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Asymmetric Cyclopropanation Catalyzed by a Series of Copper-(Schiff-Base) Complexes with Two Chiral Centers

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ABSTRACT A series of copper-(Schiff-base) complexes with two chiral centers derived from 1,2-diphenyl-2-amino-ethanol were synthesized and applied to catalyze the asymmetric cyclopropanation of ethenes with diazoacetates. A mechanism that can explain the observed results was proposed. Some of these complexes were also efficient catalysts for asymmetric cyclopropanation of 1,1-diphenylethene with ethyl diazoacetate, affording high e.e. of up to 98.6%. An e.e. of 80.7% was achieved when no solvent was used.

KEYWORDS asymmetric cyclopropanation chiral, copper-(Schiff-base), diazoacetates, diastereoselectivity

INTRODUCTION

Catalytic asymmetric cyclopropanation of diazoacetates with ethens has attracted much attention [1,2]. Certain transition metal complexes have been applied to catalyze the decomposition of diazocompounds [3,4]. The first catalytic asymmetric cyclopropanation reaction was reported in 1966 when Nozaki et al showed that the cyclopropane compound was attained by the effect of a copper(II) complex **1** bearing a salicyladimine ligand, though with a low e.e. of 6% [5]. This report initiated activities that resulted in the discovery of the Aratani' catalyst with dramatic improvements in optical yields for selected intermoleculor cyclopropanation reaction [6,7]. Some other other efficient copper-(Schiff-base) complexes were reported by Zhengling Li [8] and Cai et al [9] recently which were prepared by modification of Aratani's catalyst **2**.

However, the mechanism of the asymmetric cyclopropanation catalyzed by this kind of Schiff-base complex is still not very clear. Aratani has proposed a mechanism [7] to explain the mode of chirality transfer. Although this explanation predicts the observed predominant cyclopropane configuration, it does not adequately account for the preferential diastereoselectivity of (*E*)-product that is observed in most cases. Therefore it will be helpful to know the mechanism more thoroughly

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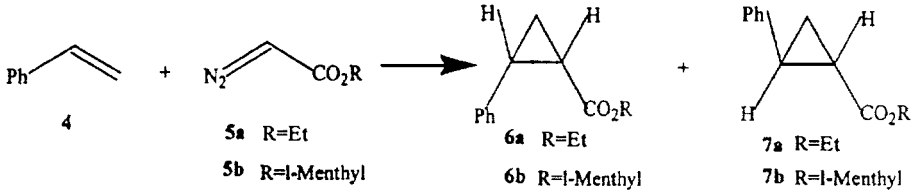
TABLE 1 Asymmetric cyclopropanation of styene **4** catalyzed by using 1 mol% of **3**[a]



Entry	***3***	***5***	*Yield (%)*[b]	*Ratio **6:7***[c]	*%ee **6***[d]	*%**7***[d]
1	a	a	63	30/70	63.2(1S, 2R)	32.8(1S, 2S)
2	b	a	65	31/69	60.6(1R, 2S)	32.3(1R, 2R)
3	c	a	54	27/73	12.1(1S, 2R)	23.4(1S, 2S)
4	d	a	57	27/73	12.9(1R, 2S)	22.7(1R, 2R)
5	e	a	75	39/61	58.8(1S, 2R)	30.5(1S, 2S)
6	a	b	54	21/79	65.4(1S, 2R)	55.3(1S, 2S)
7	b	b	59	22/78	63.9(1R, 2S)	56.7(1R, 2R)
8	c	b	60	15/85	11.3(1S, 2R)	17.2(1S, 2S)
9	d	b	51	18/82	11.4(1R, 2S)	17.8(1R, 2R)
10	e	b	70	27/73	60.1(1S, 2R)	35.0(1S, 2S)

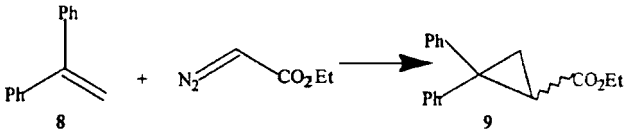
[a]All reactions were carried out at 40°C in benzene.
[b]Isolated yields of purified **6** and **7**.
[c]Determined by GC (Column: PE-5, length: 20.00 M, ID: 0.18 mm, film thickness: 0.18 um, column temp.: 250°C).
[d]For entry **1–5** the %e.e. was determined by HPLC (Chiracel OD column, elution with hexane/isopropanol 9.75:0.25, 0.4 ml/min; for entry 6–10 the %e.e. was determined by GC (Column: PE-5, length: 20.00 M, ID:0.18 mm, film thickness: 0.18 um, column temp.: 250°C). The configuration in parentheses is of the excess enatiomer, which was established on the basis of the sign of the specific rotation of the corresponding acid [10].

for developing novel efficient catalyst. Up to now, all the copper(Schiff-base) complexes that have been applied to catalyze this reaction have only one chiral center the carbon attached to the nitrogen atom. If the carbon attached to the oxygen is also a chiral center, how does it affect the enantioselectivity and which of the two chiral centers has the main effect? To explore these possibilities and to obtain more details about the catalytic mechanism, four stereoisomers of a copper-(Schiff-base) complex with double chiral centers **3a–d** and their analogue **3e**, which with a bulky group at the *ortho*-position to the phenolic hydroxyl of the complex, were synthesized and applied to catalyze the asymmetric cyclopropanation of ethenes with diazoesters in this paper.

RESULTS AND DISCUSSION

Initially, the complexes **3a–e** were applied to catalyze the reaction of styrene **4** with diazoesters **5** (Table 1). In the cases of using **3a** or **3c** as catalyst, the *1S*, *2R* for **6a–b** and the *1S*, *2S* for **7a–b** are the major enantiomers, respectively, though the configuration of C_1 in **3a** and **3c** are different. When using **3b** or **3d** as a catalyst, the *1R*, *2S* for **6a–b** and *1R*, *2R* for **7a–b** turn out to be the major enantiomers, respectively, in spite of the configurations of C_1 in **3b** and **3d** are different, too. These results indicated that the configuration of C_2 in complex **3** dominates the configurations of cyclopropanes in **6a–b** and **7a–b**. It is noteworthy that the degree of enantioselectivities for **3c** and **3d** are much lower than that for **3a** and **3b**. This suggests that the configuration of C_1 in complexes **3a–d** affect mainly the degree of enantioselectivity. A similar behavior was observed when complexes **3a–d** were used to catalyze the asymmetric cyclopropanation of 1,1-diphenylethylene **8** with ethyl diazoacetate (Table 2).

TABLE 2 Asymmetric cyclopropanation of 1,1-diphenylethene **8** with ethyl diazoacetate catalyzed by using 1 mol% of **3**[a]

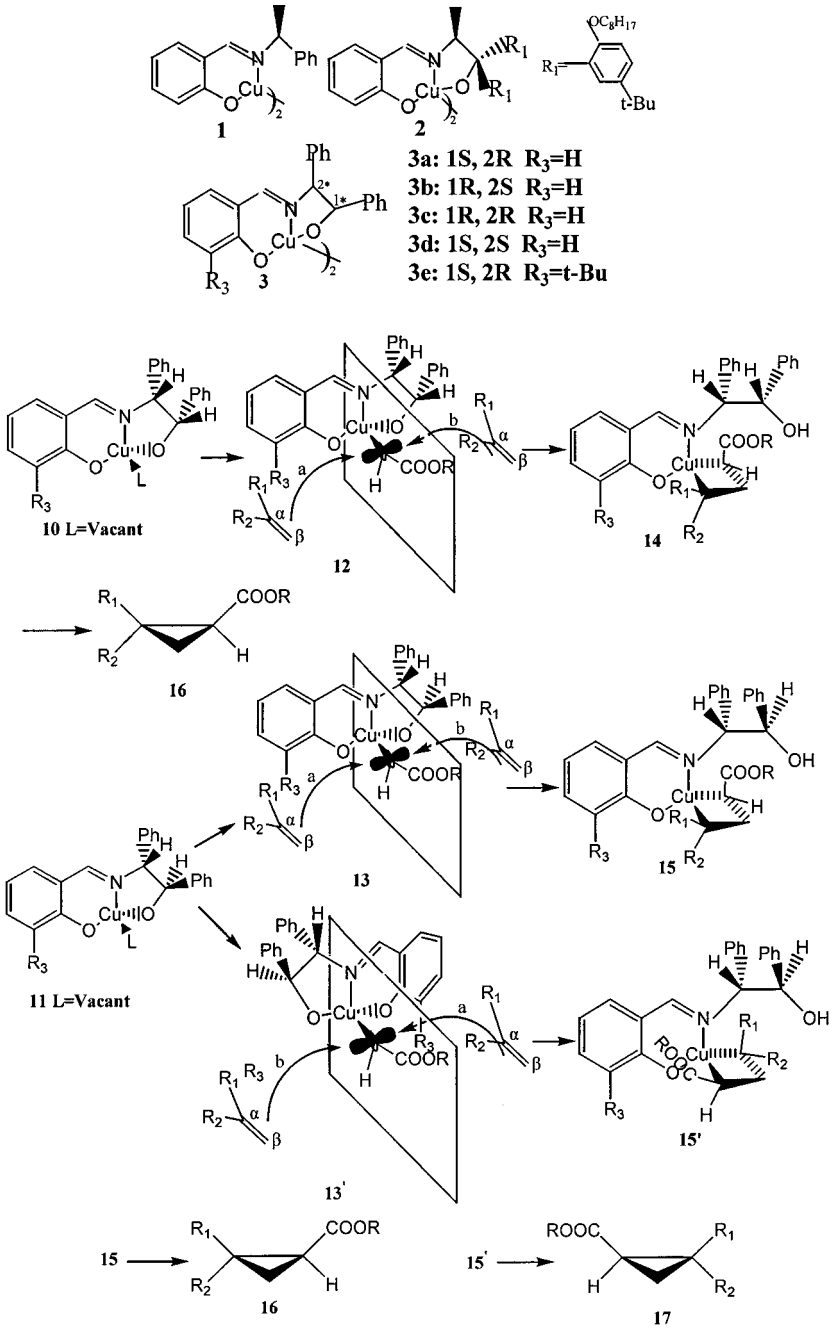


Entry	***3***	*Yield (%)*[b]	*%ee*[c]
1	a	53	90.1(S)
2	b	54	91.8(R)
3	c	58	13.4(S)
4	d	51	13.1(R)
5	e	63	87.7(S)

[a]All reactions were carried out at 40°C in benzene.
[b]Isolated yields.
[c]The %e.e. of 10 was determined by HPLC (Chiracel OD column, elution with hexane/isopropanol 9.75:0.25, 0.4 ml/min, the configuration in parentheses is of the excess enatiomer, which was established on the basis of the sign of the specific rotation of the corresponding acid [4].

Comparing the results obtained by using **3a** and **3e** as the catalysts (Table 1: entry 1, 5, 6, 10; Table 2: entry 1, 5) both the enantioselectivity and the diastereoselectivity (leading to the *E*) product are somewhat diminished when the **3e** is used. This suggests that a bulky group at the *ortho*-position to the phenolic hydroxyl of the complex is disadvantageous to the asymmetric reaction.

A possible mechanism (Scheme 1) is proposed to explain these results. Reactions employing the catalysts **3a** and **3c** are considered throughout the following discussions. There has been strong evidence indicating that the actual catalyst responsible for the asymmetric induction is a mononuclear cuprous complex such as **10** and **11**, in which copper is supposed to have a tetrahedral configuration and one of the four coordination sites is left vacant [7]. In the case of **10**, two phenyl goups in the catalyst are *syn*, and the alkyldiazoacetate will take the vacant site from the less hindered front side to give **12**. The carbene carbon bears sp^2 hybridization and the outside orientation of the alkoxycarbonyl group is selected



SCHEME 1

TABLE 3 Effect of temperature, solvent and amount of catalyst on asymmetric cyclopropanation of 1,1-diphenylethylene with ethyl diazoacetate catalyzed by **3b**

Entry	Solvent	Amt of cat. (mol%)	Temp. (°C)	Yield (%)[a]	E.e (%)[b]	Config.[c]
1	Benzene	1	80	81	68.2	R
2	Benzene	1	60	73	84.1	R
3	Benzene	1	40	53	91.8	R
4	Benzene	1	30	48	94.1	R
5	Benzene	1	20	45	97.3	R
6	Benzene	1	0	38	98.6	R
7	Benzene	0.5	40	69	78.5	R
8	Benzene	0.1	40	61	53.7	R
9	Dioxane	1	40	50	67.8	R
10	THF	1	40	23	35.6	R
11	CH_2Cl_2	1	40	65	88.5	R
12	Toluene	1	40	59	89.2	R
13[d]	—	1	40	68	80.7	R

[a]Isolated yields.
[b]The %e.e. was determined by HPLC (Chiracel OD column, elution with hexane/isopropanol 9.75:0.25, 0.4 ml/min.).
[c]Established on the basis of the sign of the specific rotation of the corresponding acid [4].
[d]No solvent was used.

to minimize steric replusion. The ethenes will approach the carbene from the less hindered **a** side and the metallacyclobutanes **14** is the main product. The copper atom forms a bond with the α-carbon atom of the alkene rather than the β-carbon atom because the carbonium ion at the α-position is more stable than that of the β-position. Collapse of the metallacycles **14** into the products **16** regenerates the true catalyst **10** to complete a catalysis cycle. In the case of **11**, the difference of the steric repulsion from rear or front is not obvious. Alkyldiazoacetate can approach the copper either from rear or front, thus **13** and **13′** are given. Intermediate **13** is somewhat predominant for C_2 is positioned a little closer to the alkoxycarbonyl group of carbene than C_1. The ethens will attack **13** or **13′** in the similar manner as that of **10** to give **16** and **17** (**16** somewhat predominant). This model explains most of the results we derived. The configuration of C_2 of the catalyst dominates the configuration of predominant cyclopropanes by governing the side the alkyldiazoacetate approaches the catalyst. A bulky group at C_1 is in favor of the enantioselectivity [8]. The enantioselectivity is diminished when two phenyl goups are *anti* in the catalyst such as **3c** and **3d**, since the difference in the approach of the diazoacetates to the catalyst from the rear or from the front is diminished. If R_2 is a more bulky group than R_1 and R_2 is at the bottom, the approach of the ethenes to the carbene is easier and the metallacycles are more stable, this leads to preference of the (*E*)-cyclopropane in most cases and a bulky group in the diazoacetates favors the diastereoselectivity. When R_3 is *tert*-butyl, the steric repulsion of the **a** side is increased so the enantioselectivity is diminished. The diastereoselectivity is also diminished because R_3 is orientated down side.

The complex **3a** and **3b** have been found to be efficient catalysts for the asymmetric cyclopropanation of 1,1-diphenylethylene with ethyl diazoacetate. The effects of temperature, solvent and the amount of catalyst on this reaction catalyzed by **3b** were also investigated (Table 3). The expected temperature effects were observed; decreasing of temperature caused increasing of enantioselectivity. The best result of 98.6% e.e was obtained at 0°C. However, the chemical yield decreased at lower temperature. Among the solvents studied, benzene was the best one. When reactions were carried out in polar solvent such as dioxane or THF, the enantioselectivity diminished. This could be a result of the strong coordinating ability of these solvents to the catalyst complex. Interestingly, a relatively high e.e. of 80.7% was obtained when no solvent was used (Entry 13). The enantioselectivity decreased when the amount of catalyst was diminished. But an e.e. of 53.7% still could be obtained when only 0.1 mol% of the catalyst was used.

MATERIALS AND METHODS

Unless otherwise stated, all reactions were carried out under an argon atmosphere with dry, freshly

distilled solvents under anhydrous conditions. All solvents were purified according to standard methods. Ethenes were purchased from Aldrich Ltd. and freshly distilled before use. NMR spectra were recorded with a Bruker DRX-500 (500 MHz). IR spectra were recorded on a RECTOR-22 instrument.

Preparation of the Racemate (1S, 2R) and (1R, 2S)-1,2-diphenyl-2-amino-ethanol

This compound was prepared according to the procedure reported by J. Weijlard et al [11] with some modifications. A mixture of 13.6 g. of benzoin oxime (0.06 mol), 112 ml of ethanol containing 2.4 g. of hydrogen chloride and 1.2 g. of 10% palladium-on-charcoal was hydrogenated at 1.06E + 05 Pa. pressure. To the reaction mixture was added 100 ml of water 5 hours later, and the catalyst was removed by filtration. The filtrate was diluted to 400 ml with water, an excess of concd. ammonia liquor was added, the precipitated base was collected, washed free from chloride with water and dried at 45–50°C; Yield 90%, m.p. 161°C. The hydrochloride was prepared by dissolving the base in hot alcohol, adding a slight excess of alcoholic HCl, and precipitating by adding an equal volume of ether. The hydrochloride was dissolved in warm water and an excess of concd. ammonia liquor was added, the precipitated base was collected, washed and dried, yield 78%, white crystal, m.p. 163°C. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 5.0 1(d, J = 7.8 Hz, 1H), 5.35 (d, J = 7.8 Hz, 1H), 6.98–7.35 (m, 10 H); IR (KBr):3440, 3332, 2920, 2887, 1639, 1592, 1454, 698 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.91; H, 7.10; N, 6.59%.

Resolution of the (1S, 2R)/(1R, 2S)-1,2-diphenyl-2-amino-ethanol [11]

A mixture of 13.4 g. of the racemate (0.063 mol) and 0.93 g. of D-glutamic acid (0.063 mol) were dissolved in 4000 ml of boiling 50% ethanol. After storage overnight at room temperature, the fine needles were collected, washed with ice-cold 50% ethanol and dried. M.p. 212°C. This solid was recrystallized twice from 50% ethanol until the m.p. reach to 215°C, yield 56%. The (1S, 2R) enantiomer was obtained by dissolving 6.2 g of the D-glutamate salt in 100 ml of warm water, precipitating with excess of ammonia, collecting, carefully washing with water and drying; yield 87%, m.p. 143°C; $[\alpha]_D^{25}$ = +7°(C = 0.6,C_2H_5OH). The mother liquor was concentrated and the obtained solid was recrystallized from 50% ethanol for five times until the m.p. reach to 196°C, yield 39%. The (1R, 2S) enantiomer was obtained as described above, yield 98% from 4.3 g. of glutamate. M.p. 143°C; $[\alpha]_D^{25}$ = −7°(C = 0.6, C_2H_5OH).

Preparation of (1R, 2R)-1,2-diphenyl-2-amino-ethanol

Prepared from (1S, 2R)-1,2-diphenyl-2-amino-ethanol in three steps in a similar manner to the literature [11]. White crystal, m.p. 116°C; $[\alpha]_D^{25}$ = −120°(C = 0.6, C_2H_5OH). ^{1}H NMR (500 MHz, CD_3COCD_3) δ 4.17 (d, J = 8.6 Hz, 1H), 4.74 (d, J = 8.6 Hz, 1H), 7.14–7.33 (10 H, m) IR (KBr): 3500, 3365, 2895, 1644, 1587, 1454, 699 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.95; H, 6.96; N, 6.51%.

Preparation of (1S, 2S)-1,2-diphenyl-2-amino-ethanol

Prepared from (1R, 2S)-1,2-diphenyl-2-amino-ethanol in three steps in a similar manner to the literature [11]. White crystal, m.p. 116°C; $[\alpha]_D^{25}$ = +121° (C = 0.6, C_2H_5OH). ^{1}H NMR (500 MHz, CD_3COCD_3) δ 4.18 (d, J = 8.6 Hz, 1H), 4.75 (d, J = 8.6 Hz 1H), 7.15–7.34 (10 H, m) IR (KBr):3489, 3330, 2826, 1638, 1590, 1454, 691 cm^{-1}. Anal Calcd for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.89; H, 7.05; N, 6.66%.

Preparation of 3-tert-Butyl-2-hydroxybenzaldehyde

Prepared by a similar method to the literature procedure [12], yield 40%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43(s, 9H), 6.90–7.80 (m, 3H), 9.89 (s, 1H), 11.80 (s, 1H); IR (KBr): 2959, 2743, 1652, 1612, 1484, 1432, 1090 cm^{-1}.

Preparation of the Schiff-Bases: General Procedure

A mixture of methanol (10 ml), amino alcohols (5 mmol), and salicyclaldehyde (6 mmol)

were refluxed for 8 hours. Most of the methanol was removed in vacuo and the residue was purified by a chromatographic column to give pure product.

Ligand of complex 3a. Yield 95%, yellow crystal, m.p. 126°C; $[\alpha]_D^{25} = +19°$(C = 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$), δ 3.08 (s, br, 1H), 5.58 (d, J = 7.0 Hz, 1H), 5.72 (d, J = 7.0 Hz, 1H), 6.86 (m, 1H), 6.95 (m, 2H), 7.06–7.27 (m, 8H), 7.41 (d, J = 7.1 Hz, 2H),7.58 (d, J = 8.2 Hz, 1H), 8.61 (s, 1H),14.2 (s, 1H) IR (KBr): 3443, 1629, 1578, 1497, 1425, 1054 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.50; H, 5.99; N, 4.42. Found: C, 79.54; H, 6.12; N, 4.41%.

Ligand of complex 3b. Yield 91%, yellow crystal, m.p. 125–126°C; $[\alpha]_D^{25} = -18°$ (C = 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 3.10 (s, br, 1H), 5.59 (d, J = 7.0 Hz, 1H), 5.74 (d, J = 7.0 Hz, 1H), 6.88 (m, 1H), 6.96 (m, 2H), 7.08–7.29 (m, 8H),7.44 (d, J = 7.1 Hz, 2H), 7.60 (d, J = 8.2 Hz, 1H), 8.62 (s, 1H), 14.3 (s, 1H) IR (KBr): 3445, 1628, 1577, 1499, 1423, 1055 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.50; H, 5.99; N, 4.42. Found: C, 79.41;H, 6.02; N, 4.35%.

Ligand of complex 3c. Yield 87%, yellow crystal m.p. 136–137°C; $[\alpha]_D^{25} = 87°$ (C = 1, C_2H_5OH); ^1H NMR (500 MHz, $CDCl_3$) δ 3.33 (s, br, 1H), 5.22 (d, J = 8.0 Hz, 1H), 5.49 (d, J = 8.0 Hz, 1H) 6.83 (m, 1H), 7.05 (d, J = 8.1 Hz, 1H), 7.14 (s, 2H), 7.22–7.47 (m, 8H), 7.50 (m, 2H), 8.77 (s, 1H) 12.15 (s, 1H) IR (KBr): 3438, 1629, 1584, 1494, 1450, 1044 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.50; H, 5.99; N, 4.42. Found: C, 79.42; H, 5.94; N, 4.45%.

Ligand of complex 3d. Yield 85%, yellow crystal, m.p. 137–138°C; $[\alpha]_D^{25} = +89°$ (C = 1, C_2H_5OH); ^1H NMR (500 MHz, $CDCl_3$) δ 3.31 (s, br, 1H), 5.21 (d, J = 8.0 Hz, 1H), 5.47 (d, J = 8.0 Hz, 1H), 6.81 (m, 1H), 7.04 (d, J = 8.1 Hz, 1H), 7.12 (s, 2H), 7.20–7.45 (m, 8H), 7.49 (m, 2H), 8.75 (s, 1H), 12.13 (s, 1H) IR (KBr): 3436, 1629, 1586, 1497, 1443, 1045 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.50; H, 5.99; N, 4.42. Found: C, 79.58; H, 6.05; N, 4.39%.

Ligand of complex 3e. Yield 89%, yellow syrup, ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.8 (br, 1H), 4.70 (d, J = 5.9 Hz, 1H), 5.14 (d, J = 5.9 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H),7.12–7.37 (m, 12H), 8.39 (d, J = 4.3 Hz, 1H),14.05 (s, 1H) IR (KBr): 3436, 2956, 1629, 1493, 1433, 1047 cm^{-1}. Anal. Calcd for $C_{25}H_{27}NO_2$: C, 80.43; H, 7.24; N, 3.75. Found: C, 80.39; H, 7.18; N, 3.81%.

Preparation of the Copper-(Schiff-Bases) Complex: General Procedure

Salicylaldimine (1 mmol) and cupric acetate monohydrate (1 mmol) were dissolved in 75 ml of ethanol. Aqueous sodioum hydroxide (10%, 3.8 ml) was added and the mixture was stirred for 1 h. The solution was diluted with water and extracted three times with benzene. The benzene extracts were dried (K_2CO_3), filtered and concentrated, the complex was obtained.

Complex 3a. Yield 92%, Anal. Calcd for $C_{25}H_{25}NO_2Cu$: C, 66.57; H, 4.49; N, 3.70. Found: C, 66.44; H, 4.31; N, 3.52%.

Complex 3b. Yield 85%, Anal. Calcd for $C_{25}H_{25}NO_2Cu$: C, 66.57; H, 4.49; N, 3.70. Found: C, 66.45; H, 4.62; N, 3.63%.

Complex 3c. Yield 89%, Anal. Calcd for $C_{25}H_{25}NO_2Cu$: C, 66.57; H, 4.49; N, 3.70. Found: C, 66.37; H, 4.51; N, 3.49%.

Complex 3d. Yield 84%, Anal. Calcd for $C_{25}H_{25}NO_2Cu$: C, 66.57; H, 4.49; N, 3.70. Found: C, 66.51; H, 4.68; N, 3.55%.

Complex 3e. Yield 81%, Anal. Calcd for $C_{25}H_{25}NO_2Cu$: C, 68.89; H, 5.97; N, 3.01. Found: C, 69.04; H, 5.84; N, 3.21%.

Cyclopropanation: General Procedure

Under an argon atmosphere, a few drops of a solution of 1.0 mmol of diazoacetates in 2.0 ml of solvent was added to a mixture of 0.01 mmol of catalyst, 1.0 ml of olefin and 3.0 ml of the solvent at 80°C to initiate the reaction. After the mixture was cooled to 40°C, the rest of the diazoacetates solution was added slowly and the mixture was stirred for another 6 h after all the diazoacetate was added. The solvent was removed in vacuo and passed through a silica gel column to obtained a pure product.

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