Asymmetric Cyclopropanation with 4-Aryloxy-1-sulfonyl-1,2,3-triazoles: Expanding the Range of Rhodium-Stabilized Donor/Acceptor Carbenes to Systems with an Oxygen Donor Group

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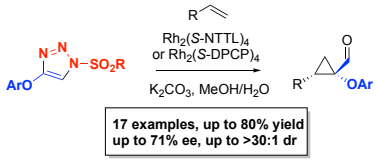
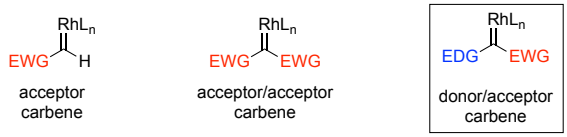


ABSTRACT: The rhodium-catalyzed enantioselective synthesis of 1-phenoxycyclopropane-1-carbaldehydes by intermolecular cyclopropanation of terminal alkenes followed by imine hydrolysis is described. This methodology utilizes 4-aryloxy-1-sulfonyl-1,2,3-triazoles as the carbene precursors and the chiral dirhodium(II) tetracarboxylates Rh_2(*S*-NTTL)$_4$ or Rh_2(S-DPCP)$_4$ as the catalysts. These reactions are considered to proceed *via* rhodium-stabilized donor/acceptor carbene intermediates, and these studies demonstrate that a heteroatom donor group is compatible with an enantioselective transformation.

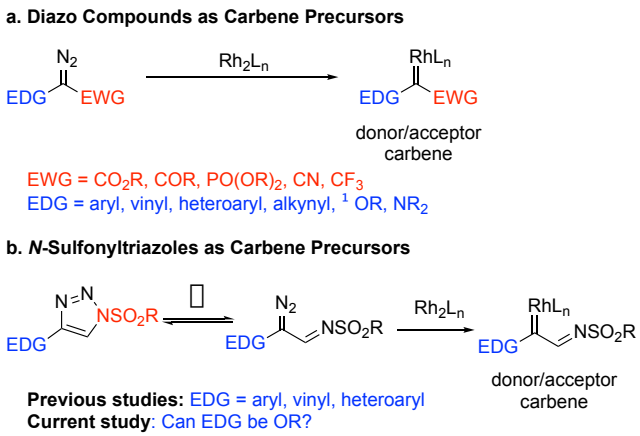
INTRODUCTION

The reactions of transient metal carbenes, most commonly generated from the corresponding diazo compounds or more recently from *N*-sulfonyltriazoles, have been shown to have broad versatility in organic synthesis.[1-2] They are capable of a wide range of reactions such as cyclopropanation, cyclopropenation, reactions involving ylide intermediates, and intra- and intermolecular C–H functionalization by means of insertion of the carbenes into C–H bonds.[1-2] The chemistry of the transient metal carbenes is strongly influenced by the groups adjacent to the carbene (Scheme 1).[1] The vast majority of the earlier work in this area was conducted with acceptor and acceptor/acceptor metal carbenes. These transient metal carbenes are highly electrophilic, and the presence of electron withdrawing (acceptor) groups make the carbenes extremely reactive and often unselective, especially in intermolecular reactions.[1] More recently, efforts have been made to modulate the reactivity of the carbene by introducing electron donating groups into the system. The donor/acceptor carbenes have become widely used because the donor group modulates their reactivity.[1] They have been especially useful in enantioselective intermolecular transformations such as cyclopropanation and C–H functionalization, often displaying exceptional levels of site-selectivity and stereoselectivity.[1]



Scheme 1. Classes of metal-stabilized carbenes

With the clear benefits associated with donor/acceptor carbenes, there has been considerable interest in broadening their structural range. Traditionally, these carbenes were derived from aryl-, heteroaryl- or vinyldiazoacetates, and even though a variety of catalysts have been used, the dirhodium tetracarboxylate catalysts are the most effective (Scheme 2A).[1] More recent studies have shown that the acceptor group can be quite variable, and enantioselective cyclopropanation with other acceptor groups such as keto, cyano, phosphonate and trifluoromethyl have been reported.[1] The donor group typically has been aryl, heteroaryl, alkenyl or alkynyl groups that are capable of resonance stabilization of the highly electrophilic carbene site.[1] Particularly useful donor groups would be oxygen or nitrogen



Scheme 2. Most widely used precursors to donor/acceptor carbenes

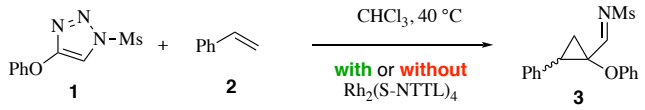
functionality, because they could lead to a versatile enantioselective approach to α-hydroxy or α-amino acids. However, enantioselective reactions with such carbenes derived from diazo compounds are not known because diazo compounds with nitrogen or oxygen donor groups are too unstable.[4a]

A decade ago, Fokin demonstrated that *N*-sulfonyltriazoles, readily generated by click-chemistry, were versatile precursors to metal carbene intermediates (Scheme 2B).[5] On warming with dirhodium tetracarboxylate catalysts, the triazoles are in equilibrium with the ring-opened α-diazo *N*-sulfonylimines, which then lose nitrogen and generate metal-bound carbenes.[4] These carbenes are capable of undergoing a variety of reactions, often with high enantioselectivity when a chiral dirhodium catalyst is used.[3,5] Most of the early studies with *N*-sulfonyltriazoles used a 4-aryl derivative, which means the donor/acceptor carbene that would be generated has an *N*-sulfonyl imino as the acceptor group and an aryl as the donor group.[3] We became interested in the use of *N*-sulfonyltriazoles as potentially viable precursors to donor/acceptor carbenes with oxygen or nitrogen functionality as the donor group. Our first foray in this area was to use 4-phthalimido-*N*-sulfonyltriazole, and even though this system leads to a highly diastereoselective cyclopropanation of styrenes, the products were formed as racemates and the reaction was equally effective in the absence of the catalysts.[4] It was concluded that the diazo compound formed on ring opening of the triazole undergoes nitrogen extrusion to the free carbene before the dirhodium catalyst can intervene. Since then, we and others have explored reactions with 4-alkoxy-*N*-sulfonyltriazoles, but as these reactions gave achiral compounds it has not been determined whether these reactions involved metal-stabilized carbenes or just free carbenes.[6] In this paper we have carried out a systematic study on the intermolecular cyclopropanation by 4-alkoxy-*N*-sulfonyl triazoles using chiral dirhodium catalysts. These studies resulted in enantioselective cyclopropanation and demonstrate that *N*-sulfonyltriazoles can be viable precursors to heteroatom-functionalized, rhodium-stabilized donor/acceptor carbenes.

RESULTS AND DISCUSSION

A major challenge for the rhodium-catalyzed reactions with the phenoxytriazole is the competing thermal reaction. To have a better understanding of the two competing processes, react-IR experiments were conducted on the thermal and the Rh_2(*S*-NTTL)$_4$-catalyzed reaction of 4-phenoxy-1-(methanesulfonyl)-1,2,3-triazole (**1**) and styrene (**2**) to form the cyclopropane **3** (Figure 1). The initial rate of the rhodium-catalyzed reaction was found to be six times faster than the purely thermal reaction. Therefore, the dirhodium complex catalyzes the reaction, so there is an opportunity for enantioselective reactions using chiral catalysts.

We began our studies by examining the reactions of 4-ethoxy- and 4-phenoxy-*N*-sulfonyl-1,2,3-triazoles. The ethoxy derivative was attractive because ethoxyacetylene is commercially available, but it failed to form any of the desired cyclopropane products under either thermal or rhodium-catalyzed conditions. Therefore, the study focused on the cyclopropanation of styrene with 4-phenoxy-*N*-sulfonyl-1,2,3-triazole **1**, and the key results are summarized in Table 1. The phenoxy derivative **1** was expected to be more effective than the ethoxy derivative because it is a weaker donating group and the ring-opened α-diazo-*N*-sulfonylimine should be more stable. The purely thermal reaction of **1** resulted in the formation in 49% yield of a 2:1 mixture of the cis and trans cyclopropanes, **4a** and **4b** (entry 1).



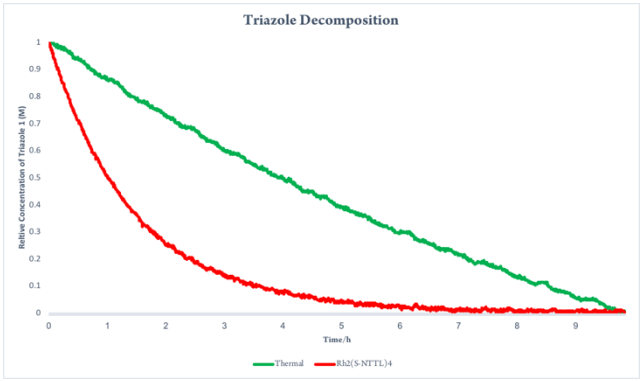
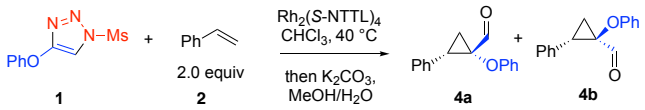


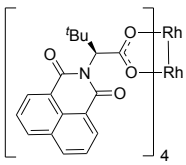
Figure 1. React IR comparison of a thermal reaction versus a rhodium catalyzed reaction of **1**.

Rh_2(*S*-NTTL)$_4$ is the most effective chiral catalyst for the reactions of 4-aryl-*N*-sulfonyltriazoles, and when the reaction of **1** was conducted with 2 mol % of Rh_2(*S*-NTTL)$_4$, the combined yield of the cyclopropanes **4a** and **4b** improved to 66% and the diastereoselectivity increased to 6.2:1 d.r. (entry 2).[3] The change in the

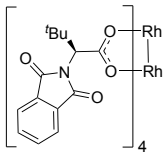
Table 1. Catalyst and triazole optimization studies



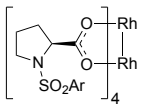
Entry	$Rh_2(L)_4$	Yield (%)	d.r.	ee 4a (%)	ee 4b (%)
1	none	49	2.0:1	n/a	n/a
2	Rh_2(*S*-NTTL)$_4$	66	6.2:1	71	29
3	Rh_2(*S*-PTTL)$_4$	67	9.5:1	47	17
4	Rh_2(*S*-DOSP)$_4$	37	2.9:1	27	0
5	Rh_2(*S*-*p*-PhTPCP)$_4$	55	2.3:1	6	6
6	Rh_2(*S*-DPCP)$_4$	80	15:1	47	28



Rh_2(*S*-NTTL)$_4$

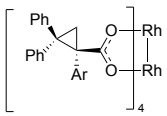


Rh_2(*S*-PTTL)$_4$



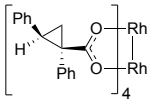
Ar = *p*-($C_{12}H_{25}$)C_6H_4

Rh_2(*S*-DOSP)$_4$



Ar = *p*-PhC_6H_4

Rh_2(*S*-*p*-PhTPCP)$_4$



Rh_2(*S*-DPCP)$_4$

a) Yields reported as combined isolated yields. b) d.r. determined by ^{1}H NMR of the crude reaction mixture. c) ee determined using HPLC of isolated mixture of diastereomers.

diastereoselectivity suggested that the rhodium was still intimately connected to the carbene during the cyclopropanation. Further evidence to support this concept is the fact that the reaction is enantioselective, with **4a** being formed in in 71% ee. The absolute and relative configuration of the major diastereomer **4a** was determined by X-ray crystallography (Figure 2) and the stereoconfiguration of the other cyclopropanes described later is tentatively assigned by analogy.

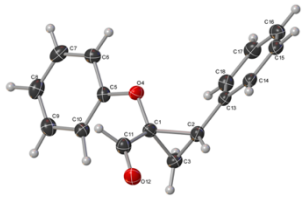
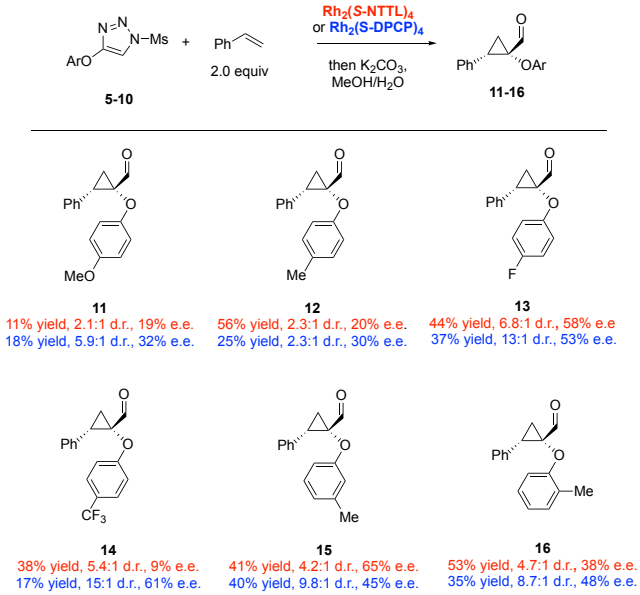


Figure 2. X-ray crystal structure of **4a**.

The catalyst screen focused on the use of less sterically crowded dirhodium catalyst to give a better chance that the complex will catalyze the nitrogen extrusion to for a metal carbene faster that the purely thermal reaction. Both Rh_2(*S*-DOSP)$_4$ and Rh_2(*S*-PTTL)$_4$ were examined (entries 3 and 4) but none were as effective as Rh_2(*S*-NTTL)$_4$, although Rh_2(*S*-PTTL)$_4$ did give a modest improvement in diastereoselectivity (9.5:1). One of the most effective bulky catalysts we have examined are the triarylcyclopropanecarboxylate catalysts, such as Rh_2(*S*-*p*-PhTPCP)$_4$.[1] As expected, the reaction with Rh_2(*S*-*p*-PhTPCP)$_4$ was not promising, giving ratios similar to what has been observed in the thermal reactions (entry 5), presumably because the catalyst is too slow at competing with the purely thermal decomposing the diazo intermediate. We had previously prepared diarylcyclopropanecarboxylate catalysts, such as Rh_2(S-DPCP)$_4$ to confirm the requirement of the three aryl groups in the ligand for the generation of a sterically bulky catalyst.[7] They performed as sterically accessible catalysts although they gave very low enantioinduction in reactions with aryldiazoacetates.[7] When tested in the reaction of the triazole **1**, however, Rh_2(S-DPCP)$_4$ was quite effective, giving the best ratio of **4a** to **4b** (15:1 d.r.), and even the enantioselectivity was quite respectable (47% ee). On the basis of these studies, Rh_2(S-NTTL)$_4$ and Rh_2(S-DPCP)$_4$ were selected for further evaluation.

The use of the phenoxy group in the triazole **1** was crucial for a successful cyclopropanation. Therefore, a study was conducted to determine the influence of using triazoles **5-10** with different types of electronic or steric influences to the 4-aryloxy group (Table 2). Triazoles with electron donating *para*-substituents gave cyclopropanes **11** and **12** with decreased yields, diastereoselectivities, and enantioselectivities. Utilizing electron withdrawing *para*-substituents

Table 2. Varying the arene component of the triazole ring.[a-c]

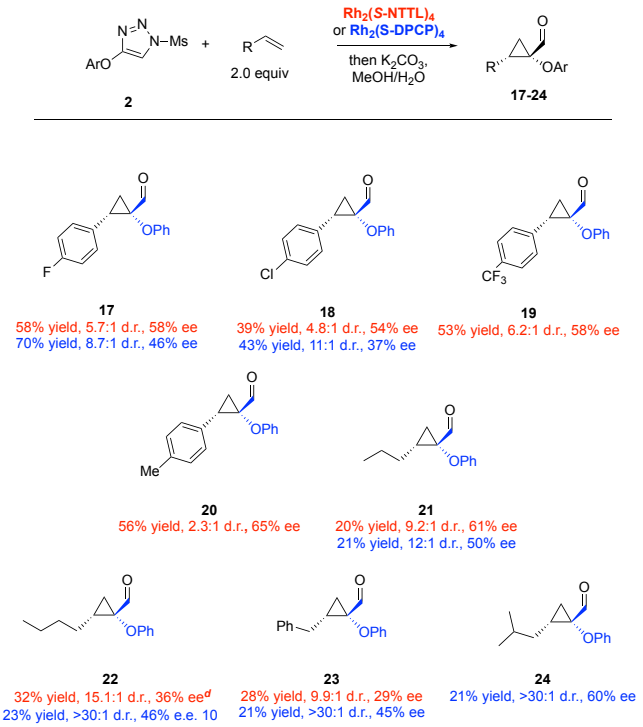


a) Yields reported as combined isolated yields. b) d.r. determined by ^{1}H NMR of the crude reaction mixture. c) % ee determined using HPLC.

gave cyclopropanes **13** and **14** with only a slight decrease in yield with similar or slightly improved diastereoselectivities. The enantioselectivity was lower for Rh_2(S-NTTL)$_4$-catalyzed reactions compared to the parent system but higher when Rh_2(S-DPCP)$_4$ was used as the catalyst. Moving the methyl group to the meta and ortho positions generated cyclopropanes **15** and **16** with higher enantioselectivities than was observed for the para methyl substituted cyclopropane (**12**), but they were still inferior to the unsubstituted system (**4**). In general, the diastereoselectivity was superior using Rh_2(S-DPCP)$_4$ compared to the Rh_2(S-NTTL)$_4$-catalyzed reactions. The enantioselectivity was dependent on the nature of the aryl substituent, and in the majority of cases, Rh_2(S-NTTL)$_4$ gave the highest levels of enantioselectivity. However, in the case of the p-CF_3 and o-CH_3 derivatives **14** and **16**, Rh_2(S-DPCP)$_4$ was the superior chiral catalyst.

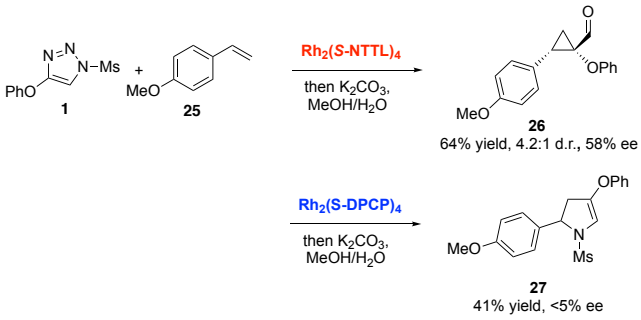
The cyclopropanation reaction of the triazole **1** was then examined with a variety of alkenes (Table 3). The reaction was effective with electron deficient styrenes as illustrated in the formation of cyclopropanes **17-19**. In the case of the electron rich *para*-methylstyrene, the Rh_2(S-NTTL)$_4$-catalyzed reaction gave **20** with diminished diastereoselectivity but slightly better enantioselectivity than the electron deficient styrenes. The cyclopropanation can also be carried out with alkyl alkenes resulting in the formation of the cyclopropanes **21-24** with improved diastereoselectivity but relatively low yields (20-32%). No improvement in yields was seen when using 5 equiv of alkene was used. In these reactions the enantioselectivity and diastereoselectivity were far superior when Rh_2(*S*-DPCP)$_4$ was used as the catalyst with **21-24** being formed in ≥20:1 d.r.

Table 3. Scope of the alkene.[a-d]



a) Yields reported as combined isolated yields. b) d.r. determined by ^{1}H NMR of the crude reaction mixture. c) ee determined using HPLC. d) Reaction ran at 5 equiv: gave 25% yield, 6.7:1 d.r., and 20% ee.

In general, both catalysts generate the same product although the stereoselectivity varied. *para*-methoxystyrene **25** is an interesting substrate because the two catalysts resulted in different products (Scheme 3). The Rh$_2$(*S*-NTTL)$_4$-catalyzed reaction resulted in the formation of the cyclopropane **26** but the Rh$_2$(*S*-DPCP)$_4$-catalyzed reaction gave the dihydropyrrole **27**, the type of product derived from a either a zwitterionic intermediate, which preferentially closes to a five-membered ring rather than the cyclopropane, or ring-opening of an intermediate cyclopropylaldimine.[8] In this case, the asymmetric induction was <5% ee.



Scheme 3. Catalyst influence on reaction outcome

CONCLUSION

In summary, we have demonstrated that a catalytic enantioselective cyclopropanation can be achieved with donor/acceptor carbenes with oxygen functionality as the donor group. The asymmetric induction by a chiral dirhodium catalyst is indicative of a reaction proceeding by means of a rhodium bound carbene rather than a free carbene. Even though donor/acceptor diazo compounds with an oxygen donor group are not isolable they can be transiently generated from 4-phenoxy-*N*-sulfonyl-1,2,3-triazoles and these results indicate that they can be intercepted by the chiral dirhodium catalysts. The highly effective chiral catalyst, Rh$_2$(*S*-NTTL)$_4$, developed for asymmetric reactions with aryl sulfonyl triazoles gave moderate enantioselectivity for phenoxy-*N*-sulfonyltriazoles. Indeed, in many instances Rh$_2$(*S*-DPCP)$_4$, a catalyst that does not perform well with aryldiazoacetates, was the best catalyst for the phenoxy-*N*-sulfonyltriazoles. As our long-term catalyst design has been directed towards carbenes with an aryl or a vinyl group as the donor group, future improvements to this methodology would require a new catalyst campaign for this novel class of carbenes. The demonstration that oxygen donor groups can be incorporated into rhodium-bound donor/acceptor carbenes offers interesting opportunities for the rapid enantioselective access of elaborate α-phenoxy acid derivatives.

EXPERIMENTAL SECTION

General methods

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry argon. All reagents were used as received from commercial suppliers, unless otherwise stated. Rh$_2$(*S*-NTTL)$_4$, Rh$_2$(*S*-DPCP)$_4$, Rh$_2$(*S*-PTTL)$_4$, Rh$_2$(*S*-p-PhTPCP)$_4$, and Rh$_2$(*S*-DOSP)$_4$ were prepared according to literature procedures and lyophilized for 24 hours from benzene prior to use with a VirTis Benchtop K lyophilizer.[9] All solvents were purchased from Sigma Aldrich and freshly distilled prior to use in synthesis. If heated, reaction temperature was maintained using an aluminum heating block. Proton (^{1}H) NMR spectra were recorded at 400 MHz on a Varian-400 or Bruker-400 spectrometer, or 600 MHz on an Inova-600 spectrometer. Proton-decoupled carbon-13 (^{13}C) NMR spectra were recorded at 100 MHz on a Varian-400 or Bruker-400 spectrometer or 151 MHz on an Inova-600 spectrometer. NMR spectra were recorded in deuterated chloroform ($CDCl_3$) solutions, with residual chloroform (δ 7.26 ppm for ^{1}H NMR and δ 77.16 ppm for ^{13}C NMR) as the internal standard and were reported in parts per million (ppm). Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sep, septet; and m, multiplet. Coupling constants were taken from the spectra directly and are uncorrected. Infrared (IR) Spectra were collected on a Nicolet Impact Series 10 FT-IR. React IR spectra were acquired using the Mettler Toledo iC IR with Microsoft Excel® used to interpret the data. Mass spectrometric determinations were carried out on a Thermo Finnigan LTQ-FTMS spectrometer with nano-spray ionization (NSI) or atmospheric pressure chemical ionization (APCI), using a Fourier-transform ion cyclotron resonance (FT-ICR) mass analyzer. Optical rotations were measured on a PerkinElmer 341 polarimeter. High performance liquid chromatography (HPLC) analysis was performed on an Agilent 1100 or 1290 with hexanes/isopropanol as eluent. Supercritical fluid chromatography (SFC) was performed on a Waters Acquity UPC2 system using methanol/isopropanol with 0.2% formic acid in supercritical carbon dioxide as eluent. Analytical thin layer chromatography (TLC) was performed on silica gel plates using ultraviolet (UV) light or stained with $KMnO_4$, ceric ammonium molybdate (CAM), or phosphomolybdic acid (PMA). Flash column chromatography was performed with silica gel 60 Å (230 – 400 mesh) according to the literature procedure.[10] Absolute stereochemical information for **4a** was elucidated by x-ray crystallographic analysis using a Rigaku SYNERGY diffractometer and assigned to similar compounds by analogy. Ynol ethers were prepared according to literature procedure directly prior to the CuAAC to arrive at 4-oxy-triazoles.[11]

Caution! Upon heating, *N*-sulfonyl-1,2,3-triazoles under ring opening to expose a diazo moiety, which is susceptible to loss of

dinitrogen. These compounds must be treated with care in handling and heating, and the chemistry is ideally done behind a blast shield.

General procedure for the synthesis of triazoles. To a stirred solution of alkyne (5 mmol, 1.0 equiv) in toluene (100 mL) was added copper(I)-thiophene-2-carboxylate (CuTC, 0.25 mmol, 0.05 equiv). The reaction mixture was cooled to 0 °C and treated dropwise with a solution of sulfonyl azide (6 mmol, 1.2 equiv) in toluene (10 mL). The reaction was stirred a further 12 h, filtered through Celite®, and then purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient) to provide the desired triazole.

1-(Methylsulfonyl)-4-phenoxy-1H-1,2,3-triazole (1). Compound **1** was prepared *via* the general procedure for the synthesis of triazoles using ethynyl benzene (511 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2 equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.30 in 2:3 EtOAc:hexanes) which afforded an off-white solid (927 mg, 83% yield). Data for **1:** ^{1}H NMR (400 MHz, $CDCl_3$) 7.67 (s, 1H), 7.43 – 7.35 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.10 (m, 2H), 3.53 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 158.2, 156.0, 130.2, 125.1, 118.3, 109.0, 42.5. IR (neat): ν_{max}/cm^{-1} 3153, 3015, 2930, 1592, 1555, 1490, 1457, 1371, 1315, 1229, 1179, 1074, 1056, 1013, 954, 844, 766, 689. HRMS (NSI): *m/z* 240.0444 [(M–H)$^+$ requires 240.0437], Calcd for $C_9H_{10}N_3O_3S$

4-(4-Methoxyphenoxy)-1-(methylsulfonyl)-1H-1,2,3-triazole (5). Compound **5** was prepared *via* general procedure for the synthesis of new triazoles using 1-ethynyl-4-methoxybenzene (661 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2 equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.34 in 2:3 EtOAc:hexanes) which afforded an off-white solid (924 mg, 73% yield). Data for **5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.12 – 7.05 (m, 2H), 6.91 – 6.84 (m, 2H), 3.79 (s, 3H), 3.50 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 159.6, 156.9, 149.4, 120.0, 119.9, 115.1, 114.8, 107.9, 55.7, 42.5. IR (neat): ν_{max}/cm^{-1} 3155, 3011, 2930, 2838, 1560, 1501, 1465, 1442, 1373, 1317, 1298, 1247, 1227, 1178, 1103, 1056, 1029, 1012, 955, 910, 835, 765, 730, 684. HRMS (NSI): *m/z* 270.0543 [(M–H)$^+$ requires 270.0543], Calcd for $C_{10}H_{12}N_3O_4S$

1-(Methylsulfonyl)-4-(3-methylphenoxy)-1H-1,2,3-triazole (6). Compound **6** was prepared *via* general procedure for the synthesis of new triazoles using 1-ethynyl-4-methylbenzene (581 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2 equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.32 in 2:3 EtOAc:hexanes) afforded an off-white solid (985 mg, 83% yield). Data for **6:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.20 – 7.15 (m, 2H), 7.06 – 6.99 (m, 2H), 3.52 (s, 3H), 2.34 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 158.9, 153.8, 134.9, 130.6, 118.4, 108.4, 42.5, 20.8. IR (neat): ν_{max}/cm^{-1} 3155, 3030, 2929, 1559, 1504, 1412, 1371, 1316, 1229, 1207, 1179, 1106, 1056, 1012, 953, 853, 824, 765, 683. HRMS (NSI): *m/z* 254.0594 [(M–H)$^+$ requires 254.0594], Calcd for $C_{10}H_{12}N_3O_3S$

4-(4-fluorophenoxy)-1-(methylsulfonyl)-1H-1,2,3-triazole (7). Compound **7** was prepared *via* general procedure for the synthesis of new triazoles using 1-ethynyl-4-fluorobenzene (601 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2 equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.30 in 2:3 EtOAc:hexanes) which afforded an off-white solid (748 mg, 62% yield). Data for **7:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.30 – 7.16 (m, 4H), 3.67 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 159.8 (d, *J* = 284 Hz), 158.5, 151.9 (d, *J* = 2.7 Hz), 120.1-120.0 (d, *J*=8.4 Hz), 116.8 (d, *J*=24 Hz), 108.8, 42.5. IR (neat): ν_{max}/cm^{-1} 3081, 3024, 2935, 1768, 1632, 1562, 1501, 1443, 1414, 1443, 1370, 1325, 1184, 1165, 1091, 1042, 1014, 969, 910, 836, 767, 747, 640. HRMS (NSI): *m/z* 258.0344 [(M–H)$^+$ requires 254.0343], Calcd for $C_9H_9N_3O_3SF$

1-(Methylsulfonyl)-4-(4-(trifluoromethyl)phenoxy)-1H-1,2,3-triazole (8). Compound **8** was prepared *via* general procedure for the synthesis of new triazoles using 1-ethynyl-4-(trifluoromethyl)benzene (851 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2 equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.24 in 2:3 EtOAc:hexanes) which afforded an off-white solid (845 mg, 58% yield). Data for **8:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.68 – 7.61 (m, 2H), 7.25 – 7.19 (m, 2H), 3.57 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 158.5, 156.5, 127.5 (q, *J* = 3.8 Hz), 127.0 (q, *J* = 33.0 Hz), 124.0 (q, *J* = 272 Hz), 118.0, 110.4, 42.6. IR (neat): ν_{max}/cm^{-1} 3157, 3029, 2936, 1616, 1560, 1513, 1417, 1375, 1321, 1233, 1164, 1121, 1105, 1065, 1015, 960, 842, 767, 602. HRMS (NSI): *m/z* 308.0313 [(M–H)$^+$ requires 308.0311], Calcd for $C_{10}H_9N_3O_3SF_3$

1-(Methylsulfonyl)-4-(3-methylphenoxy)-1H-1,2,3-triazole (9). Compound **9** was prepared *via* general procedure for the synthesis of new triazoles using 1-ethynyl-3-methylbenzene (581 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2 equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.30 in 2:3 EtOAc:hexanes) which afforded an off-white solid (1.07 g, 90% yield). Data for **9:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.01 (ddt, *J* = 7.6, 1.7, 0.8 Hz, 1H), 6.97 – 6.91 (m, 2H), 3.53 (s, 3H), 2.36 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 158.4, 156.1, 140.6, 129.9, 125.9, 119.0, 115.3, 108.9, 42.5, 21.5. IR (neat): ν_{max}/cm^{-1} 3279, 3027, 2932, 1611, 1588, 1487, 1465, 1324, 1284, 1238, 1152, 1041, 1000, 968, 929, 770, 689. HRMS (NSI): *m/z* 254.0593 [(M–H)$^+$ requires 254.0594], Calcd for $C_{10}H_{12}N_3O_3S$

1-(Methylsulfonyl)-4-(2-methylphenoxy)-1H-1,2,3-triazole (10). Compound **10** was prepared *via* general procedure for the synthesis of new triazoles using 1-ethynyl-2-methylbenzene (581 mg, 5.0 mmol, 1.0 equiv), methanesulfonyl azide (727 mg, 6.0 mmol, 1.2

equiv), CuTC (48 mg, 0.25 mmol, 5 mol %), and toluene (110 mL) at 0 °C for 30 min then room temperature for an additional 12 h. The reaction was then filtered through Celite® and toluene was removed *via* rotary evaporation. The material was purified by flash chromatography (SiO_2; EtOAc/hexanes, 1:5 to 2:3 gradient; Rf=0.29 in 2:3 EtOAc:hexanes) which afforded an off-white solid (973 mg, 82% yield). Data for **10:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.26 (ddd, J = 7.8, 1.8, 0.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.12 (td, J = 7.4, 1.4 Hz, 1H), 7.02 (dd, J = 7.9, 1.4 Hz, 1H), 3.51 (s, 3H), 2.30 (s, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 158.9, 154.1, 131.9, 129.2, 127.5, 125.5, 118.4, 107.9, 42.5, 16.0. IR (neat): ν_{max}/cm^{-1} 3027, 2931, 1629, 1558, 1490, 1463, 1317, 1226, 1159, 1108, 1042, 1014, 964, 911, 845, 751, 648. HRMS (NSI): *m/z* 254.0594 [(M–H)$^+$ requires 254.0594], Calcd for $C_{10}H_{12}N_3O_3S$

General procedure for the synthesis of new cyclopropanes. A flame dried 10 mL round bottom flask with magnetic stir bar was charged with triazole (1 mmol, 1 equiv) and Rh_2(*S*-NTTL)$_4$ or Rh_2(*S*-DPCP)$_4$ (0.02 mmol, 2 mol %) followed by three successive vacuum/argon cycles. Next, the flask was charged with styrene (2 mmol, 2 equiv) and $CHCl_3$ (2 mL) and allowed to proceed at 40 °C for 18 hrs. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (2.2 mmol, 2.2 equiv). The crude reaction mixture was extracted with dichloromethane, washed with $NaHCO_3$, and dried with $MgSO_4$. The solvent was removed *via* rotary evaporation, then the pure mixture of diastereomers was obtained by performing flash column chromatography eluting with an appropriate mixture of hexanes/ethyl acetate.

(1*S*,2*S*)-1-phenoxy-2-phenylcyclopropane-1-carbaldehyde (4a, major diastereomer), (1*R*,2*S*)-1-phenoxy-2-phenylcyclopropane-1-carbaldehyde (4b, minor diastereomer). Compound **4** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), **2** (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (6.2:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.28) afforded a tan oil containing a clean mixture of diastereomers (9.3:1 d.r.) (157 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.90 (s, 1H), 7.32 – 7.16 (m, 7H), 7.02 – 6.93 (m, 1H), 6.89 – 6.81 (m, 2H), 3.01 (dd, J = 10.3, 8.5 Hz, 1H), 2.21 (dd, J = 10.3, 6.0 Hz, 1H), 1.82 (dd, J = 8.5, 6.0 Hz, 1H); protons for minor diastereomer, δ 9.29 (s, 1H), 7.38 – 7.17 (m, 6H, overlapping with major diastereomer), 7.02 – 6.93 (m, 2H, overlapping with major diastereomer), 6.89 – 6.81 (m, 2H, overlapping with major diastereomer), 3.16-3.11 (m, 1H), 2.39 (dd, J = 8.9, 6.4 Hz, 1H), 1.96 (dd, J = 10.1, 6.4 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.2, 157.5, 134.1, 129.7, 128.6, 128.3, 127.3, 122.2, 115.5, 69.7, 35.9, 21.9; carbons for minor diastereomer, δ 198.0, 157.2, 133.7, 129.8, 129.5, 128.8, 128.8, 122.1, 115.7, 69.8, 36.6, 22.8. IR (neat): ν_{max}/cm^{-1} 3152, 1593, 1553, 1490, 1456, 1395, 1314, 1226, 1193, 1178, 1122, 1090, 1052, 1010, 978, 908, 844, 812, 756, 701, 689, 666. HRMS (NSI): *m/z* 239.1069 [(M–H)$^+$ requires 239.1067], Calcd for $C_{16}H_{15}O_2$. $[\alpha]^{20}_D$ -112.7° (*c* 0.55, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 71% ee: t_R(major enantiomer) = 24.5 min, t_R(minor enantiomer) = 22.6 min; minor diastereomer indicated 19% ee: t_R(major enantiomer) = 52.8 min, t_R(minor enantiomer) = 41.3 min. Rh_2(*S*-DPCP)$_4$ produced 4a in 80% yield (190 mg), 47% ee and 15:1 dr.

(1*S*,2*S*)-1-(4-methoxyphenoxy)-2-phenylcyclopropane-1-carbaldehyde (11). Compound **11** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **5** (269 mg, 1.0 mmol, 1.0 equiv), 2 (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (2.1:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.25) afforded a tan oil containing a clean mixture of diastereomers (1.7:1 d.r.) (30 mg, 11% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.89 (s, 1H), 7.36 – 7.16 (m, 4H, overlapping with minor diastereomer), 6.91 – 6.83 (m, 2H, overlapping with minor diastereomer), 6.77 (s, 3H, overlapping with minor diastereomer), 3.74 (s, 3H), 2.98 (dd, J = 10.2, 8.5 Hz, 1H), 2.16 (dd, J = 10.2, 6.0 Hz, 1H), 1.79 (ddd, J = 8.5, 6.0, 0.6 Hz, 1H); protons for minor diasteromer, δ 9.26 (s, 1H), 7.36 – 7.16 (m, 4H, overlapping with major diastereomer), 6.91 – 6.83 (m, 2H, overlapping with major diastereomer), 6.77 (s, 3H, overlapping with major diastereomer), 3.78 (s, 3H), 3.13 (dd, J = 10.0, 8.8 Hz, 1H), 2.35 (dd, J = 8.9, 6.3 Hz, 1H), 1.94 (dd, J = 10.0, 6.3 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$), carbons for major diastereomer, δ 201.5, 154.8, 151.4, 134.2, 128.5, 128.3, 127.3, 116.3, 114.8, 70.1, 55.8, 36.0, 21.8; carbons for minor diastereomer, δ 198.4, 154.8, 151.1, 133.9, 128.8, 128.8, 127.7, 116.7, 114.9, 70.4, 55.9, 36.5, 21.8. IR (neat): ν_{max}/cm^{-1} 2951, 2834, 1716, 1653, 1504, 1455, 1293, 1227, 1181, 1108, 1034, 826, 748, 697. HRMS (NSI): *m/z* 269.1167 [(M–H)$^+$ requires 269.1172], Calcd for $C_{17}H_{17}O_3$. $[\alpha]^{20}_D$ -20.3° (*c* 0.72, $CHCl_3$). HPLC analysis: major diasteromer (Chiralcel ADH, 1.0% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 19% ee: t_R(major enantiomer) = 24.7 min, t_R(minor enantiomer) = 21.3 min; minor diastereomer indicated 0% ee: t_R(major enantiomer) = 33.7 min, t_R(minor enantiomer) = 30.8 min. Rh_2(*S*-DPCP)$_4$ produced 11 in 18% yield (49 mg), 32% ee and 5.9:1 d.r.

(1*S*,2*S*)-2-phenyl-1-(4-methylphenoxy)cyclopropane-1-carbaldehyde (12). Compound **12** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **6** (253 mg, 1.0 mmol, 1.0 equiv), **2** (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (2.3:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.50) afforded a tan oil containing a clean mixture of diastereomers (3.5:1 d.r.) (141 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.90 (s, 1H), 7.42 – 7.16 (m, 5H, overlapping with minor diastereomer), 7.07 – 7.01 (m, 2H), 6.78 – 6.71 (m, 2H), 2.99 (dd, J = 10.2, 8.5 Hz, 1H), 2.27 (s, 3H), 2.19 (dd, J = 10.2, 6.0 Hz, 1H), 1.80 (dd, J = 8.4, 5.9 Hz, 1H); protons for minor diastereomer, δ 9.29 (s, 1H), 7.42 – 7.16 (m, 5H, overlapping with major diastereomer), 7.12 (d, J = 8.0 Hz, 2H), 6.88 – 6.83 (m, 2H), 3.13 (dd, J = 10.0, 8.9 Hz, 1H), 2.37 (dd, J = 8.9, 6.3 Hz, 1H), 2.32 (s, 3H), 1.94 (dd, J = 10.0, 6.3 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.4, 155.4, 134.2, 131.6, 130.2, 128.6, 128.2, 127.3, 115.3, 69.8, 36.0, 21.9, 20.6; carbons for minor diastereomer, δ 198.2, 155.0, 133.8, 130.2, 128.8, 128.7, 128.2, 127.6, 115.6, 70.0, 36.6, 21.4, 20.5. IR (neat): ν_{max}/cm^{-1} 3031, 2923, 2823, 2731, 1716, 1612, 1589, 1506, 1456, 1383, 1290, 1257, 1228, 1173, 1109, 1078, 1035, 1005, 942, 904, 881, 855, 774, 750, 725, 696, 611. HRMS (NSI): *m/z* 253.1217 [(M–H)$^+$ requires 253.1223], Calcd for $C_{17}H_{17}O_2$. $[\alpha]^{20}_D$ -

36.5° (*c* 3.3, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 20% ee: t_R(major enantiomer) = 29.0 min, t_R(minor enantiomer) = 22.6 min; minor diastereomer indicated 2% ee: t_R(major enantiomer) = 41.1 min, t_R(minor enantiomer) = 58.4 min. Rh_2(*S*-DPCP)$_4$ produced 12 in 25% yield (63 mg), 30% ee and 2.3:1 d.r.

(1*S*,2*S*)-1-(4-fluorophenoxy)-2-phenylcyclopropane-1-carbaldehyde (13). Compound **13** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **7** (257 mg, 1.0 mmol, 1.0 equiv), 2 (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (6.8:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.25) afforded a tan oil containing a clean mixture of diastereomers (6.2:1 d.r.) (113 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.74 (s, 1H), 7.21 – 7.11 (m, 3H, overlapping with minor diastereomer), 7.10 – 7.06 (m, 2H, overlapping with minor diastereomer), 6.84 – 6.77 (m, 2H), 6.70 – 6.64 (m, 2H), 2.92 (dd, *J* = 10.3, 8.5 Hz, 1H), 2.07 (dd, *J* = 10.2, 6.1 Hz, 1H), 1.72 (dd, *J* = 8.5, 6.1 Hz, 1H); protons for minor diastereomer, δ 9.11 (s, 1H), 7.25 (m, 4H), 7.21 – 7.11 (m, 2H, overlapping with major diastereomer), 7.10 – 7.06 (m, 1H, overlapping with major diastereomer), 6.94 – 6.88 (m, 2H), 3.04 (dd, *J* = 10.1, 8.9 Hz, 1H), 2.28 (dd, *J* = 8.8, 6.4 Hz, 1H), 1.85 (dd, *J* = 10.1, 6.4 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 200.6, 156.8 (d, *J* = 240 Hz), 153.4 (d, *J* = 2.3 Hz), 133.9, 128.5, 128.3, 127.4, 116.5 (d, *J* = 8.0 Hz), 116.1 (d, *J* = 23.3 Hz), 70.2, 35.6, 21.6. Carbons for minor diastereomer, δ 197.8, 159.6 (d, *J* = 240 Hz), 153.2 (d, *J* = 2.4 Hz), 133.6, 128.9, 128.7, 127.8, 116.9 (d, *J* =8.1 Hz), 116.2 (d, *J* =23.3 Hz), 70.3, 36.3, 21.6. IR (neat): ν_{max}/cm^{-1} 3064, 1716, 1604, 1501, 1456, 1385, 1304, 1202, 1097, 1035, 1006, 884, 829, 756, 697, 612. HRMS (NSI): *m/z* 257.0967 [(M–H)$^+$ requires 257.0972], Calcd for $C_{16}H_{14}O_2F$. $[\alpha]^{20}_D$ -71.4° (*c* 2.6, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 58% ee: t_R(major enantiomer) = 32.9 min, t_R(minor enantiomer) = 30.3 min; minor diastereomer indicated 57% ee: t_R(major enantiomer) = 24.8 min, t_R(minor enantiomer) = 22.6 min. Rh_2(*S*-DPCP)$_4$ produced 13 in 37% yield (95 mg), 53% ee and 13:1 d.r.

(1*S*,2*S*)-2-phenyl-1-(4-(trifluoromethyl)phenoxy)cyclopropane-1-carbaldehyde (14). Compound **14** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **8** (307 mg, 1.0 mmol, 1.0 equiv), **2** (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (5.4:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.23) afforded a tan oil containing a clean mixture of diastereomers (6.3:1 d.r.) (116 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.67 (s, 1H), 7.41 – 7.32 (m, 2H), 7.22 – 7.10 (m, 3H, overlapping with minor diastereomer), 7.11 – 7.04 (m, 2H, overlapping with minor diastereomer), 6.84 – 6.76 (m, 2H), 2.96 (dd, *J* = 10.3, 8.6 Hz, 1H), 2.12 (dd, *J* = 10.3, 6.2 Hz, 1H), 1.75 (dd, *J* = 8.6, 6.2 Hz, 1H); protons for minor diastereomer, δ 9.06 (s, 1H), 7.53 – 7.44 (m, 2H), 7.22 – 7.10 (m, 3H, overlapping with major diastereomer), 7.11 – 7.04 (m, 2H, overlapping with major diastereomer), 6.95 – 6.89 (m, 2H), 3.07 (dd, *J* = 8.9, 10.1 Hz, 1H), 2.34 (dd, *J* = 8.9, 6.6 Hz, 1H), 1.88 (dd, *J* = 10.1, 6.6 Hz, 1H). ^{13}C{1H} (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 199.5, 159.9, 133.4, 128.5, 128.4, 127.6, 127.1 (q, *J* = 3.6 Hz), 124.5 (q, *J* = 33.0 Hz), 124.3 (q, *J* = 272 Hz), 70.0, 35.2, 21.4; carbons for minor diastereomer, δ 196.8, 159.7, 133.3, 129.0, 128.7, 128.0, 127.0 (q, *J* = 3.6 Hz, overlapping with major diastereomer), 124.5 (q, *J* = 33.0 Hz, overlapping with major diastereomer), 124.3 (q, *J* = 272 Hz), 69.9, 36.1, 20.2. IR (neat): ν_{max}/cm^{-1} 3035, 1704, 1615, 1514, 1426, 1328, 1242, 1163, 1110, 1067, 1011, 838, 697, 655. HRMS (NSI): *m/z* 329.0755 [(M–Na)$^+$ requires 329.0760], Calcd for $C_{17}H_{13}O_2F_3Na$. $[\alpha]^{20}_D$ -23.1° (*c* 2.8, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ASH, 1.0% i-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 9% ee: t_R(major enantiomer) = 9.5 min, t_R(minor) = 10.3 min; minor diastereomer indicated 9% ee: t_R(major enantiomer) = 20.9 min, t_R(minor enantiomer) = 28.4 min. Rh_2(*S*-DPCP)$_4$ produced **14** in 17% yield (52 mg), 61% ee and 15:1 d.r.

(1*S*,2*S*)-2-phenyl-1-(3-methylphenoxy)cyclopropane-1-carbaldehyde (15). Compound **15** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **9** (253 mg, 1.0 mmol, 1.0 equiv), 2 (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (4.2:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.30) afforded a tan oil containing a clean mixture of diastereomers (4.9:1 d.r.) (103 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.79 (s, 1H), 7.25 (d, *J* = 4.4 Hz, 1H), 7.21 – 7.06 (m, 4H, overlapping with minor diastereomer), 7.01 (td, *J* = 7.6, 1.1 Hz, 1H), 6.71 – 6.65 (m, 1H), 6.58 – 6.52 (m, 2H), 2.88 (dd, *J* = 10.3, 8.5 Hz, 1H), 2.18 (s, 3H), 2.10 (dd, *J* = 10.2, 6.0 Hz, 1H), 1.70 (dd, *J* = 8.5, 6.0 Hz, 1H); protons for minor diastereomer, δ 9.20 (s, 1H), 7.21 – 7.06 (m, 4H, overlapping with major diastereomer), 6.75 (ddt, *J* = 7.5, 1.7, 0.8 Hz, 1H), 6.71 – 6.65 (m, 2H, overlapping with major diastereomer), 6.58 – 6.52 (m, 2H, overlapping with major diastereomer), 3.02 (dd, *J* = 10.1, 9.0 Hz, 1H), 2.30 – 2.22 (m, 4H), 1.84 (dd, *J* = 10.1, 6.3 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.3, 157.5, 139.9, 134.2, 129.4, 128.6, 128.2, 127.3, 123.0, 116.3, 112.4, 69.6, 35.9, 21.9, 21.6; carbons for minor diastereomer, δ 198.1, 157.2, 139.9, 133.8, 129.5, 128.8, 128.7, 127.6, 123.0, 116.5, 112.6, 69.8, 36.6, 21.7, 20.5. IR (neat): ν_{max}/cm^{-1} 3031, 2920, 2822, 2730, 1714, 1604, 1584, 1487, 1455, 1383, 1309, 1286, 1252, 1227, 1200, 1147, 1113, 1078, 1035, 1011, 936, 906, 849, 824, 771, 737, 689, 643. HRMS (NSI): *m/z* 275.1037 [(M–Na)$^+$ requires 275.1043], Calcd for $C_{17}H_{16}O_2Na$. $[\alpha]^{20}_D$ -55.4° (*c* 2.6, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 65% ee: t_R(major enantiomer) = 20.6 min, t_R(minor enantiomer) = 18.3 min; minor diastereomer indicated 24% ee: t_R(major enantiomer) = 58.4 min, t_R(minor enantiomer) = 32.4 min. Rh_2(*S*-DPCP)$_4$ produced 15 in 40% yield (100 mg), 45% ee and 9.8:1 d.r.

(1*S*,2*S*)-2-phenyl-1-(2-methylphenoxy)cyclopropane-1-carbaldehyde (16). Compound **16** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **10** (253 mg, 1.0 mmol, 1.0 equiv), 2 (208 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (4.7:1 d.r.). Purification by flash chromatography (SiO_2;

hexanes/EtOAc, 9:1; Rf 0.25) afforded a tan oil containing a clean mixture of diastereomers (5.6:1 d.r.) (138 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.78 (s, 1H), 7.20 – 7.08 (m, 5H, overlapping with minor diastereomer), 6.99 – 6.93 (m, 2H), 6.79 – 6.70 (m, 1H, overlapping with minor diastereomer), 6.66 (dd, J = 8.6, 1.2 Hz, 1H), 2.93 (dd, J = 10.2, 8.5 Hz, 1H), 2.11 (dd, J = 10.2, 6.0 Hz, 1H), 1.82 (s, 3H, overlapping with minor diastereomer), 1.69 (dd, J = 8.5, 6.0 Hz, 1H); protons for minor diastereomer, δ 9.20 (s, 1H), 7.26 – 7.23 (m, 2H), 7.20 – 7.08 (m, 2H, overlapping with major diastereomer), 7.07 – 7.01 (m, 2H), 6.83 (td, J = 7.4, 1.1 Hz, 1H), 6.79 – 6.70 (m, 2H, overlapping with major diastereomer), 3.01 (dd, J = 10.1, 8.9 1H), 2.28 (dd, J = 8.9, 6.3 Hz, 1H), 2.19 (s, 3H), 1.85 (dd, J = 8.9, 6.3 Hz, 1H, overlapping with major diastereomer). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.5, 155.4, 134.3, 131.3, 128.8, 128.2, 127.3, 127.1, 126.7, 121.7, 112.4, 69.2, 36.0, 21.7, 15.9; carbons for minor diastereomer, δ 198.2, 155.3, 133.8, 131.4, 128.8, 128.7, 127.6, 127.1, 126.8, 121.8, 113.1, 69.9, 36.8, 20.7, 16.5. IR (neat): ν_{max}/cm^{-1} 3030, 2919, 2821, 2729, 1715, 1603, 1590, 1489, 1456, 1380, 1309, 1232, 1186, 1159, 1119, 1079, 1049, 1034, 1005, 942, 883, 853, 802, 750, 696, 634. HRMS (NSI): *m/z* 253.1220 [(M–H)$^+$ requires 253.1223], Calcd for $C_{17}H_{17}O_2$. $[\alpha]^{20}_D$ -65.2° (c 2.4, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel R,R Whelk, 1.0% i-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 38% ee: t_R(major enantiomer) = 7.8 min, t_R(minor enantiomer) = 7.3 min; minor diastereomer indicated 9% ee: t_R(major enantiomer) = 12.3 min, t_R(minor enantiomer) = 13.7 min. Rh_2(*S*-DPCP)$_4$ produced 16 in 35% yield (91 mg), 48% ee and 8.7:1 d.r.

(1*S*,2*S*)-2-(4-fluorophenyl)-1-phenoxycyclopropane-1-carbaldehyde (17). Compound **17** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), 1-fluoro-4-vinylbenzene (244 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (5.7:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.30) afforded a tan oil containing a clean mixture of diastereomers (1.5:1 d.r.) (149 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.89 (s, 1H), 7.36 – 7.28 (m, 2H, overlapping with minor diastereomer), 7.27 – 7.20 (m, 1H, overlapping with minor diastereomer), 7.15 (ddd, J = 8.2, 5.2, 2.5 Hz, 1H), 7.08 – 7.01 (m, 1H, overlapping with minor diastereomer), 7.01 – 6.93 (m, 3H, overlapping with minor diastereomer), 6.88 – 6.79 (m, 1H, overlapping with minor diastereomer), 2.99 (dd, J = 10.3, 8.5 Hz, 1H), 2.20 (dd, J = 10.3, 6.1 Hz, 1H), 1.76 (dd, J = 8.5, 6.1 Hz, 1H); protons for minor diastereomer, δ 9.38 (s, 1H), 7.36 – 7.28 (m, 2H, overlapping with major diastereomer), 7.27 – 7.20 (m, 1H, overlapping with major diastereomer), 7.08 – 7.01 (m, 1H, overlapping with major diastereomer), 7.01 – 6.93 (m, 4H, overlapping with major diastereomer), 6.88 – 6.79 (m, 1H, overlapping with major diastereomer), 3.11 (dd, J = 10.1, 8.9 Hz, 1H), 2.32 (dd, J = 8.9, 6.3 Hz, 1H), 1.94 (dd, J = 10.1, 6.3 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.0, 162.2 (d, J = 246 Hz), 157.4, 130.1 (d, J = 8.1 Hz), 129.8, 122.3, 115.2 (d, J = 21.6 Hz), 115.4, 115.1, 69.4, 35.0, 22.0; carbons for minor diastereomer, δ 198.2, 162.2 (d, J = 247 Hz), 157.2, 130.5 (d, J = 8.2 Hz), 129.8, 122.3, 115.6 (d, J = 21.1 Hz), 69.9, 36.2, 20.8. IR (neat): ν_{max}/cm^{-1} 3042, 2828, 2733, 1716, 1597, 1589, 1512, 1492, 1457, 1437, 1385, 1297, 1222, 1160, 1110, 1078, 1057, 1025, 1015, 1004, 942, 905, 881, 837, 817, 753, 730, 691, 626. HRMS (NSI): m/z 256.0892 [M$^+$ requires 256.0894], Calcd for $C_{16}H_{13}FO_2$. $[\alpha]^{20}_D$ -70.9° (c 0.43, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ASH, 1.0% i-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 58% ee: t_R(major enantiomer) = 11.8 min, t_R(minor enantiomer) = 13.2 min; minor diastereomer indicated 2% ee: t_R(major enantiomer) = 19.8 min, t_R(minor enantiomer) = 26.3 min. Rh_2(*S*-DPCP)$_4$ produced 17 in 70% yield (180 mg), 46% ee and 8.7:1 d.r.

(1*S*,2*S*)-2-(4-chlorophenyl)-1-phenoxycyclopropane-1-carbaldehyde (18). Compound **18** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), 1-chloro-4-vinylbenzene (277 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (4.8:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.28) afforded a tan oil containing a clean mixture of diastereomers (2.0:1 d.r.) (106 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.89 (s, 1H), 7.30 – 7.21 (m, 5H), 7.16 – 7.10 (m, 2H), 6.87 – 6.80 (m, 2H), 2.97 (dd, J = 10.2, 8.5 Hz, 1H), 2.21 (dd, J = 10.2, 6.1 Hz, 1H), 1.77 (dd, J = 8.5, 6.1 Hz, 1H); protons for minor diastereomer, δ 9.40 (s, 1H), 7.37 – 7.30 (m, 4H), 7.08 – 7.02 (m, 1H), 6.99 (tt, J = 7.4, 1.1 Hz, 2H), 6.96 – 6.91 (m, 2H), 3.09 (dd, J = 10.1, 9.0 Hz, 1H), 2.33 (dd, J = 9.0, 6.4 Hz, 1H), 1.95 (dd, J = 10.1, 6.4 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 200.9, 157.3, 133.2, 132.8, 129.8, 129.8, 128.4, 122.4, 115.4, 69.5, 35.0, 22.0; carbons for minor diastereomer, δ 198.1, 157.1, 133.5, 132.2, 130.3, 129.9, 128.8, 122.3, 115.6, 69.9, 36.3, 20.8. IR (neat): ν_{max}/cm^{-1} 3041, 2926, 2827, 1716, 1589, 1492, 1456, 1384, 1297, 1230, 1170, 1117, 1093, 1078, 1025, 1015, 1004, 942, 881, 853, 830, 804, 787, 752, 718, 691, 651. HRMS (NSI): m/z 273.0670 [(M–H)$^+$ requires 273.0677], Calcd for $C_{16}H_{14}ClO_2$. $[\alpha]^{20}_D$ -78.3° (c 0.57, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 1.0% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 54% ee: t_R(major enantiomer) = 16.1 min, t_R(minor enantiomer) = 14.9 min; minor diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 0% ee: t_R(major enantiomer) = 56.6 min, t_R(minor enantiomer) = 70.1 min. Rh_2(*S*-DPCP)$_4$ produced 18 in 43% yield (117 mg), 37% ee and 11:1 d.r.

(1*S*,2*S*)-1-phenoxy-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbaldehyde (19). Compound **19** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), 1-(trifluoromethyl)-4-vinylbenzene (344 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). Diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (6.2:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.25) afforded a tan oil containing a clean mixture of diastereomers (1.6:1 d.r.) (162 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.92 (s, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.38 – 7.21 (m, 5H, overlapping with $CDCl_3$), 6.87 – 6.82 (m, 2H), 3.04 (dd, J = 10.2, 8.4 Hz, 1H), 2.25 (dd, J = 10.2, 6.2 Hz, 1H), 1.83 (dd, J = 8.4, 6.2 Hz, 1H); protons for minor diastereomer, δ 9.45 (s, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.06 (tt, J = 7.4, 1.1 Hz, 1H), 7.00 (tt, J = 7.3, 1.1 Hz, 2H), 6.95 (dt, J = 7.8, 1.1 Hz, 2H), 3.16 (dd, J = 10.1, 9.1 Hz, 1H), 2.39 (dd, J = 9.1, 6.4 Hz, 1H), 2.00 (dd, J = 10.1, 6.4 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$)

carbons for major diastereomer, δ 200.8, 157.2, 138.5, 129.9, 129.3, 128.9, 125.2 (q, *J* = 3.8 Hz), 122.9, 122.5, 115.4, 69.5, 35.1, 22.2; carbons for minor diastereomer, δ 198.0, 157.1, 137.7, 129.9, 129.7, 129.1, 125.6 (q, *J* = 3.7 Hz), 122.8, 122.5, 115.6, 70.0, 36.7, 20.8. IR (neat): ν_{max}/cm^{-1} 3034, 2928, 2831, 1719, 1621, 1598, 1590, 1493, 1411, 1385, 1325, 1300, 1232, 1166, 1120, 1070, 1018, 1004, 942, 882, 842, 806, 753, 723, 691, 650. HRMS (NSI): m/z 307.0932 [(M–H)$^+$ requires 307.0940], Calcd for $C_{17}H_{14}F_3O_2$. $[\alpha]^{20}_D$ -68.6° (c 0.45, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 58% ee: t_R(major enantiomer) = 24.5 min, t_R(minor enantiomer) = 28.0 min; minor diastereomer indicated 21% ee: t_R(major enantiomer) = 42.1 min, t_R(minor enantiomer) = 33.3 min.

(1*S*,2*S*)-1-phenoxy-2-(4-methylbenzene)cyclopropane-1-carbaldehyde (20). Compound **20** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), 1-methyl-4-vinylbenzene (236 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (2.3:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.35) afforded a tan oil containing a clean mixture of diastereomers (5.9:1 d.r.) (141 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.88 (s, 1H), 7.28 – 7.21 (m, 2H, overlapping with minor diastereomer), 7.12 – 7.02 (m, 4H, overlapping with minor diastereomer), 7.01 – 6.94 (m, 1H, overlapping with minor diastereomer), 6.89 – 6.84 (m, 2H), 2.97 (dd, *J* = 10.3, 8.5 Hz, 1H), 2.32 (s, 3H), 2.19 (dd, *J* = 10.3, 6.0 Hz, 1H), 1.77 (dd, *J* = 8.5, 6.0 Hz, 1H); protons for minor diastereomer, δ 9.28 (s, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H, overlapping with major diastereomer), 7.18 – 7.13 (m, 3H), 7.12 – 7.02 (m, 2H, overlapping with major diastereomer), 7.01 – 6.94 (m, 1H, overlapping with major diastereomer), 3.11 (dd, *J* = 10.0, 8.9 Hz, 1H), 2.39 – 2.34 (m, 4H), 1.93 (dd, *J* = 10.0, 6.4 Hz, 1H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.2, 157.6, 137.0, 131.0, 129.7, 129.0, 128.4, 122.2, 115.6, 69.7, 35.8, 21.8, 21.2; carbons for minor diastereomer, δ 198.1, 157.2, 137.4, 133.0, 130.7, 129.7, 129.5, 128.7, 122.1, 115.7, 69.9, 36.3, 20.5. IR (neat): ν_{max}/cm^{-1} 3029, 2921, 2822, 2730, 1715, 1596, 1519, 1492, 1456, 1382, 1300, 1254, 1230, 1170, 1154, 1123, 1100, 1078, 1035, 1024, 1004, 941, 880, 852, 819, 752, 724, 691, 629. HRMS (NSI): m/z 253.1216 [(M–H)$^+$ requires 253.1223], Calcd for $C_{17}H_{17}O_2$. $[\alpha]^{20}_D$ -102.6° (c 0.84, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 254 nm) indicated 65% ee: t_R(major enantiomer) = 22.7 min, t_R(minor enantiomer) = 20.5 min; minor diastereomer indicated 1% ee: t_R(major enantiomer) = 43.3 min, t_R(minor enantiomer) = 47.2 min.

(1*S*,2*R*)-1-phenoxy-2-propylcyclopropane-1-carbaldehyde (21). Compound **21** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), pent-1-ene (140 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^{1}H NMR of the crude reaction mixture (9.2:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.32) afforded a tan oil containing a clean mixture of diastereomers (5.6:1 d.r.) (41 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.68 (s, 1H), 7.31 – 7.25 (m, 2H, overlapping with minor diastereomer), 7.02 – 6.97 (m, 1H, overlapping with minor diastereomer), 6.96 – 6.87 (m, 2H, overlapping with minor diastereomer), 1.90 – 1.72 (m, 2H, overlapping with minor diastereomer), 1.68 – 1.36 (m, 4H, overlapping with minor diastereomer), 1.06 (m, 1H) 0.94 (t, *J* = 7.2 Hz, 3H); protons for minor diastereomer , δ 9.81 (s, 1H), 7.31 – 7.25 (m, 2H, overlapping with major diastereomer), 7.02 – 6.97 (m, 1H, overlapping with major diastereomer), 6.96 – 6.87 (m, 2H, overlapping with major diastereomer), 1.90 – 1.72 (m, 2H, overlapping with major diastereomer), 1.68 – 1.36 (m, 5H, overlapping with major diastereomer), 0.94 (m, 3H, overlapping with major diastereomer). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.7, 157.9, 129.8, 122.0, 115.5, 68.9, 31.0, 29.6, 22.7, 22.5, 14.0; carbons for minor diastereomer , δ 201.1, 157.5, 129.5, 121.9, 115.6, 60.4, 30.5, 29.7, 22.6, 22.4, 13.8. IR (neat): ν_{max}/cm^{-1} 2959, 2931, 2872, 1717, 1597, 1589, 1493, 1457, 1380, 1294, 1225, 1170, 1078, 1025, 944, 886, 815, 752, 691. HRMS (NSI): m/z 205.1218 [(M–H)$^+$ requires 205.1223], Calcd for $C_{13}H_{17}O_2$. $[\alpha]^{20}_D$ -18.1° (c 0.51, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel 4900, 0.3% i-PrOH/hexanes, 1.0 mL/min, 230 nm) indicated 61% ee: t_R(major enantiomer) = 5.8 min, t_R(minor enantiomer) = 5.0 min. Rh_2(*S*-DPCP)$_4$ produced 21 in 21% yield (43 mg), 50% ee and 12:1 d.r.

(1*S*,2*R*)-2-butyl-1-phenoxycyclopropane-1-carbaldehyde (22). Compound **22** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), hex-1-ene (168 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). Dr determined by ^{1}H NMR of the crude reaction mixture (15.1:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.30) afforded a tan oil containing a clean mixture of diastereomers (6.4:1 d.r.) (70 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.67 (s, 1H), 7.32 – 7.24 (m, 2H, overlapping with minor diastereomer), 7.00 (tt, *J* = 7.3, 1.1 Hz, 1H, overlapping with minor diastereomer), 6.96 – 6.84 (m, 2H, overlapping with minor diastereomer), 1.85 – 1.71 (m, 2H, overlapping with minor diastereomer), 1.69 – 1.29 (m, 6H, overlapping with minor diastereomer), 1.06 (q, *J* = 3.6 Hz, 1H), 0.90 (t, *J* = 7.2 Hz, 3H); protons for minor diastereomer, δ 9.81 (s, 1H), 7.32 – 7.23 (m, 2H, overlapping with major diastereomer), 7.00 (tt, *J* = 7.3, 1.1 Hz, 1H, overlapping with major diastereomer), 6.98 – 6.84 (m, 2H, overlapping with major diastereomer), 1.86 – 1.71 (m, 2H, overlapping with major diastereomer), 1.69 – 1.27 (m, 7H, overlapping with major diastereomer),), 0.90 (m, 3H, overlapping with major diastereomer). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.7, 157.9, 129.7, 122.0, 115.5, 68.9, 31.4, 31.2, 27.3, 22.7, 22.5, 14.1; carbons for minor diastereomer, δ 201.1, 157.5, 129.5, 121.8, 115.6, 60.4, 34.2, 31.7, 30.7, 26.6, 23.6, 22.4. IR (neat): ν_{max}/cm^{-1} 2957, 2930, 2860, 1719, 1598, 1590, 1494, 1457, 1380, 1301, 1224, 1170, 1078, 1026, 944, 753, 691. HRMS (NSI): m/z 219.1371 [(M–H)$^+$ requires 219.1380], Calcd for $C_{14}H_{19}O_2$. $[\alpha]^{20}_D$ -17.7° (c 0.73, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 0.3% i-PrOH/hexanes, 0.5 mL/min, 230 nm) indicated 36% ee: t_R(major enantiomer) = 18.9 min, t_R(minor enantiomer) = 29.6 min. Rh_2(*S*-DPCP)$_4$ produced **22** in 23% yield (50 mg), 46% ee and >30:1 d.r.

(1*S*,2*R*)-2-benzyl-1-phenoxycyclopropane-1-carbaldehyde (23). Compound **23** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), allylbenzene (236 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h.

Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^1H NMR of the crude reaction mixture (9.1:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.26) afforded a tan oil containing a clean mixture of diastereomers (9.9:1 d.r.) (71 mg, 28% yield). ^1H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.72 (s, 1H), 7.38 – 7.18 (m, 8H, overlapping with minor diastereomer), 7.08 – 6.94 (m, 2H, overlapping with minor diastereomer), 3.03 (dd, J = 15.0, 7.0 Hz, 1H), 2.79 (dd, J = 15.1, 7.2 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.90 (dd, J = 9.8, 5.5 Hz, 1H), 1.25 (dd, J = 8.0, 5.5 Hz, 1H); protons for minor diastereomer, δ 9.93 (s, 1H), 7.38 – 7.18 (m, 6H, overlapping with major diastereomer), 7.08 – 6.94 (m, 3H, overlapping with major diastereomer), 6.82 – 6.74 (m, 1H), 2.92 (d, J = 7.9 Hz, 1H), 2.18 – 2.11 (m, 1H), 1.76 (dd, J = 8.6, 5.6 Hz, 1H), 1.64 (dd, J = 9.9, 5.6 Hz, 1H), 1.13 (dd, J = 8.0, 5.6 Hz, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.3, 157.8, 140.1, 129.9, 128.7, 128.6, 126.5, 122.2, 115.5, 68.8, 33.5, 31.9, 22.6; carbons for minor diastereomer, δ 201.7, 157.3, 129.8, 129.7, 128.8, 128.6, 126.6, 115.6, 115.3, 68.6, 33.6, 32.5, 22.5. IR (neat): ν_{max}/cm^{-1} 3062, 3028, 2924, 2822, 2730, 1717, 1598, 1589, 1493, 1455, 1383, 1301, 1223, 1170, 1078, 1030, 946, 891, 818, 753, 692. HRMS (NSI): m/z 253.1214 [$(M–H)^+$ requires 253.1223], Calcd for $C_{17}H_{17}O_2$. $[\alpha]^{20}_D$ +0.40° (c 2.4, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel 4900, 3.0% i-PrOH/hexanes, 1.0 mL/min, 254 nm) indicated 29% ee: t_R(major enantiomer) = 18.9 min, t_R(minor enantiomer) = 29.6 min; minor diastereomer indicated 8% ee: t_R(major enantiomer) = 13.4 min, t_R(minor enantiomer) = 11.8 min. Rh_2(*S*-DPCP)$_4$ produced 23 in 21% yield (53 mg), 46% ee and >30:1 d.r.

(1*S*,2*R*)-1-phenoxy-2-isobutylcyclopropane-1-carbaldehyde (24). Compound **24** was prepared via the general procedure for the synthesis of new cyclopropanes using 1 (239 mg, 1.0 mmol, 1.0 equiv), 2-methyl-pent-1-ene (168 mg, 2.0 mmol, 2 equiv), Rh_2(S-DPCP)$_4$ (23 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by 1H NMR of the crude reaction mixture (>30:1 d.r.). Purification by flash chromatography (SiO_2; 0-10% ethyl acetate in hexanes) afforded a clear oil containing a clean mixture of diastereomers (>30:1 d.r.) (44.6 mg, 21% yield). Characterized as a pure diastereomer. ^1H NMR (600 MHz, Chloroform-d) δ 9.80 (s, 1H), 7.30-7.28 (m, 2H), 7.02-7.01 (m, 1H), 6.99 – 6.93 (m, 2H), 1.84-1.72 (m, 3H), 1.62-1.58 (dt, J = 13.2, 6.4 Hz, 1H), 1.34-1.29 (dt, J = 14.0, 7.2 Hz, 1H), 1.08-1.06 (dd, J = 7.6, 4.7 Hz, 1H), 0.97-0.95 (dd, J = 8.7, 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 201.8, 157.9, 130.0, 122.0, 115.5, 68.7, 36.3, 29.8, 28.4, 22.9, 22.7, 22.5. IR (film): vmax/cm-1 3016, 2967, 2955, 2870, 1738, 1590, 1493, 1441, 1366, 1201, 1217, 1170, 1078, 1046, 1026, 914, 888, 810, 751, 691, 624, 540, 528, 509, 412, 404. HRMS(APCI): m/z 139.0768 [$(M)^+$ requires 139.0764], Calcd for $C_8H_{11}O_2$. $[\alpha]^{20}_D$ -12.1° (c 0.5, $CHCl_3$). HPLC analysis: (Chiralcel ADH, 0.5% i-PrOH/hexanes, 0.5 mL/min, 230 nm) indicated 60% ee: t_R(major enantiomer) = 11.0 min, t_R(minor enantiomer) = 15.8 min

(1*S*,2*S*)-2-(4-methoxyphenyl)-1-phenoxycyclopropane-1-carbaldehyde (26). Compound **26** was prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene **25** (268 mg, 2.0 mmol, 2.0 equiv), Rh_2(*S*-NTTL)$_4$ (29 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 hrs. Then the reaction was quenched with MeOH (2 mL), H_2O (10 drops), and K_2CO_3 (304 mg, 2.2 mmol, 2.2 equiv). The diastereoselectivity was determined by ^1H NMR of the crude reaction mixture (4.2:1 d.r.). Purification by flash chromatography (SiO_2; hexanes/EtOAc, 9:1; Rf 0.32) afforded a tan oil containing a clean mixture of diastereomers (4.8:1 d.r.) (172 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$) protons for major diastereomer, δ 9.88 (s, 1H), 7.25 – 7.21 (m, 2H), 7.14 – 7.09 (m, 2H), 7.00 – 6.95 (m, 1H), 6.87 – 6.81 (m, 4H, overlapping with minor diastereomer), 3.79 (s, 3H), 2.96 (dd, J = 10.3, 8.6 Hz, 1H), 2.19 (dd, J = 10.3, 6.0 Hz, 1H), 1.74 (dd, J = 8.5, 6.0 Hz, 1H); protons for minor diastereomer , δ 9.30 (s, 1H), 7.34 – 7.28 (m, 3H), 7.06 – 7.01 (m, 2H), 6.87 – 6.81 (m, 4H, overlapping with major diastereomer), 3.81 (s, 3H), 3.10 (dd, J = 10.0, 8.9 Hz, 1H), 2.33 (dd, J = 8.9, 6.3 Hz, 1H), 1.92 (dd, J = 10.1, 6.3 Hz, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) carbons for major diastereomer, δ 201.2, 159.0, 157.6, 129.7, 129.6, 126.0, 122.2, 115.6, 113.8, 69.7, 55.4, 35.6, 21.9; carbons for minor diastereomer , δ 198.3, 159.1, 157.2, 129.9, 129.8, 125.7, 122.1, 115.7, 114.2, 69.9, 55.4, 36.2, 20.7. IR (neat): ν_{max}/cm^{-1} 2931, 2824, 2731, 1715, 1592, 1524, 1455, 1297, 1230, 1178, 1151, 1100, 1014, 850, 757, 687. HRMS (NSI): m/z 269.1167 [$(M–H)^+$ requires 269.1172], Calcd for $C_{17}H_{17}O_3$. $[\alpha]^{20}_D$ -22.5° (c 2.5, $CHCl_3$). HPLC analysis: major diastereomer (Chiralcel ADH, 1.0% i-PrOH/hexanes, 0.5 mL/min, 230 nm) indicated 58% ee: t_R(major enantiomer) = 21.0 min, t_R(minor enantiomer) = 20.0 min. Rh_2(*S*-DPCP)$_4$ produced **27** under the same conditions.

2-(4-Methoxyphenyl)-1-(methylsulfonyl)-4-phenoxy-2,3-dihydro-1*H*-pyrrole (27). Prepared *via* the general procedure for the synthesis of new cyclopropanes using **1** (239 mg, 1.0 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (268 mg, 2.0 mmol, 2.0 equiv), Rh_2(S-DPCP)$_4$ (23.1 mg, 0.02 mmol, 2 mol %), and $CHCl_3$ (2 mL) at 40 °C for 18 h. Purification by flash chromatography (SiO_2; 6:4 hexanes/EtOAc, Rf 0.37) afforded a white amorphous solid containing the undesired dihydropyrrole product (140 mg, 41% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.19 – 7.13 (m, 3H), 7.08 – 6.90 (m, 2H), 5.91-5.90 (dd, J = 2.3, 1.4 Hz, 1H), 5.10-5.06 (dd, J = 10.7, 5.6 Hz, 1H), 3.82 (s, 3H), 3.51 – 3.43 (ddd, J = 16.2, 10.7, 2.3 Hz, 1H), 2.78-2.72 (m, 4H). $^{13}C\{1H\}$ NMR (151 MHz, $CDCl_3$) δ δ 217.0, 172.6, 134.0, 130.0, 127.7, 124.7, 119.0, 114.4, 98.4, 61.6, 55.5, 39.5, 37.1. IR (film): ν_{max}/cm^{-1} 3012, 2930, 2837, 1663, 1612, 1589, 1512, 1489, 1456, 1335, 1302, 1244, 1227, 1176, 1150, 1111, 1070, 1030, 984, 871, 830, 809, 755, 695, 634, 591, 546, 507. HRMS (APCI): m/z 345.1029 [$(M+H)^+$ requires 305.1029]. Calc'd for $C_{18}H_{19}O_4N^{32}S$. SFC analysis: (Regis *S,S*-Whelk, 10% MeOH/i-PrOH with 0.2% formic acid in CO_2, 254 nm) indicated <5% ee: t_R (major enantiomer) = 3.68 min, t_R (minor enantiomer) = 4.97 min.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data and ^1H and ^{13}C NMR spectroscopic data (PDF)

Accession Codes

CCDC 2063334 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic DataCentre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 902 1223 336033.

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Notes

HMLD is a named inventor on a patent entitled, Dirhodium Catalyst Compositions and Synthetic Processes Related Thereto (US 8,974,428, issued March 10, 2015). The other authors have no competing financial interests.

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