400 MHz, CDCl₃) δ 9.19 (d, *J* = 0.9 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.23 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.97-7.79 (m, 8H), 7.52 (dd, *J* = 8.8, 0.5 Hz, 1H), 7.39 (ddd, *J* = 7.8, 7.0, 1.0 Hz, 1H), 7.31 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.96 (ddd, *J* = 8.8, 7.1, 1.5 Hz, 1H), 6.84 (ddd, *J* = 8.9, 7.1, 1.5 Hz, 1H), 5.94 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.53 (dd, *J* = 17.3, 0.9 Hz, 1H), 4.84 (dd, *J* = 11.0, 1.0 Hz, 1H) ; ¹³C NMR (100 MHz, CDCl₃) δ 192.3, 145.7, 137.5, 136.8, 135.0, 134.6, 134.2, 133.7, 133.5, 132.9, 131.5, 131.4, 130.5, 130.4, 130.3, 130.0, 129.7, 129.2 (2 c's), 128.9, 127.6 (2 c's), 127.1, 127.0, 126.9, 126.4 (3 c's), 125.2, 124.8, 116.9; HRMS (ESI) *m/z* calculated for C₃₁H₂₀OAg [M+Ag]⁺, 515.05664, found 515.05596.

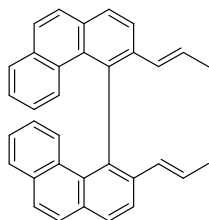


(Z)-3-styryl-3'-vinyl-4,4'-biphenanthryl (9): In a flame dried round bottom flask, is added 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl **S3** (30 mg, 1.0 eq, 0.073 mmol). Anhydrous THF (5 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to -78 °C. In a second flame dried round bottom flask, is added benzyltriphenylphosphonium chloride (0.11 mmol, 1.5 eq, 43 mg). Anhydrous tetrahydrofuran (5 mL) is added and the suspension is cooled down to -78 °C. *n*-Butyllithium (0.10 mmol, 1.4 eq, 0.04 mL of a 2.5M solution in hexanes) is added to the suspension of the phosphonium salt. The dark orange solution is warmed to rt for 10 min. and then cooled back to -78 °C. The solution of phosphorus ylide is slowly transferred via canula to the solution of 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl.

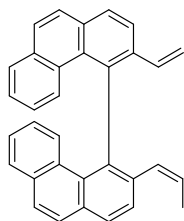
The reaction mixture is warmed to rt and stirred for 16 hours. Silica gel is added to the reaction mixture and the solvent is evaporated under vacuum. The resulting solid is dry packed and purified by silica gel column chromatography (15:1 Hexanes:Ethyl Acetate) to afford (*Z*)-3-styryl-3'-vinyl-4,4'-biphenanthryl (26 mg, 75 %) as an off-white solid. ¹H NMR (300 MHz, CDCl₃) δ 8.13-7.70 (m, 11H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.12-7.02 (m, 3H), 6.96-6.83 (m, 4H), 6.18 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.01 (d, *J* = 12.3 Hz, 1H), 5.56 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.55 (d, *J* = 13.0 Hz, 1H), 4.85 (dd, *J* = 11.0, 1.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.1, 136.2, 135.4, 134.7, 134.6, 133.2, 133.1, 133.0, 130.6, 129.5, 129.4, 129.2, 129.1, 129.0, 128.7, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.3, 127.2, 127.1, 126.5, 126.2, 126.0, 125.8, 125.7, 125.6 (2c), 124.5, 115.6, 77.4; HRMS (ESI) *m/z* calculated for C₃₈H₂₇ [M+H]⁺, 483.20883, found 483.2107.



3,3'-bis(propen-1-yl)-4,4'-biphenanthryl (6): In a flame dried round bottom flask is added 3,3'-biscarboxaldehyde-4,4'-biphenanthryl **S2** (30 mg, 1.0 eq, 0.073 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the mixture is stirred until dissolution of **S2**. The solution is cooled down to -78°C. In a second flame dried round bottom flask is added ethyltriphenylphosphonium bromide (55 mg, 2.0 eq., 0.15 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the suspension is cooled down to -78°C. *n*-Butyllithium (0.14 mmol, 1.4 eq, 0.06 mL of a 2.3M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt. for 10 min. and cooled back to -78°C. The solution of phosphorus ylide is slowly transferred via canula to the solution of 3,3'-biscarboxaldehyde-4,4'-biphenanthryl. The reaction mixture is warmed to rt. and stirred for 16 hours. Silica gel is directly added to the reaction mixture and the solvent is evaporated under vacuum. The product is dry packed and purified by silica gel column chromatography (30:1 Hexanes:Ethyl Acetate) to afford a mixture of *Z*:*E* isomers of 3,3'-bis(propen-1-yl)-4,4'-biphenanthryl (15 mg, 49 %) as an off-white solid.: ¹H NMR (400 MHz, CDCl₃) δ 8.07-7.98 (m, 1.0H), 7.92-7.67 (m, 4.2H), 7.64 (d, *J* = 8.1 Hz, 0.8H), 7.36-7.26 (m, 1.4H), 6.89 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 0.8H), 6.91-6.83 (m, 0.1H), 6.04-5.96 (m, 0.1H), 5.78-5.72 (m, 0.1H), 5.59 (dd, *J* = 11.5, 1.7 Hz, 0.7H), 5.19-5.10 (m, 0.7H), 1.43 (dd, *J* = 7.0, 1.8 Hz, 3.0H) ¹³C NMR (100 MHz, CDCl₃) δ 139.9, 139.6, 138.0, 136.5, 135.6, 134.0, 133.8, 133.6, 133.5, 133.1 (2 c's), 132.9, 131.5, 129.9, 129.8, 129.7 (2 c's), 129.3, 129.1, 128.9, 128.7 (2 c's), 128.6, 128.5, 128.2, 127.9, 127.8, 127.7, 127.6, 126.6, 126.2, 126.0 (2 c's), 125.9, 125.8, 125.3, 18.9, 18.8, 14.0 (2 c's); HRMS (ESI) *m/z* calculated for C₃₈H₂₇Ag [M+Ag]⁺, 541.10800, found 541.10777.

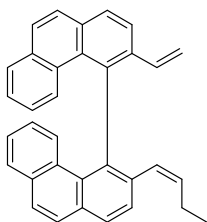


3,3'-di-((E)-prop-1-enyl)-4,4'-biphenanthryl (S4): In a flame dried sealed tube is added 3,3'-bis(propen-1-yl)-4,4'-biphenanthryl (10 mg, 1.0 eq, 0.023 mmol), Grubbs' second generation catalyst (1 mg, 0.05 eq, 0.001 mmol) and dichloromethane (3 mL). The reaction mixture is stirred at rt. for 2h. Silica gel is added to the reaction mixture and the solvent is evaporated under vacuum. The resulting solid is dry packed and purified by silica gel chromatography (30:1 Hexanes: Ethyl acetate) to afford (*E*)-3,3'-bis(propen-1-yl)-4,4'-biphenanthryl (7 mg, 70 %) as an off-white solid. ^1H NMR (300 MHz, CDCl_3) δ ppm 8.02 (d, $J = 8.3$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.8$ Hz, 2H), 7.75-7.70 (m, 4H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.26 (ddd, $J = 9.3, 7.9, 1.0$ Hz, 2H), 6.80 (ddd, $J = 8.8, 7.1, 1.5$ Hz, 2H), 5.99 (dq, $J = 15.6, 6.6$ Hz, 2H), 5.70 (dq, $J = 15.6, 1.6$ Hz), 1.41 (dd, $J = 6.6, 1.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.6, 136.5, 133.8, 133.1, 131.5, 129.9, 129.7, 129.3, 128.7, 127.8, 127.7, 127.6, 126.6, 126.0, 125.9, 125.3, 18.9; HRMS (ESI) m/z calculated for $\text{C}_{34}\text{H}_{26}$ Ag $[\text{M}+\text{Ag}]^+$, 541.10800, found 541.10728

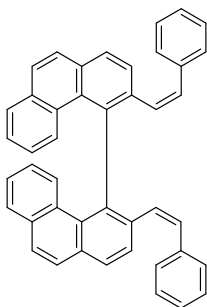


3-(prop-1-enyl)-3'-vinyl-4,4'-biphenanthryl (7): In a flame dried round bottom flask, is added 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl **S3** (70 mg, 1.0 eq, 0.17 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to -78°C . In a second flame dried round bottom flask is added ethyltriphenylphosphonium bromide (95 mg, 1.5 eq., 0.26 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the suspension is cooled down to -78°C . *n*-Butyllithium (0.10 mmol, 1.4 eq, 0.04 mL of a 2.5M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt for 10 min. and cooled back to -78°C . The solution of the phosphorus ylide is slowly transferred via canula to the solution of 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl. The reaction mixture is warmed to rt and stirred for 16 hours. Silica gel is added to the reaction mixture and the solvent is evaporated under vacuum. The resulting solid is dry packed and purified by silica gel column chromatography (15:1 Hexanes:Ethyl Acetate) to afford a mixture of isomers of 3-(prop-1-enyl)-3'-vinyl-4,4'-biphenanthryl (33 mg, 47 %) as an off-white solid. (*Note: all peaks appearing on the spectrum are listed below.*) ^1H NMR (300 MHz, CDCl_3) δ ppm 8.13-7.57 (m, 12.2H), 7.38-7.22 (m, 2.4H), 6.95-6.78 (m, 2H), 6.15-5.92 (m, 1.3H), 5.68 (dd, $J = 15.6, 1.6$ Hz, 0.4H), 5.59-5.40 (m, 1.6H), 5.13 (qd, $J = 11.5, 7.0$ Hz, 0.7H), 4.81 (dd, $J = 11.0, 1.2$ Hz, 0.3H), 4.79 (dd, $J = 11.0, 1.2$ Hz, 0.7H), 1.41 (dd, $J = 6.6, 1.6$ Hz, 1.1H), 1.35 (dd, $J = 7.0, 1.8$ Hz, 2H) ^{13}C NMR (100 MHz, CDCl_3) δ ppm 139.2, 139.0, 138.7, 137.3, 136.5, 136.4, 136.1 135.6, 135.5, 135.4, 133.8

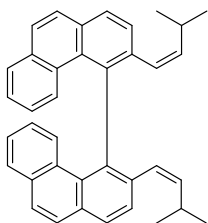
(2 c's), 133.7 (2 c's), 133.6, 133.1, 132.9, 131.5, 131.4, 131.3, 129.9 (2 c's), 129.8, 129.7, 129.5, 129.4, 129.2, 128.8, 128.7, 128.6, 128.2, 128.1, 128.0, 127.9, 127.8 (2 c's), 127.7, 126.7, 126.6, 126.4, 126.3, 126.2 (2 c's), 126.1, 126.0, 125.9, 125.4, 125.0, 124.9, 115.6, 115.5, 18.9, 14.0 HRMS (ESI) m/z calculated for $C_{33}H_{24}Ag$ $[M+Ag]^+$, 527.09235, found 527.09216.



(Z)-3-(but-1-enyl)-3'-vinyl-4,4'-biphenanthryl (8): In a flame dried round bottom flask is added 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl **S3** (30 mg, 1.0 eq, 0.073 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to $-78^{\circ}C$. In a second flame dried round bottom flask, is added *n*-propyltriphenylphosphonium bromide (43 mg, 1.5 eq., 0.11 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the suspension is cooled down to $-78^{\circ}C$. *n*-Butyllithium (0.10 mmol, 1.4 eq, 0.04 mL of a 2.5M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt for 10 min. and cooled back to $-78^{\circ}C$. The solution of the phosphorus ylide is slowly transferred via canula to the solution of 3-carboxaldehyde-3'-vinyl-4,4'-biphenanthryl. The reaction mixture is warmed to rt and stirred for 16 hours. Silica gel is added to the reaction mixture and the solvent is evaporated under vacuum. The resulting solid is dry packed and purified by silica gel column chromatography (15:1 Hexanes:Ethyl Acetate) to afford pure (Z)-3-(but-1-enyl)-3'-vinyl-4,4'-biphenanthryl (15 mg, 50 %) as an off-white solid. 1H NMR (300 MHz, $CDCl_3$) δ ppm 8.14-7.66 (m, 13.5H), 7.60 (d, $J = 8.1$ Hz, 0.5H), 7.41-7.21 (m, 2.6H), 6.97-6.75 (m, 2.3H), 6.07 (dd, $J = 17.4, 11.0$ Hz, 1.0H), 5.92 (td, $J = 15.7, 6.5, 6.5$ Hz, 0.7H), 5.70-5.35 (m, 2H), 4.99 (td, $J = 11.4, 7.4, 7.4$ Hz, 0.3H), 4.80 (dd, $J = 11.0, 1.2$ Hz, 0.7H), 4.79 (dd, $J = 11.0, 1.2$ Hz, 0.3H), 2.07-1.84 (m, 0.4H), 1.83-1.58 (m, 2.1H), 0.55 (t, $J = 7.4, 7.4$ Hz, 2.0H), 0.51 (t, $J = 7.5, 7.5$ Hz, 1.0H) ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 139.1, 139.0, 138.7, 137.4, 136.7, 136.6, 136.0, 135.6, 135.4, 135.3, 134.8, 134.1, 133.8, 133.7 (2 c's), 133.0 (2 c's), 131.5, 131.4, 131.3, 130.0 (2 c's), 129.8, 129.4, 129.3, 129.2, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0 (2 c's), 127.9, 127.8, 127.7 (2 c's), 127.6, 127.5, 126.6 (2 c's), 126.5 (2 c's), 126.4, 126.3 (2 c's), 126.2 (2 c's), 126.1 (3 c's), 126.0, 125.6, 124.9 (2 c's), 115.5 (2 c's), 26.1, 21.8, 14.2, 13.4. HRMS (ESI) m/z calculated for $C_{34}H_{26}Ag$ $[M+Ag]^+$, 541.1080, found 541.1095.

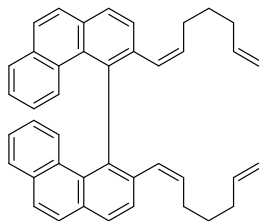


(3,3'-di-((Z)styryl)-4,4'-biphenanthryl (10): In a flame dried round bottom flask is added 3,3'-biscarboxaldehyde-4,4'-biphenanthryl **S 2** (30 mg, 1.0 eq, 0.073 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to -78°C . In a second flame dried round bottom flask, is added benzyltriphenylphosphonium chloride (35 mg, 3.0 eq., 0.22mmol). Anhydrous tetrahydrofuran (5 mL) is added and the suspension is cooled down to -78°C . *n*-Butyllithium (0.18 mmol, 2.5 eq, 0.08 mL of a 2.3M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt. for 10 min. and cooled back to -78°C . The solution of phosphorus ylide is slowly transferred via canula to the solution of 3,3'-biscarboxaldehyde-4,4'-biphenanthryl. The reaction mixture is warmed to rt. and stirred for 16 hour. Silica gel is directly added to the reaction mixture and the solvent is evaporated under vacuum. The product is dry packed and purified by silica gel column chromatography (30:1 Hexanes:Ethyl Acetate) to afford pure 3,3'-di-((Z)styryl)-4,4'-biphenanthryl (30 mg, 73%) as an off-white solid. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.03 (d, $J = 8.7$ Hz, 1H), 7.83-7.73 (m, 1H), 7.56 (d, $J = 8.3$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.11-7.00 (m, 1H), 6.97 (ddd, $J = 8.5, 7.0, 1.4$ Hz, 1H), 6.10 (d, $J = 12.3$ Hz, 1H), 5.78 (d, $J = 12.3$ Hz, 1H) ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 136.9, 135.5, 133.7, 133.4, 131.3, 130.6, 130.1, 129.8, 129.7, 129.2, 128.9, 128.4, 128.3, 128.0, 127.8, 127.2, 126.6, 126.4, 126.3; HRMS (ESI) m/z calculated for $\text{C}_{44}\text{H}_{30}\text{Ag}$ $[\text{M}+\text{Ag}]^+$, 665.1391, found 665.1393.



3,3'-di(3-methylbut-1-enyl)-4,4'-biphenanthryl (11): In a flame dried round bottom flask is added 3,3'-biscarboxaldehyde-4,4'-biphenanthryl **S2** (30 mg, 1.0 eq, 0.073 mmol). Anhydrous tetrahydrofuran (5 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to -78°C . In a second flame dried round bottom flask, is added isobutyltriphenylphosphonium bromide (0.22mmol, 3.0 eq, 88 mg). Anhydrous tetrahydrofuran (5 mL) is added and the suspension is cooled down to -78°C . *n*-Butyllithium (0.18 mmol, 2.5 eq, 0.08 mL of a 2.3M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt. for 10 min. and cooled back to -78°C . The solution of phosphorus ylide is slowly transferred via canula to the solution of 3,3'-biscarboxaldehyde-4,4'-biphenanthryl. The reaction mixture is warmed to rt. and stirred for 16 hours. Silica gel is directly added to the reaction mixture and the solvent is evaporated under vacuum. The product is dry packed and purified by silica gel column chromatography (20:1 Hexanes:Ethyl Acetate) to afford a mixture of isomers of 3,3'-di(3-methylbut-1-enyl)-4,4'-biphenanthryl (11 mg, 30%) as an off-white solid. (*Note: all peaks appearing on the spectrum are listed below.*) ^1H NMR (300 MHz, CDCl_3) δ ppm 8.01-7.71 (m, 14.3H), 7.57 (d, $J = 8.1$ Hz, 1H), 7.30 (d, $J = 6.7$ Hz, 2.2H), 6.89-6.82 (m, 2.5H), 5.75 (d, $J = 6.5$ Hz, 0.3H), 5.70 (dd, $J = 6.5, 1.0$ Hz, 0.8H), 5.64 (d, $J = 6.6$ Hz, 0.8H), 5.47 (d, $J = 15.9$ Hz, 1.6H), 5.34 (dd, $J = 11.5, 4.5$ Hz, 0.9H), 4.76 (t, $J = 11$ Hz, 1H), 2.46-2.35 (m, 1.1H), 1.90-1.76 (m, 1.9H), 0.83 (dd, $J = 13.3, 6.6, 2.9$ Hz), 0.55 (d, $J = 6.7$ Hz, 4.1H), 0.45 (d, $J = 6.7$ Hz, 3.9H), 0.23 (d, $J = 6.5$ Hz, 1.1H), 0.12 (d, $J = 6.5$ Hz, 1.1H); ^{13}C NMR (100

MHz, CDCl₃) δ 139.5 (2 c), 139.4, 139.2 (2 c), 139.1, 138.0, 137.4, 136.3, 136.1, 135.5, 135.3, 133.4, 133.2, 132.6, 132.5 (2 c), 131.3, 131.2 (2 c), 131.1, 130.0, 129.8, 129.7, 129.5, 129.2, 128.6 (2 c), 128.3, 128.2, 128.0, 127.4 (2 c), 127.2, 126.4, 126.3 (2 c), 126.2, 126.0, 125.9 (2 c), 125.7, 125.6, 125.5, 125.4, 125.3, 31.0, 30.9, 27.2, 23.3, 23.2, 22.4 (2 c), 22.0, 21.8, 21.7, 21.6; HRMS (ESI) *m/z* calculated for C₃₈H₃₄Ag [M+Ag]⁺, 597.17060, found 597.17013



3,3'-(5-hexenyl)-4,4'-biphenanthryl (12): In a flame dried round bottom flask is added 3,3'-biscarboxaldehyde-4,4'-biphenanthryl **S2** (100 mg, 1.0 eq, 0.24 mmol). Anhydrous tetrahydrofuran (10 mL) is added and the mixture is stirred until dissolution of the substrate. The solution is cooled down to -78°C. In a second flame dried round bottom flask is added 5-hexenyltriphenylphosphonium bromide (260 mg, 2.5 eq., 0.61 mmol). Anhydrous tetrahydrofuran (10 mL) is added and the suspension is cooled down to -78°C. *n*-Butyllithium (0.54 mmol, 2.2 eq, 0.22 mL of a 2.5M solution in hexanes) is added to the suspension of the phosphonium salt. The orange solution is warmed to rt. for 10 min. and cooled back to -78°C. The orange solution of phosphorus ylide is slowly transferred via canula to the solution of 3,3'-biscarboxaldehyde-4,4'-biphenanthryl. The reaction mixture is warmed to r.t. and stirred for 16 hours. Silica gel is directly added to the reaction mixture and the solvent is evaporated under vacuum. The product is dry packed and purified by silica gel column chromatography (15:1 Hexanes:Ethyl Acetate) to afford a mixture of isomers of 3,3'-(5-hexenyl)-4,4'-biphenanthryl (95 mg, 72 %) as an off-white solid. (*Note: all peaks appearing on the spectrum are listed below.*) ¹H NMR (400 MHz, CDCl₃) δ 8.08-7.93 (m, 2.0H), 7.93-7.71 (m, 4.0H), 7.61 (d, *J* = 7.98 Hz, 0.3H), 7.60 (d, *J* = 8.07 Hz, 0.6H), 7.40-7.27 (m, 1.1H), 6.97-6.80 (m, 1.0H), 6.04-5.77 (m, 0.1H), 5.74-5.54 (m, 1.0H), 5.51 (d, *J* = 11.55 Hz, 0.9H), 5.06-4.94 (m, 0.8H), 4.94-4.86 (m, 1.6H), 4.83 (m, 0.2H), 4.80-4.71 (m, 0.2H), 2.29-1.89 (m, 0.8H), 1.85-1.63 (m, 3.2H), 1.61-1.48 (m, 0.6H), 1.18-0.92 (m, 1.3H), 0.74 (m, 0.7H) ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 139.5, 138.9, 138.8, 136.2, 135.4, 133.7 (2 c's), 133.5, 133.1, 132.9, 132.5, 132.0, 131.9, 131.5, 131.4, 130.1 (2 c's), 129.7, 129.6, 129.1, 128.9, 128.7, 128.6, 128.4, 128.2, 127.9, 127.8, 127.6, 126.6 (2 c's), 126.2, 126.1, 126.0, 125.9, 125.8, 125.5, 114.4, 33.6, 32.6, 32.3, 29.1, 29.0, 28.2 (2 c's), 28.1, 7.8; HRMS (ESI) calculated for *m/z* C₄₂H₃₉ [M+H]⁺, 543.30463, found 543.30222.

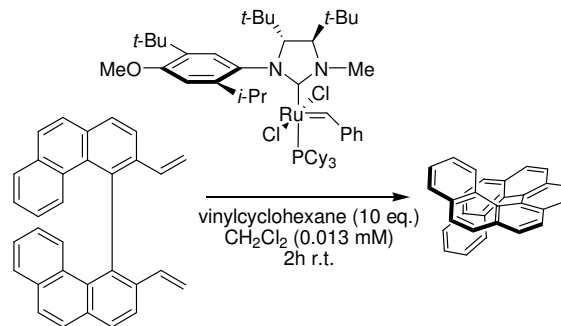
General procedure for the kinetic resolution to form [7]helicene :

In a glovebox, in a flame dried sealed tube is added precursor 3,3'-divinyl-4,4'-biphenanthryl **5** (10 mg, 0.025 mmol) and dichloromethane (1 mL). A stock solution of ruthenium catalyst (**4b**) (1 mL of a 1.0 mg/mL solution, 0.05 eq, 0.0013 mmol) is then added, the tube is sealed, removed from the glovebox and the reaction mixture is stirred at rt. for 2 hours. The reaction mixture is then filtered through a silica pad (CH₂Cl₂) and the solvent is evaporated under vacuum to afford a mixture of [7]helicene and starting material in quantitative yield. Conversions are measured directly by ¹H NMR and

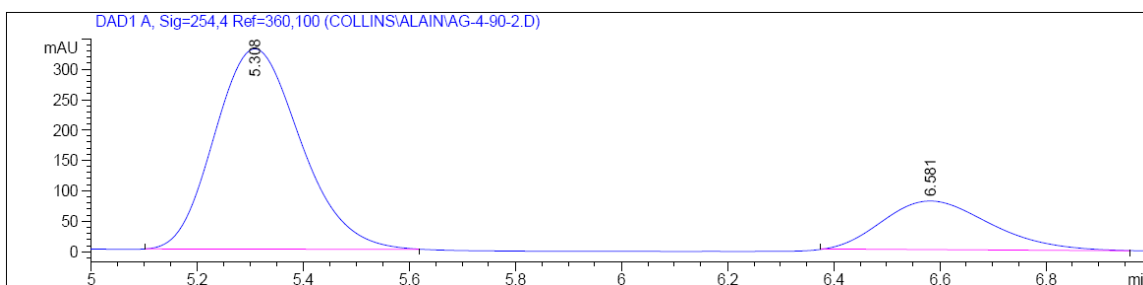
enantiomeric excess are measured by chiral HPCL (Chiralcel OD). The [7]helicene can also be purified on a preparative scale by HPLC using a Chiralcel OD preparative column.

General procedure for the kinetic resolution to form [7]helicene using olefin additives:

In a glove box, in a flame dried sealed tube is added the precursor 3,3'-divinyl-4,4'-biphenanthryl **5** (10 mg, 0.025 mmol), vinylcyclohexane (27 mg, 10 eq, 0.25 mmol) and dichloromethane (1 mL). A stock solution of ruthenium catalyst (**4b**) (1 mL of a 1.0 mg/mL solution, 0.05 eq, 0.0013 mmol) is then added, the tube is sealed and the reaction mixture is stirred at rt. for 2 hours. The reaction mixture is then filtered through a silica pad (CH₂Cl₂) and the solvent is evaporated under vacuum. Conversions are measured directly by ¹H NMR and enantiomeric excess are measured by chiral HPCL (Chiralcel OD). The [7]helicene can also be purified on a preparative scale by HPLC using a Chiralcel OD preparative column.

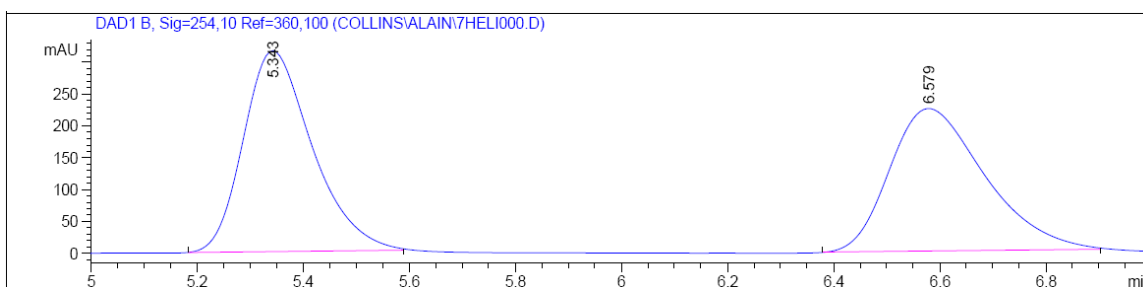


**ChiralCel OD (0.46cm ø x 25cm), 90% Hexanes, 10% *i*-PrOH,
 1 mL/min, 23°C, 10 min, 53% ee (*M*)
 [7]helicene**



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

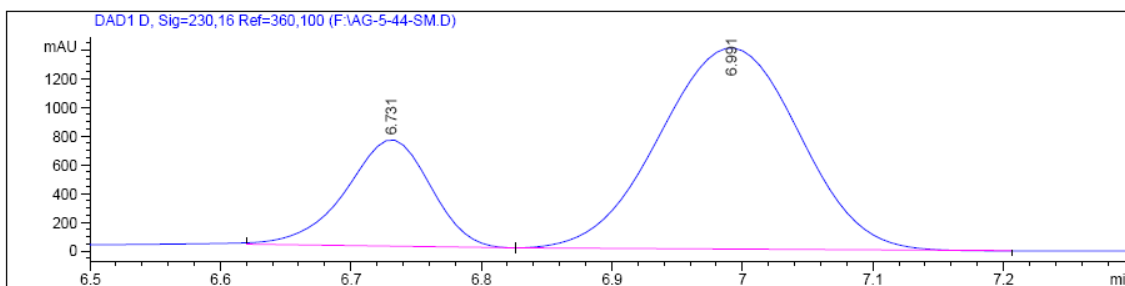
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.308	BB	0.1774	3717.51514	330.02524	76.5497
2	6.581	BB	0.2214	1138.82532	80.34509	23.4503



Signal 2: DAD1 B, Sig=254,10 Ref=360,100

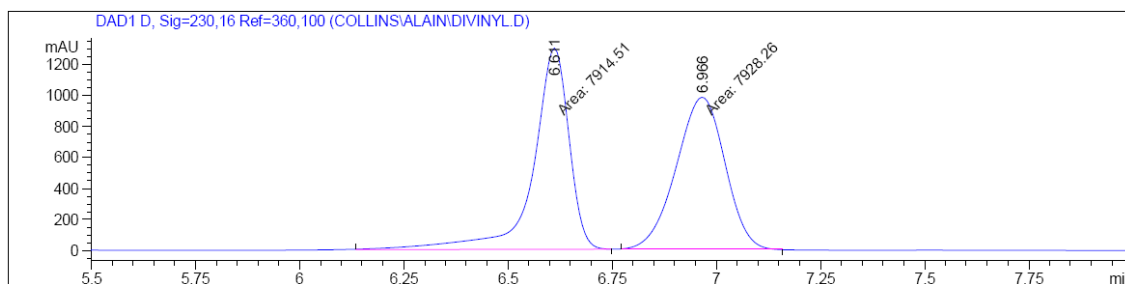
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.343	BB	0.1375	2854.48169	315.56000	50.4726
2	6.579	BB	0.1918	2801.02783	224.10204	49.5274

**ChiralPAK AD (0.46cm ø x 25cm),
98% Hexanes, 2% *i*-PrOH, 0.8 mL/min, 23°C, 10 min, 51% ee
Starting Material (5)**



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.731	BV	0.0687	3348.76099	740.90955	24.2801
2	6.991	VB	0.1191	1.04435e4	1398.99451	75.7199



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.611	MM	0.1013	7914.51123	1302.53357	49.9566
2	6.966	MM	0.1350	7928.26318	979.15698	50.0434