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Asymmetric Catalysis in the [2+2+2] Cycloaddition of Arynes and Alkynes: Enantioselective Synthesis of a Pentahelicene

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Abstract: The use of BINAP-based palladium(0) catalysts in the reaction of 7-methoxy-1,2-didehydronaphthalene (**2**) and dimethyl acetylenedicarboxylate (DMAD) affords non-racemic 9,12-dimethoxypentahelicene **1** with reasonable *ee*s, among other cycloaddition products. This is the first example of an enantioselective, metal-catalyzed cycloaddition involving arynes.

Keywords: arynes; asymmetric catalysis; [2+2+2] cycloaddition; helicenes; palladium

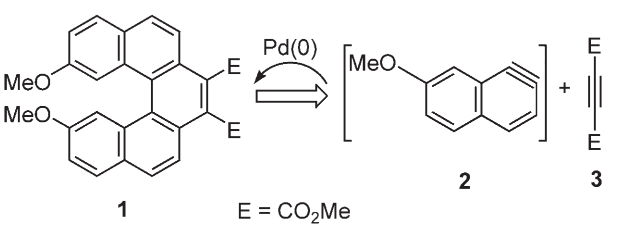
Introduction

In recent years, the palladium-catalyzed [2+2+2] cycloaddition reactions of arynes have emerged as powerful tools for the synthesis of polycyclic aromatic hydrocarbons with diverse structural arrangements,[1–4] including non-planar chiral molecules such as helicenes,[2b–d,3b] although only in racemic form. Helicenes – *ortho*-fused polycyclic aromatic molecules that exhibit helical chirality – constitute a fascinating family of organic compounds with a wide range of potential applications.[5,6] The development of novel synthetic approaches to these interesting molecules, particularly in enantioselective fashion, continues to be a challenge.[7,8] We reasoned that the use of chiral ligands in the metal-catalyzed cycloaddition of polycyclic arynes with alkynes could be applied to the development of an enantioselective synthesis of chiral helicenes, and would constitute the first example of an asymmetric [2+2+2] cycloaddition reaction involving arynes. Here we report the first results of our efforts to achieve this goal.

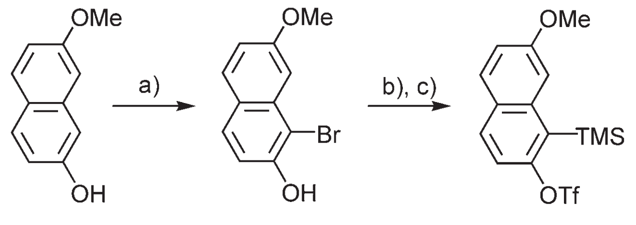
Results and Discussion

As synthetic target we chose dimethyl 9,12-dimethoxydibenzo[*c*,*g*]phenanthrene-3,4-dicarboxylate (**1**), a tetrasubstituted pentahelicene that could be easily converted to other functionalized derivatives, including potential ligands for asymmetric catalysis such as pentahelicene-9,12-diols, by common functional group transformations. Compound **1** should be obtained as one of the products in the palladium-catalyzed [2+2+2] cycloaddition of 7-methoxy-1,2-didehydronaphthalene (**2**) with dimethyl acetylenedicarboxylate (DMAD, **3**) (Scheme 1).

On the basis of our previous experience, 7-methoxy-1-trimethylsilyl-2-naphthyl triflate (**4**) should be an adequate precursor for aryne **2**. The synthesis of **4** was accomplished through the route shown in Scheme 2, which involved the regioselective monobromination of 7-methoxy-2-naphthol (**5**) by treatment with NBS and catalytic amounts of diisopropylamine in dichloromethane. The resulting bromonaphthol[9] was submitted to the one-pot/three-step procedure previously established in our group for the synthesis of *o*-trimethylsilylaryl triflates,[10] affording the



Scheme 1. Retrosynthetic analysis to 9,12-dimethoxybenzo-[*c*,*g*]phenanthrene-3,4-dicarboxylate (**1**).

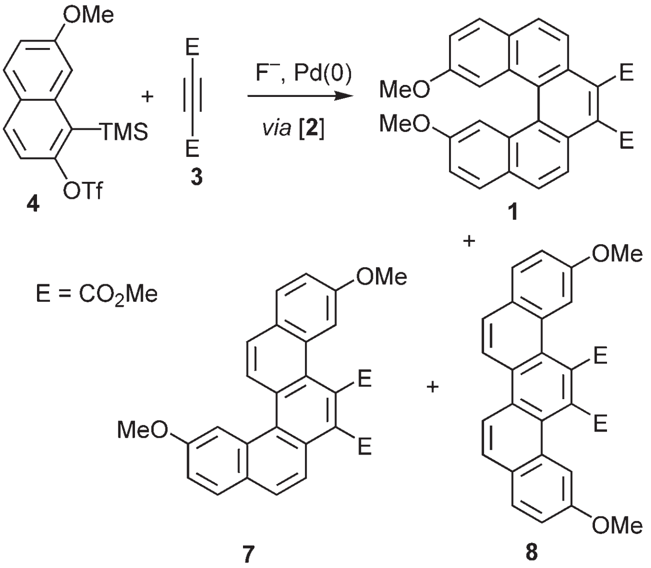


5 **6** (94%) **4** (83%)

Scheme 2. *Reaction conditions:* (a) NBS (100 mol%), *i*-Pr_2NH, CH_2Cl_2, 0°C (1 h) to room temperature. (b) HMDS (50 mol%), THF, 90°C. (c) i. *n*-BuLi (110 mol%), THF, −100°C to −80°C, 1 h; ii. Tf_2O (110 mol%), −100°C to −80°C.

expected aryne precursor **4** in a very good overall yield.

Treatment of a solution of triflate **4** with CsF, in the presence of DMAD (1.5 equivs.) and $Pd(PPh_3)_4$ (0.1 equiv.) afforded a mixture of the three possible products arising from the [2+2+2] cocycloaddition of two molecules of aryne **2** and one of DMAD (Scheme 3), in 66% overall yield and a 5.9:8.6:1 ratio (**1**:**7**:**8**). Although pentahelicene **1** was not the major product, its isolation in 25% yield (20% from commercially available naphthol **5**) was considered fairly satisfactory, taking into account the limited synthetic alternatives to functionalized helicenes.



Scheme 3. *Reaction conditions:* CsF (200 mol%), $Pd(PPh_3)_4$ (10 mol%), CH_3CN, room temperature.

The structure of pentahelicene **1** in the solid state was established by X-ray diffraction studies (Figure 1). Compound **1** crystallizes from *n*-hexane in racemic form, a common feature within the [5]helicene series.[11] Remarkably, the torsion angle at the central ring , defined by carbons C(14a)–C(14d) is 33°, larger than the value of 27.9° found for [5]helicene.[11a] The crystalline packing of compound **1** shows a herringbone-like motif, typical of polycyclic aromatic hydrocarbons with limited peripheral substitution.[12]

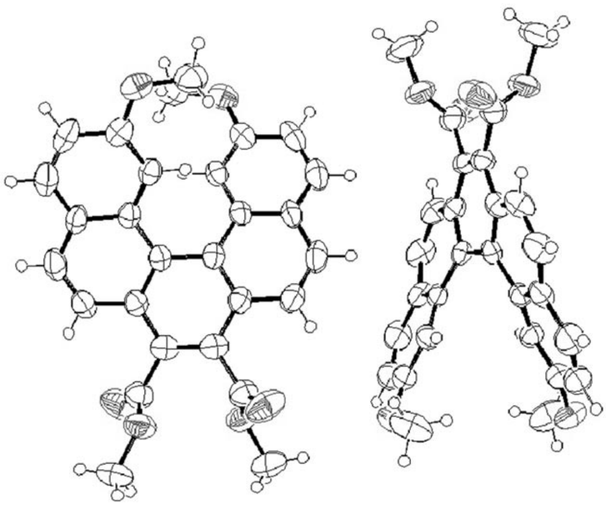


Figure 1. ORTEP view of *rac*-**1**.

Prior to exploring the possibility of developing an enantioselective version of the [2+2+2] cycloaddition reaction described above, the barrier to racemization of pentahelicene **1** was estimated by using computational methods. The ground state (**GS-1**) and the transition state (**TS-1**) for the interconversion process were located at the semiempirical AM1[13] level using the SPARTAN program.[14] The nature of any stationary structure was evaluated by way of vibrational analysis, with such structures identified as minima or transition states by the presence of zero or one imaginary vibrational frequencies, respectively. The geometries initially obtained were fully optimized using DFT calculations (B3LYP and BLYP) using the 6-31G(d,p) and 6-311G++(d,p) basis sets of the GAUSSIAN program.[15] These fully optimized geometries are represented in Figure 2, and is worth to note the excellent concordance between the calculated minimum energy conformation of **1**, and the experimentally determined crystal structure, described above (see Figure 1). On the other hand, the structure of the transition state (**TS-1**), with the terminal benzene rings oriented in pseudo-parallel disposition, is in accordance with those previously proposed for the razemization of other [*n*]helicenes ($n=5$–8).[16] The results of the computations for the racemization barrier ($\Delta G^{\neq}$) at 298 K depend on the level of calculation employed, varying from 24.8 $kcal\,mol^{-1}$ (AM1) to 25.3 $kcal\,mol^{-1}$ [BLYP/6-311G++(d,p)].[17] These values suggest a reasonable configurational stability for **1**, which should not extensively racemize in the re-

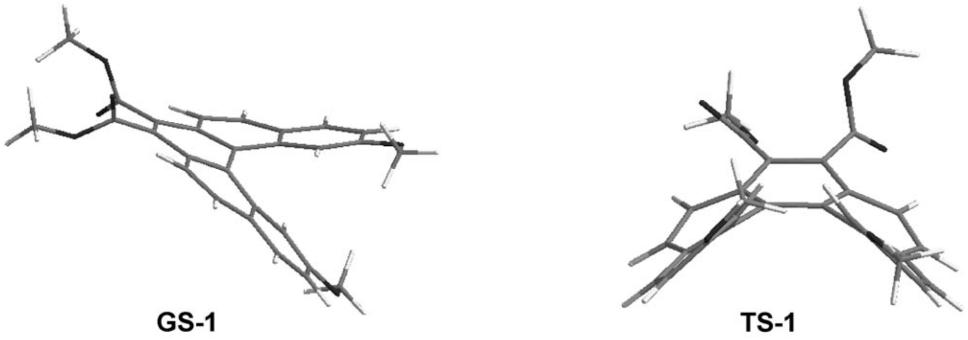


Figure 2. Minima (**GS-1**) and transition state (**TS-1**) structures of pentahelicene **1**.

action conditions previously established for the palladium-catalyzed cycloadditions of arynes (room temperature, 12–15 h).[18]

With these results in hand, we carried out preliminary experiments using palladium complexes with chiral bidentate phosphines as catalysts for the reaction of aryne **2** and DMAD (see Table 1). In a typical experiment, a solution of $Pd_2(dba)_3$ and the chiral ligand (1:2 ratio, 0.1 equiv. of Pd with respect to **4**) in CH_3CN/THF was stirred for 30 min at room temperature, and to the resulting red solution triflate **4**, DMAD (1.4 equivs.) and CsF (2 equivs.) were successively added. After stirring at room temperature for 15 h, pentahelicene **1** was quickly separated from the reaction mixture by column chromatography and analyzed by chiral HPLC.[19] Gratifyingly, we found that 2,2′-bis(diphenylphosphine)-1,1′-binaphthyl (BINAP) afforded non-racemic **1** with moderate to good enantioselectivities. The use of (*R*)-BINAP yielded (*M*)-(−)-**1** as the major enantiomer (entry 1), while (*S*)-BINAP afforded the *P* enantiomer (entry 2), as determined by comparison of their optical rotation values and CD spectra with those described for other helicenes. Other chiral diphosphines [Tol-BINAP, DIOP, BPPM, CHIRAPHOS] gave more complex reaction mixtures and lower enantiomeric excesses of pentahelicene (entries 3–7). It is worth noting that in *some* of these first essays, using $Pd_2(dba)_3$ (5 mol%) and (*R*)-BINAP (10 mol%) as catalytic system, higher *ee*s (up to 88%) were measured. Those remarkable results resulted difficult to reproduce and therefore were not included in Table 1.

Table 1. Asymmetric induction in the synthesis of pentahelicene **1** by Pd-catalyzed cycloaddition of aryne **2** with DMAD: preliminary essays.[a]

Entry	Ligand	*ee* [%][b]	Major isomer
1	(*R*)-BINAP	35–60	(−)-(*M*)-**1**[c]
2	(*S*)-BINAP	35–40	(+)-(*P*)-**1**
3	(*R*)-Tol-BINAP	30	(−)-(*M*)-**1**
4	(−)-DIOP	17	(+)-(*P*)-**1**
5	(2*S*,4*S*)-BPPM	27	(+)-(*P*)-**1**
6	(*S*,*S*)-CHIRAPHOS	5	(−)-(*M*)-**1**
7	(*R*,*R*)-Me-DUPHOS	–	–

[a] *Reaction conditions:* **4** (100 mol%), DMAD (140 mol%), CsF (200 mol%); $Pd_2(dba)_3$ (5 mol%), L* (10 mol%); CH_3CN/THF (5.5:1); room temperature, 15 h.

[b] Determined by HPLC, Chiralpak AS; *i*-PrOH/hexane, 3:97.

[c] Optical rotation measured for a sample with 60% *ee*, $[\alpha]_D^{20}$: −793° (c 0.2, CH_2Cl_2).

We centered our attention in BINAP as ligand for this reaction, and initially attributed the variable enantioselections observed in the preliminary experiments described above, to an incomplete formation of the expected monomeric Pd(BINAP) species from the achiral complex $Pd_2(dba)_3$.[20] Trying to gain insight into the catalytic species responsible for the asymmetric induction, we essayed the reaction using as catalysts the preformed palladium complexes **9** and **10**, in which one molecule of (*R*)-BINAP is chelated to the metal center, and the tetracoordinated complex $Pd[(R)\text{-BINAP}]_2$ (**11**). Having in mind the possibility of partial dissociation of BINAP, which could be acting as a chiral monodentate ligand, we also tried the cycloaddition using monophosphine analogues of (*R*)-BINAP, (*R*)-MOP (**12**) and (*R*)-BINAP(O) (**13**) (Figure 3).

Compounds **9**,[21] **11**,[22] **12**[23] and **13**[24] were prepared as described in the literature, while the previously unknown complex **10** was isolated in 97% yield by treatment of Pd(BINAP)(dba) (**9**) with DMAD in THF. The structure of complex **10**, which was established by X-ray diffraction studies (Figure 4), showed a distorted square planar geometry around the palladium centre, with a dihedral angle between the planes P(2)-Pd-P(7) and C(36)-Pd-(C37) of 11.2°.[25] The Pd–P bond distances are typical of a Pd-BINAP complex, while the C(36)-C(37) distance (1.251 Å) is slightly shorter than those observed for other palladium(0) complexes of alkynes, suggesting an important triple bond character.

The results of the use of these complexes and ligands in the cocycloaddition reaction of **4** with DMAD are summarized in Table 2, and show that for

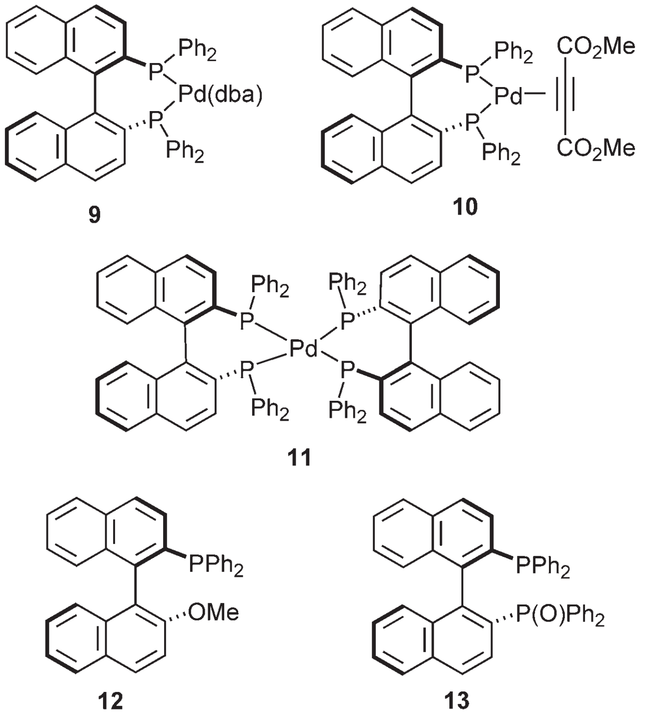


Figure 3. BINAP-based palladium complexes and phosphine ligands used in the cocycloaddition of triflate **2** and DMAD (see Table 2).

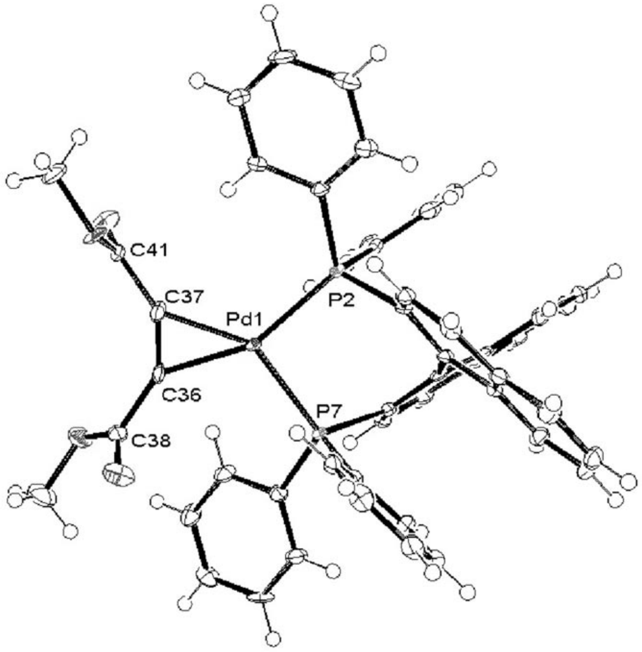


Figure 4. ORTEP view of palladium complex **10**. Significant bond lengths and angles: Pd–P(2) = 2.308 Å; Pd–P(7) = 2.317 Å; Pd–C(36) = 2.025 Å; Pd–C(37) = 2.064 Å; C(36)–C(37) = 1.251 Å; P(2)–Pd–P(7) = 94.6°; C(36)–Pd–C(37) = 35.6°.

a palladium charge of 10 mol%, the preformed Pd(BINAP)L complexes **9** and **10** afforded identical asymmetric inductions [38% *ee*, being (*M*)-**1** the major enantiomer] and product distribution (ratio **1**:**7**:**8**, around 1:2:2). The best yield was obtained with complex **10**, which afforded an 85% yield of the mixture of cycloadducts (17% yield of pentahelicene, entry 2). Remarkably, the use of 100 mol% of **10**, gave low yields of cycloadducts, but very good enantioselectivity [>90% *ee* for (*M*)-**1**, entry 3]. The enantiomeric excess obtained with **11** was much lower, and the use of monophosphine analogues of BINAP, **12** or **13**, designed to mimic a partially dissociated BINAP chelate, afforded better yields of pentahelicene (up to 33%, entry 6), but no asymmetric induction. These results support the conclusion that BINAP is chelated during the enantioselective step, and that this mode of coordination does not favor the formation of the helicene.

Next, we evaluated the effect of the solvent and the fluoride source in the outcome of the reaction (Table 3). The experiments evidenced that coordinating solvents like acetonitrile (results in Table 2), which could favor the partial dissociation of BINAP and the formation of achiral catalytic species, afforded lower enantioselectivities than solvents with lower coordination ability (Table 3). Thus, when using CsF as the fluoride source, reactions in dichloromethane gave good *ee*s (76%), but very low conversions, due to the very low solubility of CsF in this solvent (Table 3, entry 1). Better overall yields were obtained with CsF in DME or THF (entries 2, 3), although the best results were achieved when the aryne was generated by using the soluble TBAF as the fluoride source, and THF as the solvent.[26] In these conditions, and using 10 mol% of **9** as catalyst, the expected pentahelicene (*M*)-**1** was isolated in 16% yield and with reproducible enantiomeric excesses of 66–67% *ee*.

From a synthetic point of view it is worth noting that, despite the low yield of helicene obtained in the final Pd(0)/BINAP-catalyzed cycloaddition, this convergent synthesis of **1** involves only three steps and 14% overall yield from commercially available starting materials.

Finally, we carried out kinetic studies which confirmed the barrier to racemization of **1** previously predicted by computations. Enantiomerically enriched samples of **1**, dissolved in a 1:3 CH_2Cl_2/hexanes mixture, were heated at constant temperatures of 45, 60, 65 and 75 °C, and aliquots taken at different intervals of time were directly analyzed by chiral HPLC. The enantiomerization reaction rate *k* for each temperature was determined from the first order plots obtained when $\ln(ee_0/ee_t)$ was represented against time.[27] From these data, the Eyring plot gave the activation parameters $\Delta H^{\neq}$ (21.7 kcal mol^{-1}), $\Delta S^{\neq}$ (−13.7 cal mol^{-1} K) and $\Delta G^{\neq}$ (25.7 kcal mol^{-1}). This

Table 2. Cocycloaddition of 7-methoxy-1,2-didehydrophenanthrene (**2**) with DMAD catalyzed by Pd(BINAP)L and related complexes.[a]

Entry	Catalyst	Pd charge [mol %]	**1**+**7**+**8** yield [%]	**1**:**7**:**8** ratio[b]	Helicene **1**, *ee* [%][c]
1	**9**[d]	10	59	21:40:39	38
2	**9**[d]	20	68	22:42:36	37
3	**10**	10	85	21:40:39	38
4	**10**	100	18	22:36:42	>90
5	**11**	10	45	27:46:27	14
6	$Pd_2(dba)_3$+**12**[e]	10	80	41:55:4	0
7	$Pd_2(dba)_3$+**13**[e]	10	47	34:57:9	0

[a] *Reaction conditions:* **4** (100 mol %), DMAD (140 mol %), CsF (200 mol %), CH_3CN/THF (5.5:1), room temperature, 15 h.

[b] Ratio **1**:**7**:**8**, as determined by NMR.

[c] Determined by chiral HPLC.

[d] Complex prepared in solution: Pd_2 $(dba)_3$ (5 mol %) + (*R*)-BINAP (10 mol %); CH_3CN/THF (1.5:1); room temperature; 7 h (see ref.[21]).

[e] Catalyst prepared in solution: $Pd_2(dba)_3$ (5 mol %) + Ligand (20 mol %); CH_3CN; room temperature; 30 min.

Table 3. Cocycloaddition of 7-methoxy-1,2-didehydrophenanthrene (**2**) and DMAD catalyzed by $Pd_2(dba)_3$/(*R*)-BINAP: fluoride salt and solvent effects.[a,b]

Entry	Fluoride	Solvent	**1**+**7**+**8** yield [%]	**1**:**7**:**8** ratio[c]	Helicene **1**, *ee* [%][d]
1	CsF]	CH_2Cl_2	<10	-	76
2	CsF	DME	71	22:39:38	53
3	CsF	THF	66	17:42:41	67
4	KF[e]	THF	26	21:38:41	55
5	TBAF[f]	THF	66	25:36:39	66
6	TBAF[f]	CH_2Cl_2	55	30:40:30	60

[a] *Reaction conditions:* **4** (100 mol %), DMAD (140 mol %), fluoride (200 mol %); catalyst; room temperature, 15 h.

[b] Catalyst prepared in solution: $Pd_2(dba)_3$ (5 mol %) + (*R*)-BINAP (10 mol %); solvent; room temperature; 30 min.

[c] Ratio **1**:**7**:**8**, as determined by NMR.

[d] Determined by chiral HPLC.

[e] 18-Crown-6 (40 mol %) was added.

[f] Slow addition (syringe pump) of a 0.14 M solution of TBAF.

value for the free energy of activation is only 0.4 $kcal\,mol^{-1}$ higher than that previously calculated and accounts for a enantiomerization constant *k* of $4.12\times10^{-7}\,s^{-1}$ and a racemization half-life $(t_{1/2})$[27] of 9.7 days at 20 °C.

Conclusions

In summary, we have described the first enantioselective version of the palladium-catalyzed [2+2+2]-cycloaddition of arynes and alkynes. To the best of our knowledge, this is the second example of asymmetric catalysis applied to the synthesis of helicene-like compounds,[28] and the third report on asymmetric catalysis applied to a metal catalyzed-cyclotrimerization.[29]

Experimental Section

General Remarks

All reactions were performed under argon. The synthesis of organometallic complexes were performed using Schlenck techniques. Solvents were dried by distillation from a drying agent: THF, Et_2O and DME from Na/benzophenone; CH_3CN and CH_2Cl_2 from CaH_2. TMSCl and *i*-Pr_2NH were distilled from CaH_2 prior to use. Other commercial reagents were purchased from Aldrich Chemical Co. or from Strem Chemicals and were used without further purification. Reported melting points are uncorrected. TLC was performed on Merck silica gel 60 F_{254} or type E Merck aluminium oxide 60 F_{254}; chromatograms were visualized with UV light (254 and 360 nm), phosphomolybdic acid, and/or *p*-anisaldehyde. Column chromatography was performed on Merck silica gel 60 (ASTM 230–400 mesh). Enantiomeric excesses (*ee*s) were determined by HPLC (Hewlett Packard HP1100 series, with UV detector) using chiral columns Daicel Chiralpak AS (*i*-PrOH/hexane, 3:97) or OL-86[30] (CH_2Cl_2/hexane, 35:65). Optical rotation values were determined at room temperature in a JASCO DIP-370 polarimeter. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in Bruker DPX-250 MHz, Varian AMX-300, or Bruker WM-500 MHz spectrometers. LR and HR mass spectra were recorded using EI (70 eV, HP-5988 A spectrometer) or FAB (Micromass Autospec). Compounds $Pd(PPh_3)_4$,[31] (*R*)-MOP,[23] (*R*)-BINAP(O),[24a] [(*R*)-BINAP]Pd(dba)[21] and [(*R*)-BINAP]$_2$Pd[22] were prepared following published procedures.

1-Bromo-7-methoxy-2-naphthol (6)

To a solution of 7-methoxy-2-napthol (**5**, 500 mg, 2.87 mmol) and *i*-Pr_2NH (40 μL, 0.29 mmol) in CH_2Cl_2 (9 mL), a solution NBS (511 mg, 2.87 mmol) in CH_2Cl_2 (28 mL) was dropwise added (30 min). After stirring at room temperature for 1 h, the reaction mixture was poured on H_2O (50 mL) and taken to pH 1 by careful addition of concentrated H_2SO_4. The resulting mixture was extracted with CH_2Cl_2 (2×30 mL) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was chromatographed (SiO_2; CH_2Cl_2/hexanes, 1:1) to afford **6** as a white solid; yield: 684 mg (94%); mp 92–94 °C (lit. 92–93 °C)[9]; ^1H NMR (250 MHz, $CDCl_3$): $\delta=7.67$ (d, $J=8.9$ Hz, 1H), 7.65 (d, $J=8.7$ Hz, 1H), 7.32 (d, $J=2.4$ Hz, 1H), 7.12 (d, $J=8.8$ Hz, 1H), 7.04 (dd, $J=8.9$ and 2.5 Hz, 1H), 5.91 (s, 1H), 3.97 (s, 3H); ^{13}C NMR (DEPT; 63 MHz, $CDCl_3$): $\delta=159.4$ (C), 151.1 (C), 133.7 (C), 129.9 (CH), 129.0 (CH), 124.9 (C), 116.5 (CH), 114.5 (CH), 105.3 (C), 104.3 (CH), 55.4 (CH_3); LR-MS (EI), *m/z* (%)=254 (M^++2, 100), 252 (M^+, 100), 211 (47), 209 (49), 101 (28); HR-MS: $m/z=251.9788$ (calcd. for $C_{11}H_9O_2{}^{79}Br$: 251.9786), 253.9769 (calcd. for $C_{11}H_9O_2{}^{81}Br$: 253.9765).

Triflate 4

A solution of 1-bromo-7-methoxy-2-naphthol (**6**; 2.44 g, 9.64 mmol) and HMDS (1.19 mL, 5.78 mmol) in dry THF (64 mL) was refluxed for 1 h in a round-bottom flask provided with condenser and $CaCl_2$ tube. The solvent was evaporated under reduced pressure and the crude residue was subjected to vacuum in order to remove NH_3 and excess HMDS. Having proved the quantitative formation of the expected silyl ether (^1H NMR, see below), the crude product was redissolved in THF (64 mL) and cooled to −100 °C. To this solution, *n*-BuLi (4.98 mL, 2.32 M, 11.57 mmol) was dropwise added and the mixture was stirred for 30 min while the temperature reached −80 °C. The reaction mixture was again cooled to −100 °C, and Tf_2O (2.03 mL, 12.05 mmol) was dropwise added. Stirring was continued for 30 min, while the temperature reached again −80 °C. The mixture was poured on a cooled saturated aqueous solution of $NaHCO_3$ (25 mL), the phases were separated and the aqueous phase extracted with Et_2O (3×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was chromatographed (SiO_2; Et_2O/hexanes, 5:95) to afford 7-methoxy-1-(trimethylsilyl)naphth-2-yl trifluoromethanesulphonate (**4**) as a colorless oil; yield: 3.04 g (83%); ^1H NMR (250 MHz, $CDCl_3$): $\delta=7.83$ (d, $J=8.9$ Hz, 1H), 7.78 (d, $J=9.0$ Hz, 1H), 7.55 (d, $J=2.3$ Hz, 1H), 7.29 (d, $J=9.0$ Hz, 1H), 7.22 (dd, $J=9.0$ and 2.4 Hz, 1H), 3.96 (s, 3H), 0.64 (s, 9H); ^{13}C NMR (DEPT; 63 MHz, $CDCl_3$): $\delta=158.1$ (C), 153.3 (C), 139.1 (C), 132.1 (CH), 130.3 (CH), 127.6 (C), 127.2 (C), 118.7 (CH), 118.6 (C, $J=321$ Hz, CF_3), 116.6 (CH), 108.0 (CH), 55.3 (CH_3), 2.0 (3×CH_3) ppm; UV (cyclohexane): $\lambda_{max}=334$, 320, 291, 280, 234 nm; IR (KBr): $\nu=1416$, 1225, 1141, 848 cm^{-1}; LR-MS (EI): *m/z* (%)=378 (M^+, 33), 363 (38), 246 (70), 230 (74), 171 (52); HR-MS: $m/z=378.0559$ (calcd. for $C_{15}H_{17}O_4F_3SiS$: 378.0569).

Data for (1-bromo-7-methoxy-2-naphthoxy)trimethylsilane: ^1H NMR (250 MHz, $CDCl_3$): $\delta=7.67$ (d, $J=8.9$ Hz, 1H), 7.62 (d, $J=8.7$ Hz, 1H), 7.50 (d, $J=2.4$ Hz, 1H), 7.05 (dd, $J=8.9$ and 2.5 Hz, 1H), 6.97 (d, $J=8.7$ Hz, 1H), 3.97 (s, 3H), 0.35 (s, 9H); LR-MS (EI): *m/z* (%)=326 (M^++2, 100), 324 (M^+, 94), 311 (61), 309 (60), 229 (69), 171 (48), 139 (73), 73 (72); HR-MS: $m/z=324.0188$ (calcd. for $C_{14}H_{17}O_2{}^{79}BrSi$: 324.0181), 326.0175 (calcd. for $C_{14}H_{17}O_2{}^{81}BrSi$: 326.0161).

Palladium Complex 10

A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (200 mg, 0.19 mmol) and (*R*)-BINAP (241 mg, 0.39 mmol) in dry, freshly degassed THF (10.5 mL), placed into an Schlenk flask, was stirred at room temnperature for 15 h. Then, dimethyl acetylenedicarboxylate (DMAD, 48 μL, 0.39 mmol) was dropwise added, the mixture was stirred for 15 min and concentrated under reduced pressure in the vacuum line. The residue was chromatographed (SiO_2; Et_2O/CH_2Cl_2, 2:98) to afford [(*R*)-BINAP]Pd(DMAD) (**10**) as a yellow solid; yield: 328 mg (97%); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.89$ (m, 4H), 7.49–7.26 (m, 16H), 7.10–7.02 (m, 4H), 6.87–6.84 (m, 2H), 6.68–6.63 (m, 2H), 6.52–6.47 (m, 4H), 3.41 (s, 6H); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta=34.5$ (s); LR-MS (FAB): *m/z* (%)=871 (M^+, 1.6), 811 (3.3), 728 (19), 437 (100). Crystallization by slow cooling of a concentrated solution in hexanes/$CHCl_3$ afforded crystals suitable for X-ray difraction.

Cocycloaddition of Triflate with DMAD Catalyzed by $Pd(PPh_3)_4$

To a solution of **4** (106 mg, 0.28 mmol), $Pd(PPh_3)_4$ (32 mg, 0.028 mmol) and DMAD (48 μL, 0.39 mmol) in CH_3CN (5.6 mL), placed in an Schlenk tube, finely powdered anhydrous CsF (85 mg, 0.56 mmol) was added. The resulting suspension was stirred at room temperature for 15 h, concentrated under reduced pressure, and the residue was chromatographed (SiO_2; Et_2O/hexanes, 1:3) to afford a mixture of cycloadducts **1**, **7** and **8** (42 mg, 66%, ratio 5.9:8.6:1.0 as determined by ^1H NMR). Further purification by column chromatography (SiO_2; Et_2O/hexanes, 1:3) and preparative TLC (SiO_2; Et_2O/hexanes, 1:1) allowed the separation of the isomers.

Data for dimethyl 9,12-dimethoxy-3,4-dibenzo-[*c,g*]phenanthrenedicarboxylate (1): mp 221–222 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta=8.02$ (d, $J=8.9$ Hz, 2H), 7.93 (d, $J=8.9$ Hz, 2H), 7.87 (d, $J=8.8$ Hz, 2H), 7.59 (d, $J=2.3$ Hz, 2H), 7.20 (dd, $J=8.8$ and 2.5 Hz, 2H), 4.07 (s, 6H), 3.47 (s, 6H); ^{13}C- NMR - DEPT (63 MHz, $CDCl_3$): $\delta=168.5$ (C), 156.8 (C), 130.9 (C), 129.4 (CH), 129.3 (C), 128.2 (CH), 127.9 (C), 127.8 (C), 120.5 (CH), 119.1 (CH), 110.1 (CH), 54.9 (CH_3), 52.9 (CH_3); UV ($CHCl_3$): $\lambda_{máx}=321$, 286 nm; IR (KBr), 1736, 1719, 1223 cm^{-1}; LRMS (EI): *m/z* (%)=454 (M^+, 100), 407 (53), 250 (17), 125 (10); HRMS for $C_{28}H_{22}O_6$: calcd. 454.1416, found, 454.1411.

Data for dimethyl 5,11-dimethoxybenzo[*c*]chrisene-13,14-dicarboxylate (7): m.p. 180–182 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.79$ (d, $J = 9.1$ Hz, 1 H), 8.34 (d, $J = 1.9$ Hz, 1 H), 7.92–7.73 (m, 6 H), 7.32–7.29 (m, 2 H), 4.09 (s, 3 H), 4.00 (s, 3 H), 3.95 (s, 6 H); ^{13}C NMR – DEPT (63 MHz, $CDCl_3$): $\delta =$ 171.2 (C), 169.0 (C), 158.1 (C), 158.0 (C), 131.2 (C), 130.9 (C), 130.7 (C), 129.7 (CH), 129.6 (C), 129.4 (CH), 128.6 (CH), 128.4 (C), 128.2 (C), 127.4 (CH), 127.0 (C), 126.7 (C), 125.0 (C), 123.4 (CH), 120.5 (CH), 117.8 (CH), 117.5 (CH), 110.3 (CH), 107.1 (CH), 55.5 (CH_3), 55.4 (CH_3), 53.0 (2× CH_3); UV ($CHCl_3$): $\lambda_{max} = 326$, 300 nm; IR (KBr) 1722, 1221 cm^{-1}; LRMS (EI): m/z (%) = 454 (M^+, 100), 391 (9), 363 (7), 250 (7); HRMS for $C_{28}H_{22}O_6$: calcd. 454.1416, found 454.1404.

Data for dimethyl 2,11-dimethoxypicene-13,14-dicarboxylate (8): mp 171–172 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 8.52 (d, $J = 9.2$ Hz, 2 H), 7.96 (d, $J = 8.03$ Hz, 2 H), 7.94 (d, $J = 2.8$ Hz, 2 H), 7.87 (d, $J = 8.8$ Hz, 2 H), 7.29 (dd, $J = 8.8$ and 2.3 Hz, 2 H), 4.02 (s, 6 H), 3.97 (s, 6 H); ^{13}C NMR (DEPT; 63 MHz, $CDCl_3$): $\delta = 171.7$ (C), 158.5 (C), 131.0 (C), 130.9 (C), 130.0 (CH), 129.3 (CH), 128.7 (C), 127.7 (C), 124.0 (C), 119.0 (CH), 118.1 (CH), 106.4 (CH), 55.5 (CH_3), 53.2 (CH_3); UV ($CHCl_3$): $\lambda_{max} = 400$, 338, 295, 261 nm; IR (KBr): $\nu = 1738$, 1219 cm^{-1}; LR-MS (EI): m/z (%) = 454 (M^+, 100), 380 (10), 263 (15), 250 (19), 125 (15); HR-MS: $m/z = 454.1412$ (calcd. for $C_{28}H_{22}O_6$: 454.1416).

Enantioselective Cocycloaddition of Triflate 4 with DMAD

Method A: *Catalyst generated* in situ *(experiments in Table 1, and entries 6 and 7 in Table 2):* A solution of $Pd_2(dba)_3\cdot CHCl_3$ (5 mol% with respect to **4**) and the chiral ligand (10 mol%) in a CH_3CN/THF mixture (1.5:1.0, 2.5 mL) was stirred at room temperature for 20 min. Then, a solution of **4** (aprox. 0.32 mmol) in CH_3CN (4.0 mL), DMAD (140 mol%) and finely powdered anhydrous CsF (200 mol%), were successively added. After stirring at room temperature for 15 h, the reaction mixture was concentrated under reduced pressure and quickly chromatographed (SiO_2; Et_2O/hexanes, 1:3) to afford a mixture of **1**, **7** and **8**. The ratio of regioisomers was determined by integration of diagnostic signals in the ^{1}H NMR spectrum. A second chromatography allowed the isolation of pure pentahelicene **1**, which was analyzed by chiral HPLC [Chiralpak AS (*i*-PrOH/hexane, 3:97) or OL-86 (CH_2Cl_2/hexane, 35:65)] to determine the enantiomeric excess.

NOTE: The same procedure, with minor modifications (solvent, fluoride source) was followed for experiments in Table 3.

***Method B:*.** *Preformed catalyst (entries 1–5 in Table 2):* To a solution of the preformed palladium complex (**9**, **10** or **11**, 10 mol% with respect to **4**) in a CH_3CN/CH_2Cl_2 mixture (1.5:1.0, 2.5 mL), a solution of **4** (approx. 0.32 mmol) in CH_3CN (4.0 mL), DMAD (140 mol%) and finely powdered anhydrous CsF (200 mol%) were successively added. After stirring at room temperature for 15 h, the reaction mixture was concentrated under reduced pressure and quickly chromatographed (SiO_2; Et_2O/hexanes, 1:3) to afford a mixture of **1**, **7** and **8**. The ratio of regioisomers was determined by integration of diagnostic signals in the ^{1}H NMR spectrum. A second chromatography allowed the isolation of pure pentahelicene **1**, which was analyzed by chiral HPLC [Chiralpak

Table 4. Crystal data for for compounds **1** and **10**.

	1	**10**
Molecular formula	$C_{28}H_{22}O_6$	$C_{50}H_{38}O_4P_2Pd$
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	*P*2/c	*P*2/c
Unit cell dimensions	$a = 15.679(4)$ Å	$a = 11.147(4)$ Å
	$b = 13.123(3)$ Å	$b = 13.957(5)$ Å
	$c = 11.376(3)$ Å	$c = 14.524(5)$ Å
Volume	2201.08 (10) Å^3	1934.1(12) Å^3
Z	4	2
Absorption coefficient	0.096 mm^{-1}	0.611 mm^{-1}
F(000)	952	892
Crystal size	0.31 × 0.16 × 0.05 mm	0.34 × 0.13 × 0.13 mm
Theta range	1.55–22.05°	1.53–26.42°
Limiting indices	$-16 \leq h \leq 15$	$-13 \leq h \leq 13$
	$0 \leq k \leq 13$	$-17 \leq k \leq 16$
	$0 \leq l \leq 11$	$0 \leq l \leq 18$
Reflections collected/unique	34321/2707	7856/7856
*R*int	0.0685	0.0714
Absorption correction	multi-scan	multi-scan
Data/restraints/parameters	2707/0/312	7856/0/516
Goodnes-on-fit on F^2	1.072	1.031
Final *R* indices [$I > 2$ s(I)]	$R1 = 0.0415$, $wR2 = 0.0958$	$R1 = 0.0496$, $wR2 = 0.1241$
R indices (all data)	$R1 = 0.1228$, $wR2 = 0.1355$	$R1 = 0.0791$, $wR2 = 0.1440$
Largest diff. peak and hole	0.177 and −0.161	2.579 and −2.641

AS (*i*-PrOH/hexane, 3:97) or OL-86 (CH_2Cl_2/hexane, 35:65)] to determine the enantiomeric excess.

Racemization Barrier of 1

A sample of non-racemic **1** dissolved in 1:3 CH_2Cl_2/hexane (1 mL) was prepared and heated to 45 °C by immersion in a thermostatic bath. Once the constant temperature was reached, an aliquot was taken, cooled to room temperature, and quickly analyzed by HPLC [OL-86 (CH_2Cl_2/hexane, 35:65)] to determine the initial enantiomeric excess. This process was repeated at four different intervals of time. Representation of $\ln(ee_0/ee_t)$ against time resulted in a first order plot, from which the enantiomerization reaction rate k was determined [$8.86\times10^{-6}\,s^{-1}$, from the kinetic equation: $\ln(ee_0/ee_t)=2k\times t$]. The same procedure was repeated at constant temperatures of 60, 65 and 75 °C, affording k values of 4.34×10^{-5}, 8.01×10^{-5} and $1.79\times10^{-4}\,s^{-1}$, respectively. The representation of $\ln(k/T)$ against 1/T [Eyring plot, $\ln(k/T)=\ln(K_B/h)-\Delta H^{\neq}/RT+\Delta S^{\neq}/R$] gave the activation parameters $\Delta H^{\neq}$ (21.7 kcal mol^{-1}), $\Delta S^{\neq}$ (−13.7 cal mol^{-1} K) and $\Delta G^{\neq}$ (25.7 kcal mol^{-1}). See Supporting Information for details.

X-Ray Crystallographic Study of 1

The crystals were mounted on a glass fiber and collected on a Bruker SMART CCD area-detector diffractometer. Crystal data are reported in Table 4. Graphite monochromated Mo-*K*α radiation ($\lambda=0.71073$ Å) was used. The structures were solved by direct methods (SIR-97)[32] and refined with full-matrix least squares (SHELXL-97)[33] on F^2 on the basis of independent reflections. Crystallographic data (excluding structure factors) for the compounds **1** and **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications: for **1** no. CCDC-605852, for **10** no. CCDC-605851. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

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