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Guide to Enantioselective Dirhodium(II)-Catalyzed Cyclopropanation with Aryldiazoacetates

Dedicated to Professor Melanie Sanford in recognition of her receipt of the Tetrahedron Young Investigator Award

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ABSTRACT

Catalytic enantioselective methods for the generation of cyclopropanes has been of long standing pharmaceutical interest. Chiral dirhodium(II) catalysts prove to be an effective means for the generation of diverse cyclopropane libraries. $Rh_2(R-DOSP)_4$ is generaally the most effective catalyst for asymmetric intermolecular cyclopropanation of methyl aryldiazoacetates with styrene. $Rh_2(S-PTAD)_4$ provides high levels of enantioinduction with *ortho*-substituted aryldiazoacetates. The less-established $Rh_2(R-BNP)_4$ plays a complementary role to $Rh_2(R-DOSP)_4$ and $Rh_2(S-PTAD)_4$ in catalyzing highly enantioselective cyclopropanation of 3-methoxy-substituted aryldiazoacetates. Substitution on the styrene has only moderate influence on the asymmetric induction of the cyclopropanation.

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1. Introduction

Dirhodium catalysis Phenyldiazoacetate

The metal-catalyzed decomposition of diazo compounds in the presence of alkenes is a general method for the stereoselective synthesis of cyclopropanes.^{1,2} We have previously shown the rhodium-catalyzed cyclopropanation / of donor/acceptor carbenoids to be effective for the enantioselective synthesis of cyclopropanes with one or more quaternary stereogenic centers.³ As many cyclopropyl amines are known to have significant CNS activity,^{7,8} we have initiated a program to use our cyclopropanation methodology to access novel diarylcyclopropylamines as potential therapeutic agents (Scheme 1). For the methodology to be broadly useful in drug discovery, access to a range of diarylcyclopropyl derivatives with high levels of enantioenrichment is required. Herein, we define the optimal catalysts for the cyclopropanation with various types of methyl aryldiazoacetates.



Scheme 1. Route to cyclopropyl amines from aryldiazoacetates

Three chiral dirhodium-(II) catalysts were selected for this study (Figure 1). The first catalyst, $Rh_2(R$ -DOSP)₄, is considered to be the optimal catalyst for the reactions of donor/acceptor carbenoids when the acceptor group is a methyl ester.^{1,4} The





Figure 1. Dirhodium-(II) catalysts used in this study

Tetrahedror

Ph ⁄

2. Results and Discussion

The study began by exploring the effect of aryl substitution on the enantioselectivity in the cyclopropanation of styrene by aryldiazoacetates. The results for a series of aryldiazoacetates (1a-l) using the three chiral dirhodium catalysts $Rh_2(R-DOSP)_4$, $Rh_2(S-PTAD)_4$ and $Rh_2(R-BNP)_4$ are summarized in Table 1. Excellent levels of diastereoselectivity were achieved in all cases (>95:5 dr) and the isolated yields of the cyclopropanes were generally high, ranging from 63-98%. The absolute configuration of the major isomer of the cyclopropanes is tentatively assigned as $1S, 2R^{28}$ Rh₂(*R*-DOSP)₄ provided high levels of enantioinduction when unsubstituted (1a) or 4-substituted (1b-e) methyl aryldiazoacetates were employed as substrates (Table 1, entries 1-5, 87-90% ee). In general, Rh₂(S-PTAD)₄ and Rh₂(R-

 BNP_{4} gave <60% ee in the cyclopropanation reactions of unsubstituted or 4-substituted aryldiazoacetates with these same substrates. The one exception, however, is the reaction of 4methoxyphenyldiazoacetate 1e with Rh₂(S-PTAD)₄, which gave the cyclopropane 3e in exceptionally high enantioselectivity (entry 5, 96% ee). Rh₂(R-DOSP)₄ also performed well in the reactions of 2-substituted aryldiazoacetates 1f (entry 6, 92% ee) and 1g (entry 7, 86% ee), and moderately well with 3,4dichlorophenyldiazoacate 1h (entry 8, 82% ee), confirming that $Rh_2(R-DOSP)_4$ is the optimal catalyst for a range of aryldiazoacetates. The enantioselection with $Rh_2(S-PTAD)_4$ is extremely variable. However, in certain cases, it provides exceptional levels of enantioselectivity, as seen in the reaction with 2-chlorophenyldiazoacetate 1f, which generates the cyclopropane **3f** in 97% ee (entry 6).

__,CO₂Me

Table 1. Examination of the influence of substitution on aryldiazoacetate

N₂ ↓

		Ar CC 1a-I	D ₂ Me <u>1 mol%</u> so	2 Rh(II) catalyst lvent, rt	Ph Ar 3a-I	\mathbf{C}		
			$Rh_2(R-DOSP)_4^a$		$Rh_2(S-PTAD)_4^a$		$Rh_2(R-BNP)_4^b$	
entry	Ar	product	yield (%)	ee (%)	yield (%)	ee (%)	yield (%)	ee (%)
1	- The	3a	85	88	87 ^b	21 ^b	72	42
2		3b	84	87	77°	46 ^{<i>c</i>}	69	51
3	F ₃ C-	3c	93	87	67 ^c	77 ^c	80	57
4	CI	3d	87	88	71 ^{<i>c</i>}	48 ^c	89	57
5	MeO-	Зе	66	90	93 ^c	96 ^c	84	57
6	CI	3f	89	92	80 ^c	97 ^c	78	51
7	OMe	3g	92	86	87 ^c	80 ^c	69	27
8	CI	3h	88 ^b	82 ^b	88 ^b	60^b	82	63
9	MeO MeO	3i	74	56	70 ^c	94 ^{<i>c</i>}	93	97
10	MeO	3j	78^b	79 ^b	72 ^b	16^b	82	88
11	MeO OMe	3k	85 ^{b,c}	28 ^{<i>b,c</i>}	$85^{b,c}$	3 ^{<i>b,c</i>}	69 ^c	92 ^c
12	MeO MeO OMe	31	98 ^b	34 ^b	95 ^b	9 ^b	63	90

^apentane, ^btoluene, ^c0.5 mol% catalyst loading

Interestingly, $Rh_2(R-DOSP)_4$ fails to provide high levels of enantioinduction when the aryldiazoacetate contains a 3-methoxy substituent (1i-l) (entries 9-12), especially when the ring is polysubstituted (1i, k-l). In these cases, the cyclopropanes 3i, k-l are Mecoduced in 28-56% ee (entries 9, 11-12). Rev (5-117 AD) is an effective catalyst only in the case of 3,4dimethoxyphenyldiazoacetate **11**, **Berner**ating the cycloprop**2 i** in 94<u>% ee (entry 9). In contrast, $Rh_2(R-BNP)_4$ is an ext</u>remely effective catalystralywith alleactor the 3 methoxy substituted aryldiazoacates ding menerating the cyclopropanes 3i-l in 88-97% ee (entries 9-12). 1 1 93 97 0.5 83 96 1

One 30f the most attractive features sof $Rh_2(R-\Phi OSP)_4$ and Rh₂(S-PTAD)₄ as⁰ Chiral catalysts is that³ they are⁴⁰ capable of operatizes equilos syread algest loadings.²⁹ As Rh₂(R-BNP)₄ was found to be the optimal catalyst for 3-methoxyaryldiazoacetate derivatives, we investigated whether it could also operate at low catalyst loading. Reactions of aryldiazoacetate 1i, with successively lower loadings of Rh₂(R-BNP)₄ are summarized in Table 2. $Rh_2(R-BNP)_4$ was effective at catalyzing highly enantioselective cyclopropanation with catalyst loadings of 1.0 and 0.5 mol%, providing 3i with virtually the same level of enantioselectivity (entry 1 vs. 2, 97% ee vs. 96% ee). When the catalyst loading was decreased further to 0.1 mol% a more significant drop in the level of enantioselectivity was observed (entry 3, 91% ee). Further decreasing the catalyst loading to 0.01 mol%, however, caused a dramatic decrease in enantioinduction (entry 4, 40% ee). These results suggest that, although $Rh_2(R-$ BNP)₄ is capable of moderately high turnover numbers (TONs), it may not be as robust a catalyst as $Rh_2(R-DOSP)_4$ or $Rh_2(S-DOSP)_4$ PTAD)₄, which are capable of TONs as high as 850,000 and 1,800,000 in respectively asymmetric intermolecular cyclopropanation.29

Table 2. Examination of Rh₂(R-BNP)₄ Loading

At the onset of this study, the asymmetric induction of the cyclopropanation was not expected to be heavily influenced by the functionality on the aryldiazoacetate. Having observed considerable variation in enantioselectivity depending on the nature of the aryl group, we decided to explore the effect of modifying the substitution on the styrene. These studies were focused on Rh₂(R-BNP)₄-catalyzed cyclopropanation with the 3,4-dimethoxyphenyldiazoacetate 1i (Table 3), because Rh₂(R-BNP)₄ had not been previously evaluated as a catalyst for this transformation. The levels of enantioselectivity in the cyclopropanation under $Rh_2(R-BNP)_4$ -catalyzed conditions were found to be moderately influenced by the functionality on the styrene, as the cyclopropanes 5a-g were obtained with uniformly high levels of enantioinduction (80-90% ee). Previous studies have shown that $Rh_2(R-DOSP)_4$ -catalyzed cyclopropanation is also not especially influenced by the nature of the styrene^{3,4,9} and the Rh₂(R-DOSP)₄-catalyzed cyclopropanation of a range of

styrenes (**4a-g**) with **1i** gave **5a-g** with modest levels of enantioselectivity (48-67% ee).

Table 3. Substrate Scope of Styrene with Rh₂(R-BNP)₄

MeO MeC	N2 CO2Me	0.5mol ⁰ to	4a-g % Rh ₂ (<i>R</i> -BNI bluene, rt	P) ₄ ►	5a-g	_OMe OMe
			Rh ₂ (R-E	BNP) ₄	Rh ₂ (R-D	OSP) ₄
entry	Ar	product	yield (%)	ee (%)	yield (%)	ee (%)
1		5a	76	90	47	64
2	- Vi	5b	90	88	50	67
3	MeO	5c	80	90	82	62
4	O ₂ N	5d	94	80	28	50
5	F ₃ C	5e	90	90	19	63
6	CI	5f	81	89	49	67
7	Cl Cl	5g	72	86	79	48

These studies reveal subtle differences in the ability of the chiral dirhodium tetracarboxylate catalysts to induce high enantioselectivity in the cyclopropanation of styrenes, as summarized in Table 4. The previous expectation that $Rh_2(R-DOSP)_4$ would give high asymmetric induction for all aryldiazoacetates was found not to be true, although it was found

TnQTable7Table 4. A Guide to Chiral Dirhodium-(II) Catalyzed Cyclopropanation

N ₂ Ar CO ₂ Me	Ph 2 .5-1 mol% Rh(II) solvent, rt	catalyst	Ph 3a-l Ar 63-93% yield 80-97% ee		
Ar	catalyst	yield (%)	ee (%)		
R'	Rh ₂ (<i>R</i> -DOSP) ₄	66-93	82- 92		
R=H, Cl R'=H, alkyl, Cl, OMe R=Cl, OMe	Rh ₂ (S-PTAD) ₄	80-87	80- 97		
Meo R R R R H, OMe	Rh ₂ (<i>R</i> -BNP) ₄	63-93	88- 97		

to be the most effective catalyst for the broadest range of substituted methyl aryldiazoacetates. In spite of the fact that $Rh_2(S-PTAD)_4$ is the most consistent catalyst when the acceptor group of the donor/acceptor carbenoid is modified, 19-22 the level of enantioselectivity was found to be highly variable when aryl substitution of the aryldiazoacetate was modified. In particular, Rh₂(S-PTAD)₄ was very effective with 2-chlorophenyl aryldiazoacetate derivative. $Rh_2(R-BNP)_4$ becomes the best catalyst for 3-methoxyphenyl-substituted aryldiazoacetate derivatives. The cause for these subtle variations, at this stage, is not well understood. There is no clear steric or electronic trend to define which catalyst will perform best in a given system, which suggests the asymmetric induction may involve a combination of factors including π -stacking interactions. Computational studies are in progress to develop a rational model to explain these trends.

3. Conclusion

This study provides guidelines for choosing the optimal chiral dirhodium-(II) catalyst for cyclopropanation of aryldiazoacetates. The nature of the aryl group on the aryldiazoacetate strongly affects the asymmetric induction imparted by the three catalysts studied. Depending on the aryl substituent, $Rh_2(R$ -DOSP)₄, $Rh_2(S$ -PTAD)₄, or $Rh_2(R$ -BNP)₄ can be utilized to obtain the desired cyclopropane with a high level of enantioinduction. In contrast, the functionality on the styrene has only moderate influence on the level of asymmetric induction in cyclopropanation reactions. These studies set the chemical foundation for our ongoing studies to develop therapeutically useful diarylcyclopropylamines, the results of which will be reported in due course.

4. Experimental Section

4.1 General: All reactions were conducted under anhydrous conditions in oven-dried glassware under an inert atmosphere of dry argon, unless otherwise stated. Hexanes, pentane, and toluene were dried by a solvent purification system (passed through activated alumina columns). All solvents were degassed by bubbling argon through the solvent for a minimum of 10 minutes prior to use. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ¹H Nuclear Magnetic Resonance (NMR) spectra were recorded at 400 MHz or 600MHz. Data presented as follows: chemical shift (in ppm on the δ scale relative to δ H 7.27 for the residual protons in CDCl₃), coupling constant (J/Hz), integration. Coupling constants were taken directly from the spectra and are uncorrected. ¹³C NMR spectra were recorded at 100 MHz and all chemical shift values are reported in ppm on the δ scale, with an internal reference of \deltaC 77.23 for CDCl3. Mass spectral determinations were carried out by using APCI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm⁻¹. Analytical TLC was performed on silica gel plates using UV light. Flash column chromatography was performed on silica gel 60Å (230-400 mesh). Optical rotations were measured on Jasco polarimeters. Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol:hexane as gradient. Chiral HPLC conditions were determined by obtaining separation of the racemic product. $Rh_2(R/S-DOSP)_4$ was employed as the catalyst in the racemic reactions. Styrene (2) and substituted styrenes (4a-f) were commercially available and purified by pushing through a silica-filled pipette prior to use. Rh₂(R-DOSP)₄,³ Rh₂(S-PTAD)₄,¹⁹ Rh₂(*R*-BNP)₄,²³ aryldiazoacetates **1a**- \mathbf{l} ,² and styrene $4\mathbf{g}^{30}$ were all synthesized according published procedures.

4.2 General Procedure for the Synthesis of Methyl Phenyldiazoacetates³¹

The methyl arylacetate (1 equiv.) and *p*-ABSA (1.3 equiv.) were dissolved in acetonitrile and cooled to 0 °C using an ice bath under an argon atmosphere. 1,8-Diazabicycloundec-7-ene (DBU, 1.3 equiv.) was then added to the stirring mixture over the course of 5 minutes. After the addition of the DBU, the reaction mixture continued to stir at 0 °C for an additional 15 minutes. Once this allotted time had passed, the ice bath was removed and the reaction mixture was stirred for 24 hours at room temperature. The resulting orange solution was quenched with saturated NH₄Cl and the aqueous layer was extracted with diethyl ether (3x). The organic layer was then washed with deionized H₂O to remove any residual salts. The combined organic layers were dried over MgSO₄ and filtered. The organic layer was then concentrated under reduced pressure. The residue was purified via flash chromatography on silica gel (10:1 Hexanes:EtOAc).

4.3 General Procedure for the Synthesis of Methyl Phenylcyclopropanecarboxylates with Rh₂(*R*-DOSP)₄

In a 25-mL round bottom flask (Flask A) equipped with a magnetic stir bar, styrene (5 equiv.) and $Rh_2(R-DOSP)_4$ (0.01 equiv.) were dissolved in dry, degassed pentane (3 mL). The reaction mixture was then degassed using vacuum/argon cycles (x3). In a separate 25-mL round bottom flask (Flask B), the methyl phenyldiazoacetate (0.5 mmol, 1 equiv.) was dissolved in dry, degassed pentane (5 mL) and degassed using vacuum/argon cycles (x3). The contents in Flask B were then added to Flask A using a syringe pump for the duration of 1 hour. After the addition, the reaction mixture continued to stir for 1 additional hour. Once the allotted time had passed, the reaction mixture was concentrated under reduced pressure and purified using silica gel column chromatography (increasing gradient starting at 10:1 Hexanes:EtOAc).

4.4 General Procedure for the Synthesis of Methyl Phenylcyclopropanecarboxylates with Rh₂(S-PTAD)₄

In a 25-mL round bottom flask (Flask A) equipped with a magnetic stir bar, styrene (5 equiv.) and $Rh_2(S-PTAD)_4$ (0.005 equiv.) were dissolved in dry, degassed pentane (3 mL). The reaction mixture was then degassed using vacuum/argon cycles (x3). In a separate 25-mL round bottom flask (Flask B), the methyl phenyldiazoacetate (0.5 mmol, 1 equiv.) was dissolved in dry, degassed pentane (5 mL) and degassed using vacuum/argon cycles (x3). The contents in Flask B were then added to Flask A using a syringe pump for the duration of 1 hour. After the addition, the reaction mixture continued to stir for 1 additional hour. Once the allotted time had passed, the reaction mixture was concentrated under reduced pressure and purified using silica gel column chromatography (increasing gradient starting at 10:1 Hexanes:EtOAc).

4.5 General Procedure for the Synthesis of Methyl Phenylcyclopropanecarboxylates with Rh₂(*R*-BNP)₄

In a 25-mL round bottom flask (Flask A) equipped with a magnetic stir bar, styrene (5 equiv.) and $Rh_2(R-BNP)_4$ (0.01 equiv.) were dissolved in dry, degassed toluene (3 mL). The reaction mixture was then degassed using vacuum/argon cycles (x3). In a separate 25-mL round bottom flask (Flask B), the methyl phenyldiazoacetate (0.5 mmol, 1 equiv.) was dissolved in dry, degassed pentane (5 mL) and degassed using vacuum/argon cycles (x3). The contents in Flask B were then added to Flask A using a syringe pump for the duration of 1 hour. After the addition, the reaction mixture continued to stir for 1 additional hour. Once the allotted time had passed, the reaction mixture

was concentrated under reduced pressure and purified using silica gel column chromatography (increasing gradient starting at 10:1 Hexanes:EtOAc).

4.1.1. (1*R*,2*S*)-methyl 1,2-diphenylcyclopropanecarboxylate (**3***a*). Title compound was prepared by general procedure and obtained as a white solid. 85% yield for Rh₂(*R*-DOSP)₄; 87% yield for Rh₂(*S*-PTAD)₄; 72% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel SS-WHELK, 1% *i*-PrOH in hexane, 1.0 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 8.62 min (major) and 10.22 min (minor), 88% ee for Rh₂(*R*-DOSP)₄; 21% ee for Rh₂(*S*-PTAD)₄; 42% ee for Rh₂(*R*-BNP)₄; *R*_f = 0.25 (hexane: ethyl acetate 10:1); ¹H NMR (600 MHz, CDCl₃) δ 7.12-7.11 (m, 3H), 7.05-7.01 (m, 5H), 6.77-6.75 (m, 2H), 3.70 (s, 3H), 3.11 (dd, *J* = 7.2, 9.3, 1H), 2.13 (dd, *J* = 4.8, 9.3, 1H), 1.88 (dd, *J* = 4.8, 7.2, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 136.5, 134.9, 132.1, 128.2, 127.9, 127.2, 126.5, 52.8, 37.6, 33.3, 20.7; Data are consistent with the literature.^{5.6}

4.1.2. (1S, 2R)-methyl 2-phenyl-1-(ptolyl)cyclopropanecarboxylate (3b). Title compound was prepared by general procedure and obtained as a white solid. 84% yield for Rh₂(R-DOSP)₄; 77% yield for Rh₂(S-PTAD)₄; 69% yield for Rh2(R-BNP)4; HPLC: (Chiralcel SS-WHELK, 1% i-PrOH in hexane, 1.0 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 10.57 min (major) and 14.13 min (minor), 87% ee for $Rh_2(R-DOSP)_4$; 46% ee for $Rh_2(S-PTAD)_4$; 51% ee for $Rh_2(R-BNP)_4$; $R_f = 0.44$ (4:1 Hexanes:EtOAc); $[\alpha]_D^{20}$: +17.2° (c. 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.11-7.07 (m, 3H), 6.98-6.92 (m, 4H), 6.82-6.80 (m, 2H), 3.69 (s, 3H), 3.12 (dd, J = 9.2 and 7.2 Hz, 1H), 2.27 (s, 3H), 2.16 (dd, J = 9.6 and 4.8 Hz, 1H), 1.88 (dd, J = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.8, 136.8, 136.7, 131.9, 131.8, 128.7, 128.3, 127.9, 126.5, 52.9, 37.3, 33.4, 21.4, 20.9; IR (film): 3028, 2950, 1716, 1255; HRMS (APCI) calcd for C₁₈H₁₉O₂ (M+H)⁺ 267.1380 found 267.1380

2-phenyl-1-(4-413 (1S, 2R)-methyl Title (trifluoromethyl)phenyl)cyclopropanecarboxylate (3c). compound was prepared by general procedure and obtained as a transparent oil. 93% yield for Rh₂(R-DOSP)₄; 67% yield for Rh₂(S-PTAD)₄; 80% yield for Rh₂(R-BNP)₄; HPLC: (Chiralcel OD-H, 0.5% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, λ = 254 nm) retention times of 8.27 min (minor) and 10.34 min (major), 87% ee for $Rh_2(R$ -DOSP)₄; 77% ee for $Rh_2(S$ -PTAD)₄; 57% ee for Rh₂(*R*-BNP)₄; $R_f = 0.44$ (4:1 Hexanes:EtOAc); $[\alpha]^{20}_{D}$: 19.1 (c. 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.36 (d, J = 8 Hz, 2H), 7.12 (d, J = 8 Hz, 2H), 7.06 (m, 3H), 6.74 (m, 2H), 3.66 (s, 3H), 3.14 (dd, J = 9.6 and 7.6 Hz, 1H), 2.17 (dd, J = 9.2 and 5.2 Hz, 1H), 1.88 (dd, J = 7.2 and 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 139.2, 135.8, 132.4, 128.1, 126.9, 125.0, 124.9, 124.8, 124.7, 53.0, 37.2, 33.5, 20.4; IR (film): 3032, 2954, 1719, 1501, 1322, 1257; HRMS (APCI) calcd for $C_{18}H_{16}O_2F_3 (M+H)^+$ 321.1097 found 321.1097

4.1.4. (15,2*R*)-methyl 1-(4-chlorophenyl)-2phenylcyclopropanecarboxylate (3d). Title compound was prepared by general procedure and obtained as a transparent oil. 87% yield for Rh₂(*R*-DOSP)₄; 71% yield for Rh₂(*S*-PTAD)₄; 89% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OJ-H, 1% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 8.62 min (minor) and 12.58 min (major), 88% ee for Rh₂(*R*-DOSP)₄; 48% ee for Rh₂(*S*-PTAD)₄; 57% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.56 (4:1 Hexanes:EtOAc); [α]²⁰_D: 4.8 (c. 1, chloroform); ¹H NMR (300 MHz; CDCl₃) δ 7.12-7.06 (m, 5H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.79-6.76 (m, 2H), 3.67 (s, 3H), 3.12 (dd, *J* = 9.3 and 7.5 Hz, 1H), 2.15 (dd, *J* = 9.3 and 4.8 Hz, 1H), 1.85 (dd, *J* = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 136.1, 133.7, 133.4, 133.2, 128.3, 128.2, 128.1, 126.8, 52.9, 36.9, 33.4, 20.6; IR (film): 3031, 2951, 1717, 1493, 1255; HRMS (APCI) calcd for $C_{17}H_{16}O_2Cl~\left(M+H\right)^+$ 287.0833 found 287.0833.

4.1.5. (1S,2R)-methyl 1-(4-methoxyphenyl)-2phenylcyclopropanecarboxylate (3e). Title compound was prepared by general procedure and obtained as a white solid. 66% yield for Rh₂(*R*-DOSP)₄; 93% yield for Rh₂(S-PTAD)₄; 84% yield for Rh₂(R-BNP)₄; HPLC: (Chiralcel OD-H, 0.7% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 11.97 min (major) and 17.71 min (minor), 90% ee for Rh₂(R-DOSP)₄; 96% ee for Rh₂(S-PTAD)₄; 57% ee for Rh₂(R-BNP)₄; $R_f = 0.39$ (4:1 Hexanes:EtOAc); $[\alpha]_D^{20} = +5.1^\circ$ (c = 1, chloroform); ¹H NMR (400 MHz; CDCl₃) & 7.10-7.07 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 6.80-6.77 (m, 2H), 6.68 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 3.68 (s, 3H), 3.09 (dd, J = 9.2 and 7.6 Hz, 1H), 2.14 (dd, J = 9.2 and 4.8 Hz, 1H), 1.84 (dd, J = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 158.6, 136.7, 133.1, 128.3, 127.9, 127.0, 126.5, 113.4, 55.3, 52.8, 36.9, 33.4, 21.0; IR (film): 3031, 2951, 2836, 1715, 1515, 1245; HRMS (APCI) calcd for $C_{18}H_{19}O_3 (M+H)^+$ 283.1329 found 283.1328.

4.1.6 (1S, 2R)-methyl 1-(2-chlorophenyl)-2phenylcyclopropanecarboxylate (3f). Title compound was prepared by general procedure and obtained as a transparent oil. 89% yield for Rh₂(R-DOSP)₄; 80% yield for Rh₂(S-PTAD)₄; 78% yield for Rh₂(R-BNP)₄; HPLC: (Chiralcel OJ-H, 0.5% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 11.47 min (major) and 15.27 min (major), 92% ee for $Rh_2(R-DOSP)_4$; 97% ee for $Rh_2(S-PTAD)_4$; 51% ee for $Rh_2(R-PTAD)_4$ BNP)₄; $R_f = 0.43$ (4:1 Hexanes:EtOAc); $[\alpha]^{20}_{D}$: 61.8 (c. 1, chloroform); ¹H NMR (300 MHz; CDCl₃) δ 7.18-7.02 (m, 7H), 6.84-6.76 (m, 2H), 3.68 (s, 3H), 3.13 (t, J = 8.7 Hz, 1H), 2.10 (m, 1H), 1.91 (dd, J = 7.2 and 5.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 137.5, 133.5, 129.6, 128.9, 128.2, 127.6, 126.6, 126.4, 52.9, 33.5, 29.9, 21.7; IR (film): 3031, 2950, 1718, 1251, 694; HRMS (APCI) calcd for C₁₇H₁₆O₂Cl (M+H)⁺ 287.0833 found 287.0833.

4.1.7. (1S, 2R)-methyl 1-(2-methoxyphenyl)-2phenylcyclopropanecarboxylate (3g). Title compound was prepared by general procedure and obtained as a white solid. 92% yield for Rh₂(R-DOSP)₄; 87% yield for Rh₂(S-PTAD)₄; 69% yield for Rh2(R-BNP)4; HPLC: (SS-WHELK column, 1% i-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 11.65 min (minor) and 14.00 min (major), 86% ee for $Rh_2(R-DOSP)_4$; 80% ee for $Rh_2(S-PTAD)_4$; 27% ee for $Rh_2(R-DOSP)_4$; 28% ee for $Rh_2(R-DOSP)_4$ BNP)₄; $R_f = 0.45$ (4:1 Hexanes:EtOAc); $[\alpha]_{D}^{20}$: +133.3° (c. 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.19-7.10 (m, 2H), 7.04-6.98 (m, 3H), 6.86 (td, J = 7.6, 1.1 Hz, 1H), 6.81-6.74 (m, 2H), 6.53 (d, J = 8 Hz, 1H), 3.65 (s, 3H), 3.36 (s, 3H), 3.24 (dd, J = 9.6 and 7.6 Hz, 1H), 1.98 (dd, J = 9.2 and 4.8 Hz, 1H), 1.85 (dd, J = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 159.2, 137.0, 131.8, 128.9, 127.9, 127.3, 126.1, 124.1, 120.1, 110.5, 55.2, 52.7, 34.3, 32.6, 20.8; IR (film): 3030, 2950, 2835, 1716, 1496, 1242; HRMS (APCI) calcd for C₁₈H₁₉O₃ $(M+H)^+$ 283.1329 found 283.1329.

4.1.8. (1*S*,2*R*)-methyl 1-(3,4-dichlorophenyl)-2phenylcyclopropanecarboxylate (3*h*). Title compound was prepared by general procedure and obtained as a clear oil; 88% yield for Rh₂(*R*-DOSP)₄; 88% yield for Rh₂(*S*-PTAD)₄; 82% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 1% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 7.54 min (minor) and 9.78 min (major), 82% ee for Rh₂(*R*-DOSP)₄; 60% ee for Rh₂(*S*-PTAD)₄; 63% ee for Rh₂(*R*-BNP)₄; *R*_f = 0.23 (Hexane:EtOAc = 7:1); [α] ²⁰_{D:} -8.1° (c = 1.60, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.16 (m, 2H), 7.14-7.10 (m, 3H), 6.82-6.79 (m, 3H), 3.68 (s, 3H), 3.14 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.15 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.84 (dd, *J* = 7.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 135.3, 135.2, 133.7, 131.6, 131.4, 131.2, 129.6, 128.0, 127.9, 126.8, 52.8, 36.3, 33.3, 20.2; IR (film): 2925, 1719, 1257, 1163, 695; HRMS (ESI) calcd for C₁₇H₁₃O₂Cl₂ (M-H)⁺ 319.0293 found 319.0299.

4.1.9. (1S,2R)-methyl 1-(3,4-dimethoxyphenyl)-2phenylcyclopropanecarboxylate (3i). Title compound was prepared by general procedure and obtained as a white solid. 74% yield for Rh₂(R-DOSP)₄; 70% yield for Rh₂(S-PTAD)₄; 93% yield for 1 mol% Rh₂(R-BNP)₄; 83% yield for 0.5 mol% Rh₂(R-BNP)₄; 80% yield for 0.1 mol% Rh₂(R-BNP)₄; 73% yield for 0.01 mol% Rh₂(R-BNP)₄; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 13.99 min (minor) and 17.97 min (major), 56% ee for $Rh_2(R-DOSP)_4$; 94% ee for $Rh_2(S-PTAD)_4$; 97% ee for 1 mol% Rh₂(R-BNP)₄; 96% ee for 0.5 mol% Rh₂(R-BNP)₄; 91% ee for 0.1 mol% Rh₂(R-BNP)₄; 40% ee for 0.01 mol% Rh₂(R-BNP)₄; R_f = 0.20 (hexane: ethyl acetate 4:1); mp 88-89°C; $[\alpha]_{D}^{20}$ +28.4° (c = 1.51, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.07 (m, 3H), 6.81-6.79 (m, 2H), 6.69 (m, 2H), 6.36 (s, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 3.56 (s, 3H), 3.08 (dd, J = 9.2, 7.6 Hz, 1H), 2.14 (dd, J = 9.2, 4.4 Hz, 1H), 1.84 (dd, J = 7.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 147.8, 136.4, 127.9, 127.7, 127.2, 126.3, 123.9, 115.3, 110.2, 55.5, 52.6, 36.9, 33.1, 20.8; IR (film): 2924, 1716, 1518, 1455, 1434, 1413, 1341, 1229, 1208, 1177; HRMS (ESI) calcd for $C_{19}H_{21}O_4$ (M+H)⁺ 313.1440 found 313.1433.

4.1.10. (1S, 2R)-methyl 1-(3-methoxyphenyl)-2phenylcyclopropanecarboxylate (3j). Title compound was prepared by general procedure and obtained as a yellow oil. 78% yield for Rh₂(R-DOSP)₄; 72% yield for Rh₂(S-PTAD)₄; 82% yield for Rh₂(R-BNP)₄; HPLC: (Chiralcel OD-H, 0.7% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm), retention times of 9.50 min (major) and 11.38 min (minor), 79% ee for $Rh_2(R-DOSP)_4$; 16% ee for $Rh_2(S-PTAD)_4$; 88% ee for $Rh_2(R-PTAD)_4$ BNP)₄; $R_f = 0.25$ (hexane: ethyl acetate 9:1); $[\alpha]_{D}^{20} + 21.1^{\circ}$ (c = 1.25, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.03 (m, 4H), 6.81-6.79 (m, 2H), 6.69-6.63 (m, 2H), 6.53-6.52, (m, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 3.12 (dd, J = 9.6, 7.2 Hz, 1H), 2.12 (dd, J = 9.2, 4.8 Hz, 1H), 1.87 (dd, J = 7.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 158.8, 136.4, 136.2, 128.5, 127.9, 127.7, 126.3, 124.4, 117.5, 112.9, 55.0, 52.6, 37.3, 33.1, 20.6; IR (film): 2925, 1717, 1602, 1454, 1239, 697; HRMS (ESI) calcd for C₁₈H₁₉O₃ (M+H)⁺ 283.1334 found 283.1329.

4.1.11. (1S, 2R)-methyl 1-(3,5-dimethoxyphenyl)-2phenylcyclopropanecarboxylate (3k). Title compound was prepared by general procedure and obtained as a yellow oil. 85% yield for Rh₂(R-DOSP)₄; 85% yield for Rh₂(S-PTAD)₄; 69% yield for Rh₂(R-BNP)₄; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 7.33 min (major) and 9.07 min (minor), 28% ee for $Rh_2(R-DOSP)_4$; 3% ee for $Rh_2(S-PTAD)_4$; 92% ee for $Rh_2(R-DOSP)_4$ BNP)₄; $R_f = 0.31$ (hexane: ethyl acetate 5:1); $[\alpha]^{20}_{D} + 33.7^{\circ}$ (c = 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.10-7.08 (m, 3H), 6.82 (dd, J = 7.2, 2.4 Hz, 2H), 6.24 (t, J=2.4 Hz, 1H), 6.15 (d, J=2.4 Hz, 2H), 3.68 (s, 3H), 3.56 (s, 6H), 3.08 (dd, J = 9.2, 7.2 Hz, 1H), 2.10 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.84 (dd, *J* = 7.2, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 160.1, 137.2, 136.6, 128.2, 128.0, 126.6, 110.4, 99.8, 55.4, 52.9, 37.7, 33.3, 20.9; IR (film): 2951, 2840, 1715, 1594, 1456, 1425, 1260, 1203, 1151, 1046, 715, 692; HRMS (APCI) calcd for $C_{19}H_{21}O_4$ (M+H)⁺ 313.1434 found 313.1435.

4.1.12. (1S, 2R)-methyl 2-phenyl-1-(3,4,5trimethoxyphenyl)cyclopropanecarboxylate (31). Title compound was prepared by general procedure and obtained as a yellow oil. 98% yield for Rh₂(*R*-DOSP)₄; 95% yield for Rh₂(S-PTAD)₄; 63% yield for Rh₂(R-BNP)₄; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm), retention times of 10.78 min (minor) and 11.79 min (minor), 34% ee for $Rh_2(R-DOSP)_4$; 9% ee for $Rh_2(S-PTAD)_4$; 90% ee for $Rh_2(R-DOSP)_4$; 9% ee for BNP)₄; $R_f = 0.20$ (hexane: ethyl acetate 5:1); $[\alpha]_{D}^{20} + 17.5^{\circ}$ (c = 2.02, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.07 (m, 3H), 6.81-6.78 (m, 2H), 6.16 (s, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.59 (s, 6H), 3.07 (dd, J = 9.2, 7.2 Hz, 1H); 2.14 (dd, J = 9.6, 4.8 Hz, 1H), 1.82 (dd, *J* = 7.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 152.3, 136.5, 130.3, 128.0, 127.7, 126.4, 109.4, 60.7, 55.9, 52.6, 37.4, 33.1 20.8; IR (film): 2925, 1716, 1587, 1413, 1258, 1235, 1153, 1124; HRMS (ESI) calcd for C₂₀H₂₃O₄ (M+H)⁺ 345.1485 found 345.1485.

(1S,2R)-methyl 1-(3,4-dimethoxyphenyl)-2-(m-4.1.13. tolyl)cyclopropanecarboxylate (5a). Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 2-methylstyrene (148 mg, 1.25 mmol, 2.5 equiv), and Rh₂(R-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford a yellow/green oil (114 mg, 76 % yield). $R_f = 0.12$ (hexane: ethyl acetate 5:1); $[\alpha]_{D}^{20}$ $+28.7^{\circ}$ (c = 1.23, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.63 (m, 2H), 6.42 (d, J = 7.6 Hz, 1H), 6.34 (s, 1H), 3.77 (s, 3H),3.71 (s, 3H), 3.57 (s. 3H), 3.11 (dd, J = 9.2, 7.6 Hz, 1H), 2.51 (s, 3H), 2.06 (dd, J = 9.2, 5.0 Hz, 1H), 1.99 (dd, J = 7.6, 5.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 147.9, 137.8, 134.7, 129.7, 127.8, 126.7, 126.0, 125.8, 123.7, 114.7, 110.3, 55.7, 55.6, 52.8, 36.0, 31.2, 20.2, 19.5; IR (film): 2951, 1713, 1516, 1463, 1435, 1251, 1140, 1026, 740; HRMS (APCI) calcd for C₂₀H₂₃O₄ (M+H)⁺ 327.1591 found 327.1591; HPLC: (Chiralcel OD-H. 3%) *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 17.81 min (minor) and 19.31 min (major), 90% ee for Rh₂(R-BNP)₄, 64% ee for Rh₂(R-DOSP)₄.

4.1.14. (1S, 2R)-methyl 1-(3,4-dimethoxyphenyl)-2-(ptolyl)cyclopropanecarboxylate (5b). Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4-methylstyrene (148 mg, 1.25 mmol, 2.5 equiv), and Rh₂(R-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford a yellow/green oil (147 mg, 90% yield). $R_f = 0.12$ (hexane: ethyl acetate 5:1); $[\alpha]_{D}^{20}$ $+27.7^{\circ}$ (c = 1.24, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.88 (d, J = 8.0 Hz, 2H), 6.69-6.67 (m, 4H), 6.37 (s, 1H), 3.81 (s, 3H), 3.67 (s, 3H), 3.57 (s, 3H), 3.05 (dd, J = 9.2, 7.6 Hz, 1H), 2.22 (s, 3H), 2.11 (dd, J = 9.2, 4.8 Hz, 1H), 1.80 (dd, J = 7.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 147.9, 136.0, 133.5, 128.6, 128.0, 127.6, 124.1, 115.5, 110.3, 55.7, 55.6, 52.7, 36.9, 33.1, 21.0, 20.9; IR (film): 2951, 1714, 1589, 1516, 1435, 1413, 1341, 1315, 1250, 1228, 1155, 1027; HRMS (APCI) calcd for C₂₀H₂₃O₄ (M+H)⁺ 327.1591 found 327.1591; HPLC: (Chiralcel OD-H, 3% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda =$ 254 nm) retention times of 17.3 min (minor) and 20.1 min (major), 88% ee for Rh₂(*R*-BNP)₄, 67% ee for Rh₂(*R*-DOSP)₄.

4.1.15. (1S,2R)-methyl 1-(3,4-dimethoxyphenyl)-2-(4methoxyphenyl)cyclopropanecarboxylate (5c). Prepared by general procedure with methyl 2-diazo-2-(3,4dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4methoxystyrene (168 mg, 1.25 mmol, 2.5 equiv), and Rh₂(R-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv. The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford an off-white solid (137 mg, 80% yield). $R_f = 0.20$ (hexane: ethyl acetate 3:1); mp 123-125°C; $[α]^{20}_D + 33.1°$ (c = 1.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.73-6.61 (m, 6H), 6.41 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.60 (s, 3H), 3.03 (dd, J = 9.2, 7.6 Hz, 1H), 2.10 (dd, J = 9.2, 4.8 Hz, 1H), 1.76 (dd, J = 7.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 175.1, 158.6, 148.3, 129.5, 128.9, 127.9, 124.6, 115.9, 113.7, 110.7, 56.1, 55.6, 53.1, 37.1, 33.2, 21.3; IR (film): 2952, 1714, 1611, 1589, 1515, 1463, 1437, 1413, 1341, 1248, 1228, 1177, 1153; HRMS (APCI) calcd for C₂₀H₂₂O₅ (M+H)⁺ 342.14618 found 342.14589; HPLC: (Chiralcel OD-H, 5% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, λ = 254 nm) retention times of 19.2 min (minor) and 22.9 min (major), 90% ee for Rh₂(*R*-BNP)₄, 62% ee for Rh₂(*R*-DOSP)₄.

4.1.16. (1S, 2R)-methyl 1-(3,4-dimethoxyphenyl)-2-(4nitrophenyl)cyclopropanecarboxylate (5d). Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4-nitrostyrene (186 mg, 1.25 mmol, 2.5 equiv), and Rh₂(R-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford yellow oil (168 mg, 94% yield). $R_f = 0.28$ (hexane: ethyl acetate 3:1); $[\alpha]_D^{20} + 15.5^\circ$ (c = 1.07, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.2 Hz, 1H), 6.61 (dd, J = 8.2, 2.0 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.62 (s, 3H), 3.16 (dd, J = 9.2, 7.6 Hz, 1H), 2.22 (dd, J = 9.2, 5.4 Hz, 1H), 1.91 (dd, J = 7.6, 5.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 148.5, 145.1, 128.7, 126.2, 124.2, 123.0, 115.0, 110.6, 55.9, 55.8, 53.0, 38.4, 32.6, 29.8, 21.8; IR (film): 2924, 1717, 1597, 1515, 1463, 1415, 1342, 1229, 1206, 1156, 1141; HRMS (APCI) calcd for $C_{19}H_{20}O_6N_1$ (M+H)⁺ 358.12851 found 358.12836; HPLC: (Chiralcel OD-H, 6% i-PrOH in hexane, 1 mL/min, 1 mg/mL, 60 min, $\lambda = 254$ nm) retention times of 30.4 min (minor) and 41.0 min (major), 80% ee for $Rh_2(R-BNP)_4$, 50% ee for $Rh_2(R-DOSP)_4$.

4.1.17. (1S, 2R)-methyl 1-(3,4-dimethoxyphenyl)-2-(4trifluoromethyl)phenyl)cyclopropanecarboxylate (5e). Prepared bv general procedure with methyl 2-diazo-2-(3,4dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), styrene (215 mg, 1.25 mmol, 2.5 equiv), and Rh₂(R-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (6:1) to afford a yellow oil (171 mg, 90% yield); $R_f = 0.24$ (hexane: ethyl acetate 4:1); $[\alpha]_{D}^{20} + 16.5^{\circ}$ (c = 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 6.70-6.65 (m, 2H), 6.35 (s, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 3.56 (s, 3H), 3.11 (t, 1H), 3.12 (dd, J = 9.2, 7.2 Hz, 1H), 2.18 (dd, J = 9.2, 4.8 Hz, 1H), 1.85 (dd, J = 7.2, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 148.7, 148.6, 141.5, 128.7, 127.0, 124.8, 124.7, 124.6, 124.3, 115.6, 110.9, 56.1, 53.2, 38.0, 33.0, 21.7; IR (film): 2954, 1718, 1517, 1465, 1437, 1414, 1324, 1252, 1230, 1210, 1193; HRMS (APCI) calcd for $C_{20}H_{19}F_{3}O_{4}$ (M+H)⁺ 380.12300 found 380.12251; HPLC: (Chiralcel OD-H, 6% i-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 12.6 min (minor) and 15.6 min (major), 90% ee for Rh₂(R-BNP)₄, 63% ee for $Rh_2(R-DOSP)_4$.

4.1.18. (1S,2R)-methyl 2-(4-chlorophenyl)-1-(3,4dimethoxyphenyl)cyclopropanecarboxylate (5f). Prepared by general procedure with methyl 2-diazo-2-(3,4dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4chlorostyrene (173 mg, 1.25 mmol, 2.5 equiv), and Rh₂(*R*-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (6:1) to afford clear oil (123 mg, 89% yield). $R_f = 0.30$ (hexane: ethyl acetate 3:1); $[\alpha]^{20}_{D} + 13.4^{\circ}$ (c = 1.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, J = 8.4 Hz, 2H), 6.72-6.63 (m, 4H), 6.38 (d, J = 1.6 Hz, 1H), 3.81 (s, 3H), 3.67 (s. 3H), 3.61 (s, 3H), 3.04 (dd, J = 9.2, 7.2 Hz, 1H), 2.13 (dd, J = 9.2, 4.8 Hz, 1H), 1.78 (dd, J = 7.2, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 148.2, 148.2, 135.4, 132.3, 129.4, 128.0, 127.0, 124.2, 115.4, 110.5, 55.9, 55.8, 52.8, 37.2, 32.6, 21.2; IR (film): 2951, 1715, 1589, 1517, 1496, 1435, 1413, 1371, 1341, 1307, 1228,1177, 1155, 1139; HRMS (APCI) calcd for C₁₉H₁₉ClO₄ (M+H)⁺ 346.09664 found 346.09632; HPLC: (Chiralcel OD-H, 5% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 14.9 min (minor) and 18.5 min (major), 89% ee for Rh₂(*R*-BNP)₄, 67% ee for Rh₂(*R*-DOSP)₄.

2-(3,4-dichlorophenyl)-1-(3,4-4.1.19. (1S,2R)-methyl dimethoxyphenyl)cyclopropanecarboxylate (5g). Methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (2.7g, 11.6 mmol, 1 equiv) in 153 mL dry and degassed toluene was added by syringe pump over 2 h to a solution of 1,2-dichloro-4-vinylbenzene (2.4 g, 13.9 mmol, 1.2 equiv) and Rh₂(R-BNP)₄ (92.2 mg, 0.06 mmol, 0.005 equiv) in 77 mL toluene. After addition, the solution was allowed to stir overnight and toluene was removed in vacuo. The remaining residue was purified on silica gel (hexane:ethyl acetate 5:1) to afford a clear oil (3.2 g, 72% yield for Rh₂(R-BNP)₄ [enantiomer shown above]; 2.3g, 52% yield for Rh₂(*S*-BNP)₄) R_f = 0.17 (hexane: ethyl acetate 5:1); $[\alpha]^{20}_{D}$ +4.1° (c = 1.03, CHCl₃) for $Rh_2(R-BNP)_4$; $[\alpha]_{D}^{20}$ -6.9° (c = 1.05, CHCl₃) for $Rh_2(S-BNP)_4$; ¹H NMR (600 MHz, CDCl₃) δ 7.10 (d, J = 9.0 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.69 (d, J = 9.0 Hz, 1H), 6.63 (dd, J = 9.0, 2.4 Hz, 1H), 6.51 (dd, J = 9.0, 2.4 Hz, 1H), 6.44 (d, J = 1.8 Hz, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.02 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.13(dd, J = 9.0, 5.1 Hz, 1H), 1.78 (dd, J = 7.2, 5.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 148.4, 148.3, 137.4, 131.9, 130.5, 130.4, 129.7, 127.0, 126.6, 124.2, 115.2, 110.6, 55.9, 55.8, 52.9, 37.4, 32.1, 21.1; IR (film): 2951, 2836, 1716, 1559, 1516, 1413, 1229, 1178, 1137, 1027, 764; HRMS (APCI) calcd for $C_{19}H_{19}Cl_2O_4$ (M+H)⁺ 381.2498 found 381.2498; HPLC: (Chiralcel OD-H, 5% i-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 15.4 min (minor) and 17.9 min (major), 86% ee for Rh₂(R-BNP)₄; retention times of 15.3 min (major) and 19.7 min (minor) 85% ee for Rh₂(S-BNP)₄, 48% ee for Rh₂(R-DOSP)₄.

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Supplementary Material

Detailed experimental for the compounds, HPLC traces for all chiral compounds, ¹H NMR and ¹³C NMR spectra for all new compounds are described in Supplementary data. Supplementary data associated with this article can be found in the online version.

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Supplementary Material

Guide to Highly Enantioselective Chiral Dirhodium(II)-Catalyzed Cyclopropanation

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Table of Contents

General Experimental	
Details	 S-2
General procedure	
Characterization of new compounds	S-4-S-14
References	S.14
1H 13C-NMR spectra and HPLC trace	S15-875

General: All reactions were conducted under anhydrous conditions in oven-dried glassware under an inert atmosphere of dry argon, unless otherwise stated. Hexanes, pentane, and toluene were dried by a solvent purification system (passed through activated alumina columns). All solvents were degassed by bubbling argon through the solvent for a minimum of 10 minutes prior to use. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ¹H Nuclear Magnetic Resonance (NMR) spectra were recorded at 400 MHz or 600MHz. Data presented as follows: chemical shift (in ppm on the δ scale relative to δ H 7.27 for the residual protons in CDCl₃), coupling constant (J/Hz), integration. Coupling constants were taken directly from the spectra and are uncorrected. ¹³C NMR spectra were recorded at 100 MHz and all chemical shift values are reported in ppm on the δ scale, with an internal reference of δC 77.23 for CDCl₃. Mass spectral determinations were carried out by using APCI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm⁻¹. Analytical TLC was performed on silica gel plates using UV light. Flash column chromatography was performed on silica gel 60Å (230-400 mesh). Optical rotations were measured on Jasco polarimeters. Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol:hexane as gradient. Chiral HPLC conditions were determined by obtaining separation of the racemic product. $Rh_2(R/S-$ DOSP)₄ was employed as the catalyst in the racemic reactions. Styrene (2) and substituted styrenes (4a-f) were commercially available and purified by pushing through a silica-filled pipette prior to use. $Rh_2(R-DOSP)_4$, $^1 Rh_2(S-PTAD)_4$, $^2 Rh_2(R-BNP)_4$, 3 aryldiazoacetates **1a-1**, 4 and styrene $4g^5$ were all synthesized according published procedures.

General Procedure for the Synthesis of Methyl Phenyldiazoacetates⁶

The methyl arylacetate (1 equiv.) and *p*-ABSA (1.3 equiv.) were dissolved in acetonitrile and cooled to 0 °C using an ice bath under an argon atmosphere. 1,8-Diazabicycloundec-7-ene (DBU, 1.3 equiv.) was then added to the stirring mixture over the course of 5 minutes. After the addition of the DBU, the reaction mixture continued to stir at 0 °C for an additional 15 minutes. Once this allotted time had passed, the ice bath was removed and the reaction mixture was stirred for 24 hours at room temperature. The resulting orange solution was quenched with saturated NH₄Cl and the aqueous layer was extracted with diethyl ether (3x). The organic layer was then washed with deionized H₂O to remove any residual salts. The combined organic layers were

dried over $MgSO_4$ and filtered. The organic layer was then concentrated under reduced pressure. The residue was purified via flash chromatography on silica gel (10:1 Hexanes:EtOAc).

General Procedure for the Synthesis of Methyl Phenylcyclopropanecarboxylates with Rh₂(*R*-DOSP)₄

In a 25-mL round bottom flask (Flask A) equipped with a magnetic stir bar, styrene (5 equiv.) and $Rh_2(R$ -DOSP)₄ (0.01 equiv.) were dissolved in dry, degassed pentane (3 mL). The reaction mixture was then degassed using vacuum/argon cycles (x3). In a separate 25-mL round bottom flask (Flask B), the methyl phenyldiazoacetate (0.5 mmol, 1 equiv.) was dissolved in dry, degassed pentane (5 mL) and degassed using vacuum/argon cycles (x3). The contents in Flask B were then added to Flask A using a syringe pump for the duration of 1 hour. After the addition, the reaction mixture continued to stir for 1 additional hour. Once the allotted time had passed, the reaction mixture was concentrated under reduced pressure and purified using silica gel column chromatography (increasing gradient starting at 10:1 Hexanes:EtOAc).

General Procedure for the Synthesis of Methyl Phenylcyclopropanecarboxylates with Rh₂(S-PTAD)₄

In a 25-mL round bottom flask (Flask A) equipped with a magnetic stir bar, styrene (5 equiv.) and $Rh_2(S-PTAD)_4$ (0.005 equiv.) were dissolved in dry, degassed pentane (3 mL). The reaction mixture was then degassed using vacuum/argon cycles (x3). In a separate 25-mL round bottom flask (Flask B), the methyl phenyldiazoacetate (0.5 mmol, 1 equiv.) was dissolved in dry, degassed pentane (5 mL) and degassed using vacuum/argon cycles (x3). The contents in Flask B were then added to Flask A using a syringe pump for the duration of 1 hour. After the addition, the reaction mixture continued to stir for 1 additional hour. Once the allotted time had passed, the reaction mixture was concentrated under reduced pressure and purified using silica gel column chromatography (increasing gradient starting at 10:1 Hexanes:EtOAc).

General Procedure for the Synthesis of Methyl Phenylcyclopropanecarboxylates with $Rh_2(R-BNP)_4$

In a 25-mL round bottom flask (Flask A) equipped with a magnetic stir bar, styrene (5 equiv.) and $Rh_2(R$ -BNP)₄ (0.01 equiv.) were dissolved in dry, degassed toluene (3 mL). The

reaction mixture was then degassed using vacuum/argon cycles (x3). In a separate 25-mL round bottom flask (Flask B), the methyl phenyldiazoacetate (0.5 mmol, 1 equiv.) was dissolved in dry, degassed pentane (5 mL) and degassed using vacuum/argon cycles (x3). The contents in Flask B were then added to Flask A using a syringe pump for the duration of 1 hour. After the addition, the reaction mixture continued to stir for 1 additional hour. Once the allotted time had passed, the reaction mixture was concentrated under reduced pressure and purified using silica gel column chromatography (increasing gradient starting at 10:1 Hexanes:EtOAc).



(1*R*,2*S*)-methyl 1,2-diphenylcyclopropanecarboxylate (3a): Title compound was prepared by general procedure and obtained as a white solid. 85% yield for Rh₂(*R*-DOSP)₄; 87% yield for Rh₂(*S*-PTAD)₄; 72% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel SS-WHELK, 1% *i*-PrOH in hexane, 1.0 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 8.62 min (major) and 10.22 min (minor), 88% ee for Rh₂(*R*-DOSP)₄; 21% ee for Rh₂(*S*-PTAD)₄; 42% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.25 (hexane: ethyl acetate 10:1); ¹H NMR (600 MHz, CDCl₃) δ 7.12-7.11 (m, 3H), 7.05-7.01 (m, 5H), 6.77-6.75 (m, 2H), 3.70 (s, 3H), 3.11 (dd, *J* = 7.2, 9.3, 1H), 2.13 (dd, *J* = 4.8, 9.3, 1H), 1.88 (dd, *J* = 4.8, 7.2, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 136.5, 134.9, 132.1, 128.2, 127.9, 127.2, 126.5, 52.8, 37.6, 33.3, 20.7; Data are consistent with the literature.^{5,7}



(1*S*,2*R*)-methyl 2-phenyl-1-(*p*-tolyl)cyclopropanecarboxylate (3b): Title compound was prepared by general procedure and obtained as a white solid. 84% yield for Rh₂(*R*-DOSP)₄; 77% yield for Rh₂(*S*-PTAD)₄; 69% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel SS-WHELK, 1% *i*-PrOH in hexane, 1.0 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 10.57 min (major) and 14.13 min (minor), 87% ee for Rh₂(*R*-DOSP)₄; 46% ee for Rh₂(*S*-PTAD)₄; 51% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.44 (4:1 Hexanes:EtOAc); [α]²⁰_D: ⁺17.2° (c. 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.11-7.07 (m, 3H), 6.98-6.92 (m, 4H), 6.82-6.80 (m, 2H), 3.69 (s, 3H), 3.12 (dd, *J* = 9.2 and 7.2 Hz, 1H), 2.27 (s, 3H), 2.16 (dd, *J* = 9.6 and 4.8 Hz, 1H), 1.88 (dd, *J* = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.8, 136.8, 136.7, 131.9, 131.8, 128.7, 128.3,

127.9, 126.5, 52.9, 37.3, 33.4, 21.4, 20.9; IR (film): 3028, 2950, 1716, 1255; HRMS (APCI) calcd for $C_{18}H_{19}O_2$ (M+H)⁺ 267.13796 found 267.13797.



(1*S*,2*R*)-methyl 2-phenyl-1-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylate (3c): Title compound was prepared by general procedure and obtained as a transparent oil. 93% yield for Rh₂(*R*-DOSP)₄; 67% yield for Rh₂(*S*-PTAD)₄; 80% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 0.5% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 8.27 min (minor) and 10.34 min (major), 87% ee for Rh₂(*R*-DOSP)₄; 77% ee for Rh₂(*S*-PTAD)₄; 57% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.44 (4:1 Hexanes:EtOAc); [α]²⁰_D: 19.1 (c. 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.36 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 7.06 (m, 3H), 6.74 (m, 2H), 3.66 (s, 3H), 3.14 (dd, *J* = 9.6 and 7.6 Hz, 1H), 2.17 (dd, *J* = 9.2 and 5.2 Hz, 1H), 1.88 (dd, *J* = 7.2 and 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 139.2, 135.8, 132.4, 128.1, 126.9, 125.0, 124.9, 124.8, 124.7, 53.0, 37.2, 33.5, 20.4; IR (film): 3032, 2954, 1719, 1501, 1322, 1257; HRMS (APCI) calcd for C₁₈H₁₆O₂F₃ (M+H)⁺ 321.10969 found 321.10970.



(1*S*,2*R*)-methyl 1-(4-chlorophenyl)-2-phenylcyclopropanecarboxylate (3d): Title compound was prepared by general procedure and obtained as a transparent oil. 87% yield for Rh₂(*R*-DOSP)₄; 71% yield for Rh₂(*S*-PTAD)₄; 89% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OJ-H, 1% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 8.62 min (minor) and 12.58 min (major), 88% ee for Rh₂(*R*-DOSP)₄; 48% ee for Rh₂(*S*-PTAD)₄; 57% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.56 (4:1 Hexanes:EtOAc); [α]²⁰_D: 4.8 (c. 1, chloroform); ¹H NMR (300 MHz; CDCl₃) δ 7.12-7.06 (m, 5H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.79-6.76 (m, 2H), 3.67 (s, 3H), 3.12 (dd, *J* = 9.3 and 7.5 Hz, 1H), 2.15 (dd, *J* = 9.3 and 4.8 Hz, 1H), 1.85 (dd, *J* = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 136.1, 133.7, 133.4, 133.2, 128.3, 128.2, 128.1, 126.8, 52.9, 36.9, 33.4, 20.6; IR (film): 3031, 2951, 1717, 1493, 1255; HRMS (APCI) calcd for C₁₇H₁₆O₂Cl (M+H)⁺ 287.08333 found 287.08329.



(1*S*,2*R*)-methyl 1-(4-methoxyphenyl)-2-phenylcyclopropanecarboxylate (3e): Title compound was prepared by general procedure and obtained as a white solid. 66% yield for Rh₂(*R*-DOSP)₄; 93% yield for Rh₂(*S*-PTAD)₄; 84% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 0.7% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 11.97 min (major) and 17.71 min (minor), 90% ee for Rh₂(*R*-DOSP)₄; 96% ee for Rh₂(*S*-PTAD)₄; 57% ee for Rh₂(*R*-BNP)₄; *R*_f = 0.39 (4:1 Hexanes:EtOAc); $[\alpha]^{20}_{D} = +5.1^{\circ}$ (c = 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.10-7.07 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.80-6.77 (m, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.68 (s, 3H), 3.09 (dd, *J* = 9.2 and 7.6 Hz, 1H), 2.14 (dd, *J* = 9.2 and 4.8 Hz, 1H), 1.84 (dd, *J* = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 158.6, 136.7, 133.1, 128.3, 127.9, 127.0, 126.5, 113.4, 55.3, 52.8, 36.9, 33.4, 21.0; IR (film): 3031, 2951, 2836, 1715, 1515, 1245; HRMS (APCI) calcd for C₁₈H₁₉O₃ (M+H)⁺ 283.13287 found 283.13284.



(1*S*,2*R*)-methyl 1-(2-chlorophenyl)-2-phenylcyclopropanecarboxylate (3f): Title compound was prepared by general procedure and obtained as a transparent oil. 89% yield for Rh₂(*R*-DOSP)₄; 80% yield for Rh₂(*S*-PTAD)₄; 78% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OJ-H, 0.5% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 11.47 min (major) and 15.27 min (major), 92% ee for Rh₂(*R*-DOSP)₄; 97% ee for Rh₂(*S*-PTAD)₄; 51% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.43 (4:1 Hexanes:EtOAc); [α]²⁰_D: 61.8 (c. 1, chloroform); ¹H NMR (300 MHz; CDCl₃) δ 7.18-7.02 (m, 7H), 6.84-6.76 (m, 2H), 3.68 (s, 3H), 3.13 (t, *J* = 8.7 Hz, 1H), 2.10 (m, 1H), 1.91 (dd, *J* = 7.2 and 5.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 137.5, 133.5, 129.6, 128.9, 128.2, 127.6, 126.6, 126.4, 52.9, 33.5, 29.9, 21.7; IR (film): 3031, 2950, 1718, 1251, 694; HRMS (APCI) calcd for C₁₇H₁₆O₂Cl (M+H)⁺ 287.08333 found 287.08334.



(1*S*,2*R*)-methyl 1-(2-methoxyphenyl)-2-phenylcyclopropanecarboxylate (3g): Title compound was prepared by general procedure and obtained as a white solid. 92% yield for Rh₂(*R*-DOSP)₄; 87% yield for Rh₂(*S*-PTAD)₄; 69% yield for Rh₂(*R*-BNP)₄; HPLC: (SS-WHELK column, 1% *i*-PrOH in hexanes, 1.0 mL/min, 1mg/mL, 30 min, $\lambda = 254$ nm) retention times of 11.65 min (minor) and 14.00 min (major), 86% ee for Rh₂(*R*-DOSP)₄; 80% ee for Rh₂(*S*-PTAD)₄; 27% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.45 (4:1 Hexanes:EtOAc); [α]²⁰_D: ⁺133.3° (c. 1, chloroform); ¹H NMR (400 MHz; CDCl₃) δ 7.19-7.10 (m, 2H), 7.04-6.98 (m, 3H), 6.86 (td, *J* = 7.6, 1.1 Hz, 1H), 6.81-6.74 (m, 2H), 6.53 (d, *J* = 8 Hz, 1H), 3.65 (s, 3H), 3.36 (s, 3H), 3.24 (dd, *J* = 9.6 and 7.6 Hz, 1H), 1.98 (dd, *J* = 9.2 and 4.8 Hz, 1H), 1.85 (dd, *J* = 7.2 and 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 159.2, 137.0, 131.8, 128.9, 127.9, 127.3, 126.1, 124.1, 120.1, 110.5, 55.2, 52.7, 34.3, 32.6, 20.8; IR (film): 3030, 2950, 2835, 1716, 1496, 1242; HRMS (APCI) calcd for C₁₈H₁₉O₃ (M+H)⁺ 283.13287 found 283.13290.



(1*S*,2*R*)-methyl 1-(3,4-dichlorophenyl)-2-phenylcyclopropanecarboxylate (3h): Title compound was prepared by general procedure and obtained as a clear oil; 88% yield for Rh₂(*R*-DOSP)₄; 88% yield for Rh₂(*S*-PTAD)₄; 82% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 1% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 7.54 min (minor) and 9.78 min (major), 82% ee for Rh₂(*R*-DOSP)₄; 60% ee for Rh₂(*S*-PTAD)₄; 63% ee for Rh₂(*R*-BNP)₄; *R*_f = 0.23 (Hexane:EtOAc = 7:1); [α] ²⁰_{D:} -8.1° (c = 1.60, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.16 (m, 2H), 7.14-7.10 (m, 3H), 6.82-6.79 (m, 3H), 3.68 (s, 3H), 3.14 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.15 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.84 (dd, *J* = 7.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 135.3, 135.2, 133.7, 131.6, 131.4, 131.2, 129.6, 128.0, 127.9, 126.8, 52.8, 36.3, 33.3, 20.2; IR (film): 2925, 1719, 1257, 1163, 695; HRMS (ESI) calcd for C₁₇H₁₃O₂Cl₂ (M-H)⁺ 319.02927 found 319.02985.



(1S,2R)-methyl 1-(3,4-dimethoxyphenyl)-2-phenylcyclopropanecarboxylate **(3i):** Title compound was prepared by general procedure and obtained as a white solid. 74% yield for $Rh_2(R-DOSP)_4$; 70% yield for $Rh_2(S-PTAD)_4$; 93% yield for 1 mol% $Rh_2(R-BNP)_4$; 83% yield for 0.5 mol% Rh₂(*R*-BNP)₄; 80% yield for 0.1 mol% Rh₂(*R*-BNP)₄; 73% yield for 0.01 mol% Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda =$ 254 nm) retention times of 13.99 min (minor) and 17.97 min (major), 56% ee for $Rh_2(R-DOSP)_4$; 94% ee for Rh₂(S-PTAD)₄; 97% ee for 1 mol% Rh₂(R-BNP)₄; 96% ee for 0.5 mol% Rh₂(R-BNP)₄; 91% ee for 0.1 mol% Rh₂(*R*-BNP)₄; 40% ee for 0.01 mol% Rh₂(*R*-BNP)₄; $R_f = 0.20$ (hexane: ethyl acetate 4:1); mp 88-89°C; $[\alpha]_{D}^{20} + 28.4^{\circ}$ (c = 1.51, CHCl₃); ¹H NMR (400 MHz, CDCl₃) & 7.09-7.07 (m, 3H), 6.81-6.79 (m, 2H), 6.69 (m, 2H), 6.36 (s, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 3.56 (s, 3H), 3.08 (dd, J = 9.2, 7.6 Hz, 1H), 2.14 (dd, J = 9.2, 4.4 Hz, 1H), 1.84 (dd, J = 7.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 147.8, 136.4, 127.9, 127.7, 127.2, 126.3, 123.9, 115.3, 110.2, 55.5, 52.6, 36.9, 33.1, 20.8; IR (film): 2924, 1716, 1518, 1455, 1434, 1413, 1341, 1229, 1208, 1177; HRMS (ESI) calcd for $C_{19}H_{21}O_4$ (M+H)⁺ 313.14398 found 313.14332.



(1*S*,2*R*)-methyl 1-(3-methoxyphenyl)-2-phenylcyclopropanecarboxylate (3j): Title compound was prepared by general procedure and obtained as a yellow oil. 78% yield for Rh₂(*R*-DOSP)₄; 72% yield for Rh₂(*S*-PTAD)₄; 82% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 0.7% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm), retention times of 9.50 min (major) and 11.38 min (minor), 79% ee for Rh₂(*R*-DOSP)₄; 16% ee for Rh₂(*S*-PTAD)₄; 88% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.25 (hexane: ethyl acetate 9:1); $[\alpha]^{20}_{D}$ +21.1° (c = 1.25, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.03 (m, 4H), 6.81-6.79 (m, 2H), 6.69-6.63 (m, 2H), 6.53-6.52, (m, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 3.12 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.12 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.87 (dd, *J* = 7.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 158.8, 136.4, 136.2, 128.5,

127.9, 127.7, 126.3, 124.4, 117.5, 112.9, 55.0, 52.6, 37.3, 33.1, 20.6; IR (film): 2925, 1717, 1602, 1454, 1239, 697; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ (M+H)⁺ 283.13344 found 283.13288.



(1*S*,2*R*)-methyl 1-(3,5-dimethoxyphenyl)-2-phenylcyclopropanecarboxylate (3k): Title compound was prepared by general procedure and obtained as a yellow oil. 85% yield for Rh₂(*R*-DOSP)₄; 85% yield for Rh₂(*S*-PTAD)₄; 69% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 7.33 min (major) and 9.07 min (minor), 28% ee for Rh₂(*R*-DOSP)₄; 3% ee for Rh₂(*S*-PTAD)₄; 92% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.31 (hexane: ethyl acetate 5:1); [α]²⁰_D +33.7° (c = 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.10-7.08 (m, 3H), 6.82 (dd, *J* = 7.2, 2.4 Hz, 2H), 6.24 (t, *J*=2.4 Hz, 1H), 6.15 (d, *J*=2.4 Hz, 2H), 3.68 (s, 3H), 3.56 (s, 6H), 3.08 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.10 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.84 (dd, *J* = 7.2, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 160.1, 137.2, 136.6, 128.2, 128.0, 126.6, 110.4, 99.8, 55.4, 52.9, 37.7, 33.3, 20.9; IR (film): 2951, 2840, 1715, 1594, 1456, 1425, 1260, 1203, 1151, 1046, 715, 692; HRMS (APCI) calcd for C₁₉H₂₁O₄ (M+H)⁺ 313.14344 found 313.14348.



(1*S*,2*R*)-methyl 2-phenyl-1-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (3l): Title compound was prepared by general procedure and obtained as a yellow oil. 98% yield for Rh₂(*R*-DOSP)₄; 95% yield for Rh₂(*S*-PTAD)₄; 63% yield for Rh₂(*R*-BNP)₄; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm), retention times of 10.78 min (minor) and 11.79 min (minor), 34% ee for Rh₂(*R*-DOSP)₄; 9% ee for Rh₂(*S*-PTAD)₄; 90% ee for Rh₂(*R*-BNP)₄; *R_f* = 0.20 (hexane: ethyl acetate 5:1); [α]²⁰_D+17.5° (c = 2.02, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.07 (m, 3H), 6.81-6.78 (m, 2H), 6.16 (s, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.59 (s, 6H), 3.07 (dd, *J* = 9.2, 7.2 Hz, 1H); 2.14 (dd, *J* = 9.6, 4.8 Hz, 1H), 1.82 (dd, *J* = 7.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 152.3, 136.5, 130.3, 128.0, 127.7, 126.4,

109.4, 60.7, 55.9, 52.6, 37.4, 33.1 20.8; IR (film): 2925, 1716, 1587, 1413, 1258, 1235, 1153, 1124; HRMS (ESI) calcd for $C_{20}H_{23}O_4$ (M+H)⁺ 345.14852 found 345.14853.



(1*S*,2*R*)-methyl 1-(3,4-dimethoxyphenyl)-2-(*m*-tolyl)cyclopropanecarboxylate (5a): Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 2-methylstyrene (148 mg, 1.25 mmol, 2.5 equiv), and Rh₂(*R*-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford a yellow/green oil (114 mg, 76 % yield). *R_f* = 0.12 (hexane: ethyl acetate 5:1); $[\alpha]^{20}_{D}$ +28.7° (c = 1.23, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.63 (m, 2H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.34 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.57 (s. 3H), 3.11 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.51 (s, 3H), 2.06 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.99 (dd, *J* = 7.6, 5.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 147.9, 137.8, 134.7, 129.7, 127.8, 126.7, 126.0, 125.8, 123.7, 114.7, 110.3, 55.7, 55.6, 52.8, 36.0, 31.2, 20.2, 19.5; IR (film): 2951, 1713, 1516, 1463, 1435, 1251, 1140, 1026, 740; HRMS (APCI) calcd for C₂₀H₂₃O₄ (M+H)⁺ 327.15909 found 327.15909; HPLC: (Chiralcel OD-H, 3% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, λ = 254 nm) retention times of 17.81 min (minor) and 19.31 min (major), 90% ee for Rh₂(*R*-BNP)₄, 64% ee for Rh₂(*R*-DOSP)₄.



(1*S*,2*R*)-methyl 1-(3,4-dimethoxyphenyl)-2-(*p*-tolyl)cyclopropanecarboxylate (5b): Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4-methylstyrene (148 mg, 1.25 mmol, 2.5 equiv), and Rh₂(*R*-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford a yellow/green oil (147 mg, 90% yield). $R_f = 0.12$ (hexane: ethyl acetate 5:1); $[\alpha]^{20}_{\text{ D}}$ +27.7° (c = 1.24, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.88 (d, *J* = 8.0 Hz, 2H), 6.69-6.67 (m, 4H), 6.37 (s, 1H), 3.81 (s, 3H), 3.67 (s, 3H), 3.57 (s, 3H), 3.05 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.22 (s, 3H), 2.11 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.80 (dd, *J* = 7.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 147.9, 136.0, 133.5, 128.6, 128.0, 127.6, 124.1, 115.5, 110.3, 55.7, 55.6, 52.7, 36.9, 33.1, 21.0, 20.9; IR (film): 2951, 1714, 1589, 1516, 1435, 1413, 1341, 1315, 1250, 1228, 1155, 1027; HRMS (APCI) calcd for C₂₀H₂₃O₄ (M+H)⁺ 327.15909 found 327.15909; HPLC: (Chiralcel OD-H, 3% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, λ = 254 nm) retention times of 17.3 min (minor) and 20.1 min (major), 88% ee for Rh₂(*R*-BNP)₄, 67% ee for Rh₂(*R*-DOSP)₄.



(1*S*,2*R*)-methyl 1-(3,4-dimethoxyphenyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate (5c): Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4-methoxystyrene (168 mg, 1.25 mmol, 2.5 equiv), and Rh₂(*R*-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv. The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (5:1) to afford an off-white solid (137 mg, 80% yield). *R_f* = 0.20 (hexane: ethyl acetate 3:1); mp 123-125°C; $[\alpha]^{20}_{D}$ +33.1° (c = 1.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.73-6.61 (m, 6H), 6.41 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.60 (s, 3H), 3.03 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.10 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.76 (dd, *J* = 7.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 175.1, 158.6, 148.3, 129.5, 128.9, 127.9, 124.6, 115.9, 113.7, 110.7, 56.1, 55.6, 53.1, 37.1, 33.2, 21.3; IR (film): 2952, 1714, 1611, 1589, 1515, 1463, 1437, 1413, 1341, 1248, 1228, 1177, 1153; HRMS (APCI) calcd for C₂₀H₂₂O₅ (M+H)⁺ 342.14618 found 342.14589; HPLC: (Chiralcel OD-H, 5% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, λ = 254 nm) retention times of 19.2 min (minor) and 22.9 min (major), 90% ee for Rh₂(*R*-BNP)₄, 62% ee for Rh₂(*R*-DOSP)₄.



(1*S*,2*R*)-methyl 1-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)cyclopropanecarboxylate (5d): Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4-nitrostyrene (186 mg, 1.25 mmol, 2.5 equiv), and $Rh_2(R$ -BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with

hexanes : ethyl acetate (5:1) to afford yellow oil (168 mg, 94% yield). $R_f = 0.28$ (hexane: ethyl acetate 3:1); $[\alpha]^{20}{}_{D} + 15.5^{\circ}$ (c = 1.07, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.2 Hz, 1H), 6.61 (dd, J = 8.2, 2.0 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.62 (s, 3H), 3.16 (dd, J = 9.2, 7.6 Hz, 1H), 2.22 (dd, J = 9.2, 5.4 Hz, 1H), 1.91 (dd, J = 7.6, 5.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 148.5, 145.1, 128.7, 126.2, 124.2, 123.0, 115.0, 110.6, 55.9, 55.8, 53.0, 38.4, 32.6, 29.8, 21.8; IR (film): 2924, 1717, 1597, 1515, 1463, 1415, 1342, 1229, 1206, 1156, 1141; HRMS (APCI) calcd for C₁₉H₂₀O₆N₁ (M+H)⁺ 358.12851 found 358.12836; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 60 min, $\lambda = 254$ nm) retention times of 30.4 min (minor) and 41.0 min (major), 80% ee for Rh₂(*R*-BNP)₄, 50% ee for Rh₂(*R*-DOSP)₄.



(1*S*,2*R*)-methyl

1-(3,4-dimethoxyphenyl)-2-(4-

trifluoromethyl)phenyl)cyclopropanecarboxylate (5e): Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), styrene (215 mg, 1.25 mmol, 2.5 equiv), and Rh₂(*R*-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (6:1) to afford a yellow oil (171 mg, 90% yield); $R_f = 0.24$ (hexane: ethyl acetate 4:1); $[\alpha]^{20}_D + 16.5^\circ$ (c = 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 6.70-6.65 (m, 2H), 6.35 (s, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 3.56 (s, 3H), 3.11 (t, 1H), 3.12 (dd, J = 9.2, 7.2 Hz, 1H), 2.18 (dd, J = 9.2, 4.8 Hz, 1H), 1.85 (dd, J = 7.2, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 148.7, 148.6, 141.5, 128.7, 127.0, 124.8, 124.7, 124.6, 124.3, 115.6, 110.9, 56.1, 53.2, 38.0, 33.0, 21.7; IR (film): 2954, 1718, 1517, 1465, 1437, 1414, 1324, 1252, 1230, 1210, 1193; HRMS (APCI) calcd for C₂₀H₁₉F₃O₄ (M+H)⁺ 380.12300 found 380.12251; HPLC: (Chiralcel OD-H, 6% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 12.6 min (minor) and 15.6 min (major), 90% ee for Rh₂(*R*-BNP)₄, 63% ee for Rh₂(*R*-DOSP)₄.



(1*S*,2*R*)-methyl 2-(4-chlorophenyl)-1-(3,4-dimethoxyphenyl)cyclopropanecarboxylate (5f): Prepared by general procedure with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (118 mg, 0.5 mmol, 1 equiv), 4-chlorostyrene (173 mg, 1.25 mmol, 2.5 equiv), and Rh₂(*R*-BNP)₄ (4 mg, 0.0025 mmol, 0.005 equiv). The remaining residue was purified on silica gel eluting with hexanes : ethyl acetate (6:1) to afford clear oil (123 mg, 89% yield). R_f = 0.30 (hexane: ethyl acetate 3:1); $[\alpha]^{20}_{D}$ +13.4° (c = 1.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.72-6.63 (m, 4H), 6.38 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 3.67 (s. 3H), 3.61 (s, 3H), 3.04 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.13 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.78 (dd, *J* = 7.2, 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 148.2, 148.2, 135.4, 132.3, 129.4, 128.0, 127.0, 124.2, 115.4, 110.5, 55.9, 55.8, 52.8, 37.2, 32.6, 21.2; IR (film): 2951, 1715, 1589, 1517, 1496, 1435, 1413, 1371, 1341, 1307, 1228,1177, 1155, 1139; HRMS (APCI) calcd for C₁₉H₁₉ClO₄ (M+H)⁺ 346.09664 found 346.09632; HPLC: (Chiralcel OD-H, 5% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, λ = 254 nm) retention times of 14.9 min (minor) and 18.5 min (major), 89% ee for Rh₂(*R*-BNP)₄.



(1*S*,2*R*)-methyl 2-(3,4-dichlorophenyl)-1-(3,4-dimethoxyphenyl)cyclopropanecarboxylate (5g): Methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (2.7g, 11.6 mmol, 1 equiv) in 153 mL dry and degassed toluene was added by syringe pump over 2 h to a solution of 1,2-dichloro-4-vinylbenzene (2.4 g, 13.9 mmol, 1.2 equiv) and Rh₂(*R*-BNP)₄ (92.2 mg, 0.06 mmol, 0.005 equiv) in 77 mL toluene. After addition, the solution was allowed to stir overnight and toluene was removed *in vacuo*. The remaining residue was purified on silica gel (hexane:ethyl acetate 5:1) to afford a clear oil (3.2 g, 72% yield for Rh₂(*R*-BNP)₄ [enantiomer shown above]; 2.3g, 52% yield for Rh₂(*S*-BNP)₄) *R_f* = 0.17 (hexane: ethyl acetate 5:1); $[α]^{20}_{D}$ +4.1° (c = 1.03, CHCl₃) for Rh₂(*R*-BNP)₄; $[α]^{20}_{D}$ -6.9° (c = 1.05, CHCl₃) for Rh₂(*S*-BNP)₄; ¹H NMR (600 MHz, CDCl₃) δ 7.10 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 1H), 6.63 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.51 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.13(dd, *J* = 9.0, 5.1 Hz, 1H), 1.78 (dd, *J* = 7.2, 5.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 148.4, 148.3, 137.4, 131.9, 130.5, 130.4, 129.7, 127.0, 126.6, 124.2, 115.2, 110.6, 55.9, 55.8, 52.9, 37.4, 32.1, 21.1; IR (film): 2951, 2836, 1716, 1559, 1516,

1413, 1229, 1178, 1137, 1027, 764; HRMS (APCI) calcd for $C_{19}H_{19}Cl_2O_4$ (M+H)⁺ 381.24981 found 381.24982; HPLC: (Chiralcel OD-H, 5% *i*-PrOH in hexane, 1 mL/min, 1 mg/mL, 30 min, $\lambda = 254$ nm) retention times of 15.4 min (minor) and 17.9 min (major), 86% ee for Rh₂(*R*-BNP)₄; retention times of 15.3 min (major) and 19.7 min (minor) 85% ee for Rh₂(*S*-BNP)₄, 48% ee for Rh₂(*R*-DOSP)₄.

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¹H-NMR Spectrum of Compound **3a**







HPLC Trace of Compound **3a** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3b**





HPLC Trace of Compound **3b** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3c**







HPLC Trace of Compound **3c** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3d**





HPLC Trace of Compound **3d** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3e**


HPLC Trace of Racemic 3e



HPLC Trace of Compound **3e** (Rh₂(S-PTAD)₄)



HPLC Trace of Racemic 3e













HPLC Trace of Compound **3f** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3g**





HPLC Trace of Compound 3g (Rh₂(S-PTAD)₄)



HPLC Trace of Racemic **3g**



HPLC Trace of Compound **3g** (Rh₂(*R*-BNP)₄)









HPLC Trace of Compound **3h** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3i**







HPLC Trace of Compound **3i** (Rh₂(S-PTAD)₄)



HPLC Trace of Compound **3i** (Rh₂(*R*-BNP)₄, 0.5 mol%)







HPLC Trace of Compound **3i** (Rh₂(*R*-BNP)₄, 0.01 mol%)



¹H-NMR Spectrum of Compound **3**j





HPLC Trace of Compound **3j** (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3k**





HPLC Trace of Compound 3k (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **3**l





HPLC Trace of Compound 3l (Rh₂(S-PTAD)₄)



¹H-NMR Spectrum of Compound **5a**







HPLC Trace of Compound **5a** (Rh₂(*R*-DOSP)₄)



¹H-NMR Spectrum of Compound **5b**







HPLC Trace of Compound **5b** (Rh₂(*R*-DOSP)₄)



¹H-NMR Spectrum of Compound **5**c







HPLC Trace of Compound **5c** (Rh₂(*R*-DOSP)₄)


¹H-NMR Spectrum of Compound **5d**



HPLC Trace of Racemic **5d**



HPLC Trace of Compound **5d** (Rh₂(*R*-DOSP)₄)



¹H-NMR Spectrum of Compound **5e**





HPLC Trace of Compound **5e** (Rh₂(*R*-DOSP)₄)



¹H-NMR Spectrum of Compound **5**f







HPLC Trace of Compound **5f** (Rh₂(*R*-DOSP)₄)



¹H-NMR Spectrum of Compound **5**g



HPLC Trace of Racemic **5g**



HPLC Trace of Compound 5g (Rh₂(*R*-DOSP)₄)

