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# First enantioselective catalyst based on a chiral terpyridine: synthesis of new $C_2$-symmetric 2,2′:6′,2″-terpyridine ligands and copper-catalyzed enantioselective cyclopropanation of alkenes

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**Abstract**

New $C_2$-symmetric chiral 2,2′:6′,2″-terpyridines were prepared from readily available homochiral materials. Copper complexes of these ligands were prepared in situ and their catalytic activities in cyclopropanations of alkenes with alkyl diazoacetate to give cyclopropyl esters were studied. In all cases, the cyclopropyl ester yields were excellent and enantioselectivities up to 94% ee were observed. Competition experiments revealed that electron-donating substituents on styrene accelerate the reaction. A Hammett plot exhibited a good linearity with a negative $\rho^+$ value (–0.79). 

## 1. Introduction

The presence of a $C_2$-symmetry axis within a chiral auxiliary can serve the very important function of dramatically reducing the number of possible competing diastereomeric transition states.[1] Although chiral $C_2$-symmetric bidentate *N*,*N*-coordinating nitrogen heterocycles such as bisoxazoline,[2] semicorrine[3] and 2,2′-bipyridine[4] are among the most useful ligands in asymmetric catalysis, the development of chiral $C_2$-symmetric tridentate *N*,*N*,*N*-coordinating ligands represents a new challenge for chemists. One type of these ligands, 2,6-pyridinediyl-2,2′-bisoxazoline **1**, has been shown to be highly useful in a number of catalytic reactions. For example, the Rh(III) complexes are efficient enantioselective catalysts for the hydrosilylation of ketones;[5] the Ru(II) complexes are active catalysts for enantioselective cyclopropanation and epoxidation of alkenes;[6,7] and the Cu(II) complexes are efficient catalysts for asymmetric carbon–carbon bond-forming reactions[8] and allylic oxidation of cycloalkenes.[9] Terpyridines, having the general structure **2**, are

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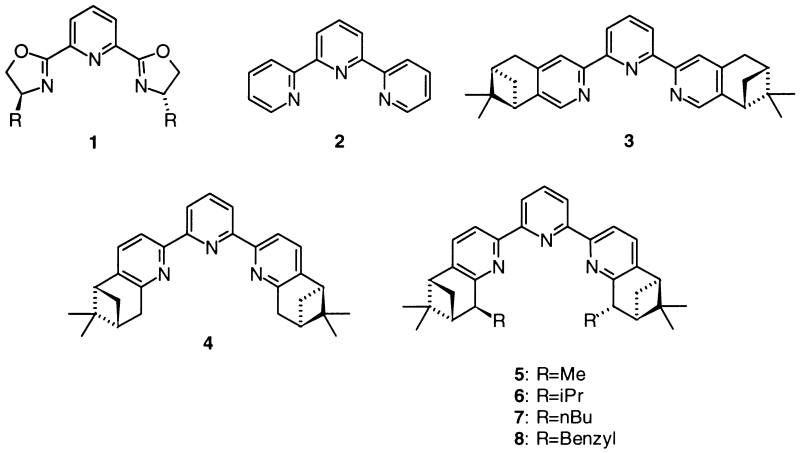
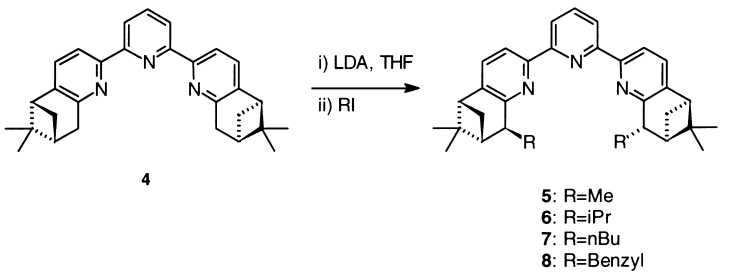
structurally similar to these ligands and are well known to form complexes with various metal ions.[10] They play important roles in supramolecular chemistry,[11] photochemistry[12] and electrochemistry.[13] The most common coordination mode is meridional,[14] although they could also form helicating or bridging structures with certain metals.[15] However, very few chiral terpyridine ligands are known and most of them have not been used in asymmetric catalysis.[16] To the best of our knowledge, only one example of utilizing chiral terpyridine in asymmetric catalysis has been reported where the cyclopropanation of styrene with ethyl diazoacetate gave an almost racemic product.[17] Recently, von Zelewsky et al. reported the synthesis of $C_2$-symmetric chiral terpyridine ligands **3** and **4** and their ruthenium and rhodium complexes.[18] Herein, we report the synthesis of a number of new chiral terpyridine ligands (ligands **5**–**8**) and their application in the copper-catalyzed asymmetric cyclopropanation of alkenes with alkyl diazoacetates.




## 2. Results and discussion

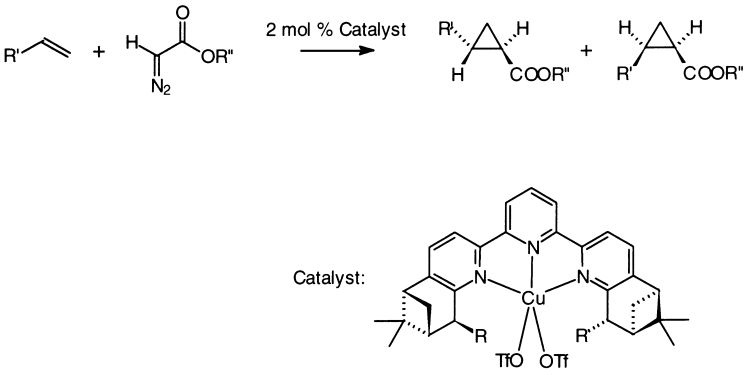
Terpyridine ligands **5**–**8** (Scheme 1) were prepared from the terpyridine **4**, which is readily accessible by the Kröhnke condensation of (1*R*)-(+)-pinocarvone with 2,6-bis(pyridinioacetyl)-pyridine diiodide.[18] The dark-blue solution of dilithiated **4**, obtained by treatment with lithium diisopropylamide (LDA) at –40°C for 2 h, was quenched with the proper alkyl iodide to give ligands **5**–**8**.




Scheme 1.

The ligands were all obtained as sole diastereomers as shown by NMR analysis of the product mixtures, and the configurations are shown in Scheme 1. The yields were between 39 and 57% which depended only slightly on the nature of the alkyl group. Similar stereoselective lithiation and alkylation have been reported previously with pinocarvone-derived bipyridine ligands.[19]

Having prepared these terpyridine ligands, we tested their efficiency in the copper-catalyzed asymmetric cyclopropanation of alkenes (Scheme 2). Although it is generally believed that the copper(I) species is the active form in the cyclopropanation, copper(II) catalysts were used in this study because of their stability in air. Unlike the previously reported catalytic systems where heating was required for the activation process,[3a] these catalysts can be easily activated by stirring with a few equivalents of alkyl diazoacetates for 30 min at room temperature.




Scheme 2.

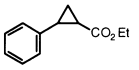
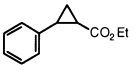
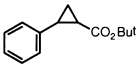
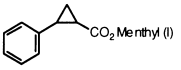
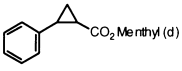
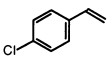
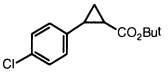
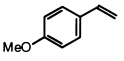
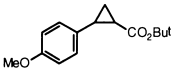
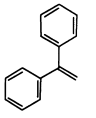
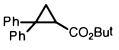
The results of asymmetric cyclopropanation of alkenes with the copper(II)–terpyridine complexes, which were generated from ligands **3**–**8** and copper(II) triflate, are shown in Table 1. All the copper–terpyridine complexes were found to be active catalysts and the yields of the isolated cyclopropyl esters were excellent (87–98%). The enantioselectivities obtained were high for ligands **5**–**8**. Analysis of the reaction mixtures by GC indicated that the *trans*/*cis* ratios were between 59:41 and 78:22 (entries 1–5 and 7). The results obtained here were much better than the previously studied 2,6-pyridinediyl-2,2′-bisoxazoline ligand.[20]

The introduction of alkyl groups at the 8-position of the tetrahydroquinoline ring of ligand **4** was crucial for the enantioselectivity of the reaction. Thus, ligand **4** gave a much lower enantiomeric excess for both the *cis*- (29%) and the *trans*-isomer (30%) than the alkyl-substituted ligands **5**–**8**. The best enantioselection was achieved with the butyl-substituted ligand **7**, where enantiomeric excesses of 86% for the *trans*- and 90% for the *cis*-isomer were obtained (entry 5).

With terpyridine **7** being the best ligand, it is used to optimize reaction conditions. Lowering the reaction temperature from room temperature to 0°C did not hamper the reaction but increased the enantioselection to 90% for the *trans*- and 94% for the *cis*-isomer (entry 6). Changing the solvent has a great effect on both the enantioselectivity and isolated yield, but only a small effect on the diastereoselectivity. Dichloromethane (entry 5) was found to be the best solvent, slightly lower enantioselectivities were obtained in toluene (entry 9) and ether (entry 10), and the enantioselectivity and isolated yield decreased significantly in THF (entry 8).

Variation on the structure of the diazo ester has a great effect on the *trans*/*cis* diastereoselectivity. As can be seen from entries 5 and 11–13 in Table 1, when the R group changes from the ethyl to bulkier groups (*tert*-butyl, *l*-menthyl and *d*-menthyl), all reactions give higher *trans*:*cis*

Table 1
Catalytic asymmetric cyclopropanation with chiral copper(II) terpyridine complexes

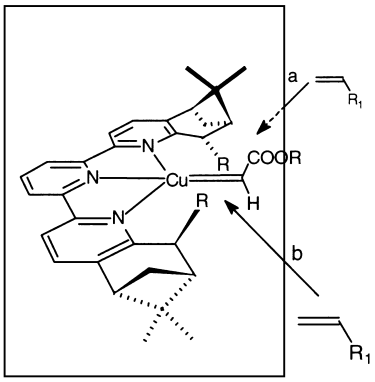
| Entry | Ligand | substrate | product | Solvent | *trans* : *cis* | % ee (*trans*)[2] | % ee (*cis*)[2] | yield %[3] |
|---|---|---|---|---|---|---|---|---|
| 1 | 3 |  |  | $CH_2Cl_2$ | 70: 30 | 3 (1R,2R) | 17 (1R,2S) | 97 |
| 2 | 4 | | | | 78 : 22 | 30 (1R,2R) | 29 (1R,2S) | 98 |
| 3 | 5 | | | | 64 : 36 | 75 (1R,2R) | 84 (1R,2S) | 87 |
| 4 | 6 | | | | 59 : 41 | 40 (1R,2R) | 51 (1R,2S) | 98 |
| 5 | 7 | | | | 68 : 32 | 86 (1R,2R) | 90 (1R,2S) | 98 |
| 6[4] | 7 | | | | 69 : 31 | 90 (1R,2R) | 94 (1R,2S) | 96 |
| 7 | 8 | | | | 61 : 39 | 72 (1R,2R) | 75 (1R,2S) | 97 |
| 8 | 7 |  |  | THF | 68 : 32 | 47 (1R,2R) | 66 (1R,2S) | 57 |
| 9 | 7 | | | Toluene | 67 : 33 | 85 (1R,2R) | 85 (1R,2S) | 95 |
| 10 | 7 | | | Ether | 64 : 36 | 81 (1R,2R) | 83 (1R,2S) | 50 |
| 11 | 7 |  |  | $CH_2Cl_2$ | 77 : 23 | 85 (1R,2R) | 90 (1R,2S) | 91 |
| 12 | 7 |  |  | $CH_2Cl_2$ | 75 : 25 | 76 (1R,2R) | 83 (1R, 2S) | 90 |
| 13 | 7 |  |  | $CH_2Cl_2$ | 91 : 9 | 83 (1R,2R) | 58 (1R,2S) | 89 |
| 14 | 7 |  |  | $CH_2Cl_2$ | 78 :22 | 83 (N.D.)[5] | 82 (N.D.)[5] | 90 |
| 15 | 7 |  |  | $CH_2Cl_2$ | 81 : 19 | 86 (1R,2R) | 87 (N.D.)[5] | 88 |
| 16 | 7 |  |  | $CH_2Cl_2$ | - | 79(1R) | | 92 |

[1]Diazoacetate (0.2 equivalent) was used for reduction of Cu(II) catalyst before the start of cyclopropanation. All reactions were run at room temperature unless otherwise stated. [2]For entry 1-10 and 16, enantiomeric excesses were determined by HPLC with a Daicel Chiralcel OJ column. For entry 11 enantiomeric excesses were determined by GC analysis using a chiral column Chiraldex β-PH column (30 m × 0.25 mm). For entries 12 and 13, enantiomeric excesses were determined by GC analysis using a Ultra 2-crosslinked 5% PhMesilcone (25 m × 0.2 mm × 0.33 μm) column. For entry 14 and 15, enantiomeric excesses were determined by a literature procedure.[6c] Absolute configurations were determined by comparing the order of elution of samples with known configurations.[6c] [3]Isolated yield after chromatography. [4]Reaction was carried out at 0 °C. [5]Not determined.

ratios for the cyclopropanation of styrene. The best result was obtained with the *d*-menthyl group, where a *trans*:*cis* ratio of 91:9 (entry 13) was obtained. This is consistent with the trend previously observed with other copper catalysts.[4a–d] However, the enantioselectivities for both the *trans*- and *cis*-isomers decreased when the bulkiness of the ester group increased.

Apart from styrene, the complex derived from ligand **7** was capable of catalyzing the cyclopropanation of various alkenes with different electronic (entries 14 and 15) and steric properties (entry 16). Higher *trans*/*cis* ratios were observed with 4-chlorostyrene (entry 14) and 4-methoxystyrene (entry 15). However, there was no improvement on the enantioselectivity for all the

substituted styrenes. By employing ligands **3**–**8**, the absolute configuration of cyclopropyl ester products formed from styrene and substituted styrenes were determined to be (1*R*,2*R*) and (1*R*,2*S*) for the *trans*- and *cis*-isomers, respectively. Based on the absolute configuration of the products obtained, the sense of asymmetric inductions observed here can be explained by the model shown in Scheme 3. This model is in agreement with the one previously cited by Pflatz for other *N*,*N*-bidentate ligands.[3a] In the model, the metal carbenoid attacks the olefinic double bond according to the pathways a and b. In the case of pathway a, a repulsive steric interaction builds up between the ester group and the adjacent bulky alkyl group of the ligand. In the case of pathway b, no such steric interaction exists and it leads to the *cis*-(1*R*)- or to the *trans*-(1*R*)-cyclopropyl esters that are consistent with the experimental results. Therefore, pathway b is more favored than pathway a.




Scheme 3.

In order to know more about the active intermediate in the reaction, the relative reaction rates were measured in the competitive cyclopropanation of EDA with substituted styrenes in the presence of the catalyst derived from ligand **7**. The reaction was enhanced by electron-donating groups but retarded by electron withdrawing groups. A Hammett plot of $\log(k_X/k_H)$ versus $\sigma(+)$ is shown in Fig. 1; a good $\sigma(+)$ correlation is obtained with $\rho = -0.79$. This value is similar to that reported by Kodadek et al.[21] (–0.68) and Pérez et al.[22] (–0.85) for the cyclopropanation of substituted

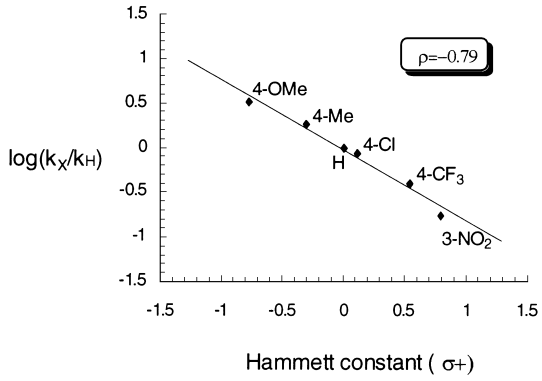



Figure 1. Hammett plot for the cyclopropanation of styrene with EDA using $Cu(OTf)_2$ and terpyridine **7** as the catalyst

styrenes using EDA/iron(II) porphyrin and EDA/copper(I) tris(pyrazolyl) borate systems, respectively. However, in both of the previous systems, correlation to σ instead of σ(+) was found. This negative value of ρ obtained supports the formation of an electrophilic metal–carbene complex intermediate with only a moderate positive charge build-up at the benzylic carbon in the transition state.

In summary, we have successfully synthesized four new $C_2$-symmetric 2,2′:6′,2″-terpyridine ligands in good yields. The copper complexes of these ligands are excellent catalysts for enantioselective cyclopropanation. Ee's up to 94% were observed. We are continuing our efforts to study the use of these ligands in other catalytic asymmetric reactions.

## 3. Experimental

### 3.1. General methods

Benzyl iodide was prepared by a literature method.[23] Toluene was distilled under $N_2$ from sodium. Dichloromethane and acetonitrile were distilled over calcium hydride. Diethyl ether and THF were distilled under $N_2$ over sodium/benzophenone. All other chemicals were of reagent grade. Infrared spectra in the range 500–4000 $cm^{-1}$ were recorded as KBr plates on a Perkin–Elmer Model FTIR-1600 spectrometer. Proton and $^{13}C$ NMR spectra were recorded on a Varian 300 MHz Mercury instrument. Positive ion FAB mass spectra as 3-nitrobenzylalcohol matrix were recorded on a Finnigan MAT 95 spectrometer. Electron ionization mass spectra were recorded on a Hewlett–Packard 5890II GC instrument coupled with a 5970 mass selective detector. Elemental analyses were performed on a Vario EL elemental analyzer. Optical rotation was measured by a JASCO DIP-370 digital polarimeter. Melting point was measured by an Electrothermal digital melting point apparatus.

### 3.2. 2,6-Bis(pyridinioacetyl)pyridine diiodide

To a pyridine solution (10 ml) of 2,6-diacetylpyridine (8 mmol, 1.31 g) was added a solution of iodine (16 mmol, 4.06 g) in pyridine (10 ml). The mixture was heated at 110°C for 3 h and, after cooling, the dull yellow solid was filtered and washed with cold ethanol. This product was characterized by $^1H$ NMR and IR. Yield = 85% (3.82 g). $^1H$ NMR ($CDCl_3$): $\delta$ 6.98 (s, 4H), 8.26 (dd, 4H), 8.43 (s, 3H), 8.76 (dd, 2H, $J = 7.8$ Hz), 9.14 (d, 4H, $J = 5.7$ Hz); IR (KBr): 3022.9 vs, 2969.5 vs, 2946.6 vs, 1719.6 vs, 1635.7 s, 1491.1 s, 1344.5 s.

### 3.3. (1R)-(+)-Pinocarvone

Following the literature procedure,[24] (1*R*)-(+)-pinocarvone was obtained in 50% yield from $SeO_2$ oxidation of β-pinene. This product was characterized by $^1H$ NMR and IR.

### 3.4. Terpyridine ligand **3**

This ligand was synthesized by Kröhnke condensation.[25] 2,6-Bis(pyridinoacetyl)pyridine diiodide (1.5 mmol, 0.84 g), (1*R*)-(–)-myrtenal (3 mmol, 0.45 g) and ammonium acetate were dissolved in glacial acetic acid (2 ml). The mixture was refluxed overnight under a $N_2$ atmosphere. The solvent

was removed under reduced pressure and the brown residue obtained was washed with ethanol, and recrystallized from dichloromethane to give 0.40 g (63%) of **3**. The product was characterized by IR, $^1$H NMR, $^{13}$C NMR and MS analyses. $[\alpha]_D^{25} = -106.7$ (*c* 0.50, $CHCl_3$); IR (KBr): 2992.4 vs, 2969.5 vs, 2931.3 vs, 2893.1 vs, 1550.5 s, 1455.2 s; $^1$H NMR ($CDCl_3$): $\delta$ 0.69 (s, 6H), 1.27 (d, 2H, $J = 9.9$ Hz), 1.44 (s, 6H), 2.37 (m, 2H), 2.74 (m, 2H), 2.90 (m, 2H), 3.14 (d, 4H), 7.93 (t, 1H, $J = 7.8$ Hz), 8.24 (s, 2H), 8.37 (d, 2H, $J = 8.1$ Hz), 8.40 (s, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ 21.46, 26.00, 31.81, 33.02, 39.23, 40.07, 44.45, 120.20, 120.31, 137.54, 142.74, 145.12, 145.26, 154.36, 155.56; positive ion FAB mass spectra *m*/*z*: 422 ($M^+$+H). Anal calcd for $C_{29}H_{31}N_3$: C, 82.62; H, 7.41; N, 9.97. Found: C, 81.89; H, 7.20; N, 9.86.

### 3.5. Terpyridine ligand *4*

This ligand was synthesized by Kröhnke condensation.[25] 2,6-Bis(pyridinoacetyl)pyridine diiodide (1.5 mmol, 0.84 g), (1*R*)-(+)-pinocarvone (3 mmol, 0.45 g) and ammonium acetate were dissolved in glacial acetic acid (2 ml). This mixture was refluxed overnight under a $N_2$ atmosphere. The solvent was removed under reduced pressure and the brown residue obtained was washed with ethanol, and recrystallized from dichloromethane to give 0.37 g (59%) of **4**. The product was characterized by IR, $^1$H NMR, $^{13}$C NMR and MS analyses. $[\alpha]_D^{25} = -149.3$ (*c* 0.40, $CHCl_3$); IR (KBr): 2969.5 s, 2908.4 vs, 2862.6 s, 1561.9 vs, 1432.4 vs; $^1$H NMR ($CDCl_3$): $\delta$ 0.70 (s, 6H), 1.33 (d, 2H, $J = 9.3$ Hz), 1.44 (s, 6H), 2.42 (m, 2H), 2.72 (m, 2H), 2.83 (dd, 2H, $J = 5.4$ Hz), 3.21 (d, 4H, $J = 2.1$ Hz), 7.37 (d, 2H, $J = 7.8$ Hz), 7.90 (t, 1H, $J = 7.8$ Hz), 8.29 (d, 2H, $J = 7.8$ Hz), 8.37 (d, 2H, $J = 7.8$ Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 21.31, 26.03, 31.91, 36.64, 39.49, 40.17, 464.4, 117.75, 119.86, 133.50, 137.42, 141.94, 153.51, 155.53, 156.04; positive ion FAB mass spectra *m*/*z*: 422 ($M^+$+H). Anal calcd for $C_{29}H_{31}N_3$: C, 82.62; H, 7.41; N, 9.97. Found: C, 81.58; H, 7.38; N, 9.65.

### 3.6. General procedures for the synthesis of terpyridine ligands *5*–*8*

A 100 ml flask was filled with dry THF (10 ml) and cooled to –40°C. Diisopropylamine (3.1 mmol, 0.44 ml) and *n*-butyllithium (1.6 M solution in hexane, 3.72 mmol, 2.3 ml) were added slowly with stirring. The temperature was then raised to 0°C and stirred for 30 min. The mixture was again cooled to –40°C and terpyridine **4** (0.77 mmol, 0.27 g) in dry THF (5 ml) was added slowly. The mixture was kept at –40°C for 2 h and a dark blue solution was obtained. The desired iodoalkane (6.14 mmol) was added slowly to this mixture. The temperature was raised to room temperature over 2 h and the mixture was stirred overnight. The reaction was quenched by the addition of water (20 ml) and the aqueous phase was extracted with dichloromethane (three times by 50 ml). The combined organic layer was dried with $Na_2SO_4$. The solvent was removed under reduced pressure and the crude product obtained was purified by silica gel column chromatography. All ligands were characterized by spectral (IR, $^1$H NMR, $^{13}$C NMR and MS) analyses.

#### 3.6.1. Terpyridine *5*

The above procedure was followed using methyl iodide. After workup and purification by column chromatography with petroleum ether:EtOAc (60:1, $R_f = 0.3$), 0.16 g (46%) of terpyridine **5** was obtained: $[\alpha]_D^{25} = -8.0$ (*c* 0.50, $CHCl_3$); IR (KBr): 2969.5 s, 2903.4 s, 2862.6 s, 1558.1 vs, 1424.8 vs; $^1$H NMR ($CDCl_3$): $\delta$ 0.69 (s, 6H), 1.35 (d, 2H, $J = 9.6$ Hz), 1.44 (s, 6H), 1.49 (d, 6H, $J = 7.2$ Hz), 2.20 (m, 2H), 2.59 (m, 2H), 2.83 (t, 2H, $J = 5.4$ Hz), 3.27 (m, 2H), 7.34 (d, 2H, $J = 7.8$ Hz), 7.91 (t, 1H, $J = 7.8$ Hz), 8.31 (d, 2H, $J = 7.5$ Hz), 8.45 (d, 2H, $J = 7.5$ Hz); $^{13}$C NMR

($CDCl_3$): $\delta$ 18.28, 20.93, 26.31, 28.59, 38.85, 41.39, 46.71, 47.09, 117.62, 119.79, 133.22, 137.30, 141.78, 153.30, 155.57, 159.79; positive ion FAB mass spectra $m/z$: 450 ($M^+$+H). Anal calcd for $C_{31}H_{35}N_3$: C, 82.81; H, 7.85; N, 9.35. Found: C, 82.65; H, 7.58; N, 9.03.

### 3.6.2. Terpyridine **6**

The above procedure was followed using isopropyl iodide. After workup and purification by column chromatography with petroleum ether:EtOAc (80:1, $R_f = 0.3$), 0.22 g (57%) of terpyridine **6** was obtained: $[\alpha]_D^{25} = +28.9$ ($c$ 0.50, $CHCl_3$); IR (KBr): 2954.2 vs, 2931.3 vs, 2870.2 s, 1558.1 vs, 1428.6 vs; $^1$H NMR ($CDCl_3$): $\delta$ 0.66 (s, 6H), 0.89 (d, 6H, $J = 6.9$ Hz), 1.20–1.70 (m, 2H), 1.27 (d, 6H, $J = 6.9$ Hz), 1.41 (d, 2H), 1.44 (s, 6H), 2.40 (m, 2H), 2.60 (m, 2H), 2.79 (t, 2H, $J = 5.4$ Hz), 2.93 (m, 2H), 7.35 (d, 2H, $J = 7.8$ Hz), 7.90 (t, 1H, $J = 7.8$ Hz), 8.34 (d, 2H, $J = 7.8$ Hz), 8.44 (d, 2H, $J = 7.8$ Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 20.21, 21.06, 22.37, 26.37, 29.33, 30.37, 41.39, 41.86, 46.74, 49.08, 117.47, 119.80, 133.23, 137.28, 142.26, 153.03, 155.68, 158.42; positive ion FAB mass spectra $m/z$: 506 ($M^+$+H). Anal calcd for $C_{35}H_{43}N_3$: C, 83.12; H, 8.57; N, 8.31. Found: C, 83.28; H, 8.43; N, 8.08.

### 3.6.3. Terpyridine **7**

The above procedure was followed using *n*-butyl iodide. After workup and purification by column chromatography with petroleum ether:EtOAc (80:1, $R_f = 0.3$), 0.22 g (54%) of terpyridine **7** was obtained: $[\alpha]_D^{25} = +25.9$ ($c$ 0.51, $CHCl_3$); IR (KBr): 2954.2 vs, 2931.3 vs, 2862.6 s, 1558.1 vs, 1432.4 vs; $^1$H NMR ($CDCl_3$): $\delta$ 0.60–1.60 (18H), 0.67 (s, 6H), 1.34 (d, 2H, $J = 9.6$ Hz), 1.45 (s, 6H), 2.39 (m, 2H), 2.56 (m, 2H), 2.81 (t, 2H, $J = 5.4$ Hz), 3.06 (m, 2H), 7.34 (d, 2H, $J = 8.1$ Hz), 7.92 (t, 1H, $J = 7.8$ Hz), 8.31 (d, 2H, $J = 7.5$ Hz), 8.45 (d, 2H, $J = 7.8$ Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 14.23, 20.96, 23.02, 28.43, 29.69, 30.14, 32.24, 41.02, 43.33, 44.21, 46.86, 117.50, 119.78, 133.16, 137.31, 141.4, 153.19, 155.58, 159.47; positive ion FAB mass spectra $m/z$: 534 ($M^+$+H). Anal calcd for $C_{37}H_{47}N_3$: C, 83.25; H, 8.87; N, 7.87. Found: C, 83.09; H, 8.80; N, 7.65.

### 3.6.4. Terpyridine **8**

The above procedure was followed using benzyl iodide. After workup and purification by column chromatography with petroleum ether:EtOAc (80:1, $R_f = 0.3$), 0.18 g (39%) of terpyridine **8** was obtained: $[\alpha]_D^{25} = -94.8$ ($c$ 0.25, $CHCl_3$); IR (KBr): 2977.1 s, 2916.0 vs, 2862.6 s, 1558.1 vs, 1428.6 vs; $^1$H NMR ($CDCl_3$): $\delta$ 0.64 (s, 6H), 1.36 (s, 6H), 1.46 (d, 2H, $J = 9.9$ Hz), 2.14 (m, 2H), 2.59 (m, 2H), 2.78 (m, 4H), 3.41 (m, 2H), 3.89 (m, 2H), 7.34 (m, 5H), 7.40 (d, 2H, $J = 7.5$ Hz), 7.94 (t, 1H, $J = 8.1$ Hz, $J = 7.8$ Hz), 8.37 (d, 2H, $J = 7.5$ Hz), 8.50 (d, 2H, $J = 8.1$ Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 20.88, 26.26, 28.26, 38.71, 41.09, 42.45, 46.19, 46.85, 117.86, 119.91, 125.58, 128.07, 129.14, 133.41, 137.36, 140.98, 141.97, 153.24, 155.49, 158.23; positive ion FAB mass spectra $m/z$: 602 ($M^+$+H). Anal calcd for $C_{43}H_{43}N_3$: C, 85.82; H, 7.20; N, 6.98. Found: C, 85.28; H, 7.10; N, 6.65.

## 3.7. Procedure for copper-catalyzed cyclopropanation

To a two-neck round-bottomed flask were added $Cu(OTf)_2$ (0.072 g, 0.02 mmol), $CH_2Cl_2$ (2.0 ml) and ligand (0.022 mmol) under nitrogen. The solution was stirred at room temperature for 2 h. Alkene (4 mmol) and diazoacetate (0.2 mmol) were then added and the mixture was stirred at room temperature for a further 0.5 h. A solution of diazoacetate (1 mmol) in $CH_2Cl_2$ (0.5 ml) was then added to the reaction mixture over a period of 4 h using a syringe pump. After the addition of diazoacetate, the mixture was stirred for 16 h at room temperature. The mixture was then

worked up by removing the solvent and the crude product obtained was purified by column chromatography (hexane/EtOAc). All the cyclopropanes obtained are known compounds and were characterized by $^1$H NMR, $^{13}$C NMR, IR and GC–MS. The enantiomeric excesses of the cyclopropanes in entries 1–10 and 16 were determined by HPLC with a Daicel Chiralcel OJ column. For entry 11 enantiomeric excesses were determined by GC analysis using a chiral column Chiraldex β-PH column (30 m×0.25 mm). For entries 12 and 13, enantiomeric excesses were determined by GC analysis using an Ultra 2-crosslinked 5% PhMesilcone (25 m×0.2 mm×0.33 μm) column. For entries 14 and 15, enantiomeric excesses were determined by a literature procedure.[6c] Absolute configurations were determined by comparing the order of elution with samples of known configurations.[6c] Diastereoselectivities (*cis*:*trans* ratio) were measured by GC with an Ultra 2-crosslinked 5% PhMesilcone (25 m×0.2 mm×0.33 μm) column.

### 3.8. General procedure for competition reactions

To a two-neck round-bottomed flask were added $Cu(OTf)_2$ (0.036 g, 0.01 mmol), $CH_2Cl_2$ (1.0 ml) and terpyridine **5** (0.011 mmol) under nitrogen. The solution was stirred at room temperature for 2 h. Styrene (1.0 mmol) and substituted styrene (1.0 mmol) were added to the stirred solution. Ethyl diazoacetate (0.5 mmol) in $CH_2Cl_2$ (0.5 ml) was then added to the reaction mixture in one portion. The mixture was allowed to stir for 16 h at room temperature. The relative amounts of the resulting cyclopropanes were determined by GC.

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