# Asymmetric Cyclopropanation of Alkenes Catalyzed by a Rhodium "Chiral Fortress" Porphyrin

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*Summary:* While a number of efficient asymmetric catalysts exist for the cyclopropanation of alkenes by diazo esters, all provide diastereomeric mixtures in which the anti product predominantes. We report here the synthesis and characterization of a chiral rhodium porphyrin catalyst that provides predominantly the syn isomers, with very good diastereoselectivity in some cases. However, the enantioselectivities observed are modest.

Due to the considerable synthetic utility of the metal-catalyzed cyclopropanation of alkenes by diazo esters,[1] there has been considerable interest in the design of asymmetric catalysts for this process. Notable recent successes in this area include the work of the Aratani,[2] Pfaltz,[3,4] Masamune,[5] and Evans[6] laboratories on chiral copper species and of Doyle and co-workers on chiral rhodium carboxamide catalysts.[7,8] For some substrates, very high enantiomeric excesses (ee's) can be realized. All of these catalysts provide a mixture of diastereomers with the anti product predominating. Thus, a catalyst able to provide optically active syn cyclopropyl esters would provide a useful complement to existing methodology. We have been working toward developing chiral porphyrin catalysts for this purpose, since Callot and co-workers have shown that bulky rhodium porphyrins produce the syn products preferentially.[9] As a first step in this direction, we recently reported the catalytic cyclopropanation activity of the iodorhodium derivative of the "chiral wall" porphyrin **1**, a macrocycle with chiral binaphthyl groups appended directly to the meso positions of the porphyrin[10,11] (Figure 1). This compound proved to be an extremely efficient catalyst for carbene transfer from ethyl diazoacetate (EDA) to alkenes with moderate to good diastereoselectivity, but only modest enantioselectivity. Studies of the geometry of alkene approach to the rhodium carbene (the putative active intermediate) using simple achiral porphyrins led us to propose a model in which the alkene $\pi$ system is perpendicular to the plane of the porphyrin and in which the alkene is tilted to some degree, allowing most of the olefin substituents to escape serious interactions with the macrocycle.[12] In this view, the low ee's provided by the chiral wall catalyst could be ascribed to the overly spacious "slot" defined by the naphthyl groups and suggested that higher ee's might be obtained by creating a more restricted pocket around the rhodium center.[12] Toward this end, we have synthesized the new macrocycle **2**, which we call the "chiral fortress" porphyrin (Figure 1). Its superstructure is closely related to that of the chiral wall catalyst **1**, but the extra bulk provided by the additional aromatic rings results in a much more hindered pocket. We hoped that this modification would increase the diastereoselectivity and enantioselectivity of cyclopropanation reactions catalyzed by the iodorhodium derivative of **2** relative to those obtained with the catalyst Rh-**1**-I. In this report, we report the synthesis, characterization, and catalytic cyclopropanation activity of this new porphyrin.

## Results and Discussion

The synthetic scheme (Figure 2) followed closely that employed in the chiral wall porphyrin synthesis.[10] The Grignard reagent derived from commercially available 1-bromopyrene was condensed with oxazoline **3**[13] to provide the naphthyl–pyrenyl product **4** in 66% yield and 73% diastereomeric excess (de). After purification by flash chromatography, **4** was converted to aldehyde **6** by hydrolysis of the oxazoline ring with ethanolic HCl, reduction with lithium aluminum hydride to alcohol **5**, and subsequent oxidation with Jones reagent (56% yield overall, unoptimized). The recrystallized aldehyde was optically pure, as judged by an NMR chiral shift experiment (splitting of the aldehyde peak induced by the shift reagent could be detected before recrystallization, but not after). The key cyclization step was effected by stirring aldehyde **6** and pyrrole in $CH_2Cl_2$ for 117 h in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$, followed by oxidation of the resultant tetrapyrrole with *p*-chloranil.[14] The total porphyrin yield was 8% (mixture of atropisomers). The desired $\alpha,\beta,\alpha,\beta$-atropisomer was obtained by chromatography on Florsil in only 0.75% yield (based on aldehyde **6**). Sequential treatment with $[Rh(CO)_2Cl]_2$ and *N*-iodosuccinimide[15] provided the iodorhodium derivative **7** in 50% yield.

The 2-D COSY $^1$H NMR spectrum of **2** (Figure 3) shows unambiguously that it is the desired atropisomer. Only the $\alpha,\beta,\alpha,\beta$-compound is expected to exhibit two $\beta$-pyrrolic resonances and only 15 aromatic proton signals (all four of the pyrene–naphthyl moieties are equivalent in the $\alpha,\beta,\alpha,\beta$-compound), which is exactly what is observed in the spectrum of porphyrin **2**.

Table I shows the results of reactions between several alkenes and EDA catalyzed by the iodorhodium derivative of porphyrin **2**. At least several hundred turnovers of the catalyst were obtained in each case for overnight runs. While respectable, the efficiency of the chiral fortress catalyst is low compared to that of simple rhodium por-

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(15) This is a modification of the metalation procedure of: Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 311–314.

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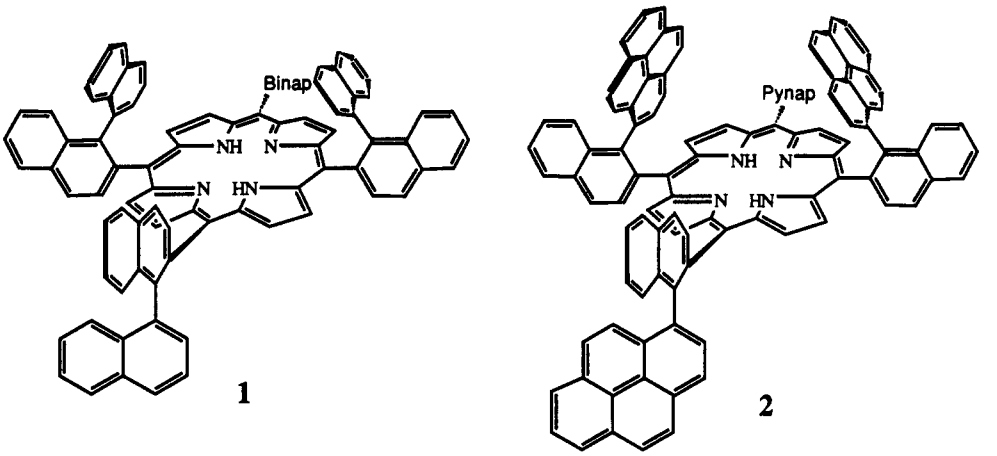



**Figure 1.** Structure of the "chiral wall" (1) and "chiral fortress" (2) porphyrins.

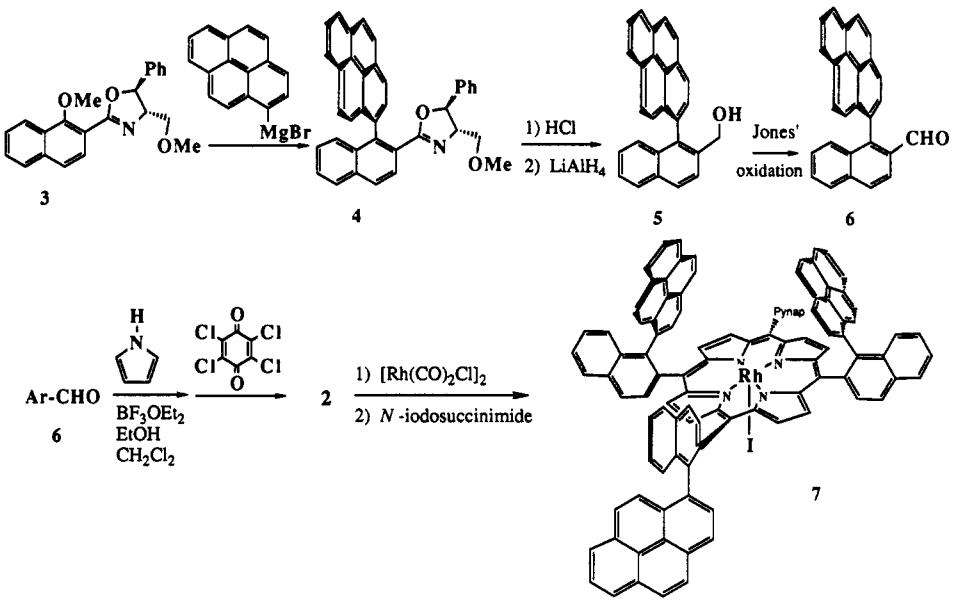



**Figure 2.** Synthesis of the "chiral fortress" porphyrin.

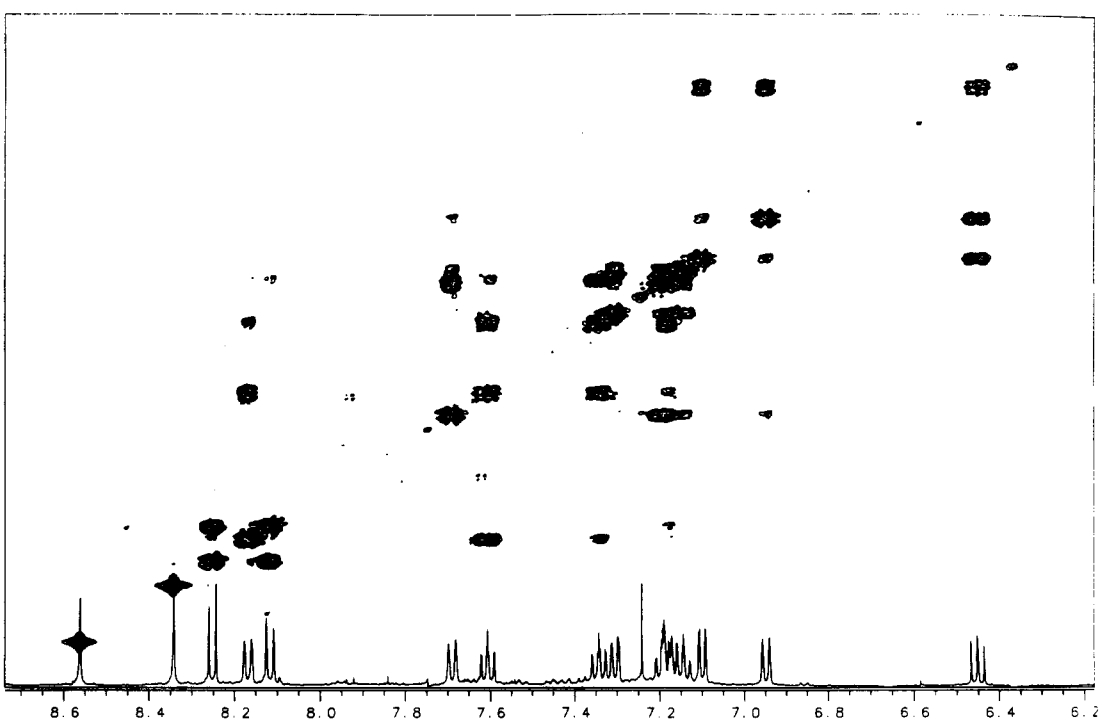
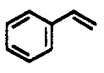
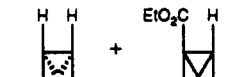
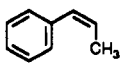
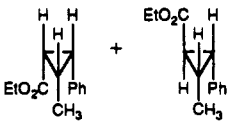
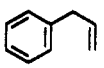
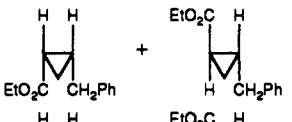
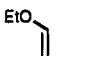
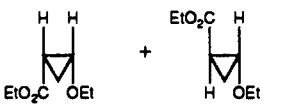



**Figure 3.** 2-D COSY $^1H$ NMR spectrum (500 MHz) of **2** at 25 °C in $CDCl_3$.

**Table I. Asymmetric Cyclopropanation of Alkenes Catalyzed by Rh-2-I[a]**

| substrate | products | T, °C | ee, % (±5%) syn | ee, % (±5%) anti | syn/anti ratio | turnovers |
|---|---|---|---|---|---|---|
|  |  (-)-1*R*,2*S* | 25 | 15 | nd[b] | 2.5 | 1600 |
|  |  | 0 | 0 | 20 | 14.2 | 720 |
| | | 25 | 25 | 20 | 5.1 | 770 |
|  |  | 0 | 20 | 40 | 3.9 | 250 |
| | | 25 | 10 | 10 | 1.0 | 420 |
|  |  | 25 | 15 | 10 | .83 | 130 |

[a] See Experimental Section for details. [b] Not determined.

phyrins and the chiral wall catalyst 1. Also, the reactions are much more sluggish, indicating that we have perhaps created a metal center that is too crowded to react rapidly with EDA. The diastereoselectivities are moderate to very good, with the syn isomer being the major product in each case, except for ethyl vinyl ether. Unfortunately, for all of the substrates examined, the ee's are not improved greatly over those observed in identical reactions using the iodorhodium derivative of porphyrin 1 and are even poorer in some cases.

In summary, due to the difficulty of obtaining large amounts of porphyrin 2 and its inability to support efficient and highly enantioselective cyclopropanation reactions, it appears that the "chiral wall" class of porphyrins, including the iodorhodium derivatives of 1 and 2, will not serve as synthetically useful cyclopropanation catalysts. However, these studies have been useful in demonstrating the feasibility of using chiral porphyrins to produce predominantly syn cyclopropyl esters in an enantioselective fashion.

It is difficult to identify precisely the flaw in the design of these catalysts, but on the basis of the mechanistic work we have carried out, some informed speculation is possible. A likely serious problem is that in a $C_2$-symmetric pocket there are a number of nonequivalent orientations of the carbene ligand (for example, the two in which the carbene p orbital eclipses the two symmetry-distinct N–Rh–N axes). On the basis of examination of molecular models, these conformational isomers might be expected to produce different enantiomers of the product. We have no reason to conclude from these studies that our previously proposed model for the orientation of the alkene with respect to the metal carbene in the transition state[12] is incorrect. The synthesis of chiral porphyrins with pockets designed to alleviate the problems of multipe carbene conformations is underway in our laboratory.

## Experimental Section

**(*R*)-2-(4-(Methoxymethyl)-5-phenyloxazolinyl)-1-(1′-pyrenyl)naphthalene (4).** Magnesium powder (11.1 mmol, 0.264 g; purchased from Aldrich and stored under argon), freshly distilled THF (13.5 mL), and 1-bromopyrene (11.1 mmol, 3.12 g) were combined with stirring in an oven-dried, argon-flushed 300-mL round-bottom flask. Grignard formation was allowed to proceed for 1 h (the mixture turned brown and became warm after about 15 min). The (1-pyrenyl)magnesium bromide solution was diluted with 55 mL of THF and cooled to 0 °C, after which a solution of (+)-1-methoxy-2-(4-(methoxymethyl)-5-phenyloxazolinyl)-naphthalene (3; 5.7 mmol, 2.0 g) in THF (32.8 mL) was added via cannula. The resulting clear yellow solution was stirred at room temperature for 92 h. After this period, the slightly green solution was quenched by the addition of a saturated $NH_4Cl$ solution (11.6 mL; the solution immediately turned yellow and then formed a white precipitate). The organic layer was separated and washed with 2 × 46 mL of saturated NaCl. Drying ($Na_2SO_4$, 10 g; 20 min) and concentrating by rotary evaporation gave a yellow-brown oily solid (4.3 g). $^1H$ NMR spectroscopy on this crude material showed a 73% diastereomeric excess (oxazoline benzylic doublets at δ 4.898 and 4.815). Purification by flash chromatography (silica, EM Science, 230–400 mesh, 4.5 cm i.d. × 27 cm, sample dissolved in 6 mL of $CH_2Cl_2$, loaded, and eluted with 100:4 $CHCl_3$–$Et_2O$) gave a light yellow foamy solid (2.0 g, 3.8 mmol, 66% yield). $^1H$ NMR (360 MHz, $CDCl_3$): δ 8.23–6.28 (complex, 20 H, naphthyl, pyrenyl, and phenyl protons), 4.90 (d, $J$ = 7.2 Hz, 1 H, benzylic *H1′*), 3.87 (m, 1 H, *H2′*), 3.21 (dd, $J$ = 9.7 Hz, 4.3 Hz, 1 H, methylene *H3′*), 3.08 (s, 3 H, methoxy), 3.04 (m, 1 H, methylene *H3′*) (note: the diagnostic benzylic proton signal for the undesired diastereomeric product occurs at δ 4.81 (d, $J$ = 7.2 Hz)). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 165.2 (oxazoline amido carbon), 140.3, 138.6, 136.4, 134.5, 133.5, 133.2, 133.0, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 127.1, 126.5, 126.4, 126.0, 125.6, 125.0 (aromatic carbons), 83.8 (benzylic *C1′*), 74.2, 74.1 (*C2′*, *C3′*), 59.0 (–$OCH_3$). IR: 3687, 3054, 1258, 830 $cm^{-1}$. Mass spectrum: $m/e$ 517.203 271 ($C_{37}H_{27}NO_2$ requires 517.204 179).

**(*R*)-(+)-2-(Hydroxymethyl)-1-(1′-pyrenyl)naphthalene (5).** (*R*)-2-(4-Methoxymethyl)-5-phenyloxazolinyl)-1-(1′-pyrenyl)naphthalene (4); 29.1 mmol, 15.1 g) was refluxed in 3 N ethanolic HCl (320 mL) for 18 h. The solution was rotary evaporated to near dryness. The ester–amine hydrochloride salt was dissolved in distilled THF (91 mL) and the solution transferred via cannula to a solution of $LiAlH_4$ at 0 °C under agron (0.21 M $LiAlH_4$; from 65 mL of 1.0 M $LiAlH_4$ in THF and 240 mL of freshly distilled THF). After the addition was complete, the solution was stirred another 1 h at 0 °C and then warmed to room temperature. The reaction was quenched by the slow addition of $H_2O$ (dropwise until a cloudy white precipitate formed, then an additional 200 mL), using an ice bath to cool the flask. The cloudy yellow mixture was extracted with $CH_2Cl_2$ (3 × 400 mL). The combined organic fractions were washed with $H_2O$ (400 mL), dried ($Na_2SO_4$, 100 g), and concentrated to give 14.4 g of a brown oil. Purification by flash column chromatography gave 5.4 g of light yellow solid alcohol (15 mmol, 52%). $^1H$ NMR (360 MHz, $CDCl_3$): δ 8.02 (complex, 15 H, aromatic), 4.43 (s, 2 H, methylene), 1.56 (s, 1 H, –O*H*). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 137.0, 136.0, 133.3, 133.1, 132.9, 131.3, 130.9, 130.0, 128.4, 128.1, 127.9, 127.7, 127.4, 126.7, 126.2, 126.1, 125.7, 125.4, 125.2, 124.9, 124.8, 124.7 (naphthyl and pyrenyl), 63.5 (methylene). IR: 3602, 3045, 1602, 1272, 1062, 824 $cm^{-1}$. Mass spectrum: $m/e$ 358.135 395

($C_{27}H_{18}O$ requires 358.135 765). $[\alpha]_D$ = +177° (*c* 0.011, $CHCl_3$).

**(*R*)-(+)-1-(1′-Pyrenyl)naphthalene-2-carboxaldehyde (6).** The alcohol **5** (5.3 mmol, 1.9 g) was dissolved in freshly distilled acetone (377 mL) in a 1-L round-bottom flask. The clear solution was cooled to 0 °C and Jone's reagent added dropwise (approximately 50 drops). The course of the reaction was monitored by TLC. After the mixture was warmed to room temperature for 15 min with stirring, the excess oxidant was quenched by the addition of isopropyl alcohol (25 mL). $H_2O$ (500 mL) was added and the resulting tan cloudy suspension poured into a separatory funnel and extracted with $CH_2Cl_2$ (3 × 400 mL). The combined organic fractions were dried and concentrated to give 3.5 g of a moist orange solid. Purification by flash column chromatography ($CH_2Cl_2$ eluant) gave a light yellow solid, which was recrystallized from boiling ether. Cooling to −10 °C gave light yellow crystals (0.40 mmol, 0.142 g; $[\alpha]_D$ = +192° (*c* 0.0063, $CHCl_3$)). A second crop was obtained by reducing the volume to 200 mL and cooling overnight (2.05 mmol, 730 mg; $[\alpha]_D$ = +1.90° (*c* 0.005, $CHCl_3$). A third crop was obtained from the remaining liquor after several days at −5 °C (0.528 mmol, 188 mg). Total yield: 2.98 mmol, 56%. $^1H$ NMR (300 MHz, $CDCl_3$): δ 9.67 (s, 1 H, −C*H*O), 8.35–7.31 (complex, 15 H, naphthyl and pyrenyl). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 145.3 (−CHO), 136.2, 133.3, 132.4, 131.5, 131.4, 130.9, 130.8, 130.0, 128.95, 128.89, 128.82, 128.5, 128.3, 128.2, 128.0, 127.3, 127.0, 126.4, 125.7, 125.5, 125.0, 125.5, 125.0, 124.5, 124.3, 122.2 (naphthyl and pyrenyl). IR: 3686, 3055, 1674, 1245, 824 $cm^{-1}$. Mass spectrum: *m/e* 356.119 689 ($C_{27}H_{16}O$ requires 356.120 115).

**5α,10β,15α,20β-Tetrakis[(*R*)-1-(1′-pyrenyl)-1-naphthalen-2-yl]porphyrin (2).** An oven-dried, argon-flushed 300-mL round-bottom flask was charged sequentially with freshly distilled $CH_2Cl_2$ (174 mL), (*R*)-(+)-1-(1′-pyrenyl)naphthalene-2-carboxaldehyde (**6**; 2.42 mmol, 0.862 mg, $[\alpha]_D$ = +190°), freshly distilled pyrrole (2.42 mmol, 169 μL), and triethylorthoacetate (451 μL). After the mixture was stirred for 15 min, a solution of $BF_3{\cdot}OEt_2$ was added (67 μL of a 2.5 M solution in $CH_2Cl_2$, made up within the hour) and the reaction was shielded with foil from ambient light. The formation of product was monitored by visible absorbance spectroscopy in the following manner: 50-μL aliquots were withdrawn from the reaction solution and injected into 300 μL of a $10^{-2}$ M solution of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in toluene to oxidize the porphyrinogen. The sample was diluted with 3:1 $CH_2Cl$–EtOH, and the intensity of the porphyrin Soret band at 436 nm was measured. After 20 h another aliquot (67 μL) of $BF_3$ catalyst was added. Additional aliquots of catalyst were added at 31, 50, 64, 85, 110, and 116 h (extra catalyst was added when the increase in the Soret intensity ceased). In addition, after 47 h more triethyl orthoacetate and newly distilled pyrrole (original amounts) were added. The reaction mixture was oxidized after 117 h, when addition of catalyst failed to cause a further increase in the porphyrin yield. Oxidation was performed by refluxing the solution with 0.75 equiv of *p*-chloranil (1.81 mmol, 446 mg) for 1 h. The resulting deep red, opaque solution was poured into a separatory funnel, and quinone components were removed by washing with 5% NaOH/5% $Na_2S_2O_4$ (2 × 112 mL). The dark green solution was dried and concentrated with 1 g of Florisil. The Florisil-adsorbed solid was placed in a Soxhlet extractor and extracted with MeOH until the rinsings were clear. The porphyrin was recovered by replacing MeOH with $CH_2Cl_2$. Concentration gave a dark solid, which was dissolved in $CH_2Cl_2$, and the solution was poured through a plug of silica (9.5 cm i.d. × 3 cm height). The reddish brown solution was concentrated with a small amount of Florsil and then purified by two successive Florisil flash columns. The mixture of atropisomers (720 mg after Soxhlet) was loaded onto a Florsil flash column (Fluka, 200–300 mesh, 8 cm i.d. × 27 cm height; 9:1 $CH_2Cl_2$–hexanes). A broad dark olive green band (mixture of atropisomer rotamers, 1.56 × $10^{-4}$ mol, 252 mg) eluted first, followed by a smaller forest green band (90–95% α,β,α,β by $^1H$ NMR, 2.63 × $10^{-5}$ mol, 42.4 mg). The α,β,α,β-compound was loaded onto a second, smaller column (Florisil, 200–300 mesh, Fluka, 2 cm i.d. × 17.5 cm height, 9:1 $CH_2Cl_2$–hexanes). The second forest green band was again collected (>95% α,β,α,β by NMR; 1.79 × $10^{-5}$ mol, 28.8 mg). Yield of isolated α,β,α,β-**2**: 0.74%. Overall porphyrin yield: 7.2%. $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.63 (s, 4 H, pyrrolic), 8.44 (s, 4 H, pyrrolic), 8.16 (dd, *J* = 8.0 Hz, 4 H, *H8*), 8.13 (d, *J* = 8.5 Hz, 4 H, *H3*), 8.05 (dd, *J* = 7.8, 0.5 Hz, 8 H), 8.04 (d, *J* = 8.0 Hz, 8 H), 7.96 (dd, *J* = 9.0, 7.0 Hz, 8 H), 7.64 (d, *J* = 9.0 Hz, 4 H), 7.59 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 4 H), 7.55 (d, *J* = 8.0 Hz, 4 H), 7.25 (m, 4 H), 7.21 (m, 4 H), 7.06 (d, *J* = 8.0 Hz, 4 H), 6.99 (d, *J* = 8 Hz, 4 H), −3.73 (sharp s, 2 H, internal porphyrinic). Mass spectrum (FAB): *m/e* 1615.567 185 ($C_{124}H_{70}N_4$ requires 1615.567 874). Visible spectrum: $\lambda_{max}$ 436 nm (ε = 1.4 × $10^5$), 275 nm (ε = 5.8 × $10^4$), 342 nm (ε = 4.4 × $10^4$), 525 nm (ε = 9.7 × $10^3$), 557 nm (ε = 3.3 × $10^3$), 595 nm (ε = 3.1 × $10^3$), 652 nm (ε = 1.7 × $10^3$). $[\alpha]_D$ = −909° (*c* 0.000 187, $CHCl_3$).

**Iodo(5α,10β,15α,20β-tetrakis[(*R*)-1-(1′-pyrenyl)-naphthalen-2-yl]porphyrinato)rhodium(III) (7).** A solution of the pyrene–naphthyl porphyrin **2** (1.79 × $10^{-5}$ mol, 28.8 mg), tetracarbonylbis(μ-chloro)dirhodium (2 equiv, 3.58 × $10^{-5}$ mol, 13.9 mg), and sodium carbonate (anhydrous, 54 mg) in dichloroethane (4.9 mL) was heated to reflux under argon for 50 h. The solution was cooled, poured into a separatory funnel, and washed with water (2 × 21 mL). The organic fraction was diluted to 30 mL with $CH_2Cl_2$, dried, and filtered and the solvent volume concentrated to 5 mL. *N*-Iodosuccinimide (3.6 equiv, 6.4 × $10^{-5}$ mol, 14.5 mg) was added, and the mixture was stirred at room temperature for 5 h. Concentration of the solution gave a brown solid. The metalated product was purified by flash chromatography on silica (2 cm i.d. × 19 cm height) with toluene as eluant. A 16.3-mg amount of reddish orange solid was collected (8.86 × $10^{-6}$ mol; 50% yield). Mass spectrum (FAB): *m/e* 1842.355 666 ($C_{124}H_{68}N_4RhI$ requires 1842.354 379). UV–visible spectrum: $\lambda_{max}$ 435 nm (ε = 5.6 × $10^4$), 395 nm (ε = 4.7 × $10^4$), 535 nm (ε = 7.9 × $10^3$).

**Cyclopropanations Catalyzed by Rh-2-I.** Catalyst **7** (3.6 × $10^{-3}$ mmol), olefin (20 mmol), $CH_2Cl_2$ (500 mL), and octane (GC standard, 5 mmol) were combined in a 10-mL round-bottom flask equipped with a nitrogen collector. Ethyl diazoacetate (5 mmol) was added and the reaction's progress monitored by GC. When product formation stopped, additional EDA was added (to a total of 20 mmol). Workup consisted of a vacuum distillation and/or flash chromatography on silica (3:1 hexanes–ether). The products of the *cis*-β-methylstyrene, allylbenzene, and ethyl vinyl ether reactions were analyzed as a mixture of syn and anti isomers. Yields were determined on a Hewlett-Packard 5890A gas chromatography equipped with a 5% SE-30-packed column using octane or dodecane as the internal standard.

**Analysis of the Asymmetric Induction.** Chiral shift NMR experiments were performed using approximately 15 mg of cyclopropyl ester with the chiral shift reagent tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III) (added in small aliquots).

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**Registry No.** **2**, 141171-37-1; **3**, 80409-54-7; **4**, 141171-38-2; **5**, 141171-39-3; **6**, 141171-40-6; **7**, 141171-41-7; DDQ, 84-58-2; $[Rh(CO)_2Cl]_2$, 14523-22-9; $PhCH{=}CH_2$, 100-42-5; (*Z*)-$PhCH{=}CHCH_3$, 766-90-5; $PhCH_2CH{=}CH_2$, 300-57-2; $EtOCH{=}CH_2$, 109-92-2; *p*-chloranil, 118-75-2; ethyl 2(*S*)-phenylcyclopropane-1(*R*)-carboxylate, 34702-97-1; ethyl 2(*R*)-phenylcyclopropane-1-(*R*)-carboxylate, 34716-60-4; ethyl 2(*R*)-phenyl-3(*S*)-methylcyclopropane-1(*S*)-carboxylate, 141269-59-2; ethyl 2(*R*)-phenyl-3(*S*)-methylcyclopropane-1(*R*)-carboxylate, 141270-66-8; ethyl 2(*S*)-(phenylmethyl)cyclopropane-1(*S*)-carboxylate, 141269-60-5; ethyl 2(*S*)-(phenylmethyl)cyclopropane-1(*R*)-carboxylate, 141315-54-0; ethyl 2(*R*)-ethoxycyclopropane-1(*S*)-carboxylate, 141269-61-6; ethyl 2(*R*)-ethoxycyclopropane-1(*R*)-carboxylate, 141269-62-7; 1-bromopyrene, 1714-29-0.

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