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Enantio- and diastereoselective cyclopropanation with *tert*-butyl α-diazopropionate catalyzed by dirhodium(II) tetrakis[*N*-tetrabromophthaloyl-(*S*)-*tert*-leucinate]

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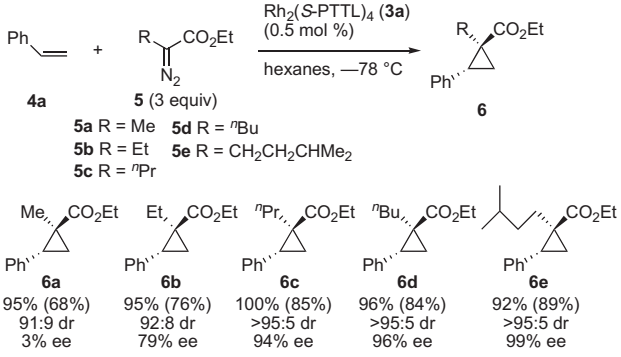
ABSTRACT

The first successful example of a catalytic asymmetric cyclopropanation with α-diazopropionates is described. The cyclopropanation reaction of 1-aryl-substituted and related conjugated alkenes with *tert*-butyl α-diazopropionate has been achieved by catalysis with dirhodium(II) tetrakis[*N*-tetrabromophthaloyl-(*S*)-*tert*-leucinate], Rh_2(*S*-TBPTTL)$_4$, providing the corresponding cyclopropane products containing a quarternary stereogenic center in good to high yields and with high diastereo- and enantioselectivities (*trans*:*cis* = 90:10 to >99:1, 81–93% ee).

Substituted cyclopropanes are commonly encountered structural subunits in a wide variety of biologically important natural products and medicinal agents.[1] Since the pioneering work of Nozaki and Noyori in 1966,[2] the transition metal-catalyzed asymmetric cyclopropanation of alkenes with diazo compounds has emerged as one of the most direct and efficient routes to optically active cyclopropane building blocks.[3] Over the past two decades, a number of powerful catalytic systems based on Cu(I),[4] Co(II),[5] Rh(II),[6] Ru(II),[7] and Ir(III)[8] complexes of well-designed chiral ligands have been developed to achieve high enantio- and diastereoselectivity for cyclopropanation reactions with various types of diazo compounds.[9–20] While the majority of successful asymmetric cyclopropanations reported involved the use of acceptor-substituted diazo compounds,[4–8,10] most commonly diazoacetates,[4–8] substantial progress in this field has recently been achieved by expanding the reaction scope to include donor/acceptor-substituted diazo compounds[11–14] such as vinyldiazoacetates[11] and aryldiazoacetates,[12] as well as acceptor/acceptor-substituted carbene precursors[15–22] such as nitrodiazoacetates,[15] nitrodiazoketones,[16] amidodiazoacetates,[17] cyanodiazoacetamides,[18] diazomalonates[19,20] and related phenyliodinium ylide variants.[21] However, asymmetric cyclopropanation with α-alkyl-α-diazoesters[23–25] has remained elusive due to the propensity to form α,β-unsaturated esters via a 1,2-hydride shift[26] in metal-carbene intermediates until a recent breakthrough by Fox et al.[27] Fox et al. developed highly enantio-, diastereo-, and chemoselective cyclopropanations of terminal aromatic alkenes and benzofuran with α-alkyl-α-diazoesters using dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-*tert*-leucinate], Rh_2(*S*-PTTL)$_4$ (**3a**),[28] as a chiral catalyst in hexanes at −78 °C. While this work was a notable landmark, the enantioselectivity was highly sensitive to the structure of the diazoester. Exceptionally high levels of enantioselectivity



Scheme 1. Catalytic asymmetric cyclopropanation of styrene with α-alkyl-α-diazoesters catalyzed by Rh_2(*S*-PTTL)$_4$ reported by Fox.[27] The isolated yields in parentheses were obtained when 1.1 equiv of styrene and 1.0 equiv of diazoesters were used.

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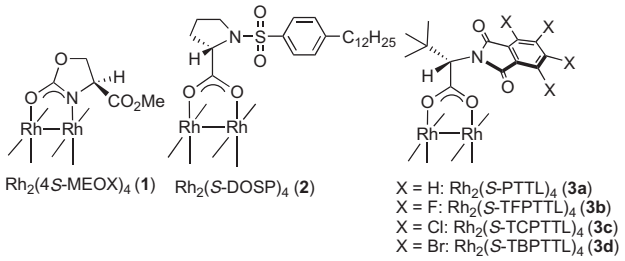
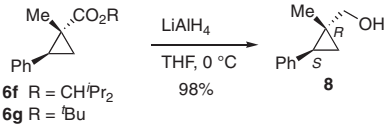
(up to 99% ee) in cyclopropanations of styrene were achieved with diazoesters bearing larger α-alkyl groups than the α-ethyl substituent as the reaction with ethyl α-diazopropionate (**5a**) and ethyl α-diazobutanoate (**5b**) gave the corresponding cyclopropane products in 3% and 79% ee, respectively (Scheme 1).[27] Very recently, we reported the first example of catalytic asymmetric cyclopropenation of 1-alkynes with α-alkyl-α-diazoesters.[29] In this process, Rh_2(*S*-TBPTTL)$_4$ (**3d**), a brominated analog of Rh_2(*S*-PTTL)$_4$ (**3a**), emerged as the catalyst of choice for achieving exceptionally high levels of asymmetric induction (up to 99% ee) as well as good to high selectivities over alkene formation via a 1,2-hydride shift. As part of our interest in further extension of the scope and utility of **3d**, we now address the issue of enantiocontrol in cyclopropanations with α-diazopropionates,[25] a virtually unmet challenge in Fox's cyclopropanation methodology.[27]



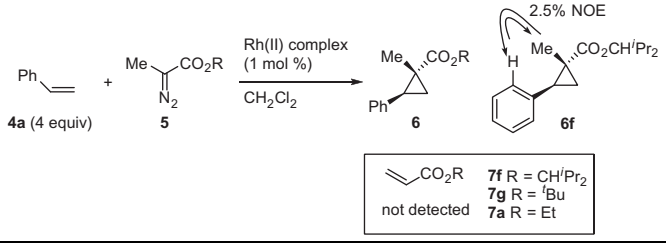
Based on our previous work,[29] we initially explored the cyclopropanation of styrene (**4a**) (4 equiv) with 2,4-dimethyl-3-pentyl α-diazopropionate (**5f**) using 1 mol % of Rh_2(*S*-TBPTTL)$_4$ (**3d**) in dichloromethane at −60 °C. The reaction proceeded to completion within 7 h, giving the *trans*-cyclopropane product **6f** in 92% yield and 97:3 dr with no signs of the formation of alkene **7f** (Table 1, entry 1). As with the Rh_2(*S*-TBPTTL)$_4$-catalyzed cyclopropenation system,[29] no slow addition of **5f** was required. The *trans*-stereochemistry of **6f** was established by ^{1}H NOE between the C1 methyl group and *ortho* protons on the benzene ring. The enantioselectivity of this reaction was determined to be 84% ee by HPLC using a



Scheme 2. Determination of the absolute stereochemistry of **6f** and **6g**.

Daicel Chiralpak IC column. The preferred absolute stereochemistry of **6f** [$[\alpha]_D^{21}$ −104.2 (*c* 1.01, $CHCl_3$) for 84% ee] was established as 1*R*,2*S* by its transformation [$LiAlH_4$, THF, 0 °C, 3 h] to the known *trans*-1-phenyl-2-methylcyclopropane-1-methanol [$[\alpha]_D^{22}$ −15.4 (*c* 0.64, $CHCl_3$); lit.,[29] $[\alpha]_D^{21}$ −17.2 (*c* 0.17, $CHCl_3$) for 95% ee of (1*R*,2*S*)-enantiomer] (Scheme 2). We next evaluated the performance of other dirhodium(II) carboxylates, Rh_2(*S*-PTTL)$_4$ (**3a**),[28] Rh_2(*S*-TFPTTL)$_4$ (**3b**)[30] and Rh_2(*S*-TCPTTL)$_4$ (**3c**).[31,32] While all of these catalysts provided the *trans*-cyclopropane **6f** in high yields and with the same sense of asymmetric induction and similar high diastereoselectivity as those observed with Rh_2(*S*-TBPTTL)$_4$ (**3d**), the highest level of enantioselectivity was only 69% ee, which was obtained using Rh_2(*S*-TCPTTL)$_4$ (**3c**) (entries 1 vs 2–4). Clearly, **3d** proved to be by far the best choice for this transformation as well as for the asymmetric cyclopropenation reaction. An examination of the temperature profile demonstrated that lowering the reaction temperature from −60 to −78 °C resulted in perfect *trans*-diastereoselectivity, though catalysis at −78 °C required a significantly longer reaction time to reach completion and resulted in 86% ee (entry 5). Not unexpectedly, increasing the reaction temperature to −40 or −20 °C was accompanied by a significant decrease in enantioselectivity while maintaining high diastereoselectivity (75% and 66% ee, entries 6 and 7). Using Rh_2(*S*-TBPTTL)$_4$ as a catalyst, the effect of the ester moiety was also evaluated at −60 °C. While the use of ethyl ester **5a** resulted in lower enantioselectivity (35% ee, entry 8), the reaction with *tert*-butyl ester **5g** afforded the *trans*-cyclopropane product **6g** as a single diastereomer in high yield and with somewhat higher enantioselectivity

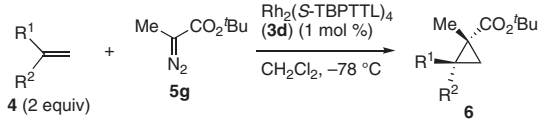
Table 1
Enantio- and diastereoselective cyclopropanation of styrene with α-diazopropionates catalyzed by dirhodium(II) carboxylates[a]



Entry	α-Diazoesters		Rh(II) catalyst	Temp (°C)	Time (h)	Cyclopropanes			
		R					Yield[b] (%)	*trans*:*cis*[c]	Ee[d] (%)
1	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−60	7	**6f**	92	97:3	84
2	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-PTTL)$_4$ (**3a**)	−60	4	**6f**	89	94:6	47
3	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-TFPTTL)$_4$ (**3b**)	−60	3	**6f**	86	92:8	33
4	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-TCPTTL)$_4$ (**3c**)	−60	3	**6f**	89	95:5	69
5	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−78	48	**6f**	86	>99:1	86
6	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−40	2	**6f**	92	96:4	75
7	**5f**	CH^{i}Pr$_2$	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−20	0.5	**6f**	90	94:6	66
8	**5a**	Et	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−60	2	**6a**	80	91:9	35
9	**5g**	^{t}Bu	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−60	2	**6g**	94	>99:1	88
10	**5g**	^{t}Bu	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−78	6	**6g**	92	>99:1	90
11[e]	**5g**	^{t}Bu	Rh_2(*S*-TBPTTL)$_4$ (**3d**)	−78	8	**6g**	87	>99:1	92

[a] All reactions were carried out as follows: Rh(II) catalyst (1 mol %) was added to a solution of **4a** (0.8 mmol, 4 equiv) and **5** (0.2 mmol) in CH_2Cl_2 (0.1 M).
[b] Isolated yield.
[c] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[d] Determined by HPLC analysis. See Supplementary data for details.
[e] 2 equiv of **4a** was used.

Table 2
Enantio- and diastereoselective cyclopropanation of alkenes with *tert*-butyl α-diazopropionate (**5g**) catalyzed by Rh_2(*S*-TBPTTL)$_4$[a]



Entry	Alkenes			Time (h)	Cyclopropanes			
		R^1	R^2			Yield[b] (%)	*trans*:*cis*[c]	ee[d] (%)
1	**4a**	C_6H_5	H	8	**6g**	87	>99:1	92
2	**4b**	4-$CH_3OC_6H_4$	H	9	**6h**	90	>99:1	90
3	**4c**	4-FC_6H_4	H	10	**6i**	86	>99:1	90
4	**4d**	4-ClC_6H_4	H	10	**6j**	89	>99:1	91
5	**4e**	4-$CF_3C_6H_4$	H	9	**6k**	81	>99:1	93
6	**4f**	1-Naphthyl	H	12	**6l**	61	98:2	88
7	**4g**	2-Naphthyl	H	12	**6m**	95	>99:1	81
8	**4h**	(*E*)-C_6H_5CH=CH	H	12	**6n**	87	90:10	92
9[e]	**4i**	$^nC_4H_9$	H	24	**6o**	59	95:5	77
10	**4j**	C_6H_5	CH_3	12	**6p**	73	91:9	70
11	**4k**	C_6H_5	C_6H_5	9	**6q**	84	–	57

[a] All reactions were carried out with 2 equiv of **4** on a 0.2 mmol scale unless otherwise stated.
[b] Isolated yield.
[c] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[d] Determined by HPLC analysis. See Supplementary data for details.
[e] 5 equiv of **4i** was used.

than that observed with 2,4-dimethyl-3-pentyl ester **5f** (88% ee, entry 9). In a similar way to **6f**, the absolute stereochemistry of **6g** was determined to be 1*R*,2*S* (Scheme 2). When the reaction with **5g** was conducted at −78 °C, the enantioselectivity was further enhanced to 90% ee without compromising the product yield or greatly affecting the reaction rate (entry 10). In addition, virtually the same result was obtained using only 2 equiv of styrene, in which a slight increase in enantioselectivity was noted (92% ee, entry 11).

Having determined the effectiveness of the combinational use of Rh_2(*S*-TBPTTL)$_4$ as a catalyst and **5g** as a carbene precursor, we then explored the scope of the reaction with respect to the alkene component (Table 2). Aside from essentially complete *trans*-diastereoselectivity, high enantioselectivity was consistently observed with styrenes bearing electron-donating or electron-withdrawing substituents at the *para* position on the benzene ring (90–93% ee, entries 2–5). The reaction with 1-vinylnaphthalene (**4f**) provided exclusively the *trans*-cyclopropane product **6l** with 88% ee, albeit in moderate yield (61% yield, entry 6), while the use of 2-vinylnaphthalene (**4g**) gave **6m** in excellent yield with a modest decrease in enantioselectivity (95% yield, 81% ee, entry 7). The regioselective cyclopropanation of (*E*)-1-phenyl-1,3-butadiene (**4h**) also proceeded cleanly and afforded predominantly the styryl-substituted *trans*-cyclopropane **6n** in high yield with 92% ee (entry 8). As might be expected from Davies' studies on cyclopropanation chemoselectivity,[33] the terminal aliphatic alkene 1-hexene (**4i**) was found to be much less reactive, as the reaction with 5 equiv of **4i** required a significantly longer reaction time (24 h) to reach completion, with **6o** being obtained in only 59% yield with 77% ee (entry 9). 1,1-Disubstituted alkenes **4j** and **4k** could be cyclopropanated in good to high yields but with only modest enantioselectivity (70% and 57% ee, entries 10 and 11).

In summary, we have demonstrated that Rh_2(*S*-TBPTTL)$_4$ is an exceptionally effective catalyst for asymmetric cyclopropanation reactions of 1-aryl-substituted and related conjugated alkenes with *tert*-butyl α-diazopropionate, in which high levels of enantioselectivity (up to 93% ee) as well as virtually complete *trans*-diastereoselectivity have been achieved. The reaction could be carried out in a one-pot fashion and would not require the slow addition of the diazo reagent, in which no signs of alkene product derived from a 1,2-hydride shift or dimer products such as carbene dimer and azine were observed. This protocol represents the first successful example of a catalytic asymmetric cyclopropanation of alkenes with α-diazopropionates and partially complements the Fox cyclopropanation methodology.[27] Further extension of this method to α-diazobutanoates as well as stereochemical studies are currently underway.

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Supplementary data

Supplementary data (detailed experimental procedures and full spectroscopic characterization data for all new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.06.008.

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